

SUPPLEMENTARY INFORMATION

Janus tricyclononene polymers bearing tri(*n*-alkoxy)silyl side groups for membrane gas separation

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1. Low temperature nitrogen adsorption/desorption analysis

The analysis was carried out at liquid nitrogen temperature (−196 °C) using Micromeritics Gemini VI surface area analyzer. For APTCNSiOMe $S_{\text{BET}} = 2.3 \text{ m}^2/\text{g}$, for APTCNSiOBu $S_{\text{BET}} = 3.5 \text{ m}^2/\text{g}$.

2. Positron annihilation lifetime spectroscopy (PALS) measurements

The positron annihilation lifetime decay curves were measured at room temperature using an EG&GOrtec “fast-fast” lifetime spectrometer. A nickel-foil-supported [⁴⁴Ti] radioactive positron source was used. Two stacks of film samples, each with a total thickness of about 1 mm, were placed on either side of the source. All the measurements were performed in inert (nitrogen)

atmosphere. The time resolution was 230 ps (full width at the halfmaximum (fwhm) of the prompt coincidence curve). The contribution from annihilation in the source material, a background, and instrumental resolution were taken into account in the PATFIT program for treating the experimental lifetime data. The resulting data were determined as an average value from the several spectra collected for the same sample, having an integral number of counts of at least 10^6 in each spectrum.

PALS is based on the measurements of positron lifetime spectra in polymers – lifetimes τ_i (ns) and corresponding intensities I_i (%). Longer lifetimes τ_3 and τ_4 can be related to the mean size of free volume elements (FVE) in polymers according to Tao-Eldrup formula:¹⁻²

$$\tau_i = \left\{ \lambda_0^T + 2 \left[1 - \frac{R_i}{R_i + \Delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R_i}{R_i + \Delta R} \right) \right] \right\}^{-1},$$

where $\tau_i = \tau_3$ or τ_4 are o-Ps lifetimes and $R_i = R_3$ or R_4 are the radii of FVE expressed in nanoseconds and angstroms respectively; λ_0^T - stands for the intrinsic *ortho*-Ps annihilation rate ($0.7 \cdot 10^9 \text{ s}^{-1}$); $\Delta R = 1.66 \text{ \AA}$ is the fitted empirical parameter.

3. Density measurements

The density of a synthesized polymer was determined using helium pycnometer AccuPyc 1340. For the determination of the density, the polymers' films were used (the thickness was 90-120 μm and the weights of samples were up to 0.7 g).

4. DMA measurements

DMA measurements were performed in the demanded temperature range at 1Hz frequency under Ar at a heating rate 3 K/min or at the constant temperature in the demanded temperature range of frequency. The samples for DMA were 0.40 mm in thickness and 9.53 mm in the diameter and the corresponding measurements were carried out using a Mettler Toledo DMA/SDTA861^e instrument. The cross-link density of the prepared rubbery polytricyclononenes was estimated using the relationship between the storage modulus (G') and cross-link density (ν):³⁻⁵

$$G' = \nu RT/2,$$

where T - is absolute temperature, R is the gas constant.

References

- 1 S. J. Tao, *J. Chem. Phys.*, 1972, **56**, 5499-5510.

- 2 M. Eldrup, D. Lightbody and J. N. Sherwood, *Chem. Phys.*, 1981, **63**, 51-58.
- 3 A. Mujtaba, M. Keller, S. Ilisch, H. J. Radusch, T. Thurn-Albrecht, K. Saalwächter and M. Beiner, *Macromolecules*, 2012, **45**, 6504-6515.
- 4 H. Jiang, W. Su, P. T. Mather and T. J. Bunning, *Polymer*, 1999, **40**, 4593-4602.
- 5 A. Hajighasem and K. Kabiri, *J. Polym. Res.*, 2013, **20**, 218.

5. Supplementary figures

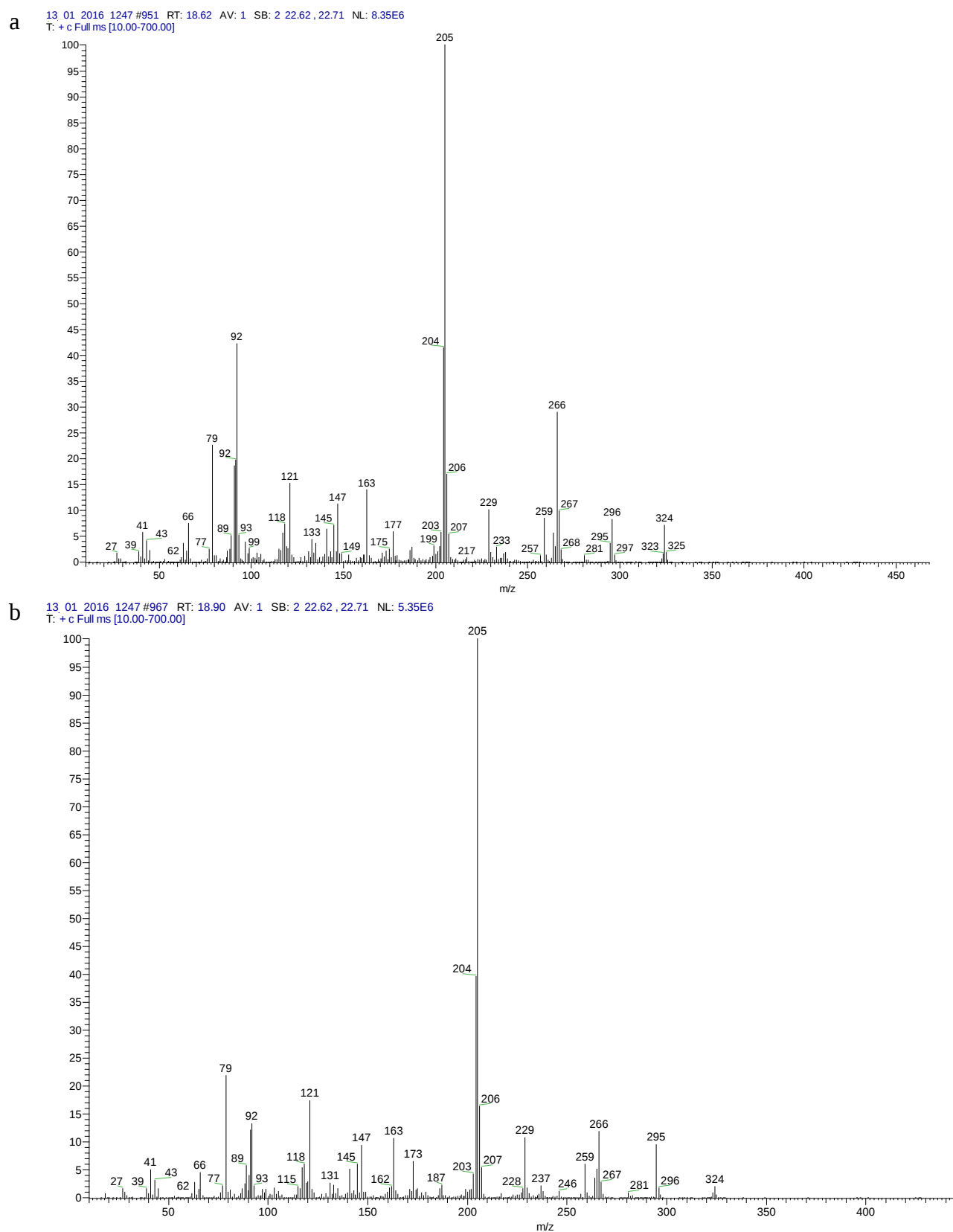


Fig. S1 Mass-spectrum of TCNSiOPr (a - *anti*-isomer, b - *syn*-isomer).

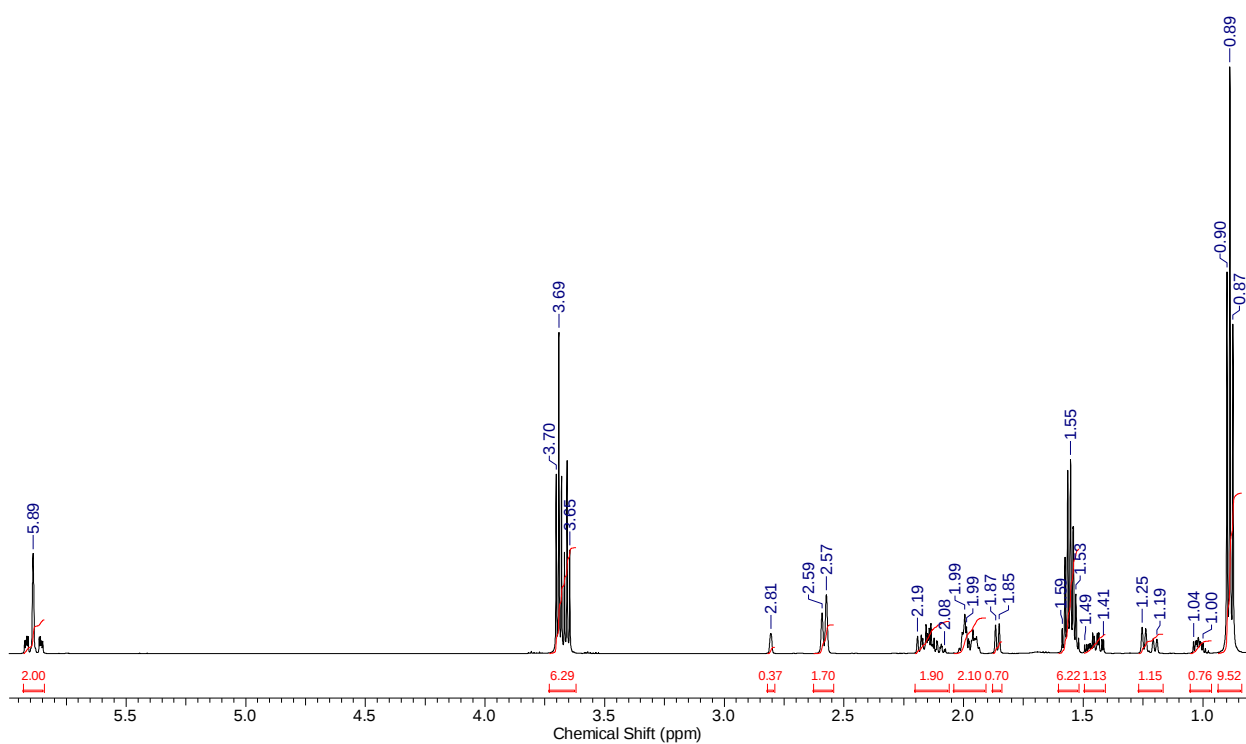


Fig. S2 ¹H NMR spectrum of TCNSiOPr (solvent: CDCl₃).

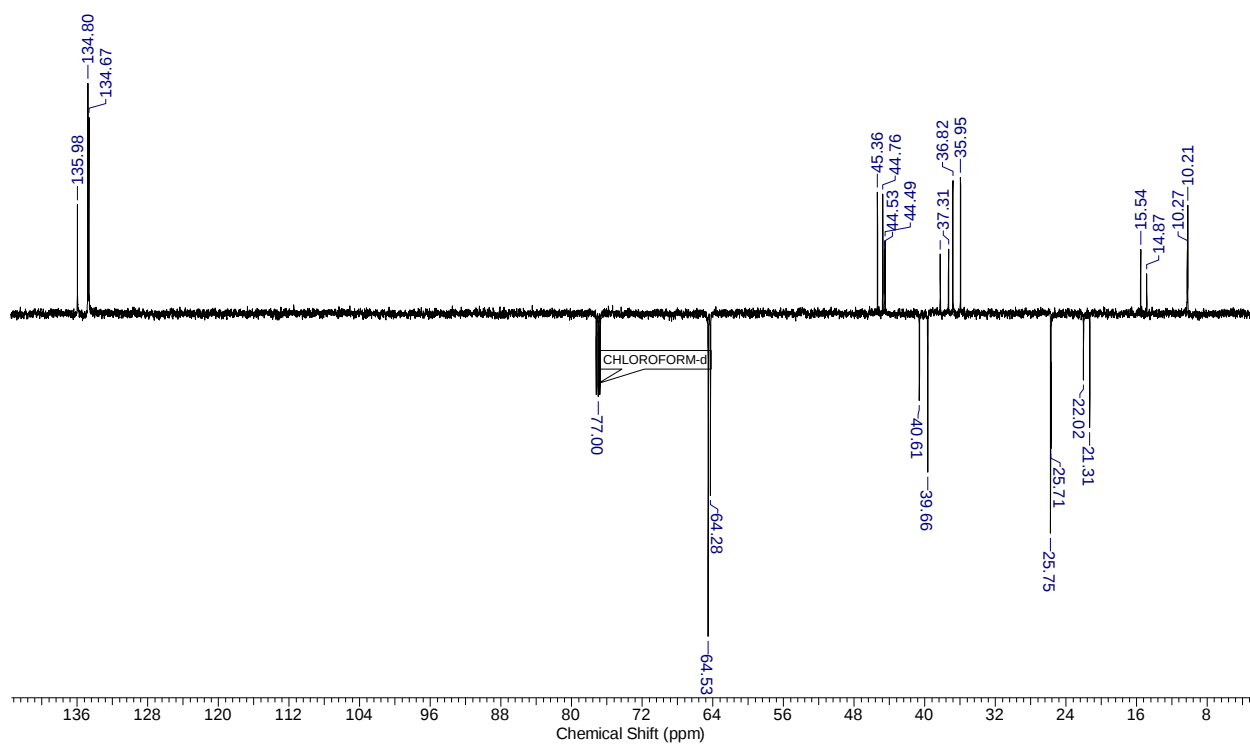


Fig. S3 ¹³C APT NMR spectrum of TCNSiOPr (solvent: CDCl₃).

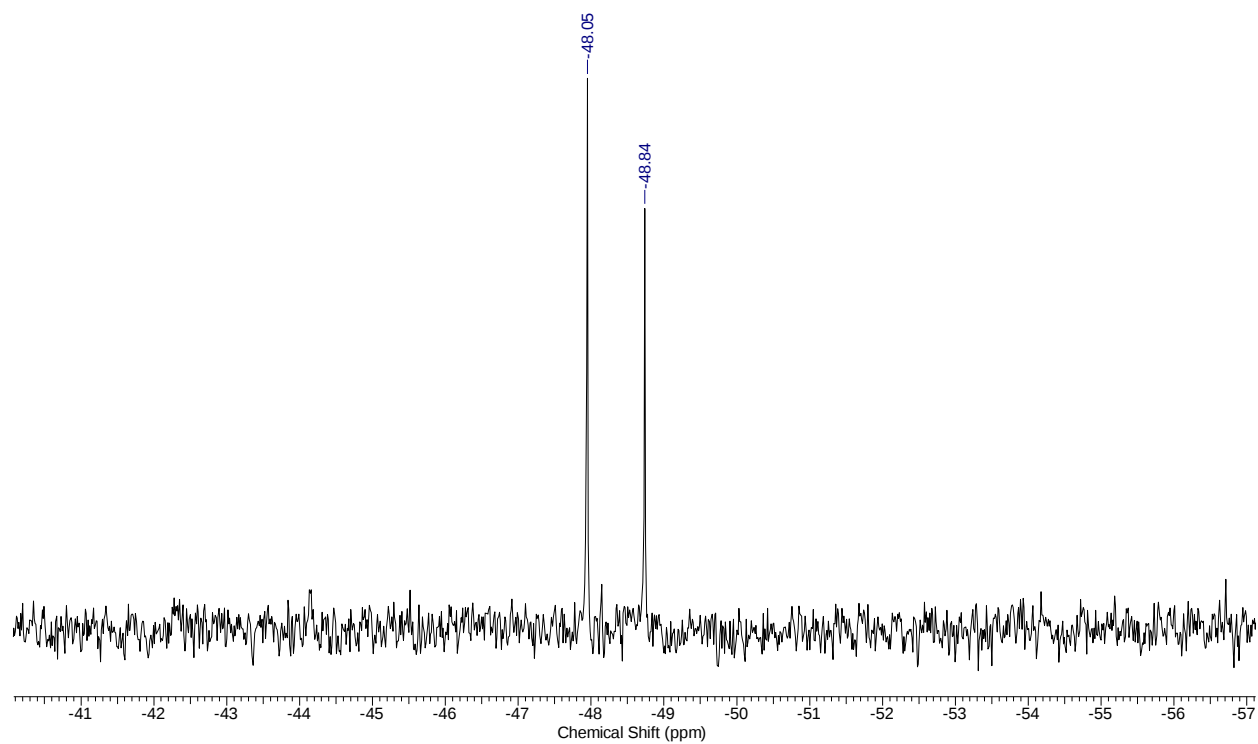


Fig. S4 ^{29}Si NMR spectrum of TCNSiOPr (solvent: CDCl_3).

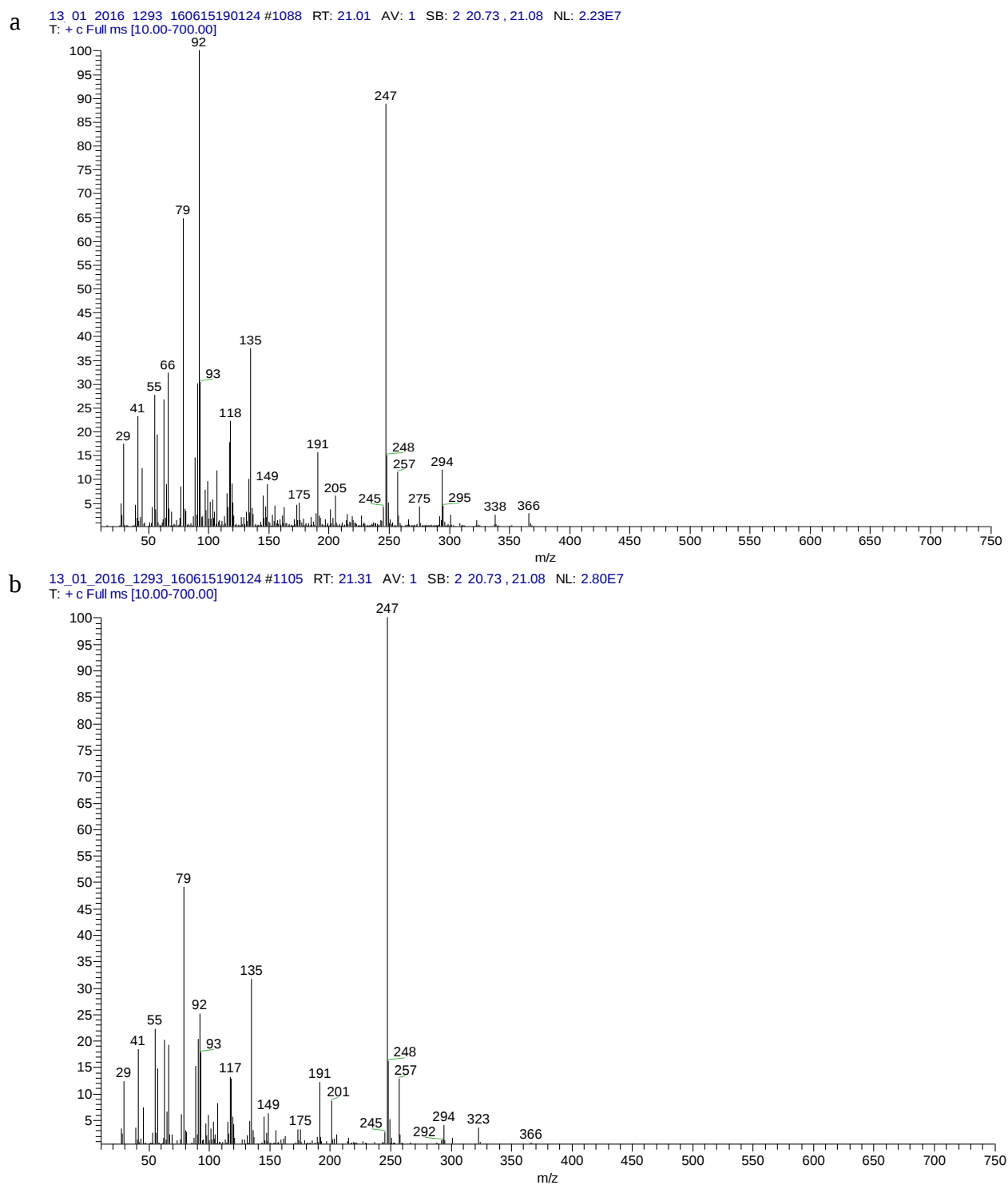


Fig. S5 Mass-spectrum of TCNSiOBu (a - *anti*-isomer, b - *syn*-isomer).

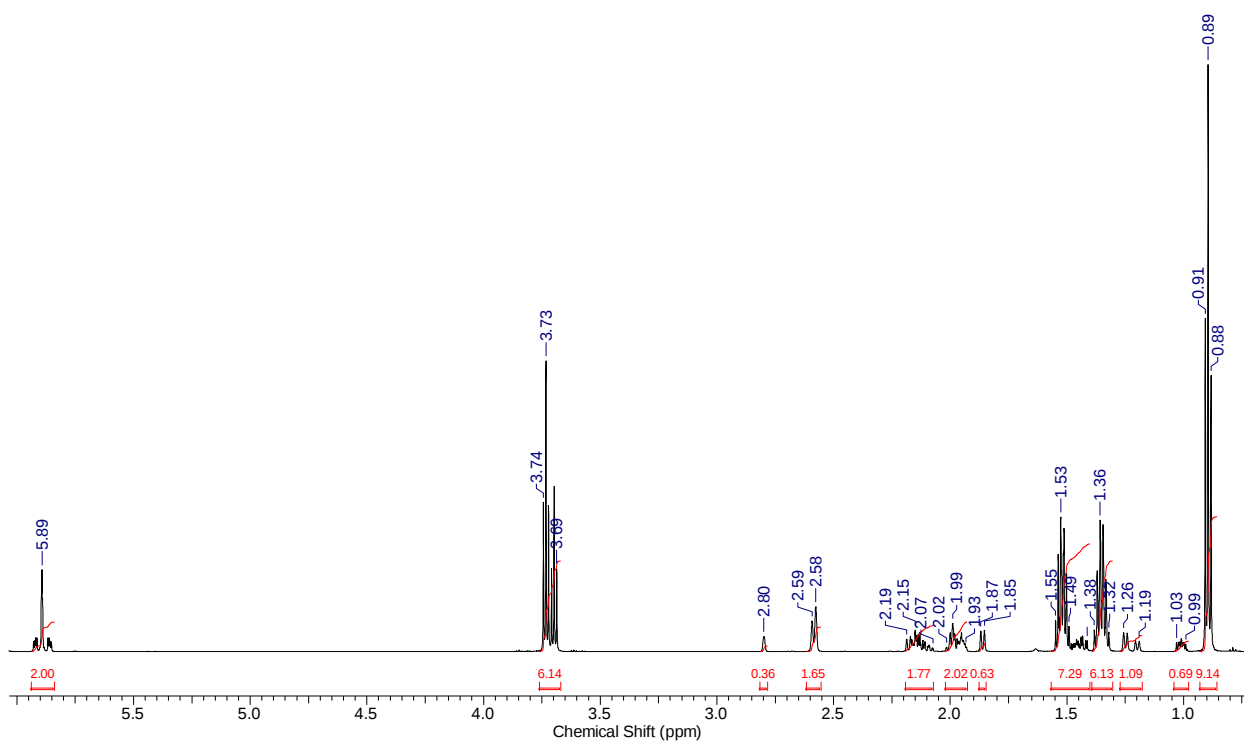


Fig. S6 ^1H NMR spectrum of TCNSiOBu (solvent: CDCl_3).

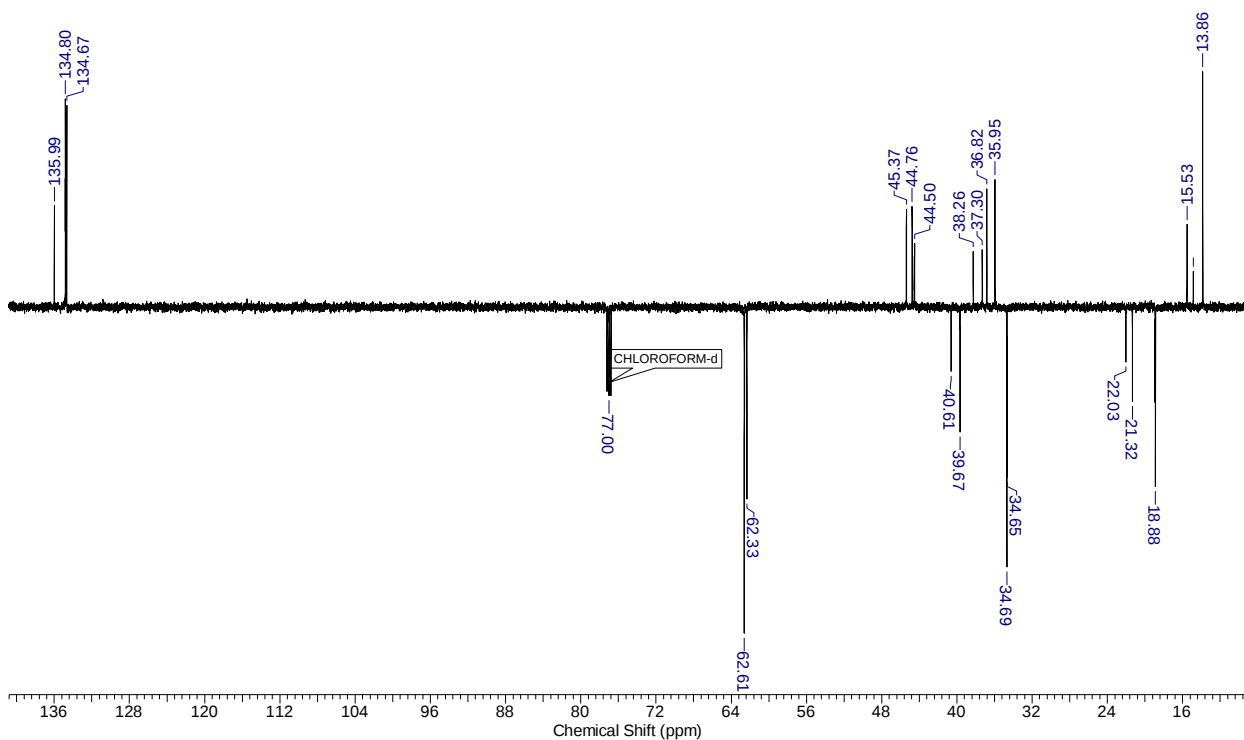


Fig. S7 ^{13}C APT NMR spectrum of TCNSiOBu (solvent: CDCl_3).

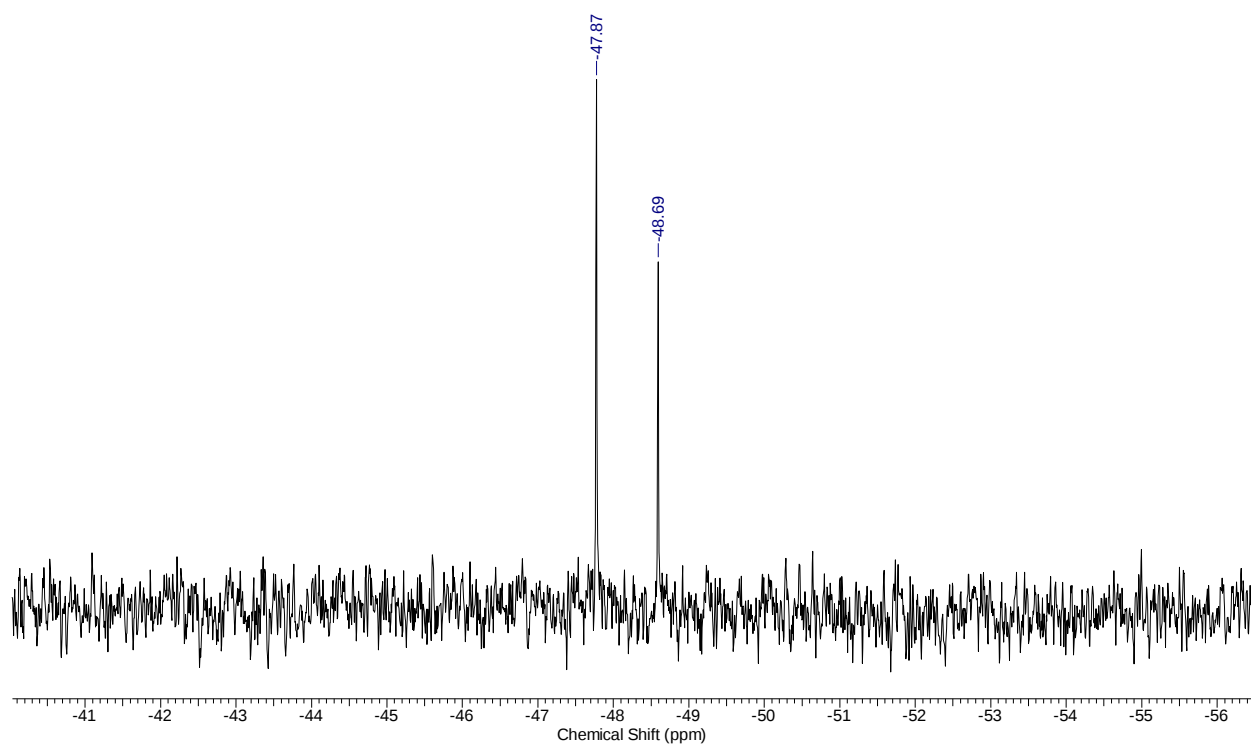


Fig. S8 ^{29}Si NMR spectrum of TCNSiOBu (solvent: CDCl_3).

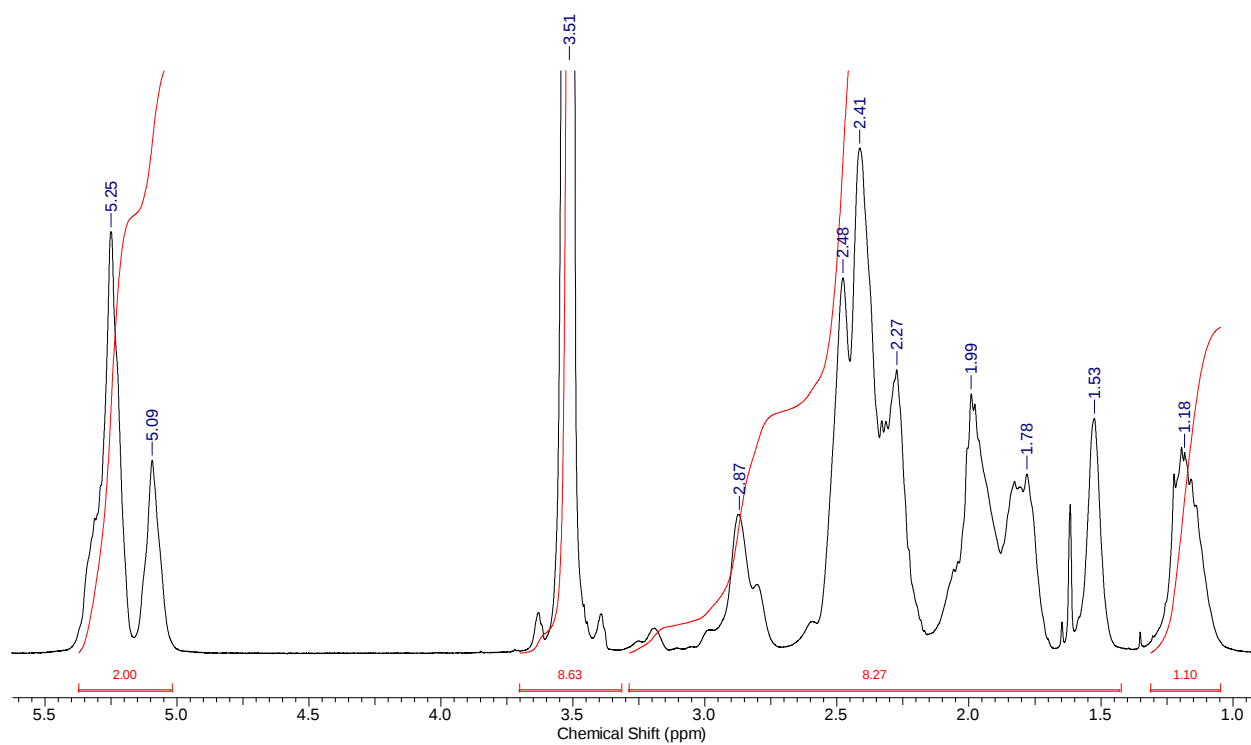


Fig. S9 ^1H NMR spectrum of MPTCNSiOMe (solvent: CDCl_3).

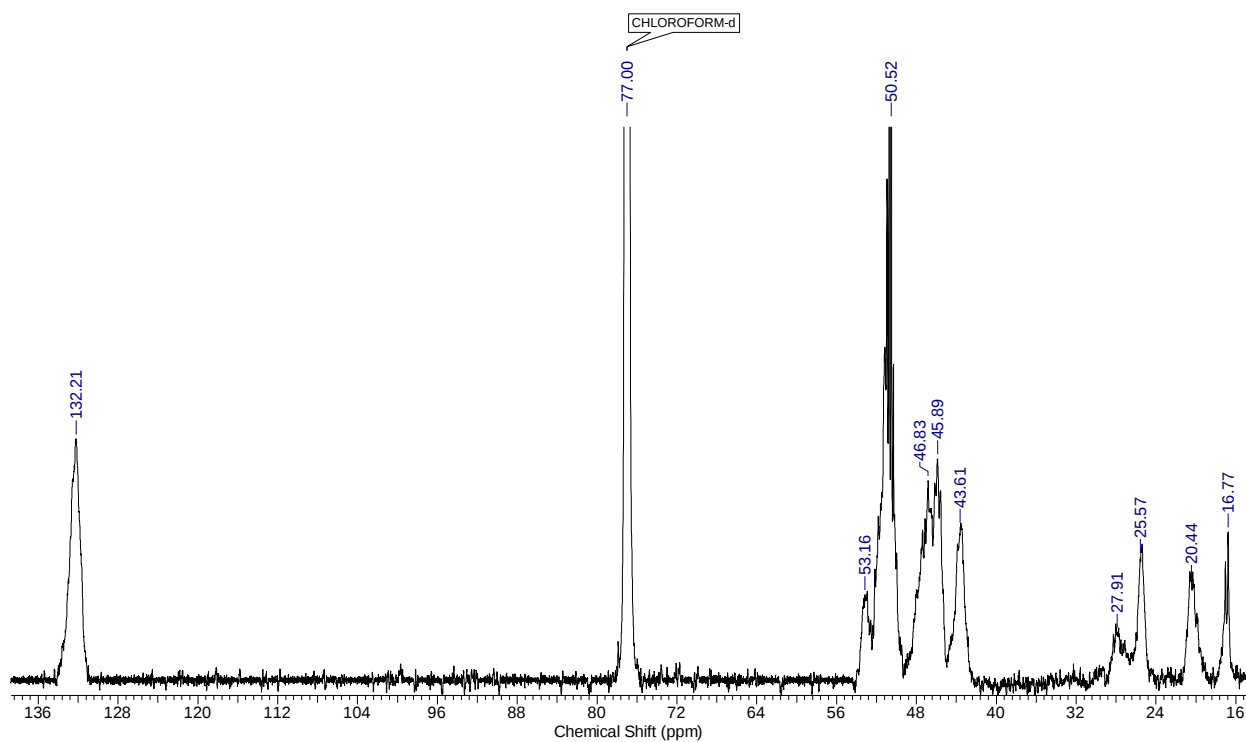


Fig. S10 ¹³C NMR spectrum of MPTCNSiOMe (solvent: CDCl₃).

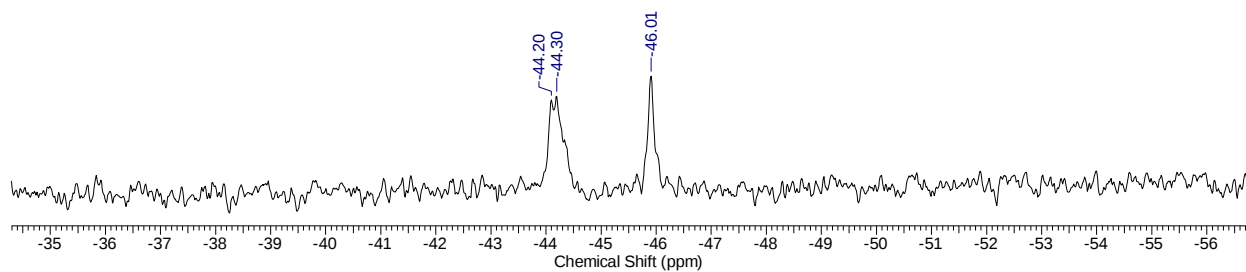


Fig. S11 ²⁹Si NMR spectrum of MPTCNSiOMe (solvent: CDCl₃).

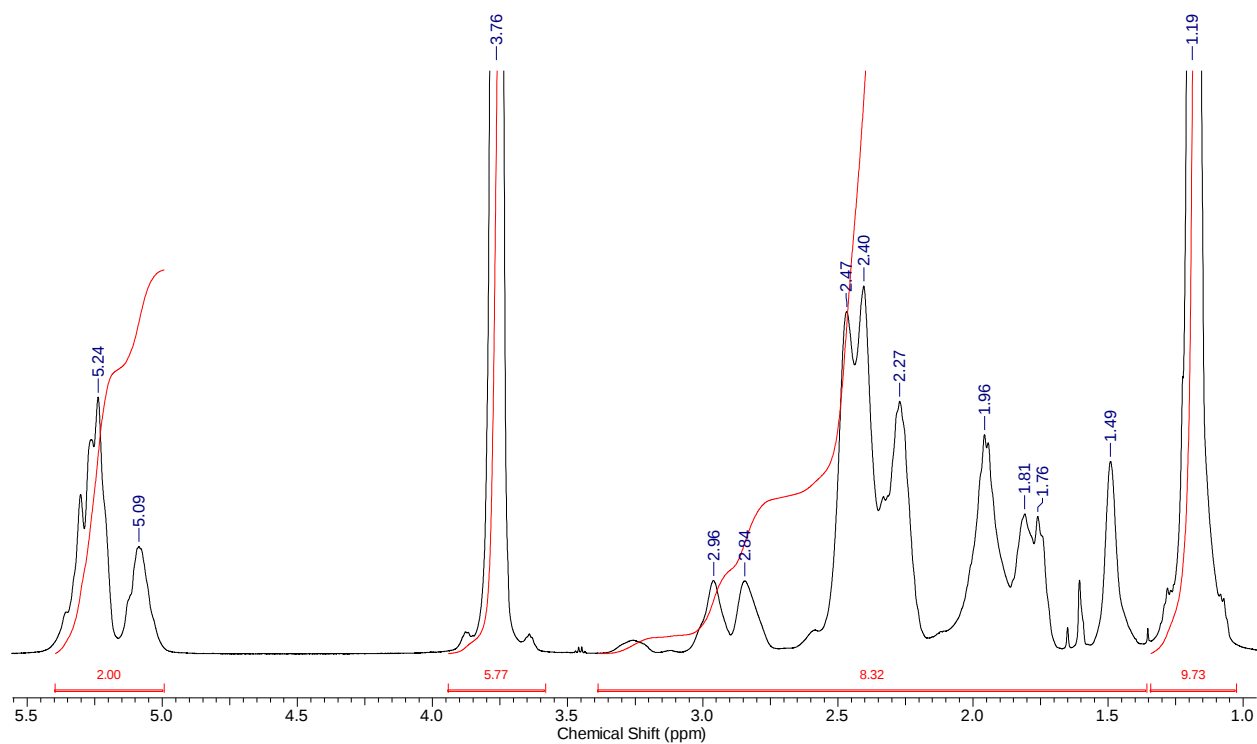


Fig. S12 ¹H NMR spectrum of MPTCNSiOEt (solvent: CDCl₃).

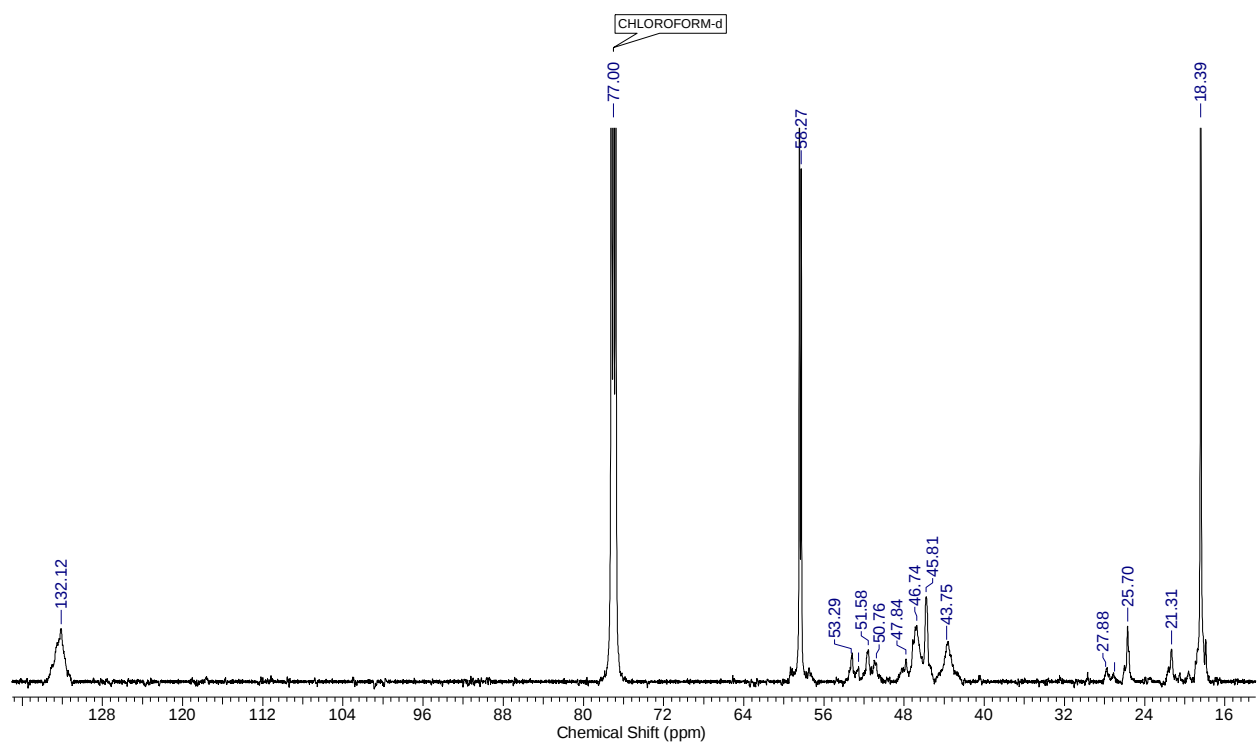


Fig. S13 ¹³C NMR spectrum of MPTCNSiOEt (solvent: CDCl₃).

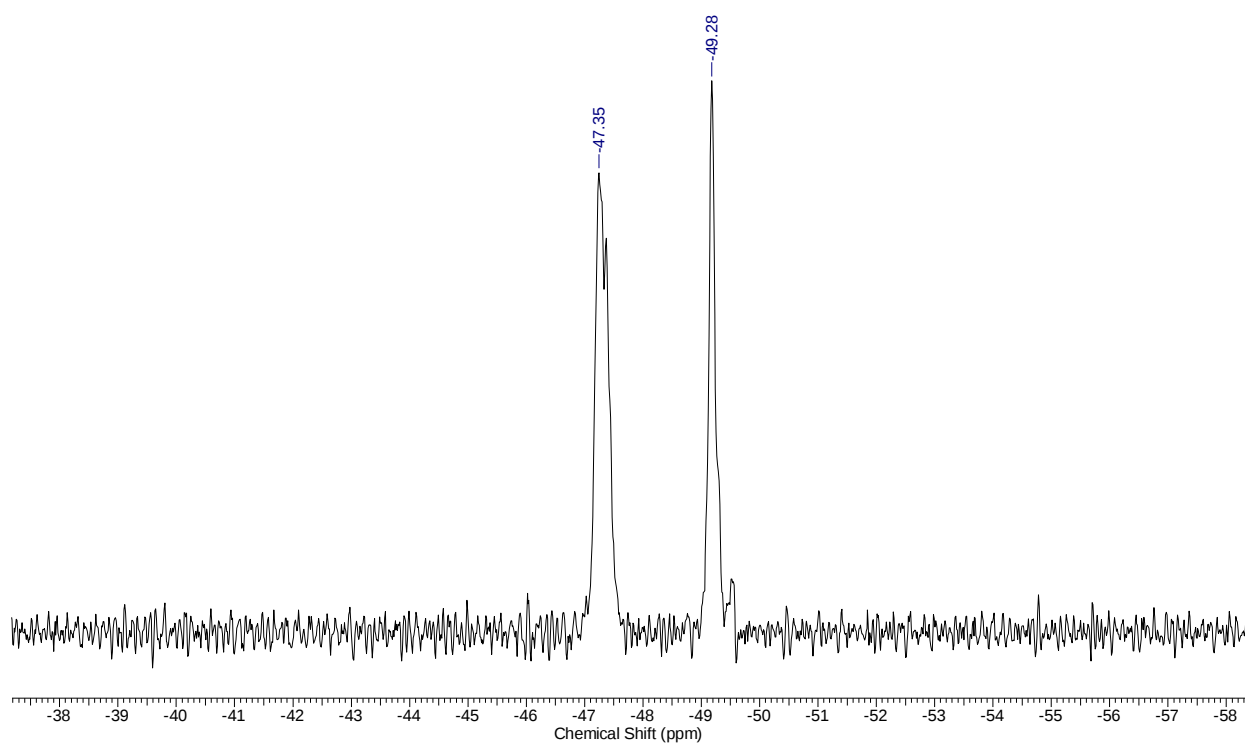


Fig. S14 ^{29}Si NMR spectrum of MPTCNSiOEt (solvent: CDCl_3).

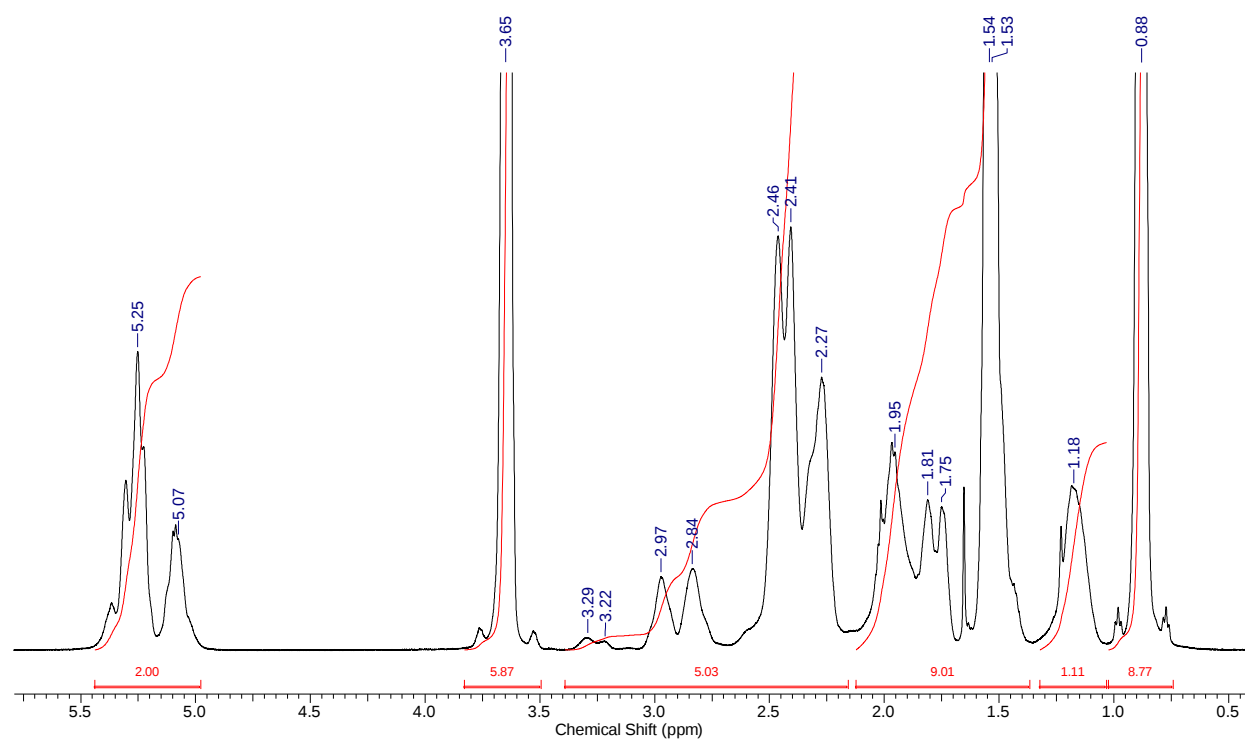


Fig. S15 ^1H NMR spectrum of MPTCNSiOPr (solvent: CDCl_3).

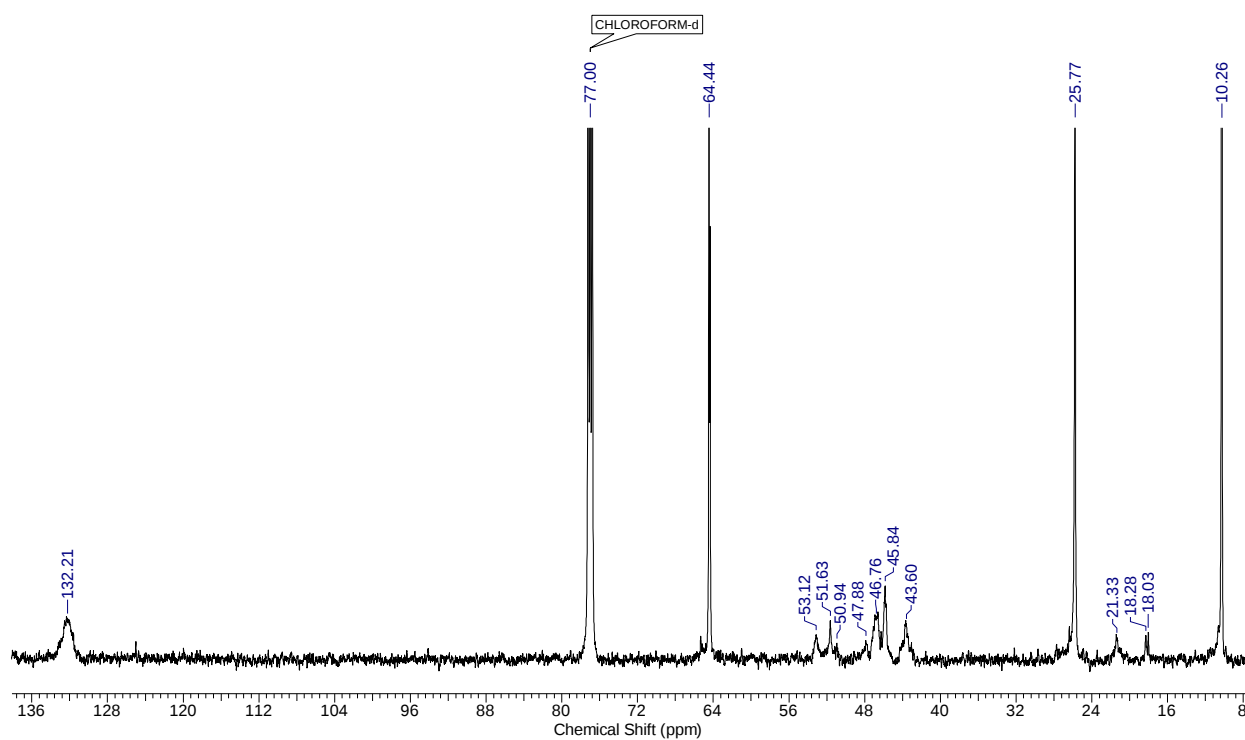


Fig. S16 ^{13}C NMR spectrum of MPTCNSiOPr (solvent: CDCl_3).

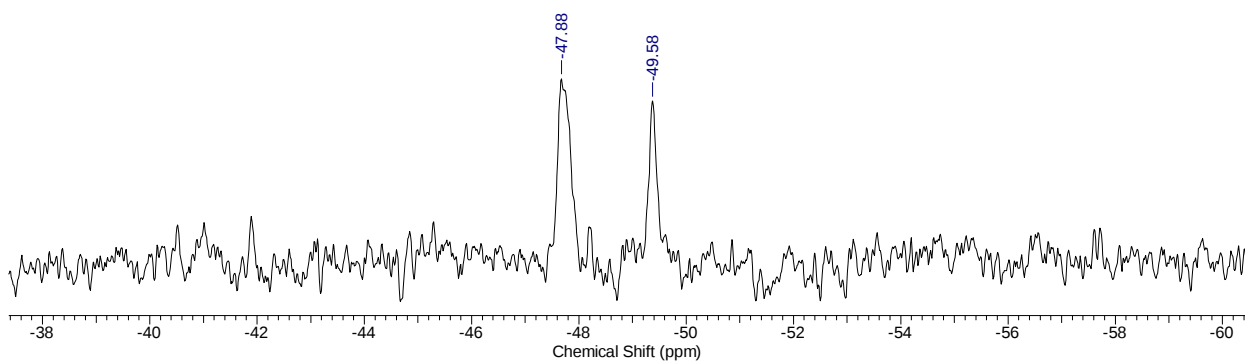


Fig. S17 ^{29}Si NMR spectrum of MPTCNSiOPr (solvent: CDCl_3).

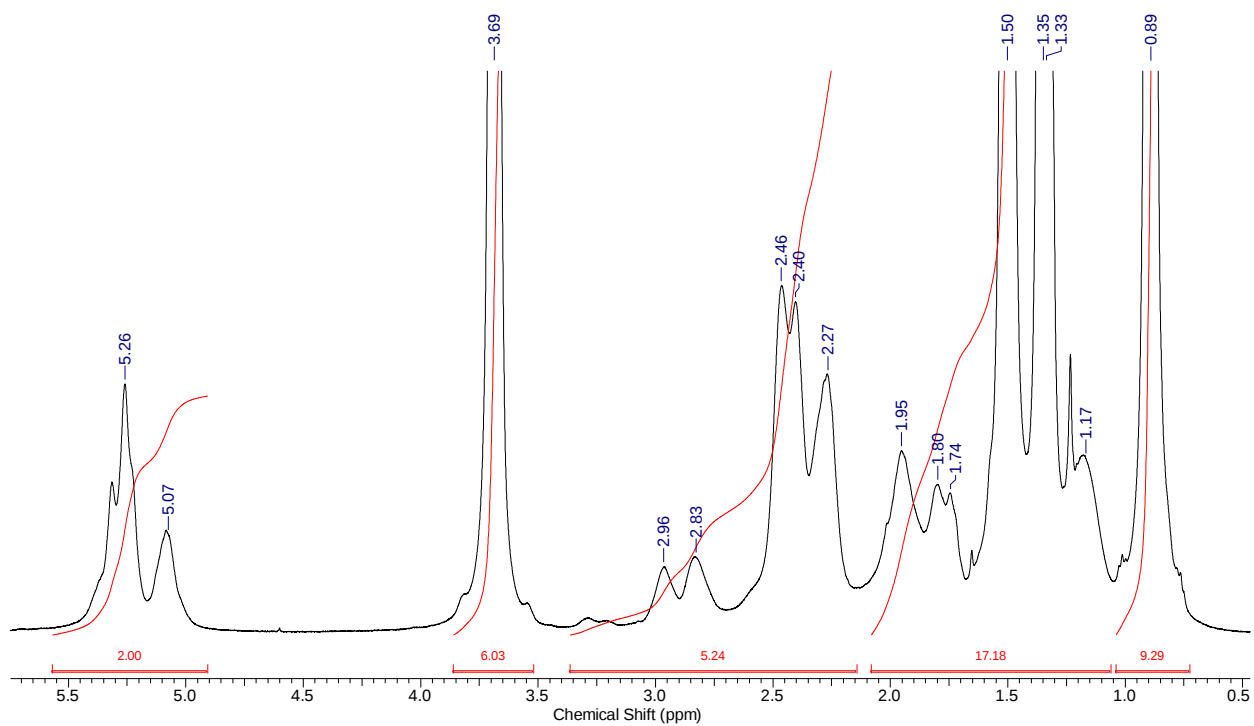


Fig. S18 ¹H NMR spectrum of MPTCNSiOBu (solvent: CDCl₃).

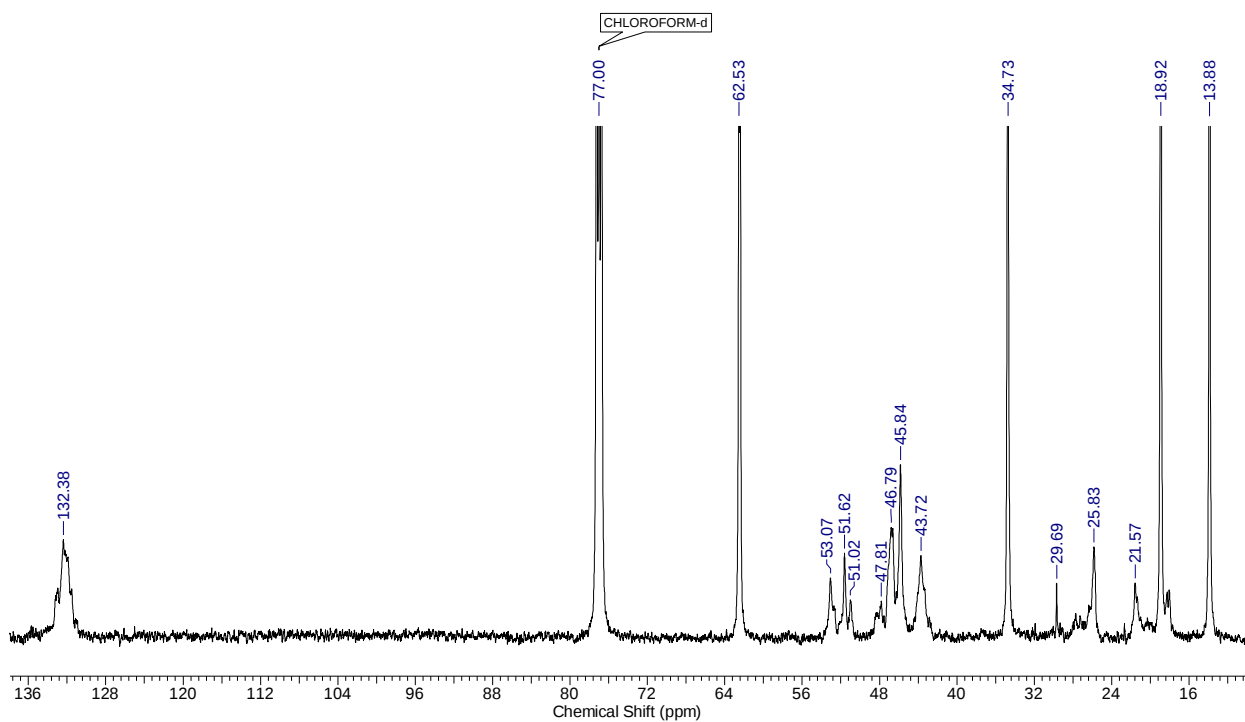


Fig. S19 ¹³C NMR spectrum of MPTCNSiOBu (solvent: CDCl₃).

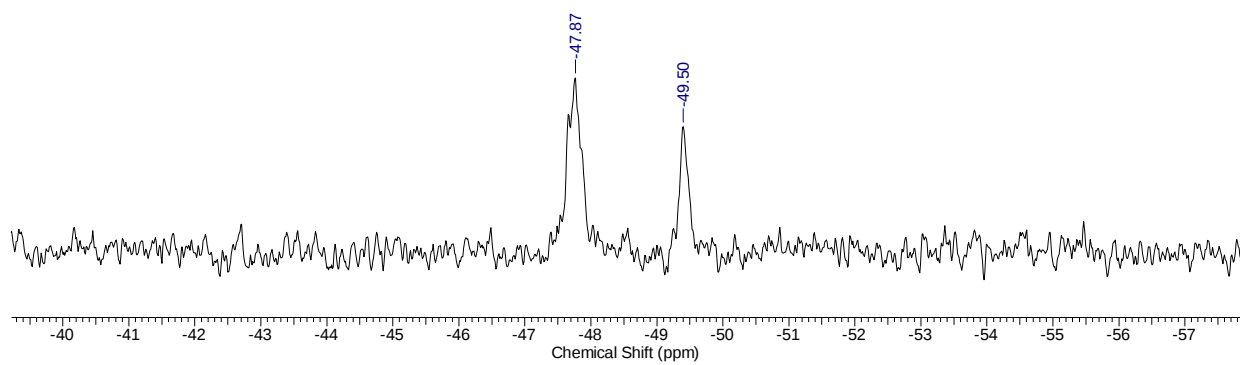


Fig. S20 ²⁹Si NMR spectrum of MPTCNSiOBu (solvent: CDCl₃).

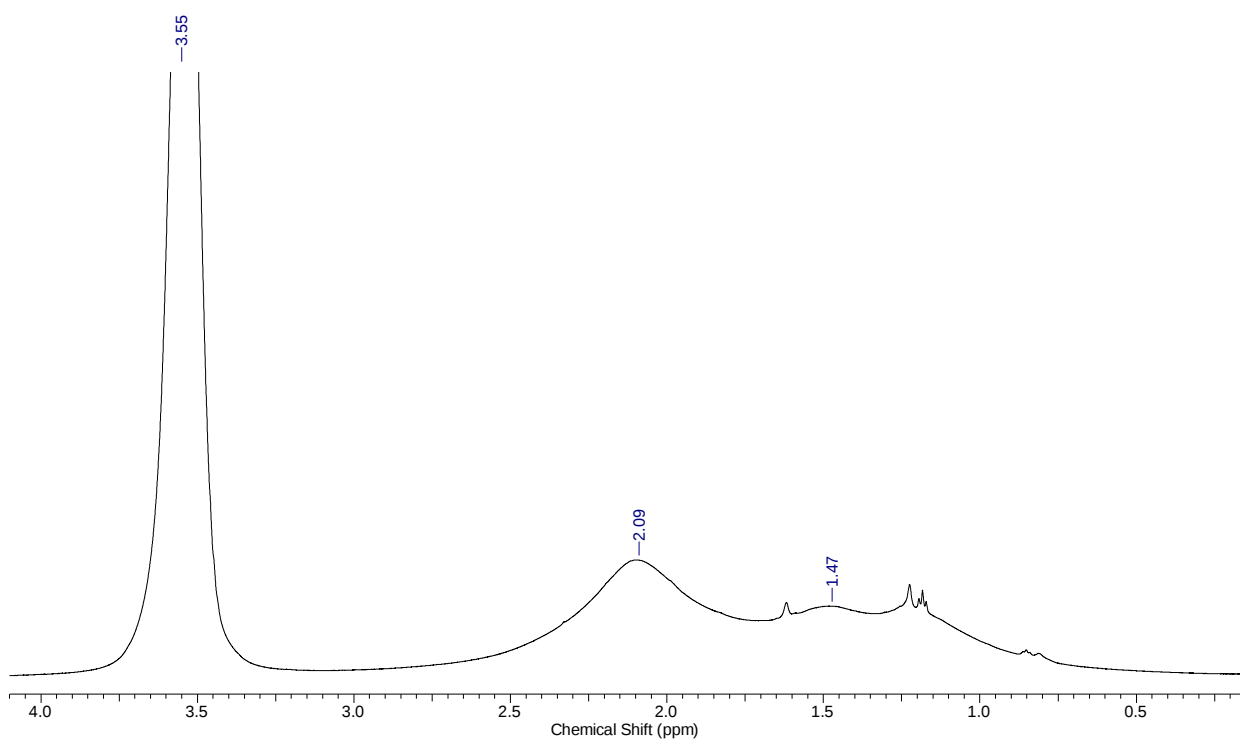


Fig. S21 ¹H NMR spectrum of APTCNSiOMe (solvent: CDCl₃).

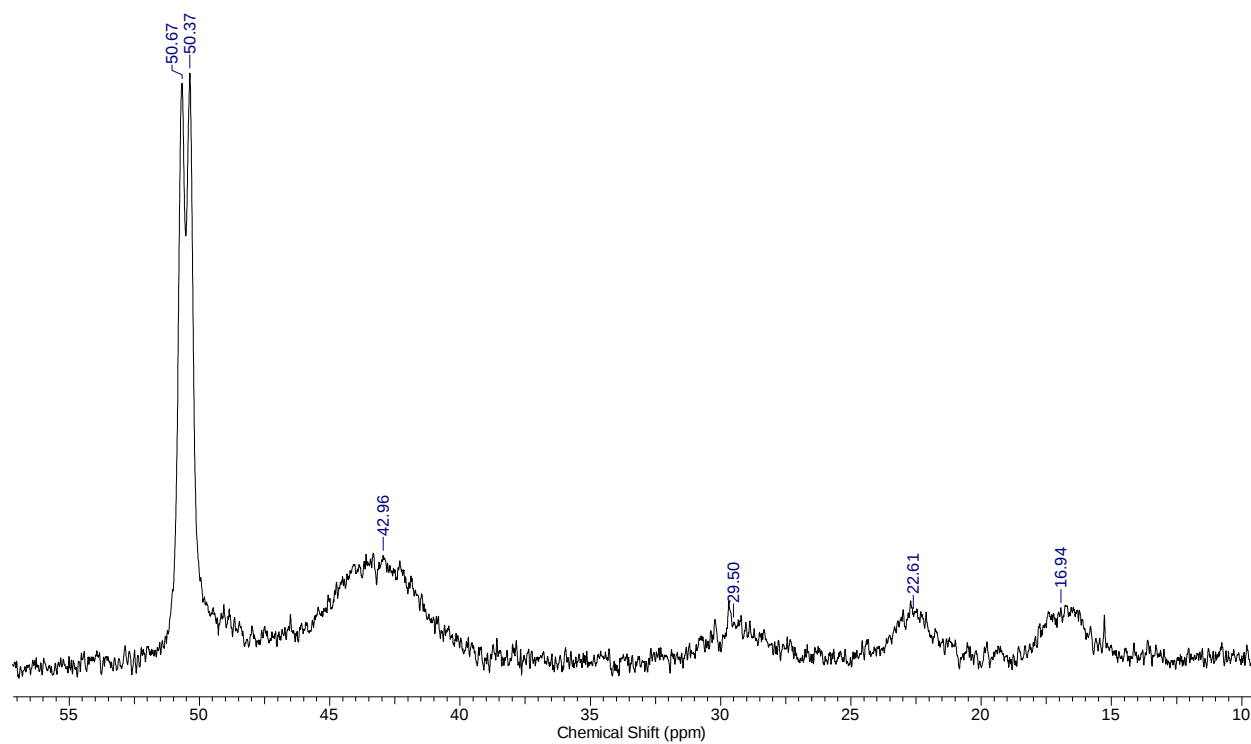


Fig. S22 ¹³C NMR spectrum of APTCNSiOMe (solvent: CDCl₃).

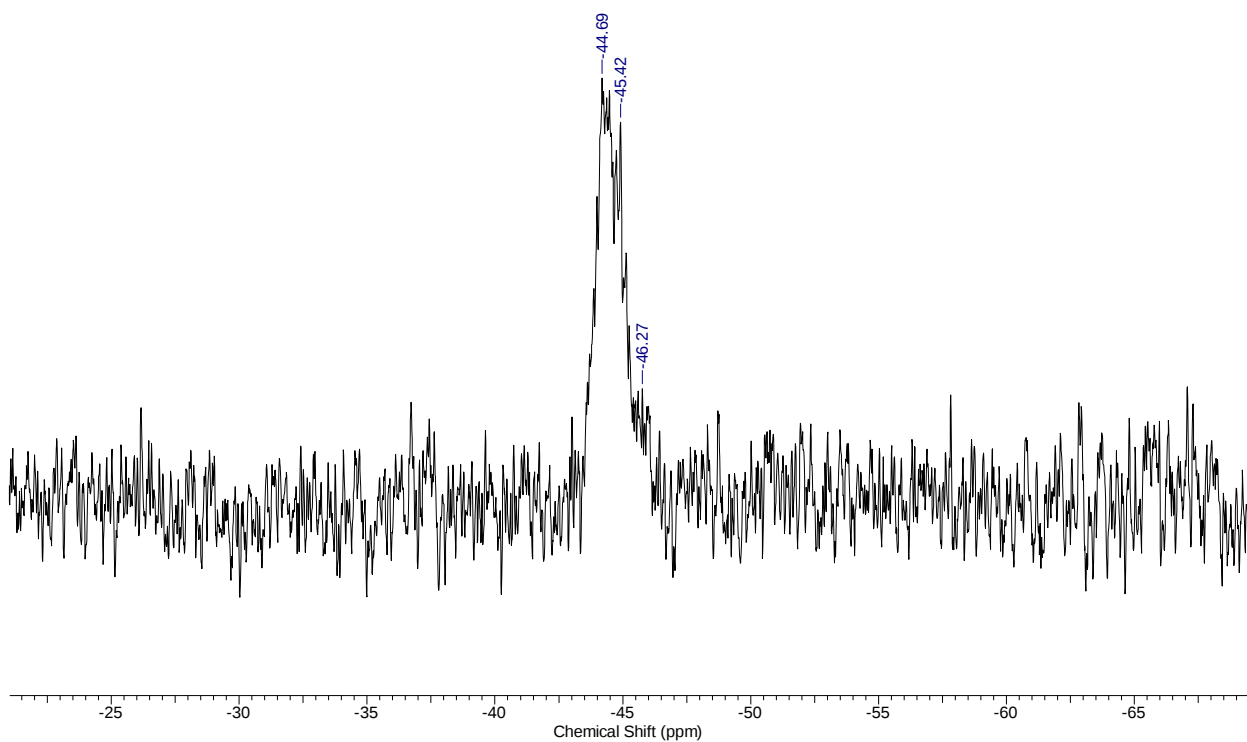


Fig. S23 ²⁹Si NMR spectrum of APTCNSiOMe (solvent: CDCl₃).

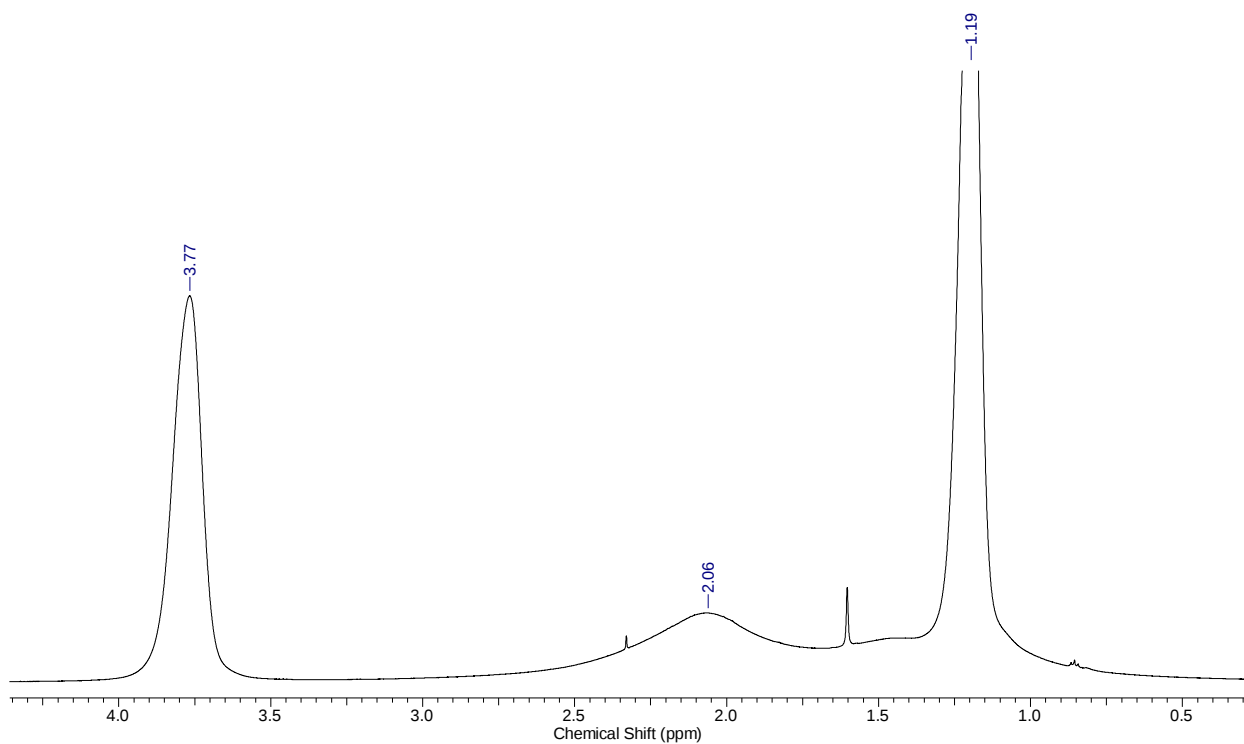


Fig. S24 ^1H NMR spectrum of APTCNSiOEt (solvent: CDCl_3).

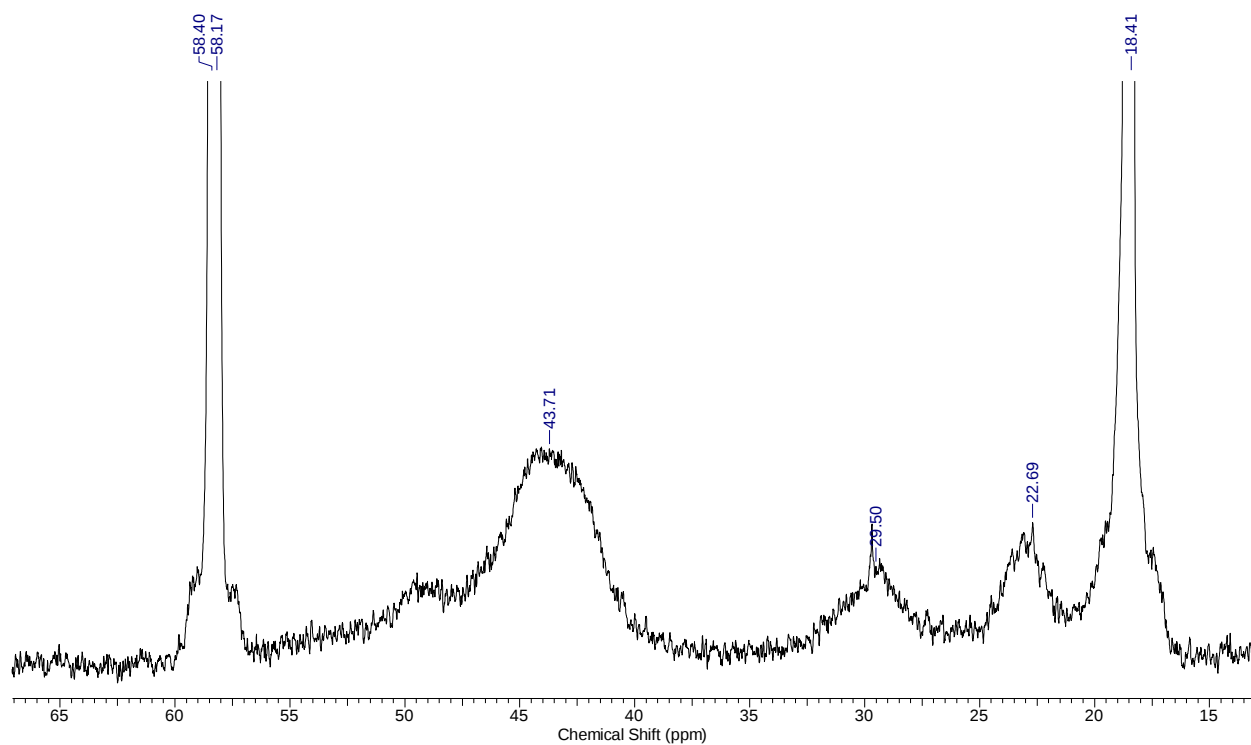


Fig. S25 ^{13}C NMR spectrum of APTCNSiOEt (solvent: CDCl_3).

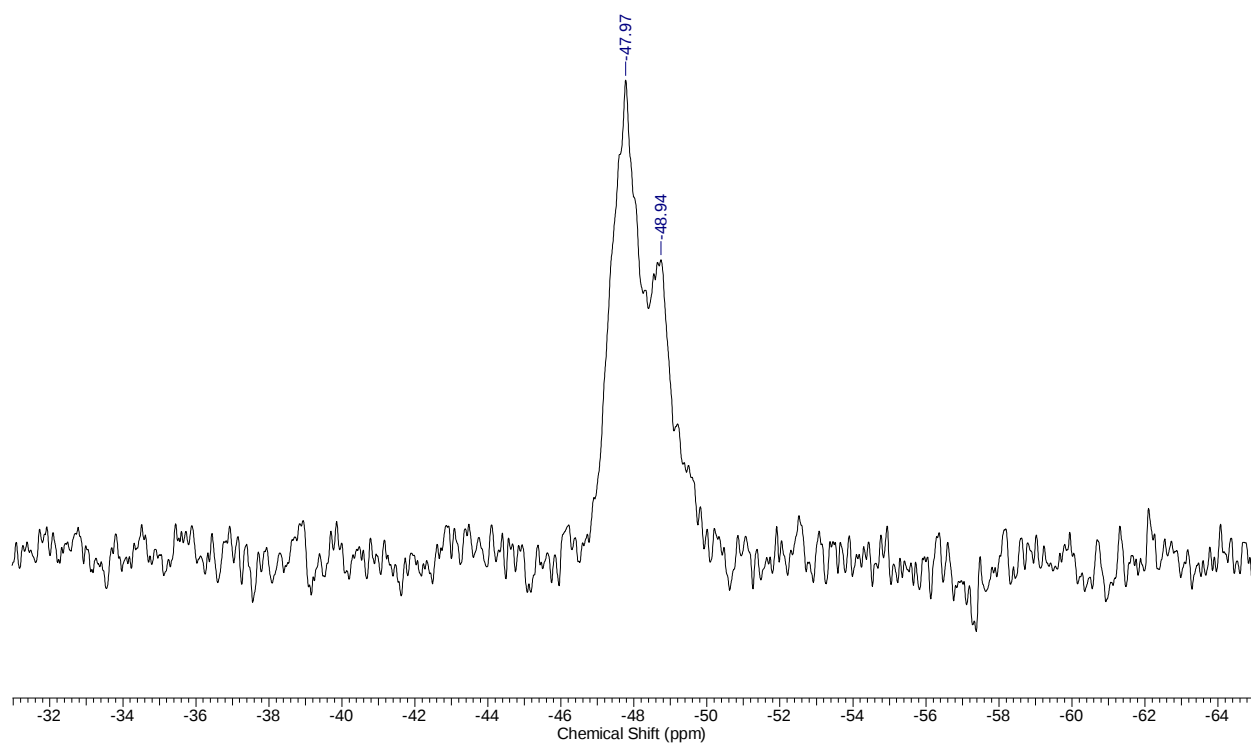


Fig. S26 ^{29}Si NMR spectrum of APTCNSiOEt (solvent: CDCl_3).

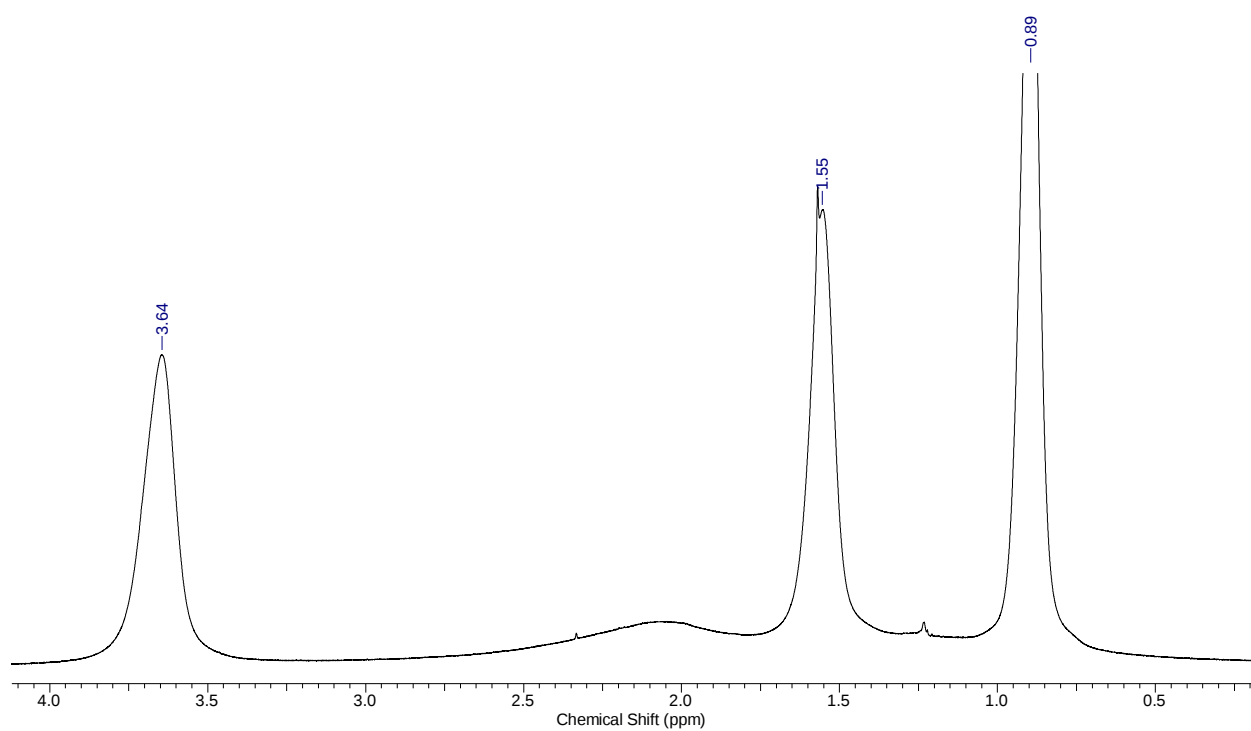


Fig. S27 ^1H NMR spectrum of APTCNSiOPr (solvent: CDCl_3).

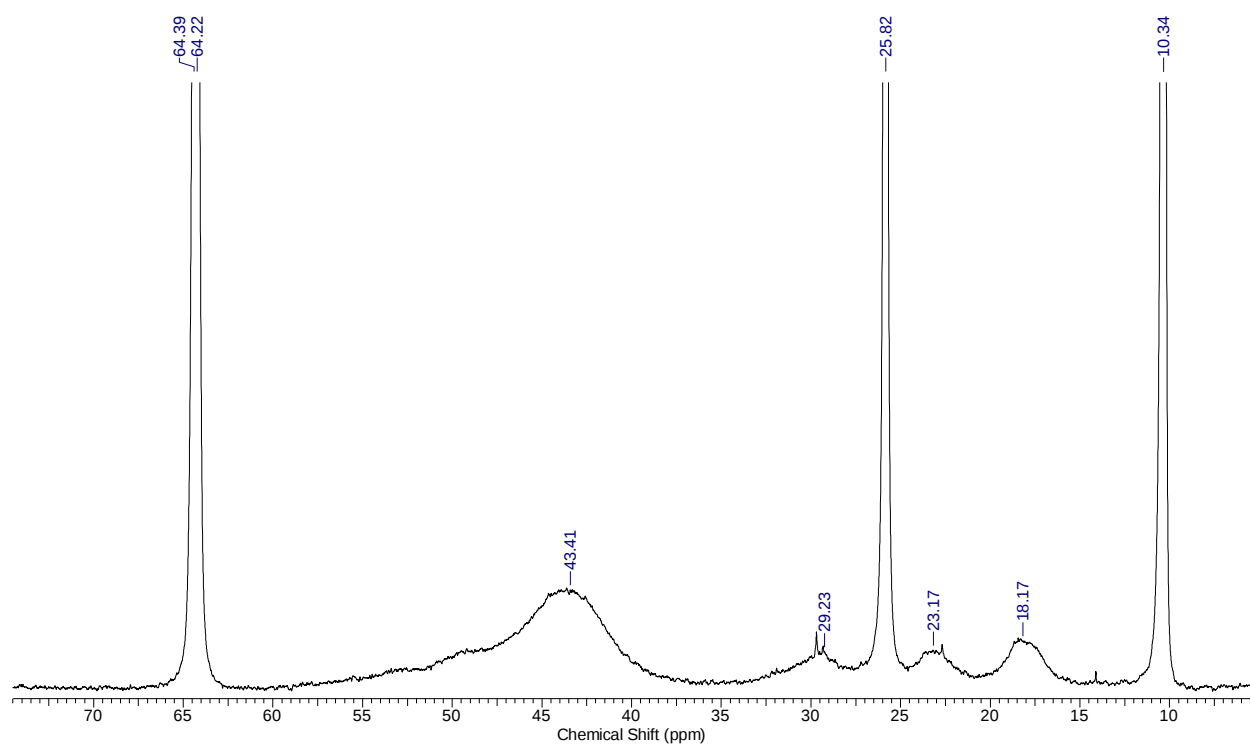


Fig. S28 ^{13}C NMR spectrum of APTCNSiOPr (solvent: CDCl_3).

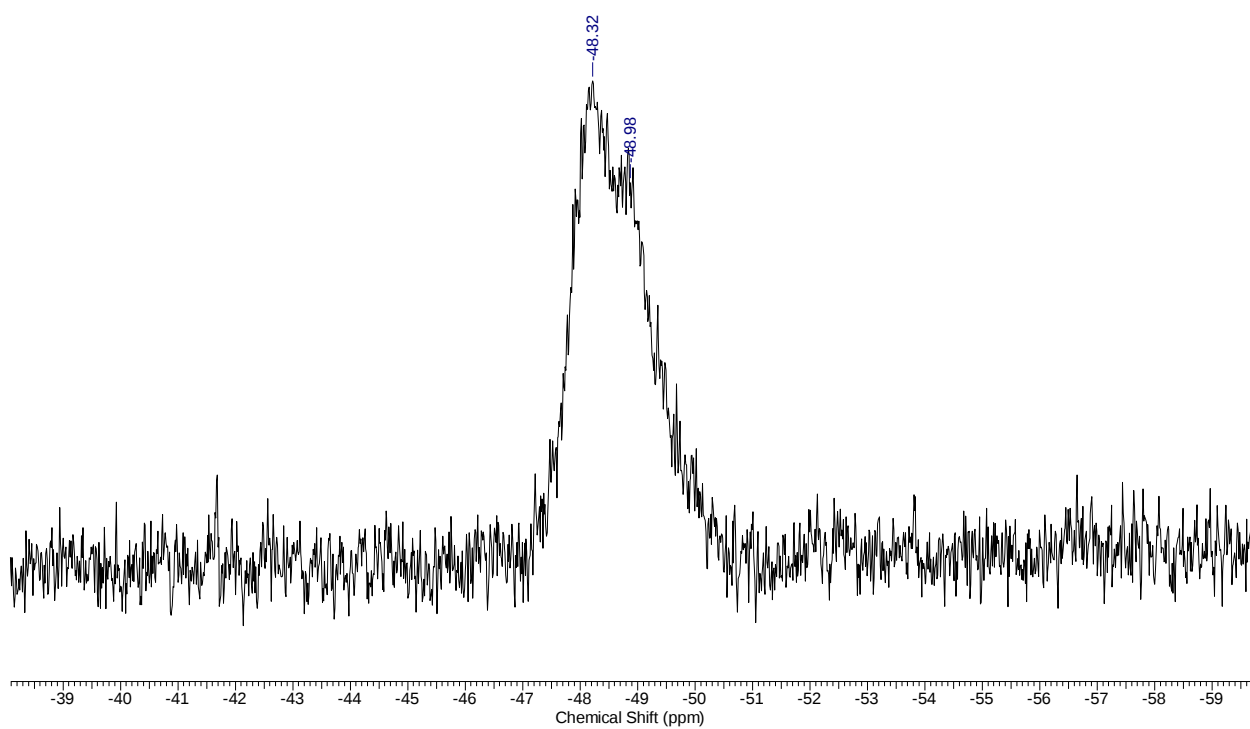


Fig. S29 ^{29}Si NMR spectrum of APTCNSiOPr (solvent: CDCl_3).

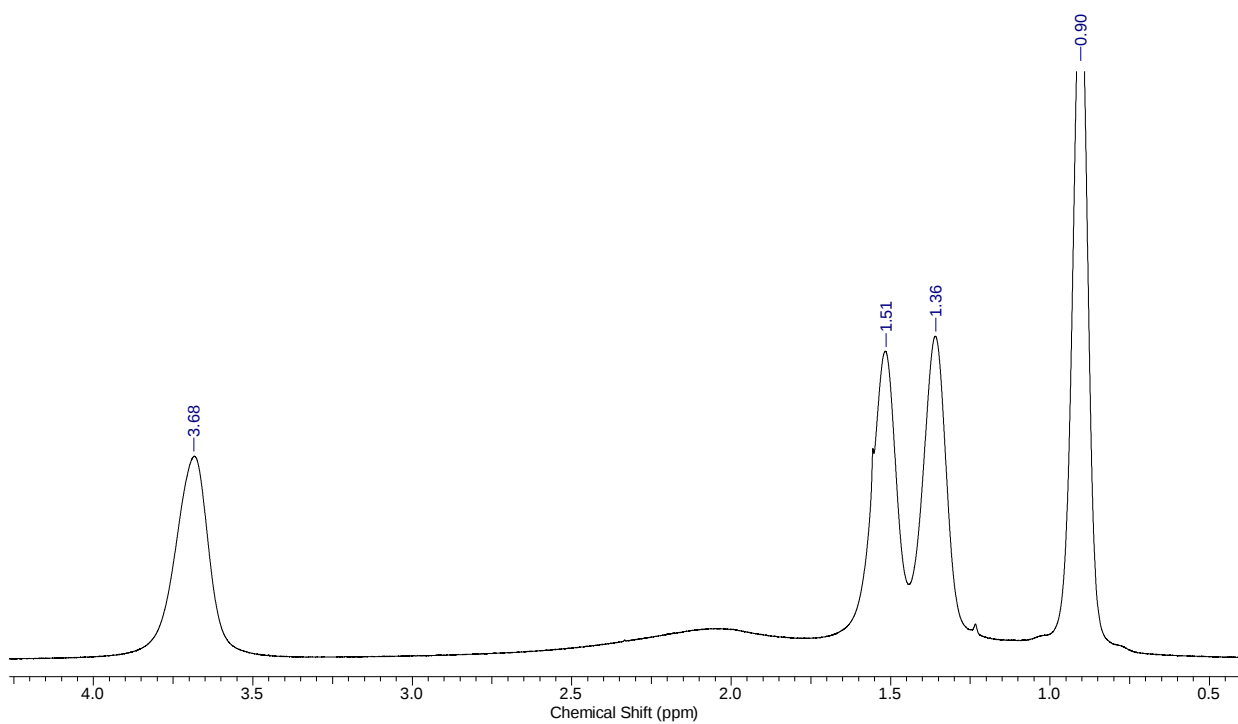


Fig. S30 ¹H NMR spectrum of APTCNSiOBu (solvent: CDCl₃).

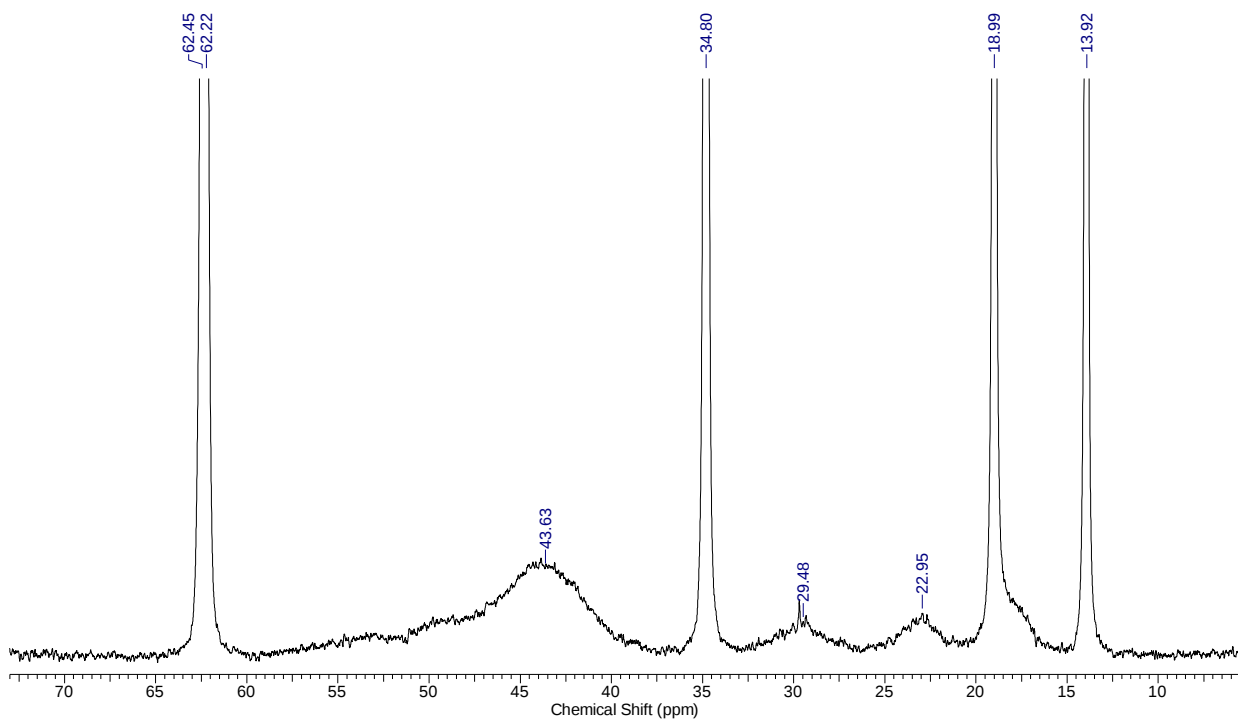


Fig. S31 ¹³C NMR spectrum of APTCNSiOBu (solvent: CDCl₃).

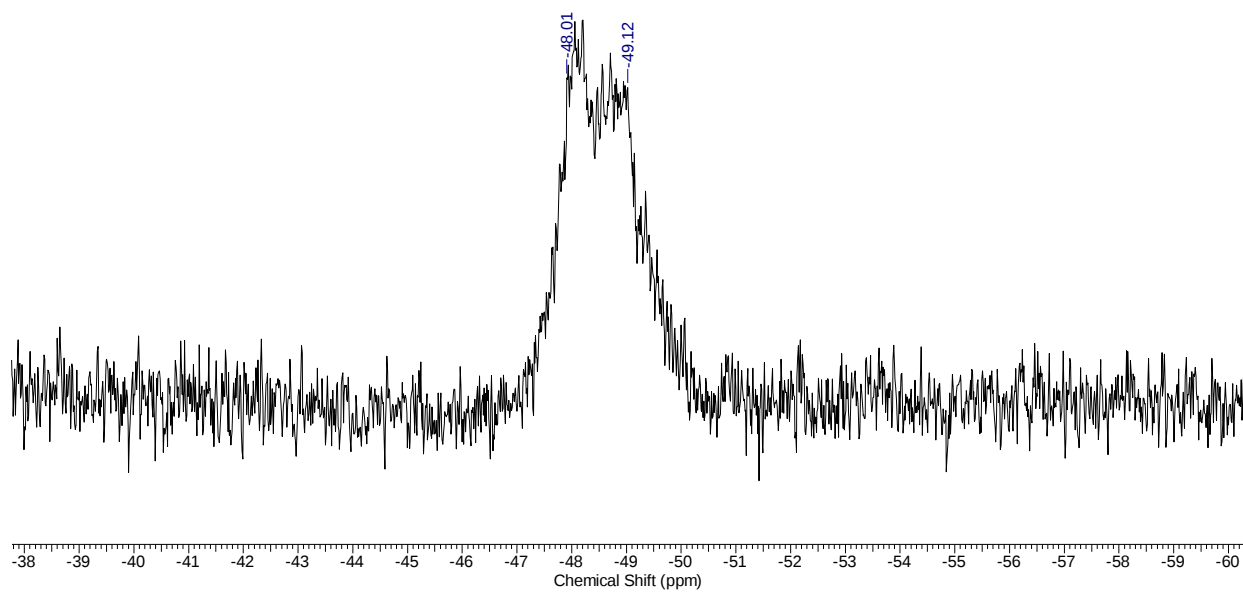


Fig. S32 ^{29}Si NMR spectrum of APTCNSiOBu (solvent: CDCl_3).

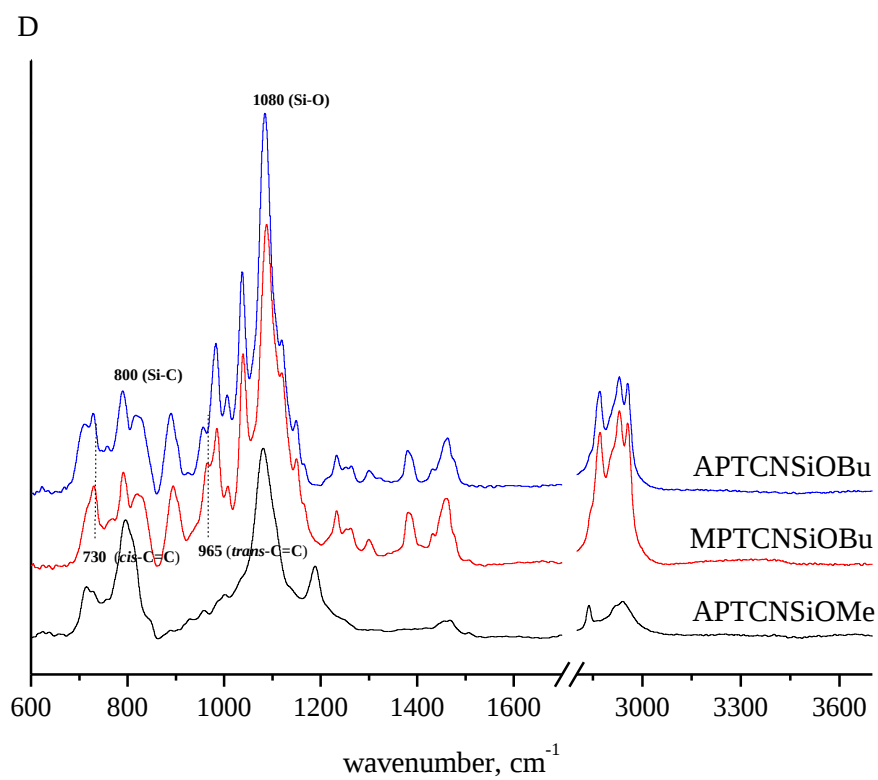


Fig. S33 IR spectra of metathesis and addition poly(TCNSiOAlk)es.

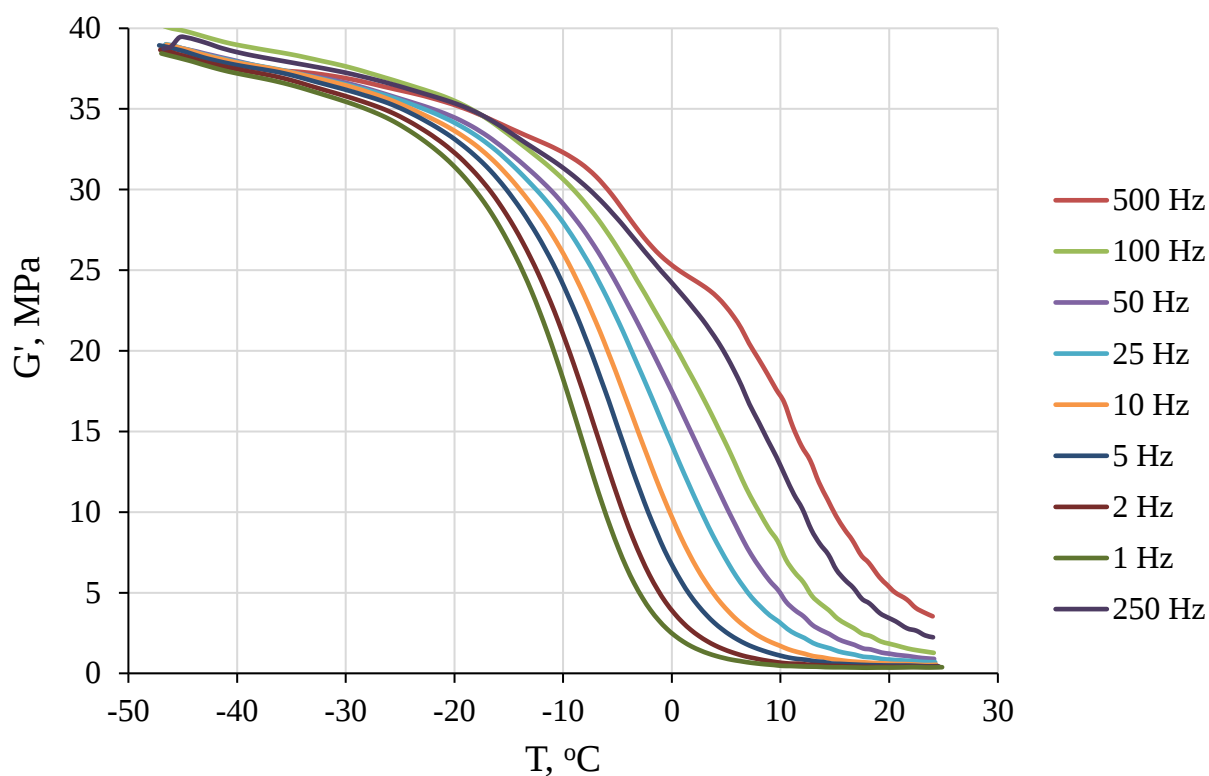


Fig. S34 Plot of storage modulus versus temperature from DMA analysis for cross-linked MPTCNSiOPr at different frequencies.

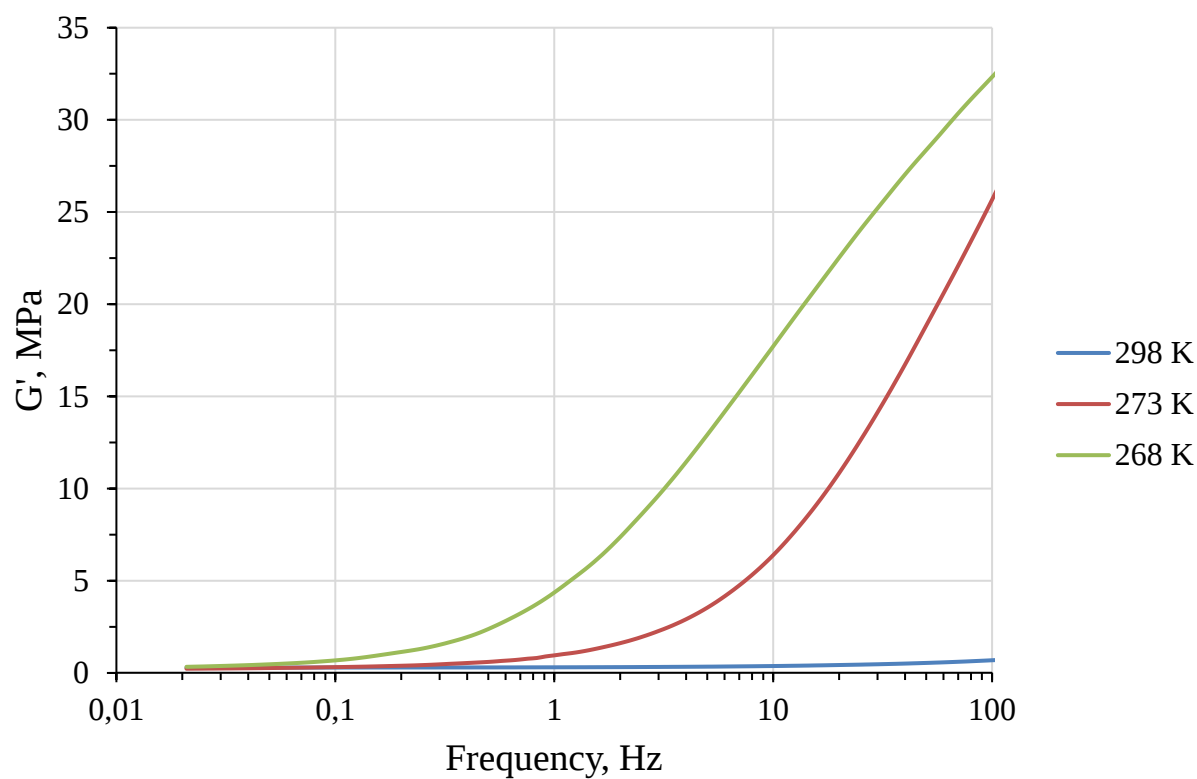


Fig. S35 Plot of storage modulus versus frequency from DMA analysis for cross-linked MPTCNSiOPr at different temperatures.