Electronic Supplementary Information

Copper Formate Supported on Sepiolite as Reusable Catalyst for Hydrosilylation of Olefins

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Experimental sections

Materials

1-octene was purchased from Aladdin Chemical Reagent Co., Ltd., 1-dodecene was purchased from Beijing Yunbang Biotechnology Co., Ltd., 1-hexadecene and 1-octadecene were purchased from Shanghai Merrill Chemical Technology Co., Ltd., 1-tetradecene and sepiolite were purchased from Shanghai Maiklin biochemical Technology Co., Ltd. Silanes were purchased from Anneji Chemical Co., Ltd and Aladdin Chemical Pharmaceutical Co., Ltd. The other reagents were purchased from Sinopharmaceutical Group Chemical Reagent Co., Ltd., and the references of $Cu(HCOO)_2$/sepiolite were prepared. All reagents were used without further purification.

Synthesis

Synthesis of $Cu(HCOO)_2$

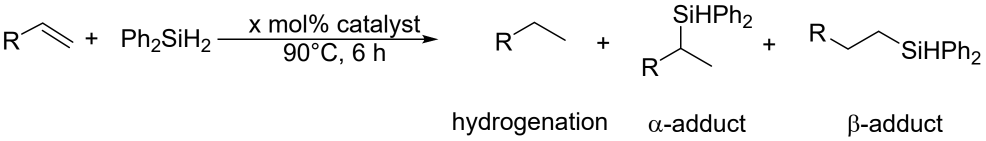
Ground a certain amount of copper sulfate pentahydrate and sodium bicarbonate in a mortar and mix evenly. Under rapid stirring, the mixture was slowly added to the near-boiling distilled water in small amounts for many times. At this time, the heating was stopped, and after the mixture was added, it was heated for nearly boiling minutes. After static clarification, the deionized water was washed to the solution without sulfate. Put the product prepared above into the beaker, added distilled water, heated and stired to about 50 °C, added formic acid drop by drop until the precipitation was completely dissolved, filtered while hot, the filtrate evaporates to about 1/3 of the original volume under the ventilation cabinet, cooled to room temperature, decompression filtration, washing with ethanol, suction filtration, vacuum drying.

Synthesis of $Cu(HCOO)_2$/sepiolite

According to the weight of copper accounting for 1% of the total mass of the catalyst, took a certain amount of sepiolite and $Cu(HCOO)_2$, dissolved the weighed $Cu(HCOO)_2$ in deionized water, poured it into a flask containing sepiolite, stired at room temperature for 6 h, spun steam to remove the solubilizer, and vacuumed 70 °C for 3 h.

Catalytic hydrosilylation

Using the reaction of 1-octene and diphenylsilane as the probe reaction, the main products are the addition products of 1-octene and the hydrosilylation products of olefins and silane (including α-addition products and β-addition products). To conduct a series of experiments.



Dry magnetic agitator, cover the seal, stir the mixture at a certain temperature, separate the solid and liquid by centrifugation, take a few drops of supernatant into the centrifuge tube, add appropriate dichloride to dilute, get the sample, analyze and test it.

The conversion and selectivity of olefins were determined and quantified by GC analysis on Agilent 7890B. The structure of the product was determined by GC-MS analysis on an Agilent 7890B-5977B instrument equipped with HP5MS column (30 mm × 0.25 mm × 0.25 μm). Gas chromatography: trace DSQ GC column, resolution = 50:1, flow rate = 1.33 ml/min constant flow rate, inlet temperature 260 ℃, column temperature = 40 ℃ (hold for 1 minute), then 15℃ min^{-1} rises from 40 ℃ to 160 ℃, then 20 ℃ min^{-1} to 280 ℃ (keep for 9 minutes). ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded on Bruker Advance spectrometer.

Cycle reaction:

The experimental procedure of hydrosilylation reaction is the same as above. After the reaction is finished, the supernatant is removed by centrifugation, and the catalyst containing the reaction is obtained. Olefin and hydrosilane are added to the test tube again, and the reaction is carried out under the condition of substrate dosage at the same temperature and time. The loop experiment was carried out repeatedly according to the above steps.

Characterization sections

Fourier transform infrared spectroscopy (FTIR)

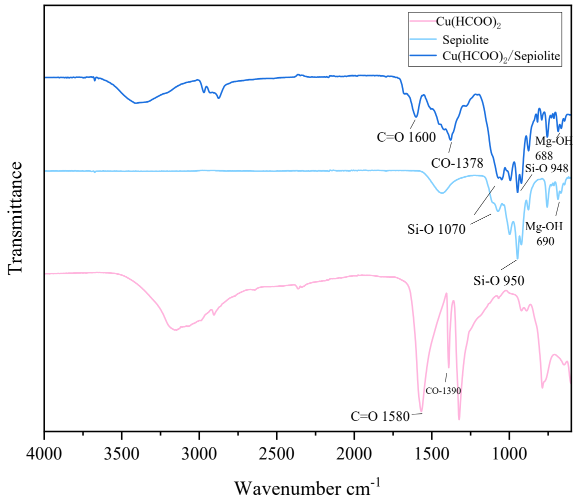


Fig. S1 Fourier transform infrared spectra of $Cu(HCOO)_2$, Sepiolite and $Cu(HCOO)_2$/sepiolite

We compared the infrared spectra of $Cu(HCOO)_2$/sepiolite with those of copper formate and sepiolite, as shown in Fig. S1: the loaded sepiolite has the characteristic peak of copper formate: There was a stretching vibration peak of saturated C-H bond in 2900cm^{-1}, an antisymmetric stretching vibration peak of CO in 1600cm^{-1}, and a symmetric stretching vibration of CO in 1300-1400 cm^{-1}. It can be seen that the infrared spectra of $Cu(HCOO)_2$/sepiolite had the characteristic peaks of sepiolite and copper formate, indicating the successful preparation of the catalyst.

Scanning electron microscopy (SEM)

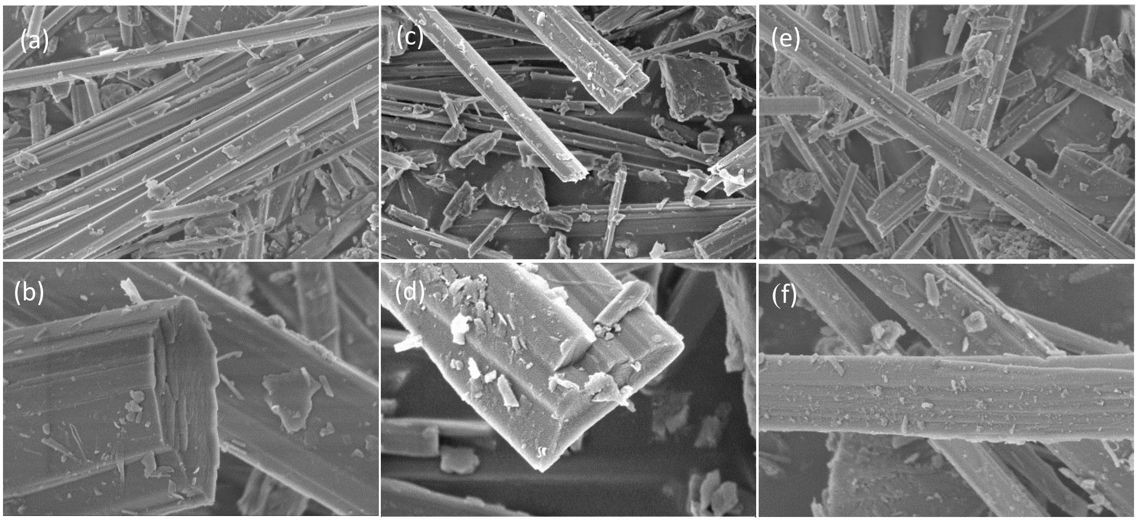


Fig. S2 Scanning electron microscope images of sepiolite (a, d), $Cu(HCOO)_2$/sepiolite before reaction (b, e) and $Cu(HCOO)_2$/sepiolite after reaction(c, f)

Fig. S2 showed scanning electron microscope images of sepiolite and $Cu(HCOO)_2$/sepiolite. As can be seen from Fig. S2-a and partially enlarged Fig. S2-b, the unloaded sepiolite showed a typical chain-like fiber structure, and the structure of loaded sepiolite had no obvious change, while the surface of sepiolite loaded with copper formate was covered with a white film, which was slightly rough (Fig. S2 c-d). Fig. S2 (e-f) showed the scanning electron microscope image of $Cu(HCOO)_2$/sepiolite after reaction. It was found that the catalytic agent after reaction still retained the typical structure and morphology of sepiolite after solvent washing, filtration and drying. At the same time, the original chain layer structure was the same as that of $Cu(HCOO)_2$/sepiolite before reaction, covered by a layer of material.

Energy dispersive spectroscopy (EDS)

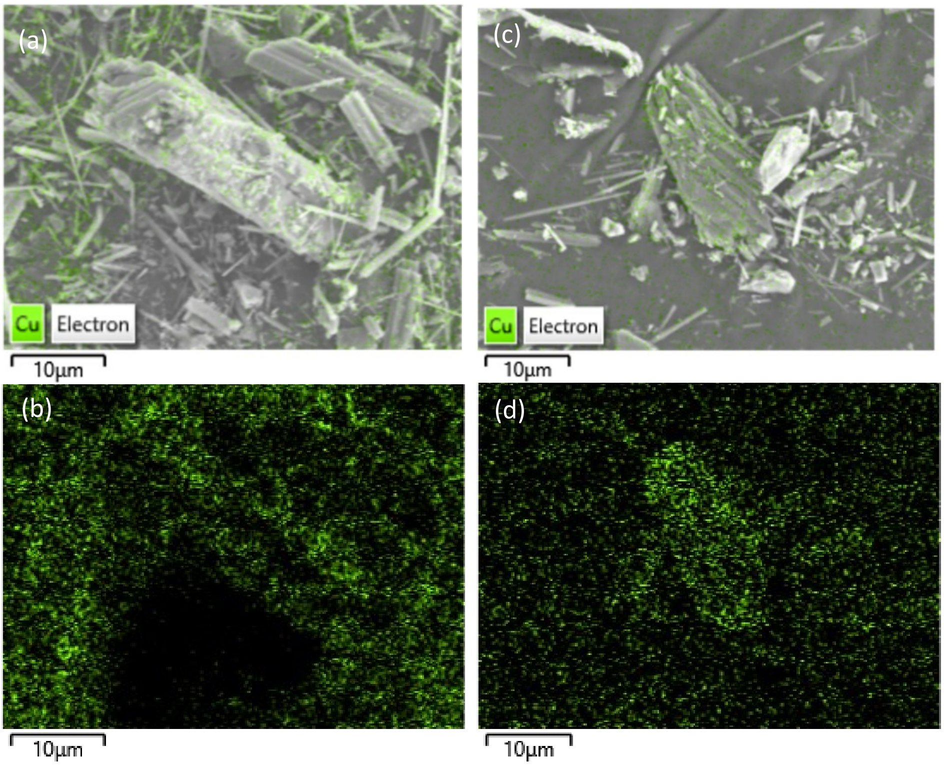


Fig. S3 Energy dispersive spectroscopy of $Cu(HCOO)_2$/sepiolite before reaction (a-b) and $Cu(HCOO)_2$/sepiolite after reaction(c-d)

EDS analysis (Fig. S3 a-d) showed that Cu was uniformly dispersed on the surface of the prepared $Cu(HCOO)_2$/sepiolite catalyst. After the catalyst has been repeatedly run for several times, the catalyst was filtered, washed and dried, and the energy spectrum of the catalyst was scanned. It was found that the loaded Cu was still well retained.

X-ray photoelectron spectroscopy (XPS)

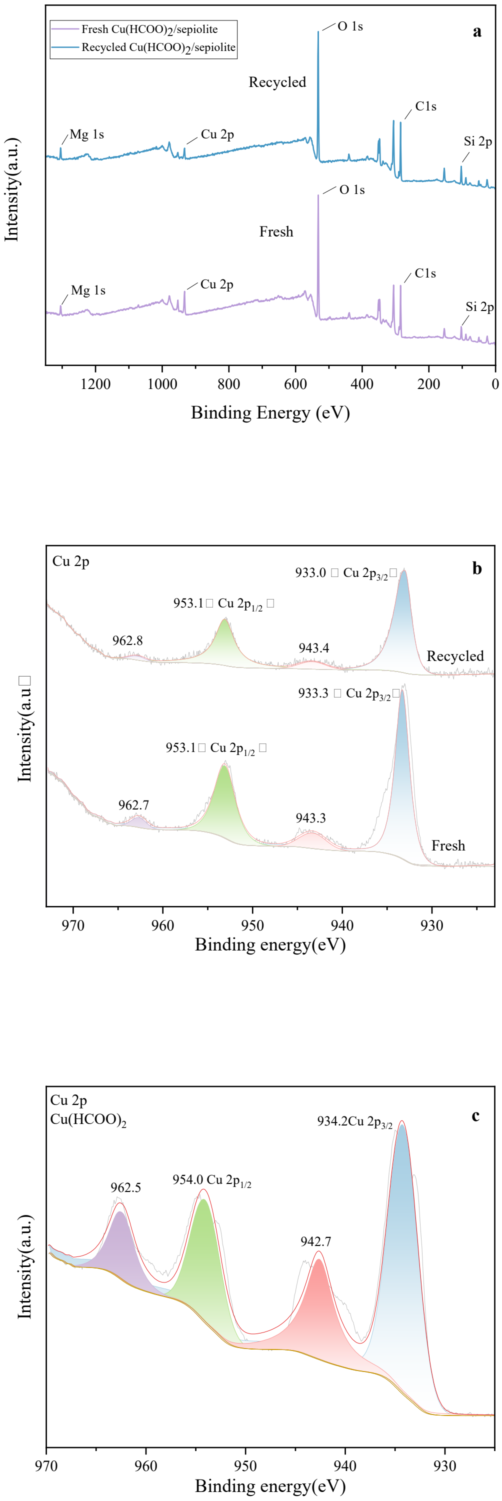


Fig. S4 (a) wide survey XPS spectra of $Cu(HCOO)_2$/sepiolite XPS; (b) Cu 2p XPS spectra of fresh $Cu(HCOO)_2$/sepiolite and recycled $Cu(HCOO)_2$/sepiolite; (c) $Cu(HCOO)_2$ Cu 2p XPS spectra

We found that there was almost no change in the XPS spectra of the catalyst and the unreacted catalyst after repeated reactions, and they all had elements such as C, O, Si, Cu, Mg and so on. 284.8eV and 531.9 (532.1eV) corresponded to the binding energies of C 1s and O 1s, and the peaks at 102.6eV (102.8eV) and 1304.4eV (1304.7eV) belonged to the binding energies of Si 2p and Mg 1s, respectively. Fig. S4-b showed the Cu 2p XPS spectra of $Cu(HCOO)_2$/sepiolite complex before and after the reaction. The peaks at 933.0 eV and 962.7 eV (962.8 eV) corresponded to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, while 943.4 eV and 962.7 eV (962.8 eV) were the characteristic satellite peaks of Cu $2p_{3/2}$ and Cu $2p_{1/2}$, belonging to surface bivalent copper. At the same time, we carried out XPS tests on a single copper formate, as shown in Fig. S4-c, and found that the $Cu(HCOO)_2$/sepiolite (fresh and recycled) XPS spectra are basically consistent with it. This result showed that we have successfully prepared $Cu(HCOO)_2$/sepiolite composites, and the valence state of Cu in $Cu(HCOO)_2$/sepiolite remained unchanged after repeated reaction, and the stability of the catalyst was good, which was consistent with the results of Fig. S1 (FTIR) and Fig. S3 (EDS).

X-Ray Diffractometer

Fig. S5 showed the X-Ray Diffractometer spectra of $Cu(HCOO)_2$, Sepiolite and $Cu(HCOO)_2$/ sepiolite.

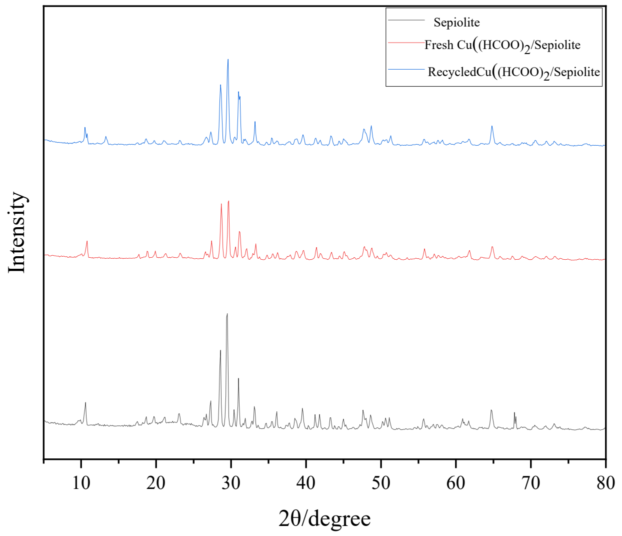
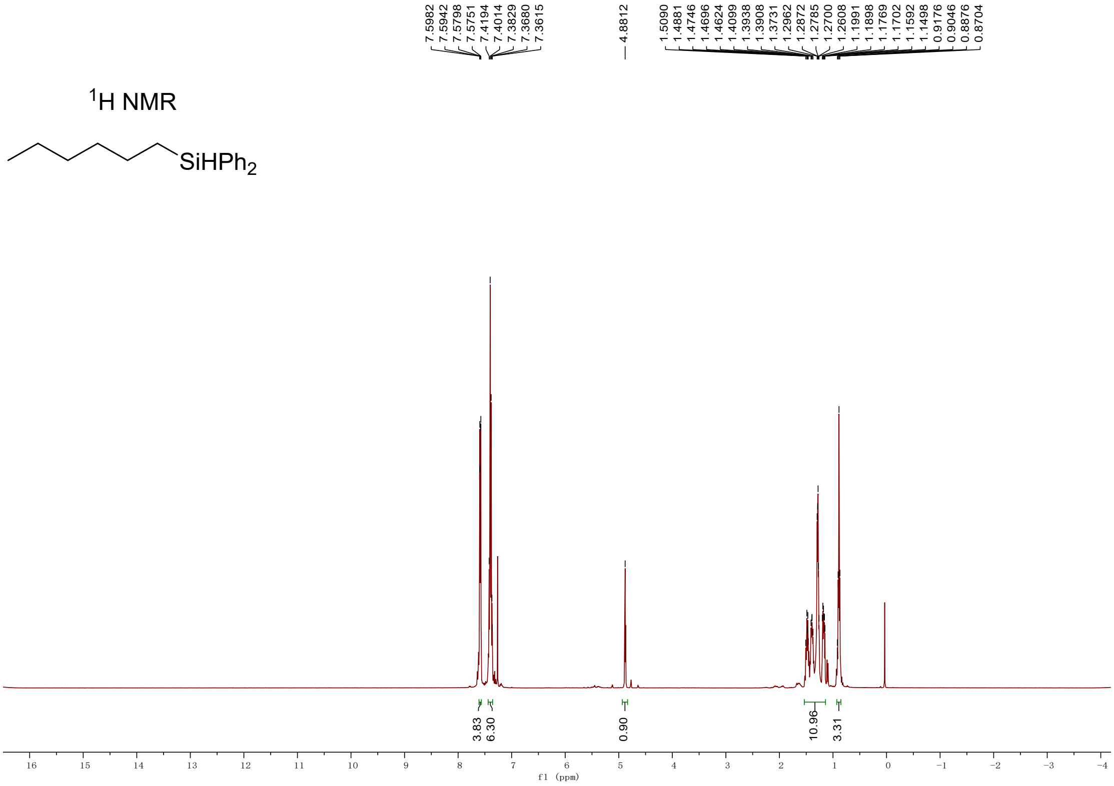
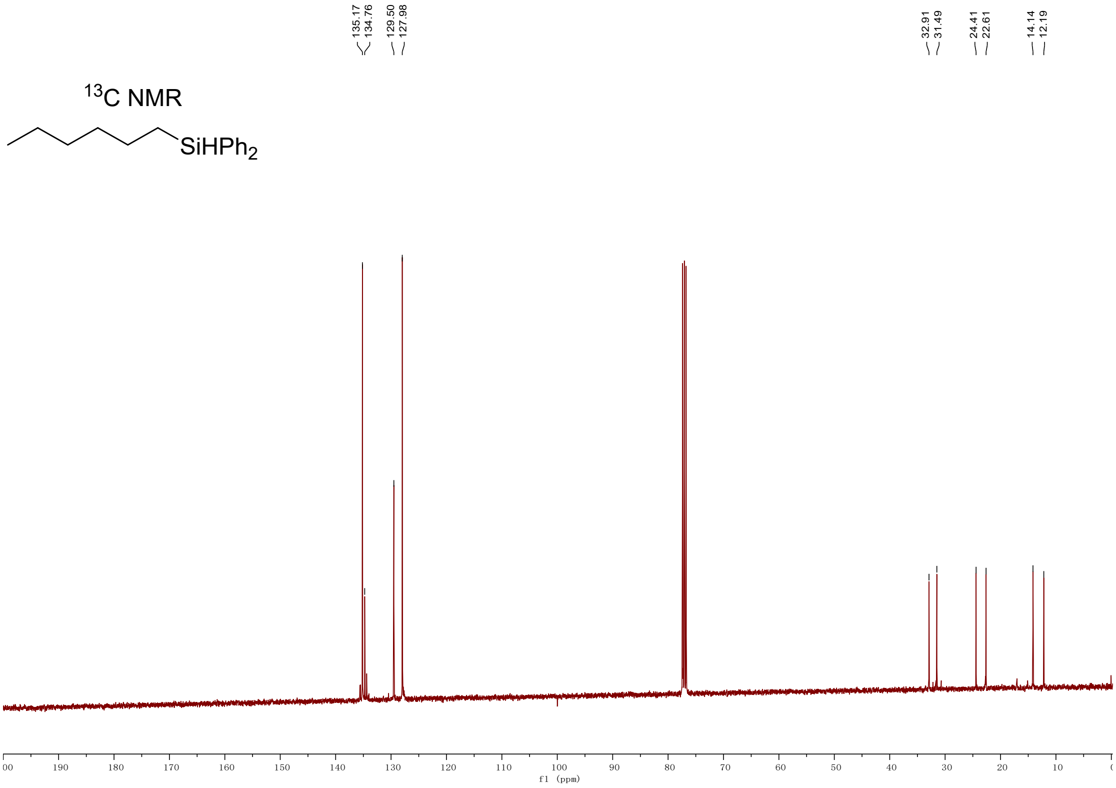


Fig. S5 X-Ray Diffractometer spectra of $Cu(HCOO)_2$, Sepiolite and $Cu(HCOO)_2$/sepiolite

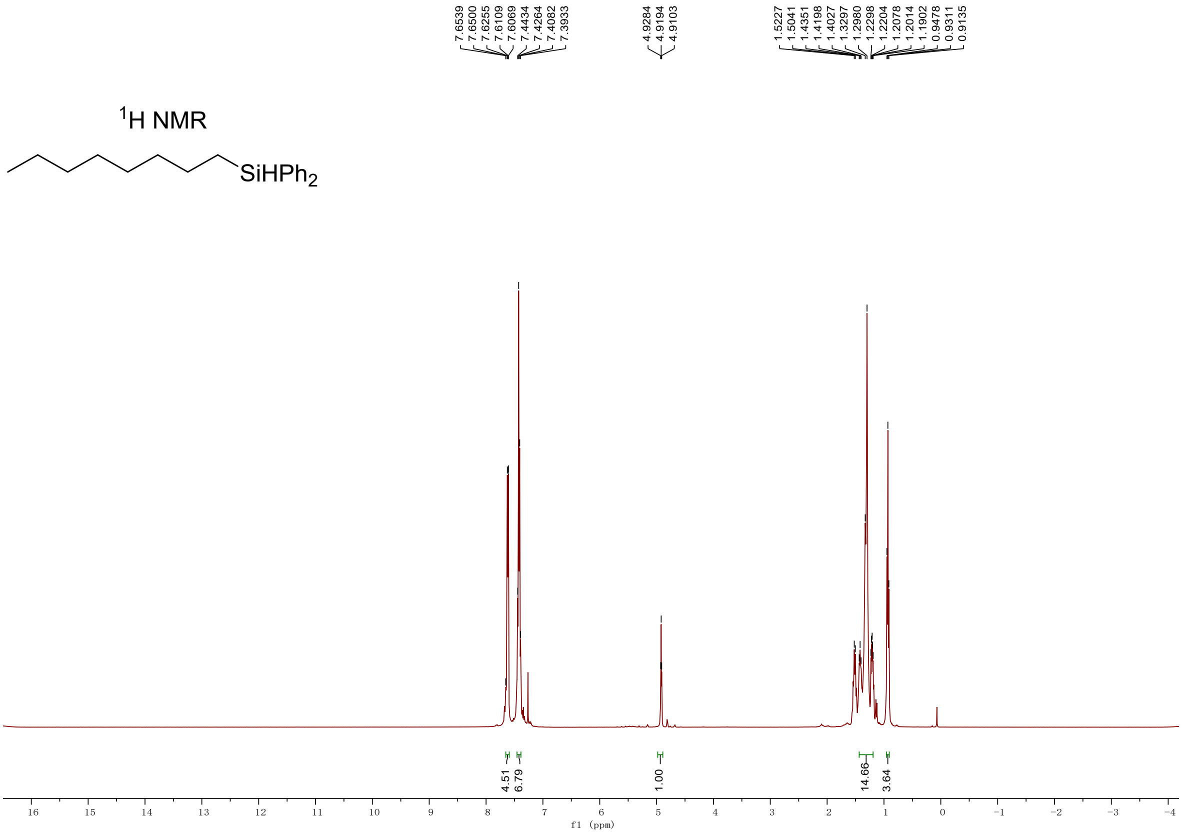
NMR data and spectra section

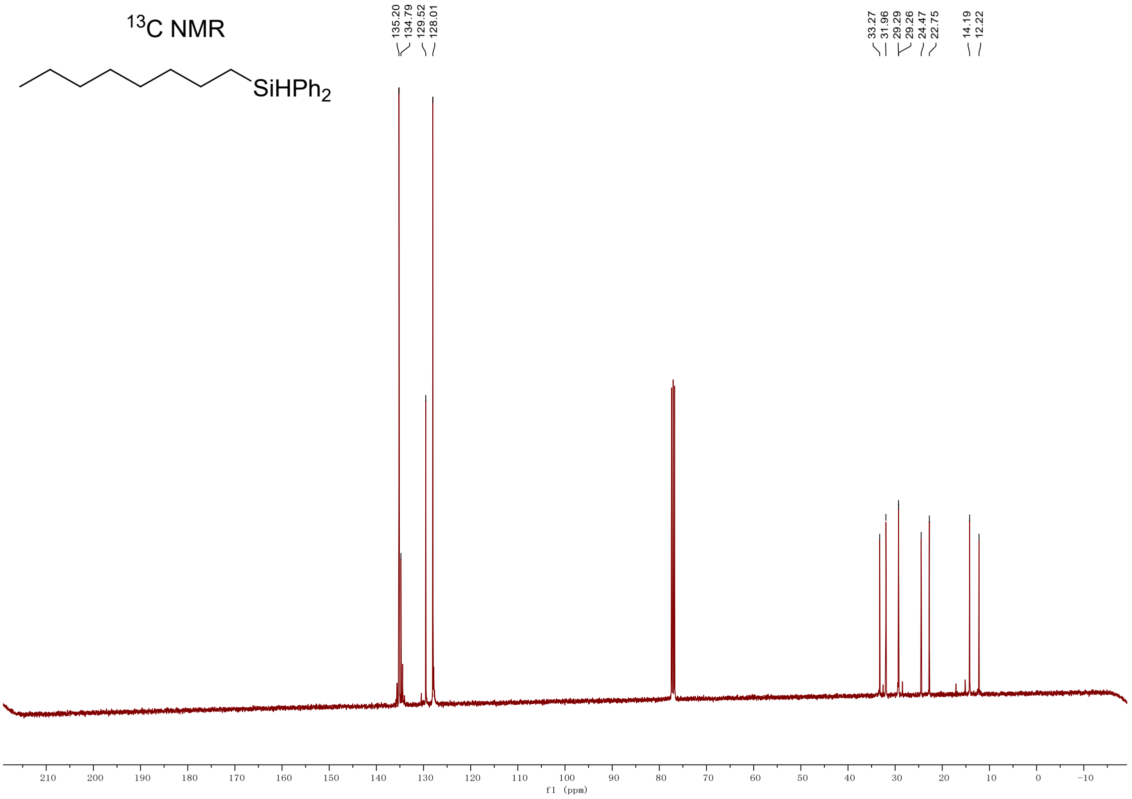
Hexyldiphenylsilane: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.59 (dd, *J* = 7.5, 1.7 Hz, 4H), 7.45 – 7.38 (m, 6H), 4.88 (t, *J* =3.7 Hz, 1H), 1.46 – 1.15 (m, 10H), 0.90 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 135.17, 134.76, 129.50, 127.98, 32.91, 31.49, 24.41, 22.61, 14.14, 12.19.



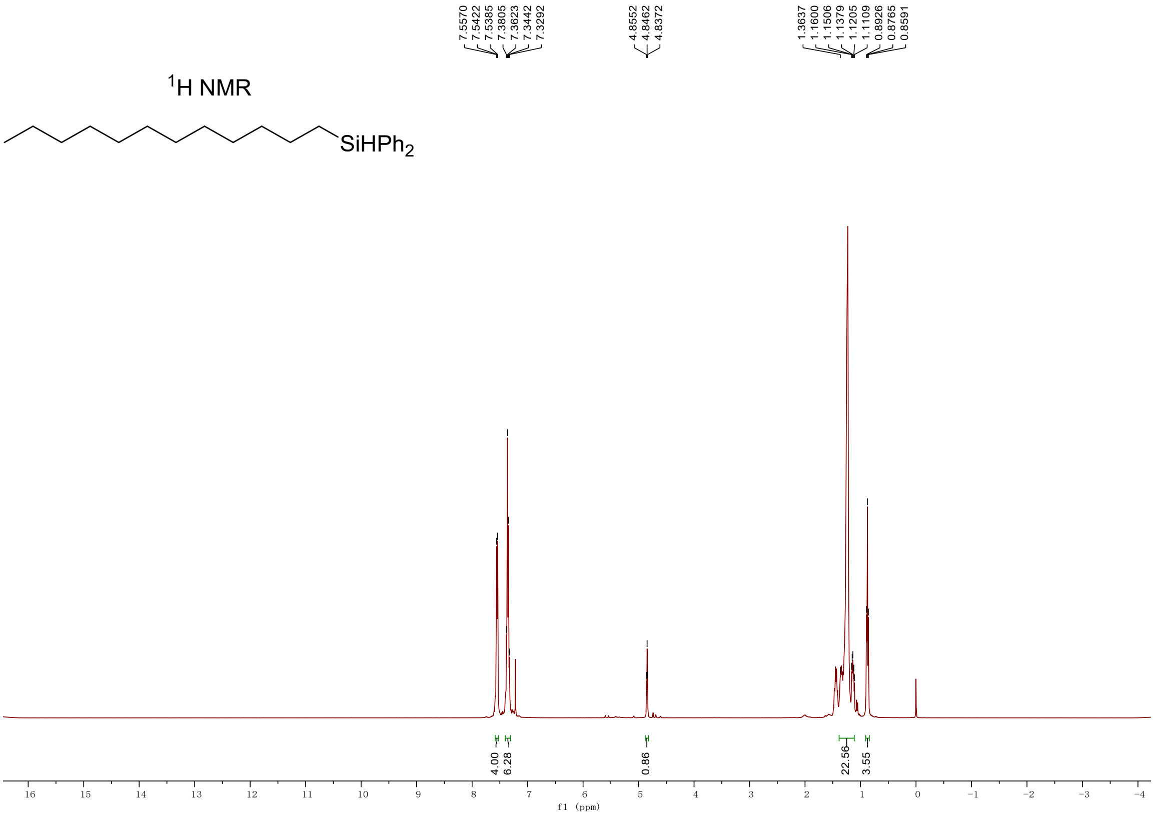


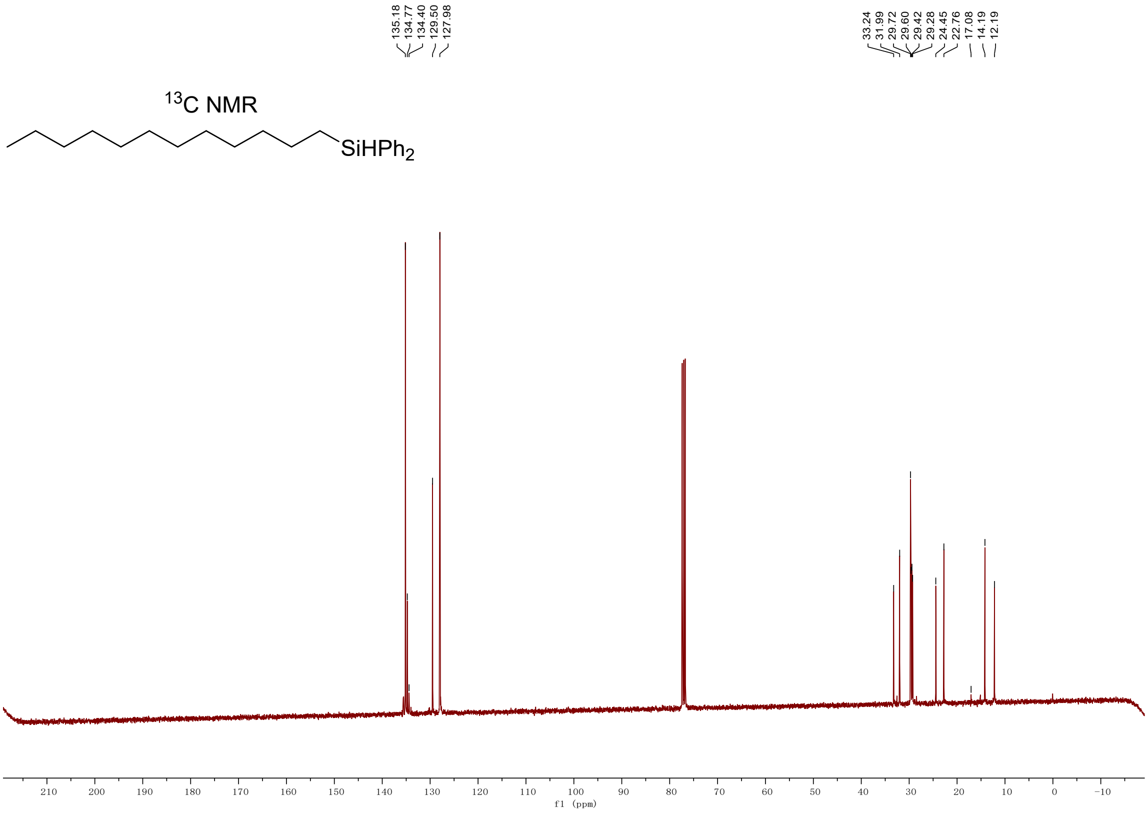
Octyldiphenysilane: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 11.5, 5.7 Hz, 4H), 7.44 – 7.39 (m, 6H), 4.92 (t, *J* =3.7 Hz, 1H), 1.52 – 1.20 (m, 14H), 0.93 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.20, 134.79, 129.52, 128.01, 33.27, 31.96, 29.28, 24.47, 22.75, 14.19, 12.22.



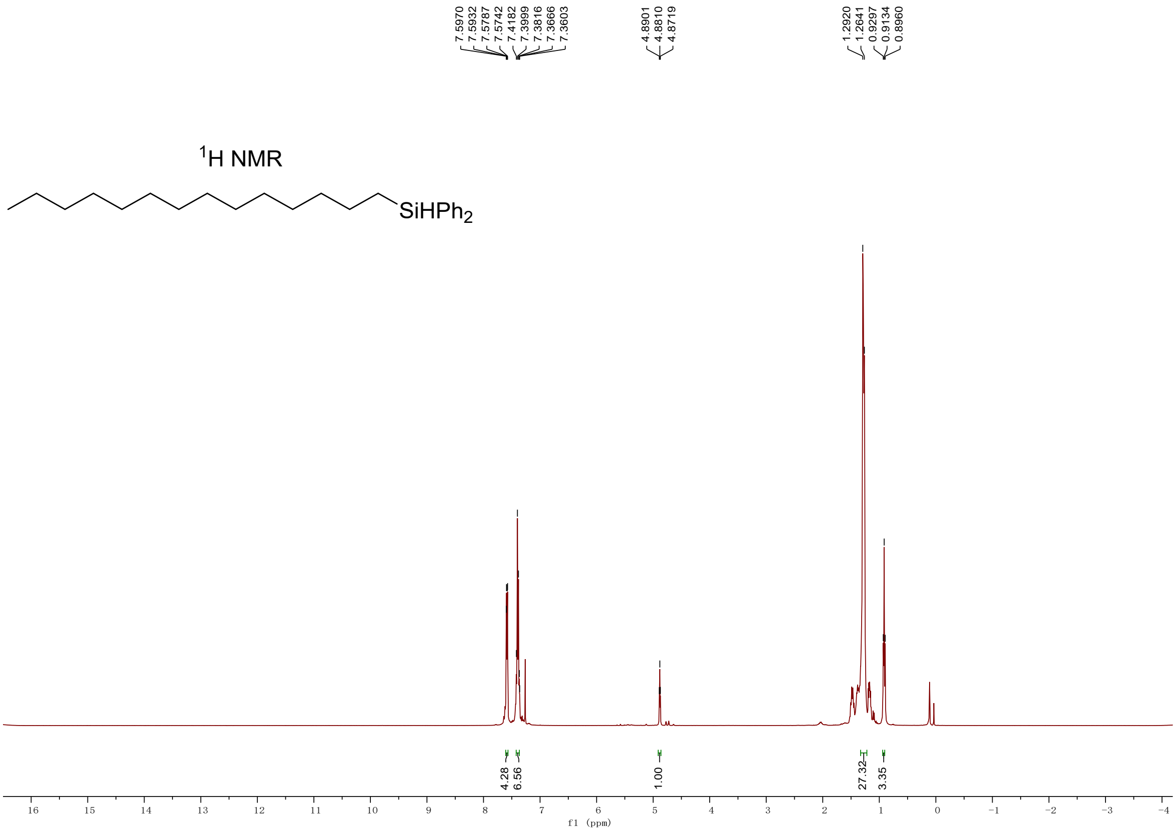


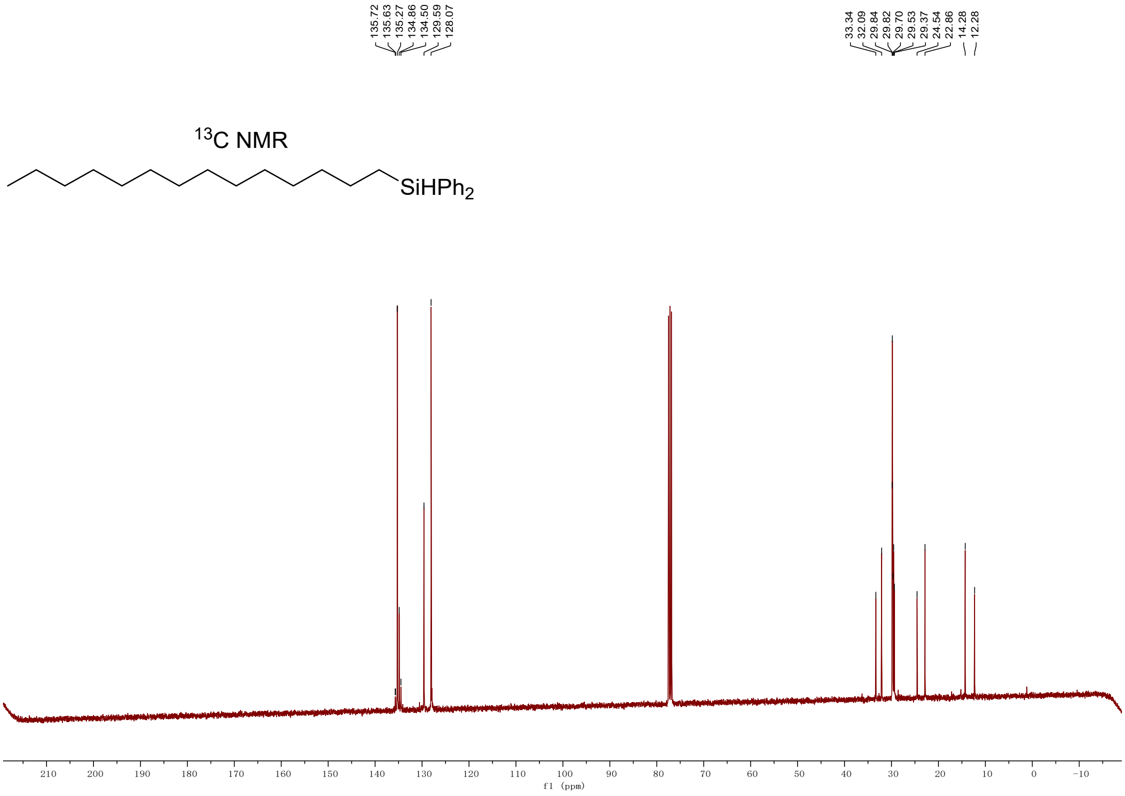
Dodecenediphenylsilane: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, 4H), 7.38 – 7.33 (m, 6H), 4.85 (t, *J* =3.7 Hz, 1H), 1.20 (m, 22H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.18, 134.77, 134.40, 129.50, 127.98, 33.24, 31.99, 29.72, 29.60, 29.42, 29.28, 24.45, 22.76, 17.08, 14.19, 12.19.



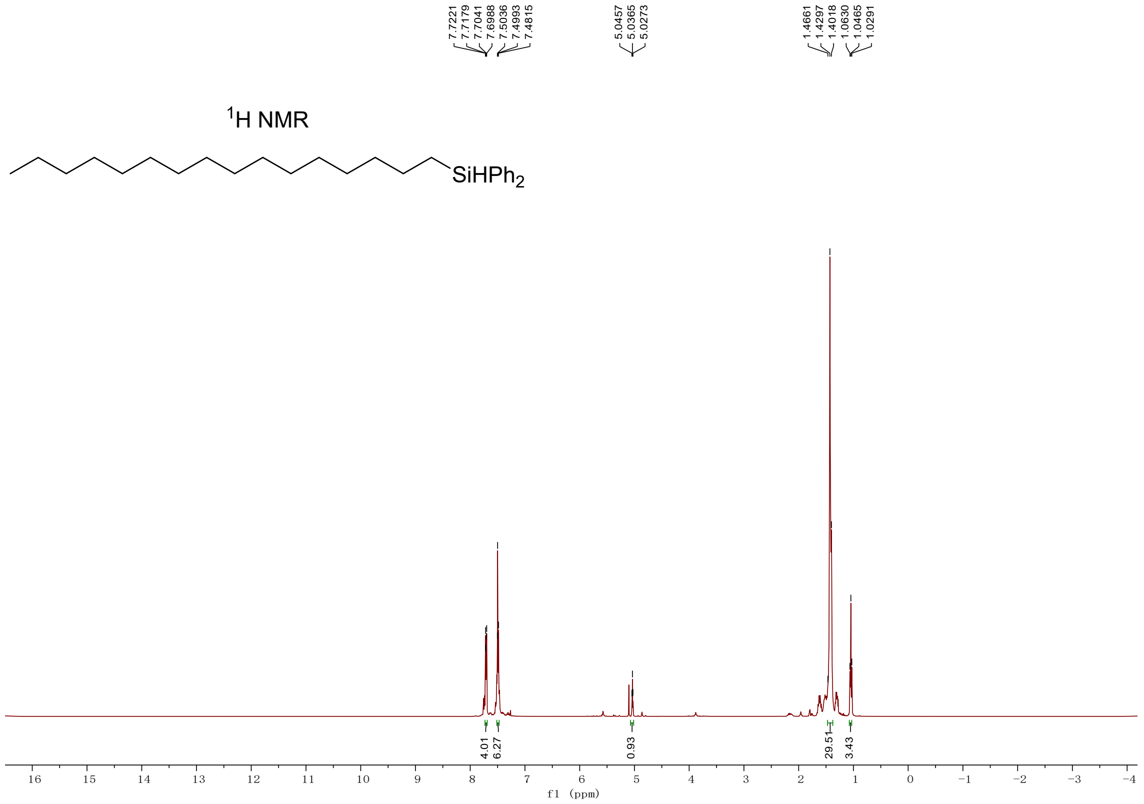


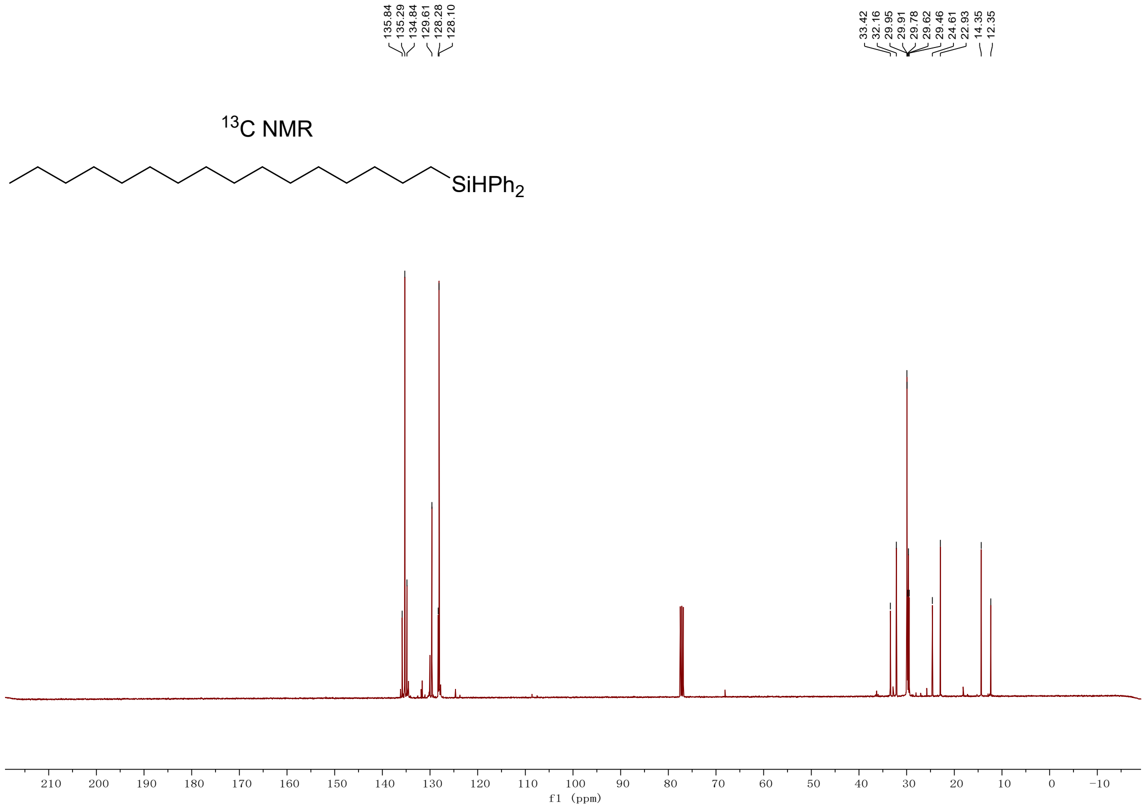
Tetradecenediphenylsilane: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 7.5, 1.7 Hz, 4H), 7.42 – 7.36 (m, 6H), 4.88 (t, *J* =3.7 Hz, 1H), 1.28 (m, *J* = 11.2 Hz, 26H), 0.92 (t, 6.5 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.62, 135.53, 135.17, 134.76, 134.40, 129.49, 127.97, 33.23, 31.98, 29.74, 29.72, 29.59, 29.42, 29.27, 24.44, 22.75, 14.18, 12.18.



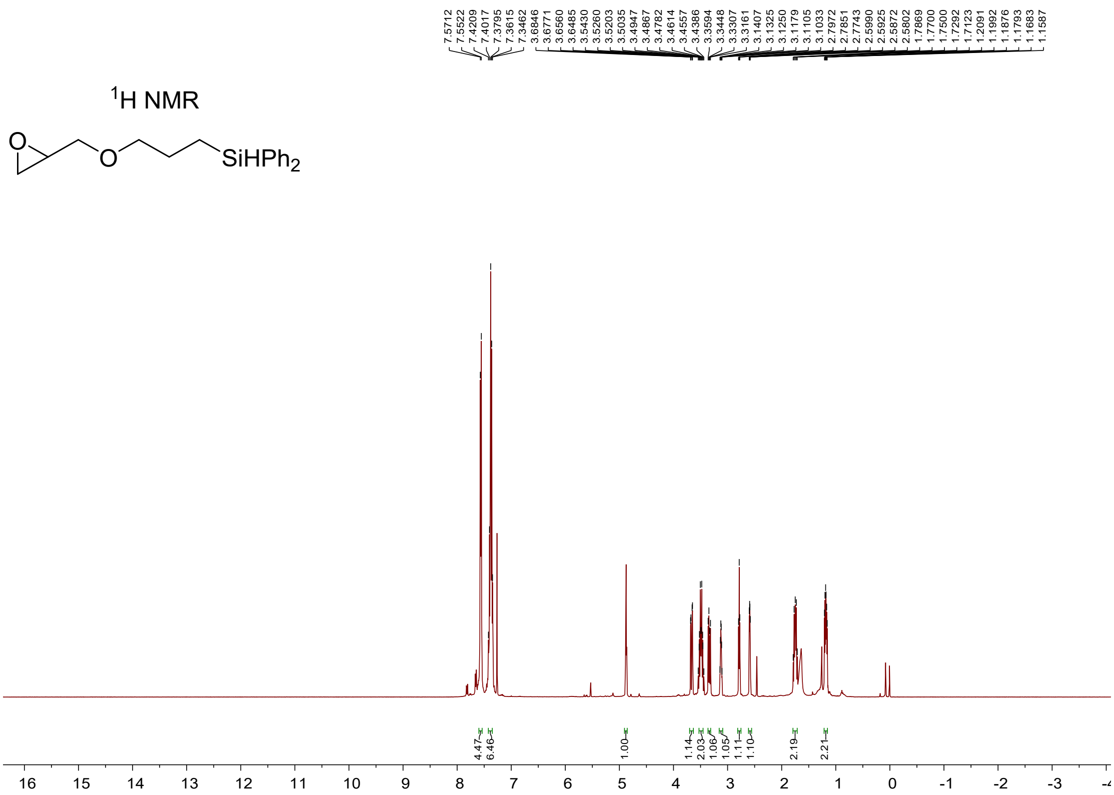


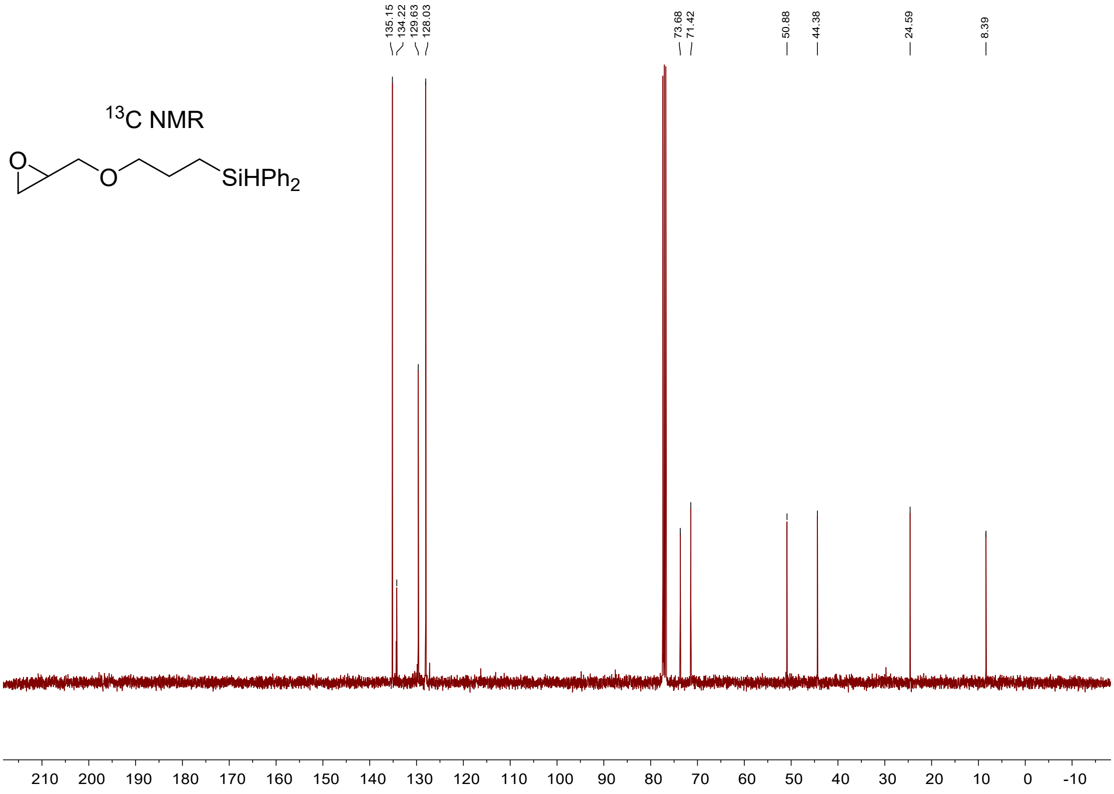
Hexadecyldiphenylsilane: ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm): 7.71 (dd, *J* = 7.4, 1.9 Hz, 4H), 7.49 (m, *J* = 4.4 Hz, 6H), 5.04 (t, *J* = 3.7 Hz, 1H), 1.42 (m, *J* = 11.2 Hz, 30H), 1.05 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm): 135.24, 134.81, 129.55, 128.04, 33.33, 32.08, 29.86, 29.82, 29.69, 29.53, 29.37, 24.53, 22.85, 14.27, 12.28.



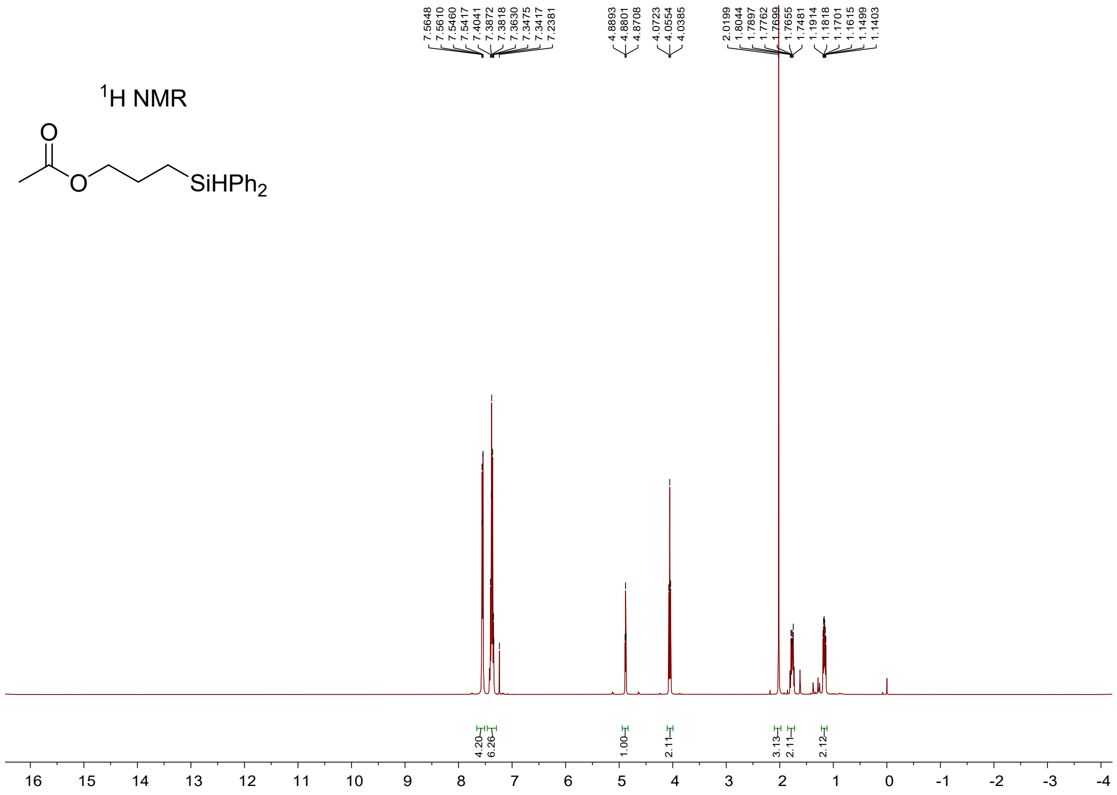


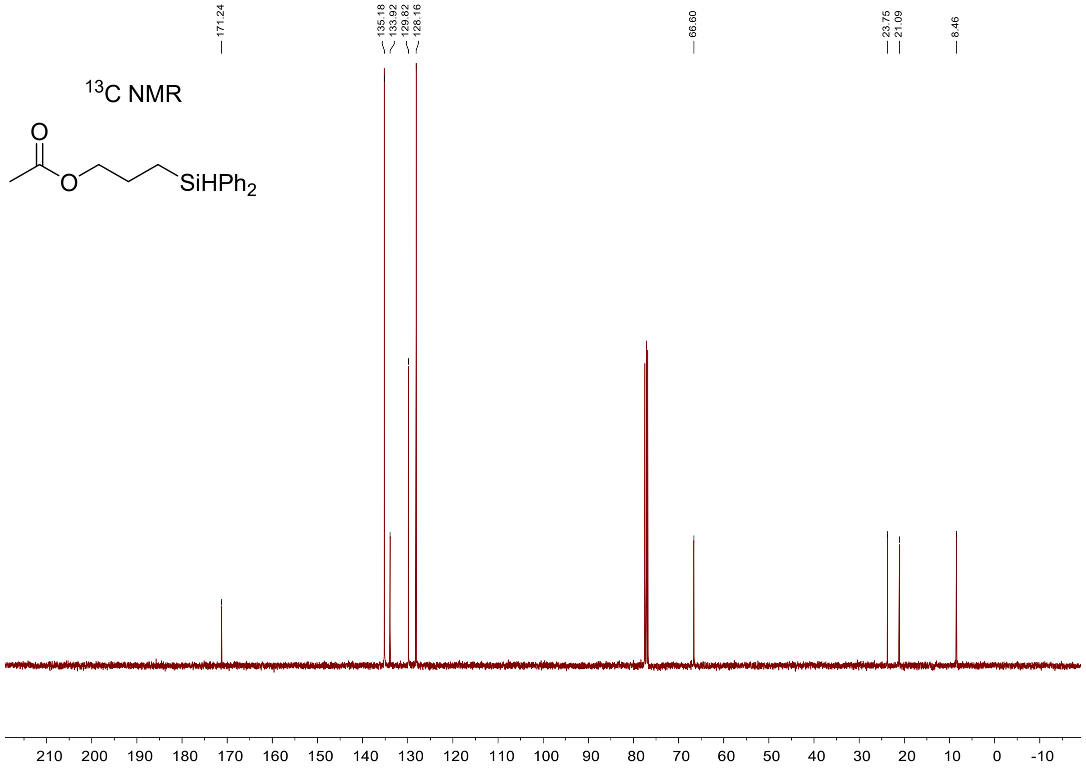
(3-(Oxiran-2-ylmethoxy)propyl)diphenylsilane：^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.6 Hz, 4H), 7.42-7.34 (m, 6H), 4.88 (t, *J* = 3.7 Hz, 1H), 3.67 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.53 – 3.45 (m, 2H), 3.34 (dd, *J* = 11.5, 5.8 Hz, 1H), 3.12 (m, 1H), 2.79 (t, *J* = 4.6 Hz, 1H), 2.59 (dd, *J* = 4.8, 2.7 Hz, 1H), 1.76 (m, 2H), 1.22 – 1.15 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.15, 134.22, 129.63, 128.03, 73.68, 71.42, 50.88, 44.38, 24.59, 8.39.



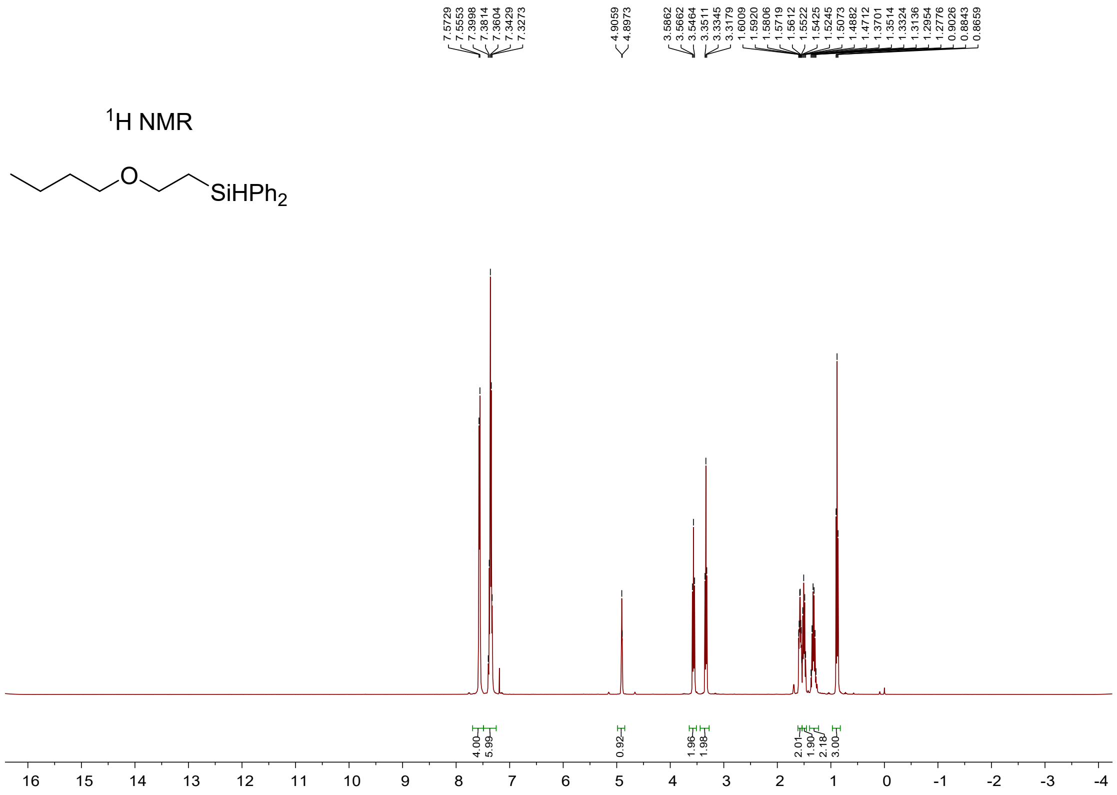


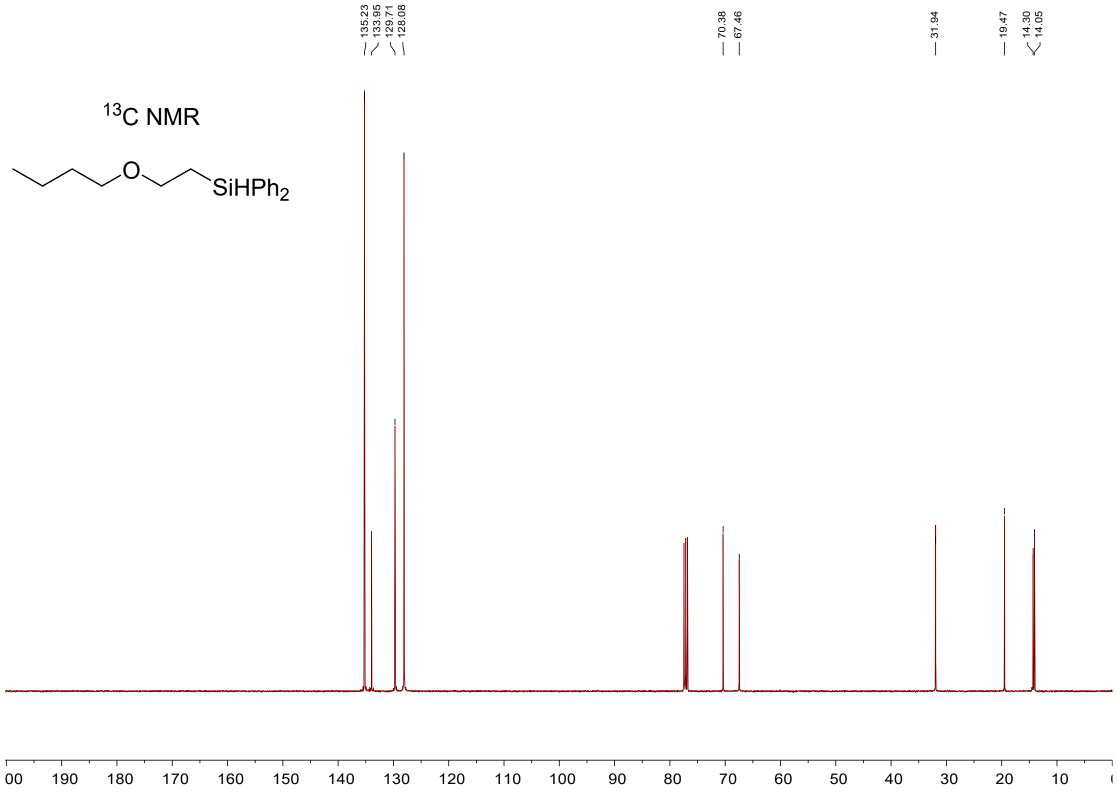
3-(Diphenylsilyl)propyl acetate：^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.6, 1.6 Hz, 4H), 7.46 – 7.29 (m, 6H), 4.88 (t, *J* = 3.7 Hz, 1H), 4.06 (t, *J* = 6.8 Hz, 2H), 2.02 (s, 3H), 1.85 – 1.72 (m, 2H), 1.22 – 1.12 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.24, 135.18, 133.92, 129.82, 128.16, 66.60, 23.74, 21.09, 8.46.





(2-Butoxyethyl)diphenylsilane: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.0 Hz, 4H), 7.36 (t, *J* = 7.7 Hz, 6H), 4.90 (t, *J* = 3.4 Hz, 1H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.33 (t, *J* = 6.6 Hz, 2H), 1.66 – 1.45 (m, 4H), 1.32 (m, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.23, 133.95, 129.71, 128.08, 70.38, 67.46, 31.94, 19.47, 14.30, 14.05.





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