Electronic Supplementary Information

Hydrosilylation of Olefins Catalyzed with Cobalt (II)-Dehydroacetic Acid Complexs and the Self-Supported Catalysts

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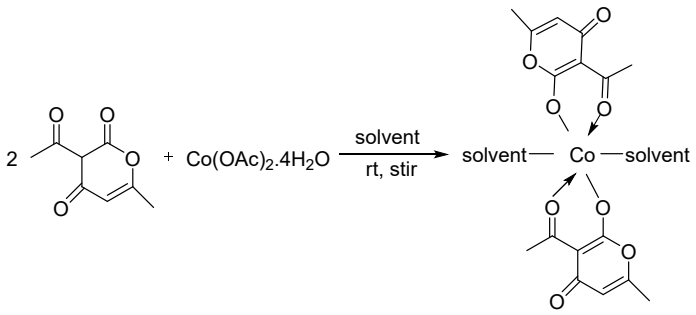
Materials

Dehydroacetic acid was purchased from Shanghai Sain Chemical Technology Co., Ltd.; 1-octene was purchased from Aladdin Chemical Reagent Co., Ltd.; 1-dodecene was purchased from Beijing Yunbang Biotechnology Co., Ltd.; 1-tetradecene was purchased from Shanghai Maiklin biochemical Technology Co., Ltd.; 1-hexadecene and 1-octadecene were purchased from Shanghai Merrill Chemical 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. All reagents were used without further purification.

Synthesis

A series of Cobalt-DHA complexes were synthesized using $Co(OAc)_2 \cdot 4H_2O$ and DHA in different aprotic polar solvents: dimethylformamide(DMF),dimethylacetamide(DMAC),diethylformamide (DEF), dimethyl sulfoxide (DMSO), and *n*-methylpyrrolidone (NMP), respectively, with reference to the literature[20]. $Co(OAc)_2 \cdot 4H_2O$ was added into round-bottomed flasks and the solvent was added to dissolve it completely, DHA (2.0 equivalents) dissolved in the same solvents was slowly dropped into the above solution. After stirring continuously at room temperature for several hours, a precipitate gradually formed in the solution. The precipitate was separated by filtration and washed several times with an appropriate amount of solvent. Finally, the precipitate was placed in a vacuum oven and dried at 80 °C for 10 hours to obtain the Cobalt-DHA complexes $Co(DHA)_2 \cdot 2[DMF]$, $Co(DHA)_2 \cdot 2[DMAC]$, $Co(DHA)_2 \cdot 2[DEF]$, $Co(DHA)_2 \cdot 2[DMSO]$ and $Co(DHA)_2 \cdot 2[NMP]$, respectively. Thus, the different cobalt carboxylate as well as different transition metal acetate were used to prepare the metal-$(DHA)_2 \cdot 2[DMF]$ complexes.



1. Cobalt Complexes

Entry	Solvent	State	Yield(%)
1	DMSO	yellow powder	87.3
2	DMF	yellow powder	88.9
3	DEF	yellow powder	80.3
4	NMP	brown powder	64.4
5	DMAC	-	-

2. The metal-$(DHA)_2 \cdot 2$[DMF] complexes

Entry	[M]	State	Yield(%)
1	Fe	reddish-brown powder	50.0
2	Cu	blue-purple powder	60.0
3	Ni	light-green powder	92.6
4	Zn	white powder	72.7

Characterization

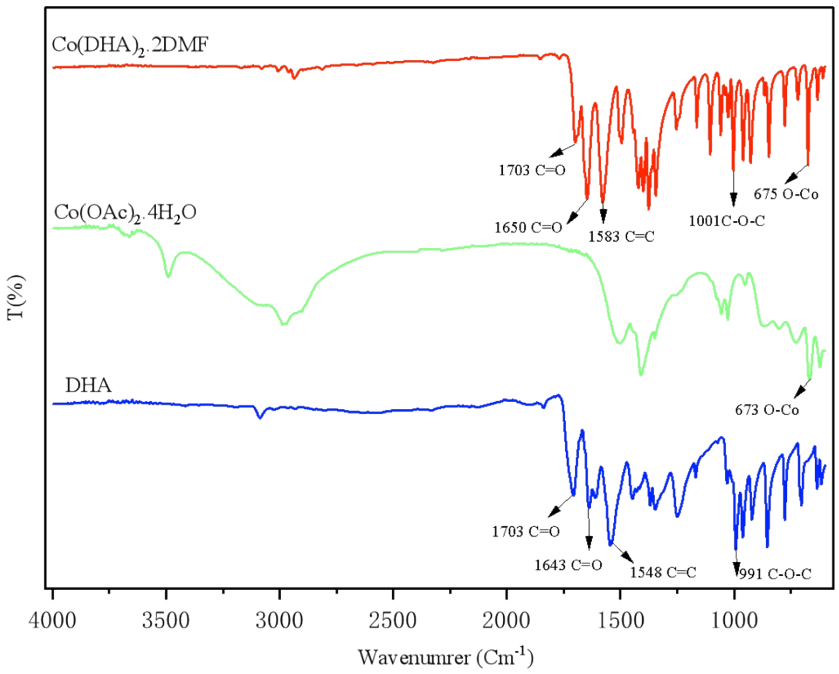
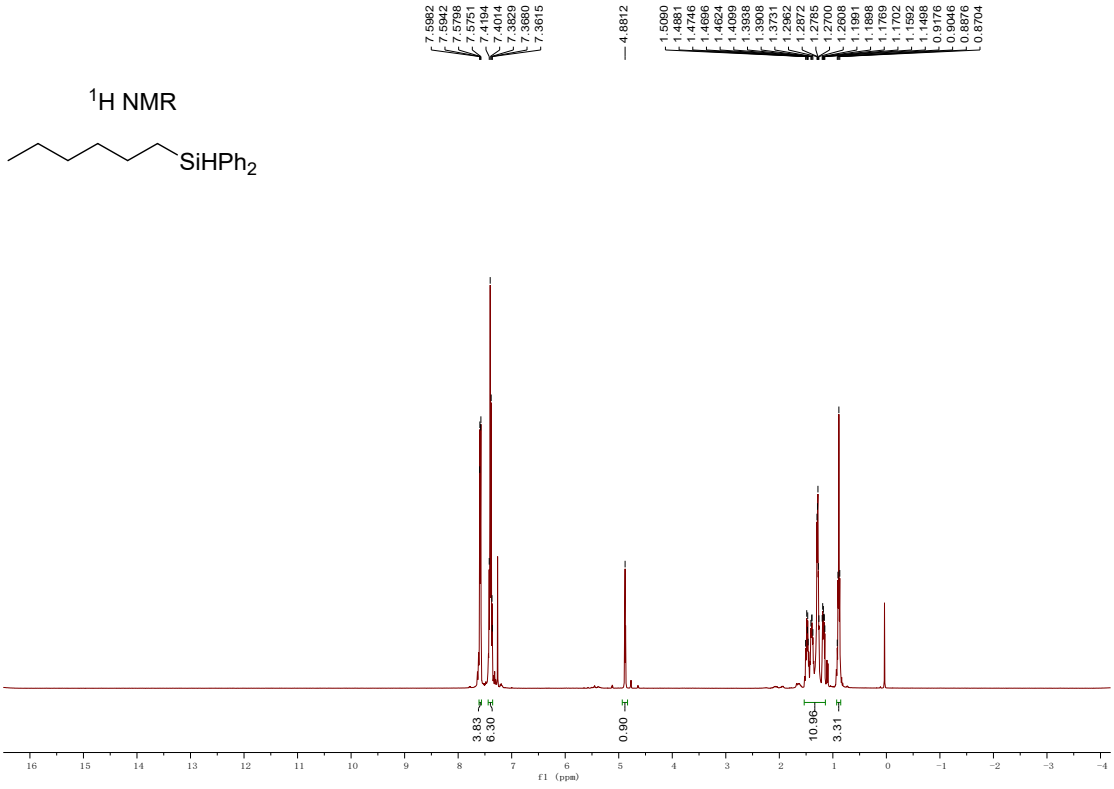
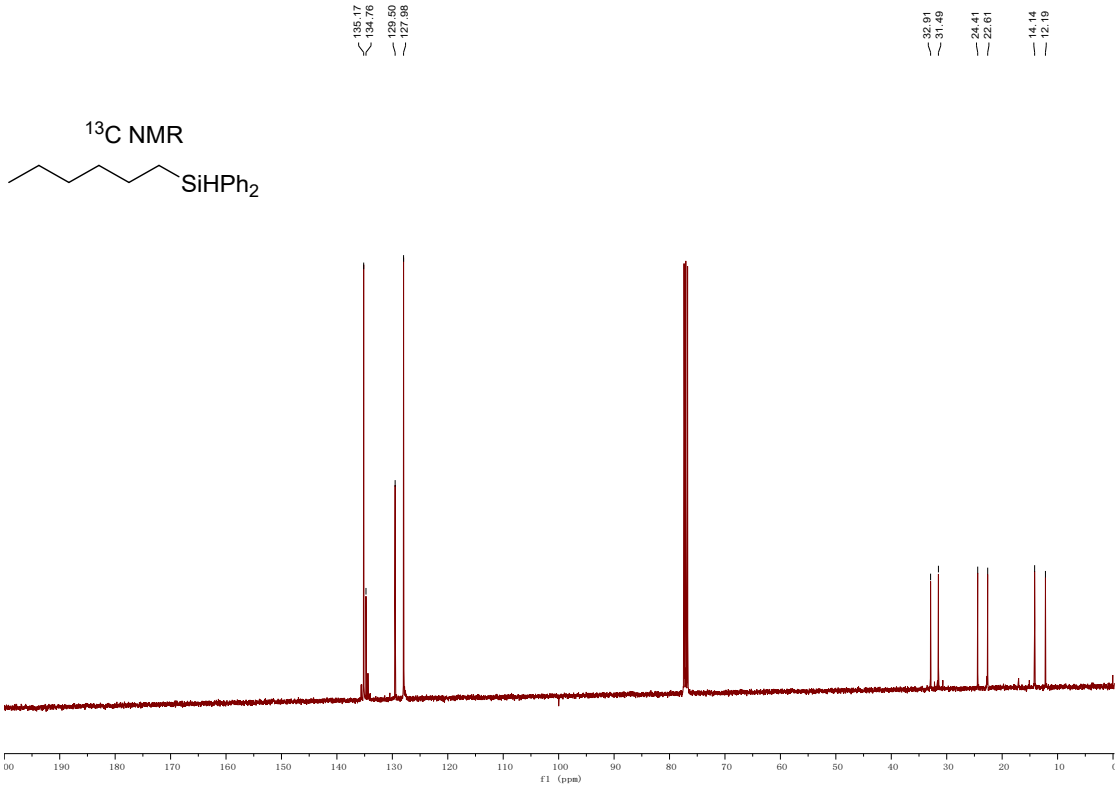


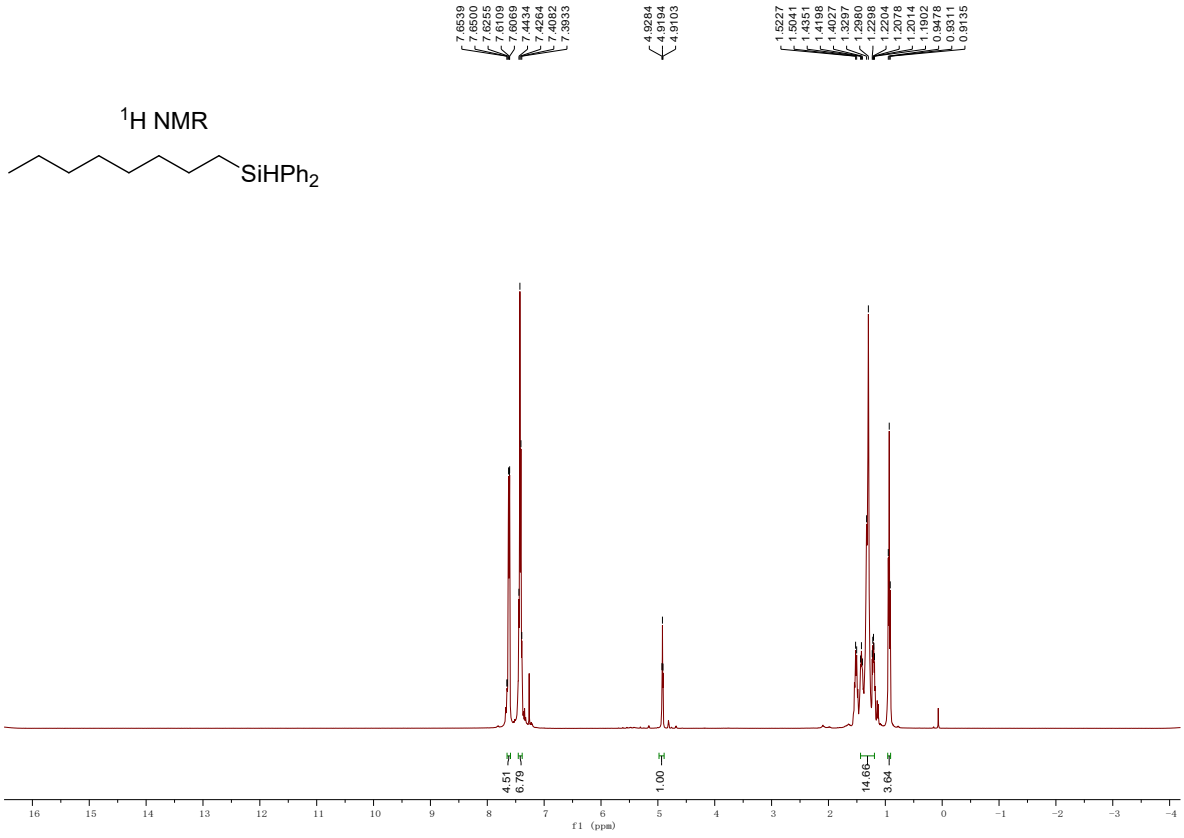
Figure 1 FTIR spectra of DHA、$Co(OAc)_2.4H_2O$ and $Co(DHA)_2.2DMF$

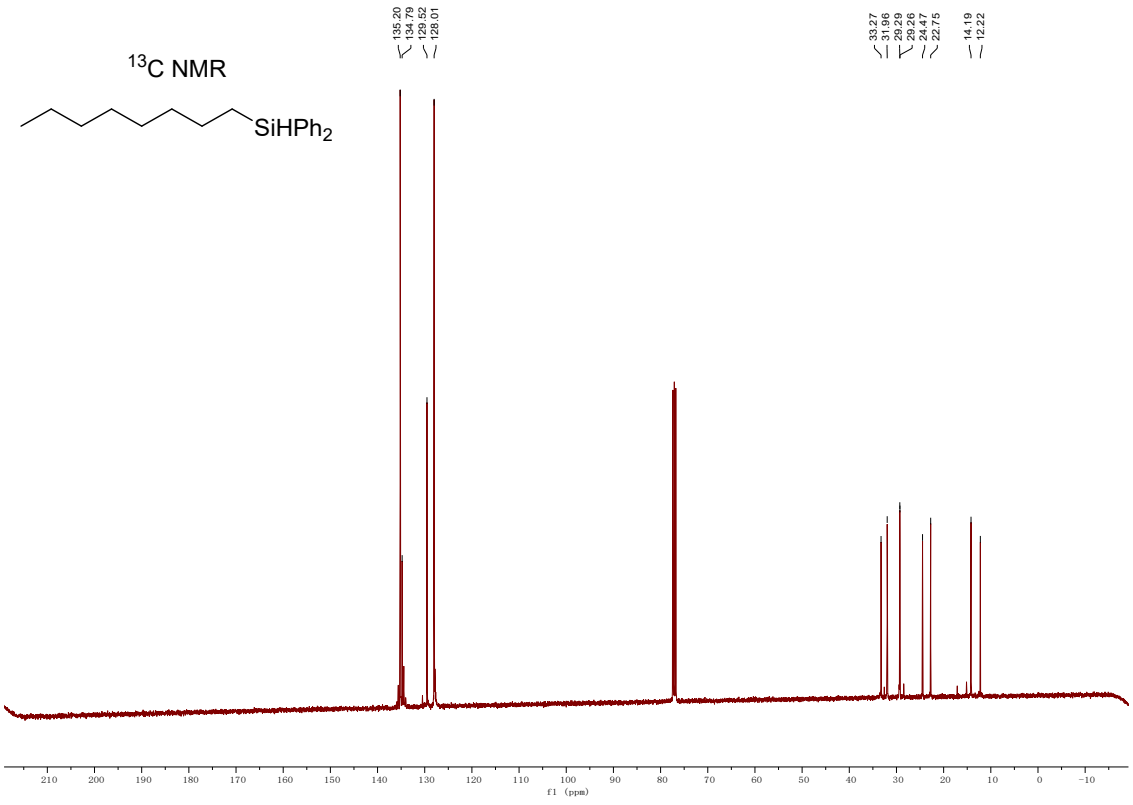
Hexyldiphenylsilane: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.59 (dd, *J* = 7.5, 1.7 Hz, 4H), 7.45 – 7.38 (m, 6H), 4.88 (t, *J* =3.7 Hz, 1H), 1.46 – 1.15 (m, 10H), 0.90 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 135.17, 134.76, 129.50, 127.98, 32.91, 31.49, 24.41, 22.61, 14.14, 12.19.



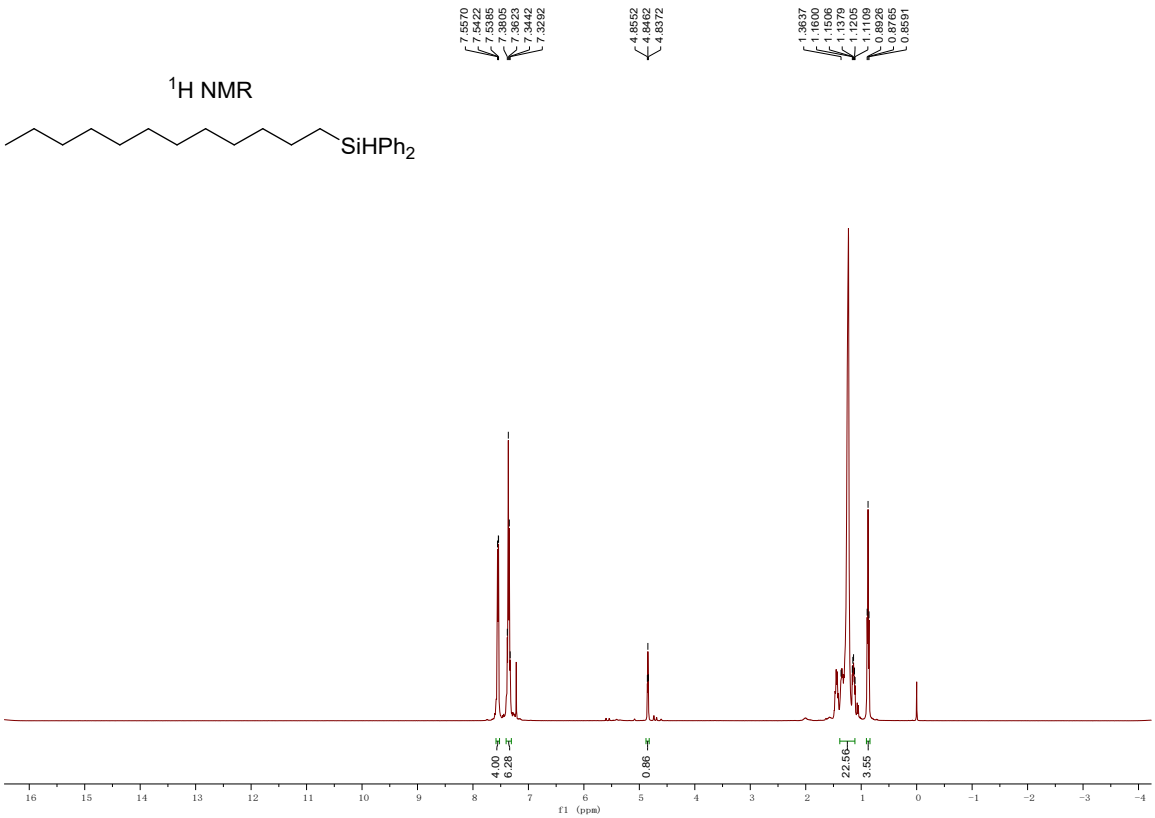


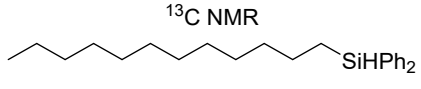
Octyldiphenysilane: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 11.5, 5.7 Hz, 4H), 7.44 – 7.39 (m, 6H), 4.92 (t, *J* =3.7 Hz, 1H), 1.52 – 1.20 (m, 14H), 0.93 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.20, 134.79, 129.52, 128.01, 33.27, 31.96, 29.28, 24.47, 22.75, 14.19,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

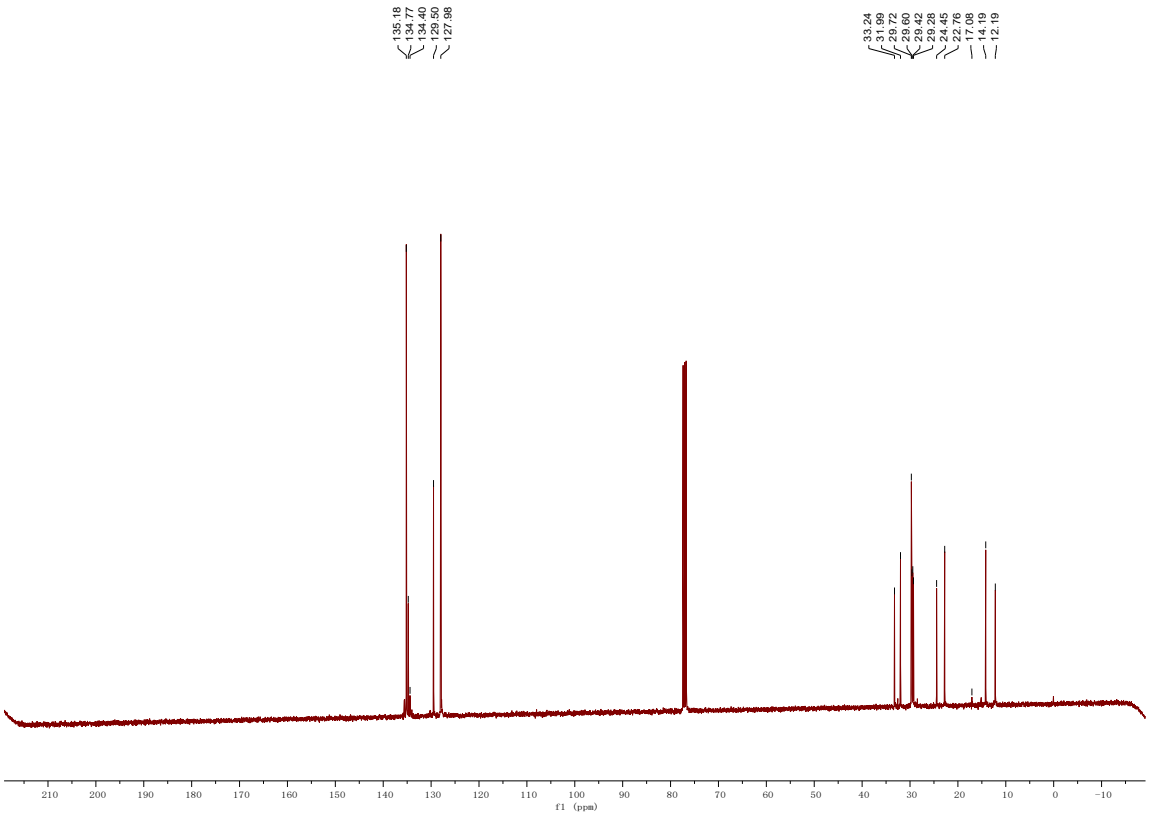




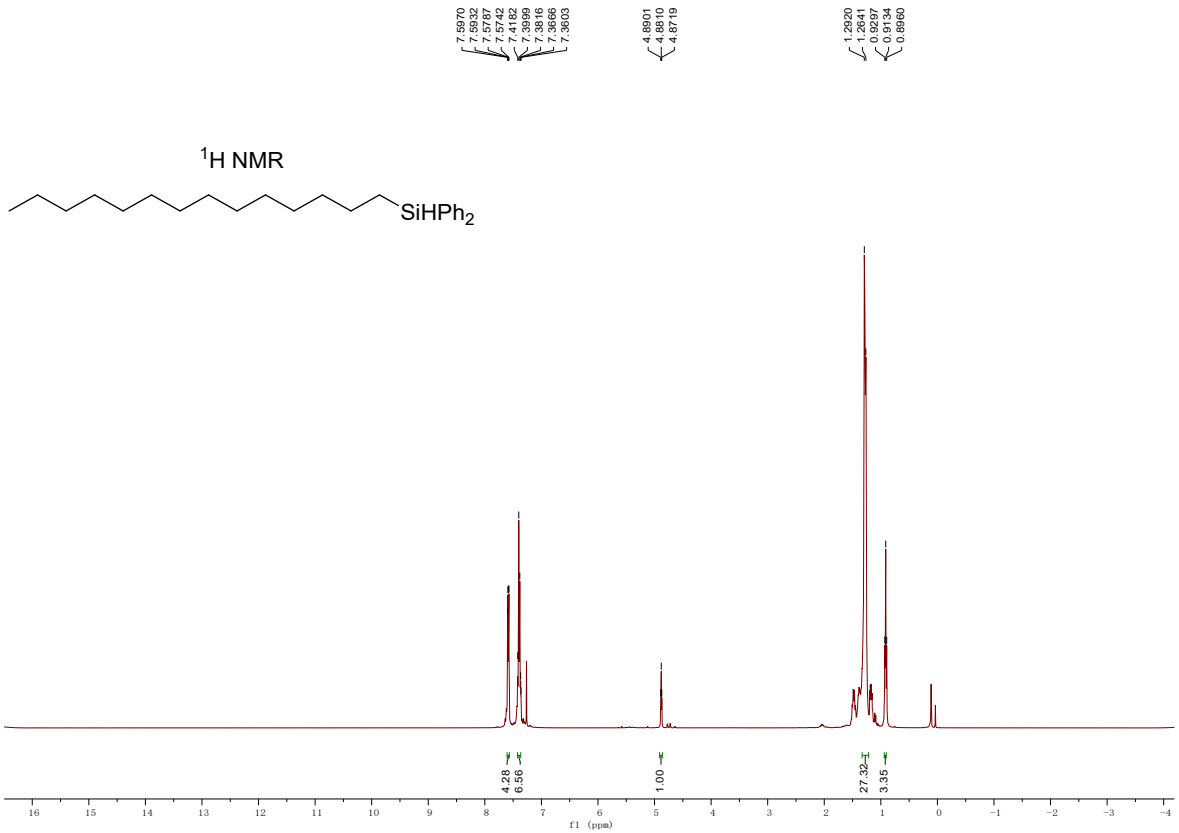
Dodecenediphenylsilane: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, 4H), 7.38 – 7.33 (m, 6H), 4.85 (t, *J* =3.7 Hz, 1H), 1.20 (m, 22H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.18, 134.77, 134.40, 129.50, 127.98, 33.24, 31.99, 29.72, 29.60, 29.42, 29.28, 24.45, 22.76,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

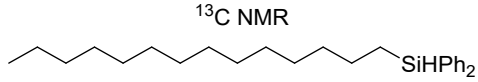


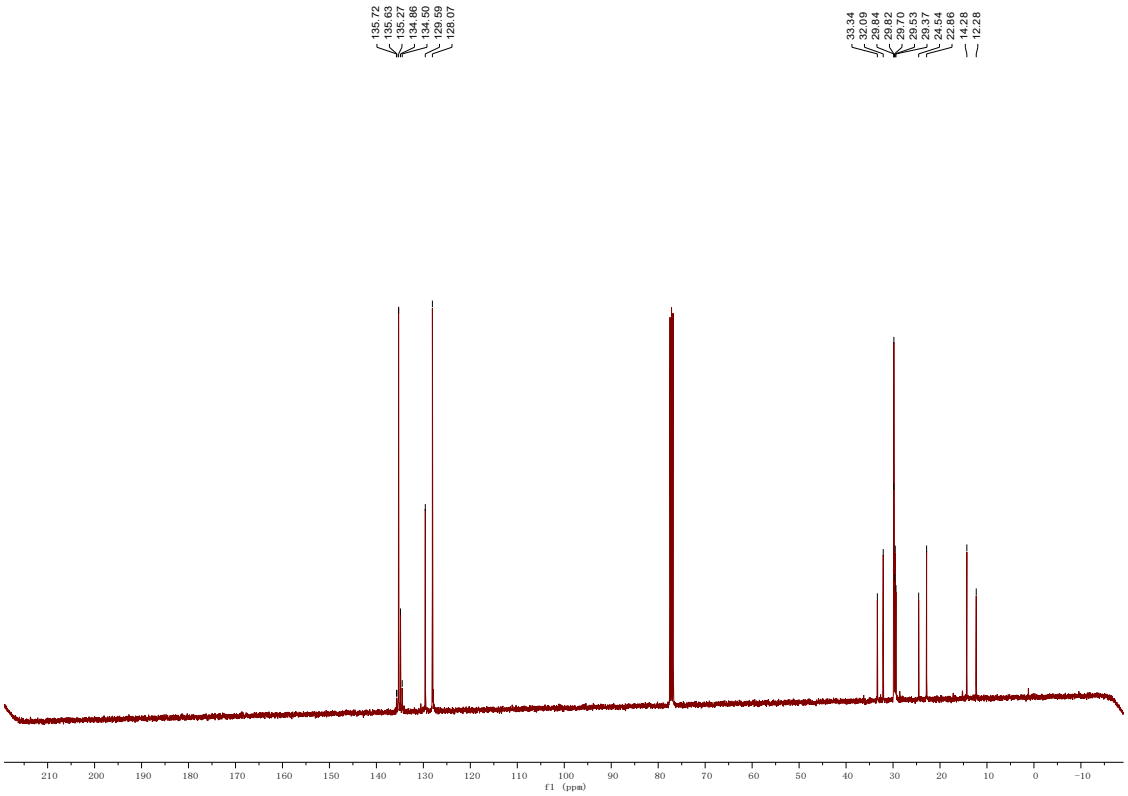




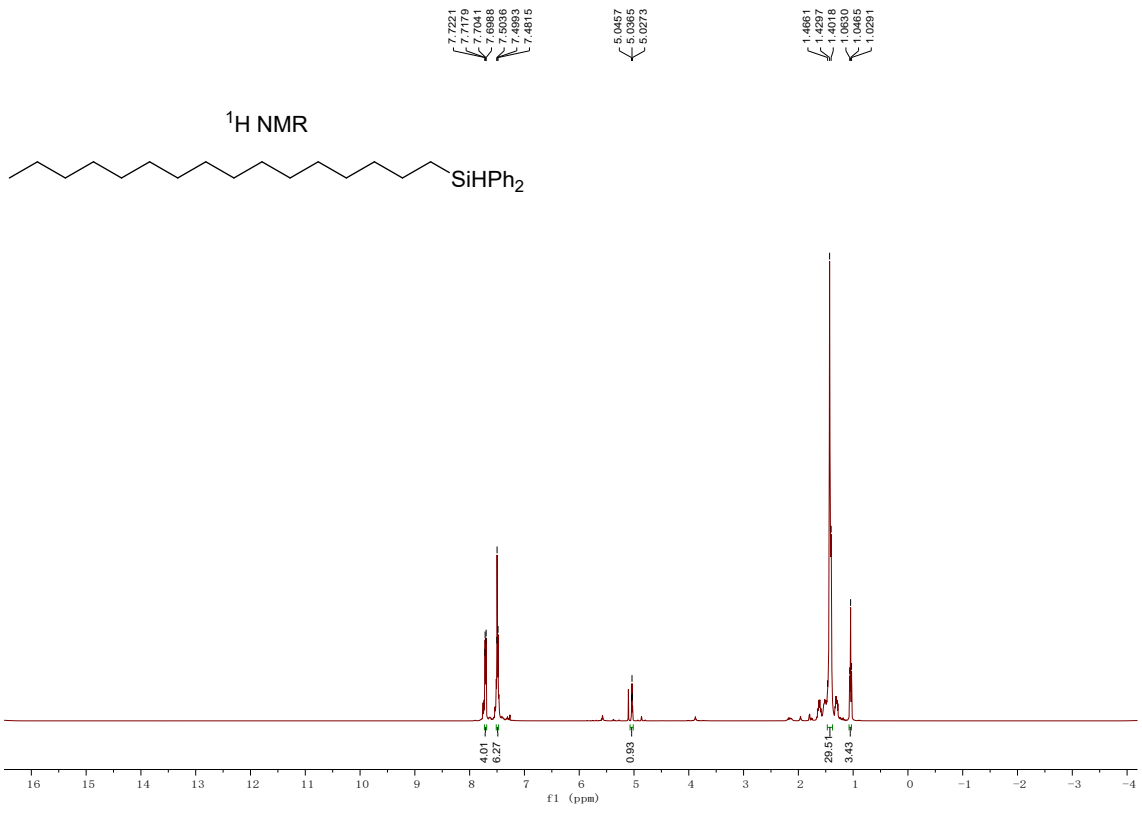
Tetradecenediphenylsilane: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 7.5, 1.7 Hz, 4H), 7.42 – 7.36 (m, 6H), 4.88 (t, *J* =3.7 Hz, 1H), 1.28 (m, *J* = 11.2 Hz, 26H), 0.92 (t, 6.5 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.62, 135.53, 135.17, 134.76, 134.40, 129.49, 127.97, 33.23, 31.98,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

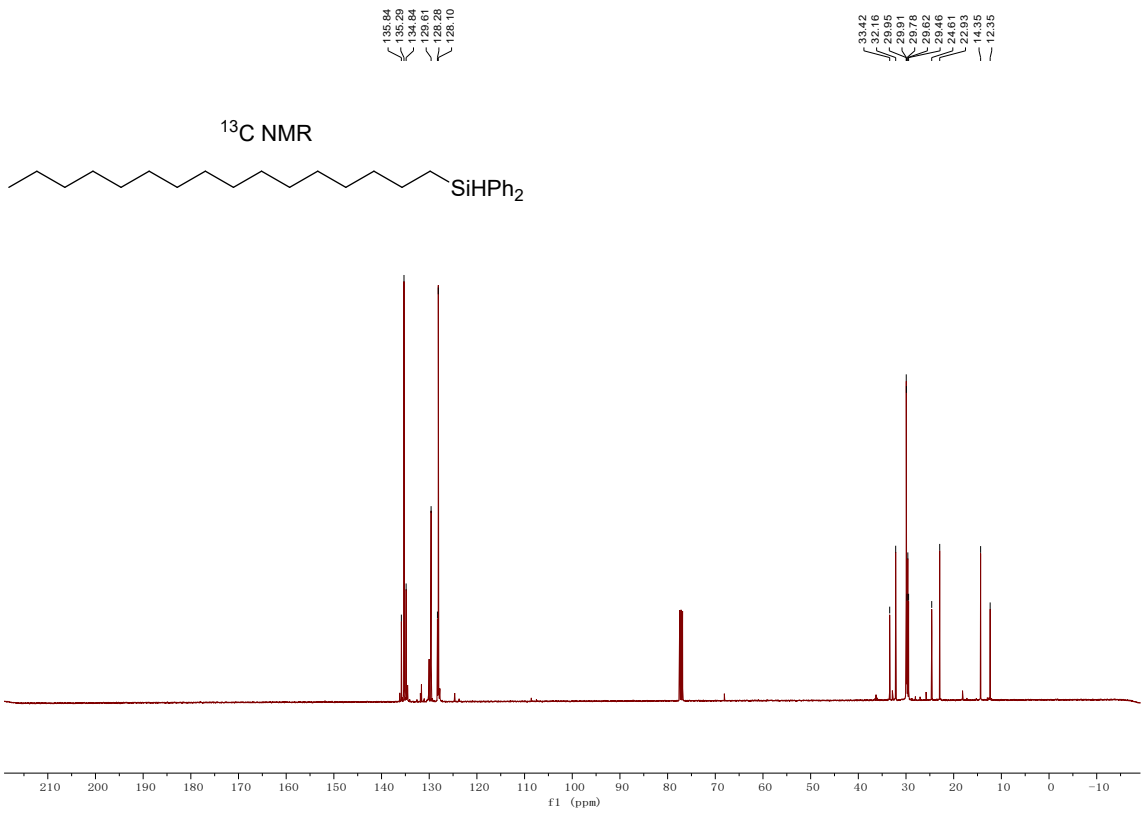




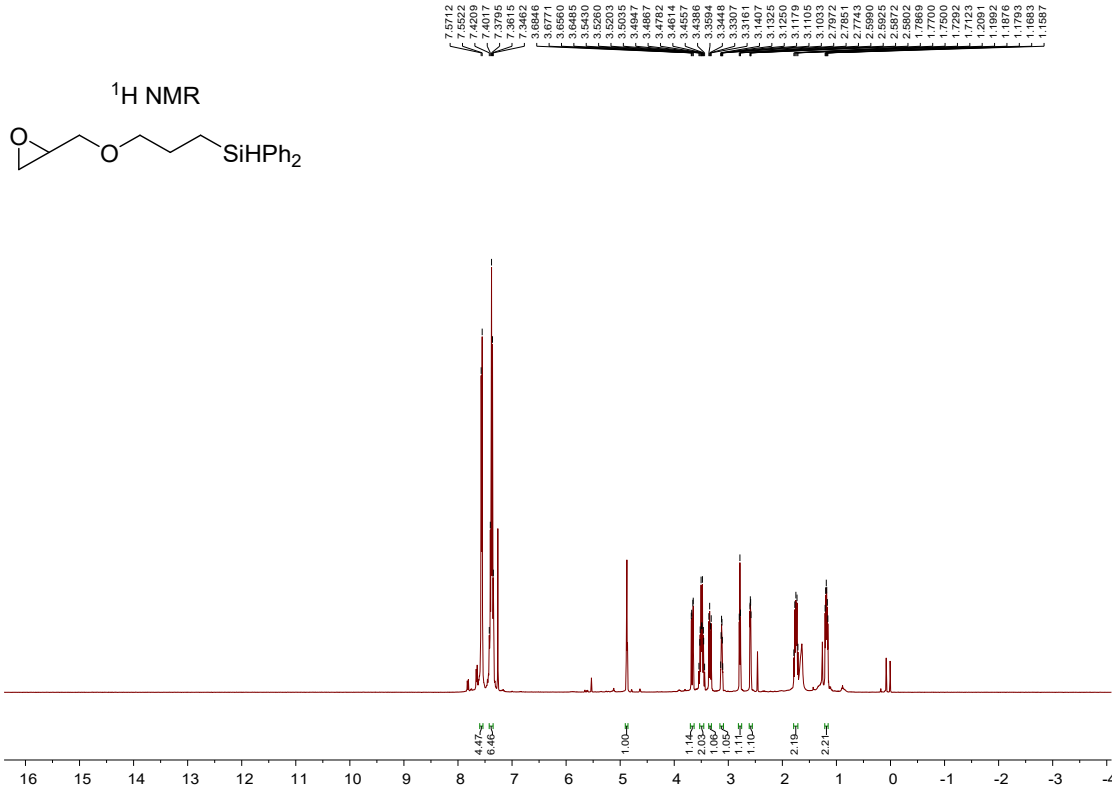


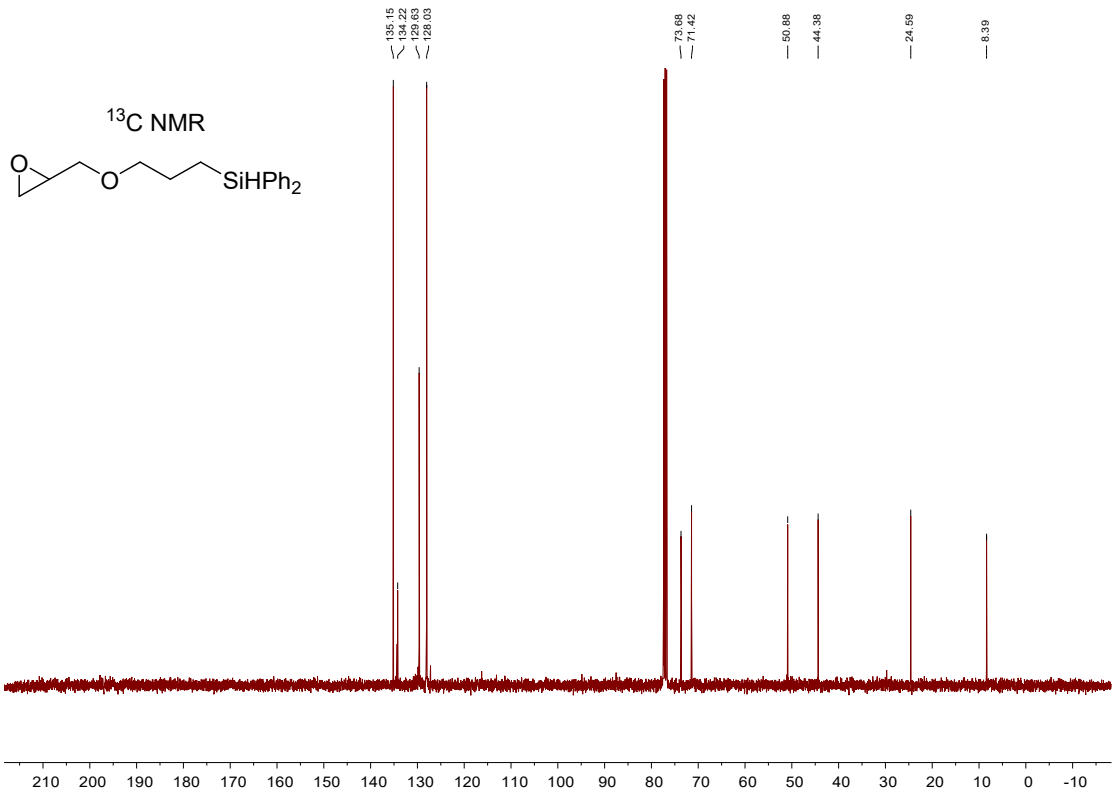
Hexadecyldiphenylsilane: ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm): 7.71 (dd, J = 7.4, 1.9 Hz, 4H), 7.49 (m, J = 4.4 Hz, 6H), 5.04 (t, J = 3.7 Hz, 1H), 1.42 (m, J = 11.2 Hz, 30H), 1.05 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm): 135.24, 134.81, 129.55, 128.04, 33.33, 32.08, 29.86,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



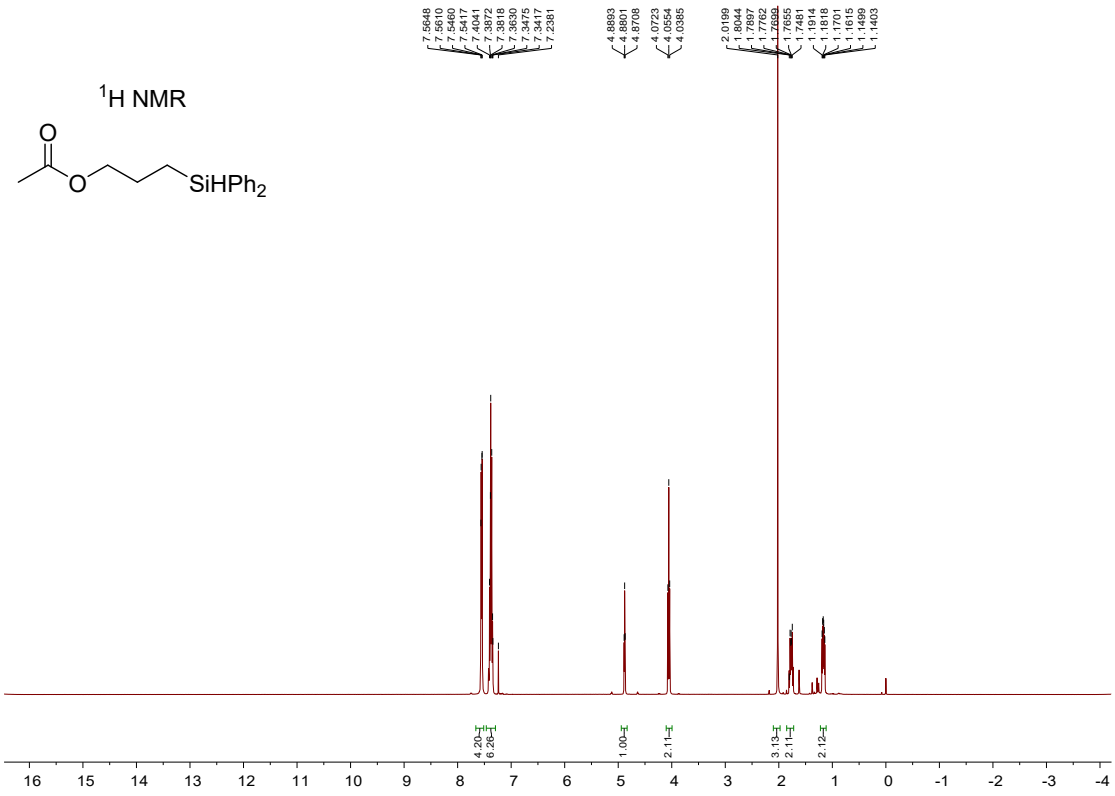


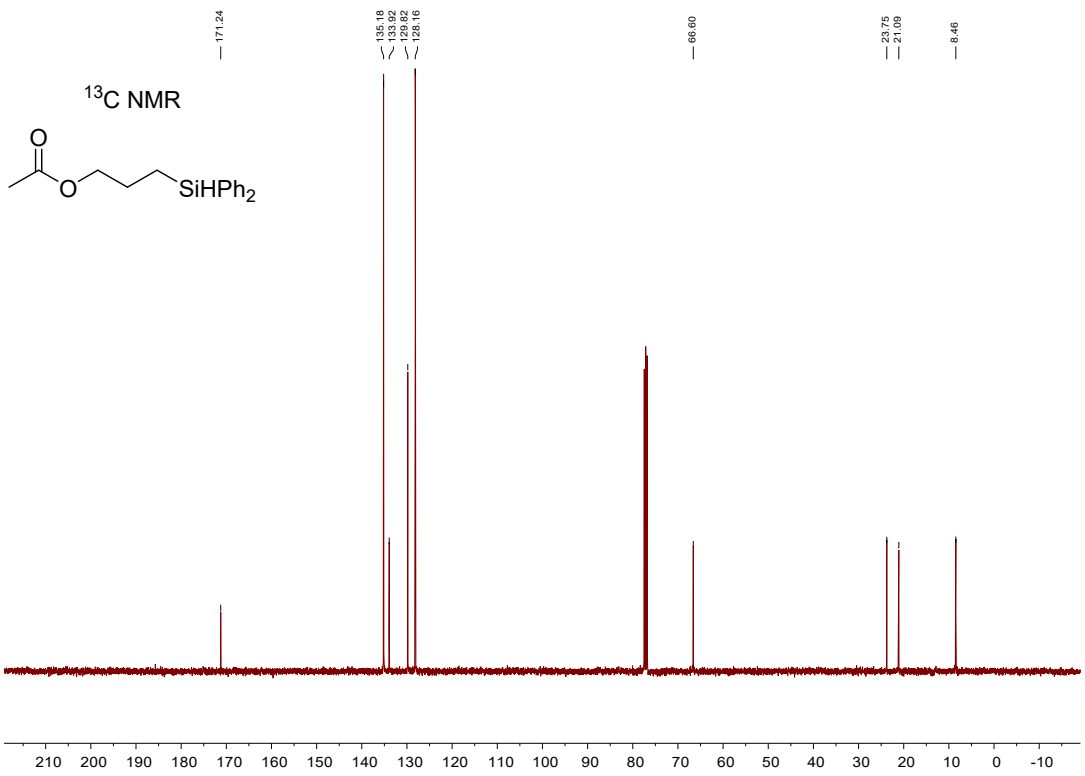
(3-(Oxiran-2-ylmethoxy)propyl)diphenylsilane：^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.6 Hz, 4H), 7.42-7.34 (m, 6H), 4.88 (t, *J* = 3.7 Hz, 1H), 3.67 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.53 – 3.45 (m, 2H), 3.34 (dd, *J* = 11.5, 5.8 Hz, 1H), 3.12 (m, 1H), 2.79 (t, *J* = 4.6 Hz, 1H), 2.59 (dd, *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.





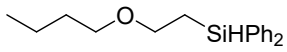
3-(Diphenylsilyl)propyl acetate：^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.6, 1.6 Hz, 4H), 7.46 – 7.29 (m, 6H), 4.88 (t, *J* = 3.7 Hz, 1H), 4.06 (t, *J* = 6.8 Hz, 2H), 2.02 (s, 3H), 1.85 – 1.72 (m, 2H), 1.22 – 1.12 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.24, 135.18, 133.92, 129.82,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

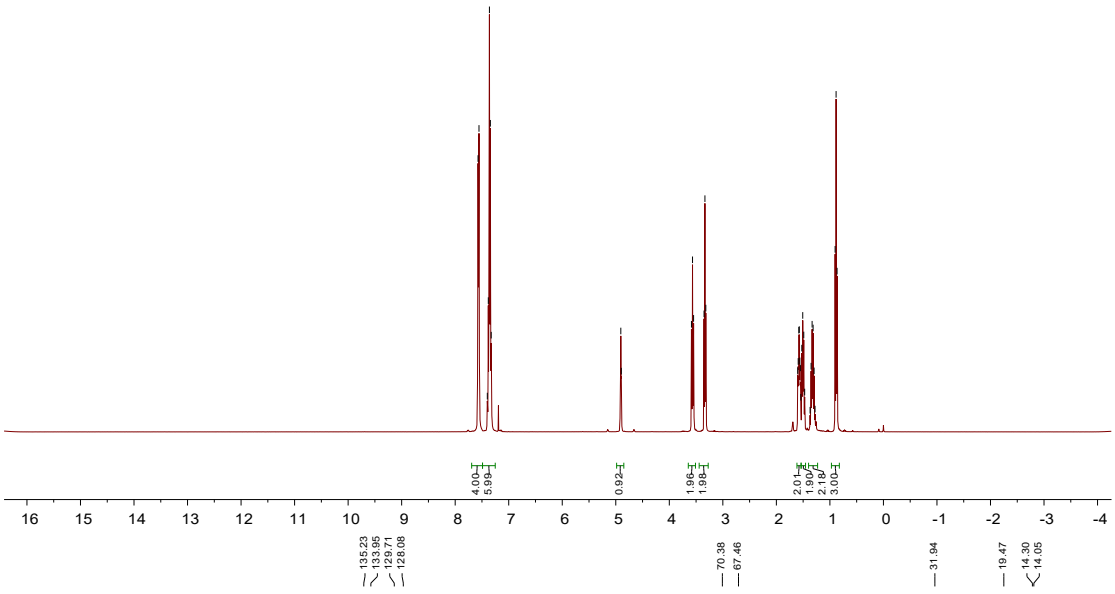




(2-Butoxyethyl)diphenylsilane: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.0 Hz, 4H), 7.36 (t, *J* = 7.7 Hz, 6H), 4.90 (t, *J* = 3.4 Hz, 1H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.33 (t, *J* = 6.6 Hz, 2H), 1.66 – 1.45 (m, 4H), 1.32 (m, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (101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

^{1}H NMR





^{13}C NMR