# Highly-active, graphene-supported platinum catalyst for the solventless hydrosilylation of olefins.

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## Supplementary Information

Table of Contents

## General Information

All commercially available reagents were purchased from Acros Organics, Sigma-Aldrich, TCI or Alfa Aesar and used as received. 1, 1, 1, 3, 5, 5, 5 heptamethyltrisiloxane was purchased from Synquest laboratories. Thin layered chromatography (TLC) was performed using silica gel 60 F254 plates. Proton nuclear magnetic resonance (1 H NMR) spectra and carbon nuclear magnetic resonance (13C NMR) spectra were recorded on a Bruker Ascend-600 MHz. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane. Chemical shifts for carbon are reported in parts per million (ppm) downfield from tetramethylsilane or referenced to residual solvent. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. High resolution mass spectra were obtained through the Virginia Commonwealth University Chemical and Proteomic Mass Spectrometry Core Facility using an Orbitrap Velos mass spectrometer from Thermo Electron Corporation. Pulse Chemisorption and Temperature Programmed Reduction experiments were performed using an AutoChem II 2920 from Micromeritics. X-ray diffraction analysis was performed at VCU in the Nanomaterials Core Characterization Facility using the PANalytical X'Pert Pro Diffractometer. The CEM Discover SP was used for the microwave reduction step.

## Preparation of Pt-GNP catalyst

The Pt-GNP catalyst was made using $K_2PtCl_4$ as the metal precursor and graphene nanoplatelets aggregates (GNP, Alfa Aesar) as the support. 2.05 mmol of $K_2PtCl_4$ was dissolved in DI water (1 L), the pH was adjusted to 3.25 using (HCl aq. or NaOH aq.), and then 2.5 grams of GNP was added to the solution. Uptake of platinum onto the GNP was determined via ICP-OES of the solution before and after addition of the GNP. After shaking for one hour (orbital shaker, 100 rpm), the solution was vacuum filtered, dried overnight at room temperature, and subsequently dried in a 100 $^0$C oven for 24 hours. The resulting, unreduced Pt-GNP catalyst was analyzed using temperature programmed reduction experiment to determine the minimum required temperature for reduction. Based on this data, the catalyst was microwaved for 10 minutes at a set temperature of 160 $^0$C in a CEM microwave to reduce the $PtCl^{4\ 2-}$ adsorbed onto GNP and thus obtain the final Pt-GNP catalyst. Reduction of $PtCl_4^{2-}$ was determined through several material characterization techniques including XRD, XPS, pulse chemisorption, and TEM.

## Pt-GNP Characterization

*BET Physical Adsorption.*

Physisorption for the GNP support was performed using a Micromeritics ASAP 2020 Plus. The surface area was measured to be 463.5 $m^2$/g.

*Temperature Programmed Reduction.*

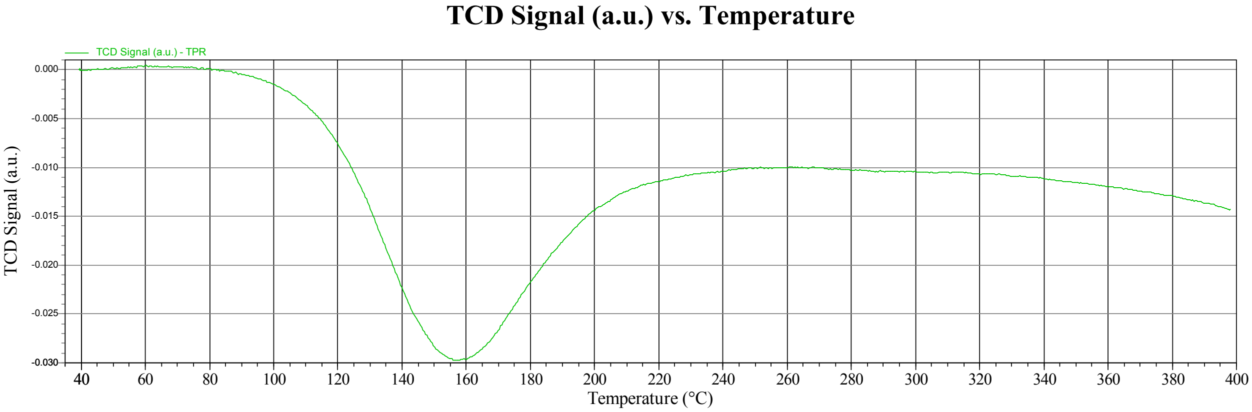


**Figure 1.** TPR plot of Pt-GNP catalyst. TPR results show that the Pt-GNP catalyst reduces around 160$^0$C.

Temperature Programmed Reduction on the unreduced Pt-GNP catalyst was performed using a Micromeritics AutoChem II. The sample was first pretreated with 50 cm$^3$/min of helium gas with a temperature ramp of 10 $^0$C/min to 120 $^0$C. The sample was then cooled to 40 $^0$C. The TPR experiment used 10% $H_2$-Ar as the carrier gas. The temperature was ramped up to 400 $^0$C at a rate of 5 $^0$C/min and the thermal conductivity detector signal was recorded every second."

*CEM Microwave.*

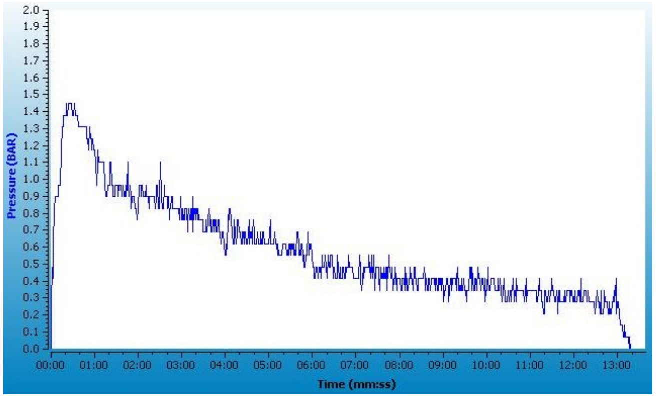


**Figure 2.** CEM recorded Pressure vs. Time graph during the microwave step.

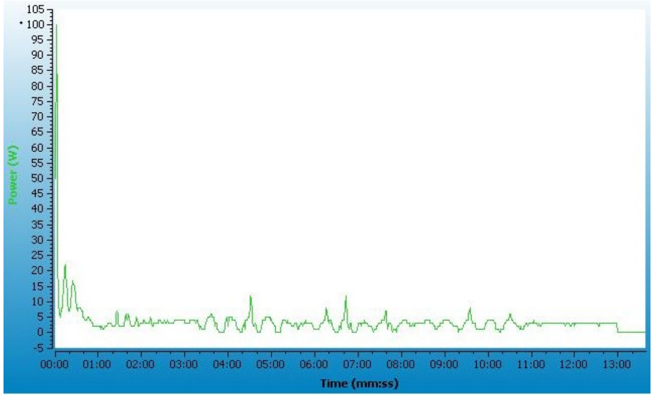


**Figure 3.** CEM recorded Power vs. Time graph during the microwave step.

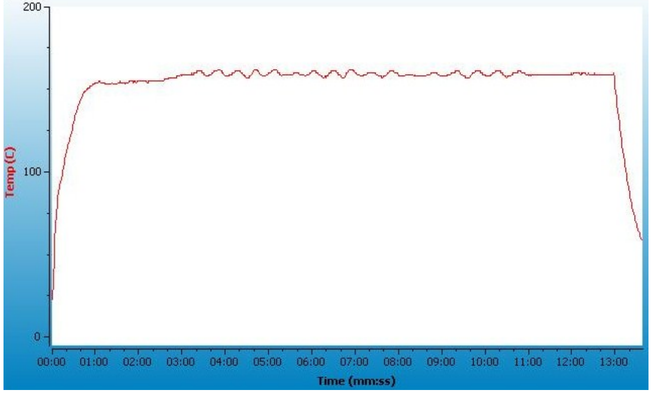


**Figure 4.** CEM recorded Temperature vs. Time graph during the microwave step.

## *X-ray Diffraction.*

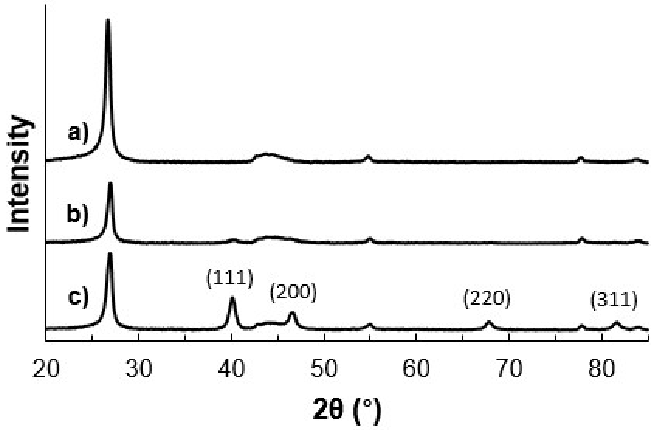


**Figure 5.** X-ray diffraction patterns for a) GNP support only, b) unreduced Pt-GNP, and c) microwaved Pt-GNP. The platinum crystal planes are labeled in c).

## *Pulse Chemisorption.*

**Table 1.** Pulse Chemisorption data for Pt-GNP

| | |
|---|---|
| Pt wt loading (%) | 3.52 |
| Cumulative Quantity (cm$^3$/g STP) | 0.39177 |
| Ns (# of active sites/g sample) | 7.02E+18 |
| Metal Dispersion (%) | 6.46 |
| Estimated Particle Diameter (nm) | 17.5 |

The cumulative quantity (cm$^3$/g STP) data from the pulse chemisorption experiment can be used to calculate the number of active sites per gram of catalyst using the following equations.

$$Cumulative\ Quantity = \frac{0.39177\ cm^3\ H_2}{g\ catalyst\ at\ STP}$$

$$\frac{\#\ molecules\ H_2}{g\ catalyst} = \frac{1\ atm \cdot \dfrac{0.39177 cm^3 H_2}{1000\dfrac{cm^3}{L} \cdot gram\ catalyst}}{0.08206\dfrac{L \cdot atm}{K \cdot mol} \cdot 273.15\ K} \cdot 6.022 \cdot 10^{23}\frac{molecules}{mol} = 1.05 \cdot 10^{19}$$

$$\frac{\#\ of\ active\ sites}{g\ catalyst} = \frac{\#\ molecules\ H_2}{g\ catalyst} \cdot stoichiometry\ factor = 1.05 \cdot 10^{19} \cdot 0.667 = 7.02 \cdot 10^{18}$$

Therefore, based on pulse chemisorption, Pt-GNP has $7.02 \cdot 10^{18}$ number of active sites per gram of catalyst.

*Platinum X-ray Photoelectron Spectroscopy.*

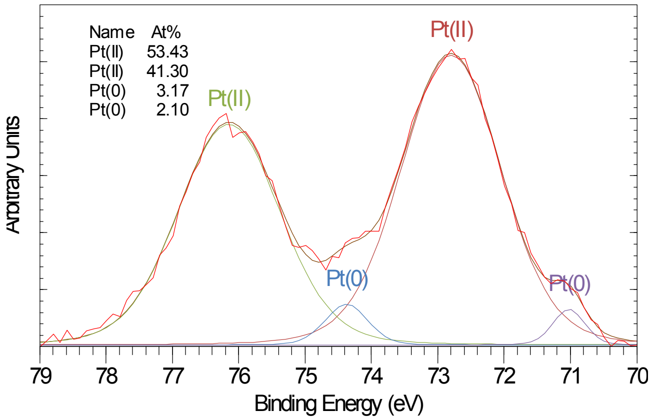


**Figure 6.** High resolution x-ray photoelectron spectroscopy Pt 4f spectrum of Pt-GNP catalyst before reaction.

## Experimental procedures for the evaluation of Pt-GNP.

*Batch hydrosilylation of 1-octene with MD'M.*

1-octene (2 mL, 12.7 mmol) was charged to an 8 mL reaction vial along with Pt-GNP(0.714 mg, 0.00125 mol%). MDM was charged (3.461 mL, 12.7 mmol) to the mixture and the reaction was heated to 40 $^0$C with magnetic stirring for 30 minutes. Pure product was isolated from Pt-GNP via vacuum filtration. $^1$H NMR (600 MHz, Chloroform-*d*) δ 1.46 – 1.06 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.52 – 0.34 (m, 2H), 0.08 (s, 18H), -0.01 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 33.51 , 32.20 , 29.60 , 29.53 , 23.32 , 22.96 , 17.88 , 14.38 , 2.11 .

*Turnover number and turnover frequency determination.*

Turnover number (TON) and turnover frequency (TOF) were determined for both Pt-GNP and Karstedt's catalyst. In order to determine TON, $3.6809*10^{-7}$ moles of Pt were charged to a 1:1 molar solution of 1-octene and MDM, and samples were taken every 30 minutes. The reaction was run at 40 $^0$C. If the conversion of 1-octene was determined to be 100%, more of the 1:1 molar solution of 1-octene and MDM would be charged. This was repeated until two consecutive samples resulted in the same conversion of 1-octene, which indicated the lifetime of the catalyst had been reached. For Pt-GNP, 0.368 micromoles Pt resulted in a 71.4% conversion of 1-octene in a 109.2 mL of a 1:1 molar solution of 1-octene and MDM. For Karstedt's catalyst, 3.59 µL of catalyst resulted in a 55% conversion of 1-octene in 271 mL of a 1:1 molar solution of 1-octene and MDM. A sample TON calculation is shown below. It was assumed that all of the Karstedt's catalyst Pt was active.

Pt-GNP

$$TON = \frac{moles\ of\ 3}{moles\ of\ active\ sites\ of\ catalyst} = \frac{0.182\ moles\ of\ 3}{1.93 \cdot 10^{-8}\ moles\ of\ actives\ sites\ of\ catalyst}$$

Pt-GNP $TON = 9{,}432{,}471$

TOF was determined by running a reaction with 0.00125 mol% catalyst at 40 $^0$C and obtaining an aliquot at a time point where the conversion is measurably less than 100%. For Pt-GNP, a sample at 8 minutes resulted in a 1-octene conversion of 41.84% of 5.461 mL of a 1:1 molar solution of 1-octene and MDM. For Karstedt's catalyst, a sample at 0.5 minutes resulted in a 1-octene conversion of 55% of 12.623 mL of a 1:1 molar solution of 1-octene and MDM. A sample TOF calculation is shown below.

Pt-GNP $TOF$

$$= \frac{moles\ of\ 3}{moles\ of\ active\ sites\ of\ catalyst \cdot time} = \frac{0.00533\ moles\ of\ 3}{8.32 \cdot 10^{-8}\ moles\ active\ sites\ of\ ca}$$

Pt-GNP $TOF = 4{,}802{,}484\ hr^{-1}$

*Continuous hydrosilylation of 1-octene with MD'M.*

The packed bed reactor was assembled through the modification of the Catalyst Cartridge system produced by Thales Nano. Empty catalyst cartridges were loaded firstly with 50 mg glass beads (0.5 mm, Sigma-Aldrich), followed by a mixture of 100 mg Pt-GNP and 400 mg glass beads and lastly, 200 mg of glass beads. Cartridges were sealed using both Teflon frits (1.5 μm). This cartridge was loaded onto a custom heating mantle, which is outfitted with a thermocouple to heat via conventional hot plate (IKA). Solutions were delivered to the packed bed system by an HPLC pump (SSI, LS-Class).

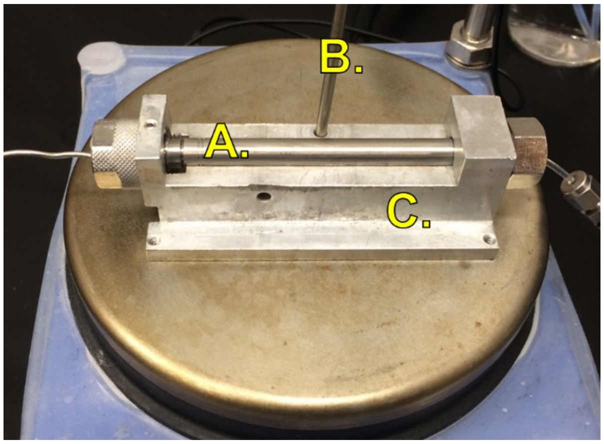


**Figure 7.** Packed bed reactor system. A: Thales Nano CatCart filled with Pt-GNP/glass beads, B: IKA thermocouple fitted to C: heating mantle ThalesNano.

An equimolar mixture of 1-octene and MDM were delivered to the reactor, preheated to 40 $^0$C, by this pump as product was collected in 40 min fractions at the outlet.

*General method for hydrosilylation of olefins for substrate evaluation.*

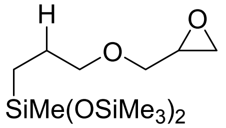
To a 4 mL reaction vial outfitted with a magnetic stir bar was charged Pt-GNP (12.4 mg, 0.05 mol%) and olefin. Silane was charged to the reaction mixture and the reaction was stirred in a heating mantle (2 hrs). To quench the reaction, product was filtered via syringe filter. Product purity was assigned by HNMR, using mesitylene as an internal standard.

## Compound Characterization.

*3. 1,1,1,3,5,5,5-heptamethyl-3-(3-(oxiran-2-ylmethoxy)propyl)trisiloxane.*

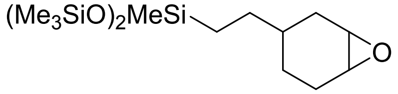
**$^{1}$H NMR (600 MHz, Chloroform-*d*)** δ 1.27 (d, *J* = 14.8 Hz, 12H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.52 – 0.37 (m, 2H), 0.08 (s, 18H), -0.01 (s, 3H). **$^{13}$C NMR (151 MHz, Chloroform-*d*)** δ 33.36 , 32.04 , 29.44 , 29.37 , 23.16 , 22.80 , 17.72 , 14.23 , 1.96 , -0.17. Spectra were recorded in agreement with previously reported data.

*6ab. 1,1,1,3,5,5,5-heptamethyl-3-(3-(oxiran-2-ylmethoxy)propyl)trisiloxane.*



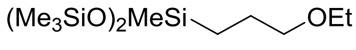
**$^{1}$H NMR (600 MHz, Chloroform-*d*)** δ 3.68 (dd, *J* = 11.5, 3.1 Hz, 1H), 3.52 – 3.27 (m, 3H), 2.80 – 2.71 (m, 1H), 2.59 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.66 – 1.57 (m, 2H), 0.56 – 0.36 (m, 2H), 0.08 (s, 18H), 0.01 (s, 3H). **$^{13}$C NMR (151 MHz, Chloroform-*d*)** δ 74.30 , 71.47 , 50.94 , 44.41 , 23.35 , 13.57 , 1.91 , -0.31. Spectra were recorded in agreement with previously reported data.[1]

*6ac. 3-(2-(7-oxabicyclo[4.1.0]heptan-3-yl)ethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane.*



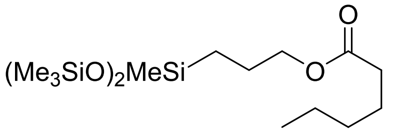
**$^{1}$H NMR (600 MHz, Benzene-$d_6$)** δ 2.93 – 2.79 (m, 4H), 2.11 – 2.04 (m, 1H), 1.97 (dt, *J* = 16.0, 1.8 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.66 – 1.60 (m, 1H), 1.49 (dtd, *J* = 10.9, 6.9, 4.2 Hz, 1H), 1.43 – 1.32 (m, 3H), 1.30 – 1.16 (m, 6H), 1.01 (ddd, *J* = 14.5, 10.4, 2.1 Hz, 1H), 0.97 – 0.86 (m, 1H), 0.65 (dtd, *J* = 13.0, 11.5, 6.5 Hz, 1H), 0.57 – 0.42 (m, 5H), 0.18 (d, *J* = 4.1 Hz, 36H), 0.13 (d, *J* = 4.1 Hz, 7H). Spectra were recorded in agreement with previously reported data.[2]

*6ad. 3-(3-ethoxypropyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane*



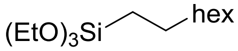
Product was isolated from crude product mixture by normal phase liquid chromatography (20% EtOAc/hexanes). **$^{1}$H NMR (600 MHz, Chloroform-*d*)** δ 3.56 – 3.42 (m, 2H), 3.36 (t, *J* = 6.9 Hz, 2H), 1.60 (td, *J* = 16.1, 14.7, 8.7 Hz, 2H), 1.20 (t, *J* = 6.7 Hz, 3H), 0.54 – 0.33 (m, 2H), 0.08 (s, 18H), 0.01 (s, 3H). **13C NMR (151 MHz, Chloroform-d)** δ 73.54, 66.10, 23.49, 15.41, 13.74, 1.99, -2.23 . **HRMS ESI/[M+Na]$^+$** *m/z* calcd. for $C_{12}H_{32}O_3Si_3Na$: 331.1557, found: 331.1554.

*6ae. 3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propyl hexanoate.*



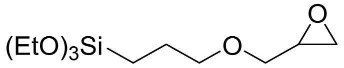
Product was isolated from crude product mixture by normal phase liquid chromatography (20% EtOAc/hexanes). **$^1$H NMR (600 MHz, Chloroform-*d*)** δ 4.01 (t, *J* = 6.7 Hz, 2H), 2.05 (s, 4H), 1.62 (s, 2H), 0.53 – 0.39 (m, 2H), 0.24 (s, 1H), 0.12 (s, 9H), 0.09 (s, 18H), 0.02 (s, 3H). **$^{13}$C NMR (151 MHz, Chloroform-*d*)** δ 171.39 , 67.09 , 23.05 , 22.65 , 21.23 , 13.69 , 2.04 , 1.69 , -0.18 , -2.63. **HRMS ESI/[M+Na]$^+$** *m/z* calcd. for $C_{16}H_{38}O_4Si_3Na$: 401.1976, found: 401.1918.

*6ba. Triethoxy(octyl)silane*



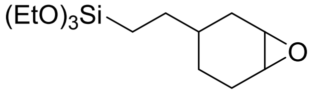
**$^1$H NMR (600 MHz, Chloroform-*d*)** δ 3.84 (q, *J* = 7.0 Hz, 6H), 1.43 (2H, m), 1.36 – 1.27 (m, 10H), 1.25 (t, *J* = 7.0 Hz, 9H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.70 – 0.60 (m, 2H). **$^{13}$C NMR (151 MHz, Chloroform-*d*)** δ 58.41, 33.34, 32.04, 29.35, 22.88, 22.81, 18.43, 14.24, 10.50 Spectra were recorded in agreement with previously reported data.[3]

*6bb. Triethoxy(3-(oxiran-2-ylmethoxy)propyl)silane.*



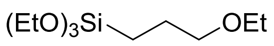
**$^1$H NMR (600 MHz, Chloroform-*d*)** δ 3.82 (q, *J* = 7.0 Hz, 6H), 3.69 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.52 – 3.41 (m, 2H), 3.38 (dd, *J* = 11.5, 5.8 Hz, 1H), 3.16 – 3.10 (m, 1H), 2.78 (t, *J* = 4.6 Hz, 1H), 2.59 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.71 (q, *J* = 15.5, 11.2 Hz, 2H), 1.63 – 1.51 (m, 1H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.72 – 0.59 (m, 2H). **$^{13}$C NMR (151 MHz, Chloroform-*d*)** δ 73.88 , 71.50 , 58.48 , 50.99 , 44.44 , 23.14 , 18.42 , 6.57. Spectra were recorded in agreement with previously reported data.[3]

*6bc. (2-(7-oxabicyclo[4.1.0]heptan-3-yl)ethyl)triethoxysilane.*



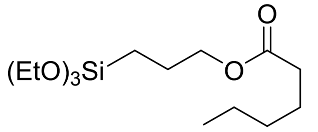
**$^1$H NMR (600 MHz, Chloroform-*d*)** δ 3.79 (q, *J* = 7.0 Hz, 7H), 3.23 – 3.03 (m, 2H), 2.23 – 2.09 (m, 1H), 2.09 – 1.92 (m, 1H), 1.80 (d, *J* = 33.4 Hz, 1H), 1.73 – 1.45 (m, 3H), 1.21 (t, *J* = 7.0 Hz, 12H), 0.66 – 0.50 (m, 2H). **$^{13}$C NMR (151 MHz, Chloroform-*d*)** δ 58.90 , 58.02 , 52.99 , 52.48 , 51.74 , 34.95 , 31.96 , 31.16 , 30.03 , 29.32 , 28.76 , 26.37 , 25.07 , 23.66 , 23.30 , 20.94 , 18.05 , 17.86 , 7.21 , 7.07. Spectra were recorded in agreement with previously reported data.[3-4]

*6bd. Triethoxy(3-ethoxypropyl)silane.*



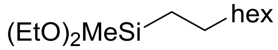
**$^1$H NMR (600 MHz, Chloroform-*d*)** δ 3.84 (q, *J* = 7.0 Hz, 6H), 1.43 (2H, m), 1.36 – 1.27 (m, 10H), 1.25 (t, *J* = 7.0 Hz, 9H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.70 – 0.60 (m, 2H). **$^{13}$C NMR (151 MHz, Chloroform-*d*)** δ 73.05 , 66.08 , 58.47 , 23.18 , 18.42 , 15.36 , 6.64 . Spectra were recorded in agreement with previously reported data.[3]

*6be. 3-(triethoxysilyl)propyl hexanoate.*



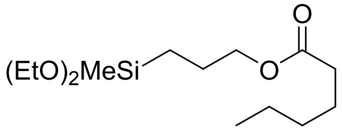
**$^1$H NMR (600 MHz, Chloroform-*d*)** δ 4.04 (t, *J* = 6.8 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 1.74 (dt, *J* = 15.6, 6.9 Hz, 2H), 1.62 (p, *J* = 7.6 Hz, 2H), 1.37 – 1.26 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 12H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.70 – 0.58 (m, 2H). **$^{13}$C NMR (151 MHz, Chloroform-*d*)** δ 173.86 , 66.25 , 58.37 , 34.29 , 31.31 , 24.68 , 22.31 , 22.22 , 18.25 , 13.87 , 6.51. Spectra were recorded in agreement with previously reported data.[1]

*6ca. Diethoxy(methyl)(octyl)silane*



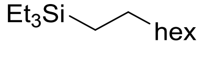
$^1$H NMR (600 MHz, Chloroform-d) δ 3.75 (q, J = 7.0 Hz, 4H), 1.37 – 1.24 (m, 12H), 1.21 (t, J = 7.0 Hz, 6H), 0.87 (t, J = 7.0 Hz, 3H), 0.65 – 0.58 (m, 2H), 0.10 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-d) δ 58.23, 33.53, 32.12, 29.48, 29.44, 23.05, 22.88, 18.60, 14.31, 14.00, -4.69. Spectra were recorded in agreement with previously reported data.[3]

*6ce. 3-(diethoxy(methyl)silyl)propyl hexanoate.*



**1H NMR (600 MHz, Chloroform-*d*)** δ 4.04 (t, *J* = 6.9 Hz, 2H), 3.77 (q, *J* = 7.0 Hz, 4H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.66 (ddt, *J* = 41.8, 14.8, 7.2 Hz, 4H), 1.40 – 1.15 (m, 12H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.69 – 0.56 (m, 2H), 0.13 (s, 3H). **13C NMR (151 MHz, Chloroform-*d*)** δ 174.08 , 66.63 , 55.83 , 34.53 , 31.53 , 24.90 , 22.52, 21.37 , 18.57 , 14. 09 , 10.13, -4.77. Spectra were recorded in agreement with previously reported data.[1]

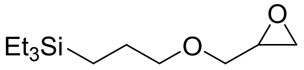
*6da. Triethyl(octyl)silane*



Product was isolated from crude product mixture by normal phase liquid chromatography (10% EtOAc/hexanes). $^1$H NMR (600 MHz, Benzene-$d_6$) δ 1.39 – 1.24

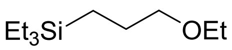
(m, 12H), 0.99 (t, *J* = 8.0 Hz, 9H), 0.92 (t, *J* = 6.9 Hz, 3H), 0.55 (q, *J* = 8.0 Hz, 8H).$^{13}$C NMR (151 MHz, Chloroform-*d*) δ 34.88, 32.67, 30.27, 30.19, 24.82, 23.60, 14.77, 12.20, 8.26, 4.21 . Spectra were recorded in agreement with previously reported data.[5]

*6db. Triethyl(3-(oxiran-2-ylmethoxy)propyl)silane.*



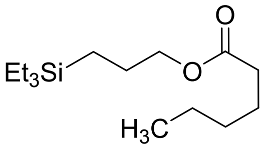
Product was isolated from crude product mixture by normal phase liquid chromatography (20% EtOAc/hexanes). **$^1$H NMR (600 MHz, Chloroform-*d*)** δ 3.71 (m, *J* = 11.5 Hz, 1H), 3.60 – 3.30 (m, 3H), 3.15 (m, 1H), 2.80 (m, 1H), 2.61 (m, 1H), 1.59 (m, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.60 – 0.38 (m, 8H). **$^{13}$C NMR (151 MHz, Chloroform-*d*)** δ 74.97 , 71.66 , 51.11 , 44.61 , 24.26 , 7.64 , 7.38 , 3.46. **HRMS ESI/[M+Na]$^+$** *m/z* calcd. for $C_{12}H_{26}O_2SiNa$: 253.1600, found: 253.1560.

*6dd. (3-ethoxypropyl)triethylsilane*



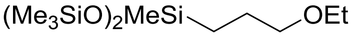
**$^1$H NMR (600 MHz, Chloroform-*d*)** δ 3.55 – 3.42 (q, *J* = 7.0, 6.3 Hz, 2H), 3.41 – 3.31 (t, *J* = 7.2 Hz, 2H), 1.67 – 1.46 (m, 2H), 1.20 (t, *J* = 6.7 Hz, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.50 (m, 8H). **$^{13}$C NMR (151 MHz, Chloroform-*d*)** δ 74.09, 66.14, 24.27, 15.41, 7.57, 7.36, 3.40. **HRMS ESI/[M+Na]$^+$** *m/z* calcd. for $C_{11}H_{26}OSiNa$: 225.1651, found: 253.1901.

*6de. 3-(triethylsilyl)propyl hexanoate.*

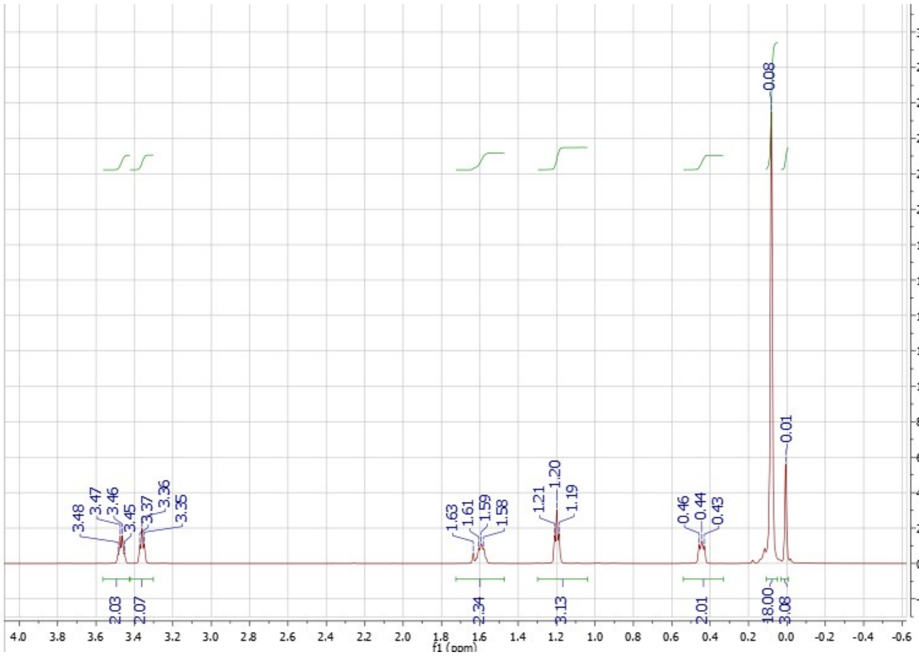


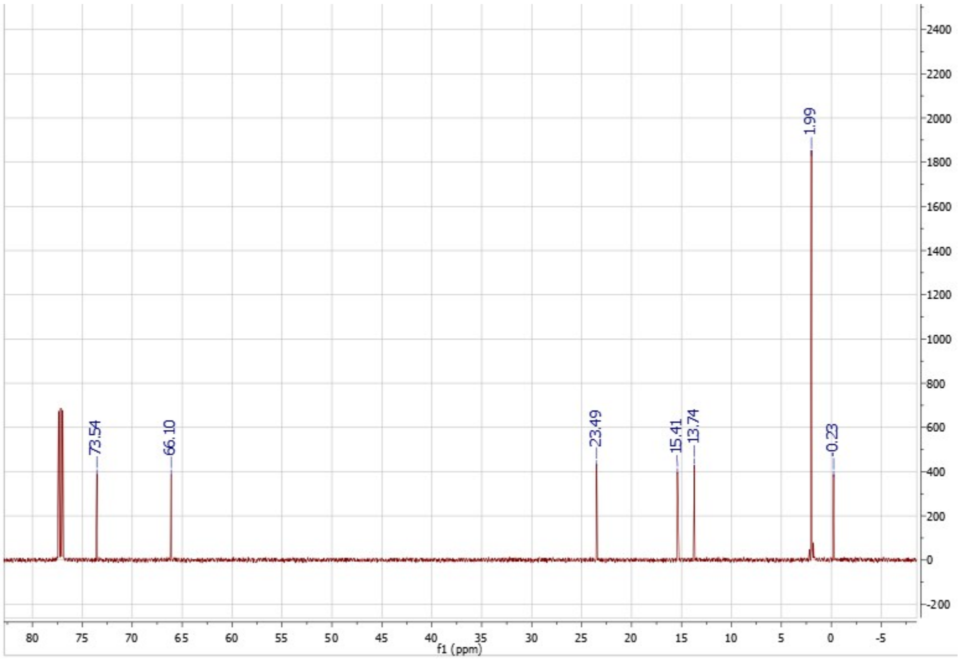
Product was isolated from crude product mixture by normal phase liquid chromatography (20% EtOAc/hexanes). **1H NMR (600 MHz, Chloroform-*d*)** δ 4.14 – 3.90 (t, J = 6.8 Hz, 2H), 2.47 – 2.12 (t, J = 7.8 Hz, 2H), 1.62 (m, 4H), 1.31 (m, 4H), 0.93 (td, *J* = 23.0, 19.7, 9.8 Hz, 12H), 0.82 – 0.43 (m, 8H). 13C NMR **(151 MHz, Chloroform-*d*)** δ 173.97 , 67.05 , 34.39 , 31.34 , 24.73 , 23.23 , 22.34 , 13.91 , 7.39 , 3.19. **HRMS ESI/[M+Na]$^+$** *m/z* calcd. for $C_{15}H_{32}O_2SiNa$: 295.2069, found: 295.2029.

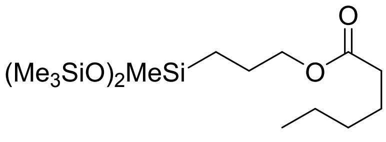
## NMR Spectra



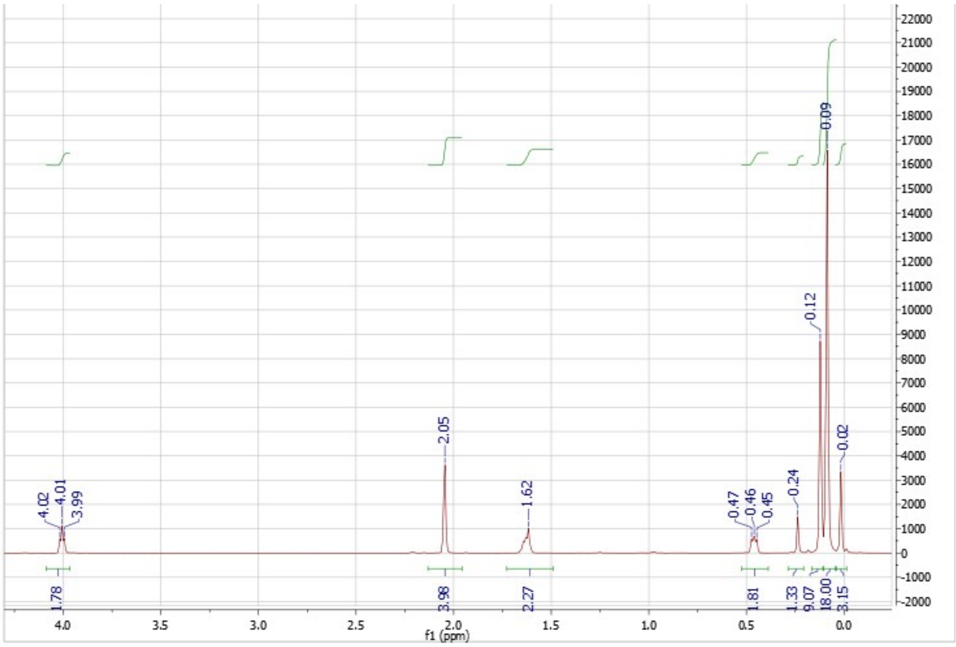
**6ad**

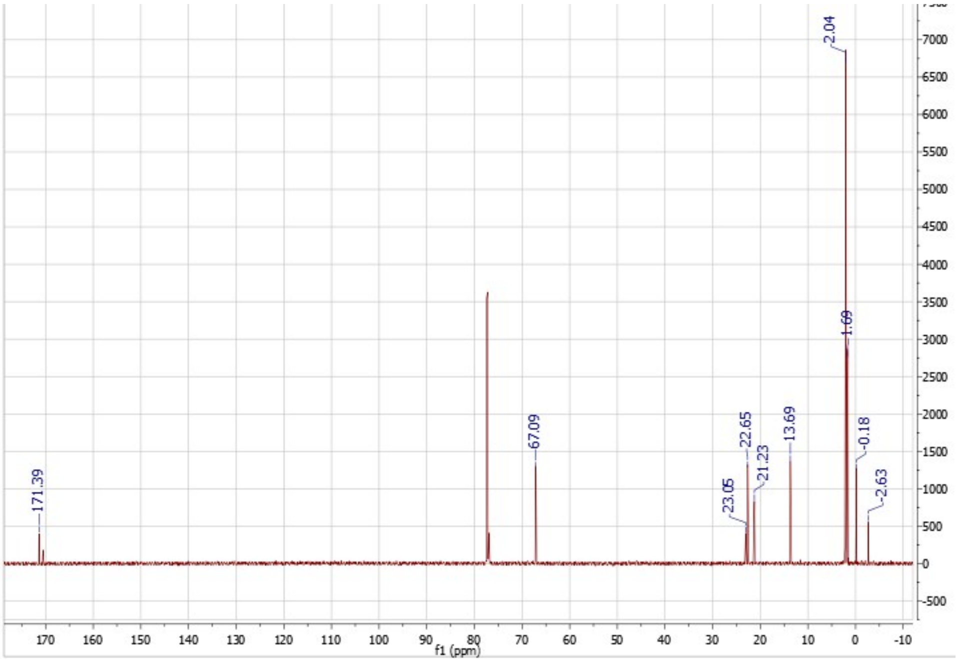


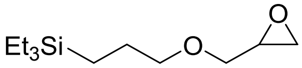



(Me3SiO)2MeSi
O
O

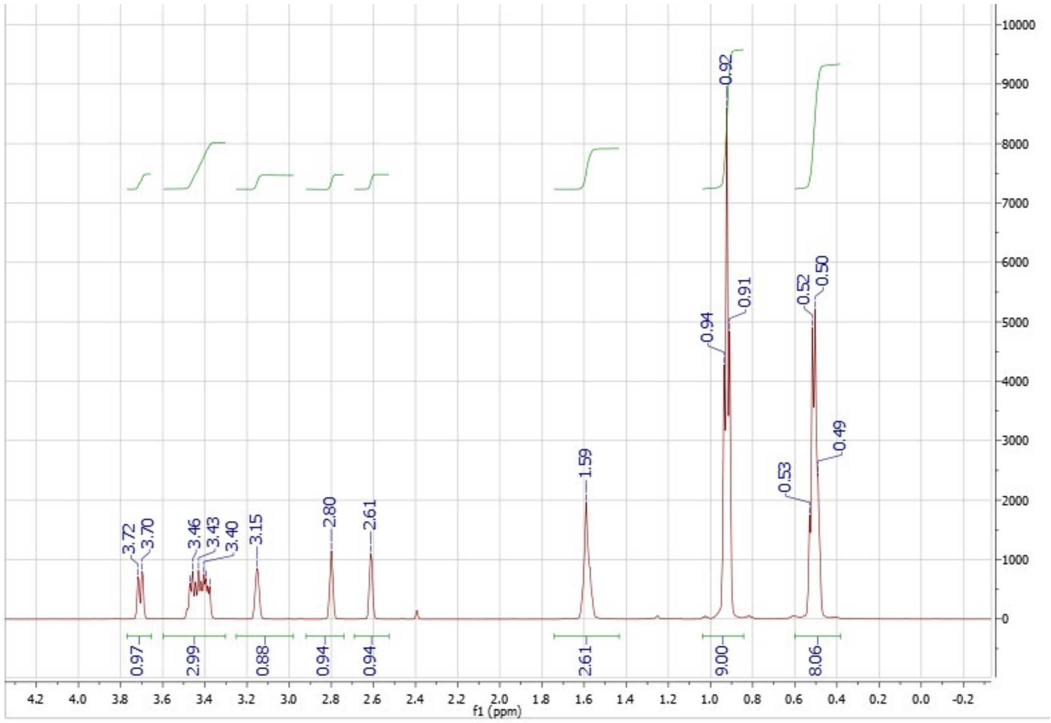
**6ae**

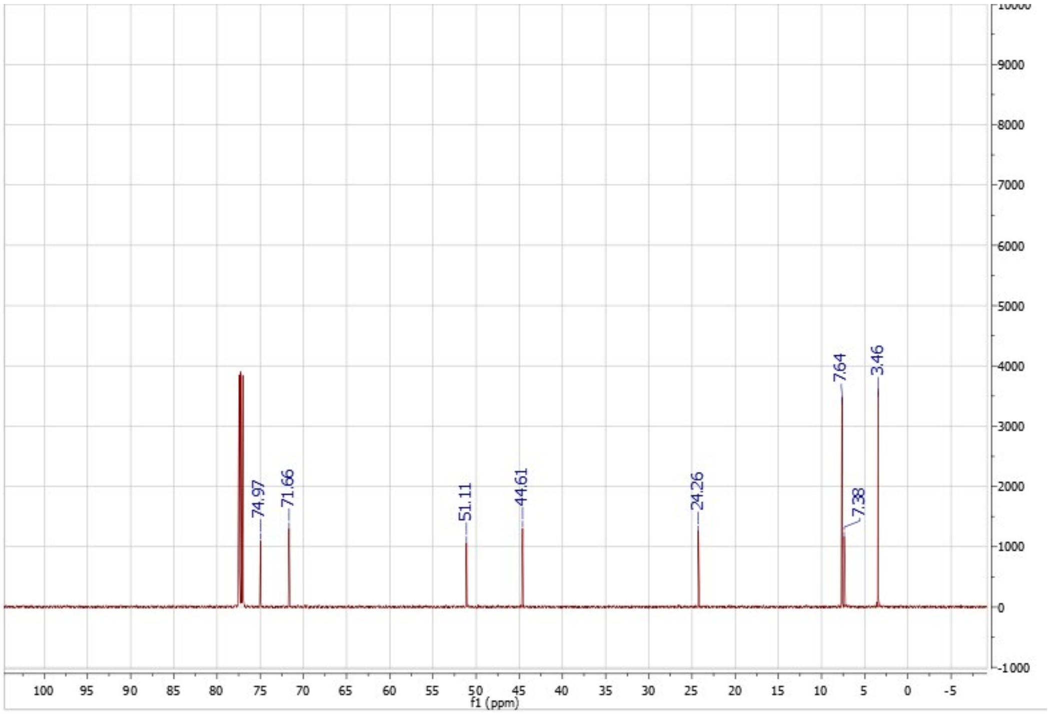

4.02
4.01
3.99
2.05
1.62
0.47
0.46
0.45
0.24
0.12
0.09
0.02
1.78
3.98
2.27
1.81
1.33
9.07
18.00
3.15
f1 (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

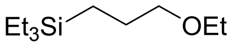

171.39
67.09
23.05
22.65
21.23
13.69
2.04
1.69
-0.18
-2.63
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


Et$_3$Si
O
O

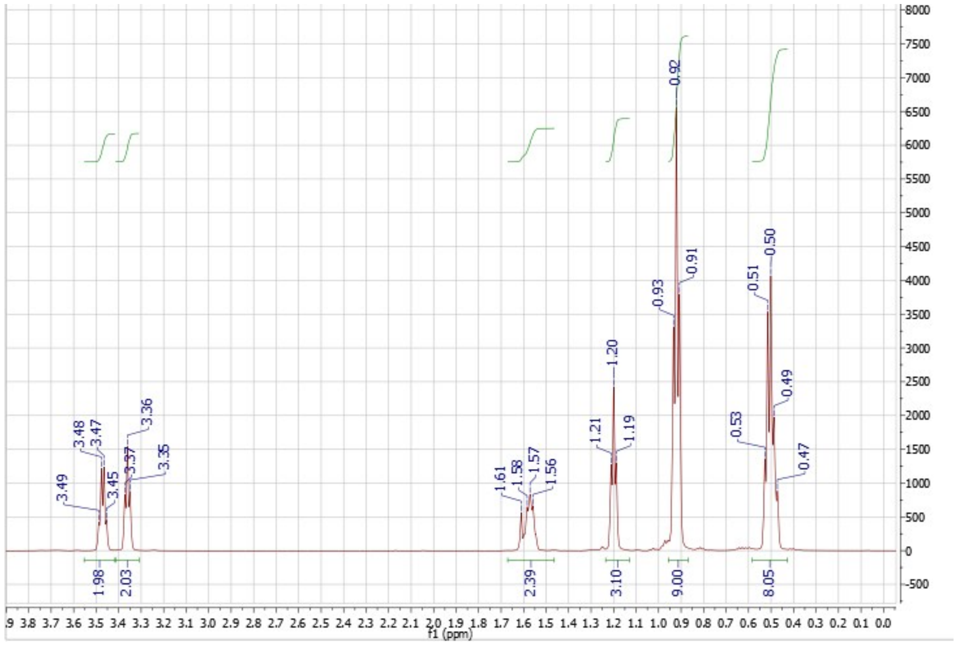
**6db**

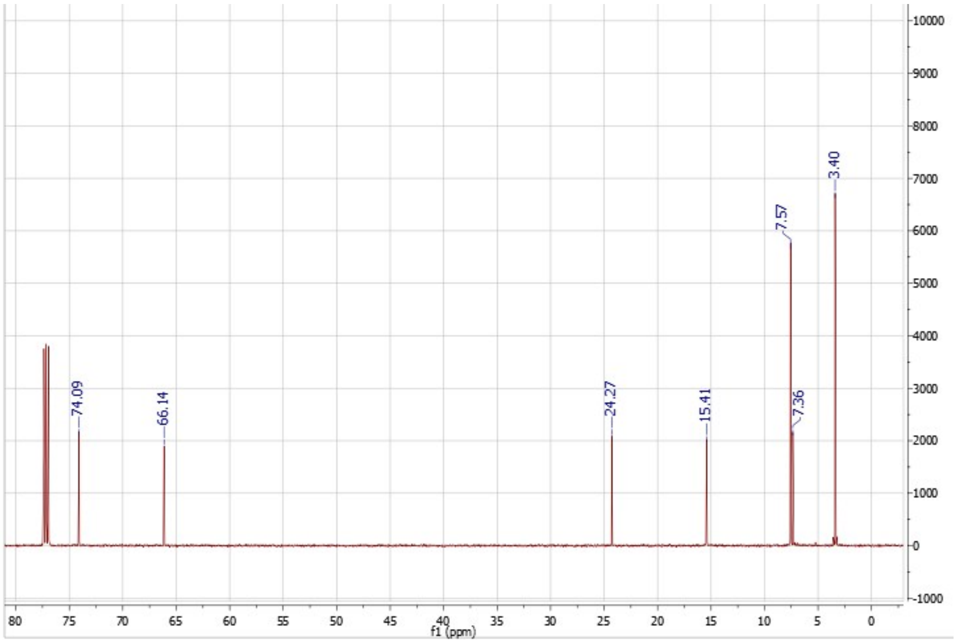

3.72
3.70
3.46
3.43
3.40
3.15
2.80
2.61
1.59
0.94
0.92
0.91
0.53
0.52
0.50
0.49
0.97
2.99
0.88
0.94
0.94
2.61
9.00
8.06
4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

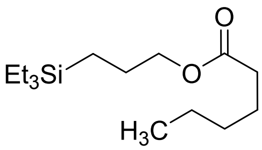

74.97
71.66
51.11
44.61
24.26
7.64
7.38
3.46
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


Et3Si
OEt

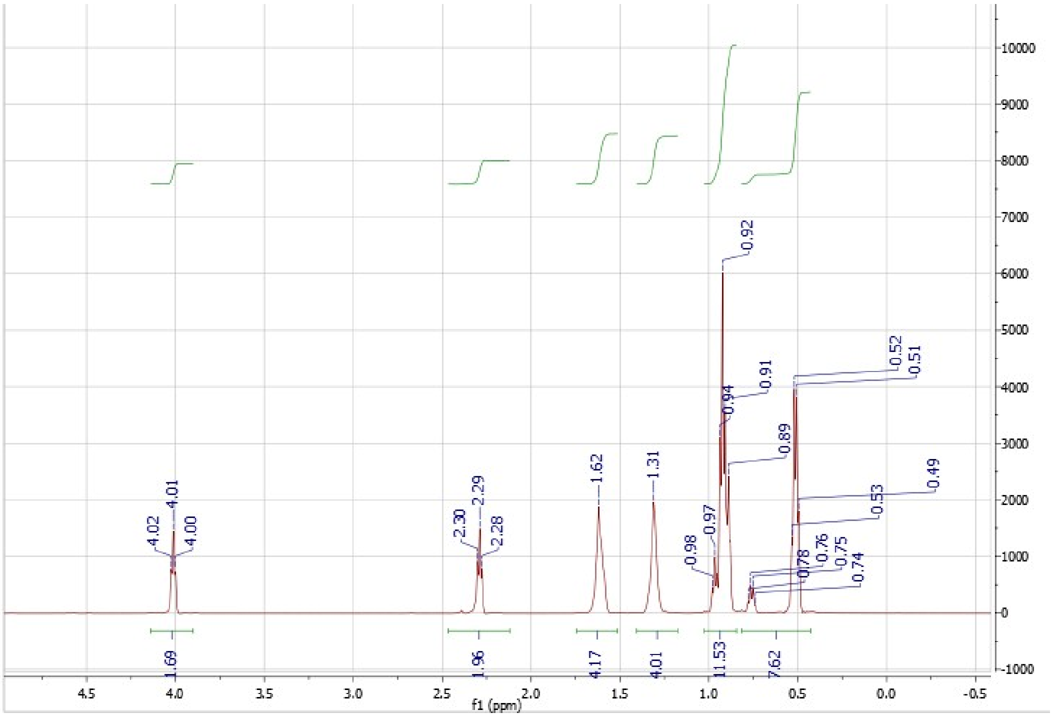
**6dd**

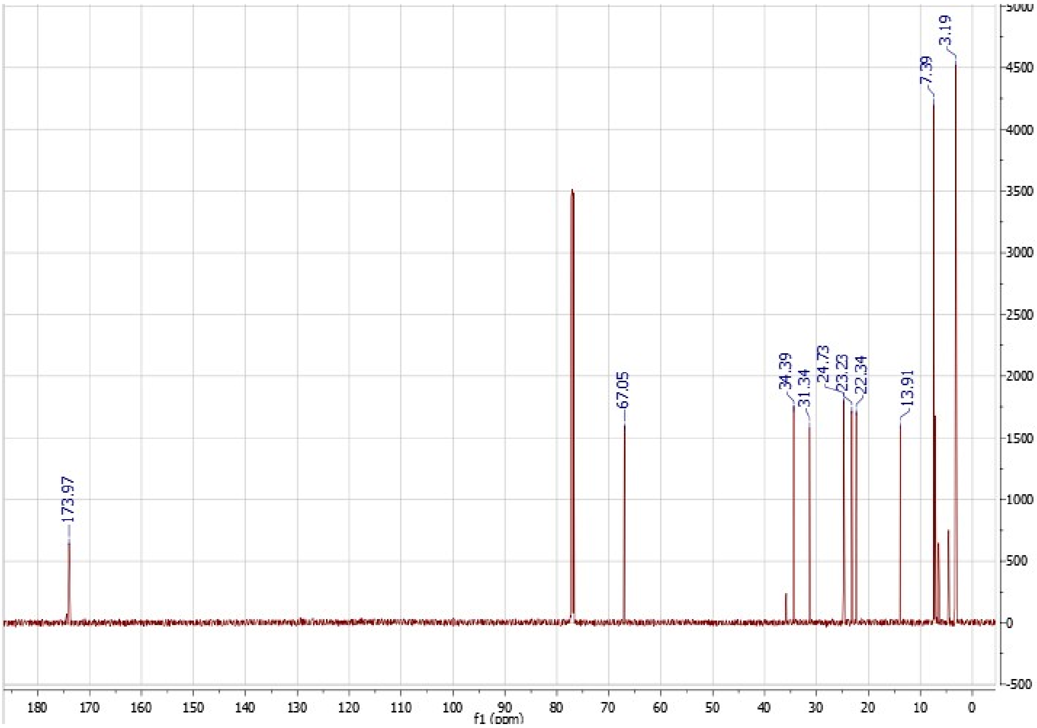

3.49
3.48
3.47
3.45
3.37
3.36
3.35
1.61
1.58
1.57
1.56
1.21
1.20
1.19
0.93
0.92
0.91
0.53
0.51
0.50
0.49
0.47
1.98
2.03
2.39
3.10
9.00
8.05
f1 (ppm)


74.09
66.14
24.27
15.41
7.57
7.36
3.40
f1 (ppm)


O
Et3Si
O
H3C

**6de**


4.02
4.01
4.00
2.30
2.29
2.28
1.62
1.31
0.98
0.97
0.94
0.92
0.91
0.89
0.78
0.76
0.75
0.74
0.53
0.52
0.51
0.49
1.69
1.96
4.17
4.01
11.53
7.62
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


173.97
67.05
34.39
31.34
24.73
23.23
22.34
13.91
7.39
3.19
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

## References.

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5. A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis and P. J. Chirik, *Science*, 2012, **335**, 567.