

Supporting Information

Novel Organic-Inorganic Hybrids Based on T₈ and T₁₀ Silsesquioxanes: Synthesis, Cage-Rearrangement and Properties

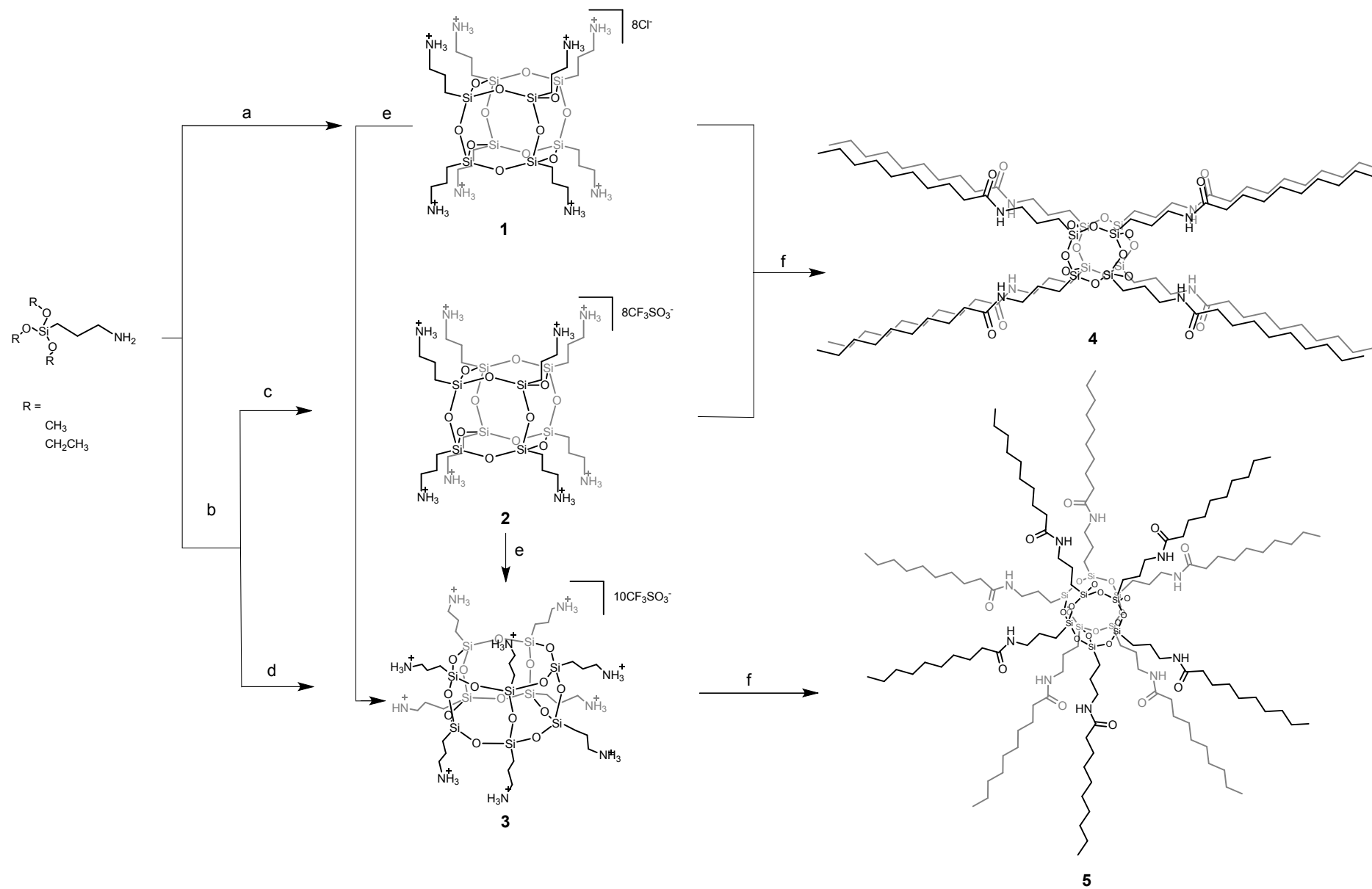
Mateusz Janeta, Łukasz John,* Jolanta Ejfler and Sławomir Szafert

*Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383
Wrocław, Poland*

*To whom correspondence should be addressed: E-mail: lukasz.john@chem.uni.wroc.pl

Table of Contents	Page
Scheme S1. Synthesis of 1–5 .	4
Figure S1. Powder XRD patterns for 1–5 .	5
Figure S2. Powder XRD patterns for 1–5 after heating to the decomposition temperature.	5
Figure S3. ^1H NMR (500 MHz, DMSO- d_6 , 300 K) spectrum of 1 .	6
Figure S4. ^{13}C NMR (126 MHz, DMSO- d_6 , 300 K) spectrum of 1 .	6
Figure S5. ^{29}Si NMR (59.6 MHz, DMSO- d_6 , 300 K) spectrum of 1 .	7
Figure S6. FT-IR (KBr pellets) spectrum of 1 .	7
Figure S7. HR-MS (ESI+, TOF, MeOH) spectrum of 1 .	8
Figure S8. EDS spectrum of 1 .	8
Figure S9. Powder XRD pattern of 1 .	9
Figure S10. ^1H NMR (500 MHz, DMSO- d_6 , 300 K) spectrum of 2 .	10
Figure S11. ^{13}C NMR (126 MHz, DMSO- d_6 , 300 K) spectrum of 2 .	10
Figure S12. ^{29}Si NMR (59.6 MHz, DMSO- d_6 , 300 K) spectrum of 2 .	11
Figure S13. FT-IR (KBr pellets) spectrum of 2 .	11
Figure S14. HR-MS (ESI+, TOF, MeOH) spectrum of 2 .	12
Figure S15. EDS spectrum of 2 .	12
Figure S16. Powder XRD pattern of 2 .	13
Figure S17. ^1H NMR (500 MHz, DMSO- d_6 , 300 K) spectrum of 3 .	14
Figure S18. ^{13}C NMR (126 MHz, DMSO- d_6 , 300 K) spectrum of 3 .	14
Figure S19. ^{29}Si NMR (59.6 MHz, DMSO- d_6 , 300 K) spectrum of 3 (method A).	15
Figure S20. ^{29}Si NMR (59.6 MHz, DMSO- d_6 , 300 K) spectrum of 3 (method B).	15
Figure S21. ^{29}Si NMR (59.6 MHz, DMSO- d_6 , 300 K) spectrum of 3 (method C).	16
Figure S22. ^{29}Si NMR (59.6 MHz, DMSO- d_6 , 300 K) spectrum of 3 (method D).	16
Figure S23. FT-IR (KBr pellets) spectrum of 3 .	17
Figure S24. HR-MS (ESI+, TOF, MeOH) spectrum of 3 (method A).	17
Figure S25. HR-MS (ESI+, TOF, MeOH) spectrum of 3 (method B).	18
Figure S26. HR-MS (ESI+, TOF, MeOH) spectrum of 3 (method C).	18
Figure S27. HR-MS (ESI+, TOF, MeOH) spectrum of 3 (method D).	19
Figure S28. EDS spectrum of 3 .	19
Figure S29. Powder XRD pattern of 3 .	20
Figure S30. ^1H DOSY (600 MHz, DMSO- d_6 , 300 K) spectrum of 2 (top) and 3 (bottom).	20
Figure S31. ^1H NMR (500 MHz, DMSO- d_6 , 300 K) spectrum of 4 .	21
Figure S32. ^{13}C NMR (126 MHz, CDCl_3 , 300 K) spectrum of 4 .	21
Figure S32. ^1H – ^1H COSY NMR (500 MHz, DMSO- d_6 , 300 K) spectrum of 4 .	22
Figure S34. ^1H DOSY (600 MHz, CDCl_3 , 300 K) spectrum of 4 .	22
Figure S35. ^{29}Si NMR (59.6 MHz, DMSO- d_6 , 300 K) spectrum of 4 .	23
Figure S36. FT-IR (KBr pellets) spectrum of 4 .	23
Figure S37. HR-MS (ESI+, TOF, CHCl_3) spectrum of 4 .	24

Figure S38. EDS spectrum of 4 .	24
Figure S39. Powder XRD pattern of 4 .	25
Figure S40. ^1H NMR (500 MHz, DMSO- d_6 , 300 K) spectrum of 5 .	26
Figure S41. ^{13}C NMR (126 MHz, CDCl_3 , 300 K) spectrum of 5 .	26
Figure S42. ^1H DOSY (600 MHz, CDCl_3 , 300 K) spectrum of 5 .	27
Figure S43. ^{29}Si NMR (59.6 MHz, DMSO- d_6 , 300 K) spectrum of 5 .	27
Figure S44. FT-IR (KBr pellets) spectrum of 5 .	28
Figure S45. HR-MS (ESI+, TOF, CHCl_3) spectrum of 5 (method A).	29
Figure S46. HR-MS (ESI+, TOF, CHCl_3) spectra of 4 and 5 before and after separation.	29
Figure S47. EDS spectrum of 5 .	30
Figure S48. Powder XRD pattern of 5 .	30
Figure S49. ^1H NMR (500 MHz, CDCl_3 , 300 K) spectrum of 6 .	31
Figure S50. ^{13}C NMR (126 MHz, CDCl_3 , 300 K) spectrum of 6 .	31
Figure S51. TG (black line), and DTA (blue line) thermogram of 1 .	32
Figure S52. TG (black line), and DTA (blue line) thermogram of 2 .	32
Figure S53. TG (black line), and DTA (blue line) thermogram of 3 .	33
Figure S54. TG (black line), and DTA (blue line) thermogram of 4 (air and nitrogen).	33
Figure S55. TG (black line), and DTA (blue line) thermogram of 5 (air and nitrogen).	34
Figure S56. TG (black line), and DTA (blue line) thermogram of 6 (air and nitrogen).	34
Figure S57. First derivative of TG (DTG) thermograms of 1–6 .	35
Figure S58. DSC of 5 , 2 nd heat and cooling cycle (in nitrogen).	35
Figure S59. DSC of 6 , 2 nd heat and cooling cycle (in nitrogen).	35
Figure S60. Selected HR-TEM images of 4 (a) and 5 (b).	36
Figure S61. ^{29}Si NMR (59.6 MHz, DMSO- d_6 , 300 K) spectrum of 1 after reaction with 0, 1, 4, 8, 12 and 16 equivalents of $\text{CH}_3\text{SO}_3\text{H}$.	37
Figure S62. HR-MS (ESI+, TOF, MeOH) spectra of C .	38
Figure S63. HR-MS (ESI+, TOF, MeOH) spectra of D .	38
Figure S64. HR-MS (ESI+, TOF, MeOH) spectra of E .	39
Figure S65. Molecular models of compound 4 (a), compound 5 (b).	39
Table S1. MM2 calculations of the minimization energies of Compound 2 , 3 , 4 , 5 .	39
Figure S66. ^{29}Si NMR (59.63 MHz, DMSO- d_6 , 300 K) spectrum of DSS and TMS.	40



a) $\text{H}_2\text{O, HCl}$; b) $\text{H}_2\text{O, CF}_3\text{SO}_3\text{H}$ c) acetone, precipitate d) acetone solution e) $\text{CF}_3\text{SO}_3\text{H, DMSO}$ f) decanoyl chloride, DMF, Et_3N

Scheme S1. Synthesis of **1–5**.

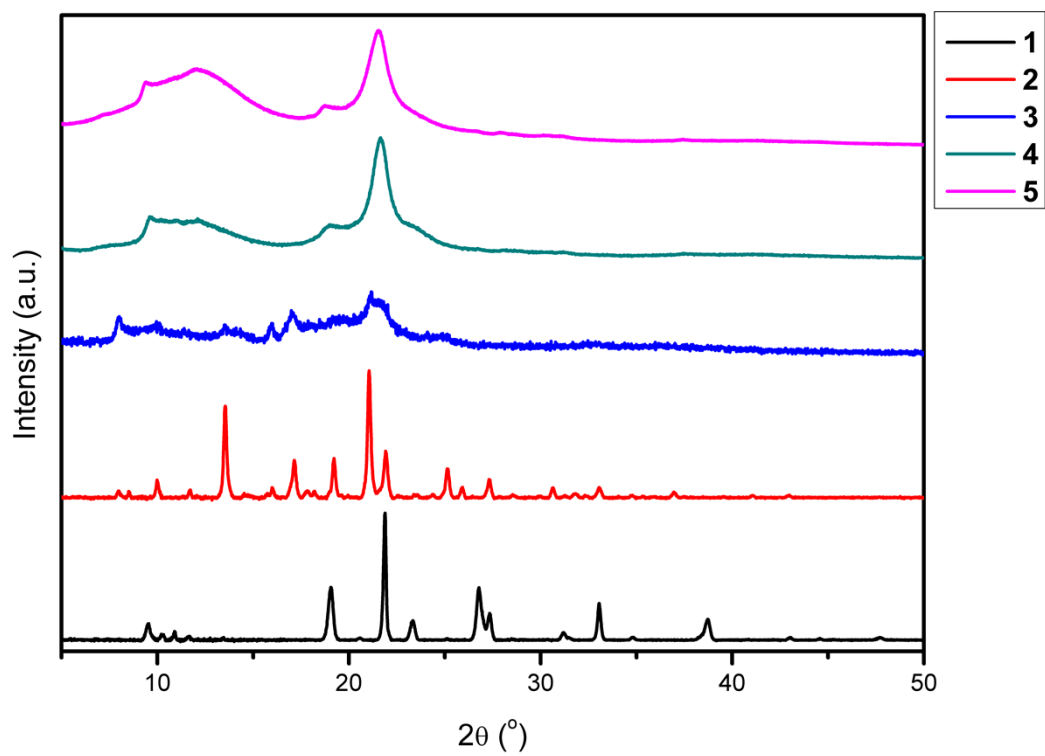


Figure S1. Powder XRD patterns for **1–5**.

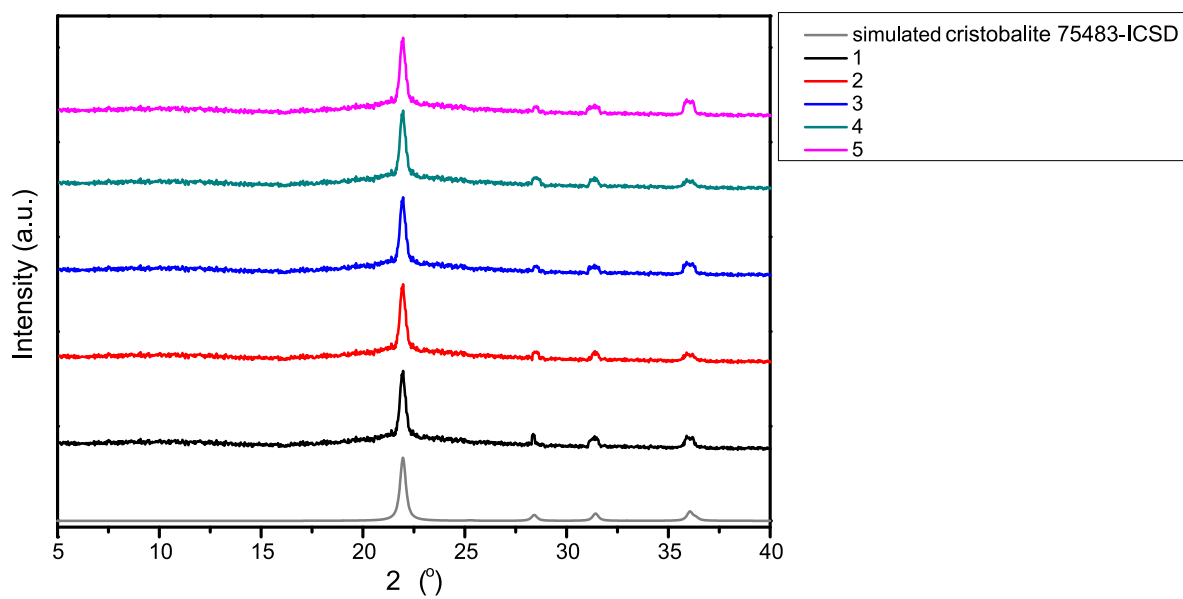


Figure S2. Powder XRD patterns for **1–5** after heating to the decomposition temperature.

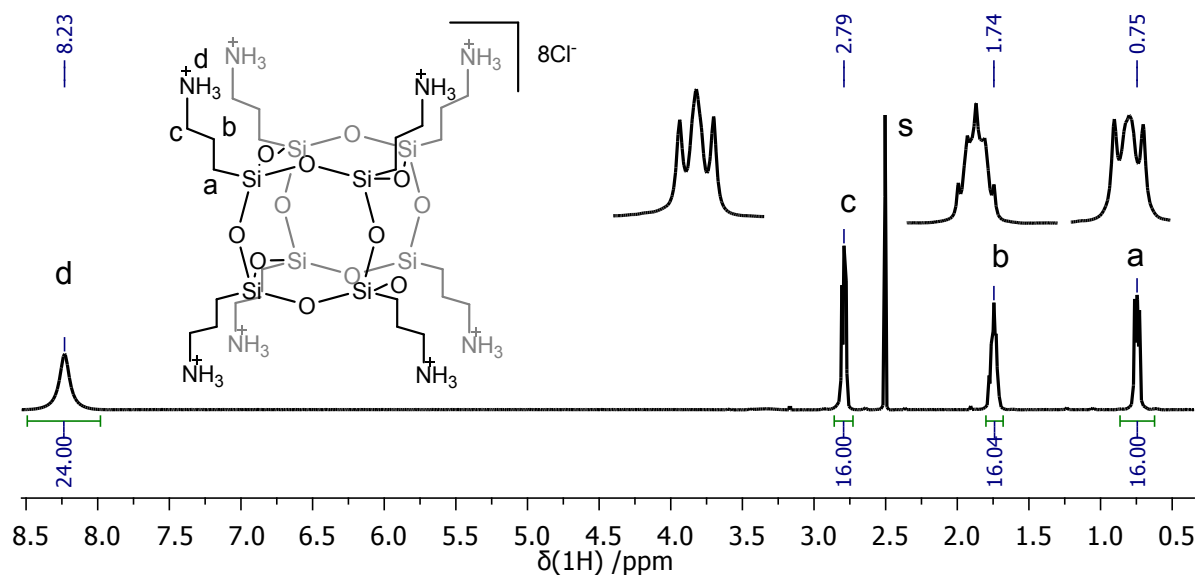


Figure S3. ^1H NMR (500 MHz, DMSO-d_6 , 300 K) spectrum of **1**, s = solvent.

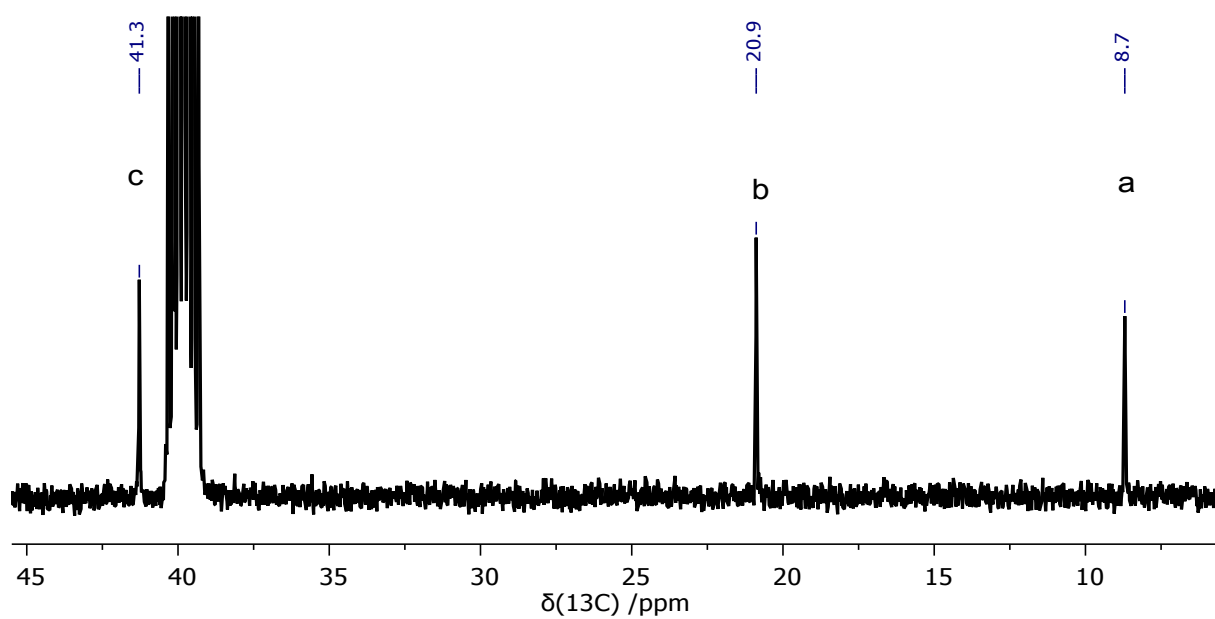


Figure S4. ^{13}C NMR (126 MHz, DMSO-d_6 , 300 K) spectrum of **1**.

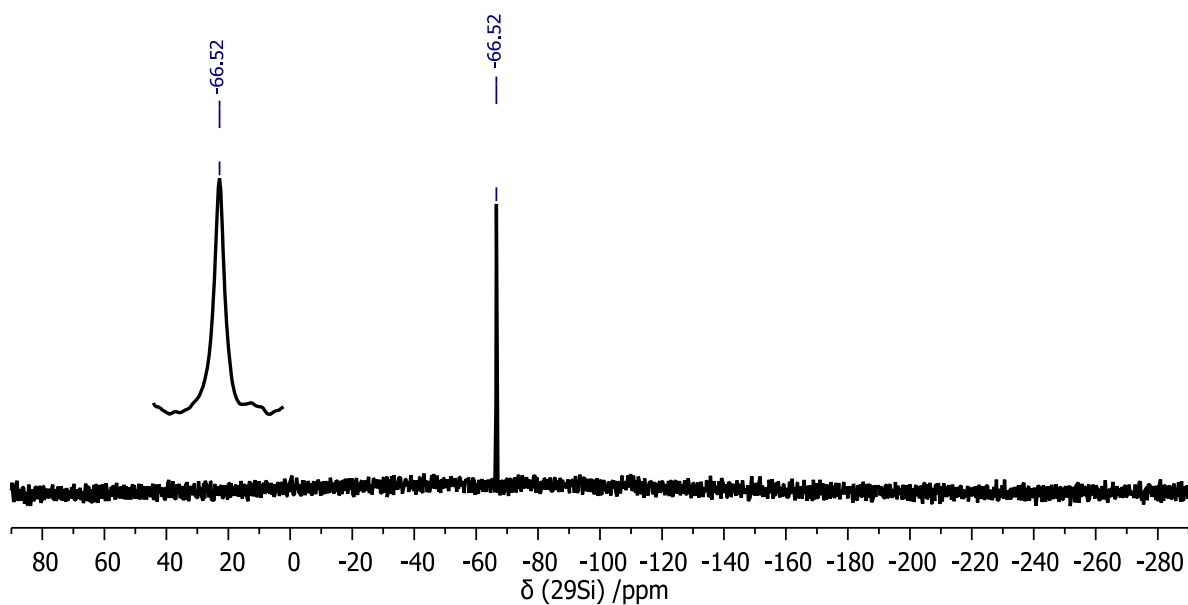


Figure S5. ^{29}Si NMR (59.6 MHz, DMSO- d_6 , 300 K) spectrum of **1**.

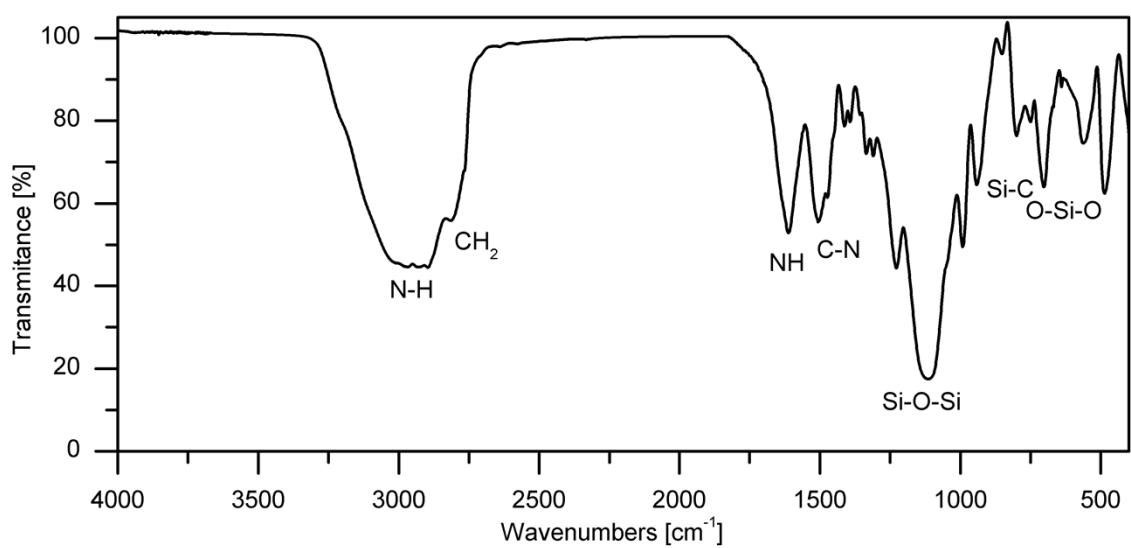


Figure S6. FT-IR (KBr pellets) spectrum of **1**.

Fi

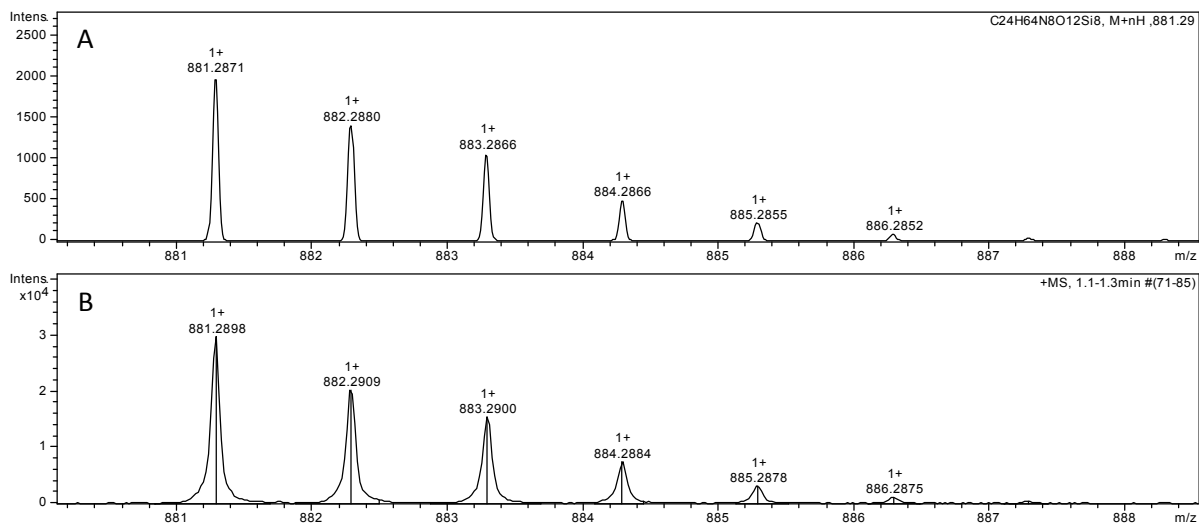


Figure S7. Simulated (A) calcd for $C_{24}H_{65}N_8O_{12}Si_8$, $[M - 8HCl + H]^+$ and measured (B) HR-MS (ESI+, TOF, MeOH) spectra of **1**.

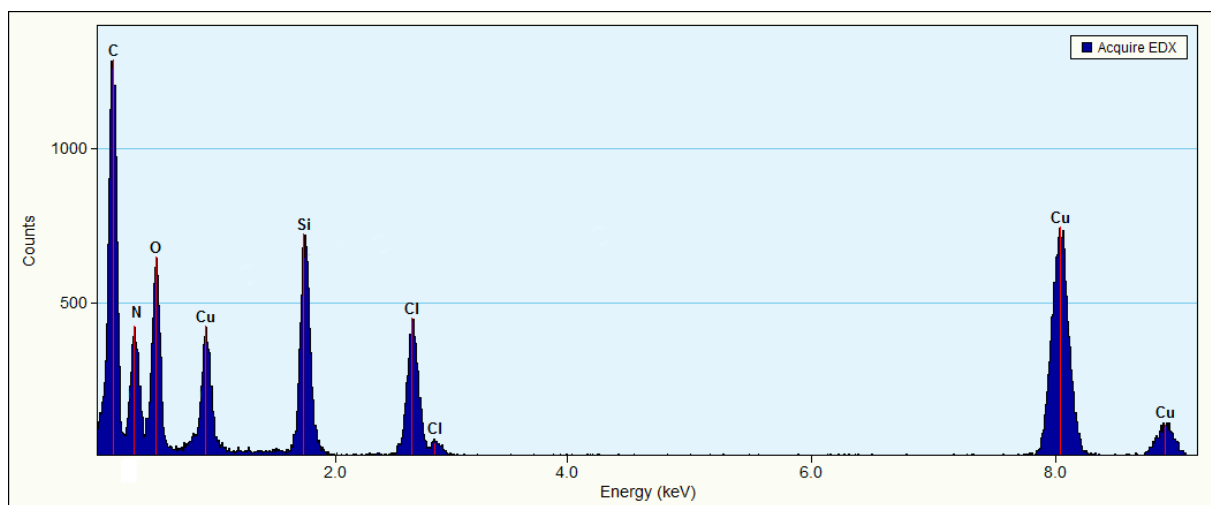


Figure S8. EDS spectrum of **1** (copper content is derived from the high-purity conducting Cu grid).

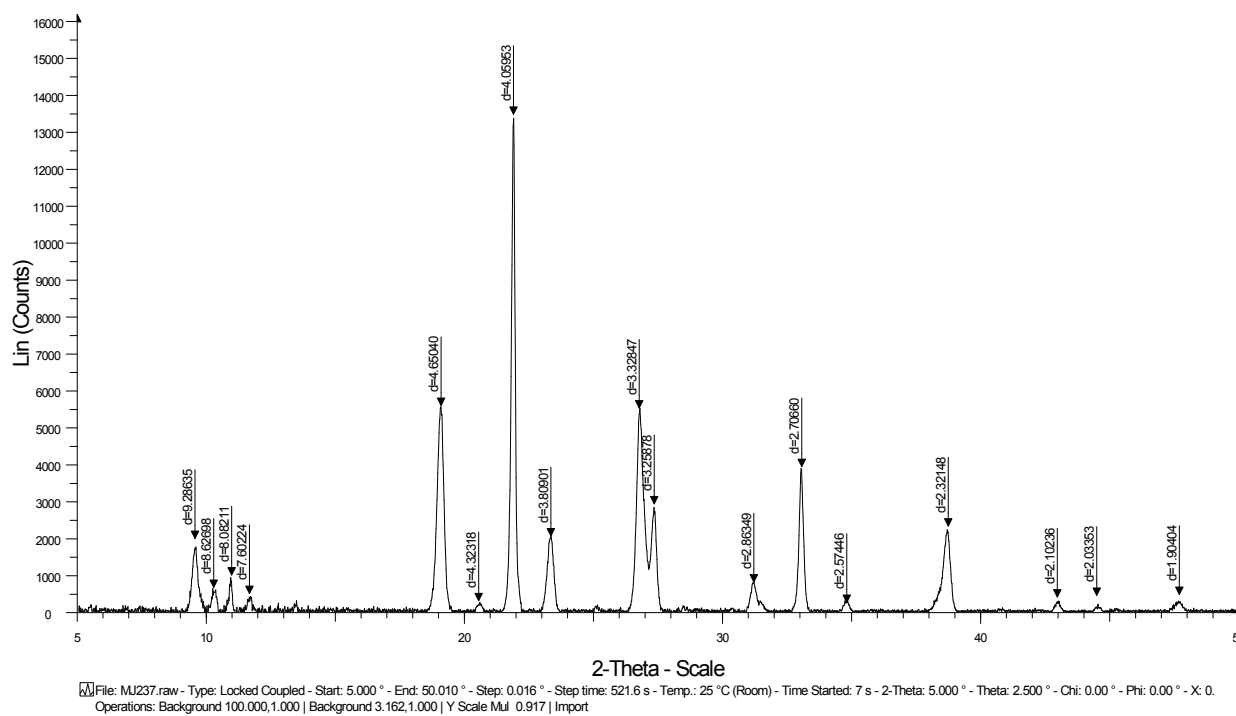


Figure S9. Powder XRD pattern of **1**.

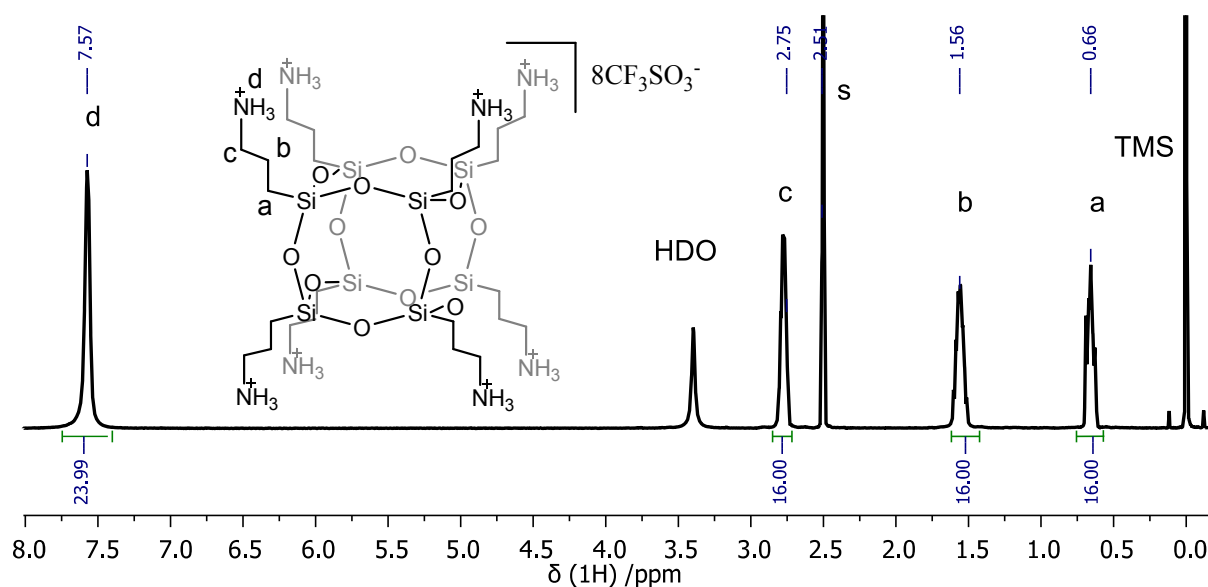


Figure S10. ^1H NMR (500 MHz, DMSO-d_6 , 300 K) spectrum of **2**, s = solvent. Chemical shifts were referenced to tetramethylsilane (TMS) (δ 0.0).

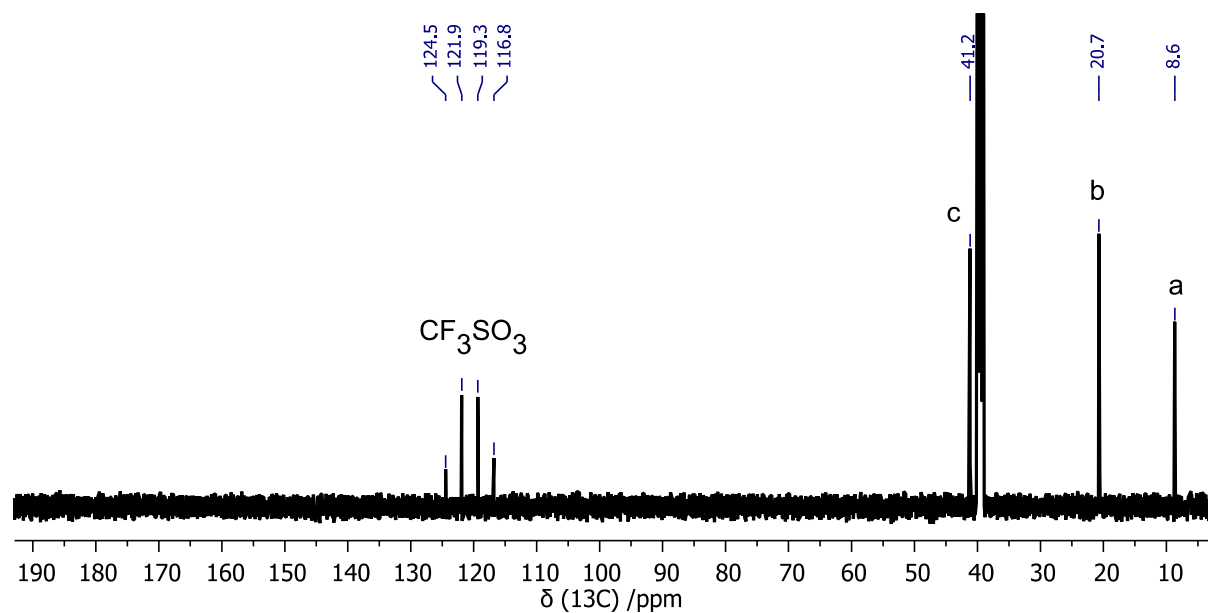


Figure S11. ^{13}C NMR (126 MHz, DMSO-d_6 , 300 K) spectrum of **2**.

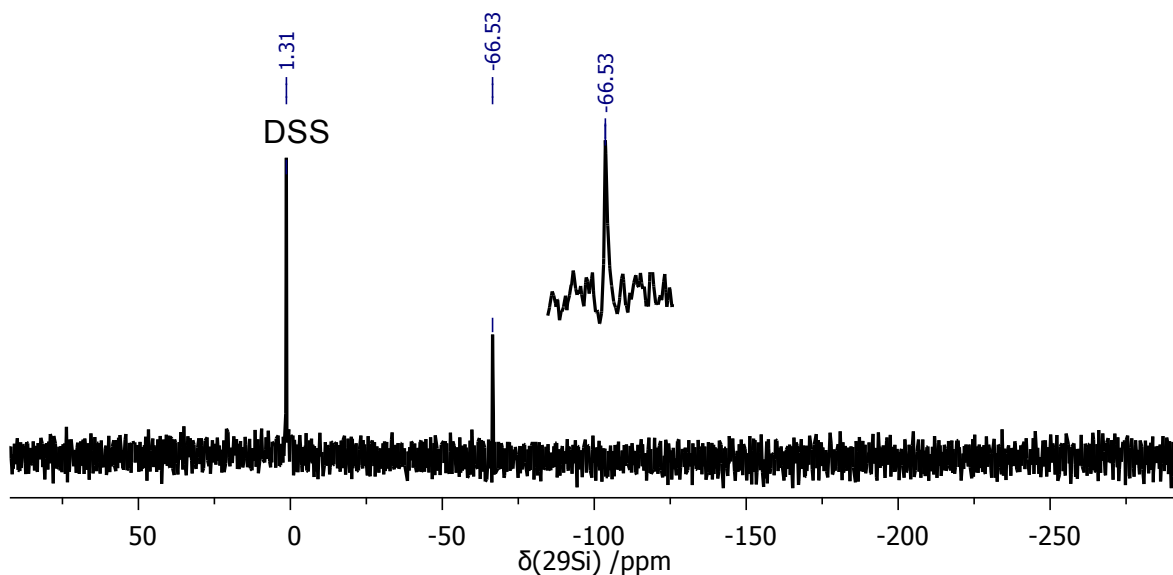


Figure S12. ^{29}Si NMR (59.6 MHz, DMSO-d_6 , 300 K) spectrum of **2**. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) (δ 1.316).

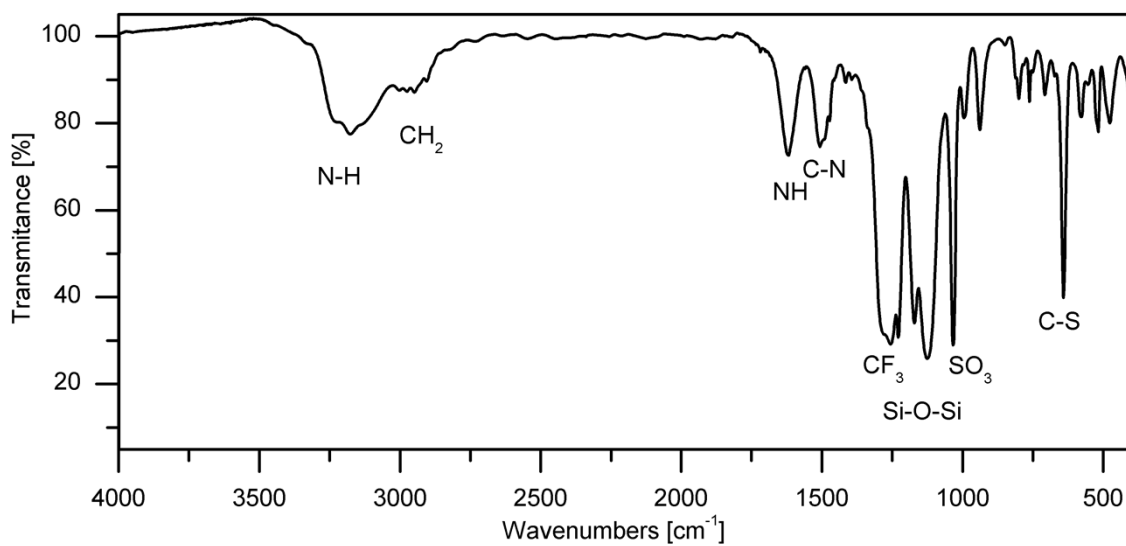


Figure S13. FT-IR (KBr pellets) spectrum of **2**.

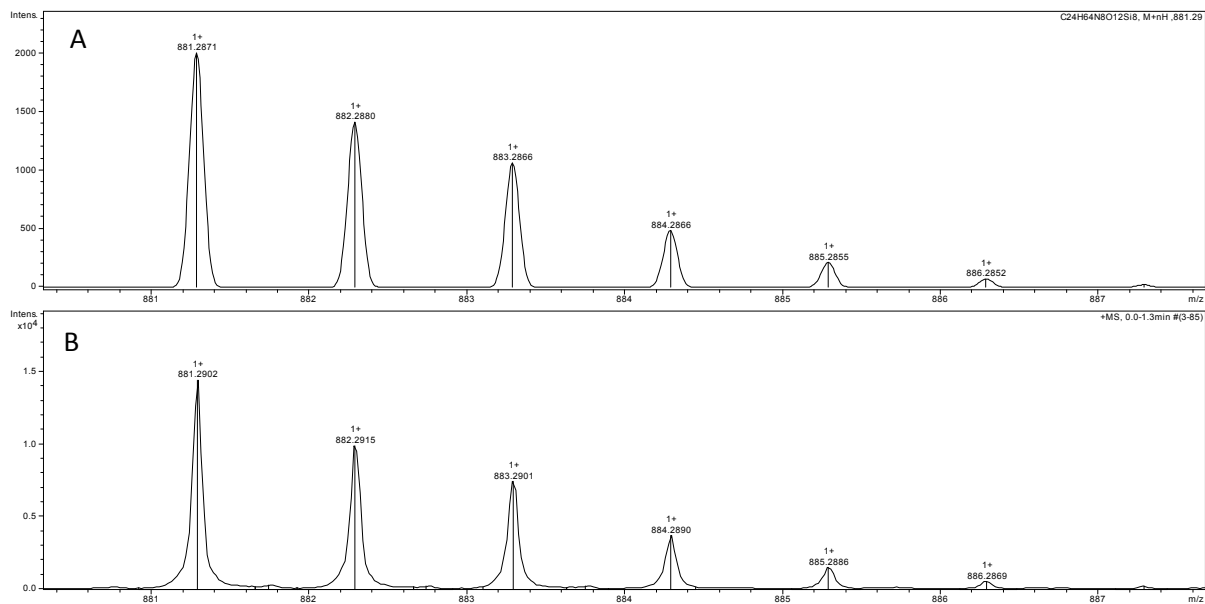


Figure S14. Simulated (A) calcd for $C_{24}H_{65}N_8O_{12}Si_8$, $[M - 8CF_3SO_3H + H]^+$ and measured (B) HR-MS (ESI+, TOF, MeOH) spectra of **2**.

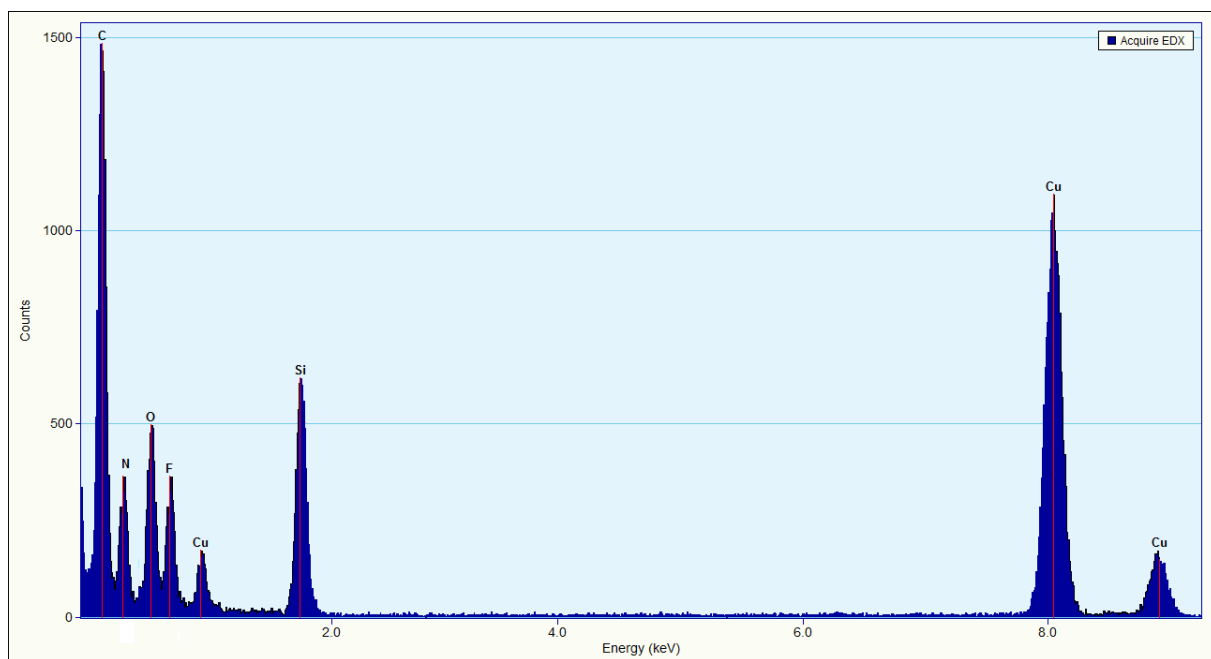


Figure S15. EDS spectrum of **2** (copper content is derived from the high-purity conducting Cu grid).

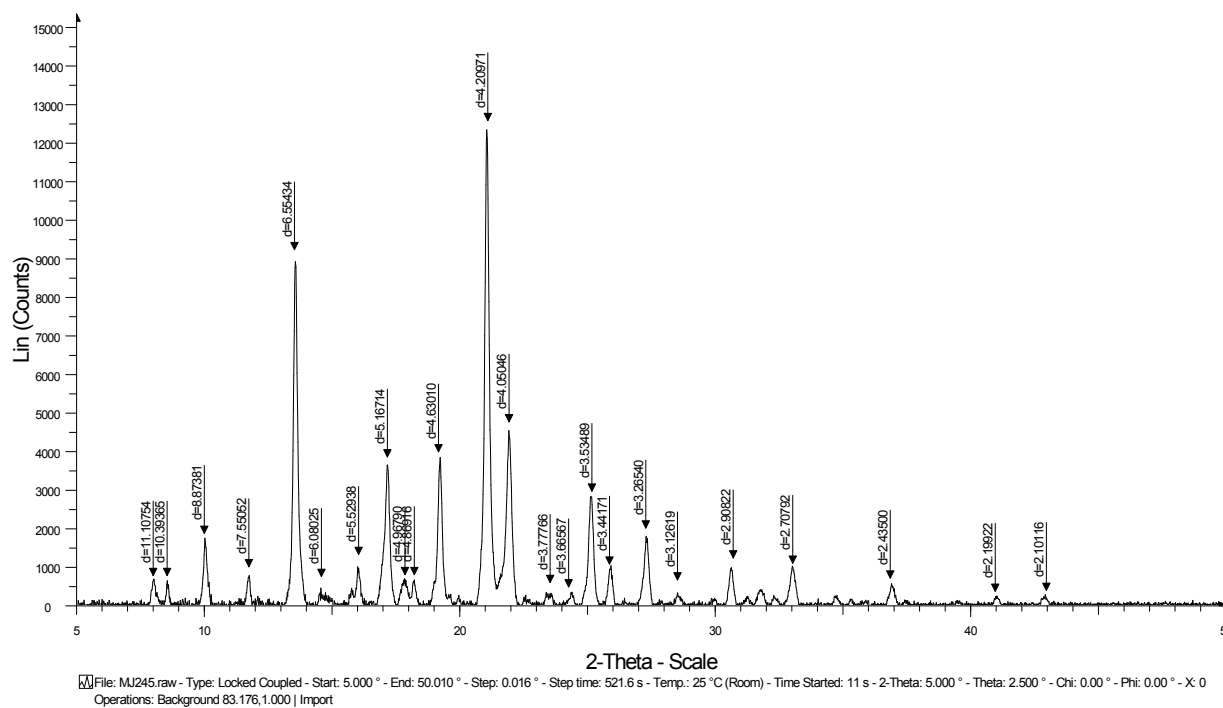


Figure S16. Powder XRD pattern of **2**.

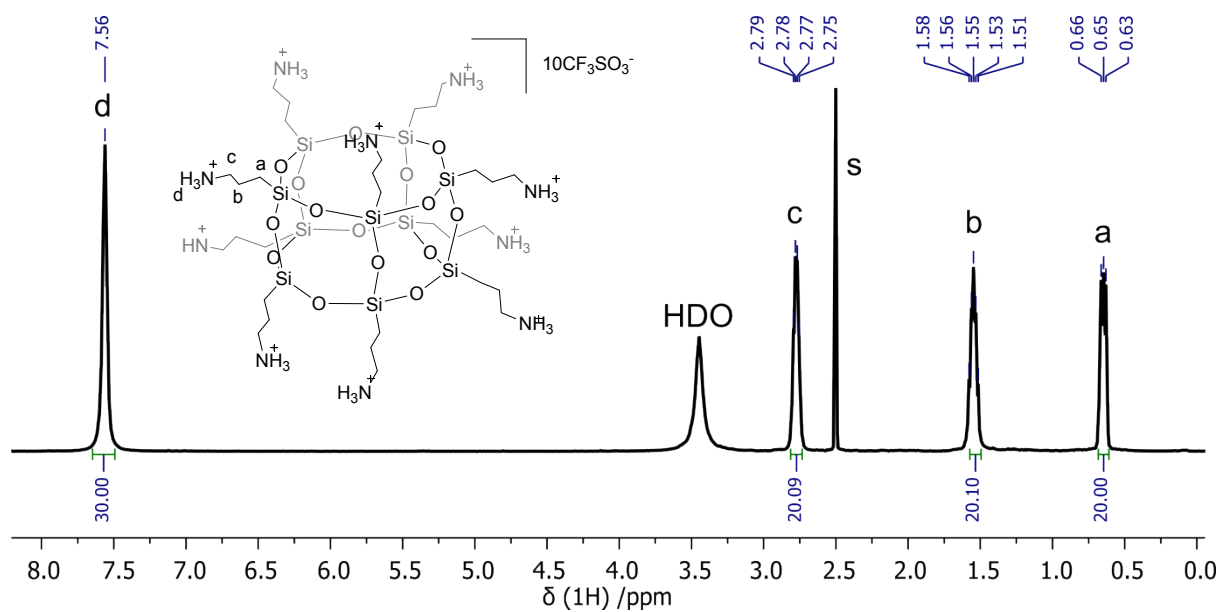


Figure S17. ^1H NMR (500 MHz, DMSO-d_6 , 300 K) spectrum of **3**, s = solvent.

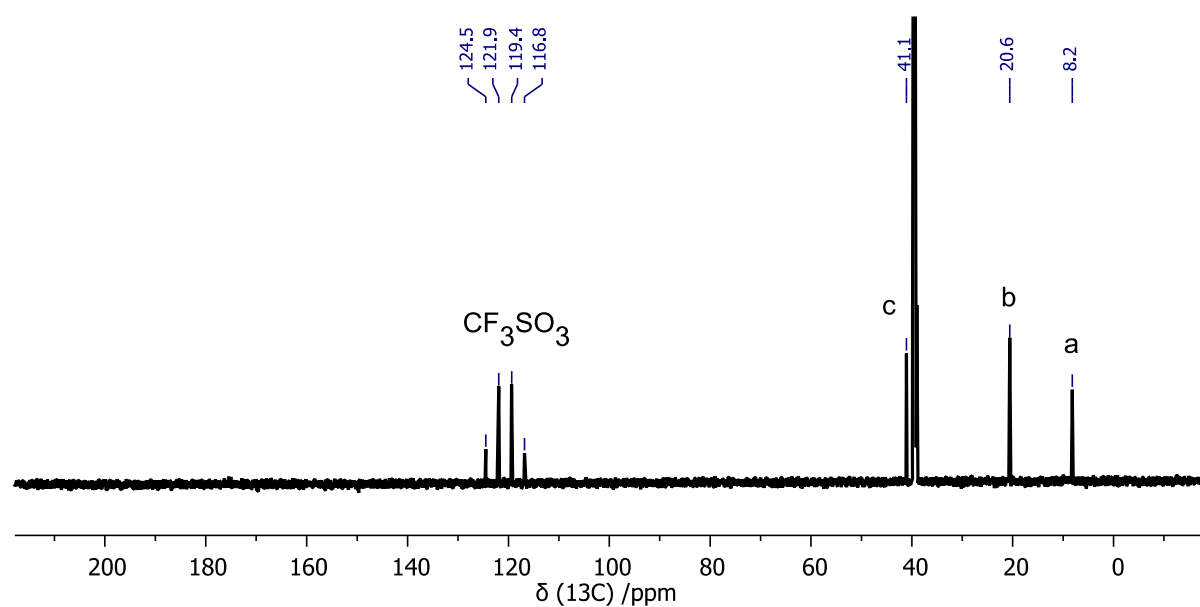


Figure S18. ^{13}C NMR (126 MHz, DMSO-d_6 , 300 K) spectrum of **3**.

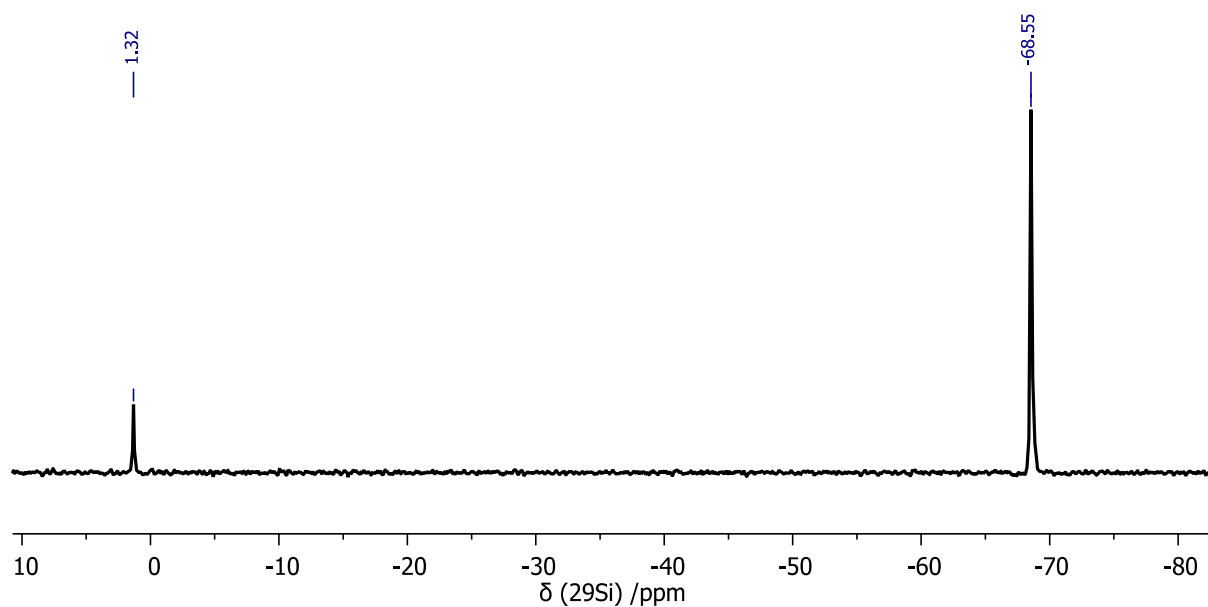


Figure S19. ^{29}Si NMR (59.6 MHz, DMSO-d_6 , 300 K) spectrum of **3** obtained in method A. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) (δ 1.316).

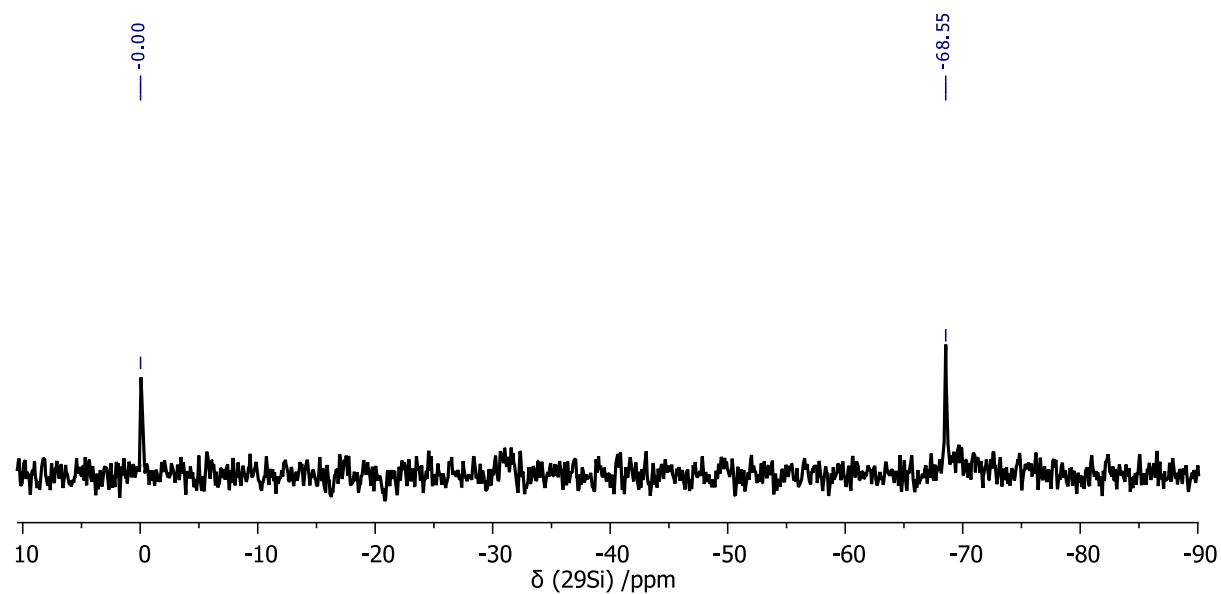


Figure S20. ^{29}Si NMR (59.6 MHz, DMSO-d_6 , 300 K) spectrum of **3** obtained in method B. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) (δ 1.316).

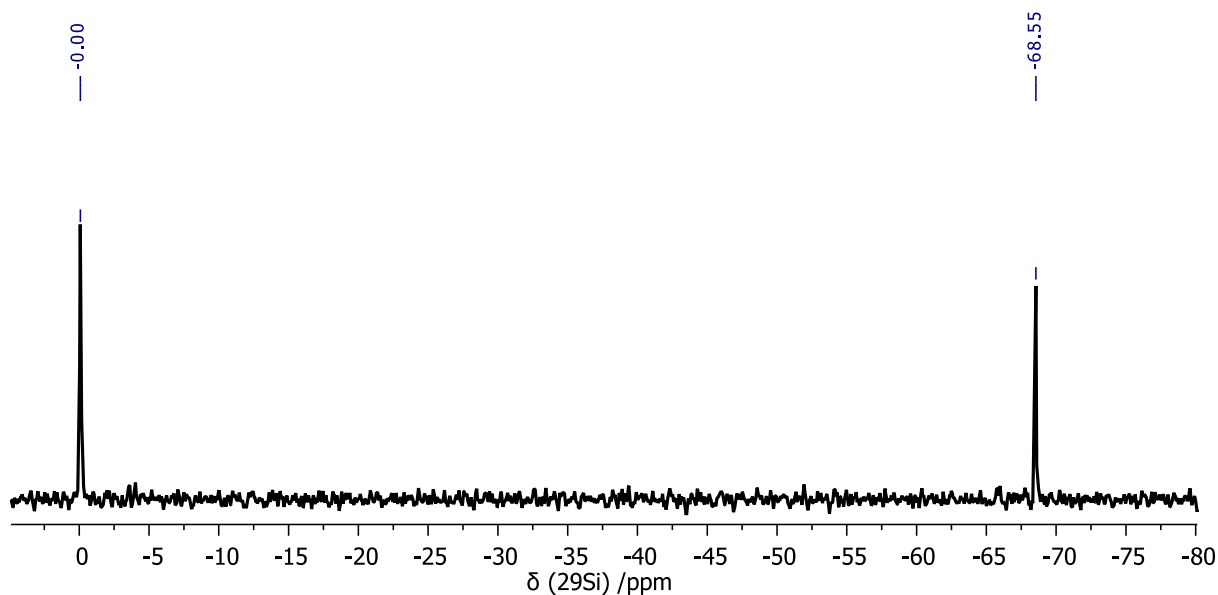


Figure S21. ^{29}Si NMR (59.6 MHz, DMSO-d_6 , 300 K) spectrum of **3** obtained in method C (by cage-rearrangement **1** $\rightarrow$ **3**). Chemical shifts were referenced to tetramethylsilane (TMS) (δ 0.00).

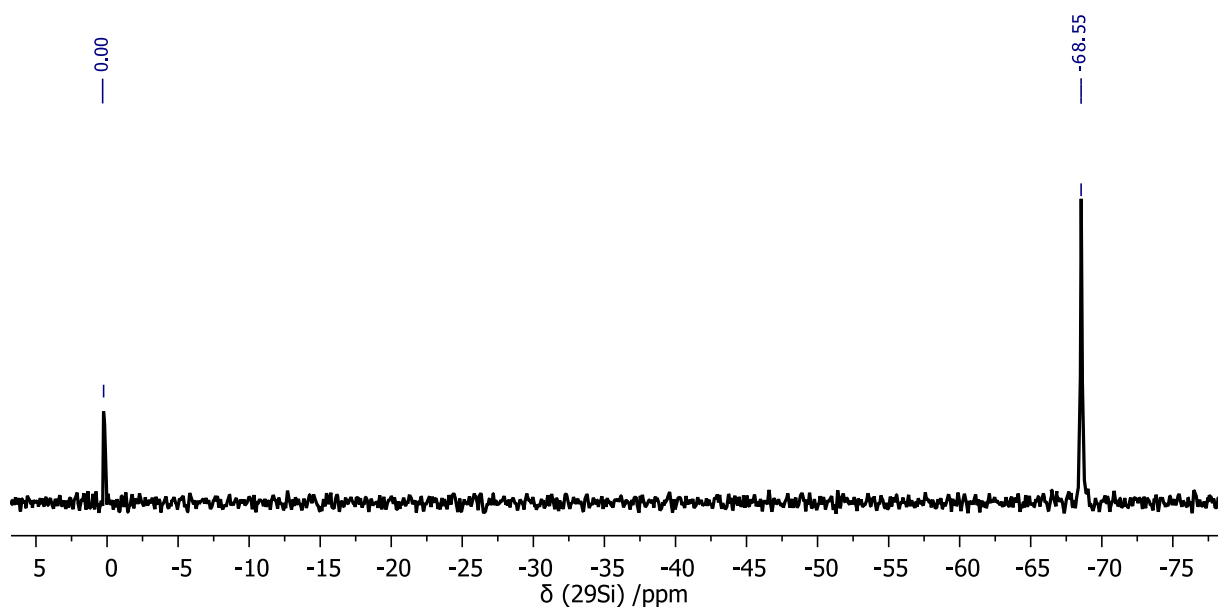


Figure S22. ^{29}Si NMR (59.6 MHz, DMSO-d_6 , 300 K) spectrum of **3** obtained in method D (by cage-rearrangement **2** $\rightarrow$ **3**). Chemical shifts were referenced to tetramethylsilane (TMS) (δ 0.00).

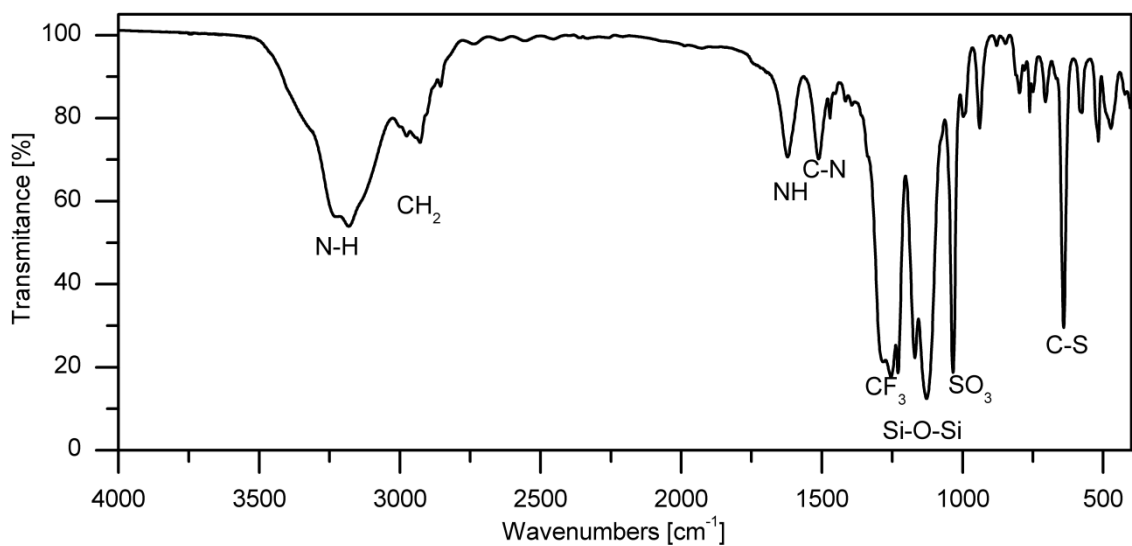


Figure S23. FT-IR (KBr pellets) spectrum of **3**.

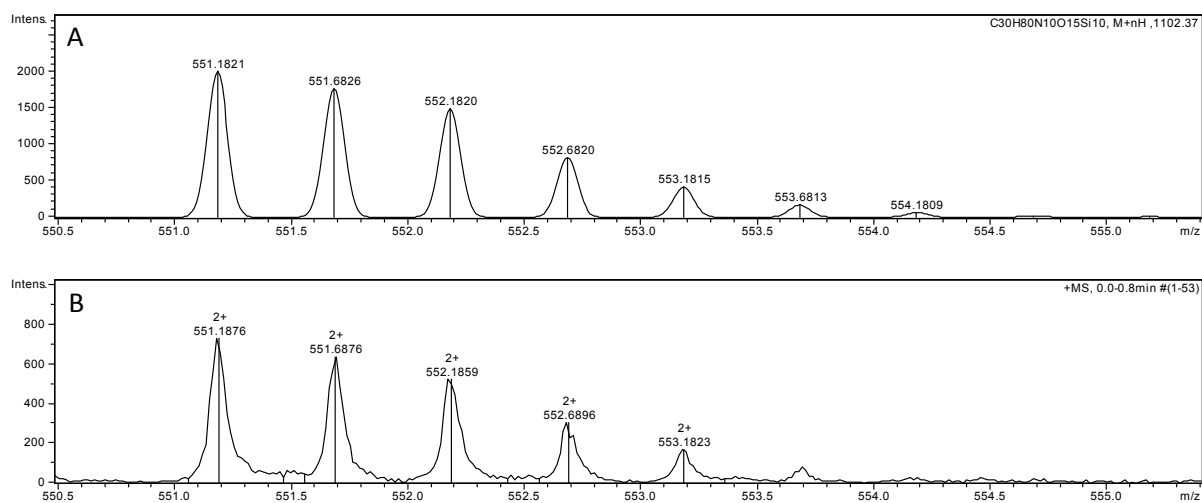


Figure S24. Simulated (A) calcd for $C_{30}H_{82}N_{10}O_{15}Si_{10}$, $[M - 10CF_3SO_3H + 2H]^{2+}$ and measured (B) HR-MS (ESI+, TOF, MeOH) spectra of **3** obtained in method A.

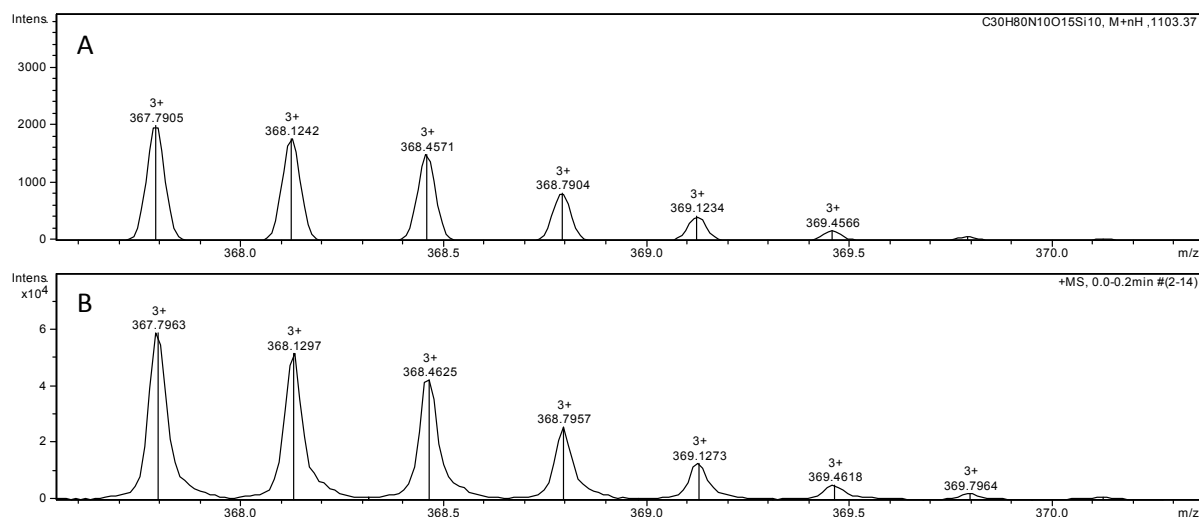


Figure S25. Simulated (A) calcd for $C_{30}H_{83}N_{10}O_{15}Si_{10}$, $[M - 10CF_3SO_3H + 3H]^{3+}$ and measured (B) HR-MS (ESI+, TOF, MeOH) spectra of **3** obtained in method B.

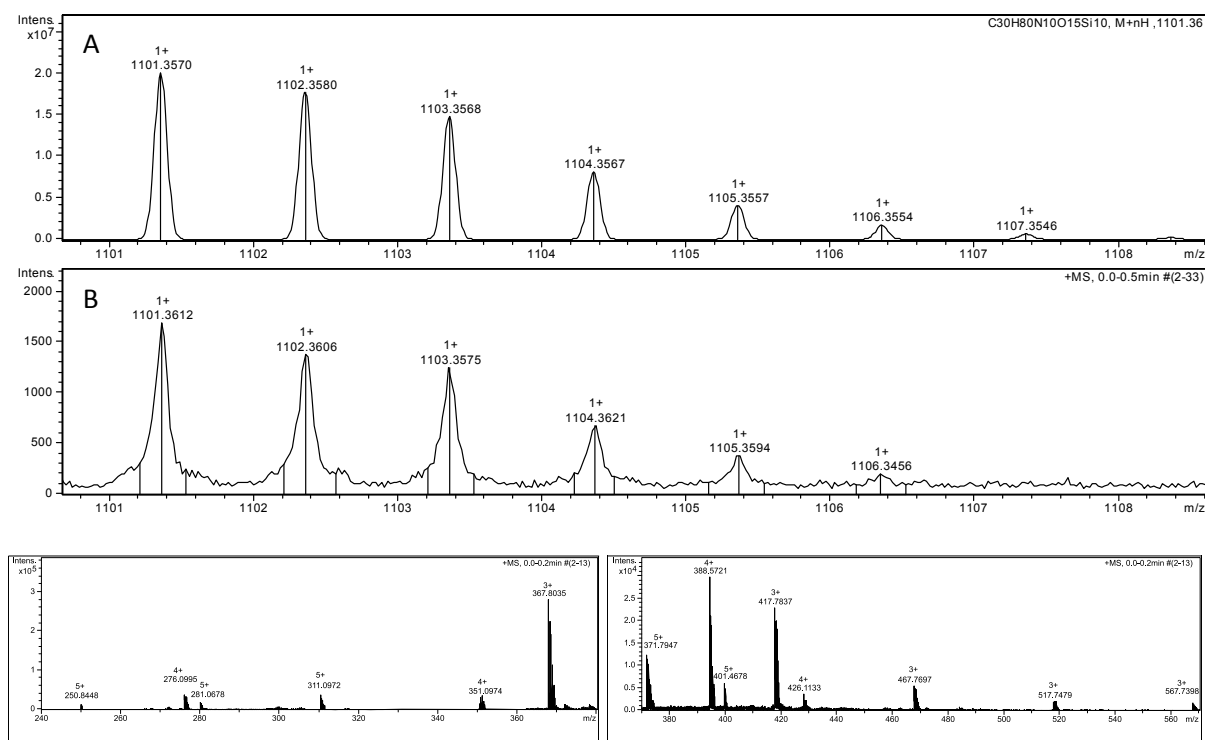


Figure S26. HR-MS (ESI+, TOF, MeOH) spectra of **3** obtained in method C (by cage-rearrangement **1** $\rightarrow$ **3**). Simulated (A) calcd for $C_{30}H_{81}N_{10}O_{15}Si_{10}$, $[M - 10CF_3SO_3H + 1H]^+$ and measured (B).

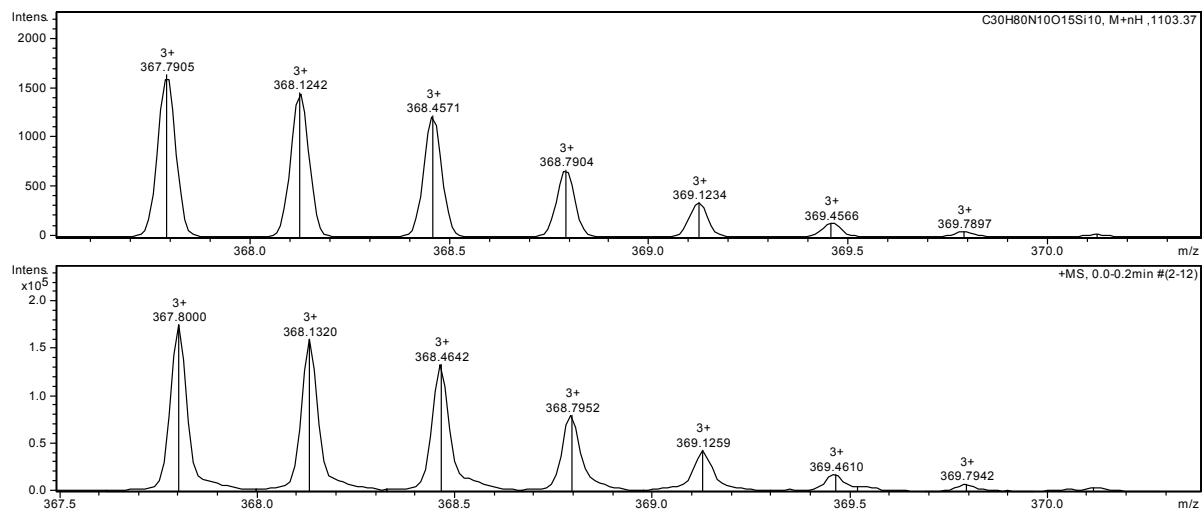


Figure S27. HR-MS (ESI+, TOF, MeOH) spectra of **3** obtained in method D (by cage-rearrangement **2** → **3**).

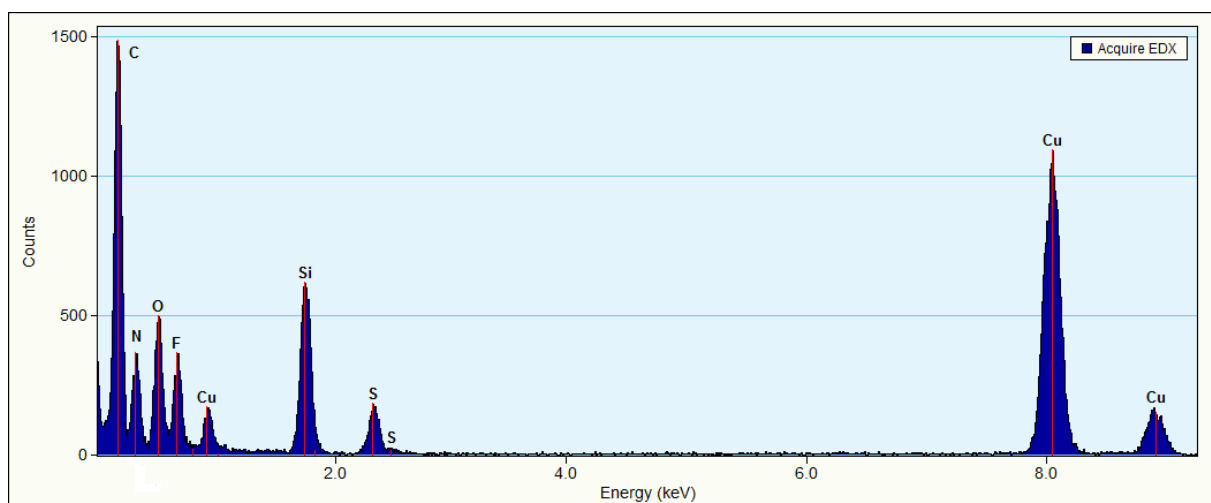


Figure S28. EDS spectrum of **3** (copper content is derived from the high-purity conducting Cu grid).

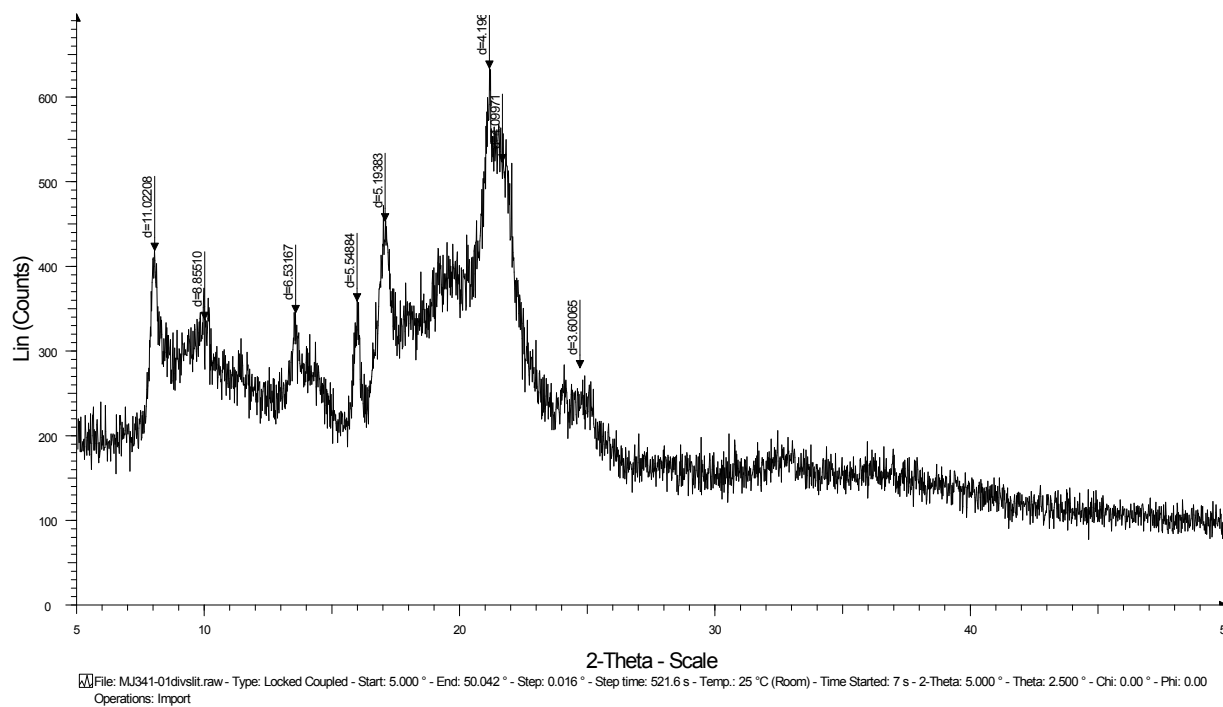


Figure S29. Powder XRD pattern of **3**.

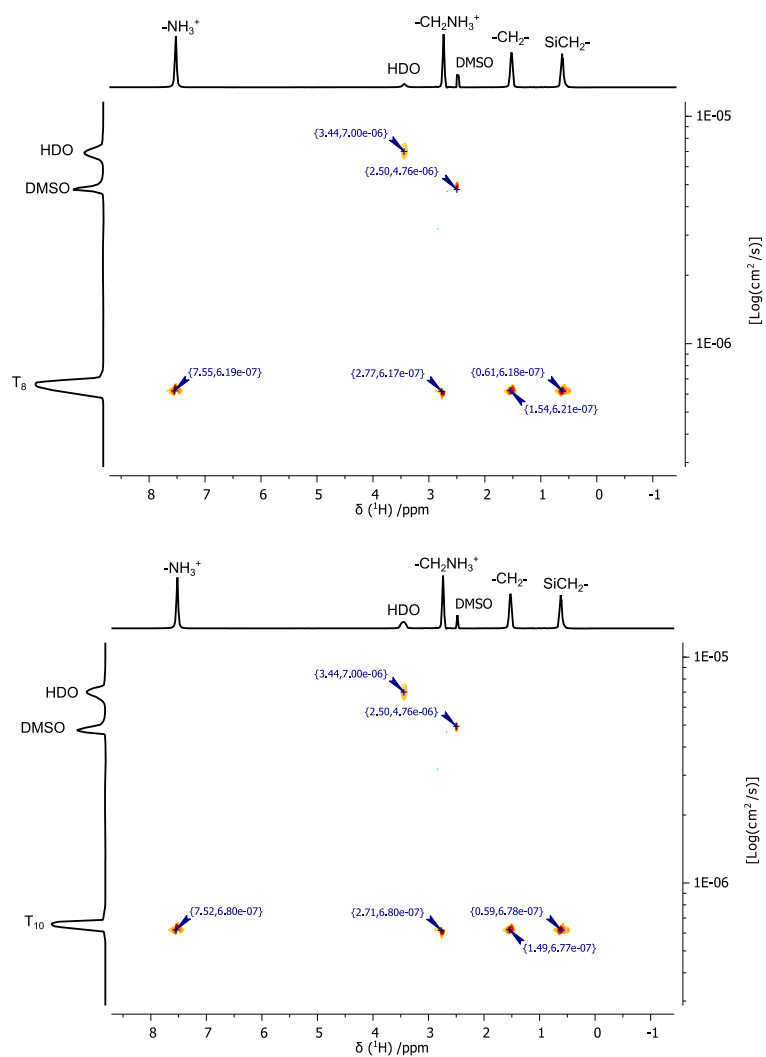


Figure S30. ^1H DOSY (600 MHz, DMSO-d_6 , 300 K) spectrum of **2** (top) and **3** (bottom).

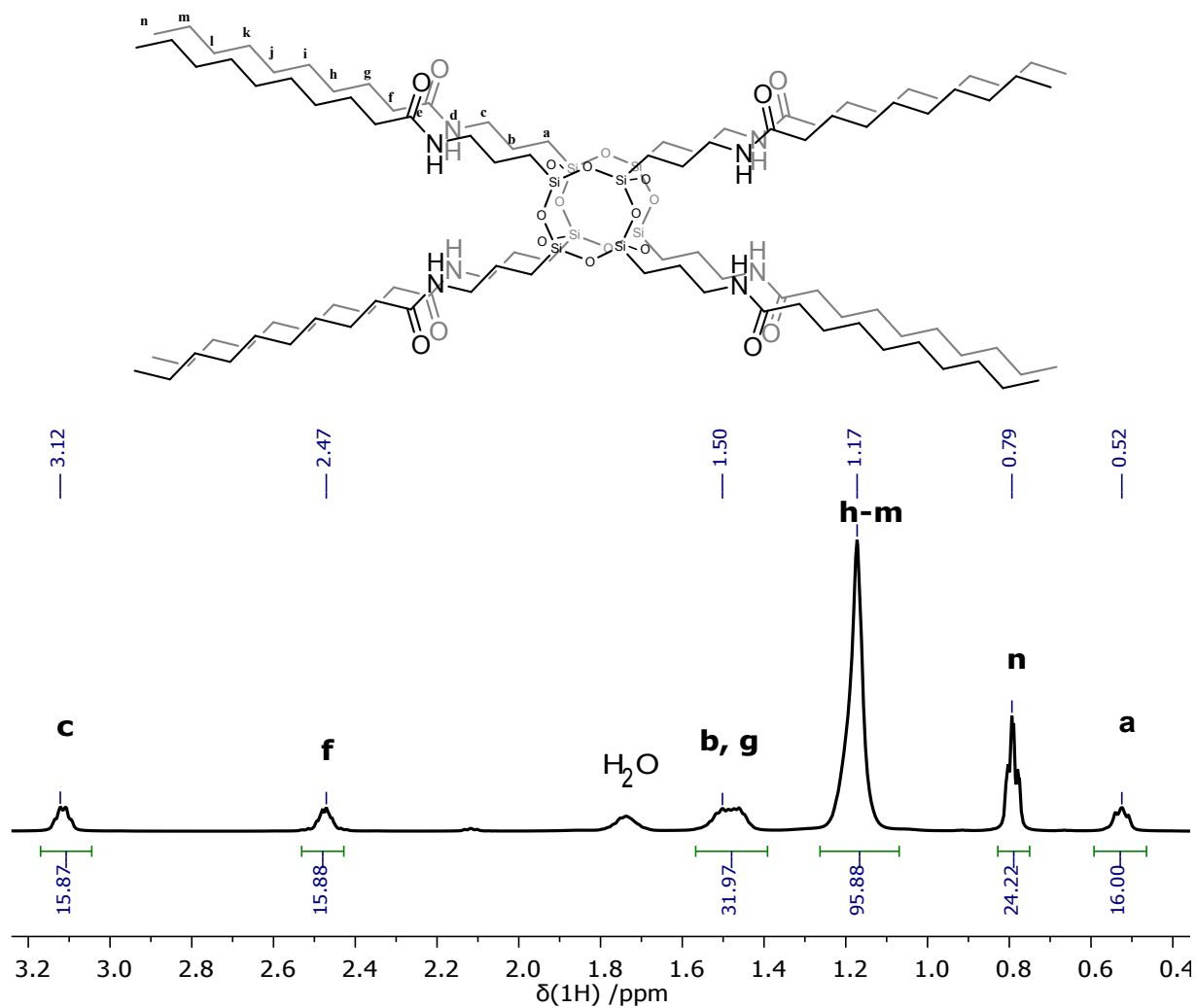


Figure S31. ^1H NMR (500 MHz, CDCl_3 , 300 K) spectrum of 4.

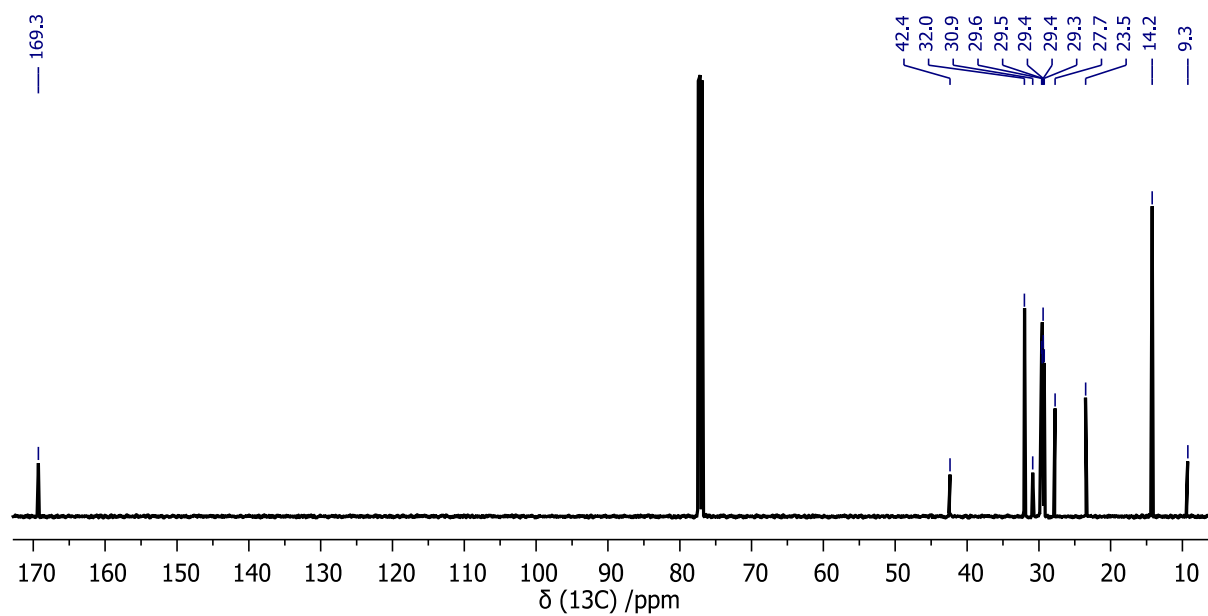
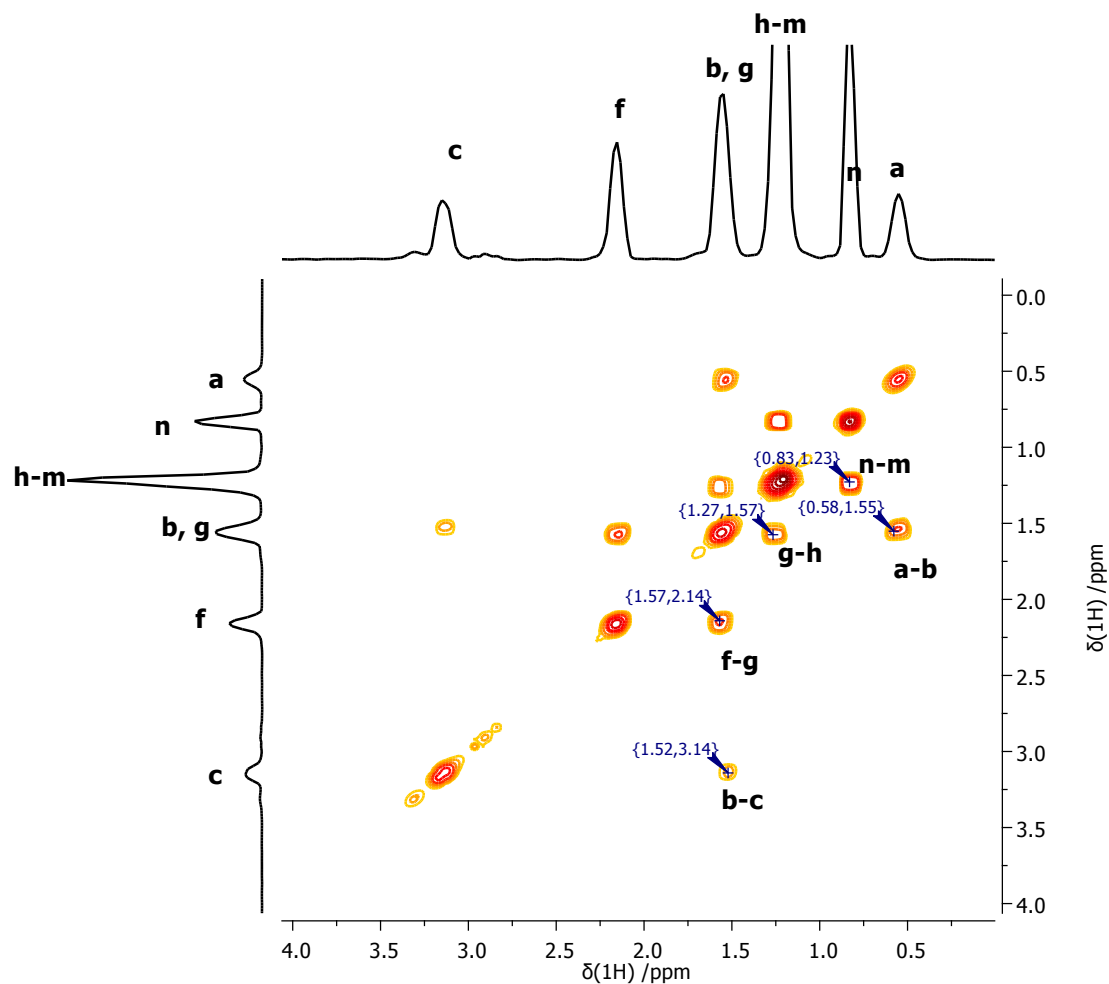


Figure S32. ^{13}C NMR (126 MHz, CDCl_3 , 300 K) spectrum of 4.



Figur

e S33. ^1H - ^1H COSY NMR (500 MHz, DMSO-d_6 , 300 K) spectrum of **4**.

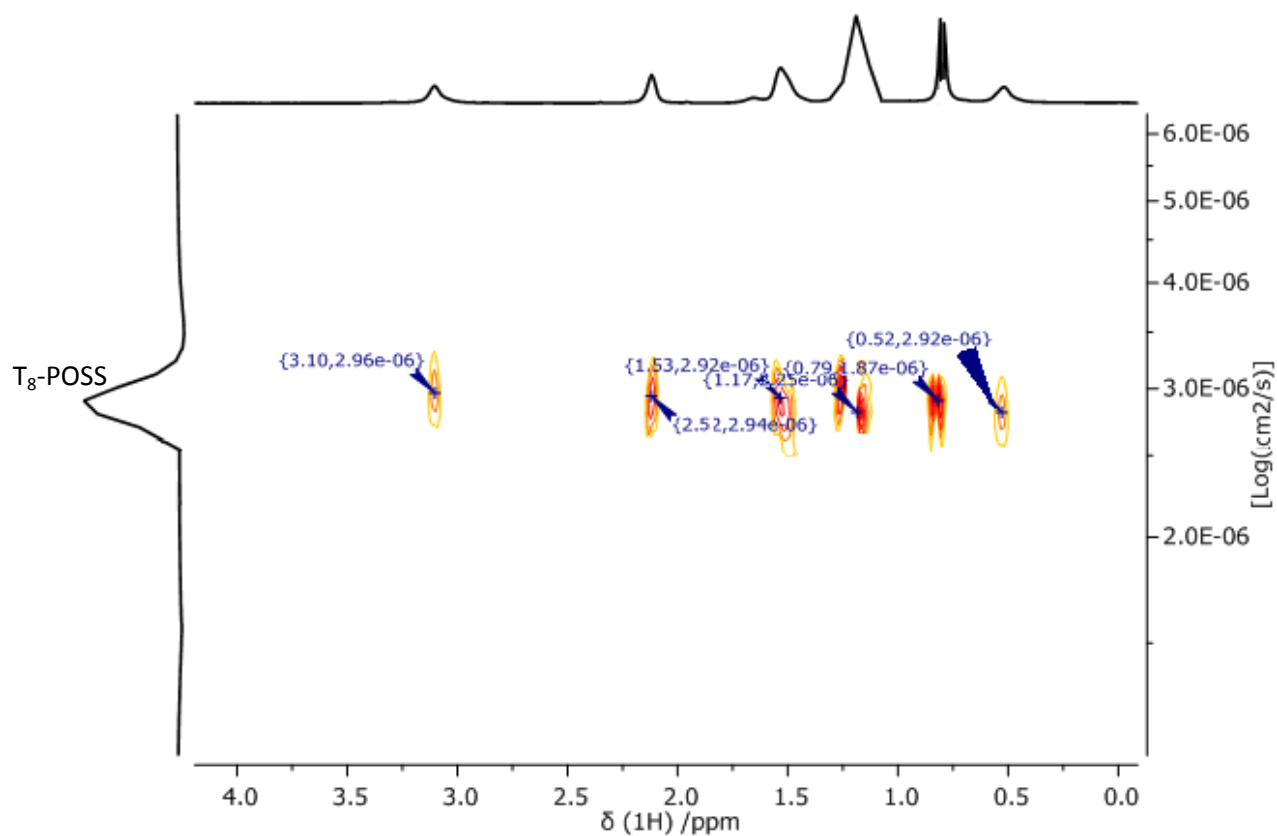


Figure S34. ^1H DOSY (600 MHz, CDCl_3 , 300 K) spectrum of **4**.

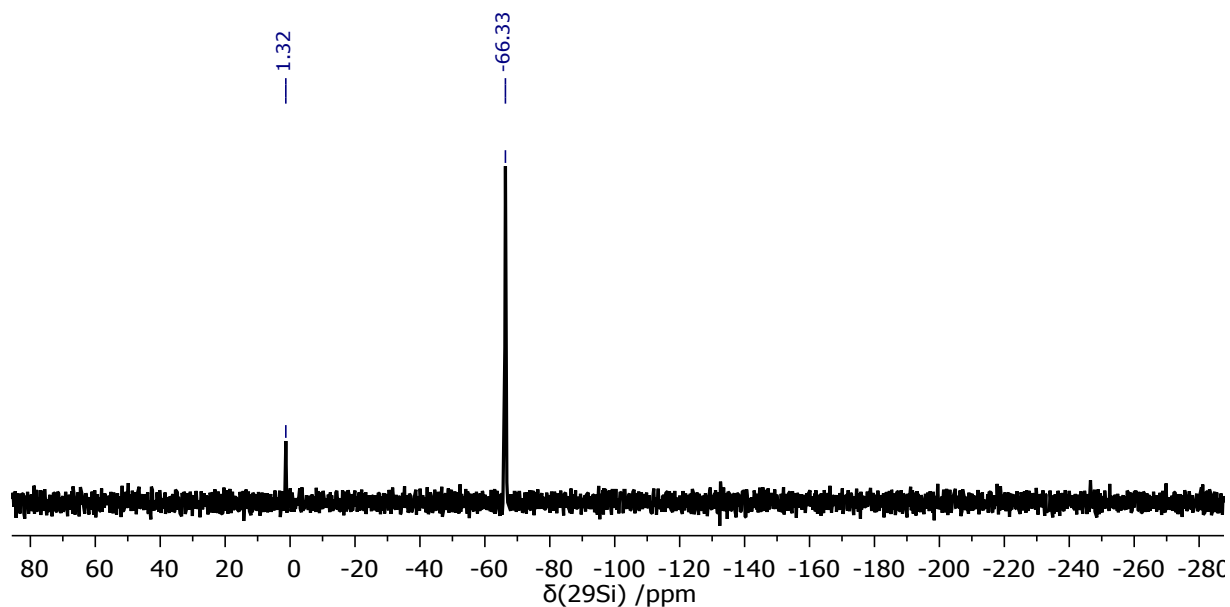


Figure S35. ^{29}Si NMR (59.6 MHz, DMSO-d_6 , 300 K) spectrum of 4. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) (δ 1.316).

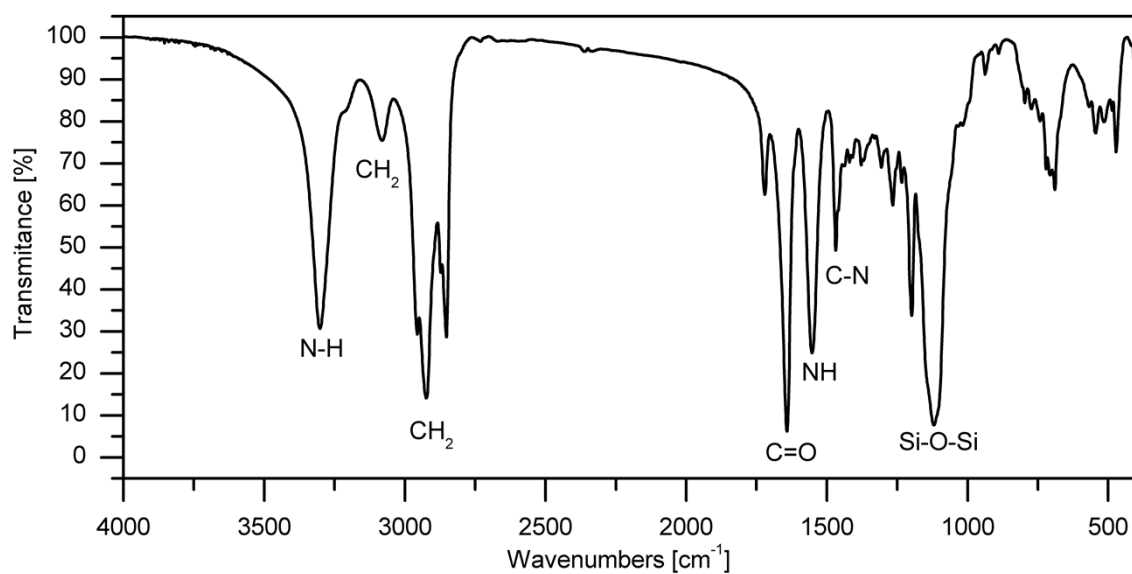


Figure S36. FT-IR (KBr pellets) spectrum of 4.

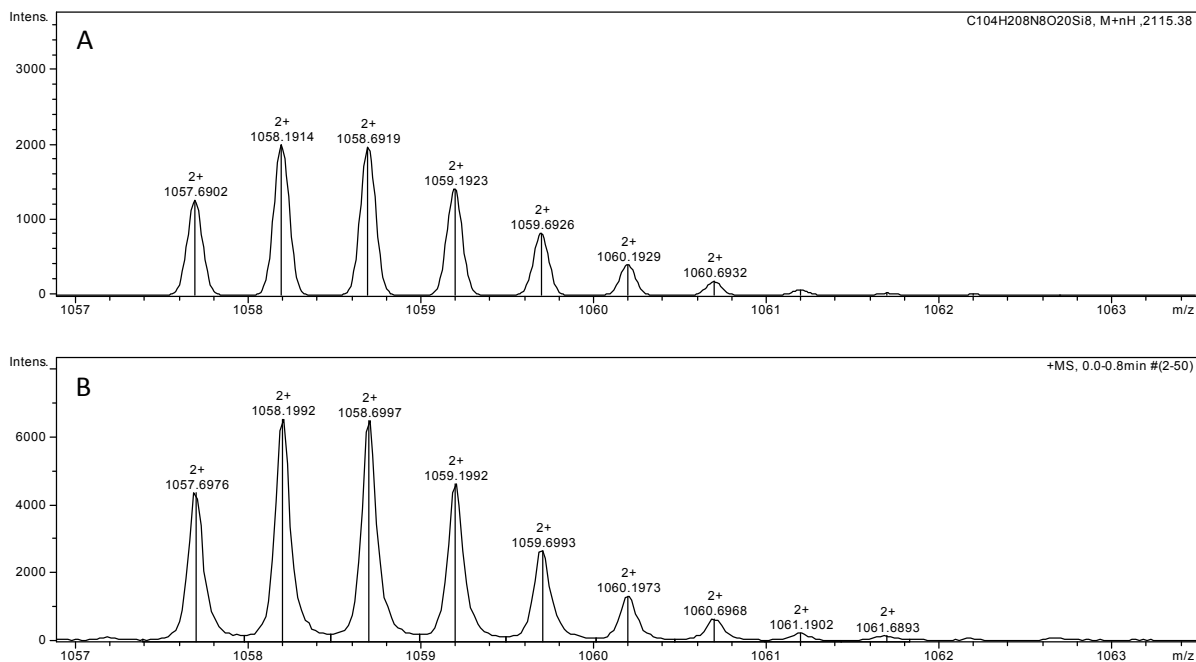


Figure S37. Simulated (A) calcd for $C_{104}H_{210}N_8O_{20}Si_8$, $[M + 2H]^{2+}$ and measured (B) HR-MS (ESI⁺, TOF, $CHCl_3$) spectra of **4**.

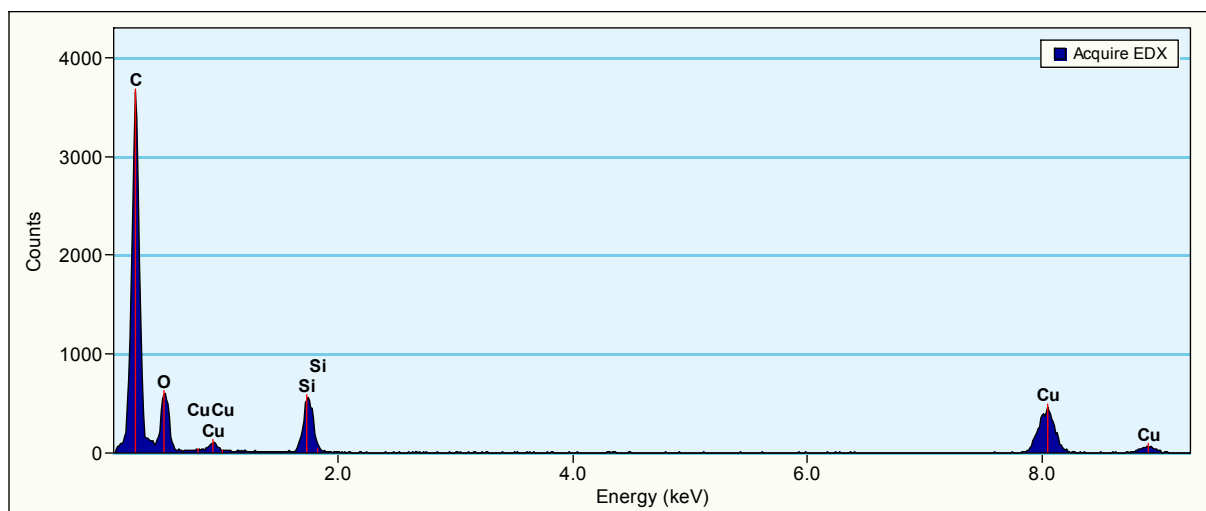


Figure S38. EDS spectrum of **4** (copper content is derived from the high-purity conducting Cu grid).

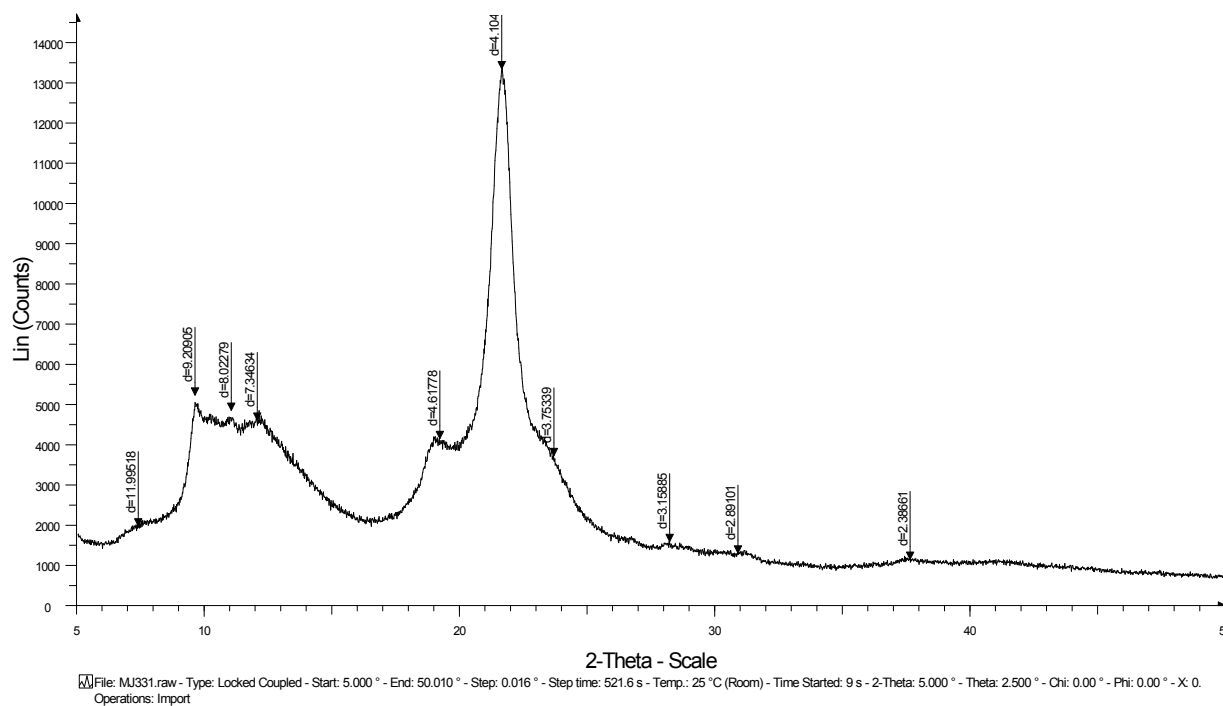
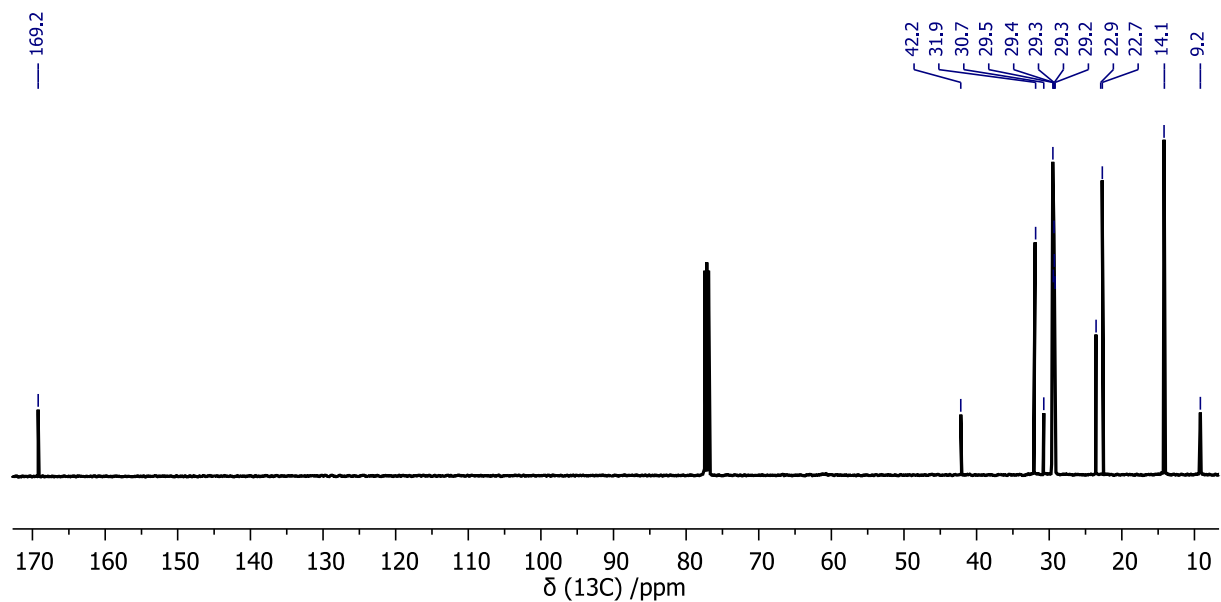
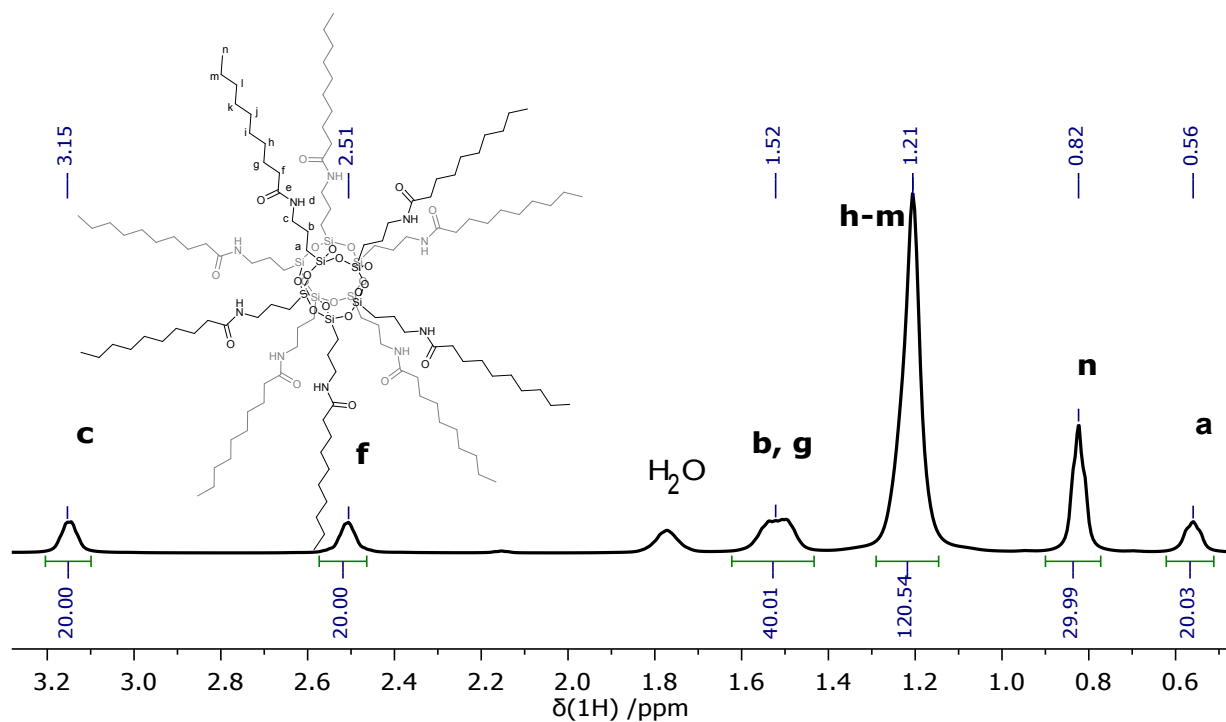


Figure S39. Powder XRD pattern of **4**.



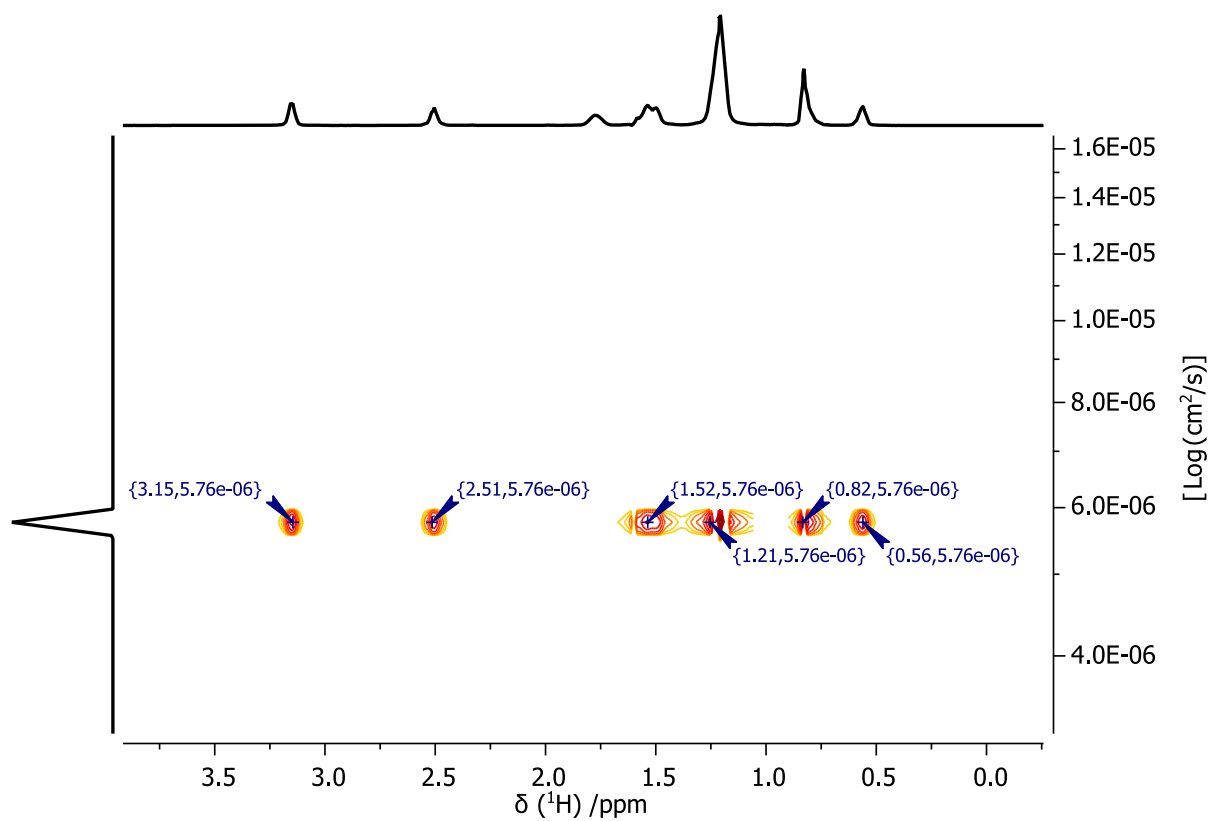


Figure S42. ^1H DOSY (600 MHz, CDCl_3 , 300 K) spectrum of **5**.

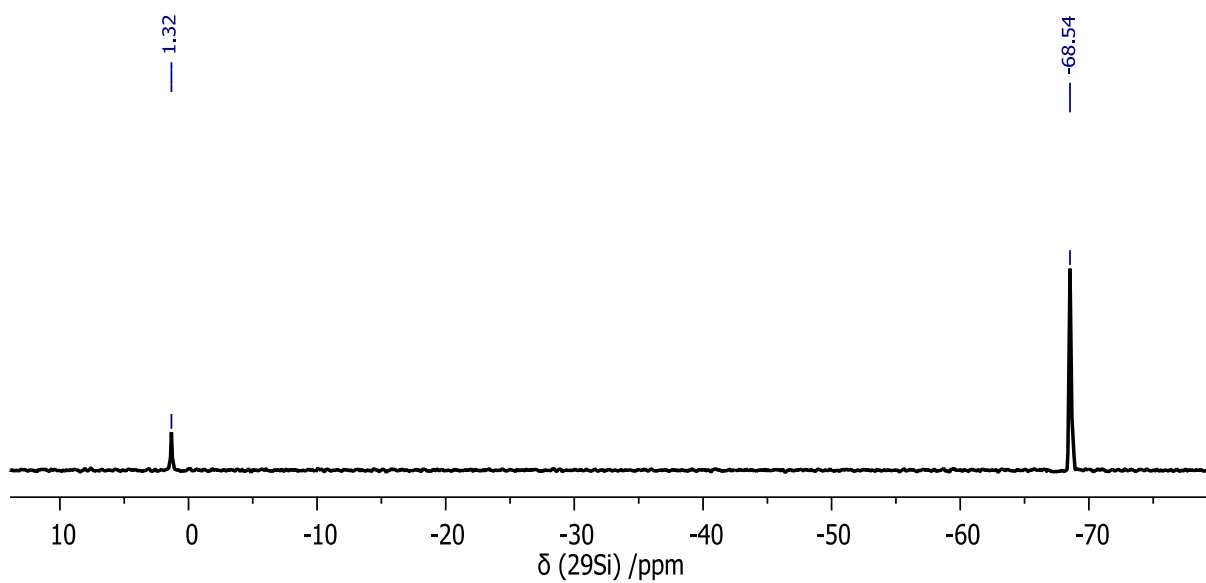


Figure S43. ^{29}Si NMR (59.6 MHz, DMSO-d_6 , 300 K) spectrum of **5**. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) (δ 1.316).

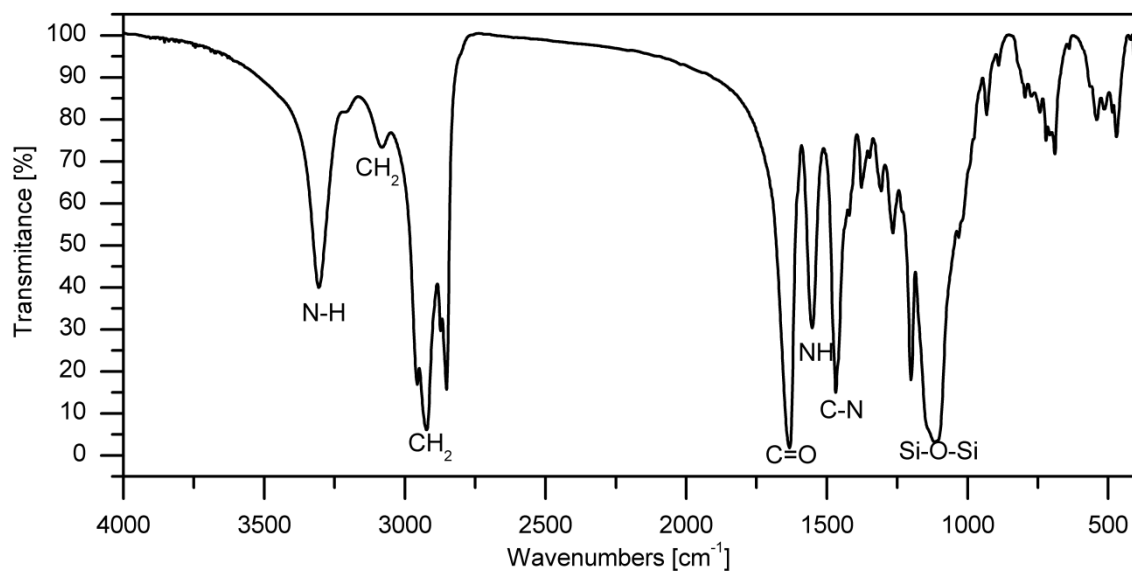


Figure S44. FT-IR (KBr pellets) spectrum of **5**.

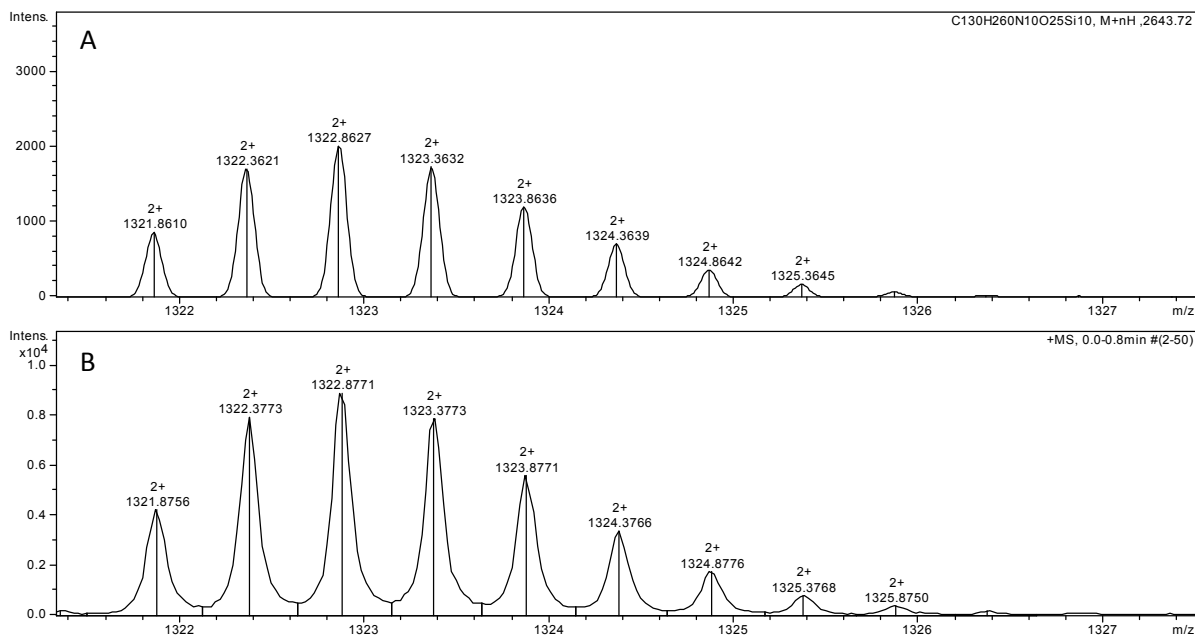
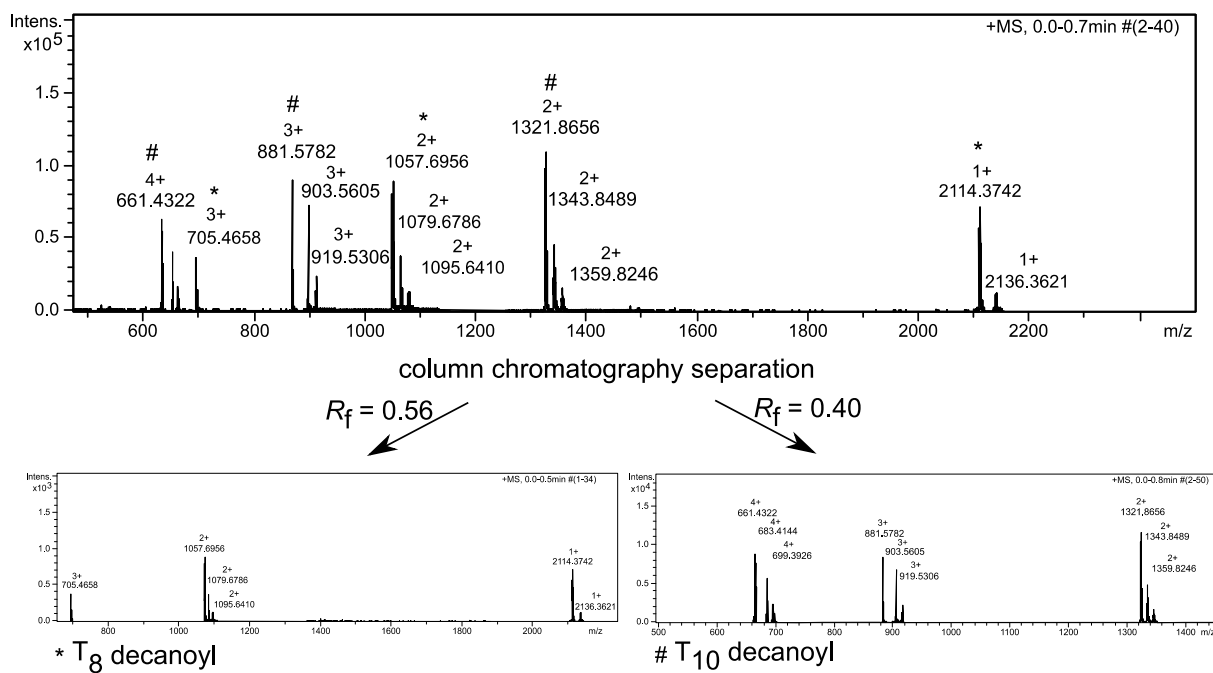


Figure S45. Simulated (A) calcd for $C_{130}H_{262}N_{10}O_{25}Si_{10}$, $[M + 2H]^{2+}$ and measured (B) HR-MS (ESI+, TOF, $CHCl_3$) spectra of **5** (method A).



T_8			
ion assignment	calcd $[m/z]$	observed $[m/z]$	error [ppm]
$[M+H]^+$	2114.3732	2114.3742	-0.5
$[M+2H]^{2+}$	1057.6902	1057.6956	5
$[M+3H]^{3+}$	705.4626	705.4658	5
$[M+Na]^+$	2136.3551	2136.3621	3
$[M+2Na]^{2+}$	1079.6721	1079.6786	6
$[M+2K]^{2+}$	1095.6461	1095.6410	-5

T_{10}			
ion assignment	calcd $[m/z]$	observed $[m/z]$	error [ppm]
$[M+2H]^{2+}$	1321.8610	1321.8656	3
$[M+3H]^{3+}$	881.5764	881.5782	2
$[M+4H]^{4+}$	661.4341	661.4322	-3
$[M+2Na]^{2+}$	1343.8429	1343.8489	4
$[M+3Na]^{3+}$	903.5583	903.5605	2
$[M+4Na]^{4+}$	683.4161	683.4144	-2
$[M+2K]^{2+}$	1359.8168	1359.8246	6
$[M+3K]^{3+}$	919.5323	919.5306	-2
$[M+4K]^{4+}$	699.3900	699.3926	4

Figure S46. HR-MS (ESI+, TOF, $CHCl_3$) spectra of **4** and **5**.

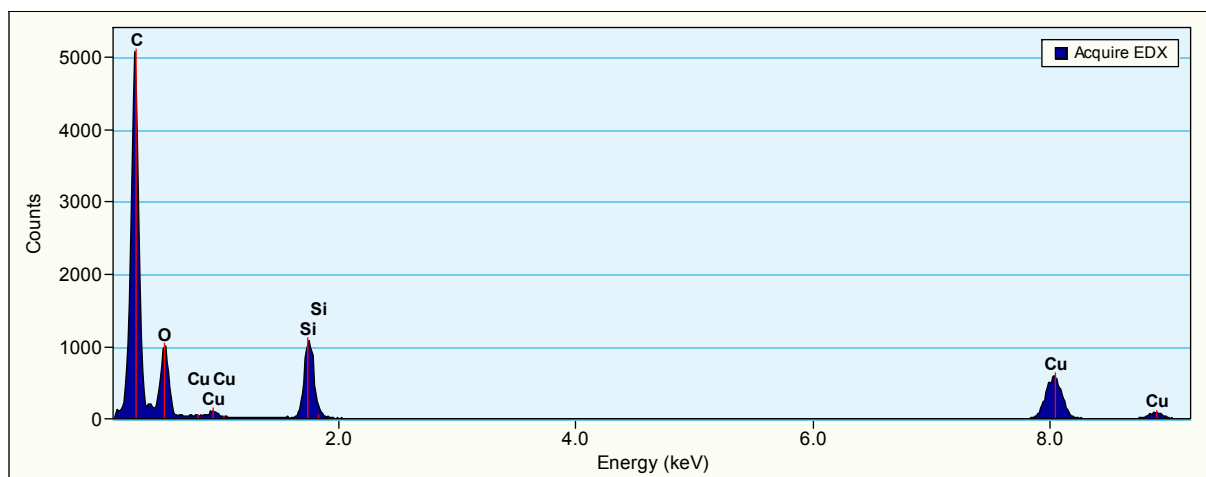


Figure S47. EDS spectrum of **5** (copper content is derived from the high-purity conducting Cu grid).

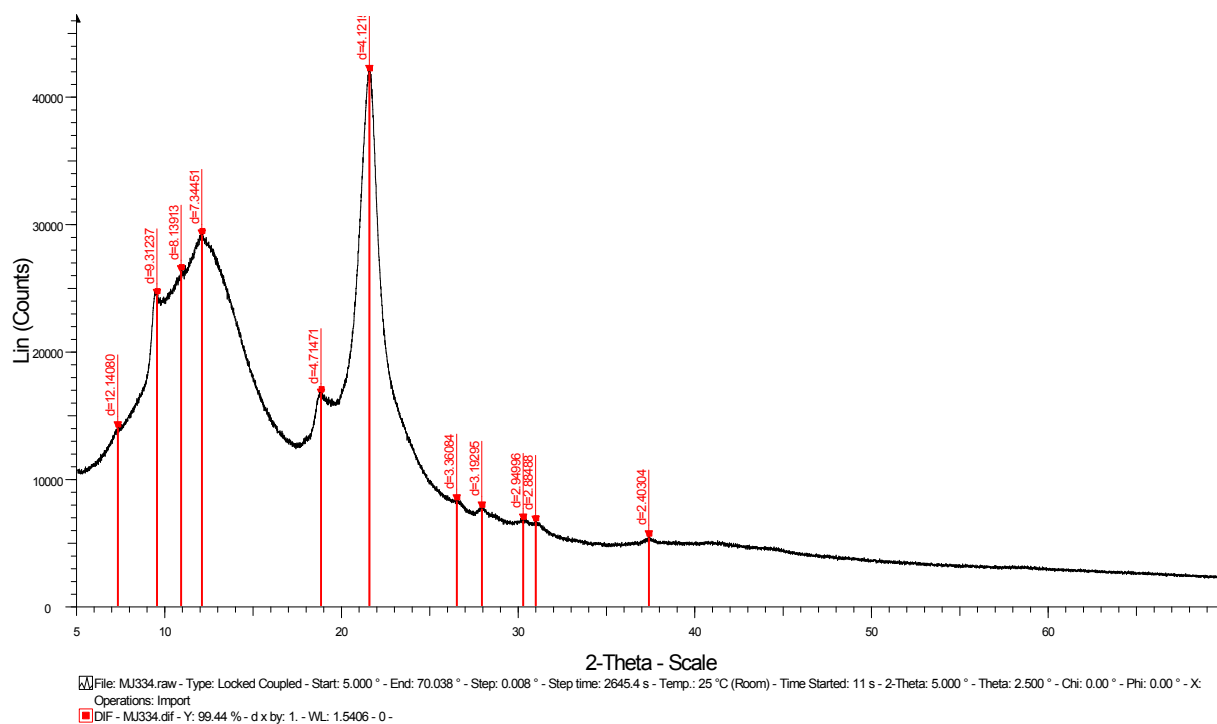


Figure S48. Powder XRD pattern of **5**.

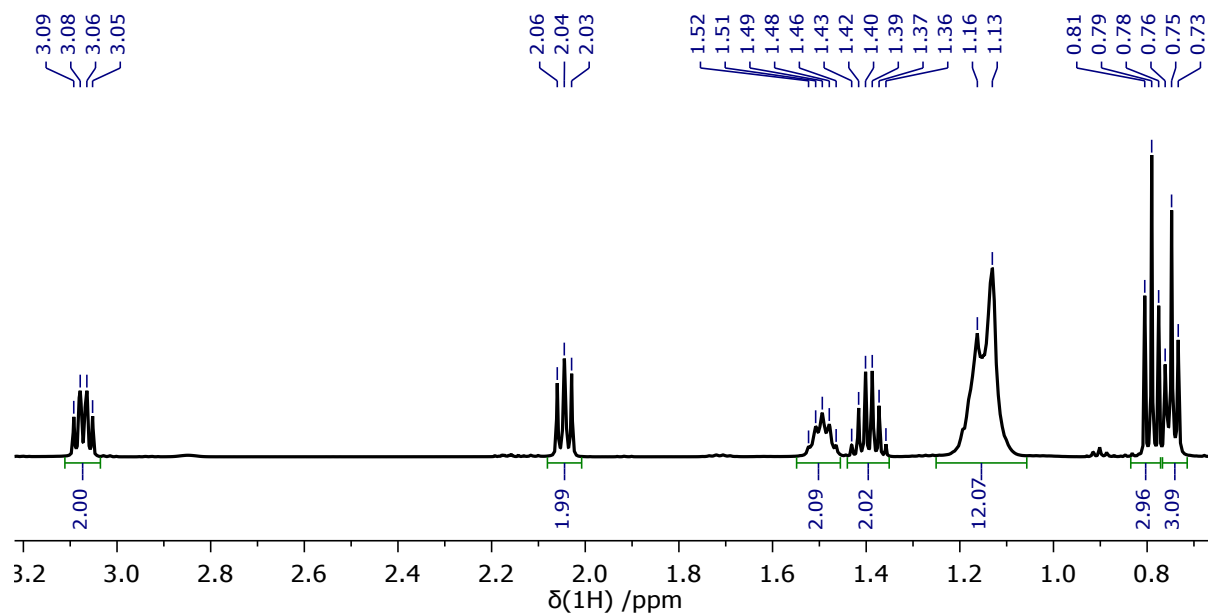


Figure S49. ^1H NMR (500 MHz, CDCl_3 , 300 K) spectrum of **6**.

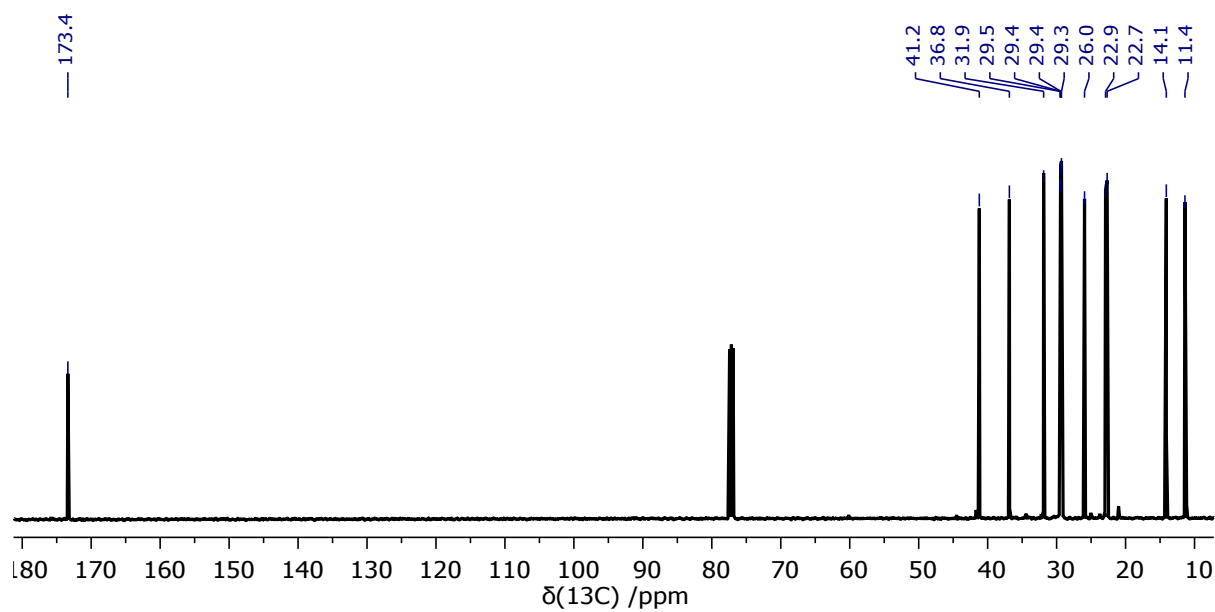


Figure S50. ^{13}C NMR (126 MHz, CDCl_3 , 300 K) spectrum of **6**.

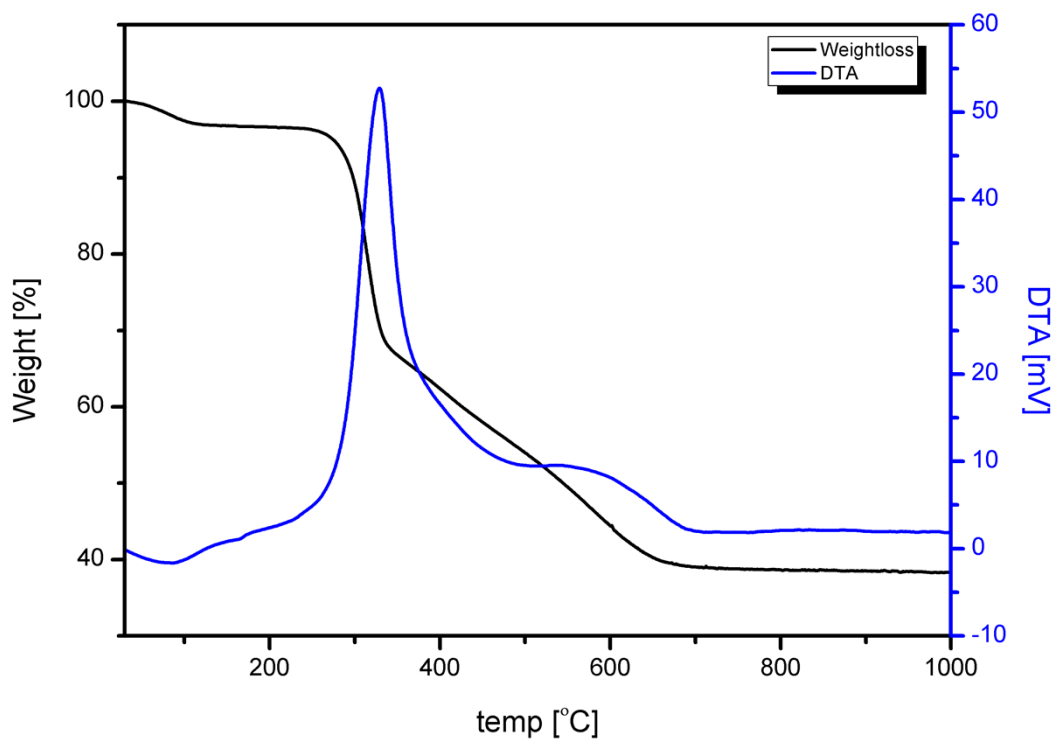


Figure S51. TG (black line), and DTA (blue line) thermogram of **1** 10 °C/min (in the air atmosphere: 60% N₂, 40% O₂).

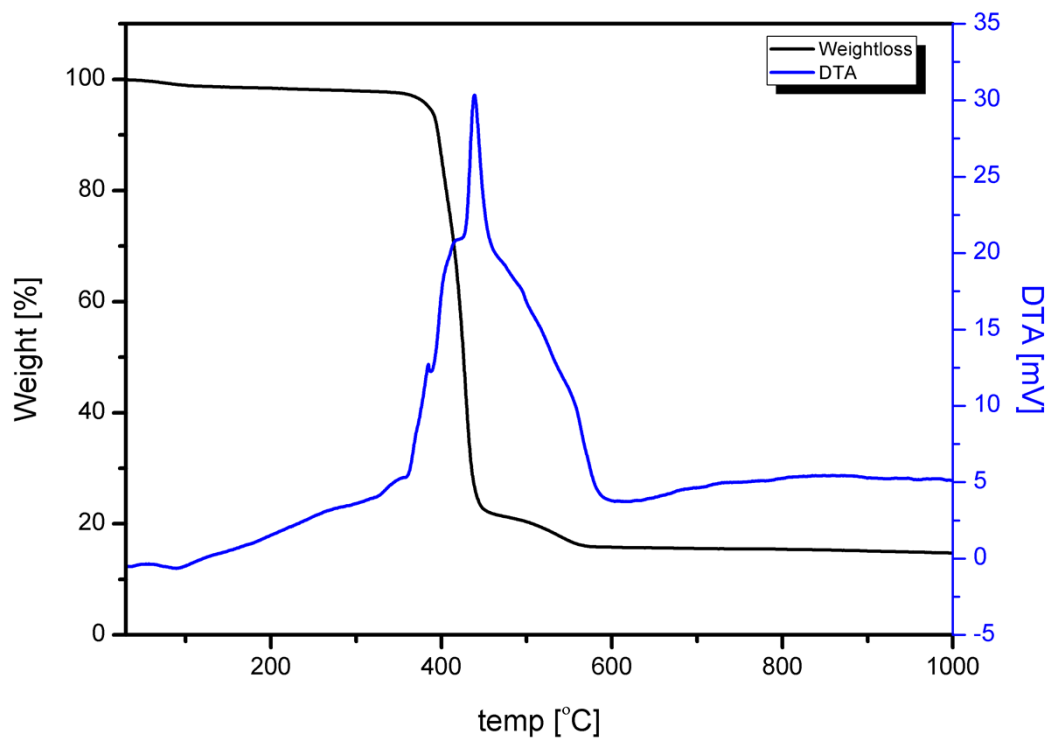


Figure S52. TG (black line), and DTA (blue line) thermogram of **2** 10 °C/min (in the air atmosphere: 60% N₂, 40% O₂).

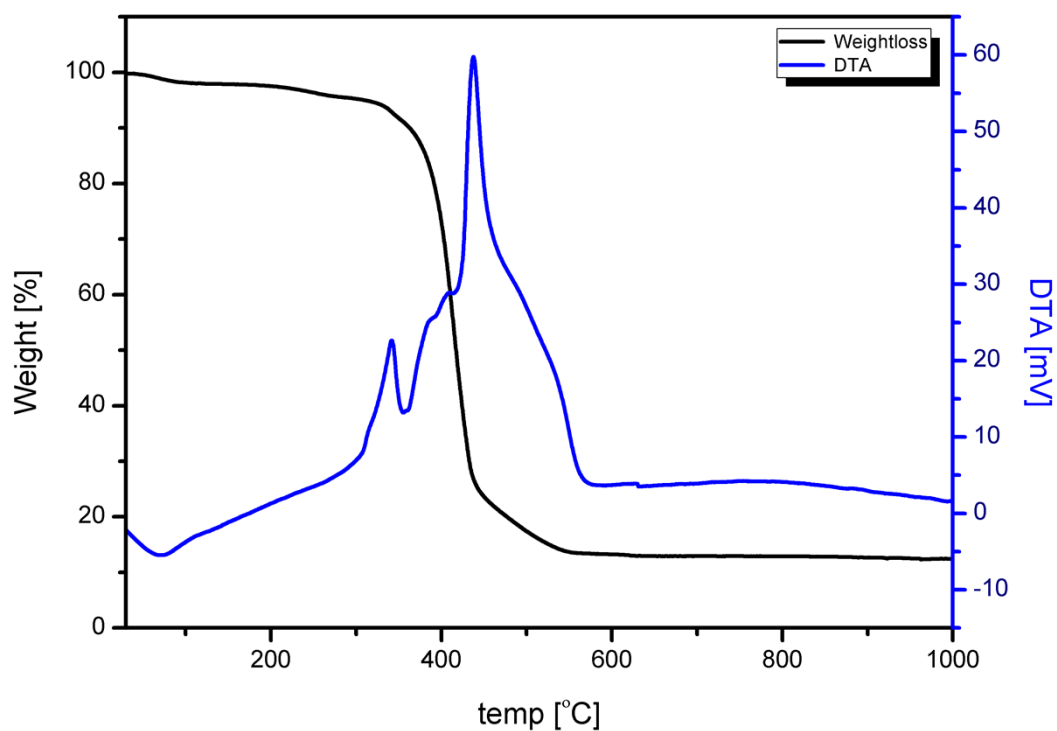


Figure S53. TG (black line), and DTA (blue line) thermogram of **3** 10 °C/min (in the air atmosphere: 60% N₂, 40% O₂).

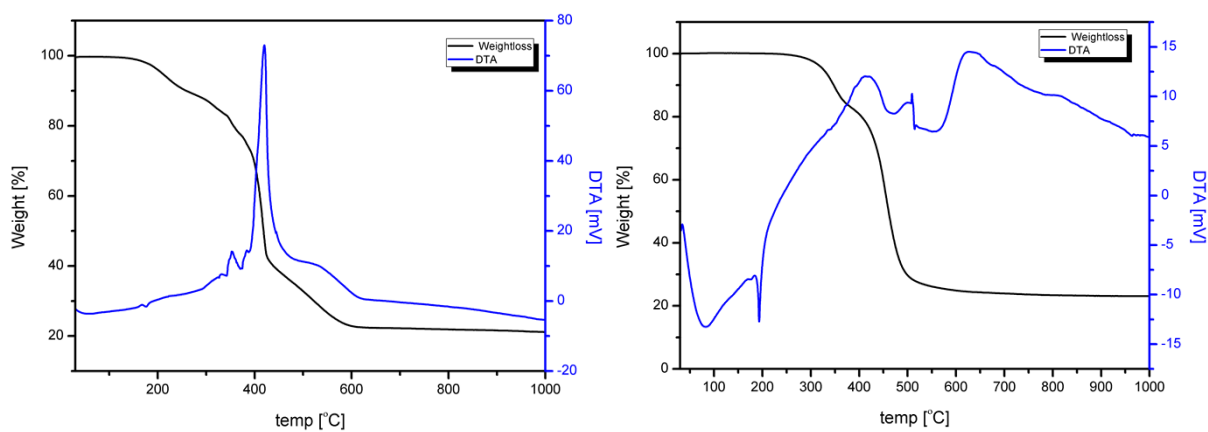


Figure S54. TG (black line), and DTA (blue line) thermogram of **4** 10 °C/min. Left graph in the air atmosphere (60% N₂, 40% O₂), right in nitrogen.

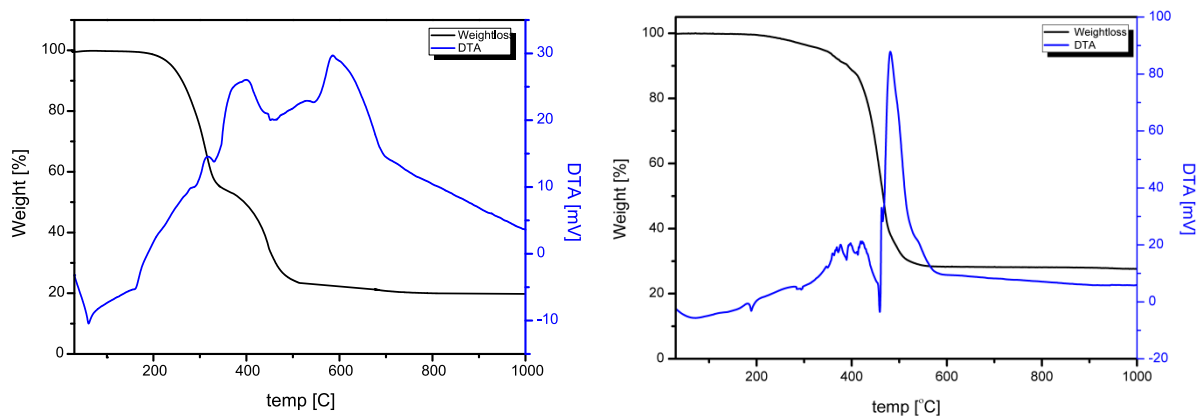


Figure S55. TG (black line), and DTA (blue line) thermogram of **5** 10 °C/min. Left graph in the air atmosphere (60% N₂, 40% O₂), right in nitrogen.

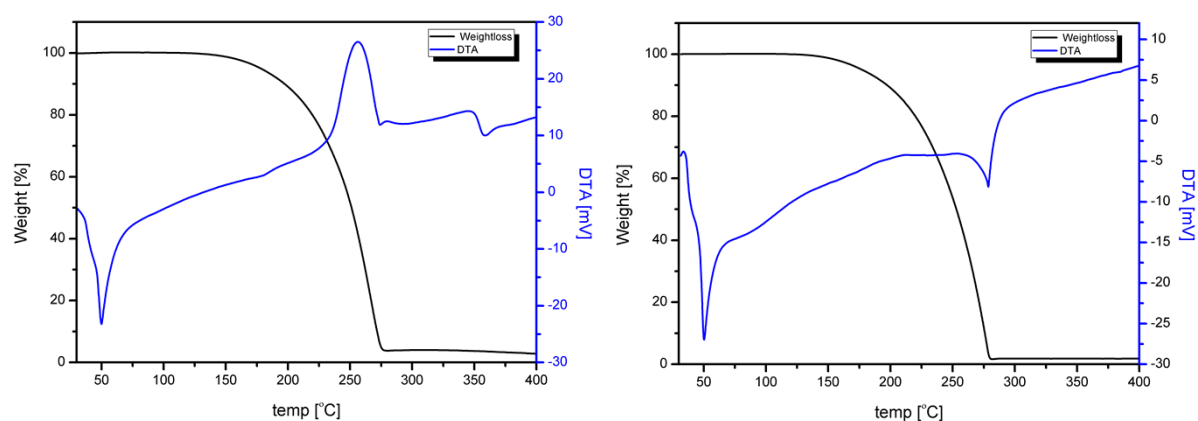


Figure S56. TG (black line), and DTA (blue line) thermogram of **6** 10 °C/min. Left graph in the air atmosphere (60% N₂, 40% O₂), right in nitrogen.

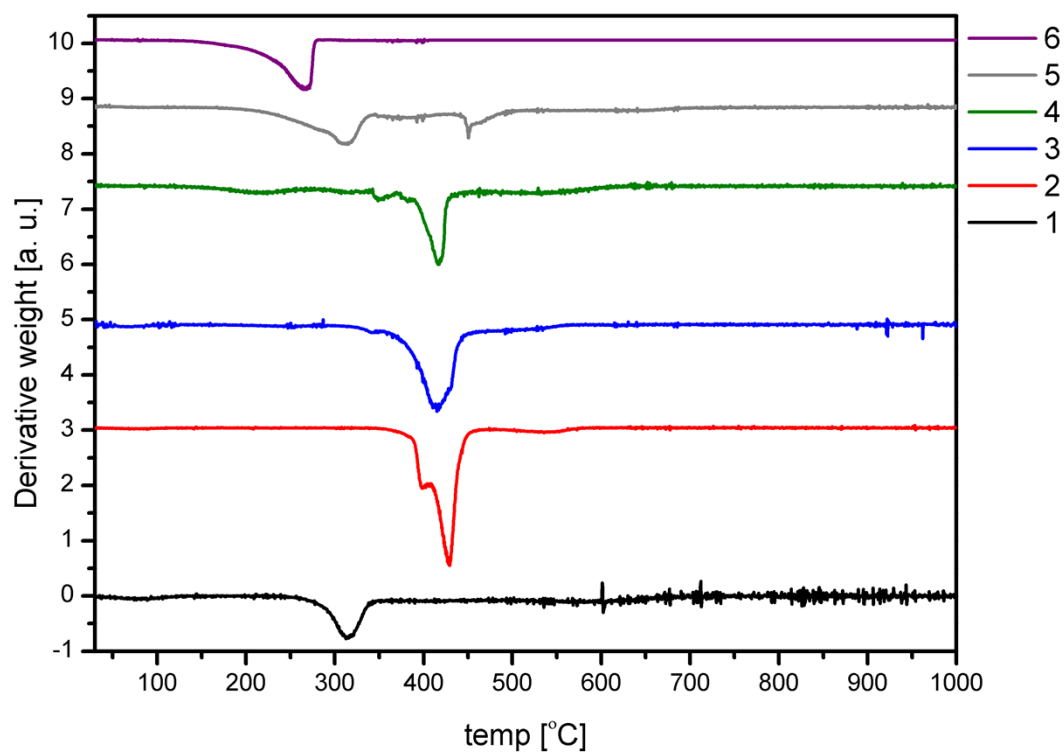


Figure S57. First derivative of TG (DTG) thermograms of **1–6** 10 °C/min (in the air atmosphere: 60% N₂, 40% O₂).

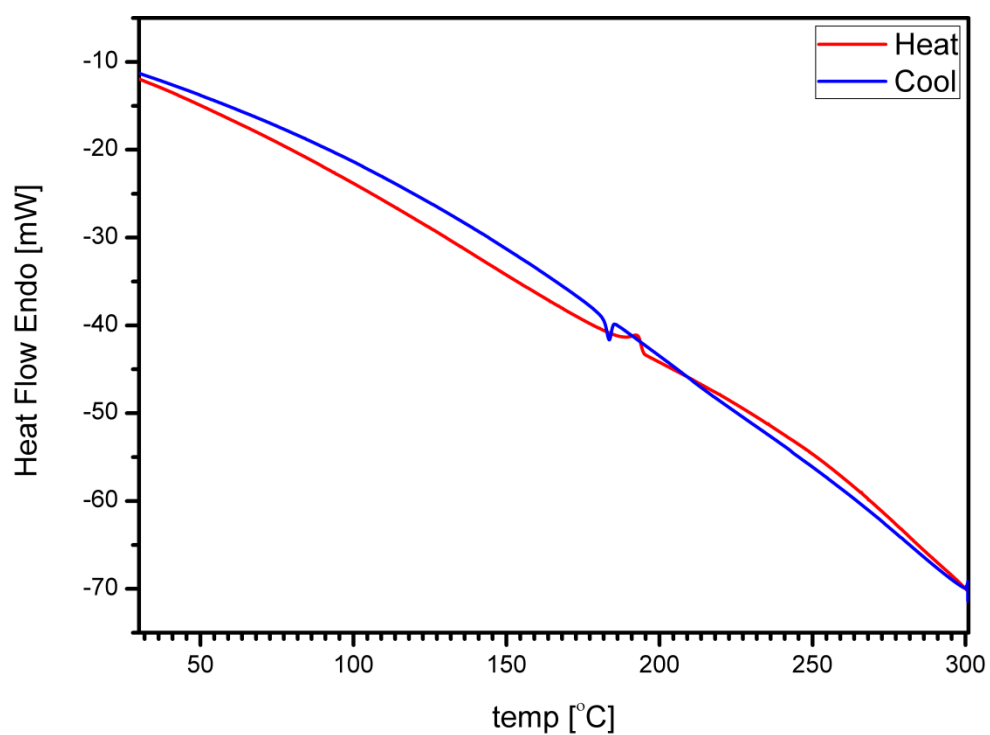


Figure S58. DSC of **5**, 2nd heat & cooling cycle (5 °C/min in the nitrogen atmosphere).

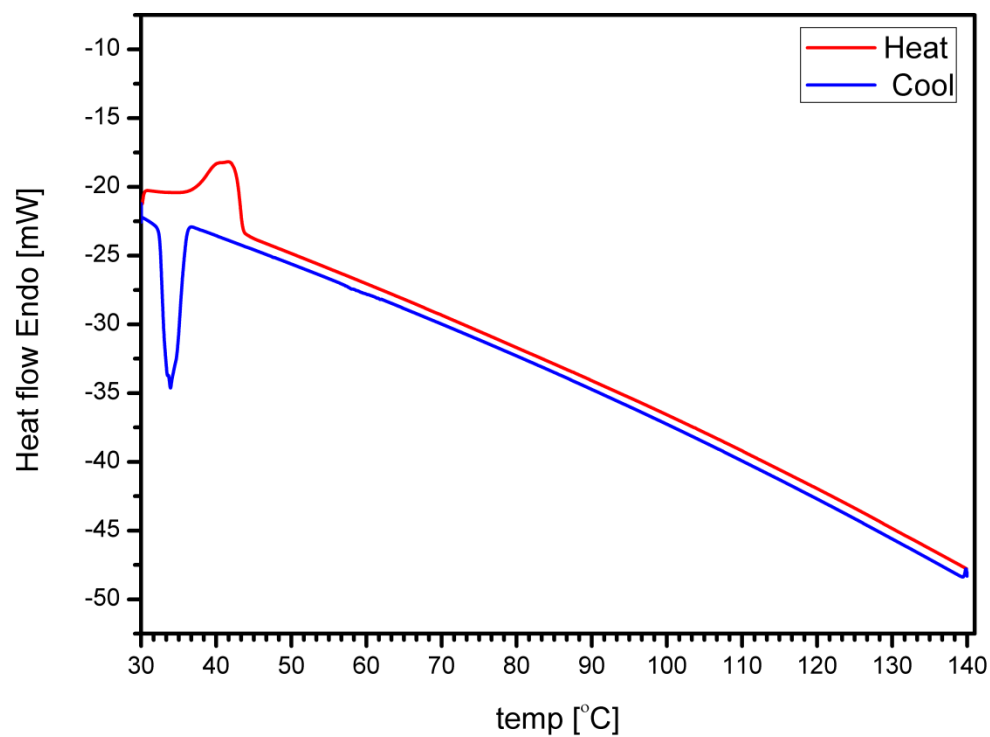


Figure S59. DSC of 6, 2nd heat & cooling cycle (5 °C/min in the nitrogen atmosphere).

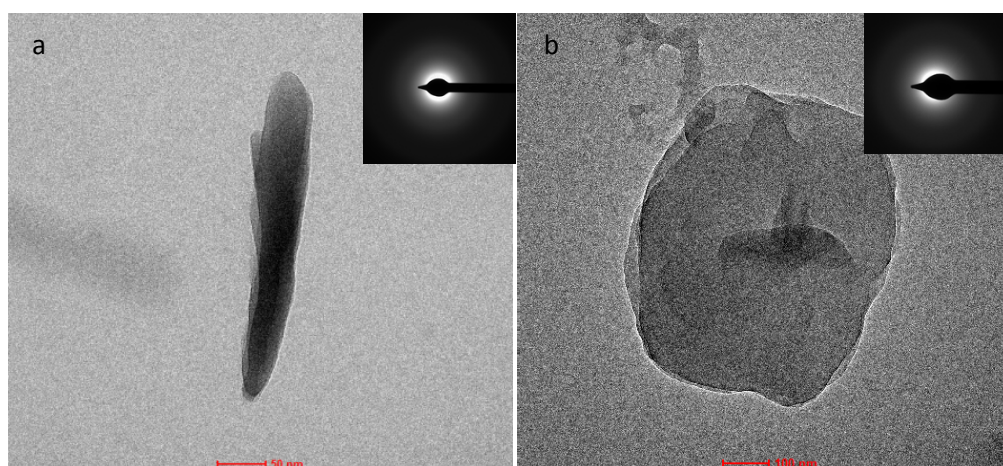


Figure S60. Selected HR-TEM images of 4 (a) and 5 (b).

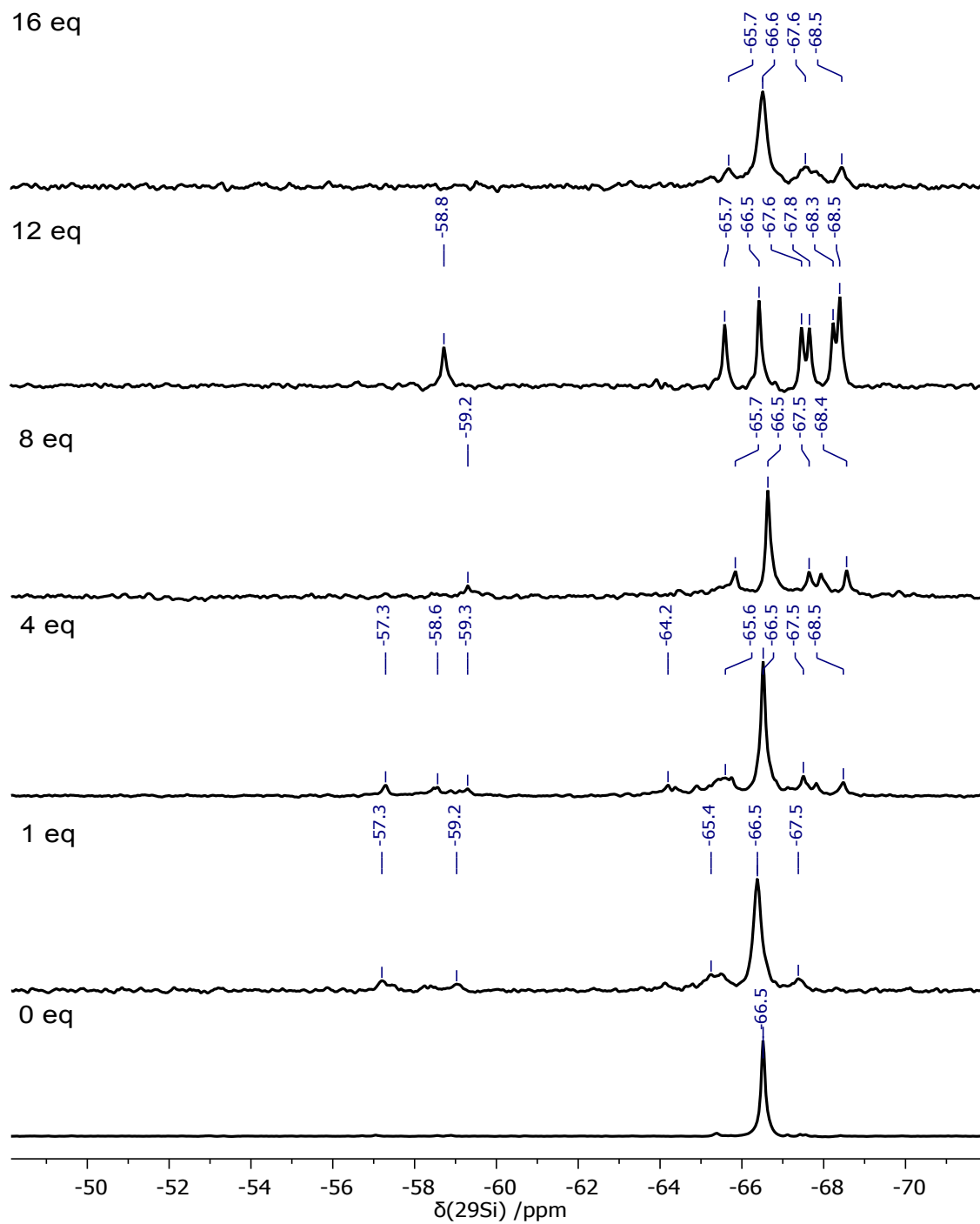


Figure S61. ^{29}Si NMR (59.6 MHz, DMSO-d_6 , 300 K) spectrum of **1** after reaction with 0, 1, 4, 8, 12 and 16 equivalents of $\text{CH}_3\text{SO}_3\text{H}$. Chemical shifts were referenced to tetramethylsilane (TMS).

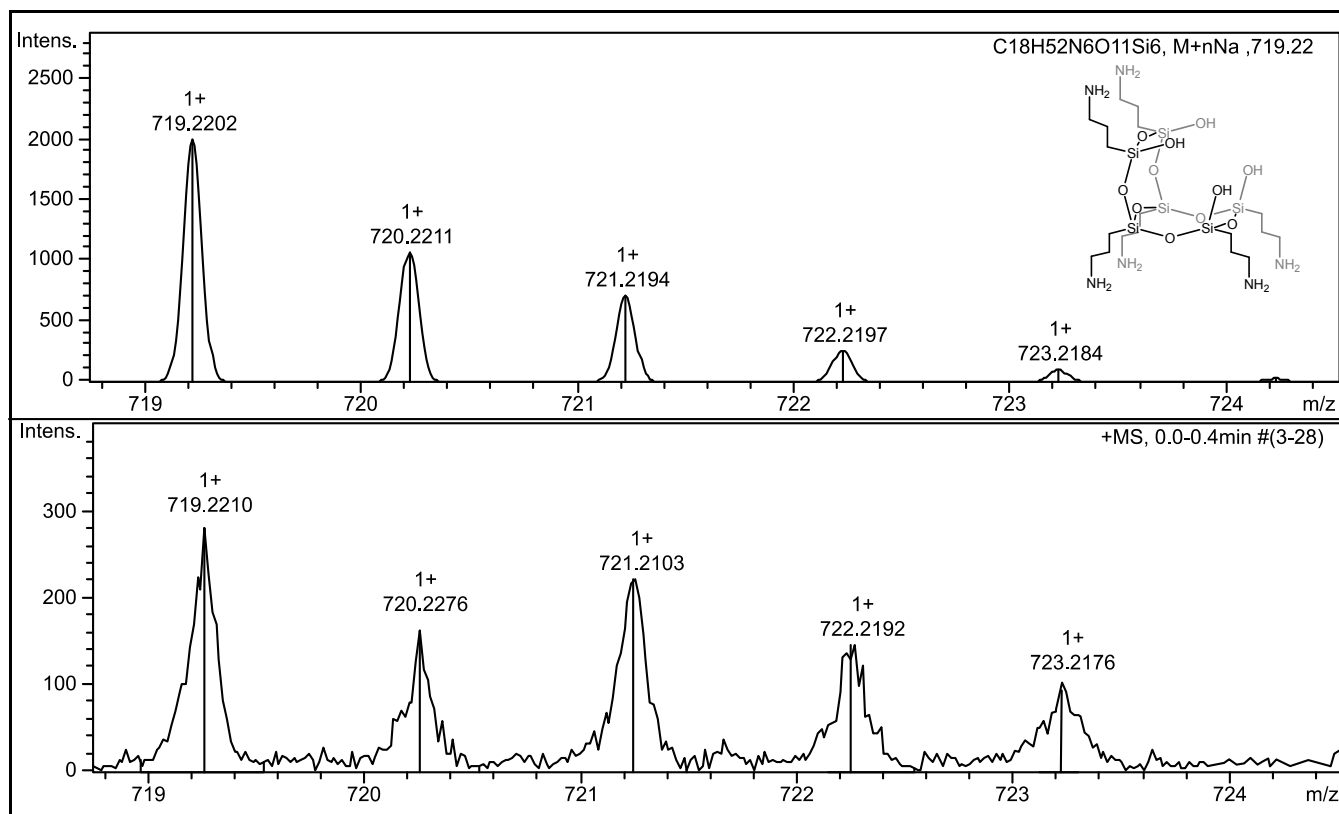


Figure S62. Simulated (up) calcd for $C_{18}H_{52}N_6O_{11}Si_6Na$, $[M + Na]^+$ and measured (down) HR-MS (ESI⁺, TOF, MeOH) spectra of C.

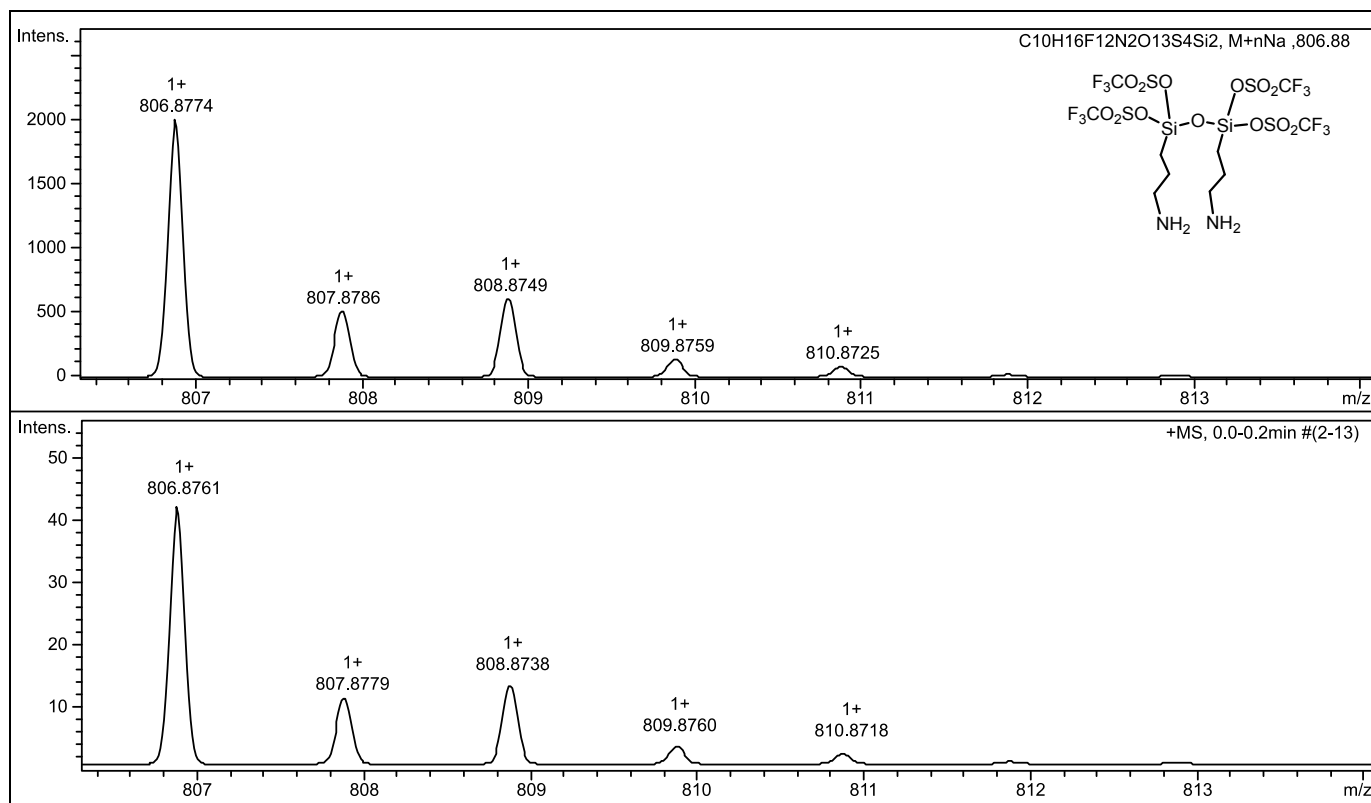


Figure S63. Simulated (up) calcd for $C_{10}H_{16}F_{12}N_2O_{13}S_4Si_2Na$, $[M + Na]^+$ and measured (down) HR-MS (ESI⁺, TOF, MeOH) spectra of D.

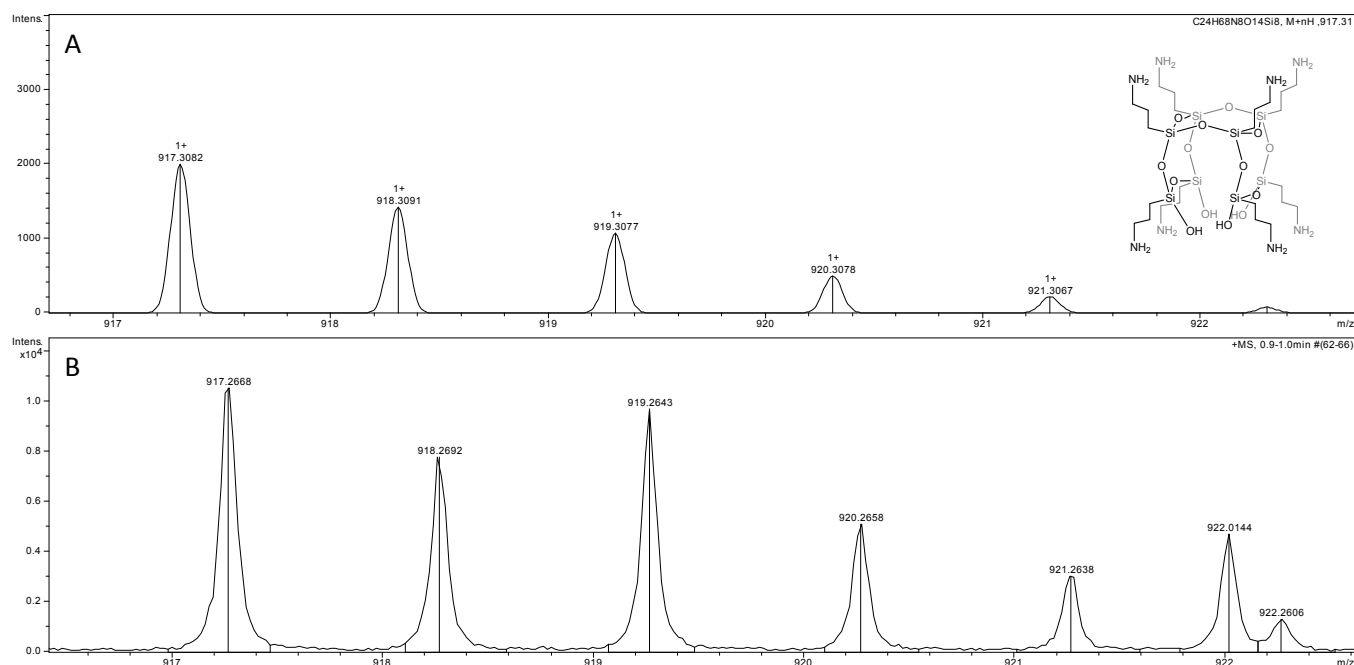


Figure S64. Simulated (up) calcd for $C_{24}H_{68}N_8O_{14}Si_8$, $[M + H]^+$ and measured (down) HR-MS (ESI+, TOF, MeOH) spectra of **E**.

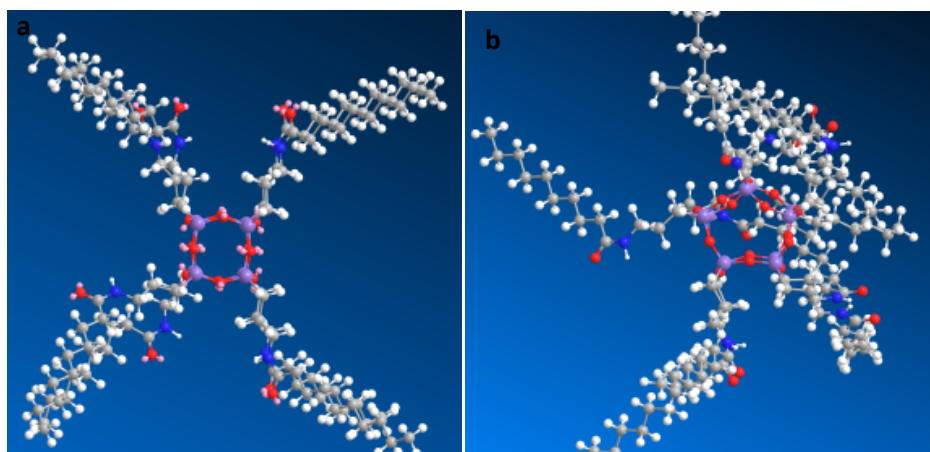


Figure S65. Molecular models of compound **4** (a), compound **5** (b).

Table S1. MM2 calculations of the minimization energies of Compound **2**, **3**, **4**, **5**.

Energy parameters*	Amine		Amide	
	Compound 2	Compound 3	Compound 4	Compound 5
Stretch:	1.7969	7.6789	7.0276	11.1709
Bend:	7.0679	58.1066	27.8027	155.4612
Stretch-Bend:	-0.6755	-4.5902	0.9053	0.4549
Torsion:	0.9477	3.1937	29.6476	39.5012
Non-1,4 VDW:	-35.4194	-53.9810	-52.8458	-123.3177
1,4 VDW:	2.4715	15.4807	44.0530	66.8356
Dipole/Dipole:	35.5346	35.0298	-25.4860	-47.7560
Total Energy:	11.7237	60.9185	31.1044	102.3501

*units of energy are kcal/mol

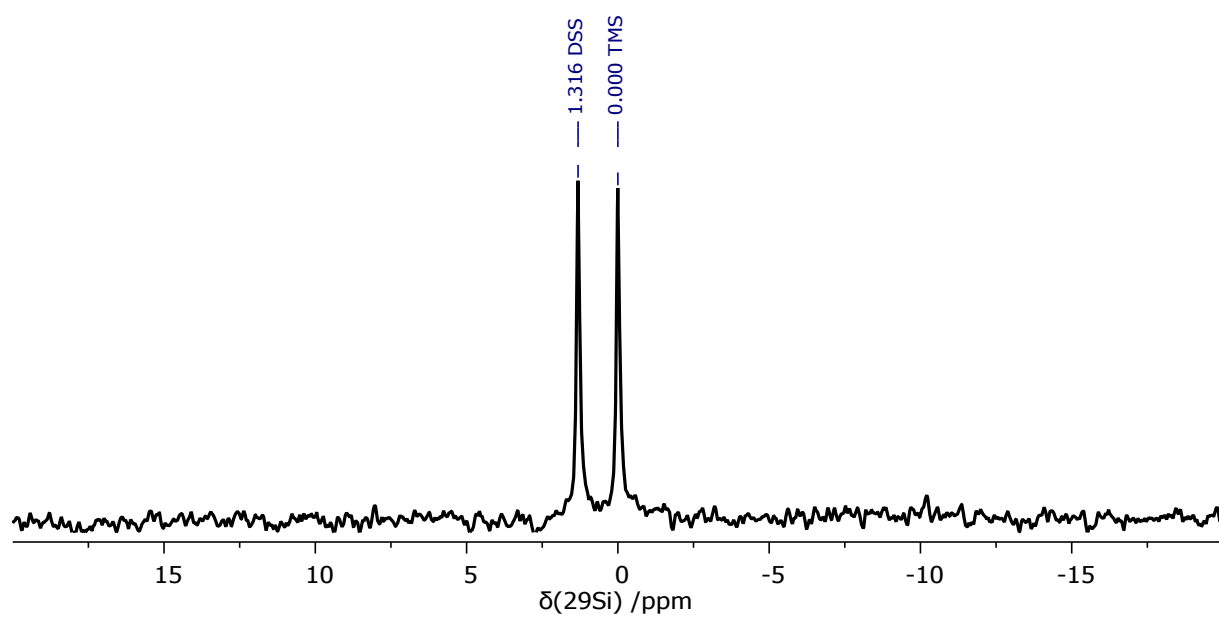


Figure S66. ^{29}Si NMR (59.63 MHz, DMSO-d_6 , 300 K) spectrum of DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid). Chemical shifts were referenced to TMS (Tetramethylsilane) (δ 0.000).