Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

One-pot strategy for synthesis of open-cage silsesquioxane monomers

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1. NMR spectra

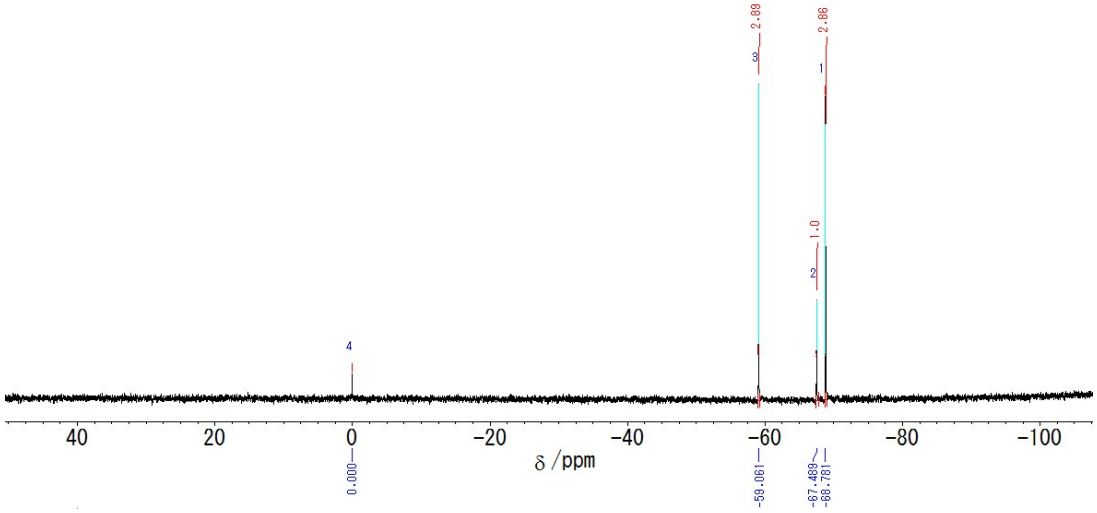


Figure S1. ^{29}Si NMR spectrum (80 MHz) of $\mathbf{1}_{\mathbf{\textit{i}Bu}}$ in $CDCl_3$.

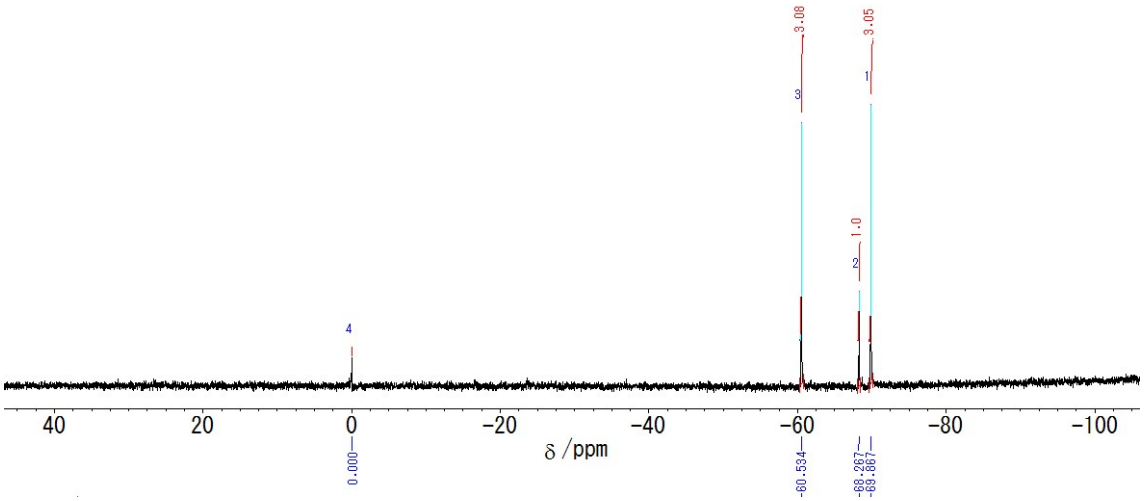


Figure S2. ^{29}Si NMR spectrum (80 MHz) of $\mathbf{1}_{\mathbf{Cyh}}$ in $CDCl_3$.

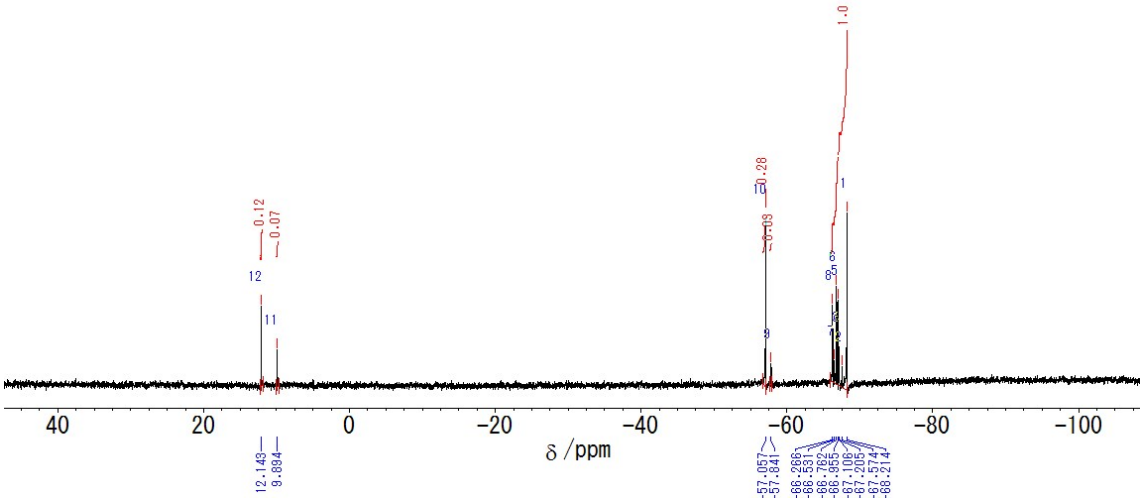


Figure S3. ^{29}Si NMR spectrum (80 MHz) of run 1 of Table 1 in $CDCl_3$.

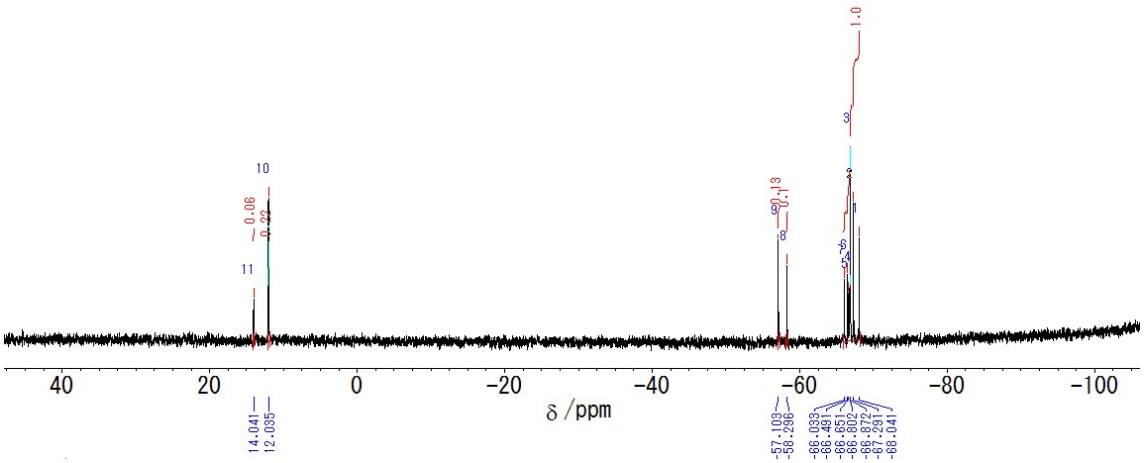


Figure S4. ^{29}Si NMR spectrum (80 MHz) of run 2 of Table 1 in $CDCl_3$.

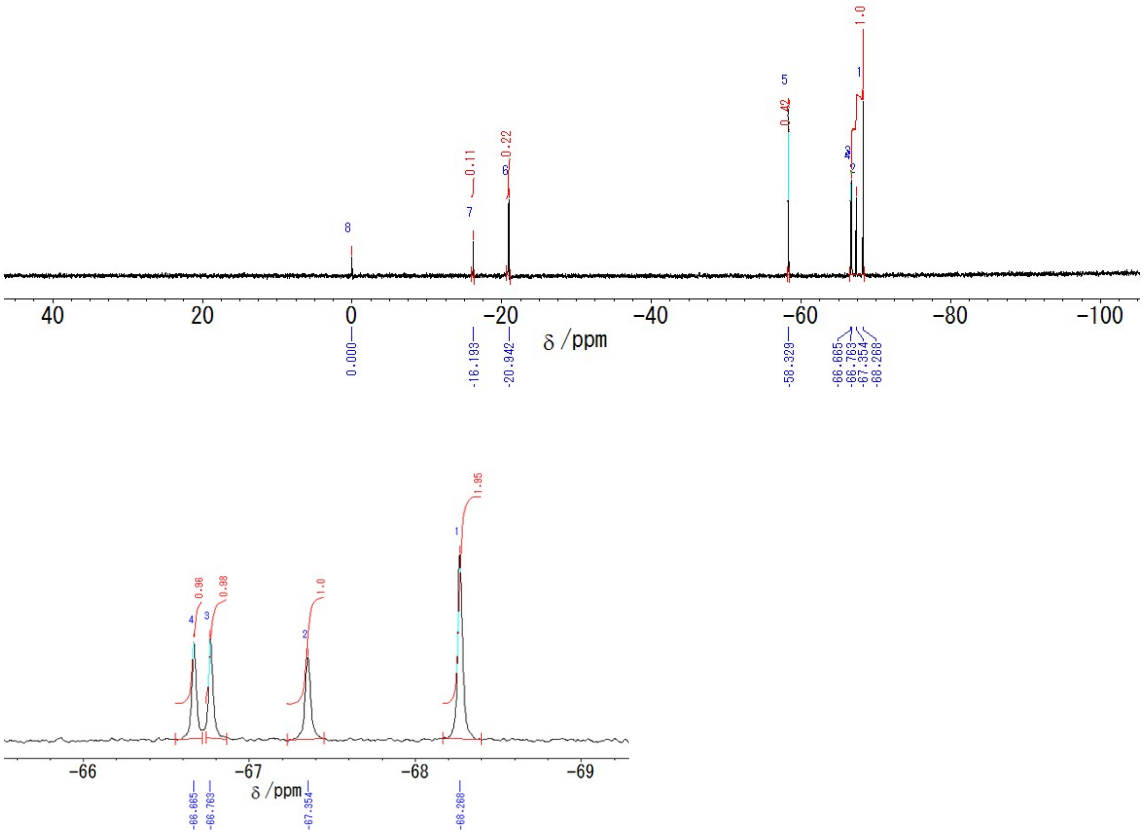


Figure S5. (Top) ^{29}Si NMR spectrum (80 MHz) of run 3 of Table 1 in $CDCl_3$. (Bottom) expanded view of ^{29}Si NMR spectrum (80 MHz) of run 3 of Table 1 in $CDCl_3$.

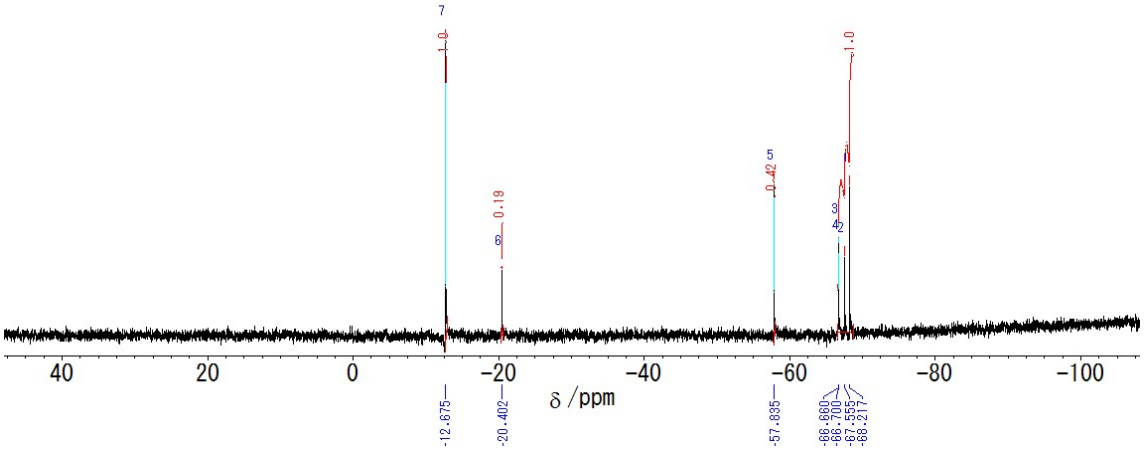


Figure S6. ^{29}Si NMR spectrum (80 MHz) of run 4 of Table 1 in $CDCl_3$.

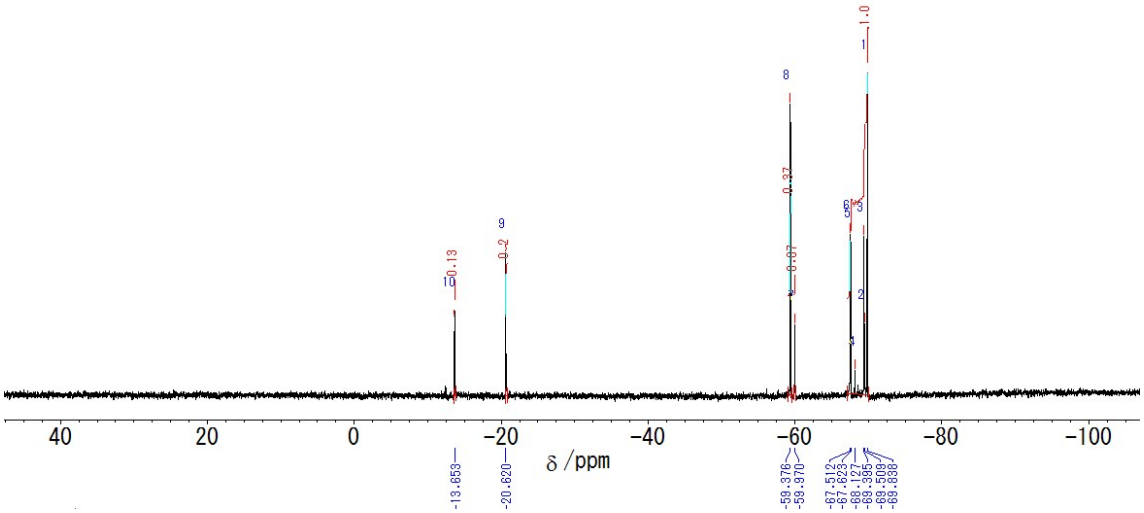


Figure S7. ^{29}Si NMR spectrum (80 MHz) of run 5 of Table 1 in $CDCl_3$.

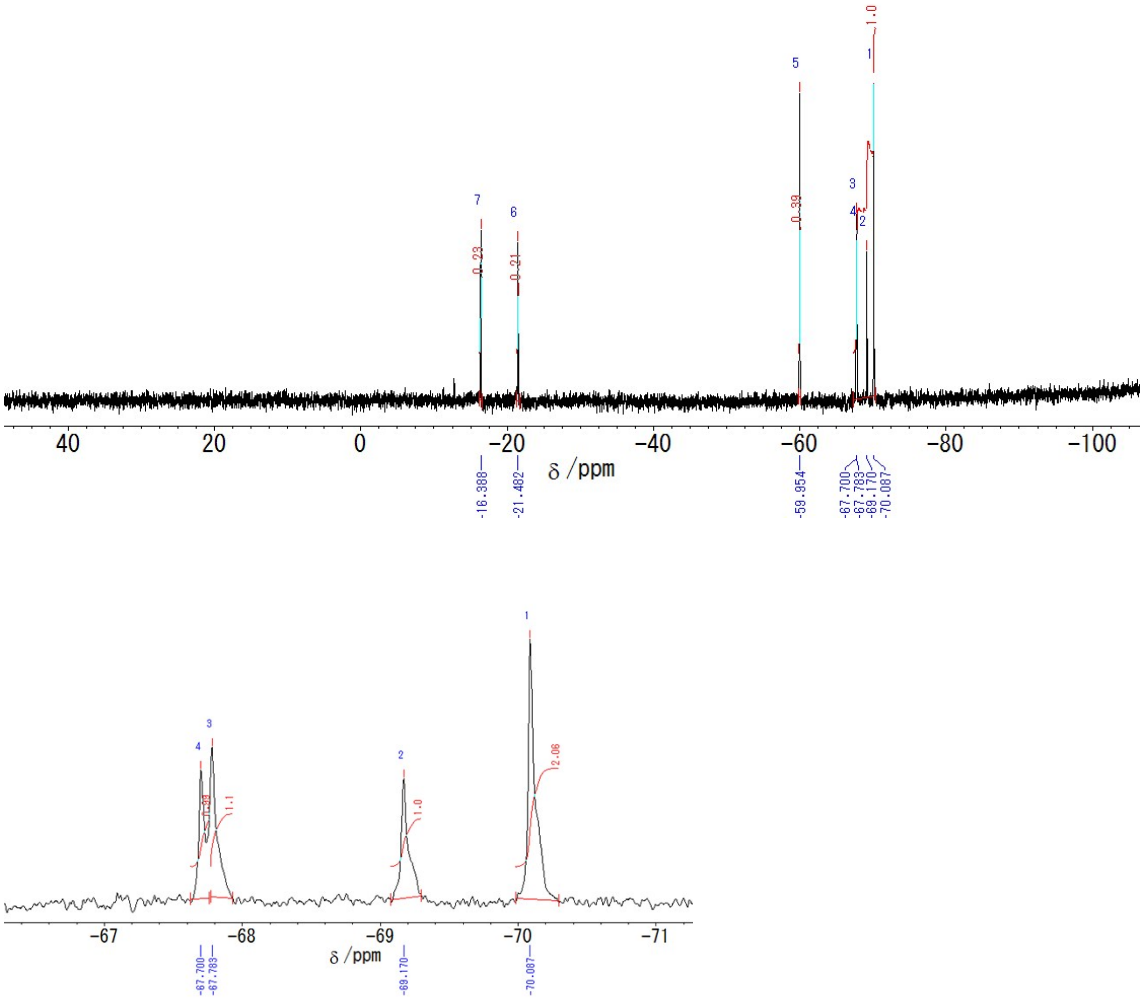


Figure S8. (Top) ^{29}Si NMR spectrum (80 MHz) of run 6 of Table 1 in $CDCl_3$. (Bottom) expanded view of ^{29}Si NMR spectrum (80 MHz) of run 6 of Table 1 in $CDCl_3$.

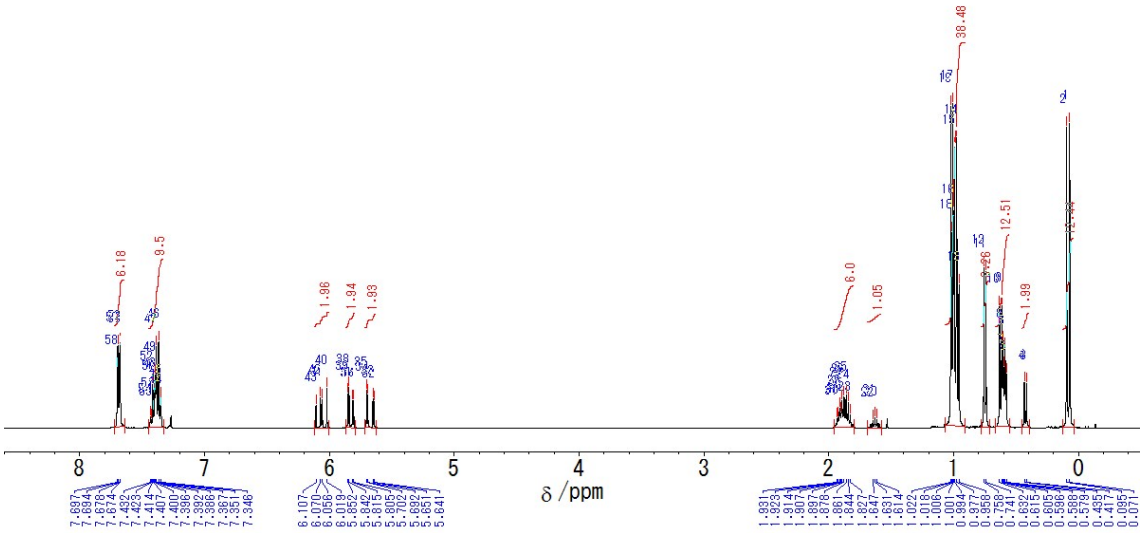


Figure S9. ^{1}H NMR spectrum (400 MHz) of $\mathbf{3}_{i\mathbf{Bu}}$ in $CDCl_3$.

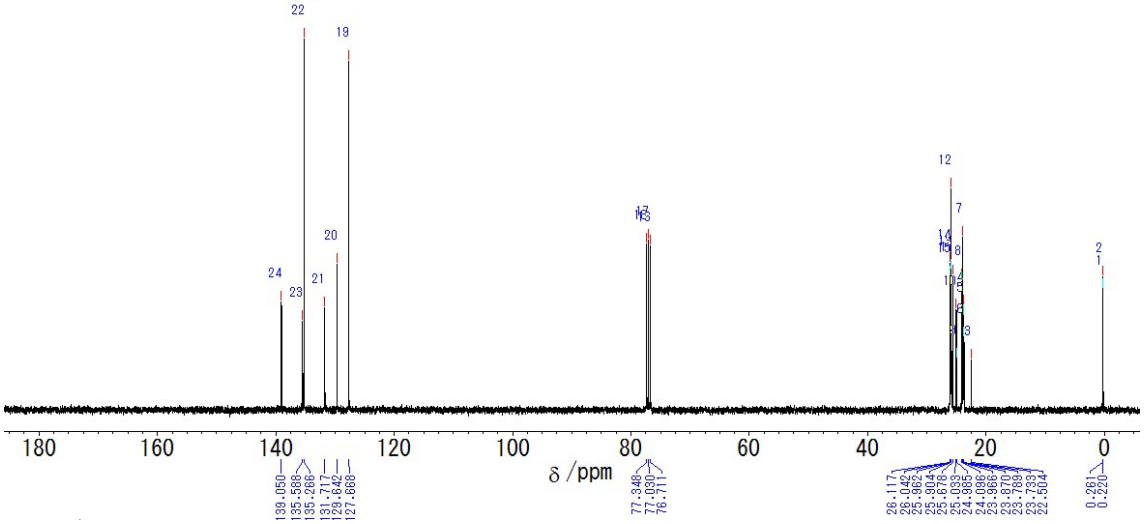


Figure S10. ^{13}C NMR spectrum (100 MHz) of $\mathbf{3}_{i\mathbf{Bu}}$ in $CDCl_3$.

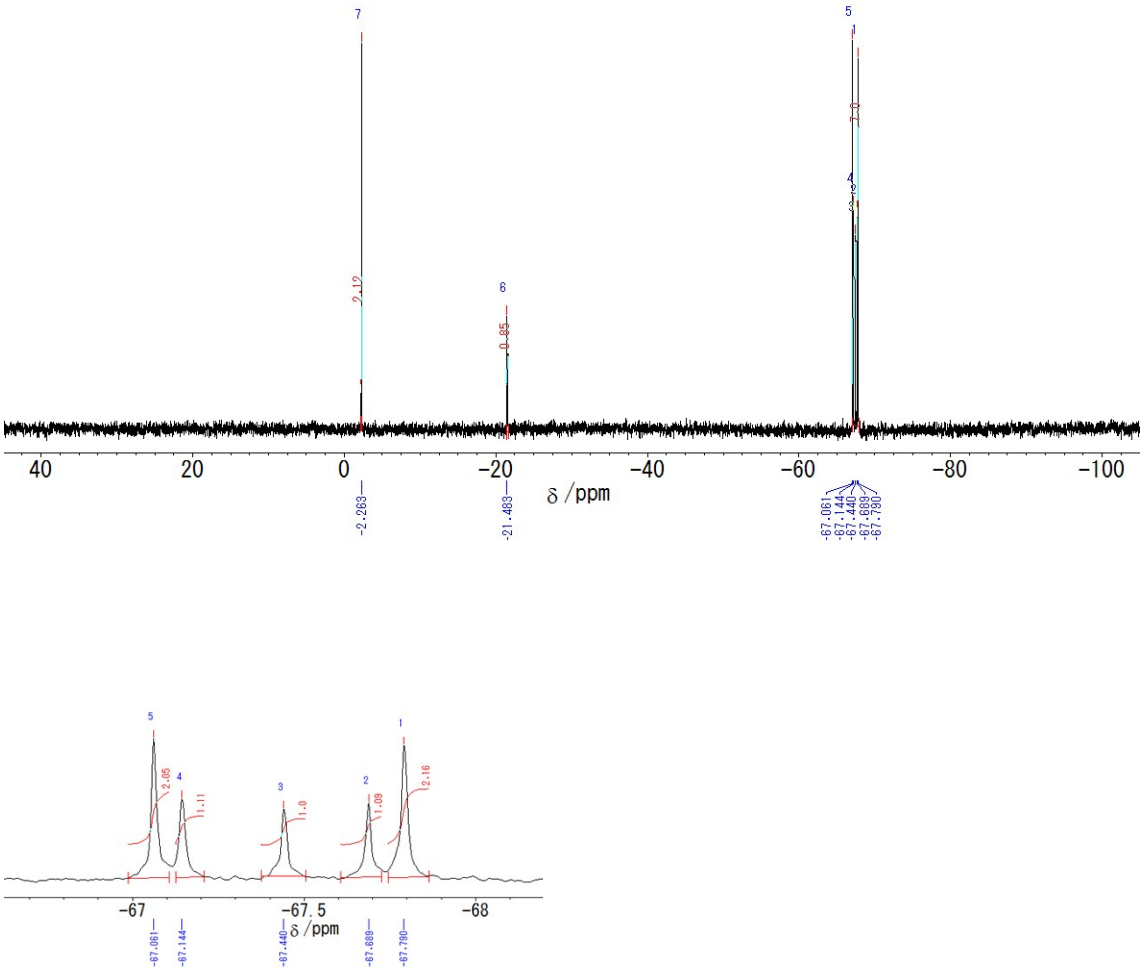


Figure S11. (Top) ^{29}Si NMR spectrum (80 MHz) of $\mathbf{3}_{i\mathbf{Bu}}$ in $CDCl_3$. (Bottom) expanded view of ^{29}Si NMR spectrum (80 MHz) of $\mathbf{3}_{i\mathbf{Bu}}$ in $CDCl_3$.

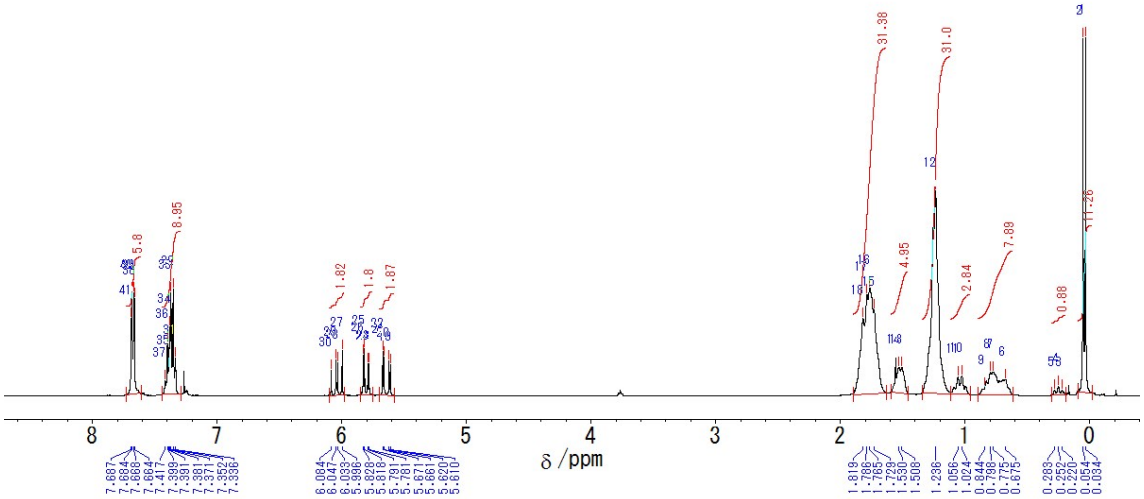


Figure S12. ^{1}H NMR spectrum (400 MHz) of $\mathbf{3_{Cyh}}$ in $CDCl_3$.

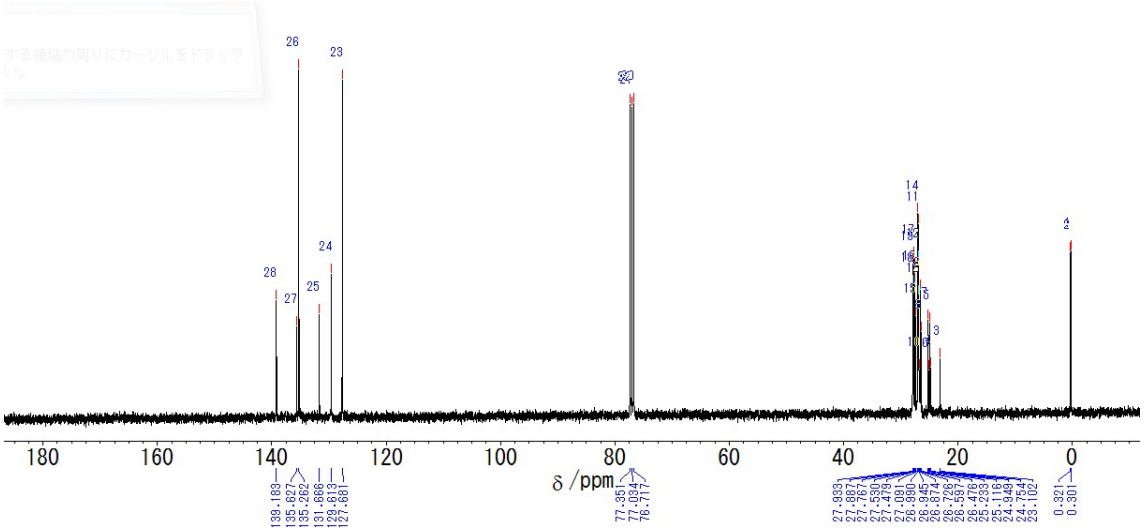


Figure S13. ^{13}C NMR spectrum (100 MHz) of $\mathbf{3_{Cyh}}$ in $CDCl_3$.

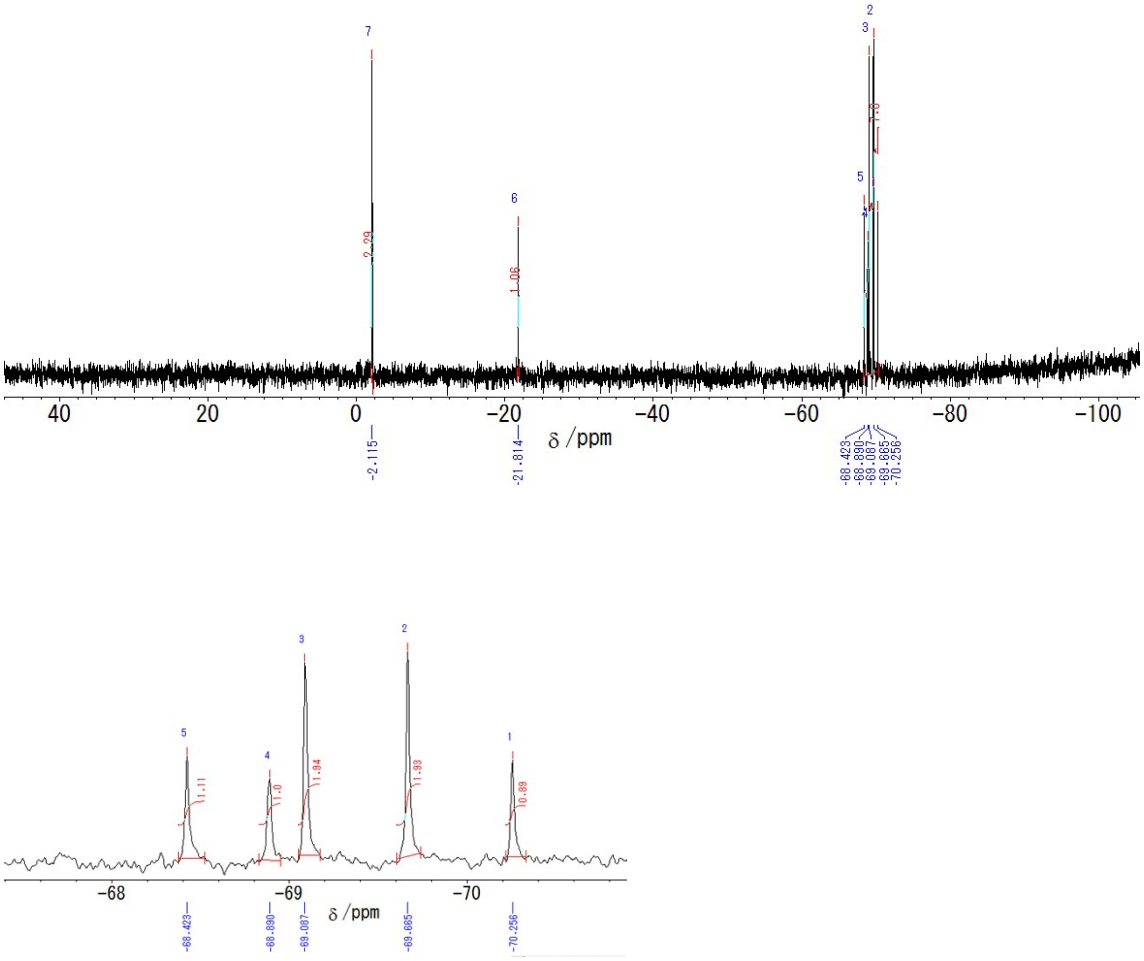


Figure S14. (Top) ^{29}Si NMR spectrum (80 MHz) of $\mathbf{3_{Cyh}}$ in $CDCl_3$. (Bottom) expanded view of ^{29}Si NMR spectrum (80 MHz) of $\mathbf{3_{Cyh}}$ in $CDCl_3$.

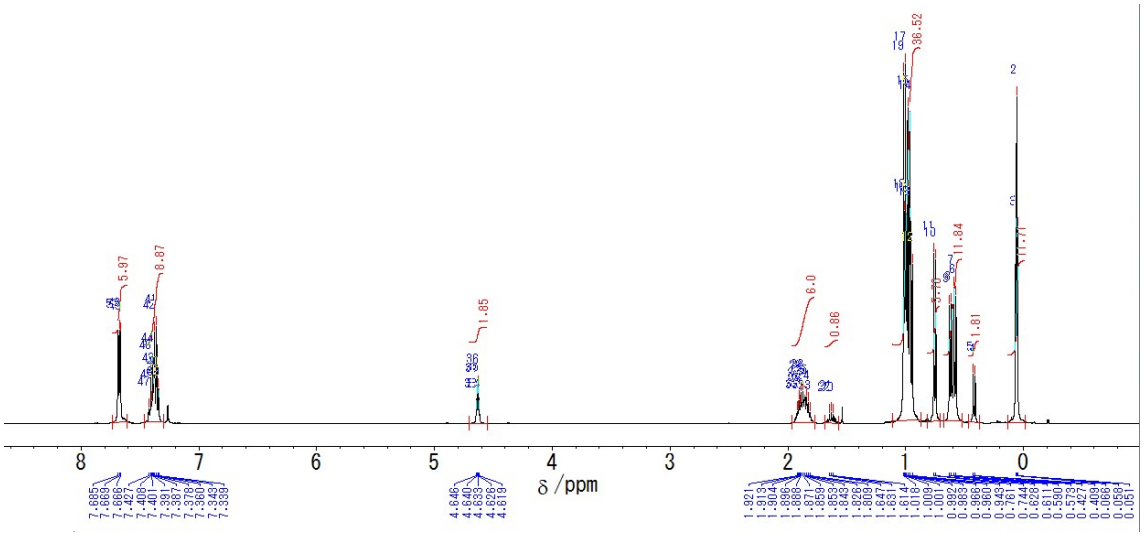


Figure S15. ^{1}H NMR spectrum (400 MHz) of $\mathbf{4}_{\boldsymbol{i}\mathbf{Bu}}$ in $CDCl_3$.

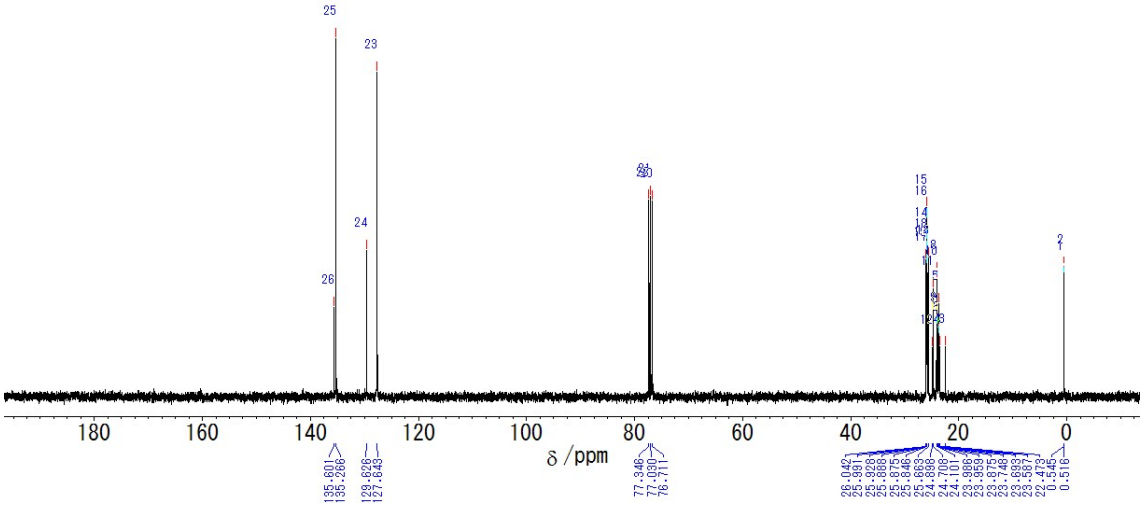


Figure S16. ^{13}C NMR spectrum (100 MHz) of $\mathbf{4}_{\boldsymbol{i}\mathbf{Bu}}$ in $CDCl_3$.

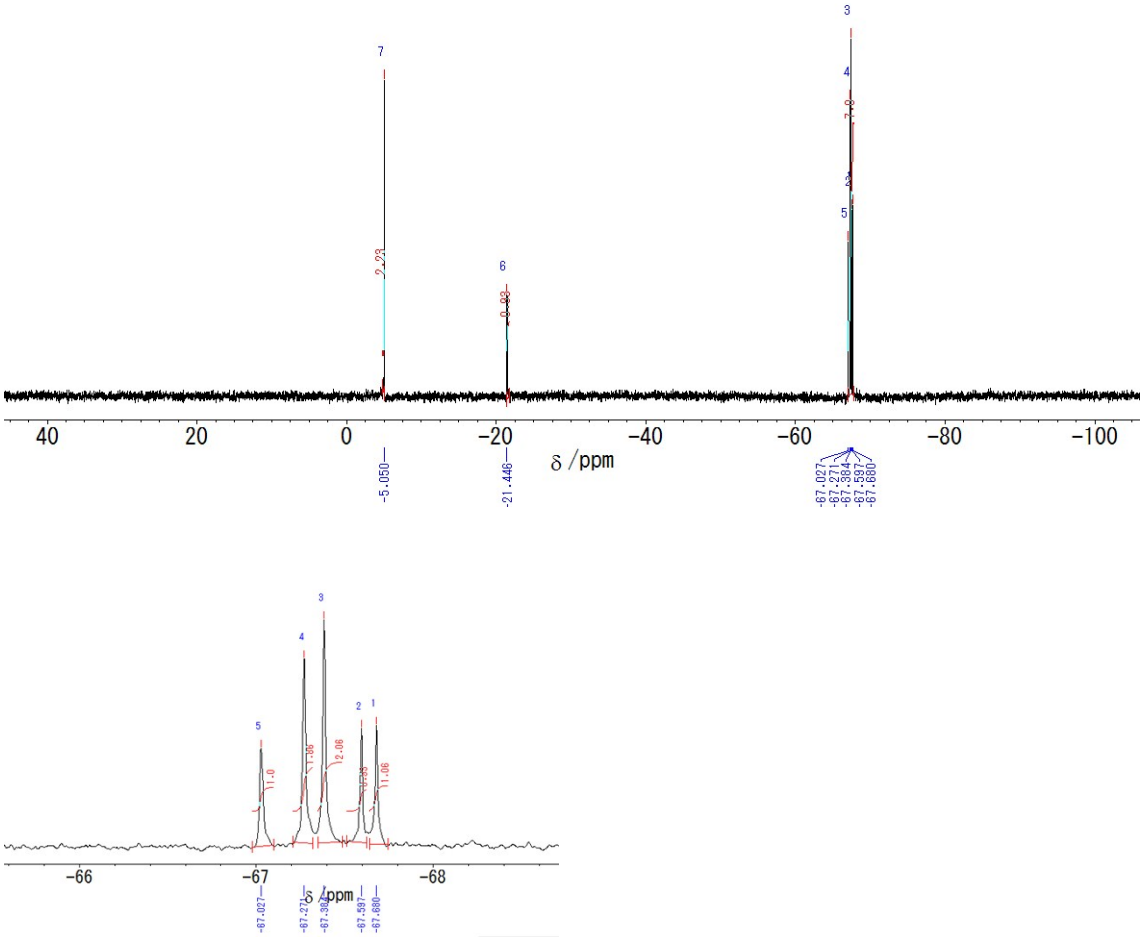


Figure S17. (Top) ^{29}Si NMR spectrum (80 MHz) of $\mathbf{4}_{\mathbf{\textit{i}Bu}}$ in $CDCl_3$. (Bottom) expanded view of ^{29}Si NMR spectrum (80 MHz) of $\mathbf{4}_{\mathbf{\textit{i}Bu}}$ in $CDCl_3$.

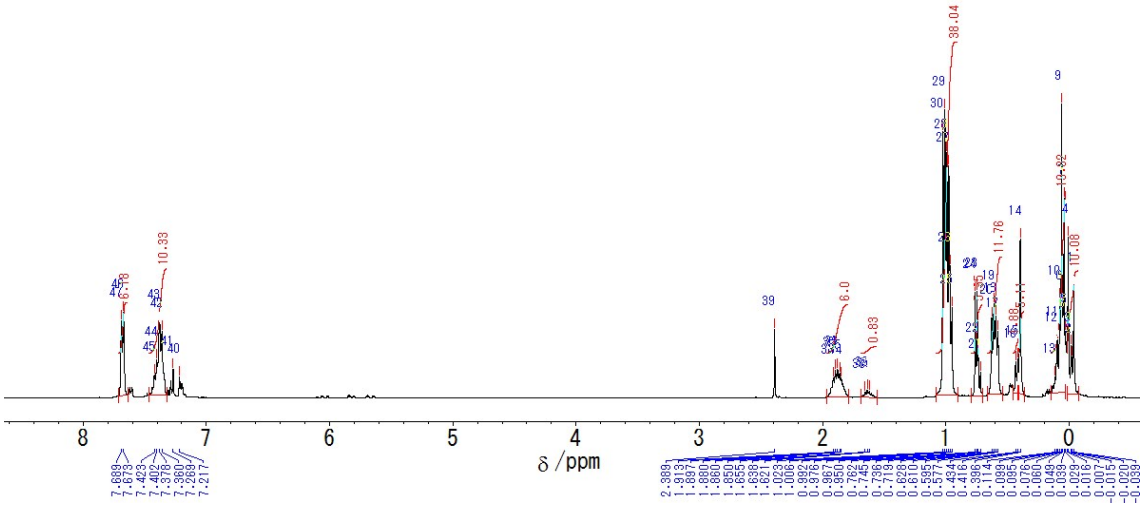


Figure S18. ^{1}H NMR spectrum (400 MHz) of $\mathbf{6}_{\mathbf{\textit{i}Bu}}$ (crude) in $CDCl_3$.

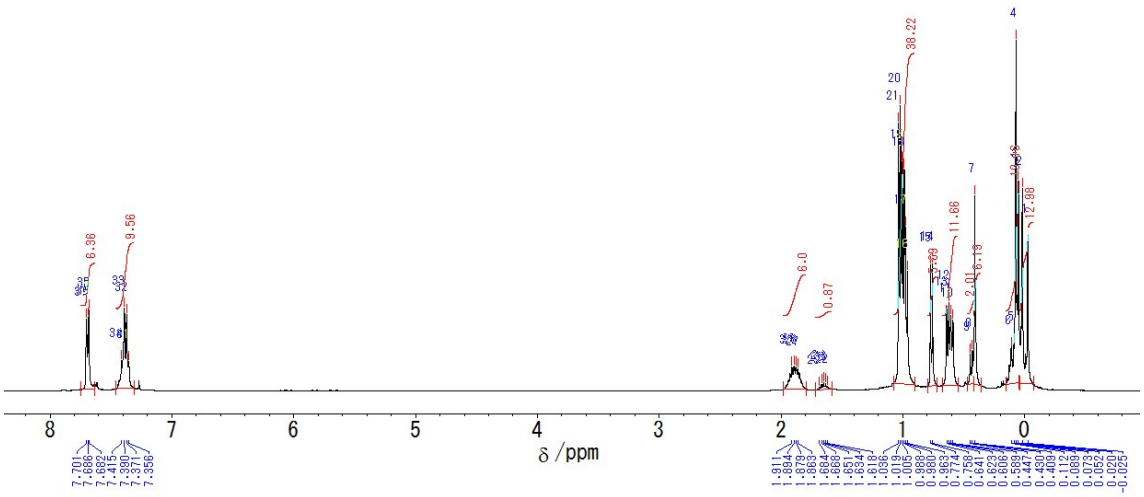


Figure S19. ^{1}H NMR spectrum (400 MHz) of $\mathbf{6}_{\mathbf{\textit{i}Bu}}$ (after purification) in $CDCl_3$.

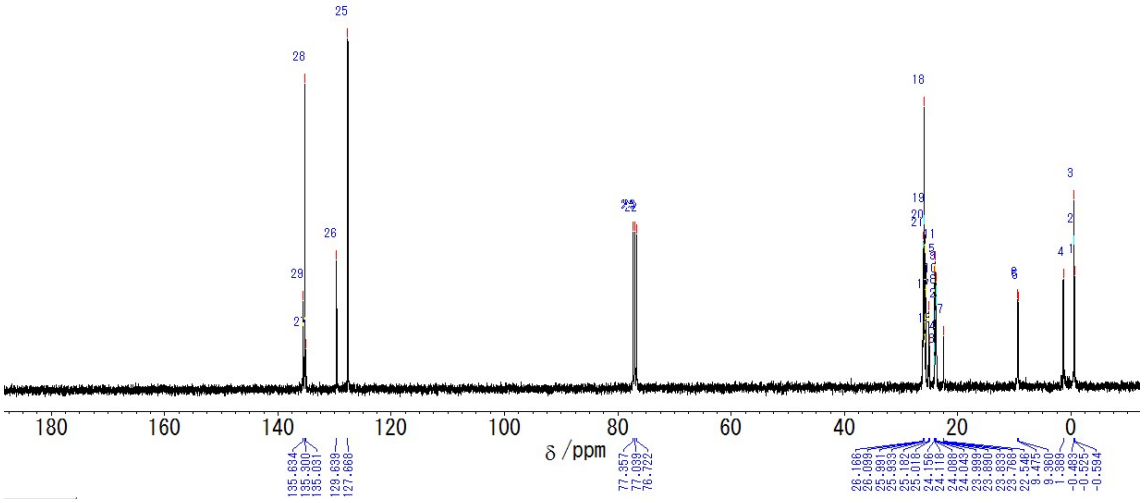


Figure S20. ^{13}C NMR spectrum (100 MHz) of $\mathbf{6}_{\mathbf{\textit{i}Bu}}$ in $CDCl_3$.

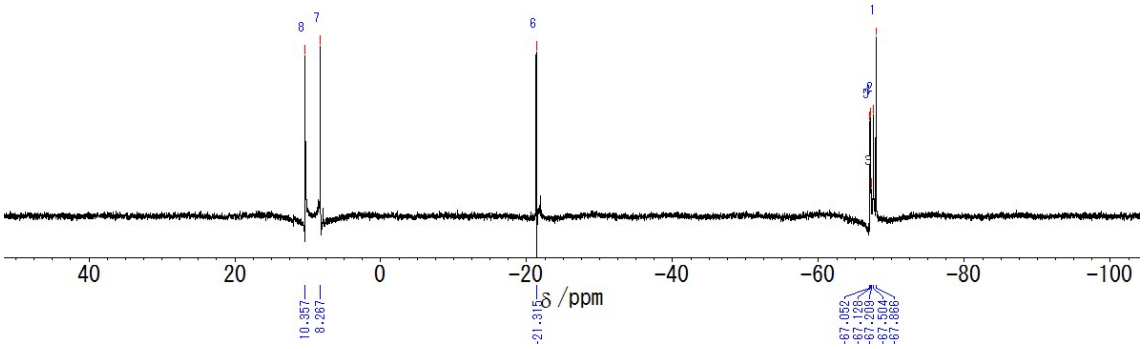


Figure S21. ^{29}Si NMR spectrum (80 MHz) of $\mathbf{6}_{\mathbf{\textit{i}Bu}}$ in $CDCl_3$.

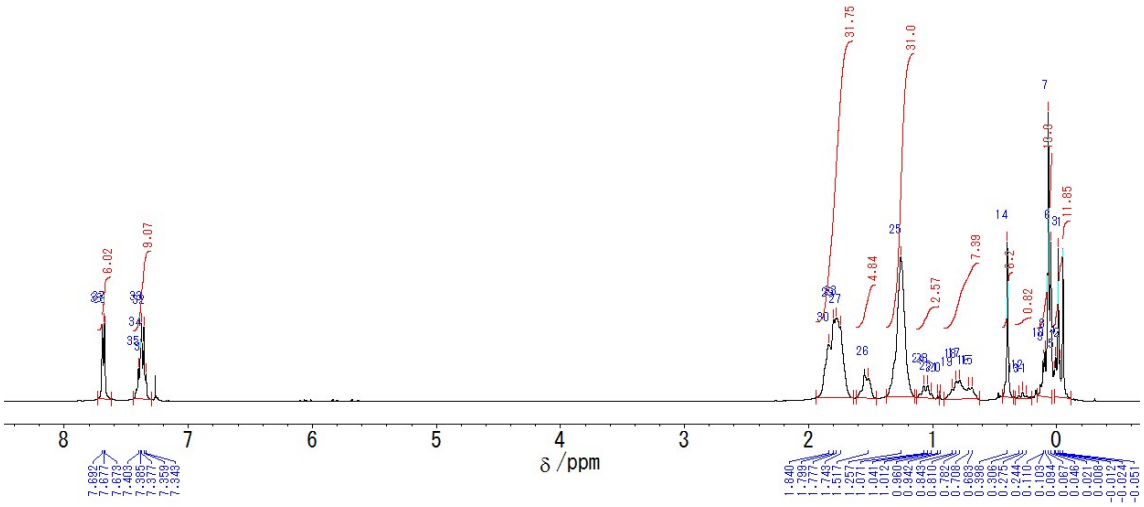


Figure S22. ^{1}H NMR spectrum (400 MHz) of $\mathbf{6_{Cyh}}$ in $CDCl_3$.

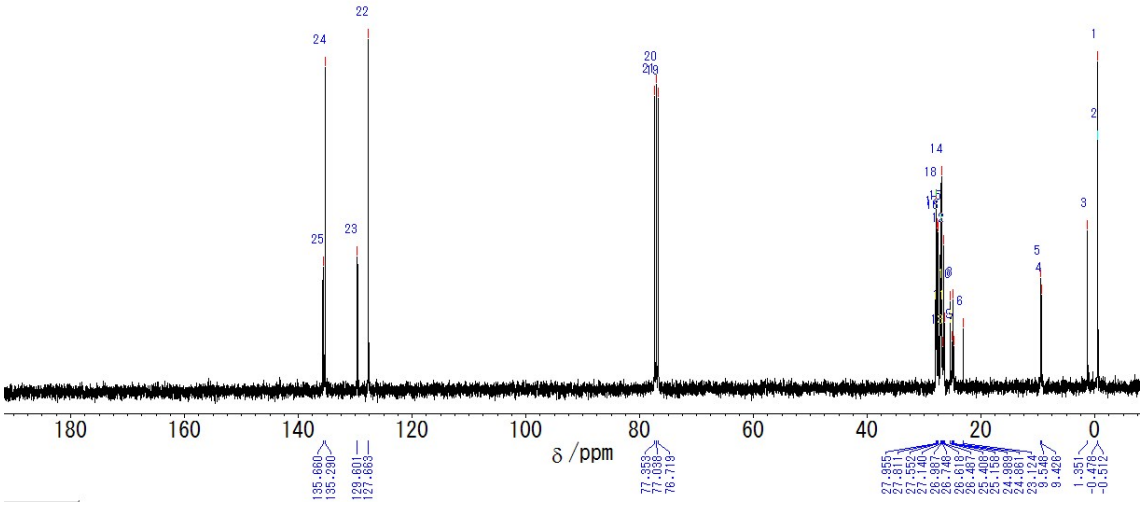


Figure S23. ^{13}C NMR spectrum (100 MHz) of $\mathbf{6_{Cyh}}$ in $CDCl_3$.

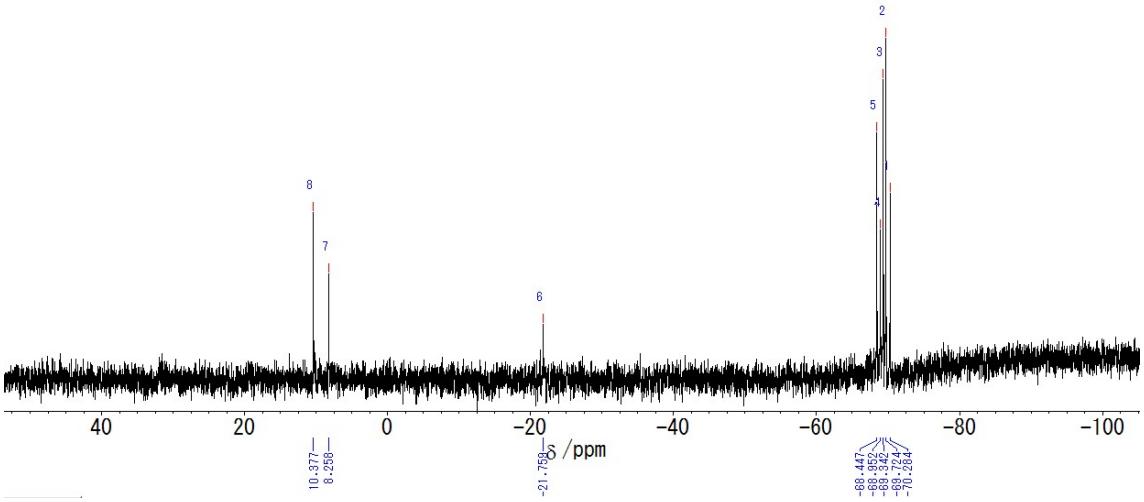


Figure S24. ^{29}Si NMR spectrum (80 MHz) of $\mathbf{6_{Cyh}}$ in $CDCl_3$.

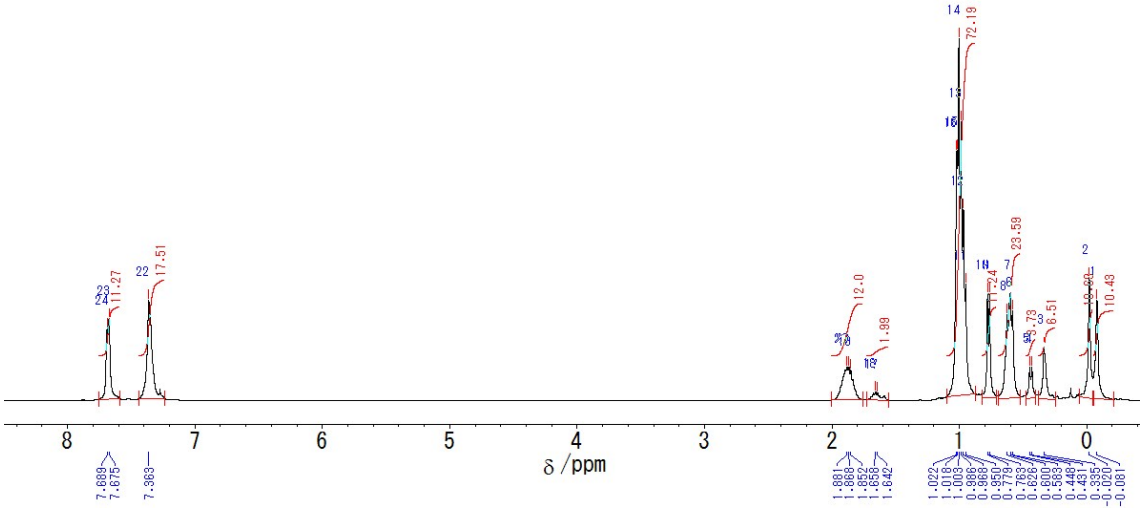


Figure S25. ^{1}H NMR spectrum (400 MHz) of $\mathbf{7_{iBu}}$ in $CDCl_3$.

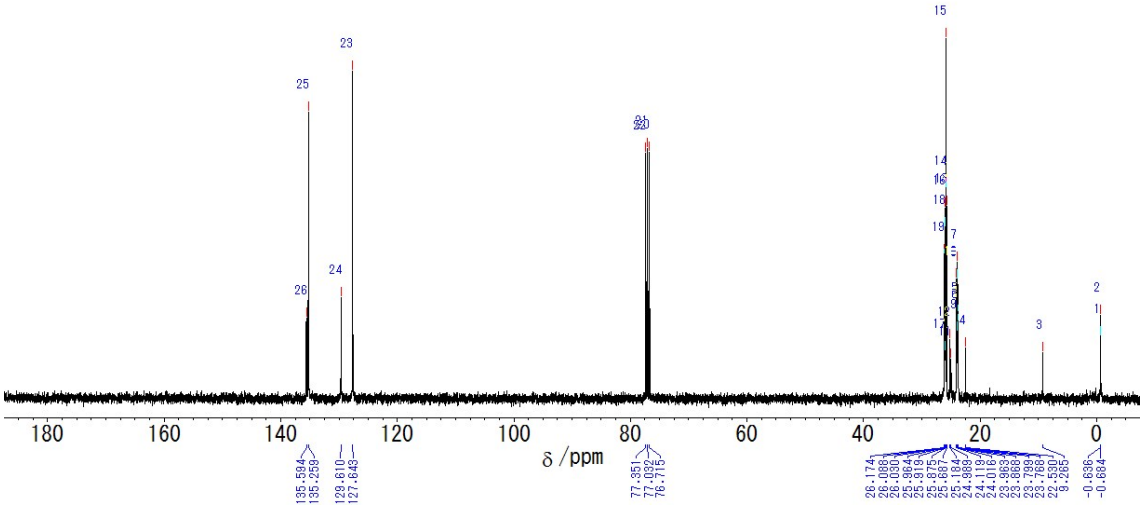


Figure S26. ^{13}C NMR spectrum (100 MHz) of $\mathbf{7}_{\mathbf{\textit{i}Bu}}$ in $CDCl_3$.

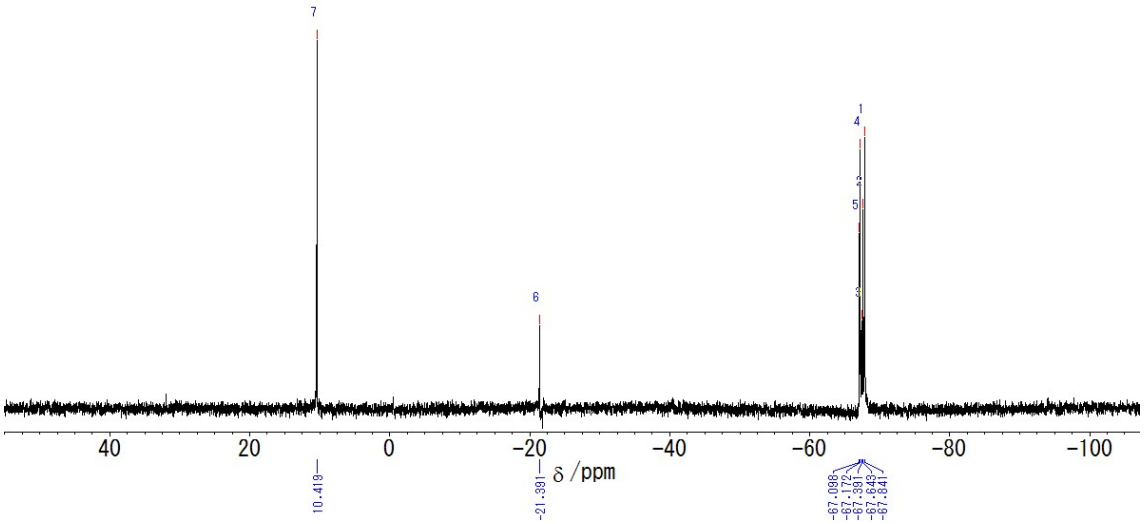


Figure S27. ^{29}Si NMR spectrum (80 MHz) of $\mathbf{7}_{\mathbf{\textit{i}Bu}}$ in $CDCl_3$.

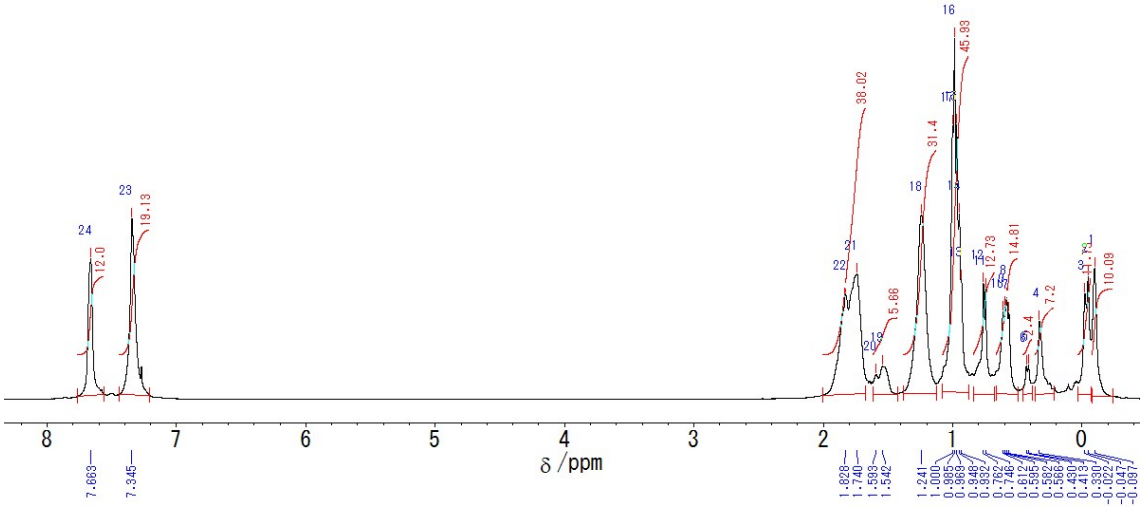


Figure S28. ^{1}H NMR spectrum (400 MHz) of $\mathbf{7_{Cyh}}$ in $CDCl_3$.

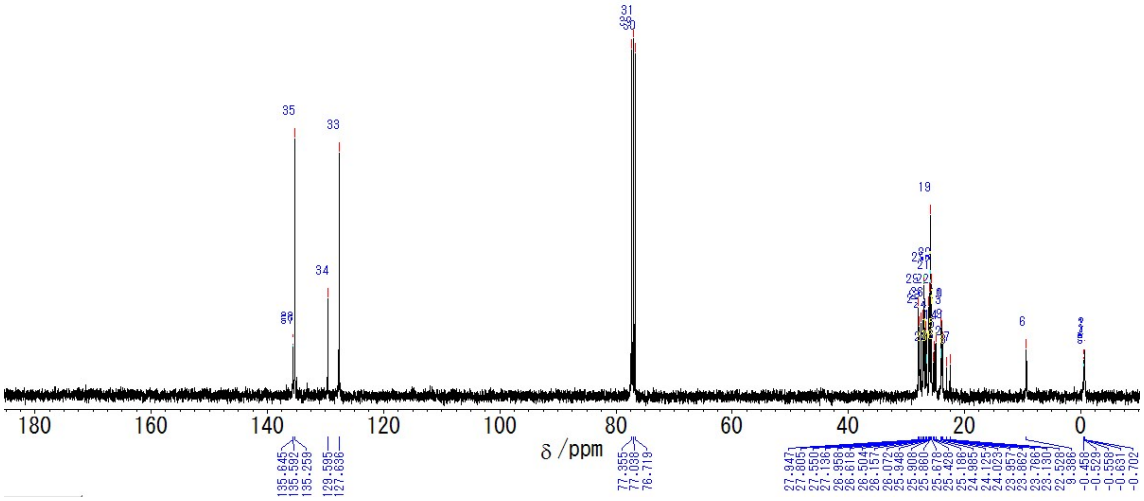


Figure S29. ^{13}C NMR spectrum (100 MHz) of $\mathbf{7_{Cyh}}$ in $CDCl_3$.

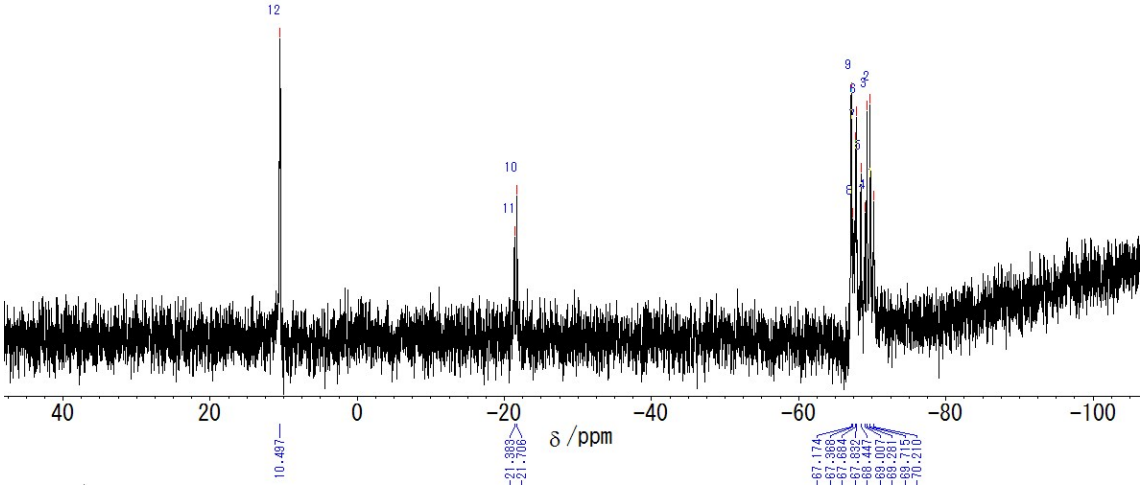


Figure S30. ^{29}Si NMR spectrum (80 MHz) of $\mathbf{7_{Cyh}}$ in $CDCl_3$.

2. SEC analysis

The signals due to the vinyl and hydrosilyl groups almost disappeared in the ^{1}H-NMR spectrum of the crude products of $\mathbf{4_{iBu}}$, though the SEC trace showed a sharp peak derived from low molecular weight by-product. This implies that the by-product is a cyclic compound, well corresponding to our previous paper.[1]

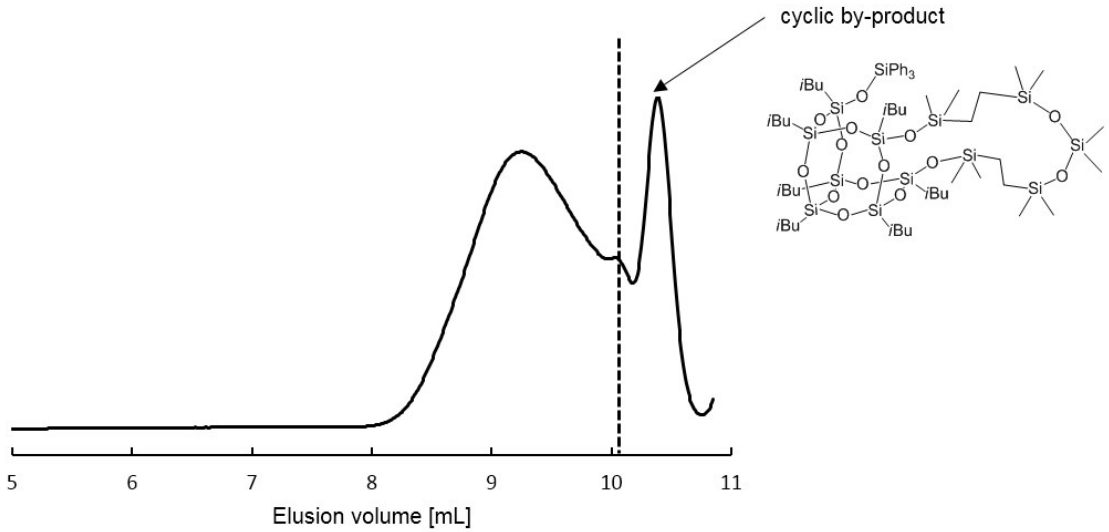
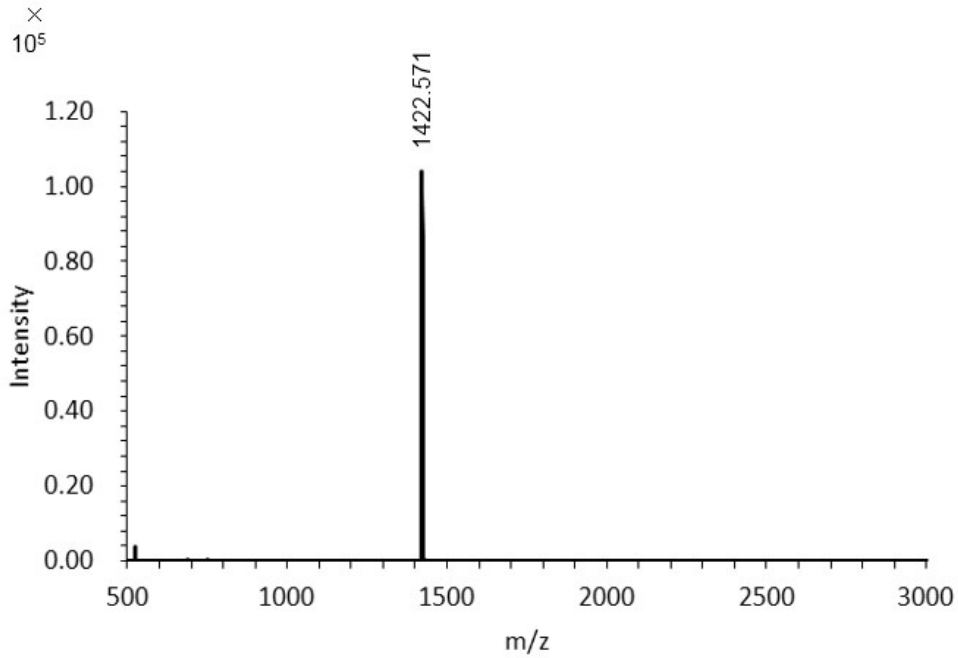


Figure S31. SEC trace of $\mathbf{4_{iBu}}$ measured in THF (1 mL/min) and detected by RI.

3. MALDI-TOF-MASS spectra

(a)



(b)

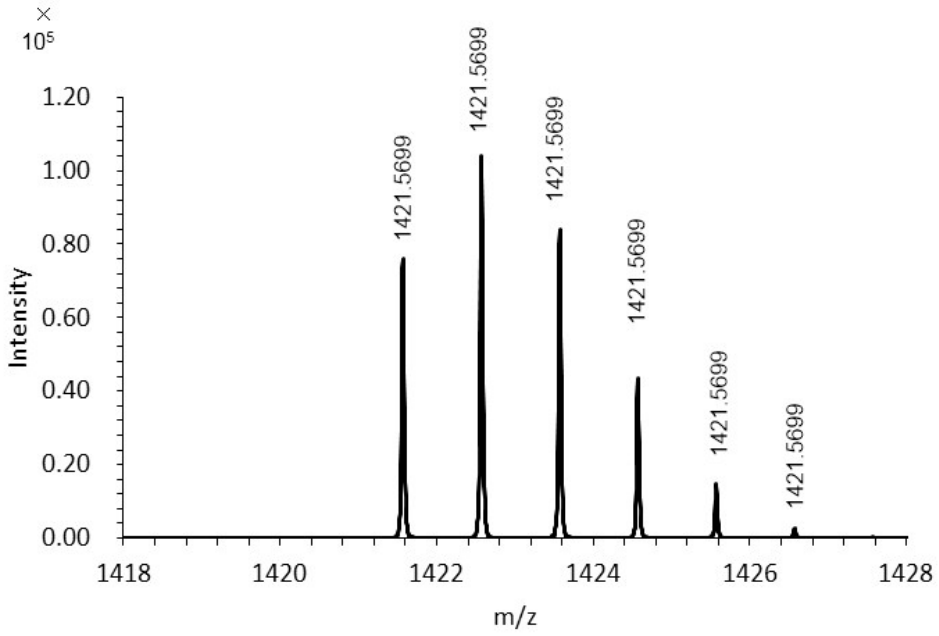
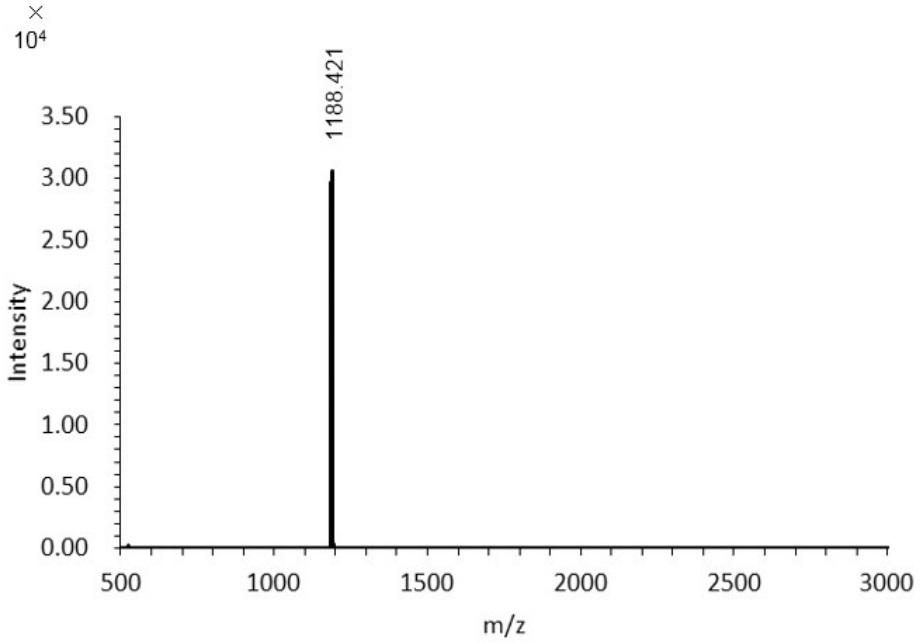


Figure S32. MALDI TOF MS spectrum of $\mathbf{3_{Cyh}}$. Matrix: DCTB (20 mg/mL in $CHCl_3$), cationizing agents: TFANa (1 mg/mL in THF). (a) Full spectrum and (b) expanded view.

(a)



(b)

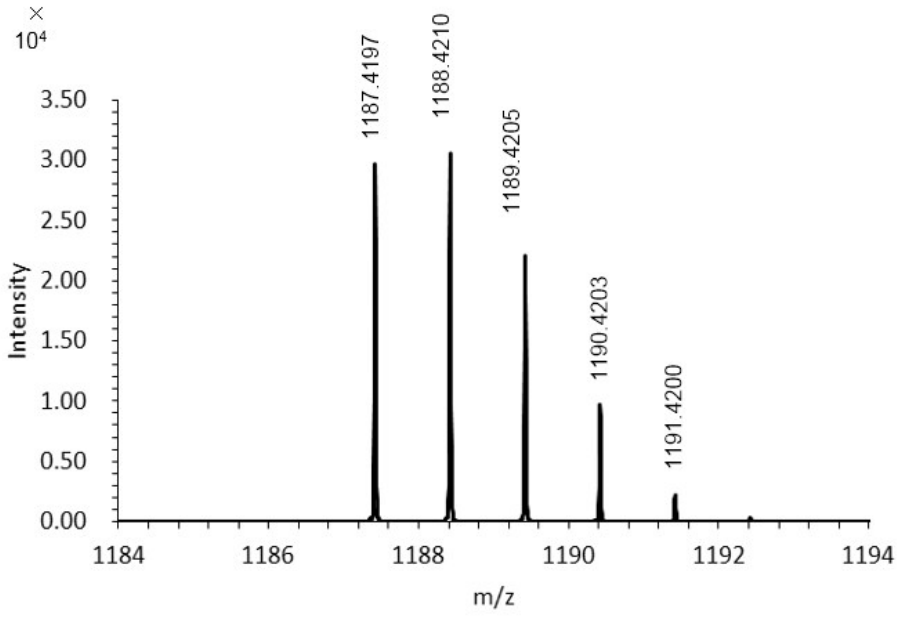


Figure S33. MALDI TOF MS spectrum of $\mathbf{4}_{i\mathbf{Bu}}$. Matrix: DCTB (20 mg/mL in $CHCl_3$), cationizing agents: TFANa (1 mg/mL in THF). (a) Full spectrum and (b) expanded view.

4. X-ray diffraction patterns

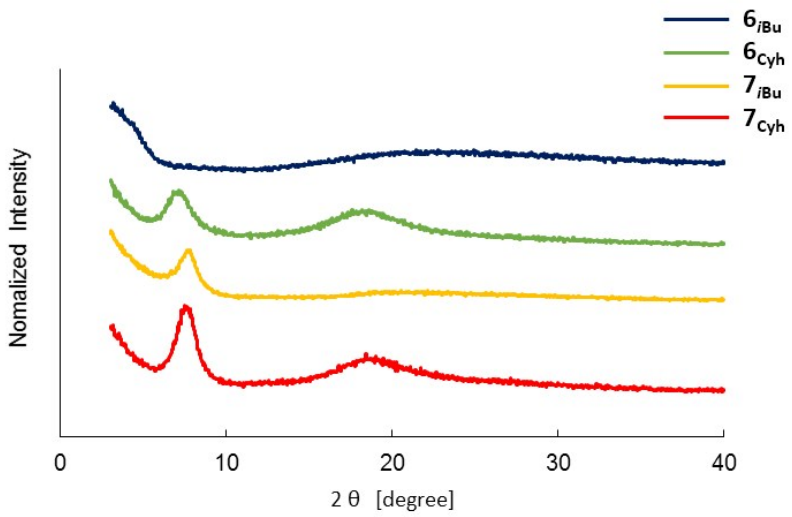


Figure S34. Powder X-ray diffraction patterns of **6-7**.

5. Chemical structure of IC-POSS polymer with CC-POSS pendants

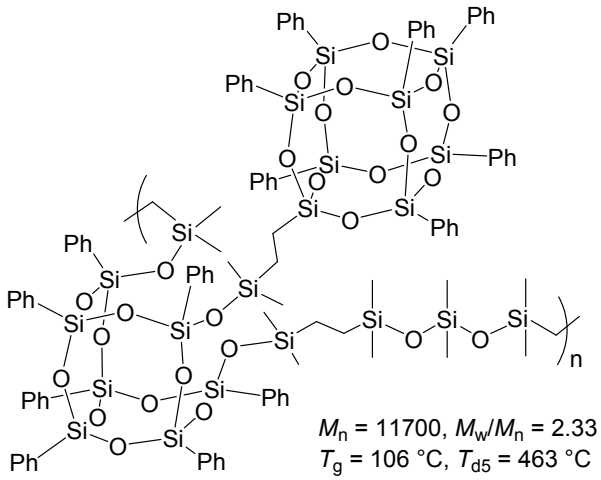


Figure S35. Chemical structures and data of previously reported IC-POSS polymer with CC-POSS pendants.[1]

[1] H. Imoto, R. Katoh and K. Naka, *Polym. Chem.*, 2018, **9**, 4108.