Electronic Supplementary Information

Styrylsilane coupling reagents for immobilization of organic functional groups on silica and glass surfaces

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Contents

1. General

Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column chromatography was monitored using analytical thin-layer chromatography (TLC) carried out on 0.25 Merck silica gel plates (60 F-254) using UV light as a visualizing agent, *p*-anisaldehyde solution, and $KMnO_4$ solution as staining solutions, and heat as developing agent. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance II/DPX 400 (400 MHz ^{1}H, 100 MHz ^{13}C) spectrometer with chemical shifts reported relative to residual deuterated solvent peaks. ^{1}H NMR spectra was referenced to residual $CDCl_3$ (for ^{1}H, δ = 7.26 ppm) as internal standard, and was reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet). ^{13}C NMR spectra was referenced to the residual $CDCl_3$ (77.26 ppm). Fluorescence spectra were obtained on a Perkin Elmer LS 55. Infrared spectra were obtained using a Nicolet Impact 400 spectrometer. Contact angle was measured using a Bioin Scientific ThetaLite 100. Elemental analysis was obtained on a Perkin Elmer 2400 Series II at YCRF of Yonsei University facility. Analytical GPC was performed on a JASCO HPLC equipped with KF-404HQ columns (ID. 4.6 X L. 250nm, Shodex, Tokyo, Japan) using THF as the eluent at a flow rate of 1.0 ml/min.

2. Materials

Reagent grade chemicals (vinyltrimethylsilane (**1h**), trifluoromethanesulfonic acid (TfOH, **3a**), **3b-3g,** dichloromethylsilane (**5**), 11-chloroundec-1-ene (**6**), allyl chloride, $LiAlH_4$ (**8**), benzylmagnesium chloride (2.0M solution in THF), phenylacetylene(**10**)) were purchased from Aldrich Chemical Company and Alfa Aesar and used as received without further purification unless otherwise stated. Polybutadiene (**12**) was purchased from Aldrich (CAS No. 9003-17-2) and its molecular weight (Mw) is determined to be 2,950 with PDI(Mw/Mn) = 1.65. Silica ball (**2**, particle/pore size: 10 μm/10 nm and surface area: 310 m^2/g) was purchased from Fuji Silysia Chemical, and glass (microscope slides) was purchased from Marienfeld. $H_2PtCl_6.xH_2O$ (**7**) was purchased from Pressure Chemical corporation. $RhCl(PPh_3)_3$ (**11**) was prepared by using reported procedures.[1] 1-(propargyloxymethyl)pyrene (**16**) was prepared by etherification of 1-pyrenylmethanol and propargyl bromide with sodium hydride.

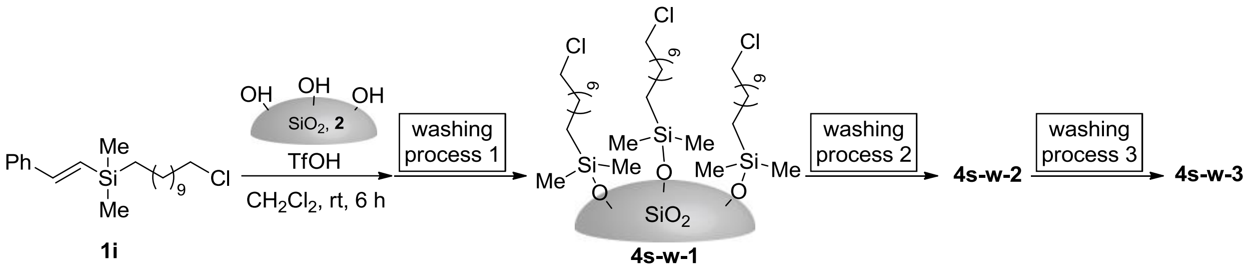
3. Experimental

- Representative procedure for immobilization of various alkenylsilane 1 onto silica surface (**Table 1 and Table 2**)

To a 1 mL pressure vial were added styrylsilane (**1a**, 0.08 mmol), silica (**2**, 20 mg), acid catalyst (**3a**, 0.004 mmol) and dichloromethane (0.1 mL). The mixture was stirred at room temperature for 6 h, filtered, and washed thoroughly with dichloromethane, H_2O and acetone. Functional group-immobilized silica **4h** (1.11 mmol/g) was obtained after drying *in vacuo*.

- Loading extent of functionalized silica by washing process

To a 2.5 mL pressure vial were added styrylsilane (**1i**, 0.8 mmol), silica (**2**, 200 mg), TfOH (**3a**, 0.04 mmol) and dichloromethane (1 mL) (Scheme S1). The reaction was carried out with stirring at room temperature for 6 h. After the reaction, the reaction mixture was filtered, washed thoroughly with dichloromethane, H_2O and acetone, and dried *in vacuo* to give functionalized silica **4s-w-1** (washing process 1), whose loading extent was determined as 0.70 mmol/g by elemental analysis. The silica **4s-w-1** was rewashed with dichloromethane, H_2O and acetone, and dried *in vacuo* to give **4s-w-2** (washing process 2), whose loading extent was determined as 0.69 mmol/g. Finally, the silica **4s-w-2** was washed with sat. aq $NaHCO_3$ solution, sat. aq NH_4Cl solution, dichloromethane, H_2O and acetone (washing process 3), and dried *in vacuo* to give functionalized silica **4s-w-3**, whose loading extent was determined as 0.71 mmol/g. These experimental results show that the sample of functionalized silica **4s-w-1** was not contaminated by other non-covalent organic species.



entry	functionalized silica	washing solvent	loading extent (mmol/g)
1	**4s-w-1**	CH_2Cl_2 / acetone / H_2O	0.70 mmol/g
2	**4s-w-2**	CH_2Cl_2 / acetone / H_2O	0.69 mmol/g
3	**4s-w-3**	sat. aq $NaHCO_3$ / sat. aq NH_4Cl and CH_2Cl_2 / acetone / H_2O	0.71 mmol/g

Scheme S1. Loading extent of functionalized silica by washing process.

- ^{13}C CP-MAS NMR spectrum of functionalized silica

When ^{13}C CP-MAS NMR spectra of functionalized silica **4s-w-1** (Figure S1b) was compared with that of the styryl silane compound **1i** (Figure S1a), carbon signals of styryl group in **1i** were completely disappeared with remaining the thirteen carbon atoms of 11-chloroundecyl and methyl groups without showing any organic carbon species. This result shows that the surface structure proposed for **4s-w-1** is right with high purity.

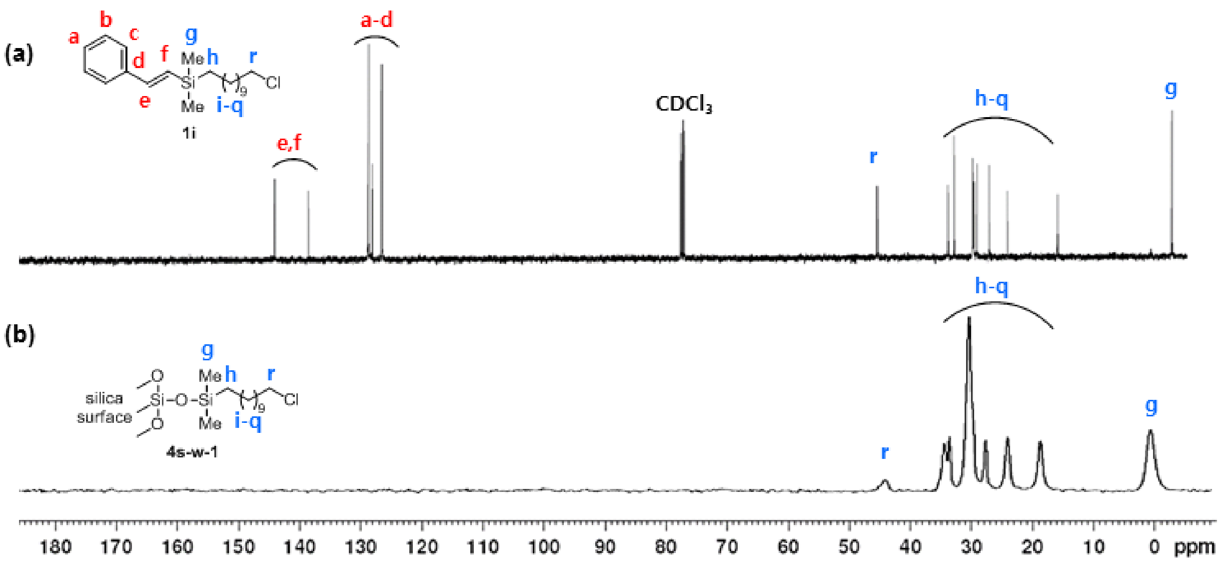


Figure S1. (a) ^{13}C NMR spectrum of **1i**. (b) ^{13}C CP-MAS NMR spectra of **4s-w-1**.

- Preparation of 1a–1g (Table 1)

A 2-neck round bottomed flask pre-equipped with reflux condenser was charged with chlorodimethylsilane (3 g, 33 mmol) and 10% H_2PtCl_6•xH_2O (16.4 mg, 0.03 mmol) in 2-propanol (0.1 mL) solution. The resulting solution was stirred for 30 min. Then, phenylacetylene (3.88 g, 38 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. Unreacted chlorodimethylsilane was removed by distillation under reduced pressure to give crude (E)-chlorodimethyl(styryl)silane, which was used for the next step without further purification. Benzylmagnesium chloride (2.0M solution in THF, 19 ml, 38mmol) was added dropwise to the crude (E)-chlorodimethyl(styryl)silane and the resulting solution was stirred at room temperature for 30 min. Saturated NH_4Cl (aq.) was added, and the mixture was extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Compound **1a** (colorless liquid, 5.76 g, 72% yield) was obtained by using column chromatography (*n*-hexane). Compound **1b-1f** were also prepared by using corresponding acetylene derivatives instead of phenylacetylene.

(E)-benzyldimethyl(styryl)silane (1a) [CAS No. 941318-08-7]; Obtained as a colorless liquid (5.76 g, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 6.8 Hz, 2H), 6.89 (d, *J* = 19.2 Hz, 1H), 6.47 (d, *J* = 19.2 Hz, 1H), 2.25 (s, 2H), 0.17 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 144.9, 140.1, 138.4, 128.8, 128.5, 128.4, 128.3, 127.6, 126.6, 124.3, 26.4, -3.1; IR (neat): 3059, 3024, 2991, 2922, 1941, 1878, 1803, 1745, 1601, 1573, 1493, 1449, 1247, 1206, 1154, 989, 833, 790, 760, 737, 698, 622 cm^{-1}.

(E)-benzyldimethyl(pent-1-en-1-yl)silane (1b); Obtained as a colorless liquid (2.15 g, 31% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 6.08 (dt, *J* = 18.8, 6.4 Hz, 1H), 5.66 (d, *J* = 18.8 Hz, 1H), 2.18-2.12 (m, 4H), 1.52-1.43 (m, 2H), 0.98-0.94 (m, 3H), 0.09 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 148.7, 140.5, 128.5, 128.3, 128.0, 124.1, 39.1, 26.5, 22.1, 13.9, -3.0; IR (neat): 3061, 3025, 2958, 2873, 1936, 1862, 1797, 1738, 1616, 1601, 1493, 1452, 1378, 1248, 1206, 1153, 1056, 989, 832, 698, 615 cm^{-1}; ESI-HRMS (negative) calcd for $C_{14}H_{21}Si$ $[M-H]^-$ 217.1418, found 217.1414.

(E)-benzyldimethyl(oct-4-en-4-yl)silane (1c); Obtained as a colorless liquid (5.78 g, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 5.77 (t, *J* = 6.8 Hz, 1H), 2.21 (s, 2H), 2.19-2.12 (m, 4H), 1.50-1.34 (m, 4H), 1.01-0.96 (m, 6H), 0.09 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 142.1, 140.7, 139.2, 128.5, 128.2, 124.0, 32.4, 30.8, 26.2, 23.8, 22.9, 14.8, 14.2, -3.1; IR (neat): 3061, 2958, 2929, 2871, 1935, 1862, 1792, 1601, 1493, 1453, 1377, 1247, 1206, 1153, 1056, 901, 830, 759, 697, 618 cm^{-1}; ESI-HRMS (positive) calcd for $C_{17}H_{28}SiNa$ $[M+Na]^+$ 283.1852, found 283.1953.

(E)-benzyl(1,2-diphenylvinyl)dimethylsilane (1d); Obtained as a white solid (5.9 g, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.19 (m, 5H), 7.11-6.96 (m, 10H), 6.79 (s, 1H), 2.22 (s, 2H), 0.11 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 145.5, 142.7, 140.0, 138.9, 137.4, 129.7, 128.9, 128.6, 128.4, 128.2, 127.8, 127.4, 126.0, 124.3, 25.2, -3.3; IR (CH_2Cl_2): 3058, 3023, 2957, 2894, 1945, 1866, 1804, 1746, 1599, 1571, 1492, 1448, 1406, 1247, 1206, 1154, 1057, 954, 903, 829, 759, 697, 627 cm^{-1}; Anal. Calcd for $C_{23}H_{24}Si$: C, 84.09; H, 7.36; found C, 82.89; H, 9.51.

(E)-benzyl(4-fluorostyryl)dimethylsilane (1e) [CAS No. 1329431-30-2]; Obtained as a colorless liquid (1.9 g, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.10-7.05 (m, 4H), 6.87 (d, *J* = 19.2 Hz, 1H), 6.40 (d, *J* = 19.2 Hz, 1H), 2.28 (s, 2H), 0.21 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 162.9 (d, J_{C-F} = 245.9 Hz), 143.6, 140.0, 134.6, 128.5, 128.2, 127.2, 124.3, 115.6 (d, J_{C-F} = 21.4 Hz), 26.3, -3.1; IR (neat): 3081, 3060, 2993, 2956, 2797, 1940, 1887, 1765, 1601, 1506, 1451, 1410, 1248, 1227, 1155, 1092, 986, 904, 831, 747, 699, 619 cm^{-1}.

(E)-benzyl(4-methoxystyryl)dimethylsilane (1f) [CAS No. 1329431-28-8]; Obtained as a colorless liquid (226 mg, 20% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 19.2 Hz, 1H), 6.26 (d, *J* = 19.2 Hz, 1H), 3.83 (s, 3H), 2.21 (s, 2H), 0.13 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 159.8, 144.3, 140.2, 131.4, 128.5, 128.3, 127.9, 124.6, 124.2, 114.1, 55.5, 26.5, -3.1; IR (neat): 3060, 2999, 2956, 2928, 2835, 2060, 1940, 1880, 1805, 1698, 1608, 1511, 1453, 1409, 1301, 1248, 1208, 1176, 1157, 1039, 835, 761, 699, 638 cm^{-1}.

- Preparation of trimethyl(1-phenylvinyl)silane (1g)[2] [CAS No. 1923-01-9]

A 10 mL flask, fitted with a rubber septum, was placed in an ice bath (0℃) and purged with nitrogen. A solution of $FeCl_3$ (8.1 mg, 0.05 mmol, 5 mol%) in dry THF (4 mL) was added via syringe followed by TMEDA (30 μL, 20 mol%). The mixture was stirred at 0°C (ice bath) for 10 min. Then, (1-bromovinyl)trimethylsilane (1M solution in THF, 1 mmol) and phenylmagnesium bromide (in 1 M solution in THF, 1 mmol) were added. After 30 min at 0 ℃, the solution was diluted with saturated aqueous $NaHCO_3$ (2 mL) and extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Trimethyl(1-phenylvinyl)silane (colorless liquid, 150 mg, 85% yield) was obtained by using column chromatography (*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.27-7.21 (m, 3H), 5.86 (d, J = 3.2 Hz, 1H), 5.64 (d, J = 3.2 Hz, 1H), 0.2 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 153.7, 145.0, 128.4, 127.4, 126.9, 126.5, -0.6; IR (neat): 3057, 3031, 2957, 2898, 1943, 1870, 1597, 1571, 1488, 1405, 1248, 1072, 1028, 931, 859, 838, 777, 759, 737, 699 cm^{-1}.

- Large scale production of (E)-(11-chloroundecyl)dimethyl(styryl)silane (1i) (Scheme 2)

A 2-neck round bottomed flask pre-equipped with a reflux condenser was charged with chlorodimethylsilane (15 g, 158 mmol) and 10% H_2PtCl_6•xH_2O (123 mg, 0.24 mmol) in 2-propanol (0.2 mL) solution. The resulting solution was stirred for 30 min. Then, 11-chloroundec-1-ene (13 g, 79 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. After the reaction, unreacted chlorodimethylsilane was removed by distillation under reduced pressure to give crude chloro(11-chloroundecyl)dimethylsilane, which was used for the next step without further purification. Chloro(11-chloroundecyl)dimethylsilane was added slowly to $LiAlH_4$ (4.5 g, 118.5 mmol) was added to diethyl ether (250 ml) at 0 °C. Resulting solution was stirred at room temperature for 1 h, diluted by slowly addiding H_2O, and extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give (11-chloroundecyl)dimethylsilane (**9**, colorless liquid, 17 g, 86% overall yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87-3.85 (m, 1H), 3.50 (t, J = 6.8 Hz, 2H), 1.79-1.72 (m, 2H), 1.44-1.40 (m, 2H), 1.3-1.27 (m, 14H), 0.56 (t, J = 6.0 Hz, 2H), 0.05 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 45.2, 33.5, 32.9, 29.9, 29.8, 29.7, 29.6, 29.2, 27.1, 24.6, 14.4, -4.2;

A 2-neck round bottomed flask pre-equipped with a reflux condenser was charged with (11-chloroundecyl)dimethylsilane (**9**, 17 g, 68 mmol) and $RhCl(PPh_3)_3$ (377 mg, 0.4 mmol) in THF (5 ml). The resulting solution was stirred for 30 min. Then, phenylacetylene (**10**, 8.3 g, 81.6 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h, diluted with saturated NH_4Cl (aq.), and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. (E)-(11-Chloroundecyl)dimethyl(styryl)silane (**1i**, colorless liquid, 20.8 g, 75% overall yield) was obtained by using column chromatography (*n*-hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 19.2 Hz, 1H), 6.51 (d, *J* = 19.2 Hz, 1H), 3.56 (t, *J* = 6.8 Hz, 2H), 1.82-1.75 (m, 2H), 1.46-1.43 (m, 2H), 1.36-1.31 (m, 14H), 0.67 (t, *J* = 7.2 Hz, 2H), 0.18 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 144.1, 138.5, 128.8, 128.7, 128.1, 126.5, 45.4, 33.8, 32.9, 29.8, 29.7, 29.6, 29.5, 29.1, 27.1, 24.1, 15.9, -2.8; IR (neat): 3078, 3059, 3028, 2988, 2925, 2853, 1941, 1875, 1801, 1604, 1573, 1494, 1464, 1446, 1288, 1247, 1215, 1070, 1028, 988, 842, 737, 689, 653 cm^{-1}; ESI-HRMS (negative) calcd for $C_{21}H_{34}ClSi$ $[M-H]^-$ 349.2124, found 349.2051.

- Preparation of 1j–1q (Scheme 3 and Table 2)[2]

- Preparation of (E)-12-(dimethyl(styryl)silyl)dodecanenitrile (1j)

A solution of (*E*)-(11-chloroundecyl)dimethyl(styryl)silane (**1i**, 2 g, 5.7 mmol) and sodium cyanide (559 mg, 11.4 mmol) in DMF (10 ml) was stirred at 120 °C for 4 h, diluted by addition of saturated NH_4Cl aqueous solution, and extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered through Celite pad, and subjected to column chromatography (*n*-hexane:ethyl acetate = 10:1) to give **1j** (1.77 g, yield: 91 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 19.2 Hz, 1H), 6.44 (d, *J* = 19.2 Hz, 1H), 2.33 (t, *J* = 6.8 Hz, 2H), 1.68-1.61 (m, 2H), 1.45-1.41 (m, 2H), 1.31-1.21 (m, 14H), 0.63 (t, *J* = 6.8 Hz, 2H), 0.13 (s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 144.0, 138.5, 128.8, 128.7, 128.1, 126.5, 120.1, 33.8, 29.7, 29.5, 29.4, 28.9, 28.8, 25.5, 24.1, 17.3, 15.9, -2.8; IR (neat) 3059, 3023, 2925, 2853, 2246, 1944, 1804, 1604, 1573, 1494, 1464, 1447, 1426, 1334, 1247, 1215, 1197, 1071, 1028, 989, 842, 777, 741, 690, 631 cm^{-1}; ESI-HRMS (negative) calcd for $C_{22}H_{34}NSi$ $[M-H]^-$ 340.2466, found 340.2481.

- Preparation of (E)-12-(dimethyl(styryl)silyl)dodecanal (1k)

The solution of (*E*)-12-(dimethyl(styryl)silyl)dodecanenitrile (**1j**, 200 mg, 0.6 mmol) in dichloromethane was cooled to -78 °C, and 1.0 M DIBAL-H in dichloromethane (0.7 ml) was slowly added. Then temperature was raised to -40 °C and the mixture was stirred for 1 h. Silica gel and water were added, and the mixture was stirred for 1 h at 0 °C. The organic layer was separated, dried over anhydrous $MgSO_4$ and K_2CO_3, and filtered through Celite pad. The filtrate was concentrated *in vacuo* to give a residue that was subjected to column chromatography (*n*-hexane:ethyl = 10:1) to give **1k** (120 mg, yield: 59 %). ^1H NMR (400 MHz, $CDCl_3$) δ 9.76 (t, *J* = 2.0 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 6.8 Hz, 2H), 6.87 (d, *J* = 19.2 Hz, 1H), 6.46 (d, *J* = 19.2 Hz, 1H), 2.43-2.39 (m, 2H), 1.62 (t, *J* = 7.6

Hz, 2H), 1.31-1.26 (m, 16H), 0.63 (t, *J* = 6.4 Hz, 2H), 0.13 (s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 203.3, 144.1, 138.6, 128.9, 128.7, 128.1, 126.5, 44.1, 33.8, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 24.1, 22.3, 15.9, -2.8; IR (neat) 3078, 3059, 3023, 2925, 2855, 1941, 1875, 1800, 1727, 1687, 1604, 1573, 1494, 1464, 1410, 1366, 1337, 1287, 1247, 1143, 988, 842, 742, 689, 631 cm^{-1}; Anal. Calcd for $C_{22}H_{36}OSi$: C, 77.68; H, 10.53; found C, 77.64; H, 12.06.

- Preparation of (E)-11-(dimethyl(styryl)silyl)undecyl acetate (1l)

A solution of (*E*)-(11-chloroundecyl)dimethyl(styryl)silane (**1i**, 1.0 g, 2.85 mmol) and sodium acetate (468 mg, 5.7 mmol) in DMF (5 mL) was stirred at 120 ºC for 12 h. After addition of saturated NH_4Cl aqueous solution, organic layer was extracted using diethyl ether. The organic layer was dried over anhydrous $MgSO_4$, filtered through Celite pad, giving a filtrate that was concentrated *in vacuo*. The resulting residue was subjected to column chromatography (*n*- hexane:ethyl acetate = 10:1) to give **ll** (854 mg, yield: 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 19.2 Hz, 1H), 6.49 (d, *J* = 19.2 Hz, 1H), 4.07 (t, *J* = 6.8 Hz, 2H), 2.06 (s, 3H), 1.67-1.60 (m, 2H), 1.35-1.30 (m, 16H), 0.66 (t, *J* = 6.8 Hz, 2H), 0.17 (s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 171.4, 144.1, 138.5, 128.8, 128.7, 128.1, 126.5, 64.8, 33.8, 29.8, 29.7, 29.6, 29.5, 29.4, 28.8, 26.1, 24.1, 21.2, 15.9, -2.8; IR (neat) 3059, 3024, 2924, 2854, 1742, 1604, 1573, 1494, 1465, 1447, 1387, 1365, 1245, 1126, 1030, 989, 842, 805, 778, 741, 723, 690, 632 cm^{-1}; ESI-HRMS (positive) calcd for $C_{23}H_{38}O_2SiNa$ $[M+Na]^+$ 397.2533, found 397.2496.

- Preparation of (E)-11-(dimethyl(styryl)silyl)undecan-1-ol (1m)

To a solution of (*E)*-11-(dimethyl(styryl)silyl)undecyl acetate (**1l**, 300 mg, 0.8 mmol) in diethylether (10 ml) was added $LiAlH_4$ (52 mg, 1.36 mol) carefully. The resulting mixture was stirred for 1 h, diluted by slow addition of $H_2O$and extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered through Celite pad, and purified by column chromatography (*n*-hexane:ethyl acetate = 5:1) to give **1m** (234 mg, yield: 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 19.2 Hz, 1H), 6.47 (d, *J* = 19.2 Hz, 1H), 3.63 (t, *J* = 6.8 Hz, 2H), 1.59-1.53 (m, 2H), 1.42 (m, 2H), 1.31-1.26 (m, 14H), 0.63 (t, *J* = 6.4 Hz, 2H), 0.13 (s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 144.0, 138.5, 128.7, 128.6, 128.0, 126.5, 62.9, 33.8, 32.9, 29.8, 29.7, 29.6, 29.5, 25.9, 24.1, 15.8, -2.8; IR (neat) 3350, 3078, 3059, 3023, 2926, 2854, 1941, 1875, 1800, 1653, 1604, 1573, 1494, 1464, 1409, 1338, 1247, 1056, 988, 842, 776, 739, 689 cm^{-1}; ESI-HRMS (negative) calcd for $C_{21}H_{35}OSi$ $[M-H]^-$ 331.2462, found 331.2466.

- Preparation of (E)-(11-azidoundecyl)dimethyl(styryl)silane (1n)

(E)-(11-chloroundecyl)dimethyl(styryl)silane (**1i**, 2 g, 5.7 mmol) and sodium azide (556 mg, 8.55 mmol) was dissolved in DMF (10 ml), and the reaction mixture was stirred at 80 ^{o}C for 4 hours. After addition of saturated NH_4Cl aqueous solution and diethyl ether, organic layer was extracted 3 times. The collected organic layer was dried over anhydrous $MgSO_4$, filtered through Celite pad, giving a filtrate that was concentrated *in vacuo*. The residue was subjected to column chromatography (*n*-hexane:ethyl acetate = 10:1) to give **1n** (1.88 g, yield: 92 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 5.6 Hz, 1H), 6.87 (d, *J* = 19.2 Hz, 1H), 6.47 (d, *J* = 19.2 Hz, 1H), 3.25 (t, *J* = 6.8 Hz, 2H), 1.63-1.56 (m, 2H), 1.31-1.27 (m, 16H), 0.63 (t, *J* = 6.4 Hz, 2H), 0.13 (s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 144.1, 138.6, 128.8, 128.7, 128.1, 126.5, 51.7, 33.8, 29.8, 29.7, 29.6, 29.4, 29.0, 26.9, 24.1, 15.9, -2.8; IR (neat) 3060, 3024, 2926, 2854, 2095, 1942, 1876, 1671, 1604, 1573, 1522, 1494, 1464, 1409, 1348, 1249, 1067, 988, 841, 741, 690 cm^{-1}; Anal. Calcd for $C_{21}H_{35}N_3Si$: C, 70.53; H, 9.86; N, 11.75 found C, 70.01; H, 11.55; N, 9.81.

- Preparation of (E)-2,5-dioxopyrrolidin-1-yl 1-(11-(dimethyl(styryl)silyl)undecyl)-1H-1,2,3-triazole-4-carboxylate (1o)

A mixture of propiolic acid (3 g, 43.4 mmol), *N*-hydroxysuccinimide (5.0 g, 43.4 mmol), *N*,*N′*-dicyclohexylcarbodiimide (9 g, 43.4 mmol) in ethyl acetate (EA; 80 mL) was stirred at 4 ^{o}C for 8 h. The mixture was filtered through a pad of Celite to remove dicyclohexylurea, and the filtrate was then concentrated *in vacuo*. The resulting crude compound, 2,5-dioxopyrrolidin-1-yl propiolate, was used in the next step without further purification. (*E*)-(11-azidoundecyl)dimethyl(styryl)silane (**1n**, 1.79 g, 5 mmol) and a mixture of $CuSO_4 \cdot 5\,H_2O$ (123 mg, 0.5 mmol) and sodium ascorbate (198 mg, 1 mmol) in water were added to a solution of crude 2,5-dioxopyrrolidin-1-yl propiolate (1.25 g, 7.5 mmol) in THF. The mixture was stirred at room temperature for 12 h, diluted with saturated aqueous NH_4Cl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered through a pad of Celite, giving a filtrate that was concentrated *in vacuo*. The resulting residue was subjected to column chromatography (*n*-hexane:ethyl acetate = 1:1) to give **1o** (1.65 g, yield: 63 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 19.2 Hz, 1H), 6.46 (d, *J* = 19.2 Hz, 1H), 4.43 (t, *J* = 7.2 Hz, 2H), 2.90 (s, 4H), 1.95-1.91 (m, 2H), 1.32-1.25 (m, 16H), 0.62 (t, *J* = 6.8 Hz, 2H), 0.13 (s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 169.2, 156.0, 144.0, 138.6, 134.8, 129.2, 128.9, 128.7, 128.1, 126.5, 51.2, 33.7, 30.3, 29.7, 29.5, 29.1, 26.5, 25.8, 24.1, 15.9, -2.8; IR (CH_2Cl_2) 3133, 3058, 3019, 2984, 2923, 2853, 1926, 1777, 1743, 1604, 1572, 1533, 1493, 1466, 1446, 1370, 1306, 1247, 1210, 1159, 1081, 1060, 991, 966, 909, 842, 814, 742, 691, 651, 609 cm^{-1}; Anal. Calcd for $C_{28}H_{40}N_4O_4Si$: C, 64.09; H, 7.68; N, 10.68 found C, 64.29; H, 7.92; N, 10.47.

- Preparation of (E)-(3-chloropropyl)dimethyl(styryl)silane (1p)

A 2-neck round bottomed flask pre-equipped with reflux condenser was charged with chlorodimethylsilane (10 g, 105.7 mmol) and 10% H_2PtCl_6•xH_2O (164 mg, 0.3 mmol) in 2-propanol (0.2 ml) solution. The resulting solution was stirred for 30 min. Then, allyl chloride (16 g, 211.4 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. After the reaction, unreacted allyl chloride and chlorodimethylsilane were removed by distillation under reduced pressure to give crude chloro(3-chloropropyl)dimethylsilane, which was used for the next step without further purification. $LiAlH_4$ (6 g, 158 mmol) was added to diethyl ether (250 ml) and then chloro(11-chloroundecyl)dimethylsilane was added slowly to the mixture of $LiAlH_4$ in diethyl ether at 0 ^oC. Resulting solution was stirred at room temperature for 2 h, diluted by slowly addiding H_2O, and extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give (3-chloropropyl)dimethylsilane (colorless liquid, 3.5 g, 30% overall yield). A 2-neck round bottomed flask pre-equipped with reflux condenser was charged with (3-chloropropyl)dimethylsilane (3.2 g, 23.4 mmol) and $RhCl(PPh_3)_3$ (130 mg, 0.14 mmol) in THF (5 ml). The resulting solution was stirred for 30 min. Then, phenyl acetylene (**10**, 2.87 g, 28 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h, diluted with saturated NH_4Cl (aq.), and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. (E)-(3-chloropropyl)dimethyl(styryl)silane (**1p**, colorless liquid, 4.84 g, 87% overall yield) was obtained by using column chromatography (*n*-hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 19.2 Hz, 1H), 6.48 (d, *J* = 19.2 Hz, 1H), 3.55 (t, *J* = 6.8 Hz, 2H), 1.89-1.81 (m, 2H), 0.80-0.75 (m, 2H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 138.2, 128.7, 128.3, 127.6, 126.6, 48.2, 27.8, 13.6, -3.0; IR (neat): 3059, 3024, 2989, 2954, 2898, 1946, 1876, 1730, 1703, 1646, 1604, 1493, 1446, 1332, 1310, 1287, 1249, 1215, 1173, 1070, 1029, 990, 910, 843, 778, 743, 690 cm^{-1}; ESI-HRMS (negative) calcd for $C_{13}H_{18}ClSi$ $[M-H]^-$ 237.0872, found 237.0909.

- Preparation of (11-chloroundecyl)(methyl)di((E)-styryl)silane (1q)

A 2-neck round bottomed flask pre-equipped with reflux condenser was charged with dichloromethylsilane (6.07 g, 52.8 mmol) and 10% H_2PtCl_6•xH_2O (41 mg, 0.08 mmol) in 2-propanol (0.1 mL) solution. The resulting solution was stirred for 30 min. Then, 11-chloroundec-1-ene (5 g, 26.4 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. After the reaction, unreacted dichloromethylsilane was removed by distillation under reduced pressure to give crude dichloro(11-chloroundecyl)(methyl)silane, which was used for the next step without further purification. $LiAlH_4$ (2 g, 56 mmol) was added to diethyl ether (250 ml) and then dichloro(11-chloroundecyl)(methyl)silane was added slowly to the mixture of $LiAlH_4$ in diethyl ether at 0 ^oC. Resulting solution was stirred at room temperature for 2 h, diluted by slowly addiding H_2O, and extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give (11-chloroundecyl)(methyl)silane (colorless liquid, 2.7 g, 44% overall yield). A 2-neck round bottomed flask pre-equipped with reflux condenser was charged with (11-chloroundecyl)(methyl)silane (2.7 g, 11.6 mmol) and $[Cp^*RhCl_2]_2$ (86 mg, 0.14 mmol) in THF (5 ml). The resulting solution was stirred for 30 min. Then, phenyl acetylene (**10**, 3 g, 29 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h, diluted with saturated NH_4Cl (aq.), and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. (11-chloroundecyl)(methyl)di((E)-styryl)silane (**1q**, colorless liquid, 1.58 g, 31% overall yield) was obtained by using column chromatography (*n*-hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.2 Hz, 4H), 7.34 (t, J = 7.2 Hz, 4H), 7.26 (t, J = 7.6 Hz, 2H), 6.95 (d, J = 19.2 Hz, 1H), 6.52 (d, J = 19.2 Hz, 1H), 3.52 (t, J = 6.8 Hz, 2H), 1.79-1.72 (m, 2H), 1.41-1.26 (m, 16H), 0.79 (t, J = 7.2 Hz, 2H), 0.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 138.4, 128.7, 128.3, 127.0, 126.6, 45.3, 33.8, 32.8, 29.7, 29.6, 29.5, 29.1, 27.0, 24.0, 14.8, -4.2; IR (neat): 3078, 3058, 3023, 2989, 2923, 2853, 1943, 1876, 1803, 1705, 1602, 1573, 1493, 1463, 1446, 1408, 1334, 1288, 1251, 1215, 1197, 1175, 1070, 1028, 989, 933, 912, 837, 799, 733, 690, 652 cm^{-1}; ESI-HRMS (positive) calcd for $C_{28}H_{40}ClSi$ $[M+H]^+$ 439.2582, found 439.2583.

- Preparation of 14–18 (Scheme 4)

- Preparation of dimethylsilanyl impregnated polybutadiene 13

A 2-neck round bottomed flask pre-equipped with a reflux condenser was charged with polybutadiene (**12**, 2 g, 31.4 mmol vinyl group of polybutadiene) and 10% $H_2PtCl_6{\bullet}xH_2O$ (48.7 mg, 0.09 mmol) in 2-propanol (0.2 mL) solution. The solution was stirred for 30 min. Then, chlorodimethylsilane (3 g, 31.4 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. Unreacted chlorodimethylsilane was removed by distillation under reduced pressure to give crude chlorosilane contained polybutadiene, which was used for the next step without further purification. Crude chlorosilane-impregnated polybutadiene was added slowly to $LiAlH_4$ (1.8 g, 47 mmol) in diethyl ether (250 ml) at 0 ^oC. The resulting solution was stirred at room temperature for 2 h, diluted by slow addition of H_2O, and extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered through Celite pad. After evaporating the solvent from filtrate, the residue was washed throughly with methanol and dried to give dimethylsilanyl group-impregnated polybutadiene **13** (colorless liquid, 3 g, 76% overall yield).

- Preparation of styryl and chloroalkyl group-impregnated polybutadiene 14

A 2-neck round bottomed flask pre-equipped with a reflux condenser was charged with dimethylsilanyl group-impregnated polybutadiene **13** (3 g, 23.9 mmol) and $RhCl(PPh_3)_3$ (133 mg, 0.14 mmol) in THF (5 ml). The resulting solution was stirred for 30 min. Then, phenyl acetylene (**10**, 1.05 ml, 9.56 mmol) and 11-chloroundec-1-ene (**6**, 9 ml, 47.8 mmol) were added dropwise and the resulting mixture was stirred at room temperature for 12 h, diluted with saturated NH_4Cl (aq.), and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The precipitate was then washed throughly with methanol and dried to give styryl and chloroalkyl group-impregnated polybutadiene **14** (5.18 g, 92% overall yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (br s, 2H), 7.30 (br s, , 3H), 6.89-6.84 (br m, 1H), 6.48-6.44 (br m, 1H), 5.37 (br s), 3.53 (br s, 3H), 1.95-1.77 (br m), 1.41-1.28 (br m) 0.48-0.03 (br m) -0.04 (br s); ^{13}C NMR (100MHz, $CDCl_3$) δ 144.2, 138.5, 128.7, 128.1, 126.5, 45.3, 34.0, 32.9, 29.9, 29.7, 29.2, 27.1, 24.2, 15.5, -2.8, -3.1; IR (CH_2Cl_2): 3078, 3059, 3023, 2930, 2853, 1940, 1875, 1800, 1726, 1604, 1573, 1494, 1447, 1412, 1338, 1288, 1247, 1214, 1178, 1070, 1028, 988, 839, 769, 690 cm^{-1}. M_w/M_n = 2.45.

- Preparation of styryl and azido group-impregnated polybutadiene 15

Styryl and chloroalkyl group-impregnated polybutadiene **14** (2.1 g, 7.2 mmol) and sodium azide (420 mg, 10.8 mmol) were dissolved in DMF and the resulting mixture was stirred at 80 ^oC for 4 hours. After addition of saturated NH_4Cl aqueous solution and diethyl ether, organic layer was extracted 3 times. The collected organic layer was dried over anhydrous $MgSO_4$, filtered, and concetrated *in vacuo*. The precipitate was then washed throughly with methanol and dried to give styryl and azido group-impregnated polybutadiene **15** (1.4 g, yield: 81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (br s, 2H), 7.30-7.23 (br m, 3H), 6.89-6.84 (br m, 1H), 6.47-6.43 (br m, 1H), 5.36 (br, s), 3.24 (br s, 3H), 2.09-1.94 (br m), 1.58-1.27 (br m), 0.47-0.03 (br m), -0.05 (br s); ^{13}C NMR (100MHz, $CDCl_3$) δ 144.3, 138.6, 128.7, 128.1, 126.6, 51.7, 34.1, 29.9, 29.8, 29.4, 29.1, 27.0, 24.2, 15.5, 7.2, -2.8, -3.1; IR (CH_2Cl_2): 3059, 3023, 2921, 2853, 2095, 1604, 1573, 1494, 1449, 1412, 1348, 1247, 1179, 1069, 988, 837, 773, 689 cm^{-1}; M_w/M_n = 2.93.

- Preparation of styryl and pyrenyl group-impregnated polybutadiene 17

Styryl and azido group-impregnated polybutadiene **15** (500 mg, 1.06 mmol) and a mixture of $CuSO_4 \cdot 5\,H_2O$ (27 mg, 0.11 mmol) and sodium ascorbate (43 mg, 0.22 mmol) in water were added to a solution of crude 1-(propargyloxymethyl)pyrene **16** in THF. The mixture was stirred at room temperature for 12 hours, diluted with saturated aqueous NH_4Cl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concetrated *in vacuo*. The precipitate was then washed throughly with methanol and dried to give styryl and pyrenyl group-impregnated polybutadiene **17** (600 mg, yield: 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (br s), 8.11-7.99 (br m), 7.37-7.26 (br m), 6.86-6.81 (br m), 6.44-6.40 (br m), 5.30 (br s), 4.78 (br s), 4.20 (br s), 1.91-1.19 (br m), 0.44-0.01 (br m), -0.08 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 138.5, 131.6, 131.4, 131.2, 130.9, 129.6, 128.7, 128.1, 127.9, 127.7, 127.6, 127.4, 126.5, 126.1, 125.4, 124.7, 123.6, 122.5, 71.2, 64.0, 50.5, 34.1, 30.4, 29.9, 29.7, 29.2, 26.7, 24.2, 15.5, -2.8, -3.1; IR (neat): 3024, 2919, 2852, 1604, 1573, 1493, 1447, 1247, 1072, 844, 774, 709 cm^{-1}; *Mw*/*Mn* = 1.78.

- Polymer 17 immobilized glass preparation (18)

A glass slide was treated by Piranha solution (H_2SO_4 : H_2O_2 = 7 : 3, 5 mL) for 1 h. Reaction of styryl and pyrenyl group-impregnated polybutadiene **17** with glass slide was performed in the presence of 5 mol% of **3a** at room temperature in dichloromethane during 12 h. After the reaction, modified glass slide was washed with dichloromethane. The contact angles of glass slide after treatment of Piranha solution and surface-modified glass slide (**18**) were measured to be 7° and 112°, respectively.

- The nitrobenzene detecting ability of 18 (Fig. 2)[3]

- Fluorescence spectra of 18 at different concentration of nitrobenzene (Fig. 2a)

Before addition of nitrobenzene, the fluorescence spectrum of **18** (2mL CH_2Cl_2) was recorded (excitation at 330 nm). To **18**, 2 mL of 1.2 mM nitrobenzene in CH_2Cl_2 was added, and the fluorescence spectra of **18** was measured again. Then **18** was washed thoroughly with dichloromethane to give recovered **18**. This procedure was repeated by increasing the concentration of nitrobenzene from 1.2 mM to 14.4 mM.

- Fluorescence intensity change during sensing and recycling of 18 (Fig. 2b)

Before addition of nitrobenzene, the fluorescence spectrum of **18** (2 mL CH_2Cl_2) was recorded (excitation at 330 nm). And then, after 2 mL of 14.4 mM nitrobenzene in CH_2Cl_2 was added, the fluorescence spectrum was measured. After **18** was washed with dichloromethane thoroughly, the fluorescence spectrum was measured. This procedure was repeated three times.

4. [1]H and [13]C NMR spectra

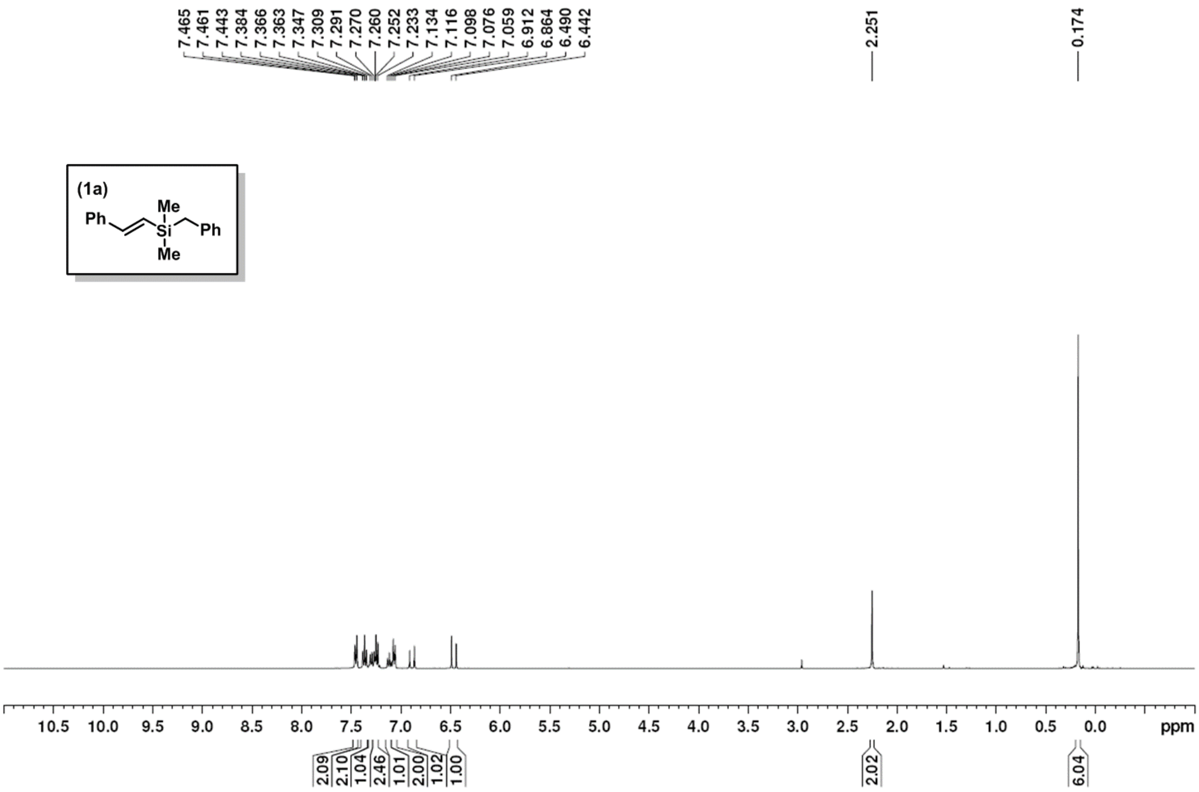


Figure S2. ^{1}H NMR spectrum of **1a**.

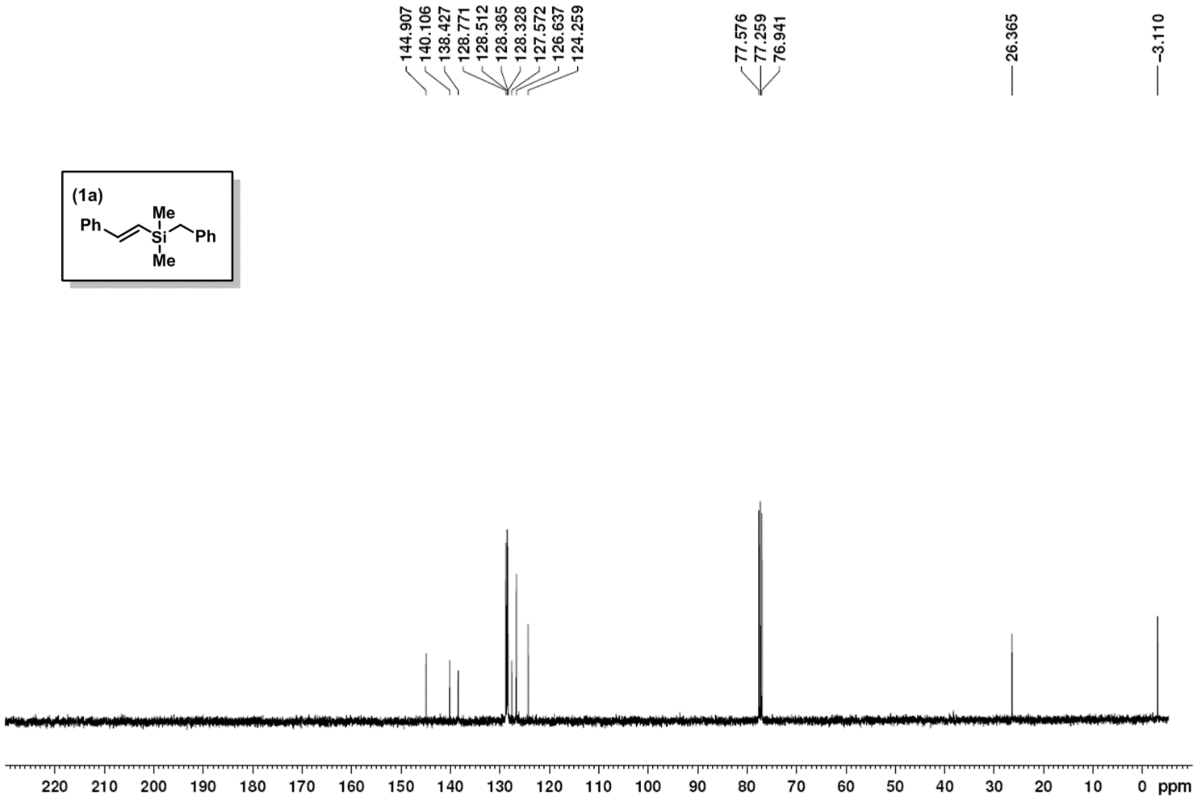


Figure S3. ^{13}C NMR spectrum of **1a**.

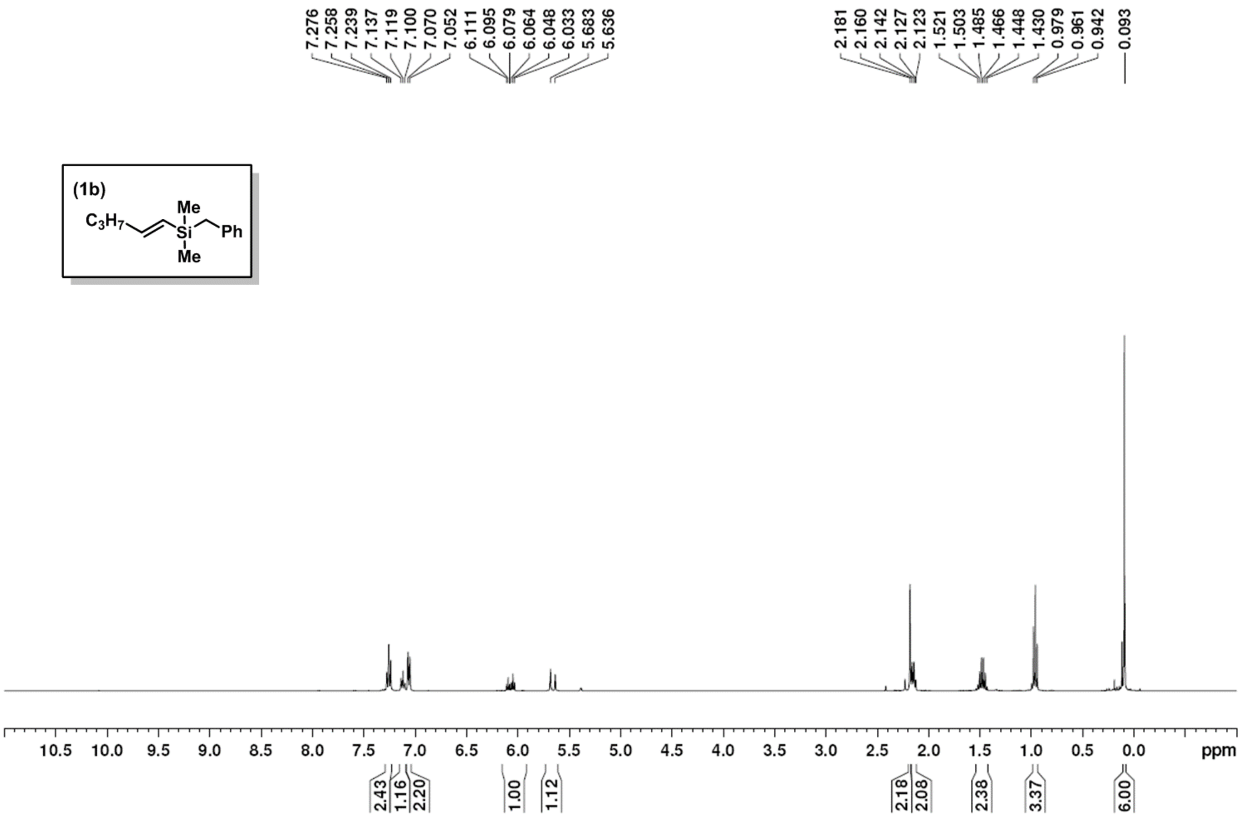


Figure S4. ^{1}H NMR spectrum of **1b**.

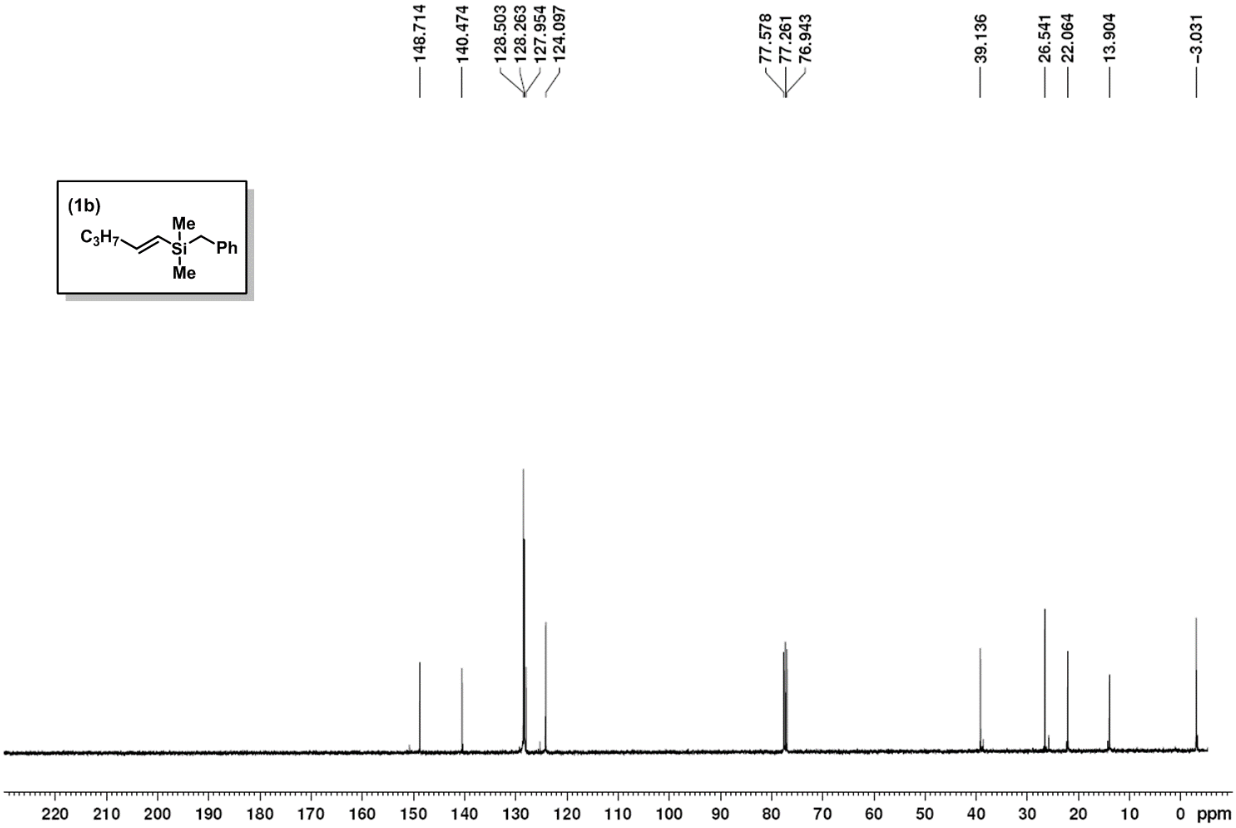


Figure S5. ^{1}H NMR spectrum of **1b**.

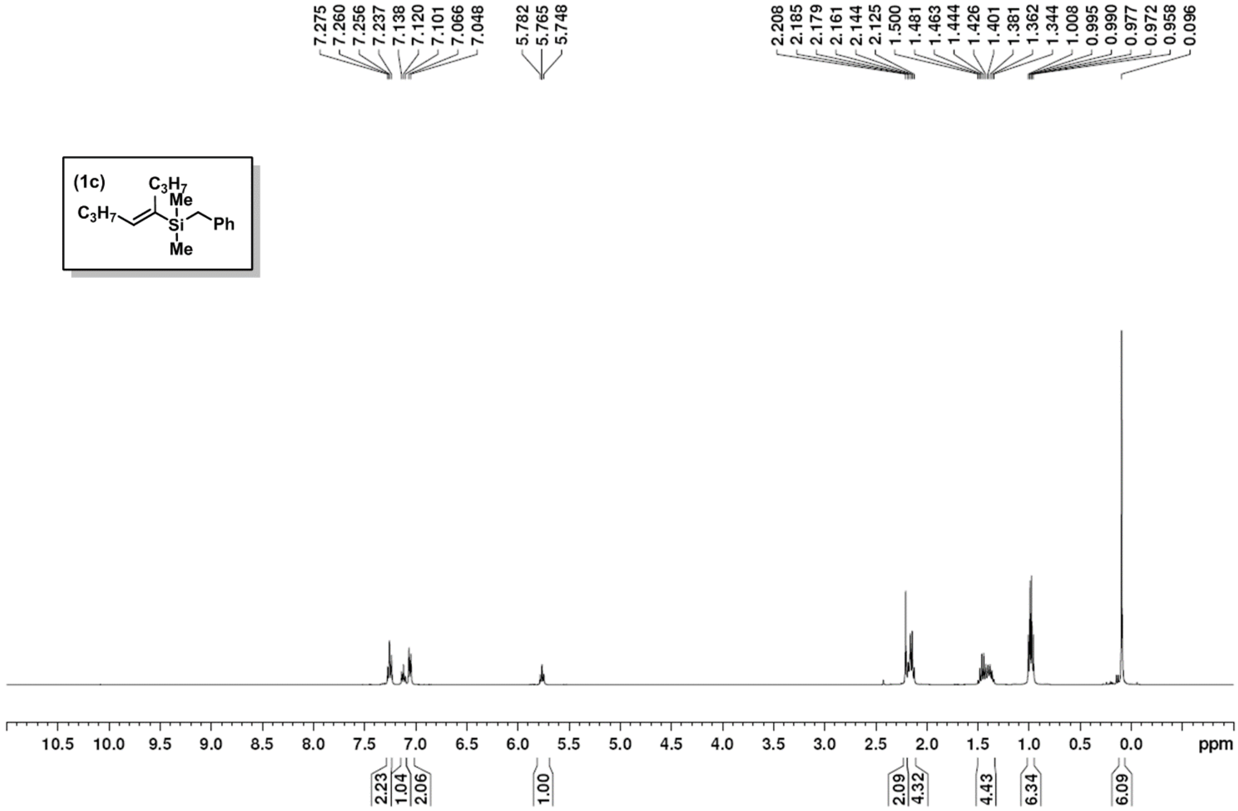


Figure S6. ^{1}H NMR spectrum of **1c**.

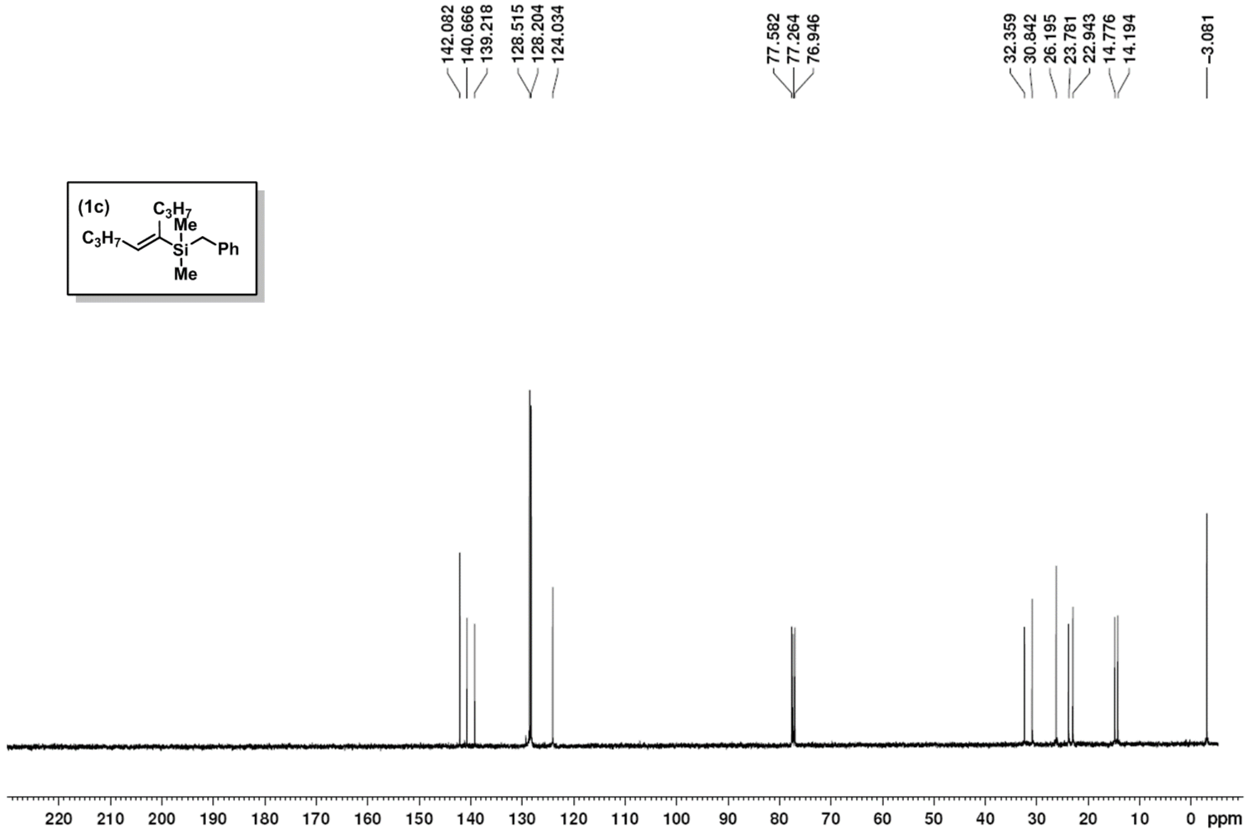


Figure S7. ^{13}C NMR spectrum of **1c**.

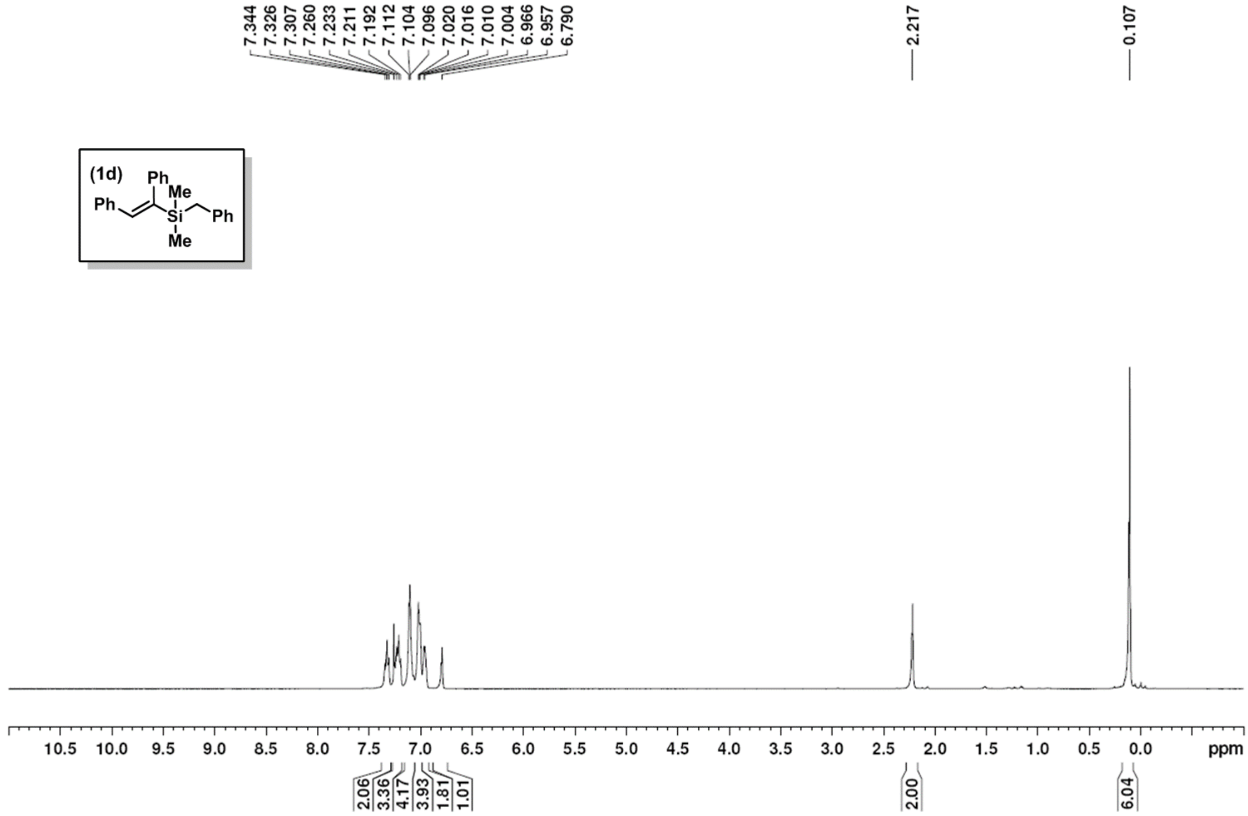


Figure S8. ^{1}H NMR spectrum of **1d**.

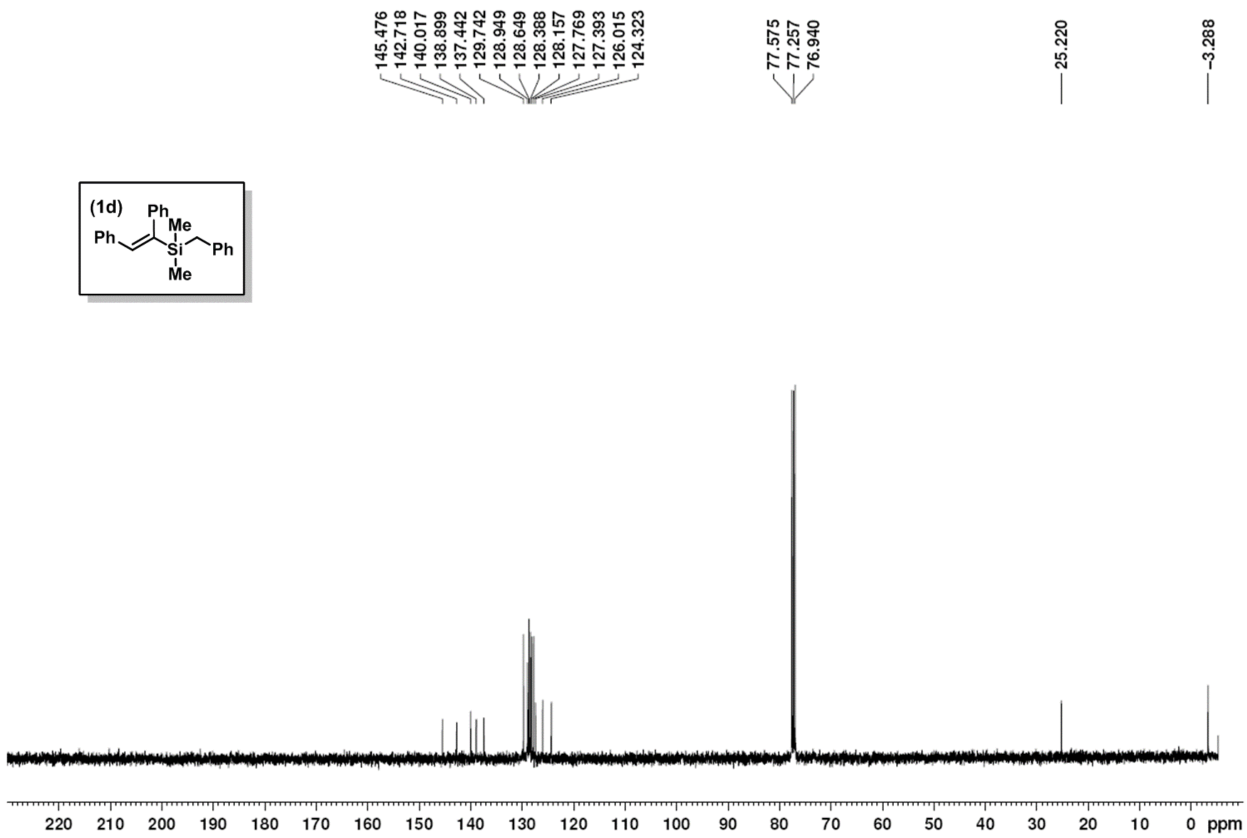


Figure S9. ^{13}C NMR spectrum of **1d**.

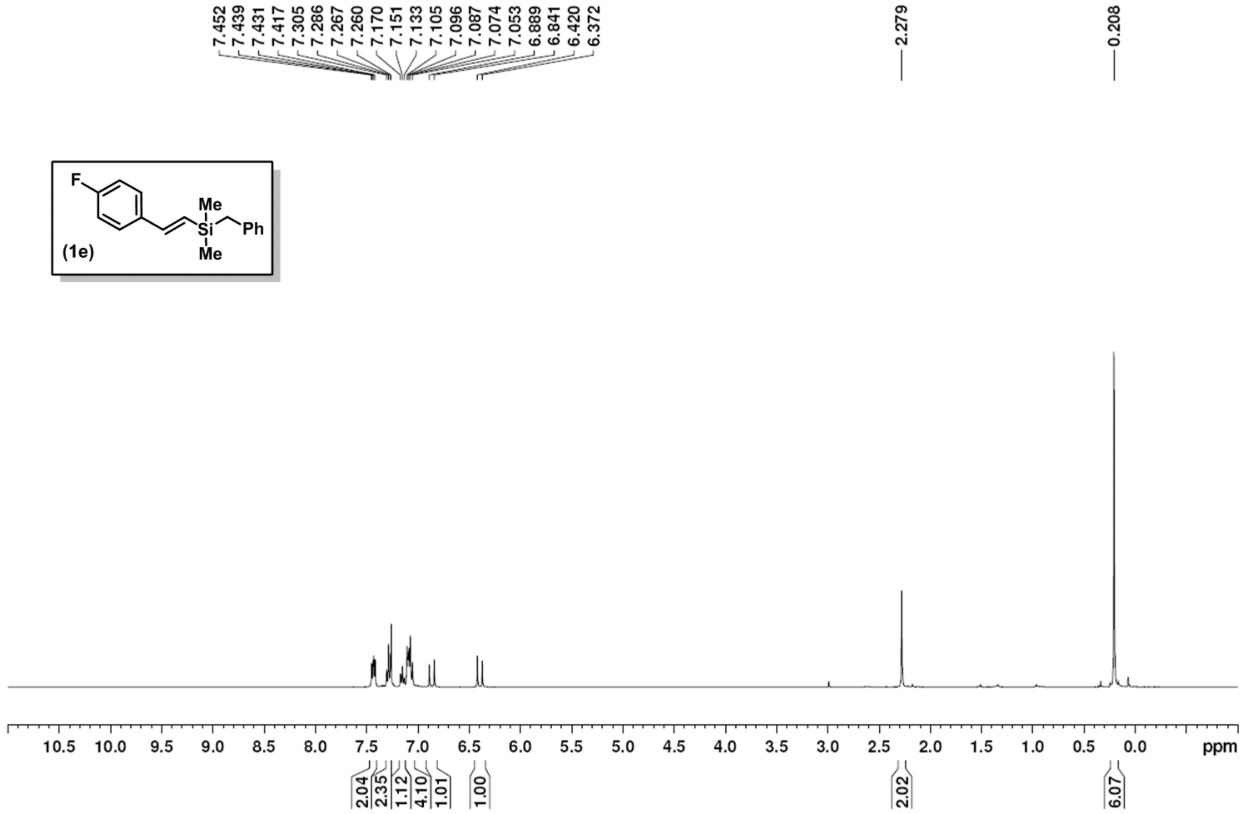


Figure S10. ^{1}H NMR spectrum of **1e**.

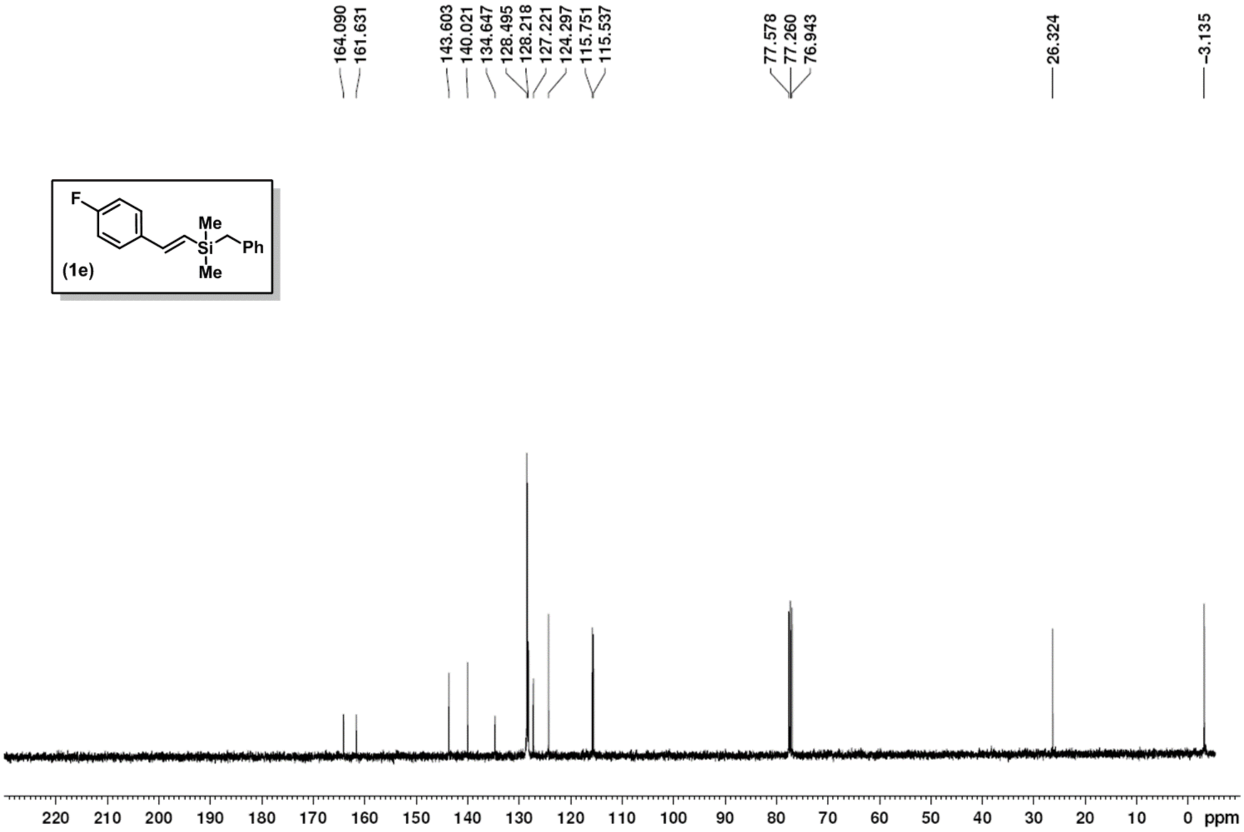


Figure S11. ^{13}C NMR spectrum of **1e**.

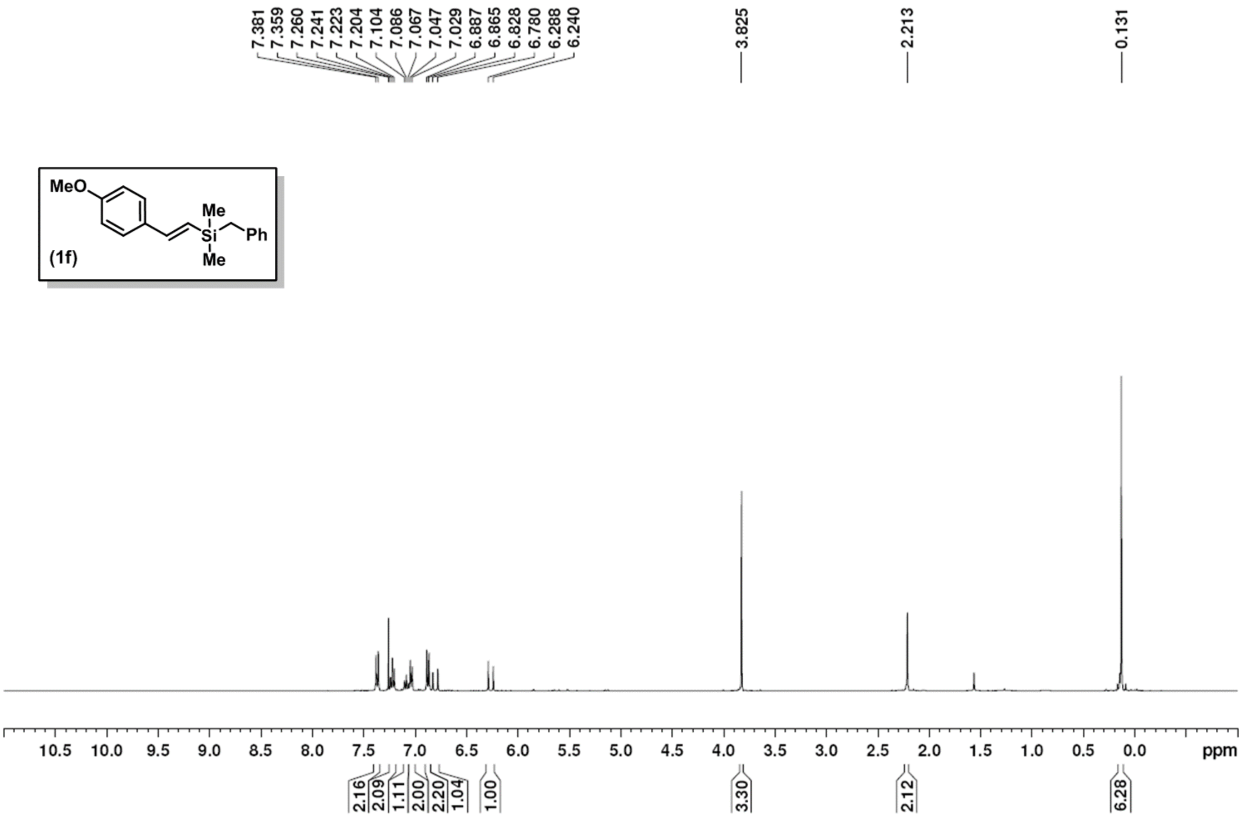


Figure S12. ^{1}H NMR spectrum of **1f**.

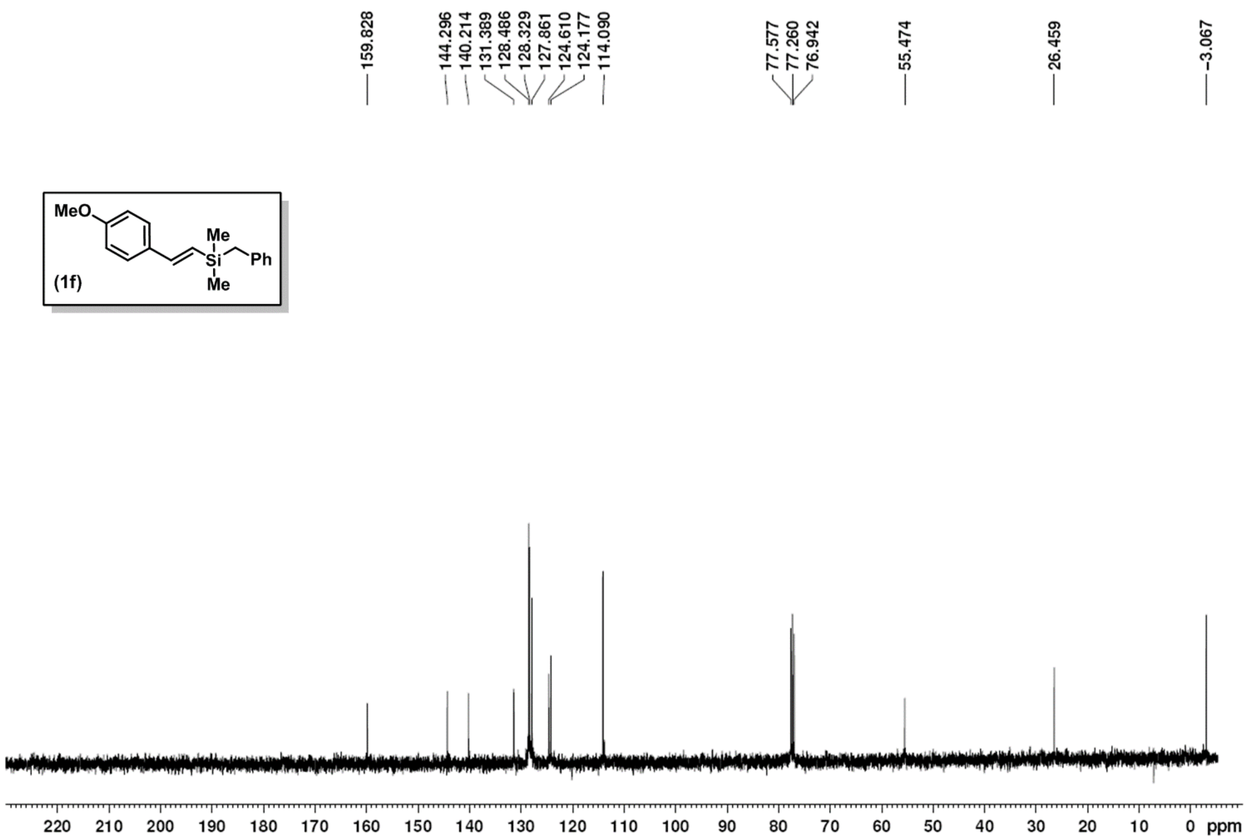


Figure S13. ^{13}C NMR spectrum of **1f**.

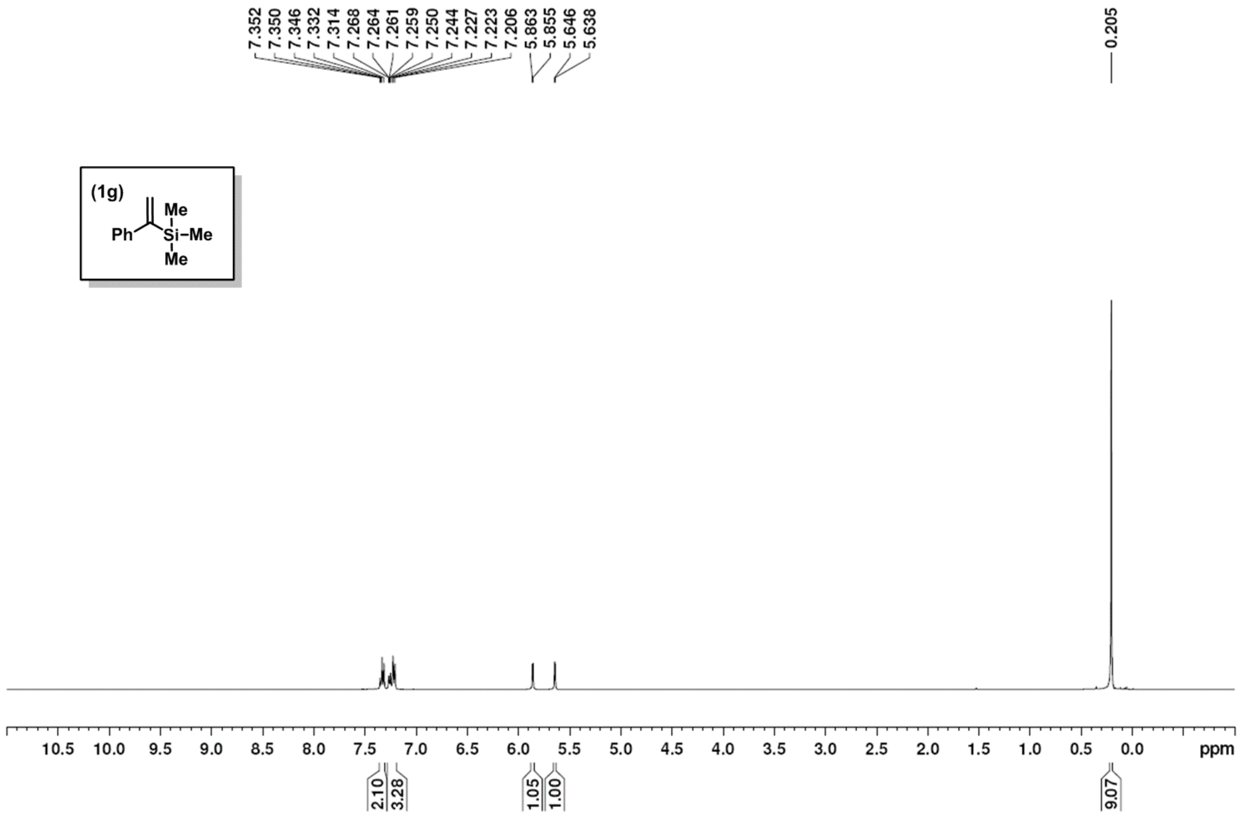


Figure S14. ^{1}H NMR spectrum of **1g**.

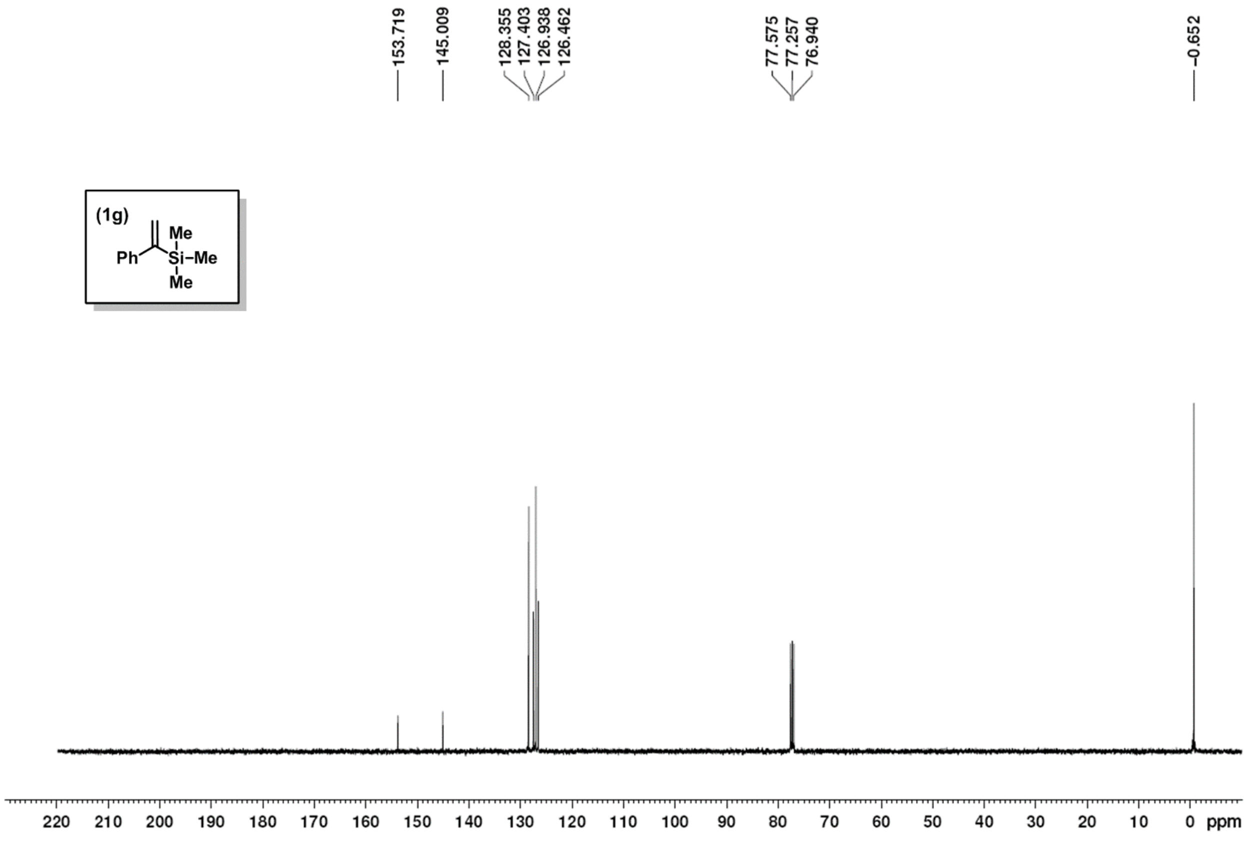


Figure S15. ^{13}C NMR spectrum of **1g**.

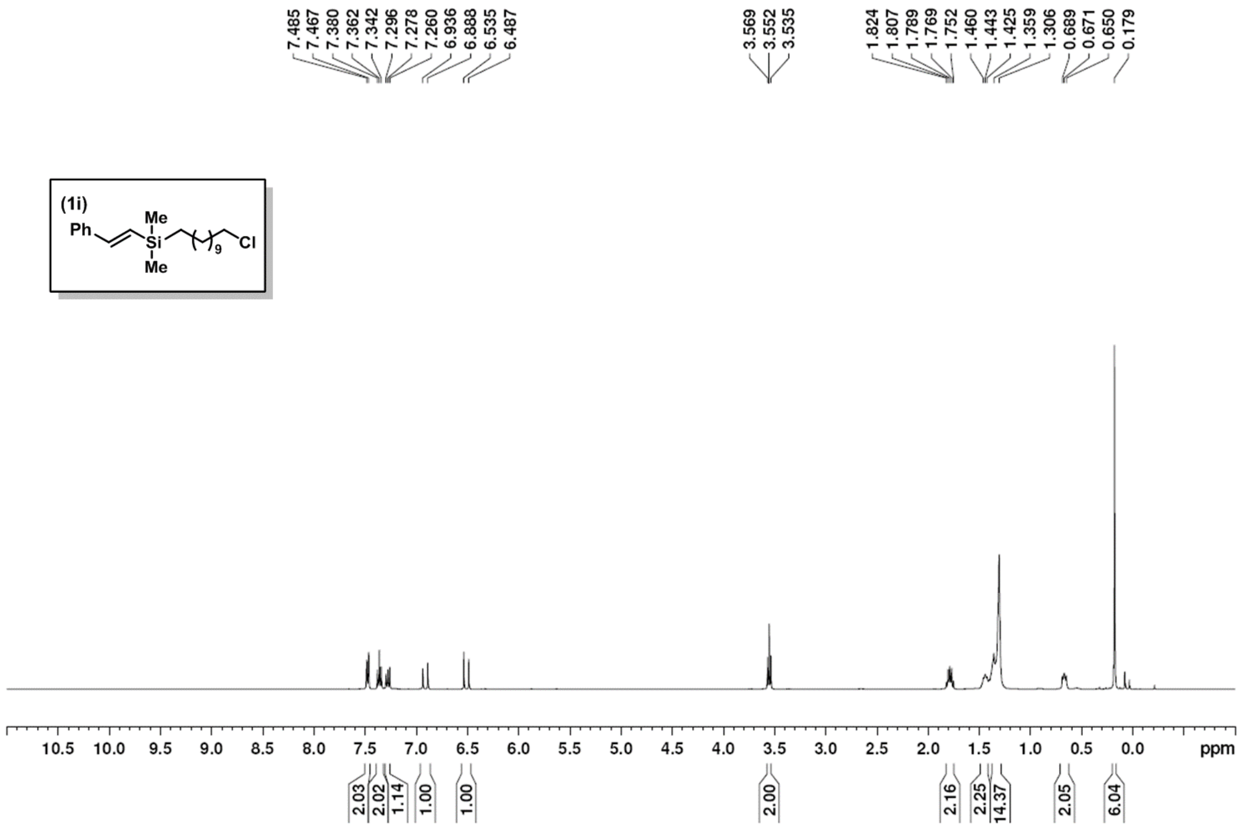


Figure S16. ^{1}H NMR spectrum of **1i**.

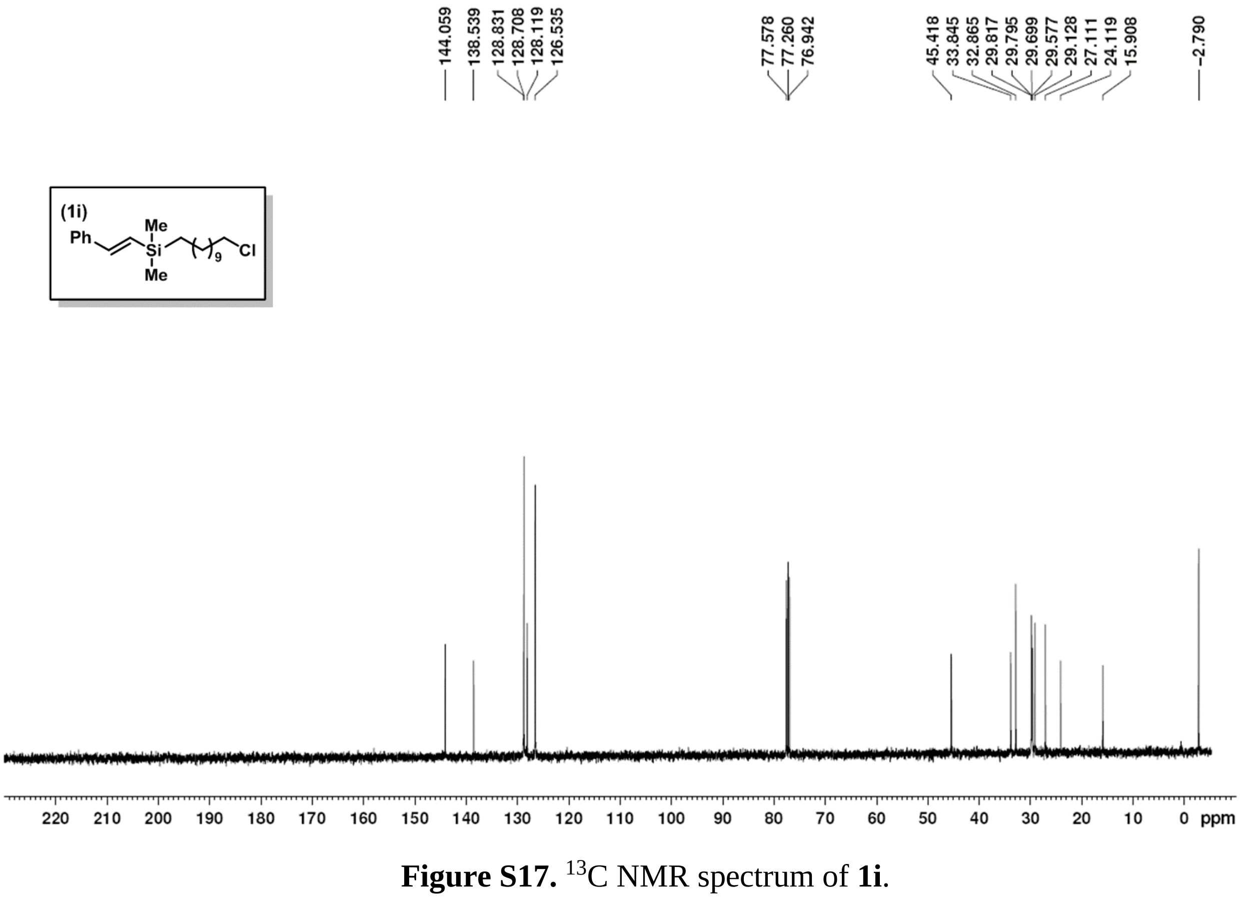


Figure S17. ^{13}C NMR spectrum of **1i**.

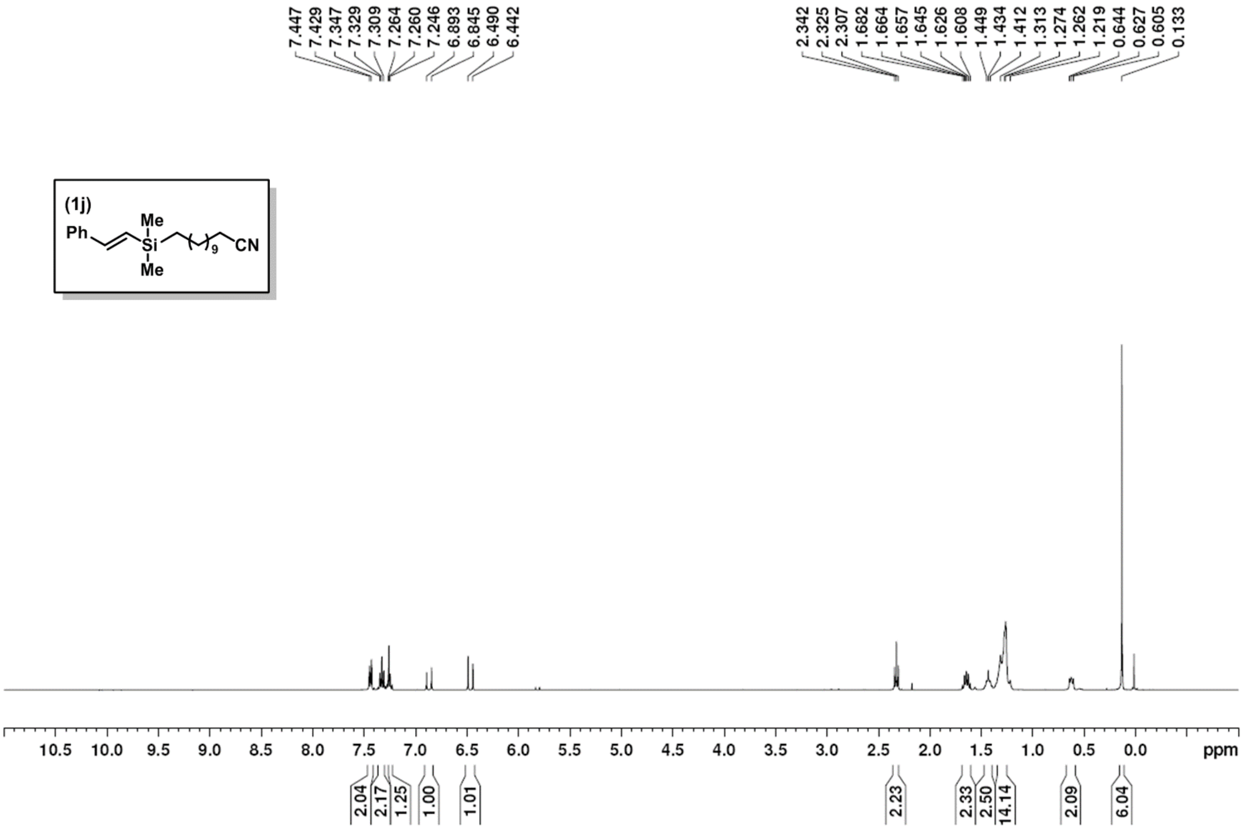


Figure S18. ^{1}H NMR spectrum of **1j**.

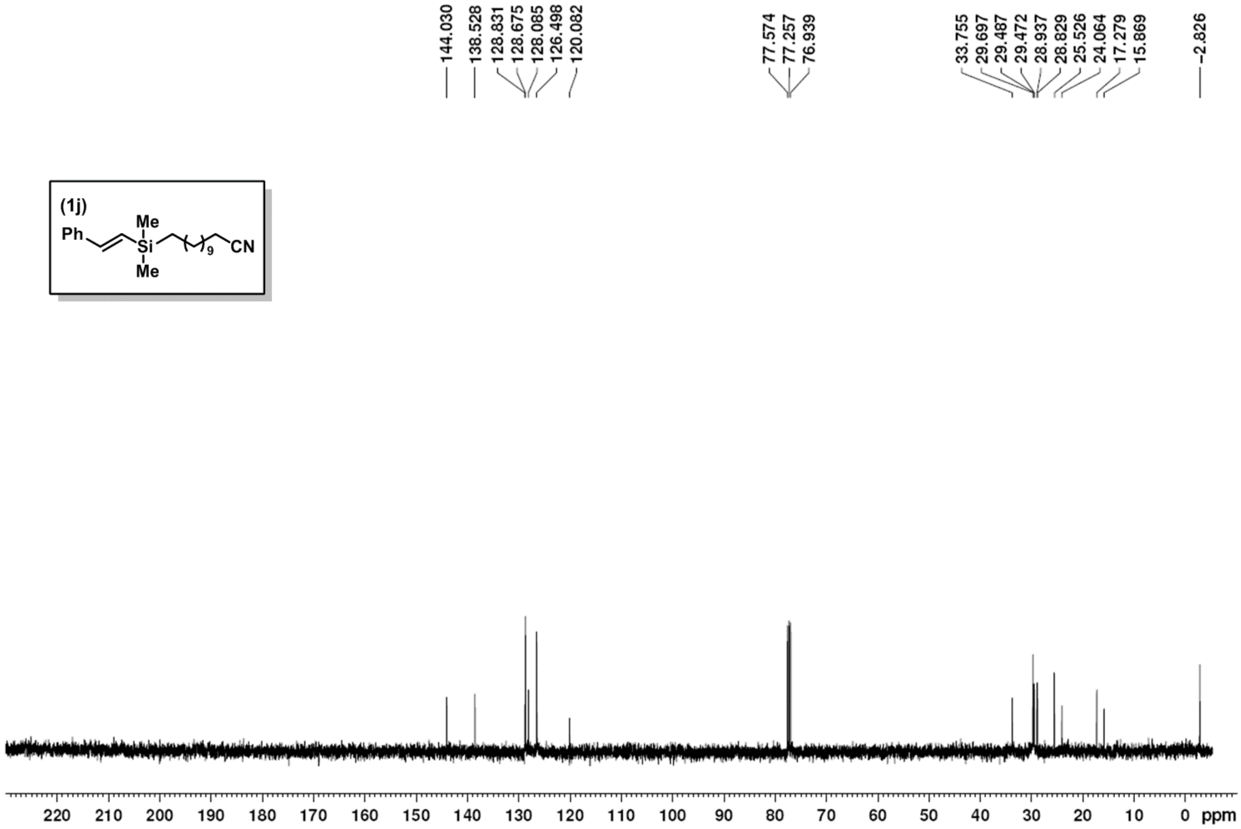


Figure S19. ^{13}C NMR spectrum of **1j**.

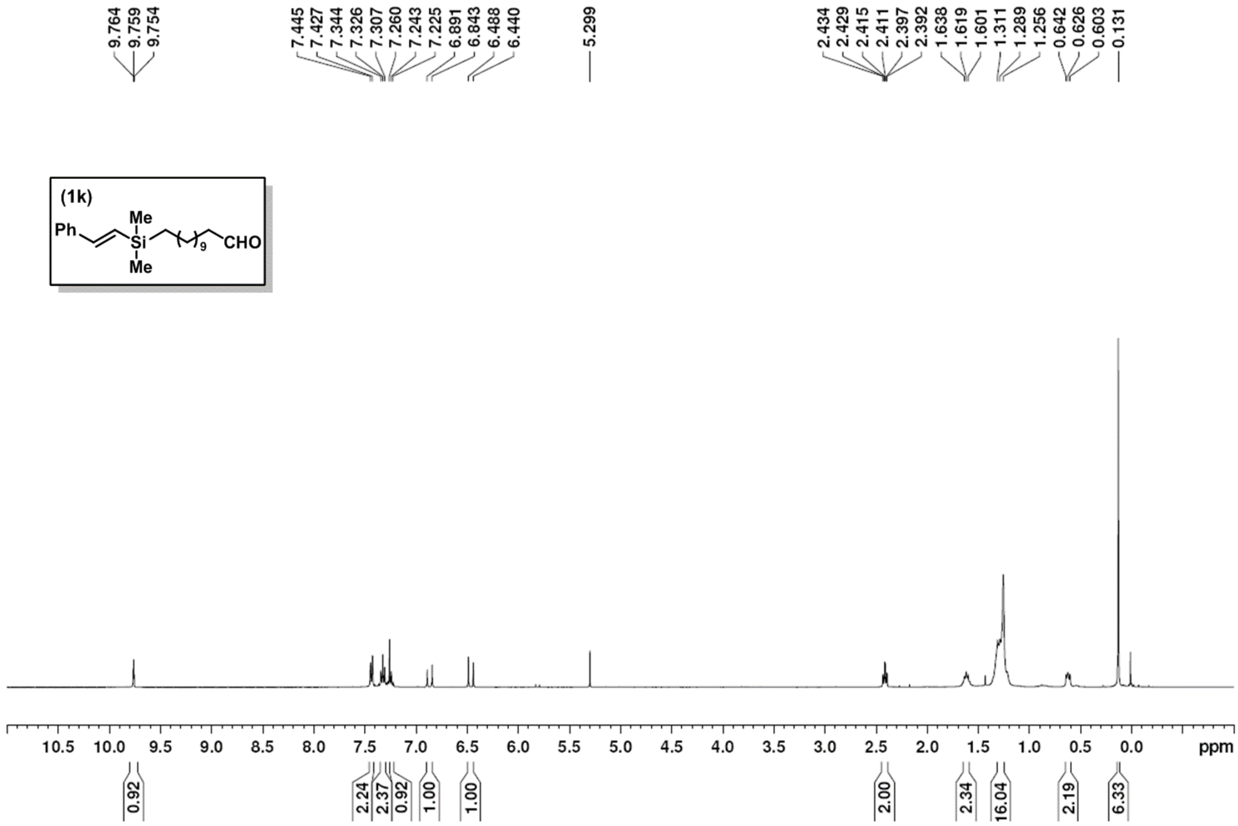


Figure S20. ^{1}H NMR spectrum of **1k**.

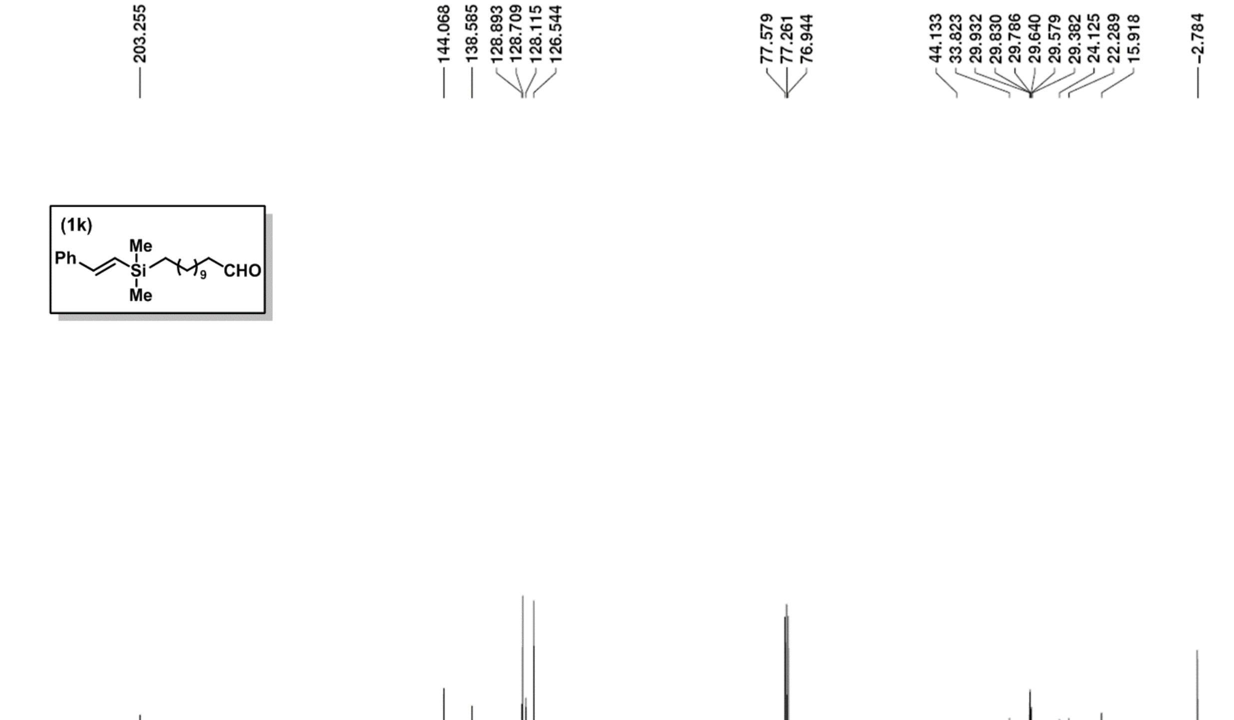


Figure S21. ^{13}C NMR spectrum of **1k**.

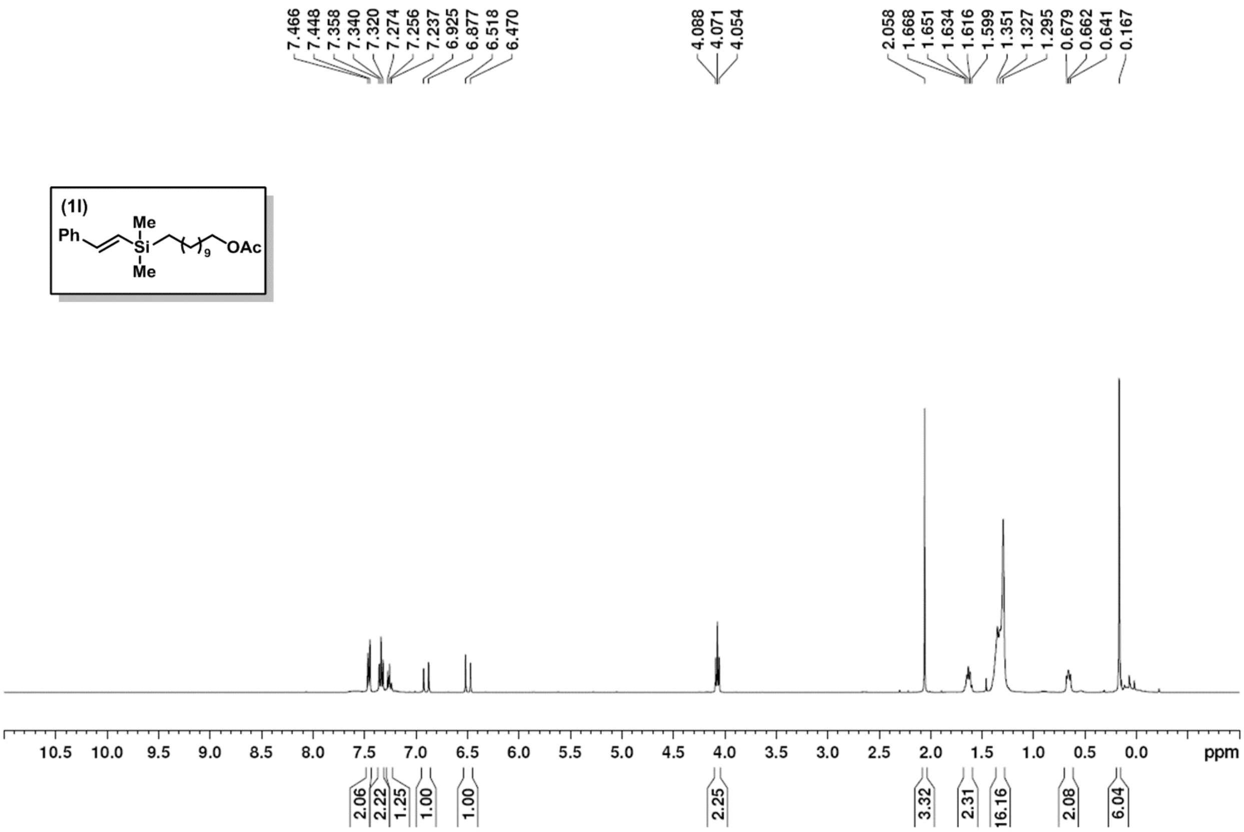


Figure S22. ^{1}H NMR spectrum of **1l**.

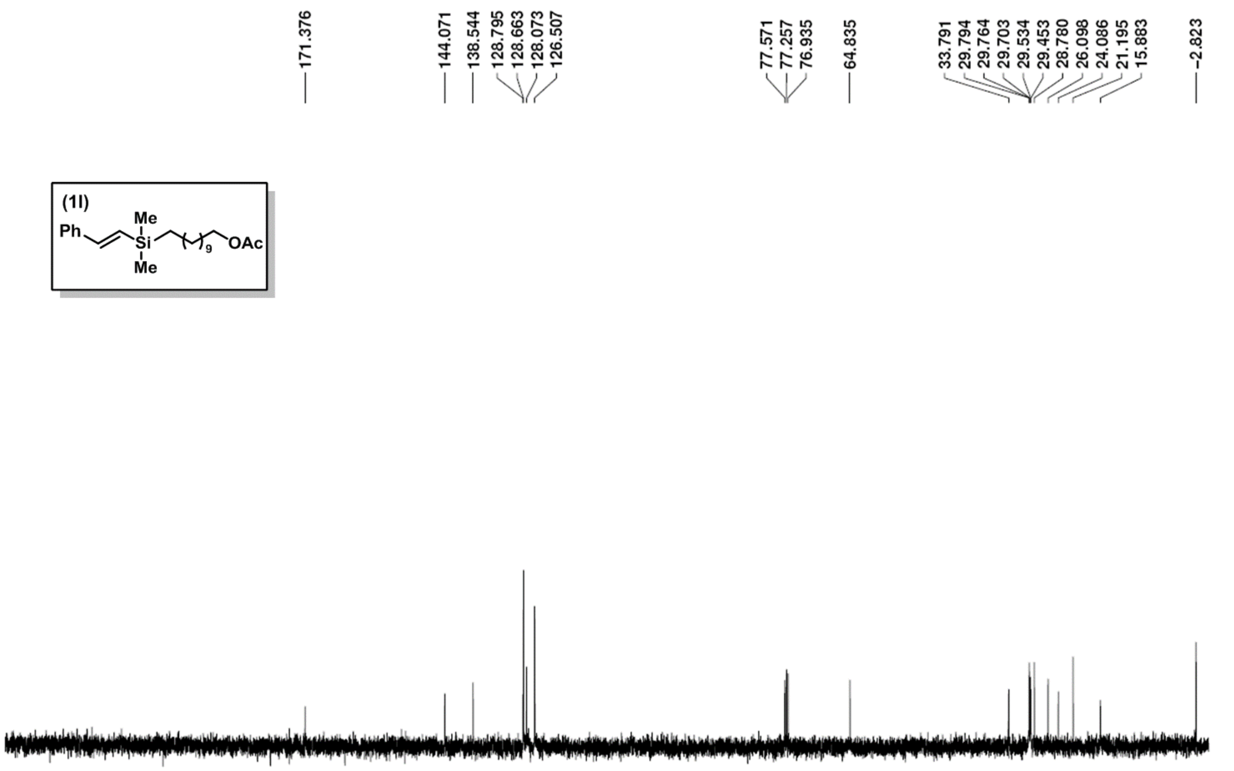


Figure S23. ^{13}C NMR spectrum of **1l**.

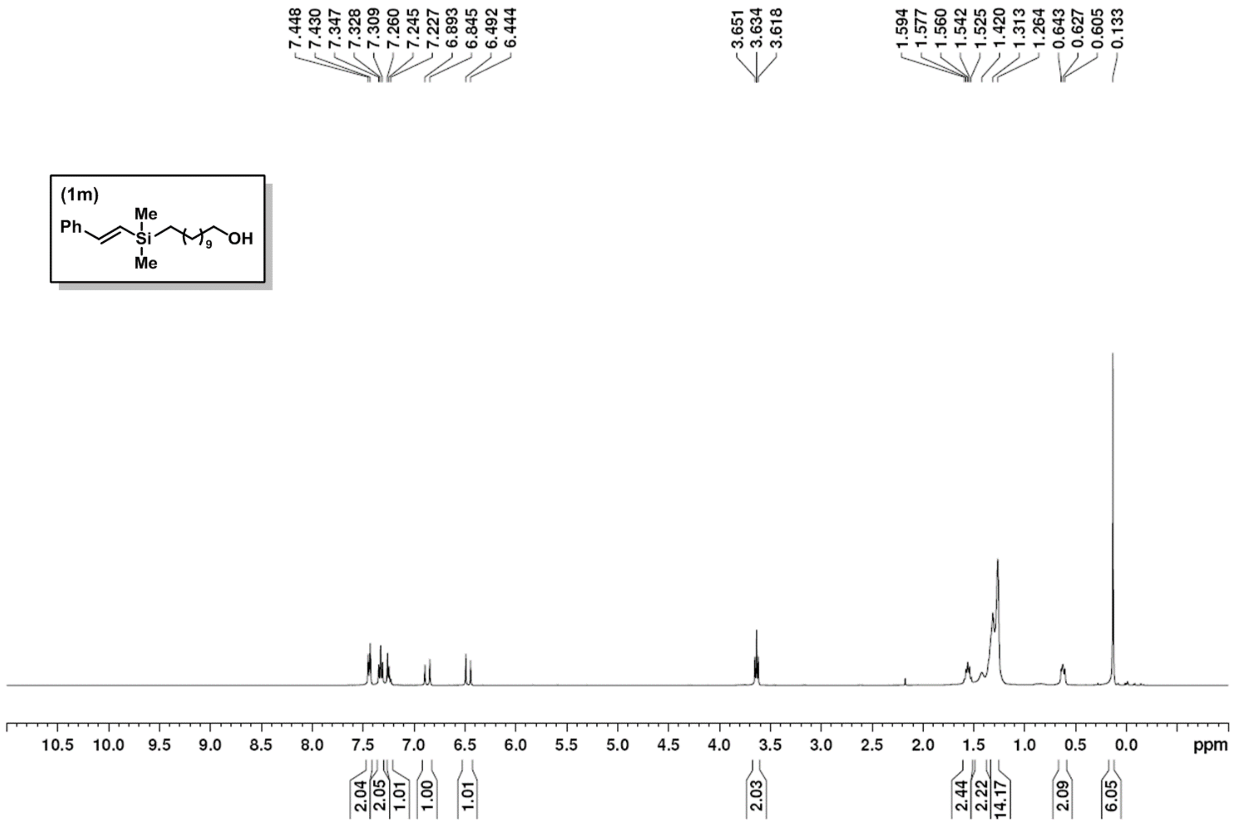


Figure S24. ^{1}H NMR spectrum of **1m**.

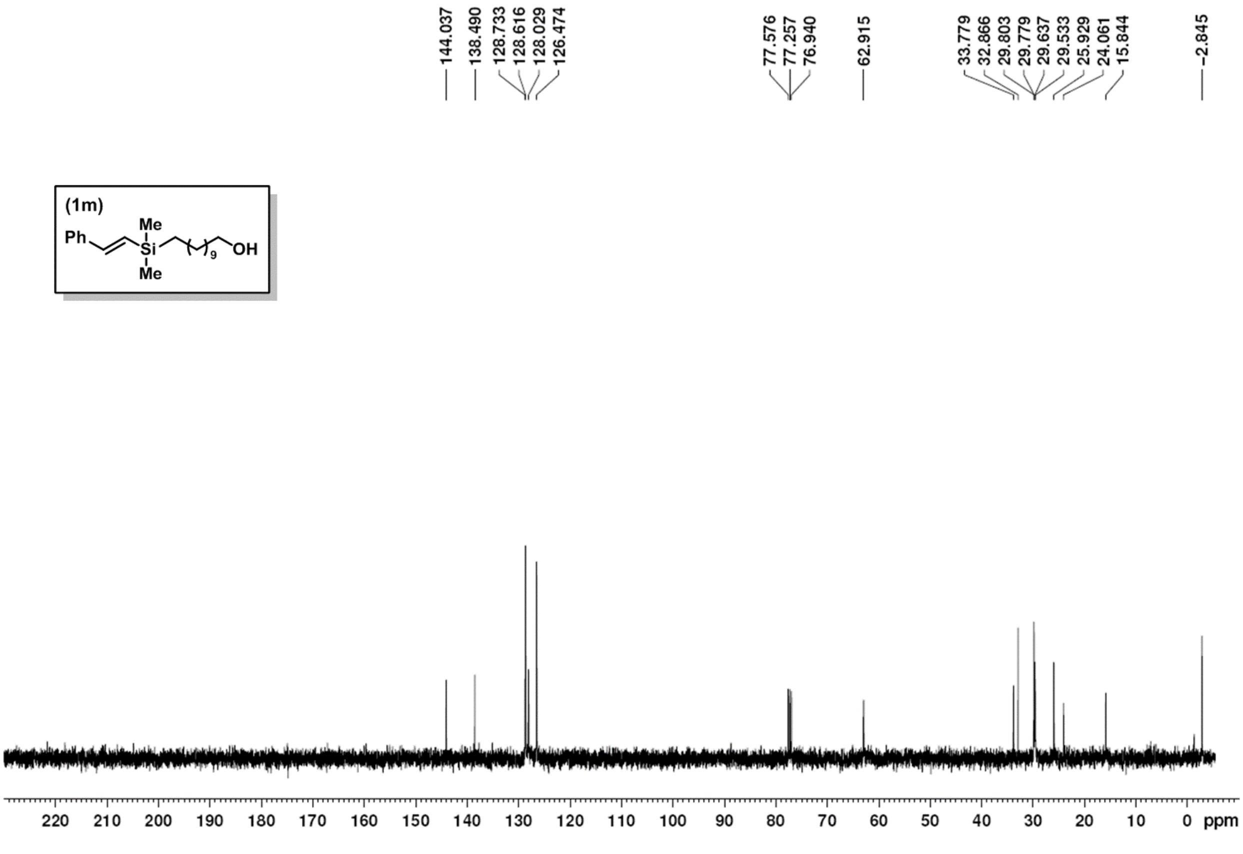


Figure S25. ^{13}C NMR spectrum of **1m**.

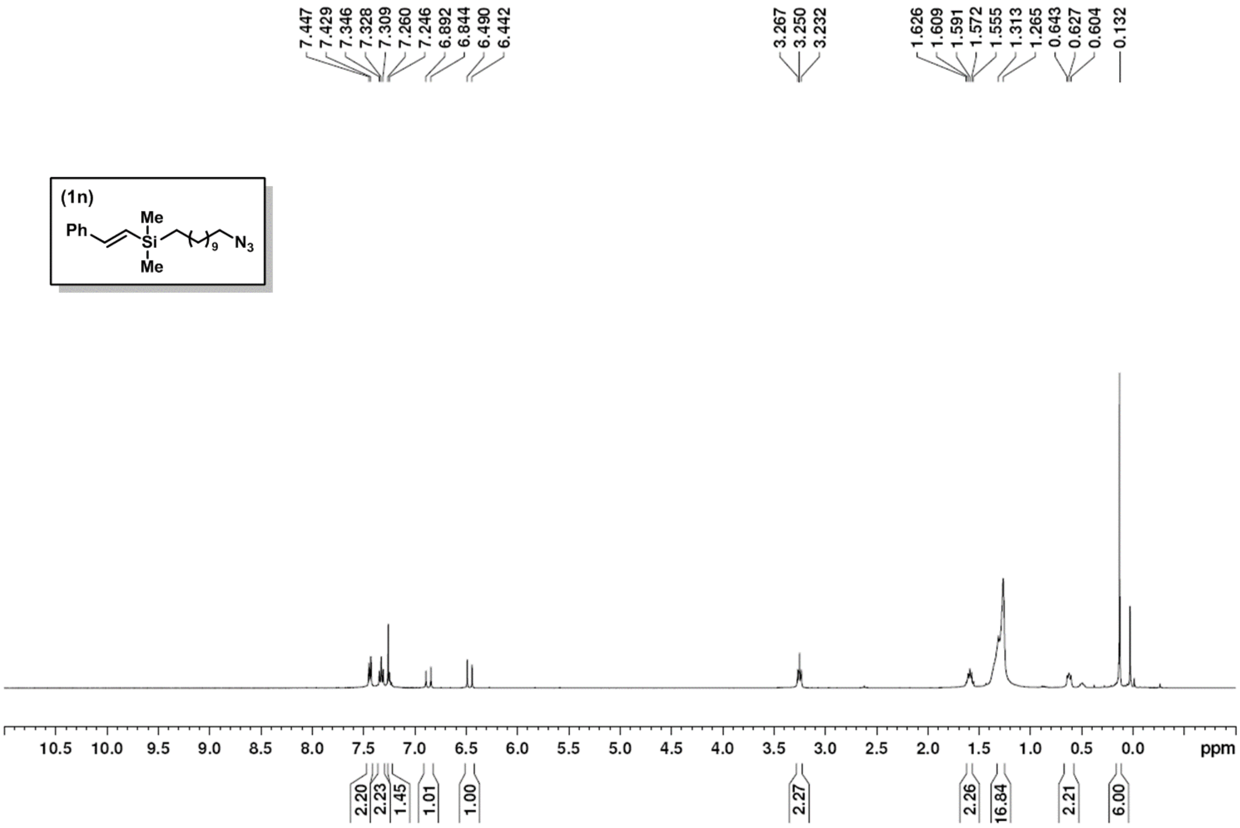


Figure S26. ^{1}H NMR spectrum of **1n**.

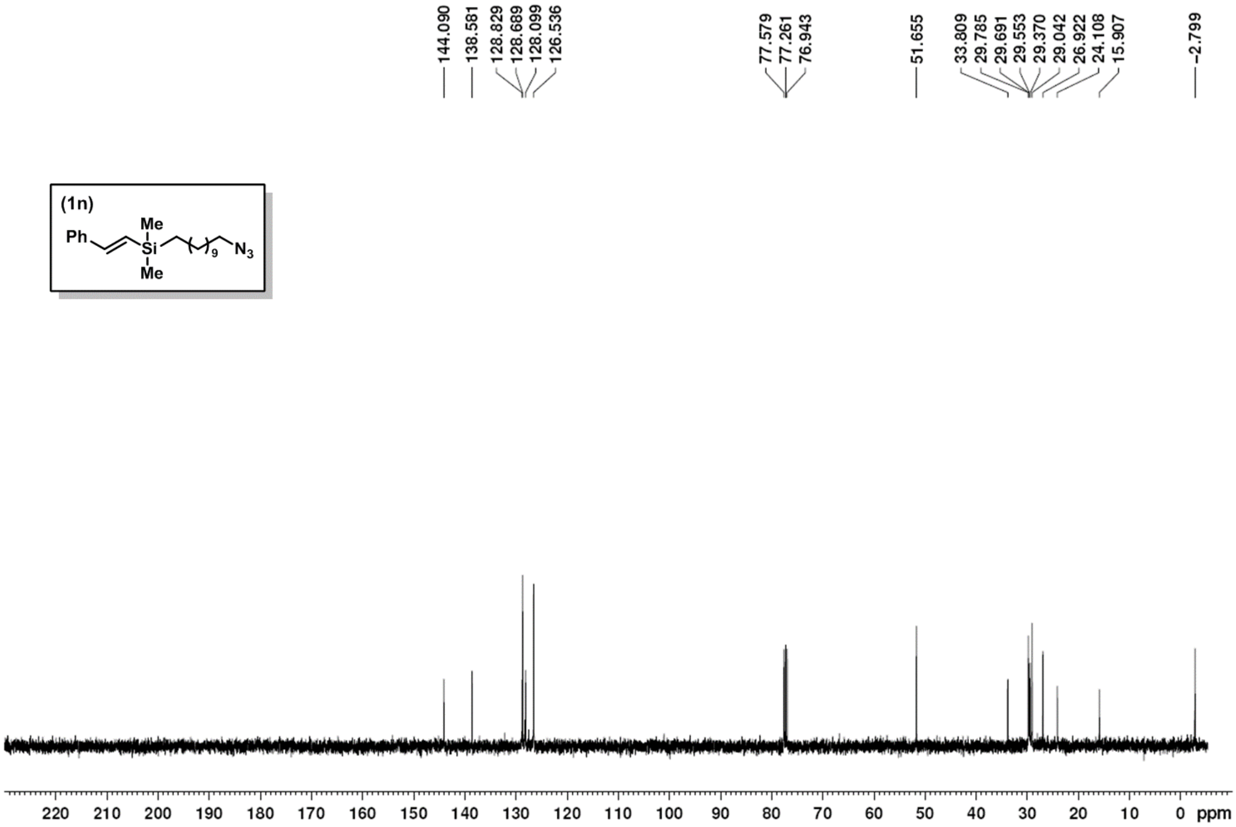


Figure S27. ^{13}C NMR spectrum of **1n**.

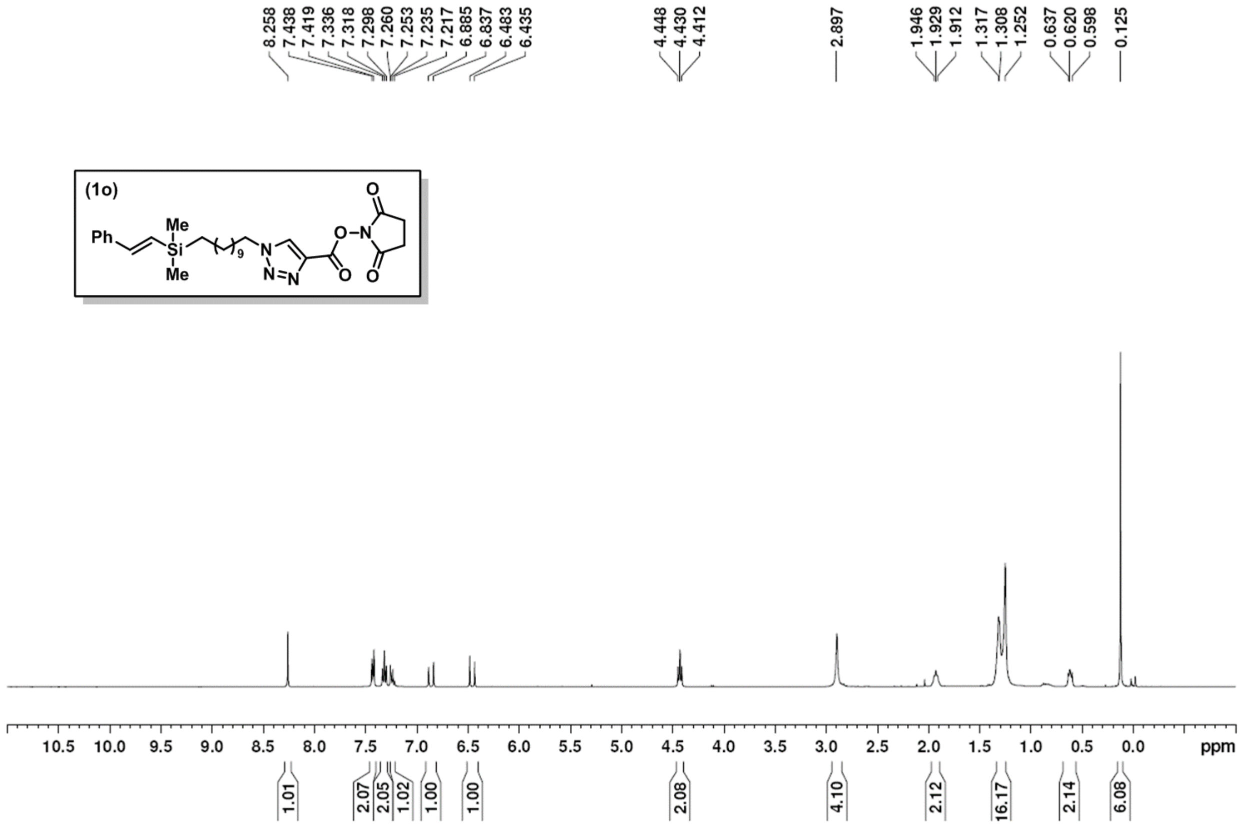


Figure S28. ^{1}H NMR spectrum of **1o**.

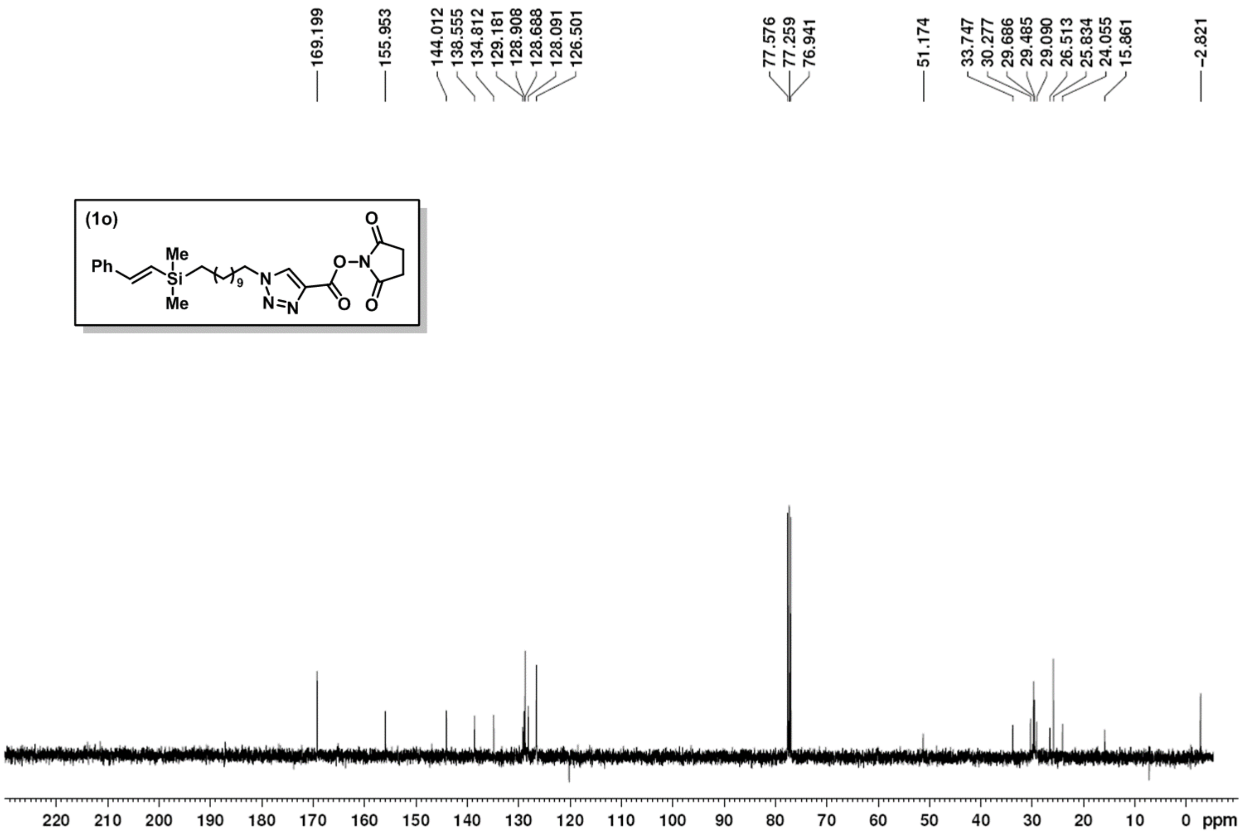


Figure S29. ^{13}C NMR spectrum of **1o**.

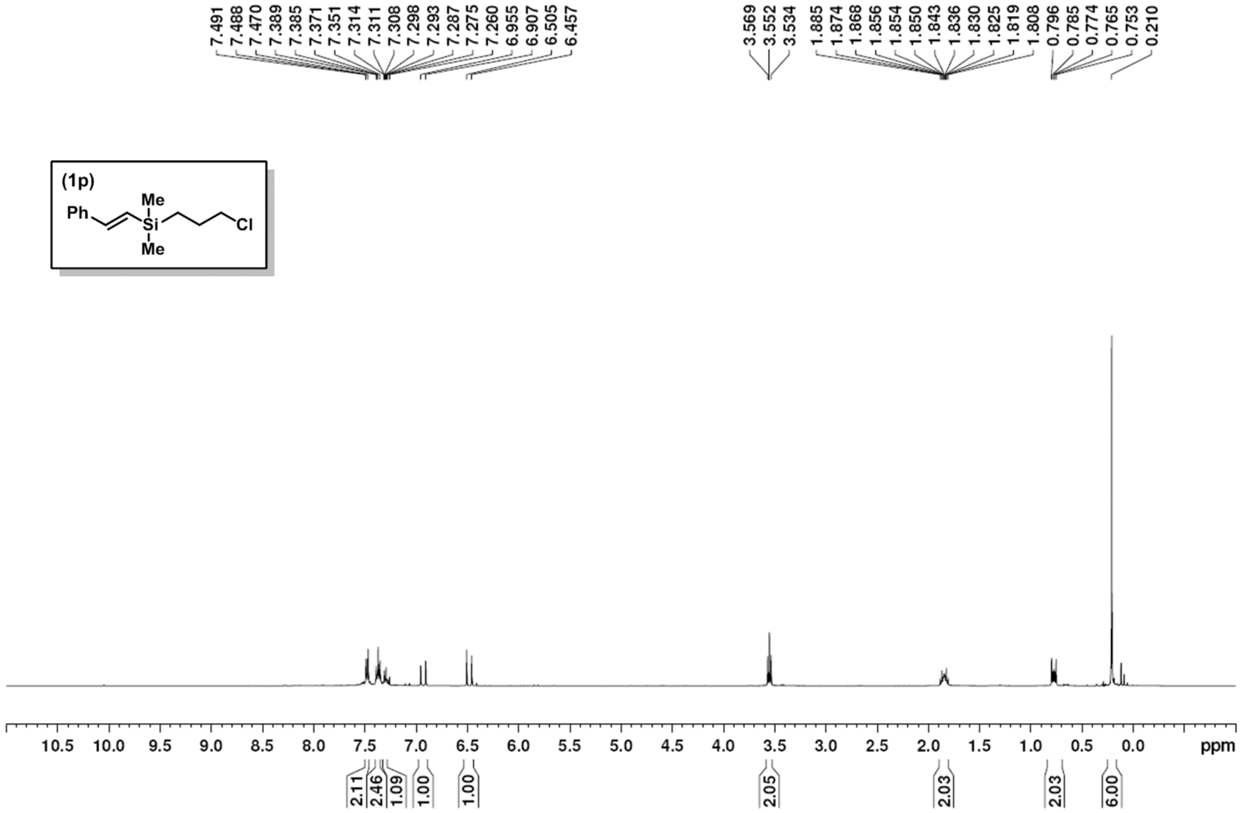


Figure S30. ^{1}H NMR spectrum of **1p**.

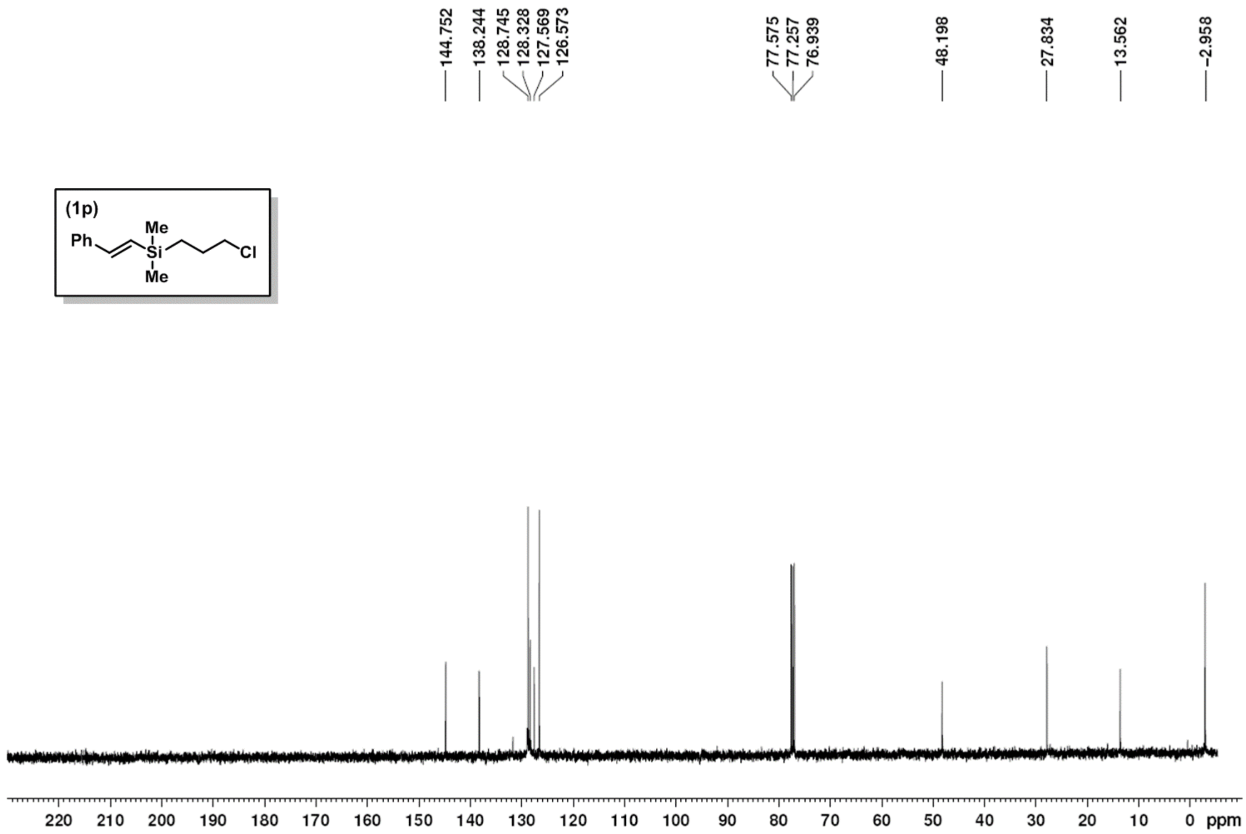


Figure S31. ^{13}C NMR spectrum of **1p**.

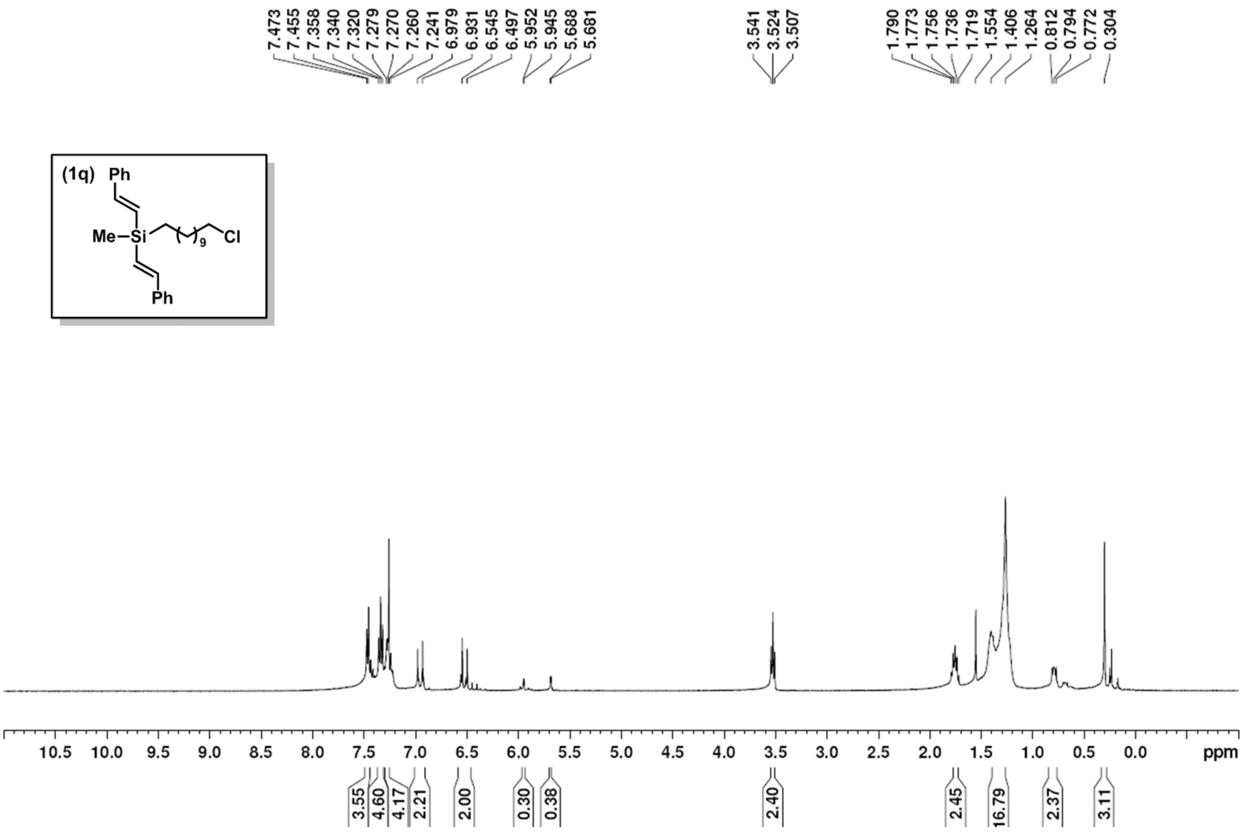


Figure S32. ^{1}H NMR spectrum of **1q**.

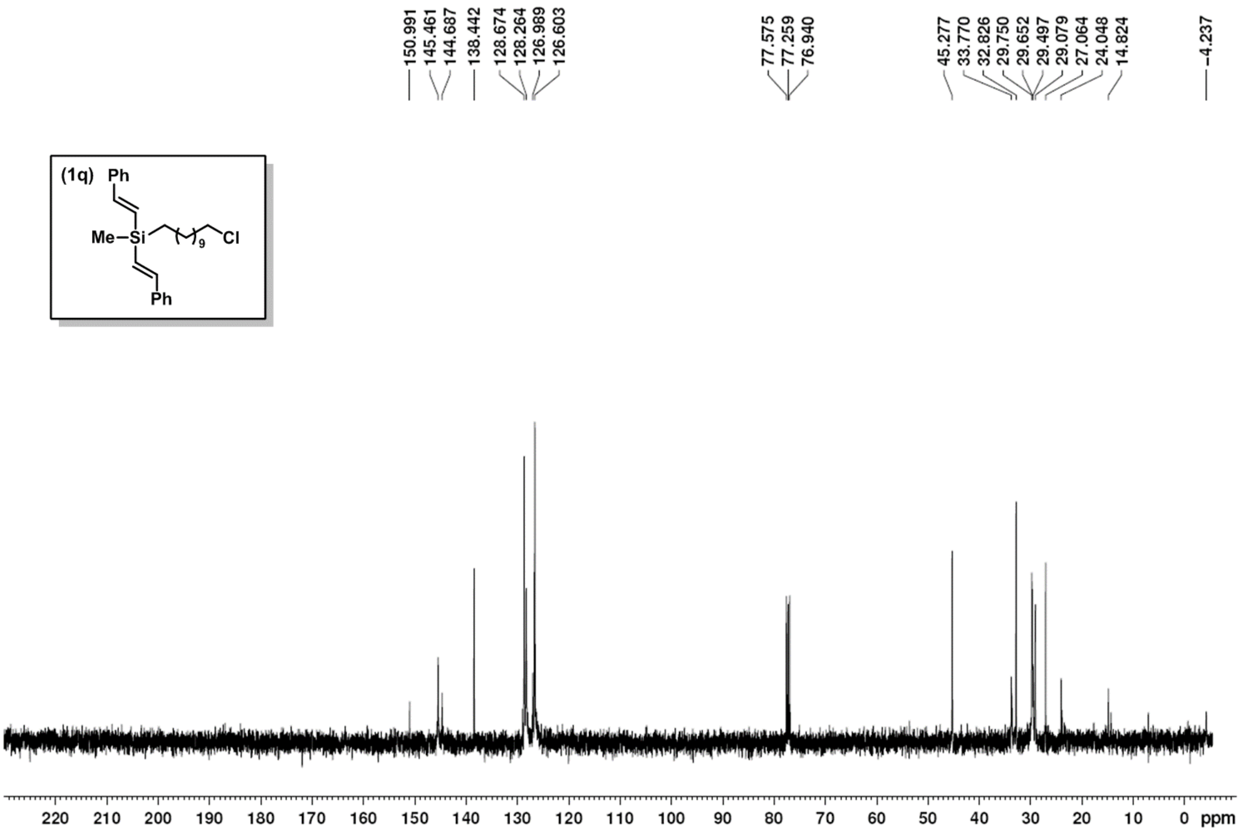


Figure S33. ^{13}C NMR spectrum of **1q**.

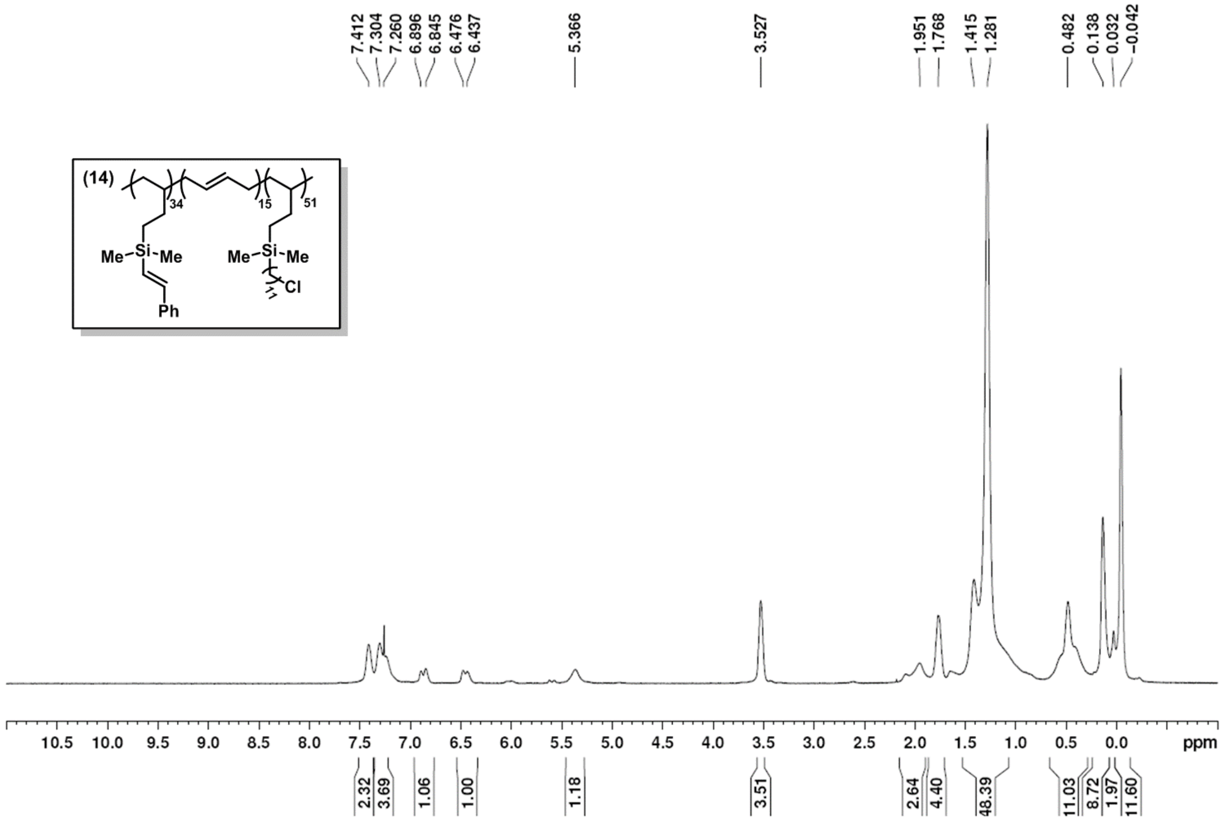


Figure S34. ^{1}H NMR spectrum of **14**.

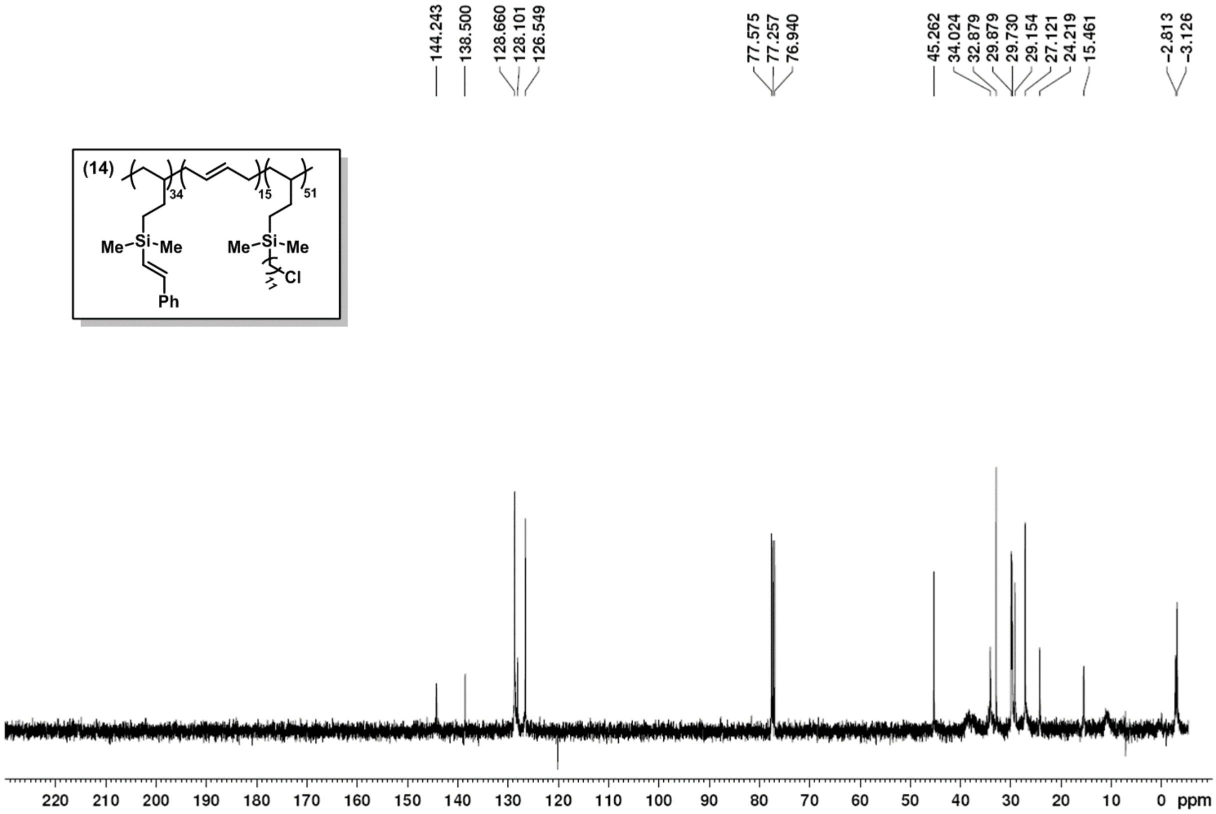


Figure S35. ^{13}C NMR spectrum of **14**.

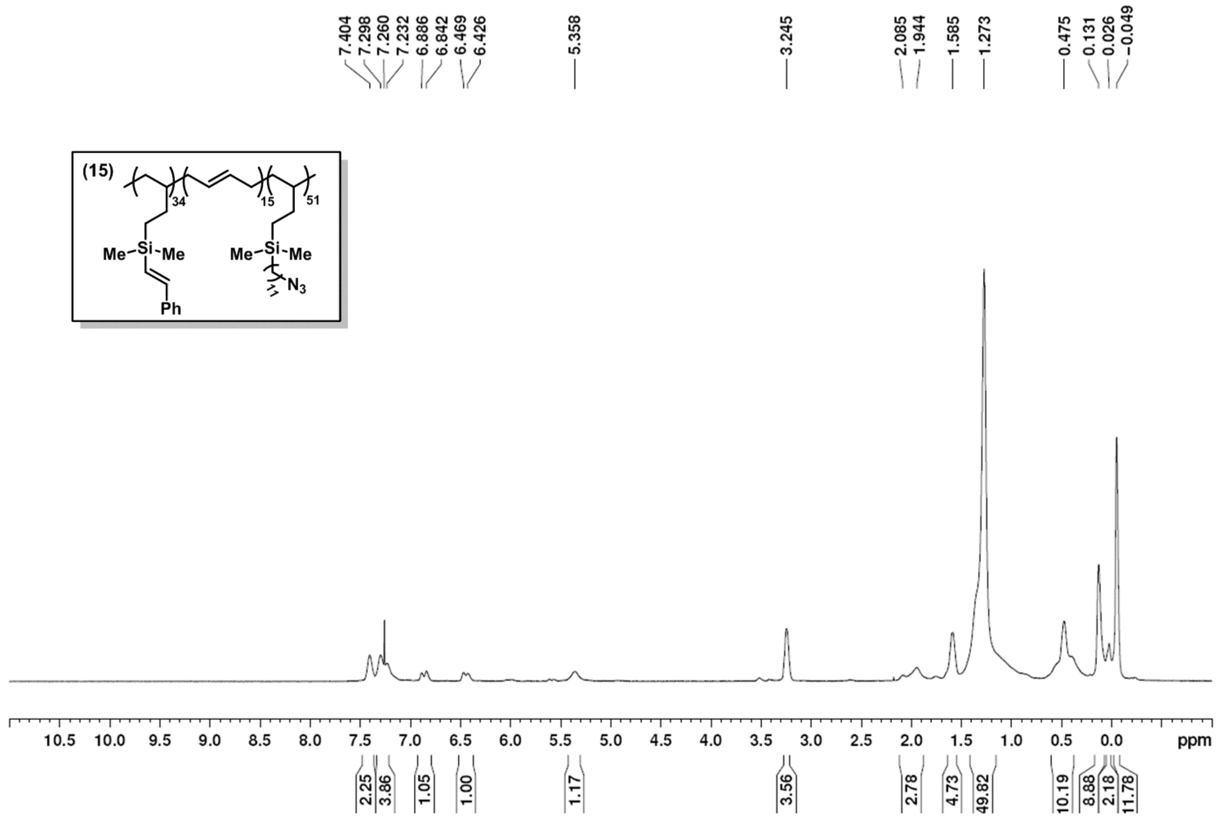


Figure S36. ^{1}H NMR spectrum of **15**.

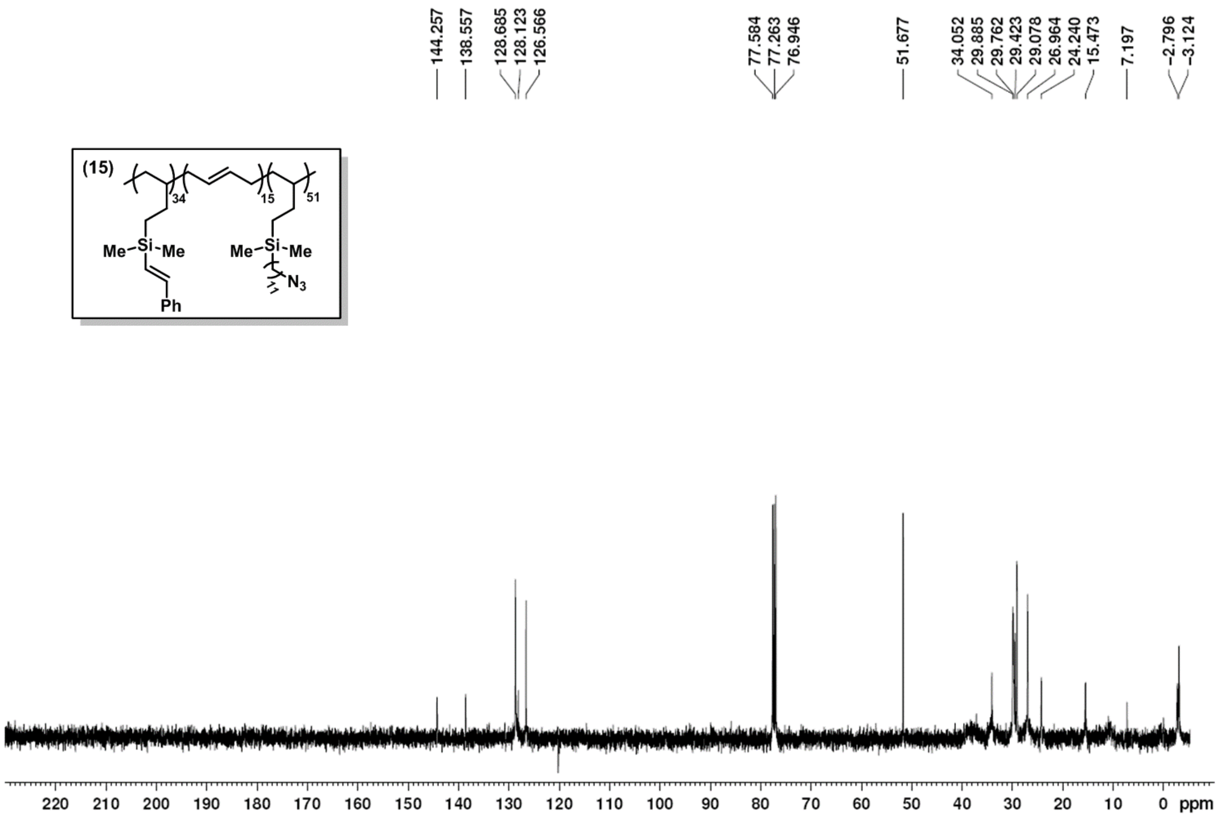


Figure S37. ^{13}C NMR spectrum of **15**.

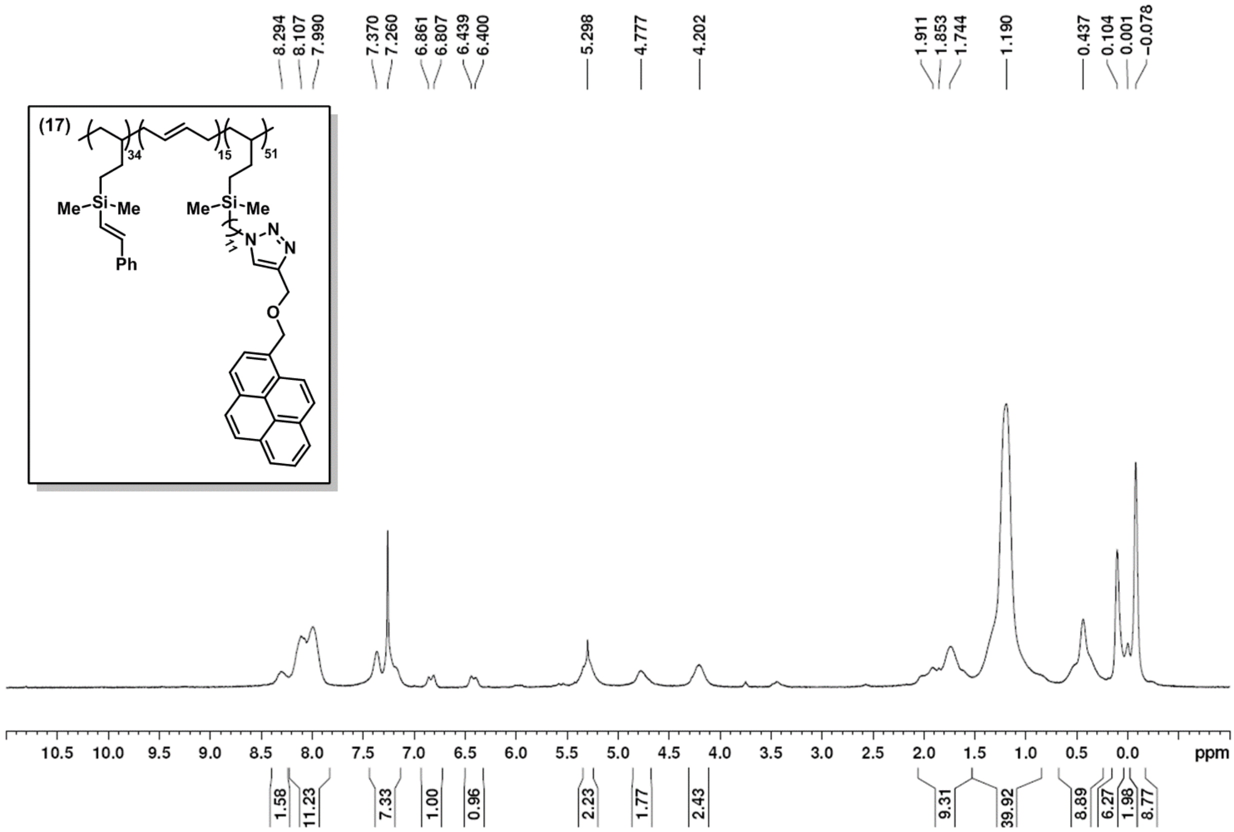


Figure S38. ^{1}H NMR spectrum of **17**.

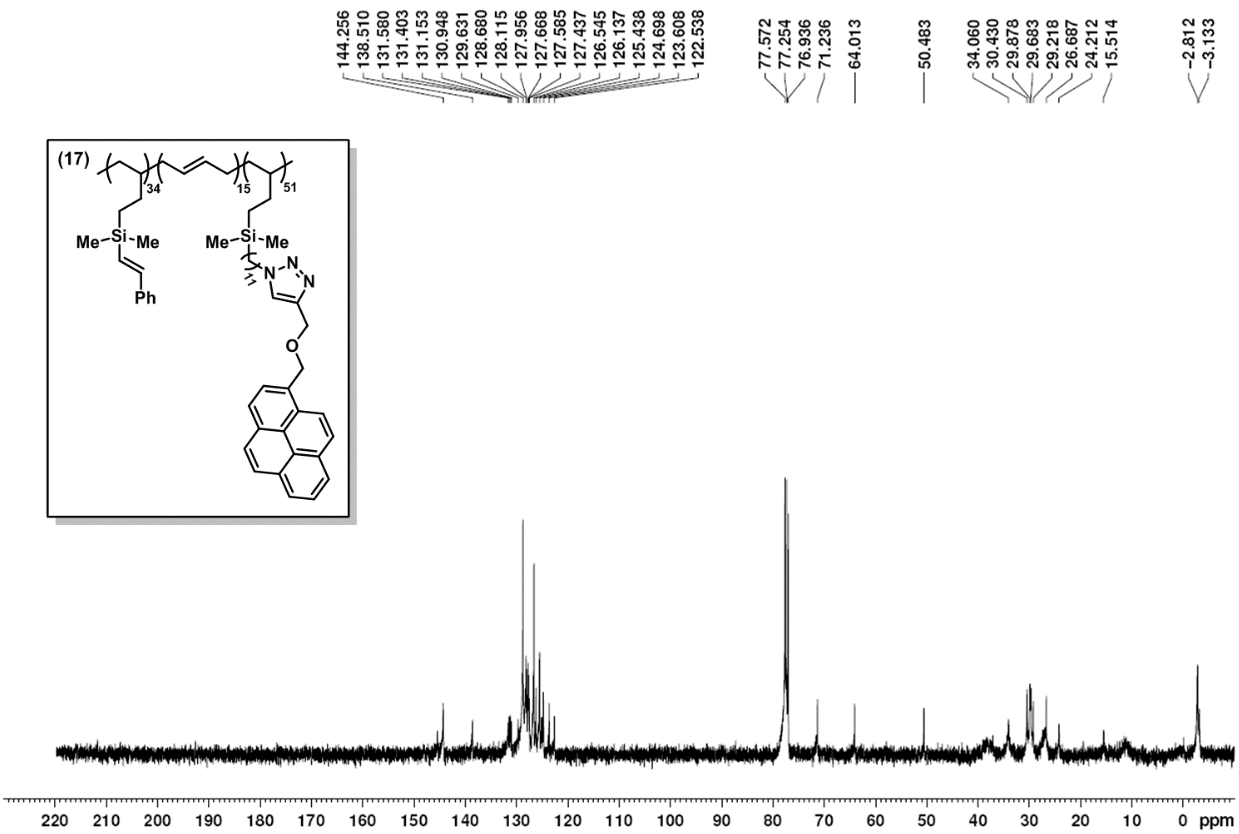


Figure S39. ^{13}C NMR spectrum of **17**.

5. Reference

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