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Conjugated microporous polymer as recyclable heterogeneous ligand for highly efficient regioselective hydrosilylation of allenes

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Contents

1. General Methods and Materials

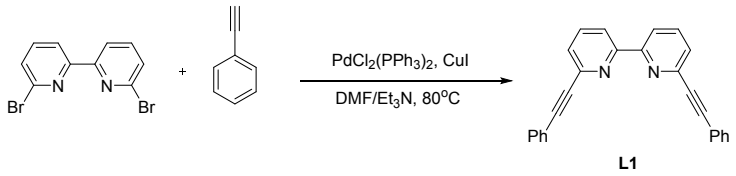
The liquid-state NMR was recorded on a 400 or 500 MHz spectrometer. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.28 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm). All ^{13}C NMR spectra were measured with complete proton decoupling. Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. The solid-state ^{13}C CP/MAS NMR was performed on a VARIAN Infinity-plus spectrometer. Nitrogen sorption isotherms at the temperature of liquid nitrogen were performed on a Quantachrome Autosorb-1 system, and the samples were degassed for 10 h at 393 K before the measurements were obtained. The specific surface areas were calculated from the adsorption data using Brunauer–Emmett–Teller (BET) methods. The total pore volume at P/Po=0.995. The pore size distribution curves were obtained from the desorption branches using the non-local density functional theory (NLDFT) method. Transmission electron microscope (TEM) images were performed using a JEM-2100 with accelerating voltage of 200 kV. The samples were pressed to tablet and were pasted on sample stage using conducting resin and the pressure of vacuum chamber was lower than 10-10mbar when testing while the step size of 0.10 eV was employed. Scanning electron microscopy (SEM) was performed using a JSM-7800 F. Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (NETZSCH STA 449 F3), the sample was heated at the rate of $10K \cdot min^{-1}$ from room temperature up to 1073K under a nitrogen atmosphere. Mass spectroscopy: We were grateful to the assistance of the Department of Chemistry, Xiamen University in obtaining the MS data.

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. The allenes[1,2,3] were prepared according to corresponding literature procedures.

Reference:

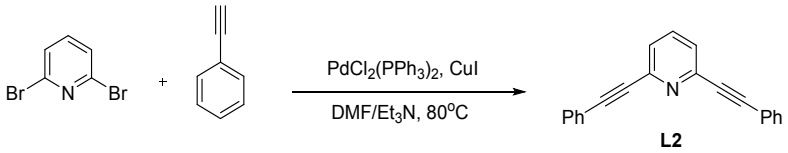
[1] J. Kuang and S. Ma, *J. Org. Chem*. **2009**, 74, 1763–1765.
[2] J. Kuang and S. Ma, *J. Am. Chem. Soc.* **2010**, 132, 1786–1787.
[3] X. Tang, Y. Han, and S. Ma, *Org. Lett*. **2015**, 17, 1176−1179.

2. Preparation of monomeric ligands (L1-L4)



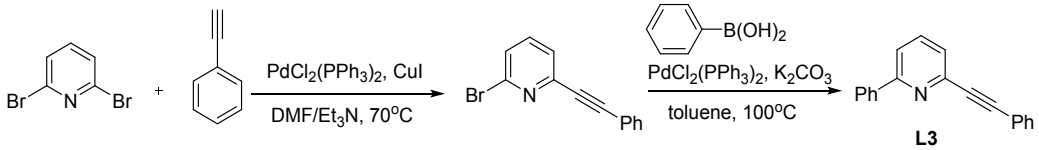
Scheme S1. Preparation of 6,6'-bis(phenylethynyl)-2,2'-bipyridine (L1)

6,6'-dibromo-2,2'-bipyridine (157 mg, 0.5 mmol), Phenyl acetylene (230 mg, 2.25 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol), CuI (6 mg, 0.03 mmol), DMF (3 mL) and Et_3N (3 mL) were added to a round bottom flask under nitrogen, and the reaction mixture was stirred at 80 °C for desired hours. When the reaction was completed, 10 mL Et_2O and 10 mL Saturated salt water were added, and the aqueous layer was extracted twice with 5 mL Et_2O. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford L1 (150 mg, 84% yield).



Scheme S2. Preparation of 2,6-bis(phenylethynyl)pyridine (L2)

2,6-bis(phenylethynyl)pyridine (118 mg, 0.5 mmol), Phenyl acetylene (230 mg, 2.25 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01mmol), CuI (6 mg, 0.03 mmol), DMF (3 mL) and Et_3N (3 mL) were added to a round bottom flask under nitrogen, and the reaction mixture was stirred at 80 °C for desired hours. When the reaction was completed, 10 mL Et_2O and 10 mL Saturated salt water were added, and the aqueous layer was extracted twice with 5 mL Et_2O. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford L2 (134 mg, 96% yield).

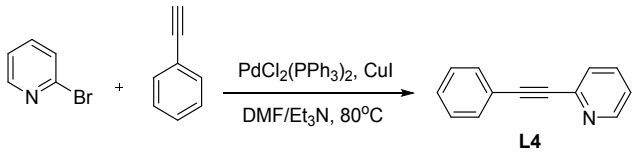


Scheme S3. Preparation of 2-phenyl-6-(phenylethynyl)pyridine (L3)

2,6-bis(phenylethynyl)pyridine (236 mg, 1 mmol), Phenyl acetylene (102 mg, 1 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (12 mg, 0.06 mmol), DMF (5 mL) and Et_3N (5 mL) were added to a round bottom flask under nitrogen, and the reaction mixture was stirred at 70 °C for desired hours. When the reaction was completed, 20 mL Et_2O and 10 mL Saturated salt water were added, and the aqueous layer was extracted twice with 10 mL Et_2O. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford 2-bromo-6-(phenylethynyl)pyridine (121 mg, 47% yield).

2-bromo-6-(phenylethynyl)pyridine (121 mg, 0.47 mmol), benzoboric acid (85 mg, 0.7 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), K_2CO_3 (138 mg, 1 mmol), toluene (5 mL) were added to a round

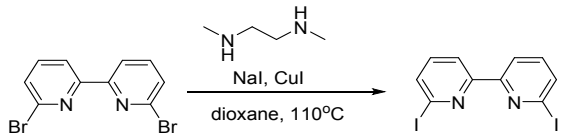
bottom flask under nitrogen, and the reaction mixture was stirred at 100 °C for desired hours. When the reaction was completed, 10 mL ethyl acetate and 5 mL Saturated salt water were added, and the aqueous layer was extracted twice with 10 mL ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford L3 (104 mg, 87% yield).



Scheme S4. Preparation of 2-(phenylethynyl)pyridine (L4)

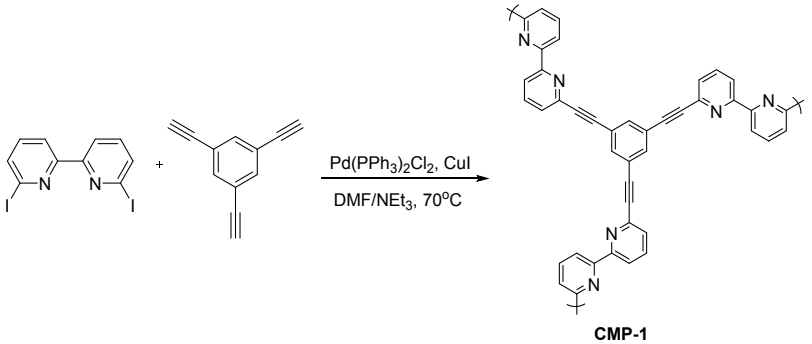
2-bromopyridine (316 mg, 2 mmol), Phenyl acetylene (306 mg, 3 mmol), $PdCl_2(PPh_3)_2$ (21 mg, 0.03 mmol), CuI (17 mg, 0.09 mmol), DMF (8 mL) and Et_3N (8 mL) were added to a round bottom flask under nitrogen, and the reaction mixture was stirred at 80 °C for desired hours. When the reaction was completed, 20 mL Et_2O and 20 mL Saturated salt water were added, and the aqueous layer was extracted twice with 10 mL Et_2O. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford L4 (276 mg, 77% yield).

3. Preparation of CMPs



Scheme S5. Preparation of 6,6'-diiodo-2,2'-bipyridine

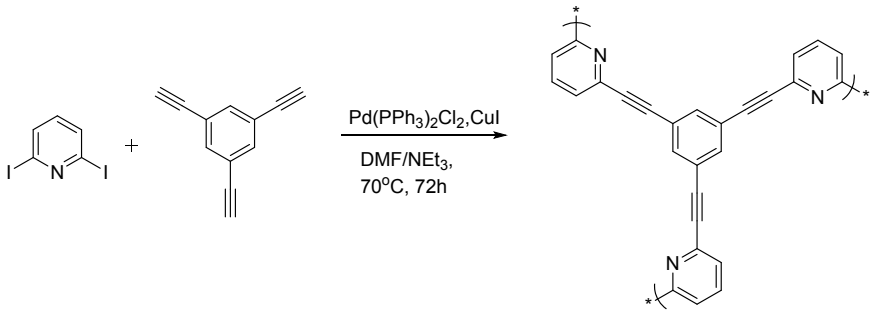
6,6'-dibromo-2,2'-bipyridine (314 mg, 1 mmol), NaI (750 mg, 5 mmol), N^1,N^2-dimethylethane-1,2-diamine (18 mg, 0.2 mmol), CuI (29 mg, 0.15 mmol) and dioxane (6 mL) were added to a round bottom flask, and the reaction mixture was stirred at 110 °C for 12 hours. The reaction solution was concentrated in vacuo and the residue was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford 6,6'-diiodo-2,2'-bipyridine (368 mg, 90%).



Scheme S6. Preparation of CMP-1

6,6'-diiodo-2,2'-bipyridine (408 mg, 1mmol), 1,3,5-triethynylbenzene (150 mg, 1mmol), $PdCl_2(PPh_3)_2$ (13 mg, 0.018 mmol), CuI (9 mg, 0.046 mmol), DMF (3 mL) and Et_3N (3 mL) were added to a round bottom flask under nitrogen, and the reaction mixture was stirred at 70 °C for 72

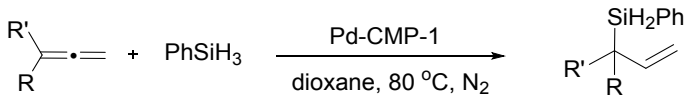
hours. The mixture was cooled to room temperature and the insoluble precipitated network polymer was filtered and washed five times with chloroform, water, acetone, methanol and CH_2Cl_2. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 24 hours. The product was dried in vacuum for 12 hours at 60 °C and isolated as fine yellow powder CMP-1 (Yield: 246 mg, 80%).



Scheme S7. Preparation of CMP-2

2,6-diiodopyridine (331 mg, 1 mmol), 1,3,5-triethynylbenzene (150 mg, 1 mmol), $PdCl_2(PPh_3)_2$ (13 mg, 0.018 mmol), CuI (9 mg, 0.046 mmol), DMF (3 mL) and Et_3N (3 mL) were added to a round bottom flask under nitrogen, and the reaction mixture was stirred at 70 °C for 72 hours. The mixture was cooled to room temperature and the insoluble precipitated network polymer was filtered and washed five times with chloroform, water, acetone, methanol and CH_2Cl_2. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 24 hours. The product was dried in vacuum for 12 hours at 60 °C and isolated as gray powder CMP-2 (Yield: 170 mg, 75%)

4. General procedure for hydrosilylation of allenes

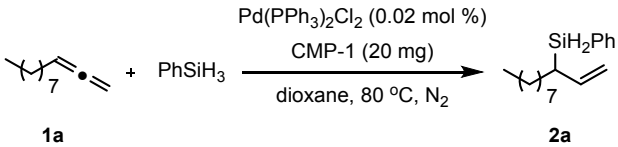


In a nitrogen filled schlenk tube, 8 mg Pd-CMP-1 (Pd, 0.02 mol %) were added. And then terminal allenes (0.25 mmol) and $PhSiH_3$ (33 mg, 0.3 mmol) were added. The reaction mixture was stirred at 80 °C. When the reaction was completed (1-5 h, monitored by TLC), 1,3,5-trimethoxybenzene (14 mg, 0.083 mmol) was added as an internal standard, filtered through a short plug of celite and the filtrate concentrated in vacuo.

A sample of the crude residue was analysed by ^1H NMR in $CDCl_3$, to determine NMR yield and the regioselectivity of the reaction. The crude product was purified by column chromatography.

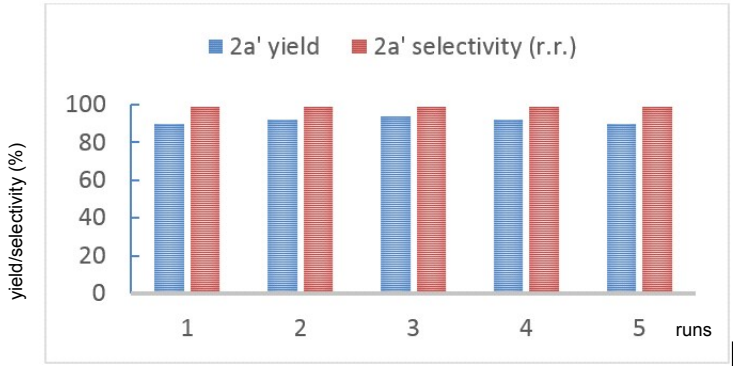
Note: Analysis of CMP-1 by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) showed that 0.27 wt % Pd was remained, the control experiments and the scope of the reaction were both performed with CMP-1 without additional $Pd(PPh_3)_2Cl_2$.

Studies on recycling of CMP-1 for the Hydrosilylation of 1-Octylallene and $PhSiH_3$.



1a **2a**

In a nitrogen filled schlenk tube, 20 mg Pd-CMP-1 (Pd, 0.05 mol %) were added in the first run. And then 1-Octylallene (38 mg, 0.25 mmol) and $PhSiH_3$ (33 mg, 0.3 mmol) were added. The reaction mixture was stirred at 80 °C for 1 h. Upon completion, Centrifuge and pour out the supernatant, CMP-1 was separated and recycled. And 1,3,5-trimethoxybenzene (14 mg, 0.083 mmol) was added to supernatant as an internal standard, concentrated in vacuo. A sample of the crude residue was analysed by ^1H NMR in $CDCl_3$, to determine NMR yield and the regioselectivity of the reaction. Next time, in a nitrogen filled schlenk tube, the recycled CMP-1 was added, then the additional $Pd(PPh_3)_2Cl_2$ (0.02 mol %) was added. Then 1-Octylallene (38 mg, 0.25 mmol) and $PhSiH_3$ (33 mg, 0.3 mmol) were added. After reaction, analysed by ^1H NMR. This operation was repeated four times. As can be seen, the catalyst system was recycled five times with nearly no loss of activity and selectivity.



Scheme S8. recycling of CMP-1 for the Hydrosilylation of 1-Octylallene and $PhSiH_3$

5. Characterization of polymers

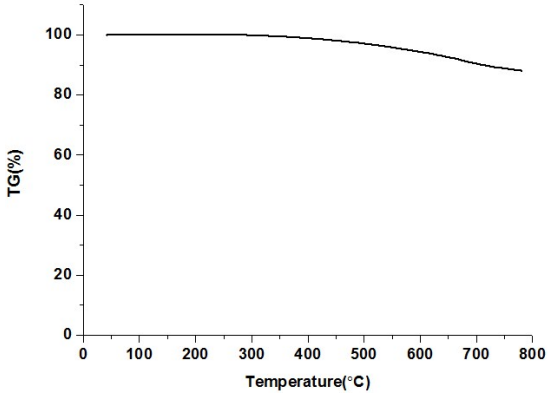


Figure S1. Thermogravimetric analysis (TGA) curve of Pd-CMP-1.

The TG shows that Pd-CMP-1 remains intact at temperatures up to 400 °C, even with only about 15% weight loss at 800 °C, indicating its good thermal stability.

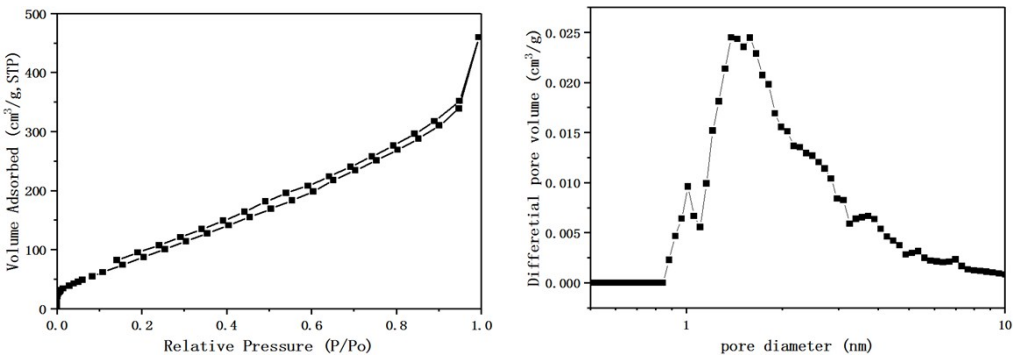


Figure S2. Nitrogen sorption isotherms and pore size distribution of Pd-CMP-1.

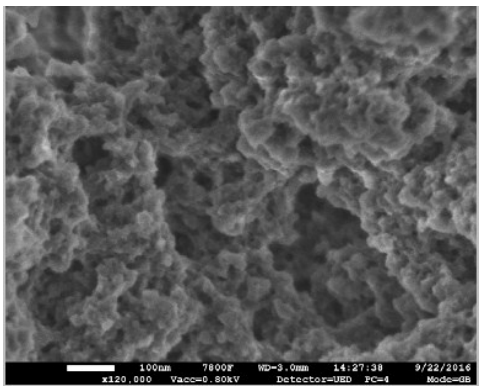


Figure S3. Scanning electron microscopy (SEM) of Pd-CMP-1.

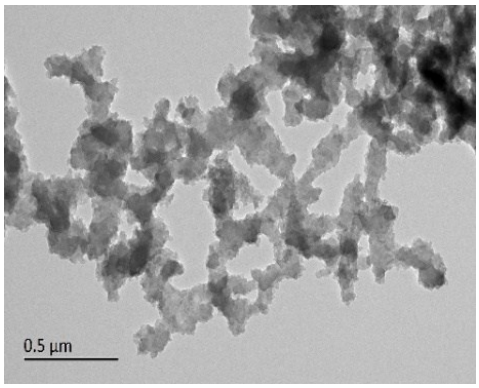


Figure S4. TEM images of Pd-CMP-1.

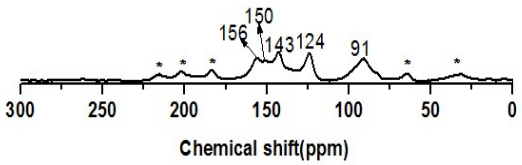
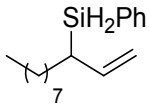


Figure S5. ^{13}C CP/MAS Pd-CMP-1 (100 MHz) δ 91, 124, 143, 150, 156.

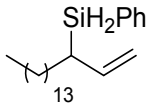
6. Analytical data for compounds

(undec-1-en-3-yl)(phenyl)silane (2a)



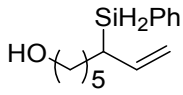
colorless liquid (90%, 59 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60-7.54 (m, 2H), 7.44-7.32 (m, 3H), 5.74 (ddd, J_1 = 17.1 Hz, J_2 = 10.3 Hz, J_3 = 9.0 Hz, 1H), 4.98-4.86 (m, 2H), 4.28-4.22 (m, 2H), 2.07-1.95 (m, 1H), 1.60-1.48 (m, 1H), 1.47-1.37 (m, 1H), 1.35-1.17 (m, 12H), 0.89 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.5, 135.7, 131.4, 129.7, 127.9, 113.2, 31.9, 30.14, 30.10, 29.49, 29.46, 29.3, 29.1, 22.7, 14.1. **HRMS** (ESI) m/z Calculated for $C_{17}H_{28}NaSi^+$ $[M+Na]^+$: 283.1852, found: 283.1853.

(heptadec-1-en-3-yl)(phenyl)silane (2b)



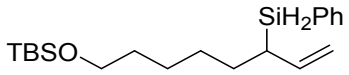
colorless liquid (94%, 81 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62-7.56 (m, 2H), 7.45-7.33 (m, 3H), 5.75 (apparent dt, J_1 = 17.1 Hz, J_2 = 9.2 Hz, 1H), 4.96 (d, J = 10.2 Hz, 1H), 4.92 (d, J = 17.0 Hz, 1H), 4.30-4.23 (m, 2H), 2.09-1.98 (m, 1H), 1.60-1.50 (m, 1H), 1.48-1.38 (m, 1H), 1.36-1.18 (m, 24H), 0.91 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.6, 135.8, 131.4, 129.7, 127.9, 113.2, 32.0, 30.15, 30.1, 29.73, 29.71, 29.69, 29.66, 29.53, 29.46, 29.4, 29.1, 22.7, 14.1. **HRMS** (ESI) m/z Calculated for $C_{23}H_{40}NaSi^+$ $[M+Na]^+$: 367.2791, found: 367.2790.

6-(phenylsilyl)oct-7-en-1-ol (2c)



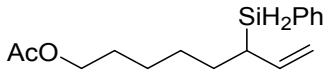
colorless liquid (64%, 38 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60-7.55 (m, 2H), 7.43-7.33 (m, 3H), 5.73 (ddd, J_1 = 17.1 Hz, J_2 = 10.3 Hz, J_3 = 9.0 Hz, 1H), 4.98-4.94 (m, 1H), 4.94-4.88 (m, 1H), 4.28-4.22 (m, 2H), 3.61 (t, J = 6.6 Hz, 2H), 2.08-1.95 (m, 1H), 1.64-1.42 (m, 5H), 1.38-1.23 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.4, 135.7, 131.3, 129.7, 127.9, 113.3, 62.9, 32.6, 30.1, 30.0, 28.8, 25.5. **HRMS** (ESI) m/z Calculated for $C_{14}H_{22}NaOSi^+$ $[M+Na]^+$: 257.1332, found: 257.1338.

tert-butyldimethyl((6-(phenylsilyl)oct-7-en-1-yl)oxy)silane (2d)



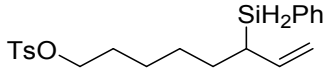
colorless liquid (85%, 74 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61-7.52 (m, 2H), 7.43-7.30 (m, 3H), 5.73 (apparent dt, J_1 = 17.0 Hz, J_2 = 9.4 Hz, 1H), 4.94 (d, J = 10.1 Hz, 1H), 4.90 (d, J = 17.2 Hz, 1H), 4.28-4.20 (m, 2H), 3.58 (t, J = 6.6 Hz, 2H), 2.05-1.95 (m, 1H), 1.58-1.43 (m, 5H), 1.35-1.23 (m, 3H), 0.89 (s, 9H), 0.05 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.5, 135.7, 131.4, 129.7, 127.9, 113.2, 63.2, 32.7, 30.08, 30.05, 28.8, 26.0, 25.6, 18.4, -5.3. **HRMS** (ESI) m/z Calculated for $C_{20}H_{36}NaOSi_2^+$ $[M+Na]^+$: 371.2197, found: 371.2198.

6-(phenylsilyl)oct-7-en-1-yl acetate (2e)



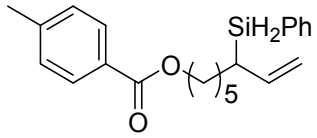
colorless liquid (63%, 44 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60-7.53 (m, 2H), 7.45-7.30 (m, 3H), 5.73 (ddd, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 9.0 Hz, 1H), 5.01-4.85 (m, 2H), 4.28-4.20 (m, 2H), 4.03 (t, J = 6.7 Hz, 2H), 2.06-2.02 (m, 4H), 1.65-1.50 (m, 4H), 1.38-1.21 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.2, 139.3, 135.7, 131.2, 129.7, 127.9, 113.4, 64.5, 30.1, 29.9, 28.7, 28.5, 25.7, 21.0. **HRMS** (ESI) m/z Calculated for $C_{16}H_{24}NaO_2Si^+$ $[M+Na]^+$: 299.1438, found: 299.1440.

6-(phenylsilyl)oct-7-en-1-yl 4-methylbenzenesulfonate (2f)



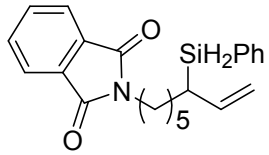
colorless liquid (84%, 82 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.75 (m, 2H), 7.58-7.52 (m, 2H), 7.45-7.30 (m, 5H), 5.56 (apparent dt, J_1 = 17.3 Hz, J_2 = 9.3 Hz, 1H), 4.93 (d, J = 10.2 Hz, 1H), 4.87 (d, J = 17.1 Hz, 1H), 4.26-4.19 (m, 2H), 3.99 (t, J = 6.5 Hz, 2H), 2.44 (s, 3H), 1.90-1.99 (m, 1H), 1.67-1.55 (m, 2H), 1.55-1.41 (m, 2H), 1.35-1.14 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.6, 139.2, 135.7, 133.3, 131.1, 129.80, 129.78, 127.92, 127.88, 113.4, 70.6, 30.0, 29.8, 28.7, 28.3, 25.1, 21.6. **HRMS** (ESI) m/z Calculated for $C_{21}H_{28}NaO_3SSi^+$ $[M+Na]^+$: 411.1421, found: 411.1427.

6-(phenylsilyl)oct-7-en-1-yl 4-methylbenzoate (2g)



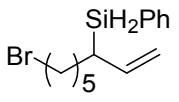
colorless liquid (80%, 71 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95-7.89 (m, 2H), 7.59-7.52 (m, 2H), 7.42-7.30 (m, 3H), 7.25-7.15 (m, 2H), 5.72 (ddd, J_1 = 17.2 Hz, J_2 = 10.3 Hz, J_3 = 9.1 Hz, 1H), 4.97-4.92 (m, 1H), 4.89 (apparent dt, J_1 = 17.1 Hz, J_2 = 1.4 Hz, 1H), 4.29-4.21 (m, 4H), 2.40 (s, 3H), 2.08-1.95 (m, 1H), 1.78-1.67 (m, 2H), 1.60-1.30 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 143.4, 139.3, 135.7, 131.3, 129.7, 129.6, 129.1, 127.9, 127.8, 113.4, 64.9, 30.1, 30.0, 28.73, 28.65, 25.9, 21.7. **HRMS** (ESI) m/z Calculated for $C_{22}H_{28}NaO_2Si^+$ $[M+Na]^+$: 375.1751, found: 375.1748.

2-(6-(phenylsilyl)oct-7-en-1-yl)isoindoline-1,3-dione (2h)



colorless liquid (55%, 50 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90-7.77 (m, 2H), 7.76-7.64 (m, 2H), 7.59-7.49 (m, 2H), 7.43-7.29 (m, 3H), 5.70 (ddd, J_1 = 17.1 Hz, J_2 = 10.2 Hz, J_3 = 9.1 Hz, 1H), 4.92 (d, J = 10.2 Hz, 1H), 4.88 (d, J = 17.2 Hz, 1H), 4.27-4.18 (m, 2H), 3.65 (t, J = 7.3 Hz, 2H), 2.06-1.91 (m, 1H), 1.75-1.58 (m, 2H), 1.58-1.41 (m, 2H), 1.40-1.20 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.4, 139.3, 135.7, 133.8, 132.2, 131.2, 129.7, 127.9, 123.2, 113.4, 38.0, 30.0, 29.9, 28.6, 28.5, 26.7. **HRMS** (ESI) m/z Calculated for $C_{22}H_{25}NNaO_2Si^+$ $[M+Na]^+$: 386.1547, found: 386.1550.

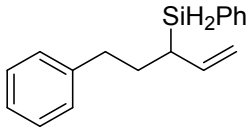
(8-bromooct-1-en-3-yl)(phenyl)silane (2i)



colorless liquid (81%, 60 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62-7.53 (m, 2H), 7.45-7.33 (m, 3H), 5.73 (ddd, J_1 = 17.1 Hz, J_2 = 10.1 Hz, J_3 = 9.2 Hz, 1H), 4.97 (d, J = 10.1 Hz, 1H), 4.92 (d, J = 17.1 Hz, 1H), 4.29-4.22 (m, 2H), 3.38 (t, J = 6.8 Hz, 2H), 2.08-1.98 (m, 1H), 1.89-1.77 (m, 2H), 1.63-1.50 (m, 2H), 1.49-1.26 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.3, 135.7, 131.2, 129.8,

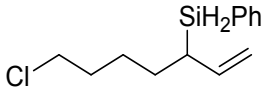
127.9, 113.5, 33.9, 32.7, 30.0, 29.9, 28.2, 27.9. **HRMS** (ESI) m/z Calculated for $C_{14}H_{21}BrNaSi^+$ $[M+Na]^+$: 319.0488, found: 319.0490.

phenyl(5-phenylpent-1-en-3-yl)silane (2j)



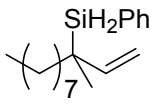
colorless liquid (89%, 56 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59-7.48 (m, 2H), 7.42-7.36 (m, 1H), 7.36-7.29 (m, 2H), 7.29-7.21 (m, 2H), 7.19-7.09 (m, 3H), 5.77 (ddd, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 9.1 Hz, 1H), 5.01 (d, J = 10.2 Hz, 1H), 4.95 (d, J = 17.2 Hz, 1H), 4.33-4.20 (m, 2H), 2.83-2.67 (m, 1H), 2.65-2.49 (m, 1H), 2.12-1.98 (m, 1H), 1.95-1.74 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.2, 139.1, 135.8, 131.1, 129.8, 128.6, 128.4, 128.0, 125.8, 114.0, 35.1, 32.0, 29.6. **HRMS** (ESI) m/z Calculated for $C_{17}H_{20}NaSi^+$ $[M+Na]^+$: 275.1226, found: 275.1227.

(7-chlorohept-1-en-3-yl)(phenyl)silane (2k)



colorless liquid (71%, 42 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59-7.51 (m, 2H), 7.43-7.30 (m, 3H), 5.71 (ddd, J_1 = 17.0 Hz, J_2 = 10.1 Hz, J_3 = 9.2 Hz, 1H), 4.96 (d, J = 10.3 Hz, 1H), 4.91 (d, J = 17.1 Hz, 1H), 4.28-4.22 (m, 2H), 3.50 (t, J = 6.7 Hz, 2H), 2.06-1.95 (m, 1H), 1.80-1.65 (m, 2H), 1.63-1.48 (m, 3H),1.46-1.36 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.0, 135.8, 131.1, 129.8, 128.0, 113.7, 44.9, 32.4, 30.0, 29.4, 26.4. **HRMS** (ESI) m/z Calculated for $C_{13}H_{19}ClNaSi^+$ $[M+Na]^+$: 261.0837, found: 261.0839.

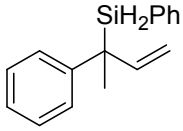
(3-methylundec-1-en-3-yl)(phenyl)silane (2l)



colorless liquid (86%, 59 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.48 (m, 2H), 7.44-7.28 (m, 3H), 5.93-5.82 (dd, J_1 = 17.3 Hz, J_2 = 10.7 Hz, 1H), 5.00 (dd, J_1 = 10.7 Hz, J_2 = 1.3 Hz, 1H), 4.80 (dd, J_1 = 17.4 Hz, J_2 = 1.2 Hz, 1H), 4.19-4.11 (m, 2H), 1.55-1.42 (m, 2H), 1.36-1.20 (m, 12H), 1.16-

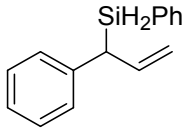
1.06 (s, 3H), 0.93-0.83 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.5, 136.2, 131.4, 129.7, 127.7, 111.4, 37.4, 31.9, 30.4, 29.9, 29.6, 29.3, 24.2, 22.7, 19.1, 14.1. **HRMS** (ESI) m/z Calculated for $C_{18}H_{30}NaSi^+$ $[M+Na]^+$: 297.2009, found: 297.2016.

phenyl(2-phenylbut-3-en-2-yl)silane (2m)



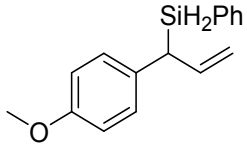
colorless liquid (56%, 33 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.33 (m, 1H), 7.33-7.27 (m, 6H), 7.27-7.22 (m, 2H), 7.18-7.13 (m, 1H), 6.34 (dd, J_1 = 17.3 Hz, J_2 = 10.7 Hz, 1H), 5.14 (dd, J_1 = 10.7 Hz, J_2 = 0.9 Hz, 1H), 5.02 (dd, J_1 = 17.3 Hz, J_2 = 0.8 Hz, 1H), 4.42 (d, J = 7.3 Hz, 1H), 4.37 (d, J = 7.3 Hz, 1H), 1.55 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.1, 143.3, 136.2, 130.9, 129.9, 128.4, 127.7, 126.8, 125.4, 112.7, 36.0, 21.2. **HRMS** (ESI) m/z Calculated for $C_{16}H_{18}NaSi^+$ $[M+Na]^+$: 261.1070, found: 261.1066.

phenyl(1-phenylallyl)silane (2n)



colorless liquid (60%, 34 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42-7.33 (m, 3H), 7.31-7.22 (m, 4H), 7.17-7.08 (m, 3H), 6.16 (ddd, J_1 = 17.0 Hz, J_2 = 10.2 Hz, J_3 = 8.6 Hz, 1H), 5.08-4.98 (m, 2H), 4.45-4.38 (m, 2H) , 3.47-3.39 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.1, 137.7, 135.8, 130.8, 129.9, 128.6, 127.9, 127.8, 125.5, 114.4, 38.8. **HRMS** (ESI) m/z Calculated for $C_{15}H_{16}NaSi^+$ $[M+Na]^+$: 247.0913, found: 247.0915.

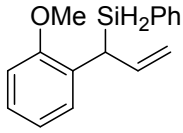
(1-(4-methoxyphenyl)allyl)(phenyl)silane (2o)



colorless liquid (83%, 53 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.33 (m, 3H), 7.32-7.26 (m, 2H), 7.04 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 6.14 (ddd, J_1 = 17.0 Hz, J_2 = 10.2 Hz, J_3 =

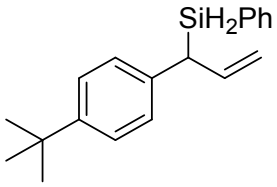
8.4 Hz, 1H), 5.07-4.93 (m, 2H), 4.44-4.36 (m, 2H), 3.77 (s, 3H), 3.41-3.32 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.6, 138.1, 135.8, 132.9, 131.0, 129.9, 128.8, 127.9, 114.13, 114.11, 55.3, 37.6. **HRMS** (ESI) m/z Calculated for $C_{16}H_{18}NaOSi^+$ $[M+Na]^+$: 277.1019, found: 277.1025.

(1-(2-methoxyphenyl)allyl)(phenyl)silane (2p)



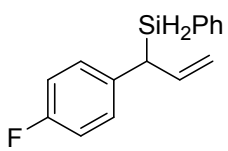
colorless liquid (80%, 51 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.37-7.31 (m, 1H), 7.30-7.24 (m, 2H), 7.17-7.08 (m, 2H), 6.92-6.86 (m, 1H), 6.77 (d, J = 8.1 Hz, 1H), 6.25-6.14 (m, 1H), 5.06-4.95 (m, 2H), 4.40 (dd, J_1 = 7.3 Hz, J_2 = 3.3 Hz, 1H), 4.32 (dd, J_1 = 7.3 Hz, J_2 = 2.8 Hz, 1H), 3.84-3.76 (m, 1H), 3.66 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.1, 137.6, 135.6, 132.1, 129.9, 129.6, 128.1, 127.7, 126.5, 120.8, 114.1, 110.5, 55.1, 31.9. **HRMS** (ESI) m/z Calculated for $C_{16}H_{18}NaOSi^+$ $[M+Na]^+$: 277.1019, found: 277.1020.

(1-(4-(*tert*-butyl)phenyl)allyl)(phenyl)silane (2q)



colorless liquid (64%, 45 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43-7.35 (m, 3H), 7.32-7.25 (m, 4H), 7.08-7.04 (m, 2H), 6.15 (ddd, J_1 = 17.0 Hz, J_2 = 10.3 Hz, J_3 = 8.7 Hz, 1H), 5.06-4.95 (m, 2H), 4.45-4.37 (m, 2H), 3.45-3.36 (m, 1H), 1.30 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.3, 137.89, 137.87, 135.8, 131.0, 129.8, 127.8, 127.3, 125.5, 114.2, 38.1, 34.3, 31.4. **HRMS** (ESI) m/z Calculated for $C_{19}H_{24}NaSi^+$ $[M+Na]^+$: 303.1539, found: 303.1541.

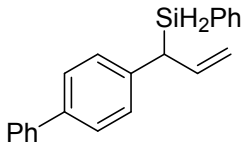
(1-(4-fluorophenyl)allyl)(phenyl)silane (2r)



colorless liquid (65%, 39 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42-7.36 (m, 3H), 7.32-7.27 (m,

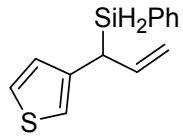
2H), 7.08-7.03 (m, 2H), 6.97-6.92 (m, 2H), 6.11 (ddd, J_1 = 17.0 Hz, J_2 = 10.2 Hz, J_3 = 8.4 Hz, 1H), 5.05 (apparent dt, J_1 = 10.2 Hz, J_2 = 1.3 Hz, 1H), 5.02 (apparent dt, J_1 = 17.0 Hz, J_2 = 1.3 Hz, 1H), 4.45-4.35 (m, 2H), 3.45-3.35 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.0 (d, J = 243 Hz), 137.6, 136.6 (d, J = 2.9 Hz), 135.7, 130.5, 130.0, 129.0 (d, J = 8.0 Hz), 127.9, 115.4 (d, J = 21.1 Hz), 114.6, 37.8. **HRMS** (ESI) m/z Calculated for $C_{15}H_{15}FNaSi^+$ $[M+Na]^+$: 265.0819, found: 265.0827.

(1-([1,1'-biphenyl]-4-yl)allyl)(phenyl)silane (2s)



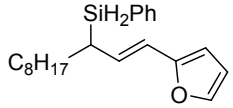
colorless liquid (60%, 45 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62-7.55 (m, 2H), 7.53-7.47 (m, 2H), 7.46-7.39 (m, 5H), 7.34-7.28 (m, 3H), 7.19 (d, J = 8.1 Hz, 2H), 6.19 (ddd, J_1 = 17.0 Hz, J_2 = 10.3 Hz, J_3 = 8.7 Hz, 1H), 5.11-5.01 (m, 2H), 4.50-4.41 (m, 2H), 3.53-3.45 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.0, 140.2, 138.3, 137.5, 135.8, 130.7, 130.0, 128.7, 128.1, 127.9, 127.3, 127.1, 126.9, 114.6, 38.5. **HRMS** (ESI) m/z Calculated for $C_{21}H_{20}NaSi^+$ $[M+Na]^+$: 323.1226, found: 323.1231.

phenyl(1-(thiophen-3-yl)allyl)silane (2t)



colorless liquid (64%, 37 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.35 (m, 3H), 7.34-7.27 (m, 2H), 7.27-7.22 (m, 1H), 6.89 (dd, J_1 = 5.0 Hz, J_2 = 1.2 Hz, 1H), 6.86-6.82 (m, 1H), 6.09 (ddd, J_1 = 17.0 Hz, J_2 = 10.3 Hz, J_3 = 8.7 Hz, 1H), 5.09-4.95 (m, 2H), 4.44-4.37 (m, 2H), 3.62-3.50 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.7, 137.4, 135.7, 130.7, 130.0, 127.9, 127.7, 125.5, 119.3, 114.3, 33.9. **HRMS** (ESI) m/z Calculated for $C_{13}H_{14}NaSSi^+$ $[M+Na]^+$: 253.0478, found: 253.0485.

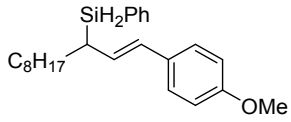
(E)-(1-(furan-2-yl)pent-1-en-3-yl)(phenyl)silane (2u)



colorless liquid (60%, 49 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58-7.53 (m, 2H), 7.41-7.37 (m,

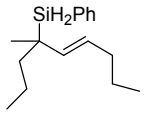
1H), 7.37-7.32 (m, 2H), 7.29 (d, J = 1.7 Hz, 1H), 6.33 (dd, J_1 = 3.2 Hz, J_2 = 1.8 Hz, 1H), 6.13-6.03 (m, 3H), 4.29 (d, J = 2.90 Hz, 2H), 2.17-2.05 (m, 1H), 1.64-1.55 (m, 1H), 1.30-1.16 (m, 13H), 0.86 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 141.0, 135.8, 131.2, 131.1, 129.8, 127.9, 117.4, 111.1, 105.4, 31.9, 30.5, 29.6, 29.5, 29.3, 22.7, 14.1. **HRMS** (ESI) m/z Calculated for $C_{21}H_{30}NaOSi^+$ $[M+Na]^+$: 349.1958, found: 349.1964.

(E)-(1-(4-methoxyphenyl)undec-1-en-3-yl)(phenyl)silane (2v)



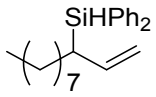
colorless liquid (68%, 62 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (dd, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 2H), 7.42-7.36 (m, 1H), 7.36-7.31(m, 2H), 7.23-7.19 (m, 2H), 6.82 (d, J = 8.6 Hz, 2H), 6.21 (d, J = 15.8 Hz, 1H), 5.98 (dd, J_1 = 15.8 Hz, J_2 = 9.3 Hz, 1H), 4.33-4.26 (m, 2H), 3.79 (s, 3H), 2.18-2.08 (m, 1H), 1.67-1.55 (m, 2H), 1.49-1.38 (m, 1H), 1.34-1.16 (m, 11H), 0.86 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 135.8, 131.4, 131.0, 129.8, 129.7, 128.1, 127.9, 126.8, 113.9, 55.3, 31.9, 30.7, 29.7, 29.48, 29.46, 29.3, 22.7, 14.1. **HRMS** (ESI) m/z Calculated for $C_{24}H_{34}NaOSi^+$ $[M+Na]^+$: 389.2271, found: 389.2277.

(E)-(4-methylnon-5-en-4-yl)(phenyl)silane (2w)



colorless liquid (72%, 44 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.50 (m, 2H), 7.41-7.30 (m, 3H), 5.45 (dt, J_1 = 15.6 Hz, J_2 = 1.3 Hz, 1H), 5.16 (dt, J_1 = 15.6 Hz, J_2 = 6.8 Hz, 1H), 4.14 (s, 2H), 2.05-1.95 (m, 2H), 1.49-1.22 (m, 6H), 1.11 (s, 3H), 0.91-0.83 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.2, 131.8, 129.5, 127.71, 127.66, 127.46, 40.3, 35.2, 28.4, 23.0, 20.0, 17.5, 14.8, 13.6. **HRMS** (ESI) m/z Calculated for $C_{16}H_{26}NaSi^+$ $[M+Na]^+$: 269.1696, found: 269.1699.

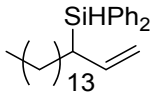
pent-1-en-3-yldiphenylsilane (3a)



colorless liquid (77%, 65 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.58 (m, 4H), 7.46-7.35 (m,

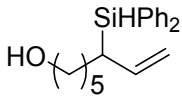
6H), 5.75 (ddd, J_1 = 17.2 Hz, J_2 = 10.3 Hz, J_3 = 9.3 Hz, 1H), 4.99-4.88 (m, 2H), 4.81 (d, J = 2.8 Hz, 1H), 2.33-2.21 (m, 1H), 1.69-1.59 (m, 1H), 1.51-1.42 (m, 1H), 1.36-1.17 (m, 12H), 0.90 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.2, 135.7, 135.6, 133.5, 133.2, 129.6, 128.2, 127.9, 127.8, 113.7, 31.9, 31.6, 29.5, 29.4, 29.3, 29.0, 22.7, 14.1. **HRMS** (ESI) m/z Calculated for $C_{23}H_{32}NaSi^+$ $[M+Na]^+$: 359.2165, found: 359.2167.

heptadec-1-en-3-yldiphenylsilane (3b)



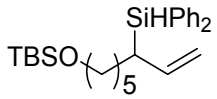
colorless liquid (71%, 75 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64-7.58 (m, 4H), 7.44-7.34 (m, 6H), 5.73 (ddd, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 9.3 Hz, 1H), 4.95 (dd, J_1 = 10.3 Hz, J_2 = 1.2 Hz, 1H), 4.90 (apparent dt, J_1 = 17.1 Hz, J_2 = 1.4 Hz ,1H), 4.79 (d, J = 2.7 Hz, 1H), 2.31-2.20 (m, 1H), 1.68-1.58 (m, 1H), 1.49-1.40 (m, 1H), 1.37-1.14 (m, 24H), 0.91 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.1, 135.7, 135.6, 133.5, 133.2, 129.60, 129.58, 127.9, 127.8, 113.7, 32.0, 31.6, 29.73, 29.70, 29.69, 29.68, 29.66, 29.54, 29.50, 29.40, 29.37, 29.0, 22.7, 14.2. **HRMS** (ESI) m/z Calculated for $C_{29}H_{44}NaSi^+$ $[M+Na]^+$: 443.3104, found: 443.3102.

6-(diphenylsilyl)oct-7-en-1-ol (3c)



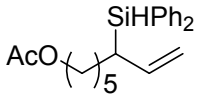
colorless liquid (58%, 45 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64-7.56 (m, 4H), 7.45-7.33 (m, 6H), 5.72 (ddd, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 9.4 Hz, 1H), 4.95 (dd, J_1 = 10.2 Hz, J_2 = 1.2 Hz, 1H), 4.90 (apparent dt, J_1 = 17.1 Hz, J_2 = 1.2 Hz ,1H), 4.79 (d, J = 2.8 Hz, 1H), 3.60 (t, J = 6.6 Hz, 2H), 2.31-2.20 (m, 1H), 1.68-1.59 (m, 1H), 1.59-1.44 (m, 3H), 1.39-1.22 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.0, 135.7, 135.6, 133.3, 133.1, 129.7, 129.6, 128.0, 127.9, 113.8, 63.0, 32.6, 31.5, 29.4, 28.8, 25.4. **HRMS** (ESI) m/z Calculated for $C_{20}H_{26}NaOSi^+$ $[M+Na]^+$: 333.1645, found: 333.1647.

tert-butyl((6-(diphenylsilyl)oct-7-en-1-yl)oxy)dimethylsilane (3d)



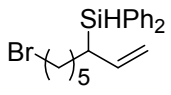
colorless liquid (85%, 90 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66-7.56 (m, 4H), 7.45-7.34 (m, 6H), 5.73 (apparent dt, J_1 = 17.0 Hz, J_2 = 9.4 Hz, 1H), 4.96 (d, J = 10.2 Hz, 1H), 4.90 (d, J = 17.2 Hz, 1H), 4.79 (d, J = 2.7 Hz, 1H), 3.58 (t, J = 6.6 Hz, 2H), 2.31-2.20 (m, 1H), 1.69-1.59 (m, 1H), 1.59-1.41 (m, 4H), 1.38-1.19 (m, 3H), 0.91 (s, 9H), 0.06 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.0, 135.7, 135.6, 133.4, 133.2, 129.62, 129.61, 127.9, 127.8, 113.8, 63.3, 32.8, 31.6, 29.5, 28.8, 26.0, 25.6, 18.4, -5.2. **HRMS** (ESI) m/z Calculated for $C_{26}H_{40}NaOSi_2^+$ $[M+Na]^+$: 447.2510, found: 447.2513.

6-(diphenylsilyl)oct-7-en-1-yl acetate (3e)



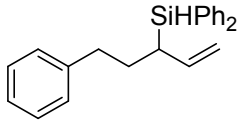
colorless liquid (55%, 48 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63-7.55 (m, 4H), 7.43-7.32 (m, 6H), 5.70 (ddd, J_1 = 17.2 Hz, J_2 = 10.3 Hz, J_3 = 9.4 Hz, 1H), 4.94 (dd, J_1 = 10.3 Hz, J_2 = 1.2 Hz, 1H), 4.88 (apparent dt, J_1 = 17.2 Hz, J_2 = 1.2 Hz ,1H), 4.77 (d, J = 2.8 Hz, 1H), 4.01 (t, J = 6.7 Hz, 2H), 2.29-2.18 (m, 1H), 2.03 (s, 3H), 1.62-1.43 (m, 5H), 1.36-1.21 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.2, 138.9, 135.7, 135.6, 133.3, 133.0, 129.7, 129.6, 127.93, 127.85, 113.9, 64.6, 31.5, 29.4, 28.7, 28.5, 25.7, 21.0. **HRMS** (ESI) m/z Calculated for $C_{22}H_{28}NaO_2Si^+$ $[M+Na]^+$: 375.1751, found: 375.1756.

(8-bromooct-1-en-3-yl)diphenylsilane (3f)



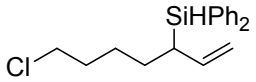
colorless liquid (71%, 66 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63-7.53 (m, 4H), 7.43-7.31 (m, 6H), 5.72 (apparent dt, J_1 = 17.1 Hz, J_2 = 9.8 Hz, 1H), 4.94 (d, J = 10.3 Hz, 1H), 4.88 (d, J = 17.2 Hz, 1H), 4.76 (d, J = 2.6 Hz, 1H), 3.60 (t, J = 6.7 Hz, 2H), 2.27-2.18 (m, 1H), 1.83-1.74 (m, 2H), 1.66-1.56 (m, 1H), 1.55-1.21 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.8, 135.7, 135.6, 133.2, 133.0, 129.69, 129.67, 128.0, 127.9, 113.9, 33.9, 32.7, 31.5, 29.3, 28.1, 27.9. **HRMS** (ESI) m/z Calculated for $C_{20}H_{25}BrNaSi^+$ $[M+Na]^+$: 395.0801, found: 395.0802.

diphenyl(5-phenylpent-1-en-3-yl)silane (3g)



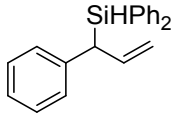
colorless liquid (65%, 53 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58-7.49 (m, 4H), 7.42-7.29 (m, 6H), 7.27-7.20 (m, 2H), 7.19-7.13 (m, 1H), 7.13-7.06 (m, 2H), 5.76 (apparent dt, J_1 = 17.2 Hz, J_2 = 9.4 Hz, 1H), 5.02 (d, J = 10.1 Hz, 1H), 4.93 (d, J = 17.2 Hz, 1H), 4.77 (d, J = 2.6 Hz, 1H), 2.84-2.72 (m, 1H), 2.60-2.47 (m, 1H), 2.32-2.22 (m, 1H), 1.99-1.87 (m, 1H), 1.87-1.76(m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.2, 138.7, 135.7, 135.6, 133.1, 132.9, 129.72, 129.69, 128.6, 128.3, 128.0, 127.9, 125.8, 114.4, 35.0, 31.3, 30.9. **HRMS** (ESI) m/z Calculated for $C_{23}H_{24}NaSi^+$ $[M+Na]^+$: 351.1539, found: 351.1540.

(7-chlorohept-1-en-3-yl)diphenylsilane (3h)



colorless liquid (72%, 57 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63-7.53 (m, 4H), 7.42-7.31 (m, 6H), 5.69 (apparent dt, J_1 = 17.1 Hz, J_2 = 9.6 Hz, 1H), 4.95 (d, J = 10.5 Hz, 1H), 4.89 (d, J = 17.2 Hz, 1H), 4.77 (d, J = 2.6 Hz, 1H), 3.45 (t, J = 6.7 Hz, 2H), 2.28-2.18 (m, 1H), 1.80-1.48 (m, 5H), 1.42-1.34 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.6, 135.7, 135.6, 133.1, 132.9, 129.8, 129.7, 128.0, 127.9, 114.2, 45.0, 32.4, 31.5, 28.8, 26.4. **HRMS** (ESI) m/z Calculated for $C_{19}H_{23}ClNaSi^+$ $[M+Na]^+$: 337.1150, found: 337.1153.

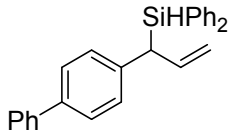
diphenyl(1-phenylallyl)silane (3i)



colorless liquid (70%, 53 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.43-7.37(m, 3H), 7.36-7.31 (m, 3H), 7.29-7.23 (m, 2H), 7.22-7.15 (m, 2H), 7.13-7.07 (m, 1H), 7.06-7.00 (m, 2H), 6.16 (ddd, J_1 = 17.0 Hz, J_2 = 10.1 Hz, J_3 = 8.9 Hz, 1H), 5.04-4.95 (m, 2H), 4.93 (d, J = 3.2 Hz, 1H) , 3.63 (dd, J_1 = 8.7 Hz, J_2 = 3.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.9, 137.7, 135.9, 135.7,

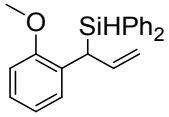
132.7, 132.5, 129.9, 129.7, 128.5, 128.3, 127.9, 127.8, 125.4, 114.5, 40.8. **HRMS** (ESI) m/z Calculated for $C_{21}H_{20}NaSi^+$ $[M+Na]^+$: 323.1226, found: 323.1224.

(1-([1,1'-biphenyl]-4-yl)allyl)diphenylsilane (3j)



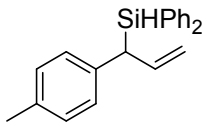
colorless liquid (73%, 69 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58-7.51 (m, 4H), 7.46-7.42 (m, 4H), 7.41-7.36 (m, 3H), 7.36-7.31(m, 3H), 7.30-7.23 (m, 3H), 7.12-7.06 (m, 2H), 6.18 (ddd, J_1 = 17.0 Hz, J_2 = 10.2 Hz, J_3 = 8.8 Hz, 1H), 5.06-4.98 (m, 2H), 4.97 (d, J = 3.2 Hz, 1H) , 3.63 (dd, J_1 = 8.7 Hz, J_2 = 3.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.0, 140.1, 138.2, 137.6, 136.0, 135.7, 132.7, 132.5, 130.0, 129.8, 128.8, 128.7, 128.0, 127.9, 127.1, 127.0, 126.9, 114.7, 40.6. **HRMS** (ESI) m/z Calculated for $C_{27}H_{24}NaSi^+$ $[M+Na]^+$: 399.1539, found: 399.1540.

(1-(2-methoxyphenyl)allyl)diphenylsilane (3k)



colorless liquid (89%, 74 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61-7.53 (m, 2H), 7.42-7.32 (m, 5H), 7.22-7.26 (m, 1H), 7.25-7.18 (m, 2H), 7.12-7.04 (m, 2H), 6.85 (t, J = 7.4 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 6.23-6.13(m, 1H), 5.01-4.92 (m, 2H), 4.85 (d, J = 3.3 Hz, 1H), 4.08 (dd, J_1 = 9.0 Hz, J_2= 3.2 Hz, 1H), 3.53 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.0, 137.5, 135.8, 135.4, 133.61, 133.55, 129.7, 129.6, 129.3, 128.4, 127.8, 127.5, 126.2, 120.5, 114.3, 110.4, 55.0, 33.2. **HRMS** (ESI) m/z Calculated for $C_{22}H_{22}NaOSi^+$ $[M+Na]^+$: 353.1332, found: 353.1331.

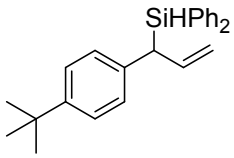
diphenyl(1-(p-tolyl)allyl)silane (3l)



colorless liquid (50%, 39 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54-7.49 (m, 2H), 7.44-7.37 (m, 3H), 7.37-7.31 (m, 3H), 7.29-7.24 (m, 2H), 7.01 (d, J = 7.9 Hz, 2H), 6.93 (d, J = 7.9 Hz, 2H), 6.13 (ddd, J_1 = 17.0 Hz, J_2 = 9.8 Hz, J_3 = 9.1 Hz, 1H), 5.01-4.90 (m, 3H), 3.59 (dd, J_1 = 8.6 Hz, J_2 = 2.6

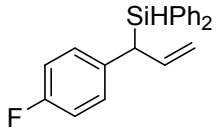
Hz, 1H), 2.28 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.0, 137.7, 135.9, 135.7, 134.8, 132.9, 132.7, 129.8, 129.7, 129.2, 128.2, 127.9, 127.8, 114.3, 40.2, 21.0. **HRMS** (ESI) m/z Calculated for $C_{22}H_{22}NaSi^+$ $[M+Na]^+$: 337.1383, found: 337.1381.

(1-(4-(tert-butyl)phenyl)allyl)diphenylsilane (3m)



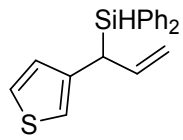
colorless liquid (65%, 58 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54-7.49 (m, 2H), 7.42-7.29 (m, 6H), 7.27-7.19 (m, 4H), 7.01-6.94 (m, 2H), 6.15 (apparent dt, J_1 = 17.1 Hz, J_2 = 9.4 Hz, 1H), 5.01-4.94 (m, 2H), 4.93 (d, J = 3.1 Hz, 1H), 3.60 (dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz, 1H), 1.28 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.2, 137.9, 137.7, 136.0, 135.7, 135.3, 133.0, 132.7, 129.8, 129.6, 127.9, 127.7, 125.3, 114.3, 40.2, 34.3, 31.5. **HRMS** (ESI) m/z Calculated for $C_{25}H_{28}NaSi^+$ $[M+Na]^+$: 379.1852, found: 379.1853.

(1-(4-fluorophenyl)allyl)diphenylsilane (3n)



colorless liquid (66%, 53 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.42-7.38 (m, 3H), 7.38-7.32 (m, 3H), 7.31-7.25 (m, 2H), 7.00-6.94 (m, 2H), 6.91-6.85 (m, 2H), 6.11 (ddd, J_1 = 17.0 Hz, J_2 = 10.2 Hz, J_3 = 8.6 Hz, 1H), 5.02 (apparent dt, J_1 = 10.3 Hz, J_2 = 1.2 Hz, 1H), 4.96 (apparent dt, J_1 = 17.0 Hz, J_2 = 1.3 Hz, 1H), 4.92 (d, J = 3.3 Hz, 1H), 3.60 (dd, J_1 = 8.6 Hz, J_2 = 3.2 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.9 (d, J = 242.9 Hz), 137.5, 136.4 (d, J = 2.8 Hz), 135.8, 135.6, 132.4, 132.2, 130.0, 129.8, 129.5 (d, J = 7.4 Hz), 128.0, 127.8, 115.2 (d, J = 20.9 Hz), 114.7, 39.9. **HRMS** (ESI) m/z Calculated for $C_{21}H_{19}FNaSi^+$ $[M+Na]^+$: 341.1132, found: 341.1134.

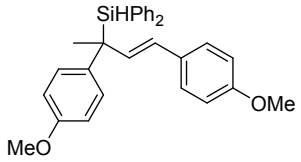
diphenyl(1-(thiophen-3-yl)allyl)silane (3o)



colorless liquid (58%, 44 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, J = 7.2 Hz, 2H), 7.46-7.32

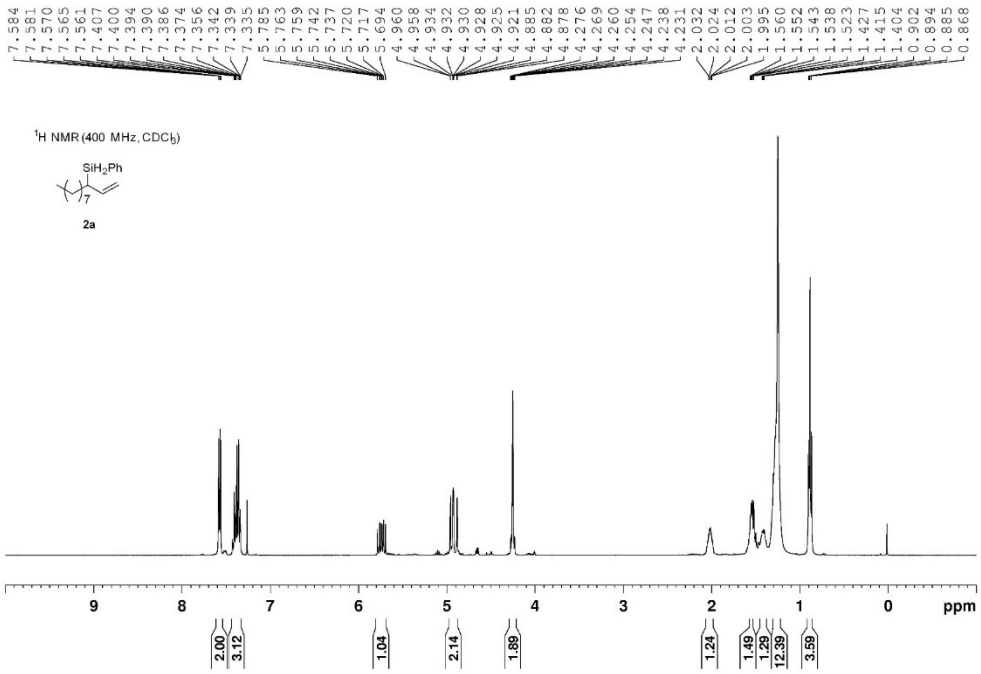
(m, 6H), 7.31-7.26 (m, 2H), 7.18 (dd, J_1 = 4.7 Hz, J_2 = 3.0 Hz, 1H), 6.78 (d, J = 4.7 Hz, 1H), 6.75 (d, J = 1.7 Hz, 1H), 6.08 (ddd, J_1 = 17.3 Hz, J_2 = 9.9 Hz, J_3 = 9.0 Hz, 1H), 5.06-4.88 (m, 3H), 3.77 (apparent d, J = 8.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.4, 137.3, 135.8, 135.7, 132.6, 132.5, 129.9, 129.8, 128.2, 127.96, 127.86, 125.2, 119.7, 114.4, 35.9. **HRMS** (ESI) m/z Calculated for $C_{19}H_{18}NaSSi^+$ $[M+Na]^+$: 329.0791, found: 329.0797.

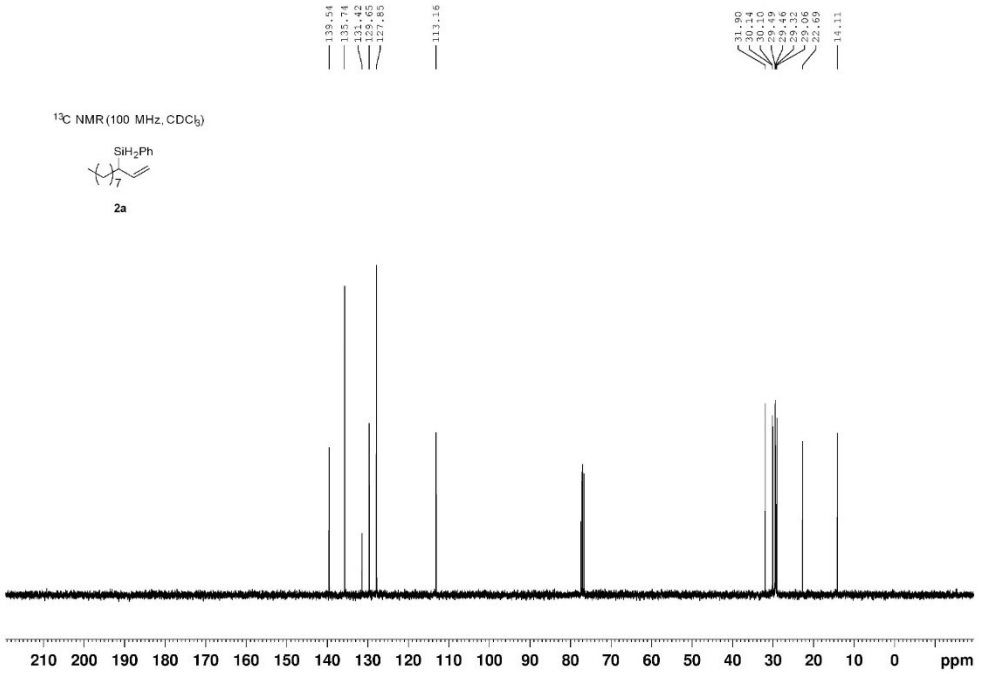
(E)-(2,4-bis(4-methoxyphenyl)but-3-en-2-yl)diphenylsilane (3p)



colorless liquid (70%, 79 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 2H), 7.38-7.31 (m, 4H), 7.31-7.17 (m, 8H), 6.89-6.78 (m, 4H), 6.60 (d, J = 16.1 Hz, 1H), 6.22 (d, J = 16.1Hz, 1H), 5.00 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 1.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 157.4, 137.7, 136.3, 136.1, 133.6, 132.93, 132.88, 131.1, 129.8, 129.7, 128.5, 127.7, 127.2, 127.1, 114.0, 113.7, 55.33, 55.28, 36.1, 22.5. **HRMS** (ESI) m/z Calculated for $C_{30}H_{30}NaO_2Si^+$ $[M+Na]^+$: 473.1907, found: 473.1911.

7. NMR spectra


7.584
7.581
7.570
7.565
7.561
7.407
7.400
7.394
7.390
7.386
7.374
7.356
7.342
7.339
7.335
5.785
5.763
5.759
5.742
5.737
5.720
5.717
5.694
4.960
4.958
4.934
4.932
4.930
4.928
4.925
4.921
4.885
4.882
4.878
4.276
4.269
4.260
4.254
4.247
4.238
4.231
2.032
2.024
2.012
2.003
1.995
1.560
1.552
1.543
1.538
1.523
1.427
1.415
1.404
0.902
0.894
0.885
0.868
1H NMR (400 MHz, CDCl3)
SiH2Ph
7
2a
9
8
7
6
5
4
3
2
1
0
ppm
2.00
3.12
1.04
2.14
1.89
1.24
1.49
1.29
12.39
3.59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135.74
133.42
129.65
127.85
113.16
31.90
30.14
30.10
29.49
29.46
29.32
29.06
22.69
14.11
13C NMR (100 MHz, CDCl3)
SiH2Ph
7
2a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
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10
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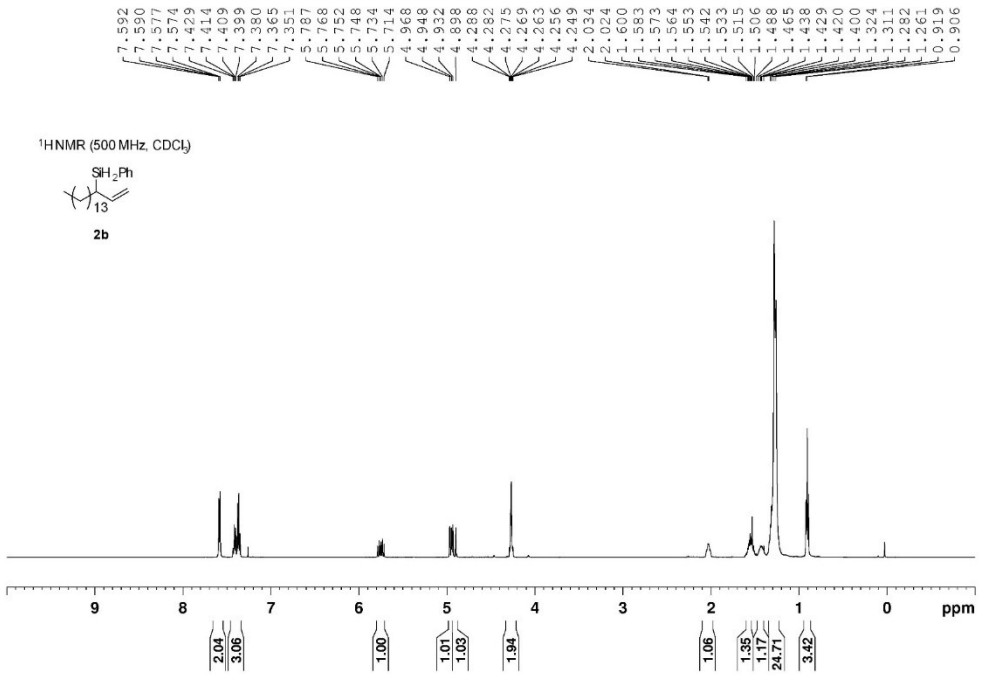
ppm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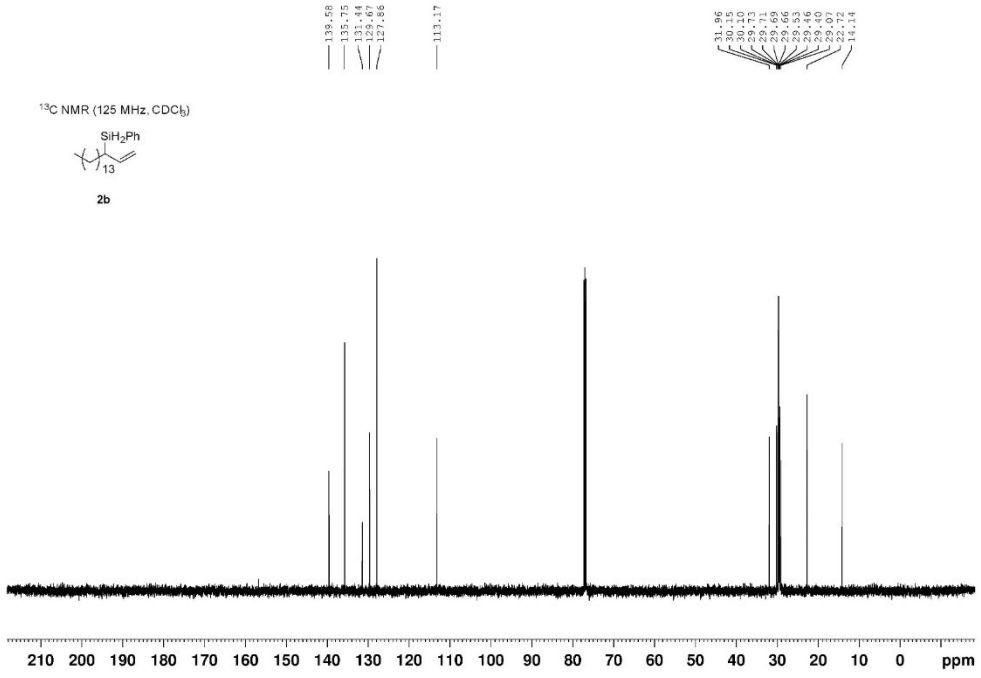
7.399
7.380
7.365
7.351
5.787
5.768
5.752
5.748
5.734
5.714
4.968
4.948
4.932
4.898
4.288
4.282
4.275
4.269
4.263
4.256
4.249
2.034
2.024
1.600
1.583
1.573
1.564
1.553
1.542
1.533
1.515
1.506
1.488
1.465
1.438
1.429
1.420
1.400
1.324
1.311
1.282
1.261
0.919
0.906
1H NMR (500 MHz, CDCl3)
SiH2Ph
13
2b
9
8
7
6
5
4
3
2
1
0
ppm
2.04
3.06
1.00
1.01
1.03
1.94
1.06
1.35
1.17
24.71
3.42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129.67
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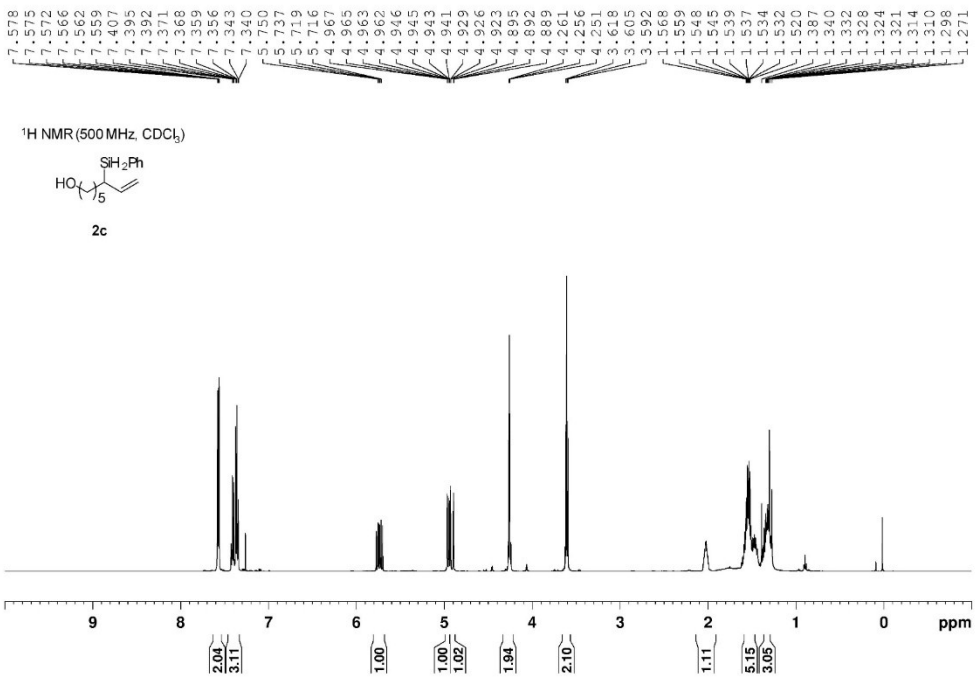
113.17
31.96
30.15
30.10
29.73
29.71
29.69
29.66
29.53
29.46
29.40
29.00
22.72
14.14
13C NMR (125 MHz, CDCl3)
SiH2Ph
13
2b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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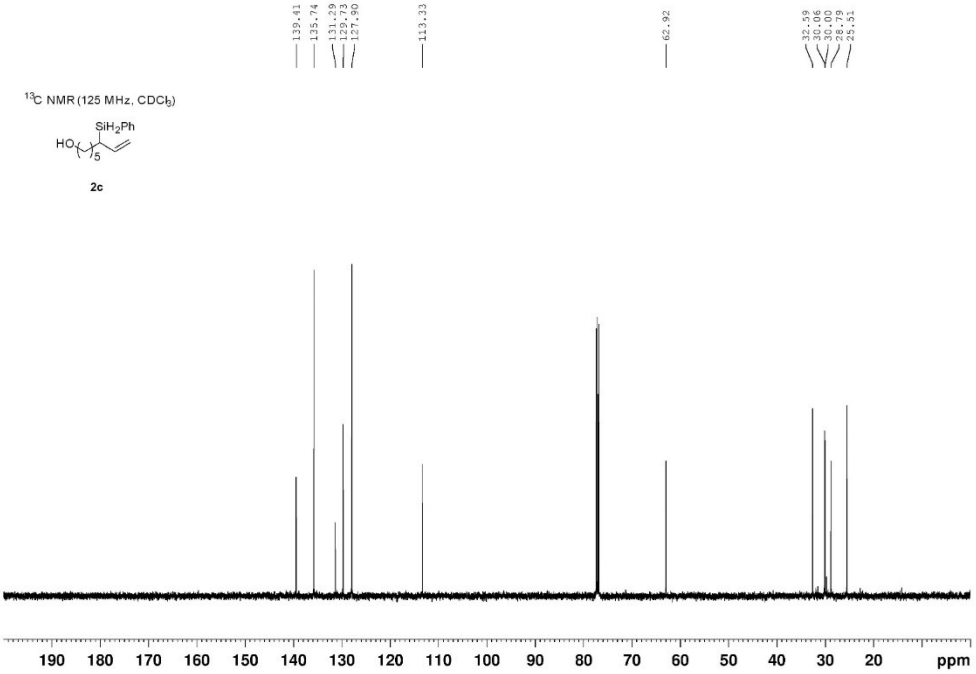
7.575
7.572
7.566
7.562
7.559
7.407
7.395
7.392
7.371
7.368
7.359
7.356
7.343
7.340
5.750
5.737
5.719
5.716
4.967
4.965
4.963
4.962
4.946
4.945
4.943
4.941
4.929
4.926
4.923
4.895
4.892
4.889
4.261
4.256
4.251
3.618
3.605
3.592
1.568
1.559
1.548
1.545
1.539
1.537
1.534
1.532
1.520
1.387
1.340
1.332
1.328
1.324
1.321
1.314
1.310
1.298
1.271
1H NMR (500 MHz, CDCl3)
SiH2Ph
HO
5
2c
9
8
7
6
5
4
3
2
1
0
ppm
2.04
3.11
1.00
1.00
1.02
1.94
2.10
1.11
5.15
3.05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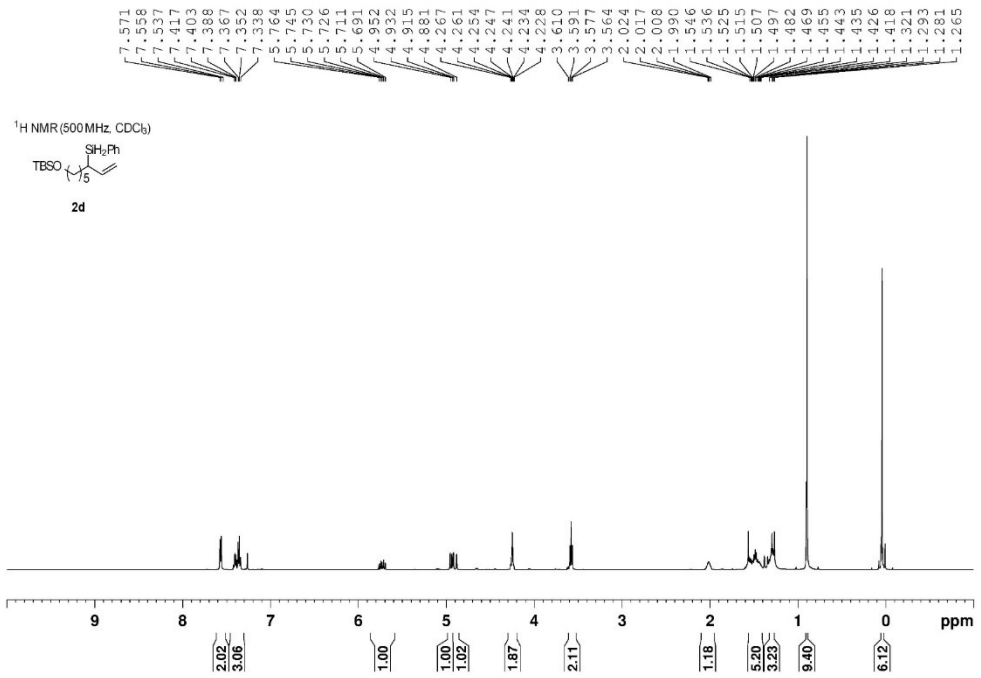
131.29
129.73
127.90
113.33
62.92
32.59
30.06
29.00
28.79
25.51
13C NMR (125 MHz, CDCl3)
SiH2Ph
HO
5
2c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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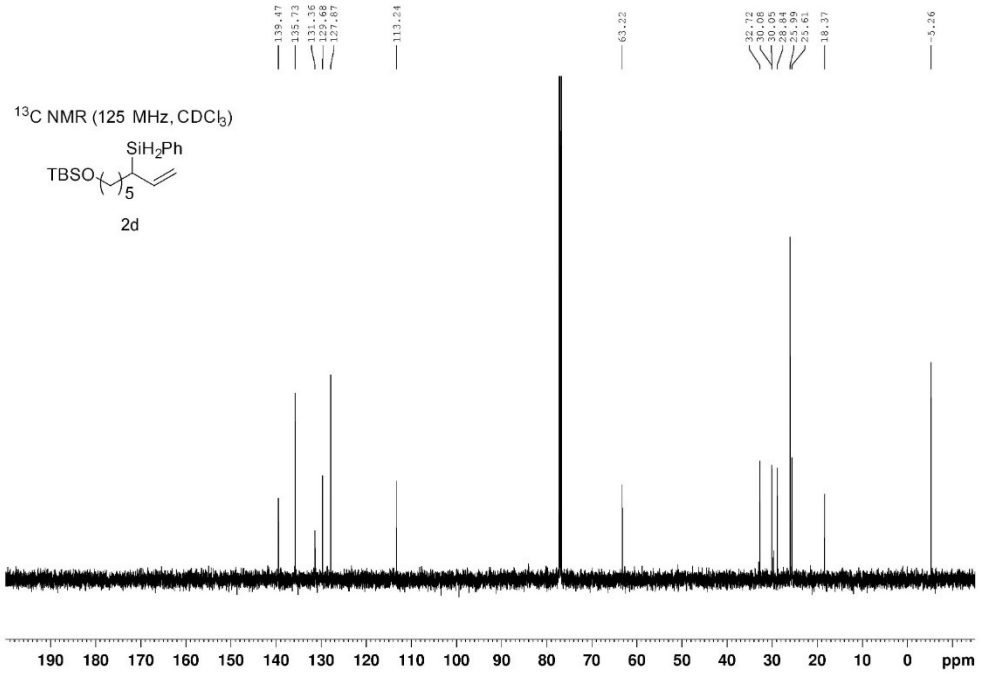
7.558
7.537
7.417
7.403
7.388
7.367
7.352
7.338
5.764
5.745
5.730
5.726
5.711
5.691
4.952
4.932
4.915
4.881
4.267
4.261
4.254
4.247
4.241
4.234
4.228
3.610
3.591
3.577
3.564
2.024
2.017
2.008
1.990
1.546
1.536
1.525
1.515
1.507
1.497
1.482
1.469
1.455
1.443
1.435
1.426
1.418
1.321
1.293
1.281
1.265
1H NMR (500 MHz, CDCl3)
SiH2Ph
TBSO
5
2d
9
8
7
6
5
4
3
2
1
0
ppm
2.02
3.06
1.00
1.00
1.02
1.87
2.11
1.18
5.20
3.23
9.40
6.12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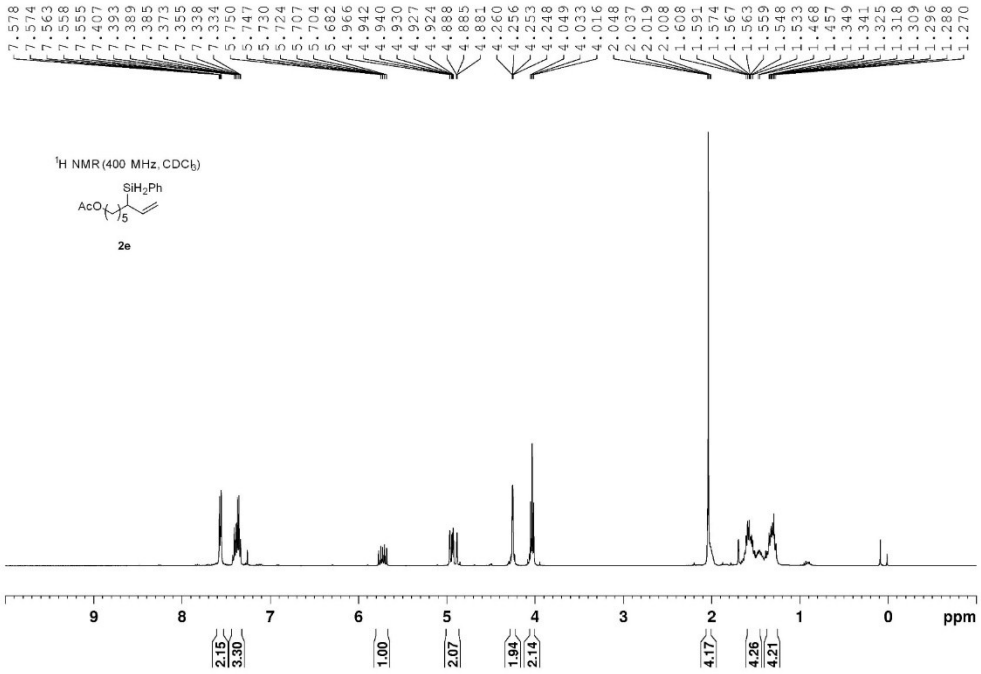
131.36
129.68
127.87
113.24
63.22
32.72
30.88
30.05
28.84
25.99
25.61
18.37
-5.26
13C NMR (125 MHz, CDCl3)
SiH2Ph
TBSO
5
2d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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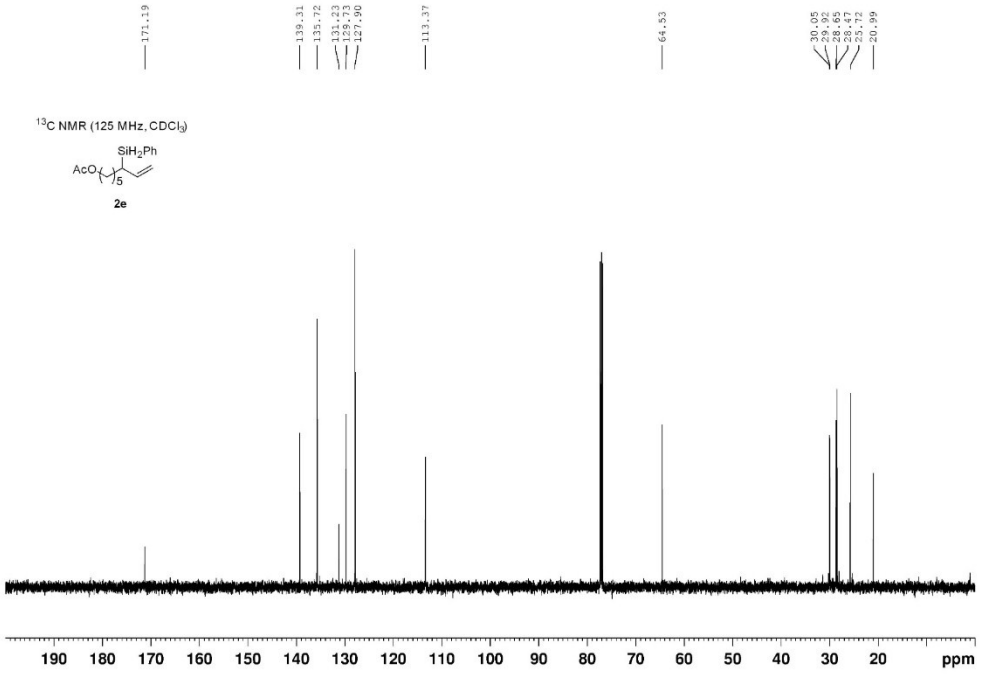
7.574
7.563
7.558
7.555
7.407
7.393
7.389
7.385
7.373
7.355
7.338
7.334
5.750
5.747
5.730
5.724
5.707
5.704
5.682
4.966
4.942
4.940
4.930
4.927
4.924
4.888
4.885
4.881
4.260
4.256
4.253
4.248
4.049
4.033
4.016
2.048
2.037
2.019
2.008
1.608
1.591
1.574
1.567
1.563
1.559
1.548
1.533
1.468
1.457
1.349
1.341
1.325
1.318
1.309
1.296
1.288
1.270
1H NMR (400 MHz, CDCl3)
SiH2Ph
AcO
5
2e
9
8
7
6
5
4
3
2
1
0
ppm
2.15
3.30
1.00
2.07
1.94
2.14
4.17
4.26
4.21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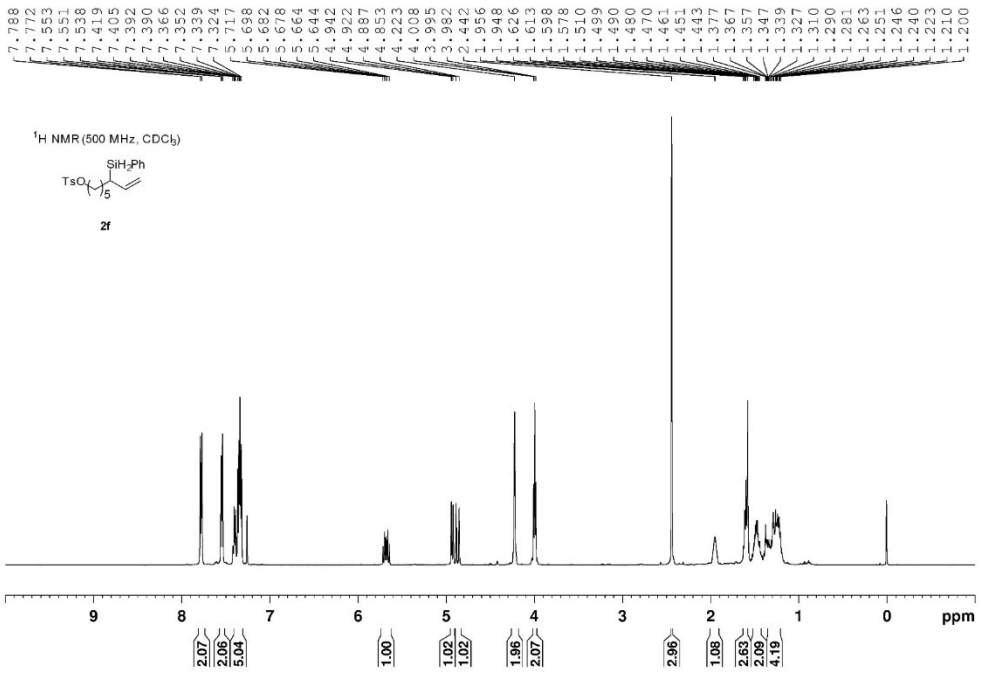
139.31
135.72
131.23
129.73
127.90
113.37
64.53
30.05
29.92
28.65
28.47
25.72
20.99
13C NMR (125 MHz, CDCl3)
SiH2Ph
AcO
5
2e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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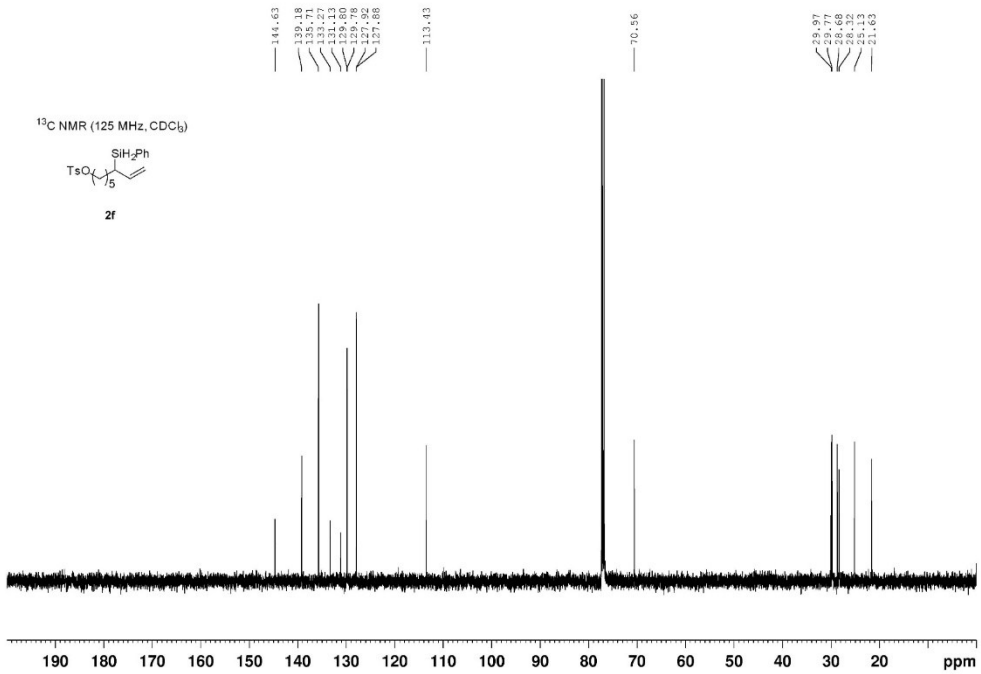
7.553
7.551
7.538
7.419
7.405
7.392
7.390
7.366
7.352
7.339
7.324
5.717
5.698
5.682
5.678
5.664
5.644
4.942
4.922
4.887
4.853
4.223
4.008
3.995
3.982
2.442
1.956
1.948
1.626
1.613
1.598
1.578
1.510
1.499
1.490
1.480
1.470
1.461
1.451
1.443
1.377
1.367
1.357
1.347
1.339
1.327
1.310
1.290
1.281
1.263
1.251
1.246
1.240
1.223
1.210
1.200
1H NMR (500 MHz, CDCl3)
SiH2Ph
TsO
5
2f
9
8
7
6
5
4
3
2
1
0
ppm
2.07
2.06
5.04
1.00
1.02
1.02
1.96
2.07
2.96
1.08
2.63
2.09
4.19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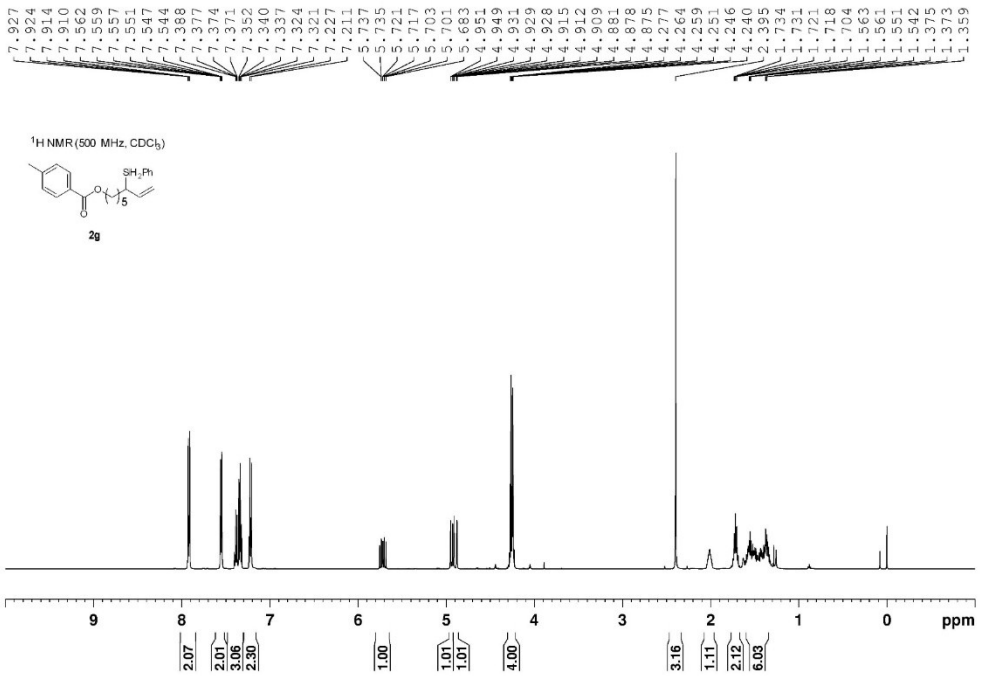
135.71
133.27
131.13
129.60
129.38
127.92
127.88
113.43
70.56
29.97
29.77
28.68
28.32
25.13
21.63
13C NMR (125 MHz, CDCl3)
SiH2Ph
TsO
5
2f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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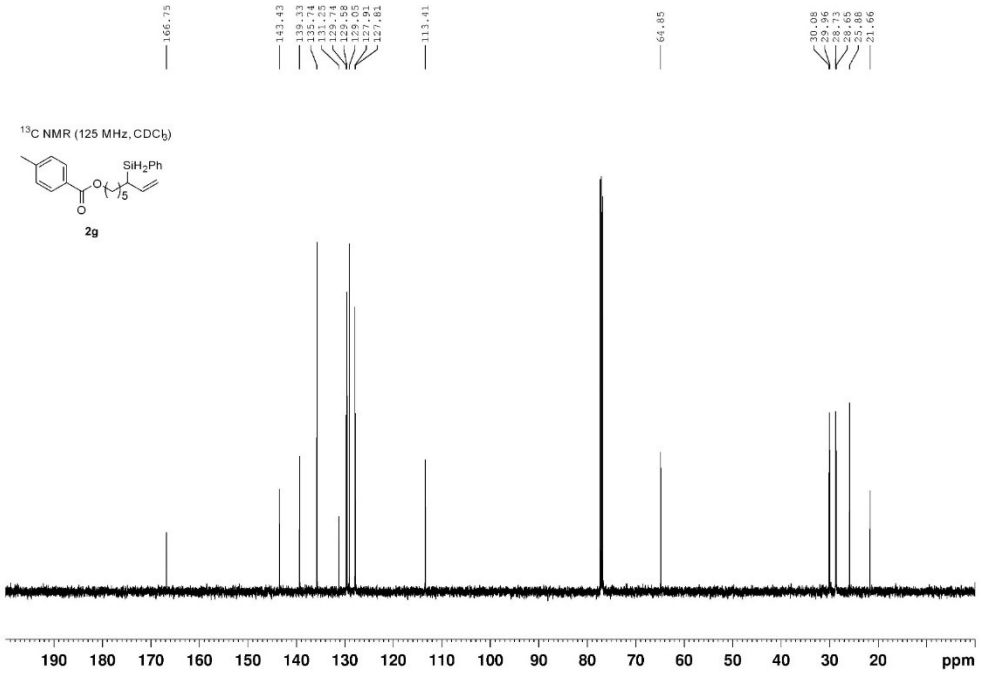
7.914
7.910
7.562
7.559
7.557
7.551
7.547
7.544
7.388
7.377
7.374
7.371
7.352
7.340
7.337
7.324
7.321
7.227
7.211
5.737
5.735
5.721
5.717
5.703
5.701
5.683
4.951
4.949
4.931
4.929
4.928
4.915
4.912
4.909
4.881
4.878
4.875
4.277
4.264
4.259
4.251
4.246
4.240
2.395
1.734
1.731
1.721
1.718
1.704
1.563
1.561
1.551
1.542
1.375
1.373
1.359
1H NMR (500 MHz, CDCl3)
SiH2Ph
5
2g
9
8
7
6
5
4
3
2
1
0
ppm
2.07
2.01
3.06
2.30
1.00
1.01
1.01
4.00
3.16
1.11
2.12
6.03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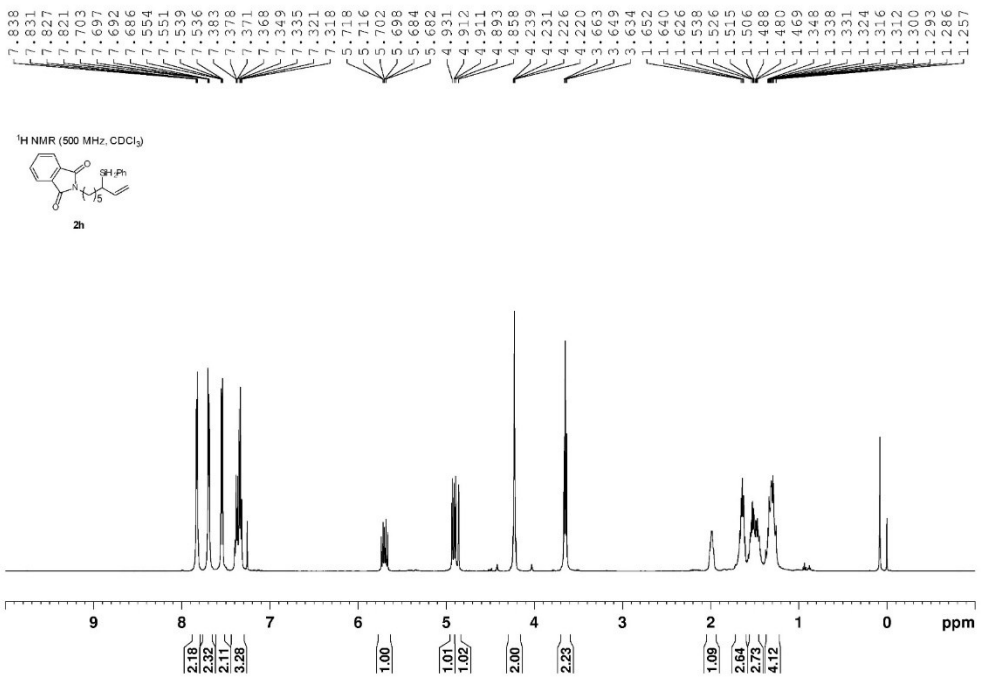
133.74
131.25
129.74
129.58
129.05
127.91
127.61
113.41
64.85
30.08
29.96
28.73
28.65
25.68
21.66
13C NMR (125 MHz, CDCl3)
SiH2Ph
5
2g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.821
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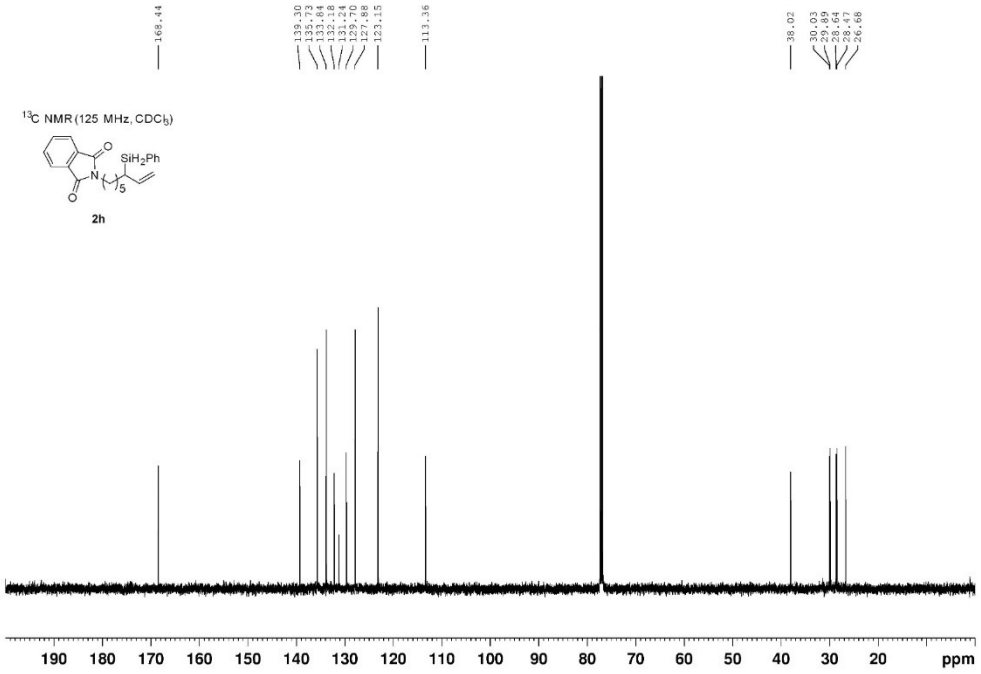
7.697
7.692
7.686
7.554
7.551
7.539
7.536
7.383
7.378
7.371
7.368
7.349
7.335
7.321
7.318
5.718
5.716
5.702
5.698
5.684
5.682
4.931
4.912
4.911
4.893
4.858
4.239
4.231
4.226
4.220
3.663
3.649
3.634
1.652
1.640
1.626
1.538
1.526
1.515
1.506
1.488
1.480
1.469
1.348
1.338
1.331
1.324
1.316
1.312
1.300
1.293
1.286
1.257
1H NMR (500 MHz, CDCl3)
SiH2Ph
2h
9
8
7
6
5
4
3
2
1
0
ppm
2.18
2.32
2.11
3.28
1.00
1.01
1.02
2.00
2.23
1.09
2.64
2.73
4.12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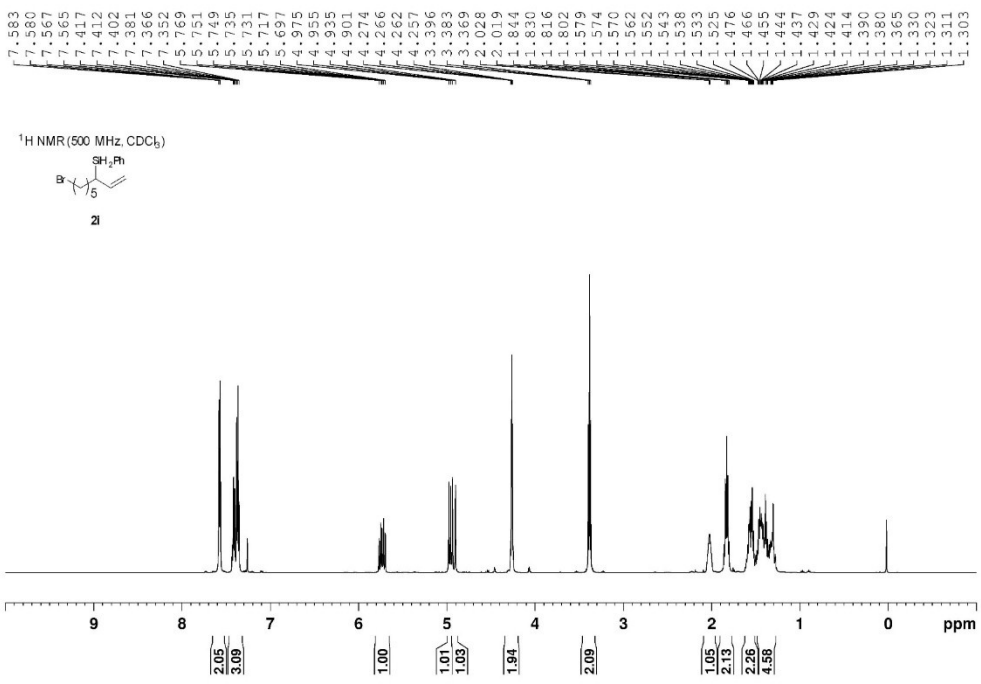
135.73
133.84
132.18
131.24
129.70
127.88
123.15
113.36
38.02
30.03
29.89
28.64
28.47
26.68
13C NMR (125 MHz, CDCl3)
SiH2Ph
2h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.565
7.417
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7.381
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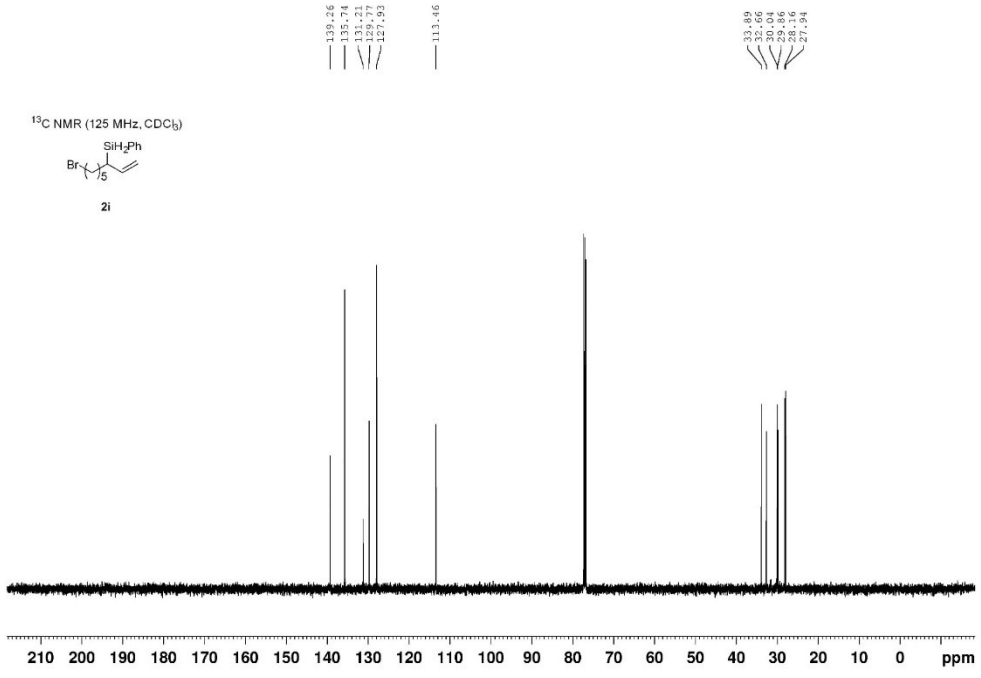
7.352
5.769
5.751
5.749
5.735
5.731
5.717
5.697
4.975
4.955
4.935
4.901
4.274
4.266
4.262
4.257
3.396
3.383
3.369
3.028
2.019
1.844
1.830
1.816
1.802
1.579
1.574
1.570
1.562
1.552
1.543
1.538
1.533
1.525
1.476
1.466
1.455
1.444
1.437
1.429
1.424
1.414
1.390
1.380
1.365
1.330
1.323
1.311
1.303
1H NMR (500 MHz, CDCl3)
SiH2Ph
Br
5
2i
9
8
7
6
5
4
3
2
1
0
ppm
2.05
3.09
1.00
1.01
1.03
1.94
2.09
1.05
2.13
2.26
4.58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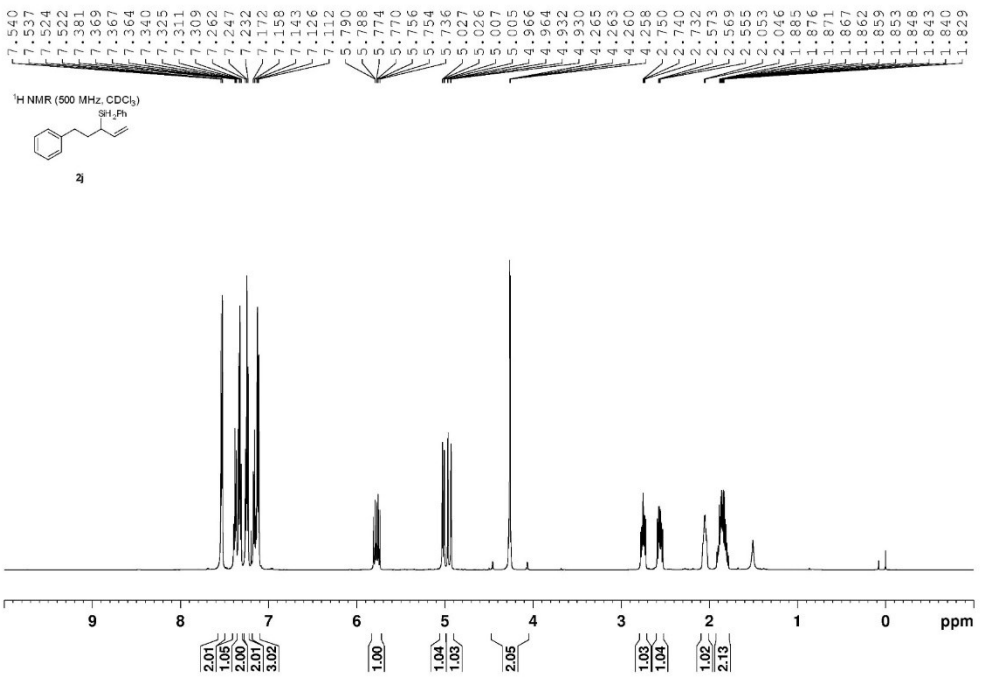
135.74
131.21
129.77
127.83
113.46
33.89
32.66
30.04
29.86
28.16
27.94
13C NMR (125 MHz, CDCl3)
SiH2Ph
Br
5
2i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.537
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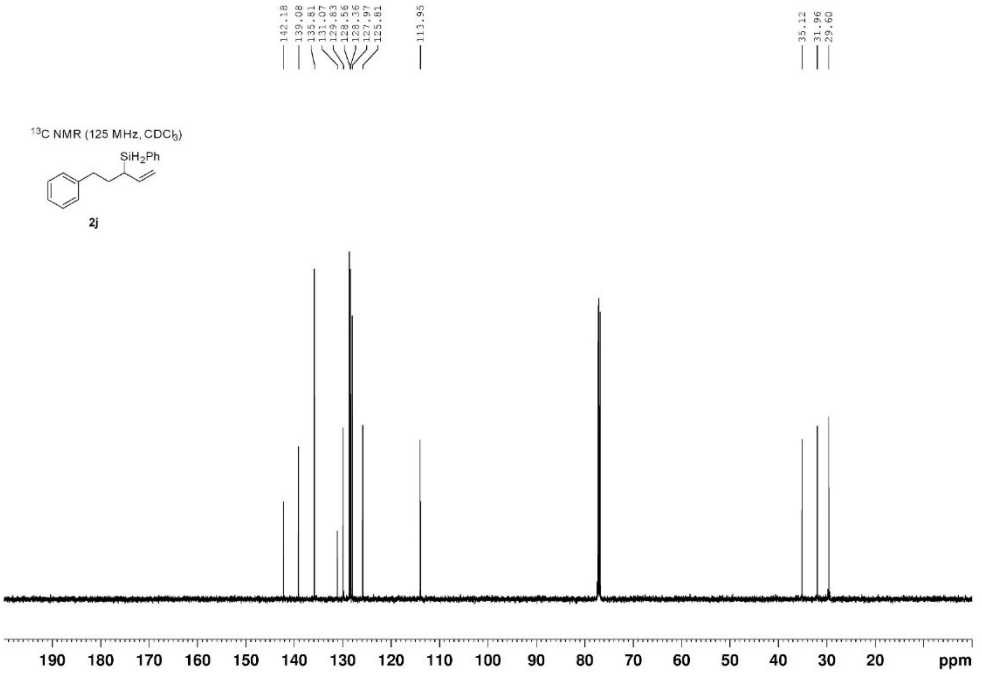
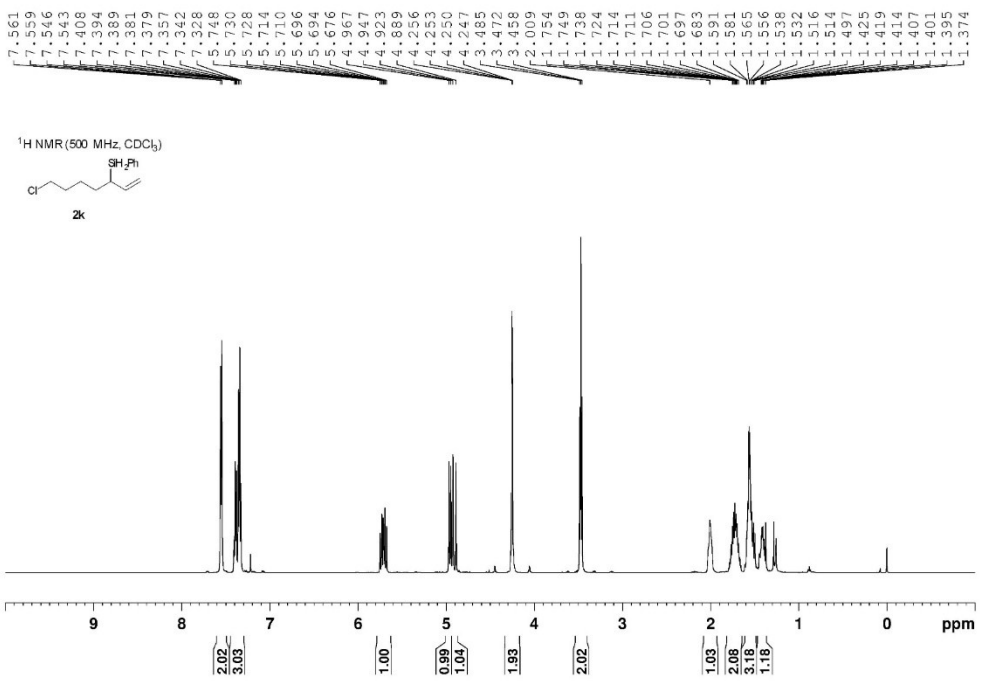
7.522
7.381
7.369
7.367
7.364
7.340
7.325
7.311
7.309
7.262
7.247
7.232
7.172
7.158
7.143
7.126
7.112
5.790
5.788
5.774
5.770
5.756
5.754
5.736
5.027
5.026
5.007
5.005
4.966
4.964
4.932
4.930
4.265
4.263
4.260
4.258
2.750
2.740
2.732
2.573
2.569
2.555
2.053
2.046
1.885
1.876
1.871
1.867
1.862
1.859
1.853
1.848
1.843
1.840
1.829
^{1}H NMR (500 MHz, CDCl$_3$)
SiH$_2$Ph
2j
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.05
2.00
2.01
3.02
1.00
1.04
1.03
2.05
1.03
1.04
1.02
2.13


142.18
139.08
135.81
133.07
129.83
128.56
128.36
127.97
125.81
113.95
35.12
31.96
29.60
^{13}C NMR (125 MHz, CDCl$_3$)
SiH$_2$Ph
2j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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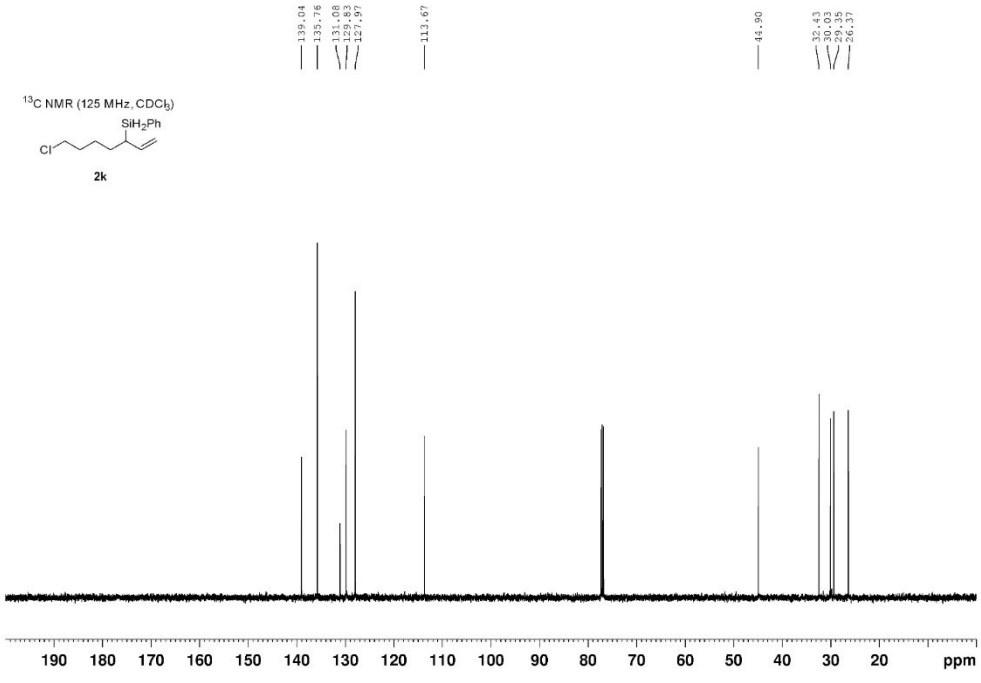
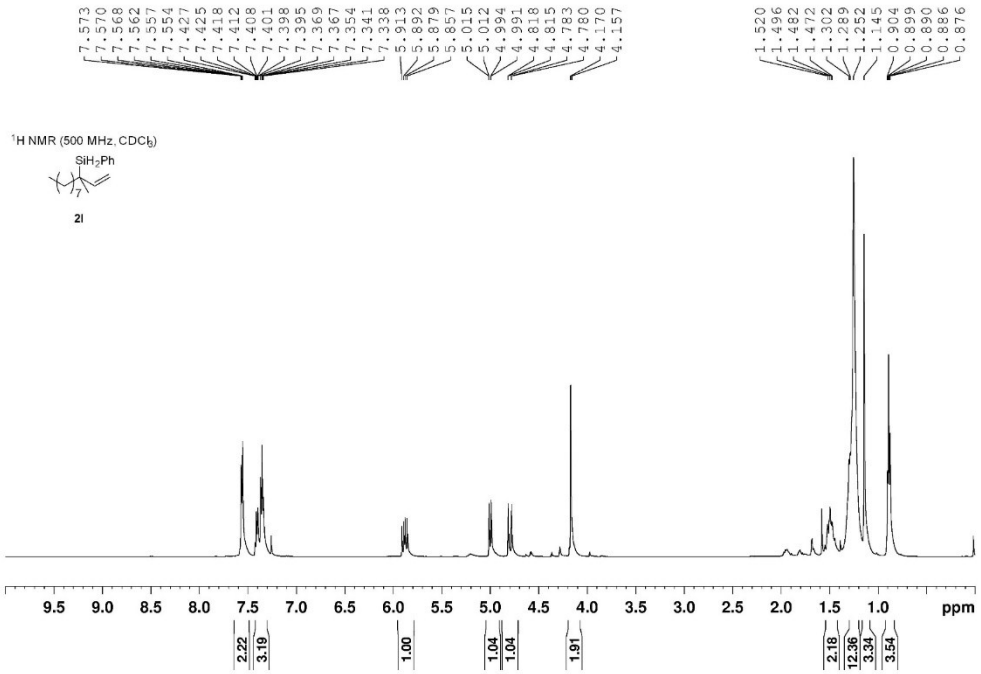
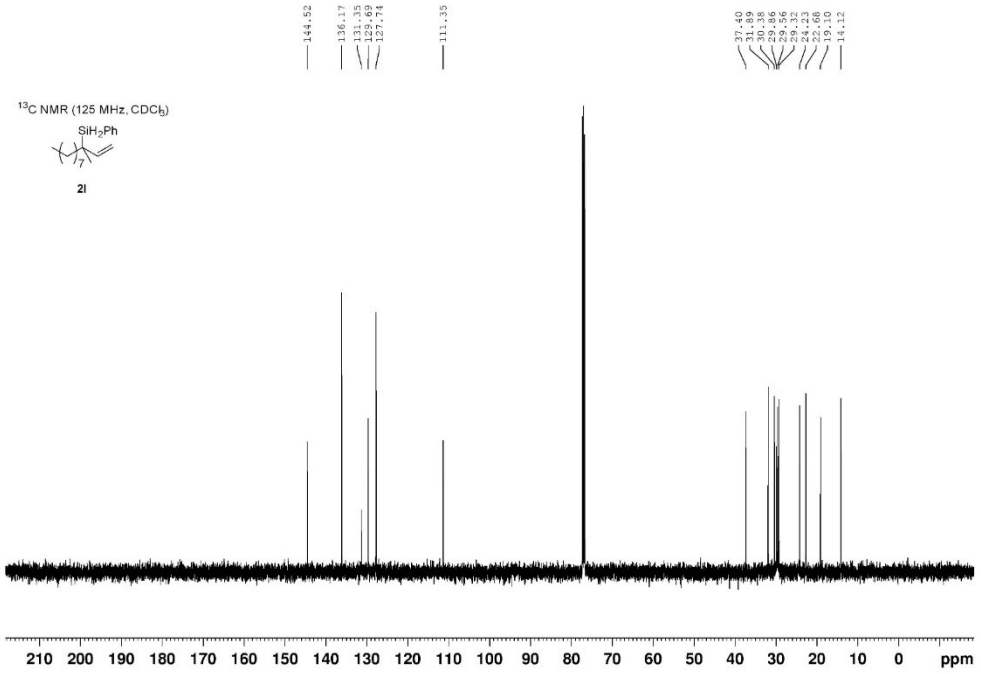
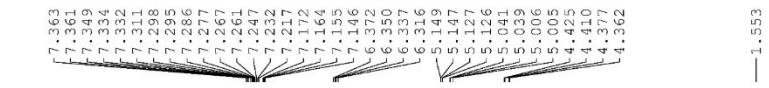
7.559
7.546
7.543
7.408
7.394
7.389
7.381
7.379
7.357
7.342
7.328
5.748
5.730
5.728
5.714
5.710
5.696
5.694
5.676
4.967
4.947
4.923
4.889
4.256
4.253
4.250
4.247
3.485
3.472
3.458
2.009
1.754
1.749
1.738
1.724
1.714
1.711
1.706
1.701
1.697
1.683
1.591
1.581
1.565
1.556
1.538
1.532
1.516
1.514
1.497
1.425
1.419
1.414
1.407
1.401
1.395
1.374
1H NMR (500 MHz, CDCl3)
SiH2Ph
Cl
2k
9
8
7
6
5
4
3
2
1
0
ppm
2.02
3.03
1.00
0.99
1.04
1.93
2.02
1.03
2.08
3.18
1.18

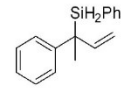

139.04
135.76
131.08
129.83
127.97
113.67
44.90
32.43
30.03
29.35
26.37
13C NMR (125 MHz, CDCl3)
SiH2Ph
Cl
2k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.573
7.570
7.568
7.562
7.557
7.554
7.427
7.425
7.418
7.412
7.408
7.401
7.398
7.395
7.369
7.367
7.354
7.341
7.338
5.913
5.892
5.879
5.857
5.015
5.012
4.994
4.991
4.818
4.815
4.783
4.780
4.170
4.157
1.520
1.496
1.482
1.472
1.302
1.289
1.252
1.145
0.904
0.899
0.890
0.886
0.876
1H NMR (500 MHz, CDCl3)
SiH2Ph
7
2l
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.22
3.19
1.00
1.04
1.04
1.91
2.18
12.36
3.34
3.54

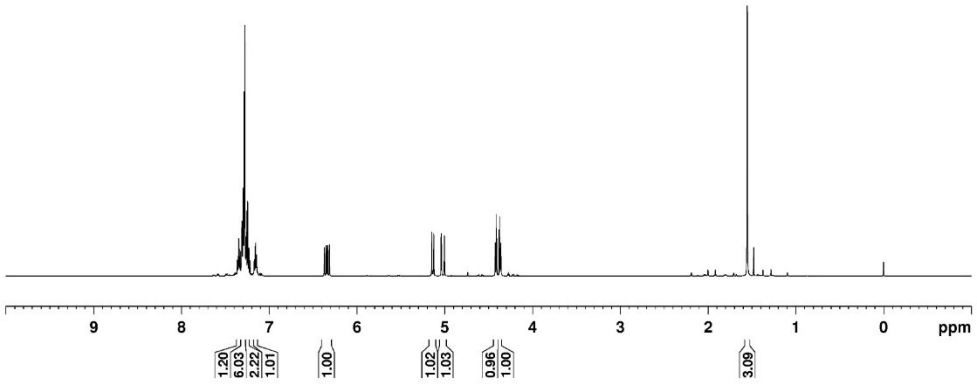

144.52
136.17
131.35
130.69
127.74
111.35
37.40
31.89
29.38
29.36
29.56
29.32
24.23
22.66
19.10
14.12
13C NMR (125 MHz, CDCl3)
SiH2Ph
7
2l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



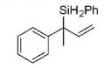
^{1}H NMR (500 MHz, $CDCl_3$)



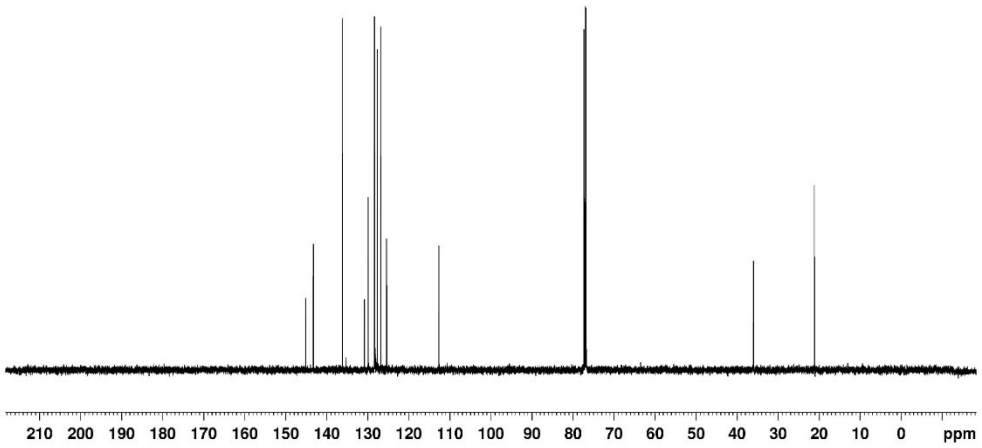
2m

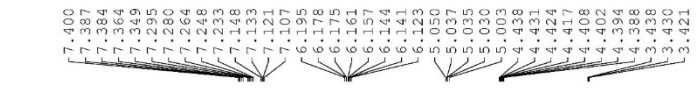


^{13}C NMR (125 MHz, $CDCl_3$)



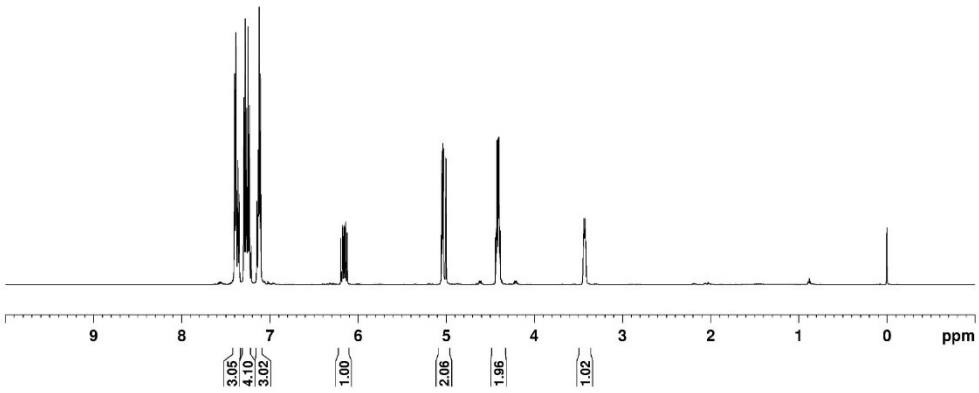
2m





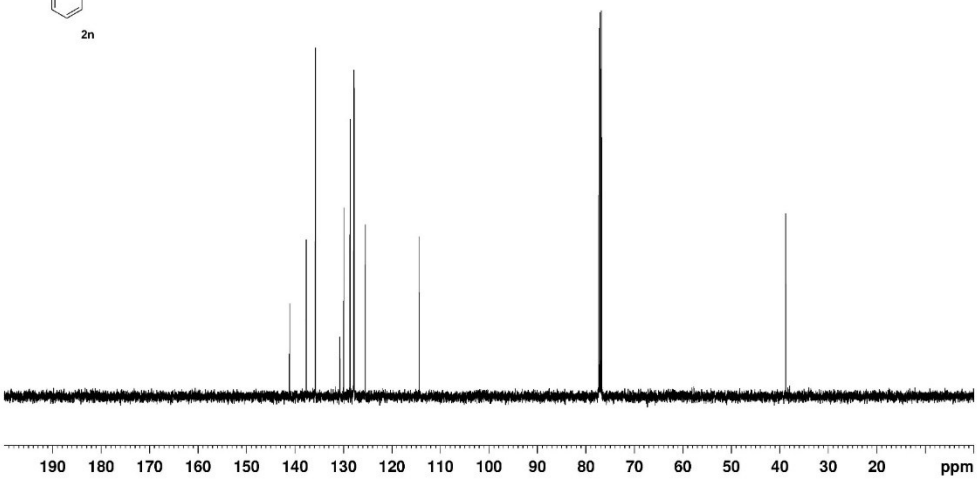
^{1}H NMR (500 MHz, $CDCl_3$)

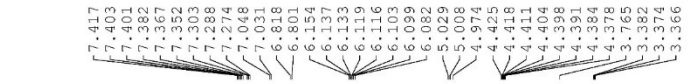
2n

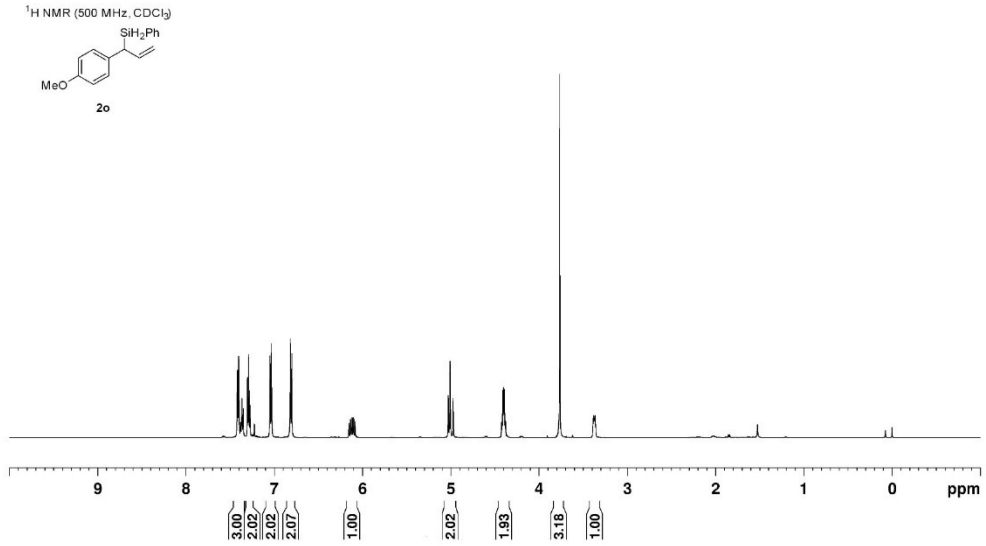


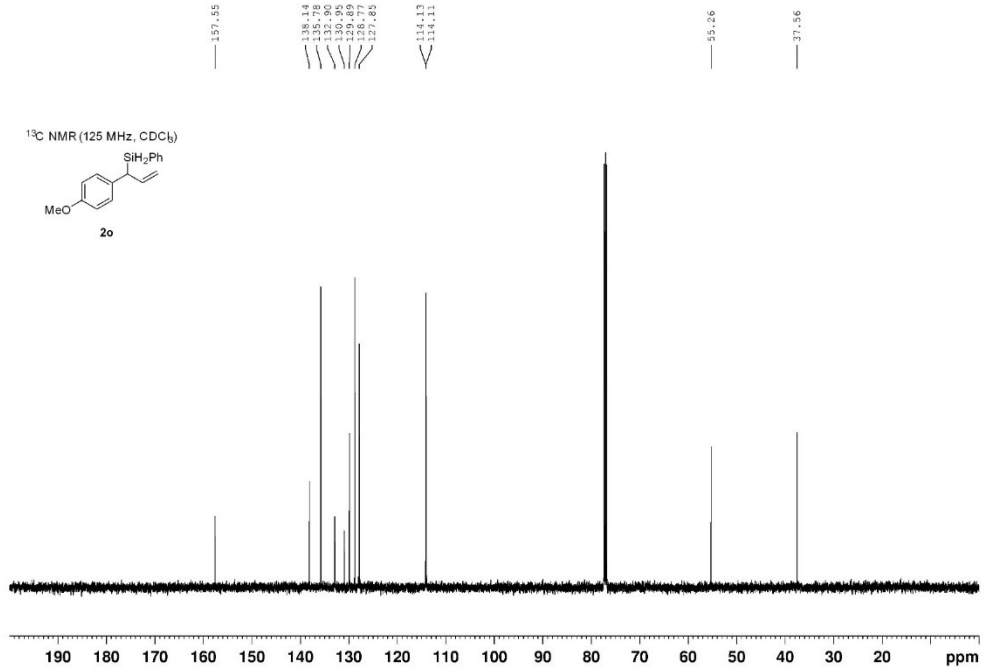
^{13}C NMR (125 MHz, $CDCl_3$)

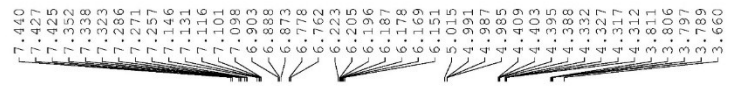
2n



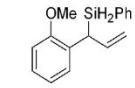

7.417
7.403
7.401
7.382
7.367
7.352
7.303
7.288
7.274
7.048
7.031
6.818
6.801
6.154
6.137
6.133
6.119
6.116
6.103
6.099
6.082
5.029
5.008
4.974
4.425
4.418
4.411
4.404
4.398
4.391
4.384
4.378
3.765
3.382
3.374
3.366


^{1}H NMR (500 MHz, CDCl$_3$)
SiH$_2$Ph
MeO
2o
9
8
7
6
5
4
3
2
1
0
ppm
3.00
2.02
2.02
2.07
1.00
2.02
1.93
3.18
1.00

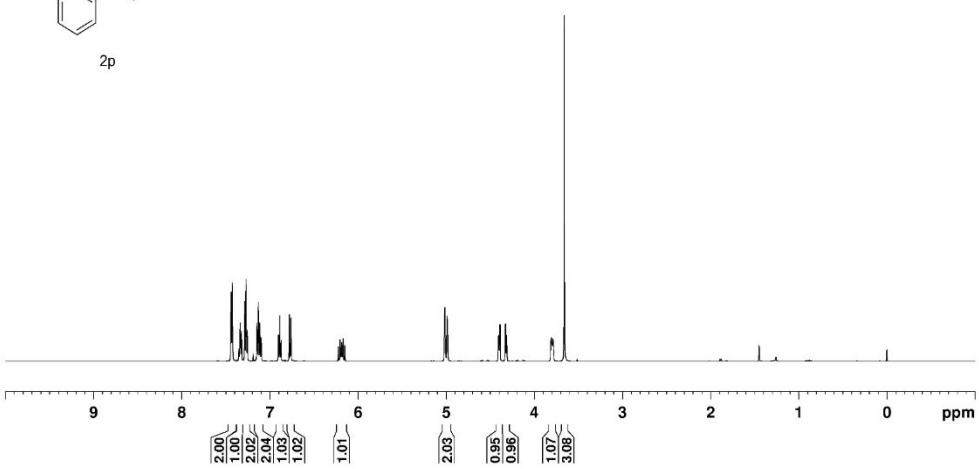

157.55
138.14
135.78
132.90
130.95
129.89
128.77
127.85
114.13
114.11
55.26
37.56
^{13}C NMR (125 MHz, CDCl$_3$)
SiH$_2$Ph
MeO
2o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

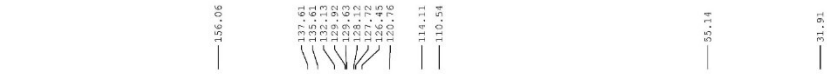


^{1}H NMR (500 MHz, $CDCl_3$)

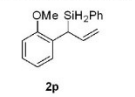


2p

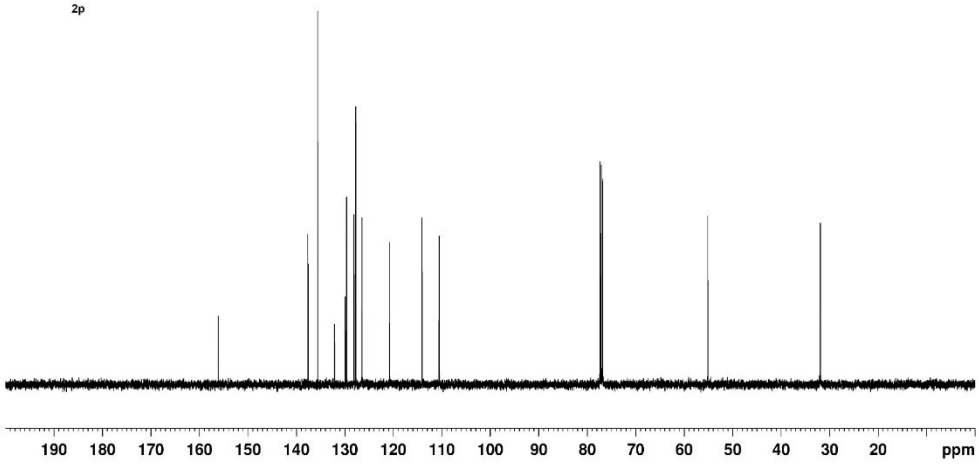


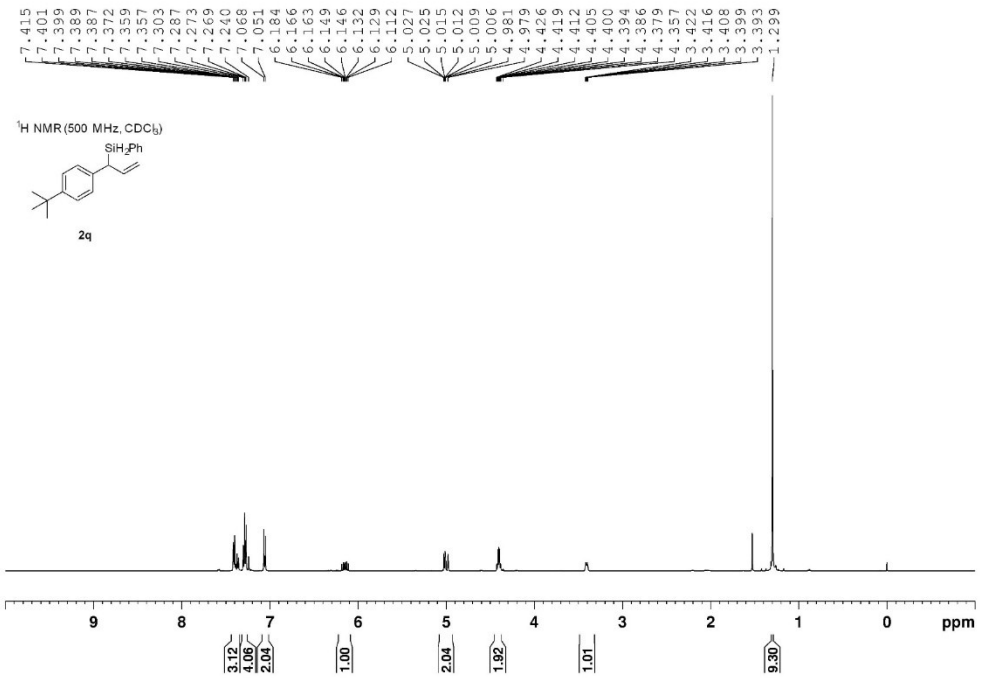


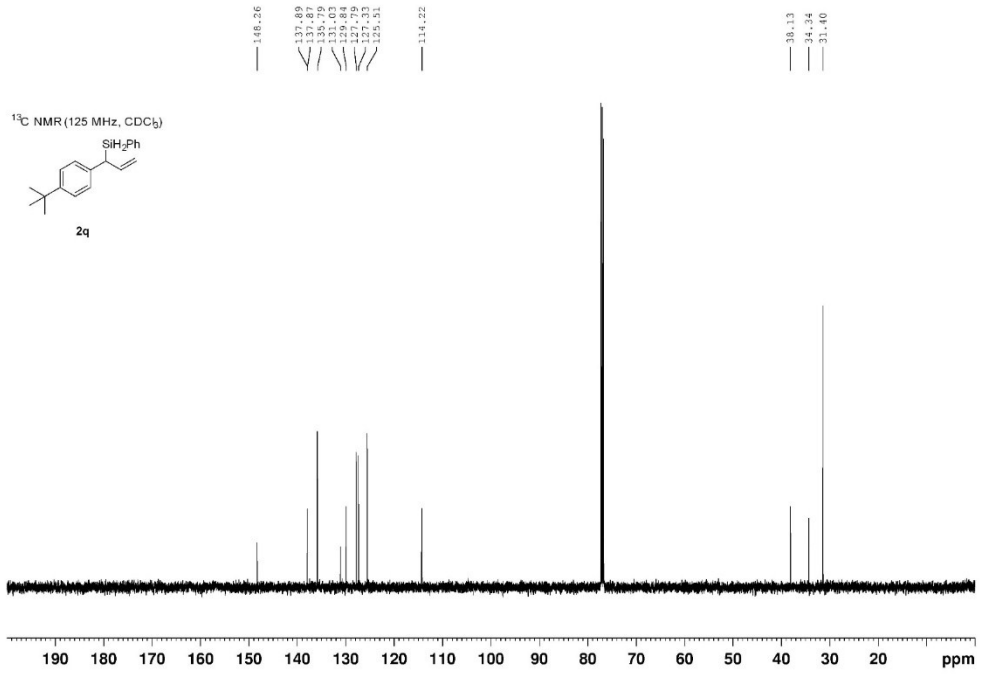
^{13}C NMR (125 MHz, $CDCl_3$)

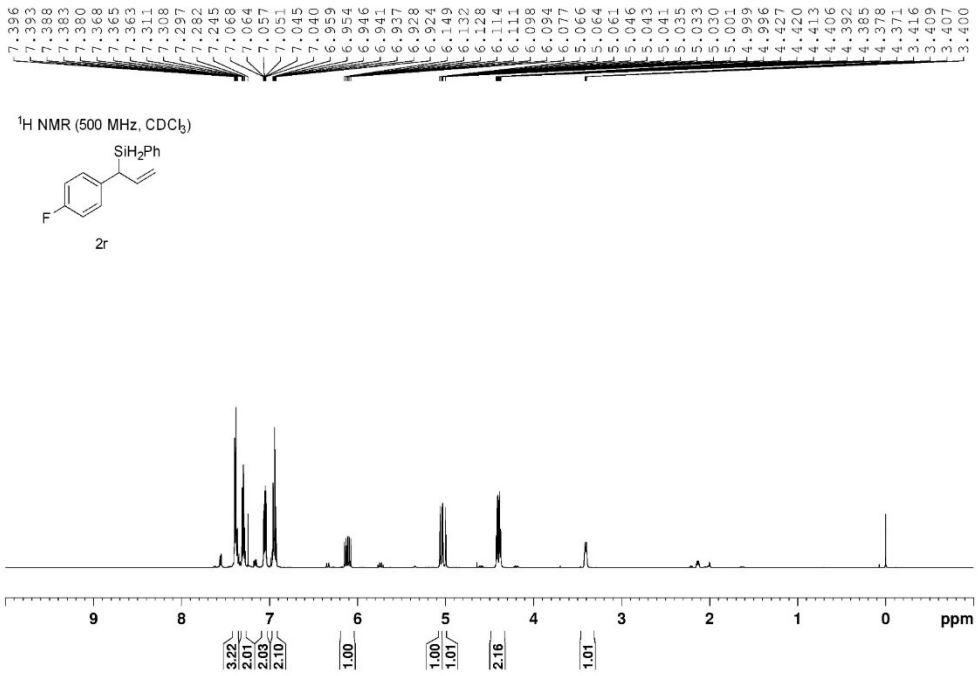


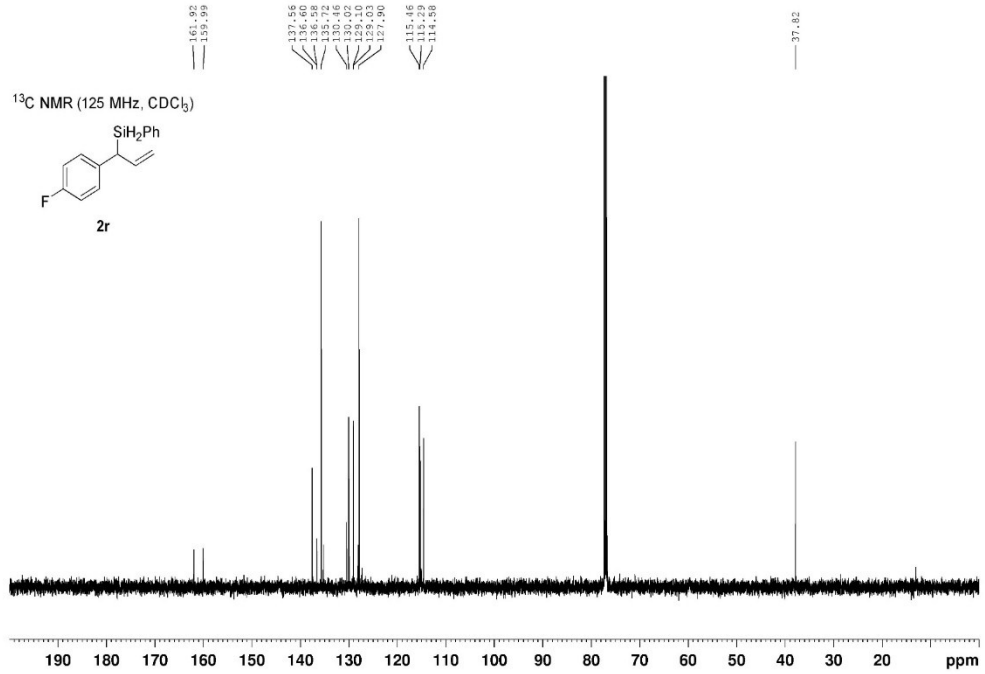
2p

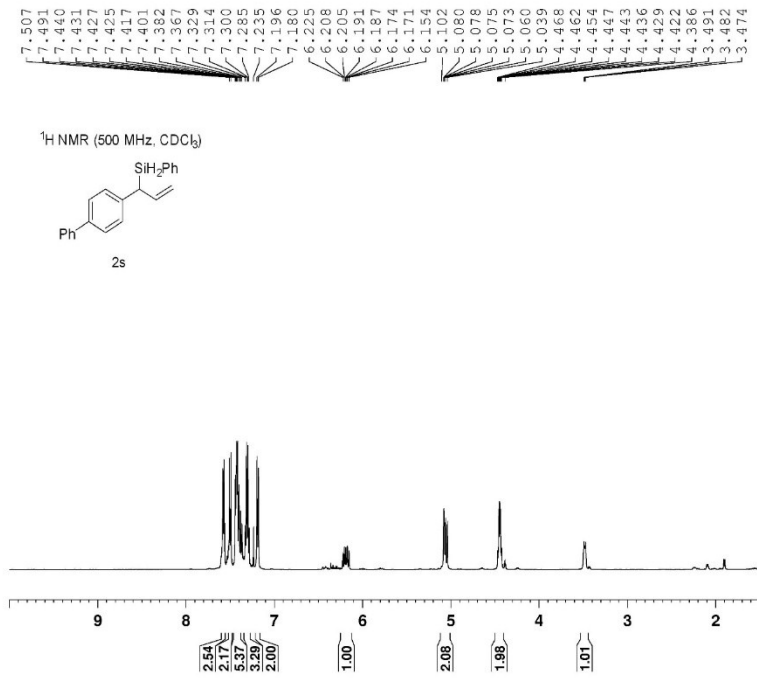


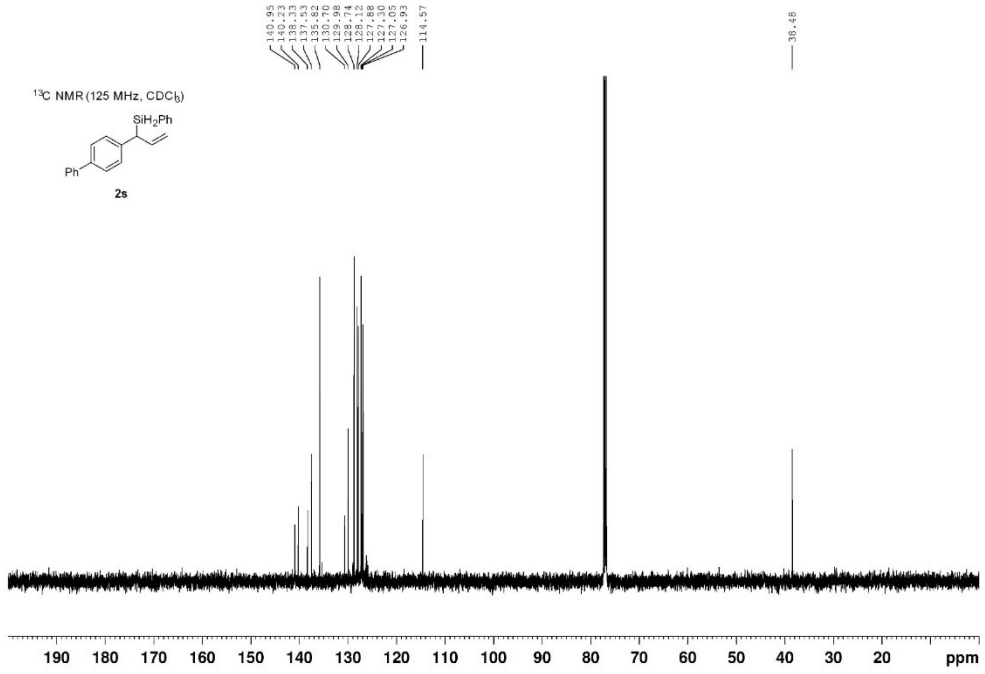

7.415
7.401
7.399
7.389
7.387
7.372
7.359
7.357
7.303
7.287
7.273
7.269
7.240
7.068
7.051
6.184
6.166
6.163
6.149
6.146
6.132
6.129
6.112
5.027
5.025
5.015
5.012
5.009
5.006
4.981
4.979
4.426
4.419
4.412
4.405
4.400
4.394
4.386
4.379
4.357
3.422
3.416
3.408
3.399
3.393
1.299
1H NMR (500 MHz, CDCl3)
SiH2Ph
2q
9
8
7
6
5
4
3
2
1
0
ppm
3.12
4.06
2.04
1.00
2.04
1.92
1.01
9.30

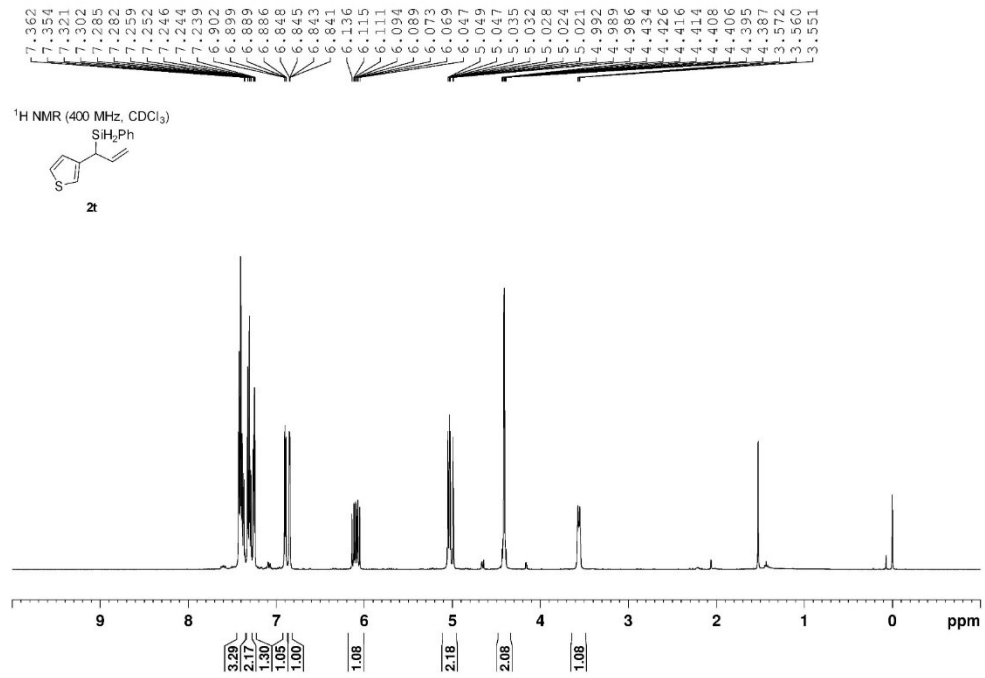

148.26
137.89
137.87
135.79
131.03
129.84
127.79
127.33
125.51
114.22
38.13
34.34
31.40
13C NMR (125 MHz, CDCl3)
SiH2Ph
2q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

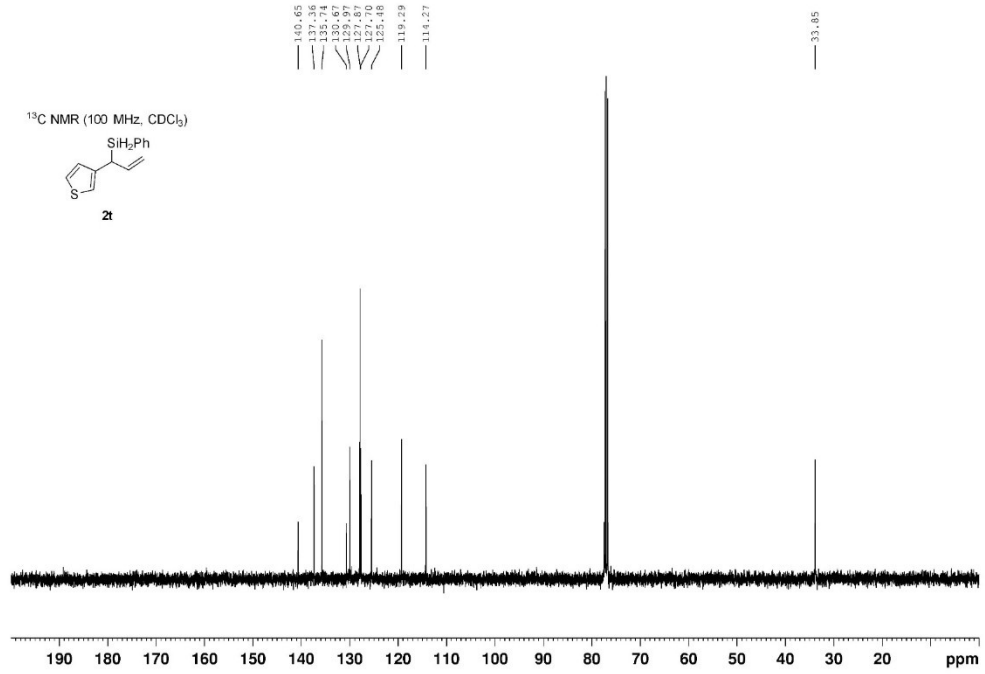

7.396
7.393
7.388
7.383
7.380
7.368
7.365
7.363
7.311
7.308
7.297
7.282
7.245
7.068
7.064
7.057
7.051
7.045
7.040
6.959
6.954
6.946
6.941
6.937
6.928
6.924
6.149
6.132
6.128
6.114
6.111
6.098
6.094
6.077
5.066
5.064
5.061
5.046
5.043
5.041
5.035
5.033
5.030
5.001
4.999
4.996
4.427
4.420
4.413
4.406
4.392
4.385
4.378
4.371
3.416
3.409
3.407
3.400
1H NMR (500 MHz, CDCl3)
SiH2Ph
F
2r
9
8
7
6
5
4
3
2
1
0
ppm
3.22
2.01
2.03
2.10
1.00
1.00
1.01
2.16
1.01

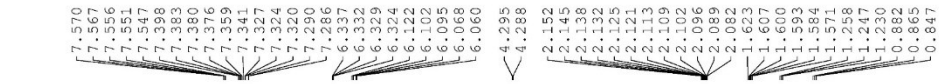

161.92
159.99
137.56
136.60
136.58
135.72
130.46
130.02
129.50
128.03
127.90
115.46
115.29
114.58
37.82
13C NMR (125 MHz, CDCl3)
SiH2Ph
F
2r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.507
7.491
7.440
7.431
7.427
7.425
7.417
7.401
7.382
7.367
7.329
7.314
7.300
7.285
7.235
7.196
7.180
6.225
6.208
6.205
6.191
6.187
6.174
6.171
6.154
5.102
5.080
5.078
5.075
5.073
5.060
5.039
4.468
4.462
4.454
4.447
4.443
4.436
4.429
4.422
4.386
3.491
3.482
3.474
1H NMR (500 MHz, CDCl3)
SiH2Ph
Ph
2s
9
8
7
6
5
4
3
2
1
0
ppm
2.54
2.17
5.37
3.29
2.00
1.00
2.08
1.98
1.01

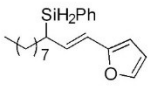

140.95
140.23
138.33
137.53
135.82
130.70
129.98
128.74
128.12
127.88
127.30
127.05
126.93
114.57
38.48
13C NMR (125 MHz, CDCl3)
SiH2Ph
Ph
2s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.362
7.354
7.321
7.302
7.285
7.282
7.259
7.252
7.246
7.244
7.239
6.902
6.899
6.889
6.886
6.848
6.845
6.843
6.841
6.136
6.115
6.111
6.094
6.089
6.073
6.069
6.047
5.049
5.047
5.035
5.032
5.028
5.024
5.021
4.992
4.989
4.986
4.434
4.426
4.416
4.414
4.408
4.406
4.395
4.387
3.572
3.560
3.551
1H NMR (400 MHz, CDCl3)
SiH2Ph
S
2t
9
8
7
6
5
4
3
2
1
0
ppm
3.29
2.17
1.30
1.05
1.00
1.08
2.18
2.08
1.08

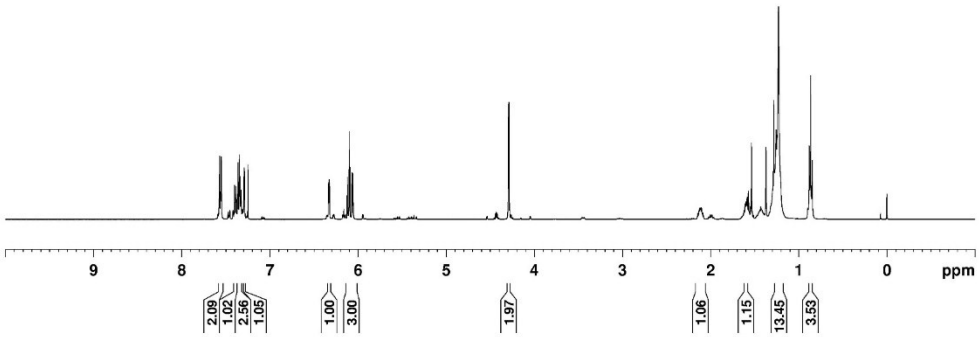

140.65
137.36
135.74
130.67
129.97
129.87
127.70
125.48
119.29
114.27
33.85
13C NMR (100 MHz, CDCl3)
SiH2Ph
S
2t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

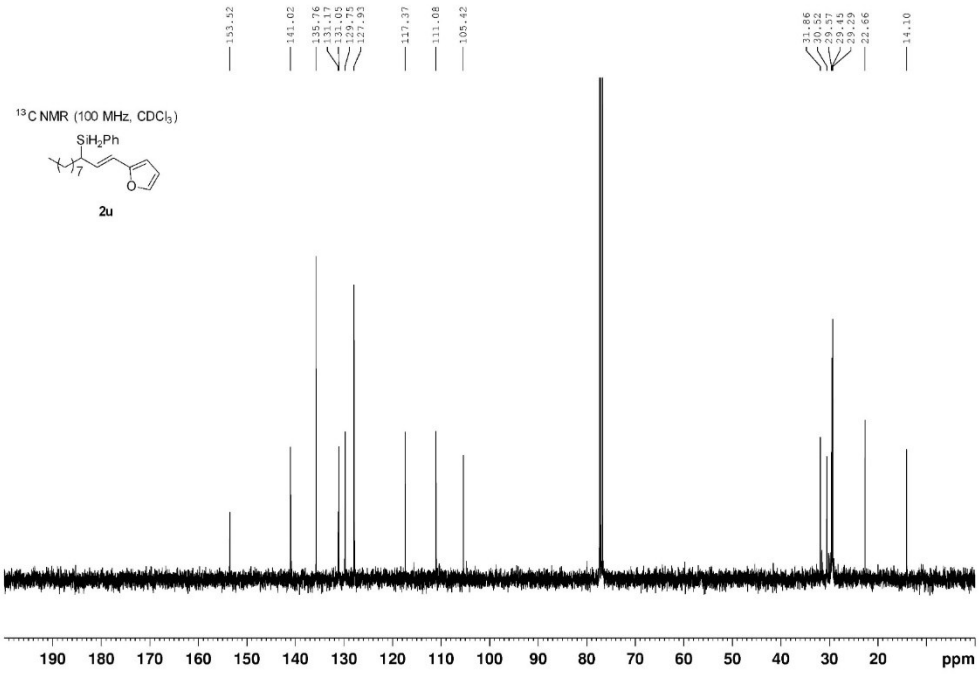


^{1}H NMR (400 MHz, $CDCl_3$)



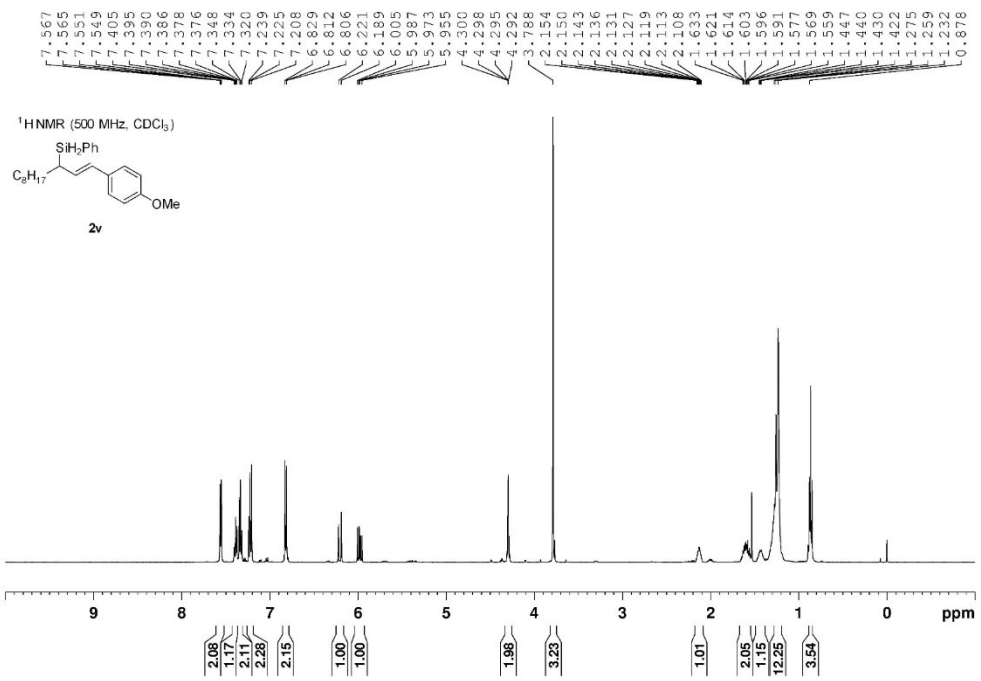
2u

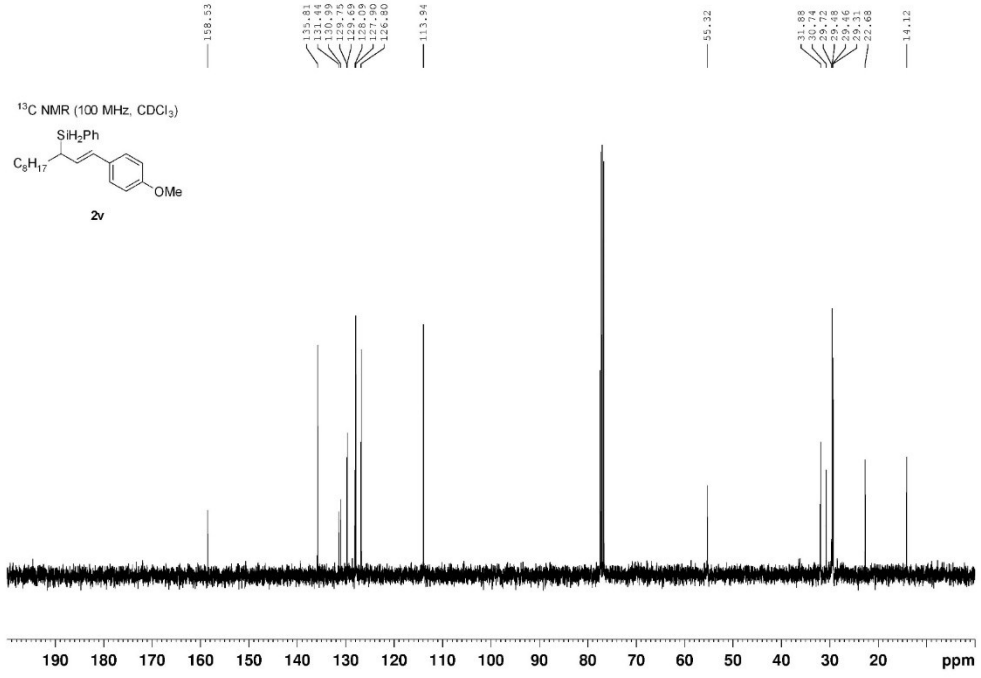




^{13}C NMR (100 MHz, $CDCl_3$)

2u


7.567
7.565
7.551
7.549
7.405
7.395
7.390
7.386
7.378
7.376
7.348
7.334
7.320
7.239
7.225
7.208
6.829
6.812
6.806
6.221
6.189
6.005
5.987
5.973
5.955
4.300
4.298
4.295
4.292
3.788
2.154
2.150
2.143
2.136
2.131
2.127
2.119
2.113
2.108
1.633
1.621
1.614
1.603
1.596
1.591
1.577
1.569
1.559
1.447
1.440
1.430
1.422
1.275
1.259
1.232
0.878
1H NMR (500 MHz, CDCl3)
SiH2Ph
C8H17
OMe
2v
9
8
7
6
5
4
3
2
1
0
ppm
2.08
1.17
2.11
2.28
2.15
1.00
1.00
1.98
3.23
1.01
2.05
1.15
12.25
3.54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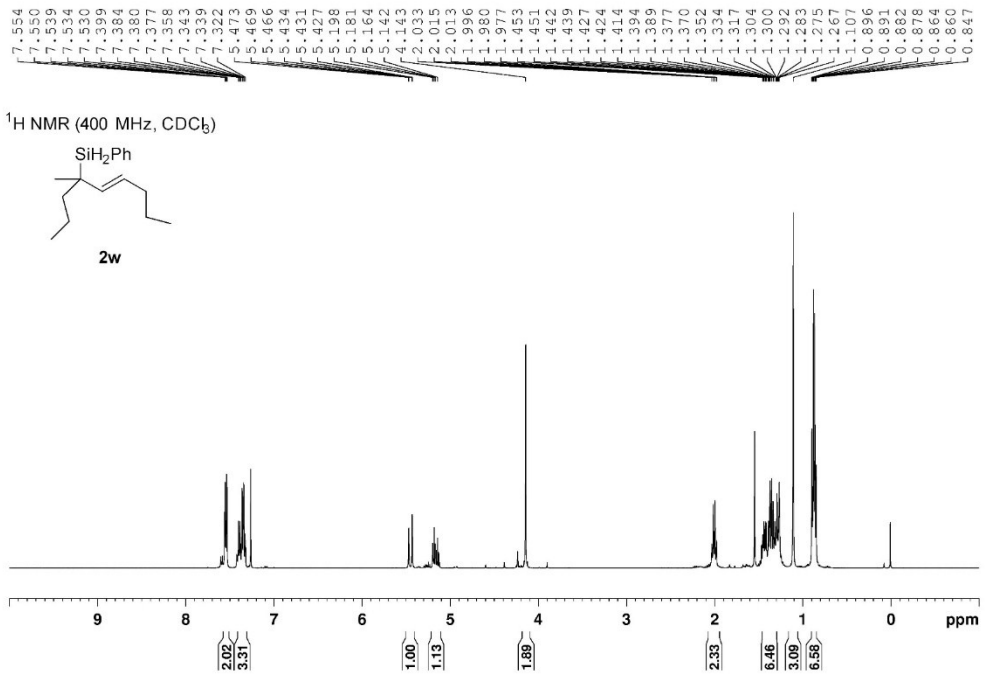
135.81
131.44
130.99
129.35
129.69
128.09
127.90
126.80
113.84
55.32
31.88
30.74
29.72
29.48
29.46
29.31
22.68
14.12
13C NMR (100 MHz, CDCl3)
SiH2Ph
C8H17
OMe
2v
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.539
7.534
7.530
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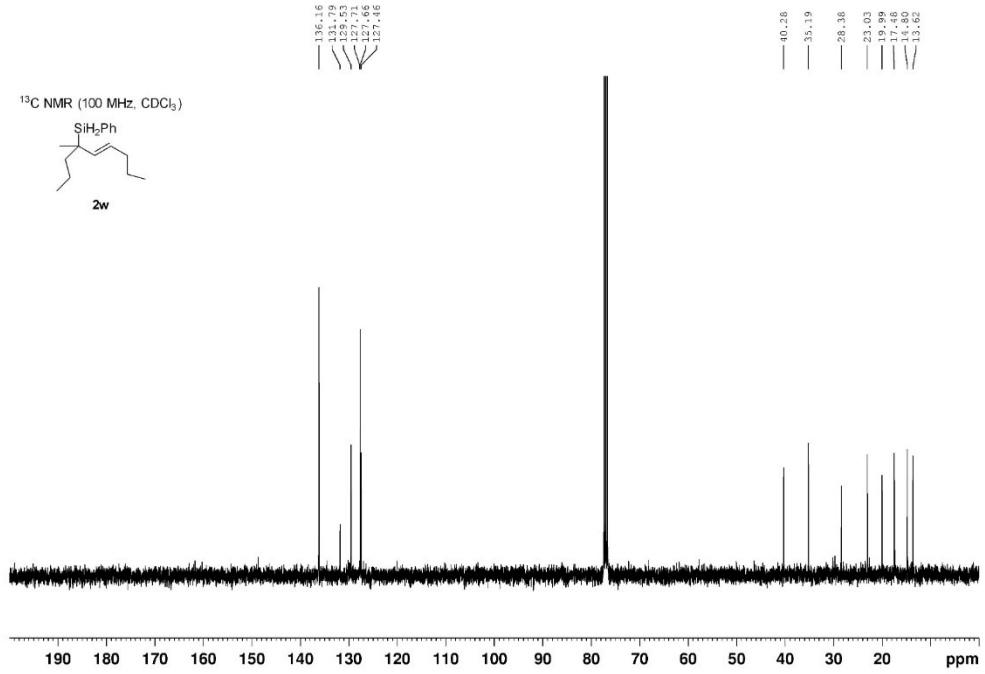
7.384
7.380
7.377
7.358
7.343
7.339
7.322
5.473
5.469
5.466
5.434
5.431
5.427
5.198
5.181
5.164
5.142
4.143
2.033
2.015
2.013
1.996
1.980
1.977
1.453
1.451
1.442
1.439
1.427
1.424
1.414
1.394
1.389
1.377
1.370
1.352
1.334
1.317
1.304
1.300
1.292
1.283
1.275
1.267
1.107
0.896
0.891
0.882
0.878
0.864
0.860
0.847
1H NMR (400 MHz, CDCl3)
SiH2Ph
2w
9
8
7
6
5
4
3
2
1
0
ppm
2.02
3.31
1.00
1.13
1.89
2.33
6.46
3.09
6.58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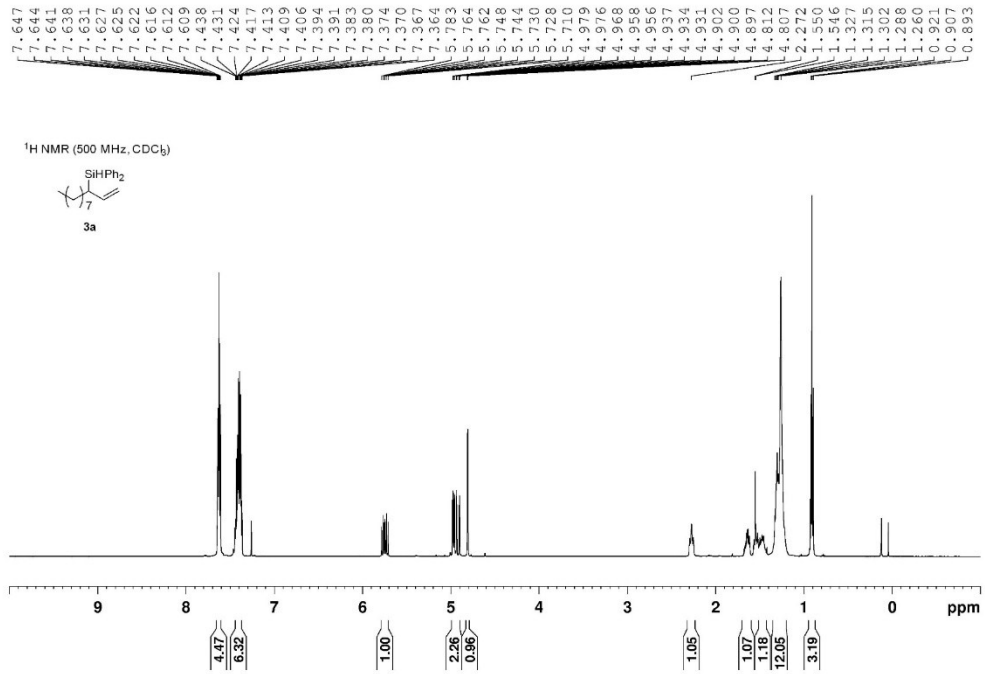
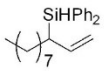
133.79
129.53
127.71
127.66
127.46
40.28
35.19
28.38
23.03
19.99
17.48
14.60
13.62
13C NMR (100 MHz, CDCl3)
SiH2Ph
2w
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



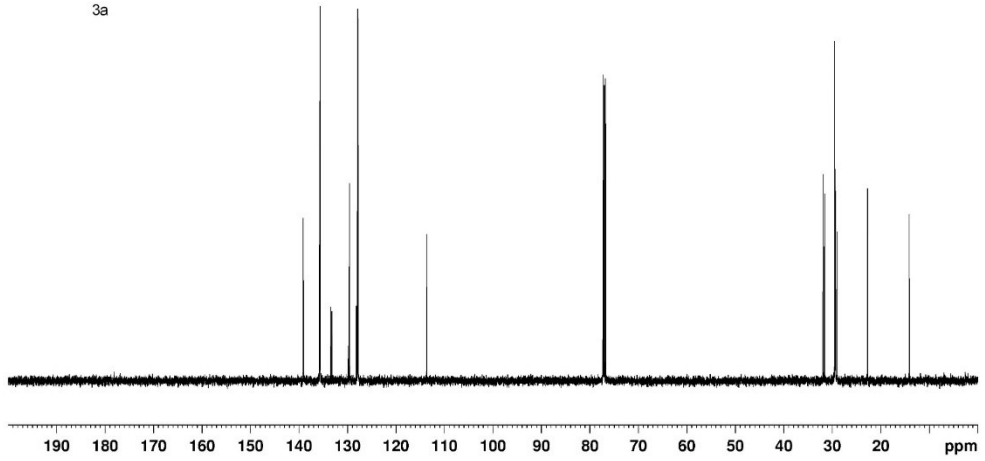
^{1}H NMR (500 MHz, $CDCl_3$)

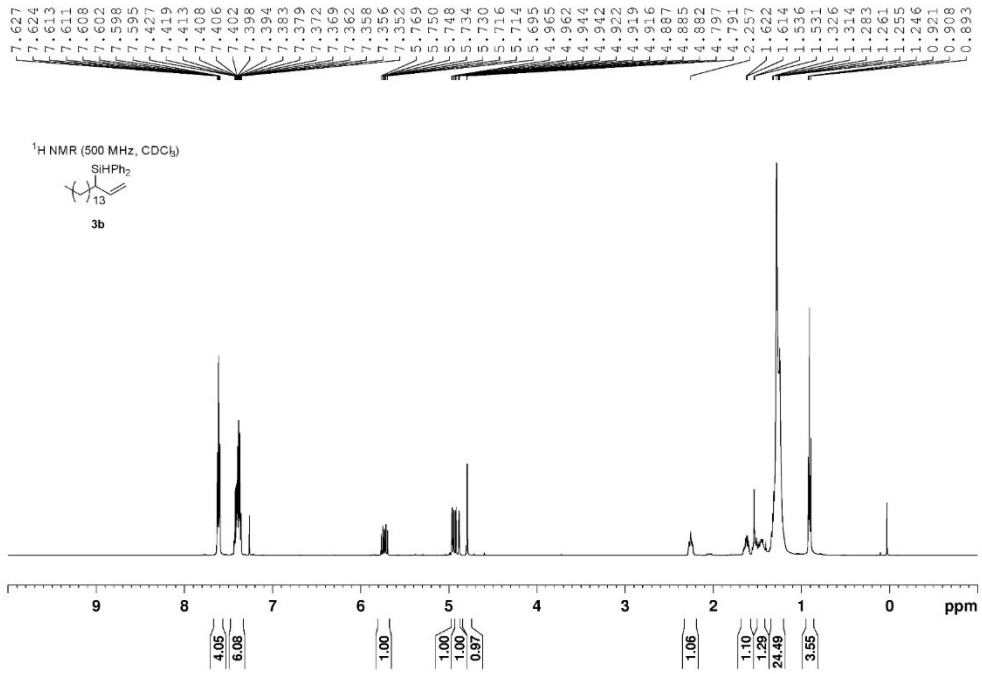
3a

^{13}C NMR (125 MHz, $CDCl_3$)



3a

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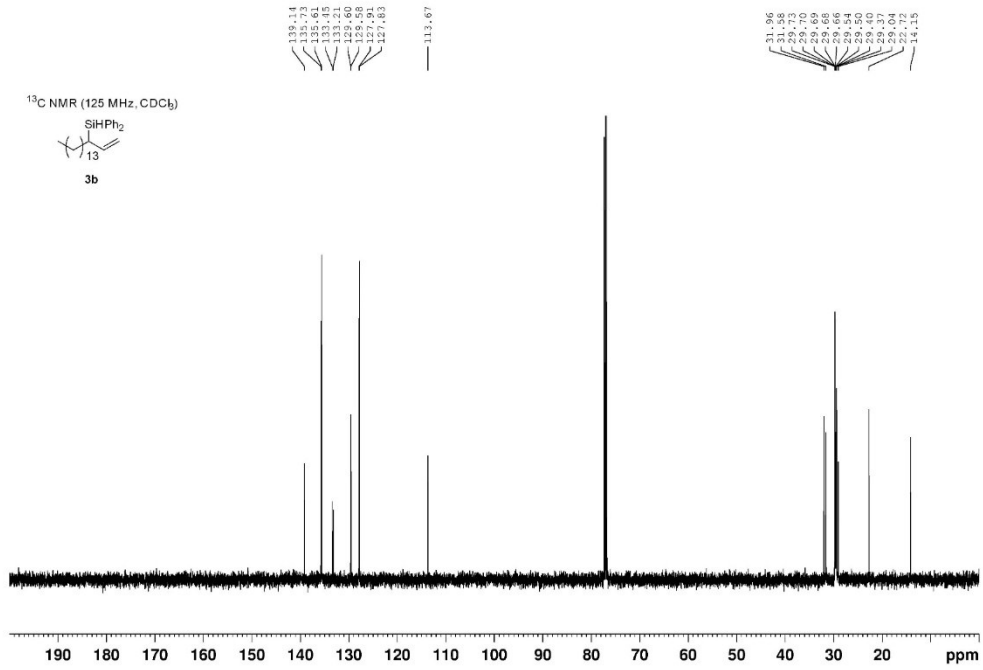
7.624
7.613
7.611
7.608
7.602
7.598
7.595
7.427
7.419
7.413
7.408
7.406
7.402
7.398
7.394
7.383
7.379
7.372
7.369
7.362
7.358
7.356
7.352
5.769
5.750
5.748
5.734
5.730
5.716
5.714
5.695
4.965
4.962
4.944
4.942
4.922
4.919
4.916
4.887
4.885
4.882
4.797
4.791
2.257
1.622
1.614
1.536
1.531
1.326
1.314
1.283
1.261
1.255
1.246
0.921
0.908
0.893
1H NMR (500 MHz, CDCl3)
SiHPh2
13
3b
9
8
7
6
5
4
3
2
1
0
ppm
4.05
6.08
1.00
1.00
1.00
0.97
1.06
1.10
1.29
24.49
3.55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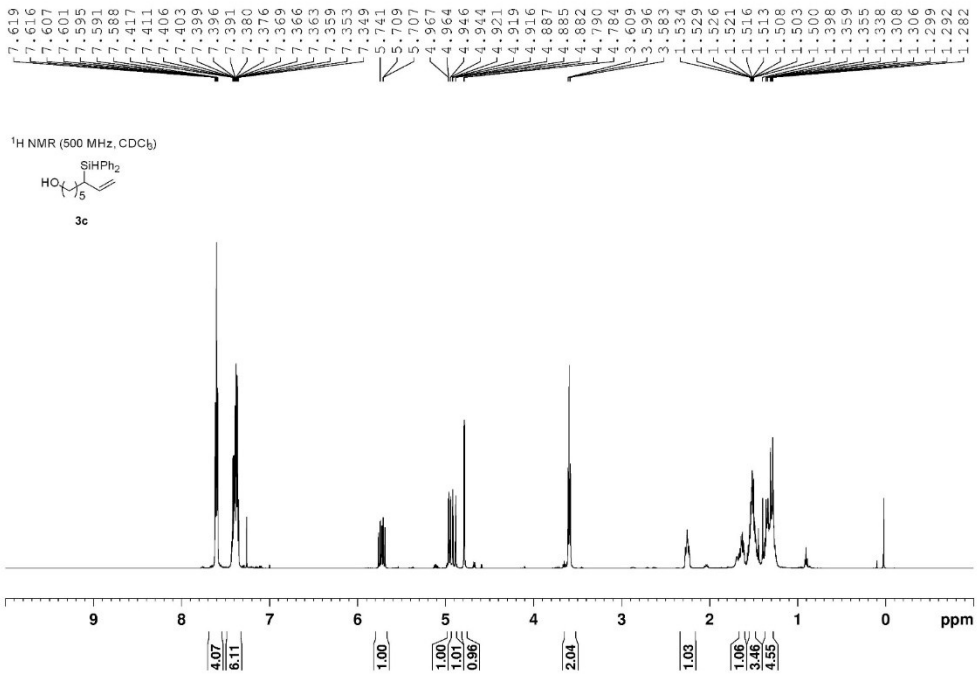
135.73
135.61
133.45
133.21
129.60
129.58
127.91
127.83
113.67
31.96
31.58
30.13
29.70
29.69
29.68
29.66
29.54
29.50
29.40
29.37
29.04
28.72
14.15
13C NMR (125 MHz, CDCl3)
SiHPh2
13
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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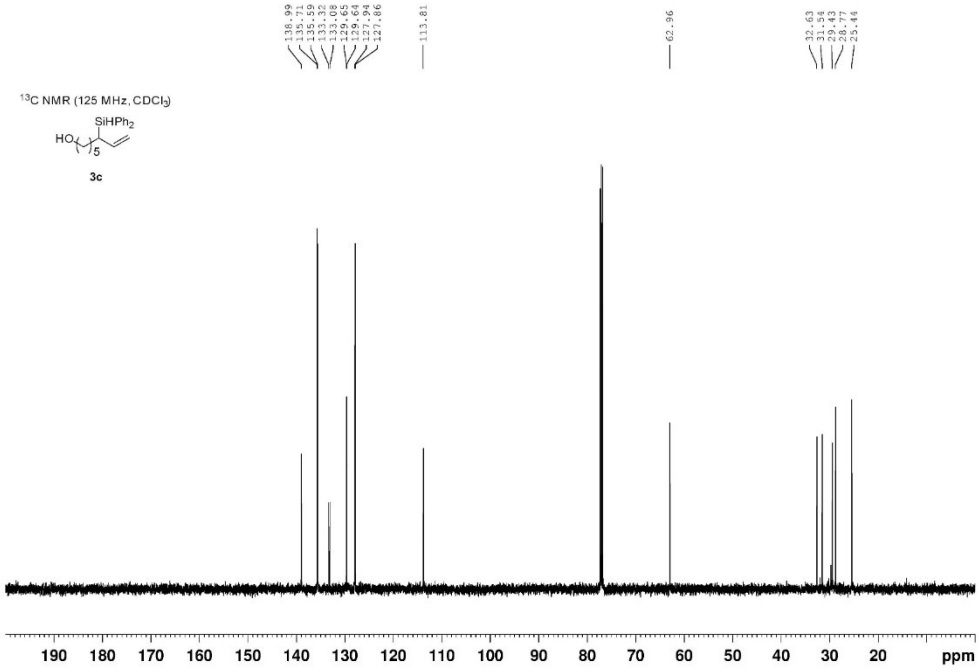
7.616
7.607
7.601
7.595
7.591
7.588
7.417
7.411
7.406
7.403
7.399
7.396
7.391
7.380
7.376
7.369
7.366
7.363
7.359
7.353
7.349
5.741
5.709
5.707
4.967
4.964
4.946
4.944
4.921
4.919
4.916
4.887
4.885
4.882
4.790
4.784
3.609
3.596
3.583
1.534
1.529
1.526
1.521
1.516
1.513
1.508
1.503
1.500
1.398
1.359
1.355
1.338
1.308
1.306
1.299
1.292
1.282
1H NMR (500 MHz, CDCl3)
SiHPh2
HO
5
3c
9
8
7
6
5
4
3
2
1
0
ppm
4.07
6.11
1.00
1.00
1.01
0.96
2.04
1.03
1.06
3.46
4.55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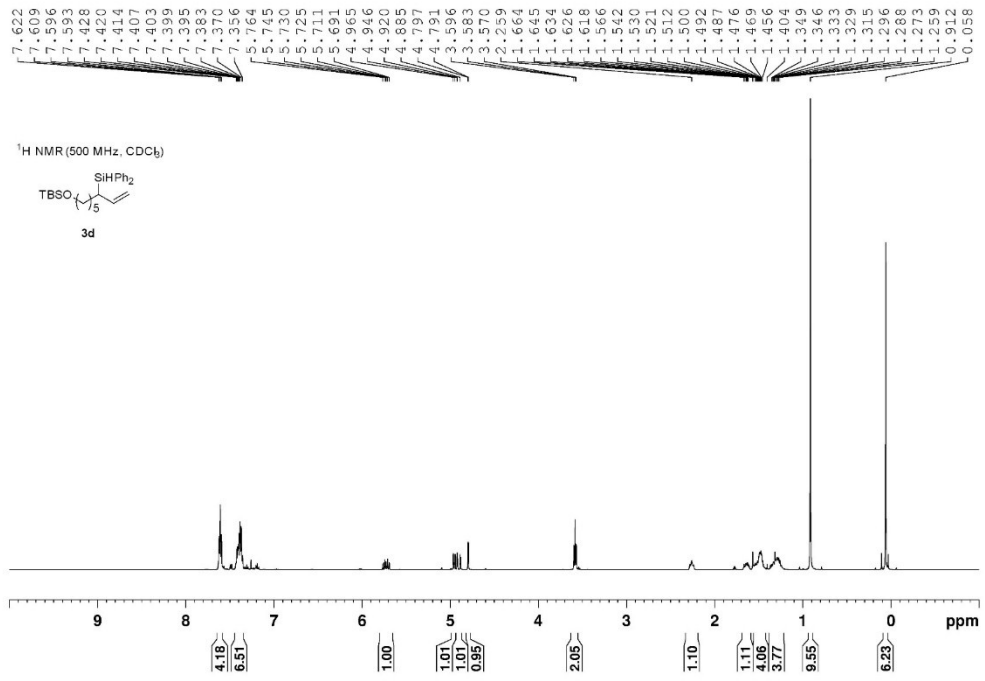
135.71
135.59
133.32
133.08
129.65
129.64
127.94
127.86
113.81
62.96
32.63
31.54
29.43
28.77
25.46
13C NMR (125 MHz, CDCl3)
SiHPh2
HO
5
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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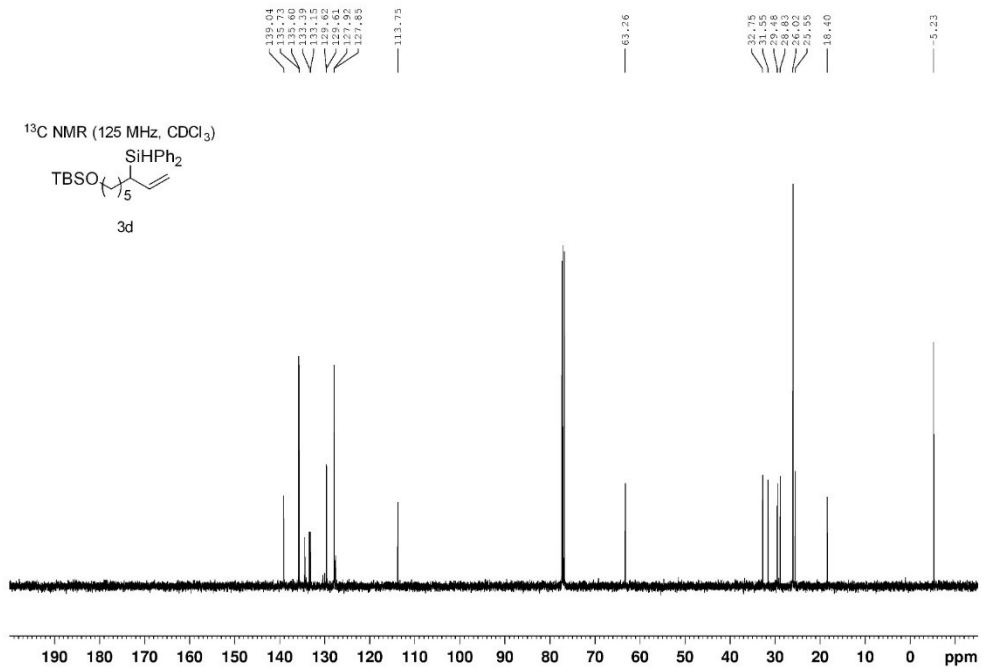
7.609
7.596
7.593
7.428
7.420
7.414
7.407
7.403
7.399
7.395
7.383
7.370
7.356
5.764
5.745
5.730
5.725
5.711
5.691
4.965
4.946
4.920
4.885
4.797
4.791
3.596
3.583
3.570
2.259
1.664
1.645
1.634
1.626
1.618
1.566
1.542
1.530
1.521
1.512
1.500
1.492
1.487
1.476
1.469
1.456
1.404
1.349
1.346
1.333
1.329
1.315
1.296
1.288
1.273
1.259
0.912
0.058
1H NMR (500 MHz, CDCl3)
SiHPh2
TBSO
5
3d
9
8
7
6
5
4
3
2
1
0
ppm
4.18
6.51
1.00
1.01
1.01
0.95
2.05
1.10
1.11
4.06
3.77
9.55
6.23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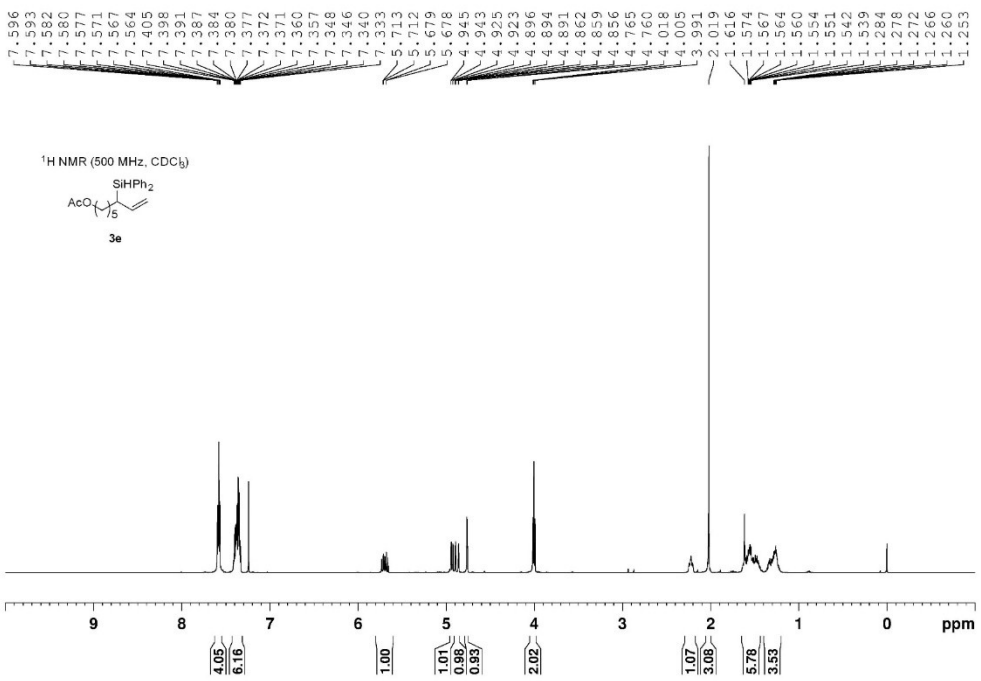
135.73
135.60
133.39
133.15
129.62
129.61
127.92
127.85
113.75
63.26
32.75
31.55
29.48
28.83
26.02
25.55
18.40
-5.23
13C NMR (125 MHz, CDCl3)
SiHPh2
TBSO
5
3d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.593
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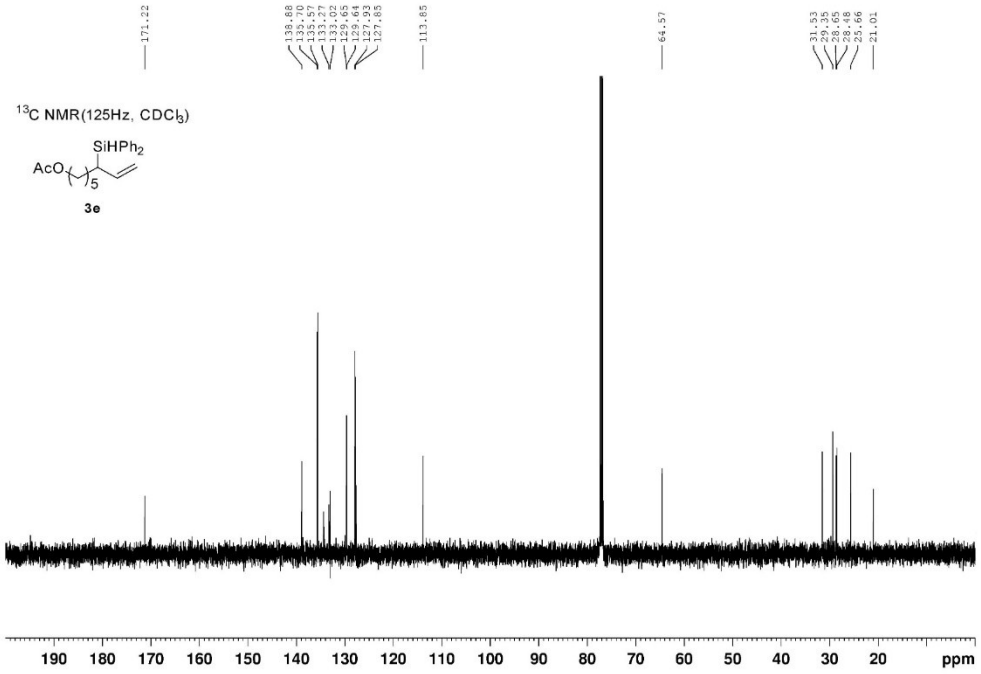
7.580
7.577
7.571
7.567
7.564
7.405
7.398
7.391
7.387
7.384
7.380
7.377
7.372
7.371
7.360
7.357
7.348
7.346
7.340
7.333
5.713
5.712
5.679
5.678
4.945
4.943
4.925
4.923
4.896
4.894
4.891
4.862
4.859
4.856
4.765
4.760
4.018
4.005
3.991
2.019
1.616
1.574
1.567
1.564
1.560
1.554
1.551
1.542
1.539
1.284
1.278
1.272
1.266
1.260
1.253
1H NMR (500 MHz, CDCl3)
SiHPh2
AcO
5
3e
9
8
7
6
5
4
3
2
1
0
ppm
4.05
6.16
1.00
1.01
0.98
0.93
2.02
1.07
3.08
5.78
3.53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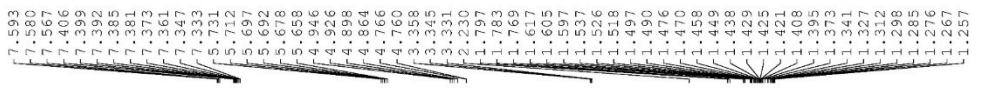
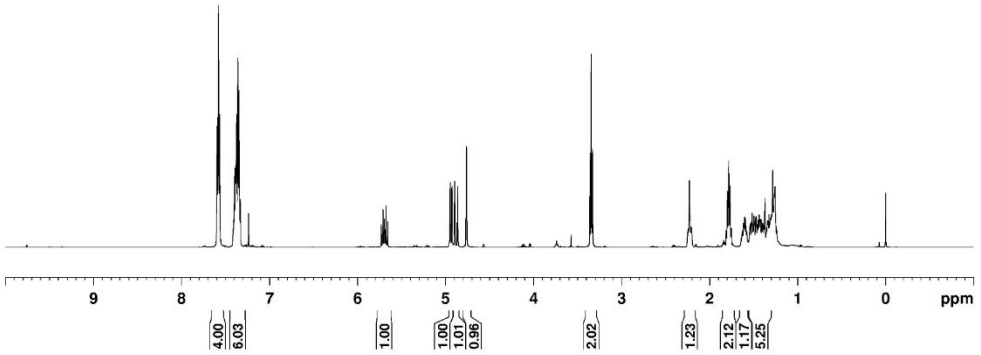
135.70
133.57
133.27
133.02
129.65
129.64
127.93
127.85
113.85
64.57
31.53
29.35
28.65
28.48
25.66
21.01
13C NMR(125Hz, CDCl3)
SiHPh2
AcO
5
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



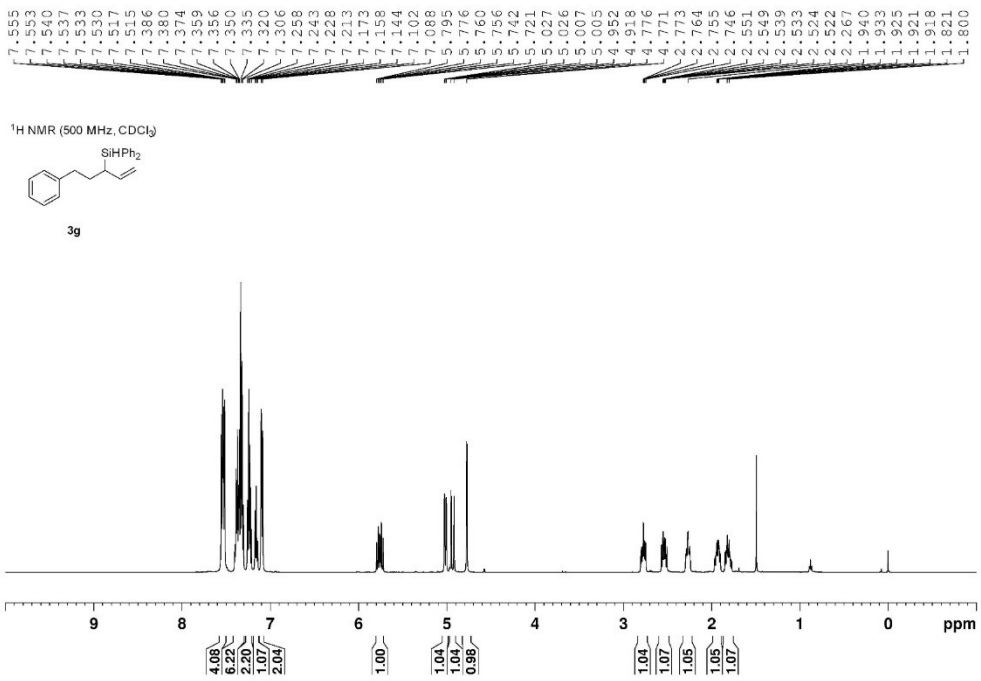
^{1}H NMR (500 MHz, $CDCl_3$)

3f



^{13}C NMR (125 MHz, $CDCl_3$)

3f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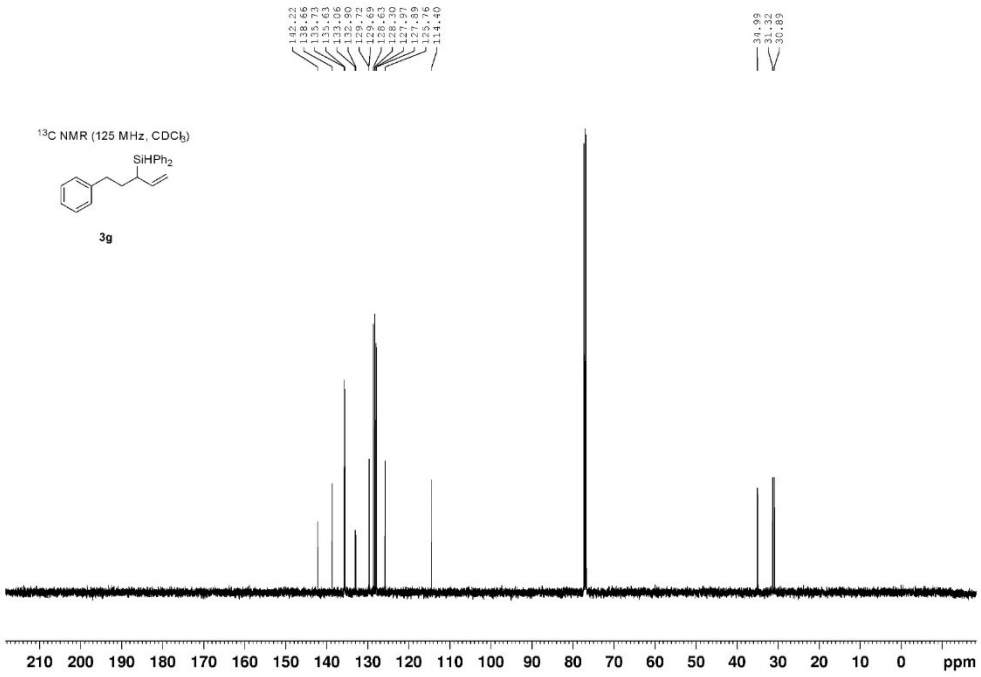
7.537
7.533
7.530
7.517
7.515
7.386
7.380
7.374
7.359
7.356
7.350
7.335
7.320
7.306
7.258
7.243
7.228
7.213
7.173
7.158
7.144
7.102
7.088
5.795
5.776
5.760
5.756
5.742
5.721
5.027
5.026
5.007
5.005
4.952
4.918
4.776
4.771
2.773
2.764
2.755
2.746
2.551
2.549
2.539
2.533
2.524
2.522
2.267
1.940
1.933
1.925
1.921
1.918
1.821
1.800
1H NMR (500 MHz, CDCl3)
SiHPh2
3g
9
8
7
6
5
4
3
2
1
0
ppm
4.08
6.22
2.20
1.07
2.04
1.00
1.04
1.04
0.98
1.04
1.07
1.05
1.05
1.07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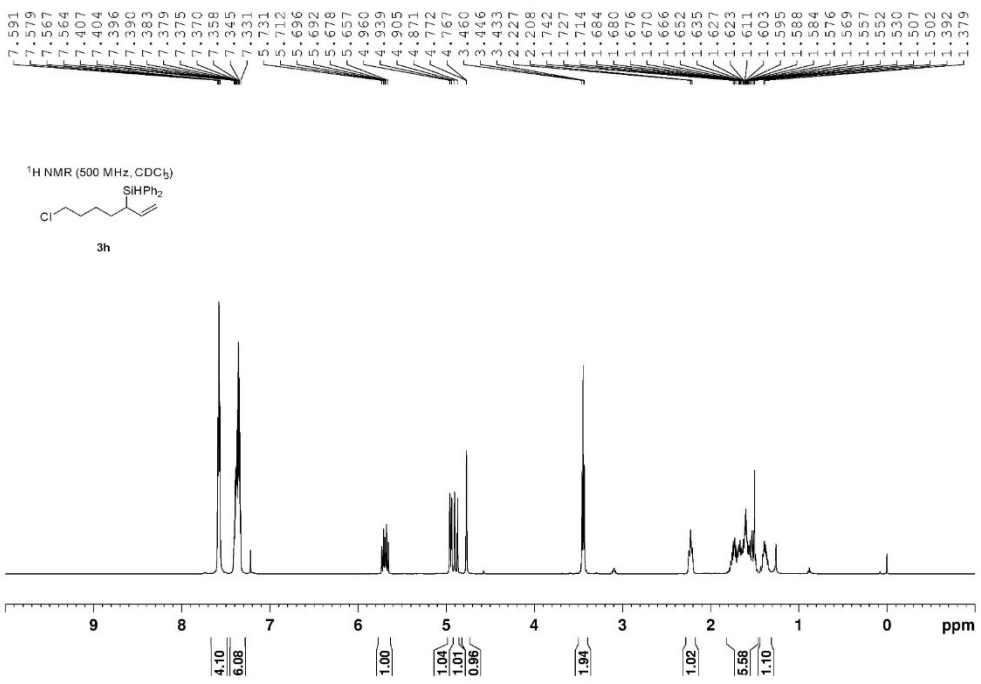
133.06
132.90
129.72
129.69
128.63
128.30
127.97
127.89
125.76
114.40
34.99
31.32
30.89
13C NMR (125 MHz, CDCl3)
SiHPh2
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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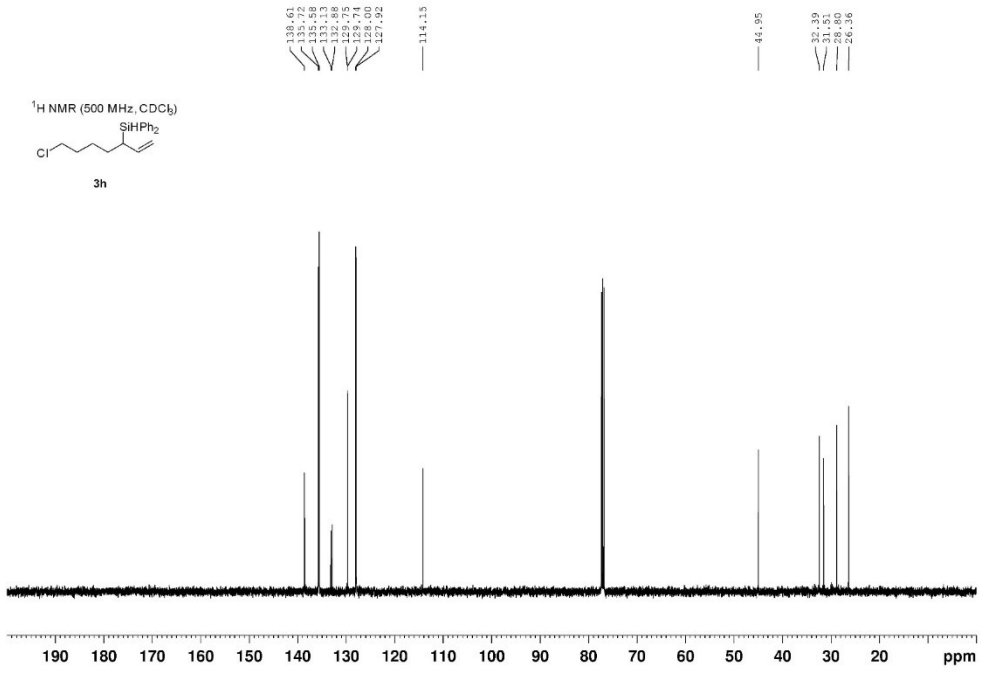
7.407
7.404
7.396
7.390
7.383
7.379
7.375
7.370
7.358
7.345
7.331
5.731
5.712
5.696
5.692
5.678
5.657
4.960
4.939
4.905
4.871
4.772
4.767
3.460
3.446
3.433
2.227
2.208
1.742
1.727
1.714
1.684
1.680
1.676
1.670
1.666
1.652
1.635
1.627
1.623
1.611
1.603
1.595
1.588
1.584
1.576
1.569
1.557
1.552
1.530
1.507
1.502
1.392
1.379
1H NMR (500 MHz, CDCl3)
SiHPh2
Cl
3h
9
8
7
6
5
4
3
2
1
0
ppm
4.10
6.08
1.00
1.04
1.01
0.96
1.94
1.02
5.58
1.10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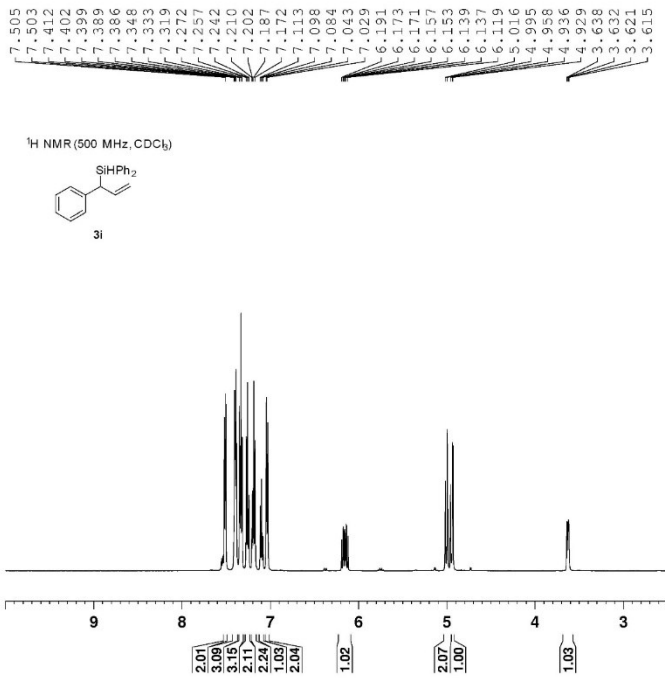
135.72
135.58
133.11
132.88
129.75
129.74
128.00
127.92
114.15
44.95
32.39
31.51
28.80
26.36
1H NMR (500 MHz, CDCl3)
SiHPh2
Cl
3h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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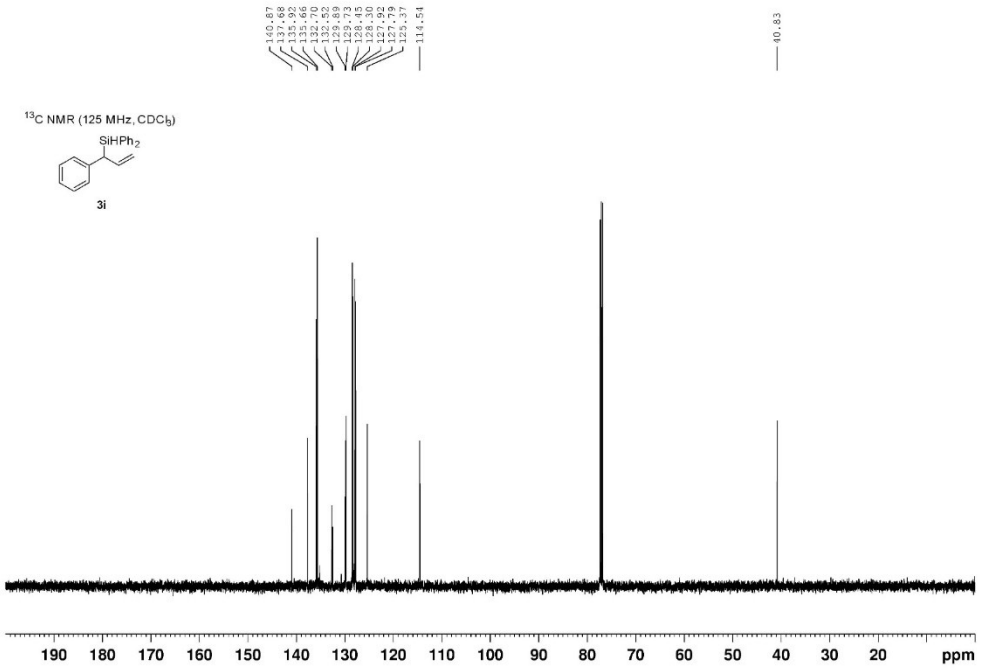
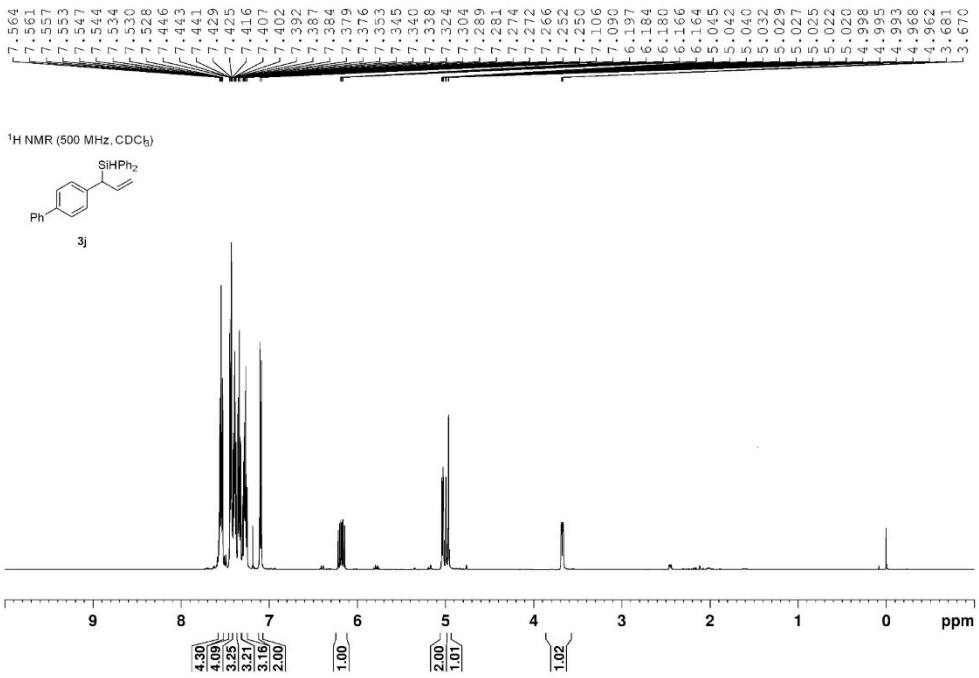
7.402
7.399
7.389
7.386
7.348
7.333
7.319
7.272
7.257
7.242
7.210
7.202
7.187
7.172
7.113
7.098
7.084
7.043
7.029
6.191
6.173
6.171
6.157
6.153
6.139
6.137
6.119
5.016
4.995
4.958
4.936
4.929
3.638
3.632
3.621
3.615
^{1}H NMR (500 MHz, CDCl$_3$)
SiHPh$_2$
3i
9
8
7
6
5
4
3
2
1
0
ppm
2.01
3.09
3.15
2.11
2.24
1.03
2.04
1.02
2.07
1.00
1.03


140.87
137.68
135.92
135.66
132.70
132.53
129.83
129.73
128.45
128.30
127.83
127.79
125.37
114.54
40.83
^{13}C NMR (125 MHz, CDCl$_3$)
SiHPh$_2$
3i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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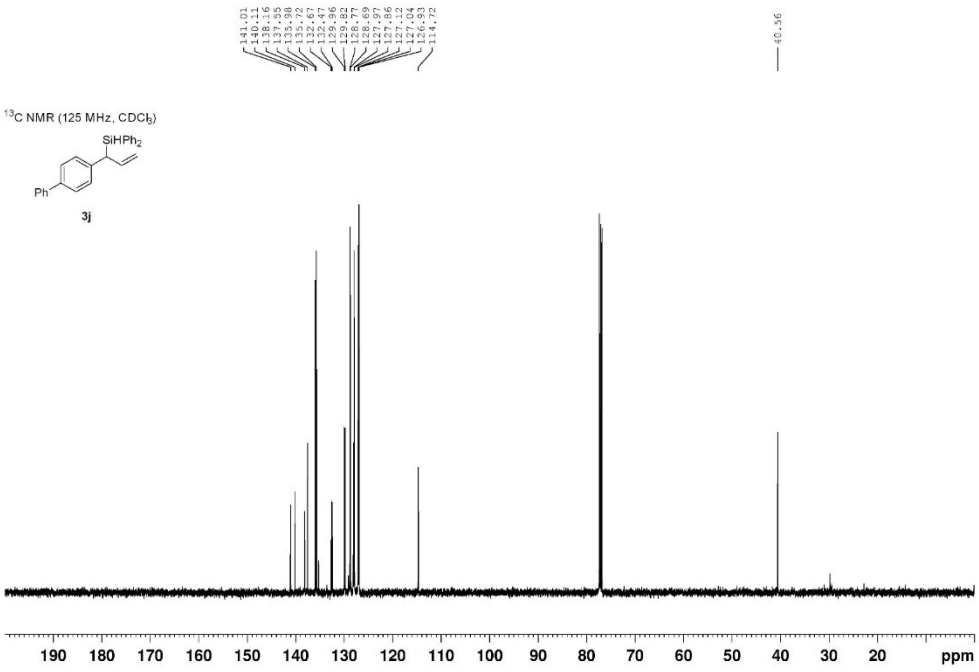
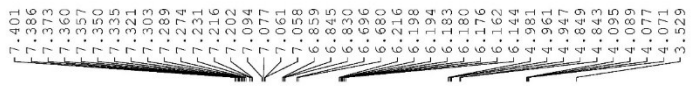
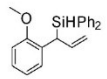
7.561
7.557
7.553
7.547
7.544
7.534
7.530
7.528
7.446
7.443
7.441
7.429
7.425
7.416
7.407
7.402
7.392
7.387
7.384
7.379
7.376
7.353
7.345
7.340
7.338
7.324
7.304
7.289
7.281
7.274
7.272
7.266
7.252
7.250
7.106
7.090
6.197
6.184
6.180
6.166
6.164
5.045
5.042
5.040
5.032
5.029
5.027
5.025
5.022
5.020
4.998
4.995
4.993
4.968
4.962
3.681
3.670
1H NMR (500 MHz, CDCl3)
SiHPh2
Ph
3j
9
8
7
6
5
4
3
2
1
0
ppm
4.30
4.09
3.25
3.21
3.16
2.00
1.00
2.00
1.01
1.02

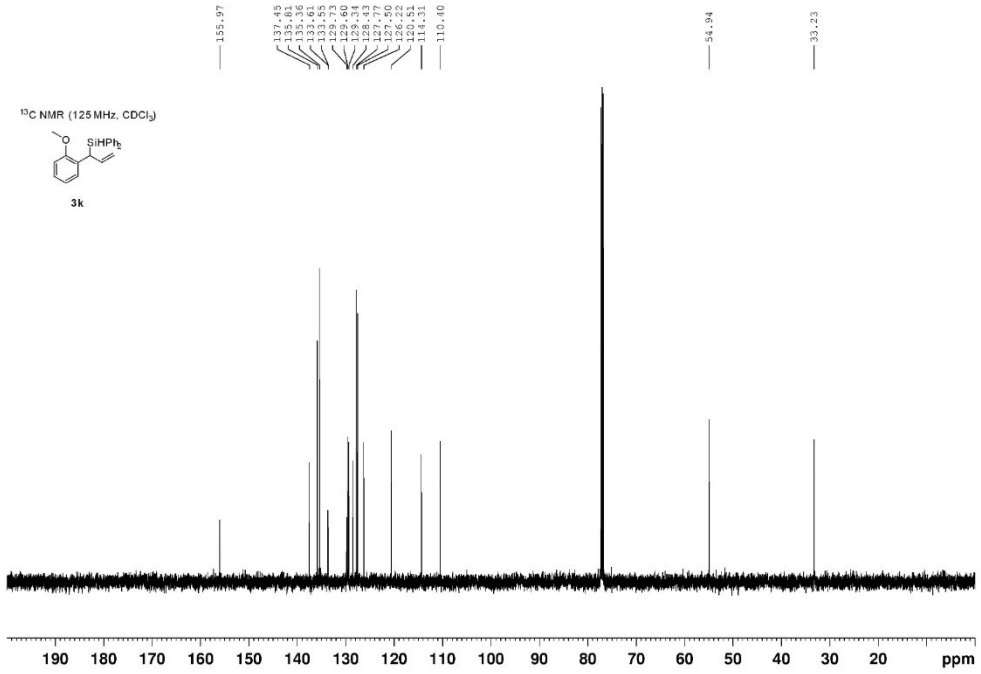

141.01
140.11
138.16
137.55
135.98
135.72
132.67
132.47
129.96
129.82
128.77
128.69
127.97
127.86
127.12
127.04
116.93
114.72
40.56
13C NMR (125 MHz, CDCl3)
SiHPh2
Ph
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



^{1}H NMR (500 MHz, $CDCl_3$)

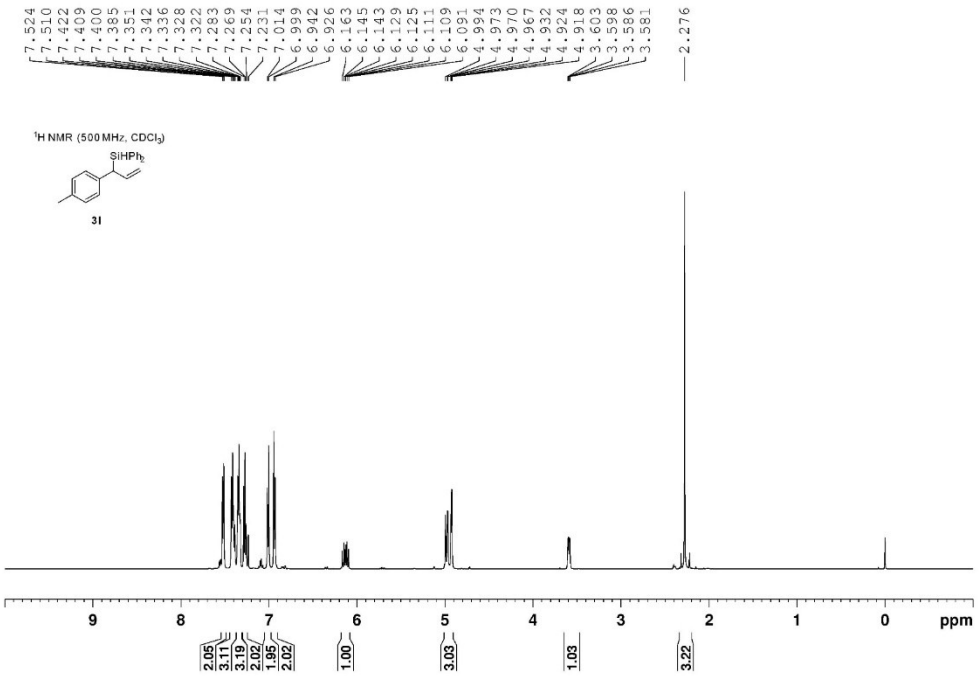


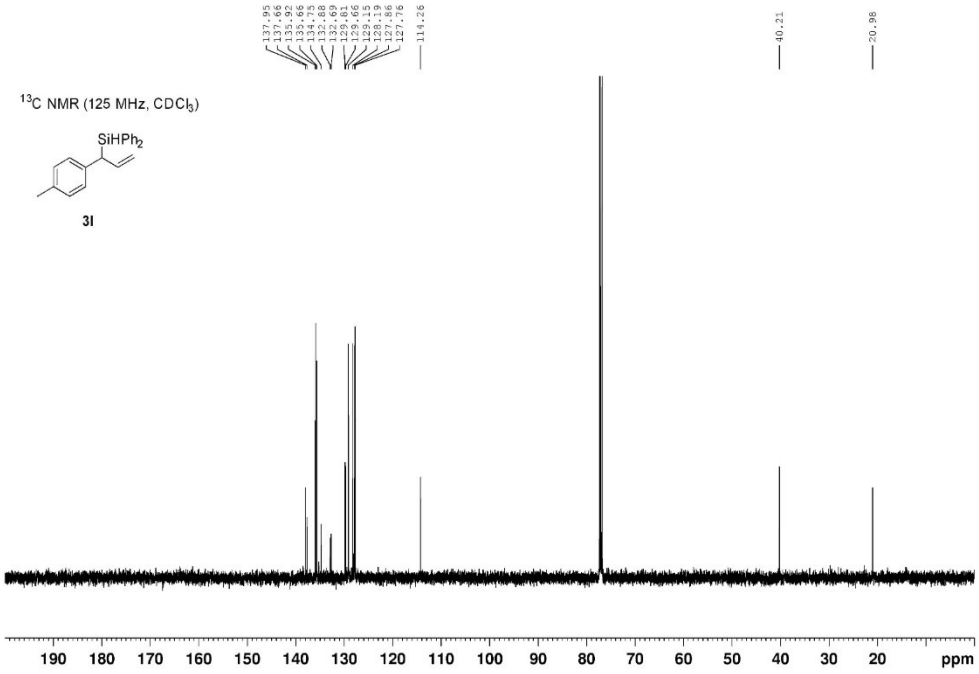
3k

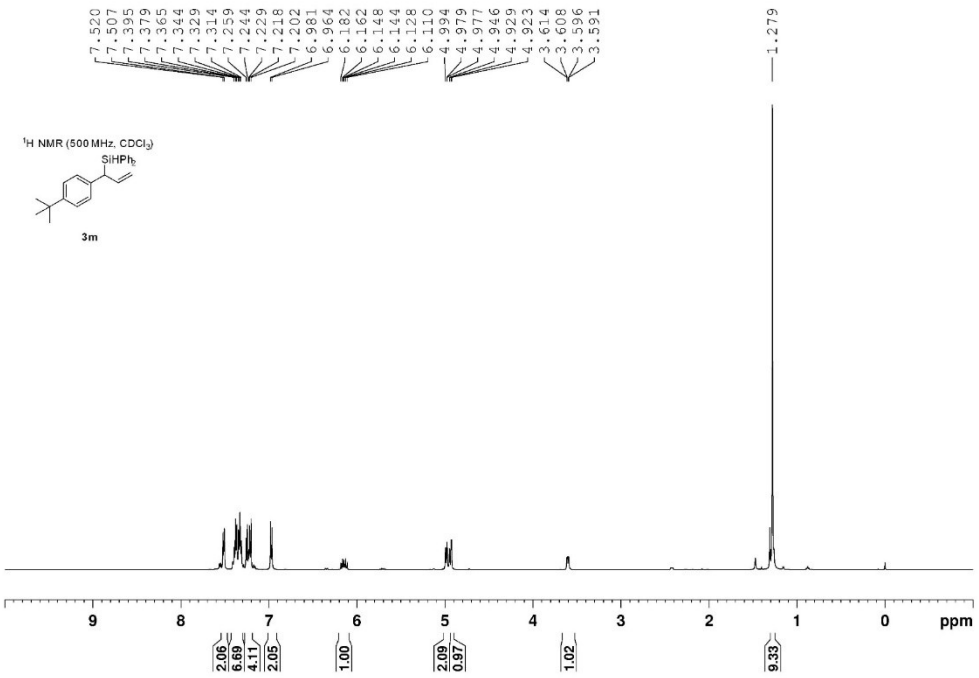


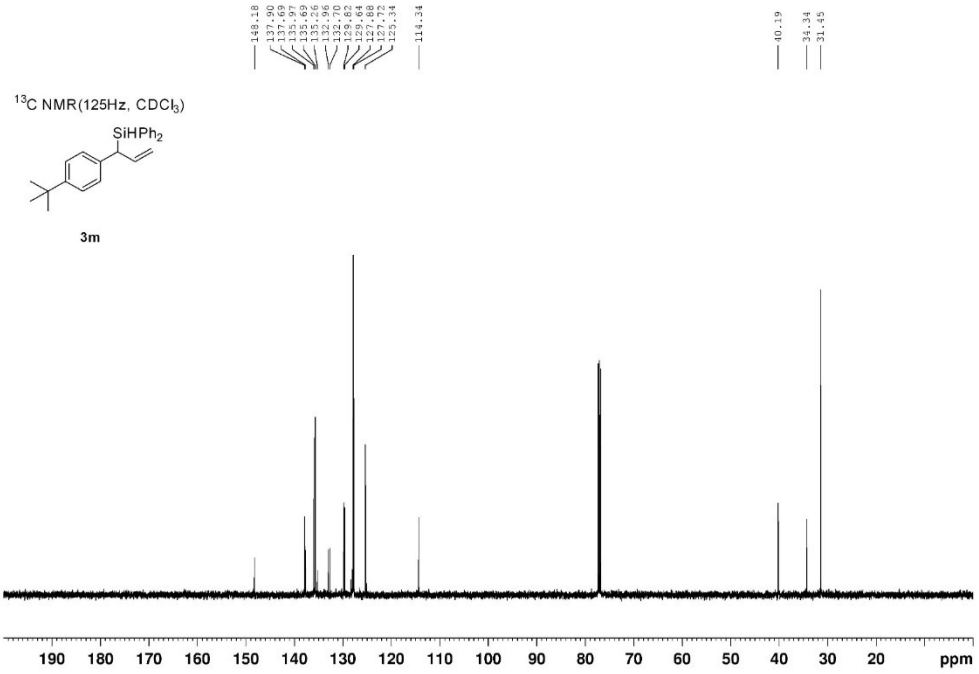
^{13}C NMR (125 MHz, $CDCl_3$)

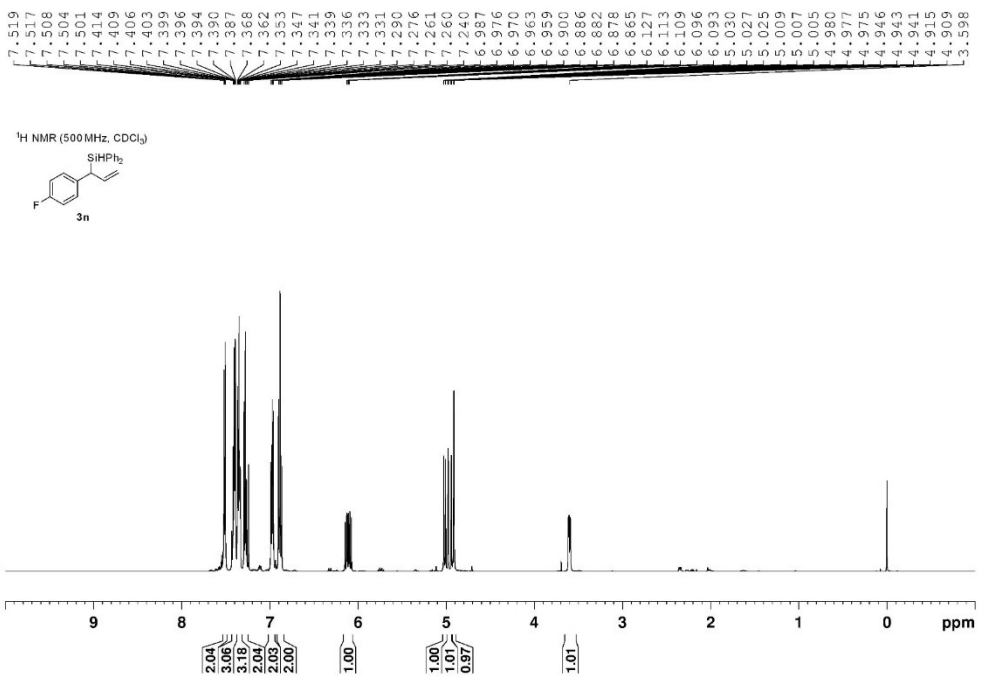
3k

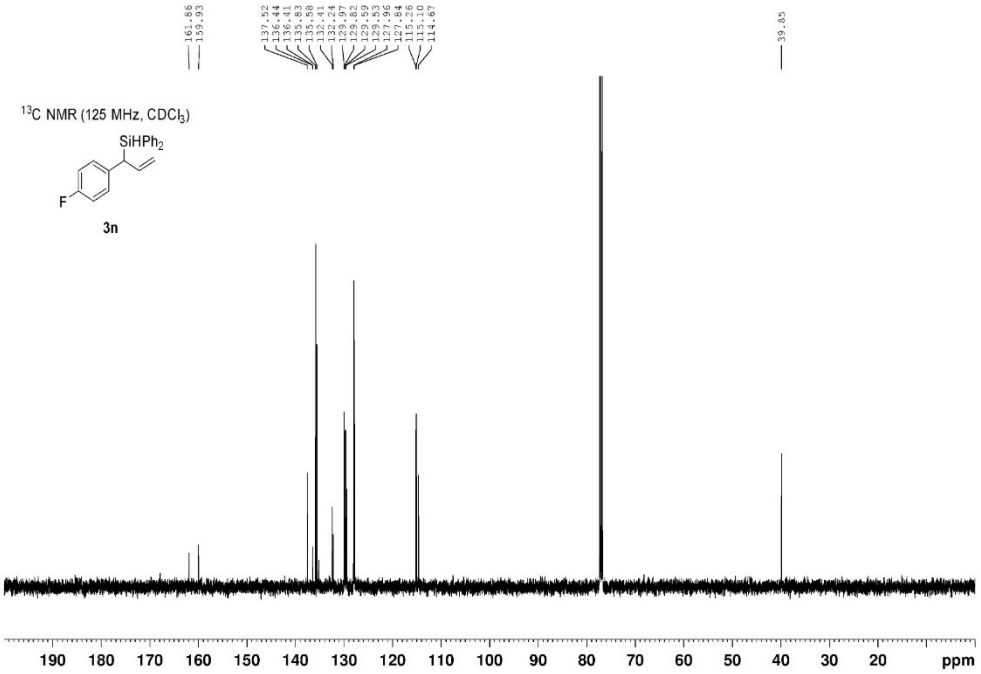

7.524
7.510
7.422
7.409
7.400
7.385
7.351
7.342
7.336
7.328
7.322
7.283
7.269
7.254
7.231
7.014
6.999
6.942
6.926
6.163
6.145
6.143
6.129
6.125
6.111
6.109
6.091
4.994
4.973
4.970
4.967
4.932
4.924
4.918
3.603
3.598
3.586
3.581
2.276
1H NMR (500 MHz, CDCl3)
SiHPh2
3l
9
8
7
6
5
4
3
2
1
0
ppm
2.05
3.11
3.19
2.02
1.95
2.02
1.00
3.03
1.03
3.22

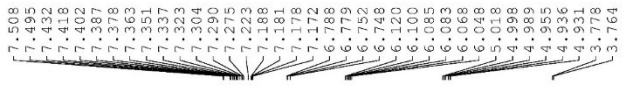

137.95
137.66
135.92
133.66
133.35
133.08
132.69
129.81
129.66
129.15
128.13
127.86
127.76
114.26
40.21
20.98
13C NMR (125 MHz, CDCl3)
SiHPh2
3l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.520
7.507
7.395
7.379
7.365
7.344
7.329
7.314
7.259
7.244
7.229
7.218
7.202
6.981
6.964
6.182
6.162
6.148
6.144
6.128
6.110
4.994
4.979
4.977
4.946
4.929
4.923
3.614
3.608
3.596
3.591
1.279
1H NMR (500 MHz, CDCl3)
SiHPh2
3m
9
8
7
6
5
4
3
2
1
0
ppm
2.06
6.69
4.11
2.05
1.00
2.09
0.97
1.02
9.33

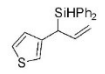

148.18
137.90
135.69
135.97
135.69
135.26
132.96
132.70
129.82
129.64
127.88
127.72
126.34
114.34
40.19
34.34
31.45
13C NMR(125Hz, CDCl3)
SiHPh2
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.519
7.517
7.508
7.504
7.501
7.414
7.409
7.406
7.403
7.399
7.396
7.394
7.390
7.387
7.368
7.362
7.353
7.347
7.341
7.339
7.336
7.333
7.331
7.290
7.276
7.261
7.260
7.240
6.987
6.976
6.970
6.963
6.959
6.900
6.886
6.882
6.878
6.865
6.127
6.113
6.109
6.096
6.093
5.030
5.027
5.025
5.009
5.007
5.005
4.980
4.977
4.975
4.946
4.943
4.941
4.915
4.909
3.598
1H NMR (500 MHz, CDCl3)
SiHPh2
F
3n
9
8
7
6
5
4
3
2
1
0
ppm
2.04
3.06
3.18
2.04
2.03
2.00
1.00
1.00
1.01
0.97
1.01

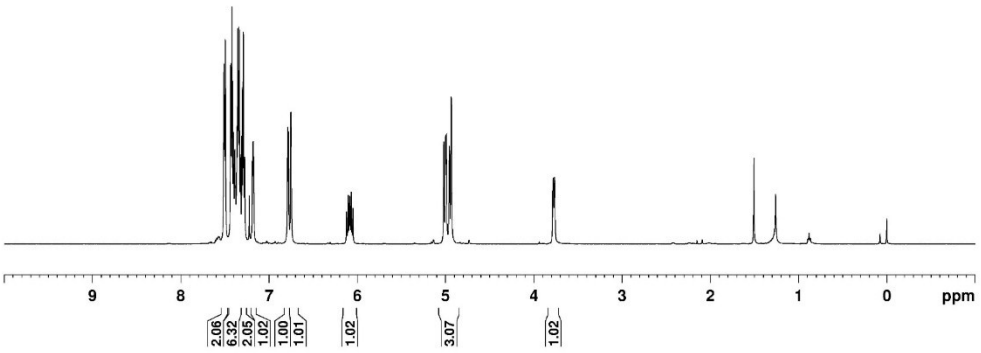

161.86
159.93
137.52
136.44
136.41
136.33
135.58
132.41
132.24
129.97
129.88
129.59
129.53
127.96
127.64
115.26
115.10
114.67
39.85
13C NMR (125 MHz, CDCl3)
SiHPh2
F
3n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



^{1}H NMR (500 MHz, $CDCl_3$)

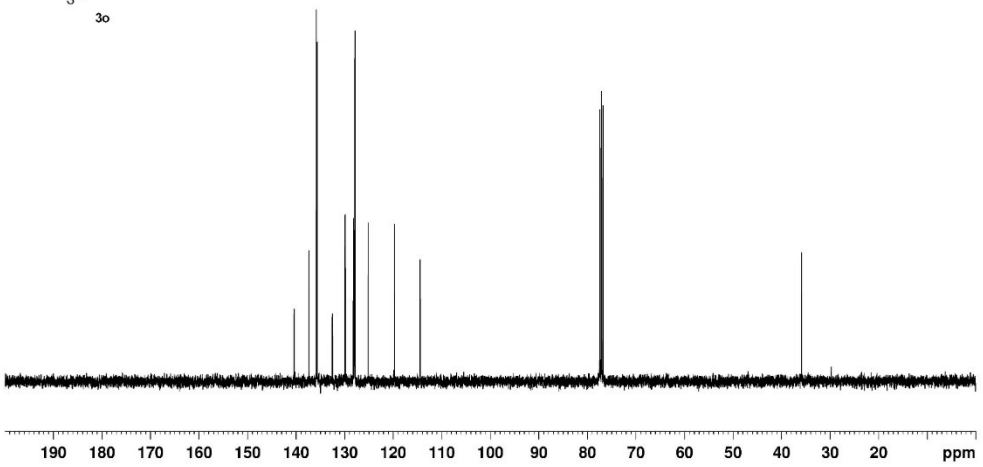


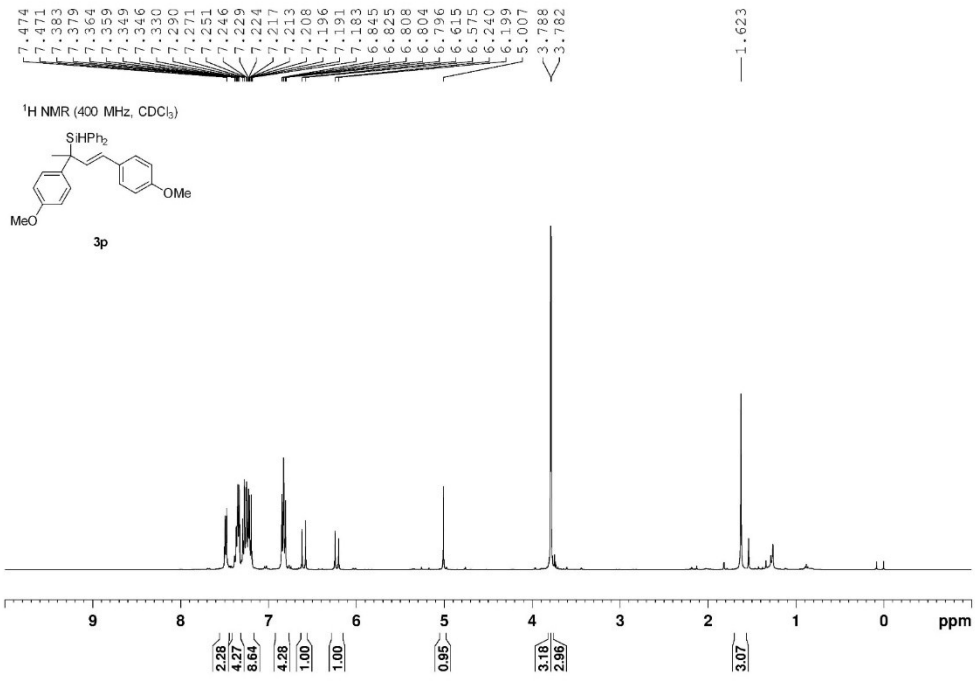
3o

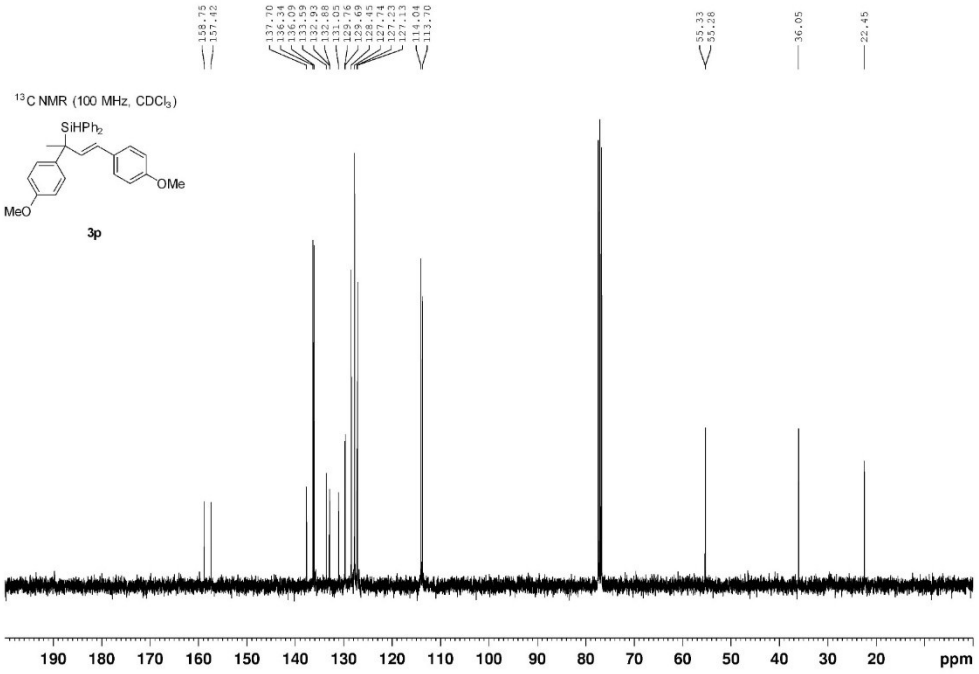


^{13}C NMR (100 MHz, $CDCl_3$)

3o




7.474
7.471
7.383
7.379
7.364
7.359
7.349
7.346
7.330
7.290
7.271
7.251
7.246
7.229
7.224
7.217
7.213
7.208
7.196
7.191
7.183
6.845
6.825
6.808
6.804
6.796
6.615
6.575
6.240
6.199
5.007
3.788
3.782
1.623
1H NMR (400 MHz, CDCl3)
SiHPh2
OMe
MeO
3p
9
8
7
6
5
4
3
2
1
0
ppm
2.28
4.27
8.64
4.28
1.00
1.00
0.95
3.18
2.96
3.07


158.75
157.42
137.70
136.34
136.09
133.59
132.93
132.68
131.05
129.76
129.69
128.45
127.74
127.23
127.13
114.04
113.70
55.33
55.28
36.05
22.45
13C NMR (100 MHz, CDCl3)
SiHPh2
OMe
MeO
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm