Supplementary Information for:

Energetic silicones: synthesis and characterization of pentaoxadiazole-PDMS copolymers

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1. Experimental Data

Starting materials: hydride terminated polydimethylsiloxane (2-3 cst, 4-6 cst, and 7-10 cst, Gelest), pentamethyldisiloxane (Gelest), 1,1,3,3,5,5-hexamethyltrisiloxane (Gelest), 1,1,3,3,tetramethyldisiloxane (Gelest), Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Pt ~ 2% in xylene, Sigma Aldrich), and toluene (Sigma Aldrich) were all used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification.

Physical Measurements

Nuclear magnetic resonance (NMR, ^{1}H, ^{13}C and ^{29}Si) were collected on a Bruker AVANCE III HD 500 MHz spectrometer with a Bruker cryoprobe and chemical shifts were referenced to residual protic species in the respective solvent. Infrared spectra were measured under ambient conditions on a Bruker Alpha FTIR spectrometer with a zinc selenide ATR crystal. GPC measurements were carried out on an PL-GPC 200 High Temperature using Agilent ResiPore 300 x 7.5 mm columns with THF as eluent. The calibration curve was established with Polystyrene medium EasiVials (2 ml) from Agilent. DSC measurements were performed on a TA instruments DSC Q2000 calibrated to indium and performed with aluminum pans with pinhole lids at 3 °C/min with nitrogen purge gas at 50 ml/min**.** TGA measurements were carried out on an TA instruments TGA 5000 in a platinum pan without a lid at 10 °C/min with nitrogen purge gas at 25 ml/min.

Synthesis of polymers

3,4-bis(3-(4-(2-(2-(vinyloxy)ethoxy)ethoxy)-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-yl)-1,2,5-oxadiazole (1).

1 was synthesized and provided by Dr. Mao-Xi Zhang from Lawrence Livermore National Laboratory and used as received.

3,4-bis(3-(4-(2-(2-(2-(1,1,3,3,3-pentamethyldisiloxaneyl)ethoxy)ethoxy)ethoxy)-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-yl)-1,2,5-oxadiazole (2).

A 3 mL vial was charged with **1** (40 mg, 0.066 mmol), pentamethyldisiloxane (21 mg, 0.14 mmol), and toluene (0.5 mL). The solution was stirred for 5 min at ambient temperature, after which platinum(0)-1,3-divinyl-1,1,3,3,-tetramethyldisiloxane (2% Pt solution in xylene, 15 µL, 0.0013mmol) was added. The reaction stirred for 24 h and was then concentrated via rotary evaporation followed by high vacuum to yield a viscous brown oil.

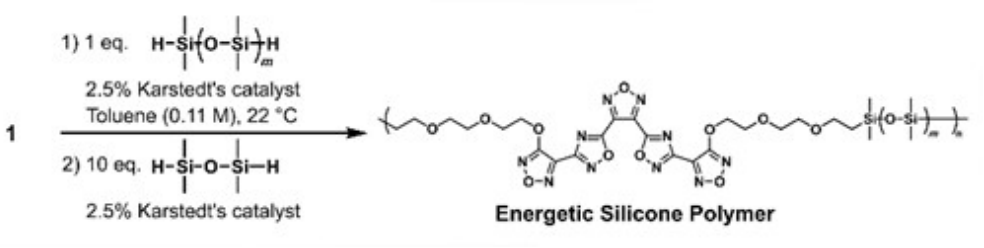
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.73 – 4.63 (m, 4H), 4.01 – 3.94 (m, 4H), 3.76 – 3.69 (m, 4H), 3.60 – 3.49 (m, 8H), 1.03 – 0.93 (m, 4H), 0.06 (s, 12H), 0.05 (s, 18H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 164.6, 163.9, 160.1, 141.6, 136.4, 73.1, 71.2, 69.7, 68.9, 68.1, 20.2, 2.1, 1.0.

General procedure for synthesis of 1 : PDMS copolymers.

A 3 mL scintillation vial was charged with **1** (40 mg, 0.066 mmol), dihydride terminated PDMS (0.066 mmol), and toluene (0.5 mL). The solution was stirred for 5 min at ambient temperature, after which platinum(0)-1,3-divinyl-1,1,3,3,-tetramethyldisiloxane (2% Pt solution in xylene, 15 µL, 0.0013 mmol) was added. The reaction stirred for 24 h, then 1,1,3,3-tetramethyldisiloxane (233 µL, 1.32 mmol) and platinum(0)-1,3-divinyl-1,1,3,3,-tetramethyldisiloxane (2% Pt solution in xylene, 15 µL, 0.0013 mmol) were added. After an additional 24 h, the reaction was then concentrated via rotary evaporation followed by high vacuum to yield a viscous brown oil.

Table S1 Measured data showing the length of PDMS component used for polymerization (*m*), weight average molecular weight (M_w), number average molecular weight (M_n), and TGA decomposition temperature (°C) for polymers **2-7**. [a]Trimer synthesized with **1** and pentamethyldisiloxane.

Material	PDMS (m)	M_w (kDa)	M_n (kDa)	TGA (°C)
2[a]	-	—	—	316
3	1	3.2	1.9	333
4	2	5.2	2.7	325
5	5-6	6.9	3.1	337
6	6-7	12.1	4.1	340
7	8-9	15.3	5.1	343



2. ^{1}H, ^{13}C, & ^{29}Si NMR Spectra

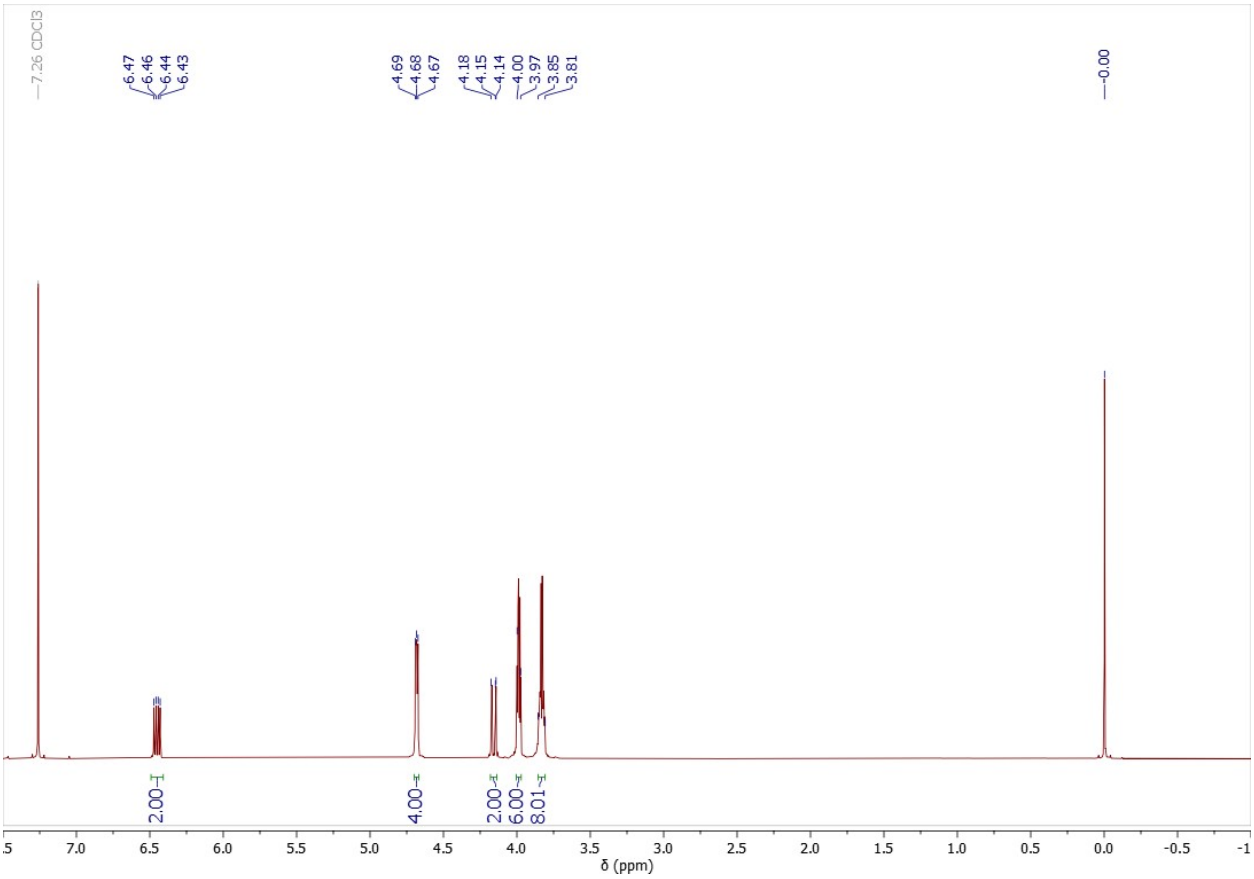


Figure S1. ^{1}H-NMR spectrum of **1** in $CDCl_3$.

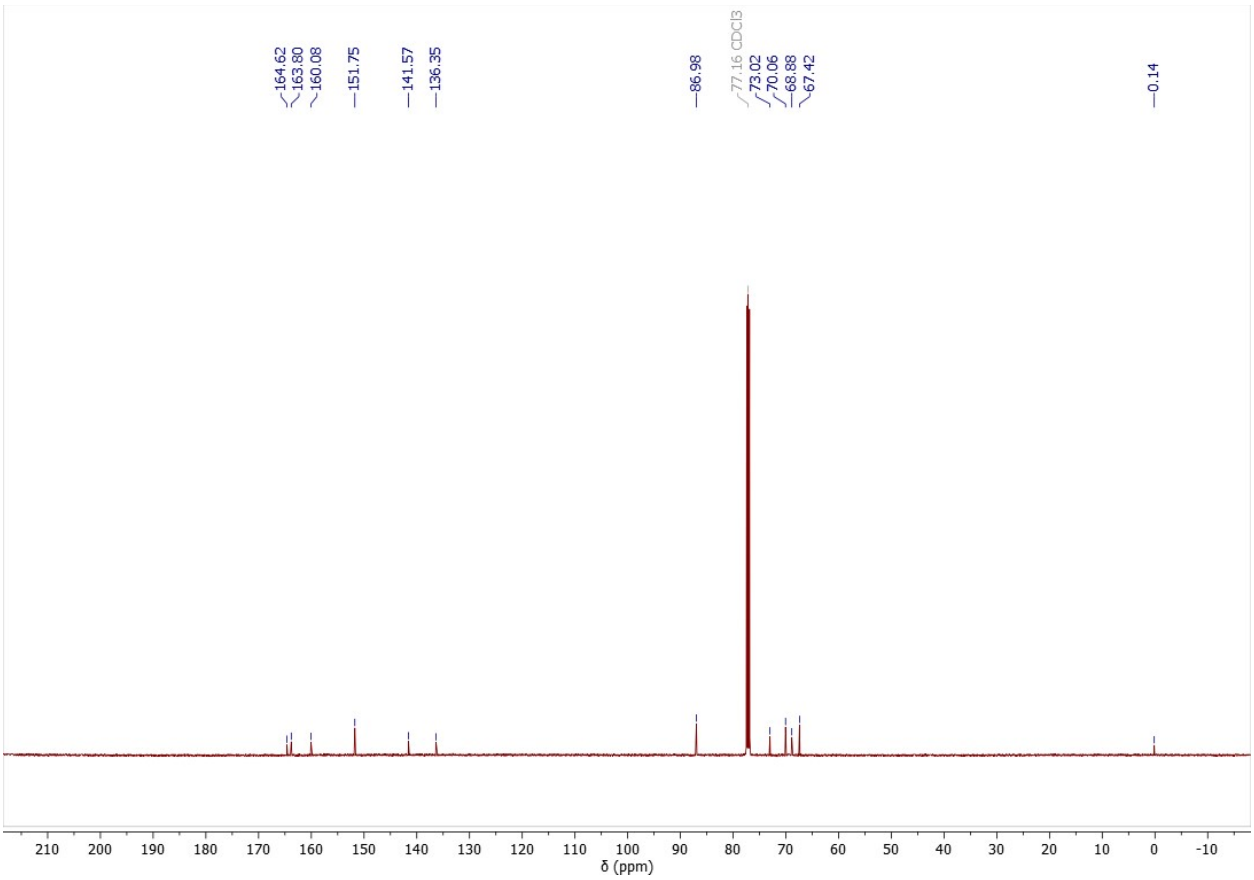


Figure S2. ^{13}C-NMR spectrum of **1** in $CDCl_3$.

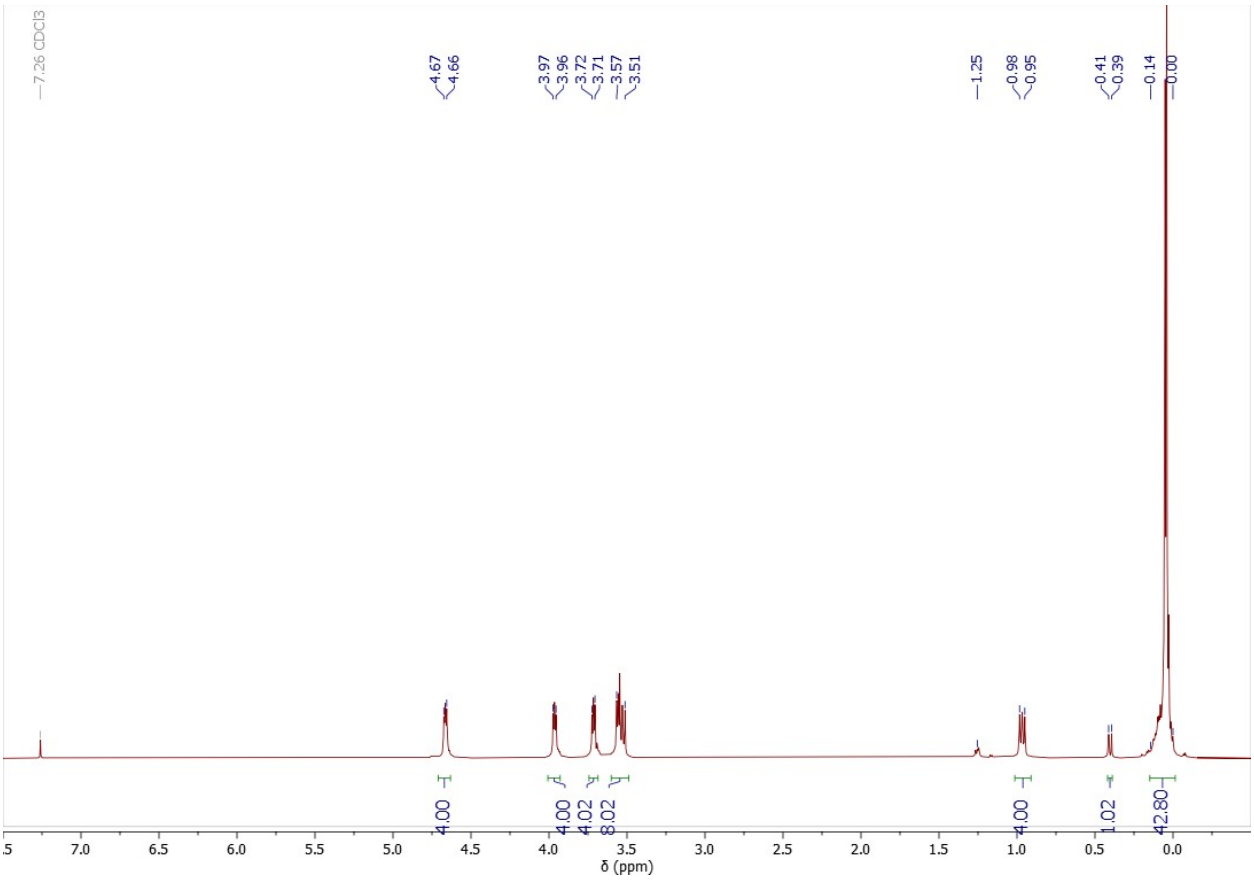


Figure S3. ^{1}H-NMR spectrum of **2** in $CDCl_3$.

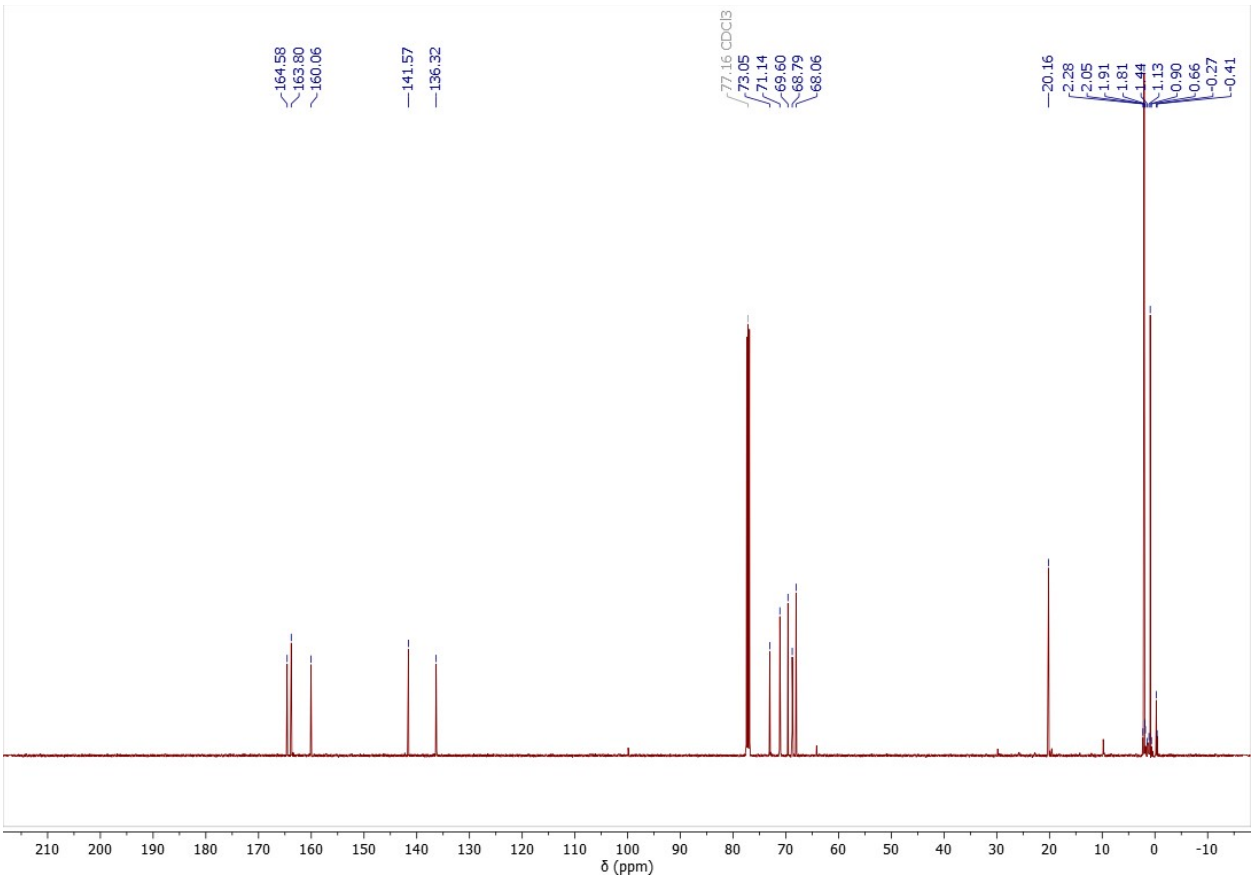


Figure S4. ^{13}C-NMR spectrum of **2** in $CDCl_3$.

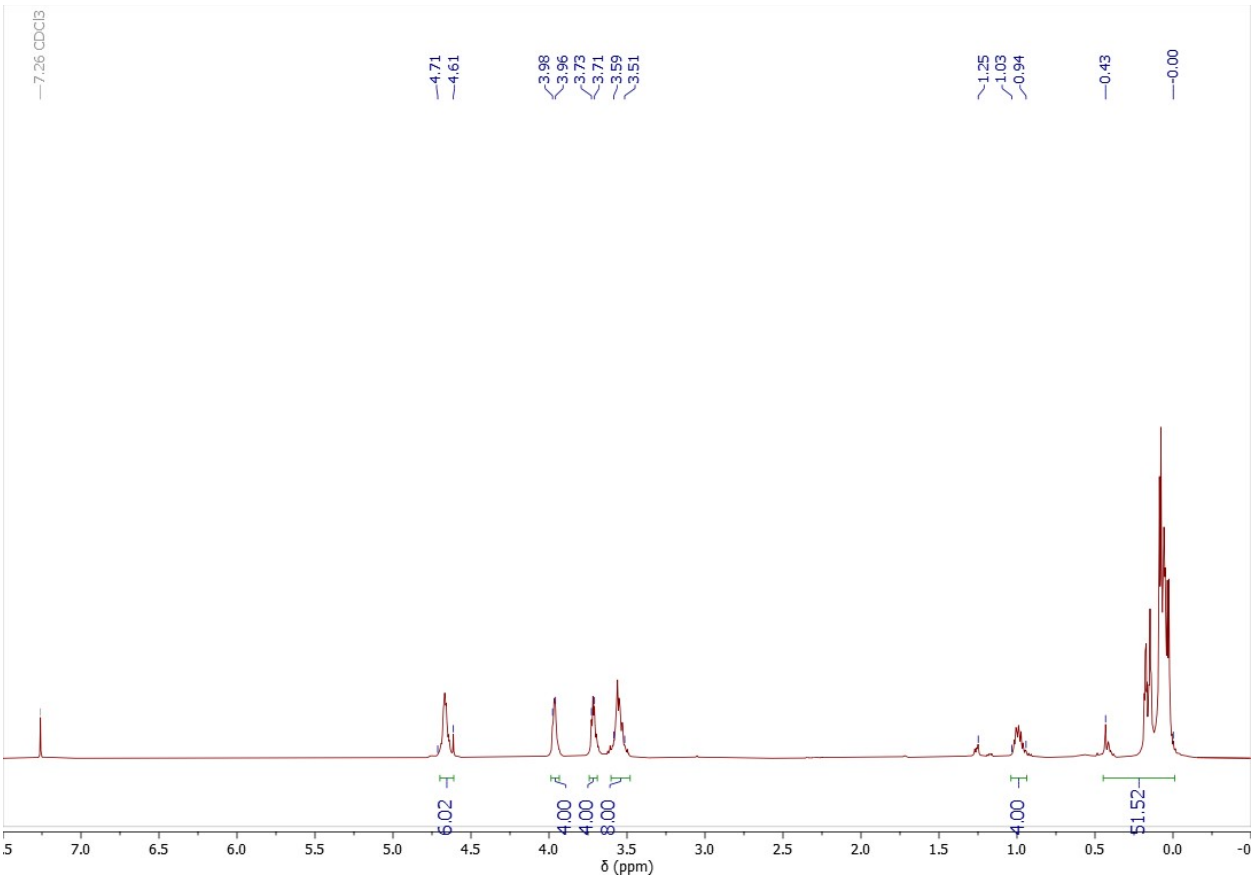


Figure S5. ^{1}H-NMR spectrum of **3** in $CDCl_3$.

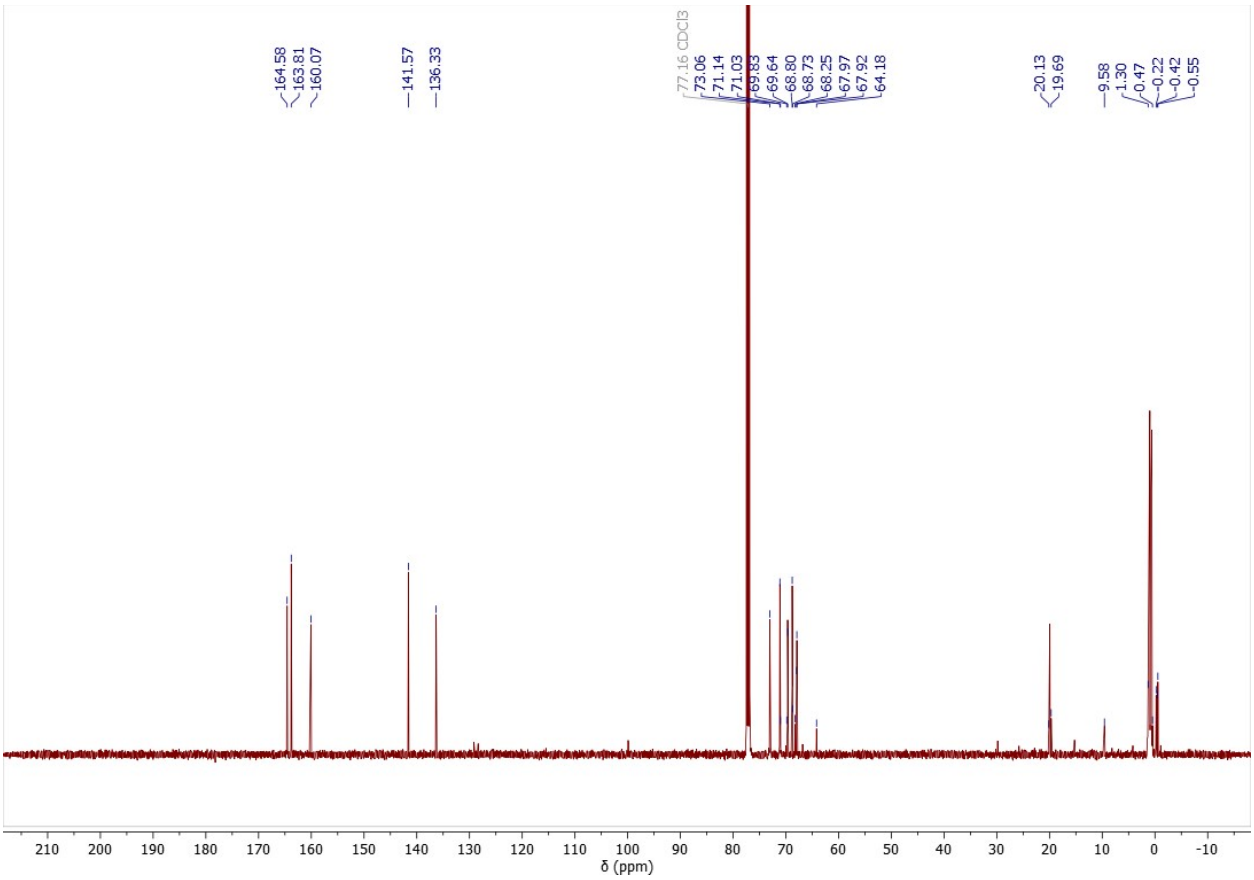


Figure S6. ^{13}C-NMR spectrum of **3** in $CDCl_3$.

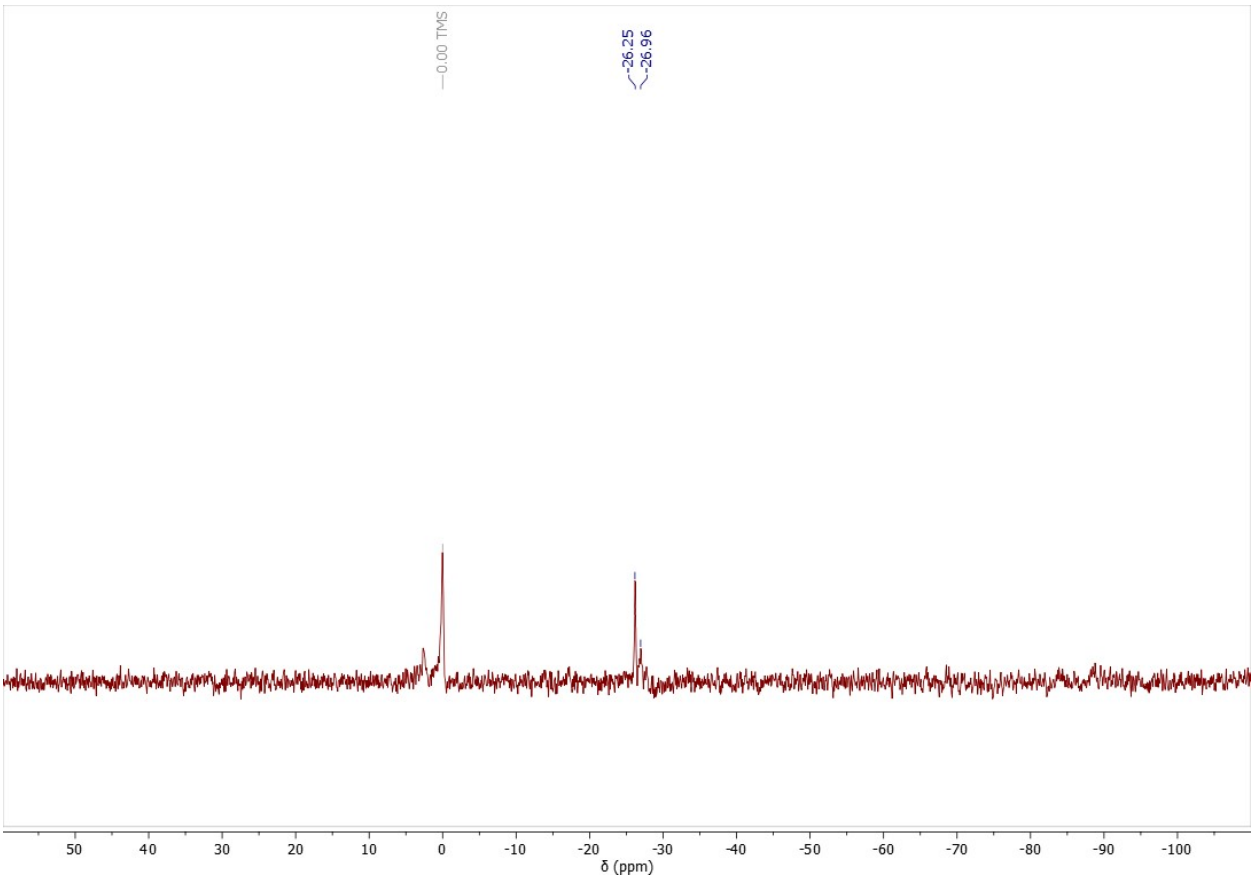


Figure S7. ^{29}Si-NMR spectrum of **3** in $CDCl_3$, referenced to TMS.

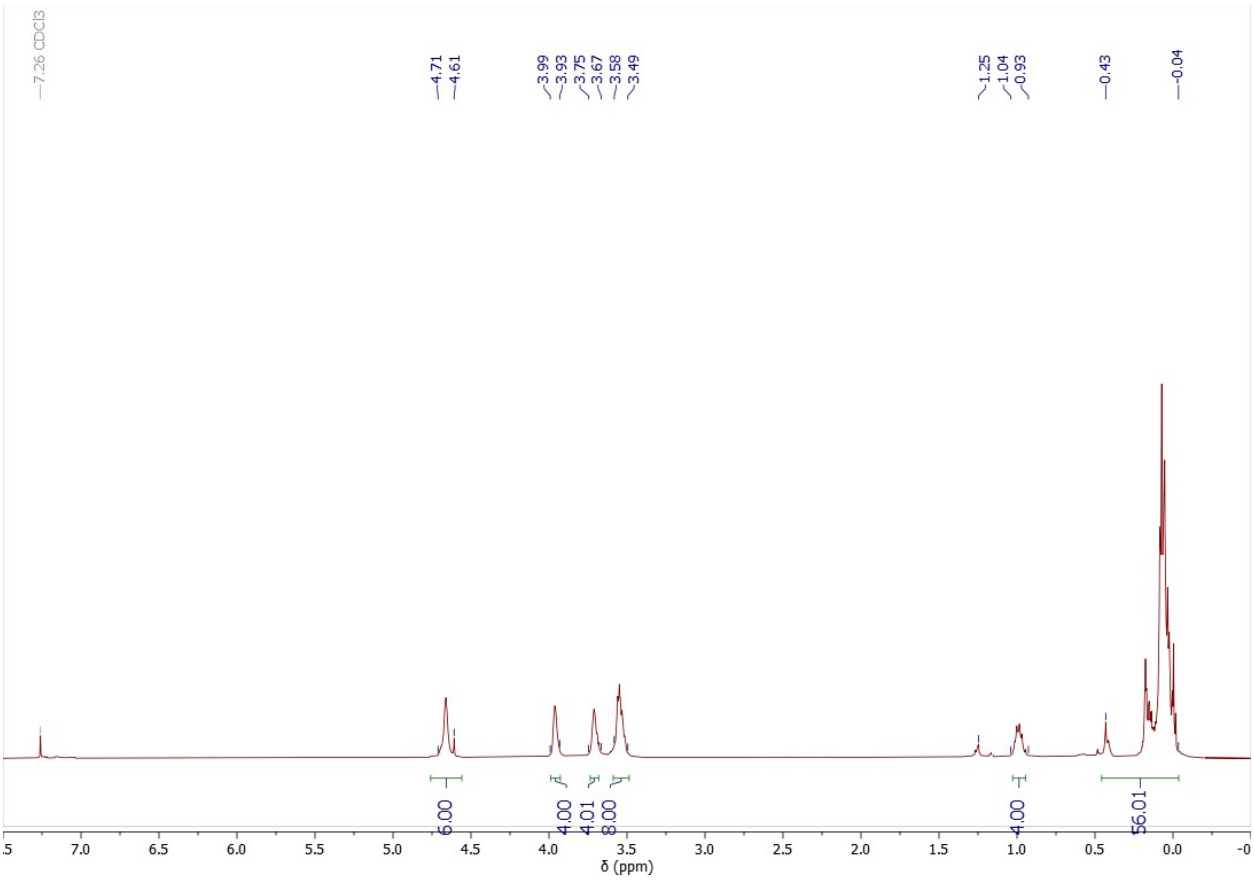


Figure S8. ^{1}H-NMR spectrum of **4** in $CDCl_3$.

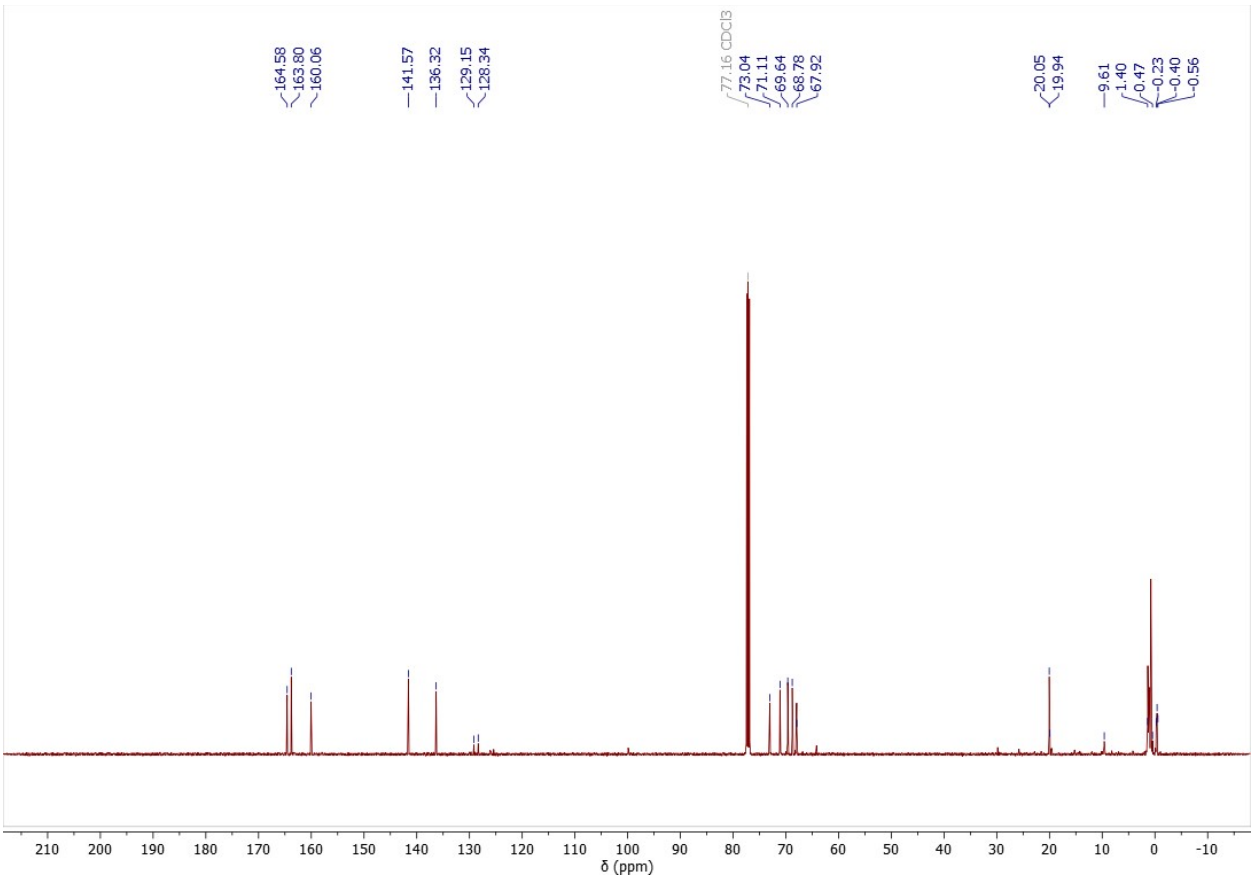


Figure S9. ^{13}C-NMR spectrum of **4** in $CDCl_3$.

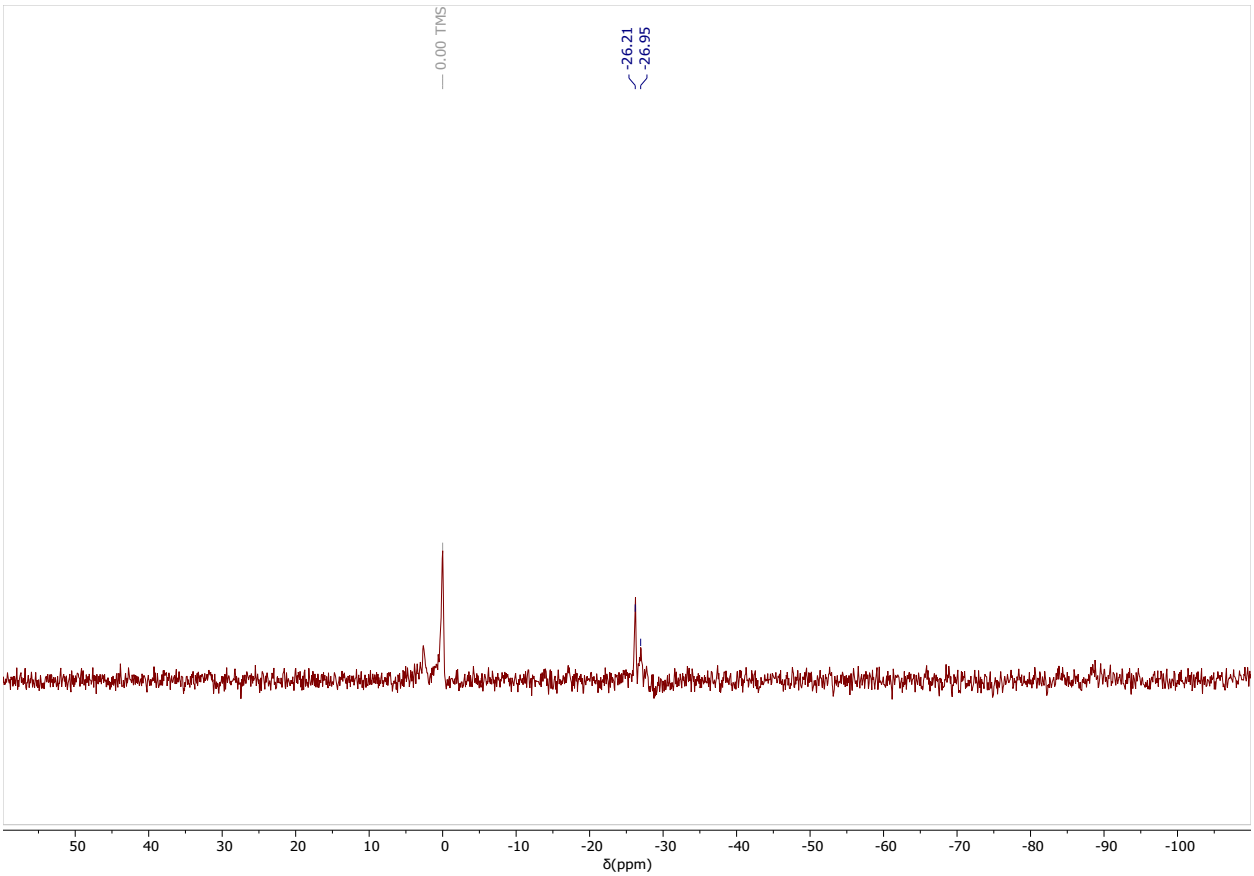


Figure S10. ^{29}Si-NMR spectrum of **4** in $CDCl_3$, referenced to TMS.

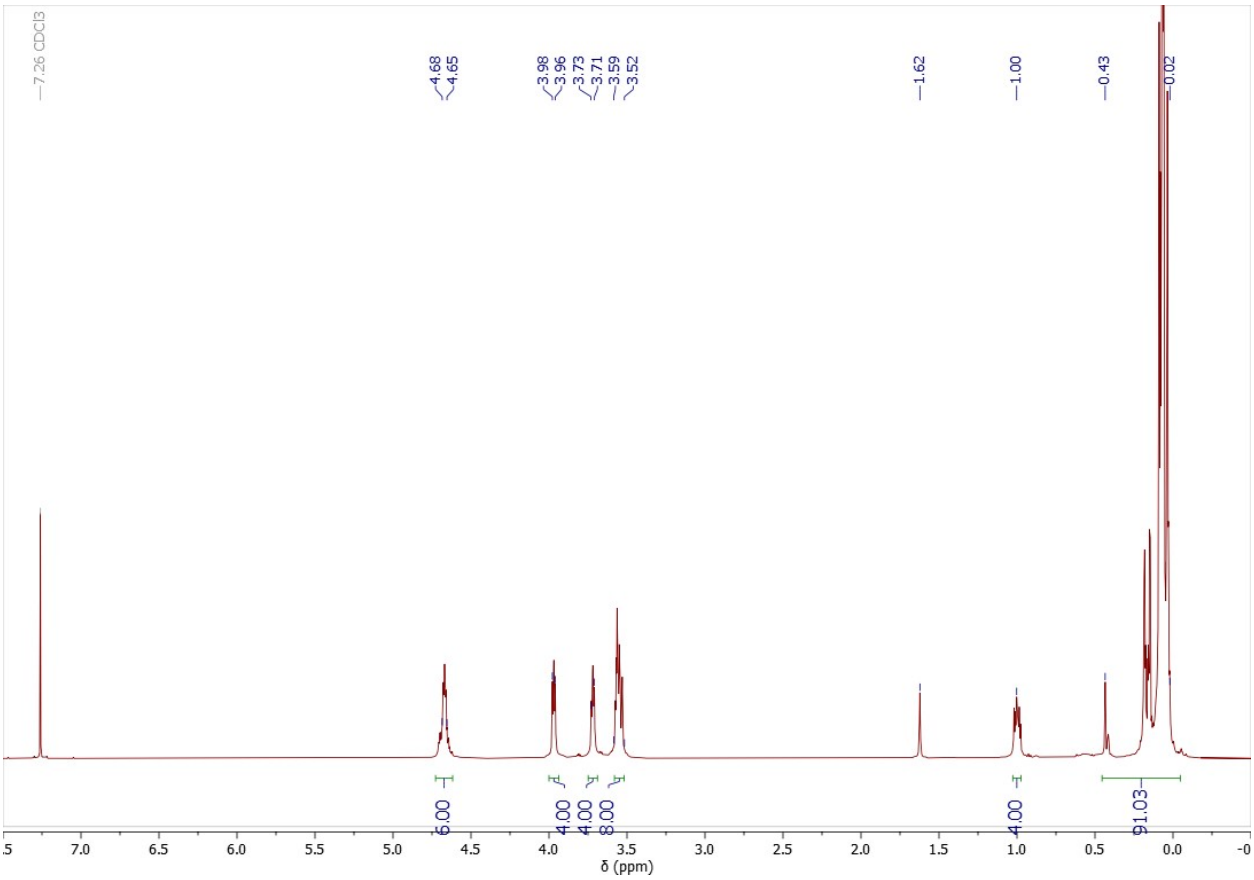


Figure S11. ^{1}H-NMR spectrum of **5** in $CDCl_3$. Peak at 1.62 ppm = H_2O

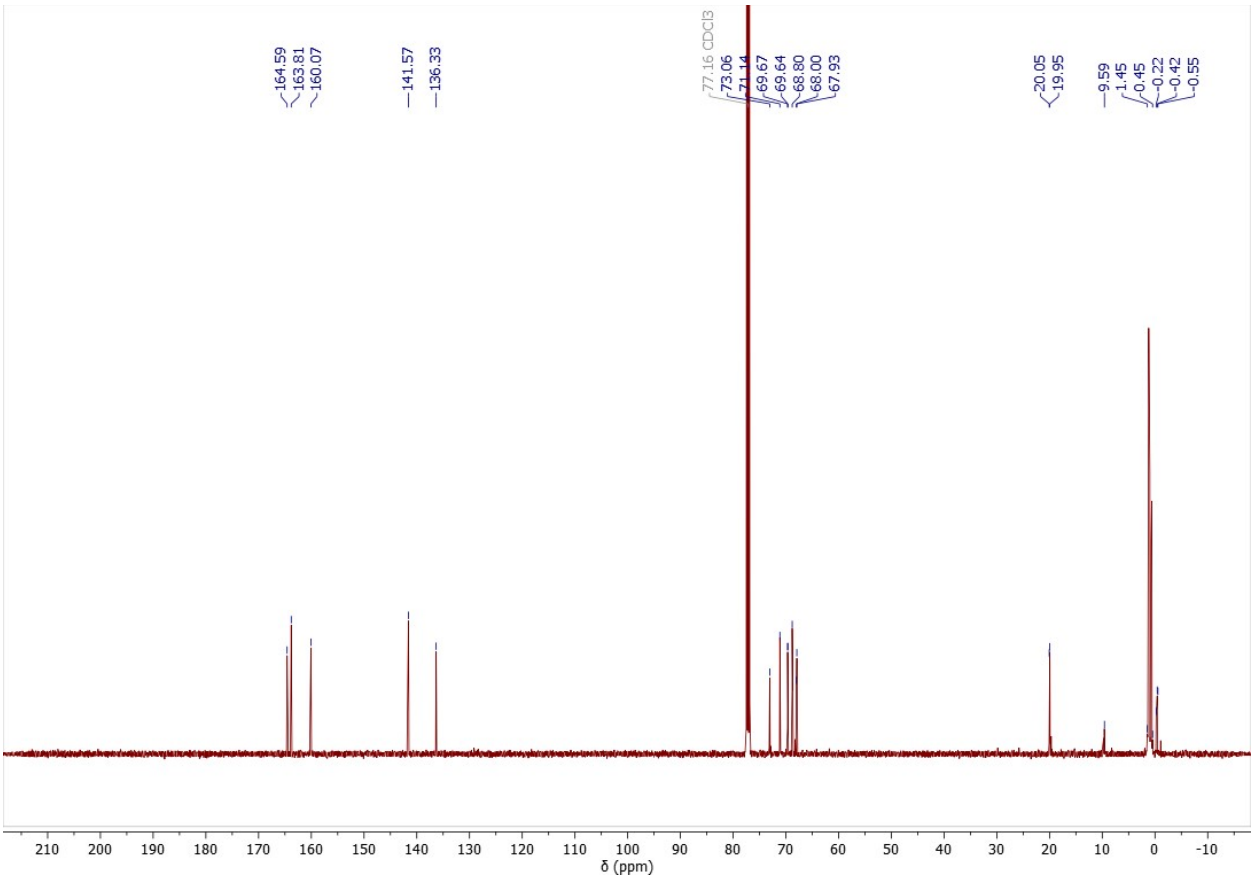


Figure S12. ^{13}C-NMR spectrum of **5** in $CDCl_3$.

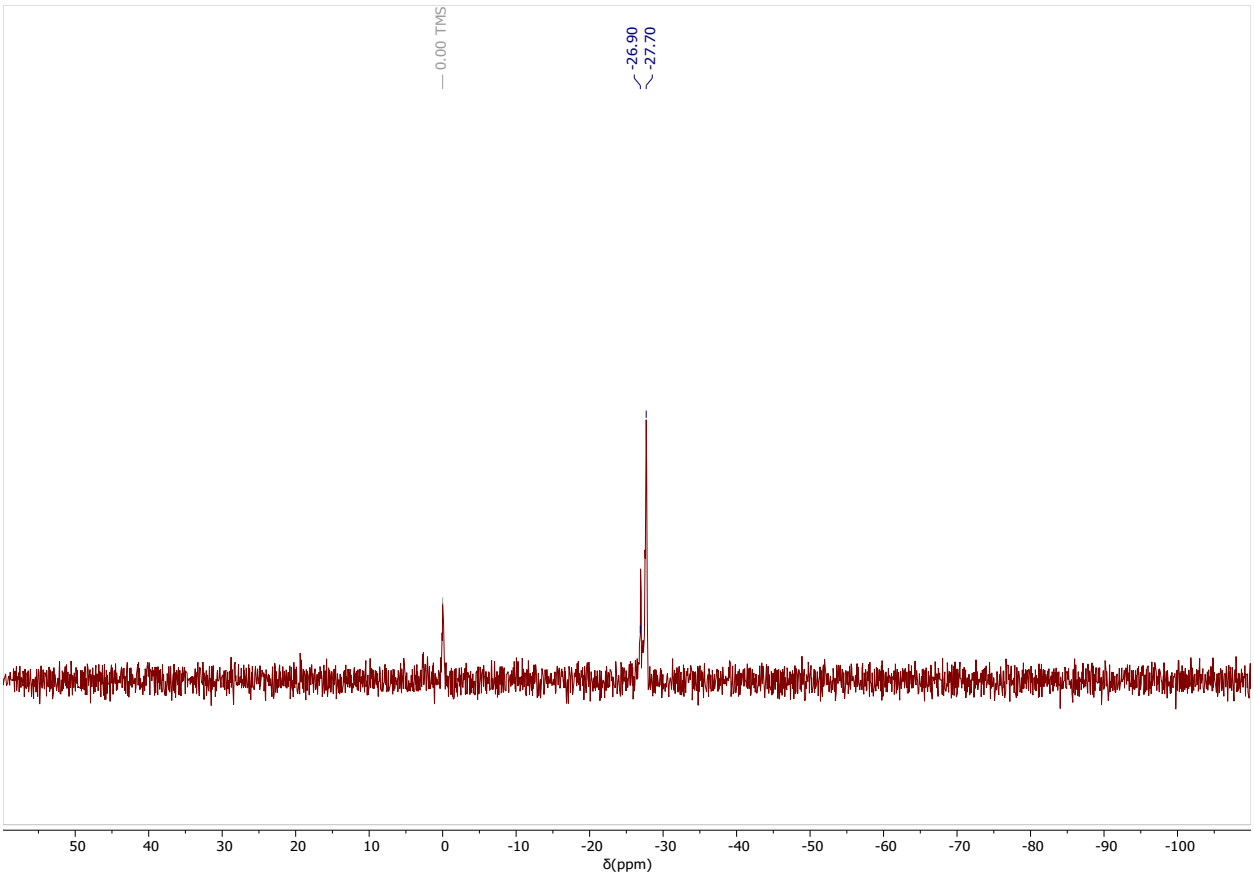


Figure S13. ^{29}Si-NMR spectrum of **5** in $CDCl_3$, referenced to TMS.

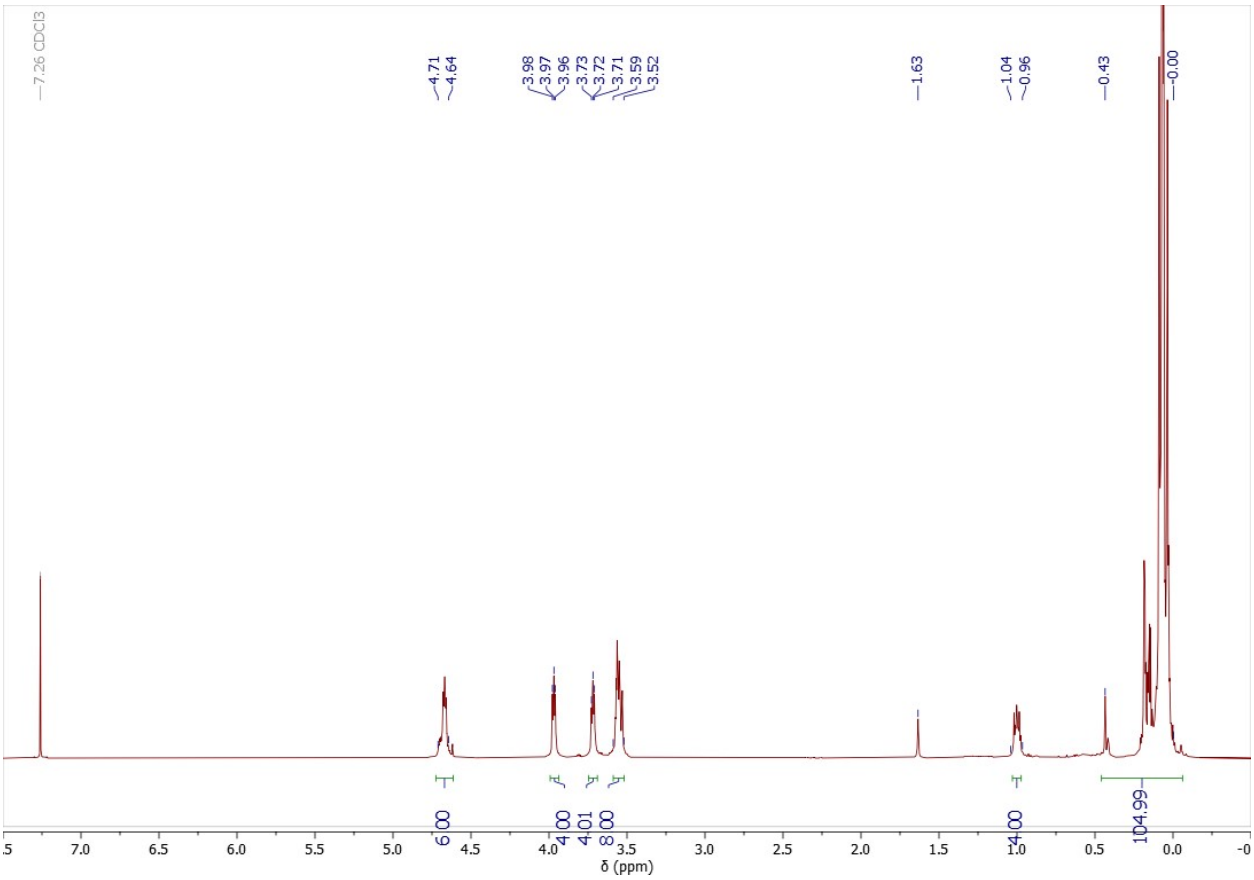


Figure S14. ^{1}H-NMR spectrum of **6** in $CDCl_3$. Peak at 1.63 ppm = H_2O

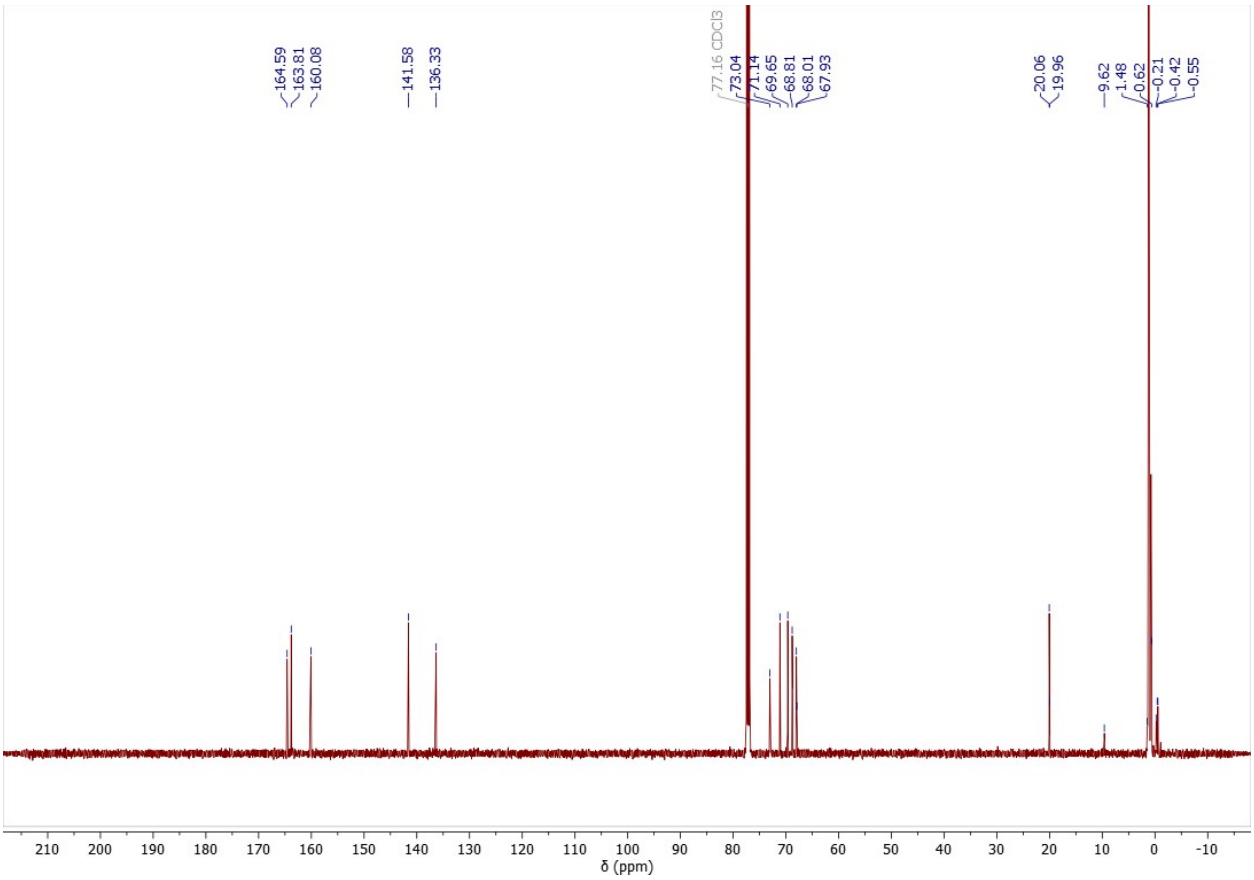


Figure S15. ^{13}C-NMR spectrum of **6** in $CDCl_3$.

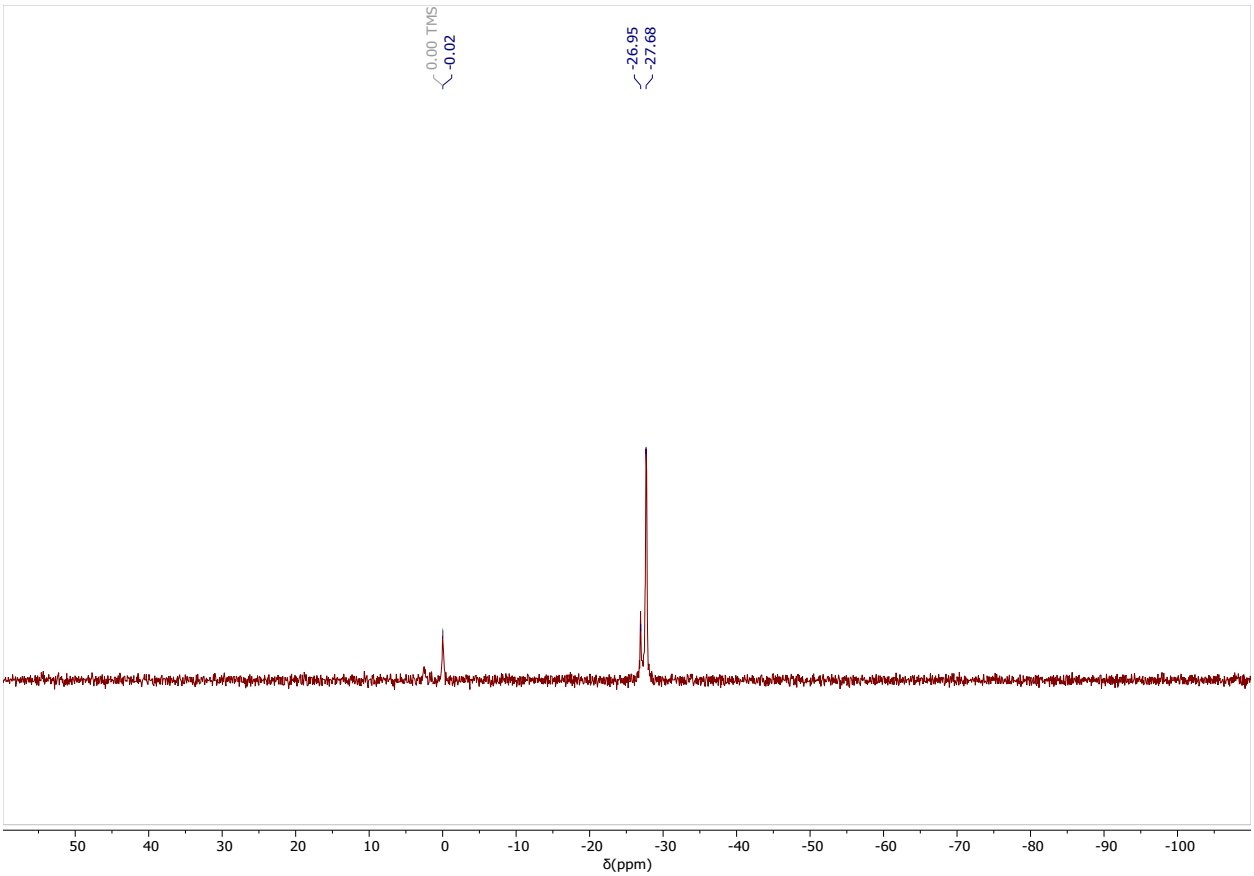


Figure S16. ^{29}Si-NMR spectrum of **6** in $CDCl_3$, referenced to TMS.

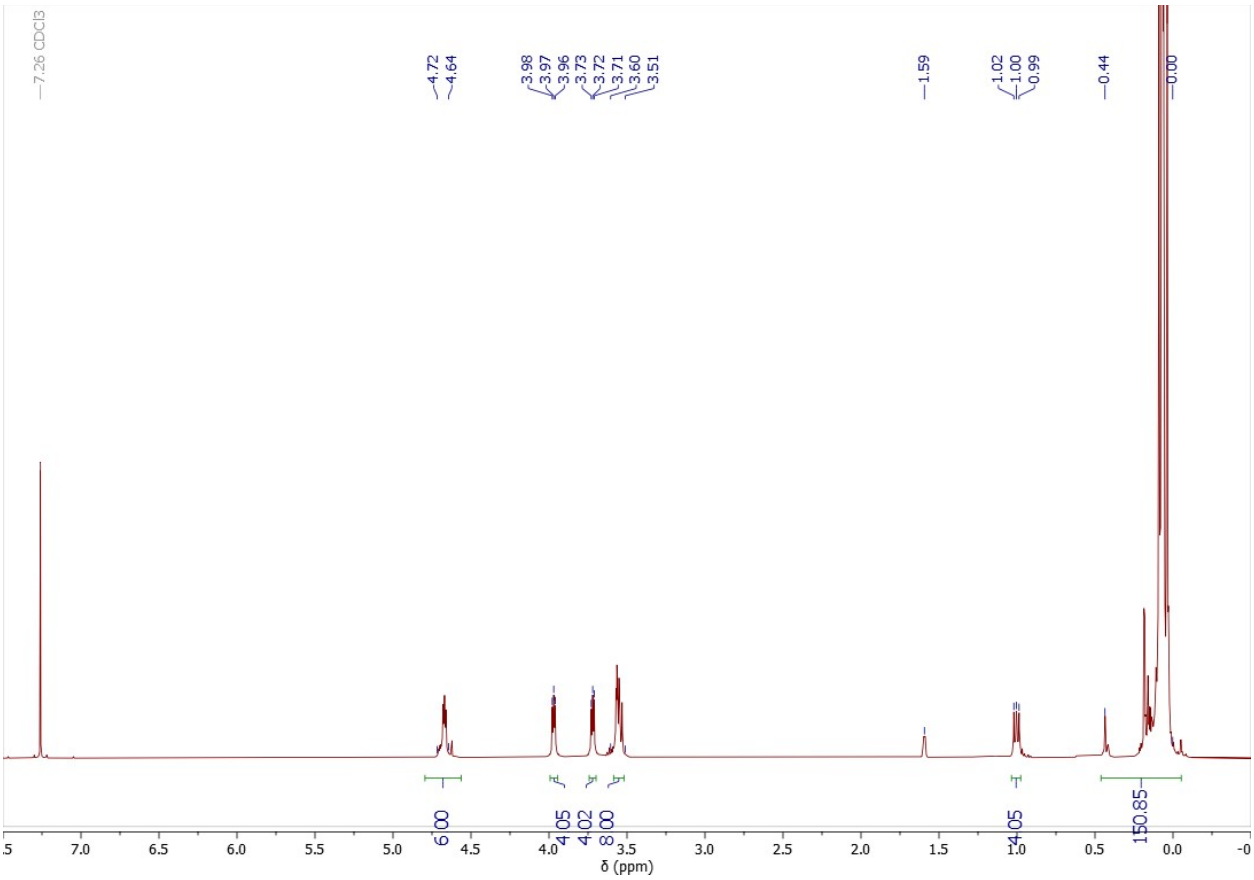


Figure S17. ^{1}H-NMR spectrum of **7** in $CDCl_3$. Peak at 1.59 ppm = H_2O

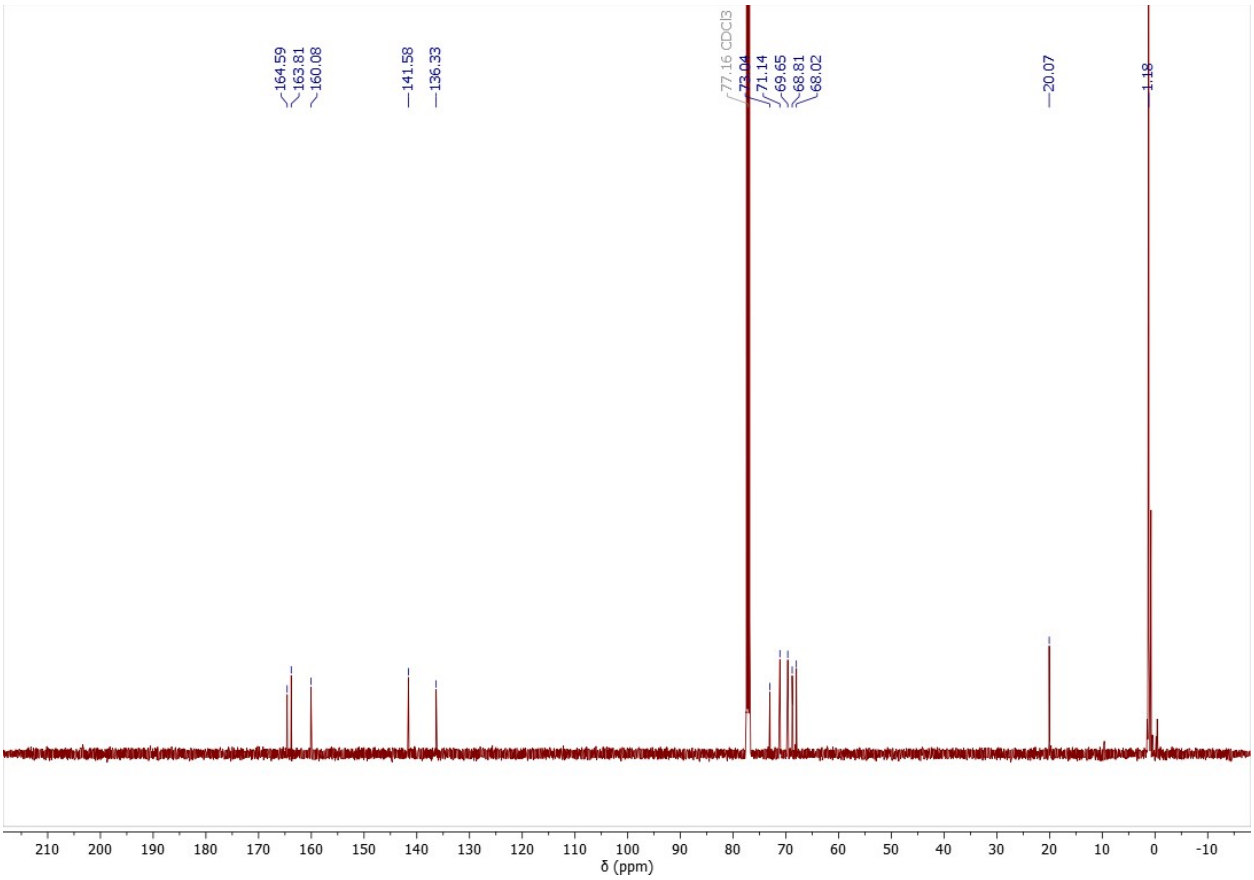


Figure S18. ^{13}C-NMR spectrum of **7** in $CDCl_3$.

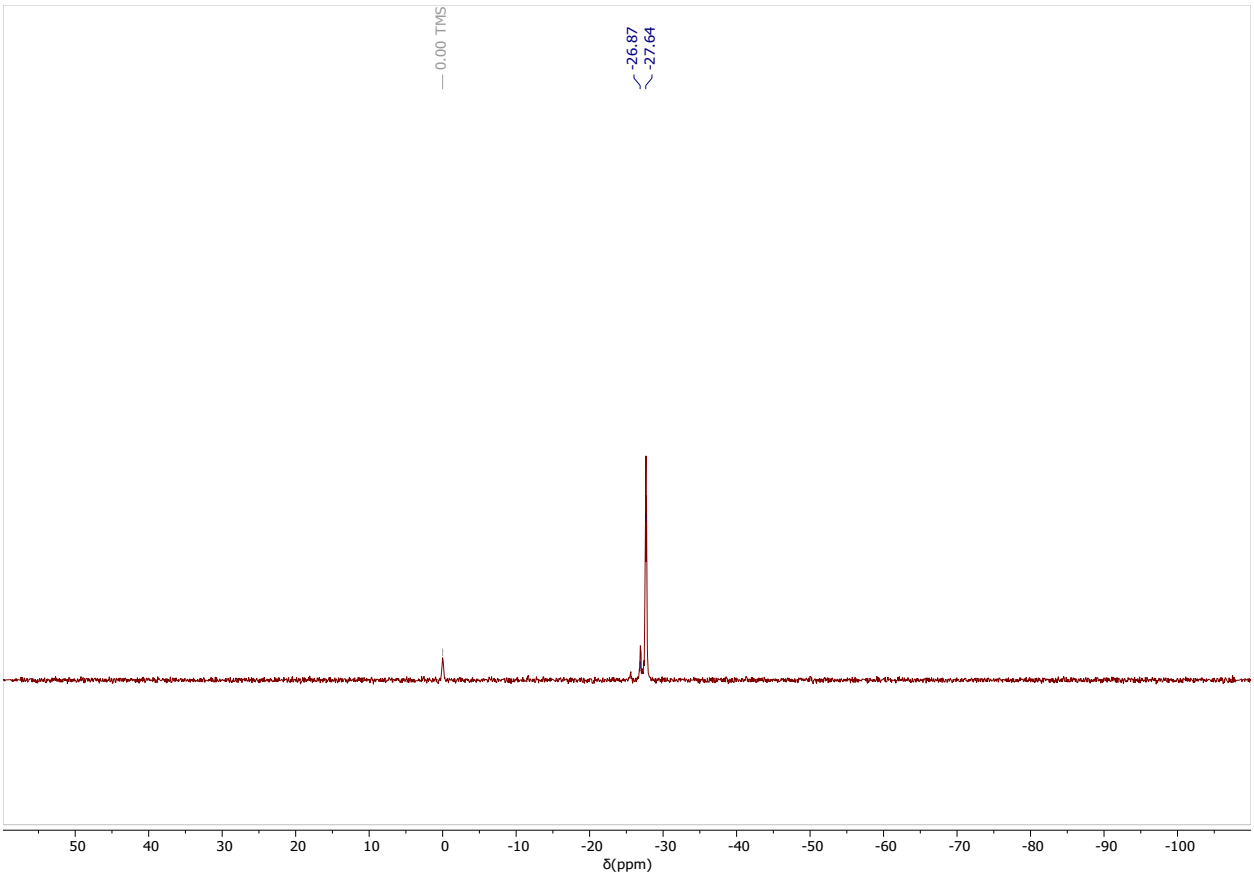


Figure S19. ^{29}Si-NMR spectrum of **7** in $CDCl_3$, referenced to TMS.

3. DSC Data

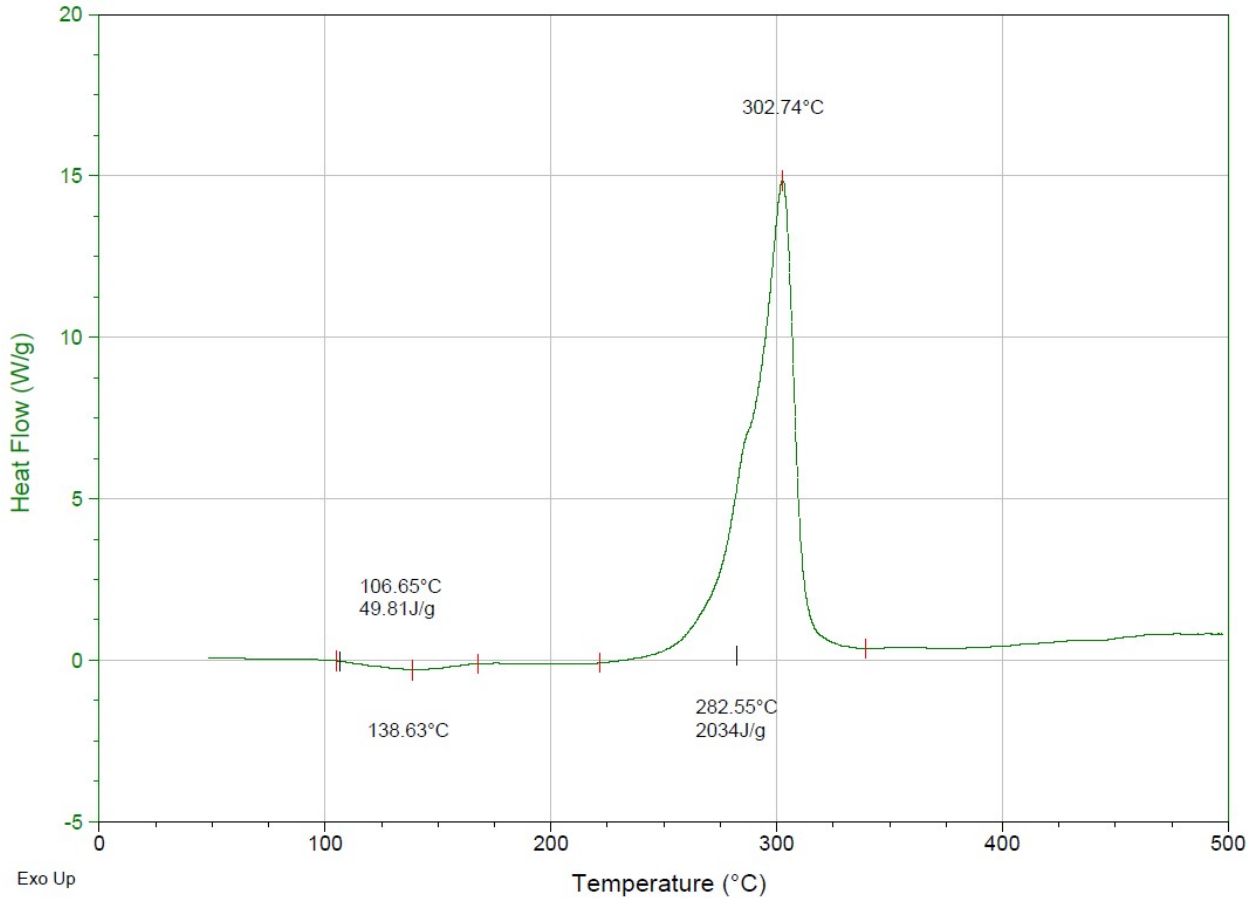


Figure S20. High temperature DSC trace of **1**.

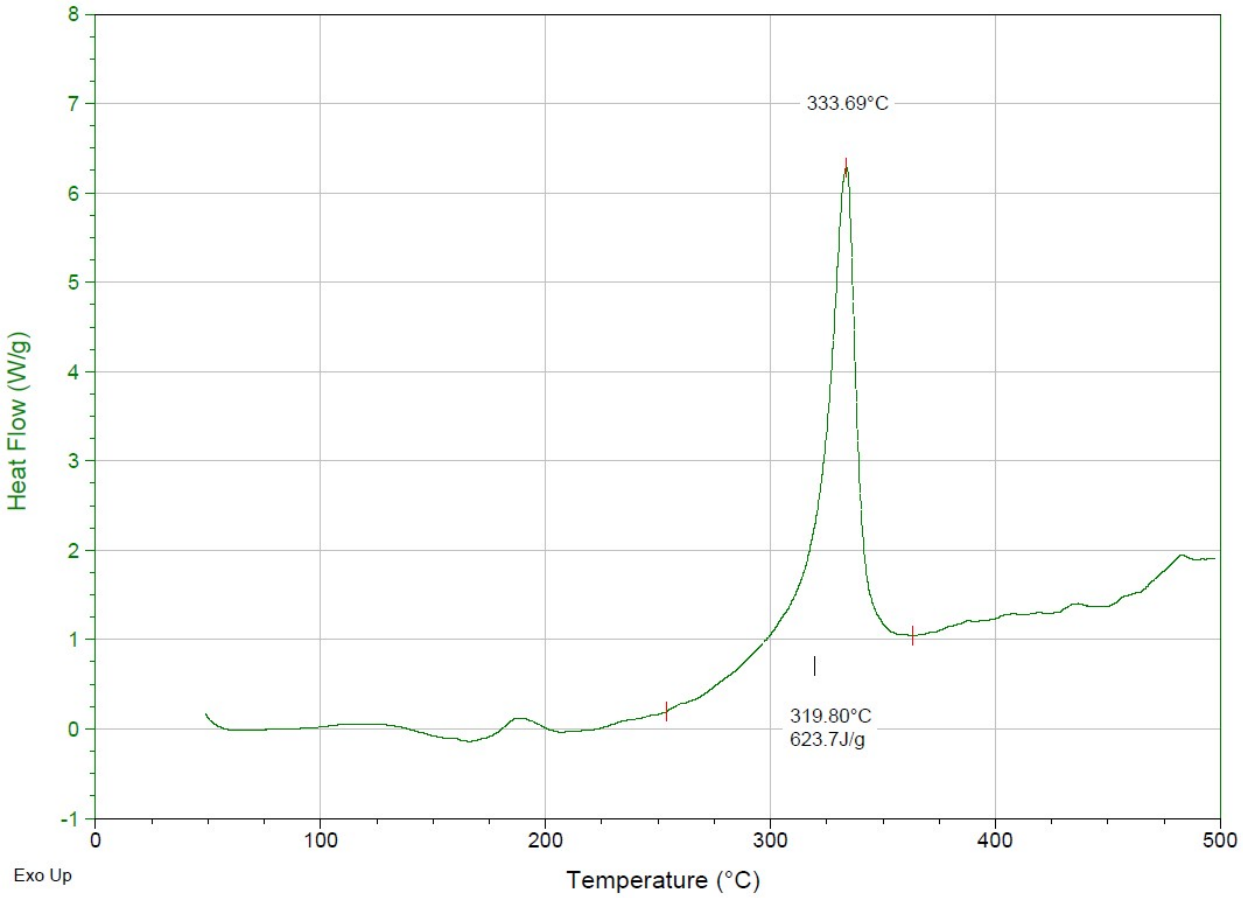


Figure S21. High temperature DSC trace of **2**.

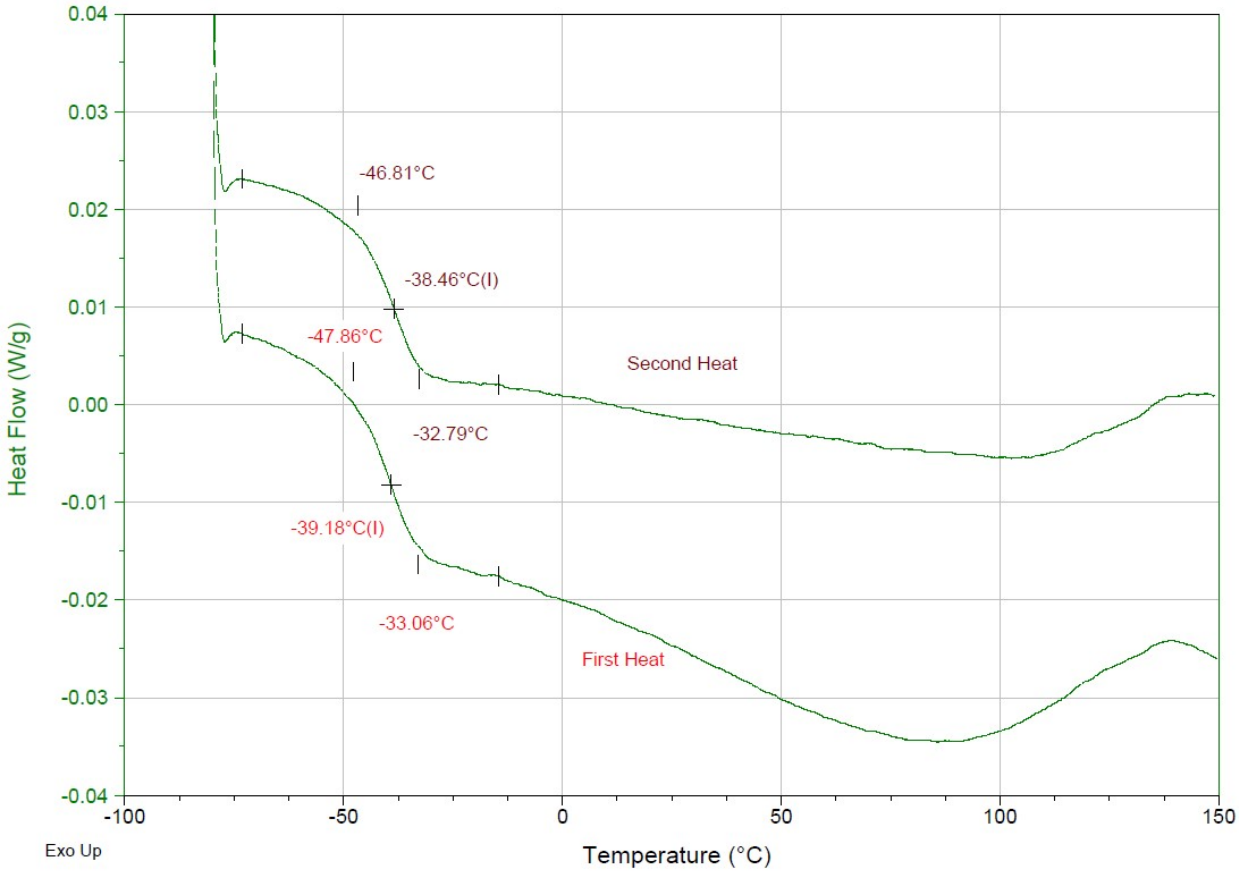


Figure S22. Low temperature DSC trace of **2**.

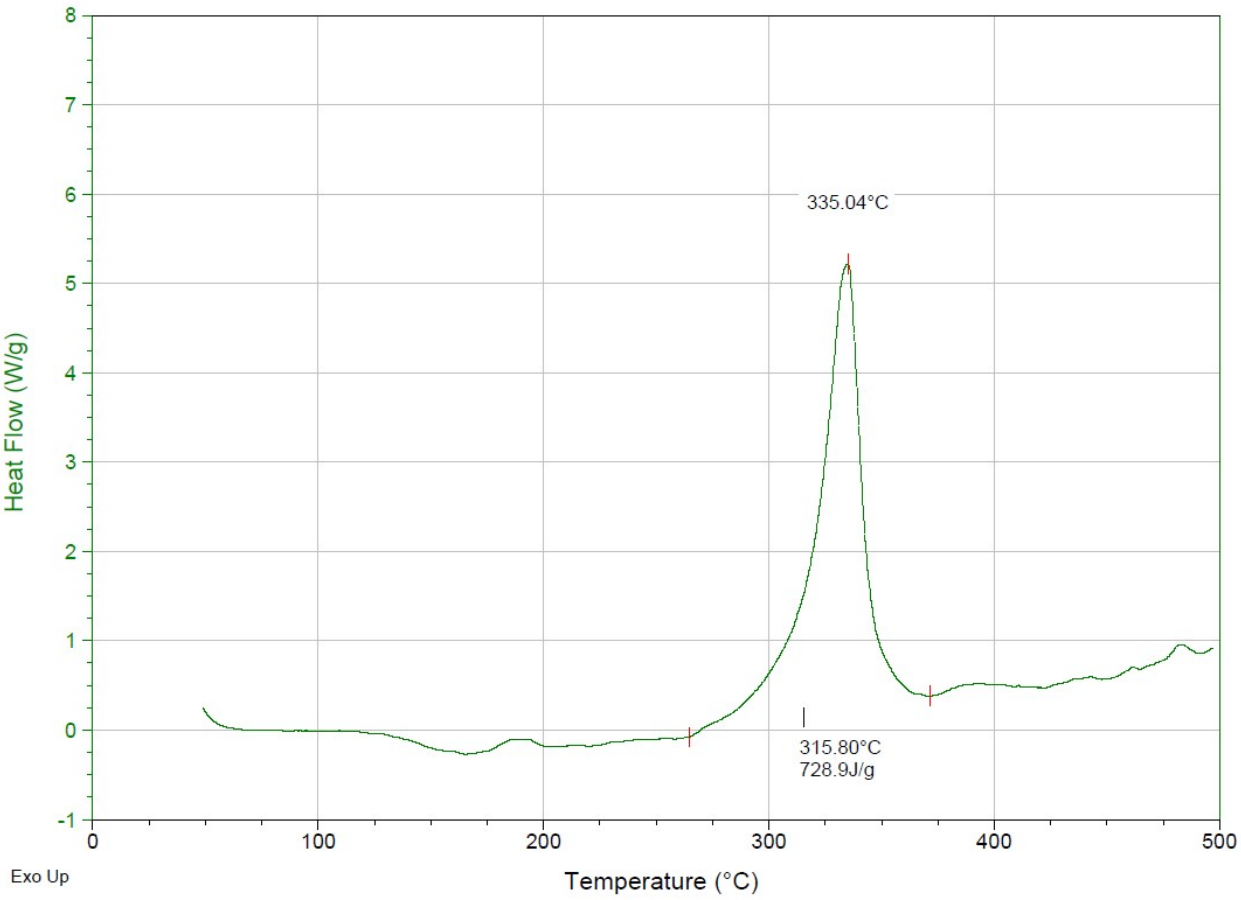


Figure S23. High temperature DSC trace of **3**.

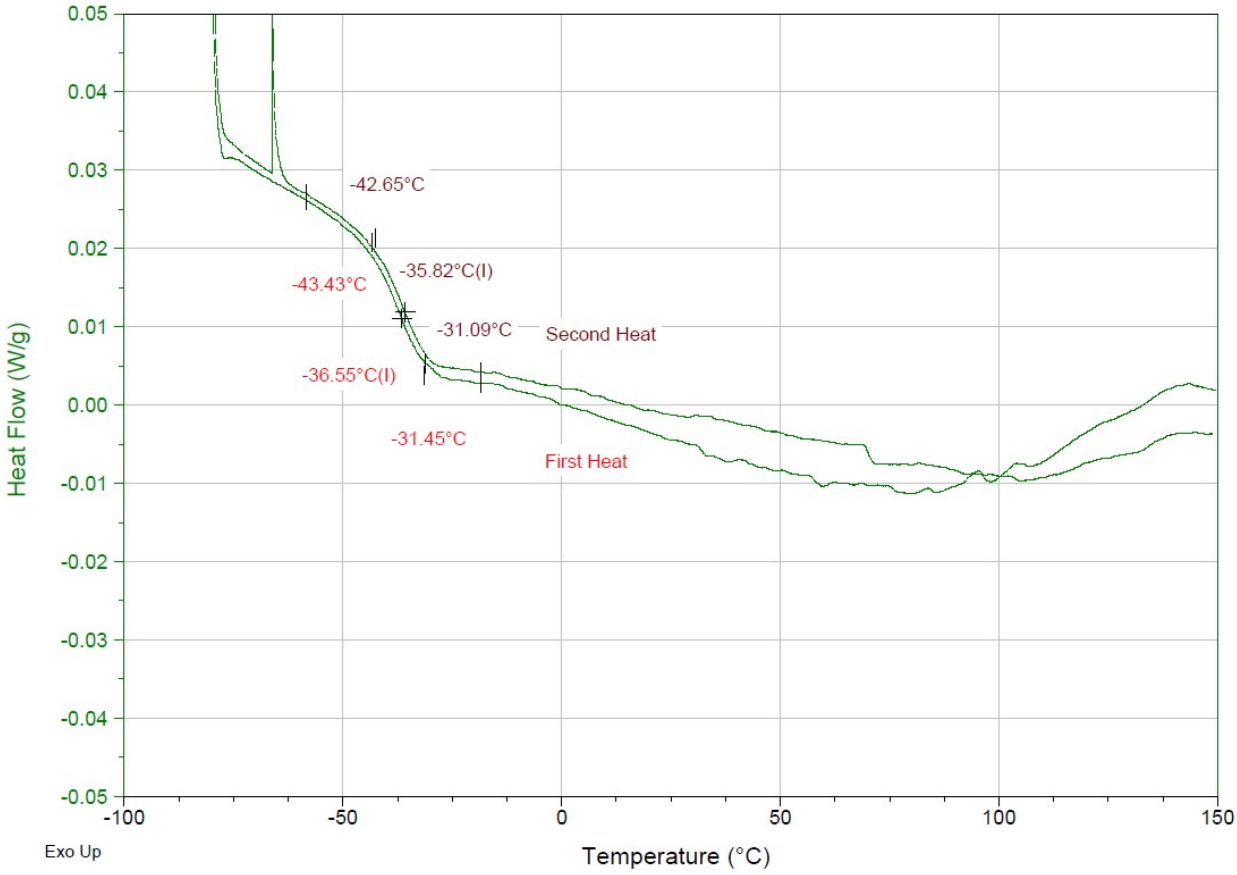


Figure S24. Low temperature DSC trace of **3**.

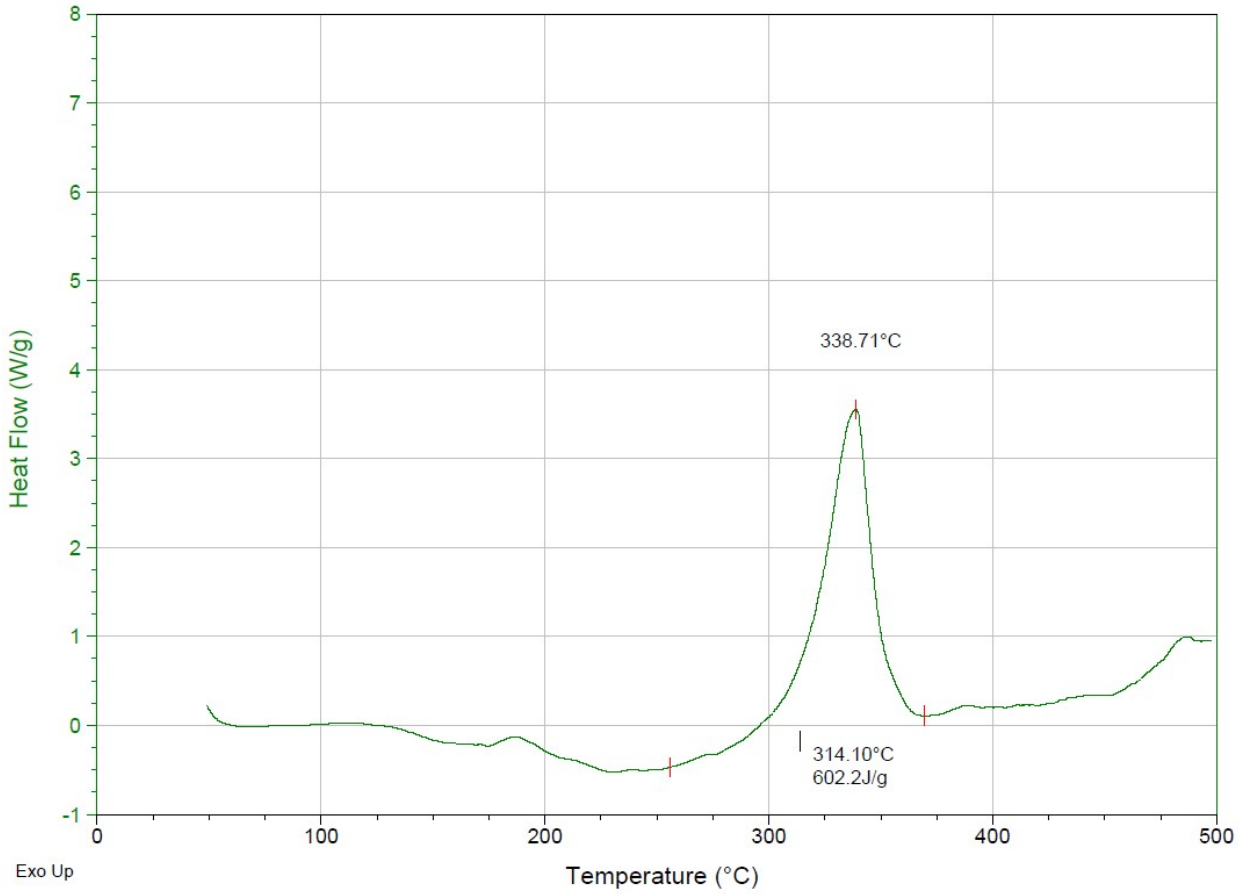


Figure S25. High temperature DSC trace of **4**.

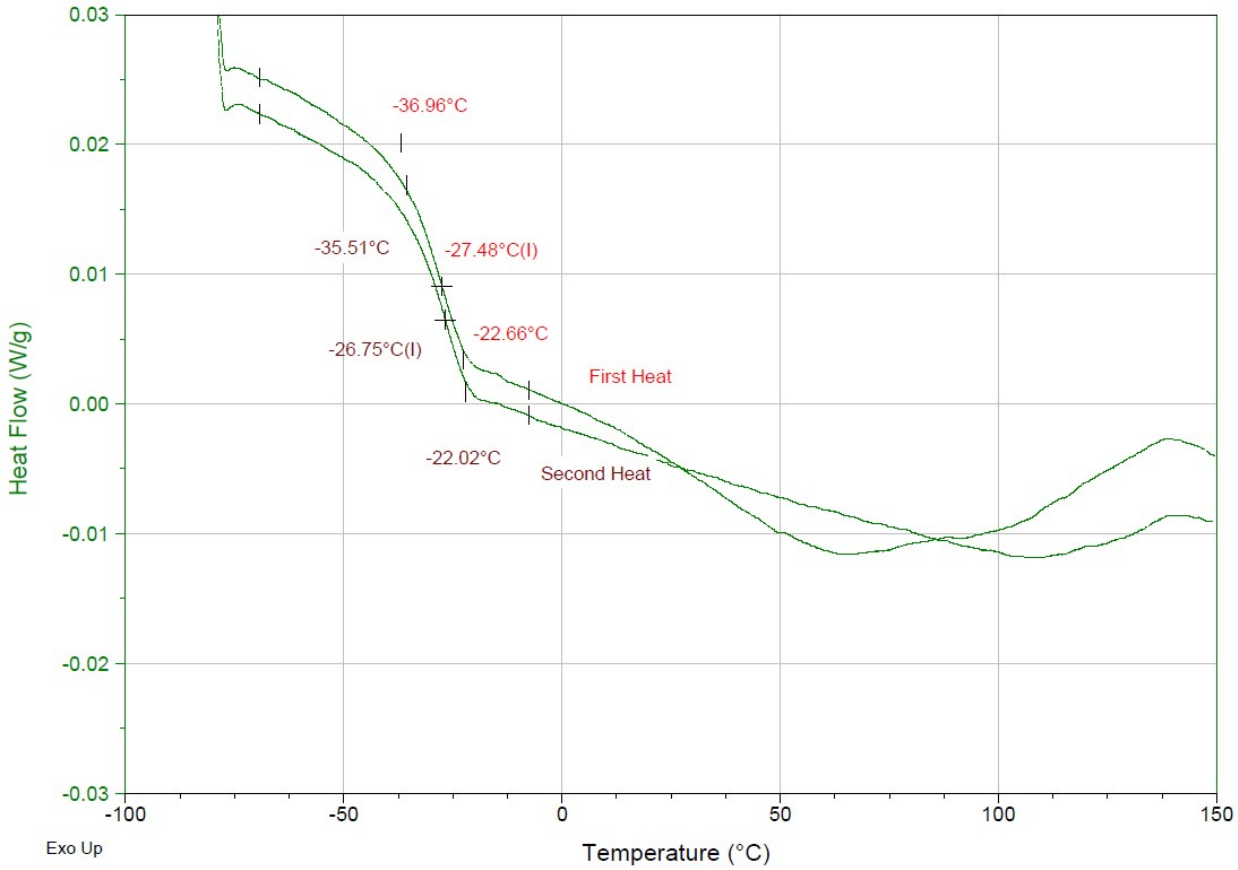


Figure S26. Low temperature DSC trace of **4**.

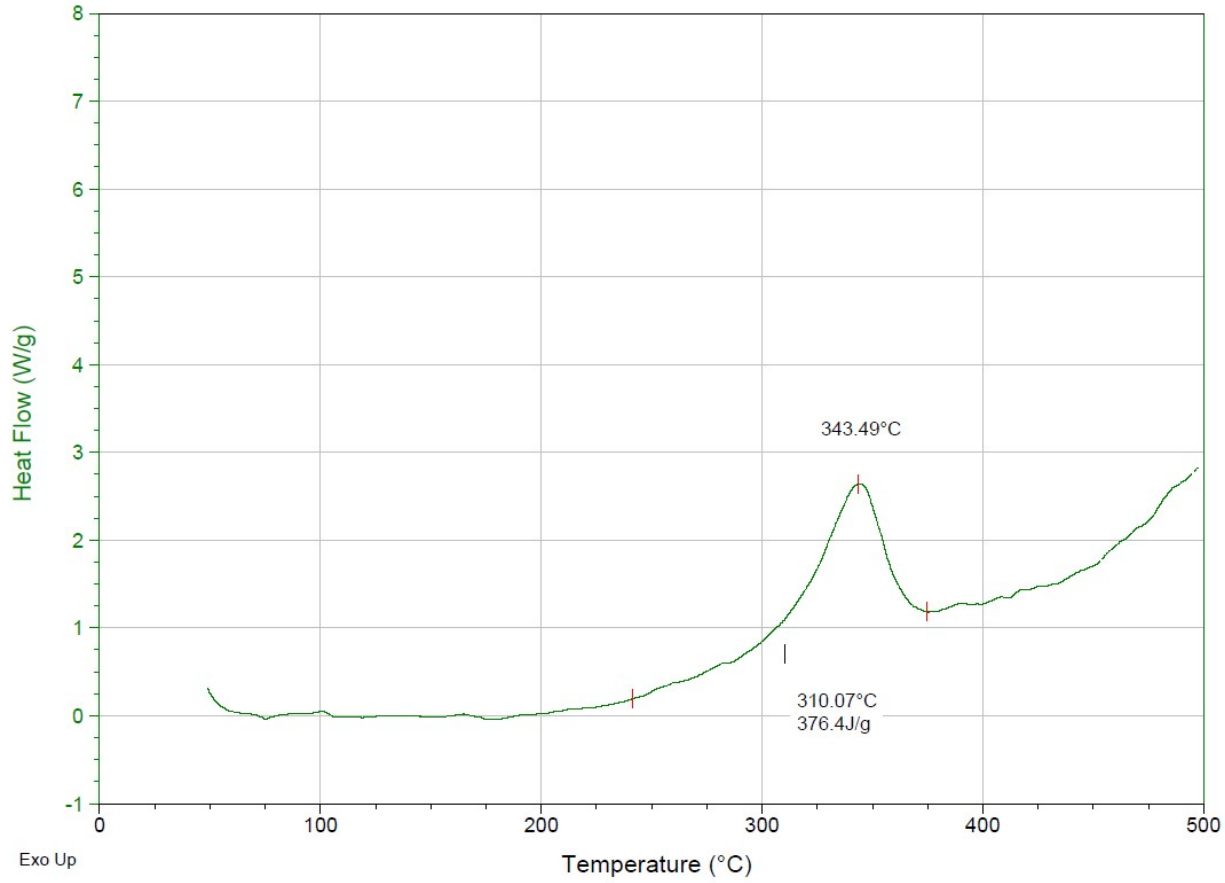


Figure S27. High temperature DSC trace of **5**.

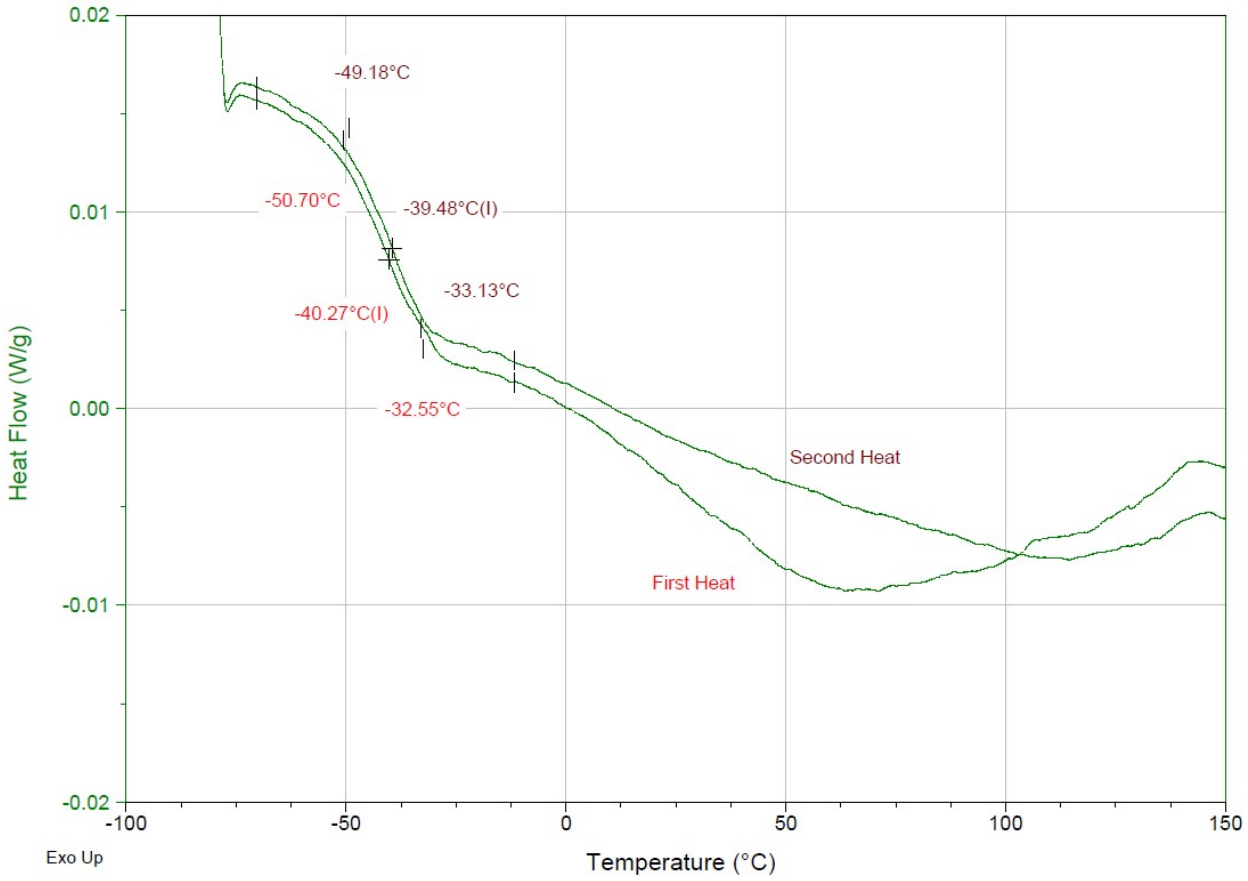


Figure S28. Low temperature DSC trace of **5.**

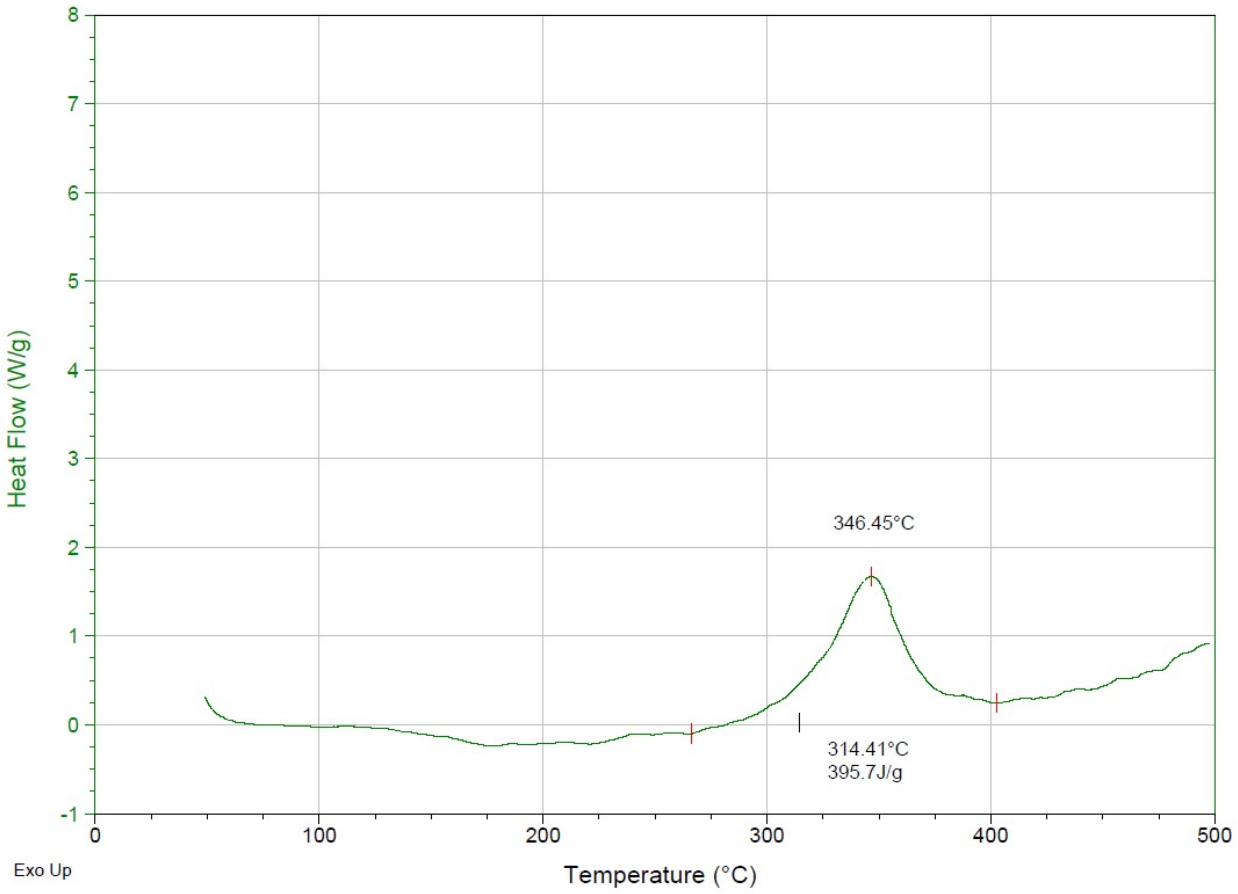


Figure S29. High temperature DSC trace of **6**.

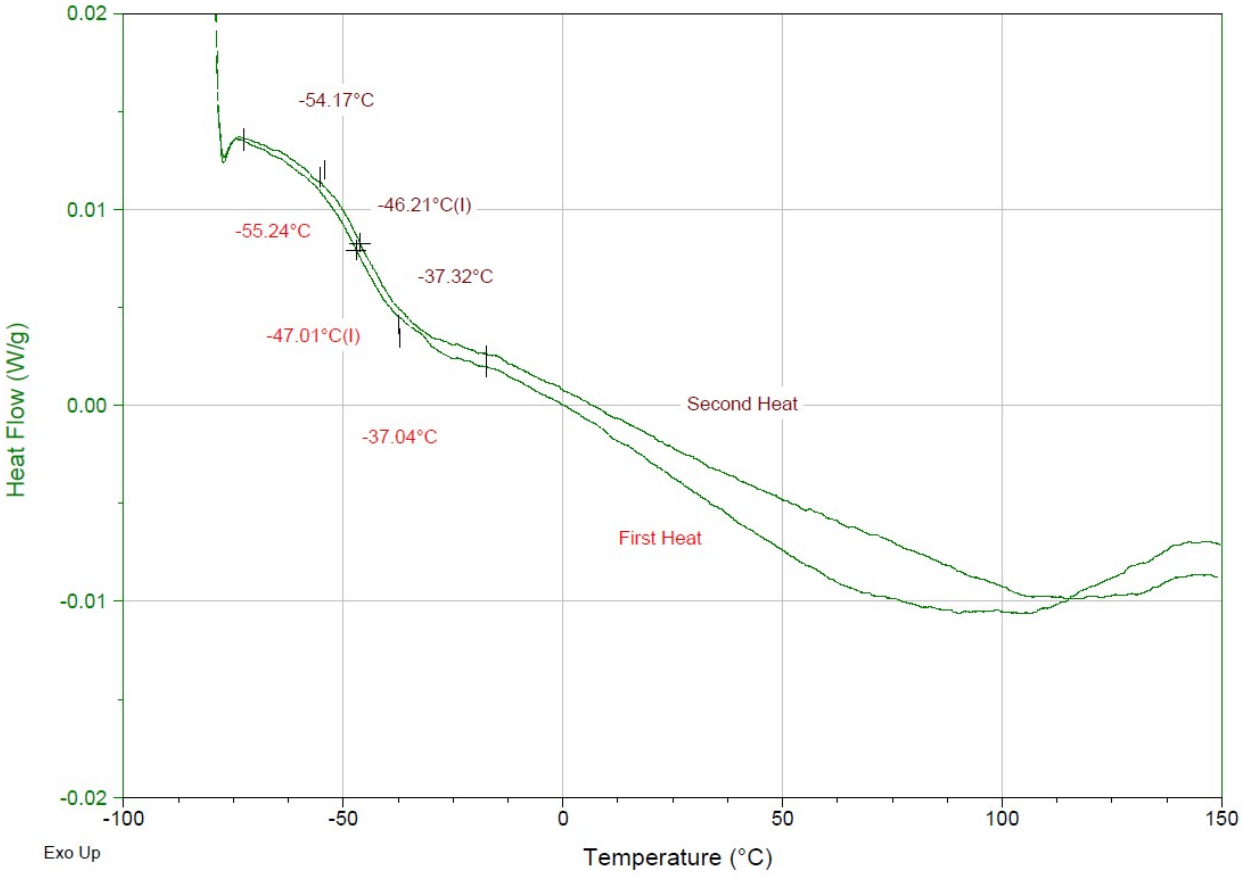


Figure S30. Low temperature DSC trace of **6**.

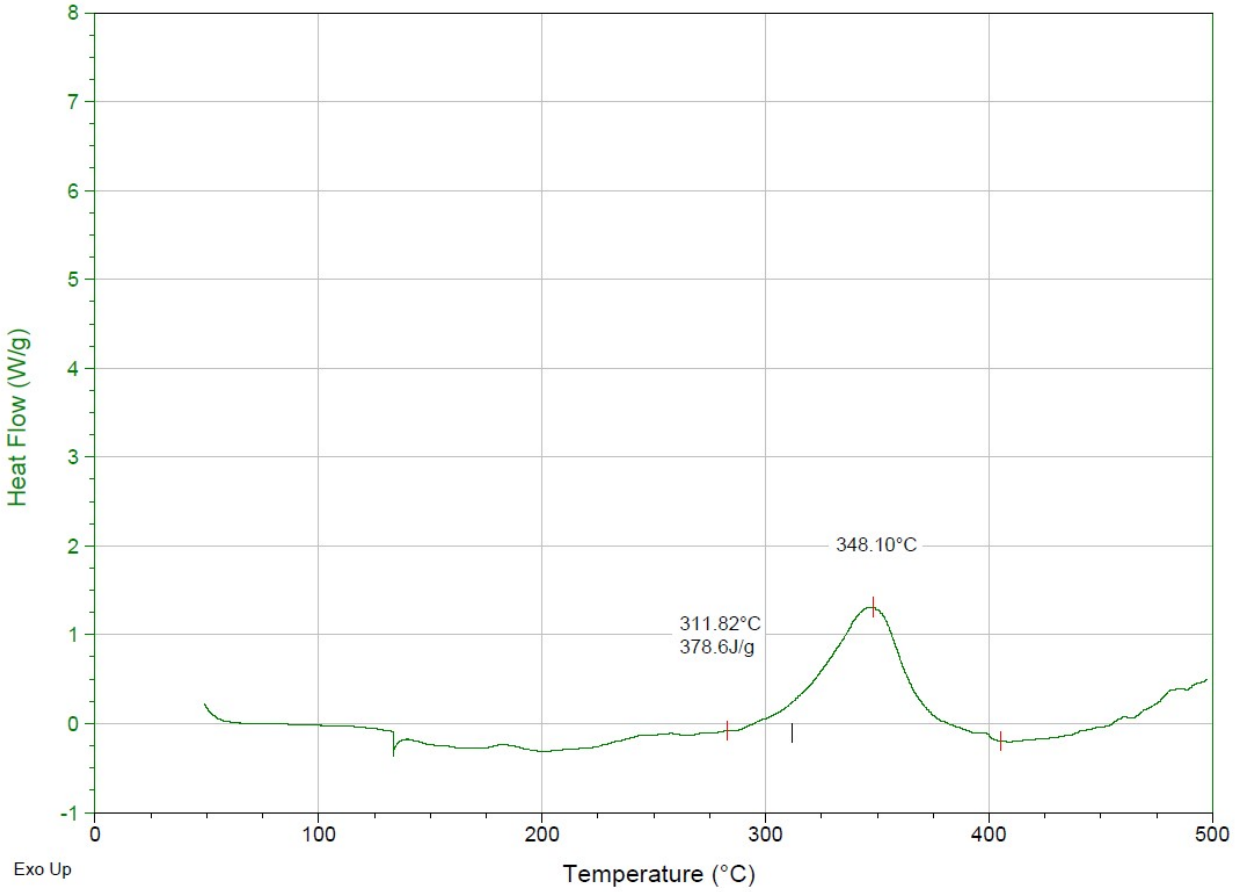


Figure S31. High temperature DSC trace of **7**.

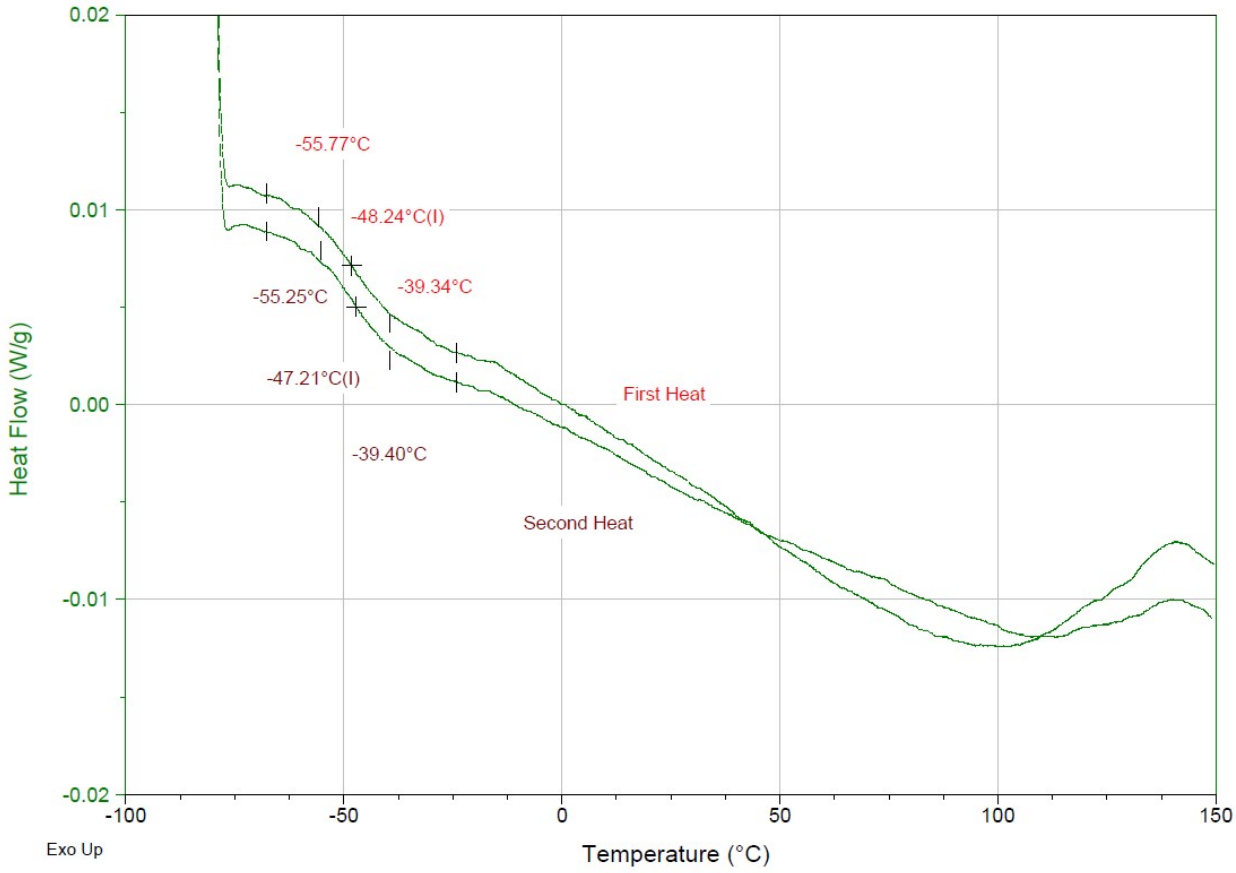


Figure S32. Low temperature DSC trace of **7**.

4. TGA Data

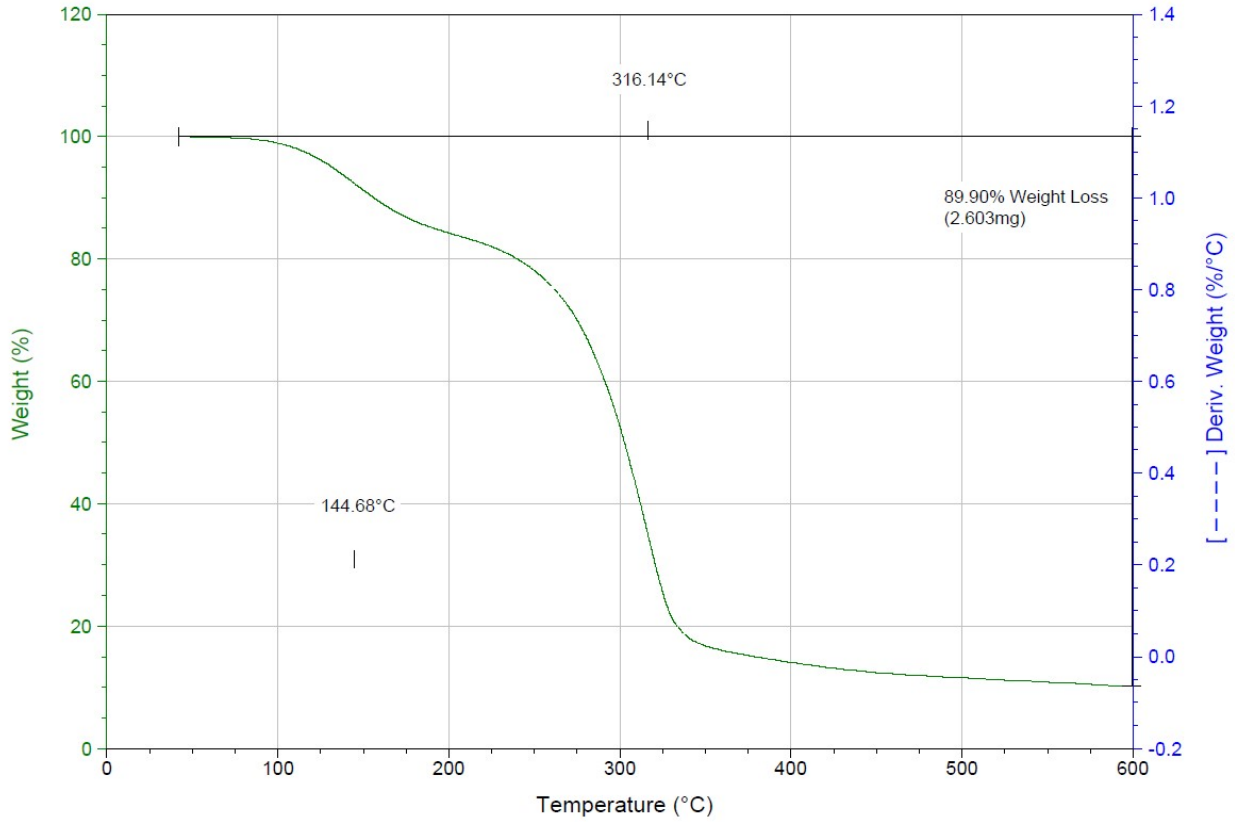


Figure S33. TGA trace of **2**.

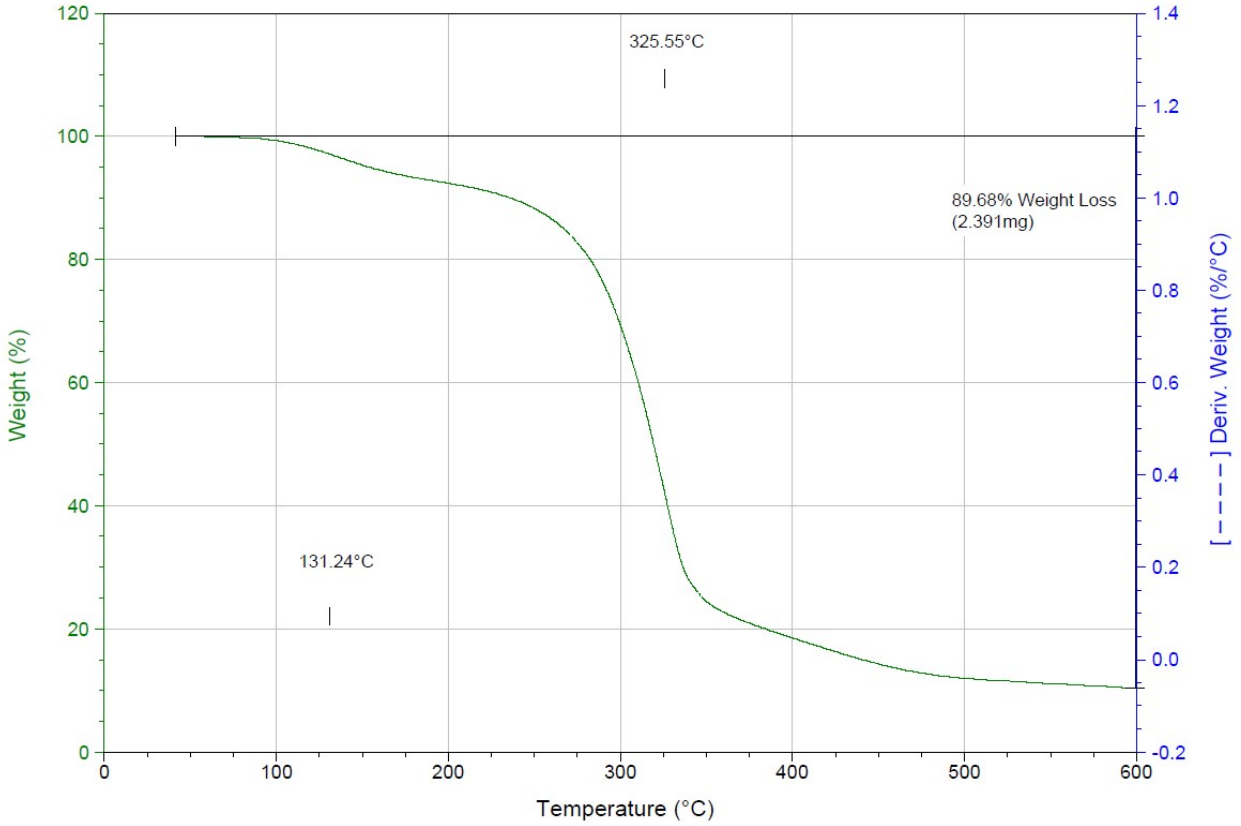


Figure S34. TGA trace of **3**.

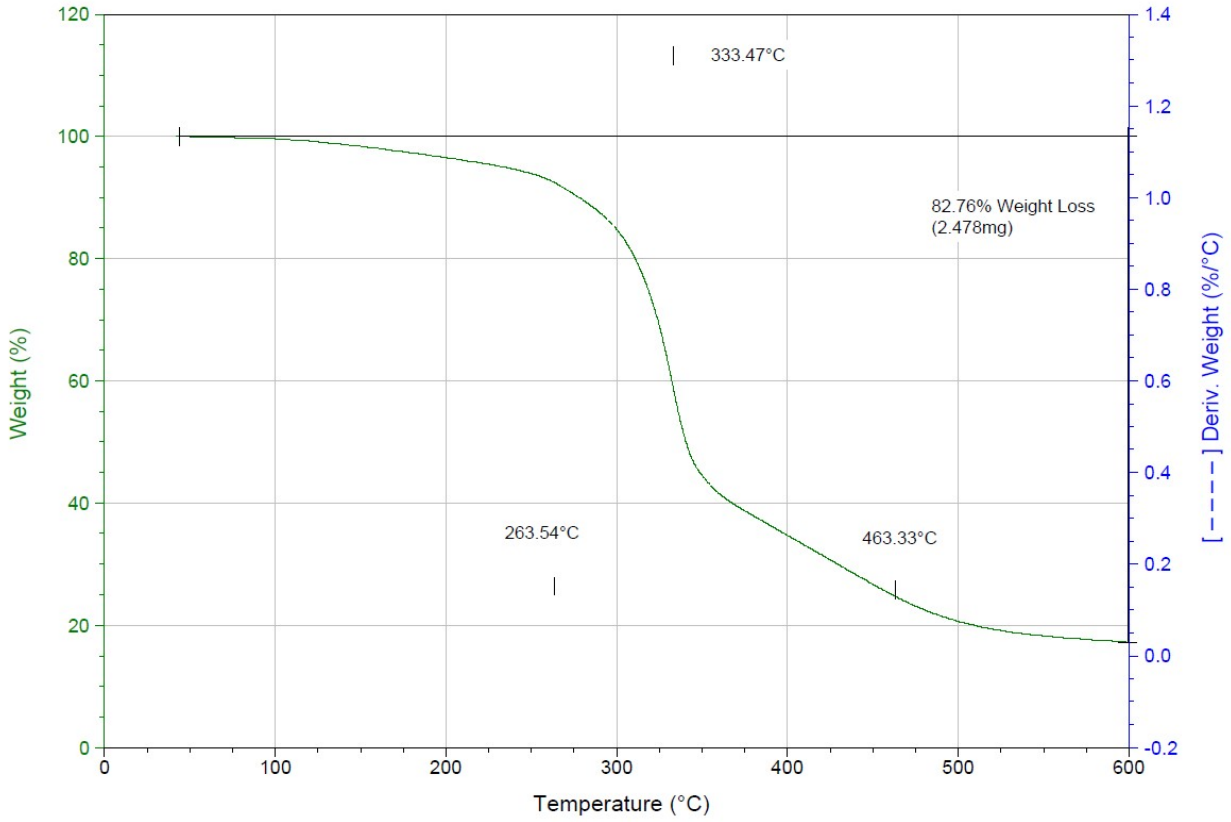


Figure S35. TGA trace of **4**.

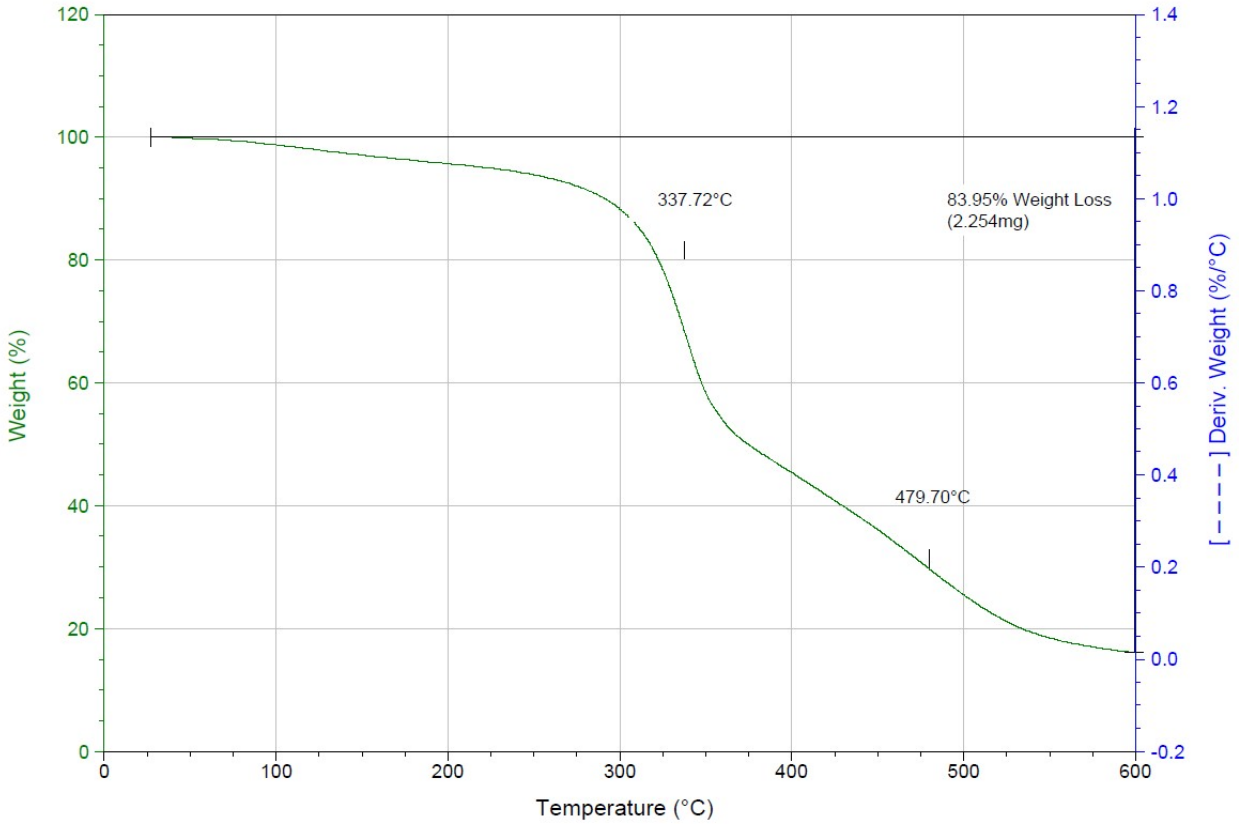


Figure S36. TGA trace of **5**.

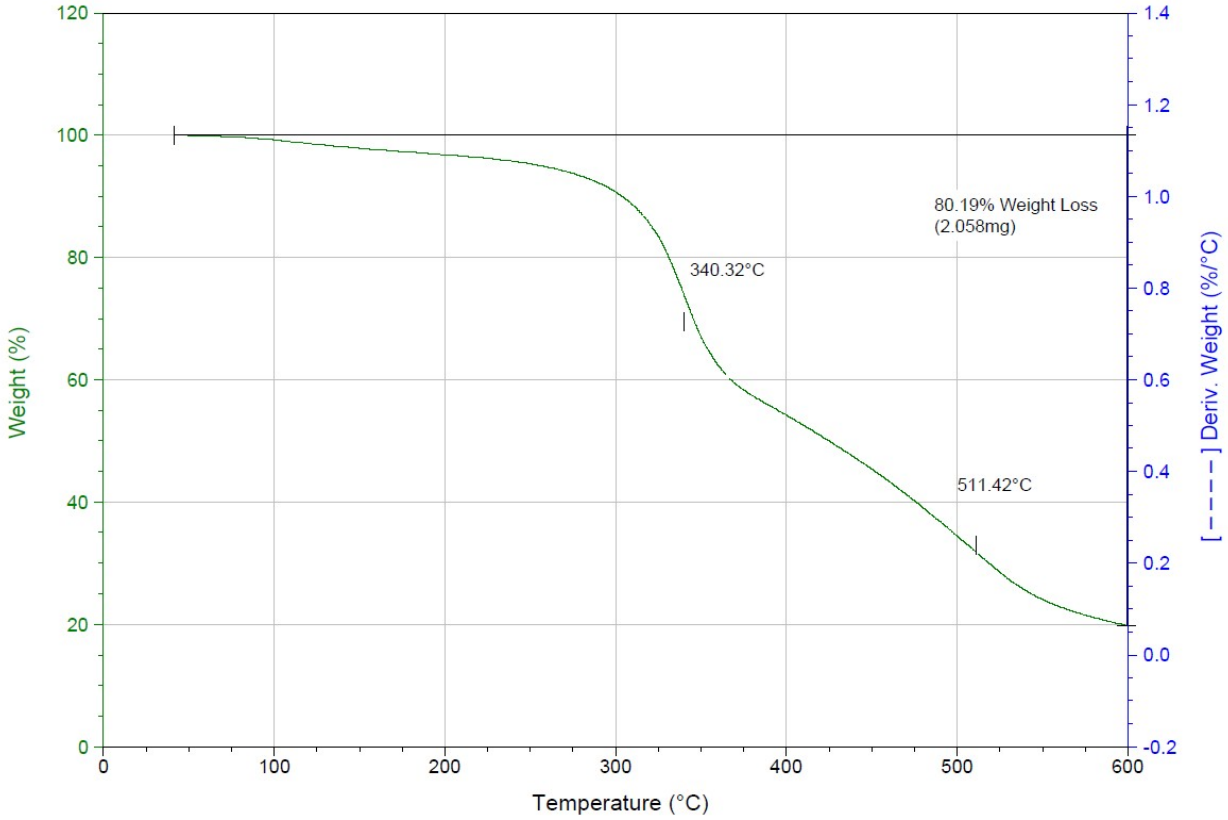


Figure S37. TGA trace of **6**.

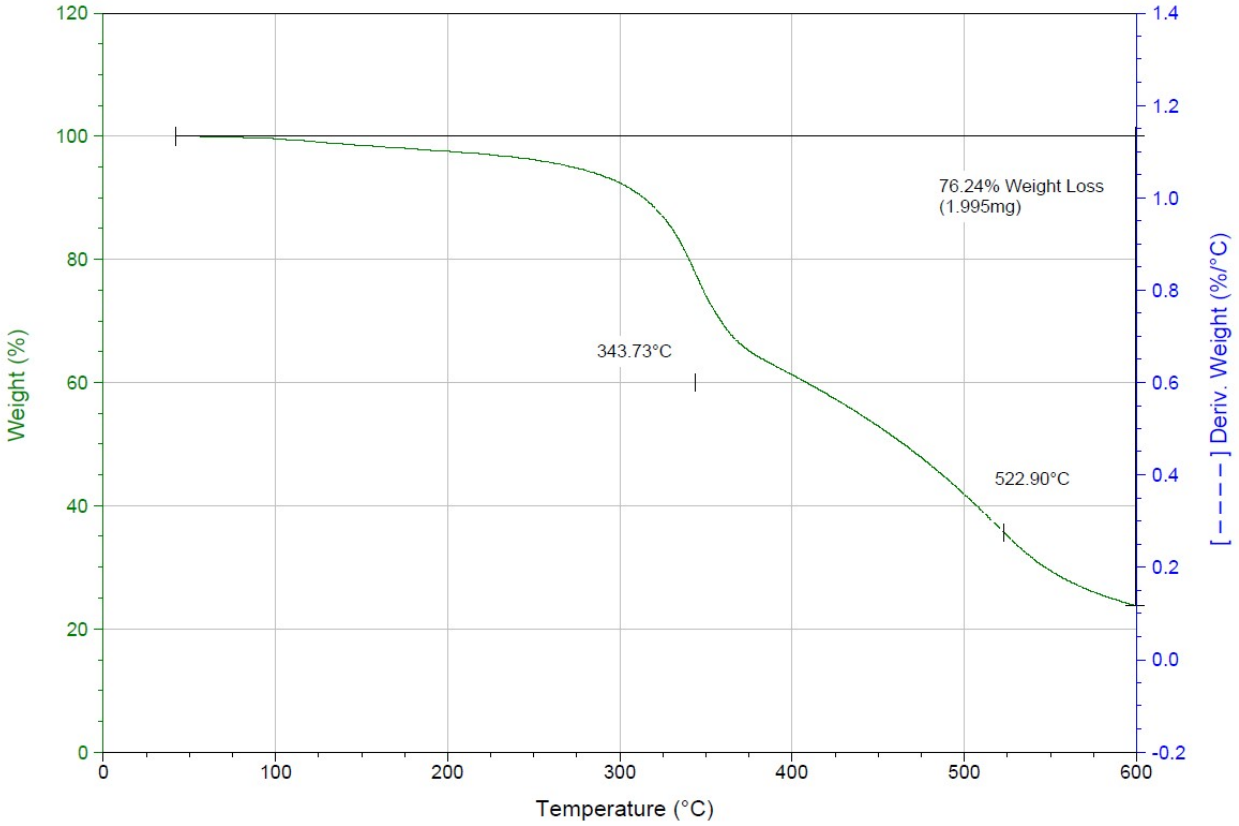
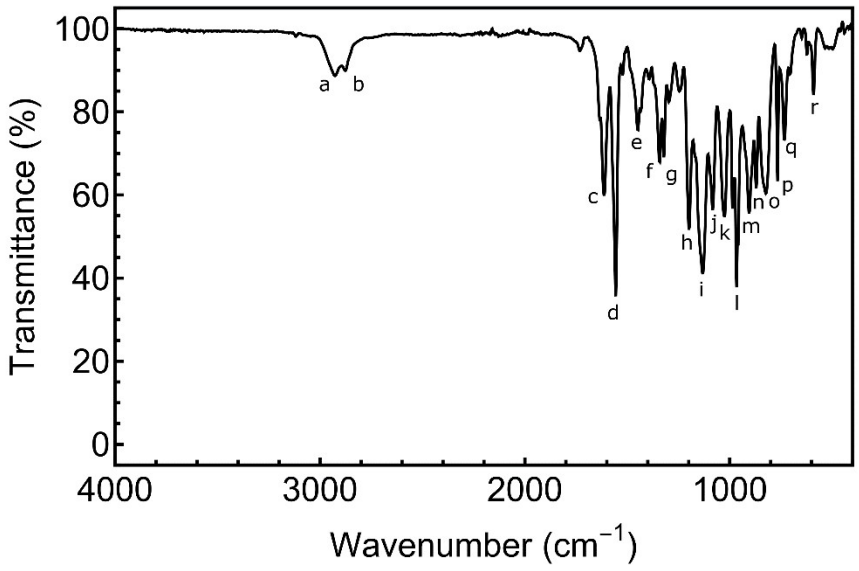


Figure S38. TGA trace of **7**.

5. IR Spectra

The IR spectrum for compound **1** and polymers **3** and **7** are marked with corresponding peaks. Polymers **4**, **5**, and **6** were not labeled as only a change in the relative intensity of the peaks was observed as the PDMS co-monomer size increased.



Peak	Wavenumber (cm^{-1})
a	2929
b	2876
c	1614
d	1556
e	1450
f	1344
g	1322
h	1199
i	1133
j	1082
k	1027
l	967
m	906
n	871
o	823
p	767
q	734
r	591

Figure S39. IR Spectrum of **1**.

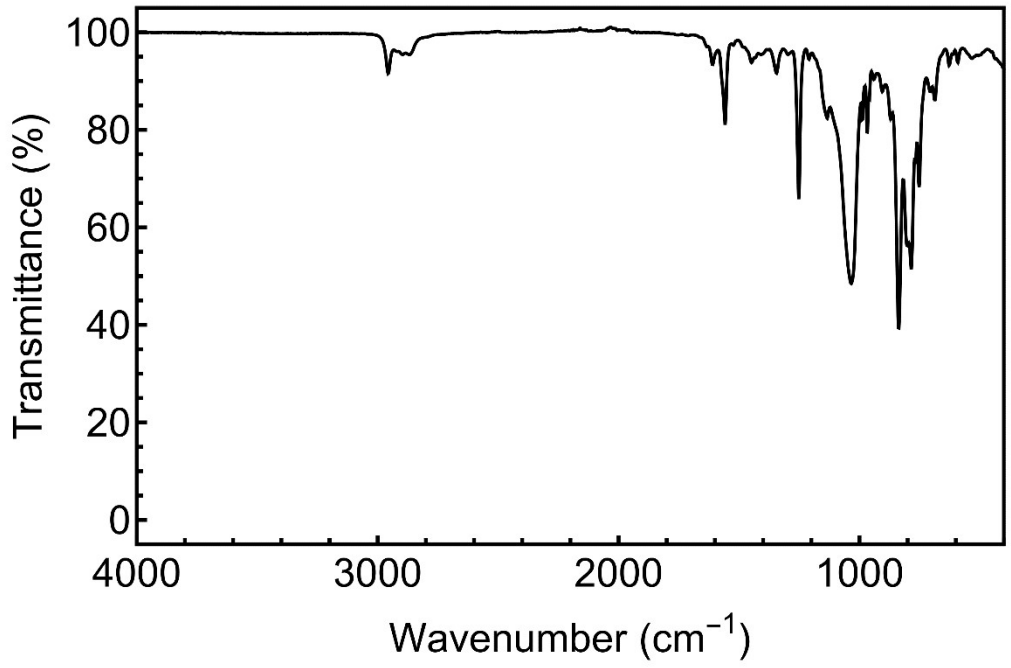
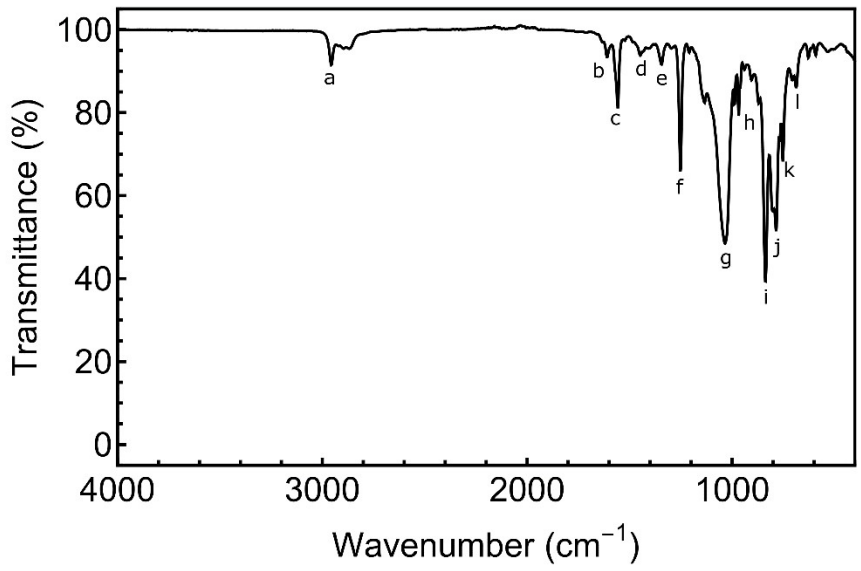


Figure S40. IR Spectrum of **2**.



Peak	Wavenumber (cm^{-1})
a	2957
b	1610
c	1559
d	1448
e	1345
f	1252
g	1035
h	968
i	837
j	785
k	753
l	688

Figure S41. IR Spectrum of **3**.

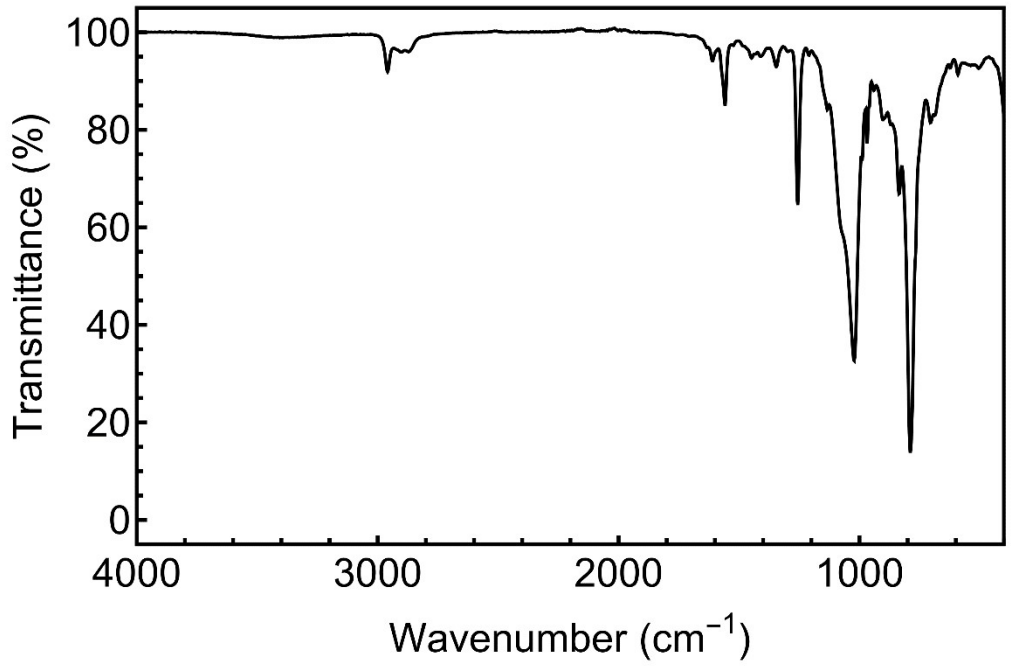


Figure S42. IR Spectrum of **4**.

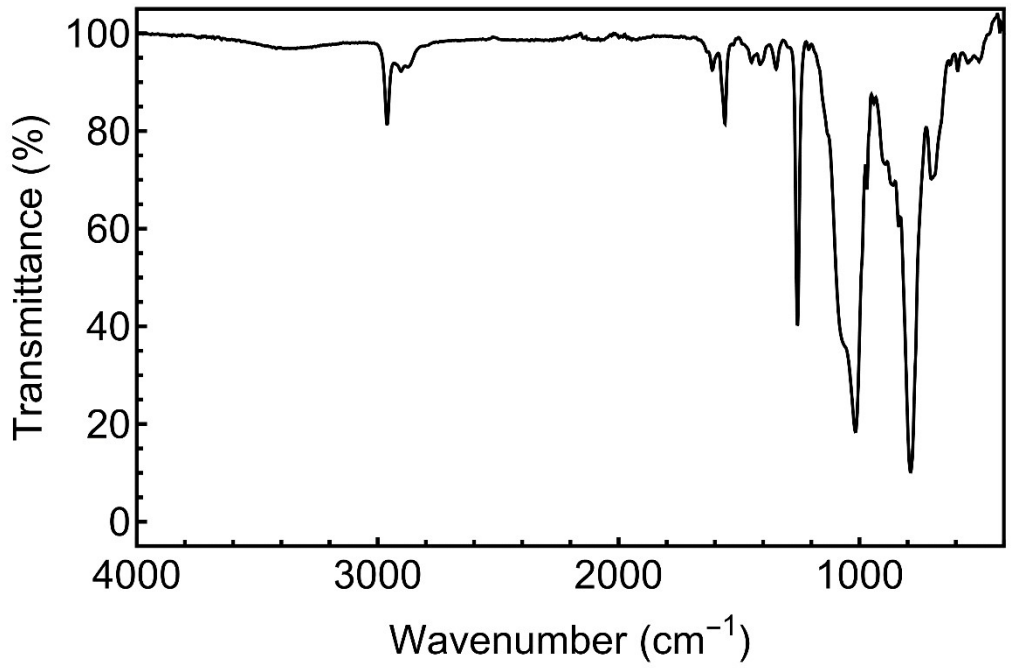


Figure S43. IR Spectrum of **5**.

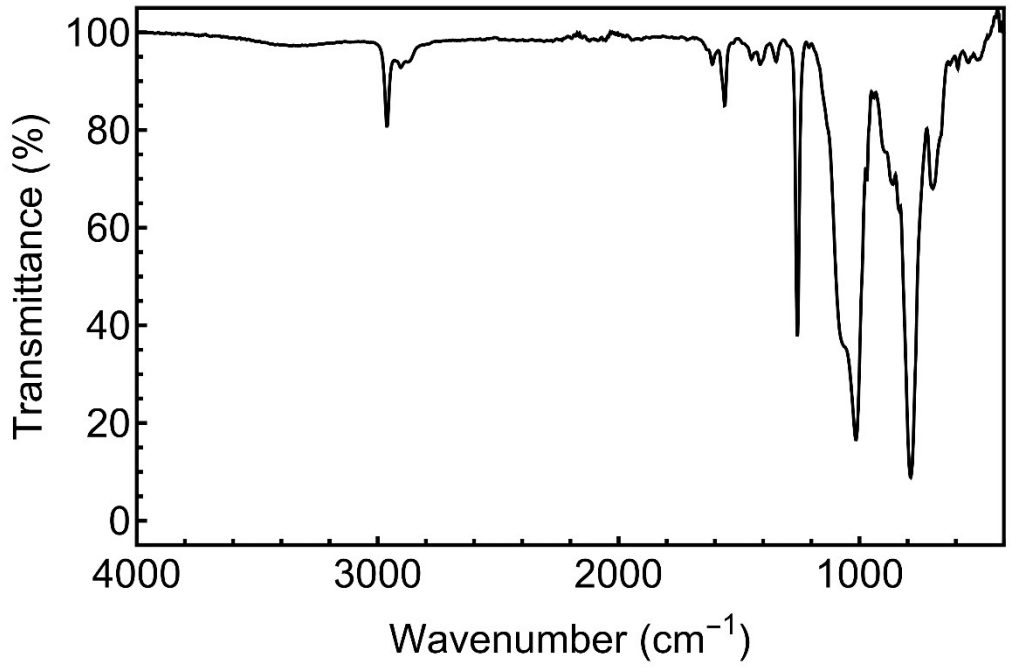
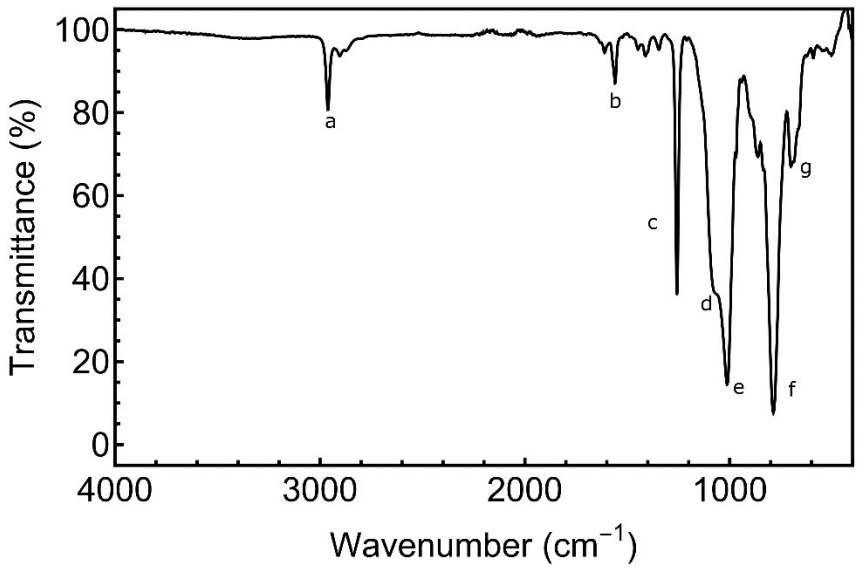


Figure S44. IR Spectrum of **6**.



Peak	Wavenumber (cm^{-1})
a	2962
b	1559
c	1258
d	1079
e	1014
f	788
g	701

Figure S45. IR Spectrum of **7**.