Supporting Information

Synthesis of Polysilylethers *via* Iridium-Catalyzed Dehydrocoupling Polymerization

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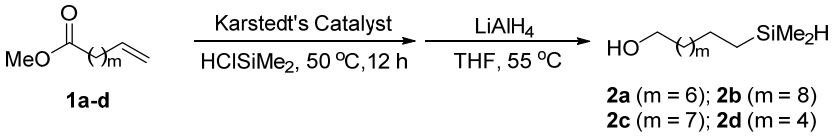
1. General

All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Flash column chromatography was performed on silica gel. GPC was performed on a Waters 1515 chromatography system equipped with Agilent PL1110 column using THF as the eluent (35 ^{o}C, 1 mL/min). Polystyrene standards were used for calibration. DSC was performed on a DSC Instruments 204 HP calorimeter (purge gas: N_2, flow rate: 20 mL/min, ramp rate: 10 ^{o}C/min, temperature range: -100 to 300 ^{o}C). TGA was performed on a STA instrument 449 F3 thermogravimetric analyzer (purge gas: N_2, flow rate: 20 mL/min, ramp rate: 10 ^{o}C/min, temperature range: 40 to 600 ^{o}C).

2. Synthesis of Monomers

Monomers **2a-e** were conveniently prepared according to the literature method.[1] The first step is the hydrosilylation catalyzed by Karstedt's catalyst.[2] The following step is the reduction using $LiAlH_4$. Monomer **2b** is known compound and its NMR data matched the literature data.[1]

2.1. The synthesis of monomer 2a-2d



Scheme S1. The synthesis of monomers **2a-d**

To a mixture of chlorodimethylsilane (7.896 g, 86 mmol) and **1** (72 mmol) in a 125 mL sealed tube was added Karstedt's catalyst (~2% xylene solution, 7 μL, 0.001 mol%). The tube was heated under nitrogen at 50 °C for 12 h. After cooled to room temperature, the content of the flask was added dropwise to a stirring suspension of $LiAlH_4$ (4.819 g, 129 mmol) in dry THF (350 mL) in an oven-dried 1 L flask under nitrogen at 0 °C. The flask was shaken by hand occasionally to break up the chunk formed. After the addition of the chlorosilane intermediate, the flask was heated at 55 °C for 2 h before cooled to 0 °C. The reaction mixture was quenched by slow addition of ethyl acetate (80 mL). To the mixture was added dropwise an aqueous solution of Rochelle salt (40 g in 150 mL water). The mixture was stirred vigorously. Then the aqueous layer was extracted with hexanes (100 mL × 2). The combined organic layer was washed with water (100 mL × 2) and brine (100 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (50:1-20:1 hexanes:ethyl acetate) and then distilled to give monomer **2** as a colorless liquid. To impove the polymerization performance of monomers, an anhydration process is necessary to reduce moisture content of monomers. Toluene (30 mL) and ethanol (7 mL) were added to the monomer **2**, the azeotropic solvent was evaporated by fractional distillation, and the mixture was distilled under reduced pressure to obtain anhydrous monomer **2** as a colorless liquid.

9-(Dimethylsilyl)nonan-1-ol (2a): 90 mmol scale, 4.049 g, 22% overall yield, colorless liquid, new compound, R_f = 0.24 (hexanes/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87-3.79 (m, 1H), 3.63 (t, *J* = 6.6 Hz, 2H), 1.62-1.50 (m, 2H), 1.41-1.27 (m, 13H), 0.63-0.50 (m, 2H), 0.05

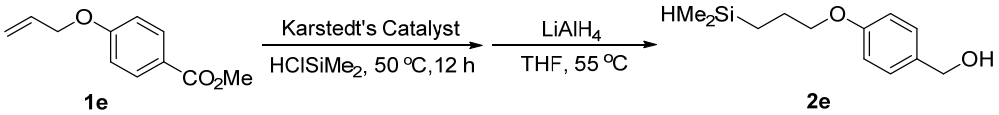
(d, *J* = 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.3, 33.4, 33.0, 29.7, 29.6, 29.5, 25.9, 24.5, 14.3, -4.2. HRMS-ESI Calculated for $C_{11}H_{25}OSi$ $[M-H]^+$ 201.1669; found 201.1670.

11-(Dimethylsilyl)undecan-1-ol (2b): 31 mmol scale, 2.200 g, 31% overall yield, colorless liquid, known compound,[1] R_f = 0.20 (hexanes/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88-3.77 (m, 1H), 3.63 (t, *J* = 6.6 Hz, 2H), 1.62-1.51 (m, 2H), 1.38-1.25 (m, 17H), 0.61-0.53 (m, 2H), 0.05 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.3, 33.4, 33.0, 29.8, 29.8, 29.63, 29.6, 25.9, 24.6, 14.4, -4.2.

10-(Dimethylsilyl)decan-1-ol (2c): 72 mmol scale, 2.388 g, 15% overall yield, colorless liquid, new compound, R_f = 0.34 (hexanes/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87-3.78 (m, 1H), 3.63 (t, *J* = 6.6 Hz, 2H), 1.61-1.50 (m, 2H), 1.38-1.26 (m, 15H), 0.64-0.49 (m, 2H), 0.05 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.3, 33.4, 33.0, 29.8, 29.7, 29.6, 29.5, 25.9, 24.6, 14.4, -4.2. HRMS-ESI Calculated for $C_{12}H_{27}OSi$ $[M-H]^+$, 215.1826; found, 215.1825.

7-(Dimethylsilyl)heptan-1-ol (2d): 142 mmol scale, 3.516 g, 14% overall yield, colorless liquid, new compound, R_f = 0.27 (hexanes/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87-3.78 (m, 1H), 3.63 (t, *J* = 6.6 Hz, 2H), 1.62-1.50 (m, 2H), 1.37-1.30 (m, 9H), 0.64-0.52 (m, 2H), 0.05 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.3, 33.3, 33.0, 29.3, 25.9, 24.5, 14.3, -4.2. HRMS-ESI Calculated for $C_9H_{21}OSi$ $[M-H]^+$, 173.1356; found, 173.1359.

2.2. The synthesis of monomer 2e

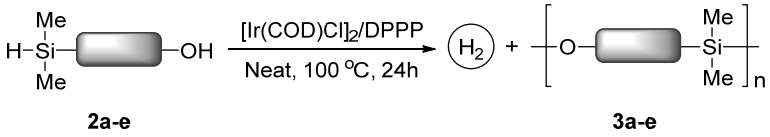


Scheme S2. The synthesis of monomer **2e**

The synthesis of monomer **2e** was conducted following the general procedure for the synthesis of monomer **2a** to **2d**.

(4-(3-(Dimethylsilyl)propoxy)phenyl)methanol (2e): 95 mmol scale, 5.770 g, 27% overall yield, colorless liquid, new compound, R_f = 0.19 (hexanes/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.60 (s, 2H), 3.87-3.95 (m, 3H), 1.89-1.77 (m, 2H), 1.67-1.60 (br, 1H), 0.76-0.66 (m, 2H), 0.11 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 133.1, 128.8, 114.8, 70.5, 65.3, 24.4, 10.5, -4.3. HRMS-ESI Calculated for $C_{12}H_{19}O_2Si$ $[M-H]^+$, 223.1149; found, 223.1147.

3. General Procedure for the Polymerization of Monomers



Scheme S3. The synthesis of PSEs

To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged DPPP (4.2 mg, 0.01 mmol), $[Ir(COD)Cl]_2$ (3.4 mg, 0.005 mmol) and dichloromethane (3 mL) under nitrogen. The solution was stirred at room temperature for 10 min. Then the solvent was removed under reduced pressure to *in situ* prepare the catalyst. Monomer **2** (1 mmol) was added into the flask under nitrogen. The flask was heated at 100 °C for 24 h under nitrogen (connected to a nitrogen Schlenk line). During the last 6 h of the reaction time, H_2 produced during the reaction was replaced with nitrogen every 2 h. After the polymerization, the reaction mixture was cooled to room temperature, and the content was purified by the precipitation method.

All of the polymers are soluble in tetrahydrofuran and insoluble in methanol, so these two solvents were used in the precipitation process. The reaction mixture was first homogenized by the addition of as low as possible amount of THF (1-2 mL), then, cold methanol was added portionwise (15-20 mL) until it turned to a biphasic mixture. The top layer was taken out, and the bottom viscous/solid layer was washed with methanol two times until it gave a white/light yellow color viscous/solid polymer. The resulting polymer was dried to a constant weight and characterized by ^{1}H NMR, ^{13}C NMR, GPC, TG and DSC.

Polysilylether (**3a**): 0.158 g, 79% yield, colorless soft solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (t, *J* = 6.7 Hz, 2H), 1.57-1.45 (m, 2H), 1.35-1.24 (m, 12H), 0.64-0.50 (m, 2H), 0.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.0, 33.7, 33.0, 29.8, 29.7, 29.5, 26.1, 23.4, 16.6, -1.9.

Polysilylether (**3b**): 0.183 g, 80% yield, colorless soft solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (t, J = 6.7 Hz, 2H), 1.57-1.46 (m, 2H), 1.34-1.24 (m, 16H), 0.64-0.49 (m, 2H), 0.08 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.0, 33.7, 33.0, 29.9, 29.8, 29.7, 29.6, 26.1, 23.4, 16.6, -1.9.

Polysilylether (**3c**): 0.210 g, 98% yield. colorless soft solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (t, *J* = 6.7 Hz, 2H), 1.58-1.45 (m, 2H), 1.34-1.23 (m, 14H), 0.65-0.49 (m, 2H), 0.08 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.0, 33.7, 33.0, 29.9, 29.8, 29.7, 29.6, 26.1, 23.4, 16.6, -1.9.

Polysilylether (**3d**): 0.166 g, 96% yield, colorless viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.55 (t, *J* = 6.7 Hz, 2H), 1.56-1.44 (m, 2H), 1.34-1.26 (m, 8H), 0.62-0.51 (m, 2H), 0.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.0, 33.7, 33.0, 29.4, 26.0, 23.4, 16.5, -1.9.

Polysilylether (**3e**): 0.166 g, 75% yield, light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 4.64 (s, 2H), 3.90 (t, J = 6.7 Hz, 2H), 1.91-1.76 (m, 2H), 0.81-0.66 (m, 2H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 133.0, 128.2, 114.5, 70.6, 64.7, 23.4, 12.6, -1.8.

Polysilylether (***3f***) 0.175 g, 78% yield, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.19 (m, 2H), 6.90-6.81 (m, 2H), 4.62 (d, *J* = 7.3 Hz, 2H), 3.90 (dd, *J* = 12.4, 6.4 Hz, 2H), 3.57 (dd, *J* = 14.7, 6.9 Hz, 2H), 1.88-1.78 (m, 2H), 1.56-1.46 (m, 2H), 1.36-1.24 (m, 16H), 0.80-0.64 (m, 2H), 0.64-0.54 (m, 2H), 0.20-0.05 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5,

133.2, 133.0, 129.6, 128.8, 128.2, 114.8, 114.5, 71.7, 70.6, 64.7, 64.6, 63.1, 63.0, 33.7, 33.0, 29.8, 29.7, 29.6, 26.0, 23.4, 18.6, 16.6, 14.5, 12.7, 12.6, 0.5, -0.1, -1.8, -1.9.

4. Methanolysis of PSEs

To a 10 mL flask were added the polymer **3e** (20 mg) and tetrahydrofuran (2 mL). After the polymer dissolved completely, methanol (0.5 mL) was added to the solution. A small amount of the solution was taken for GPC analysis after stirring for a certain time.

Table S1. methanolysis of polymer **3e**

Entry	t/h	M_n	M_w	D
1	0	21500	36500	1.70
2	2	17700	34700	1.96
3	25	17400	32200	1.85
4	49	17300	29500	1.70
5	97	11300	21200	1.88
7	145	9700	16400	1.69
9	193	7400	13400	1.81
10	253	6500	10400	1.60
11	325	4400	7400	1.68
12	397	3600	5600	1.56

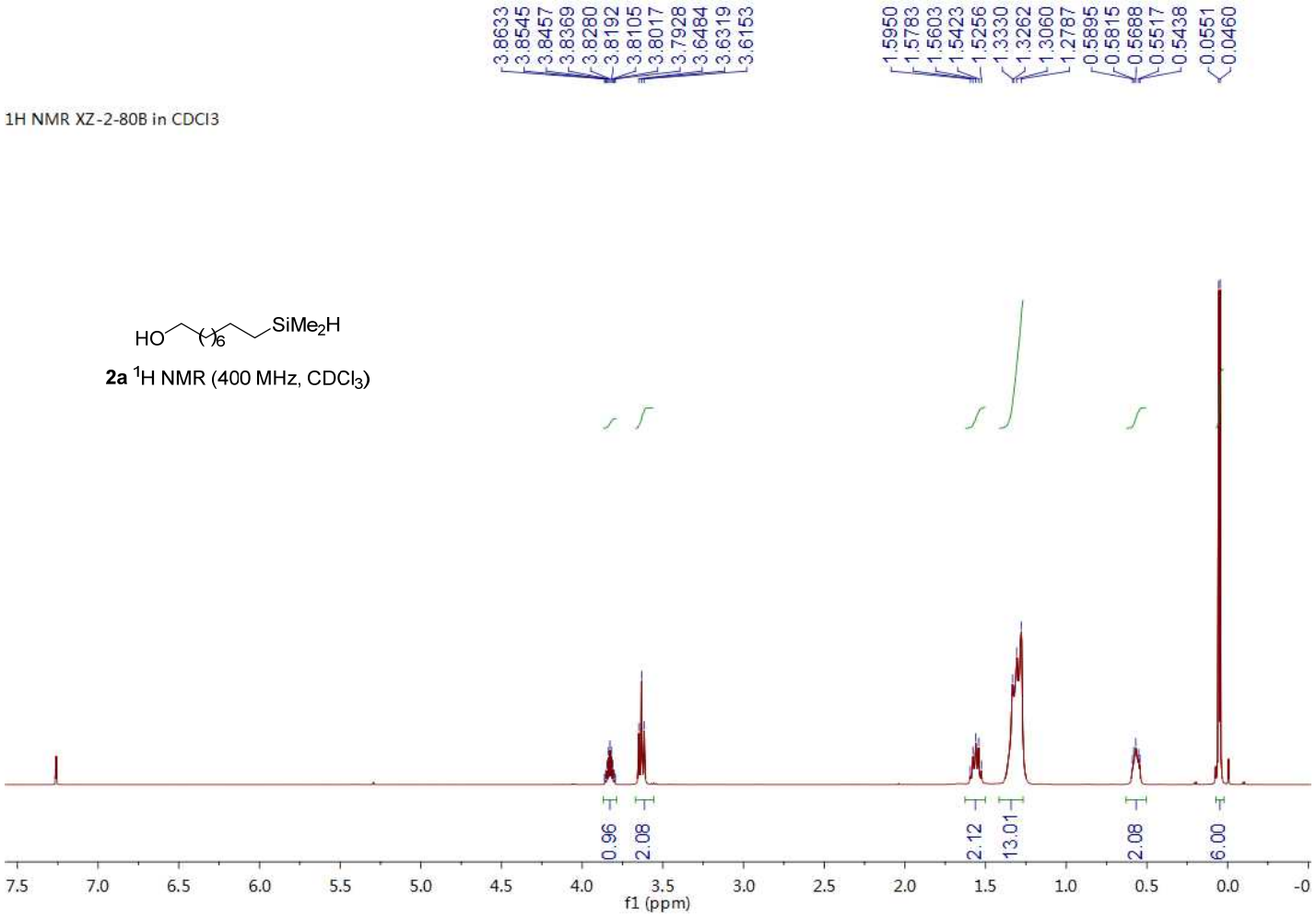


Figure S1, ^{1}H NMR of monomer **2a**

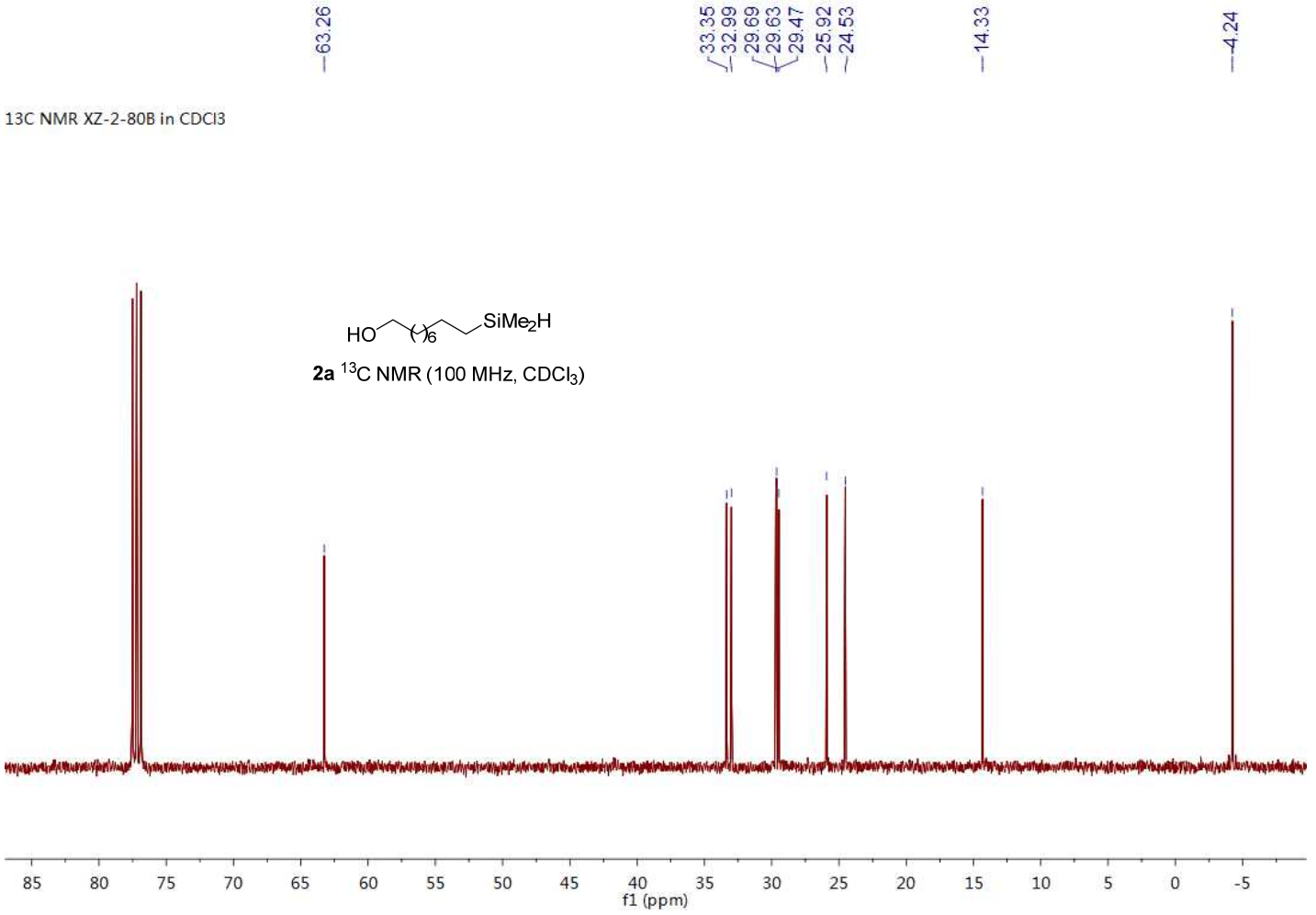


Figure S2, ^{13}C NMR of monomer **2a**

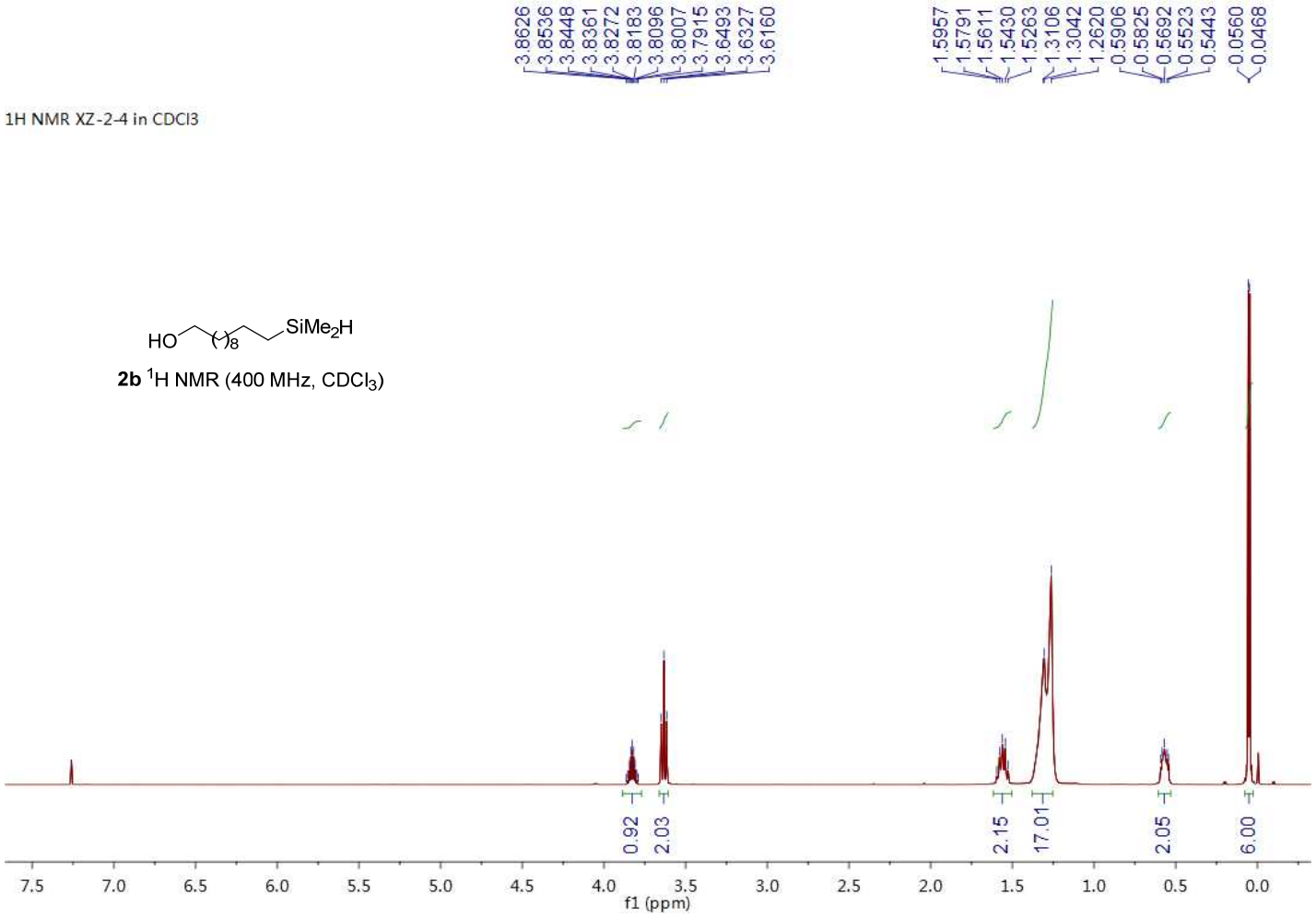


Figure S3, ^{1}H NMR of monomer **2b**

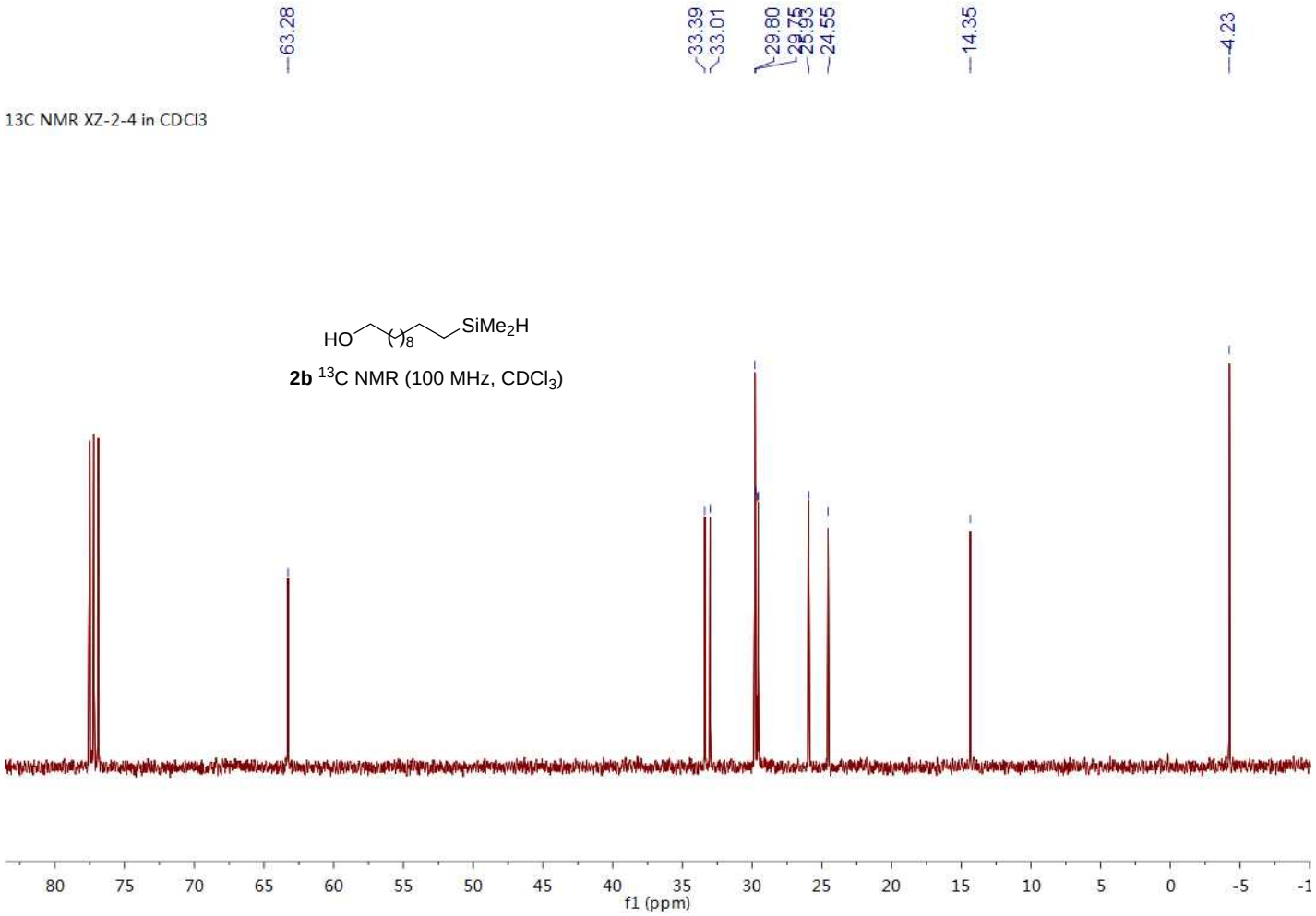


Figure S4, ^{13}C NMR of monomer **2b**

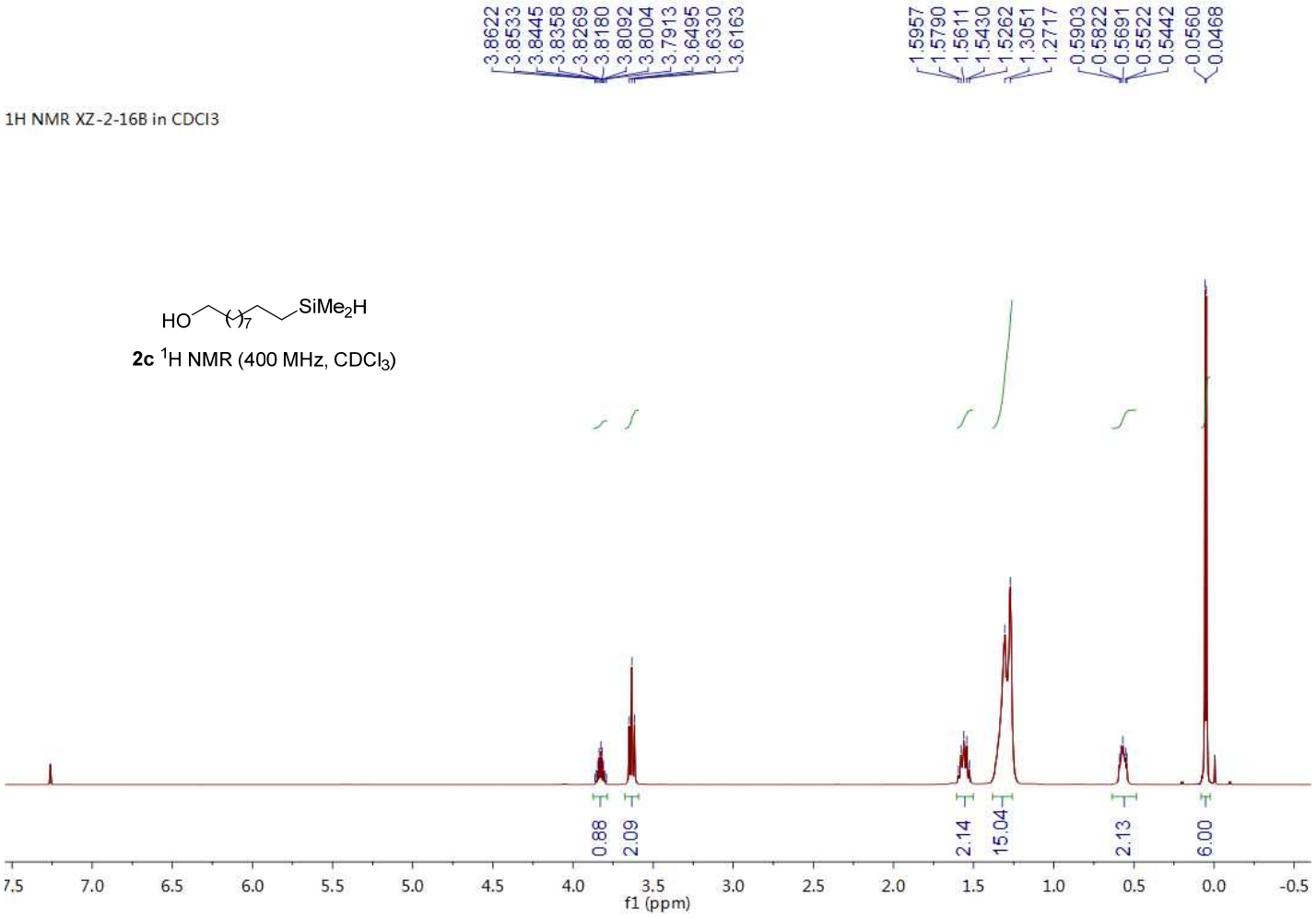
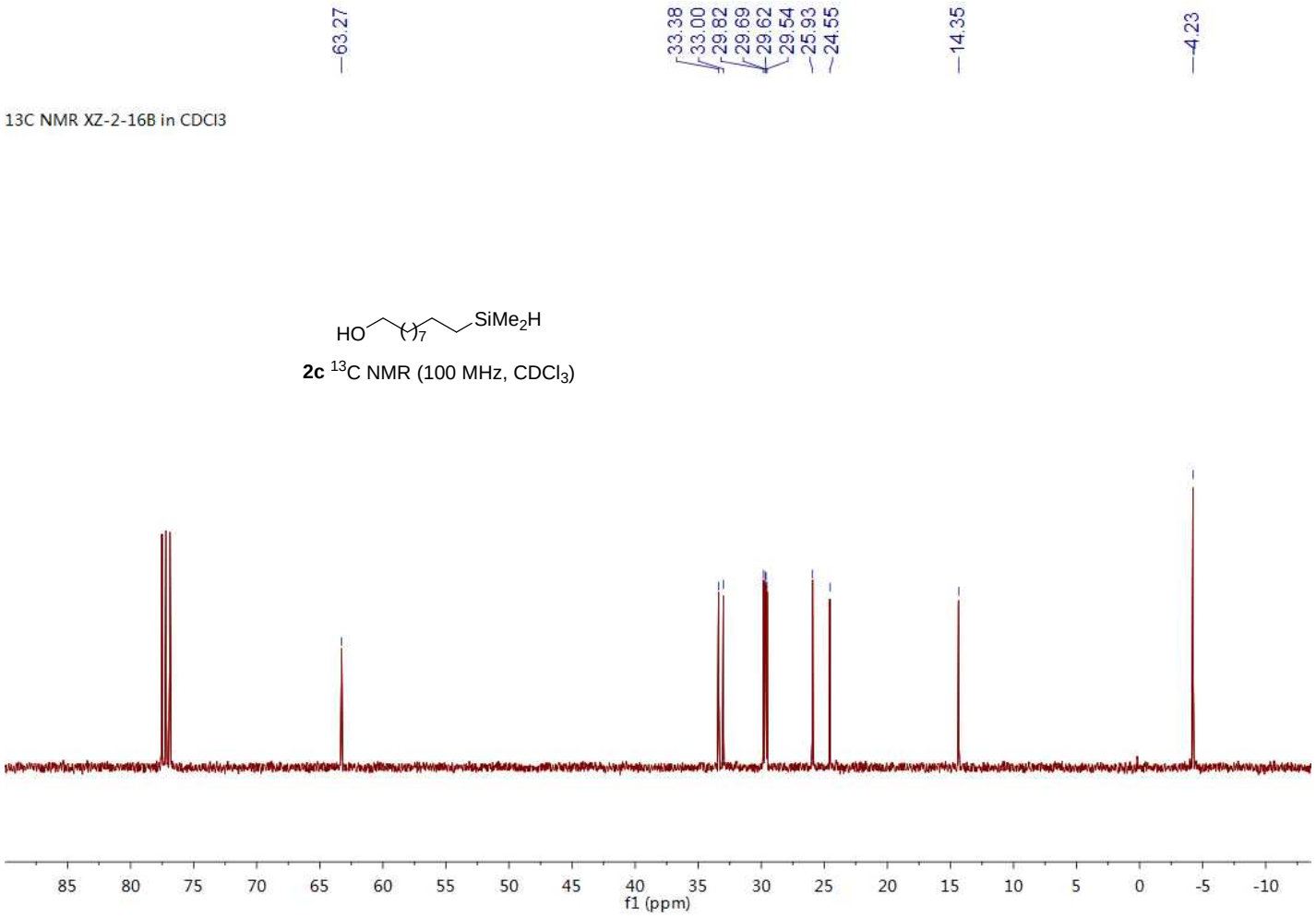


Figure S5, ^{1}H NMR of monomer **2c**



2c ^{13}C NMR (100 MHz, $CDCl_3$)

Figure S6, ^{13}C NMR of monomer **2c**

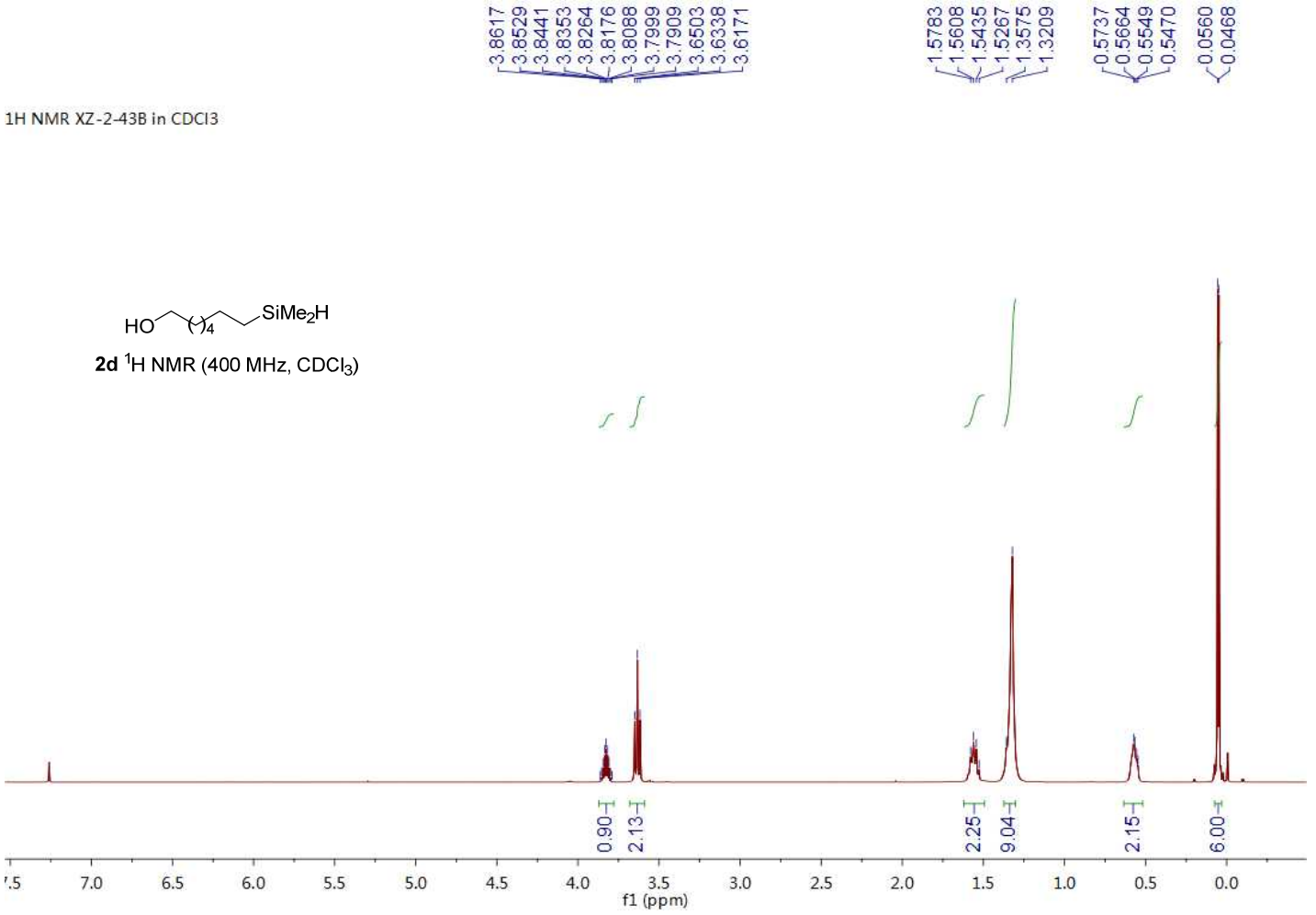


Figure S7, ^{1}H NMR of monomer **2d**

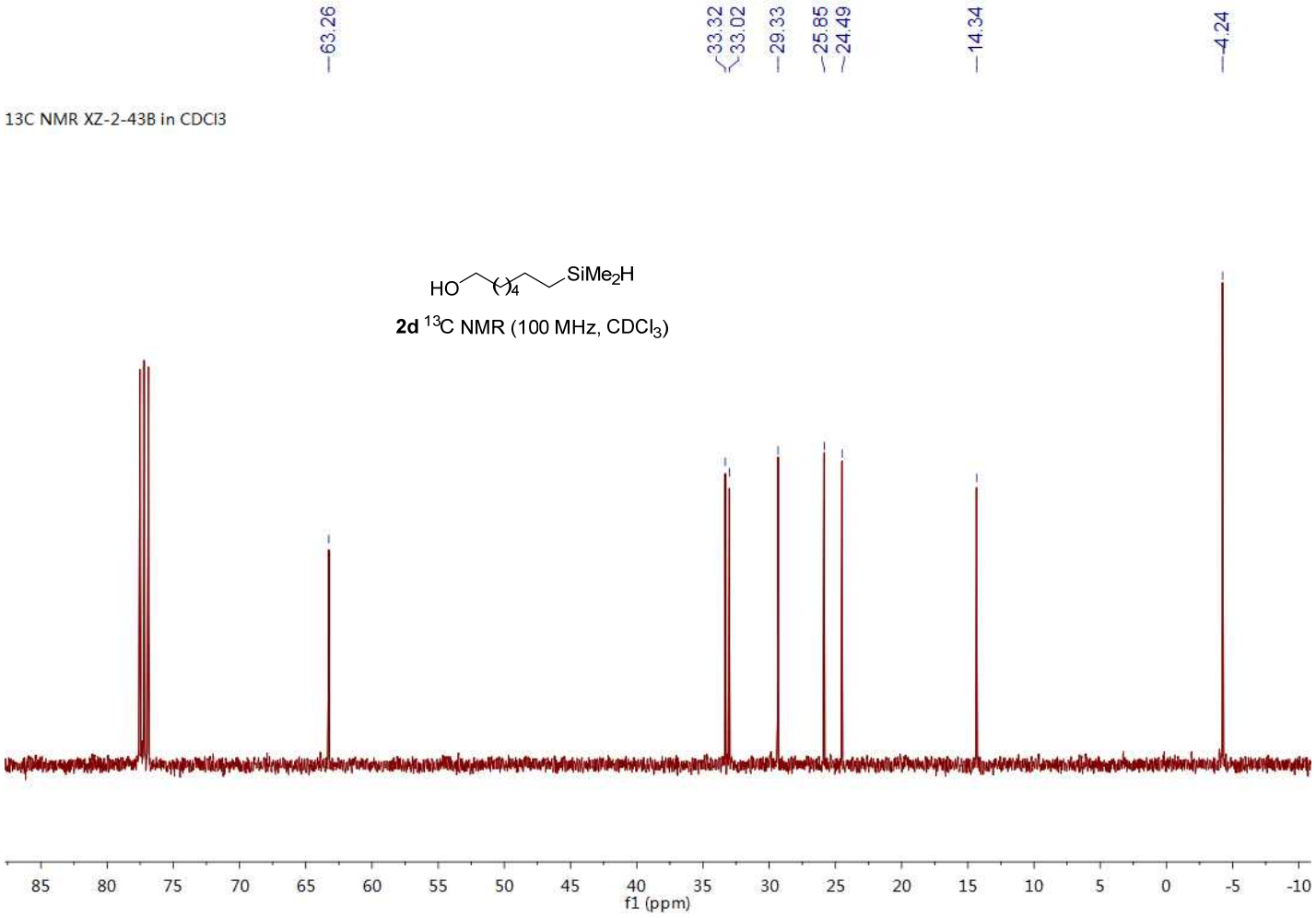


Figure S8, ^{13}C NMR of monomer **2d**

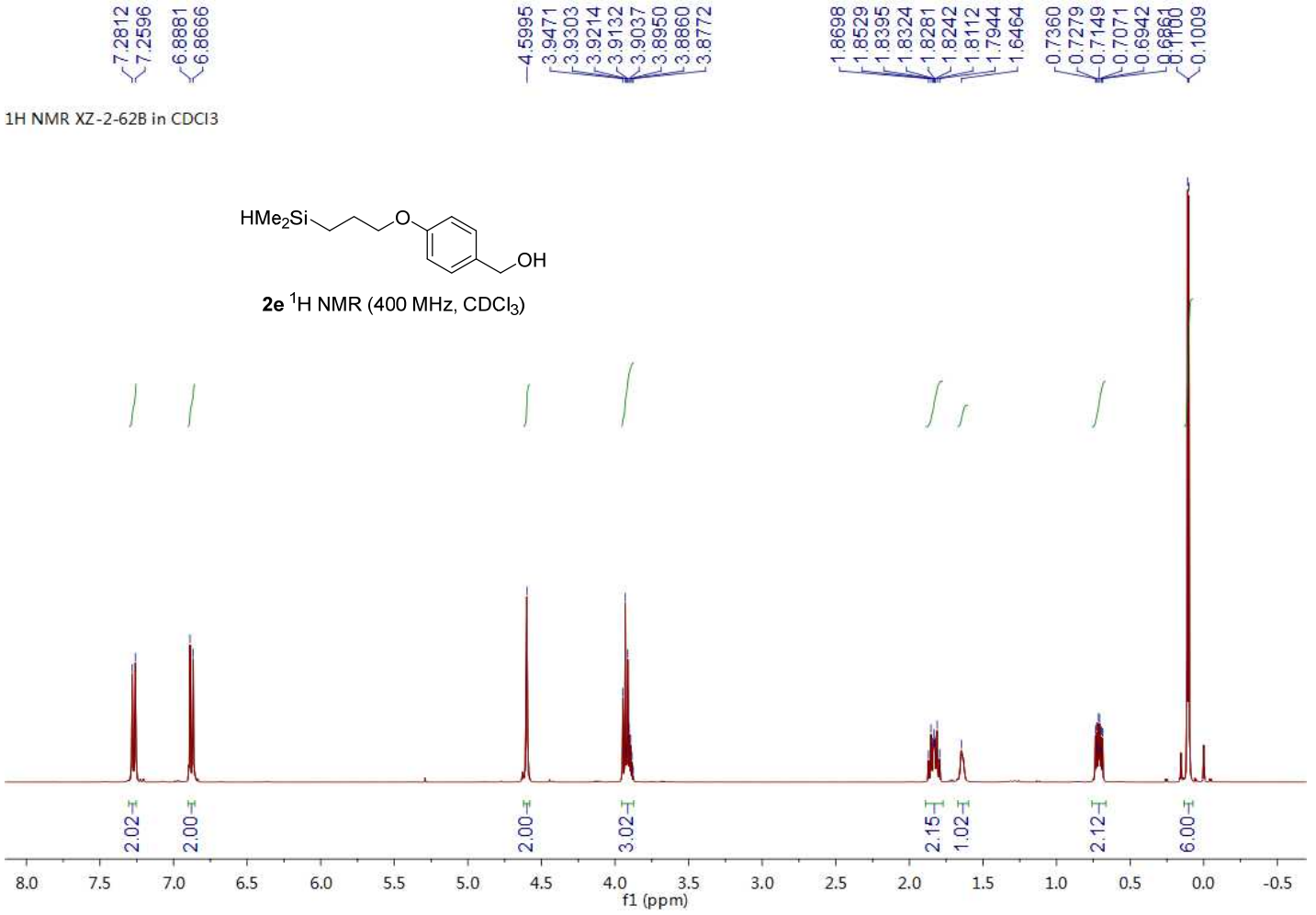


Figure S9, ^{1}H NMR of monomer **2e**

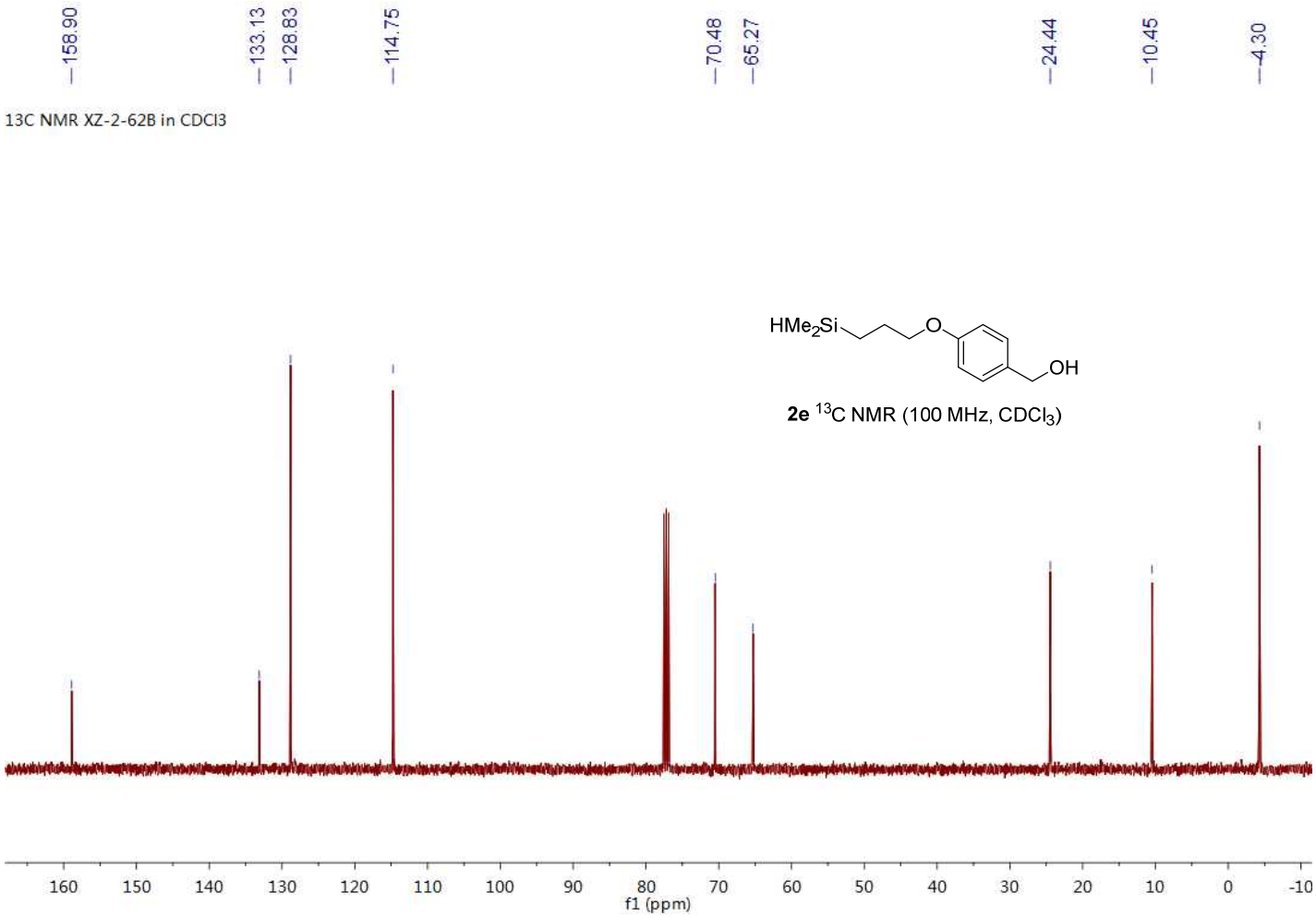


Figure S10, ^{13}C NMR of monomer **2e**

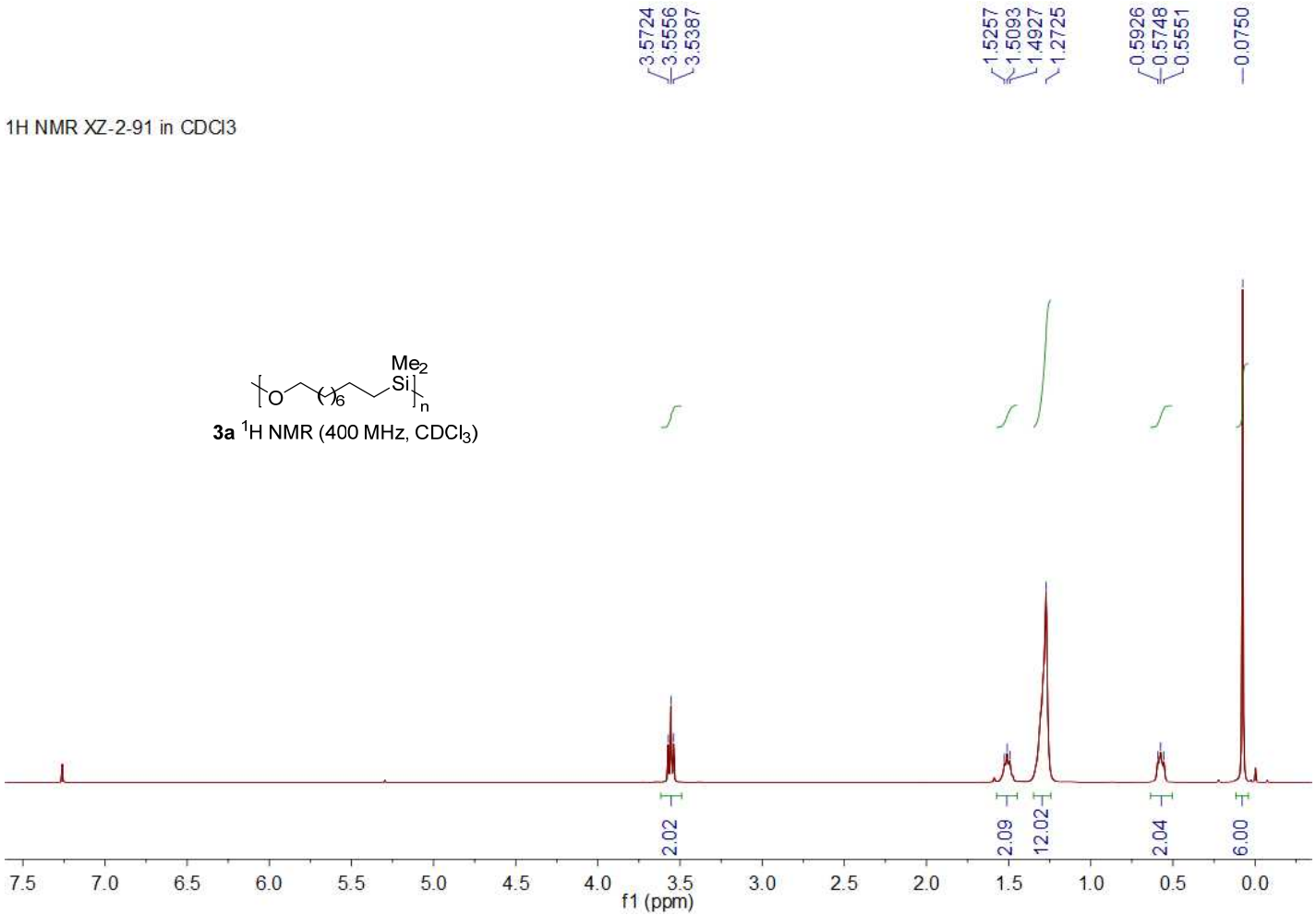


Figure S11, ^{1}H NMR of polymer **3a**

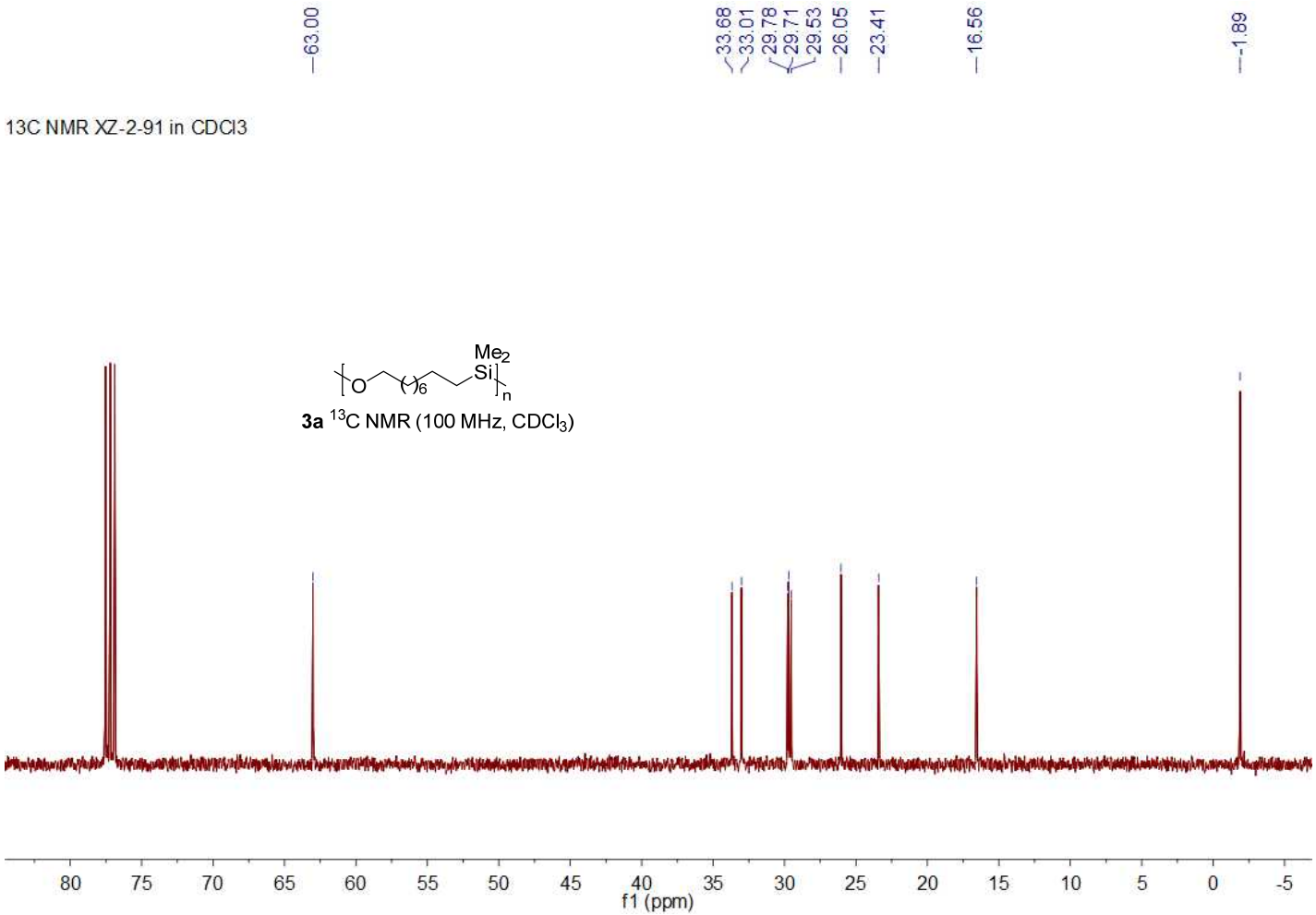


Figure S12, ^{13}C NMR of polymer **3a**

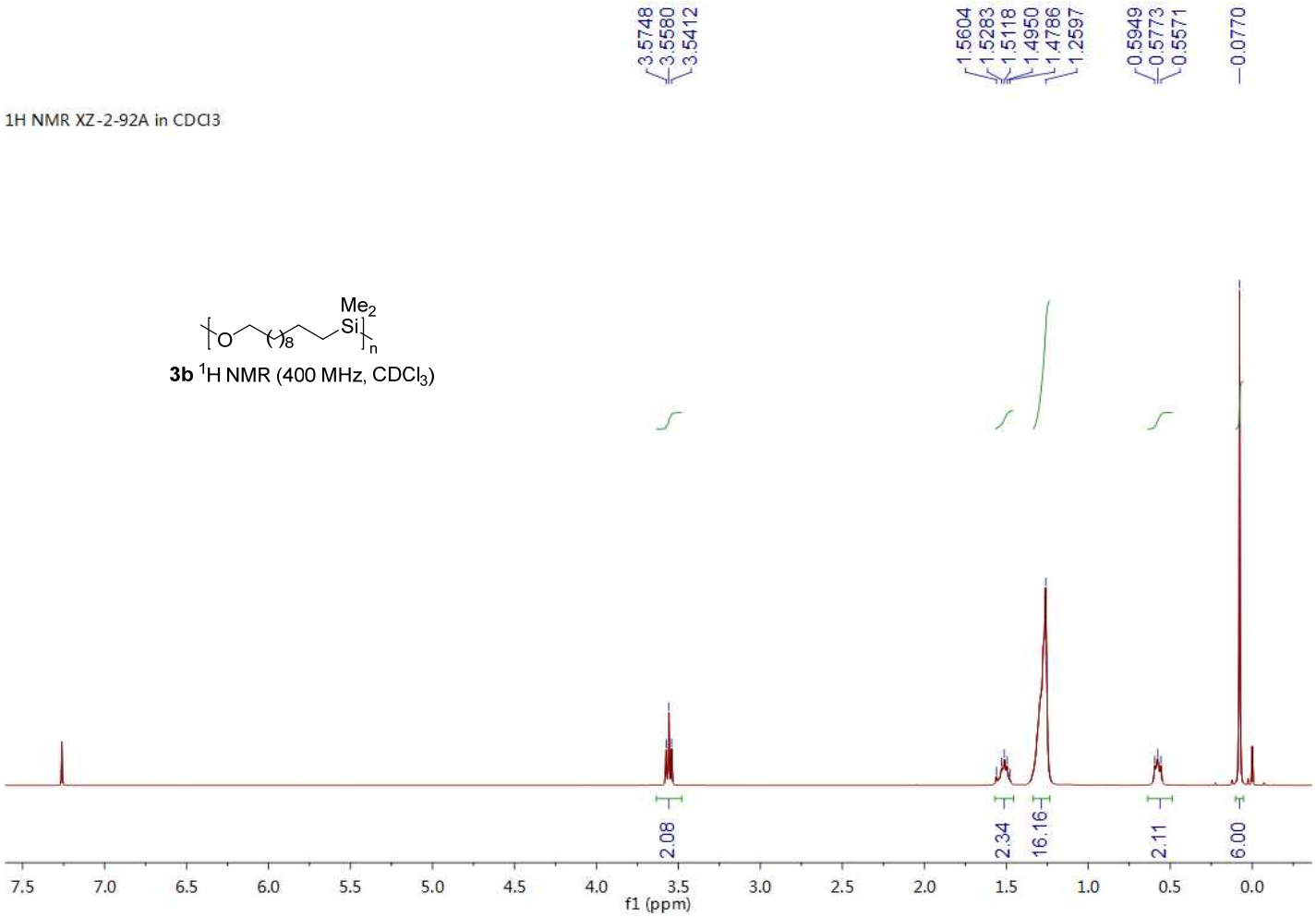


Figure S13, ^{1}H NMR of polymer **3b**

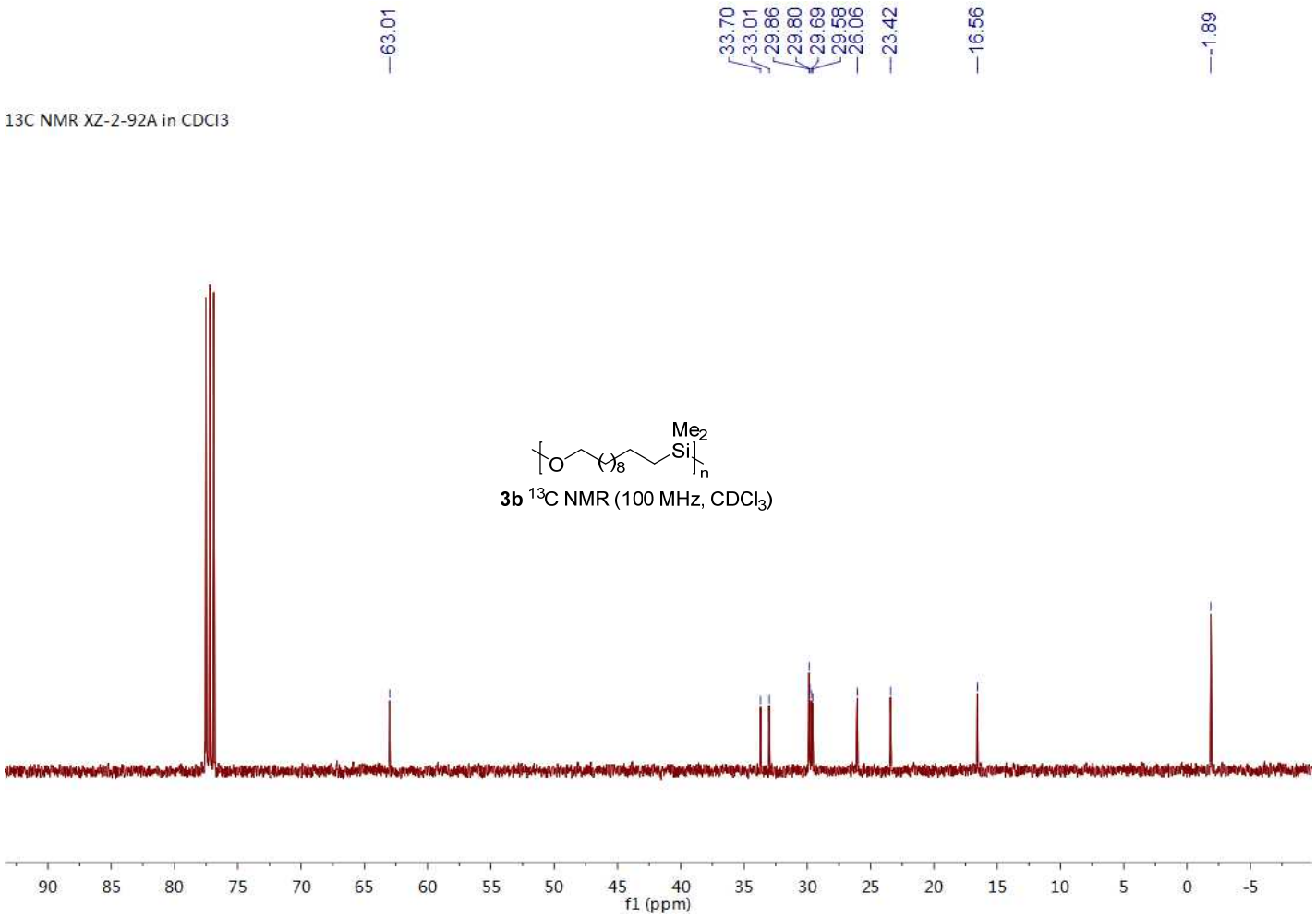


Figure S14, ^{13}C NMR of polymer **3b**

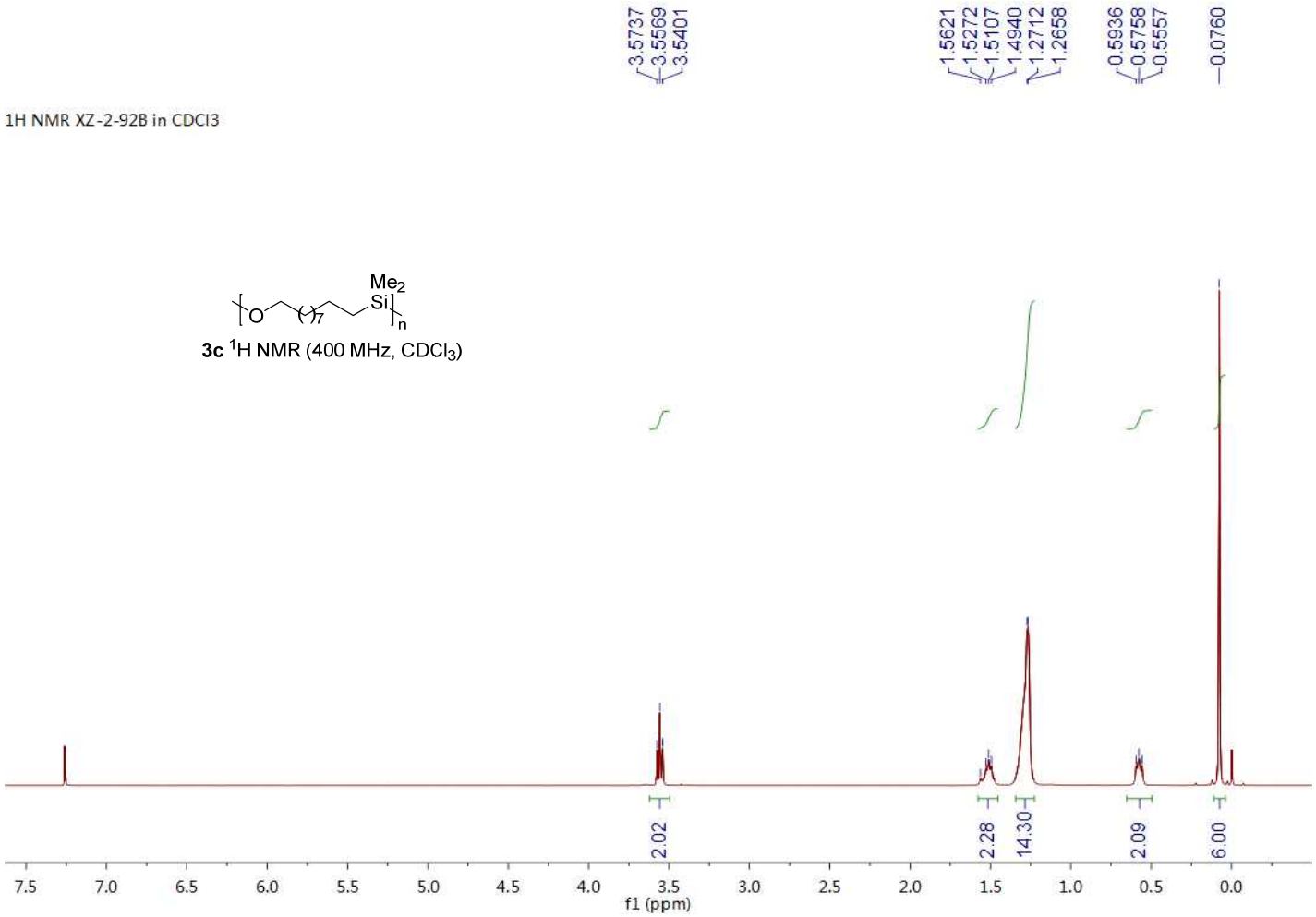


Figure S15, ^{1}H NMR of polymer **3c**

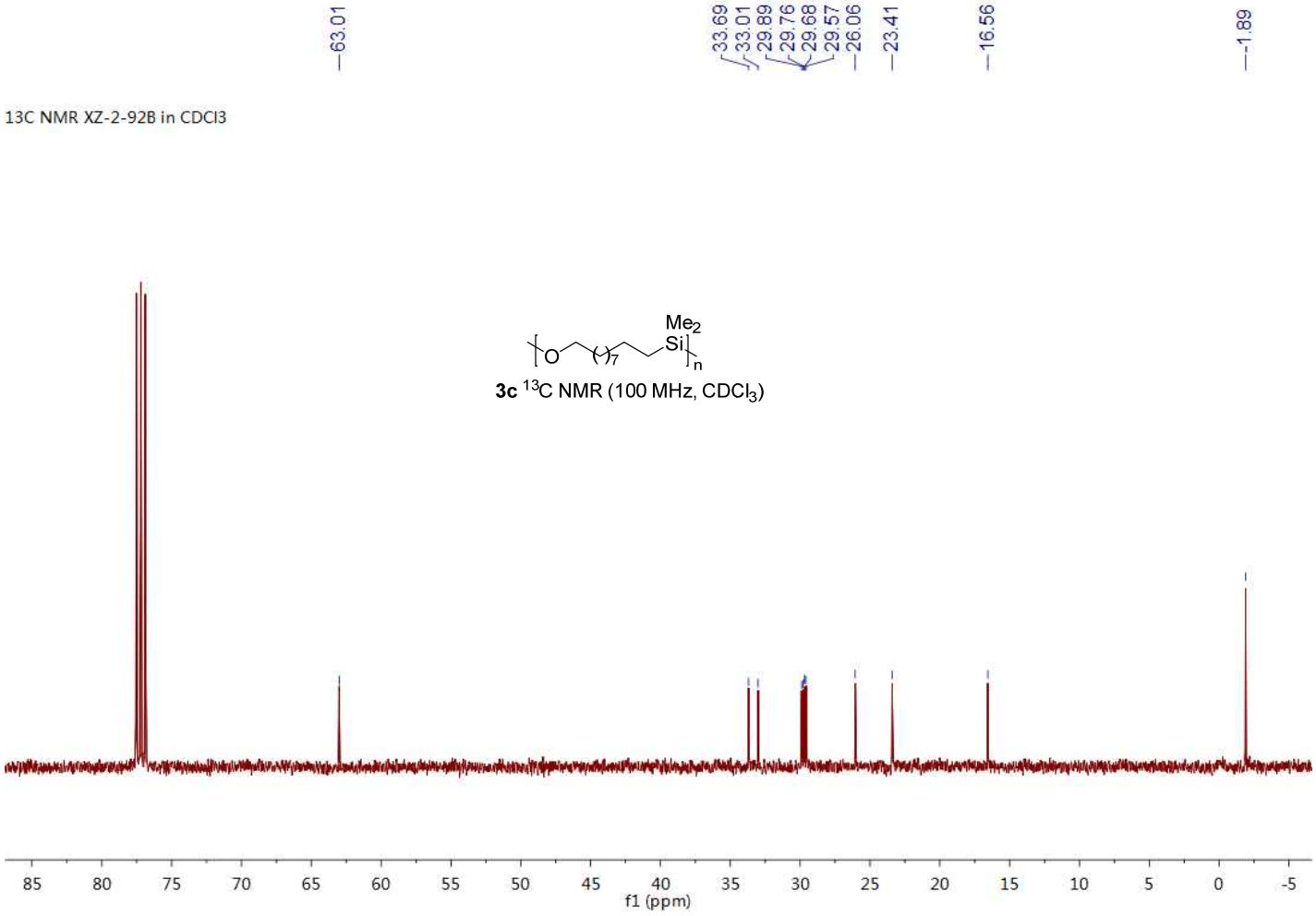


Figure S16, ^{13}C NMR of polymer **3c**

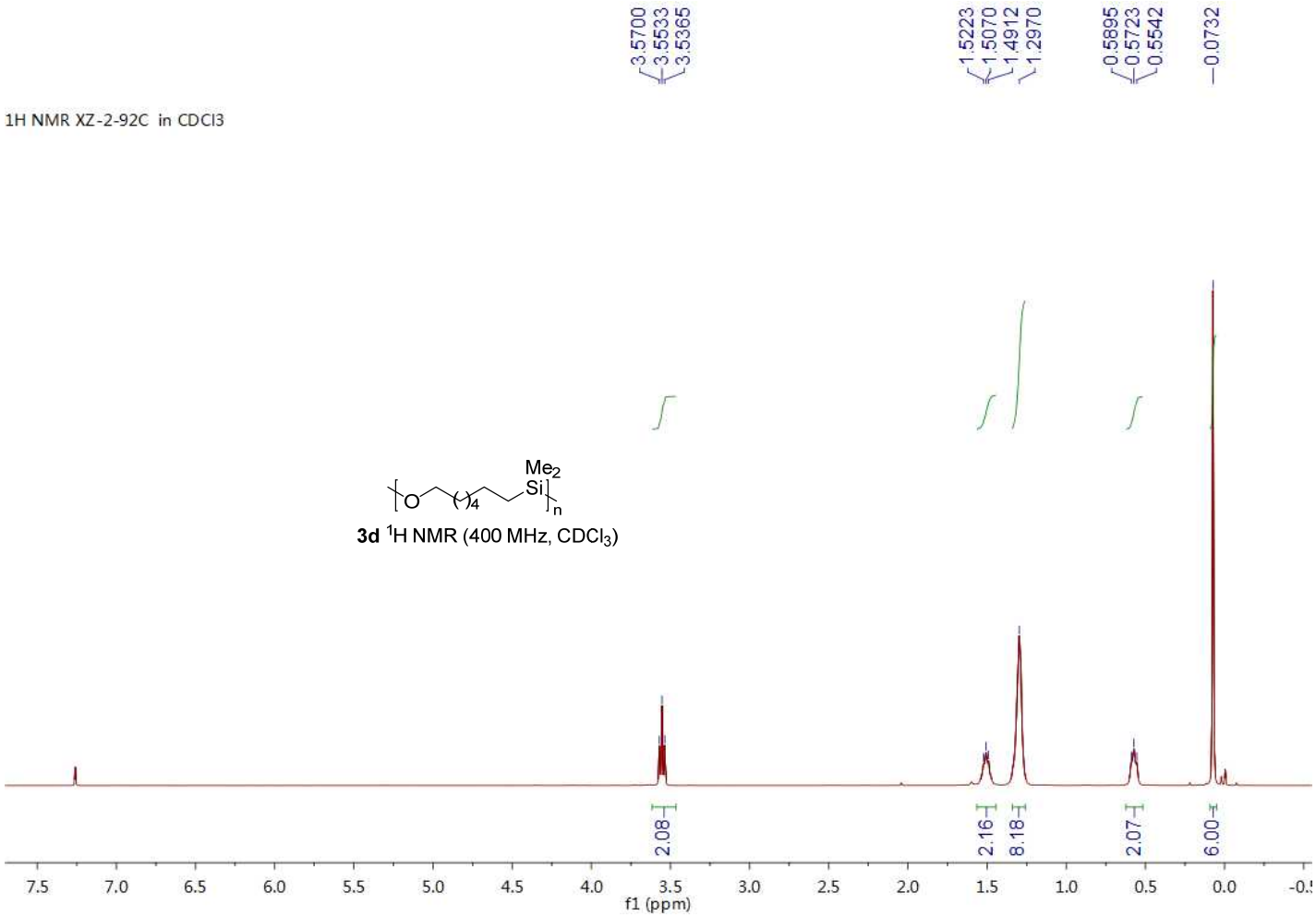
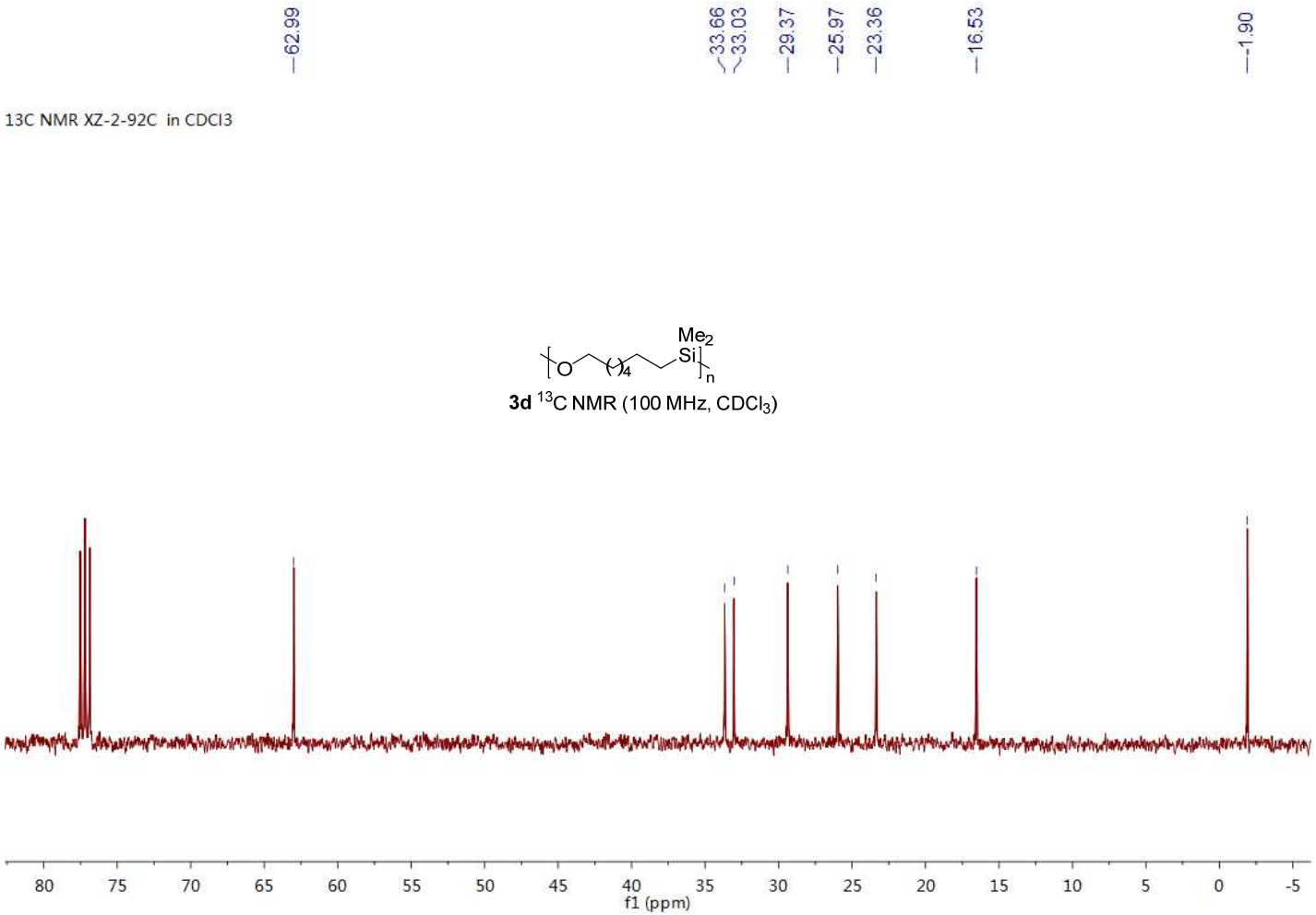


Figure S17, ^{1}H NMR of polymer **3d**



3d ^{13}C NMR (100 MHz, $CDCl_3$)

Figure S18, ^{13}C NMR of polymer **3d**

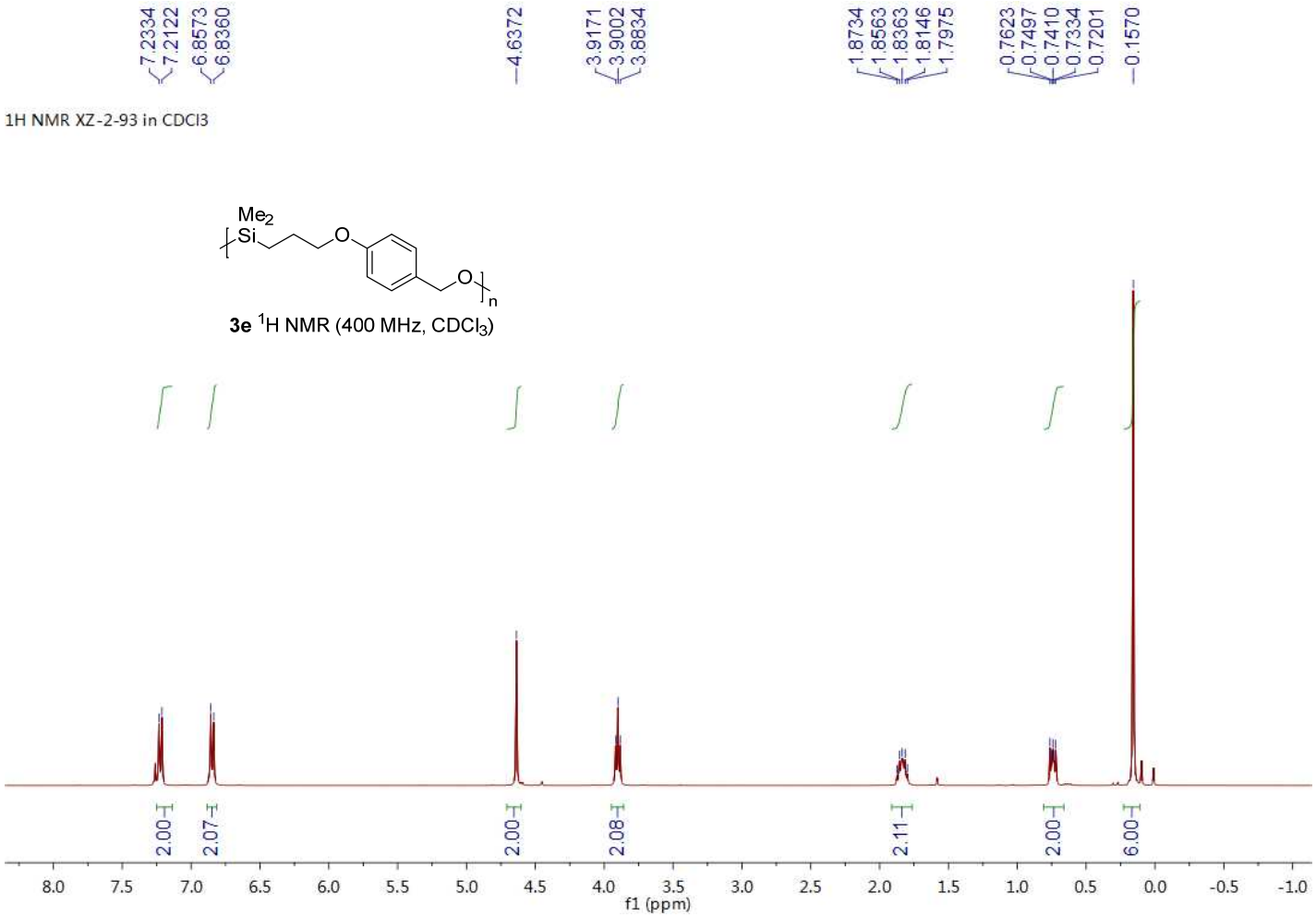


Figure S19, ^{1}H NMR of polymer **3e**

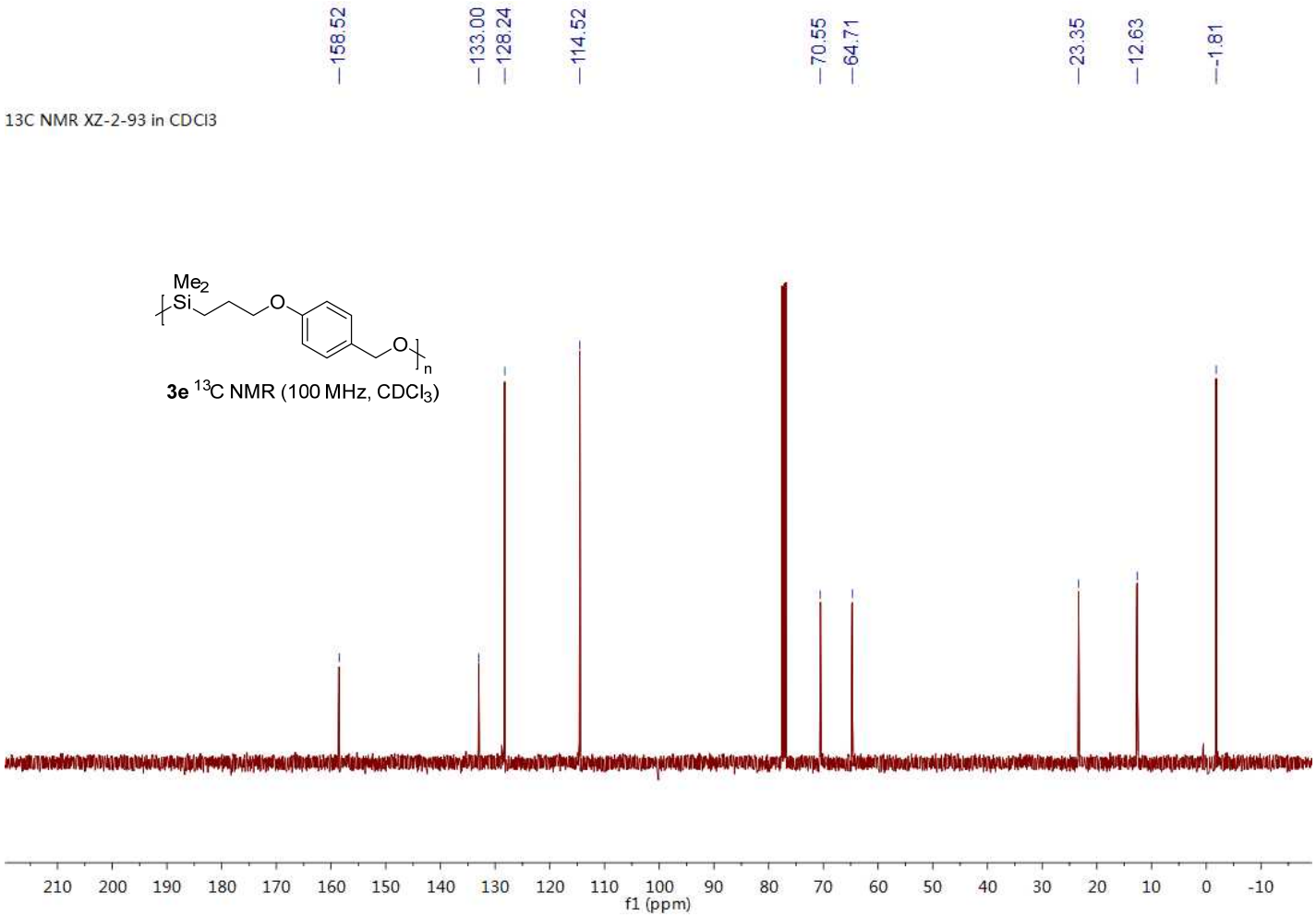


Figure S20, ^{13}C NMR of polymer **3e**

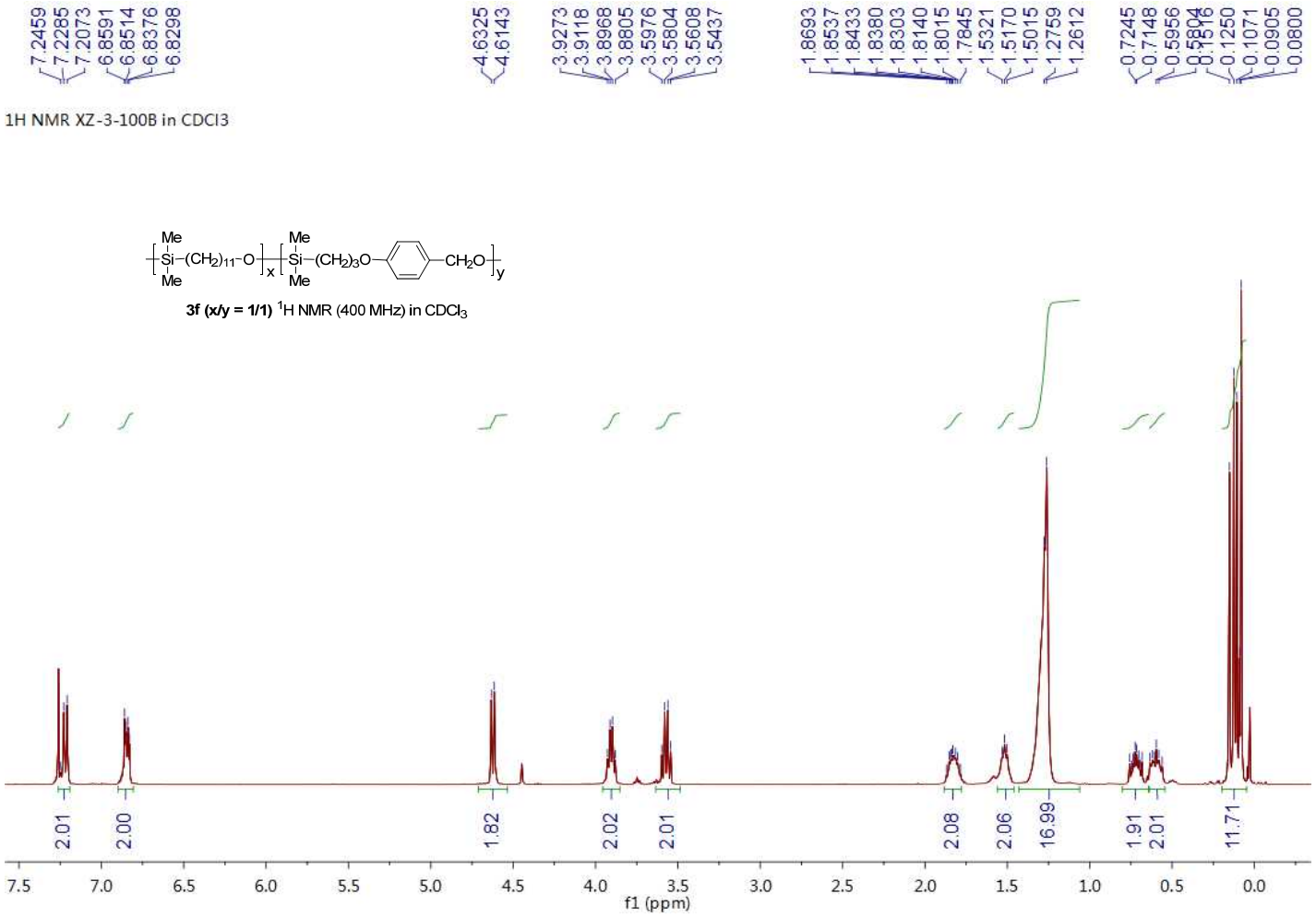


Figure S21, ^{1}H NMR of polymer **3f**

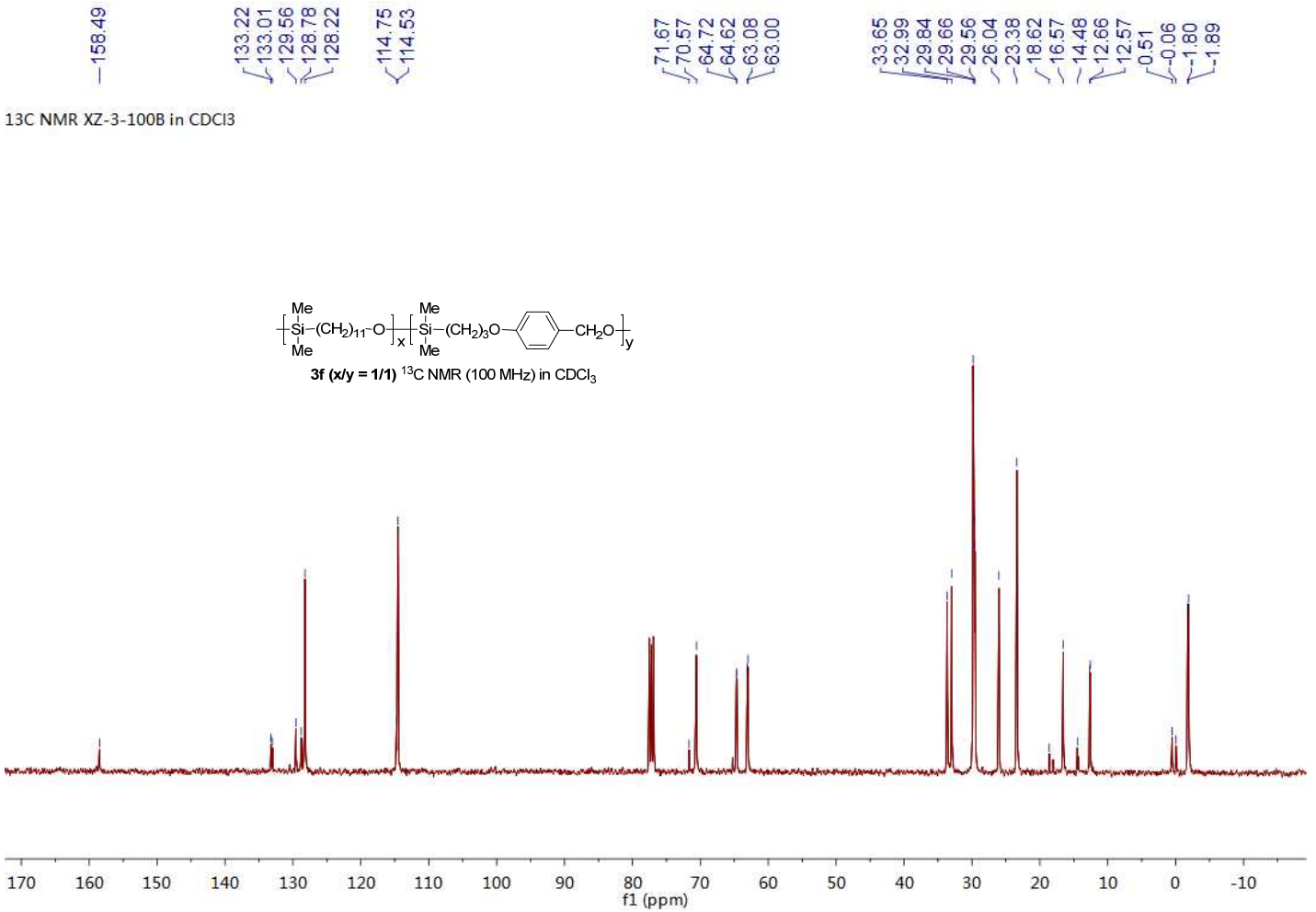


Figure S22, ^{13}C NMR of polymer **3f**

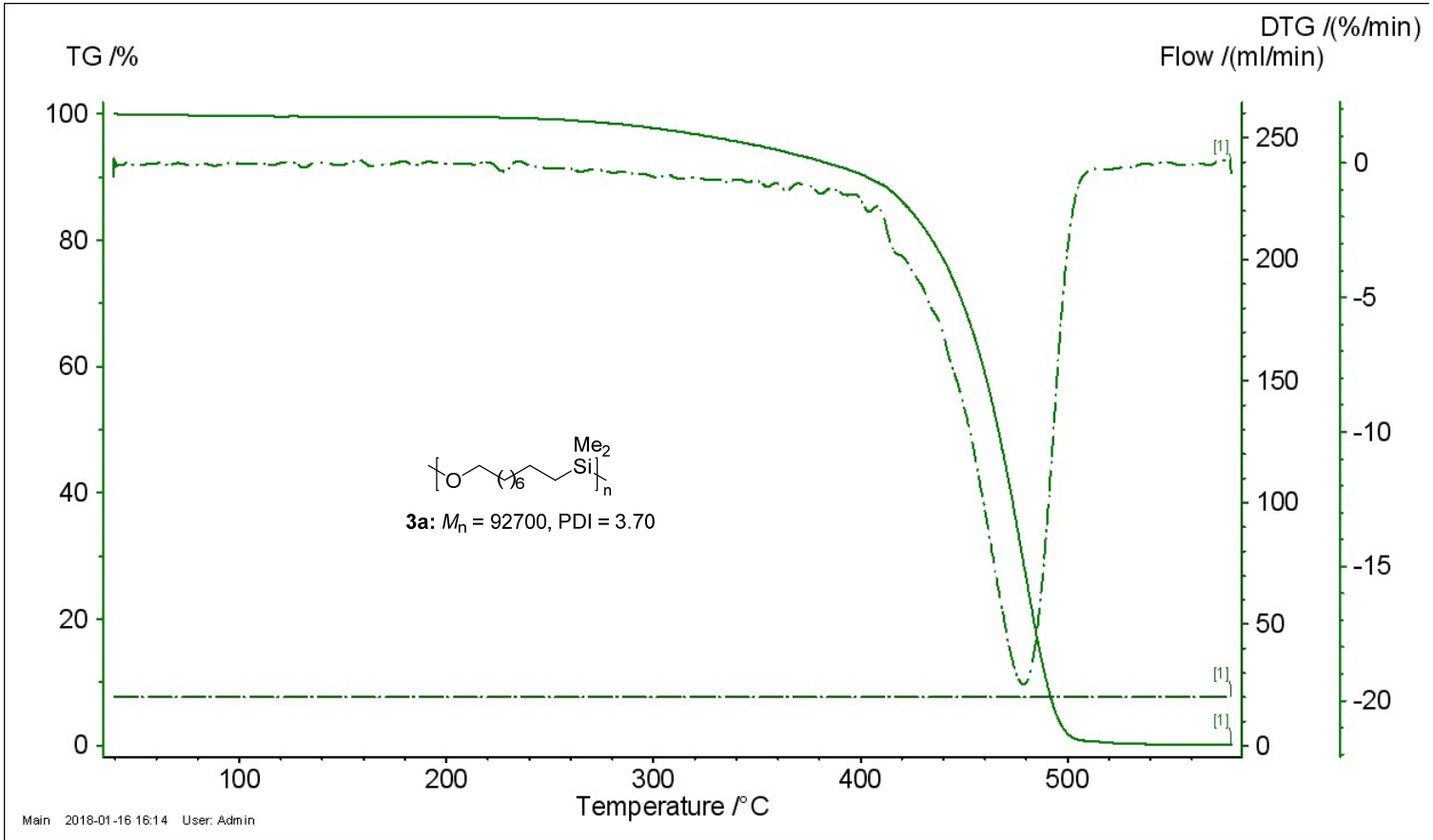


Figure S23, TG of polymer **3a**

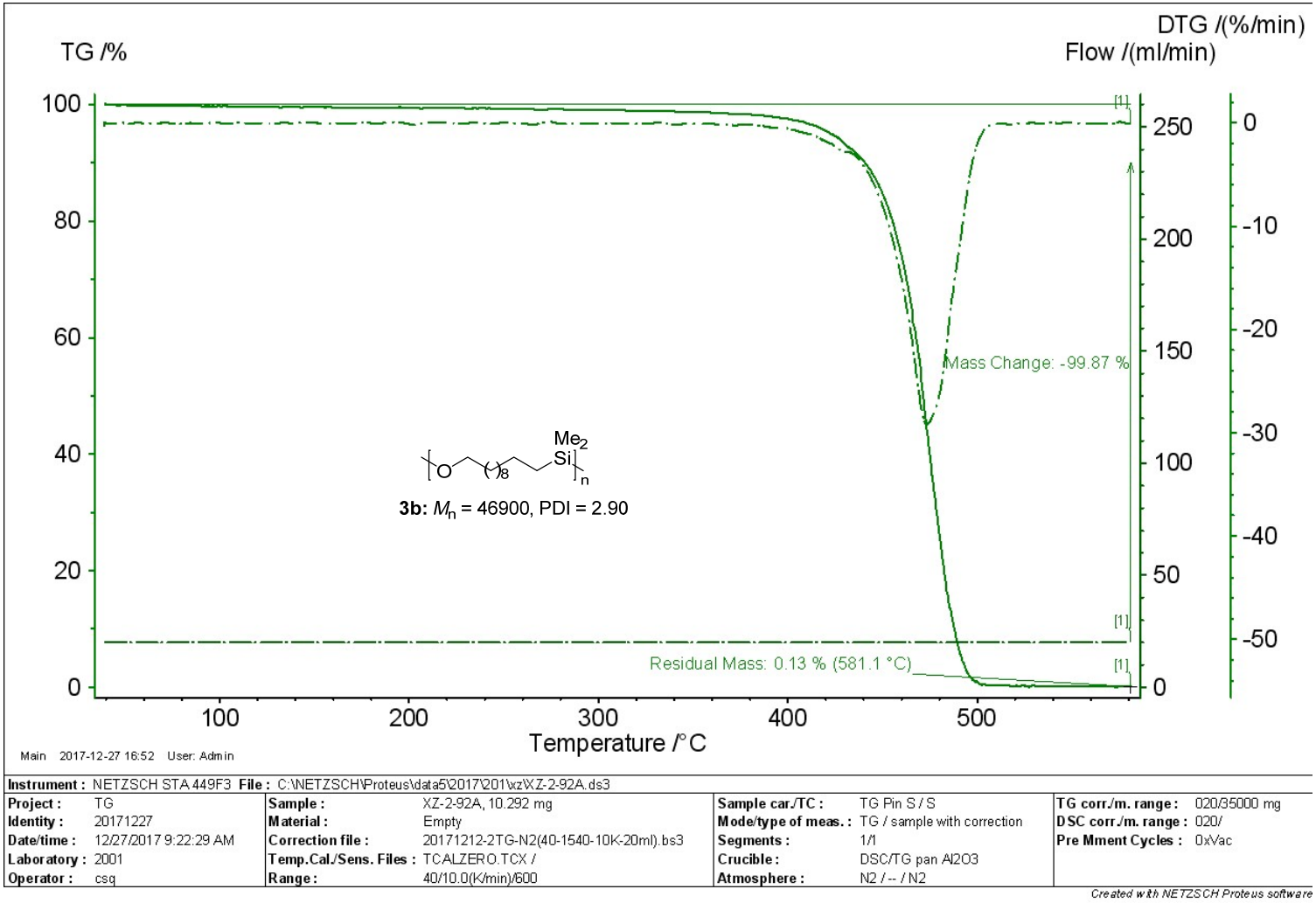


Figure S24, TG of polymer **3b**

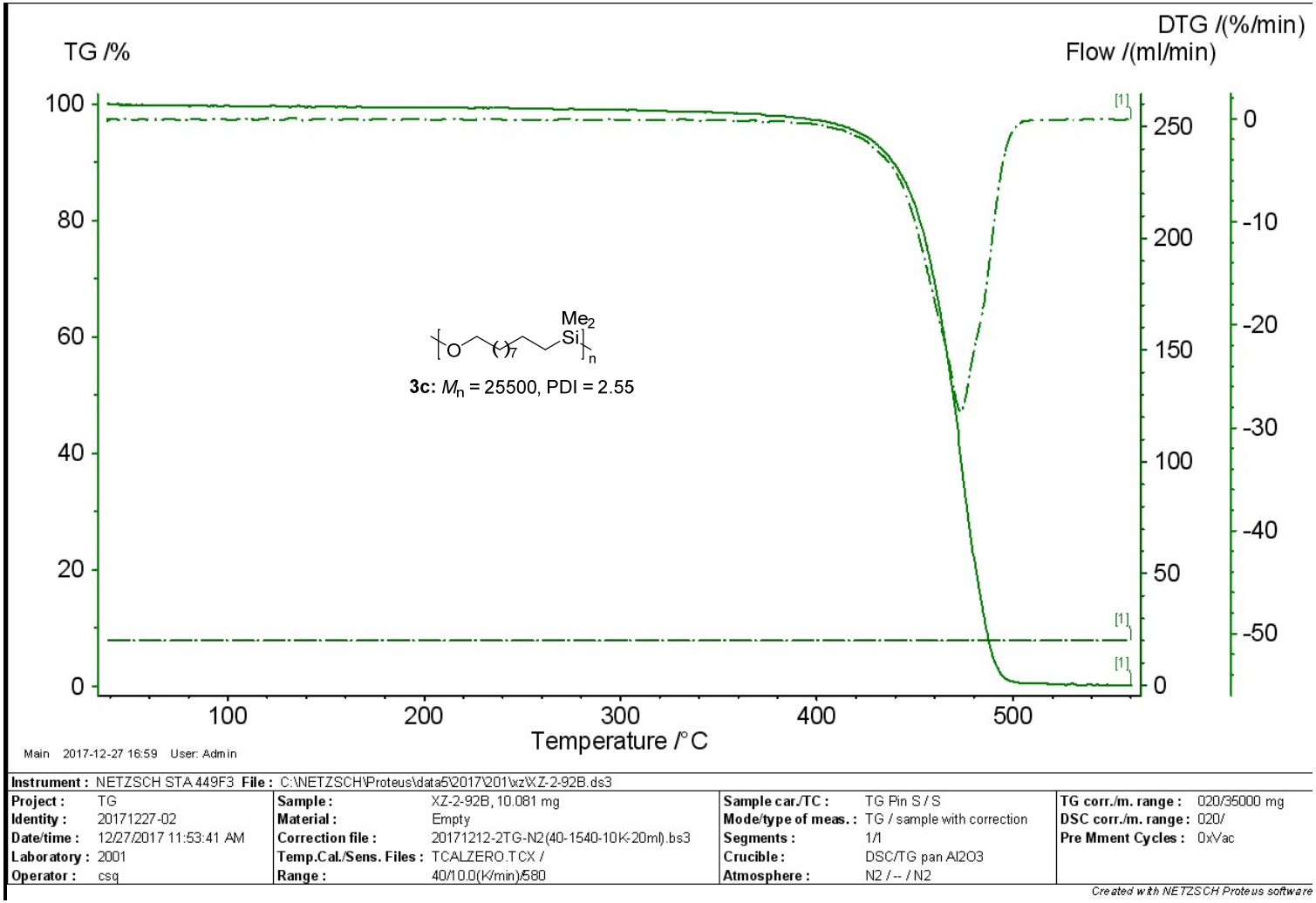


Figure S25, TG of polymer **3c**

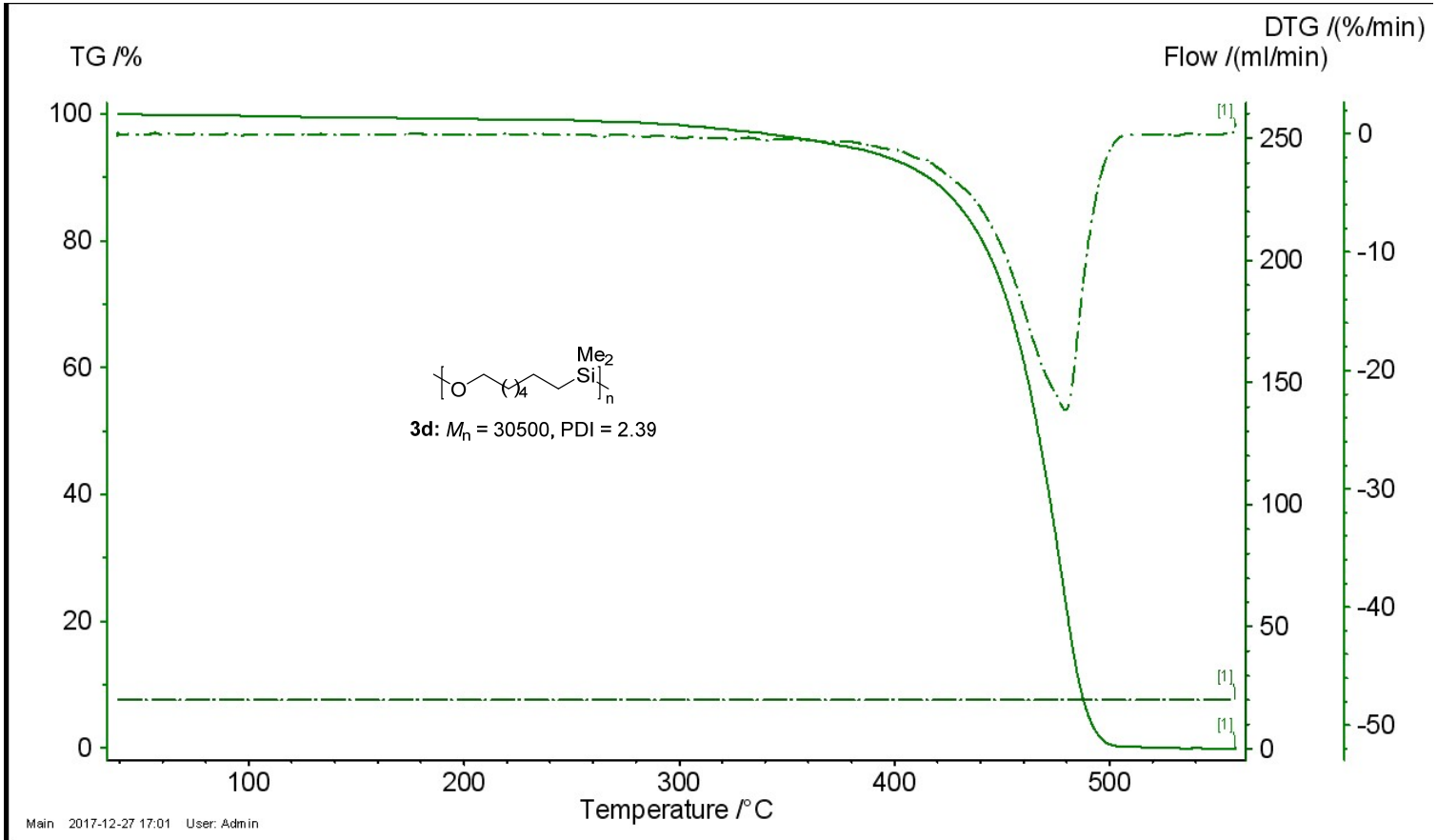


Figure S26, TG of polymer **3d**

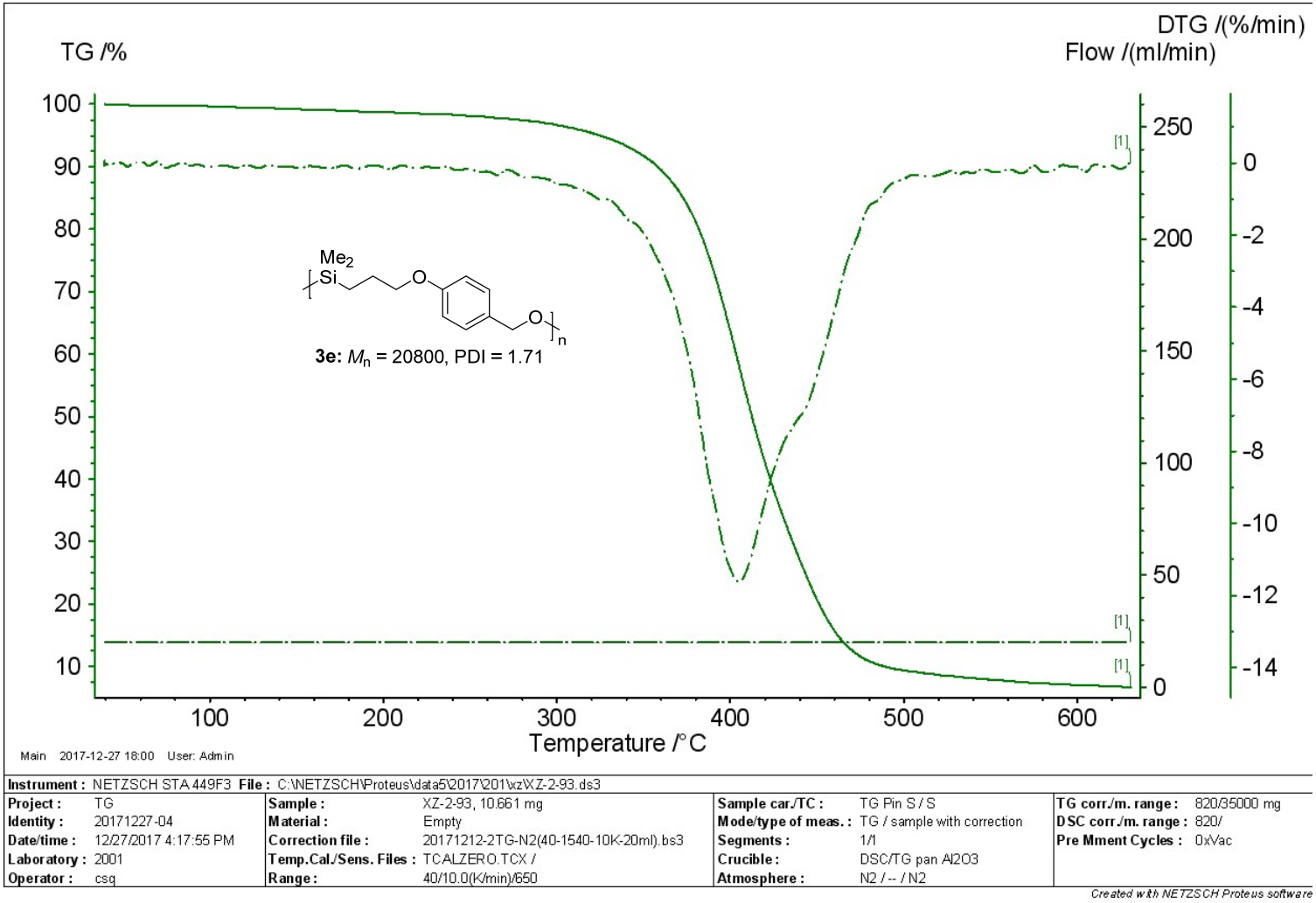


Figure S27, TG of polymer **3e**

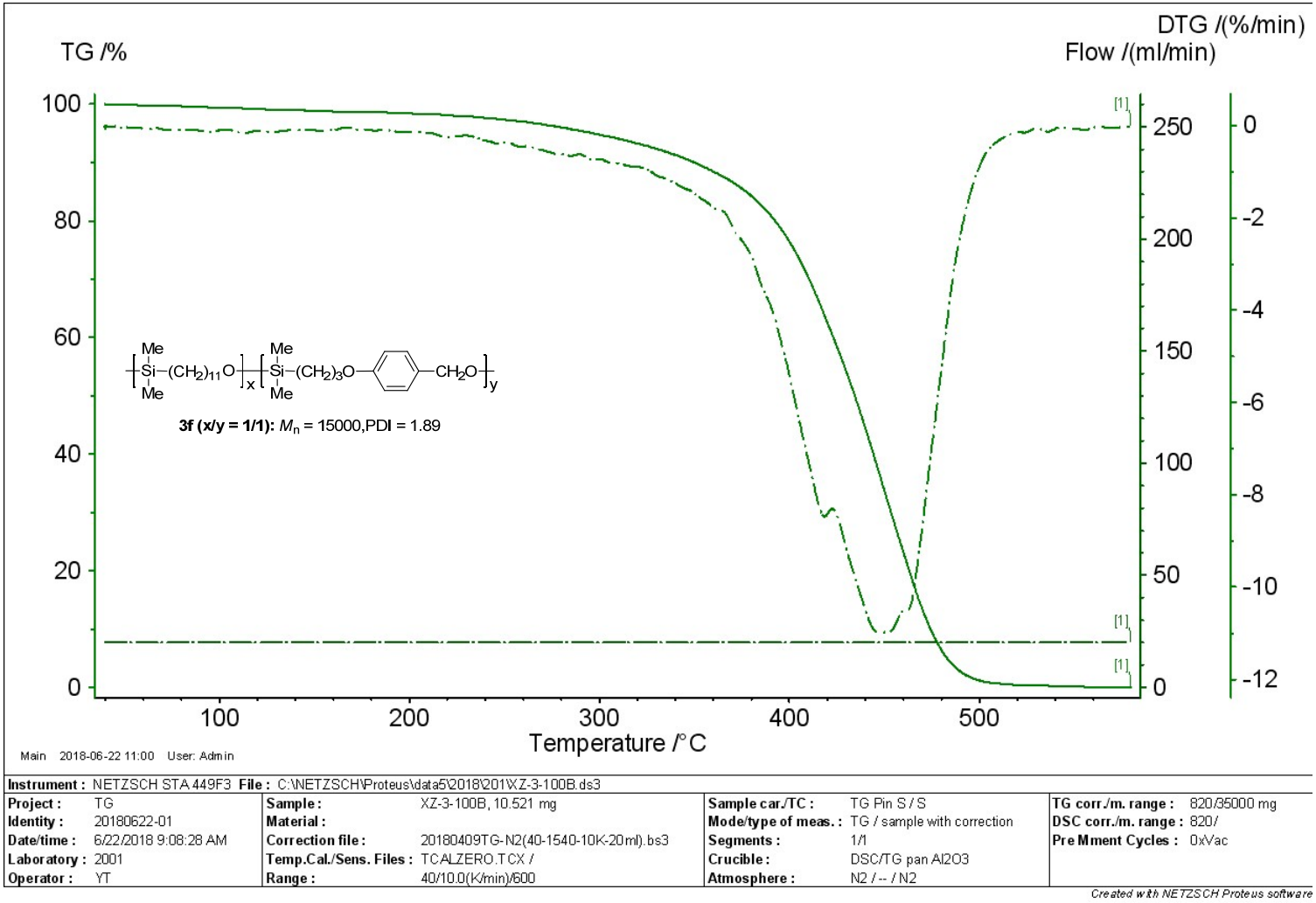


Figure S28, TG of polymer **3f**

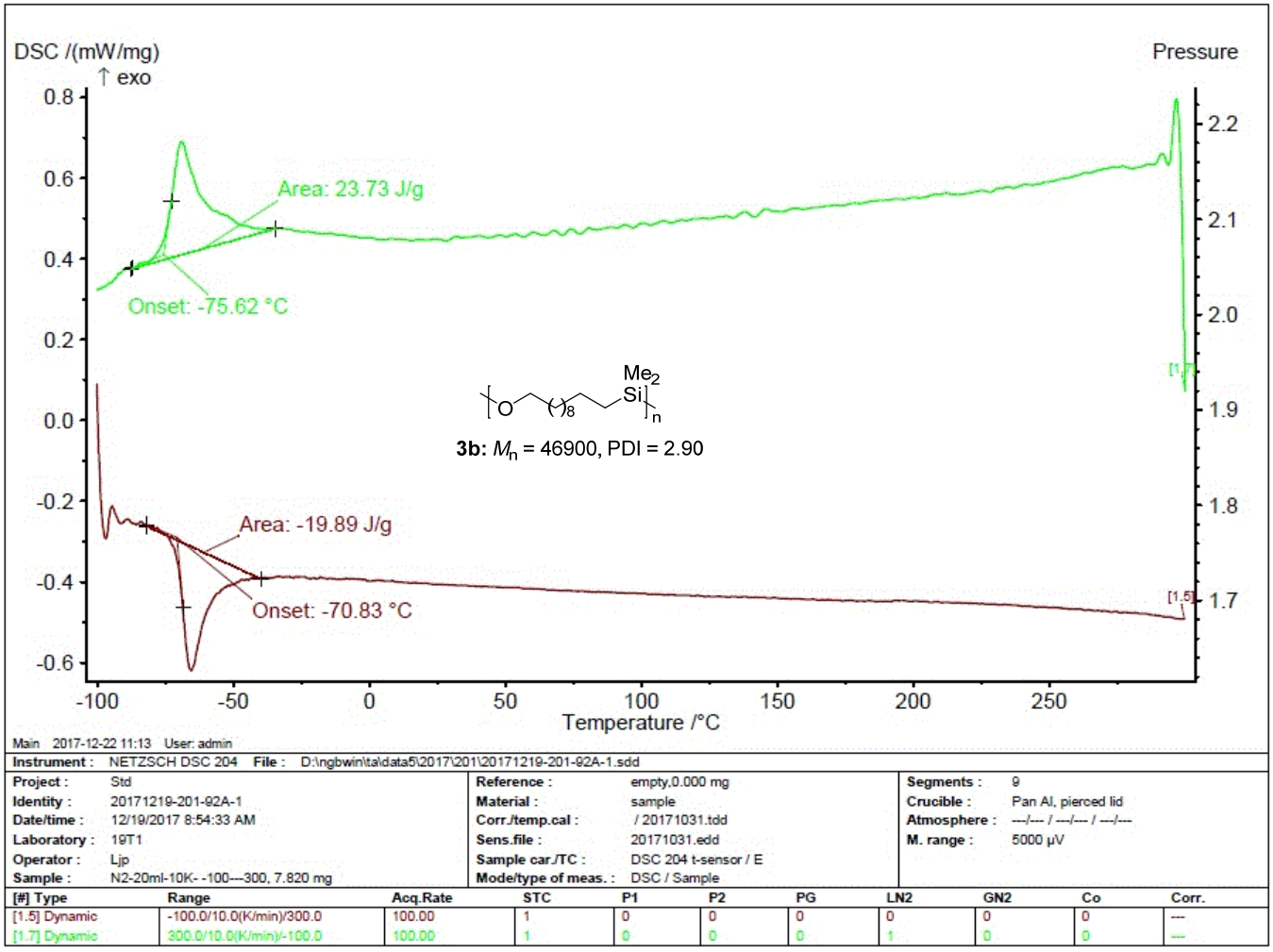


Figure S29, DSC of polymer **3b**

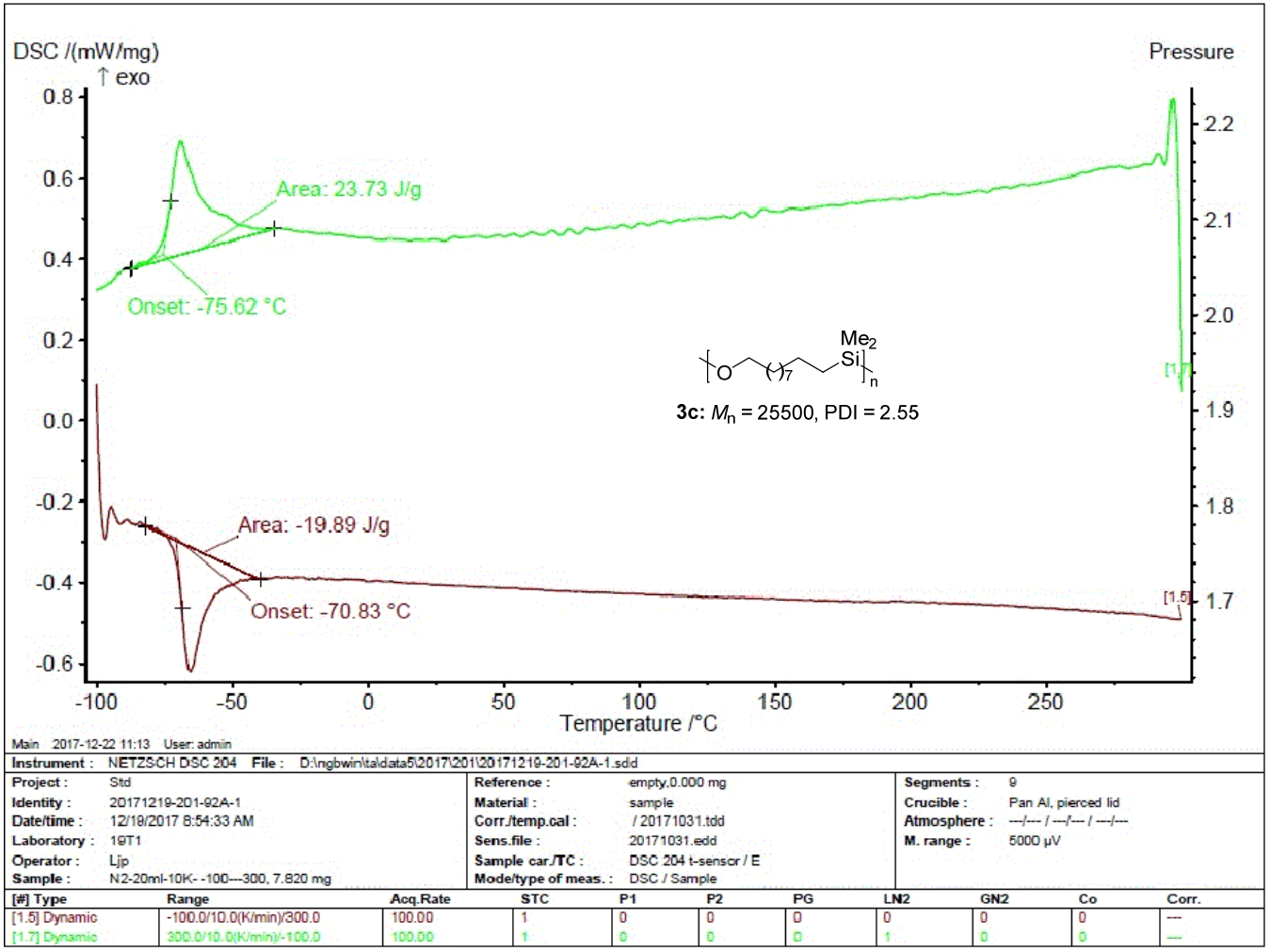


Figure S30, DSC of polymer **3c**

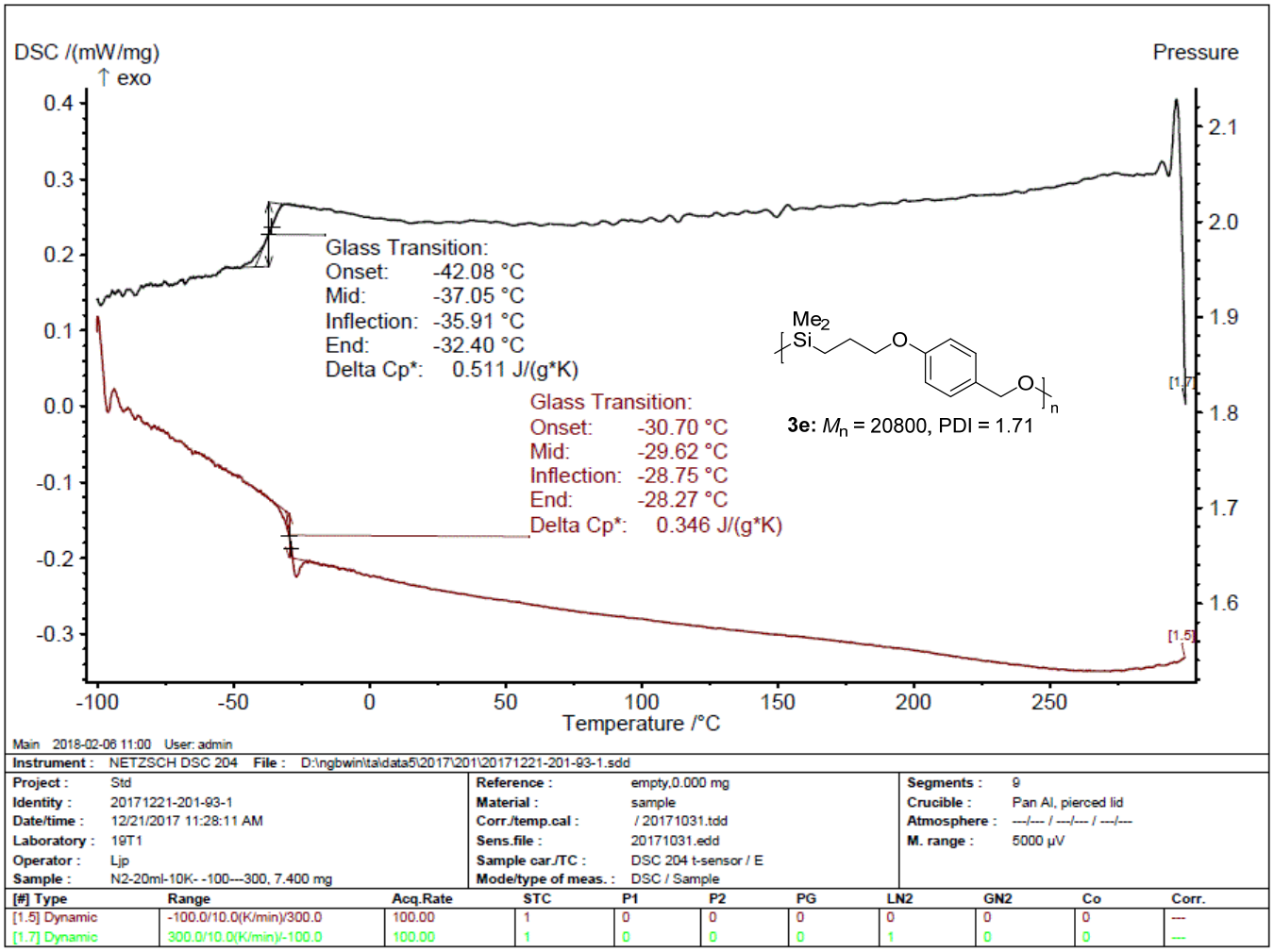


Figure S31, DSC of polymer **3e**

8. References

[1] Cheng, C.; Watts, A.; Hillmyer, M. A.; Hartwig, J. F. Polysilylether: A Degradable Polymer from Biorenewable Feedstocks. *Angew. Chem. Int. Ed.* **2016**, *55*, 11872.

[2] (a) Karstedt, B. D.; Charlotte, N. C. *US 3775452A* **1973** [*Chem. Abstr.* **1974**, *80*, 135655]. (b) Lewis, L. N.; Stein, J.; Gao, Y.; Colborn, R. E.; Hutchins, G. Platinum Catalysts Used in the Silicones Industry. *Platinum Met. Rev.* **1997**, *41*, 66.