Electronic Supplementary Information

Hydrosilylation of ω-hydroxyalkenes catalysed with 2-methacryloyloxyethyl-phosphorylcholine-protected ruthenium nanoparticles

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1. General information

$RuCl_3 \cdot nH_2O$ was obtained from TANAKA Kikinzoku Kogyo. Ethanol of guaranteed reagent grade was supplied by FUJIFILM Wako Pure Chemical Corporation. 2-Methacryloyloxyethyl phosphorylcholine (MPC) was purchased from NOF Co., Japan. Unless otherwise specified, all starting materials were commercially available and were employed without further purification. Diisopropylamine was purified by distillation under reduced pressure (0.3 mmHg) before use. Gas chromatography (GC) analyses were carried out using a Shimadzu GC-2025 instrument equipped with a flame-ionization detector (FID) and fitted with a BP-5 capillary column (25 m length, 0.22 mm internal diameter, film thickness 0.25 μm). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECZ-400S spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements. Spectra were referenced to $CDCl_3$ using the residual solvent signals (δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). Compounds **3b**,[1] **3d**,[1] **3e**,[1] **3f**,[1] **3i**,[1] **3j**,[1] **3k**,[1] **3l**,[1] and **3n**[2] were previously reported in the literature. The obtained products were analyzed and confirmed using ^{1}H NMR, ^{13}C NMR, and GC-mass spectrometry (GC-MS). In addition, compounds **3a**, **3c**, **3g**, **3h**, **3m** were further characterized by infrared (IR) spectroscopy and high-resolution mass spectrometry (HRMS), along with ^{1}H NMR, ^{13}C NMR, analyses. GC-MS measurements were performed using a Shimadzu GCMS-QP2010 SE system. IR spectroscopy was recorded with a Fourier-transform infrared (FT-IR) spectrometer (Shimadzu IRAffinity-1). HRMS were obtained using a Bruker microTOF mass spectrometer equipped with an electrospray ionization (ESI) source. Product yields were estimated from the GC peak areas using an internal standard method. Ultraviolet-visible (UV–vis) absorption spectra were measured using a JASCO V-670 spectrometer. Photoluminescence emission measurements were conducted with a Shimadzu RF-6000 spectrofluorometer using an excitation wavelength of 350 nm. Dynamic light scattering (DLS) measurements were performed in ethanol at 25 °C with a Zetasizer Nano ZSP instrument (Malvern Panalytical Ltd.). The resulting data were evaluated using the cumulant analysis method. Thermogravimetric (TG) analysis was conducted using a PerkinElmer TGA4000 instrument under a nitrogen atmosphere at a heating rate of 10 °C/min with an Al sample pan. Annular dark-field scanning transmission electron microscopy (ADF-STEM) observations were carried out using a JEOL JEM-ARM200F microscope operated at an accelerating voltage of 200 kV. Small-angle X-ray scattering (SAXS) experiments were conducted at the BL19B2 beamline at SPring-8 (Hyogo, Japan) using an X-ray beam energy of 25 keV. Scattered X-ray profiles were recorded with a PILATUS 2M area detector. For SAXS measurements, the sample-to-detector distance was set to 2040 mm. Calibration of this distance was performed using the diffraction pattern of a standard silver behenate sample. Each SAXS profile was acquired with an exposure time of 60 s. The two-dimensional SAXS patterns were transformed into one-dimensional scattering profiles by circular averaging. The SAXS intensity profiles were plotted as a function of the scattering vector, q, which is defined as $q = 4\pi \sin\theta / \lambda$, where

θ represents half of the scattering angle and λ corresponds to the wavelength of the X-ray beam. Curve fitting of the SAXS data was carried out using spherical particle models based on previously reported methods.[3,4] X-ray photoelectron spectroscopy (XPS) measurements (Contents **4**) were performed with a SHIMADZU KRATOS ULTRA2 system using monochromatic Al Kα radiation. The binding energy scale was calibrated with reference to the C 1s peak of adventitious carbon at 284.8 eV. For spectral processing, a Shirley background was subtracted, and peak deconvolution was conducted using a mixed Gaussian-Lorentzian fitting function. XPS measurements (Contents **14**) were performed with a ULVAC-PHI PHI5000 VersaProbe system using monochromatic Al Kα radiation. The binding energy scale was calibrated with reference to the C 1s peak of adventitious carbon at 284.8 eV. For spectral processing, a Shirley background was subtracted, and peak deconvolution was conducted using a mixed Gaussian-Lorentzian fitting function. X-ray absorption spectroscopy (XAS) measurements were conducted at the BL14B2 beamline at SPring-8. Ru K-edge spectra were collected in transmission mode at ambient temperature. A Si(311) double-crystal monochromator was used to monochromatize the incident beam. Data processing and analysis were carried out using the Athena software (version 0.9.25) included in the Demeter package.[5]

2. Experimental procedures

Synthesis of thiolated 2-methacryloyloxyethyl phosphorylcholine (PC-SH)[6]

MPC (1.47 g, 5 mmol) and 1,6-hexanedithiol (1.50 g, 10 mmol) were dissolved in 10 mL degassed chloroform. Michael-type addition was conducted by adding distilled diisopropylamine (0.028 mL, 0.2 mmol) for 22 h at 25 °C under Ar. The mixture was precipitated into acetone and was vacuumed with an oil pump for 1 h to eliminate the residual acetone (0.3 mmHg). The sample was dissolved in pure water. PC-SH was obtained as a white powder after collection and lyophilization. PC-SH was kept under dry nitrogen until use.

Synthesis of (PC-SH) Ru NPs

Preparation of 0.1 M ethanol solution of $RuCl_3 \cdot nH_2O$. A mixture of $RuCl_3 \cdot nH_2O$ (225 mg) and ethanol (10 mL) was added to a vial and allowed to stand at room temperature overnight.

The $RuCl_3 \cdot nH_2O$ solution (0.1 M, 0.05 mmol) and PC-SH (111 mg, 0.25 mmol) were dissolved in 2.5 mL of ethanol. After stirring for 30 min at 25 °C, $NaBH_4$ (9.45 mg, 0.25 mmol) was added in four parts every 15 min with stirring. After all the $NaBH_4$ was added, the solution was stirred for 24 h at 25 °C. The mixture was then dialyzed using a dialysis membrane (MWCO: 3500) for 6 h to eliminate any unreacted PC-SH and $RuCl_3 \cdot nH_2O$. The ethanol was removed from the mixture using an evaporator and oil pump (0.3 mmHg). Finally, the sample was dissolved in pure water (2 mL) and lyophilized. After that, the sample (1 mM) was obtained for adding ethanol (50 mL).

Hydrosilylation reaction of 9-decene-1-ol (1a) with methyldiphenylsilane (2a) (Table 1, entry 1)

A dispersion (1 mM) of the synthesized (PC-SH) Ru NPs (2.0 mL, 0.2 mol%) was introduced into a 20 mL Schlenk flask. The ethanol was subsequently removed by evaporation. Diethylene Glycol Dimethyl Ether (diglyme, 1 mL), **1a** (0.156 g 1.0 mmol), and **2a** (0.793 g, 4.0 mmol) were added to the flask. The reaction mixture was then stirred at 120 °C for 24 h under Ar. Conversion of the substrates and the yield of product **3a** were determined from the GC peak areas using nonane as an internal standard.

Preparation of (PC-SH) Ru NPs_ar

1-Dodecene (**1e**, 1 mmol) and methyl diphenylsilane (**2a**, 4 mmol) were reacted at 120°C for 24 h in a mixture of diglyme (1 mL) solvent using (PC-SH) Ru NPs (2.0 mL, 0.2 mol%) as the catalyst. After the reaction, the catalyst was separated from the mixture using a membrane filter with a pore size of 1.0 μm and recovered; this was used as (PC-SH) Ru NPs_ar.

Catalyst recycling procedure

9-decene-1-ol (**1a**, 1 mmol) and methyl diphenylsilane (**2a**, 4 mmol) were reacted at 120°C for 24 h in a mixture of diglyme (1 mL) solvent using (PC-SH) Ru NPs (2.0 mL, 0.2 mol%) as the catalyst. After the reaction, the catalyst was separated from the mixture using a membrane filter with a pore size of 1.0 μm. The catalyst was then dissolved in methanol (1 mL). This solution was placed in a Schlenk flask and the methanol was removed under vacuum. Then, **1a**, **2a** and the solvent were added to the flask for use in the next cycle.

Preparation of samples for ADF-STEM

Ethanol was removed from the (PC-SH) Ru NPs (1 mL, 1 mM) under reduced pressure using a rotary evaporator. The obtained NPs were then redispersed in ethanol (2 mL). The resulting suspension was filtered through a membrane filter (RephiQuik polytetrafluoroethylene (PTFE), 0.22 μm).

Preparation of samples for SAXS

After the lyophilization, (PC-SH) Ru NPs solid was dissolved in ethanol (0.1 mL). The solution of (PC-SH) Ru NPs in ethanol (0.5 M) was transferred to a glass capillary.

Preparation of samples for DLS

An ethanol solution of (PC-SH) Ru NPs (1 mM) was passed through a membrane filter (RephiQuik PTFE, 0.22 μm) and subsequently transferred to a glass cell with dimensions of 12 mm × 12 mm. The catalyst particles were dispersed in filtered ethanol (2 mL), and the resulting suspension (0.25 mM) was placed into the glass cell at 25 °C.

Preparation of samples for TG

Ethanol was removed from the (PC-SH) Ru NPs with an evaporator and oil pump (0.3 mmHg). The solid sample (5 mg) was placed on an Al sample cup.

Preparation of samples for XPS (Contents **4**)

The solutions obtained after the reactions of 9-decene-1-ol with methyldiphenylsilane (2:1, 1:1, 2:1, 1:4) were filtered through a membrane filter using hexane. The resulting catalysts after the reaction were dried in a desiccator (100 °C for 2 hours, followed by 16 hours under vacuum).Each sample was placed on an indium foil for analysis.

Preparation of samples for XPS (Contents **14**)

Ethanol was removed from the (PC-SH) Ru NPs (50 mL, 1 mM) under reduced pressure using a rotary evaporator. The remaining samples were further dried under reduced pressure in a desiccator equipped with a diaphragm pump at 100 °C for 10 h. Subsequently, additional drying was conducted for 1 h using a turbomolecular pump (Edwards EXT70) at 90 Pa. The resulting sample was mounted onto an Ag plate measuring 5 mm × 5 mm.

Preparation of samples for XAS

For the XAS measurements, powdered samples were diluted with boron nitride to obtain an appropriate concentration for analysis, and pellet samples with a thickness of approximately 1 mm were prepared. For analysis of the (PC-SH) Ru NPs, after lyophilization, (PC-SH) Ru NPs solid was dissolved in ethanol (1.43 mL). The solution of (PC-SH) Ru NPs in ethanol (35 mM) was transferred to a PTFE cell (light path: 40 mm).

Preparation of samples for ICP-OES

For metal quantification samples, 2 ml of 1 mM (PC-SH) Ru NPs were taken, the solvent was removed and the sample dissolved in 2 ml of HNO_3 and 18 ml of distilled water. For the leaching test, the mixture obtained after the reaction was filtered through a PTFE T100A025A ADVANTEC® membrane filter using hexane. The solvent was then evaporated and removed, and the residue dissolved in 2 ml of HNO_3 and 18 ml of distilled water.

3. Results of Fluorescence (PL) and UV-visible (UV-Vis) spectroscopic analyses

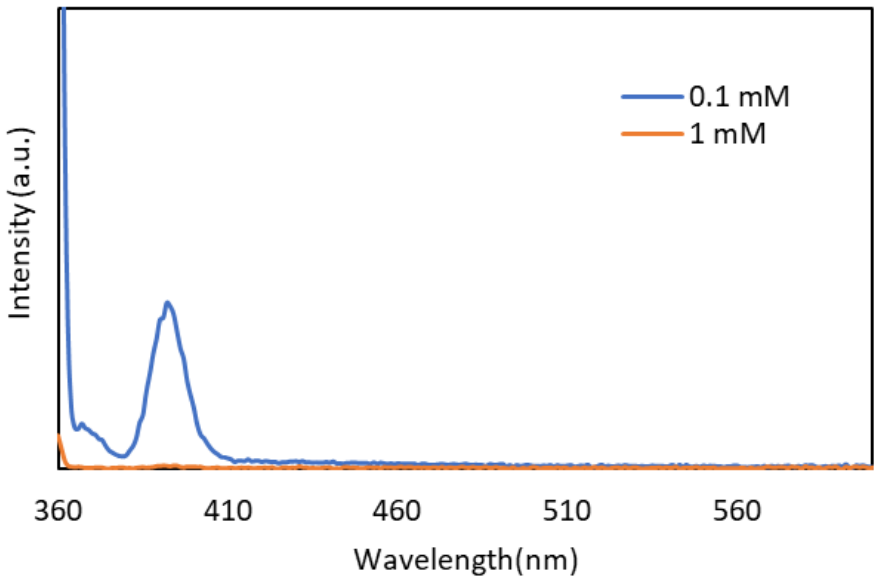


Figure S1. Fluorescence spectra of (PC-SH) Ru NPs under irradiation with 350 nm excitation light. The decrease in fluorescence of the 1 mM confirms concentration quenching.

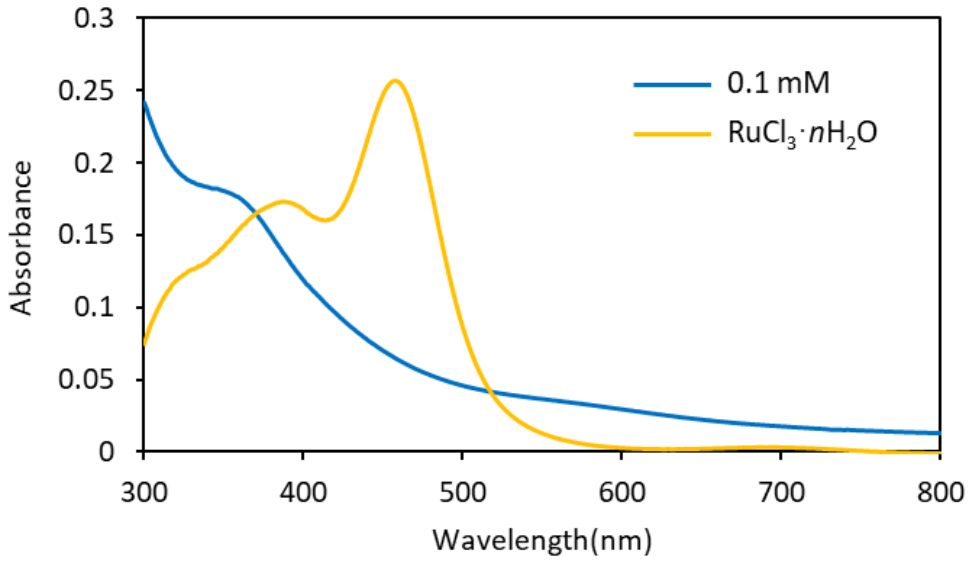


Figure S2. UV-visible spectra of (PC-SH) Ru NPs (blue) and precursor (yellow, $RuCl_3 \cdot nH_2O$). The absence of precursor peak at approximately 400 nm indicates that no unreacted precursor remains in the synthesized (PC-SH) Ru NPs.

4. 1H- and 31P-NMR measurements of the interaction between -OH and MPC

^{1}H-NMR

Preparation of sample

Samples of MPC (0.1 mmol), 9-decene-1-ol (0.1 mmol), 3-butene-1-ol (0.1 mmol), MPC (0.05 mmol) + 9-decene-1-ol (0.05 mmol), and MPC (0.05 mmol) + 3-butene-1-ol (0.05 mmol) were prepared in $CDCl_3$ (0.5 mL) in NMR tubes and mixed using a vortex mixer.

Table S1. Chemical shifts of ^{1}H-NMR spectra

	Chemical shift (ppm)	peak shift (ppm)
9-decene-1-ol	1.37-1.31	-
MPC + 9-decene-1-ol	2.38	1.01-1.07
3-butene-1-ol	1.45	-
MPC + 3-butene-1-ol	2.77	1.32

9-decene-1-ol

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.86-5.76 (1H, m), 5.02-4.91 (2H, m), 3.64 (2H, t, J = 6.6 Hz), 2.05-2.02 (2H, m), 1.60-1.53 (2H, m), 1.37-1.31 (11H, m, overlapping signals).

MPC + 9-decene-1-ol

MPC : ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.08-6.08 (1H, m), 5.56-5.54 (1H, m), 4.30-4.25 (4H, m), 4.06-4.03 (2H, m), 3.78-3.77 (2H, m), 3.34 (9H, s), 1.90 (3H, s).

9-decene-1-ol : ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.83-5.73 (1H, m), 4.99-4.88 (2H, m), 3.57 (2H, t, J = 6.7 Hz), 2.38 (1H, br s), 2.02-1.99 (2H, m), 1.55-1.48 (2H, m), 1.35-1.29 (10H, m).

3-butene-1-ol

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.86-5.75 (1H, m), 5.16-5.13 (2H, m), 3.68 (2H, t, J = 6.0 Hz), 2.36-2.31 (2H, m), 1.45 (1H, s).

MPC + 3-butene-1-ol

MPC : ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.08-6.08 (1H, m), 5.55-5.55 (1H, m), 4.29-4.26 (4H, m), 4.06-4.03 (2H, m), 3.78-3.75 (2H, m), 3.34 (9H, s), 1.90 (3H, s).

3-butene-1-ol : ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.81-5.75 (1H, m), 5.11-5.05 (2H, m), 3.62 (2H, t, J = 6.0 Hz), 2.77 (1H, br s), 2.31-2.26 (2H, m).

MPC

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.06-6.03 (1H, m), 5.54-5.51 (1H, m), 4.26-4.23 (4H, m), 4.02-3.99 (2H, m), 3.77-3.75 (2H, m), 3.33 (9H, s), 1.87 (3H, s).

^{31}P-NMR

Preparation of sample

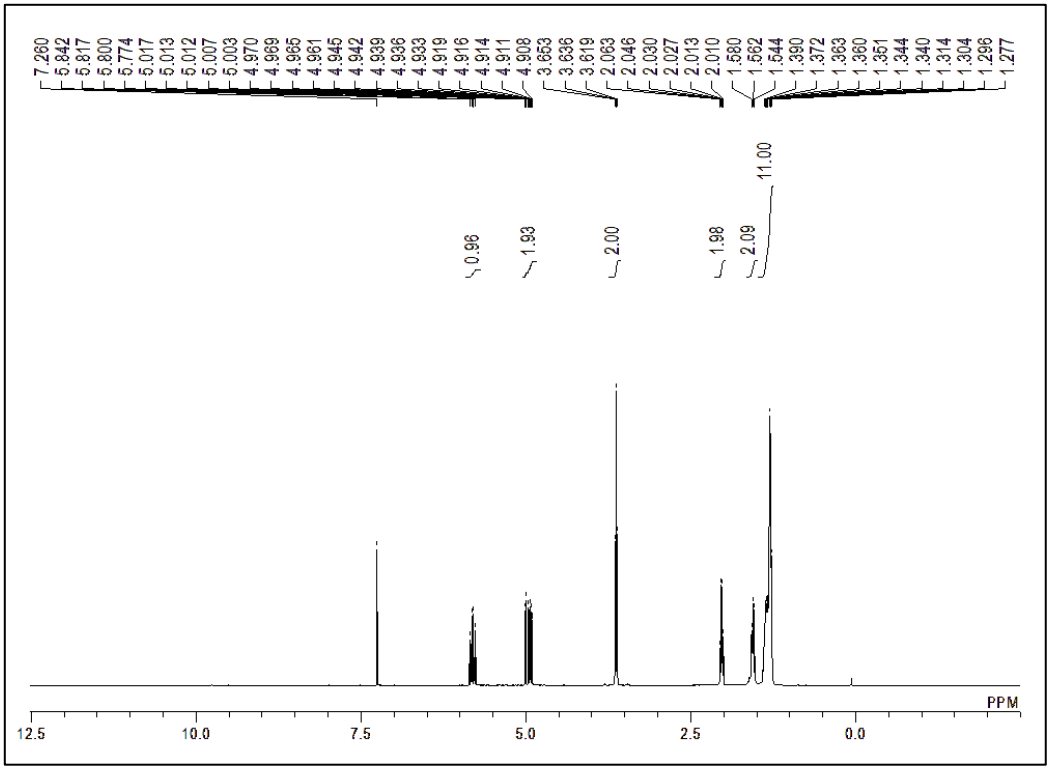
MPC (0.01 mmol), either with or without 9-decene-1-ol (0.01 mmol) or 3-butene-1-ol (0.01 mmol), was dissolved in 0.5 mL of $CDCl_3$ in an NMR tube and mixed using a vortex mixer. The peak of triphenyl phosphate was used as the internal standard (-17.0 ppm).

Table S2. Chemical shifts of ^{31}P-NMR spectra

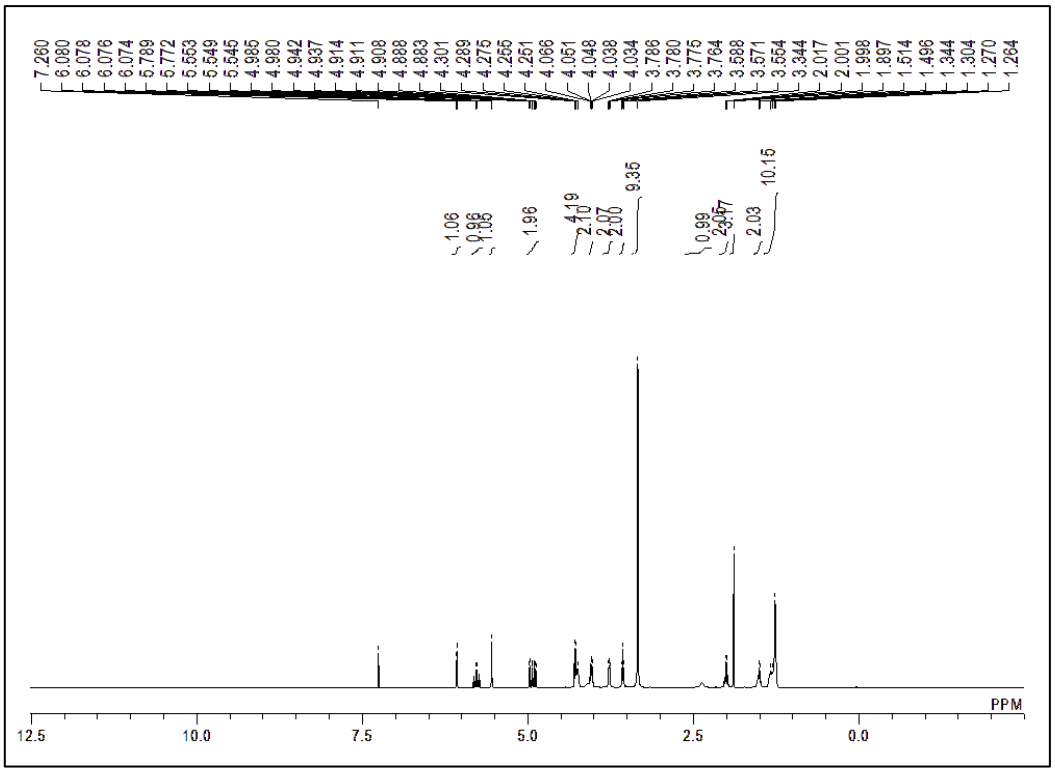
	Chemical shift (ppm)	peak shift (ppm)
MPC	0.09	-
MPC + 9-decene-1-ol	-0.04	-0.13
MPC + 3-butene-1-ol	-0.30	-0.39

^{1}H-NMR

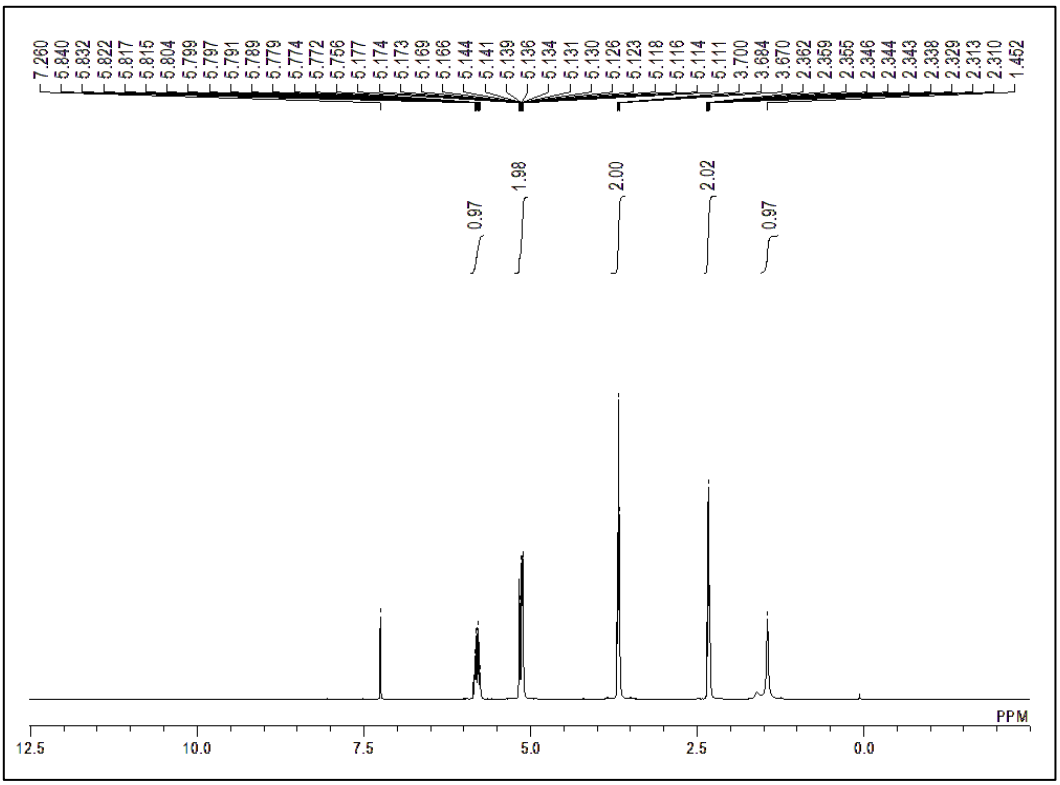
9-decene-1-ol



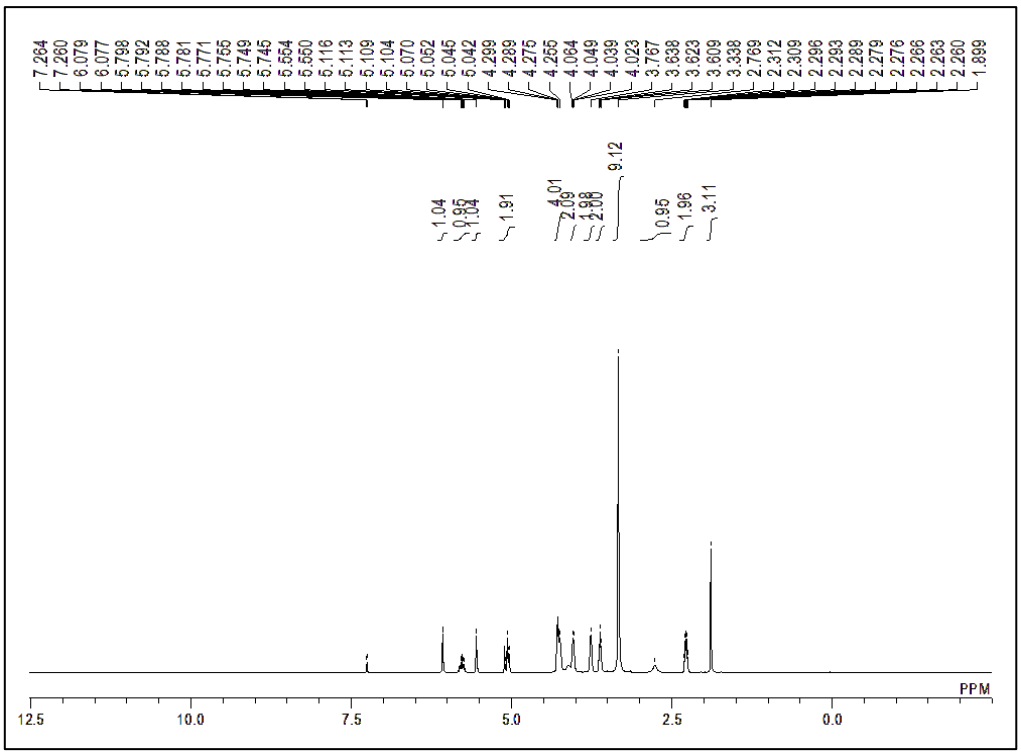
MPC + 9-decene-1-ol



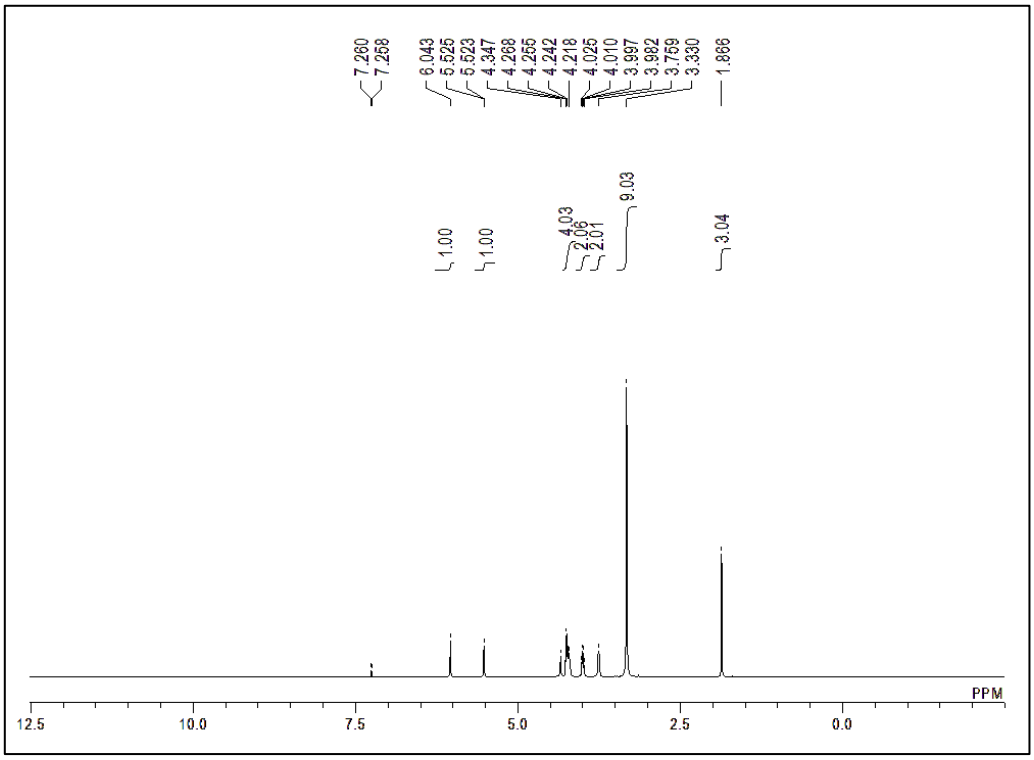
3-butene-1-ol



MPC + 3-butene-1-ol

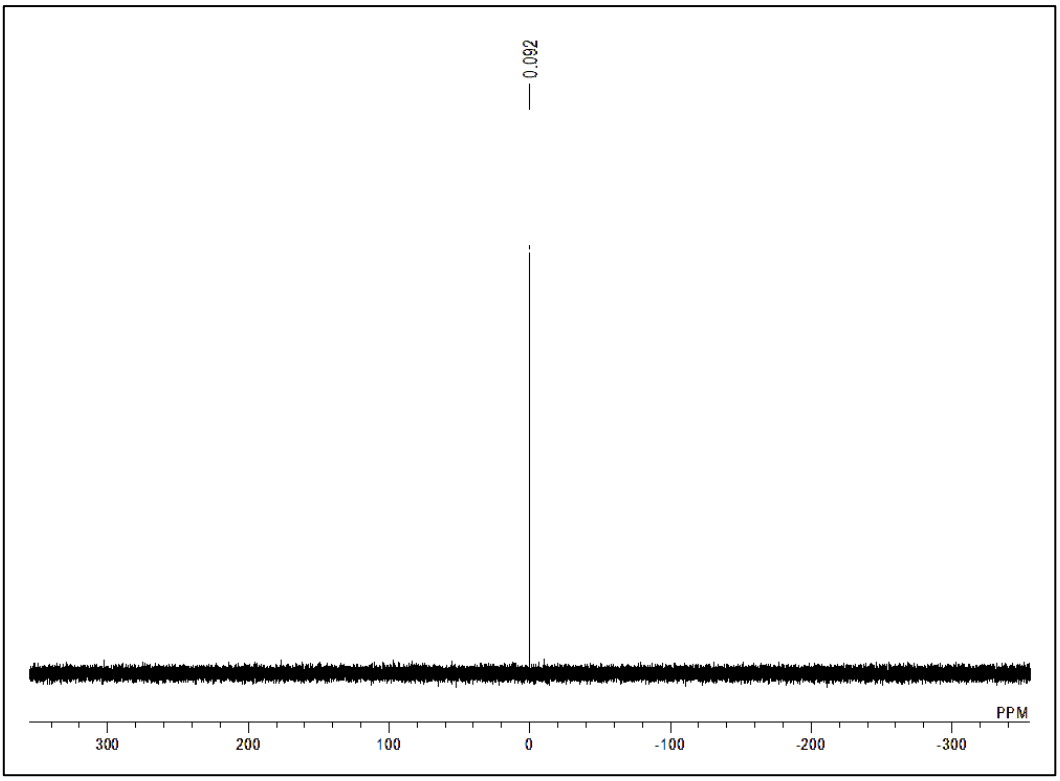


MPC

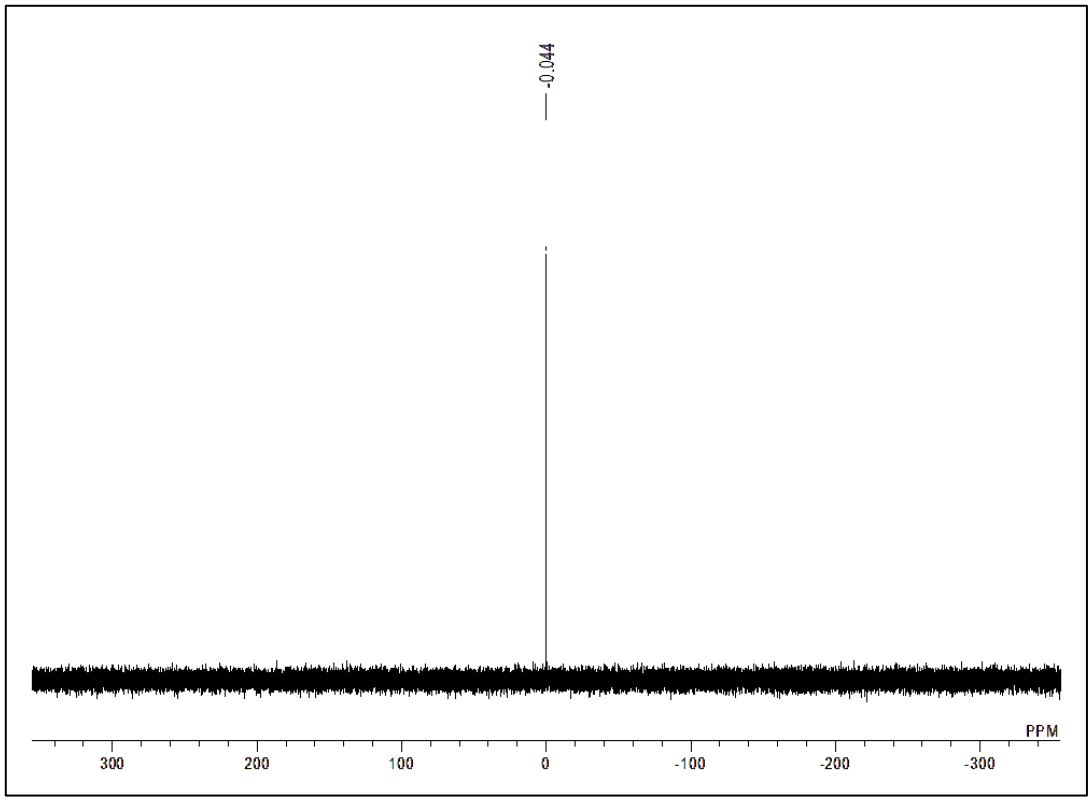


^{31}P-NMR

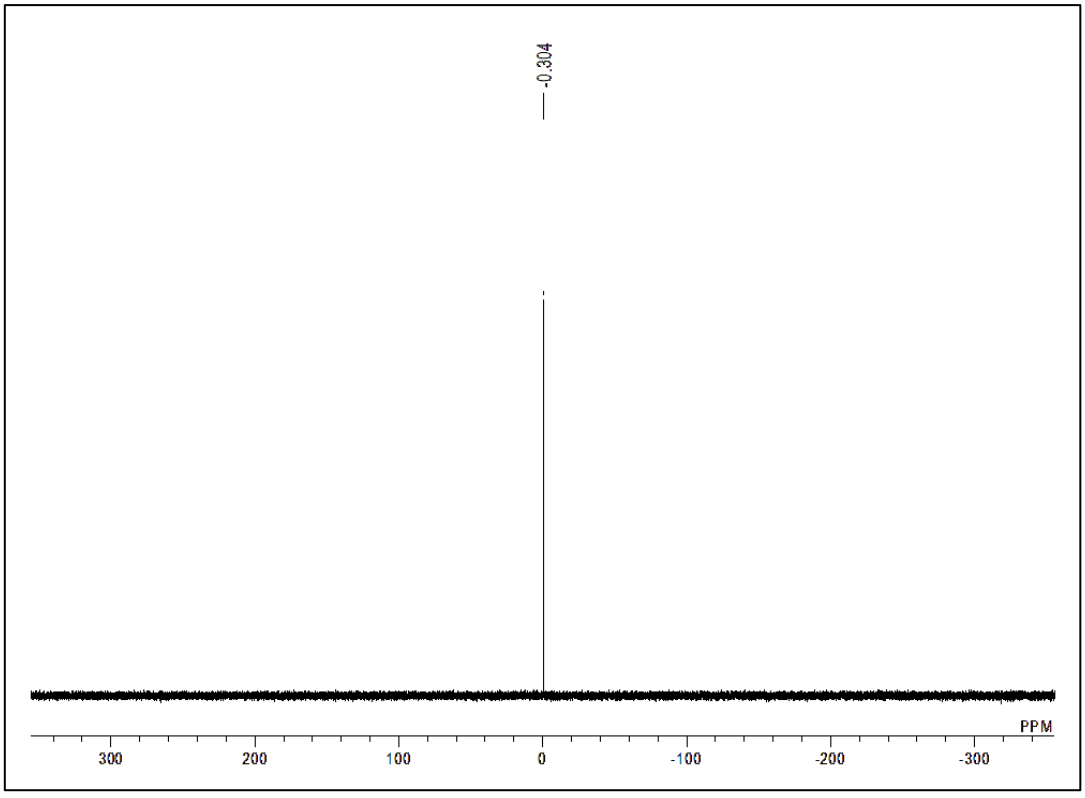
MPC



MPC + 9-decene-1-ol

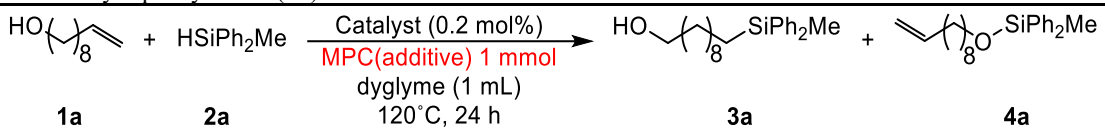


MPC + 3-butene-1-ol



5. A study of MPC as an additive

Table S3. A study of MPC as an additive with Ru-catalysts as a catalysed hydrosilylation of 9-decen-1-ol (**1a**) with methyldiphenylsilane (**2a**)[a]



1a **2a** **3a** **4a**

Entry	Catalyst	Additive	Conv. (%)	Yield (%)	
			1a	**3a**	**4a**
1	DMF-Ru NPs	MPC 1 mmol	>99	trace	6
2		w/o MPC	>99	nd	22
3	$RuCl_3 \cdot nH_2O$	MPC 1 mmol	78	19	6
4		w/o MPC	>99	nd	34

[a]Reaction conditions: **1a** (1 mmol), **2a** (4 mmol), DMF-Ru NPs (0.2 mol%) dissolved in diglyme (1 mL) were stirred at 120 °C for 24 h under Ar. [b]Yields were determined by GC based on **1a** used (nonane as internal standard).

6. X-ray photoelectron spectroscopy (XPS) measurements of (PC-SH)Ru NPs after reaction with varying alkene (1a)-to-silane (2a) ratios

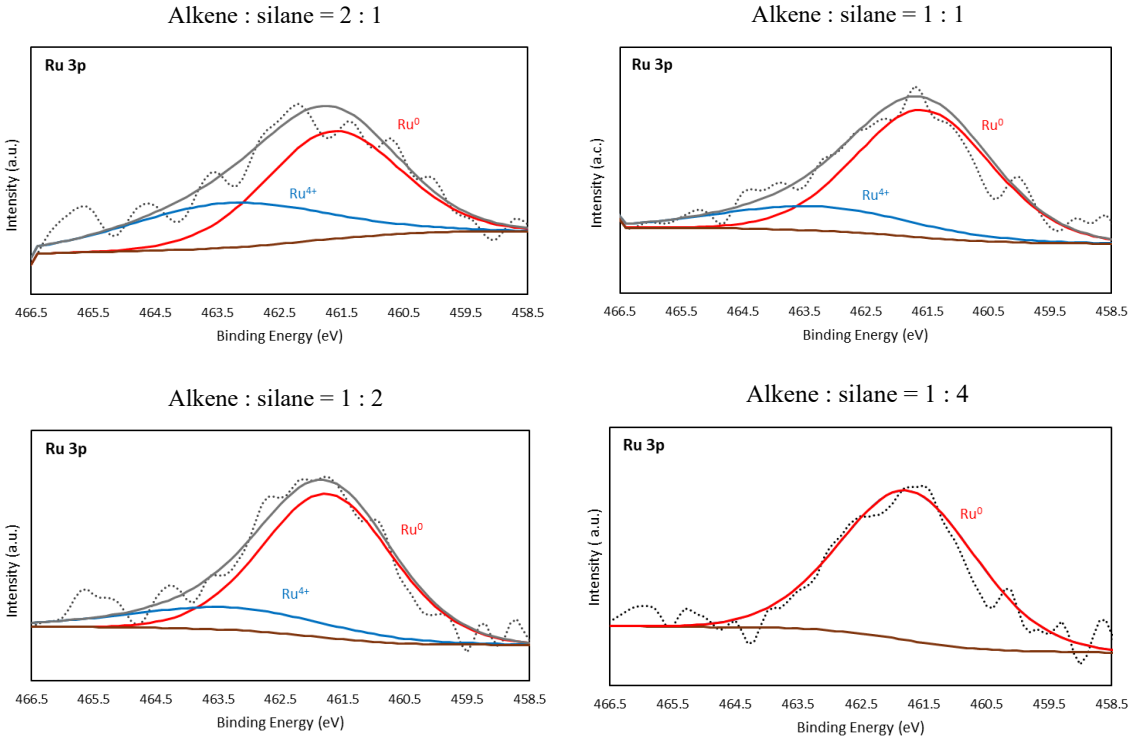


Figure S3. XPS profiles for the Ru 3p region for (PC-SH) Ru NPs after reaction with varying alkene (**1a**)-to-silane (**2a**) ratios

Table S4. XPS peak positions and full-width at half-maximum (FWHM) values (Ru $3p_{3/2}$)

Sample (Alkene : Silane)		Binding Energy (eV)	FWHM	Ratio (%)
2:1	Ru^0	461.6	2.6	62.45
	Ru^{4+} (RuO_2)	463.3	3.7	37.55
1:1	Ru^0	461.6	2.6	78.70
	Ru^{4+} (RuO_2)	463.3	3.9	21.30
1:2	Ru^0	461.7	2.5	80.73
	Ru^{4+} (RuO_2)	463.3	3.9	19.27
1:4	Ru^0	461.7	2.6	100
	Ru^{4+} (RuO_2)	-	-	-

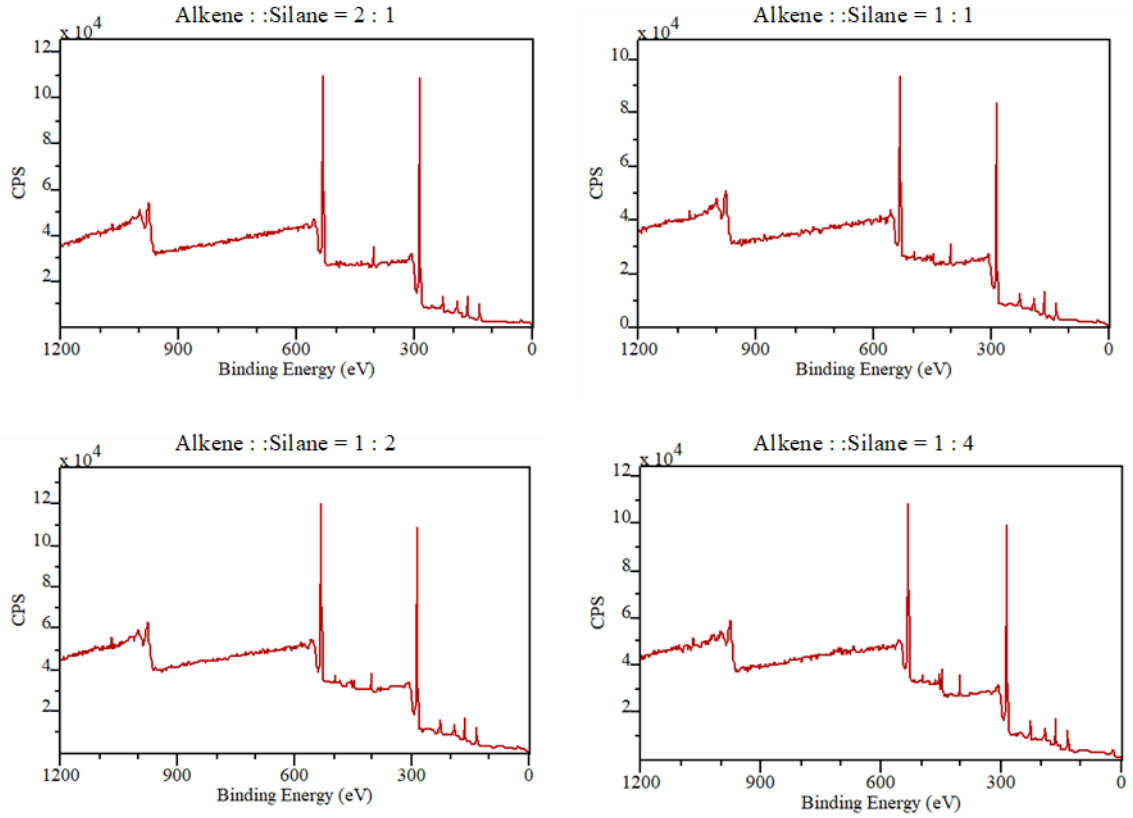


Figure S4. Survey scan XPS spectrum of (PC-SH) Ru NPs with varying alkene (**1a**)-to-silane (**2a**) ratios.

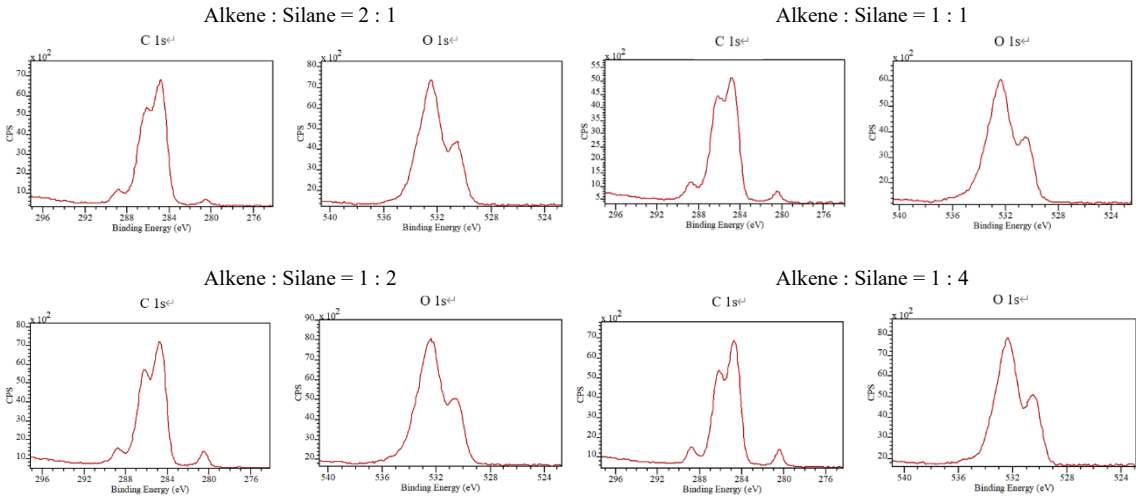
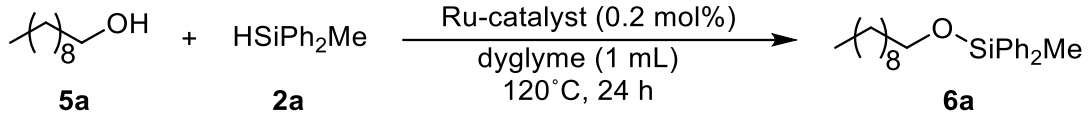


Figure S5. Narrow scan XPS spectrum of (PC-SH) Ru NPs with varying alkene (**1a**)-to-silane (**2a**) ratios.

7. Comparative reactivity

Table S5. Study of Ru-catalyst-catalysed O-silylation of 1-decanol (**5a**) with methyldiphenylsilane (**2a**)[a]

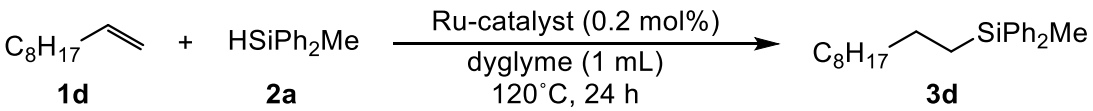


5a **2a** **6a**

Entry	Ru-catalyst	Conv.[b] (%)		Yield[b] (%)
		5a	**2a**	**6a**
1	(PC-SH) Ru NPs	53	32	36
2	DMF-Ru NPs	67	28	45
3	$RuCl_3 \cdot nH_2O$	95	44	87
4	Ru(*p*-cymene)Cl_2	81	31	81

[a]Reaction conditions: **5a** (1 mmol), **2a** (4 mmol), Ru catalyst (0.2 mol%) dissolved in diglyme (1 mL) were stirred at 120 °C for 24 h under Ar. [b]Yields were determined by GC based on **5a** used (nonane as internal standard).

Table S6. Study of Ru-catalyst-catalysed hydrosilylation of 1-decene (**1d**) with methyldiphenylsilane (**2a**)[a]

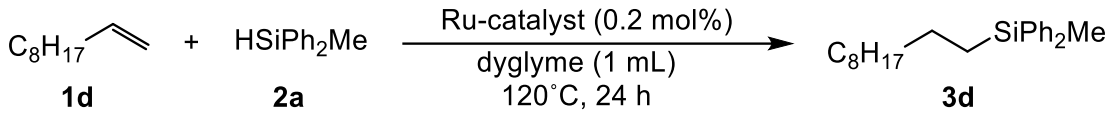


1d **2a** **3d**

Entry	Ru-catalyst	Conv.[b] (%)		Yield[b] (%)
		1d	**2a**	**3d**
1	(PC-SH) Ru NPs	27	49	7
2	DMF-Ru NPs	51	53	5
3	$RuCl_3 \cdot nH_2O$	92	57	6
4	Ru(*p*-cymene)Cl_2	80	91	5

[a]Reaction conditions: **1d** (2 mmol), **2a** (1 mmol), Ru catalyst (0.2 mol%) dissolved in diglyme (1 mL) were stirred at 120 °C for 24 h under Ar. [b]Yields were determined by GC based on **2a** used (nonane as internal standard).

Table S7. Study of Ru-catalyst-catalysed hydrosilylation of 1-decene (**1d**) with methyldiphenylsilane (**2a**)[a]

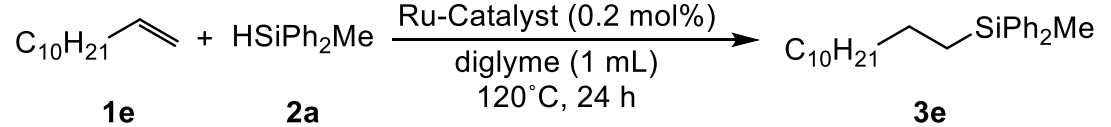


1d **2a** **3d**

Entry	Ru-catalyst	Conv.[b] (%)		Yield[b] (%)
		1d	**2a**	**3d**
1	(PC-SH) Ru NPs	>99	55	92
2	DMF-Ru NPs	>99	32	64
3	$RuCl_3 \cdot nH_2O$	88	16	51
4	Ru(*p*-cymene)Cl_2	57	50	17

[a]Reaction conditions: **1d** (1 mmol), **2a** (4 mmol), Ru catalyst (0.2 mol%) dissolved in diglyme (1 mL) were stirred at 120 °C for 24 h under Ar. [b]Yields were determined by GC based on **1d** used (nonane as internal standard).

Table S8. Study of H_2PtCl_6-catalysed hydrosilylation of 1-dodecene (**1e**) with methyldiphenylsilane (**2a**)[a]

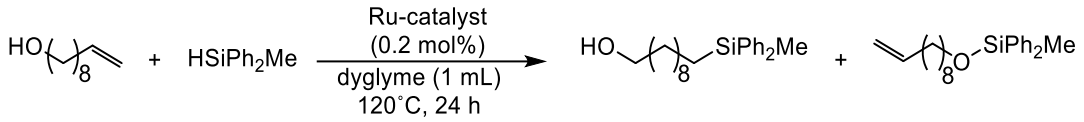


1e **2a** **3e**

Entry	Ru-Catalyst	Conv.[b] (%)		Yield[b] (%)
		1e	**2a**	**3e**
1	(PC-SH) Ru NPs	>99	78	80 [400][c]
2	H_2PtCl_6	69	26	23 [115][c]

[a]Reaction conditions: **1e** (1 mmol), **2a** (4 mmol), Ru-catalyst (0.2 mol%) dissolved in diglyme (1 mL) were stirred at 120 °C for 24 h under Ar. [b]Yields were determined by GC based on **1e** used (nonane as internal standard). [c]Number in square brackets show TON.

Table S9. Study of H_2PtCl_6-catalysed hydrosilylation of 9-decene-1-ol (**1a**) with methyldiphenylsilane (**2a**)[a]



1a **2a** **3a** **4a**

Entry	Ru-Catalyst	Conv.[b] (%)		Yield[b] (%)	
		1a	**2a**	**3a**	**4a**
1	(PC-SH) Ru NPs	>99	96	51 [39][c]	nd
2	H_2PtCl_6	>99	40	nd	5

[a]Reaction conditions: **1a** (1 mmol), **2a** (4 mmol), Ru-catalyst (0.2 mol%) dissolved in diglyme (1 mL) were stirred at 120 °C for 24 h under Ar. [b]Yields were determined by GC based on **1a** used (nonane as internal standard). [c]Number in square brackets show the isolated yield.

(PC-SH) Ru NPs were compared with H_2PtCl_6, an industrial standard. The results showed that the turnover number (TON) was higher for (PC-SH) Ru NPs when 1-dodecene was used (Table S8). Furthermore, when ω-hydroxyalkenes were used, H_2PtCl_6 did not produce **3a** and only a small amount of **4a** was formed (Table S9).

8. Unsuccessful substrates

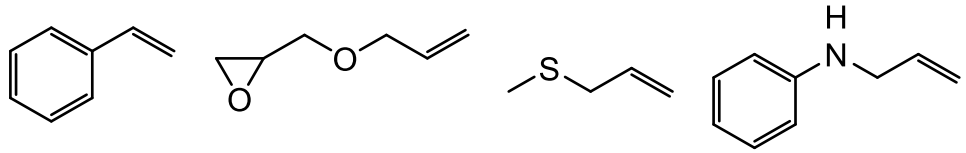


Figure S6. Unsuccessful substrates of (PC-SH) Ru NPs-catalyzed hydrosilylaion

9. Results of Small-Angle X-ray Scattering (SAXS) analysis

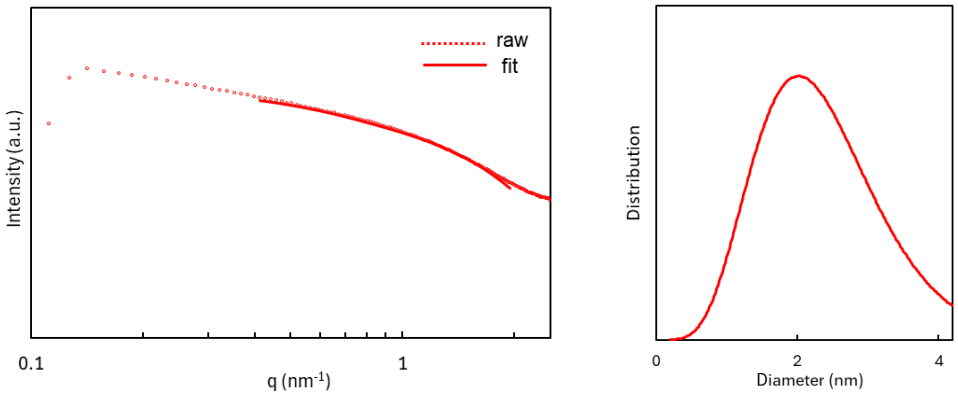


Figure S7. SAXS profiles and particle distributions of the (PC-SH) Ru NPs

Table S10. Fitting results for the SAXS profiles

Sample		Radius[a] (nm)	sigma	η^b	R^2	Ratio[c]
(PC-SH) Ru NPs	fit 1	1.17	0.201	0 (fixed)	0.9996	97 : 3
	fit 2	1.99	0.807	0 (fixed)		

[a]average particle radius, [b]volume fraction, [c]ratio of (fit 1 : fit 2) estimated from their relative intensity.

10. Results of Dynamic Light Scattering (DLS) analyses

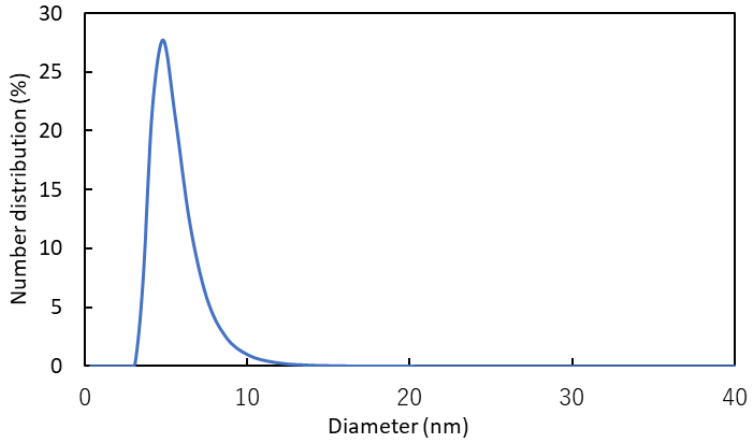
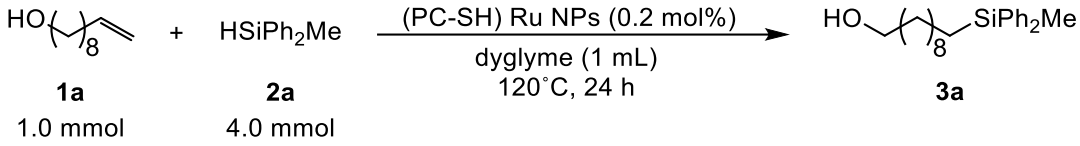


Figure S8. DLS curves for (PC-SH) Ru NPs (green).

11. Recycling experiments



1a 1.0 mmol **2a** 4.0 mmol **3a**

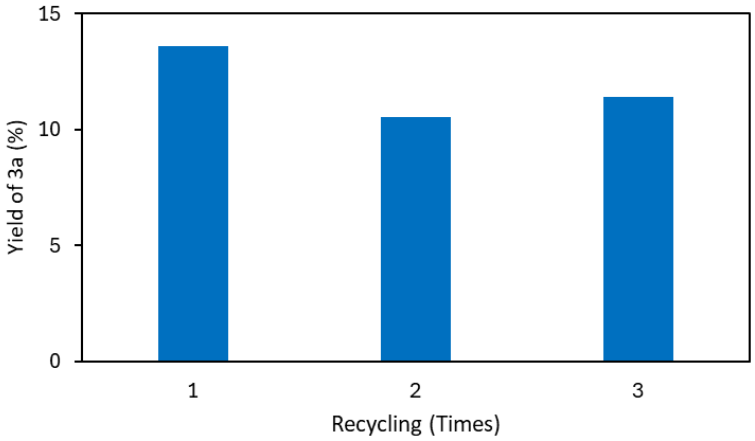


Figure. S9 Recycling experiment result for (PC-SH) Ru NPs catalyzed hydrosilylation of **1a** with **2a**.

12. Results of Fourier Transform Infrared Spectroscopy (FT-IR) analyses

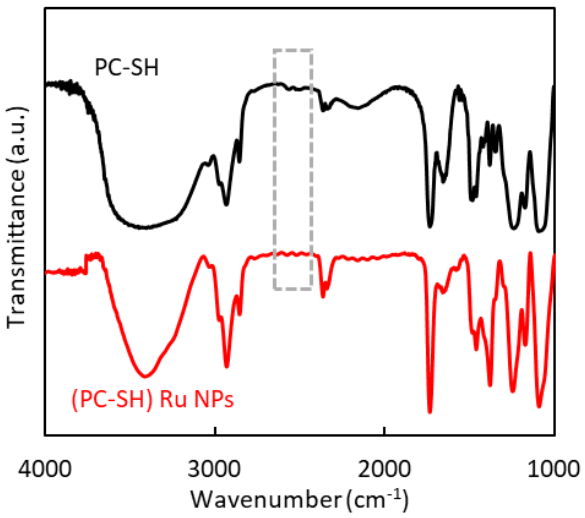


Figure S10. FT-IR spectra of PC-SH (black) and (PC-SH) Ru NPs (red).

13. Results of Thermogravimetric (TG) analysis

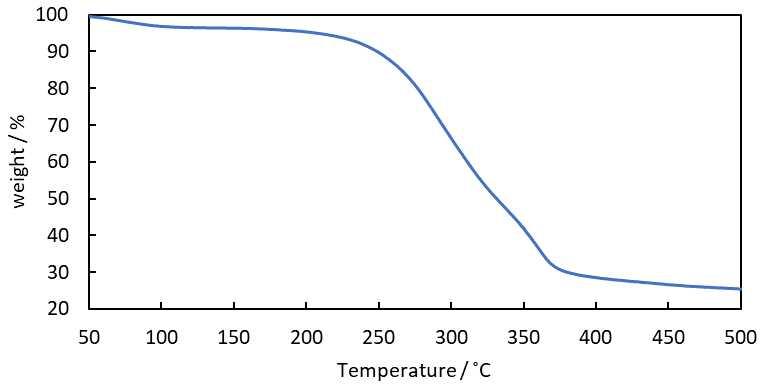
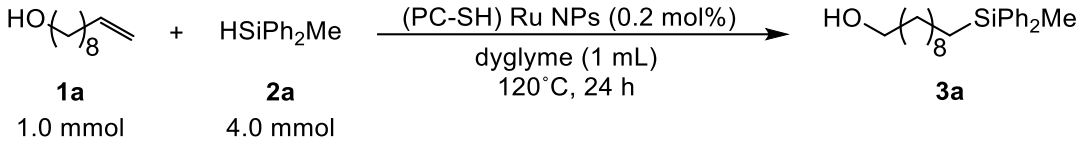


Figure. S11. Thermogravimetric analysis of (PC-SH) Ru NPs

Td_5: 210 °C.

14. Results of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis



1a 1.0 mmol **2a** 4.0 mmol **3a**

Table S11. Quantification of the Ru content in (PC-SH) Ru NPs and the amount eluted after the reaction.

	SD	DL	ppm
(PC-SH) Ru NPs	4.2×10^{-2}	5.4×10^{-1}	2.9
filtrate after the reaction	3.4×10^{-3}	4.4×10^{-2}	8.9×10^{-3}

15. Results of XPS analysis of (PC-SH) Ru NPs before and after the reaction

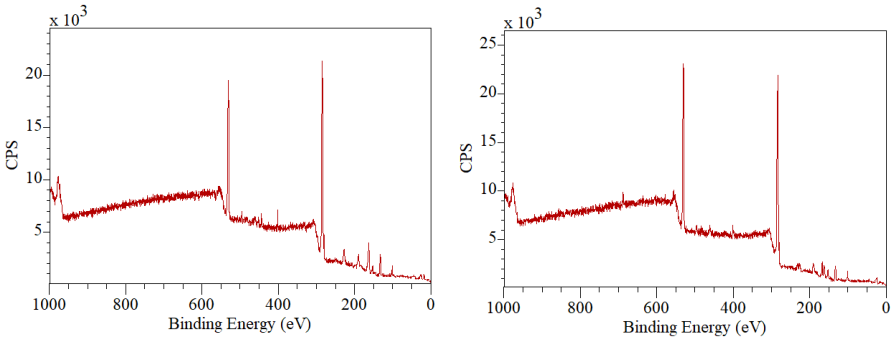


Figure S12. Survey scan XPS spectrum of (PC-SH) Ru NPs before(left) and after(right) reaction.

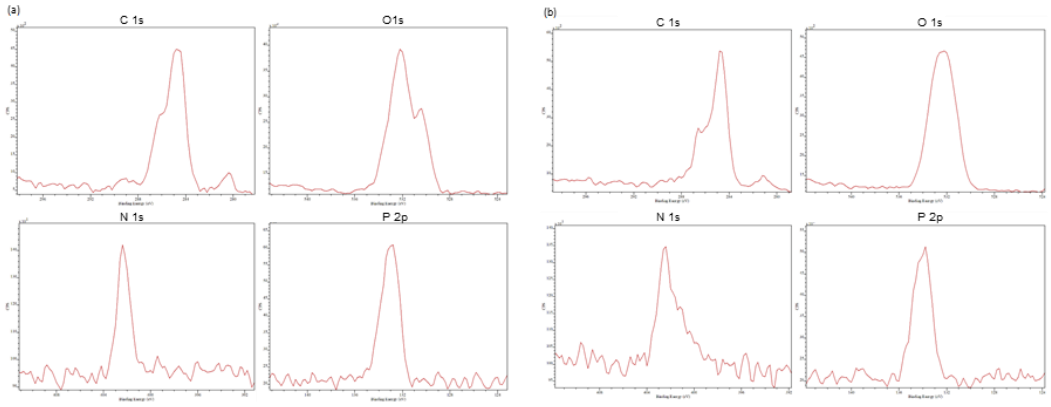


Figure S13. Narrow scan XPS spectrum of (PC-SH) Ru NPs before(left) and after(right) reaction.

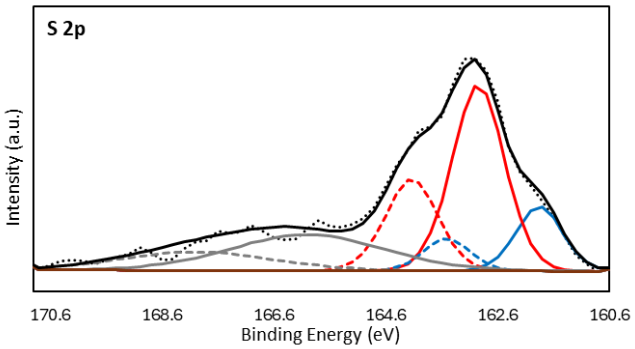


Figure S14. XPS profiles for the S 2p region for (PC-SH) Ru NPs_br

Table S12. XPS peak positions and full-width at half-maximum (FWHM) values (Ru $3p_{3/2}$)

Sample		Binding Energy (eV)	FWHM	Ratio (%)
(PC-SH) Ru NPs Before reaction	Ru^0	462.0	2.7	82.7
	Ru^{4+} (RuO_2)	463.3	3.8	17.3
(PC-SH) Ru NPs After reaction	Ru^0	462.0	2.7	65.6
	Ru^{4+} (RuO_2)	463.3	3.8	34.4

Surface analysis of the (PC-SH) Ru NPs using XPS at Ru 3p region before and after the reaction revealed the presence of peaks originating from the zero-valent state (462.0 eV) and the tetravalent oxide state (RuO_2, 463.3 eV) on the ruthenium surface in both cases.

16. Results of X-ray absorption near-edge structure (XANES) analysis

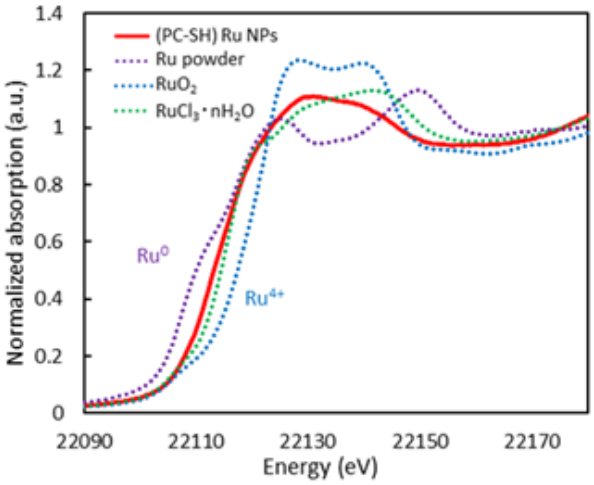
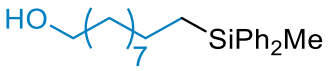


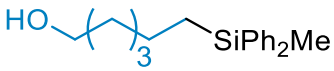
Figure S15. Ru K-edge XANES spectra of the reference Ru compounds and (PC-SH) Ru NPs

17. Characterization data



3a：The desired product was purified by Kugelrohr distillation (155 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (7:3) as the eluent, and further purified by Kugelrohr distillation (180 °C, 0.3 mmHg, 1 h). The desired product was obtained as a colorless oil in 39% yield (138 mg).

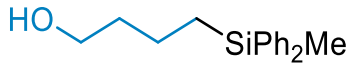
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.54-7.53 (m, 4H), 7.37-7.35 (m, 6H), 3.64 (t, 2H, J = 6.6 Hz), 1.60-1.54 (m, 2H), 1.32-1.28 (m, 15H, overlapping signals), 1.09-1.06 (m, 2H), 0.56 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 137.51 (C), 134.42 (CH), 129.00 (CH), 127.73 (CH), 63.04 (CH_2), 33.60 (CH_2), 32.76 (CH_2), 29.56 (CH_2), 29.45 (CH_2), 29.37 (CH_2), 29.16 (CH_2), 25.67 (CH_2), 23.76 (CH_2), 14.12 (CH_2), -4.48 (CH_3); IR (neat, cm^{-1}) 731, 1112, 1426, 2853, 2924, 3068, 3362; HRMS (APCI) *m/z* Calcd for $C_{23}H_{34}OSi$ $[M+H]^+$ 393.2011, found 393.1997.



3b：The desired product was purified by Kugelrohr distillation (155 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (2:1) as the eluent. The desired product was obtained as a colorless oil in 45% yield (134 mg).

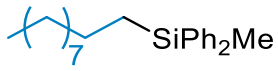
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.53-7.53 (m, 4H), 7.39-7.35 (m, 6H), 3.61 (t, 2H, J = 6.6 Hz), 1.54-1.52 (m, 2H), 1.39-1.36 (m, 6H), 1.34 (br, 1H), 1.10-1.08 (m, 2H), 0.55 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 137.38 (C), 134.40 (CH), 129.03 (CH), 127.74 (CH), 62.97 (CH_2), 33.29 (CH_2), 32.62 (CH_2), 25.25 (CH_2), 23.72 (CH_2), 14.06 (CH_2), -4.50 (CH_3); GC-MS (EI) *m/z* (relative intensity) 283(5) $[M-CH_3]^+$, 197(100), 199(62), 142(17), 221(16), 205(15).

The spectroscopic data correspond to those reported in the literature.[1]



3c：The desired product was purified by Kugelrohr distillation (140 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (17:3) as the eluent. The desired product was obtained as a colorless oil in 23% yield (62 mg).

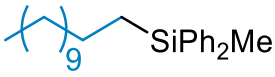
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.54-7.52 (m, 4H), 7.38-7.37 (m, 6H), 3.62 (t, 2H, J = 6.4 Hz), 1.64-1.60 (m, 2H), 1.50-1.48 (m, 2H), 1.28 (br, 1H), 1.11-1.06 (m, 2H), 0.57 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 137.16 (C), 134.40 (CH), 129.11 (CH), 127.79 (CH), 62.52 (CH_2), 36.51 (CH_2), 20.05 (CH_2), 14.00 (CH_2), -4.52 (CH_3); IR (neat, cm^{-1}) 673, 733, 1111, 1427, 2868, 2929, 3048, 3356; HRMS (APCI) *m/z* Calcd for $C_{17}H_{22}OSi$ $[M+H]^+$ 293.1332, found 293.1339.



3d：The desired product was purified by Kugelrohr distillation (140 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane as the eluent. The desired product was obtained as a colorless oil in 78% yield (264 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.56-7.51 (m, 4H), 7.38-7.35 (m, 6H), 1.42-1.26 (m, 16H), 1.11-1.07 (m, 2H), 0.90 (t, 3H, J = 6.9 Hz), 0.56 (s, 3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 137.56 (C), 134.44 (CH), 129.01 (CH), 127.74 (CH), 33.64 (CH_2), 31.90 (CH_2), 29.63 (CH_2), 29.57 (CH_2), 29.32 (CH_2), 29.22 (CH_2), 23.79 (CH_2), 22.67 (CH_2), 14.15 (CH_2), 14.11 (CH_3), -4.46 (CH_3); GC-MS (EI) *m/z* (relative intensity) 323(1) $[M-CH_3]^+$, 197(100), 198(19), 260(12), 182(10), 105(5).

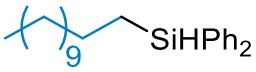
The spectroscopic data correspond to those reported in the literature.[1]



3e：The desired product was purified by Kugelrohr distillation (155 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (9:1) as the eluent. The desired product was obtained as a colorless oil in 72% yield (264 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.56-7.52 (m, 4H), 7.41-7.34 (m, 6H), 1.38-1.31 (m, 20H), 1.09 (t, 2H, J = 8.0 Hz), 0.91 (t, 3H, J = 6.9 Hz), 0.57 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 137.57 (C), 134.45 (CH), 129.01 (CH), 127.75 (CH), 33.64 (CH_2), 31.92 (CH_2), 29.67 ($2CH_2$), 29.64 (CH_2), 29.57 (CH_2), 29.35 (CH_2), 29.22 (CH_2), 23.79 (CH_2), 22.69 (CH_2), 14.16 (CH_2), 14.11 (CH_3), -4.45 (CH_3); GC-MS (EI) *m/z* (relative intensity) 351(1) $[M\text{-}CH_3]^+$ 197(100), 198(19), 183(8), 288(6), 105(5).

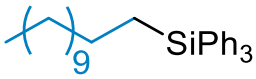
The spectroscopic data correspond to those reported in the literature.[1]



3f：The desired product was purified by Kugelrohr distillation (155 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane as the eluent. The desired product was obtained as a colorless oil in 58% yield (205 mg).

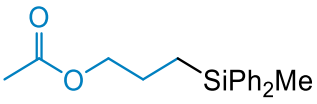
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.58-7.57 (m, 4H), 7.41-7.35 (m, 6H), 4.87 (t, 1H, J = 3.7 Hz), 1.50-1.14 (m, 22H), 0.90 (t, 3H, J = 6.9 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 135.12 (CH), 134.73 (C), 129.43 (CH), 127.92 (CH), 33.17 (CH_2), 31.92 (CH_2), 29.66 ($2CH_2$), 29.53 (CH_2), 29.35 (CH_2), 29.21 (CH_2), 24.39 (CH_2), 22.69 (CH_2), 14.11 (CH_3), 12.14 (CH_2); GC-MS (EI) *m/z* (relative intensity) 351(0.2) $[M\text{-}H]^+$ 183(100), 175(36), 196(25), 105(25), 180(18).

The spectroscopic data correspond to those reported in the literature.[1]



3g：The desired product was purified by Kugelrohr distillation (155 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (19:1) as the eluent. The desired product was obtained as a colorless oil in 67% yield (287 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.57-7.54 (m, 6H), 7.42-7.36 (m, 9H), 1.52-1.47 (m, 2H), 1.43-1.26 (m, 20H), 0.91 (t, 3H, J = 6.9 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 135.63 (CH), 135.43 (C), 129.28 (CH), 127.79 (CH), 33.79 (CH_2), 31.91 (CH_2), 29.66 ($2CH_2$), 29.63 (CH_2), 29.57 (CH_2), 29.34 (CH_2), 29.14 (CH_2), 23.90 (CH_2), 22.68 (CH_2), 14.11 (CH_3), 13.25 (CH_2); IR (neat, cm-1) 735, 1001, 1109, 1463, 1590, 2845, 2955, 3061; HRMS (APCI) *m/z* Calcd for $C_{30}H_{40}OSi$ $[M+H]^+$ 428.2894, found 428.2882.



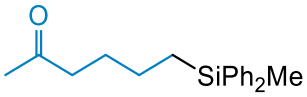
3h：The desired product was purified by Kugelrohr distillation (155 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (9:1) as the eluent. The desired product was obtained as a colorless oil in 37% yield (110 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.54-7.52 (m, 4H), 7.38-7.37 (m, 6H), 4.05 (t, 2H, J = 5.8 Hz), 2.04-2.04 (m, 3H), 1.72-1.70 (m, 2H), 1.12-1.07 (m, 2H), 0.58 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 171.11 (C), 136.63 (C), 134.39 (CH), 129.26 (CH), 127.87 (CH), 66.84 (CH_2), 23.15 (CH_2), 20.96 (CH_3), 10.19 (CH_2), -4.57 (CH_3); IR (neat, cm-1) 666, 734, 1111, 1237, 1427, 1739, 3069; HRMS (APCI) *m/z* Calcd for $C_{18}H_{22}O_2Si$ $[M+H]^+$ 321.1281, found 321.1289.

3i：The desired product was purified by Kugelrohr distillation (155 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane as the eluent. The desired product was obtained as a colorless oil in 69% yield (225 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.54-7.53 (m, 4H), 7.40-7.36 (m, 6H), 4.04 (t, 2H, J = 6.8 Hz), 2.05 (s, 3H), 1.64-1.61 (m, 2H), 1.44-1.42 (m, 4H), 1.12-1.10 (m, 2H), 0.58 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 171.15 (C), 137.21 (C), 134.39 (CH), 129.08 (CH), 127.77 (CH), 64.54 (CH_2), 29.79 (CH_2), 28.17 (CH_2), 23.51 (CH_2), 20.96 (CH_3), 14.12 (CH_2), -4.51 (CH_3); GC-MS (EI) *m/z* (relative intensity) 311 (3) $[M\text{-}CH_3]^+$, 197 (100), 249 (42), 179 (42), 241 (23), 198 (19).

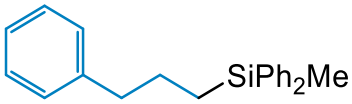
The spectroscopic data correspond to those reported in the literature.[1]



3j：The desired product was purified by Kugelrohr distillation (155 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (20:1) as the eluent. The desired product was obtained as a colorless oil in 43% yield (127 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.53-7.51 (m, 4H), 7.38-7.36 (m, 6H), 2.41 (t, 2H, J = 7.5 Hz), 2.11 (s, 3H), 1.65-1.61 (m, 2H), 1.41-1.39 (m, 2H), 1.09 (t, 2H, J = 7.6 Hz), 0.56 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 209.11 (C), 137.09 (C), 134.37 (CH), 129.11 (CH), 127.78 (CH), 43.37 (CH_2), 29.79 (CH_3), 27.60 (CH_2), 23.47 (CH_2), 14.05 (CH_2), -4.54 (CH_3); GC-MS (EI) *m/z* (relative intensity) 281 (2) $[M\text{-}CH_3]^+$, 197 (100), 219 (60), 137 (31), 199 (26), 105 (13).

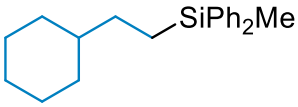
The spectroscopic data correspond to those reported in the literature.[1]



3k：The desired product was purified by Kugelrohr distillation (155 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (9:1) as the eluent. The desired product was obtained as a colorless oil in 37% yield (117 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.54-7.52 (m, 4H), 7.43-7.35 (m, 6H), 7.32-7.28 (m, 2H), 7.23-7.15 (m, 3H), 2.68 (t, 2H, J = 7.5 Hz), 1.79-1.72 (m, 2H), 1.18-1.13 (m, 2H), 0.58 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 142.30 (C), 137.18 (C), 134.43 (CH), 129.09 (CH), 128.50 (CH), 128.20 (CH), 127.78 (CH), 125.66 (CH), 39.70 (CH_2), 25.79 (CH_2), 13.89 (CH_2), -4.46 (CH_3); GC-MS (EI) *m/z* (relative intensity) 301 (2) $[M\text{-}CH_3]^+$, 197 (100), 238 (47), 209 (19), 104 (11), 239 (11).

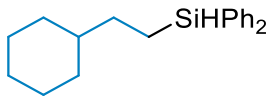
The spectroscopic data correspond to those reported in the literature.[1]



3l：The desired product was purified by Kugelrohr distillation (140 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (17:3) as the eluent. The desired product was obtained as a colorless oil in 26% yield (80 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.54-7.53 (m, 4H), 7.38-7.37 (m, 6H), 1.71-1.61 (m, 5H), 1.30-1.07 (m, 8H), 0.88-0.86 (m, 2H), 0.55 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 137.53 (C), 134.43 (CH), 129.00 (CH), 127.74 (CH), 40.72 (CH), 32.92 (CH_2), 31.18 (CH_2), 26.75 (CH_2), 26.41 (CH_2), 11.05 (CH_2), -4.57 (CH_3); GC-MS (EI) *m/z* (relative intensity) 293 (1) $[M\text{-}CH_3]^+$, 197 (100), 230 (29), 198 (19), 183 (11), 202 (8).

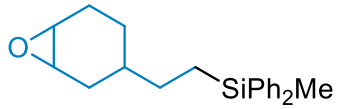
The spectroscopic data correspond to those reported in the literature.[1]



3m：The desired product was purified by Kugelrohr distillation (140 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (17:3) as the eluent. The desired product was obtained as a colorless oil in 52% yield (153 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.58-7.57 (m, 4H), 7.41-7.36 (m, 6H), 4.85 (t, 1H, J = 3.7 Hz), 1.74-1.67 (m, 5H), 1.37-1.36 (m, 2H), 1.29-1.11 (m, 6H), 0.90-0.87 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 135.11 (CH), 134.72 (C), 129.43 (CH), 127.92 (CH), 40.46 (CH), 32.89 (CH_2), 31.82 (CH_2), 26.73 (CH_2), 26.38 (CH_2), 9.17 (CH_2); GC-MS (EI) *m/z* (relative intensity) 293 (0.2) $[M-H]^+$, 182 (100), 216 (53), 188 (42), 138 (41), 104 (37).

The spectroscopic data correspond to those reported in the literature.[2]

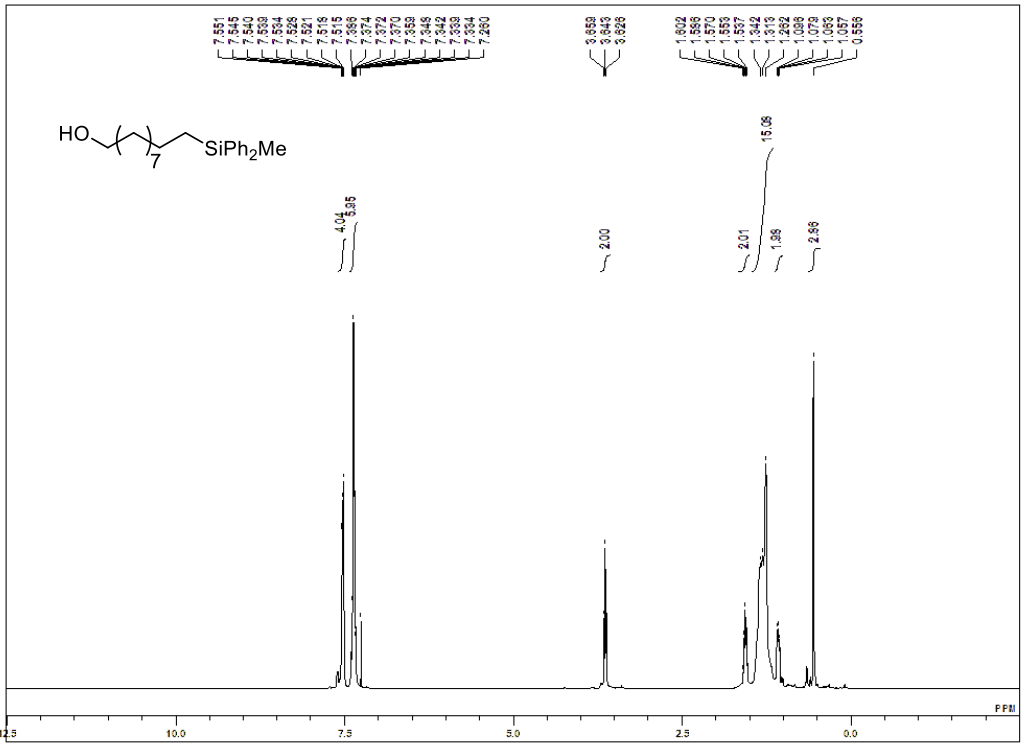


3n：The desired product was purified by Kugelrohr distillation (130 °C, 0.3 mmHg, 1 h), followed by column chromatography on silica gel using hexane/ethyl acetate (10:1) as the eluent. The desired product was obtained as a colorless oil in 47% yield (152 mg).

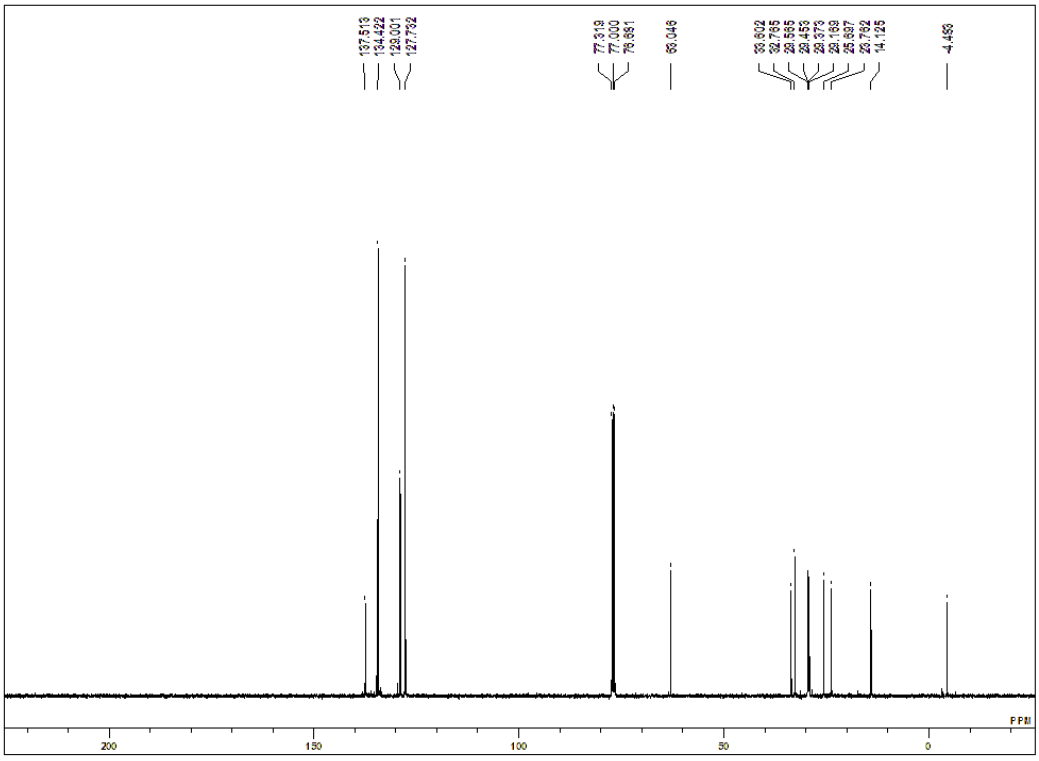
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.52-7.50 (m, 4H), 7.39-7.34 (m, 6H), 3.16-3.13 (m, 2H), 2.18-2.01 (m, 2H, overlapping signals), 1.81-1.71 (m, 1H), 1.53-1.25 (m, 6H), 1.06-1.05 (m, 2H), 0.55 (s, 3H); ^{13}C-NMR (100 MHz, CDCl3) δ: 137.13 (C), 134.37 (CH), 129.09 (CH), 127.78 (CH), 53.25 (CH), 52.71 (CH), 51.97 (CH), 51.87 (CH), 35.45 (CH), 32.51 (CH), 31.49 (CH_2), 30.58 (CH_2), 30.25 (CH_2), 30.05 (CH_2), 26.65 (CH_2), 25.27 (CH_2), 23.88 (CH_2), 23.56 (CH_2), 11.05 (CH_2), 10.89 (CH_2), -4.62 (CH_3), -4.64 (CH_3); IR (neat, cm-1) 701, 734, 881, 1111, 1254, 1428, 2917, 3067; HRMS (APCI) *m/z* Calcd for $C_{21}H_{26}OSi$ $[M+H]^+$ 323.1826, found 323.1822.

18. NMR-Spectra

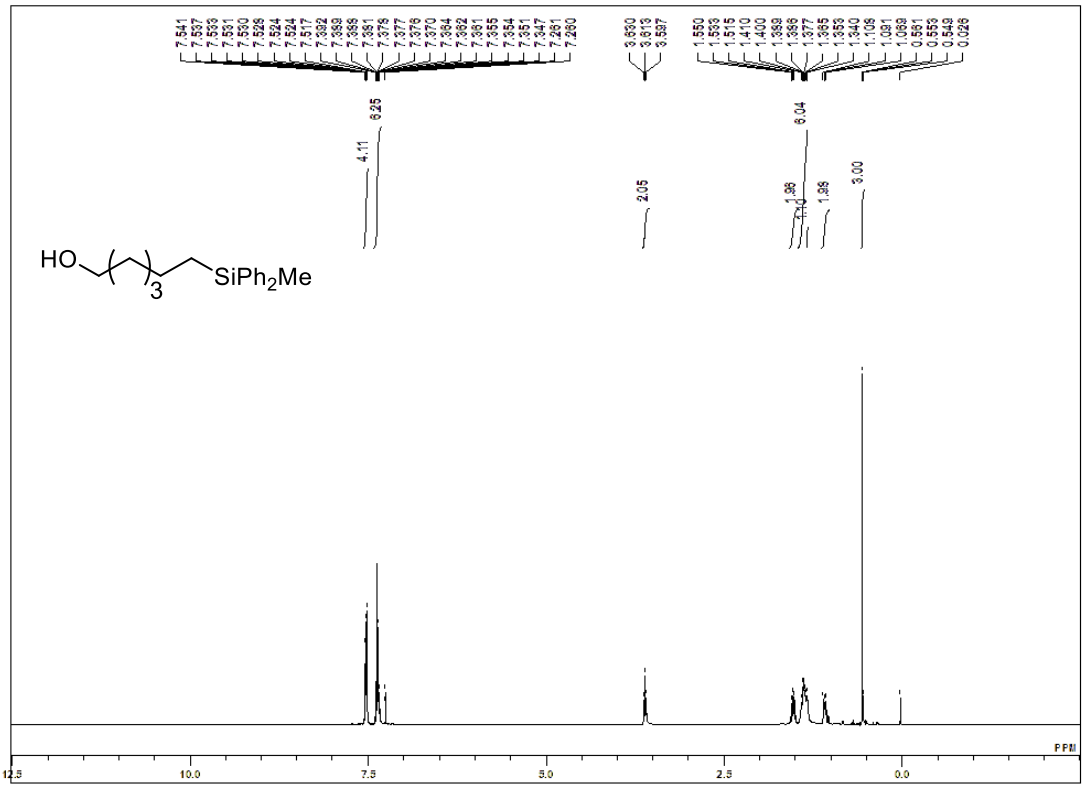
3a ^{1}H-NMR (400 MHz, $CDCl_3$)



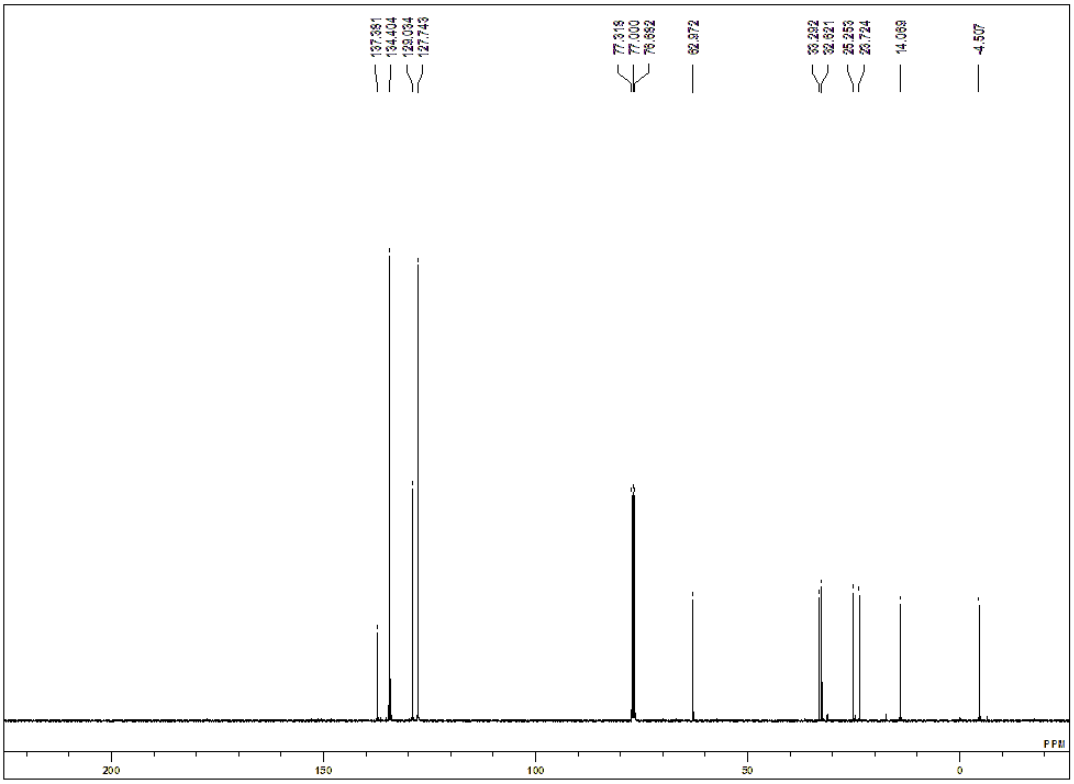
^{13}C-NMR (100 MHz, $CDCl_3$)



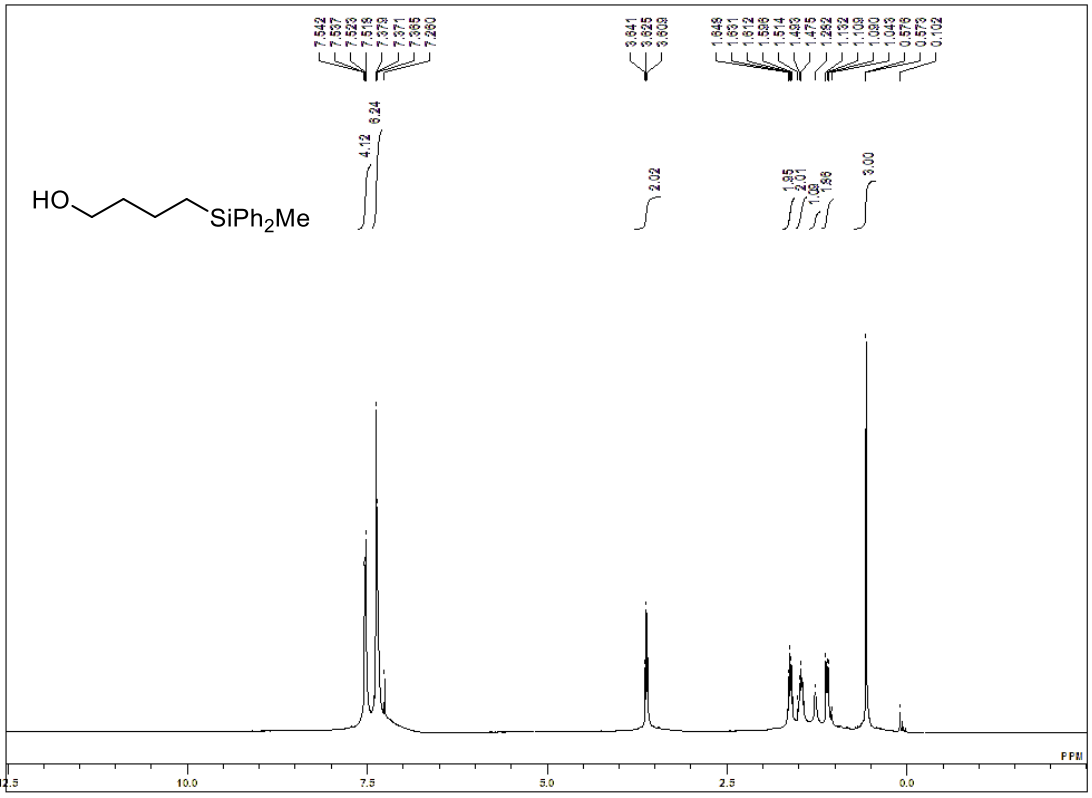
3b ^{1}H-NMR (400 MHz, $CDCl_3$)



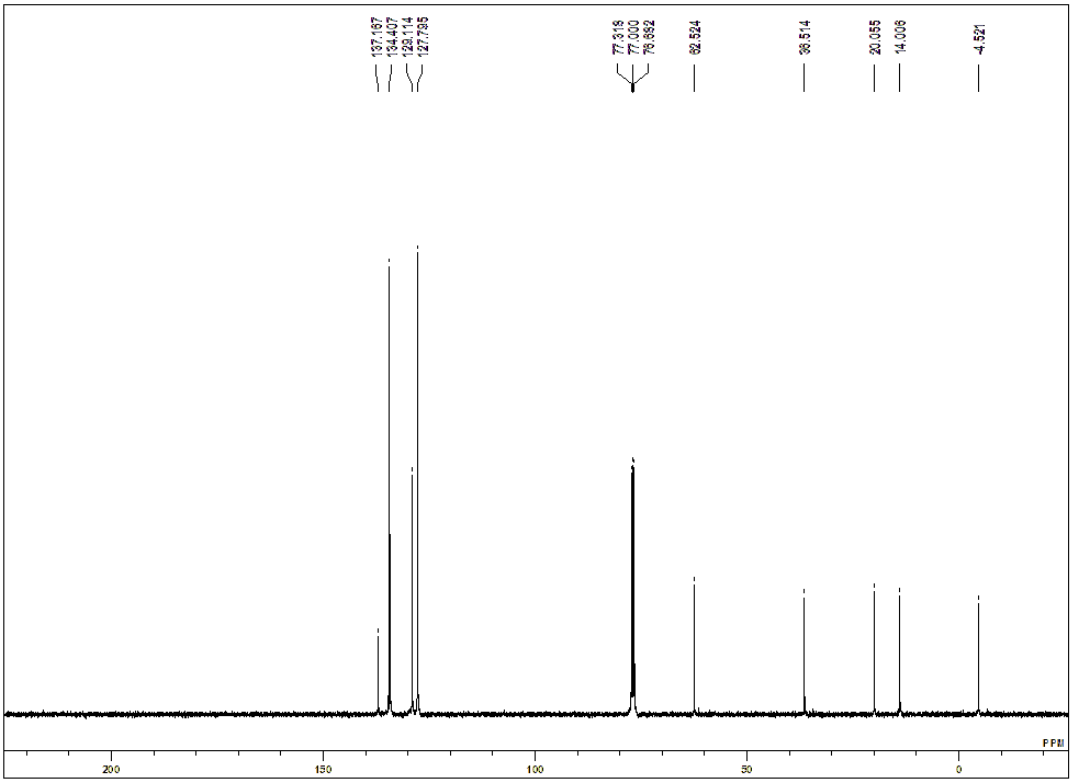
^{13}C-NMR (100 MHz, $CDCl_3$)



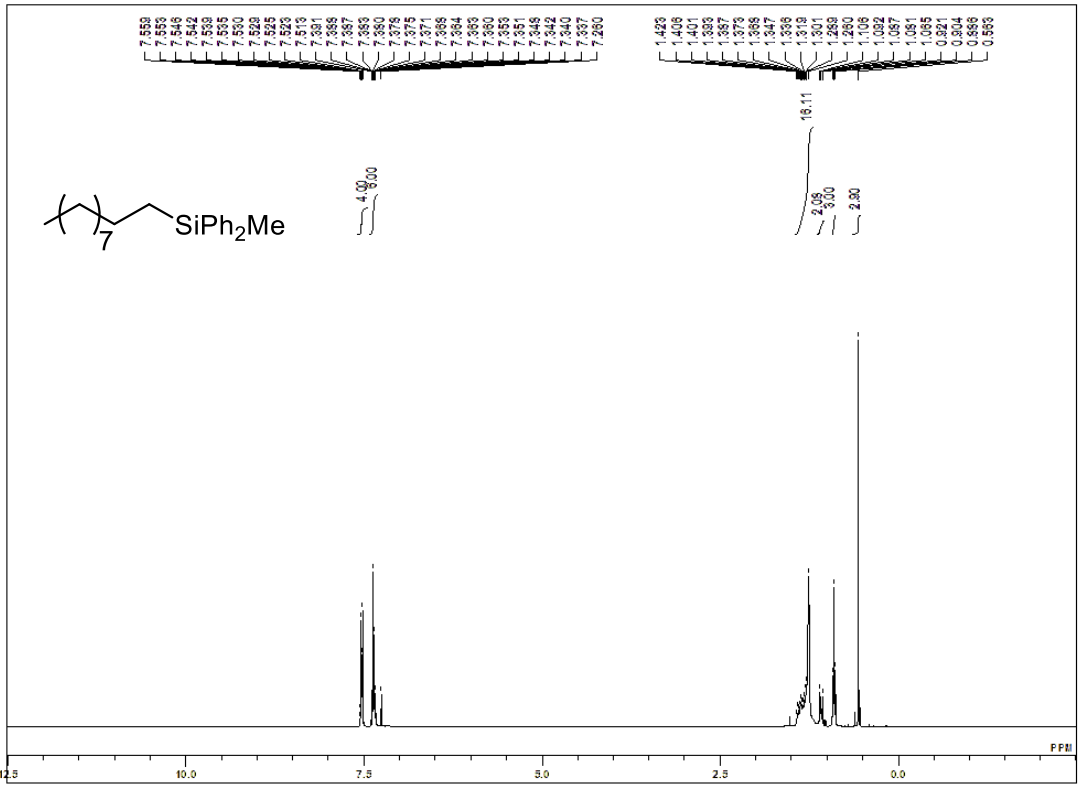
3c ^{1}H-NMR (400 MHz, $CDCl_3$)



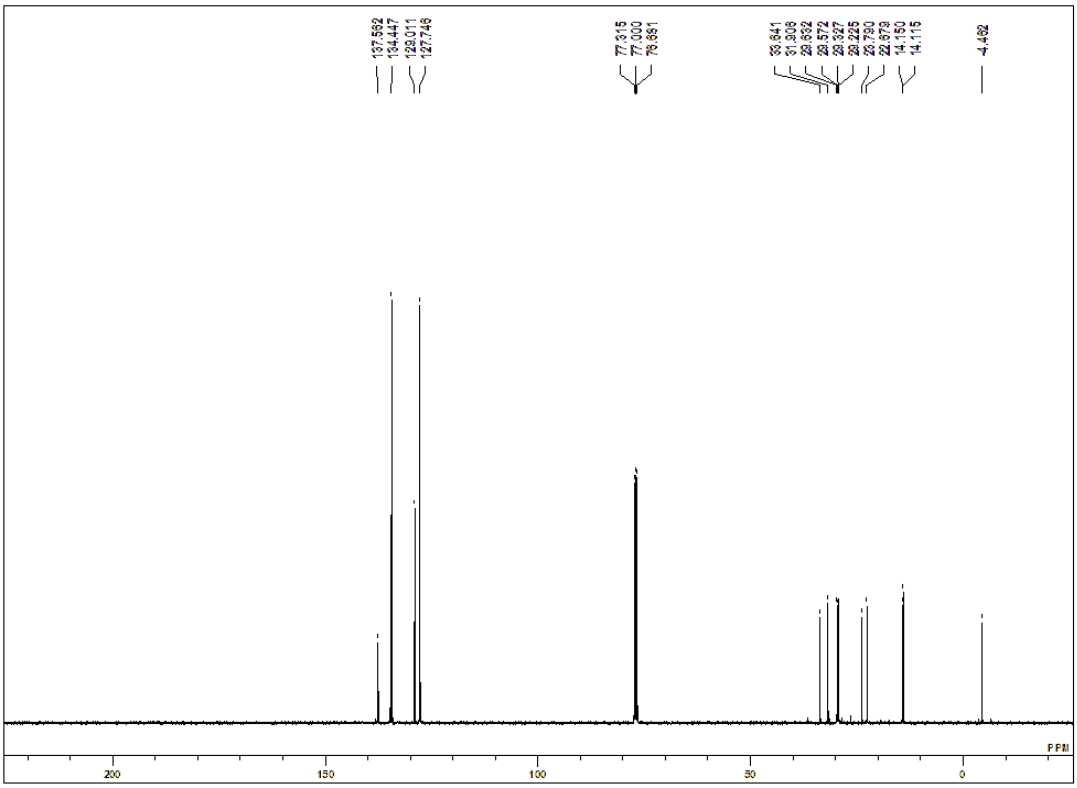
^{13}C-NMR (100 MHz, $CDCl_3$)



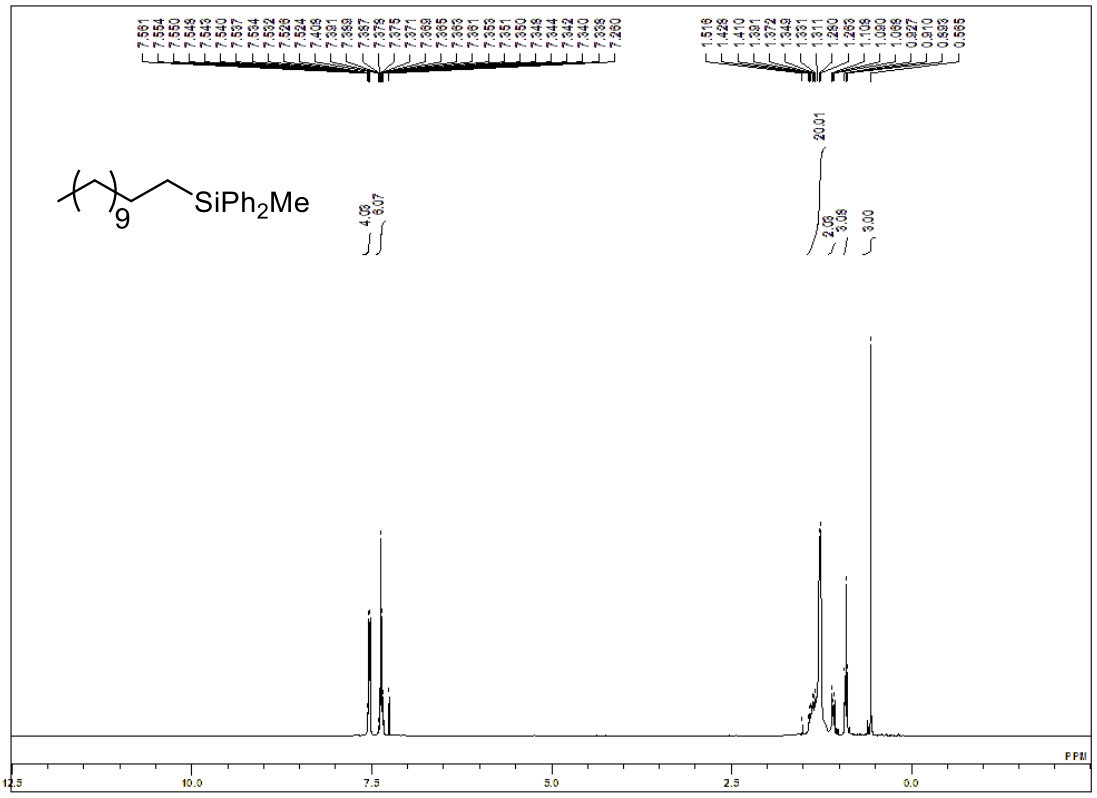
3d ^{1}H-NMR (400 MHz, $CDCl_3$)



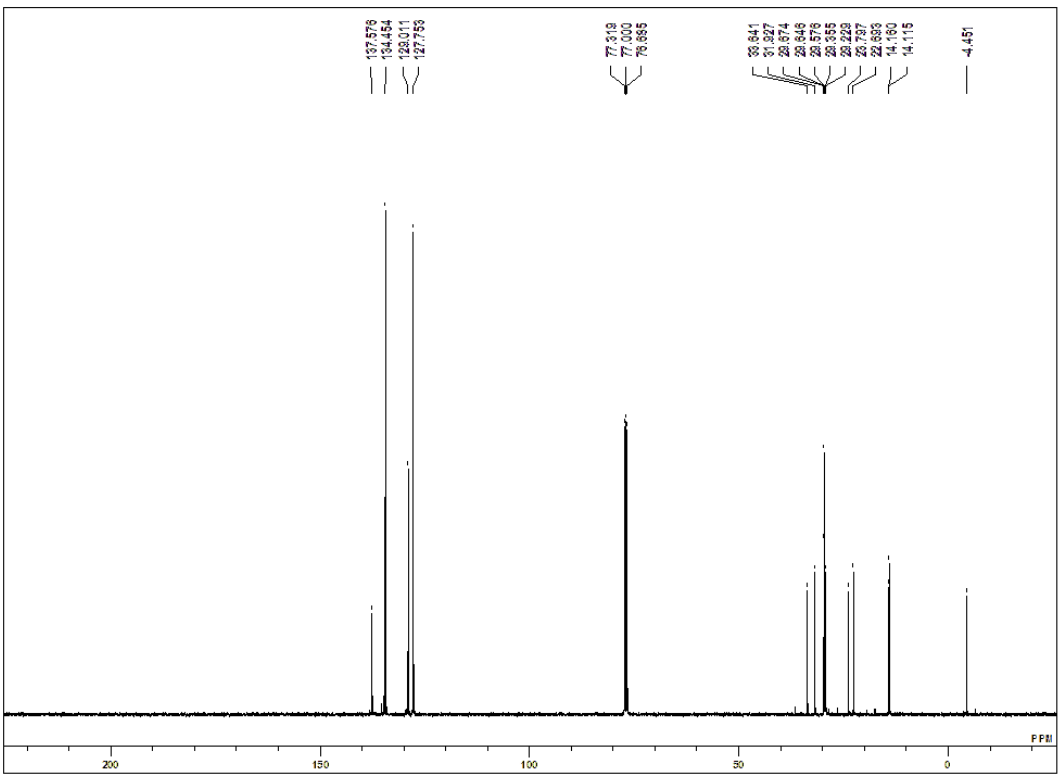
^{13}C-NMR (100 MHz, $CDCl_3$)



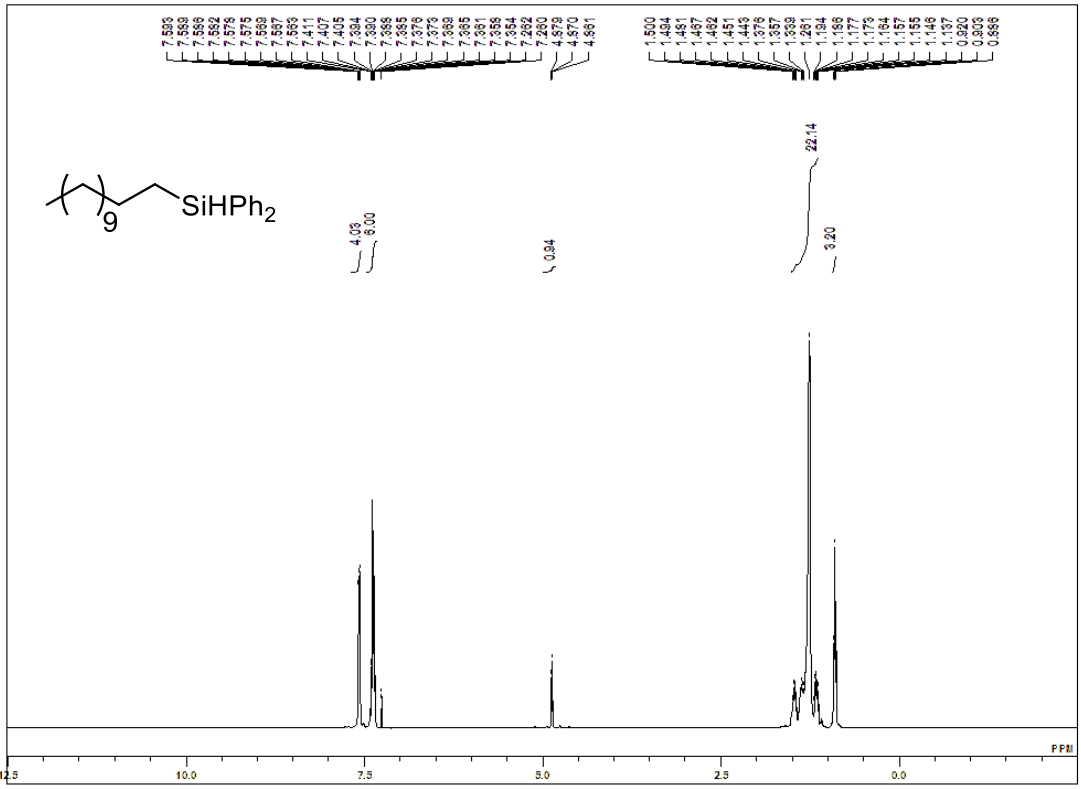
3e ^{1}H-NMR (400 MHz, $CDCl_3$)



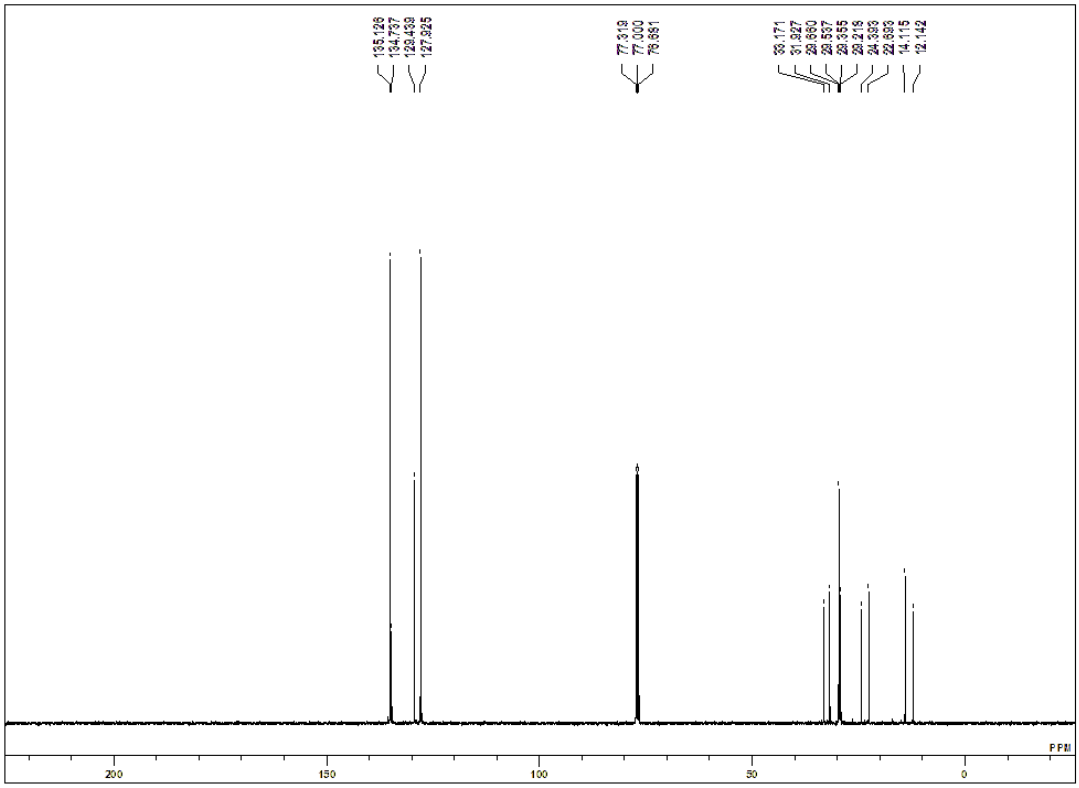
^{13}C-NMR (100 MHz, $CDCl_3$)



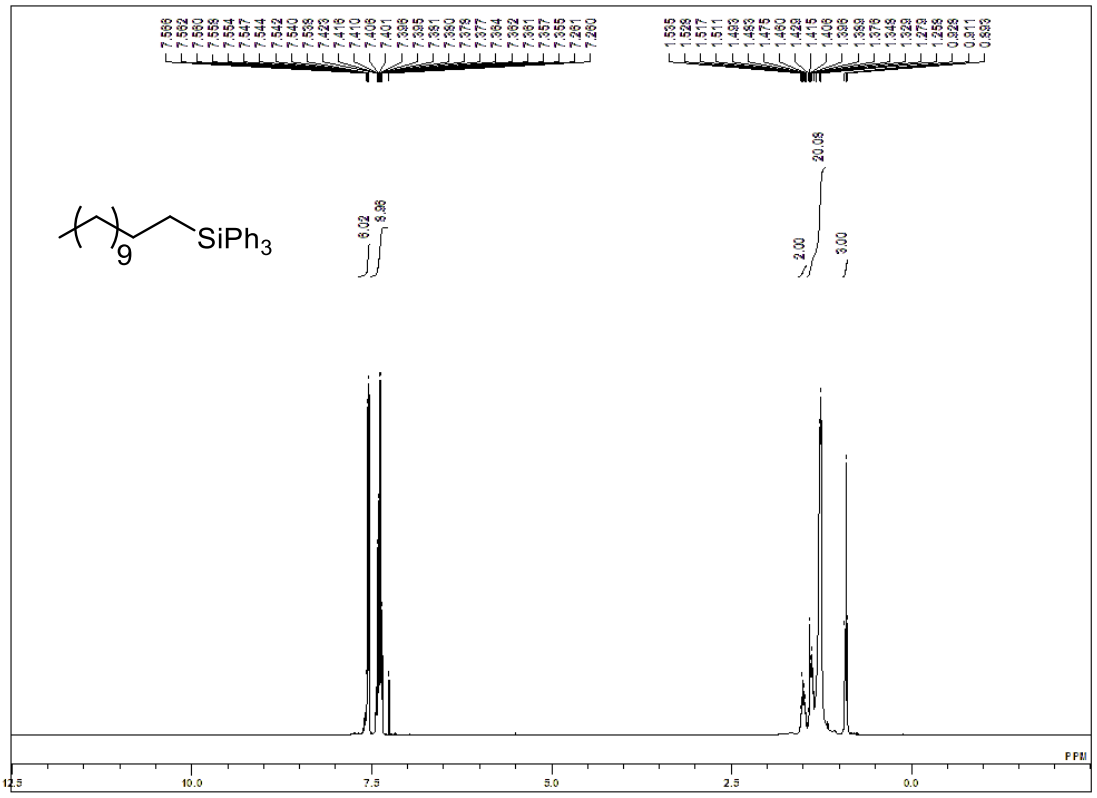
3f ^{1}H-NMR (400 MHz, $CDCl_3$)



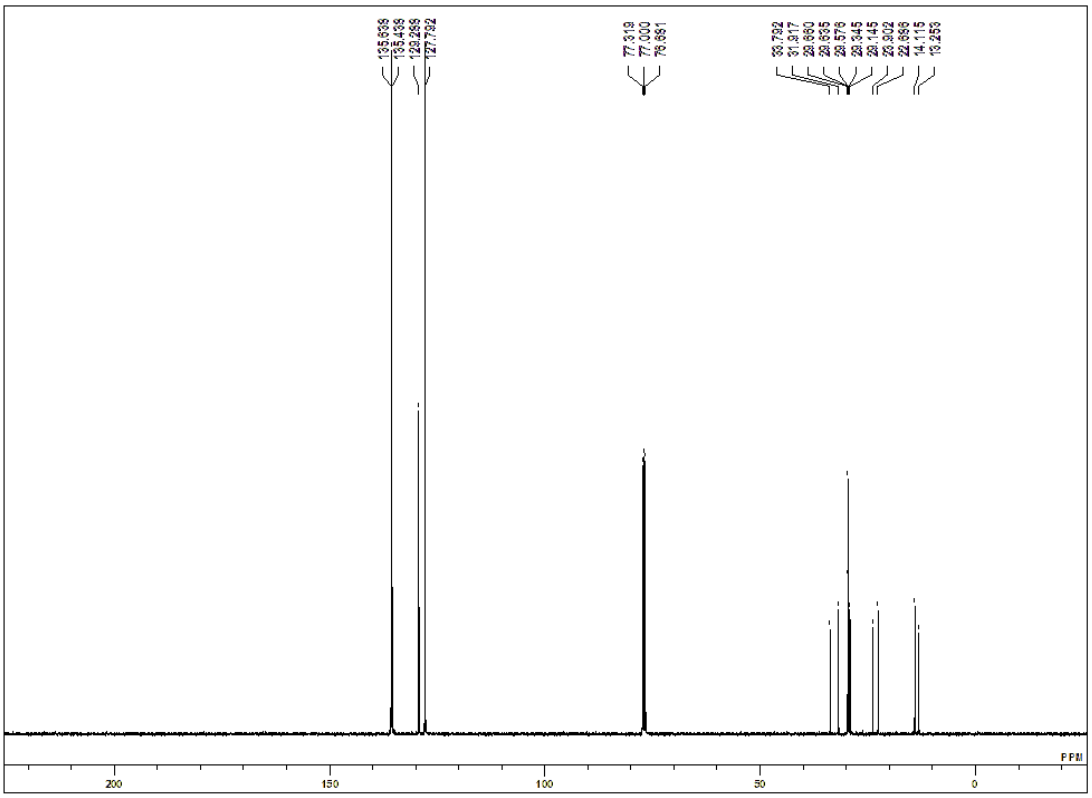
^{13}C-NMR (100 MHz, $CDCl_3$)



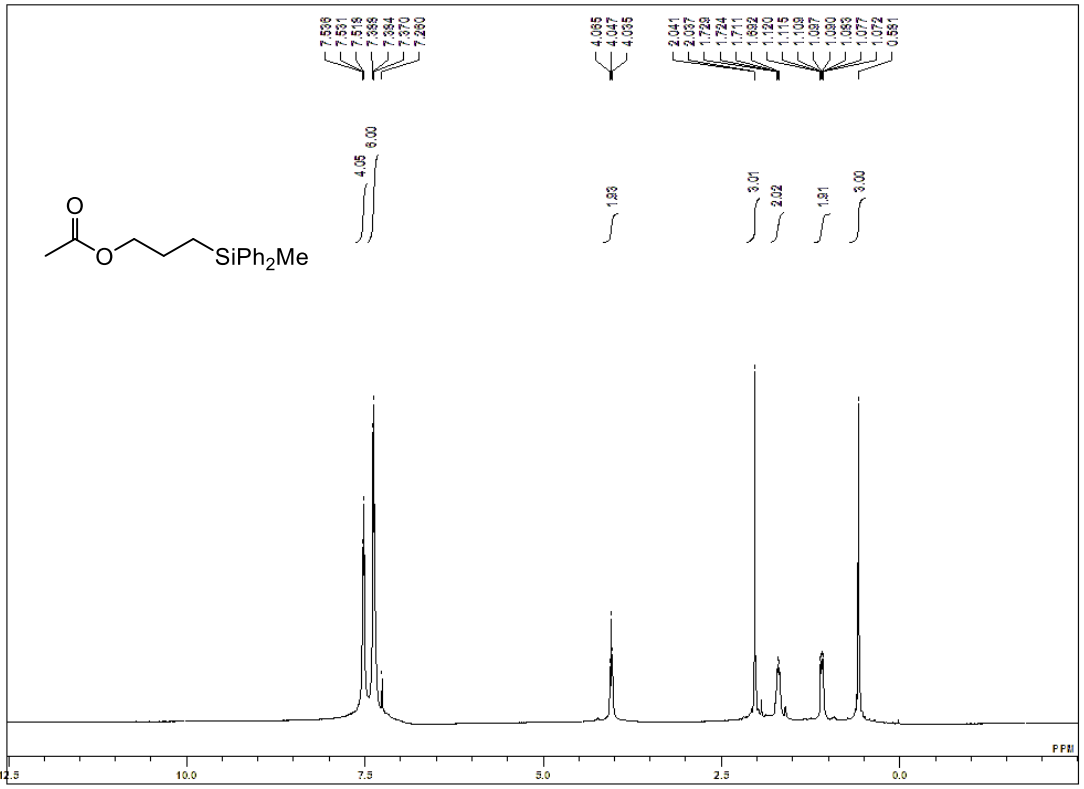
3g ^{1}H-NMR (400 MHz, $CDCl_3$)



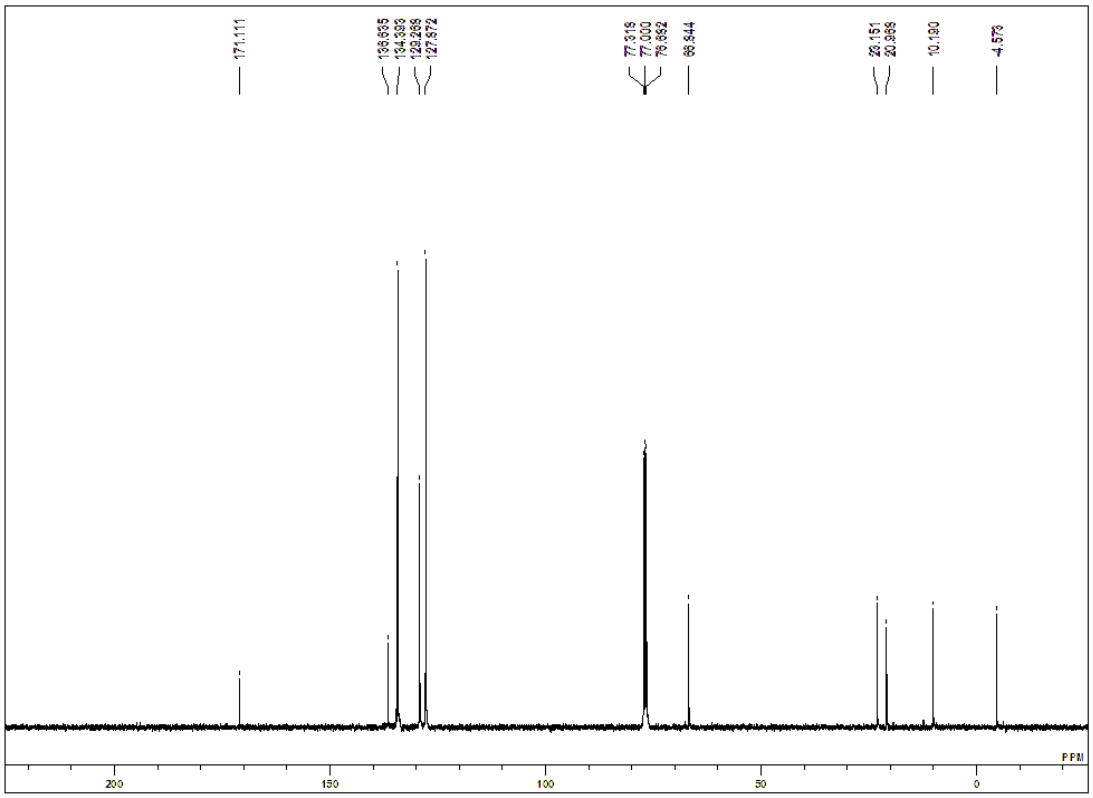
^{13}C-NMR (100 MHz, $CDCl_3$)



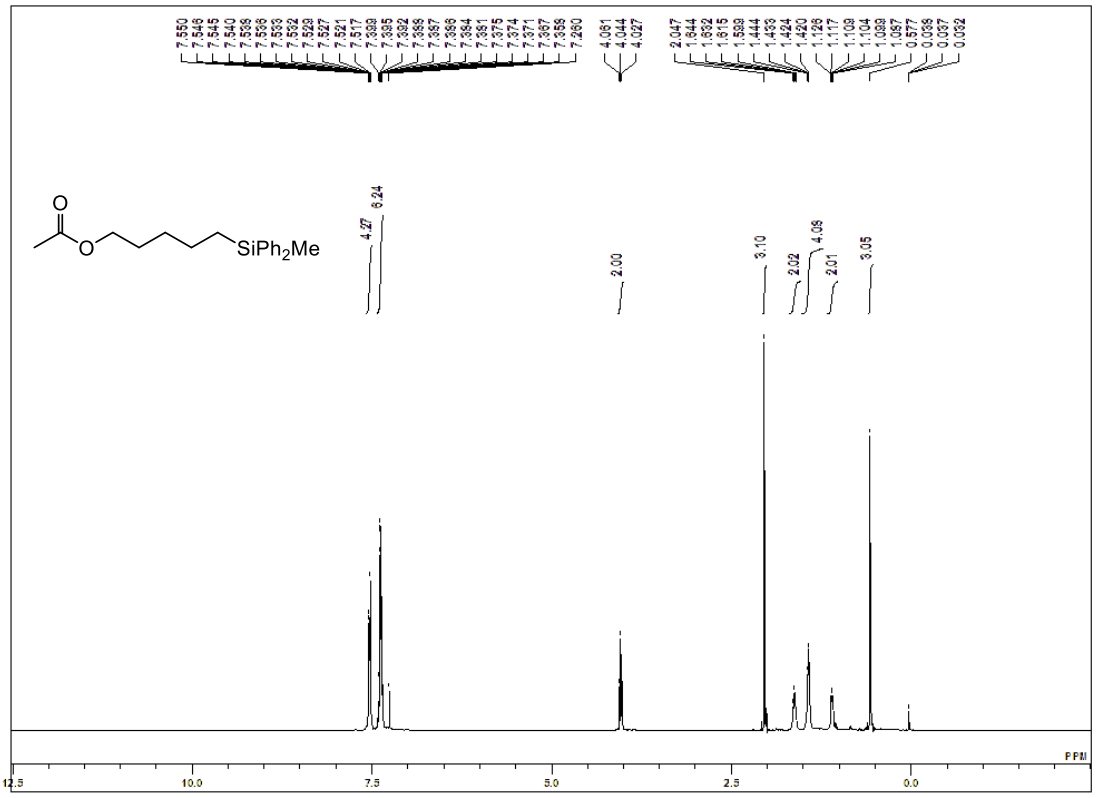
3h ^{1}H-NMR (400 MHz, $CDCl_3$)



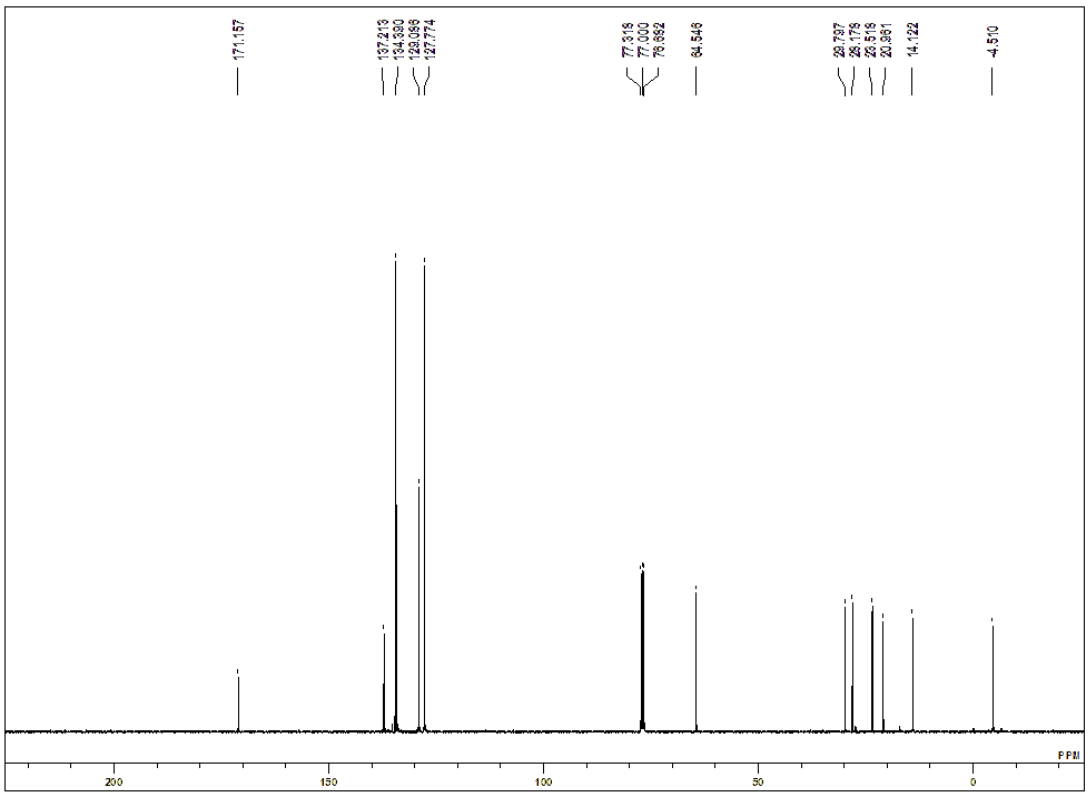
^{13}C-NMR (100 MHz, $CDCl_3$)



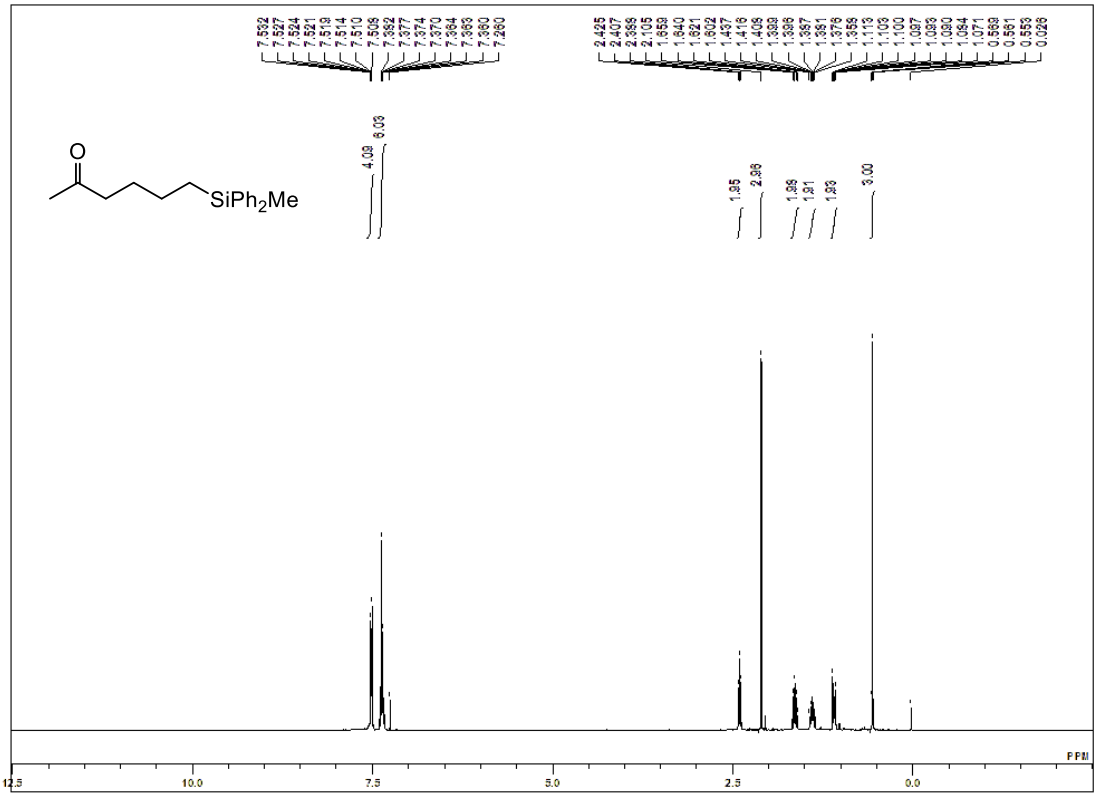
3i ^{1}H-NMR (400 MHz, $CDCl_3$)



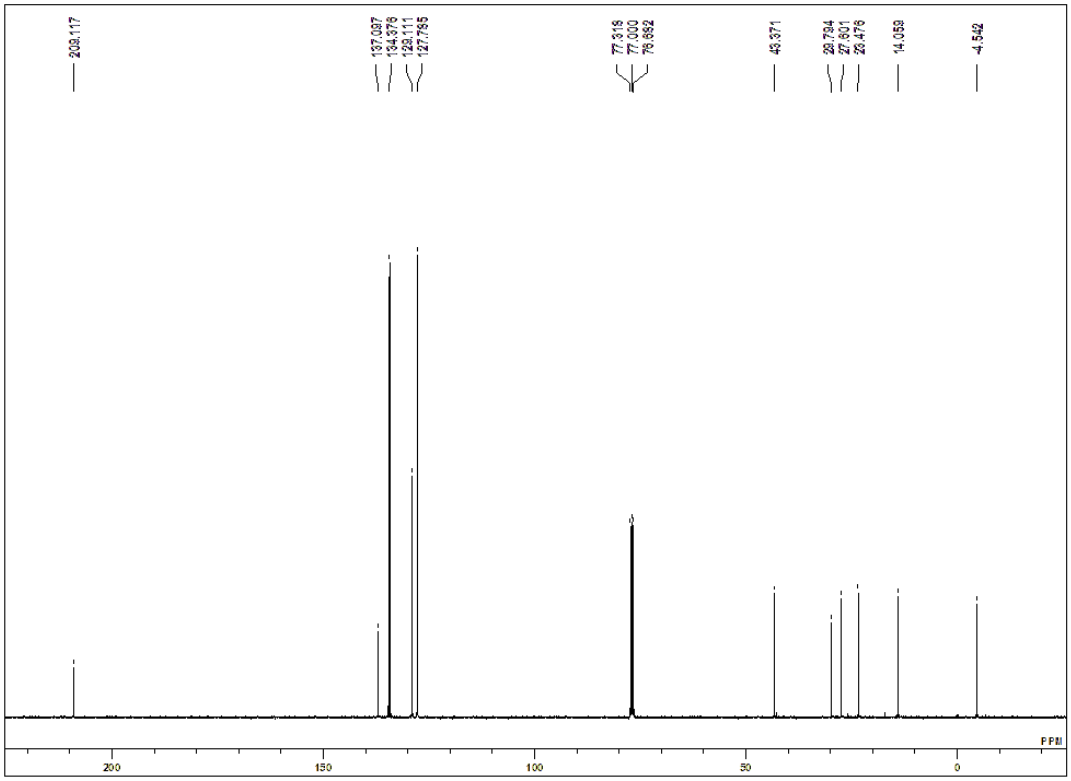
^{13}C-NMR (100 MHz, $CDCl_3$)



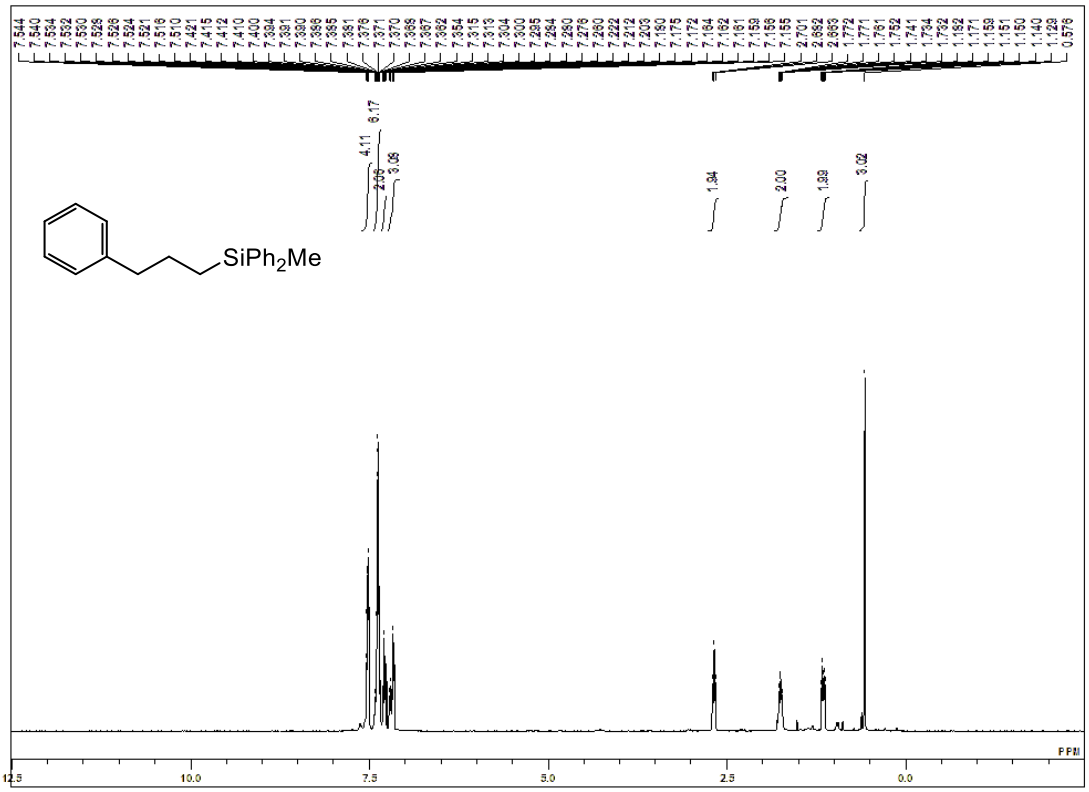
3j ^{1}H-NMR (400 MHz, $CDCl_3$)



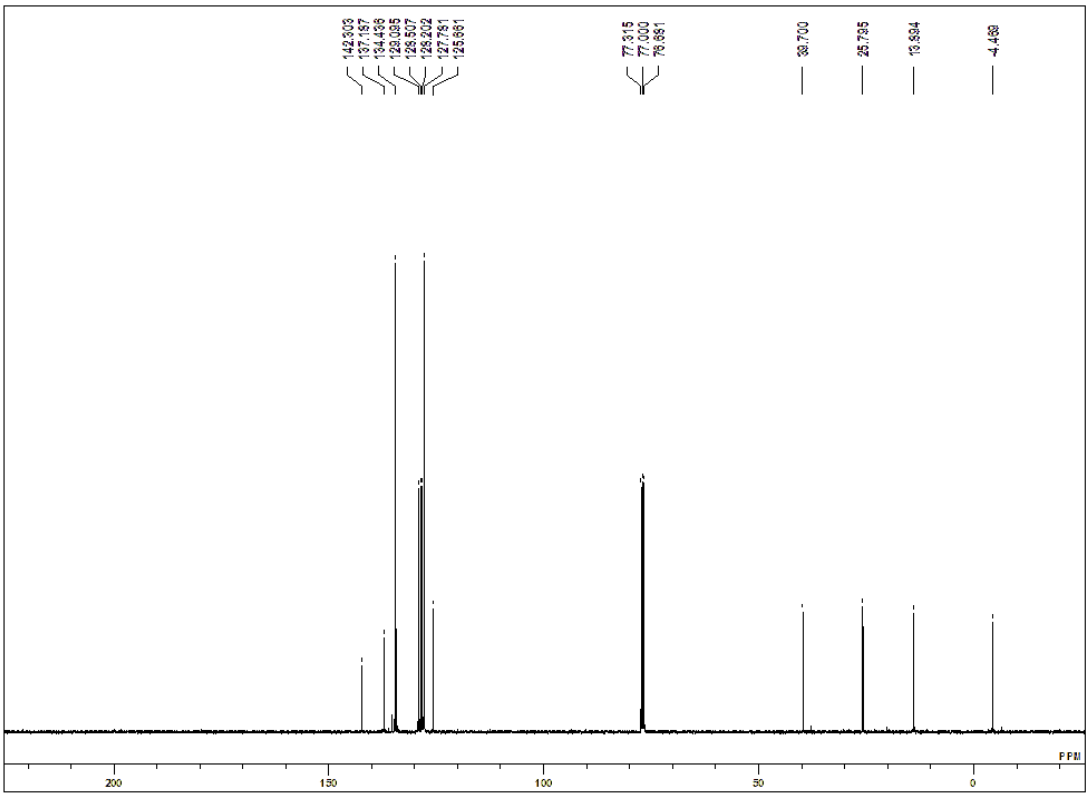
^{13}C-NMR (100 MHz, $CDCl_3$)



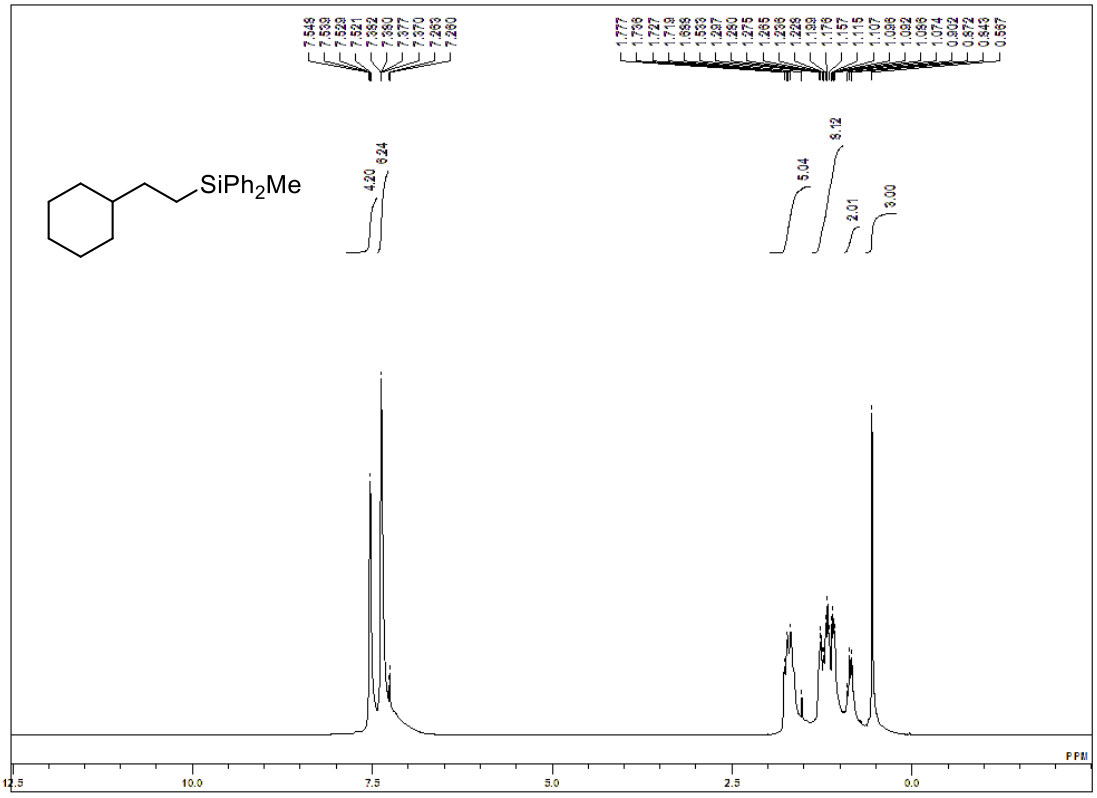
3k ^{1}H-NMR (400 MHz, $CDCl_3$)



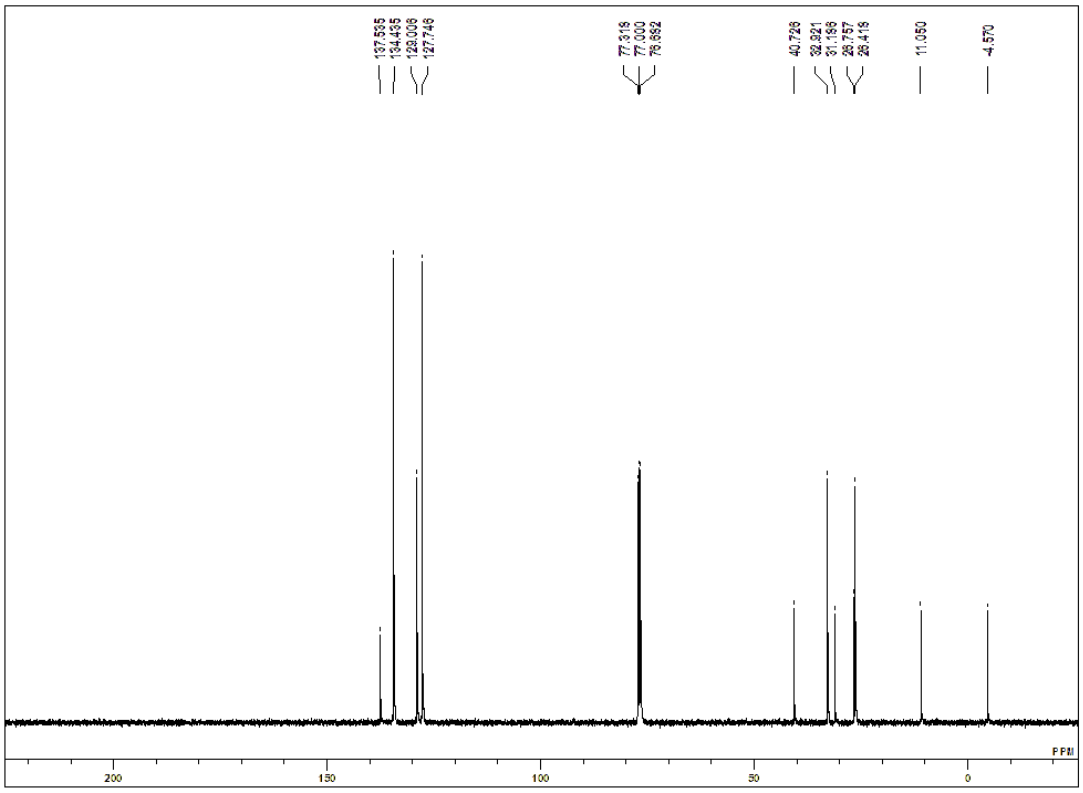
^{13}C-NMR (100 MHz, $CDCl_3$)



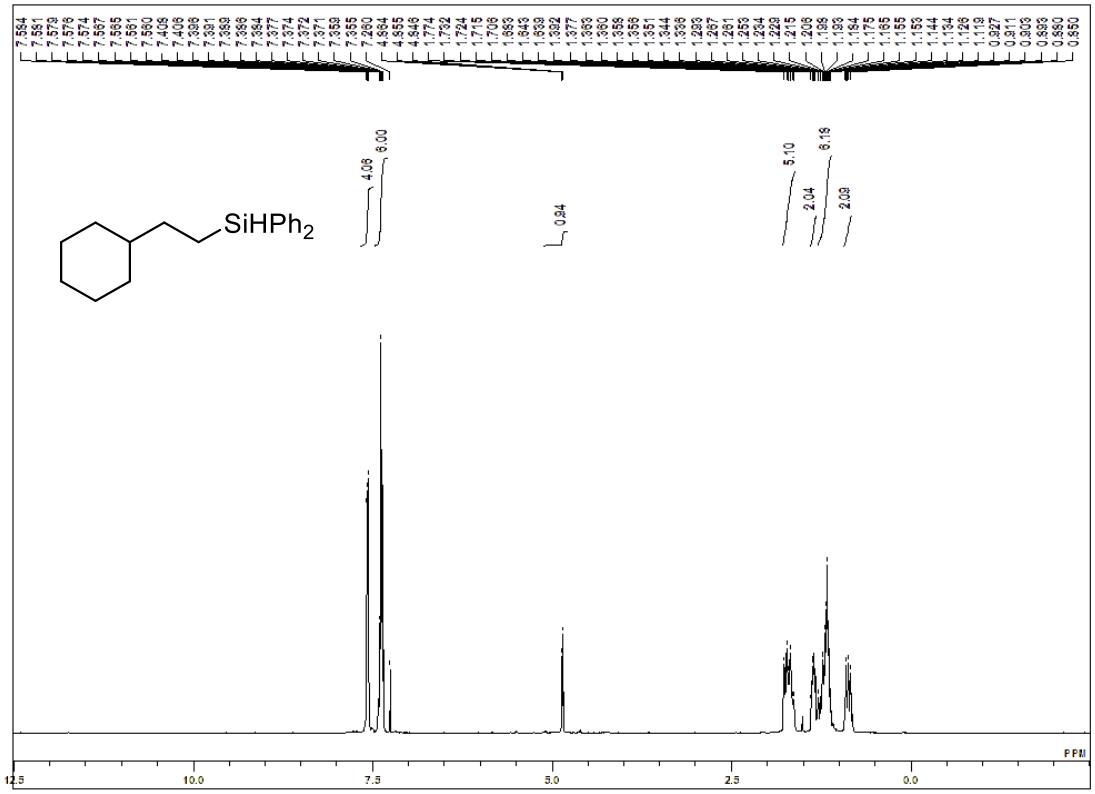
3l ^{1}H-NMR (400 MHz, $CDCl_3$)



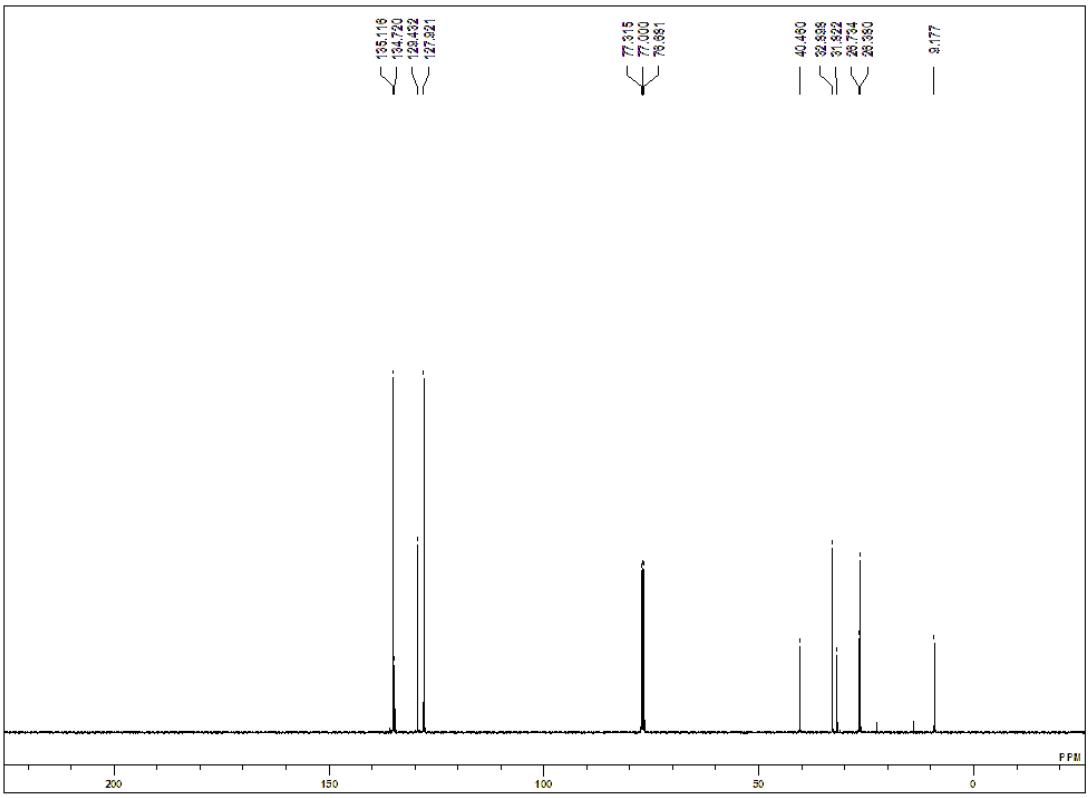
^{13}C-NMR (100 MHz, $CDCl_3$)



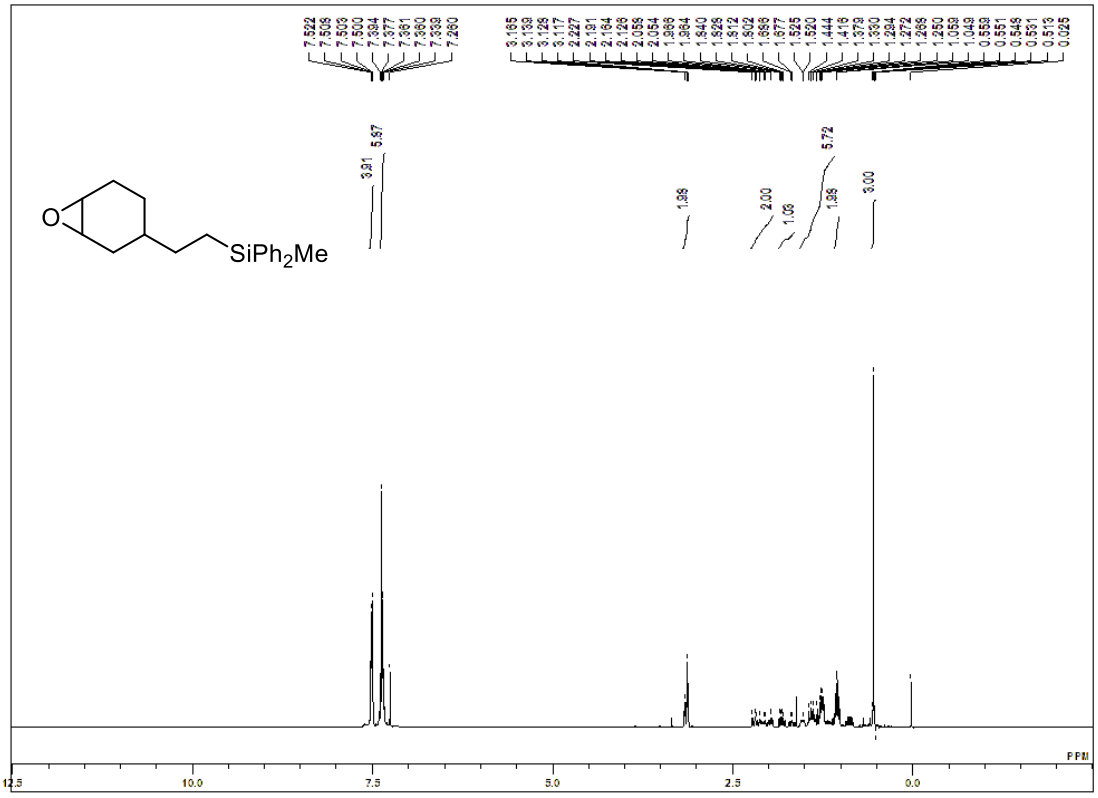
3m ^{1}H-NMR (400 MHz, $CDCl_3$)



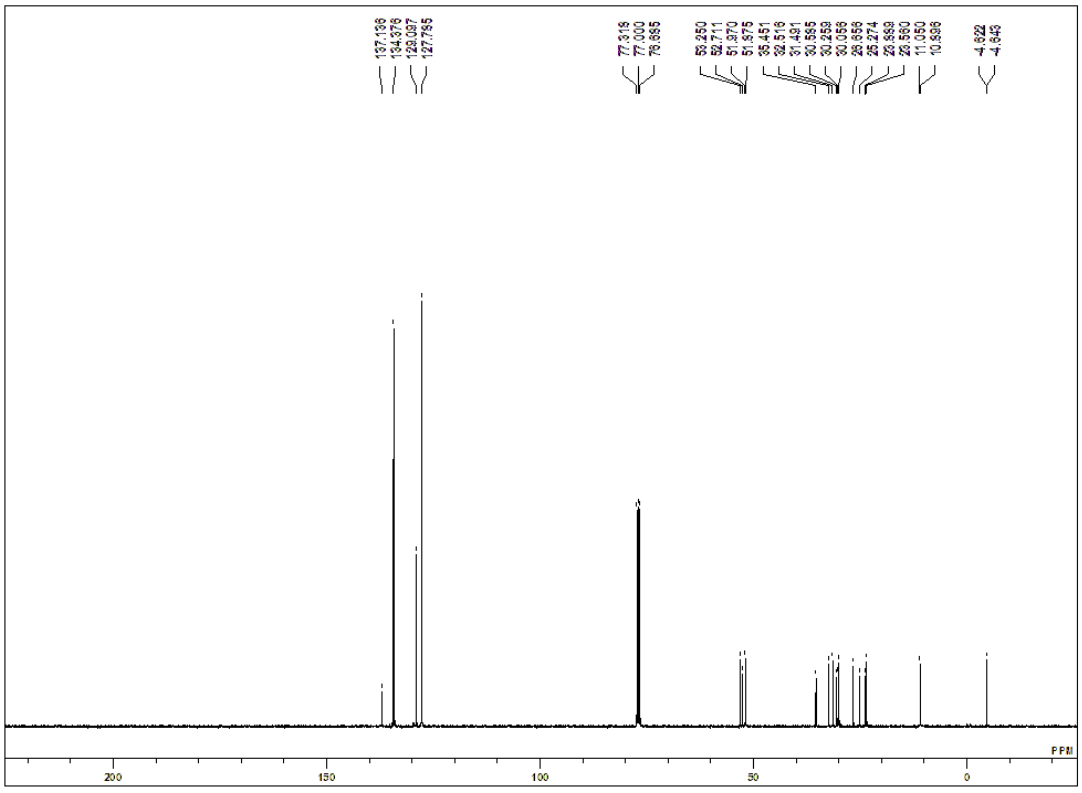
^{13}C-NMR (100 MHz, $CDCl_3$)



3n ^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)



19. References

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