

Highly efficient and reusable alkyne hydrosilylation catalysts based on rhodium complexes ligated by imidazolium-substituted phosphine

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1. Analytical data of complexes **1** and **2**

{1,2-dimethyl-3-(diphenylphosphine)butylimidazoliumbromide}bis(triphenylphosphine)chloridorhodium(I) [RhCl(PPh₃)₂(BMMIMP(PPh₃)₂)]Br (**1**)

¹H NMR (CDCl₃) ppm: 9.05 and 8.74 (s, 2H, imidazolium -CH=), 7.80-7.18 (m, 40H, Ar-H), 4.15 (dt, 2H, N-CH₂), 3.72 (s, 3H, N-CH₃), 2.55 (d, *J* = 3.7 Hz, 2H, CH₂), 2.52 (dt, *J* = 15.7 Hz, *J* = 8.2 Hz 2H, CH₂), 2.3 (s, 3H, CH₃) 1.2 (m, 4H, *J* = 7.5, CH₂). ¹³C NMR (CDCl₃) ppm: 138 (NC(CH₃)N), 135, 134, 133, 132, 131, 130, 129, 128, 127 (Ar-C), 123 (CH=CH), 121 (CH=CH), 49 (N-CH₃), 35 (N-CH₂), 32, 28 (CH₂), 13 (CH₃). ³¹P NMR (CDCl₃) ppm: 28. 35 (P-Ar).

Elem. Anal. Calcd. for C₅₇H₅₆BrClN₂P₃Rh : C 63.38; H 5.23; N 2.59; Found C 63.57; H 5.19; N 2.67 (%).

{1,2-dimethyl-3-(diphenylphosphine)butylimidazoliumbromide}(η⁴-cycloocta-1,5-diene)chloridorhodium(I) [RhCl(cod)(BMMIMP(PPh₃)₂)]Br (**2**)

¹H NMR (CDCl₃) ppm: 8.57 and 8.16 (s, 2H, imidazolium -CH=), 7.85-7.18 (m, 10H, Ar-H), 5.45 (m, 2H, *J* = 7.5, -CH=), 4.34 (dt, 2H, N-CH₂), 4.24 (m, 4H, =CH-), 3.71 (s, 3H, N-CH₃), 3.1 (m, 2H, -CH=), 2.6 (d, *J* = 3.4 Hz, 2H, CH₂), 2.2 (dt, *J* = 13.5, 2H, CH₂), 1.8 (s, 3H, CH₃), 1.4 (m, 4H, *J* = 7.1, CH₂). ¹³C NMR (CDCl₃) ppm: 139 (NC(CH₃)N), 135, 132, 131, 129, (Ar-C), 122 (-CH=CH-), 121 (-CH=CH), 101(cod, =CH-), 64.8, 64 (cod, -CH=), 47 (N-CH₃), 34 (N-CH₂), 33, 31 (cod, CH₂), 30, 29 (CH₂), 14 (CH₃) ³¹P NMR(CDCl₃) ppm: 26 (P-Ar).

Elem. Anal. Calcd. for C₃₂H₄₆BrClN₂PRh: C 54.29; H 6.55; N 3.96; Found C 54.46; H 6.44; N 3.99 (%).

2. NMR spectra of isolated products

2.1. 1,1,1,3,5,5,5-Heptamethyl-3-[(1*Z*)hept-1-enyl]trisiloxane

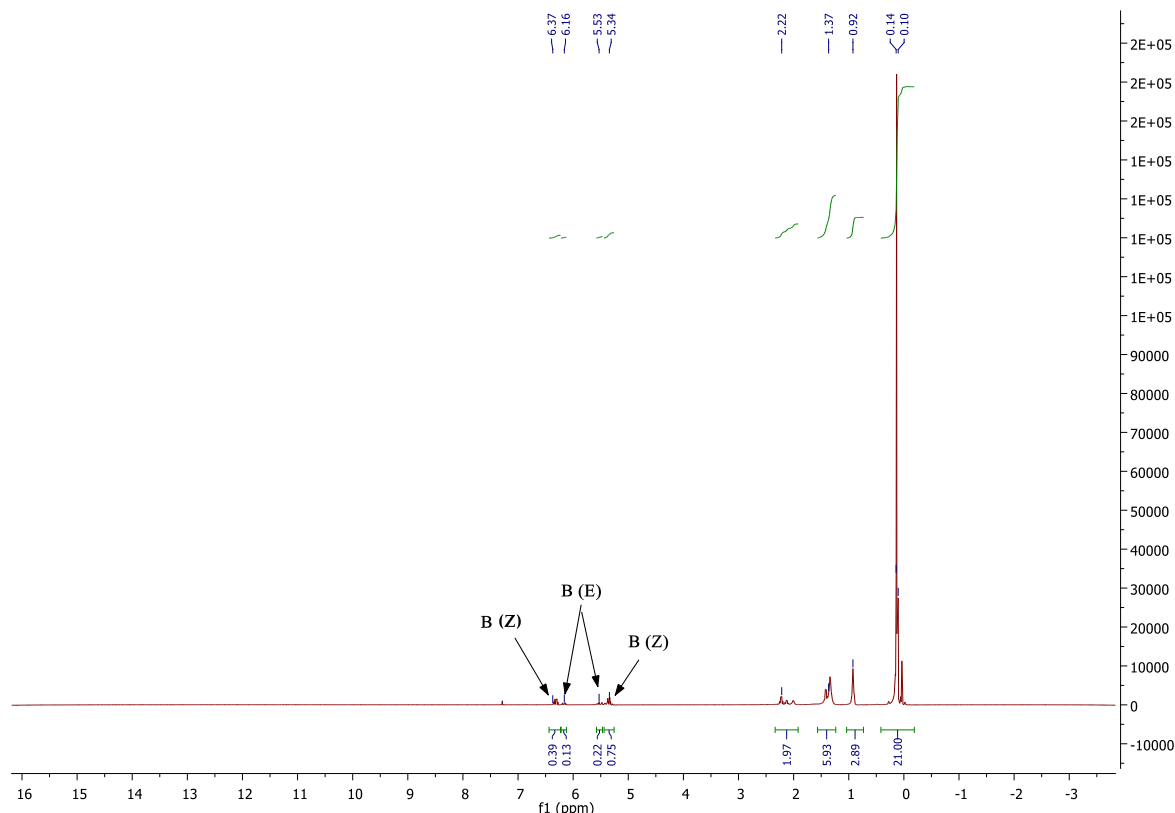


Fig. S1. ¹H NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1*Z*)hept-1-enyl]trisiloxane.

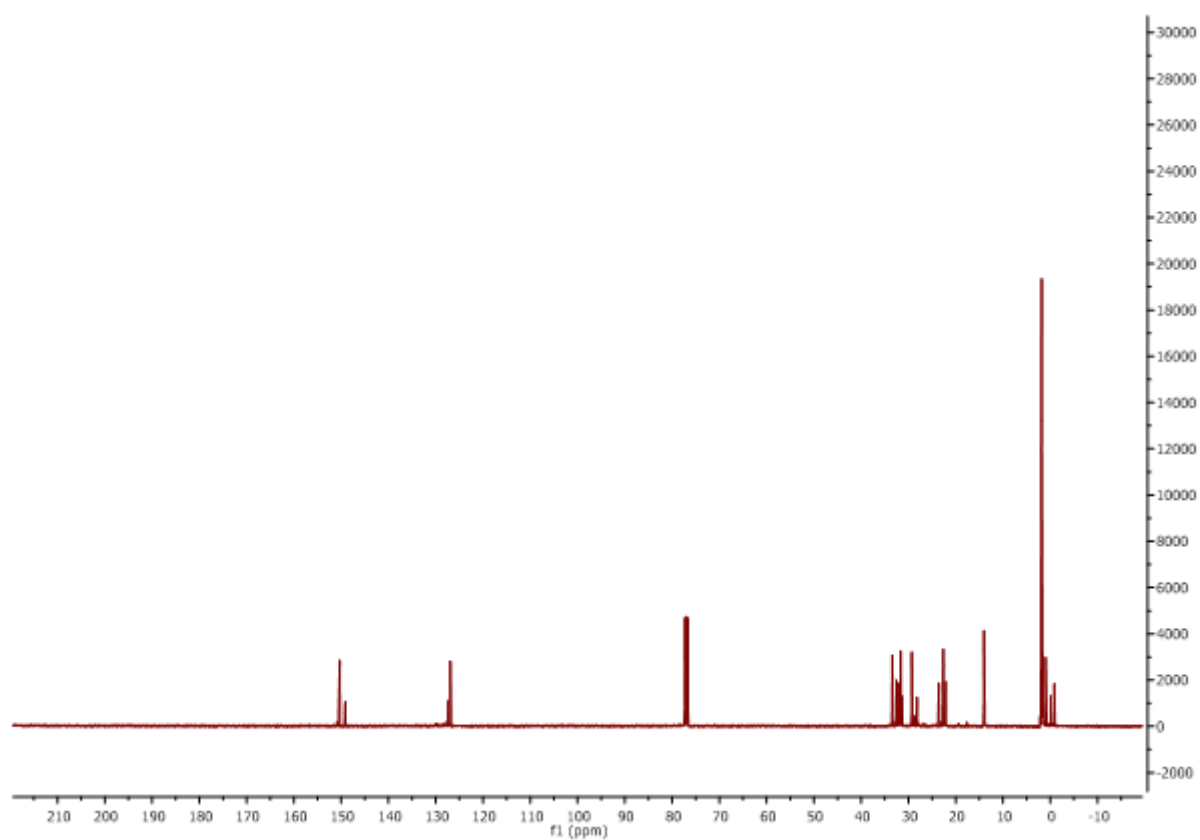


Fig. S2. ^{13}C NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)hept-1-enyl]trisiloxane.

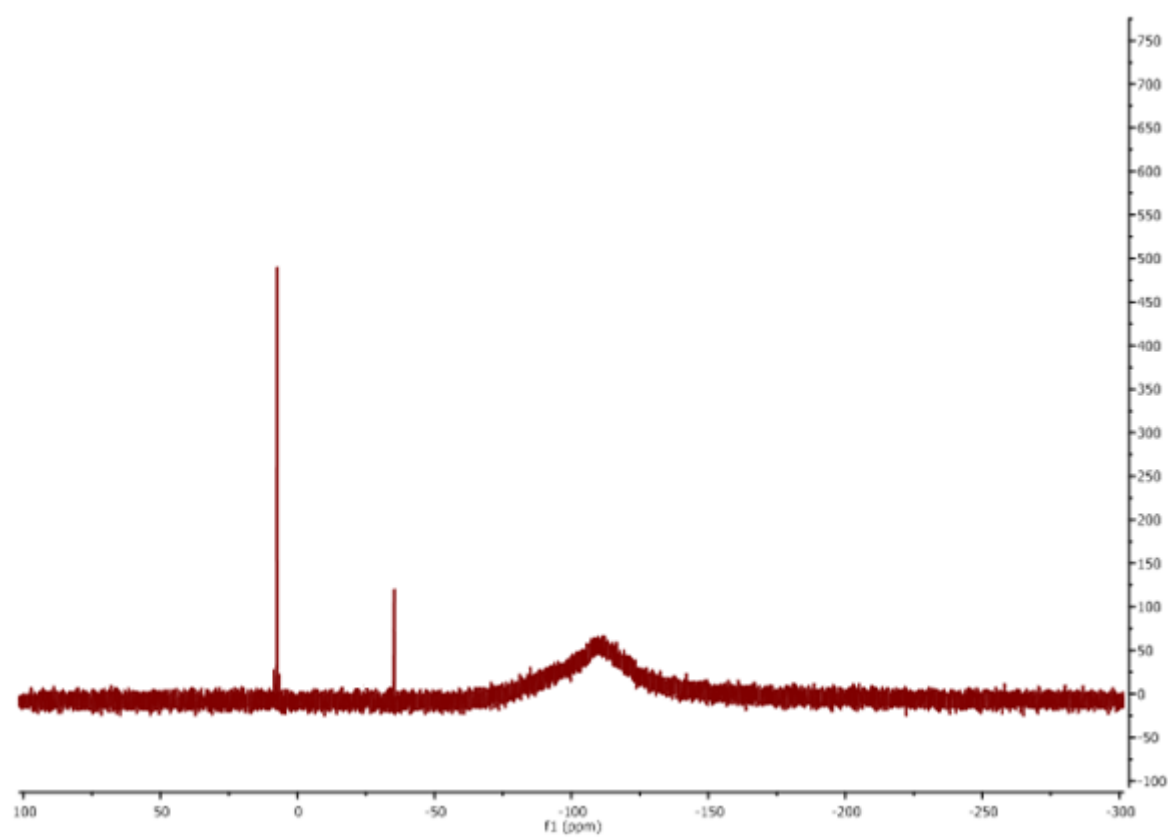


Fig. S3. ^{29}Si NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)hept-1-enyl]trisiloxane.

2.2. 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)oct-1-enyl]trisiloxane

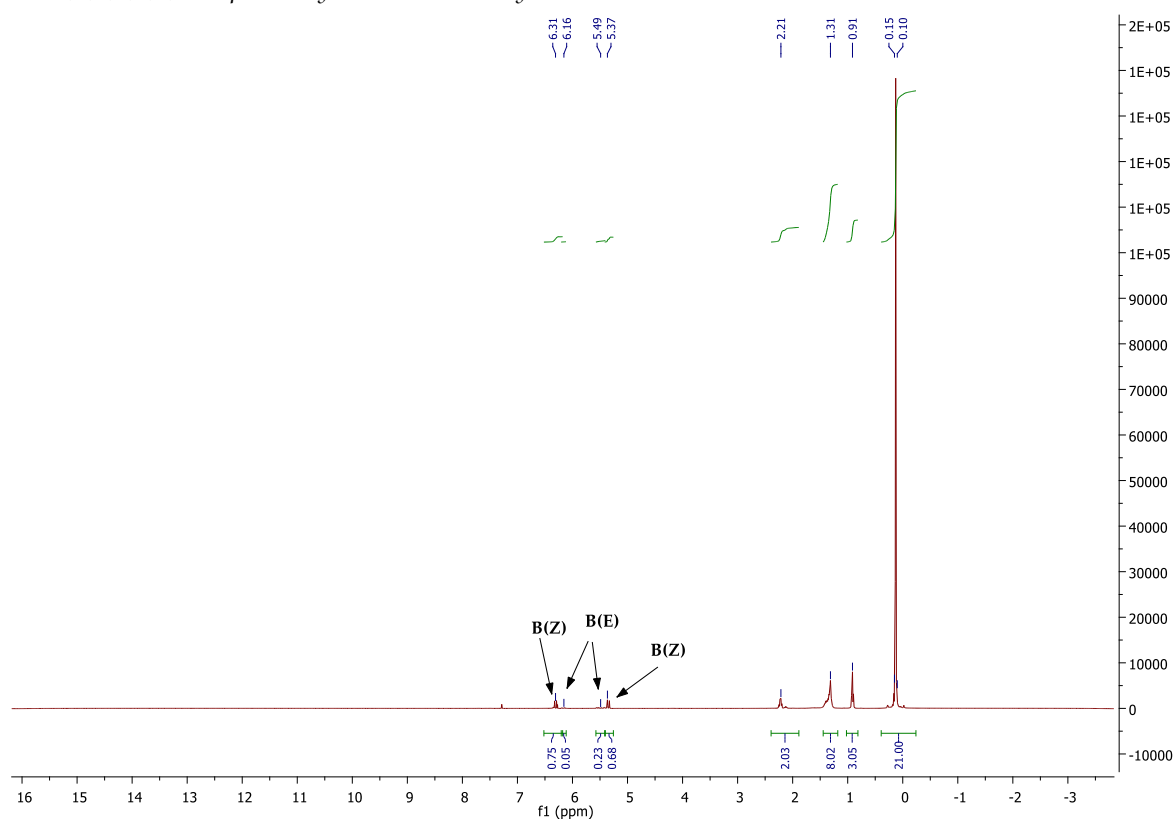


Fig. S4. ^1H NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)oct-1-enyl]trisiloxane.

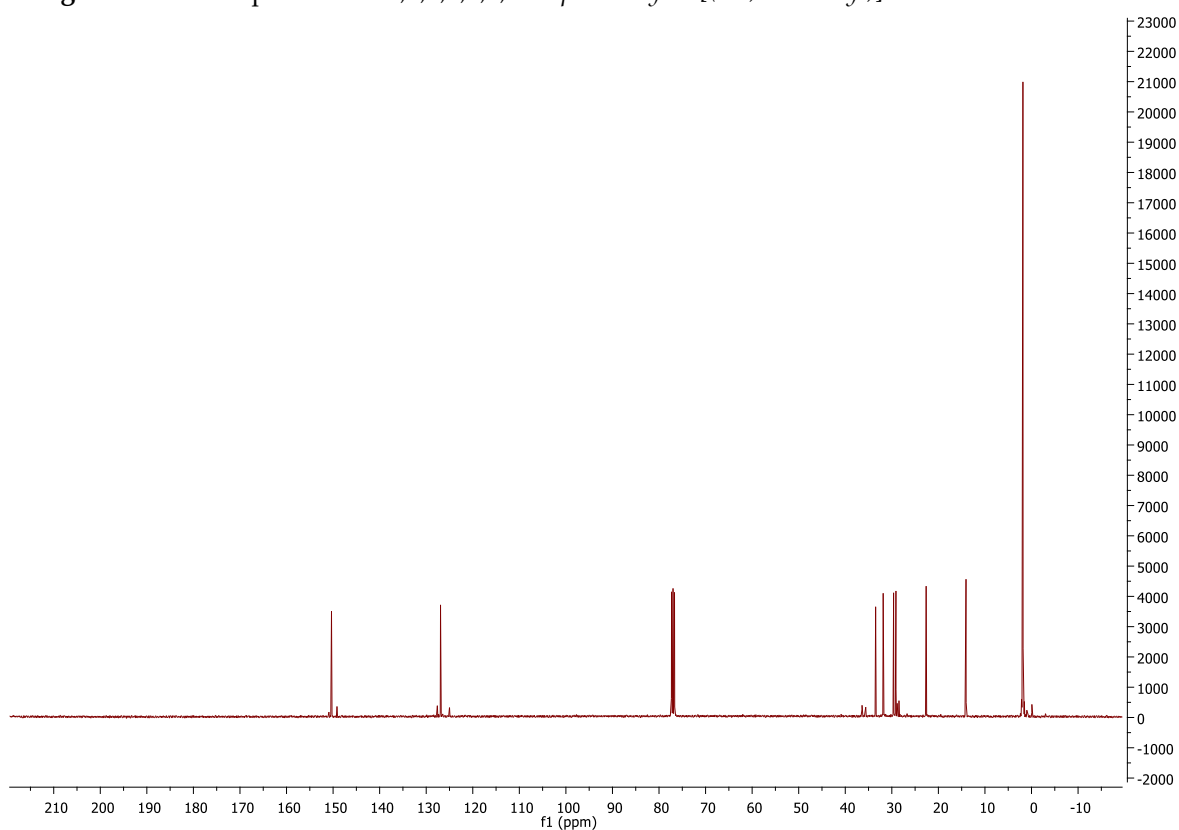


Fig. S5. ^{13}C NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)oct-1-enyl]trisiloxane.

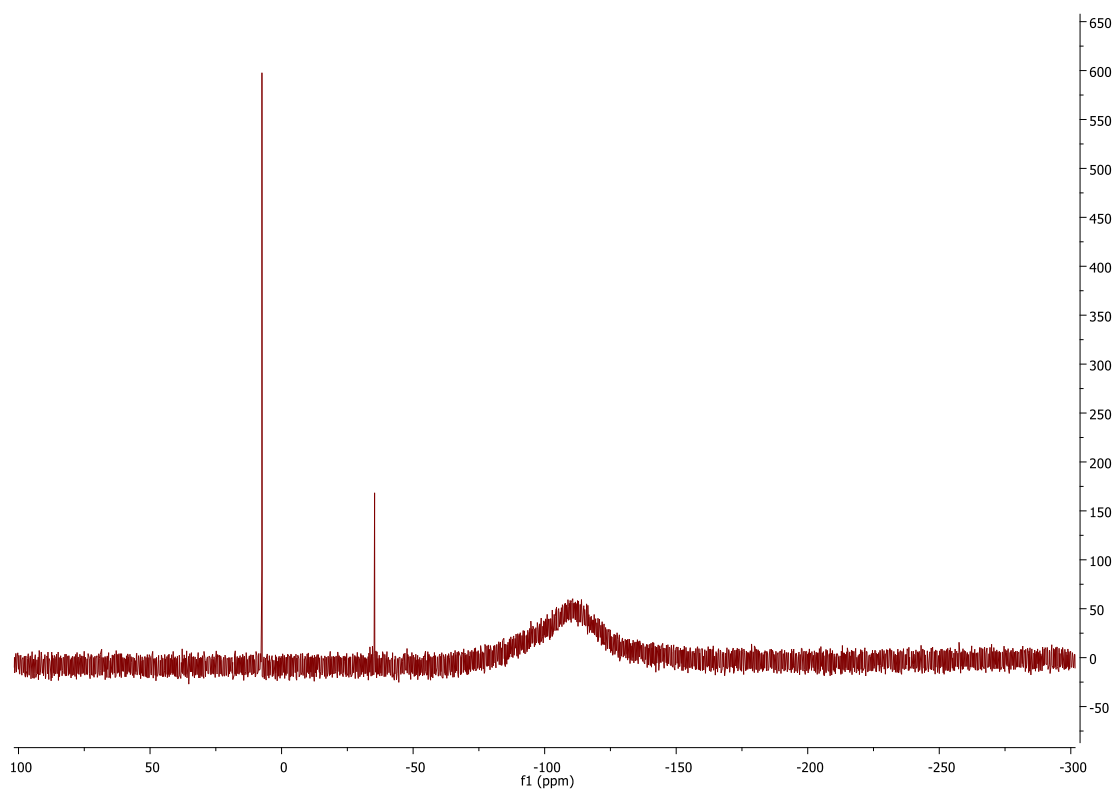


Fig. S6. ^{29}Si NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)oct-1-enyl]trisiloxane.

2.3. 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]trisiloxane

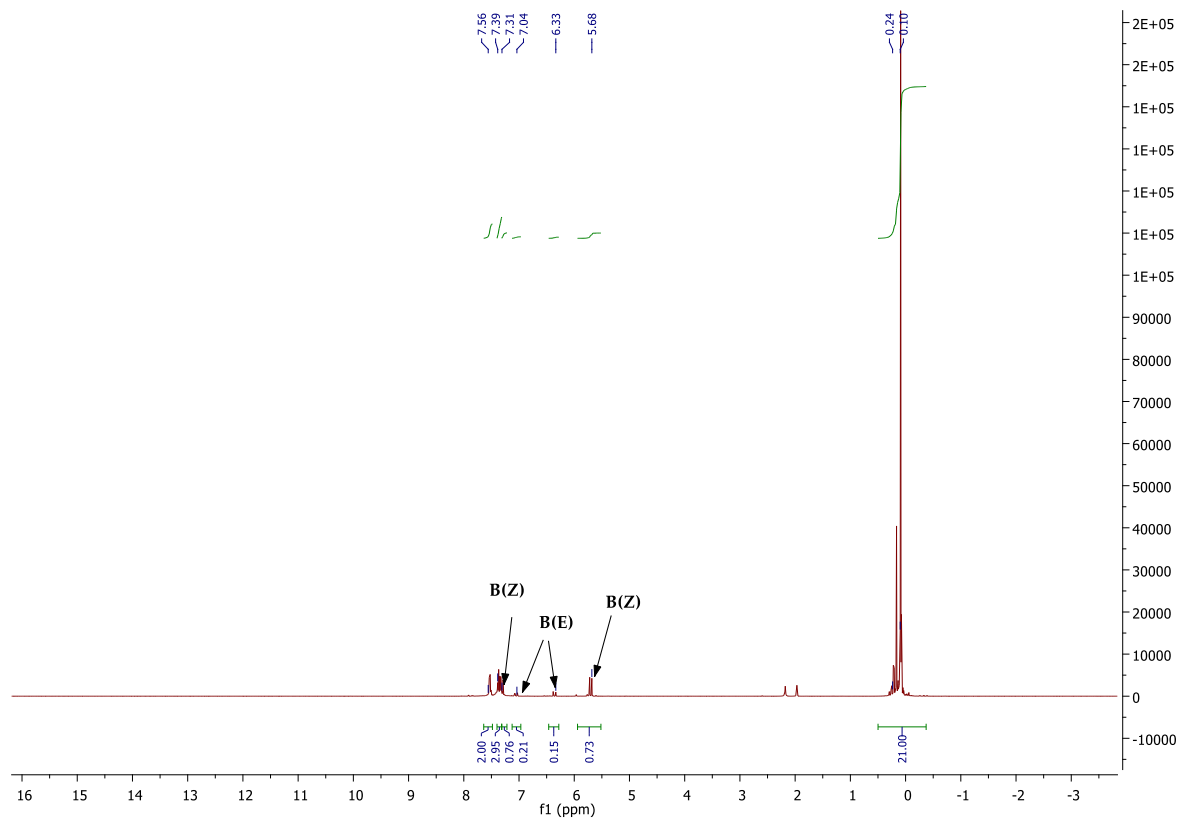


Fig. S7. ^1H NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]trisiloxane.

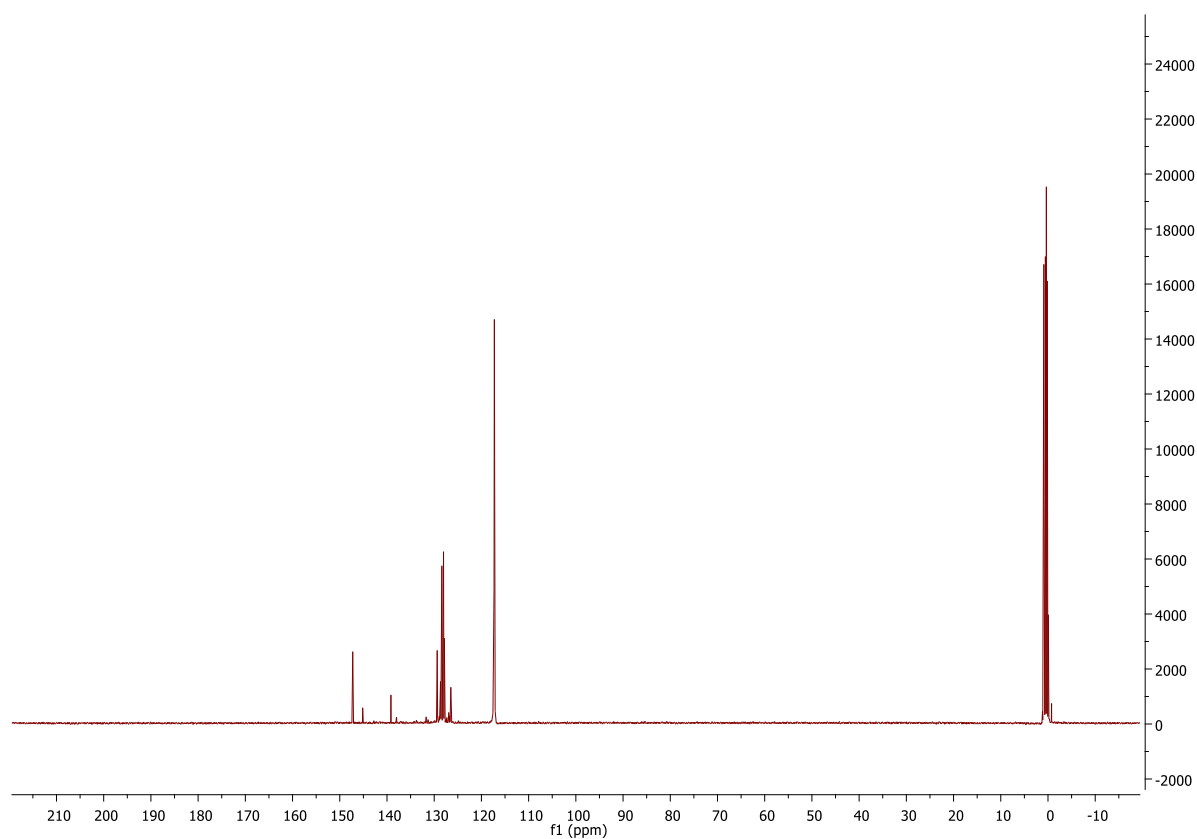


Fig. S8. ^{13}C NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]trisiloxane.

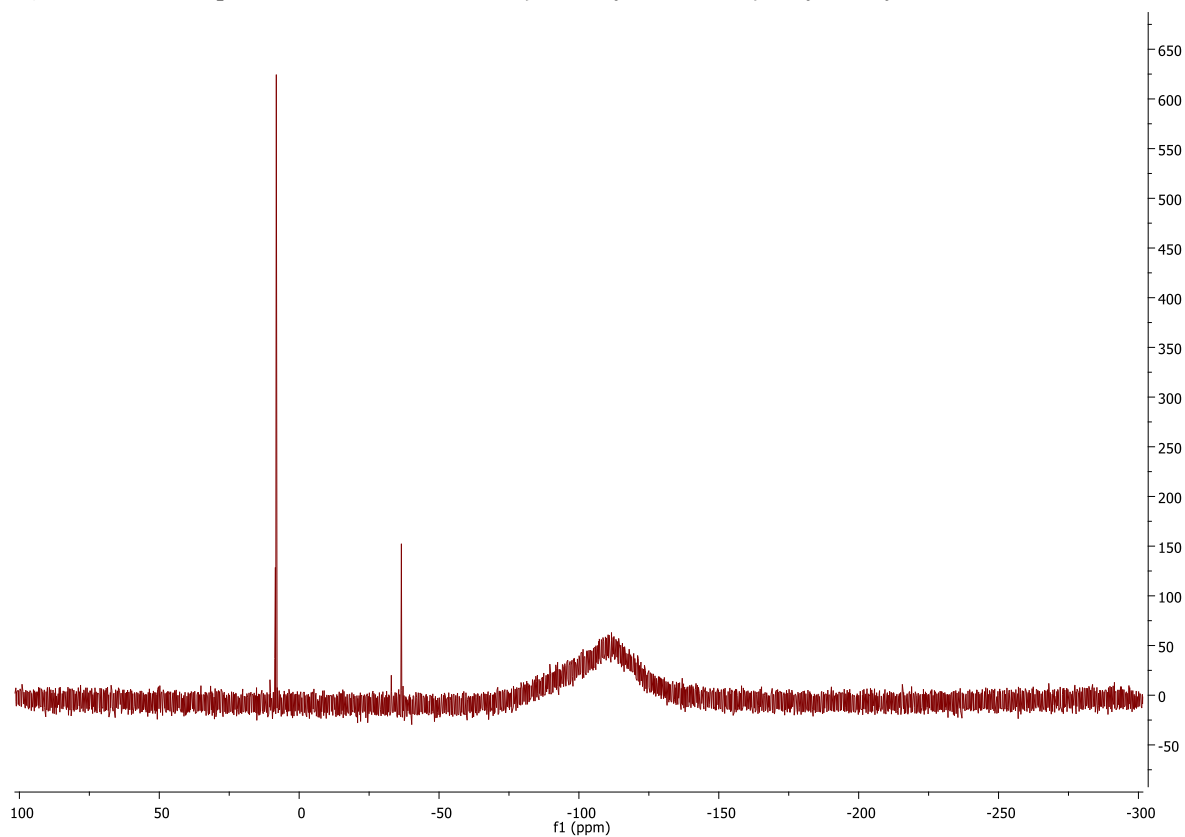


Fig. S9. ^{29}Si NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]trisiloxane.

2.4. (Z)-triethyl(hept-1-enyl)silane

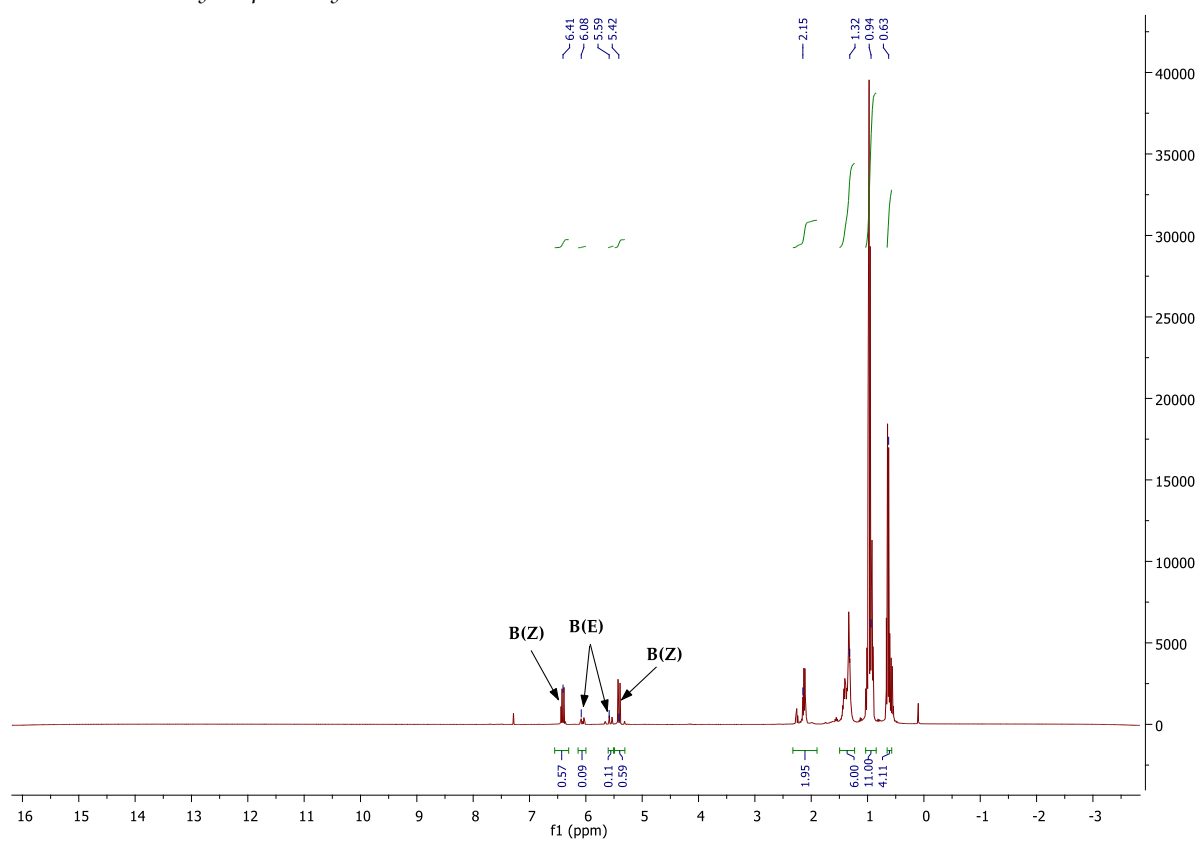


Fig. S10. ^1H NMR spectrum of (Z)-triethyl(hept-1-enyl)silane.

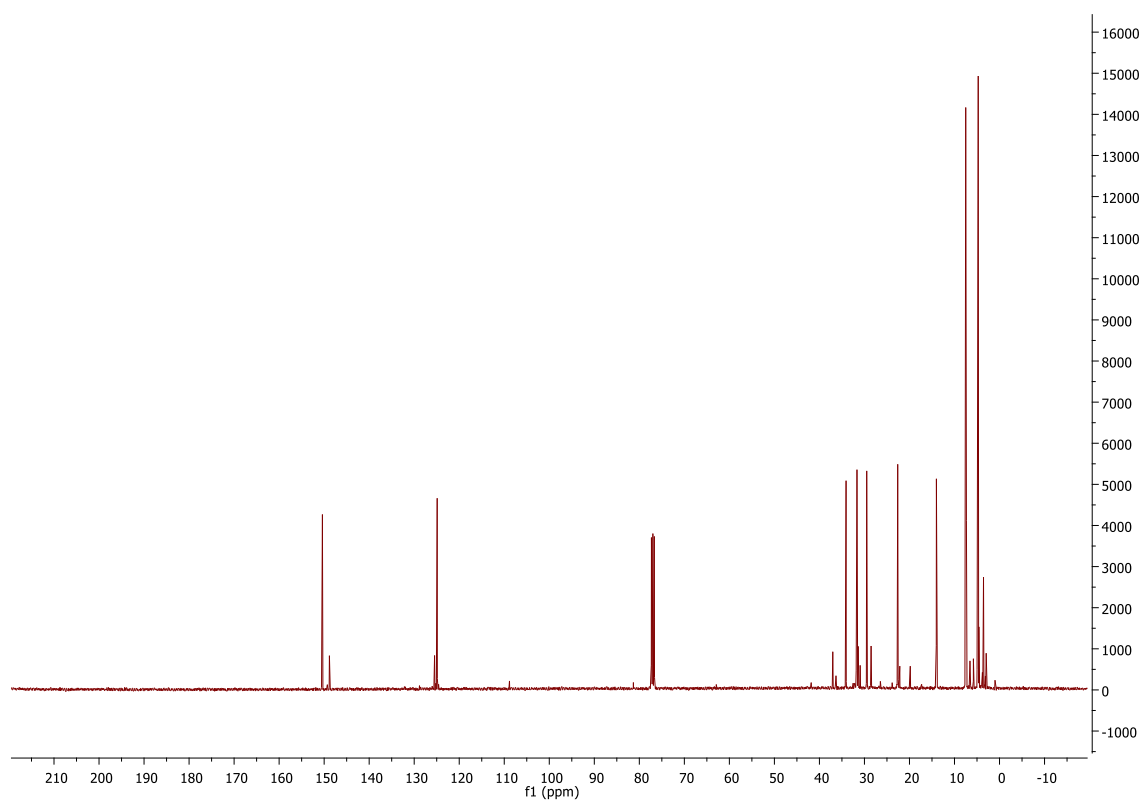


Fig. S11. ^{13}C NMR spectrum of (Z)-triethyl(hept-1-enyl)silane.

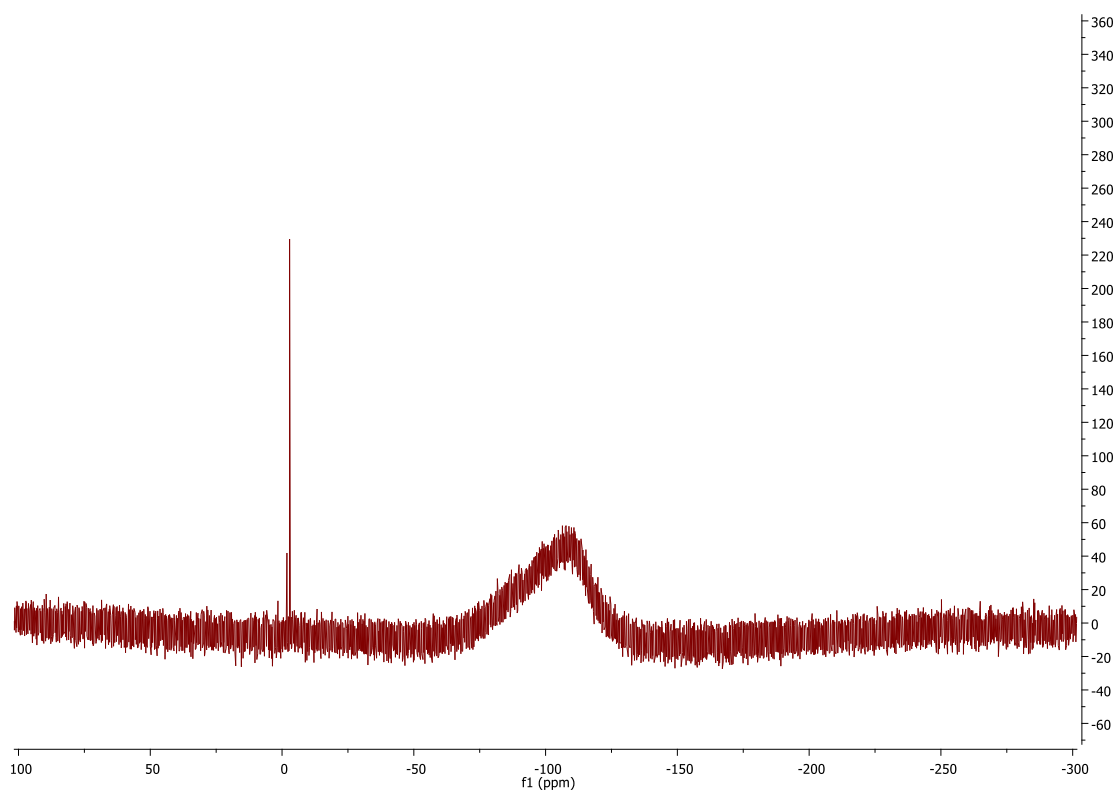


Fig. S12. ^{29}Si NMR spectrum of (Z)-triethyl(oct-1-enyl)silane.

2.5. (Z)-triethyl(oct-1-enyl)silane

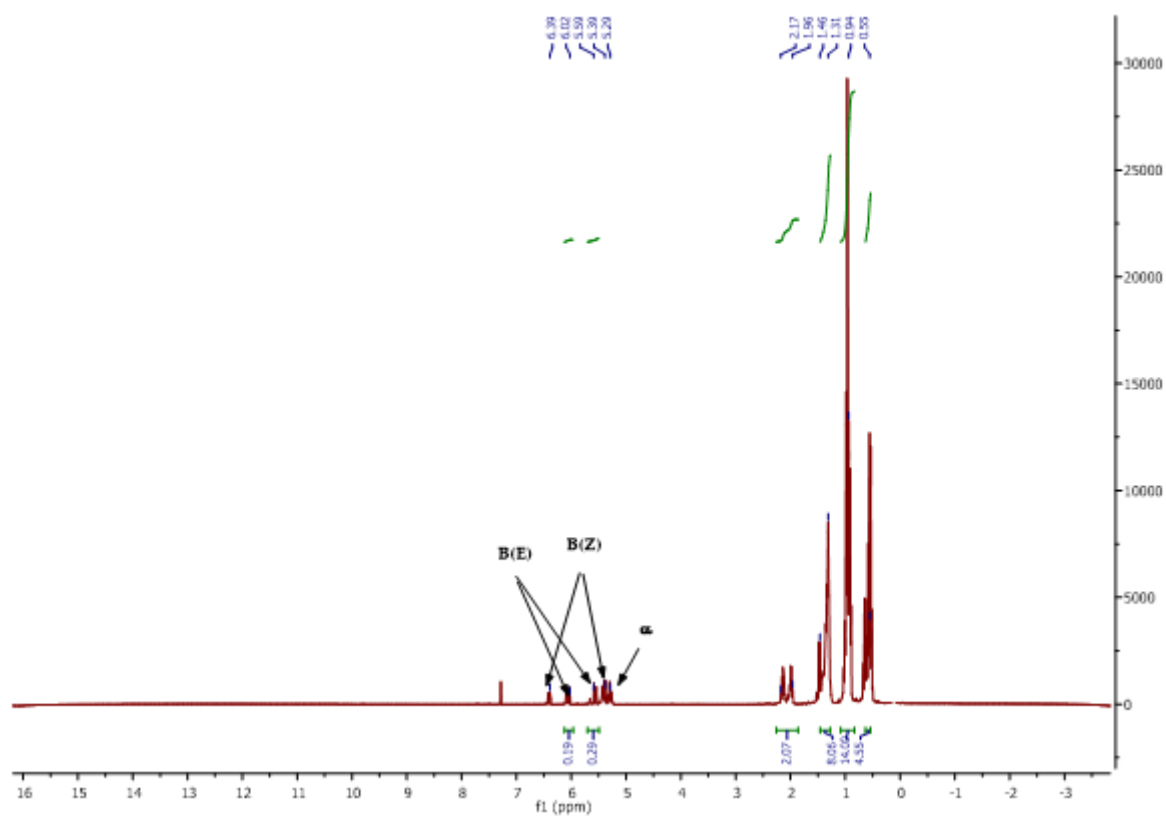


Fig. S13. ^1H NMR spectrum of (Z)-triethyl(oct-1-enyl)silane.

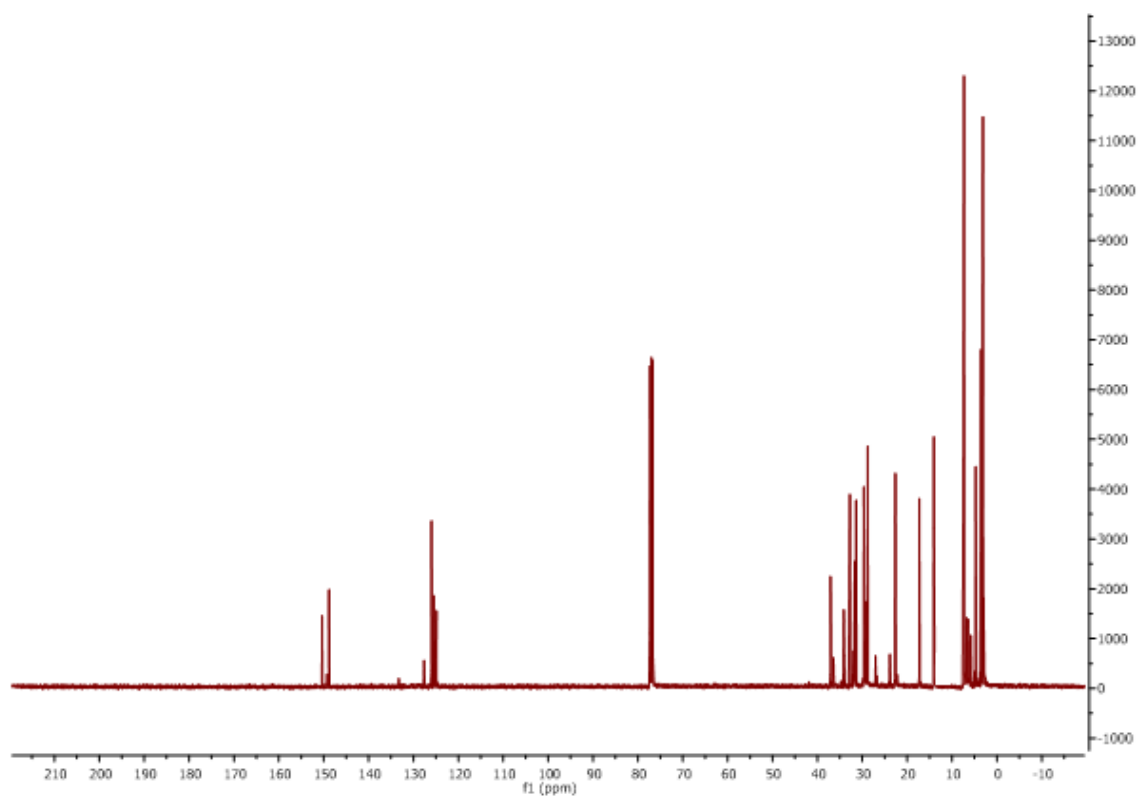


Fig. S14. ^{13}C NMR spectrum of *(Z)*-triethyl(oct-1-enyl)silane.

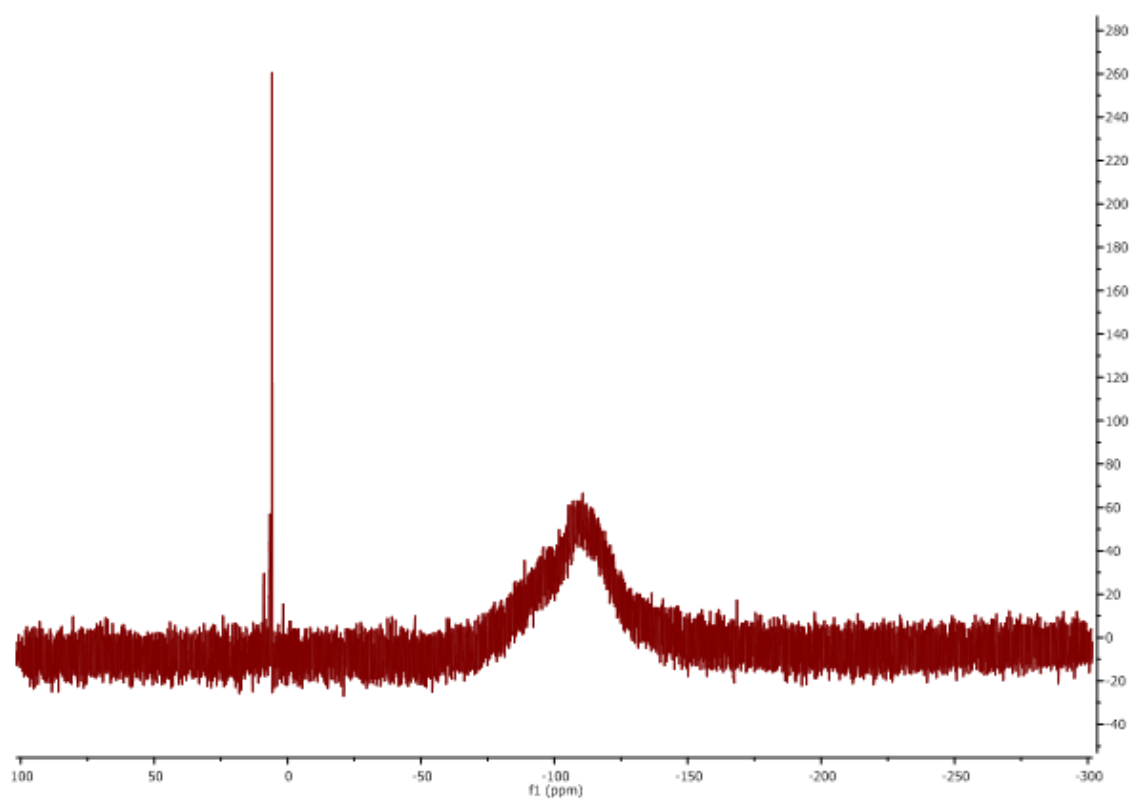


Fig. S15. ^{29}Si NMR spectrum of *(Z)*-triethyl(oct-1-enyl)silane.

2.6. *(E)*-triethyl(phenyl-1-ethene)silane

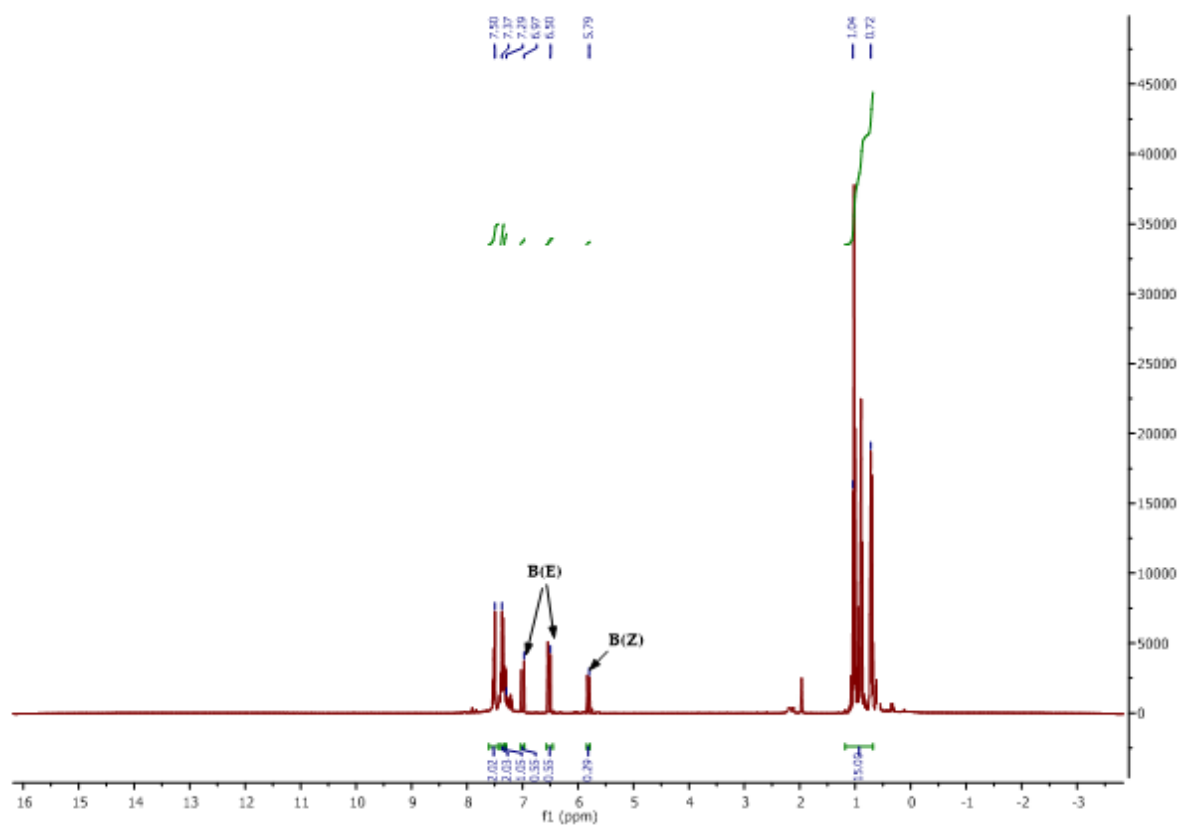


Fig. S16. ¹H NMR spectrum of *(E)*-triethyl(phenyl-1-ethene)silane.

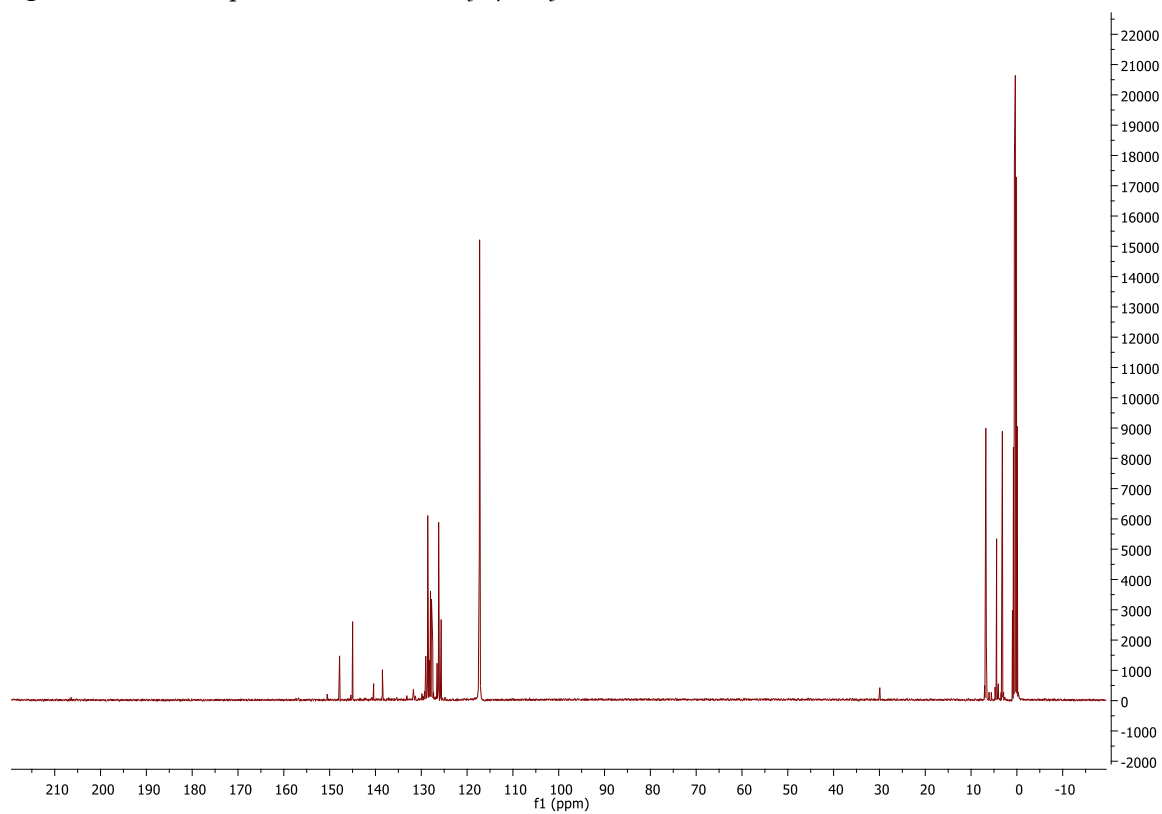


Fig. S17. ¹³C NMR spectrum of *(E)*-triethyl(phenyl-1-ethene)silane.

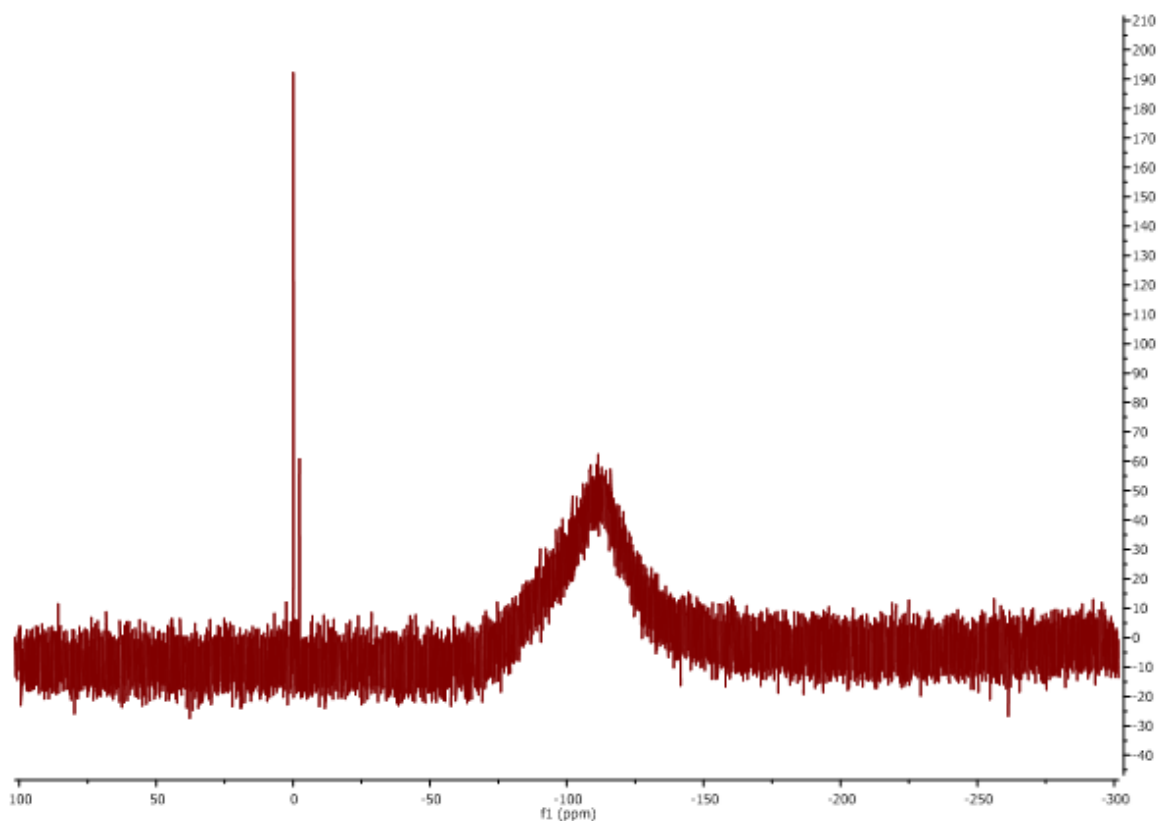


Fig. S18. ^{29}Si NMR spectrum of (*E*)-triethyl(phenyl-1-ethene)silane.

3. GC-MS spectra of isolated products

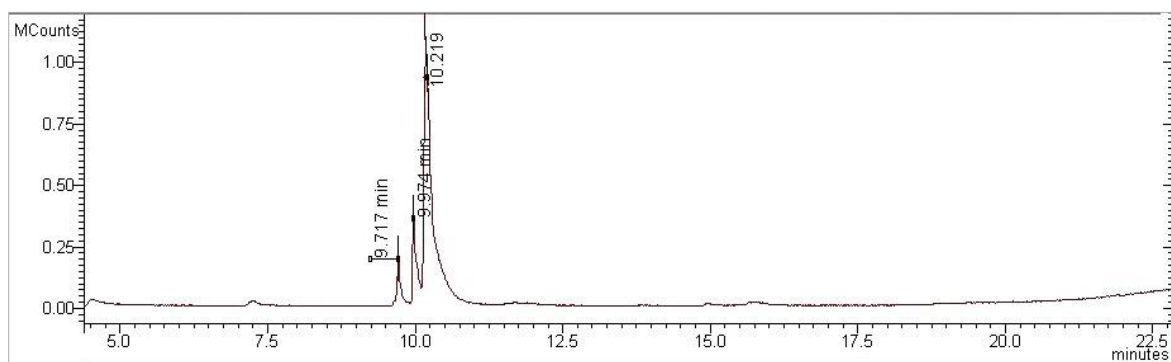


Fig. S19. GC chromatogram of 1,1,1,3,5,5,5-Heptamethyl-3-[(1*Z*)hept-1-enyl]trisiloxane, 1,1,1,3,5,5,5-Heptamethyl-3-[(1*E*)hept-1-enyl]trisiloxane and 1,1,1,3,5,5,5-Heptamethyl-3-[(α)hept-1-enyl]trisiloxane.

Retention time: 10.219 min.

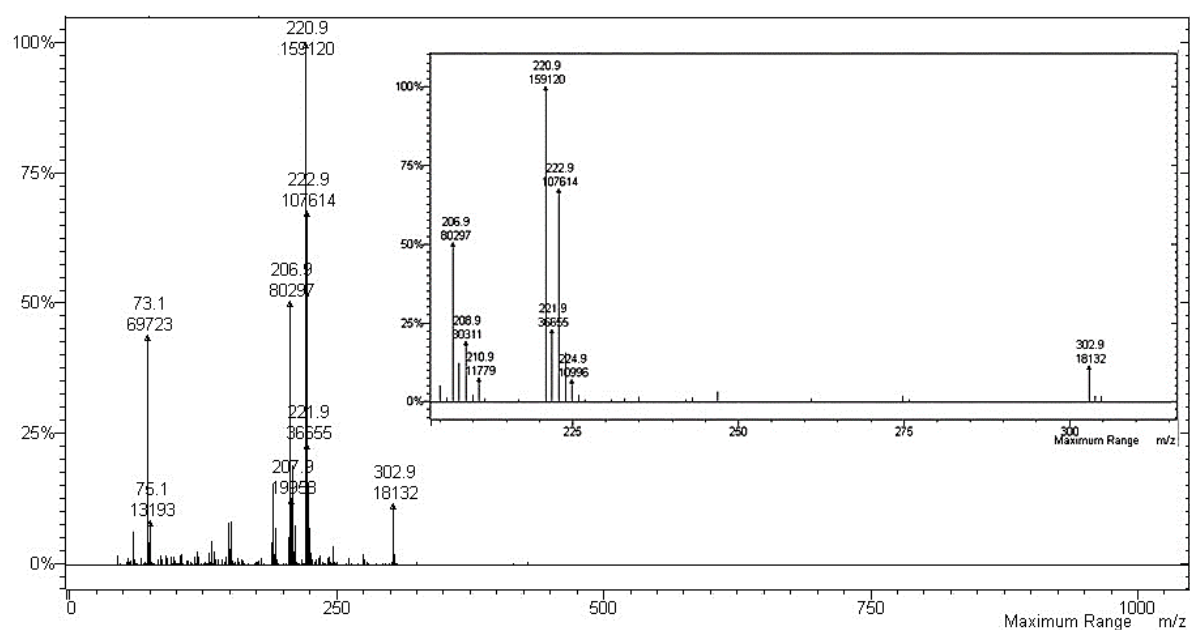


Fig. S20. MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)hept-1-enyl]trisiloxane.

Retention time: 9.974 min.

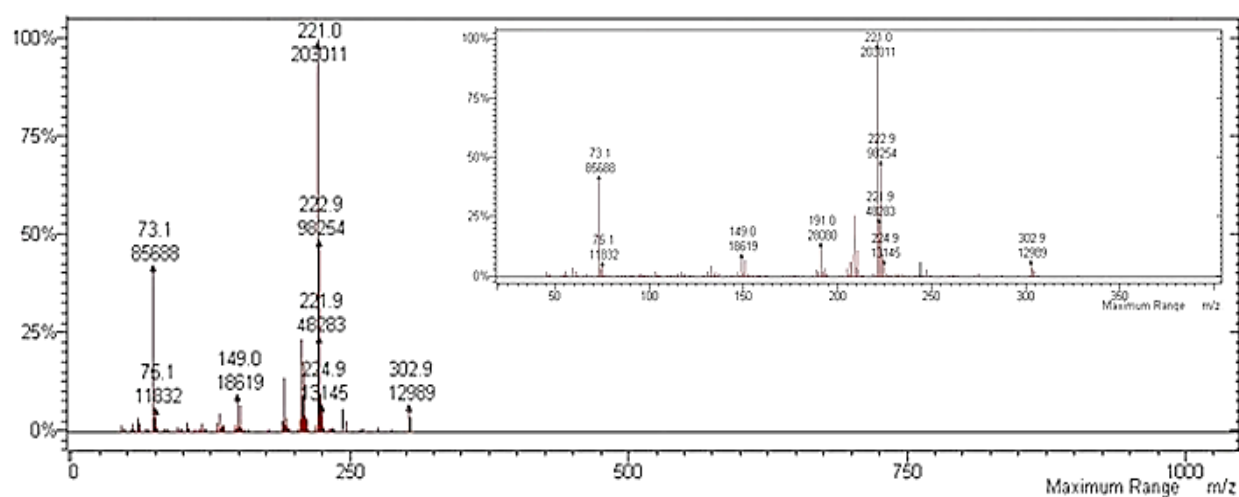


Fig. S21. MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1E)hept-1-enyl]trisiloxane.

Retention time: 9.917 min.

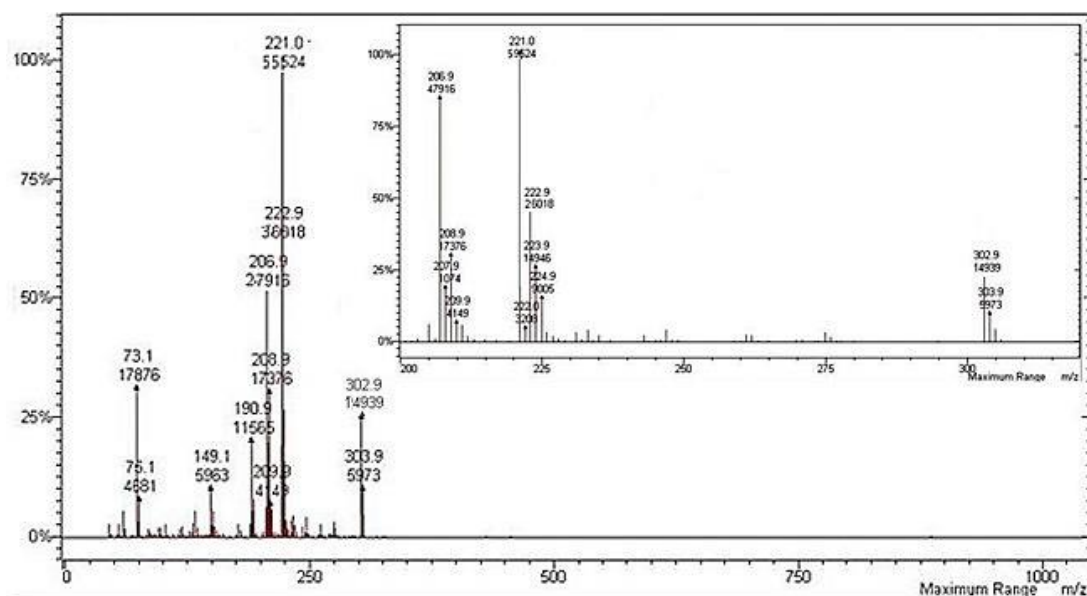


Fig. S22. MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1 α)hept-1-enyl]trisiloxane.

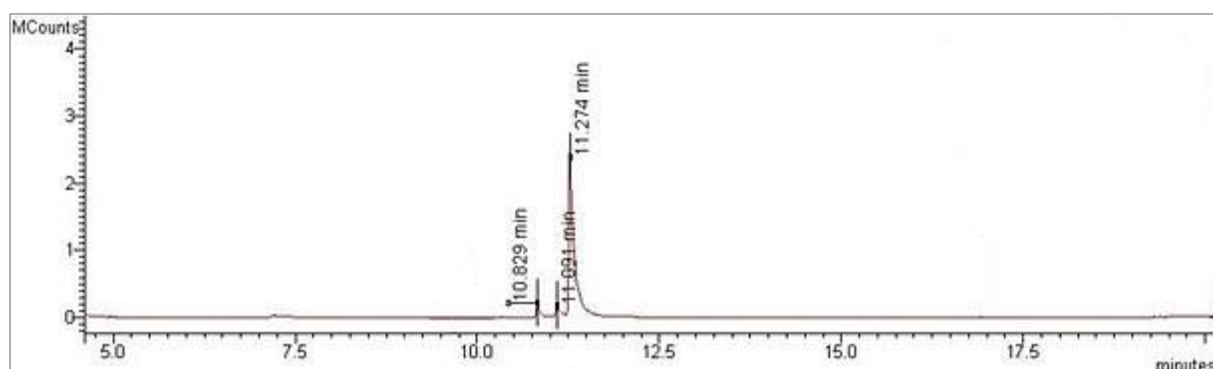


Fig. S23. GC chromatogram of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)oct-1-enyl]trisiloxane, 1,1,1,3,5,5,5-Heptamethyl-3-[(1E)oct-1-enyl]trisiloxane and 1,1,1,3,5,5,5-Heptamethyl-3-[(1 α)oct-1-enyl]trisiloxane.

Retention time: 11.274 min.

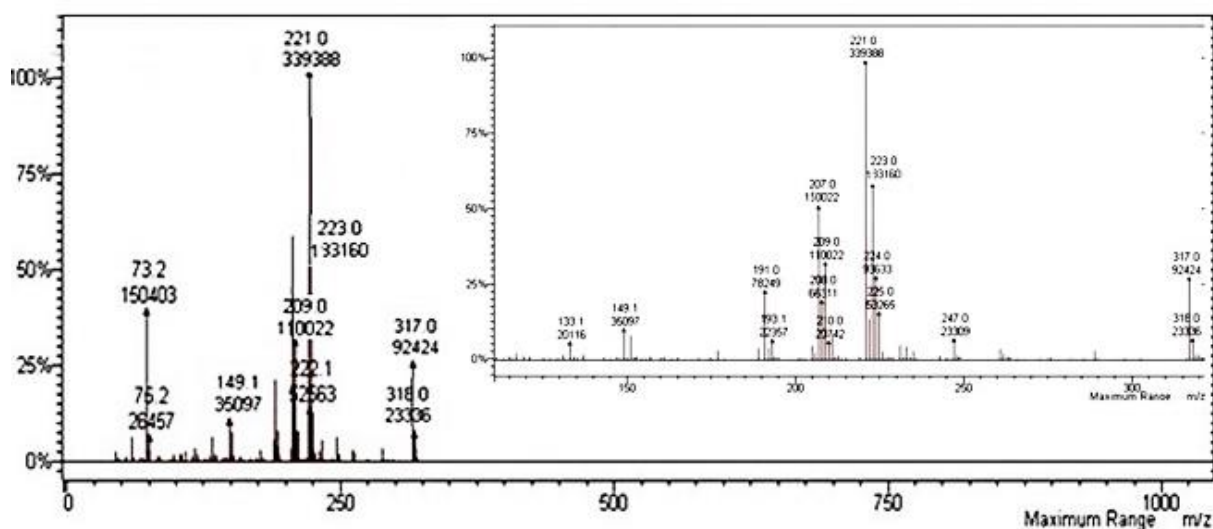


Fig. S24. MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)oct-1-enyl]trisiloxane.

Retention time: 11.091 min.

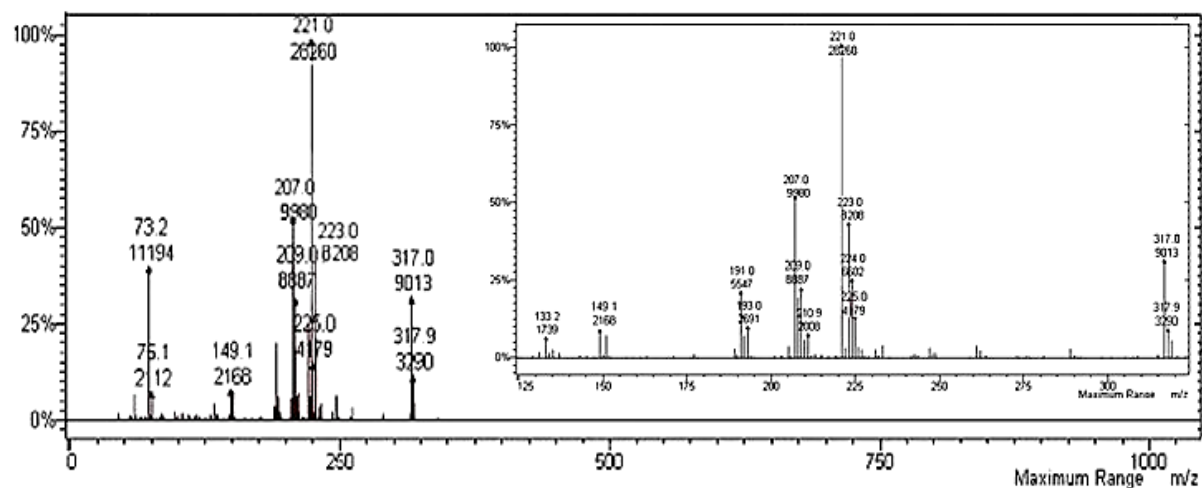


Fig. S25. MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1E)oct-1-enyl]trisiloxane.

Retention time: 10.829 min.

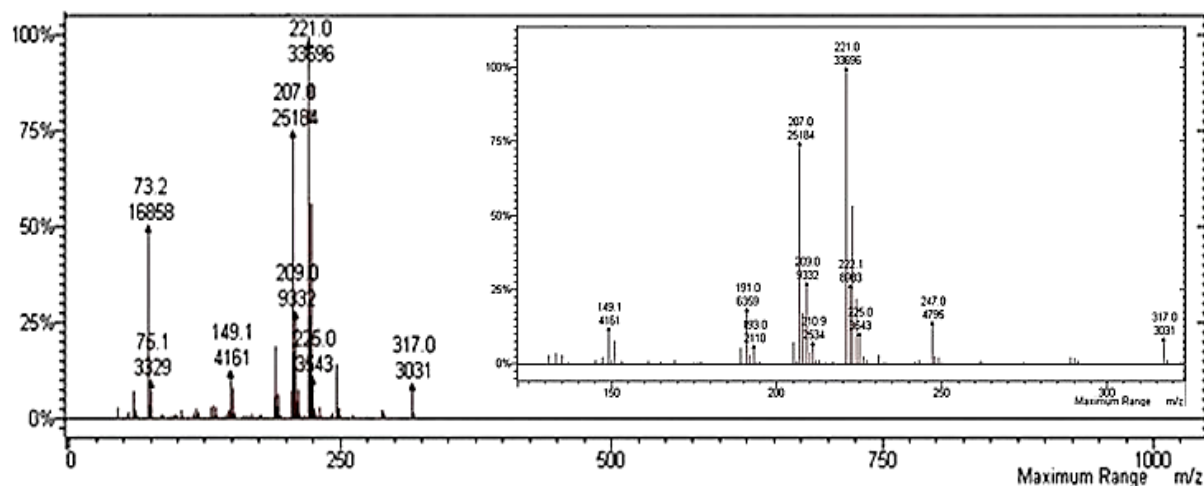


Fig. S26. MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1α)oct-1-enyl]trisiloxane.

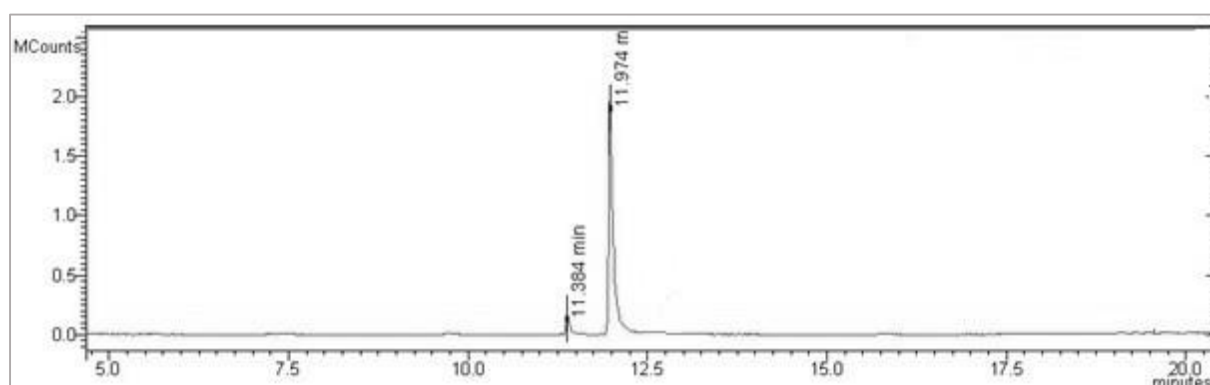


Fig. S27. GC chromatogram of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]trisiloxane and 1,1,1,3,5,5,5-Heptamethyl-3-[(1E)-2-phenylethenyl]trisiloxane.

Retention time: 11.974 min.

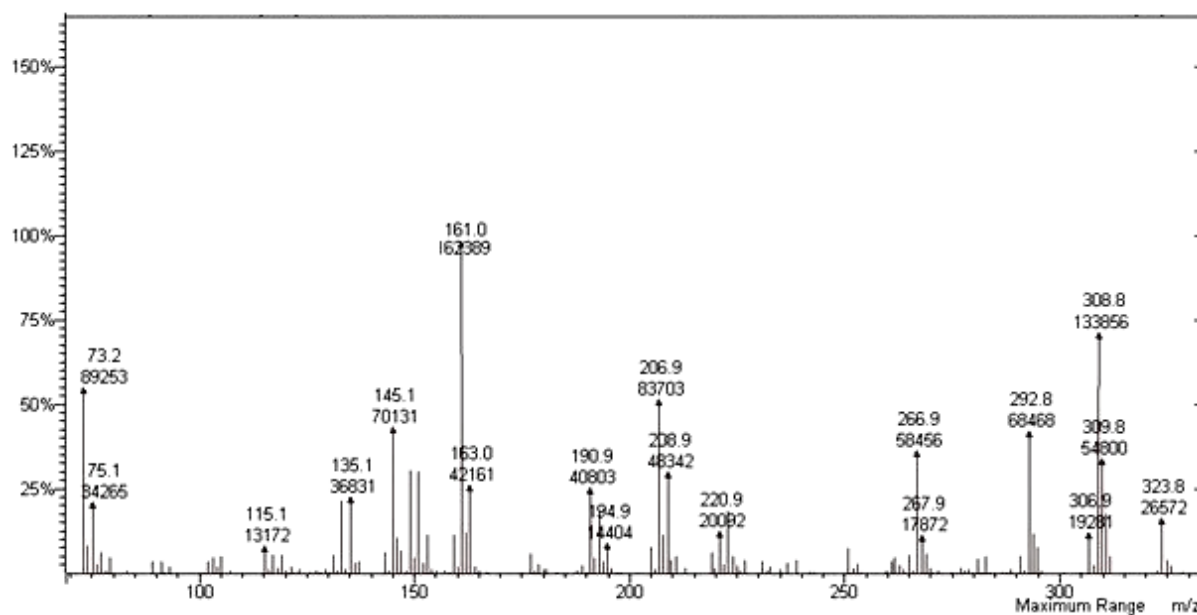


Fig. S28. MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]trisiloxane.

Retention time: 11.384 min.

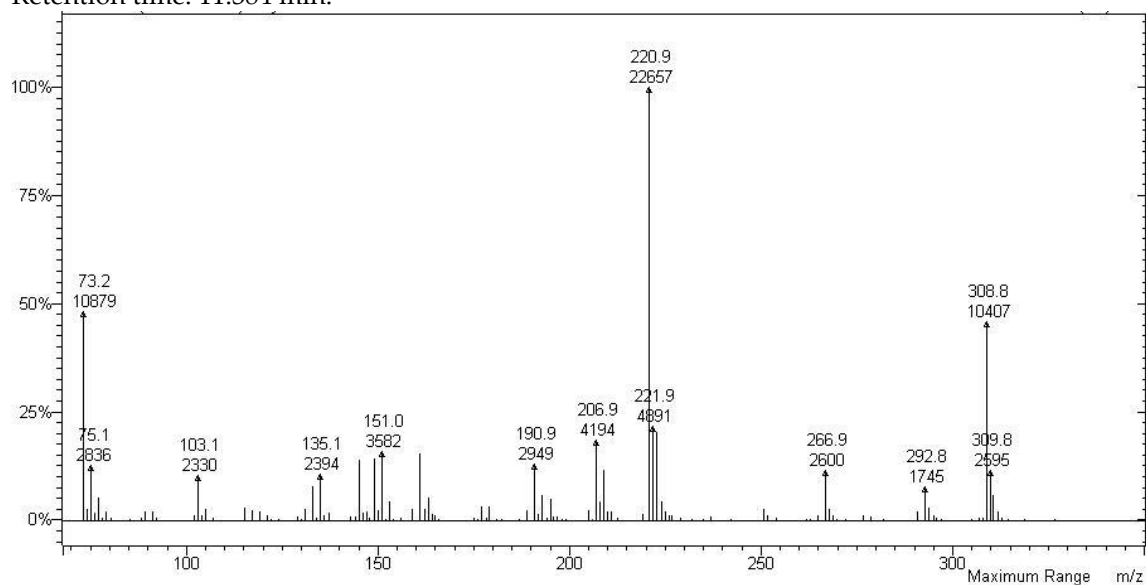


Fig. S29. MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1E)-2-phenylethenyl]trisiloxane.

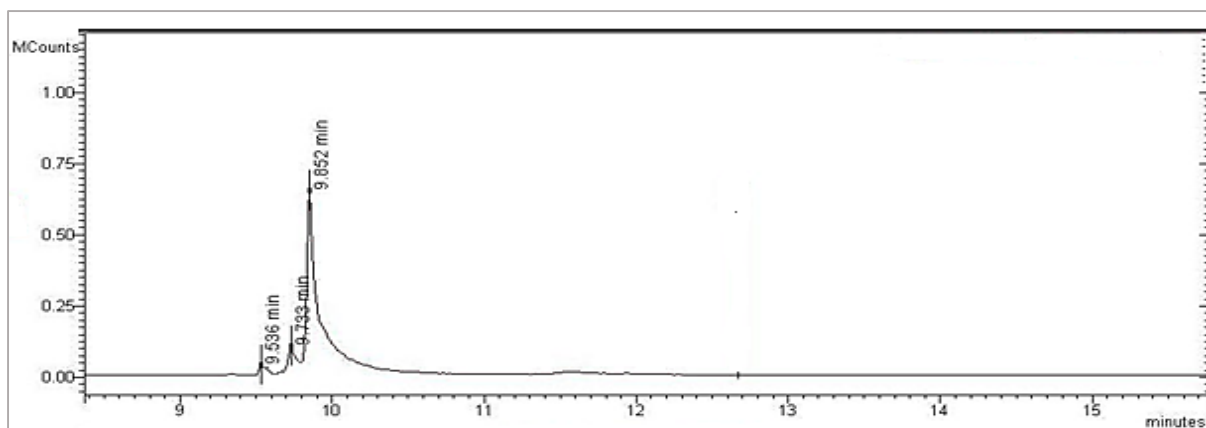


Fig. S30. GC chromatogram of *(Z)*-triethyl(hept-1-enyl)silane, *(E)*-triethyl(hept-1-enyl)silane and (α) -triethyl(hept-1-enyl)silane.

Retention time: 9.852 min.

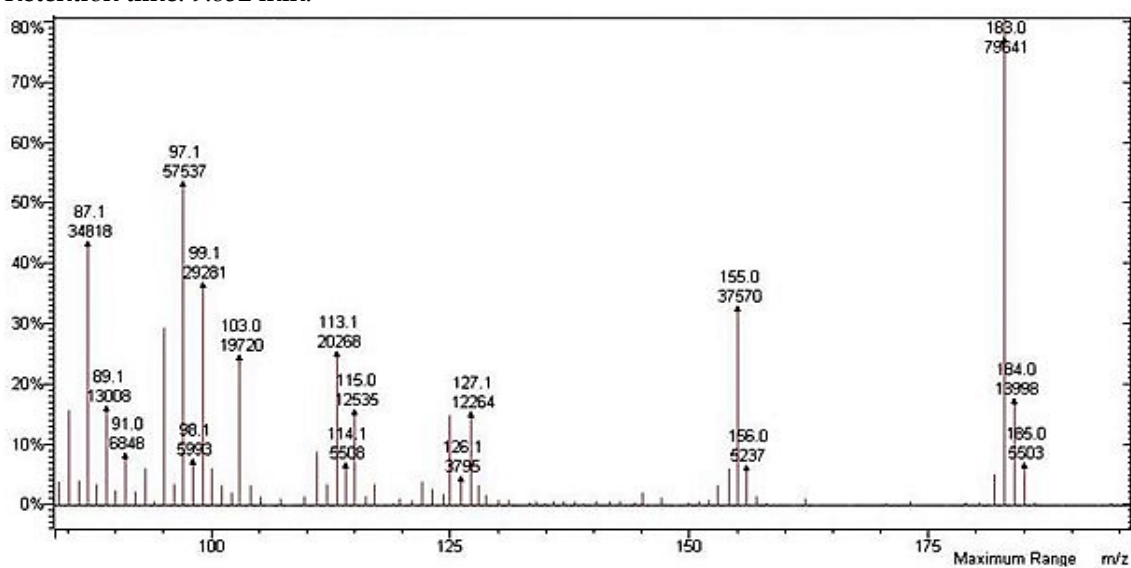


Fig. S31. MS spectrum of *(Z)*-triethyl(hept-1-enyl)silane.

Retention time: 9.733 min.

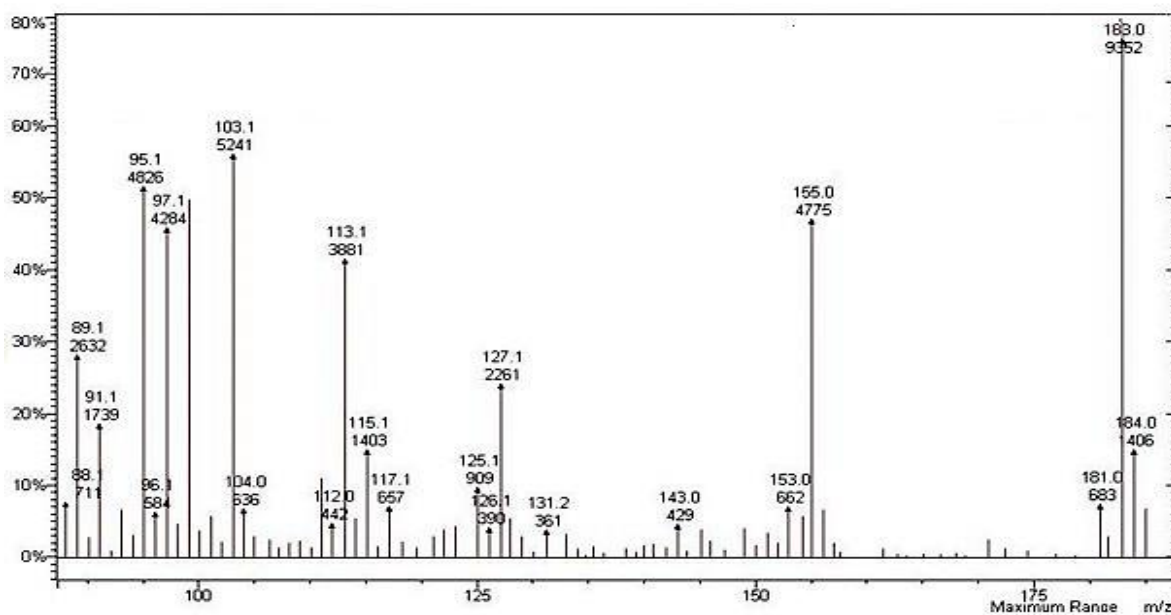


Fig. S32. MS spectrum of *(E)*-triethyl(hept-1-enyl)silane.

Retention time: 9.536 min.

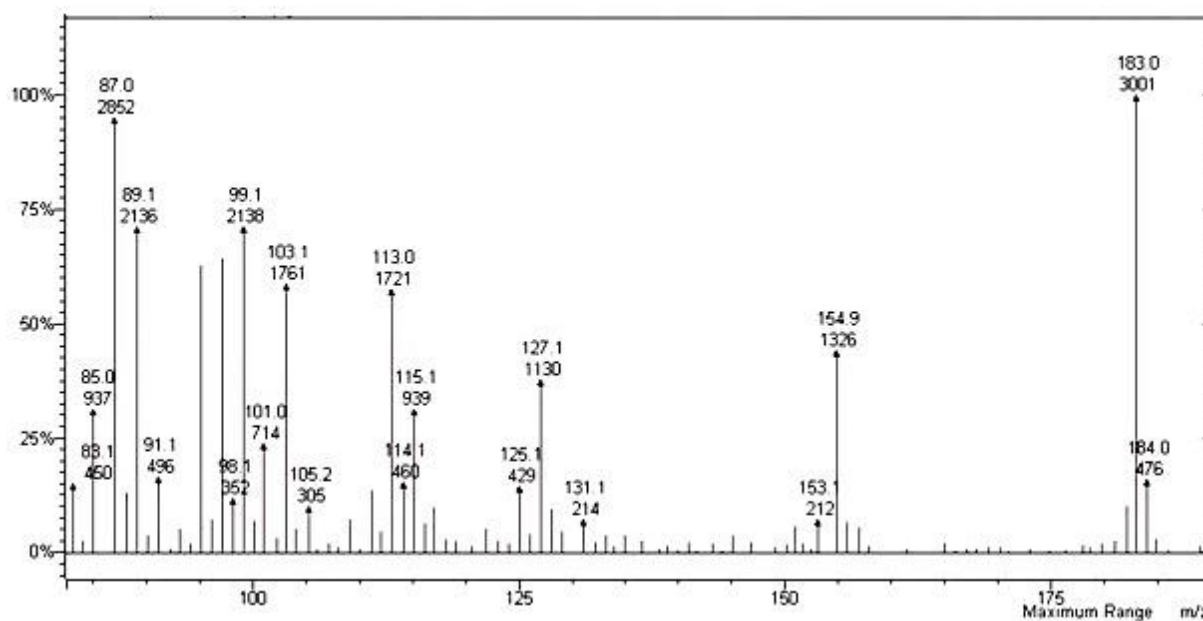


Fig. S33. MS spectrum of (α)-triethyl(hept-1-enyl)silane.

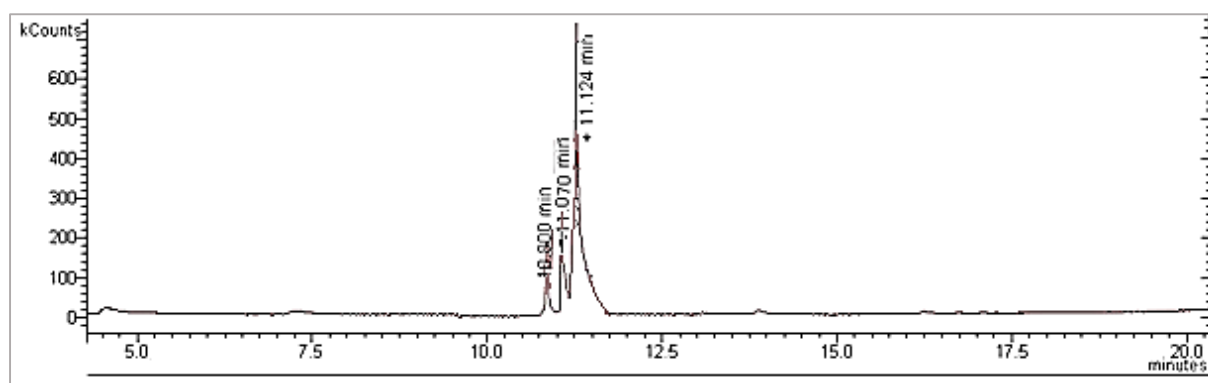


Fig. S34. GC chromatogram of (*Z*)-triethyl(oct-1-enyl)silane, (*E*)-triethyl(oct-1-enyl)silane and (α)-triethyl(oct-1-enyl)silane.

Retention time: 11.124 min.

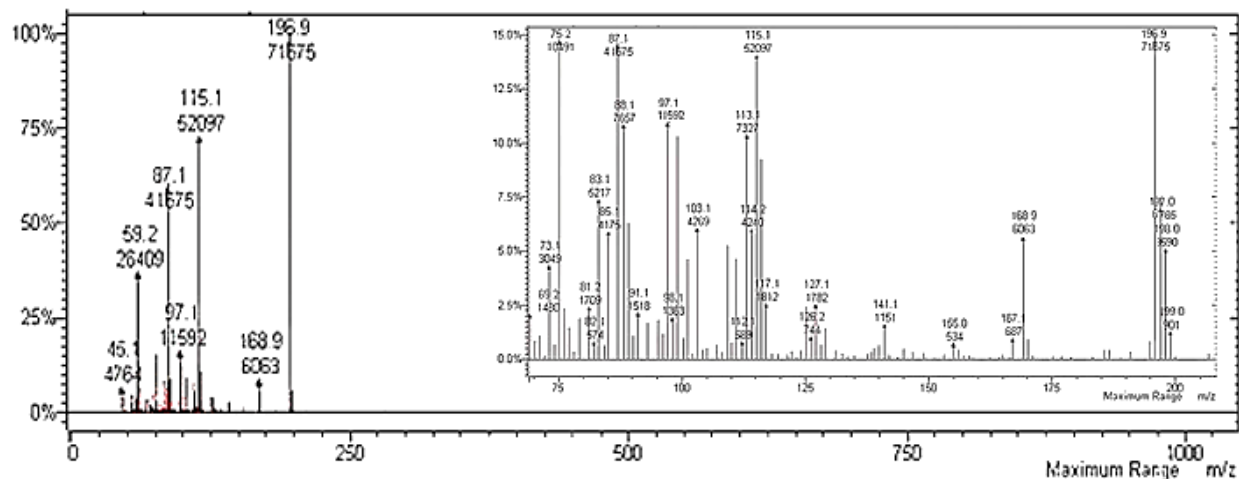


Fig. S35. MS spectrum of (*Z*)-triethyl(oct-1-enyl)silane.

Retention time: 11.070 min.

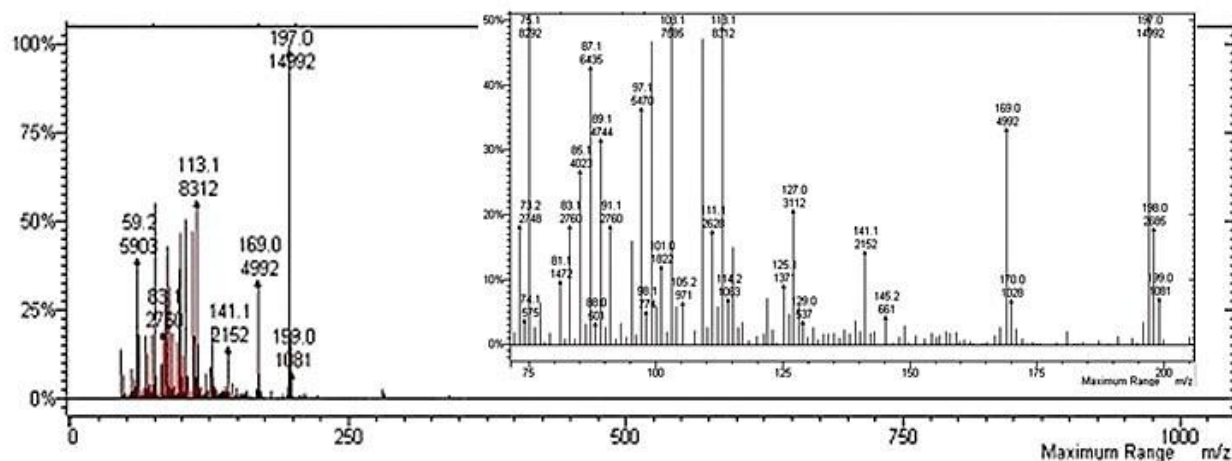


Fig. S36. MS spectrum of *(E)*-triethyl(oct-1-enyl)silane.

Retention time: 10.800 min.

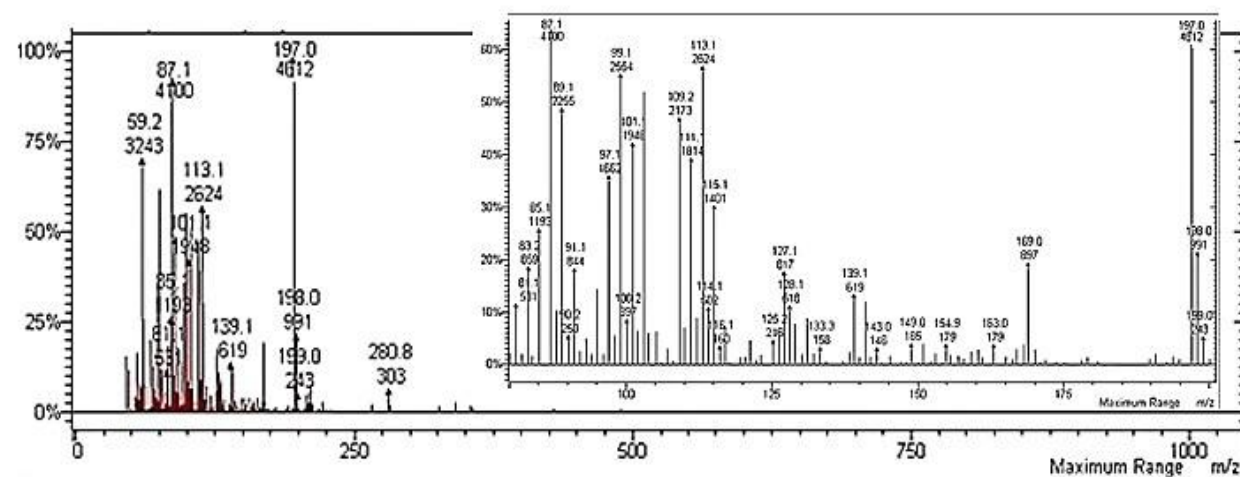


Fig. S37. MS spectrum of (α) -triethyl(oct-1-enyl)silane.

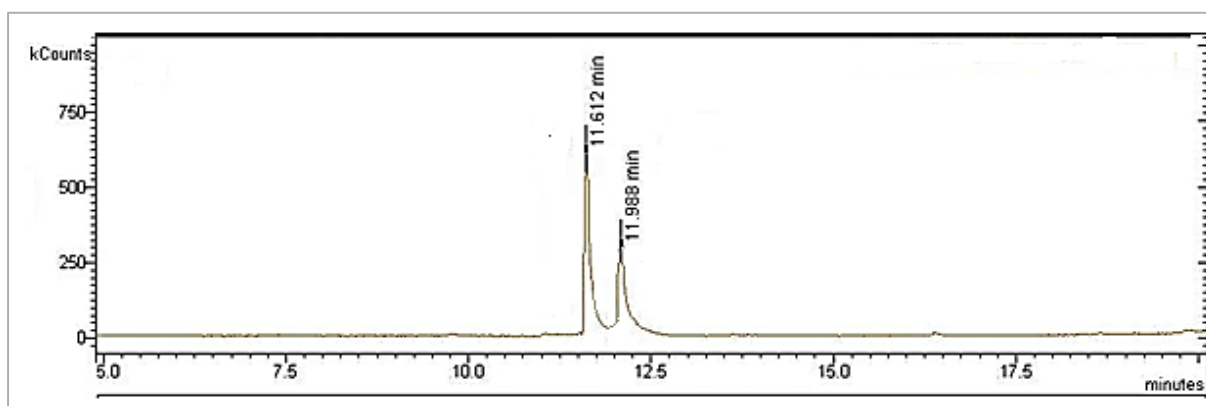


Fig. S38. GC chromatogram of *(E)*-triethyl(phenyl-1-ene)silane and *(Z)*-triethyl(phenyl-1-ene)silane.

Retention time: 11.612 min.

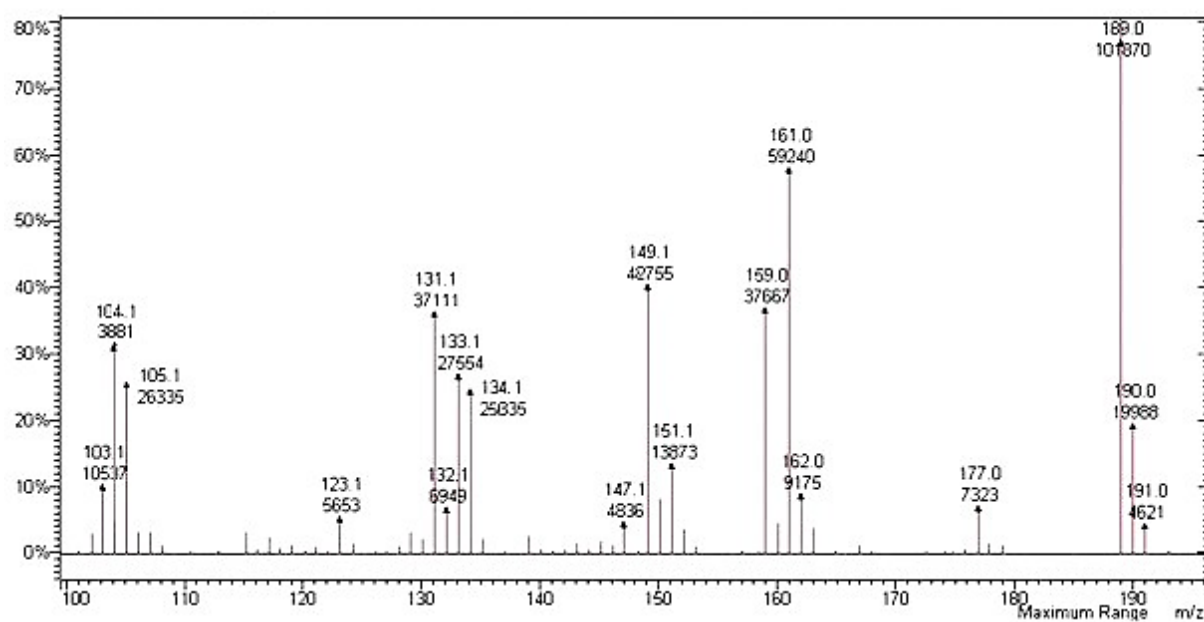


Fig. S39. MS spectrum of (E)-triethyl(phenyl-1-ethene)silane.

Retention time: 11.988 min.

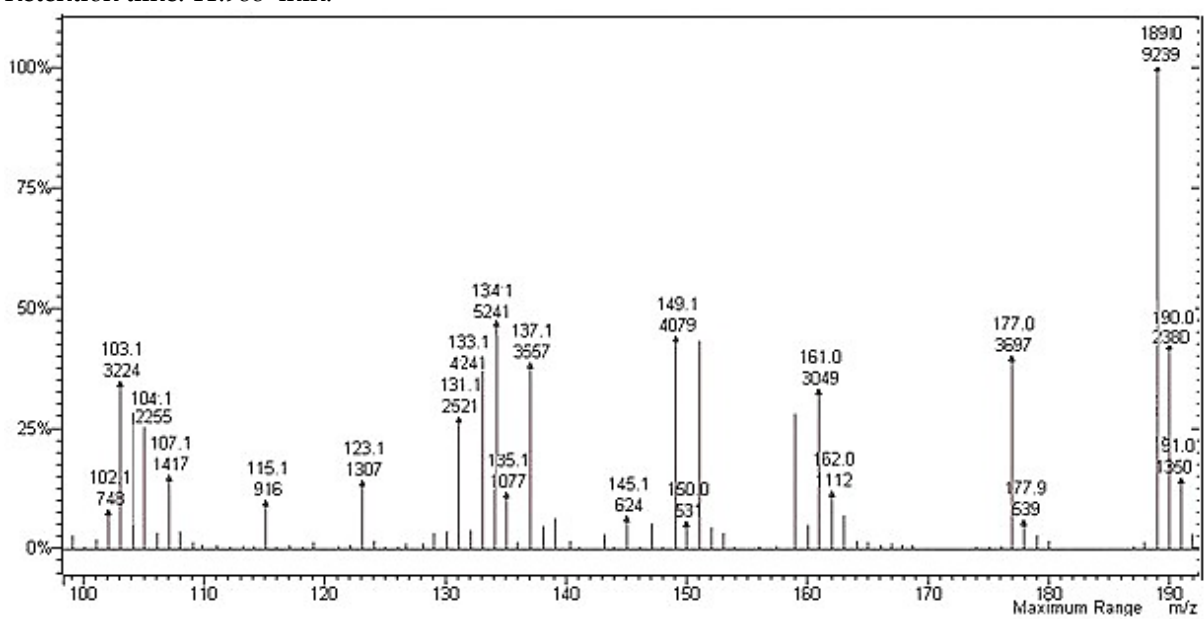


Fig. S40. MS spectrum of (Z)-triethyl(phenyl-1-ethene)silane.

4. FT-IR spectra

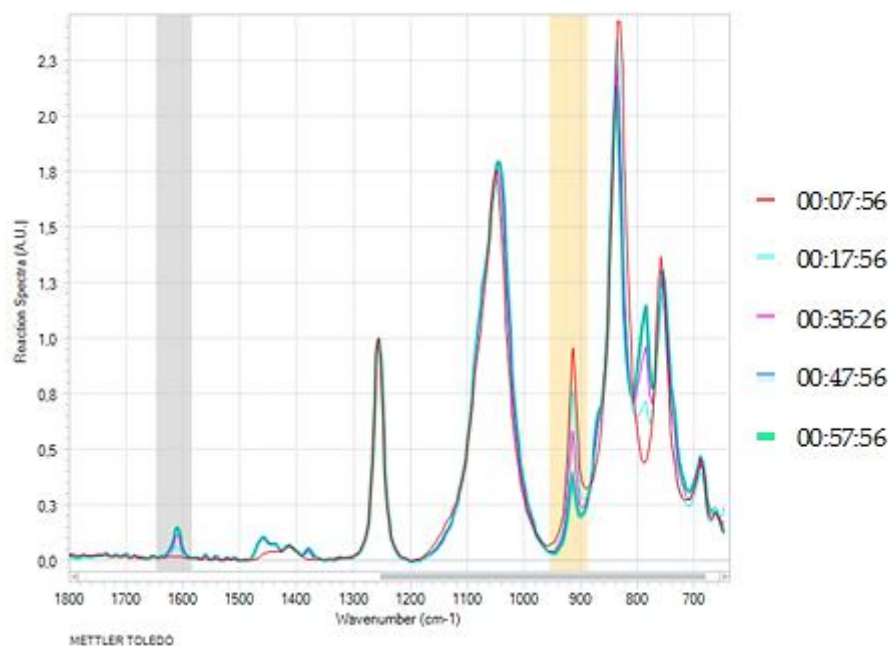


Fig. S41. FT-IR spectra with characteristic peaks at 1600 cm^{-1} and 913 cm^{-1} which change with time of the hydrosilylation reaction between 1-octyne and HMTS, carried out in the presence of the Wilkinson's catalyst.

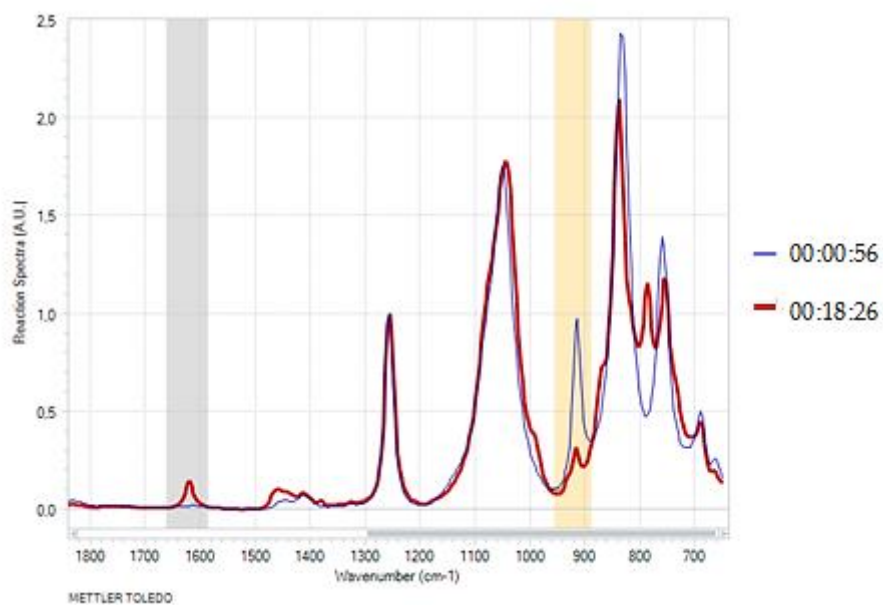


Fig. S42. FT-IR spectra with characteristic peaks at 1600 cm^{-1} and 913 cm^{-1} which change with time of the hydrosilylation reaction between 1-octyne and HMTS, carried out in the presence of catalyst **1**.