Supporting Information

Valorization of Polyoxymethylene (POM) Waste as a C_1 Synthon for Industrially Relevant Dialkoxymethanes and Cyclic Aminals

Matthew J. Cullen[a],[b], Matthew G. Davidson*[a],[b], Matthew D. Jones*[a],[b], and Jack A. Stewart[a]

[a] Department of Chemistry, University of Bath, Claverton Down, Bath, United Kingdom, BA2 7AY. E-mail: mj205@bath.ac.uk

[b] Institute of Sustainability and Climate Change, University of Bath, Claverton Down, Bath, United Kingdom, BA2 7AY. E-mail: chsmgd@bath.ac.uk

Table of Contents

1. Methods and Characterisation

1.1 General Considerations, Methods, and Materials

All depolymerisations were conducted under an argon atmosphere using standard air-sensitive techniques with oven-dried glassware and a Schlenk Line or argon-filled MBraun LABmaster dp glovebox unless otherwise stated.

Polyoxymethylene (POM) was purchased from Merck (Goodfellow homopolymer, POMH, 3 mm nominal granule size) and was used for all alcoholysis and aminolysis scope reactions. Keck® branded laboratory glassware clips purchased from Merck were used as post-consumer POM waste. Poly(lactic acid) (PLA) was purchased commercially (PLLA cup, M_n ~ 45,500 g/mol, *Vegware*™, R600Y-VW). Poly(bisphenol A carbonate) (BPA-PC) pellets were purchased from Merck (M_n ~ 45,000 g/mol). Poly(butylene terephthalate) pellets were purchased from Merck (M_v ~ 38,000 g/mol). Poly(ethylene terephthalate) (PET) was purchased locally (UK, Fanta bottle, *The Coca-Cola Company*™, M_n ~ 40,000 g/mol) and washed and dried before use.

All non-polymer reagents and solvents were purchased from Merck or Fisher Scientific and used without further purification.

All reaction temperatures noted in the manuscript and experimental procedures are the temperatures the oil baths were set to. The actual temperature inside the reaction vessel is likely slightly lower due to refluxing reagents. An unsealed J Young's ampoule containing 1,4-dioxane was immersed in an oil bath held at 100.0 °C. A thermocouple inside the ampoule measured a stable internal temperature of 96.5 °C.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 400 MHz instrument and referenced to residual solvent peaks. Depolymerisation conversion to product was calculated using trimethoxybenzene (TMB) as an internal standard. Typically, a 65 µL aliquot of the crude reaction mixture was taken using a micropipette. This was spiked with 25 µL of a stock solution of TMB in toluene of known concentration and dissolved in an appropriate deuterated solvent. A diagnostic product peak, typically the methylene bridge protons found at ~4.6 ppm on the ^{1}H NMR spectrum, was integrated against the aromatic protons of the TMB internal standard to calculate conversion to product. Diffusion ordered spectroscopy (DOSY) spectra were recorded on a Bruker 500 MHz instrument. Thermogravimetric analysis (TGA) was conducted on a Setsys

Evolution TGA 16/18 (Setaram). Samples, under a constant flow of argon, were heated from room temperature to 300 °C at a heating rate of 10 °C/min to determine if thermal degradation would occur at reaction temperatures.

Mixed plastic depolymerisations were conducted identically to single plastic depolymerisations (the methods of which are described below) with the addition of the 'contaminant' plastic at the start of the reaction. Upon observation of complete consumption of the plastic being degraded, the contaminant was washed with acetone, dried, and weighed.

$Zn(BAP)_2$, structure shown in Figure S1, was used for mixed plastic depolymerisations. It was reported by Jones *et al.* in a 2022 paper, and is referred to in the original paper as $Zn(2)_2$.[1] The ligand has been abbreviated to BAP for readability, the full name is: 2,4-di**b**romo-6-(((3-(dimethylamino)propyl)**a**mino)methyl)**p**henol.

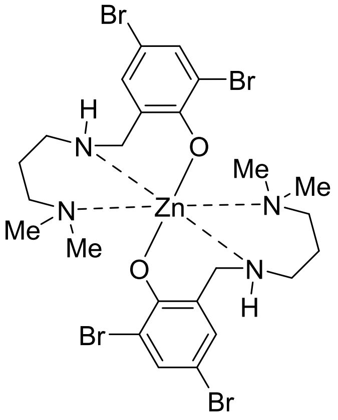


Figure S1 – Structure of $Zn(BAP)_2$, the catalyst used for BPA-PC, PET, and PBT depolymerisations. Reported by Jones *et al.*[1]

1.2 POM Characterisation

As discussed above, the POM granules used in this manuscript are POM homopolymer purchased from Merck and produced by Goodfellow. Due to the polymer's general insolubility, measuring the molecular weight of POM is extremely difficult. Berer *et al.* in 2014 used SEC to measure the molecular weight and dispersity of Delrin 100, reporting a M_w of 146 kDa and a Đ of 2.6.[2] To determine if the POM samples used in this manuscript were of similarly high molecular weight, diffusion-ordered spectroscopy (DOSY) was used to measure the diffusion coefficient of both the POM granules used in all alcoholysis and aminolysis reactions as well as the Keck® clips used for mixed plastic depolymerisations. Spectra were collected in neat 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) without the addition of a deuterated solvent, shimming directly on the HFIP methine proton. The measured diffusion coefficient was then used to estimate the material's molecular weight using Mass Determination Diffusion Ordered Spectroscopy (MaDDOSY), a technique recently published by Haddleton *et al*.[3] Results are presented in Table S1.

Table S1 – Diffusion coefficients and estimated molecular weights of POM samples.

Entry	POM Sample	Supplier	Material Trade Name	Diffusion Coefficient [m²/s]	Estimated M_w [kDa]
1	Keck® Clip	Merck (DuPont)	Delrin	9.95×10^{-12}	125
2	Granules	Merck (Goodfellow)	-	8.61×10^{-12}	159
3	Granules, mid-reaction[a]	-	-	3.88×10^{-11}	12.7

[a] – Polymer taken from a POM ethanolysis reaction in standard reaction conditions (see Section 1.3) after 1.5 hrs. Pellets were rinsed with acetone, air dried, dissolved in HFIP, and analysed by DOSY to demonstrate a reduction in M_w as a result of the reaction.

The MaDDOSY estimated molecular weights of both the Keck® clip and the virgin granules broadly agree with the data reported by Berer *et al*. While this is by no means a definitive or absolute measure of the samples' molecular weights, it does strongly suggest that the samples are of high molecular weight. The MaDDOSY technique does not estimate M_n, so the dispersity of the samples could not be estimated.

The acetyl end groups of the polymer were not found in any analysis. Due to the high molecular weight of the polymer, the acetyl end groups make up <0.1% of the mass of an average chain and are too low in abundance to be detected. The mass of the end groups was deemed to be negligible and omitted when calculating polymer equivalents and catalyst loading.

Thermogravimetric analysis was conducted on a POM granule and a portion of a Keck® clip. Each sample was heated under a constant flow of argon to 300 °C to demonstrate the thermal stability of the polymers under reaction conditions (100 – 130 °C, under argon). Results are presented in Figure S2, and clearly show that the onset of thermal degradation is significantly above the temperature of the reactions.

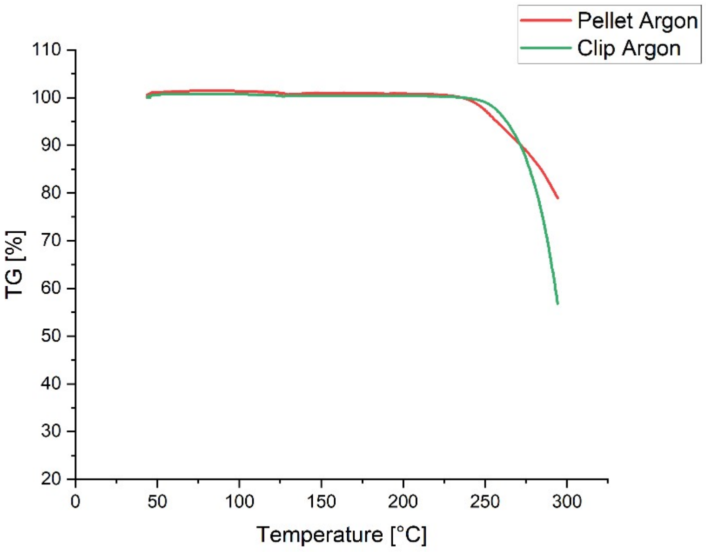


Figure S2 – TGA of POM samples to 300 °C.

1.3 General Procedure for POM Alcoholysis

An oven-dried J Young's ampoule was charged with POM pellets (0.25 g, 8.3 mmol of repeat unit) and a stirrer bar. $Bi(OTf)_3$ (5 mol% loading relative to repeat unit, 0.272 g, 0.415 mmol) was added in a glovebox filled with argon. 1,4-Dioxane (5 mL) and an alcohol (10 eq, 83 mmol) were added by syringe under dynamic argon flow. The ampoule was submerged in a 100 °C oil bath and allowed to warm up before being sealed. Aliquots of the crude (65 µL) were taken under a flow of argon, spiked with trimethoxybenzene as an internal standard, and analysed by ^1H NMR spectroscopy to determine conversion.

1.4 General Procedure for POM Aminolysis

An oven-dried J Young's ampoule was charged with POM pellets (0.25 g, 8.3 mmol of repeat unit) and a stirrer bar. The ampoule was evacuated and flushed with argon three times using a Schlenk line. 1,4-Dioxane or DMSO (5 mL) and a diamine (1.2 eq, 10 mmol) were added by syringe under dynamic argon flow. TfOH (15 mol% loading relative to the repeat unit, 0.11 mL, 1.25 mmol) was added by glass graduated pipette under dynamic argon flow and an argon blanket. The ampoule was submerged in a 130 °C oil bath and allowed to warm up before being sealed. Aliquots of the crude (65 μL) were taken under a flow of argon, spiked with trimethoxybenzene as an internal standard, and analysed by ^{1}H NMR spectroscopy to determine conversion.

1.5 Procedure for Sequential Degradation of BPA-PC / POM Sample

BPA-PC glycolysis proceeded according to a method reported by Jones *et al*.[1]

An oven-dried J Young's ampoule was charged with BPA-PC (0.25 g, 0.98 mmol of repeat unit) sourced from a broken pair of laboratory safety glasses and POM (0.25 g, 8.3 mmol of repeat unit) sourced from a broken keck clip. Zn(BAP)$_2$ (0.01 g, 1.3 mol% relative to BPA-PC repeat unit, 4 wt% relative to BPA-PC) was added in a glovebox filled with argon. 2-MeTHF (4 mL) and *rac*-1,3-butanediol (1.2 eq relative to BPA-PC repeat unit, 0.90 mL, 10 mmol) were added by syringe under dynamic flow of argon. The ampoule was submerged in a 75 °C oil bath for two hours. An aliquot of the crude was taken under a dynamic flow of argon, spiked with trimethoxybenzene as an internal standard, and analysed by ^{1}H NMR spectroscopy to determine conversion to BPA. The unreacted POM was washed with acetone, dried in a vacuum oven at 40 °C for 1.5 h, and weighed to assess mass loss. The POM then underwent ethanolysis according to the general procedure for POM alcoholysis, at a reduced ethanol loading (3 : 1 relative to POM repeat unit) and Bi(OTf)$_3$ loading (1 mol% relative to POM repeat unit).

1.6 Procedure for Sequential Degradation of POM / PET Sample

PET glycolysis proceeded according to a method reported by Jones *et al.*[1]

An oven-dried J Young's ampoule was charged with POM (0.25 g, 8.3 mmol of repeat unit) sourced from a broken keck clip and PET (0.25 g, 1.3 mmol of repeat unit) sourced from a soft drink bottle. The POM then underwent ethanolysis according to the general procedure for POM alcoholysis, at a reduced ethanol loading (3 : 1 relative to POM repeat unit) and $Bi(OTf)_3$ loading (1 mol% relative to POM repeat unit). The unreacted PET was washed with acetone, dried in a vacuum oven at 40 °C for 1.5 h, and weighed to assess mass loss. $Zn(BAP)_2$ (0.01 g, 4 wt% relative to PET) was added in a glovebox filled with argon. Ethylene glycol (20.6 eq relative to the PET repeat unit, 2 mL) was added under a dynamic flow of argon. The ampoule was submerged in a 180 °C oil bath until full consumption of the solid polymer was observed. An aliquot of the crude was taken under a dynamic flow of argon, spiked with trimethoxybenzene as an internal standard, and analysed by ^1H NMR spectroscopy to determine conversion to BHET.

1.7 Procedure for Catalyst Reuse Experiment

An oven-dried 250 mL J Young's ampoule was charged with POM pellets (5.00 g, 167 mmol of repeat unit). $Bi(OTf)_3$ (10.0 wt% loading relative to the polymer, 0.500 g, 0.762 mmol, 0.46 mol% loading relative to the repeat unit) was added in a glovebox filled with argon. Ethanol (48.8 mL, 38.5 g, 835 mmol, 5 eq) and 1,4-dioxane (50 mL) were added by syringe under dynamic argon flow. The ampoule was submerged in a 100 °C oil bath and allowed to warm up before being sealed. The reaction was allowed to proceed for 24h before being cooled to room temperature. A 65 μL aliquot of the crude reaction mixture was taken, spiked with trimethoxybenzene as an internal standard, and analysed by ^1H NMR spectroscopy to determine conversion. The reaction was then reloaded with POM pellets (5.00 g, 167 mmol of repeat unit) and ethanol (19.5 mL, 15.4 g, 334 mmol, 2 eq) were added under dynamic argon flow. The ampoule was submerged in a 100 °C oil bath and allowed to warm up before being sealed. The reaction was allowed to proceed for 24 h before being cooled to room temperature. A 65 μL aliquot of the crude reaction mixture was taken, spiked with trimethoxybenzene as an internal standard, and analysed by ^1H NMR spectroscopy to determine conversion. The reloading procedure was repeated once more for a total of three reactions. Results presented in Table S5.

1.8 Procedure for Scaled-Up Isolation of Bis(allyloxymethane) (2k)

An oven-dried 250 mL J Young's ampoule was charged with POM pellets (5.00 g, 167 mmol of repeat unit). $Bi(OTf)_3$ (10.0 wt% loading relative to the polymer, 0.500 g, 0.762 mmol, 0.46 mol% loading relative to the repeat unit) was added in a glovebox filled with argon. Allyl alcohol (27.3 mL, 23.2 g, 400 mmol, 2.4 eq) was added by syringe under dynamic argon flow. The ampoule was submerged in a 90 °C oil bath and allowed to warm up before being sealed. The reaction was allowed to proceed overnight (20 h in total), before being cooled to room temperature. A 65 μL aliquot of the crude reaction mixture was taken, spiked with trimethoxybenzene as an internal standard, and analysed by ^{1}H NMR spectroscopy to determine conversion (42% conversion by ^{1}H NMR spectroscopy). The product was isolated from the crude reaction mixture by silica plug (eluent: diethyl ether – hexane, 1:4; TLC visualisation: $KMnO_4$) to give **2k** (8.42 g, 40%).

2. Tables

Table S2 – POM ethanolysis co-solvent screen, using typical conditions (0.25 g POM, 10 equivalents of ethanol, 5 mol % $Bi(OTf)_3$, 100 °C, 5 mL co-solvent).

Co-Solvent	Time to Full Consumption of Polymer [h]	Conversion by NMR [%]
1,4-dioxane	2	79
2-MeTHF	4.5	71
THF	4.5	78
Water	Incomplete at 24 h	27
No co-solvent	4.5	80

Table S3 – POM ethanolysis catalyst loading investigation using typical conditions (10 equivalents of ethanol, 100 °C, 5 mL 1,4-dioxane).

Catalyst	Loading [mol %]	Scale [g POM]	Time to Full Consumption of Polymer [h]	Conversion by NMR [%]
$Bi(OTf)_3$	5	0.25	2	74
$Bi(OTf)_3$	1.67	0.25	2.5	71
$Bi(OTf)_3$	0.5	0.25	5	76
$Bi(OTf)_3$	0.1	0.25	22	77

Table S4 – Ethanol loading relative to POM repeat unit investigation using typical conditions (0.25 g POM, 5 mol % $Bi(OTf)_3$, 100 °C, 5 mL 1,4-dioxane).

Ethanol Loading Relative to POM Repeat Unit	Ethanol Volume [mL]	Conversion by NMR [%]
20:1	9.70	86
10:1	4.85	84
5:1	2.43	85
4:1	1.94	88
3:1	1.46	81
2:1	0.97	68

Table S5 – Catalyst reuse experiment for POM ethanolysis (5:1 loading EtOH, 50 mL 1,4-dioxane, 100 °C, see SI Section 1.7 for details). Conversion determined by ^{1}H NMR spectroscopy with TMB internal standard. Low conversion likely due to poor stirring and therefore poor mass transfer in larger reaction vessel.

Cycle	POM Loading	Total $Bi(OTf)_3$ Loading [wt%]	Total $Bi(OTf)_3$ Loading [mol%]	Reaction Duration [h]	Conversion
First Run	5 g 167 mmol	10 wt%	0.46 mol%	24 h	52%
First Reloading	5 g 167 mmol	5.0 wt%	0.23 mol%	24 h	38%
Second Reloading	5 g 167 mmol	3.3 wt%	0.15 mol%	24 h	33%
Overall	15 g 500 mmol	3.3 wt%	0.15 mol%	72 h	41%

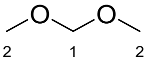
Table S6 – Control experiments for POM alcoholysis and aminolysis. Reactions proceeded according to general procedures for alcoholysis and aminolysis described in Section 1 without the addition of $Bi(OTf)_3$ or TfOH. No conversion to product was observed by ^{1}H NMR with TMB internal standard, and no mass loss of POM was observed.

Entry	Alcohol / Amine	Product	Co-solvent	Temperature [°C]	Reaction Duration [h]	Conversion by ^{1}H NMR [%]	Mass Loss of Polymer [%]
1	Ethanol	**2b**	1,4-dioxane	100	19	<1	<1
2	Allyl alcohol	**2k**	-	100	20	<1	<1
3	2,2-dimethyl-1,3-diaminopropane	**4a**	1,4-dioxane	130	19	<1	<1
4	1,2-diaminoproane	**4e**	DMSO	130	6	<1	<1

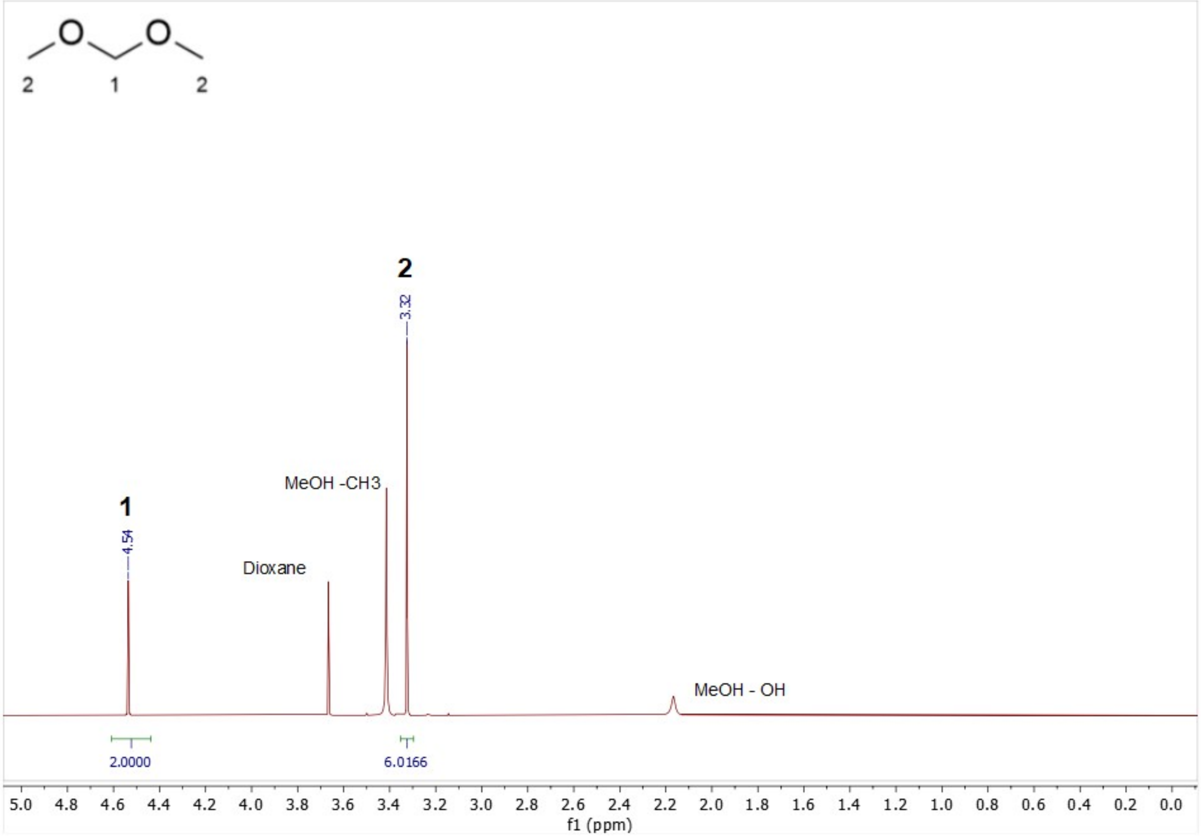
3. Spectral Information

3.1 POM Alcoholysis

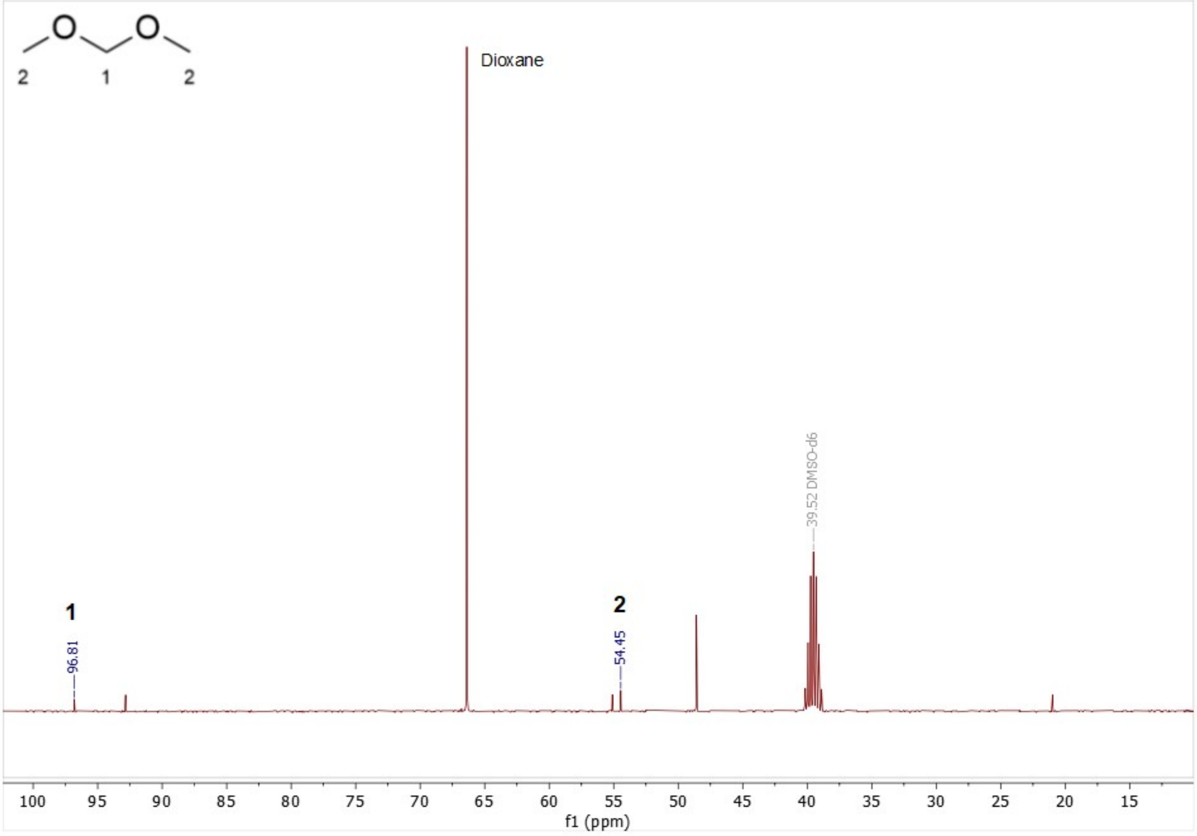
2a (dimethoxymethane)



2a was prepared according to the general procedure for POM alcoholysis using methanol (10 equiv., 3.36 mL, 83 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H ppm 4.54 (2H, s, H_1), 3.32 (6H, s, H_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6) δ_C ppm 96.81 (C_1), 54.45 (C_2). 60% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

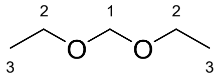


<u>Figure S3</u> - ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of DMM (**2a**).



<u>Figure S4</u> - $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6, 100.6 MHz) of **2a**.

2b (diethoxymethane)



2b was prepared according to the general procedure for POM alcoholysis using ethanol (10 equiv., 4.85 mL, 83 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ_H ppm 4.66 (2H, s, H$_1$), 3.59 (4H, q, J = 7.1 Hz, H$_2$), 1.21 (6H, t, J = 7.0 Hz, H$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ_C ppm 95.0 (C$_1$), 63.2 (C$_2$), 15.3 (C$_3$). 86% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

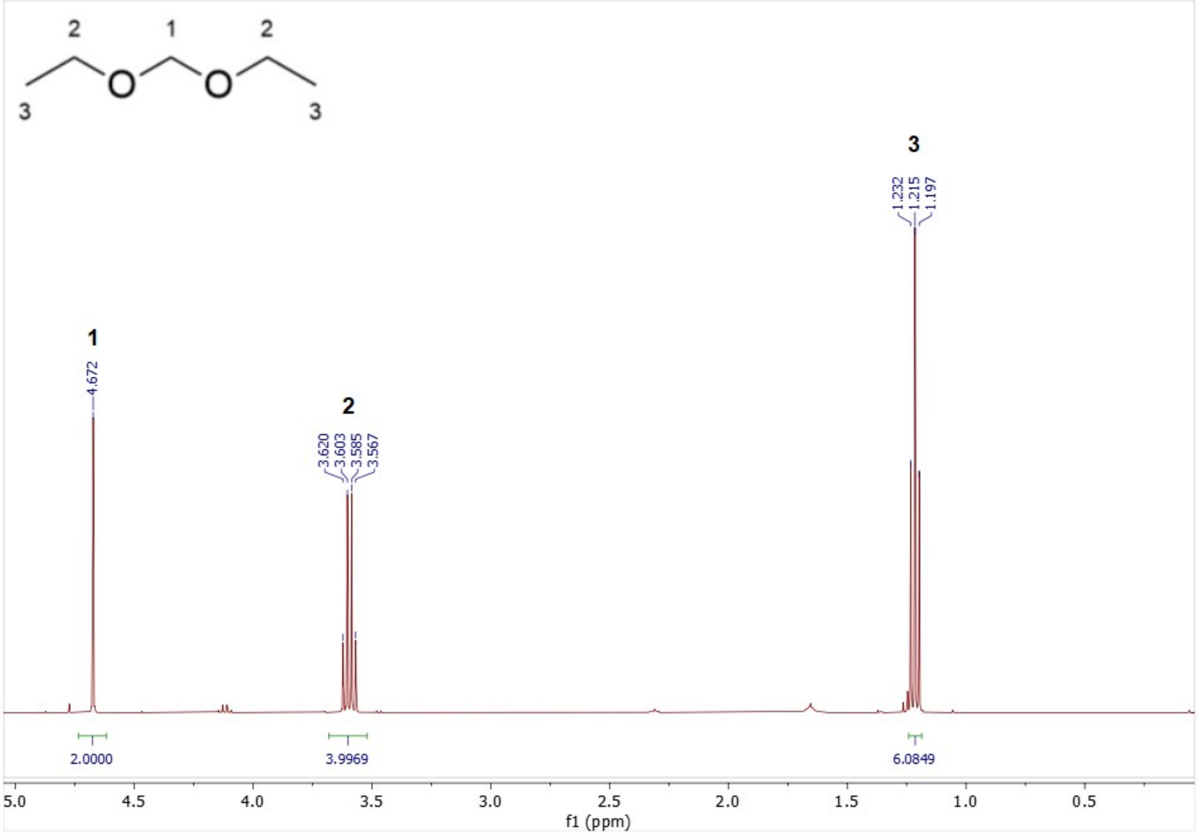


Figure S5 - ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of DEM (**2b**).

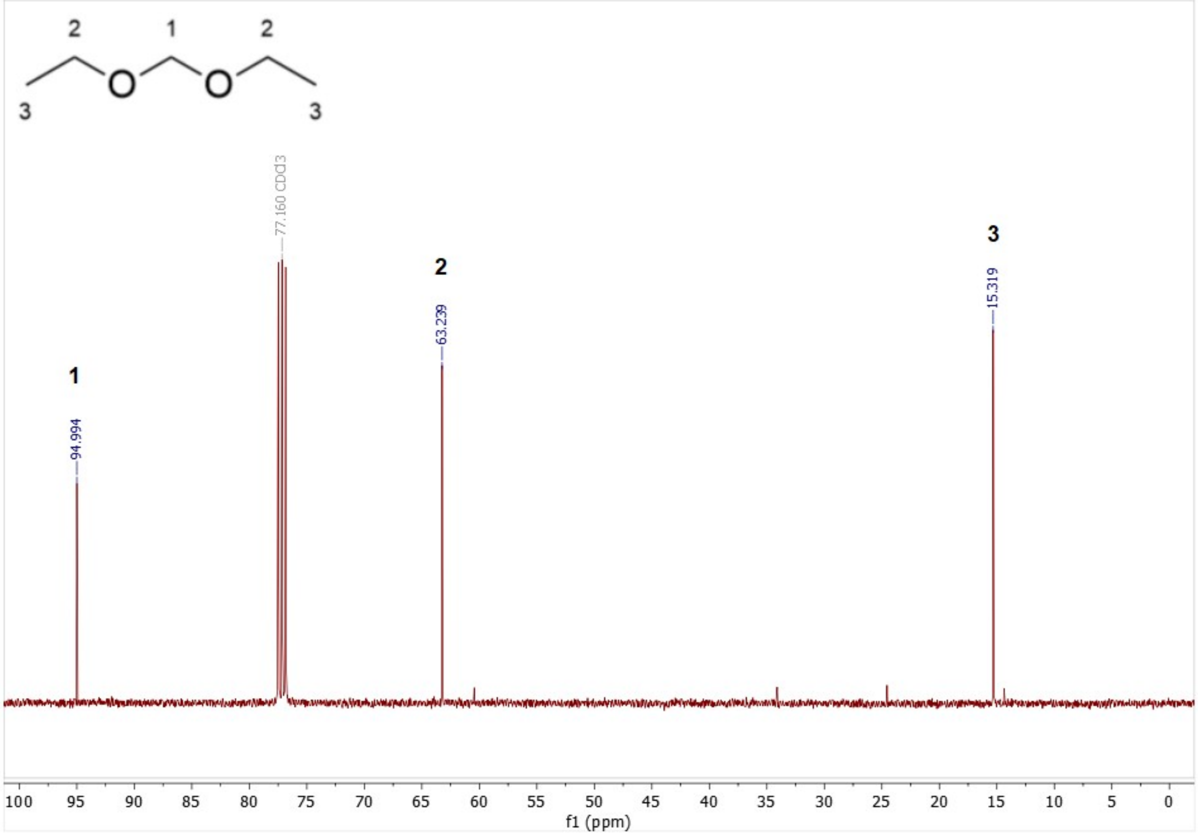
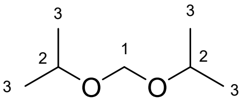


Figure S6 – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **2b**.

2c (diisopropoxymethane)



2c was prepared according to the general procedure for POM alcoholysis using isopropyl alcohol (10 equiv., 6.35 mL, 83 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H ppm 4.67 (2H, s, H_1), 3.86 (2H, sept, J = 6.0 Hz, H_2), 1.13 (12H, d, J = 6.0 Hz, H_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ_C ppm 90.9 (C_1), 68.6 (C_2), 22.6 (C_3). 80% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

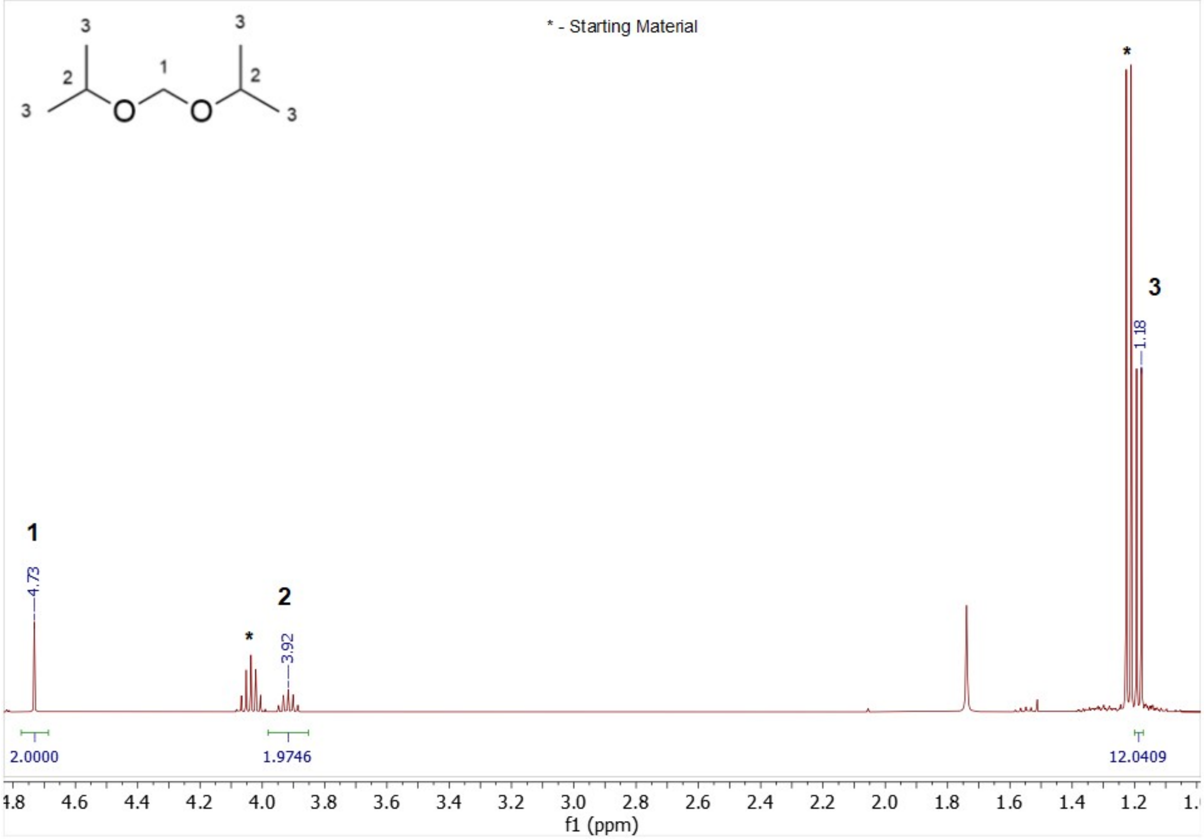


Figure S7 - ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2c**.

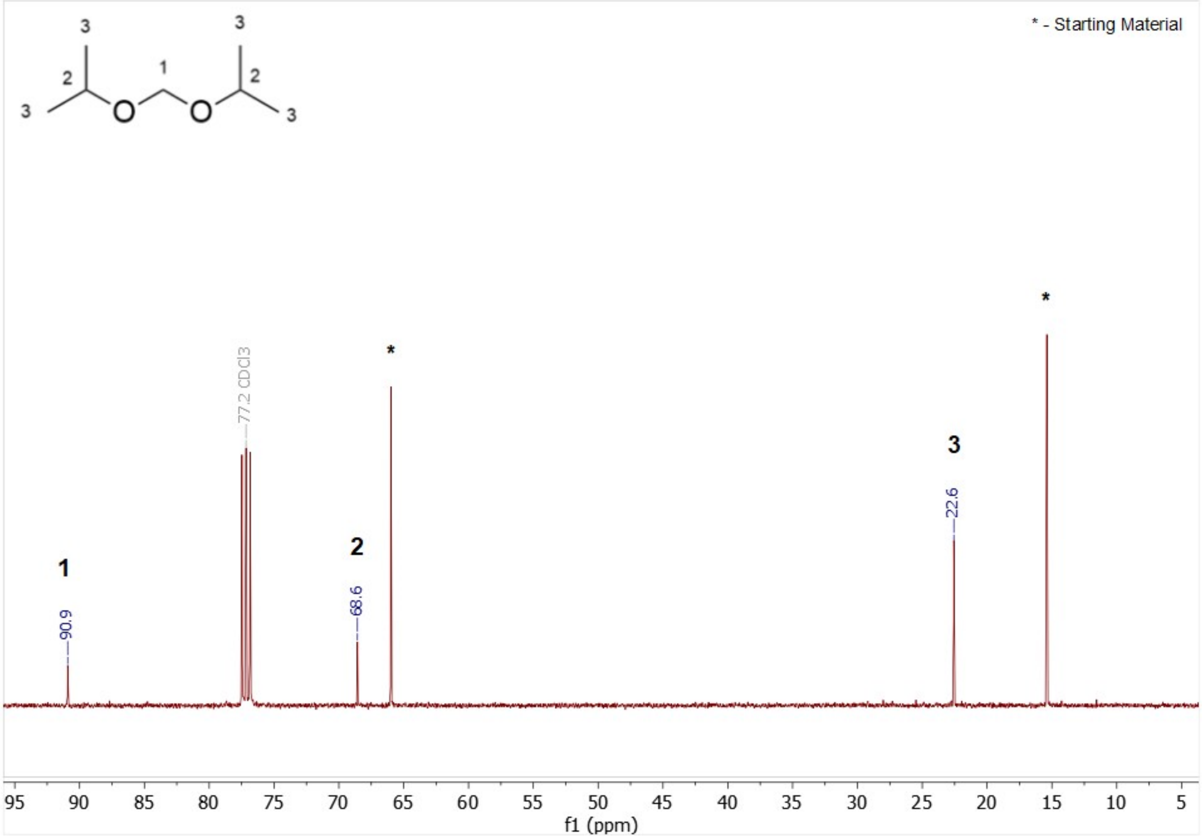
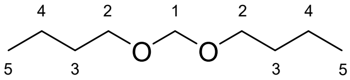


Figure S8 – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **2c**.

2d (dibutoxymethane)



2d was prepared according to the general procedure for POM alcoholysis using n-butanol (2.4 equiv., 1.3 mL, 20 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H ppm 4.63 (2H, s, H_1), 3.50 (4H, t, *J* = 6.6 Hz, H_2), 1.54 (4H, m (1.50 - 1.59 ppm), H_3), 1.35 (4H, m (1.31 - 1.41 ppm), H_4), 0.90 (6H, t, *J* = 7.4 Hz, H_5). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ_C ppm 95.3 (C_1), 67.7 (C_2), 31.9 (C_3), 18.9 (C_4), 13.9 (C_5). 79% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

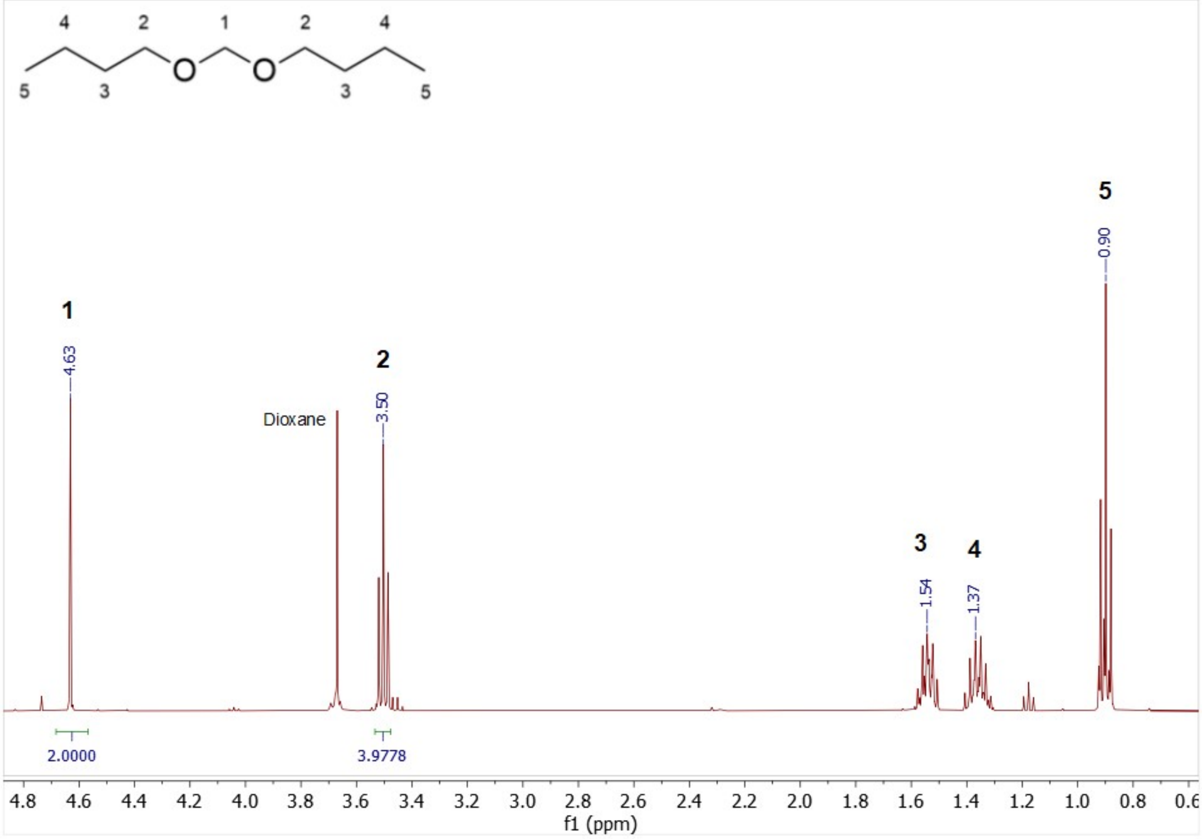


Figure S9 – ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2d**.

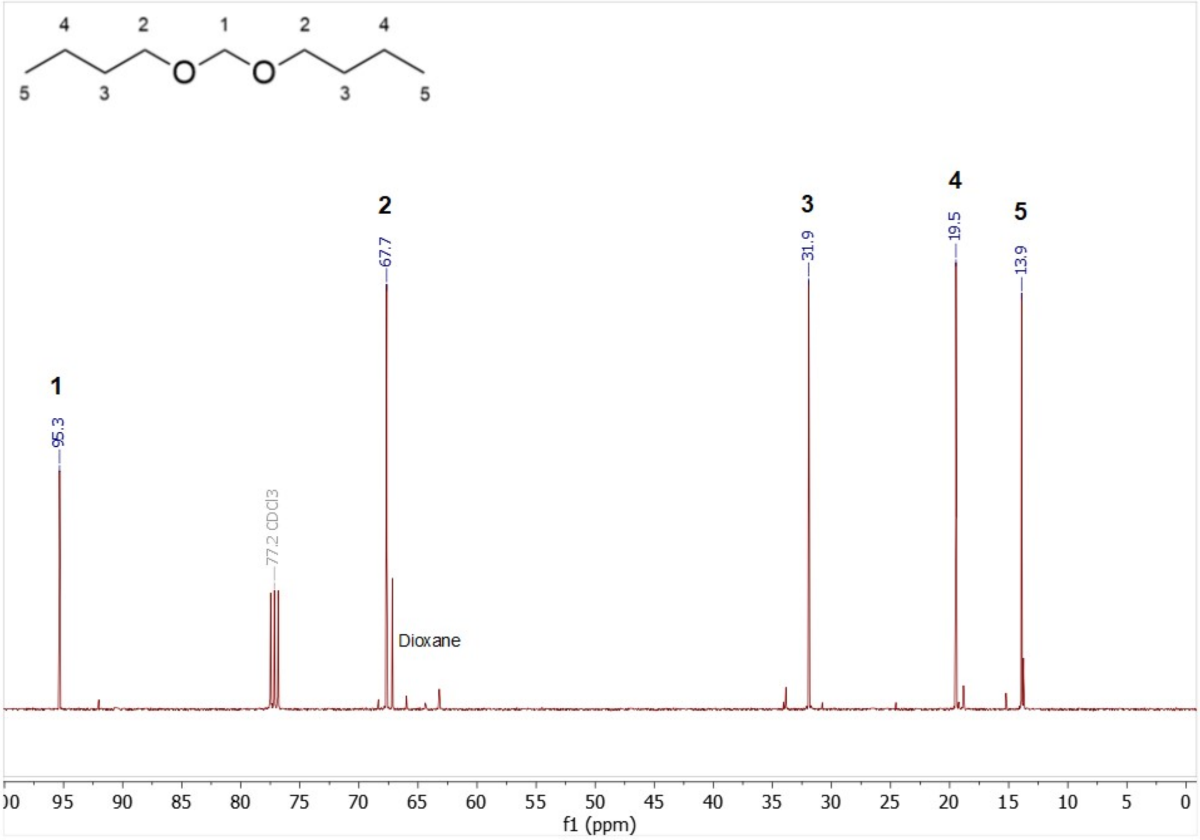
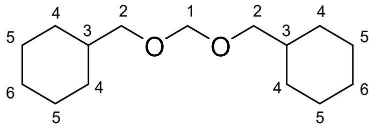


Figure S10 – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **2d**.

2e (bis(cyclohexylmethoxy)methane)



6e was prepared according to the general procedure for POM alcoholysis using cyclohexanemethanol (10 equiv., 2.6 mL, 21 mmol) at a lower scale due to the high price of the alcohol. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H ppm 4.63 (2H, s, H_1), 3.31 (4H, d, *J* = 6.5 Hz, H_2), 1.71 (5H, br m (1.61 - 1.77 ppm), $H_{4,5,6}$), 1.54 (2H, m (1.52 - 1.59 ppm), H_3), 1.19 (4H, br m (1.08 - 1.30 ppm), $H_{5,6}$), 0.92 (2H, br m (0.85 - 0.99 ppm), H_6). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ_C ppm 95.6 (C_1), 73.7 (C_2), 38.2 (C_3), 30.2 (C_4), 26.7 (C_5), 26.0 (C_6). 79% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

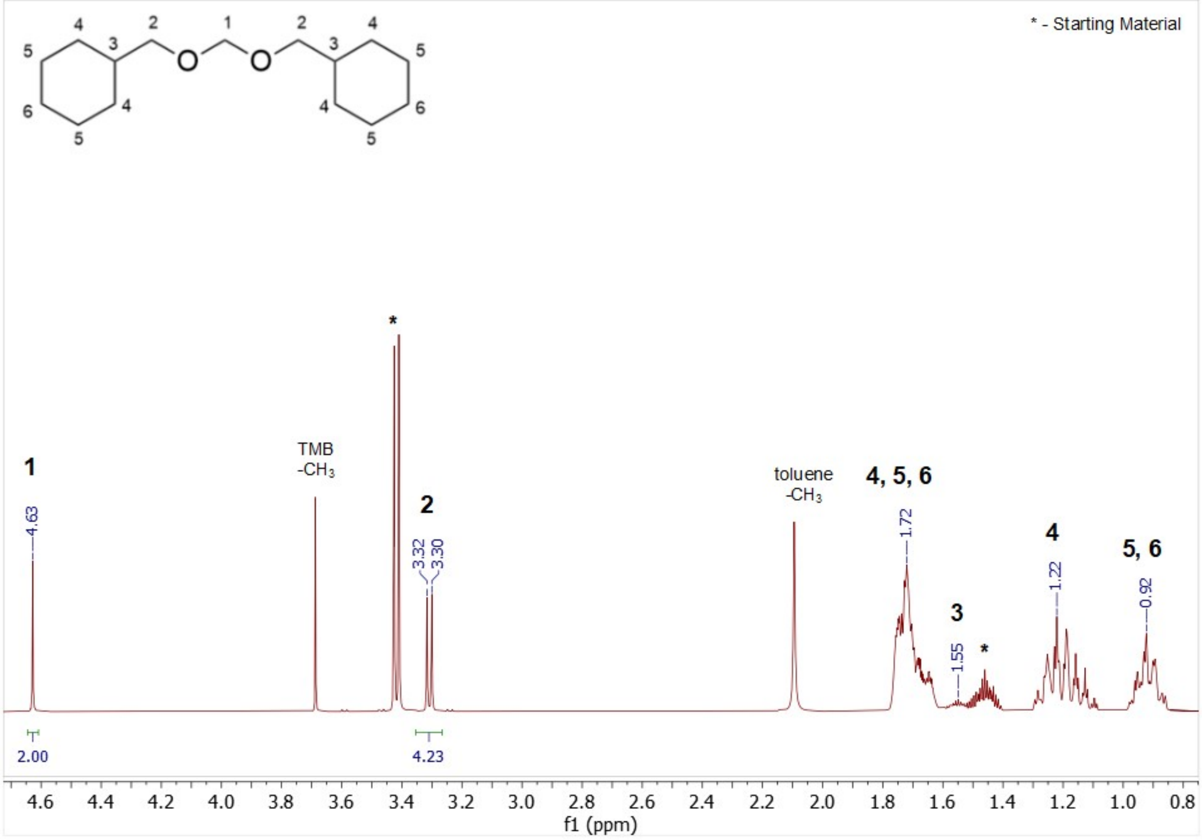


Figure S11 – ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **2e**.

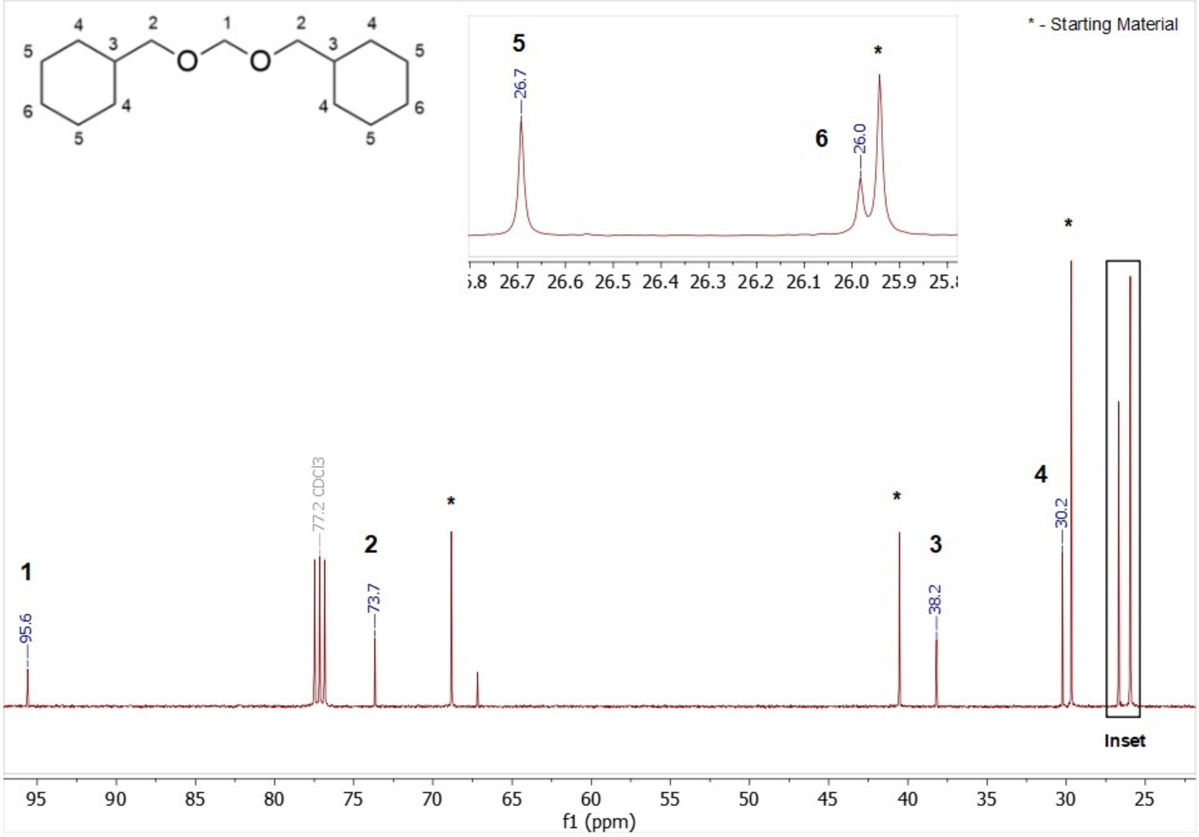
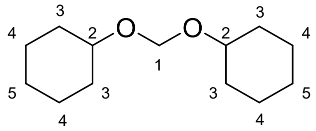


Figure S12 – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **2e**.

2f (bis(cyclohexyloxy)methane)



2f was prepared according to the general procedure for POM alcoholysis using cyclohexanol (10 equiv., 8.35 g, 83 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ_H ppm 4.76 (2H, s, H$_1$), 3.59 (2H, m, H$_2$), 1.88 (2H, br m (1.82 - 1.93 ppm), H$_3$), 1.71 (2H, br m (1.64 - 1.77), H$_5$), 1.52 (2H, br m (1.48 - 1.57), H$_4$), 1.25 (4H, br m (1.20 - 1.32), H$_{3,5}$), 1.16 (2H, br m (1.08 - 1.20), H$_4$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ_C ppm 90.6 (C$_1$), 74.8 (C$_2$), 32.8 (C$_3$), 25.8 (C$_4$), 24.4 (C$_5$). 78% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

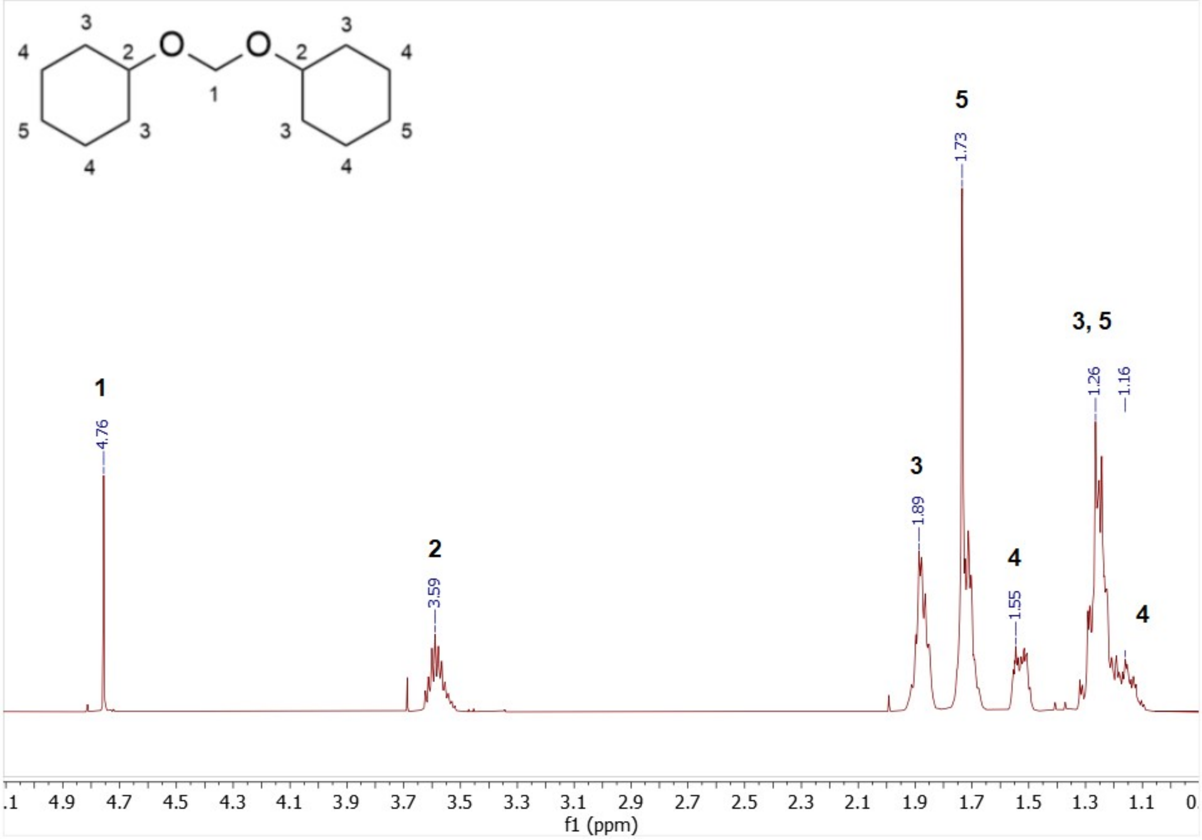


Figure S13 – ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **2f**.

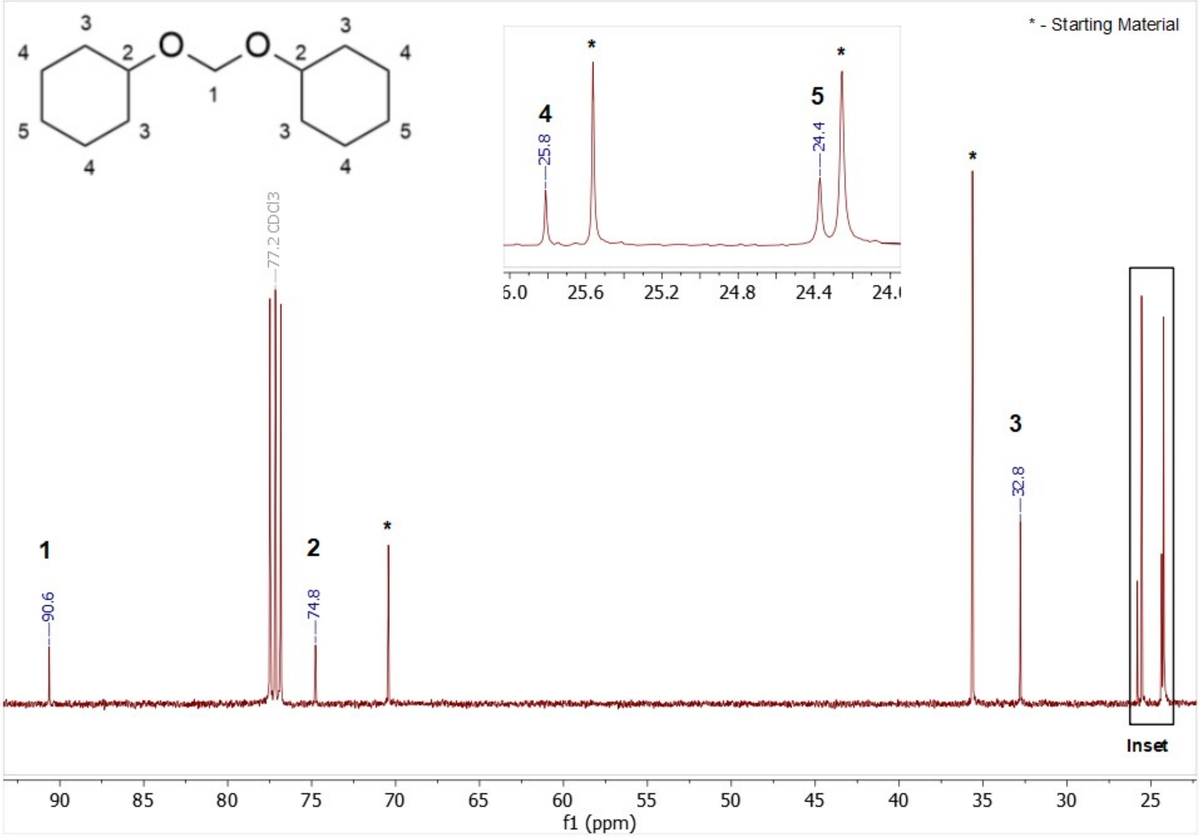
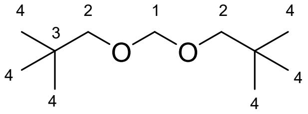


Figure S14 – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **2f**.

2g (bis(neopentyloxy)methane)



2g was prepared according to the general procedure for POM alcoholysis using neopentanol (10 equiv., 5 g, 57 mmol) on a smaller scale due to the price of the alcohol. ^1H NMR (400 MHz, $CDCl_3$) δ_H ppm 4.67 (2H, s, H_1), 3.19 (4H, s, H_2), 0.92 (18H, s, H_4). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ_C ppm 96.0 (C_1), 78.2 (C_2), 31.9 (C_3), 26.9 (C_4). 89% conversion calculated by ^1H NMR spectroscopy with TMB internal standard.

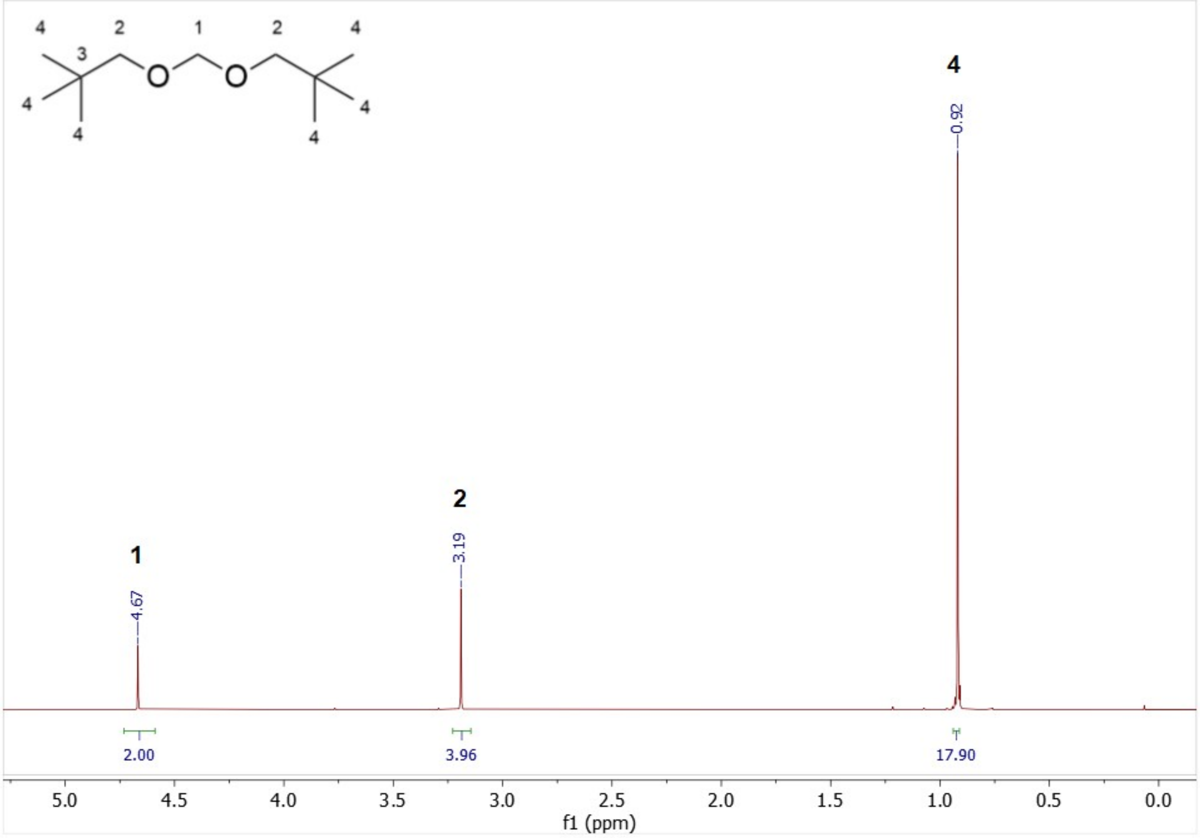


Figure S15 - ^1H NMR spectrum ($CDCl_3$, 400 MHz) of **2g.**

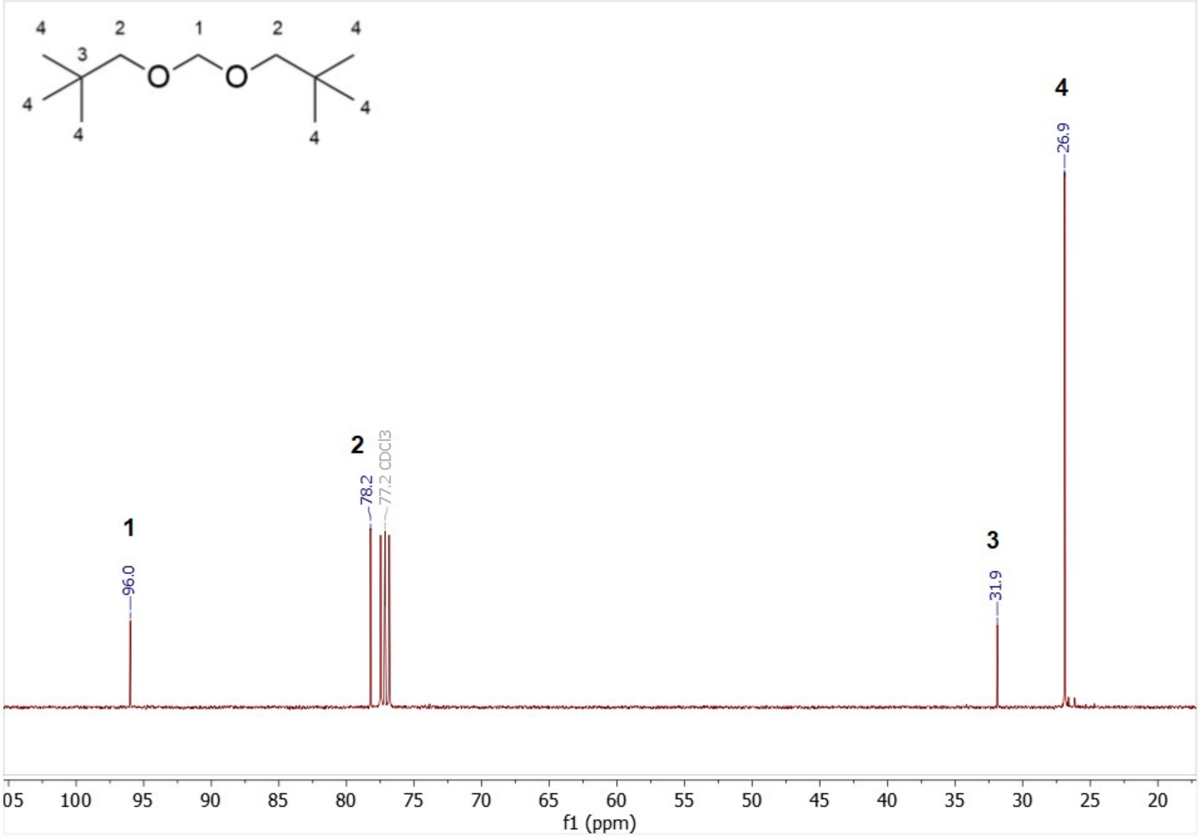
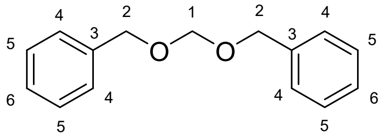


Figure S16 - $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **2g**.

2h (bis(benzyloxy)methane)



2h was prepared according to the general procedure for POM alcoholysis using benzyl alcohol (2.4 equiv., 2.08 mL g, 20 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ$_H$ ppm 7.29 (10H, m (7.10 - 7.48 ppm), H$_{4\text{-}6}$), 4.90 (2H, s, H$_1$), 4.71 (4H, s, H$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ$_C$ ppm 137.9 (C$_3$), 128.4 (C$_4$), 127.9 (C$_5$), 127.7 (C$_6$), 93.9 (C$_1$), 69.5 (C$_2$). 99% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

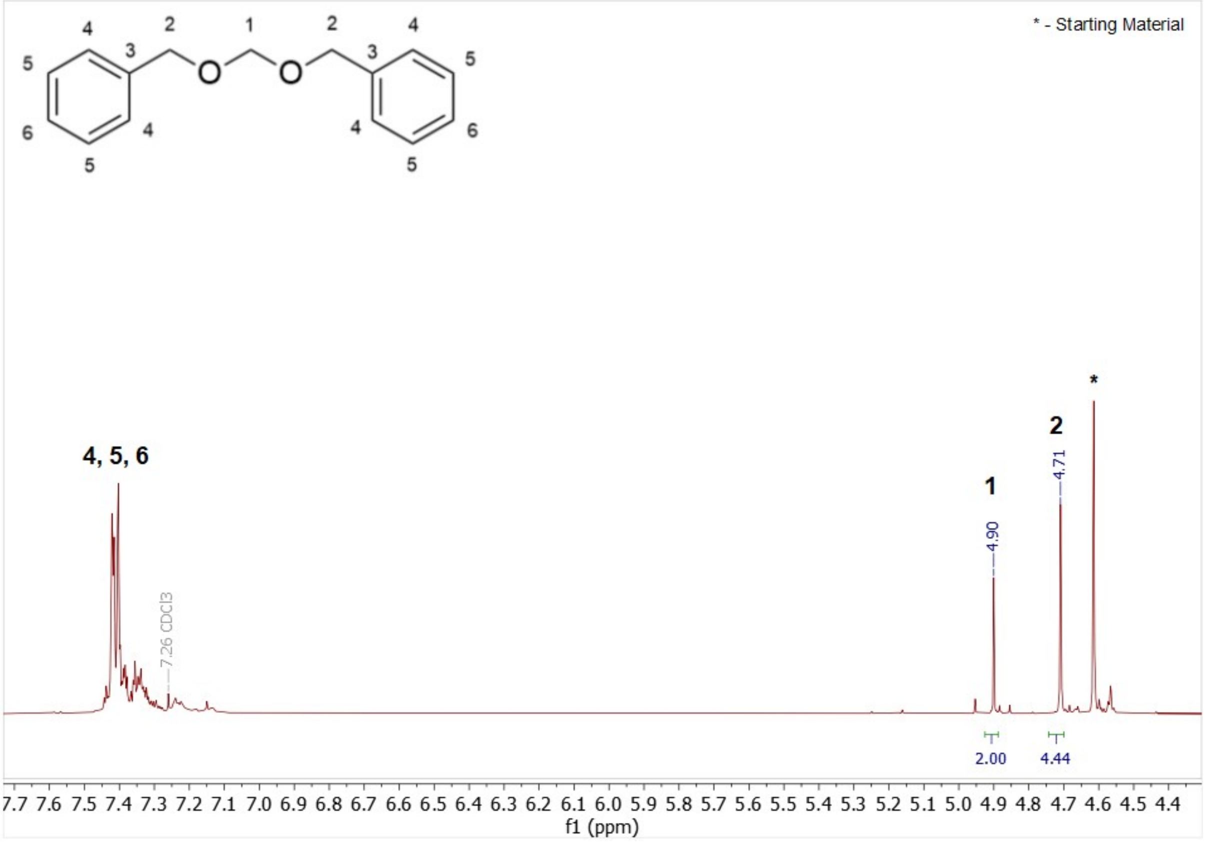


Figure S17 – ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **2h**.

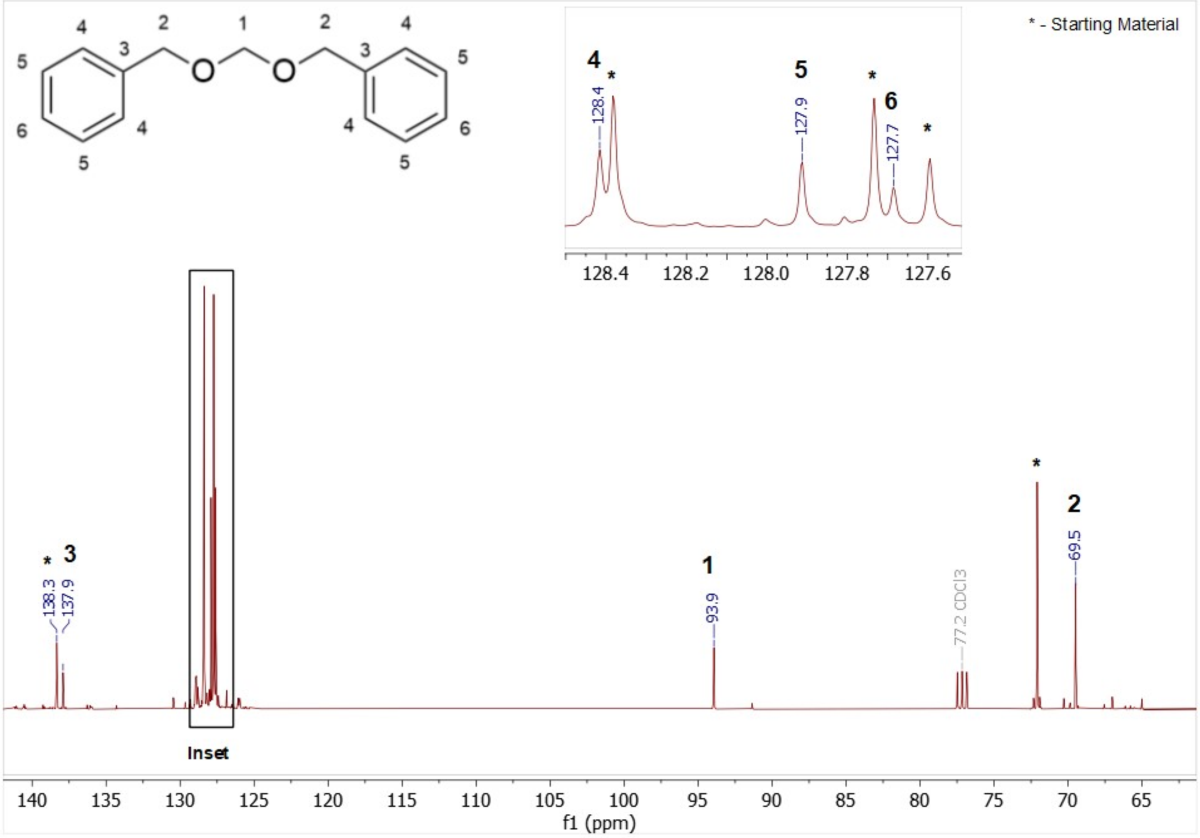
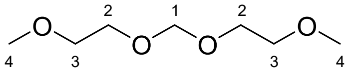


Figure S18 – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **2h**.

2i (2,5,7,10-tetraoxaundecane)



2i was prepared according to the general procedure for POM alcoholysis using 2-methoxyethanol (10 equiv., 6.58 mL, 83 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ_H ppm 4.76 (2H, s, H$_1$), 3.71 (4H, m (3.70 - 3.72 ppm), H$_2$), 3.56 (4H, m (3.55 - 3.57 ppm), H$_3$), 3.39 (6H, s, H$_4$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ_C ppm 95.8 (C$_1$), 71.9 (C$_3$), 66.9 (C$_2$), 59.2 (C$_4$). 79% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

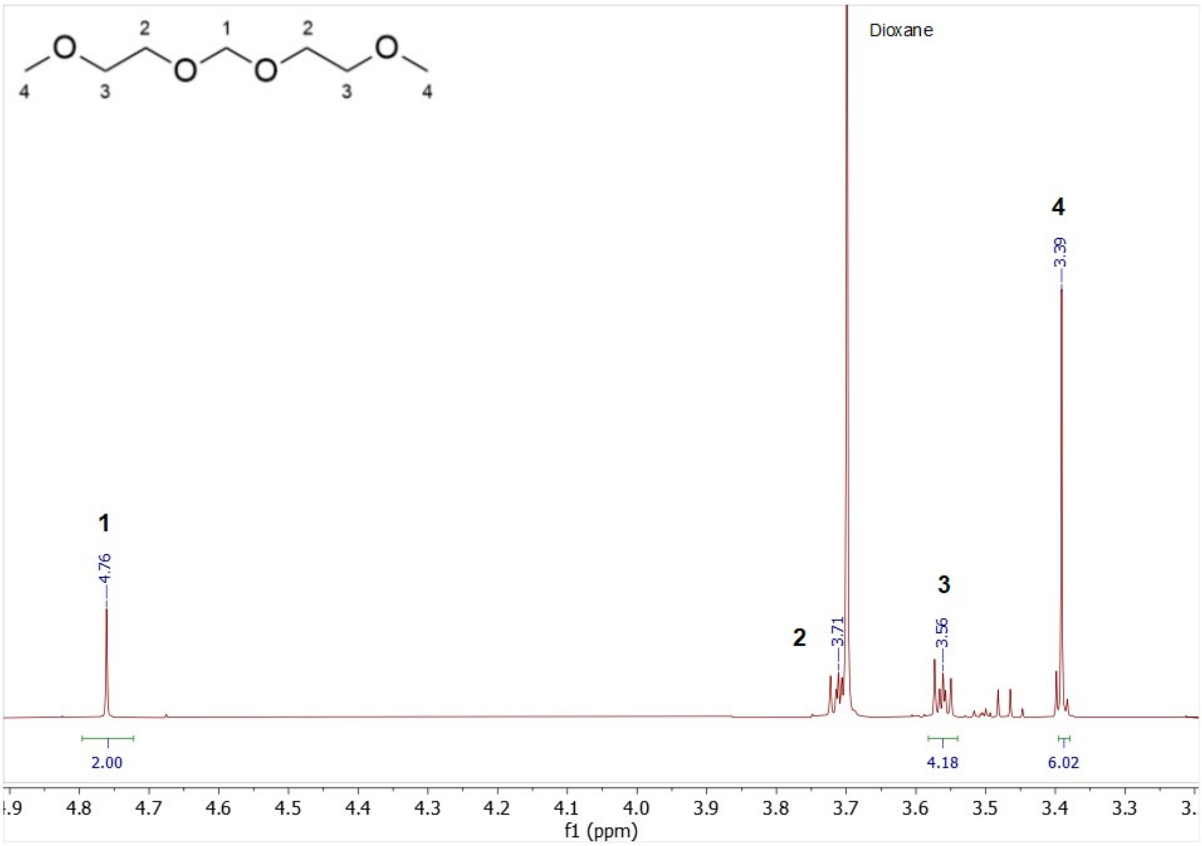
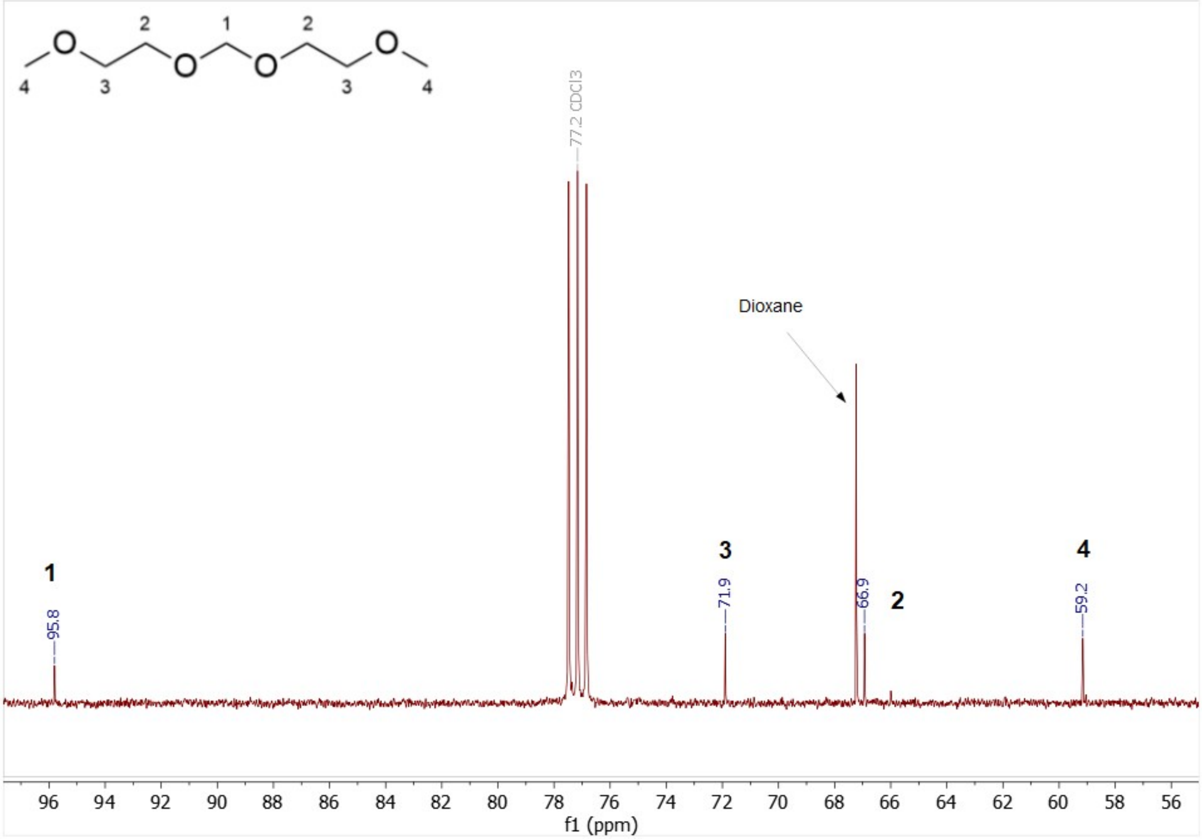
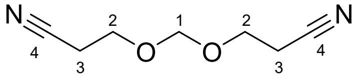


Figure S19 – ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **2i**.



<u>Figure S20</u> – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **2i**.

2j (3,3'-(methylenebis(oxy))dipropanenitrile)



2j was prepared according to the general procedure for POM alcoholysis using 3-propionitrile (10 equiv., 5.67 mL g, 83 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ_H ppm 4.76 (2H, s, H$_1$), 3.81 (4H, t, *J* = 6.1 Hz, H$_2$), 2.65 (4H, t, *J* = 6.1 Hz, H$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ_C ppm 117.9 (C$_4$), 97.2 (C$_1$), 62.9 (C$_2$), 19.1 (C$_3$). 83% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

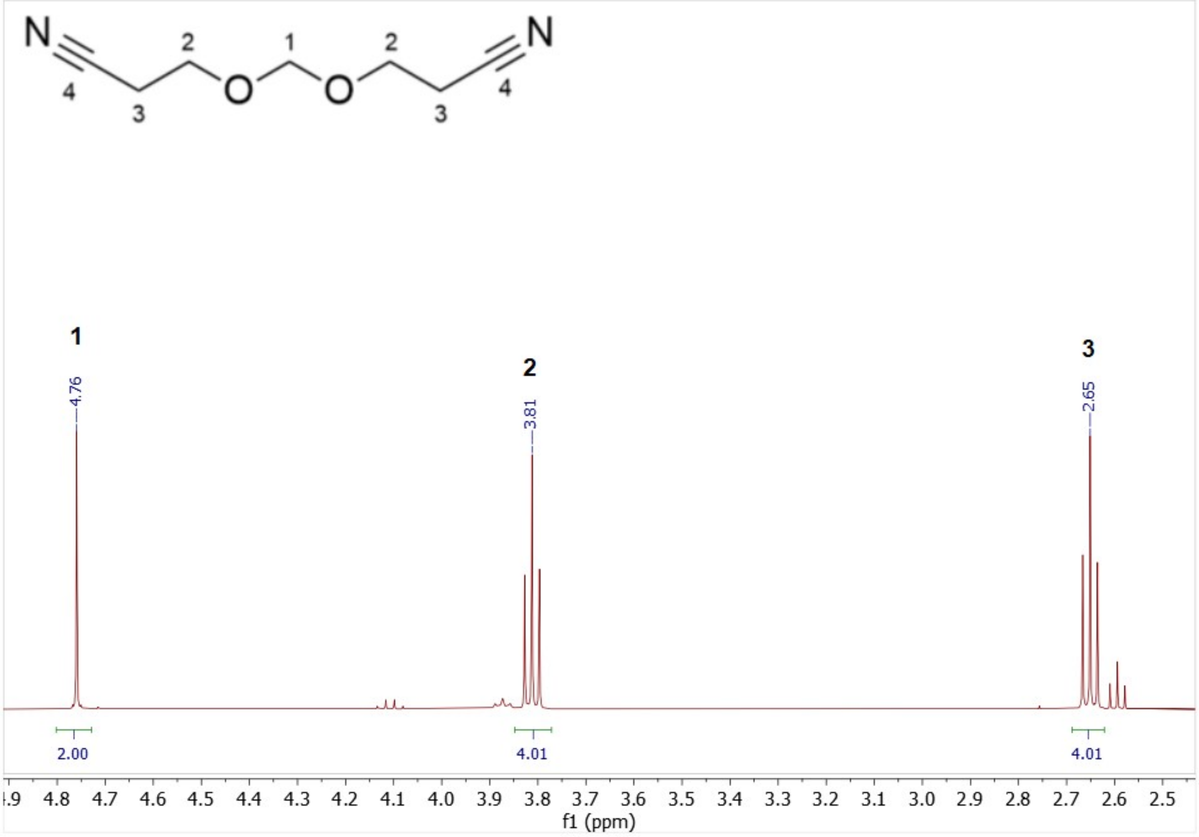


Figure S21 – ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **2j**.

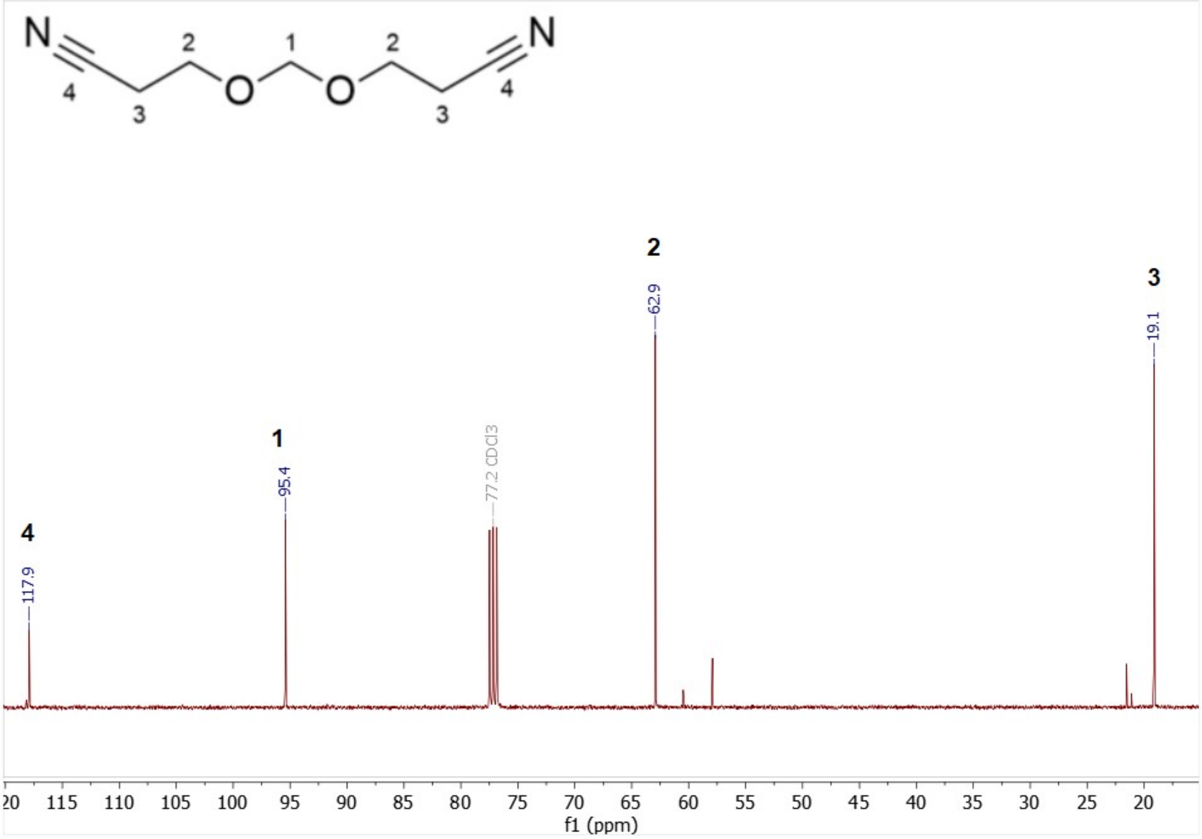
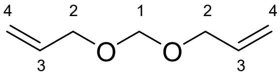


Figure S22 – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **2j**.

2k (bis(allyloxy)methane)



2k was prepared according to the general procedure for POM alcoholysis using allyl alcohol (10 equiv., 5.67 mL g, 83 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ_H ppm 5.91 (2H, ddt, *J* = 17.2, 10.4, 5.6 Hz, H$_3$), 5.29 (2H, dq, *J* = 17.2, 1.7 Hz, H$_4$(cis)), 5.18 (2H, ddt, *J* = 10.4, 1.8, 1.3 Hz, H$_4$(trans)), 4.71 (2H, s, H$_1$), 4.08 (4H, dt, *J* = 5.6, 1.4 Hz, H$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ_C ppm 134.5 (C$_3$), 117.2 (C$_4$), 93.9 (C$_1$), 68.5 (C$_2$). 62% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard. Literature source assisted with assignments.[4]

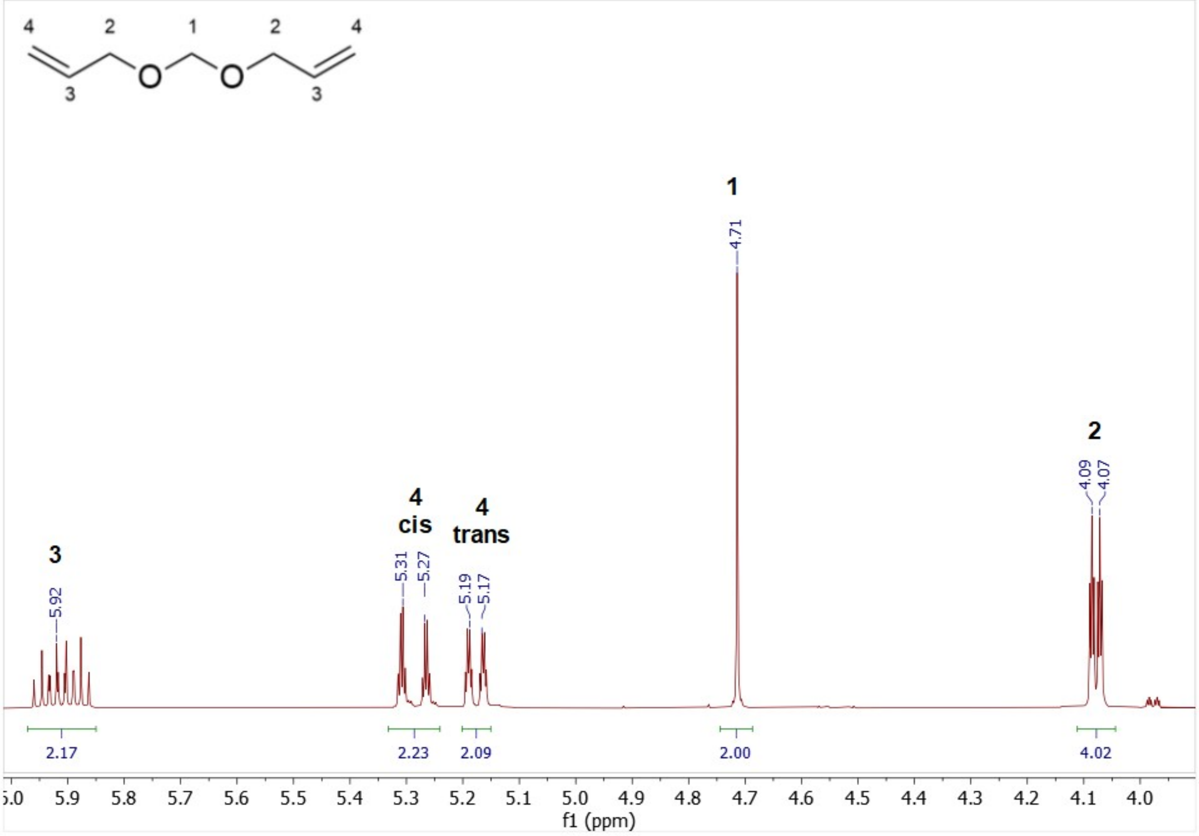
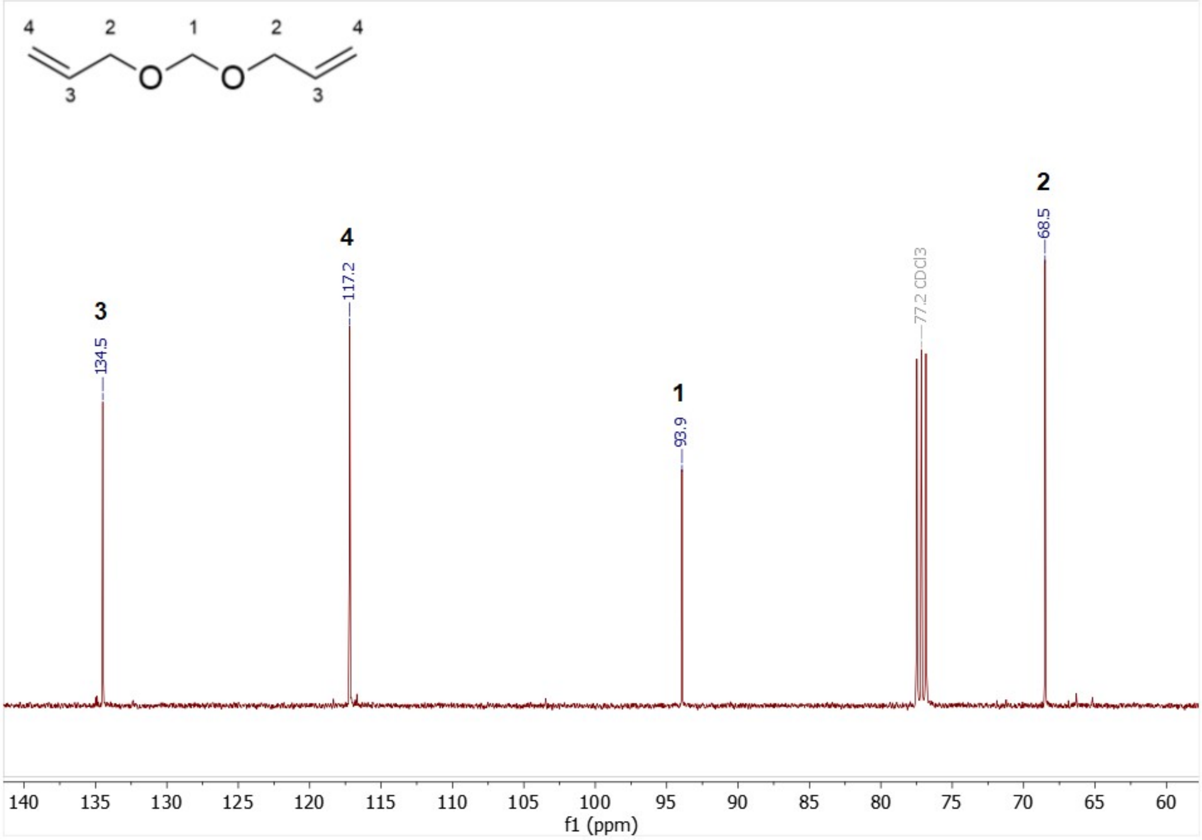
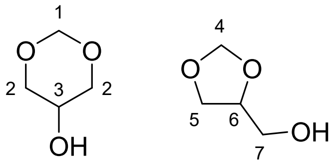


Figure S23 – ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **2k**.



<u>Figure S24</u> – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **2k**.

2t (glycerol formal, a 3:2 mixture of 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane)



2t was prepared according to a modified procedure for POM alcoholysis using glycerol (1.2 equiv., 0.74 mL g, 10 mmol) without the addition of 1,4-dioxane and heating to 130 °C. 63% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

5-hydroxy-1,3-dioxane: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H ppm 4.92 (1H, d, J = 6.2 Hz, H_{1A}), 4.76 (1H, d, J = 6.2 Hz, H_{1A}), 3.92 (2H, m (3.90 - 3.94 ppm), H_{2A}), 3.85 (2H, m (3.83 - 3.88 ppm), H_{2B}), 3.62 (1H, m (3.59 - 3.65 ppm), H_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ_C ppm 94.2 (C_1), 71.8 (C_2), 64.2 (C_3).

4-hydroxymethyl-1,3-dioxolane: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H ppm 5.05 (1H, s, H_{4A}), 4.87 (1H, s, H_{4B}), 4.17 (1H, dddd, J = 7.0, 6.0, 5.5, 3.7 Hz, H_6), 3.94 (1H, m (3.92 - 3.96 ppm), H_{5A}), 3.76 (1H, m (3.74 - 3.77 ppm), H_{5B}), 3.74 (1H, m (3.71 - 3.75 ppm), H_{7A}), 3.62 (1H, m (3.59 - 3.65 ppm), H_{7B}). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ_C ppm 95.4 (C_4), 76.1 (C_6), 66.2 (C_5), 62.9 (C_7).

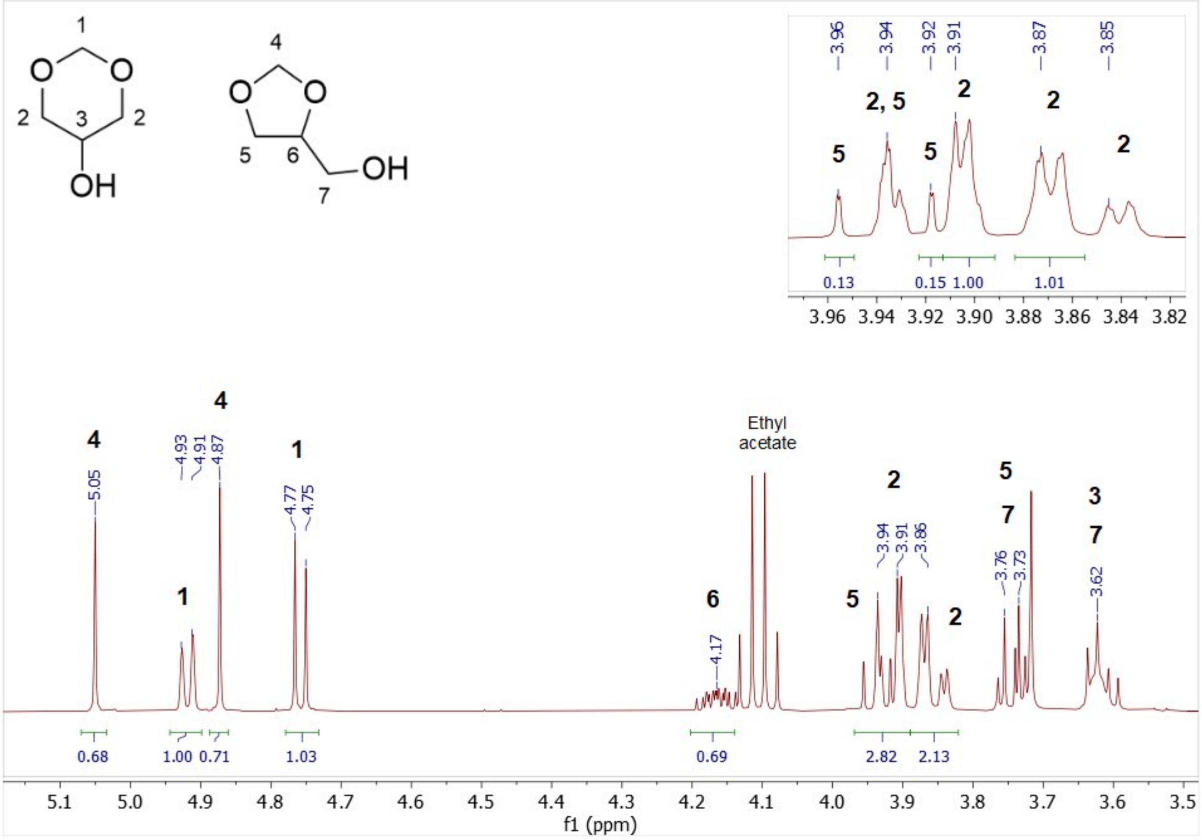


Figure S25 - ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **2t.**

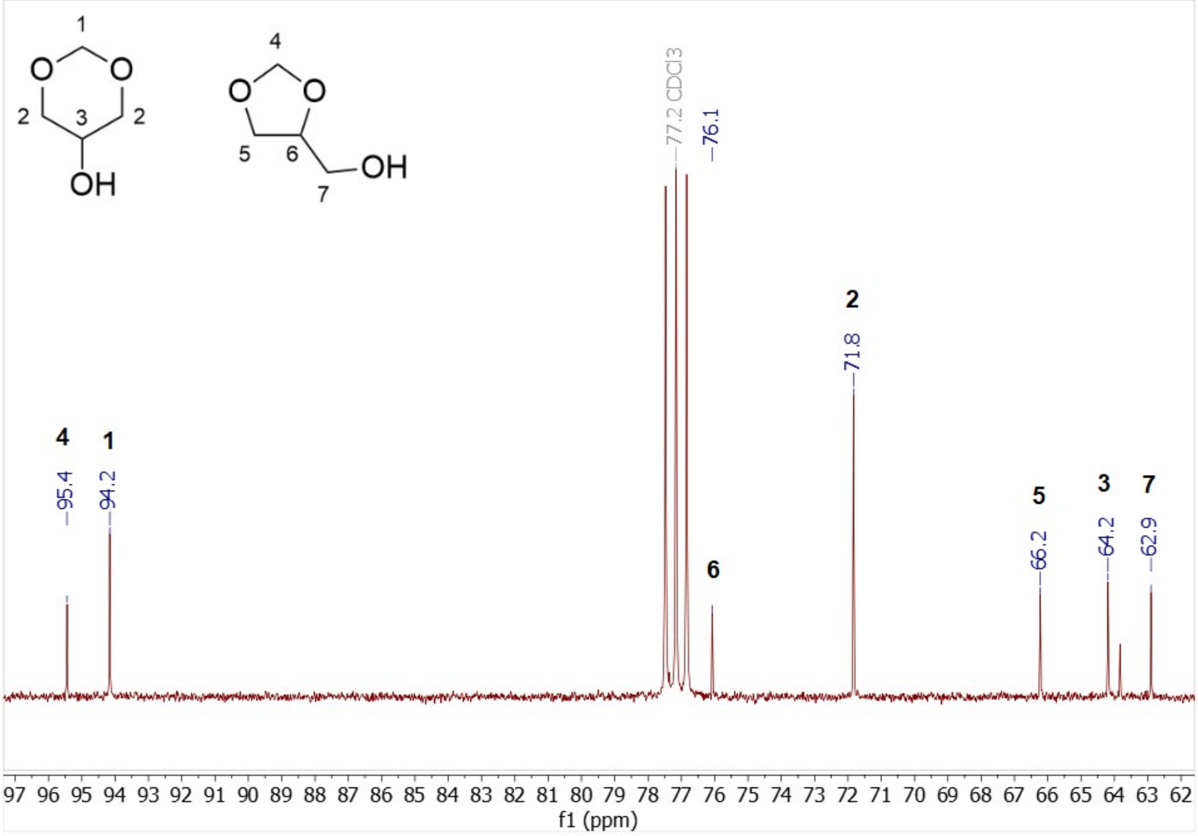


Figure S26 - ^{13}C{^{1}H} NMR spectrum (CDCl$_3$, 100.6 MHz) of **2t**.

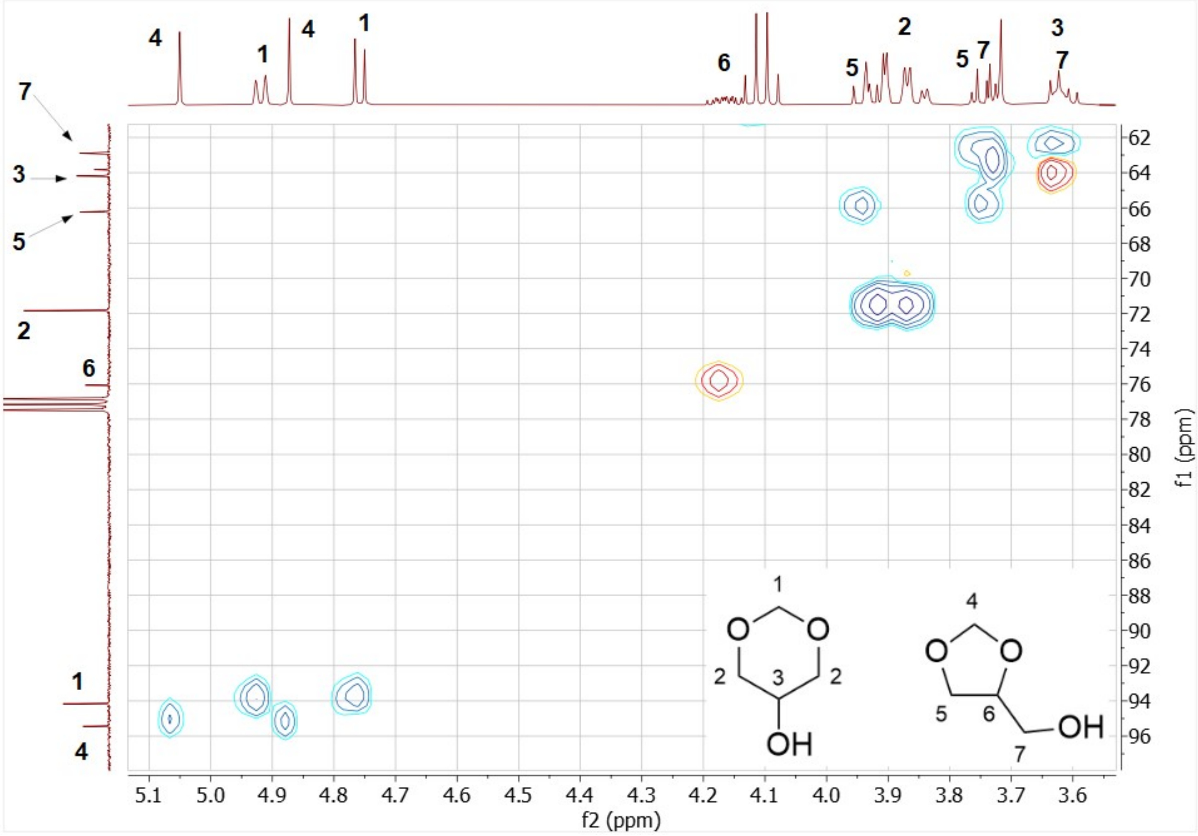
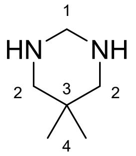


Figure S27 – HSQC NMR spectrum ($CDCl_3$) of **2t**. Blue peaks indicate -CH_2- units, red peaks indicate -CH- or -CH_3 units.

3.2 POM Aminolysis

4a (4,4-dimethylhexahydropyrimidine)



4a was prepared according to the general procedure for POM aminolysis using 2,2-dimethyl-1,3-diaminopropane (1.2 equiv., 0.85 g, 10 mmol) in 5 mL of 1,4-dioxane. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H ppm 3.69 (2H, s, H_1), 2.60 (4H, s, H_2), 0.86 (6H, s, H_4). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ_C ppm 62.1 (C_1), 57.2 (C_2), 29.0 (C_3), 24.3 (C_4). 77% conversion estimated by ^{1}H NMR spectroscopy integral ratios.

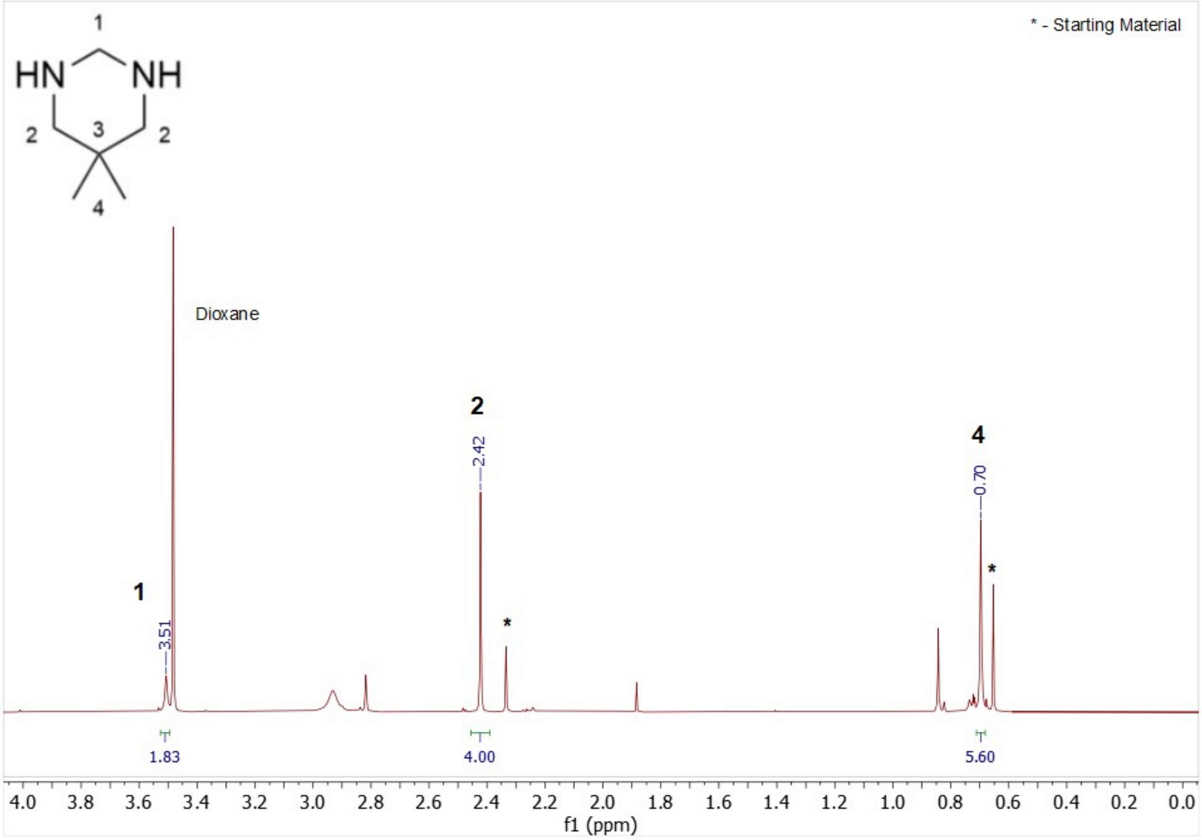


Figure S28 – ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4a**.

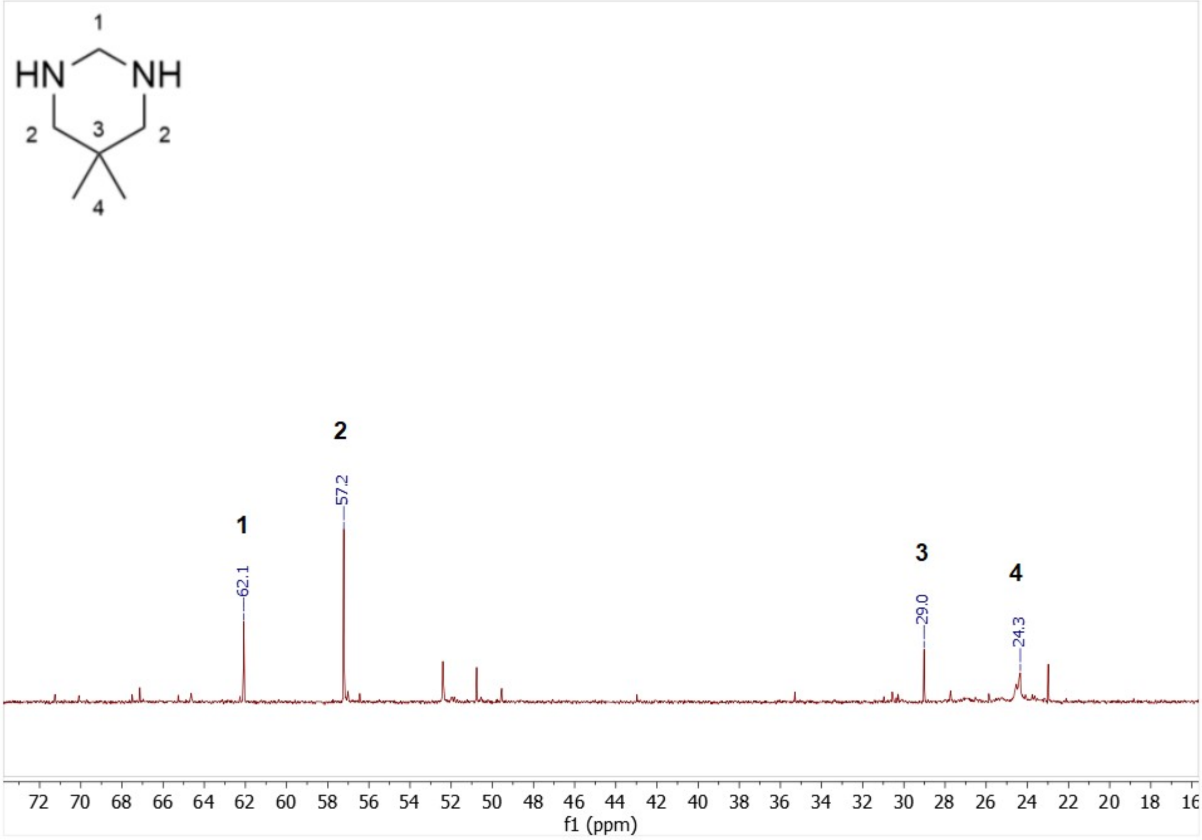
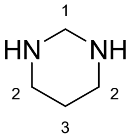


Figure S29 - $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **4a**.

4b (hexahydropyrimidine)



4b was prepared according to the general procedure for POM aminolysis using 1,3-diaminopropane (1.2 equiv., 0.83 mL, 10 mmol) in 5 mL of DMSO. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H ppm 3.51 (2H, s, H_1), 2.76 (4H, m (2.73 - 2.78 ppm), H_2), 0.78 (2H, p, J = 5.6 Hz, H_3). ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6) δ_C ppm 62.6 (C_1), 45.4 (C_2), 28.4 (C_3). 50% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

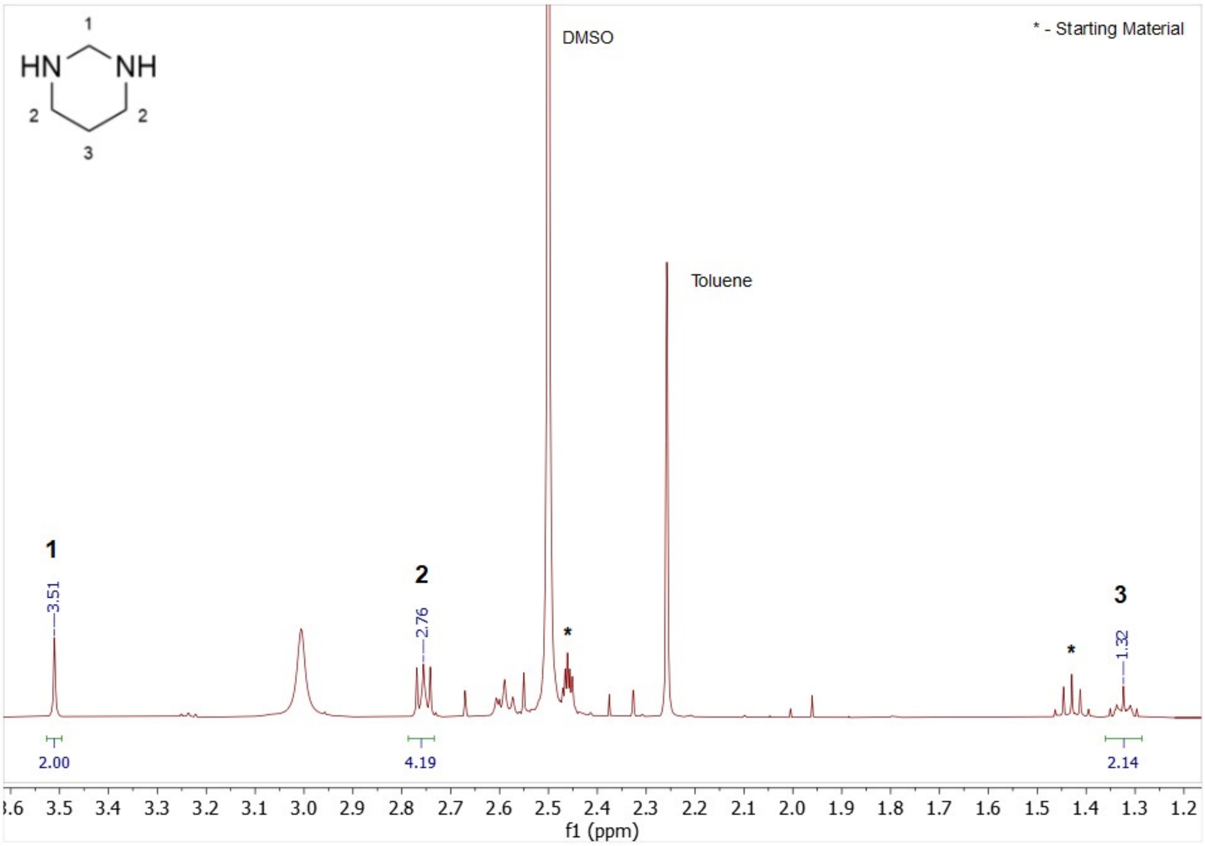


Figure S30 – ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of **4b**.

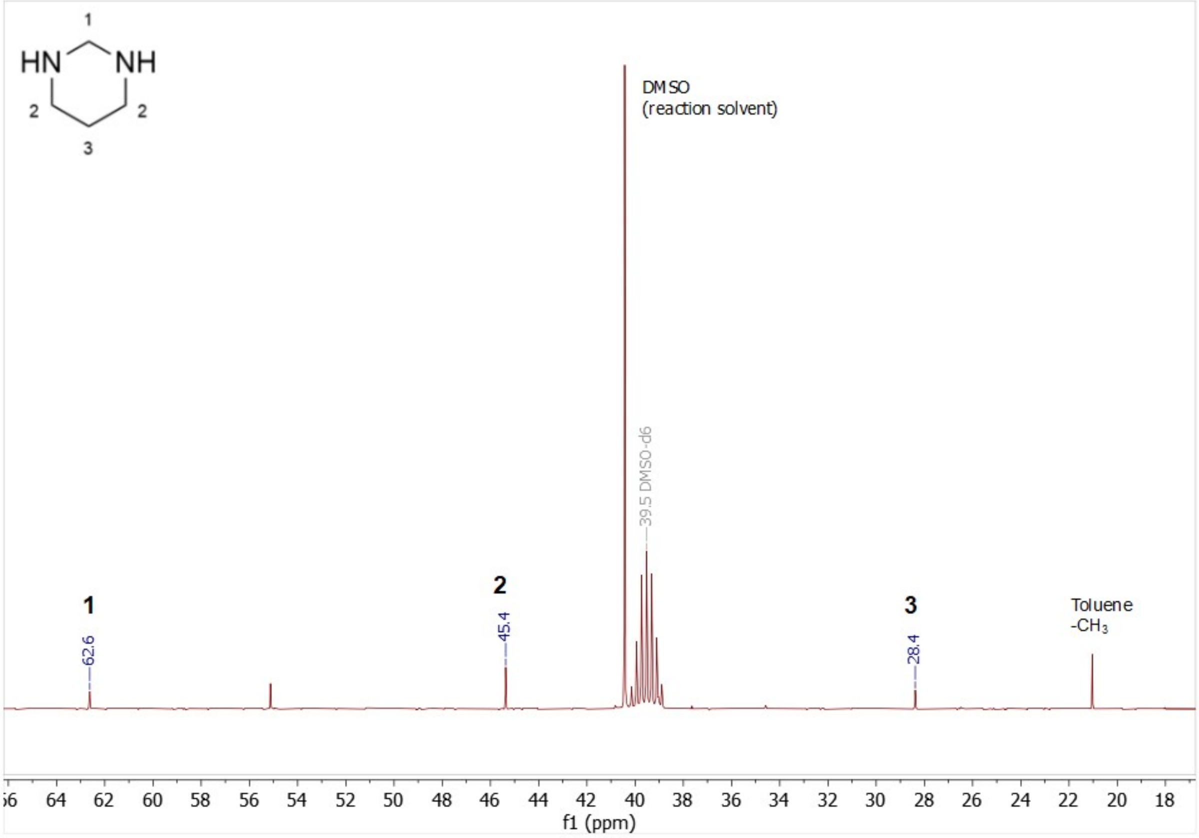
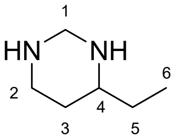


Figure S31 - $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6, 100.6 MHz) of **4b**.

4c (4-ethylhexahydropyrimidine)



4c was prepared according to the general procedure for POM aminolysis using 1,3-diaminopentane (1.2 equiv., 1.19 mL, 10 mmol) in 5 mL of 1,4-dioxane. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H ppm 3.84 (1H, d, J = 12.1 Hz, H$_{1A}$), 3.48 (1H, d, J = 12.1 Hz, H$_{1B}$), 2.99 (1H, ddt, J = 13.3, 4.0, 1.8 Hz, H$_{2A}$), 2.60 (1H, td, J = 12.8, 2.8 Hz, H$_{2B}$), 2.41 (1H, dtd, J = 10.9, 6.5, 2.8, H$_4$), 1.45 (1H, m (1.41- 1.48), H$_{3A}$), 1.23 (2H, m (1.11 - 1.34), H$_5$), 0.99 (1H, tdd, J = 12.8, 11.0, 4.4 Hz, H$_{3B}$), 0.76 (3H, t, J = 7.4 Hz, H$_6$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ_C ppm 62.3 (C$_1$), 56.7 (C$_4$), 45.1 (C$_2$), 33.5 (C$_3$), 29.8 (C$_5$), 9.7 (C$_6$). 57% conversion estimated by ^{1}H NMR spectroscopy integral ratios.

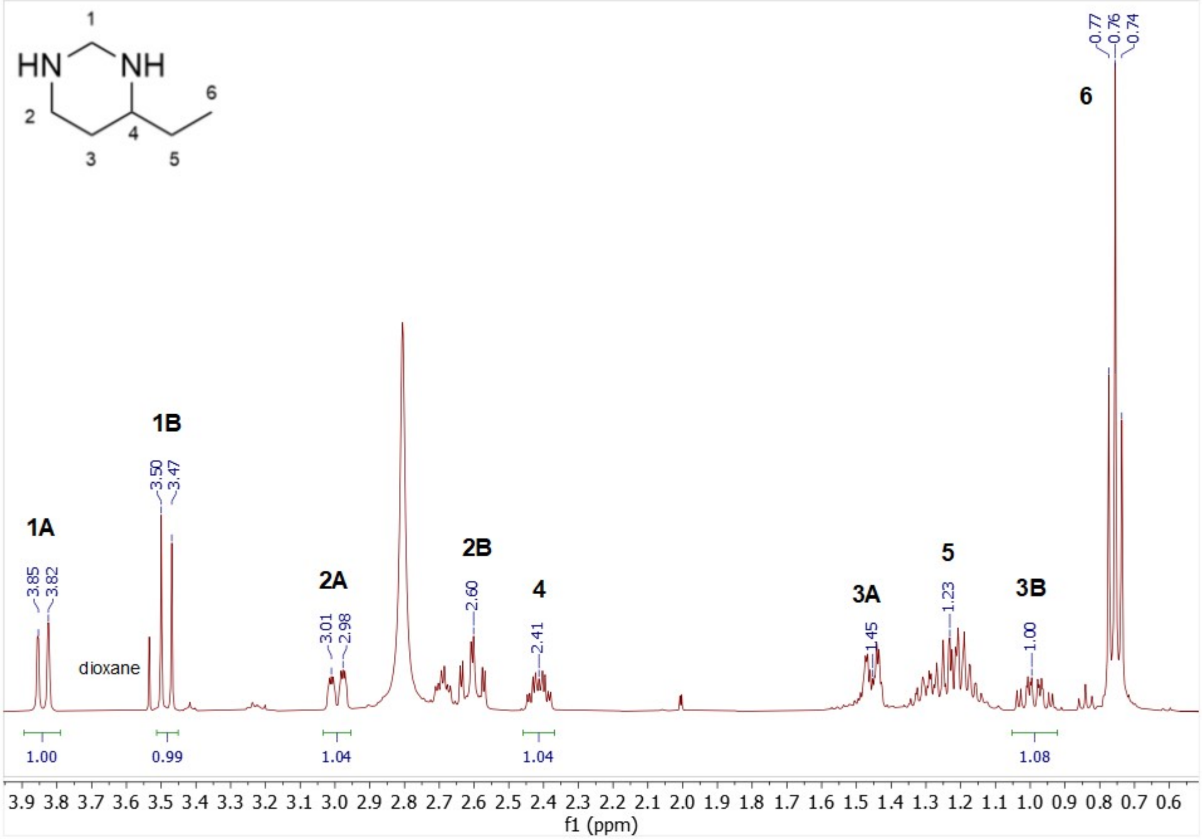


Figure S32 – ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **4c**.

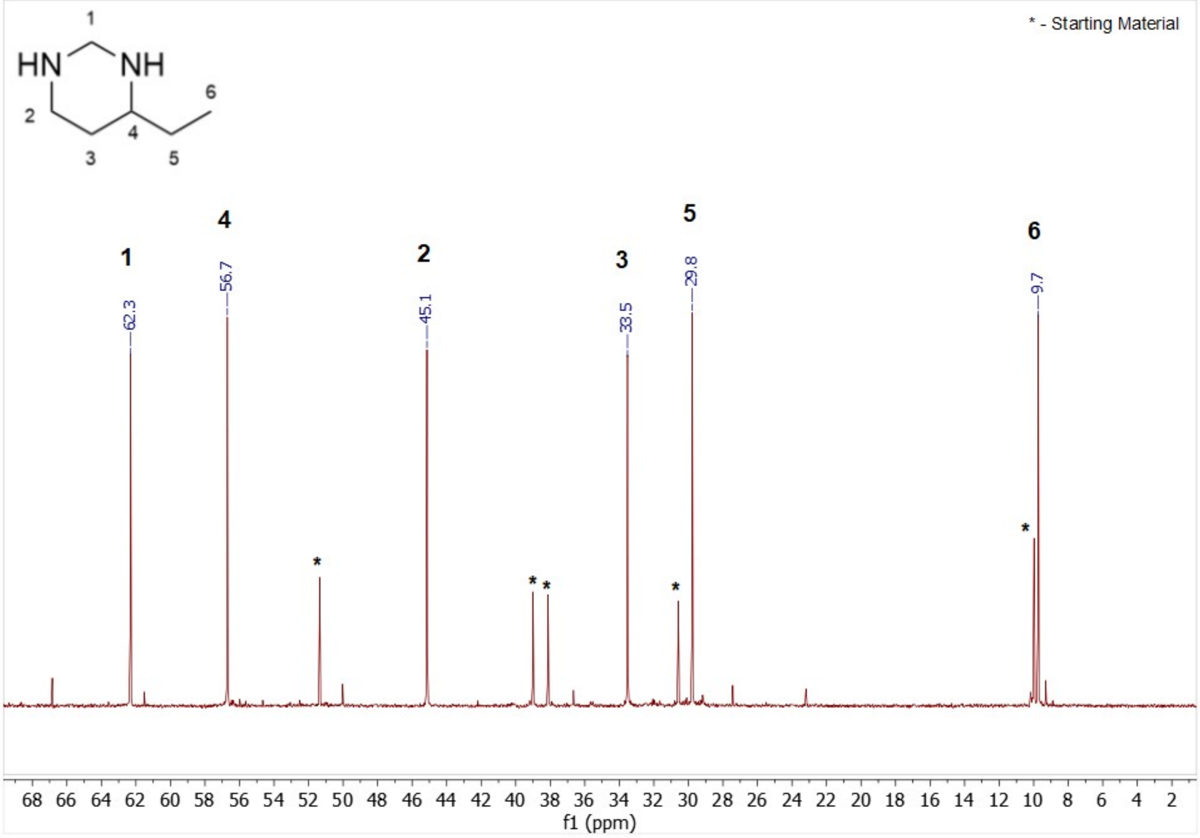
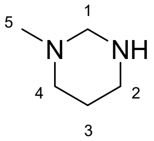


Figure S33 - $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **4c**.

4d (1-methylhexahydropyrimidine)



4d was prepared according to the general procedure for POM aminolysis using N-methyl-1,3-diaminopropane (1.2 equiv., 1.04 mL, 10 mmol) in 5 mL of 1,4-dioxane. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H ppm 3.57 (2H, s, H$_1$), 2.60 (2H, m (2.58 - 2.62 ppm), H$_2$), 2.40 (2H, m (2.37 - 2.42 ppm), H$_4$), 2.01 (3H, s, H$_5$), 1.48 (2H, m (1.42 – 1.51 ppm), H$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ_C ppm 66.9 (C$_1$), 55.1 (C$_4$), 44.3 (C$_2$), 42.7 (C$_5$), 27.0 (C$_3$). 43% conversion estimated by ^{1}H NMR spectroscopy integral ratios.

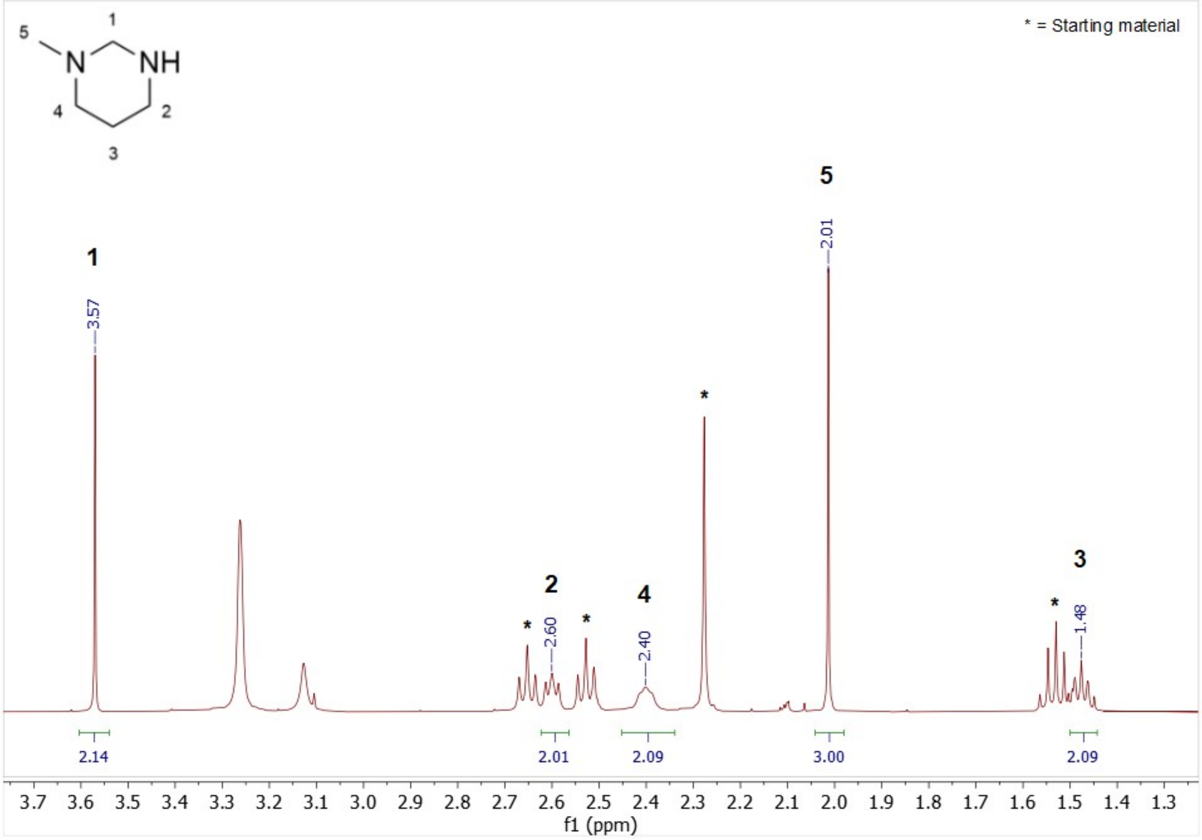


Figure S34 – ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **4d**.

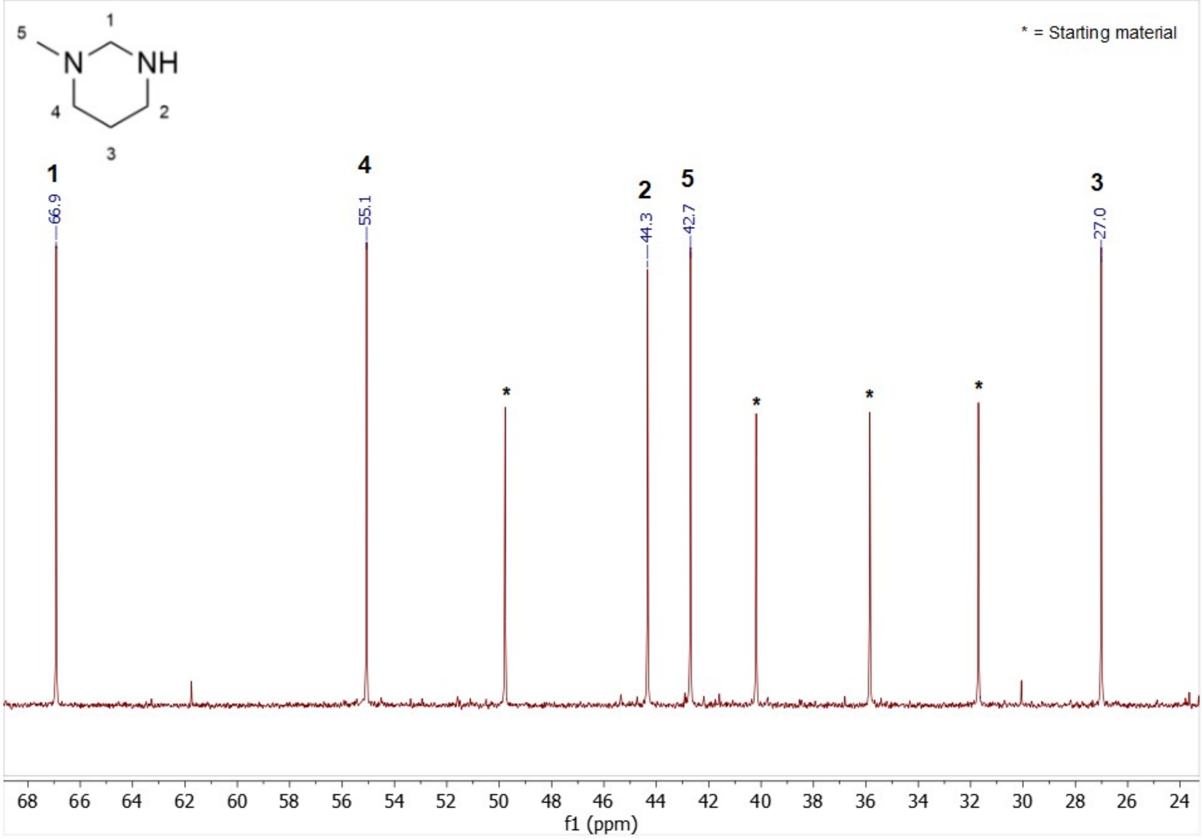
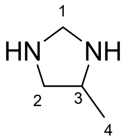


Figure S35 – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **4d**.

4e (4-methylimidazolidine)



4e was prepared according to the general procedure for POM aminolysis using 1,2-propandiamine (1.2 equiv., 0.86 mL, 10 mmol) in 5 mL of DMSO. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H ppm 3.56 (1H, d, *J* = 9.5 Hz, H$_{1A}$), 3.44 (1H, d, *J* = 9.5 Hz, H$_{1B}$), 2.88 (1H, m (2.82 - 2.92 ppm), H$_3$), 2.78 (1H, m (2.70 - 2.82 ppm), H$_{2A}$), 2.06 (1H, m (1.98 - 2.07 ppm), H$_{2B}$), 0.88 (3H, d, *J* = 6.4 Hz, H$_4$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ_C ppm 64.0 (C$_1$), 52.8 (C$_3$), 52.7 (C$_2$), 19.2 (C$_4$). 30% conversion calculated by ^{1}H NMR spectroscopy with TMB internal standard.

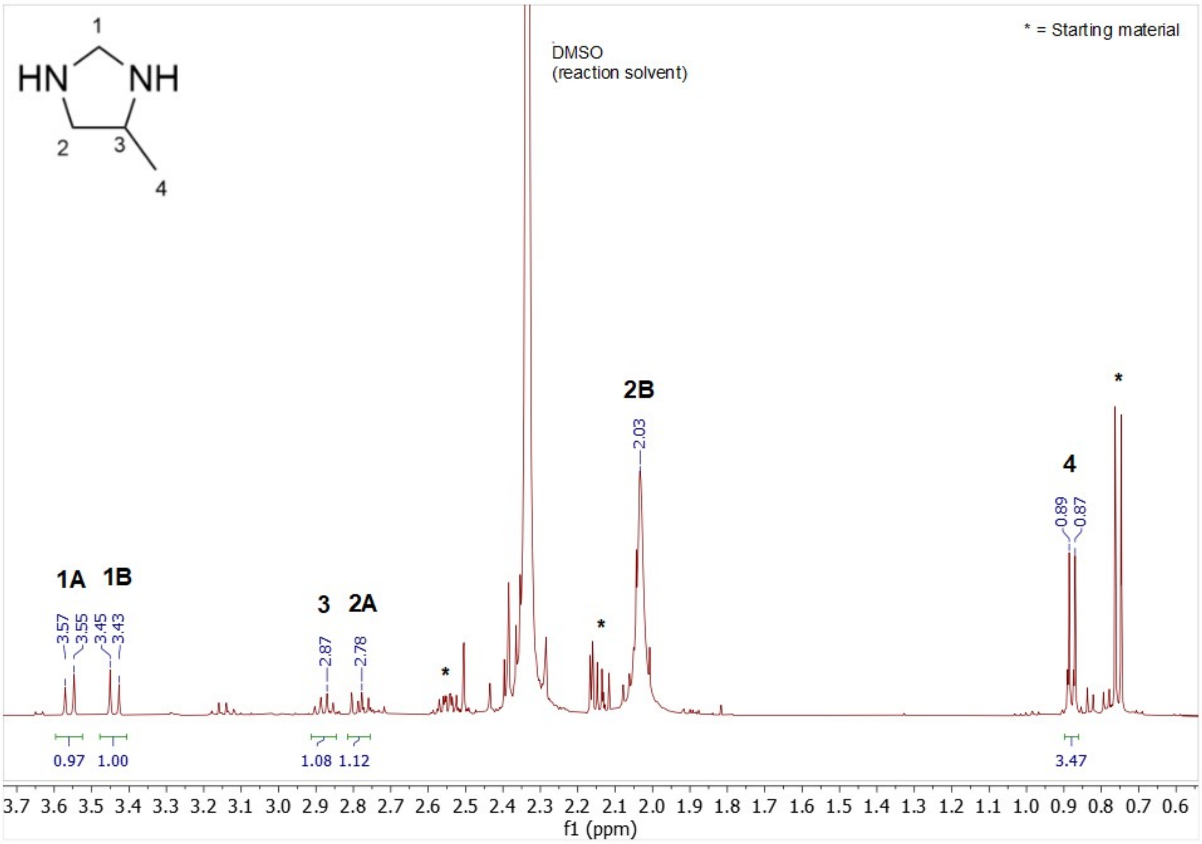
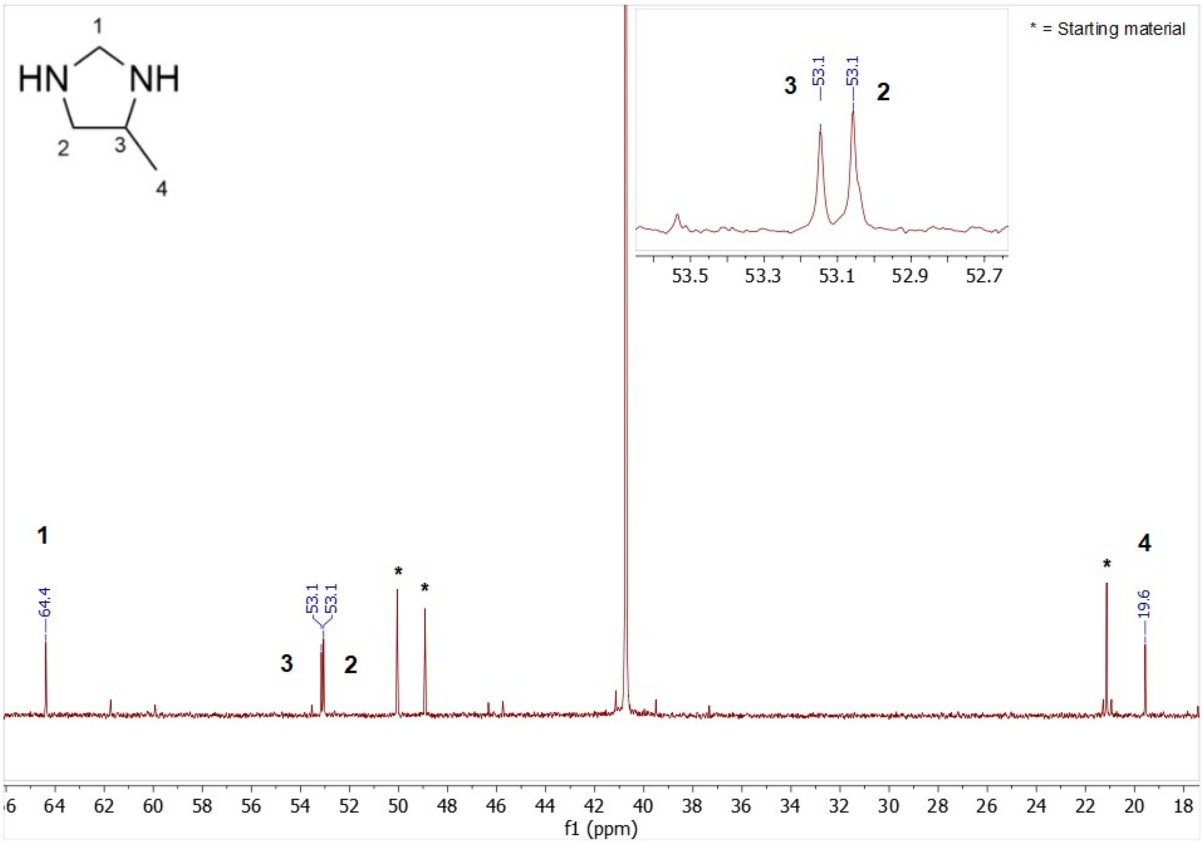


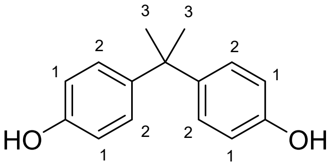
Figure S36 – ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **4e**.



<u>Figure S37</u> – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100.6 MHz) of **4e**.

3.3 Sequential Degradation Spectra

BPA (Bisphenol A)



BPA was prepared according to the procedure for the glycolysis of BPA-PC as part of a sequential degradation as described above in the general methods section. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H ppm 7.04 (4H, m (7.01 – 7.06 ppm), H_1), 6.69 (4H, m (6.66 – 6.71 ppm), H_2), 1.59 (6H, s, H_3).

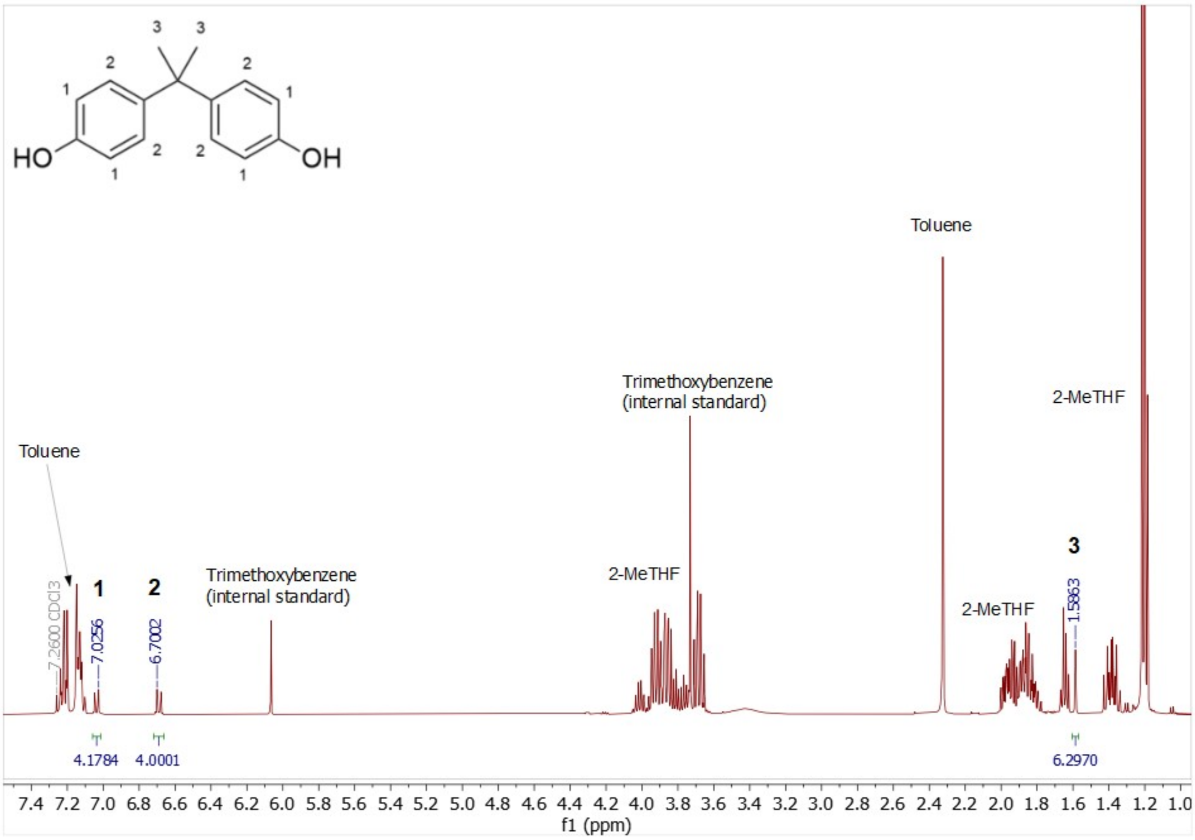
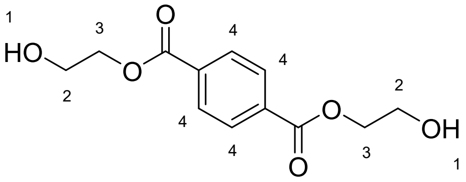


Figure S38 - ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **BPA**.

BHET (Bis(2-hydroxyethyl) terephthalate)



BHET was prepared according to the procedure for the glycolysis of PET as part of a sequential degradation as described above in the general methods section. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H ppm 8.12 (4H, s, H$_4$), 4.95 (2H, t, *J* = 5.7 Hz, H$_1$), 4.32 (4H, m (4.30 – 4.34 ppm), H$_3$), 3.73 (4H, q, *J* = 5.4 Hz, H$_2$).

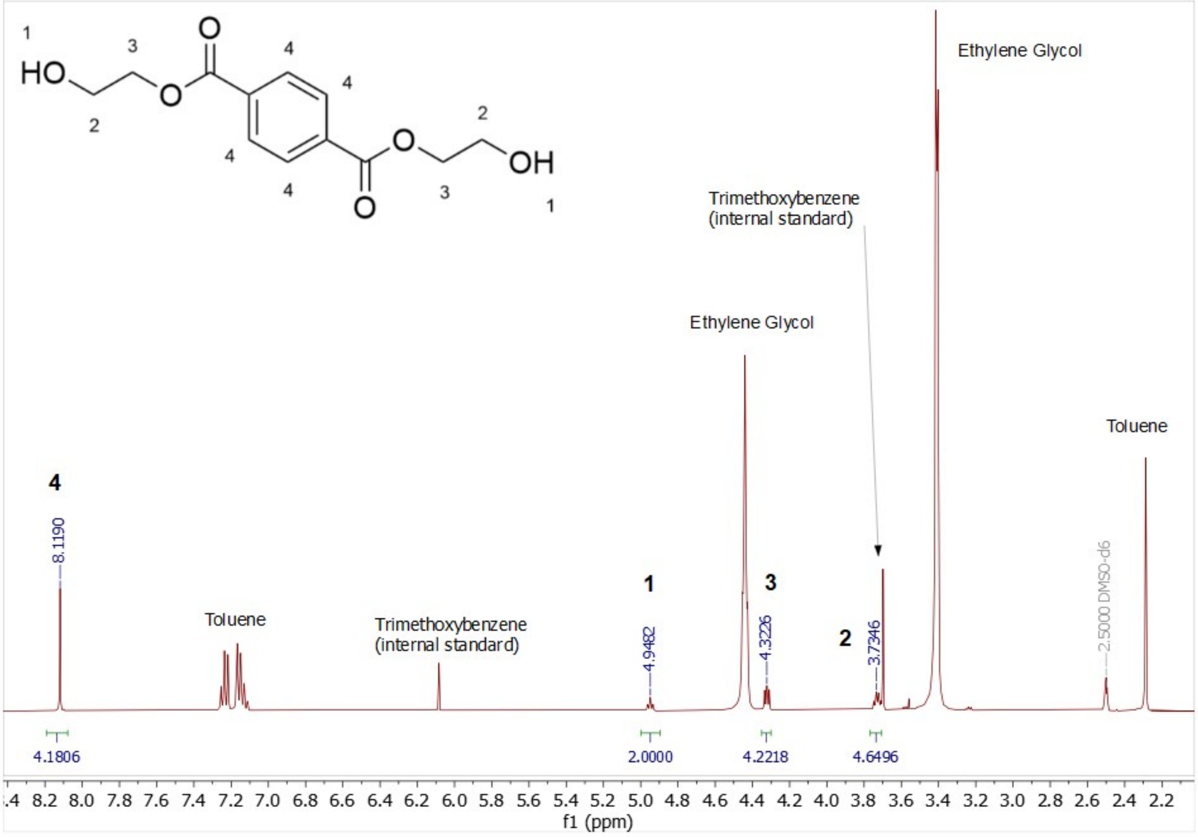


Figure S34 – ^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz) of **BHET**.

4. References

1. J. M. Payne, M. Kamran, M. G. Davidson and M. D. Jones, *ChemSusChem*, 2022, **15**, e202200255.
2. M. Berer, G. Pinter and M. Feuchter, *Journal of Applied Polymer Science*, 2014, **131**.
3. O. Tooley, W. Pointer, R. Radmall, M. Hall, T. Swift, J. Town, C. Aydogan, T. Junkers, P. Wilson, D. Lester and D. Haddleton, *ACS Polymers Au*, 2024, **4**, 311-319.
4. D. Sánchez-Roa, M. E. G. Mosquera and J. Cámpora, *The Journal of Organic Chemistry*, 2021, **86**, 16725-16735.