Supporting information

Back-to-cyclic-monomers: chemical recycling of silicone wastes using a [polydentate ligand-potassium silanolate] complex

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1. General information

All silicone oils, catalysts and solvents used were purchased from commercial suppliers (*e.g.* Sigma-Aldrich, TCI Chemical, Fisher, abcr) or supplied by our industrial partner (Elkem Silicones©) then were used without further purification. Nuclear magnetic resonance spectra were recorded on a Brüker DRX 300 (^{1}H-300 MHz, ^{13}C-75 MHz and ^{29}Si-59.6 MHz). Chemical shifts are given in ppm with reference to residual $CHCl_3$ central peaks: 7.26 ppm for proton, 77.16 ppm for carbon, respectively; residue acetone-d6 central peaks: 2.05 ppm for proton, 206.26 and 29.84 ppm for carbon, respectively; J values are given in Hertz (Hz). Abbreviations are defined as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quadruplet, m = multiplet, br = broad.

2. General procedures

*2.1. General procedure for the depolymerisation of siloxanes oil **1** (decagram scale)*

In a flask (50 mL) connecting with a short Vigreux column, siloxane oil **1** (10 mL, 9.5 g, 120 mmol Me_2SiO unit), $KOSiMe_3$ (14 mg, 0.1 mol%), 18C6 (30 mg, 0.1 mol%) were introduced then this mixture was heated at 140°C for 1 hour. Then, the reaction mixture was distillated under reduced pressure (140°C, 10mbar) to give a mixture of cyclosiloxanes D_3, D_4, D_5 (9.2 g, 97% yield) as a colourless liquid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H= 0.17 ($C\underline{H_3}$ in D_3), 0.09 ($C\underline{H_3}$ in D_4), 0.08 ($C\underline{H_3}$ in D_5); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C= 1.08 ($\underline{C}H_3$ in D_3), 0.93 ($\underline{C}H_3$ in D_4), 1.05 ($\underline{C}H_3$ in D_5); **^{29}Si-NMR** (59.6 MHz, $CDCl_3$): δ_{Si}= 7.2 ($(Me_3\underline{Si})_2O$), -8.4 ($\underline{Si}Me_2O$ in D_3), -19.2 ($\underline{Si}Me_2O$ in D_4), -21.6 ($\underline{Si}Me_2O$ in D_5).

*2.2. General procedure for the depolymerisation of waste siloxanes oil **2** (100 g scale)*

In a flask (250 mL) connecting with a long Vigreux column, waste siloxane oil **2** (100 g), $KOSiMe_3$ (142 mg, 0.1 mol%), 18C6 (300 mg, 0.1 mol%) were introduced then this mixture was heated at 140°C for 1 hour. Then, the reaction mixture was distillated under reduced pressure (140°C, 10mbar) in 3 hours to give a mixture of cyclosiloxanes D_3, D_4, D_5 (99 g, 99% yield) as a colourless liquid.

2.3. General procedure for the polymerisation of a mixture of cyclic siloxanes oil (100 g scale)

An obtained mixture of siloxanes from the depolymerisation of waste silicone oil **2** (99 g) and hexamethyldisiloxane (0.6 g) were introduced in a three-neck round bottom flask then this mixture was heated to 160°C. At this temperature, $KOSiMe_3$ (50 ppm) and 18C6 (4 ppm) were added and the polymerisation experiment were performed at 160°C for 3 hours. Then, the reaction was cooled down to room temperature and a neutralized solution containing phosphoric acid was introduced. Finally, the result mixture was evaporated (devolatilization step) under reduced pressure (170°C, 1 mbar) for 3 hours to give a silicone oil (87 g, 87% yield) as a colourless liquid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H= 0.07 (s); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C= 1.2; **^{29}Si-NMR** (59.6 MHz, $CDCl_3$): δ_{Si}= -21.9 ($SiMe_2O$), 7.3 ($OSiMe_3$); SEC (toluene): M_n= 8200 g/mol (DPI = 2).

2.4. General procedure for the catalyst recycling (decagram scale)

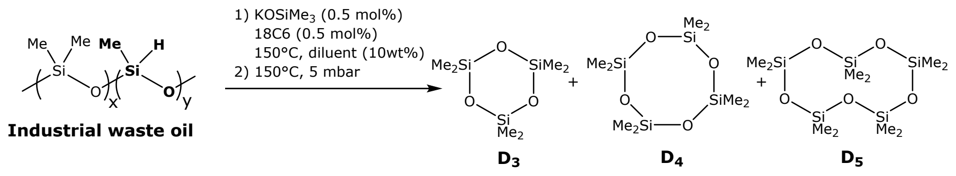
In a flask (50 mL) connecting with a short Vigreux column, siloxane oil **1** (10 mL, 9.5 g, 120 mmol Me_2SiO unit), $KOSiMe_3$ (14 mg, 0.1 mol%), 18C6 (30 mg, 0.1 mol%) were introduced then this mixture was heated at 140°C for 1 hour. Then, the reaction mixture was distillated under reduced pressure (140°C, 10mbar) to give a mixture of cyclosiloxanes (D_3, D_4, D_5) (9.15 g, 96% yield) as a colourless liquid. After removing most of volatile products, the catalysts were remained in a residue with a little of polysiloxanes. The catalyst was reused by adding further amounts of silicone oil after complete turnover. A small amount of silicone oil is always kept in the flask at the end of the distillation to prevent the sublimation of pure catalyst or complexing agent ($KOSiMe_3$, 18C6). Finally, after 5 cycles, the flask was cooled down, then a small amount of $CDCl_3$ was introduced to dissolve this residue and analysed it in ^{29}Si-NMR.

*2.5. General procedure for depolymerization of fluorosilicone **12***

In a flask (50 mL) connecting with a short Vigreux column, siloxane oil **12** (10.6 g, 120 mmol Me_2SiO unit), $KOSiMe_3$ (14 mg, 0.1 mol%), 18C6 (30 mg, 0.1 mol%) were introduced then this mixture was heated at 160°C for 1 hour. Then, the reaction mixture was distillated under reduced pressure (160°C, 0.1 mbar) to give a mixture of fluoro-substituted cyclosiloxanes D_4^F (2 enantioisomers), D_5^F, D_6^F (9.6 g, 92% yield) as a colourless oil. A higher temperature and lower pressure are required due to the formation of D_4^F (2 enantioisomers), D_5^F, D_6^F that are higher boiling point products than conventional cyclosiloxanes (D_3, D_4, D_5). **^{1}H-NMR** (300 MHz, acetone-d_6): δ_H= 0.26 (*t*, J =1.9, Si-**CH_3**, D_4), 0.28 (s, Si-**CH_3**, D_5), 0.30 (s, Si-**CH_3**, D_6), 0.87 (m, CH_2-**CH_2**-CF_3 in D_4, D_5, D_6), 2.24 (m, **CH_2**-CH_2-CF_3 in D_4, D_5, D_6); **^{13}C-NMR** (75 MHz, acetone-d_6): δ_C= -0.7 (Si-**CH_3**, D_4), -0.6 (Si-**CH_3**, D_5), -0.2 (Si-**CH_3**, D_6), 9.7 (**CH_2**-CH_2-CF_3 in D_4), 9.9 (**CH_2**-CH_2-CF_3 in D_5), 10.3 (**CH_2**-CH_2-CF_3 in D_6), 28.6 (CH_2-**CH_2**-CF_3 in D_4), 29.0 (CH_2-**CH_2**-CF_3 in D_5), 28.1 (CH_2-**CH_2**-CF_3 in D_6), 127.4 (CH_2-CH_2-**CF_3** in D_4), 131.1 (CH_2-CH_2-**CF_3** in D_5), 134.8 (CH_2-CH_2-**CF_3** in D_6); **^{29}Si-NMR** (59.6 MHz, acetone-d_6): -20.2 and -20.4 (2 enantioisomers in D_4), -22.2 (D5), -22.4 (D6); **^{19}F-NMR** (282 MHz, acetone-d_6) : -68.77, -68.80,-68.83, -68.86 (2 isomers D_4+D_5+D_6); Ratio of each cyclosiloxane was determined by ^{29}Si-NMR: $D_4/D_5/D_6$=47/48/5.

3. Optimised conditions

Table S1: Screening diluents for the depolymerisation of industrial waste oil



Diluent	Reaction conditions	Yield of cyclosiloxanes (%)
n-$C_{18}H_{37}$-OH	150°C, 5 mbar	75
n-$C_{16}H_{33}$-OH	150°C, 5 mbar	74
n-$C_{22}H_{45}$-OH	150°C, 5 mbar	74
2-decyl-1-tetradecanol	150°C, 5 mbar	74
$C_{30}H_{62}$ (squalane)	150°C, 5 mbar	0
n-$C_{22}H_{46}$	150°C, 5 mbar	61

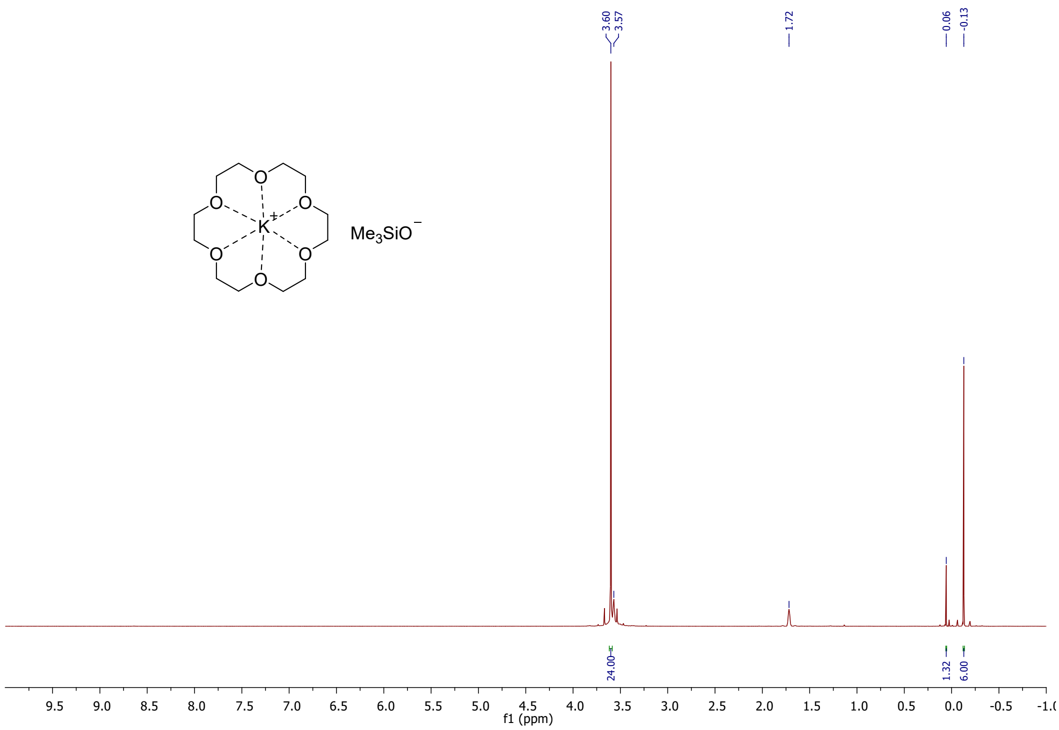


Figure S1a: ^{1}H-NMR of [KOSiMe$_3$-18C6] complex in d_8-THF (25°C, 300 MHz)

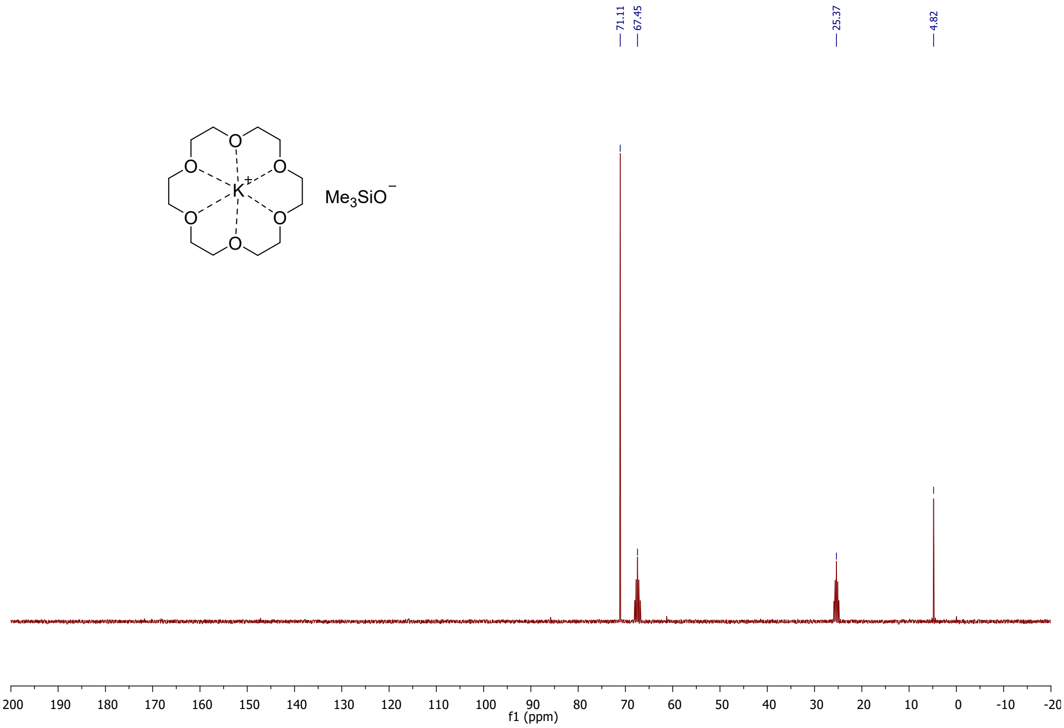


Figure S1b: [13]C-NMR of [$KOSiMe_3$-18C6] complex in d_8-THF (25°C, 75 MHz)

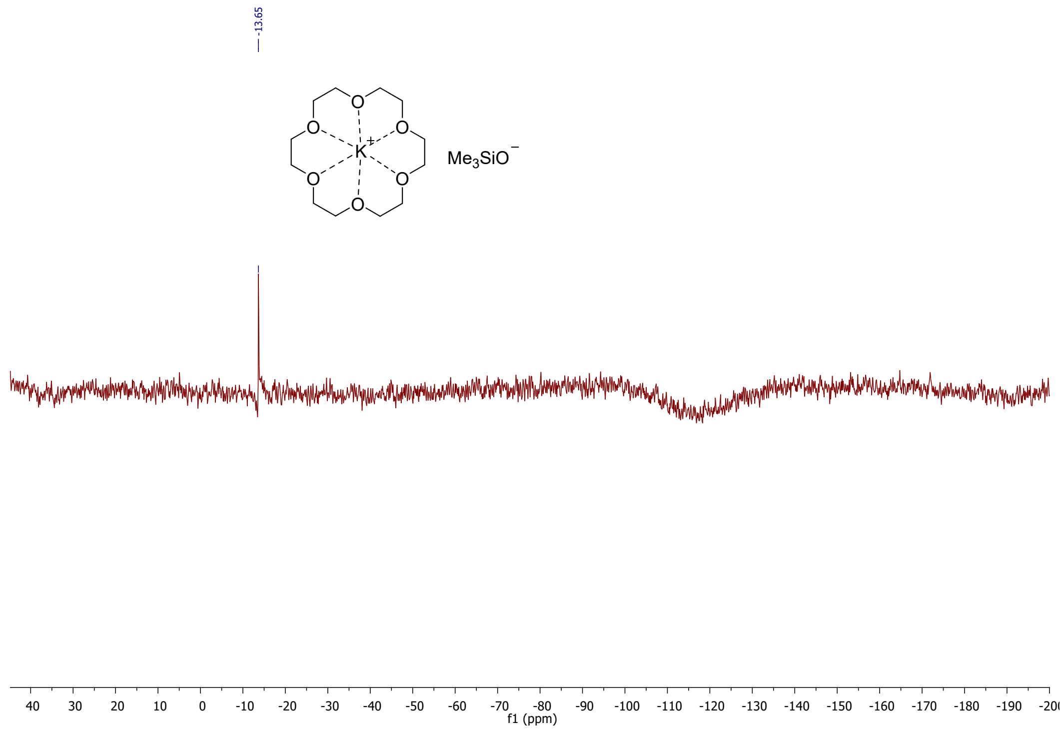


Figure S1c: [29]Si-NMR of [$KOSiMe_3$-18C6] complex in d_8-THF (25°C, 59.6 MHz)

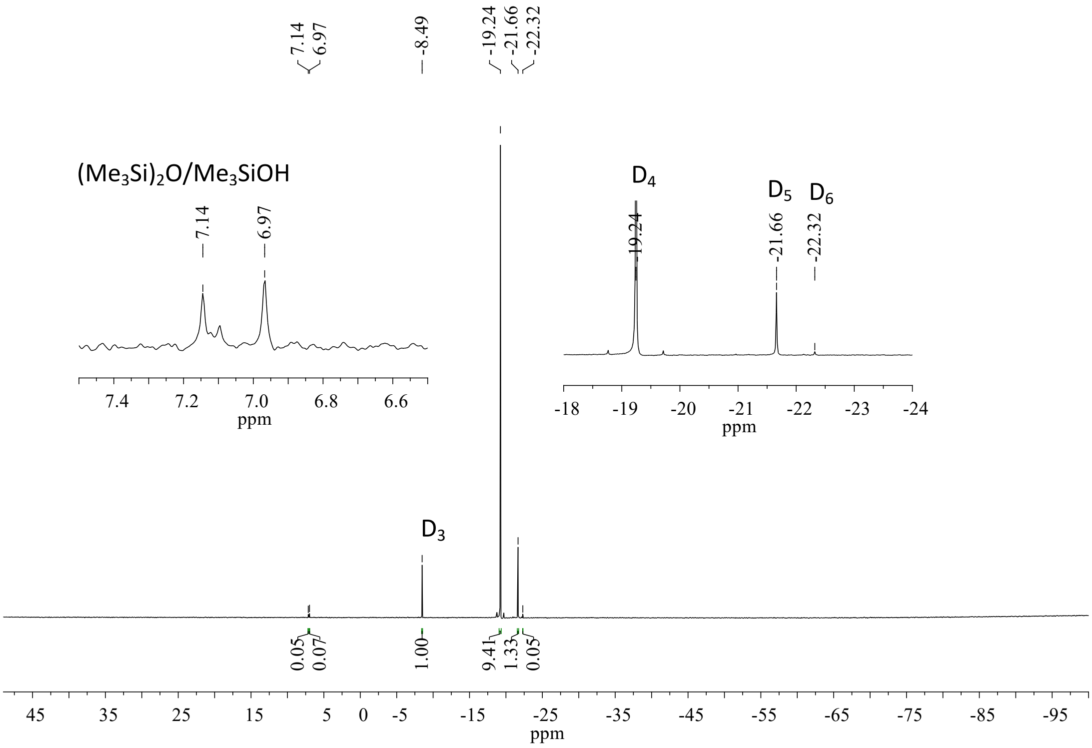


Figure S2: [29]Si-NMR of distillation fraction in d-chloroform (150 mg in 0.5 mL $CDCl_3$, 25°C)

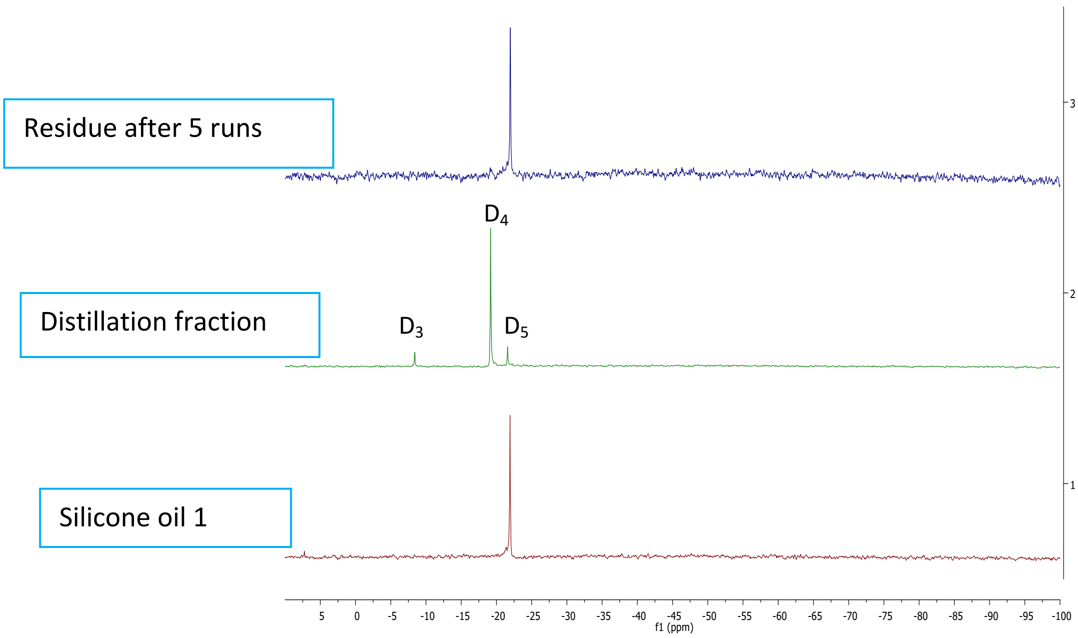


Figure S3: [29]Si-NMR of initial oil, distillation fraction and residue in d-chloroform

4. ^{1}H, ^{13}C, ^{19}F and ^{29}Si-NMR spectrum

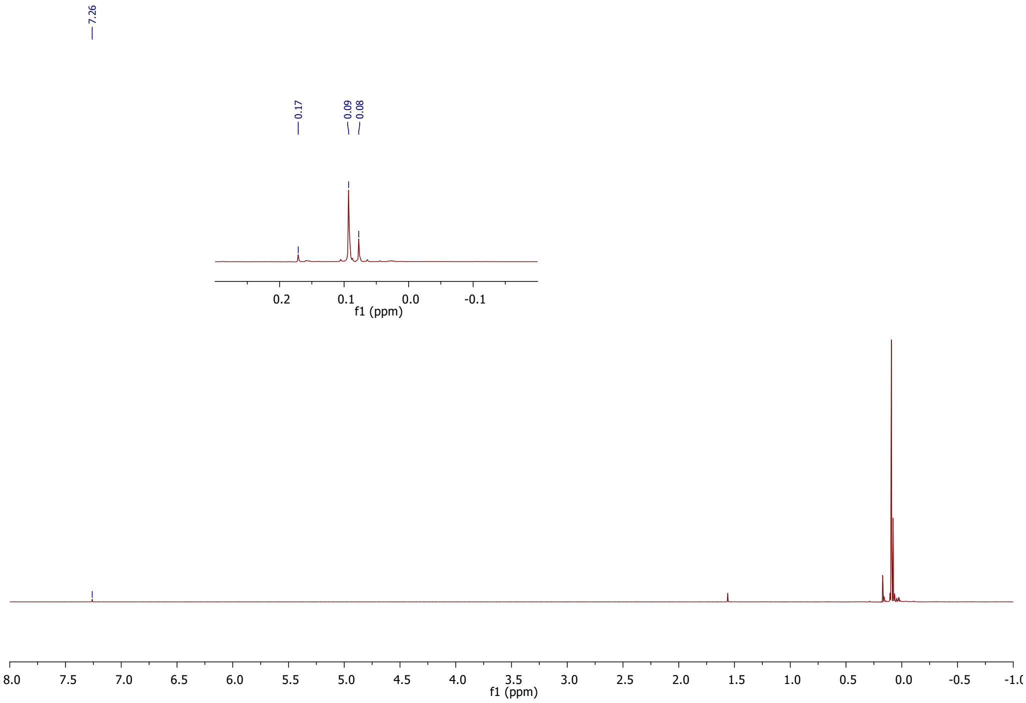


Figure S4: ^{1}H-NMR spectrum of depolymerization products of silicone oil ***1*** *(D_3, D_4, D_5) (25°C, $CDCl_3$, 300 MHz)*

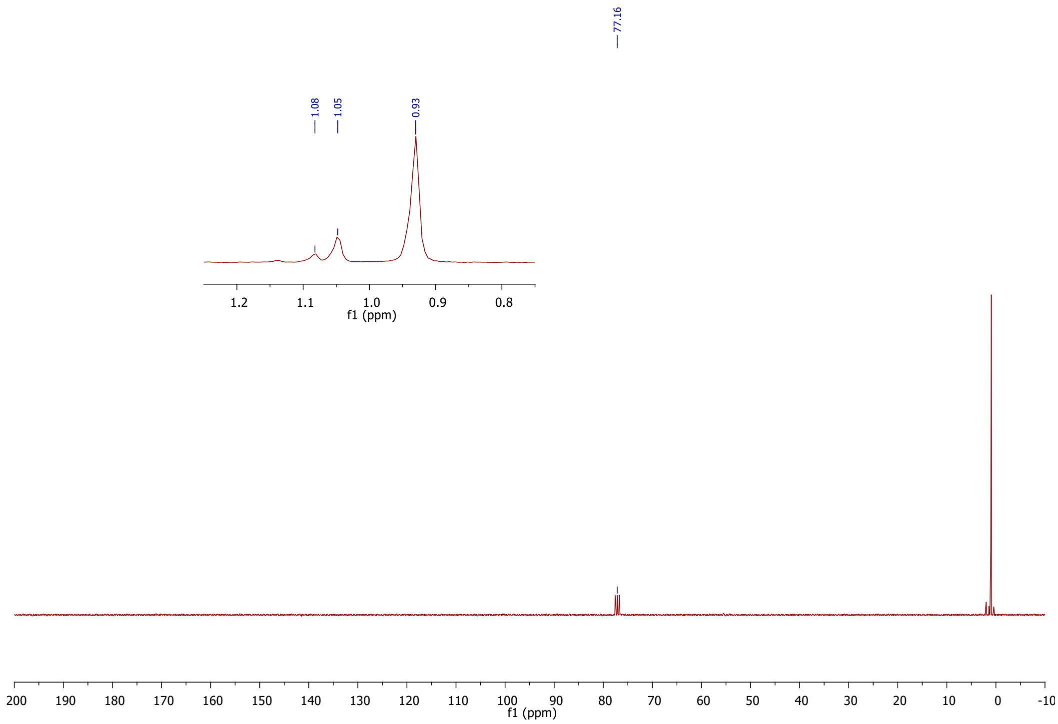


Figure S5: ^{13}C-NMR spectrum of depolymerization products of silicone oil ***1*** *(D_3, D_4, D_5) (25°C, $CDCl_3$, 75 MHz)*

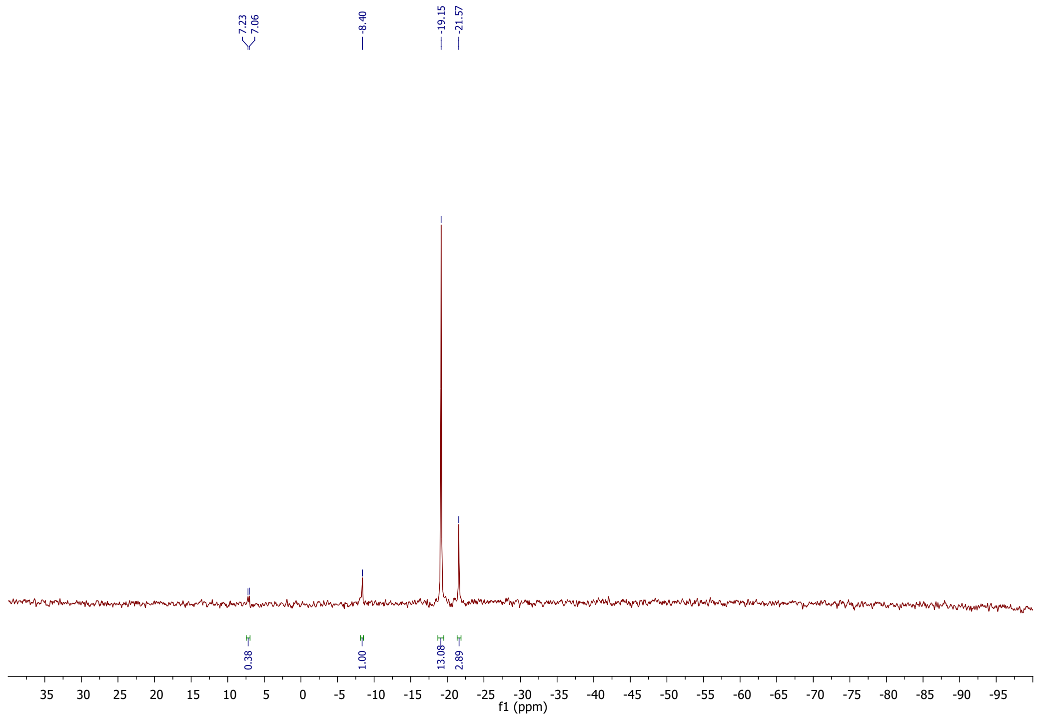


*Figure S6: ^{29}Si-NMR spectrum of depolymerization products of silicone oil **1** (D_3, D_4, D_5) (25°C, $CDCl_3$, 59.6 MHz)*

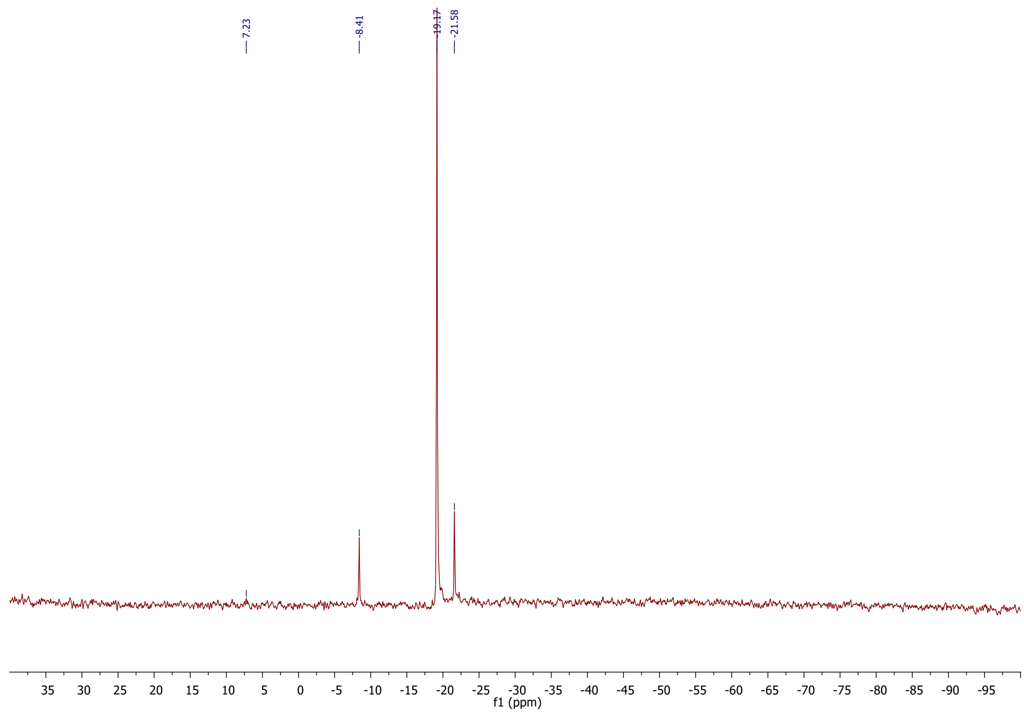


*Figure S7: ^{29}Si-NMR spectrum of depolymerization products of silicone oil **2** (D_3, D_4, D_5) (25°C, $CDCl_3$, 59.6 MHz)*

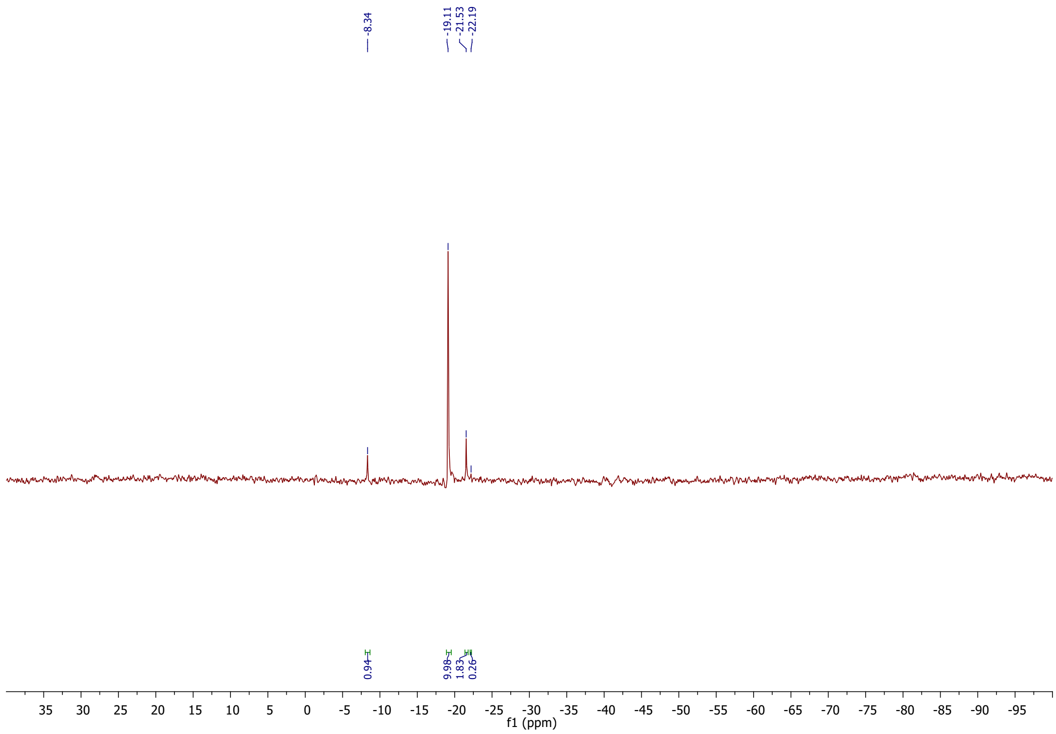


*Figure S8: [29]Si-NMR spectrum of depolymerization products of silicone gum **4 + 1** (D_3, D_4, D_5) (25°C, $CDCl_3$, 59.6 MHz)*

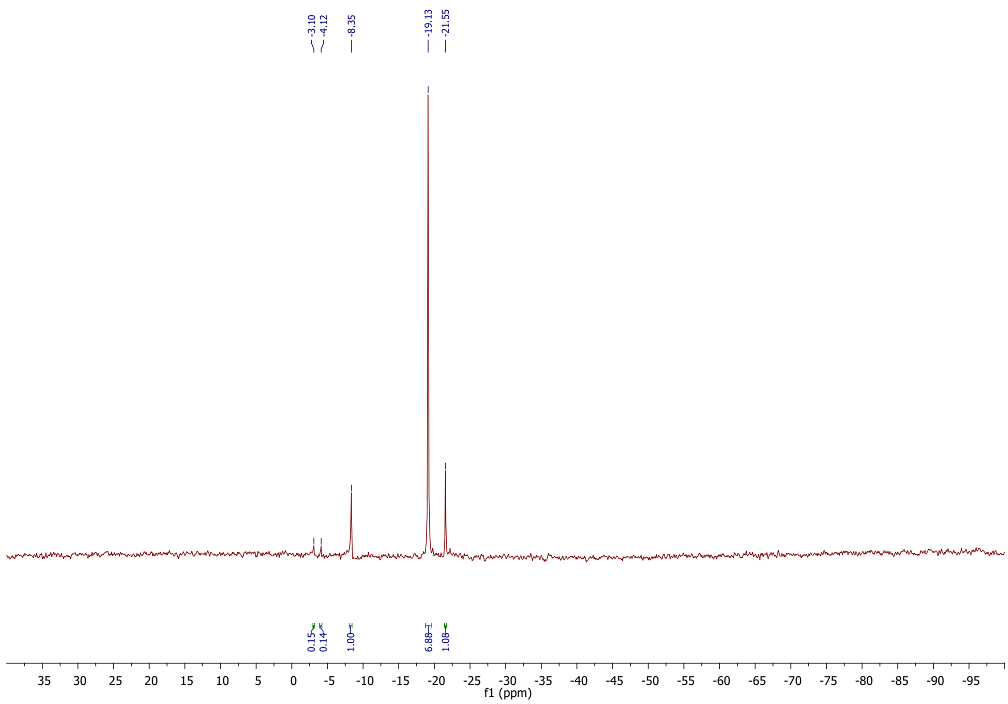


*Figure S9: [29]Si-NMR spectrum of depolymerization products of silicone oil **5** (D_3, D_4, D_5) (25°C, $CDCl_3$, 59.6 MHz)*

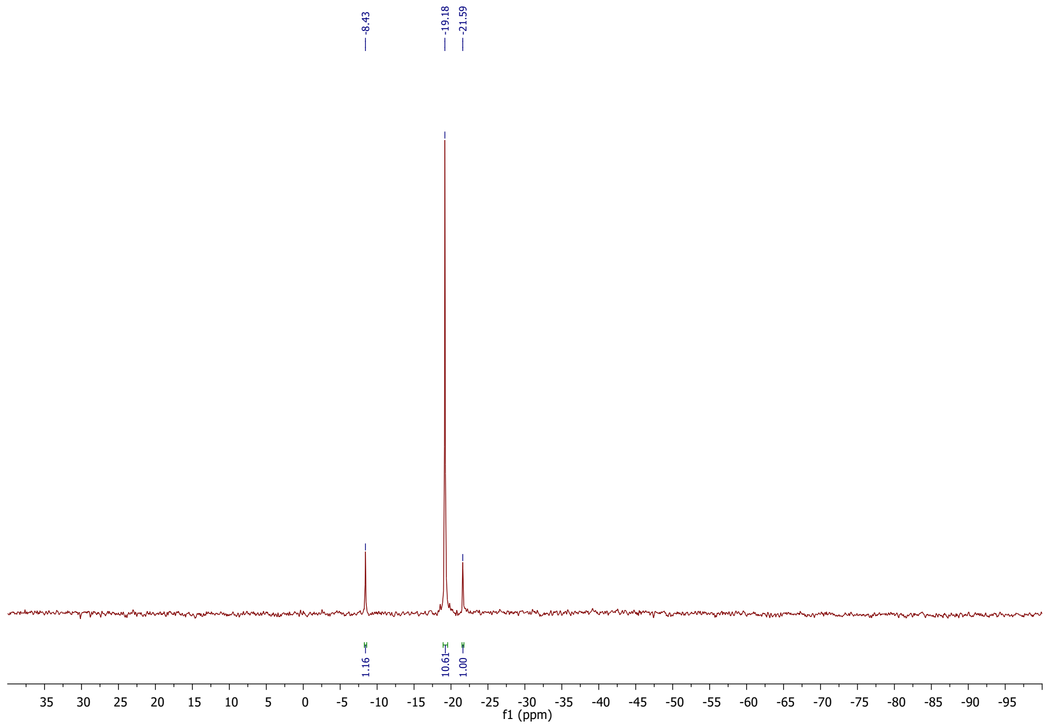


*Figure S10: ^{29}Si-NMR spectrum of depolymerization products of silicone oil **6** (D_3, D_4, D_5) (25°C, $CDCl_3$, 59.6 MHz)*

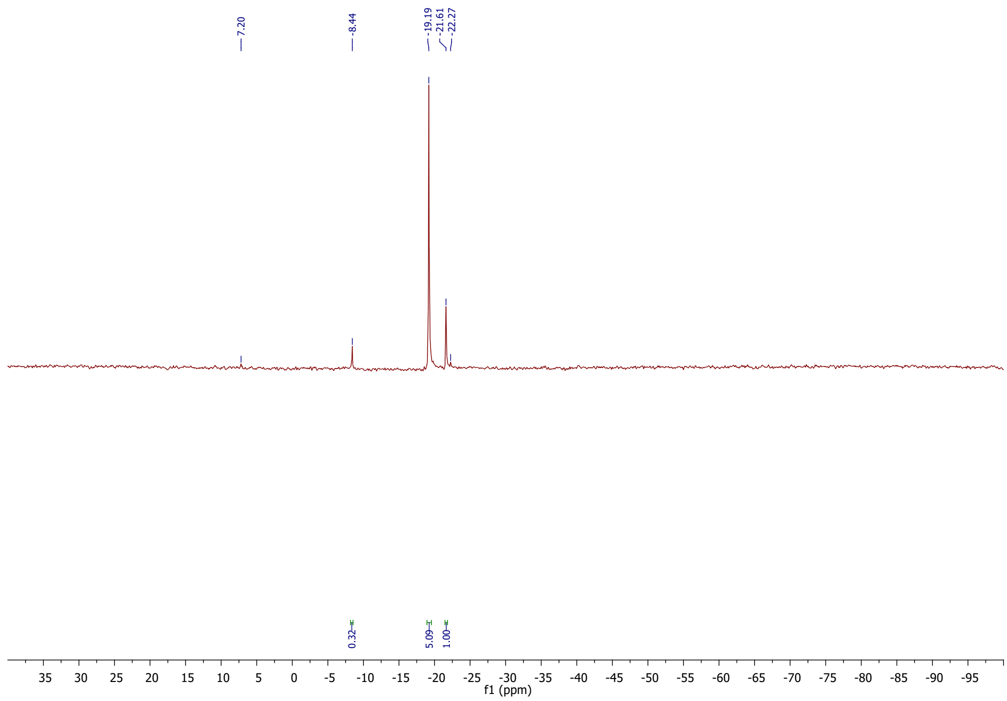


*Figure S11: ^{29}Si-NMR spectrum of depolymerization products of silicone oil **6 + 1** (D_3, D_4, D_5) (25°C, $CDCl_3$, 59.6 MHz)*

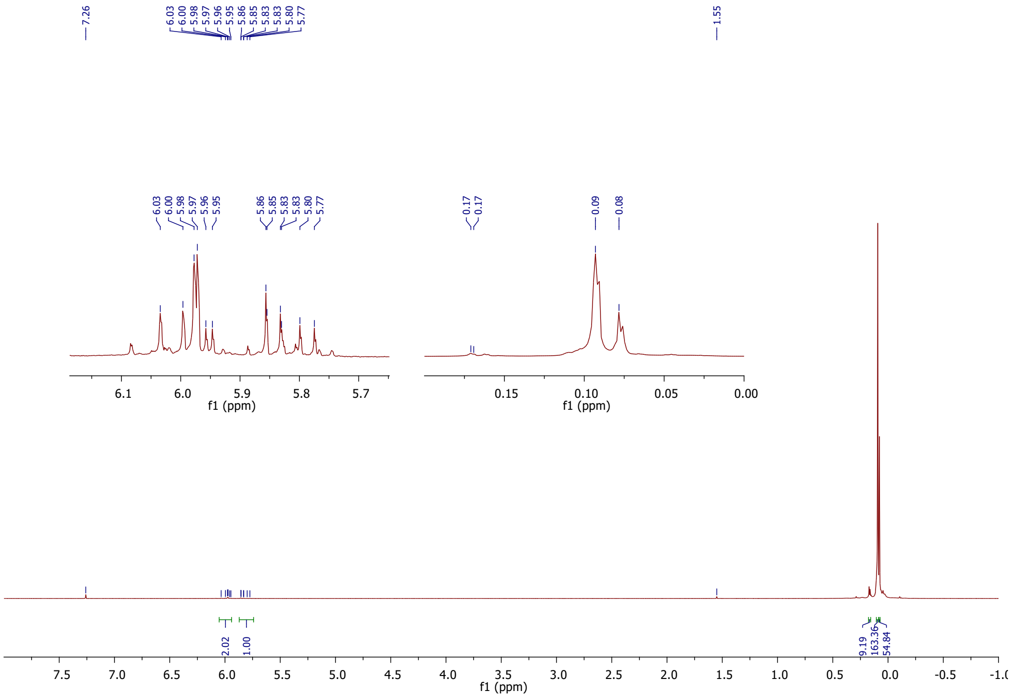


*Figure S12: ^{1}H-NMR spectrum of depolymerization products of silicone oil **7** (D_3, D_4, D_5) (25°C, $CDCl_3$, 300 MHz)*

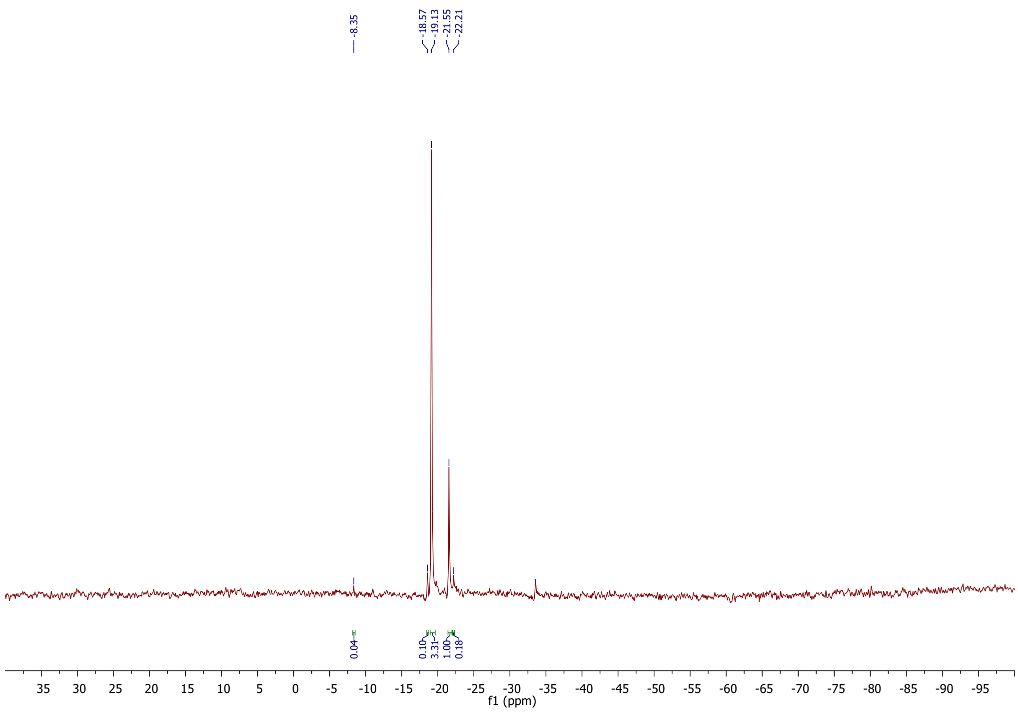


*Figure S13: ^{29}Si-NMR spectrum of depolymerization products of silicone oil **7** (D_3, D_4, D_5) (25°C, $CDCl_3$, 59.6 MHz)*

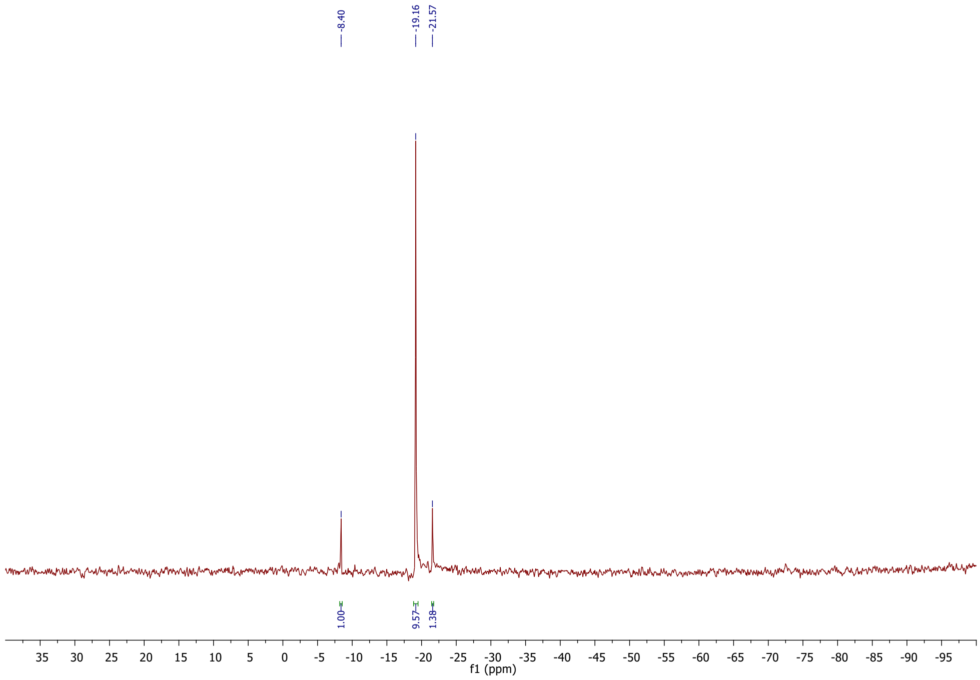


*Figure S14: ^{29}Si-NMR spectrum of depolymerization products of silicone oil **8 + 1** (D_3, D_4, D_5) (25°C, $CDCl_3$, 59.6 MHz)*

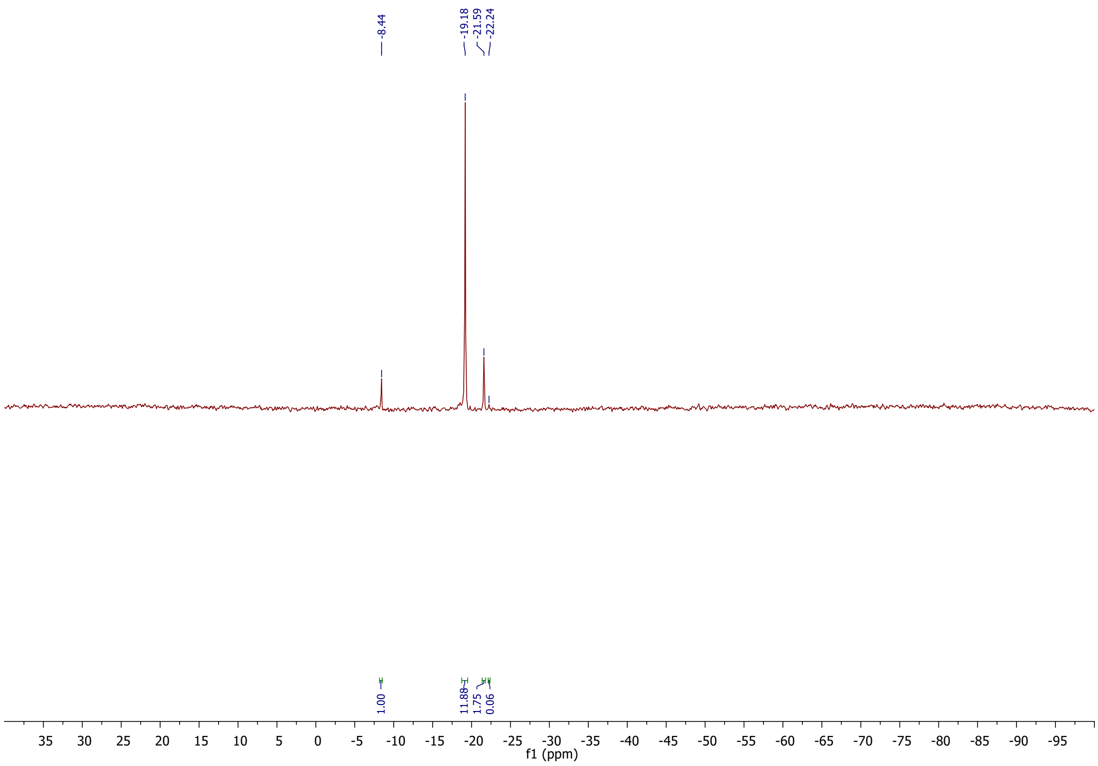


*Figure S15: ^{29}Si-NMR spectrum of depolymerization products of silicone oil **9 + 1** (D_3, D_4, D_5) (25°C, $CDCl_3$, 59.6 MHz)*

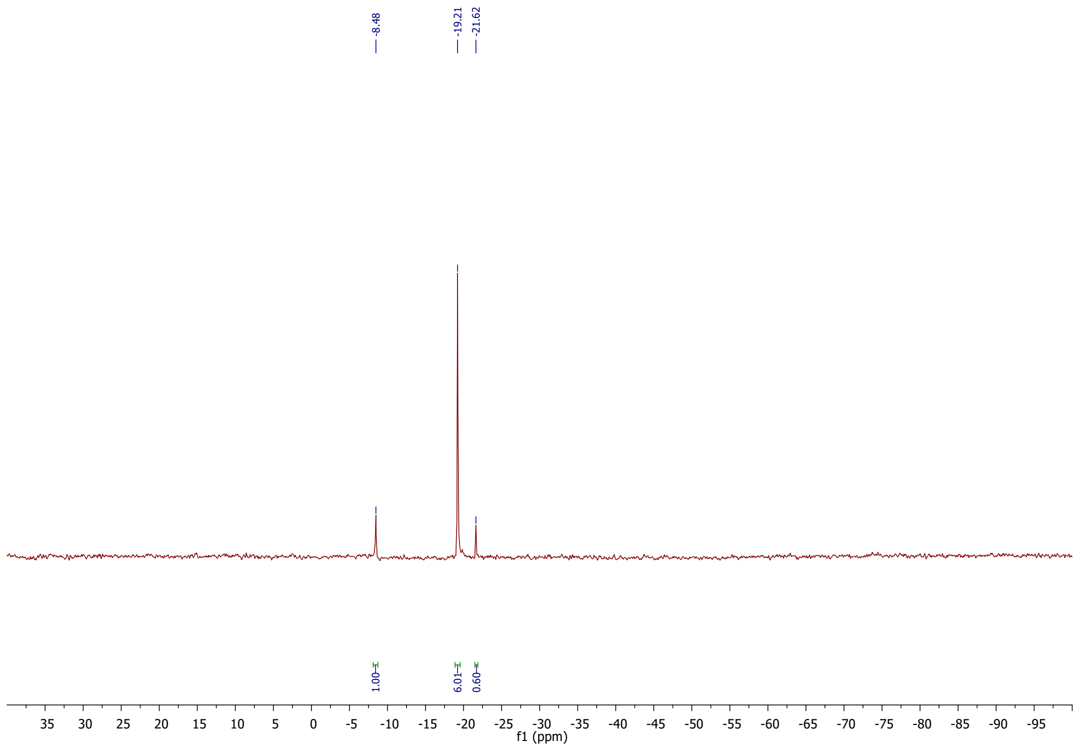


*Figure S16: ^{29}Si-NMR spectrum of depolymerization products of silicone oil **10 + 6 + 1** (25°C, $CDCl_3$, 59.6 MHz)*

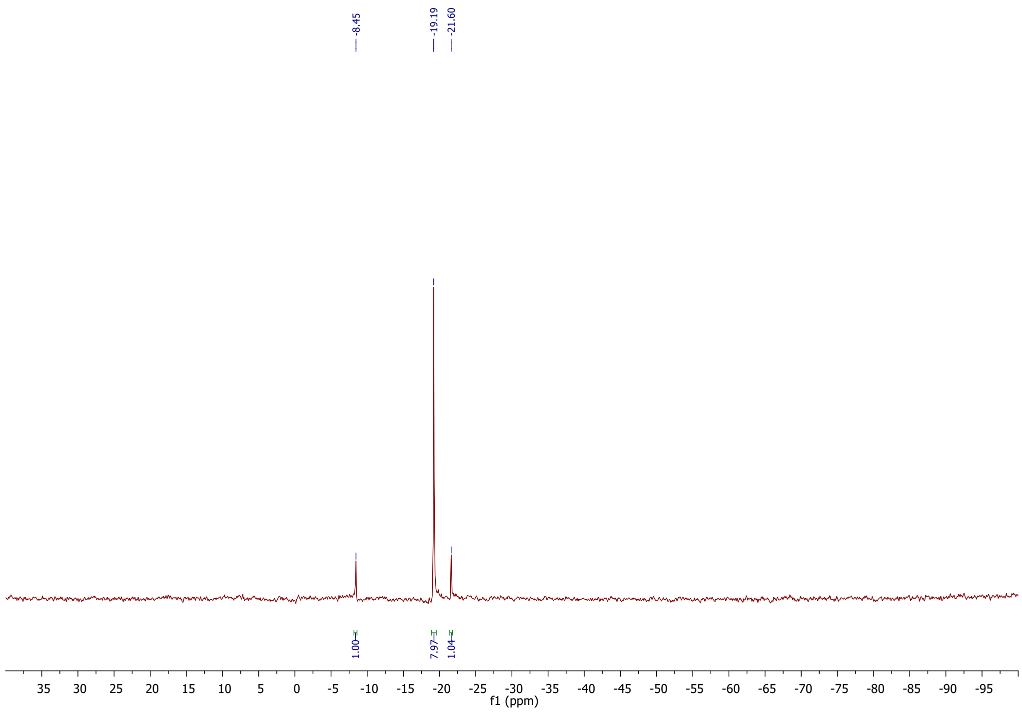


*Figure S17: ^{29}Si-NMR spectrum of depolymerization products of silicone oil **11** (25°C, $CDCl_3$, 59.6 MHz)*

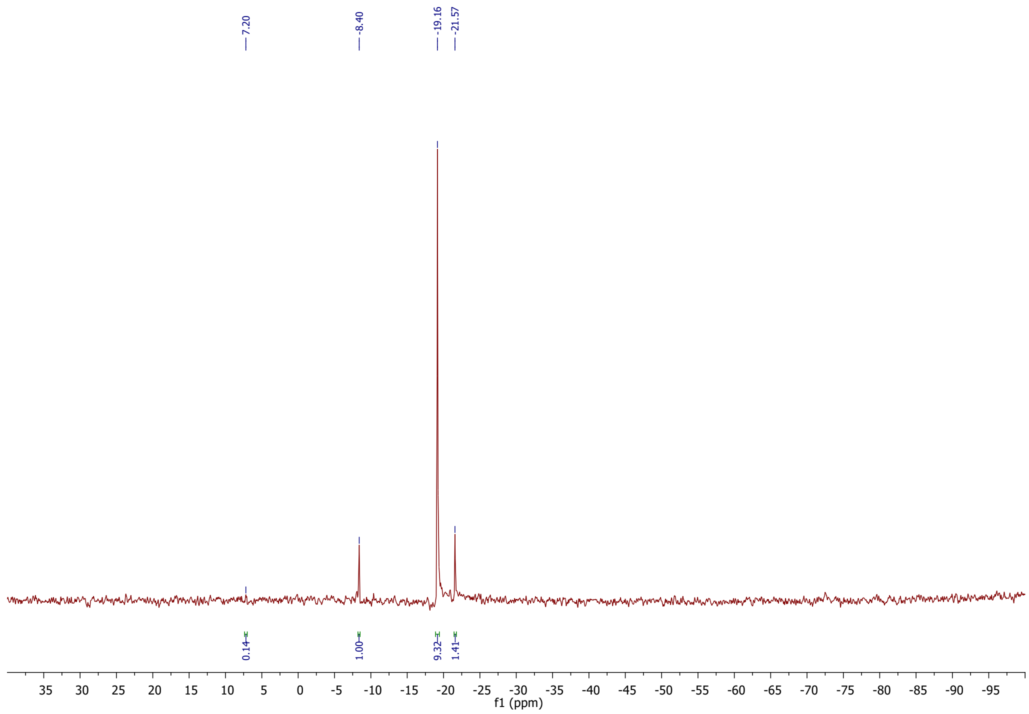


*Figure S18: ²⁹Si-NMR spectrum of depolymerization products of RTV2 + **1** (25°C, $CDCl_3$, 59.6 MHz)*

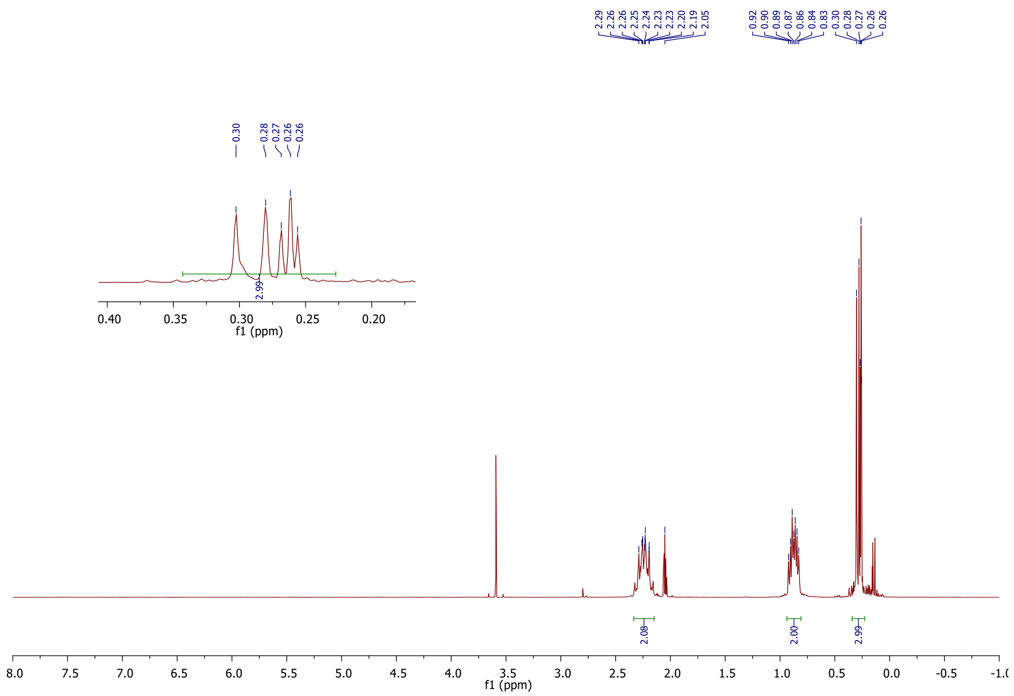


*Figure S19: ¹H-NMR spectrum of depolymerization products of silicone oil **12** (25°C, d_6-acetone, 300 MHz)*

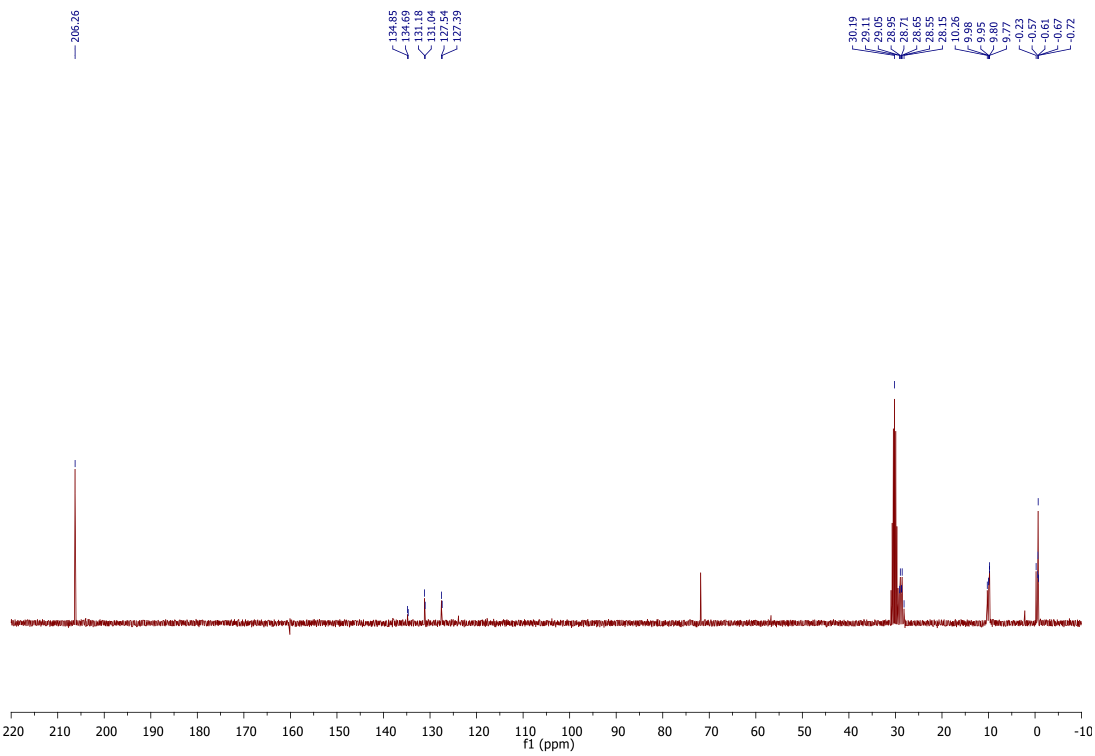


*Figure S20: ^{13}C-NMR spectrum of depolymerization products of silicone oil **12** (25°C, d_6-acetone, 75 MHz)*

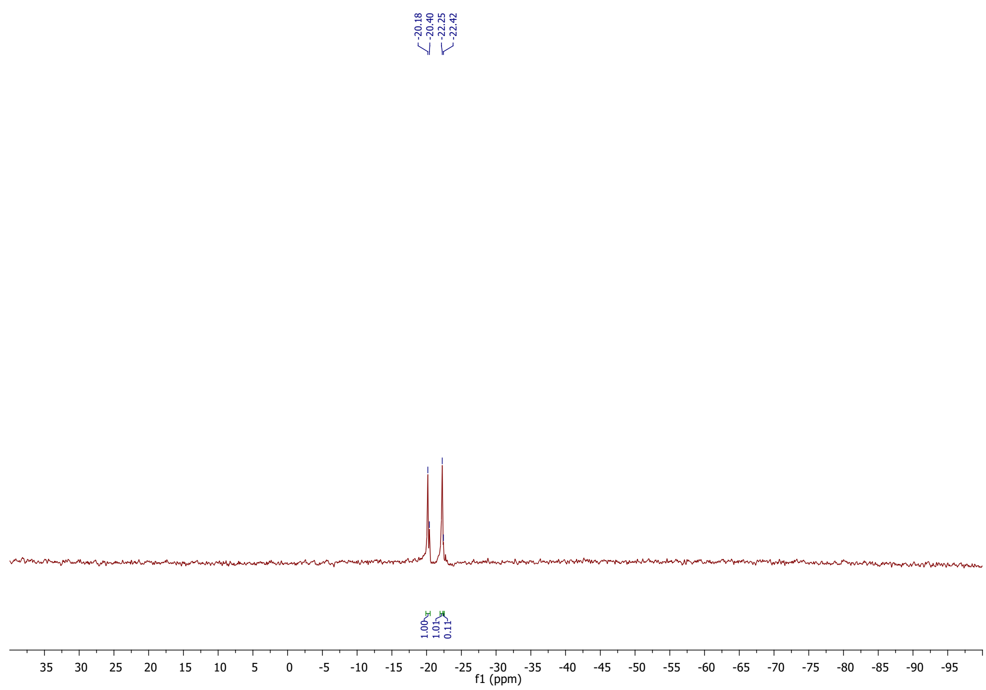


*Figure S21: ^{29}Si-NMR spectrum of depolymerization products of silicone oil **12** (25°C, d_6-acetone, 59.6 MHz)*

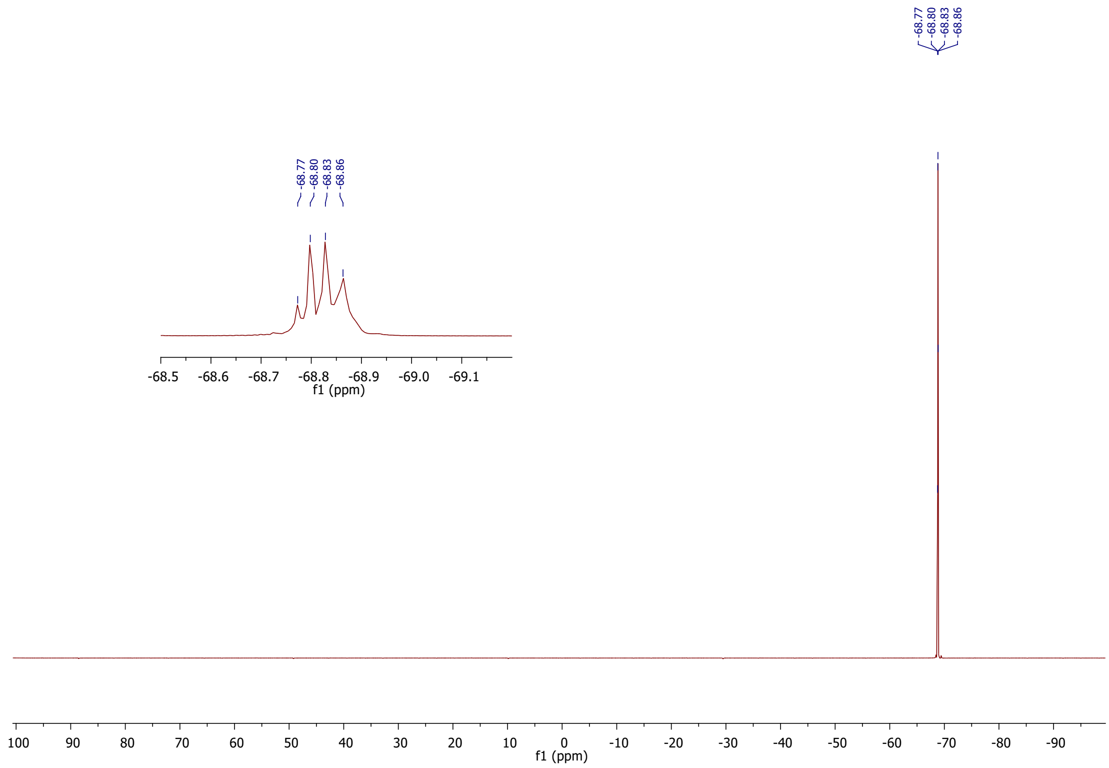


*Figure S22: ^{19}F-NMR spectrum of depolymerization products of silicone oil **12** (25°C, d_6-acetone, 284 MHz)*

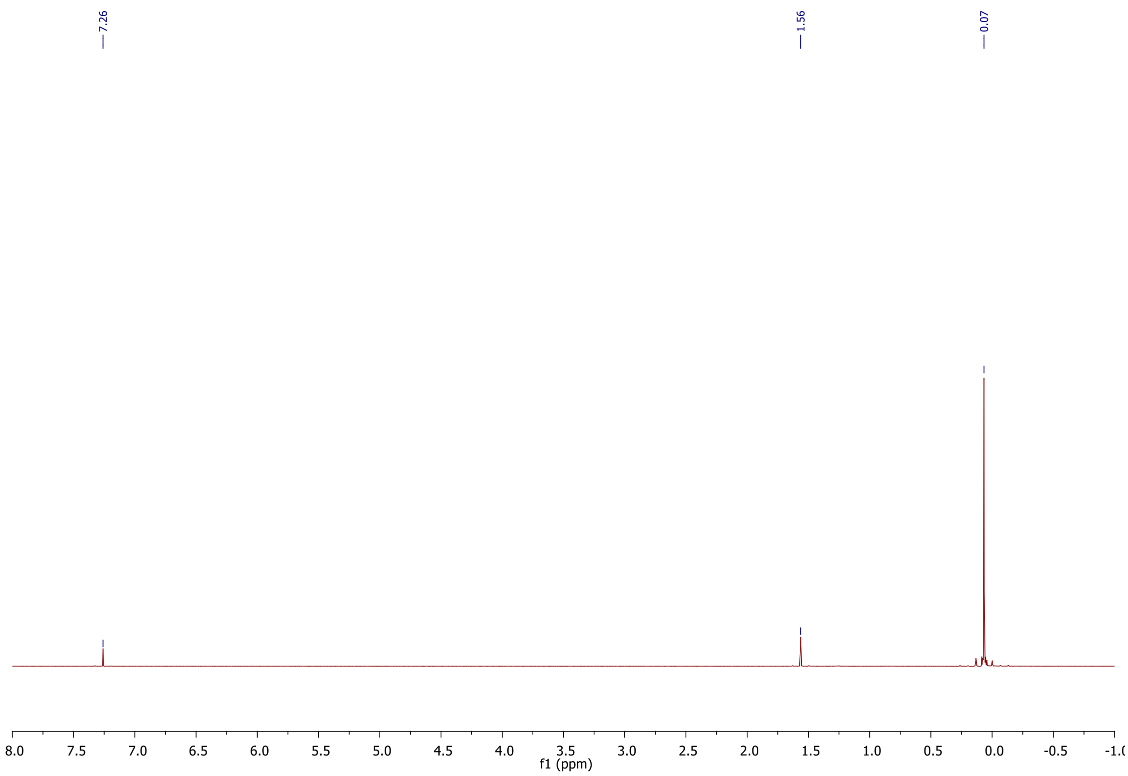


Figure S23: ^{1}H-NMR spectrum of lab-synthesized silicone oil (25°C, $CDCl_3$, 300 MHz)

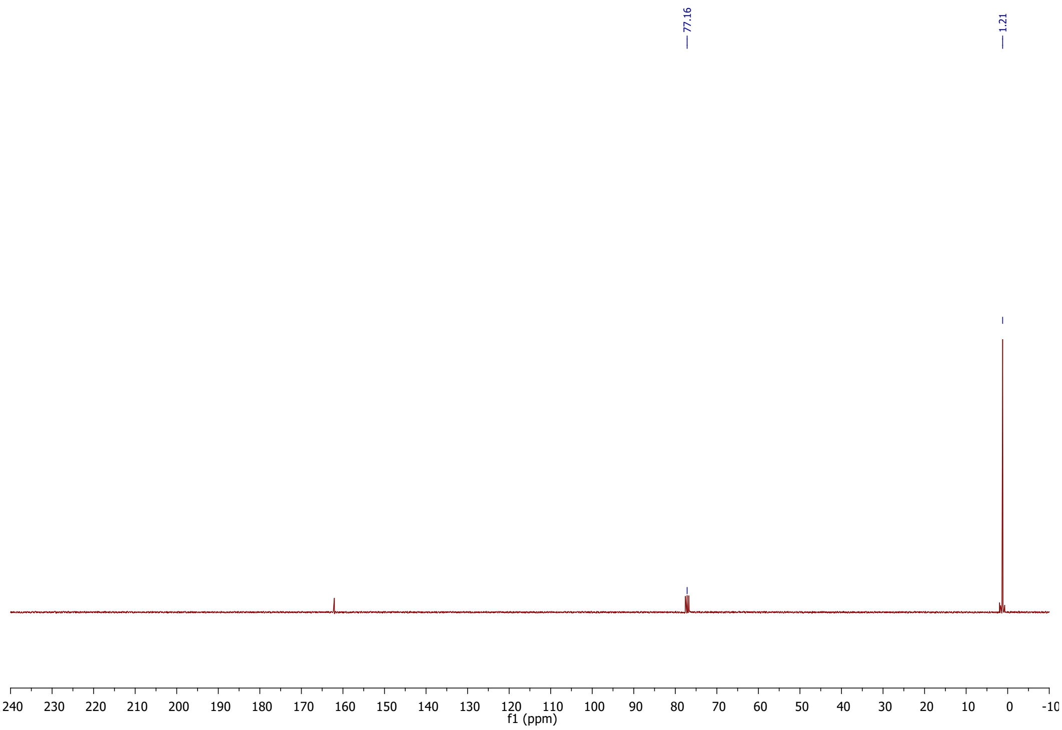


Figure S24: ^{13}C-NMR spectrum of lab-synthesized silicone oil (25°C, $CDCl_3$, 75 MHz)

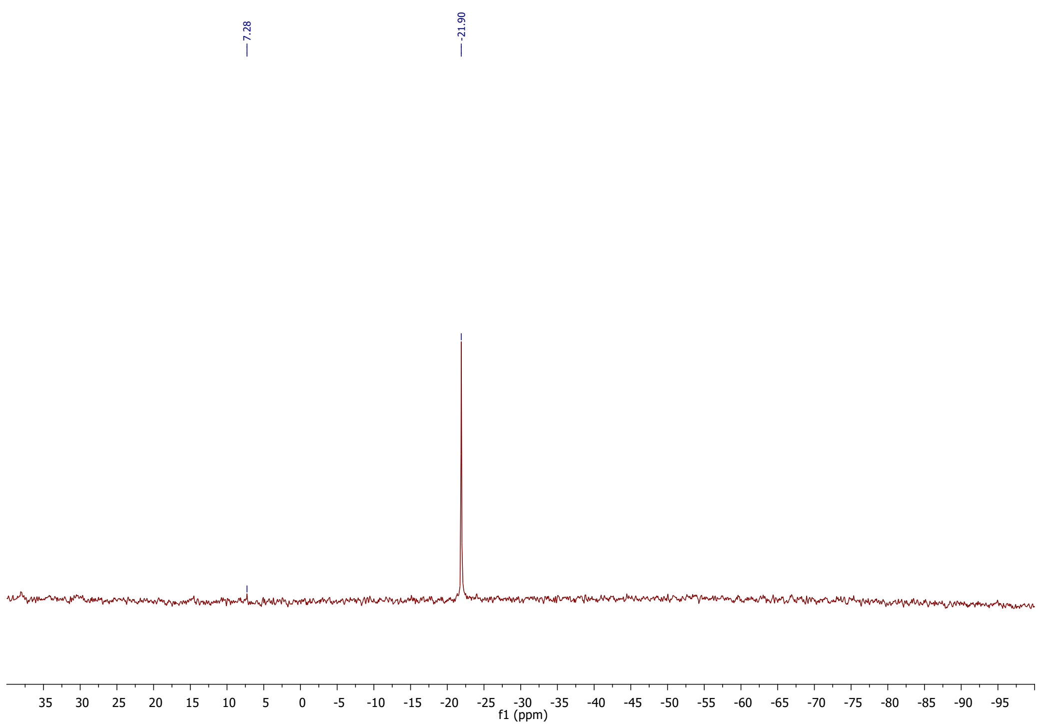


Figure S25: ^{29}Si-NMR spectrum of lab-synthesized silicone oil (25°C, $CDCl_3$, 59.6 MHz)

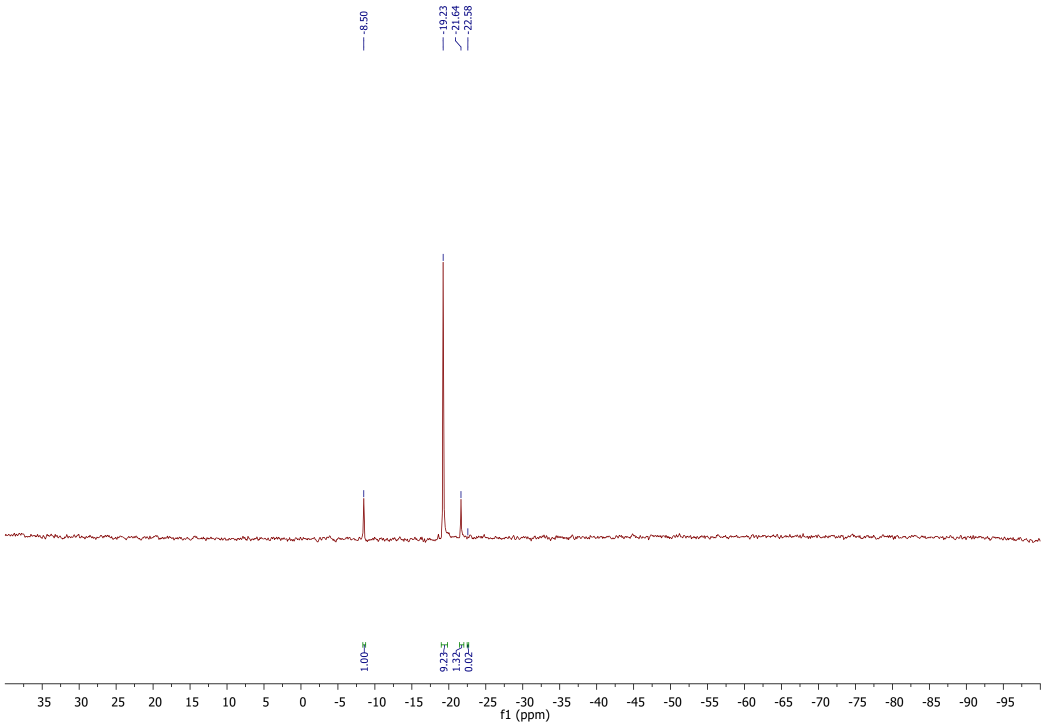
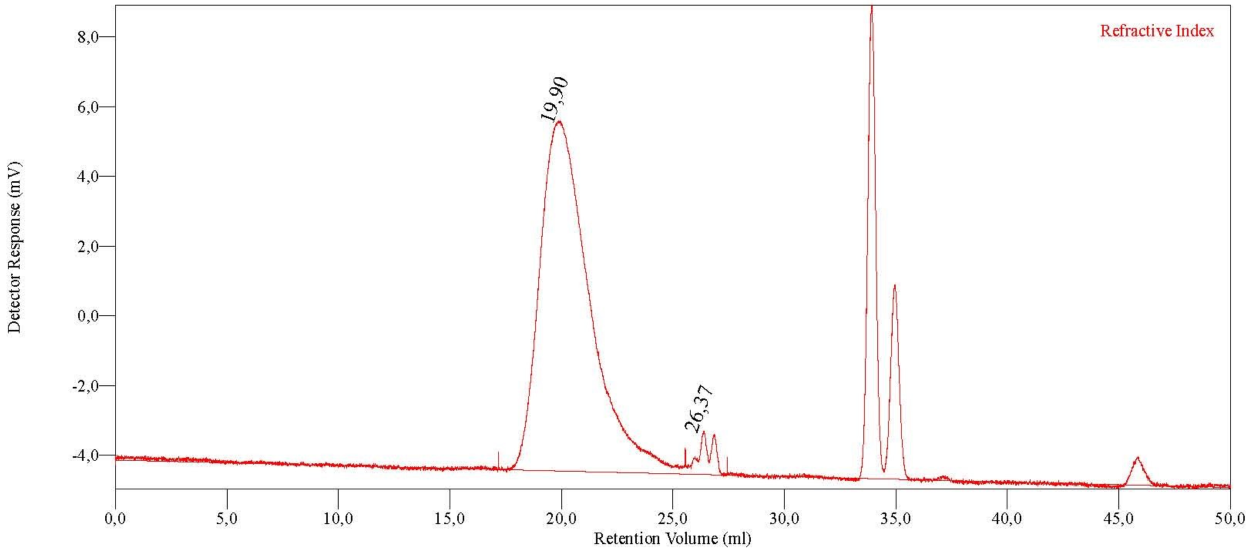


Figure S26: ^{29}Si-NMR spectrum of depolymerization products of industrial silicone waste (25°C, $CDCl_3$, 59.6 MHz)

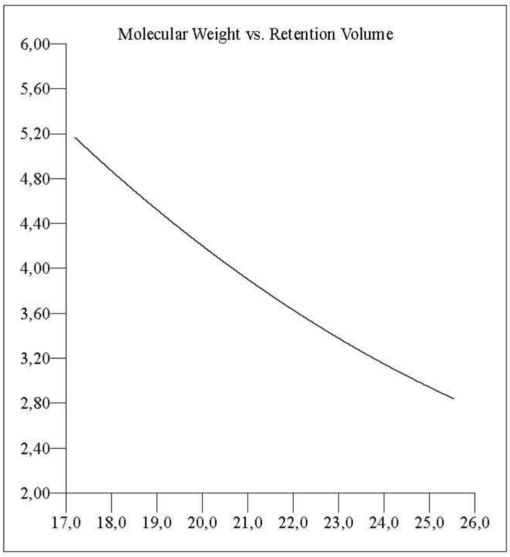
5. SEC analysis of lab-synthesized silicone oil



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	19,897	26,373
Mn - (Daltons)	8 180	473
Mw - (Daltons)	16 468	484
Mz - (Daltons)	25 440	495
Mp - (Daltons)	17 072	490
Mw / Mn	2,013	1,022
Percent Above Mw: 0	100,000	100,000
Percent Below Mw: 0	0,000	0,000
Mw 10.0% Low	2 473	387
Mw 10.0% High	42 319	624
Wt Fr (Peak)	0,966	0,034
RI Area - (mvml)	26,12	0,91
UV Area - (mvml)	0,00	0,00

Annotation	
Method File	05-04-2022 sans FRM-0006.vcm
Limits File	
Date Acquired	Apr 29, 2022 - 09:25:19
Solvent	Toluène
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	GMHxl
System	Viscotek.Toluène
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	100,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	35,0
Column Temp. - (deg C)	35,0
OmniSEC Build Number	406



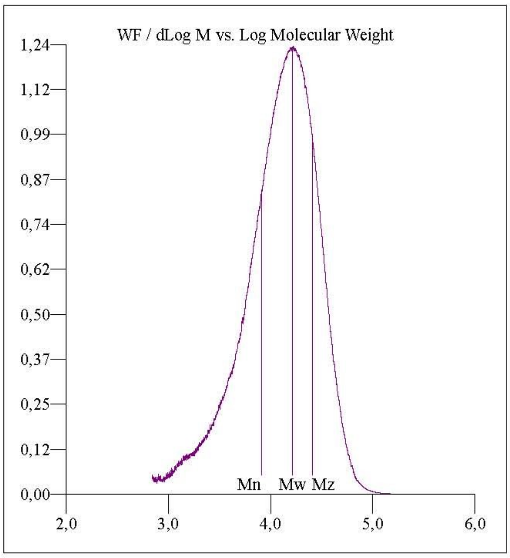
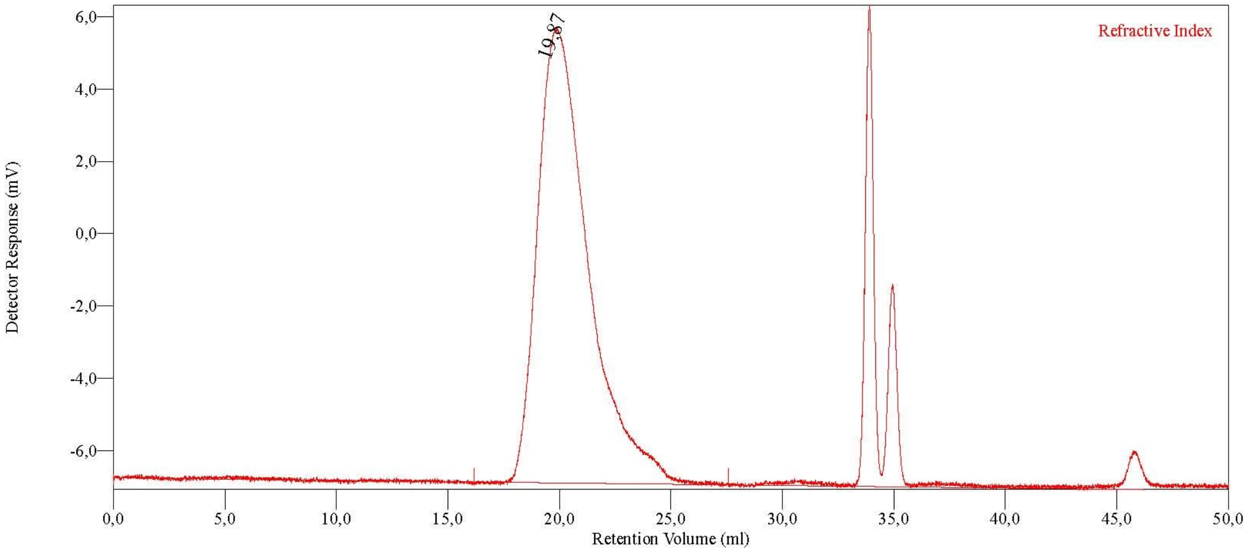


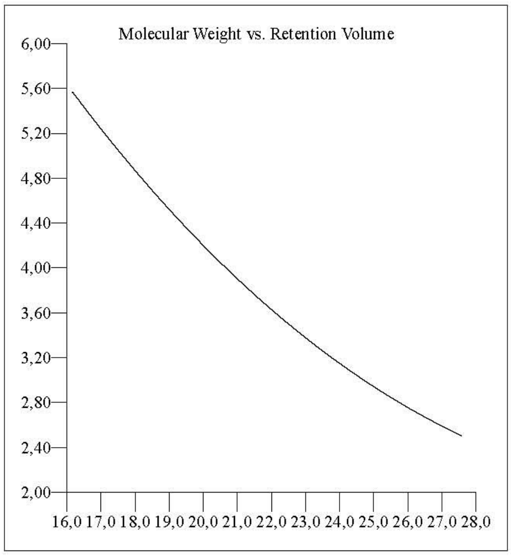
Figure S27: SEC chromatogram after incomplete devolatilization (some cyclics are still present, elution after 26mL or 26min)



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	19,873
Mn - (Daltons)	7 866
Mw - (Daltons)	16 385
Mz - (Daltons)	25 647
Mp - (Daltons)	17 333
Mw / Mn	2,083
Percent Above Mw: 0	100,000
Percent Below Mw: 0	0,000
Mw 10.0% Low	2 336
Mw 10.0% High	41 053
Wt Fr (Peak)	1,000
RI Area - (mvml)	33,12
UV Area - (mvml)	0,00

Annotation	
Method File	05-04-2022 sans FRM-0006.vcm
Limits File	
Date Acquired	Apr 29, 2022 - 13:02:58
Solvent	Toluène
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	GMHxl
System	Viscotek.Toluène
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	100,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	35,0
Column Temp. - (deg C)	35,0
OmniSEC Build Number	406



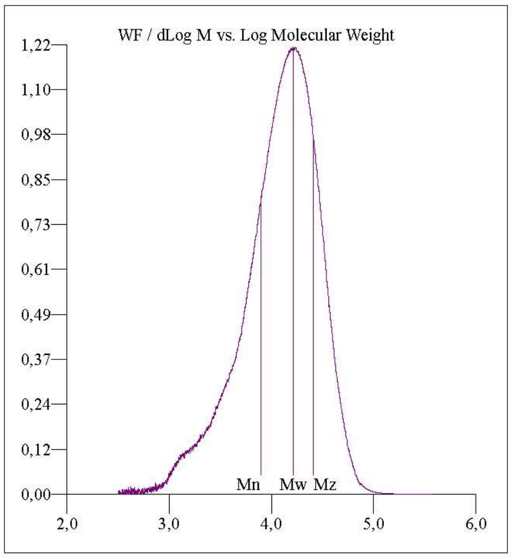


Figure S28: SEC chromatogram after complete devolatilization (absence of volatile cyclics: D3/D4/D5)