Supporting information

Depolymerization of polydimethylsiloxanes in ammonia – a new approach to silicone recycling

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Experimental

Anhydrous ammonia was purchased from Spectra Gases Inc.

Trimethylsiloxy terminated polydimethylsiloxane (PMS-200), silanol terminated polydimethylsiloxane (PDMS-$(OH)_2$), trimethylsiloxy terminated methylhydrosiloxane, K-18 catalyst (25 % solution of tin diethyldicaprylate in TEOS) were purchased from LLC "SILANE".

Karstedt's catalyst (a xylene solution of a platinum (0) complex with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, Pt ~2%) was purchased from Aldrich.

DMS-V25 was purchased from Gelest.

Chlorotrimethylsilane (TMSCl), Tetramethylammonium hydroxide (25% w/w in methanol), Amberlyst 15 were purchased from abcr GmbH.

Benzoyl peroxide was purchased from Acros.

Technical silicone rubber IVb – product of JSC "Polymer-Apparat".

Water was deionised by deionizer MILLIPORE MILLI-Q SYNTHESIS.

^{29}Si NMR spectra were recorded on a Bruker Avance™ 500 spectrometer (Germany) operating at 79 MHz. The chemical shifts for ^{29}Si were measured with TMS as an external standard.

SEC analysis was performed on a Shimadzu chromatograph using a RID - 20A refractometer as the detector, a PSS SDV analytical 10^3 Å column (Size 300 x 8 mm) and 10^4 Å column (Size 300 x 8 mm), and toluene as an eluent.

Gas chromatography (GC) analysis was performed on a chromatograph (Crystallux 4000, Russia) at 50–280 °C, 20° min−1; catharometer detector, columns (2 mm × 2 m) with 5% SE-30 stationary phase deposited onto Chromaton-N-AW-HMDS, helium as a carrier gas (30 mL min−1). Data were recorded and processed using the NetChrom 2.0 program package (Crystallux, Russia).

General procedure for depolymerization of trimethylsiloxy terminated polydimethylsiloxane (PMS-200) in ammonia (samples 1-4)

PMS-200 and required amount of H_2O were loaded into an autoclave equipped with a magnetic stirrer, then the autoclave was filled with required amount of NH_3 under chill-down using an IN-FLOW mass flow meter (Bronkhorst, Netherlands). The reaction mixture was heated at **T**°C for **t** h and then decompressed. The depolymerization products were obtained as transparent viscous liquids. Reagent loads, temperature and duration of synthesis are shown in Table S1. The products obtained were isolated in quantitative yields. The yield of HMDS was calculated using the M_n^{NMR} (Fig S34) of the initial PMS for depolymerizates that do not contain a high molecular weight fraction.

Table S1.

№	m(PMS-200), g	PMS-200, mmol	V(H_2O), mL	H_2O, mmol	m(NH_3), g	T, °C	t, hours	HMDS yield, %
1a	1	14	1	56	5	150	24	83.7
1b	1	14	1	56	5	150	12	91.6
1c	1	14	1	56	5	150	10	-
1d	1	14	1	56	5	150	8	-
1e	1	14	1	56	5	150	6	-
2a	1	14	0.5	28	5	150	24	84.2
2b	1	14	0.25	14	5	150	24	69.5
2c	1	14	0.1	5.5	5	150	24	-
2d	1	14	0	0	5	150	24	-
3a	1	14	0.5	28	4	150	24	42.1
3b	1	14	0.5	28	3	150	24	-
3c	1	14	0.25	14	4	150	24	75.8
3d	1	14	0.25	14	3	150	24	-
4a	1	14	1	56	5	50	48	-
4b	1	14	1	56	5	125	24	-
4c	1	14	1	56	5	125	48	-

General procedure for depolymerization of silanol terminated polydimethylsiloxane (PDMS-(OH)$_2$) in ammonia (sample 5)

PDMS-(OH)$_2$ and required amount of H_2O were loaded into an autoclave equipped with a magnetic stirrer, then the autoclave was filled with 5 g of NH_3 under chill-down using an IN-FLOW mass flow meter (Bronkhorst, Netherlands). The reaction mixture was heated at 150°C for 24 h and then decompressed. The depolymerization products were obtained as transparent viscous liquids. Reagent loads are shown in Table S2. The products obtained were isolated in quantitative yields.

Table S2.

№	m(PDMS-(OH)$_2$), g	PDMS-(OH)$_2$, mmol	V(H_2O), ml	H_2O, mmol	m(NH_3), g	T, °C	t, hours
5	1	14	0.25	14	5	150	24
5a	1	14	1	56	5	150	24
5b	1	14	0.5	28	5	150	24
5c	1	14	0.1	5.5	5	150	24
5d	1	14	0	0	5	150	24

Synthesis of model silicone rubbers

Synthesis of silicone rubber IIIa

20 µL of Karstedt's catalyst was placed added to a vial containing 9.1 g (0.5 mmol) of DMS-V25. This mixture was then quickly added to the 30 % solution of 10 g (1 mmol) of methylhydrosiloxane in toluene, stirred, and poured into a PTFE mold to cure. After evaporation of the solvent, the silicone rubber IIIa was heated at 80 °C/1 mbar. The transparent cross-linked material was obtained, the gel fraction was 98%.

Synthesis of silicone rubber IIIb

The mixture of 50 % solution of 10 g (0.14 mmol (calculated for dimethylsiloxane unit)) of silanol terminated polydimethylsiloxane PDMS-$(OH)_2$ in toluene and 1 mL of K-18 was poured into a PTFE mold to cure. After evaporation of the solvent, the silicone rubber IIIb was heated at 80 °C/1 mbar. The transparent cross-linked material was obtained, the gel fraction was 93%.

Synthesis of silicone rubber IIIc

The mixture of 10 g (0.14 mmol (calculated for dimethylsiloxane unit)) of silanol terminated polydimethylsiloxane PDMS-$(OH)_2$ and 0.1 g (1 wt. %) of benzoyl peroxide was poured into a PTFE mold to cure in a circulating air oven at 150° C for 24 hours. The transparent cross-linked material was obtained, the gel fraction was 62%.

General procedure for depolymerization of silicone rubbers IIIa – IIIc and industrial silicone waste IVa – IVb in ammonia (samples 6-10)

1 g of silicone and 0.25 mL (14 mmol) of H_2O were loaded into an autoclave equipped with a magnetic stirrer, then the autoclave was filled with 5 g of NH_3 under chill-down using an IN-FLOW mass flow meter (Bronkhorst, Netherlands). The reaction mixture was heated at 150°C for 24 h and then decompressed. The depolymerization products were obtained as transparent viscous liquids in case of samples 6-8 and as paste in case of samples 9-10.

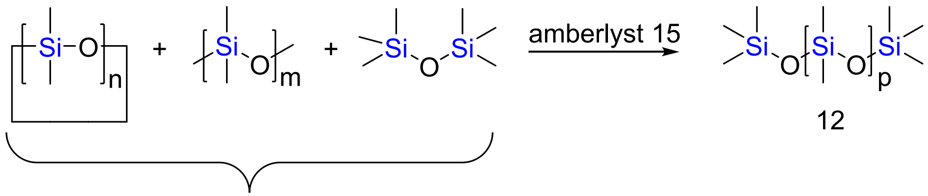
Isolation of reaction products 9-10

The mixtures of low molecular weight products obtained in experiments **8** and **9** were separated from the fillers by centrifugation in pentane solution. The solutions obtained were further decanted. The solvent was distilled off on a rotary vacuum evaporator at 50 °C/850 mbar. The filler was evacuated at rt/2 mbar. The filler content of the original sample was 25% in the case of IVa and 50% in the case of IVb. The product mass of 8 after isolation was 0.68 g, the yield was 91 %. The product mass of 9 after isolation was 0.45 g, the yield was 90 %.

General procedure for scaling up for depolymerization of industrial silicone waste IVa in ammonia (sample 11)

4.25 g of IVa and 1.06 mL (59 mmol) H_2O were loaded into an autoclave equipped with a mechanical stirrer, then the autoclave was filled with 21.25 g of NH_3 under chilldown using an IN-FLOW mass flow meter. The reaction mixture was heated at 150°C for 24 h and then decompressed. The depolymerization product was obtained as white paste. Then the sample 11 was separated from the fillers by centrifugation in pentane solution. The solution obtained was further decanted. The solvent was distilled off on a rotary vacuum evaporator at 50 °C/850 mbar. The product mass after isolation was 2.98 g, the yield was 93 %.

Preparation of polysiloxane by cationic polymerization of depolymerizate 2b (sample 12)



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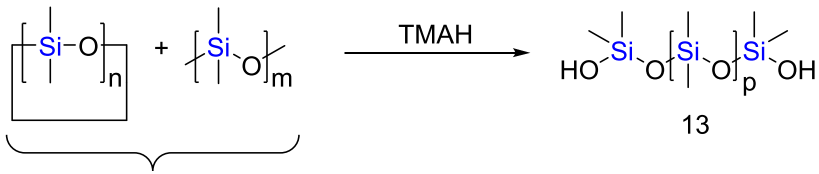
2b

A flask equipped with a magnetic stirrer was loaded with 3.09 g (41.76 mmol) of 2b and 0.062 g (2 wt%) of Amberlyst 15. The mixture was stirred for 8 hours at a temperature of 80 °C. Then the reaction mixture was dissolved in hexane. Amberlyst 15 was removed by filtration through a folded filter in a hexane solution. The solvent was distilled off on a rotary vacuum evaporator at 50 °C/360 mbar. Final polymer was analyzed by SEC.

Preparation of polysiloxane by anionic polymerization of depolymerizate 9 (sample 13)



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A test tube equipped with a magnetic stirrer was loaded with 0.18 g (2.5 mmol) of 9, 7 µL (0.018 mmol) of TMAH (25% w/w in methanol) and 0.2 mL of dry toluene. The mixture was stirred at 100 °C for 20 h under argon conditions. Then 0.0019 g (0.018 mmol) of TMSCl was added. Furthermore, the mixture was stirred at 100 °C for 2 h. Final polymer was analyzed by SEC.

GC data

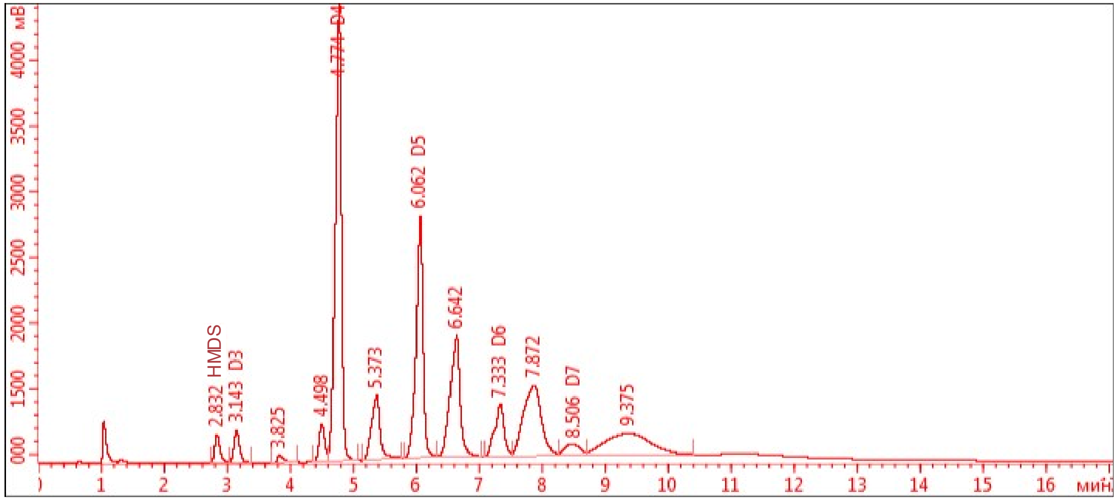


Fig S1. GC spectra of **1a**

Component	Time, min	Concentration, %	Area
HMDS	2.832	1.5957	1304.181
D3	3.143	1.9337	1580.432
L3	3.825	0.49096	401.261
	4.498	2.2279	1820.875
D4	4.774	28.917	23634.041
L4	5.373	5.7101	4666.888
D5	6.062	16.899	13811.166
L5	6.642	12.357	10099.293
D6	7.333	4.9375	4035.459
L6	7.872	12.97	10600.470
D7	8.506	1.8587	1519.108
L7	9.375	10.103	8256.820

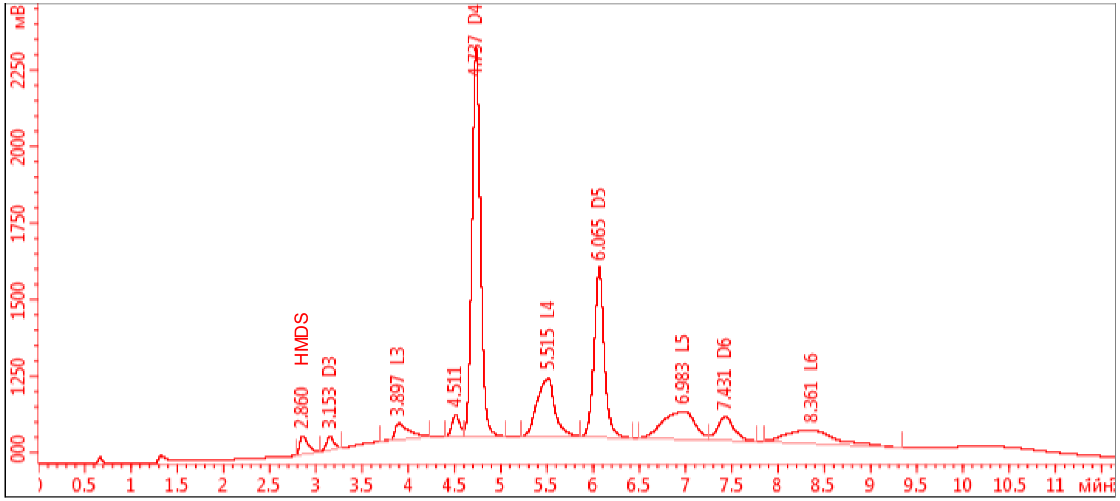


Fig S2. GC spectra of **1b**

Component	Time, min	Concentration, %	Area
HMDS	2.860	1.7382	372.331
D3	3.153	1.1199	239.875
L3	3.897	2.5349	542.989
	4.511	2.052	439.534
D4	4.737	38.171	8176.395
L4	5.515	12.281	2630.647
D5	6.065	20.222	4331.549
L5	6.983	10.092	2161.788
D6	7.431	4.419	946.553
L6	8.361	7.3697	1578.617

Component	Time, min	Concentration, %	Area
	1.289	0.52896	191.318
HMDS	2.841	1.6525	597.679
D3	3.154	1.6572	599.396
L3	3.828	3.0322	1096.718
	4.491	1.8424	666.375
D4	4.741	36.272	13119.221
L4	5.355	11.924	4312.801
D5	6.027	14.539	5258.558
L5	6.523	10.816	3912.176
	7.186	1.1334	409.955
D6	7.307	2.1165	765.509
L6	7.622	7.5182	2719.253
D7	8.339	1.345	486.476

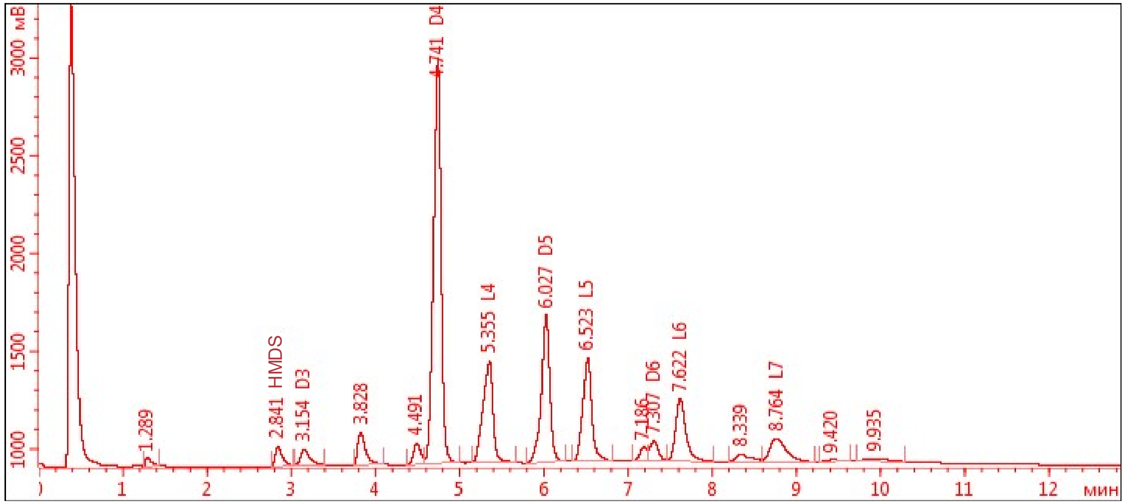


Fig S3. GC spectra of **1c**

L7	8.764	4.6103	1667.494
D8	9.420	0.3312	119.792
L8	9.935	0.68096	246.298

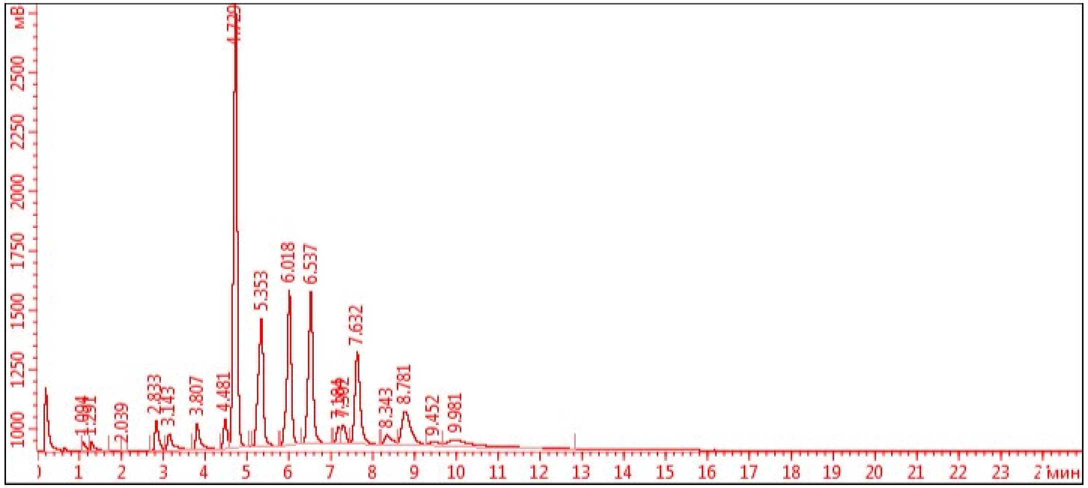
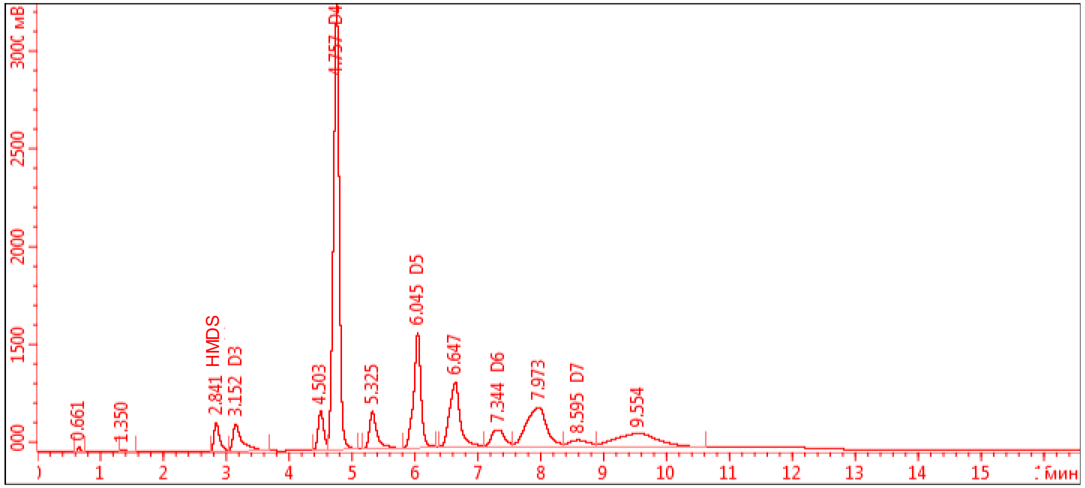


Fig S4. GC spectra of **1d**

Component	Time, min	Concentration, %	Area
	1.291	0.6473	246.171
	2.039	0.0095477	3.631
HMDS	2.833	2.1773	828.041
D3	3.143	1.8592	707.057
L3	3.807	2.1766	827.761
	4.481	1.9459	740.030
D4	4.729	30.693	11672.733
L4	5.353	12.106	4604.116
D5	6.018	12.387	4710.700
L5	6.537	13.316	5063.920
	7.184	1.1359	431.976
D6	7.302	1.5673	596.046
L6	7.632	9.1947	3496.774
D7	8.343	1.2489	474.968
L7	8.781	5.8247	2215.158
	9.452	0.75781	288.197
	9.981	2.9527	1122.918

Component	Time, min	Concentration, %	Area
	0.661	0.24052	91.599
	1.350	0.18552	70.654
HMDS	2.841	2.4663	939.248
D3	3.152	3.7153	1414.925
L3	4.503	3.2202	1226.366
D4	4.757	38.516	14668.258
L4	5.325	4.0871	1556.528
D5	6.045	12.259	4668.833
L5	6.647	9.9183	3777.271



D6	7.344	3.2685	1244.764
L6	7.973	11.72	4463.323
D7	8.595	1.9349	736.888
L7	9.554	8.4688	3225.247
D9	0.000	0	0.000
L9	0.000	0	0.000

Fig S5. GC spectra of **1e**

Component **Time,** **Concentration,** **Area**

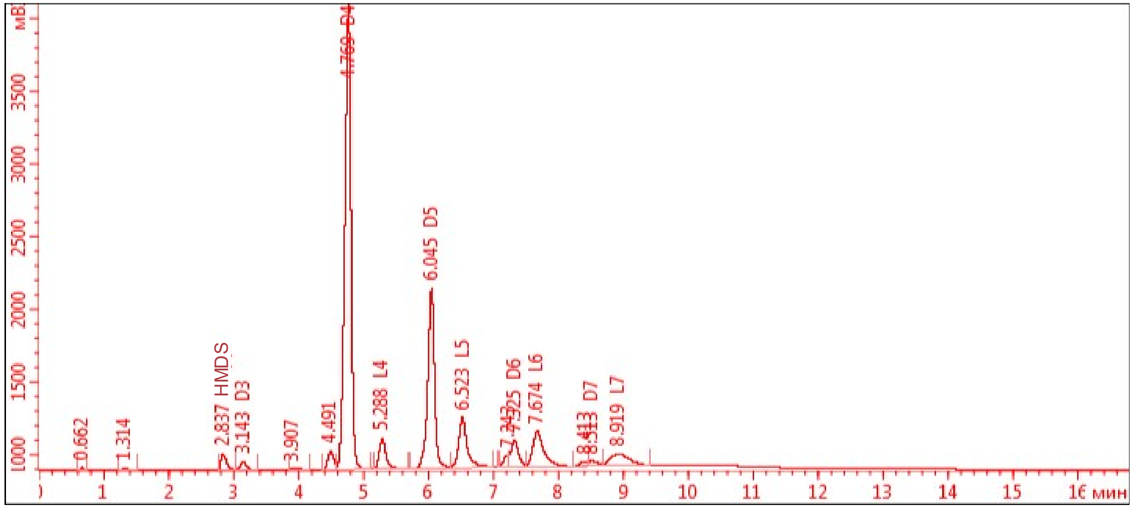


Fig S6. GC spectra of **2a**

	min	%	
	0.662	0.16459	72.149
	1.314	0.22871	100.259
HMDS	2.837	1.6025	702.466
D3	3.143	0.87898	385.314
L3	3.907	0.2294	100.562
	4.491	1.7835	781.817
D4	4.769	48.784	21385.077
L4	5.288	3.5038	1535.924
D5	6.045	20.138	8827.840
L5	6.523	6.8568	3005.755
	7.243	0.96565	423.305
D6	7.325	3.2529	1425.943
L6	7.674	6.4802	2840.667
	8.413	0.56874	249.316
D7	8.513	0.75028	328.897
L7	8.919	3.812	1671.040

Component	**Time, min**	**Concentration, %**	**Area**
	0.261	0.16215	56.459
	0.703	0.84345	293.679
	1.322	0.10893	37.927
HMDS	2.844	1.3246	461.225
D3	3.147	0.75743	263.726
L3	4.490	1.6199	564.045
D4	4.768	61.784	21512.395
L4	5.262	2.5899	901.771
D5	6.027	14.997	5221.836
L5	6.487	4.8135	1675.985
	7.189	1.0959	381.570

D6	7.312	2.1856	760.981
L6	7.628	4.7238	1644.782
D7	8.356	0.33857	117.887
L7	8.827	2.655	924.439

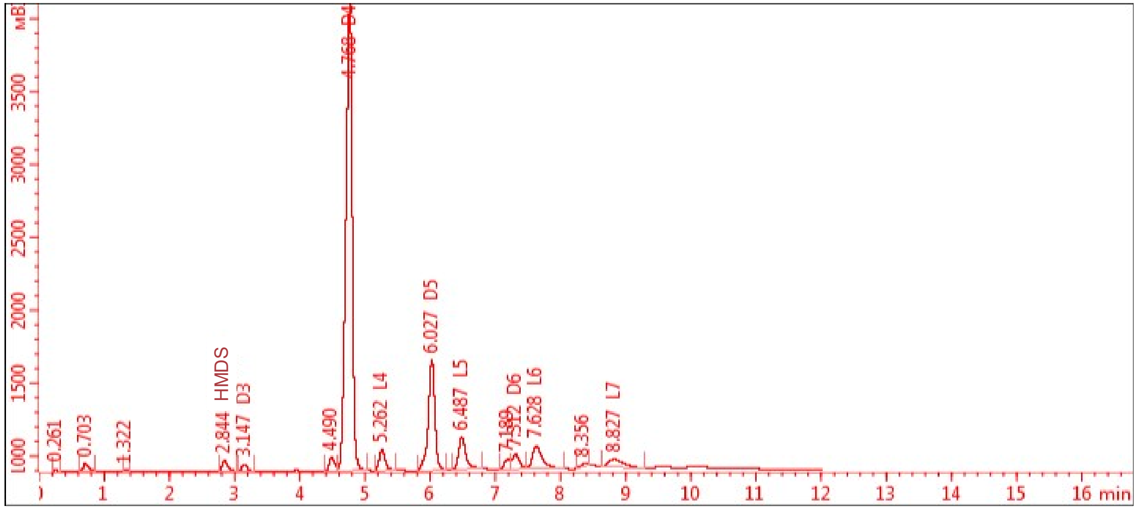


Fig S7. GC spectra of **2b**

Component	Time, min	Concentration, %	Area
HMDS	2,823	0,942	107,885
D3	3,147	5,097	583,767
	4,462	2,119	242,628
D4	4,720	61.784	21512.395
	5,897	1,473	168,671
D5	6,009	11,655	1334,770
L5	6,410	1,021	116,931
	7,168	1,941	222,274
D6	7,307	2,063	236,283

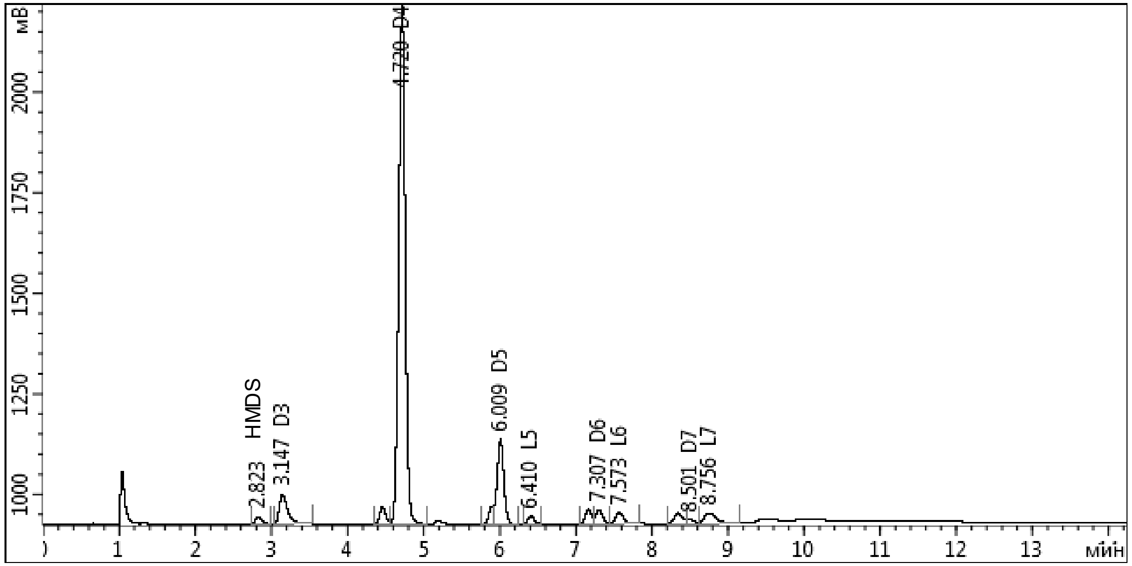


Fig S8. GC spectra of **2c**

Component	Time, min	Concentration, %	Area
HMDS	2,809	0,798	173,614
D3	3,135	0,902	196,292
L3	3,712	2,019	439,163
	4,458	2,014	437,959
D4	4,710	27,606	6004,355
	5,253	8,461	1840,183
D5	5,925	1,359	295,498
L5	6,025	19,832	4313,418
	6,513	14,065	3059,057
D6	7,194	1,417	308,174
L6	7,325	4,399	956,749
L6	7,573	1,810	207,288
	8,343	1,891	216,517
D7	8,501	0,619	70,935
L7	8,756	2,590	296,599

D7	8,390	0,397	86,370
L7	8,756	2,590	296,599

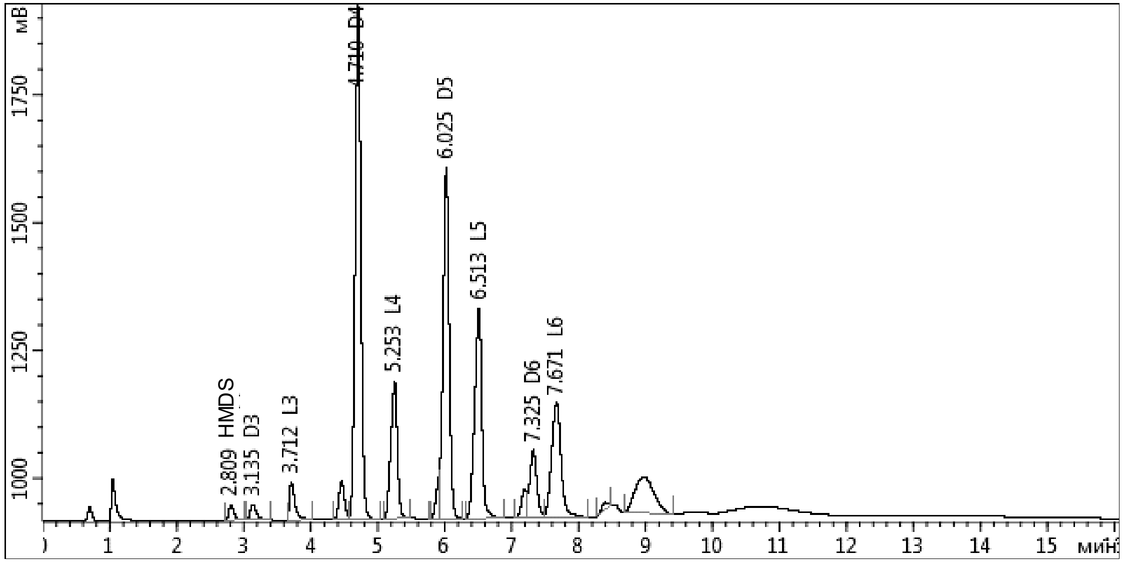


Fig S9. GC spectra of **3a**

Component	Time,	Concentration, %	Area

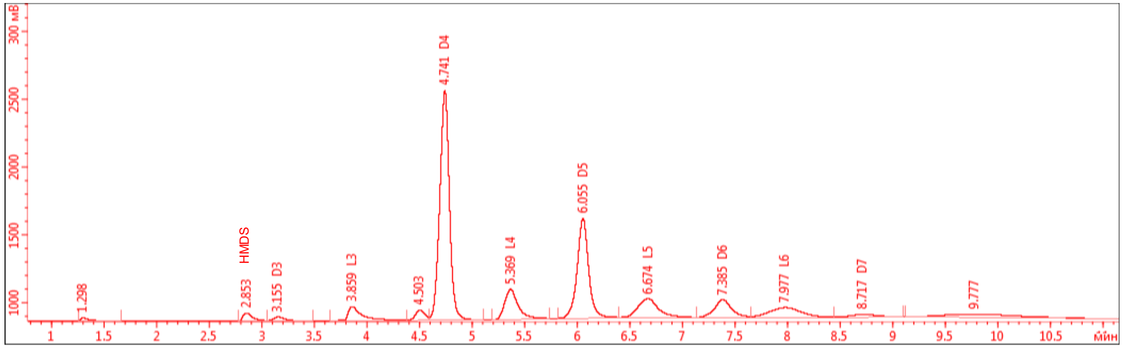


Fig S10. GC spectra of **3b**

	min		
	1.298	0.65718	181.421
HMDS	2.853	1.4691	405.574
D3	3.155	0.92414	255.118
L3	3.859	3.7068	1023.292
	4.503	1.715	473.455
D4	4.741	39.308	10851.401
L4	5.369	7.0388	1943.141
D5	6.055	20.291	5601.632
L5	6.674	7.3494	2028.877
D6	7.385	5.6155	1550.209
L6	7.977	5.6737	1566.293
D7	8.717	1.3389	369.621
L7	0.000	2,590	0.000
D9	0.000	0	0.000
	9.777	0	1356.068
L9	0.000	4.9122	0.000

Component	**Time, min**	**Concentration, %**	**Area**
HMDS	2.842	1.44	887.372
D3	3.151	1.0844	668.264
L3	3.911	0.14015	86.370
	4.501	1.5571	959.581
D4	4.802	52.035	32066.629
L4	5.303	2.7816	1714.147
D5	6.061	18.702	11524.913
L5	6.525	5.1013	3143.674
	7.205	1.1179	688.905
D6	7.328	2.9107	1793.737
L6	7.660	5.3622	3304.455
D7	8.386	1.765	1087.652
L7	8.879	4.2981	2648.662

L9	10.257	1.1816	728.145

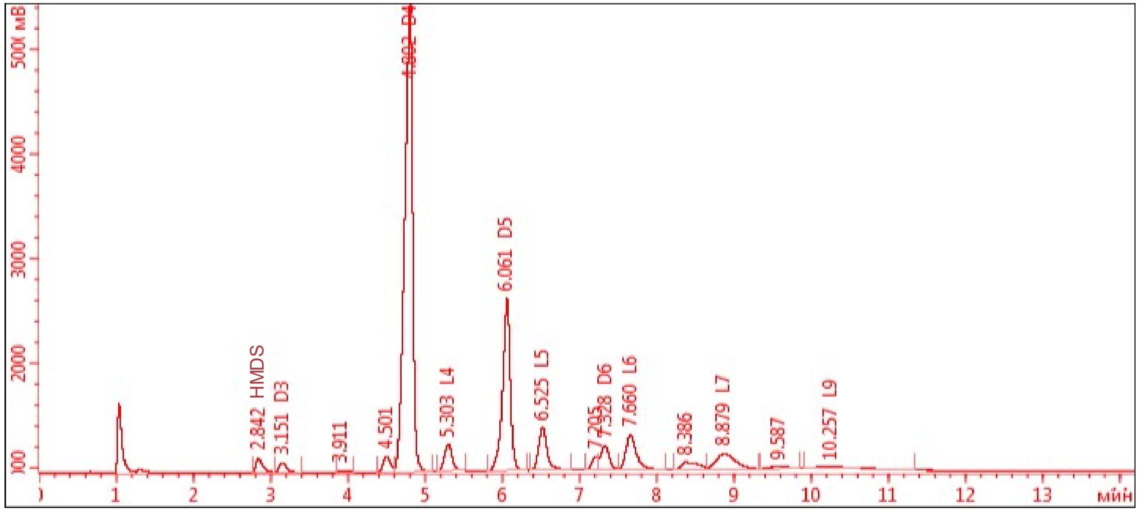


Fig S11. GC spectra of **3c**

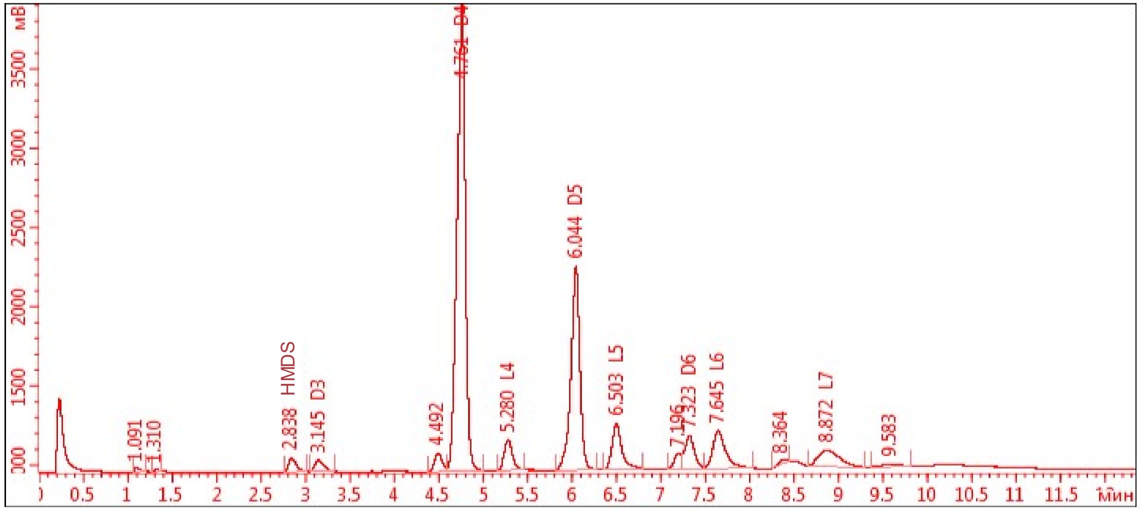


Fig S12. GC spectra of **3d**

Component	**Time, min**	**Concentration, %**	**Area**
	1.091	0.28795	115.430
	1.310	0.10007	40.115
HMDS	2.838	1.367	547.975
D3	3.145	1.1899	477.014
	4.492	1.7154	687.669
D4	4.761	48.08	19273.910
L4	5.280	3.1375	1257.755
D5	6.044	22.307	8942.200
L5	6.503	5.467	2191.576
	7.196	1.2498	501.020
D6	7.323	4.015	1609.483
L6	7.645	5.9734	2394.554
D7	8.364	0.40542	162.522
L7	8.872	4.1705	1671.837
	9.583	0.53424	214.160

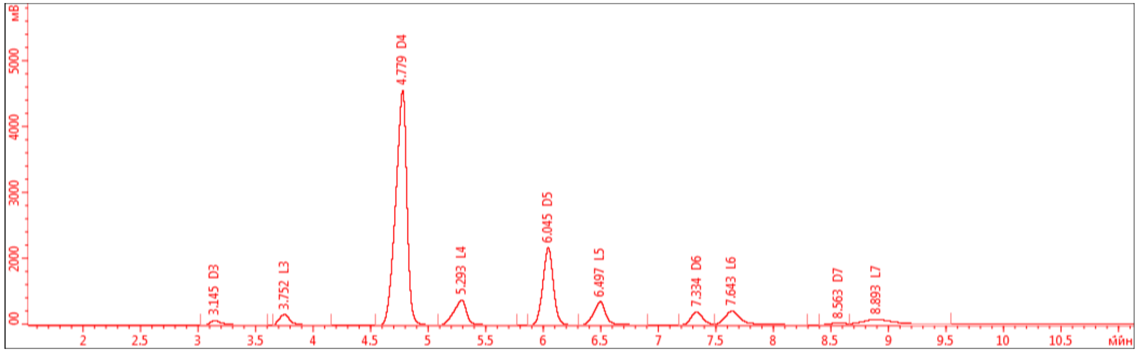


Fig S13. GC spectra of **5**

Component	**Time, min**	**Concentration, %**	**Area**
D3	3.145	1.3586	602.431
L3	3.752	2.5069	1111.585
D4	4.779	54.8	24299.326
L4	5.293	6.8272	3027.310
D5	6.045	16.807	7452.533
L5	6.497	5.835	2587.350
D6	7.334	3.1766	1408.551
L6	7.643	4.5733	2027.865
D7	8.563	0.54608	242.140
L7	8.893	3.5693	1582.687

Component	**Time,**	**Concentration, %**	**Area**

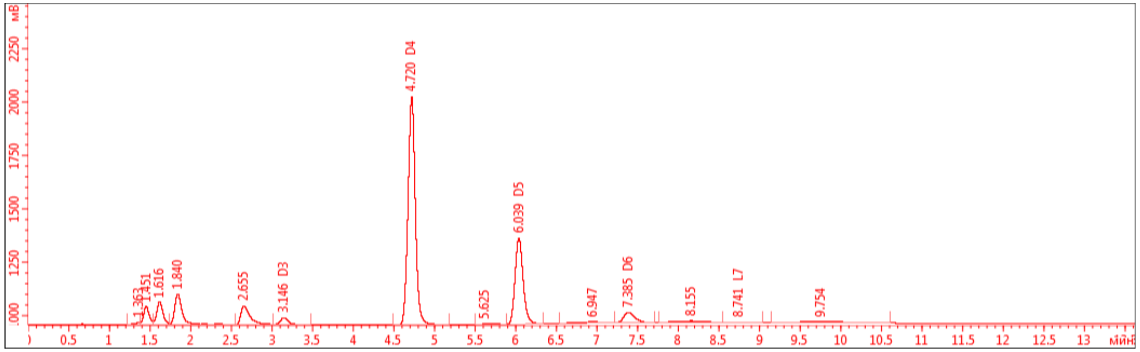


Fig S14. GC spectra of **6**

	min		
	1.363	0.49899	68.169
	1.451	3.132	427.871
	1.616	4.3269	591.121
	1.840	7.3866	1009.116
	2.655	5.2028	710.769
D3	3.146	1.7017	232.473
L3	0.000	0.000	0.000
D4	4.720	48.98	6691.335
L4	5.625	0.24967	34.108
D5	6.039	20.395	2786.228
L5	6.947	1.0259	140.157
D6	7.385	3.3344	455.523
D7	8.155	1.5072	205.909
L7	8.741	0.29424	40.198
	9.754	1.9648	268.420

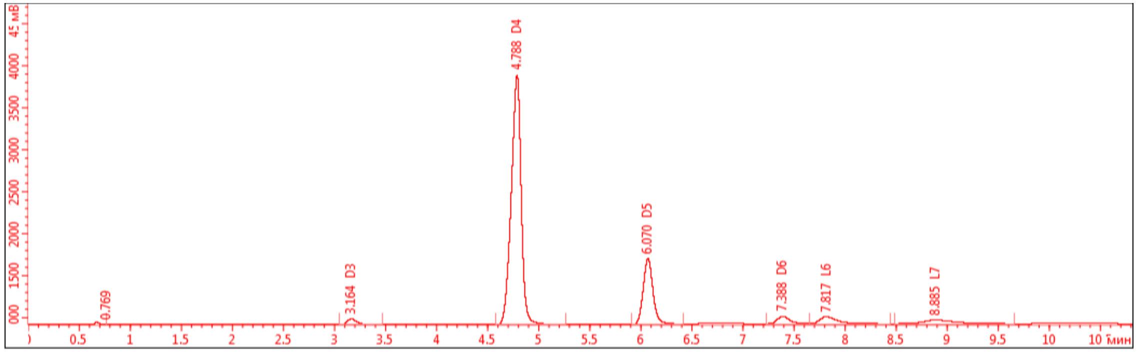


Fig S15. GC spectra of **7**

Component	**Time, min**	**Concentration, %**	**Area**
D3	3.164	1.6413	467.863
L3	0.000	0	0.000
D4	4.788	70.266	20029.083
L4	0.000	0	0.000
D5	6.070	18.247	5201.285
L5	0.000	0	0.000
D6	7.388	2.6056	742.731
L6	7.817	3.5755	1019.182
D7	0.000	0	0.000
L7	8.885	3.665	1044.697

Component	**Time,**	**Concentration, %**	**Area**

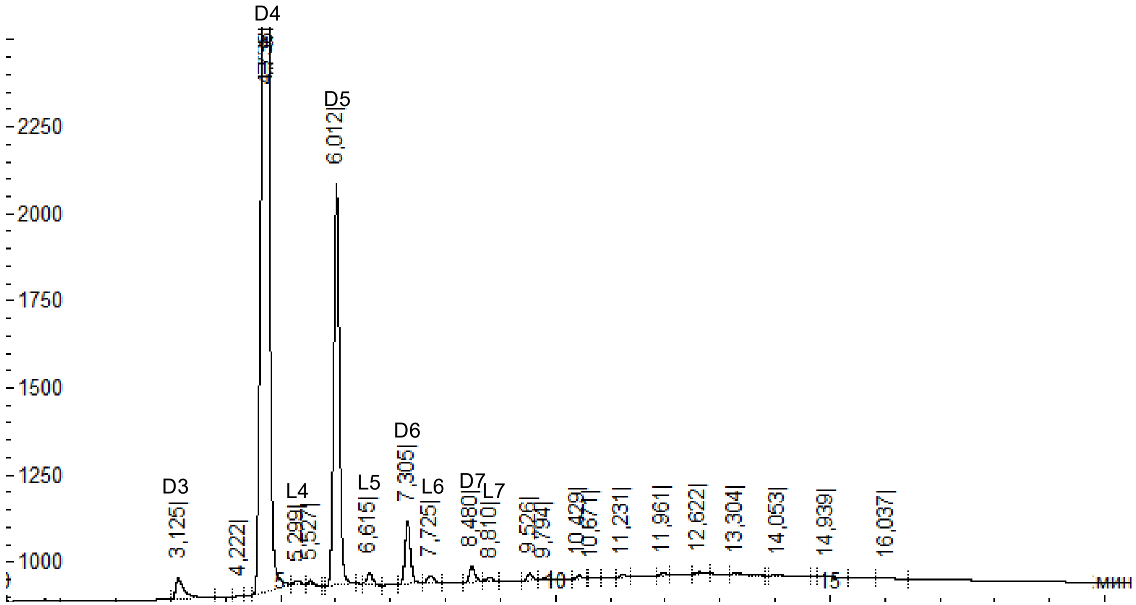


Fig S16. GC spectra of **8**

	min		
D3	3.125	1.715	676.088
L3	4.222	0.041	16.195
D4	4.738	69.947	27577.284
L4	5.299	0.206	81.298
	5.527	0.229	90.138
D5	6.012	20.962	8264.372
L5	6.615	0.641	252.576
D6	7.305	3.255	1283.441
L6	7.725	0.475	187.359
D7	8.480	0.782	308.266
L7	8.810	0.239	94.372
D8	9.526	0.346	136.376
L8	9.794	0.069	27.377
D9	10.429	0.202	79.629
L9	10.671	0.034	13.555
	11.231	0.127	50.010
	11.961	0.099	38.859
	12.622	0.111	43.928
	13.304	0.146	57.441
	14.053	0.139	54.692
	14.939	0.129	50.980
	16.037	0.107	42.000

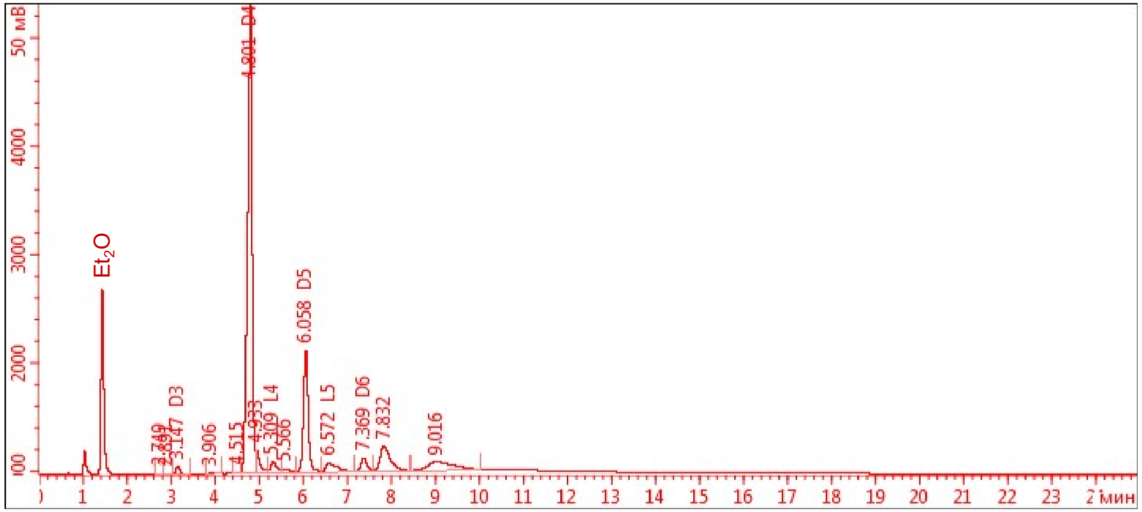


Fig S17. GC spectra of **9**

Component	Time, min	Concentration, %	Area
	2.749	0.077256	41.116
	2.891	0.085607	45.560
D3	3.147	0.90481	481.541
L3	3.906	0.2534	134.858
	4.515	0.12066	64.216
D4	4.801	59.916	31887.402
	4.933	2.5943	1380.660
L4	5.309	1.9678	1047.275
	5.566	0.8213	437.095
D5	6.058	15.519	8259.149
L5	6.572	2.8392	1511.037
D6	7.369	2.3327	1241.450
L6	7.832	6.8592	3650.441
L7	9.016	5.7086	3038.103

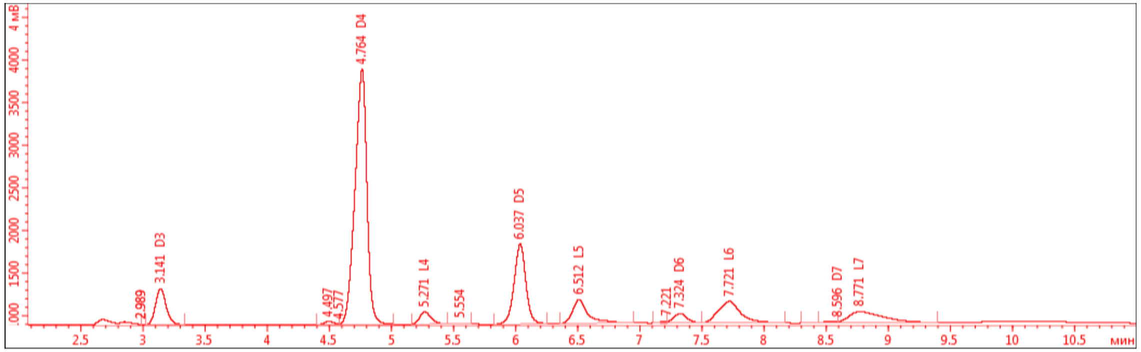


Fig S18. GC spectra of **10**

Component	Time, min	Concentration, %	Area
D3	3.141	6.3813	2478.797
L3	0.000	0.000	0.000
	4.497	0.50419	195.853
D4	4.764	51.181	19881.213
L4	5.271	2.3305	905.268
	5.554	0.1183	45.954
D5	6.037	15.777	6128.550
L5	6.512	6.1659	2395.132
D6	7.221	0.19607	76.163
	7.324	2.1386	830.733
L6	7.721	8.1838	3178.961
D7	8.596	0.3189	123.875
L7	8.771	6.704	2604.144

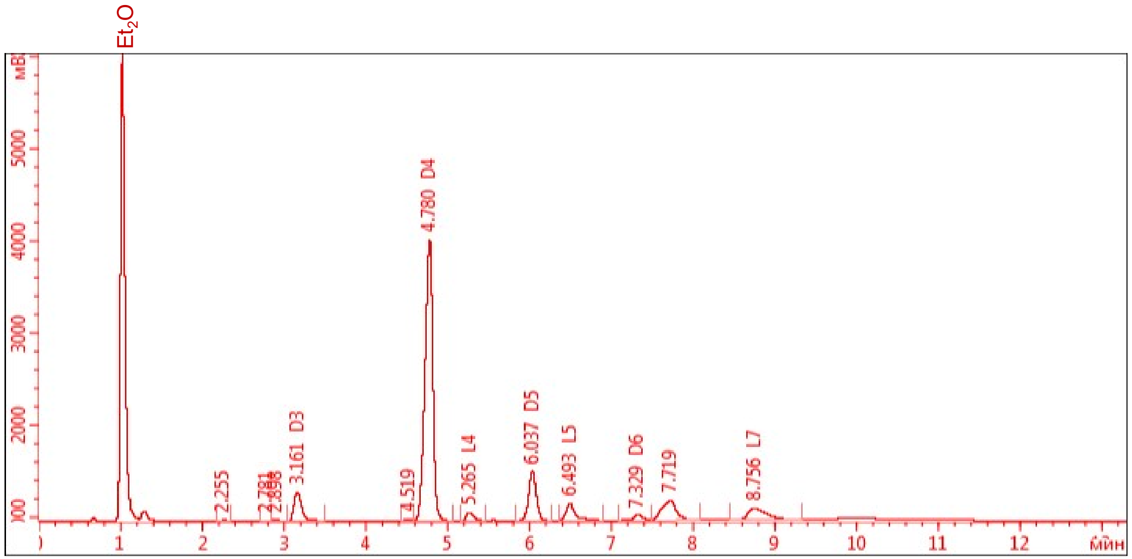


Fig S19. GC spectra of **11**

Component	**Time, min**	**Concentration, %**	**Area**
	2.255	0.20039	66.723
	2.781	0.23228	77.339
	2.898	0.34489	114.834
D3	3.161	6.197	2063.356
L3	0.000	0	0.000
	4.519	0.33544	111.690
D4	4.780	60.561	20164.681
L4	5.265	1.6556	551.251
D5	6.037	10.559	3515.881
L5	6.493	4.3457	1446.948
D6	7.329	1.4739	490.743
L6	7.719	7.8474	2612.875
L7	8.756	6.2467	2079.917

SEC data

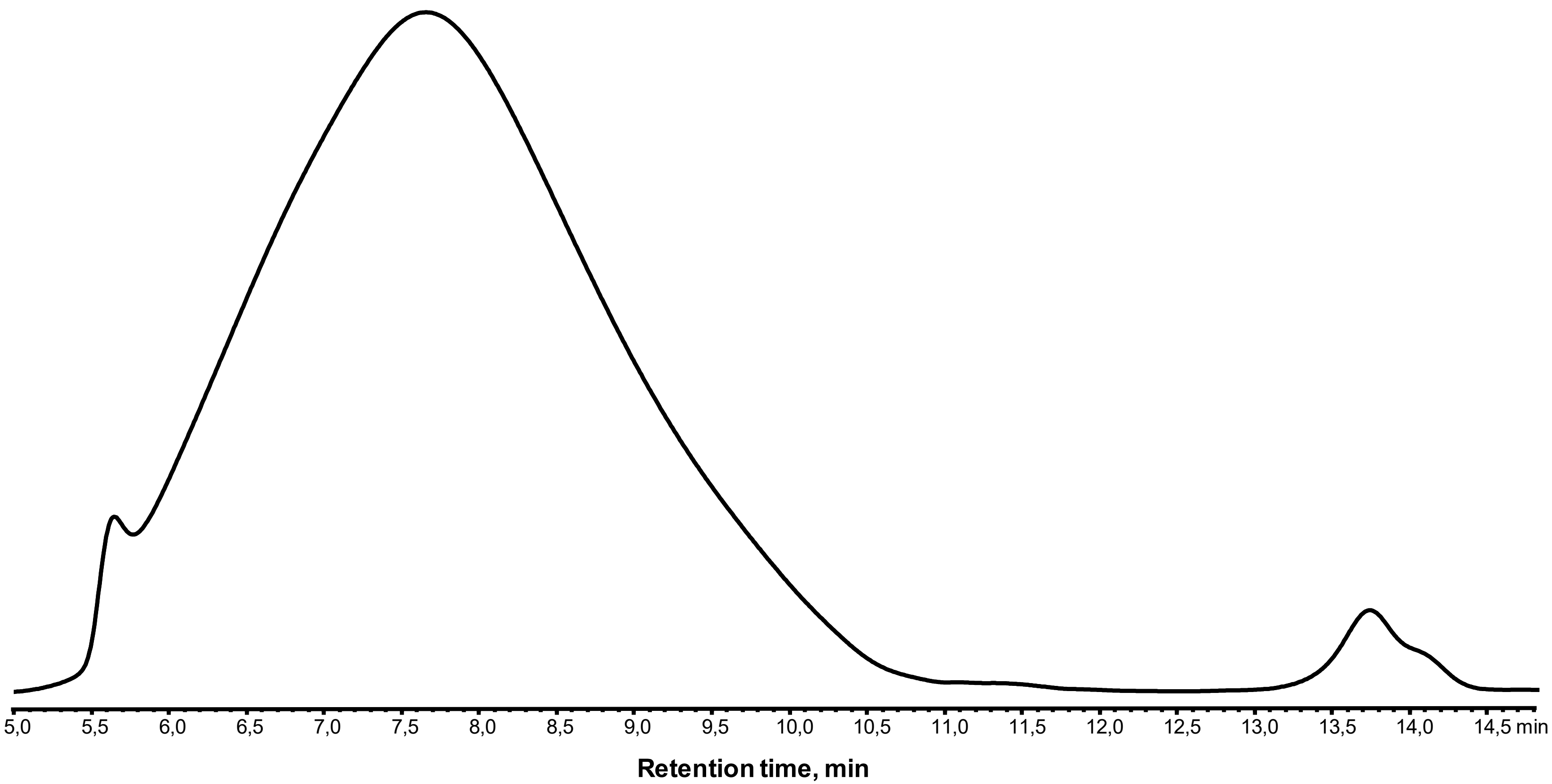


Fig S20. SEC curve of PMS-200

Table S3.

sample	Mp, kDa	Mn, kDa	Mw, kDa	PDI	Column size, Å
PMS-200 (I)	14.1	8.6	19.3	2.25	10^3

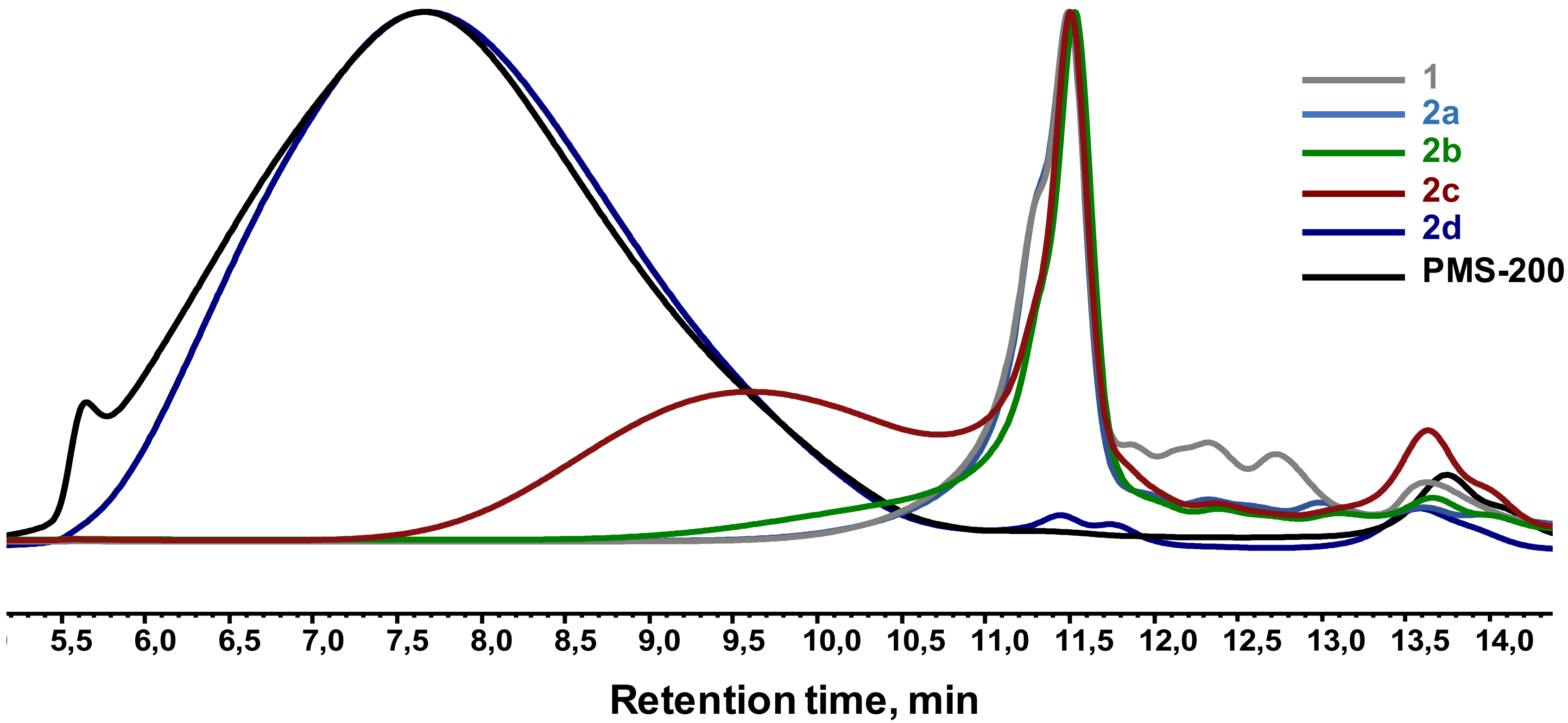


Fig S21. SEC curves of products 2a-2b after ammonia decompression

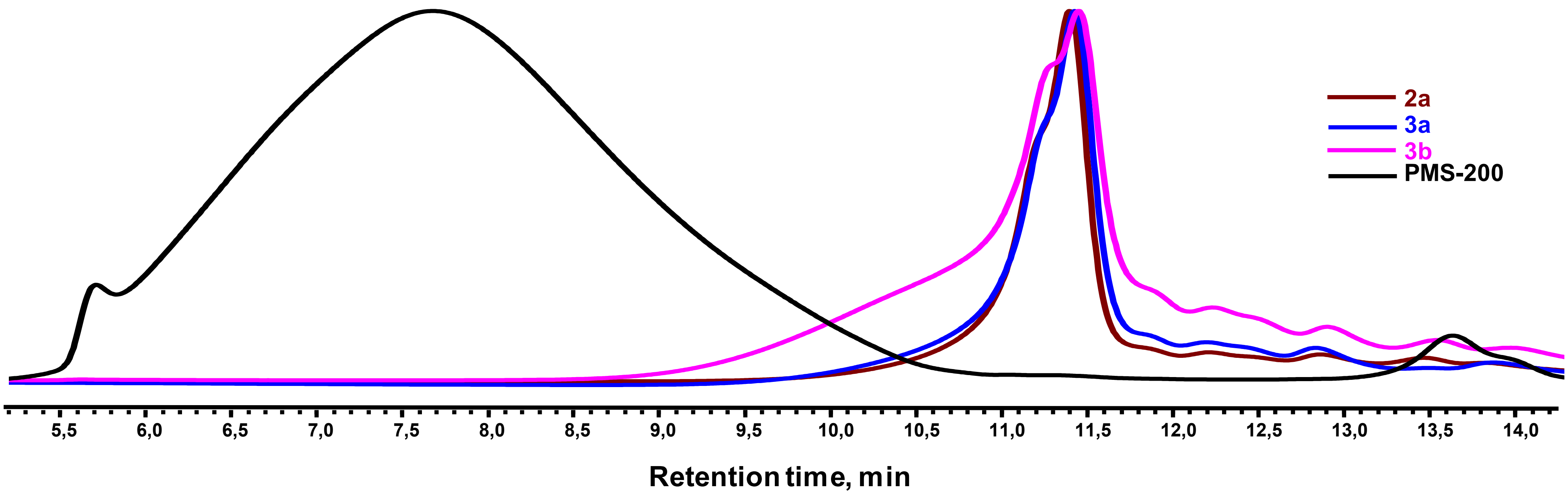


Fig S22. SEC curves of depolymerization products **3a** – **3b** after decompression

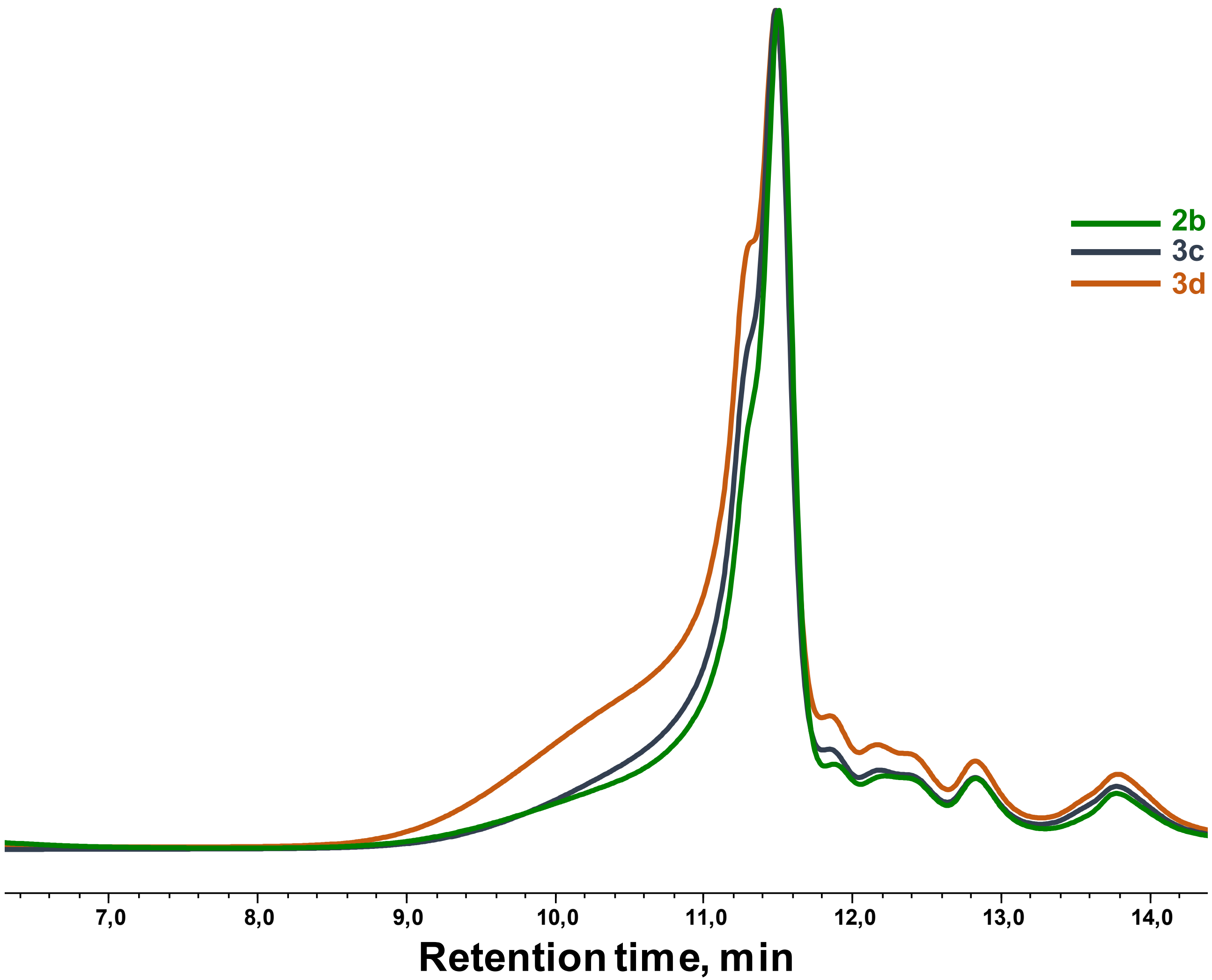


Fig S23. SEC curves of depolymerization products **3c** – **3d** after decompression

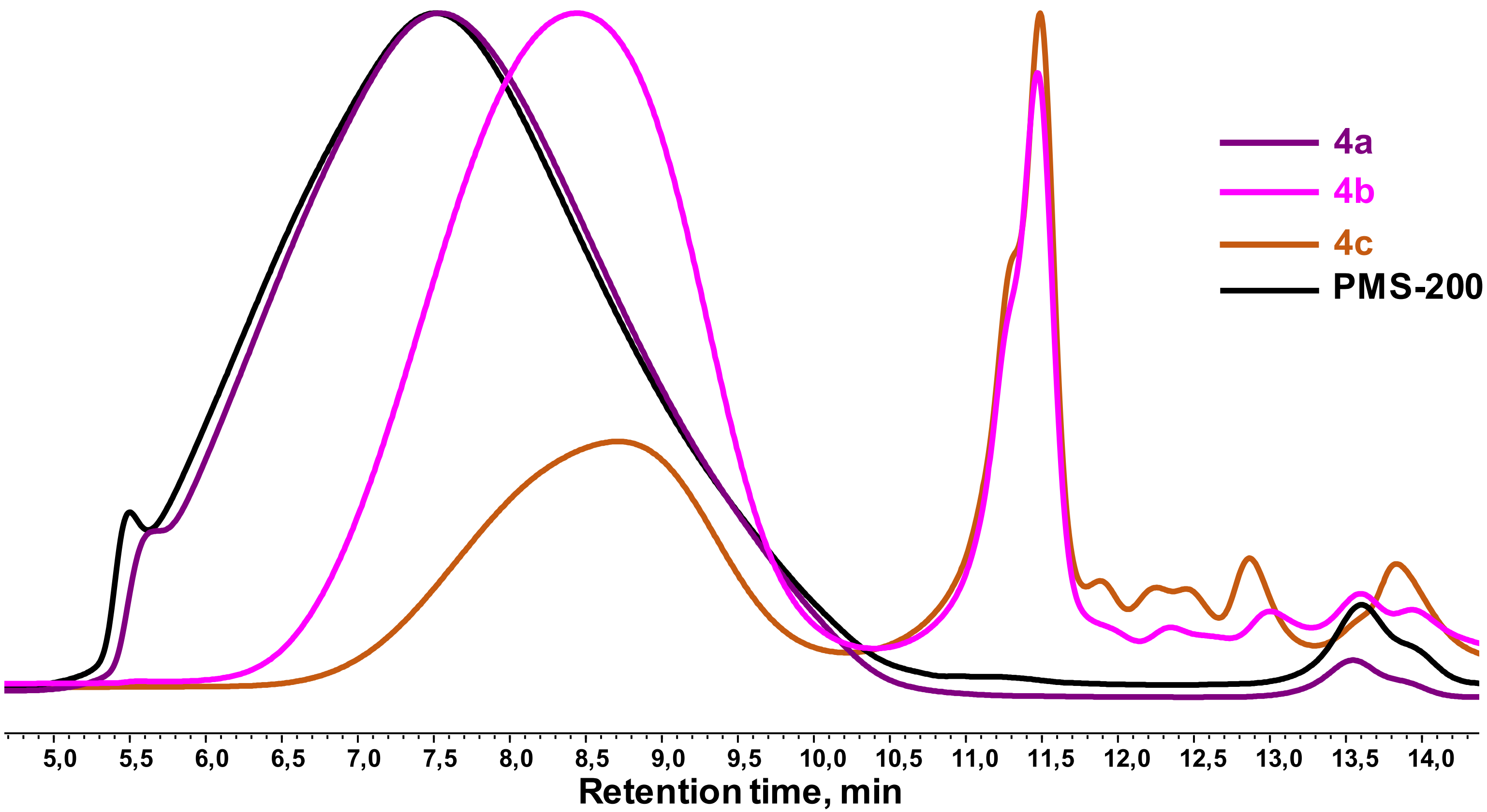


Fig S24. SEC curves of depolymerization products **4a** – **4c** after decompression

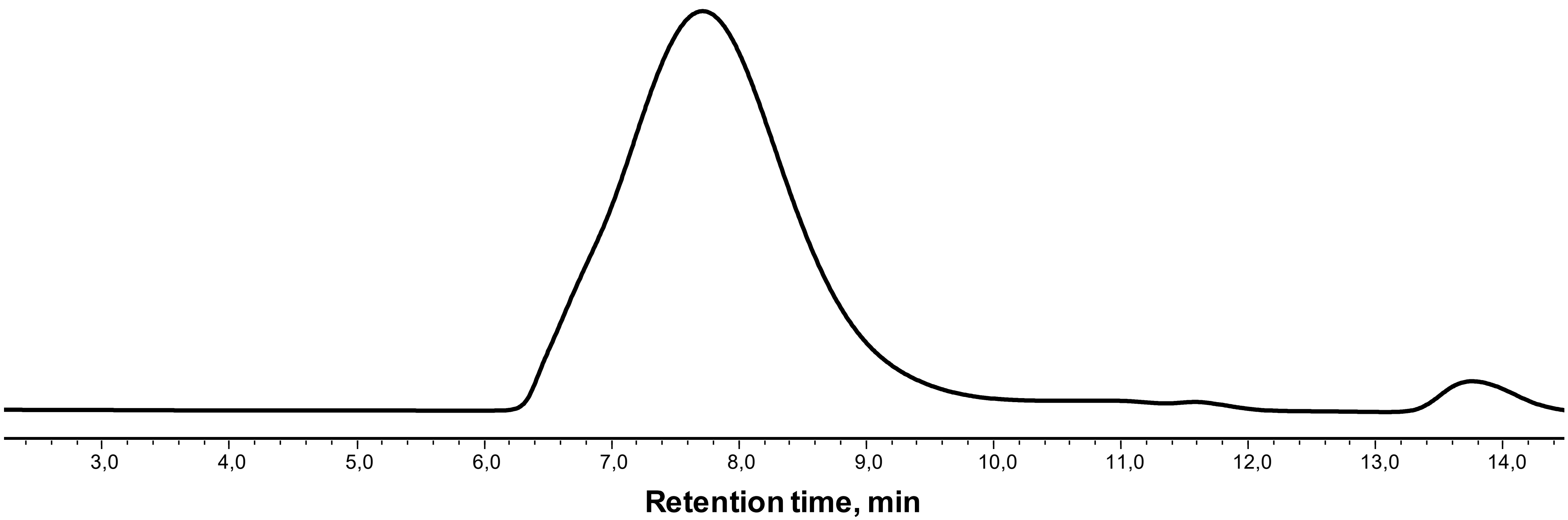


Fig S25. SEC curve of PDMS-$(OH)_2$

Table S4.

sample	Mp, kDa	Mn, kDa	Mw, kDa	PDI	Column size, Å
PDMS-$(OH)_2$ (II)	68.9	56.6	75.9	1.34	10^4

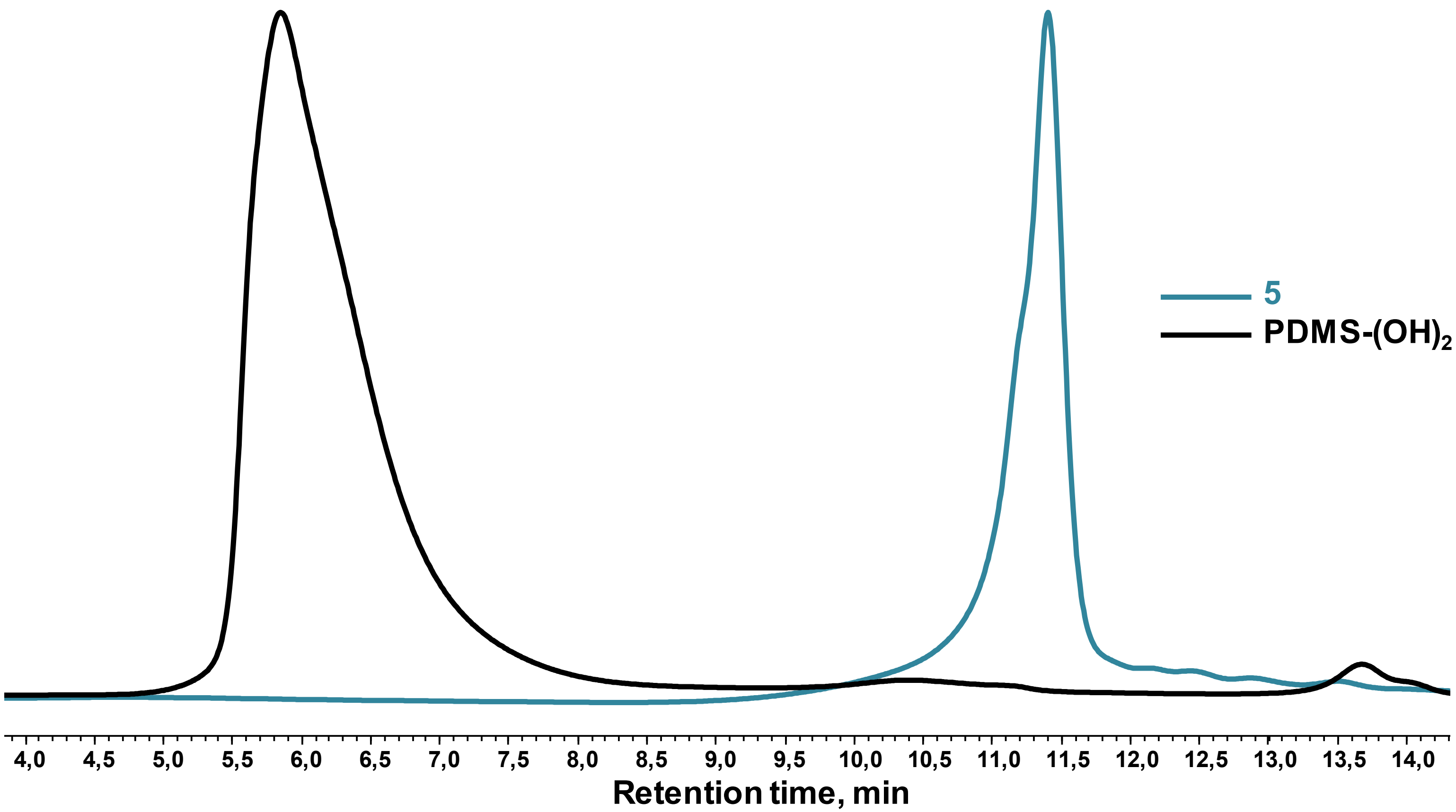


Fig S26. SEC curves of initial PDMS-(OH)$_2$ **II** and its depolymerization product **7** after ammonia decompression

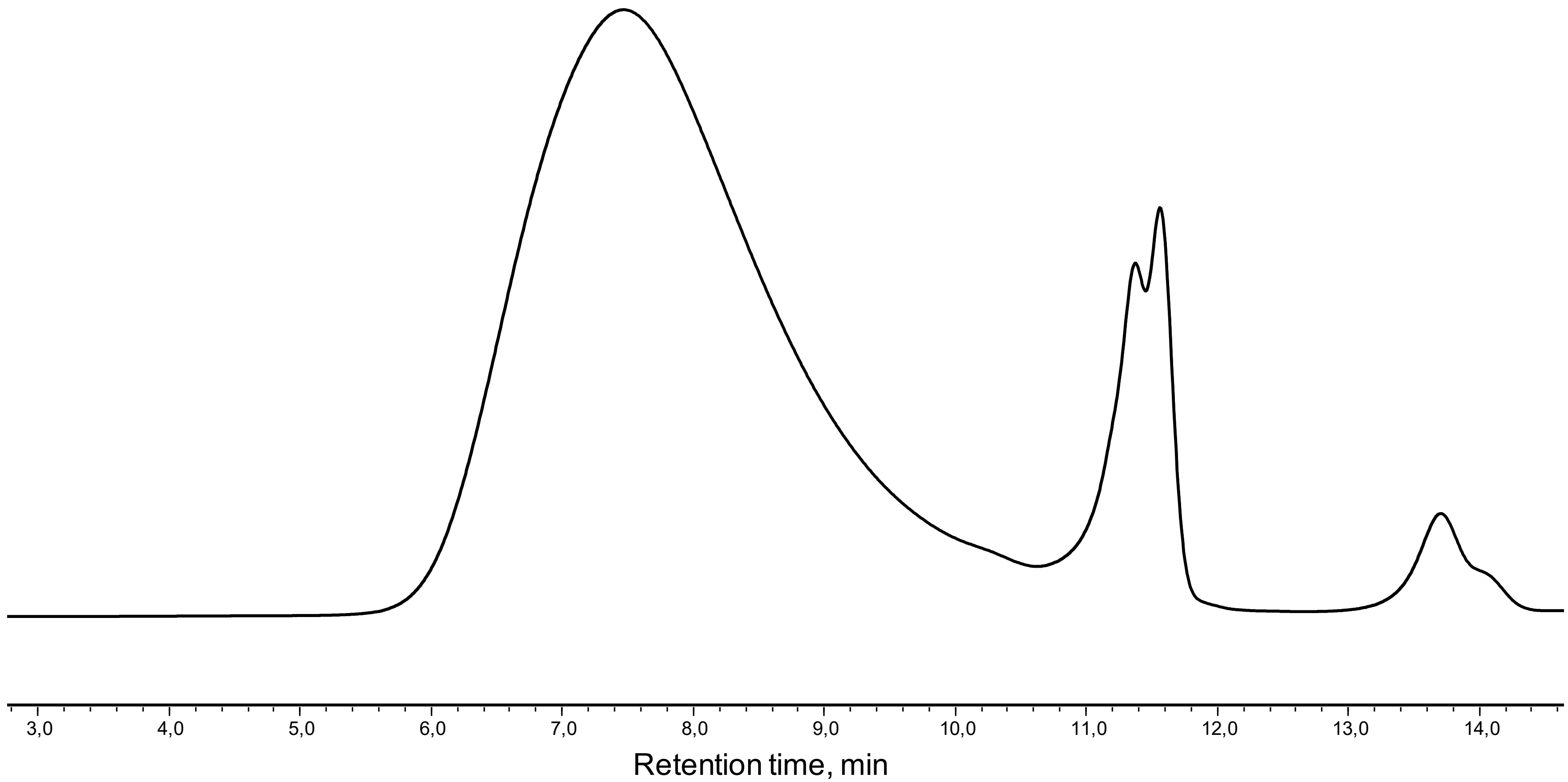


Fig S27. SEC curve of product 12

Table S5.

sample	Mp, kDa	Mn, kDa	Mw, kDa	PDI	Column size, Å
12	16.5	8.4	16.3	1.95	10^3

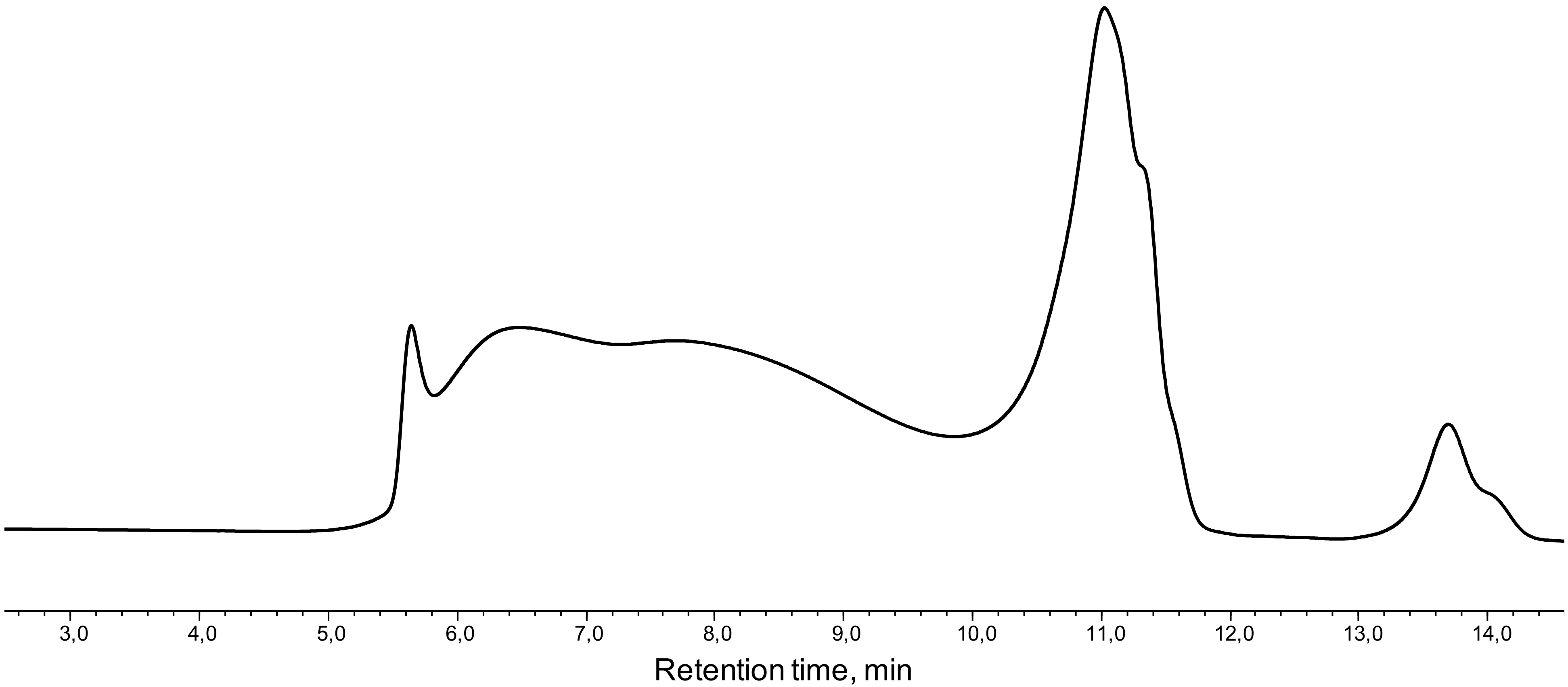


Fig S28. SEC curve of product 13

Table S6.

sample	Mp, kDa	Mn, kDa	Mw, kDa	PDI	Column size, Å
13	79.6	9.6	24.5	2.56	10^3

NMR data

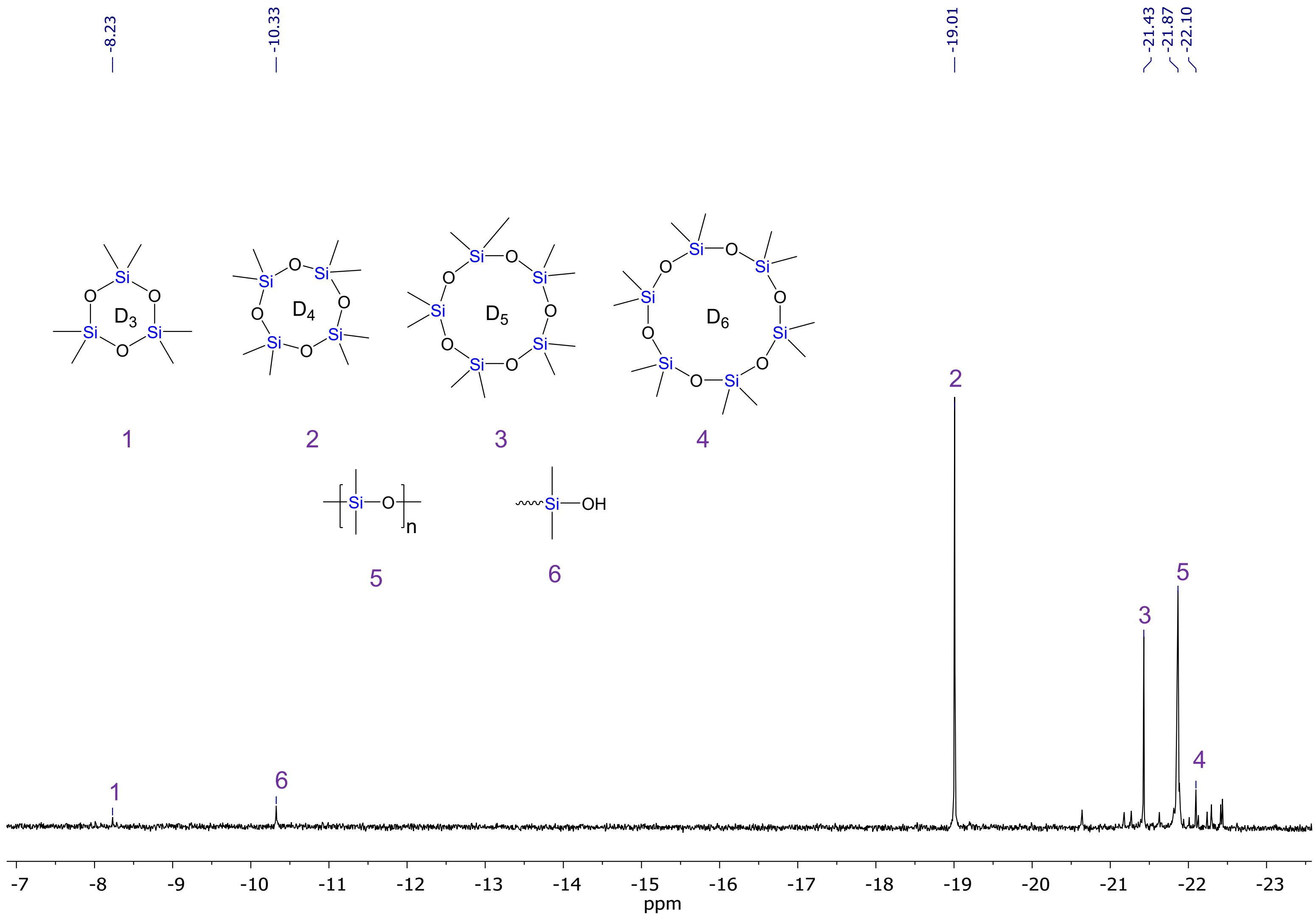


Fig S29. ^{29}Si NMR spectrum of **6**

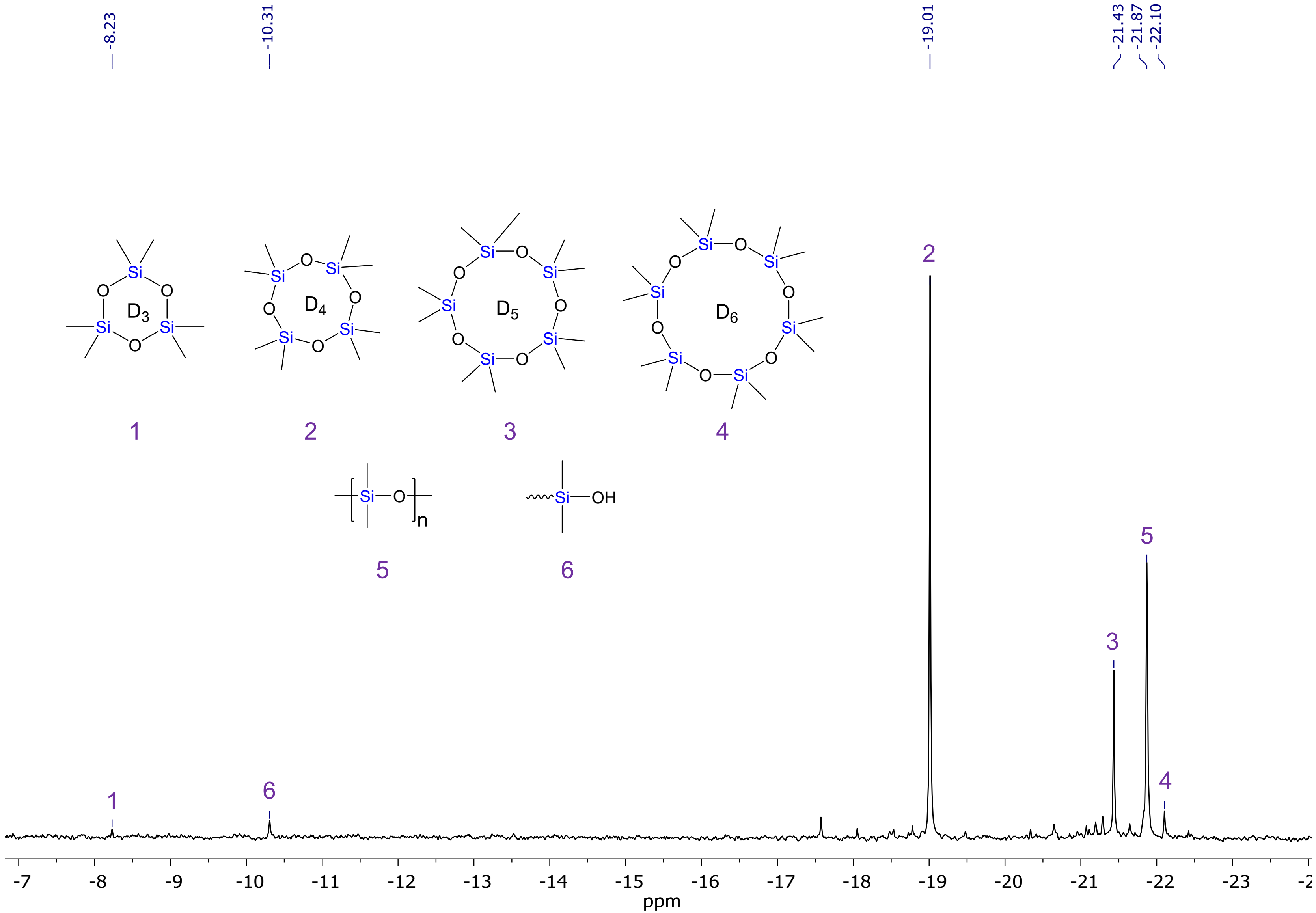


Fig S30. ^{29}Si NMR spectrum of **7**

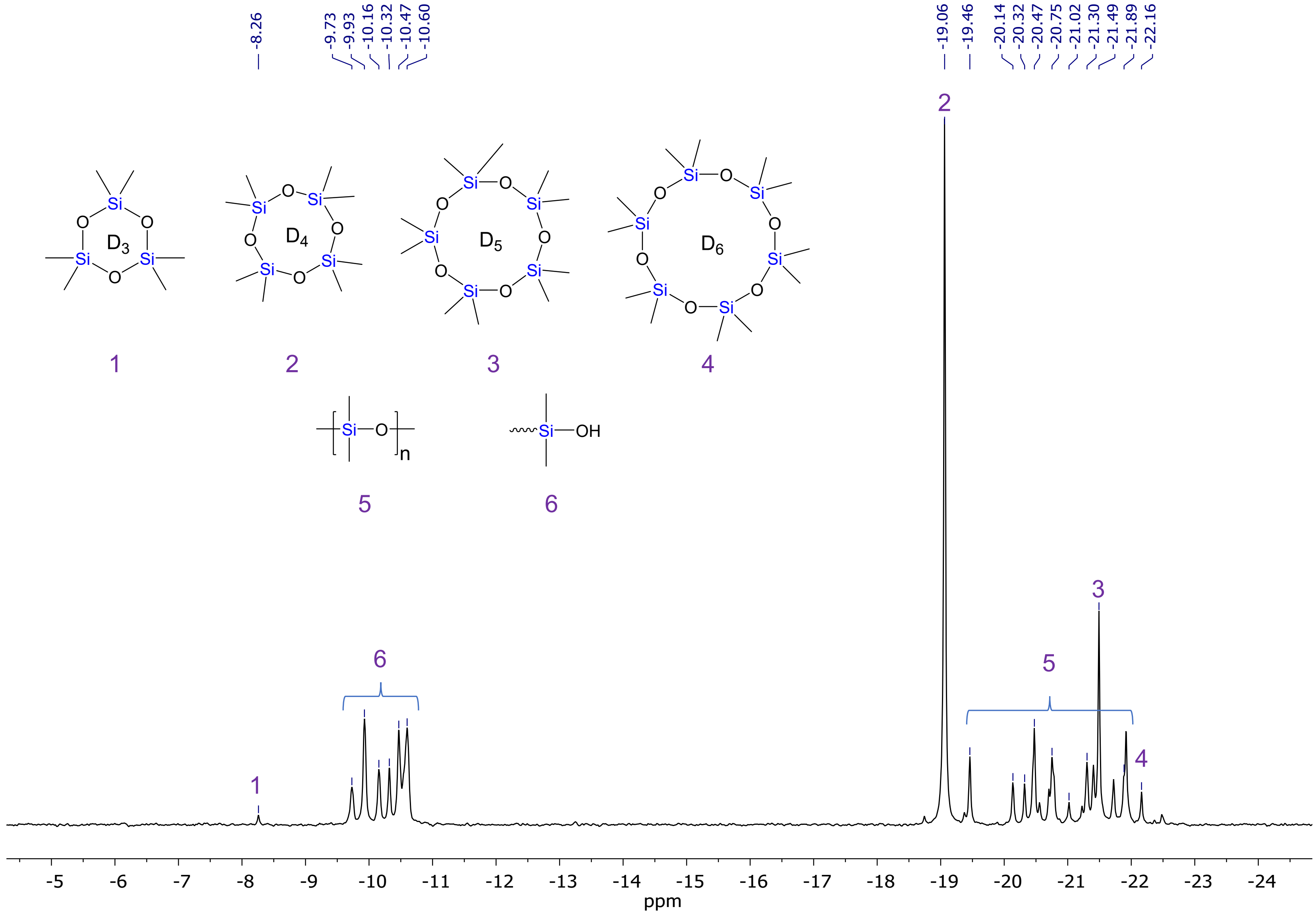


Fig S31. ^{29}Si NMR spectrum of **8**

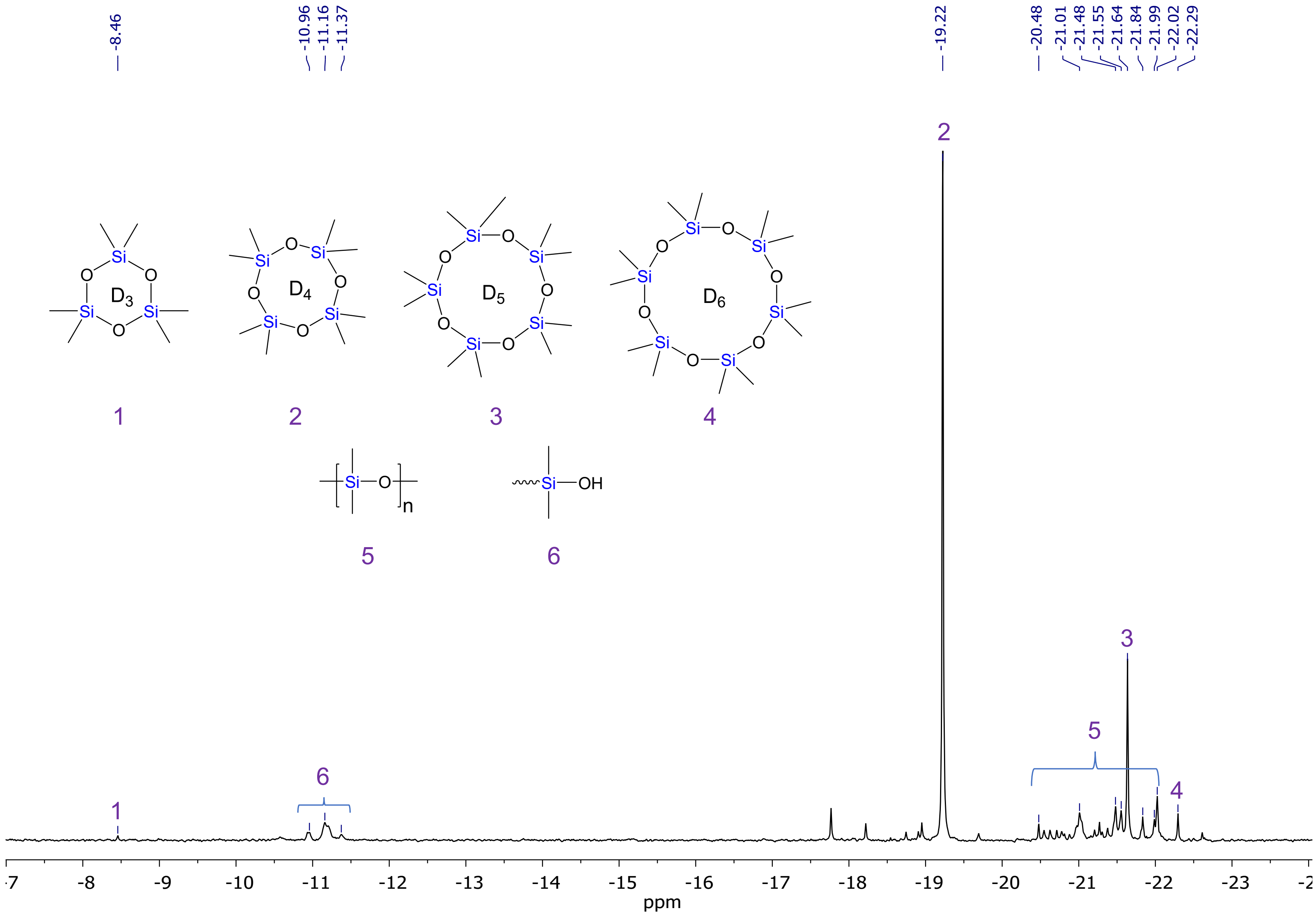


Fig S32. ^{29}Si NMR spectrum of **9**

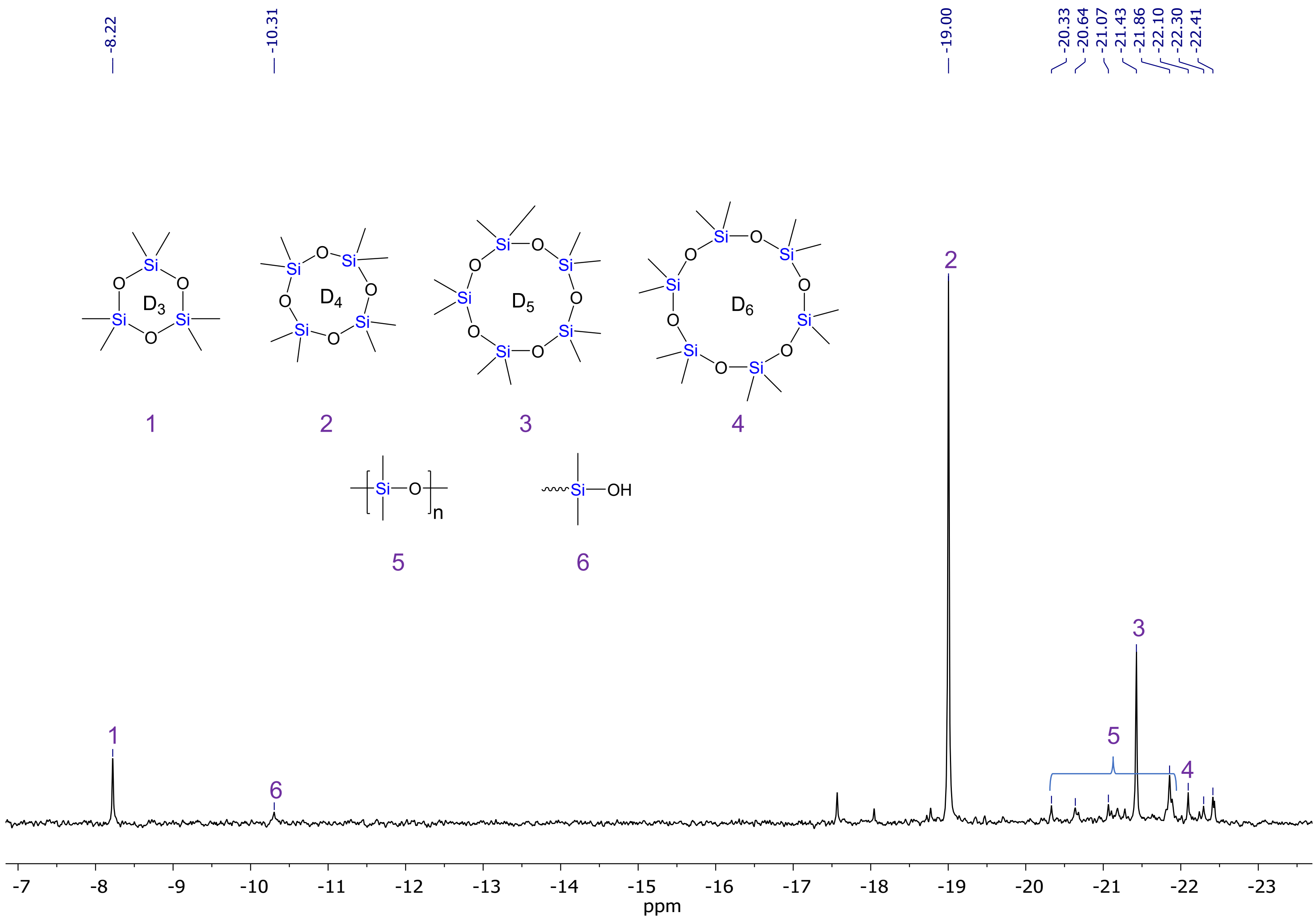


Fig S33. ^{29}Si NMR spectrum of **10**

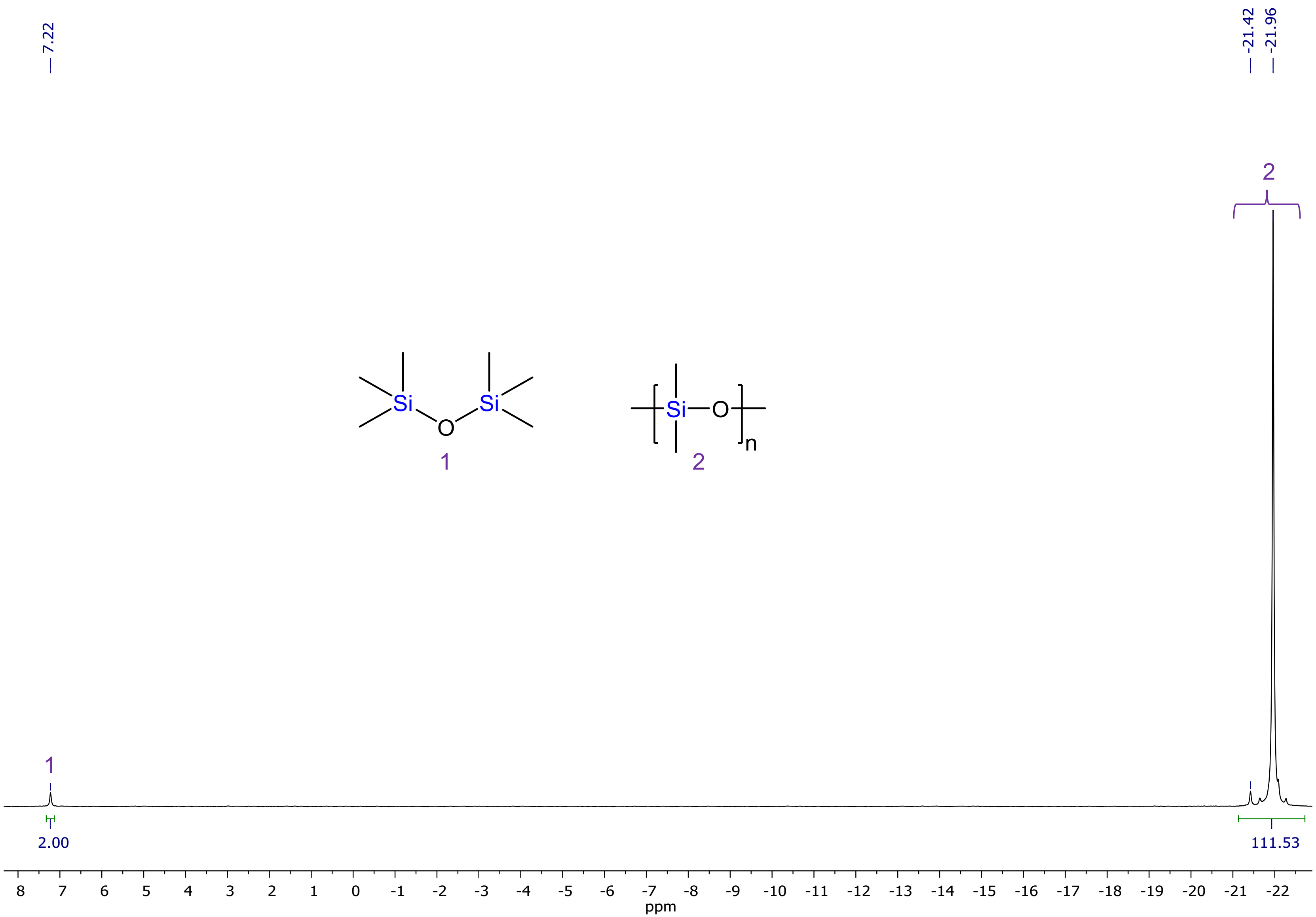
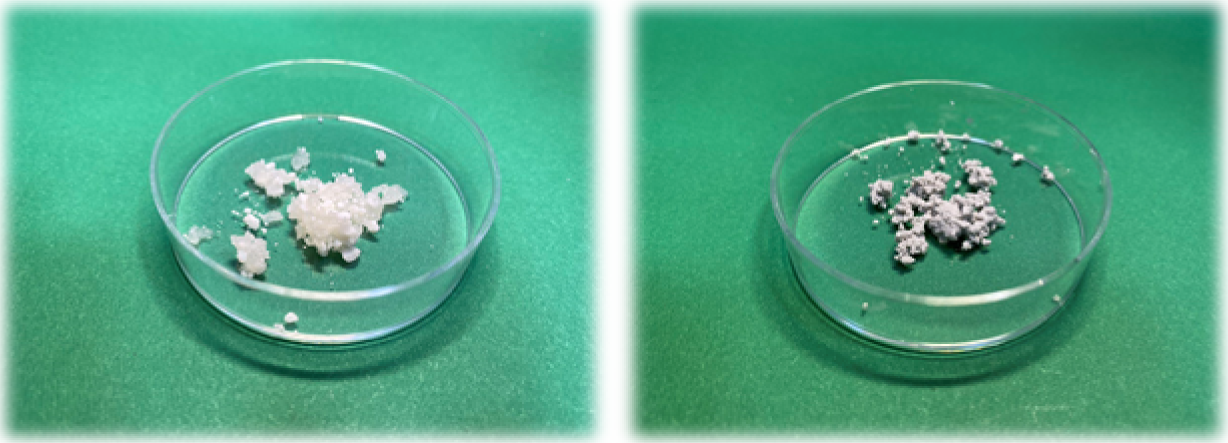


Fig S34. ^{29}Si ($CDCl_3/Cr(C_5H_8O_2)_3$) NMR spectrum of **PMS-200**

Photo



sample 9 sample 10

Fig S35. Photographs of depolymerization products of silicone industrial waste after ammonia decompression

Fig S36. Autoclave for scaling the depolymerization process