Supporting Information for

# Phosphorus-containing polycarbosilazanes: Synthesis via dehydrocoupling catalysis and flame-retardant properties†

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† Dedicated to Professor Cristian Silvestru, in celebration of his 70th birthday.

‡ These two co-authors have contributed equally to the work and must be considered as first co-authors.

**Contents**

**General procedures.**

All manipulations were performed under an inert atmosphere by using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; $O_2$ < 1 ppm, $H_2O$ < 3 ppm). THF was distilled under argon from Na/benzophenone prior to use. Hexanes (petroleum ether), toluene, dichloromethane, and $Et_2O$ were collected from MBraun SPS-800 purification alumina columns and thoroughly degassed with argon before being stored on 4 Å molecular sieves. Deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and degassed by a minimum of three freeze–thaw cycles. Standard NMR spectra were recorded with Bruker AM-400 or AM-500 spectrometers. All chemical shifts (δ) [ppm] were determined relative to the residual signal of the deuterated solvent or to an external standard in [$D_6$]benzene or [$D_8$]toluene: $Si(SiMe_3)_4$ for $^{29}Si\{^1H\}$ NMR. Assignment of the signals was assisted by 1D ($^1H$, $^{13}C$) and 2D (COSY, HMBC, and HMQC) NMR experiments. (*p*-xylylene-*N*-methyldiamine 1,4-$(HN(CH_3)CH_2)_2C_6H_4$,[1] diphenyl(*p*-tolyl)phosphine,[2] phenylbis(*p*-tolyl)phosphine,[2] benzyldiphenylphosphine,[3] 4-$Ph_2P$-$C_6H_4CH_2NH_2$[4] (**B**) and $[Ba\{N(SiMe_3)_2\}_2]_2$ (**1**)[5] were prepared by modification of literature procedures. Phenylsilane [$PhSiH_3$] was purified by distillation, stored in an ampoule under Ar and checked for purity by $^1H$ NMR twice per month. All other chemicals were provided by commercial suppliers and used as received.

The polymers prepared herein where too sensitive and not soluble enough for characterisation by size exclusion chromatography. The determination of molecular weight was instead achieved by DOSY NPR analysis (see below).

**Standard dehydrocoupling and dehydropolymerisation procedures**

In a glovebox, the catalyst ($[Ba(N\{SiMe_3\}_2)]_2$, 5 or 10 mol% in Ba contents vs. the limiting substrate) was weighed directly into a Schlenk flask equipped with a stir bar. In a separate flask (also equipped with a stir bar), the amine (*p*-xylylene-*N*-methyldiamine, 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) or *p*-xylylenediamine, 1,4-$(H_2NCH_2)_2$-$C_6H_4$ was weighed into a flask, along with the phosphine-substituted silane 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**) (if used). The two flasks were sealed, removed from the glovebox and attached to a Schlenk line. Phenylsilane [$PhSiH_3$] or diphenylsilane [$Ph_2SiH_2$] (if used) was added via syringe to the amine containing Schlenk flask. The contents were dissolved in solvent (benzene or toluene) that would give a final concentration of 0.34 M of the limiting reagent, and heated to the desired temperature using a water or oil bath. The catalyst solution was added via cannula to the monomer solution, resulting in significant gas evolution (assumed to be $H_2$). The flask was then sealed and left to stir for 16 h. After this time, the solution was concentrated to 1-2 mL and the polymer was precipitated with either wet pentane or wet hexanes. The solid was isolated by cannula filtration and washed again with wet pentane or wet hexanes. After another filtration, the polymer was dried under reduced pressure ($1\times10^{-3}$ mbar) at 55 °C to constant weight. The polymer was then transferred into a glovebox and stored at room temperature under inert atmosphere.

**DOSY Measurements**

The polymers were not suitable to be analysed via GPC, likely due to their hydrolytic sensitivity. However, by using the method previously described by Grubbs *et al.*, the molecular weight of the polymers could be established using diffusion ordered NMR spectroscopy (DOSY).[6] Molecular weights were estimated using the method described by Grubbs *et al.*, that has also been used specifically for the qualification of molecular weight of polycarbosilazanes previously, both by our group[7] and by others.[8] By using seven monodisperse polystyrene standards (traditionally for use in GPC calibration) of known molecular weight from 580 g $mol^{-1}$ to 70,500 g $mol^{-1}$, a monotonous correlation could be established between molecular weight ($M_n$) and diffusion coefficient (D). The plot of log D against log $M_n$ produced a linear calibration curve (vide infra), to which our polycarbosilazanes were compared. Both the samples and the polystyrene standard were analysed at a concentration of approximately 1 mg $mL^{-1}$ in dry benzene[$D_6$]. The Bruker dstebpgp3s convection corrected pulse sequence was used, with a diffusion delay of $\Delta = 60$ ms and gradient pulse length of $\delta = 5$ ms. Spectra were obtained over a 16-step gradient range from 10% to 90%. Mathematical fittings were made of the diffusion data, and averaged to obtain the given diffusion coefficient D for each sample. Spectra were processed using the *MestReNova* Bayesian DOSY transform function at a resolution factor of 0.1, 5 repetitions, and 512 points in the diffusion dimension over the range from $1\times10^{-7}$ to $1\times10^{-4}$ $cm^2s^{-1}$. The relationship $\log D = -0.5172 \log M_n - 7.6921$ is similar to that of Grubbs *et. al.* ($\log D = -0.537 \log M_n - 7.697$)[6] and of Hill *et al.* ($\log D = -0.5089 \log M_n - 7.8635$).[8] The $R^2$ value of 0.9825 is slightly lower than that of Grubbs ($R^2 = 0.9991$), but still indicates the overall quality of the mathematical fit (Figure S1).

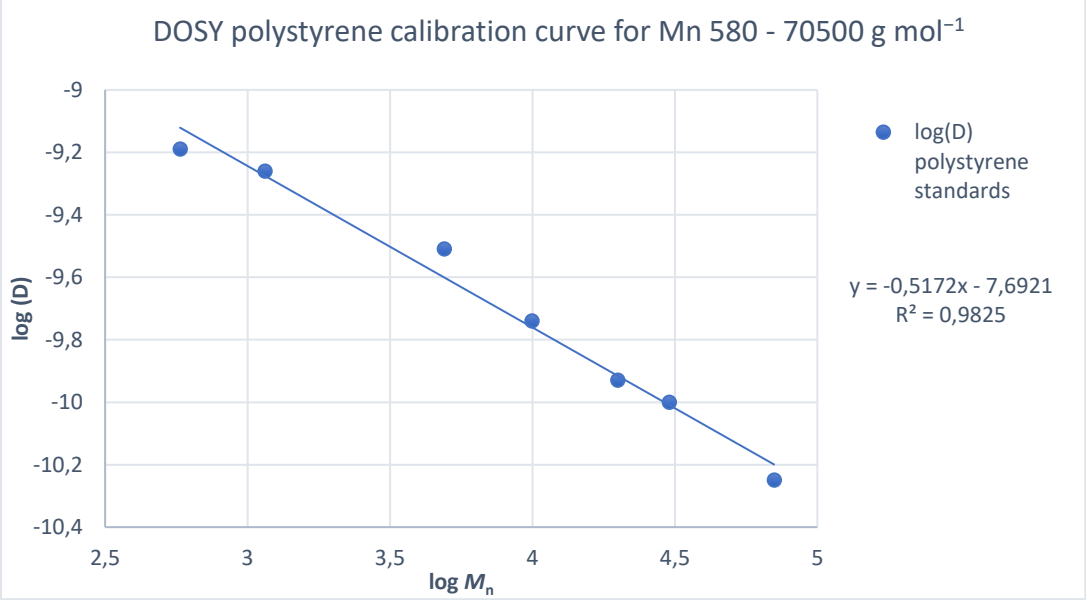



**Figure S1.** Graph of log D vs log $M_n$ for a series of monodisperse polystyrene standards designed for GPC calibration.

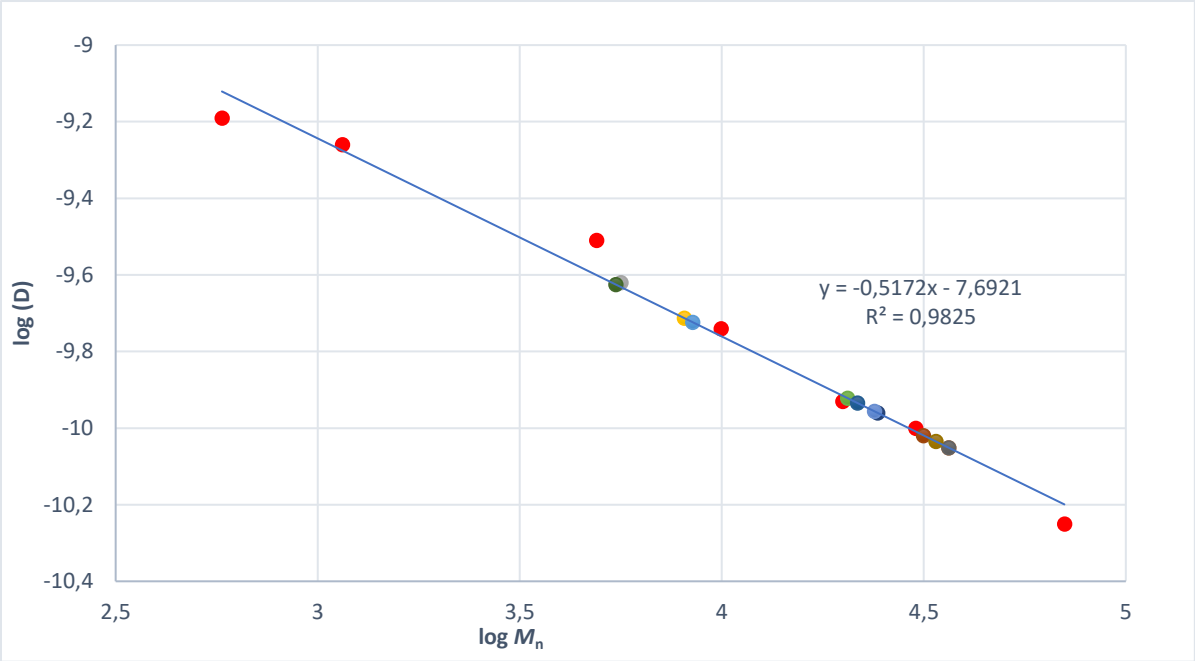



**Figure S2.** Graph showing the polycarbosilazanes plotted on the DOSY calibration curve as a function of their diffusion coefficients D. The polystyrene calibration data points from Figure S1 are in red, the data points for the polycarbosilazanes of unknown molecular weights are in other colours.

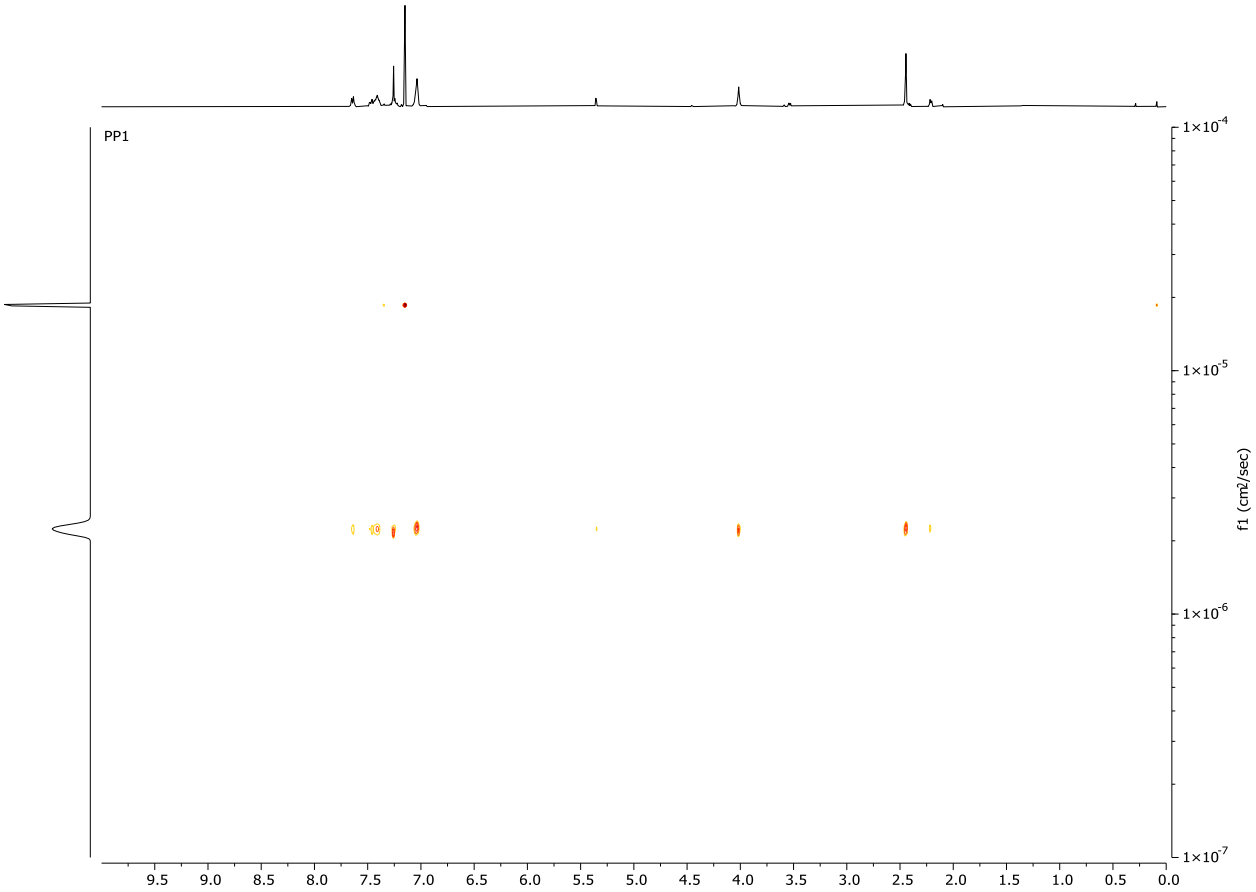
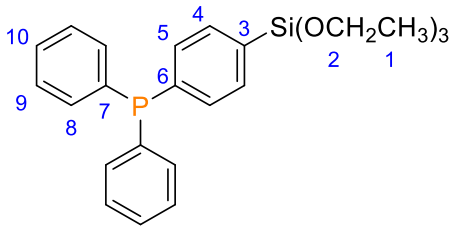



**Figure S3.** Illustrative example of the DOSY $^{1}$H NMR Spectrum of co-PhPZ-1 in benzene[$D_6$].

**Flame retardancy analysis**

A pyrolysis-combustion flow calorimeter (PCFC from *Fire Testing Technologies*) was used to study the flammability of the phosphorus-containing polycarbosilazanes. This apparatus allows for the separation of the anaerobic pyrolysis of the condensed phase from the combustion step in gas phase. Typically, small samples (around 3 mg) undergo anaerobic pyrolysis (heating rate 1 °C $s^{-1}$) from 100 to 750 °C under a nitrogen flow (100 mL $min^{-1}$). The gases produced during heating are sent to a second chamber, called combustor, where they are completely oxidized at 900 °C in excess of oxygen (nitrogen-oxygen mixture 80/20). The heat release rate (HRR) is calculated according to the well-known Huggett relation (1 g of oxygen consumed corresponds to 13.1 kJ of energy released[9]). The total heat release (THR) is the area under the curve in the plot of HRR versus temperature of pyrolysis. The residue content is measured at the end of the test. The heat of complete combustion $\Delta h$ (kJ $g^{-1}$) is the ratio between the THR (i.e. the area) and the mass loss fraction.

**Synthesis of $Ph_2P(p\text{-}Si(OEt_3)_3C_6H_4)$**




A 250 mL round bottom flask was loaded with magnesium turnings (850 mg, 0.35 mmol), a stir bar and diethyl ether (150 mL). A small volume of diiodoethane was added to the flask which was briefly heated until ethane evolution was observed. A solution of [$Ph_2PC_6H_4Br$] (10.0 g, 29.3 mmol) in diethyl ether (50 mL) was added dropwise, generating a slight orange colour. After complete addition, a reflux condenser was attached to the flask and the contents were refluxed for 2.5 h, generating a dark 'cola' coloured suspension. The flask was cooled to room temperature, and the decanted solution was added dropwise to a solution of tetraethylorthosilicate (neat, 100 mL) in thf (100 mL) at 0 °C, generating a colourless solution. The solution was left to stir overnight. The solution was quenched with degassed $H_2O$ (200 mL), and the organic phase was isolated by cannula, dried over $MgSO_4$ and filtered to give a clear solution (all under argon). Removal of the volatiles under reduced pressure (100 °C, $1 \times 10^{-3}$ mbar) gave a slightly orange oil, consisting of a mixture of the desired product, along with the di- and tri- substituted orthosilicates as well. The desired compound was isolated by Kugelrohr distillation (280 °C, $1 \times 10^{-3}$ mbar) to give the title compound as a colourless oil. Yield: 4.72 g (38%).

NMR spectra are provided below as Figures S6-S9.

**$^{1}$H NMR** (300.13 MHz, [$D_6$]benzene, 298 K): δ 7.77 (m, 2H, $C_4$**H**); 7.47 (m, 2H, $C_5$**H**); 7.41 (m, 4H, $C_9$**H**); 7.05 (m, 6H, $C_8$**H** + $C_{10}$**H**); 3.83 (q, $^{3}J_{HH}$ = 7.0 Hz, 6H, $C_2$**H**); 1.15 (t, $^{3}J_{HH}$ = 7.0 Hz, 9H, $C_1$**H**) ppm.

**$^{13}$C{$^{1}$H} NMR** (75.48 MHz, [$D_6$]benzene, 298 K): δ 140.71 (d, $^{1}J_{CP}$ = 13.2 Hz, **C**$_6$); 137.73 (d, $^{1}J_{CP}$ = 12.1 Hz, **C**$_7$); 135.31 (d, $^{3}J_{CP}$ = 6.3 Hz, **C**$_4$); 134.34 (d, $^{2}J_{CP}$ = 19.9 Hz, $C_8$); 133.38 (d, $^{2}J_{CP}$ = 18.8 Hz, **C**$_5$); 132.56 (**C**$_3$); 128.98 (**C**$_{10}$); 128.88 (d, $^{3}J_{CP}$ = 6.9 Hz, **C**$_9$); 58.96 (**C**$_2$); 15.51 (**C**$_1$) ppm.

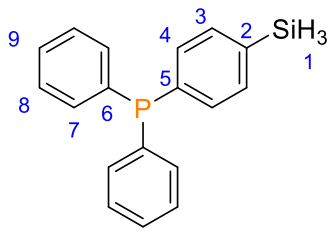
**$^{31}$P NMR** (161.99 MHz, [$D_6$]benzene, 298 K): δ –5.18 ($J_{PC}$ = 19.4 Hz) ppm.

**$^{29}$Si{$^{1}$H} INEPT NMR** (79.49 MHz, [$D_6$]benzene, 302 K): δ –58.79 ppm.

**HRMS (ESI)**: $(M+H)^+$ Calc(m/z): 425.16964 Found: 425.1696 (0 ppm).

**Elemental Analysis**: theoretical: C 67.90 H 6.89. Found: C 68.03 H 6.78.

**Synthesis of 4-$Ph_2P$-$C_6H_4SiH_3$ (A)**




To a suspension of $LiAlH_4$ (0.50 g, 13.1 mmol) in diethyl ether (150 mL) at 0 °C was added a solution of [$Ph_2P$(*p*-Si($OEt_3$)$_3C_6H_4$)] (5.00 g, 11.8 mmol) in diethyl ether (50 mL) dropwise. After the complete addition, the resulting suspension was left to stir overnight at room temperature. The volatiles were removed under reduced pressure, and the solid was extracted with toluene or benzene (100 mL × 3) and filtered to give a colourless solution. The combined fractions had the solvent evaporated under reduced pressure to give the title compound as a white solid. Yield: 3.32 g (96%). Recrystallisation from $Et_2O$ gave a sample used for analytical results and XRD analysis.

NMR spectra are provided below as Figures S10-S13.

**$^1$H NMR** (300.13 MHz, [$D_6$]benzene, 299 K): δ 7.38 (m, 4H, $C_8$**H**); 7.19 (m, 4H, $C_7$**H**); 7.05 (overlapping m, 6H, $C_3$**H** + $C_4$**H** + $C_9$**H**); 4.17 (s, $^1J_{HSi}$ = 201.0 Hz, 3H, Si**H**) ppm.

**$^{13}$C{$^1$H} NMR** (75.48 MHz, [$D_6$]benzene, 299 K): δ 140.40 (d, $^1J_{CP}$ = 13.6 Hz, **C**$_5$); 137.62 (d, $^1J_{CP}$ = 12.1 Hz, **C**$_6$); 136.19 (d, $^3J_{CP}$ = 6.0 Hz, **C**$_3$); 134.27 (d, $^2J_{CP}$ = 19.6 Hz, **C**$_7$); 133.61 (d, $^2J_{CP}$ = 18.9 Hz, **C**$_4$); 129.05 (**C**$_9$); 128.89 (d, $^3J_{CP}$ = 6.8 Hz, **C**$_8$); 128.70 (**C**$_2$) ppm.

**$^{31}$P NMR** (121.50 MHz, [$D_6$]benzene, 300 K): δ –5.34 ($J_{PC}$ = 19.4 Hz) ppm.

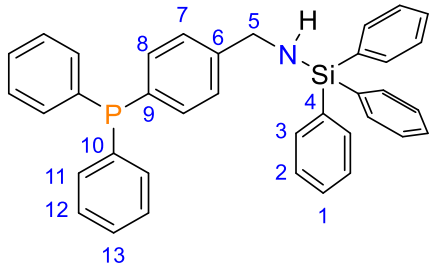
**$^{29}$Si{$^1$H} INEPT NMR** (79.49 MHz, [$D_6$]benzene, 300 K): δ –60.40 ppm.

**HRMS (ESI)**: $(M+H)^+$ Calc(m/z): 293.09099. Found: 293.0911 (0 ppm).

**Elemental Analysis**: theoretical: C 73.94 H 5.86. Found: C 73.15 H 5.80.

Single crystals were obtained, and the molecular solid-state structure of the compound was established by X-ray diffraction analysis (see below).

**4-$Ph_2P$-$C_6H_4CH_2NHSiPh_3$**




Following the standard procedure, the dehydrocoupling between **B** and excess triphenylsilane (2.1 equiv) catalysed by **1** (2.5 mol-%) in benzene-$d_6$ at 60 °C proceeded smoothly and quantitatively within 1 h to give the monocoupled silazane 4-$Ph_2P$-$C_6H_4CH_2NHSiPh_3$, see Scheme 3 in the manuscript. Single crystals of the title compound were obtained, and the molecular solid-state structure of the compound was established by X-ray diffraction analysis (see XRD section below for details).

NMR spectra are provided below as Figures S15-S18.

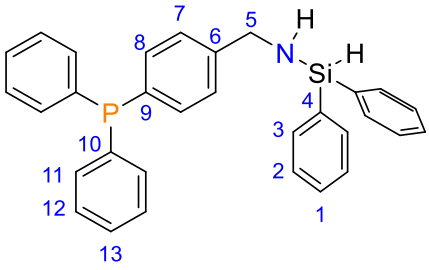
**$^1$H NMR** (400.16 MHz, [$D_6$]benzene, 298 K): δ 7.67 (dd, $^3J_{HH}$ = 7.4 and 2.1 Hz, 6H, $C_2$**H**); 7.43 (td, $J_{HH}$ = 7.5 and 1.9 Hz, 4H, $C_{11}$**H**); 7.38 (t, $^3J_{HH}$ = 7.8 Hz, 2H, $C_8$**H**); 7.20 (overlapping m, 8H, $C_{12}$**H** + $C_{13}$**H** + $C_7$**H**); 7.08 (overlapping m, 9H, $C_1$**H** + $C_3$**H**); 3.95 (d, $^3J_{HH}$ = 7.9 Hz, 2H, $C_5$**H**); 1.25 (t, $^3J_{HH}$ = 7.9 Hz, 1H, N**H**) ppm.

**$^{13}$C{$^1$H} NMR** (100.63 MHz, [$D_6$]benzene, 298 K): δ 144.67 (**C**$_6$); 138.41 (d, $^1J_{CP}$ = 12.2 Hz, **C**$_9$); 136.01 (**C**$_2$); 135.98 (**C**$_{10}$, coupling not observable due to overlapping resonance); 134.38 (d, $^2J_{CP}$ = 20.4 Hz, **C**$_8$); 134.16 (d, $^2J_{CP}$ = 19.5 Hz, **C**$_{11}$); 129.96 (**C**$_1$); 128.81 (**C**$_{13}$); 128.81 (d, $^3J_{CP}$ = 6.8 Hz, **C**$_{12}$); 128.22 (**C**$_3$); 127.69 (d, $^3J_{CP}$ = 7.9 Hz, **C**$_7$); 46.65 (**C**$_5$) ppm. The resonance for $C_4$ could not be detected.

**$^{31}$P NMR** (161.99 MHz, [$D_6$]benzene, 298 K): δ –5.99 ppm.

**HRMS (ESI).** $(M+H)^+$ Calc(m/z): 550.21114. Found: 550.2115 (0 ppm).

**4-$Ph_2P$-$C_6H_4CH_2NHSiPh_2H$**




Following the standard procedure, the equimolar dehydrocoupling between **B** and excess diphenylsilane catalysed by **1** (2.5 mol-%) in benzene-$d_6$ at 60 °C proceeded smoothly and quantitatively within 1 h to give the monocoupled silazane 4-$Ph_2P$-$C_6H_4CH_2NHSiPh_2H$, see Scheme 3 in the manuscript. The final product was contaminated by another unassigned compound, assumed to be the cyclic disilazane $[(4\text{-}Ph_2P\text{-}C_6H_4CH_2)NSiPh_2]_2$, although no conclusive evidence confirms this hypothesis.

NMR spectra are provided below as Figures S19-S21.

**$^1$H NMR** (500.13 MHz, [$D_6$]benzene, 300 K): δ 7.64 (dd, $^3J_{HH}$ = 7.4 and 2.1 Hz, 4H, $C_2$**H**); 7.43 (td, $J_{HH}$ = 7.5 and 1.9 Hz, 4H, $C_{11}$**H**); 7.40 (t, $^3J_{HH}$ = 7.8 Hz, 2H, $C_8$**H**); 7.18 (m, 6H, $C_{12}$**H** + $C_{13}$**H**); 7.07 (overlapping m, 8H, $C_1$**H** + $C_3$**H** + $C_7$**H**); 5.59 (d, $^3J_{HH}$ =2.2 Hz, $^1J_{HSi}$ = 203.8 Hz, 1H, Si**H**); 3.80 (d, $^3J_{HH}$ = 8.0 Hz, 2H, $C_5$**H**); 0.94 (m, 1H, N**H**) ppm.

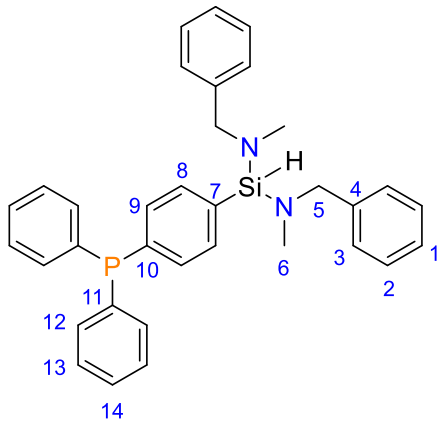
**$^{13}$C{$^1$H} NMR** (125.77 MHz, [$D_6$]benzene, 300 K): δ 144.47 (**C**$_6$); 138.41 (d, $^1J_{CP}$ = 12.2 Hz, **C**$_9$); 135.52 (**C**$_{10}$); 135.30 (**C**$_2$); 134.39 (d, $^2J_{CP}$ = 20.0 Hz, **C**$_8$); 134.16 (d, $^2J_{CP}$ = 19.5 Hz, **C**$_{11}$); 130.29 (**C**$_1$); 128.82 (**C**$_{13}$); 128.81 (d, $^3J_{CP}$ = 6.8 Hz, **C**$_{12}$); 128.34 (**C**$_3$); 127.68 (d, $^3J_{CP}$ = 7.2 Hz, **C**$_7$); 46.82 (**C**$_5$) ppm. The resonance for $C_4$ could not be detected.

**$^{31}$P NMR** (202.46 MHz, [$D_6$]benzene, 300 K): δ –5.99 ppm.

**$^{29}$Si{$^1$H} INEPT NMR** (79.49 MHz, [$D_6$]benzene, 298 K): δ –16.81 ppm.

**HRMS(ESI).** $(M+H)^+$ Calc (m/z): 474.18014. Found: 474.1801 (0 ppm).

**4-$PPh_2$-$C_6H_4SiH\{N(Me)CH_2Ph\}_2$**




Following the standard procedure, the dehydrocoupling of trihydrosilane **A** with a threefold excess of *N*-methylbenzylamine catalysed by **1** (2.5 mol-% vs. **A**) at 25 °C in benzene[$D_6$] generates the product of double dehydrocoupling, 4-$PPh_2$-$C_6H_4SiH\{N(Me)CH_2Ph\}_2$, isolated as a colourless oil. See Scheme 4 in the manuscript.

NMR spectra are provided below as Figures S22-S25.

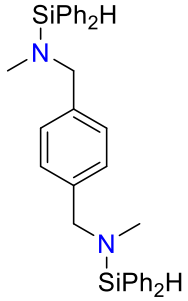
**$^1$H NMR** (500.13 MHz, [$D_6$]benzene, 300 K): δ 7.62 (m, 2H, $C_8$**H**); 7.44 (overlapping m, 6H, $C_{12}$**H** + $C_9$**H**); 7.20 (m, 8H, $C_2$**H** + $C_3$**H**); 7.07 (m, 8H, $C_1$**H** + $C_{13}$**H** + $C_{14}$**H**); 5.32 (s, $^1J_{HSi}$ = 219.4 Hz, 1H, Si**H**); 3.97 (s. 4H, $C_5$**H**); 2.41(s, 6H, $C_6$**H**).

**$^{13}$C{$^1$H} NMR** (125.77 MHz, [$D_6$]benzene, 300 K): δ 140.97 (s, **C**$_4$); 140.30 (d, $^1J_{CP}$ = 13.2 Hz, **C**$_{10}$); 137.79 (d, $^1J_{CP}$ = 12.1 Hz, **C**$_{11}$); 136.75 (s, **C**$_7$); 135.18 (d, $^3J_{CP}$ = 6.2 Hz, **C**$_8$); 134.36 (d, $^2J_{CP}$ = 19.6 Hz, **C**$_{12}$); 133.65 (d, $^2J_{CP}$ = 18.8 Hz, **C**$_9$); 128.99 (s, **C**$_{14}$); 128.88 (d, $^3J_{CP}$ = 6.9 Hz, **C**$_{13}$); 128.62 (s, **C**$_2$); 128.11 (s, **C**$_3$, partially obscured by residual solvent signal); 127.03 (s, **C**$_1$); 54.68 (s, **C**$_5$) 34.33 (s, **C**$_6$).

**$^{31}$P{$^1$H} NMR** (202.46 MHz, [$D_6$]benzene, 300 K): δ –5.19 ppm.

**Elemental Analysis**: theoretical: C 76.95 H 6.65 N 5.28. Found: C 75.59 H 6.53 N 4.64. We could not obtain reproducible and reliable results, despite multiple attempts. We assume this is because of (1) the presence of Si atoms (known to form SiC and thus to lower C amounts), and (2) the hydrolytically sensitive nature of the sample.

**NMR scale reaction of 1,4-{$CH_2NHMe$}$_2$-$C_6H_4$ (C) with 2 equivalents of $Ph_2SiH_2$**




In the glove-box, the two substrates **C** (16.4 mg, 100 µmol) and $Ph_2SiH_2$ (36.9 mg, 200 µmol) were mixed in an NMR tube, and the precatalyst **1** (6.9 mg, 7.5 µmol) was added. The tube was removed from the glove-box, and, using a Schlenk line and standard Schlenk techniques, [$D_6$]benzene was injected into the NMR tube, which was then sealed off. The mixture was stirred manually for a few seconds, and the immediate release of $H_2$ was observed. The reaction was pursued at 60 °C, using a stainless-steel heating block for temperature control. Conversion was monitored by $^1$H NMR spectroscopy.

**$^1$H NMR** (400.13 MHz, [$D_6$]benzene, 300 K): δ 5.69 (s, $^1J_{SiH}$ = 204 Hz, 2H, Si**H**), 4.00 (s, 4H, NC**H**$_2$Ar), 2.45 (s, 6H, NC**H**$_3$) ppm. The spectrum also shows multiples resonances in the aromatic region (δ 7.84, 7.76, 7.68, 7.32-7.15 ppm) and resonances at 4.13 (s) and 2.60 (s) ppm which could not be assigned.

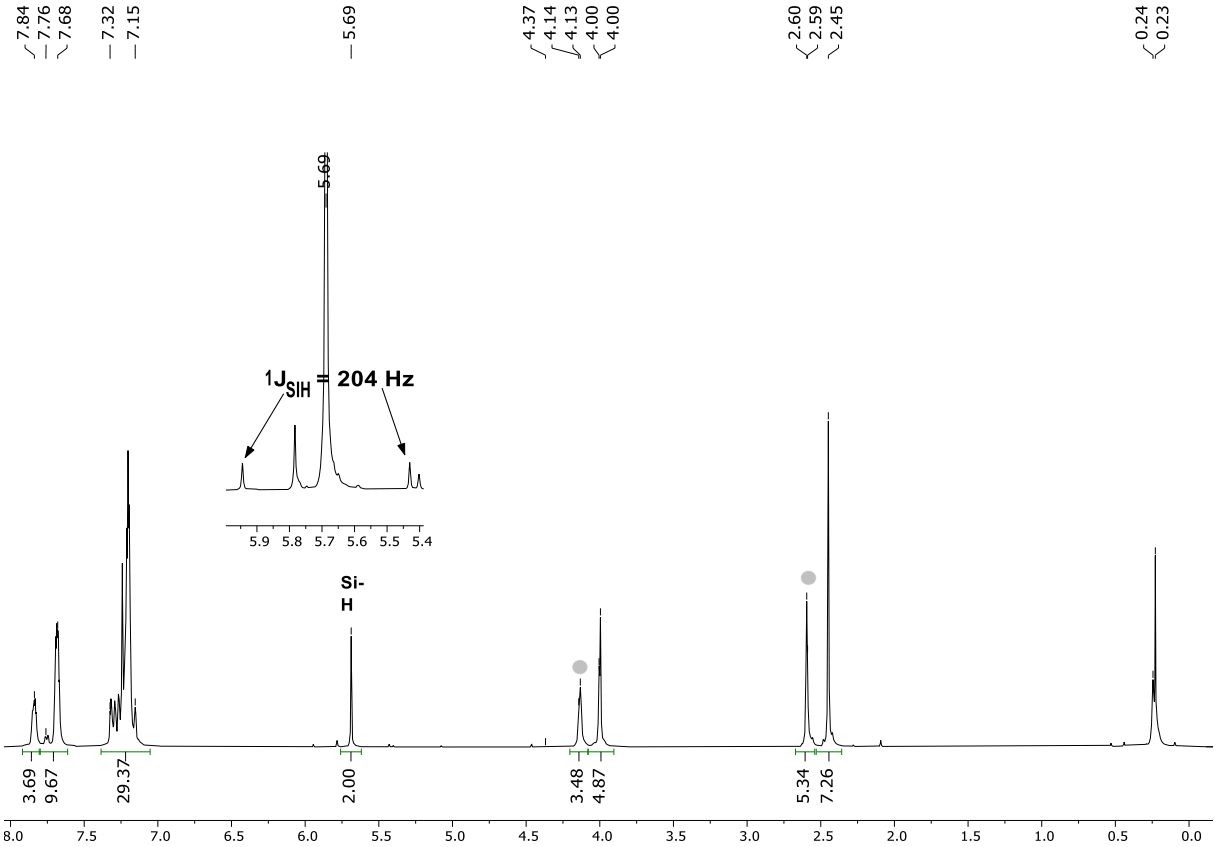
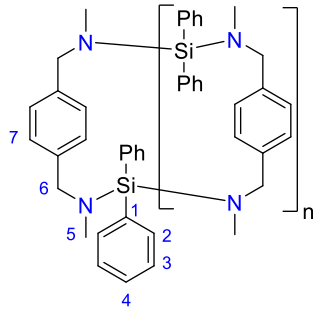



**Figure S4.** $^1$H NMR spectrum ([$D_6$]benzene, 400.16 MHz, 298 K) of the monitoring (after 48 h) of the reaction between 1,4-($CH_2NHMe$)$_2$-$C_6H_4$ (**C**) with two equivalents of diphenylsilane, showing formation of the desired α,ω-disilazane 1,4-{$CH_2N(Me)SiPh_2H$}$_2$-$C_6H_4$ along another unidentified species in minor proportions (grey dots), and full consumption of the starting amine **C**. No presence of **C** (δ 3.55, 2.23 and 0.71 ppm, see Figure S14 below) can be seen.

**NMR scale reaction of 1,4-{$CH_2NHMe$}$_2$-$C_6H_4$ (C) with 1 equivalent of $Ph_2SiH_2$**




In the glove-box, the two substrates **C** (24.6 mg, 150 µmol) and $Ph_2SiH_2$ (27.6 mg, 150 µmol) were mixed in an NMR tube, and the precatalyst **1** (6.9 mg, 7.5 µmol) was added. The tube was removed from the glove-box, and, using a Schlenk line and standard Schlenk techniques, [$D_6$]benzene was injected into the NMR tube, which was then sealed off. The mixture was stirred manually for a few seconds, and the immediate release of $H_2$ was observed. The reaction was pursued at 60 °C, using a stainless-steel heating block for temperature control. Conversion was monitored by $^1$H NMR spectroscopy. The absence of detectable endgroups is consistent with the formation of a cyclic chain.

**$^1$H NMR** (400.13 MHz, [$D_6$]benzene, 298 K): δ 7.83 (m, 4H, $C_7$**H**), 7.32 (m, 4H, $C_2$**H**), 7.21 (overlapping m, 6H, $C_3$**H** + $C_4$**H**), 4.14 (s, 4H, $C_6$**H**), 2.60 (s, 6H, $C_5$**H**) ppm.

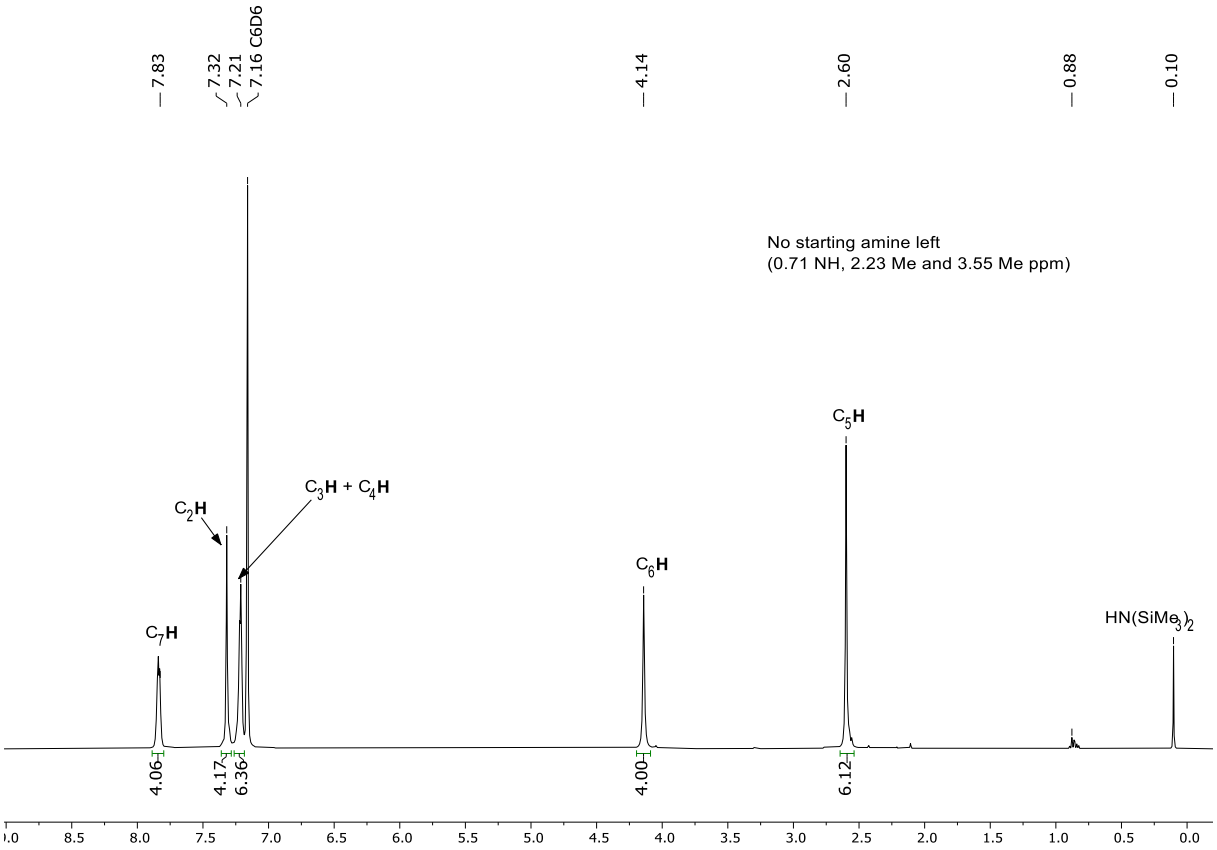
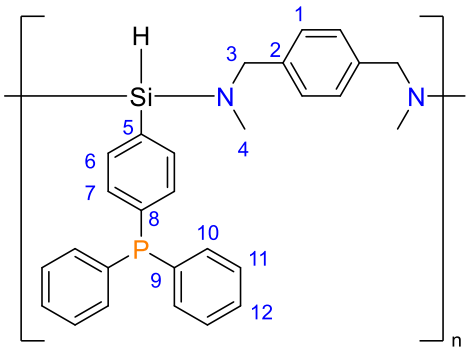



**Figure S5.** $^1$H NMR spectrum ([$D_6$]benzene, 400.16 MHz, 298 K) of the monitoring of the reaction between 1,4-($CH_2NHMe$)$_2$-$C_6H_4$ (**C**) with one equivalent of diphenylsilane, showing formation of the polycarbosilazane [-$Ph_2$Si-(Me)N$CH_2$-$C_6H_4$-$CH_2$NMe-]$_n$, with full consumption of the starting amine **C**. No residual presence of **C** (δ 3.55, 2.23 and 0.71 ppm, see Figure S14 below) can be seen. No endgroup can be detected, suggesting the formation of a cyclic chain.

**co-PhPZ-0. NMR reaction of 4-$Ph_2P$-$C_6H_4SiH_3$ (A) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**




In the glove-box, the two substrates **A** (29.9 mg, 102 µmol) and **C** (16.8 mg, 102 µmol) were mixed in an NMR tube, and the precatalyst **1** (6.9 mg, 7.5 µmol, 15 mol-% in Ba) was added. The tube was removed from the glove-box, and, using a Schlenk line and standard Schlenk techniques, [$D_6$]benzene (0.5 ml) was injected into the NMR tube, which was then sealed off. The mixture was stirred manually for a few seconds, and the immediate release of $H_2$ was observed. The reaction was carried out at 60 °C, using a stainless-steel heating block for temperature control. Conversion was monitored by $^1$H NMR spectroscopy over the course of 37.5 h.

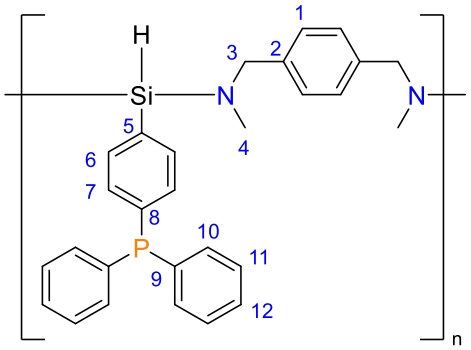
**$^1$H NMR** (300.13 MHz, [$D_6$]benzene, 298 K): δ 7.67-7.64 (m, 2H, arom-**H**), 7.49-7.42 (m, 6H, arom-**H**), 7.27 (s, 4H, $C_1$**H** + $C_2$**H**), 7.05 (m, 6H, arom-**H**), 5.37 (s, $^1J_{SiH}$ = 219 Hz, 1H, Si**H**), 4.03 (s, 4H, $C_4$**H**), 2.46 (4, 6H, $C_5$**H**) ppm.

**$^{13}$C{$^1$H} NMR** (75.48 MHz, [$D_6$]benzene, 299 K): δ 140.27 (d, $^1J_{CP}$ = 12.8 Hz, **C**$_8$), 139.46 (s, **C**$_2$), 137.75 (d, $^1J_{CP}$ = 12.1 Hz, **C**$_9$), 136.80 (s, **C**$_1$), 135.21 (d, $^3J_{CP}$ = 6.0 Hz, **C**$_6$), 134.31 (d, $^2J_{CP}$ = 19.6 Hz, **C**$_{10}$), 133.64 (d, $^2J_{CP}$ = 18.1 Hz, **C**$_7$), 129.01 (s, **C**$_{12}$), 128.89 (d, $^3J_{CP}$ = 6.8 Hz, **C**$_{11}$), 128.29 (s, **C**$_5$), 54.49 (s, **C**$_3$), 34.41 (s, **C**$_4$) ppm.

**$^{31}$P{$^1$H} NMR** (121.50 MHz, [$D_6$]benzene, 298 K): δ –5.26 ppm (see Figure 5 in the manuscript).

**$^{29}$Si{$^1$H} INEPT NMR** ([$D_6$]benzene, 79.49 MHz, 302 K): δ –15.22 ppm

**Co-PhPZ-1. 100:100 polymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (A) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**




The reaction was conducted as per standard procedure, at 60 °C using **A** (607 mg, 2.08 mmol) and **C** (325 mg, 1.98 mmol), catalysed by **1** (90.7 mg, 99 µmol, 10 mol-% loading in Ba). Substrate conversion was quantitative according to $^1$H NMR. Isolated yield after purification: 532 mg (58%).

The relevant NMR spectra are provided below in Figures S29-S32.

**$^1$H NMR** (500.13 MHz, [$D_6$]benzene, 300 K): δ 7.65 (m, 2H, $C_6$**H**); 7.47 (m, 2H, $C_7$**H**); 7.42 (m, 4H, $C_{10}$**H**); 7.27 (br s, 4H, $C_1$**H**); 7.05 (m, 6H, $C_{11}$**H** + $C_{12}$**H**); 5.37 (s, $^1J_{HSi}$ = 218.1 Hz, 1H, Si**H**); 4.03 (m, 4H, $C_3$**H**); 3.55 (d, $^2J_{HH}$ = 6.4 Hz, $C_2$**H** terminal); 2.46 (s, 6H, $C_4$**H**); 2.22 (m, $C_4$**H** terminal); 0.62 (m, N**H** terminal) ppm.

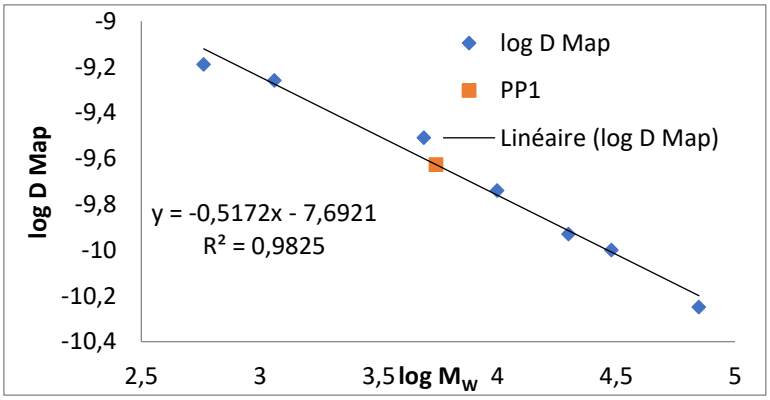
**$^{13}$C{$^1$H} NMR** (125.77 MHz, [$D_6$]benzene, 300 K): δ 140.28 (d, $^1J_{CP}$ = 13.2 Hz, **C**$_8$ terminal); 140.25 (d, $^1J_{CP}$ = 13.1 Hz, **C**$_8$ backbone); 139.47 (s, **C**$_2$ backbone); 139.41 (s, **C**$_2$ terminal); 137.79 (d, $^1J_{CP}$ = 12.2 Hz, **C**$_9$ terminal); 137.78 (d, $^1J_{CP}$ = 12.2 Hz, **C**$_9$ backbone); 136.87 (s, **C**$_5$ terminal); 136.81 (s, **C**$_5$ backbone); 135.22 (d, $^3J_{CP}$ = 6.2 Hz, **C**$_6$); 134.37 (d, $^2J_{CP}$ = 19.7 Hz, **C**$_{10}$); 133.65 (d, $^2J_{CP}$ = 18.8 Hz, **C**$_7$); 129.00 (**C**$_1$); 128.90 (d, $^3J_{CP}$ = 7.1 Hz, **C**$_{11}$); 128.29 (**C**$_{12}$); 56.17 (**C**$_3$, terminal); 54.52 (**C**$_3$, backbone); 36.22 (**C**$_4$, terminal); 34.40 (**C**$_4$, backbone) ppm.

**$^{31}$P{$^1$H} NMR** (161.99 MHz, [$D_6$]benzene, 298 K): δ –5.18 (major, backbone P), –5.40 (minor terminal P) ppm.

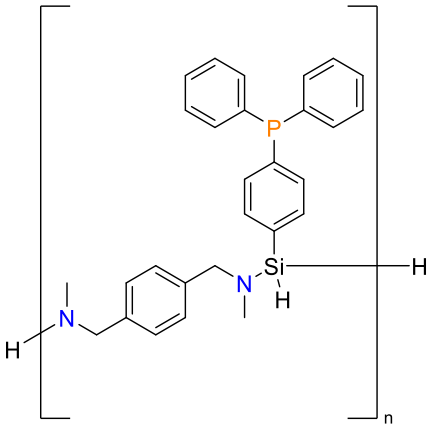
**$^{29}$Si{$^1$H} INEPT NMR** (79.49 MHz, [$D_6$]benzene, 302 K): δ –15.23 (major, backbone Si), –15.37 (minor, terminalSi)ppm.

**DOSY molecular weight determination**

log D = −9.60, D = 2.36217 ×$10^{-10}$ $m^2$ $s^{-1}$. Calculated $M_n$ = 5502 g $mol^{-1}$.



**Co-PhPZ-2. 100:80 polymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (A) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**



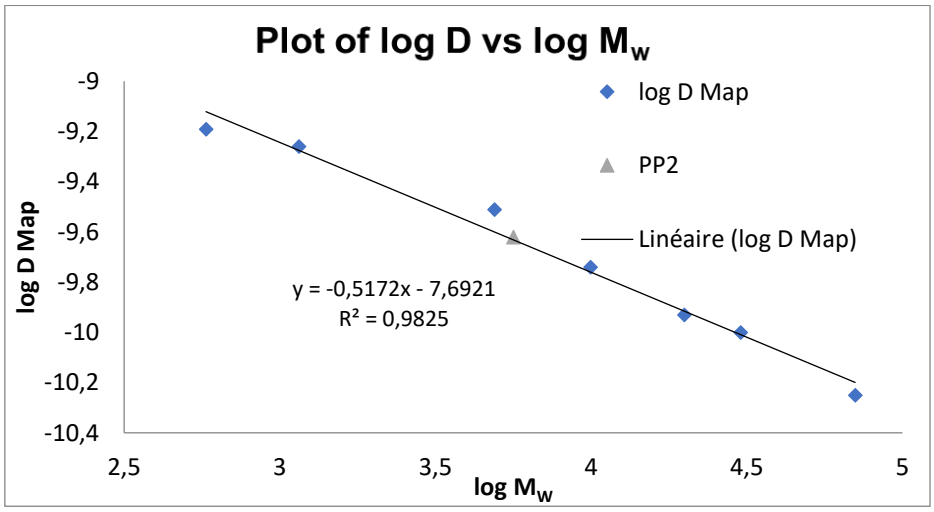

The reaction was conducted as per standard procedure, at 60 °C, using toluene as solvent, with **A** (300 mg, 1.03 mmol) and **C** (135 mg, 0.82 mmol), catalysed by **1** (37.6 mg, 41.0 µmol, 10 mol-% loading in Ba). Conversion of the default substrate was quantitative according to $^1$H NMR.

Isolated yield after purification: 271 mg (73%).

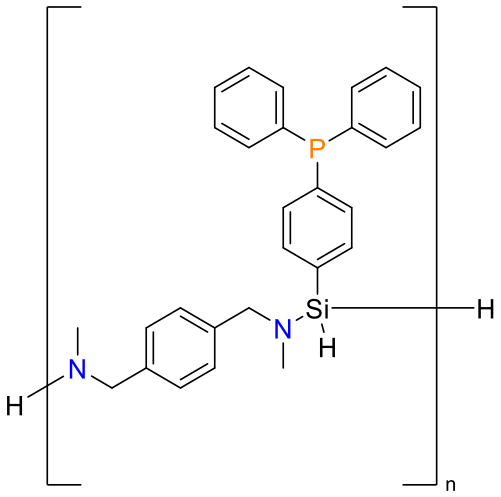
The NMR data for **Co-PhPZ-2** are essentially identical to those for **Co-PhPZ-1**, except for the absence of detectable endgroups (see above and Figures S29-S32).

**DOSY molecular weight determination**

log D = −9.62, D = 2.33433 ×$10^{-10}$ $m^2$ $s^{-1}$. Calculated $M_n$ = 5629 g $mol^{-1}$.



**Co-PhPZ-3. 95:100 polymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (A) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**



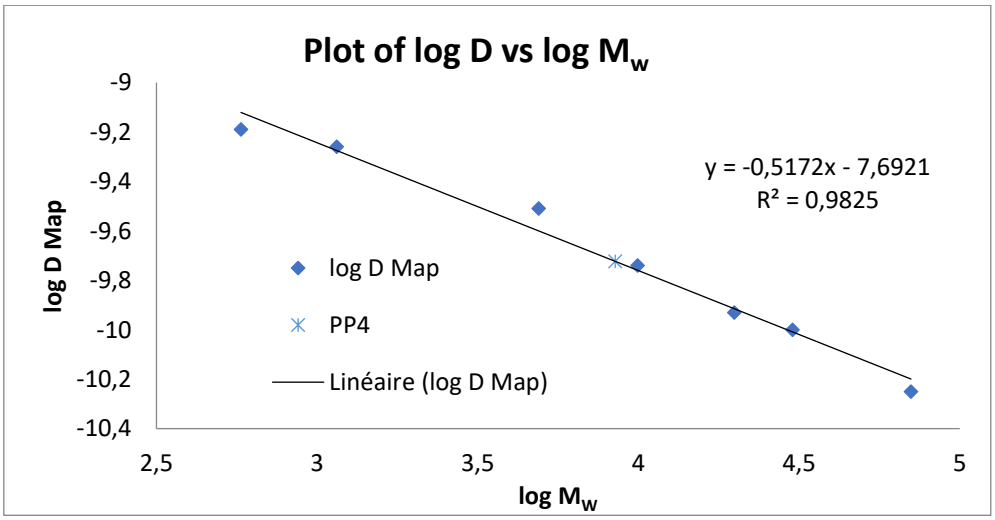

The reaction was conducted as per standard procedure, at 25 °C, with **A** (200 mg, 684 µmol) and **C** (101 mg, 615 µmol), catalysed by **1** (28.2 mg, 30.7 µmol, 10 mol-% loading in Ba). Conversion of the default substrate was quantitative according to $^1$H NMR.

Isolated yield after purification: 148 mg (48%).

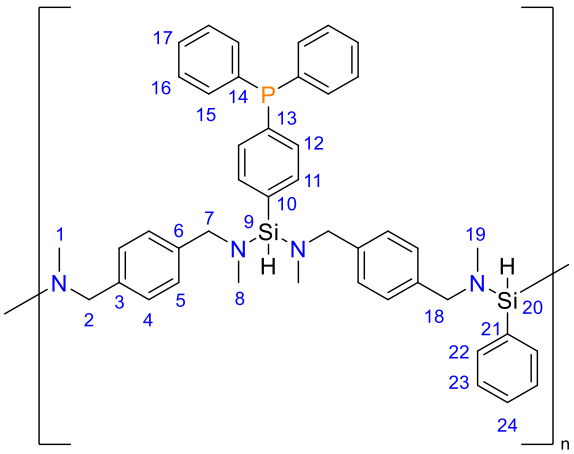
The NMR data for **Co-PhPZ-2** are essentially identical to those for **Co-PhPZ-1** (see above and Figures S29-S32).

**DOSY molecular weight determination**

log D = −9.73, D = 1.89033 ×$10^{-10}$ $m^2$ $s^{-1}$. Calculated $M_n$ = 8465 g $mol^{-1}$.



**Ter-PhCZ-4. 50:50:95 polymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (A), $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**




The reaction was conducted as per standard procedure, at 25 °C, with **A** (188 mg, 642 µmol), $PhSiH_3$ (75 mg, 693 µmol) and **C** (210 mg, 1.28 mmol), catalysed by **1** (58.6 mg, 63.9 µmol, 10 mol-% loading in Ba). Conversion of the default substrate was quantitative according to $^1$H NMR. Isolated yield after purification: 274 mg (58%). It proved impossible to remove entirely all solvent residues.

NMR spectra are provided below as Figures S33-S36.

**$^1$H NMR** (500.13 MHz, [$D_6$]benzene, 300 K): δ 7.74 (m, $C_{22}$**H**); 7.64 (m, $J_{HH}$ = 7.4 Hz, $C_{11}$**H**); 7.49-7.42 (m, arom-**H**); 7.37-7.22 (m, arom-**H**); 7.04 (m, $C_{16}$H + $C_{17}$H); 5.41 (m, $^1J_{HSi}$ = 217.9 Hz, 1H, $Si_{20}$**H**); 5.36 (m, $^1J_{HSi}$ = 219.1 Hz, $Si_9$**H**); 4.06 and 4.02 (m, $C_7$**H** and $C_{18}$**H**); 2.49 and 2.45 (s, $C_8$**H** and $C_{19}$**H**). A number of resonances could not be assigned. They belonged to unidentified impurities we could not remove, and potentially coming from degradation of the polymer during the work-up procedure.

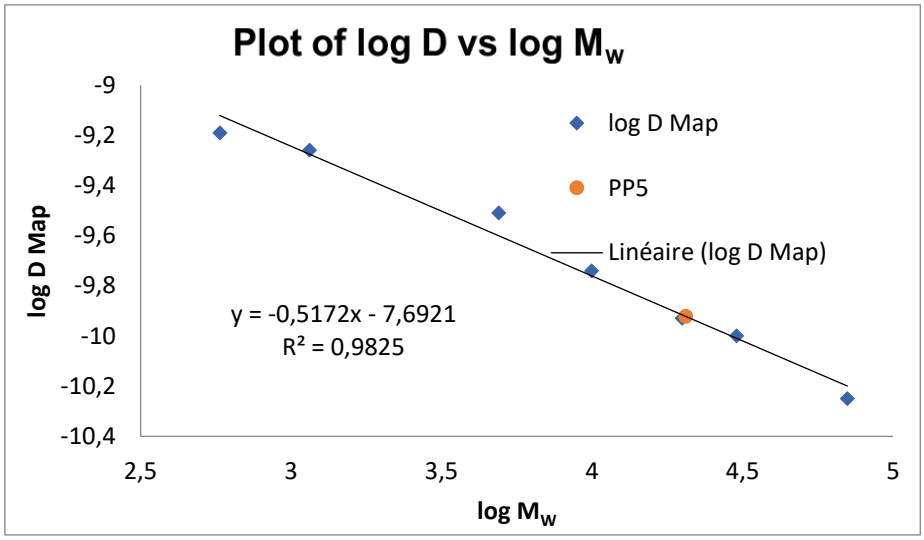
**$^{13}$C{$^1$H}NMR** (125.77 MHz, [$D_6$]benzene, 300 K): δ 139.53 (**C**$_{21}$); 139.48 (**C**$_6$); 137.79 (d, $^1J_{CP}$ = 12.2 Hz, **C**$_{15}$); 136.40 (**C**$_{21}$); 135.23 (d, $^3J_{CP}$ = 6.2 Hz, **C**$_{11}$); 135.11 (**C**$_{22}$); 134.37 (d, $^2J_{CP}$ = 20.0 Hz, **C**$_{15}$); 133.64 (d, $^2J_{CP}$ = 18.8 Hz, **C**$_{12}$); 130.18 (**C**$_{24}$); 129.20, 129.00, 128.92, 128.85, 128.45 and other resonances hidden by the solvent (arom-**C**); 54.21 (br, **C**$_7$ + **C**$_{18}$); 34.39 (br, $C_8$ + $C_{19}$) ppm. A more detailed assignment could not be achieved.

**$^{31}$P{$^1$H} NMR** (161.99 MHz, [$D_6$]benzene, 298 K): δ –5.21 ppm. A residual resonance at –6.40 could not be assigned.

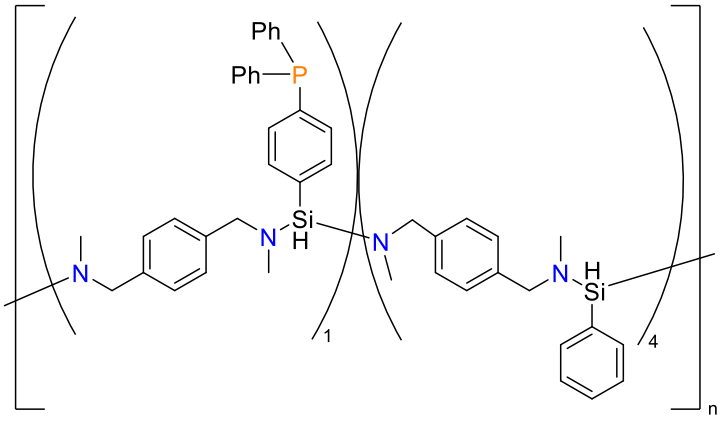
**$^{29}$Si{$^1$H} INEPT NMR** (79.49 MHz, [$D_6$]benzene, 302 K): δ –14.77; –15.24 ppm.

**DOSY molecular weight determination for Ter-PhCZ-4**

log D = −9.92, D = 1.1975 ×$10^{-10}$ $m^2$ $s^{-1}$.Calculated $M_n$ = 20,462 g $mol^{-1}$.



**Ter-PhCZ-5. 20:80:95 polymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (A), $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**

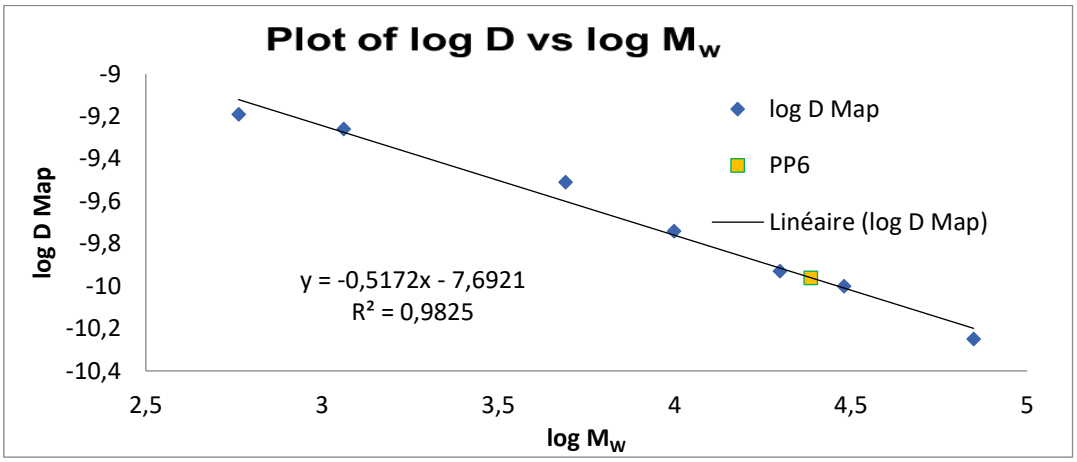



The reaction was conducted as per standard procedure, at 25 °C, with **A** (75 mg, 256 µmol), $PhSiH_3$ (111 mg, 1.02 mmol) and **C** (210 mg, 1.28 mmol), catalysed by **1** (58.6 mg, 63.9 µmol, 10 mol-% loading in Ba).
Isolated yield after purification: 136 mg (35%).

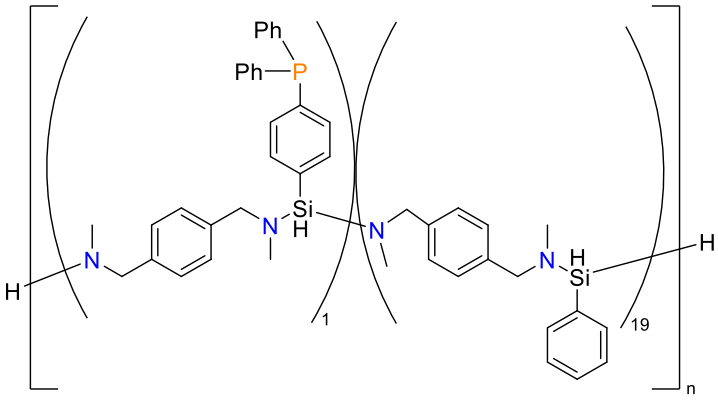
The NMR data for **Ter-PhCZ-5** are similar to those for **Ter-PhCZ-4** (see above and Figures S33-S36).

**DOSY molecular weight determination**

log D = −9.96, D = 1.09567 ×$10^{-10}$ $m^2$ $s^{-1}$. Calculated $M_n$ = 24298 g $mol^{-1}$.



**Ter-PhCZ-6. 5:95:95 polymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (A), $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**

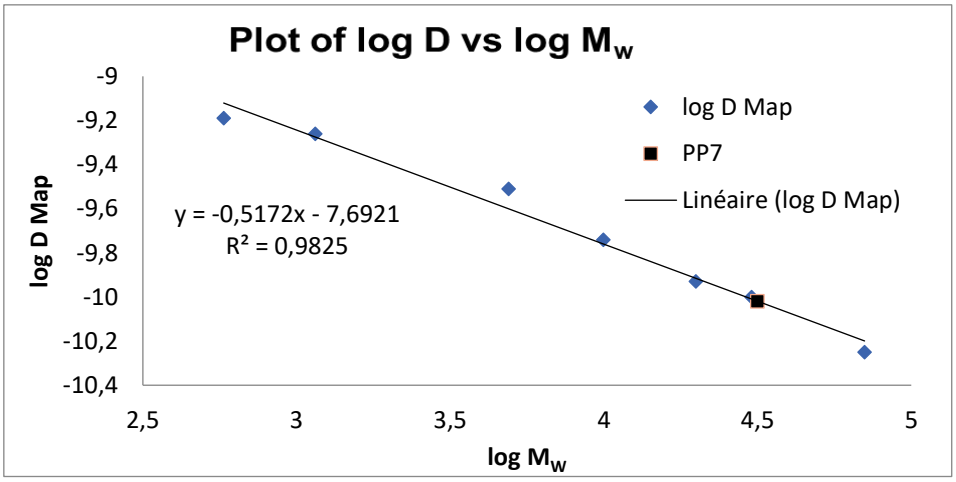



The reaction was conducted as per standard procedure, at 25° C, with **A** (51 mg, 174 µmol), $PhSiH_3$ (356 mg, 3.29 mmol) and **C** (568 mg, 3.46 mmol), catalysed by **1** (158 mg, 172 µmol, 10 mol-% loading in Ba). Isolated yield after purification: 480 mg (50%).

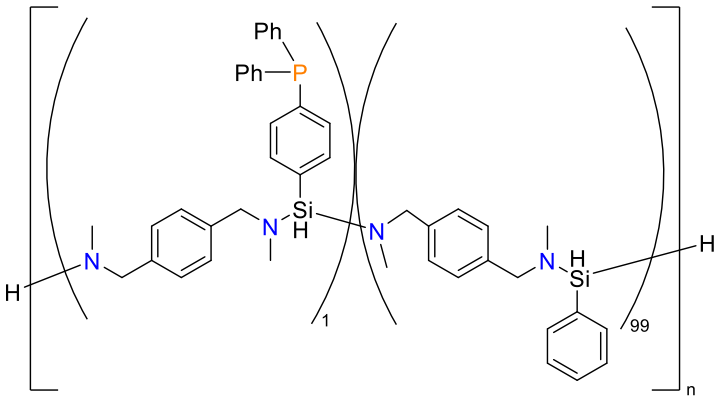
The NMR data for **Ter-PhCZ-6** are similar to those for **Ter-PhCZ-4** (see above and Figures S33-S36).

**DOSY molecular weight determination**

log D = −10.02, D = 9.56833 ×$10^{-10}$ $m^2$ $s^{-1}$. Calculated $M_n$ = 31575 g $mol^{-1}$.



**Ter-PhCZ-7. 1:99:100 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (A), $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**



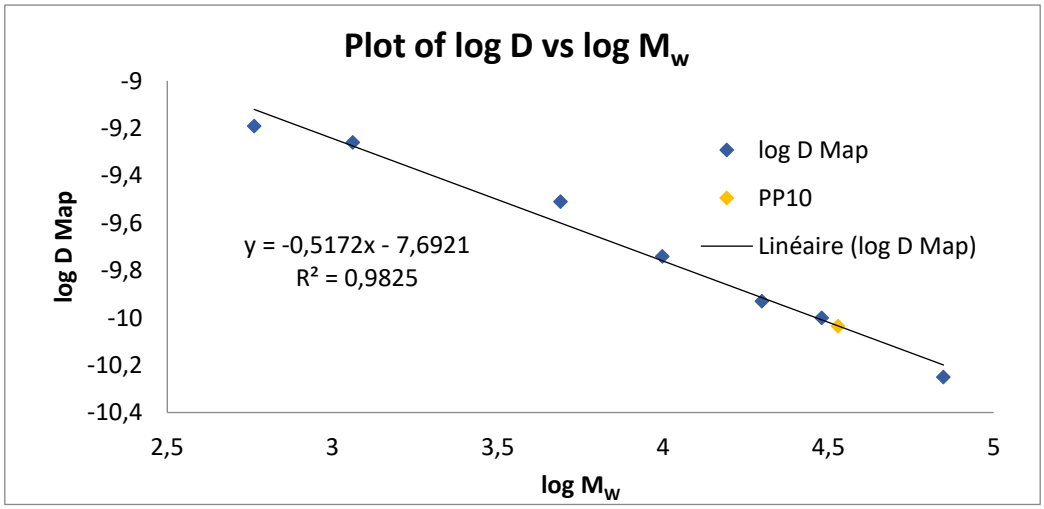

The reaction was conducted as per standard procedure, at 25 °C, with **A** (18 mg, 61.5 µmol), $PhSiH_3$ (652 mg, 6.02 mmol) and **C** (1.00 g, 6.09 mmol), catalysed by **1** (278 mg, 303 µmol, 10 mol-% loading in Ba).

Isolated yield after purification: 927 mg (56%).

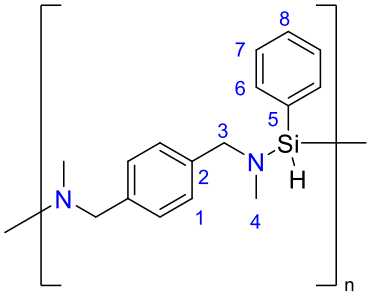
The NMR data for **Ter-PhCZ-7** are similar to those for **Ter-PhCZ-4** (see above and Figures S33-S36). Note however that most of the carbon signals of the phosphine phenyl rings are so weak they could be clearly assigned after 8000 scans on a concentrated sample.

**DOSY molecular weight determination**

log D = −10.03, D = 9.2298 ×$10^{-10}$ $m^2$ $s^{-1}$. Calculated $M_n$ = 33,853 g $mol^{-1}$.



**Co-PZ-8. 100:100 dehydropolymerisation of $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**




The reaction was conducted as per standard procedure, at 25 °C, with $PhSiH_3$ (329 mg, 3.04 mmol) and **C** (500 mg, 3.04 mmol), catalysed by **1** (139 mg, 152 µmol, 10 mol-% loading in Ba).
Isolated yield after purification: 450 mg (55%).

NMR spectra are provided below as Figures S37-S39.

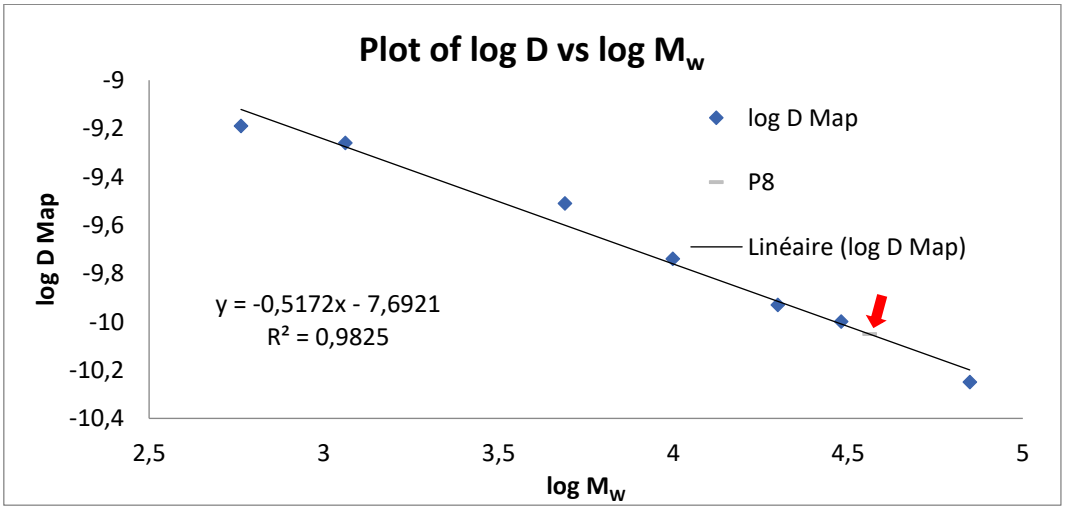
**$^1$H NMR** (500.13 MHz, [$D_6$]benzene, 300 K): δ 7.74 (m, 2H, $C_6$**H**); 7.29 (br s, 4H, $C_1$**H**); 7.22 (m, 3H, $C_7$**H** + $C_8$**H**); 5.41 (s, $^1J_{HSi}$ = 220 Hz, 1H, Si**H**); 4.06 (m, 4H, $C_3$**H**); 2.49 (s, 6H, $C_4$**H**) 2.21 (m, $C_4$**H** terminal) ppm.

**$^{13}$C{$^1$H} NMR** (125.77 MHz, [$D_6$]benzene, 300 K): δ 139.53 (**C**$_2$); 136.41 (**C**$_5$); 135.11(**C**$_6$); 130.17 (**C**$_8$); 128.44 (**C**$_7$); 128.28 (**C**$_1$, obscured by solvent signal); 54.51 (**C**$_3$); 34.38 (**C**$_4$) ppm.

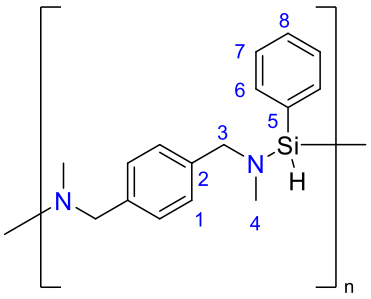
**$^{29}$Si{$^1$H} INEPT NMR** (79.46 MHz, [$D_6$]benzene, 300 K): δ – 14.78 ppm

**DOSY molecular weight determination**

log D = −10.05, D = 8.88783 ×$10^{-10}$ $m^2$ $s^{-1}$. Calculated $M_n$ = 36,417 g $mol^{-1}$.



**Co-PZ-9. 100:80 dehydropolymerisation of $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**

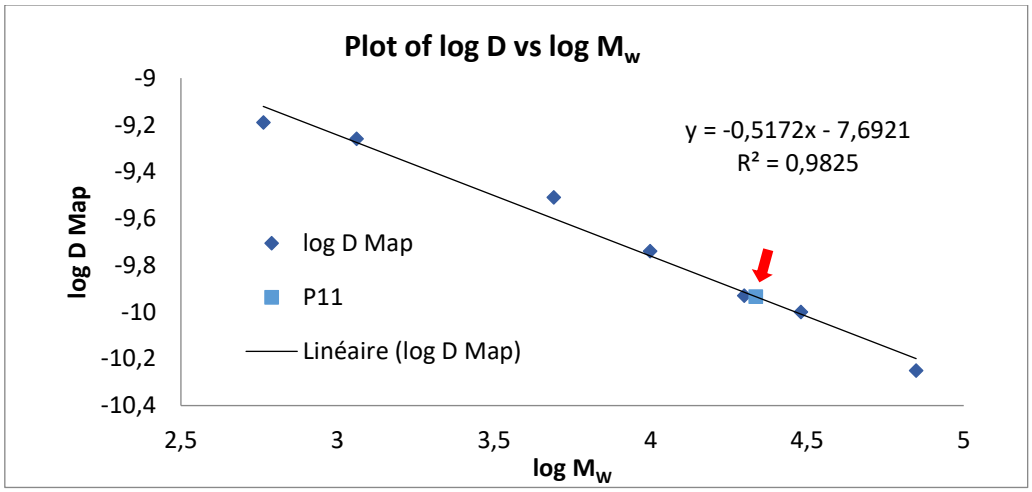



The reaction was conducted as per standard procedure, at 25 °C, with $PhSiH_3$ (632 mg, 5.84 mmol) and **C** (800 mg, 4.87 mmol), catalysed by **1** (22.3 mg, 24.3 µmol, 1 mol-% loading in Ba).
Isolated yield after purification: 740 mg (56%).

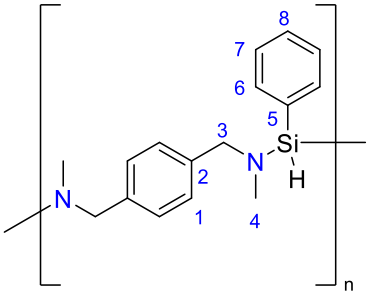
The NMR data for **Co-PZ-9** are identical to those for **Co-Pz-8** (see Figures S37-S39 below).

**DOSY molecular weight determination**

log D = −9.93, D = 1.16267 ×$10^{-10}$ $m^2$ $s^{-1}$. Calculated $M_n$ = 21,664 g $mol^{-1}$.



**Co-PZ-10. 80:100 dehydropolymerisation of $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**

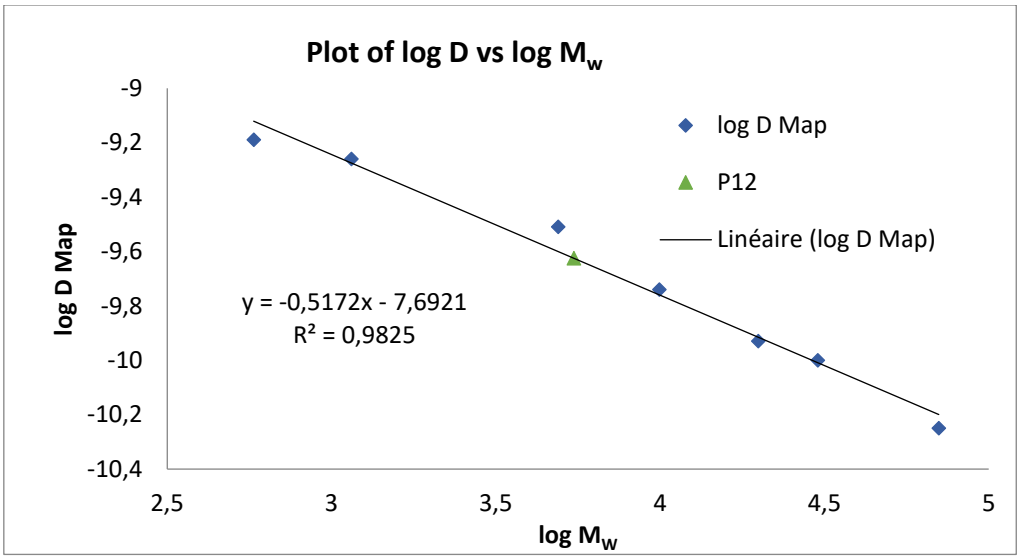



The reaction was conducted as per standard procedure, at 25 °C, with $PhSiH_3$ (527 mg, 4.87 mmol) and **C** (960 mg, 5.84 mmol), catalysed by **1** (22.3 mg, 24.3 µmol, 1 mol-% loading in Ba).
Isolated yield after purification: 200 mg (15%).

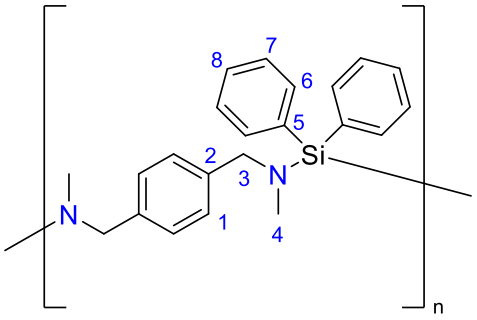
The NMR data for **Co-PZ-10** are identical to those for **Co-Pz-8** (see Figures S37-S39 below).

**DOSY molecular weight determination**

log D = −9.63, D = 2.37083 ×$10^{-10}$ $m^2$ $s^{-1}$. Calculated $M_n$ = 5463 g $mol^{-1}$.



**Co-PZ-11. 100:100 dehydropolymerisation of $Ph_2SiH_2$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (C)**




The reaction was conducted as per standard procedure, at 25 °C, with $Ph_2SiH_2$ (921 mg, 5.00 mmol) and **C** (821 mg, 5.00 mmol), catalysed by **1** (229 mg, 250 µmol, 10 mol-% loading in Ba).

Isolated yield after purification: 1.06 g (62%).

NMR spectra are provided below as Figures S40-S42.

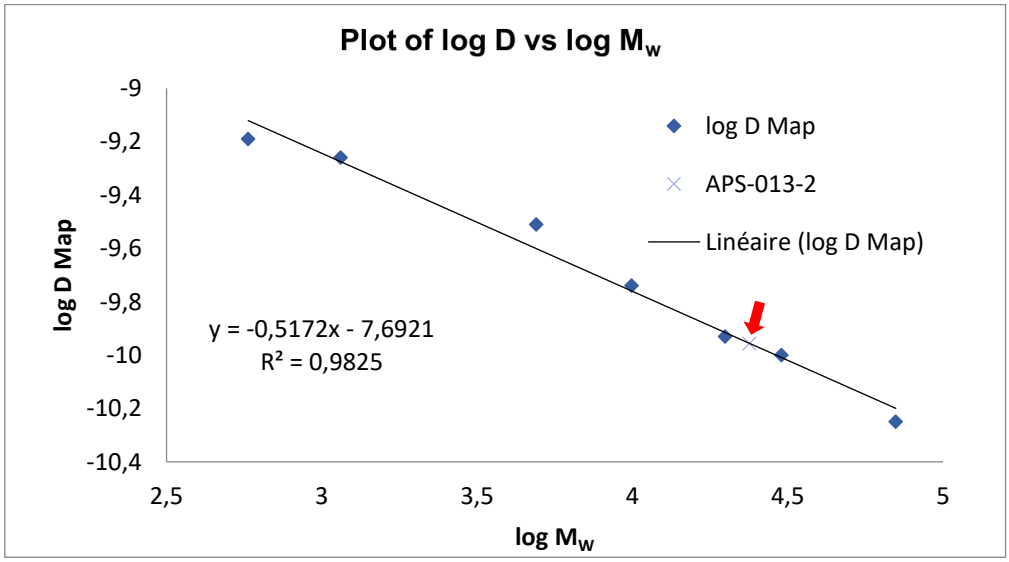
**$^1$H NMR** (500.13 MHz, [$D_6$]benzene, 300 K): δ 7.83 (m, 4H, $C_6$**H**); 7.32 (br s, 4H, $C_1$**H**); 7.21 (m, 6H, $C_7$**H** + $C_8$**H**); 4.14 (s, 4H, $C_3$**H**); 2.60 (s, 6H, $C_4$**H**) ppm.

**$^{13}$C{$^1$H} NMR** (125.77 MHz, [$D_6$]benzene, 300 K): δ 139.60 (**C**$_2$); 136.26 (**C**$_5$); 136.15 (**C**$_6$); 129.84 (**C**$_8$); 128.62 (**C**$_7$); 128.36 (**C**$_1$); 54.79 (**C**$_3$); 35.66 (**C**$_4$) ppm.

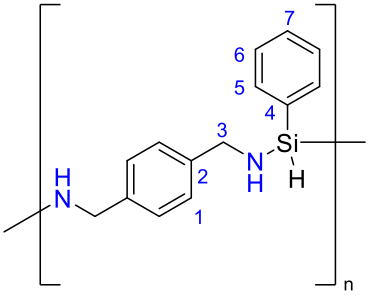
**$^{29}$Si{$^1$H} {INEPT} NMR** (79.46 MHz, [$D_6$]benzene): δ –15.97 ppm

**DOSY molecular weight determination**

log D = −9.96, D = 1.1064 ×$10^{-10}$ $m^2$ $s^{-1}$. Calculated $M_n$ = 23,845 g $mol^{-1}$.



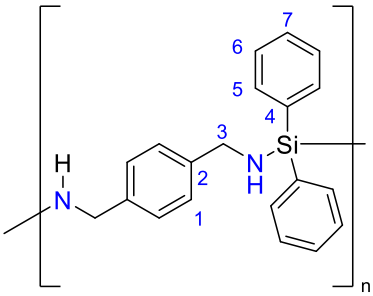
**Co-PZ-12. 100:100 dehydropolymerisation of $PhSiH_3$ and 1,4-$(CH_2NH_2)_2$-$C_6H_4$**



The reaction was conducted as per standard procedure, at 25 °C, with $PhSiH_3$ (329 mg, 3.83 mmol) and 1,4-$(CH_2NH_2)_2$-$C_6H_4$ (520 mg, 3.82 mmol), catalysed by **1** (175 mg, 191 µmol, 10 mol-% loading in Ba). Isolated yield after work-up: 808 mg (96%).

The insolubility of this polymer in available solvents ([$D_8$]thf. [$D_8$]toluene, [$D_6$]benzene, [$D_2$]methylene chloride, [$D_1$]chloroform, [D6]DMSO, [D6]acetone, [D4]methanol) precluded its characterisation in solution and DOSY molecular weight estimation.

**Co-PZ-13. 100:100 dehydropolymerisation of $Ph_2SiH_2$ and 1,4-$(CH_2NH_2)_2$-$C_6H_4$**



The reaction was conducted as per standard procedure, at 25 °C, with $Ph_2SiH_2$ (735 mg, 3.99 mmol) and 1,4-$(CH_2NH_2)_2$-$C_6H_4$ (545 mg, 4.00 mmol), catalysed by **1** (183 mg, 200 µmol, 10 mol-% loading in Ba).
Isolated yield after work-up: 1.20 g (94%).

The insolubility of this polymer in available solvents ([$D_8$]thf. [$D_8$]toluene, [$D_6$]benzene, [$D_2$]methylene chloride, [$D_1$]chloroform, [D6]DMSO, [D6]acetone, [D4]methanol) precluded its characterisation in solution and DOSY molecular weight estimation.

**Crystallographic data**

| Compound | Compound label | Experiment number | CCDC number |
|---|---|---|---|
| 4-$Ph_2P$-$C_6H_4CH_2NHSiPh_3$ | n/a | PC04160 | 2384912 |
| 4-$Ph_2P$-$C_6H_4SiH_3$ | **A** | 0138alb | 2384976 |

**4-$Ph_2P$-$C_6H_4CH_2NHSiPh_3$** ($C_{37}H_{32}NPSi$); $M$ = 549.69 g mol$^{-1}$. A suitable crystal for X-ray diffraction single crystal experiment (colourless plate, dimensions = 0.550 × 0.420 × 0.100 mm) was selected and mounted on the goniometer head of a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-$K\alpha$ radiation ($\lambda$ = 0.71073 Å, multilayer monochromator) at $T$ = 150 K. The crystal structure was described in triclinic symmetry and $P$-1 (I.T.#2) space group. Cell parameters have been refined as follows: $a$ = 9.4488(11), $b$ = 17.913(2), $c$ = 17.982(2) Å, $\alpha$ = 89.561(5), $\beta$ = 79.782(5), $\gamma$ = 83.183(4) °, $V$ = 2973.8(6) Å$^3$. The number of formula unit $Z$ is equal to 4 and the calculated density $d$ and absorption coefficient $\mu$ values are 1.228 g cm$^{-3}$ and 0.159 mm$^{-1}$ respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,[10] and then refined with full-matrix least-squares methods based on $F^2$ (*SHELXL*).[11] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on $F^2$ with 11213 unique intensities and 578 parameters converged at $\omega R_F^2$ = 0.3788 ($R_F$ = 0.1424) for 9426 observed reflections with $I > 2\sigma(I)$.

**4-$Ph_2P$-$C_6H_4SiH_3$** ($C_{18}H_{17}PSi$); $M$ = 292.37 g mol$^{-1}$. A suitable crystal for X-ray diffraction single crystal experiment (colourless block, dimensions = 0.196 × 0.125 × 0.020 mm) was selected and mounted using a MiTeGen MicroMount loop, on the goniometer head of a D8 VENTURE Bruker AXS dual source diffractometer equipped with a (CPAD) PHOTON II detector, using Mo-$K\alpha$ radiation from an IμS 3.0 source ($\lambda$ = 0.71073 Å, multilayer optics) at $T$ = 100 K. The crystal structure was solved in monoclinic symmetry and $P2_1/n$ (I.T.#14) space group. Cell parameters have been refined as follows: $a$ = 10.8294(9), $b$ = 8.7426(7), $c$ = 16.9192(10) Å, $\alpha$ = 90, $\beta$ = 91.869(3), $\gamma$ = 90 °, $V$ = 1601.0(2) Å$^3$. The number of formula unit $Z$ is equal to 4 and the calculated density $d$ and absorption coefficient $\mu$ values are 1.213 g cm$^{-3}$ and 0.234 mm$^{-1}$ respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,[10] and then refined with full-matrix least-squares methods based on $F^2$ (*SHELXL*)[11] within the APEX5 software suite.[12] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters, except for the hydrogen atoms bonded to Si, which were found from the Fourier difference electron density map and their thermal parameters were freely refined. The residual bond electron densities were modelled using the IDEAL (Invariom Derived Electron Analysis)[13] plugin within the APEX5 software suite. The final

refinement on $F^2$ with 3981 unique intensities and 196 parameters converged at w$R_F^2$ = 0.0541 ($R_F$ = 0.0213) for 3654 observed reflections with $I > 2\sigma(I)$.

## References


1 PCT Int. Appl., 2015, WO 2015030071 A1 Mar 05, 2015.

2 Y-Y. Huang, H-L. Zhang, G-J. Deng, W-J. Tang, X-Y. Wang, Y-M. He and Q-H. Fan, *J. Mol. Catal. A: Chem.*, 2005, **227**, 91.

3 K. Izod, J. Stewart, E. R. Clark, W. McFarlane, B. Allen, W. Clegg and R. W. Harrington, *Organometallics*, 2009, **28**, 3327–3337.

4 R. C. Larock, *Comprehensive Organic Transformations - A Guide to Functional Group Preparations*, 2nd edition, page 876, 1999, Wiley-VCH.

5 M. Westerhausen, *Inorg. Chem.*, 1991, **30**, 96.

6 W. Li, H. Chung, C. Daeffler, J. A. Johnson and R. H. Grubbs, *Macromolecules*, 2012, **45**, 9595.

7 a) C. Bellini, J.-F. Carpentier, S. Tobisch and Y. Sarazin, *Angew. Chem. Int. Ed.*, 2015, **54**, 7679; *Angew. Chem.*, 2015, **127**, 7789. b) C. Bellini, V. Dorcet, J.-F. Carpentier, S. Tobisch and Y. Sarazin, *Chem. Eur. J.*, 2016, **22**, 4564.

8 L. J. Morris, G. R. Whittell, J.-C. Eloi, M. F. Mahon, F. Marken, I. Manners and M. S. Hill, *Organometallics*, 2019, **38**, 3629.

9 C. Huggett, *Fire Mater.*, 1980, **4**, 61.

10 G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3.

11 G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3.

12 APEX5, Bruker AXS Inc., Madison, Wisconsin, USA, 2023.

13 J. Lübben, C. M. Wandtke, C. B. Hübschle, M. Ruf, G. M. Sheldrick and B. Dittrich, *Acta Crystallogr. A*, 2019, **75**, 50.


## Author contributions

P. M. Chapple and A. Soran performed synthetic experimental work and data analysis, and assisted in the writing of the draft. participated to the design of experiments and analysis of experimental data. C. Longuet and R. Sonnier conducted the analysis of polymer properties, and participated to the preparation of the manuscript. J.-F. Carpentier and Y. Sarazin secured the funding, participated to the design of experiments, analysis of experimental data and writing of the draft.

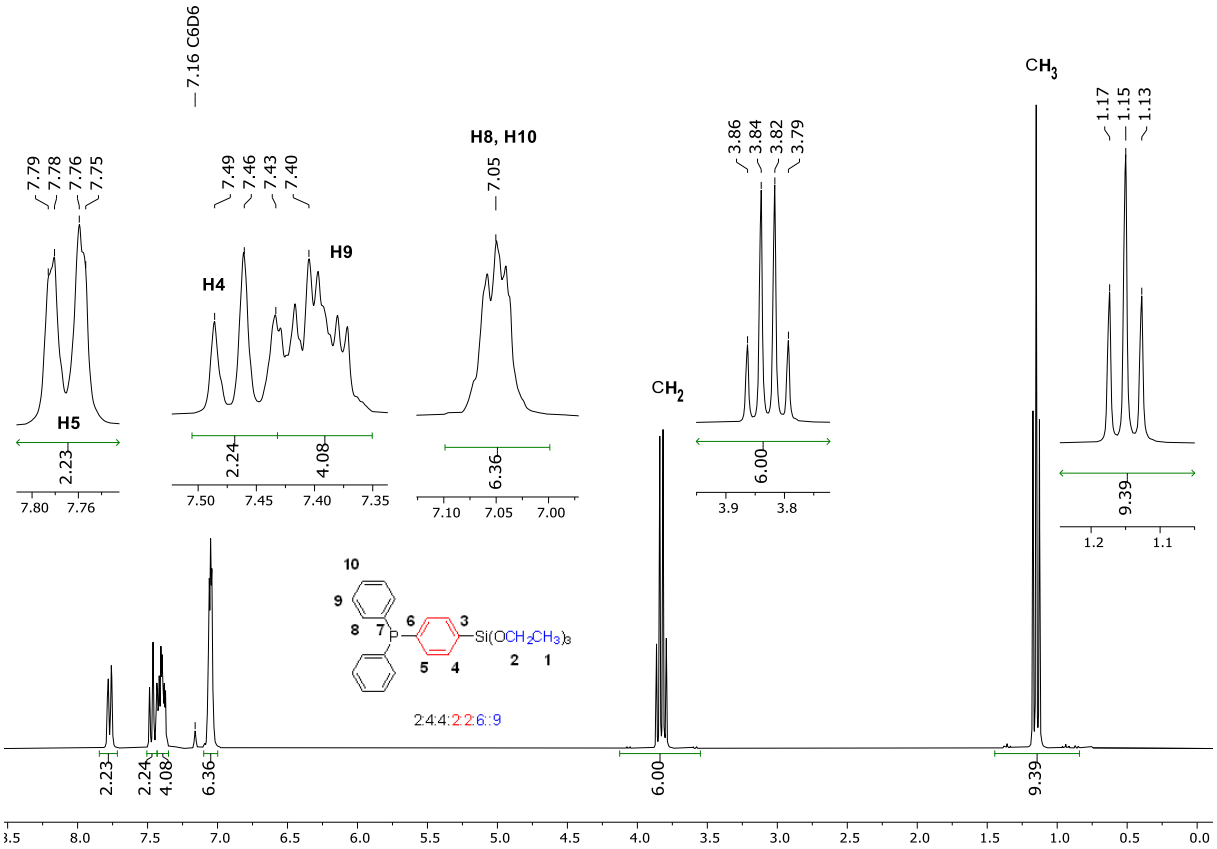



**Figure S6.** $^{1}H$ NMR spectrum ([$D_6$]benzene, 300.13 MHz, 298 K) of $Ph_2P(p\text{-}Si(OEt_3)_3C_6H_4)$.

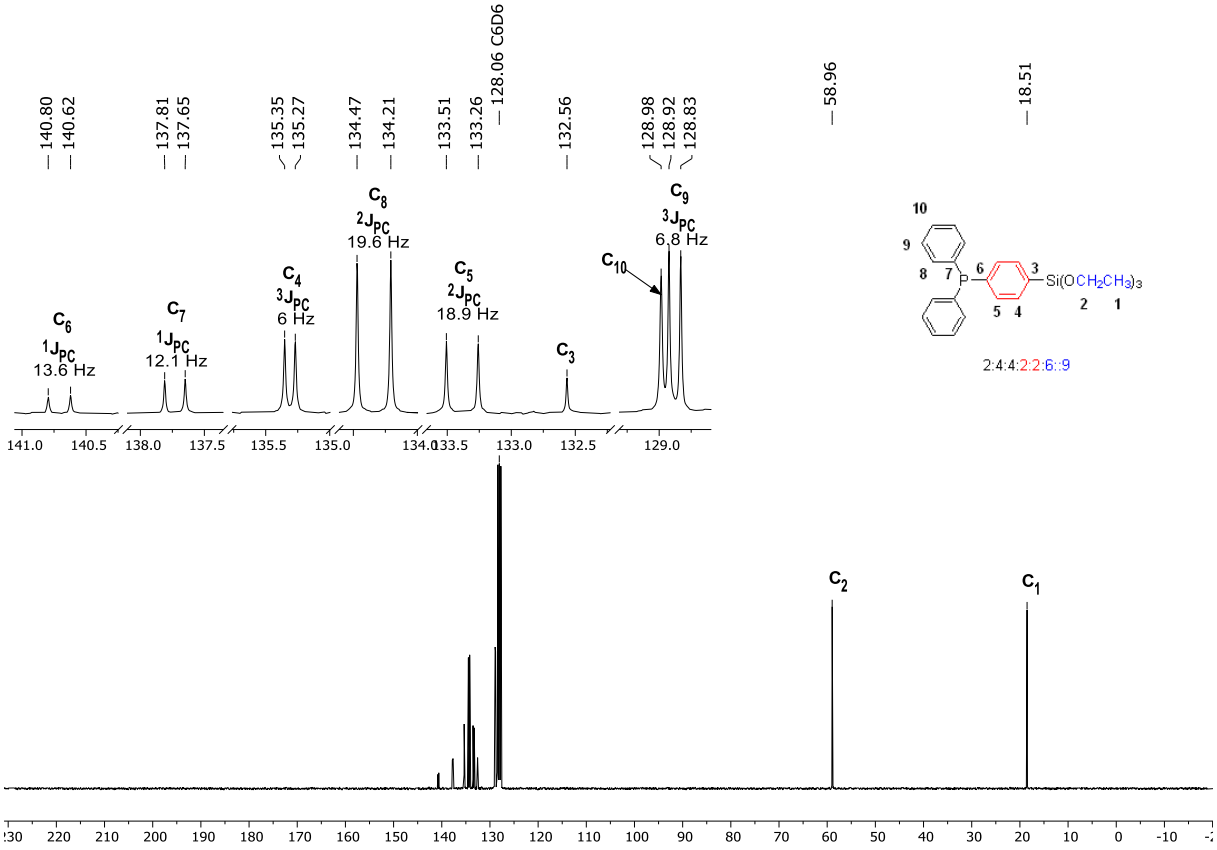



**Figure S7.** $^{13}C\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 75.48 MHz, 298 K) of $Ph_2P(p\text{-}Si(OEt_3)_3C_6H_4)$.

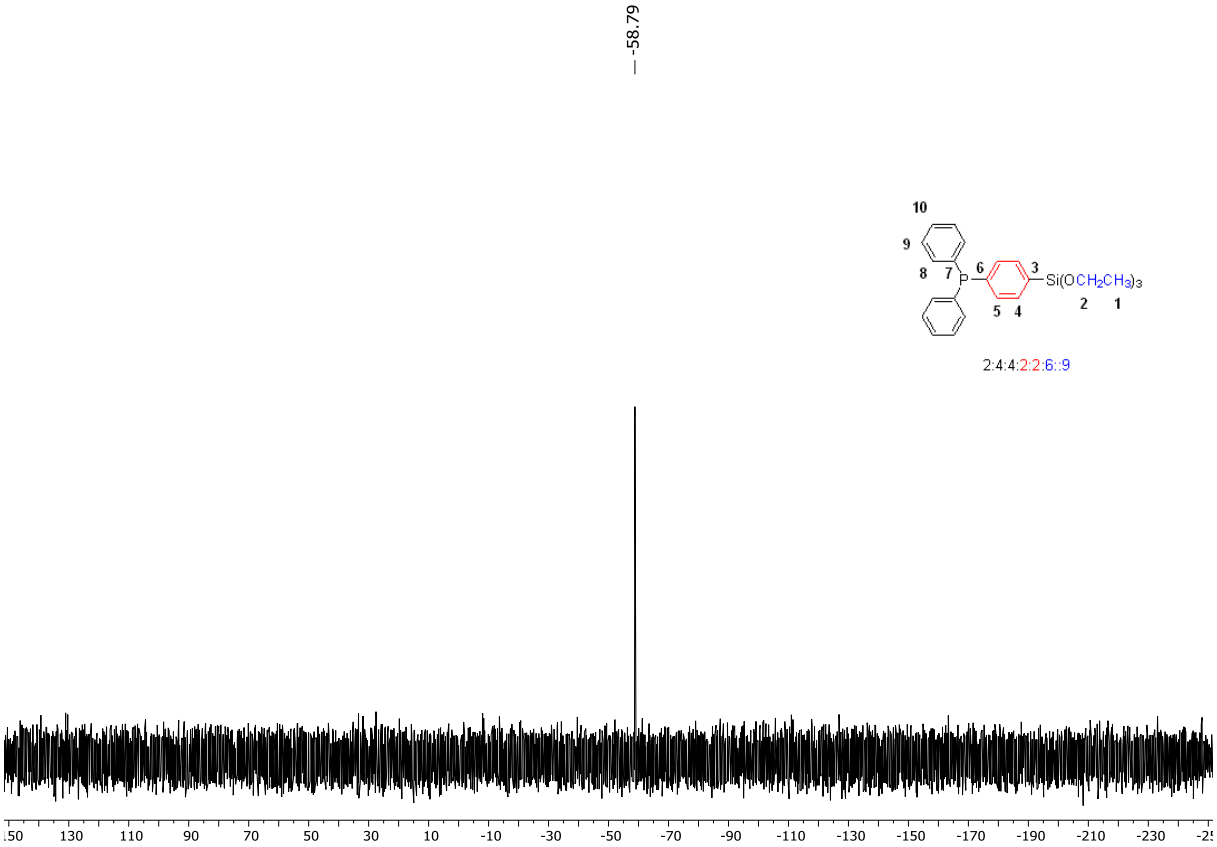



**Figure S8.** $^{29}Si\{^{1}H\}$ INEPT NMR spectrum ([$D_6$]benzene, 79.49 MHz, 302 K) of $Ph_2P(p\text{-}Si(OEt_3)_3C_6H_4)$.

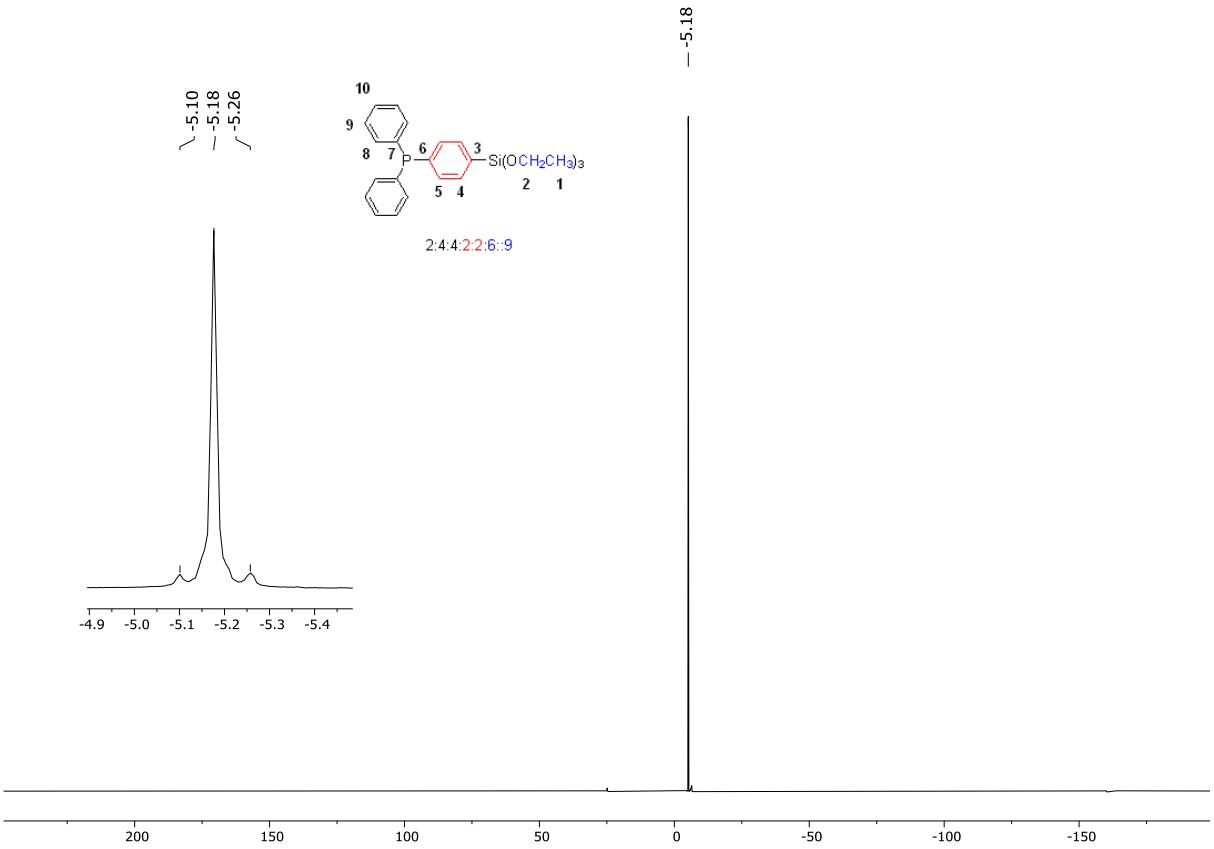



**Figure S9.** $^{31}P\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 121.50 MHz, 298 K) of $Ph_2P(p\text{-}Si(OEt_3)_3C_6H_4)$.

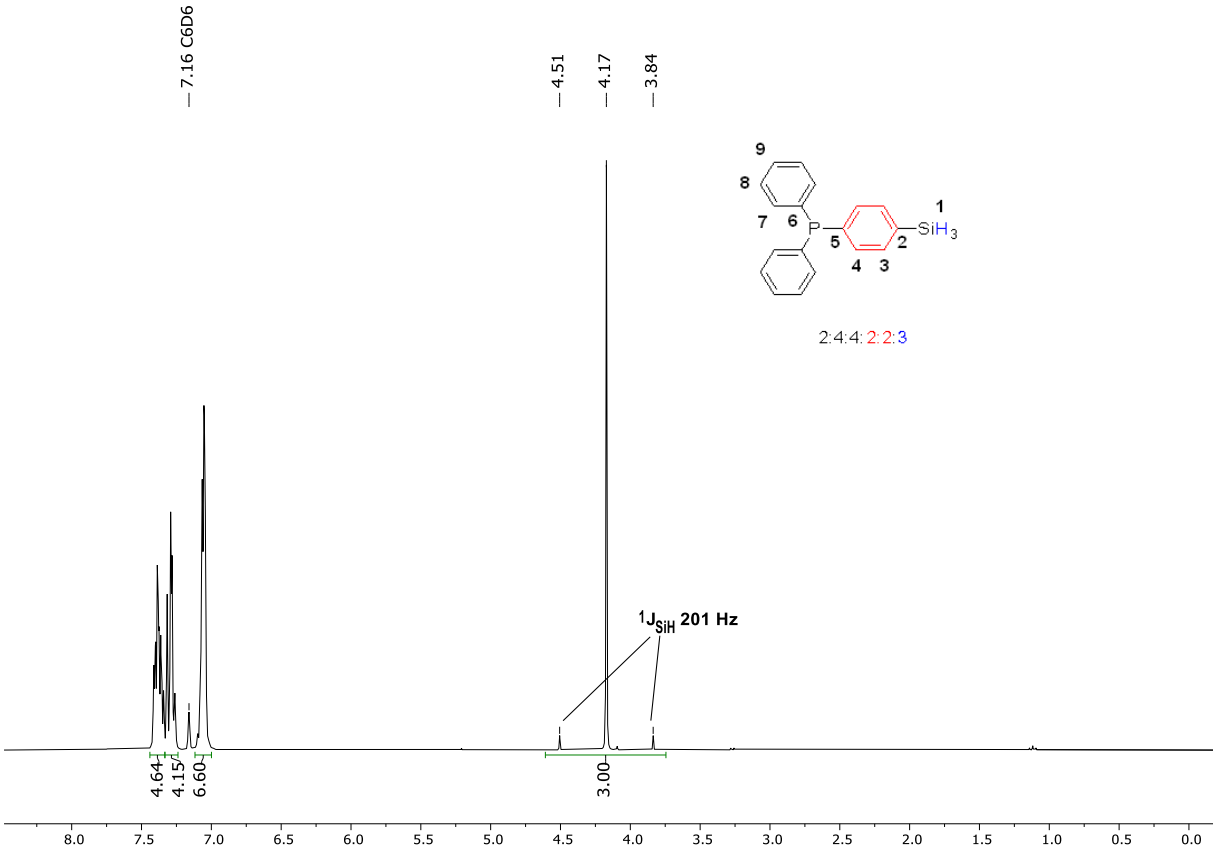



**Figure S10.** $^{1}$H NMR spectrum ([$D_6$]benzene, 300.13 MHz, 299 K) of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**).

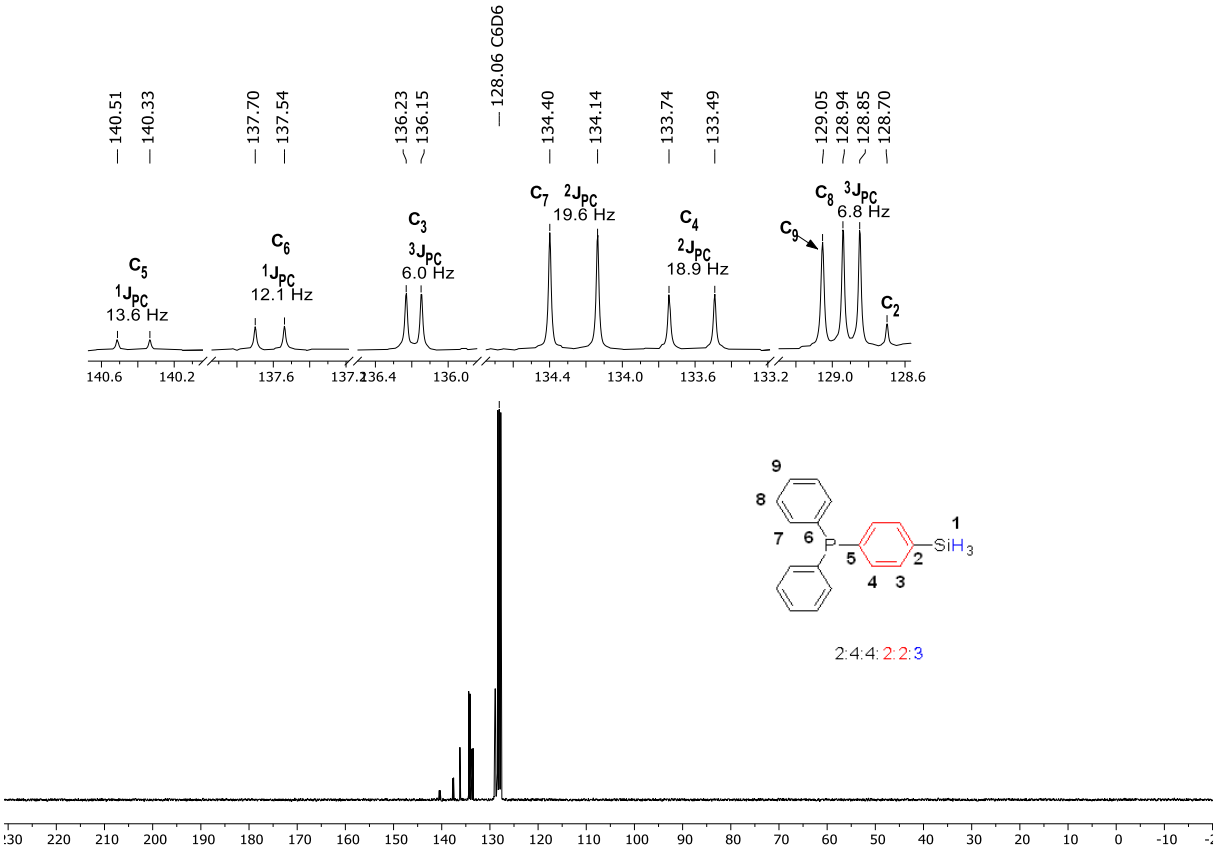



**Figure S11.** $^{13}C\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 75.48 MHz, 299 K) of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**).

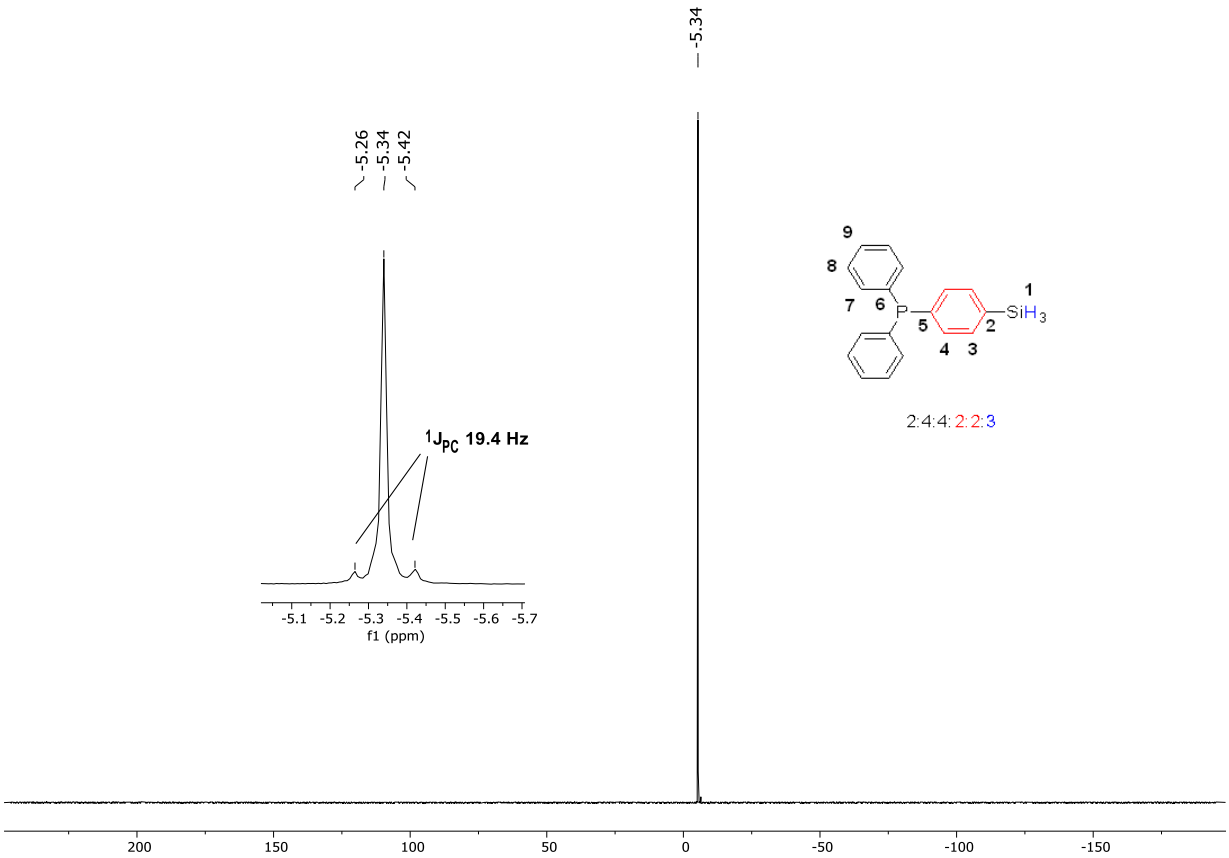



**Figure S12.** $^{31}P\{^1H\}$ NMR spectrum ([$D_6$]benzene, 121.50 MHz, 300 K) of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**).

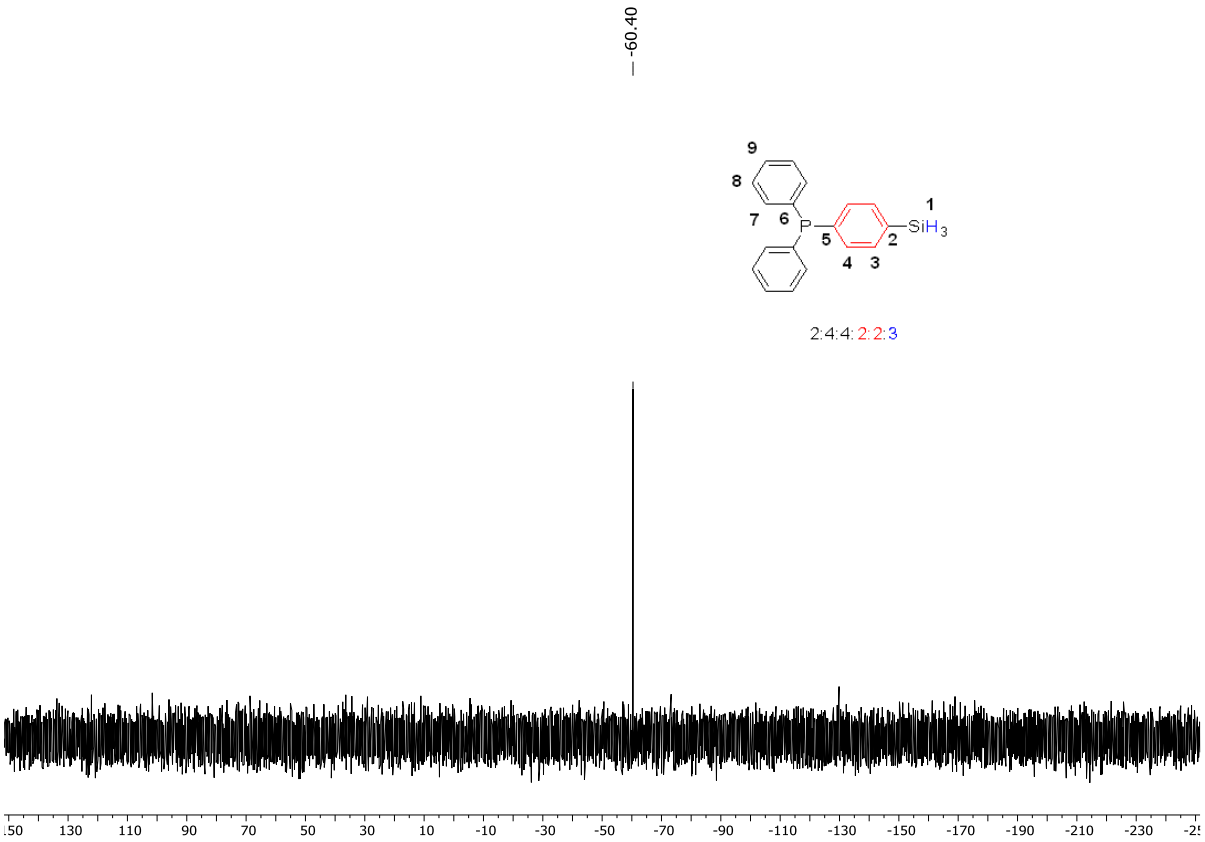



**Figure S13.** $^{29}Si\{^{1}H\}$ INEPT NMR spectrum ([$D_6$]benzene, 79.49 MHz, 302 K) of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**).

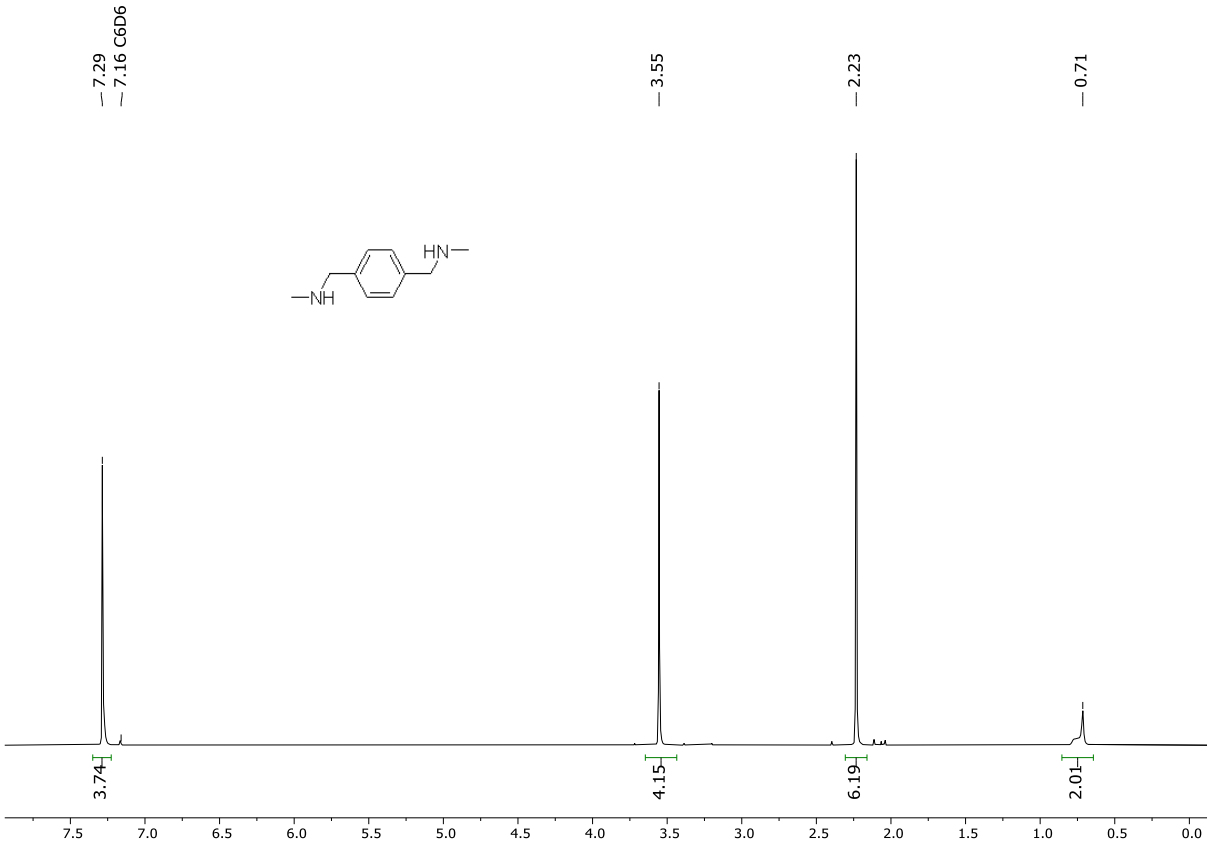



**Figure S14.** $^{1}$H NMR spectrum ([$D_6$]benzene, 400.13 MHz, 298 K) of 1,4-($CH_2NHMe)_2$-$C_6H_4$ (**C**).

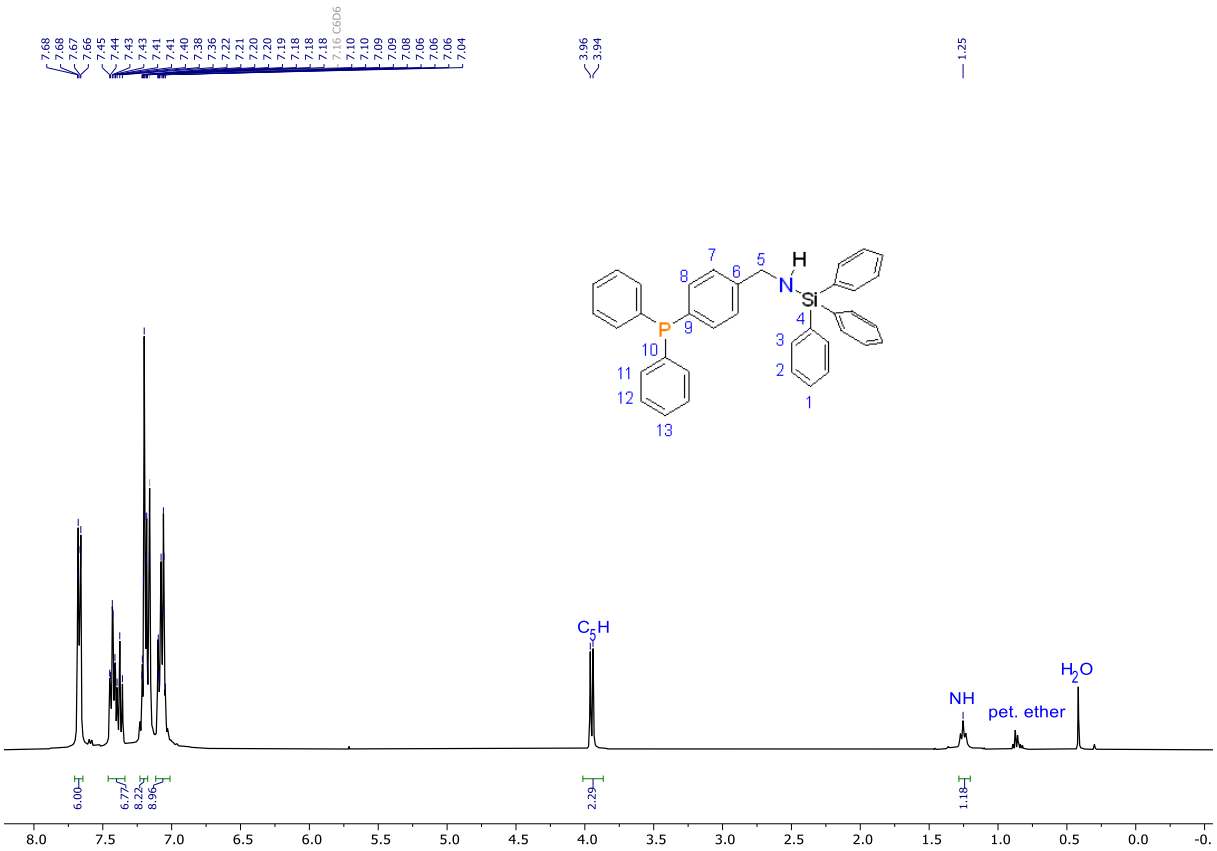



**Figure S15.** $^{1}$H NMR spectrum ([$D_6$]benzene, 400.16 MHz, 298 K) of 4-$Ph_2P$-$C_6H_4CH_2NHSiPh_3$.

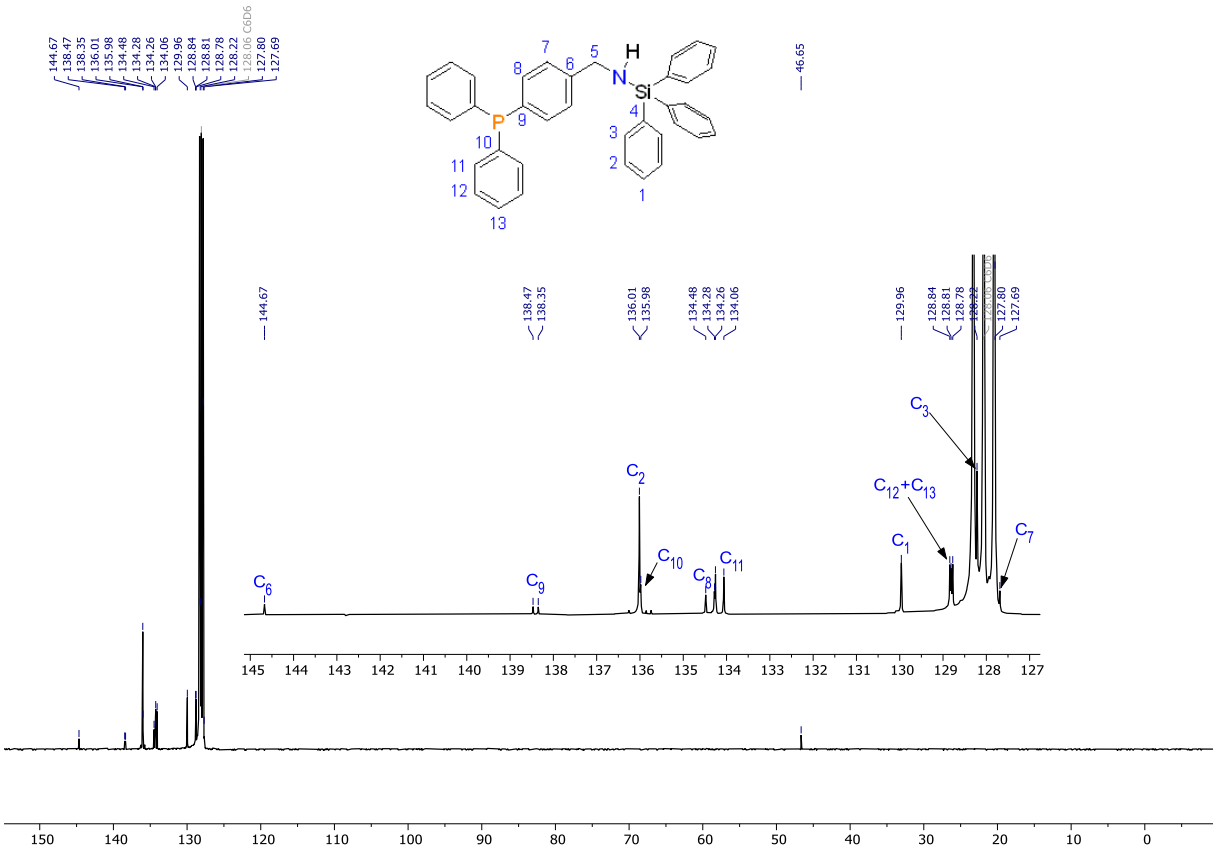



**Figure S16.** $^{13}C\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 100.63 MHz, 298 K) of 4-$Ph_2P$-$C_6H_4CH_2NHSiPh_3$.

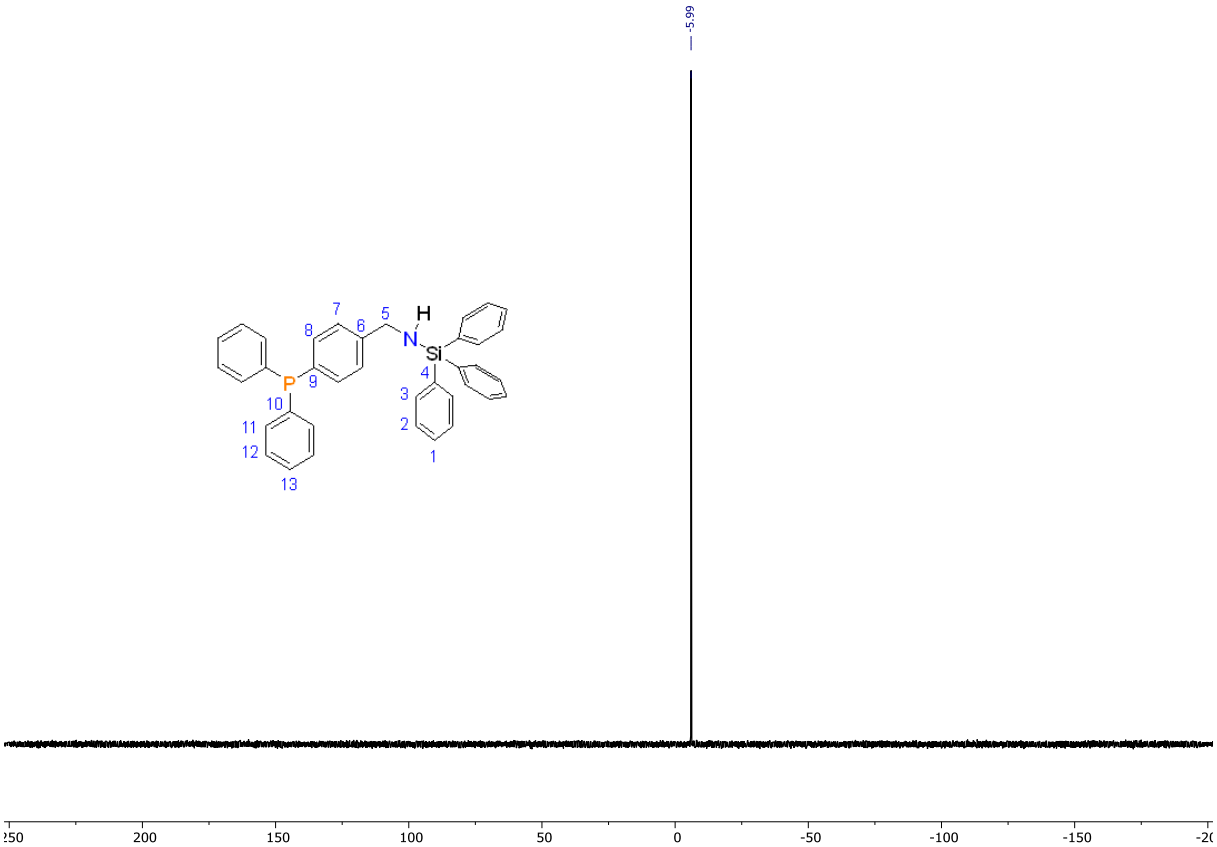



**Figure S17.** $^{31}P\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 161.99 MHz, 298 K) of 4-$Ph_2P$-$C_6H_4CH_2NHSiPh_3$.

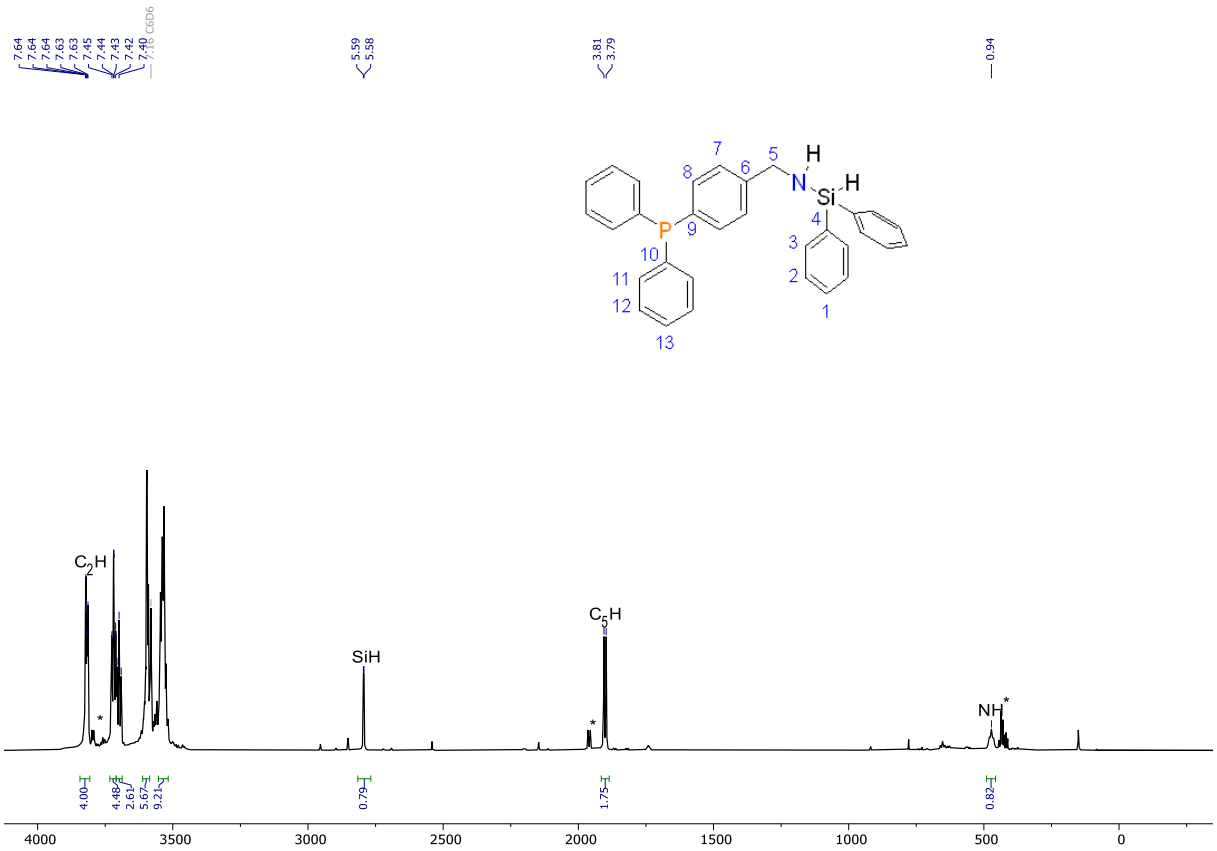



**Figure S18.** $^{1}$H NMR spectrum ([$D_6$]benzene, 500.13 MHz, 300 K) of 4-$Ph_2P$-$C_6H_4CH_2NHSiPh_2H$. The final product is contaminated by another compound assumed to be [(4-$Ph_2P$-$C_6H_4CH_2$)$NSiPh_2$]$_2$ (*).

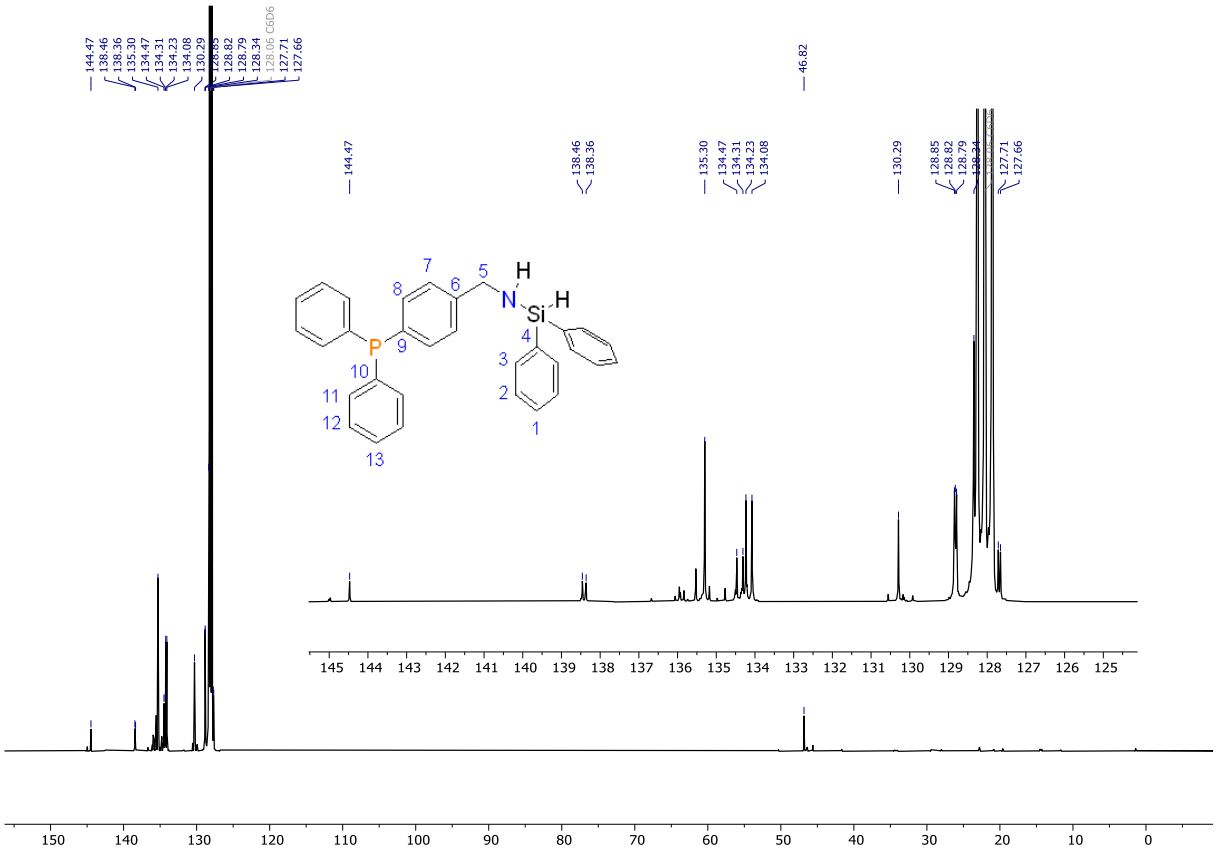



**Figure S19.** $^{13}C\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 125.77 MHz, 300 K) of 4-$Ph_2P$-$C_6H_4CH_2NHSiPh_2H$.

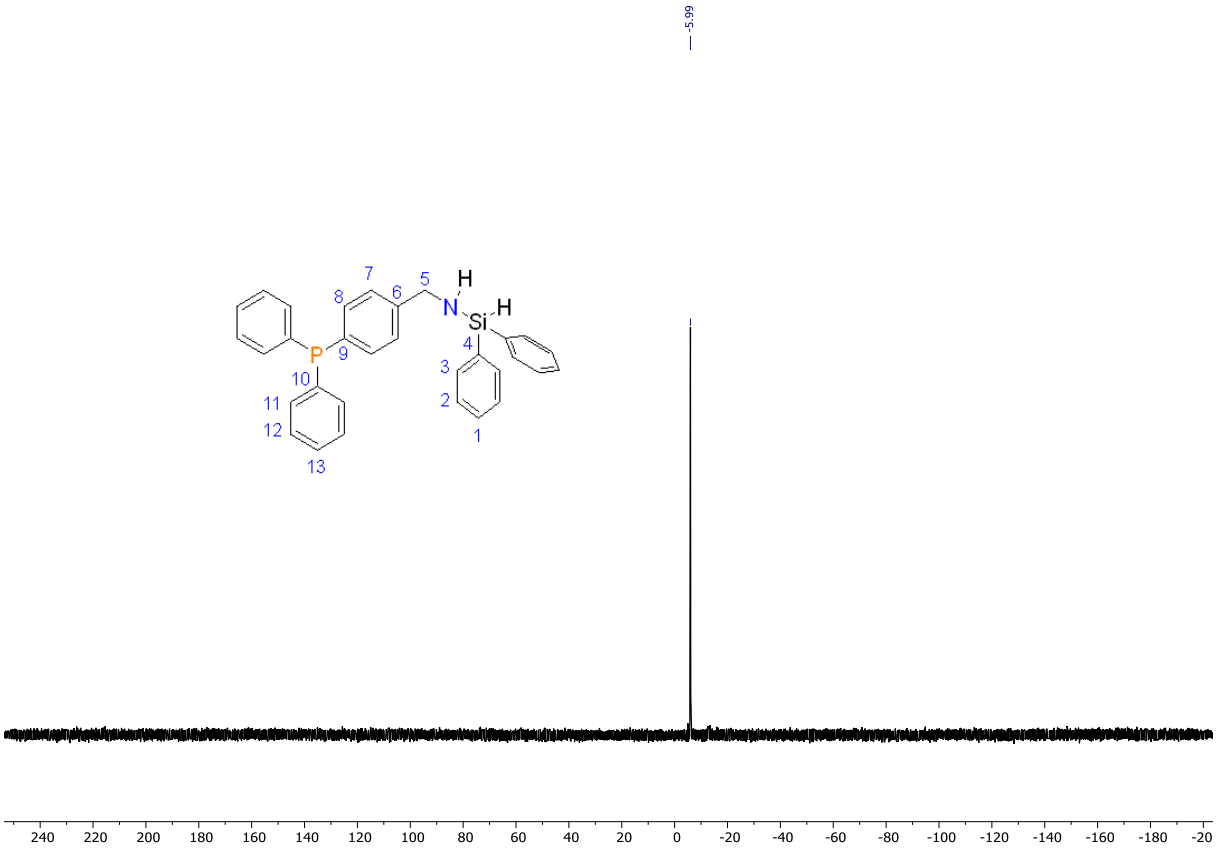



**Figure S20.** $^{31}P\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 202.46 MHz, 300 K) of 4-$Ph_2P$-$C_6H_4CH_2NHSiPh_2H$.

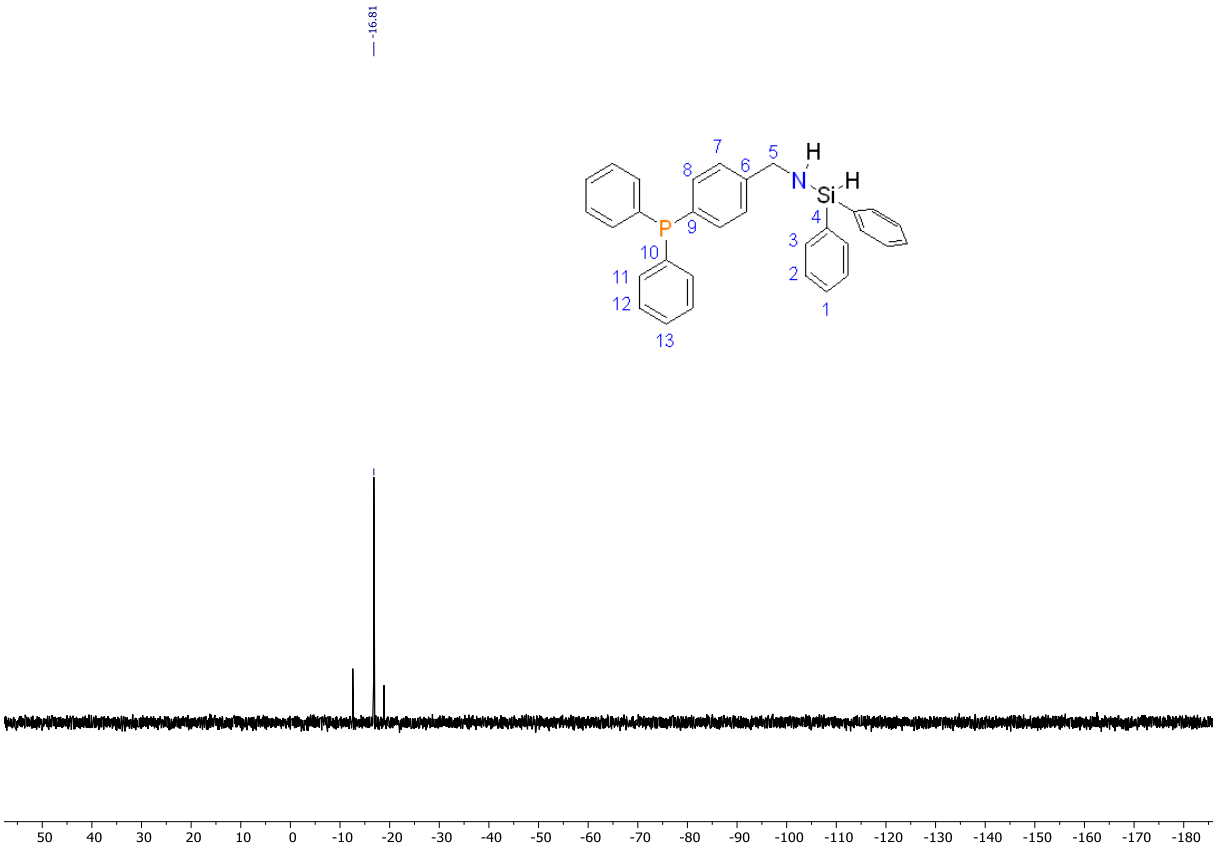



**Figure S21.** $^{29}Si\{^{1}H\}$ INEPT NMR spectrum ([$D_6$]benzene, 79.49 MHz, 298 K) of 4-$Ph_2P$-$C_6H_4CH_2NHSiPh_2H$.

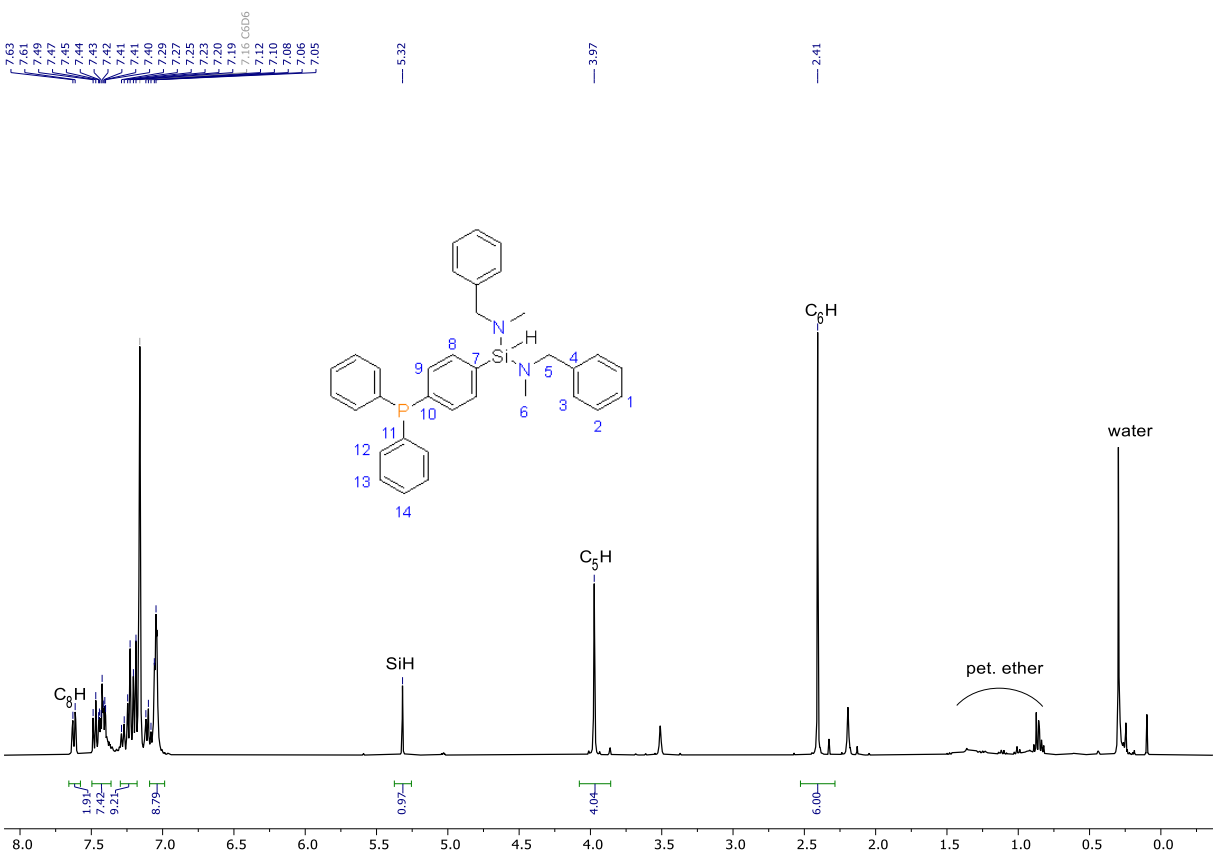



**Figure S22.** $^{1}H$ NMR spectrum ([$D_6$]benzene, 400.16 MHz, 298 K) of 4-$PPh_2$-$C_6H_4SiH\{N(Me)CH_2Ph\}_2$.

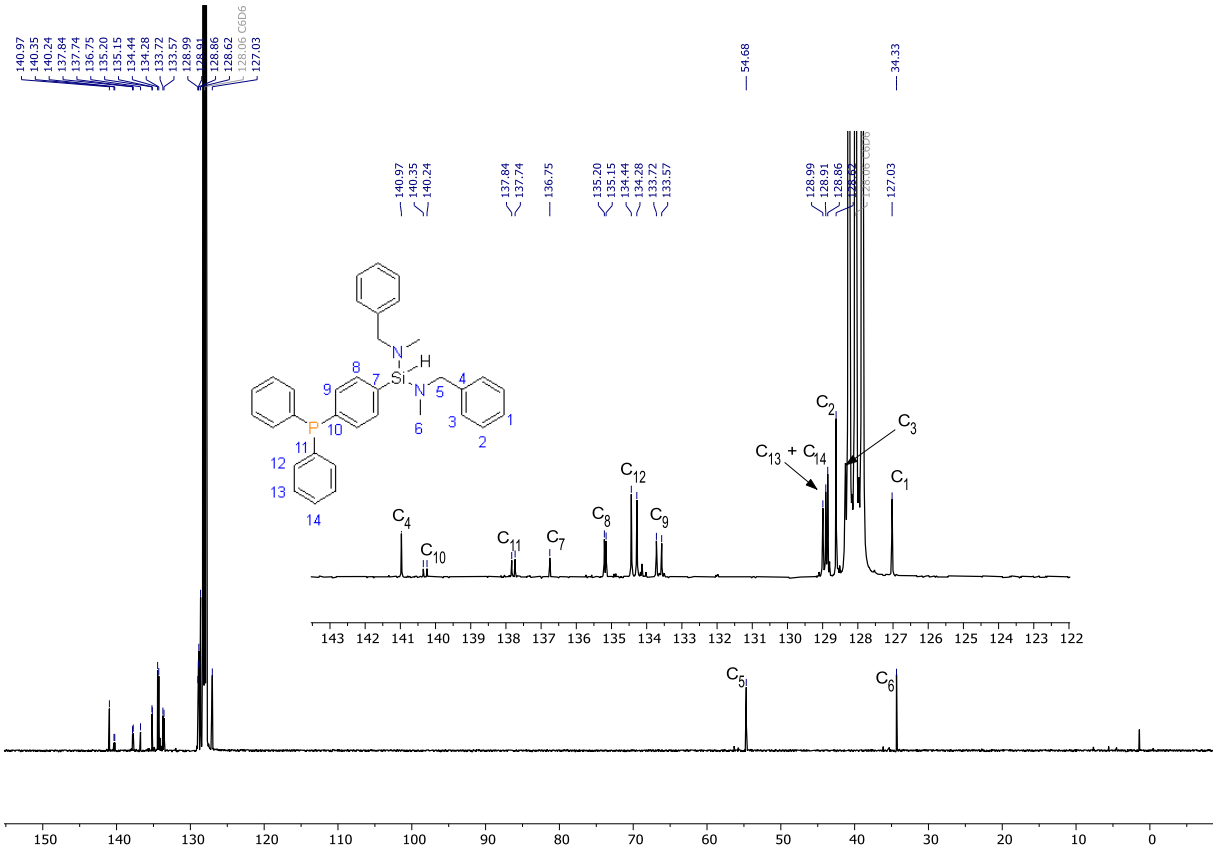



**Figure S23.** $^{13}C\{^{1}H\}$ NMR spectrum of 4-$PPh_2$-$C_6H_4SiH\{N(Me)CH_2Ph\}_2$ ([$D_6$]benzene, 125.77 MHz, 300 K).

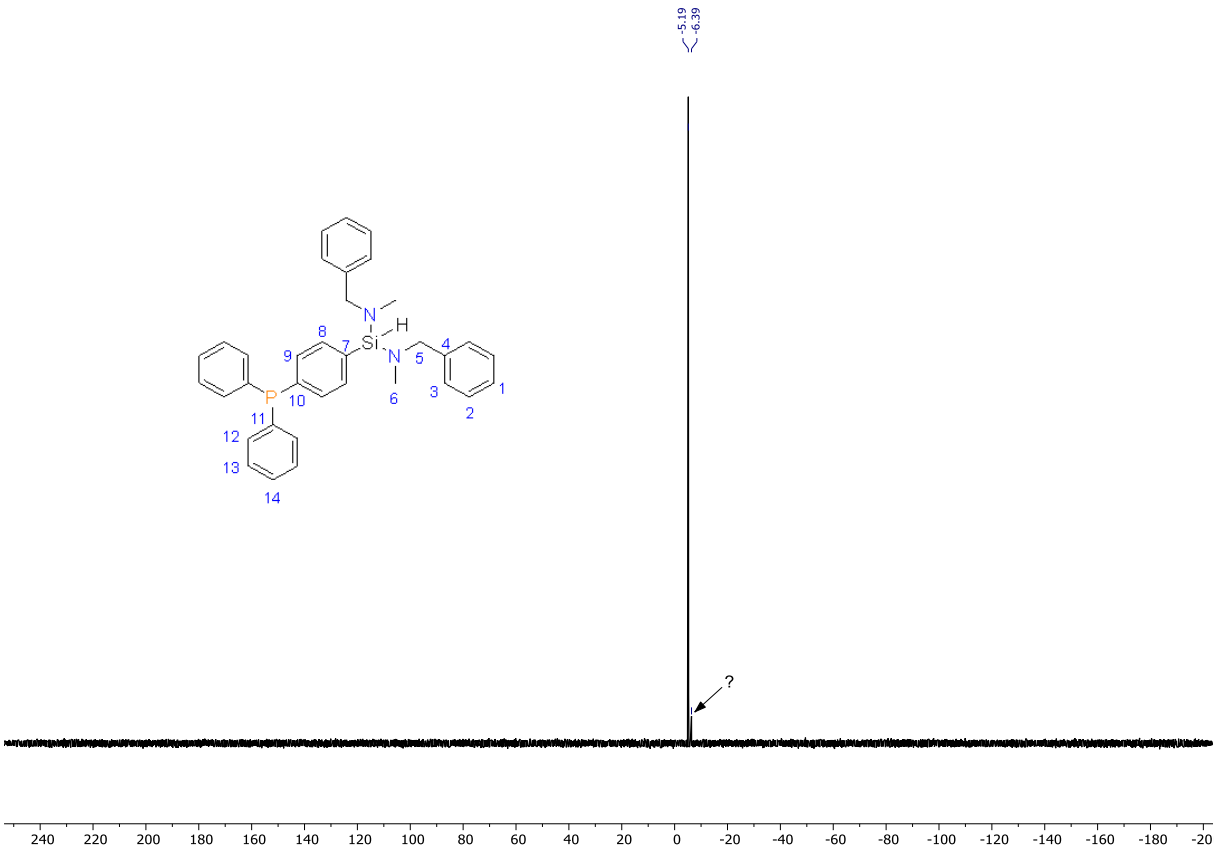



**Figure S24.** $^{31}P\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 202.46 MHz, 300 K) of 4-$PPh_2$-$C_6H_4SiH\{N(Me)CH_2Ph\}_2$. The minor impurity at $\delta_P$ –6.39 ppm could not be identified.

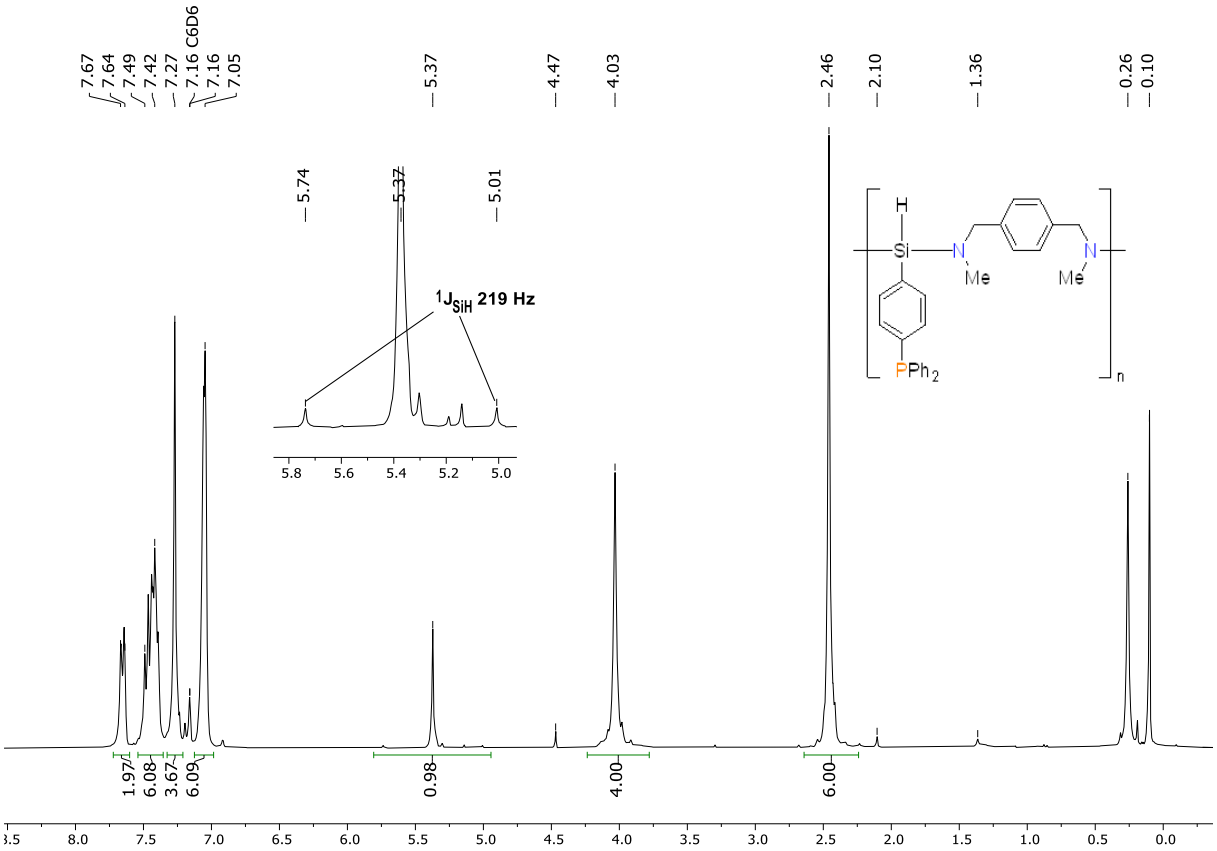



**Figure S25.** $^1$H NMR spectrum ([$D_6$]benzene, 300.13 MHz, 298 K) of **co-PhPZ-0**, product of the 1:1 dehydropolymerisation of 4-$Ph_2$P-$C_6H_4SiH_3$ (**A**) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (7.5 mol-%).

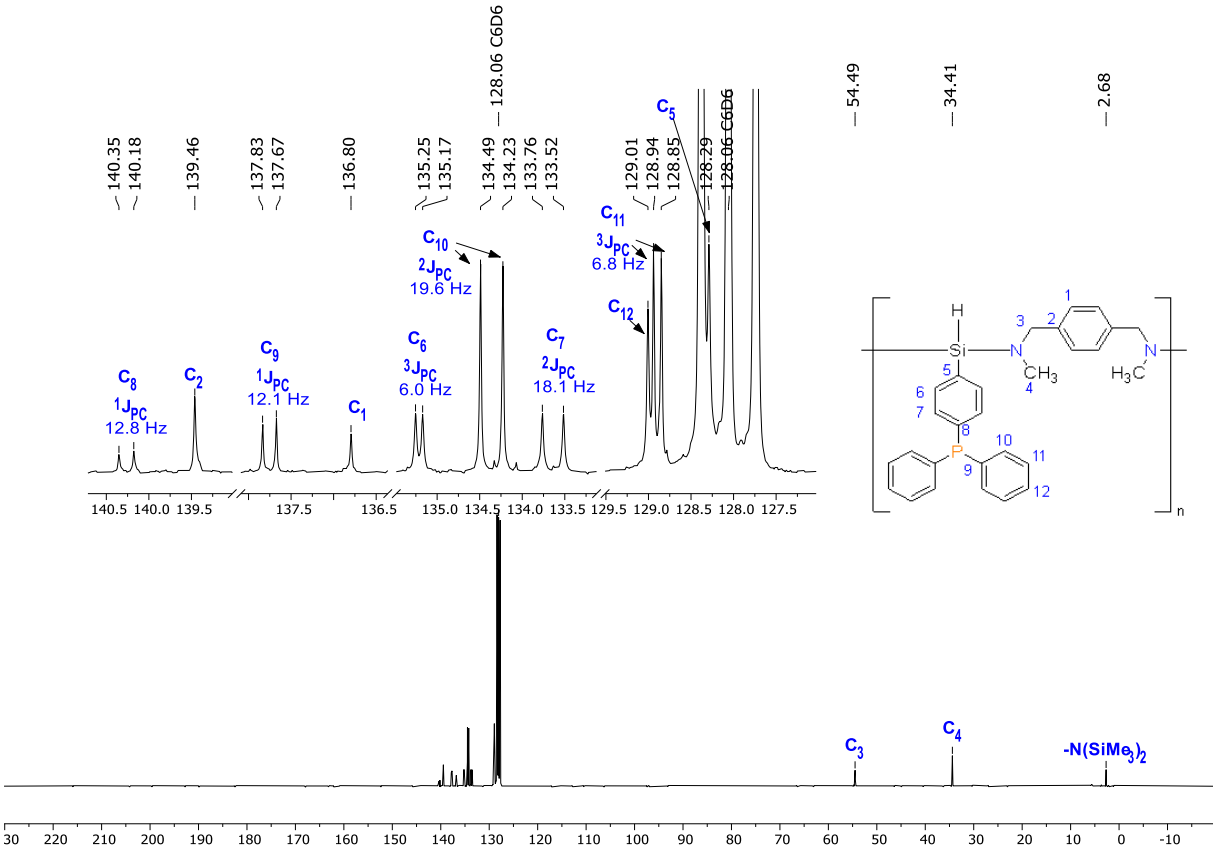



**Figure S26.** $^{13}C\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 75.48 MHz, 299 K) of **co-PhPZ-0**, product of the 1:1 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (7.5 mol-%).

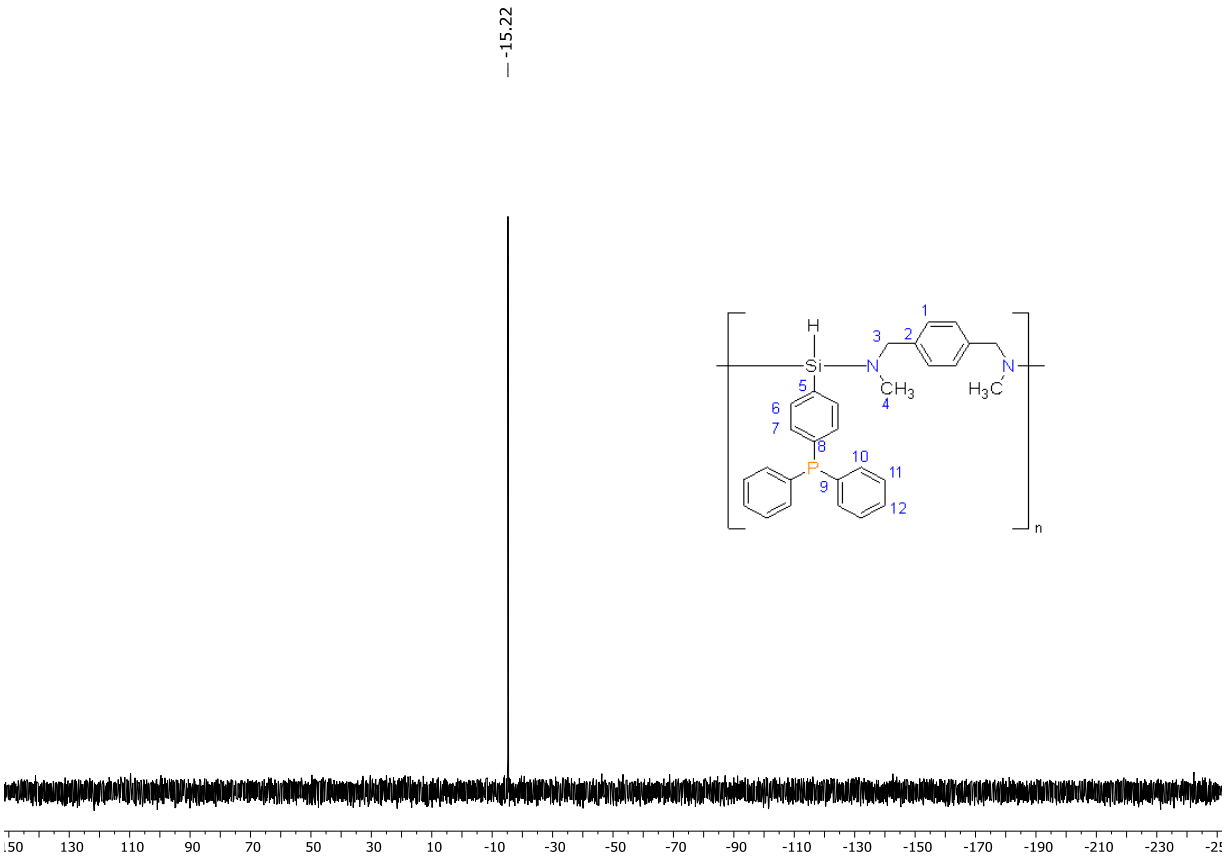



**Figure S27.** $^{29}Si\{^{1}H\}$ INEPT NMR spectrum ([$D_6$]benzene, 79.49 MHz, 302 K) of **co-PhPZ-0**, product of the 1:1 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (7.5 mol-%).

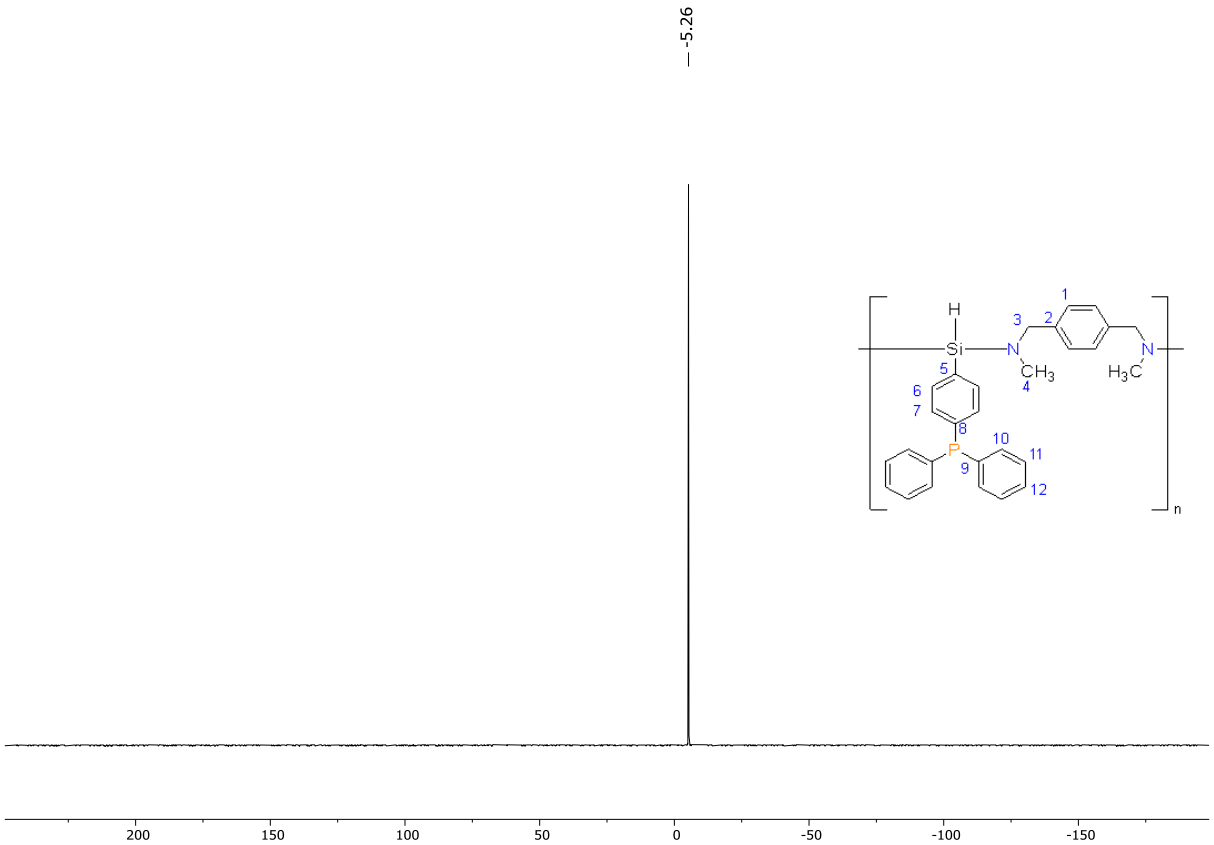



**Figure S28.** $^{31}P\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 121.50 MHz, 298 K) of **co-PhPZ-0**, product of the 1:1 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (7.5 mol-%).

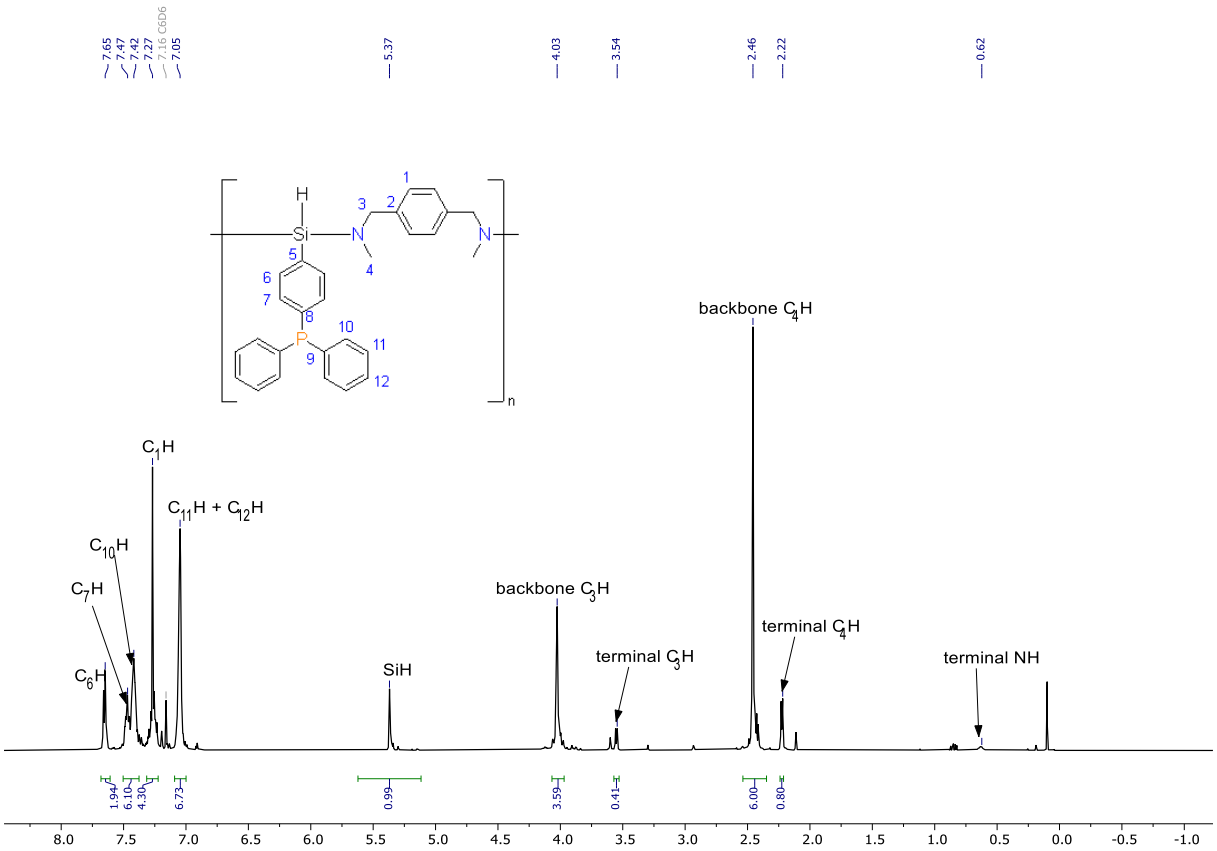



**Figure S29.** $^{1}$H NMR spectrum ([$D_6$]benzene, 300.13 MHz, 298 K) of **co-PhPZ-1**, product of the 1:1 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

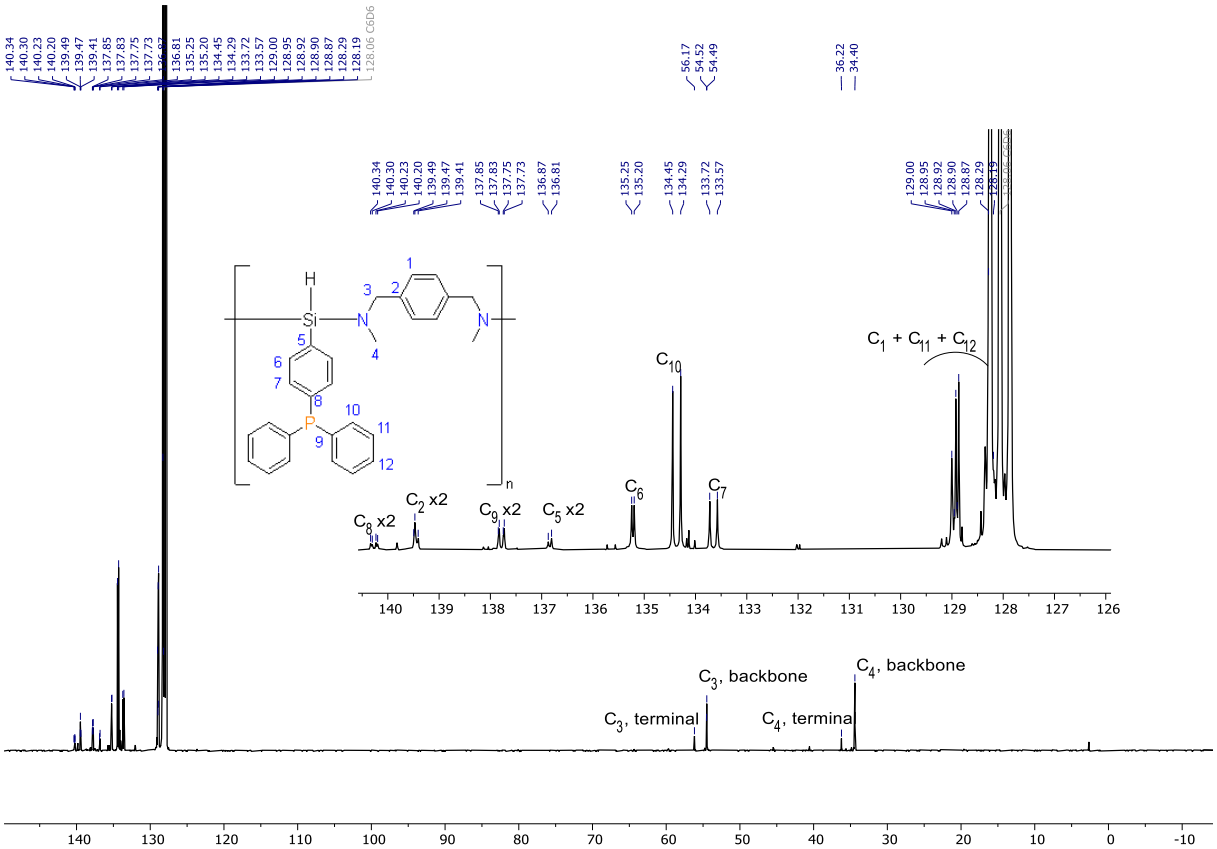



**Figure S30.** $^{13}C\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 125.77 MHz, 300 K) of **co-PhPZ-1**, product of the 1:1 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

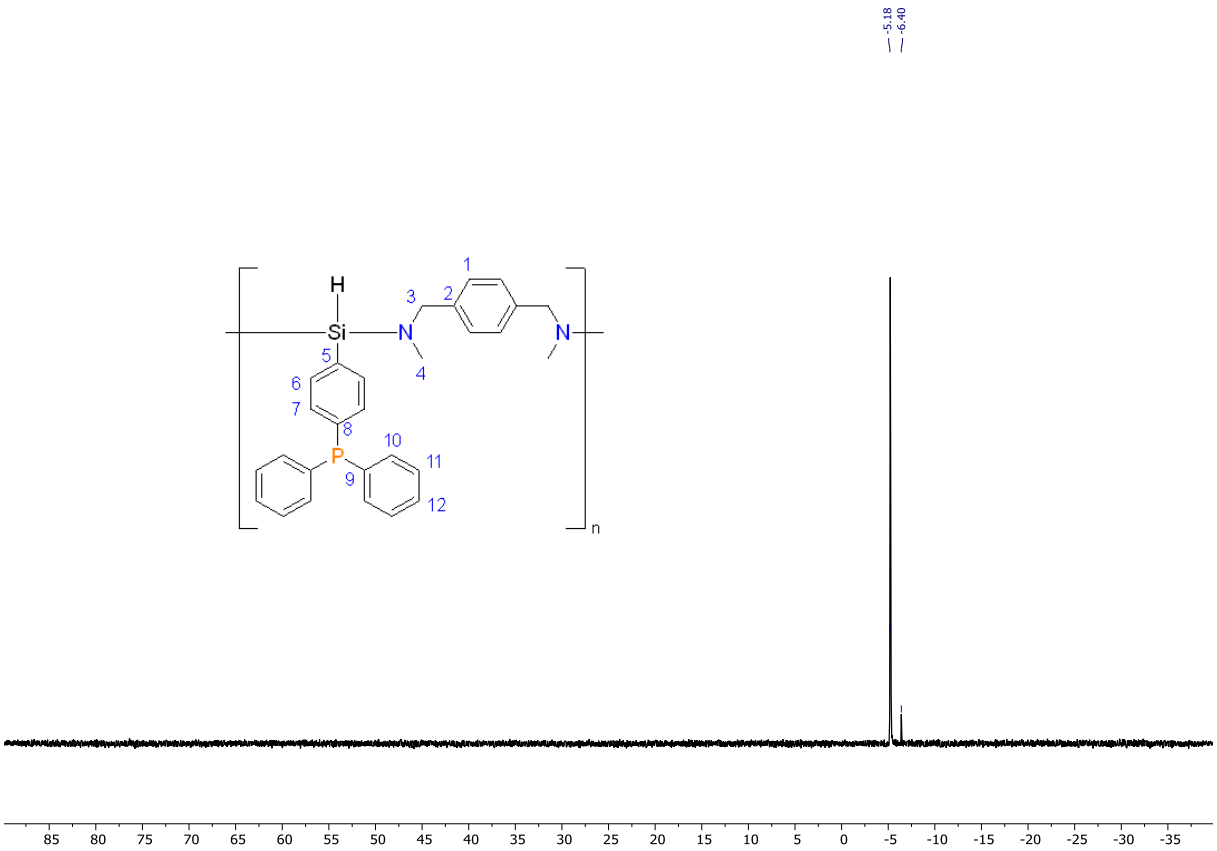



**Figure S31.** $^{31}P\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 161.99 MHz, 298 K) of **co-PhPZ-1**, product of the 1:1 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

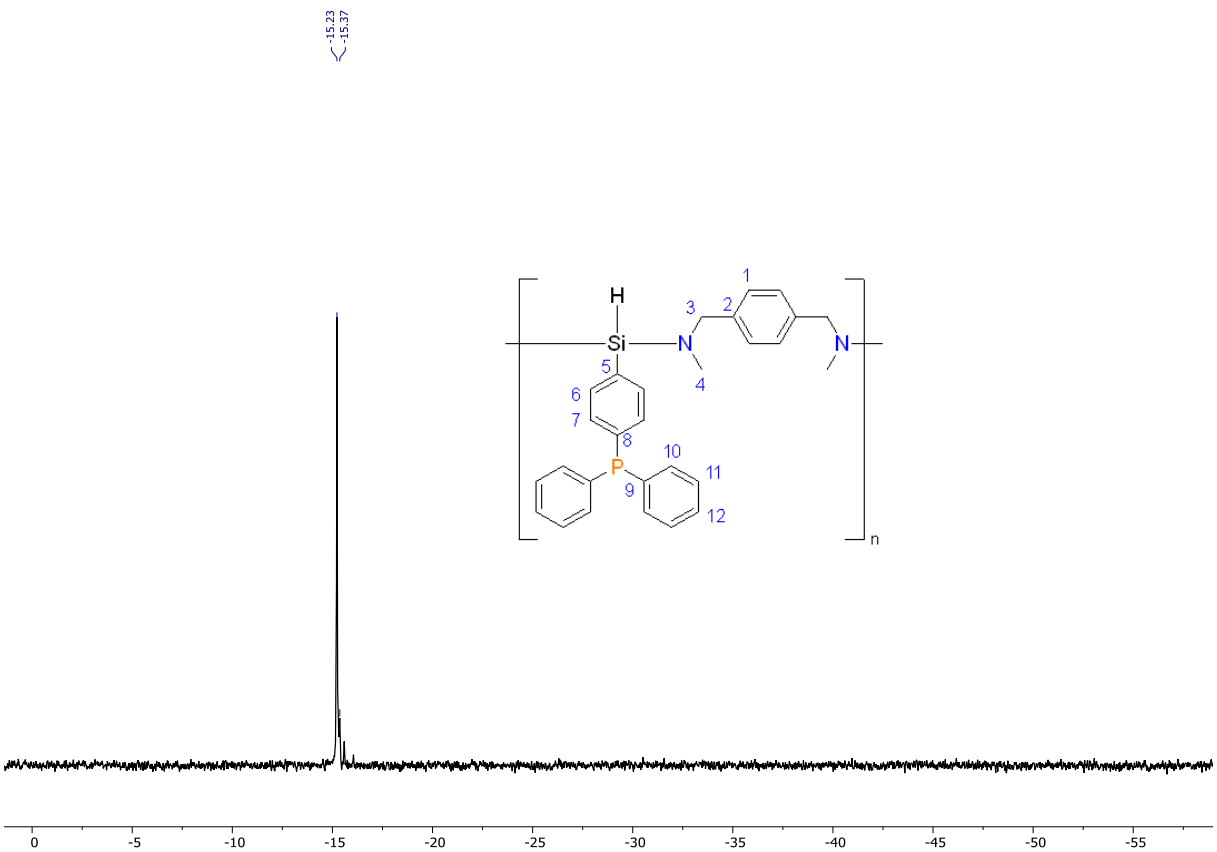



**Figure S32.** $^{29}Si\{^{1}H\}$ INEPT NMR spectrum ([$D_6$]benzene, 79.49 MHz, 302 K) of **co-PhPZ-1**, product of the 1:1 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

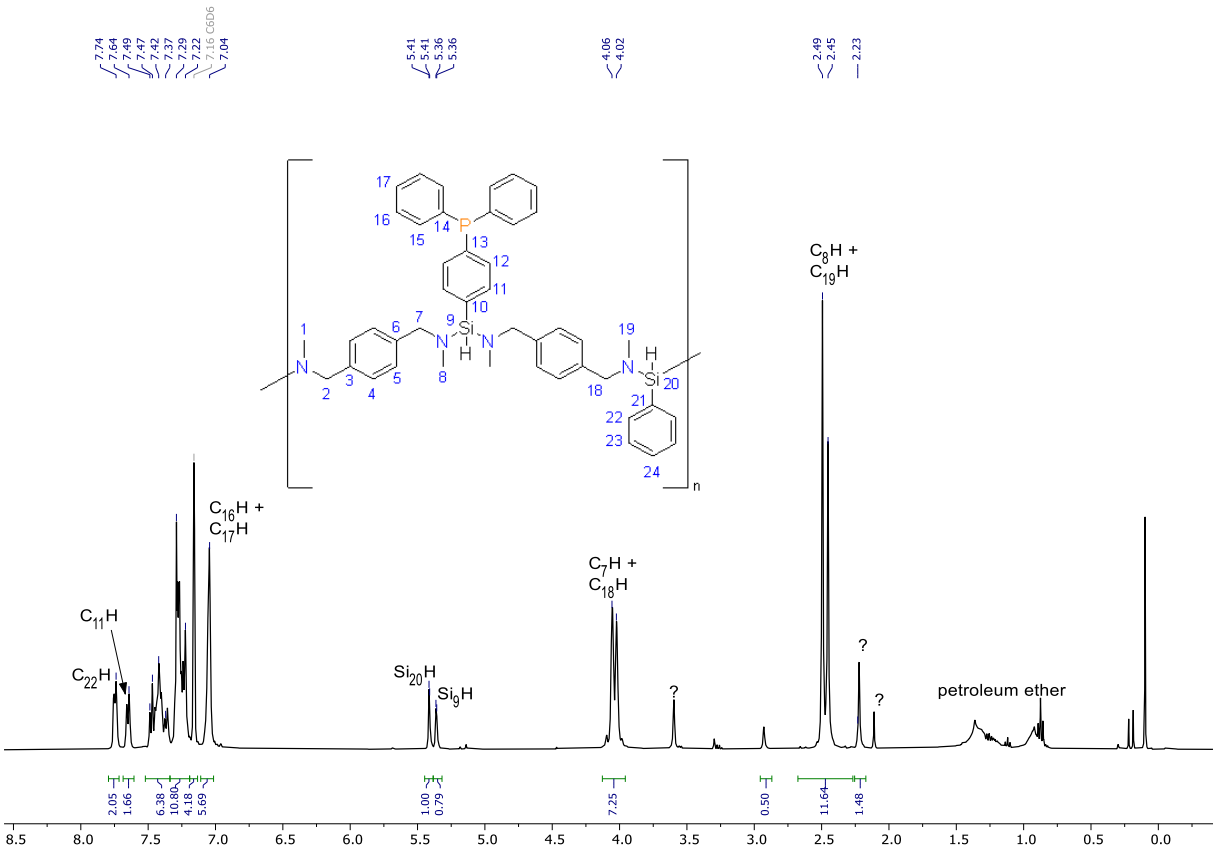



**Figure S33.** $^{1}$H NMR spectrum ([$D_6$]benzene, 400.16 MHz, 298 K) of **ter-PhCZ-4**, product of the 50:50:95 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**), $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%). A number of unidentified resonances (?) could not be assigned.

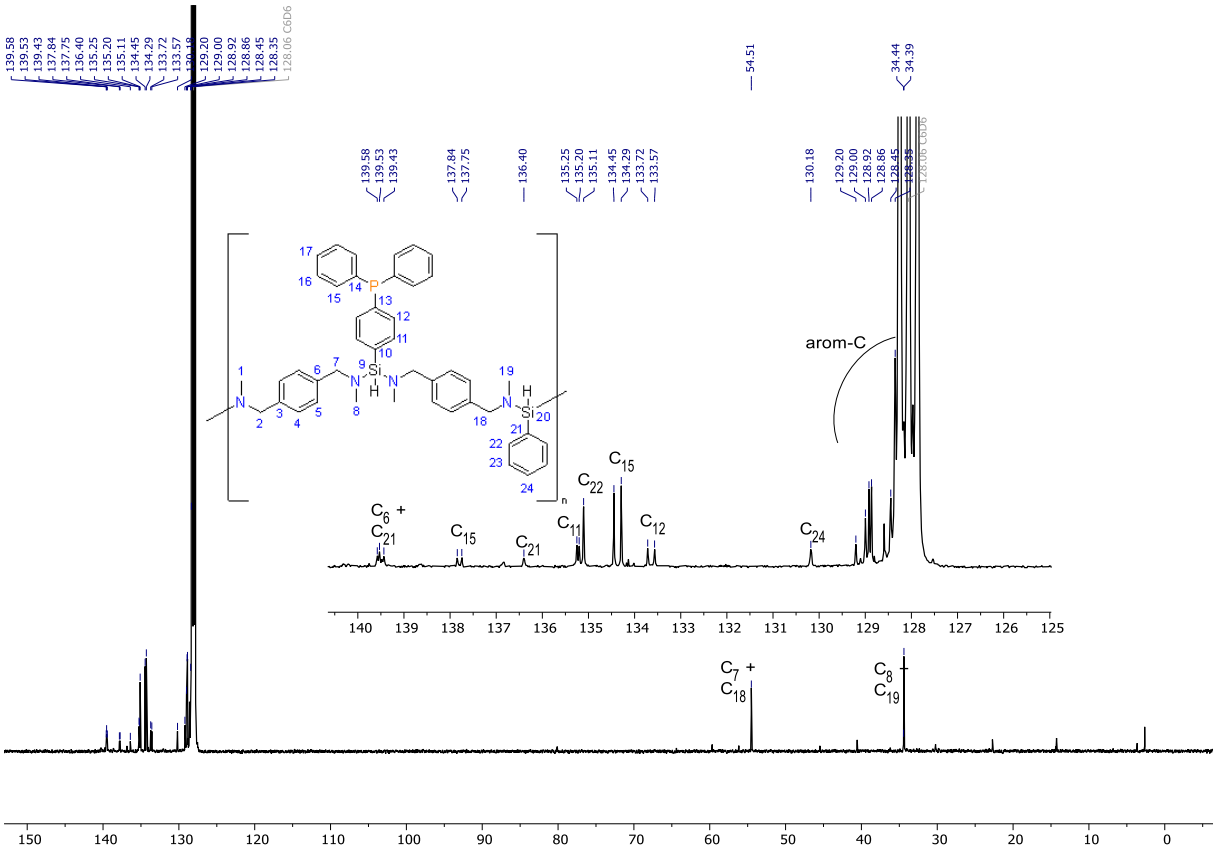



**Figure S34.** $^{13}C\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 125.77 MHz, 300 K) of **ter-PhCZ-4**, product of the 50:50:95 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**), $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

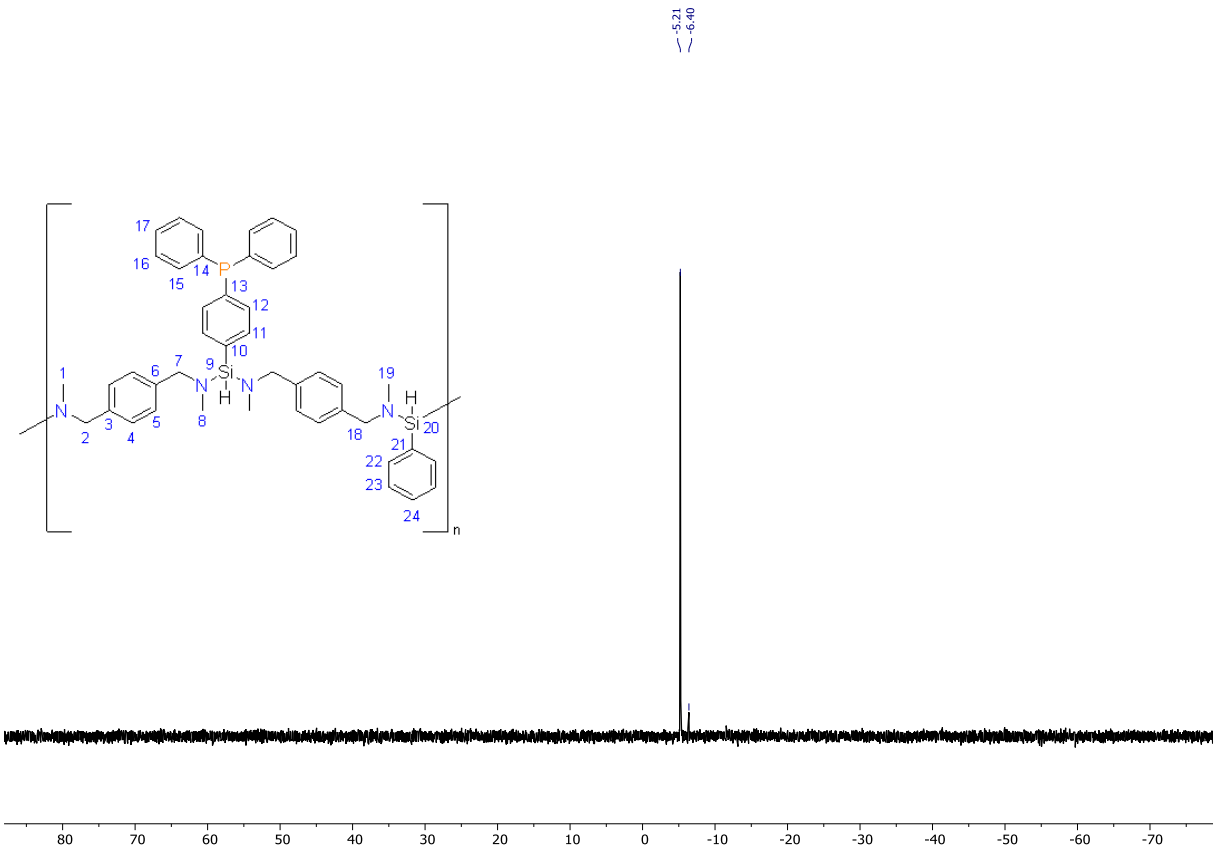



**Figure S35.** $^{31}P\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 161.99 MHz, 298 K) of **ter-PhCZ-4**, product of the 50:50:95 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**), $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%). The residual resonance at –6.40 could not be assigned.

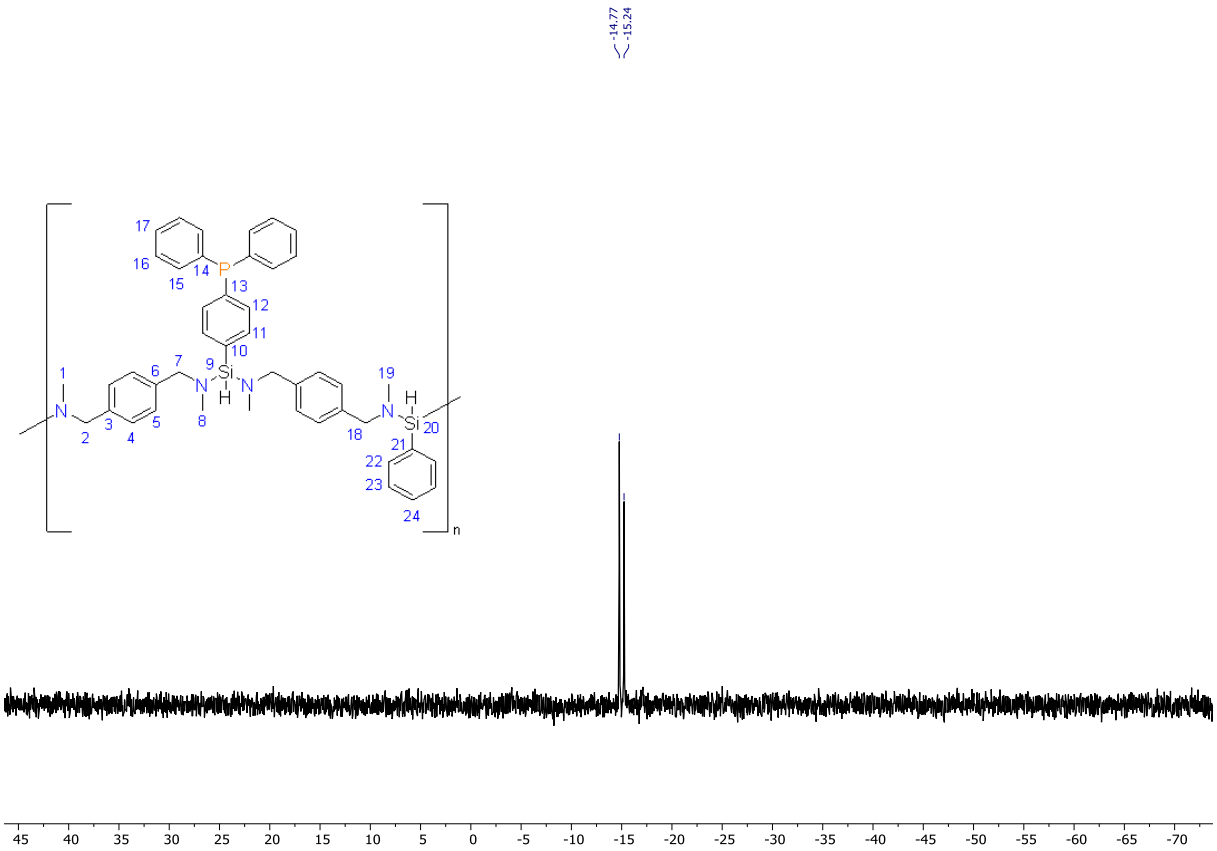



**Figure S36.** $^{29}Si\{^{1}H\}$ INEPT NMR spectrum ([$D_6$]benzene, 79.49 MHz, 302 K) of **ter-PhCZ-4**, product of the 50:50:95 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**), $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

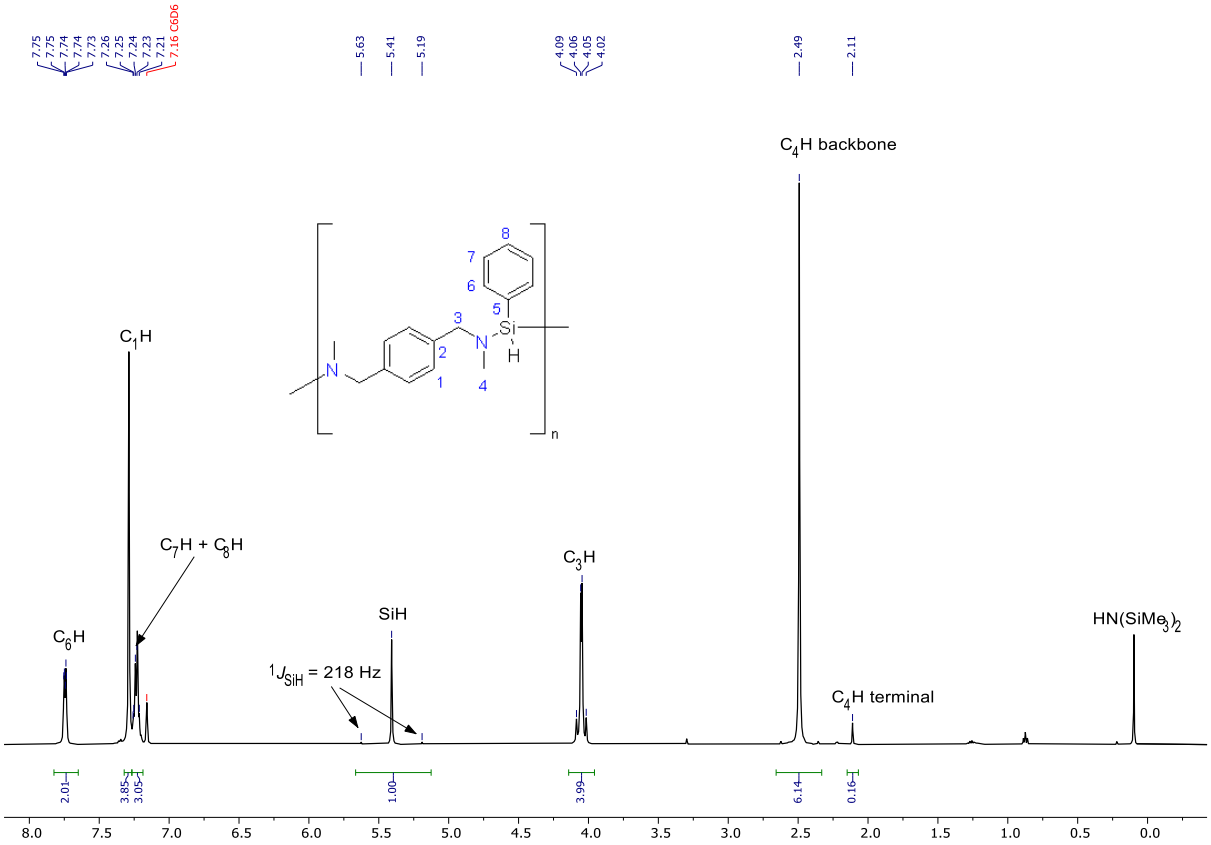



**Figure S37.** $^{1}$H NMR spectrum ([$D_6$]benzene, 500.13 MHz, 300 K) of **co-PZ-8**, product of the 100:100 dehydropolymerisation of $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

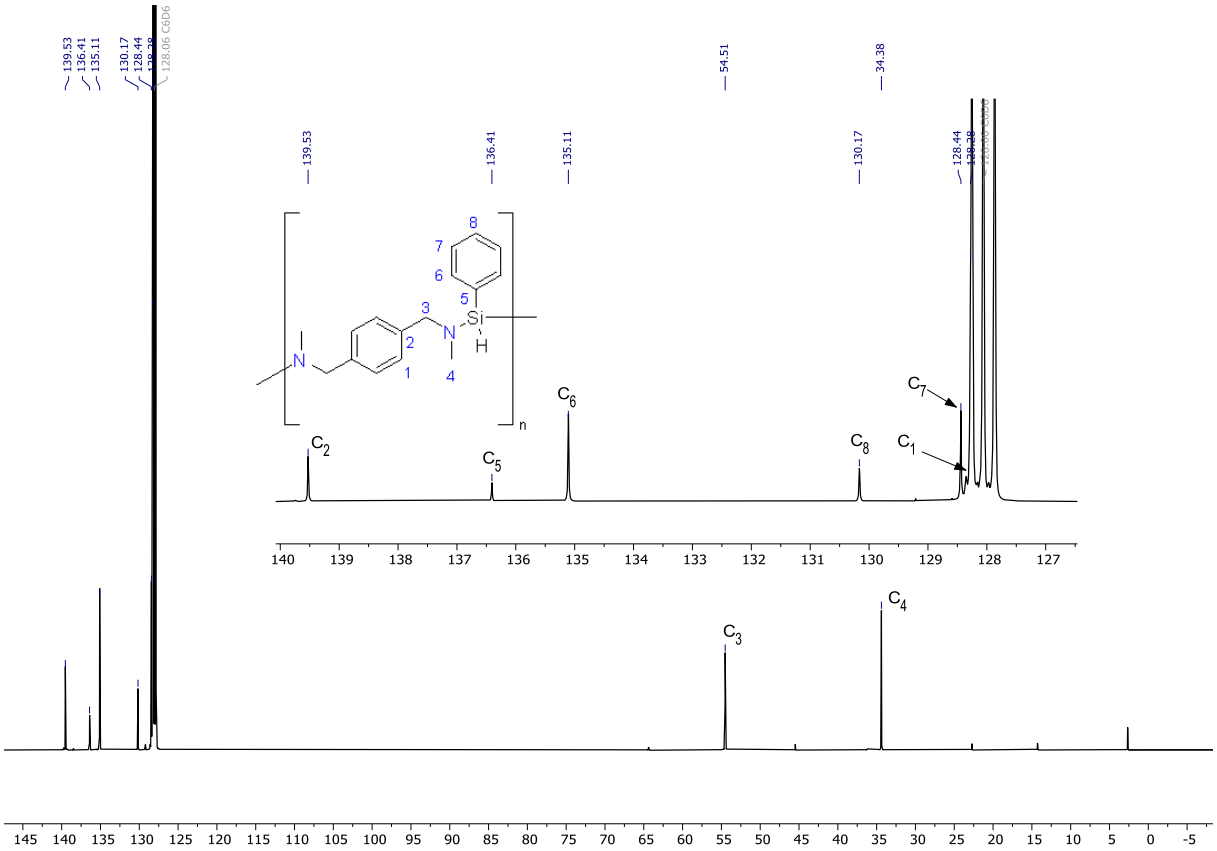



**Figure S38.** $^{13}C\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 125.77 MHz, 300 K) of **co-PZ-8**, product of the 100:100 dehydropolymerisation of $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

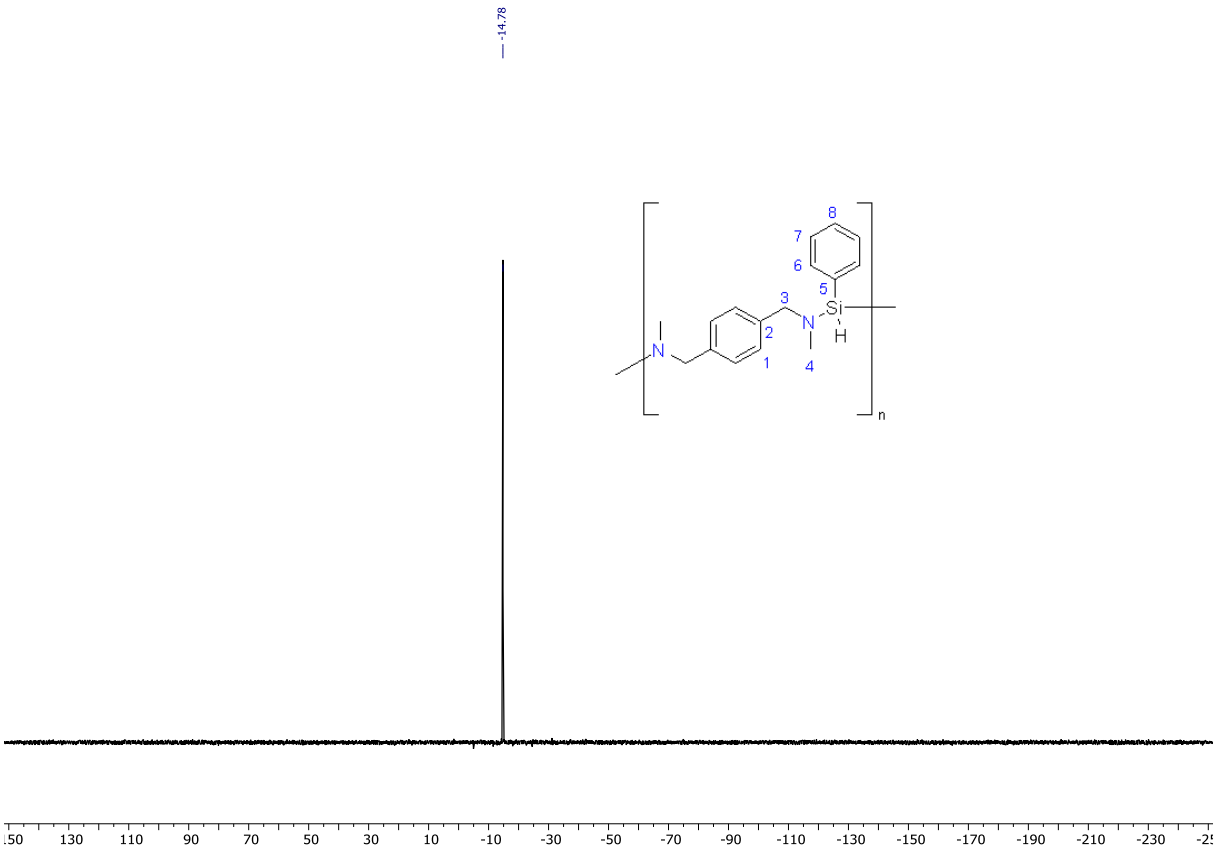



**Figure S39.** $^{29}Si\{^{1}H\}$ INEPT NMR spectrum ([$D_6$]benzene, 79.49 MHz, 302 K) of **co-PZ-8**, product of the 100:100 dehydropolymerisation of $PhSiH_3$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

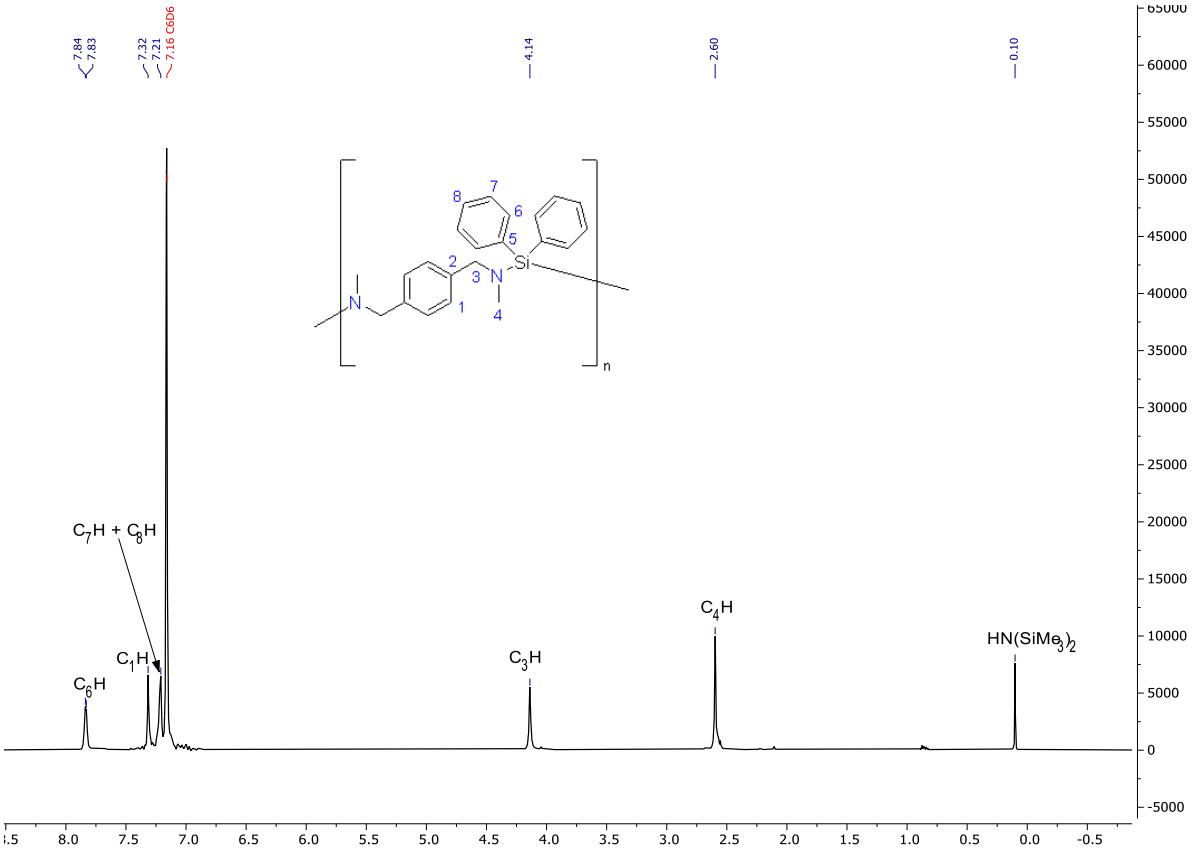



**Figure S40.** $^{1}$H NMR spectrum ([$D_6$]benzene, 500.13 MHz, 300 K) of **co-PZ-11**, product of the 100:100 dehydropolymerisation of $Ph_2SiH_2$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

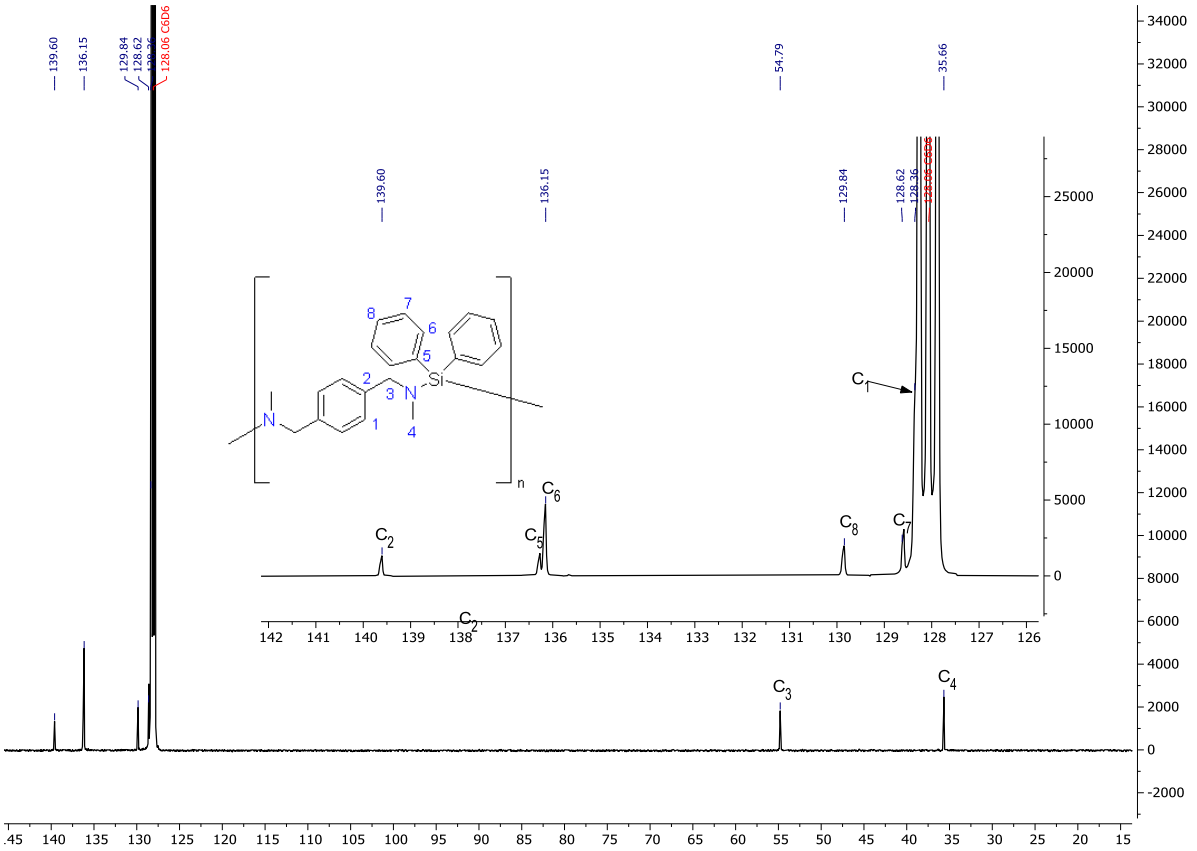



**Figure S41.** $^{13}C\{^{1}H\}$ NMR spectrum ([$D_6$]benzene, 125.77 MHz, 300 K) of **co-PZ-11**, product of the 100:100 dehydropolymerisation of $Ph_2SiH_2$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

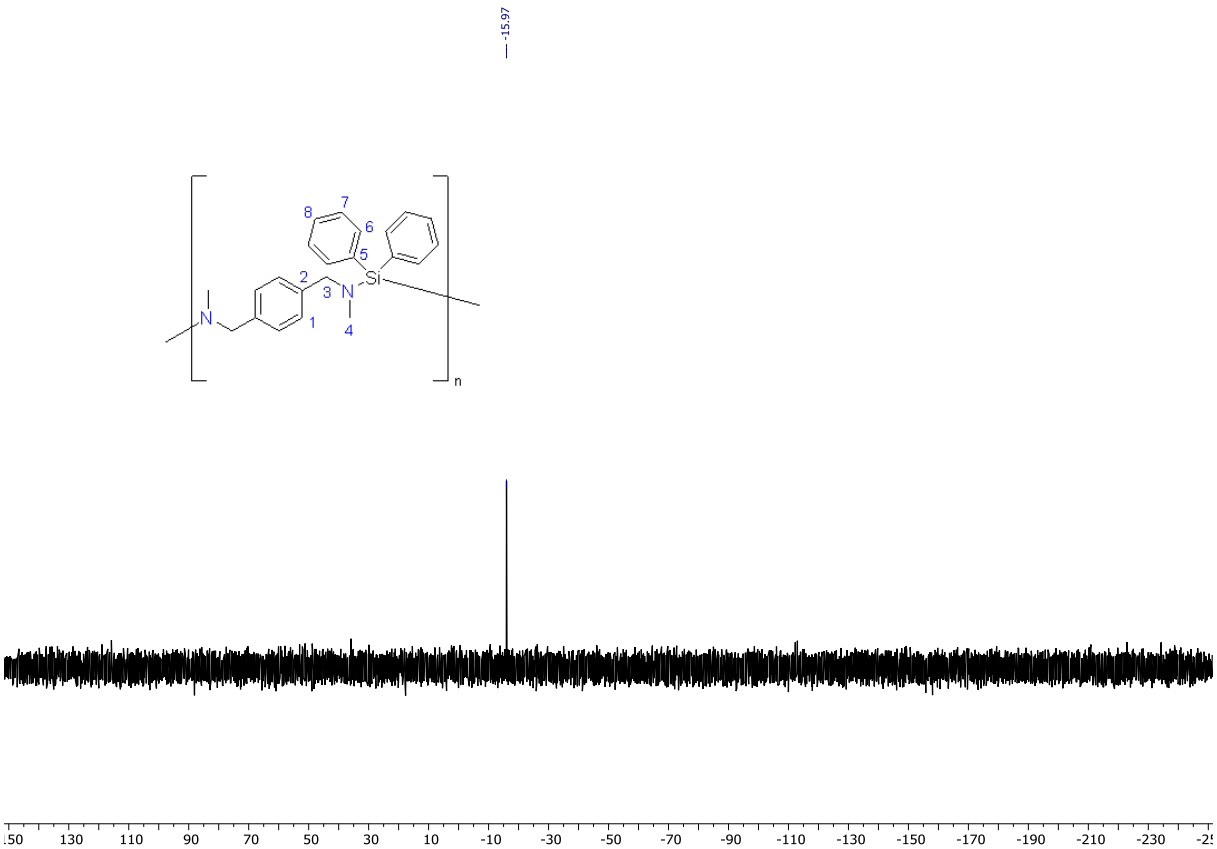



**Figure S42.** $^{29}Si\{^{1}H\}$ INEPT NMR spectrum ([$D_6$]benzene, 79.49 MHz, 302 K) of **co-PZ-11**, product of the 100:100 dehydropolymerisation of $Ph_2SiH_2$ and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%).

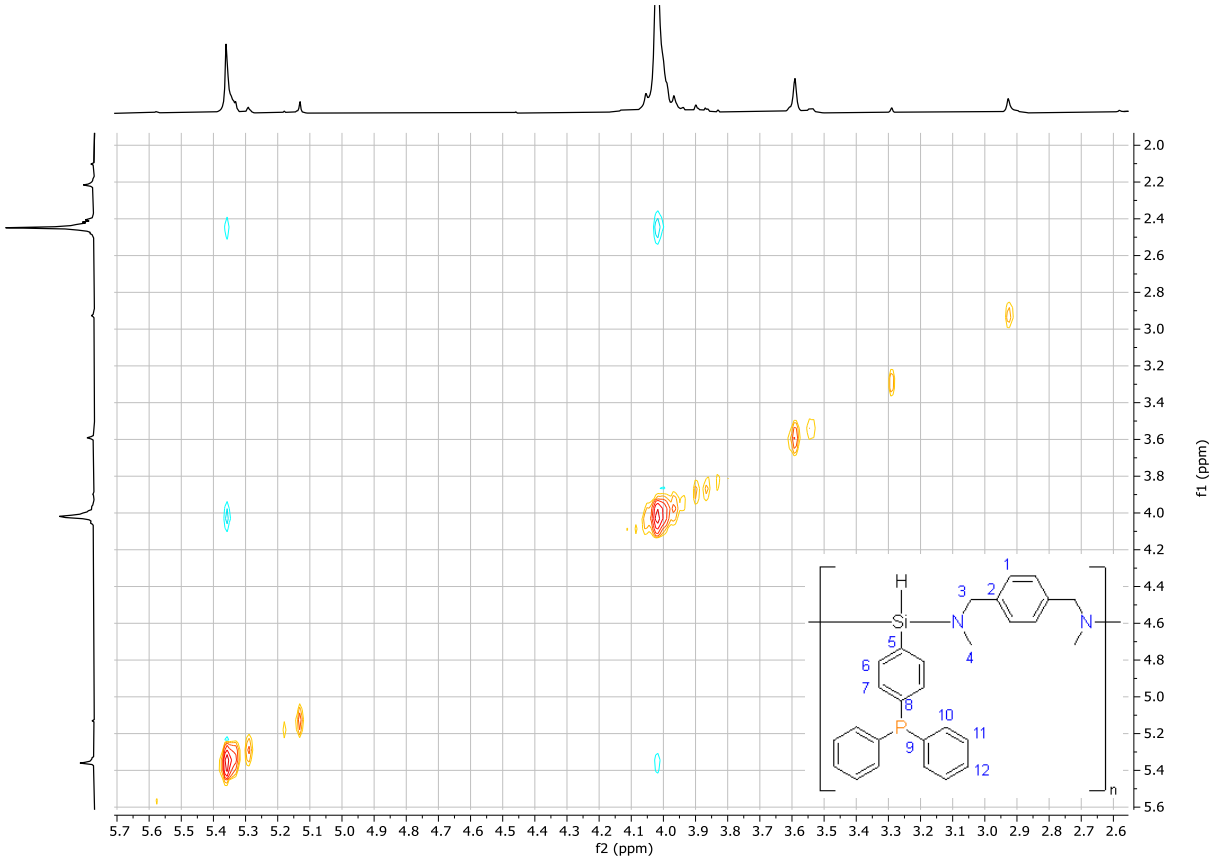



**Figure S43.** 2D ROESY NMR spectrum of **co-PhPZ-3**, product of the 1:1 dehydropolymerisation of 4-$Ph_2P$-$C_6H_4SiH_3$ (**A**) and 1,4-$(CH_2NHMe)_2$-$C_6H_4$ (**C**) catalysed by $[Ba\{N(SiMe_3)_2\}_2]_2$ (10 mol-%). It shows clear through-bond coupling between the hydrosilane, methylene protons and methyl protons.