Highly Regio- and Stereoselective Heterogeneous Hydrosilylation of Terminal Alkynes over Cobalt-Metalated Porous Organic Polymer

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1. General Information

Tetrahydrofuran(THF) was freshly distilled from Na prior to use. Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. All reaction mixtures were stirred with a magnetic bar in a flame-dried glassware.

Chromatography

Thin layer chromatography (TLC) was performed on Huanghai pre-coated glass-backed TLC plates and visualized by UV lamp (254 nm). Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 ^{o}C petroleum ether (distillated prior to use) and analytical grade EtOAc (without further purification). Concentration under reduced pressure was performed by rotary evaporation. Purified compounds were further addressed under high vacuum (3-5 mmHg). Yields refer to chromatographically purified compounds.

Nuclear magnetic resonance spectra

^{1}H and ^{13}C spectra were recorded on a 400MHz and 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.

IR spectra and Mass spectroscopy

IR spectra were recorded on a Nicolet AVATER FTIR360 spectrometer as a thin film. Absorptions were given in wavenumbers (cm^{-1}). Mass spectroscopy: HRMS spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization.

Solid-state CP/MAS NMR, Nitrogen sorption isotherms, Pore size distribution curves, Transmission electron microscope, Scanning electron microscopy and Thermogravimetric analysis

The solid-state 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 was 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. 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•min^{-1} from room temperature up to 1073K under a nitrogen atmosphere. The X-ray photoelectron spectroscopy(XPS)was conducted using a Thermo Scientific ESCALAB 250Xi with the Al Kα irradiation at θ = 90^{o} for X-ray sources, and the spectrometer binding energy was calibrated through the reference C 1s (284.9 eV).

2. Experimental detail

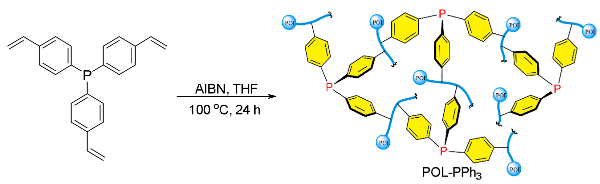
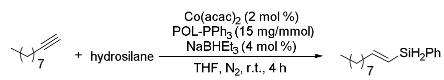


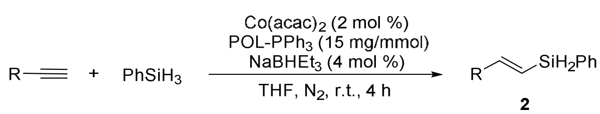
Figure S1. Preparation of POL-PPh_3

Table S1. Hydrosilane Screen for Hydrosilylation of 1-decyne[a]



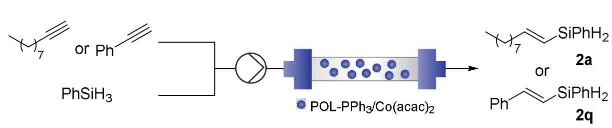
entry	hydrosilane	yield/%
1	$PhSiH_3$	93
2[a,b]	Ph_2SiH_2	N.R[c]
3[a,b]	Ph_3SiH	N.R.
4[a,b]	Ph_2MeSiH	N.R.
5[a,b]	$PhMe_2SiH$	N.R.
6[a,b]	$(MeO)_2MeSiH$	N.R.

[a]Reaction conditions: 1-decyne (1.0 mmol), silane (1.1 mmol), Co(acac)$_2$ (2 mol %), POL-PPh_3 (15 mg/ mmol), $NaBHEt_3$ (4 mol %), THF (2 mL), room temperature, N_2 atmosphere, 4 h. [b]reflux. [c]N.R. = No Reaction.



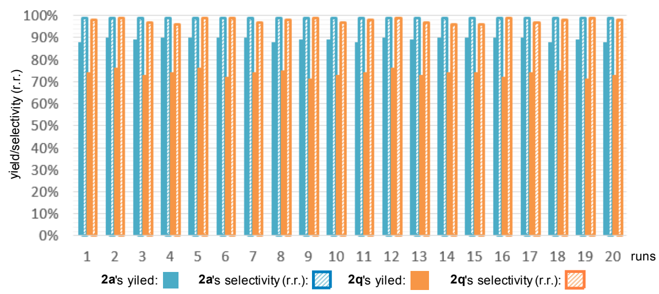
In a nitrogen filled schlenk tube, Co(acac)$_2$ (2 mol %), POL-PPh_3 (15 mg/mmol), $NaBHEt_3$ (4 mol %) and THF (2 mL) were added and the mixture was stirred at room temperature for 10 minutes, then alkyne (1.0 mmol) and phenylsilane (1.1 mmol) were added under N_2. The reaction mixture was stirred at room temperature. Upon completion, the solvent was removed by vacuum and the crude residue was purified by silica gel column chromatography to afford the corresponding products **2** (eluent: petroleum ether/EtOAc = 100/1).

3. General procedure for synthesis of vinylsilane products 2a and 2q in flow system



In a stationary phase, a mixed powder of POL-PPh_3 (30 mg) and silica sands (100 mg, 0.65-0.85 mm) was charged into a glass column (ϕ 0.6 cm × 8.0 cm) and washed by THF (2 mL). A solution of $Co(acac)_2$ (5.1 mg) in THF (1 mL) and $NaBHEt_3$ (4 mol %) in THF (1 mL) was subjected to the column respectively. After a residence time, the reactant alkyne (1.0 mmol) and $PhSiH_3$ (1.1 mmol) dissolving in THF (2 mL) slowly passed through the glass column (the flow rate of 0.3 mL/h), then eluted by THF (0.5 mL, the flow rate of 1 mL/h). Concentration of the eluent and the yield was determined by ^1H NMR analysis of the crude reaction mixture using diethyl phthalate as the internal standard. Next time, the solution of alkyne (1.0 mmol), $PhSiH_3$ (1.1 mmol) and $NaBHEt_3$ (4 mol %) passed through the glass column (the flow rate of 0.3 mL/h), then eluted by THF (0.5 mL, the flow rate of 1 mL/h). Concentration of the eluent and the yield was determined by ^1H NMR analysis. This operation was repeated nineteen times. $Co(acac)_2$ (5.1 mg) in THF (1 mL) needed to be subjected to the column once every five runs. As can be seen, the catalyst system was recycled twenty times with nearly no loss of activity and selectivity.

Scheme S1. Synthesis in flow system and reuse of Co/POL-PPh_3 towards hydrosilylation.



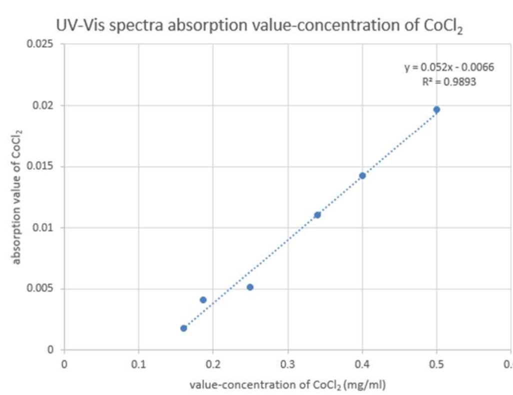


Table S2. Standard curve of aqueous solution of $CoCl_2$ in 516 nm wavelength.

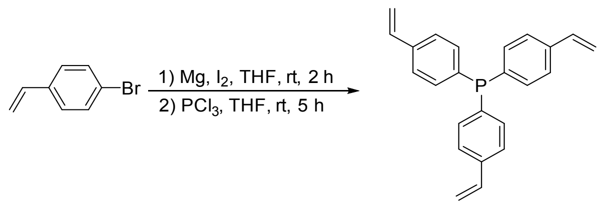
run	Absorption value	mg/ml($CoCl_2$)	mg($CoCl_2$)	mg($Co(acac)_2$)	Co leaching (%)
1	0.00383	0.200	0.400	0.790	15.5
2	0.00401	0.204	0.408	0.800	15.7
3	0.00421	0.208	0.416	0.819	16.1
4	0.0041	0.206	0.412	0.812	15.9
5	0.00392	0.202	0.404	0.796	15.6

Table S3. Leached of $CoCl_2$ in five runs

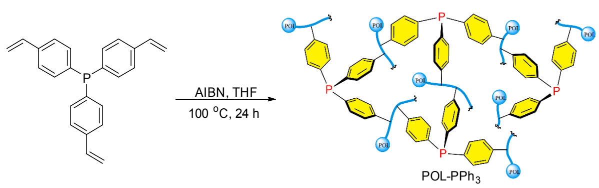
To determine the release of Cobalt, the eluent added aqueous solution of NaOH 2 mL (1.0 M), filtrate and washed by water, then added aqueous solution of HCl (1.0 M) afford to $CoCl_2$ solvent (2 mL). The solvent was examined by UV-Vis spectra in 516 nm wavelength.

Through UV-Vis spectra absorption value, we know each run leached 15.5% to 16.1% of Co, corresponding to 0.790 mg to 0.819 mg of $Co(acac)_2$(total amount of $Co(acac)_2$: 5.1 mg).

4. General procedure for synthesis of POL-PPh_3



Mg turnings (2.40g, 100 mmol) was added to a round bottom flask under nitrogen, and were activated by treatment with a grain of I_2 in THF (80 mL). *p*-bromostyrene (14.64g, 80 mmol) was slowly added to the flask, and the mixture was stirred for 1 h at room temperature. Next, PCl_3 (3.43g, 25 mmol) was slowly added to the solution in the ice water bath over 30 min followed by stirring at room temperature for 4 h. The reaction was quenched by aq.NH_4Cl, and the mixture was extracted with ethyl acetate. The organic layer was washed by H_2O twice, dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford tris(4-vinylphenyl)phosphane (5.45 g, 64% yield).



Under nitrogen, tris(4-vinylphenyl)phosphane (5.0 g) was dissolved in THF (50 mL), followed by the addition of AIBN (1.0 g) at room temperature. Next, the mixture was transferred into an autoclave at 100 ^{o}C for 24 h. After evaporation of THF under vacuum, a white solid (4.8 g, 96% yield) was obtained.

5. Characterization of POL-PPh_3 and $Co(acac)_2$/POL-PPh_3

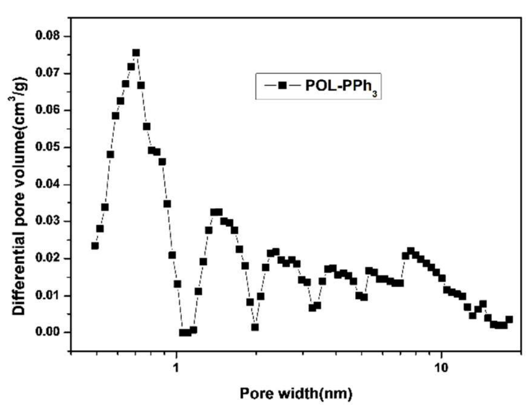


Figure S2. Pore size distribution of POL-PPh_3

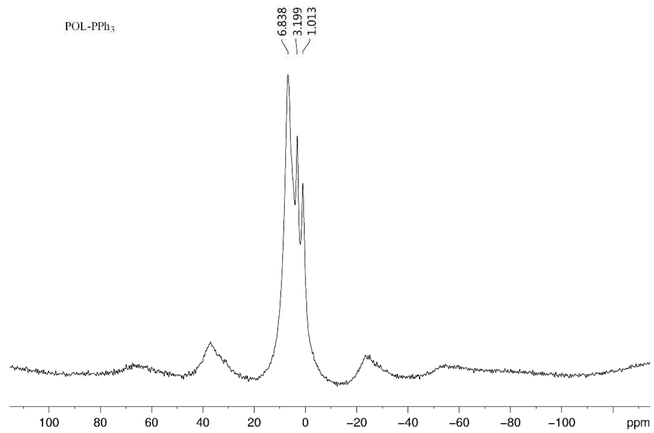


Figure S3. 1H CP/MAS of POL-Ph3P (400 MHz) δ 1.01-6.84

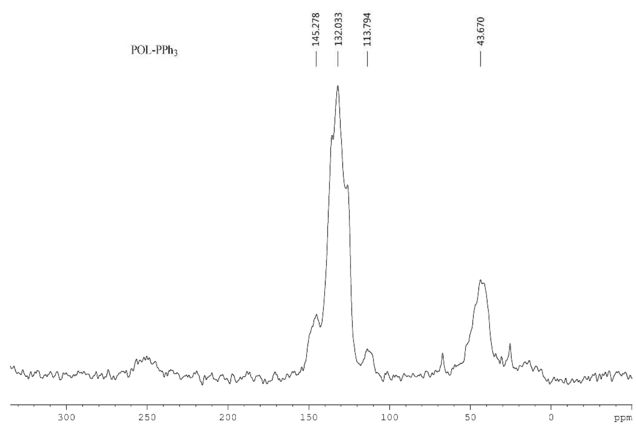


Figure S4. ^{13}C CP/MAS of POL-Ph_3P (100 MHz) δ 43.67, 113.79, 132.03, 145.28

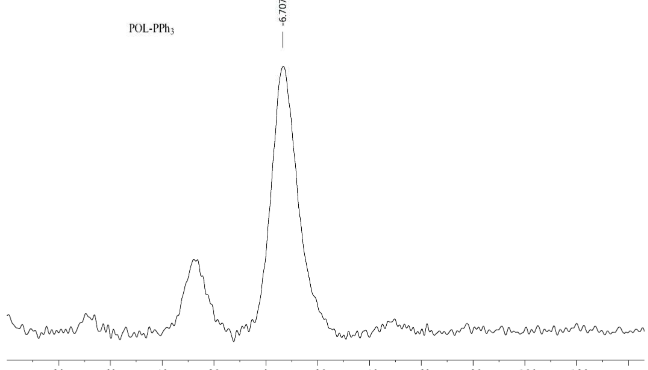


Figure S5. ^{31}P CP/MAS of POL-Ph_3P (161.8 MHz) δ -6.71

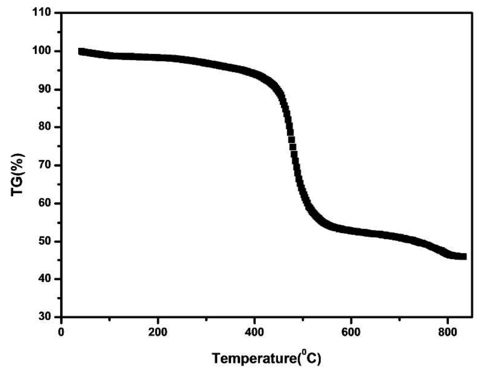


Figure S6. TG curve of POL-PPh_3

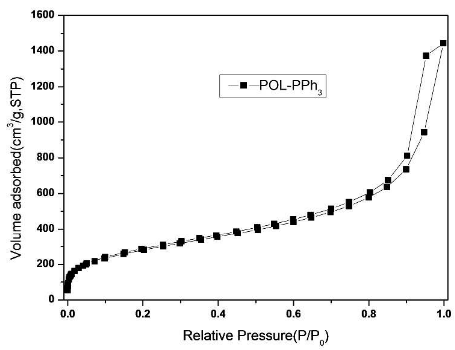


Figure S7. N_2 sorption isotherms of POL-PPh_3.

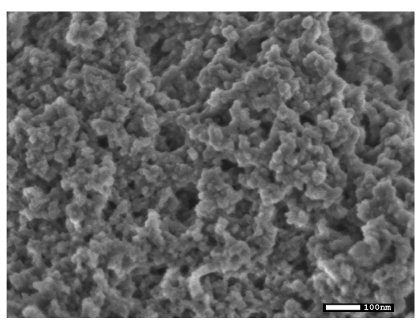


Figure S8. Scanning electron microscopy (SEM) of POL-PPh_3.

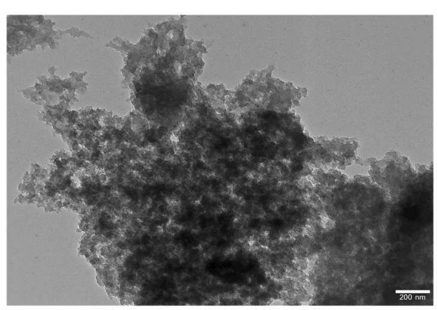


Figure S9. Transmission electron microscopy (TEM) of POL-PPh_3.

The $Co(acac)_2/POL\text{-}PPh_3$ was characterized by N_2 adsorption–desorption analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS).

Nitrogen adsorption–desorption analysis (Figure S10) shows that $Co(acac)_2/POL\text{-}PPh_3$ possesses very favorable hierarchical pore size distributions, which is further confirmed by SEM (Figure S12) and TEM (Figure S13) images. The pore sizes were mainly distributed at 0.40-0.80 nm, which was calculated by the method of non-local density functional theory (NLDFT) (Figure S11). The BET surface areas and total pore volumes of $Co(acac)_2/POL\text{-}PPh_3$ are up to 868 m^2/g and 1.16 cm^3/g, respectively. No obvious change in the pore size distribution emerged between $POL\text{-}PPh_3$ and $Co(acac)_2/POL\text{-}PPh_3$.

Furthermore, XPS confirmed the coordination of Cobalt with phosphorus of PPh_3 (Figure S14). In addition, the elemental distribution in the $Co(acac)_2/POL\text{-}PPh_3$ was determined by using the energy-dispersive X-ray spectroscopy (EDX) mapping technique in scanning electron microscopy. The highly dispersed character of all functional elements (C, P and Co) demonstrates the excellent integration of homogeneously distributed active functional sites (Figure S15).

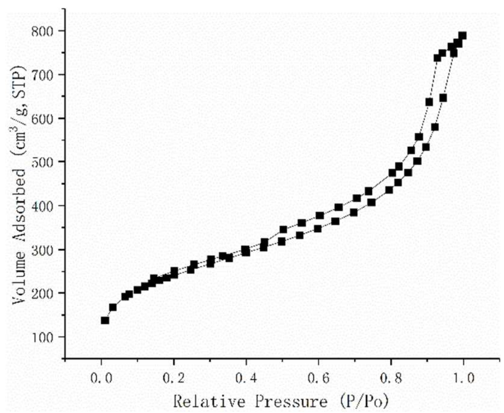


Figure S10. N_2 sorption isotherms of $Co(acac)_2/POL\text{-}PPh_3$

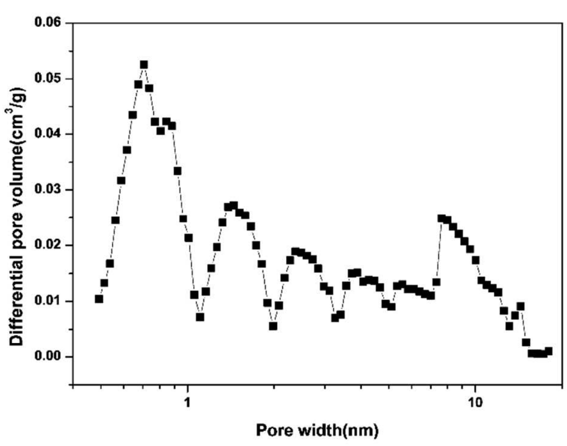


Figure S11. Pore size distribution of $Co(acac)_2/POL\text{-}PPh_3$

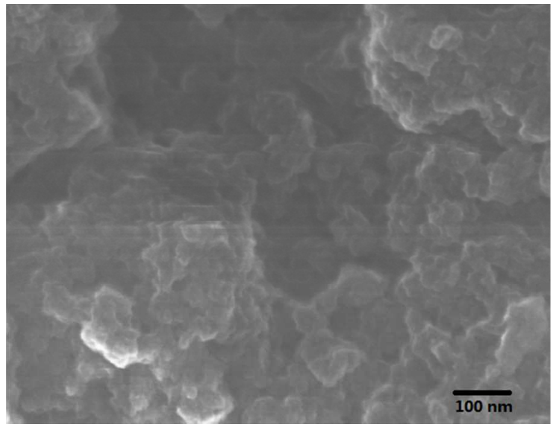


Figure S12. Scanning electron microscopy (SEM) of $Co(acac)_2$/POL-PPh_3

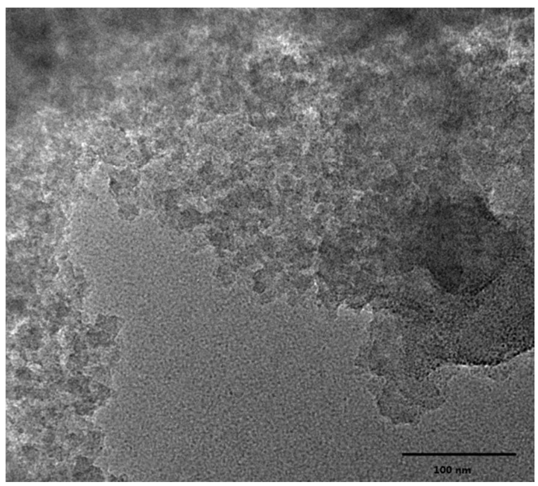


Figure S13. Transmission electron microscopy (TEM) of $Co(acac)_2$/POL-PPh_3

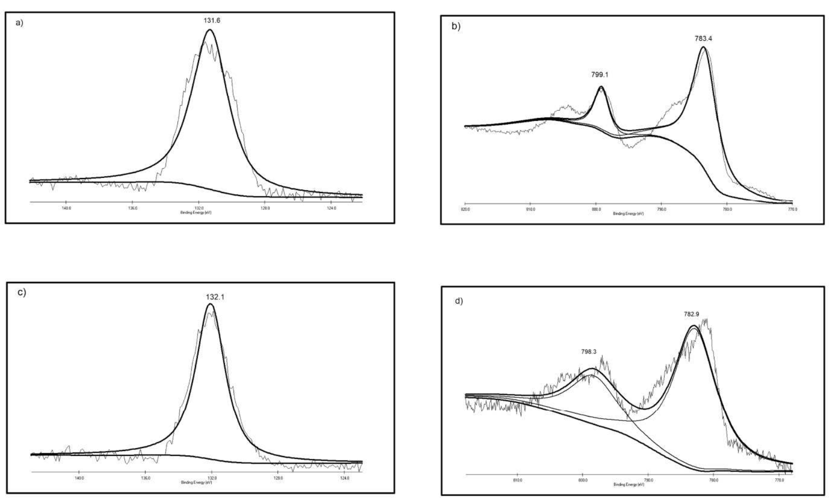


Figure S14. (a) P_{2p} XPS spectra of POL-PPh_3 and (b) Co_{2p} XPS spectra of $Co(acac)_2$,(c) P_{2p} XPS spectra of in $Co(acac)_2$/POL-PPh_3, (d) Co_{2p} XPS spectra of in $Co(acac)_2$/POL-PPh_3

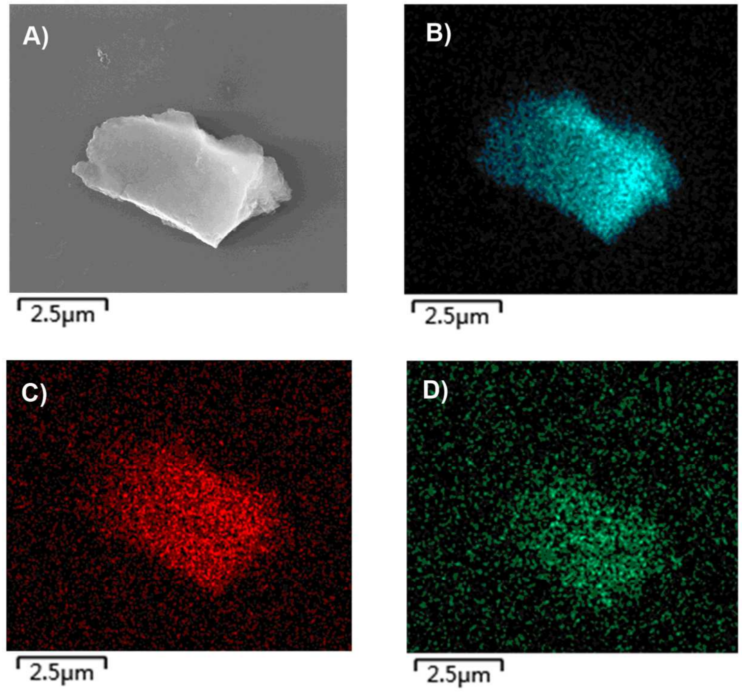
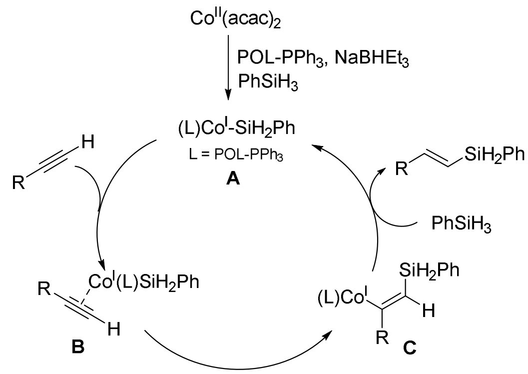


Figure S15. Elemental distribution in Co(acac)$_2$/POL-PPh$_3$ determined by SEM-EDS mapping, (A) SEM images, (B) Carbon, (C) Phosphorus and (D) Cobalt.

6. NBO charges for intermediate B

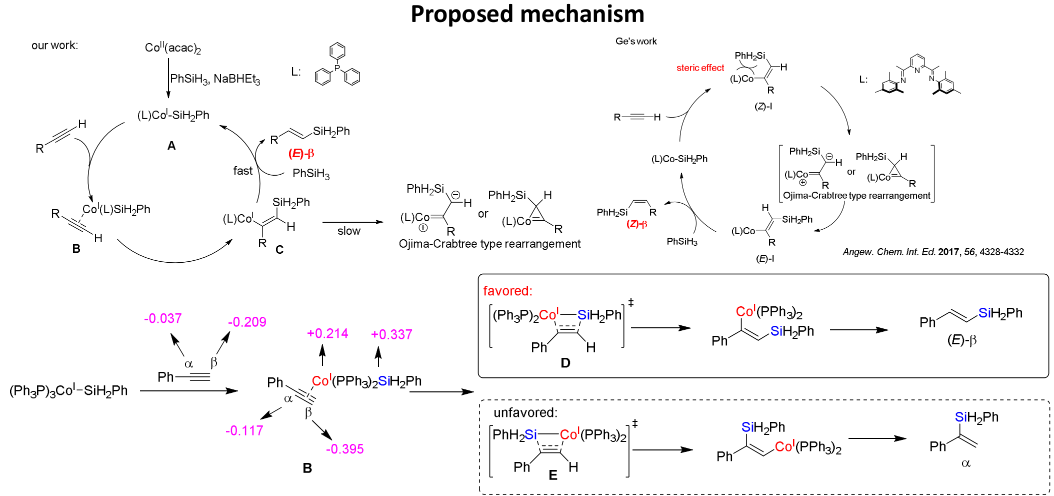
In our work on the mechanism, we accounted a mechanism for the formation of (*E*)-β-vinylsilane. On the basis of the precedents of Co-catalyzed hydrosilylation processes[a-c], we propose that the catalytic cycle involves a low-valent Co(I) silyl intermediate (**A**). Once formed, migratory insertion of the silyl moiety to the C≡C triple bond in **B** will produce the alkenyl metal species **C**. Due to the monodentate phosphine ligand (PPh$_3$) more flexibility than tridentate ligands, the steric repulsion between the bulky silyl group and the metal moiety is less than tridentate ligands', complex **C** did not undergo isomerization to form a sterically less demanding (*E*)-I (Ojima–Crabtree type rearrangement)[b,c]. Complex **C** could further react with PhSiH$_3$ to yield the hydrosilylation product (*E*)-β-vinylsilane and regenerate **A**.

Scheme S2. Proposed mechanism



Atomic charge is one of the simplest and most intuitive description of charge distribution in chemical systems. In general, an atom with more negative (positive) atomic charge is more likely to be the favorable site of electrophilic (nucleophilic) attack. Here we check the natural bond orbital (NBO) charge of intermediate **B** as shown in Scheme S3. The NBO charge located on the α and β carbons in alkyne are -0.117 and -0.395, respectively. While for the NBO charge on the silicon atom is much more positive than the cobalt. Apparently, the silicon with more positive atomic charge is more likely to be the favorable site of nucleophilic attack to the β carbon in alkyne, thus more likely to generate intermediate (**D**). In addition, we have found that the β is more stable than α by 4.7 kcal mol^{-1}. This could be one of the reason that we get the main product β-vinylsilane not α-vinylsilane.

Proposed mechanism



Scheme S3. The possible reaction paths and selected NBO charges for intermediate **B**

[a] Mo, Z.; Xiao, J.; Gao, Y.; Deng, L. Regio- and Stereoselective Hydrosilylation of Alkynes Catalyzed by Three-Coordinate Cobalt(I) Alkyl and Silyl Complexes. *J. Am. Chem. Soc*. **2014**, *136*, 17414−17417. [b] Teo, W. J.; Wang, C.; Tan, Y. W.; Ge, S. Cobalt-Catalyzed *Z*-Selective Hydrosilylation of Terminal Alkynes. *Angew. Chem. Int. Ed.* **2017**, *56*, 4328-4332. [c] Du, X. Y.; Hou, W. J.; Zhang, Y. L.; Huang, Z. Pincer cobalt complex-catalyzed *Z*-selective hydrosilylation of terminal alkynes. *Org. Chem. Front.*, **2017**, *4*, 1517-1521.

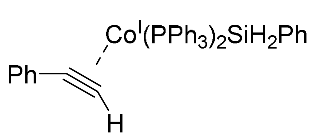
Computational details

The B3LYP[1] level of density functional theory was applied to optimize all of the structures studied in using the PCM[2] model with tetrahydrofuran as the solvent. Frequency calculations were performed at the same level of theory to confirm that all stationary points were minima (no imaginary frequency). A combination of Stuttgart/Dresden small-core RECP (relativistic effective core potential) plus valence double-ζ basis set (SDD)[3] for Co, P and Si atoms and the standard 6-31G(d) basis set for C and H atoms. Reported energies are relative Gibbs free energies at 298 K. Natural bond orbital (NBO) atomic charges calculations were carried out using the NBO 6.0 program[4]. All calculations were carried out using the Gaussian 09 software[5].

References:

1. (a) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.,* **1989**, *157*, 200; (b) A. D. Becke, *J. Chem. Phys.,* **1993**, *98*, 5648; (c) P. Stephens, F. Devlin, C. Chabalowski and M. J. Frisch, *J. Phys. Chem.,* **1994**, *98*, 11623; (d) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* **1988**, *37*, 785.
2. Scalmani, G. & Frisch, M. J. Continuous surface charge polarizable continuum models of solvation. I. General formalism. *J. Chem. Phys.* **2010**, *132*, 114110.
3. Fuentealba, P.; Preuss, H.; Stoll, H.; von Szentpaly, L. *Chem. Phys. Lett.* **1989**, *89*, 418.
4. NBO 6.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013.
5. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr. , J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox,
J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

Cartesian coordinates and electronic energies for all the species calculated in this study



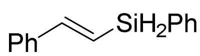
E = -3049.0834866 a.u.

Co	-0.19301000	0.32068000	-0.03699500

P	2.08024700	0.53412900	-0.57602200
P	-2.43456300	-0.44236100	-0.13418000
Si	0.21365100	-1.09583900	1.91332600
H	0.60590800	-0.22501600	3.10188200
H	-1.03974900	-1.76868300	2.44861100
C	1.45957200	-2.58349100	2.07734400
C	2.76210500	-2.43836800	2.59109600
C	1.06961900	-3.88052200	1.69053500
C	3.63594700	-3.52524600	2.69809400
H	3.10451900	-1.46120700	2.92111100
C	1.93583000	-4.97260900	1.79064000
H	0.06325500	-4.04896500	1.31212700
C	3.22813000	-4.79862300	2.29299600
H	4.63410200	-3.37736400	3.10485300
H	1.59887900	-5.96082900	1.48489100
H	3.90448400	-5.64574800	2.37719500
C	-0.64013400	1.83222000	-1.24972700
H	-0.78488500	2.08612800	-2.28953100
C	-0.62694400	2.23074400	-0.03892400
C	-0.72876100	3.29188800	0.94333200
C	-0.48604400	3.06528100	2.31227900
C	-1.06919200	4.60037200	0.53246000
C	-0.58133200	4.10718700	3.23637500
H	-0.22520000	2.06371400	2.64049600
C	-1.16441500	5.63576700	1.45877500
H	-1.25714300	4.78970500	-0.52079900
C	-0.92096200	5.39528300	2.81614300
H	-0.39018800	3.91030100	4.28816900
H	-1.42904700	6.63500500	1.12213000
H	-0.99614800	6.20499200	3.53681200
C	2.32626000	-1.03100700	-1.57942600
C	3.08344000	-2.11482200	-1.11730000
C	1.62364200	-1.15425500	-2.79056500
C	3.15495300	-3.29312700	-1.86576800
H	3.60732800	-2.05325900	-0.17050000
C	1.70034800	-2.33148600	-3.53664000
H	1.02221000	-0.32697900	-3.15653700
C	2.46909200	-3.40394900	-3.07661800
H	3.74640100	-4.12516600	-1.49416700
H	1.15883700	-2.40870500	-4.47544100
H	2.53046800	-4.32010800	-3.65747500
C	3.51393800	0.63951000	0.63485900
C	4.83192100	0.35747200	0.24725200
C	3.26800200	1.12729800	1.92335600

C	5.88296000	0.53344000	1.14809300
H	5.04438000	0.00350200	-0.75729300
C	4.32381000	1.31644800	2.82067700
H	2.25284800	1.35687800	2.22971100
C	5.63080500	1.01311100	2.43713000
H	6.89946200	0.30358500	0.84048500
H	4.12018200	1.69690000	3.81782400
H	6.45125900	1.15467100	3.13520800
C	2.60261200	1.92062800	-1.74984500
C	3.28360400	1.68259500	-2.94968200
C	2.35198600	3.24445200	-1.35942700
C	3.69667800	2.75032200	-3.75273200
H	3.49809400	0.66763700	-3.26663200
C	2.77093300	4.30900800	-2.15910200
H	1.82921300	3.44946900	-0.43133300
C	3.44078500	4.06497400	-3.36090300
H	4.22418600	2.54931000	-4.68143300
H	2.56992500	5.32901500	-1.84269800
H	3.76319600	4.89403300	-3.98494000
C	-3.57121100	0.51584200	-1.29647900
C	-4.67554800	1.24538900	-0.84502300
C	-3.26900800	0.51443500	-2.66665400
C	-5.46683800	1.96204300	-1.74973200
H	-4.92905100	1.25924000	0.20961200
C	-4.06210500	1.22324700	-3.56867200
H	-2.41212800	-0.04530300	-3.03210900
C	-5.16461100	1.95188600	-3.11132000
H	-6.32285800	2.52292400	-1.38416200
H	-3.81865300	1.20751400	-4.62768800
H	-5.78202900	2.50604000	-3.81294400
C	-2.56544800	-2.16413800	-0.87741800
C	-3.78517700	-2.65153800	-1.37278100
C	-1.42164500	-2.96527900	-0.97715200
C	-3.85946100	-3.92466100	-1.93990100
H	-4.67763500	-2.03489300	-1.32438600
C	-1.49517600	-4.23726300	-1.55295900
H	-0.46757100	-2.59726600	-0.61392100
C	-2.71398500	-4.72061800	-2.03058800
H	-4.81093400	-4.29152700	-2.31500300
H	-0.59658500	-4.84281600	-1.62890900
H	-2.77201400	-5.70962700	-2.47675800
C	-3.42826300	-0.50469100	1.46202400
C	-3.35901300	0.60644700	2.31478900
C	-4.21123100	-1.60308300	1.83378600

C	-4.07512800	0.62377200	3.51311900
H	-2.73960400	1.45802300	2.04972800
C	-4.92026000	-1.58746200	3.03815200
H	-4.26693000	-2.47831100	1.19583000
C	-4.85732300	-0.47453400	3.87845100
H	-4.01299800	1.49252200	4.16282700
H	-5.52002300	-2.44944200	3.31776600
H	-5.40940100	-0.46476800	4.81421700



***(E)*-β** E = -831.3705031 a.u.

Si	-1.30994300	-1.62438300	-0.01846100
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H	-1.68635600	-2.70692100	0.94774700
C	-2.74175900	-0.36613000	-0.04133600
C	-2.58894200	0.89452000	-0.64554700
C	-3.98446200	-0.67804900	0.53542000
C	-3.64353100	1.80917700	-0.67967700
H	-1.63555800	1.17053500	-1.09150400
C	-5.04347800	0.23351700	0.50343300
H	-4.13097000	-1.64232000	1.01732900
C	-4.87428200	1.47893800	-0.10531400
H	-3.50534900	2.77873000	-1.15135600
H	-5.99689100	-0.02731900	0.95567900
H	-5.69567900	2.19026200	-0.12999100
C	0.34063700	-0.84469800	0.44969900
C	1.40303100	-0.80586700	-0.37843000
C	2.72967600	-0.21841700	-0.12217200
C	3.70520900	-0.28976500	-1.13344400
C	3.07355800	0.41512600	1.08760300
C	4.97811700	0.25031300	-0.94841300
H	3.45717700	-0.77559600	-2.07434700
C	4.34360400	0.95473400	1.27371800
H	2.34327100	0.48686500	1.88833100
C	5.30248600	0.87546900	0.25716100
H	5.71456700	0.18274200	-1.74455600
H	4.58875400	1.43977400	2.21478600
H	6.29241500	1.29771300	0.40619500
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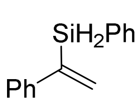
H	1.30560400	-1.25520900	-1.36841300



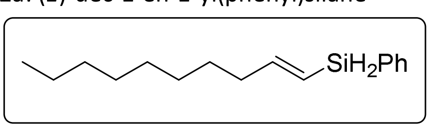
α E = -831.3639579 a.u.

C	3.60604800	-1.23316700	-0.73092000
C	3.75919900	-1.50997000	0.62924300
C	2.67111800	-0.28232000	-1.14934100
C	2.97456900	-0.83420100	1.56797500
H	4.48402600	-2.25059700	0.95686100
C	1.87723400	0.41072700	-0.22004800
H	2.56022500	-0.08171800	-2.21273900
C	2.04292000	0.11590200	1.14490900
H	3.08716600	-1.04873400	2.62757600
H	1.43658100	0.62875700	1.88869300
C	-1.46030000	2.64439900	0.84642300
C	-1.04897400	1.59973600	0.10452200
C	-1.85645200	0.35319400	0.01052100
C	-2.54468700	-0.14761000	1.13176900
C	-1.95546000	-0.36159200	-1.19686600
C	-3.31833800	-1.30445800	1.04329000
H	-2.45360100	0.36779800	2.08367400
C	-2.73245300	-1.51733800	-1.28767400
H	-1.43769500	0.00053200	-2.08078300
C	-3.41811100	-1.99407800	-0.16826000
H	-3.83624400	-1.67339000	1.92476100
H	-2.80100900	-2.04522500	-2.23513200
H	-4.01711200	-2.89801400	-0.23645100
H	-2.41482900	2.63923700	1.37147100
H	4.21040900	-1.75872500	-1.46575500
Si	0.63187900	1.73103700	-0.79459500
H	0.47672400	1.59060900	-2.27691100
H	1.14852300	3.10963100	-0.51976100
H	-0.86734900	3.54998900	0.94556900

7. ^{1}H, ^{13}C-NMR, IR and HRMS Data of products 2

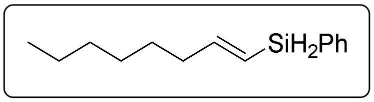
Compound **2a**[6], **2b**[7], **2d**[8], **2e**[9], **2g**[8] and **2t**[8] were known in the literature.

2a: (*E*)-dec-1-en-1-yl(phenyl)silane



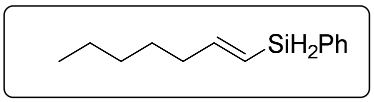
colorless liquid (90%, 221.9 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 0.99 (t, 3H, *J*= 6.8 Hz), 1.38-1.41 (m, 10H), 1.49-1.54 (m, 2H), 2.25-2.31 (m, 2H), 4.65 (d, 2H, *J*= 3.2 Hz), 5.79-5.85 (m, 1H), 6.46 (dt, 1H, J_1= 18.5 Hz, J_2=6.4 Hz), 7.44-7.48 (m, 3H), 7.66-7.68 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 28.4, 29.2, 29.3, 29.5, 31.9, 37.0, 119.9, 128.0, 129.5, 132.4, 135.3, 154.2; **IR** (film): 3068, 2131, 1613 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{16}H_{27}Si^+$ $[M+H]^+$ 247.1877, found: 247.1875.

2b: (*E*)-oct-1-en-1-yl(phenyl)silane



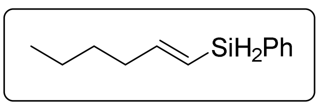
colorless liquid (91%, 198.7 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 0.96 (t, 3H, *J*= 6.8 Hz), 1.33-1.38 (m, 6H), 1.47-1.51 (m, 2H), 2.22-2.27 (m, 2H), 4.61 (d, 2H, *J*= 3.2 Hz), 5.76-5.82 (m, 1H), 6.43 (dt, 1H, J_1= 18.5 Hz, J_2=6.4 Hz), 7.40-7.45 (m, 3H), 7.62-7.65 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 28.4, 28.8, 31.7, 36.9, 119.8, 128.0, 129.5, 132.4, 135.3, 154.2; **IR** (film): 3069, 2134, 1617 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{14}H_{23}Si^+$ $[M+H]^+$ 219.1564, found: 219.1562.

2c: (*E*)-hept-1-en-1-yl(phenyl)silane



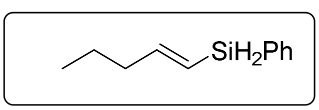
colorless liquid (93%, 190.1 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 0.94 (t, 3H, *J*= 6.9 Hz), 1.32-1.37 (m, 4H), 1.44-1.51 (m, 2H), 2.20-2.25 (m, 2H), 4.58 (d, 2H, *J*= 3.2 Hz), 5.73-5.79 (m, 1H), 6.41 (dt, 1H, J_1= 18.4 Hz, J_2=6.4 Hz), 7.38-7.45 (m, 3H), 7.60-7.62 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 14.0, 22.5, 28.1, 31.4, 36.9, 119.8, 128.0, 129.5, 132.4, 135.3, 154.2; **IR** (film): 3068, 2133, 1616 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{13}H_{21}Si^+$ $[M+H]^+$ 205.1408, found: 205.1405.

2d: (*E*)-hex-1-en-1-yl(phenyl)silane



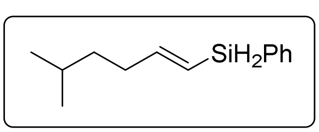
colorless liquid (89%, 169.5 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 0.98 (t, 3H, *J*= 7.1 Hz), 1.34-1.43 (m, 2H), 1.45-1.52 (m, 2H), 2.25-2.28 (m, 2H), 4.61 (d, 2H, *J*= 3.2 Hz), 5.76-5.82 (m, 1H), 6.43 (dt, 1H, J_1= 18.4 Hz, J_2=6.4 Hz), 7.40-7.46 (m, 3H), 7.62-7.66 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 13.9, 22.2, 30.6, 36.6, 119.8, 128.0, 129.5, 132.4, 135.3, 154.1; **IR** (film): 3065, 2130, 1619 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{12}H_{19}Si^+$ $[M+H]^+$ 191.1251, found: 191.1250.

2e: (*E*)-pent-1-en-1-yl(phenyl)silane



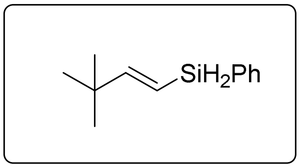
colorless liquid (83%, 146.3 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 1.01 (t, 3H, *J*= 7.3 Hz), 1.50-1.60 (m, 2H), 2.23-2.28 (m, 2H), 4.64 (d, 2H, *J*= 3.2 Hz), 5.79-5.86 (m, 1H), 6.45 (dt, 1H, J_1= 18.4 Hz, J_2=6.3 Hz), 7.42-7.49 (m, 3H), 7.65-7.67 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 13.6, 21.6, 39.0, 120.1, 128.0, 129.5, 132.4, 135.3, 153.9; **IR** (film): 3065, 2131, 1614 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{11}H_{17}Si^+$ $[M+H]^+$ 177.1095, found: 177.1093.

2f: (*E*)-(5-methylhex-1-en-1-yl)(phenyl)silane



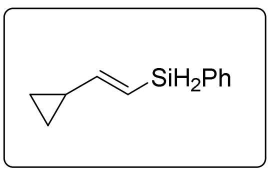
colorless liquid (89%, 181.9 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 0.96 (d, 6H, *J*= 6.7 Hz), 1.35-1.41 (m, 2H), 1.60-1.67 (m, 1H), 2.22-2.28 (m, 2H), 4.60 (d, 2H, *J*= 3.2 Hz), 5.76-5.82 (m, 1H), 6.43 (dt, 1H, J_1= 18.4 Hz, J_2=6.3 Hz), 7.40-7.45 (m, 3H), 7.62-7.65 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 22.5, 27.6, 34.8, 37.6, 119.7, 128.0, 129.5, 132.4, 135.3, 154.3; **IR** (film): 3069, 2132, 1618 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{13}H_{21}Si^+$ $[M+H]^+$ 205.1408, found: 205.1407.

2g: (*E*)-(3,3-dimethylbut-1-en-1-yl)(phenyl)silane



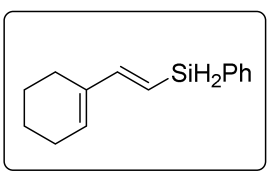
colorless liquid (31%, 59.0 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9H), 4.60 (d, 2H, *J*= 3.2 Hz), 5.68 (dt, 1H, J_1= 18.8 Hz, J_2=3.2 Hz), 6.44 (d, 1H, *J*= 18.8 Hz), 7.40-7.45 (m, 3H), 7.60-7.63 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 28.9, 35.7, 113.4, 128.0, 129.5, 132.5, 135.3, 164.1; **IR** (film): 3062, 2131, 1613 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{12}H_{19}Si^+$ $[M+H]^+$ 191.1251, found: 191.1250.

2h: (*E*)-(2-cyclopropylvinyl)(phenyl)silane



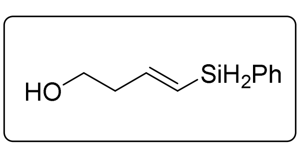
colorless liquid (89%, 155.1 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 0.47-0.51 (m, 2H), 0.76-0.80 (m, 2H), 1.50-1.58 (m, 1H), 4.52 (d, 2H, *J*= 2.7 Hz), 5.71-5.84 (m, 2H), 7.32-7.40 (m, 3H), 7.55-7.58 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 7.6, 17.7, 116.3, 128.0, 129.5, 132.4, 135.3, 157.4; **IR** (film): 3063, 2133, 1619 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{11}H_{15}Si^+$ $[M+H]^+$ 175.0938, found: 175.0936.

2i: (*E*)-(2-(cyclohex-1-en-1-yl)vinyl)(phenyl)silane



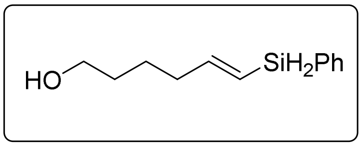
colorless liquid (84%, 180.1 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 1.60-1.64 (m, 2H), 1.68-1.70 (m, 2H), 2.17-2.18 (m, 4H), 4.62 (d, 2H, *J*= 3.2 Hz), 5.74 (dt, 1H, J_1= 18.7 Hz, J_2=3.2 Hz), 5.89 (t, *J*= 3.4 Hz, 1H), 6.80 (d, 1H, *J*= 18.7 Hz), 7.36-7.41 (m, 3H), 7.59-7.60 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 22.4, 22.5, 23.9, 26.0, 114.1, 128.0, 129.6, 132.4, 132.9, 135.4, 137.3, 153.1. **IR** (film): 3068, 2133, 1615 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{14}H_{19}Si^+$ $[M+H]^+$ 215.1251, found: 215.1252.

2j: (*E*)-4-(phenylsilyl)but-3-en-1-ol



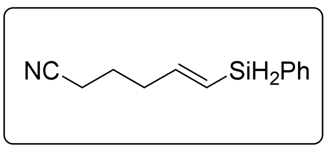
colorless liquid (68%, 121.2 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 1H), 2.47-2.52 (m, 2H), 3.75 (t, 2H, *J*= 6.4 Hz), 4.61 (d, 2H, *J*= 3.2 Hz), 5.88-5.95 (m, 1H), 6.39 (dt, 1H, J_1= 18.5 Hz, J_2=6.4 Hz), 7.39-7.47 (m, 3H), 7.61-7.62 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 40.0, 61.2, 123.6, 128.0, 129.6, 131.7, 135.3, 149.4; **IR** (film): 3068, 2131, 1616 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{10}H_{15}OSi^+$ $[M+H]^+$ 179.0887, found: 179.0889.

2k: (*E*)-6-(phenylsilyl)hex-5-en-1-ol



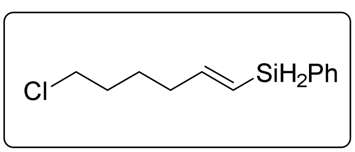
colorless liquid (88%, 181.6 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 1.51-1.64 (m, 4H), 1.80 (s, 1H), 2.23-2.28 (m, 2H), 3.67 (t, 2H, *J*= 6.5 Hz), 4.58 (d, 2H, *J*= 3.1 Hz), 5.76-5.81 (m, 1H), 6.39 (dt, 1H, J_1= 18.4 Hz, J_2=6.3 Hz), 7.37-7.43 (m, 3H), 7.59-7.62 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 24.5, 32.1, 36.5, 62.6, 120.4, 127.9, 129.5, 132.2, 135.3, 153.4; **IR** (film): 3064, 2132, 1613 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{12}H_{19}OSi^+$ $[M+H]^+$ 207.1200, found: 207.1201.

2l: (*E*)-6-(phenylsilyl)hex-5-enenitrile



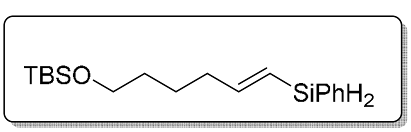
colorless liquid (84%, 169.2 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 1.79-1.87 (m, 2H), 2.35-2.39 (m, 4H), 4.58 (d, 2H, *J*= 3.1 Hz), 5.84-5.91 (m, 1H), 6.30 (dt, 1H, J_1= 18.4 Hz, J_2=6.4 Hz), 7.39-7.47 (m, 3H), 7.56-7.60 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 16.4, 24.0, 35.2, 119.3, 122.9, 128.0, 129.7, 131.5, 135.2, 150.2; **IR** (film): 3063, 2235, 2131, 1614 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{12}H_{16}NSi^+$ $[M+H]^+$ 202.1047, found: 202.1046.

2m: (*E*)-(6-chlorohex-1-en-1-yl)(phenyl)silane



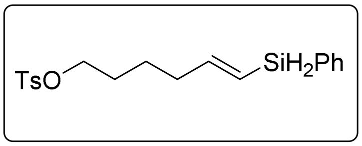
colorless liquid (74%, 166.4 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 1.54-1.62 (m, 2H), 1.75-1.82 (m, 2H), 2.18-2.24 (m, 2H), 3.52 (t, 2H, *J*= 6.6 Hz), 4.53 (d, 2H, *J*= 3.1 Hz), 5.72-5.78 (m, 1H), 6.33 (dt, 1H, J_1= 18.5 Hz, J_2=6.4 Hz), 7.33-7.41 (m, 3H), 7.54-7.58 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 25.6, 32.0, 34.0, 44.8, 120.9, 128.0, 129.6, 132.1, 135.3, 152.8; **IR** (film): 3068, 2133, 1616 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{12}H_{18}ClSi^+$ $[M+H]^+$ 225.0861, found: 225.0860.

2n: (*E*)-tert-butyldimethyl((6-(phenylsilyl)hex-5-en-1-yl)oxy)silane



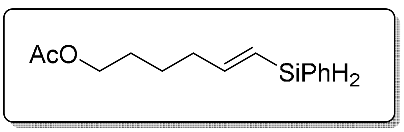
colorless liquid (55%, 176.3 mg); **^{1}H** NMR (500 MHz, $CDCl_3$) δ 0.08 (s, 6H), 0.92 (s, 9H), 1.49-1.59 (m, 4H), 2.21-2.25 (m, 2H), 3.64 (t, 2H, *J*= 5.9 Hz), 4.56 (d, 2H, *J*= 2.8 Hz), 5.74-5.78 (m, 1H), 6.39 (dt, 1H, J_1= 18.5 Hz, J_2=6.3 Hz), 7.34-7.43 (m, 3H), 7.59-7.60 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ -5.3, 18.4, 24.7, 26.0, 32.3, 36.6, 63.0, 120.1, 128.0, 129.6, 132.3, 135.4, 153.9; **IR** (film): 3065, 2132, 1614 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{18}H_{33}OSi_2^+$ $[M+H]^+$ 321.2065, found: 321.2066.

2o: (*E*)-6-(phenylsilyl)hex-5-en-1-yl 4-methylbenzenesulfonate



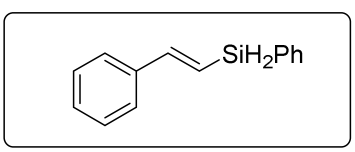
colorless liquid (86%, 310.0 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 1.45-1.51 (m, 2H), 1.65-1.72 (m, 2H), 2.14-2.19 (m, 2H), 2.46 (s, 3H), 4.07 (t, 2H, *J*= 6.4 Hz), 4.56 (d, 2H, *J*= 3.2 Hz), 5.69-5.76 (m, 1H), 6.30 (dt, 1H, J_1= 18.4 Hz, J_2=6.4 Hz), 7.35-7.40 (m, 3H), 7.41-7.43 (m, 2H), 7.57-7.60 (m, 2H), 7.80-7.83 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 21.5, 24.0, 28.1, 35.8, 70.2, 120.9, 127.7, 127.9, 129.6, 129.7, 131.9, 133.1, 135.2, 144.6, 152.5; **IR** (film): 3069, 2131, 1618 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{19}H_{25}O_3SSi^+$ $[M+H]^+$ 361.1289, found: 361.1290.

2p: (*E*)-6-(phenylsilyl)hex-5-en-1-yl acetate



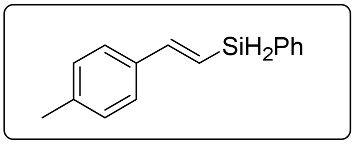
colorless liquid (61%, 151.5 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 1.50-1.56 (m, 2H), 1.64-1.70 (m, 2H), 2.07 (s, 3H), 2.22-2.26 (m, 2H), 4.10 (t, 2H, *J*= 6.4 Hz), 4.55 (d, 2H, *J*= 2.6 Hz), 5.75-5.80 (m, 1H), 6.36 (dt, 1H, J_1= 18.3 Hz, J_2=6.2 Hz), 7.37-7.44 (m, 3H), 7.58-7.60 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 21.0, 24.7, 28.1, 36.4, 64.3, 120.7, 128.0, 129.6, 132.2, 135.4, 153.1, 171.2; **IR** (film): 3062, 2139, 1750, 1616 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{14}H_{21}O_2Si^+$ $[M+H]^+$ 249.1306, found: 249.1304.

2q: (*E*)-phenyl(styryl)silane



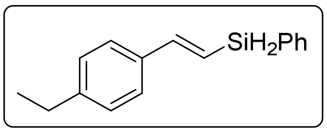
colorless liquid (74%, 155.7 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 4.70 (d, 2H, *J*= 3.2 Hz), 6.50 (dt, 1H, J_1= 19.0 Hz, J_2=3.2 Hz), 7.15 (d, 1H, *J*= 19.0 Hz), 7.24-7.40 (m, 6H), 7.44-7.45 (m, 2H) 7.61-7.63 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 119.3, 126.7, 128.1, 128.6, 128.6, 129.8, 131.6, 135.5, 137.7, 149.3; **IR** (film): 3065, 2136, 1604 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{14}H_{15}Si^+$ $[M+H]^+$ 211.0938, found: 211.0936.

2r: (E)-(4-methylstyryl)(phenyl)silane



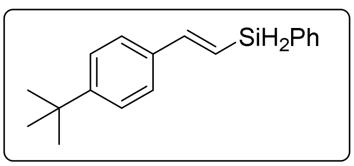
colorless liquid (78%, 174.8 mg); **^{1}H** NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 4.79 (d, 2H, *J*= 3.2 Hz), 6.52 (dt, 1H, J_1= 19.0 Hz, J_2=3.2 Hz), 7.20-7.23 (m, 3H), 7.43-7.49 (m, 5H), 7.70-7.72 (m, 2H); **^{13}C** NMR (125 MHz, $CDCl_3$) δ 21.2, 117.9, 126.6, 128.1, 129.3, 129.7, 131.8, 135.1, 135.5, 138.6, 149.3; **IR** (film): 3067, 2133, 1616 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{15}H_{17}Si^+$ $[M+H]^+$ 225.1095, found: 225.1094.

2s: (*E*)-(4-ethylstyryl)(phenyl)silane



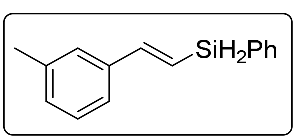
colorless liquid (65%, 155.0 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 1.22 (t, 3H, *J*= 7.6 Hz), 2.63 (q, 2H, *J*= 7.6 Hz), 4.69 (d, 2H, *J*= 3.3 Hz), 6.44 (dt, 1H, J_1= 19.0 Hz, J_2=3.3 Hz), 7.11-7.17 (m, 3H), 7.34-7.40 (m, 5H), 7.60-7.63 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 15.5, 28.7, 118.0, 126.7, 128.1, 128.1, 129.7, 131.8, 135.3, 135.5, 145.0, 149.3; **IR** (film): 3067, 2135, 1596 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{16}H_{19}Si^+$ $[M+H]^+$ 239.1251, found: 239.1253.

2t: (*E*)-(4-(tert-butyl)styryl)(phenyl)silane



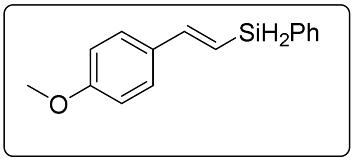
colorless liquid (83%, 221.2 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 4.78 (d, 2H, *J*= 3.2 Hz), 6.54 (dt, 1H, J_1= 19.0 Hz, J_2=3.2 Hz), 7.24 (d, 1H, *J*= 19.0 Hz), 7.44-7.50 (m, 7H), 7.69-7.71 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 31.2, 34.7, 118.2, 125.5, 126.4, 128.1, 129.7, 131.9, 135.1, 135.5, 149.2, 151.9; **IR** (film): 3068, 2133, 1609 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{18}H_{23}Si^+$ $[M+H]^+$ 267.1564, found: 267.1561.

2u: (*E*)-(3-methylstyryl)(phenyl)silane



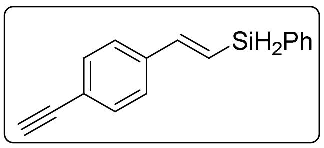
colorless liquid (83%, 186.3 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.69 (d, 2H, *J*= 3.2 Hz), 6.48 (dt, 1H, J_1= 19.0 Hz, J_2=3.3 Hz), 7.09-7.15 (m, 2H), 7.20-7.27 (m, 3H), 7.35-7.43 (m, 3H), 7.61-7.63 (m, 2H), **^{13}C** NMR (100 MHz, $CDCl_3$) δ 21.3, 119.0, 123.9, 127.4, 128.1, 128.5, 129.4, 129.8, 131.7, 135.5, 137.7, 138.2, 149.5; **IR** (film): 3066, 2135, 1594 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{15}H_{17}Si^+$ $[M+H]^+$ 225.1095, found: 225.1096.

2v: (*E*)-(4-methoxystyryl)(phenyl)silane



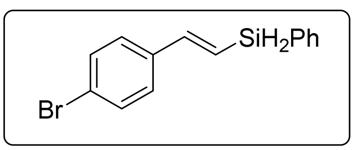
colorless liquid (84%, 201.9 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 4.78 (d, 2H, *J*= 3.2 Hz), 6.41 (dt, 1H, J_1= 19.0 Hz, J_2=3.2 Hz), 6.94-6.96 (m, 2H), 7.19 (d, 1H, *J*= 19.0 Hz), 7.40-7.51 (m, 5H), 7.70-7.72 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 55.2, 113.9, 116.2, 128.0, 128.0, 129.7, 130.7, 131.9, 135.4, 148.8, 160.0; **IR** (film): 3069, 2132, 1606 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{15}H_{17}OSi^{+}$ $[M+H]^{+}$ 241.1044, found: 241.1043.

2w: (*E*)-(4-ethynylstyryl)(phenyl)silane



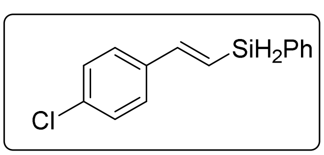
colorless liquid (45%, 105.5 mg); **^{1}H** NMR (500 MHz, $CDCl_3$) δ 3.12 (s, 1H), 4.69 (d, 2H, *J*= 3.2 Hz), 6.53 (dt, 1H, J_1= 19.0 Hz, J_2=3.2 Hz), 7.11 (d, 1H, *J*= 18.9 Hz), 7.37-7.46 (m, 7H), 7.61-7.62 (m ,2H); **^{13}C** NMR (125 MHz, $CDCl_3$) δ 78.2, 83.6, 121.2, 122.2, 126.6, 128.2, 129.9, 131.3, 132.4, 135.5, 138.0, 148.3; **IR** (film): 3301, 2137, 1601 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{16}H_{15}Si^{+}$ $[M+H]^{+}$ 235.0938, found: 235.0935.

2x: (*E*)-(4-bromostyryl)(phenyl)silane



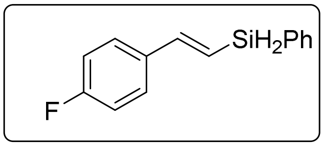
colorless liquid (66%, 190.9 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 4.68 (d, 2H, *J*= 3.2 Hz), 6.49 (dt, 1H, J_1= 19.0 Hz, J_2=3.2 Hz), 7.06 (d, 1H, *J*= 19.0 Hz), 7.29-7.30 (m, 2H), 7.36-7.42 (m, 3H), 7.44-7.46 (m, 2H), 7.60-7.62 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 120.6, 122.6, 128.1, 128.1, 129.9, 131.3, 131.7, 135.5, 136.6, 147.8; **IR** (film): 3065, 2134, 1608 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{14}H_{14}BrSi^{+}$ $[M+H]^{+}$ 289.0043, 291.0023 found: 289.0042, 291.0022.

2y: (*E*)-(4-chlorostyryl)(phenyl)silane



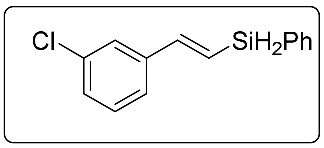
colorless liquid (63%, 154.2 mg); **^{1}H** NMR (500 MHz, $CDCl_3$) δ 4.69 (d, 2H, *J*= 3.0 Hz), 6.48 (dt, 1H, J_1= 18.9 Hz, J_2=3.1 Hz), 7.08 (d, 1H, *J*= 18.5 Hz), 7.29-7.31 (m, 2H), 7.36-7.42 (m, 5H), 7.61-7.62 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 120.4, 127.9, 128.2, 128.8, 129.9, 131.4, 134.4, 135.5, 136.2, 147.8; **IR** (film): 3067, 2134, 1610 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{14}H_{14}ClSi^{+}$ $[M+H]^{+}$ 245.0548, found: 245.0549.

2z: (*E*)-(4-fluorostyryl)(phenyl)silane



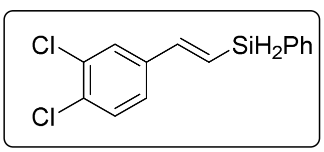
colorless liquid (60%, 137.0 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 4.69 (d, 2H, *J*= 3.3 Hz), 6.41 (dt, 1H, J_1= 18.9 Hz, J_2=3.2 Hz), 7.00-7.04 (m, 2H), 7.10 (d, 1H, *J*= 18.8 Hz), 7.34-7.44 (m, 5H), 7.61-7.63 (m, 2H); **^{13}C** NMR (125 MHz, $CDCl_3$) δ 115.5 (d, *J*= 22.1 Hz), 119.2 (d, *J*= 2.0 Hz), 128.2, 128.3 (d, *J*= 8.2 Hz), 129.9, 131.5, 134.1, 135.5, 148.0, 163.0 (d, *J*= 248.8 Hz); **IR** (film): 3068, 2137, 1600 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{14}H_{14}FSi^+$ $[M+H]^+$ 229.0844, found: 229.0846.

2aa: (*E*)-(3-chlorostyryl)(phenyl)silane



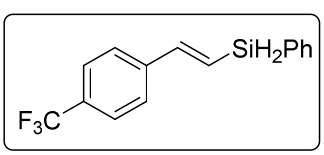
colorless liquid (68%, 166.5 mg); **^{1}H** NMR (500 MHz, $CDCl_3$) δ 4.69 (d, 2H, *J*= 3.1 Hz), 6.53 (dt, 1H, J_1= 18.9 Hz, J_2=3.2 Hz), 7.07 (d, 1H, *J*= 18.9 Hz), 7.25-7.31 (m, 3H), 7.37-7.43 (m, 4H), 7.60-7.62 (m, 2H); **^{13}C** NMR (125 MHz, $CDCl_3$) δ 121.6, 124.9, 126.6, 128.2, 128.5, 129.8, 130.0, 131.2, 134.7, 135.5, 139.6, 147.6; **IR** (film): 3068, 2138, 1591 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{14}H_{14}ClSi^+$ $[M+H]^+$ 245.0548, found: 245.0547.

2ab: (*E*)-(3,4-dichlorostyryl)(phenyl)silane



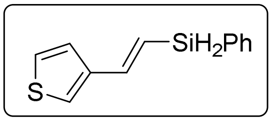
colorless liquid (42%, 117.3 mg); **^{1}H** NMR (500 MHz, $CDCl_3$) δ 4.68 (d, 2H, *J*= 3.1 Hz), 6.51 (dt, 1H, J_1= 18.9 Hz, J_2=3.0 Hz), 7.02 (d, 1H, *J*= 19.0 Hz), 7.25-7.27 (m, 1H), 7.38-7.43 (m, 4H), 7.51-7.52 (m, 1H), 7.60-7.61 (m, 2H); **^{13}C** NMR (125 MHz, $CDCl_3$) δ 122.4, 125.8, 128.2, 128.4, 130.0, 130.5, 131.0, 132.4, 132.9, 135.5, 137.8, 146.4; **IR** (film): 3064, 2140, 1616 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{14}H_{13}Cl_2Si^+$ $[M+H]^+$ 279.0159, 281.0129, found: 279.0160, 281.0131.

2ac: (*E*)-phenyl(4-(trifluoromethyl)styryl)silane



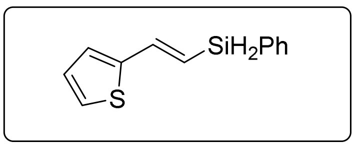
colorless liquid (47%, 130.8 mg); **^{1}H** NMR (500 MHz, $CDCl_3$) δ 4.71 (d, 2H, *J*= 3.1 Hz), 6.63 (dt, 1H, J_1= 19.0 Hz, J_2=3.1 Hz), 7.16 (d, 1H, *J*= 18.7 Hz), 7.38-7.43 (m, 3H), 7.52-7.53 (m, 2H), 7.58-7.59 (m, 2H), 7.61-7.63 (m, 2H); **^{13}C** NMR (125 MHz, $CDCl_3$) δ 123.2, 124.1 (q, *J*= 272.1 Hz), 125.6 (q, *J*= 3.7 Hz), 126.8, 128.2, 130.0, 130.3 (q, *J*= 32.6 Hz), 131.0, 135.5, 141.0,147.6; **IR** (film): 3068, 2141, 1614 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{15}H_{14}F_3Si^+$ $[M+H]^+$ 279.0812, found: 279.0810.

2ad: (*E*)-phenyl(2-(thiophen-3-yl)vinyl)silane



colorless liquid (74%, 160.1 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 4.67 (d, 2H, *J*= 3.2 Hz), 6.27 (dt, 1H, J_1= 18.9 Hz, J_2=3.2 Hz), 7.13 (d, 1H, *J*= 19.0 Hz), 7.22-7.29 (m, 3H), 7.35-7.41 (m, 3H), 7.60-7.62 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 118.9, 123.9, 124.9, 126.1, 128.1, 129.8, 131.6, 135.5, 141.5, 142.9; **IR** (film): 3069, 2134, 1604 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{12}H_{13}SSi^+$ $[M+H]^+$ 217.0502, found: 217.0500.

2ae: (*E*)-phenyl(2-(thiophen-2-yl)vinyl)silane



colorless liquid (75%, 162.3 mg); **^{1}H** NMR (400 MHz, $CDCl_3$) δ 4.76 (d, 2H, *J*= 3.1 Hz), 6.35 (dt, 1H, J_1= 18.9 Hz, J_2=3.1 Hz), 7.21 (d, 1H, *J*= 18.9 Hz), 7.28-7.37 (m, 3H), 7.46-7.50 (m, 3H), 7.69-7.71 (m, 2H); **^{13}C** NMR (100 MHz, $CDCl_3$) δ 118.9, 123.9, 124.8, 126.1, 128.1, 129.8, 131.6, 135.5, 141.5, 142.9; **IR** (film): 3066, 2132, 1605 cm^{-1}; **HRMS** (ESI) m/z Calculated for $C_{12}H_{13}SSi^+$ $[M+H]^+$ 217.0502, found: 217.0501.

Reference:

(6) Takahashi, T.; Bao, F.; Gao, G.; Ogasawara, M. *Org. Lett.,* **2003**, *19*, 3479.
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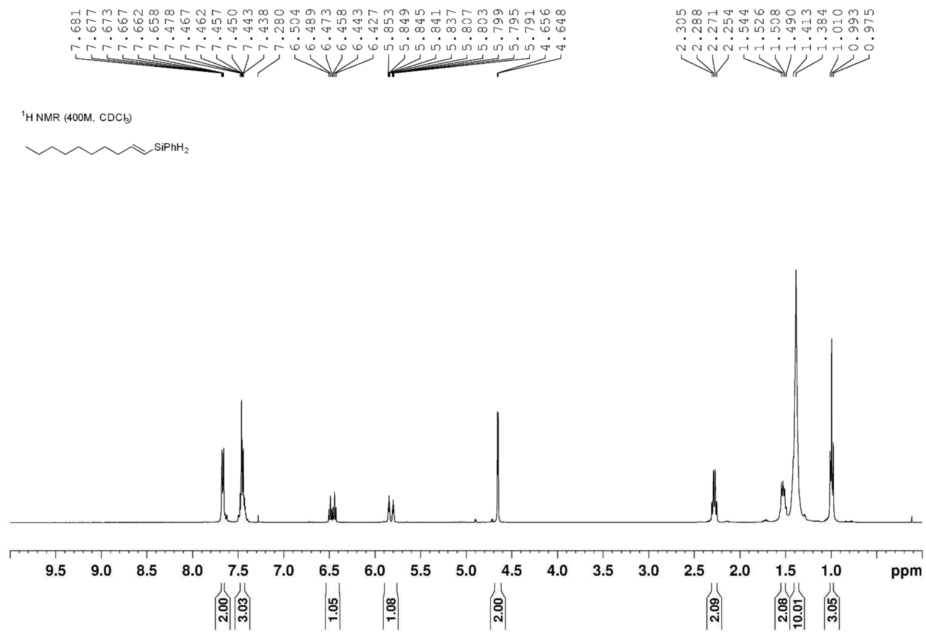
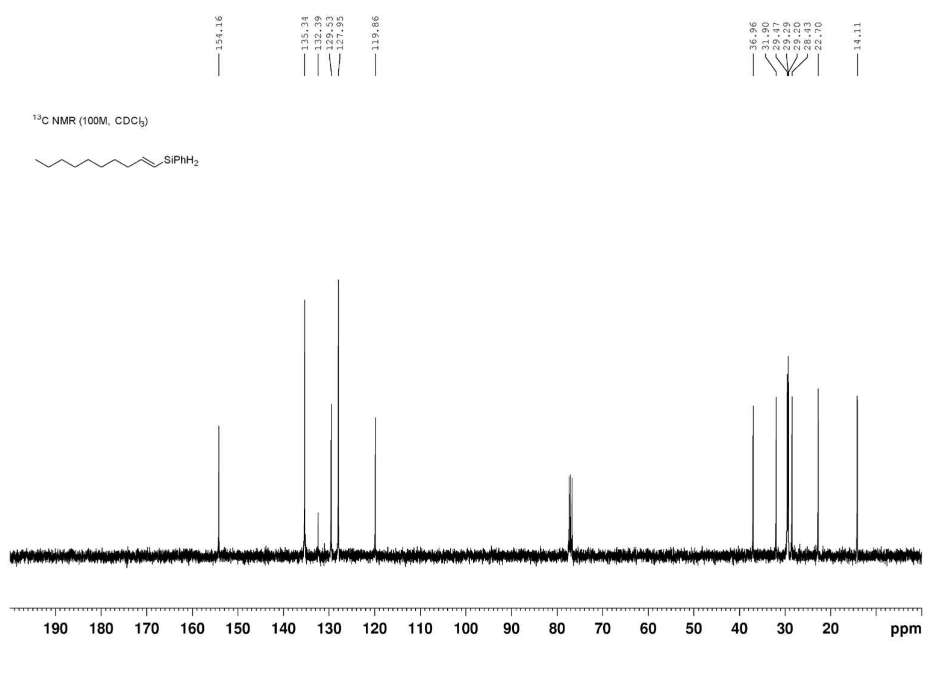
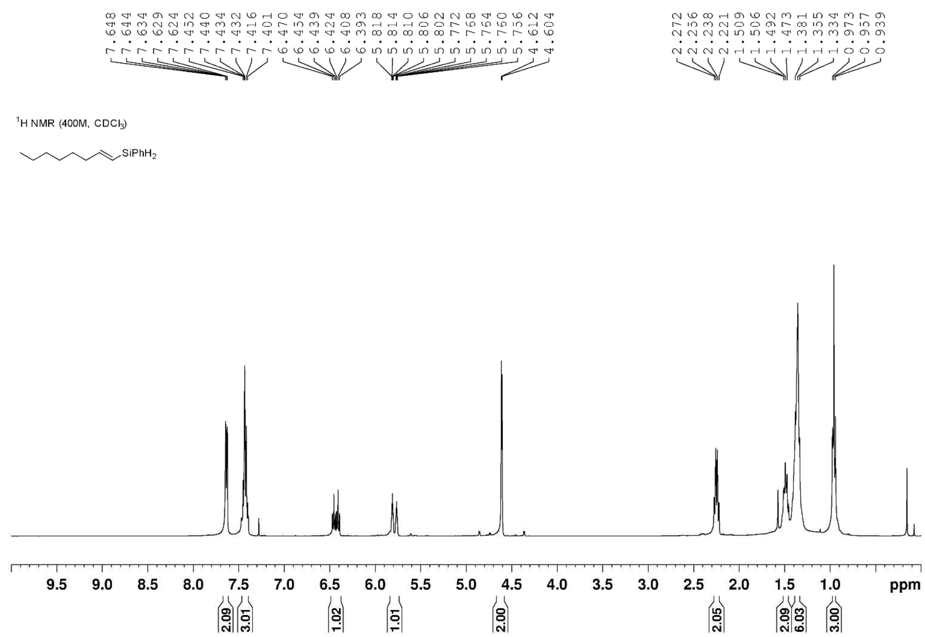
8. ^{1}H, ^{13}C-NMR Spectra of products 2

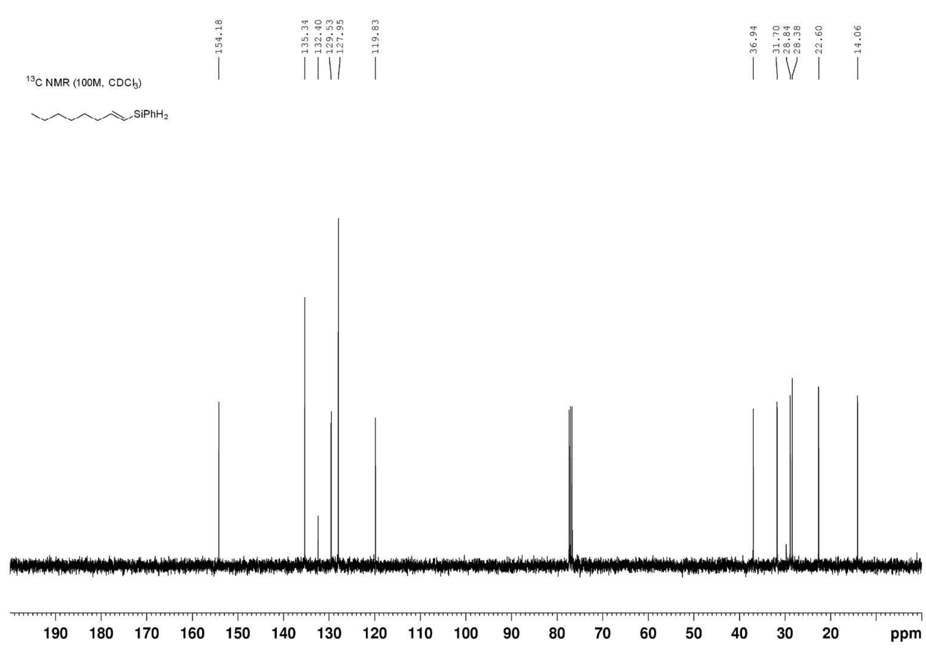
2a: (*E*)-dec-1-en-1-yl(phenyl)silane



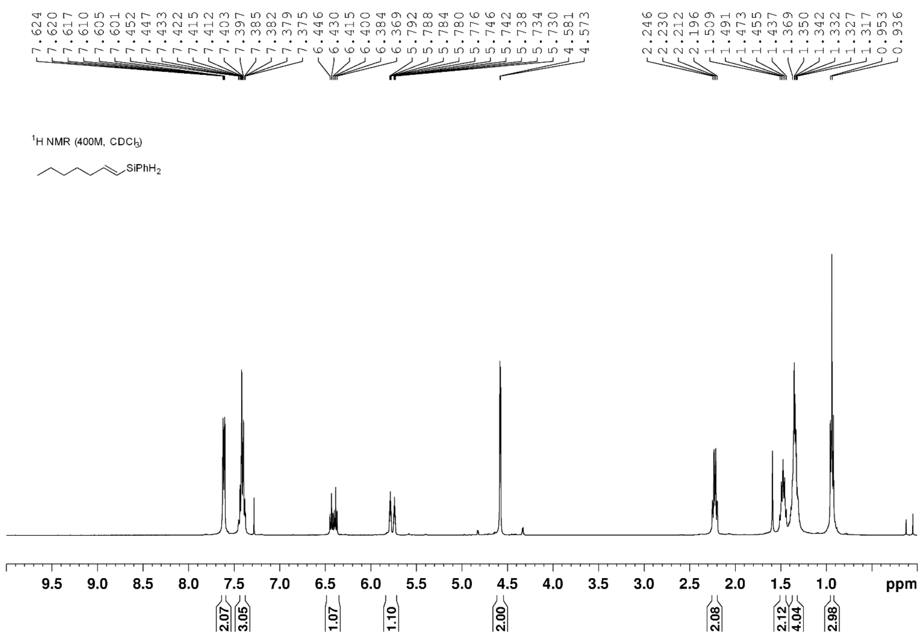


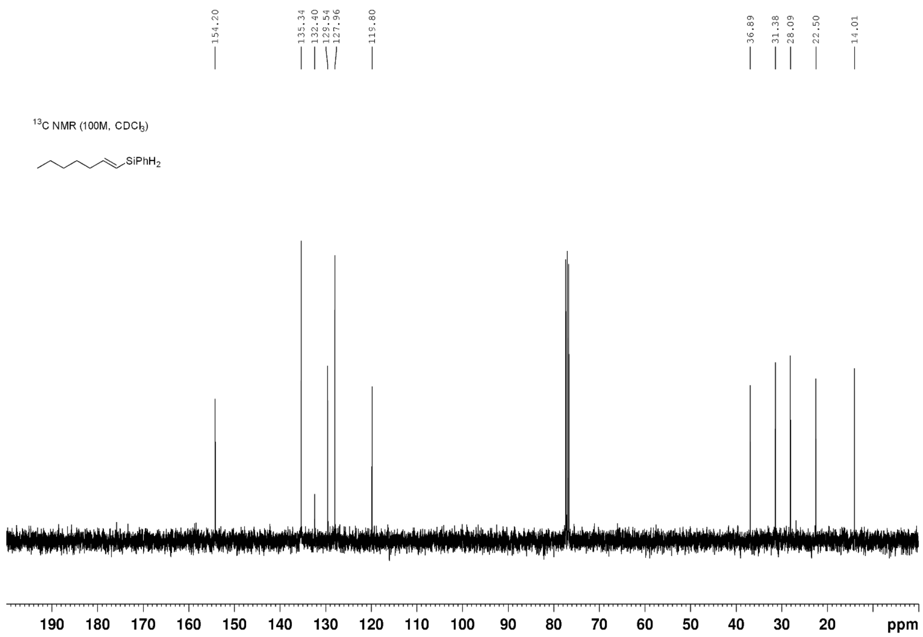
2b: (*E*)-oct-1-en-1-yl(phenyl)silane



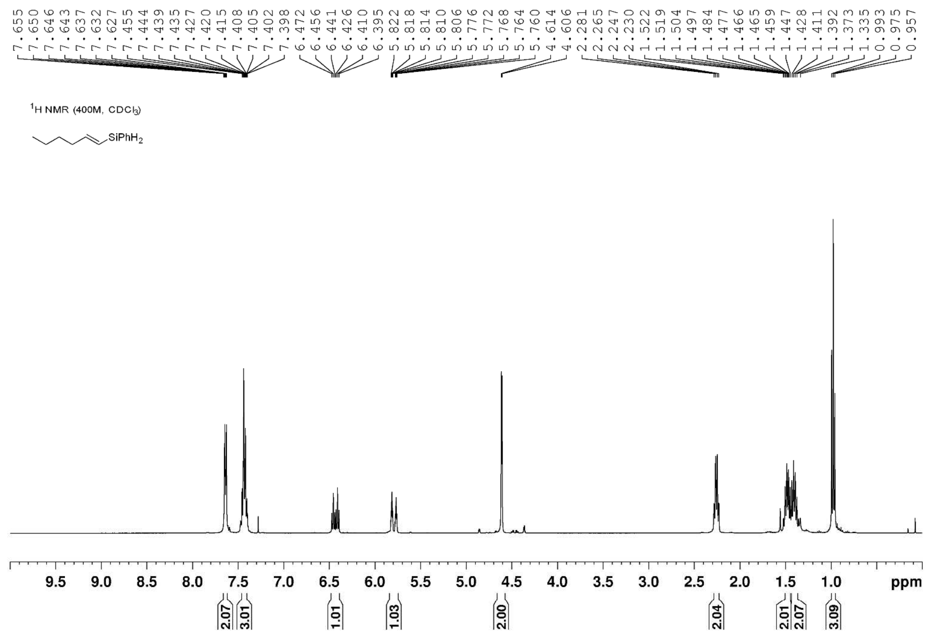


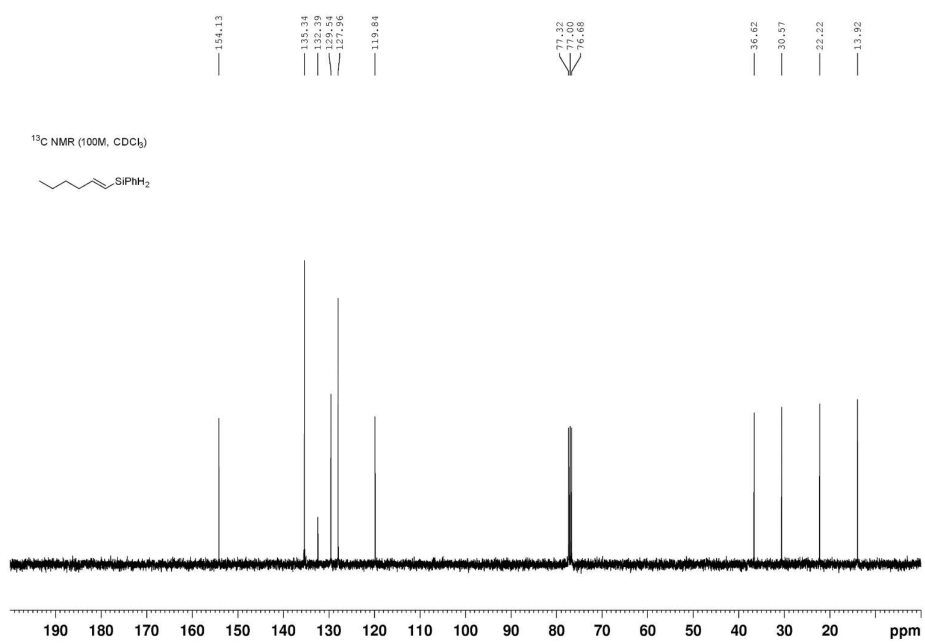
2c: (*E*)-hept-1-en-1-yl(phenyl)silane



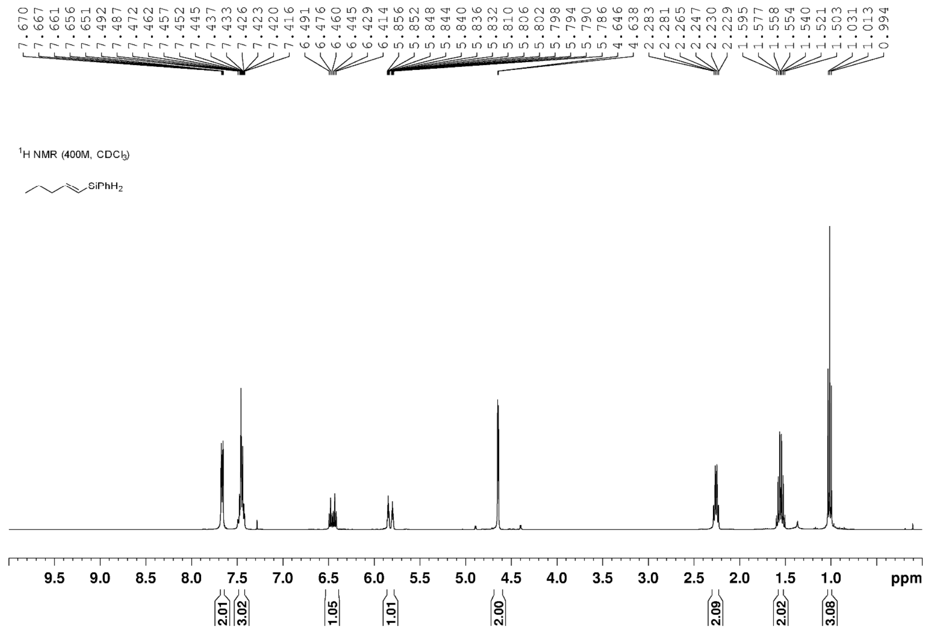


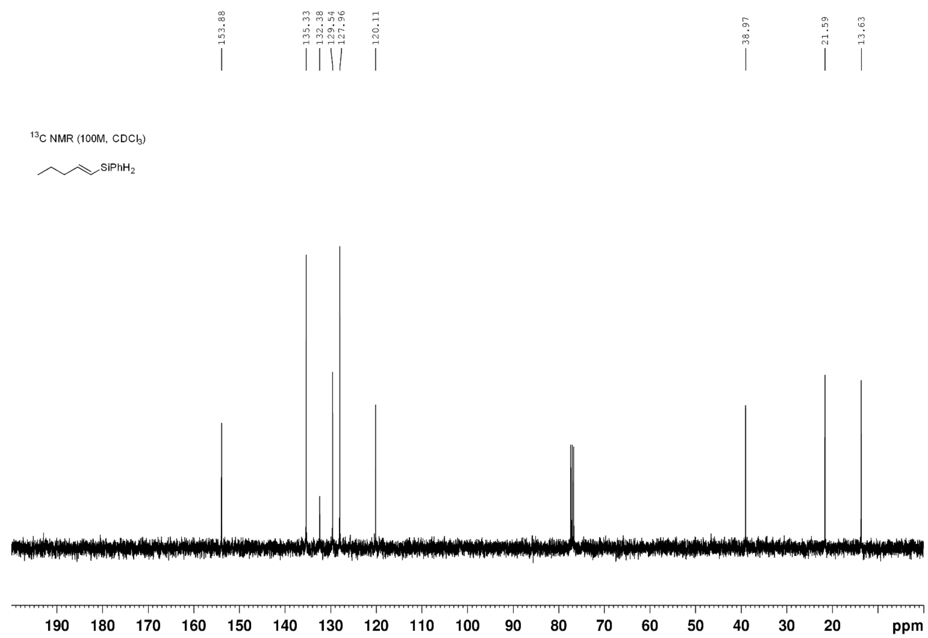
2d: (*E*)-hex-1-en-1-yl(phenyl)silane



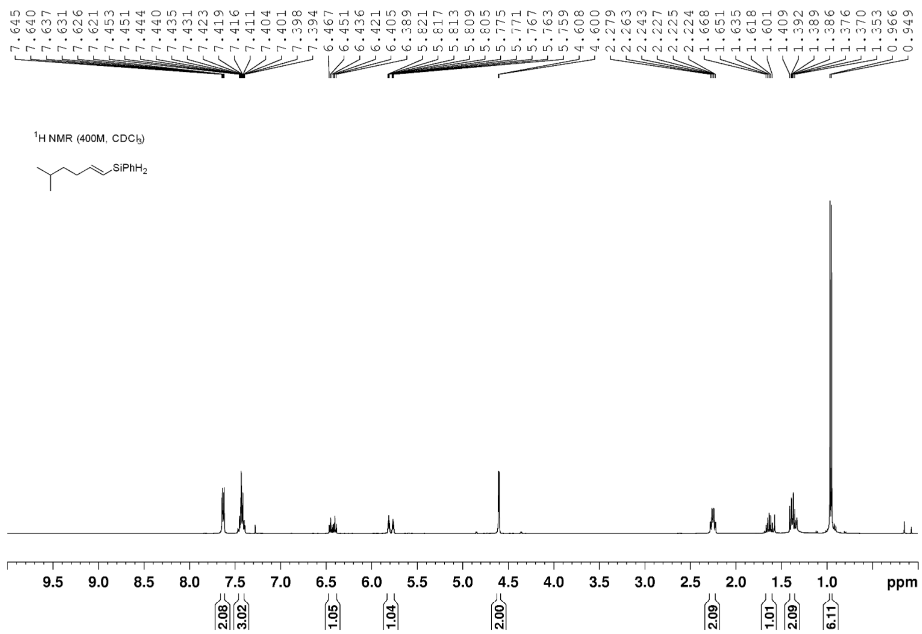


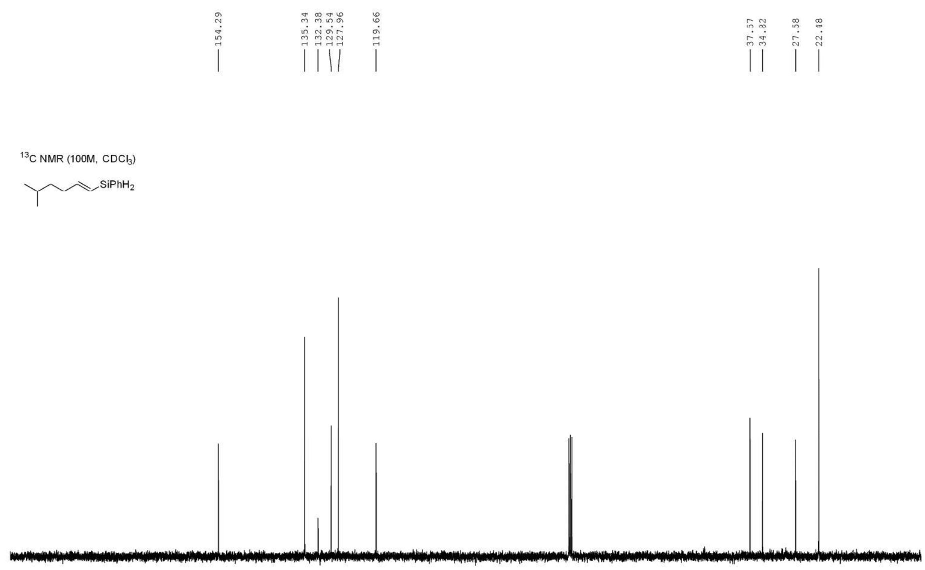
2e: (*E*)-pent-1-en-1-yl(phenyl)silane



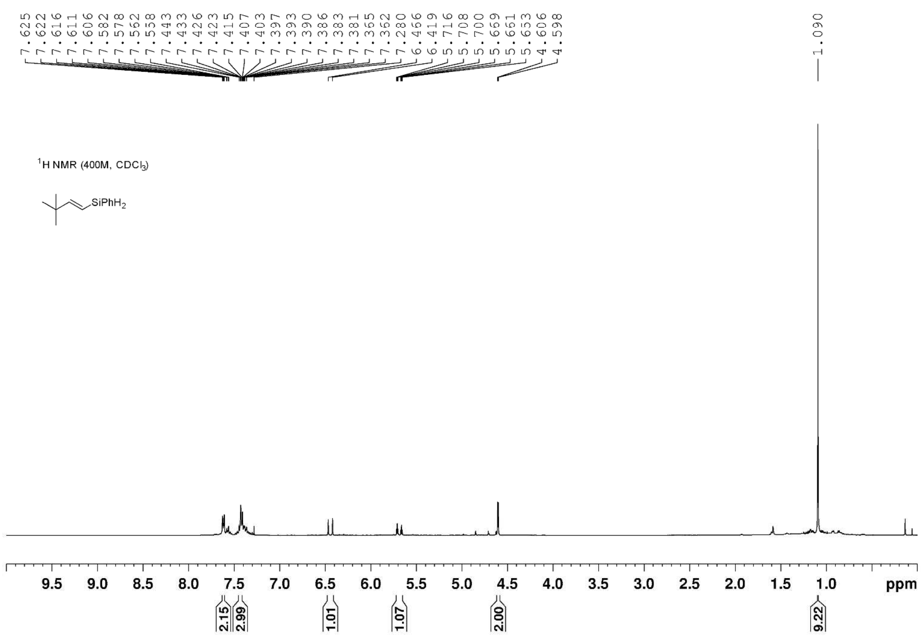


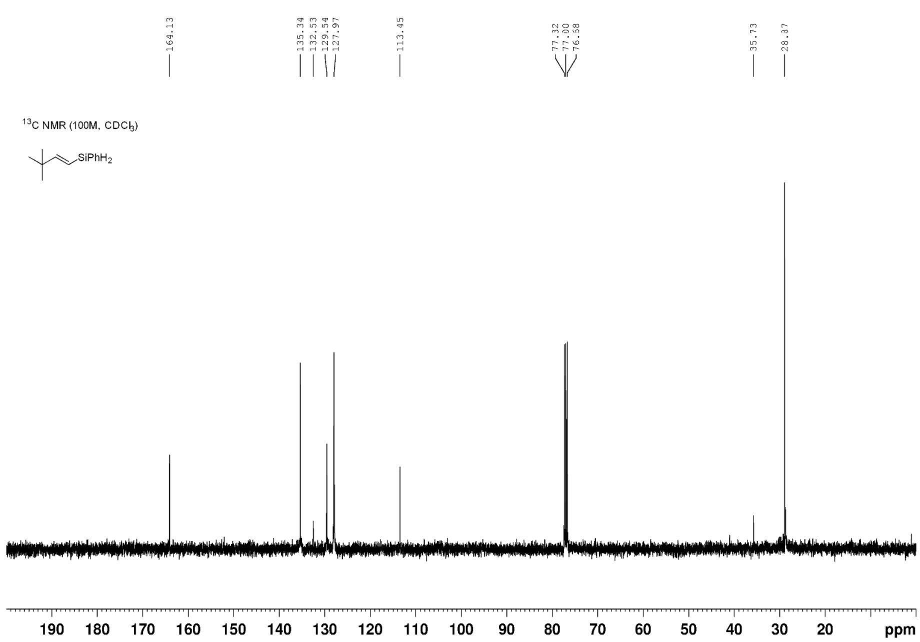
2f: (*E*)-(5-methylhex-1-en-1-yl)(phenyl)silane



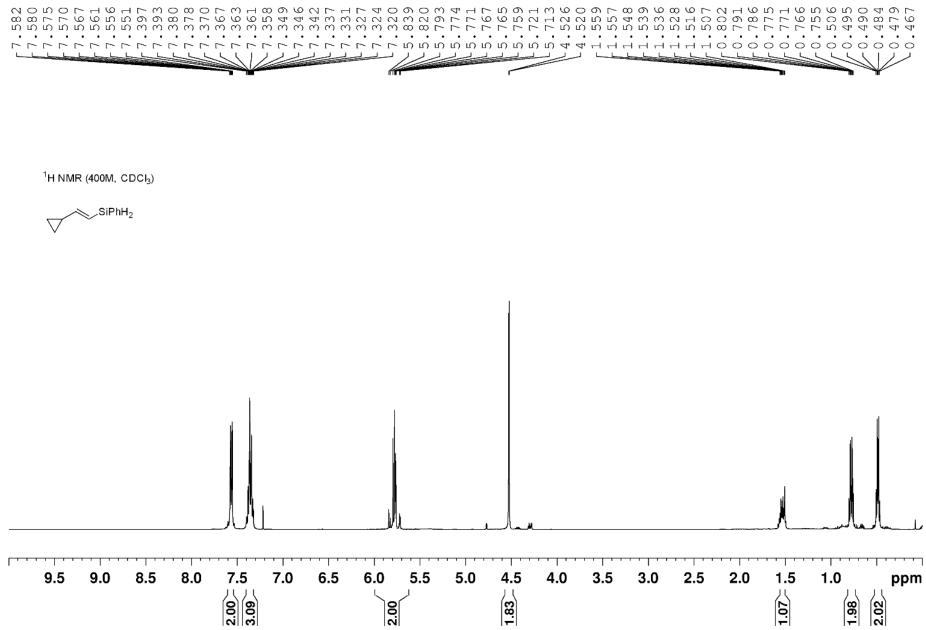


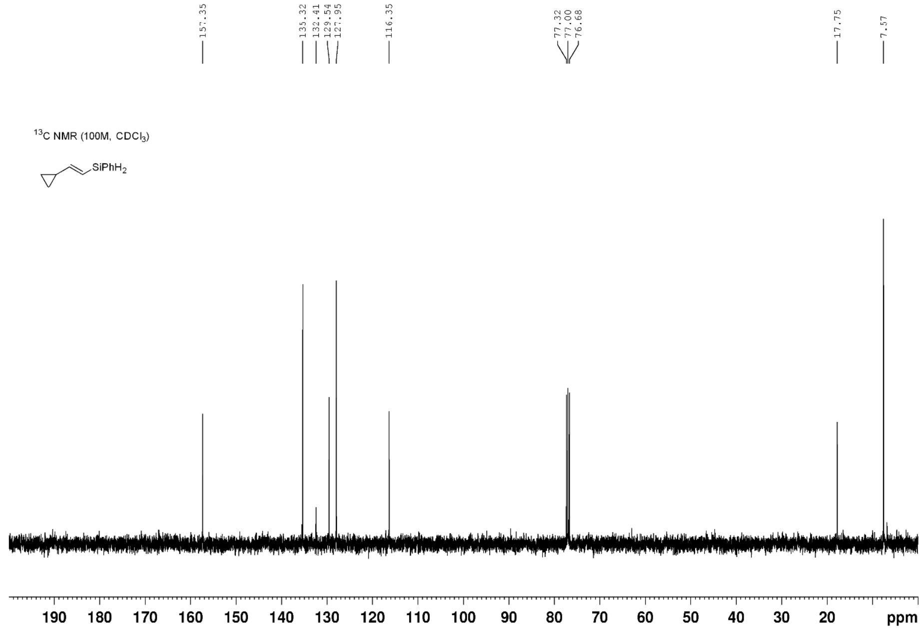
2g: (*E*)-(3,3-dimethylbut-1-en-1-yl)(phenyl)silane



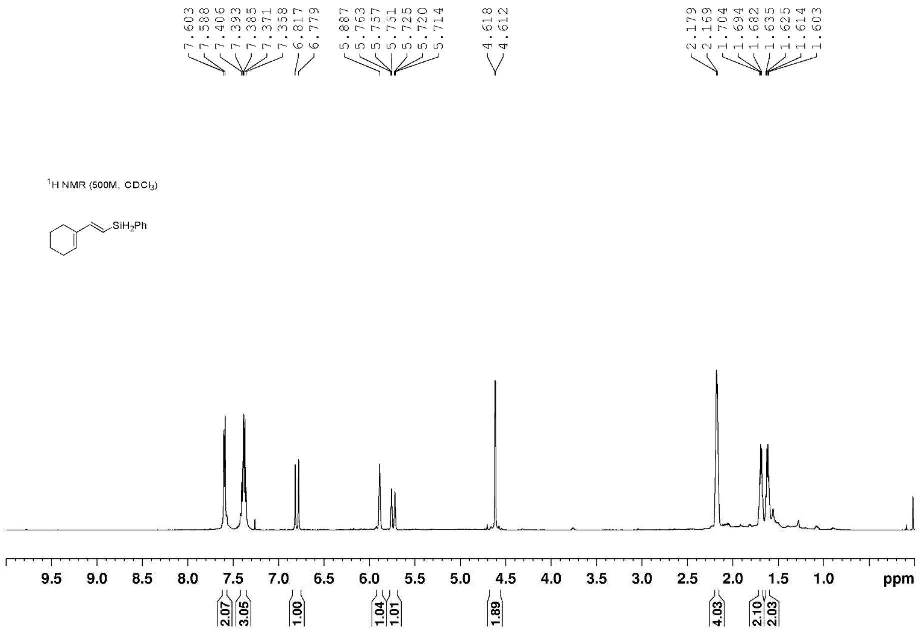


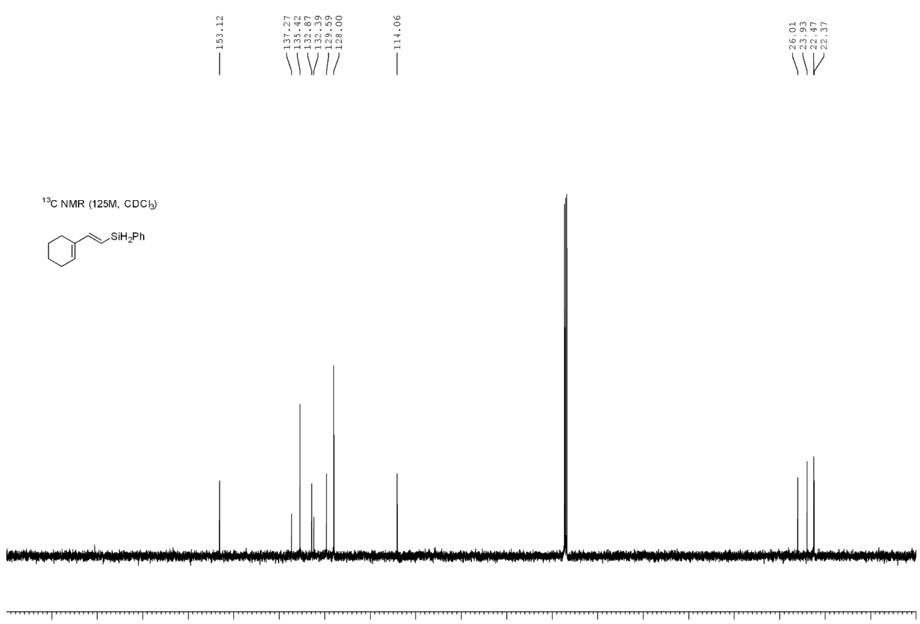
2h: (*E*)-(2-cyclopropylvinyl)(phenyl)silane



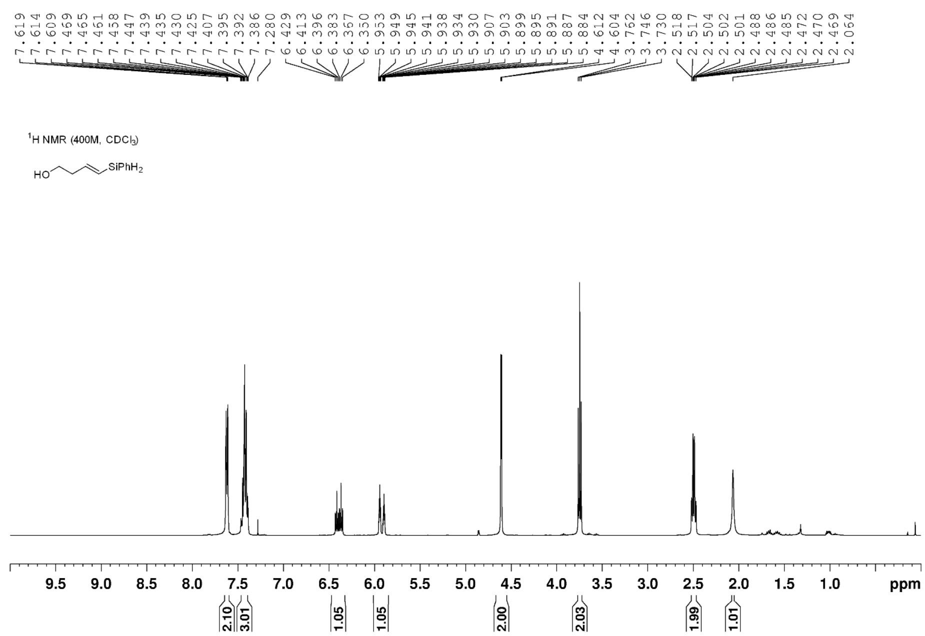


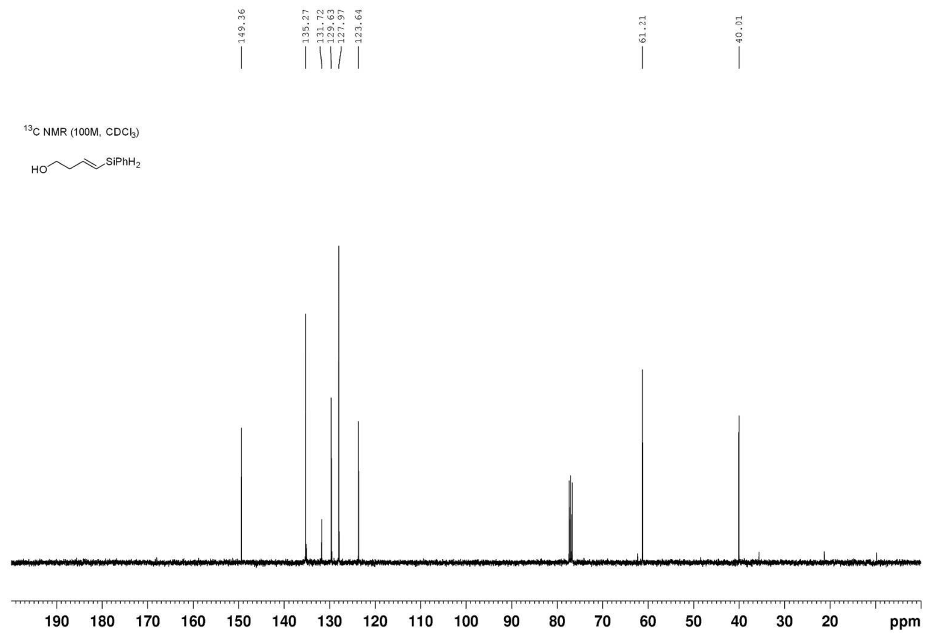
2i: (*E*)-(2-(cyclohex-1-en-1-yl)vinyl)(phenyl)silane



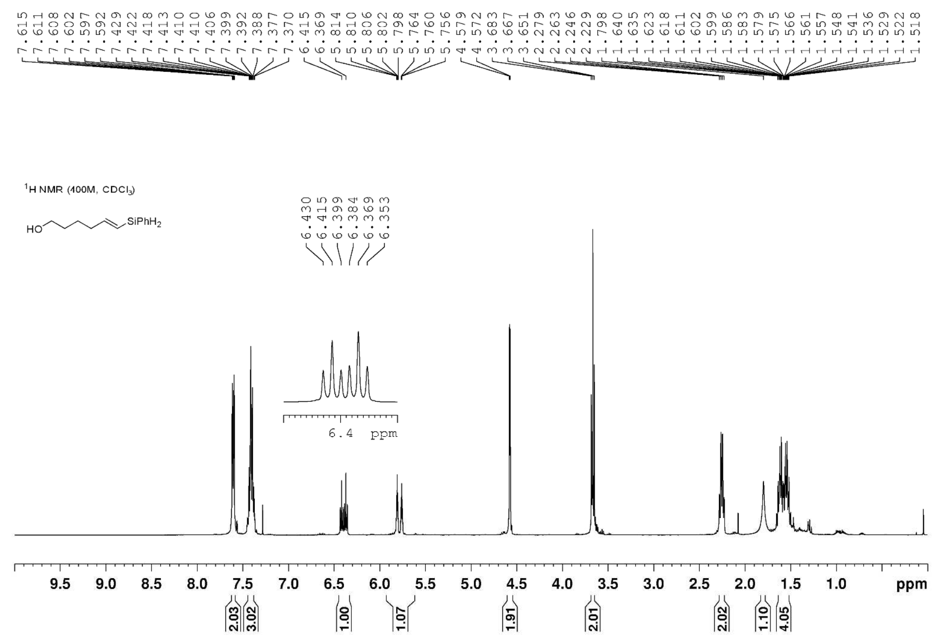


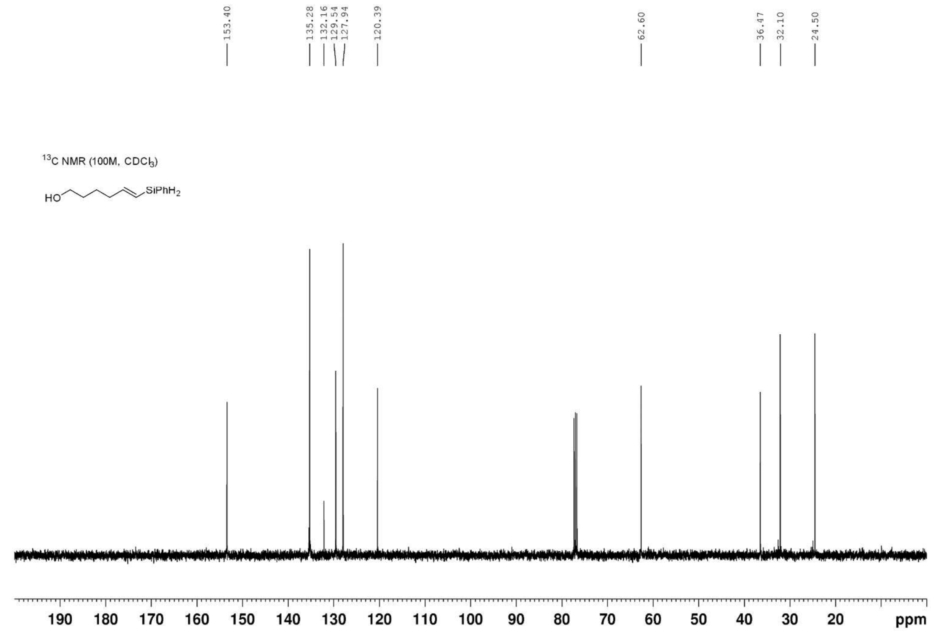
2j: (*E*)-4-(phenylsilyl)but-3-en-1-ol



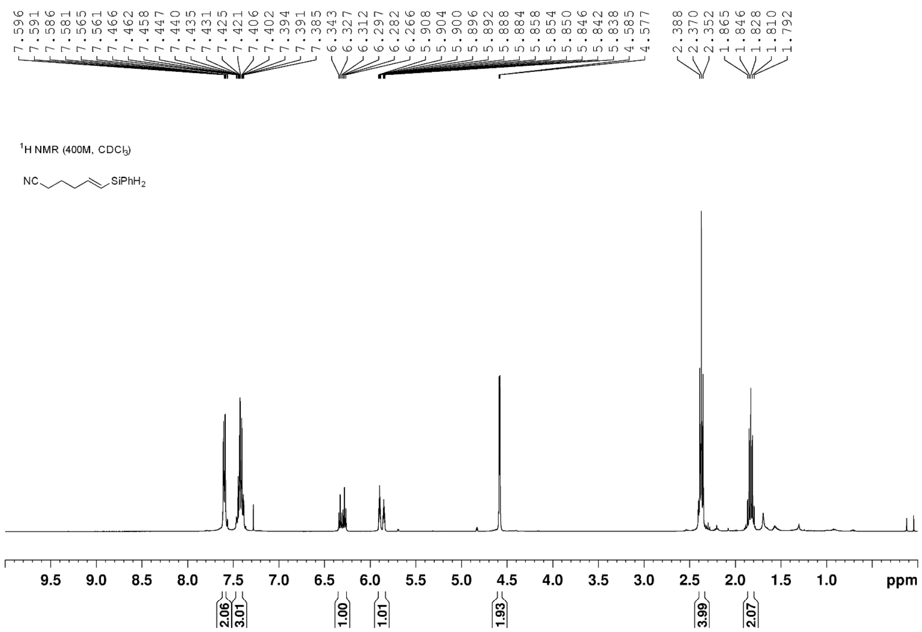


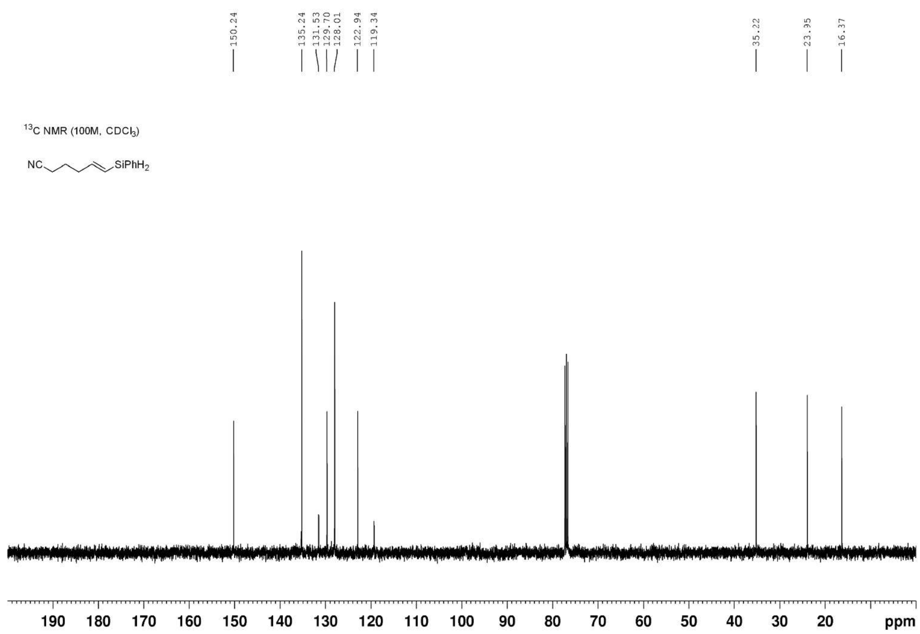
2k: (*E*)-6-(phenylsilyl)hex-5-en-1-ol



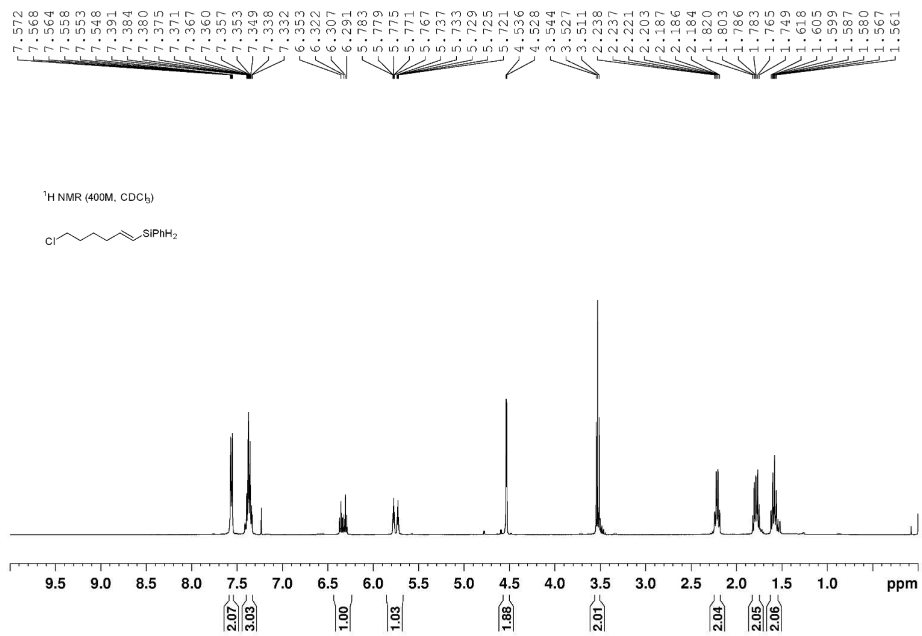


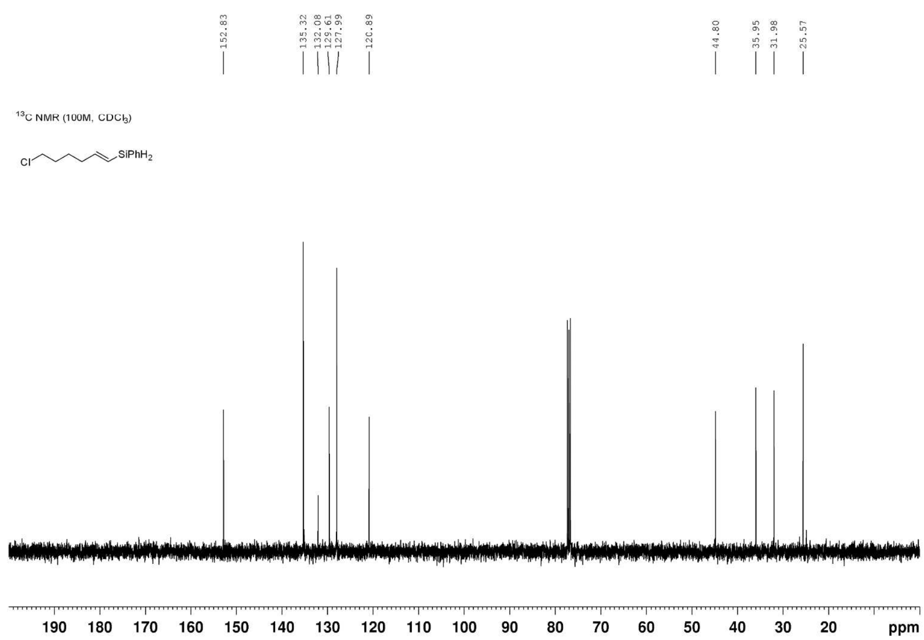
2l: (*E*)-6-(phenylsilyl)hex-5-enenitrile



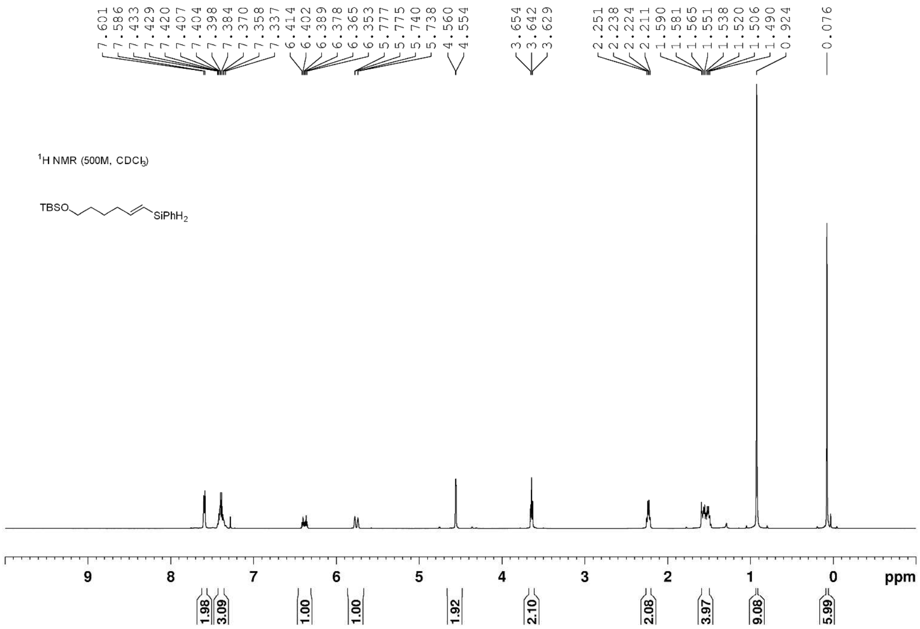


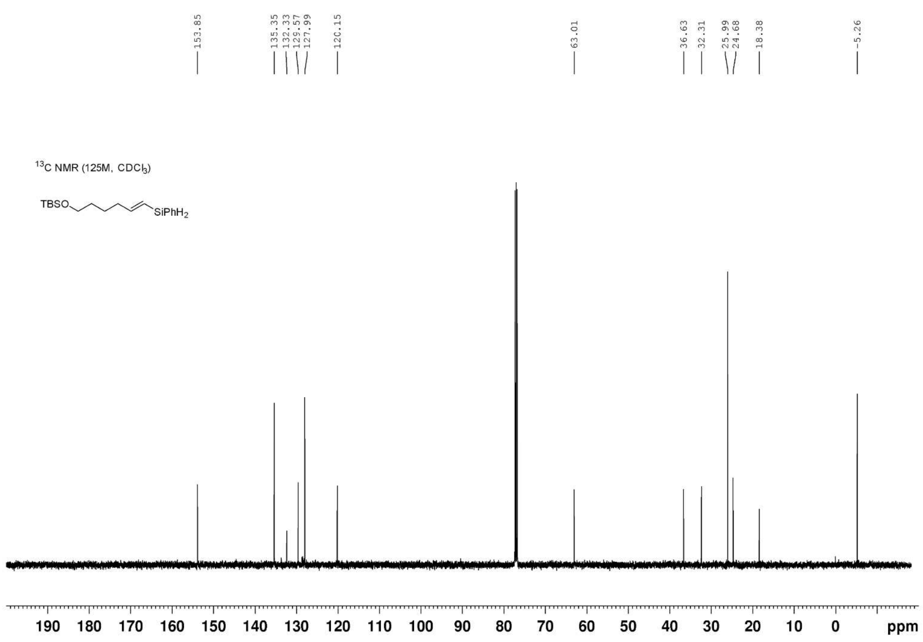
2m: (*E*)-(6-chlorohex-1-en-1-yl)(phenyl)silane



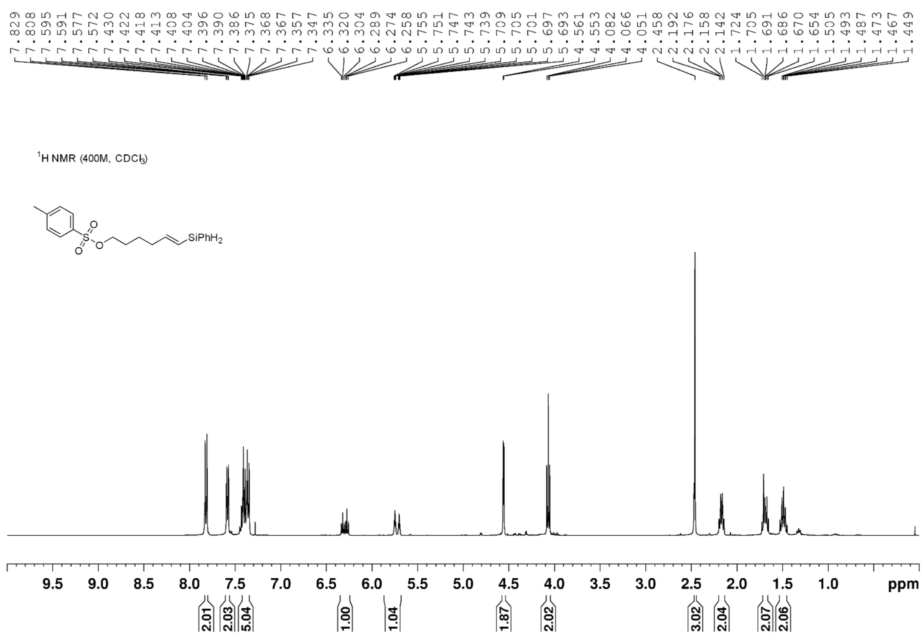


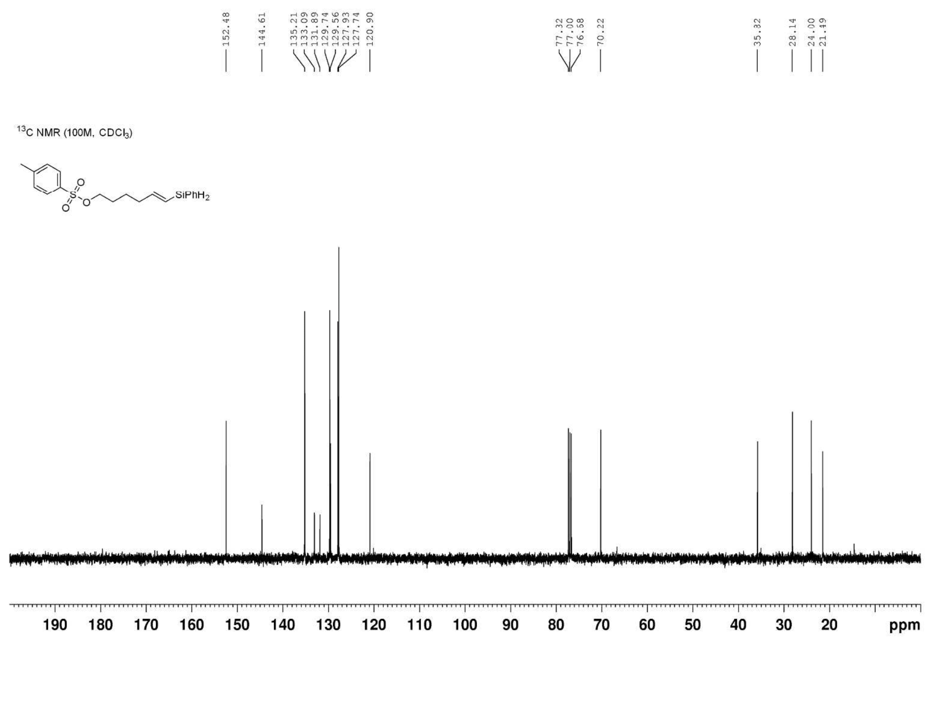
2n: (*E*)-tert-butyldimethyl((6-(phenylsilyl)hex-5-en-1-yl)oxy)silane



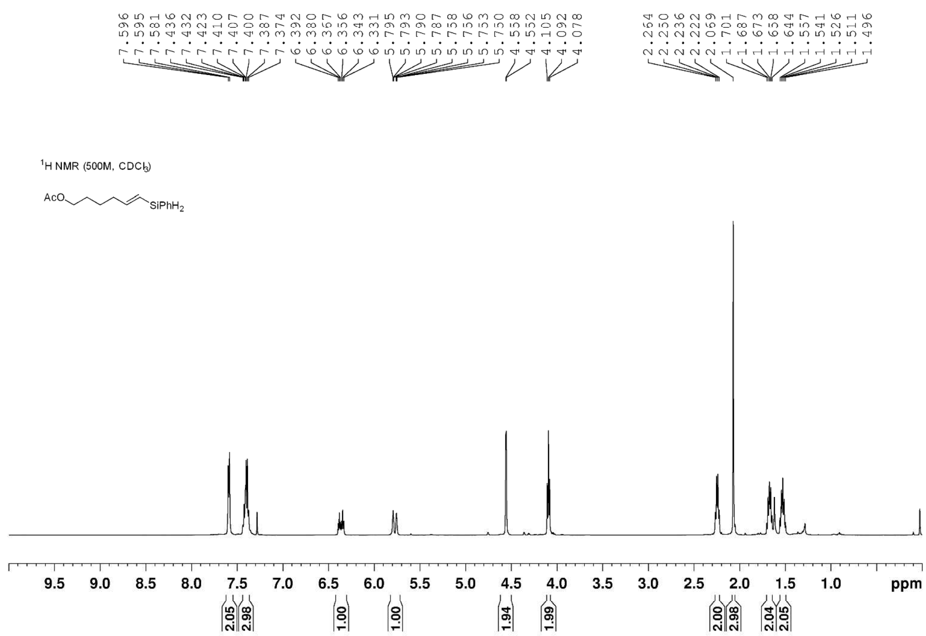


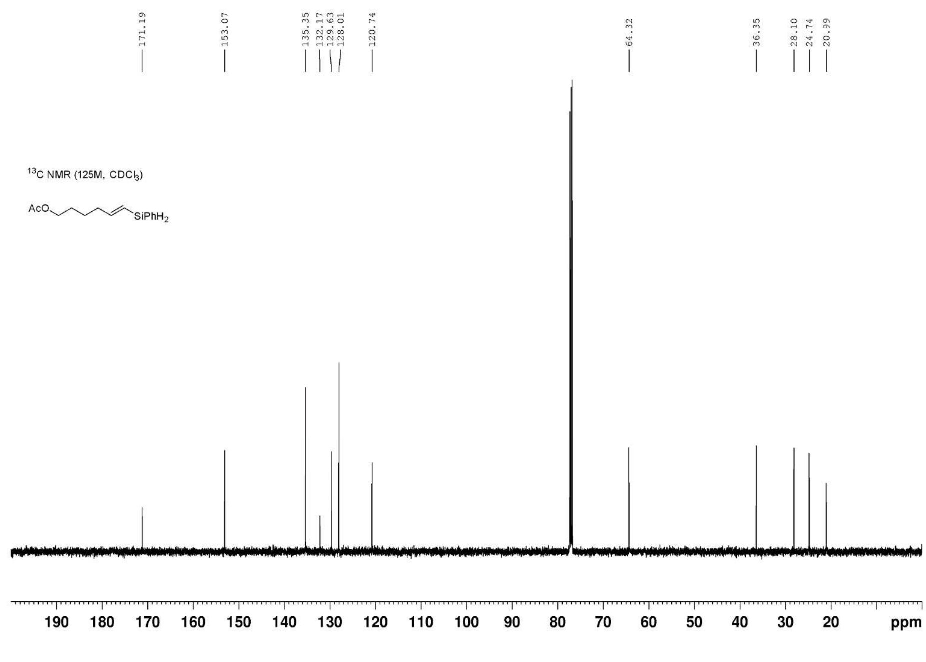
2o: (*E*)-6-(phenylsilyl)hex-5-en-1-yl 4-methylbenzenesulfonate



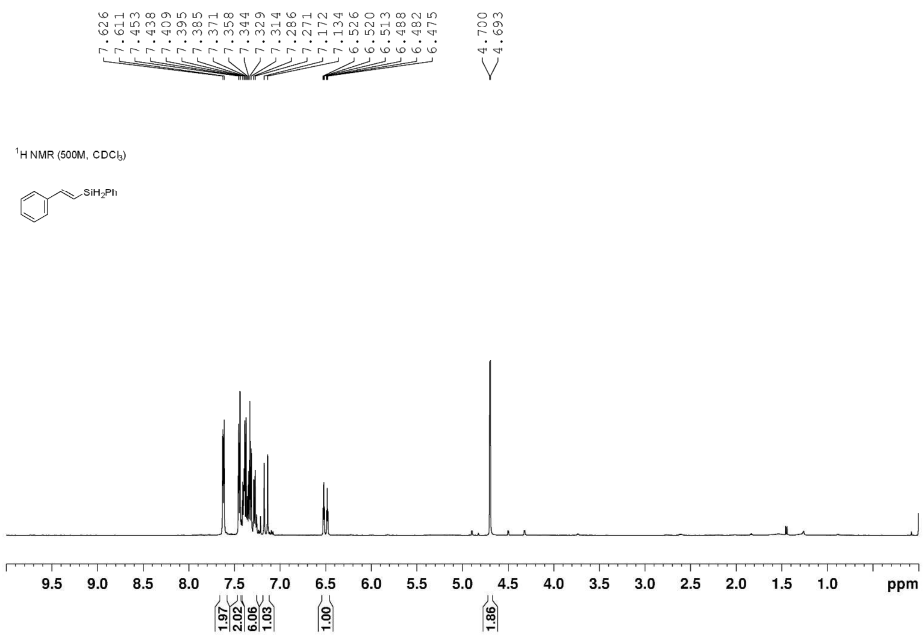


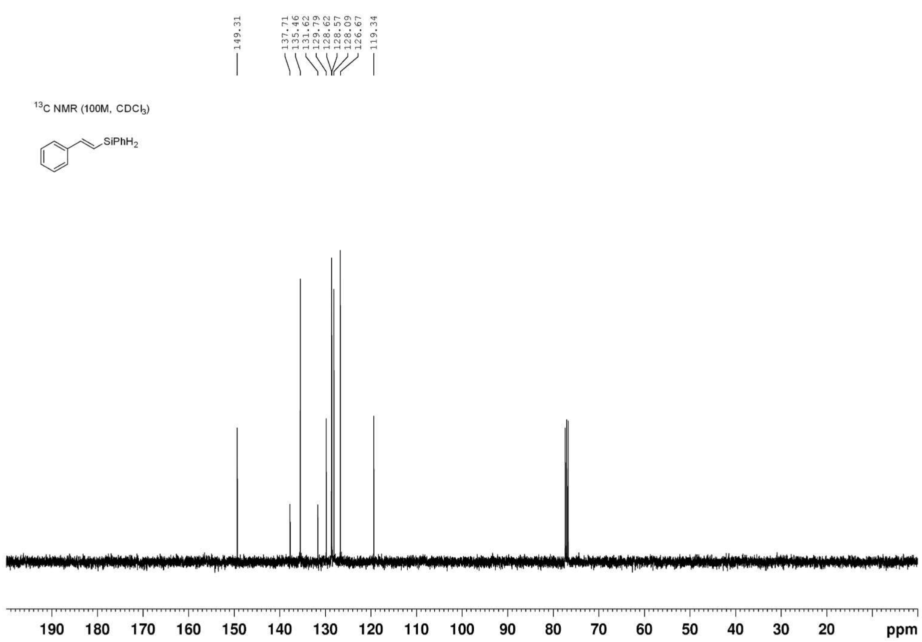
2p: (*E*)-6-(phenylsilyl)hex-5-en-1-yl acetate



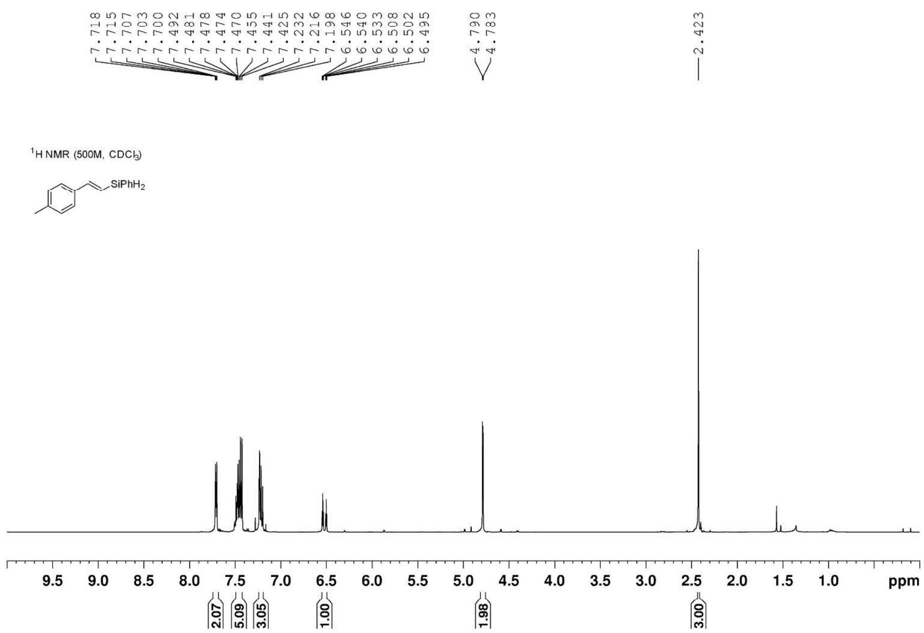


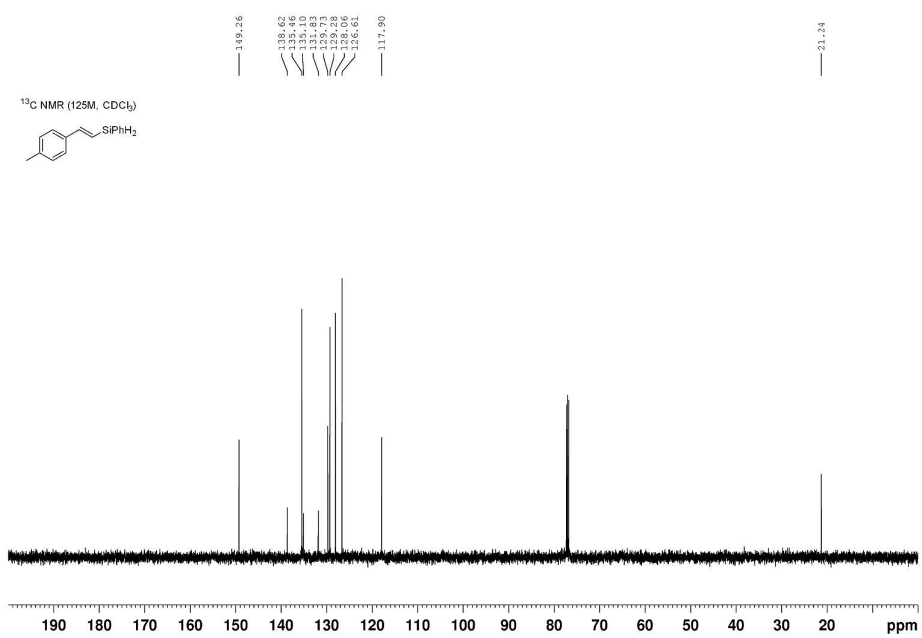
2q: (*E*)-phenyl(styryl)silane



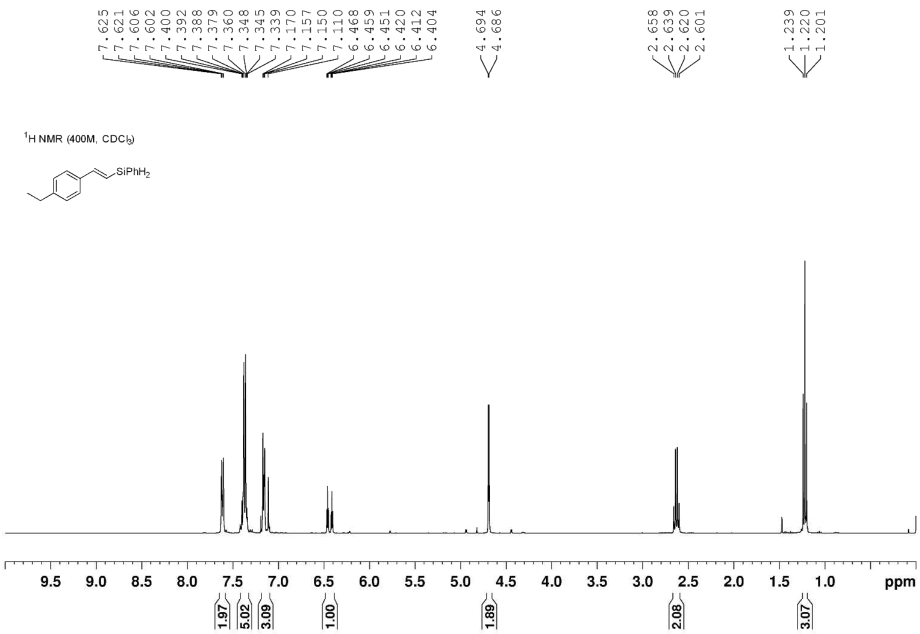


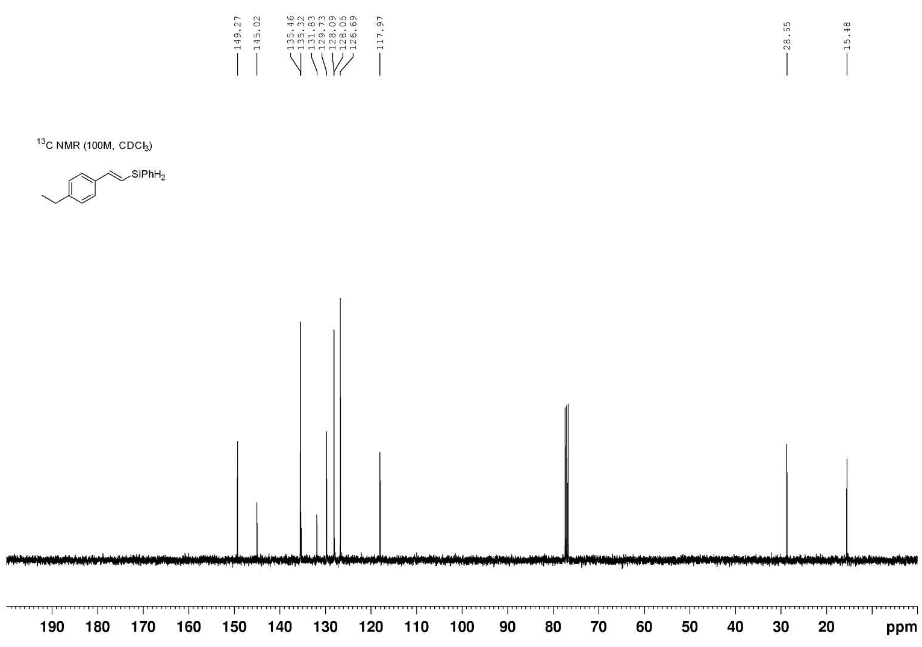
2r: (E)-(4-methylstyryl)(phenyl)silane



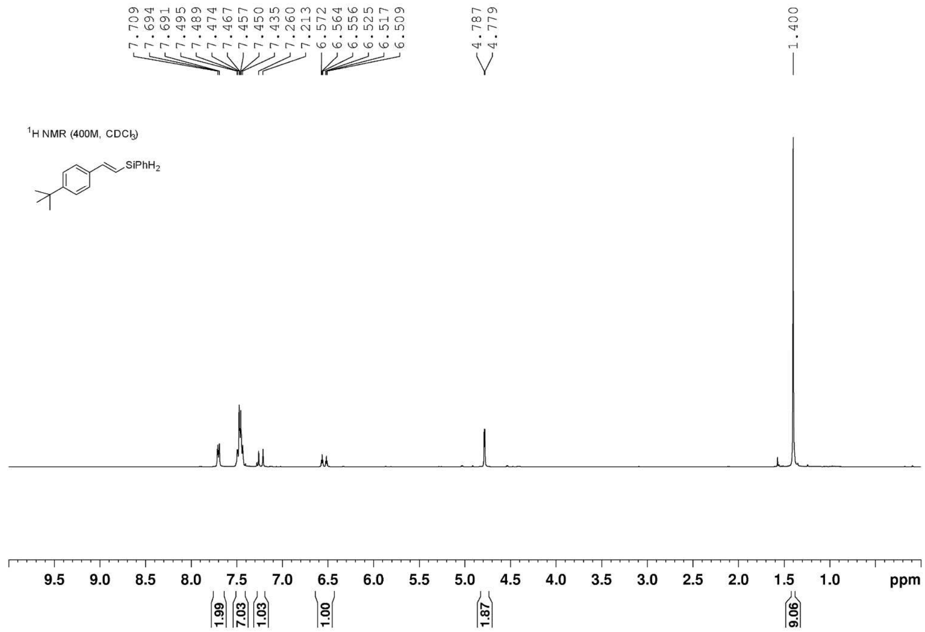


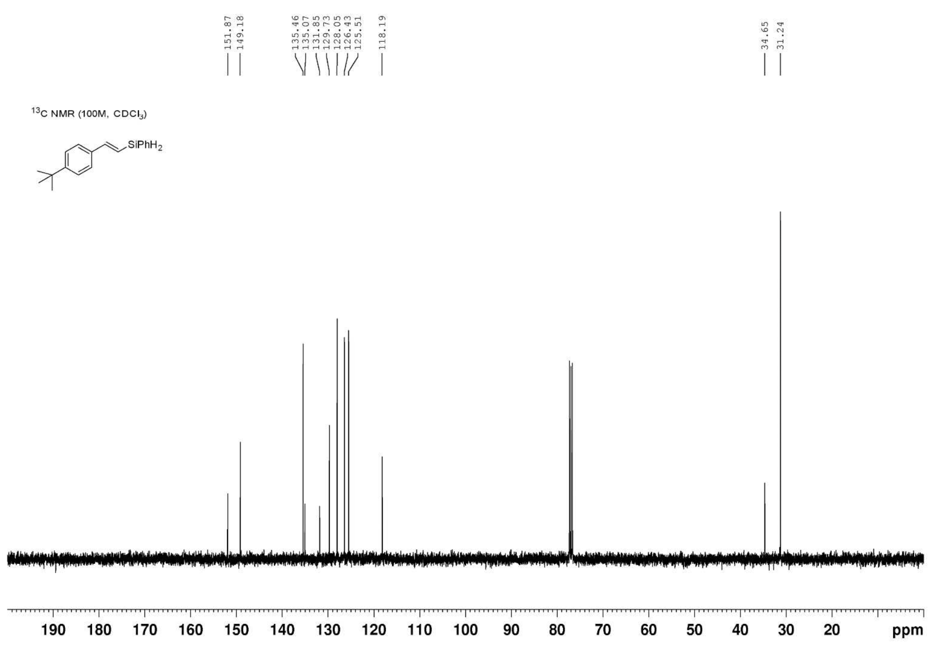
2s: (*E*)-(4-ethylstyryl)(phenyl)silane



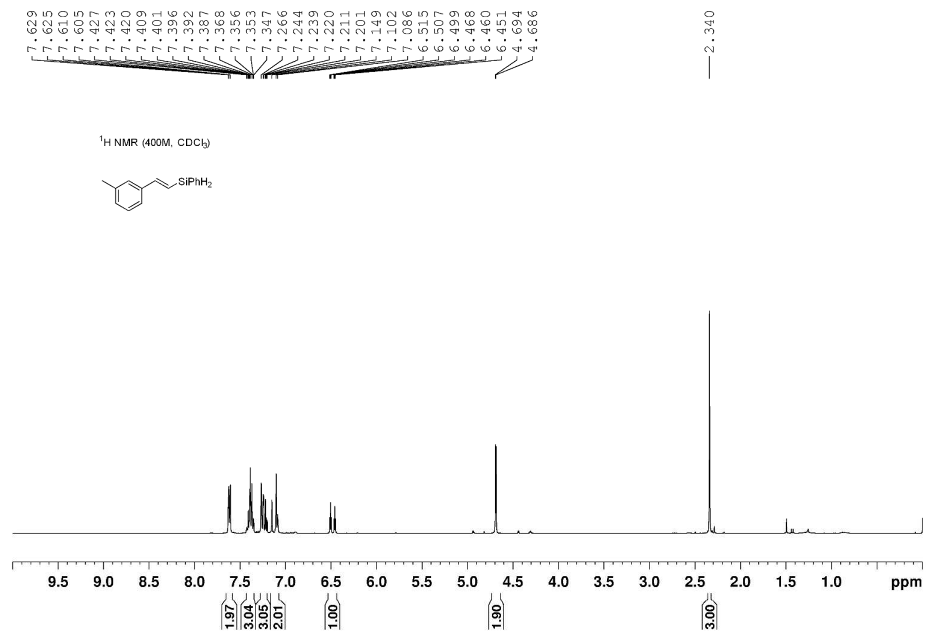


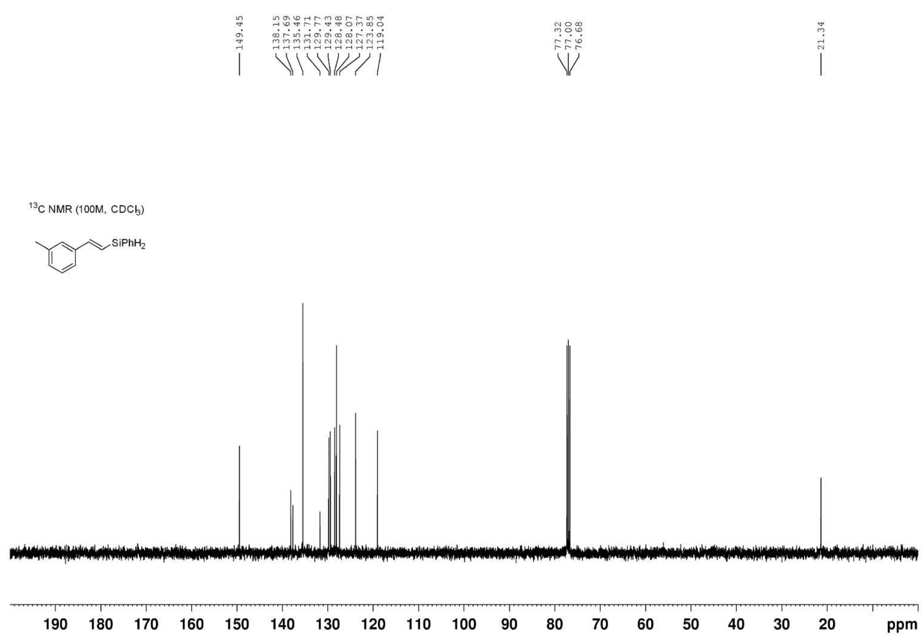
2t: (*E*)-(4-(tert-butyl)styryl)(phenyl)silane



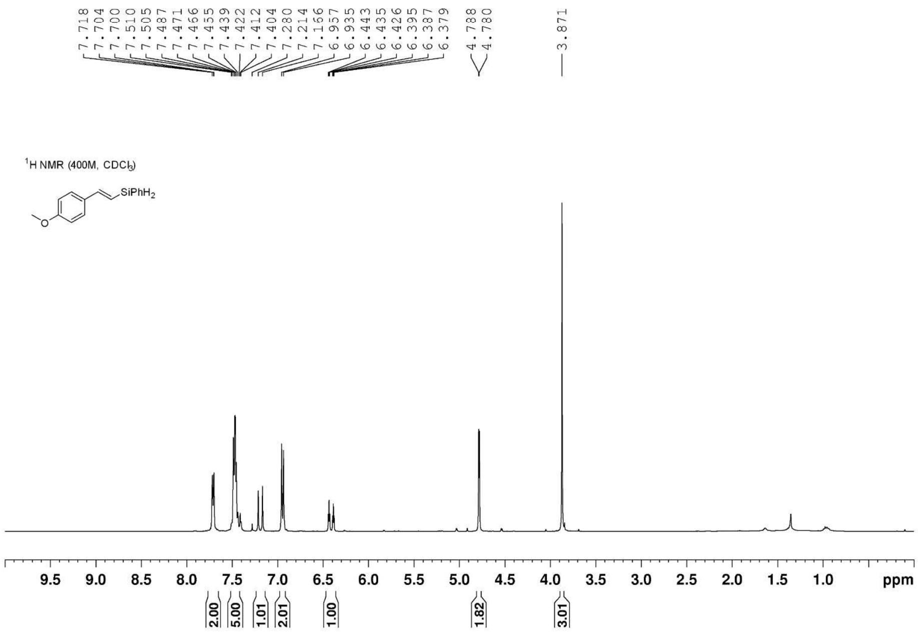


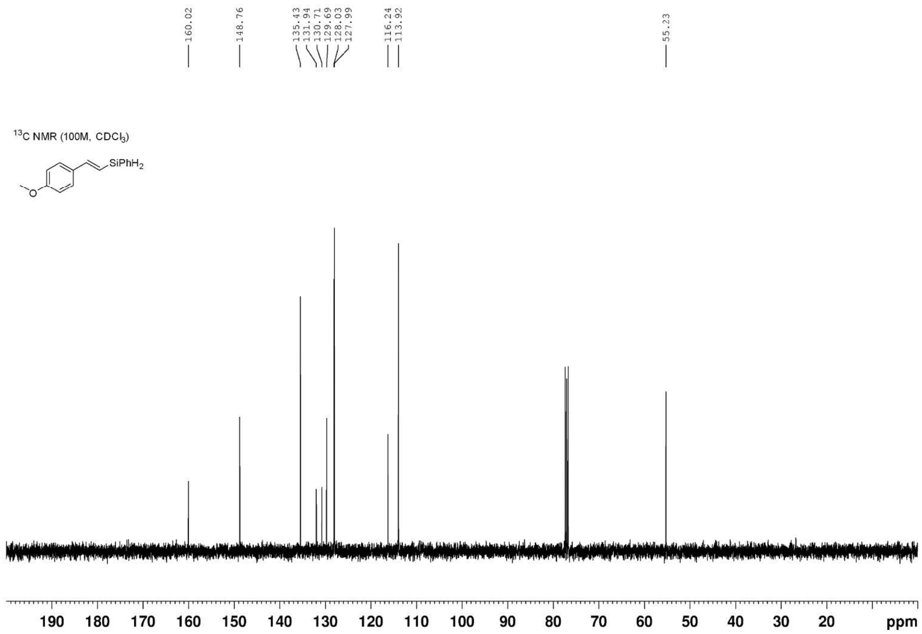
2u: (*E*)-(3-methylstyryl)(phenyl)silane



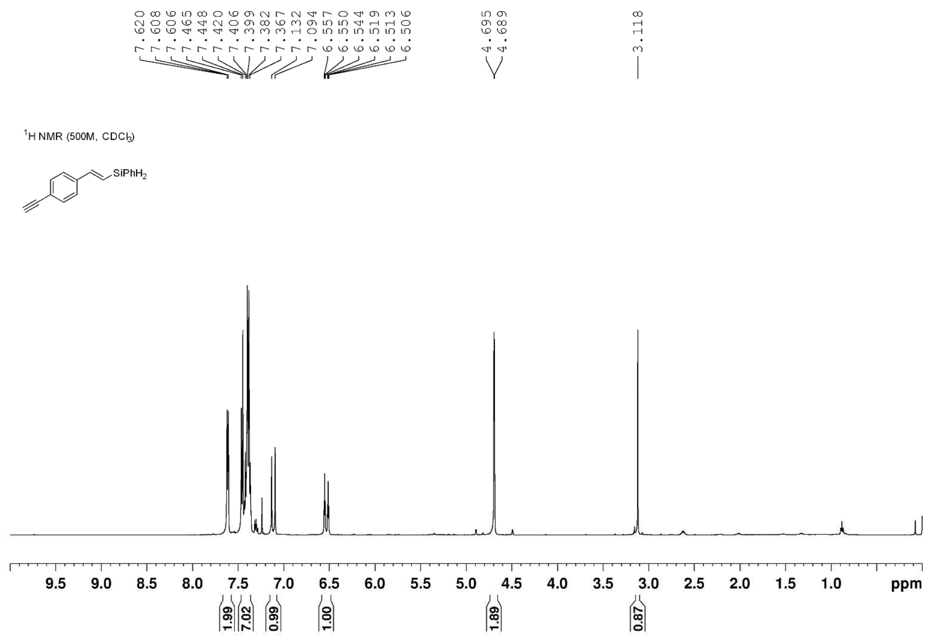


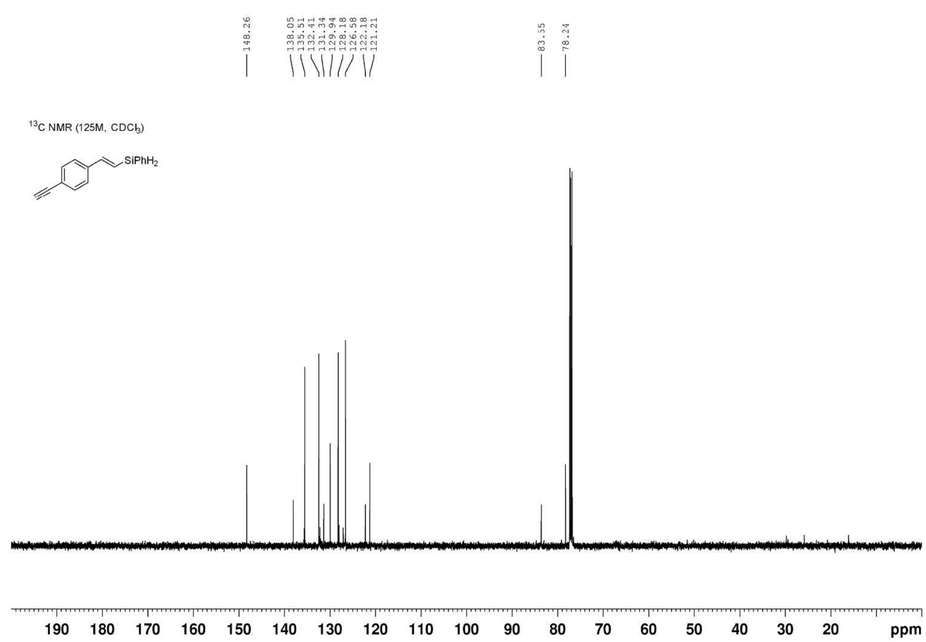
2v: (*E*)-(4-methoxystyryl)(phenyl)silane



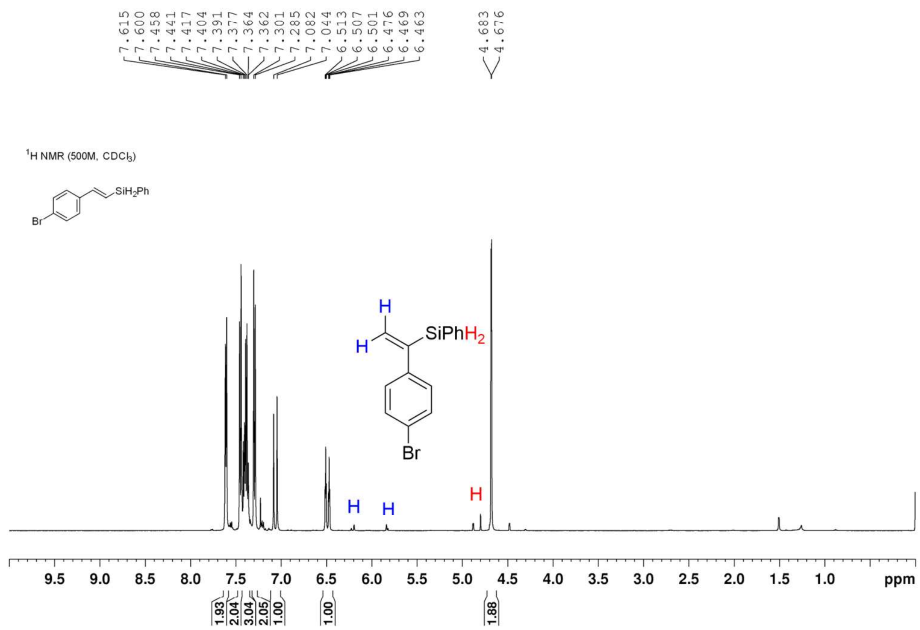


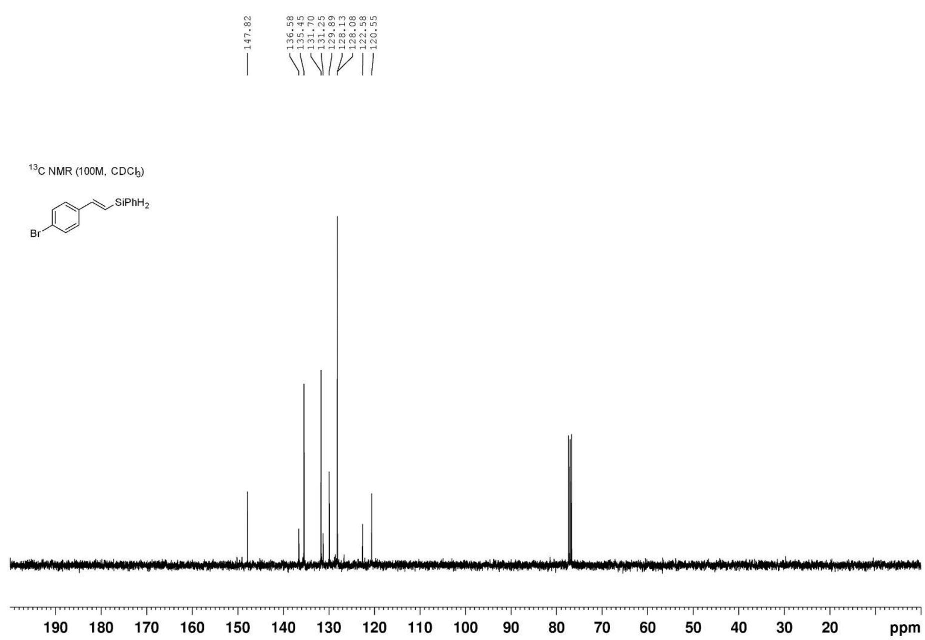
2w: (*E*)-(4-ethynylstyryl)(phenyl)silane



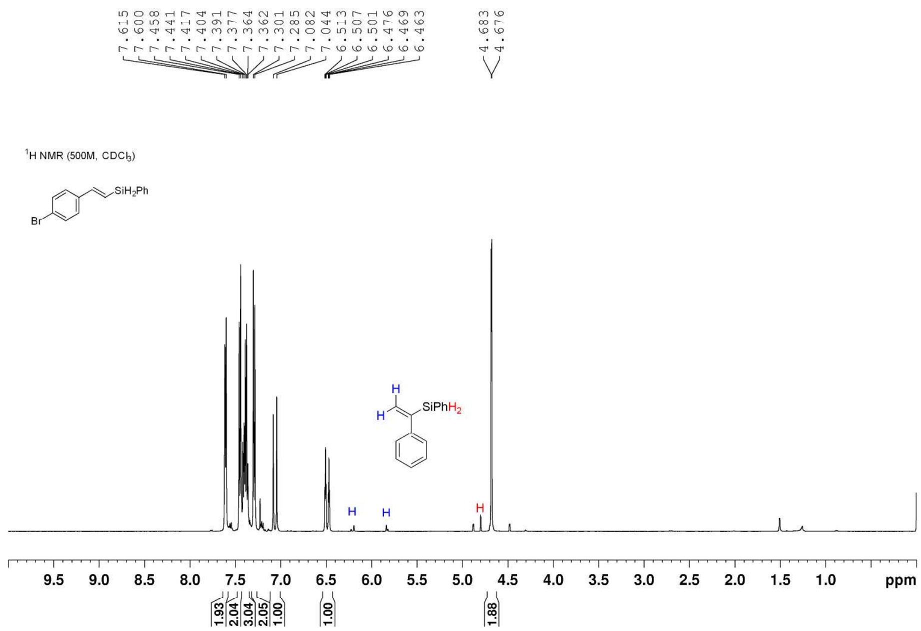


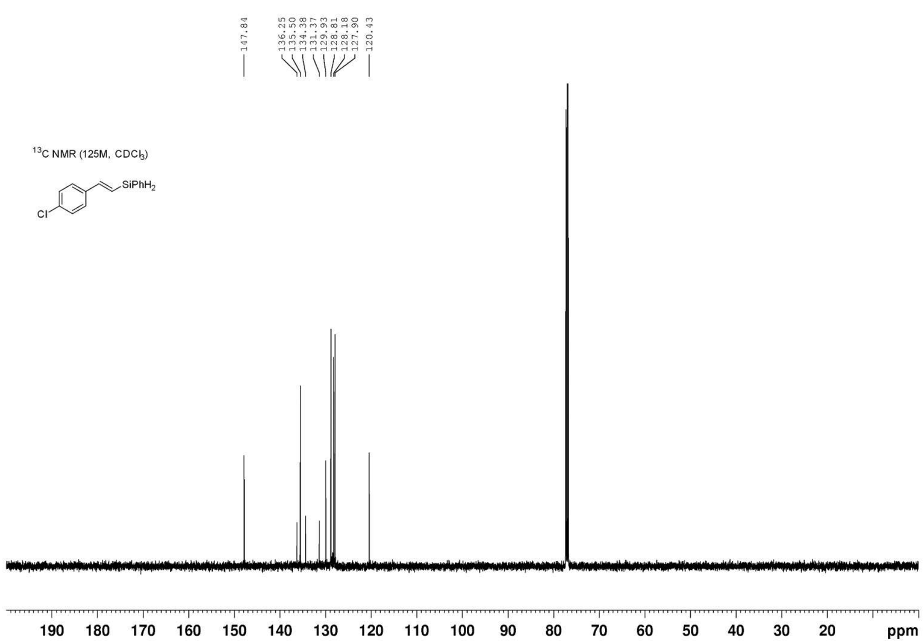
2x: (*E*)-(4-bromostyryl)(phenyl)silane



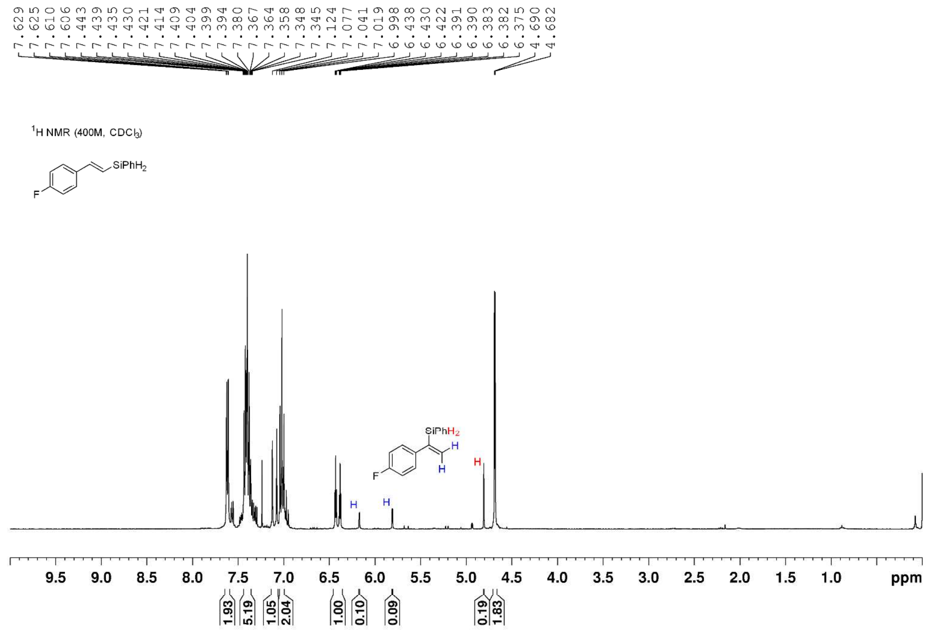


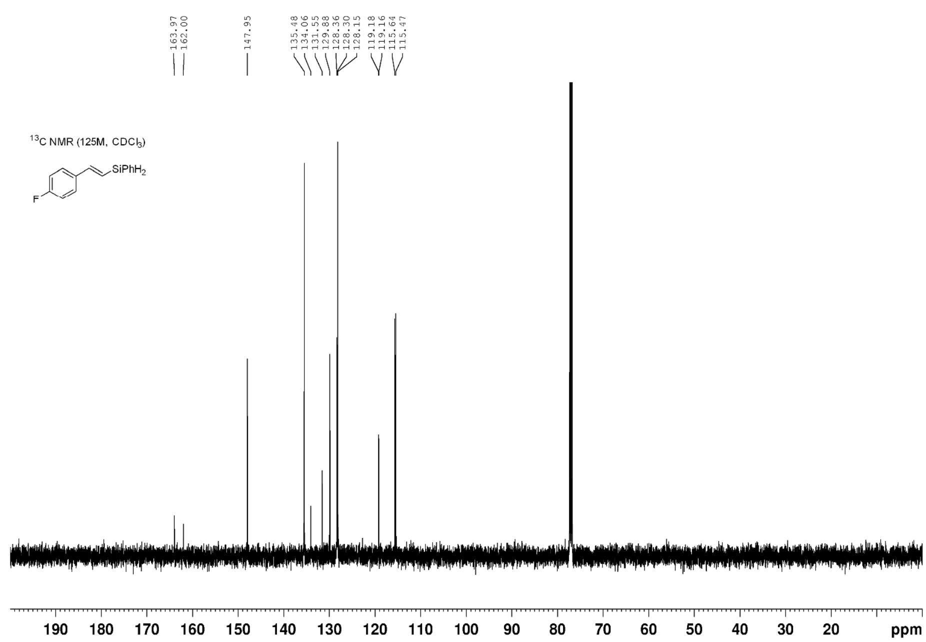
2y: (E)-(4-chlorostyryl)(phenyl)silane



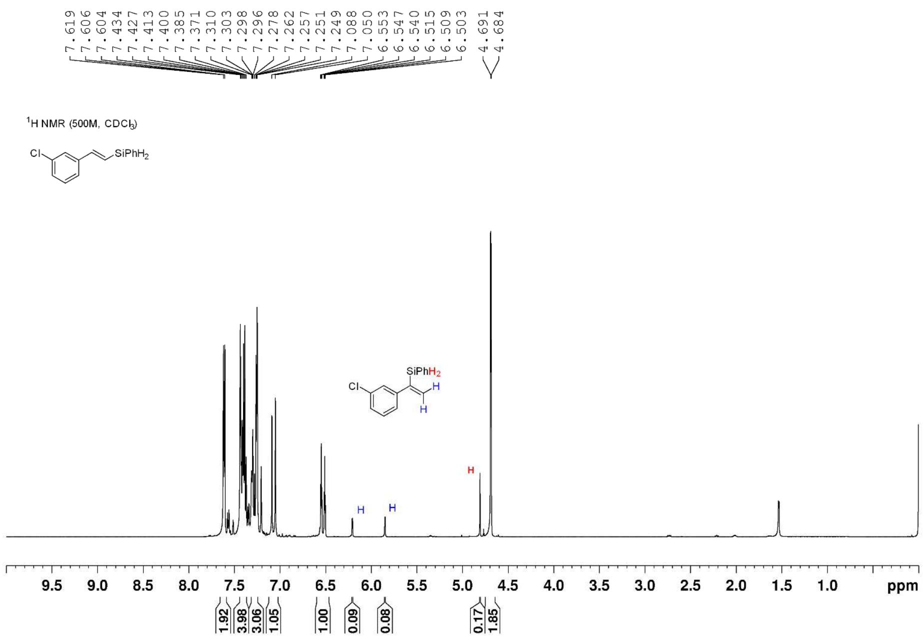


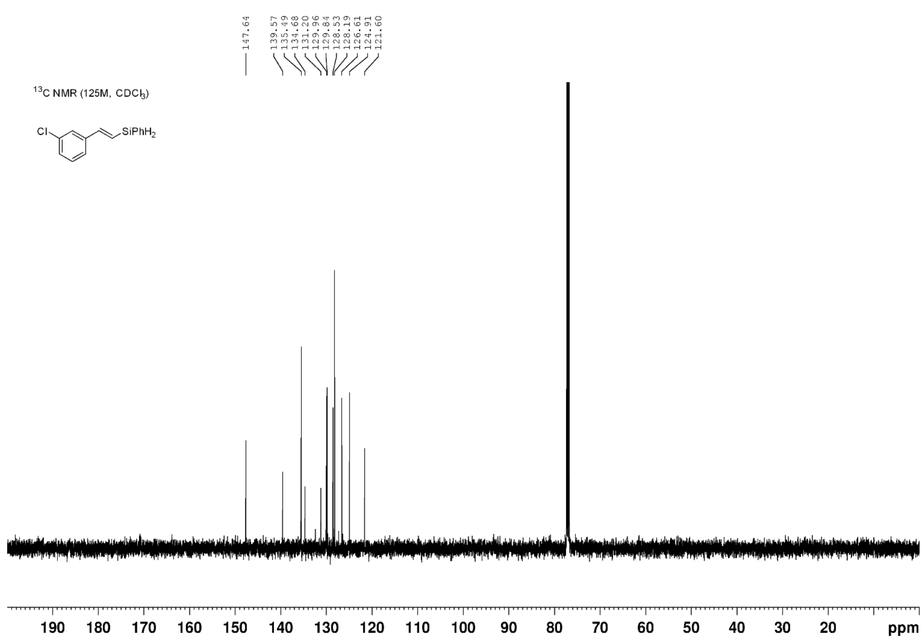
2z: (*E*)-(4-fluorostyryl)(phenyl)silane



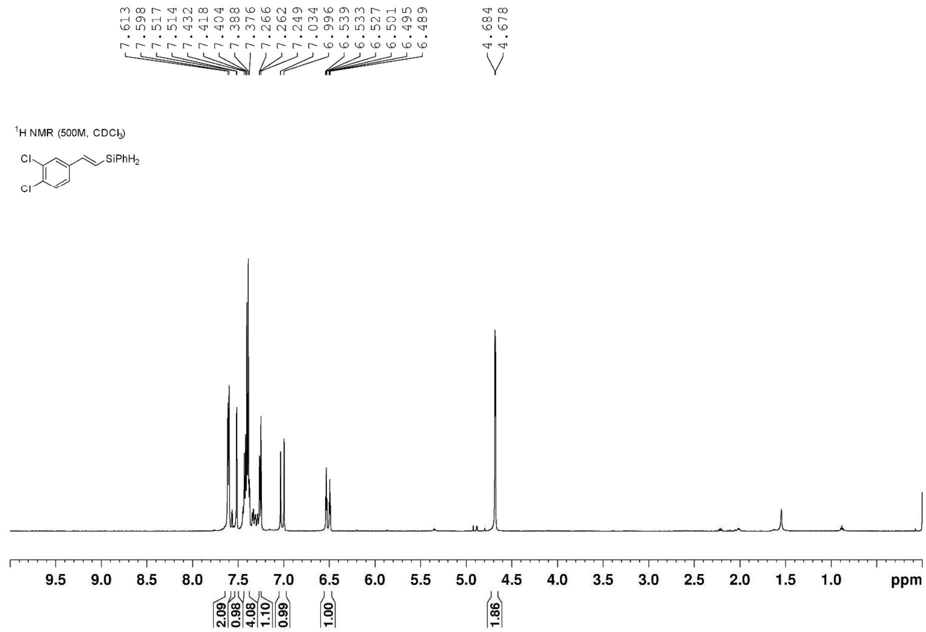


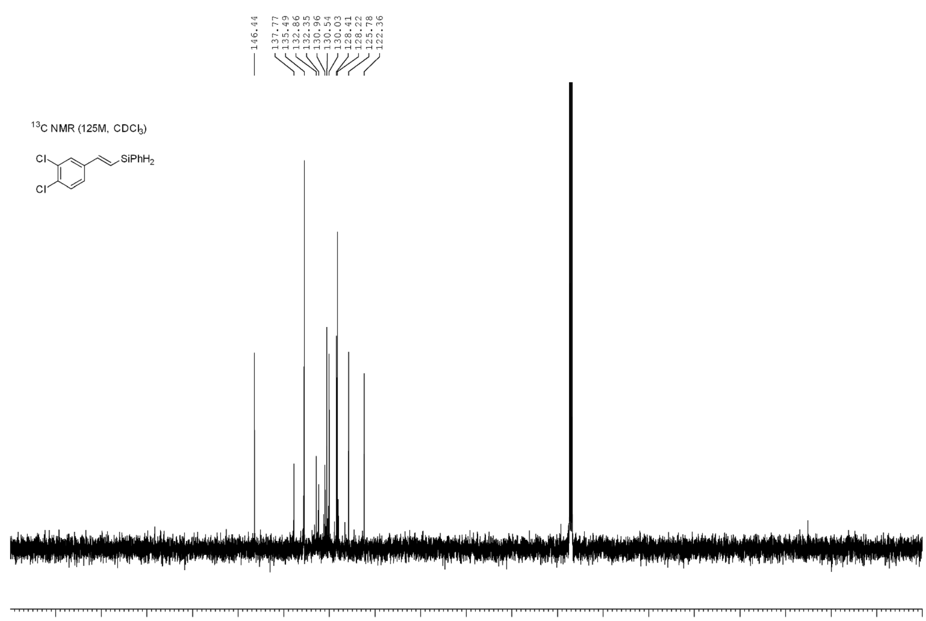
2aa: (*E*)-(3-chlorostyryl)(phenyl)silane



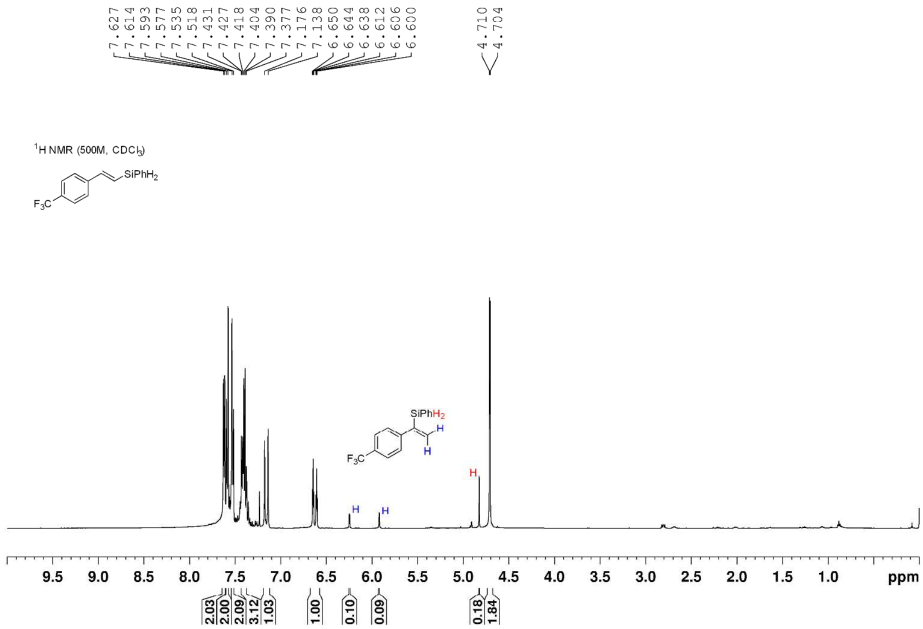


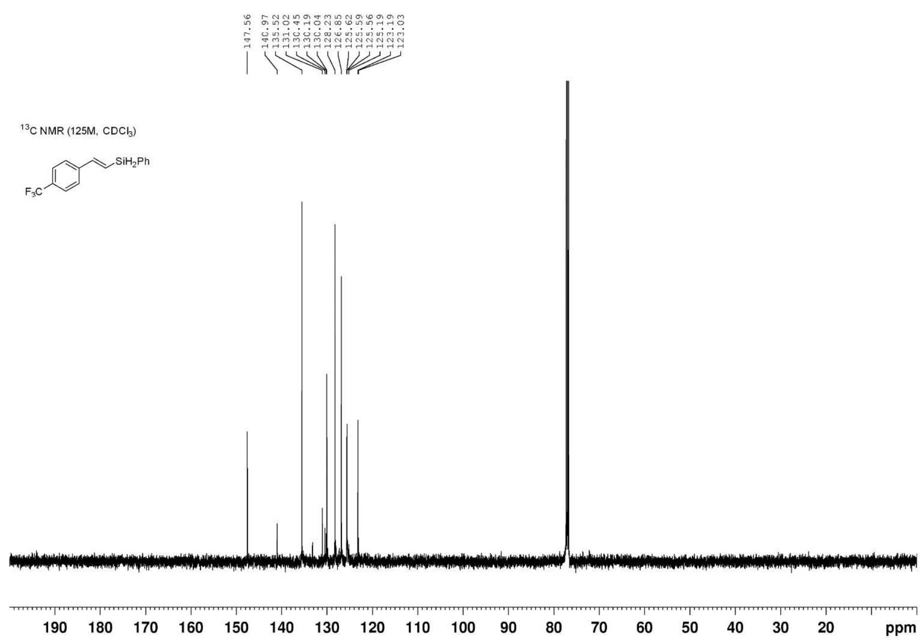
2ab: (*E*)-(3,4-dichlorostyryl)(phenyl)silane



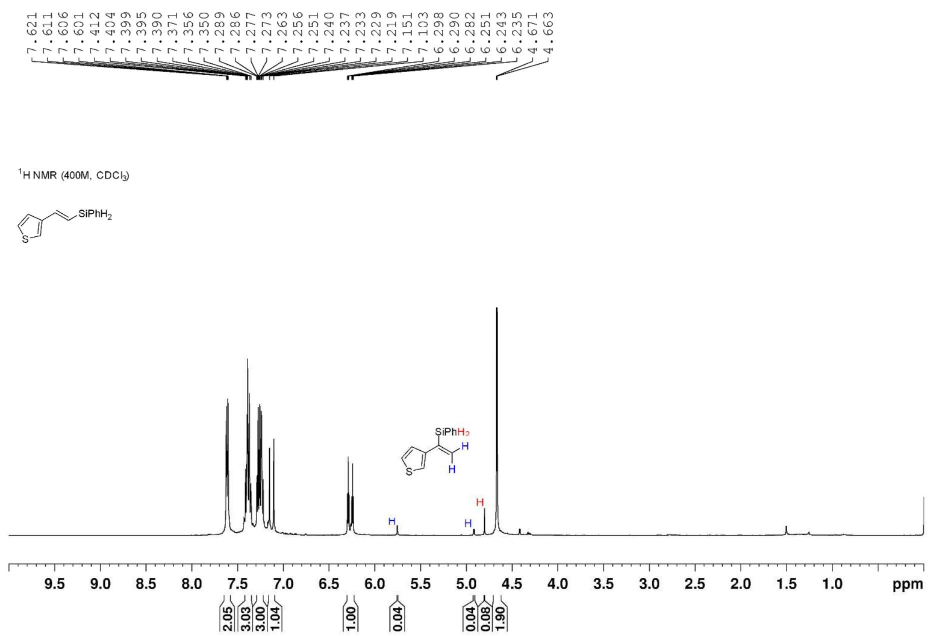


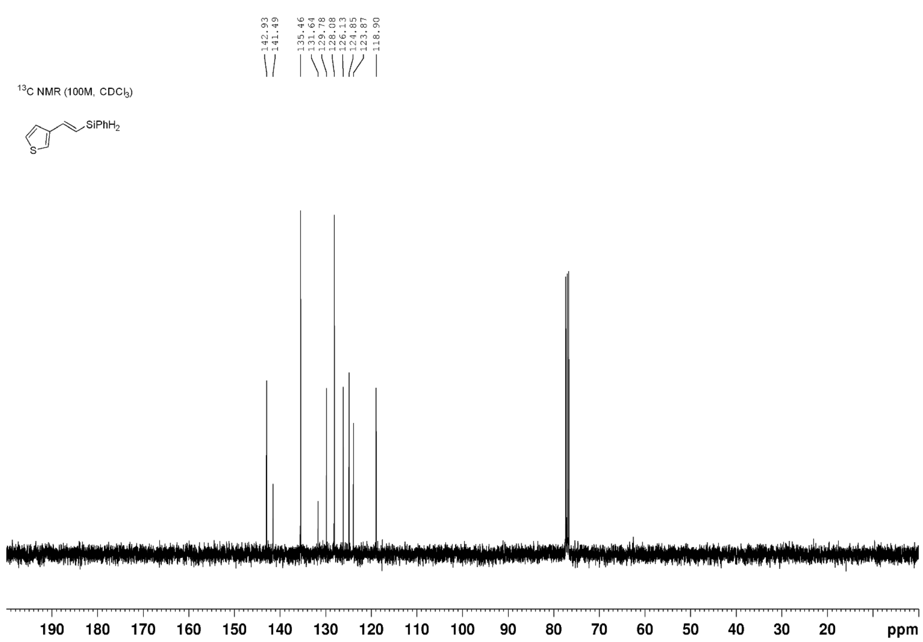
2ac: (*E*)-phenyl(4-(trifluoromethyl)styryl)silane





2ad: (*E*)-phenyl(2-(thiophen-3-yl)vinyl)silane





2ae: (*E*)-phenyl(2-(thiophen-2-yl)vinyl)silane