

Supporting Information

Optimized synthesis of functional organosilicon monomers and polymers exploiting new type of CuAAC recoverable heterogeneous catalyst

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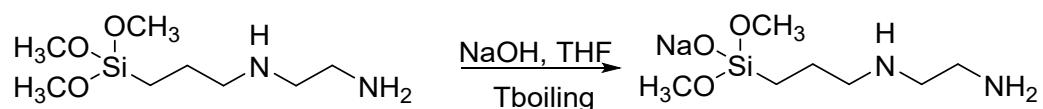
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1. Synthesis of hyperbranched poly[3-(2-Aminoethylamino)propyl]methoxysiloxane poly(en-propyl-methoxysiloxane)

Hyperbranched poly[3-(2-Aminoethylamino)propyl]methoxysiloxane was synthesized in the process of heterofunctional polycondensation of the corresponding AB₂-type Sodiumoxy-[3-(2-Aminoethylamino)propyl]dimethoxysilane monomer according to the procedure previously described in ¹

2. Synthesis of Sodiumoxy-[3-(2-Aminoethylamino)propyl]dimethoxysilane



¹H NMR (300 MHz, THF) δ : 2,81-2,73 ppm (m, 2H, -CH₂-NH₂), 2,66-2,62 ppm (m, 2H, -NH-CH₂-), 2,66-2,62 ppm (m, 2H, -CH₂-NH-), 1,73-1,63 ppm (q, 2H, -CH₂-CH₂-NH-, J= 7 Hz), 0,52 ppm (t, 2H, -Si-CH₂-, J= 7,6 Hz), 3,45 ppm (s, 6H, CH₃O-), 1,38 ppm (t, 2H, -NH₂, J= 6,5 Hz), 1,63-1,54 ppm (q, 1H, -NH-, J= 7 Hz); ¹³C NMR (THF) δ : 9,25 ppm (-Si-CH₂-CH₂-), 24,54 ppm (-Si-CH₂-CH₂-), 52,57 ppm or 52,54 ppm (-CH₂-CH₂-NH-), 52,57 ppm or 52,54 ppm (-NH-CH₂-CH₂-), 41,64 ppm (CH₂-CH₂-NH₂); ²⁹Si (THF), δ : -44,46 ppm; ¹⁵N (THF), δ : 34 ppm (-NH-), 16 ppm (-NH₂); ²³Na (THF) 13 ppm; HRMS calcd for C₇H₁₉N₂NaO₃Si: 231.1135; found: [M+nNa] = 231.1132.

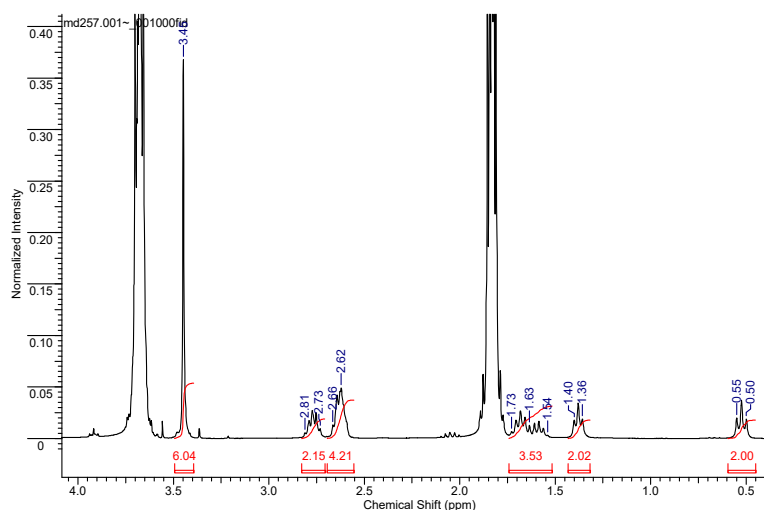


Figure S1. ¹H NMR Spectral data of Sodiumoxy-[3-(2-Aminoethylamino)propyl]dimethoxysilane

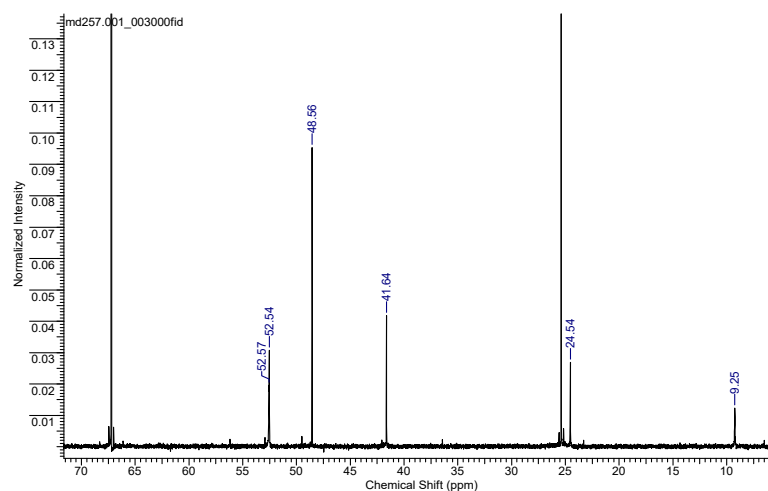


Figure S2. ^{13}C NMR Spectral data of Sodiumoxy-[3-(2-Aminoethylamino)propyl]dimethoxysilane

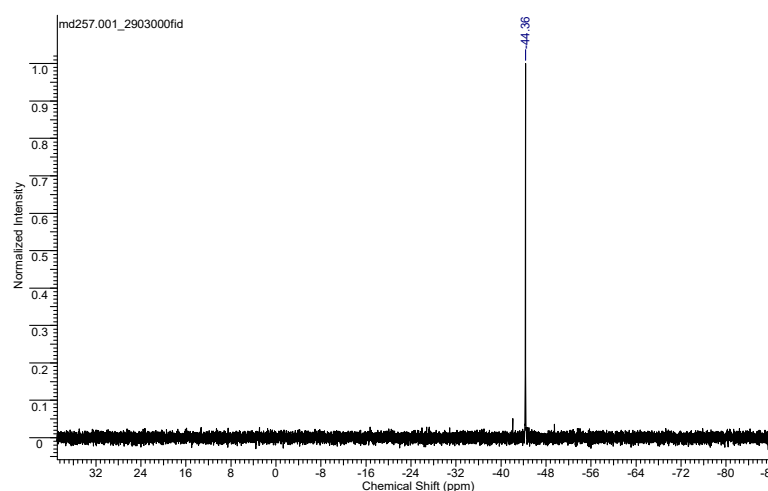


Figure S3. ^{29}Si NMR Spectral data of Sodiumoxy-[3-(2-Aminoethylamino)propyl]dimethoxysilane

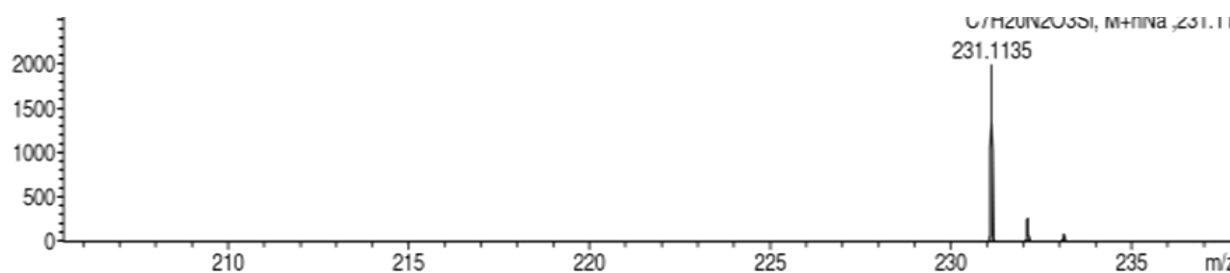
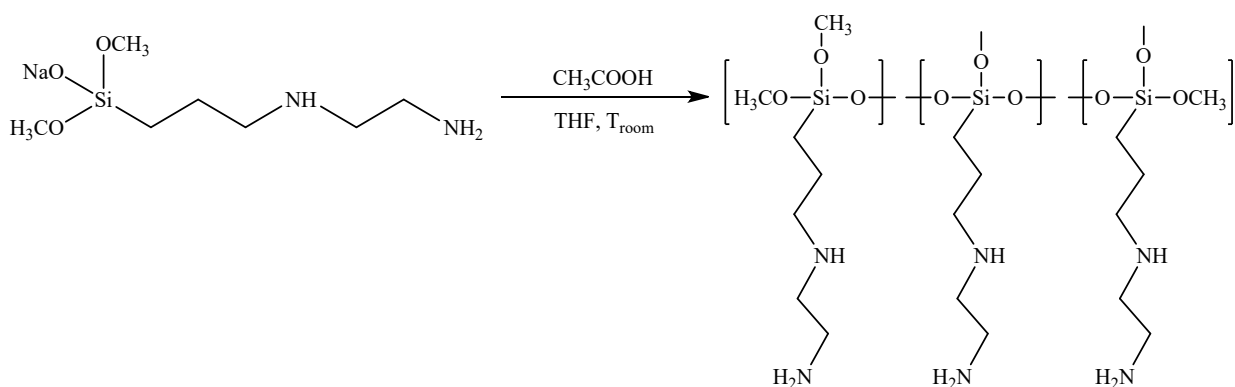


Figure S4. Mass spectra of Sodiumoxy-[3-(2-Aminoethylamino)propyl]dimethoxysilane

3. Synthesis of hyperbranched poly[3-(2-Aminoethylamino)propyl]methoxysiloxane poly(en-propyl-siloxane)



^1H NMR (300 MHz, THF) δ : 2,84-2,73 ppm (m, 2H, $-\text{CH}_2-\text{NH}_2$), 2,70-2,54 ppm (m, 2H, $-\text{NH}-\text{CH}_2-$), 2,70-2,54 ppm (m, 2H, $-\text{CH}_2-\text{NH}-$), 1,66-1,50 ppm (q, 2H, $-\text{CH}_2-\text{CH}_2-\text{NH}-$), 0,72-0,57 ppm (m, 2H, $-\text{Si}-\text{CH}_2-$), 3,58-3,48 ppm (m, 6H, $\text{CH}_3\text{O}-$), 1,20-1,06 ppm (m, 2H, $-\text{NH}_2$), 1,20-1,06 ppm (m, 1H, $-\text{NH}-$); ^{29}Si (THF), δ : 49,18-49,93 ppm (m, R-Si(OCH₃)₂O-), 56,45-59,16 (m, R-Si(OCH₃)(O-)₂), 63,75-68,62 (m, R-Si(O-)₃).

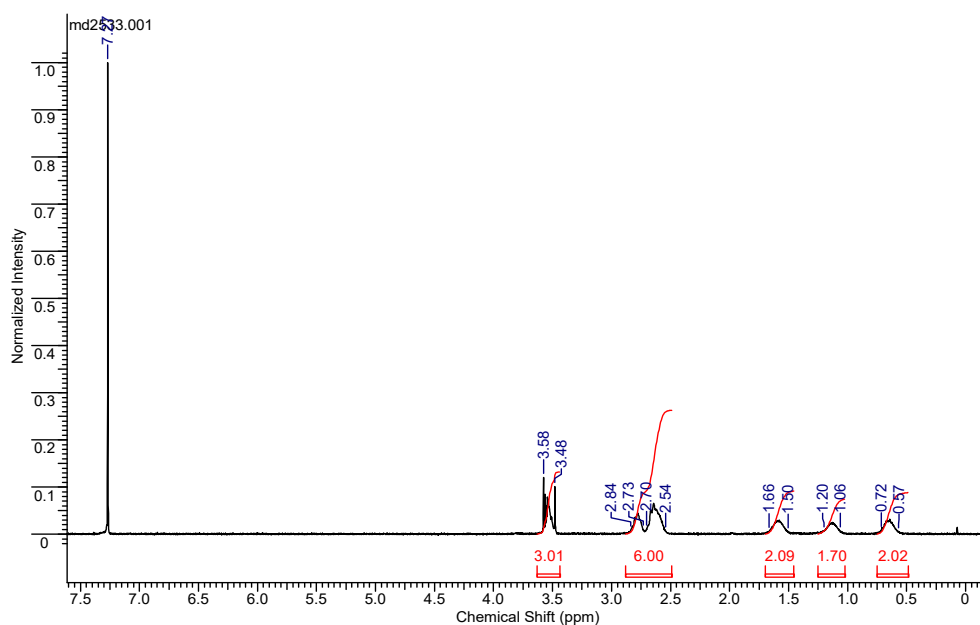


Figure S5. ^1H NMR Spectral data of poly(en-propyl-siloxane)

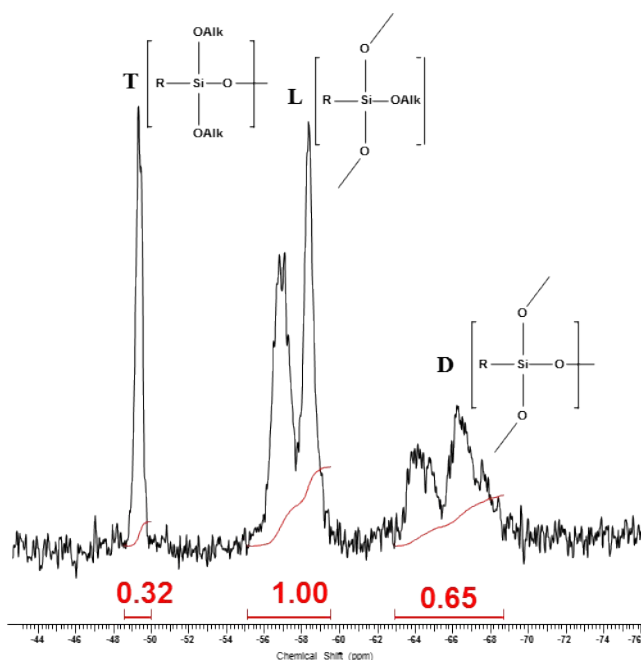


Figure S6. ^{29}Si NMR Spectral data of ^1H NMR Spectral data of poly(en-propyl-siloxane) with the addition of paramagnetic relaxation agent Chromium (III) Acetylacetonate

4. Synthesis of hyperbranched poly(3-(4-((dimethylamino)methyl)-1H-1,2,3-triazol-1-yl)propyl)ethoxysiloxane - poly(DMA-1,2,3-triazole-siloxane)

Hyperbranched DMA-1,2,3-triazole-siloxane was synthesized according to the procedure previously described in ².

^1H NMR (300 MHz, CDCl_3) δ 7.7-7.4 (m, 1H), 4.3-4.1 (m, 2H), 3.7- 3.5 (m, 1.5H), 3.6 -3.3 (m, 2H), 2.1 (br.s, 3H), 1.9 - 1.7 (m, 2H), 1.0-0.8 (m, 2H), 0.6-0.3 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 144.4, 122.5, 58.0, 53.9, 51.9, 44.8, 25.2, 23.8, 17.8, 9.9, 9.2, 8.7, 8.0; ^{29}Si NMR (60 MHz, CDCl_3) δ : (-53.6) - (-54.5) (R-Si(OCH₂CH₃)₂O_{0.5}), (-59.0) – (-62.6) (R-Si(OCH₂CH₃)O), (-64.0) –(-70.0) (R-SiO_{1.5}). MALDI: M_w =2348 g/mol, M_w/M_n =1.1.

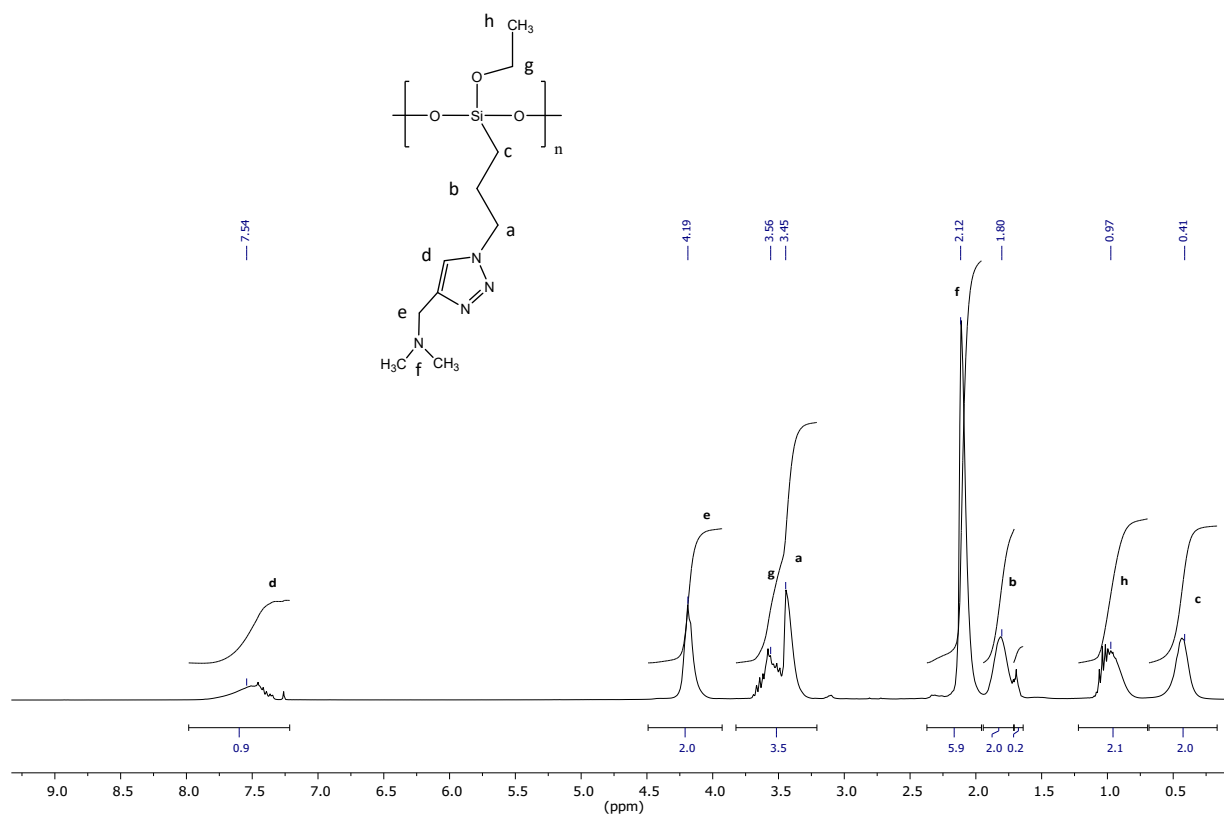


Figure S7. ^1H NMR Spectra of poly(DMA-1,2,3-triazole-siloxane)

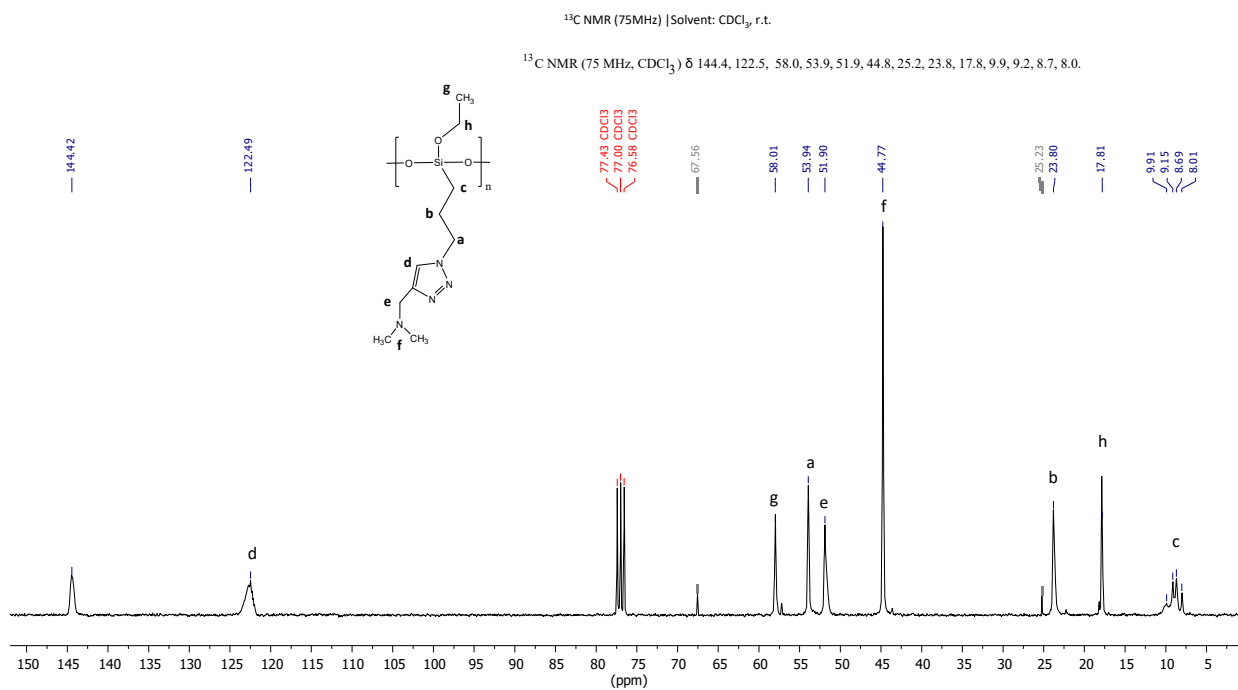


Figure S8. ^{13}C NMR Spectra of poly(DMA-1,2,3-triazole-siloxane)

^{13}C NMR (75MHz) APT | Solvent: CDCl_3 , r.t.

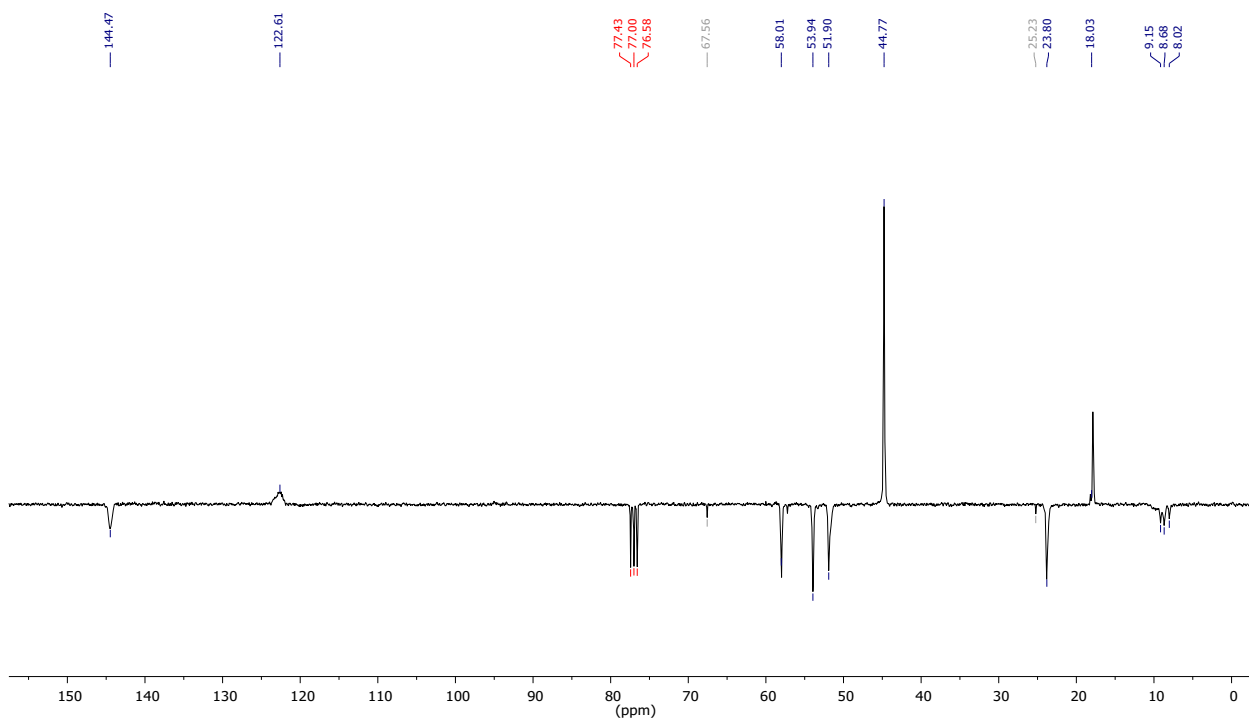


Figure S9. ^{13}C NMR APT Spectra of poly(DMA-1,2,3-triazole-siloxane)

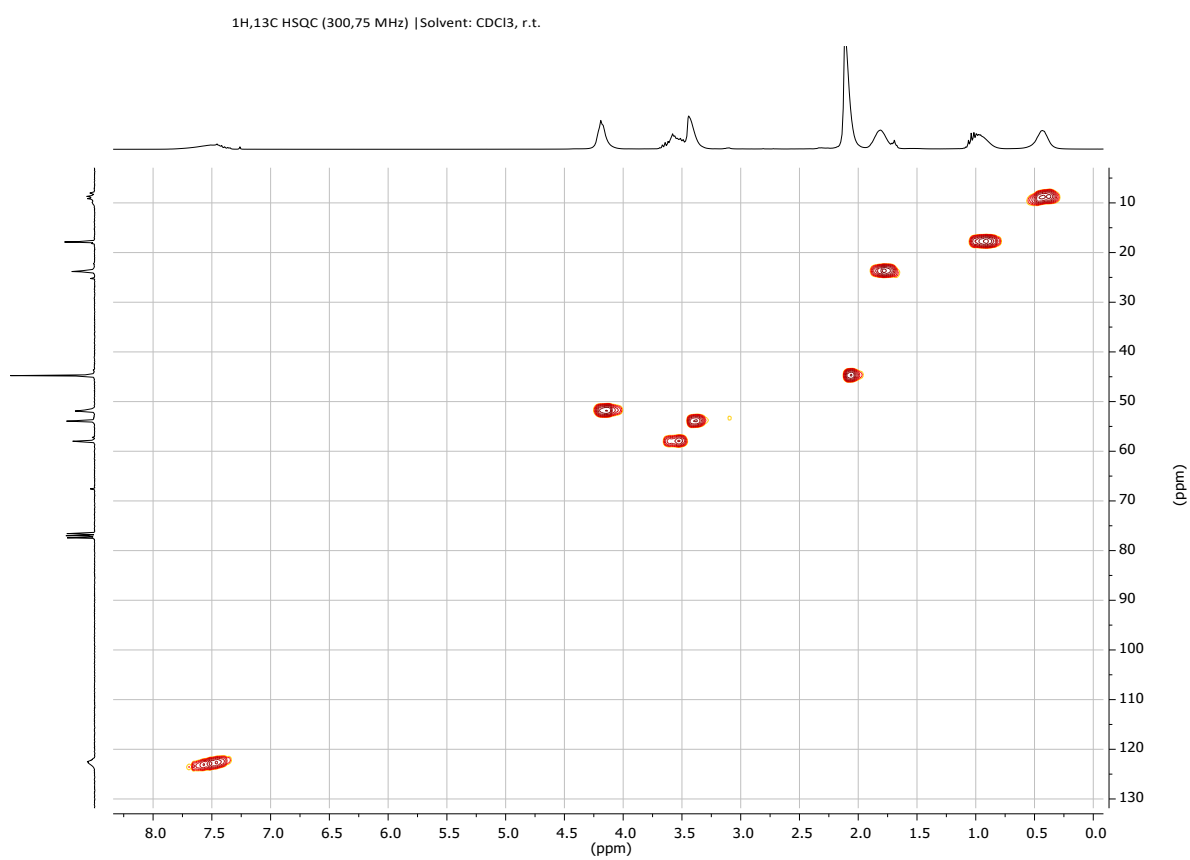


Figure S10. ^1H , ^{13}C NMR HSQC Spectra of poly(DMA-1,2,3-triazole-siloxane)

MHz) | Solvent: CDCl₃, r.t.

²⁹Si NMR (60 MHz, CDCl₃) δ: (-53.6) - (-54.5), (-59) - (-62.6), (-64) - (-70).

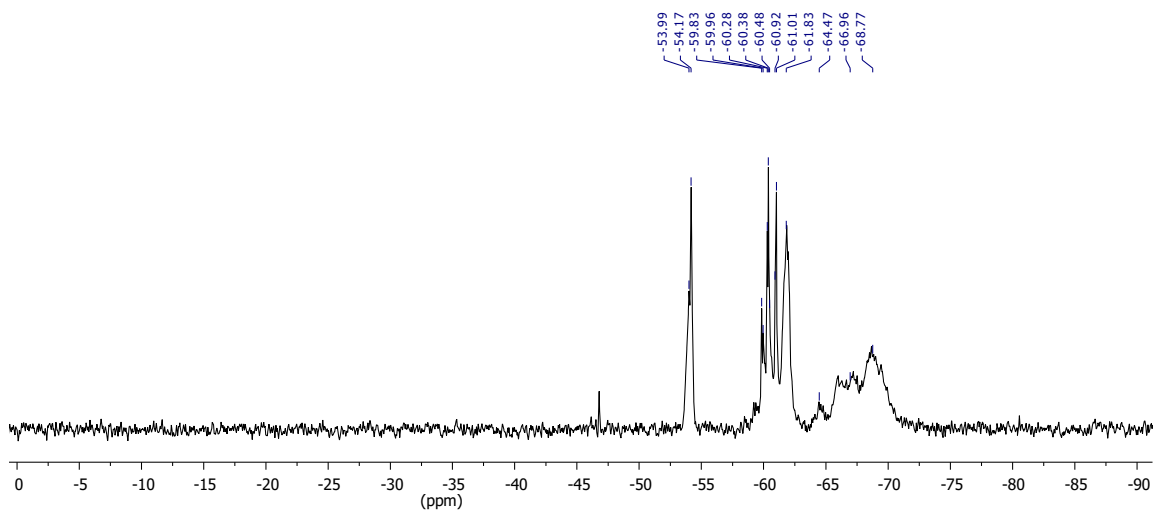


Figure S11. ²⁹Si NMR Spectra of DMA-1,2,3-triazole-siloxane

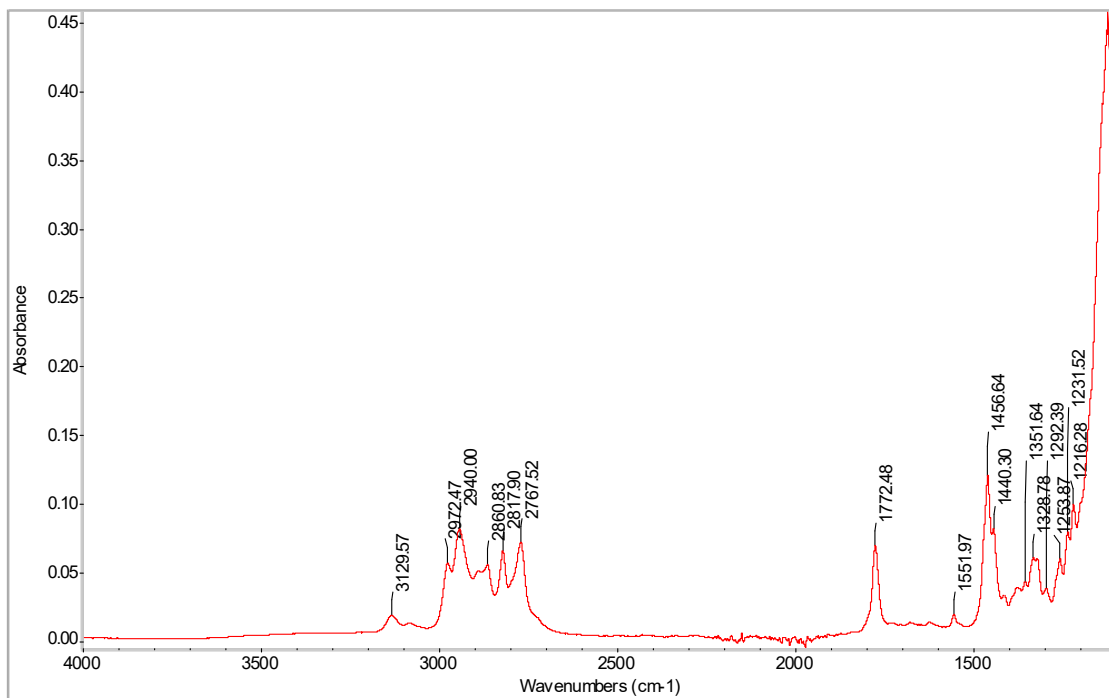


Figure S12. FTIR Spectra of poly(DMA-1,2,3-triazole-siloxane)

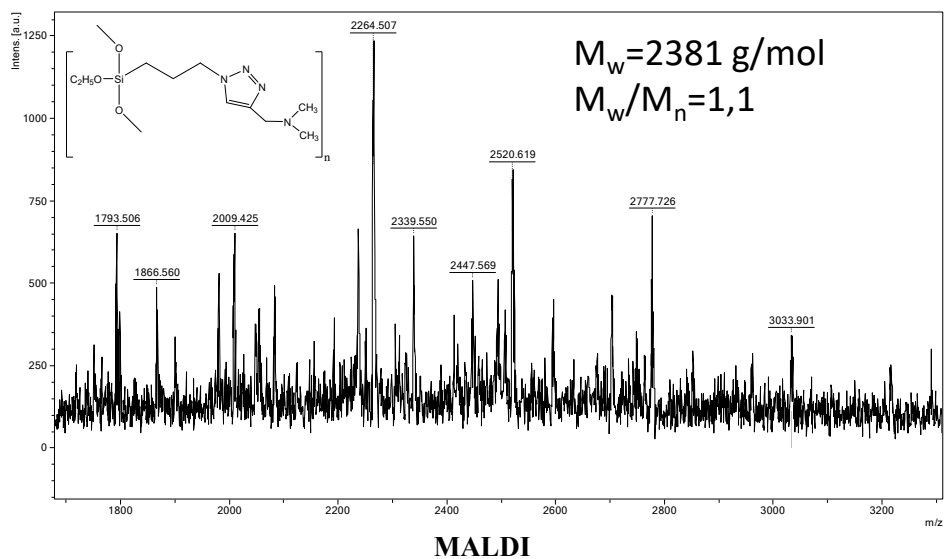


Figure S13. MALDI spectra of poly(DMA-1,2,3-triazole-siloxane)

5. NMR spectra and GPC curves of functional siloxanes

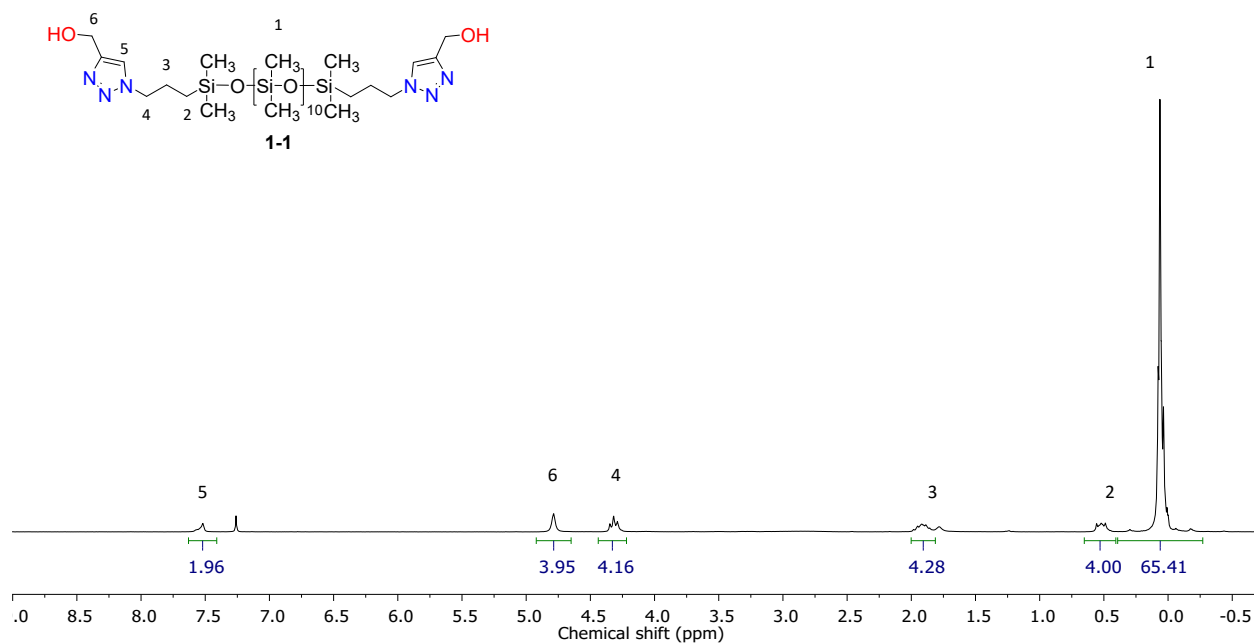


Figure S14. ^1H NMR spectrum of 1-1

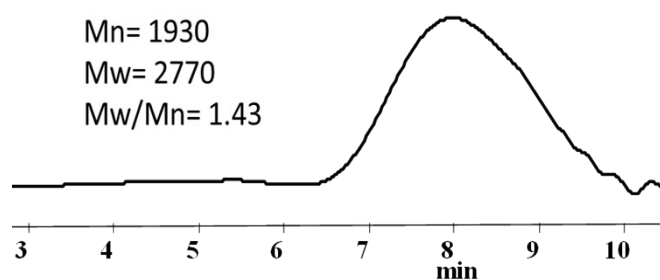


Figure S15. GPC curve of 1-1

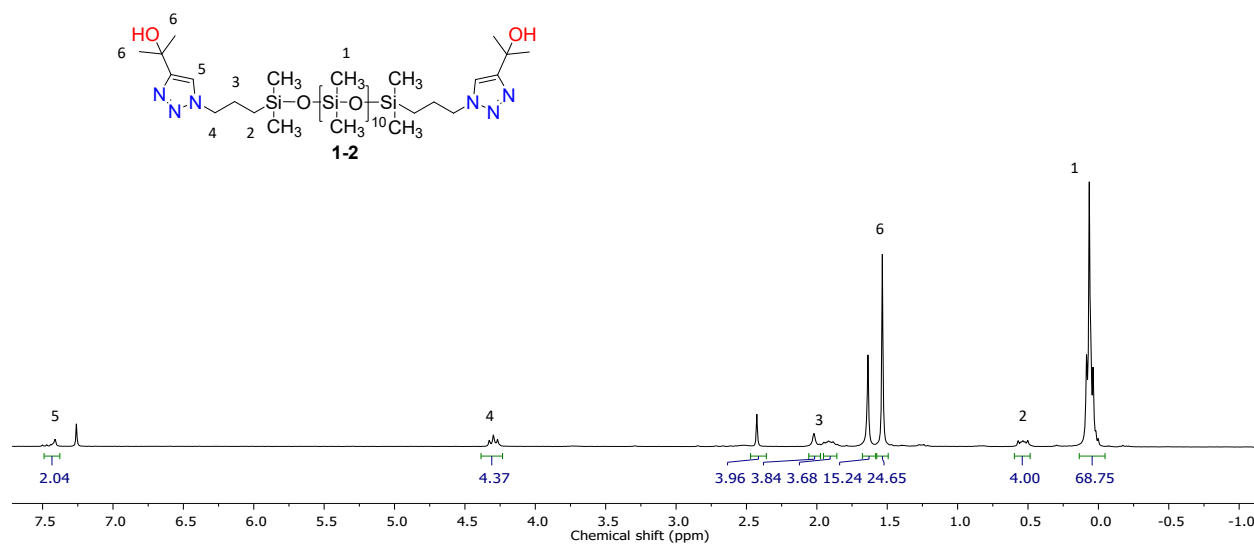


Figure S16. ^1H NMR spectrum of 1-2

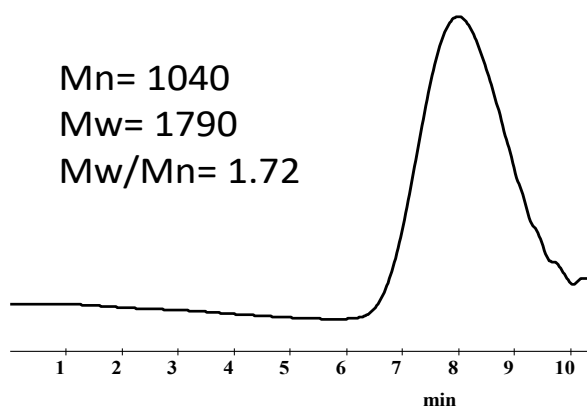


Figure S17. GPC curve of 1-2

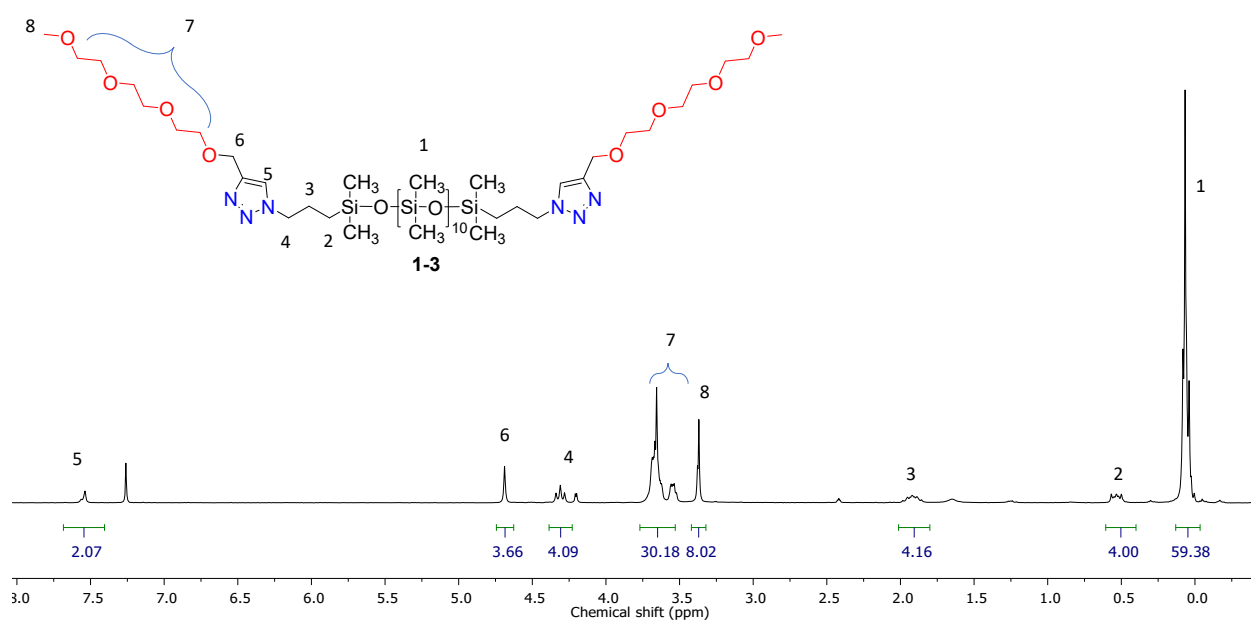


Figure S18. ¹H NMR spectrum of 1-3

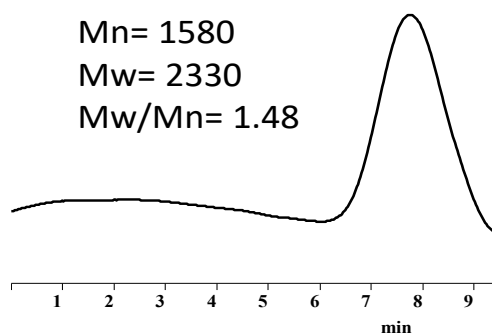


Figure S19. GPC curve of 1-3

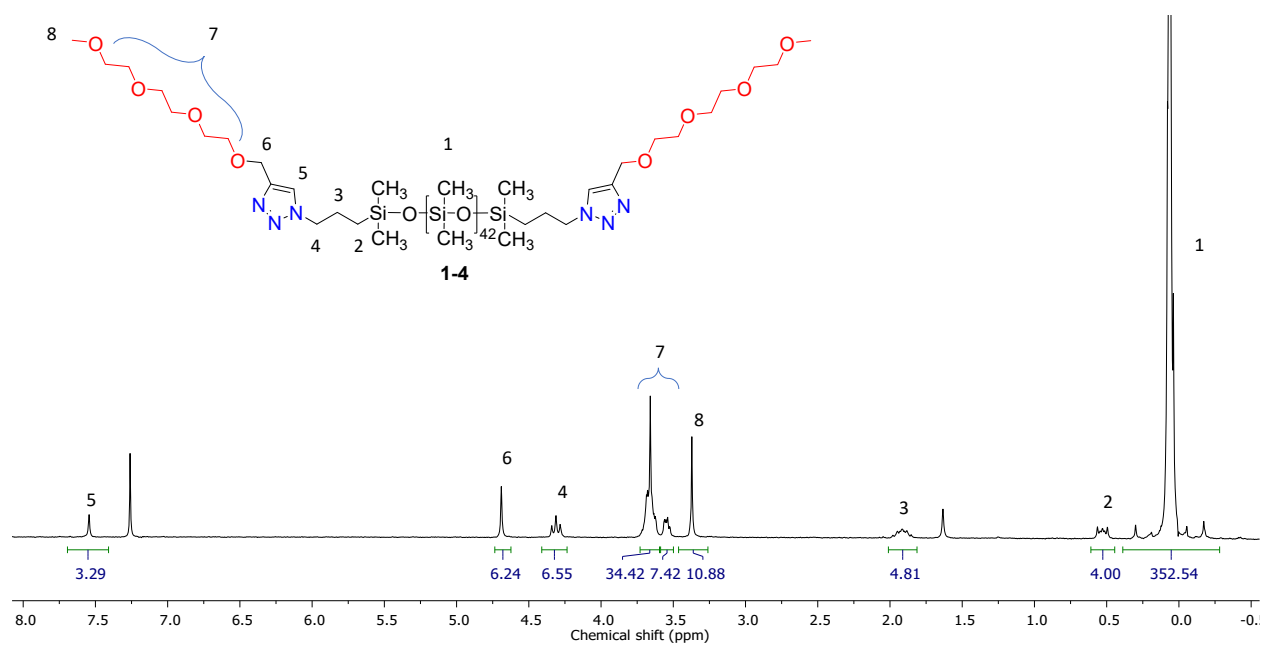


Figure S20. ¹H NMR spectrum of 1-4

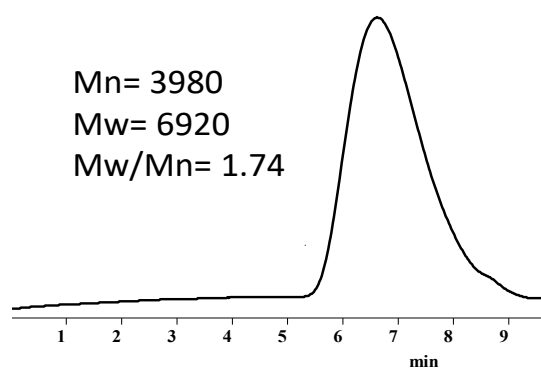


Figure S21. GPC curve of 1-4

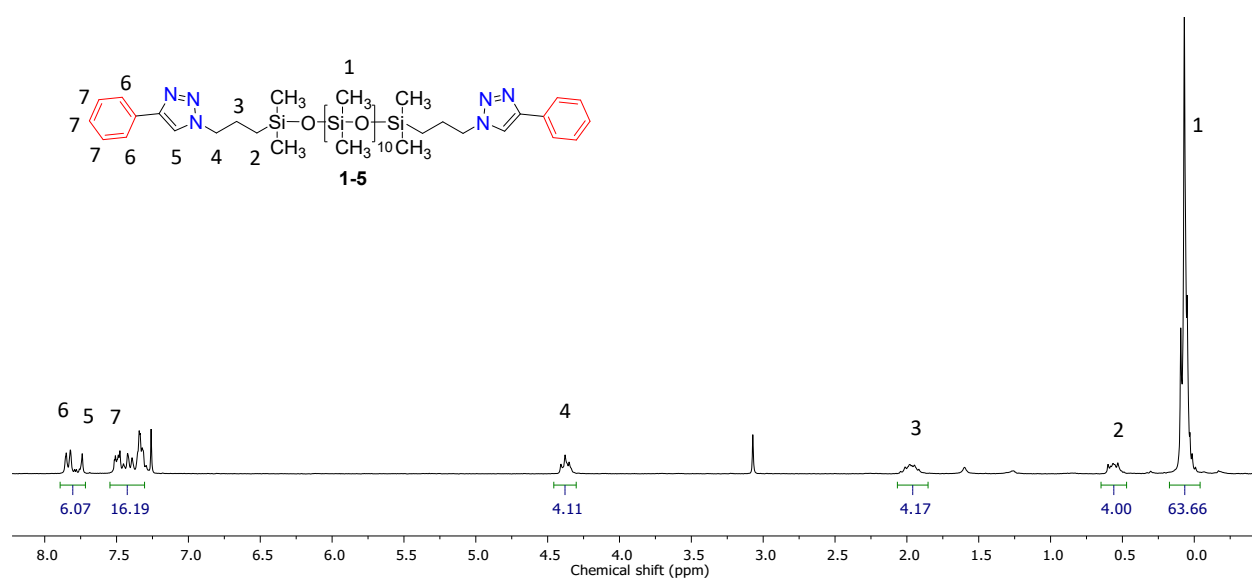


Figure S22. ¹H NMR spectrum of 1-5

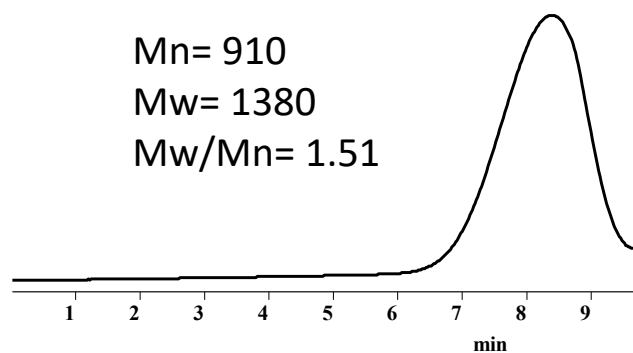


Figure S23. GPC curve of 1-5

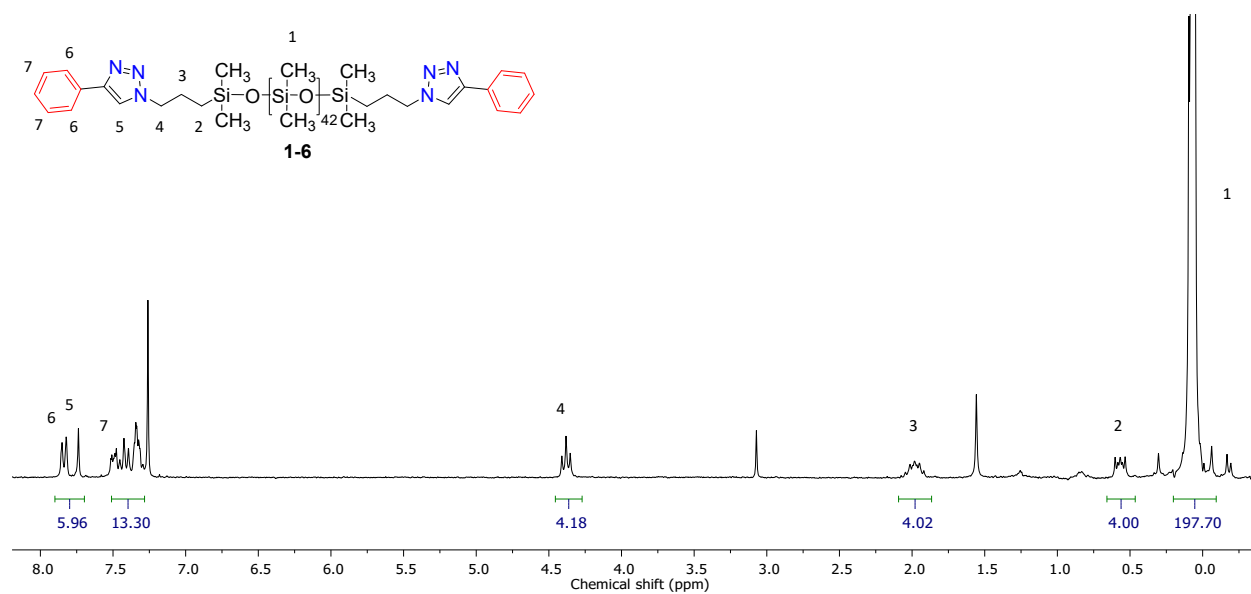


Figure S24. ^1H NMR spectrum of 1-6

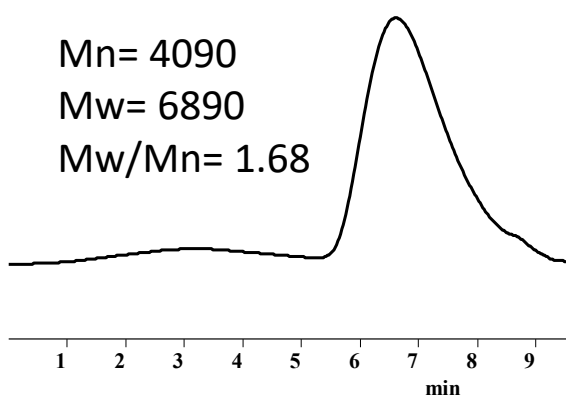


Figure S25. GPC curve of 1-6

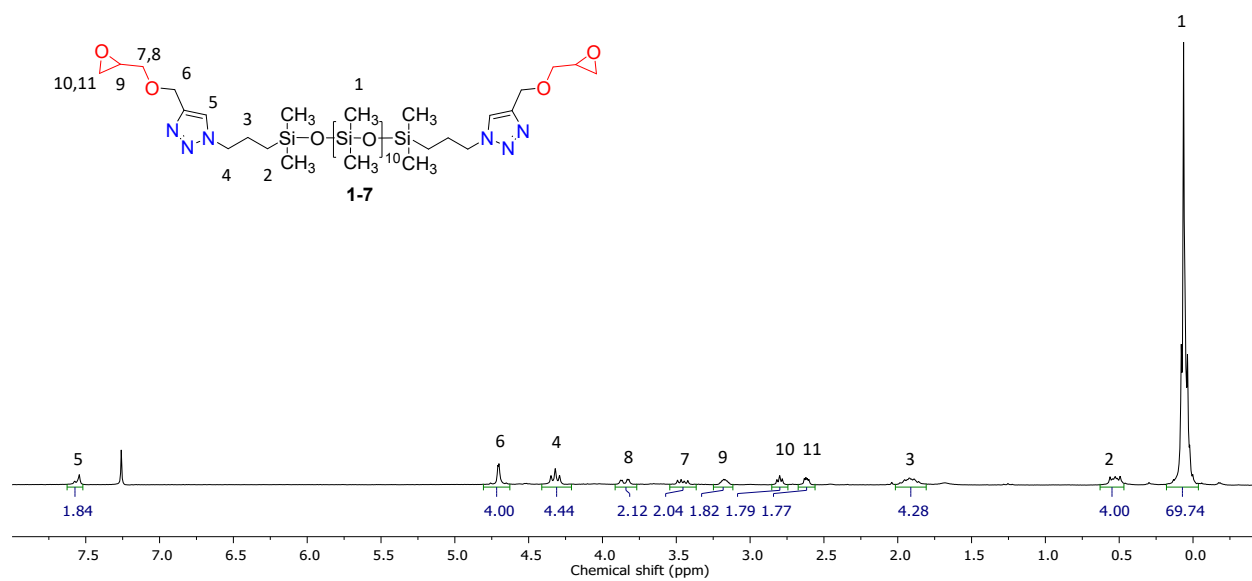


Figure S26. ¹H NMR spectrum of 1-7

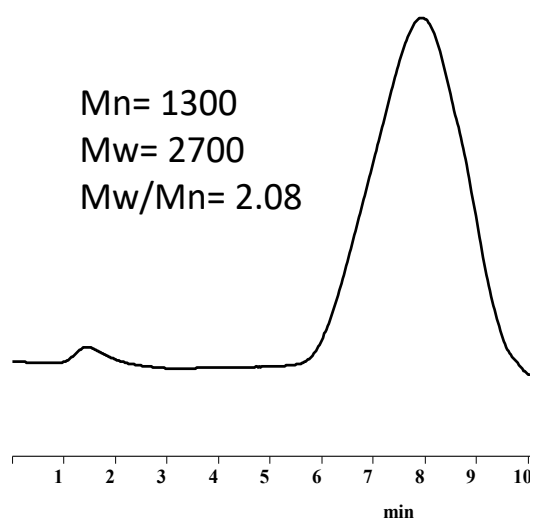


Figure S27. GPC curve of 1-7

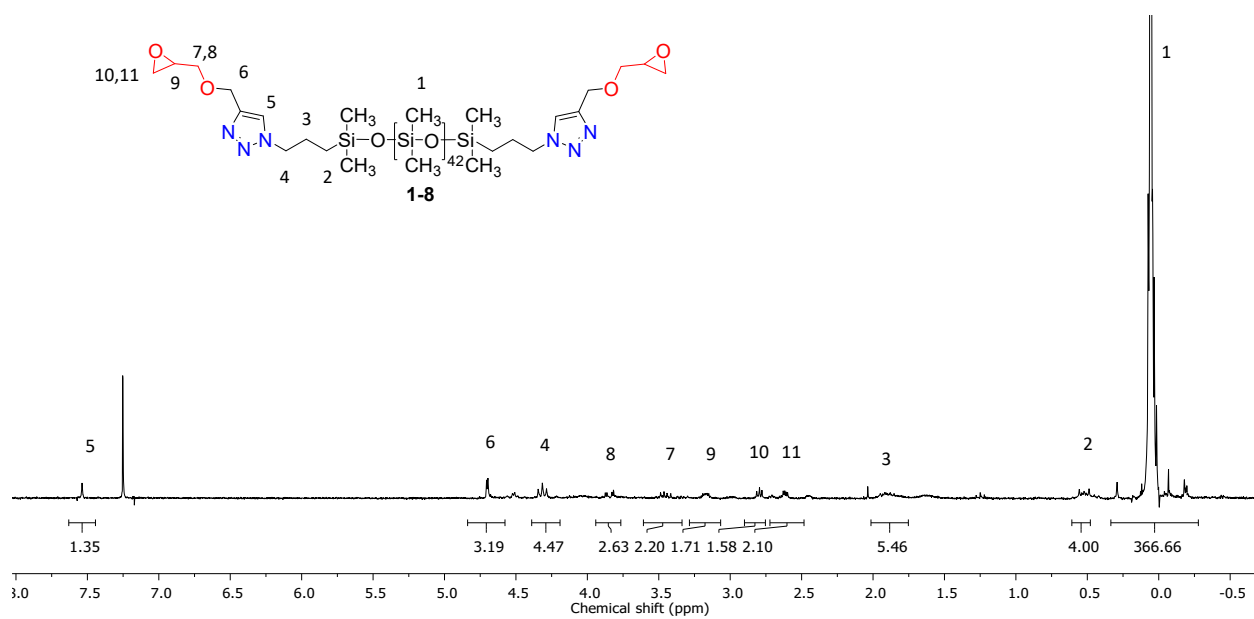


Figure S28. ^1H NMR spectrum of 1-8

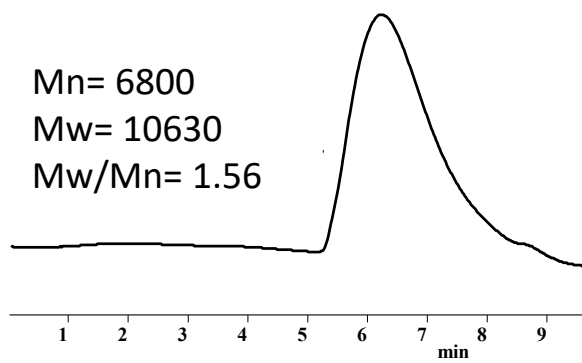


Figure S29. GPC curve of 1-8

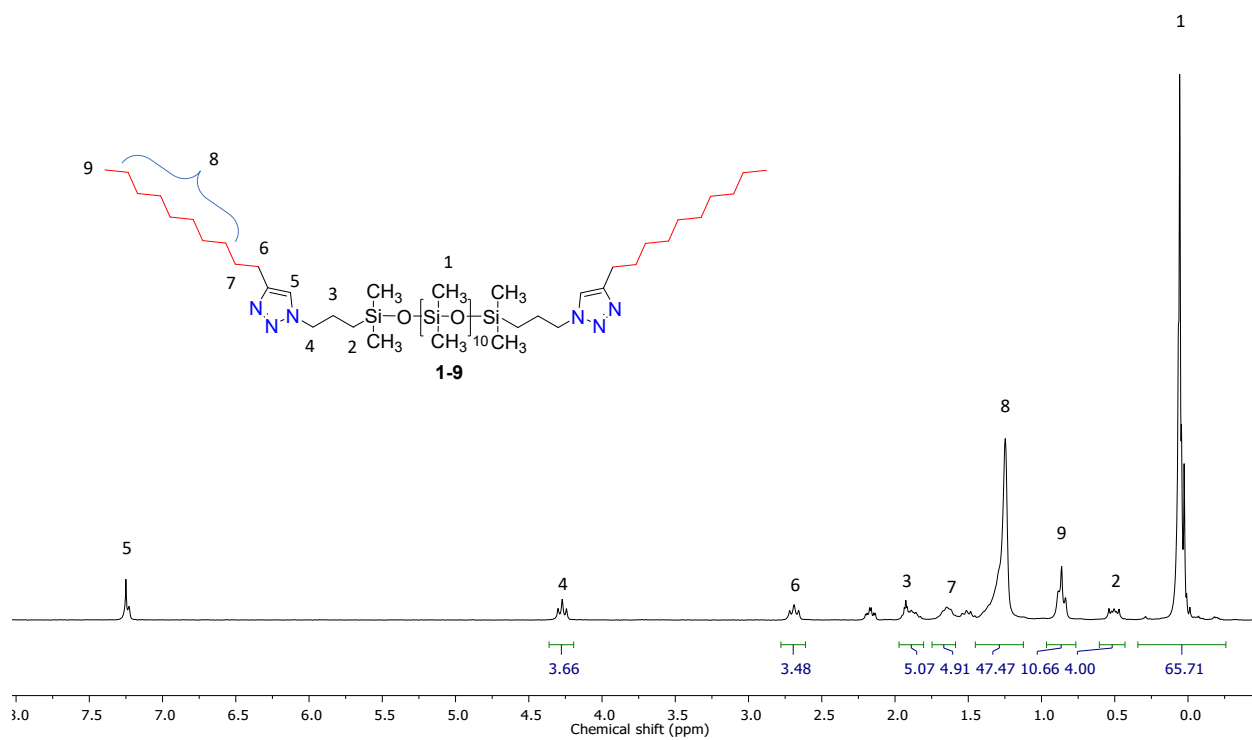


Figure S30. ^1H NMR spectrum of 1-9

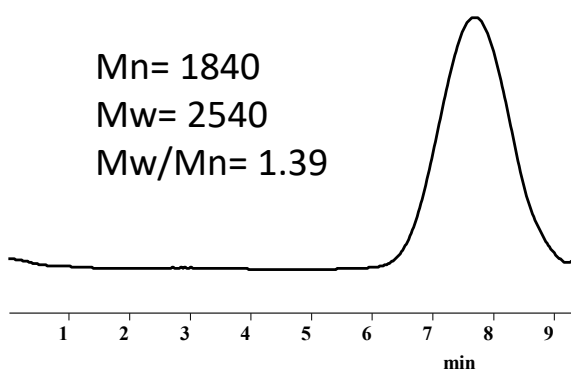


Figure S31. GPC curve of 1-9

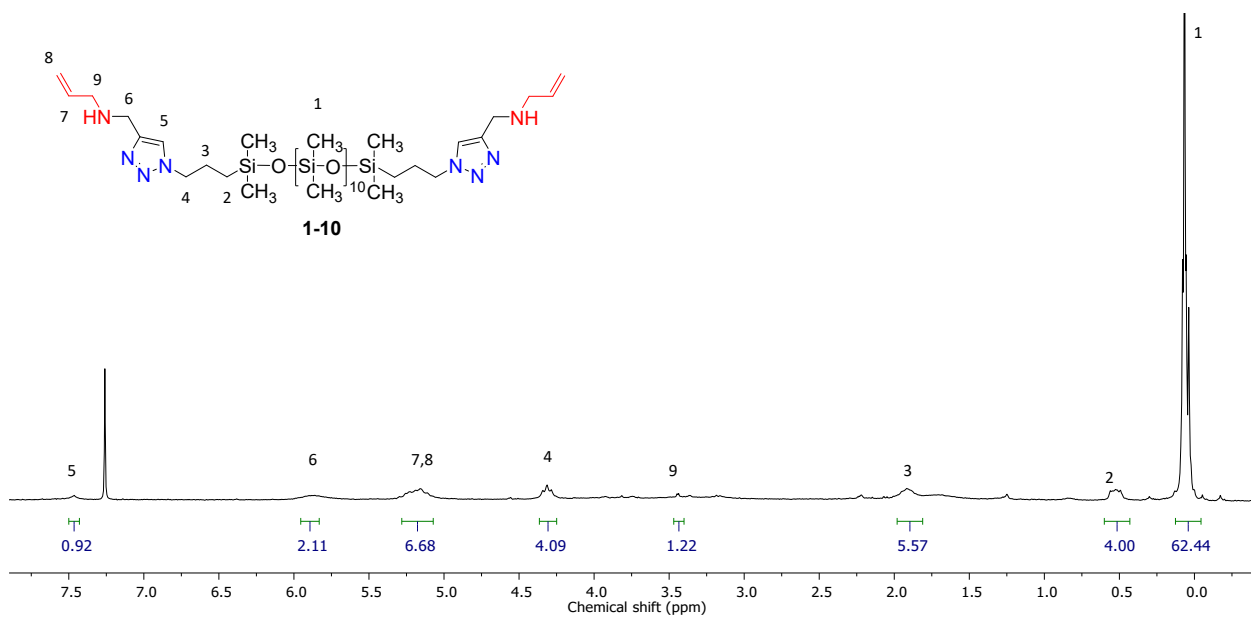


Figure S32. ¹H NMR spectrum of 1-10

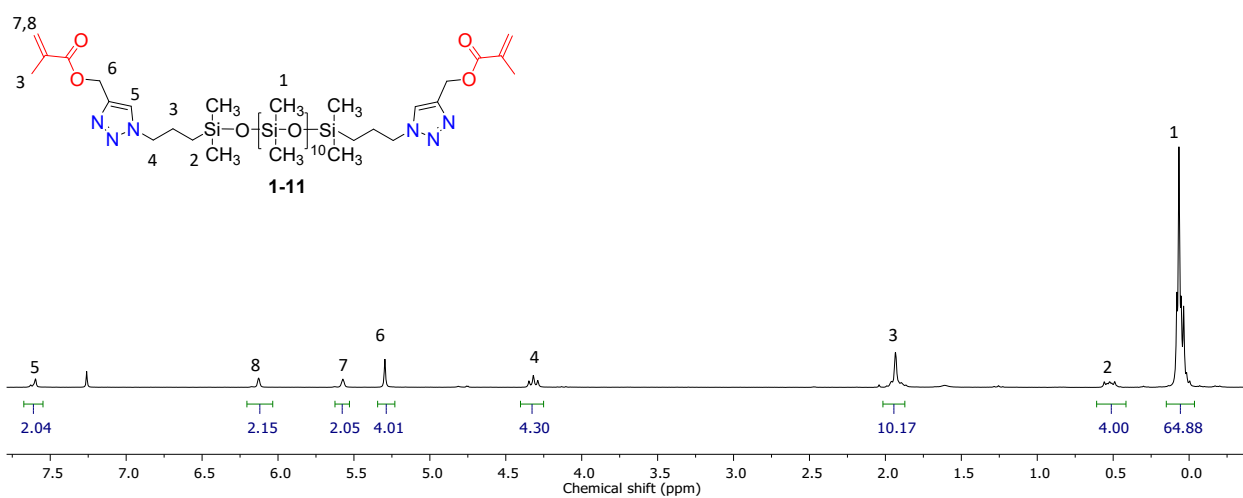


Figure S33. ¹H NMR spectrum of 1-11

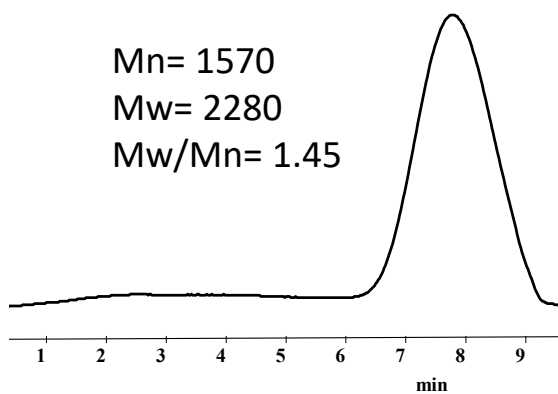


Figure S34. GPC curve of 1-11

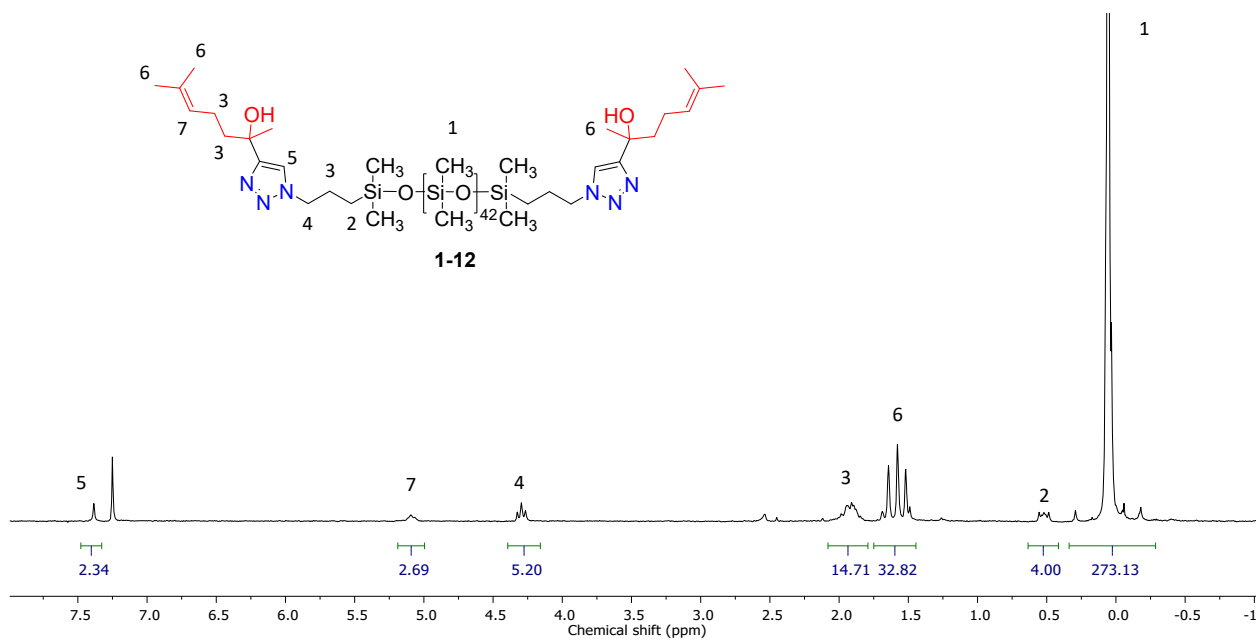


Figure S35. ¹H NMR spectrum of 1-12

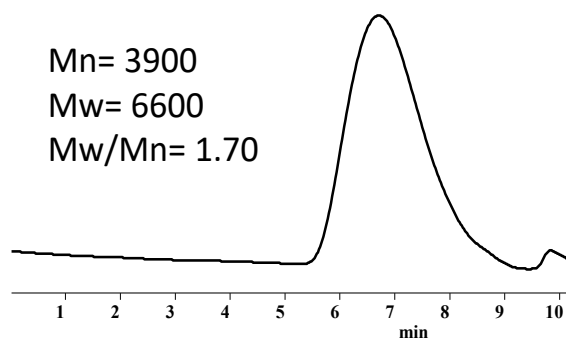


Figure S36. GPC curve of 1-12

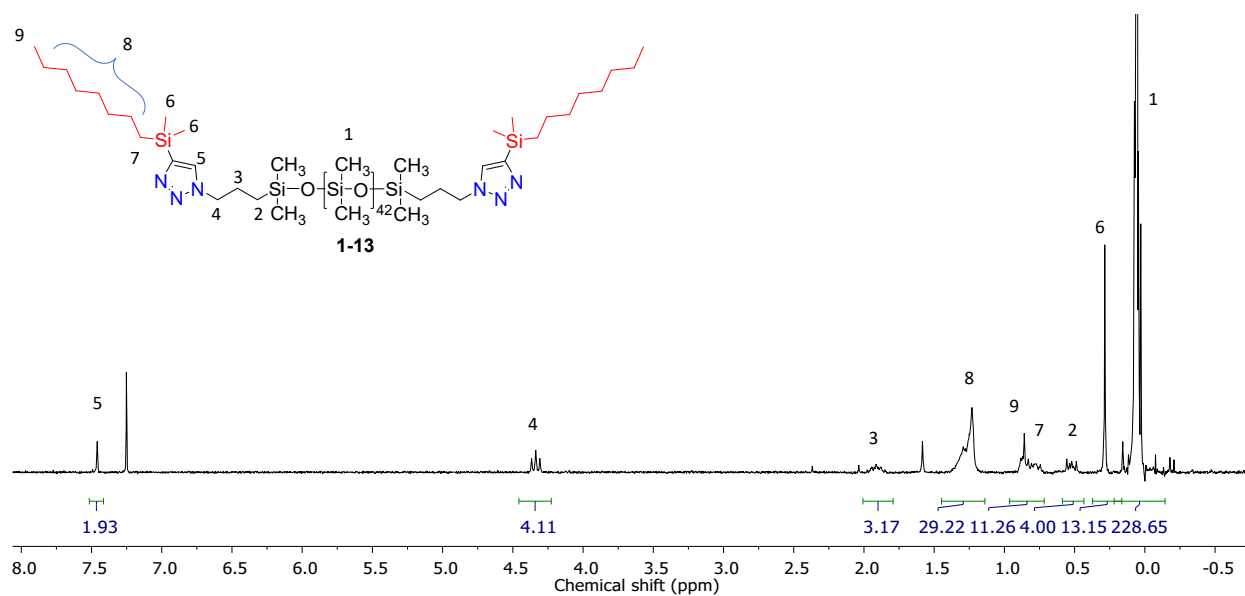


Figure S37. ¹H NMR spectrum of 1-13

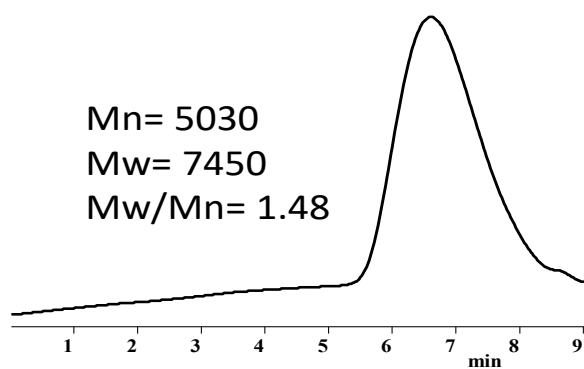


Figure S38. GPC curve of 1-13

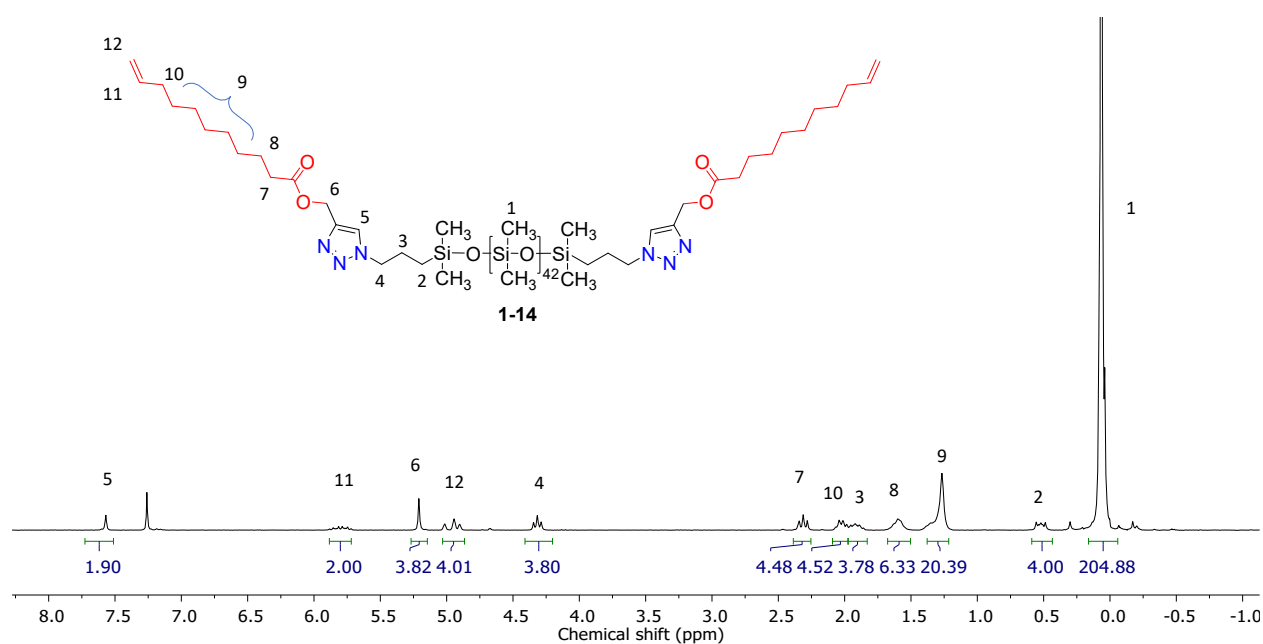


Figure S39. ¹H NMR spectrum of 1-14

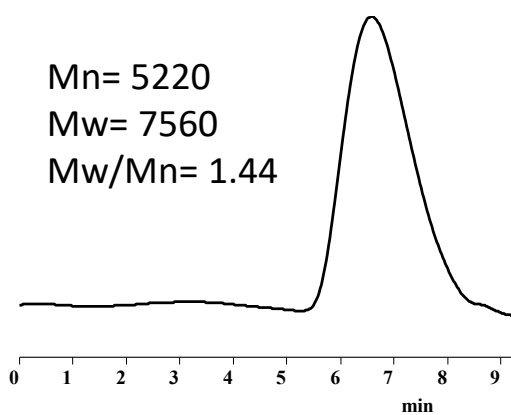


Figure S40. GPC curve of 1-14

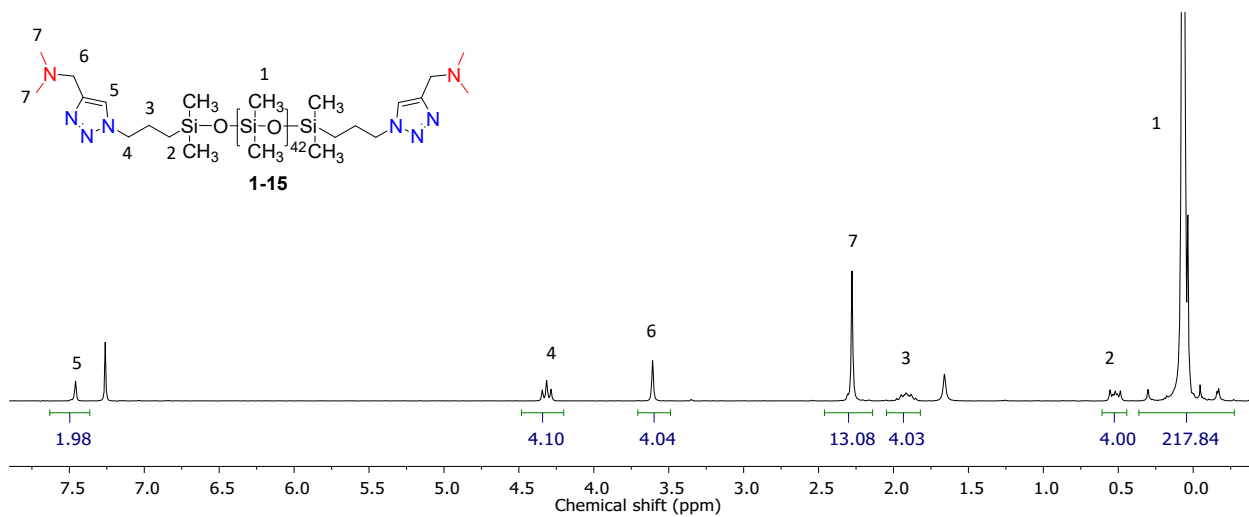


Figure S41. ¹H NMR spectrum of 1-15

6. NMR spectra of functional silanes

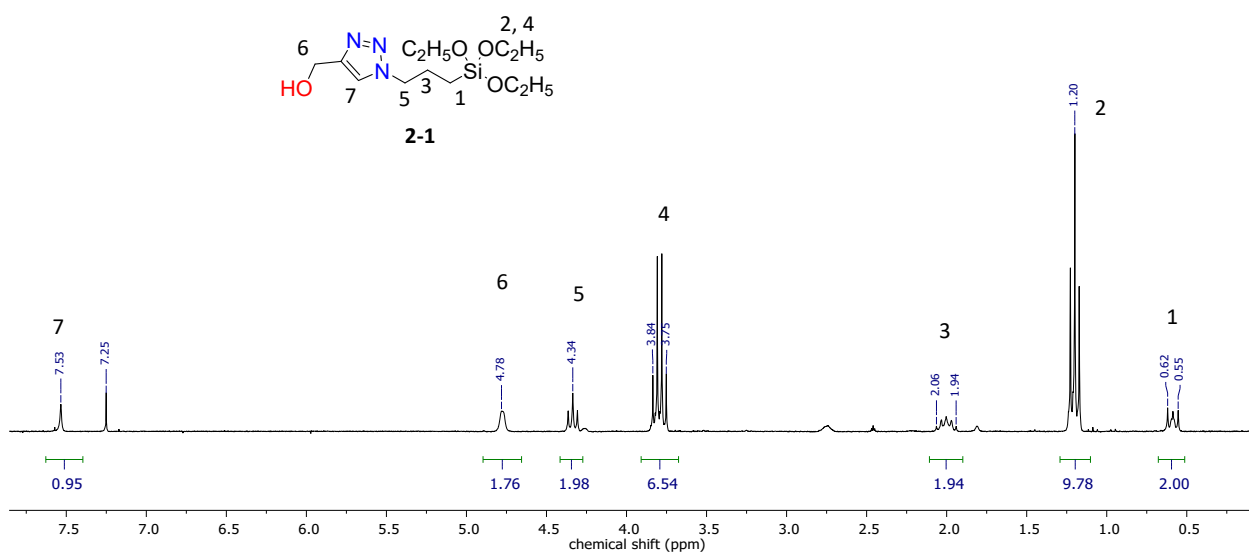


Figure S42. ¹H NMR spectrum of 2-1

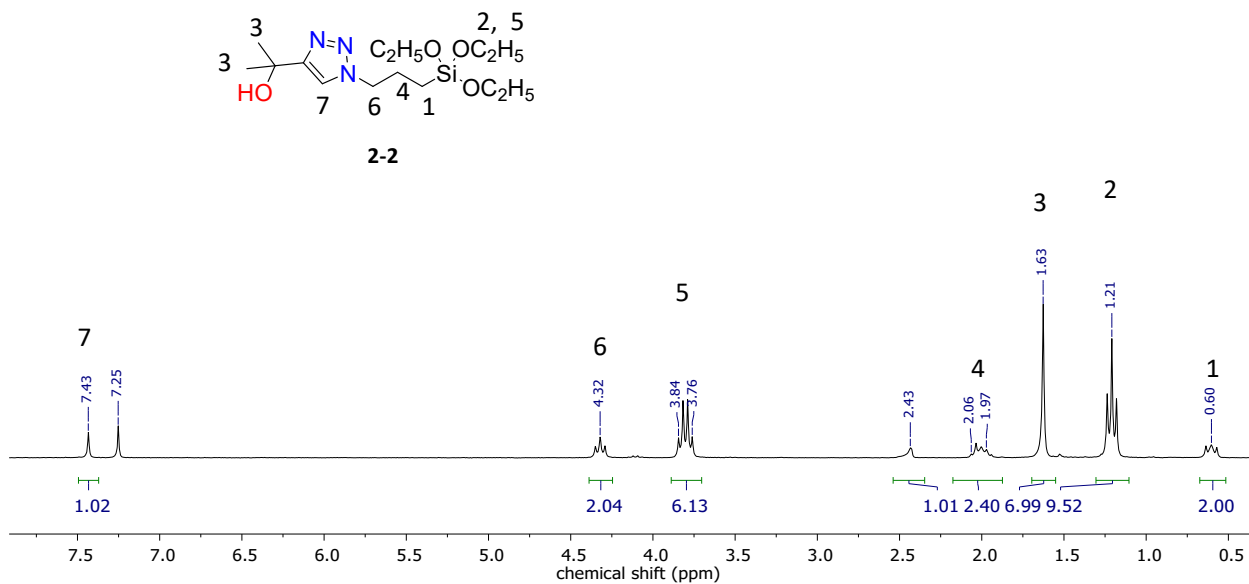


Figure S43. ¹H NMR spectrum of 2-2

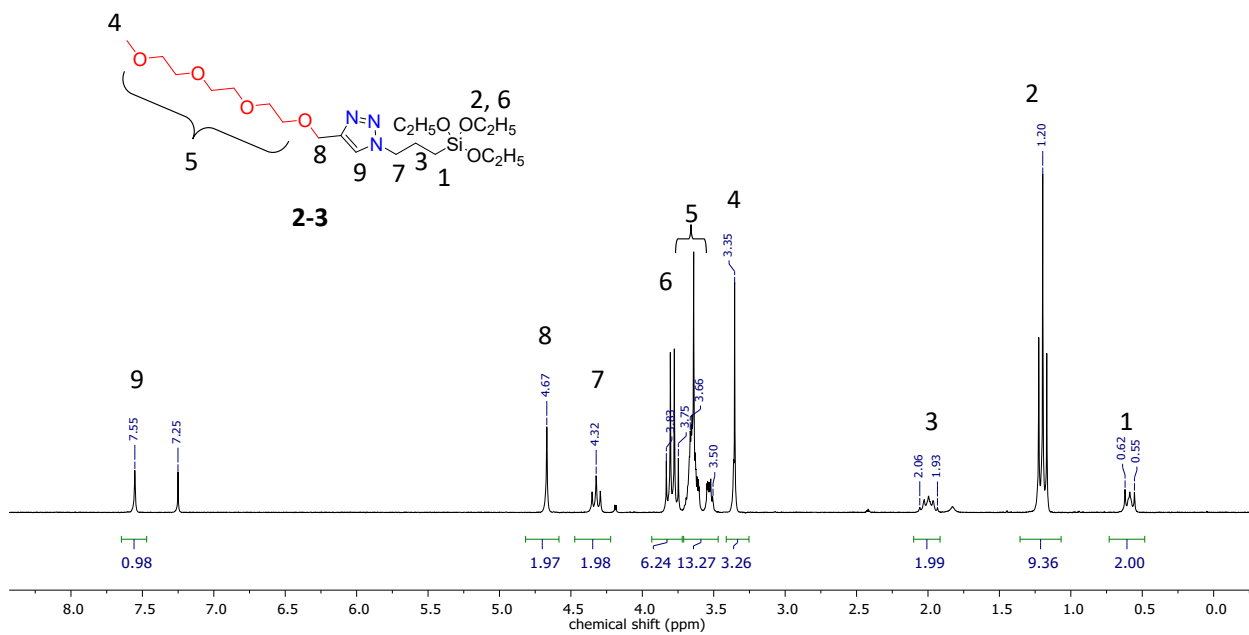


Figure S44. ¹H NMR spectrum of 2-3

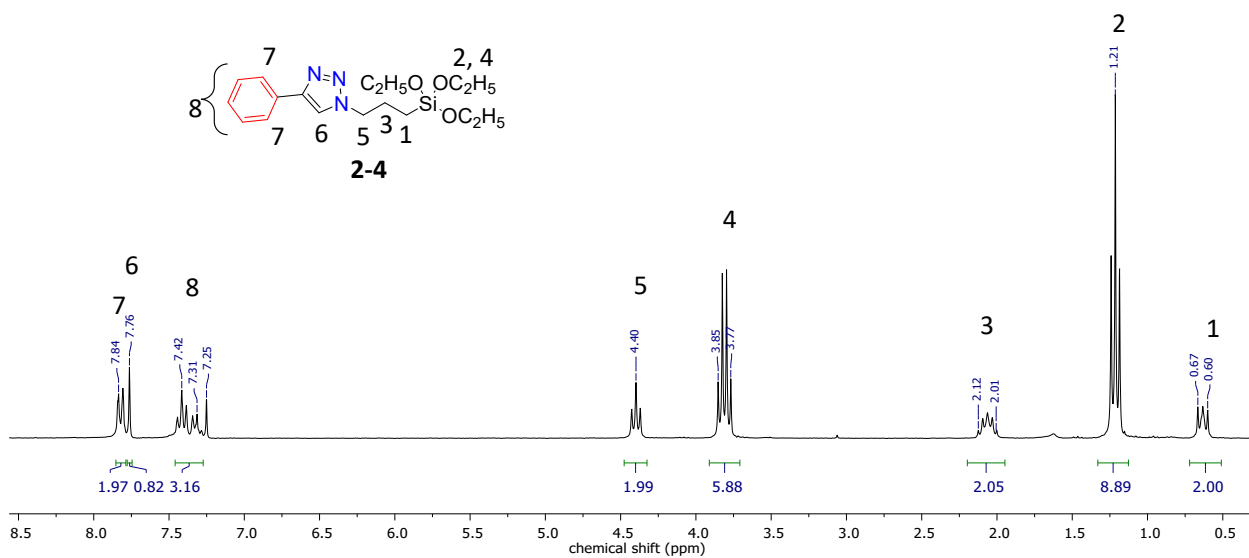


Figure S45. ^1H NMR spectrum of 2-4

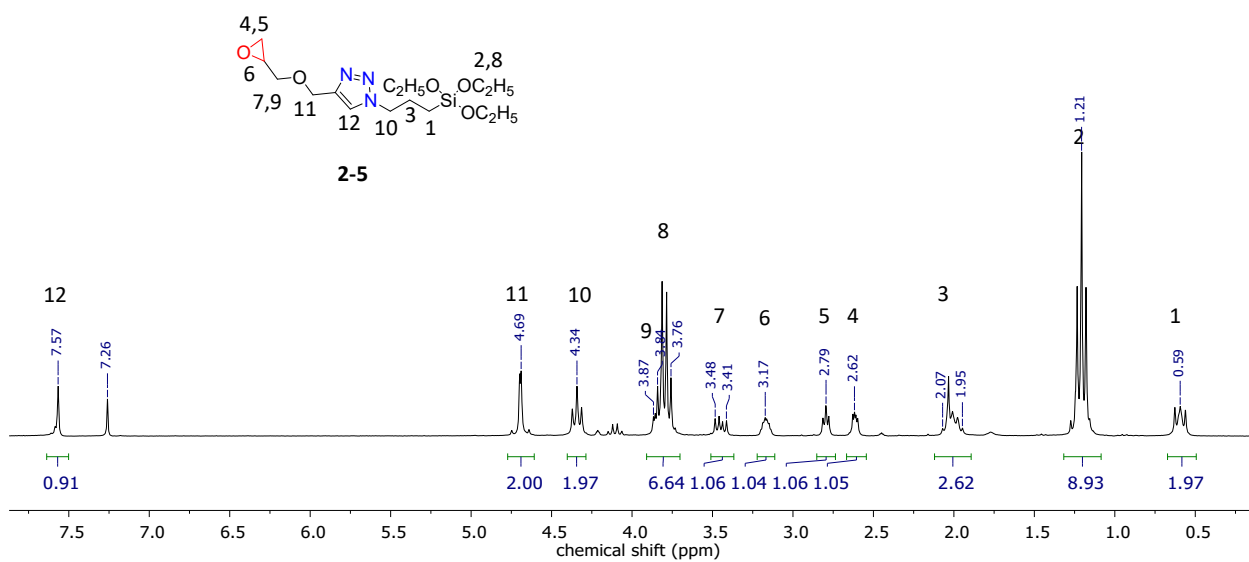


Figure S46. ^1H NMR spectrum of 2-5

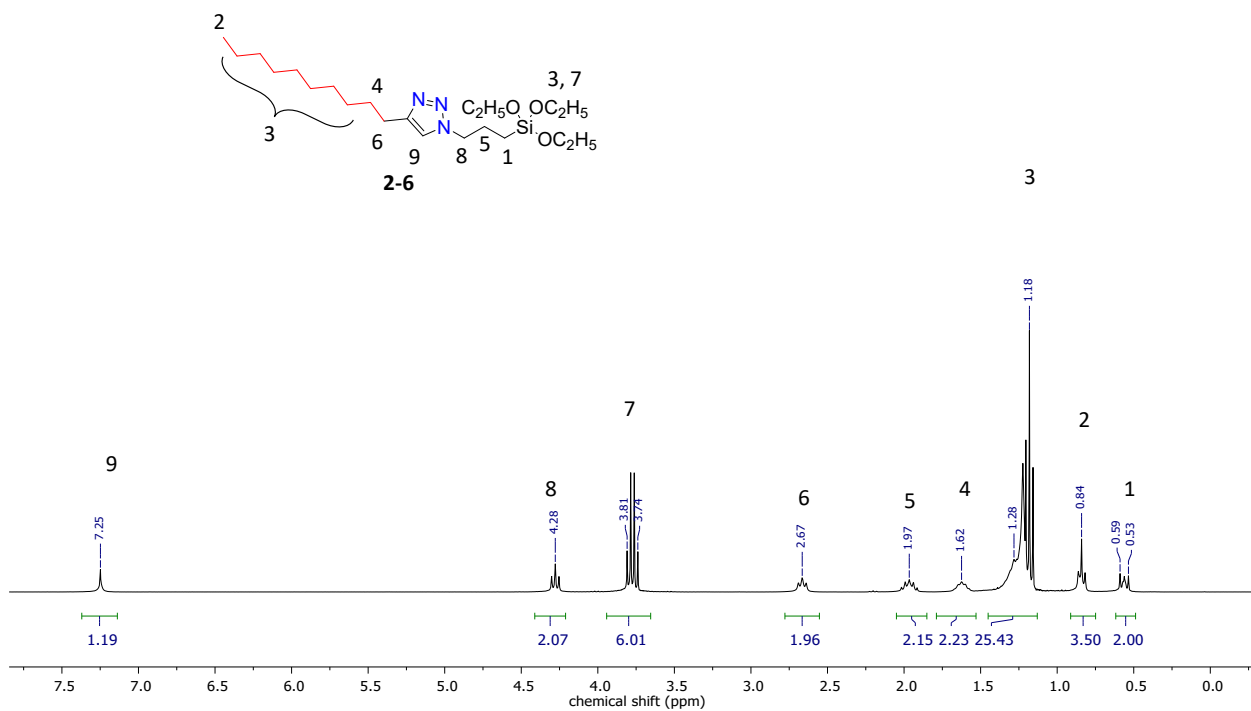


Figure S47. ¹H NMR spectrum of 2-6

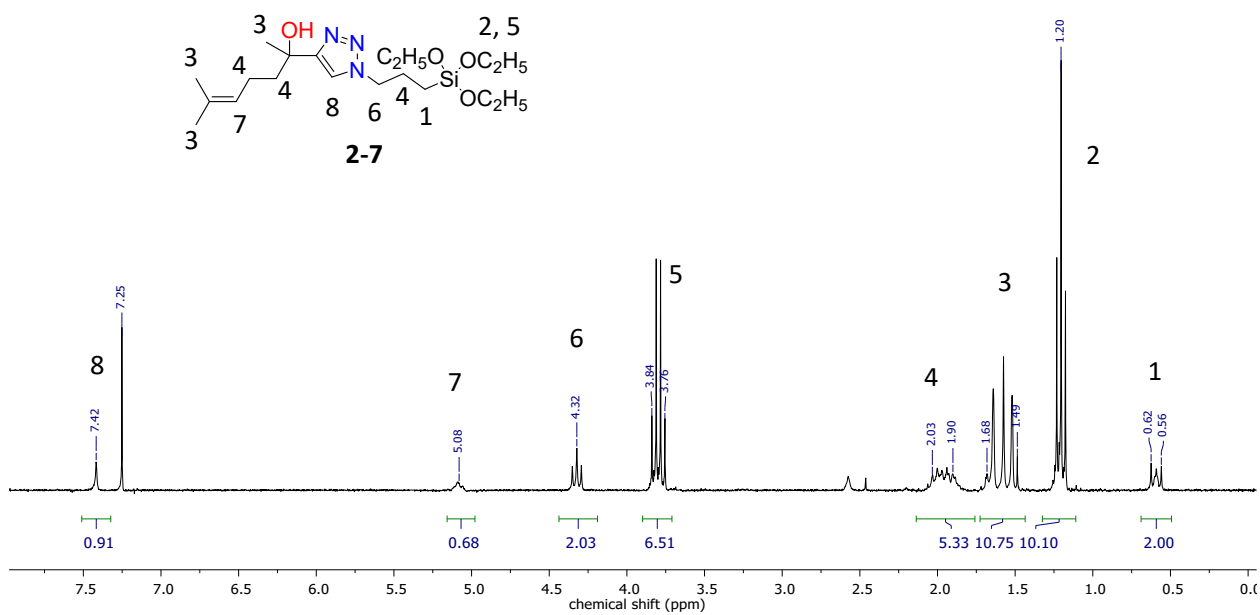


Figure S48. ¹H NMR spectrum of 2-7

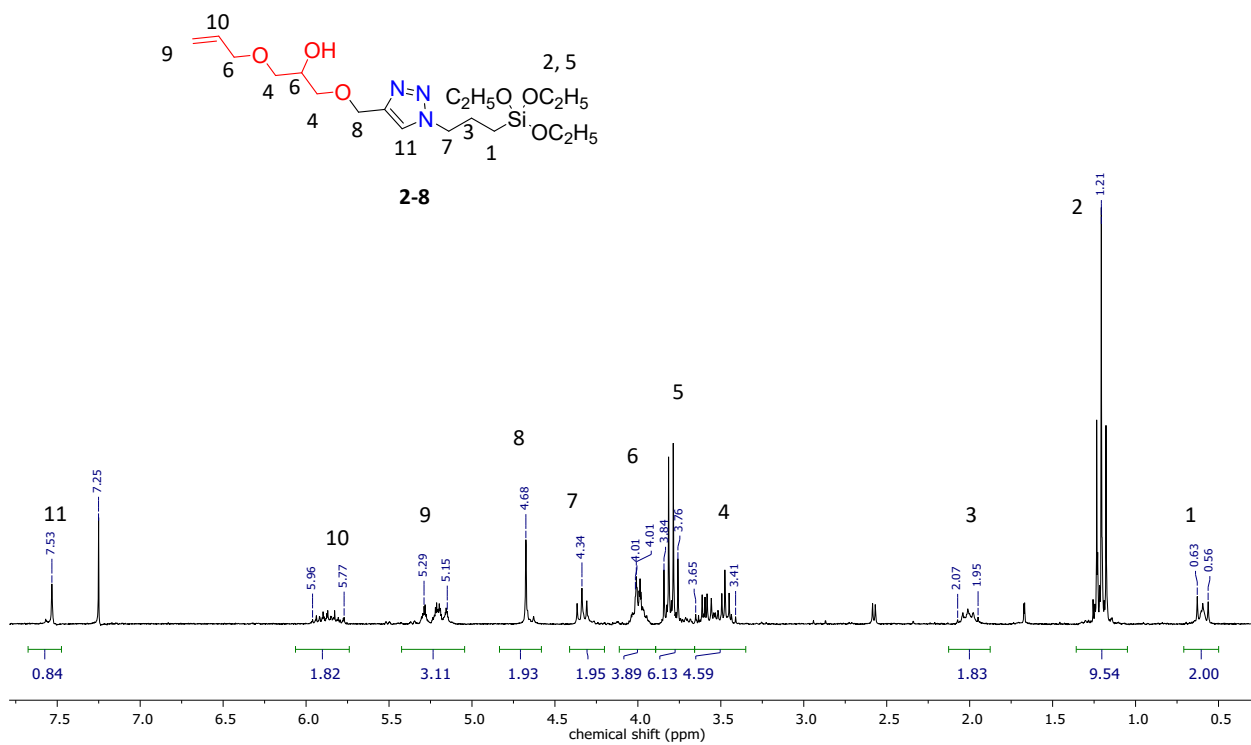


Figure S49. ¹H NMR spectrum of 2-8

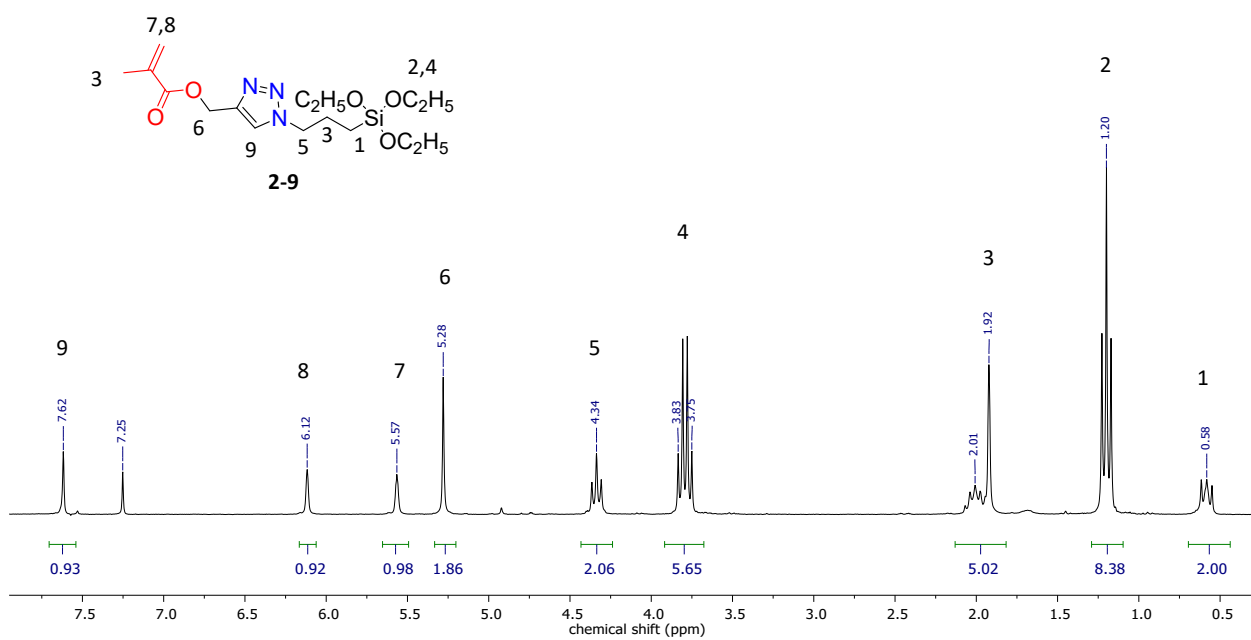


Figure S50. ¹H NMR spectrum of 2-9

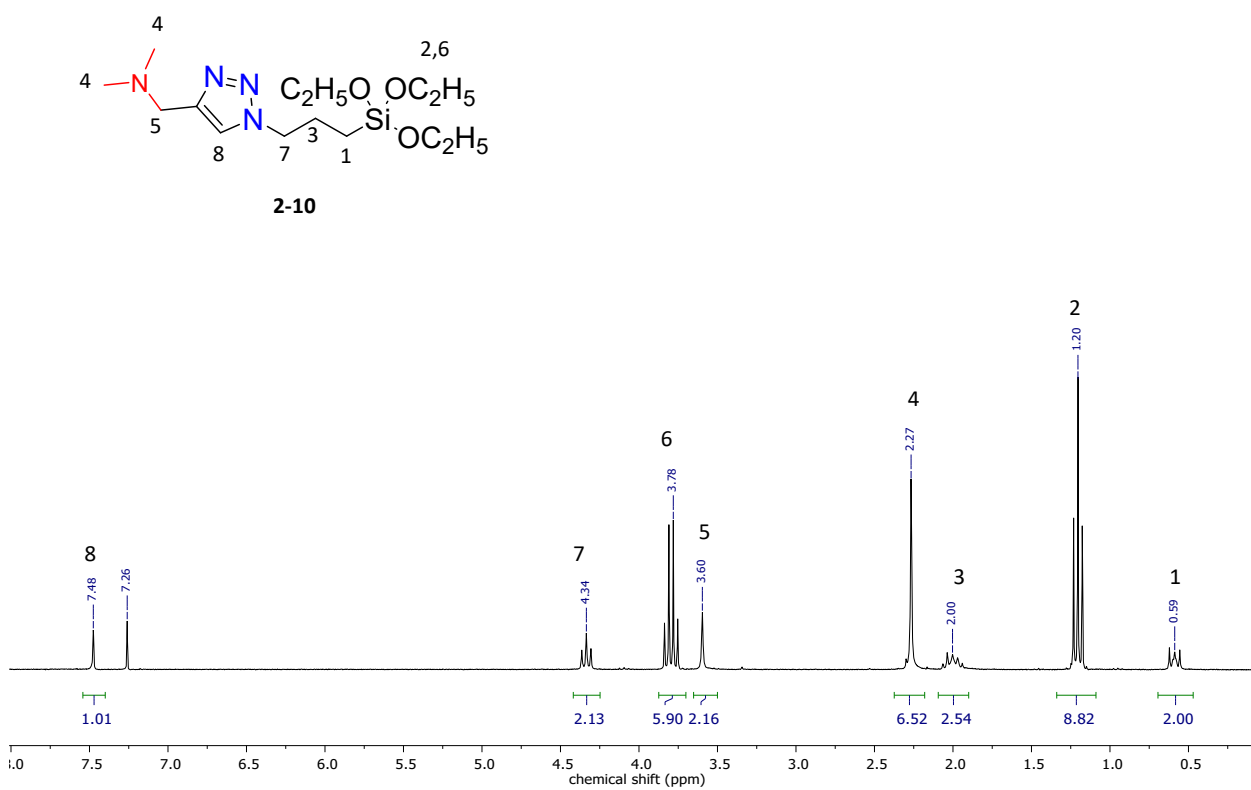
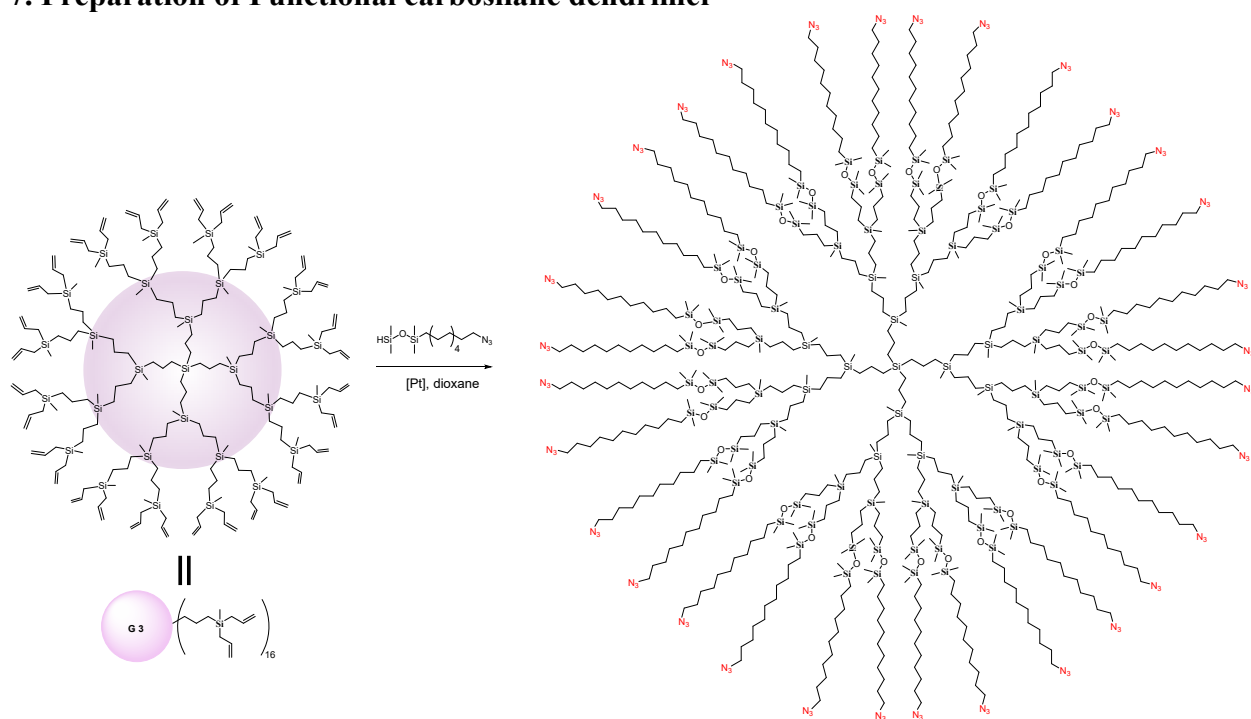
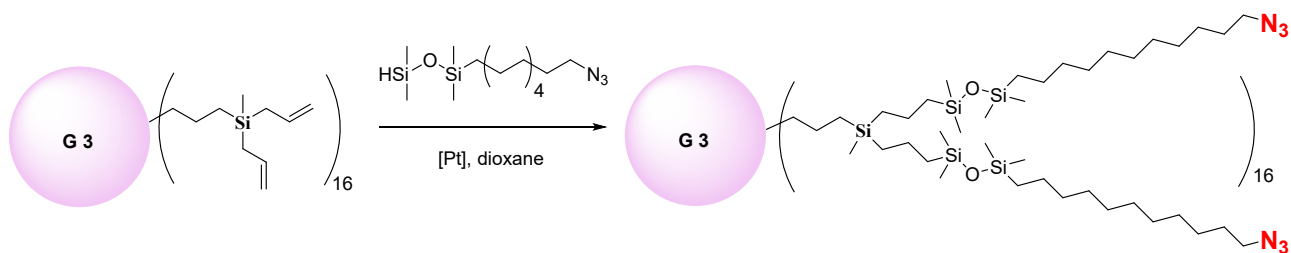


Figure S51. ^1H NMR spectrum of 2-10

7. Preparation of Functional carbosilane dendrimer





G₃Si₉₃(N₃)₃₂ The allyl-terminated **carbosilane** dendrimer G₃Si₂₉All₃₂ (312 mg, 8.4×10^{-5} mol) was dissolved in 5 mL of dry dioxane, then 1-(11-azidoundecyl)-1,1,3,3-tetramethyldisiloxane (0.89 g, 2.7×10^{-3} mol) and Karstedt's catalyst were added to the solution. The obtained mixture was stirred at room temperature for 48 h. The reaction was monitored by ¹H NMR. The reaction mixture was concentrated under reduced pressure (80 °C/0.5 mbar). The product was obtained as a colorless oil with a 99% yield (1.19 g, 99% of purity according to GPC). And then the product was purified on a preparative chromatograph from excess low-molecular compounds with a yield of 80% (0.952 g, 99% of purity according to GPC).

¹H NMR (300 MHz, CDCl₃): δ 3.25 (m, 16H, CH₂-N₃), 1.64-1.55 (m, 16H, CH₂-CH₂-N₃), 1.36-1.28 (m, 158H, -CH₂), 0.61-0.48 (m, 76H, Si-CH₂), 0.03 -0.07 (m, 117H, Si-CH₃). ¹³C NMR (77.5 MHz, CDCl₃): δ 51.48, 33.48, 33.41, 29.62, 29.53, 29.42, 29.19, 28.86, 26.75, 23.32, 23.26, 19.11, 19.01, 18.54, 18.45, 17.93, 0.56, 0.46, -4.99. ²⁹Si NMR (59.6 MHz, CDCl₃): δ 7.19, 6.62, 1.03, 0.86, 0.72.

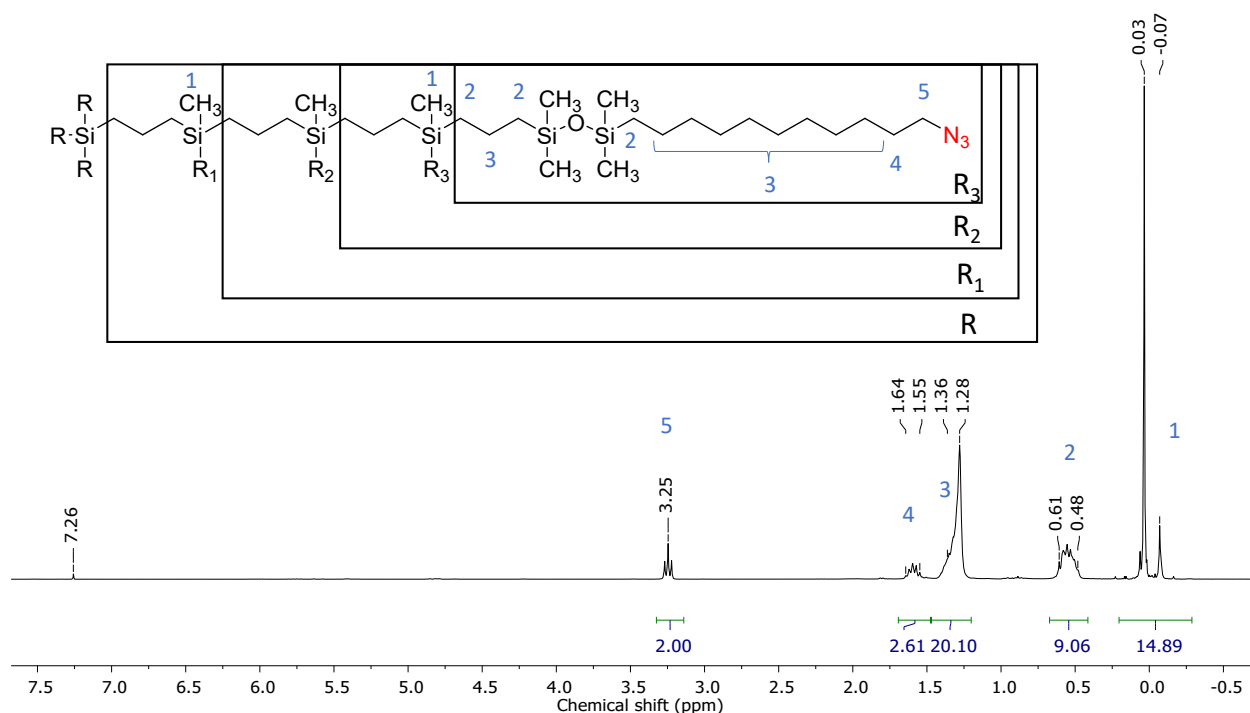


Figure S52. ^1H NMR spectrum of $\text{G}_3\text{Si}_9(\text{N}_3)_{32}$

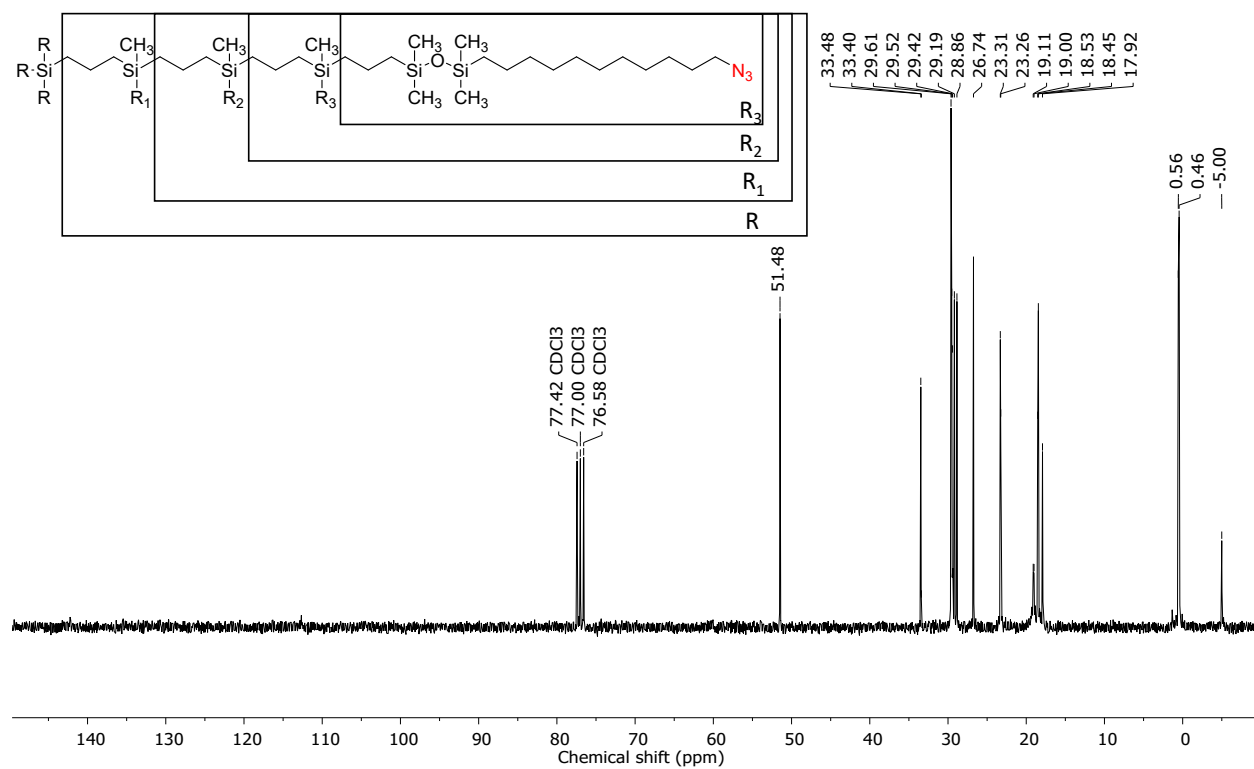


Figure S53. ^{13}C NMR spectrum of $\text{G}_3\text{Si}_9(\text{N}_3)_{32}$

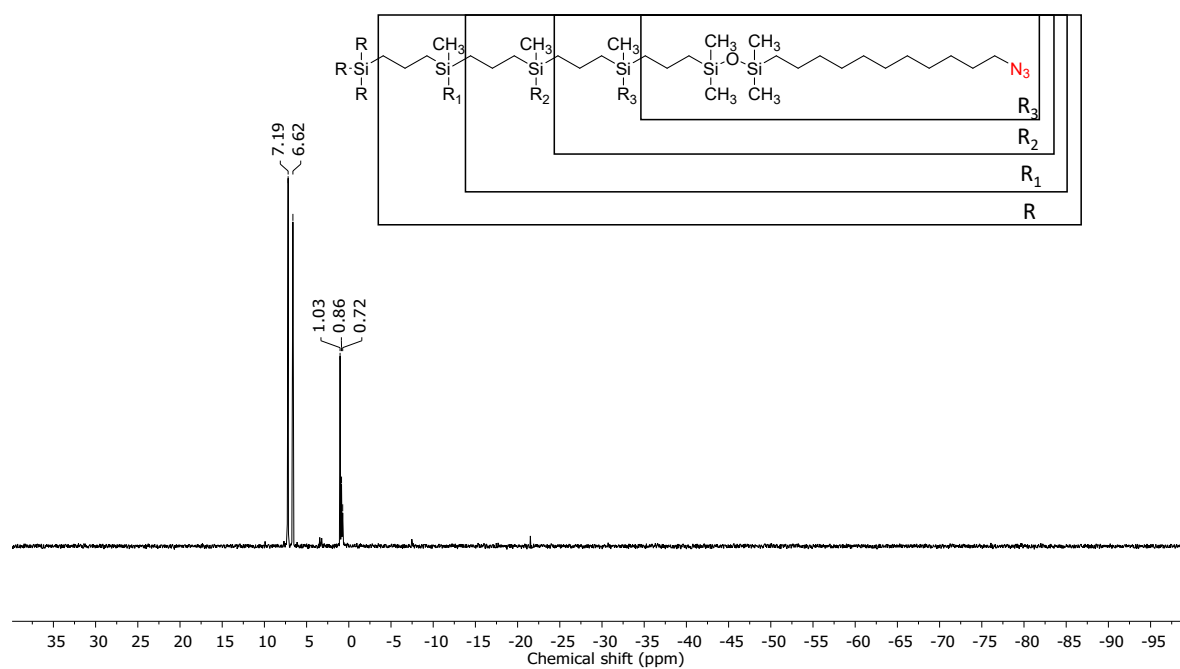


Figure S54. ^{29}Si NMR spectrum of $\text{G}_3\text{Si}_9(\text{N}_3)_{32}$

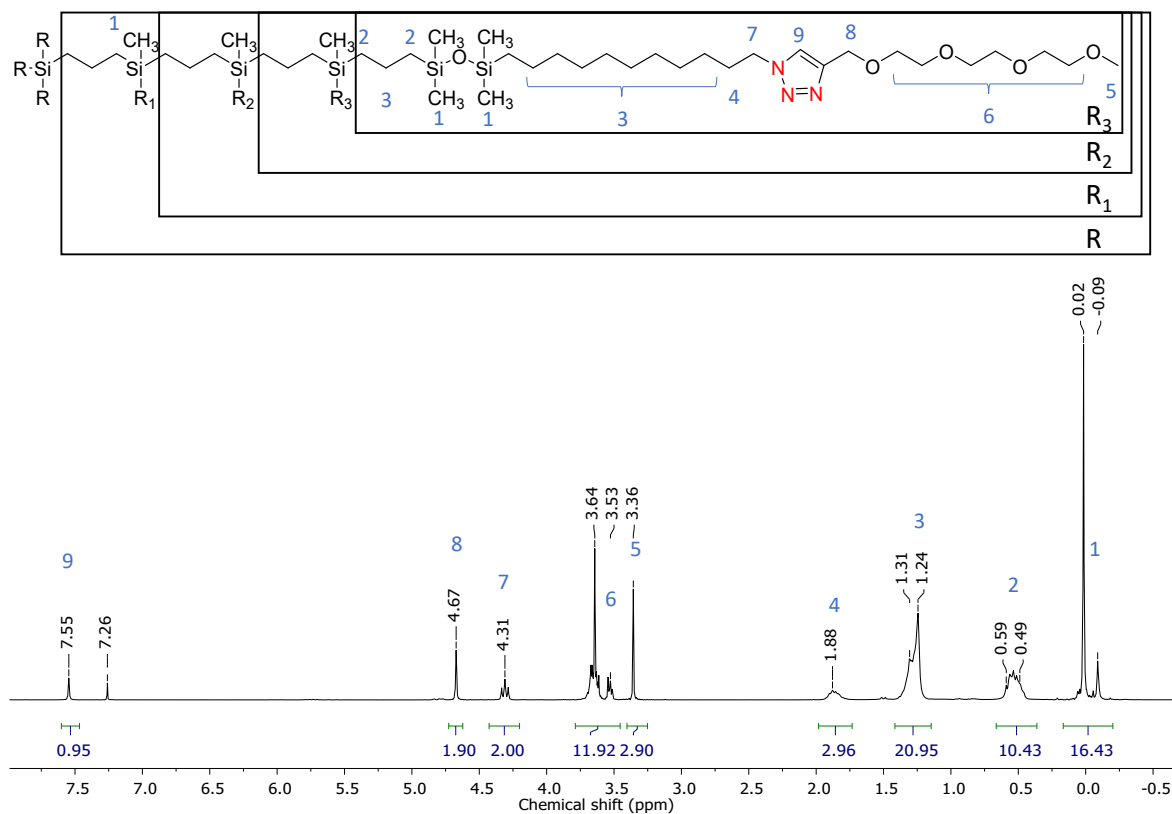


Figure S55. ^1H NMR spectrum of $\text{G}_3\text{Si}_9(\text{TEG})_{32}$ (3-1)

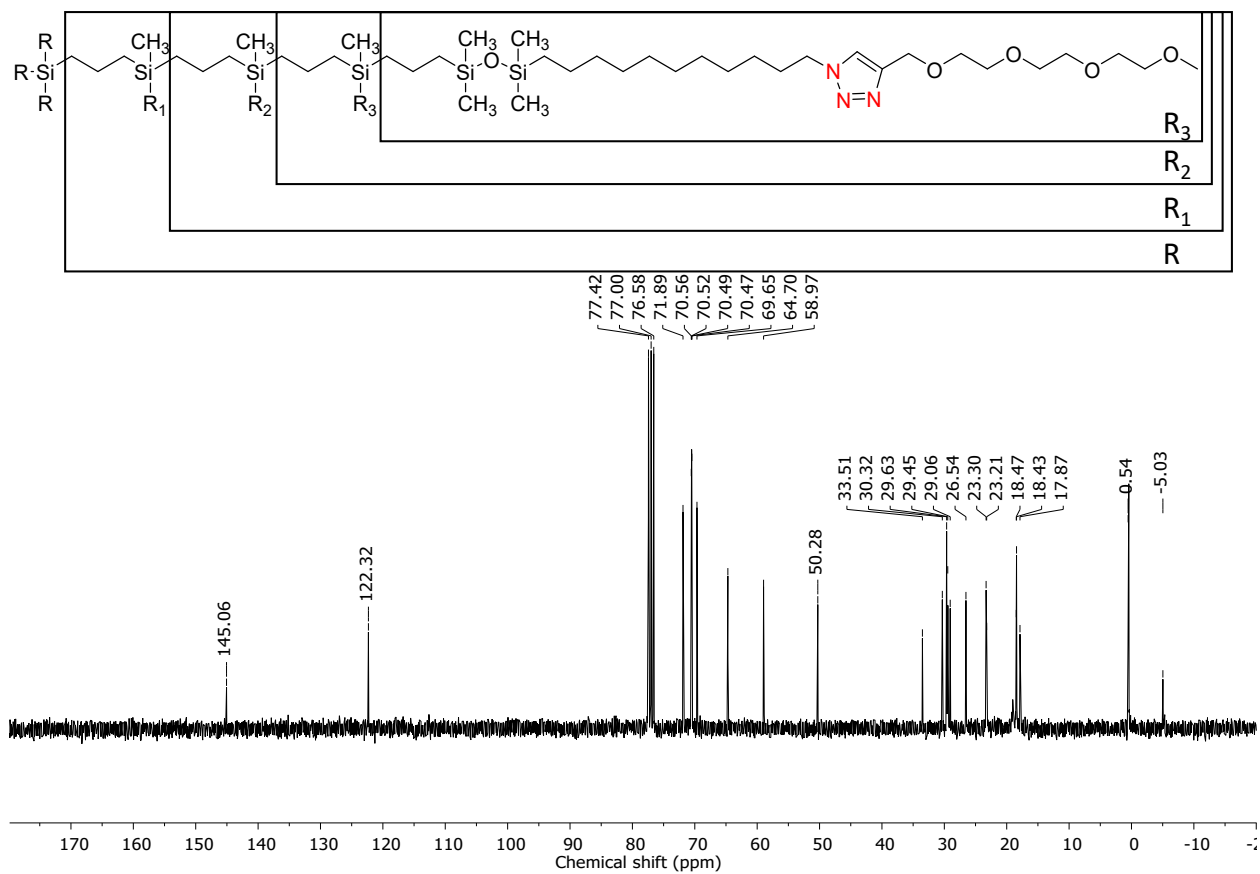


Figure S56. ^{13}C NMR spectrum of $\text{G}_3\text{Si}_{193}(\text{TEG})_{32}$ (3-1)

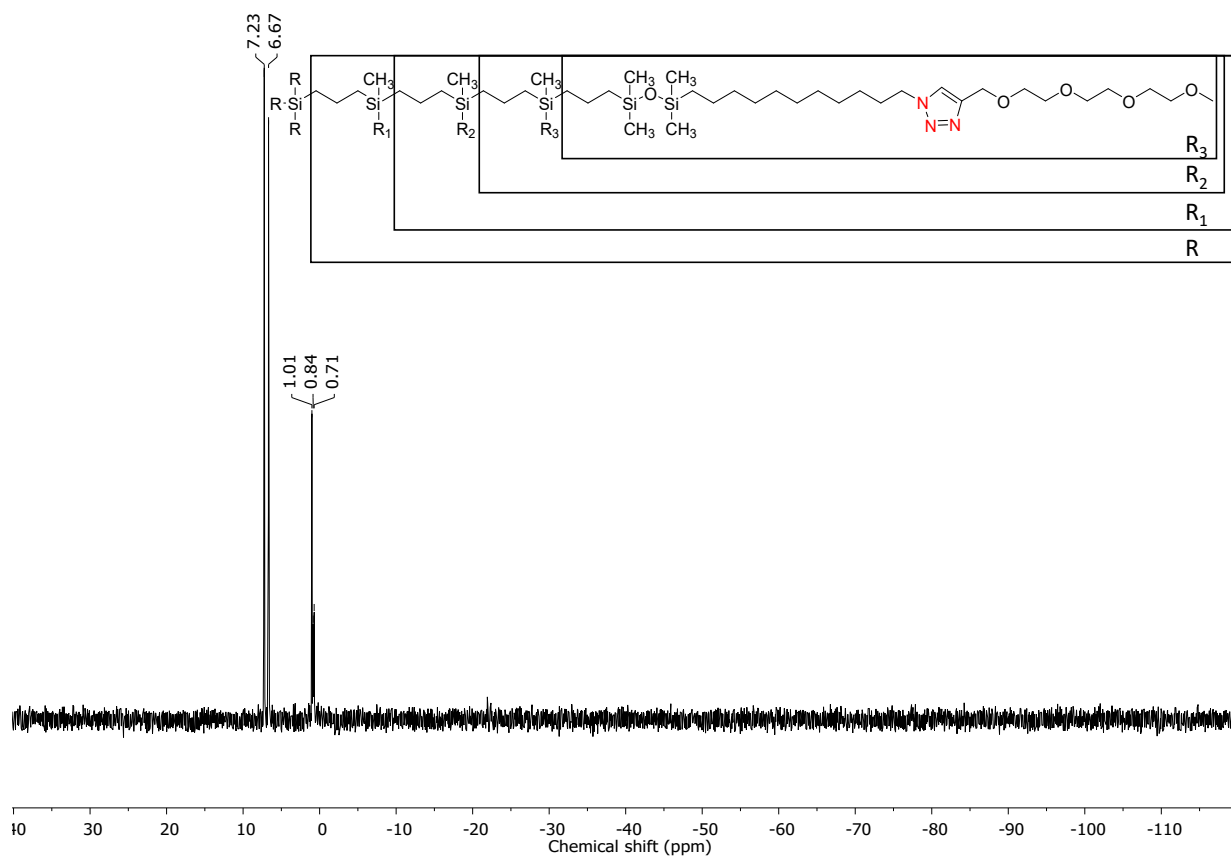


Figure S57. ^{29}Si NMR spectrum of $\text{G}_3\text{Si}_{193}(\text{TEG})_{32}$ (3-1)

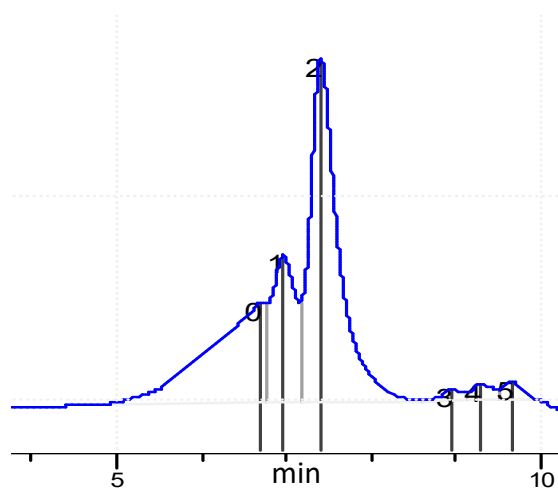


Figure S58. GPC of $\text{G}_3\text{Si}_{193}(\text{TEG})_{32}$ (3-1) before purification on a preparative chromatograph

8. Cell culture and cytotoxicity assay

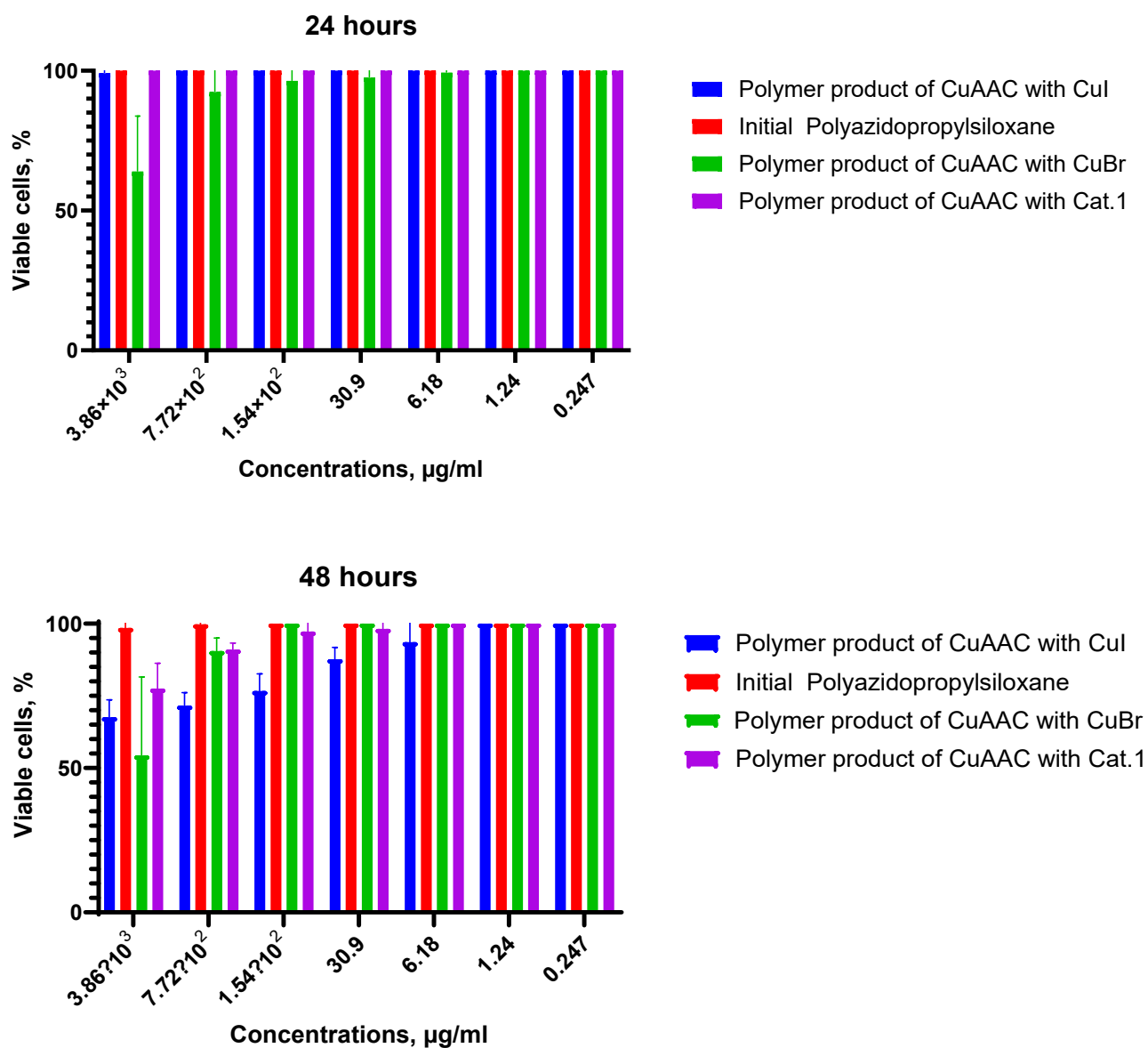


Figure S59. Induced cell death by the components.

9. References

- 1 D. Migulin, S. Milenin, G. Cherkaev, E. Svidchenko, N. Surin and A. Muzafarov, *J Organomet Chem*, 2018, **859**, 24–32.
- 2 D. A. Migulin, J. V. Rozanova, V. A. Migulin, G. V. Cherkaev, I. B. Meshkov, A. A. Zezin and A. M. Muzafarov, *Soft Matter*, 2022, **18**, 2441–2451.