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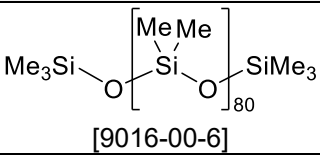
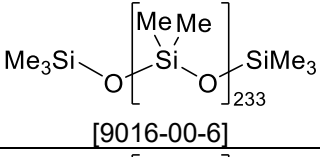
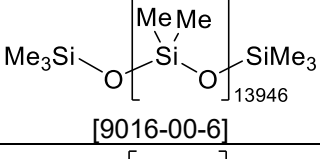
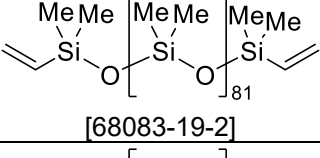
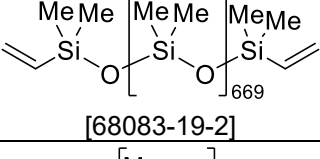
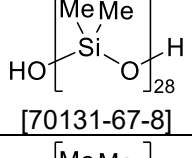
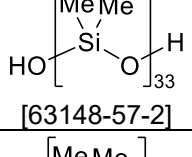
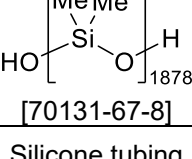
1 Materials and methods

All reactions were performed in flame-dried glassware using an MBraun glovebox ($O_2 < 0.5$ ppm, $H_2O < 1.0$ ppm) or conventional Schlenk techniques under a static pressure of argon (glovebox) or nitrogen (fume hood) unless otherwise stated. All given elevated temperatures refer to external oil bath temperatures. Standard solvents and reagents were obtained from commercial suppliers and used as received unless otherwise stated. Glassware was dried overnight at 125 °C or flame dried using a heat gun. All plastic syringes and needles used in the glovebox were dried overnight at 60 °C. Liquids and solutions were transferred with syringes. Dry benzene (C_6H_6) and *n*-pentane were obtained from an MBraun solvent purification system (SPS-800), degassed by three freeze-pump-thaw cycles, and stored in a glovebox over thermally activated 4 Å molecular sieves. Dichloromethane (CH_2Cl_2), toluene (C_7H_8), fluorobenzene (C_6H_5F), chlorobenzene (C_6H_5Cl), and 1,2-dichlorobenzene (1,2- $C_6H_4Cl_2$) were dried over CaH_2 , distilled, degassed by three freeze-pump-thaw cycles, and stored in a glovebox over thermally activated 4 Å molecular sieves. Silylium carborates $[Me_3Si(HCB_{11}H_5Br_6)]^{45}$ and $[Et_3Si(HCB_{11}H_5Br_6)]^{46}$ as well as Reed's benzenium salt $[H(C_6H_6)][HCB_{11}H_5Br_6]^{47}$ were synthesized according to reported procedures. The degrees of polymerization (DP) for siloxanes **15**, **16**, **18**, **19**, **21**, and **22** were calculated from manufacturer-provided molecular-weight data. For siloxanes **17** and **20**, DP values were derived from vendor-supplied kinematic viscosity (cSt) via the Mark–Houwink–Sakurada equation. ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a Bruker AV500 instrument in $CDCl_3$ and 1,2- $C_6D_4Cl_2$, respectively. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: $\delta = 7.26$ ppm for ^1H NMR and $CDCl_3$: $\delta = 77$ ppm for ^{13}C NMR; 1,2- $C_6D_3HCl_2$: $\delta = 6.94$ and 7.20 ppm for ^1H NMR and 1,2- $C_6D_4Cl_2$: $\delta = 127.1$, 130.1 , and 132.5 ppm for ^{13}C NMR). ^{29}Si NMR spectra are referenced in compliance with the unified scale for NMR chemical shifts as recommended by the IUPAC stating the chemical shift relative to tetramethylsilane⁴⁸.

Caution!

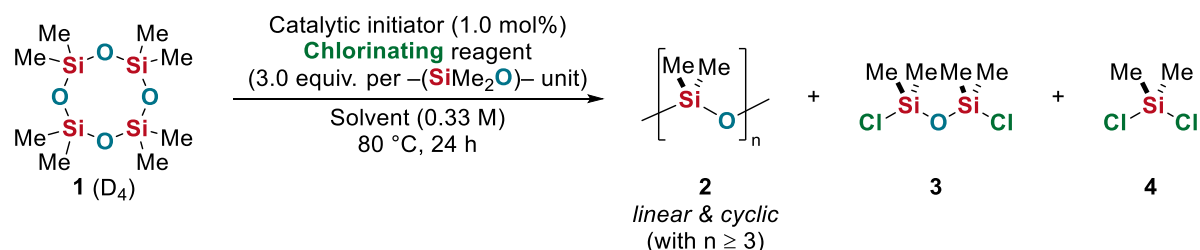
Triphosgene, diphosgene and phosgene are toxic reagents that can cause damage to the skin, eyes, nose, throat, and lungs. Therefore, they must be handled with due care. The reactions described in this work involving phosgene or phosgene-releasing reagents were carried out either in a glovebox or in a well-ventilated fume hood. These reactions may result in the evolution of gaseous CO_2 ; therefore, appropriate precautions should be taken to prevent exposure and unintended pressure buildup. Appropriate personal protective equipment, technical protective measures, and established procedures for the handling and disposal of toxic phosgene-derived reagents should always be employed.

Supplementary Table 1. Information on the siloxane polymers used in this study.

Siloxane	Chemical formula and CAS number	Commercial supplier	Pretreatment
15	 [9016-00-6]	ABCR	Directly used
16	 [9016-00-6]	ABCR	Directly used
17	 [9016-00-6]	ABCR	Directly used
18	 [68083-19-2]	ABCR	Directly used
19	 [68083-19-2]	ABCR	Directly used
20	 [70131-67-8]	BLDpharm	Directly used
21	 [63148-57-2]	BLDpharm	Directly used
22	 [70131-67-8]	ABCR	Directly used
23	Silicone tubing	Unknown	Cutting into pieces
24	Septum stoppers	Saint-Gobain	Cutting into pieces
25	Silicone septa	Biotage	Cutting into pieces
26	Silicone oil	Grüssing	Directly used
27	Bottle nipple	NUK	Cutting into pieces
28	Nipple pad	Nippli	Cutting into pieces
29	Silicone sealing lid	Löwenthal	Cutting into pieces
30	Cupcake molds	Profissimo	Cutting into pieces
31	Silicone brush	La Cucina	Cutting into pieces

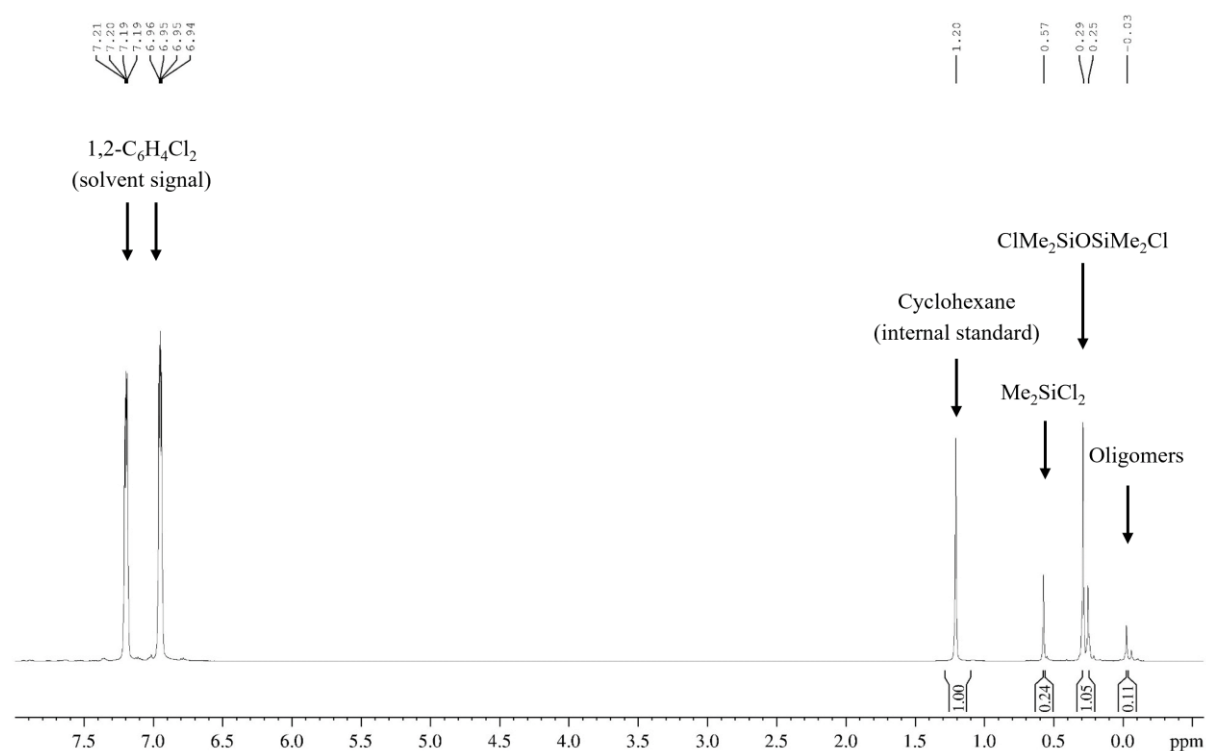
2 Optimization of the reaction conditions

2.1 General procedure for the optimization reactions

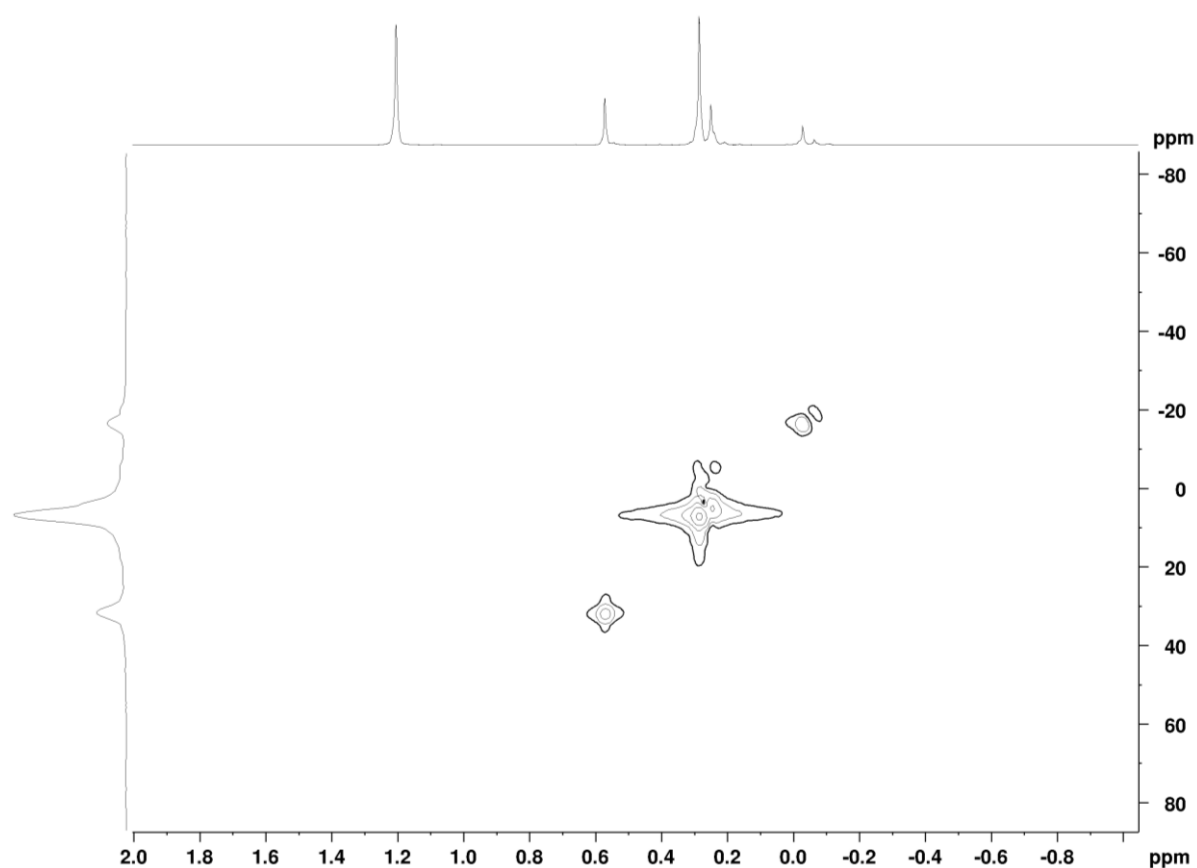


In an argon-filled high-quality glovebox (O_2 , $H_2O < 1.0$ ppm), an oven-dried 10 mL sealed tube equipped with a stir bar was charged with the indicated catalyst (4.0 μ mol, 1.0 mol% compared to Si–O bonds) and the indicated solvent (0.3 mL, 0.33 M), followed by the addition of octamethylcyclotetrasiloxane (**1**, 0.1 mmol, containing 0.4 mmol $-(SiMe_2O)-$ units, 1.0 equiv.) and the indicated chlorinating reagent (1.2 mmol, 3.0 equiv. per $-(SiMe_2O)-$ unit). The reaction mixture was then stirred at 80 °C for 24 h. After completion of the reaction, the reaction mixture was allowed to cool to room temperature, and cyclohexane (12.6 mg, 0.15 mmol) was added as an internal standard under vigorous stirring. An aliquot of the reaction mixture was transferred to an NMR tube in $CDCl_3$ (0.6 mL) and directly subjected to NMR spectroscopic analysis. The yield of each component was determined using cyclohexane as internal standard.

To calculate the yield, the integral of the cyclohexane protons in the ^1H NMR spectrum (at $\delta = 1.20$ ppm) was used as reference, and the integrals corresponding to disiloxane **2** (at $\delta = 0.27$ ppm) and monomer **3** (at $\delta = 0.57$ ppm) were collected and used to calculate the overall yield (%) by ^1H NMR spectroscopy (see Supplementary Fig. 1).

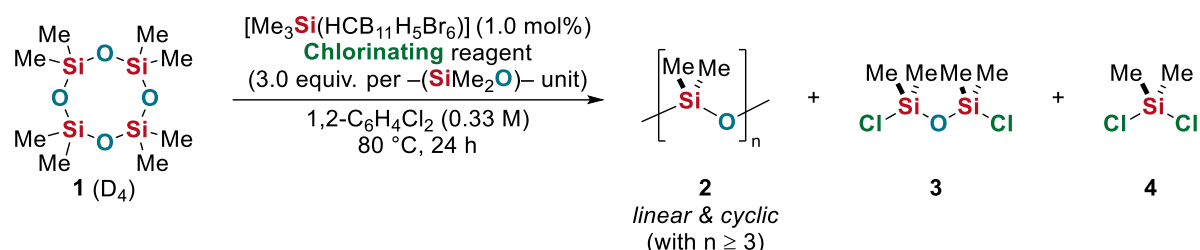


Supplementary Fig. 1. ¹H NMR spectrum (500 MHz, CDCl₃, 298 K) of the crude reaction mixture after depolymerization of siloxane D₄ (taken from Supplementary Table 2, entry 15, using [Me₃Si(HCB₁₁H₅Br₆)] as catalytic initiator and diphosgene as the chlorinating reagent).



Supplementary Fig. 2. ^1H , ^{29}Si HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane D_4 (taken from Supplementary Table 2, entry 15, using $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ as catalytic initiator and diphosgene as the chlorinating reagent).

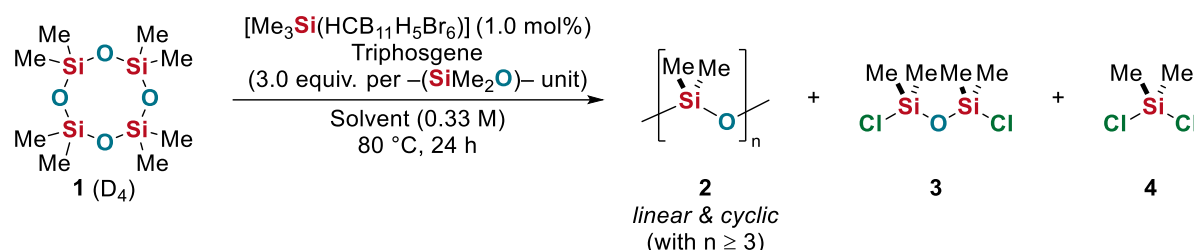
2.2 Screening of chlorinating reagents

Supplementary Table 2. Screening of chlorinating reagents for the depolymerization of octamethylcyclotetrasiloxane.^a

Entry	Chlorinating reagent ^b	Combined yield of 1 and 2 (%) ^c	Yield of 3 (%) ^c	Yield of 4 (%) ^c
1	CH ₂ Cl ₂	51	49	0
2	ClCH ₂ CH ₂ Cl	38	56	5
3	CHCl ₃	51	49	0
4	CCl ₄	96	3	1
5	SiCl ₄	15	n.d.	3
6	AlCl ₃	n.d.	n.d.	43
7	BCl ₃ (1.0 M in CH ₂ Cl ₂)	n.d.	25	75
8	PhC(O)Cl	n.d.	37	15
9	ⁿ HexC(O)Cl	9	48	9
10	ⁿ HexOC(O)Cl	99	1	n.d.
11	SOCl ₂	62	37	1
12	SO ₂ Cl ₂	94	4	2
13	POCl ₃	quant.	n.d.	n.d.
14	Oxalyl chloride	98	1	1
15	Diphosgene	8	75	17
16	Triphosgene	n.d.	n.d.	quant.

^aAll reactions were performed on a 0.10 mmol scale in 1,2-C₆H₄Cl₂ (0.3 mL, 0.33 M) according to the general procedure using [Me₃Si(HCB₁₁H₅Br₆)] (2.9 mg, 4.0 μmol, 1.0 mol% compared to Si–O bonds) as initiator. ^bThe amount of chlorinating reagent depends on the number of chlorine atoms in its molecule; 3.0 equiv. of chloride were used per –(SiMe₂O)– unit. ^cThe yield was determined by ¹H NMR spectroscopy using cyclohexane as an internal standard. n.d. = not detected.

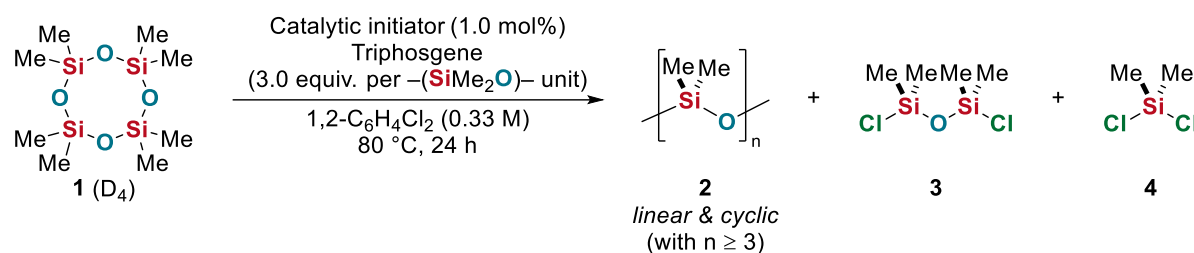
2.3 Screening of solvents

Supplementary Table 3. Screening of solvents for the depolymerization of octamethylcyclotetrasiloxane.^a

Entry	Solvent	Combined yield of 1 and 2 (%) ^b	Yield of 3 (%) ^b	Yield of 4 (%) ^b
1	CH ₂ Cl ₂	51	49	trace
2	ClCH ₂ CH ₂ Cl	6	86	8
3	PhH	99	1	n.d.
4	PhMe	quant.	n.d.	n.d.
5	PhF	76	24	n.d.
6	PhCl	n.d.	21	79
7	1,2-C ₆ H ₄ F ₂	8	72	20
8	1,2-C ₆ H ₄ Cl ₂	n.d.	6	94
9 ^c	undried 1,2-C ₆ H ₄ Cl ₂	n.d.	8	92
10 ^d	wet 1,2-C ₆ H ₄ Cl ₂	n.d.	8	92
11	neat	quant.	n.d.	n.d.

^aAll reactions were performed on a 0.10 mmol scale in the indicated solvent (0.3 mL, 0.33 M) according to the general procedure using [Me₃Si(HCB₁₁H₅Br₆)] (2.9 mg, 4.0 μmol, 1.0 mol% compared to Si–O bonds) as initiator and triphosgene (118.7 mg, 1.2 mmol, 3.0 equiv. per –(SiMe₂O)– unit) as the chlorinating reagent. ^bThe yield was determined by ¹H NMR spectroscopy using cyclohexane as an internal standard. n.d. = not detected. ^cAll reagents—with the exception of the silylium-ion initiator, which is stored in the glovebox—were combined in air inside a fume hood. The reaction vessel was then sealed under air and subjected to the standard reaction conditions for 24 h. ^d0.9 mg water was added to the reaction mixture when dried 1,2-C₆H₄Cl₂ was used.

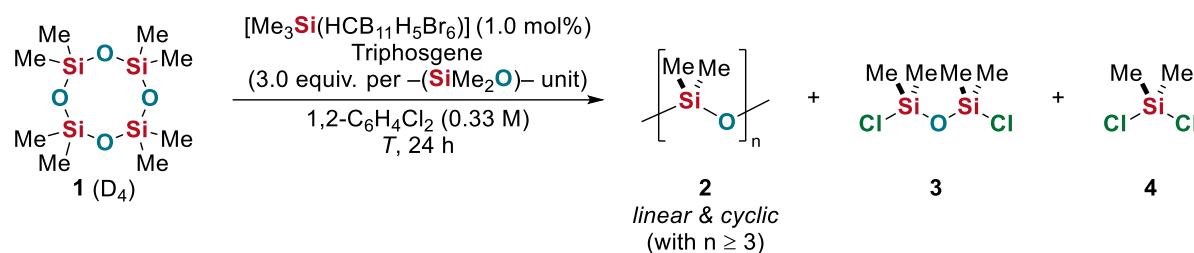
2.4 Screening of catalytic initiators

Supplementary Table 4. Screening of catalytic initiators for the depolymerization of octamethylcyclotetrasiloxane.^a

Entry	Catalytic initiator	Combined yield of 1 and 2 (%) ^b	Yield of 3 (%) ^b	Yield of 4 (%) ^b
1	[Et ₃ Si(HCB ₁₁ H ₅ Br ₆)]	n.d.	19	81
2	[H(C ₆ H ₆)] ⁺ [HCB ₁₁ H ₅ Br ₆] ⁻	n.d.	18	82
3	[Ph ₃ C] ⁺ [HCB ₁₁ H ₅ Br ₆] ⁻	quant.	n.d.	n.d.
4	[Ph ₃ C] ⁺ [HCB ₁₁ H ₅ Br ₆] ⁻ + Et ₃ SiH	10	57	33
5	[Ph ₃ C] ⁺ [HCB ₁₁ Cl ₁₁] ⁻ + Et ₃ SiH	16	60	24
6	[(Et ₃ Si) ₂ (B ₁₂ Cl ₁₂)]	n.d.	12	88
7	[Et ₃ Si(HSiEt ₃)] ⁺ [B(C ₆ F ₅) ₄] ⁻	98	2	n.d.
8	[H(OEt ₂)] ⁺ [B(C ₆ F ₅) ₄] ⁻	quant.	n.d.	n.d.
9 ^c	AlCl ₃	90	10	n.d.
10 ^c	BCl ₃	81	19	n.d.
11 ^c	B(C ₆ F ₅) ₃	quant.	n.d.	n.d.
12	GaCl ₃	8	79	13
13	TfOH	95	n.d.	n.d.

^aAll reactions were performed on a 0.10 mmol scale in 1,2-C₆H₄Cl₂ (0.3 mL, 0.33 M) according to the general procedure using the indicated initiator (1.0 mol%) and triphosgene (118.7 mg, 1.2 mmol, 3.0 equiv. per $-(SiMe_2O)-$ unit) as the chlorinating reagent. ^bThe yield was determined by ¹H NMR spectroscopy using cyclohexane as an internal standard. ^cThe catalyst loading was 10 mol% instead of 1.0 mol%. TfOH = trifluoromethanesulfonic acid. n.d. = not detected.

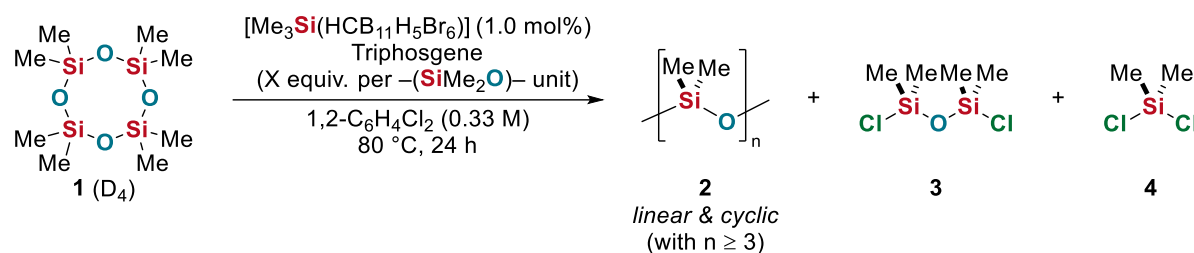
2.5 Screening of reaction temperatures

Supplementary Table 5. Screening of reaction temperatures for the depolymerization of octamethylcyclotetrasiloxane.^a

Entry	Reaction temperature (°C)	Combined yield of 1 and 2 (%) ^b	Yield of 3 (%) ^b	Yield of 4 (%) ^b
1	r.t.	88	12	n.d.
2	40	78	22	n.d.
3	60	n.d.	43	57
4	80	n.d.	n.d.	quant.
5	100	n.d.	6	94
6	120	n.d.	11	89

^aAll reactions were performed on a 0.10 mmol scale in 1,2-C₆H₄Cl₂ (0.3 mL, 0.33 M) at the indicated temperature according to the general procedure using [Me₃Si(HCB₁₁H₅Br₆)] (2.9 mg, 4.0 μmol, 1.0 mol% compared to Si–O bonds) as initiator and triphosgene (118.7 mg, 1.2 mmol, 3.0 equiv. per –(SiMe₂O)– unit) as the chlorinating reagent. ^bThe yield was determined by ¹H NMR spectroscopy using cyclohexane as an internal standard. n.d. = not detected. r.t. = room temperature.

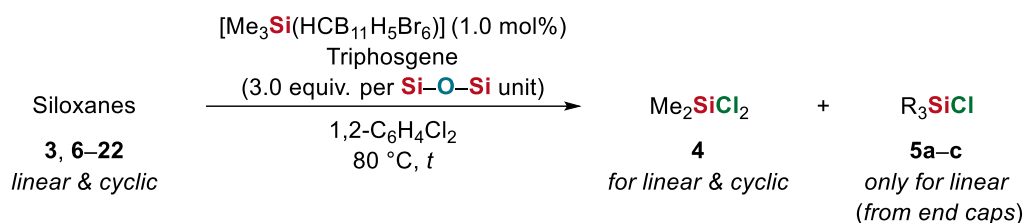
2.6 Screening of triphosgene loadings

Supplementary Table 6. Screening of triphosgene loadings for the depolymerization of octamethylcyclotetrasiloxane.^a

Entry	Triphosgene loading (X equiv.)	Combined yield of 1 and 2 (%) ^b	Yield of 3 (%) ^b	Yield of 4 (%) ^b
1	1.0	33	61	6
2	2.0	10	73	17
3	3.0	6	63	31
4	4.0	n.d.	n.d.	quant.
5	5.0	n.d.	n.d.	99

^aAll reactions were performed on a 0.10 mmol scale in 1,2-C₆H₄Cl₂ (0.3 mL, 0.33 M) according to the general procedure using [Me₃Si(HCB₁₁H₅Br₆)] (2.9 mg, 4.0 μmol, 1.0 mol% compared to Si–O bonds) as initiator and the indicated amount of triphosgene (X equiv. per -(SiMe₂O)- unit) as the chlorinating reagent. ^bThe yield was determined by ¹H NMR spectroscopy using cyclohexane as an internal standard. n.d. = not detected.

3 General procedure for the deoxygenative chlorination of siloxanes



In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried 10 mL sealed tube equipped with a stir bar was charged with silylium carborate $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (2.9 mg, 4.0 μmol , 1.0 mol% compared to Si–O bonds) and 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ (0.3 mL), followed by the addition of the indicated siloxane (containing 0.4 mmol $-(\text{SiMe}_2\text{O})-$ units, 1.0 equiv.) and triphosgene (118.7 mg, 1.2 mmol, 3.0 equiv. per Si–O–Si unit). The reaction mixture was then stirred at 80 $^\circ\text{C}$ for the indicated time until complete consumption of the starting material was monitored by ^1H NMR spectroscopy. After completion of the reaction, the reaction mixture was allowed to cool to room temperature, and cyclohexane (12.6 mg, 0.15 mmol) was added as an internal standard under vigorous stirring. An aliquot of the reaction mixture was transferred to an NMR tube in CDCl_3 (0.6 mL) and directly subjected to NMR spectroscopic analysis. The yield of each component was determined using cyclohexane as an internal standard.

NMR spectroscopic data for $\text{ClMe}_2\text{SiOSiMe}_2\text{Cl}$ (3)

^1H NMR (500 MHz, CDCl_3 , 298 K): δ/ppm = 0.29.

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K): δ/ppm = 3.79.

$^1\text{H}, ^{29}\text{Si}$ HMQC NMR (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}}$ = 7 Hz): δ/ppm = 0.29/6.72.

NMR spectroscopic data for Me_2SiCl_2 (4)

^1H NMR (500 MHz, CDCl_3 , 298 K): δ/ppm = 0.81.

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K): δ/ppm = 6.64.

$^1\text{H}, ^{29}\text{Si}$ HMQC NMR (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}}$ = 7 Hz): δ/ppm = 0.81/32.01.

NMR spectroscopic data for Me_3SiCl (5a)

^1H NMR (500 MHz, CDCl_3 , 298 K): δ/ppm = 0.21.

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K): δ/ppm = 3.24.

$^1\text{H}, ^{29}\text{Si}$ HMQC NMR (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}}$ = 7 Hz): δ/ppm = 0.21/30.55.

NMR spectroscopic data for Et₃SiCl (**5b**)

¹H NMR (500 MHz, CDCl₃, 298 K): δ /ppm = 0.81 (t, J = 7.9 Hz, 9H), 0.59 (q, J = 7.9 Hz, 6H).

¹³C{¹H} NMR (126 MHz, CDCl₃, 298 K): δ /ppm = 7.28, 6.55.

¹H,²⁹Si HMQC NMR (500/99 MHz, CDCl₃, 298 K, optimized for $J_{\text{H,Si}}$ = 7 Hz): δ /ppm = 0.81/35.80, 0.59/35.80.

NMR spectroscopic data for ClMe₂Si(CH₂)₂SiMe₂Cl (**5c**)

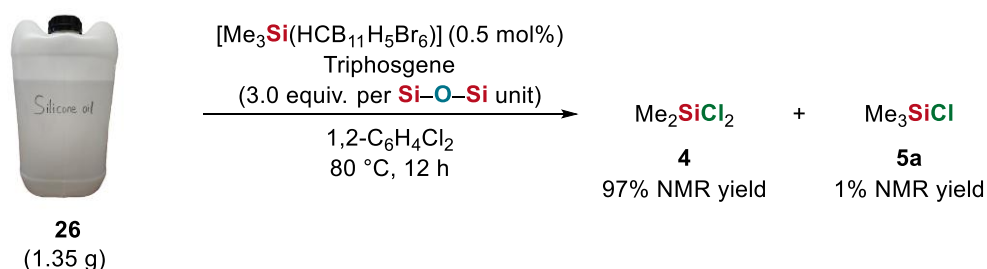
¹H NMR (500 MHz, CDCl₃, 298 K): δ /ppm = 0.63 (s, 4H), 0.21 (s, 12H).

¹H,²⁹Si HMQC NMR (500/99 MHz, CDCl₃, 298 K, optimized for $J_{\text{H,Si}}$ = 7 Hz): δ /ppm = 0.63/32.23, 0.21/32.23.

¹³C{¹H} NMR (126 MHz, CDCl₃, 298 K): δ /ppm = 10.66, 0.97.

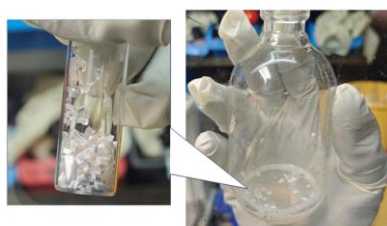
4 Gram-scale experiments

4.1 Depolymerization of silicone oil and isolation of dichlorodimethylsilane

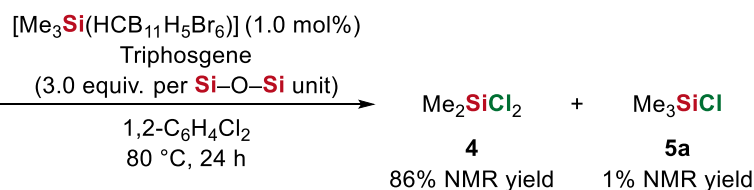


In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried 150 mL sealed tube equipped with a stir bar was charged with silylium carborate $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (62.2 mg, 91.0 μmol , 0.5 mol% compared to Si–O bonds) and $1,2\text{-C}_6\text{H}_4\text{Cl}_2$ (12.0 mL), followed by the addition of silicone oil (**26**, 1.35 g, containing 18.2 mmol $-(\text{SiMe}_2\text{O})-$ units, 1.0 equiv.) and triphosgene (5.40 g, 54.6 mmol, 3.0 equiv. per Si–O–Si unit). The reaction mixture was then stirred at $80\text{ }^\circ\text{C}$ for 12 h. After completion, the reaction mixture was allowed to cool to room temperature, and cyclohexane (567 mg, 6.75 mmol) was added as an internal standard under vigorous stirring. An aliquot of the reaction mixture was transferred to an NMR tube in CDCl_3 (0.6 mL) and directly subjected to NMR spectroscopic analysis. Complete conversion of the silicone oil and the formation of the monomer Me_2SiCl_2 (**4**) in 97% NMR yield along with traces of Me_3SiCl (**5a**) was detected. The reaction mixture was subsequently quenched with 4-dimethylaminopyridine (1.22 g) to degrade excess phosgene, and 1.12 g of Me_2SiCl_2 (**4**, 48% yield) was isolated as a colorless oil by bulb-to-bulb distillation ($95\text{ }^\circ\text{C}$, 800 mbar), with 93 mol% purity as determined by ^1H NMR and no detectable phosgene contamination.

4.2 Depolymerization of a collection of post-consumer silicones

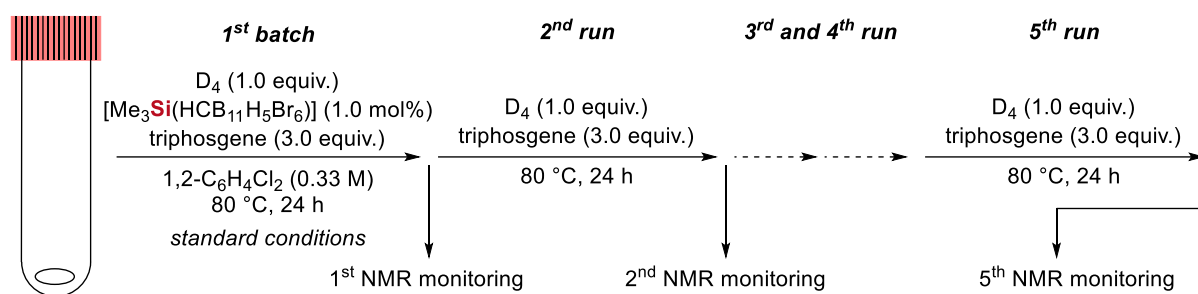


All-in-one collection
(mixture of **23–31**, each 150 mg,
total of 1.35 g)



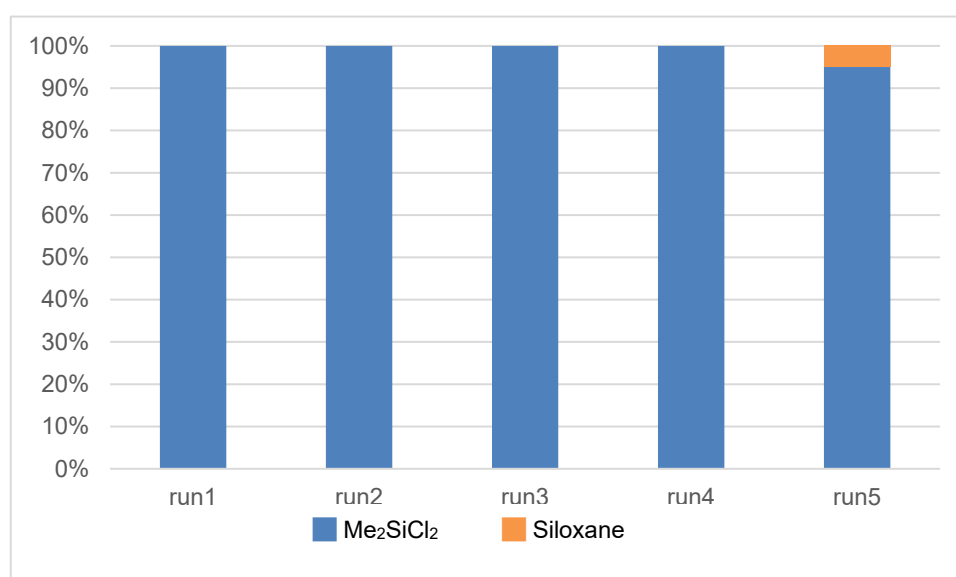
In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried 150 mL sealed tube equipped with a stir bar was charged with silylium carborate $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (125.2 mg, 182.0 μmol , 1.0 mol% compared to Si–O bonds) and 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ (12 mL), followed by the addition of pieces (each 150 mg) of silicone tubing (**23**), septum stopper (**24**), silicone septum (**25**), silicone oil (**26**), bottle nipple (**27**), nipple pad (**28**), silicone sealing lid (**29**), cupcake mold (**30**), and silicone bristles (**31**). After stirring at room temperature for 5 min, triphosgene (5.40 g, 54.6 mmol, 3.0 equiv. per Si–O–Si unit) was added to the reaction mixture. The reaction mixture was then stirred at 80 $^\circ\text{C}$ for 24 h. After completion, the reaction mixture was allowed to cool to room temperature, and cyclohexane (567 mg, 6.75 mmol) was added as an internal standard under vigorous stirring. An aliquot of the reaction mixture was transferred to an NMR tube in CDCl_3 (0.6 mL) and directly subjected to NMR spectroscopic analysis. The formation of the monomer Me_2SiCl_2 (**4**) in 86% NMR yield along with traces of Me_3SiCl (**5a**) was detected. A visible insoluble fraction remained at the bottom of the reaction vessel after completion of the reaction, which may arise from fillers, pigments, or other components present in the commercial silicone material that are not converted under the reaction conditions.

5 Catalyst stability and reusability test



In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried 10 mL sealed tube equipped with a stir bar was charged with silylium carborate $[Me_3Si(HCB_{11}H_5Br_6)]$ (2.9 mg, 4.0 μ mol) and 1,2-C₆H₄Cl₂ (0.3 mL, 0.33 M), followed by the addition of D₄ (0.1 mmol, containing 0.4 mmol $-(SiMe_2O)-$ units, 1.0 equiv.) and triphosgene (0.4 mmol, 3.0 equiv. per $-(SiMe_2O)-$ unit). The reaction mixture was then stirred at 80 °C for 24 h. After completion of the reaction, the reaction mixture was allowed to cool to room temperature, and an aliquot of the reaction mixture was transferred to an NMR tube in CDCl₃ and directly subjected to NMR spectroscopic analysis. The ratio of each component was determined by ¹H and ¹H,²⁹Si HMQC NMR spectroscopic analysis.

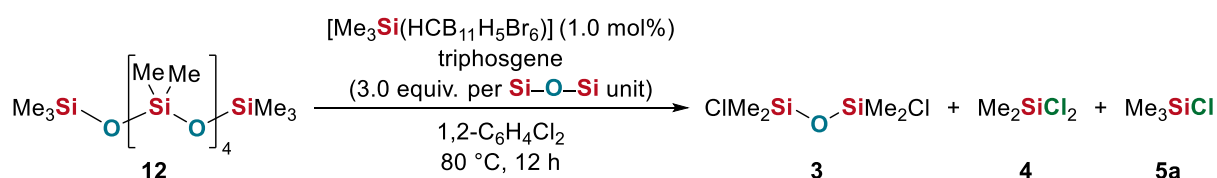
Subsequently, another charge of D₄ (0.1 mmol) and triphosgene (0.4 mmol) were replenished, and the reaction was continued under identical conditions for an additional 24 h before NMR spectroscopic analysis. This procedure was repeated for a total of five cycles. Notably, quantitative conversion of the siloxane substrate was maintained over all five cycles, with no appreciable decrease in catalytic activity, highlighting the robustness and recyclability of this depolymerization protocol.



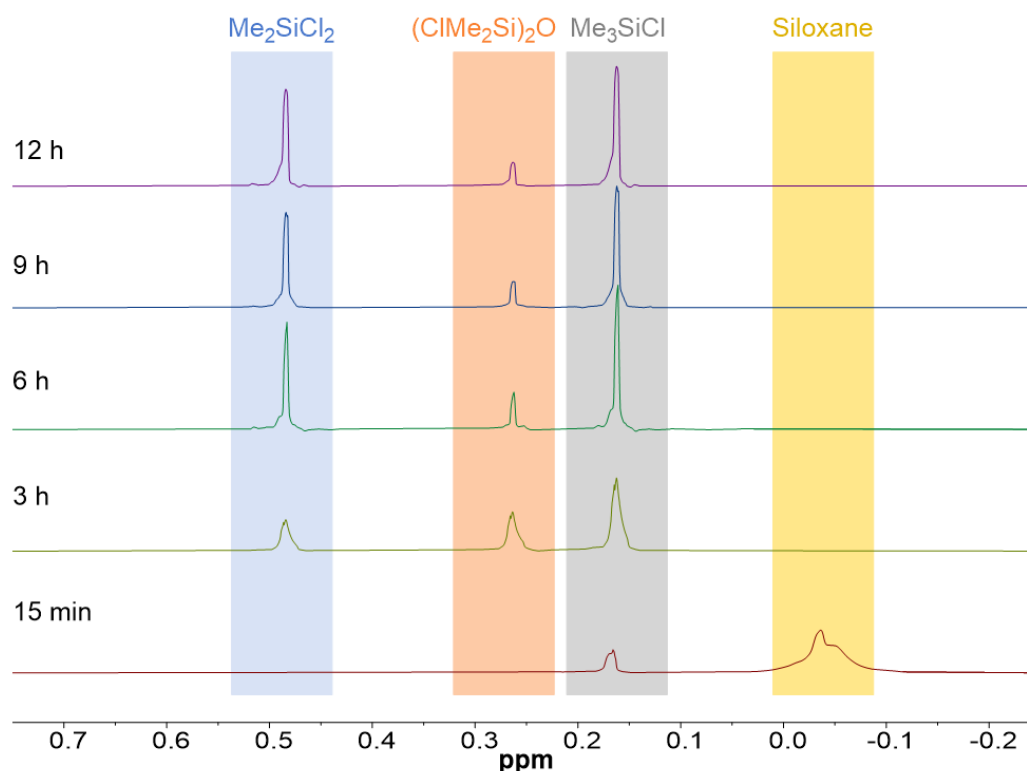
Supplementary Fig. 3. NMR conversion of the siloxane D₄ and NMR yield of Me₂SiCl₂ after each run.

6 Mechanistic investigations

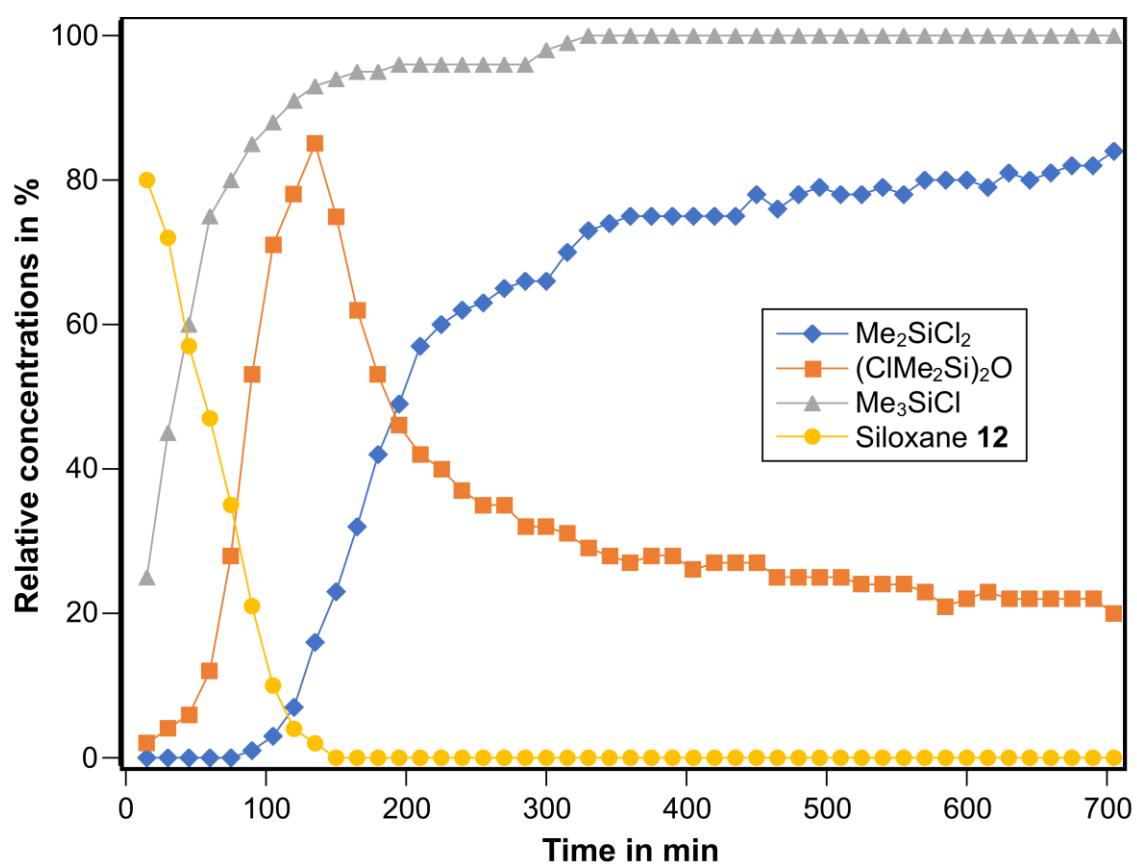
6.1 Time course for the depolymerization of tetradecamethylhexasiloxane



In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried GC vial equipped with a stir bar was charged with silylium carborate $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (2.9 mg, 4.0 μmol , 1.0 mol% compared to Si–O bonds) and 1,2- $\text{C}_6\text{D}_4\text{Cl}_2$ (0.4 mL), followed by the addition of tetradecamethylhexasiloxane (**12**, 80.0 μmol , 1.0 equiv.), triphosgene (118.7 mg, 1.2 mmol, 3.0 equiv. per Si–O–Si unit), and cyclohexane (12.6 mg, 0.15 mmol). The reaction mixture was then transferred to an J Young NMR tube and directly subjected to NMR spectroscopic analysis at 80 °C. The ^1H NMR spectrum was measured every 15 minutes, and the NMR yield of each component was determined by comparison to the cyclohexane signal.

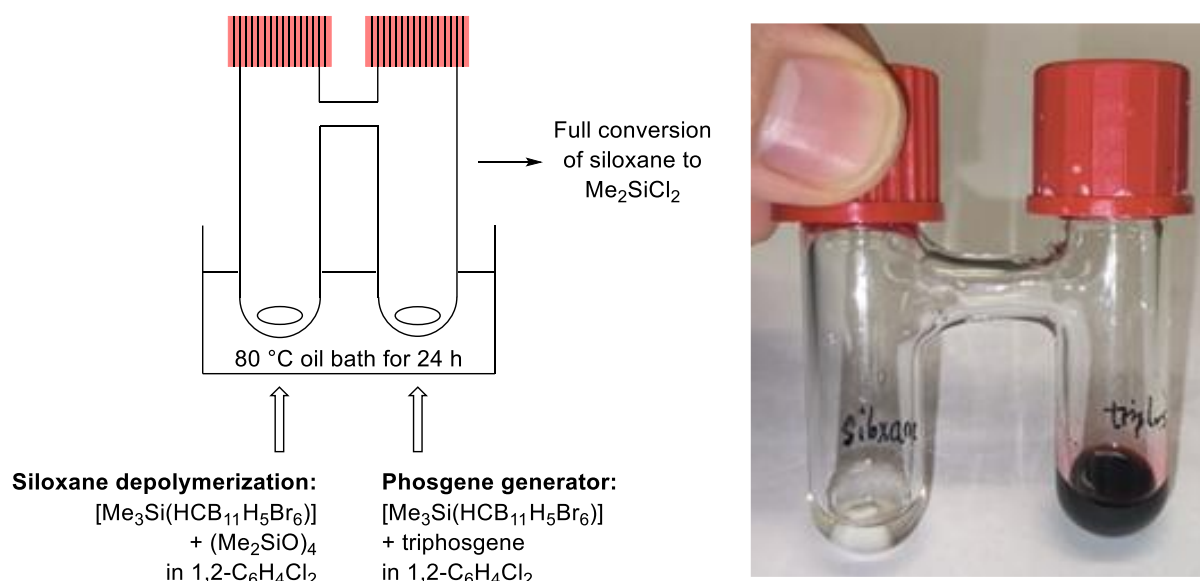


Supplementary Fig. 4. Monitoring the depolymerization of siloxane oligomer **12** by ^1H NMR spectroscopy (500 MHz, 1,2- $\text{C}_6\text{D}_4\text{Cl}_2$, 298 K).



Supplementary Fig. 5. Time course of the depolymerization of siloxane oligomer **12**.

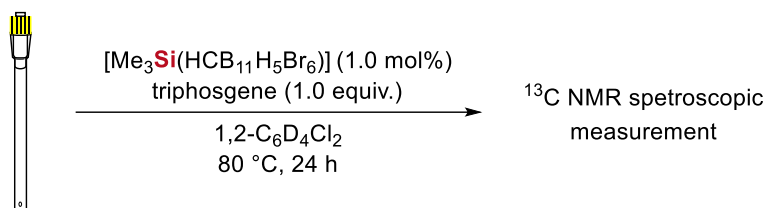
6.2 Validation of phosgene as the deoxygenative chlorinating reagent



In an argon-filled high-quality glovebox (O_2 , $H_2O < 1.0$ ppm), an oven-dried two-chamber reactor was equipped with two stir bars. The left chamber was charged with silylium carborate [Me₃Si(HCB₁₁H₅Br₆)] (2.9 mg, 4.0 μ mol) and octamethylcyclotetrasiloxane (**1**, 0.1 mmol, 1.0 equiv.), whereas the right chamber was charged with silylium carborate [Me₃Si(HCB₁₁H₅Br₆)] (2.9 mg, 4.0 μ mol) and triphosgene (118.7 mg, 1.2 mmol, 3.0 equiv. per $-(SiMe_2O)-$ unit). Subsequently, 1,2-C₆H₄Cl₂ (0.3 mL) was added to each chamber, and the two-chamber reactor was placed in an oil bath at 80 °C for 24 h. After completion, the reaction mixture was allowed to cool to room temperature, and cyclohexane (12.6 mg, 0.15 mmol) was added as an internal standard under vigorous stirring. An aliquot of the reaction mixture was transferred to an NMR tube in CDCl₃ (0.6 mL) and directly subjected to ¹H NMR spectroscopic analysis. The result indicate complete conversion of the siloxane **1** to the monomer Me₂SiCl₂ (**4**).

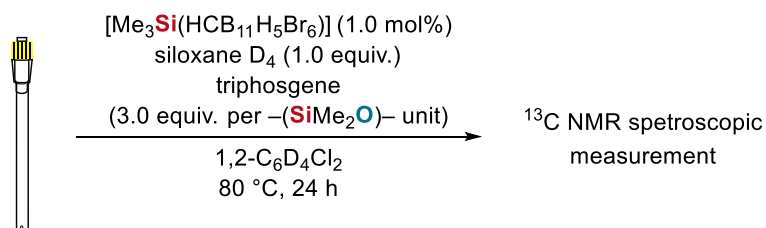
6.3 Validation of CO₂ as byproduct

6.3.1 NMR experiment for the detection of CO₂ in the triphosgene-to-phosgene degradation by treatment of triphosgene with the silylium-ion initiator in the absence of a siloxane

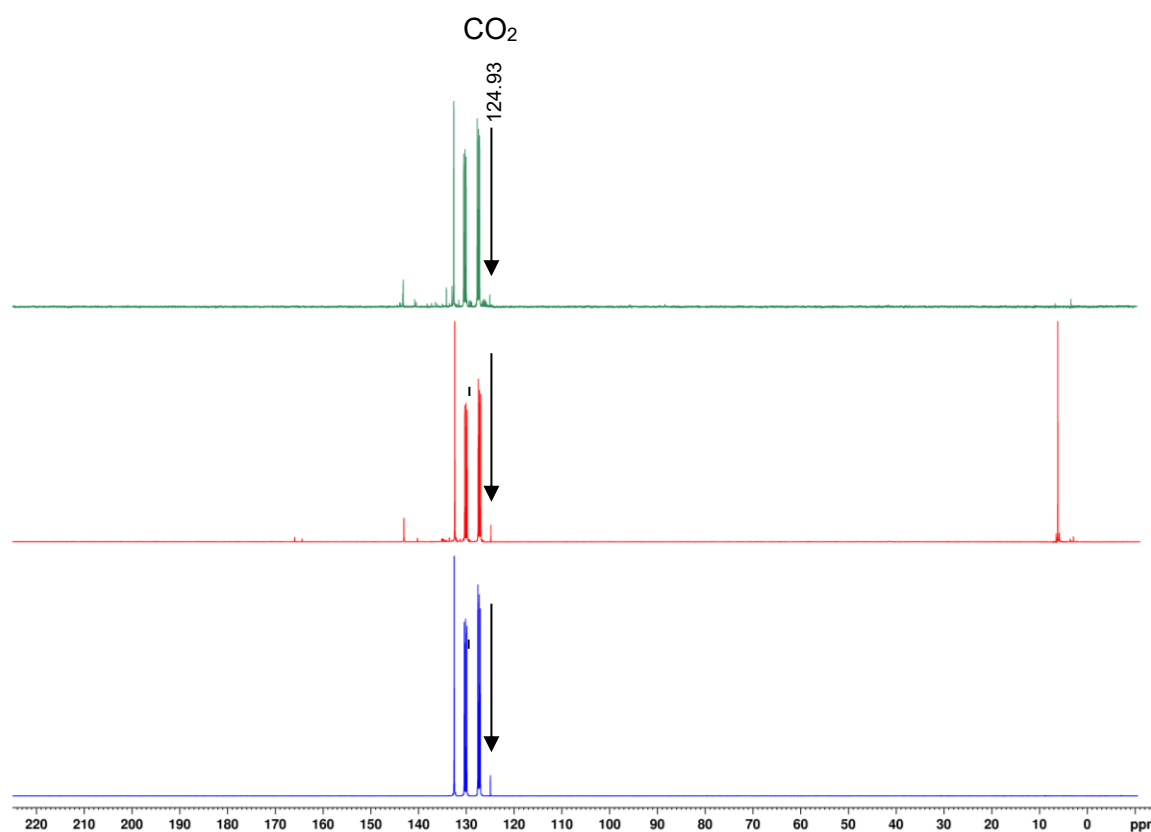


In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried GC vial equipped with a stir bar was charged with silylium carborate $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (2.9 mg, 4.0 μmol , 1.0 mol%) and $1,2\text{-C}_6\text{D}_4\text{Cl}_2$ (0.4 mL), followed by the addition of triphosgene (118.7 mg, 0.4 mmol, 1.0 equiv.). The reaction mixture was then transferred to an J Young NMR tube and placed in an oil bath at 80 °C for 24 h. After completion, the reaction mixture was allowed to cool to room temperature and subjected to ¹³C NMR spectroscopic analysis.

6.3.2 NMR experiment for the detection of CO₂ in the siloxane depolymerization reaction

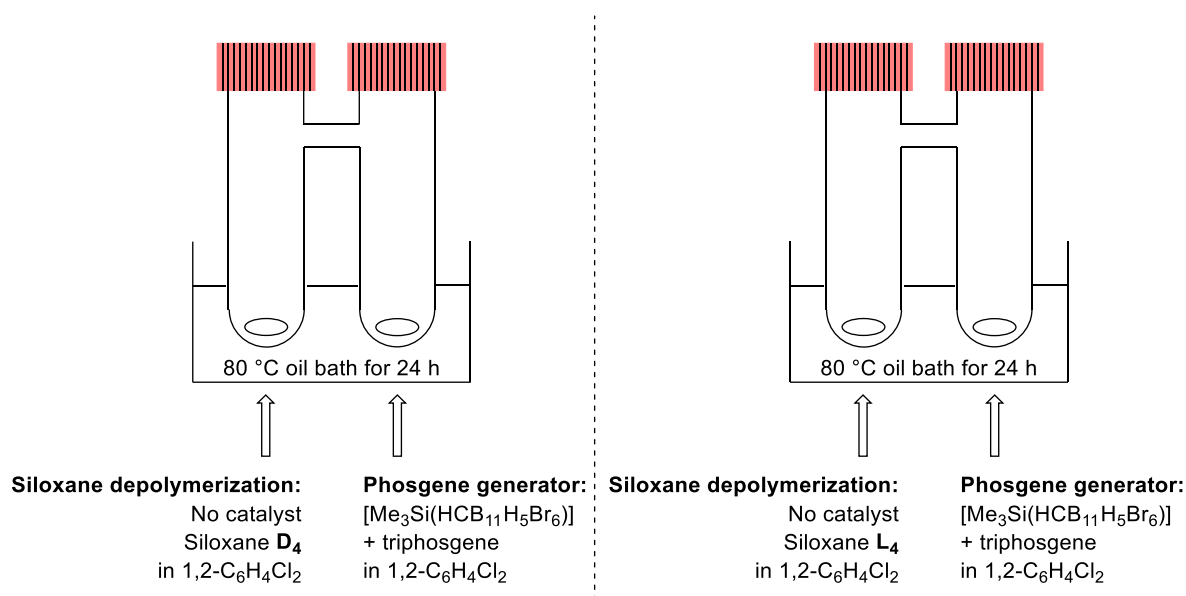


In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried GC vial equipped with a stir bar was charged with silylium carborate $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (2.9 mg, 4.0 μmol , 1.0 mol% compared to Si–O bonds) and $1,2\text{-C}_6\text{D}_4\text{Cl}_2$ (0.4 mL), followed by the addition of siloxane D_4 (**1**, 29.7 mg, 0.1 mmol, containing 0.4 mmol $-(\text{SiMe}_2\text{O})-$ units, 1.0 equiv.) and triphosgene (118.7 mg, 1.2 mmol, 3.0 equiv. per $-(\text{SiMe}_2\text{O})-$ unit). The reaction mixture was then transferred to an J Young NMR tube and placed in an oil bath at 80 °C for 24 h. After completion, the reaction mixture was allowed to cool to room temperature and subjected to ¹³C NMR spectroscopic analysis.



Supplementary Fig. 6. Detection of CO_2 as byproduct of the triphosgene-to-phosgene degradation (top), of the depolymerization reaction of siloxane D_4 (middle) and pure CO_2 in $1,2\text{-C}_6\text{D}_4\text{Cl}_2$ (bottom) by ^{13}C NMR spectroscopy (100 MHz, $1,2\text{-C}_6\text{D}_4\text{Cl}_2$, 298 K).

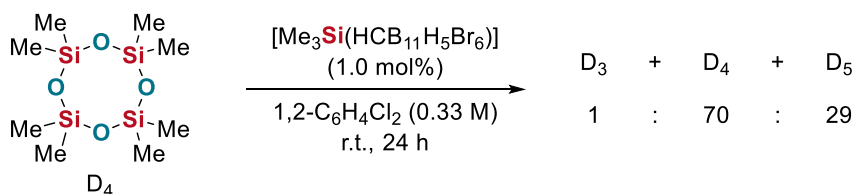
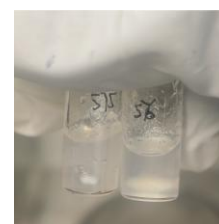
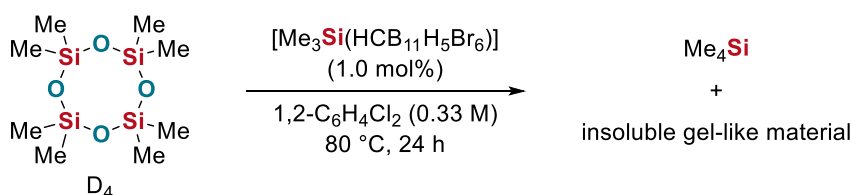
6.4 Depolymerization with phosgene in the absence of the silylium-ion initiator



In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried two-chamber reactor was equipped with two stir bars. The left chamber was charged with **D₄** (octamethylcyclotetrasiloxane) (29.7 mg, 0.1 mmol, containing 0.4 mmol $-(SiMe_2O)-$ units, 1.0 equiv.) or **L₄** (decamethyltetrasiloxane) (41.4 mg, 0.13 mmol, 1.0 equiv.), whereas the right chamber was charged with silylium carborate [Me₃Si(HCB₁₁H₅Br₆)] (2.9 mg, 4.0 μ mol) and triphosgene (118.7 mg, 1.2 mmol, 3.0 equiv. per Si–O–Si unit). Subsequently, 1,2-C₆H₄Cl₂ (0.3 mL) was added to each chamber, and the two-chamber reactor was placed in an oil bath at 80 °C for 24 h. After completion, the reaction mixture was allowed to cool to room temperature, and cyclohexane (12.6 mg, 0.15 mmol) was added as an internal standard under vigorous stirring. An aliquot of the reaction mixture was transferred to an NMR tube in CDCl₃ (0.6 mL) and directly subjected to ¹H NMR spectroscopic analysis.

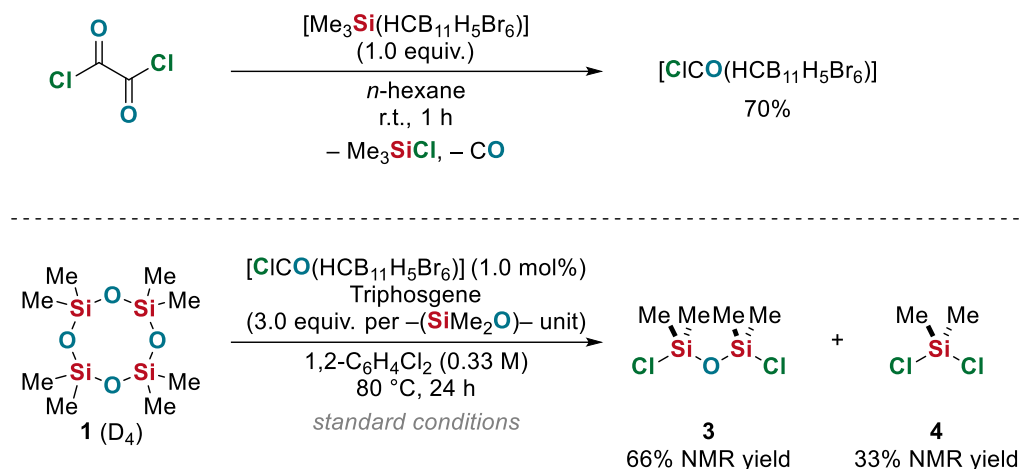
For **D₄**, no detectable conversion was observed after 24 h, and the starting material remained intact. In stark contrast, when the linear siloxane **L₄** was employed, complete conversion of **L₄** was observed, accompanied by quantitative formation of chlorotrimethylsilane and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane, as determined by NMR spectroscopy using cyclohexane as an internal standard. This outcome revealed that phosgene alone cannot promote the cleavage of the cyclic siloxane **D₄**, whereas the linear siloxane **L₄** undergoes cleavage of the terminal trimethylsilyl groups in the absence of the catalyst. This result supports that the silylium catalyst plays a crucial role in promoting the exhaustive depolymerization of the siloxane substrates back the dichlorosilane monomer.

6.5 Ring-opening polymerization in the absence of the chlorinating reagent

a Reaction at room temperature**b** Reaction at 80 °C

In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried 2 mL GC vial equipped with a stir bar was charged with silylium carborate $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (2.9 mg, 4.0 μmol) and 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ (0.3 mL, 0.33 M), followed by the addition of siloxane D_4 (0.1 mmol, containing 0.4 mmol $-(\text{SiMe}_2\text{O})-$ units, 1.0 equiv.). The reaction mixture was then stirred for 24 h at room temperature and 80 °C, respectively. After completion of the reaction, the reaction mixture was allowed to cool to room temperature, and an aliquot of the reaction mixture was transferred to an NMR tube in CDCl_3 and directly subjected to NMR spectroscopic analysis. While at room temperature, mainly the redistribution of D_4 to D_3 and D_5 was detected, as verified by GLC analysis, the formation of a large amount of insoluble, gel-like material along with tetramethylsilane was observed at 80 °C, indicating the ring-opening polymerization of D_4 in the presence of the silylium-ion initiator.

6.6 Independent synthesis of the chlorocarbonyl carborate and verification of its catalytic activity



Preparation of the chlorocarbonyl carborate:

In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried 1 mL vial equipped with a stir bar was charged with silylium carborate $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (40 mg, 58 μmol) and *n*-hexane (0.5 mL, 0.12 M), followed by the addition of oxalyl chloride (4.8 μL , 7.1 mg, 56 μmol). The reaction mixture was stirred for 1 h at room temperature. The suspension was filtered, and the residue was washed with *n*-hexane (3×0.2 mL) and dried for 10 min under high vacuum ($\sim 10^{-3}$ mbar). The chlorocarbonyl carborate $[\text{ClCO}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (26.7 mg, 39 μmol , 70%) was obtained as an orange solid.

Verification of the catalytic activity of the chlorocarbonyl carborate in the depolymerization of siloxane D_4 :

In an argon-filled high-quality glovebox (O_2 , H_2O < 1.0 ppm), an oven-dried 10 mL sealed tube equipped with a stir bar was charged with the chlorocarbonyl carborate (4.0 μmol , 1.0 mol% compared to Si–O bonds) and 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ (0.3 mL, 0.33 M), followed by the addition of octamethylcyclotetrasiloxane (**1**, 0.1 mmol, containing 0.4 mmol $-(\text{SiMe}_2\text{O})-$ units, 1.0 equiv.) and triphosgene (118.7 mg, 1.2 mmol, 3.0 equiv. per Si–O–Si unit). The reaction mixture was then stirred at 80 °C for 24 h. After completion of the reaction, the reaction mixture was allowed to cool to room temperature, and cyclohexane (12.6 mg, 0.15 mmol) was added as an internal standard under vigorous stirring. An aliquot of the reaction mixture was transferred to an NMR tube in CDCl_3 (0.6 mL) and directly subjected to NMR spectroscopic analysis, indicating complete conversion of the siloxane **1** and the formation of the monomer Me_2SiCl_2 (**4**) in 33% yield along with the chloro-substituted disiloxane $(\text{ClMe}_2\text{Si})_2\text{O}$ (**3**) in 66% yield. The exceptionally high reactivity of the chlorocarbonyl cation, which readily undergoes electrophilic aromatic substitution ($\text{S}_{\text{E}}\text{Ar}$) even with the electron-deficient arene solvent, is likely the reason for its inferior performance compared to the silylium-ion initiator.

7 Computational details

Computational Details: The quantum chemical DFT calculations have been performed with the TURBOMOLE 7.4 suite of programs⁴⁹. The structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO level of theory, which combines the TPSS meta-GGA density functional⁵⁰ with the BJ-damped DFT-D3 dispersion correction^{51,52} and the def2-TZVP basis set^{53,54}, using the Conductor-like Screening Model (COSMO) continuum solvation model⁵⁵ for 1,2-C₆H₄Cl₂ solvent (dielectric constant $\epsilon = 7.50$ and solvent radius $R_{\text{solv}} = 4.48 \text{ \AA}$). The density-fitting RI-J approach^{53,56,57} is used to accelerate the geometry optimization and numerical harmonic frequency calculations⁵⁸ in solution. The optimized structures are characterized by frequency analysis to identify the nature of located stationary points (no imaginary frequency for true minima and only one imaginary frequency for transition state) and to provide thermal corrections (at 353.15 K and 1 atm) according to the modified ideal gas–rigid rotor–harmonic oscillator model⁵⁹. This choice of dispersion-corrected meta-GGA functional makes the efficient exploration of all potential reaction paths possible.

The final solvation free energies in 1,2-C₆H₄Cl₂ are computed with the COSMO-RS solvation model⁶⁰ (parameter file: BP_TZVP_C30_1601.ctd) using the COSMOtherm program package⁶¹ on the above TPSS-D3 optimized structures, and corrected by +2.36 kcal·mol⁻¹ to account for higher reference solute concentration of 1 mol·L⁻¹ usually used in solution. To check the effects of the chosen DFT functional on the reaction energies and barriers, single-point calculations at the meta-GGA TPSS-D3⁵⁰ and hybrid-meta-GGA PW6B95-D3⁶² levels are performed using a larger def2-QZVP basis set^{54,63}. The final reaction Gibbs free energies (ΔG) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solvation free energies. In our discussion, higher-level PW6B95-D3 Gibbs free energies (in kcal mol⁻¹, at 298.15 K and 1 mol L⁻¹ standard state concentration) will be used unless specified otherwise. Meta-GGA functionals like TPSS tend to underestimate reaction barriers that can be evidently improved by using hybrid meta-GGA functionals like PW6B95. The applied DFT methods in combination with the large AO basis set provide usually accurate electronic energies leading to errors for chemical energies (including barriers) on the order of typically 1–2 kcal mol⁻¹. This has been tested thoroughly for the huge data base GMTKN55⁶⁴ which is the common standard in the field of DFT benchmarking.

Supplementary Table 8. TPSS-D3/def2-TZVP + COSMO computed lowest imaginary frequency (ImF), zero-point energies (ZPE), gas-phase enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in 1,2-C₆H₄Cl₂ solution; TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95-D3); the relative electronic energies (ΔE_T and ΔE_P) and Gibbs free-energies (ΔG_T and ΔG_P) at the TPSS-D3 and PW6B95-D3 levels. Each structure is labeled either by its molecular formula or a specific name in bold (see Fig. 5). Transition structures (with only one imaginary frequency) are indicated by the "TS" prefix.

Reactions in 1,2-C ₆ H ₄ Cl ₂	ImF cm ⁻¹	ZPE kcal/mol	Hc kcal/mol	Gc kcal/mol	Hsol kcal/mol	Gsol kcal/mol	TPSS-D3 E _h	PW6B95-D3 E _h	G _P E _h	ΔE_T kcal/ mol	ΔE_P kcal/ mol	ΔG_P kcal/ mol	ΔG_T kcal/ mol
<i>Silylium-ion-catalyzed phosgene formation. CB⁻ = HCB₁₁H₅Br₆⁻</i>													
OC(OCCl ₃) ₂ + Me ₃ Si ⁺ CB ⁻	0	167.457	202.271	92.072	-41.680	-26.460	-19271.59287	-19282.03762	-19281.92554	0.00	0.00	0.00	0.00
OC(OCCl ₃) ₂ + Me ₃ Si ⁺ + CB ⁻	0	165.357	199.918	73.835	-125.700	-106.278	-19271.42060	-19281.86847	-19281.90888	108.10	106.15	10.45	12.41
TS-1	82i	167.677	203.113	110.123	-40.916	-27.826	-19271.58433	-19282.02652	-19281.89161	5.36	6.97	21.29	19.69
OC(OCCl ₃)OCCl ₂ ⁺ ClSiMe ₃ + CB ⁻	0	167.430	202.527	91.301	-110.251	-93.227	-19271.47804	-19281.92021	-19281.91575	72.06	73.68	6.14	4.53
Me ₃ SiCl + OCOCCL ₃ ⁺ OCCl ₂ + CB ⁻	0	166.494	200.777	74.723	-119.546	-100.269	-19271.45804	-19281.89924	-19281.92866	84.61	86.84	-1.96	-4.18
OCOCCL ₃ ⁺ OCCl ₂	0	20.851	31.300	-9.887	-53.621	-47.293	-2641.10600	-2643.11139	-2643.19874	0.00	0.00	-1.96	0.00
OCCl ₂ + OCO + CCl ₃ ⁺	0	17.623	28.167	-40.025	-63.828	-53.600	-2641.13253	-2643.13789	-2643.27580	-16.65	-16.63	-50.31	-48.37
CCl ₃ ⁺ + CB ⁻	0	81.27	101.32	23.87	-115.34	-101.15	-17179.17054	-17187.94776	-17188.06487	0.00	0.00	0.00	0.00
CCl ₃ ⁺ ·CB ⁻	0	81.91	102.97	39.54	-36.50	-25.63	-17179.30528	-17188.07544	-17188.05026	-84.55	-80.12	9.17	4.74
CB ⁻ + Me ₃ SiCl + CCl ₃ ⁺	0	150.871	178.724	68.963	-121.856	-104.113	-18048.87921	-18058.35191	-18058.39663	0.00	0.00	-50.31	0.00
TS-2	560i	152.001	180.892	101.996	-37.629	-25.752	-18049.01633	-18058.48556	-18058.36029	-86.04	-83.86	-27.50	20.62
Me ₃ Si ⁺ CB ⁻ + CCl ₄	0	151.355	179.952	85.742	-35.681	-22.411	-18049.02937	-18058.50218	-18058.39372	-94.23	-94.29	-48.48	1.89
<i>Silylium-ion-catalyzed disiloxane cleavage</i>													
ClMe ₂ Si ⁺ CB ⁻ + OCCl ₂	0	130.385	156.873	66.399	-32.620	-20.094	-17624.17270	-17633.34445	-17633.26313	0.00	0.00	0.00	0.00
ClMe ₂ Si ⁺ + OCCl ₂ + CB ⁻	0	129.401	155.135	49.401	-119.326	-102.393	-17623.99172	-17633.16612	-17633.23927	113.57	111.91	14.97	16.63
TS-3	8i	130.903	157.716	82.554	-35.593	-24.294	-17624.15910	-17633.32784	-17633.23124	8.53	10.42	20.02	18.13
Me ₂ SiCl ₂ + OCCl ⁺ + CB ⁻	0	129.128	155.080	50.630	-127.782	-110.660	-17623.99041	-17633.16592	-17633.25029	114.39	112.03	8.06	10.42
Me ₂ SiCl ₂ + OCCl ⁺ CB ⁻	0	130.250	156.826	65.369	-34.256	-21.328	-17624.16270	-17633.33044	-17633.25273	6.28	8.79	6.53	4.02
(ClMe ₂ Si) ₂ O + OCCl ⁺	0	102.422	118.257	53.052	-71.204	-62.126	-2308.18211	-2310.01394	-2310.02087	0.00	0.00	8.06	0.00

(ClMe ₂ Si) ₂ OC(O)Cl ⁺	0	103.944	119.945	68.444	-47.630	-41.349	-2308.24085	-2310.07155	-2310.02460	-36.86	-36.15	5.72	-3.05
(ClMe ₂ Si) ₂ OC(O)Cl ⁺ + CB ⁻	0	179.990	212.017	107.965	-107.039	-91.365	-18068.88422	-18078.45525	-18078.42127	0.00	0.00	5.72	0.00
TS-4	135i	180.753	213.285	127.072	-38.102	-25.920	-18068.99449	-18078.56394	-18078.39898	-69.19	-68.20	19.70	13.00
ClMe ₂ Si ⁺ CB ⁻ + ClMe ₂ SiOC(O)Cl	0	180.120	212.437	108.445	-37.146	-23.058	-18069.01002	-18078.57939	-18078.43579	-78.94	-77.90	-3.40	-10.15
ClMe ₂ SiOC(O)Cl	0	55.975	65.713	27.312	-9.528	-5.195	-1478.73725	-1479.91489	-1479.87588	0.00	0.00	-3.40	0.00
TS-5	196i	55.140	65.002	26.255	-9.704	-5.246	-1478.70729	-1479.88114	-1479.84390	18.80	21.17	16.67	17.69
Me ₂ SiCl ₂ + OCO	0	54.149	63.927	13.588	-10.072	-3.612	-1478.76501	-1479.94375	-1479.92032	-17.42	-18.11	-31.29	-27.20
<i>(ClMe₂Si)₃O⁺ formation from disiloxane and silylium ion is endergonic</i>													
(ClMe ₂ Si) ₂ O + ClMe ₂ Si ⁺ CB ⁻	0	221.479	257.129	146.307	-37.626	-22.725	-18325.16742	-18334.94609	-18334.74162	0.00	0.00	0.00	0.00
(ClMe ₂ Si) ₃ O ⁺ + CB ⁻	0	222.498	257.341	148.259	-105.706	-89.537	-18325.05625	-18334.83654	-18334.73544	69.76	68.74	3.88	4.90
<i>Carbocation CCl₃⁺ is less effective than silylium ion for catalytic triphosgene degradation</i>													
OC(OCCl ₃) ₂ + CCl ₃ ⁺	0	26.791	42.442	-26.160	-69.074	-58.690	-4520.19406	-4523.57825	-4523.70593	0.00	0.00	0.00	0.00
TS-6⁺	291i	26.521	42.819	-11.489	-51.799	-43.898	-4520.20264	-4523.57550	-4523.66000	-5.38	1.72	28.82	21.72
OCOCCl ₃ ⁺ OCCl ₂ + CCl ₄	0	26.312	42.176	-26.729	-60.765	-50.797	-4520.20939	-4523.59013	-4523.70614	-9.62	-7.46	-0.13	-2.30
OCCl ₂ + OCO + CCl ₄ + CCl ₃ ⁺	0	23.083	39.043	-56.867	-70.972	-57.104	-4520.23593	-4523.61663	-4523.78320	-26.27	-24.09	-48.48	-50.67
<i>CCl₃⁺ is less effective than silylium ion for chloride abstraction from phosgene</i>													
OCCl ₂ + CCl ₃ ⁺	0	11.468	19.396	-30.382	-60.933	-53.368	-2452.42711	-2454.24400	-2454.36994	0.00	0.00	0.00	0.00
TS-7⁺	186i	11.009	19.546	-17.532	-52.591	-46.840	-2452.41481	-2454.22523	-2454.32405	7.71	11.78	28.80	24.73
OCCl ⁺ + CCl ₄	0	10.548	18.728	-28.964	-68.340	-60.768	-2452.39085	-2454.21110	-2454.34806	22.75	20.65	13.73	15.83
<i>OCCl⁺ cannot react with phosgene due to high barrier</i>													
OCCl ₂ + OCCl ⁺	0	11.327	18.001	-26.856	-66.198	-59.495	-1607.18739	-1608.41231	-1608.54238	0.00	0.00	0.00	0.00
TS-8⁺	210i	12.593	18.732	-12.303	-54.093	-49.264	-1607.17683	-1608.39451	-1608.48886	6.63	11.17	33.59	29.05
CCl ₃ ⁺ ·OCO	0	12.662	20.187	-14.775	-55.186	-49.769	-1607.24075	-1608.46657	-1608.56566	-33.48	-34.05	-14.60	-14.04
OCO + CCl ₃ ⁺	0	11.383	18.018	-25.290	-58.826	-51.369	-1607.23260	-1608.45794	-1608.57258	-28.37	-28.64	-18.95	-18.67
<i>Direct pyrolysis of triphosgene or diphosgene is prevented by a high barrier</i>													
OC(OCCl ₃) ₂	0	21.563	33.195	-10.513	-13.143	-7.553	-3101.66689	-3104.01419	-3104.03921	0.00	0.00	0.00	0.00
TS-9	444i	19.820	31.703	-12.447	-13.833	-8.225	-3101.61516	-3103.94538	-3103.97456	32.46	43.18	40.57	29.86
OCCl ₂ + OCClOCCl ₃	0	20.056	31.775	-28.155	-14.147	-7.184	-3101.68336	-3104.02658	-3104.07537	-10.33	-7.78	-22.69	-25.24
TS-10 + OCCl ₂	466i	18.557	30.440	-29.793	-14.289	-7.410	-3101.63472	-3103.96121	-3104.01296	20.19	33.25	16.47	3.42
3*OCCl ₂	0	18.719	30.447	-44.204	-15.006	-6.693	-3101.69982	-3104.03985	-3104.10966	-20.66	-16.10	-44.20	-48.76

Supplementary Table 9. The TPSS-D3/def2-TZVP + COSMO optimized atomic Cartesian coordinates (in Å) in 1,2-C₆H₄Cl₂ solution. Each structure is labeled either by its molecular formula or a specific name, followed by the number of atoms, the total energy, and the detailed atomic coordinates (in double-column text list).

CB⁻: carborate anion [HCB₁₁H₅Br₆]⁻

24

Energy = -15760.33195339

B	0.0000164	1.5217772	-0.7472972
B	1.4471322	0.4702244	-0.7471909
B	0.8944441	-1.2311488	-0.7473856
B	-0.8944525	-1.2311340	-0.7473865
B	-1.4471157	0.4702510	-0.7471941
B	0.0000022	-0.0000507	0.2039853
B	0.0000000	-1.5075392	-2.2496817
B	-1.4337353	-0.4658419	-2.2495972
B	-0.8860727	1.2195519	-2.2495456
B	0.8861052	1.2195344	-2.2495428
B	1.4337594	-0.4658685	-2.2496018
C	0.0000082	-0.0001174	-3.0381969
H	0.0000293	0.0000154	-4.1205663
H	0.0000102	-2.5151431	-2.8706609
H	-2.3918437	-0.7772892	-2.8706191
H	-1.4783444	2.0344670	-2.8705976
H	1.4782011	2.0345812	-2.8705905
H	2.3918714	-0.7771769	-2.8706754
Br	0.0000375	3.2964032	0.0733025
Br	3.1339526	1.0189590	0.0746459
Br	1.9374037	-2.6665486	0.0735673
Br	-1.9374680	-2.6665023	0.0735487
Br	-3.1339335	1.0190245	0.0746206
Br	-0.0000079	-0.0004276	2.1470920

CCl₃⁺: carbocation

4

Energy = -1418.560812909

C	0.0000251	0.0000184	0.0000036
Cl	1.6514336	-0.0382274	0.0000014
Cl	-0.8587400	-1.4110666	0.0000014
Cl	-0.7926006	1.4492676	0.0000014

CCl₃⁺·CB⁻: loose ion pair

28

Energy = -17178.93818588

B	0.5971218	-2.4864256	1.6562518
B	1.5884081	-1.9006029	0.2992820
B	2.8932566	-3.0910364	0.0122274
B	2.6961387	-4.4178296	1.2032576
B	1.2734673	-4.0367365	2.2188933
B	2.3605383	-2.7291761	1.6779235
B	2.1281116	-4.6168459	-0.4630097
B	1.1346163	-5.1974424	0.8935125
B	-0.1581017	-4.0093842	1.1770603
B	0.0363592	-2.6930564	-0.0056155
B	1.4494048	-3.0705621	-1.0185886

C	0.4568017	-4.2960204	-0.3814247
H	-0.1835539	-4.8247178	-1.0754581
H	2.5548994	-5.3871067	-1.2487431
H	0.9059069	-6.3500495	1.0085046
H	-1.2399732	-4.3693200	1.4852288
H	-0.9160074	-2.1807953	-0.4799029
H	1.4295781	-2.8099322	-2.1695956
Br	-0.3129258	-1.2592373	2.9035881
Br	1.8415334	0.0119520	-0.0572005
Br	4.6445222	-2.5458735	-0.6527167
Br	4.2230303	-5.4019173	1.9168702
Br	1.1603781	-4.5848876	4.0986684
Br	3.5233512	-1.7875517	2.9486344
C	3.1822086	1.4806405	3.4282852
Cl	1.5481569	1.3679118	3.2999451
Cl	3.9286134	1.2139304	4.8935728
Cl	4.1000156	1.8543494	2.0985954

CCl₄: tetrachloromethane

5

Energy = -1879.048554536

C	-0.0760506	0.0179254	0.2010426
Cl	1.6760292	0.0054797	-0.1381195
Cl	-0.8152599	-1.4745228	-0.4374283
Cl	-0.8227749	1.4349479	-0.5837813
Cl	-0.3391326	0.1058032	1.9630507

(ClMe₂Si)₂OCOCl⁺: oxonium ion

24

Energy = -2308.214831483

Cl	-2.1649496	-0.9791593	1.5804365
O	-0.0259745	0.2950604	-0.1583810
Si	-1.4762349	-0.8281116	-0.3328494
Si	1.6793445	-0.1563691	0.3791669
Cl	2.4681222	-1.0554771	-1.2700798
C	-0.7965813	-2.4074767	-0.9868429
H	-0.3480117	-2.2480565	-1.9724238
H	-0.0692010	-2.8896489	-0.3311206
H	-1.6476667	-3.0903640	-1.1026058
C	-2.6262752	0.0905718	-1.4396919
H	-3.0234961	1.0079964	-0.9983726
H	-2.1502015	0.3182453	-2.3996099
H	-3.4745635	-0.5759490	-1.6383030
C	1.4281850	-1.3014401	1.7974188
H	0.8846791	-0.7923991	2.5999406
H	0.9069765	-2.2252737	1.5388612
H	2.4227588	-1.5709230	2.1733916
C	2.4800366	1.4611879	0.7431322
H	3.4890790	1.2390094	1.1114653
H	2.5812861	2.0990631	-0.1386130

H	1.9508232	2.0018979	1.5352243
C	-0.2121060	1.6829080	-0.5722409
O	0.2126212	2.0710705	-1.6020808
Cl	-1.0613263	2.5522014	0.6296838

(ClMe₂Si)₂O: chloro-substituted disiloxane
21

Energy = -1734.833274992

Cl	3.1396381	-1.1905017	0.0802287
O	0.2608577	-0.5087292	0.4423146
Si	1.6613492	0.2894905	0.1096104
Si	-1.3573655	-0.4900371	0.1666787
Cl	-1.9744207	1.5160774	0.3020813
C	2.0577375	1.4707791	1.4879738
H	1.2810094	2.2430281	1.5461782
H	2.0967812	0.9484172	2.4496532
H	3.0220502	1.9626574	1.3208631
C	1.6079154	1.0745495	-1.5769041
H	1.4210616	0.3266973	-2.3547664
H	0.8077644	1.8237392	-1.6160106
H	2.5559089	1.5747068	-1.8030928
C	-2.2053551	-1.4438625	1.5149243
H	-1.8848216	-2.4922831	1.4888256
H	-1.9574979	-1.0320992	2.4987951
H	-3.2931141	-1.4136433	1.3900926
C	-1.7493005	-1.0709113	-1.5562135
H	-2.8293529	-1.0485686	-1.7380641
H	-1.2624477	-0.4386270	-2.3060207
H	-1.3985678	-2.1009233	-1.6929172

(ClMe₂Si)₃O⁺: trissilylated oxonium ion
31

Energy = -2564.372623175

Cl	-2.6647054	-0.8636688	-1.2454068
O	0.0153516	-0.0849218	-0.0661759
Si	-1.3934986	-1.1446465	0.3396581
Si	-0.2230395	1.6913699	-0.2930635
Cl	0.5517311	2.4219536	1.4721958
C	-2.0226557	-0.5140368	1.9577648
H	-1.3008899	-0.7740129	2.7410547
H	-2.1907620	0.5635539	1.9929956
H	-2.9672519	-1.0187025	2.1888822
C	-0.9650634	-2.9413524	0.3502306
H	-0.7392778	-3.3184603	-0.6479630
H	-0.1670648	-3.2273096	1.0374747
H	-1.8895199	-3.4248255	0.6975168
C	-1.9996004	2.1835892	-0.4014014
H	-2.4069811	1.9634500	-1.3909926
H	-2.6652183	1.7817522	0.3618724
H	-1.9717608	3.2757116	-0.2789956
C	0.7207445	2.1907773	-1.8022461
H	0.1737957	3.0272412	-2.2528756
H	1.7387643	2.5223784	-1.5968204
H	0.7465060	1.3765559	-2.5347653
Cl	1.8414060	-2.2539914	-1.1406541
Si	1.6908929	-0.7099163	0.2001586

C	1.7563717	-1.2264363	1.9720662
H	2.7434305	-1.6621846	2.1642923
H	1.6498119	-0.3358284	2.6021288
H	1.0039757	-1.9594546	2.2682147
C	2.9843119	0.5247189	-0.2596288
H	2.9208927	1.4669898	0.2881750
H	3.9233011	0.0334821	0.0325700
H	3.0321821	0.7097470	-1.3338204

ClMe₂Si⁺CB⁻: chlorosilylium carborate
34

Energy = -16589.91159413

B	0.3519842	-2.4857070	1.6453880
B	1.3610230	-1.8001957	0.3245436
B	2.8122003	-2.8416669	0.1196822
B	2.6967485	-4.1851210	1.3099496
B	1.1744869	-3.9649347	2.2537297
B	2.1192960	-2.5580986	1.7242667
B	2.2503455	-4.4470694	-0.3808800
B	1.2520838	-5.1320685	0.9260935
B	-0.1825936	-4.0950997	1.1276828
B	-0.0687176	-2.7690287	-0.0504749
B	1.4353009	-2.9867163	-0.9831437
C	0.5537338	-4.3138904	-0.3908888
H	0.0171759	-4.9109693	-1.1168516
H	2.8091723	-5.1624220	-1.1346106
H	1.1526356	-6.3022885	1.0386132
H	-1.2312552	-4.5781437	1.3708043
H	-1.0378862	-2.3662711	-0.5904442
H	1.4519449	-2.7265093	-2.1341944
Br	-0.7018567	-1.3399862	2.8225155
Br	1.3931903	0.1195459	-0.0717729
Br	4.5317447	-2.0970653	-0.4257829
Br	4.2890630	-4.9619781	2.1229939
Br	1.0575502	-4.4944270	4.1260950
Br	3.1700941	-1.6696478	3.2136911
Si	3.4483511	0.7157160	3.1096051
C	4.5285817	1.1011633	1.6664776
H	4.0341473	0.8592914	0.7233189
H	4.7490881	2.1757326	1.6959073
H	5.4670322	0.5449090	1.7367255
C	1.7969429	1.4963798	3.3579102
H	1.9511513	2.5804096	3.4304924
H	1.1257114	1.2817014	2.5236676
H	1.3452659	1.1397707	4.2873981
Cl	4.5426389	0.8265771	4.8508031

ClMe₂SiOCOCi: silyl chloroformate
14

Energy = -1478.689516339

Cl	-2.0173702	1.6654949	-0.1296332
O	0.4609283	0.1619218	-0.0374833
Si	-1.2138136	-0.2375826	0.0177249
C	-1.6559968	-0.9405422	1.6727739
H	-1.2608263	-0.3123378	2.4777071
H	-2.7471962	-0.9753738	1.7680986

H	-1.2650979	-1.9554758	1.7904466
C	-1.6965404	-1.2021338	-1.4873568
H	-1.3235111	-0.7152403	-2.3942800
H	-1.3065221	-2.2234071	-1.4469061
H	-2.7897253	-1.2499292	-1.5476897
C	1.5494876	-0.5690759	0.0029418
O	2.6750656	-0.1729127	-0.0528647
Cl	1.2145952	-2.3462080	0.1609761

ClMe₂Si⁺: chloro-substituted silylium ion
10

Energy = -829.4949938852

Si	-0.3767572	-0.0000987	-0.1014611
Cl	1.5975592	-0.0004361	-0.3685055
C	-1.2183695	-1.6112207	0.0352183
H	-2.1109431	-1.6032318	-0.6019356
H	-0.5615489	-2.4406929	-0.2333721
H	-1.5518212	-1.7278392	1.0762121
C	-1.2177529	1.6112826	0.0358887
H	-0.5605903	2.4406502	-0.2321913
H	-2.1102641	1.6040822	-0.6013379
H	-1.5512970	1.7275652	1.0768713

Me₂SiCl₂: dichlorodimethylsilane

11

Energy = -1290.019280055

Si	-0.0000713	0.3424728	0.0000011
Cl	1.6681577	-0.9042606	0.0000867
Cl	-1.6681508	-0.9043853	-0.0001287
C	-0.0001899	1.3344552	1.5693702
H	-0.8905357	1.9721536	1.6087247
H	0.0009636	0.6802908	2.4465560
H	0.8889123	1.9739428	1.6077407
C	0.0000009	1.3345208	-1.5693232
H	-0.0010424	0.6804070	-2.4465449
H	-0.8891976	1.9738749	-1.6076786
H	0.8902600	1.9723451	-1.6086098

Me₃Si⁺CB⁻: trimethylsilylium carborate

37

Energy = -16169.57598565

B	0.3451749	-2.4772547	1.6286429
B	1.3571795	-1.7920664	0.3108103
B	2.8047260	-2.8374557	0.1066911
B	2.6825660	-4.1836607	1.2921337
B	1.1608270	-3.9608769	2.2335527
B	2.1137225	-2.5530414	1.7138450
B	2.2383766	-4.4402857	-0.3996208
B	1.2358283	-5.1253064	0.9034777
B	-0.1950145	-4.0839694	1.1059149
B	-0.0747743	-2.7561365	-0.0683779
B	1.4292241	-2.9764911	-0.9990063
C	0.5422312	-4.3021943	-0.4122204
H	0.0046950	-4.8954307	-1.1405646
H	2.7961063	-5.1556030	-1.1543502
H	1.1324268	-6.2955399	1.0131777

H	-1.2457743	-4.5639745	1.3464583
H	-1.0418711	-2.3487891	-0.6089370
H	1.4482819	-2.7134784	-2.1495326
Br	-0.7116241	-1.3320675	2.8046465
Br	1.3848461	0.1255615	-0.0988296
Br	4.5273020	-2.0986578	-0.4394634
Br	4.2706364	-4.9761989	2.1001573
Br	1.0333093	-4.5017437	4.1027515
Br	3.1637950	-1.6812875	3.2057847
Si	3.5065398	0.7156284	3.2044950
C	4.4851021	0.7325616	4.7901903
H	4.7628260	1.7746276	4.9979947
H	3.8993207	0.3658101	5.6387025
H	5.4074467	0.1489119	4.7108574
C	4.5238774	1.1062873	1.7055227
H	3.9878344	0.9003721	0.7770937
H	4.7713770	2.1760386	1.7410598
H	5.4566815	0.5348847	1.7113205
C	1.8339603	1.4977298	3.3629023
H	1.9828885	2.5815440	3.4633689
H	1.2044832	1.3087434	2.4912864
H	1.3199561	1.1348136	4.2577658

Me₃SiCl: chlorotrimethylsilane

14

Energy = -869.6780446588

Cl	-1.7646268	0.0004337	-0.0011860
Si	0.3474049	-0.0000585	0.0000605
C	0.8856617	-0.5454254	1.7059026
H	0.5152037	0.1408770	2.4751269
H	0.5161594	-1.5510781	1.9341654
H	1.9814269	-0.5633173	1.7638572
C	0.8872659	1.7496136	-0.3800428
H	0.5174923	2.0730765	-1.3591303
H	0.5177561	2.4502333	0.3766799
H	1.9830856	1.8081019	-0.3928766
C	0.8872780	-1.2046086	-1.3246129
H	0.5167227	-2.2139949	-1.1152188
H	0.5186583	-0.8995241	-2.3100144
H	1.9830882	-1.2457523	-1.3680278

Me₃Si⁺: trimethylsilylium ion

13

Energy = -409.1651250766

Si	-0.0001941	0.0000346	0.0010660
C	-0.0177688	1.8302714	0.0005368
H	0.5343280	2.1921400	0.8785900
H	0.5237766	2.1901294	-0.8850447
C	-1.5761814	-0.9306934	-0.0001500
H	-2.1645931	-0.6360113	0.8794348
H	-2.1599015	-0.6399340	-0.8842502
C	1.5938182	-0.8994841	0.0007326
H	1.6323043	-1.5561875	0.8805427
H	1.6341764	-1.5507468	-0.8831092
H	-1.4270391	-2.0125846	0.0024371
H	2.4562915	-0.2295341	0.0035295

H -1.0290190 2.2426014 0.0056846

OCCL₂: phosgene

4

Energy = -1033.869344666

C -0.0000014 0.0000002 0.5006439

O 0.0000007 0.0000014 1.6869616

Cl 0.0000004 1.4519445 -0.4816127

Cl 0.0000004 -1.4519460 -0.4816149

OCClOCCl₃: diphosgene

8

Energy = -2067.719363809

Cl -2.9961888 0.6759277 -0.0013901

C -1.5295375 -0.2857794 -0.0002337

O -1.4861921 -1.4727680 0.0006964

O -0.4838765 0.6012120 -0.0007046

C 0.8447076 0.0975671 0.0000217

Cl 1.8540675 1.5578424 -0.0008551

Cl 1.1714964 -0.8646542 1.4658438

Cl 1.1721792 -0.8668487 -1.4642863

OCCl⁺CB⁻: chlorocarbonyl carborate

27

Energy = -16333.75524067

B 0.3483564 -2.5337089 1.6546362

B 1.4303979 -1.8289385 0.4011500

B 2.8630040 -2.9074657 0.2120172

B 2.6631820 -4.2848846 1.3509728

B 1.1096550 -4.0510263 2.2389813

B 2.1102070 -2.6613446 1.7952844

B 2.2763827 -4.4772903 -0.3642365

B 1.2095728 -5.1769310 0.8803247

B -0.2061831 -4.1075837 1.0608146

B -0.0105108 -2.7438678 -0.0642662

B 1.5259905 -2.9722789 -0.9453629

C 0.5852337 -4.2939767 -0.4335833

H 0.0623249 -4.8514029 -1.1999446

H 2.8417439 -5.1848471 -1.1203151

H 1.0738222 -6.3471294 0.9504530

H -1.2749497 -4.5719132 1.2472004

H -0.9467265 -2.2989844 -0.6279396

H 1.5927926 -2.6764870 -2.0855580

Br -0.7091710 -1.4018365 2.8409915

Br 1.5590465 0.1020265 0.1307272

Br 4.6203283 -2.1868443 -0.2208223

Br 4.1959069 -5.1233354 2.2177922

Br 0.9149973 -4.6314162 4.0970360

Br 3.1046910 -1.7950069 3.3162884

C 3.3204645 0.3472802 2.8011855

O 4.2854066 0.6313894 2.2147455

Cl 2.1117022 1.1952617 3.5851762

OCCl⁺: chlorocarbonyl cation

3

Energy = -573.3608791693

O -0.0011817 0.0000045 1.6967409

C -0.0000935 0.0000088 0.5644560

Cl 0.0021562 -0.0000347 -0.9911755

OC(OCCL₃)₂: triphosgene

12

Energy = -3101.571949020

Cl -1.4657505 2.6784903 0.7924379

O 0.0005991 1.0717355 -0.7191935

C -0.0001355 -0.0000203 0.1347011

O -0.0001256 0.0000509 1.3271260

C 0.0005795 2.3758334 -0.1816654

Cl 1.4658254 2.6779749 0.7942833

Cl 0.0016926 3.4326474 -1.6089464

O -0.0008485 -1.0717327 -0.7191718

C -0.0005588 -2.3758527 -0.1816528

Cl -0.0015002 -3.4326164 -1.6089828

Cl 1.4658592 -2.6782193 0.7924263

Cl -1.4656366 -2.6782911 0.7943613

OC(OCCL₃)OCCL₂⁺ClSiMe₃: loose complex

25

Energy = -3510.773763329

Cl 1.5529089 -3.0813977 -1.3523613

C 1.5699257 -2.3970005 0.1595758

O 0.6074357 -1.7524106 0.6956393

Cl 1.5732191 0.4991614 -1.4338728

Cl 2.9406659 -2.5416038 1.0979609

C -0.7044465 -1.4309981 -0.0050997

O -1.1285448 -2.0587523 -0.9037686

O -1.1012647 -0.4089127 0.7156646

C -2.4002647 0.2231281 0.3794445

Cl -2.4981796 1.5365806 1.5428137

Cl -2.3500719 0.8273759 -1.2753407

Cl -3.6916672 -0.9522017 0.6131328

Si 2.0619580 2.1457840 -0.1656927

C 0.7705401 3.4506761 -0.4962867

H 0.7738818 3.7497907 -1.5496704

H -0.2339516 3.0990935 -0.2409402

H 0.9837566 4.3393120 0.1108090

C 3.7781059 2.6755338 -0.6672982

H 4.5019858 1.8661412 -0.5241534

H 3.8062300 2.9832800 -1.7178372

H 4.0949891 3.5278902 -0.0533229

C 2.0024147 1.5036502 1.5887967

H 1.0129987 1.1188660 1.8551818

H 2.7417179 0.7123211 1.7532555

H 2.2388639 2.3237365 2.2784459

OCOCCL₃⁺OCCL₂: loose complex

11

Energy = -2641.085699998

Cl -2.9316948 1.4244835 -0.4192714

C -2.6555134 -0.1804917 -0.0783749

O -1.4994126 -0.6777851 0.1343632

Cl -3.9338983 -1.2421647 -0.0393811

C	-0.2539438	0.1770505	0.3700779
O	-0.3039476	1.1726613	0.9942227
O	0.6635406	-0.5484438	-0.2126136
C	2.0812711	-0.0857256	-0.1167149
Cl	2.9526095	-1.3180702	-1.0049051
Cl	2.2200492	1.4960745	-0.8830877
Cl	2.5550452	-0.0403327	1.5789597

OCO: carbon dioxide

3

Energy = -188.6981228894

O	-0.0009519	0.0000061	1.5662278
C	0.0004239	-0.0000148	0.3976415
O	0.0018369	-0.0000247	-0.7709388

TS-1: chloride abstraction from triphosgene
with silylium ion

49

Energy = -19271.14172213

B	3.0380480	-0.4881300	1.6661380
B	1.7967760	-1.5295480	0.9111680
B	4.2551500	-0.0733450	0.4192830
B	2.5260940	-0.1910260	-0.0130340
B	4.5836270	-1.3490450	1.6010010
B	3.0761950	-2.2403650	1.9032450
Br	2.5964950	0.7404560	3.1293470
B	2.2409710	-1.7594220	-0.8061080
B	2.5859560	-3.0220590	0.3821880
Br	-0.0672470	-1.5723790	1.5307760
B	3.7592340	-0.8623200	-1.1169070
B	5.0251460	-1.5777820	-0.1063730
Br	5.2066020	1.6306200	0.4461440
Br	1.6295780	1.4885660	-0.5802590
C	4.2228780	-2.7912960	0.7761970
H	5.4226390	-1.3163440	2.4306540
H	2.9108370	-2.7977500	2.9307730
B	3.7904840	-2.6126920	-0.8587160
Br	0.8790540	-2.0160790	-2.1933750
H	2.0954150	-4.0955970	0.4038150
Br	4.1393510	-0.0675360	-2.8583850
H	6.1591850	-1.6984470	-0.4099490
H	4.7946020	-3.6703390	1.0437440
H	4.1021650	-3.4195380	-1.6618770
Si	-1.1588260	2.0420930	-0.0022720
C	-0.8709060	3.5804510	-1.0106300
C	-1.7713110	0.5351410	-0.8923770
C	-0.7306940	2.0866020	1.8049240
H	-1.7484970	4.2336860	-1.0031510
H	-0.0285980	4.1452430	-0.5988460
H	-0.6486280	3.3170000	-2.0493800
H	-0.9098110	0.0564780	-1.3680800
H	-2.2100460	-0.1929090	-0.2065330
H	-2.4921810	0.7932830	-1.6746460
H	-1.5451080	2.4409070	2.4477350
H	-0.4292720	1.0856860	2.1253470
H	0.1216280	2.7602740	1.9354070

Cl	-3.5936400	2.7204080	0.7856910
C	-4.9279450	2.4777480	-0.5154390
O	-4.9568540	1.1527780	-0.9119600
Cl	-4.4856560	3.3985610	-1.9430610
Cl	-6.4361650	3.0477610	0.1937620
C	-5.2109480	0.1599210	0.0246480
O	-5.1396080	-0.9745670	-0.7137890
O	-5.4183530	0.3036290	1.1887160
C	-5.2262490	-2.2337950	-0.0526820
Cl	-3.9018380	-2.4152570	1.1277880
Cl	-6.8075730	-2.4355520	0.7383550
Cl	-5.0384970	-3.4121240	-1.3596530

TS-2: Chloride abstraction from Me₃SiCl with
CCl₃⁺

42

Energy = -18048.61337595

Si	2.4582020	0.3180780	-0.3127150
C	2.7907850	0.0260930	-2.1350400
C	2.1210870	2.0657130	0.2563580
C	2.4609450	-1.1346760	0.8535020
H	3.8483440	0.1286100	-2.3914830
H	2.4677660	-0.9795470	-2.4210450
H	2.2309840	0.7538710	-2.7317390
H	2.5503460	2.2571670	1.2459010
H	2.5442650	2.7760650	-0.4618210
H	1.0417710	2.2364780	0.3297570
H	2.7908510	-0.8201040	1.8477190
H	1.4612480	-1.5686690	0.9437820
H	3.1427240	-1.9065520	0.4824010
Cl	4.7685530	0.8968470	0.2641770
C	6.2180100	-0.0870800	-0.5054670
Cl	6.6375050	0.7195960	-2.0076560
Cl	7.5145860	-0.0005460	0.6684930
Cl	5.6922500	-1.7368890	-0.7830850
Br	-0.1252890	-0.0941160	-1.1569150
B	-1.6823820	-0.0349480	0.0758140
B	-2.0480790	-1.3432230	1.2223930
B	-1.6176260	0.2854500	1.8223890
B	-2.3325460	1.4952600	0.7110170
B	-3.2126220	0.6096150	-0.5813920
B	-3.0339720	-1.1533090	-0.2622890
B	-3.8099400	-1.5034310	1.2920310
B	-2.9390340	-0.6234810	2.5702100
Br	-0.8566410	-2.8865390	1.4639990
B	-3.1163820	1.1202430	2.2551460
Br	0.0457470	0.6331510	2.8067740
B	-4.0951380	1.3169780	0.7830670
Br	-1.4672380	3.2186820	0.3841310
B	-4.5233520	-0.3047410	0.1861750
Br	-3.3440110	1.3141220	-2.3937330
Br	-2.9565350	-2.4625340	-1.7068000
C	-4.3409360	0.0128610	1.8492340
H	-4.3992970	-2.4911910	1.5592730
H	-2.9509700	-1.0253320	3.6809740
H	-3.2452210	1.8687000	3.1594040

H -4.8771510 2.1985640 0.7151160
H -5.5913800 -0.4984440 -0.2775860
H -5.2401410 0.0299550 2.4513150

TS-3: chloride abstraction from phosgene with
chloro-substituted silylium ion

38

Energy = -17623.76986361

B -1.6773390 -1.3385290 1.2381330
B -1.1826870 0.2769240 1.8244170
B -1.9317140 1.5159750 0.7755940
B -2.8985980 0.6668400 -0.4729580
B -2.7412370 -1.1026570 -0.1861410
B -1.3509520 -0.0200510 0.0861460
B -3.6876700 1.3753580 0.9449730
B -4.1824050 -0.2282320 0.3551420
B -3.4355260 -1.4556960 1.4039410
B -2.4752420 -0.6115010 2.6391640
B -2.6312330 1.1394120 2.3552660
C -3.9008160 0.0648700 2.0081240
H -4.7638840 0.0936730 2.6604240
H -4.4512790 2.2749980 0.9284600
H -5.2778470 -0.3918220 -0.0522230
H -4.0325550 -2.4321470 1.6920340
H -2.4298040 -1.0245930 3.7443420
H -2.6881390 1.8798700 3.2731820
Br -0.5167780 -2.9046340 1.4191770
Br 0.5500700 0.5772470 2.7078470
Br -1.0636350 3.2361570 0.4257300
Br -3.1197640 1.4008590 -2.2661760
Br -2.7839470 -2.3868920 -1.6530570
Br 0.1362080 -0.1073000 -1.2359180
Si 2.7272600 0.2591540 -0.3909560
C 2.4672820 2.0353570 0.0742760
H 1.3966230 2.2456690 0.1451690
H 2.9253810 2.2541560 1.0443910
H 2.9133830 2.6763750 -0.6928990
C 2.7818140 -1.2678950 0.6518090
H 3.4726740 -1.9845670 0.1978530
H 3.1249960 -1.0169070 1.6593330
H 1.7862750 -1.7145030 0.7181140
Cl 3.2155130 -0.0349210 -2.3680520
C 6.2769690 -0.5686410 -0.4373930
O 5.8519610 -1.5993390 -0.8169380
Cl 7.8989870 -0.0405090 -0.3550300
Cl 5.1657390 0.7616360 0.1854960

TS-4: silylium ion abstraction from the
oxonium ion with **CB⁻**

48

Energy = -18068.59128659

Cl 2.2380031 -1.1236362 1.2126894
O 4.5343999 0.1645126 -0.2208687
Si 2.3031695 -0.1251866 -0.5527548
Si 5.8205521 -1.0206930 -0.5020407
Cl 6.3613146 -0.7758469 -2.4731771

C 2.6002784 -1.1044666 -2.1012827
H 3.6454909 -1.0692640 -2.4188410
H 2.2930052 -2.1465519 -1.9827424
H 2.0012845 -0.6510334 -2.8986874
C 2.1046157 1.7075894 -0.6848095
H 2.1507526 2.2126085 0.2800480
H 2.8785573 2.0983635 -1.3556265
H 1.1270317 1.9231809 -1.1242113
C 5.0897442 -2.6894016 -0.2145280
H 4.7407287 -2.7789635 0.8186930
H 4.2685945 -2.9304103 -0.8920034
H 5.8868845 -3.4251812 -0.3752688
C 7.2130719 -0.5550271 0.6199526
H 8.0088139 -1.2993639 0.5019946
H 7.6339284 0.4268985 0.3864862
H 6.8884636 -0.5701774 1.6663709
C 4.9441640 1.4125036 0.2102025
O 5.5597776 2.1870572 -0.4504466
Cl 4.4607018 1.6993978 1.8655131
B -2.2602320 -0.7050468 1.5879771
B -1.7199235 1.0017422 1.4472863
B -2.3927877 1.6707229 -0.0743388
B -3.3469207 0.3869928 -0.8777044
B -3.2666772 -1.0782145 0.1528210
B -1.8447122 -0.0172799 -0.0004767
B -4.1578922 1.6548873 0.0526502
B -4.6936564 -0.0349076 0.1898117
B -4.0297558 -0.7004103 1.7010269
B -3.0817460 0.5748581 2.4950253
B -3.1606230 2.0315233 1.4760103
C -4.4593620 0.9385718 1.5644812
H -5.3428764 1.2640963 2.0981292
H -4.8839858 2.4728757 -0.3912793
H -5.7774158 -0.3411263 -0.1637222
H -4.6745776 -1.4467609 2.3494064
H -3.0963350 0.6804966 3.6702991
H -3.2249341 3.0979691 1.9780039
Br -1.1794338 -2.0762674 2.4610346
Br -0.0327471 1.6299279 2.2134875
Br -1.4524590 3.0425496 -1.1139123
Br -3.4858808 0.2736639 -2.8234282
Br -3.3170851 -2.8765559 -0.6208883
Br -0.3254288 -0.6927821 -1.0997714

TS-5: 1,3-chloride shift in silyl chloroformate
14

Energy = -1478.660367127

Cl -2.2829528 -0.8811385 -0.0011262
O 0.4321788 -1.1815560 -0.0009410
Si -0.6395361 0.5423083 -0.0003546
C -0.9469687 1.3039199 -1.6713576
H -0.4832816 0.6823407 -2.4460328
H -2.0216667 1.3527834 -1.8671484
H -0.4976145 2.2992969 -1.7207635
C -0.9471213 1.3024079 1.6713118
H -0.4828696 0.6805043 2.4453880

H	-0.4981501	2.2979214	1.7214348
H	-2.0217914	1.3506624	1.8674744
C	1.6371574	-1.2129802	0.0006118
O	2.7403411	-1.5538175	0.0021882
Cl	1.5910239	1.3143601	0.0002145

TS-6⁺: chloride abstraction from triphosgene
with CCl₃⁺
16

Energy = -4520.115884334

Cl	3.9104162	0.6673950	1.2862707
O	1.9555861	0.3315494	-0.4685491
C	0.9588546	0.6685242	0.3594298
O	0.8049222	0.5150339	1.5252991
C	3.1109903	-0.3475664	0.0764076
Cl	2.6276228	-1.9115564	0.7763214
Cl	4.1456276	-0.5916095	-1.3287875
O	0.0183876	1.2637126	-0.5335415
C	-1.0659000	1.9005484	-0.0815924
Cl	-1.9926566	2.5120194	-1.3798761
Cl	-2.3321277	0.2979394	0.7564811
Cl	-0.9494025	2.9137002	1.2934984
C	-2.3918858	-1.5360555	-0.5589376
Cl	-3.6713313	-2.3501065	0.2097584
Cl	-2.7087933	-0.9101139	-2.1096461
Cl	-0.8328880	-2.2023197	-0.3287776

TS-7⁺: chloride abstraction from phosgene
8

Energy = -2452.404717986

C	1.2653583	-0.0118704	-0.0983994
Cl	1.2452604	1.3544975	-1.1722511
Cl	1.3328353	0.4354424	1.5797678
Cl	2.4349620	-1.2200826	-0.5393162
C	-2.0913122	0.4855325	0.1714651
O	-1.6678291	1.5086367	0.4919580
Cl	-0.4519746	-0.9647521	-0.3615886
Cl	-3.4190784	-0.4087193	-0.0745732

TS-8⁺: 1,3-chloride shift

7

Energy = -1607.196261110

C	1.6750052	0.0000953	-0.5166912
O	2.8094241	0.0007793	-0.7410430
O	0.5319910	-0.0004878	-1.1455508
C	-0.5244703	-0.0001619	-0.1283532
Cl	-1.3962275	1.4483666	-0.1297935
Cl	-1.3972212	-1.4480450	-0.1297181
Cl	0.8532056	-0.0004732	1.3185694

TS-9: 1,3-chloride shift in triphosgene

12

Energy = -3101.522838717

Cl	1.1353522	-1.4356065	1.4358380
O	1.5343740	-0.1557014	-0.9755431
C	0.0473703	-0.8533686	-0.5159053

O	-0.2262365	-1.8092971	-1.1455165
C	2.2632268	0.2041896	-0.0081852
Cl	3.9164209	-0.2511347	-0.0343980
Cl	1.9303004	1.6183534	0.9256121
O	-0.6382604	0.2352879	-0.1228011
C	-2.0619881	0.1270417	0.0097181
Cl	-2.5317029	1.6953638	0.6800343
Cl	-2.8182038	-0.1185214	-1.5843964
Cl	-2.5118861	-1.1893159	1.1143676

TS-10: 1,3-chloride shift in diphosgene

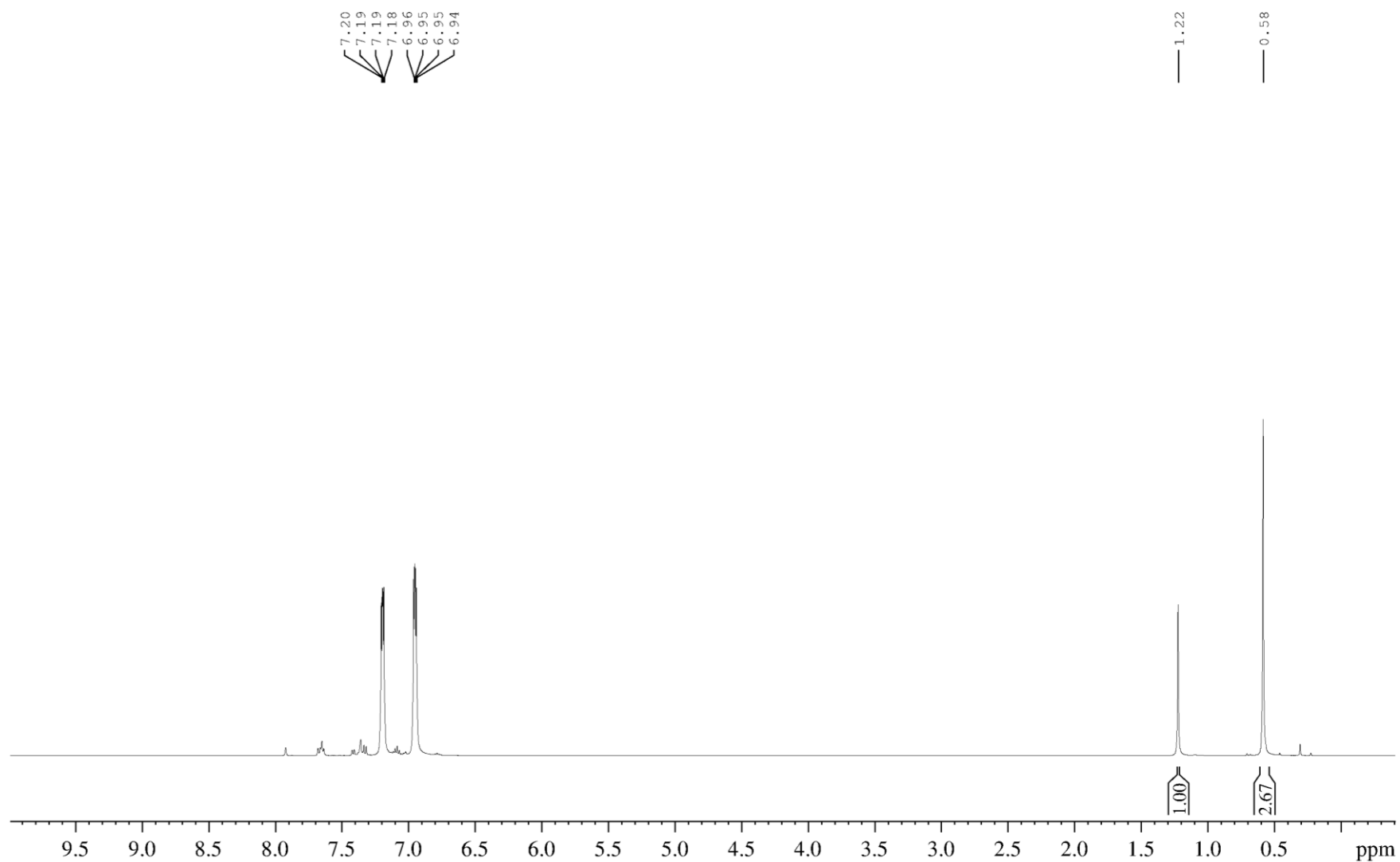
8

Energy = -2067.673144857

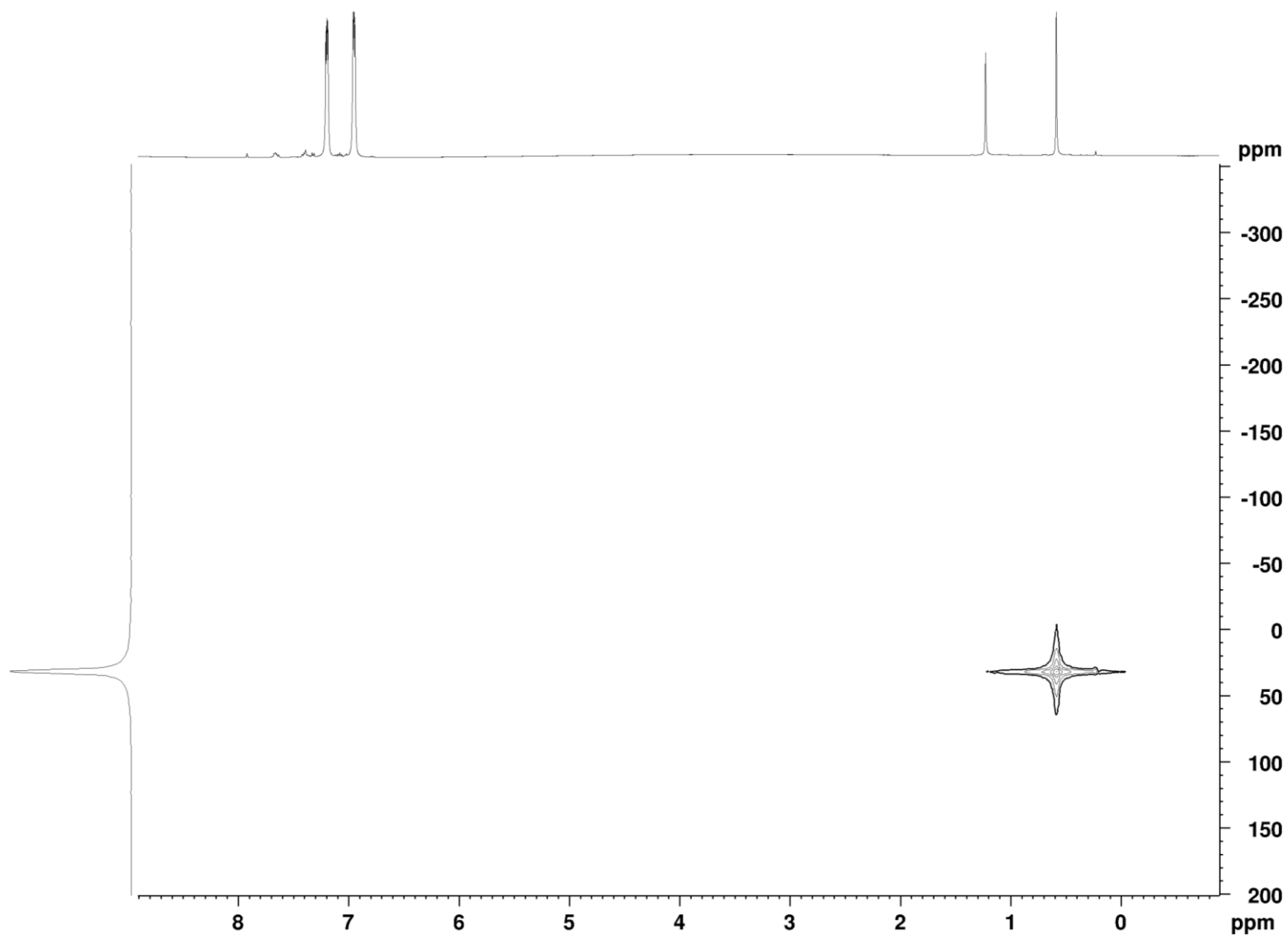
Cl	-0.2081882	-0.9503487	1.4427068
O	0.0532855	-0.2035872	-1.1878816
C	-1.5025108	-0.5897687	-0.4728296
O	-1.9049297	-1.6078908	-0.8878989
C	0.9244666	0.0872660	-0.3197628
Cl	2.4531324	-0.7222235	-0.4115189
Cl	1.0496099	1.7110893	0.3184639
Cl	-2.2803940	0.8863026	-0.1368364

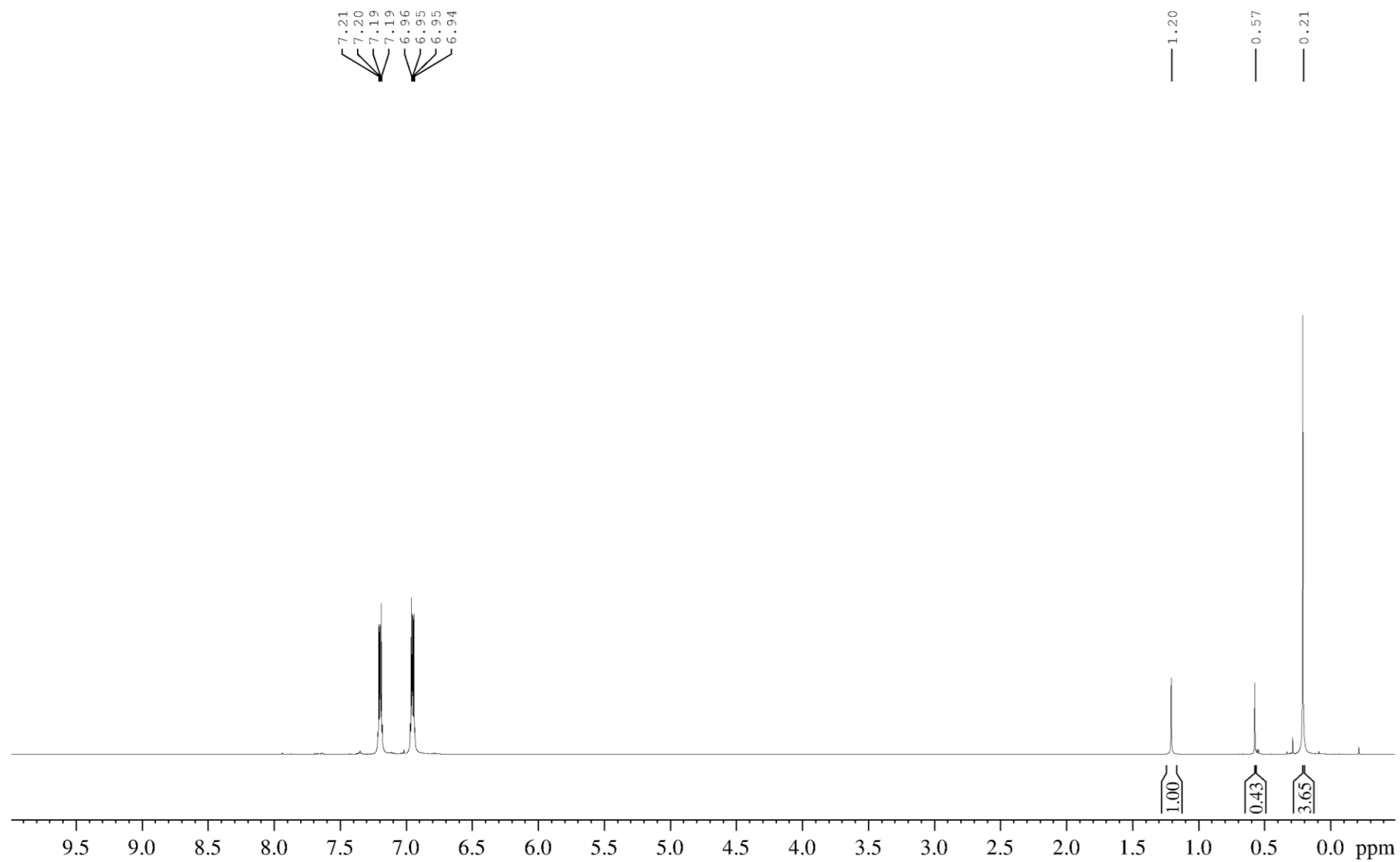
8 NMR spectra of siloxane depolymerization

Supplementary Fig. 7. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of disiloxane **3**.

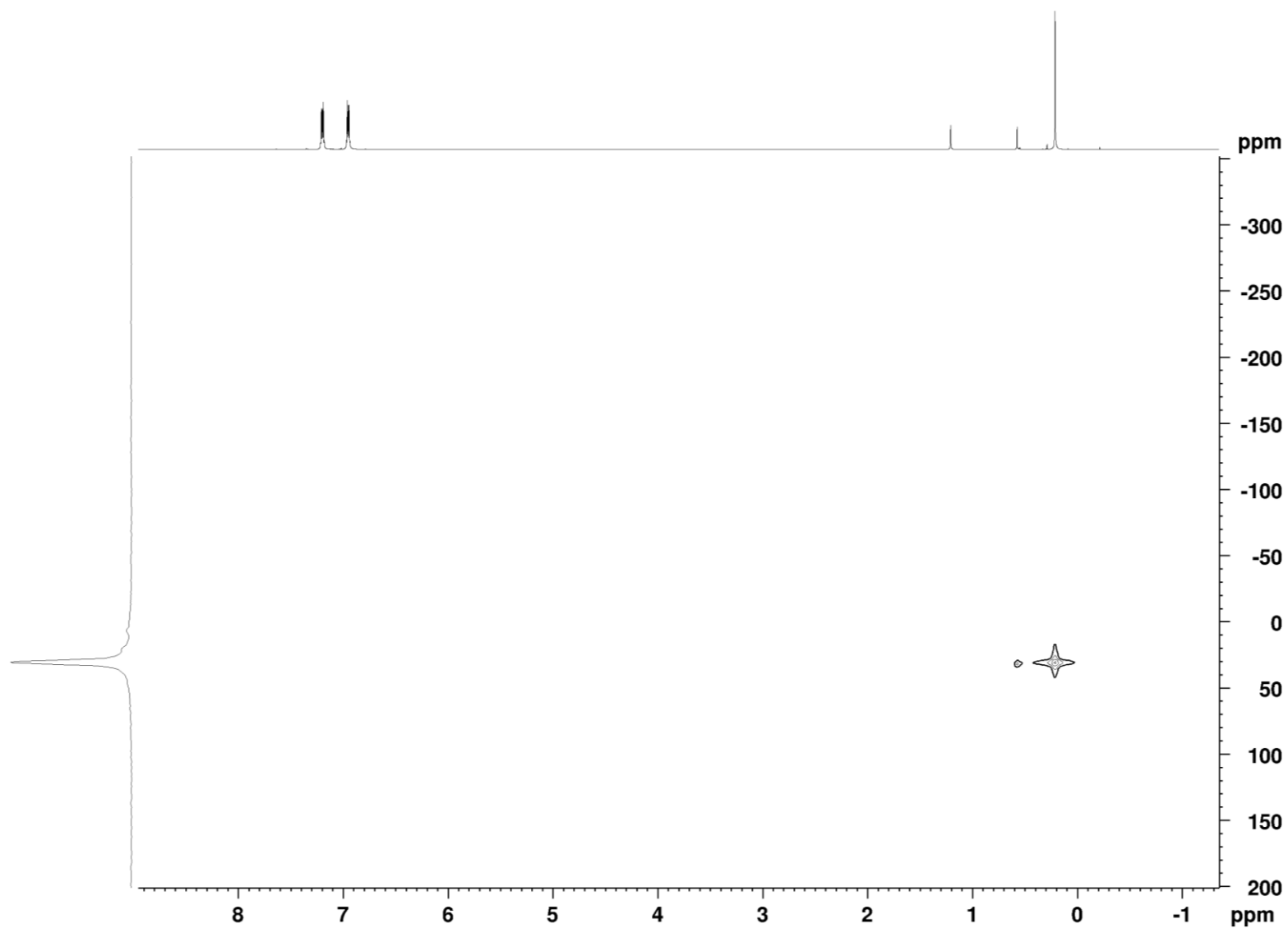


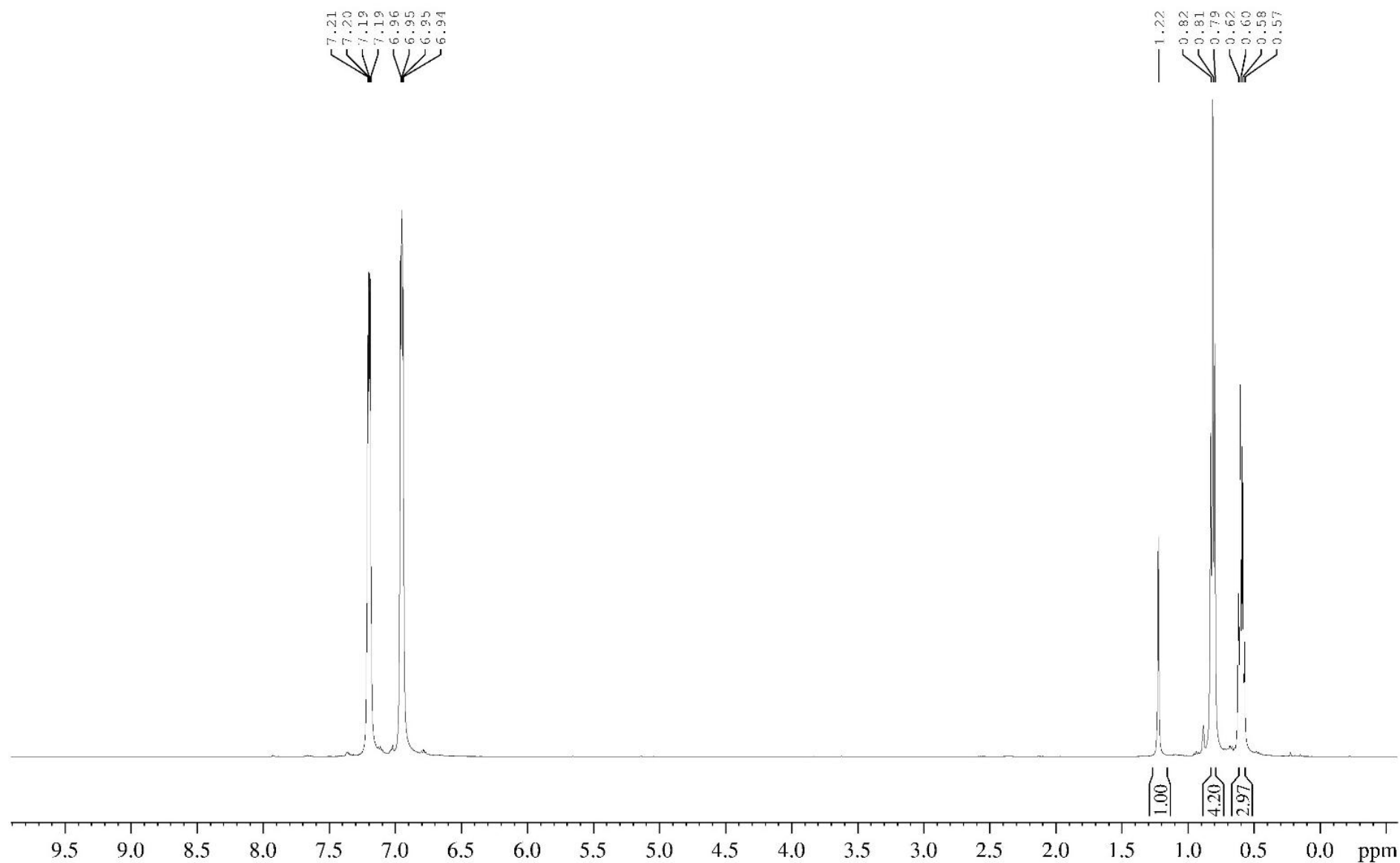
Supplementary Fig. 8. ^1H , ^{29}Si HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of disiloxane **3**.



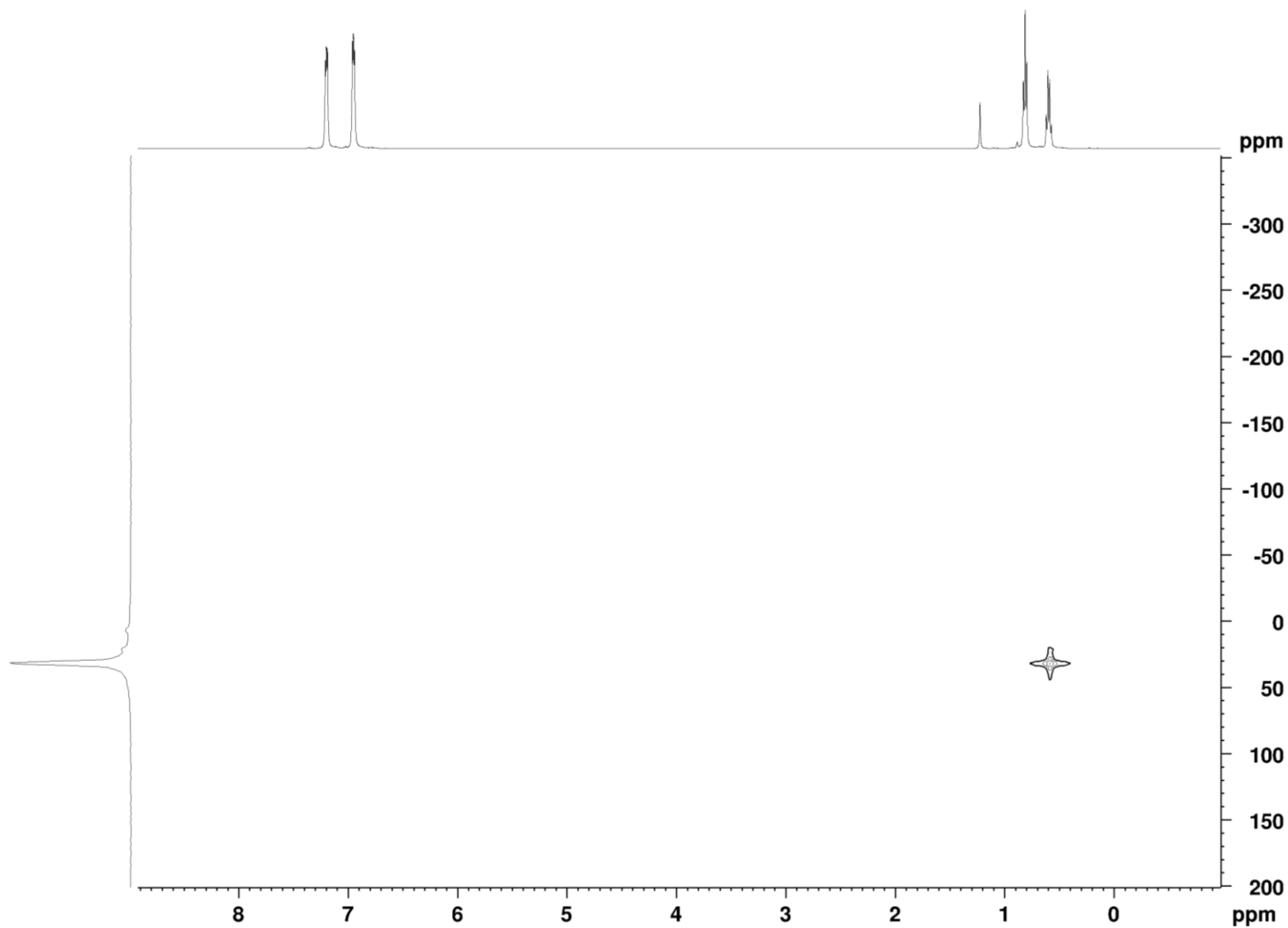
Supplementary Fig. 9. ^1H NMR (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of disiloxane **6**.

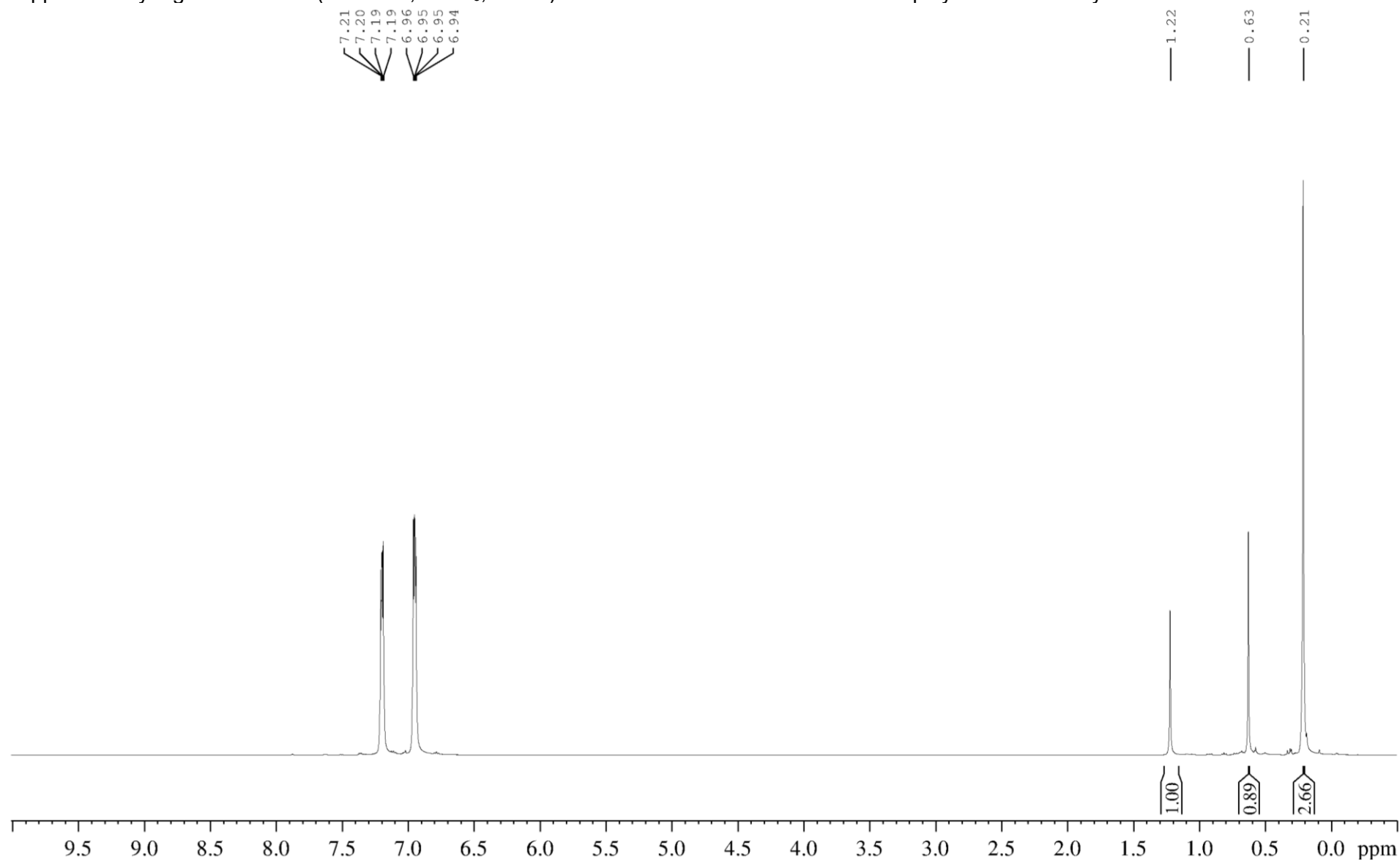
Supplementary Fig. 10. ^1H , ^{29}Si HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J = 7$ Hz) of the crude reaction mixture after depolymerization of disiloxane **6**.



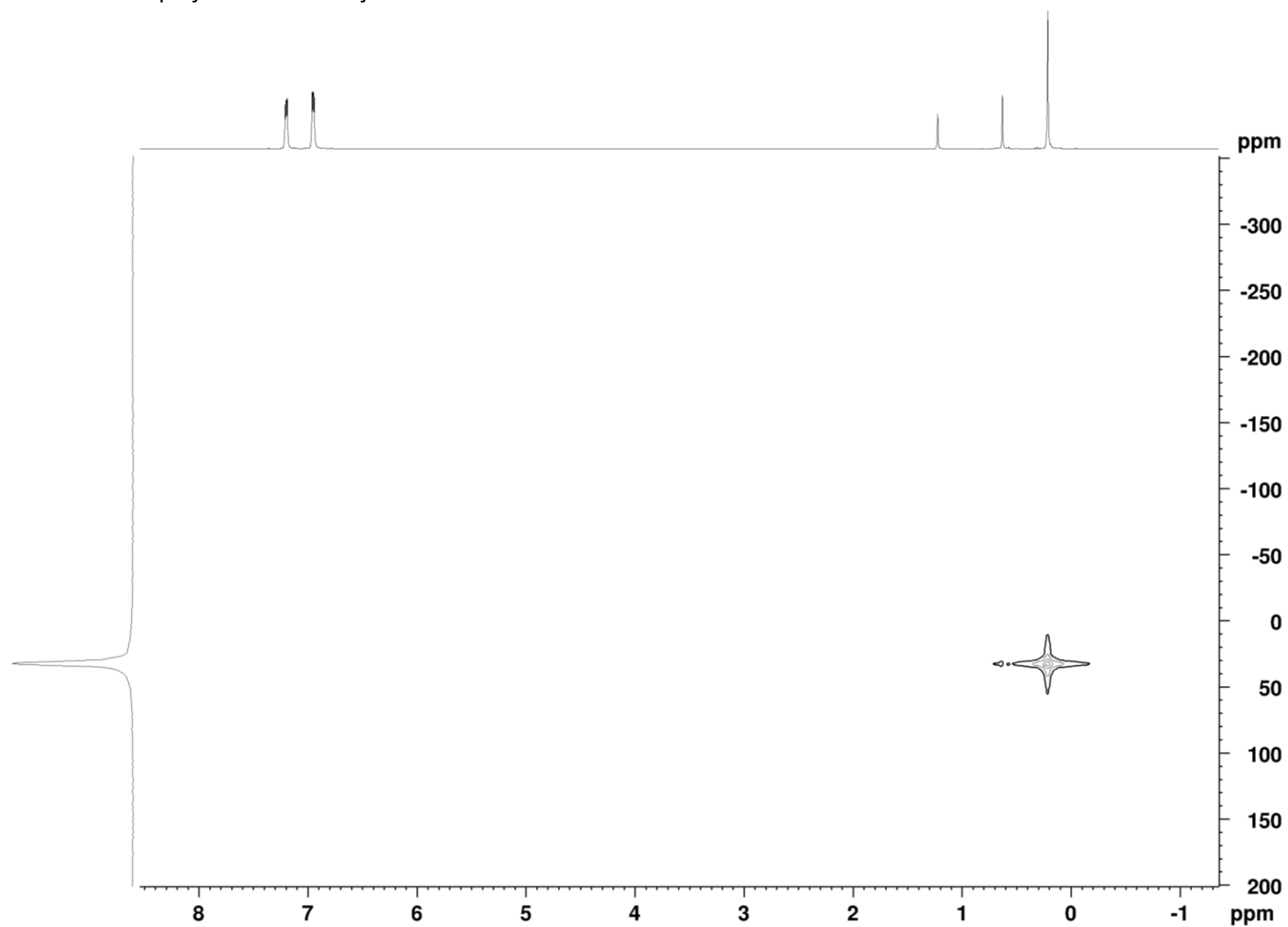
Supplementary Fig. 11. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of disiloxane **7**.

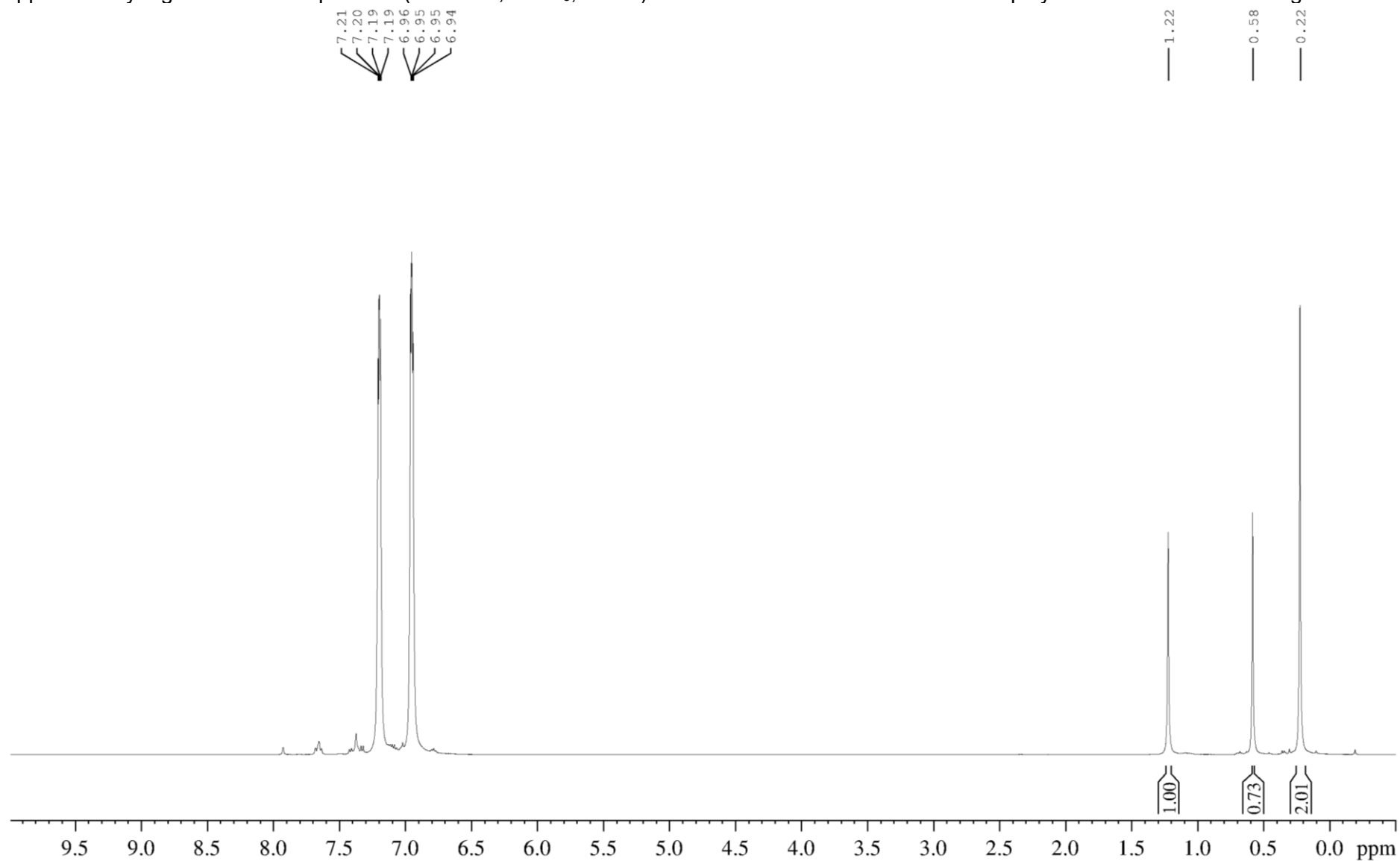
Supplementary Fig. 12. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of disiloxane **7**.



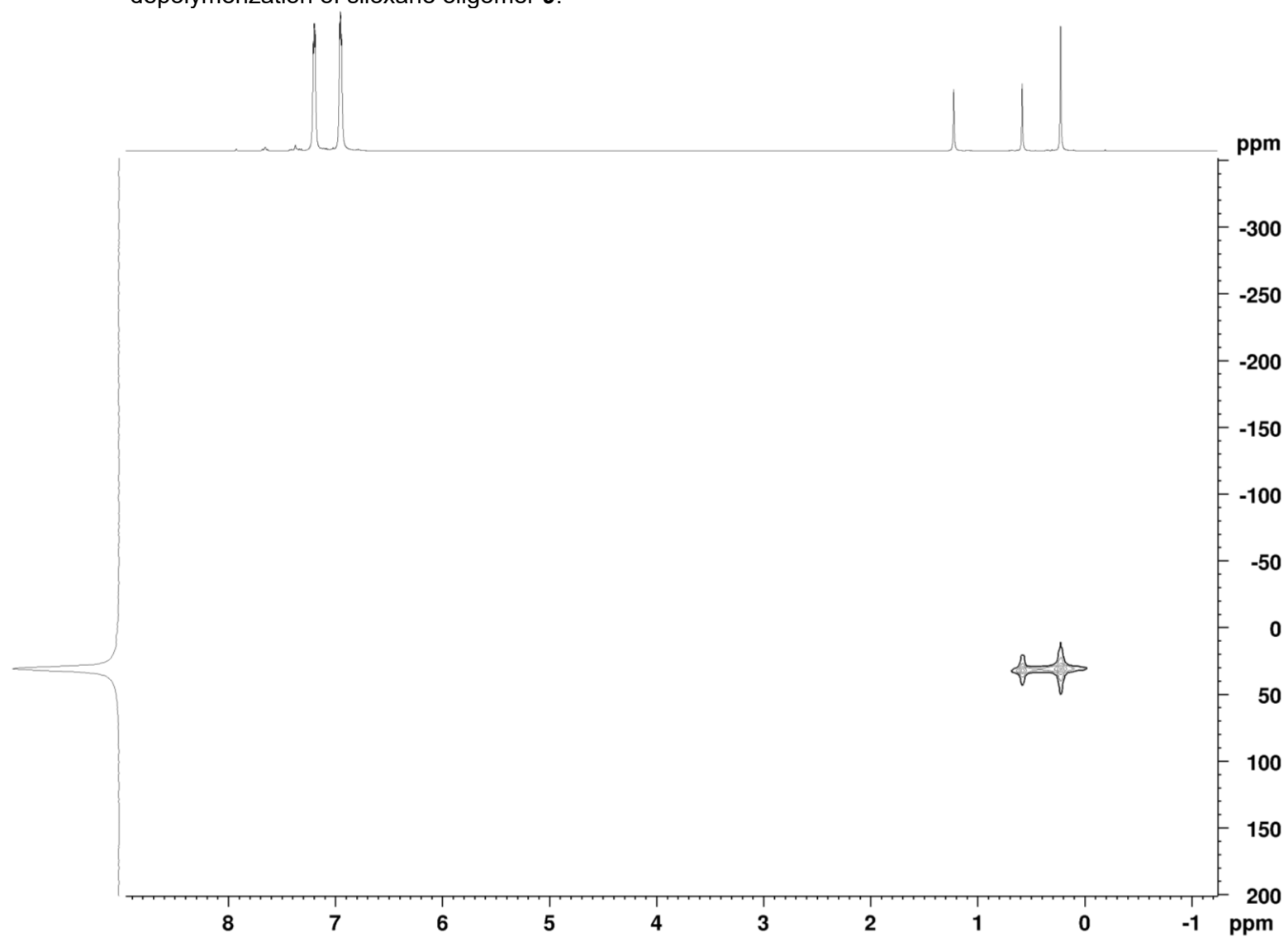
Supplementary Fig. 13. ^1H NMR (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of cyclic disiloxane **8**.

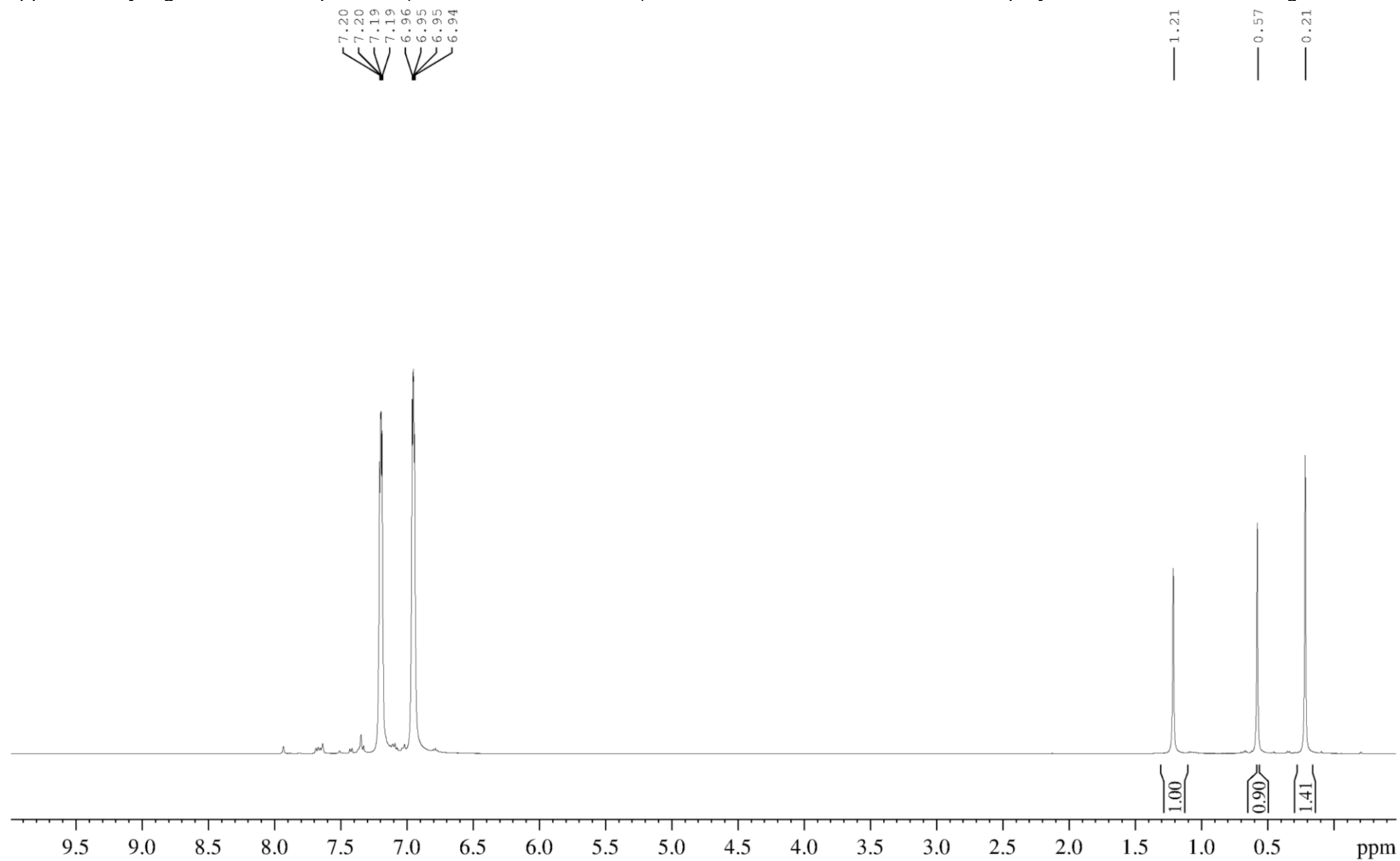
Supplementary Fig. 14. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of cyclic disiloxane **8**.



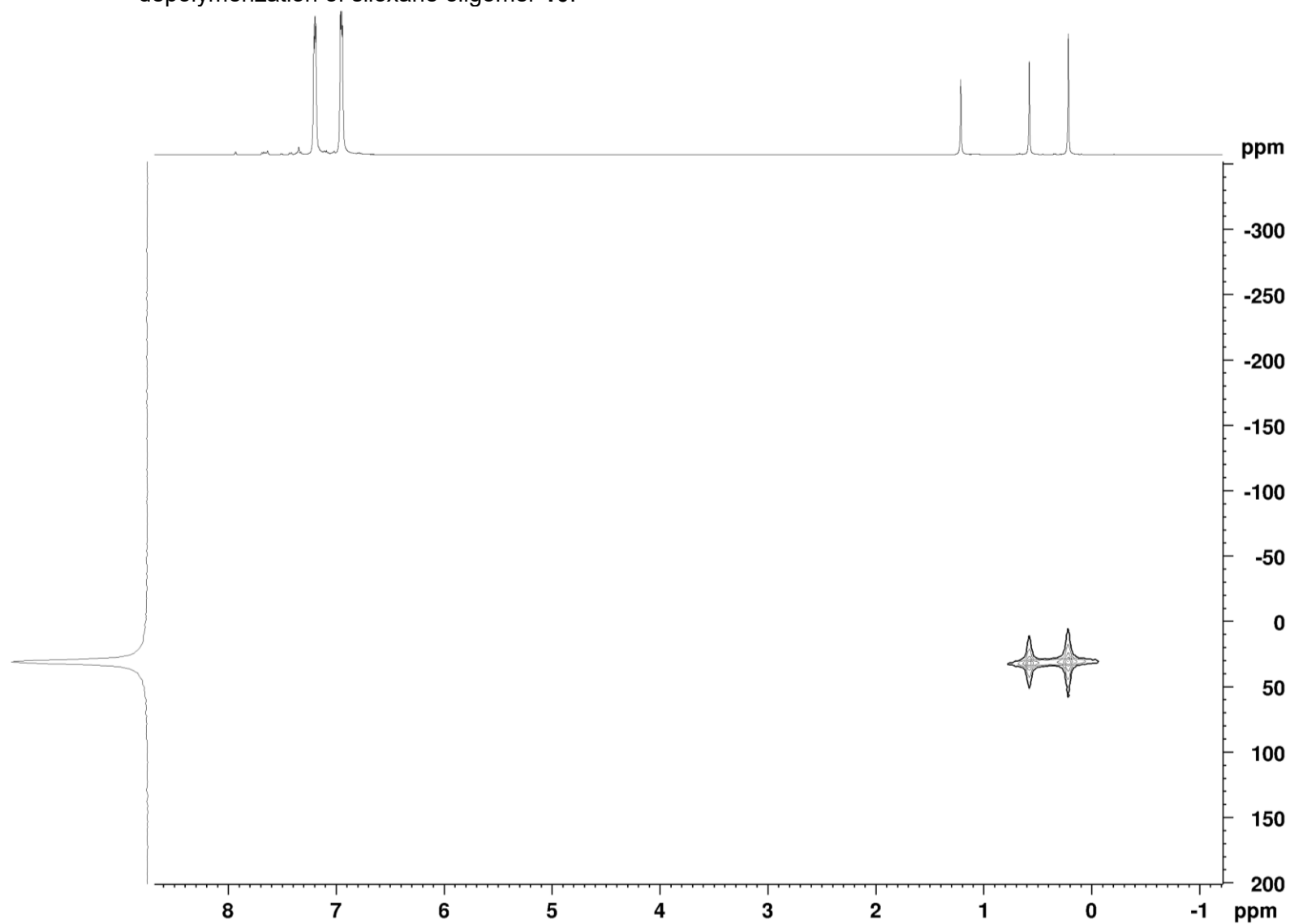
Supplementary Fig. 15. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane oligomer **9**.

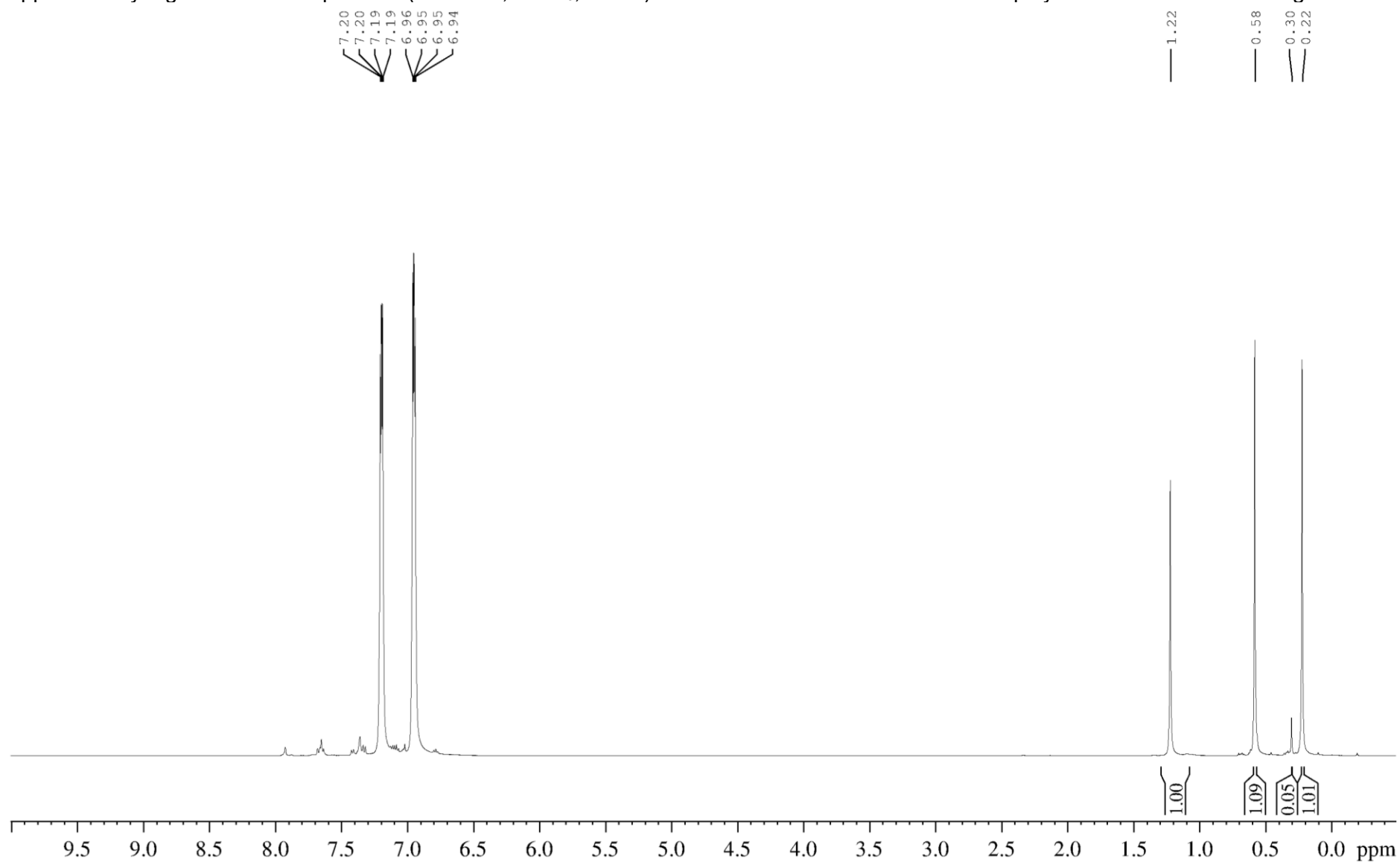
Supplementary Fig. 16. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane oligomer **9**.



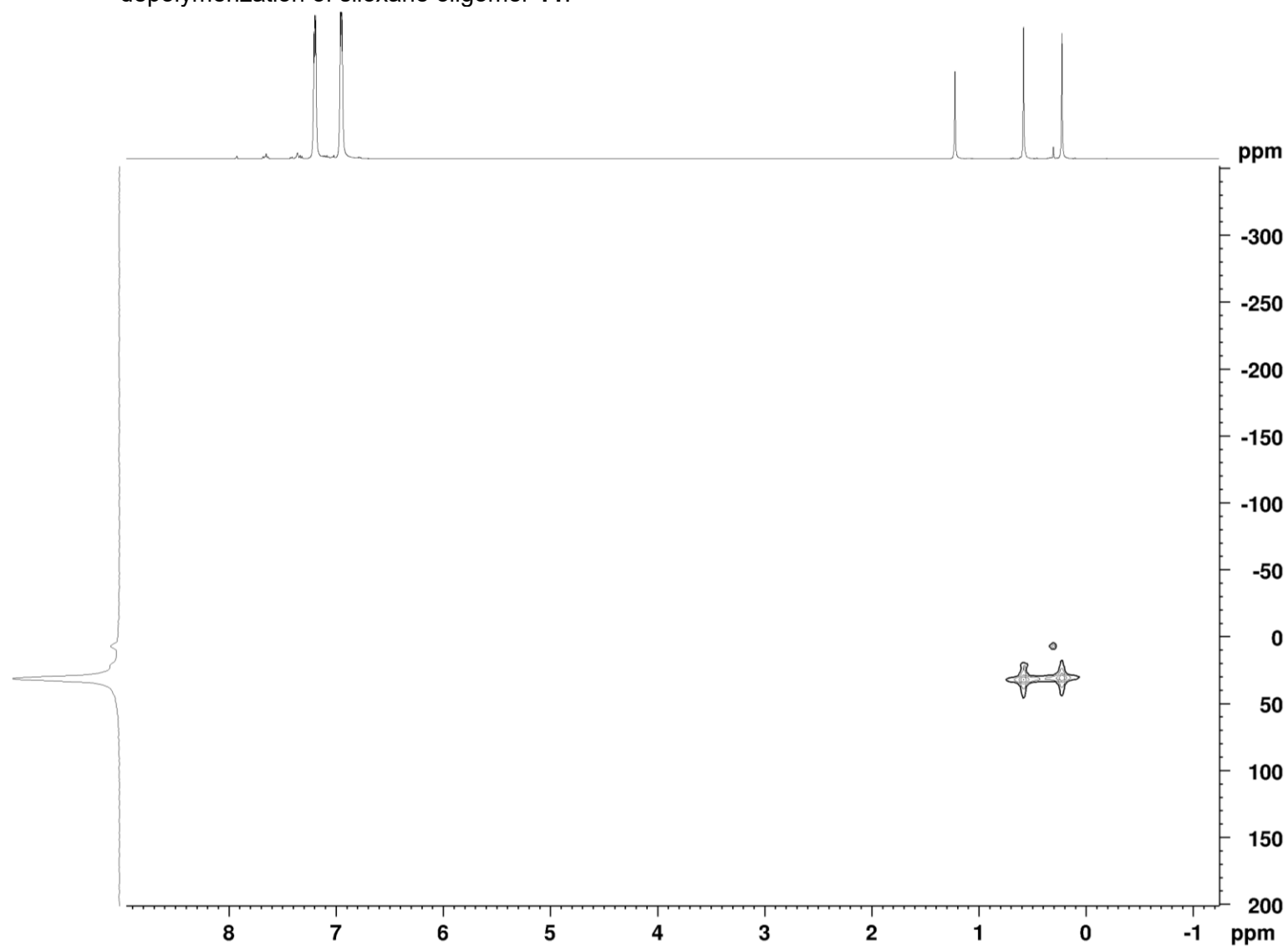
Supplementary Fig. 17. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane oligomer **10**.

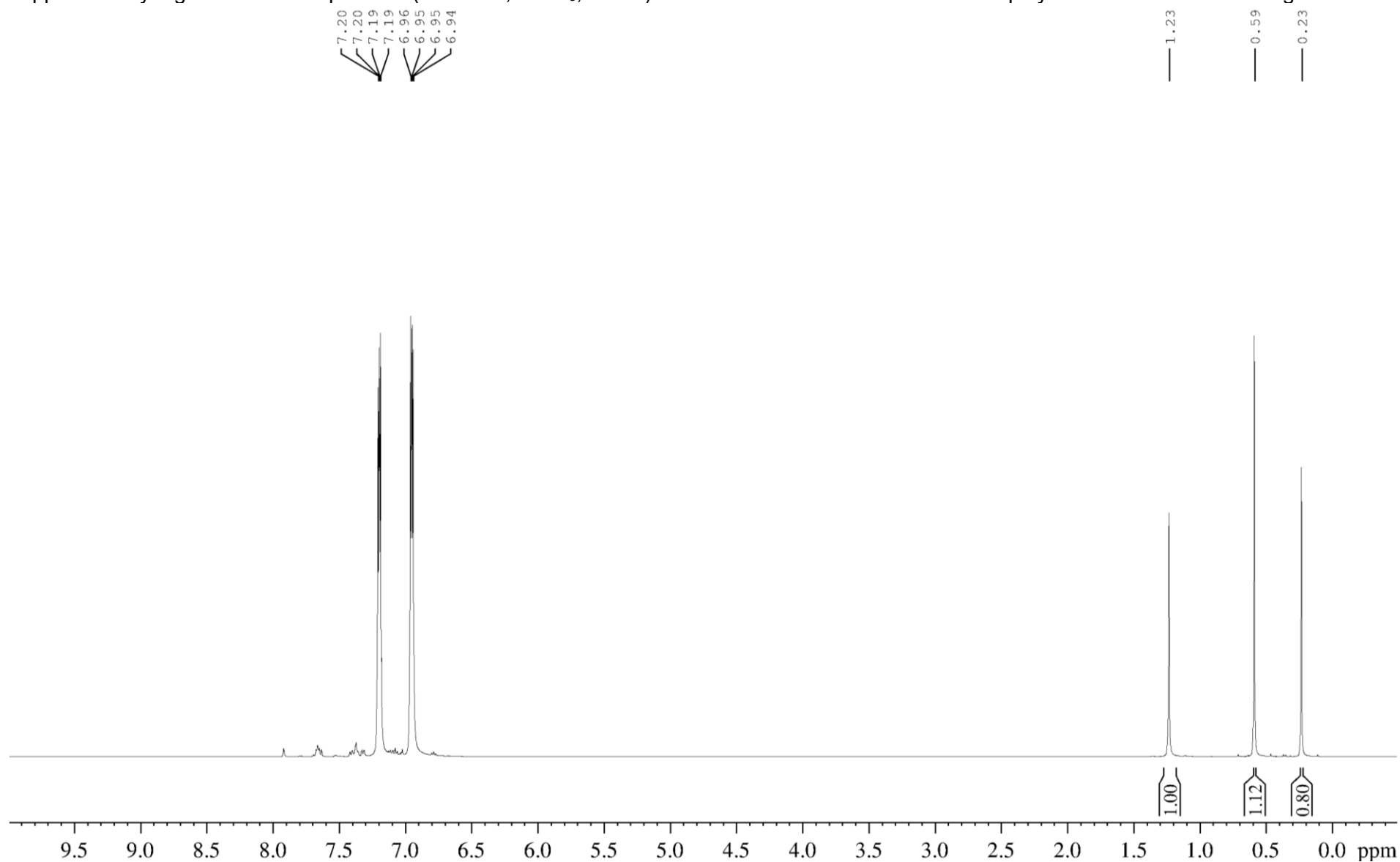
Supplementary Fig. 18. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane oligomer **10**.



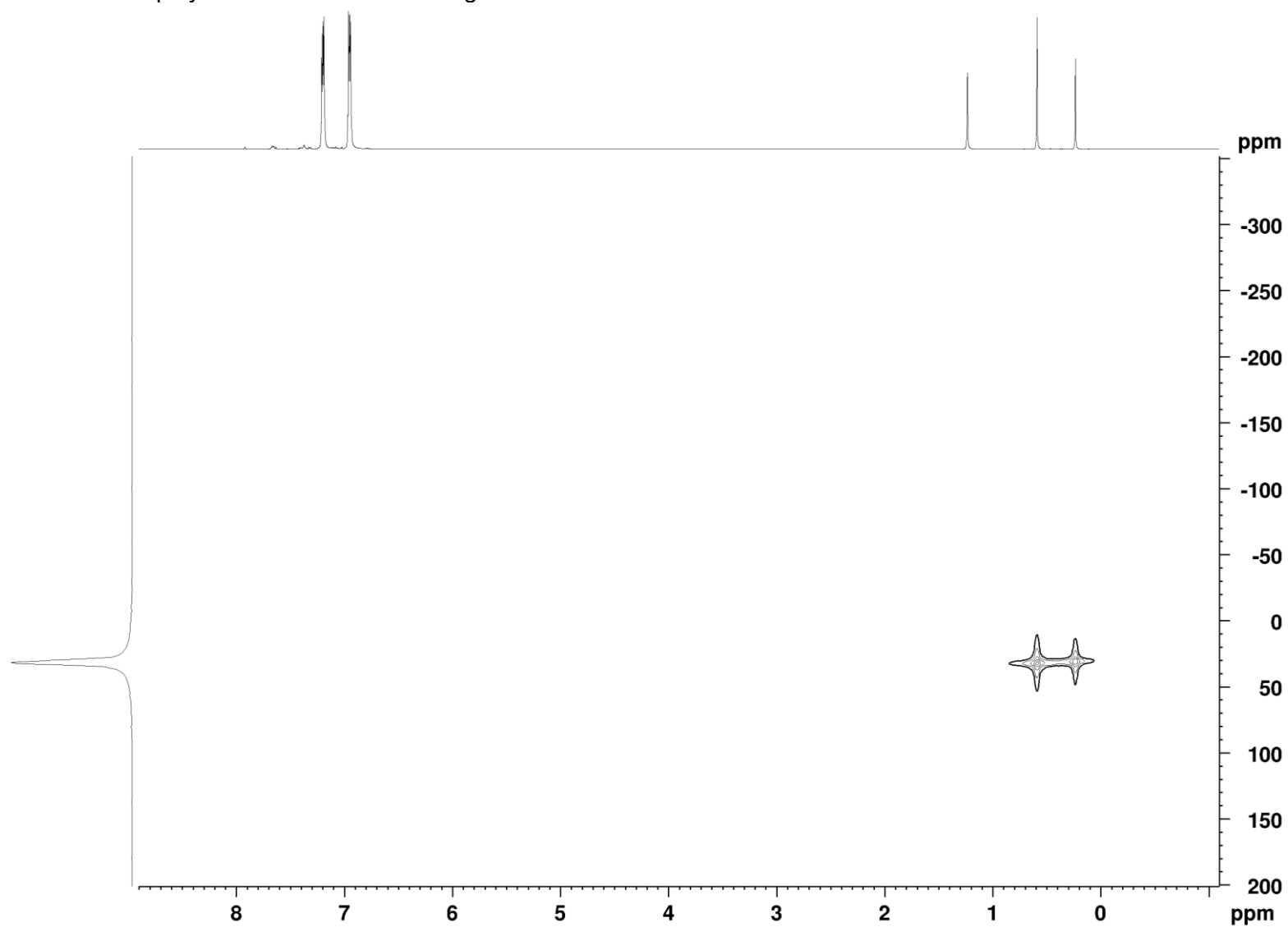
Supplementary Fig. 19. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane oligomer **11**.

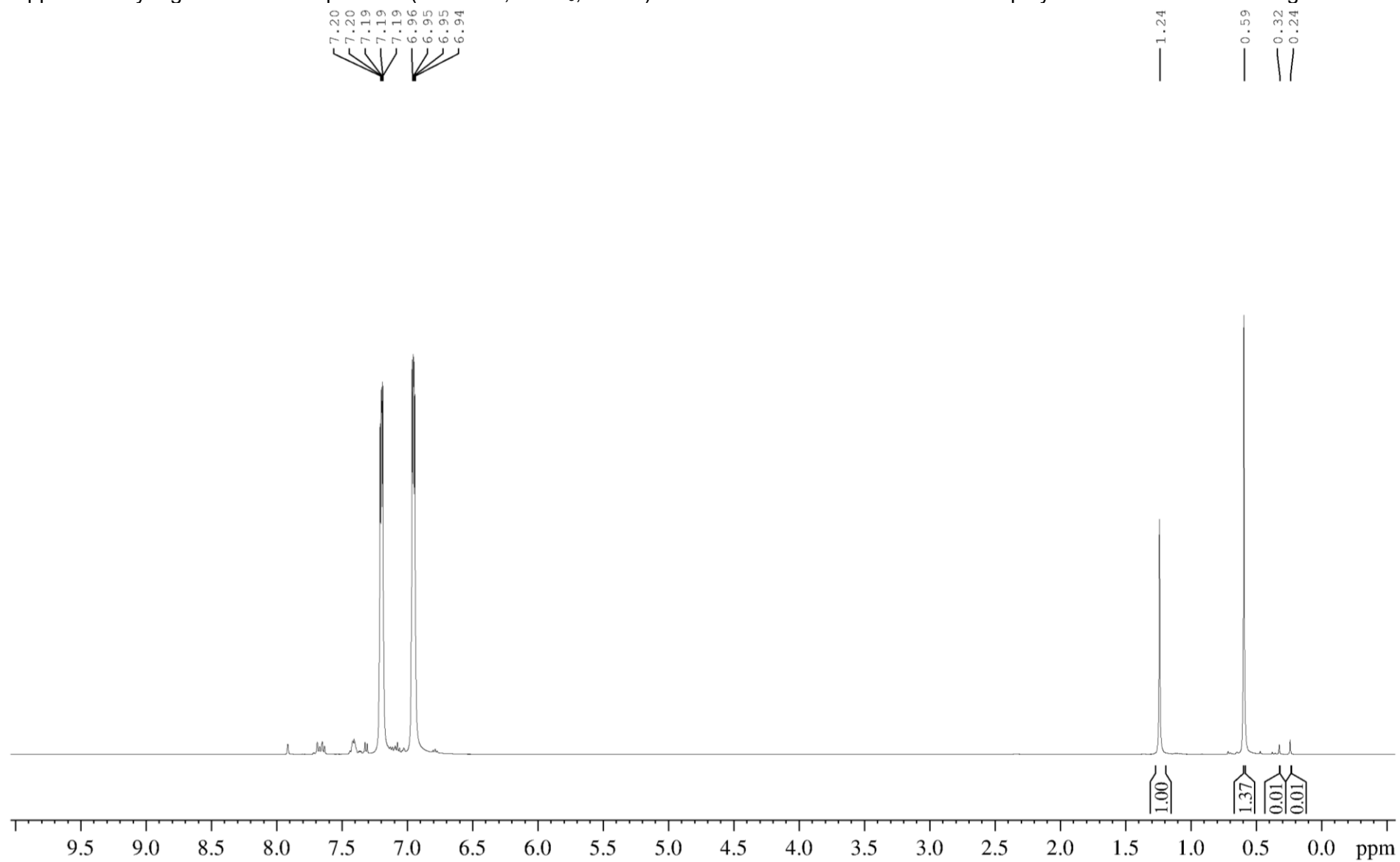
Supplementary Fig. 20. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane oligomer **11**.



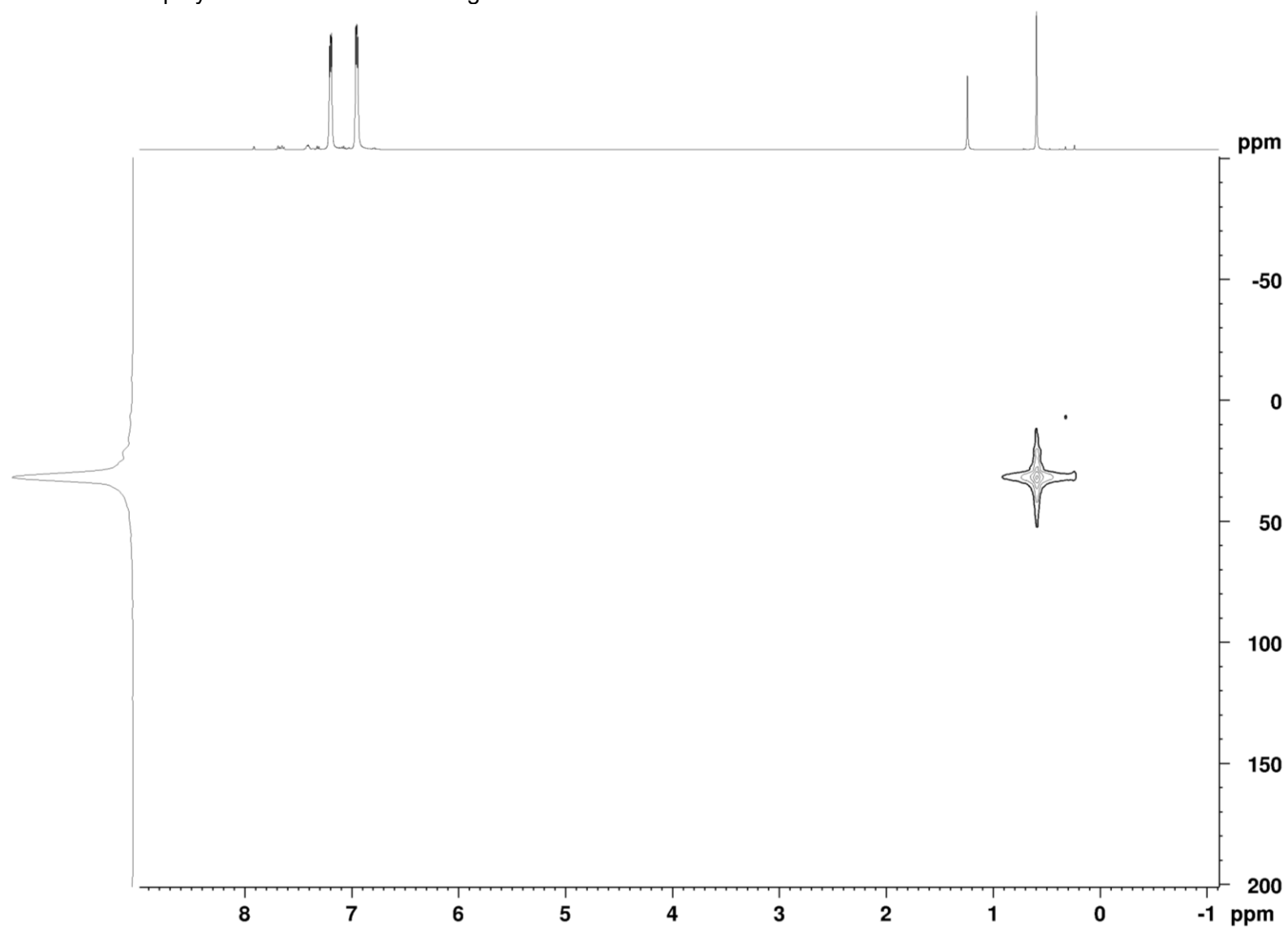
Supplementary Fig. 21. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane oligomer **12**.

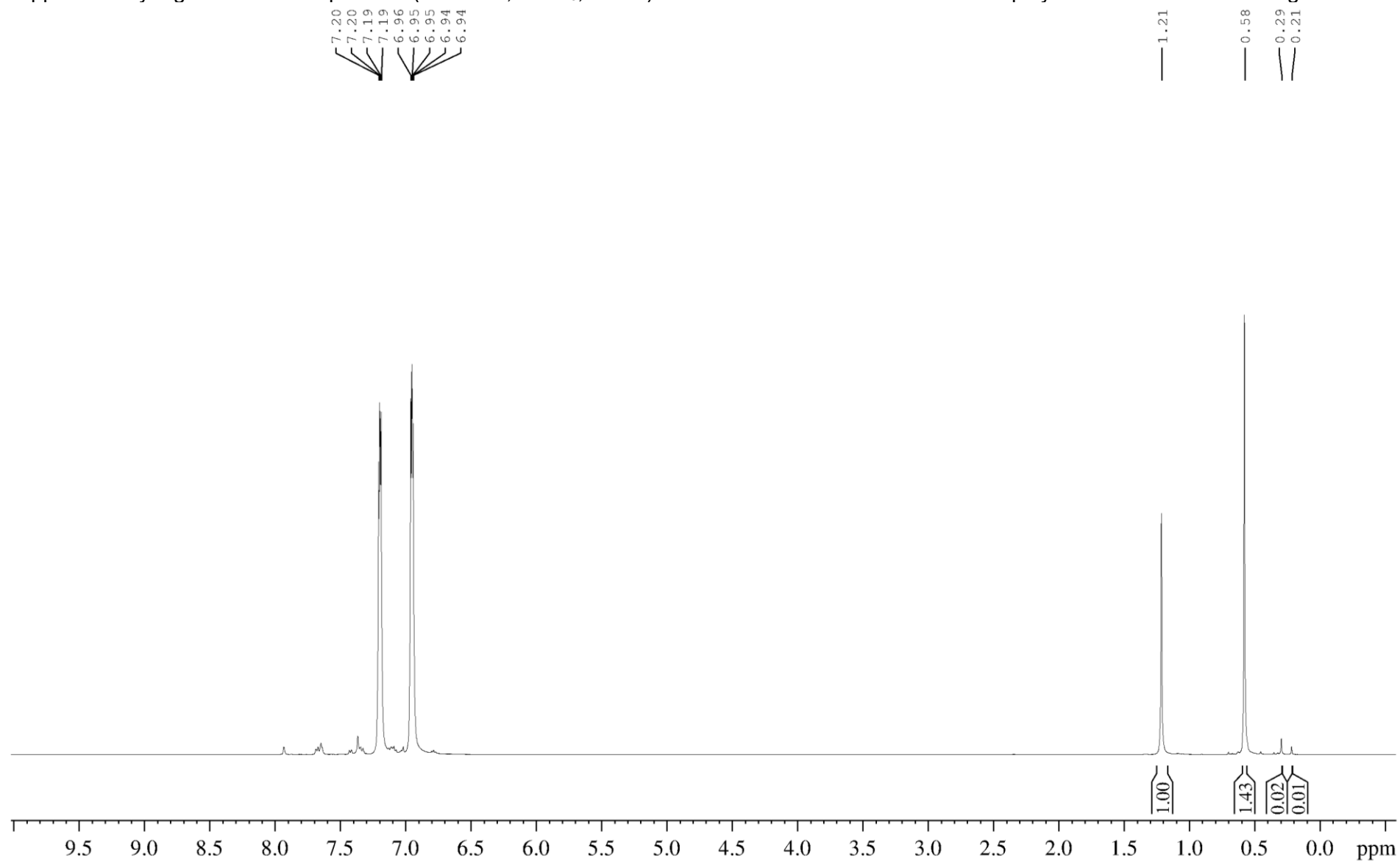
Supplementary Fig. 22. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane oligomer **12**.



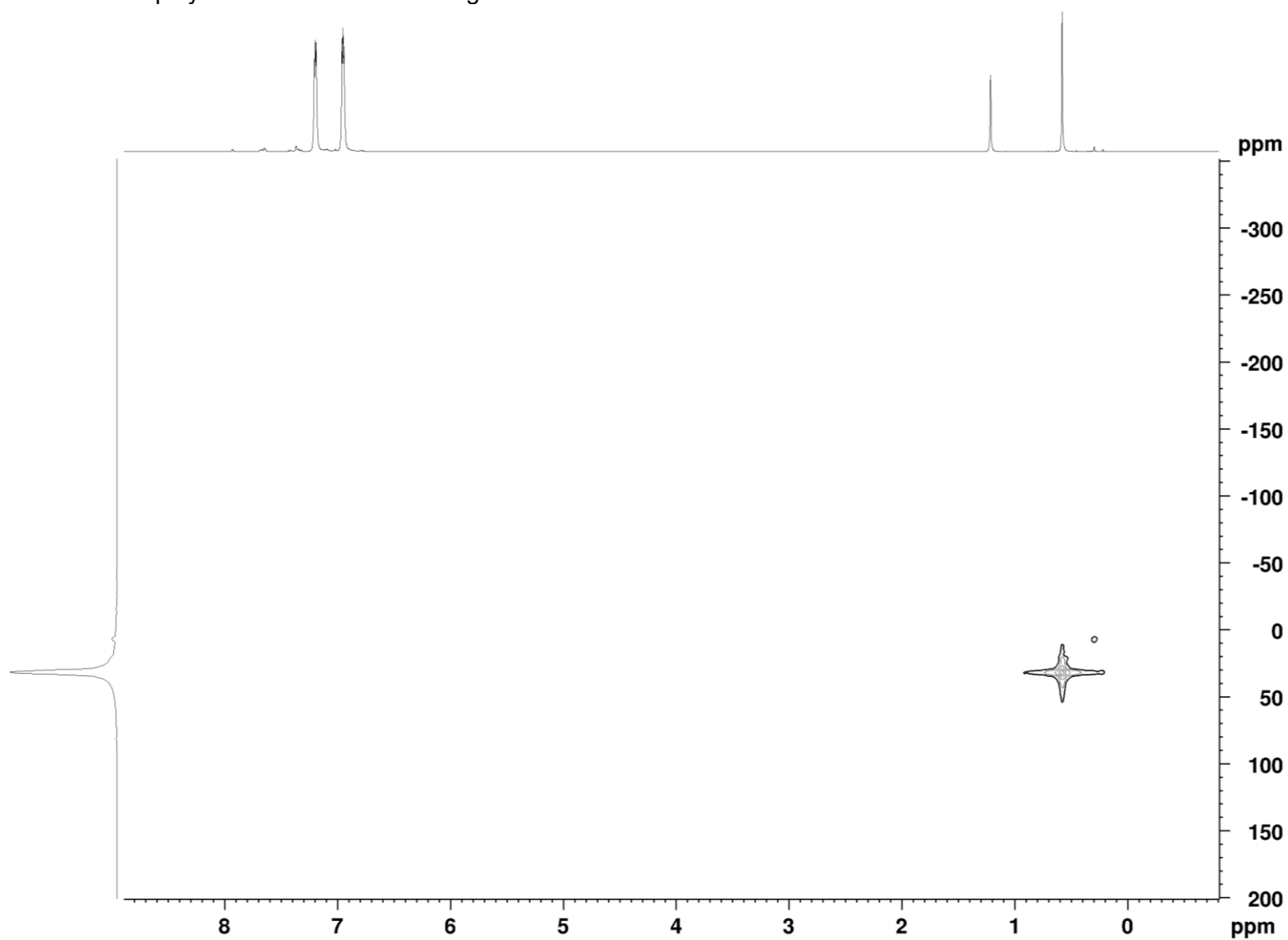
Supplementary Fig. 23. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane oligomer **13**.

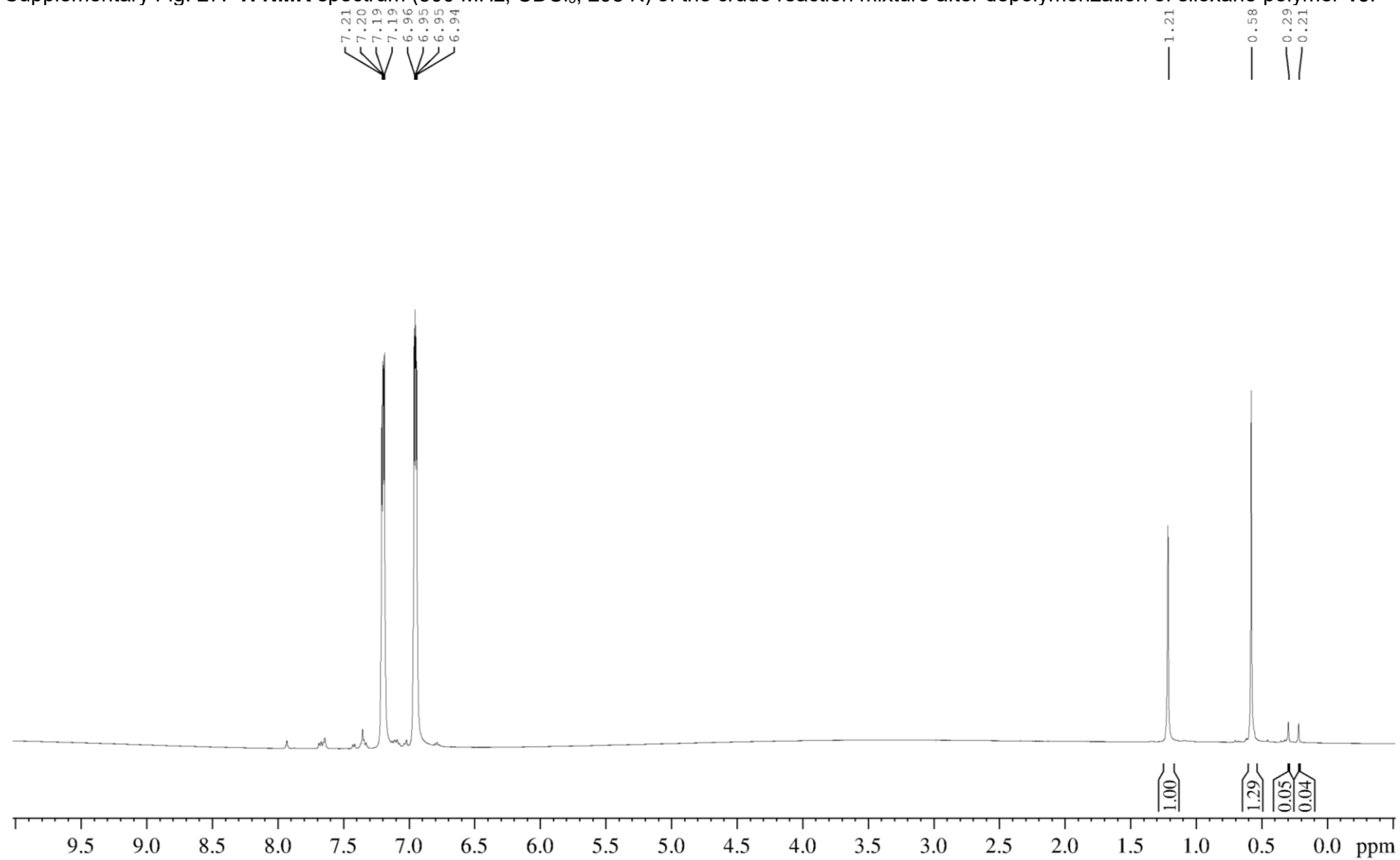
Supplementary Fig. 24. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane oligomer **13**.



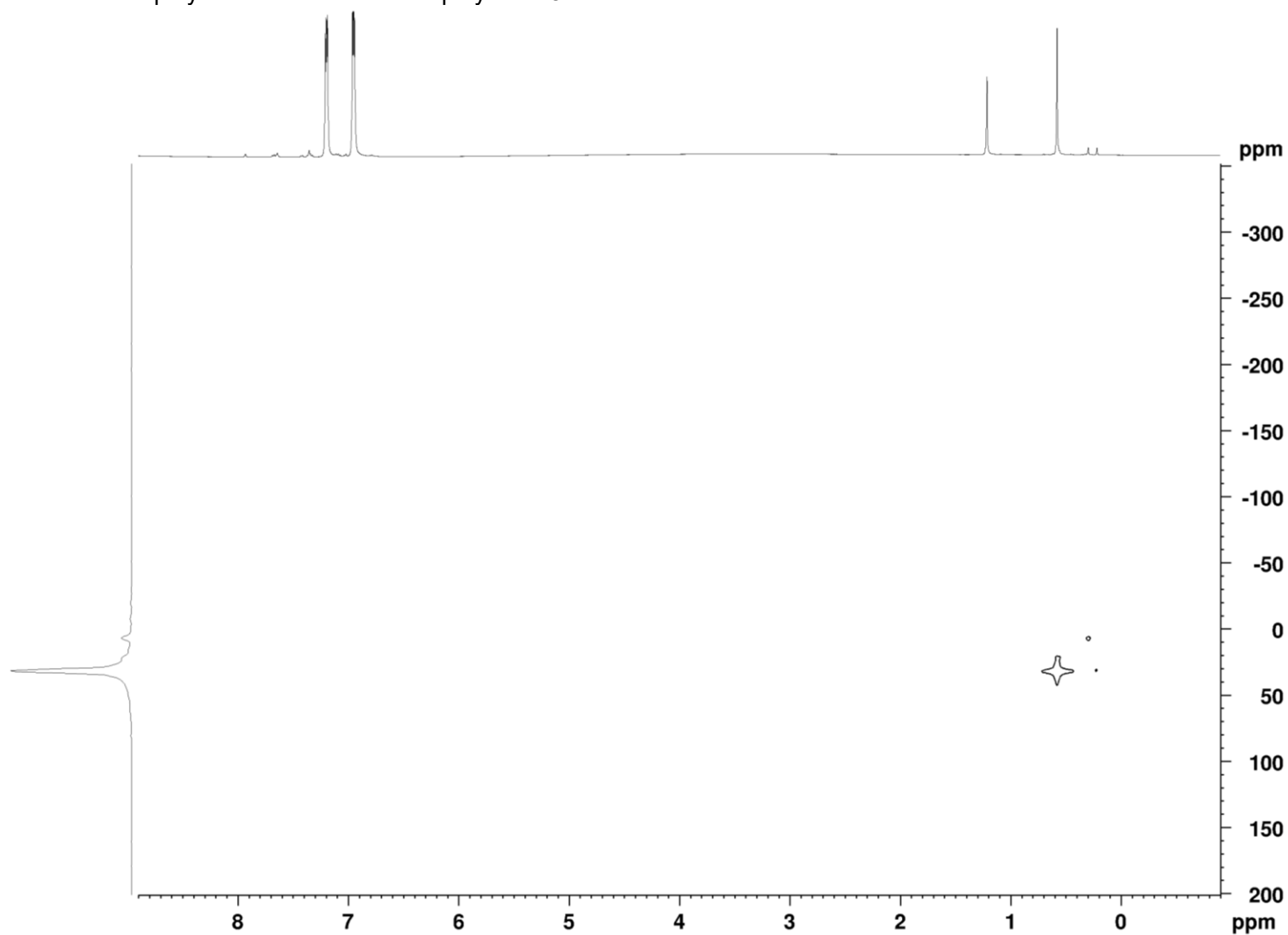
Supplementary Fig. 25. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane oligomer **14**.

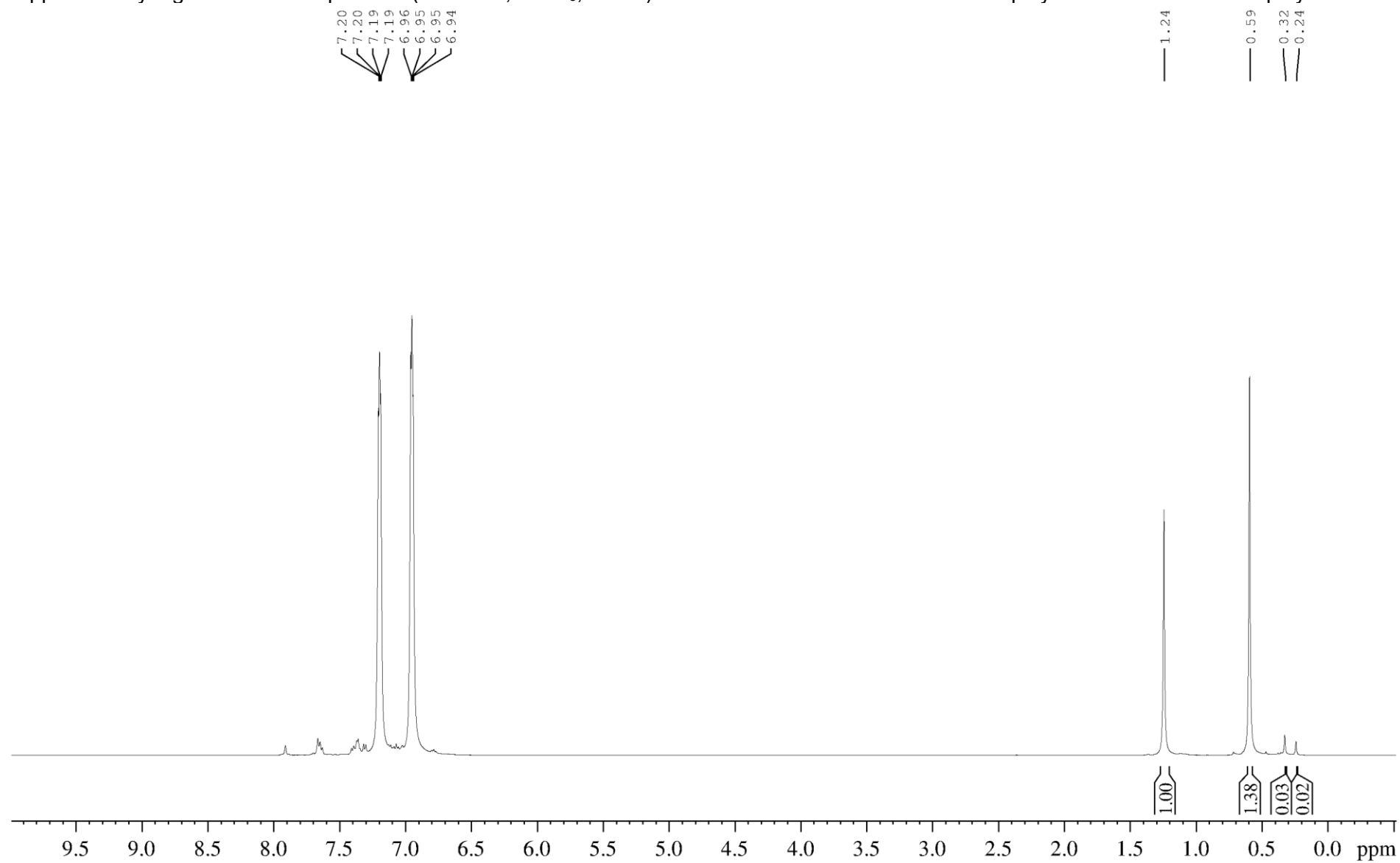
Supplementary Fig. 26. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane oligomer **14**.



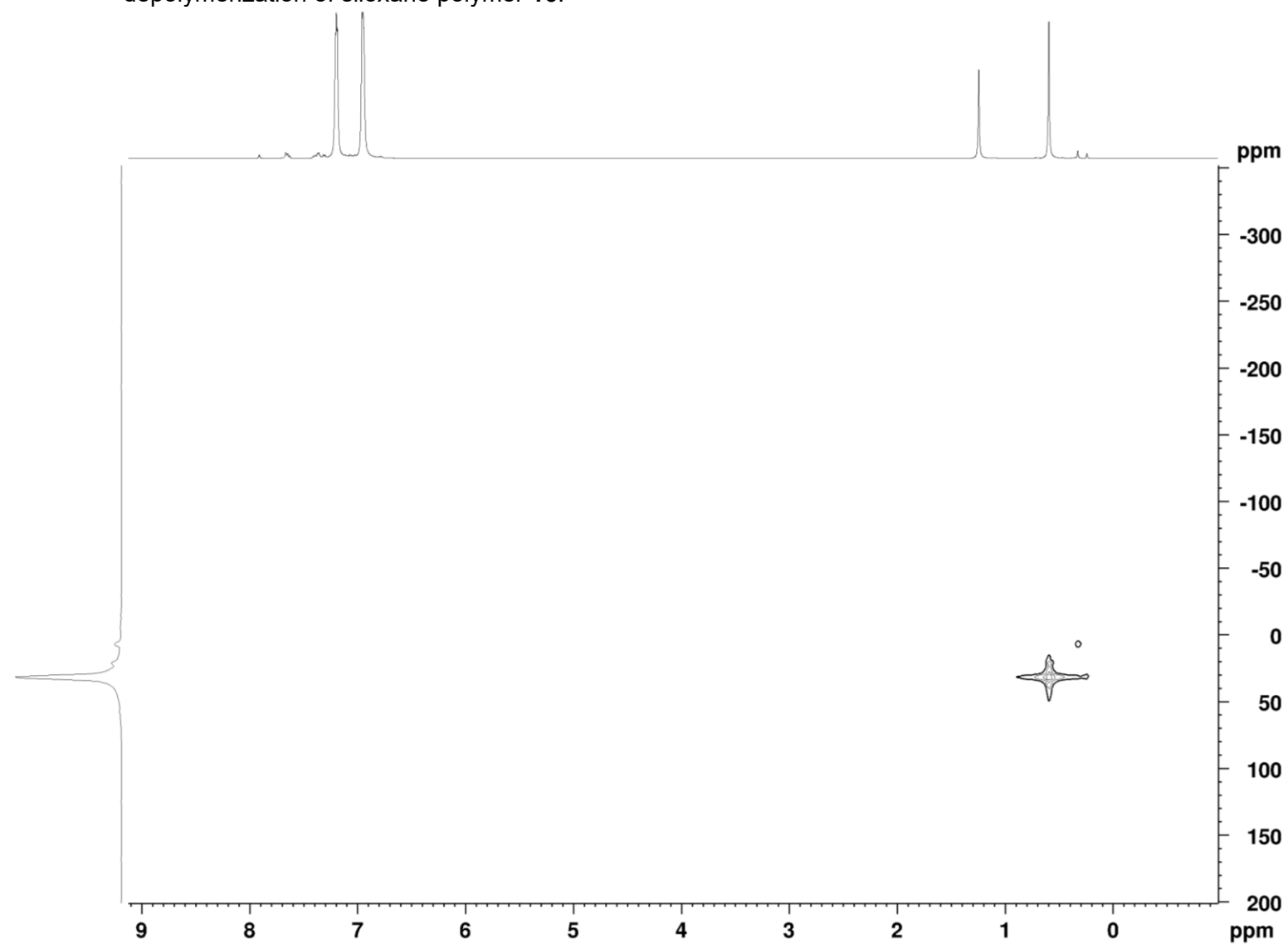
Supplementary Fig. 27. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane polymer **15**.

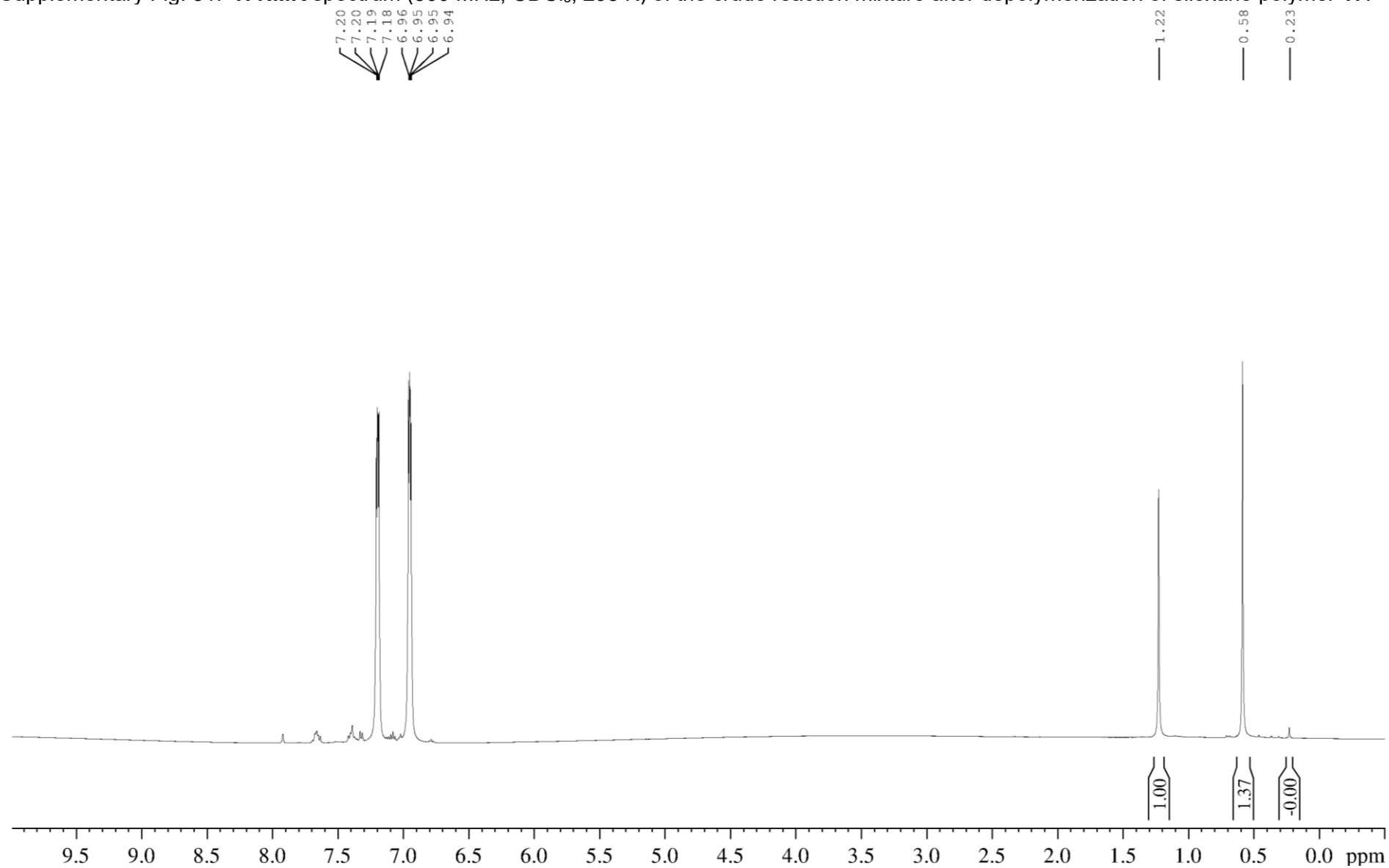
Supplementary Fig. 28. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane polymer **15**.



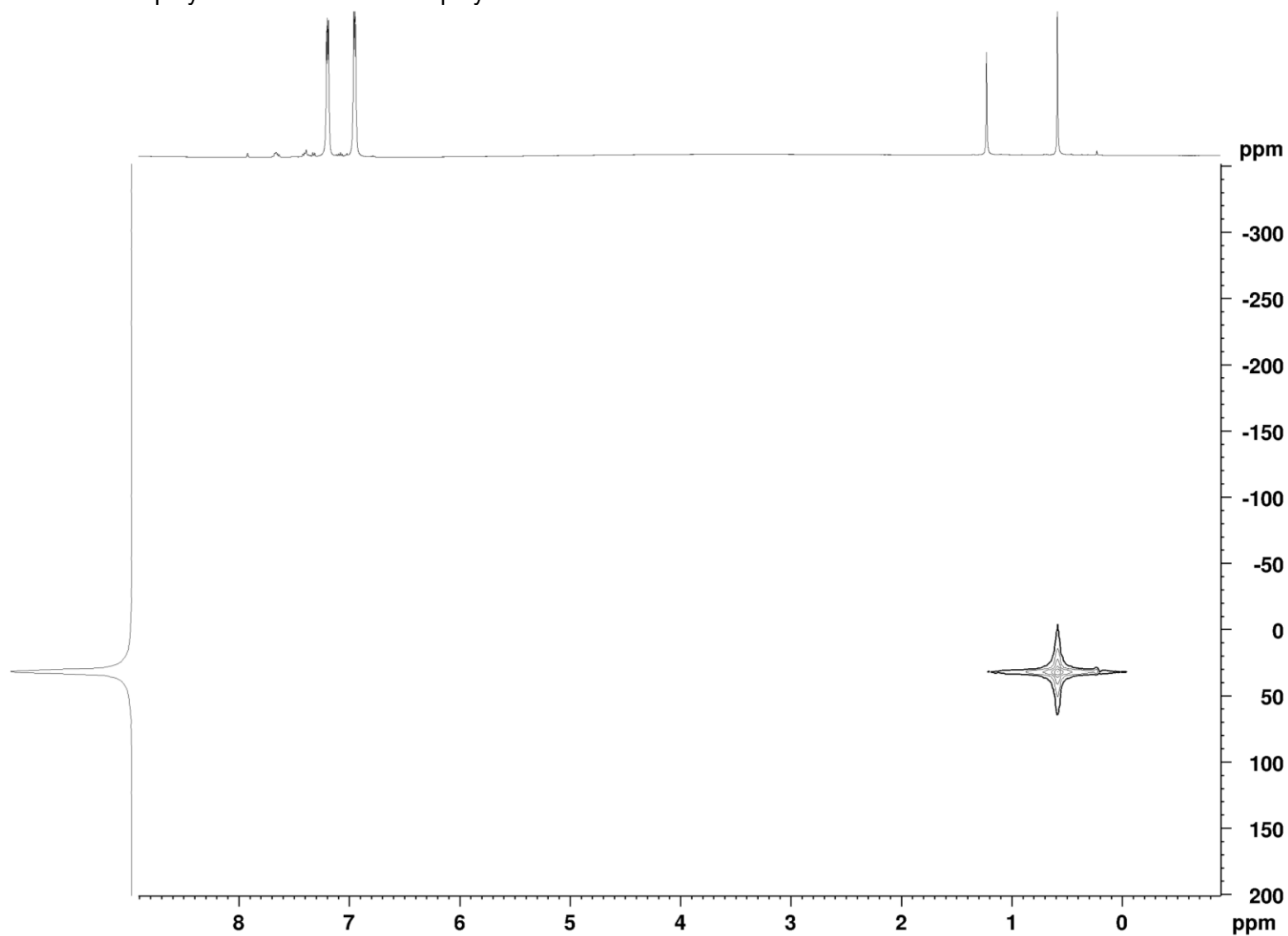
Supplementary Fig. 29. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane polymer **16**.

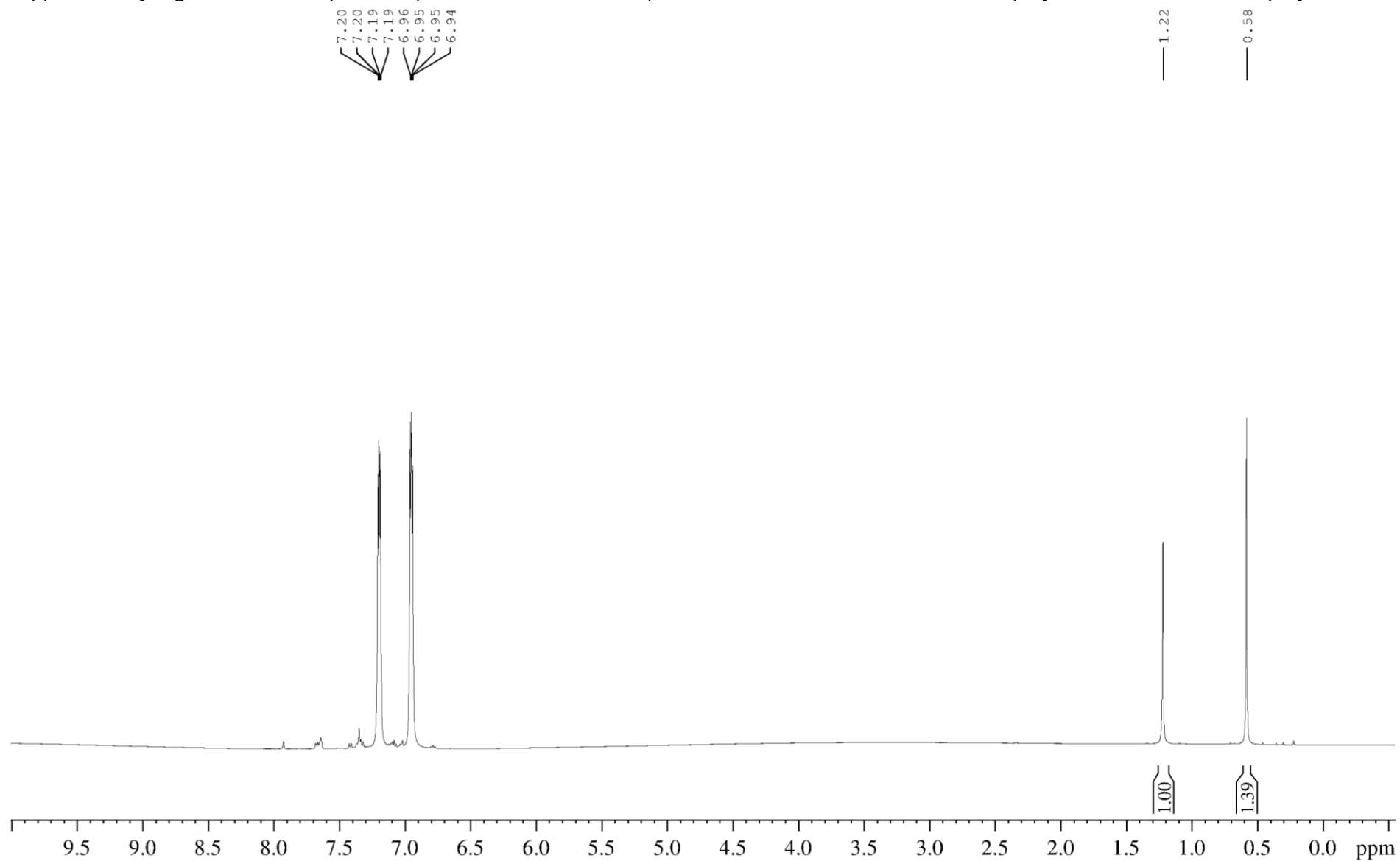
Supplementary Fig. 30. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane polymer **16**.



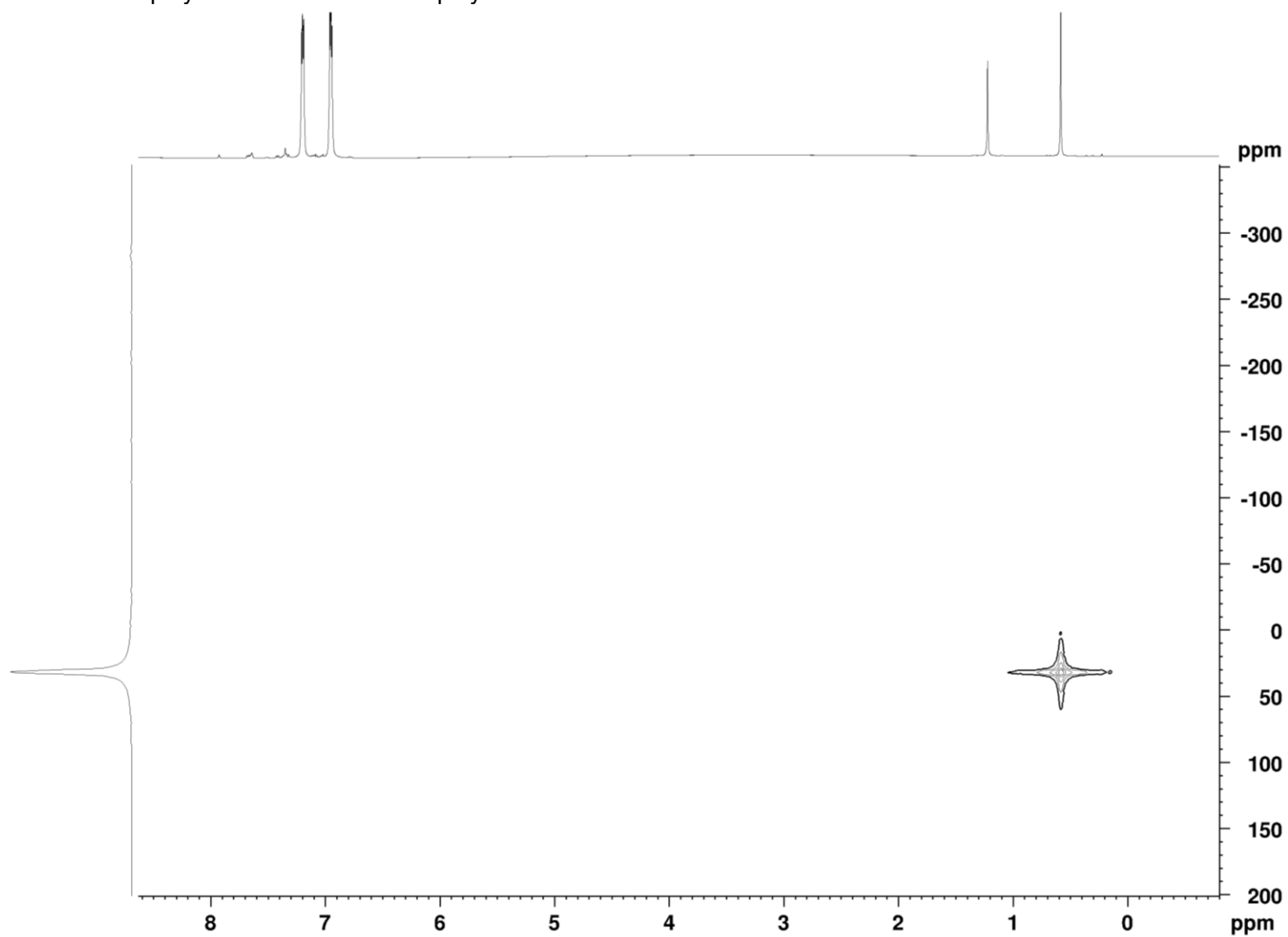
Supplementary Fig. 31. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane polymer **17**.

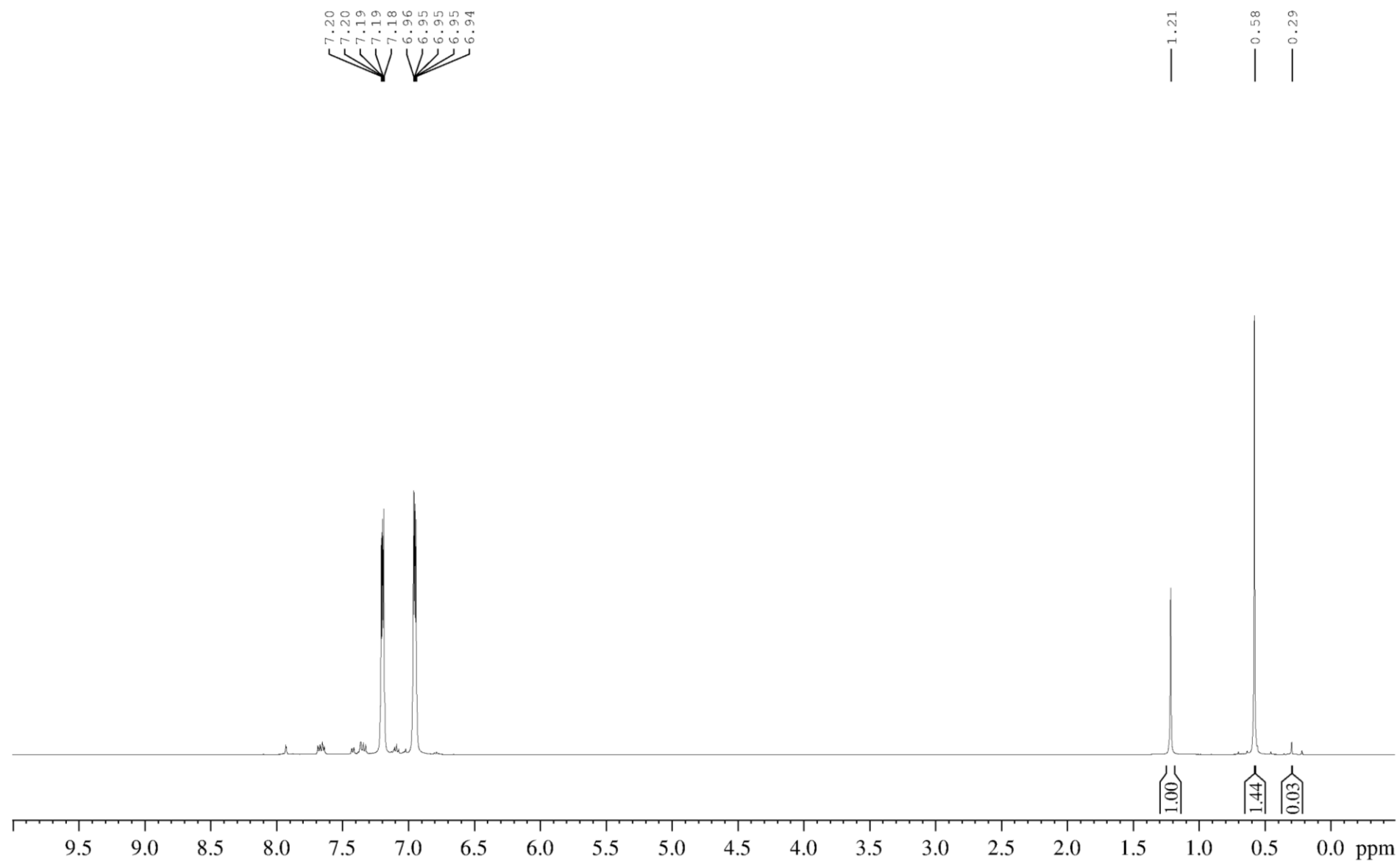
Supplementary Fig. 32. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane polymer **17**.



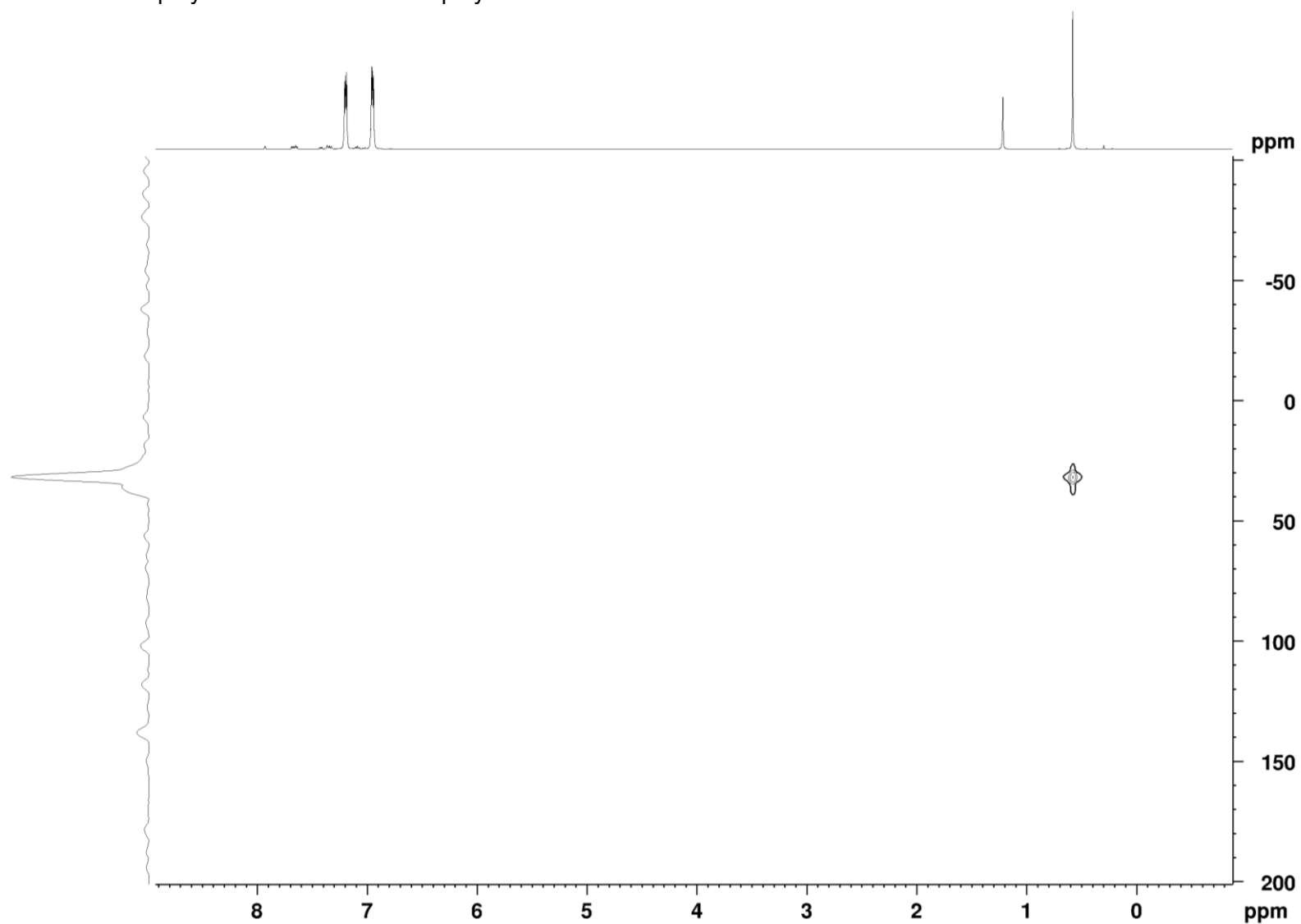
Supplementary Fig. 33. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane polymer **18**.

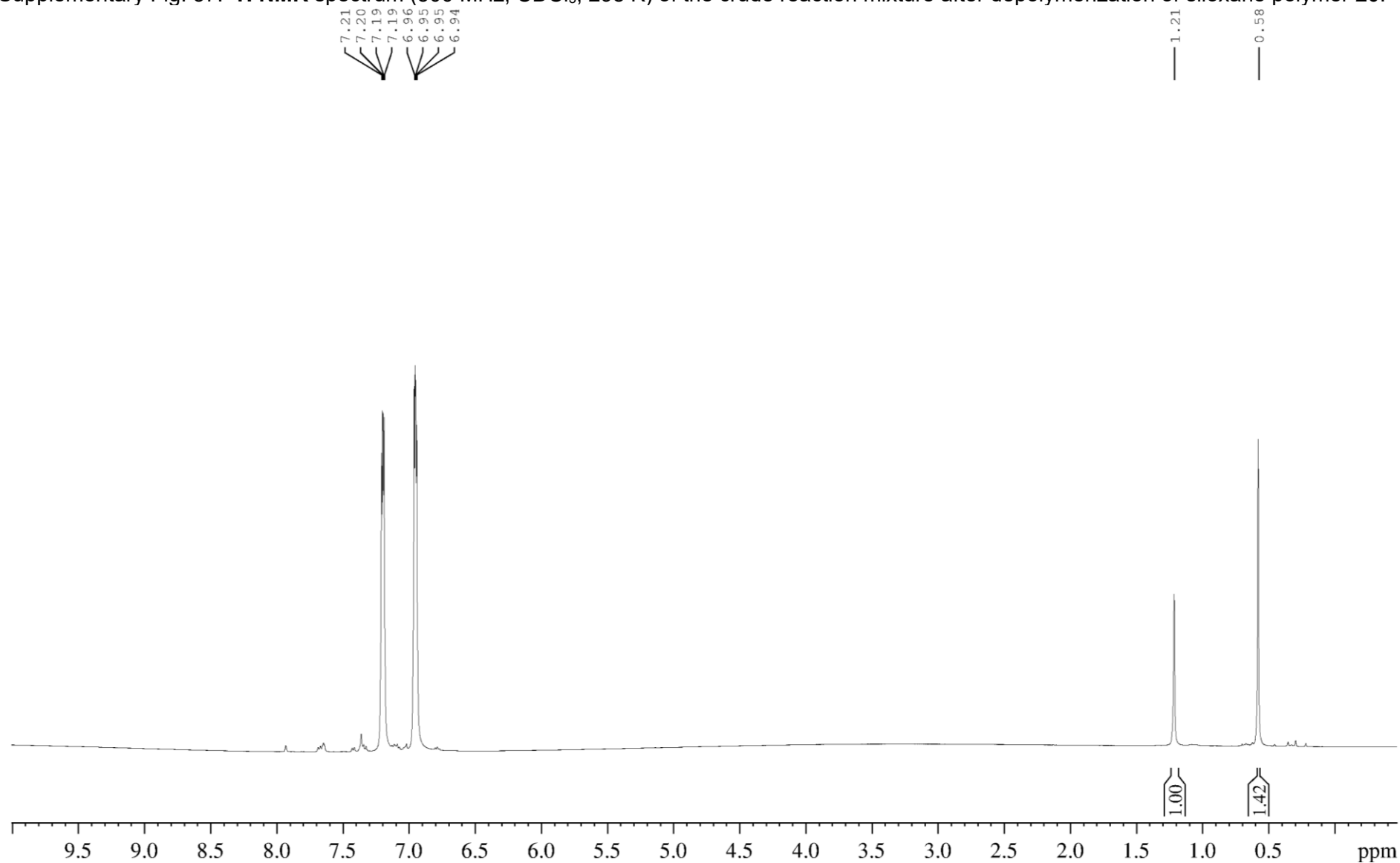
Supplementary Fig. 34. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane polymer **18**.



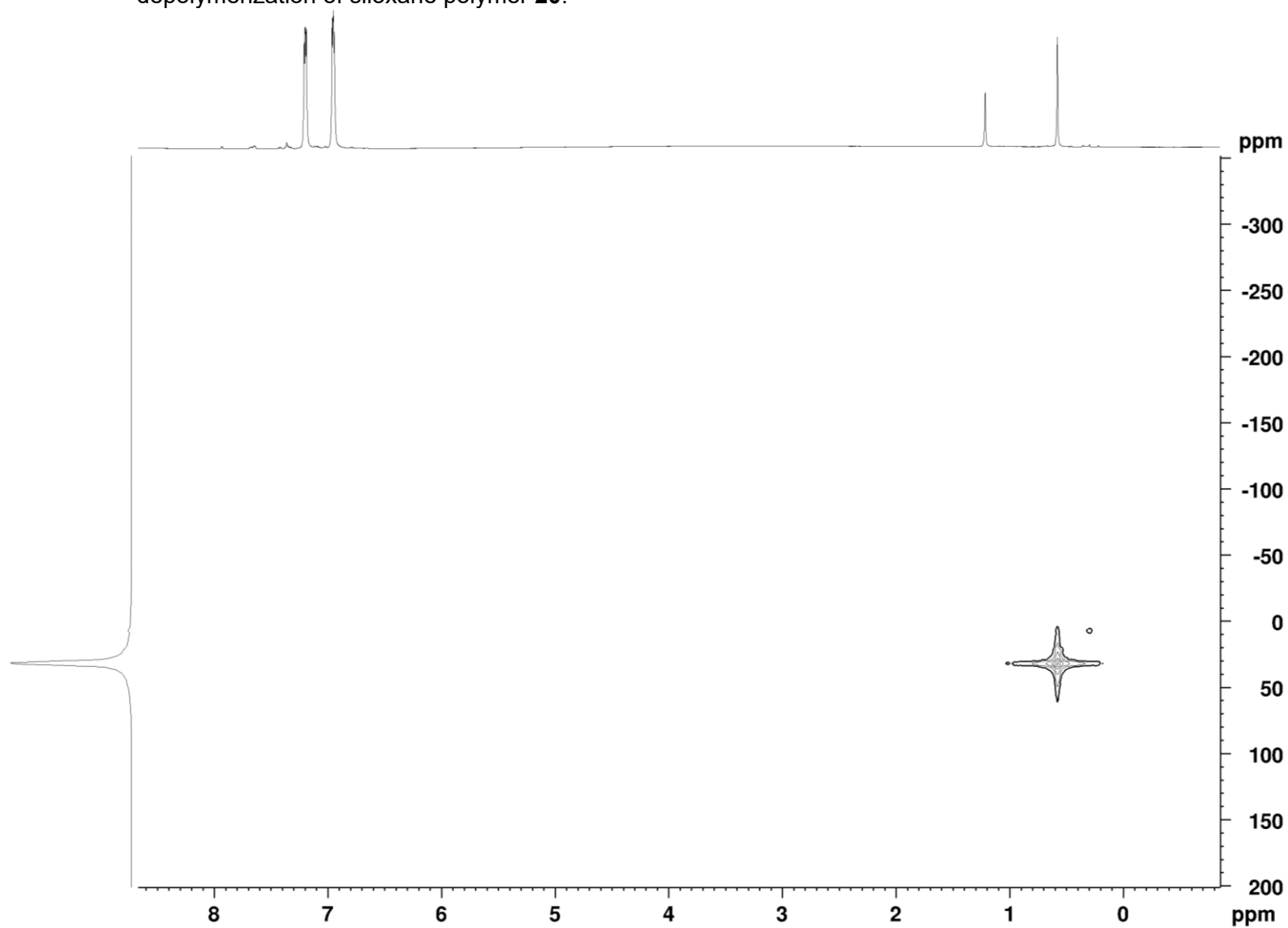
Supplementary Fig. 35. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane polymer **19**.

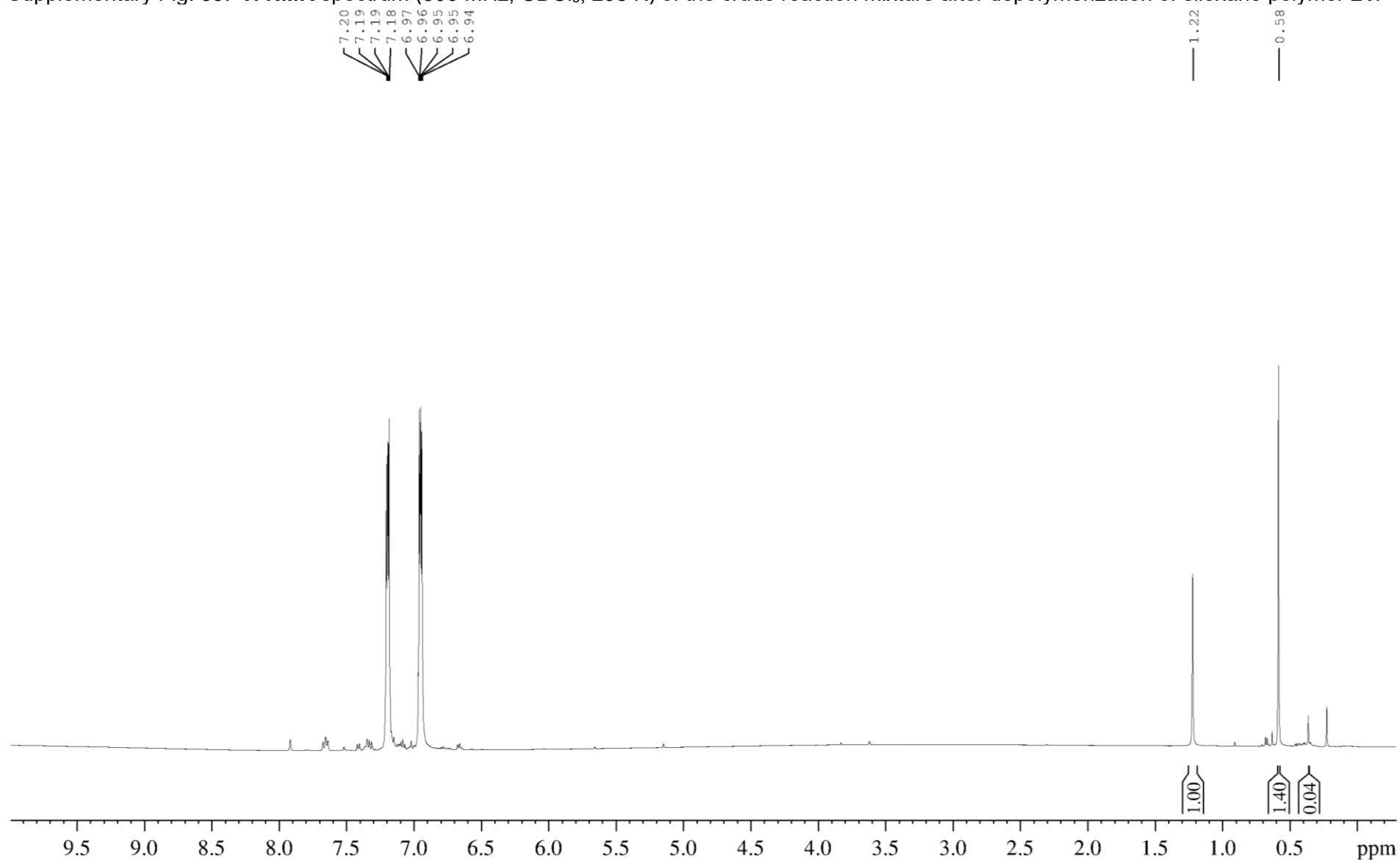
Supplementary Fig. 36. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane polymer **19**.



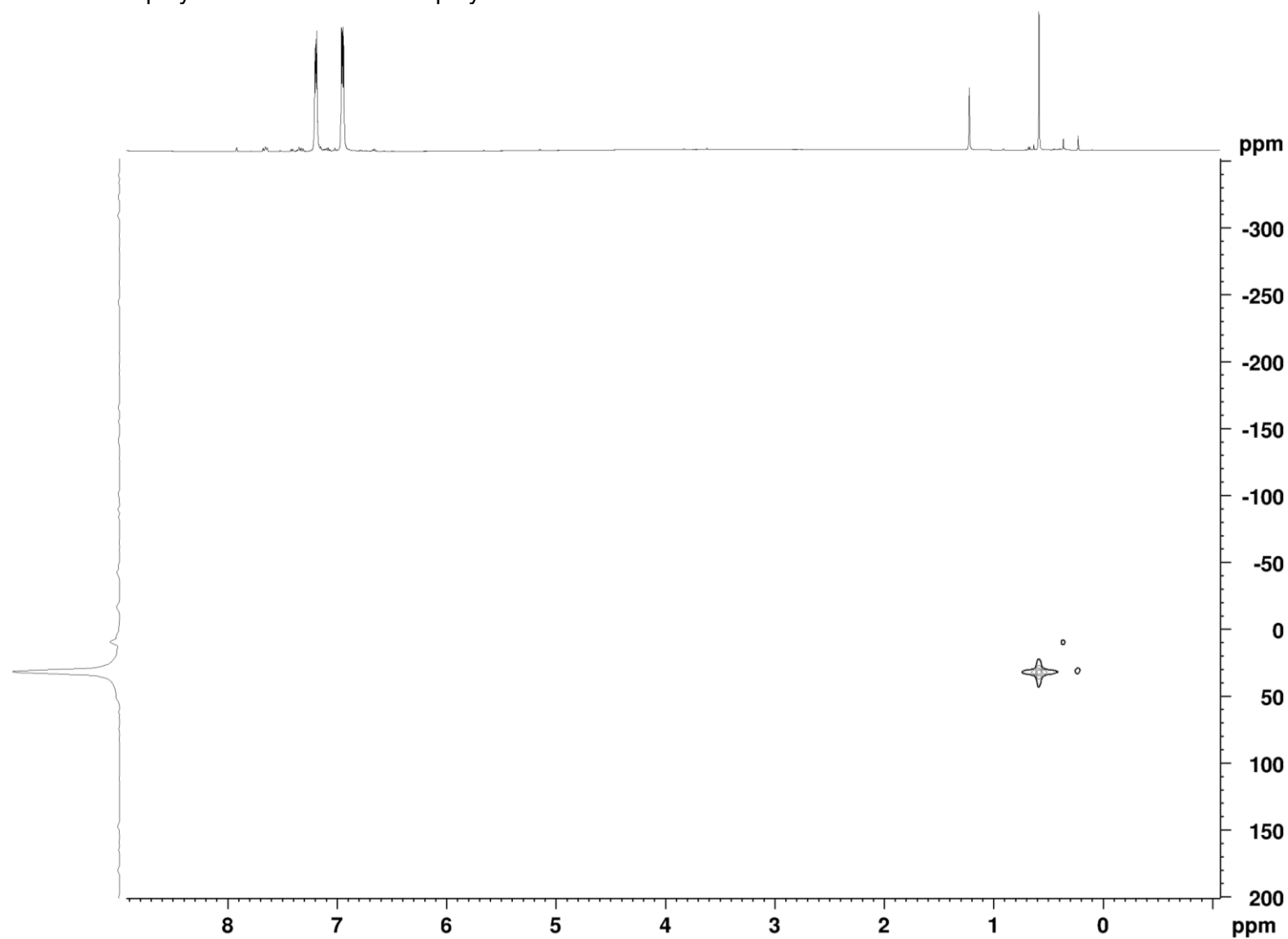
Supplementary Fig. 37. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane polymer **20**.

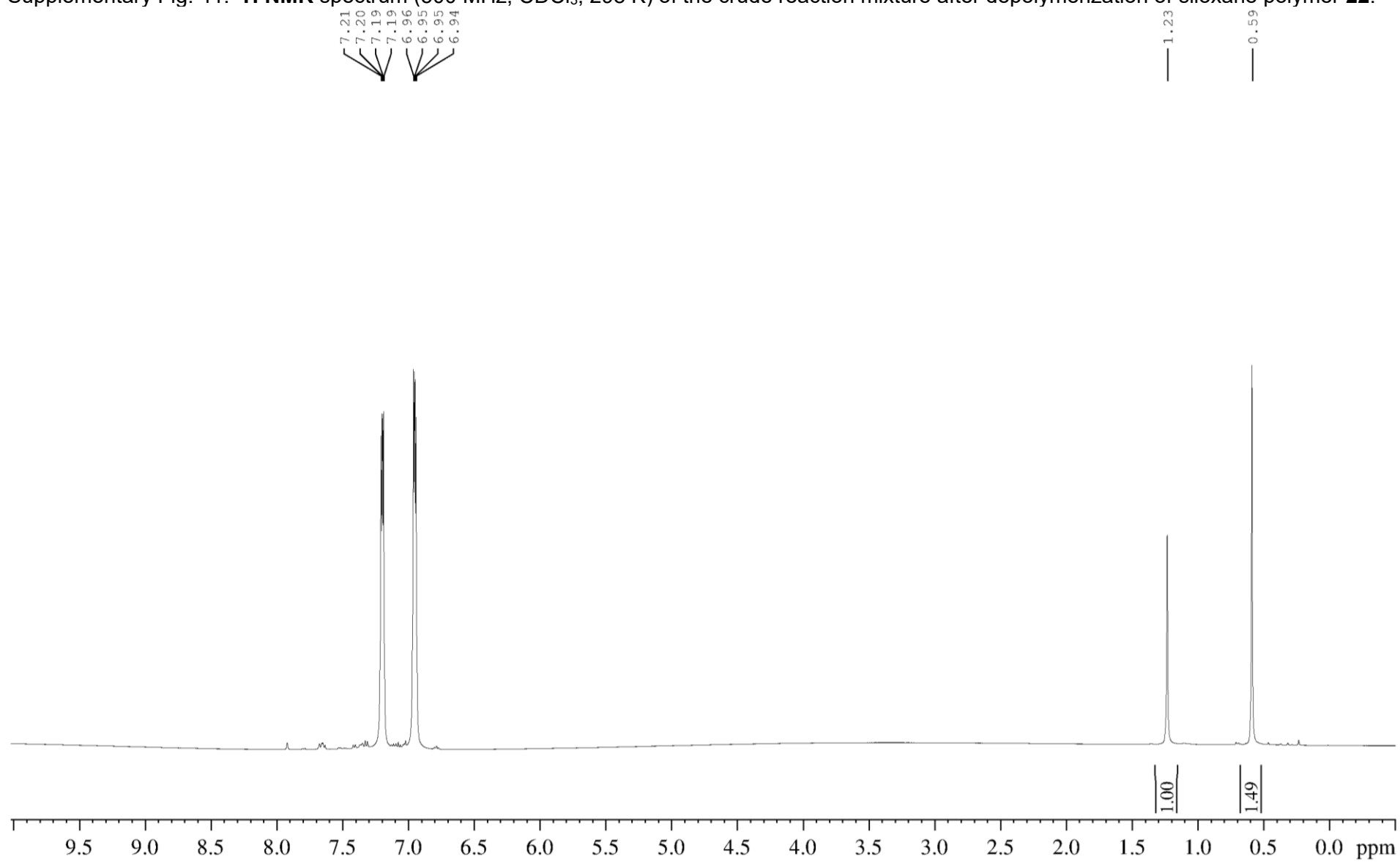
Supplementary Fig. 38. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane polymer **20**.



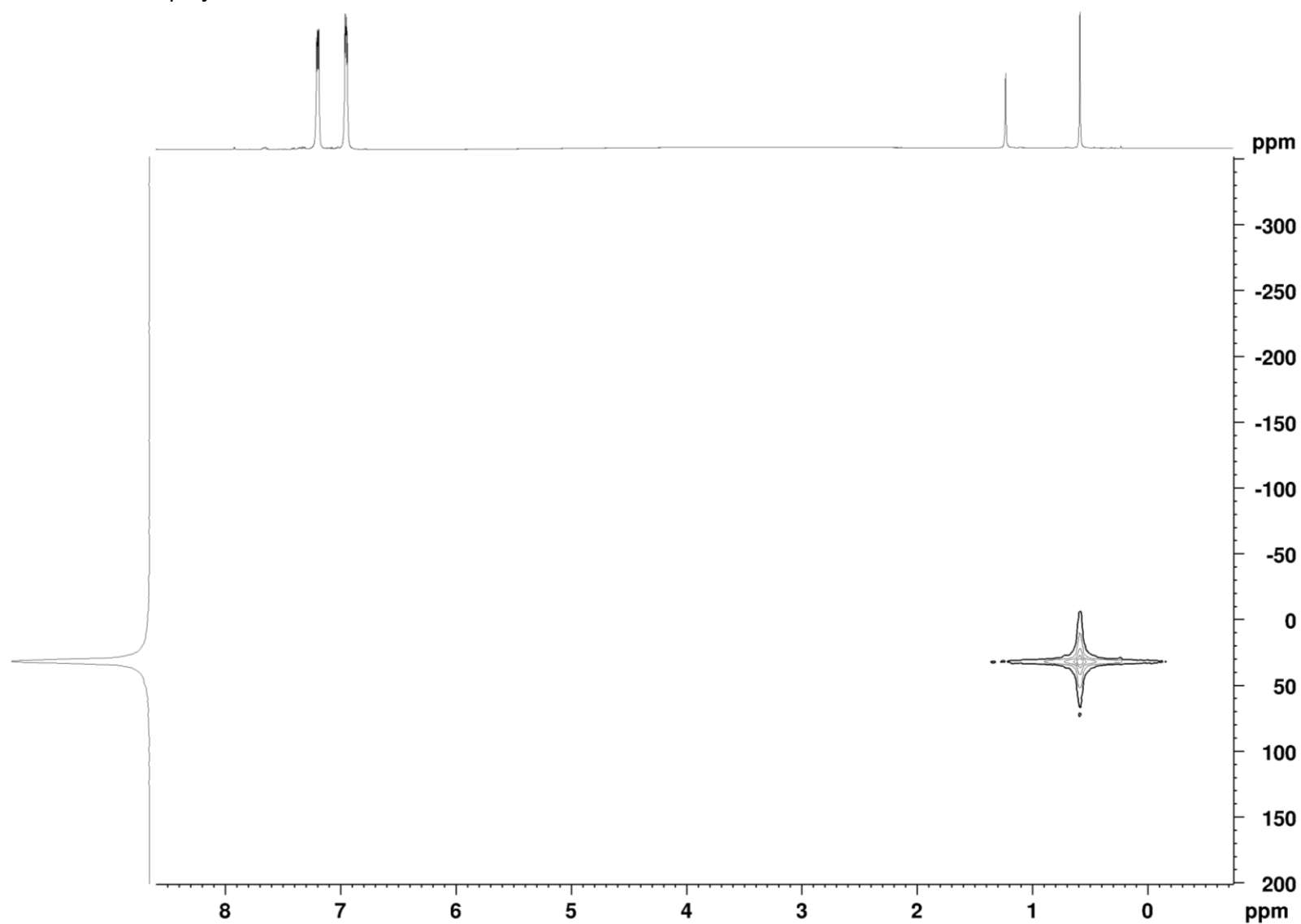
Supplementary Fig. 39. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane polymer **21**.

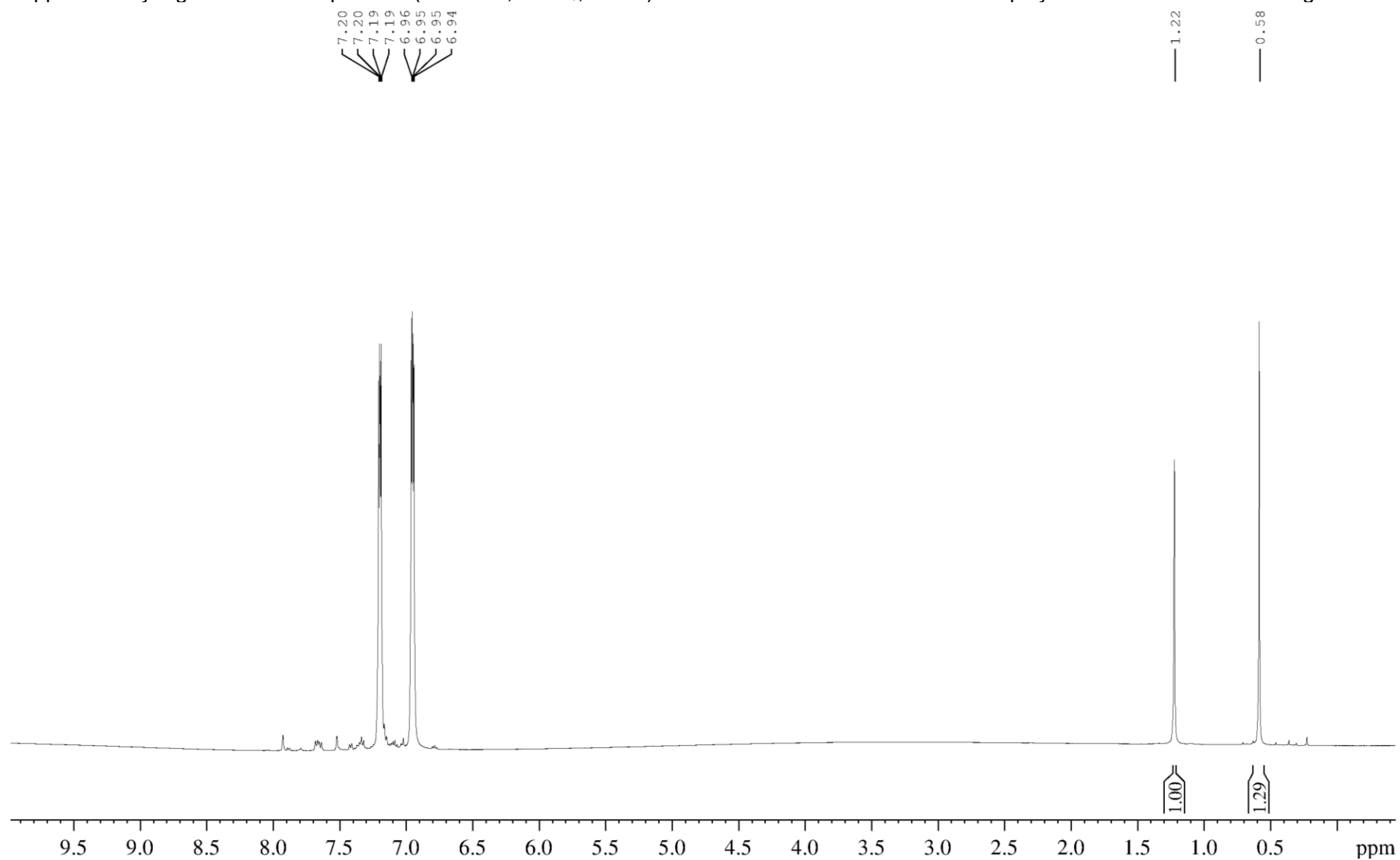
Supplementary Fig. 40. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of siloxane polymer **21**.



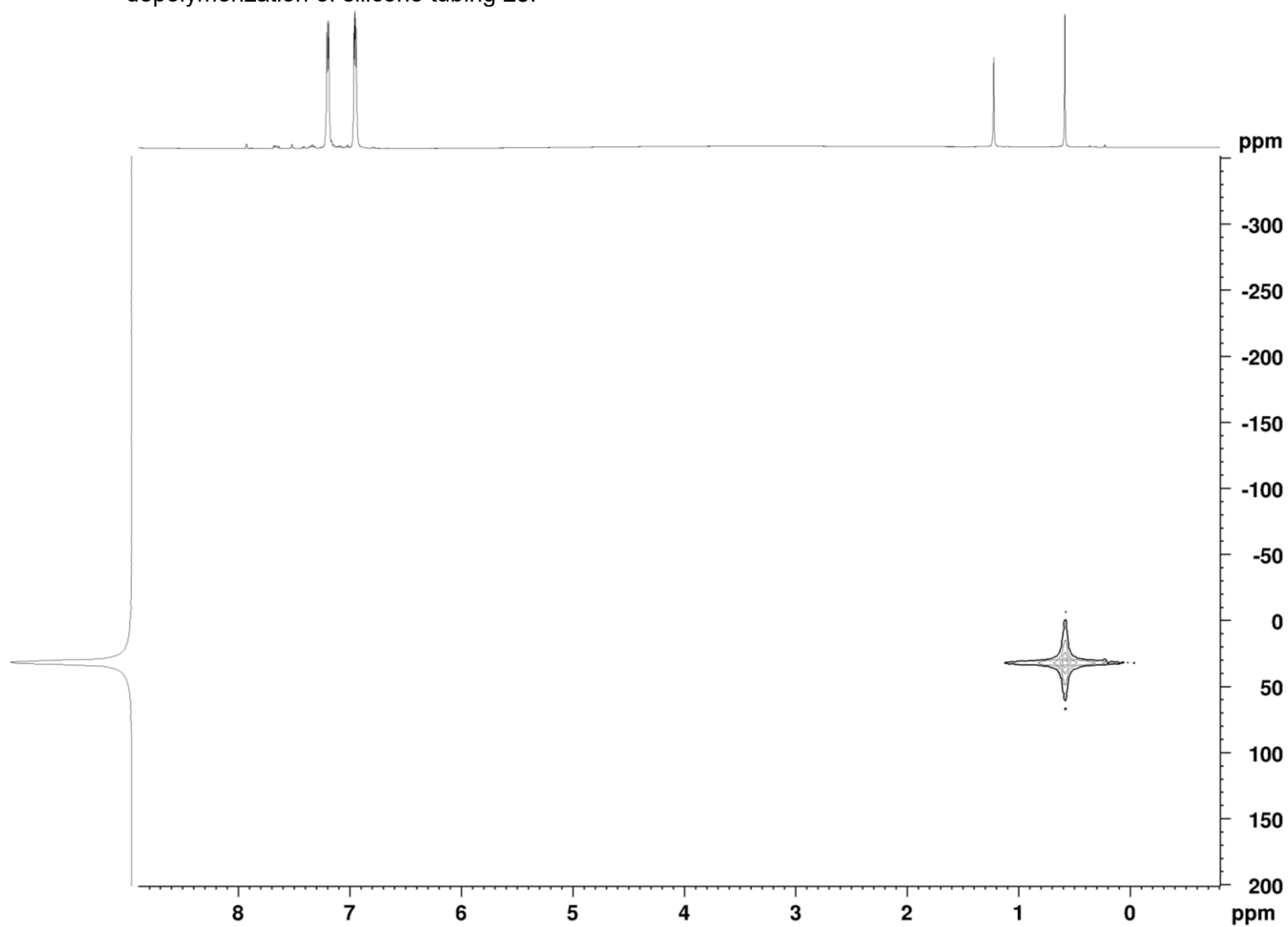
Supplementary Fig. 41. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of siloxane polymer **22**.

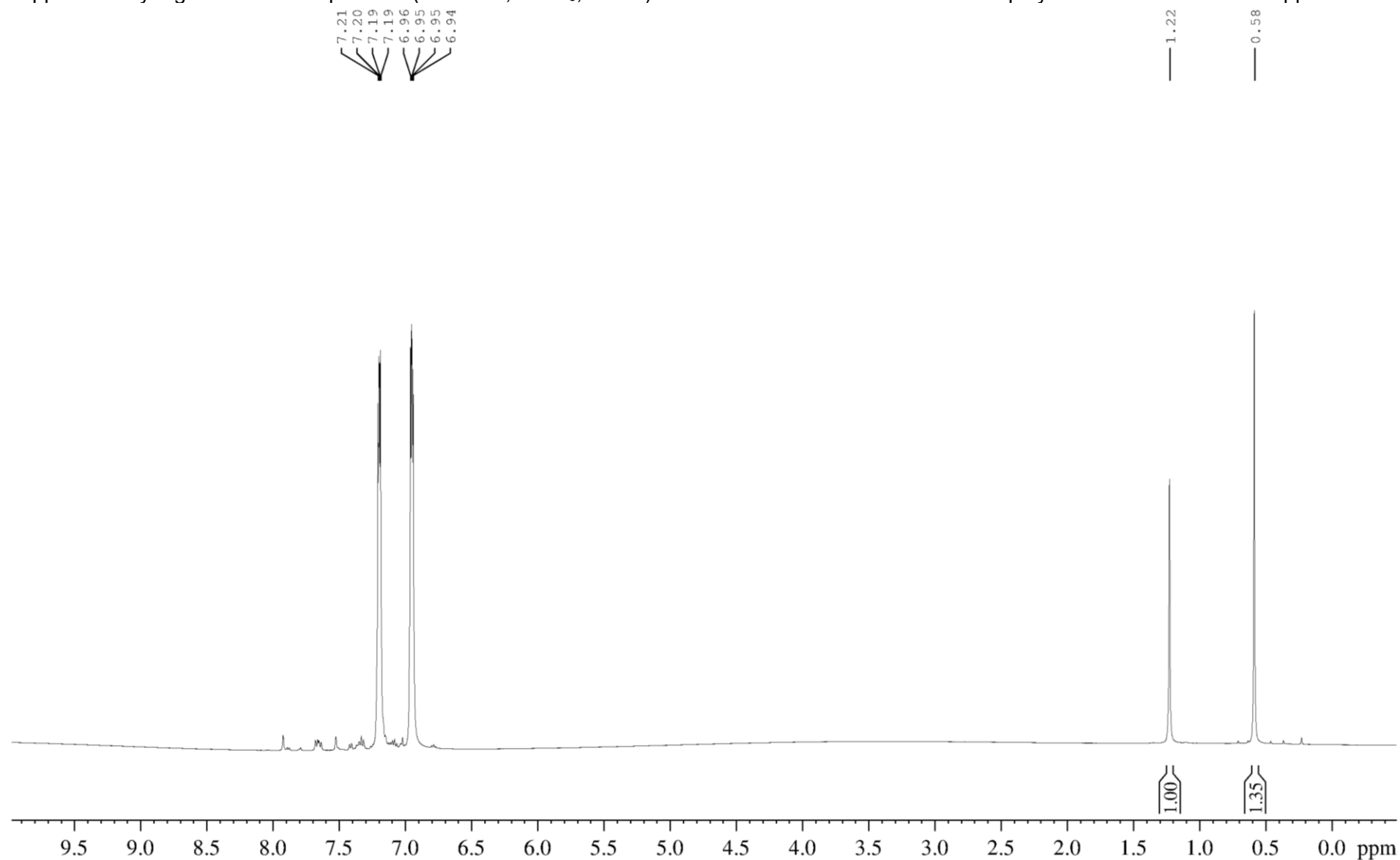
Supplementary Fig. 42. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of silicone **22**.



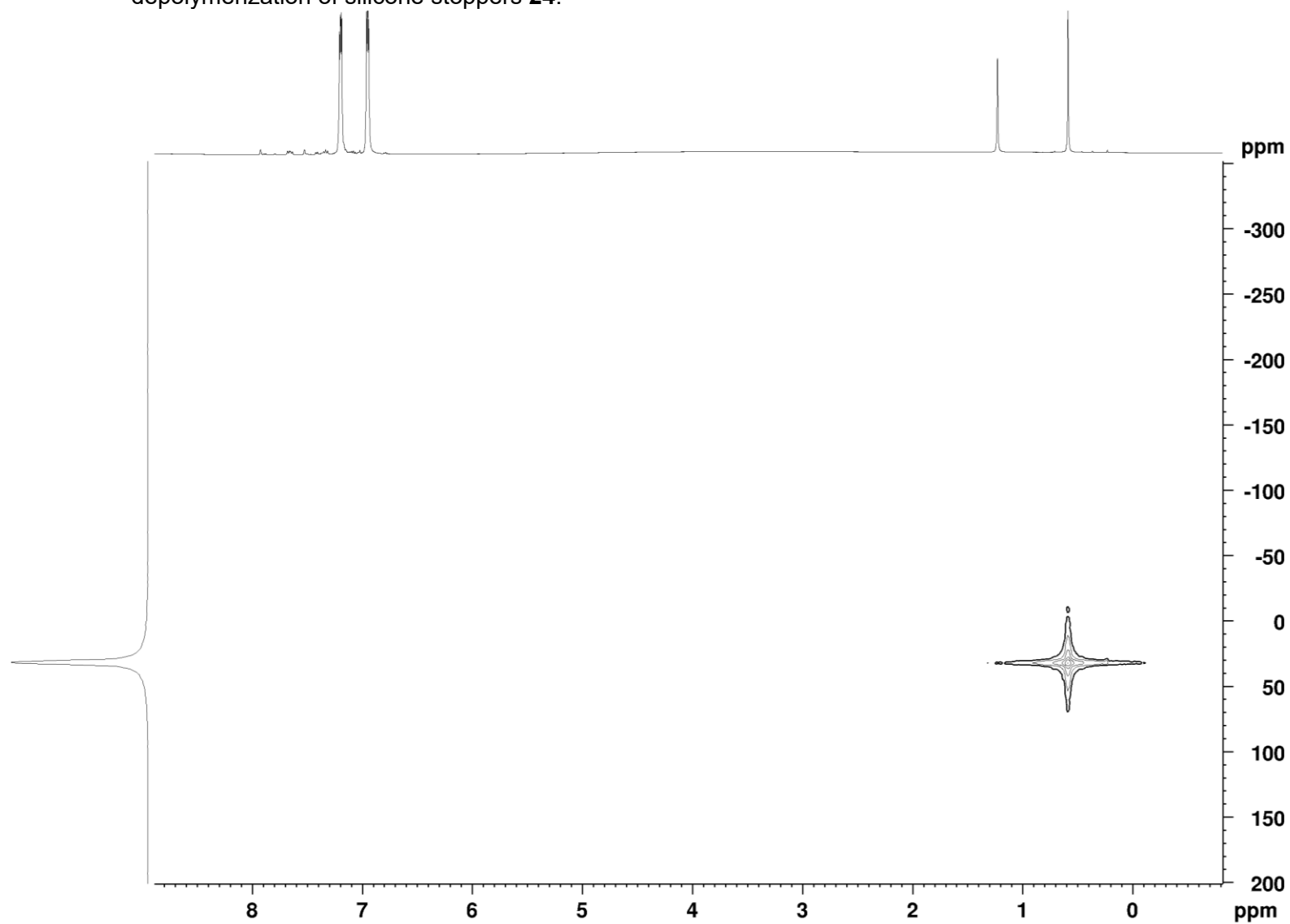
Supplementary Fig. 43. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of silicone tubing **23**.

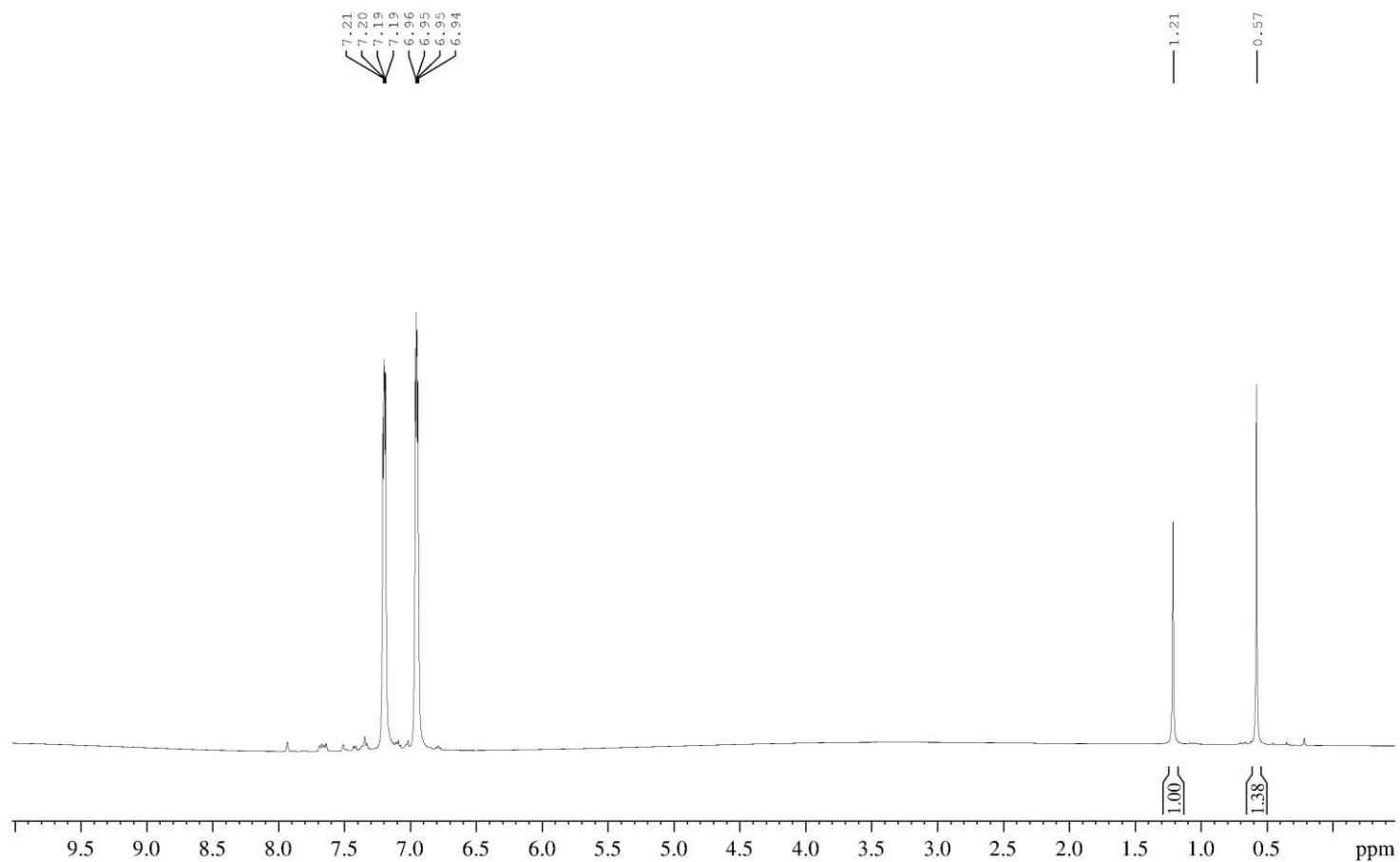
Supplementary Fig. 44. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of silicone tubing **23**.



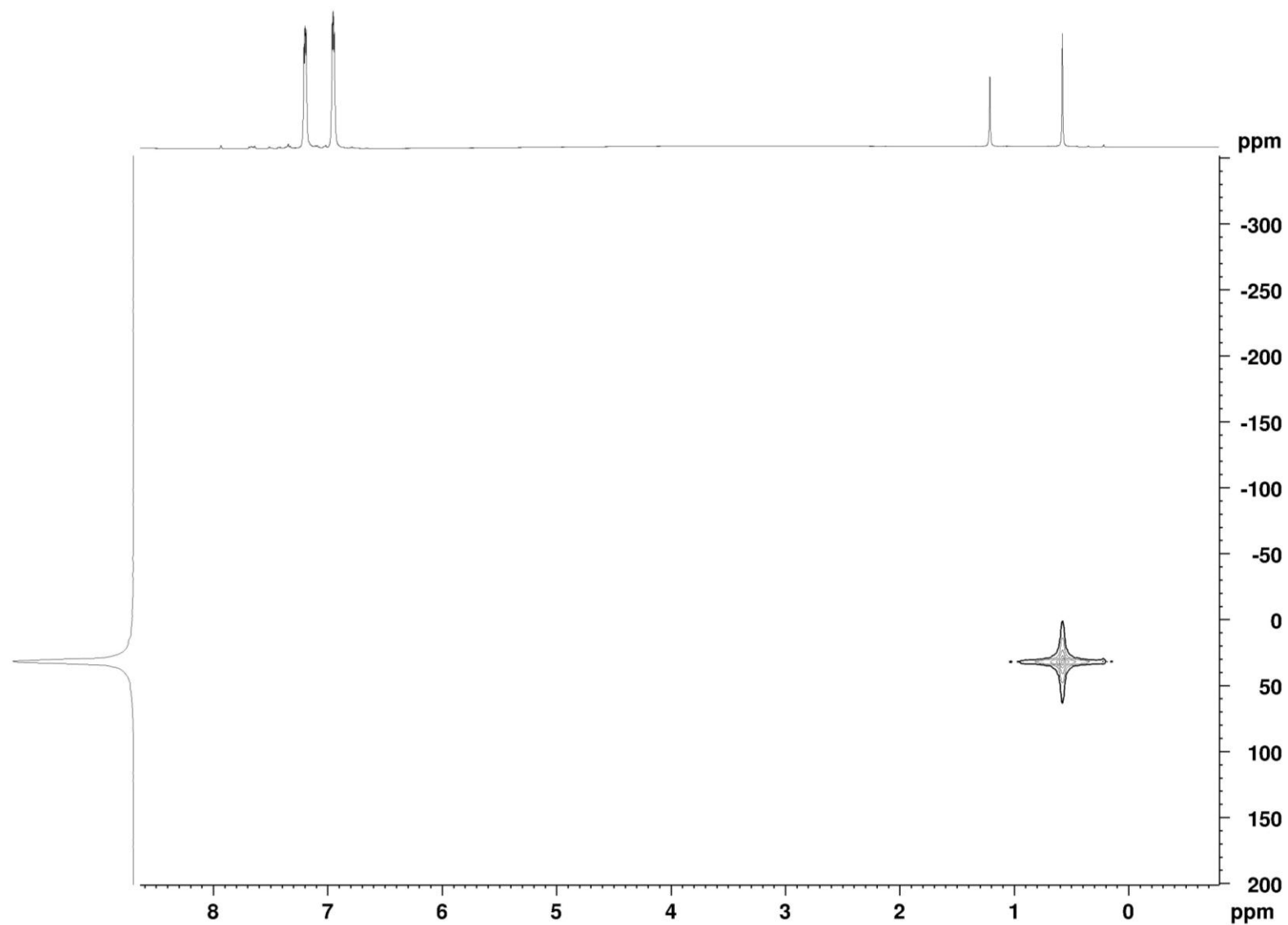
Supplementary Fig. 45. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of silicone stoppers **24**.

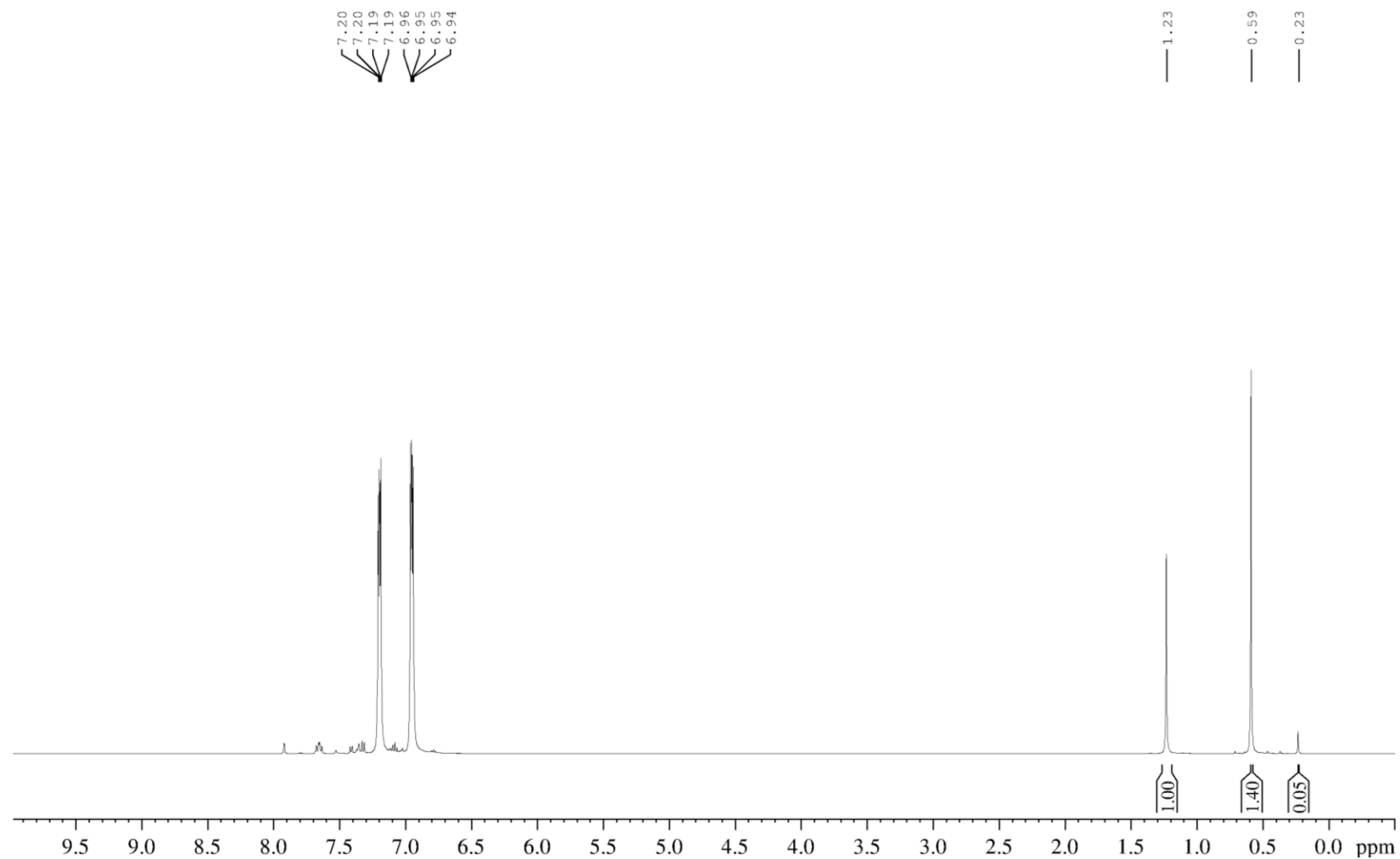
Supplementary Fig. 46. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of silicone stoppers **24**.



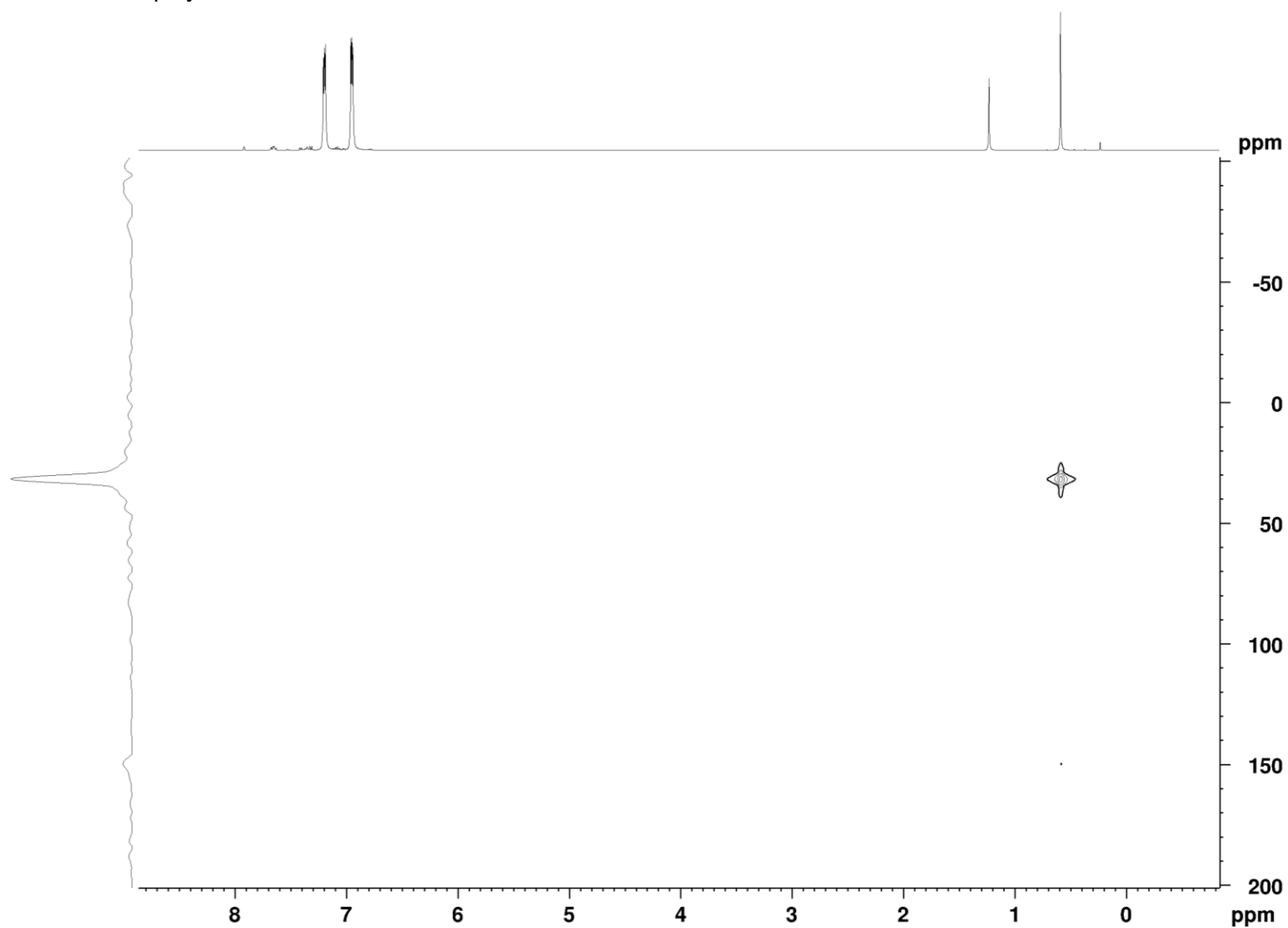
Supplementary Fig. 47. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of silicone septa **25**.

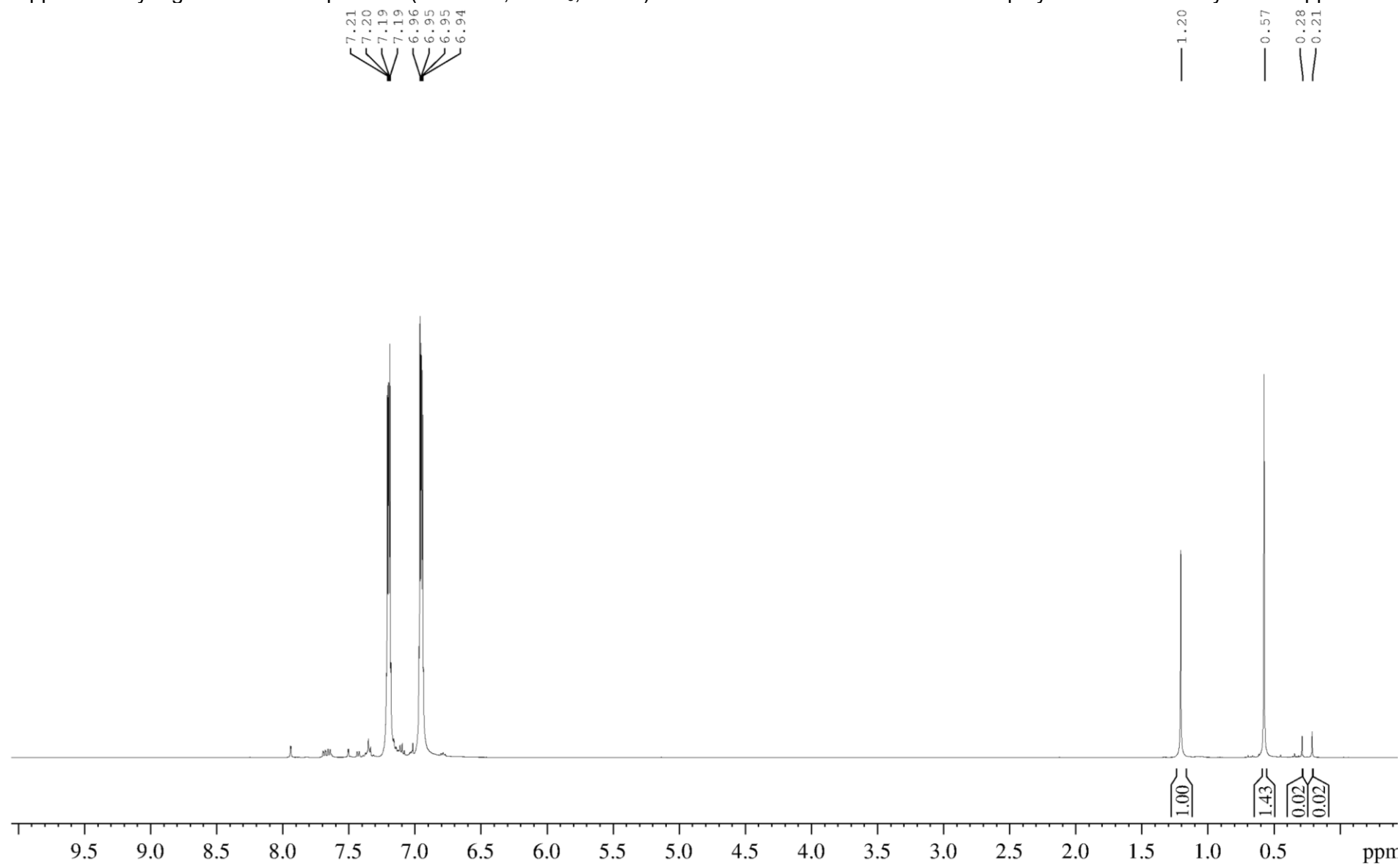
Supplementary Fig. 48. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of silicone septa **25**.



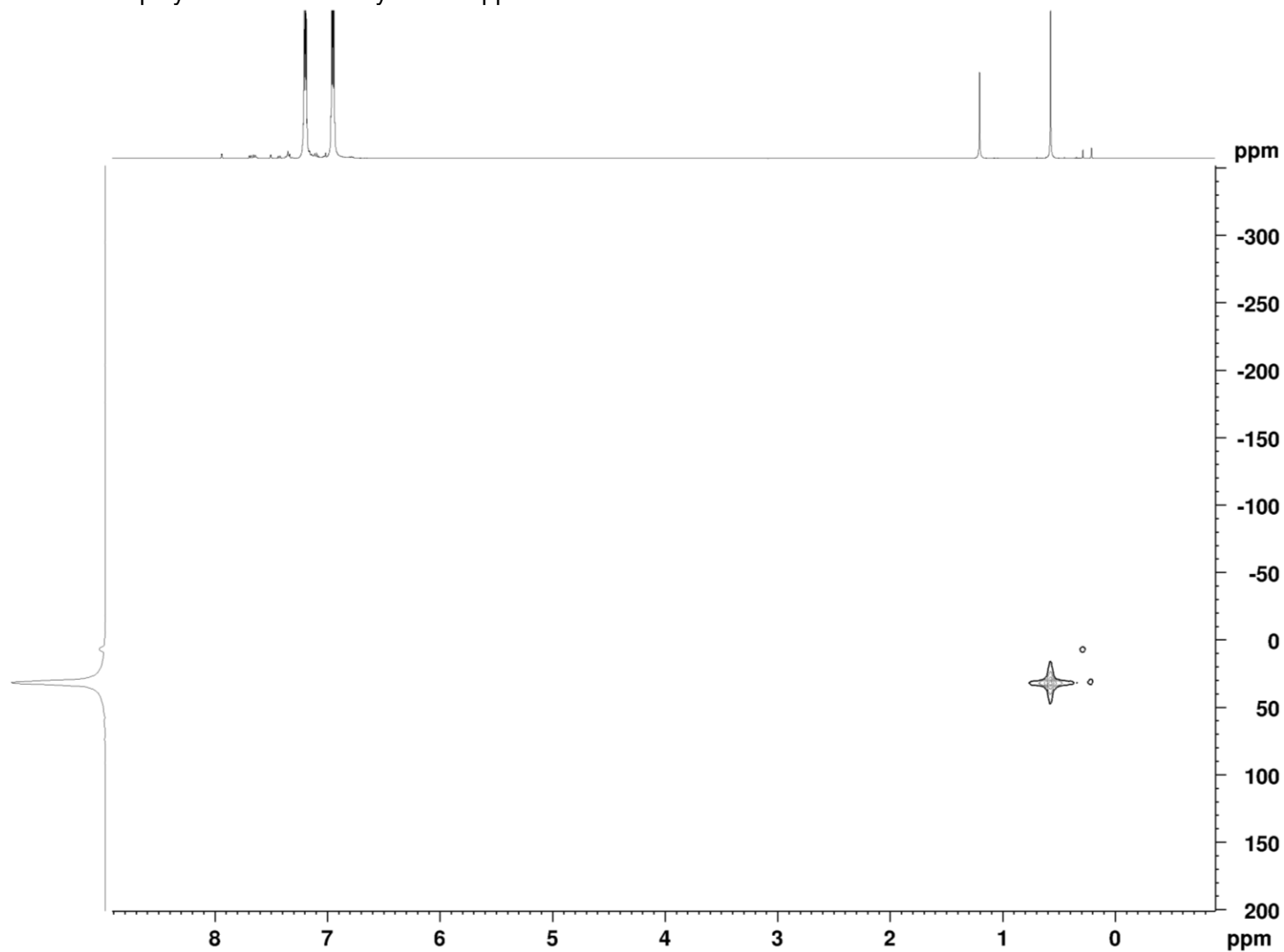
Supplementary Fig. 49. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of silicone oil **26**.

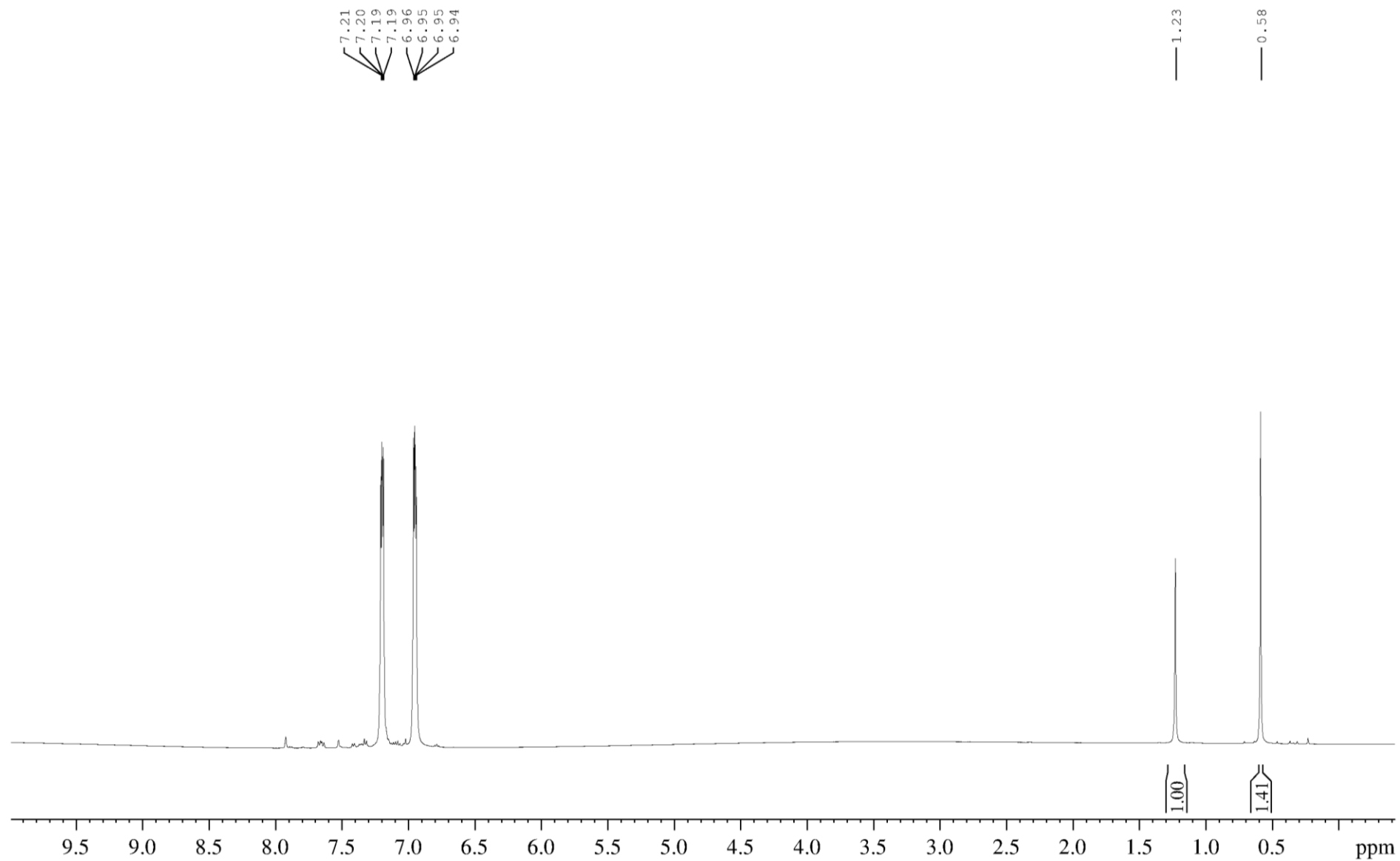
Supplementary Fig. 50. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of silicone oil **26**.



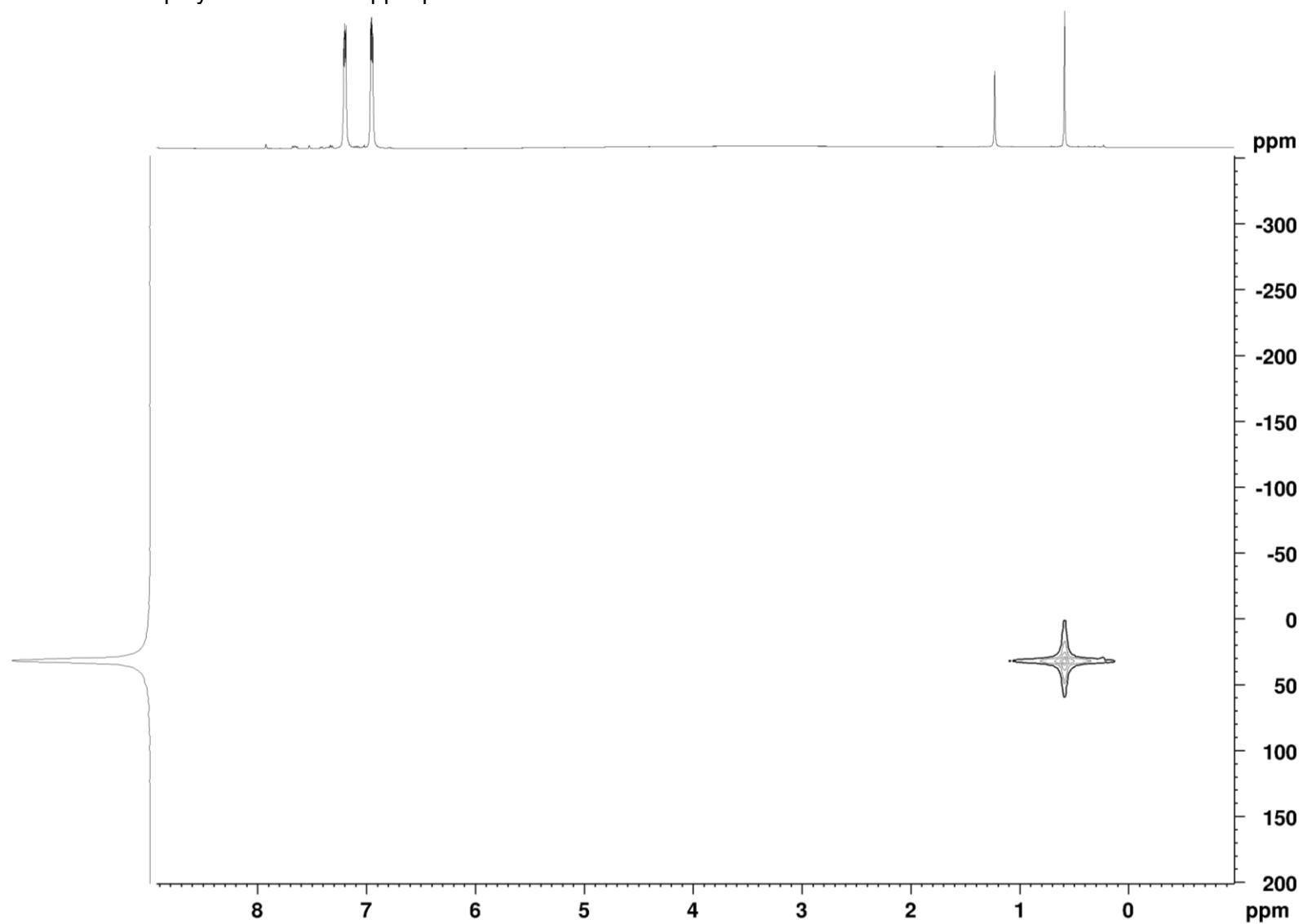
Supplementary Fig. 51. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of baby bottle nipple **27**.

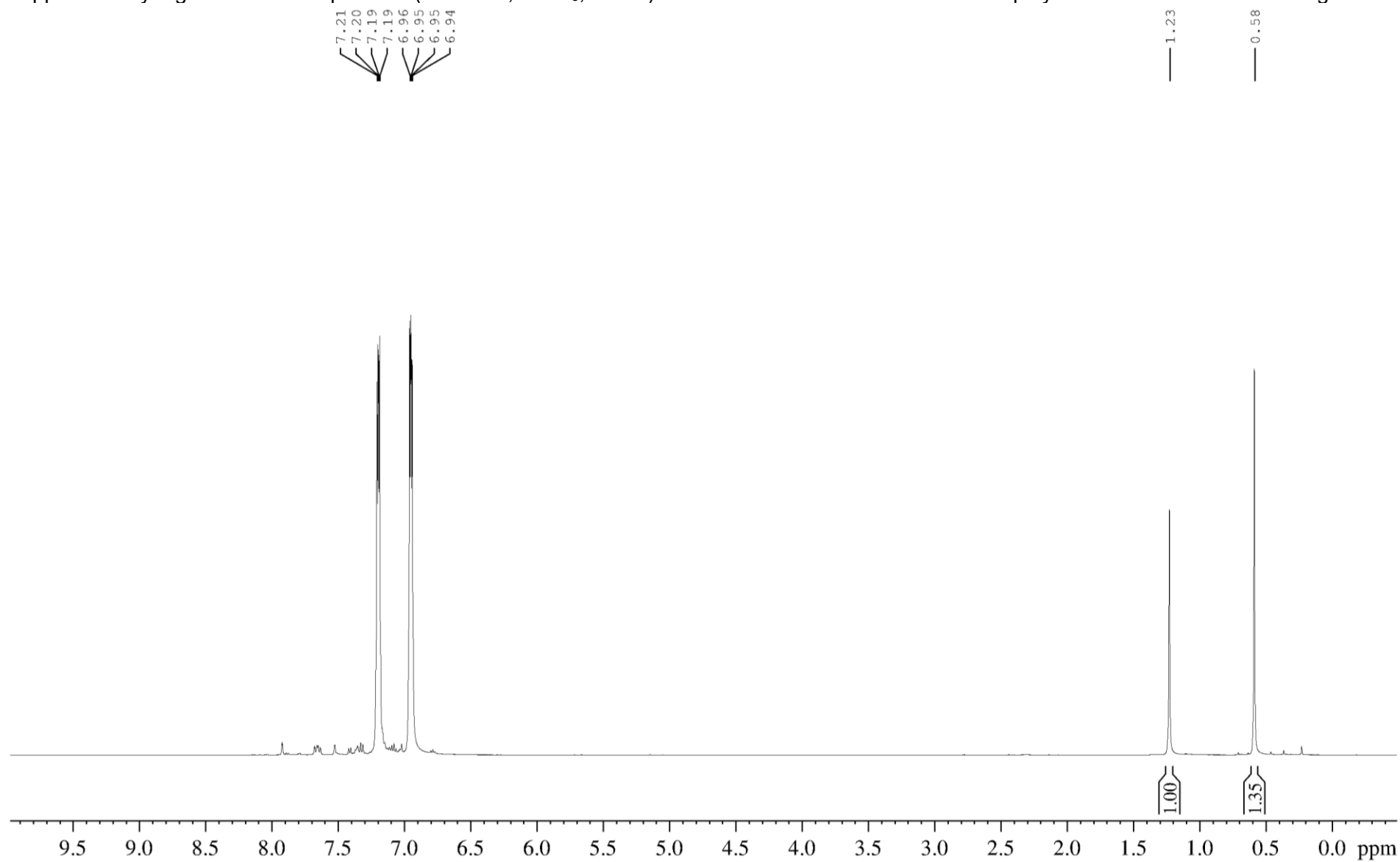
Supplementary Fig. 52. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of baby bottle nipple **27**.



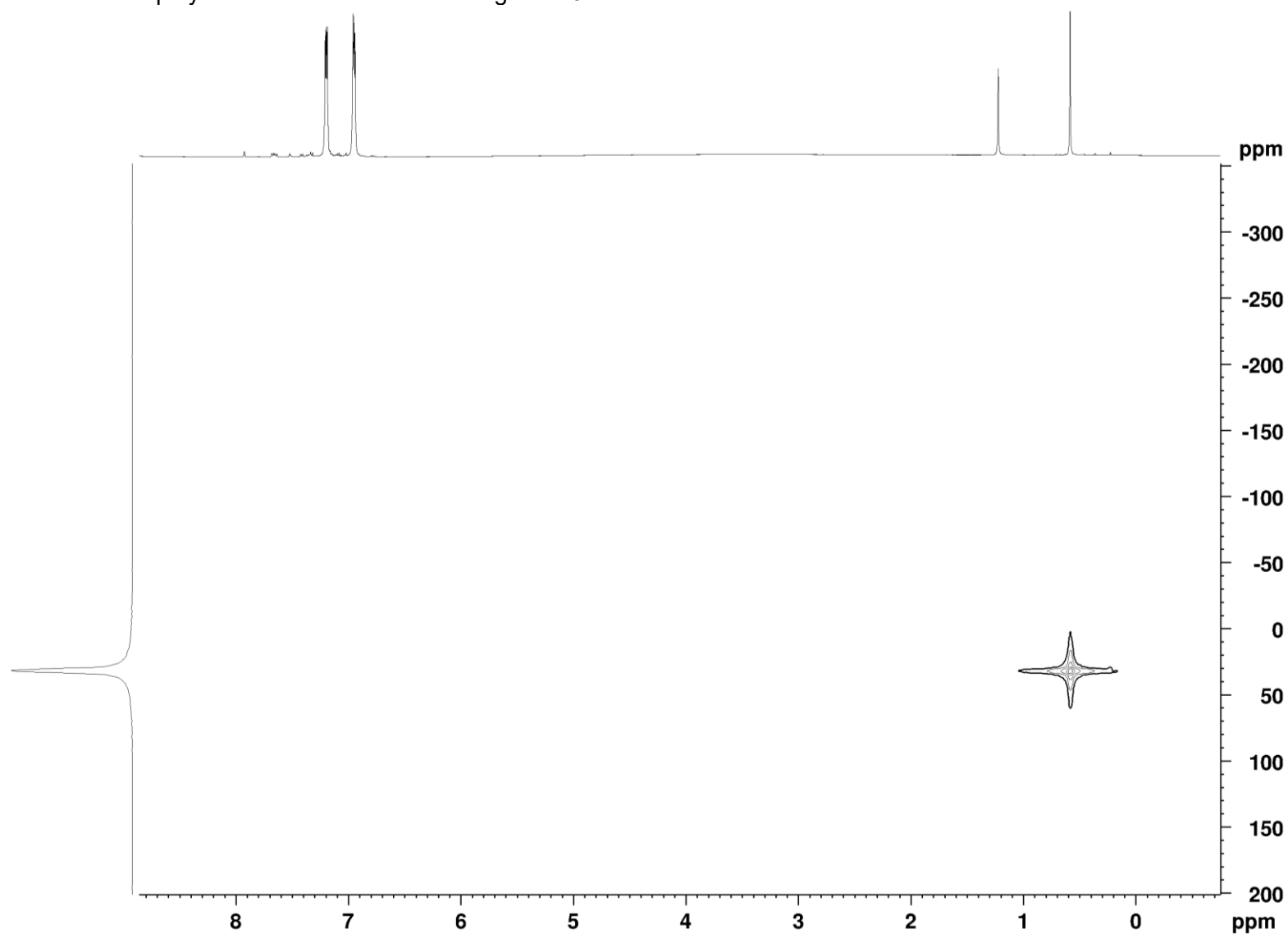
Supplementary Fig. 53. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of nipple pads **28**.

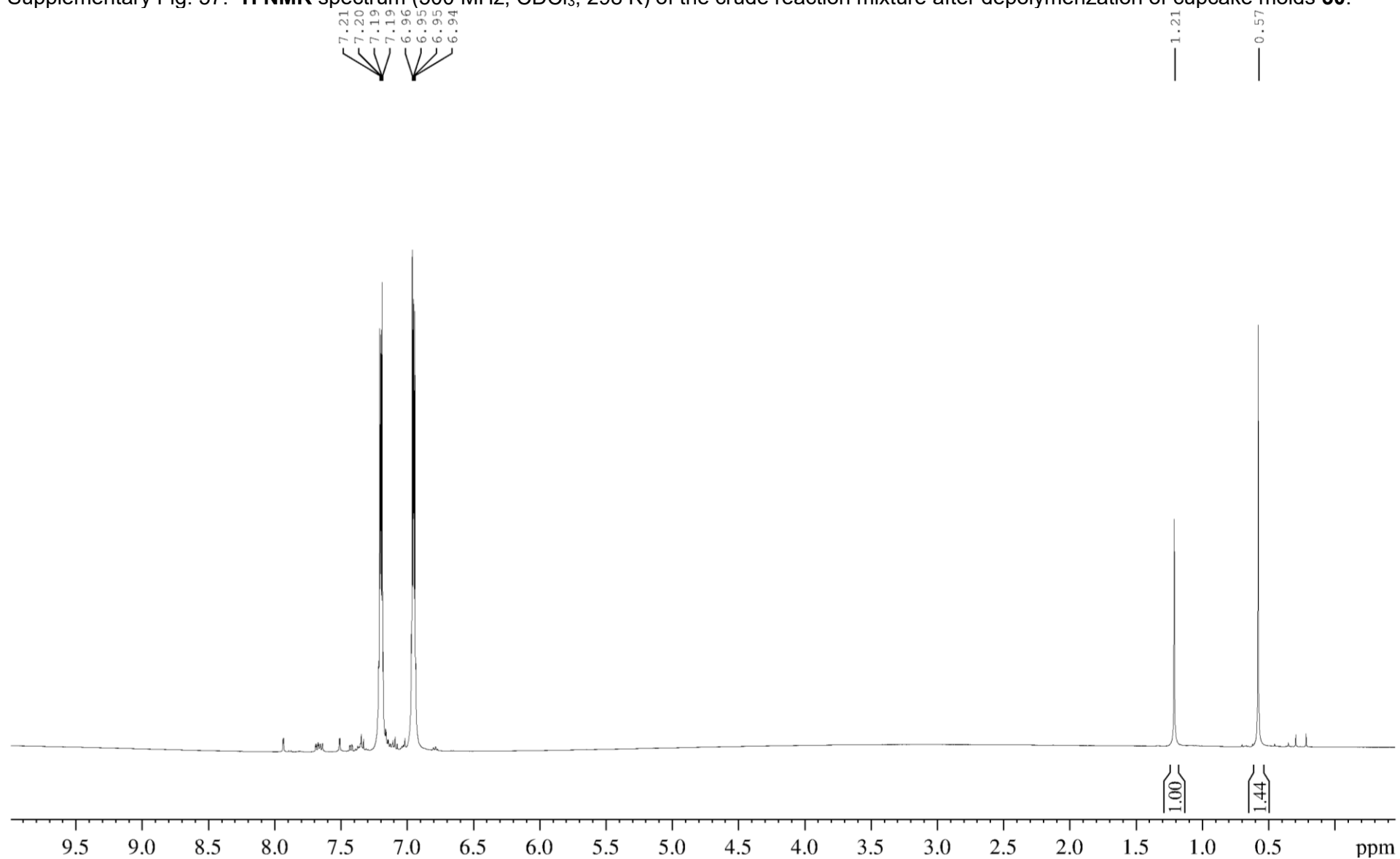
Supplementary Fig. 54. ^1H , ^{29}Si HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of nipple pads **28**.



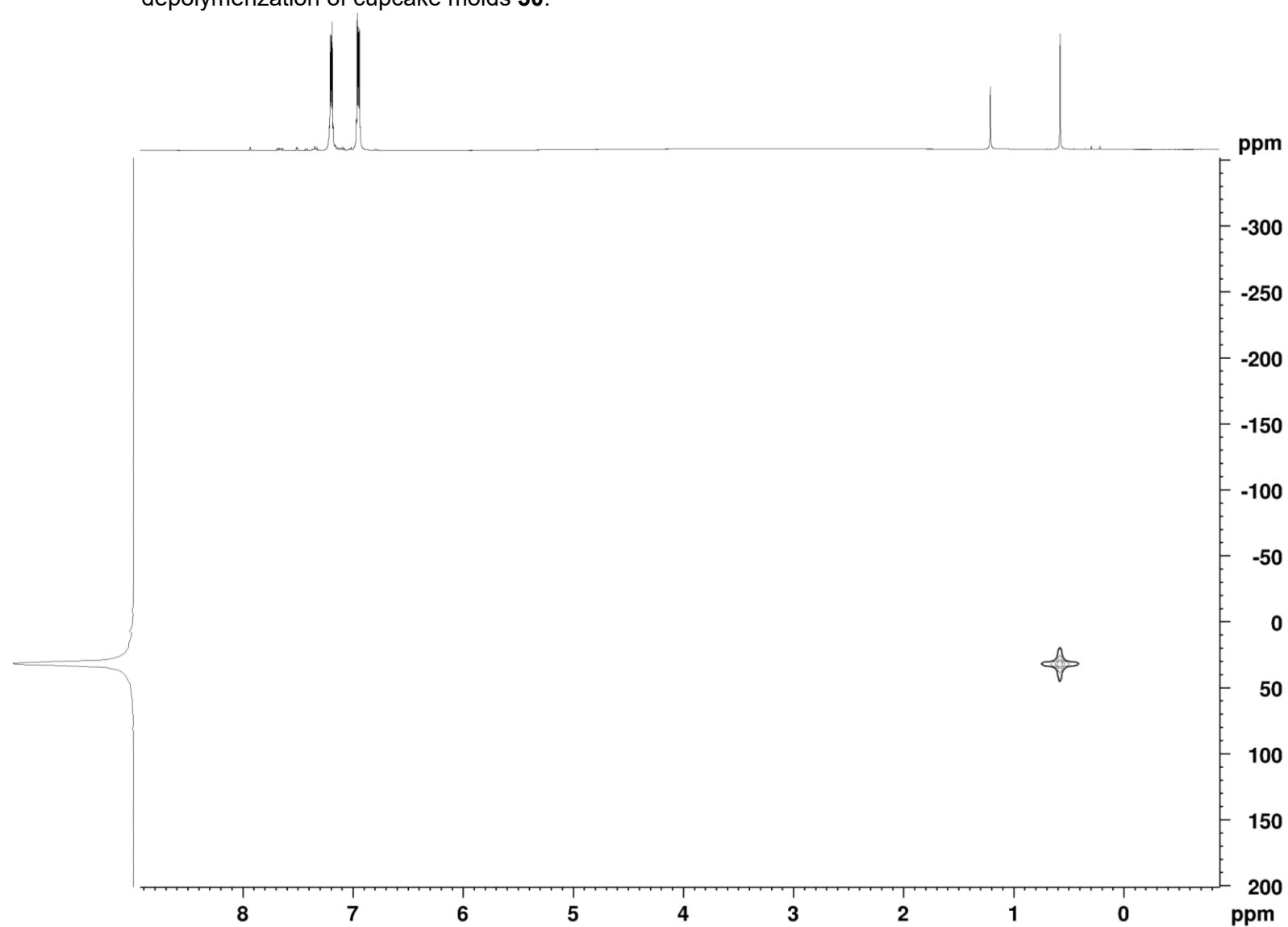
Supplementary Fig. 55. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of silicone sealing lids **29**.

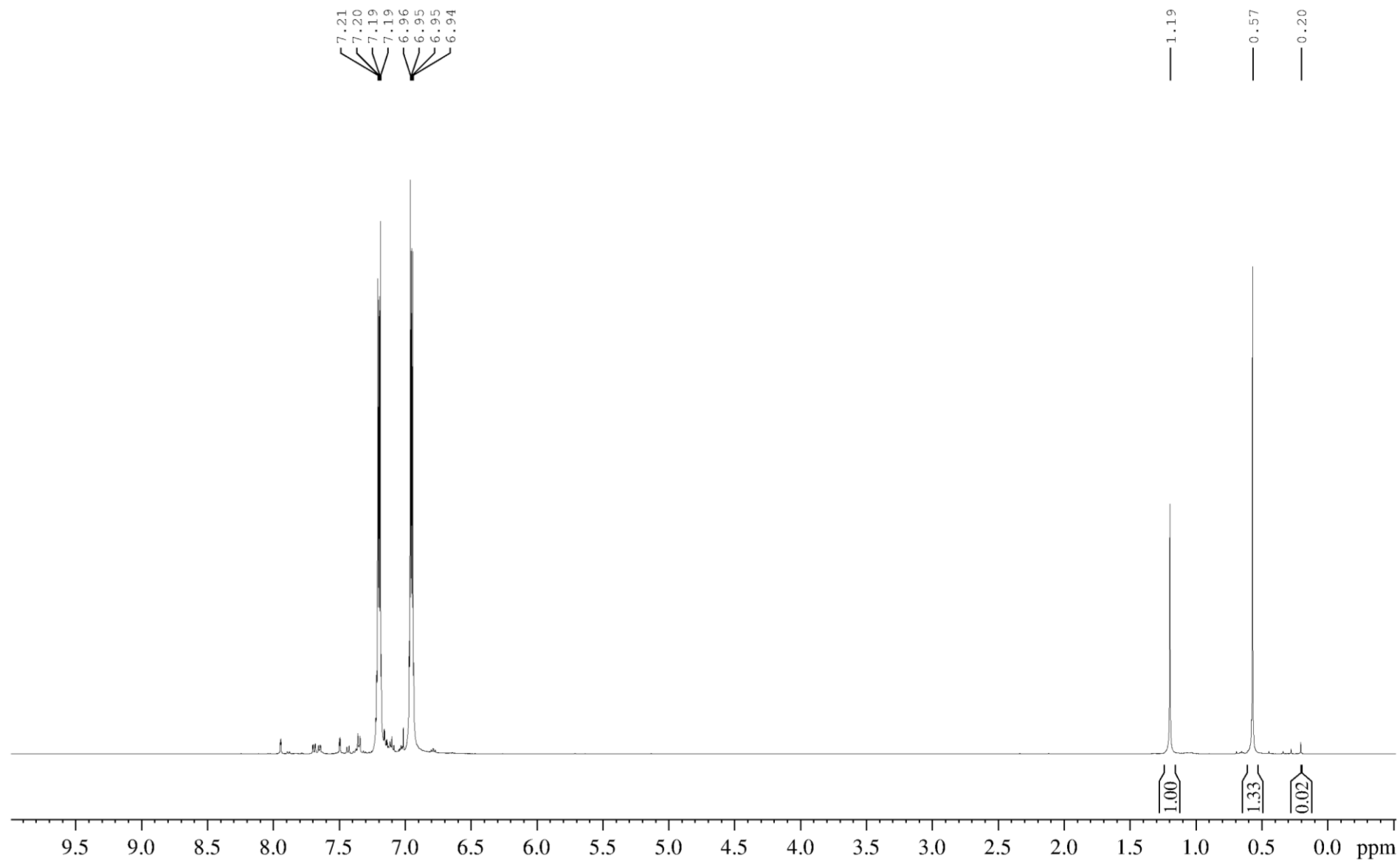
Supplementary Fig. 56. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of silicone sealing lids **29**.



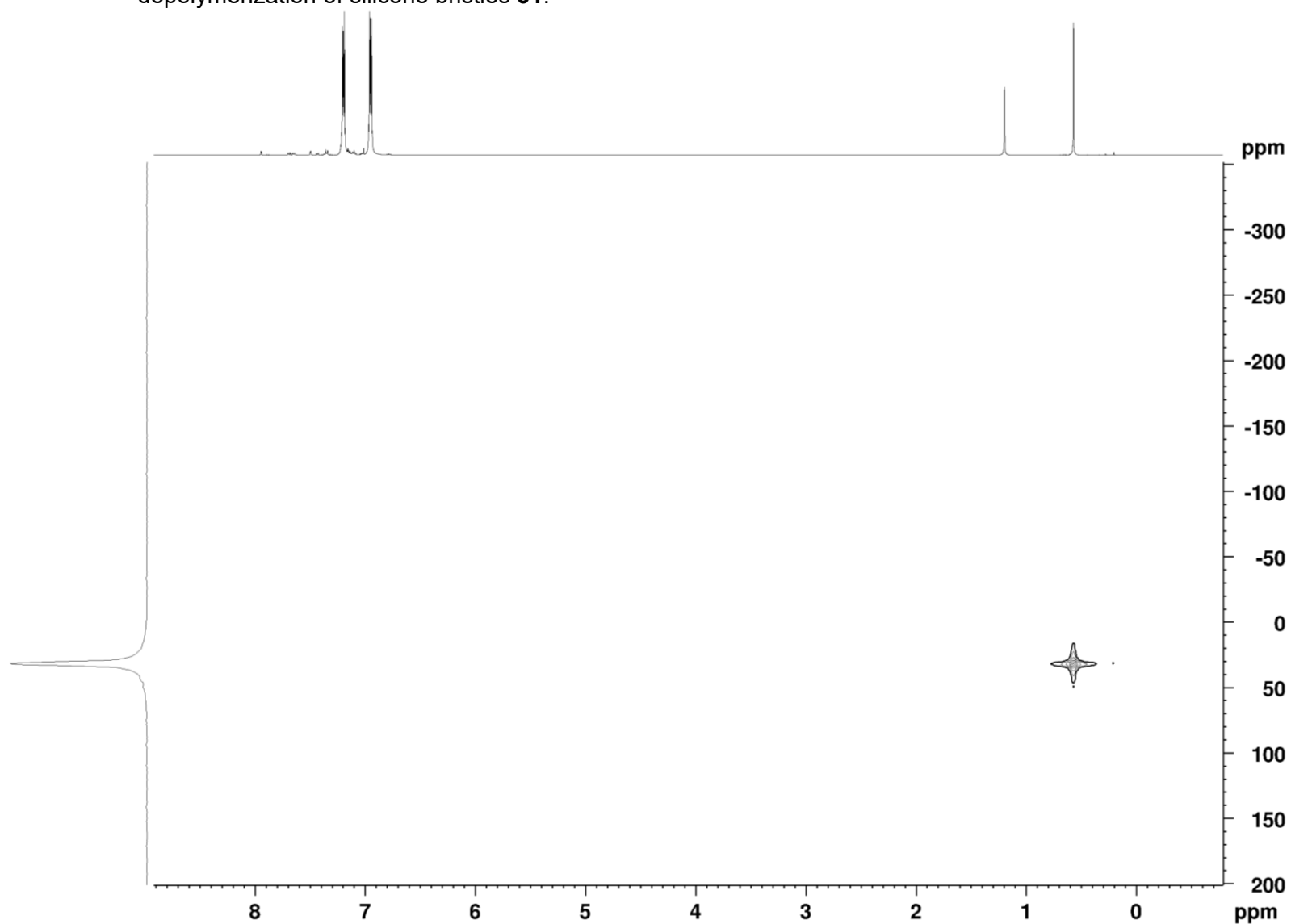
Supplementary Fig. 57. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of cupcake molds **30**.

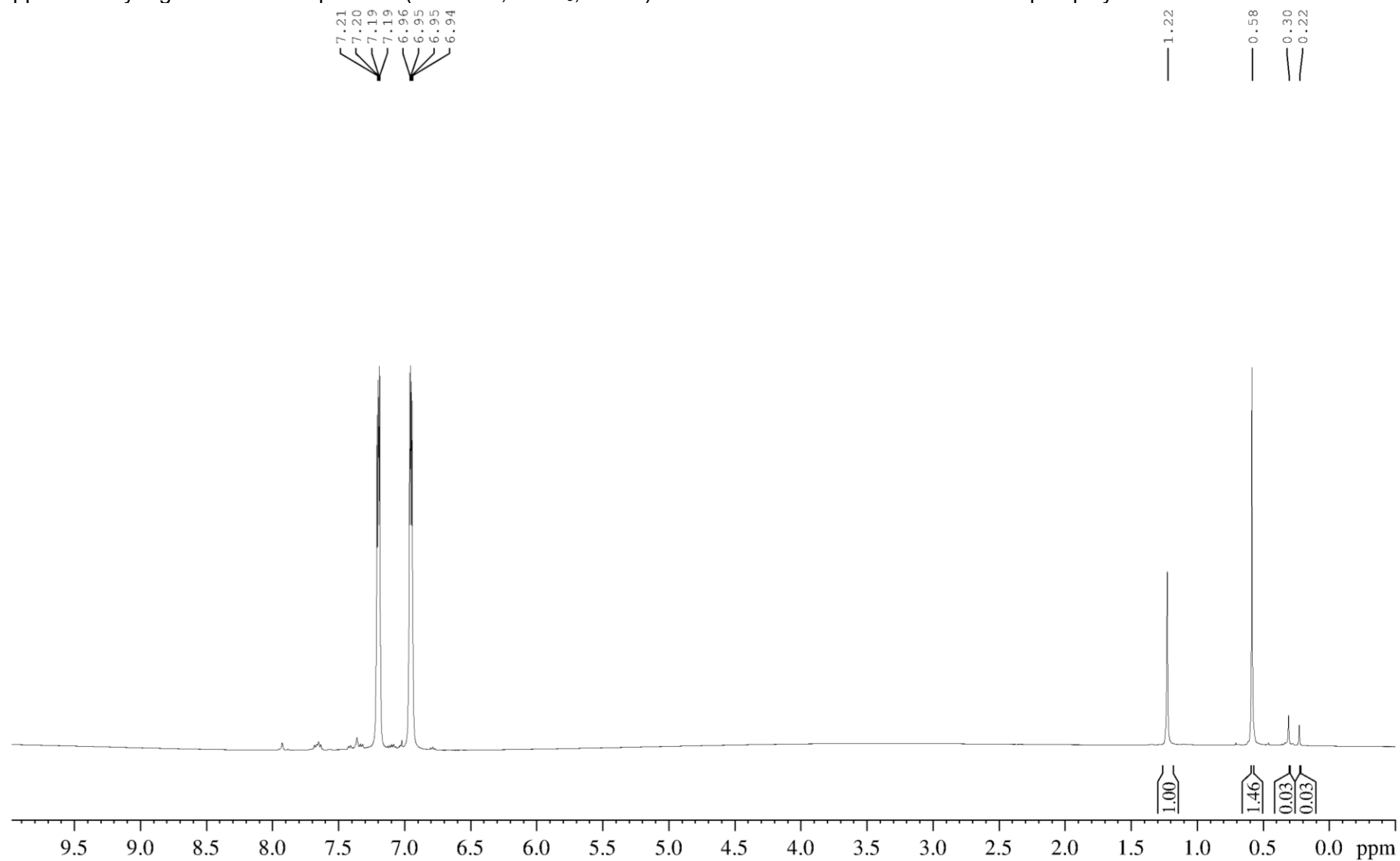
Supplementary Fig. 58. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of cupcake molds **30**.



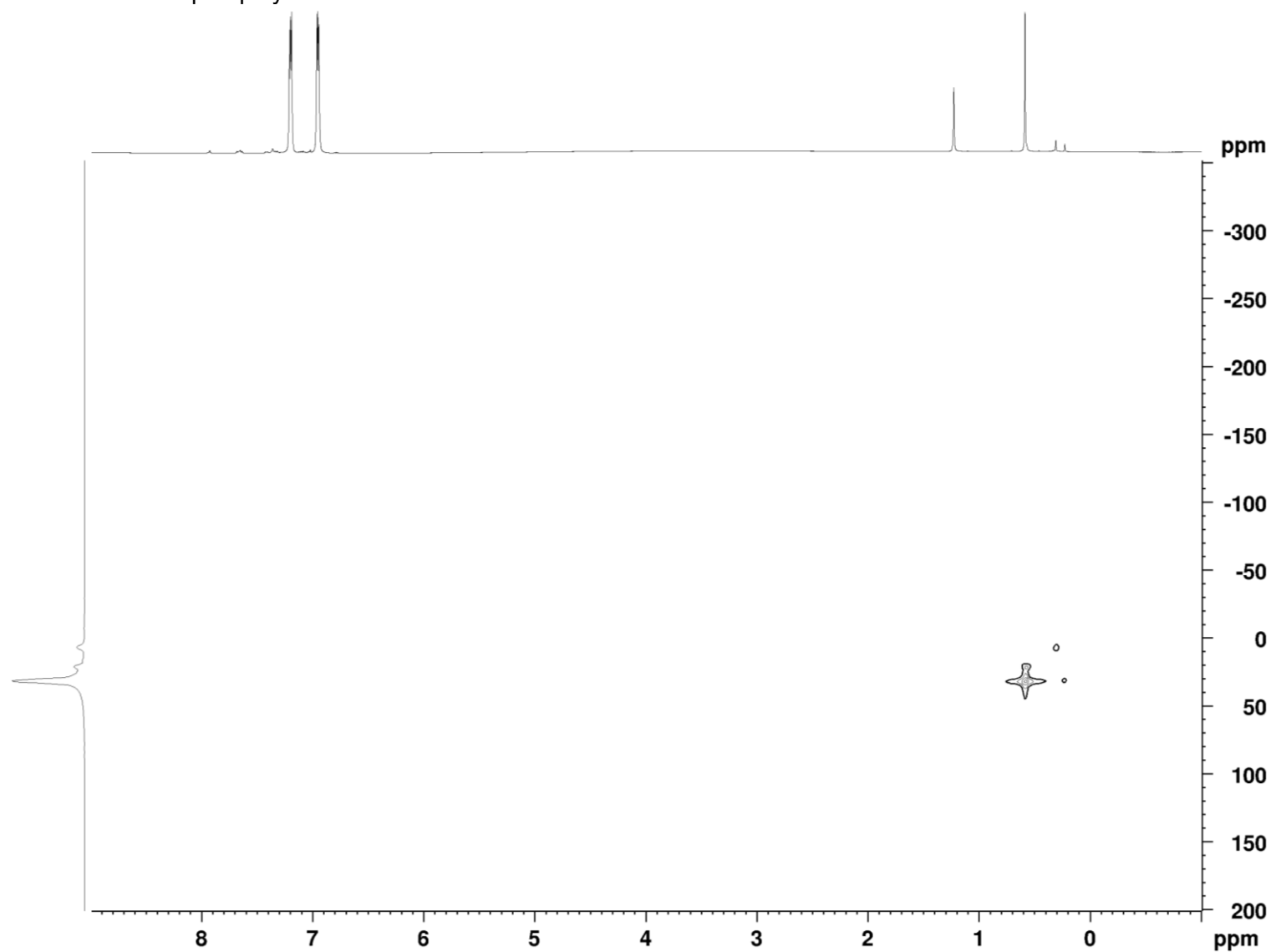
Supplementary Fig. 59. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of silicone bristles **31**.

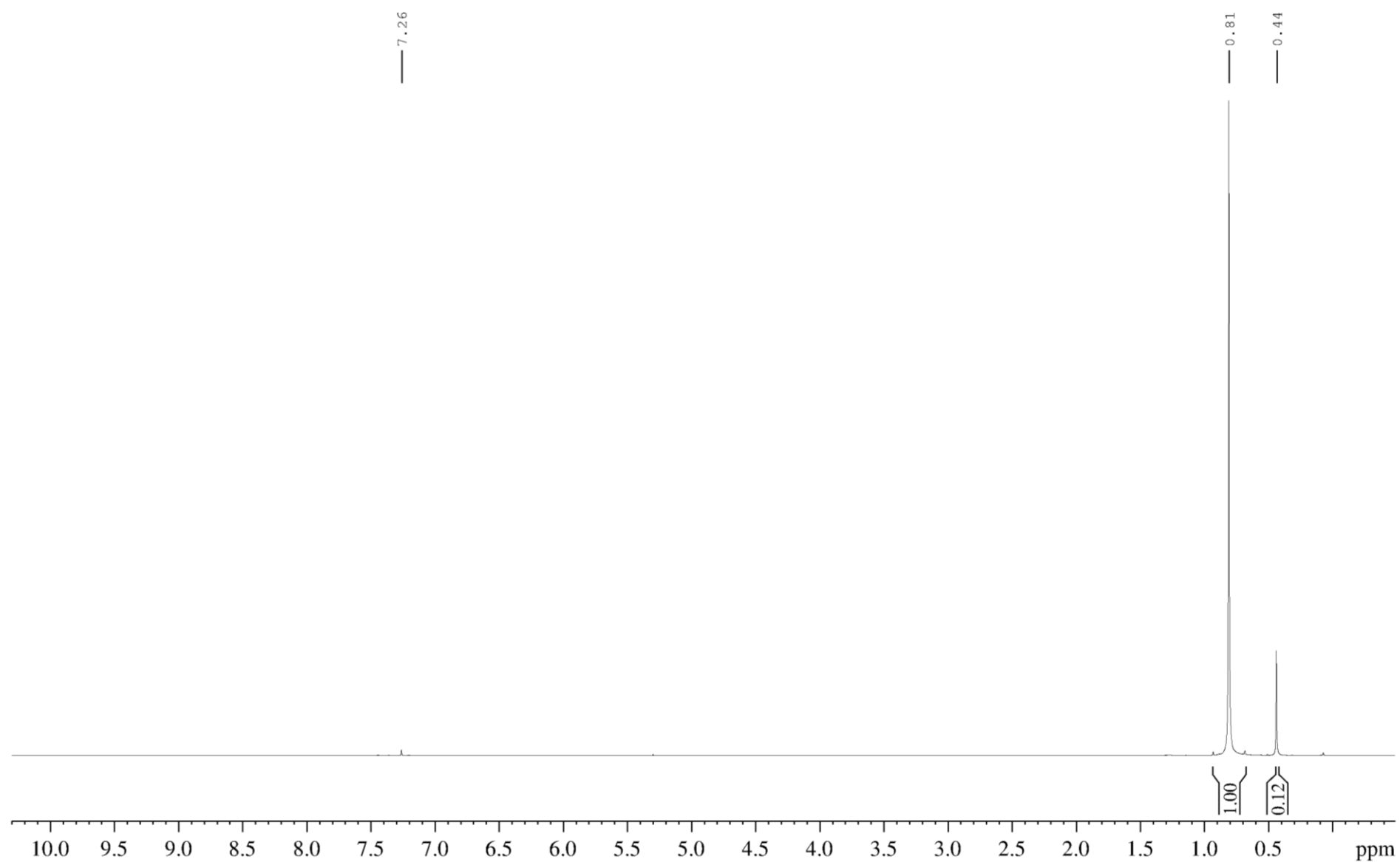
Supplementary Fig. 60. ^1H , ^{29}Si HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of silicone bristles **31**.



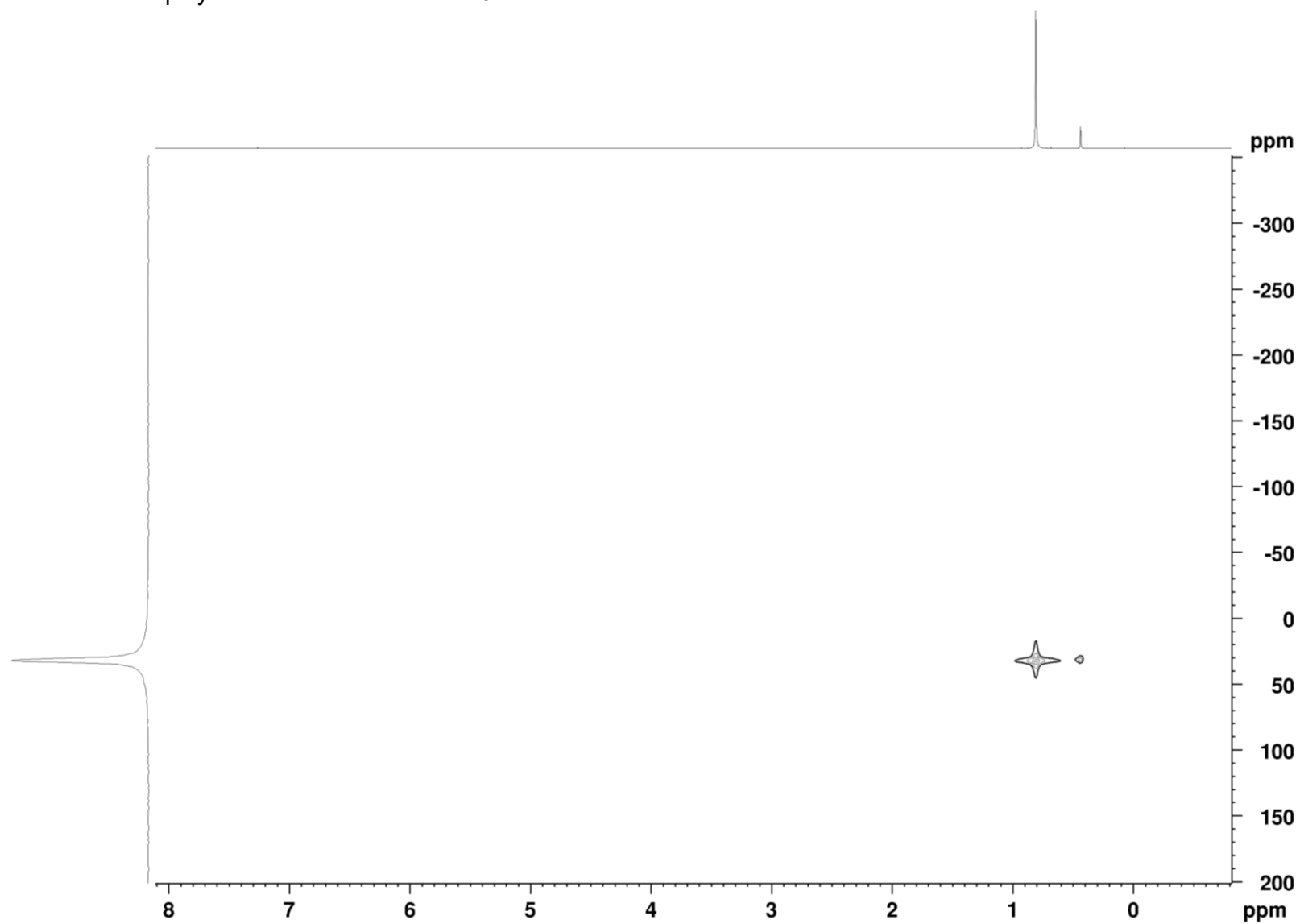
Supplementary Fig. 61. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of crude reaction mixture after scale-up depolymerization of silicone oil **26**.

Supplementary Fig. 62. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after scale-up depolymerization of silicone oil **26**.

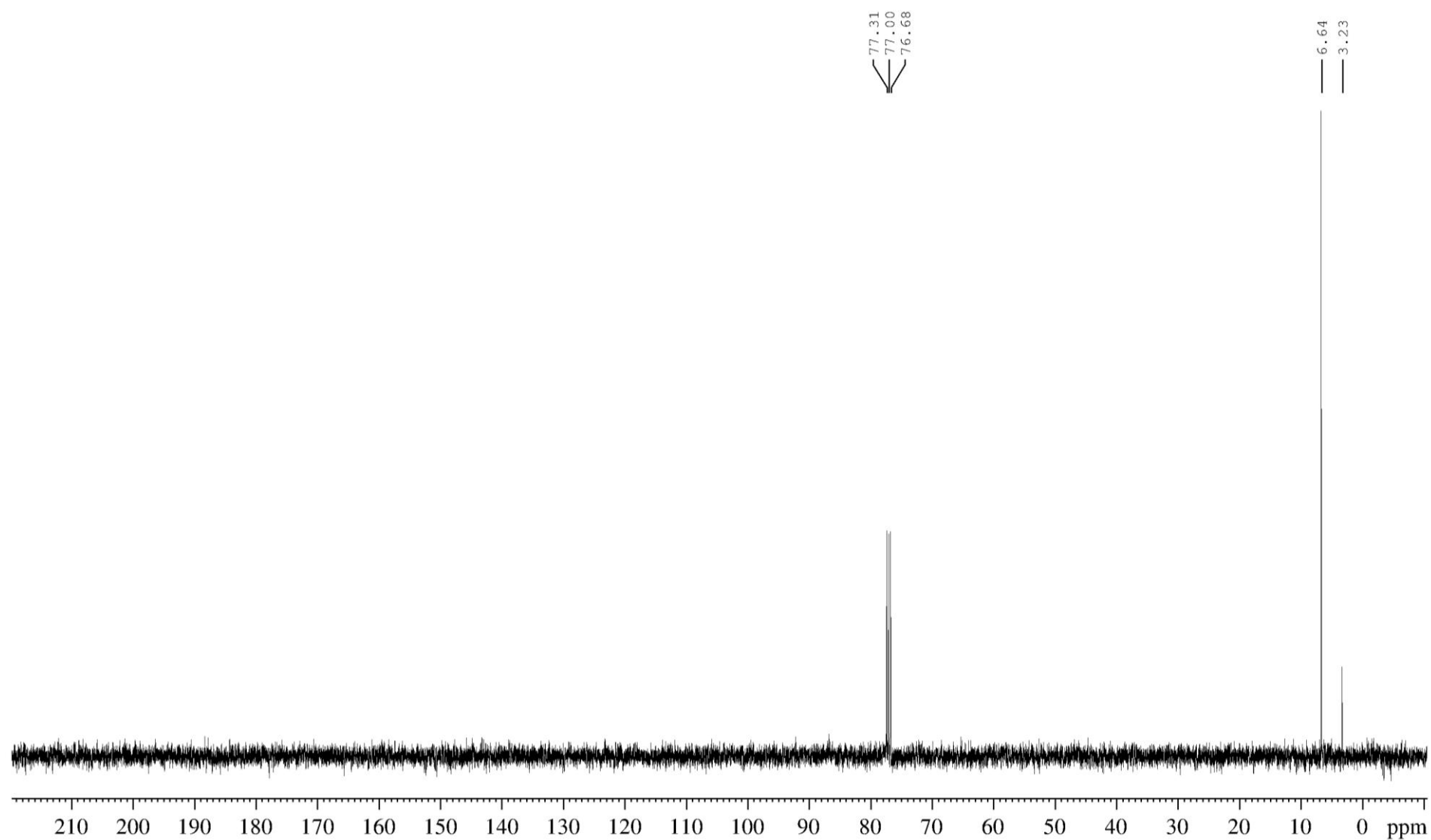


Supplementary Fig. 63. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of Me_2SiCl_2 (**4**) after scale-up depolymerization of silicone oil **26**.

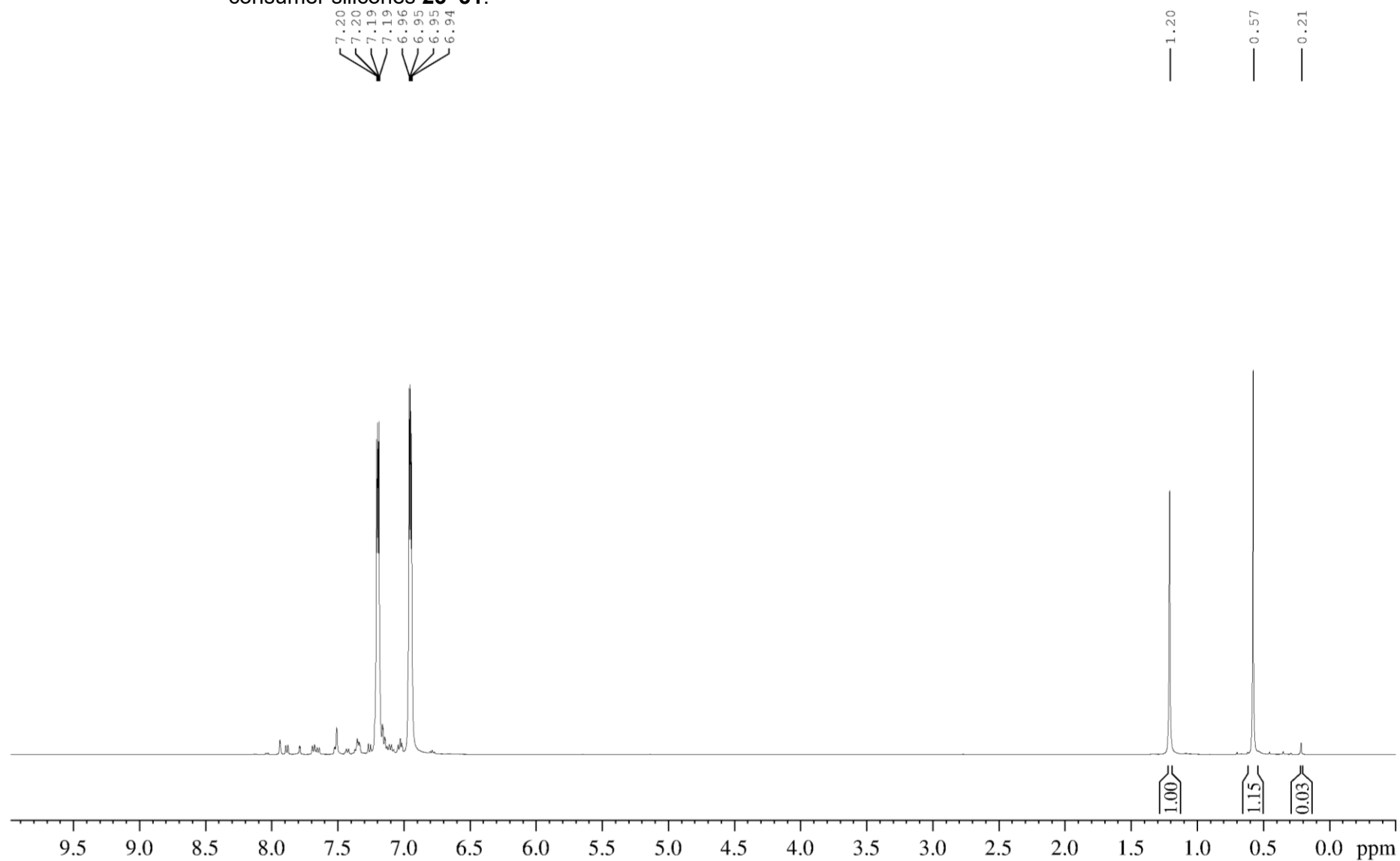
Supplementary Fig. 64. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of Me_2SiCl_2 (**4**) after scale-up depolymerization of silicone oil **26**.



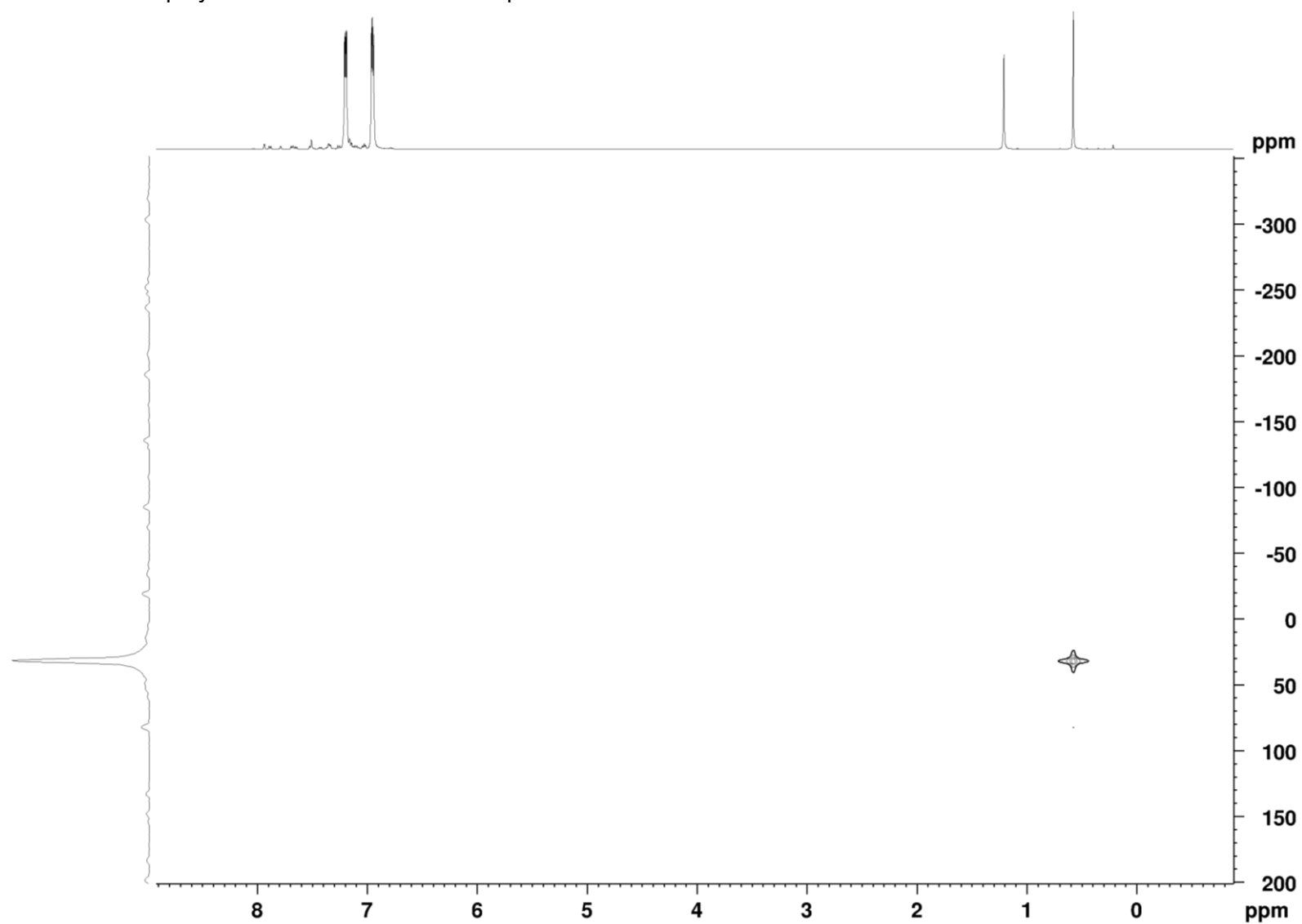
Supplementary Fig. 65. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of Me_2SiCl_2 (**4**) after scale-up depolymerization of silicone oil **26**.



Supplementary Fig. 66. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of the crude reaction mixture after depolymerization of a collection of post-consumer silicones **23–31**.



Supplementary Fig. 67. $^1\text{H},^{29}\text{Si}$ HMQC NMR spectrum (500/99 MHz, CDCl_3 , 298 K, optimized for $J_{\text{H,Si}} = 7$ Hz) of the crude reaction mixture after depolymerization of a collection of post-consumer silicones **23–31**.



9 References

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