Electronic Supplementary Information for

Borane-Catalysed Postpolymerisation Modification of the Si-H Bonds in Poly(phenylsilane)

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^{1}H and ^{13}C NMR spectra

Spectra for polymers **8**, **10**, and **11** were previously reported.[1] In polymer structures shown here and throughout the ESI, the "•" symbol represents chain termini ($SiPhH_2$, SiPhHX, $SiPhX_2$) or repeat units (SiPhH, SiPhX), where X is the modified sidechain.
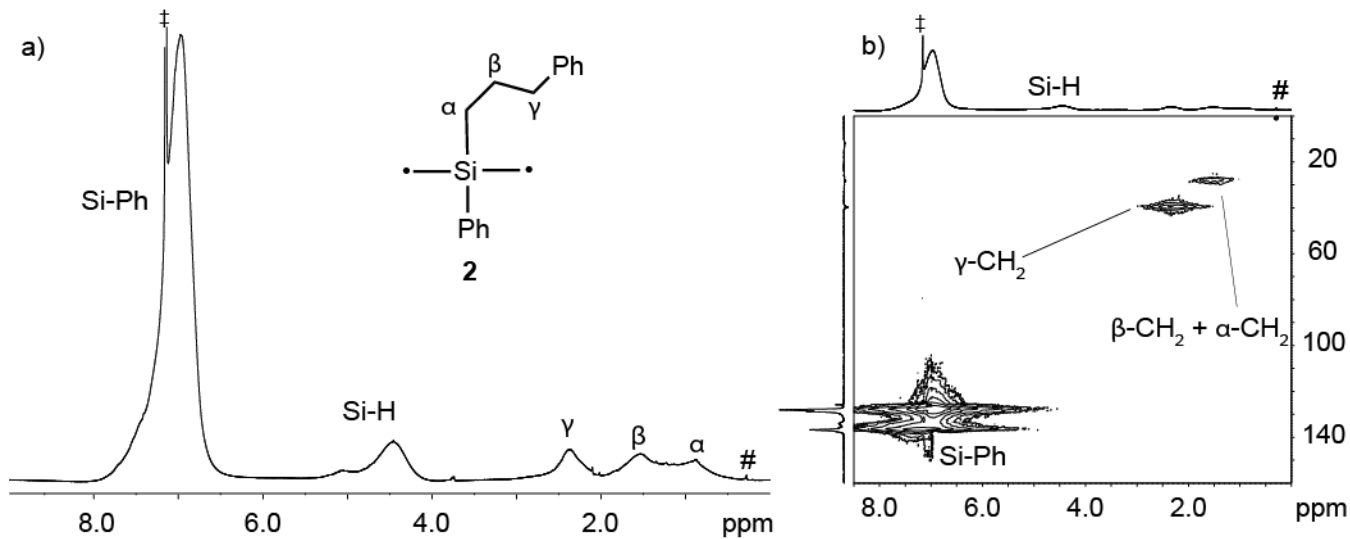

Figure S1. a) ^{1}H NMR (300 MHz) and **b)** ^{1}H-^{13}C HSQC (^{1}H 300 MHz) of modified polymer **2** (X = $(CH_2)_5CH_3$) in C_6D_6. The "‡" is C_6D_5H and "#" is grease.
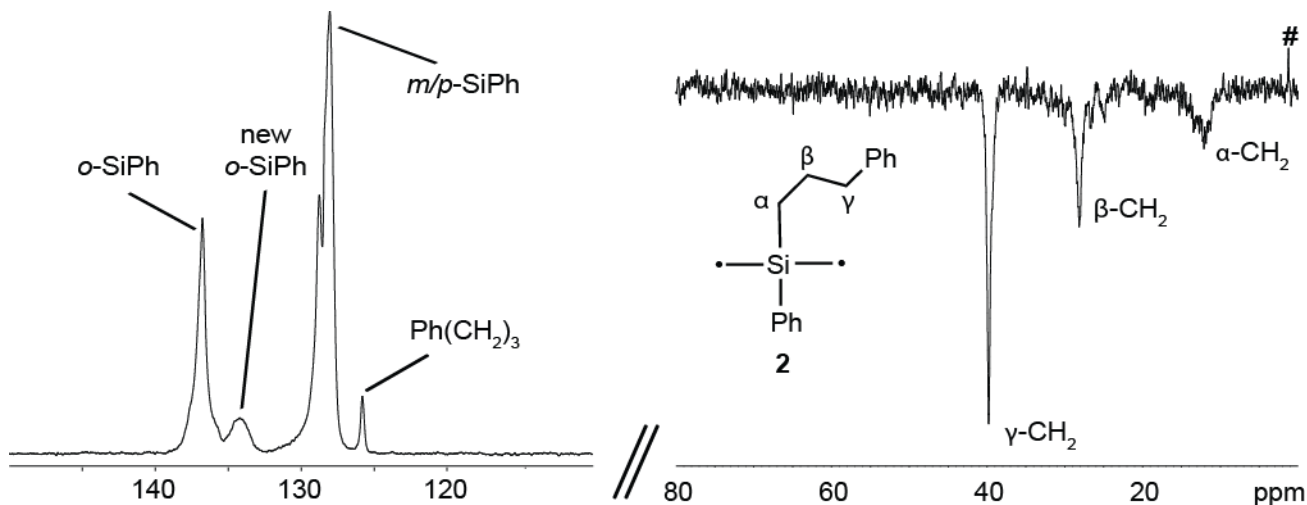

Figure S2. Aromatic and alkyl regions of the DEPT135 ^{13}C NMR (75 MHz) of modified polymer **2** (X = $(CH_2)_5CH_3$) in C_6D_6. The alkyl region (0-80 ppm) has been vertically expanded and horizontally compressed relative to the aromatic region (100-160 ppm). The "#" is grease.

[1] P. T. K. Lee, M. K. Skjel and L. Rosenberg, *Organometallics*, 2013, **32**, 1575
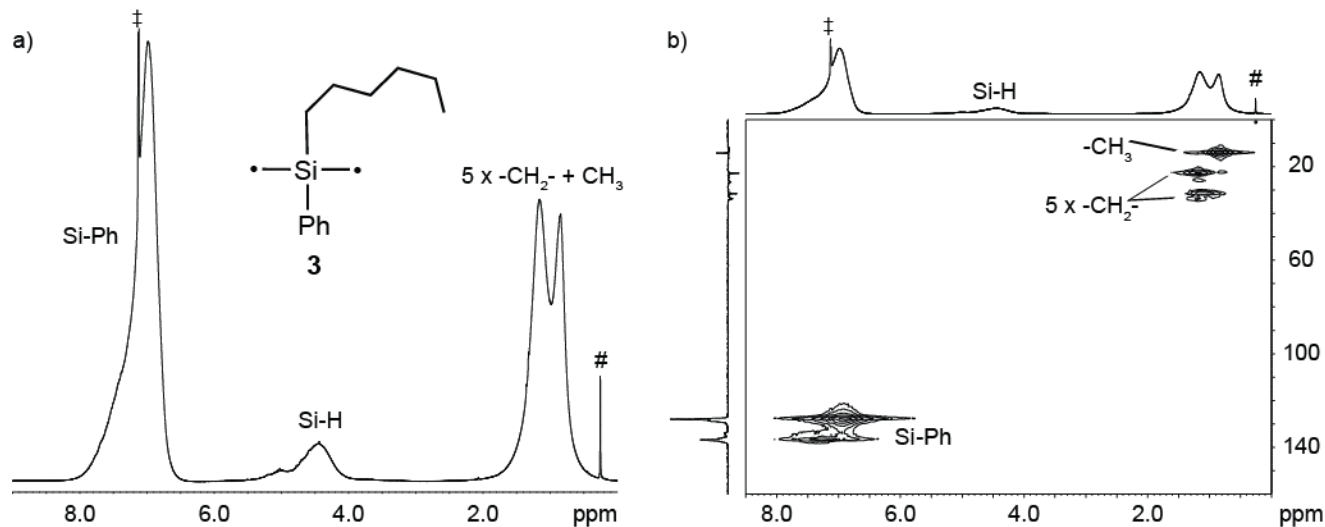
Figure S3. a) ^{1}H NMR (300 MHz) and **b)** ^{1}H-^{13}C HSQC (^{1}H 300 MHz) of modified polymer **3** (X = (CH$_2$)$_5$CH$_3$) in C$_6$D$_6$. The "‡" is C$_6$D$_5$H and "#" is grease.

Figure S4. Aromatic and alkyl regions of the DEPT135 ^{13}C NMR (75 MHz) of modified polymer **3** (X = (CH$_2$)$_3$Ph**)** in C$_6$D$_6$. The alkyl region (0-80 ppm) has been vertically expanded and horizontally compressed relative to the aromatic region (100-160 ppm). The "#" is grease.

Figure S5. a) ^{1}H NMR (300 MHz) and **b)** ^{1}H-^{13}C HSQC (^{1}H 300 MHz) of modified polymer **4** (X = N(Ph)CH$_2$Ph) in C$_6$D$_6$. The "‡" is C$_6$D$_5$H, "#" is grease, and "*" marks traces of N-benzylideneaniline released partial hydrolysis of the Si-N bonds.
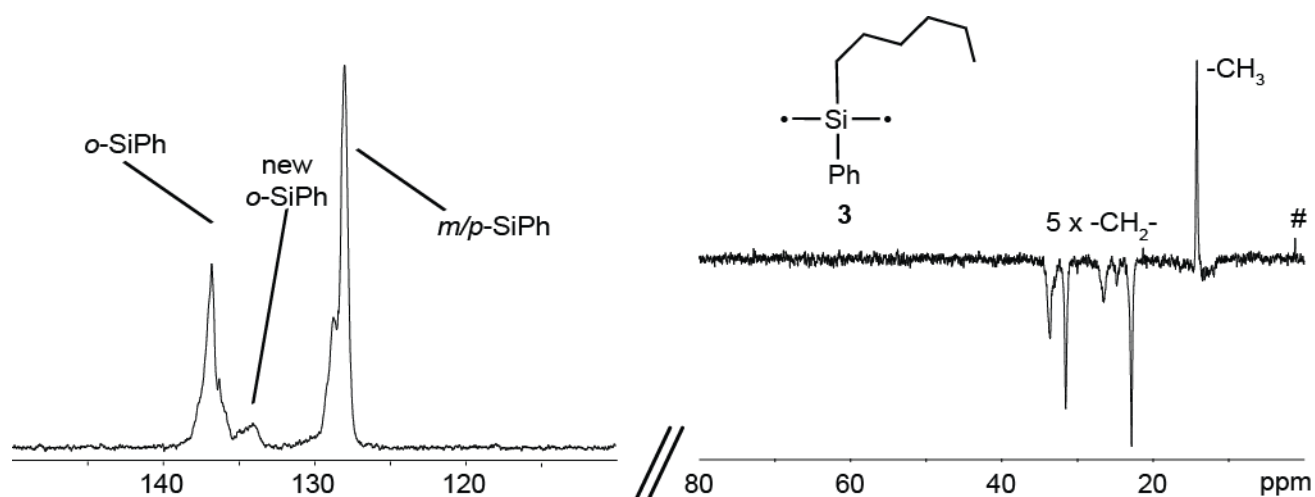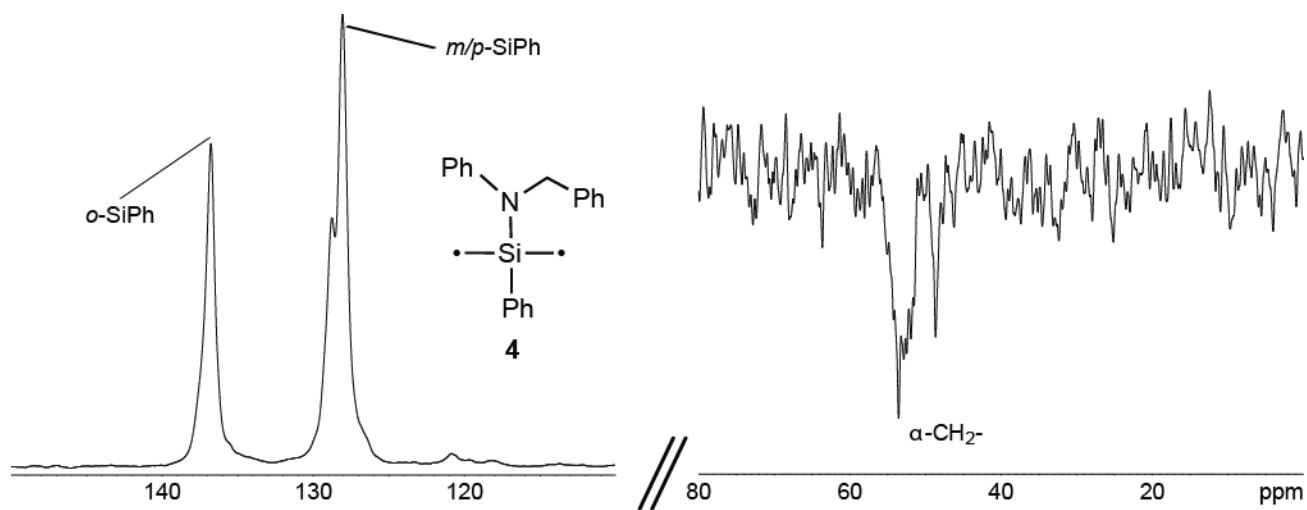

Figure S6. Aromatic and alkyl regions of the DEPT135 ^{13}C NMR (75 MHz) of modified polymer **4** (X = N(Ph)CH$_2$Ph) in C$_6$D$_6$. The alkyl region (0-80 ppm) has been vertically expanded and horizontally compressed relative to the aromatic region (100-160 ppm). The "#" is grease.
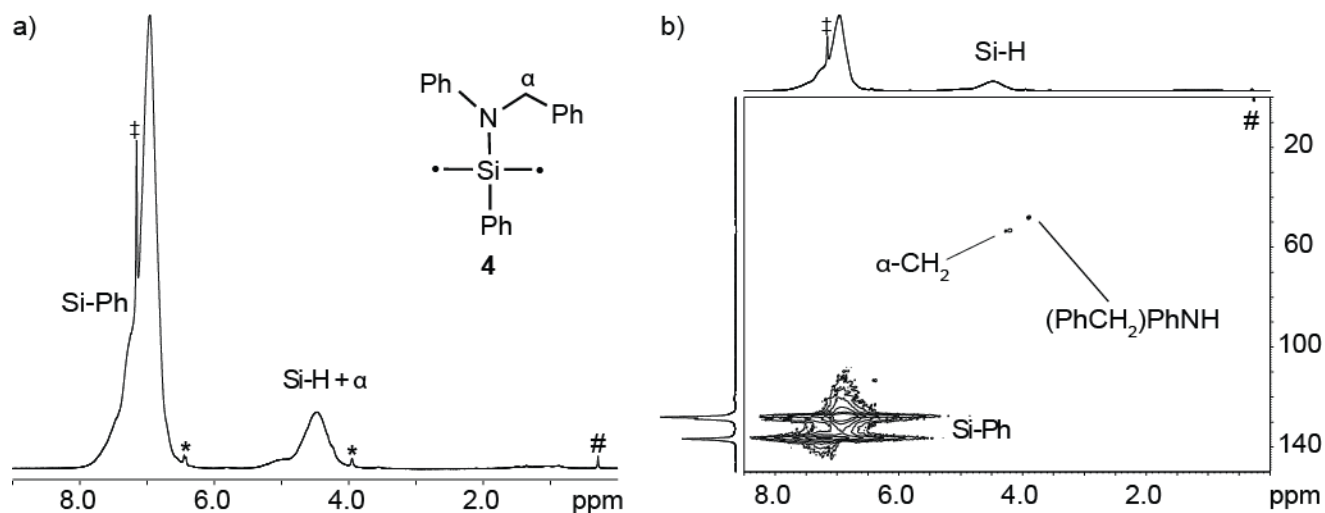
Figure S7. a) ^{1}H NMR (300 MHz) and **b)** ^{1}H-^{13}C HSQC (^{1}H 300 MHz) of modified polymer **5** (X = OCH(CH$_3$)$_2$) in C$_6$D$_6$. The "‡" is C$_6$D$_5$H, "#" is grease.

Figure S8. Aromatic and alkyl regions of the DEPT135 ^{13}C NMR (75 MHz) of modified polymer **5** (X = OCH(CH$_3$)$_2$**)** in C$_6$D$_6$. The alkyl region (0-80 ppm) has been vertically expanded and horizontally compressed relative to the aromatic region (100-160 ppm). The "#" is grease.
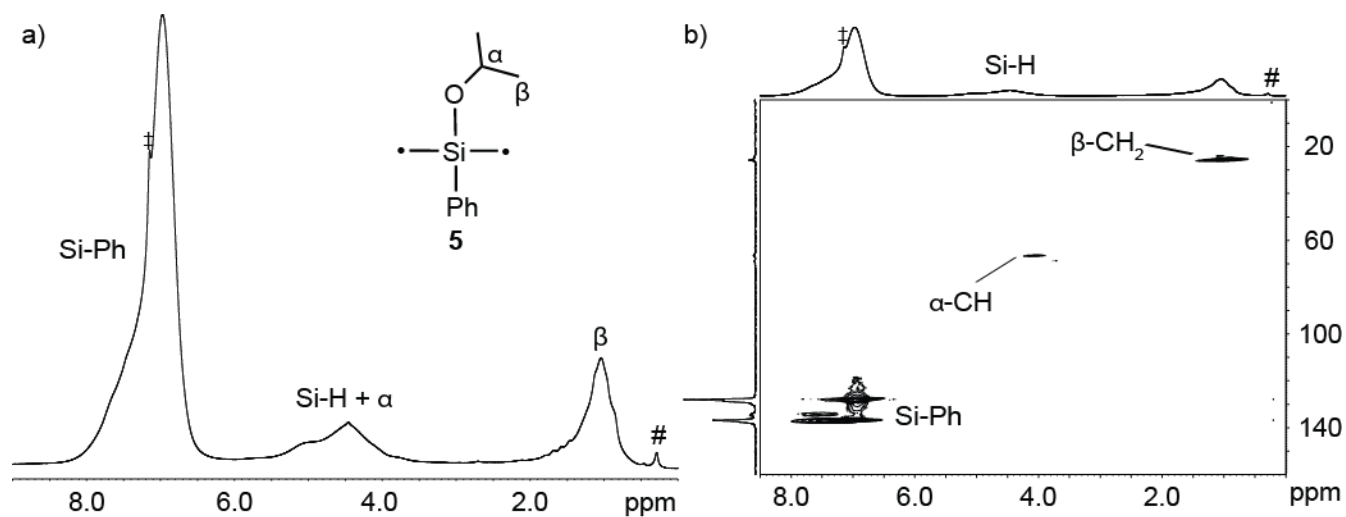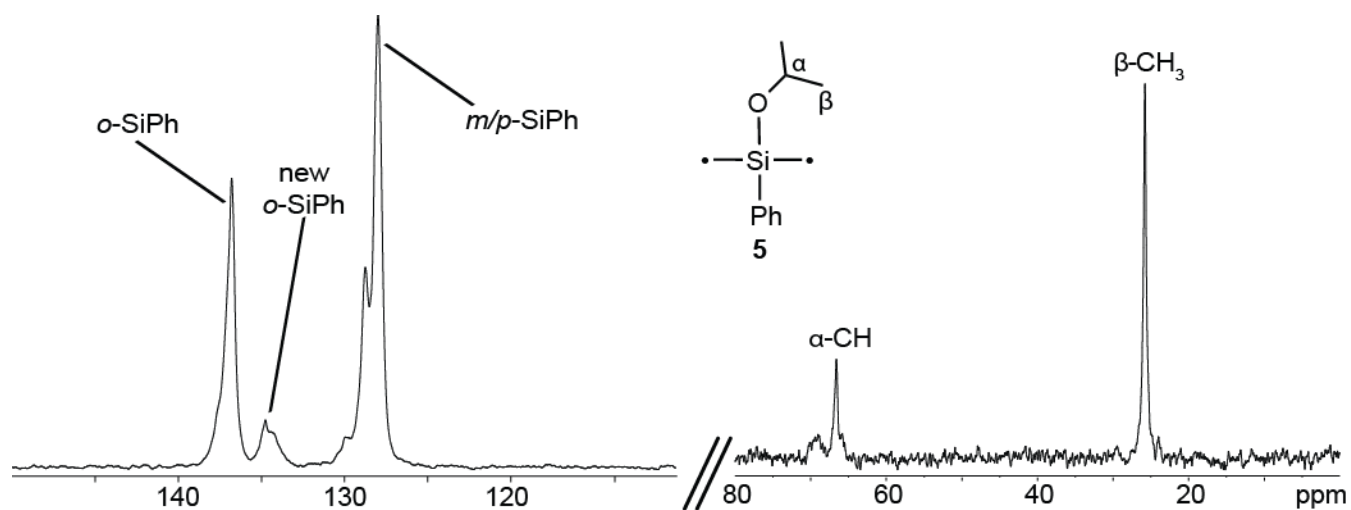
Figure S9. a) ^{1}H NMR (300 MHz) and **b)** ^{1}H-^{13}C HSQC ([1]H 300 MHz) of modified polymer **6** (X = O(CH$_2$)$_2$CH$_3$) in C$_6$D$_6$. The "‡" is C$_6$D$_5$H, and "#" is grease. Quotation marks have been added around the polymer structure here and in Figure S10 below since it is likely to contain a number of Si-O-Si linkages (see text).

Figure S10. Aromatic and alkyl regions of the DEPT135 ^{13}C NMR (75 MHz) of modified polymer **6** (X = O(CH$_2$)$_2$CH$_3$) in C$_6$D$_6$. The alkyl region (0-80 ppm) has been vertically expanded and horizontally compressed relative to the aromatic region (100-160 ppm). The "#" is grease.
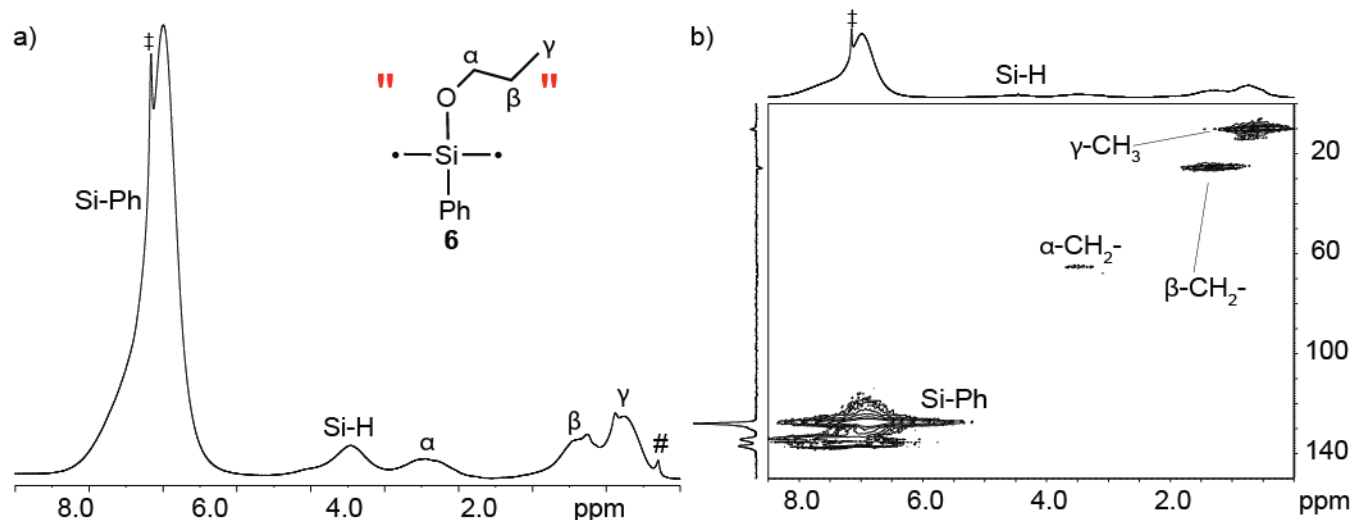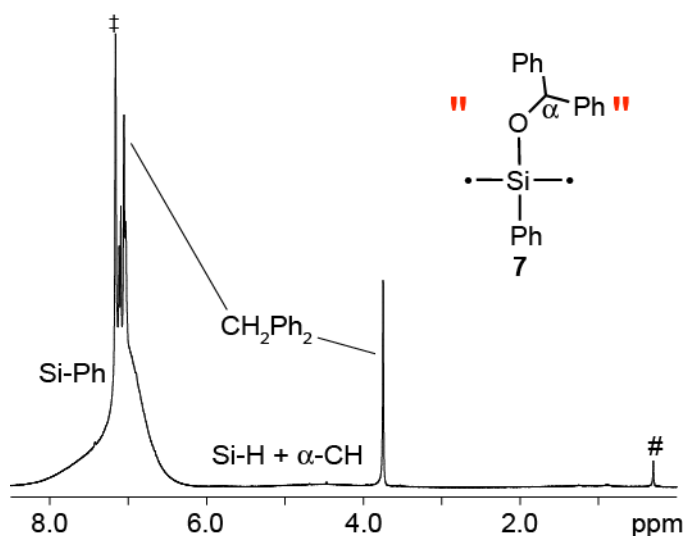
Figure S11. a) ^{1}H NMR (300 MHz) of modified polymer **7** (X = OCHPh$_2$) in C$_6$D$_6$. The "‡" is C$_6$D$_5$H, and "#" is grease. The ^{1}H-^{13}C HSQC is not included, since the alkyl region of the ^{13}C dimension shows only a singlet due to the Ph$_2$CH$_2$ byproduct. Quotation marks have been added around the polymer structure here and in Figure S12 below, since it is likely to contain a number of Si-O-Si linkages (see text).
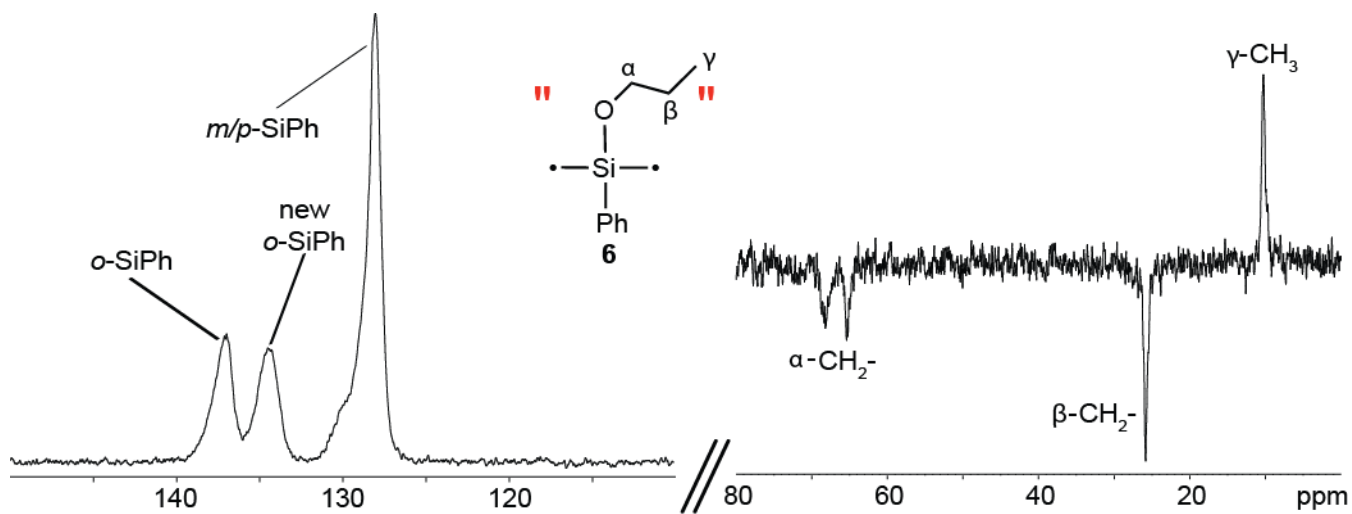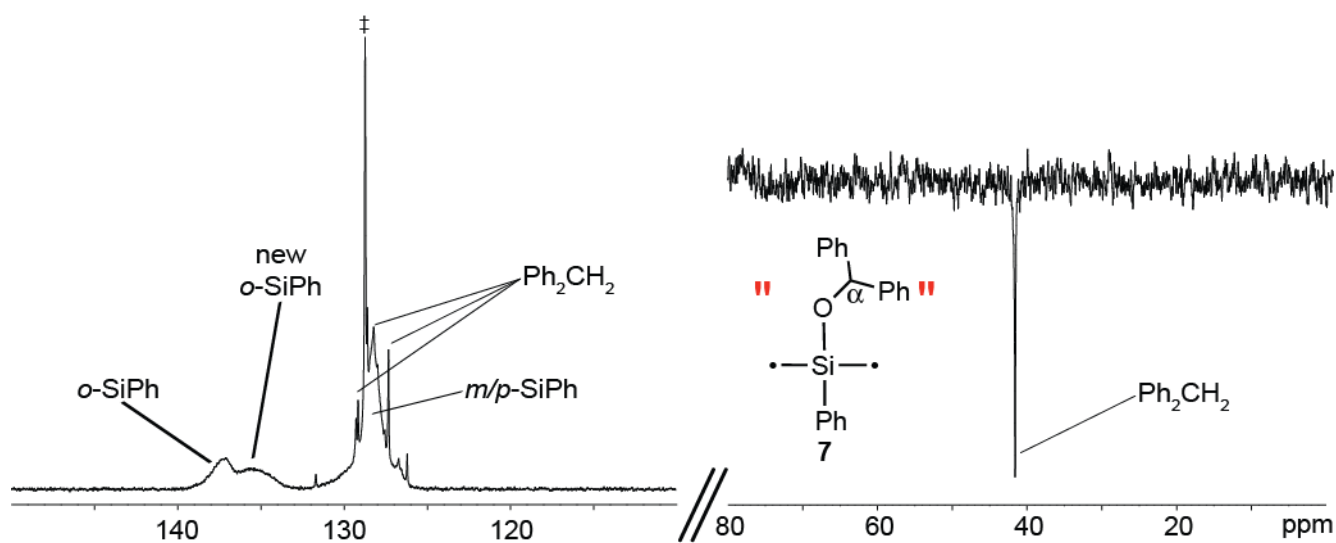

Figure S12. Aromatic and alkyl regions of the DEPT135 ^{13}C NMR (75 MHz) of modified polymer **7** (X = OCHPh$_2$) in C$_6$D$_6$. The alkyl region (0-80 ppm) has been vertically expanded and horizontally compressed relative to the aromatic region (100-160 ppm). The "‡" is C$_6$D$_5$H, and the "#" is grease.
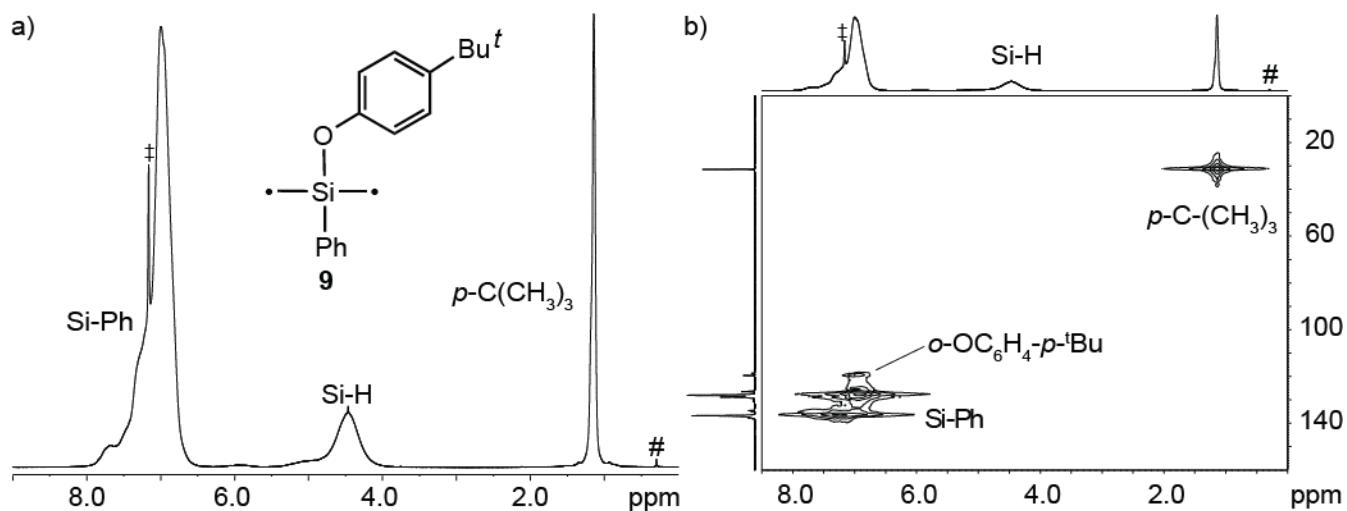
Figure S13. a) ^{1}H NMR (300 MHz) and **b)** ^{1}H-^{13}C HSQC (^{1}H 300 MHz) of modified polymer **9** (X = OC$_6$H$_4$-p-Bu^t) in C$_6$D$_6$. The "‡" is C$_6$D$_5$H and "#" is grease.
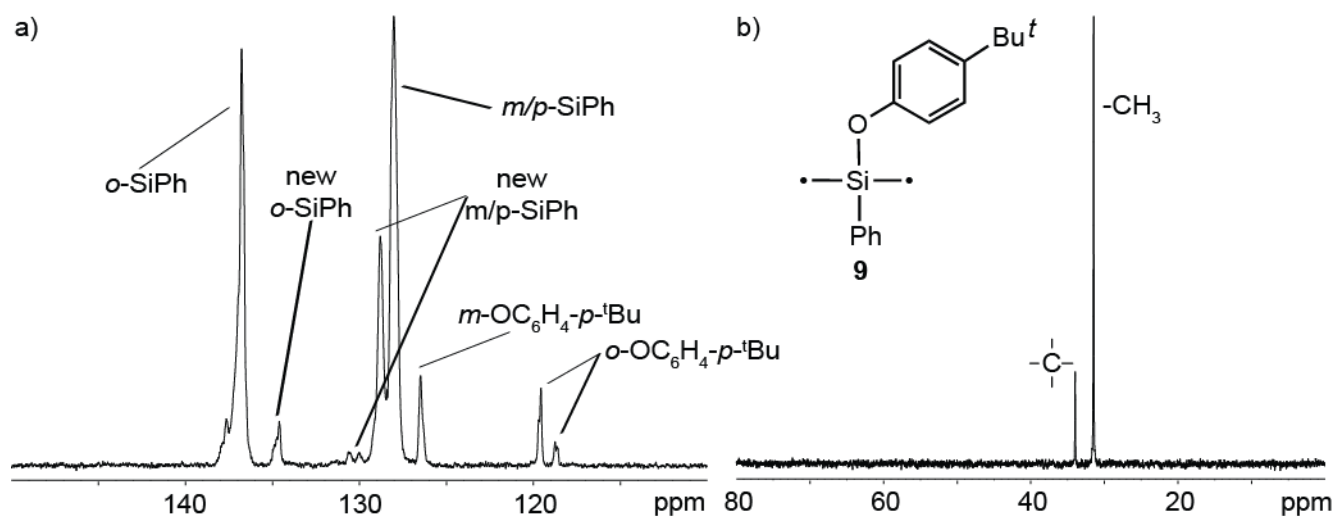
Figure S14. a) DEPT135 ^{13}C NMR (75 MHz) of the aryl region (100-160 ppm) and **b)** ^{13}C{^{1}H} NMR (75 MHz) of the alkyl region (0-80 ppm) of modified polymer **9** (X = OC$_6$H$_4$-p-Bu^t) in C$_6$D$_6$.

Figure S15. a) ^{1}H NMR (300 MHz) and **b)** ^{1}H-^{13}C HSQC (^{1}H 300 MHz) of modified polymer **12** (X = OC$_6$H$_4$-p-CH$_3$) in C$_6$D$_6$. The "‡" is C$_6$D$_5$H.

Figure S16. Aromatic and alkyl regions of the DEPT135 ^{13}C NMR (75 MHz) of modified polymer **12** (X = OC$_6$H$_4$-p-CH$_3$) in C$_6$D$_6$. The alkyl region (0-80 ppm) has been vertically expanded and horizontally compressed relative to the aromatic region (100-160 ppm).
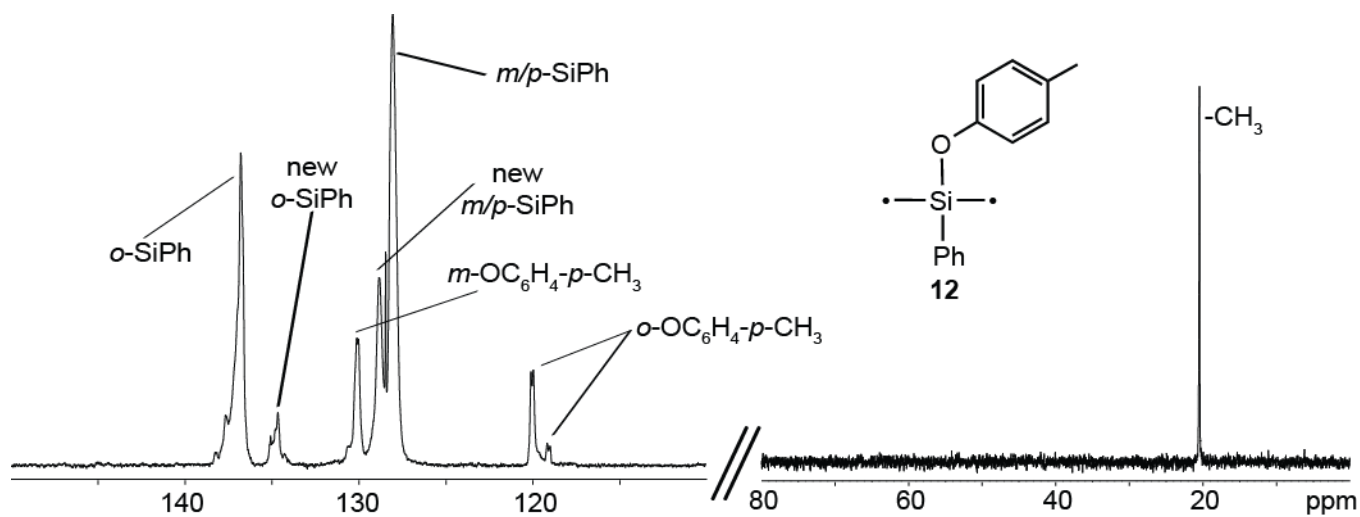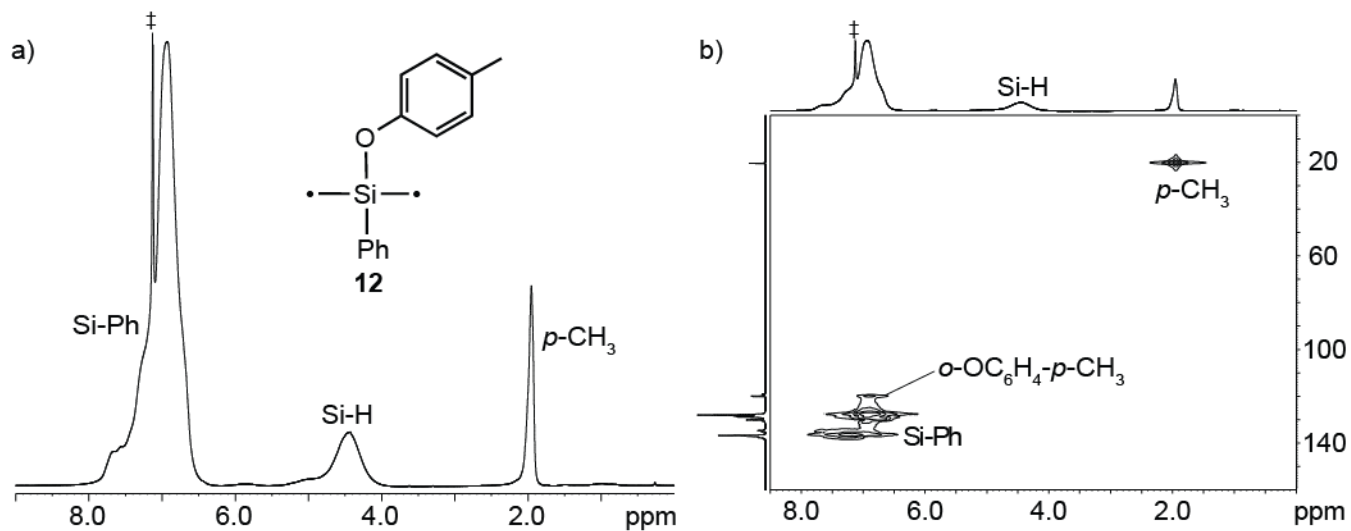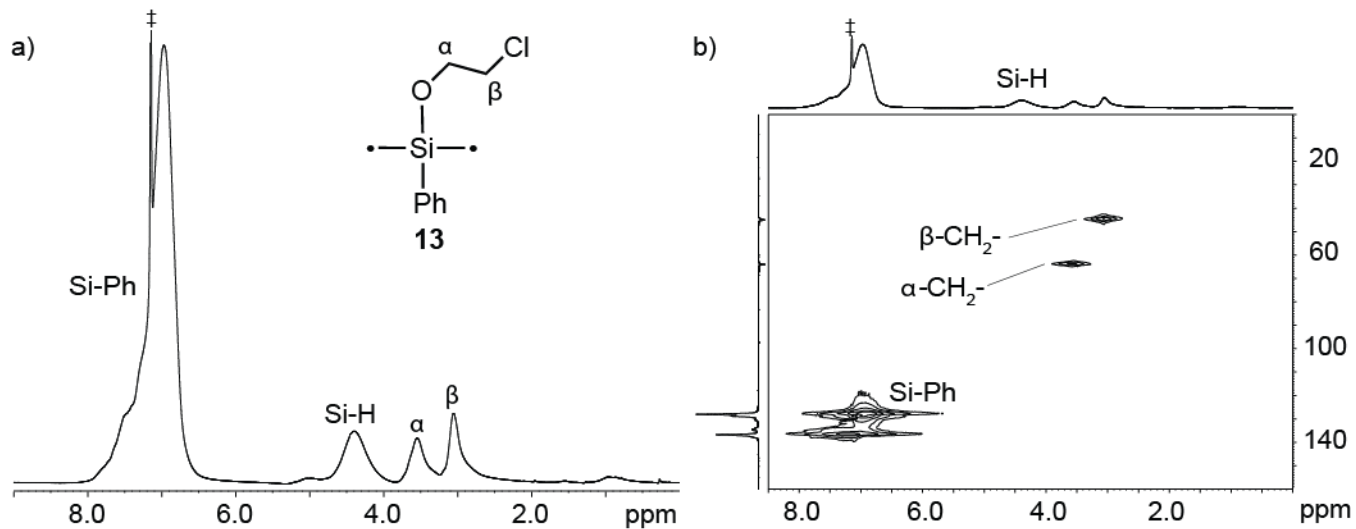
Figure S17. a) ^{1}H NMR (300 MHz) and **b)** ^{1}H-^{13}C HSQC (^{1}H 300 MHz) of modified polymer **13** (X = O(CH$_2$)$_2$Cl) in C$_6$D$_6$. The "‡" is C$_6$D$_5$H.
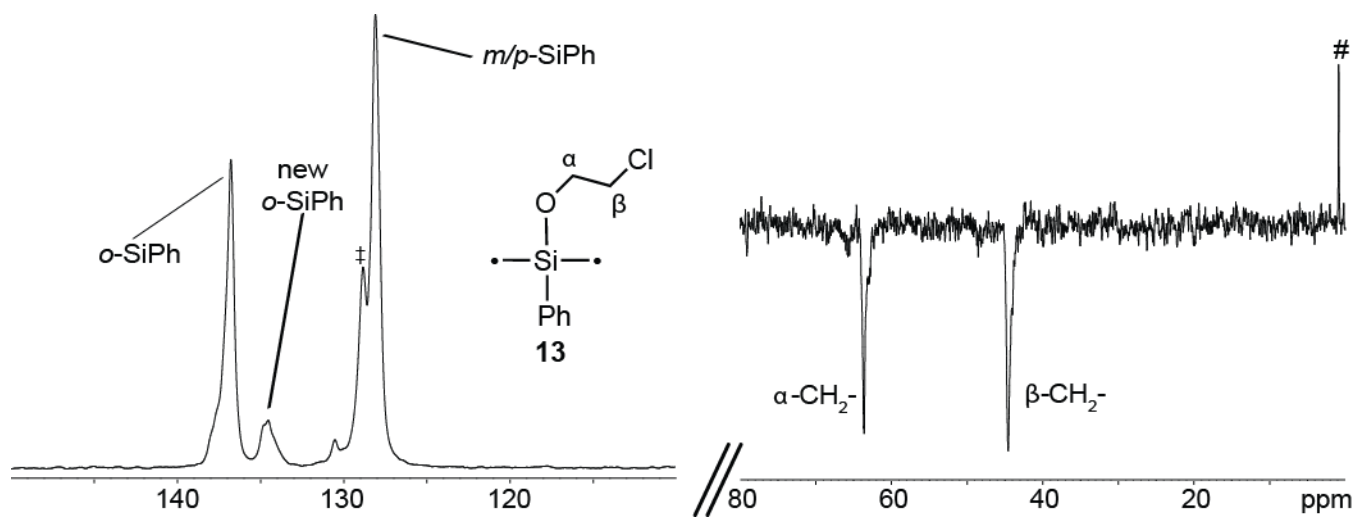
Figure S18. Aromatic and alkyl regions of the DEPT135 ^{13}C NMR (75 MHz) of modified polymer **13** (X = O(CH$_2$)$_2$Cl) in C$_6$D$_6$. The alkyl region (0-80 ppm) has been vertically expanded and horizontally compressed relative to the aromatic region (100-160 ppm). The "‡" is C$_6$D$_5$H and the "#" is grease.

Representative IR spectra

IR spectra were obtained for KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer. Spectra for polymers **8**, **10**, and **11** were previously reported.[1] Spectrum for polymer **7** was not recorded due to impurities of diphenylmethane in this sample. The spectrum for polymer **9** is not included; similar to polymer **4**, at 10% sidechain modification it provided no diagnostic peaks.
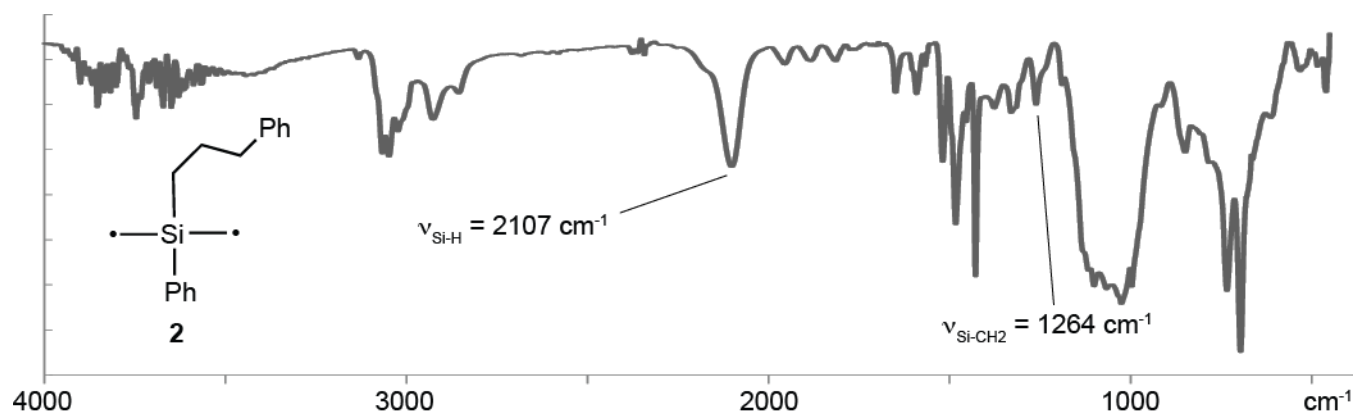
Figure S19. IR spectrum for modified polymer **2** (X = (CH$_2$)$_3$Ph).
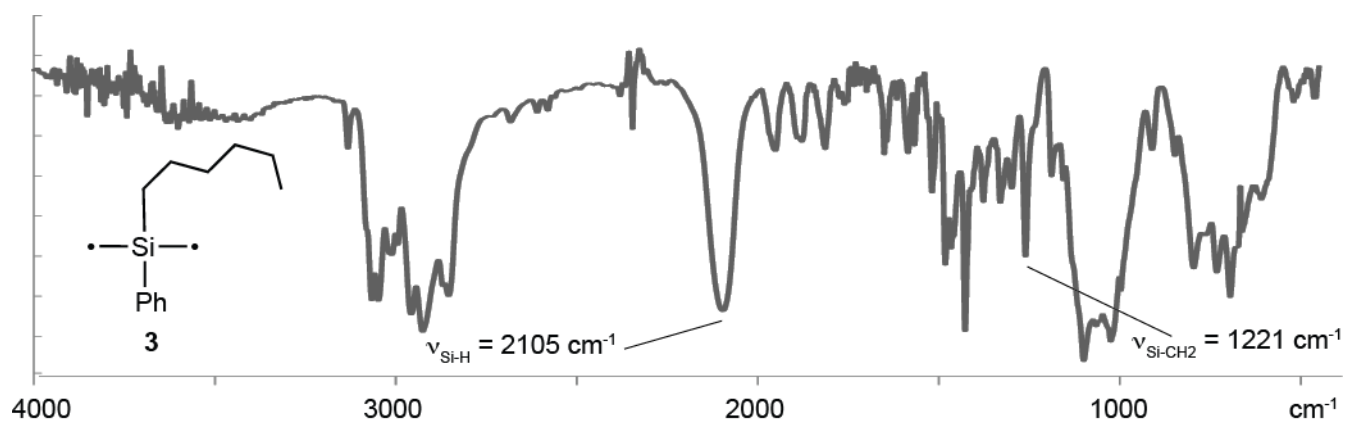
Figure S20. IR spectrum for modified polymer **3** (X = (CH$_2$)$_5$CH$_3$).
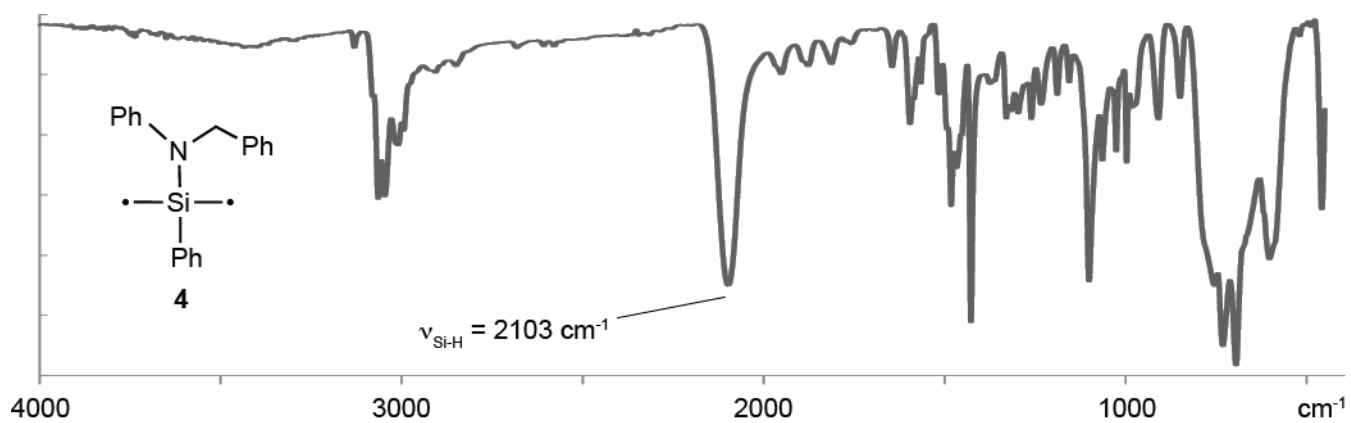
Figure S21. IR spectrum for modified polymer **4** (X = N(Ph)CH$_2$Ph).
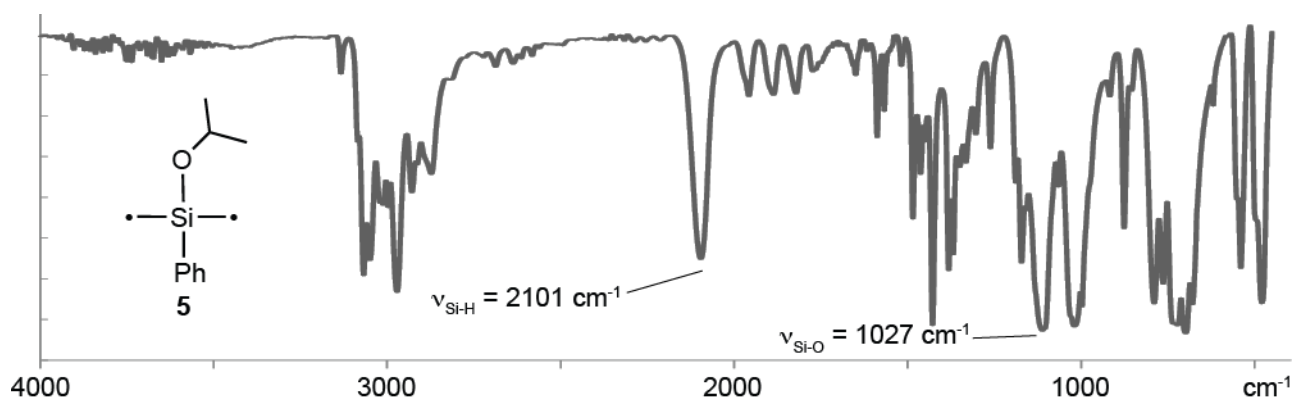
Figure S22. IR spectrum for modified polymer **5** (X = OCH(CH$_3$)$_2$).
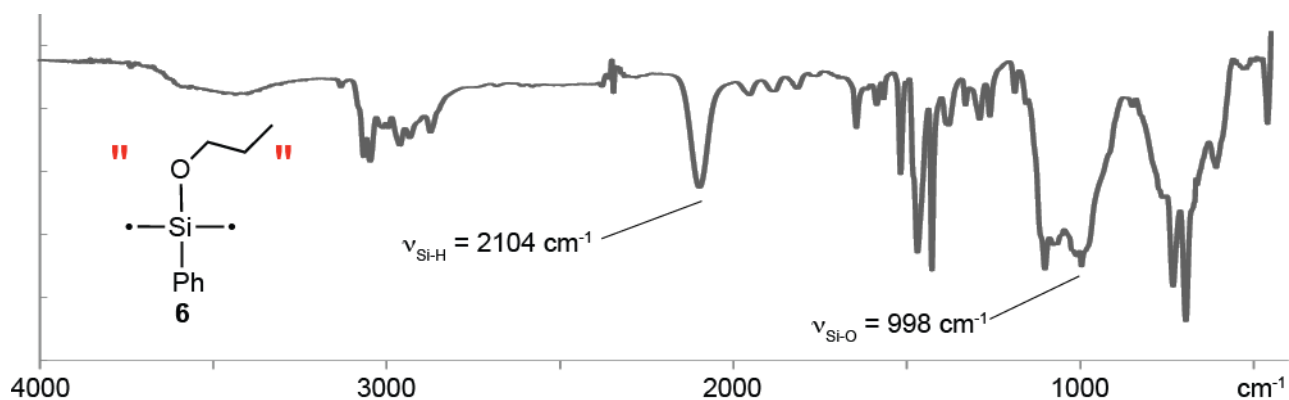
Figure S23. IR spectrum for modified polymer **6** ($X = O(CH_2)_2CH_3$), a polymer for which over-reduction occurred.
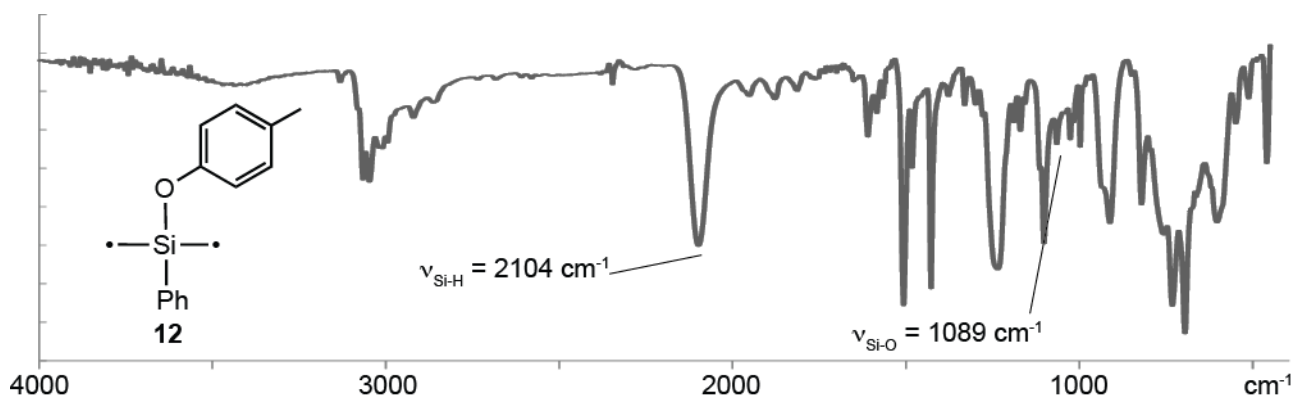
Figure S24. IR spectrum for modified polymer **12** ($X = OC_6H_4\text{-}p\text{-Me}$).
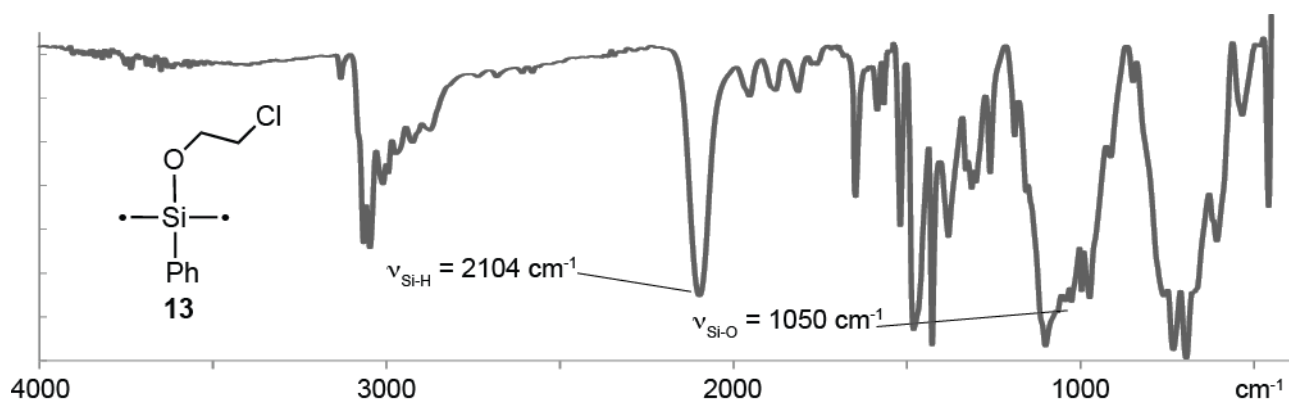
Figure S25. IR spectrum for modified polymer **13** (X = OCH$_2$CH$_2$Cl).

^{29}Si{^{1}H} NMR details and spectra

^{29}Si{^{1}H} DEPT NMR experiments were performed on saturated samples in d_6-benzene (typically ~100 mg/mL). For polymer samples, two experiments were attempted: DEPT90, optimized for a single proton directly bound to Si, with $^{1}J_{SiH}$ ~ 188 Hz, and DEPT45, optimized for two H$_{ortho}$ in SiPh, with $^{3}J_{SiH}$ ~ 8 Hz. Thus, the DEPT90 experiment detects "SiH" groups, while the DEPT45 detects "SiPh" groups. The DEPT45 experiment gave much lower signal intensities; useful spectra were obtained only for polymers **2**, **3**, **5**, **12**, and **13**. Spectra for polymers **8**, **10**, and **11** were previously reported.[1]
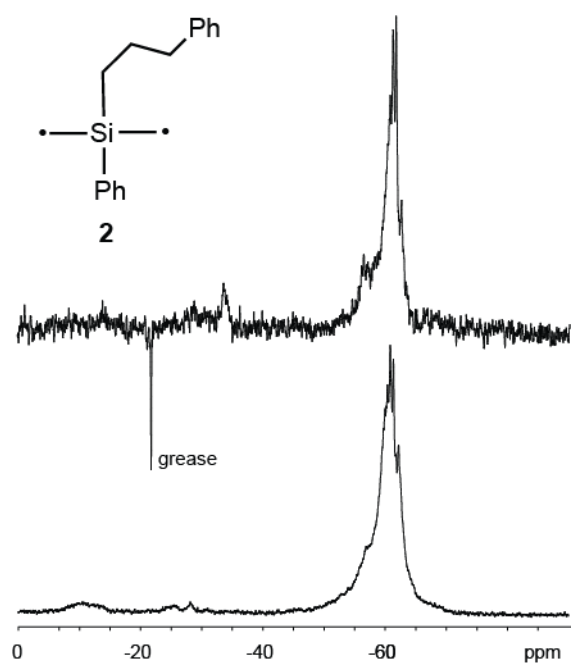
Figure S26. 99 MHz ^{29}Si{^{1}H} DEPT45 (top) and DEPT90 (bottom) NMR spectra of modified polymer **2** (X = (CH$_2$)$_3$Ph) in C$_6$D$_6$.
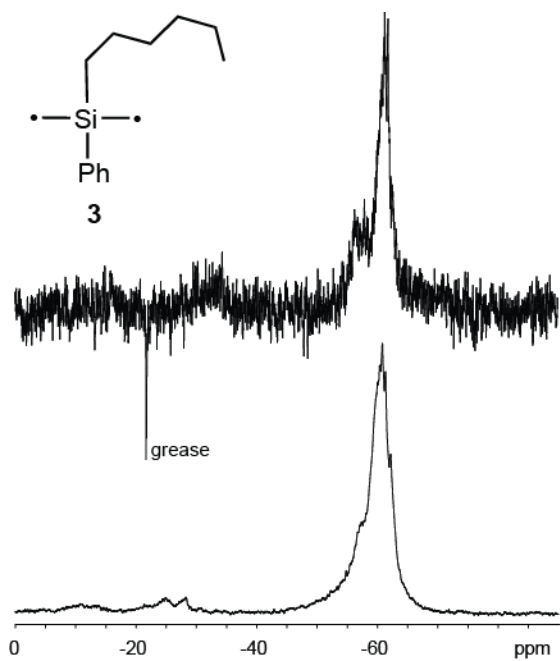
Figure S27. 99 MHz $^{29}Si\{^1H\}$ DEPT45 (top) and DEPT90 (bottom) NMR spectra of modified polymer **3** (X = (CH$_2$)$_5$CH$_3$) in C$_6$D$_6$.
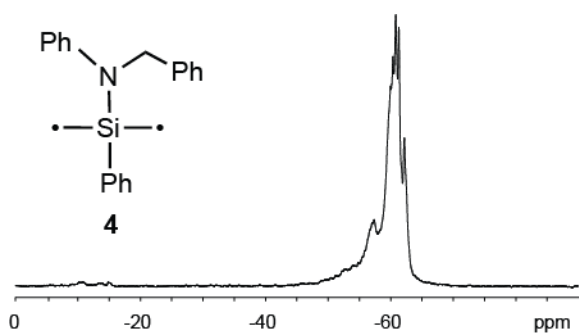
Figure S28. 99 MHz $^{29}Si\{^1H\}$ DEPT90 NMR spectrum of modified polymer **4** (X = N(Ph)CH$_2$Ph) in C$_6$D$_6$.
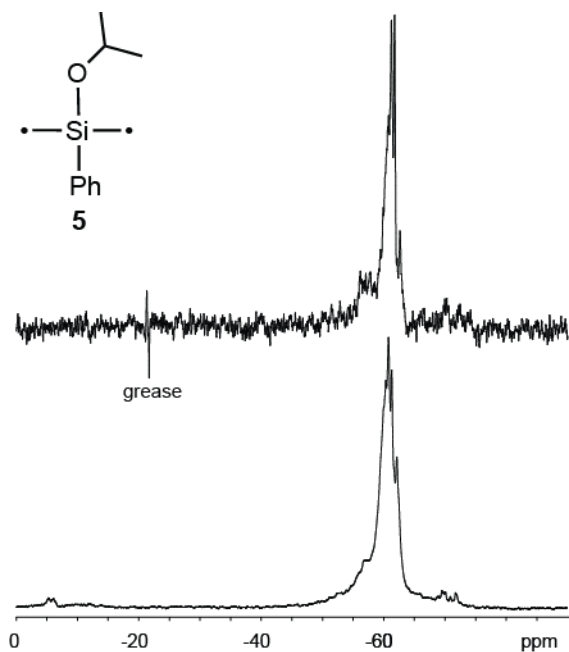
Figure S29. 99 MHz $^{29}Si\{^1H\}$ DEPT45 (top) and DEPT90 (bottom) NMR spectra of modified polymer **5** (X = OCH(CH$_3$)$_2$) in C$_6$D$_6$.
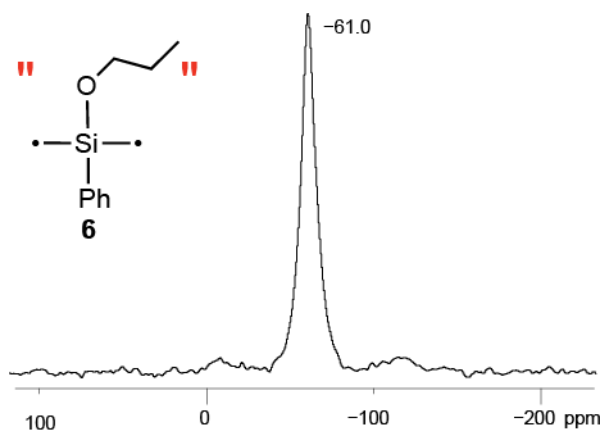
Figure S30. 72 MHz $^{29}Si\{^1H\}$ DEPT90 NMR spectrum of modified polymer **6** (X = O(CH$_2$)$_2$CH$_3$) in C$_6$D$_6$. The structure is shown in quotation marks since over-reduction has occurred to install Si-O-Si units (see text).
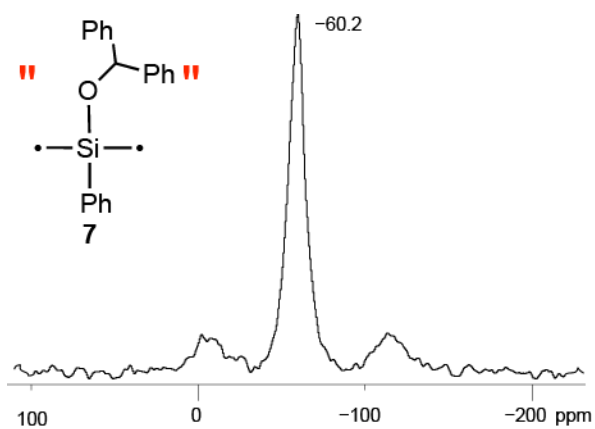
Figure S31. 72 MHz ^{29}Si{^{1}H} DEPT90 NMR spectrum of modified polymer **7** (X = OCHPh$_2$) in C$_6$D$_6$. The structure is shown in quotation marks since over-reduction has occurred to install Si-O-Si units (see text).
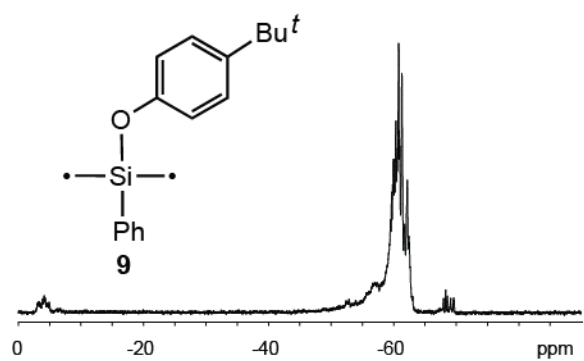
Figure S32. 99 MHz ^{29}Si{^{1}H} DEPT90 NMR spectra of modified polymer **9** (X = OC$_6$H$_4$-*p*-Bu^t) in C$_6$D$_6$.
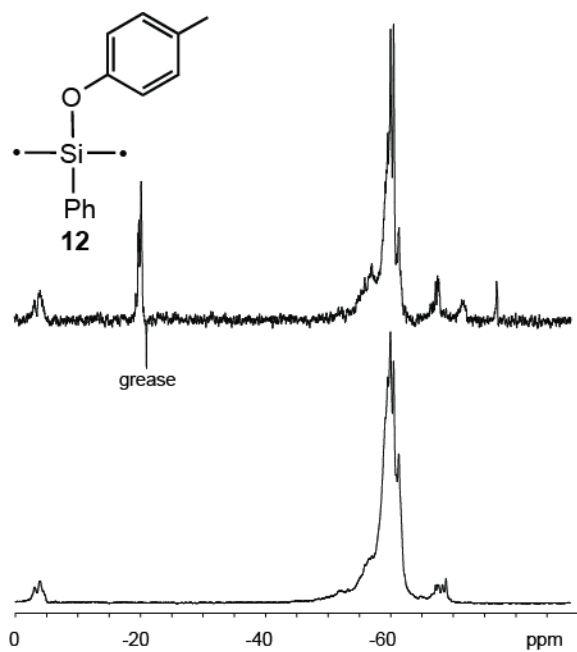
Figure S33. 99 MHz ^{29}Si{^{1}H} DEPT45 (top) and DEPT90 (bottom) NMR spectra of modified polymer

12 (X = OC$_6$H$_4$-*p*-CH$_3$) in C$_6$D$_6$.
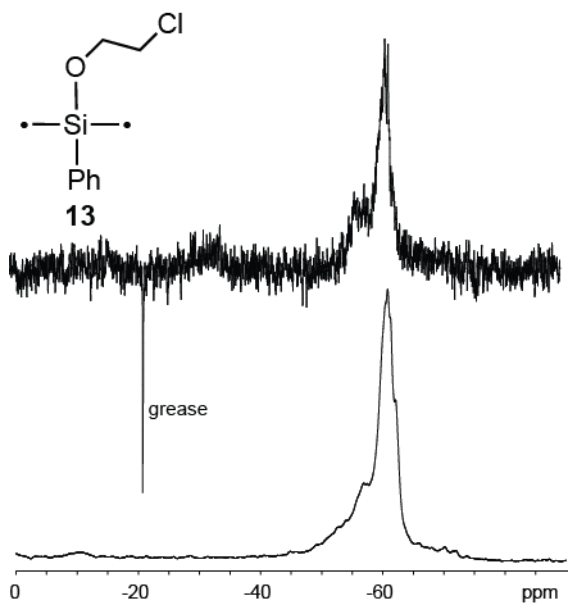
Figure S34. 99 MHz ^{29}Si{^{1}H} DEPT45 (top) and DEPT90 (bottom) NMR spectra of modified polymer

13 (X = O(CH$_2$)$_2$Cl) in C$_6$D$_6$.

Evaluation of catalyst selectivity for Si-H bond modification over Si-Si bond cleavage

GC-MS data was obtained using a Polaris Trace Q-DSQ instrument (GC column was DB5-MS 15 m length, 0.25 mm inner diameter, 25 μm coating; temperature was increased from 50 to 250°C at 25°C/min and held for 22 min for a total 30 min chromatogram; flow rate was 1 mL/min; EI-MS used 70 eV ionization.

As reported previously for the synthesis of polymers **8**, **10**, and **11**,[1] pentane or hexanes washings obtained during the syntheses of the new modified polymers in this work were diluted with pentane or hexanes, respectively, to approximately 100 mL total volume. An aliquot (1.5-2 mL) of solution was removed and this was analyzed by GC-MS. The major chromatogram trace peaks were unreacted (if non-volatile) substrate (e.g. for **4** ($m/z = 181$), **7** ($m/z = 182$), **9** ($m/z = 150$), and **12** ($m/z = 122$)) and $B(C_6F_5)_3$ (usually detected as hydrolyzed/degraded by-product, pentafluorobenzene (C_6HF_5) $m/z = 168$).

The pentane or hexanes was removed under vacuum from the remaining solution, leaving a white or slightly yellow residue, which was dissolved in C_6D_6 for analysis by ^{1}H and ^{19}F NMR. The ^{1}H NMR spectra showed unreacted substrate (for polymers **4**, **7**, **9**, and **12**) and/or trace amounts (signals just above the ^{1}H NMR baseline) of the X-modified poly(phenylsilane). No discrete or sharp signals were detected in the Si-H region (4-6 ppm) or elsewhere that could be attributed to mono- or disilane products resulting from polymer degradation. The ^{19}F NMR showed $B(C_6F_5)_3$ and/or substrate-coordinated $B(C_6F_5)_3$ (three ^{19}F peaks slightly displaced from free $B(C_6F_5)_3$).

Molecular weight analysis by MALS-GPC

MALS-GPC was carried out using an Agilent liquid chromatograph equipped with an Agilent 1200 series isocratic pump, Agilent 1200 series standard autosampler, Phenomenex Phenogel 5 μm narrow bore columns (4.6 x 300 mm) 10^4 Å (1000-75000), Wyatt Optilab rEX differential refractometer (λ = 658 nm, 40 ºC), and a Wyatt TriStar miniDAWN (laser light scattering detector at λ = 690 nm). A flow rate of 0.5 mL/min was used and samples were dissolved in THF or CHCl$_3$ (ca. 2-3 mg/mL). The dη/dc values of all polymers were calculated using 100% mass recovery methods using the ASTRA software version 5. All analyses were run in triplicate, in air.
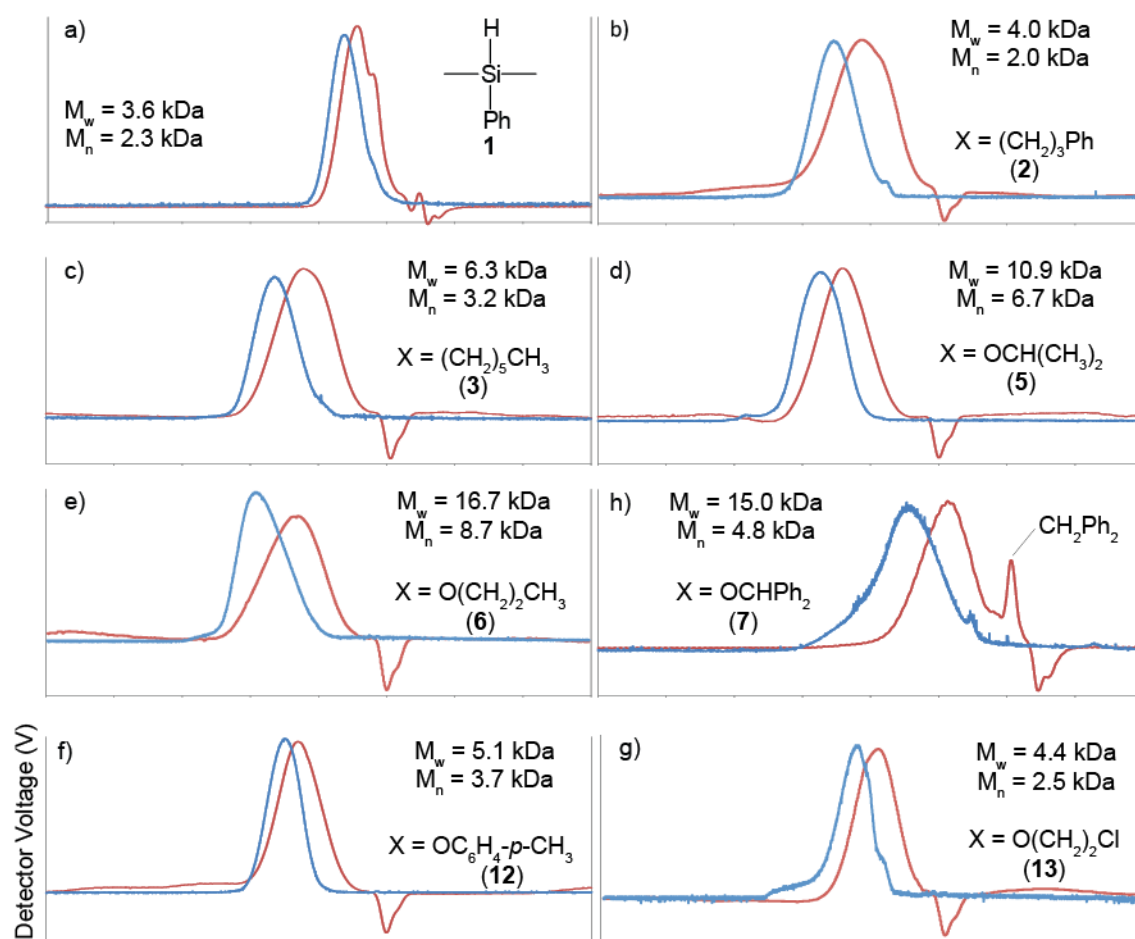
Figure S35. Representative differential RI (red) and multi-angle LS (blue) traces for modified polymers.

Thermogravimetric analysis (TGA)

TGA was carried out on a TA Instruments SDT Q600 with temperature increased from 20 to 1000 °C at a rate of 10 °C/min. The oven was flushed with nitrogen during analysis, in an attempt to limit sample oxidation to SiO_2. However we note that some of the traces in Figure 6 show minimum masses at 600-700°C and slight increases in mass on further heating to 1000°C; these may be attributed to some surface oxidation.

Table S1 TGA data for modified polymers that did not undergo over-reduction. Data for polymers **8**, **10**, and **11** is new since we first reported the synthesis of these the S-substituted derivatives.[1]

polymer	X	inflection temperature (± 10 °C)	ceramic yield (%)
1	H	320	37
2	$(CH_2)_3Ph$	340	58
3	$(CH_2)_5CH_3$	340	44
4	$N(Ph)CH_2Ph$	300	52
5	$OCH(CH_3)_2$	280	58
10	SC_6H_4-*p*-CH_3	310	46
11	$S(CH_2)_2CH_3$	270	67
12	OC_6H_4-*p*-CH_3	340	59
13	$O(CH_2)_2Cl$	320	60

UV-visible spectra

UV-visible spectra were acquired for samples in spectroscopic grade dichloromethane (0.1-0.4 mg/mL) at room temperature on a Varian Cary-1 or Cary-5 spectrophotometer.
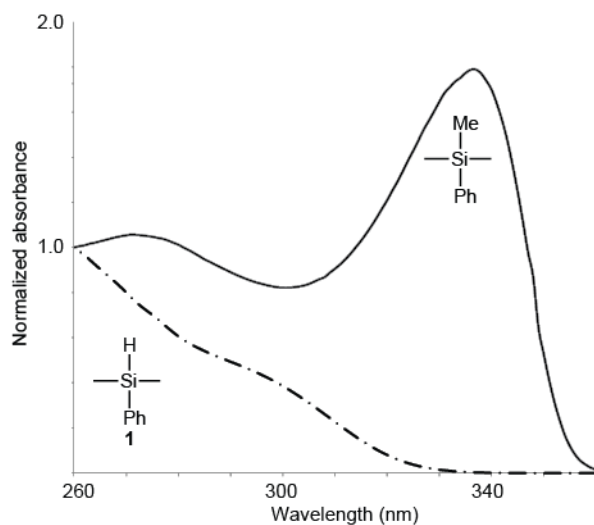
Figure S36 UV-visible spectra of poly(phenylsilane) **1** prepared via catalytic dehydrocoupling (M_W/M_n = 3500/2200) and poly(methylphenylsilane) prepared via Wurtz coupling (M_w/M_n = 16,900/5,600)[2].

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[2]The MW of the poly(methylphenylsilane) sample was calculated from MALS-GPC data using the random coil model. However, it has been suggested that for fully substituted polysilanes such as this, the rigid rod calculation may be a more suitable model. W. J. Welsh, J. R. Damewood and R. C. West, *Macromolecules*, 1989, **22**, 2947.
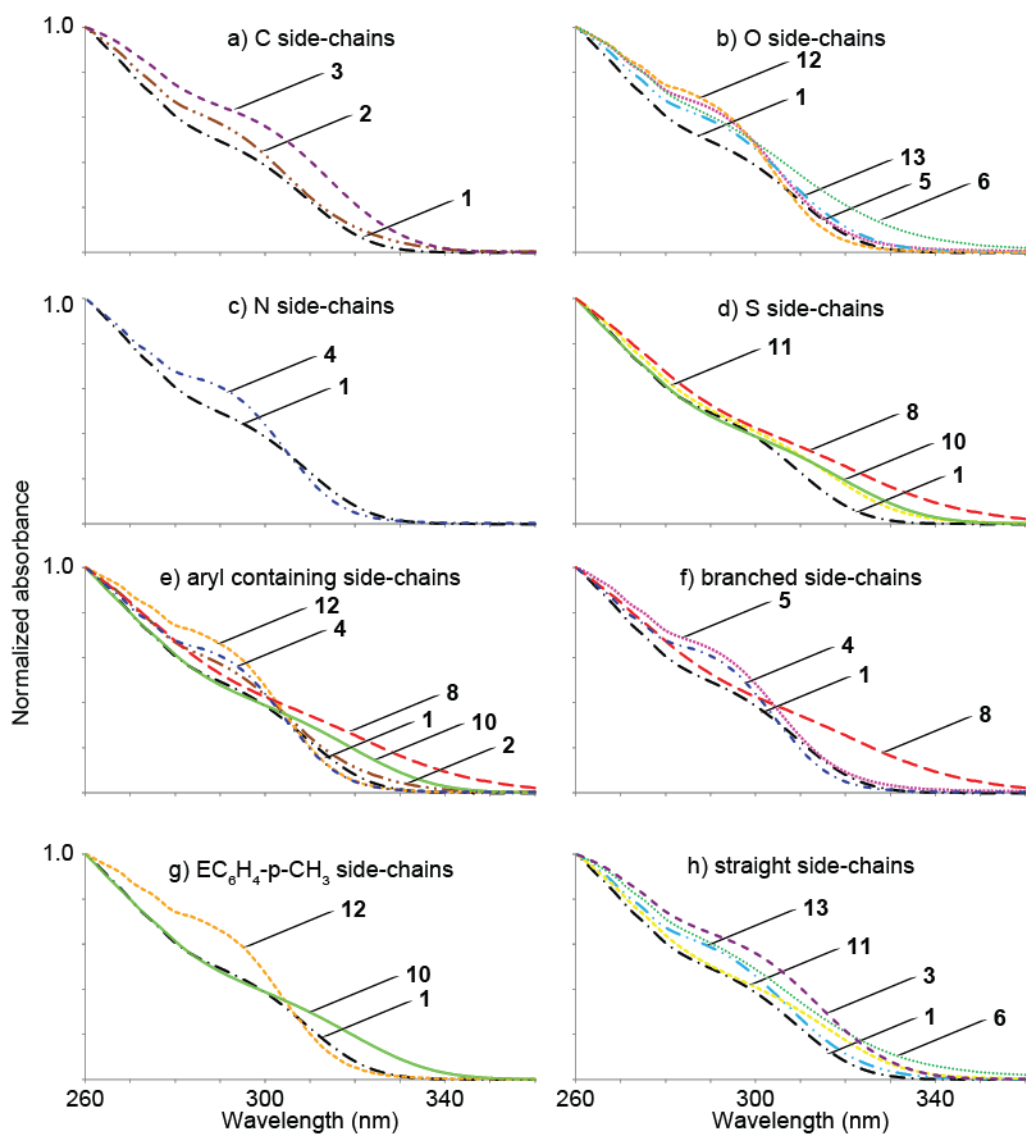
Figure S37 Groupings of UV-visible spectra recorded for poly(phenylsilane) (**1**) and selected modified polysilanes.

Elemental analyses

Microanalysis was performed by Canadian Microanalytical Service Ltd., Delta, BC, Canada.

Combustion analysis is not routinely used to characterize polysilanes, probably due to the common perception that SiC is likely to form during combustion, leading to low %C values. Nevertheless, elemental analyses (EA) have been reported for some polysilanes, including some with heteroatom substituents, that match reasonably well the calculated percentages based on established polymer repeat units.[3] We previously reported the EA obtained for poly(phenylsilane) **1** (Table S2), which is consistent with the formula based on the repeat unit $[PhSiH]_n$.[1]

Our generic formulae for the modified polymers, $[PhSiX]_n[PhSiH]_{(1-n)}$, give elemental compositions that vary considerably with respect to the sensitivity of their %C, H, N values to the %X content. Table S2 provides a range of calculated values for each polymer to illustrate this variability, and also shows the calculated values based on our ^{1}H NMR estimates of the %X incorporated into each polymer. The results for the polymers for which over-reduction occurs (**6** and **7**) are reported separately in Table S3, since they pose the additional challenge of assessing numbers of "Si-O-Si" repeat units in addition to %X. The EA results for polymers **8**, **10**, and **11** were previously reported.[1]

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[3] See for example: a) M. Fujino, T. Hisaki, M. Fujiki, N. Matsumoto, *Macromolecules,* 1992, **25**, 1079; b) Y.-L. Hsiao and R. M. Waymouth, *J. Am. Chem. Soc.*, 1994, **116**, 9779 c) H. Tang, Y. Liu, B. Huang, J. Qin, C. Fuentes-Hernandez, B. Kippelen, S. Li and C. Ye, *J. Mater. Chem.*, 2005, **15**, 778.

Table S2. Elemental analysis data for modified polymers of general formulae $[PhSiX]_n[PhSiH]_{(1-n)}$.

		Found	Calcd for %X (best fit in bold)		Calcd for X% (^{1}H NMR)	
	X	**%C/H(/N)**	**%X**	**%C/H(/N)**	**%X**	**%C/H(/N)**
1	H	67.99/5.69	**100**	**67.86/5.69**	100	67.86/5.69
			10	70.22/5.98		
2	$(CH_2)_3Ph$	68.51/5.35	**5**	**69.10/5.84**	20	72.16/6.21
			0	67.86/5.69		
			20	70.29/6.88		
3	$(CH_2)_5CH_3$	68.82/7.24	**15**	**69.75/6.62**	40	72.14/7.78
			10	69.16/6.33		
			10	70.53/5.76/1.40		
4	$N(Ph)CH_2Ph$	66.49/5.93/0.70	**5**	**69.30/5.73/0.61**	5	69.30/5.73/0.61
			0	67.86/5.69/0		
			95	65.87/7.31		
5	$OCH(CH_3)_2$	60.31/6.25	**25**	**67.16/6.26**	25	67.16/6.26
			5	67.70/5.82		
			25	66.45/5.46		
12	$OC_6H_4\text{-}p\text{-}CH_3$	68.42/5.58	**20**	**69.75/5.70**	20	69.75/5.70
			15	73.05/5.93		
			35	60.20/21.01		
13	$O(CH_2)_2Cl$	61.20/4.92	**30**	**61.10/5.36**	25	62.05/5.41
			25	62.05/5.41		

The EA results for modified polymers containing heteroatoms adjacent to Si (**4**, **12**, **13**, and the S-containing polymers **10** and **11**[1]) fit the formulae derived from ^{1}H NMR relatively well, within the estimated ± 5% deviation. The polymers containing alkyl sidechains (**2** and **3**) gave %C (and %H) values that fit a [PhSiX]$_n$[PhSiH]$_{(1-n)}$ formula in which %X is low relative that estimated from ^{1}H integrations (EA values low in %C). We note that the [Si-CH$_2$-] groups in these polymers may make them the most susceptible to loss of carbon during combustion due to the formation of SiC.[4]

The %C for the isopropoxy-substituted polymer (**5**) is extremely low relative to the calculated value based on ^{1}H NMR. It is even low relative to the expected value for 100% substitution of the Si-H bonds in this polymer! This result, along with the unexpectedly high MWs obtained for this polymer (vide supra), is consistent with the possible introduction of Si-O-Si units, leading to some crosslinking. We do not think over-reduction is occurring for this substrate; previous studies[5] suggest it should not be favoured for branched alkoxides, and NMR analysis of this polymer does not indicate similar polymer architectures to those we apparently see for polymers **6**, **7**, and **8**, where over-reduction is occurring. The inconsistencies between EA, GPC and NMR data for this polymer may be attributable to hydrolysis of the small alkoxy sidechains during EA and GPC analysis.

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[4] See for example: a) S. Yajima, K. Okamura, j. Hayashi, M. Omori, *J. Am. Ceram. Soc.*, 1976, **59**, 324; b) W. R. Schmidt, L. V. Interrante, R. H. Doremus, T. K. Trout, P. S. Marchetti and G. E. Maciel, *Chem. Mater.*, 1991, **3**, 257; and references therein.

[5] See discussion and references in: P. T. K. Lee and L. Rosenberg, *J. Organomet. Chem.*, 2016, **809**, 86.

Table S3. Elemental analysis data for modified polymers for which over-reduction occurred.

		Found	Calcd (best fit in bold)	
	X	**%C/H**	**[PhSiH]/[PhSiX]/[PhSiO$_{1/2}$](/Ph$_2$CH$_2$)**	**%C/H**
1	H	67.99/5.69	**100**	**67.86/5.69**
6	O(CH$_2$)$_2$CH$_3$	62.65/5.18	2/5/93	63.90/4.68
			0/0/100	**63.37/4.45**
			30/70/0 (^{1}H estimate)	66.65/7.00
7	OCHPh$_2$	64.21/4.31	**0.5/0.5/98/1**	**64.21/4.50**
			0/0/99/1	64.10/4.49

Table S3 shows that EA results for polymers **6** and **7** are consistent with a substantial contribution of the Si-O-Si repeat unit to the polymer structure; in particular the %C values are very low. For polymer **6**, however, even assuming complete replacement of SiH and SiOPr^n groups with Si-O-Si (which is not supported by NMR characterization of this polymer (vide supra)) does not give a low enough %C. As noted in the text, when this polymer is heated above 50°C under vacuum it undergoes some as-yet uncharacterized transformation that renders it completely insoluble – this process may be occurring also during combustion, and may be complicating the analysis. Although we are able to identify a formula for polymer **7** that matches the EA results (ratios of SiH, SiCHPh$_2$, and PhCH$_2$ were crudely estimated from ^{1}H NMR), it also seems to underestimate the remaining SiH and SiCHPh$_2$ groups in the polymer. We cannot rule out the possibility that the over-reduction chemistry is simply yielding highly non-homogeneous polymer samples in these cases.