

Supplementary Information: Alkoxysilyl Functionalized Polynorbornenes with Enhanced Selectivity for Heavy Hydrocarbon Separations

Synthesis of the trimethylsilyl norbornene monomer

Under nitrogen, a 100-mL Schlenk flask was charged with cyclopentadiene (4.75 ml, 35.2 mmol) and vinyltrimethyl silane (31 mL, 211.6 mmol), heated to 205 °C, and stirred for 3 hours. After 3 hours, the reaction mixture was cooled to room temperature before it was distilled and isolated as a clear liquid at 74% yield.

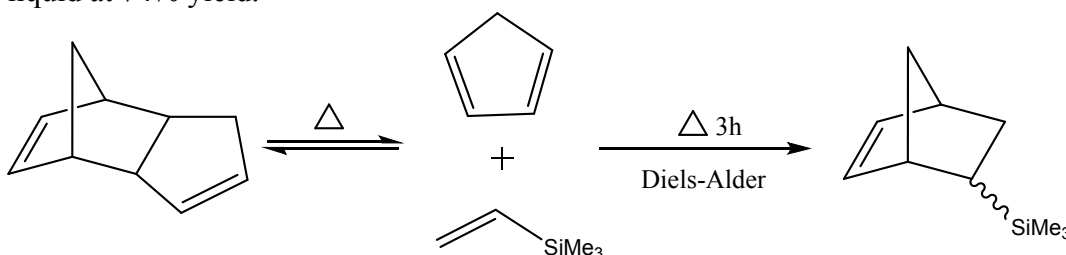


Figure S1. Cracking of dicyclopentadiene and subsequent Diels-Alder reaction with vinyl trimethylsilane

Viscosity testing of low molecular weight addition-type oligomers produced from nickel catalysis

Inherent viscosity results of addition-type polymers prepared from nickel naphthenate (Nph) catalyst conditions. Viscosity testing performed using 1.0 g/dL solution in toluene at 35 °C.

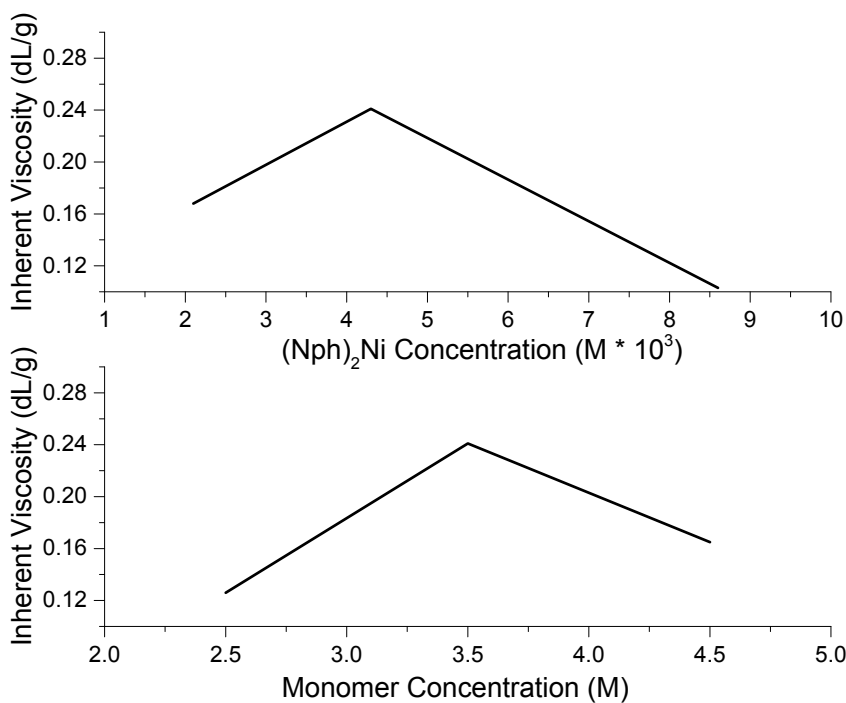


Figure S2. Nickel catalysts gave low inherent viscosities in toluene for several monomer and catalyst concentrations

Gel permeation chromatography (GPC) of ROMP-SiMe₃, and GPC of APN-SiMe₃ synthesized from nickel (Ni) catalyst and palladium (Pd) catalyst

Table S1. GPC confirmed that nickel naphthenate produced molecular weight species of insufficient molecular weight for film formation

30 °C	APN-SiMe ₃ [Ni(nph) ₂ catalyst]
M _n	28774
M _w	63998
M _z	117740
M _p	57165
M _w /M _n	2.224
Intrinsic Viscosity	0.1589
Sample Recovery (%)	99.26
dn/dc	2.738

Table S2. GPC results for high molecular polymers used for film casting

30 °C	ROMP-SiMe ₃	APN-SiMe ₃ (Pd catalyst)
M _n	60194	122070
M _w	102180	153110
M _z	236270	172770
M _p	80227	176610
M _w /M _n	1.698	1.254
Intrinsic Viscosity	0.5506	0.3387
Sample Recovery (%)	99.673	106.35
dn/dc	0.0373	0.0405

Thermogravimetric analysis showed high thermal stability of the synthesized polymers

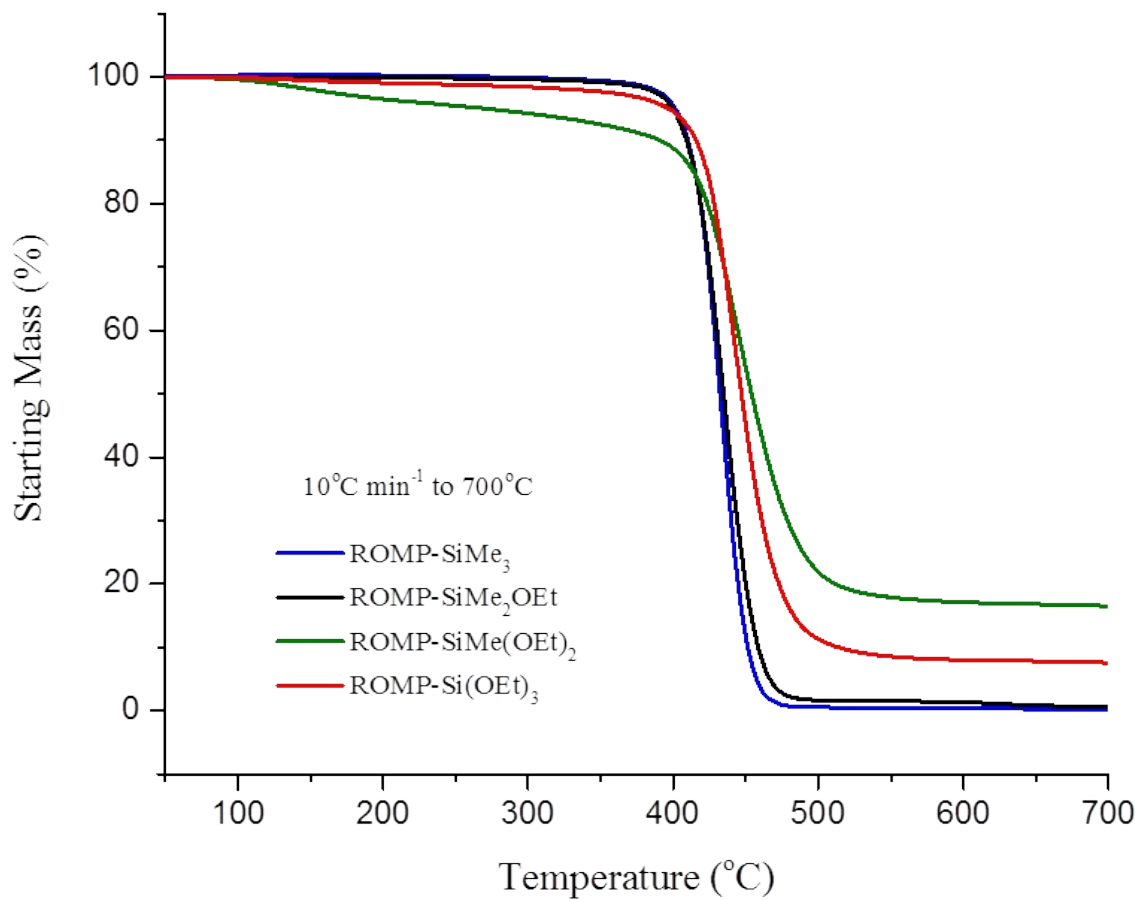


Figure S3. Thermal stability comparison of the ROMP polymers

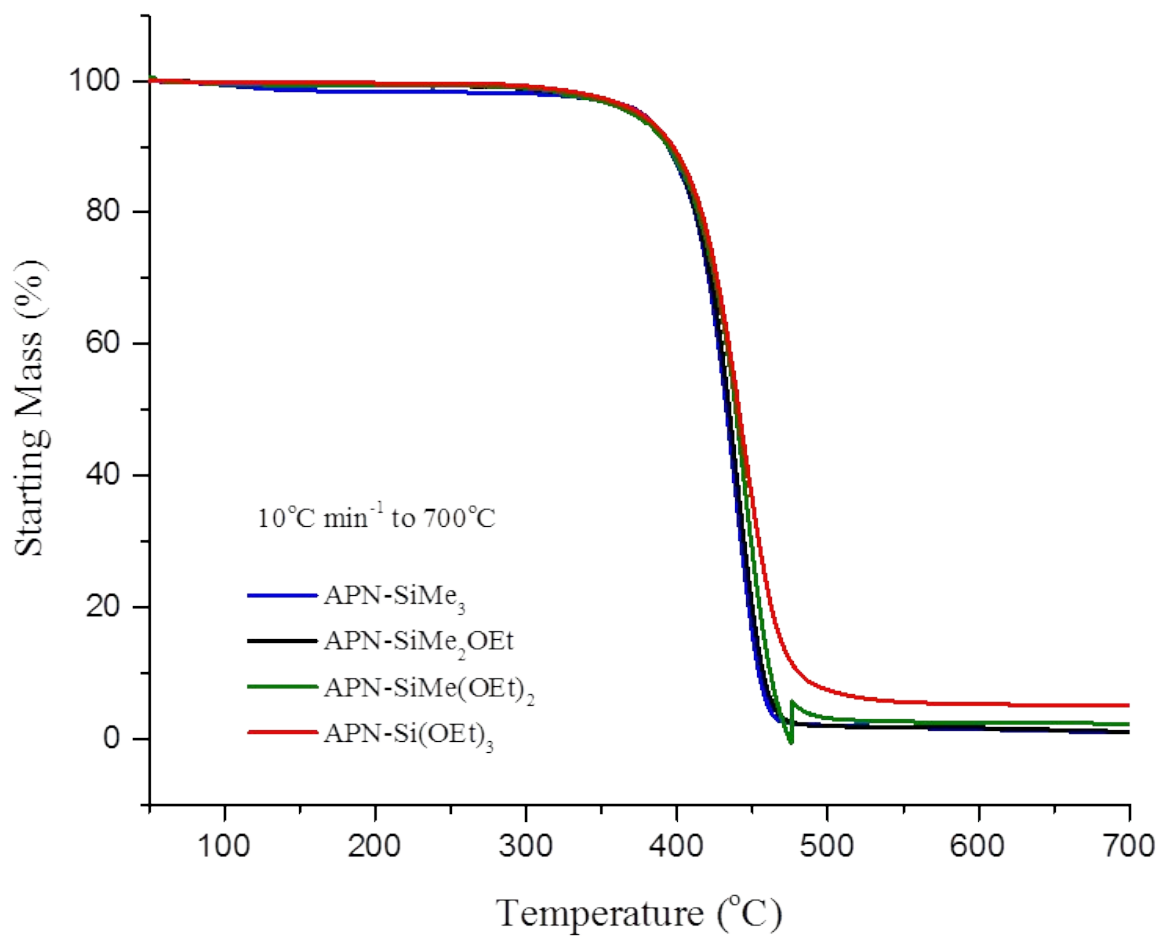


Figure S4. Thermal stability comparison of the addition-type polymers

Infrared spectroscopy of the synthesized polymers

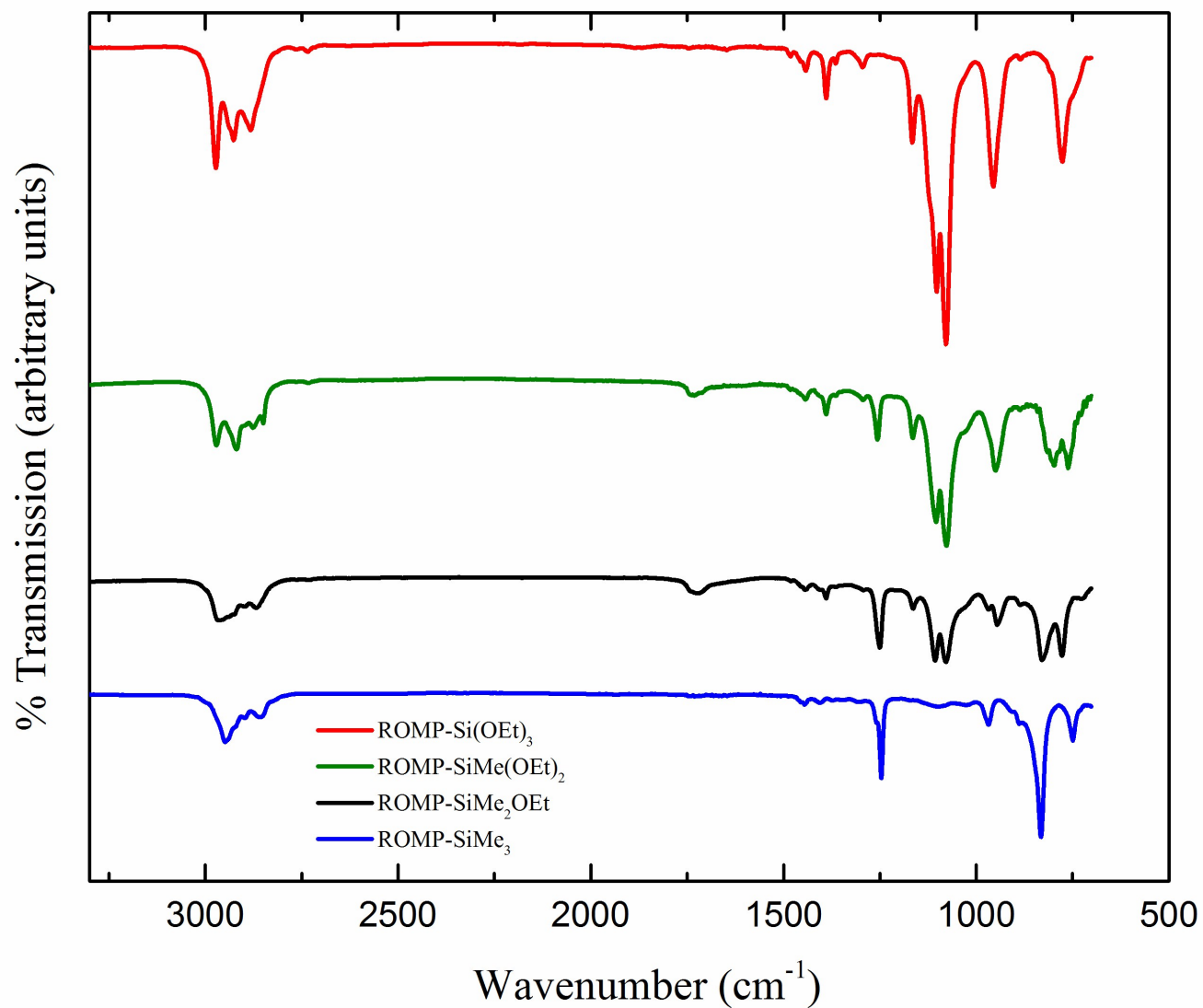


Figure S5. ATR-FTIR shows varying ethoxysilyl and methylsilyl content in the ROMP polymers

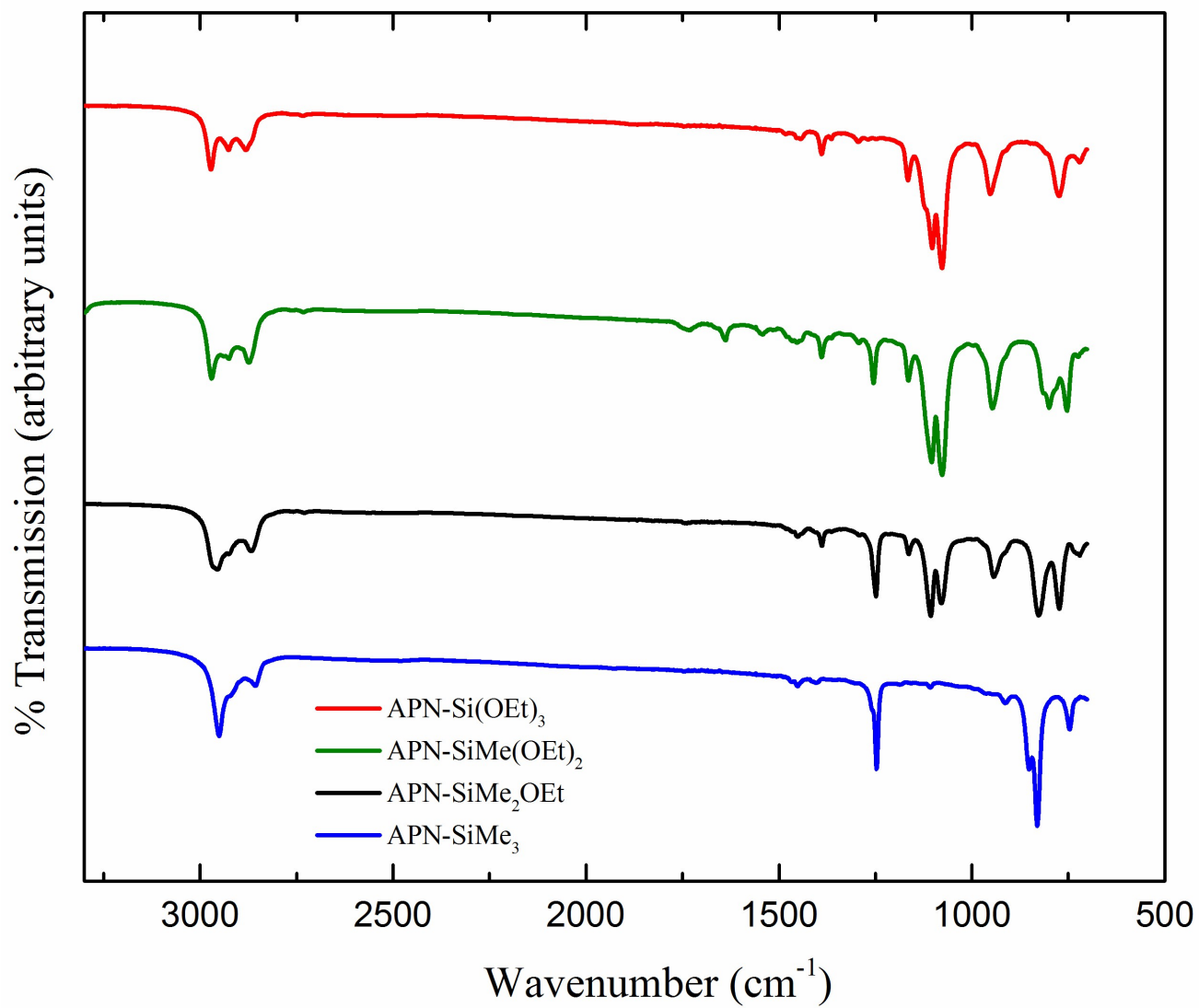


Figure S6. ATR-FTIR shows varying ethoxysilyl and methylsilyl content in the addition-type polymers

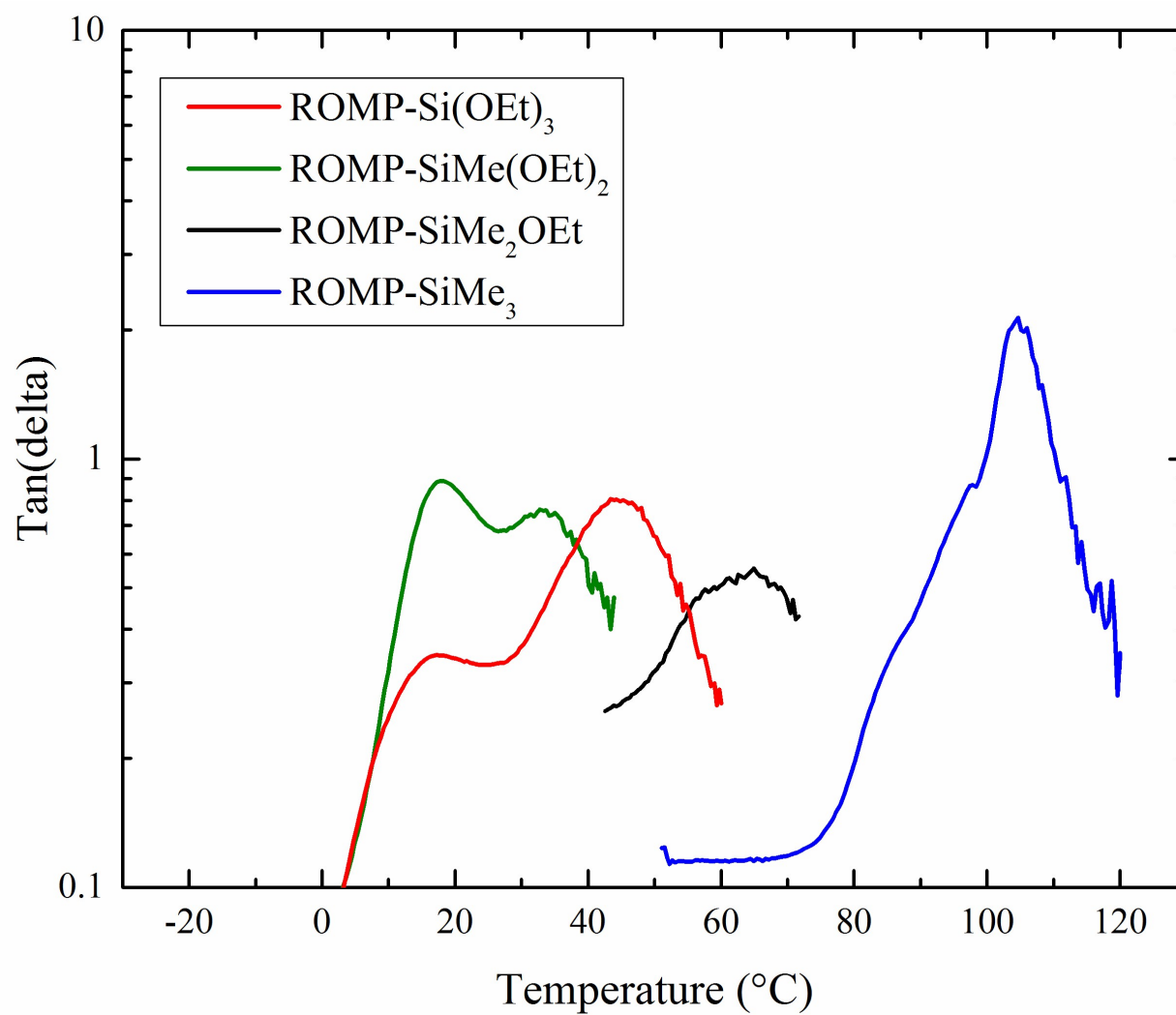


Figure S7. Glass transition temperatures of ROMP polymers from Tan (delta) peaks

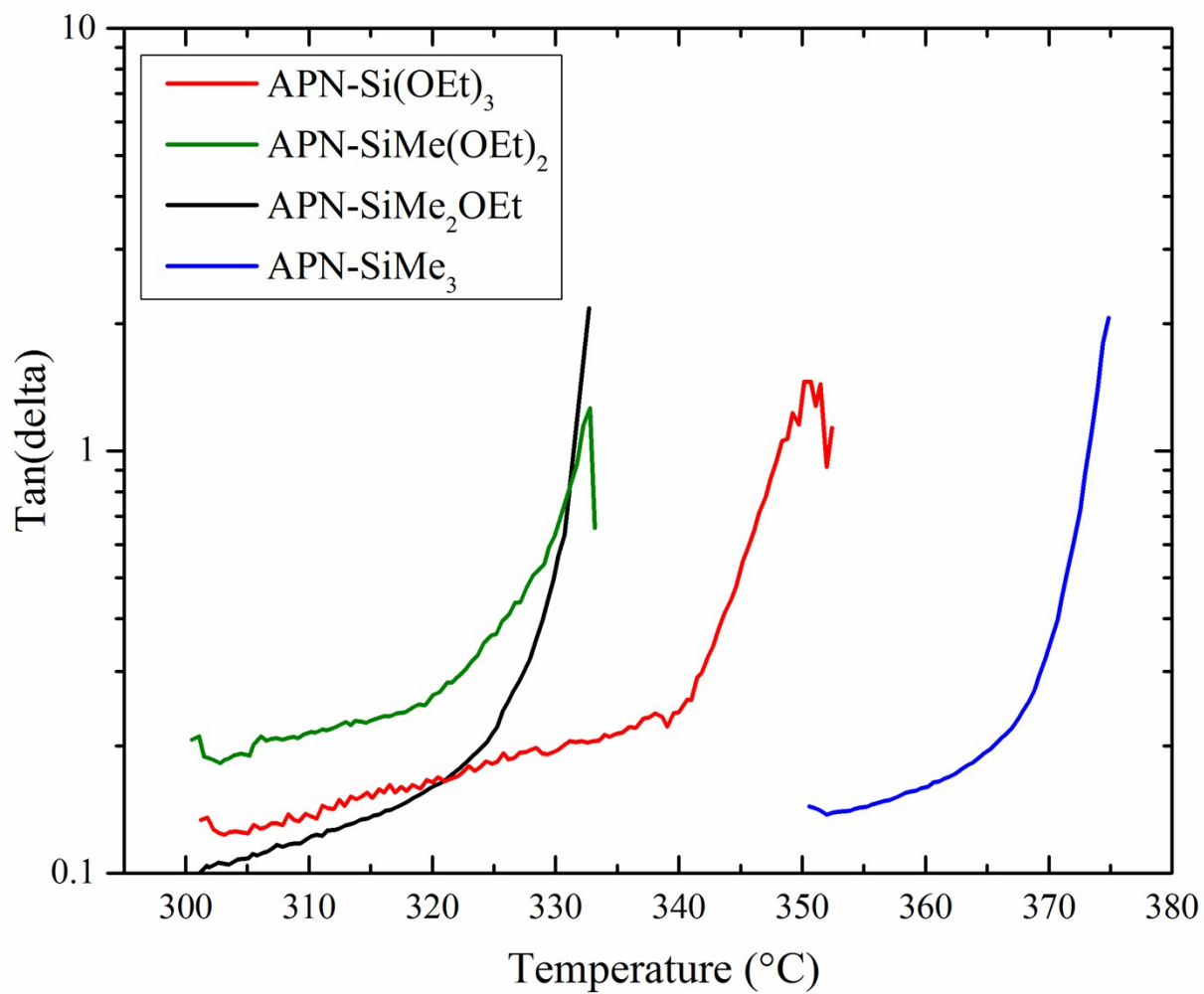


Figure S8. Glass transition temperatures of addition-type polymers from Tan (δ) peaks

¹H-NMR and ¹³C-NMR spectroscopy of monomers and ¹H-NMR of polymers with appropriate integrations and peak designations

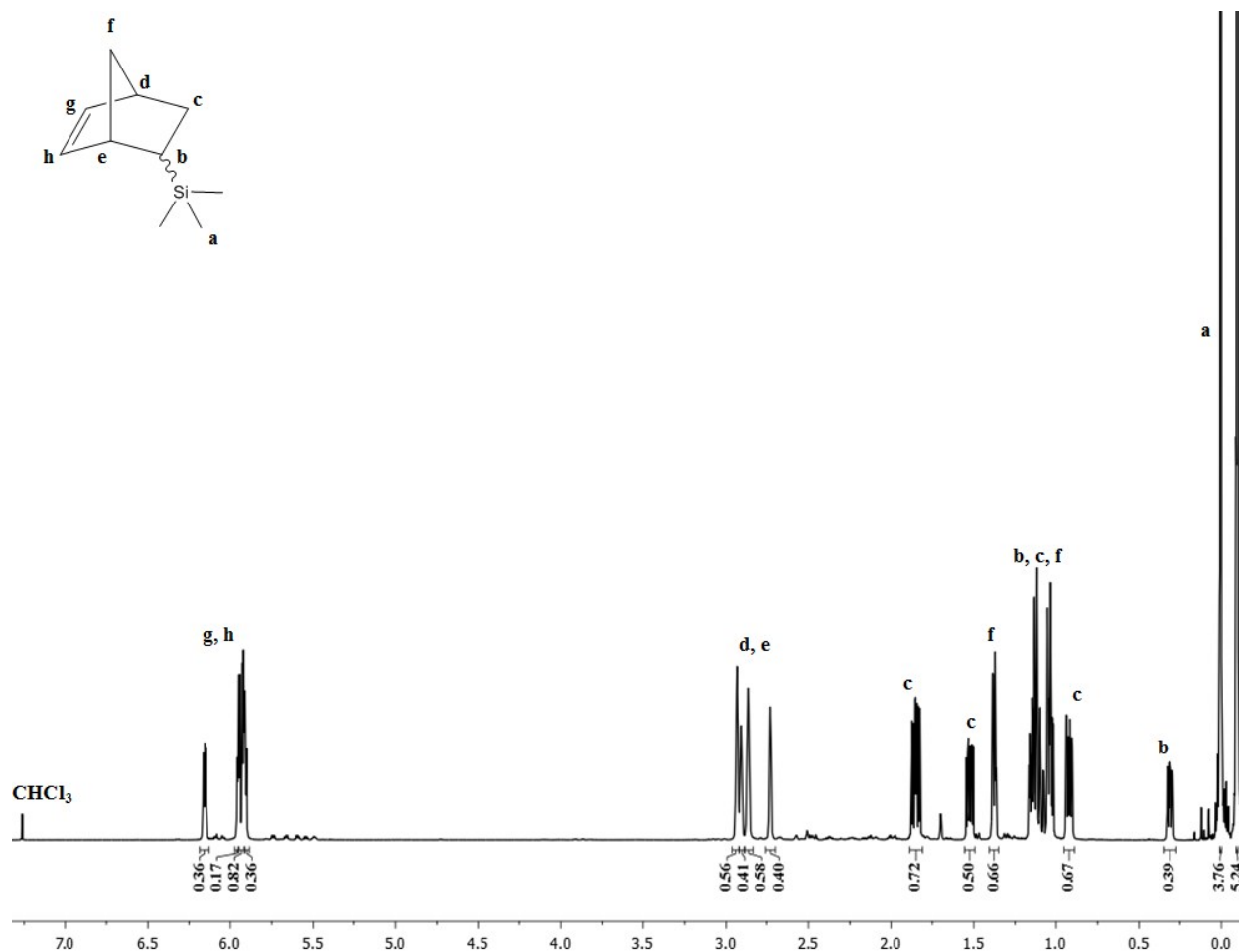


Figure S9. ¹H-NMR with appropriate peak positions and integrations for trimethylsilyl norbornene

NMR spectra are in agreement with the formation of trimethylsilyl norbornene.

¹H NMR (CDCl₃): δ 6.16 (dd, 1H, minor), 5.95 (dd, 1H, minor), 5.93 (dd, 1H, major), 5.92 (dd, 1H, major), 2.93 (br s, 1H, major), 2.91 (br s, 1H, minor), 2.87 (br s, 1H, major), 2.73 (br s, 1H, minor), 1.85 (ddd, 1H, major), 1.52 (ddd, 1H, minor), 1.38 (ddd, 1H, major), 1.16 (m, 1H, minor), 1.15 (m, 1H, major), 1.13 (m, 1H, minor), 1.12 (m, 1H, major), 1.05 (m, 1H, minor), 1.03 (m, 1H, major), 0.92 (ddd, 1H, major), 0.31 (ddd, 1H, minor), 0.00 (s, 3H, minor), -0.10 (s, 3H, major)

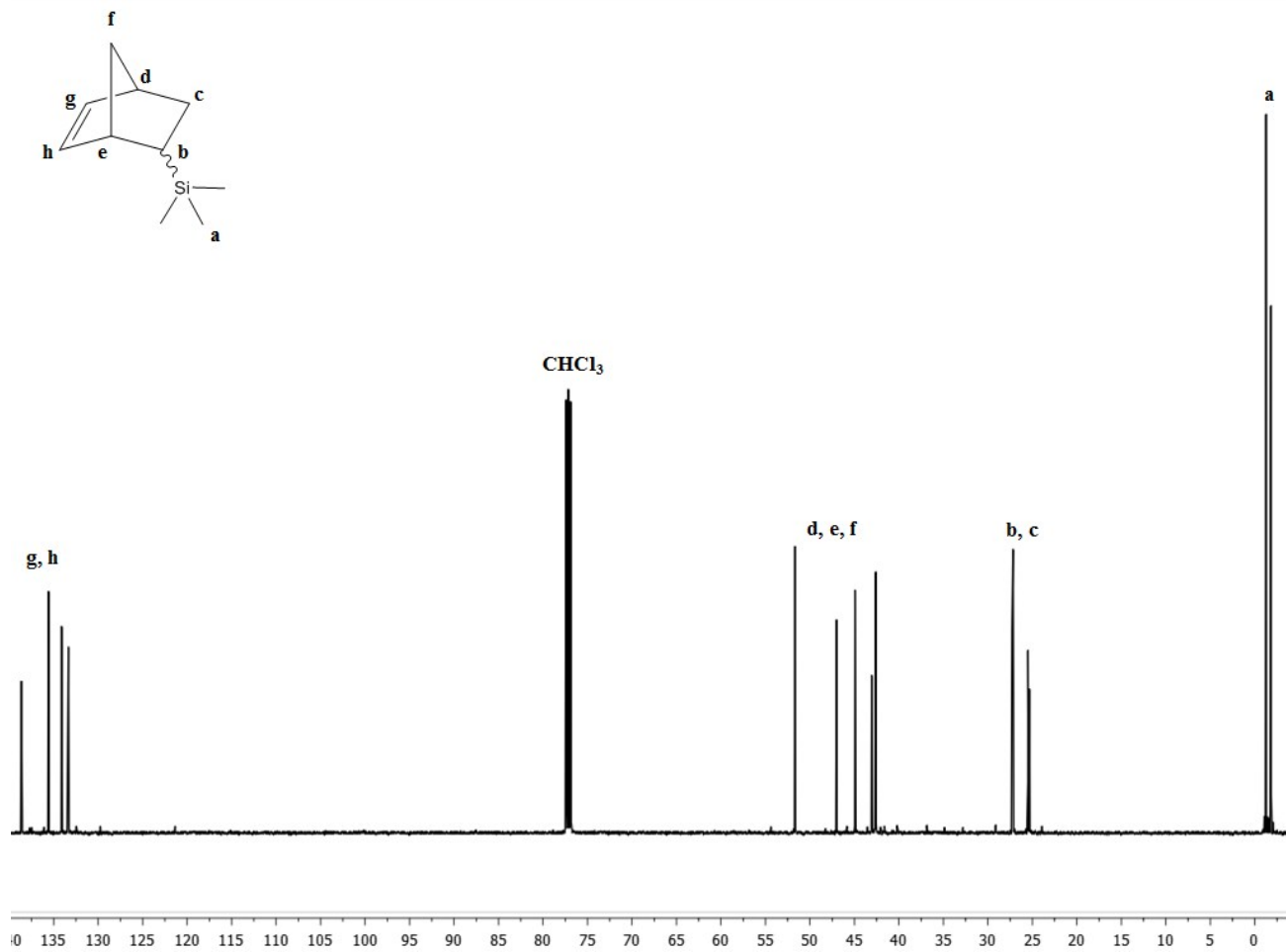


Figure S10. ^{13}C -NMR with appropriate peak positions for trimethylsilyl norbornene

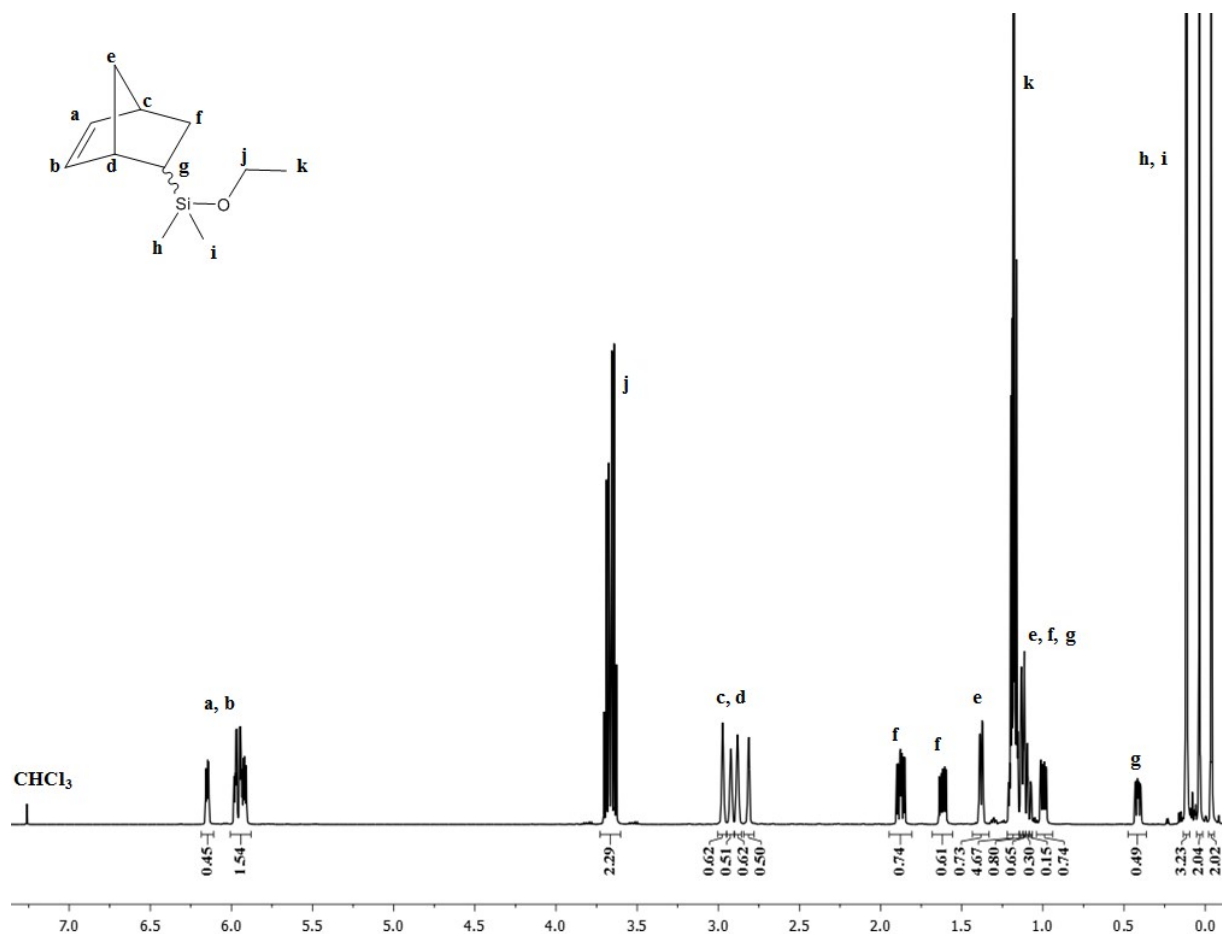


Figure S11. ¹H-NMR with appropriate peak positions and integrations for dimethylethoxysilyl norbornene

NMR spectra for dimethylethoxysilyl norbornene:

¹H NMR (CDCl₃): δ 6.15 (dd, 1H, minor), 5.98 (dd, 1H, major), 5.94 (dd, 1H, major), 5.92 (dd, 1H, minor), 3.68 (q, 2H, minor), 3.65 (q, 2H, major), 2.97 (br s, 1H, major), 2.92 (br s, 1H, minor), 2.88 (br s, 1H, major), 2.81 (br s, 1H, minor), 1.88 (ddd, 1H, major), 1.62 (ddd, 1H, minor), 1.38 (ddd, 1H, major), 1.19 (t, 3H, minor), 1.18 (t, 3H, major), 1.17 (m, 1H, minor), 1.16 (m, 1H, major), 1.13 (m, 1H, major), 1.12 (m, 1H, major), 1.05 (m, 1H, minor), 1.03 (m, 1H, minor), 1.00 (ddd, 1H, major), 0.41 (ddd, 1H, minor), 0.12 (s, 3H, minor), 0.11 (s, 3H, minor), 0.04 (s, 3H, major), -0.04 (s, 3H, major)

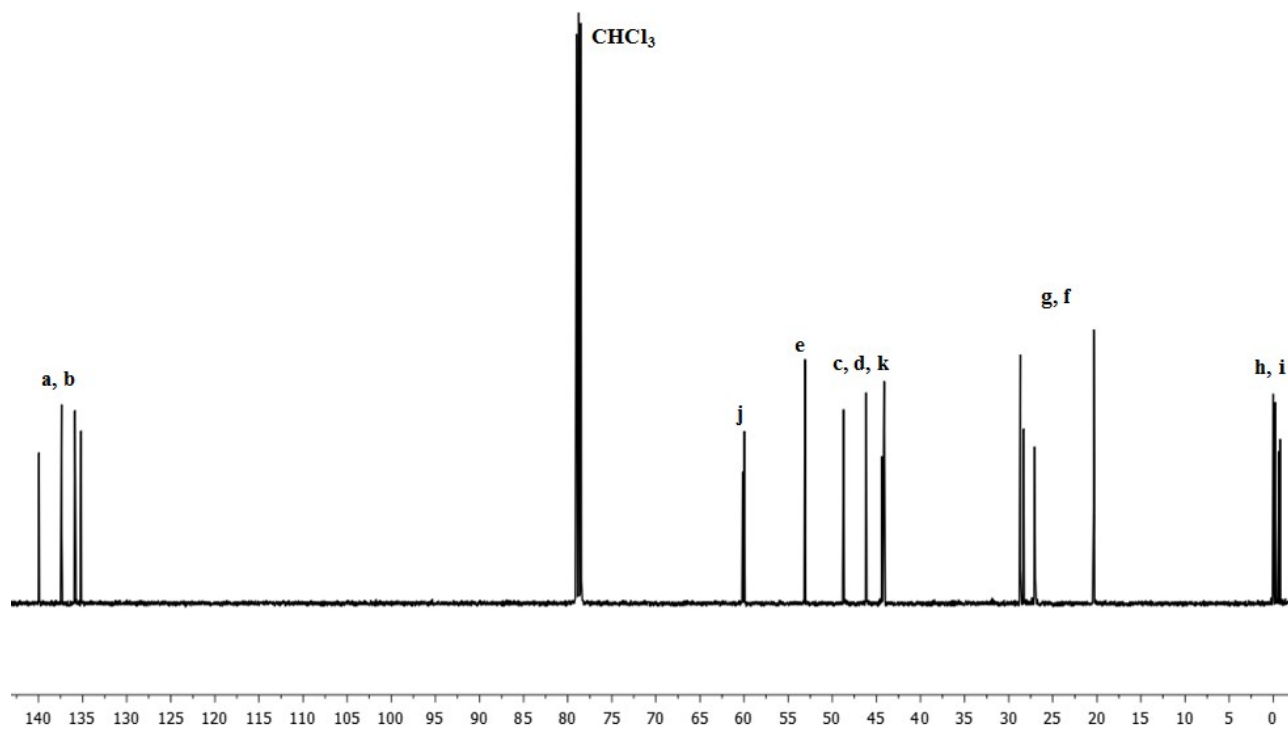
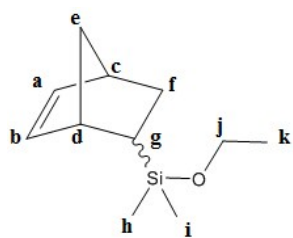


Figure S12. ^{13}C -NMR with appropriate peak positions for dimethylethoxysilyl norbornene

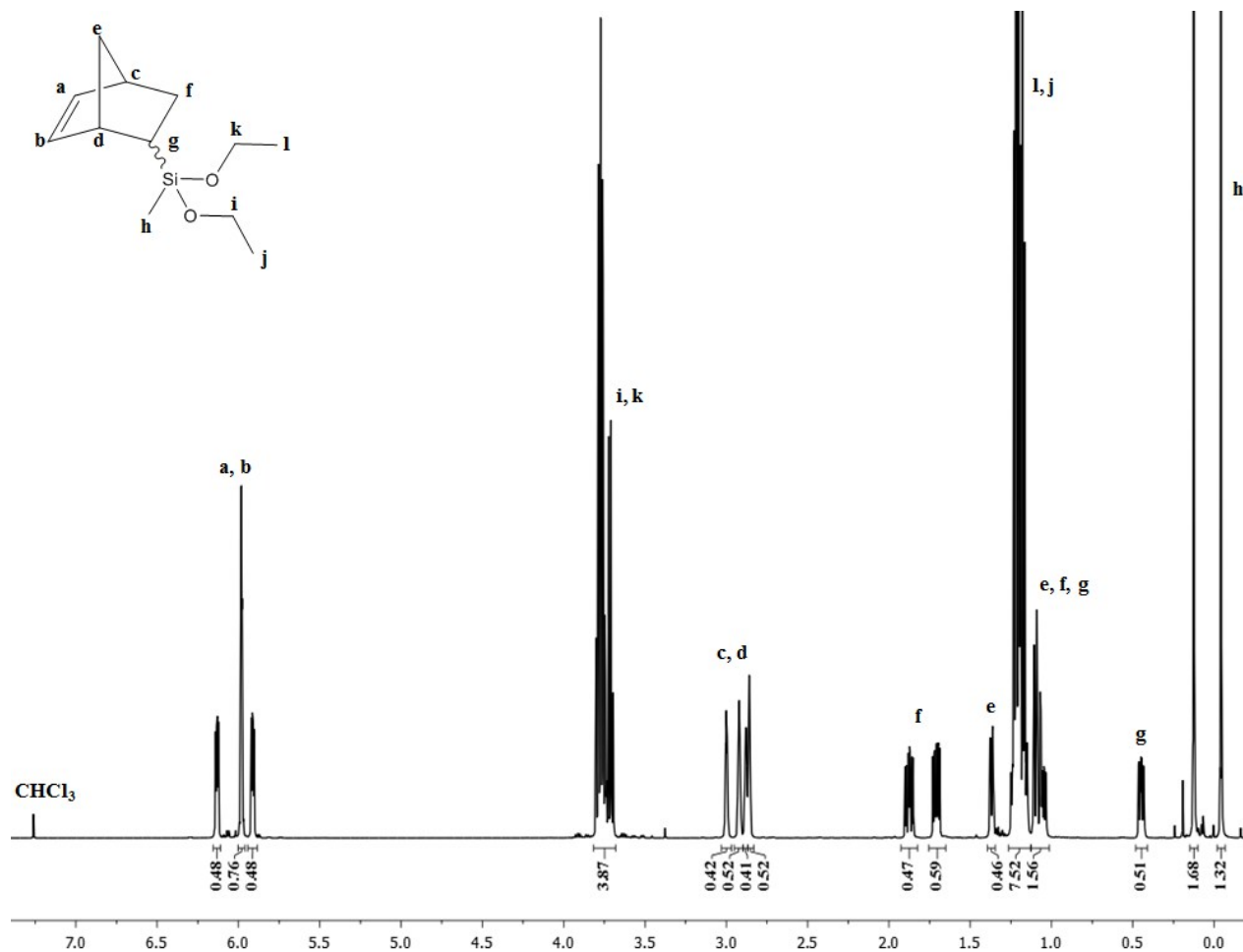


Figure S13. ¹H-NMR with appropriate peak positions and integrations for methyldiethoxysilyl norbornene

NMR spectra for methyldiethoxysilyl norbornene:

¹H NMR (CDCl₃): δ 6.13 (dd, 1H, major), 5.98 (m, 2H, minor), 5.91 (dd, 1H, major), 3.78 (q, 2H, major), 3.78 (q, 2H, major), 3.76 (q, 2H, minor), 3.72 (q, 2H, minor), 3.00 (m, 1H, minor), 2.92 (br s, 1H, major), 2.88 (m, 1H, minor), 2.86 (br s, 1H, major), 1.88 (ddd, 1H, minor), 1.70 (ddd, 1H, major), 1.38 (m, 1H, minor), 1.36 (m, 1H, major), 1.22 (t, 3H, major), 1.21 (t, 3H, major), 1.20 (t, 3H, minor), 1.18 (t, 3H, minor), 1.17 (m, 1H, major), 1.15 (m, 1H, minor), 1.11 (m, 1H, minor), 1.09 (m, 1H, major), 1.05 (ddd, 1H, minor), 0.45 (ddd, 1H, major), 0.13 (s, 3H, major), -0.04 (s, 3H, minor)

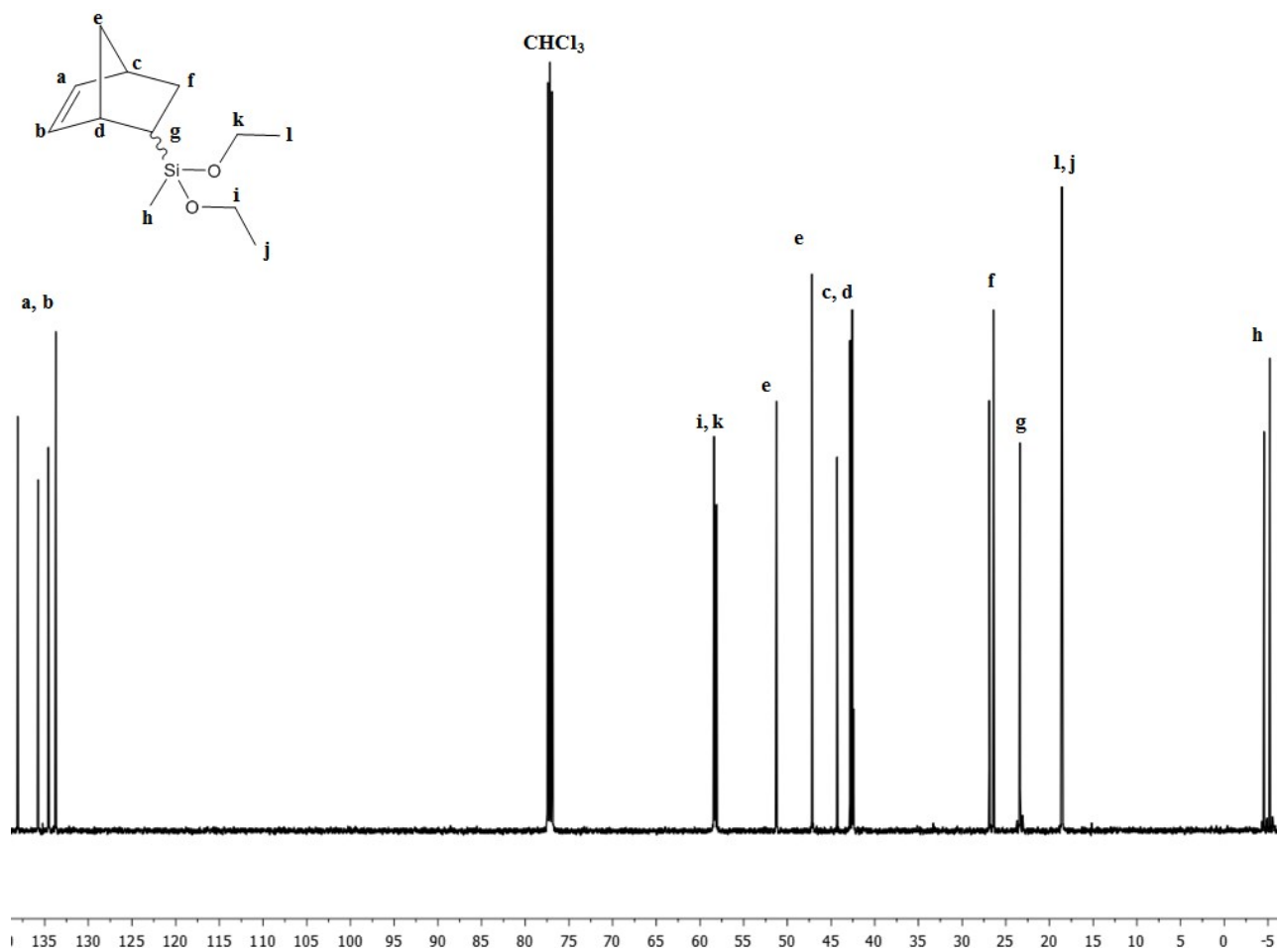


Figure S14. ^{13}C -NMR with appropriate peak positions for methyldiethoxysilyl norbornene

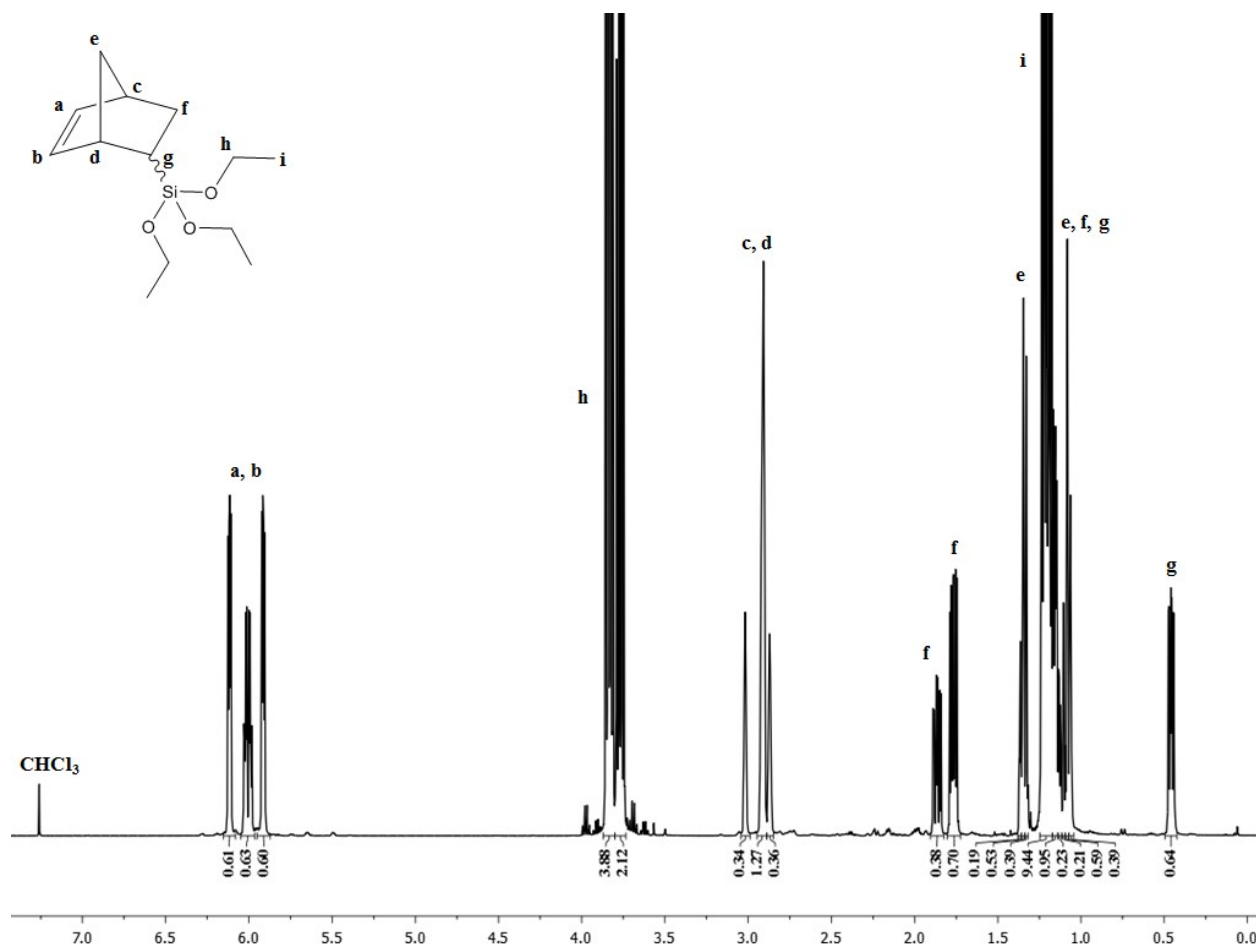


Figure S15. ¹H-NMR with appropriate peak positions and integrations for triethoxysilyl norbornene

NMR spectra for triethoxysilyl norbornene:

¹H NMR (CDCl₃): δ 6.12 (dd, 1H, major), 6.01 (m, 2H, minor), 5.91 (dd, 1H, major), 3.83 (q, 6H, major), 3.77 (q, 6H, minor), 3.02 (m, 1H, minor), 2.92 (br s, 1H, major), 2.91 (br s, 1H, major), 2.27 (br s, 1H, minor), 1.86 (ddd, 1H, minor), 1.77 (ddd, 1H, major), 1.37 (m, 1H, minor), 1.35 (m, 1H, major), 1.35 (br s, 1H, minor), 1.33 (br s, 1H, major), 1.22 (t, 9H, major), 1.19 (t, 9H, minor), 1.17 (m, 1H, major), 1.15 (m, 1H, minor), 1.08 (m, 1H, minor), 0.45 (ddd, 1H, major)

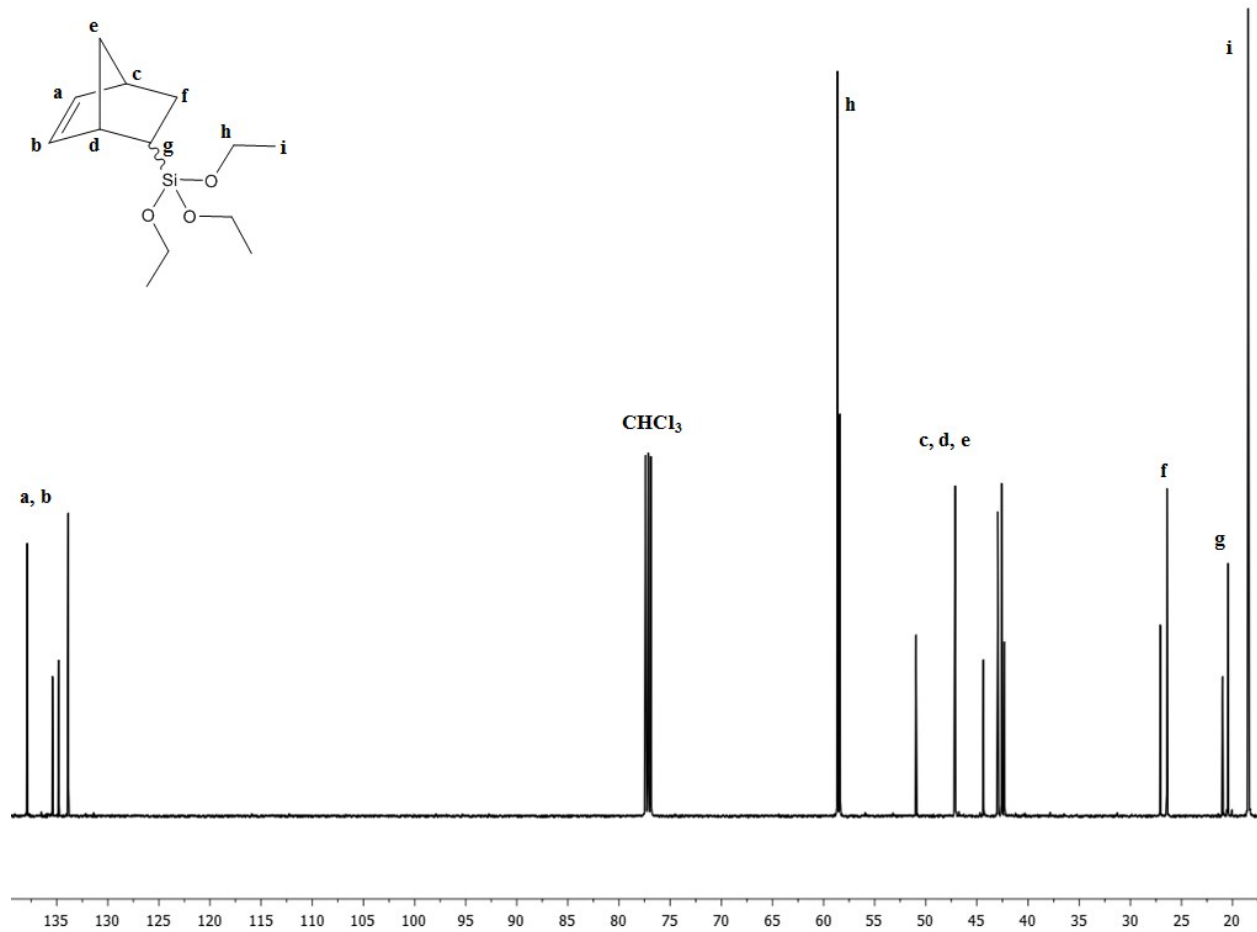


Figure S16. ¹³C-NMR with appropriate peak positions for triethoxysilyl norbornene

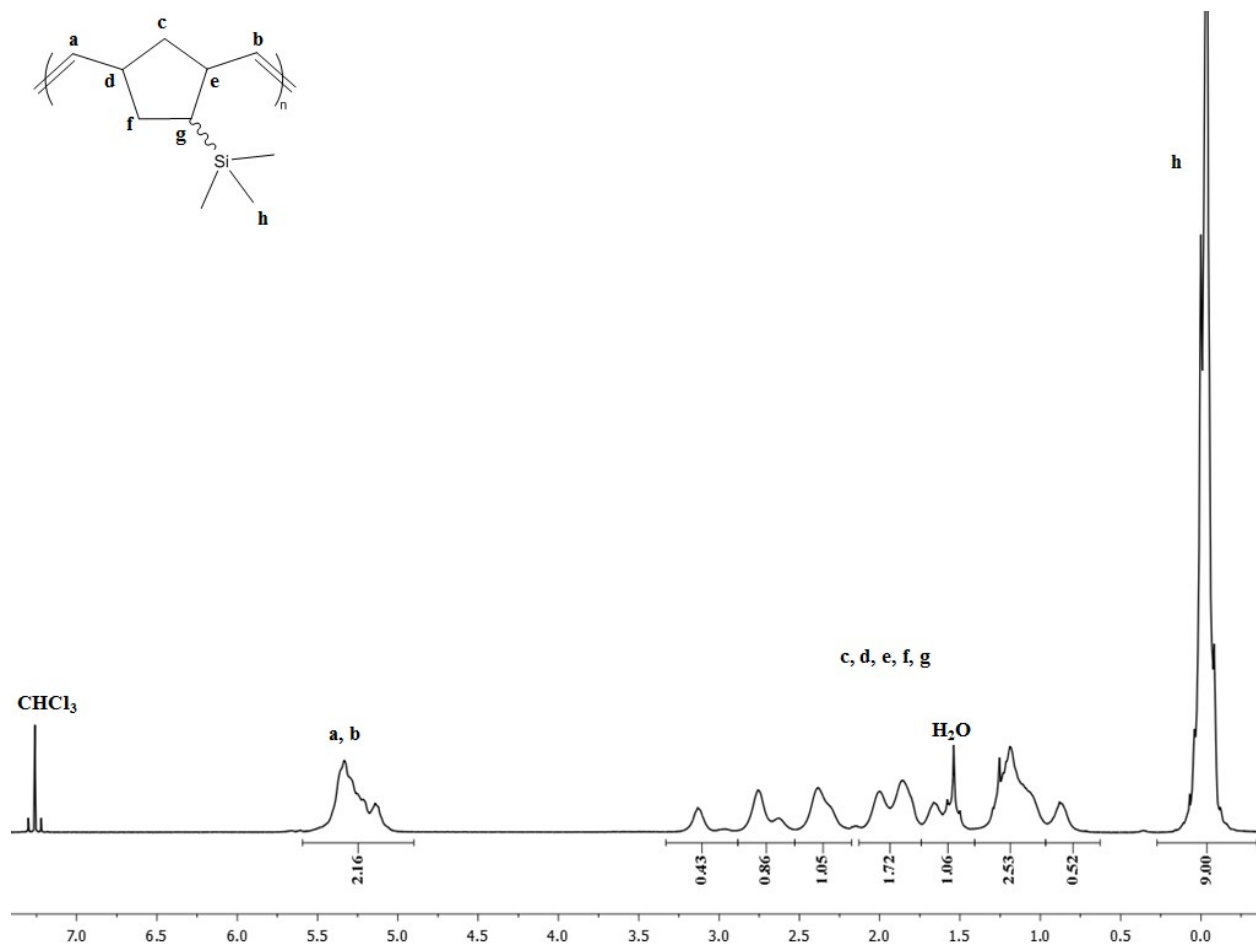


Figure S17. ¹H-NMR with appropriate peak positions and integrations for ROMP-SiMe₃

NMR spectra are in agreement with the formation of ROMP-SiMe₃.

¹H NMR (CDCl₃): δ 5.25 (several broad peaks, 2H, alkenyl), 3.32-0.63 (several broad peaks, aliphatic, 7H), 0.00 and -0.04 (singlets, -Si(CH₃)₃, 9H)

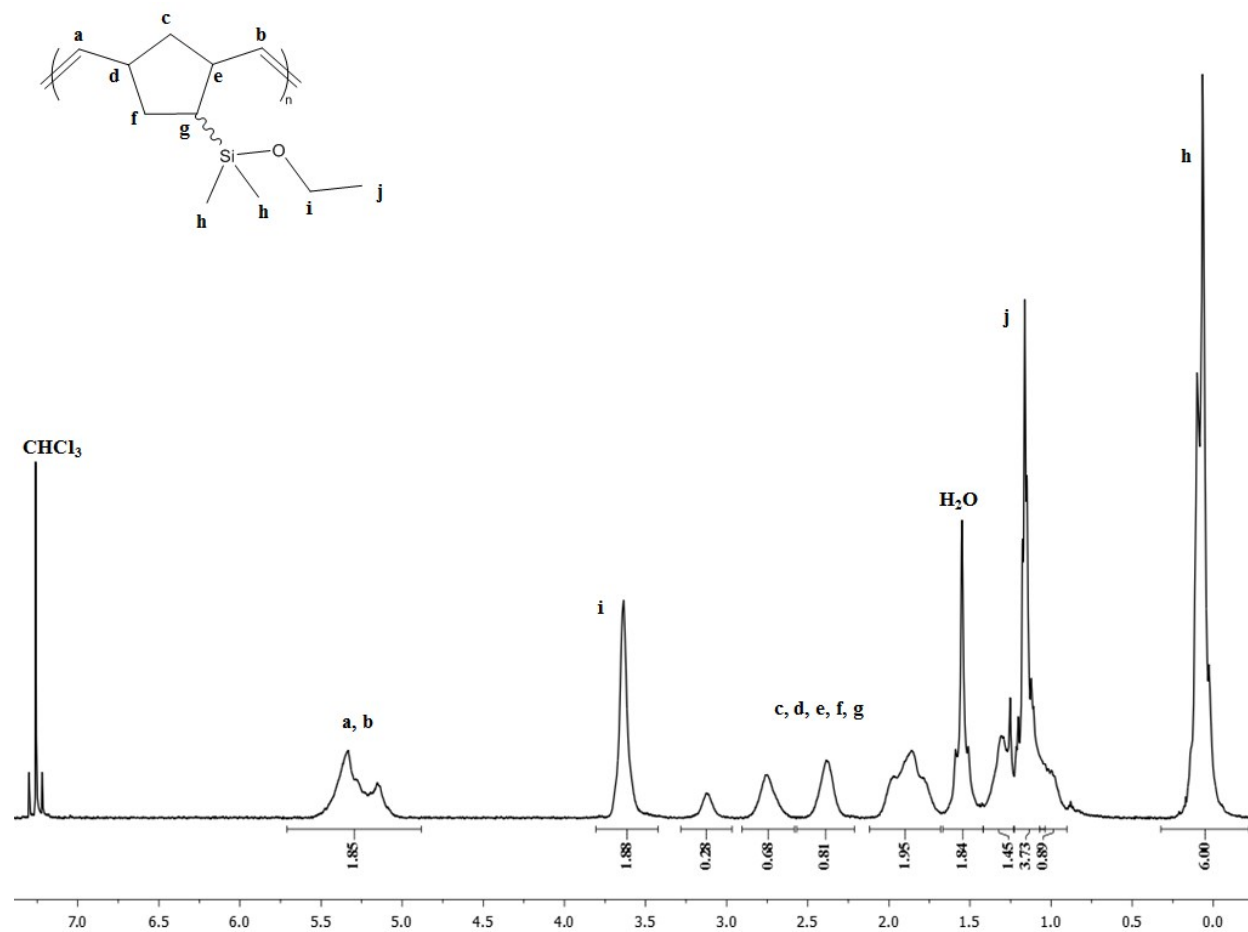


Figure S18. ¹H-NMR with appropriate peak positions and integrations for ROMP-SiMe₂OEt

NMR spectra are in agreement with the formation of ROMP-SiMe₂OEt.

¹H NMR (CDCl₃): δ 5.26 (several broad peaks, 2H, alkenyl), 3.36 (br s, Si(OCH₂CH₃), 2H) 3.32-1.42 (several broad peaks, aliphatic, 5H + H₂O), 1.30 (br s, aliphatic, 1H), 1.17 (s, Si(OCH₂CH₃), 3H), 0.16 (br shoulder, aliphatic, 1H), 0.10 and 0.06 (singlets, -Si(CH₃)₃, 6H)

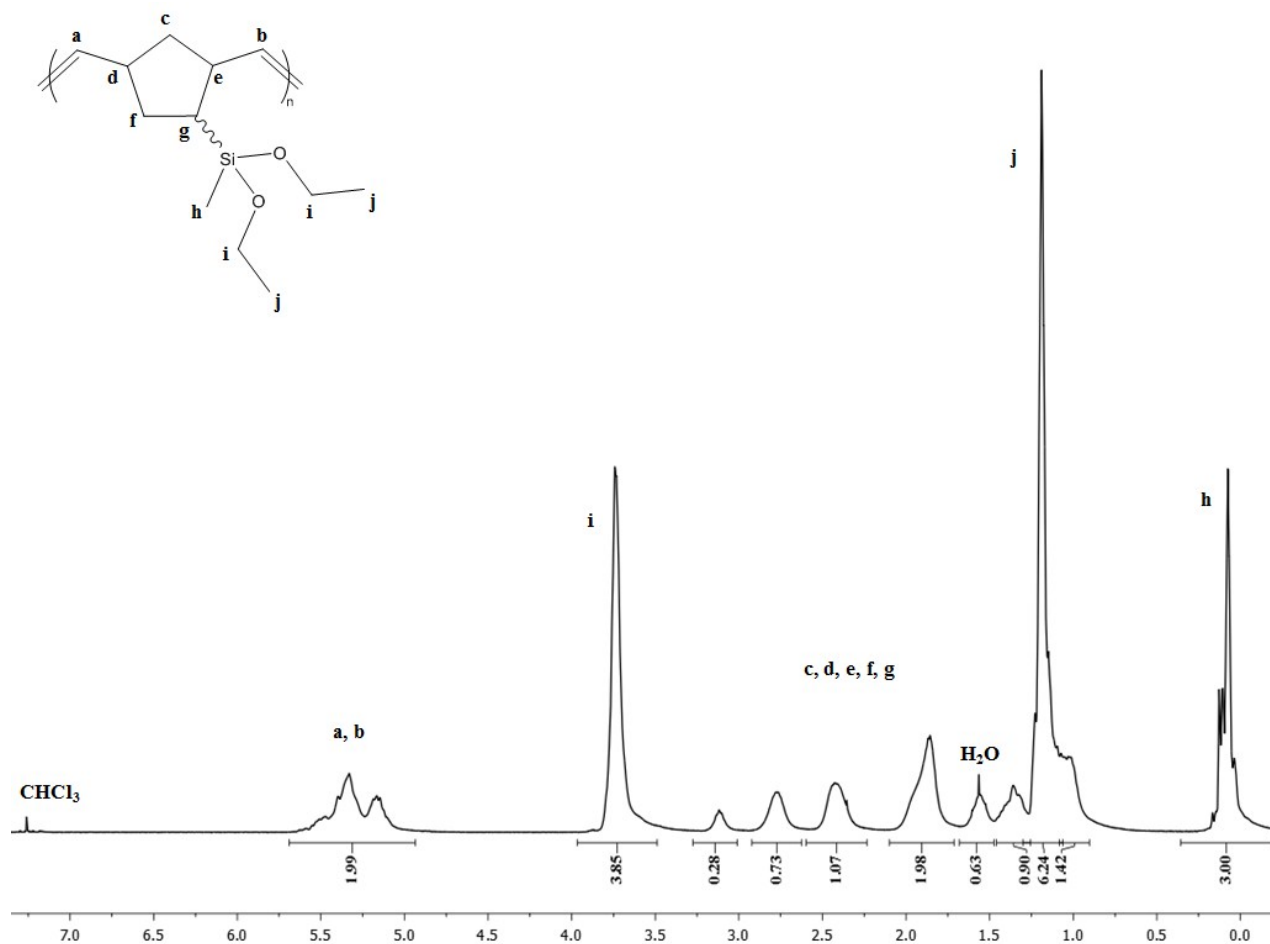


Figure S19. ¹H-NMR with appropriate peak positions and integrations for ROMP-SiMe(OEt)₂

NMR spectra are in agreement with the formation of ROMP-SiMe(OEt)₂.

¹H NMR (CDCl₃): δ 5.28 (several broad peaks, 2H, alkenyl), 3.73 (br s, Si(OCH₂CH₃), 4H) 3.27-1.27 (several broad peaks, aliphatic, 6H + H₂O), 1.19 (s, Si(OCH₂CH₃), 6H), 0.16 (br shoulder, aliphatic, 1H), 0.13/0.10 and 0.06 (singlets, -Si(CH₃)₃, 3H)

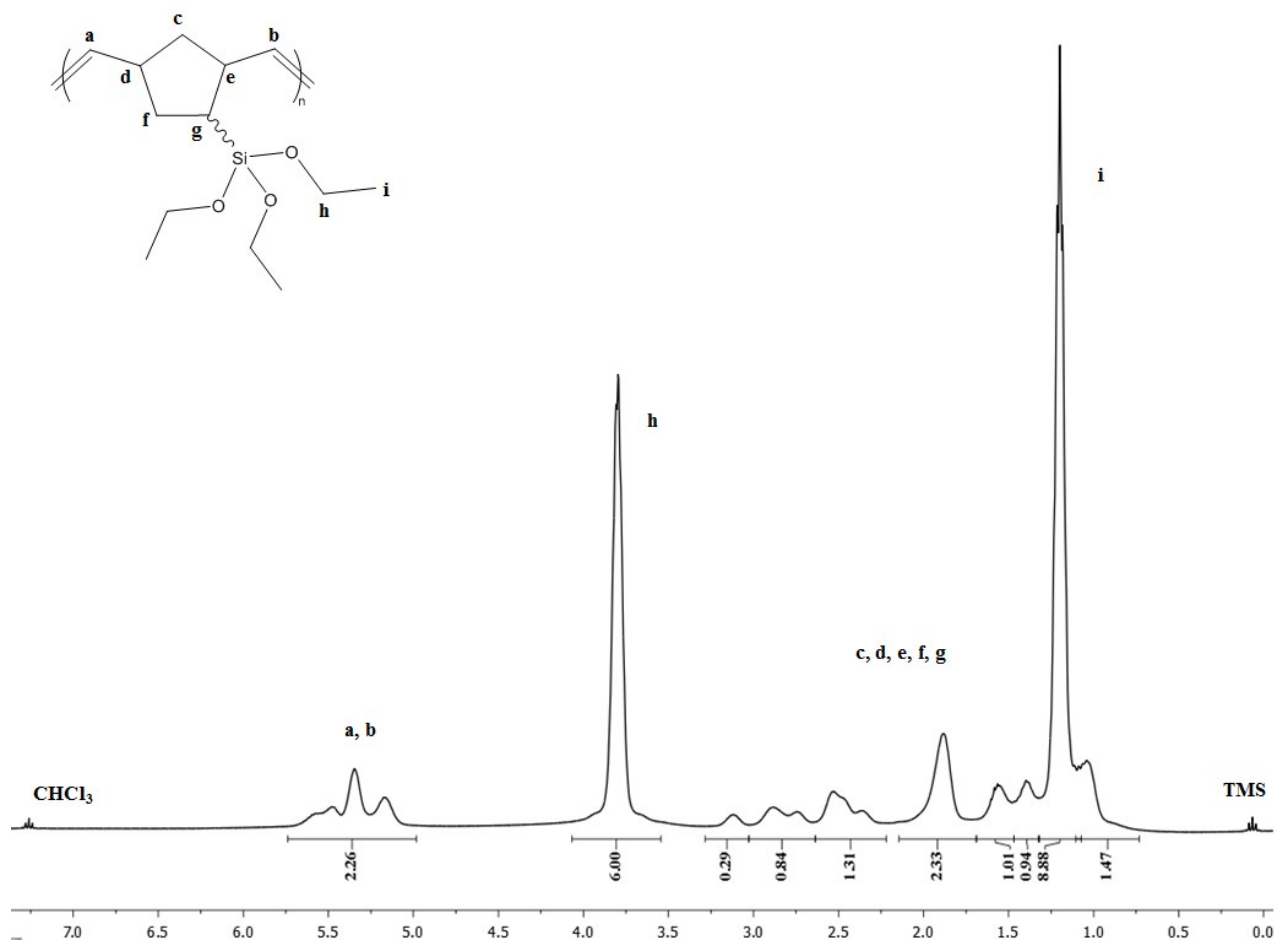


Figure S20. ^1H -NMR with appropriate peak positions and integrations for ROMP-Si(OEt) $_3$

NMR spectra are in agreement with the formation of ROMP-Si(OEt) $_3$.

^1H NMR (CDCl $_3$): δ 5.34 (several broad peaks, 2H, alkenyl), 3.80 (br s, Si(OCH $_2$ CH $_3$), 6H) 3.27-1.30 (several broad peaks, aliphatic, 6H + H $_2$ O), 1.20 (s, Si(OCH $_2$ CH $_3$), 9H), 0.16 (br shoulder, aliphatic, 1H)

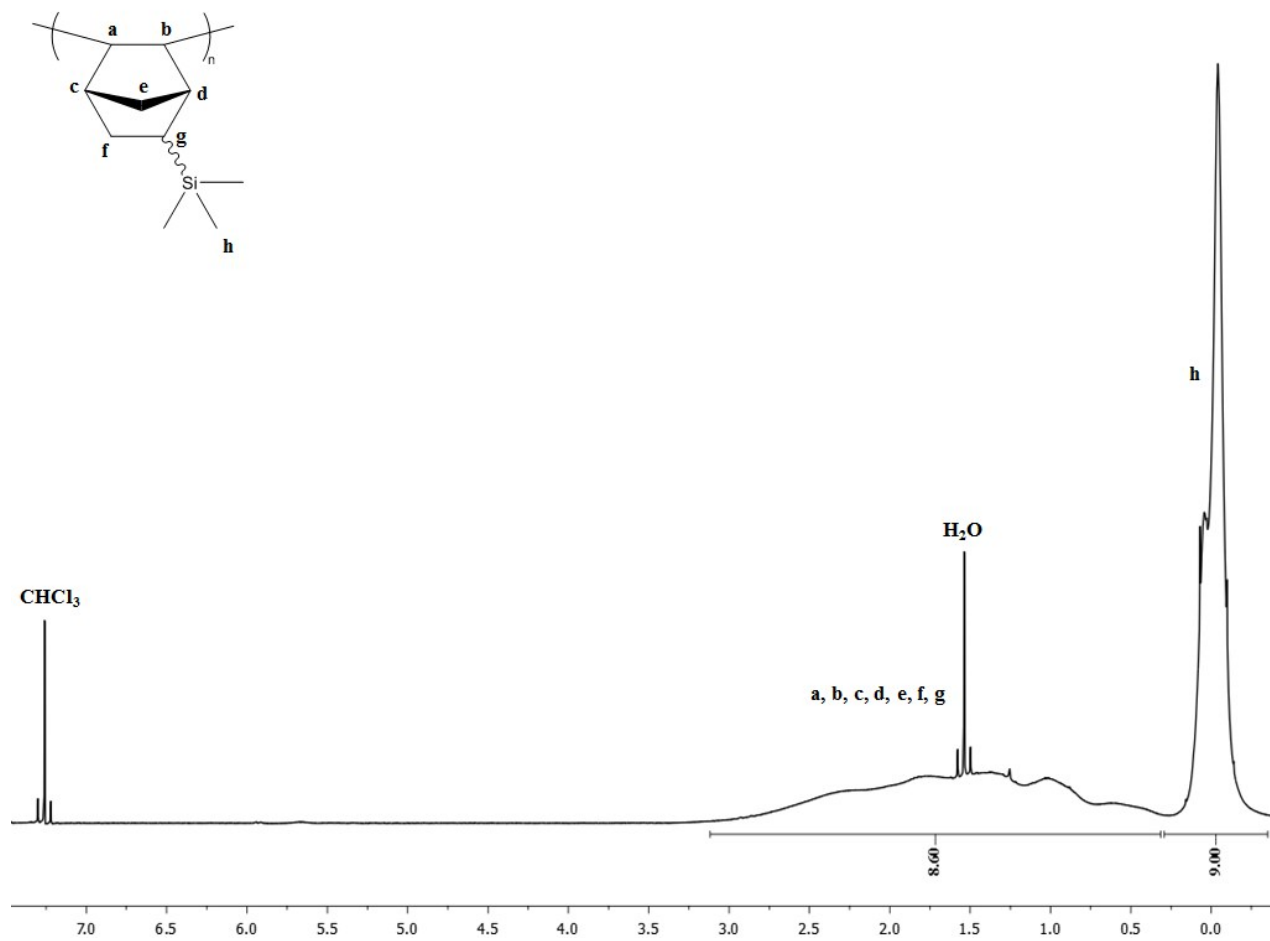


Figure S21. ¹H-NMR with appropriate peak positions and integrations for APN-SiMe₃

NMR spectra are in agreement with the formation of APN-SiMe₃.

¹H NMR (CDCl₃): δ 3.24-0.25 (several broad peaks, aliphatic, 9H), 0.04 and -0.04 (singlets, - Si(CH₃)₃, 9H)

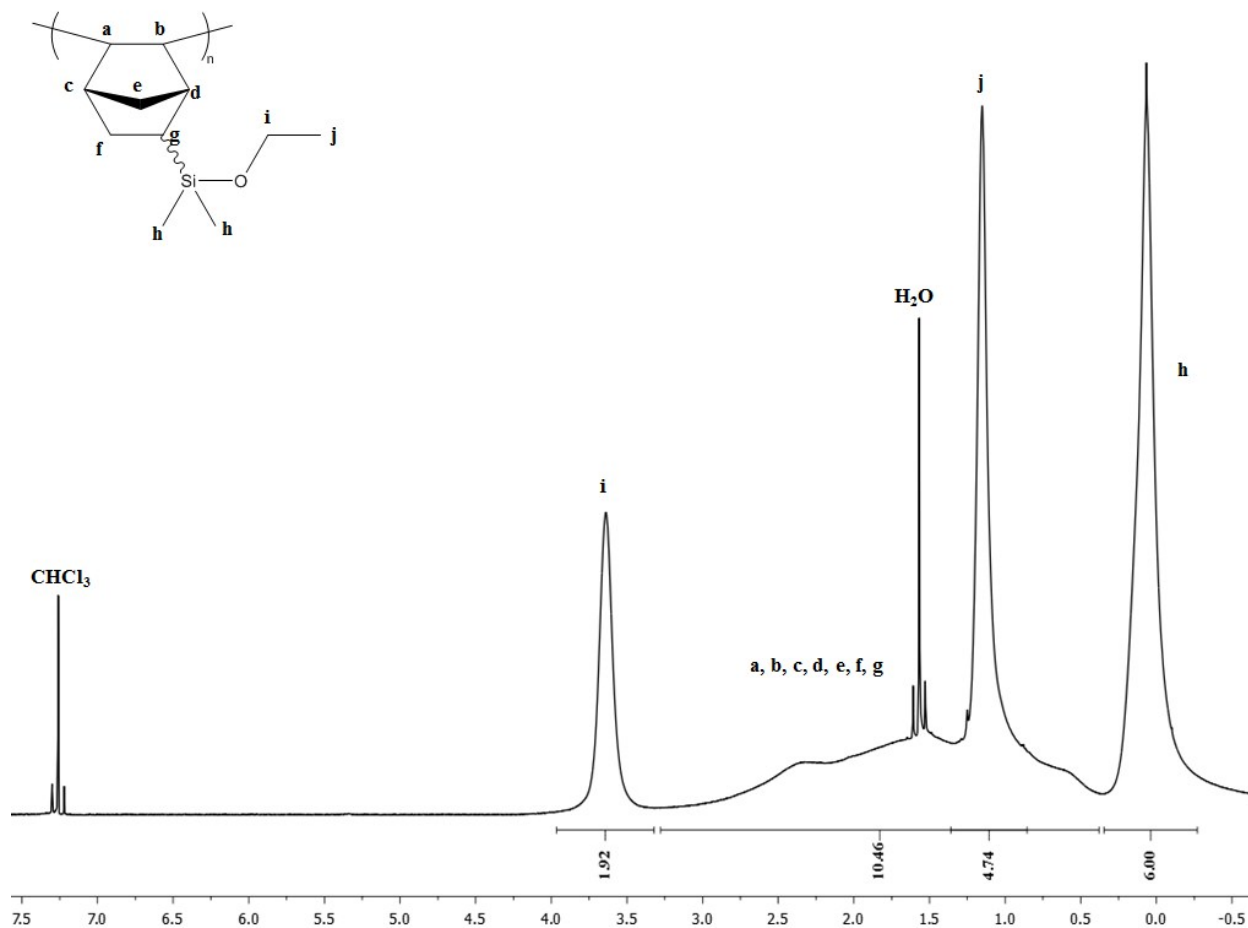


Figure S22. ^1H -NMR with appropriate peak positions and integrations for APN-SiMe₂OEt

NMR spectra are in agreement with the formation of APN-SiMe₂OEt.

^1H NMR (CDCl₃): δ 3.64 (br s, Si(OCH₂CH₃), 2H), 1.14 (br s, Si(OCH₂CH₃), 3H), 3.28-0.35 (several broad peaks, aliphatic, 9H), 0.06 (br s, -Si(CH₃)₃, 6H)

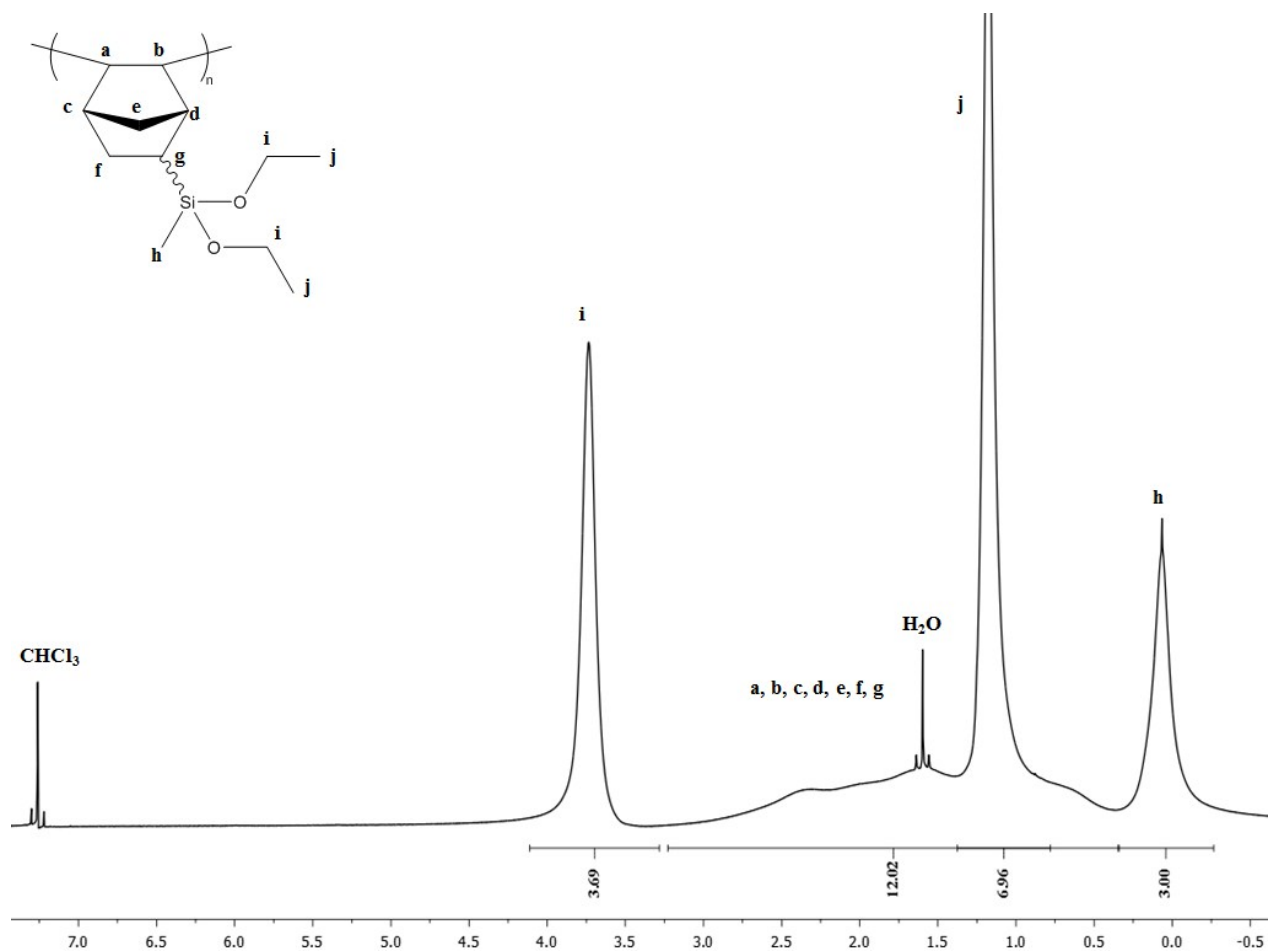


Figure S23. ¹H-NMR with appropriate peak positions and integrations for APN-SiMe(OEt)₂

NMR spectra are in agreement with the formation of APN-SiMe(OEt)₂.

¹H NMR (CDCl₃): δ 3.74 (br s, Si(OCH₂CH₃), 4H), 1.17 (br s, Si(OCH₂CH₃), 6H), 3.46-0.35 (several broad peaks, aliphatic, 9H), 0.07 (br s, -Si(CH₃)₃, 3H)

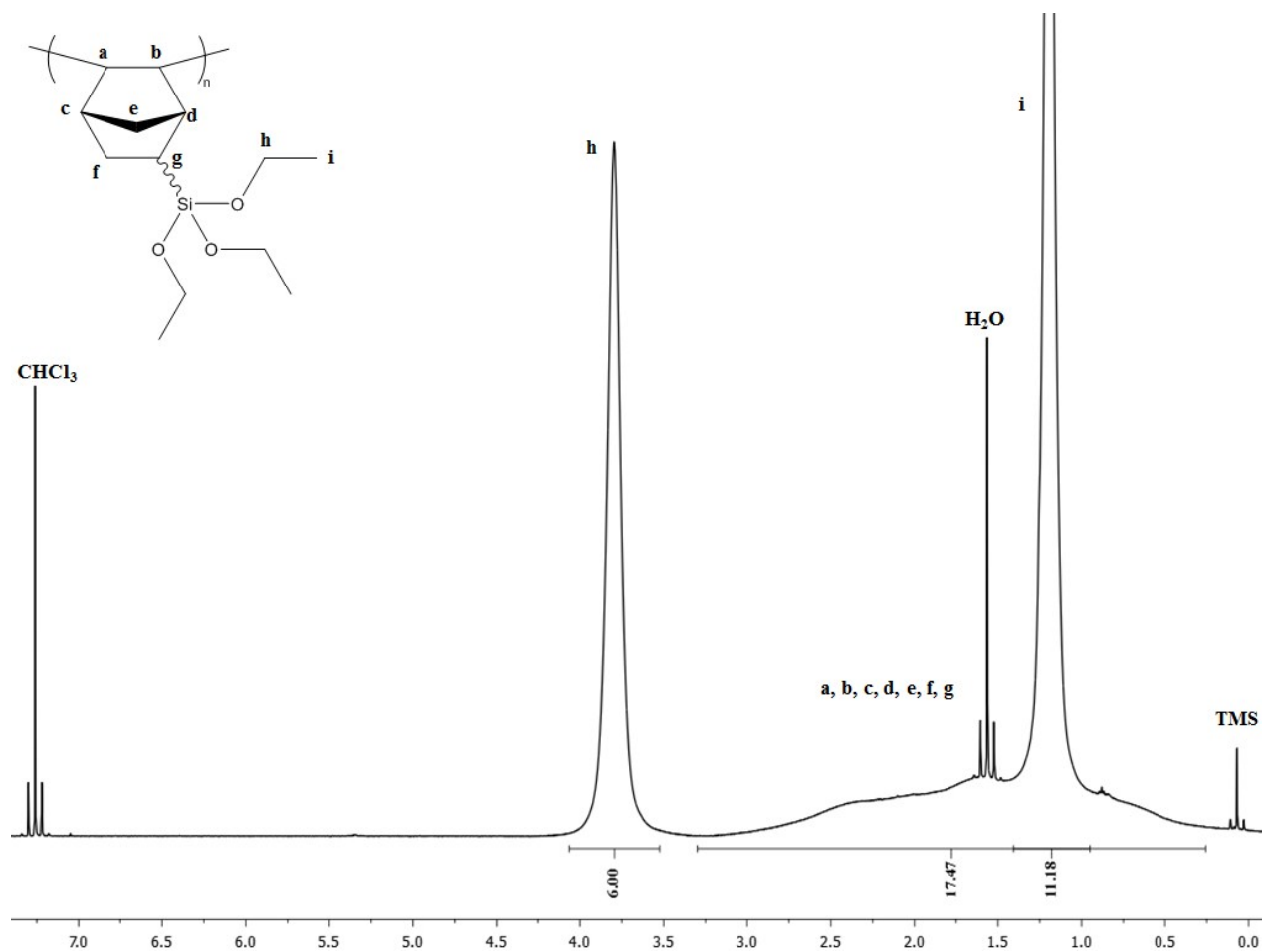


Figure S24. ¹H-NMR with appropriate peak positions and integrations for APN-Si(OEt)₃

NMR spectra are in agreement with the formation of APN-Si(OEt)₃.

¹H NMR (CDCl₃): δ 3.79 (br s, Si(OCH₂CH₃), 6H), 1.19 (br s, Si(OCH₂CH₃), 9H), 3.42-0.16 (several broad peaks, aliphatic, 9H)