Electronic Supplementary Information for:

A library of multisubstituted cyclotriphosphazenes – molecular scaffolds for hybrid materials

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Methods and materials

All commercially available chemicals were used without further purification. Allyl glycidyl ether, 1-octene, N,N-dimethylallylamine, (±)-3,7-dimethyl-1,6-octadien-3-ol, 2-chloroethyl vinyl ether, hept-1-yne, ethynyltrimethylsilane, ethynyldimethyl(phenyl)silane and Karstedt's complex were obtained from Sigma-Aldrich while vinyltriethoxysilane and ethynyltriisopropylsilane were purchased from ABCR. 5-allyl-1,1,2,2,3,3,4,4-octafluoropentyl ether was synthesized according to the published procedure[1]. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 300 MHz spectrometer using $CDCl_3$ as a solvent. The ^{29}Si and ^{31}P NMR spectra were recorded using Bruker Ascend 400 spectrometer using $CDCl_3$ as a solvent. FT-IR spectra were recorded on a Nicolet iS50 (Thermo Scientific) Fourier transform spectrophotometer equipped with a diamond ATR unit. In all cases, 16 scans at a resolution of 2 cm^{-1} were collected, to record the spectra in a range of 4000-650 cm^{-1}. Elemental analyses were carried out using a Vario EL III instrument (Elementar Analysensysteme GmbH).

General procedure for cyclotriphosphazene (1) functionalization

A mixture prepared from 0.5 g (0.62 mmol) of (**1**), 10mL of toluene and 1.24 mmol of alkene (**b**-**f**) (1.37 mmol in case of olefin (**a**)) was heated up to 90°C, then Karstedt's catalyst was added [SiH]:[C=C]:[Pt] = [1]:[1]:[5×10^{-5}] for all alkenes except N,N-dimethylallylamine and allyl-glycidyl ether. For allyl-glycidyl ether the stoichiometry of substrates was [SiH]:[C=C]:[Pt] = [1]:[1.1]:[5×10^{-5}] and for N,N-dimethylallylamine [SiH]:[C=C]:[Pt] = [1]:[1]:[1.25×10^{-4}]. Reactions were continued until total disappearance of the band at 2116 cm^{-1} characteristic for Si-H bond present in the substrate (**1**) structure observed in the FT-IR spectrum of the reaction mixture. After the reaction completion, the mixture was cooled down to the room temperature and filtered through silica gel for the catalyst separation. Evaporation of the solvent gave pure products as white solids.

General procedure for cyclotriphosphazene (2) functionalization

A mixture prepared from 0.5 g (0.48 mmol) of (**2**), 10mL of toluene and 2.875 mmol of alkene/alkyne (**b**-**j**) (3.165 mmol in case of allyl-glycidyl ether (**a**)) was heated up to 90°C, then Karstedt's catalyst was added [SiH]:[C=C]:[Pt] = [1]:[1]:[$5x10^{-5}$] for all alkynes and alkenes except N,N-dimethylallylamine and allyl-glycidyl ether. For allyl-glycidyl ether the stoichiometry of substrates was [SiH]:[C=C]:[Pt] = [1]:[1.1]:[$5x10^{-5}$] and for N,N-dimethylallylamine [SiH]:[C=C]:[Pt] = [1]:[1]:[$1.25x10^{-4}$]. Reactions were continued until total disappearance of the band at 2116 cm^{-1}, characteristic for Si-H bond present in the substrate (**2**) structure observed in the FT-IR spectrum of the reaction mixture. After the reaction completion, the mixture was cooled down to the room temperature and filtered through silica gel for the catalyst separation. Evaporation of the solvent gave pure products as colorless or pale yellow oils.

Literature:

[1] R. Januszewski, I. Kownacki, H. Maciejewski, B. Marciniec, *J. Organomet. Chem.* 2017, **846**, 263.

Spectra of: 2,2-bis(4-dimethylsilylphenoxy)-4,4,6,6-bis[spiro(2',2''-dioxy-1'-1''-biphenyl)]cyclotriphosphazene (1)

Elemental Analysis Calc. for $C_{40}H_{38}N_3O_6P_3Si_2$: C, 59.62; H, 4.75; N, 5.21; O, 11.91; P, 11.53; Si, 6.97%; Found: C, 59.65; H, 4.74; N, 5.23%.

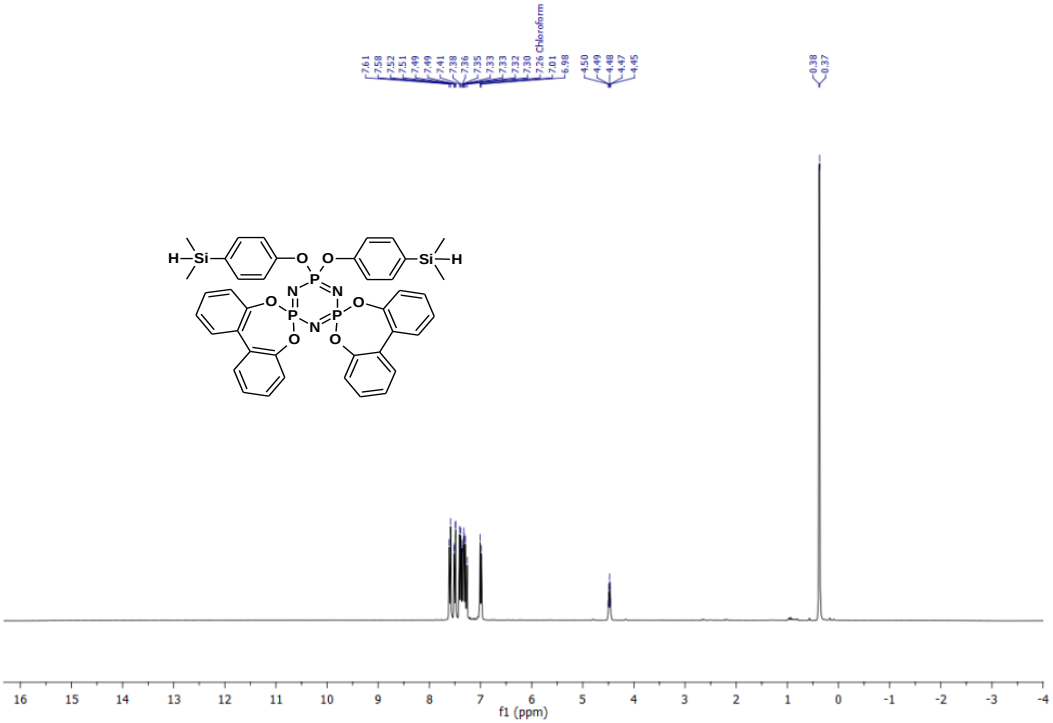

Fig.1. ^{1}H NMR spectrum of Substrate (**1**).

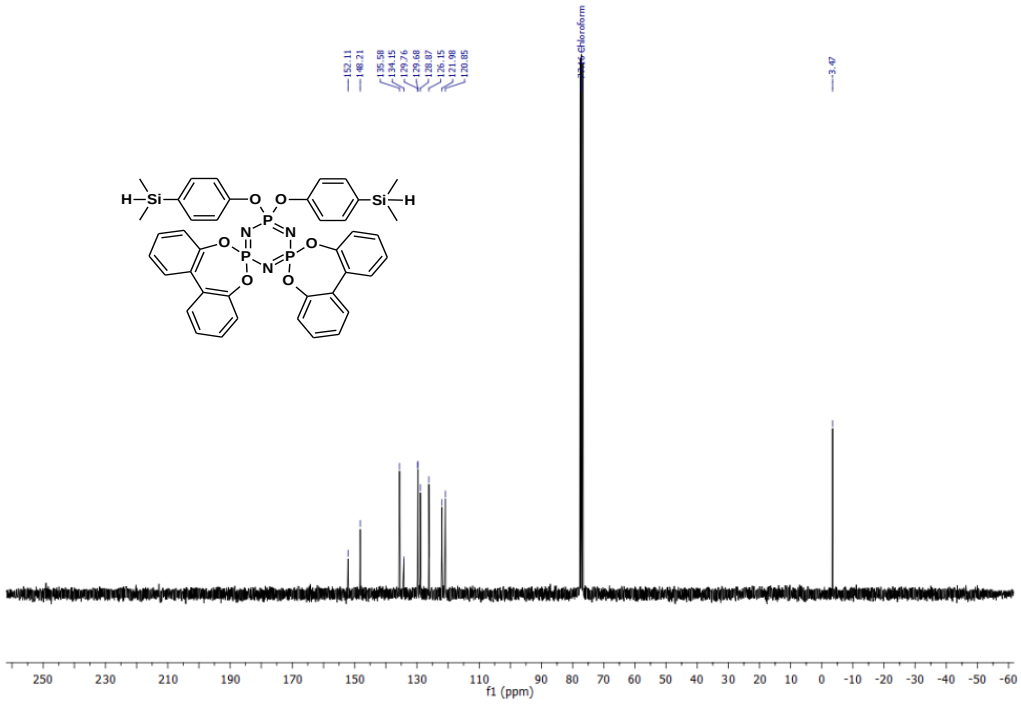

Fig. 2. ^{13}C NMR spectrum of Substrate (**1**).

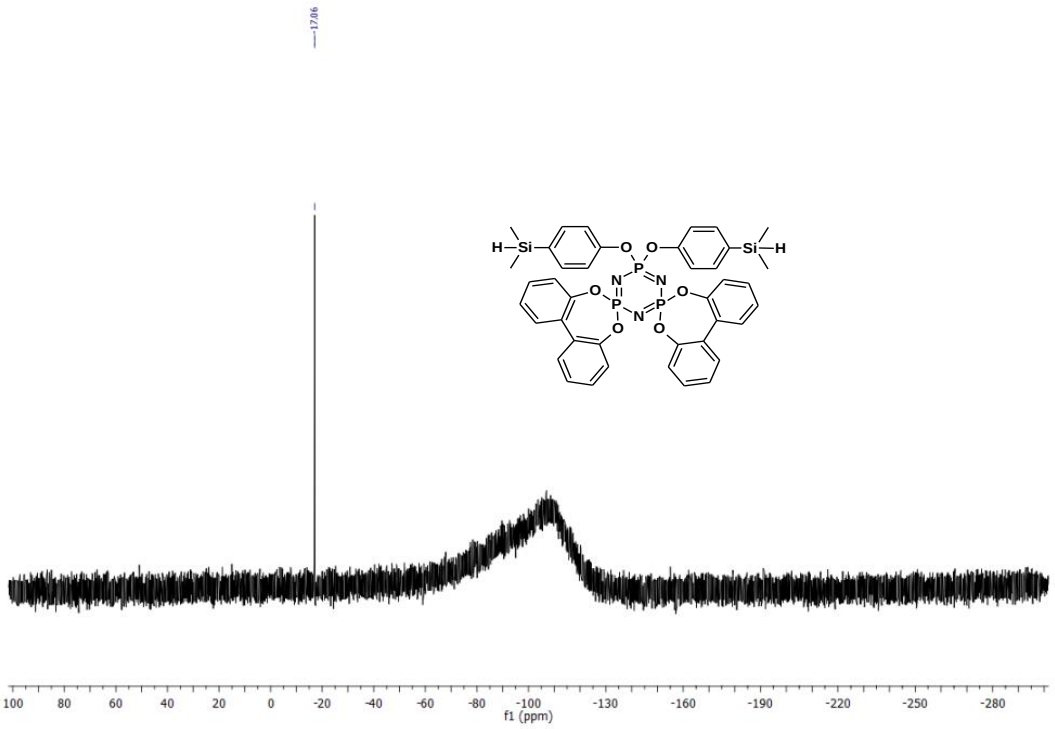

Fig. 3. ^{29}Si NMR spectrum of Substrate (**1**).

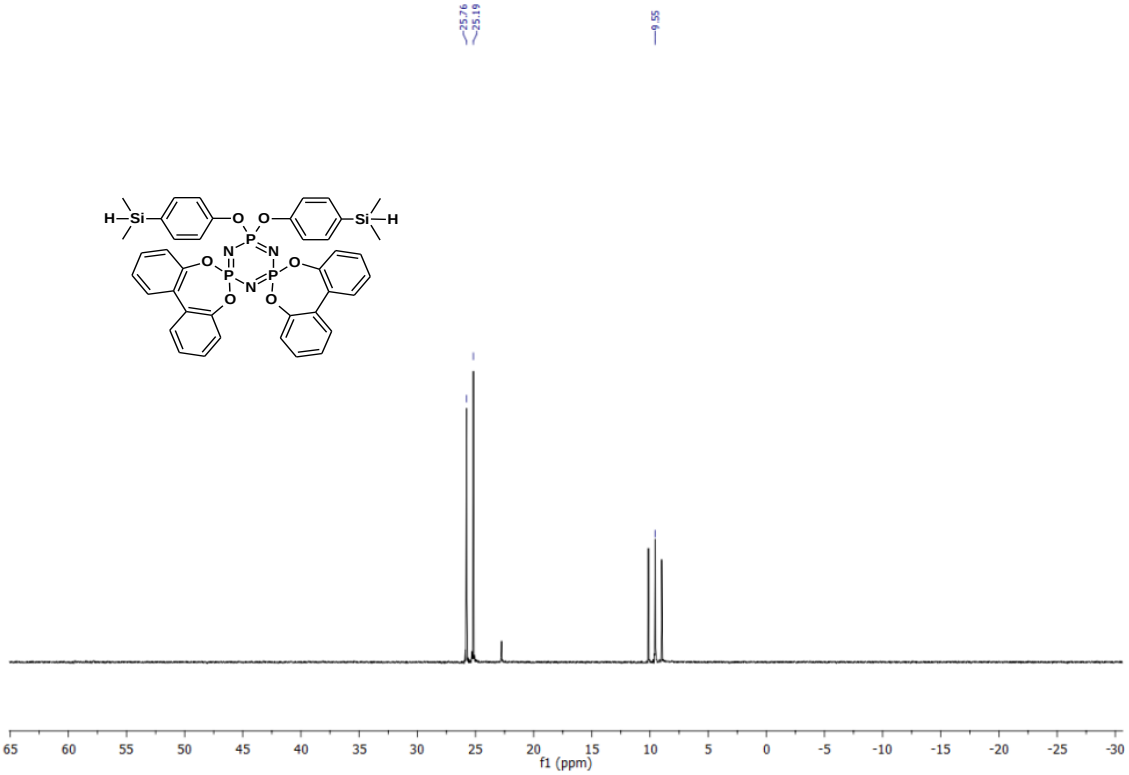

Fig. 4. ^{31}P NMR spectrum of Substrate (**1**).

Spectra of Product (1a): Yield 94%. ^{1}H NMR ($CDCl_3$): δ = 7.56 (d, 4H, *J*=10.6 Hz), 7.50 (dd, 4H, *J*=9.9, 2.4Hz), 7.41-7.30 (m, 12H), 6.99 (d, 4H *J*=10.2Hz), 3.65 (dd, 2H, *J*=15.3, 4.1Hz), 3.49-3.39 -CH-$\underline{CH_2}(O)_{oxirane}$ (m, 4H), 3.32 $C\underline{H}_{oxirane}(O)$ (m, 2H), 3.10 (m, 2H), 2.75 (m, 2H), 2.56 (m, 2H), 1.63 -$\underline{CH_2}CH_2Si$ (m, 4H), 0.78 $CH_2\underline{CH_2}Si$ (m, 4H), 0.30 $SiCH_3$ (s, 12H), **^{13}C NMR** ($CDCl_3$): δ = 151.78, 148.20, 135.87, 135.10, 129.76, 129.67, 128.87, 126.14, 121.98, 120.67, 74.30, 71.53, 50.97, 44.43, 24.19 -$\underline{CH_2}CH_2Si$, 11.89 $CH_2\underline{CH_2}Si$, -2.84 $SiCH_3$, **^{29}Si NMR** ($CDCl_3$): δ = -2.40, **^{31}P NMR** ($CDCl_3$): δ = 25.48, 9.46. **Elemental Analysis** Calc. for $C_{52}H_{58}N_3O_{10}P_3Si_2$: C, 60.39; H, 5.65; N, 4.06; O, 15.47; P, 8.99; Si, 5.43%; Found: C, 60.24; H, 5.67; N, 4.05%.

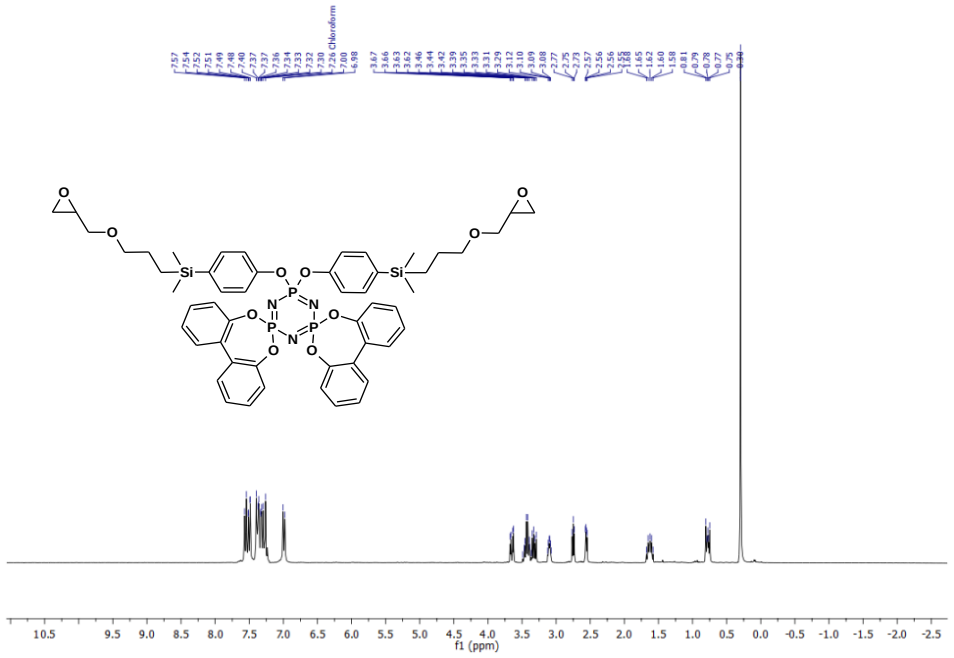

Fig. 5. ^{1}H NMR spectrum of Product (**1a**).

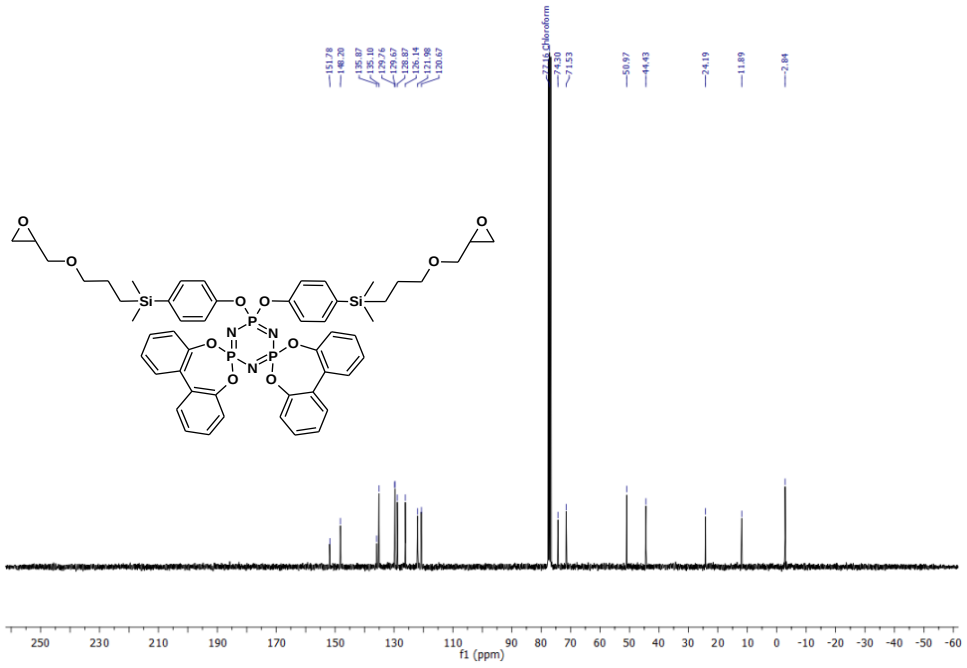

Fig. 6. ^{13}C NMR spectrum of Product (**1a**).

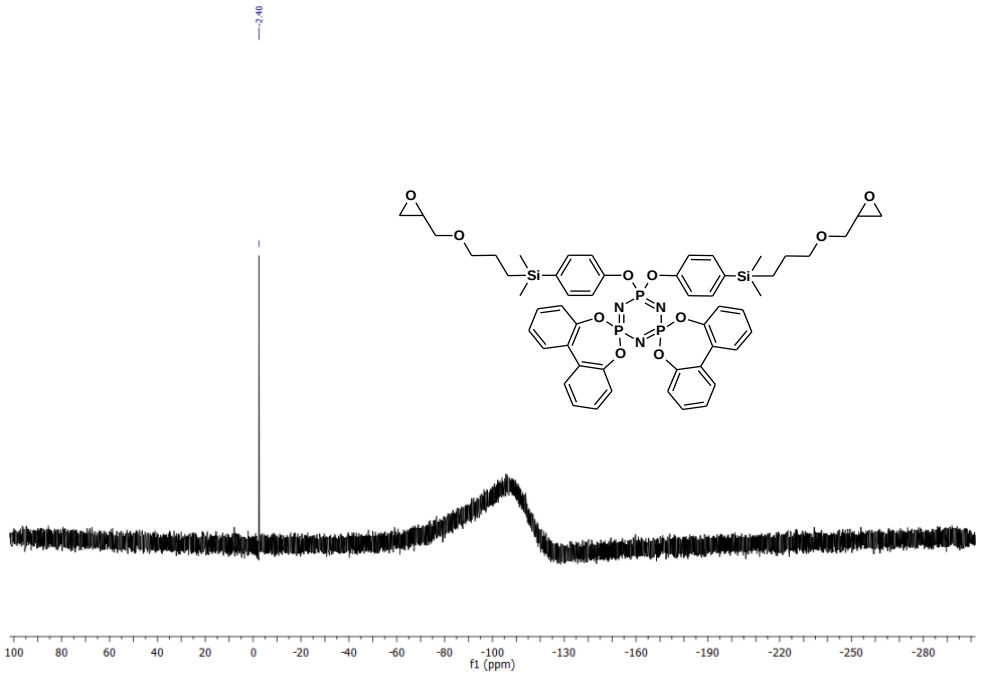

Fig. 7. ^{29}Si NMR spectrum of Product (**1a**).

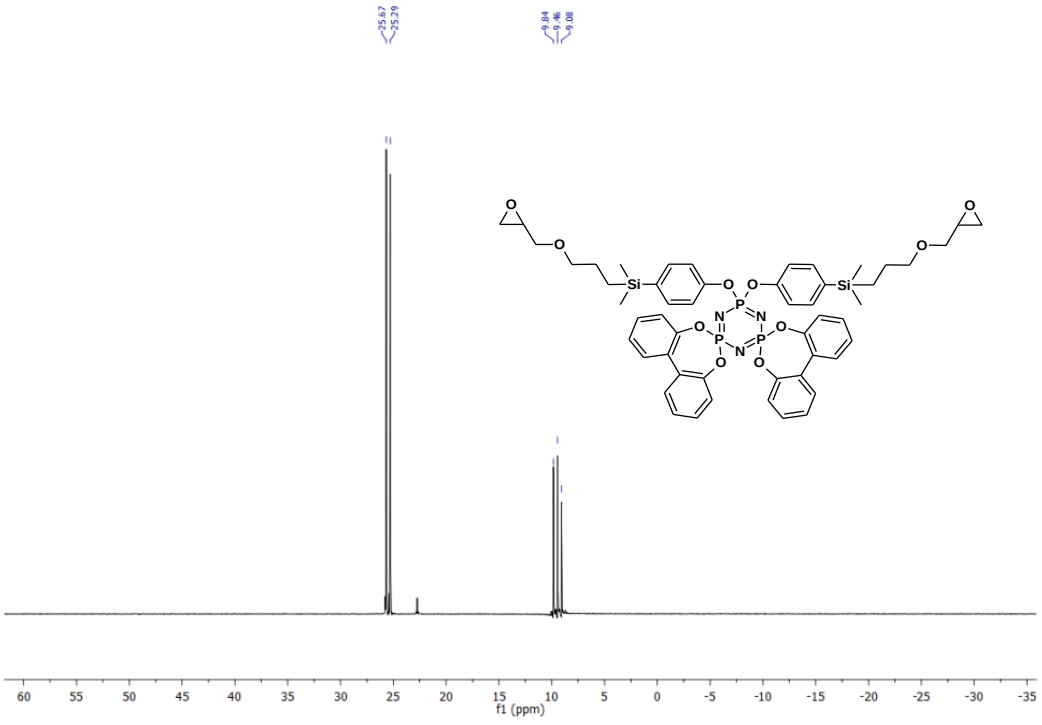

Fig. 8. ^{31}P NMR spectrum of Product (**1a**).

Spectra of Product (1b): Yield 91%.^{1}H NMR ($CDCl_3$): δ = 7.57 (d, 4H, *J*=11.1 Hz), 7.50 (dd, 4H), 7.41-7.30 (m, 12H, 9.8, 2.1 Hz), 7.0 (d, 4H, *J*=10.3 Hz) 3.56 $\underline{CH_2}O\underline{CH_2CH_2}Cl$ (m, 12H), 1.22 -CH_2Si (m, 4H), 0.33 $SiCH_3$ (s, 12H) **^{13}C NMR** ($CDCl_3$): δ = 151.87, 148.20, 135.74, 135.09, 129.77, 129.71, 128.88, 126.17, 121.96, 120.81, 70.43 $CH_2O\underline{CH_2}CH_2Cl$, 68.34 $\underline{CH_2}OCH_2CH_2Cl$, 43.05 CH_2Cl, 17.58 -CH_2Si, -2.38 $SiCH_3$, **^{29}Si NMR** ($CDCl_3$): δ = -4.18, **^{31}P NMR** ($CDCl_3$): δ = 25.47, 9.48. **Elemental Analysis** Calc. for $C_{48}H_{52}Cl_2N_3O_8P_3Si_2$: C, 56.58; H, 5.14; Cl, 6.96; N, 4.12; O, 12.56; P, 9.12; Si, 5.51%; Found: C, 56.77; H, 5.14; N, 4.12%.

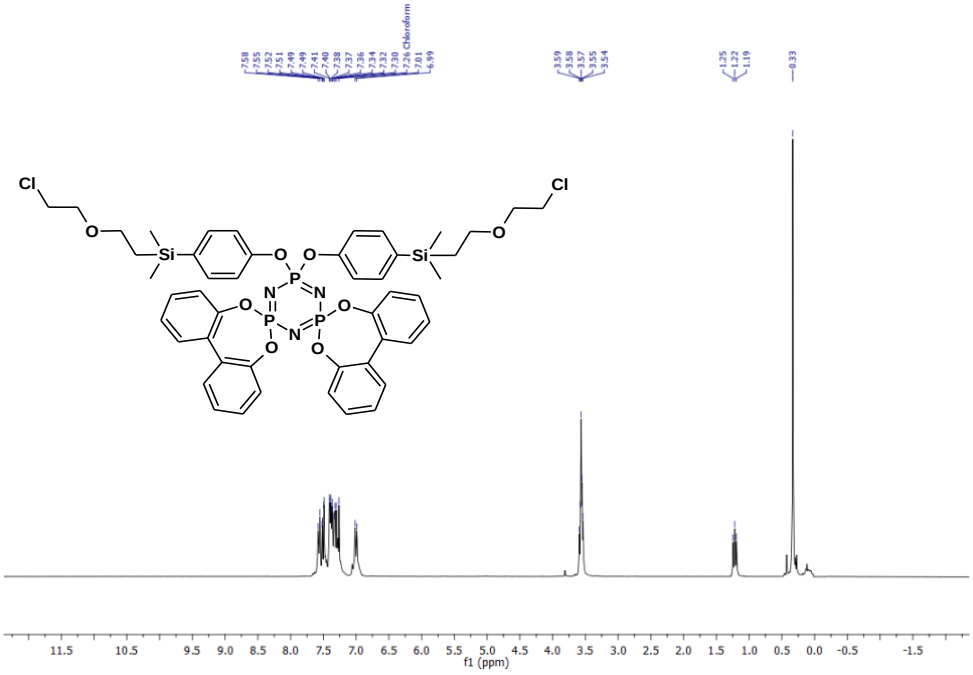

Fig. 9. ^{1}H NMR spectrum of Product (**1b**).

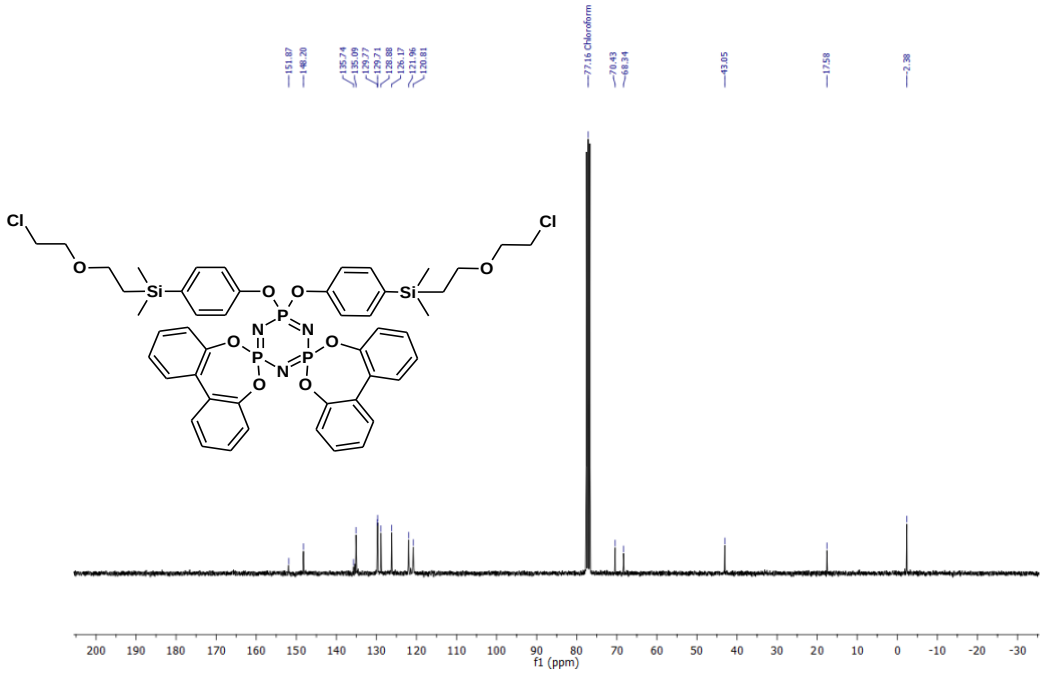

Fig. 10. ^{13}C NMR spectrum of Product (**1b**).

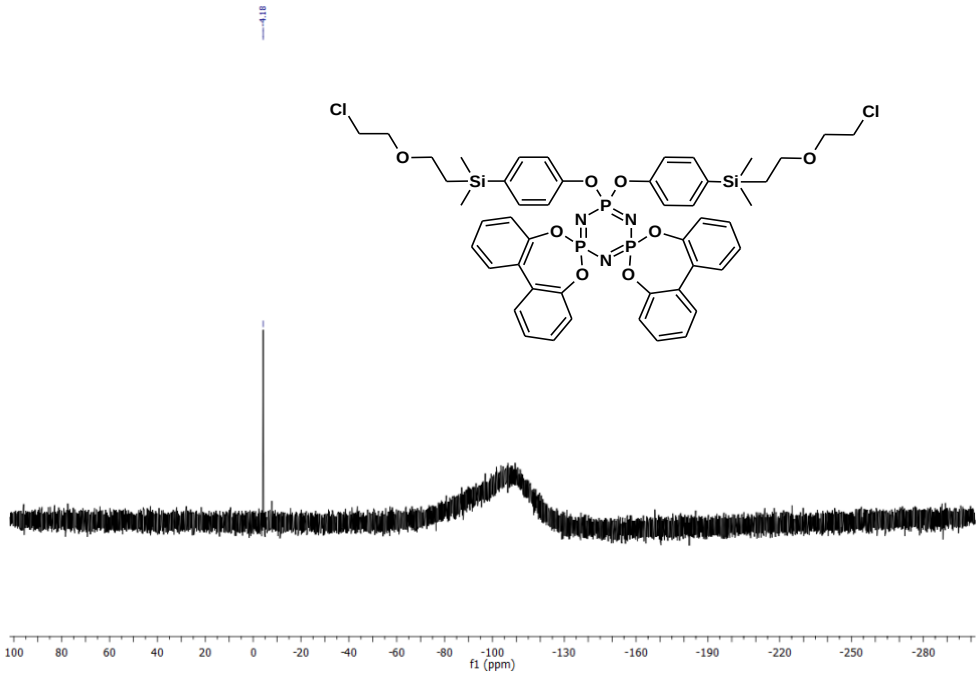

Fig. 11. ^{29}Si NMR spectrum of Product (**1b**).

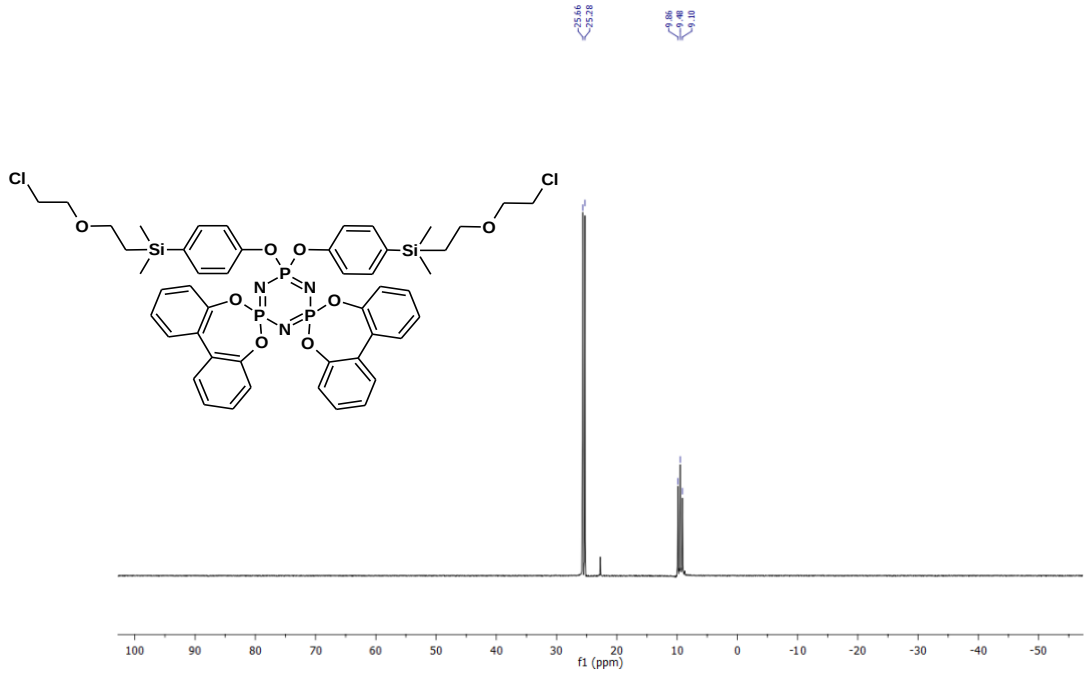

Fig. 12. ^{31}P NMR spectrum of Product (**1b**).

Spectra of Product (1c): Yield 94%. ^{1}H NMR ($CDCl_3$): δ = 7.55 (d, 4H, *J*= 10.8 Hz), 7.50 (dd, 4H, *J=9.8, 2.3 Hz*), 7.40-7.32 (m.12H), 6.98 (d, 4H, *J*=10.0 Hz), 1.30-1.23 (24H), 0.87 (m, 6H), 0.76 (m, 4H) CH_2Si, 0.28 $SICH_3$ (s, 12H), **^{13}C NMR ($CDCl_3$):** δ = 151.68, 148.24, 136.44, 135.08, 129.74, 129.66, 128.90, 126.11, 122.02, 120.70, 33.78, 32.05, 29.40, 24.01, 22.78, 15.94, 14.25 CH_2Si, -2.70 $SiCH_3$, **^{29}Si NMR** ($CDCl_3$): δ = -2.95, **^{31}P NMR** ($CDCl_3$): δ = 25.51, 9.56. **Elemental Analysis** Calc. for $C_{56}H_{70}N_3O_6P_3Si_2$: C, 65.28; H, 6.85; N, 4.08; O, 9.32; P, 9.02; Si, 5.45%; Found: C, 65.22; H, 6.87; N, 4.10%.

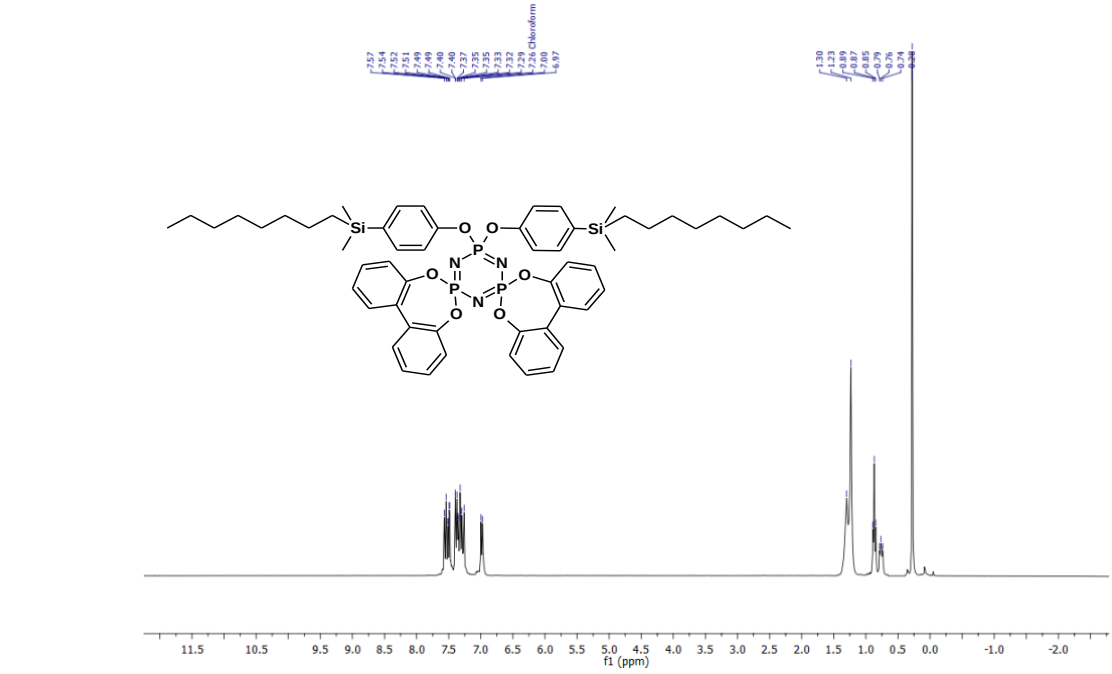

Fig. 13. ^{1}H NMR spectrum of Product (**1c**).

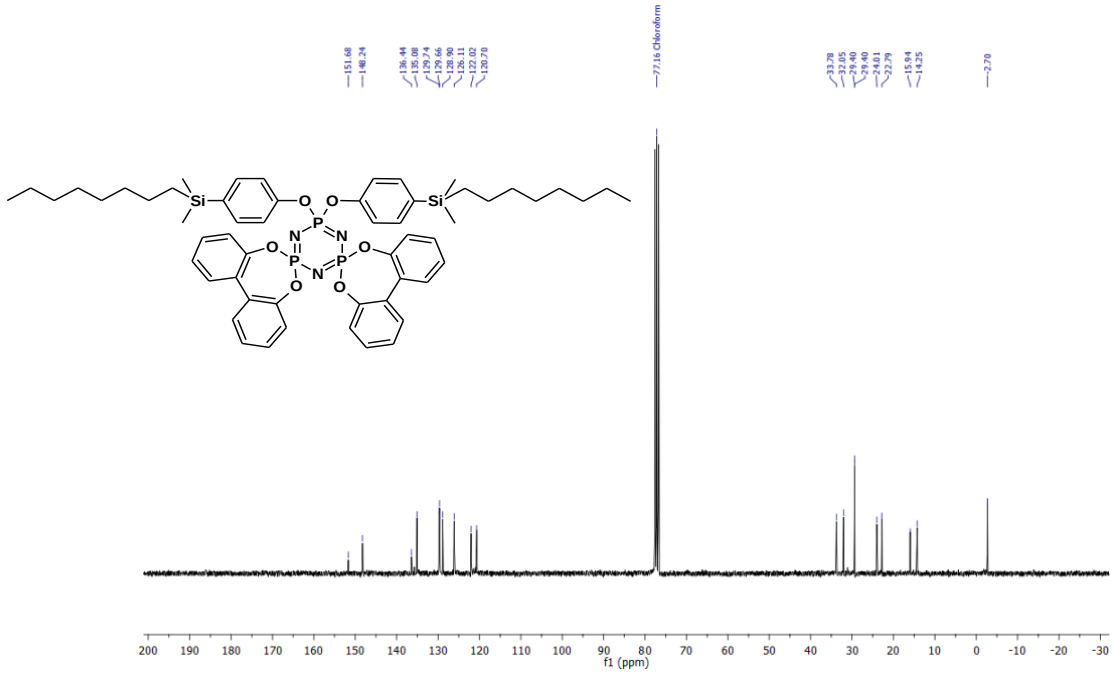

Fig. 14. ^{13}C NMR spectrum of Product (**1c**).

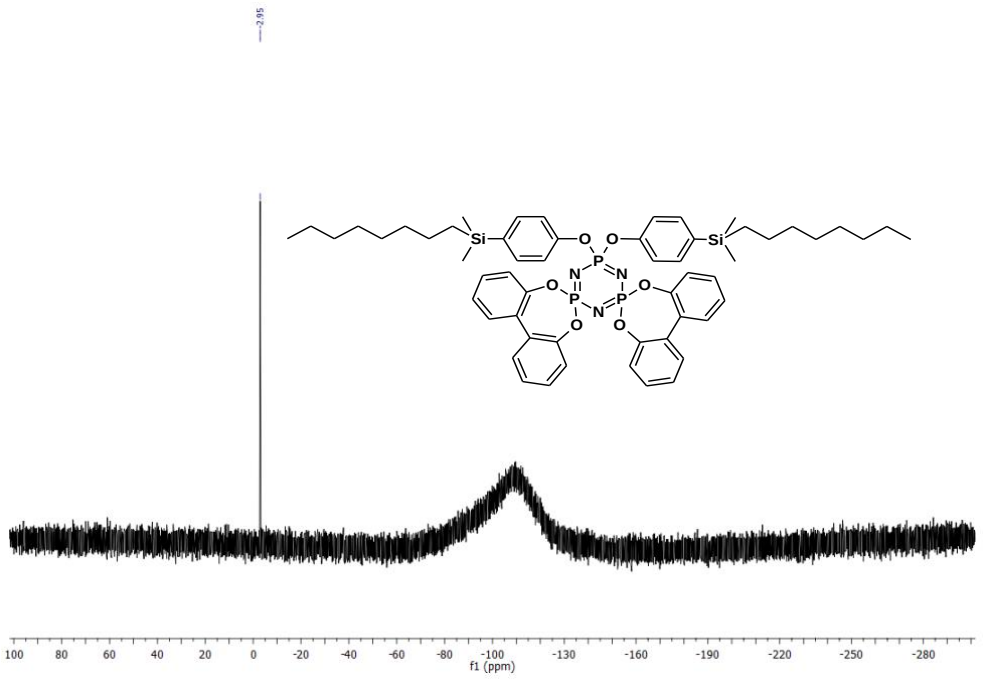

Fig. 15. ^{29}Si NMR spectrum of Product (**1c**).

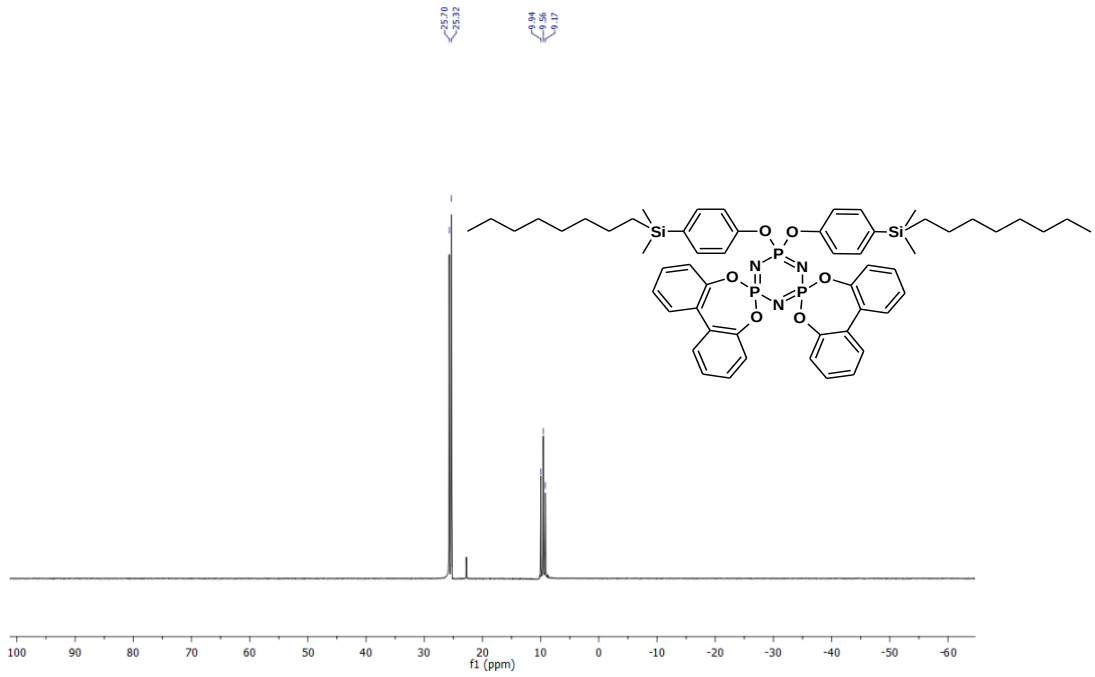

Fig. 16. ^{31}P NMR spectrum of Product (**1c**).

Spectra of Product (1d): Yield 98%. ^{1}H NMR ($CDCl_3$): δ = 7.55 (d, 4H, *J*=11.0 Hz), 7.50 (dd, 4H, *J*=9.9, 2.4 Hz)), 7.40-7.30 (m.12H), 6.99 (d, 4H, *J*=10.1 Hz), 6.04 CF_2H(tt, 2H, *J*=69.3, 7.3 Hz), 3.86 CH_2O (t, 4H, *J*=18.7 Hz), 3.51 OCH_2- (t, 4H, *J*=8.9 Hz), 1.62 $\underline{CH_2}CH_2Si$ (m, 4H), 0.77 CH_2Si (m, 4H), 0.30 $SiCH_3$ (s, 12H), **^{13}C NMR** ($CDCl_3$): δ = 151.95, 148.21, 135.61, 135.08,129.74, 129.70, 128.89, 126.16, 121.96, 120.78, 75.82, 67.72, 24.05 $\underline{CH_2}CH_2Si$, 11.65 CH_2Si, -2.90 $SiCH_3$, **^{29}Si NMR** ($CDCl_3$): δ = -2.40, **^{31}P NMR** ($CDCl_3$): δ = 25.37, 9.41. **Elemental Analysis** Calc. for $C_{56}H_{54}F_{16}N_3O_8P_3Si_2$: C, 49.82; H, 4.03; F, 22.51; N, 3.11; O, 9.48; P, 6.88; Si, 4.16%; Found: C, 49.72; H, 4.04; N, 3.11%.

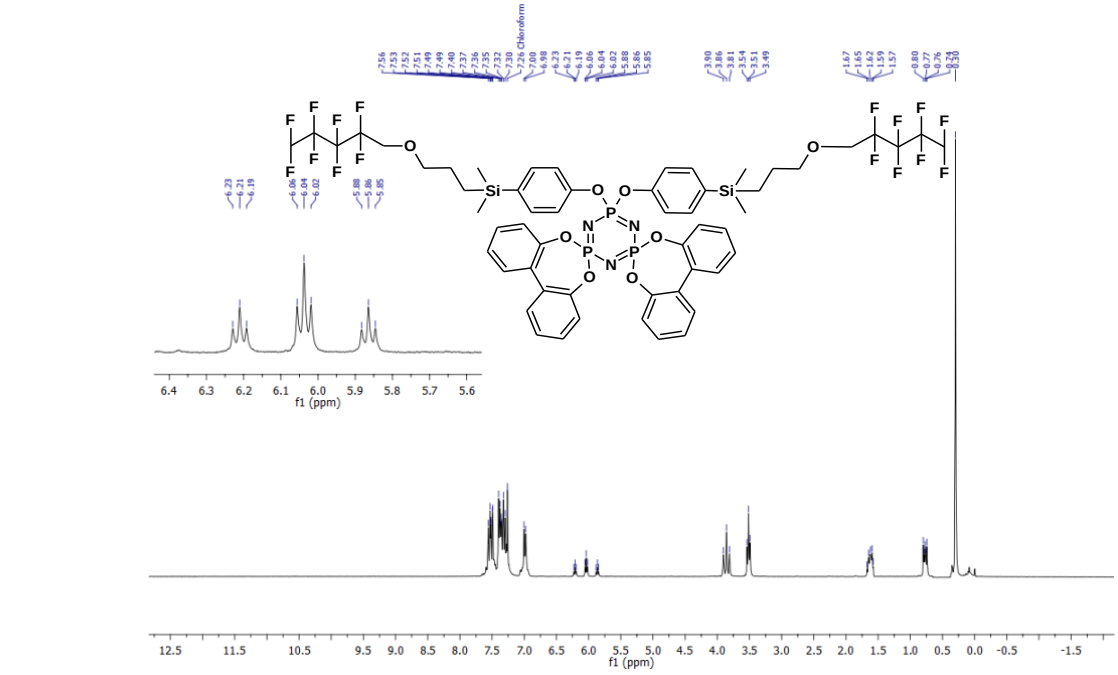

Fig. 17. ^{1}H NMR spectrum of Product (**1d**).

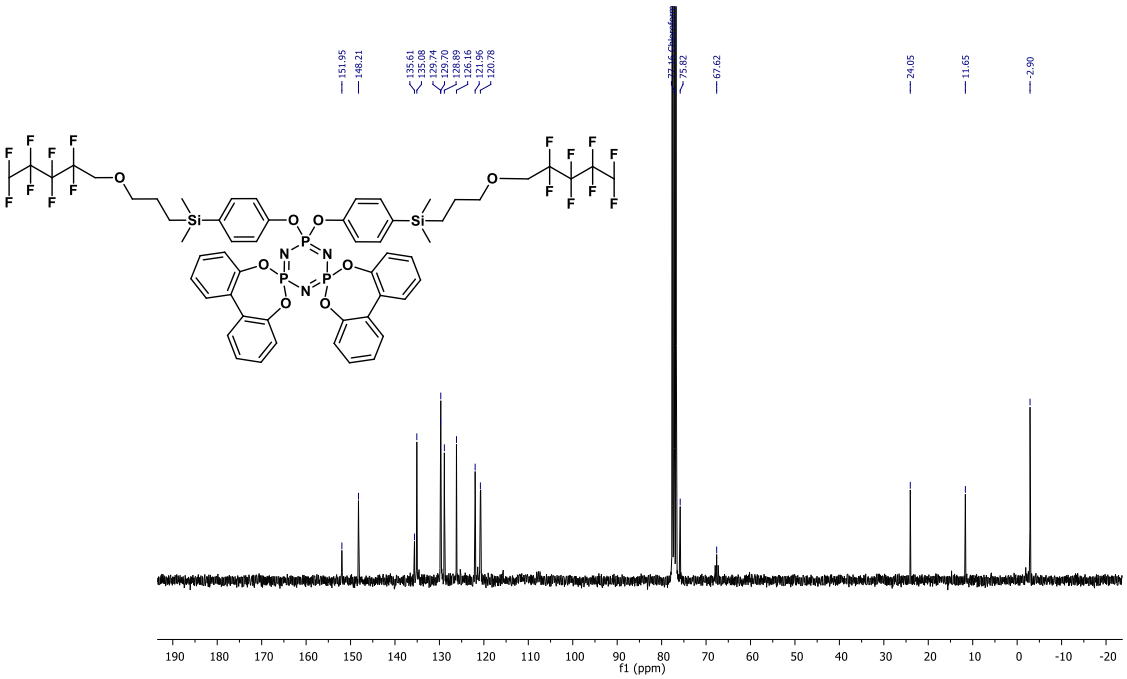

Fig. 18. ^{13}C NMR spectrum of Product (**1d**).

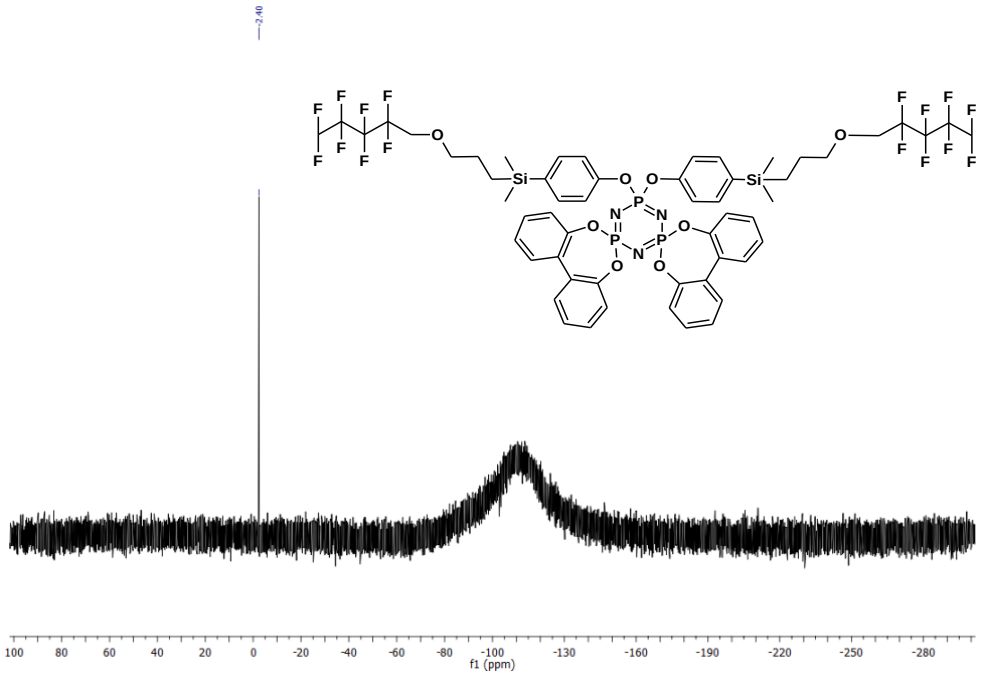

Fig. 19. ^{29}Si NMR spectrum of Product (**1d**).

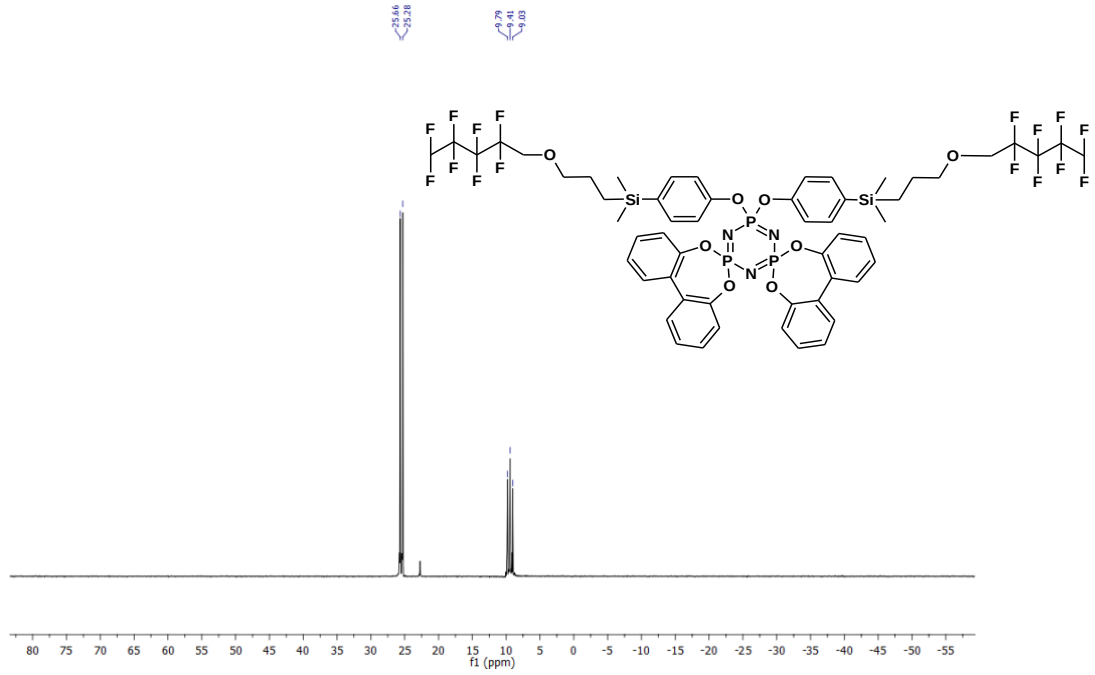

Fig. 20. ^{31}P NMR spectrum of Product (**1d**).

Spectra of Product (1e) Yield 98%. ^{1}H NMR ($CDCl_3$): δ = 7.55 (d, 4H, *J*=8.1 Hz), 7.50 (dd, 4H, *J*=7.4, 1.7Hz), 7.40-7.32 (m, 12H), 7.0 (d, 4H), 5.10 -C=CH-CH_2 (m, 2H), 1.98 -C=CH-CH_2 (m, 4H), 1.66 (s, 6H), 1.58 (s, 6H), 1.45 (m, 8H), 1.13 (s, 6H), 0.76 (m, 4H) CH_2Si, 0.30 $SiCH_3$ (s, 12H), **^{13}C NMR** ($CDCl_3$): δ = 151.81, 148.21, 135.78, 135.09, 131.80, 129.76, 129.68, 128.88, 126.14, 124.61, 121.98, 120.78, 73.44, 40.82, 35.90, 26.39, 25.83, 22.75, 17.76, 9.50 CH_2Si, -2.92 $SiCH_3$**, ^{29}Si NMR** ($CDCl_3$): δ = -1.85, **^{31}P NMR** ($CDCl_3$): δ = 25.48, 9.44. **Elemental Analysis** Calc. for $C_{60}H_{74}N_3O_8P_3Si_2$: C, 64.67; H, 6.69; N, 3.77; O, 11.49; P, 8.34; Si, 5.04%; Found: C, 64.50; H, 6.69; N, 3.76%.

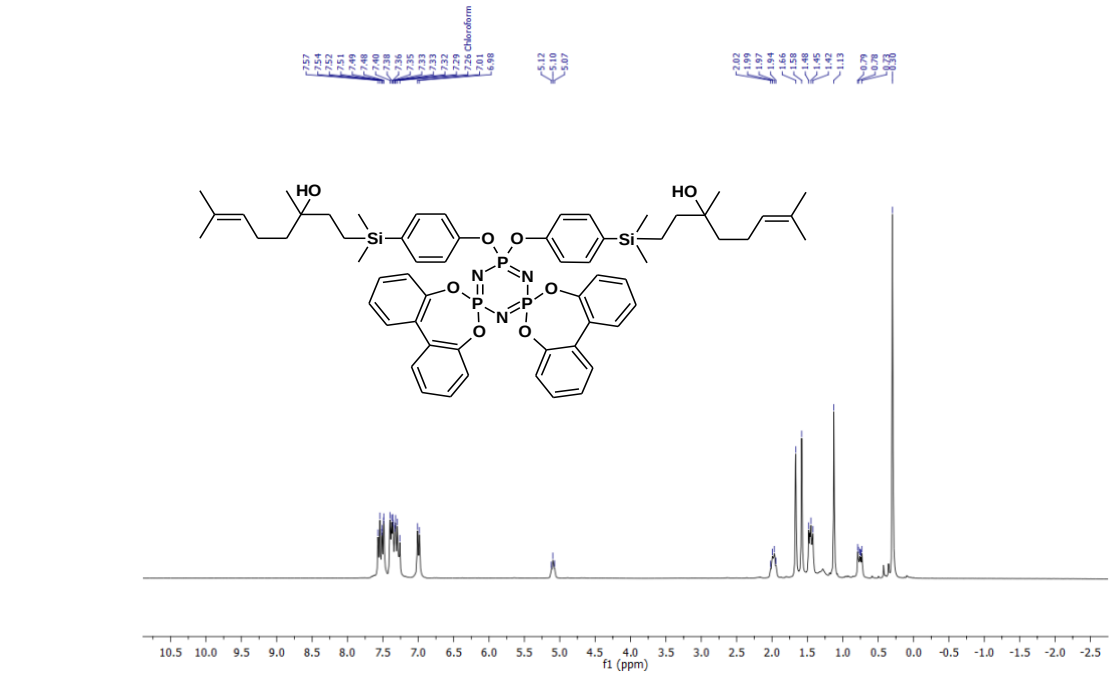

Fig. 21. ^{1}H NMR spectrum of Product (**1e**).

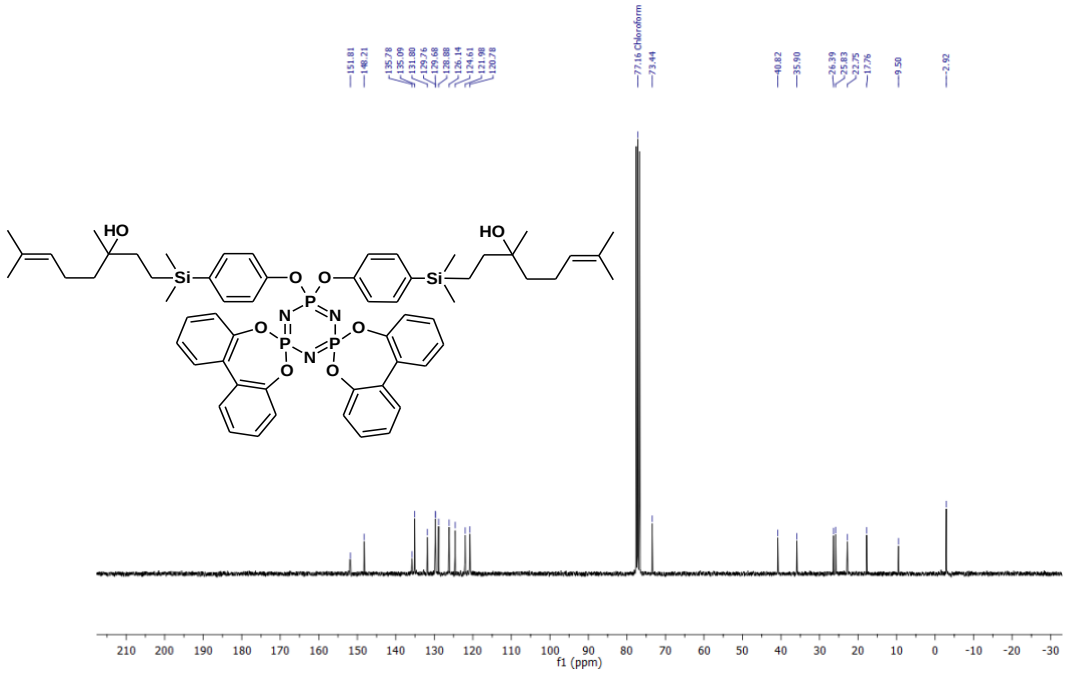

Fig. 22. ^{13}C NMR spectrum of Product (**1e**).

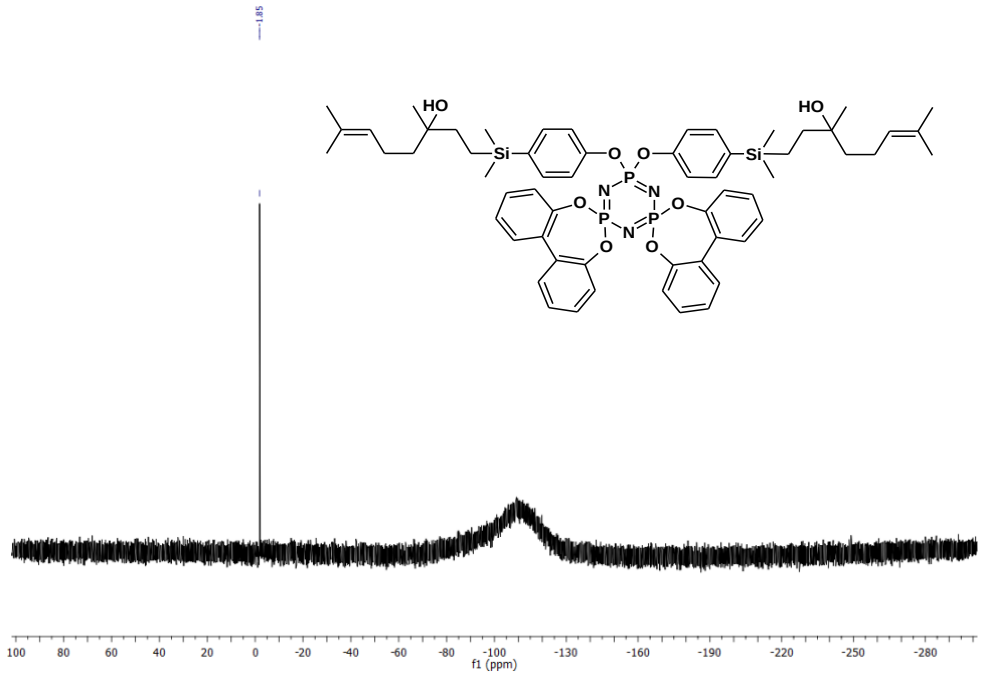

Fig. 23. ^{29}Si NMR spectrum of Product (**1e**).

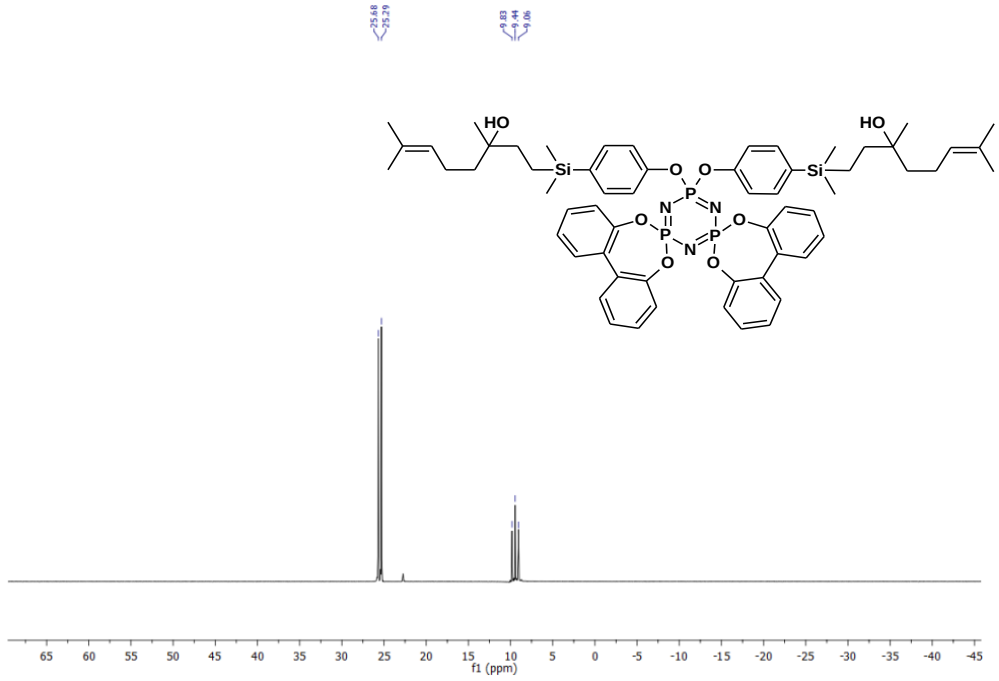

Fig. 24. ^{31}P NMR spectrum of Product (**1e**).

Spectra of Product (1f) Yield 93%. ^{1}H NMR ($CDCl_3$): δ = 7.55 (d, 4H), 7.50 (dd, 4H), 7.38-7.29 (m, 12H), 6.99 (d, 4H), 2.23 N-CH_2 (m 4H), 2.16 NMe_2 (s, 12H), 1.47 $\underline{CH_2}CH_2Si$ (m, 4H), 0.75 $CH_2\underline{CH_2}Si$ (m, 4H), 0.29 $SiCH_3$ (s, 12H), **^{13}C NMR** ($CDCl_3$): δ = 151.96, 148.23, 136.04, 135.08, 129.76, 129.67, 128.89, 126.14, 122.00, 120.72, 63.20 N-CH_2, 45.51 NMe_2, 22.10 $\underline{CH_2}CH_2Si$, 13.44 $CH_2\underline{CH_2}Si$, -2.79 $SiCH_3$, **^{29}Si NMR** ($CDCl_3$): δ = -2.61, **^{31}P NMR** ($CDCl_3$): δ = 25.48, 9.42. **Elemental Analysis** Calc. for $C_{50}H_{60}N_5O_6P_3Si_2$: C, 61.52; H, 6.20; N, 7.17; O, 9.83; P, 9.52; Si, 5.75%; Found: C, 61.41; H, 6.21; N, 7.16%.

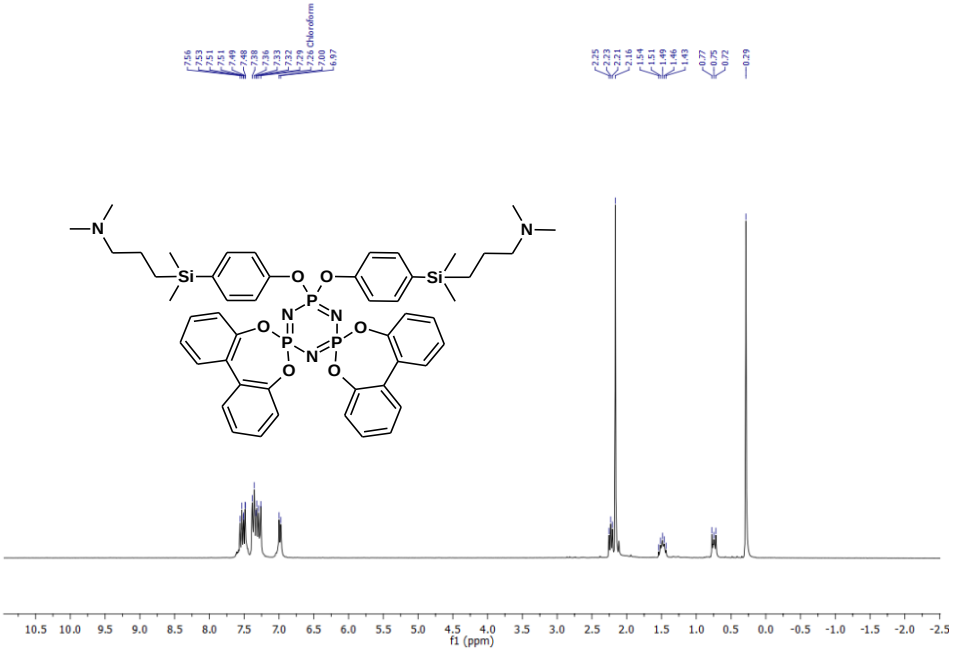

Fig. 25. ^{1}H NMR spectrum of Product (**1f**).

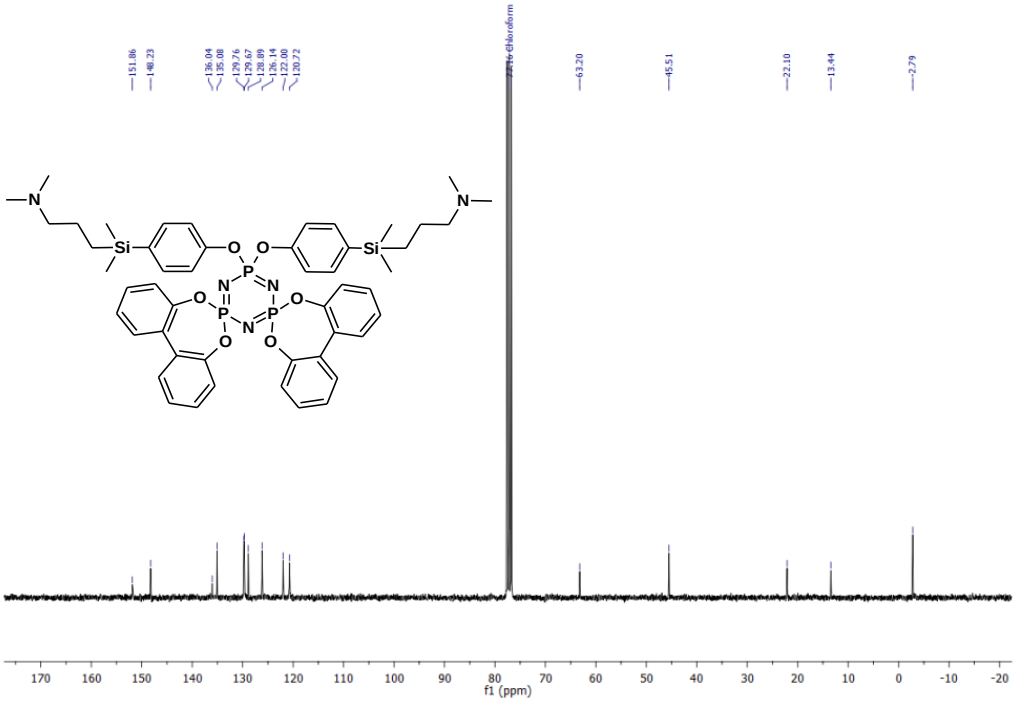

Fig. 26. ^{13}C NMR spectrum of Product (**1f**).

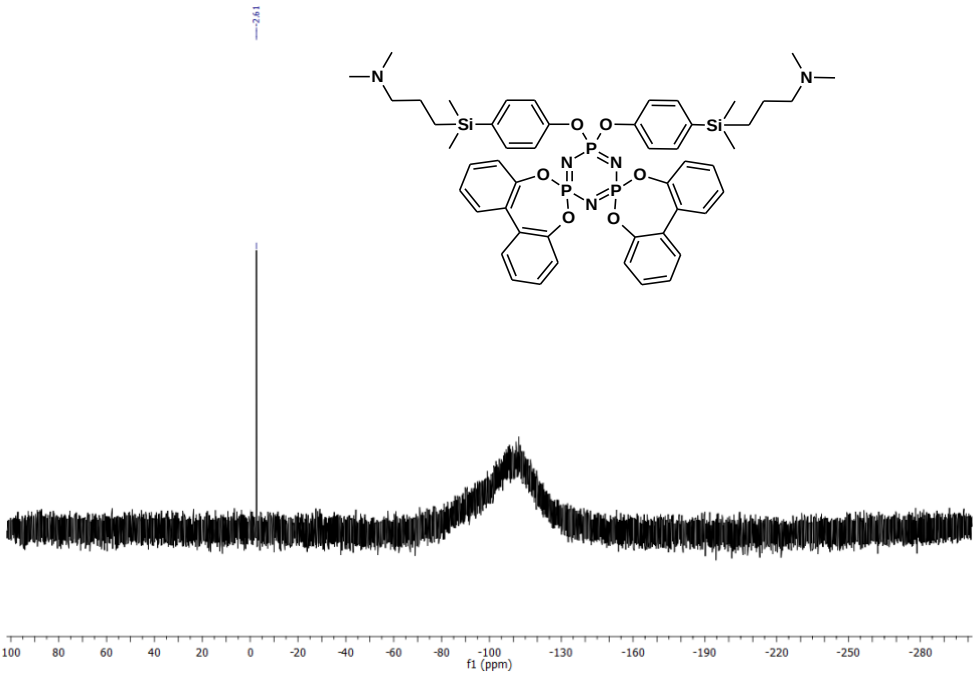

Fig. 27. ^{29}Si NMR spectrum of Product (**1f**).

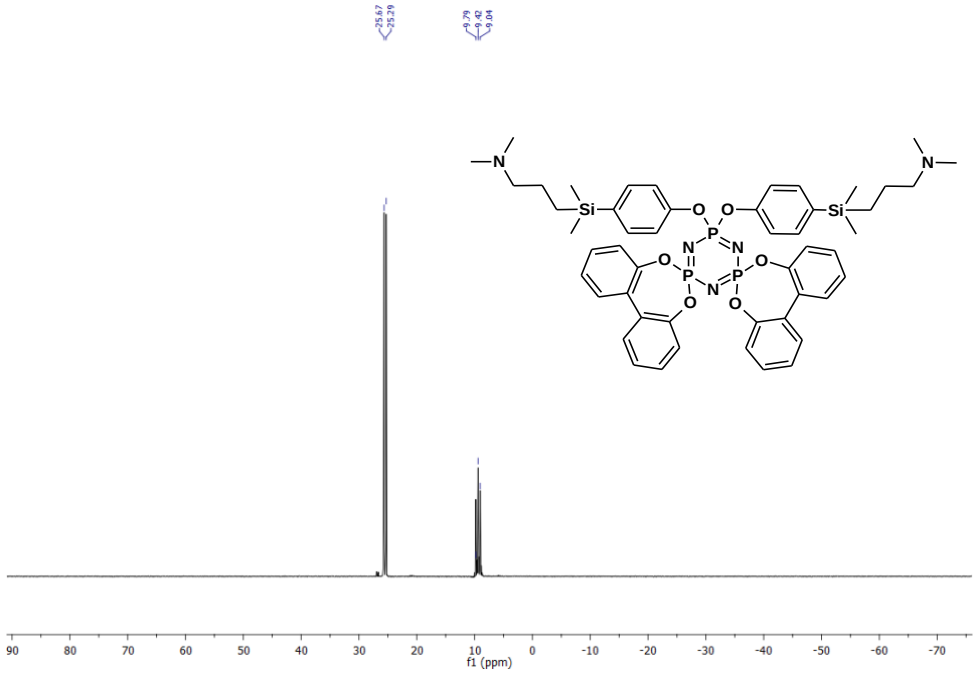

Fig. 28. ^{31}P NMR spectrum of Product (**1f**).

Spectra of Hexakis((4-dimethylsilyl)phenoxy)cyclotriphosphazene (2)

Elemental Analysis Calc. for $C_{48}H_{66}N_3O_6P_3Si_6$: C, 55.30; H, 6.38; N, 4.03; O, 9.21; P, 8.91; Si, 16.16%; Found: C, 55.13; H, 6.40; N, 4.02%.

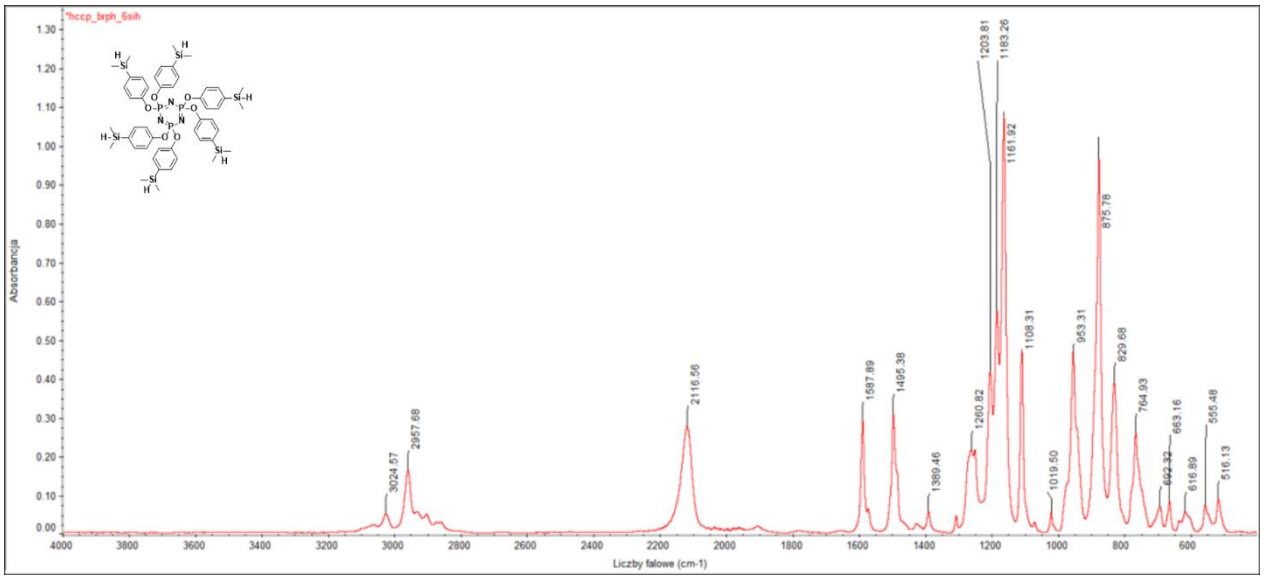

Fig. 29. FT-IR spectrum of Substrate (**2**).

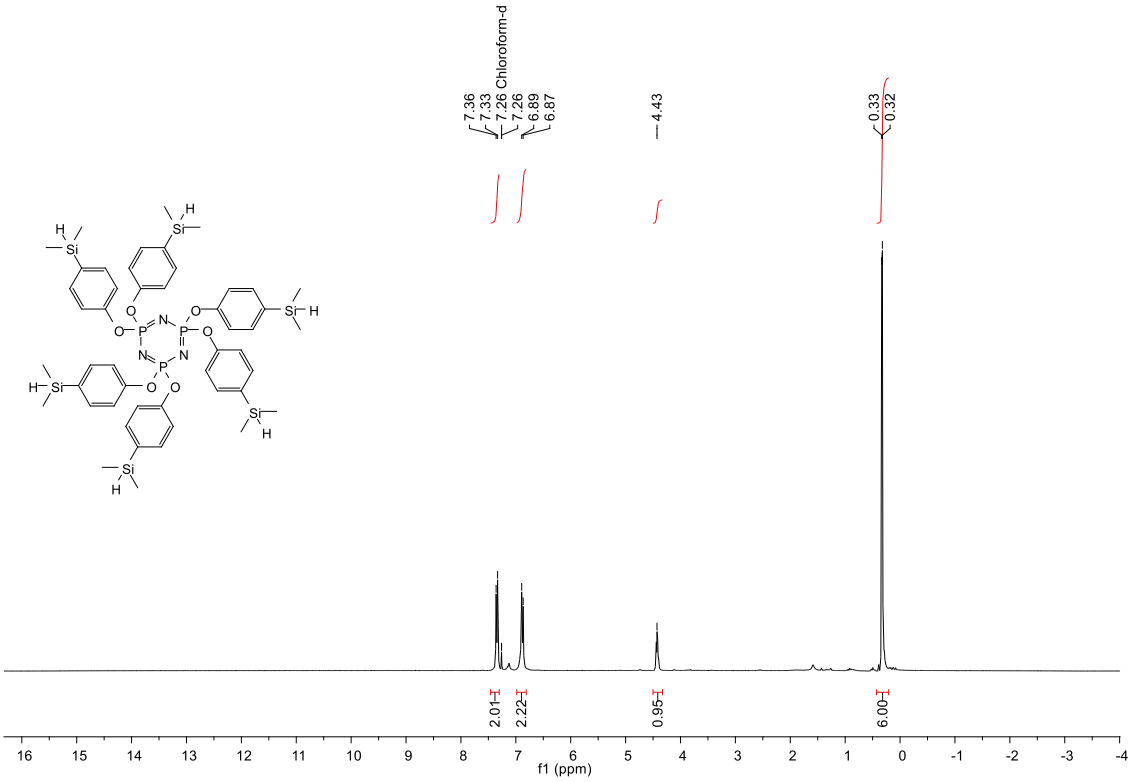

Fig. 30. ^{1}H NMR spectrum of Substrate (**2**).

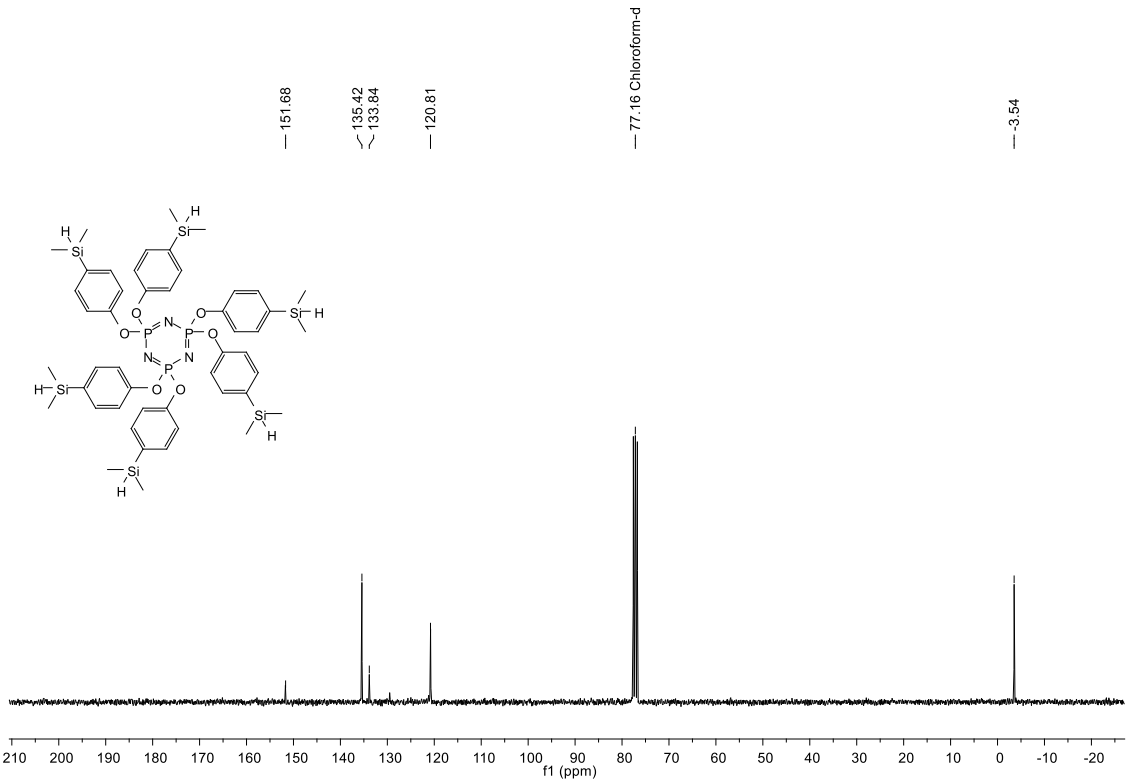

Fig. 31. ^{13}C NMR spectrum of Substrate (**2**).

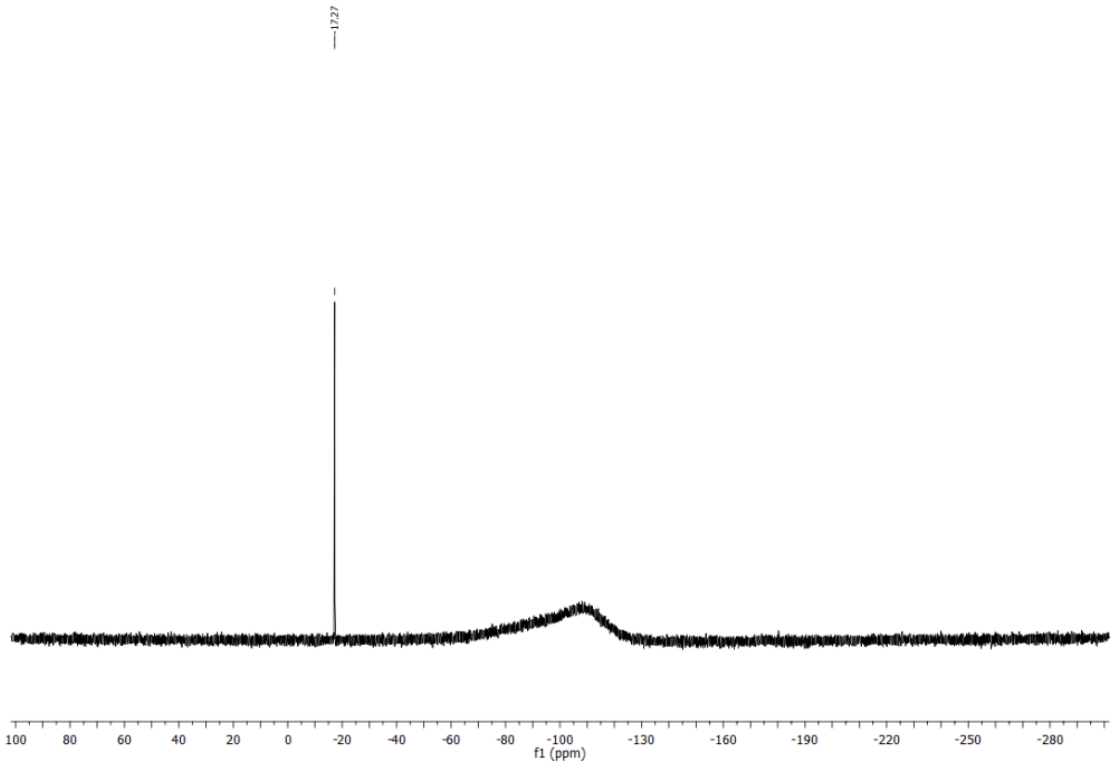

Fig. 32. ^{29}Si NMR spectrum of Substrate (**2**).

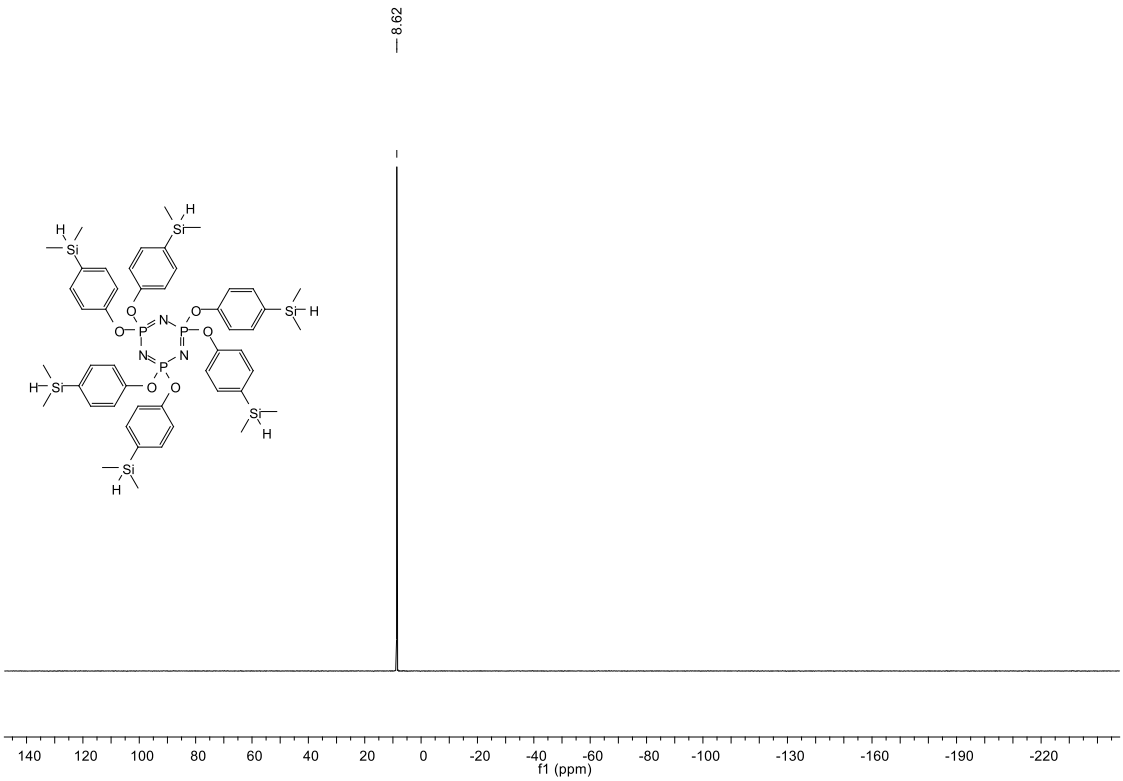

Fig. 33. ^{31}P NMR spectrum of Substrate (**2**).

Spectra of Product (2a): Yield 93%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.33 (d, 12H, *J*=8.3 Hz), 6.91 (d, 12H, *J*=8.1 Hz), 3.65 (dd, 6H, *J*=11.5, 3.0 Hz), 3.51 – 3.24 (m, 18H), 3.10 (m, 6H), 2.79 – 2.73 (m, 6H), 2.57 (m, 6H), 1.57 $\underline{CH_2}CH_2Si$ (m, 12H), 0.71 $CH_2\underline{CH_2}Si$ (m, 12H), 0.24 $SiCH_3$ (s, 36H). **^{13}C NMR** ($CDCl_3$; 75 MHz) δ = 151.57 (C-O), 135.56 (CPh-Si), 134.89, 120.65, 74.30, 71.55, 50.96, 44.42, 24.16 $\underline{CH_2}CH_2Si$, 11.86 $CH_2\underline{CH_2}Si$, -3.86 $SiCH_3$. **^{31}P NMR** ($CDCl_3$; 162 MHz) δ: = 8.22. **^{29}Si NMR** ($CDCl_3$; 79 MHz) δ = -2.56. **Elemental Analysis** Calc. for $C_{84}H_{126}N_3O_{18}P_3Si_6$: C, 58.41; H, 7.35; N, 2.43; O, 16.67; P, 5.38; Si, 9.76%; Found: C, 58.45; H, 7.34; N, 2.43%.

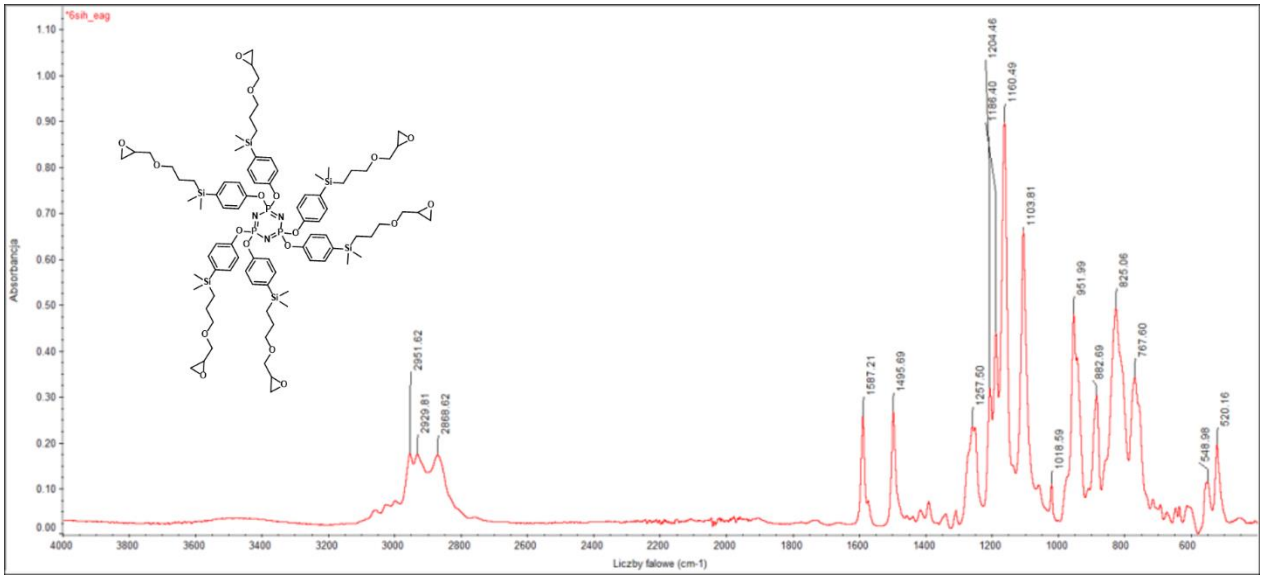

Fig. 34. FT-IR spectrum of Product (**2a**).

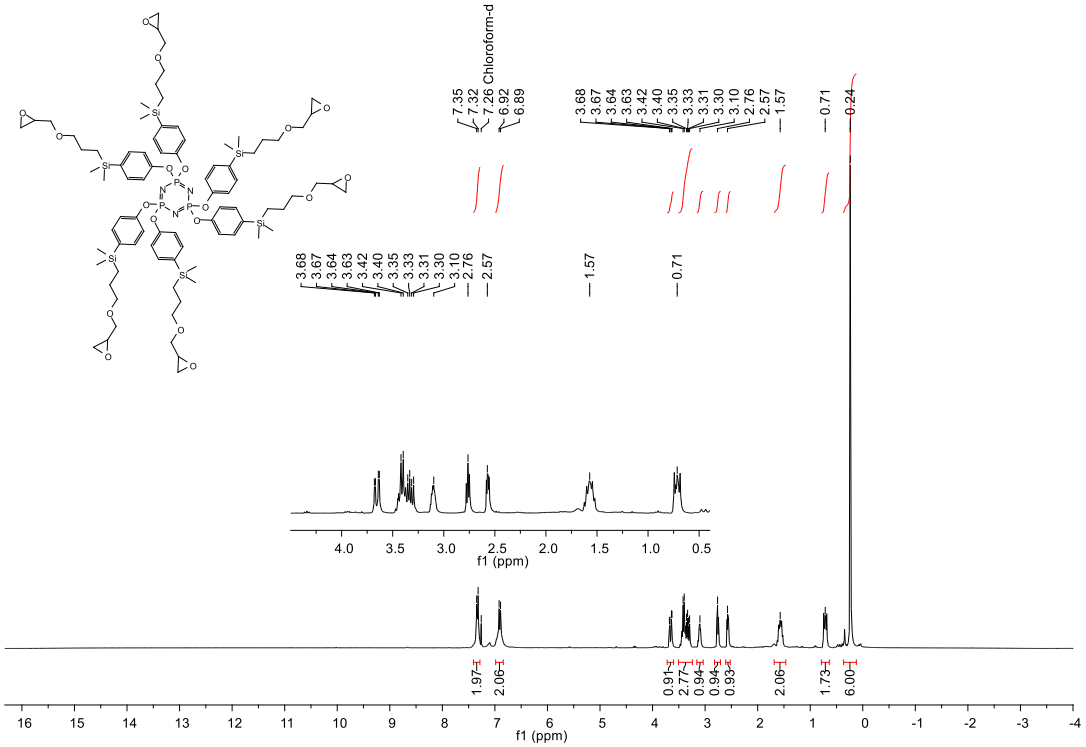

Fig. 35. ^{1}H NMR spectrum of Product (**2a**).

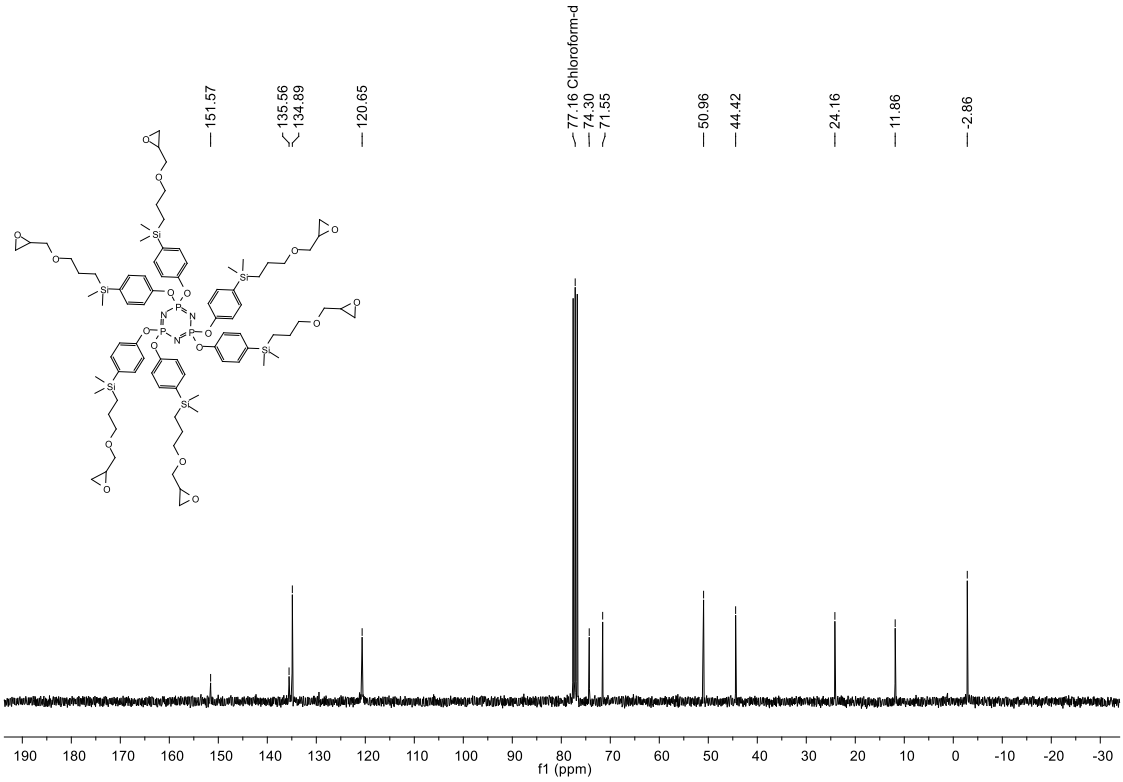

Fig. 36. ^{13}C NMR spectrum of Product (**2a**).

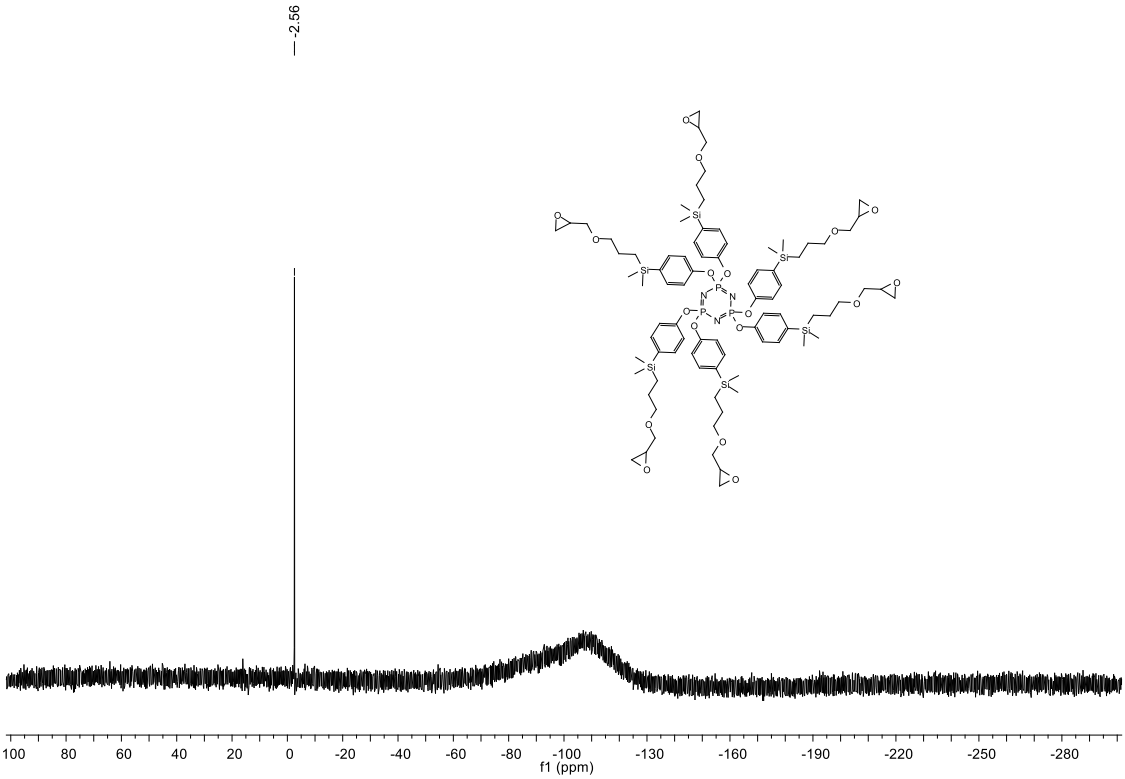

Fig. 37. ^{29}Si NMR spectrum of Product (**2a**).

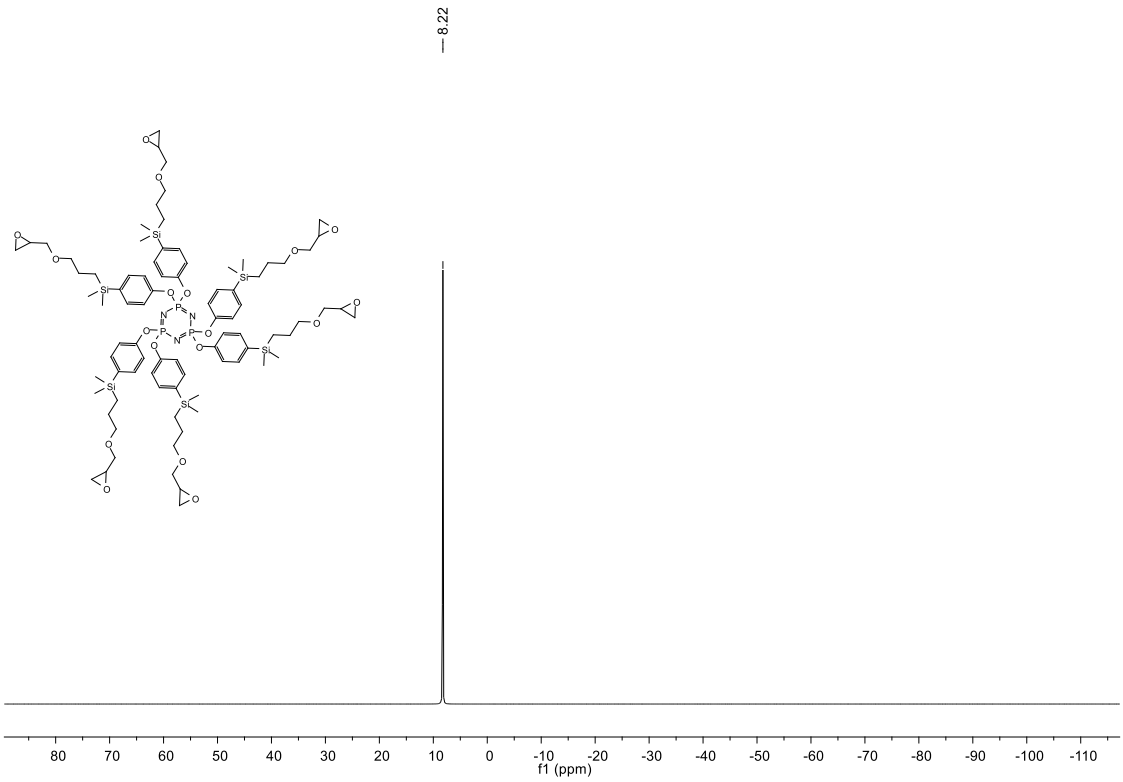

Fig. 38. ^{31}P NMR spectrum of Product (**2a**).

Spectra of Product (2b): Yield 95%. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 8.3 Hz, 12H), 6.94 (d, *J* = 8.3 Hz, 12H), 3.56 $ClCH_2CH_2OCH_2$- (m, 18H), 1.17 CH_2Si (t, J = 8.0 Hz, 12H), 0.29 $SiCH_3$ (s, 36H). **^{13}C NMR** ($CDCl_3$; 75 MHz) δ = 151.67 C-O, 135.20 C_{Ph}-Si, 134.89, 120.69, 70.43 OCH_2, 68.28 OCH_2, 43.02 CH_2Cl, 17.51 $SiCH_2$, -2.40 $SiCH_3$. **^{31}P NMR** ($CDCl_3$; 162 MHz) δ = 8.20. **^{29}Si NMR** ($CDCl_3$; 79 MHz) δ: -4.29. **Elemental Analysis** Calc. for $C_{72}H_{108}Cl_6N_3O_{12}P_3Si_6$: C, 51.42; H, 6.47; Cl, 12.65; N, 2.50; O, 11.42; P, 5.53; Si, 10.02%; Found: C, 51.42; H, 6.45; N, 2.49%.

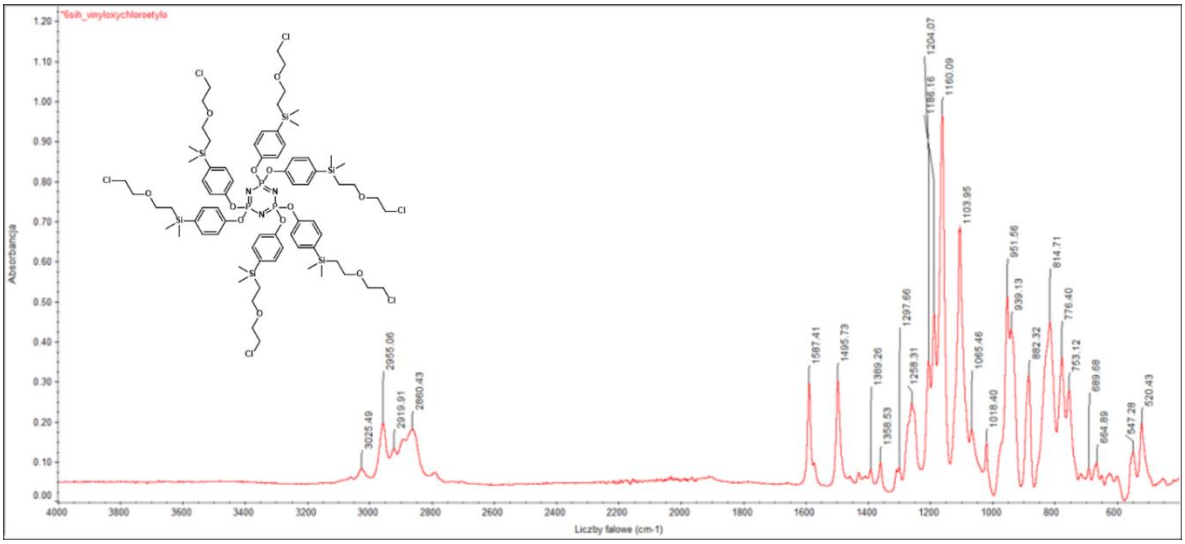

Fig. 39. FT-IR spectrum of Product (**2b**).

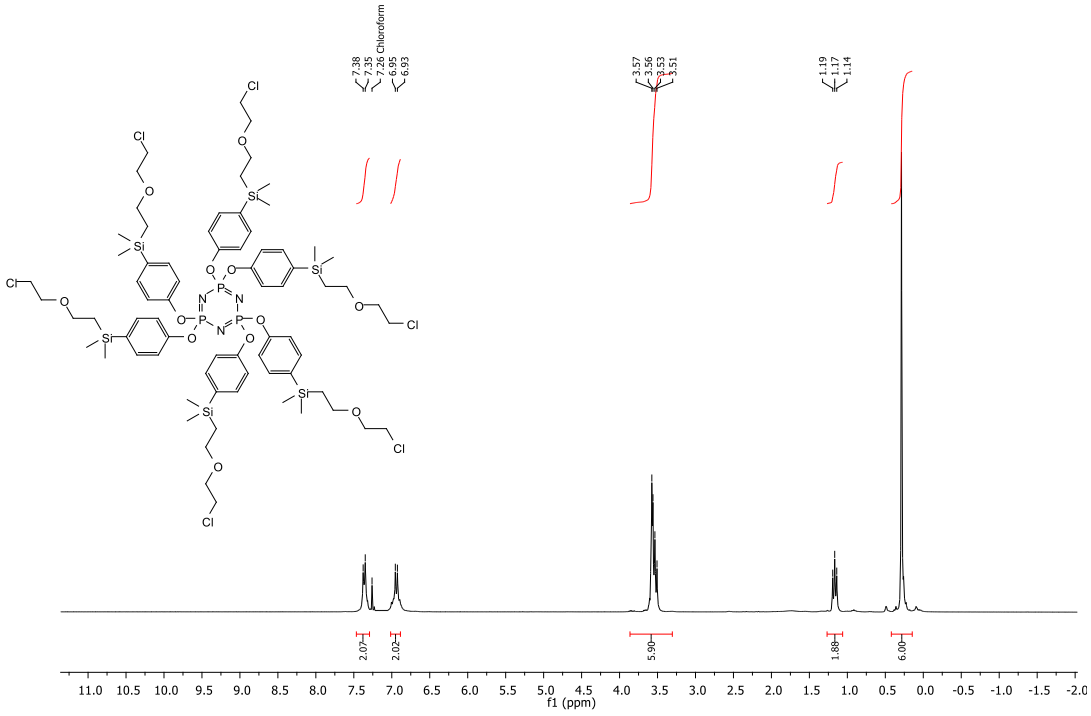

Fig. 40. ^{1}H NMR spectrum of Product (**2b**).

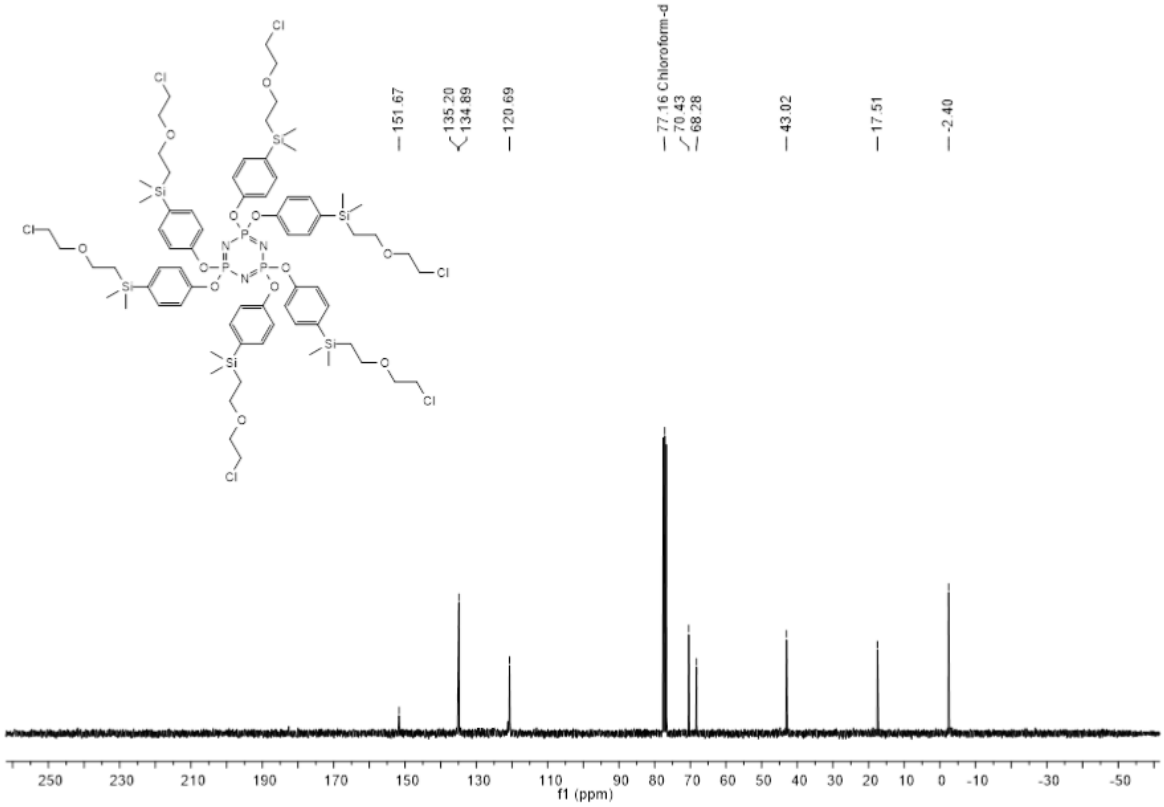

Fig. 41. ^{13}C NMR spectrum of Product (**2b**).

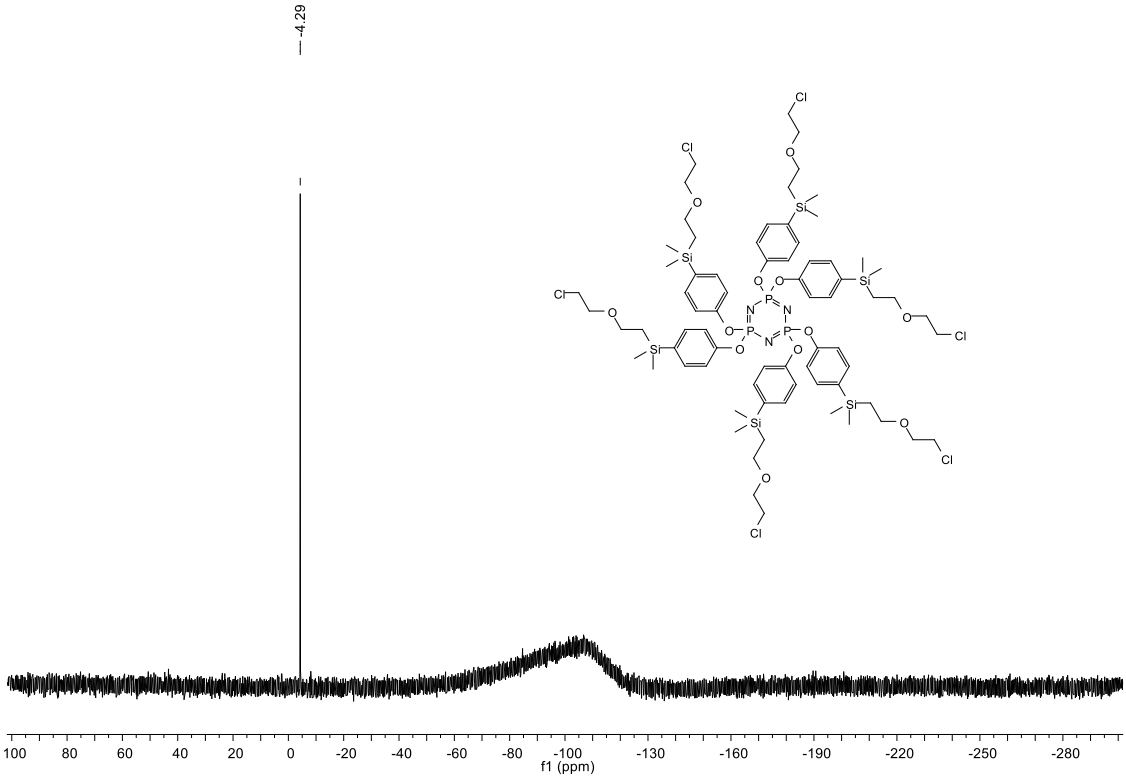

Fig. 42. ^{29}Si NMR spectrum of Product (**2b**).

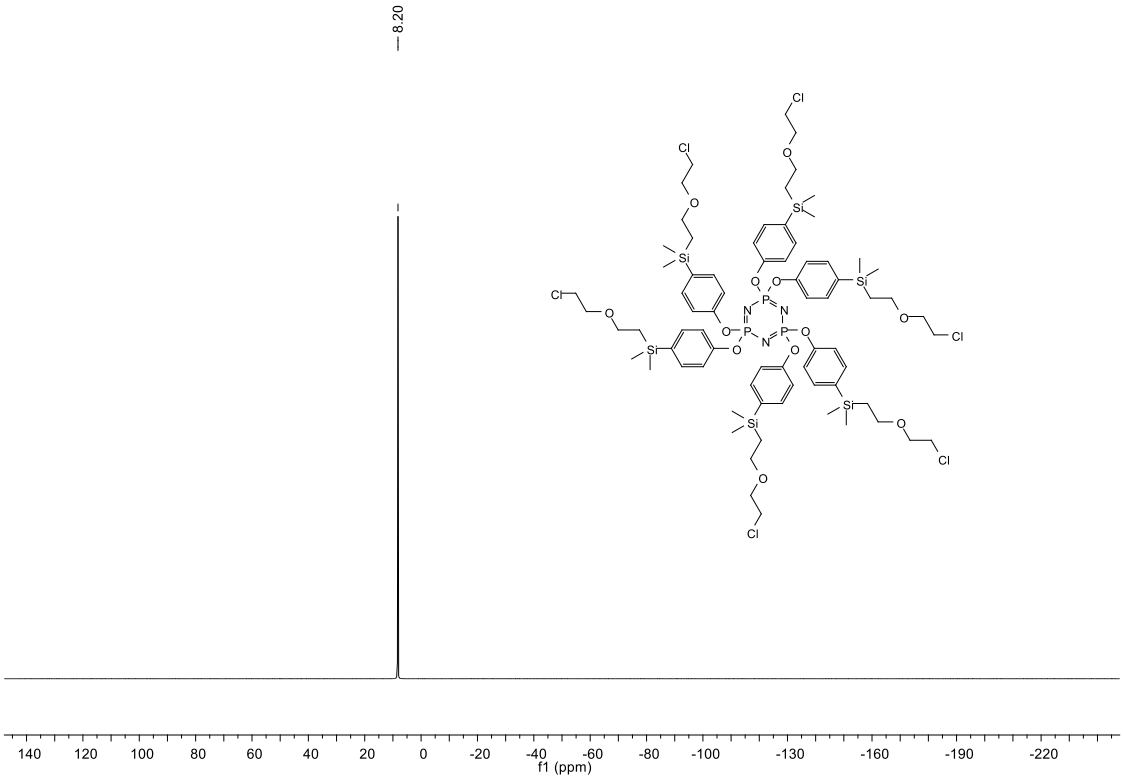

Fig. 43. ^{31}P NMR spectrum of Product (**2b**).

Spectra of Product (2c): Yield 98%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 8.2 Hz, 12H), 6.92 (d, *J* = 8.1 Hz, 12H), 3.77 OCH_2CH_3 (q, *J* = 7.0 Hz, 36H), 1.19 OCH_2CH_3 (t, *J* = 7.0 Hz, 54H), 0.74 $SiCH_2$ (m, 12H), 0.52 $SiCH_2$ (m, 12H), 0.23 $SiCH_3$ (s, 36H). **^{13}C NMR** ($CDCl_3$; 75 MHz) δ = 151.63 (C-O), 135.51 (CPh-Si), 134.97, 120.98, 58.51 OCH_2CH_3, 18.43 OCH_2CH_3, 6.95 $SiCH_2$, 2.65 $SiCH_2$, -3.41 $SiCH_3$. **^{31}P NMR** ($CDCl_3$; 162 MHz) δ = 8.11. **^{29}Si NMR** ($CDCl_3$; 79 MHz) δ = -1.20 (Ph-Si), -45.07 [$Si(OEt)_3$]. **Elemental Analysis** Calc. for $C_{96}H_{174}N_3O_{24}P_3Si_{12}$: C, 52.79; H, 8.03; N, 1.92; O, 17.58; P, 4.25; Si, 15.43%; Found: C, 52.80; H, 8.03; N, 1.93%.

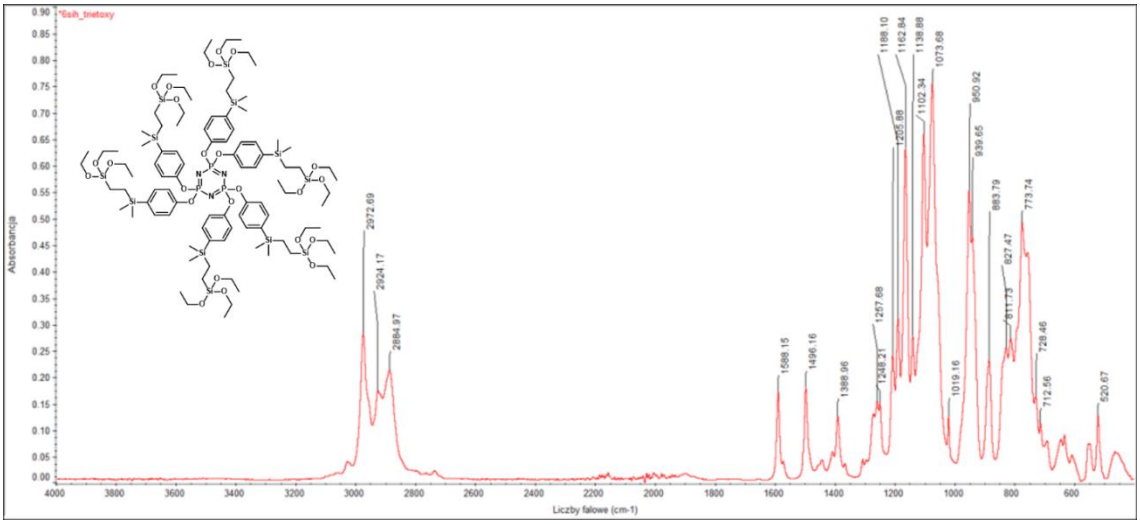

Fig. 44. FT-IR spectrum of Product (**2c**).

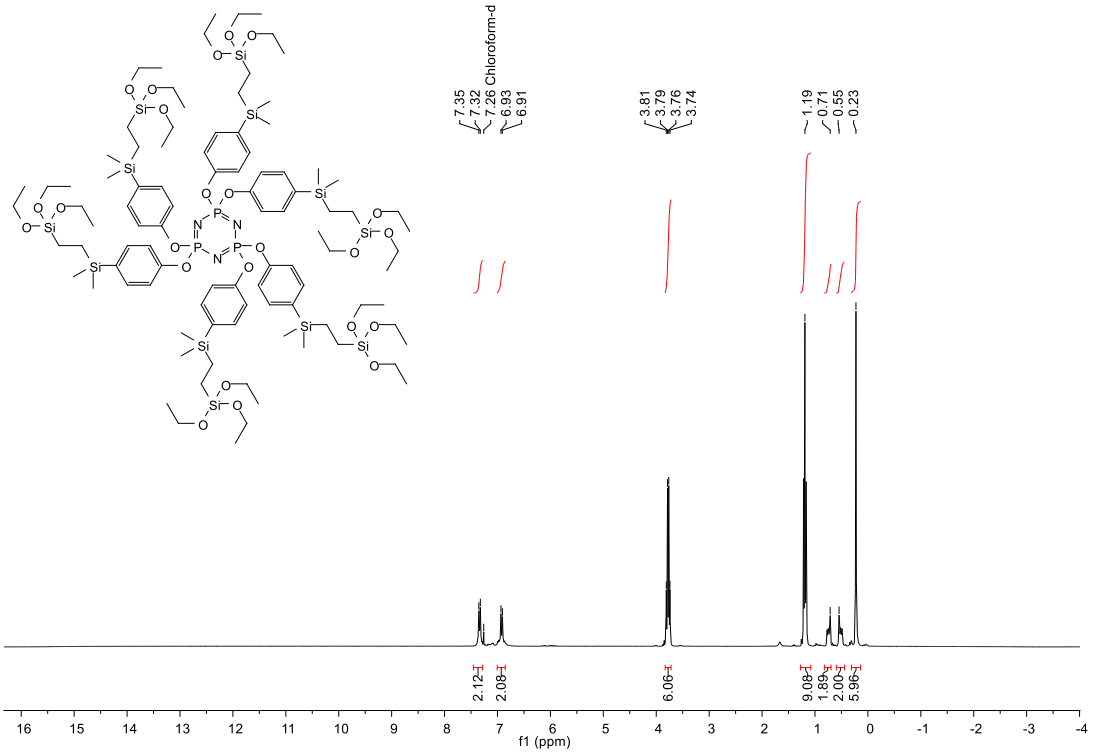

Fig. 45. ^{1}H NMR spectrum of Product (**2c**).

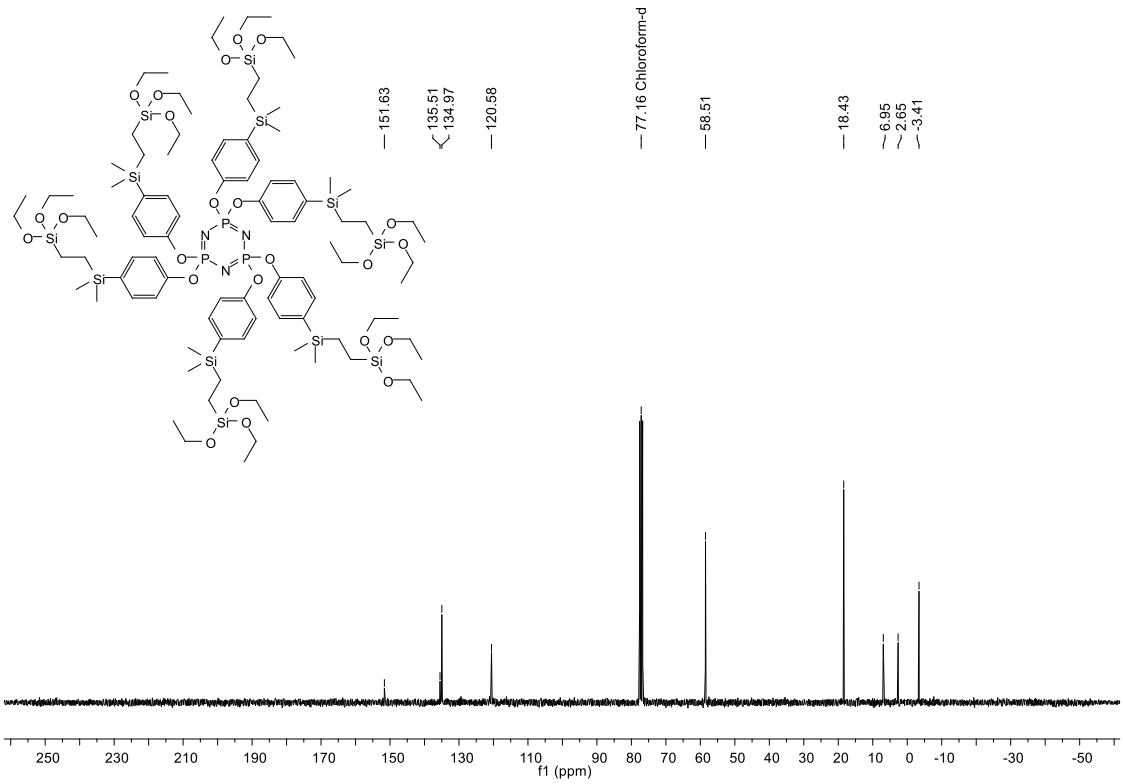

Fig. 46. ^{13}C NMR spectrum of Product (**2c**).

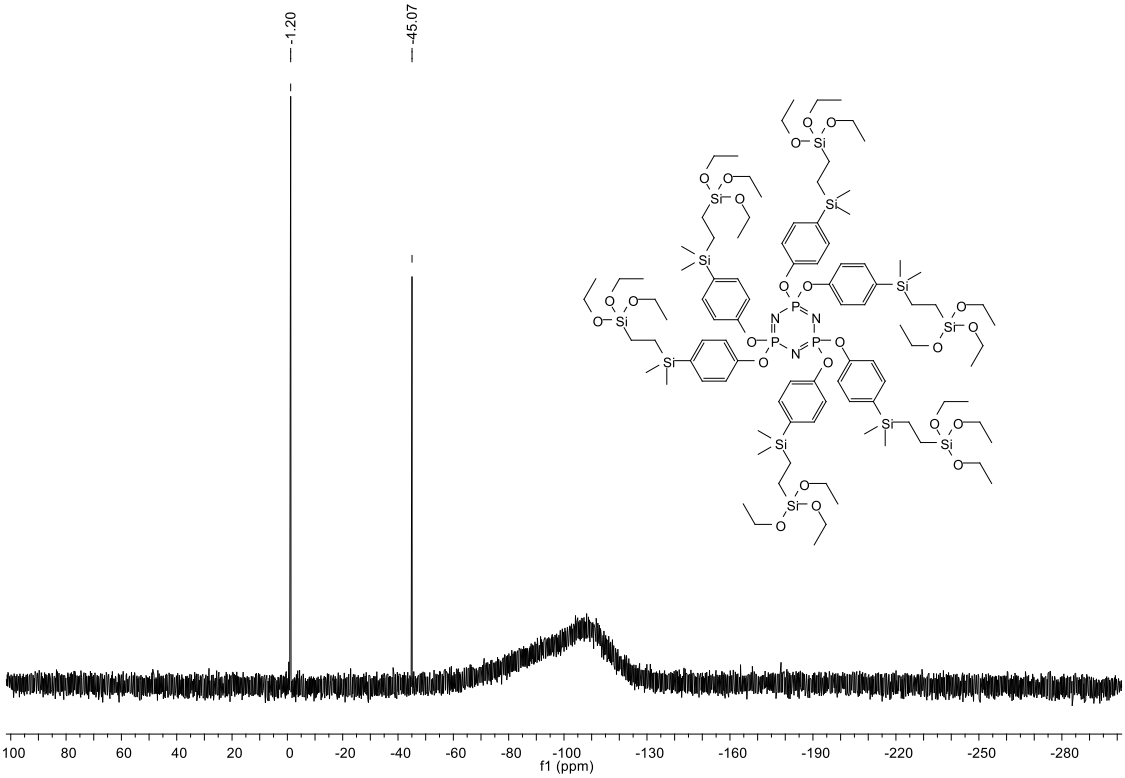

Fig. 47. ^{29}Si NMR spectrum of Product (**2c**).

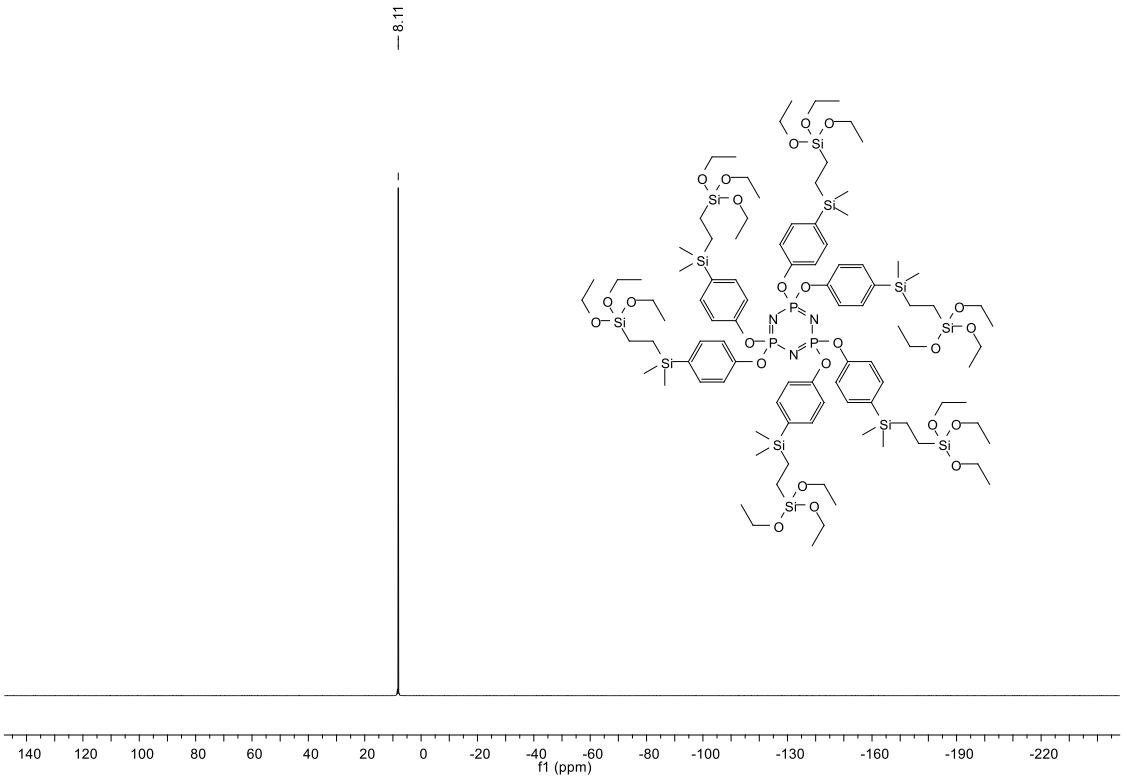

Fig. 48. ^{31}P NMR spectrum of Product (**2c**).

Spectra of Product (2d): Yield 93%. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.3 Hz, 12H), 6.92 (d, *J*=8.2 Hz, 12H), 6.03 CF_2H (tt, *J*=52.1, 5.5 Hz, 6H), 3.86 OCH_2 (t, *J* = 14.0 Hz, 12H), 3.49 OCH_2 (t, *J* = 6.7 Hz, 12H), 1.57 $\underline{CH_2}CH_2Si$ (m, 12H), 0.71 $CH_2\underline{CH_2}Si$ (m, 12H), 0.24 $SiCH_3$ (s, 36H). **^{13}C NMR** ($CDCl_3$; 75 MHz) δ = 151.62, 135.40, 134.89, 120.72, 75.80 OCH_2, 67.62 OCH_2, 24.02 $\underline{CH_2}CH_2Si$, 11.62 $CH_2\underline{CH_2}Si$, -2.96 $SiCH_3$. **^{31}P NMR** ($CDCl_3$; 162 MHz) δ = 8.25. **^{29}Si NMR (**$CDCl_3$; 79 MHz) δ = -2.55. **Elemental Analysis** Calc. for $C_{96}H_{114}F_{48}N_3O_{12}P_3Si_6$: C, 44.40; H, 4.60; F, 33.05; N, 1.52; O, 6.96; P, 3.37; Si, 6.11%; Found: C, 44.55; H, 4.58; N, 1.52%.

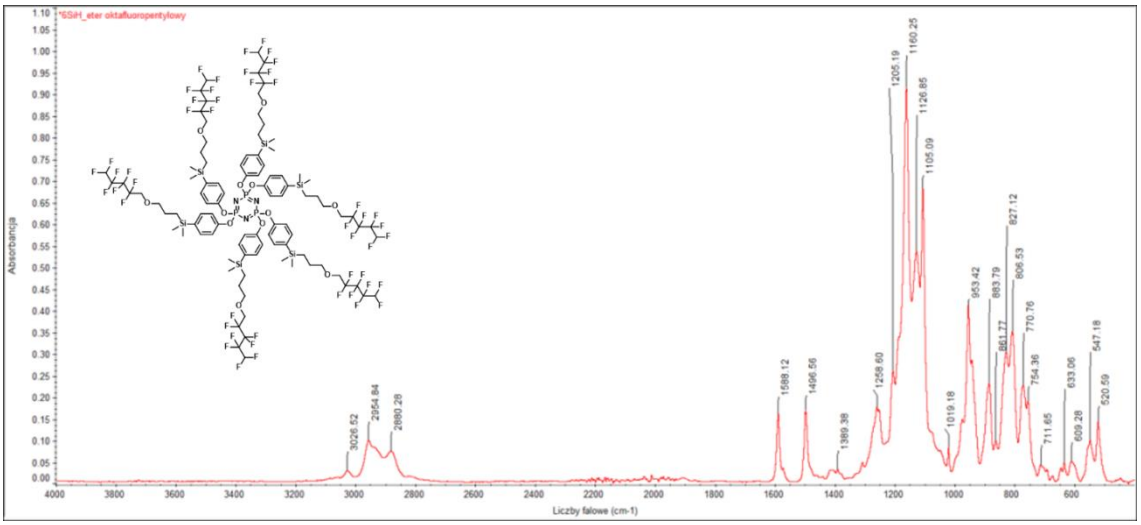

Fig. 49. FT-IR spectrum of Product (**2d**).

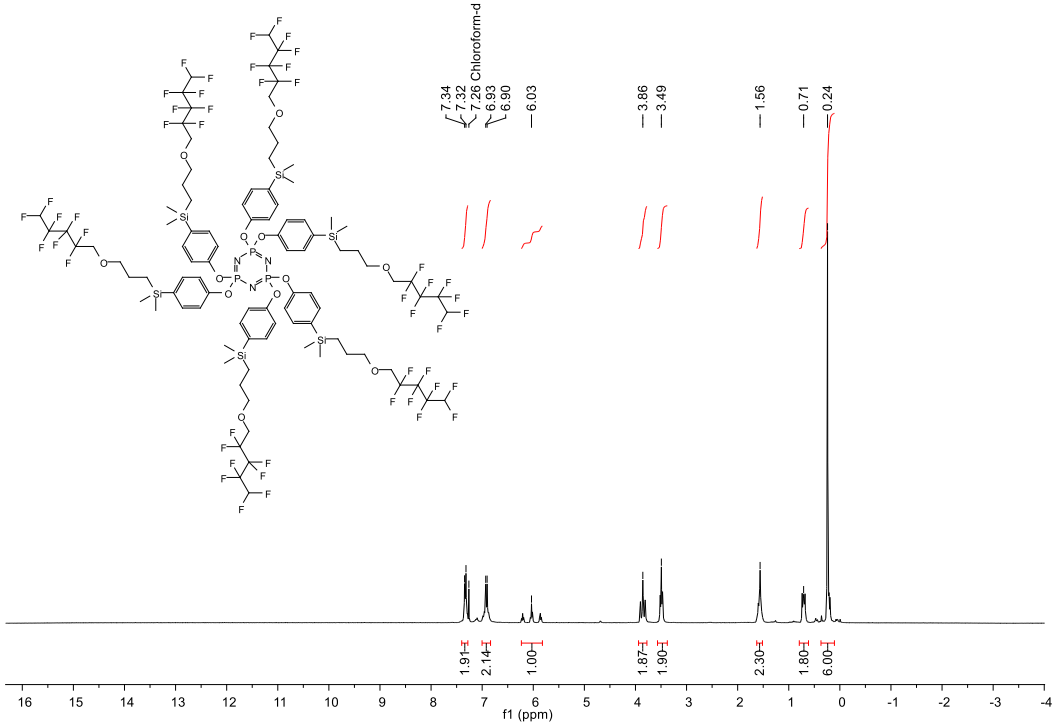

Fig. 50. ^{1}H NMR spectrum of Product (**2d**).

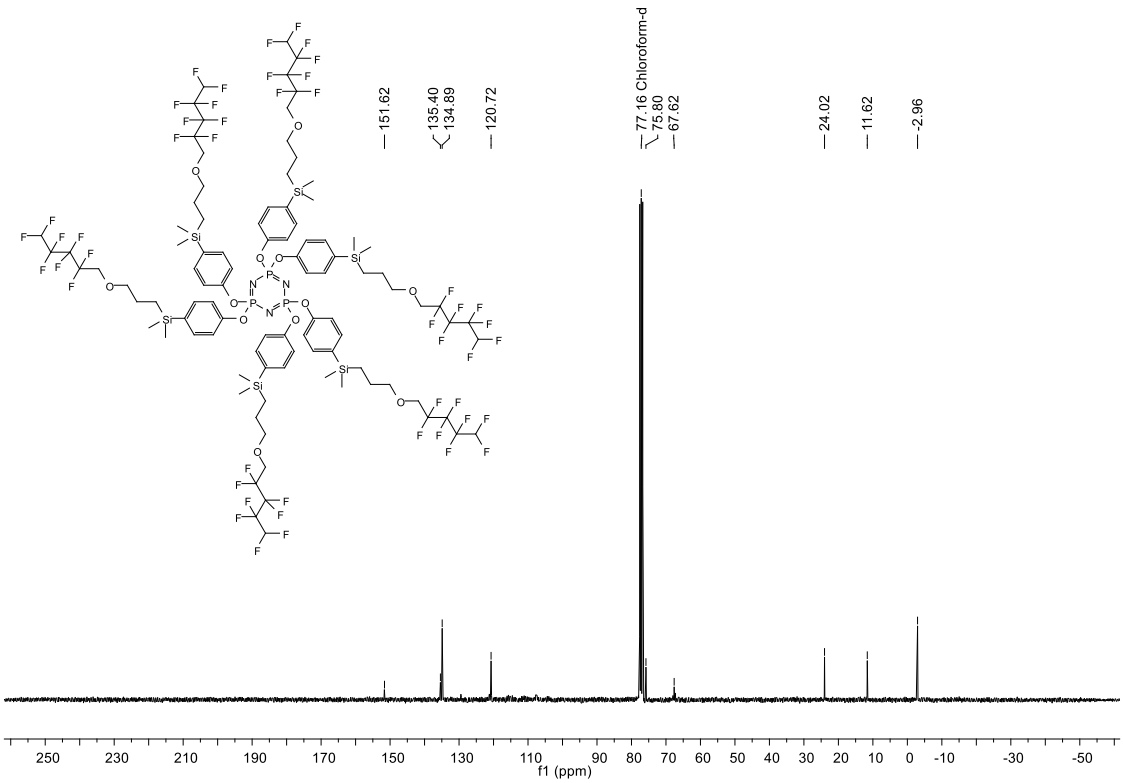

Fig. 51. ^{13}C NMR spectrum of Product (**2d**).

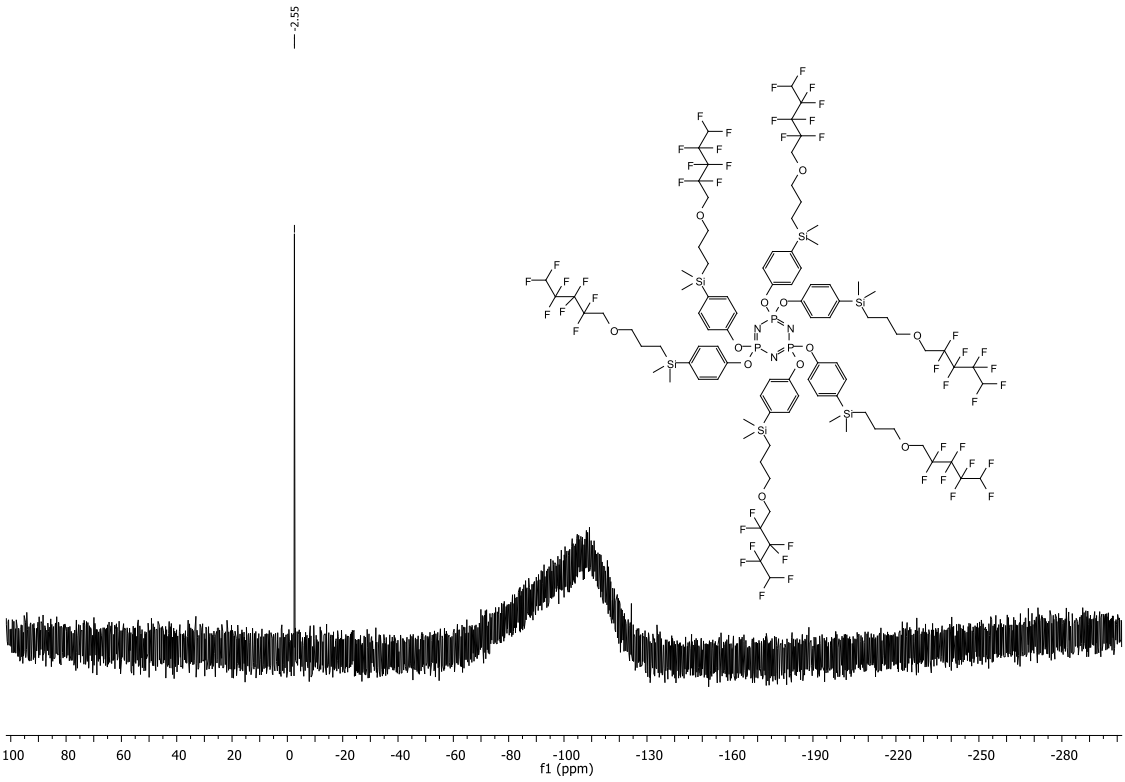

Fig. 52. ^{29}Si NMR spectrum of Product (**2d**).

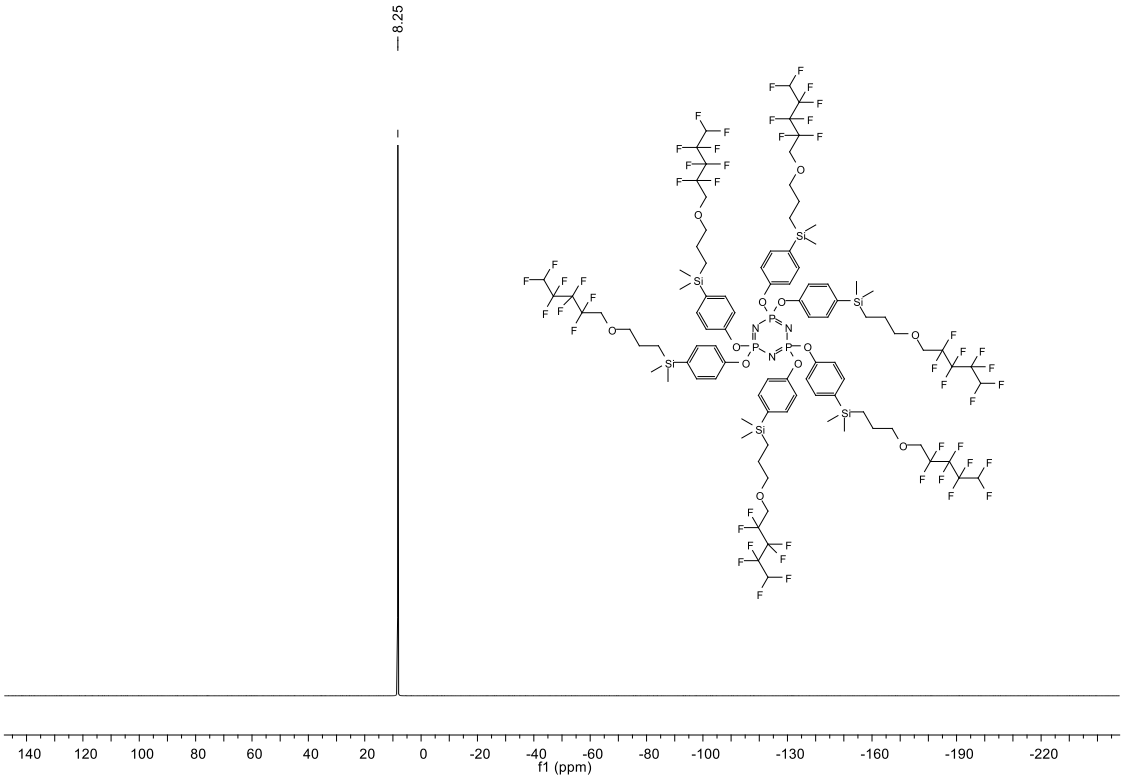

Fig. 53. ^{31}P NMR spectrum of Product (**2d**).

Spectra of Product (2e) Yield 97%. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.3 Hz, 12H), 6.91 (d, *J* = 8.1 Hz, 12H), 5.09 (m, 6H), 1.97 (m, 12H), 1.66 (s, 18H), 1.58 (s, 18H), 1.49 – 1.35 (m, 24H), 1.10 (s, 18H), 0.7 $SiCH_2$ (m, 12H), 0.24 $SiCH_3$ (s, 36H). **^{13}C NMR** ($CDCl_3$; 75 MHz) δ: 151.62, 135.57, 134.93, 131.78, 124.64, 120.74, 77.39, 40.86, 35.89, 26.36, 25.85, 22.77, 17.79, 9.43 $SiCH_2$, 2.89 $SiCH_3$. **^{31}P NMR** ($CDCl_3$; 162 MHz) δ = 8.27. **^{29}Si NMR** ($CDCl_3$; 79 MHz) δ = -2.00. **Elemental Analysis** Calc. for $C_{107}H_{172}N_3O_{12}P_3Si_6$: C, 66.72; H, 9.14; N, 2.05; O, 9.36; P, 4.53; Si, 8.21%; Found: C, 66.50; H, 9.13; N, 2.06%.

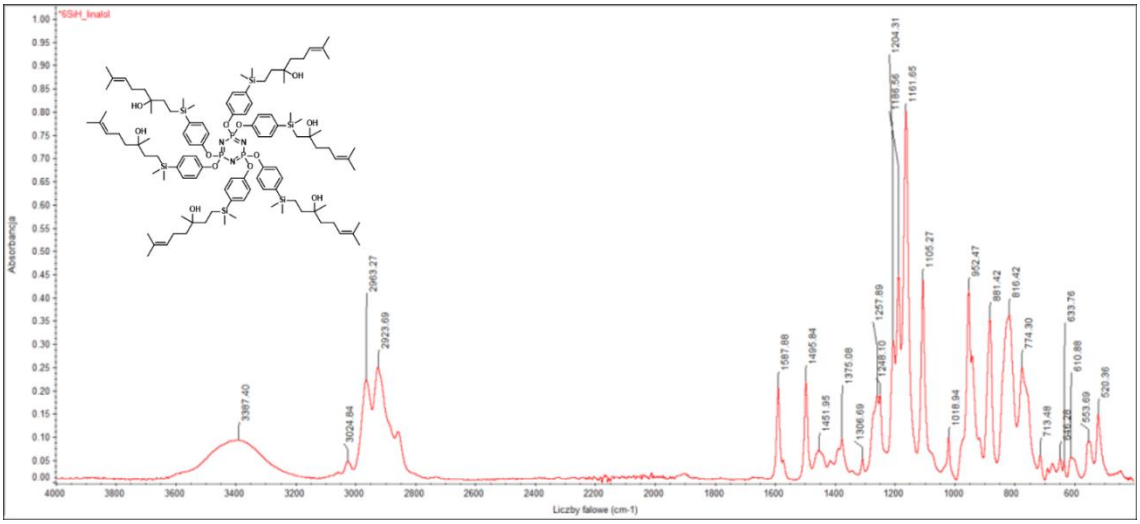

Fig. 54. FT-IR spectrum of Product (**2e**).

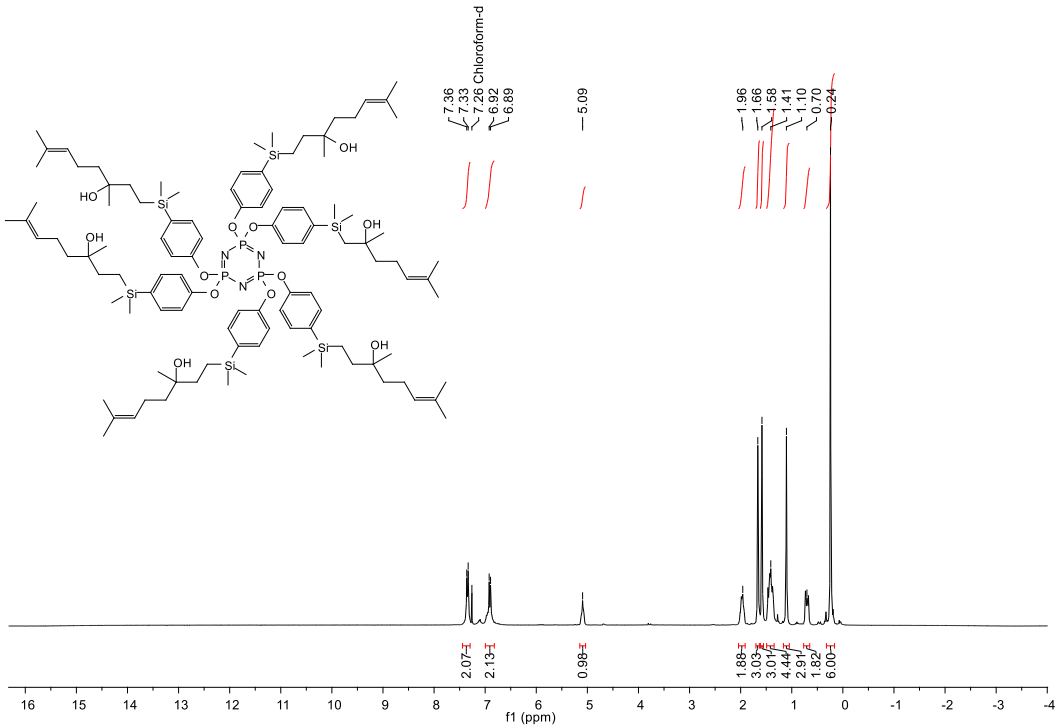

Fig. 55. ^{1}H NMR spectrum of Product (**2e**).

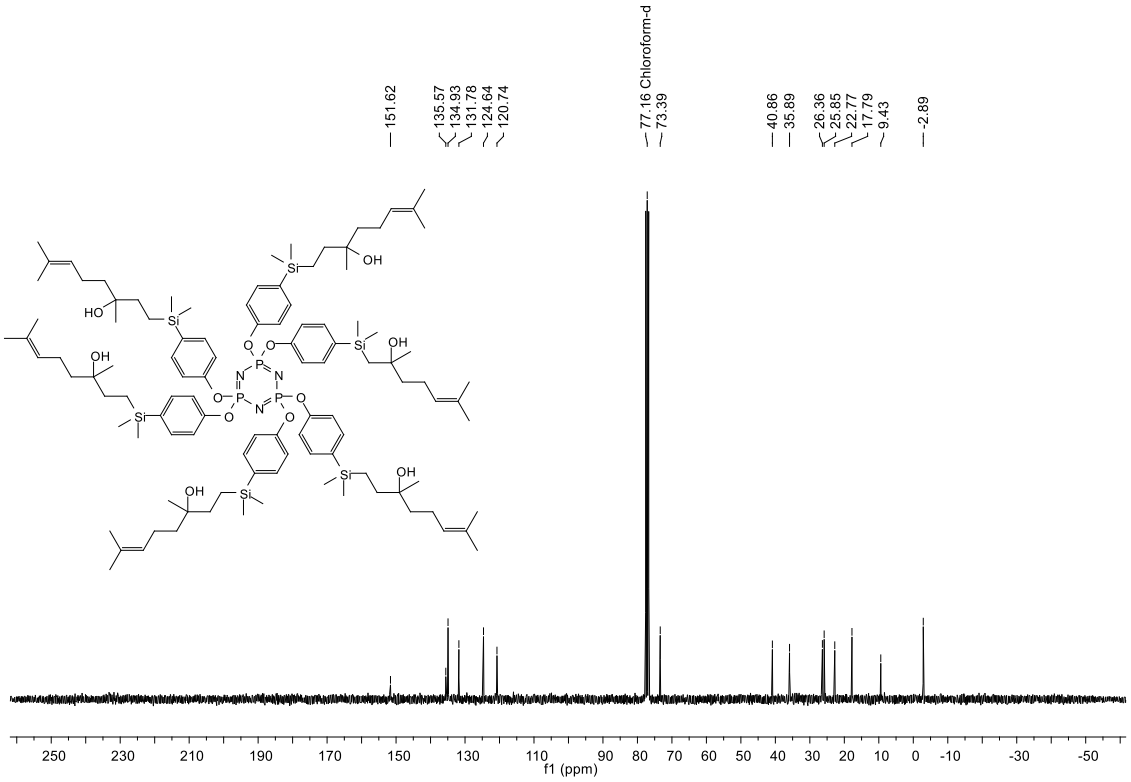

Fig. 56. ^{13}C NMR spectrum of Product (**2e**).

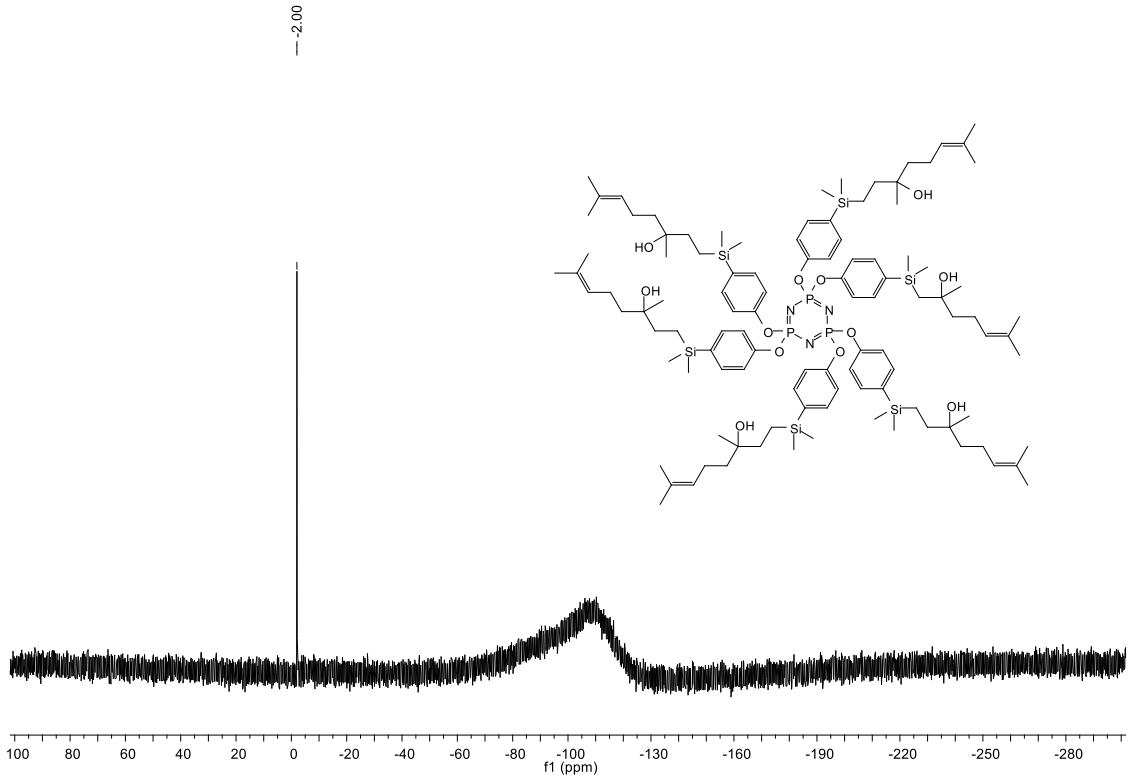

Fig. 57. ^{29}Si NMR spectrum of Product (**2e**).

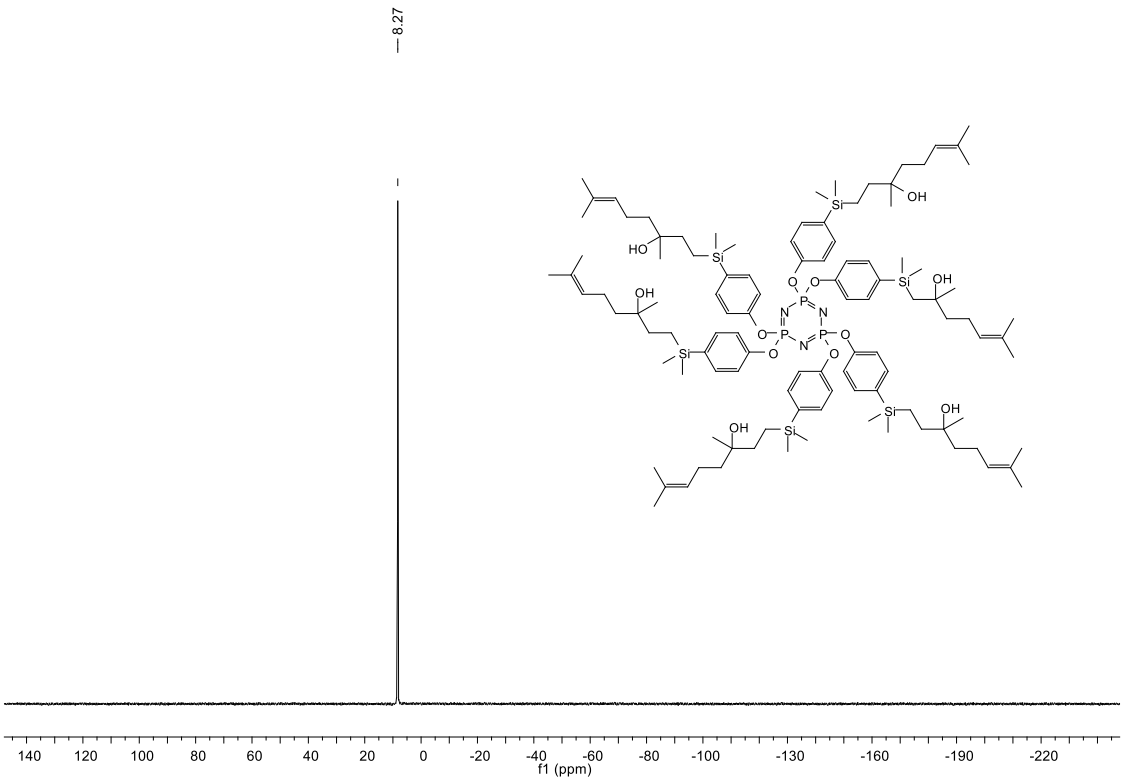

Fig. 58. ^{31}P NMR spectrum of Product (**2e**).

Spectra of Product (2f) Yield 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.1 Hz, 12H), 6.89 (d, *J* = 8.1 Hz, 12H), 2.26 – 2.05 N-CH_2, NMe_2 (48H), 1.44 $\underline{CH_2}CH_2Si$ (m, 12H), 0.76 – 0.61 $CH_2\underline{CH_2}Si$ (m, 12H), 0.23 $SiCH_3$ (s, 36H). **^{13}C NMR** ($CDCl_3$; 75 MHz) δ: 151.57 C-O, 135.70, 134.87, 120.67, 63.26 N-CH_2, 45.55 NMe_2, 22.12 $\underline{CH_2}CH_2Si$, 13.43 $CH_2\underline{CH_2}Si$, -2.80 $SiCH_3$. **^{31}P NMR** ($CDCl_3$; 162 MHz) δ = 8.26. **^{29}Si NMR** ($CDCl_3$; 79 MHz) δ = -2.78. **Elemental Analysis** Calc. for $C_{78}H_{132}N_9O_6P_3Si_6$: C, 60.31; H, 8.57; N, 8.12; O, 6.18; P, 5.98; Si, 10.85%; Found: C, 60.02; H, 8.59; N, 8.14%.

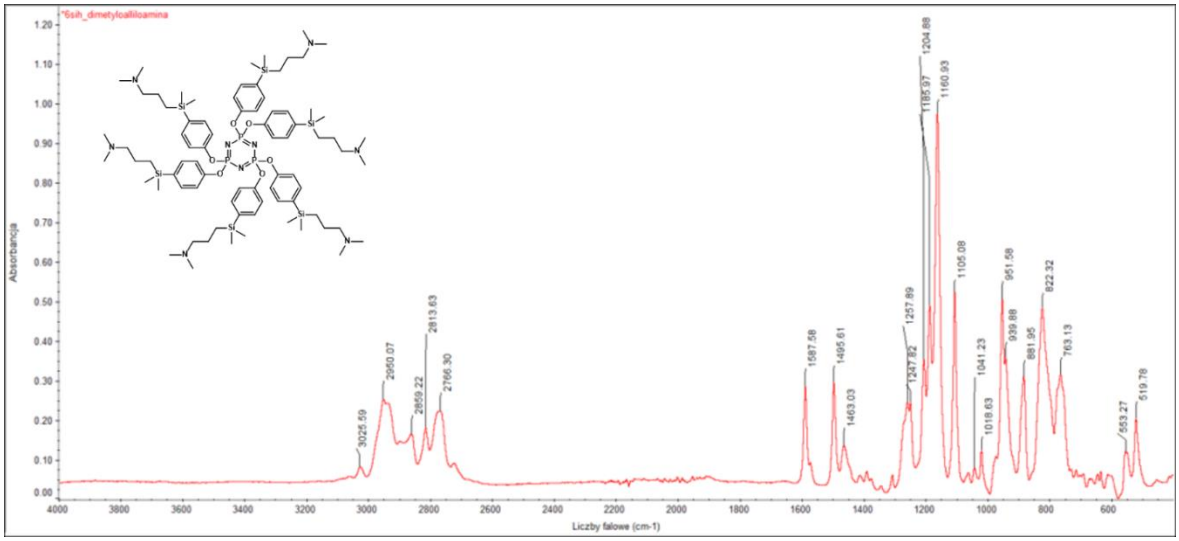

Fig. 59. FT-IR spectrum of Product (**2f**).

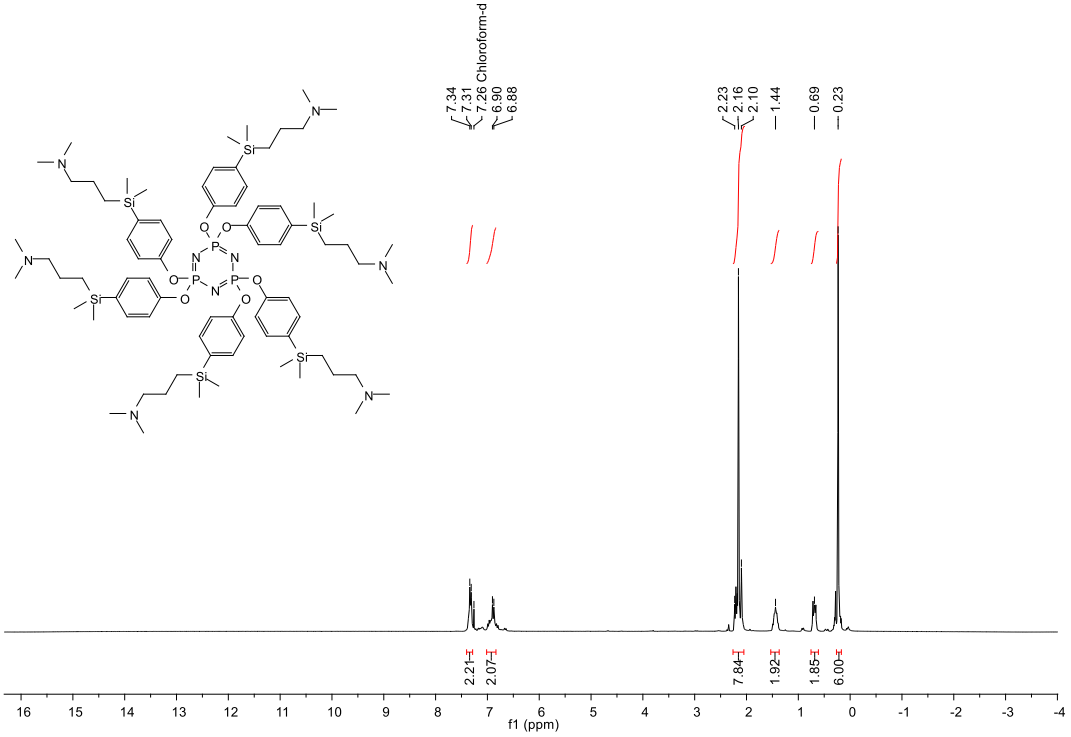

Fig. 60. ^{1}H NMR spectrum of Product (**2f**).

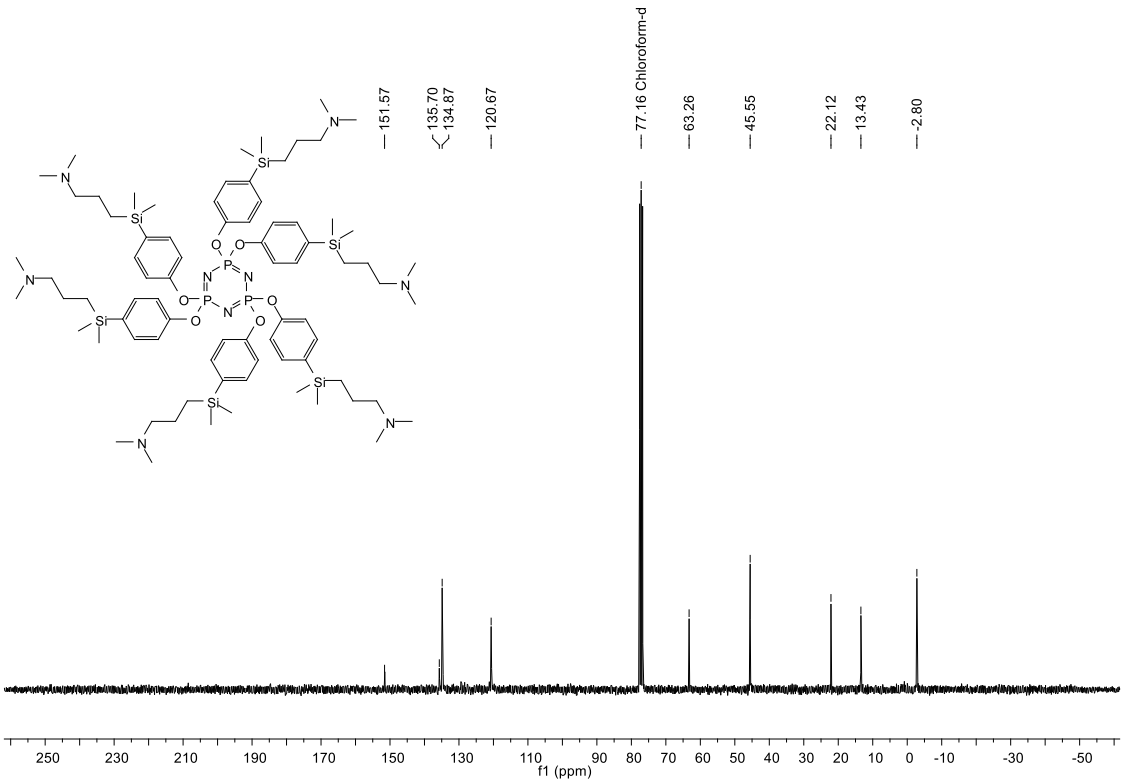

Fig. 61. ^{13}C NMR spectrum of Product (**2f**).

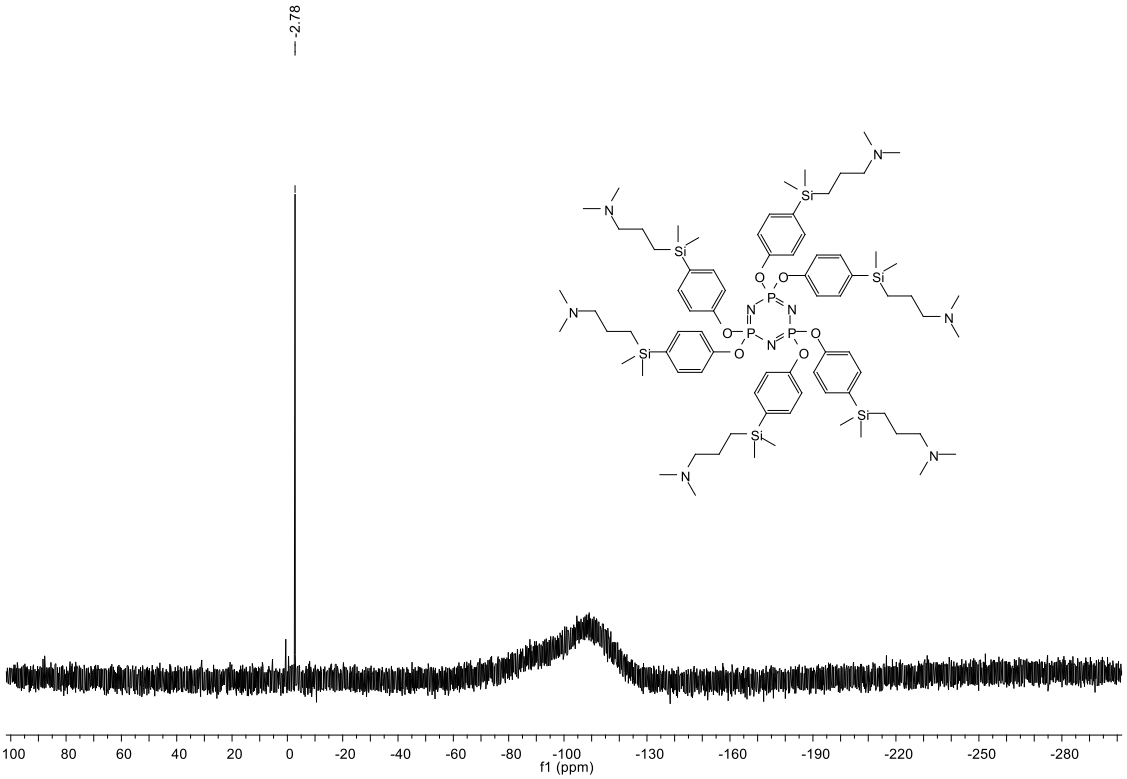

Fig. 62. ^{29}Si NMR spectrum of Product (**2f**).

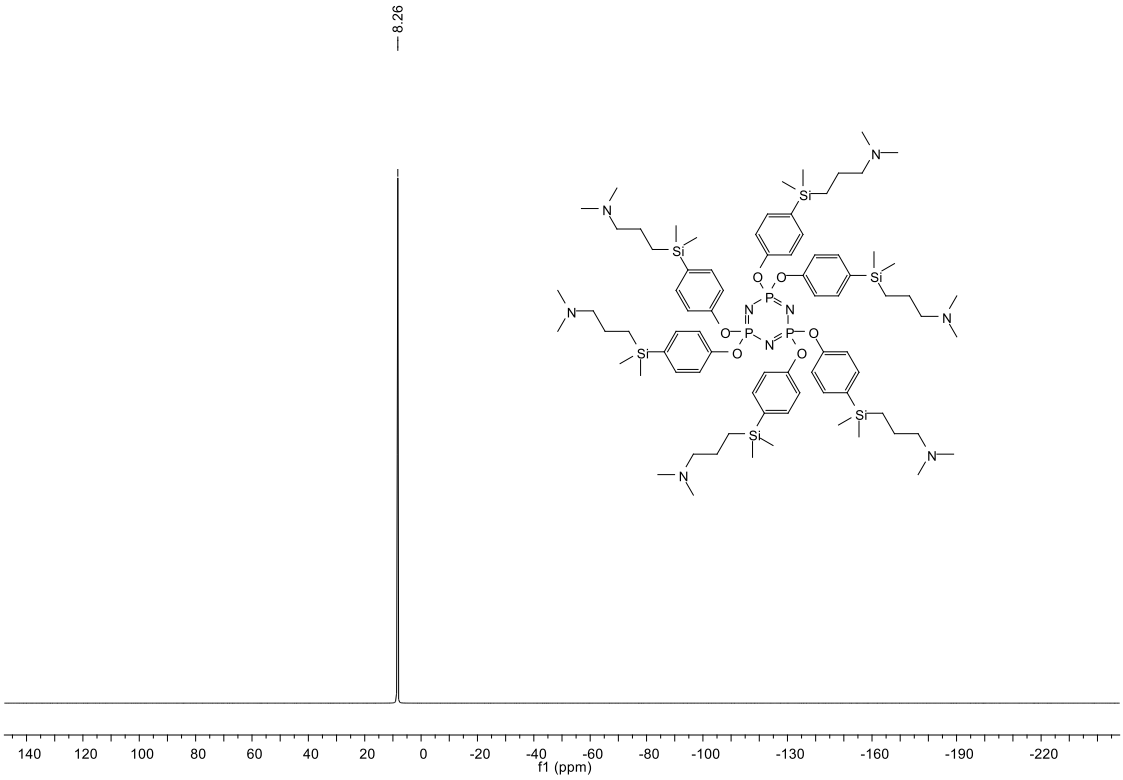

Fig. 63. ^{31}P NMR spectrum of Product (**2f**).

Spectra of Product (2g) Yield 92%. α/β-E: (25/75). **^{1}H NMR (**300 MHz, $CDCl_3$) δ = *Isomer β-E*: 7.34 (d, *J*=7.3 Hz, 12H), 6.88 (d, *J*=7.5 Hz, 12H), 6.10 (dt, *J*=18.4 Hz, 6H), 5.71 (d, *J*=18.6 Hz, 6H), 2.10 (m, 12H), 1.39-1.21 (m, 36H), 0.85 (m,18H), 0.29 (s, 36H), *Isomer α*: (d, *J*=7.3 Hz, 12H), 6.88 (d, *J*=7.5 Hz, 12H), 5.66 (*d*, J=2.70 Hz, 6H), 5.36 (*d*, J=2.66 Hz, 6H), 2.10 (m, 12H), 1.39-1.21 (m, 36H), 0.85 (m,18H), 0.33 (s, 36H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = *Isomer β-E*: 151.61, 149.81 (Si-CH=), 135.31, 135.21, 127.09 (Si-CH=CH-), 120.66, 36.94, 31.61, 28.44, 22.66, 14.19, 2.09 (Si-CH_3), *Isomer α*: 151.61, 150.45 (Si-CH=), 135.73, 135.21, 125.96 (Si-CH=CH), 120.66, 35.99, 31.76, 28.66, 22.66, 14.19, 2.57. **Elemental Analysis** Calc. for $C_{90}H_{138}N_3O_6P_3Si_6$: C, 66.75; H, 8.59; N, 2.59; O, 5.93; P, 5.74; Si, 10.41%; Found: C, 66.74; H, 8.59; N, 2.60%.

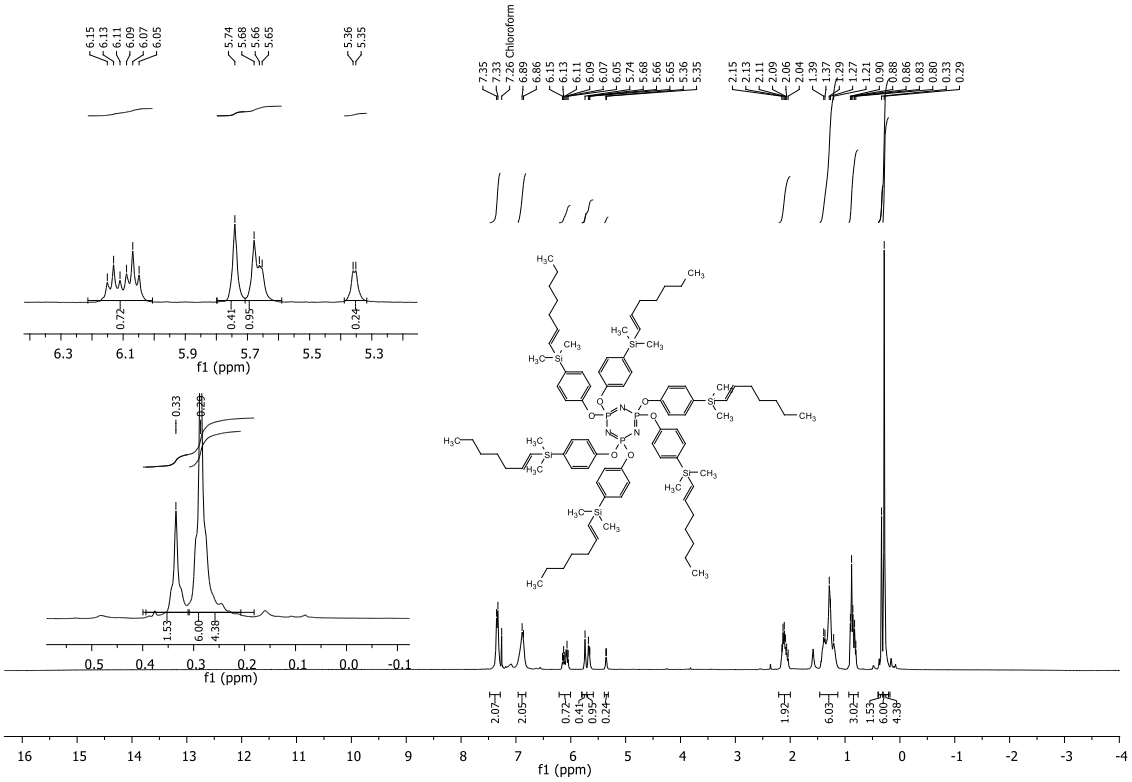

Fig. 64. ^{1}H NMR spectrum of Product (**2g**) - α and β-E isomers.

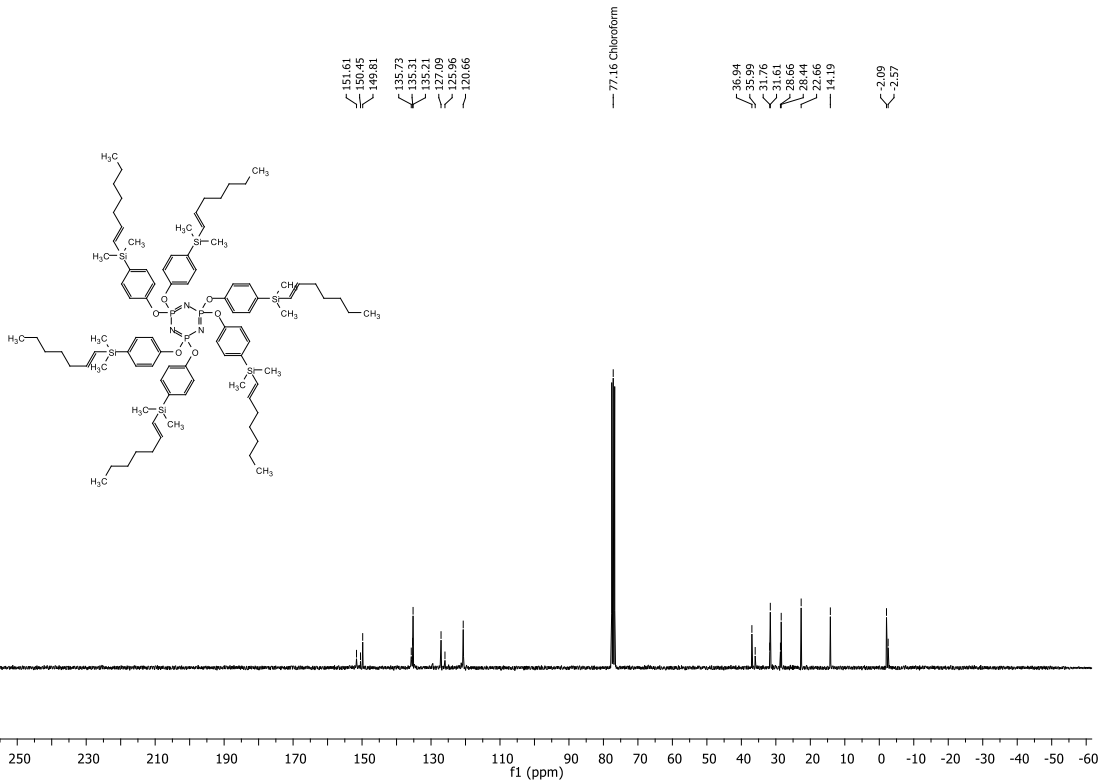

Fig. 65. ^{13}C NMR spectrum of Product (**2g**) - α and β-E isomers.

Spectra of Product 2h α/β-E: Yield 92%. (4/96) ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34 (d, *J*=8.2 Hz, 12H), 6.90 (d, *J*=8.2 Hz, 12H), 6.66 (d, *J*=22.68 Hz, 12H), 0.31 (s, 36H), 0.05 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 153.43 (Si-CH=), 151.62 C-O, 147.89 (=CH-Si), 135.29, 135.19, 120.69, 1.46, -2.54. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 8.35. **^{29}Si NMR** (79 MHz, $CDCl_3$) δ = -7.41, -12.08. **Elemental Analysis** Calc. for $C_{78}H_{126}N_3O_6P_3Si_{12}$: C, 57.41; H, 7.78; N, 2.58; O, 5.88; P, 5.69; Si, 20.65%; Found: C, 57.37; H, 7.77; N, 2.57%.

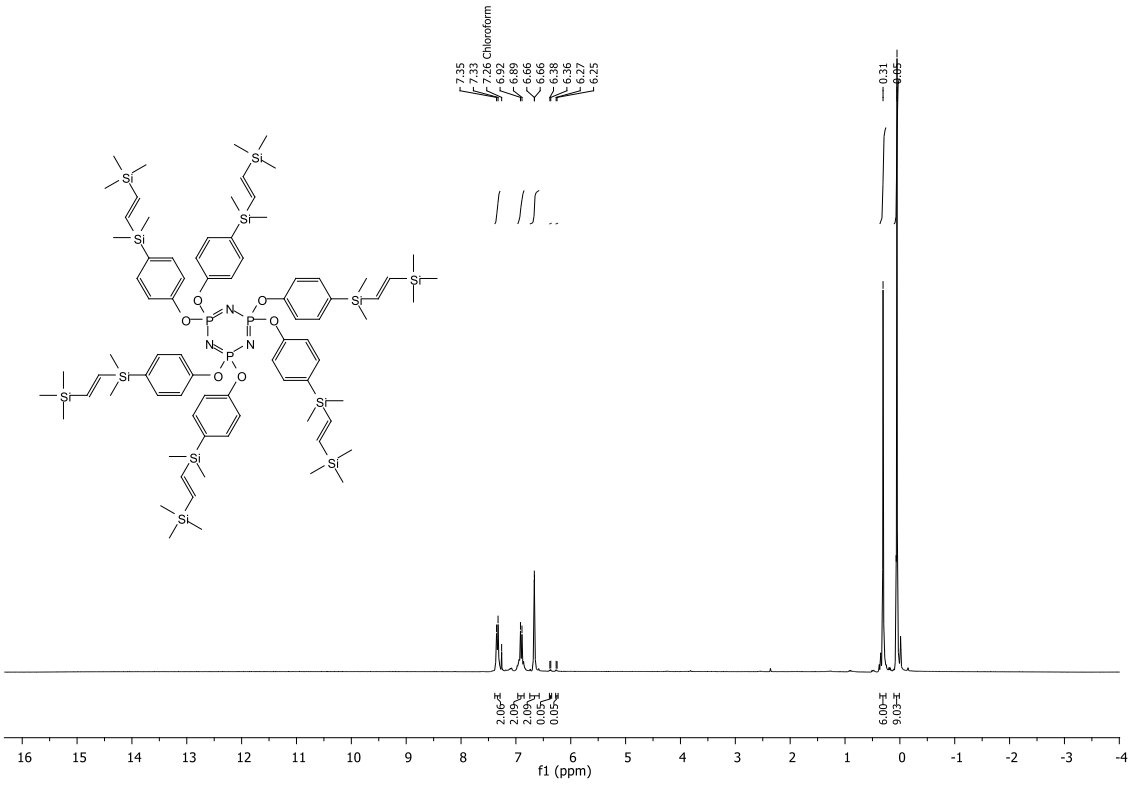

Fig. 66. ^{1}H NMR spectrum of Product (**2h**) - α and β-E isomers.

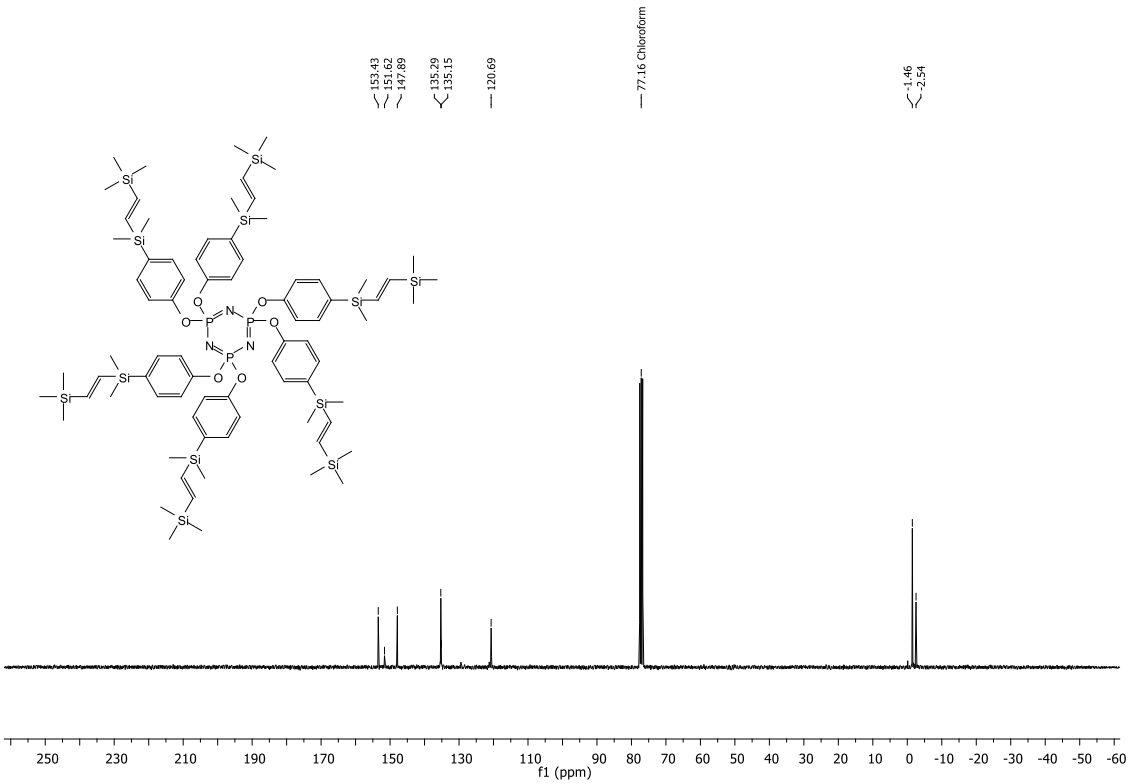

Fig. 67. ^{13}C NMR spectrum of Product (**2h**) - α and β-E isomers.

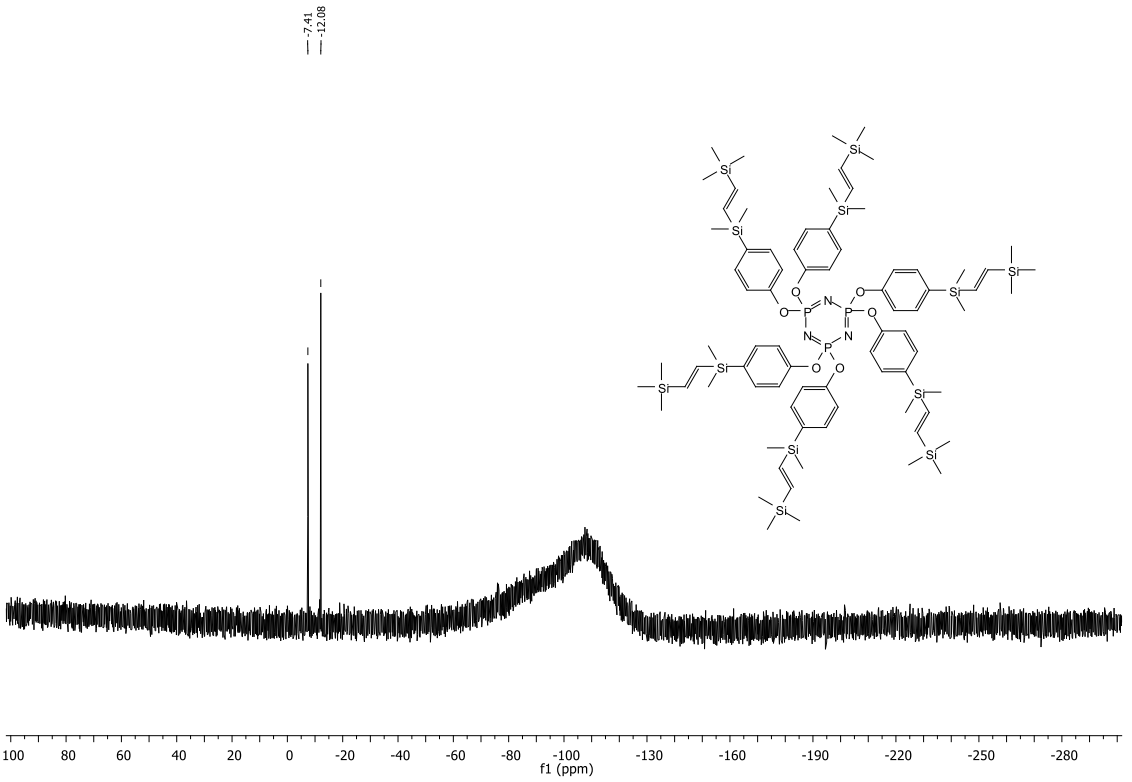

Fig. 68. ^{29}Si NMR spectrum of Product (**2h**) - α and β-E isomers.

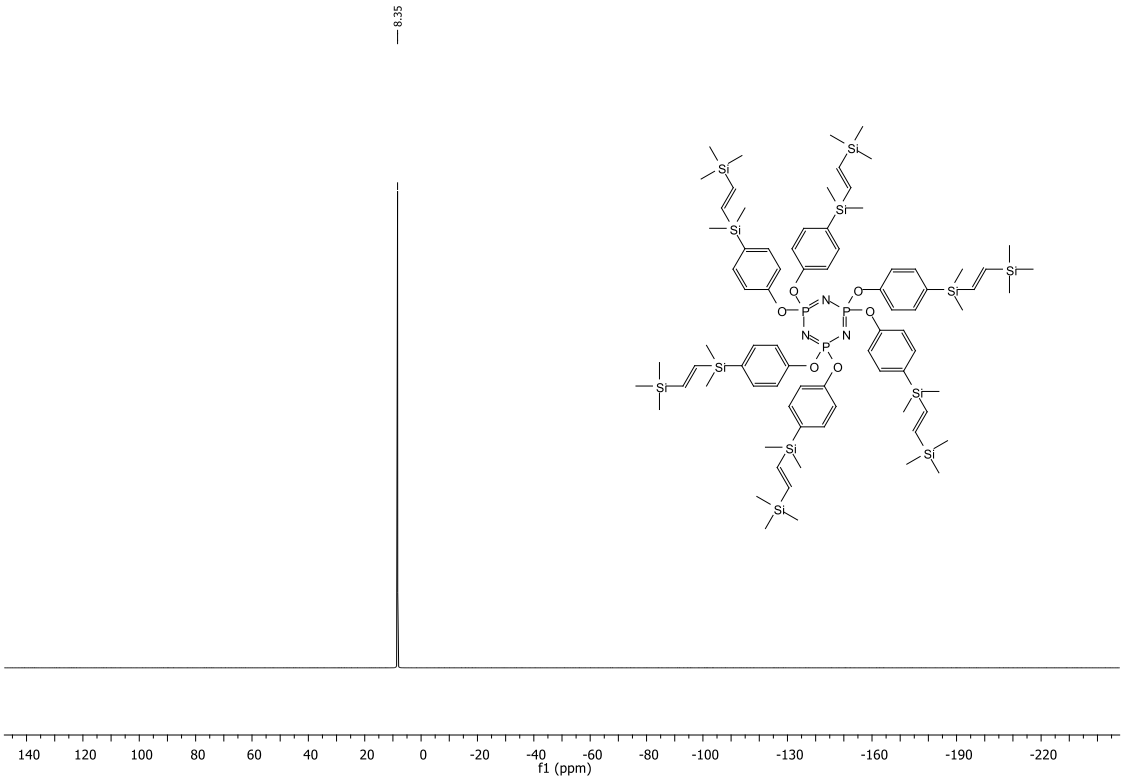

Fig. 69. ^{31}P NMR spectrum of Product (**2h**) - α and β-E isomers.

Spectra of Product (2i) α/β-E: Yield 96% (4/96). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.35 (d, *J*=10.7 Hz, 12H), 6.92 (d, *J*=10.8 Hz, 12H), 6.66 Si-CH= (d, *J*=30.50 Hz, 12H), 1.03 Si[$CH(CH_3)_2$]$_3$ (126H), 0.30 $SiCH_3$ (s, 36H). **^{13}C** NMR (75 MHz, $CDCl_3$) δ = 151.64 C-O, 150.91 Si-CH=CH-Si, 147.96 Si-CH=CH-Si, 135.44, 135.22, 120.64, 18.77 SiCH($\underline{CH_3}$)$_2$, 10.81 Si$\underline{CH}$(CH_3)$_2$, -2.47 $SiCH_3$. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 8.22. **^{29}Si NMR** (79 MHz, $CDCl_3$) δ = -1.63, -12.21. **Elemental Analysis** Calc. for $C_{114}H_{198}N_3O_6P_3Si_{12}$: C, 64.08; H, 9.34; N, 1.97; O, 4.49; P, 4.35; Si, 15.77%; Found: C, 64.14; H, 9.33; N, 1.98%.

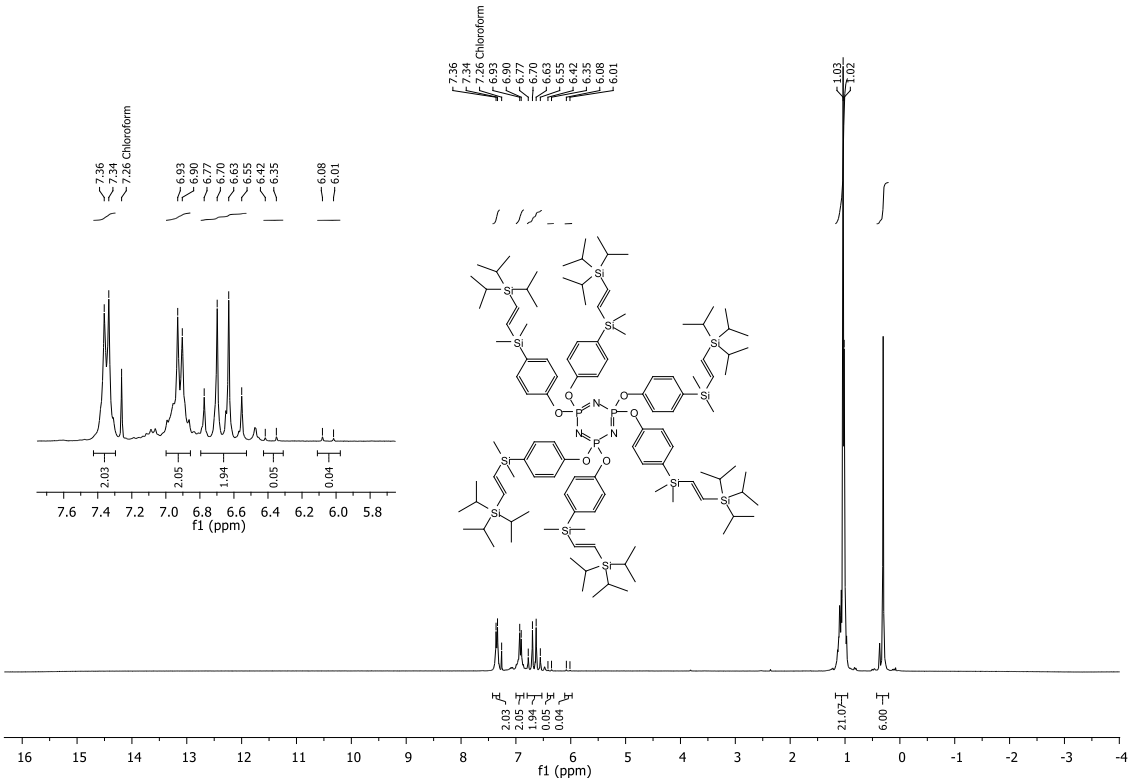

Fig. 70. ^{1}H NMR spectrum of Product (**2i**) - α and β-E isomers.

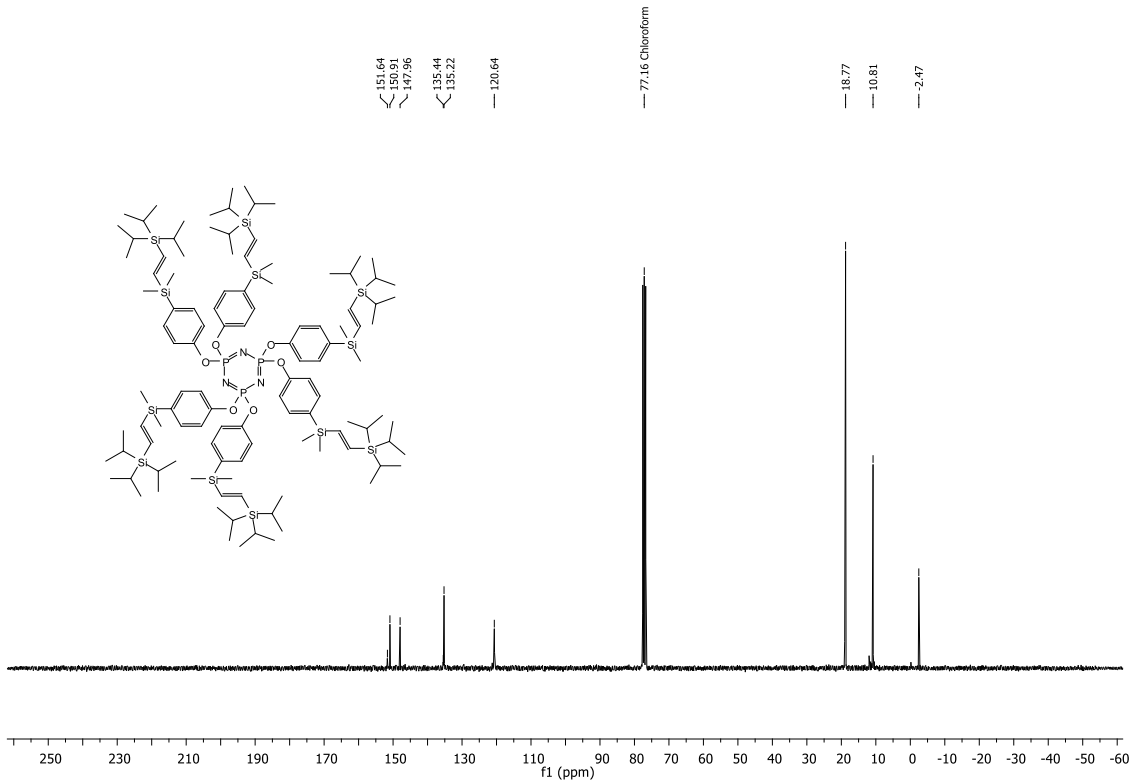

Fig. 71. ^{13}C NMR spectrum of Product (**2i**) - α and β-E isomers.

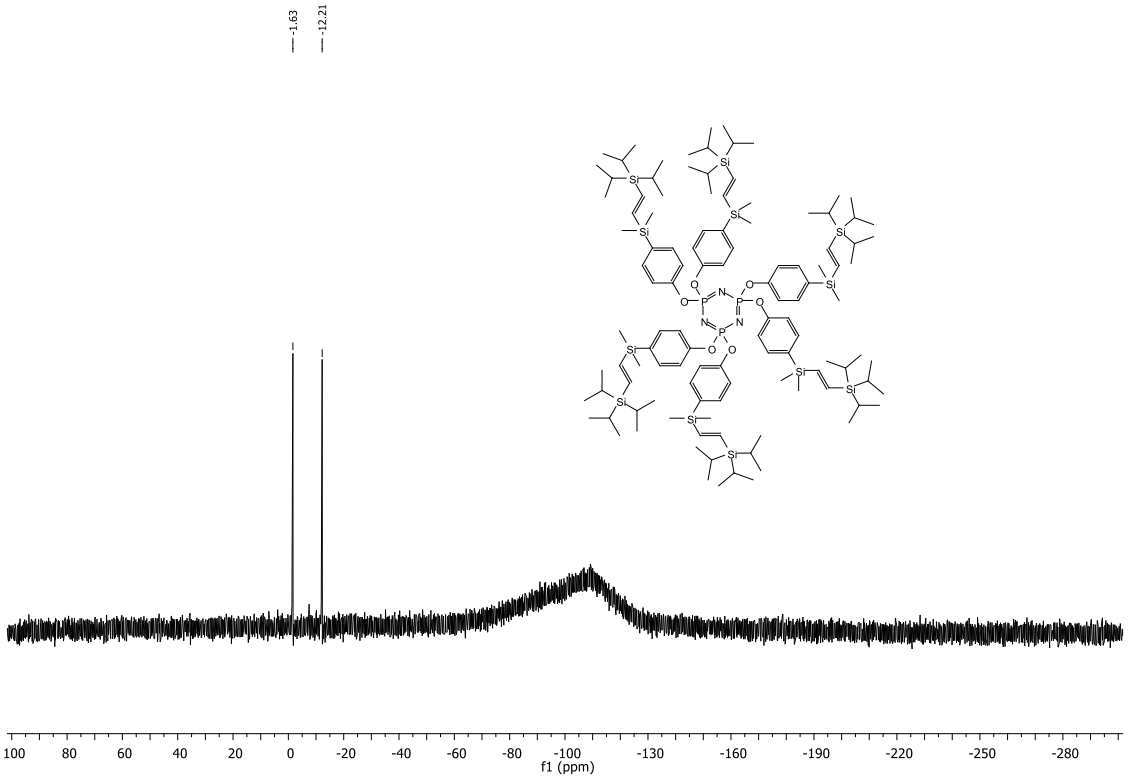

Fig. 72. ^{29}Si NMR spectrum of Product (**2i**) - α and β-E isomers.

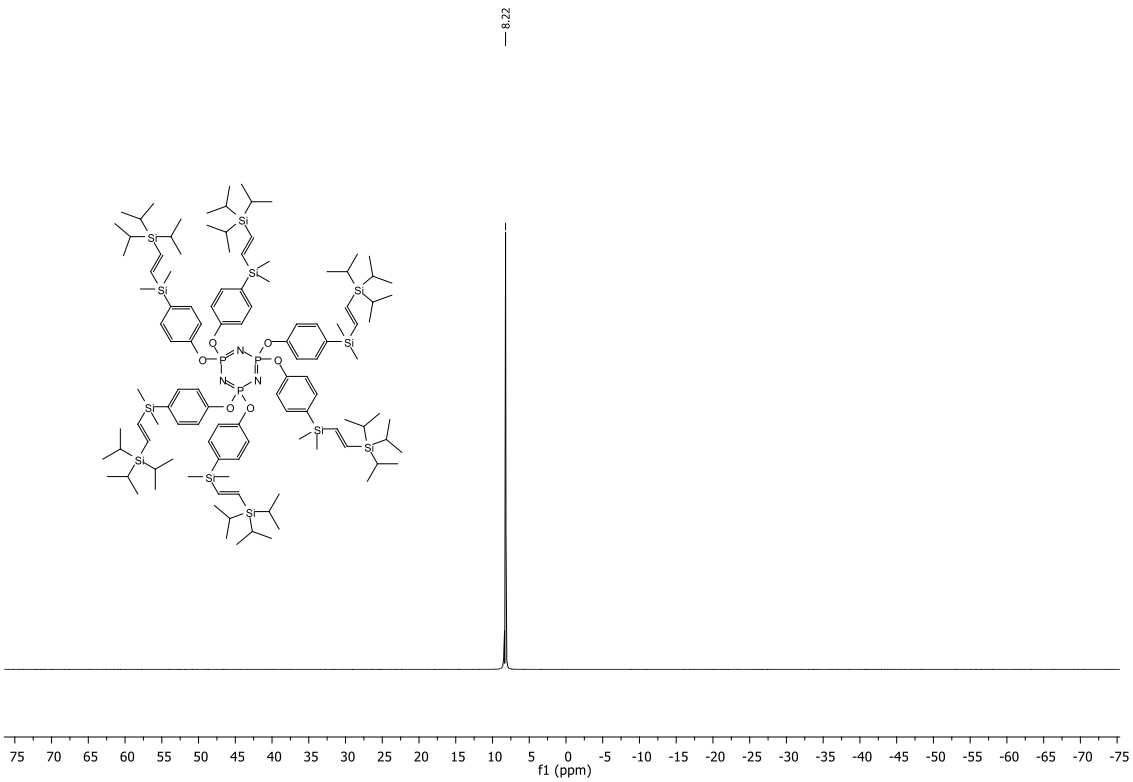

Fig. 73. ^{31}P NMR spectrum of Product (**2i**) - α and β-E isomers.

Spectra of Product (2j) Product 2j α/β-E: Yield 94% (10/90). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.49 (m, 12H), 7.34 (m, 30H), 6.93 (d, *J*= 8.07 Hz, 12H), 6.79 Si-CH= (d, *J*=22.60 Hz, 12H), 0.33, 0.31 $SiCH_3$ (s, 72H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 151.62 C-O, 150.78 Si-CH=CH-Si, 150.15 Si-CH=CH-Si, 138.52, 135.28, 134.94, 133.99, 129.11, 127.92, 120.69, -2.57 $SiCH_3$, -2.77 $SiCH_3$. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 8.31. **^{29}Si NMR** (79 MHz, $CDCl_3$) δ = -11.74, -11.82. **Elemental Analysis** Calc. for $C_{108}H_{138}N_3O_6P_3Si_{12}$: C, 64.72; H, 6.94; N, 2.10; O, 4.79; P, 4.64; Si, 16.82%; Found: C, 64.56; H, 6.92; N, 2.09%.

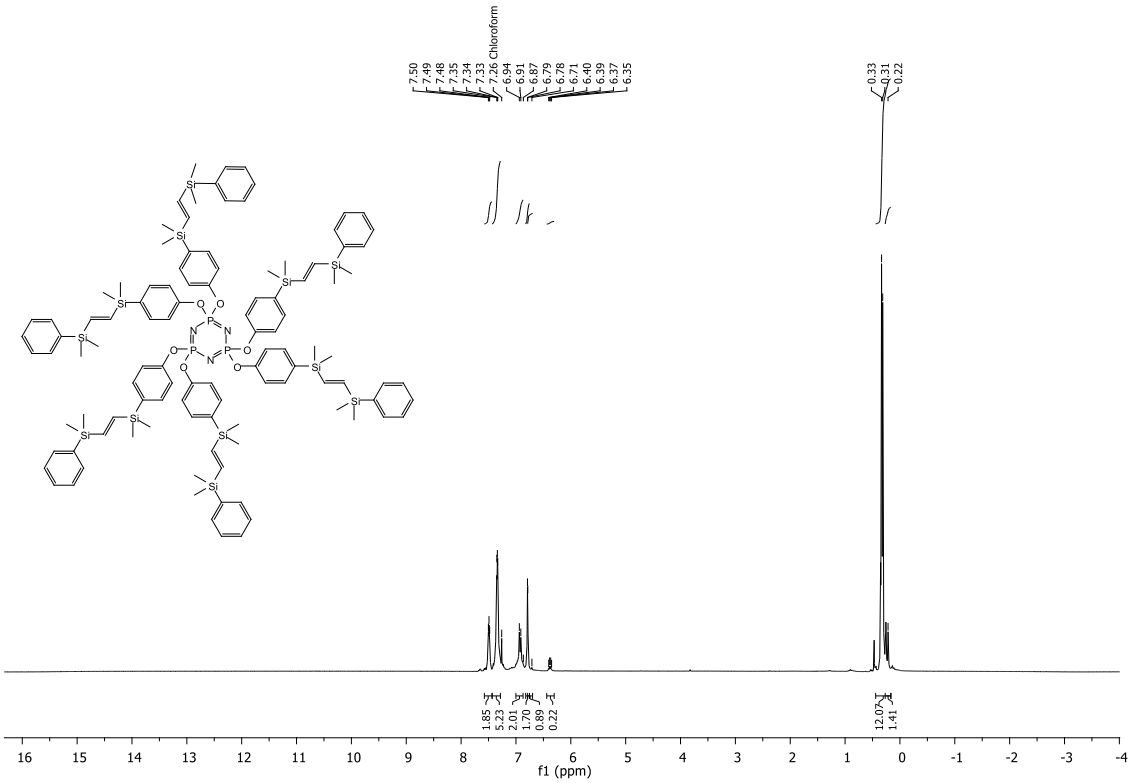

Fig. 74. ^{1}H NMR spectrum of Product (**2j**) - α and β-E isomers.

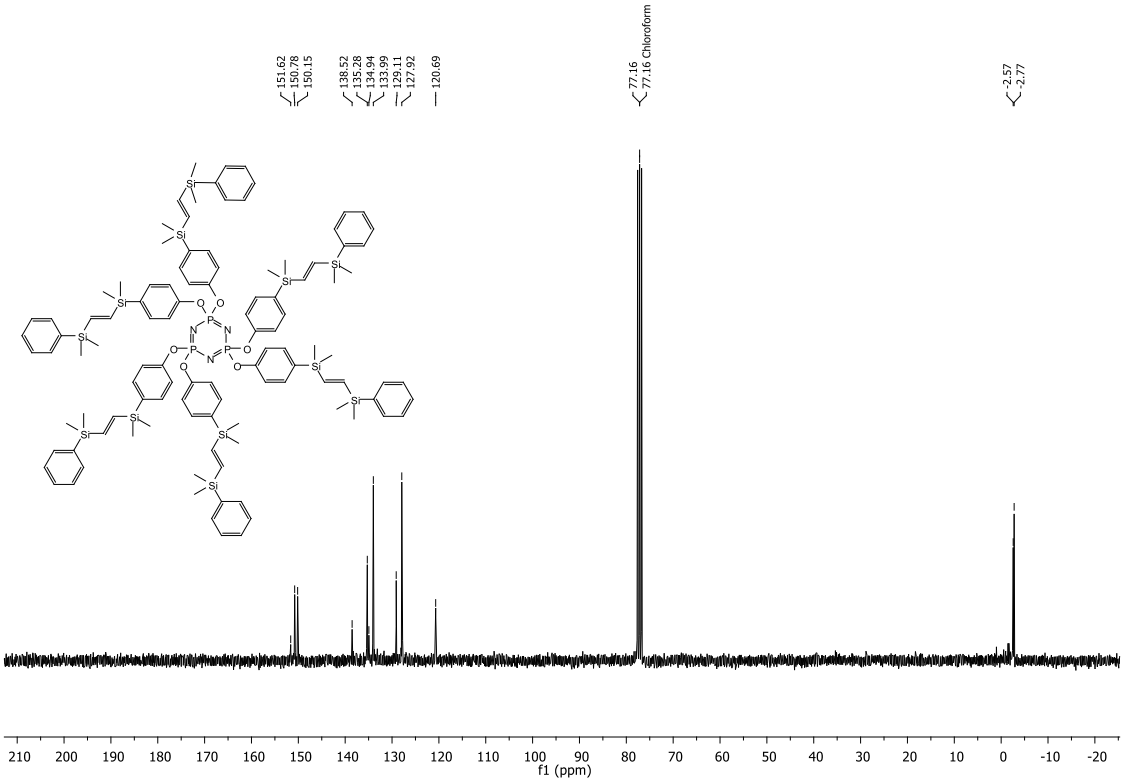

Fig. 75. ^{13}C NMR spectrum of Product (**2j**) - α and β-E isomers.

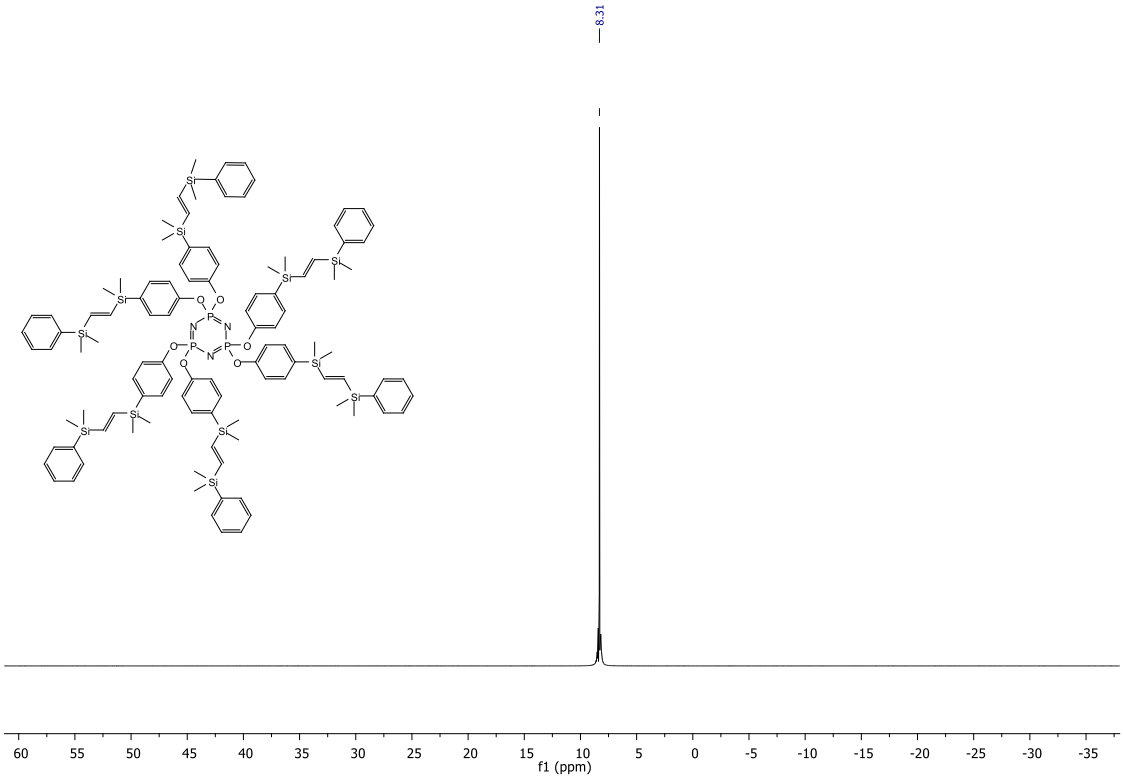

Fig. 77. ^{31}P NMR spectrum of Product (**2j**) - α and β-E isomers.

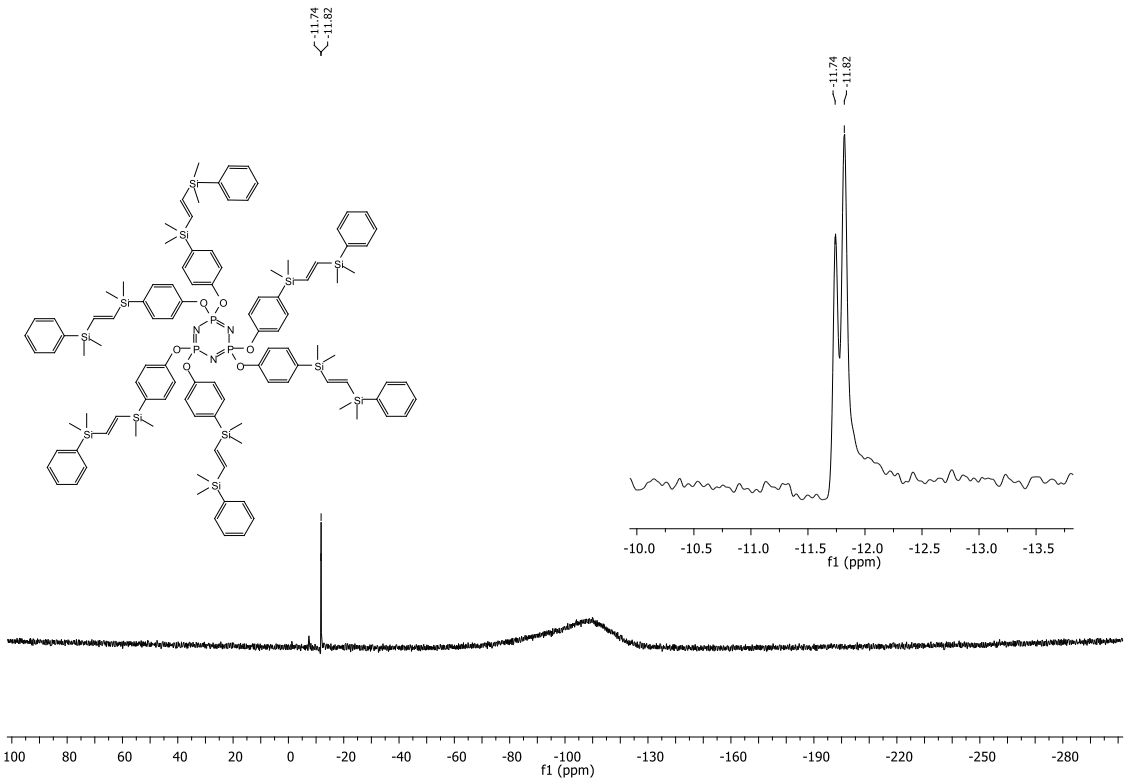

Fig. 76. ^{29}Si NMR spectrum of Product (**2j**) - α and β-E isomers.