Secondary diamines as monomer from *bis*-hydroaminomethylation of industrial cyclic dienes

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Supporting Information:

Catalytic Experiments

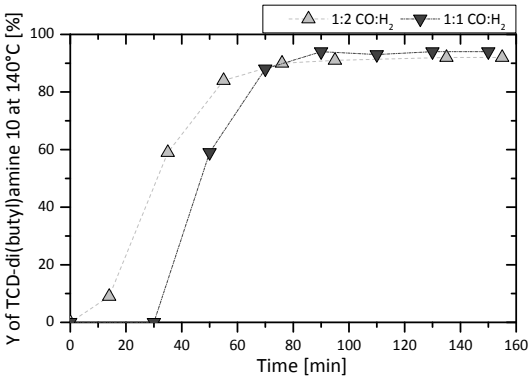
Catalyst screening

Table 4. Effect of different rhodium precursors on the hydroaminomethylation of dcpd

Entry	precursor	X_1 [%]	Yield [%]			
			Y_4	Y_6	Y_9	Y_{10}
S1.1	$Rh(acac)_3$	14	0	0	0	0
S1.2	$[Rh(cod)Cl]_2$	100	0	39	0	20
S1.3	$[Rh(cod)_2]BF_4$	100	0	40	8	23
S1.4	$Rh(acac)(CO_2)$	100	0	19	3	29

Reaction conditions: 1 mmol dcpd, 0.25 mol% precursor, 2 mmol *n*-butyl amine, 5 mL toluene, t = 3 h, T = 120°C, p = 60 bar syngas (1:1), 450 rpm. Yield (Y) is given as sum of the isomers and reported in % determined with dibutylether as internal standard based on GC–FID analysis.

Syngas variation at 140°C



Scheme 5. Influence of syngas ration. Reaction conditions: 17 mmol dcpd, 0.5 mol% $[Rh(octanoate)_2]_2$, 102 mmol *n*-butyl amine, 45 mL toluene, p 60 bar syngas, 450 rpm. Yield (Y) is given as sum of the isomers and reported in % determined with dibutylether as internal standard based on GC–FID analysis.

Reactive Extraction

$$Extraction\ yield\ \% = \frac{m_{extraced\ TCD-di(butyl)amine\ 10}}{m_{produced\ TCD-di(butyl)amine\ 10}} \times 100$$

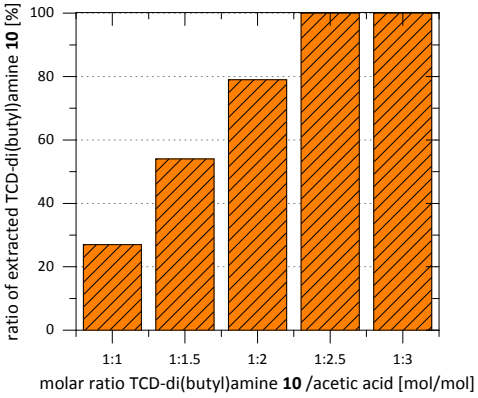
Influence of the temperature

Table 5. Reactive extraction at 30°C and 40°C

Entry	molar concentration of acetic acid	0.25 M	0.5M	0.75 M	1 M
2.1	Extraction yield at 30°C [%]	0	52	100	100
2.2	Extraction yield at 40°C [%]	0	42	100	100

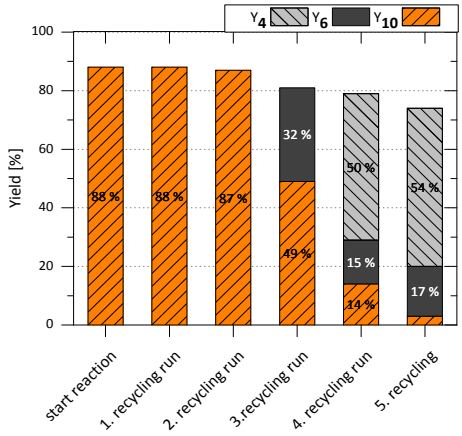
Reaction conditions: 5 g reaction mixture and 5 g extraction solution, extract time = 1h;

Influence of the acetic acid concentration



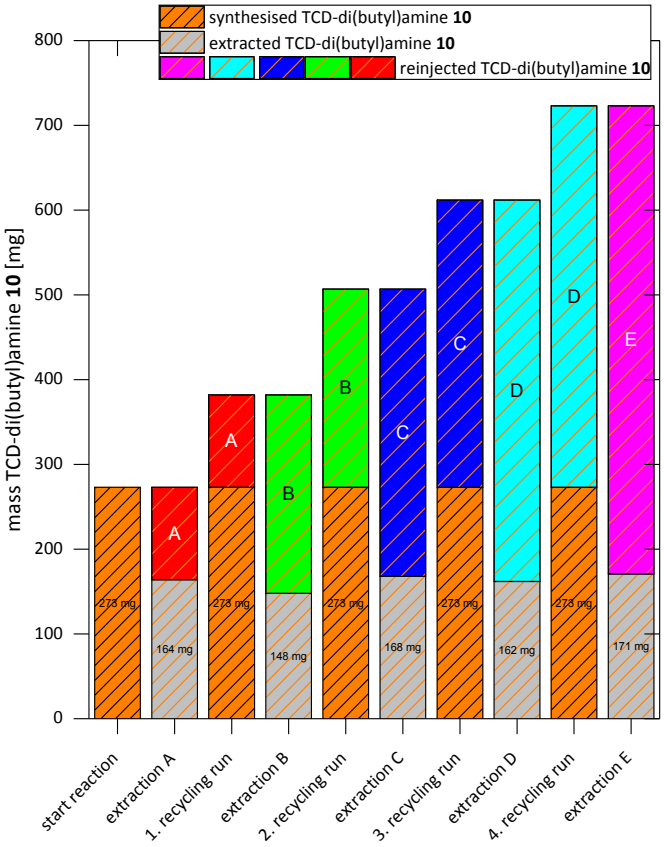
Scheme 6. Influence of the acetic acid concentration. Reaction conditions: 5 g reaction mixture and 5 g extraction solution, extract time = 1h

Recycling of the catalyst through reactive extraction with 2M acetic acid



Scheme 7. Recycling of the catalyst through reactive extraction with 2M acetic acid. Reaction conditions: 1 mmol dcpd **1**, 0.5 mol% $[Rh(octanoate)_2]_2$, 6 mmol *n*-butyl amine, 5 mL toluene, t = 3 h, T = 120°C, p = 60 bar syngas (1:1), 1250 rpm. Condition for the recycling: The reaction solution was washed twice with 5 mL water to remove the *n*-butyl amine followed by the reactive extraction with 5 mL aqueous acetic acid 2 M and then 1 mmol dcpd **1** and 6 mmol *n*-butyl amine were added and the reaction was run again. Mass (M) is given as sum of the isomers and reported in g determined with dibutylether as internal standard based on GC–FID analysis.

Recycling of the catalyst through reactive extraction with 0.8 M acetic acid



Scheme 8. Recycling of the catalyst through reactive extraction with 0.8 M acetic acid. Reaction conditions: 1 mmol dcpd **1**, 0.5 mol% $[Rh(octanoate)_2]_2$, 6 mmol *n*-butyl amine, 5 mL toluene, t = 3 h, T = 120°C, p = 60 bar syngas (1:1), 1250 rpm. Condition for the recycling: The reaction solution was washed twice with 5 mL water to remove the *n*-butyl amine followed by the reactive extraction with 5 mL aqueous acetic acid 0.8 M and then 1 mmol dcpd **1** and 6 mmol *n*-butyl amine were added and the reaction was run again. Mass (M) is given as sum of the isomers and reported in g determined with dibutylether as internal standard based on GC–FID analysis.

Increased reaction time

Table 6. Influence of the reaction time on the HAM of divinylbenzene.

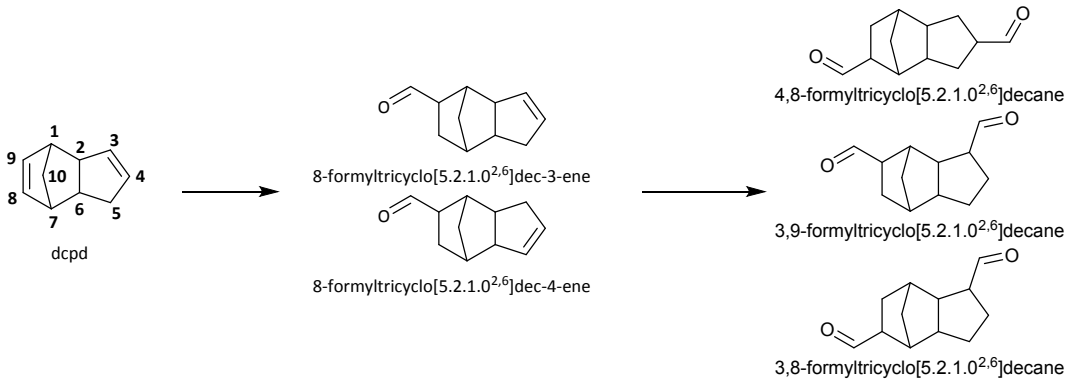
Entry	T [h]	diene	Conv. [%]	Yield [%]		
				$Y_{monoamine}$	$Y_{amine\text{-}imine}$	$Y_{diamine}$
S3.1	4	divinylbenzene	100	2	24	65
S3.2	5	divinylbenzene	100	0	0	86

Reaction conditions: 17 mmol divinylbenzene, 0.5mol% $[Rh(octanoate)_2]_2$, 102 mmol *n*-butyl amine, 45 mL toluene, T = 120°C, p = 60 bar syngas (1:1), 450 rpm. X_1=100%, missing yield is the sum of the high boiler (oligomerisation products). Yield (Y) is given as sum of the isomers and reported in % determined with dibutylether as internal standard based on GC–FID analysis.

Product characterisation of dcpd in the literature

When dcpd was used as starting material, an isomeric mixture is obtained. A special challenge is the separation of the different possible isomers and Table 7 describes the products and the characterisation of the hydroformylation of dcpd in the literature. Isomeric mixtures were obtained by several authors in the hydroformylation of dcpd. The quantification was carried out via GC-FID and identification of the isomeric mixtures was done by GC-MS and NMR. The isomers were separated on the gas chromatographic column; however the single isomers were not separable via column chromatography.

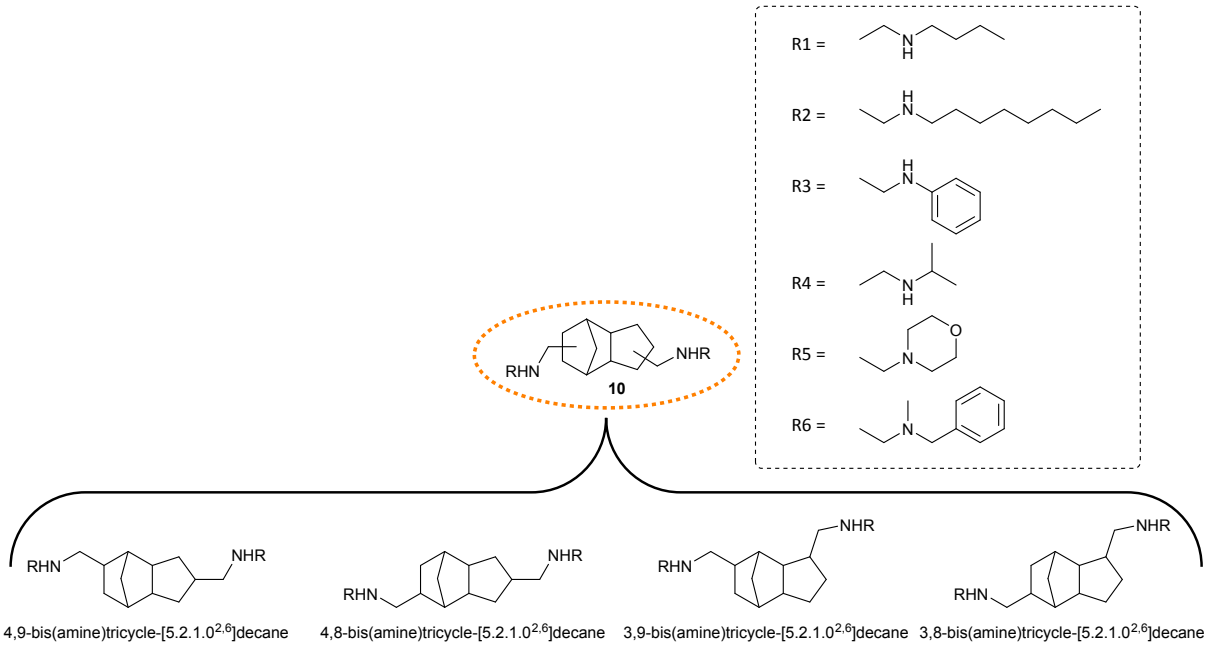
Table 7. Hydroformylation of dcpd over the past decades.



Authors [Ref]	Products and characterisation
Fujikura, Y [1]	Product mixture of 8- and 9-formyltricyclo[5.2.1.0^{2,6}]dec-3-ene was obtained. Hydroformylation occurred at the norbornenyl moiety and two possible isomers are obtained. By comparison of dcpd the same IR $\nu_{C=C}$ and ^{1}H-NMR olefinic proton signals as those of 3,4-bond in dcpd were shown. However, it could not be determined which component had which of the two alternative structures.
Garlaschelli, L. [2]	Two major isomers of 8-formyltricyclo[5.2.1.0^{2,6}]dec-3-ene and 8-formyl-tricyclo[5.2.1.0^{2,6}]dec-4 -ene were identified via GC-MS and NMR. ^{1}H and ^{13}C-NMR-Spectra showed presence of two isomers in roughly the same ratio. By comparison, the data shows hydroformylation at the norbornenyl moiety. Three isomers of diformyltricyclo[5.2.1.0^{2,6}]decanes were clearly separated by GC. The presence of three isomers was also observed in ^{1}H- and ^{13}C-NMR-spectra. Separation of the isomers was not possible.
Trzeciak, A. [3]	Two isomers of formyltricyclodec-4-ene, with different aldehyde group positions in the norbornenyl ring. Products were distinguished via MS chromatography, but are not fully characterised.
Pi, X. [4]	Two major isomers, 8- and 9-formyltricyclo[5,2,1,0^{2,6}]dec-3-ene were obtained. Isomers were separated on the GC, but individual identities could not be determined. According to the retention time a ratio between "E" earlier isomer and "L" later isomer was shown.
Luo, R. [5]	A mixture of 8- and 9-formyltricyclo[5,2,1,0^{2,6}]dec-3- ene and mixture of 3(4),8(9)-diformyltricyclo[5,2,1,0^{2,6}]decane was obtained. Product mixtures were identified by GC-MS and NMR spectra. It is not stated if the mixtures could be separated.
MA, Y.[6–8]	The analysation of product mixtures was carried out with GC-FID and GC–MS.

Isomers of the *bis*-HAM products of dcpd with different amines

Varoius amines were used for the *bis*-HAM with dcpd. Scheme 9 shows possible isomers of the *bis*-HAM product of dcpd.



Scheme 9. Isomers of the *bis*-HAM products of dcpd with different amines

Product distribution of *bis*-HAM product

A distribution approximate ratio of 34:31:33:2 the isomers was identified. Unfortunalty individual identities of the different isomers was not possible to determine. Table 8 shows the *bis*-HAM product distribution.

Table 8. Product distribution of the *bis*-HAM products of dcpd.

Entry	amine	Yield [%] of Y_{10}					
		$Y_{10\ ISO\ I}$	$Y_{10\ ISO\ II}$	$Y_{10\ ISO\ III}$	$Y_{10\ ISO\ IV}$	$Y_{\Sigma 10}$	Ratio of Isomers
S4.1	*n*-butyl amine	31	27	28	2	88	35:31:32:2
S4.2[a]	*n*-butyl amine	28	26	24	2	80	35:32:30:3
S4.3[b]	*n*-butyl amine	20	20	19	2	60	23:33:31:3
S4.4	octylamine	25	27	19	2	73	34:37:26:3
S4.5	aniline	22	24	24	2	72	30:33:34:3
S4.6	isopropylamine	22	1	32	0	54	40:1:59
S4.7	morpholine	37	32	31	0	99	37:32:31
S4.8	benzylmethylamine	26	29	30	0	85	31:34:35

Reaction conditions: 1 mmol dcpd, 0.5 mol% $[Rh(octanoate)_2]_2$, dcpd: amine = 1:6, 5 mL toluene, t = 3 h, T = 120°C, p = 60 bar syngas (1:1), 450 rpm, a) 5mL cyclohexane, b) 5 mL isopropanol. X_1=100%, missing yield is the sum of the high boiler (oligomerisation products). Yield (Y) is given as sum of the isomers and reported in % determined with dibutylether as internal standard based on GC–FID analysis.

Isolated yields of the isomeric mixture of *bis*-HAM products 10

[Rh(octanoate)$_2$)$_2$] (0.5 mol%), substrate (17 mmol), amine (102 mmol) were dissolved in 45 mL toluene in a 300 mL Parr stainless steel autoclave. The autoclave was pressurised with 60 bar syngas (CO:H_2) and the mixture was stirred at 120°C for 4 h. The autoclave was cooled in a ice bath, carefully depressurised and degassed with agon. The reaction mixture was purified by coloumn chromatography (ethyl acetat to methanol 1:0-1:10) yielding an isomeric mixture of **10** (Table 9). The eluates were filtered with syring filters to remove accesses silica gel.

Table 9. Isolated yields of the *bis*-HAM products

Entry	diene	amine	Isolated yields of **∑10** [g]
.1	dcpd	*n*-butyl amine	3.66
.2	dcpd	octylamine	5.25
.3	dcpd	aniline	6.7
.4	dcpd	isopropylamine	2.35
.5	dcpd	morpholine	5.09
.6	dcpd	benzylmethylamine	4.53
.7	4-vinylcyclohexene	*n*-butyl amine	2.62
.8	5-vinyl-2-norbornene	*n*-butyl amine	2.98
.9	divinylbenzene	*n*-butyl amine	2.83

Reaction conditions: 17 mmol dcpd, 0.5 mol% [Rh(octanoate$_2$)$_2$]$_2$, dcpd: amine = 1:6, 45 mL toluene, t = 4 h, T = 120°C, p = 60 bar syngas (1:1), 450 rpm. X_1=100%, missing yield is the sum of the high boiler (oligomerisation products). Yield (Y) is given as sum of the isomers and reported in % determined with dibutylether as internal standard based on GC–FID analysis.

Materials and methods

Chemicals

All chemicals were purchased from commercial suppliers like Sigma Aldrich, Acros Organics and were used without further purification. The synthesis gas was used as received from Messer Industriegas GmbH. Selected rhodium catalysts were donated from Umicore AG & Co. KG (Hanau, Germany).

Chemical	purity	supplier
4-vinyl-1-cyclohexene	97 %	ACROS
divinylbenzene (isomer mix)	80 %	Alfa Aesar
5-vinyl-2-norbornene	98 %	ACROS
morpholine	99 %	Alfa Aesar
N-benzylmethylamin	97 %	Aldrich Chemistry
aniline	99.8 %	ACROS
n-octylamine	99 %	ABCR
cyclohexane	98 %	ACROS
isopropylamine	99 %	ACROS
methanol	99.9 %	ACROS
acetonitrile	99.8 %	ACROS
dicyclopentadiene	95 %	ACROS
toluene	99.9 %	VWR Chemicals
n-butyl amine	99 %+	ACROS
[Rh(octaonate)$_2$]$_2$	98 %	Umicore

Autoclaves

The experiments (Table 1, figure 1 and Table 3) and were performed in 45 mL stainless steel autoclaves with magenetic stirring bar. (figure 5, left). The conversion/time, the temperature and the substrate experiments were performed in 300 mL Parr-Autoclave. (Figure 5, right)

Figure 5. 45 mL stainless steel autoclave (left) and 300 mL stainless steel Parr-Autoclave

Characterization of the oligomers via MALDI-TOF

Especially with low *n*-butyl amine concentrations, the formation of the oligomers occurs. Due to the lack of amine the obtained imines reacted with the obtained aldehydes. The fragmentation pattern shows the formation of oligomers of up to nine repetition unites (Figure 6). Typical fragment sizes are 233, 177 and 56.

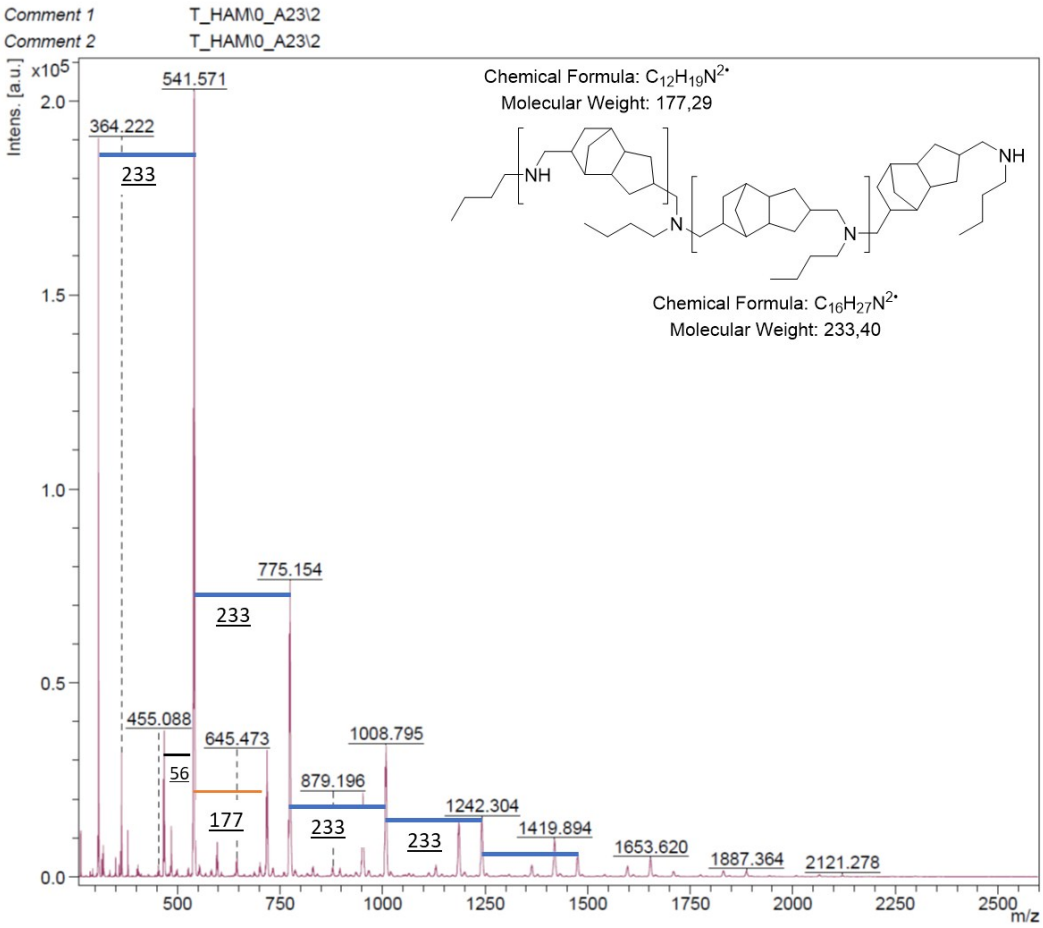


Figure 6. MALDI-TOF spectra of experiment 1.3

Characterization of the Product via Mass-Spectroscopy and NMR

Gas chromatographic analyses were done with an Agilent Technologies 7890B GC-System equipped with a flame ionisation detector (FID) and a HP5 capillary column (30 m, diameter 0.25 mm, film thickness 0.25 µm, method starting with 3 minutes at 40 °C, heating rate 15 °C/min to 320 °C, holding for 5 minutes)) connected to an auto sampler. GC:MS analyses were conducted with an Algilent Technologies 7890 B GC-System (70 eV). N_2 is used as carrier gas (v = 1.0 ml/min, 30 cm/s) with an injection volume 1 µL and a split of 15:1. An example of a typical GC-chromatogram of the product solution is shown below (Figure 7). Conversion of substrate and yields were determined with dibutylether as internal standard.

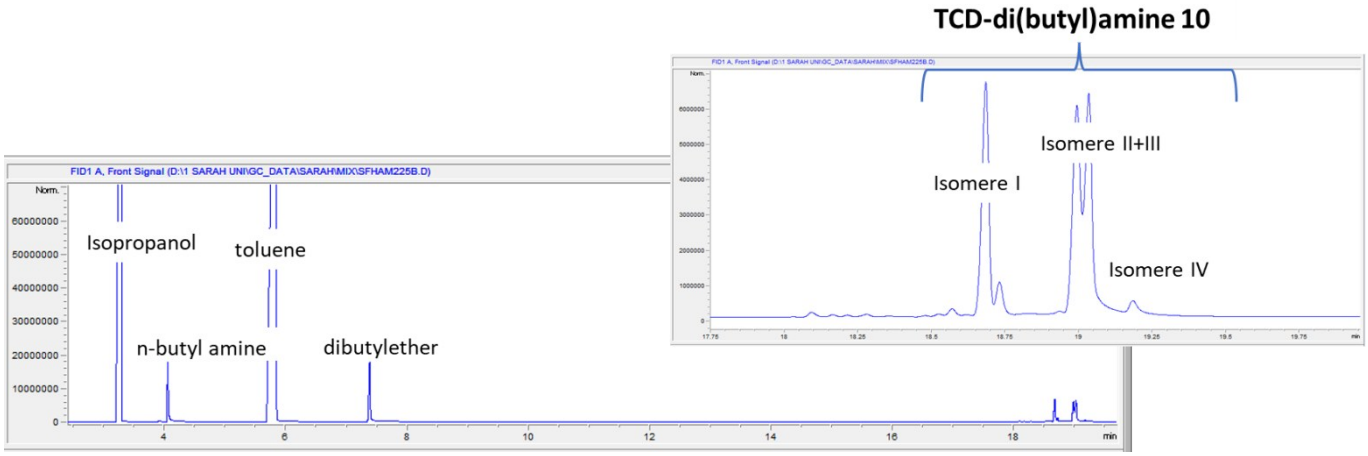


Figure 7. Typical GC-FID chromatogram

Quantification of products via GC-FID

Calculation of product mass $m_{GC-Produkt}$ of the GC-vial under consideration of calibration factors and the areas of the product $A_{Produkt}$and the standard $A_{Standard}$:

$$\frac{m_{Standard} \cdot A_{product\ I} \cdot f_K}{A_{standard}} = m_{GC-product\ I}$$

Factor $F_{overall}$ is the multiplication factor to transfer the results to the overall weighted sampel:

$$\frac{m_{weighted\ sample}}{m_{GC-\ weight\ of\ probe\ reaction\ mixture} - m_{GC-weight\ of\ standard}} = F_{overall}$$

The overall product mass $m_{overall}$ is calculated:

$$m_{GC-produkt\ I} \cdot F_{overall} = m_{overall-product\ I}$$

Calculation of the product yield $Y_{product\ I}$ in procent:

$$\frac{n_{product}}{n_{educt}} = \frac{\frac{m_{overall-product\ I}}{M_{product\ I}}}{\frac{m_{educt}}{M_{educt}}} \cdot 100\% = Y_{product\ I}$$

Analyses GC-FID

The isomeric mixtures were separated on the gas chromatographic column and analysed via GC-Fid and GC-MS. According to their retion time, the isomers were reffered to as isomer I-IV, with isomer I as the first detected one. As expected the *bis*-HAM products with the different amines showed similar peak patterns (Figure 8). Analysis of the reaction mixtures revealed four products, which feature the same molecular mass weight and with identical main fragmentation pattern.

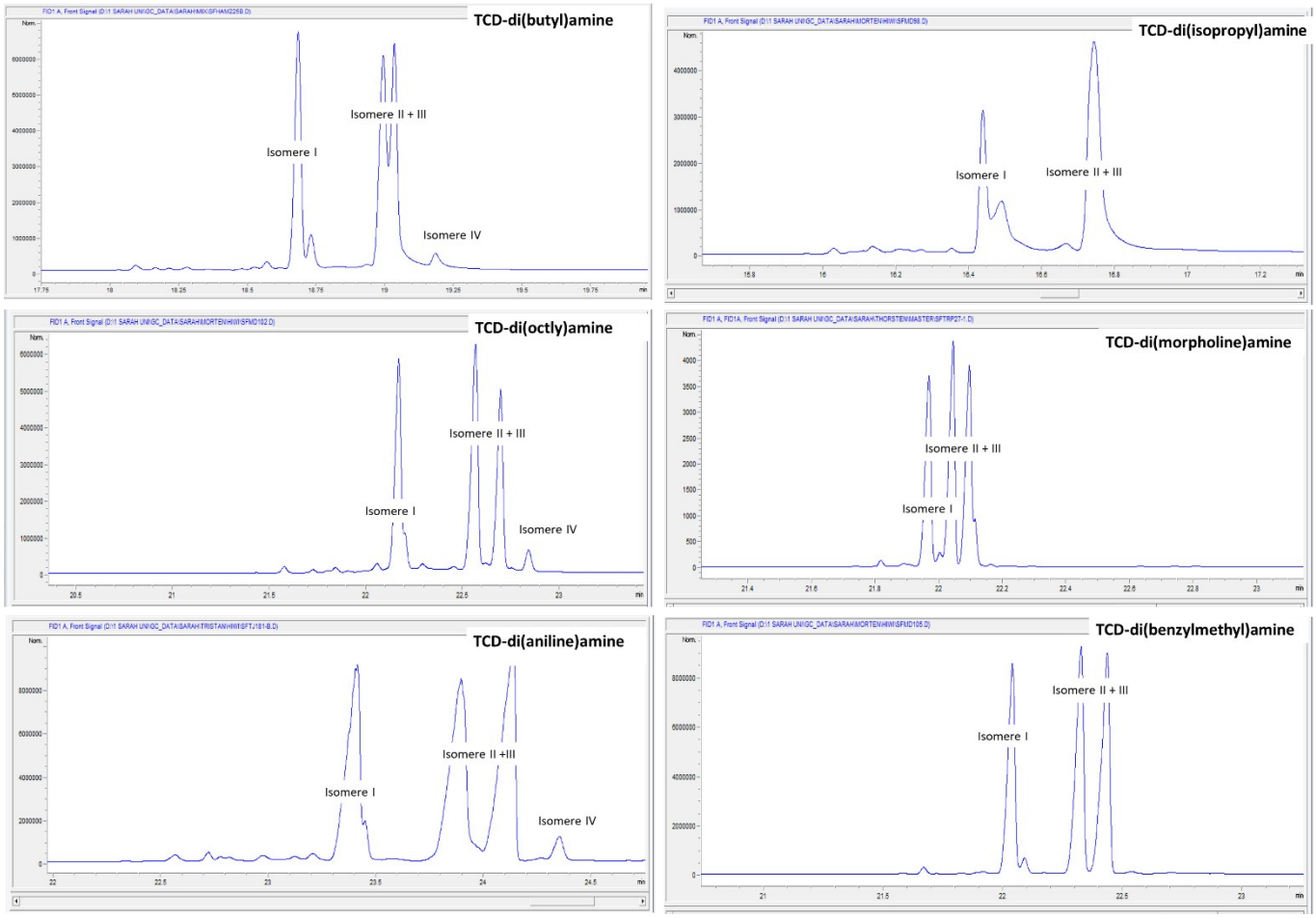
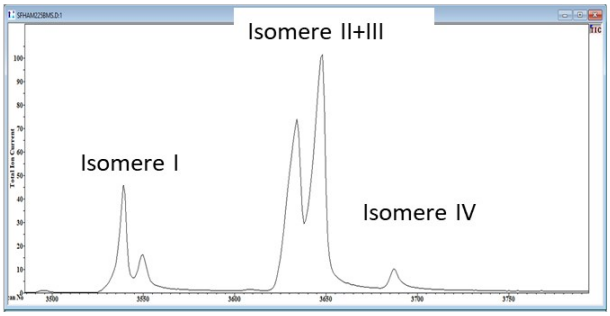
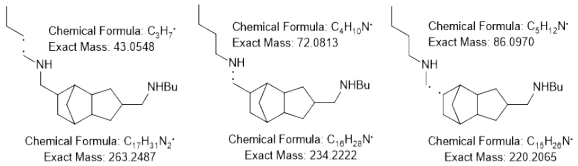


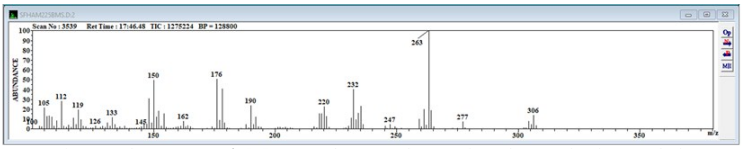
Figure 8. GC-FID *bis*-HAM products isomers of dcpd with different amines

Analyses GC-MS

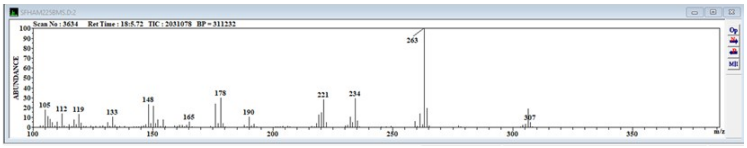
The analyses via GC-MS showed four isomers with the same molecular weight and identical main fragmation patterns. For TCD-di(butyl)amine the main fragmentation pattern is as follows: 306.3(M+), 263.3, 234.2, 220.2, 178.2, 154.2, 112.1, 105.1 and is shown in Figure 9.



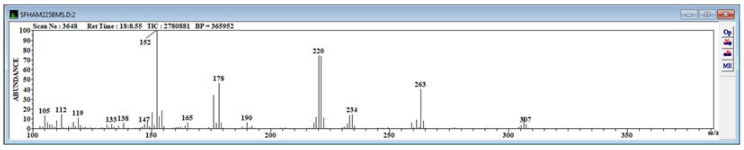




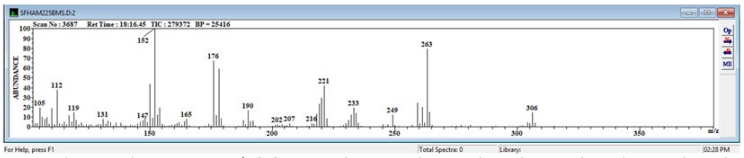
GC-MS (EI, 70 eV): **Isomer I:** m/z [%] = 306.3 (M+, 13.85), 264.2 (18.97), 263.2 (100), 261.2 (20), 235.2 (23.5), 234.2 (16.13), 232.2 (40.42), 220.2 (22.6), 219.2 (15.53), 218.2 (15.45), 190.1 (23.8), 178.20 (41.03), 176.10 (50.76), 154.20 (15.83), 152.20 (18.17) 150.1 (49.88), 148.1 (30.85), 119.1 (19.51), 112.10 (28.39), 107.1 (13.37), 106.1 (13.15), 105.1 (21.57)



GC-MS (EI, 70 eV): **Isomer II:** m/z [%] = 306.3 (M+, 18.79), 264.2 (19.4), 263.2 (100), 234.2 (29.29), 221.2 (28.06), 178.2 (29.84), 176.1 (23.87), 150.1 (21.79), 148.1 (23.56), 105.1 (17.67)



GC-MS (EI, 70 eV): **Isomer III:** m/z [%] = 306.3 (M+, 12.17), 263.2 (40.38), 234.2 (14.79), 233.2 (14.23), 221.2 (73.99), 220.2 (74.27), 219.2 (12.05), 178.2 (46.19), 176.1 (34.25), 154.2 (18.53), 153.2 (12.25), 152.2 (100), 150.1 (16.99), 112.1 (14.69), 105.1 (13.44)

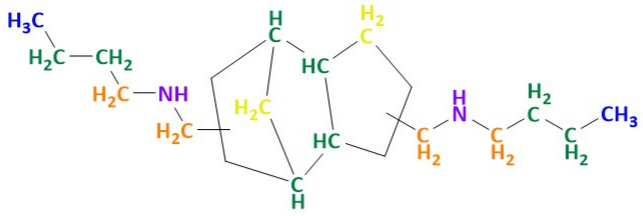


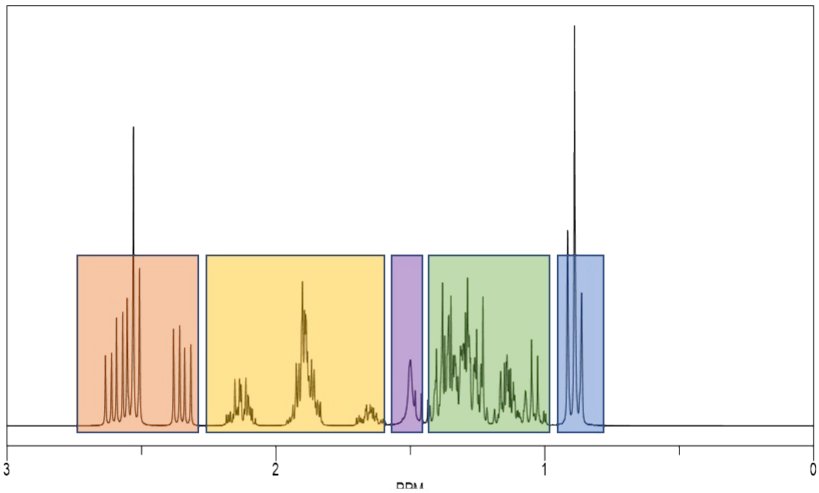
GC-MS (EI, 70 eV): **Isomer IV:** m/z [%] = 306.3 (M+, 14.81), 264.2 (15.09), 263.2 (79.32), 261.2 (20.11), 259.2 (24.23), 233.2 (19.71), 221.2 (41.85), 220.2 (29.5), 219.2 (23.42), 190.1 (16.83), 178.2 (58.79), 176.1 (67.08), 154.1 (19.3), 152.1 (100), 150.1 (43.7), 119.1 (14.53), 112.1 (37.43), 110.1 (19.05), 105.1 (19.39)

Figure 9. GC-MS of *bis*-HAM products of different isomers of dcpd and *n*-butylamine

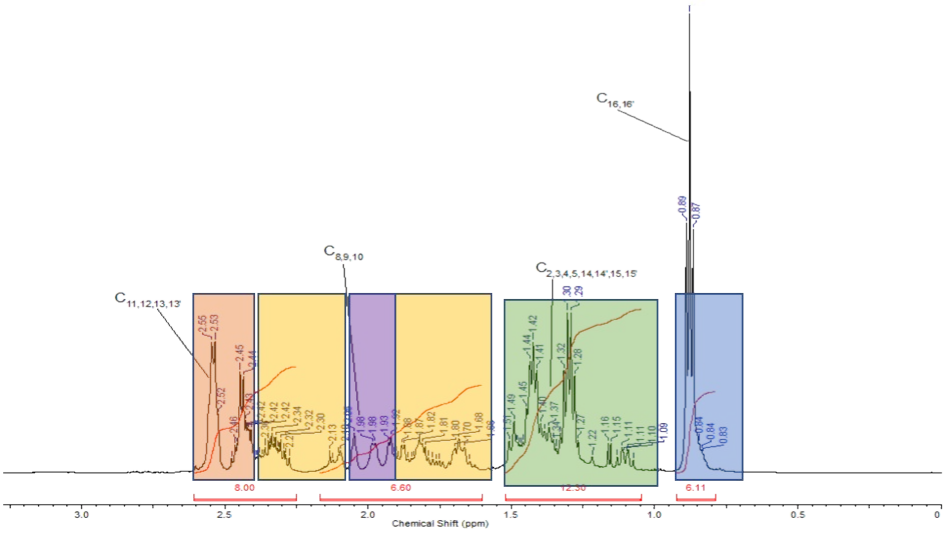
Comparison of predicted and obtained ^{1}H-NMR spectra

The sum of all isomers was analysed via NMR. The evaluation of the NMR spectra was due to the isomeric mixtures very challenging. ^{1}H-NMR and ^{13}C- NMR of the isomeric mixtures are attached. We thoroughly analysed and compared the spectra and identified the *bis*-HAM products. Unfortunately, an exact assignment is not possible (Figure 10).





^{1}H-NMR spectra predicted with Chemdraw of the TCD-di(butyl)amine isomers

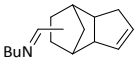


^{1}H-NMR spectra of the TCD-di(butyl)amine isomers

Figure 10. Comparison of the ^{1}H-NMR spectra and a predicted 1H-NMR spectra (Chemdraw) of the TCD-di(butyl)amine isomers

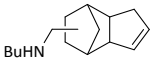
Products of the HAM of dcpd and *n*-butyl amine

*TCD-(butyl)imine **4***



GC-MS (EI, 70 eV): m/z [%] = 217.20 (M+, 5.93), 174.1 (15.15), 150.16 (93.67), 112.15 (100)

*TCD-mono(butyl)amine **6***

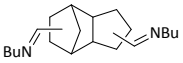


GC-MS (EI, 70 eV): m/z [%] = 219.20 (M+, 35.98), 176.20 (100), 105.10 (28.03)

ESI-HRMS: Calculated for $C_{15}H_{26}N$ ([M+H]$^+$): 220.20598

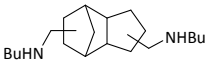
Measured ([M+H]$^+$): 220.20549

*TCD-di(butyl)imin **7***



GC-MS (EI, 70 eV): m/z [%] = 302.30 (M+, 16.57), 259.20 (100), 230.20 (39.7), 150.10 (50.87)

*TCD-di(butyl)amine **10***



GC-MS (EI, 70 eV): m/z [%] = 306.3 (M+, 20.84), 263.3 (100), 221.20 (66.5), 178.20 (58.18), 152.20 (69.44)

ESI-HRMS: Calculated for $C_{20}H_{39}N_2$ ([M+H]$^+$): 307.31078

Measured ([M+H]$^+$): 307.31040

^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 0.82-0.91 (m, 6H, CH_3), 1.06-1.52 (m, 12H, CH, CH_2), 1.70-2.32 (m, 7H, CH, CH_2), 2.25-2.60 (m, 8H, CH_2).

^{13}C-NMR ($CDCl_3$, 150 MHz): δ = 13.94, 20.43, 24.42, 25.25, 29.46, 29.96, 30.34, 32.06, 32.21, 32.29, 34.12, 35.06, 35.23, 38.89, 39.37, 39.79, 40.50, 40.56, 40.72, 40.75, 41.73, 42.19, 43.88, 44.03, 44.60, 45.05, 45.11, 45.80, 49.74, 49.82, 50.02, 51.38, 55.65, 55.90, 56.88.

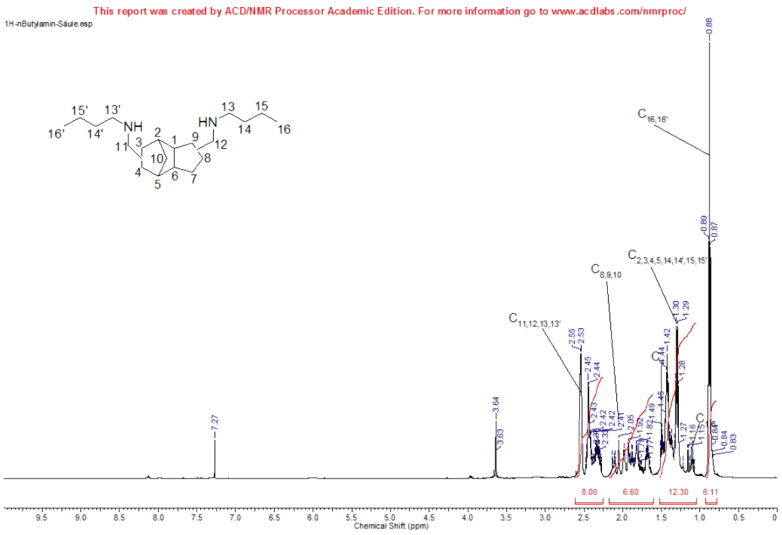


Figure 11. ^{1}H-NMR TCD-di(butyl)amine **10**.

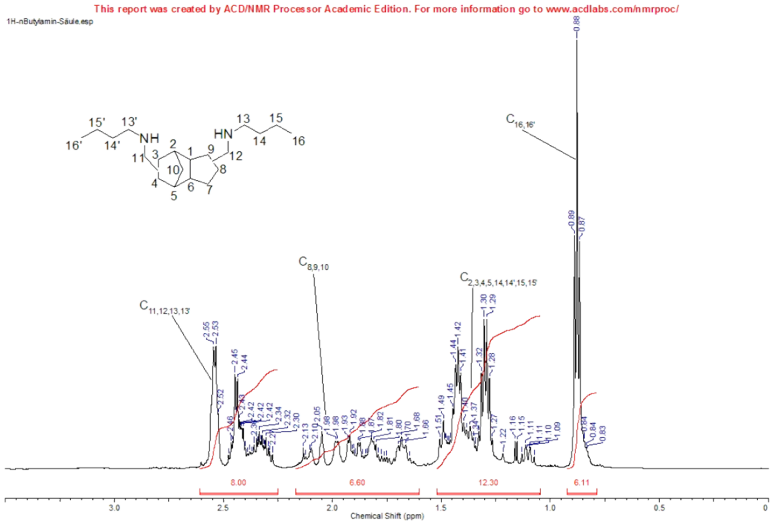


Figure 12. Zoom of ^{1}H-NMR TCD-di(butyl)amine **10**.

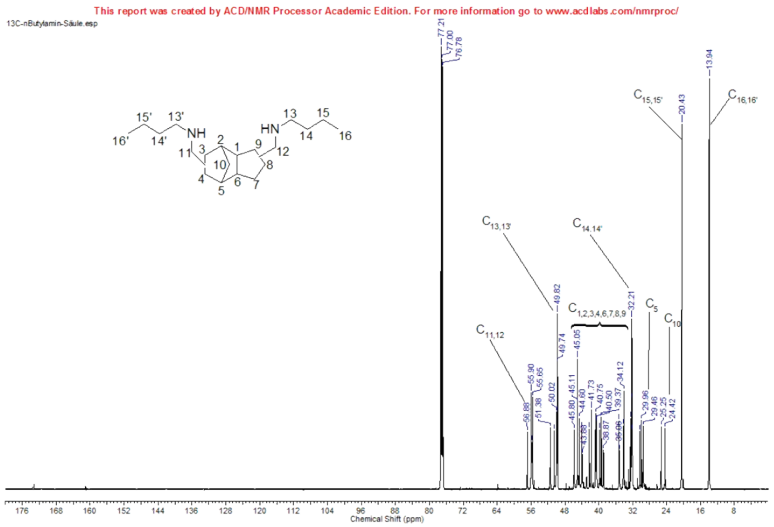


Figure 13. ^{13}C-NMR TCD-di(butyl)amine **10**.

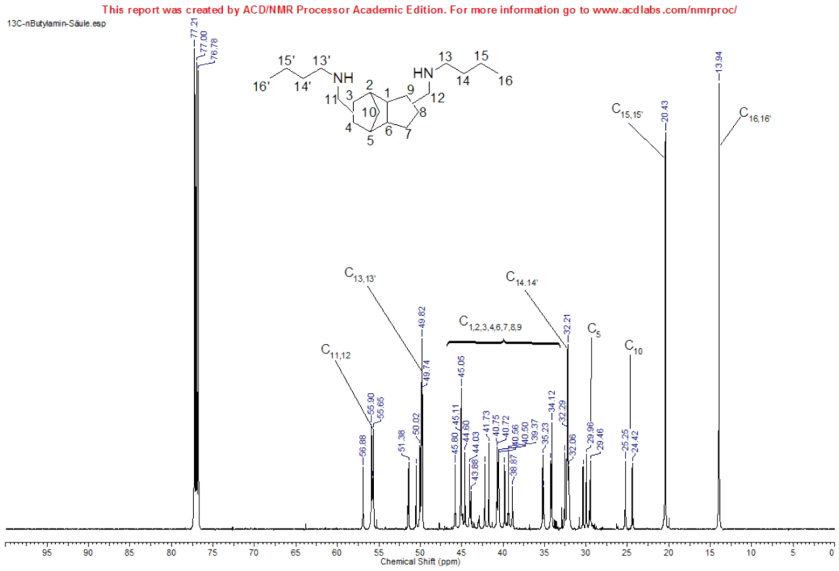
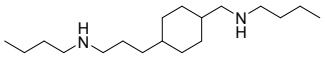


Figure 14. Zoom of ^{13}C-NMR TCD-di(butyl)amine **10**.

Products of the HAM of 4-Vinylcyclohexene and *n*-butyl amine

4-Vinylcyclohexene-di(butyl)amine



GC-MS (EI, 70 eV): m/z [%] = 282.30 (M+, 4.43), 239.20 (100), 225.20 (24.52), 210.20 (19.68), 197.20 (43.66), 154.11 (92.40)

ESI-HRMS: Calculated for $C_{18}H_{39}N_2$ ($[M+H]^+$): 283.31078

Measured ($[M+H]^+$): 283,30986

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 0.80-0.92 (m, 9H, CH_3), 1.20-1.52 (m, 12H, CH, CH_2), 1.53-1.65 (m, 2H, CH_2), 1.65-1.79 (m, 2H, CH_2), 2.25-2.45 (m, 4H, CH_2), 2.50-2.61 (m, 4H, CH_2).

^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 13.47, 13.59, 13.91, 14.67, 19.90, 20.41, 25.12, 26.06, 27.15, 27.75, 30.12, 31.18, 31.31, 31.45, 31.95, 32.69, 33.14, 34.22, 37.65, 37.76, 37.87, 38.02, 49.52, 49.77, 51.14, 53.87, 56.55.

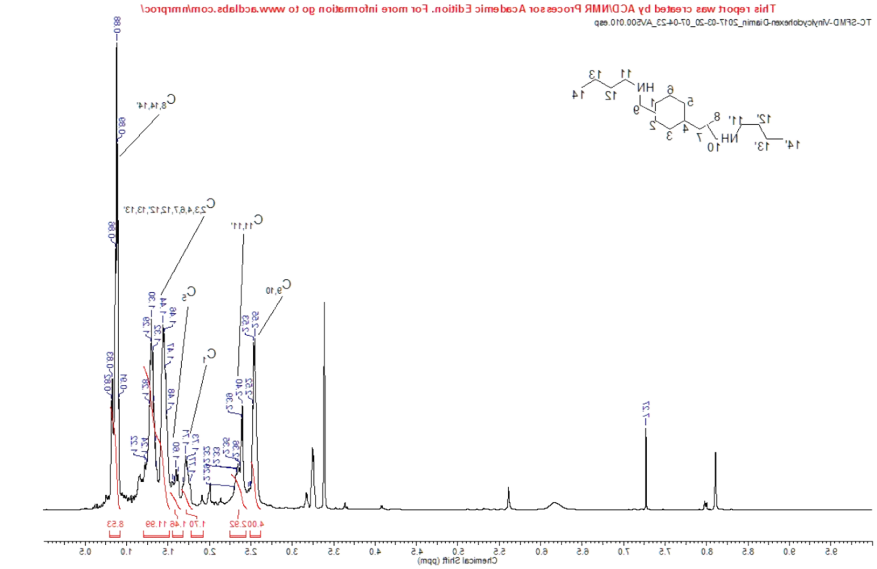


Figure 15**. ^{1}H-NMR** of 4-Vinylcyclohexendiamin.

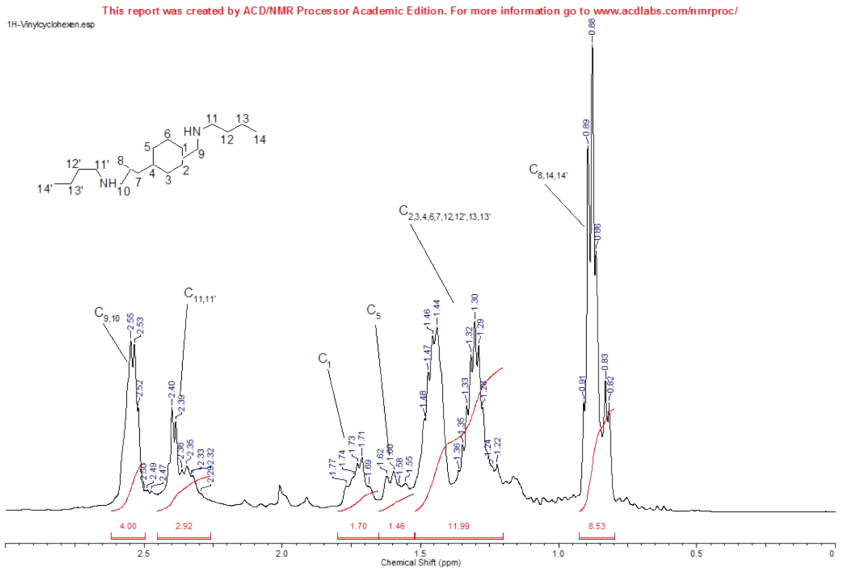


Figure 16**. Zoom of ^{1}H-NMR** of 4-Vinylcyclohexendiamin.

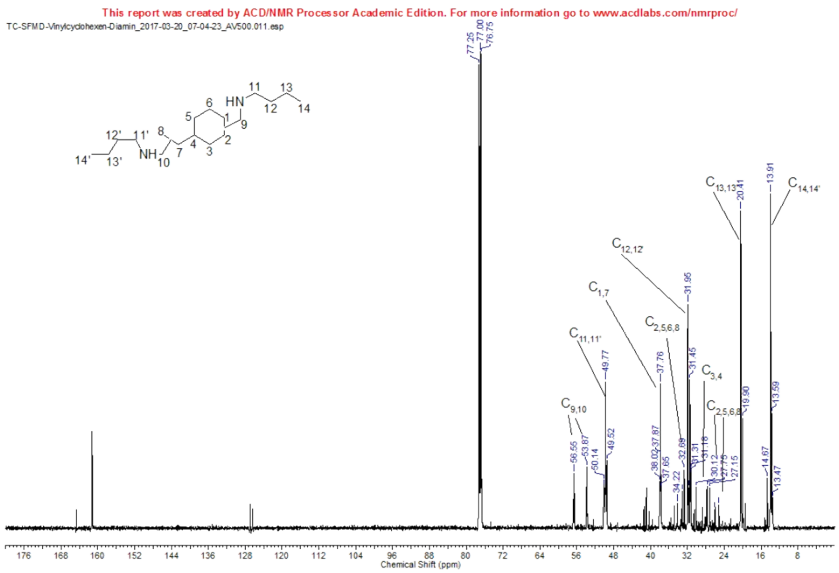


Figure 17**. ^{13}C-NMR** of 4-Vinylcyclohexendiamin.

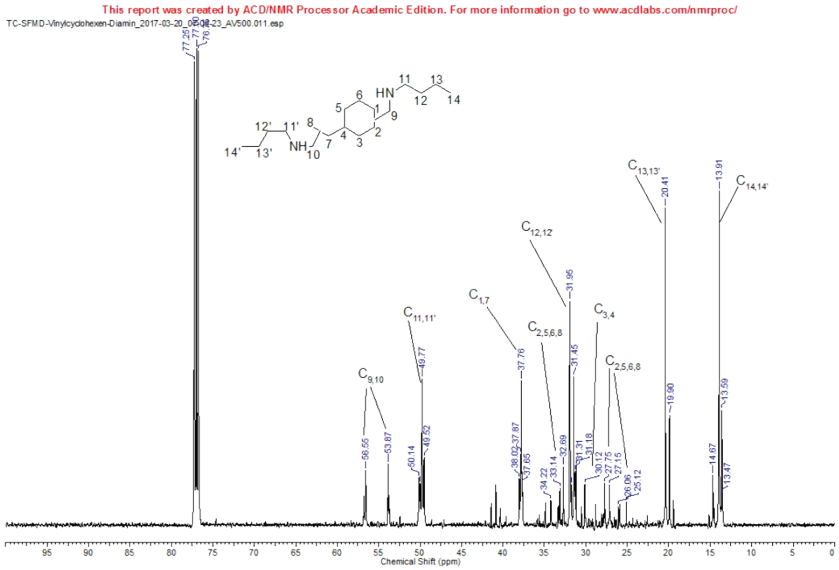
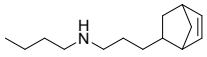


Figure 18**. Zoom of ^{13}C-NMR** of 4-Vinylcyclohexendiamin.

Products of the HAM of 5-vinylnorbornen and *n*-butyl amine

5-Vinyl-2-norbornene-mono(butyl)amine

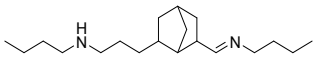


GC-MS (EI, 70 eV): m/z [%] = 207.08 (M+, 1.96), 192.08 (2.59), 178.1 (3.16), 164.09 (41.42), 151.1 (15.54)

ESI-HRMS: Calculated for $C_{14}H_{26}N$ ([M+H]$^+$): 208.20652

Measured ([M+H]$^+$): 208.20507

5-Vinyl-2-norbornene-(butyl)amine-imine

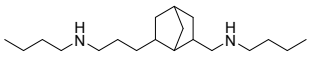


GC-MS (EI, 70 eV): m/z [%] = 292.16 (M+, 0.87), 249.20 (15.21), 235.20 (100), 219.20 (20.79), 204.13 (8.07)

ESI-HRMS: Calculated for $C_{19}H_{37}N_2$ ([M+H]$^+$): 293.29513

Measured ([M+H]$^+$): 293.29467

5-Vinylnorbornen-di(butyl)amine



GC-MS (EI, 70 eV): m/z [%] = 294.30 (M+, 4.61), 265.21 (3.23), 251.20 (100), 237.20 (21.23), 222.20 (50.92), 209.20 (33.25)

ESI-HRMS: Calculated for $C_{19}H_{39}N_2$ ([M+H]$^+$): 295,31078

Measured ([M+H]$^+$): 295.30986

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 0.77-0.93 (m, 6H, CH_3), 0.94-1.80 (m, 13H, CH, CH_2), 1.80-2.90 (m, 8H, CH_2), 3.10-3.45 (m, 2H, CH_2).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 13.46, 13.58, 13.91, 19.40, 19.89, 20.39, 29.10, 30.03, 31.44, 32.01, 33.13, 34.20, 35.17, 35.90, 36.16, 36.37, 36.50, 36.89, 37.75, 39.82, 39.96, 41.40, 41.51, 44.34, 46.23, 48.11, 48.20, 49.60, 49.68, 49.80, 49.93, 50.17, 50.40, 55.48.

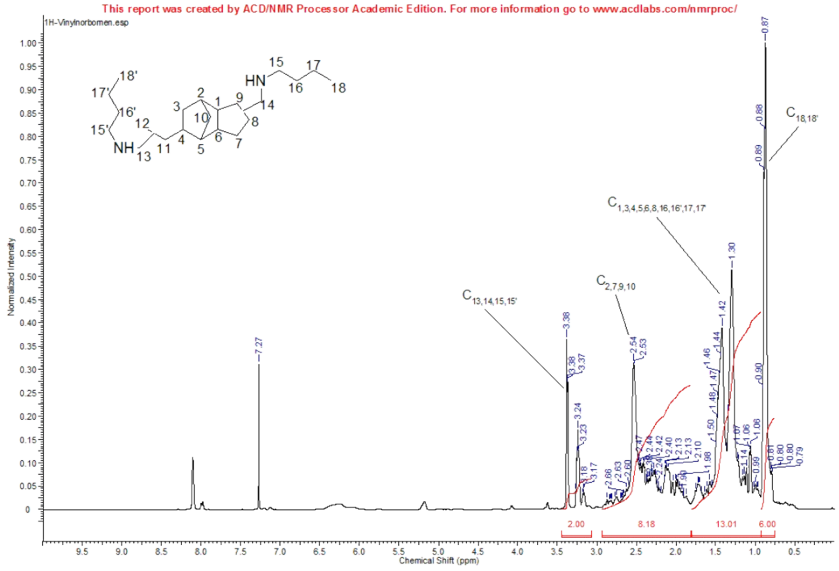


Figure 19. **^{1}H-NMR** 5-Vinylnorbornen-di(butyl)amine**.**

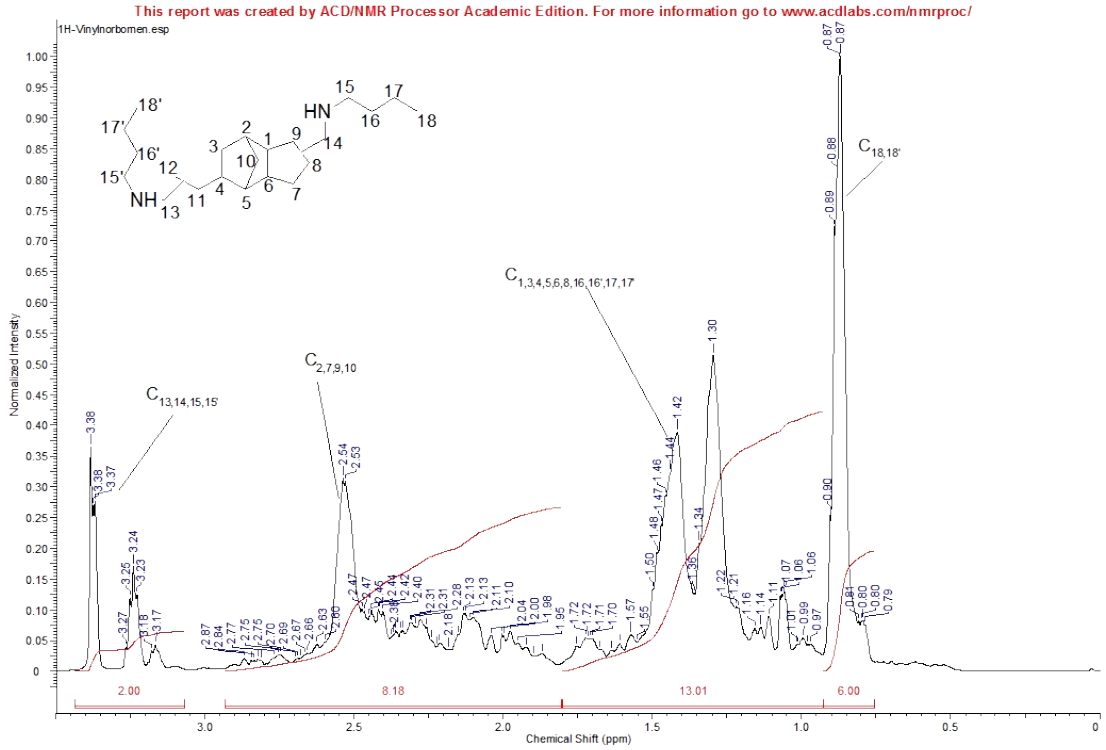


Figure 20. **Zoom of ^{1}H-NMR** 5-Vinylnorbornen-di(butyl)amine**.**

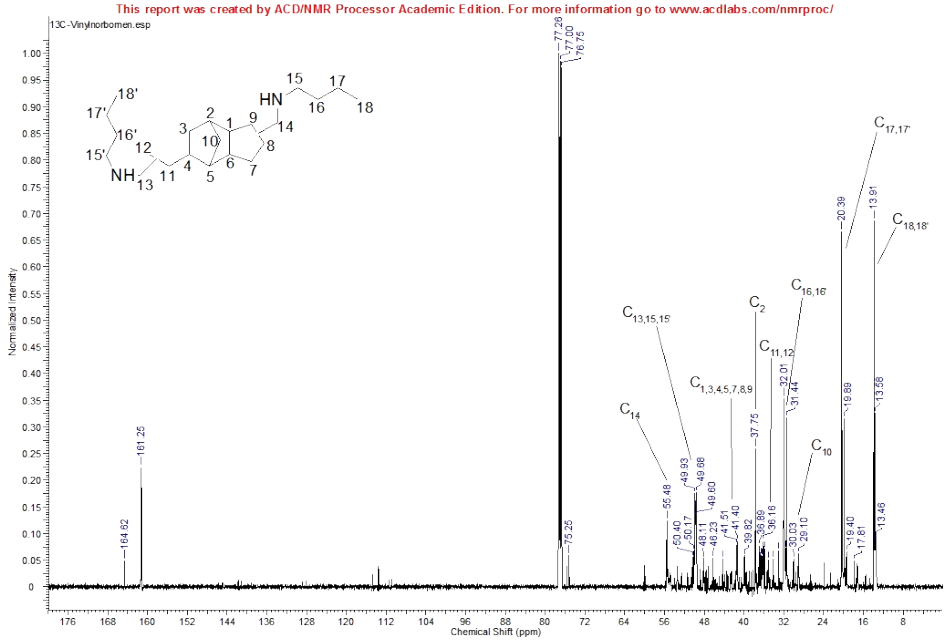


Figure 21. **^{13}C-NMR** 5-Vinylnorbornen-di(butyl)amine**.**

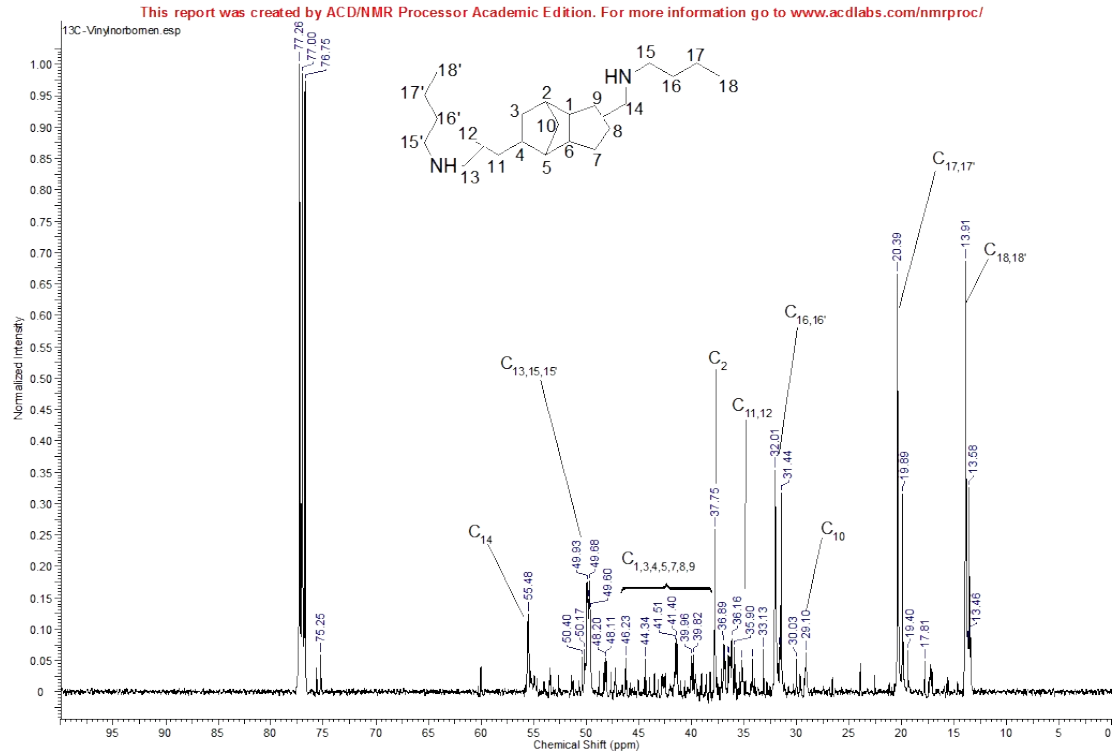
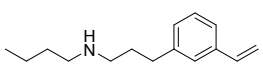


Figure 22. **Zoom. ^{13}C-NMR** 5-Vinylnorbornen-di(butyl)amine**.**

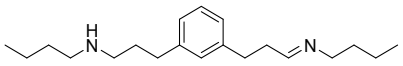
Products of the HAM of Divinylbenzene and *n*-butyl amine

Divinylbenzene-mono(butyl)amine



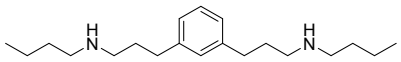
GC-MS (EI, 70 eV): m/z [%] = 218.14 (M+, 3.06), 204.05 (0.3), 176.09 (15.94), 160.04 (1.73)

Divinylbenzene-(butyl)amine-imine



GC-MS (EI, 70 eV): m/z [%] = 303.25 (M+, 0.47), 275.23 (0.18), 261.20 (3.7), 219.20 (100)

Divinylbenzene-di(butyl)amine



GC-MS (EI, 70 eV): m/z [%] = 305.30 (M+, 0.35), 275.20 (0.1), 261.20 (0.13), 219.20 (100)

ESI-HRMS: Calculated for $C_{20}H_{37}N_2$ ([M+H]$^+$): 305.29513

Measured ([M+H]$^+$): 305,29436

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 0.75-0.98 (m, 6H, CH_3), 1.10-1-56 (m, 12 H, CH_2), 1.75-2.15 (m, 2H, NH), 2.46-2.65 (m, 4H, CH_2), 2.68-2.78 (m, 2H, CH_2), 2.84-3.00 (m, 2H, CH_2), 6.95-7.26 (m, 4H, CH).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 13.48, 13.59, 13.86, 15.43, 15.52, 19.84, 19.90, 20.00, 20.31, 31.46, 31.87, 37.76, 39.31, 39.72 49.37, 49.44, 56.83, 56.91, 56.99, 124.87, 124.96, 125.21, 156.94, 127.20, 127.92, 128.17, 128.70, 128.83, 143.13, 145.07, 145.36, 161.19.

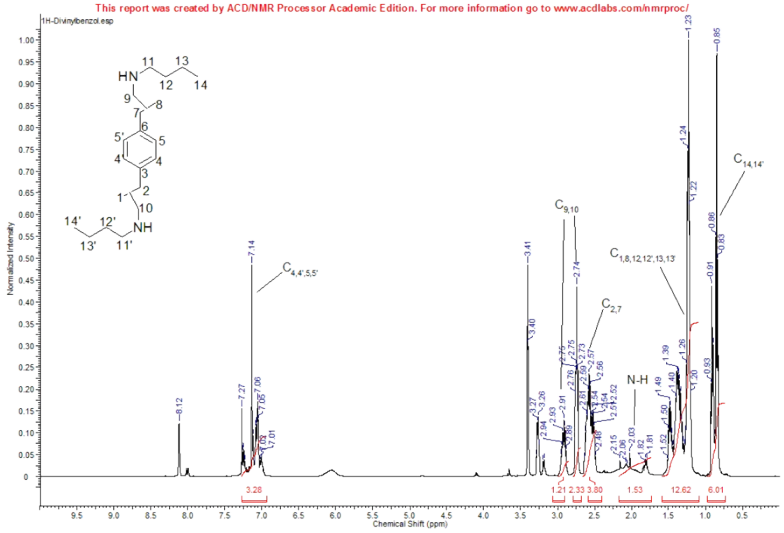


Figure 23. **^{1}H-NMR** Divinylbenzene-di(butyl)amine**.**

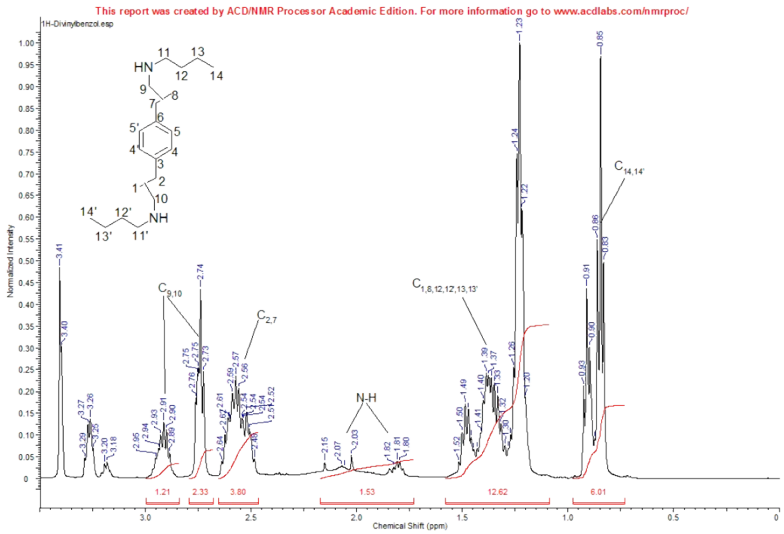


Figure 24. **Zoom of ^{1}H-NMR** Divinylbenzene-di(butyl)amine.

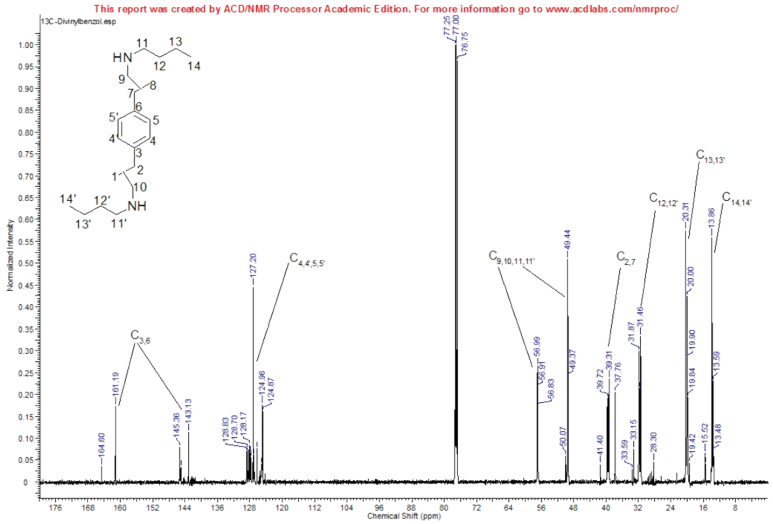
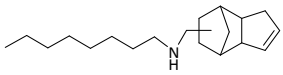


Figure 25. **^{13}C-NMR** Divinylbenzene-di(butyl)amine**.**

Products of the HAM of dcpd and ocytlamine

TCD-mono(octyl)amine

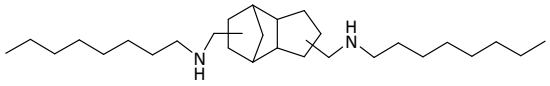


GC-MS (EI, 70 eV): m/z [%] = 241.21 (3.62), 226.21 (0.38), 212.20 (3.62), 198.20 (2.47)

ESI-HRMS: Calculated for $C_{19}H_{34}N$ ([M+H]$^+$): 276.26858

Measured ([M+H 276.26805

TCD-di(octyl)amine



ESI-HRMS: Calculated $C_{28}H_{55}N_2$ ([M+H]$^+$): 419.43598

Measured ([M+H]$^+$): 419.43580

GC-MS (EI, 70 eV): m/z [%] = 375.35 (0.31), 333.31 (0.92), 319.30 (28.7), 305.30 (0.73), 276.28 (10.37)

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.15-1.18 (m, 4H, CH_2), 1.19-1.55 (m, 26 H, CH, CH_2), 1.72-1.94 (m, 4H, CH, CH_2), 1.97-2.23 (m, 8H, CH_2), 2.79-3.16 (m, 8H, CH_2).

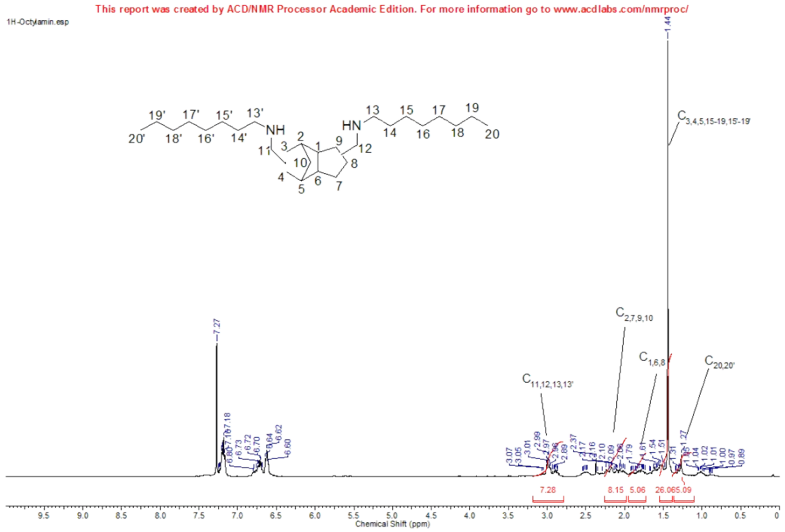


Figure 26. **^{1}H-NMR** of TCD-di(octyl)amine**.**

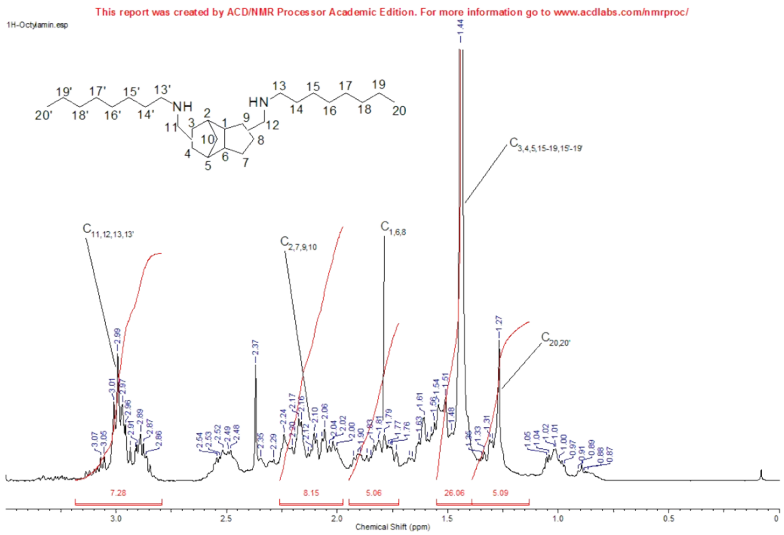


Figure 27. Zoom of **^{1}H-NMR** of TCD-di(octyl)amine**.**

^{13}C-NMR ($CDCl_3$, 176 MHz): δ = 13.88, 14.04, 22.61, 24.47, 25.30, 26.34, 26.81, 27.37, 29.05, 29.14, 29.23, 29.51, 30.12, 31.71, 31.79, 32.34, 34.18, 35.30, 38.14, 39.43, 40.55, 40.76, 40.81, 41.78, 42.27, 44.08, 44.66, 45.10, 45.17, 45.86, 50.16, 50.21, 50.43, 51.44, 55.70, 55.92, 55.97, 56.95.

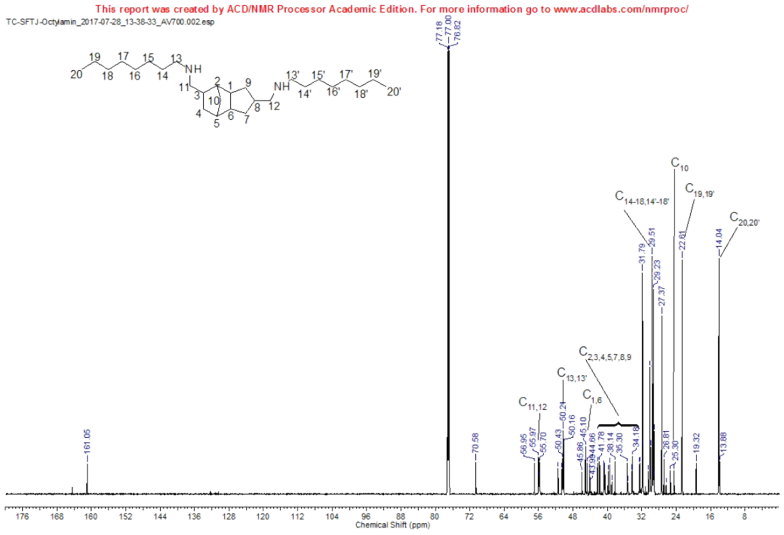
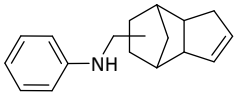


Figure 28. ^{13}C-NMR of TCD-di(octyl)amine.

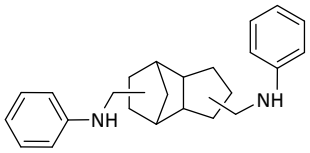
Products of the HAM of dcpd and aniline

TCD-mono(aniline)amine



ESI-HRMS: Calculated for $C_{17}H_{22}N$ ([M+H]$^+$): 240.17468
Measured ([M+H]$^+$): 240.17412

TCD-di(aniline)amine



GC-MS (EI, 70 eV): m/z [%] = 346.20 (M+, 26.49), 241.10 (2.1), 196.99 (0.14)

ESI-HRMS: Calculated for $C_{24}H_{31}N_2$ ($[M+H]^+$): 347.24782

Measured ($[M+H]^+$): 347.24802

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.95-1.08 (m, 1H, CH), 1.25-1.32 (m, 1H, CH), 1.46-1.95 (m, 7H, CH, CH_2), 1.96-2.07 (m, 2H, CH_2), 2.08-2.20 (m, 2H, CH_2), 2.20-2.34 (m, 1H, CH), 2.41-2.60 (m, 2H, CH_2), 2.80-3.07 (m, 4H, CH_2), 6.51-6.66 (m, 4H, CH), 6.68-6.74 (m, 2H, CH), 7.15-7.22 (m, 4H, CH).

^{13}C-NMR ($CDCl_3$, 150 MHz): δ = 24.50, 25.26, 26.89, 29.12, 29.72, 30.10, 32.03, 32.28, 33.99, 34.09, 34.17, 35.08, 35.17, 38.65, 39.53, 40.60, 40.77, 40.80, 43.73, 43.95, 44.56, 44.89, 45.05, 45.17, 45.75, 49.23, 49.47, 49.53, 50.29, 50.35, 51.23, 112.69, 112.73, 112.90, 115.08, 117.10, 117.15, 117.23, 117.43, 118.55, 129.22, 148.48.

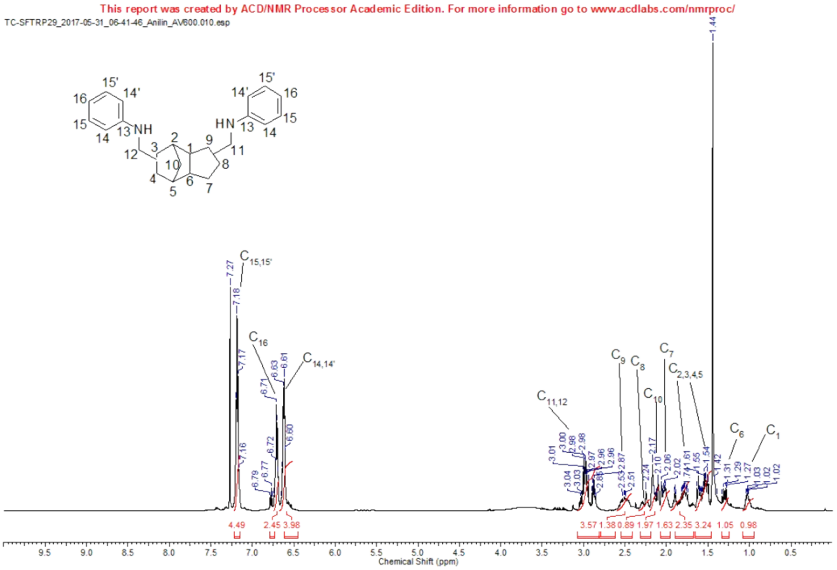


Figure 29. **^{1}H-NMR** of TCD-di(aniline)amine.

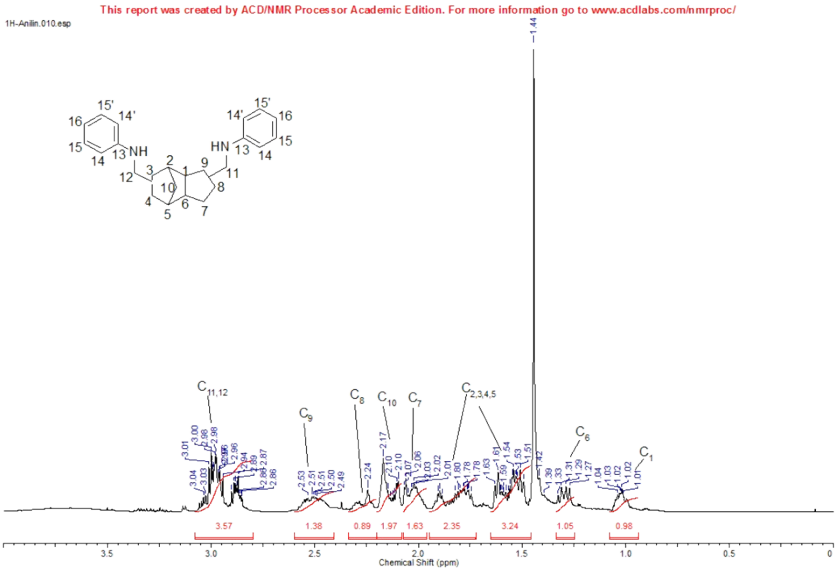


Figure 30. **Zoom of ^{1}H-NMR of** TCD-di(aniline)amine**.**

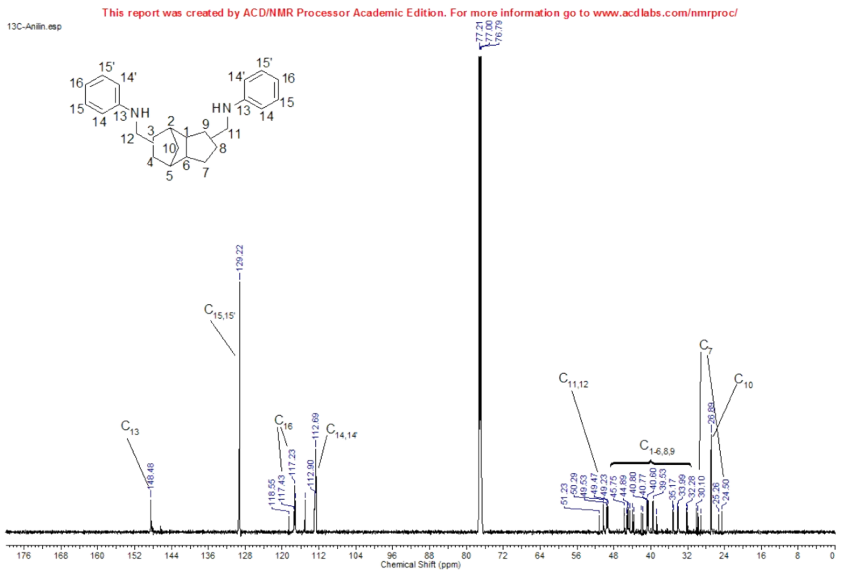
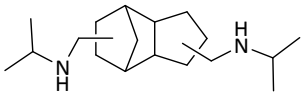


Figure 31. **^{13}C-NMR** of TCD-di(aniline)amine.

Products of the HAM of dcpd and isopropyl amine

TCD-Di(isopropyl)amine



GC-MS (EI, 70 eV): m/z [%] = 278.3 (M+, 7.31), 263.20 (100), 221.20 (44.01), 207.20 (65.16), 192.20 (24.42)

ESI-HRMS: Calculated for $C_{18}H_{35}N_2$ ([M+H]$^+$): 279.27948

Measured ([M+H]$^+$): 279.27835

^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 0.90-1.04 (m, 12H, CH_2), 1.05-1.20 (m, 2H, CH), 1.37-1.44 (m, 2H, CH), 1.45-1.55 (m, 1H, CH), 1.69-1.85 (m, 3H, CH), 1.86-2.00 (m, 2H, CH_2), 2.03-2.16 (m, 2H, CH), 2.30-2.55 (m, 4H, CH_2), 2.71-281 (m, 2H, CH), 3.43 (s, 2H, N-H).

^{13}C-NMR ($CDCl_3$, 125 MHz) : δ = 22.35, 22.84, 22.91, 24.45, 25.23, 29.50, 30.12, 30.47, 30.87, 32.65, 34.18, 34.39, 35.40, 39.46, 39.94, 40.55, 40.83, 41.76, 42.27, 44.62, 45.16, 18.77, 48.81, 48.93, 50.61, 51.59, 53.15, 53.51, 54.44.

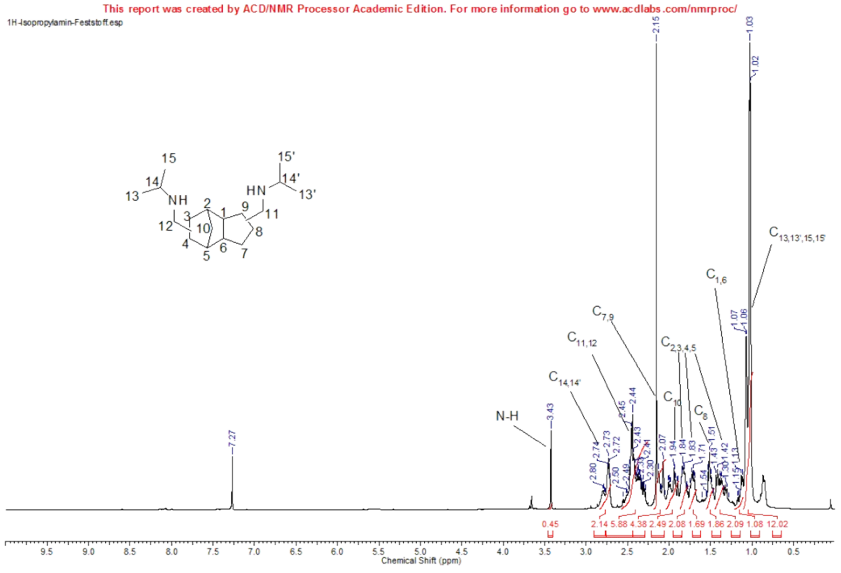


Figure 32. **^{1}H-NMR** of TCD-di(isopropyl)amin**.**

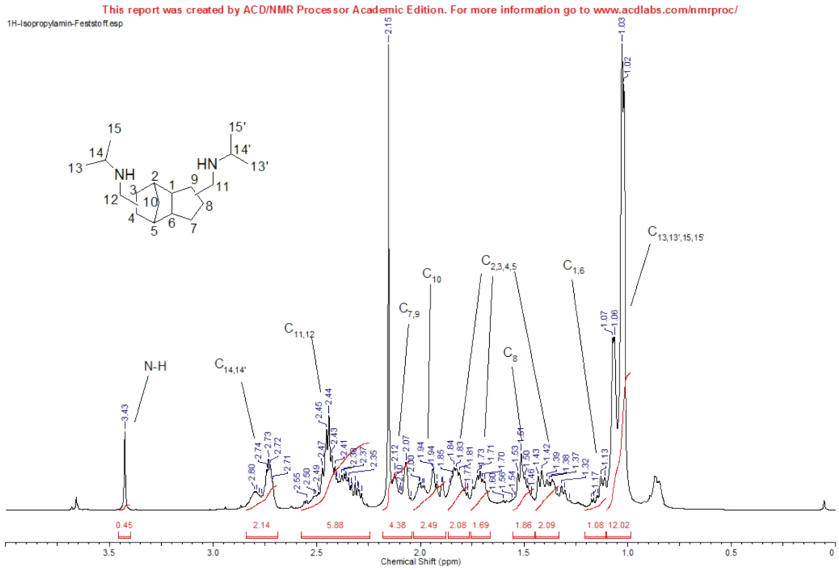


Figure 33. **Zoom of ^{1}H-NMR** of TCD-di(isopropyl)amin**.**

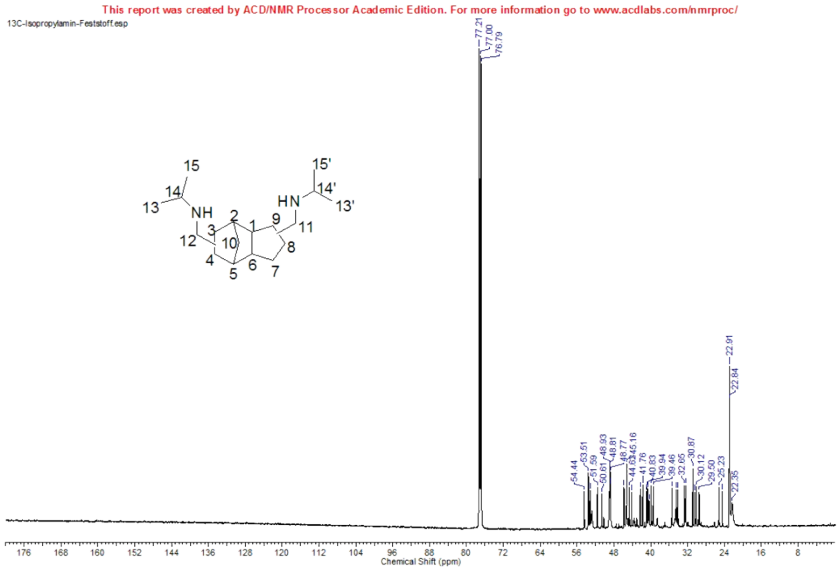


Figure 34. **^{13}C-NMR** of TCD-di(isopropylamine)**.**

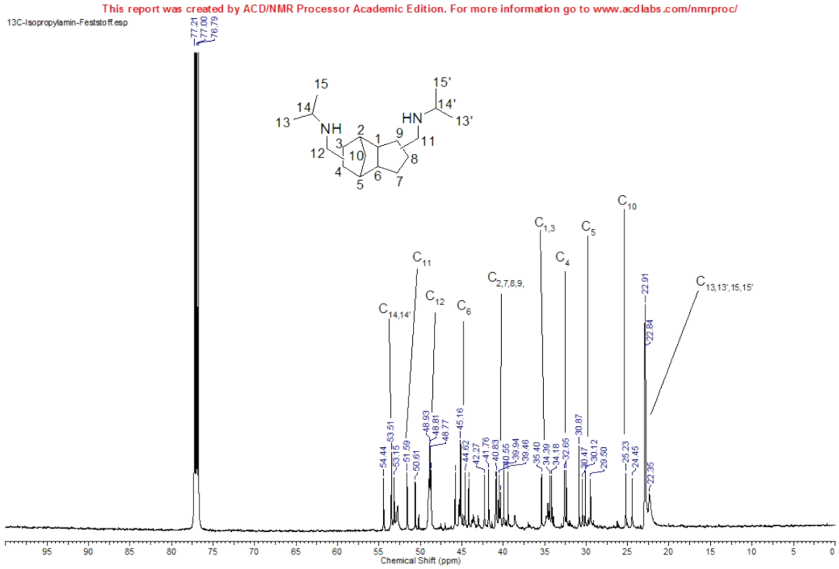
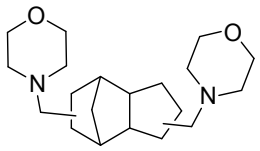


Figure 35. **Zoom of ^{13}C-NMR** of TCD-di(isopropylamine)**.**

Products of the HAM of dcpd and morpholine

TCD-di(morpholine)amine



GC-MS (EI, 70 eV): m/z [%] = 334.20 (M+,3.67), 304.20 (1.58), 289.20 (0.92)

ESI-HRMS: Calculated for $C_{20}H_{35}O_2N_2$ ([M+H]$^+$): 335.26930

Measured ([M+H]$^+$):335.26845

^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 1.15-1.57 (m, 7H, CH, CH_2), 1.58-1.81 (m, 3H, CH, CH_2), 1.84-2.12 (m, 6H, CH_2), 2.12-2.30 (m, 4H, CH_2), 2.31-2.53 (m, 8H, CH_2), 3.55-3.85 (m, 8H, CH_2).

^{13}C-NMR ($CDCl_3$, 150 MHz): δ = 24.54, 25.27, 30.00, 30.47, 30.85, 31.76, 31.82, 32.85, 33.37, 34.18, 35.80, 36.53, 39.32, 39.43, 40.59, 40.63, 40.88, 41.76, 44.46, 44.75, 44.89, 45.51, 50.29, 51.21, 53.93, 54.07, 60.34, 64.60, 64.70, 65.23, 65.27, 65.50, 65.96, 66.90, 66.97.

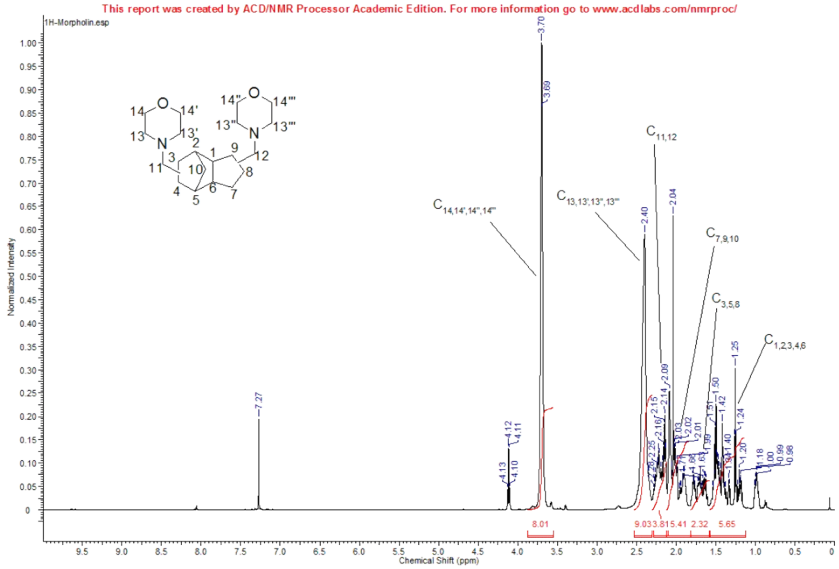


Figure 36. **^{1}H-NMR** of TCD-dimorpholine.

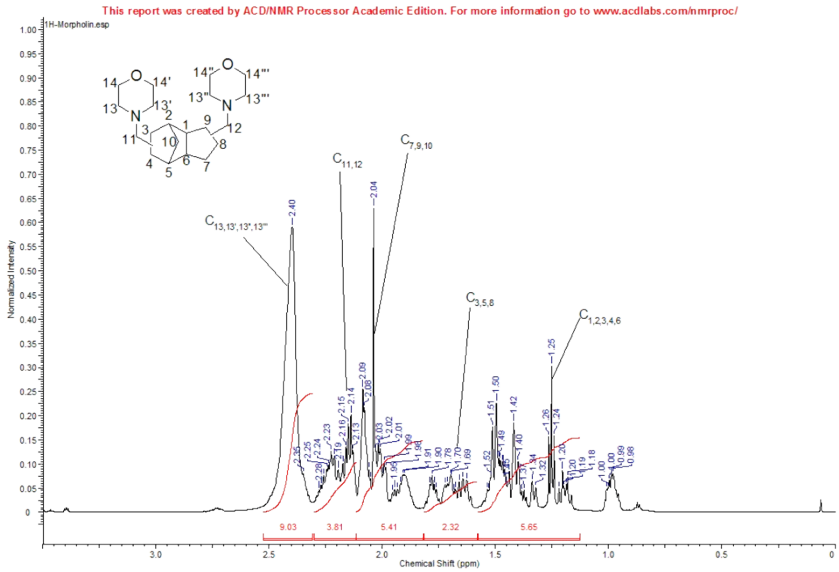


Figure 37. **Zoom of ^{1}H-NMR** of TCD-dimorpholine.

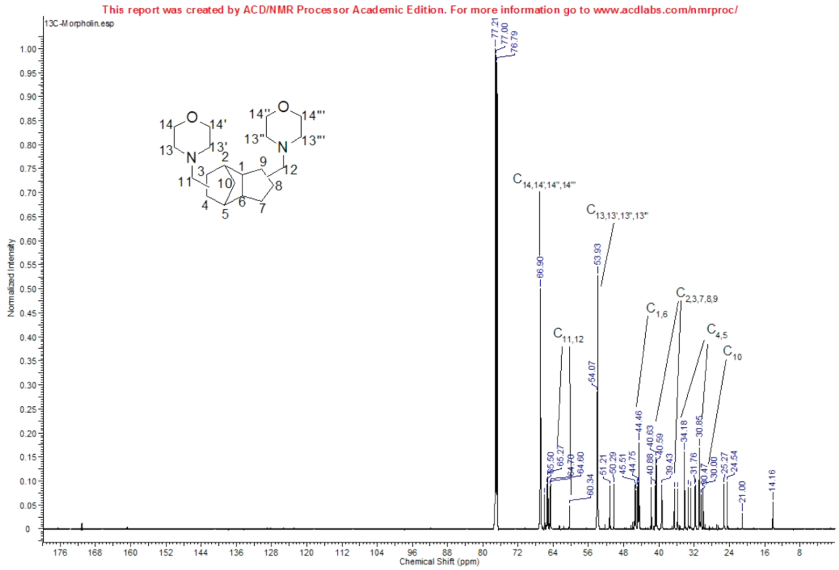


Figure 38. **^{13}C-NMR** of TCD-dimorpholin**.**

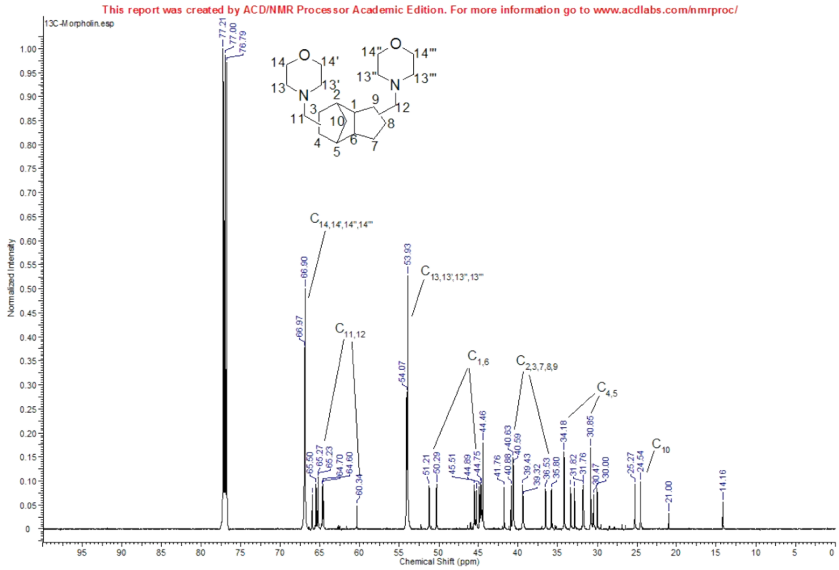
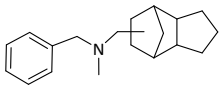


Figure 39. **Zoom of ^{13}C-NMR** of TCD-dimorpholin**.**

Products of the HAM of dcpd and methylbenzyl amine

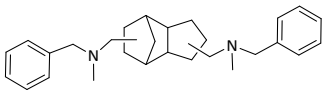
TCD-mono(methylbenzyl)amine



ESI-HRMS: Calculated for $C_{19}H_{26}N$ ([M+H]$^+$): 268.20598

Measured ([M+H]$^+$): 268.20509

TCD-di(methylbenzyl)amine



GC-MS (EI, 70 eV): m/z [%] = 325.24 (0.06), 311.20 (5.59), 268.20 (0.43), 190.12 (0.33), 176.08 (0.09), 160.09 (0.31), 134.10 (100)

ESI-HRMS: Calculated for $C_{28}H_{39}N_2$ ([M+H]$^+$): 403.31078

Measured ([M+H]$^+$): 403.30992

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.85-0.95 (m, 1H, CH), 1.00-1.14 (m, 1H, CH), 1.18-1.48 (m, 4H, CH), 1.53-1.76 (m, 2H, CH_2), 1.85-2.40 (m, 16H, CH_2, CH_3), 3.30-3.50 (m, 4H, CH_2), 7.10-7.30 (m, 10H, CH).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 24.55, 25.25, 29.53, 30.03, 30.45, 31.92, 32.65, 32.76, 32.94, 33.86, 37.14, 37.76, 39.37, 40.16, 40.37, 40.42, 40.80, 41.10, 41.83, 42.65, 44.32, 44.80, 45.00, 45.47, 50.31, 51.01, 61.83, 62,46, 62.58, 63.54, 62.24, 126.70, 126.87, 128.07, 128.88, 128.92, 139.56, 139.66.

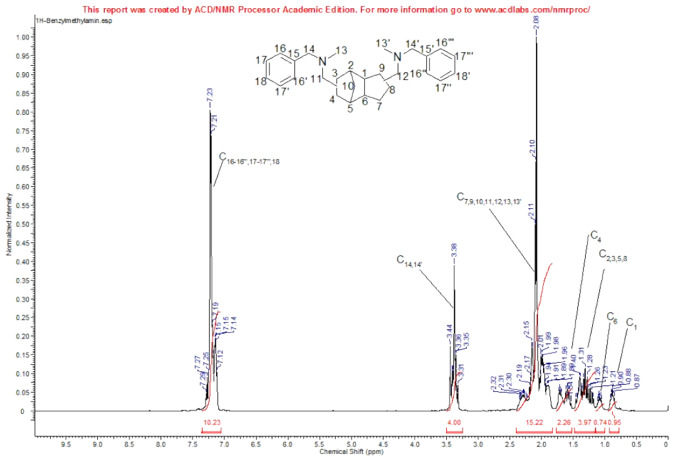


Figure 40. ^{1}H-NMR of TCD-di(methylbenzyl)amine.

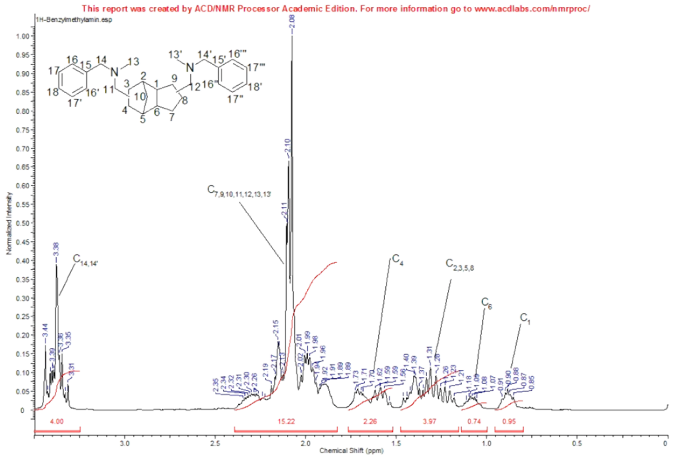


Figure 41. Zoom of ^{1}H-NMR of TCD-di(methylbenzyl)amine.

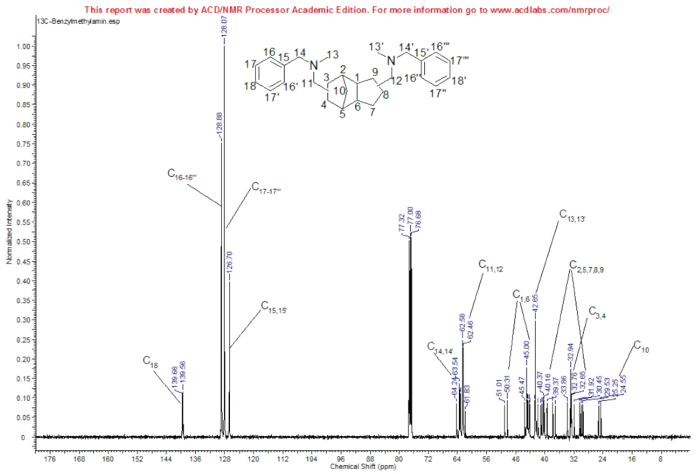


Figure 42. ^{13}C-NMR of TCD-di(methylbenzyl)amine.

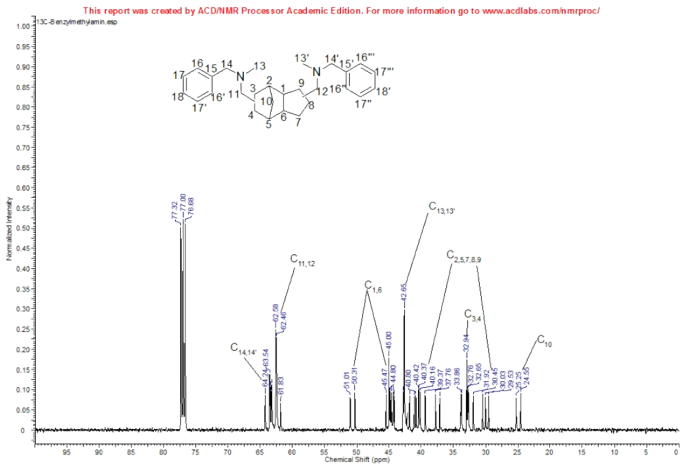


Figure 43. Zoom of ^{13}C-NMR of TCD-di(methylbenzyl)amine.

TCD-diamine as reference substance

^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 0.89 (m, 1H, CH2), 1.15 (s, 4H, NH2), 1.39-1.43 (m, 2H, CH2), 1.48-1.52 (m, 3H, CH2), 1.70-1.71 (m, 3H, CH, CH_2), 1.78-1.84 (m, 1H, CH2), 1.93-1.96 (m, 2H, CH), 2.13 (s, 1H, CH), 2.41-2.43 (m, 2H, CH2), 2.49-2.55 (m, 3H, CH, CH_2) ppm.

^{13}C-NMR ($CDCl_3$, 600 MHz): δ = 24.6 (1C, CH2), 30.0 (1C, CH2), 33.6 (1C, CH2), 38.28 (1C, CH), 40.7 (1C, CH2), 40.8 (1C, CH), 43.7 (2C, CH), 45.9 (1C, CH), 47.8 (1C, CH2), 47.9 (1C, CH2), 50.2 (1C, CH) ppm.

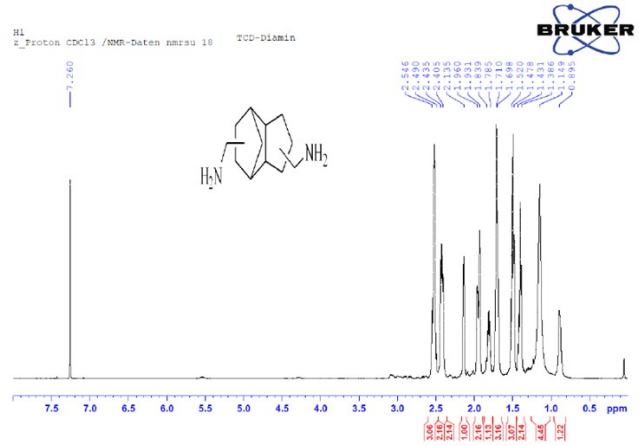


Figure 44. **^{1}H-NMR** of TCD-diamine.

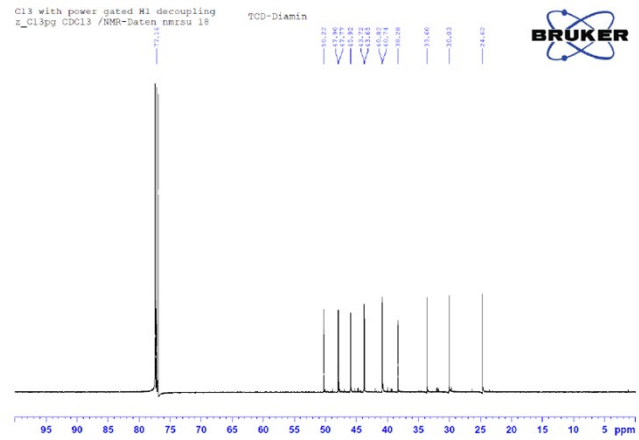


Figure 45. **^{13}C-NMR** of TCD-diamine.

Inductively coupled plasma mass spectrometry (ICP-MS)

The rhodium leaching of the water extraction phase was determined with inductively coupled plasma mass spectrometry (ICP - MS). A spectrometer from Thermo Scientific IRIS Intrepid Elemente ICP was used.

Reference

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