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BACHELOR THESIS

**Diglycolamide-functionalized amino
group-containing platforms for nuclear
waste processing**

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Abstract

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Diglycolamide-functionalized amino group-containing platforms for nuclear waste processing

by Anna Maria Wouda

Diglycolamide-functionalized tris(2-aminoethyl)amine (**4**) and diglycolamide-functionalized triazacyclononane (**5**) were successfully synthesized. This was done by reaction of *p*-nitrophenol activated diglycolamide and the appropriate amino group-containing platform. The extraction properties towards actinides and lanthanides, two components of nuclear waste, will be determined in the BARC institute in Mumbai, India.

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Abbreviations

HLW	H igh L evel W aste
PUREX	P lутonium U Ranium EX traction
DIAMEX	DI AMide EX traction
SANEX	S elective Acti Nide EX traction
DGA	Di Glycol A mide
Ln(III)	L anthanide
An(III)	A ctinide
TBP	Tri-<i>n</i>-Butyl P hosphate
TRPO	TR ialkyl P hosphine O xides
CMPO	octyl(phenyl)- <i>N,N</i> -diisobutyl C arbamoyl M ethyl P hosphine O xide
DMDBTTDMA	<i>N,N'</i> - Di Methyl- <i>N,N'</i> - Di Butyl Tetra Decyl M alon A mide
DMDOHEMA	<i>N,N'</i> - Di Methyl- <i>N,N'</i> - Di Octyl-2-(2- H exyl O xy E thyl) M alon A mide
TODGA	<i>N,N,N',N'</i> - Tetra Octyl Di Glycol A mide
TREN	TR is(2-amino E thyl)amine
EDC	1- E thyl-3-(3- D imethylaminopropyl) C arbodiimide hydrochloride
DCC	Di Cyclohexyl C arbodiimide
HOBt	1- H ydroxy B enzotriazole
FTIR	F ourier T ransform I nfrared spectroscopy
HRMS	H igh R esolution M ass S pectrometry

Chapter 1

Introduction

1.1 Problem description

A nuclear energy plant produces high level waste (HLW). The most common solution is to bury the waste in glass matrices for more than 100 years, but this is not long enough to decay to the level of natural uranium. The waste contains minor actinides like Tc, Pb, Zr, I, Cs and Sr, lanthanides, unextracted U and Pu, activation products, structural elements and process chemicals. The half-life times of all the HLW components range from a few 100 to millions of years [1]. Now it is simply impossible to store all the HLW that nuclear plants are producing, and in the future, with the growing number of plants, this will become an ever bigger problem.

1.2 Solution

The biggest problems of nuclear energy harvesting are the enormous amount of HLW produced and the long storage time that is needed for the waste to decay back to natural radiation levels. The size and time of storage can be reduced if there would be a possibility to separate different HLW components. In Figure 1.1 the radiotoxic decay from the different components is represented. If the components are not separated the decay will take millions of years, but when the components are separated, the decay of some of them will be only a few hundreds of years. So the waste can be separated in

parts, based on storage time: long term and short term storage. The amount of waste that has to be put away for a long time can be reduced by this matter.

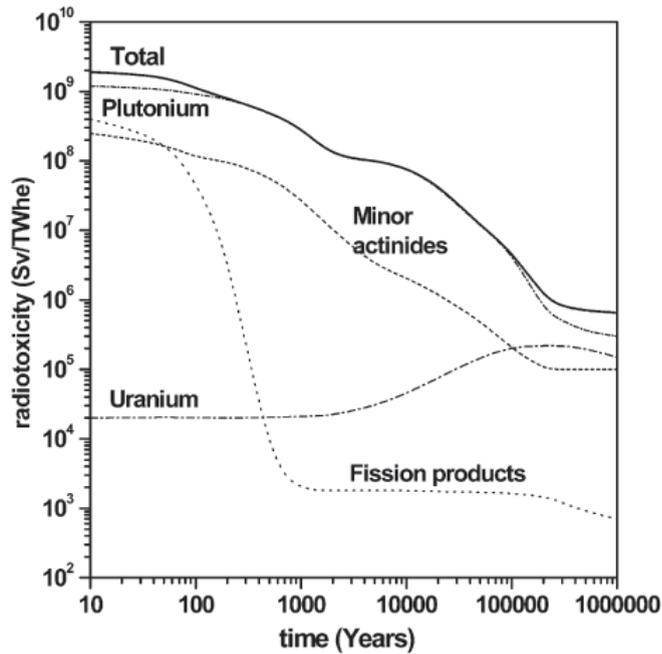


FIGURE 1.1: Partitioning of minor actinides and radiotoxicity of residual waste [1].

1.2.1 Separation processes

HLW can be separated by using several processes. The process to get the uranium, plutonium and neptunium out of the dissolved spent fuel is called the PUREX (Plutonium URanium EXtraction) process. The fission and corrosion products are being extracted with the DIAMEX (DIAMide EXtraction) process. That leaves the lanthanides and actinides to be separated. This is currently done with the SANEX (Selective ActiNide EXtraction) process. But there is no process known yet that directly can separate individual actinides selectively from the spent fuel [2][3].

Chapter 2

Ligands for nuclear waste treatment

There are several ligands that have been researched to extract the lanthanides (Ln(III)) and actinides(An(III)) from the HLW. Since this research is about diglycolamide(DGA)-based ligands, this chapter is divided into two parts: non DGA-based and DGA-based ligands. Only a selection of all possible ligands will be described, because there are too many possibilities. So a few ligand types are chosen to look into: organophosphorous ligands, malonamides and DGA-based ligands.

2.1 Non DGA-based ligands

The non DGA-based ligands can be divided again themselves into several classes. organophosphorous ligands and malonamides. Both have been extensively investigated and applied in a process [4].

2.1.1 Organophosphorous ligands

Tri-*n*-butyl phosphate (TBP) is being used for the chemical separation of uranium and plutonium from the waste. A variation to this, diamylamyl phosphonate, cannot only separate uranium and plutonium, but also Am(III) in *n*-dodecane solution out of the waste.

In China a process for the removal of transuranic elements out of HLW was developed by using trialkylphosphine oxides (TRPOs) [5]. This was further developed by coupling two of these groups via a CH_2 -bridge. More complex structures based on the CH_2 -bridged organophosphorous ligands were developed like octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) [6] and diphenyl(diisobutylcarbamoylmethyl)phosphine oxide ($\text{Ph}_2\text{iBu}_2\text{-CMPO}$) [7]. A process to extract all minor actinides and lanthanides from a HNO_3 medium was developed, by using a mixture of CMPO and TBP [3]. The chemical structures of the organophosphorous ligands can be found in Figure 2.1.

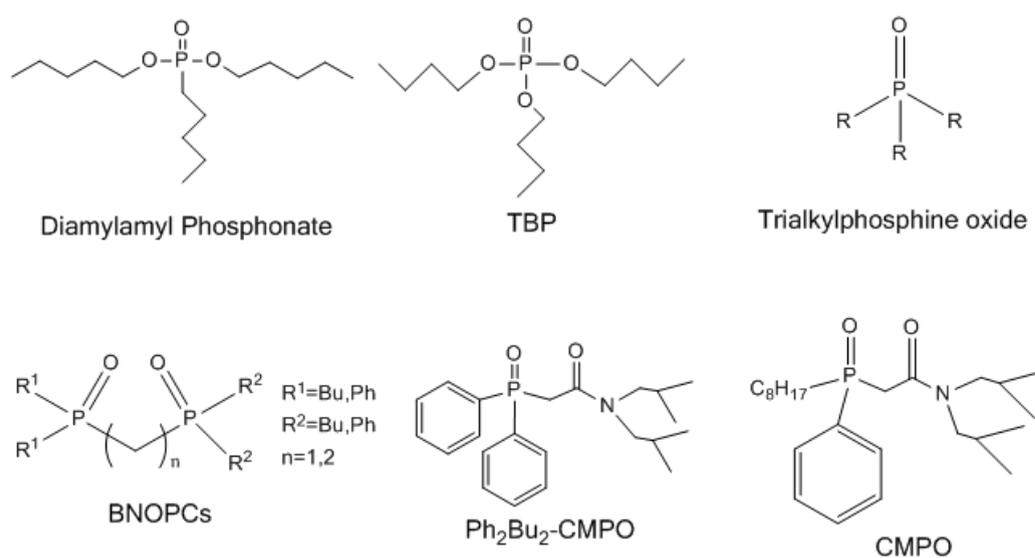


FIGURE 2.1: Different organophosphorous ligands

2.1.2 Malonamides

Malonamides are bidentate oxygen donor ligands and are used for the extraction of An(III) and Ln(III) in the PUREX process. Compared to the phosphorous ligands there is less secondary waste produced in this process. The DIAMEX process proved to proceed better using of $\text{R}^1\text{R}^2\text{NCOCHR}^3\text{CONR}^2\text{R}^1$ -based ligands [8]. Several useful ligands involve: *N,N'*-dimethyl-*N,N'*-dibutyltetradecylmalonamide (DMDBTDMA), *N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-hexyl-oxylethyl)malonamide (DMDOHEMA) [9] and bicyclic malonamides [3]. The structures of the different malonamides are shown in Figure 2.2.

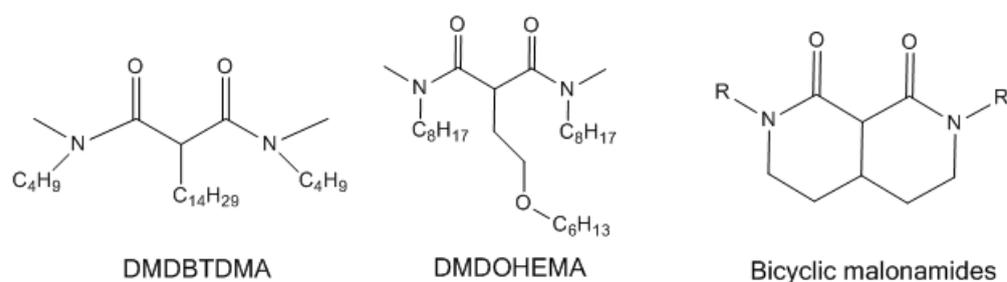


FIGURE 2.2: Different malonamides

2.2 DGA-based ligands

In 1996 Choppin and Sasaki proved that glycolamide-based structures have better extraction properties towards lanthanides than the ligands described above [10]. Because of the use of a tridentate ligand instead of a bidentate ligand also the affinity for lanthanides was increased [11]. DGA derivatives have been synthesized with varying chain lengths, however, *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) was proven to have the best extraction properties, highest stability and best solubility in aliphatic solvents. (Figure 2.3) However, three TODGA units need to cluster around an actinide or lanthanide to be able to extract it. The extraction efficiency can be considerably enhanced by preorganizing DGA units on a molecular platform [12]. Excellent results were obtained with DGA-containing di- [13] and tripodal- [14] [15] and calix[4]arene-based ligands [16].

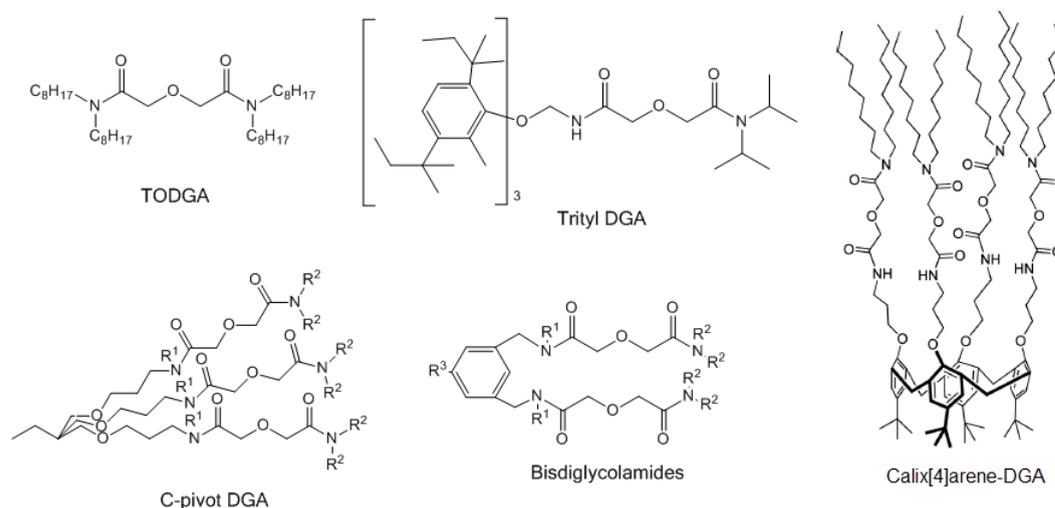


FIGURE 2.3: Different glycolamides

2.3 Thesis project

There are many more possibilities to preorganize ligands, but if you want to do decent research in ten weeks, a choice has to be made among all of them. The structures should be simpler than the ones studied before and relatively easy to make, because mass production has to be possible. That is why the thesis project is limited to coupling of DGA to simple commercially available platforms. Both platforms used are amino group-containing platforms that can preorganize 3 DGA ligands. The first platform is tris(2-aminoethyl)amine (TREN), a structure with 3 aminoethyl groups, connected to a central amine. The second platform is triazacyclononane, a cyclic compound. The structures of both platforms can be found in Figure 2.4.

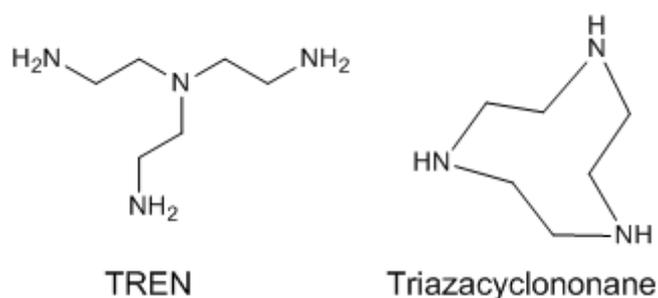


FIGURE 2.4: TREN and Triazacyclononane platforms

Chapter 3

Results and discussion

The synthesis of the target compounds **4** and **5** is summarized in Scheme 3.1. It involves the reaction of glycolic anhydride (**1**) with di-*n*-octylamine followed by activation of the carboxylic acid group by reaction with *p*-nitrophenol [3]. Subsequently, the *p*-nitrophenol activated DGA (**3**) is reacted with the appropriate amino group-containing platforms.

3.1 Synthesis DGA

The diglycolamide (**2**) was synthesised by a nucleophilic addition of di-*n*-octylamine to a glycolic anhydride (**1**) in a 99% yield following the procedure reported by Djedovič et al. [17]. The formation of DGA clearly followed from the characteristic triplets in the ¹H NMR spectrum at 3.09 ppm and 3.35 ppm.

3.2 Synthesis *p*-nitrophenol activated DGA

The synthesis of *p*-nitrophenol activated DGA (**3**) was carried out in two different ways. Namely in acetonitrile with EDC as water scavenger and HOBT as activator and in pyridine with DCC as water scavenger. The procedure using DCC was described in literature, but the formed 'DCC urea' is much harder to remove than 'EDC urea'. DGA (**2**) was reacted with *p*-nitrophenol via an esterification reaction to afford the *p*-nitrophenol

activated DGA ester (**3**). For both reactions the procedure was the same. The purification of the product proved to be difficult. Following the procedure described in ref [16]. During the washing with base and the column chromatography the product decomposed into the starting materials. This because the activation of the ester gives rise to not only a higher reactivity with the platform, but also with other chemical such as the basic solution and the silica.

By adding the reactants in a one to one ratio and only washing with Milli-Q water the product (**3**) was obtained in 60% yield. The formation of the ester followed from the ^1H NMR spectrum as the peaks of the protons on the *p*-nitrophenol ring shifted from 6.91 ppm to 7.33 ppm and from 8.10 ppm to 8.28 ppm.

3.3 Functionalization of the amino group-containing platform

3.3.1 Coupling to tris(2-aminoethyl)amine

Tris(2-aminoethyl)amine (TREN) has three amino groups to which the DGA can be attached. This can be done in two ways, direct coupling, or via activated DGA (**3**). Earlier studies done by Iqbal [3] have shown that indirect coupling of DGA to an amino group-containing platforms via *p*-nitrophenol activated DGA gives a 3 times higher yield than direct coupling.

p-Nitrophenol activated DGA (**3**) was reacted with tris(2-aminoethyl)amine via an amidation in a 86% yield. There was some product lost during the work-up, because it was difficult to get the product out of the column, due to the polarity.

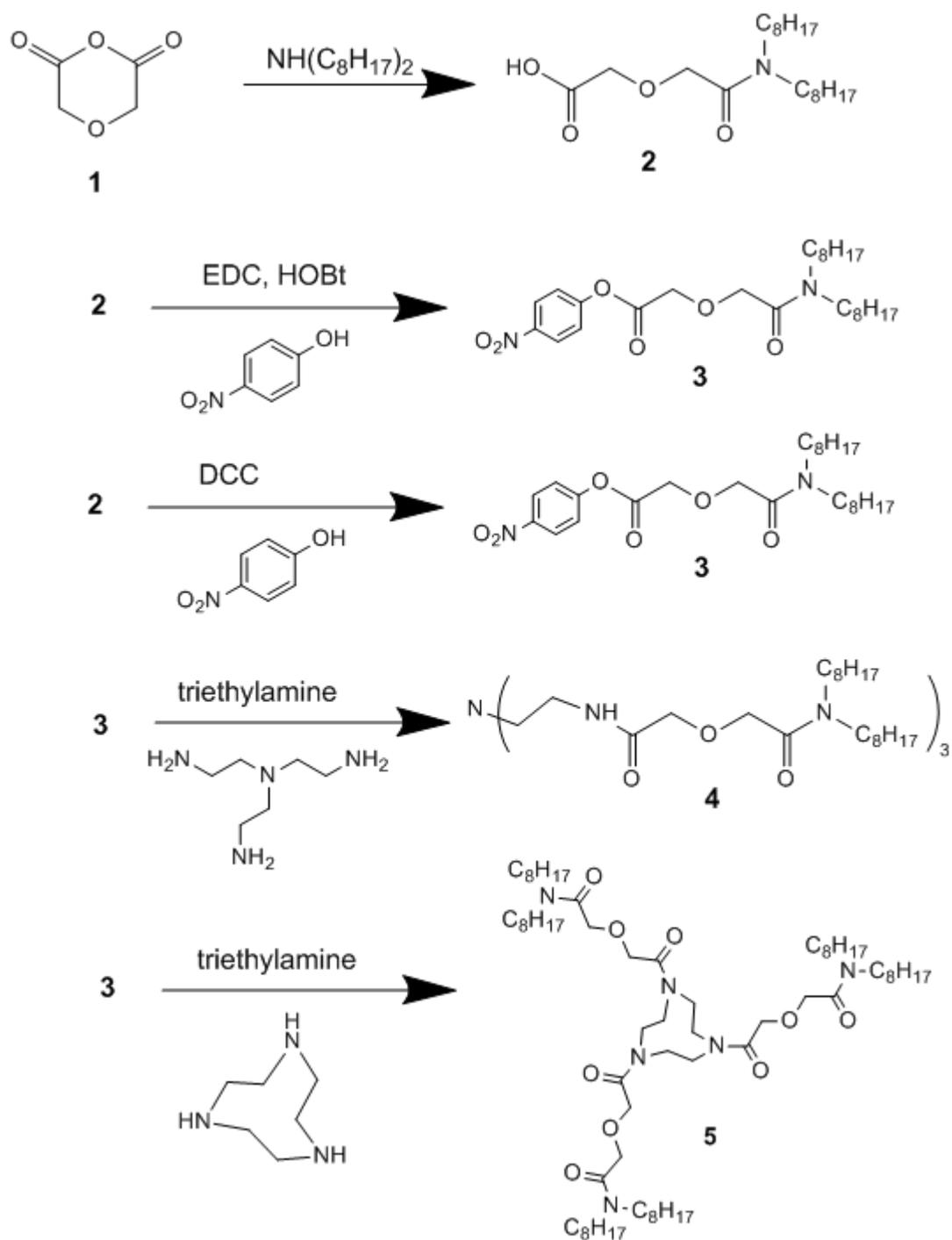
The formation of the product followed from the ^1H NMR spectrum, because of the characteristic peak at 7.85 ppm that shows the three NH groups where the DGA and TREN are coupled. Also the mass spectrum shows a nice result, the mass of 1164.7916 which is the molecular weight of the molecule plus a proton.

3.3.2 Coupling to triazacyclononane

The same procedure as the functionalization of TREN was used, because of the high yield afforded there.

p-Nitrophenol activated DGA (**3**) was reacted with triazacyclononane via an amidation in a 35% yield. There was product lost during the work-up, because it was difficult to get the product out of the column, due to the polarity, and there were some mixed fractions from which the product could not be separated.

The ^1H NMR spectrum shows some inconsistency of the integrals, but the total number is correct, probably because the different signals from the NCH_2 bonds in the ring are divided over several peaks, due to ring strain. The mass spectrum shows the mass of 1148.7599 which is the molecular weight of the molecule plus a proton.



SCHEME 3.1: Overview of reactions

Chapter 4

Conclusion and outlook

Two different diglycolamide-functionalized tripodal ligands were successfully prepared by reaction of a *p*-nitrophenol activated ester with TREN and triazocyclononane. The extraction properties towards An(III) and Ln(III) will be determined in the BARC institute in Mumbai, India.

If preorganization shows improvement of the extraction properties, other commercially available platforms can be synthesised, using the procedure that now has been developed. Possible structures are: different generations of dendrimers or *1,3,5*-triamino-*1,3,5*-trideoxy-*cis*-inositol shown in Figure 4.1.

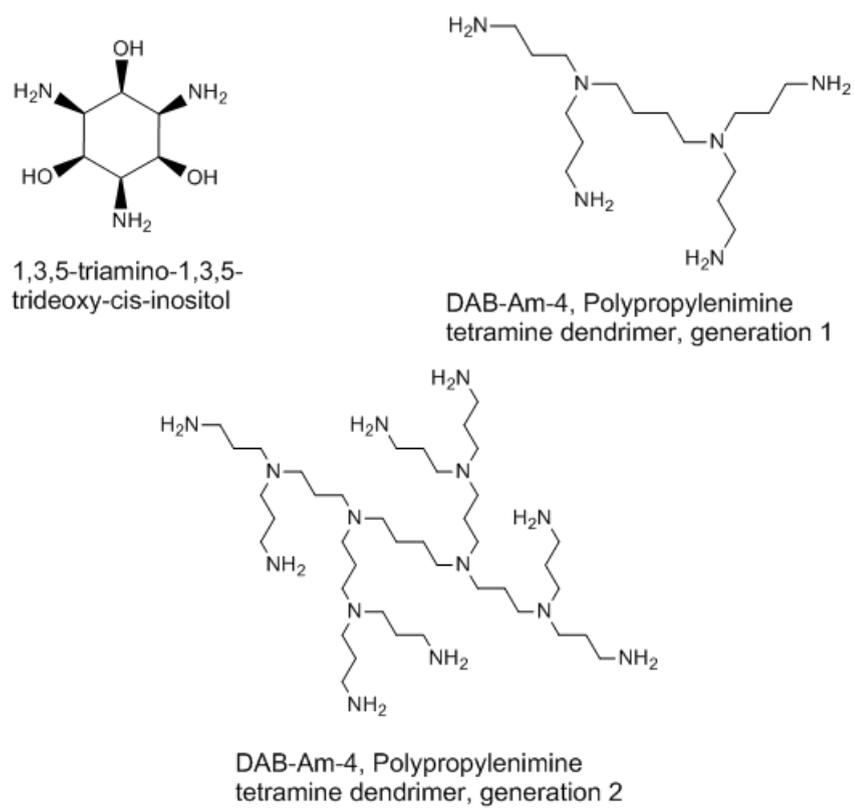


FIGURE 4.1: Platform suggestions for further research

Chapter 5

Experimental

All moisture-sensitive reactions were carried out under a nitrogen atmosphere. The represented reaction times are not optimized for the reactions. The solvents and all reagents were obtained from commercial sources and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Ascend (400 MHz) spectrometer. ^1H NMR (400 MHz) and ^{13}C NMR (75 MHz) chemical shift values are reported as δ using the CDCl_3 solvent signal as an internal standard. High resolution mass spectra were recorded on a Waters Micromass LCT mass spectrometer. Infrared spectra were recorded on a Thermo Scientific. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). Analytical TLC was done using Merck prepared plates (silica gel 60 F-254 on aluminium).

5.1 Synthesis DGA (**2**)

The synthesis of DGA (**2**) was done following a procedure described by Djedovič et al. [17].

A solution of di-*n*-octylamine (27.12 g, 112.32 mmol) and diglycolic anhydride (**2**) (16.30 g, 140.40 mmol) in THF (600 mL) was refluxed over the weekend under a N_2 atmosphere. The solvent was evaporated and the crude product was dissolved in CH_2Cl_2 (50 mL), washed with 10% aq. HCl (3x 50mL). The organic layer was dried with anhydrous MgSO_4 and the organic layer was evaporated to dryness to obtain DGA (**2**) in 99% yield.

^1H NMR: δ 0.80-0.91 (6H, m, CH_3), 1.20-1.35 (20H, m, $\text{CH}_3(\text{CH}_2)_5$), 1.44-1.61 (4H, m, NCH_2CH_2), 3.08 (2H, t, $J=1.44$ Hz, $\text{CH}_2\text{CH}_2\text{N}$), 3.35 (2H, t, $J=1.44$ Hz, $\text{CH}_2\text{CH}_2\text{N}$), 4.21 (2H, s, COCH_2O), 4.38 (2H, s, COCH_2O).

5.2 Synthesis *p*-nitrophenol activated DGA (**3**) method A

The synthesis of *p*-nitrophenol activated DGA (**3**) was performed by an adapted procedure reported by Mohapatra et al. [16].

A solution of *N,N*-dioctylglycolic acid (**2**) (1.0 g, 2.8 mmol), *p*-nitrophenol (0.405 g, 2.75 mmol), EDC (0.55 g, 2.8 mmol), HOBT (0.39 g, 2.8 mmol) and triethylamine (0.6 g, 3.0 mmol) in acetonitrile (30 mL) was stirred overnight at room temperature. The solvent was evaporated and the residue was dissolved in *n*-hexane (50 mL), filtered and the filtrate was washed with 4% NaHCO_3 (8x 50 mL) solution. The organic layer was dried with anhydrous MgSO_4 and concentrated under reduced pressure.

After the purification the ^1H NMR spectrum showed so many peaks that it was impossible to analyse the different components.

5.3 Synthesis *p*-nitrophenol activated DGA (**3**) method B

(*Method B1*) The synthesis of *p*-nitrophenol activated DGA (**3**) was performed by an adapted procedure reported by Mohapatra et al. [16].

A solution of *N,N*-dioctylglycolic acid (2.0 g, 5.6 mmol), *p*-nitrophenol (0.81 g, 5.7 mmol) and DCC (1.22 g, 5.6 mmol) in pyridine (60 mL) was stirred overnight at room temperature. The solvent was evaporated and the residue was dissolved in *n*-hexane (50 mL), filtered and the filtrate was washed with 4% NaHCO_3 (6x 50 mL) solution. The organic layer was dried with anhydrous MgSO_4 and concentrated under reduced pressure. The residue was separated by column chromatography (CH_2Cl_2 :MeOH, 98:2) giving DGA and *p*-nitrophenol and almost no activated DGA.

(*Method B2*) Because the product kept falling apart the procedure was changed to a 1 to 1 ratio of *p*-nitrophenol to DGA and all the purification steps after the filtration were replaced by washing with Milli-Q water, drying with anhydrous MgSO_4 and evaporation

of the organic layer to obtain *p*-nitrophenol activated DGA in 60% yield.

^1H NMR: δ 0.80-0.91 (6H, m, CH_3), 1.14-1.38 (20H, m, $\text{CH}_3(\text{CH}_2)_5$), 1.45-1.60 (4H, m, NCH_2CH_2), 3.18 (2H, t, $J=1.2$ Hz, $\text{CH}_2\text{CH}_2\text{N}$), 3.32 (2H, t, $J=1.2$ Hz, $\text{CH}_2\text{CH}_2\text{N}$), 4.37 (2H, s, OCH_2O), 4.58 (2H, s, OCH_2O), 7.33 (2H, d, ArH), 8.28 (2H, d, ArH)

5.4 Functionalization of the amino group-containing platforms

5.4.1 DGA-functionalized TREN(4)

A mixture of TREN (0.0395 g, 0.27 mmol), *p*-nitrophenol activated DGA (**3**) (0.48 g, 1 mmol) and triethylamine (0.13 g, 1.3 mmol) in toluene (30 mL) was refluxed for 1 day. The crude reaction mixture was washed with 1M NaOH (5x 50 mL) and H_2O (5x 50 mL) to remove *p*-nitrophenol, filtered and washed again with H_2O . The organic layer was dried with anhydrous MgSO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2 , CH_2Cl_2 :MeOH = 96 : 4 \rightarrow 85 : 15) to afford **4** as a light brown oil in 86% yield.

^1H NMR: δ 0.80-0.91 (18H, m, CH_3), 1.19-1.38 (66H, m, $\text{CH}_3(\text{CH}_2)_5$, NHCH_2CH_2), 1.42-1.51 (12H, m, NCH_2CH_2), 2.56 (6H, t, $J=0.78$ Hz, $\text{CH}_2\text{CH}_2\text{N}$), 3.09 (6H, t, $J=0.78$ Hz, $\text{CH}_2\text{CH}_2\text{N}$), 3.28 (6H, t, $J=1.08$ Hz, NHCH_2), 3.34 (6H, q, $J=0.72$ Hz, $\text{N}(\text{CH}_2)_3$), 4.07 (6H, s, OCH_2O), 4.27 (6H, s, OCH_2O), 7.85 (3H, s, NH)

^{13}C NMR: δ 14.1, 22.6, 27.1, 27.7, 28.9, 29.2, 29.25, 29.3, 29.4, 31.7, 37.2, 46.1, 46.8, 53.9, 69.4, 71.4, 76.7, 77.0, 77.2, 168.3, 169.7

5.4.2 DGA-functionalized Triazacyclononane (5)

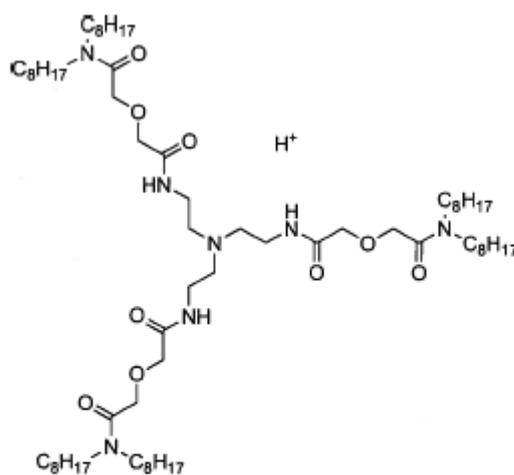
A mixture of triazacyclononane (0.0430 g, 0.27 mmol), *p*-nitrophenol activated DGA (**3**) (0.48 g, 1 mmol) and triethylamine (0.114 g, 1 mmol) in toluene (30 mL) was refluxed for 2 days. The crude reaction mixture was washed with 1M NaOH (10x 50 mL) and H_2O (5x 50 mL) to remove *p*-nitrophenol. The organic layer was dried with anhydrous MgSO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2 , CH_2Cl_2 :MeOH = 97 : 3 \rightarrow 85 : 15) to afford the product in 35% yield. ^1H NMR: δ 0.80-0.91 (18H, m, CH_3), 1.19-1.38 (60H, m, $\text{CH}_3(\text{CH}_2)_5$),

1.38-1.58 (12H, m, NCH₂CH₂), 1.8-2.3 (7H, m, CH₂CH₂N), 2.9-3.5 (14H, m, OCH₂O, CH₂CH₂N), 3.7-4.4 (15H, m, OCH₂O, CH₂CH₂N)

¹³C NMR: δ 14.1, 22.6, 22.7, 26.9, 27.2, 27.5, 29.2, 29.4, 29.4, 29.5, 31.7, 31.8, 76.7, 77.0, 77.2

Appendix A

DGA-functionalized TREN



Chemical Formula: $C_{86}H_{130}N_7O_9^+$

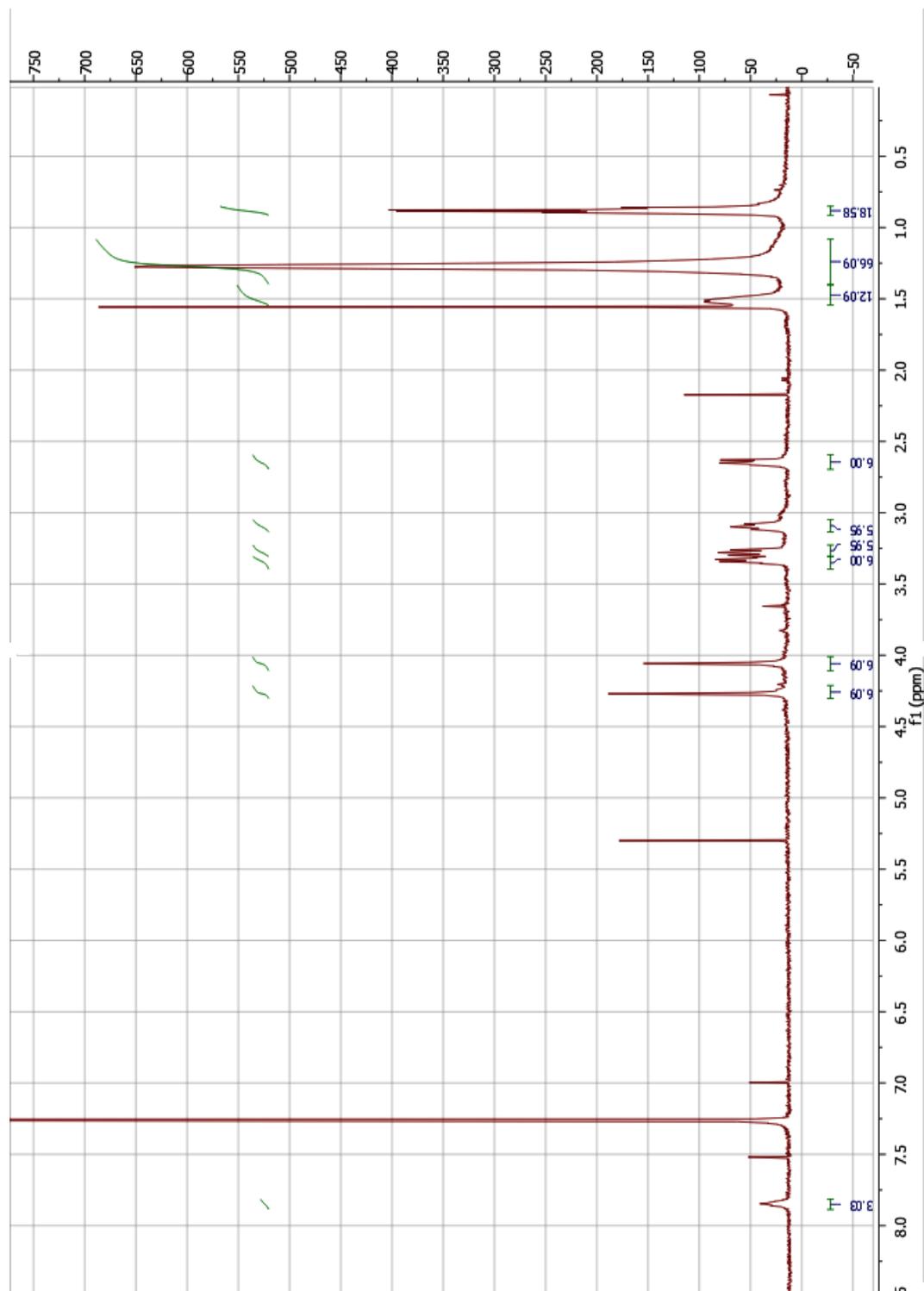
Exact Mass: 1164,9925

Molecular Weight: 1165,7794

m/z: 1164.9930 (100.0%), 1165.9964 (71.4%), 1166.9997 (25.1%), 1168.0031 (5.8%), 1165.9900 (2.6%), 1166.9972 (1.8%), 1166.9934 (1.8%), 1165.9993 (1.5%), 1168.0006 (1.3%), 1167.0026 (1.1%)

Elemental Analysis: C, 68.00; H, 11.24; N, 8.41; O, 12.35

FIGURE A.1: Analysis of DGA-functionalized TREN

FIGURE A.2: ^1H NMR of DGA-functionalized TREN

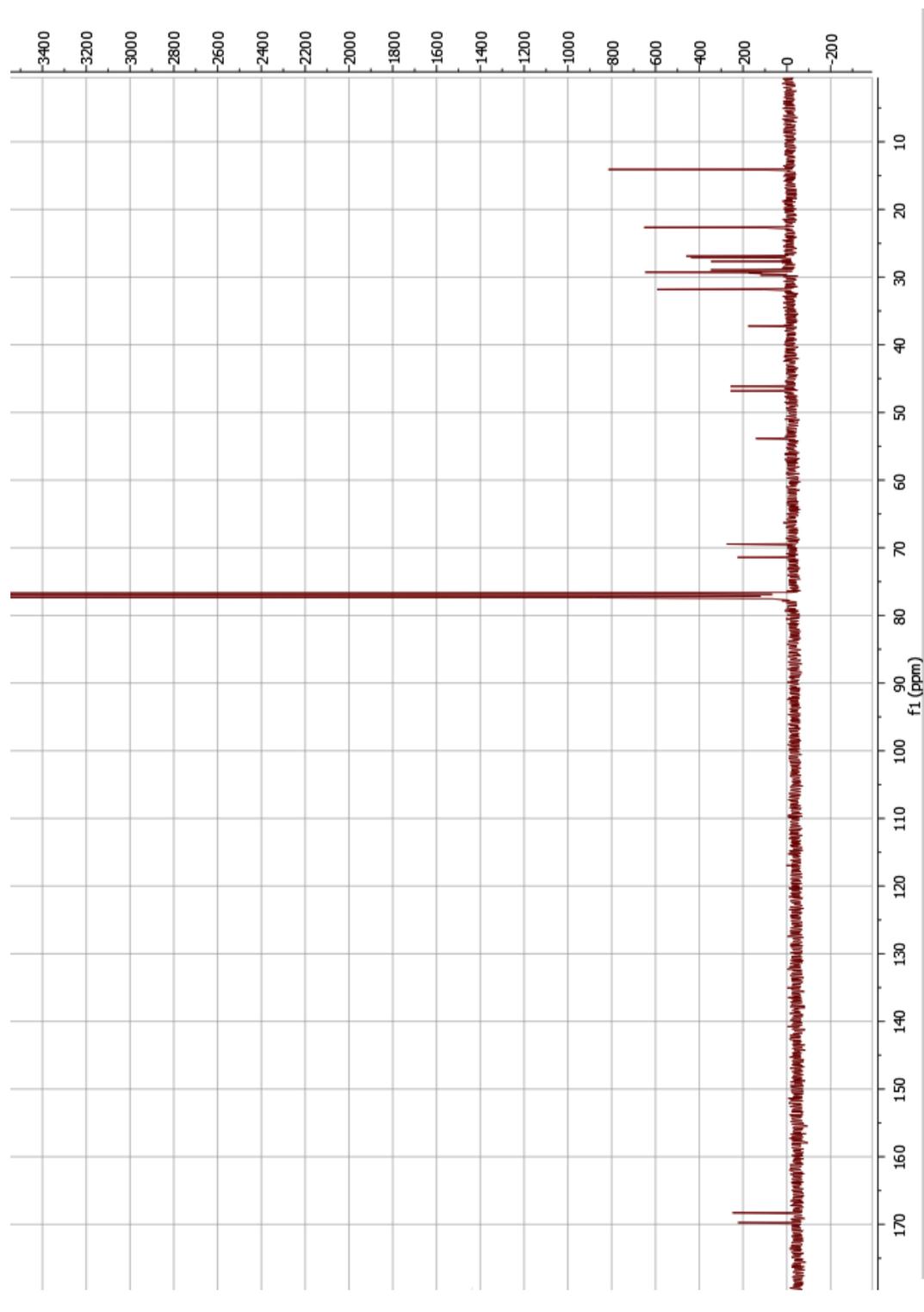
FIGURE A.3: ^{13}C NMR of DGA-functionalized TREN



FIGURE A.4: Mass spectrum of DGA-functionalized TREN

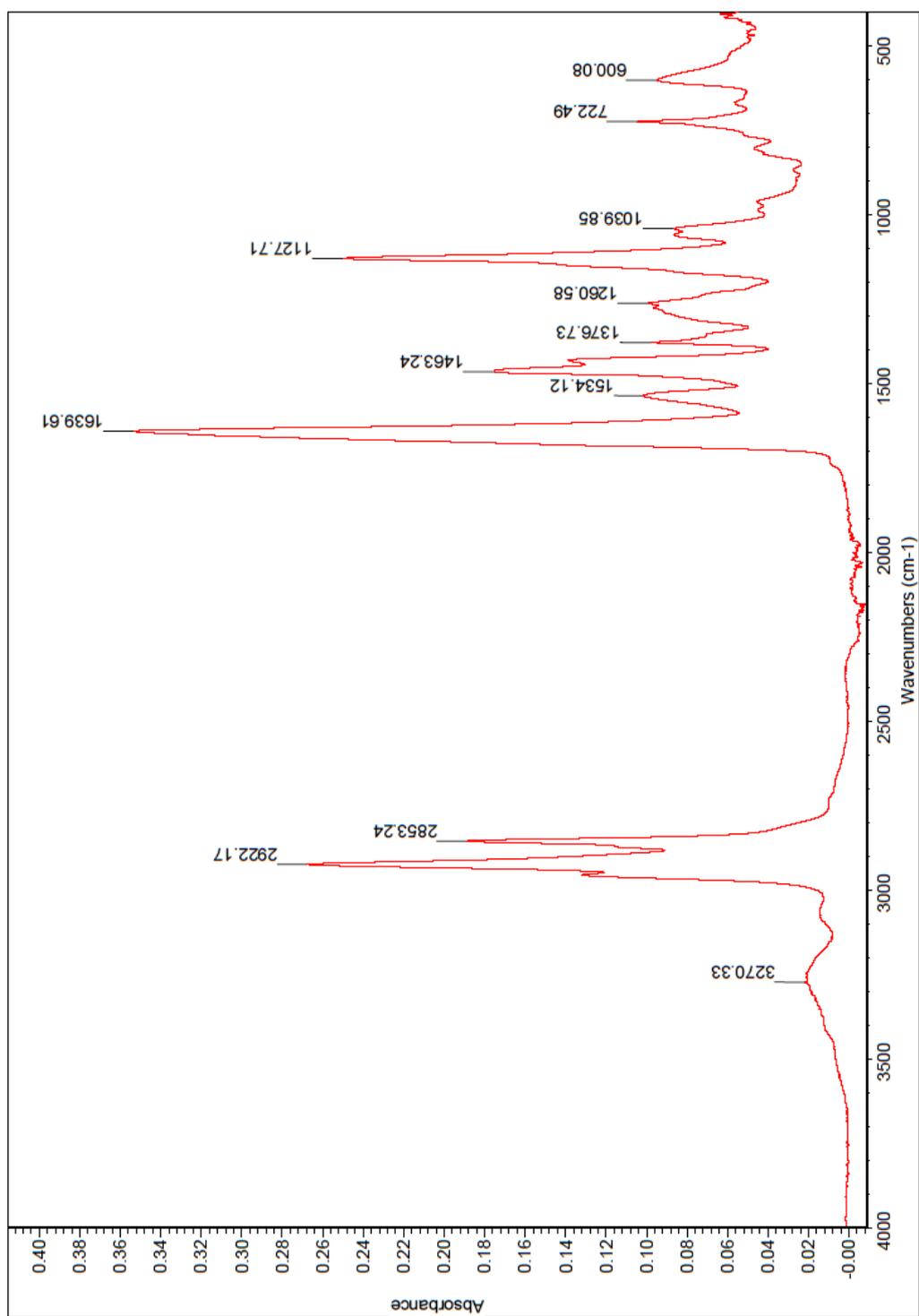
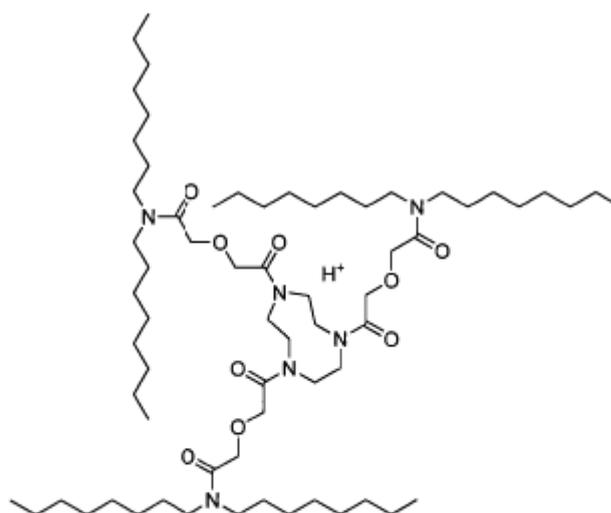


FIGURE A.5: Infrared spectrum of DGA-functionalized TREN

Appendix B

DGA-functionalized triazacyclononane



Chemical Formula: $C_{65}H_{127}N_6O_9^+$

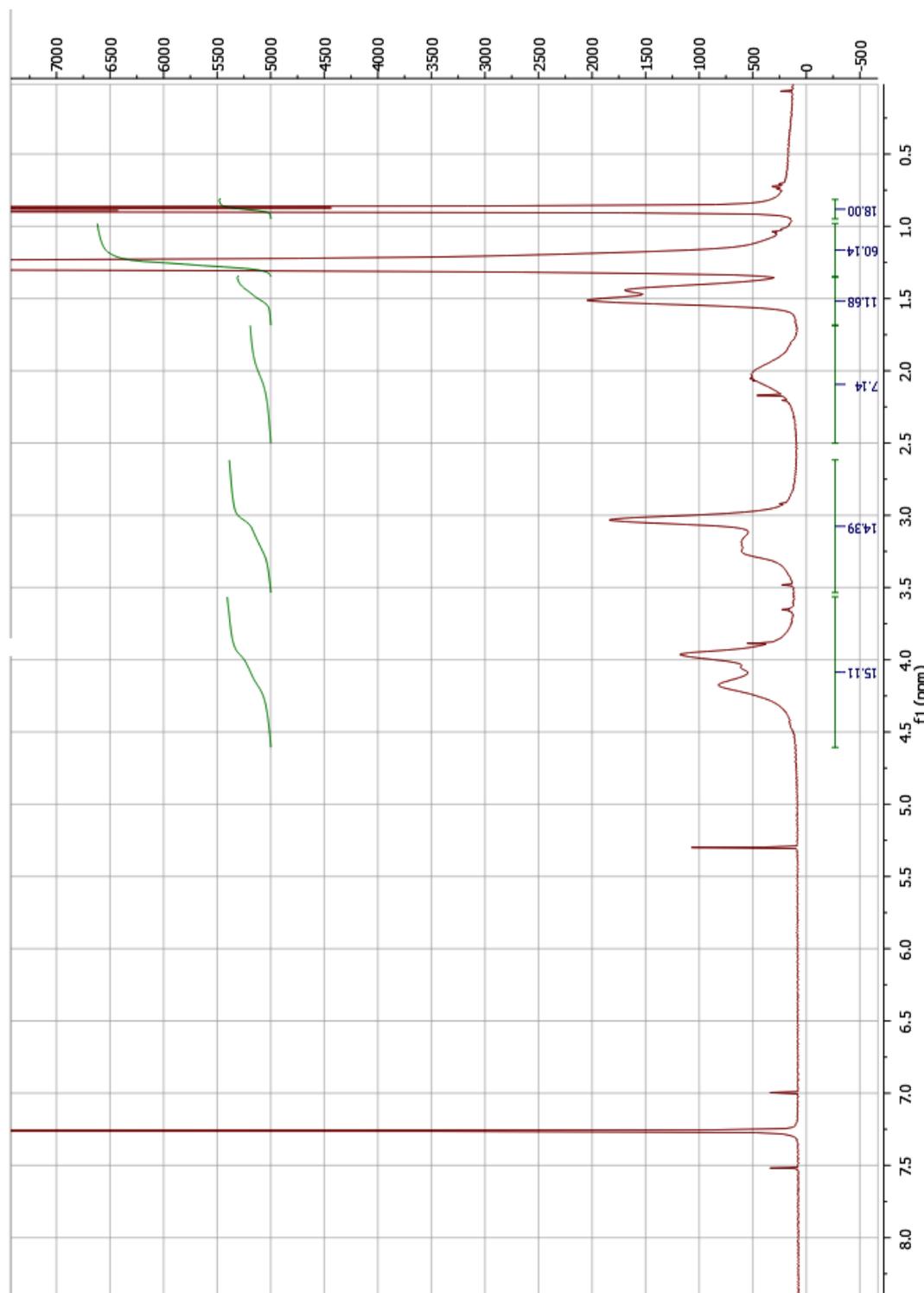
Exact Mass: 1147,9659

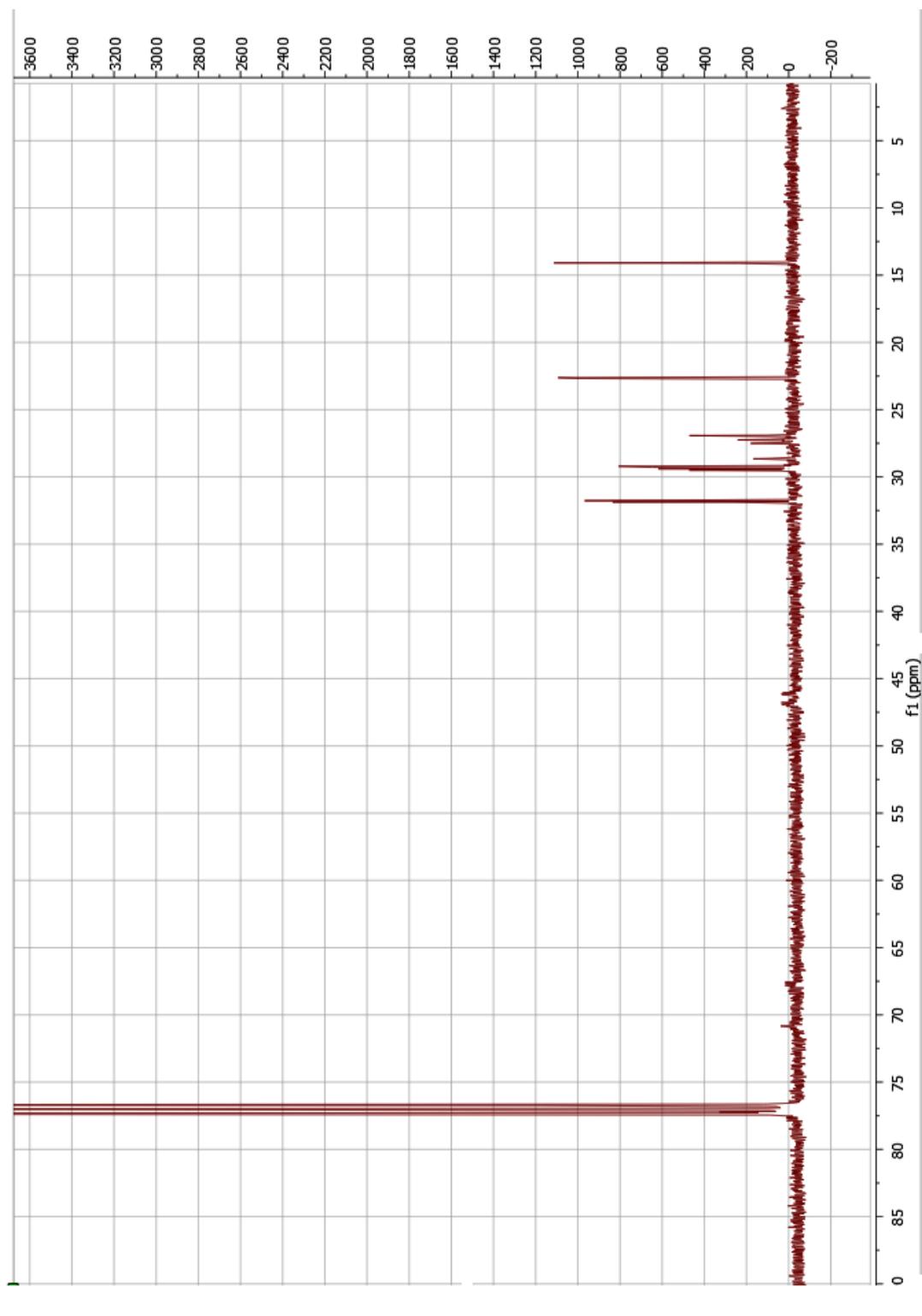
Molecular Weight: 1148,7488

m/z : 1147.9665 (100.0%), 1148.9698 (71.4%), 1149.9732 (25.1%), 1150.9765 (5.8%), 1148.9635 (2.2%),
1149.9707 (1.8%), 1149.9668 (1.6%), 1148.9727 (1.5%), 1150.9741 (1.3%), 1149.9761 (1.0%)

Elemental Analysis: C, 69.01; H, 11.14; N, 7.32; O, 12.53

FIGURE B.1: Analysis of DGA-functionalized triazacyclononane

FIGURE B.2: ^1H NMR of DGA-functionalized triazacyclononane

FIGURE B.3: ^{13}C NMR of DGA-functionalized triazacyclononane

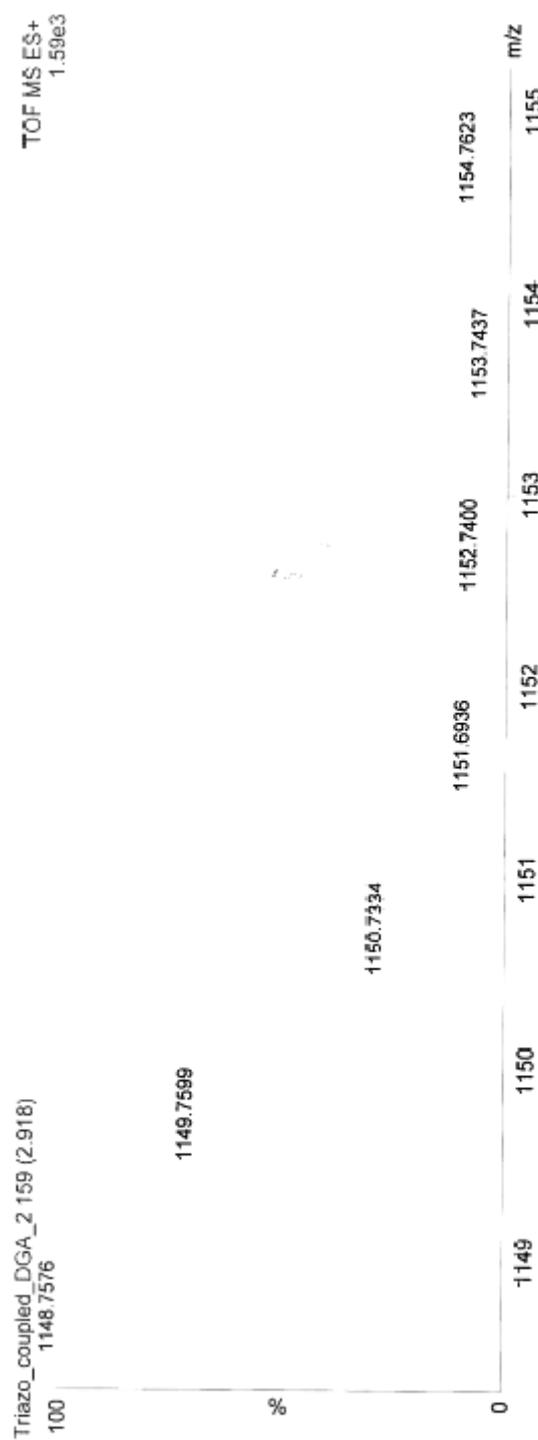


FIGURE B.4: Mass spectrum of DGA-functionalized triazacyclononane

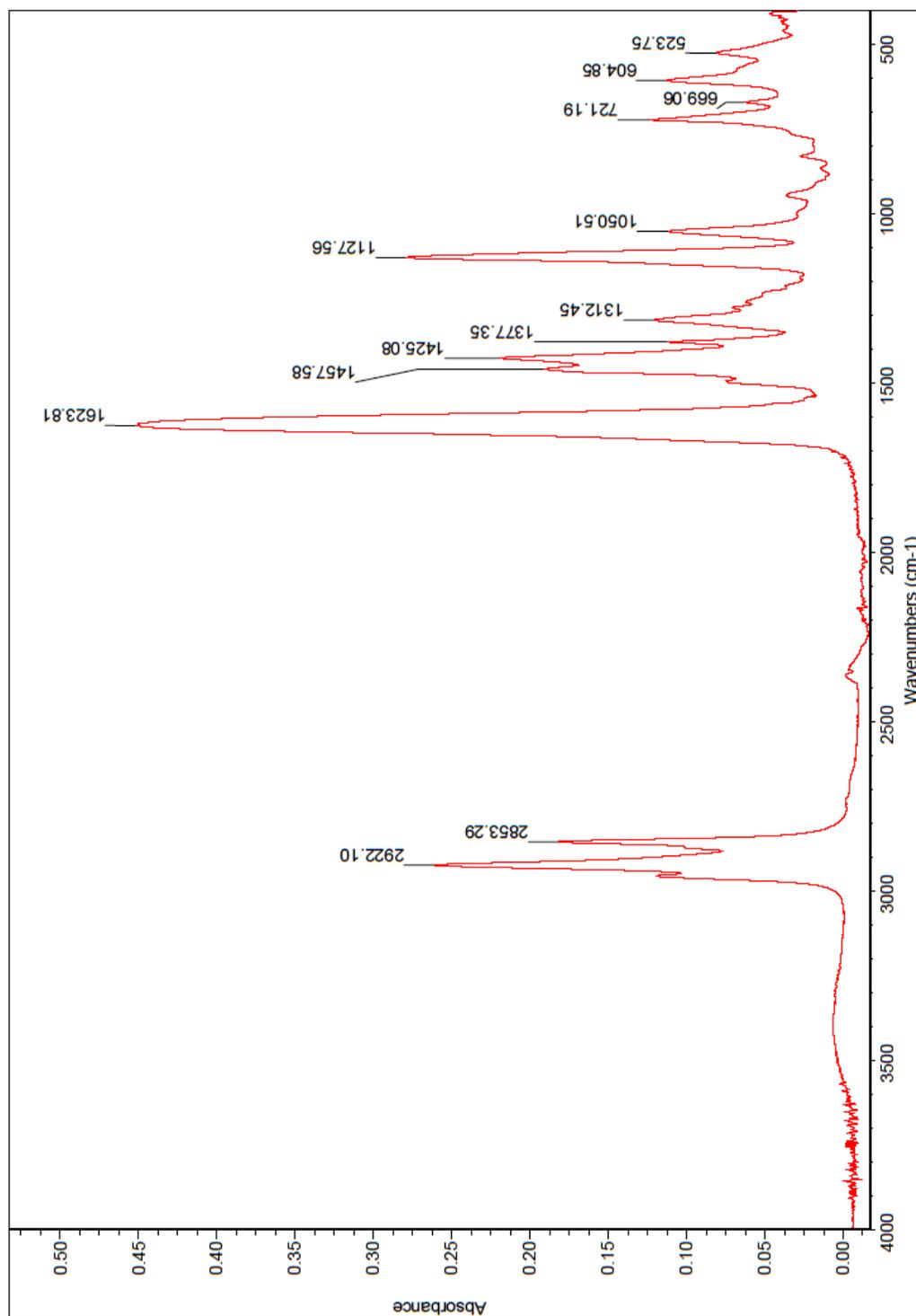


FIGURE B.5: Infrared spectrum of DGA-functionalized triazacyclononane

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