Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Highly Regio- and Stereo-Selective Heterogeneous 1,3-Diyne Hydrosilylation Controlled by Nickel-Metalated Porous Organic Polymer

Ying Yang[§], Ya-Nan Jiang[§], Zhi-Yi Lin, Jia-Hao Zeng, Zhi-Kai Liu, and Zhuang-Ping Zhan*

Department of Chemistry and Key Laboratory for Chemical Biology of Fujian Province, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

zpzhan@xmu.edu.cn

Contents

S1. 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 NMR was recorded on a Bruker AVANCE III400 WB spectrometer equipped with a 4 mm standard bore CP/MAS probehead whose channel was tuned to 400.18 MHz. The samples were packed in the ZrO_2 rotor closed with Kel-F cap which was spun at 12 kHz. ^{1}H CP/MAS and ^{13}C CP/MAS spectra were referenced to adamantane($C_{10}H_{16}$) as standard (1.63 ppm). ^{31}P CP/MAS were referenced to adenosine diphosphate (ADP) (0.0 ppm). The specific surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore size distribution curves were obtained from the desorption branches using the nonlocal density functional theory (NLDFT) method.

High resolution mass spectrometry

The instruments used in high resolution mass spectrometry are as follows: Ultra-High Resolution Hybrid Qh-Fourier Transform Mass Spectrometer (En Apex ultra 7.0 FT-MS)

Nitrogen adsorption desorption analysis

The instrument used is autosorb-1 physicochemical adsorber of quantachrome.

High resolution scanning electron microscope

JSM-7800F is used for HRSEM.

Transmission electron microscope

JEM-2100 is used for TEM.

TLC method: UV (254 nm UV lamp); Molybdophosphoric Acid developer: 5% $(NH_4)_6Mo_7O_{24}$ and 0.2% $Ce(SO_4)_2$ were added into 5% H_2SO_4 solution, stirred overnight to obtain chromogenic agent. TCL plate was soaked and heated to 110 ^{o}C for baking.

If there is no special description, the reagents used in the experiment are commercial analytical pure. The 1,3-diynes were prepared according to corresponding literature procedures.[1,2]

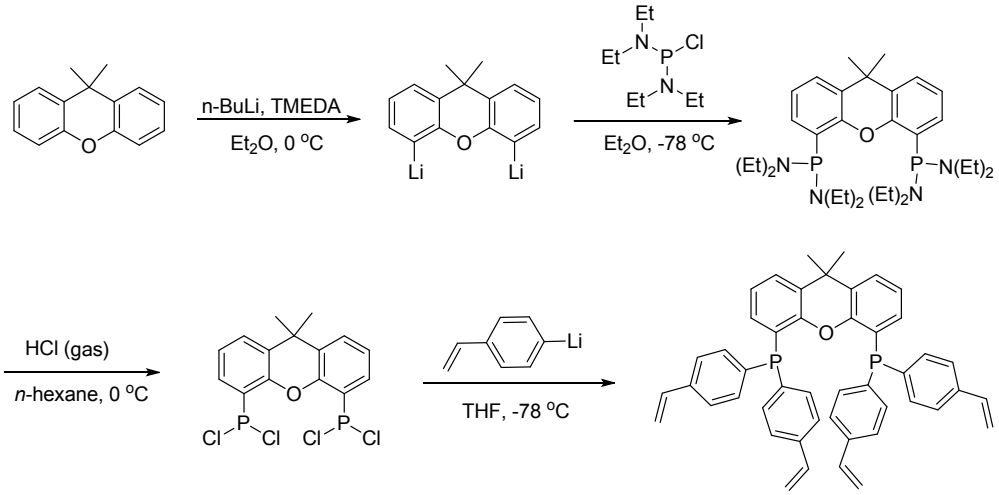
References:

[1] Shi, W.; Lei, A. *Tetrahedron Lett.* **2014**, *55*, 2763-2772.

[2] Burghart, J.; Brückner, R. *Eur. J. Org. Chem.* **2011**, 150–165.

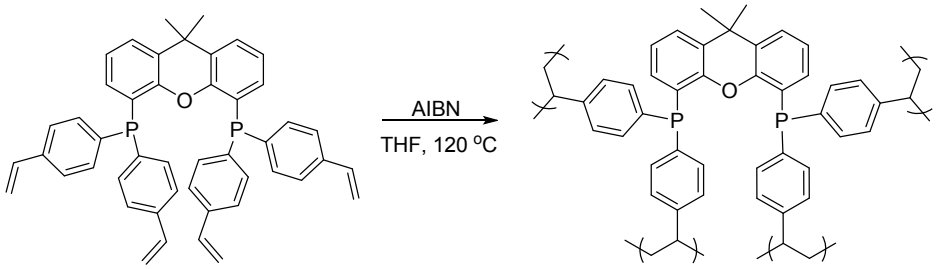
S2. General procedure for polymer synthesis

The synthesis of POL-xantphos



Under the protection of nitrogen atmosphere, 9,9-dimethyl-9*H*-xanthene (5.0 g, 24 mmol) was successively added into a 500 ml round bottom flask, and then tetramethylethylenediamine (TMEDA, 7.0 g, 60 mmol) and anhydrous ether (40 ml) were added into a syringe. Then, the reaction system was cooled to 0 °C, and then n-butyl lithium solution (24 ml, 60 mmol, 2.5 min THF) was added to the reaction solution drop by drop with a syringe. After dropping, the temperature was slowly raised to room temperature, and the reaction system was continuously stirred for 12 hours to prepare lithium salt intermediate **2**. Then the reaction system was further cooled to - 78 °C, and 50 ml of newly prepared CLP $(NEt_2)_2$ ether solution (12.6 g, 60 mmol) was added dropwise into the reaction solution with a syringe. Then return to room temperature, continue stirring and overnight. A small amount of reaction liquid was extracted by syringe, and the reaction was monitored by nuclear magnetic resonance spectroscopy [^{31}P NMR (161.8 MHz), δ 91.5]. Intermediate compound **3** was prepared after the reaction was completely transformed. The reaction system was directly pumped out with solvent ether by oil pump, and then 200 ml of new anhydrous hexane was added. Then, under the protection of nitrogen atmosphere, the filter was filtered with sand plate filter tube, and then the filter cake was washed with n-hexane. After that, the filtrate was cooled to 0 °C, and the newly prepared dry HCl gas was introduced into the bottom of the reaction solution (dried by two concentrated sulfuric acid drying bottles). The step lasted for 0.5-1 h, and a large amount of white salt was precipitated from the reaction solution. After passing through HCl gas, the filter tube with sand plate was used for filtration again under the protection of nitrogen, and the filter cake was washed with new tetrahydrofuran. The intermediate **4** was obtained by pumping the solvent tetrahydrofuran and n-hexane with an oil pump. The NMR was used to track and monitor [^{31}P NMR (161.8 MHz), δ 158.8]. Intermediate **4** was stored in nitrogen and used directly in the next step.

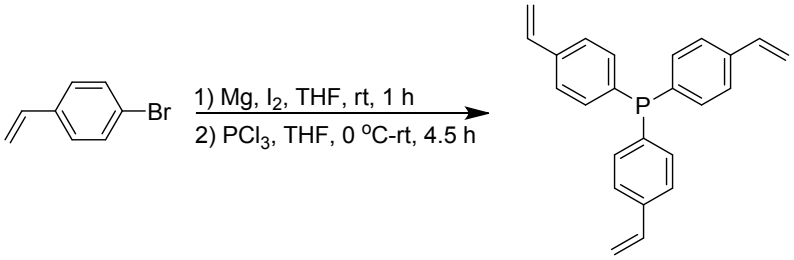
Under the protection of nitrogen atmosphere, p-bromophenylethylene (5.0 g, 27.5 mmol) and 60 ml fresh treated anhydrous tetrahydrofuran were added into the round bottom flask. The reaction solution was cooled to -78 °C, and n-butyl lithium solution (11 ml, 27.5 mmol, 2.5 min THF) was added dropwise into the reaction solution with a syringe. After the dropping of butyl lithium was finished, the solution was stirred continuously for 1 hour to obtain p-vinyl phenyl lithium solution. At -78 °C, p-vinylphenyl lithium solution was added dropwise to THF solution of Intermediate **4** by syringe. After dropping, return the temperature to room temperature naturally, and then keep stirring and overnight. Finally, saturated ammonium chloride solution was added, and then ethyl acetate was added for extraction (20 ml * 3). Anhydrous Na_2SO_4 was dried, filtered and steamed. Finally, the final product 4V-xantphos **5** (1.3 g) was obtained by silica gel column chromatography and the total yield was 9%.



POL-Xantphos

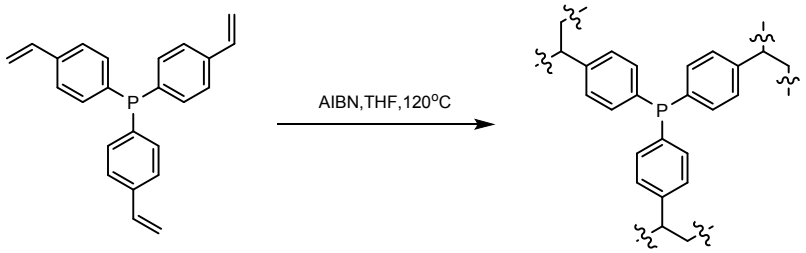
Under the protection of nitrogen, 1.3 g of monomer **5**, AIBN (0.1 g) and anhydrous tetrahydrofuran (3 ml) were successively added into the pressure resistant reaction tube. At 120 °C for 24 hours, white solid precipitated. After the reaction, the solvent was removed under reduced pressure and dried in vacuum for 6 hours. Finally, the white polymer POL-xantphos (1.2 g) was obtained.

The synthesis of POL-PPh_3



Under the protection of nitrogen atmosphere, magnesium chips (2.40g, 100 mmol) were added into the round bottom bottle, and then a particle of iodine and a small amount of 1-bromo-4-vinylbenzene were added to activate the magnesium chips. The magnesium chips were heated until the reaction refluxed, and then the p-bromophenylethylene (14.64g, 100 mmol) was added into the bottom bottle, 80 mmol) of tetrahydrofuran solution (80 ml), the dropping acceleration should be controlled, and the reaction solution should be kept in a slightly boiling state. After dropping, the mixture should be continuously stirred and refluxed for 1 h. After that, the reaction was cooled to 0 °C, and the newly distilled phosphorus trichloride (3.43g, 25 mmol) was added to the reaction solution with a syringe, continuously stirred for 0.5 h, and then slowly heated to room temperature, and the reaction was stirred for 4 h. The reaction was quenched by adding saturated

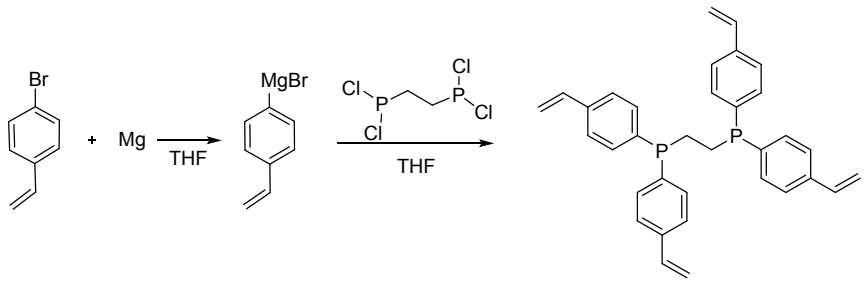
ammonium chloride aqueous solution (20 ml), and extracted with ethyl acetate twice (20 ml * 2). Na_2SO_4 was dried, filtered, evaporated, and purified by silica gel column chromatography. Finally, the vinyl monomer tris (4-vinyl phenyl) phosphine (5.5 g, 65%) was obtained.



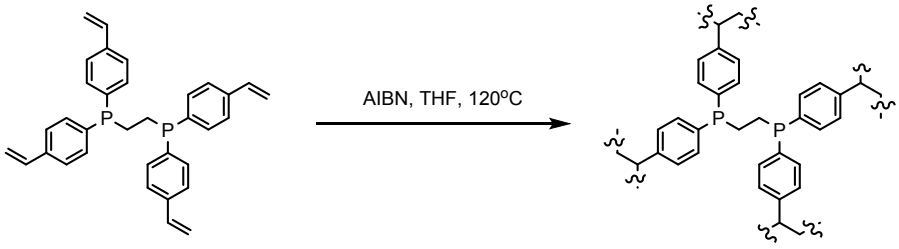
POL-PPh$_3$

Under the protection of nitrogen atmosphere, 2 g tris(4-vinylphenyl) phosphine, 0.2 g AIBN and anhydrous tetrahydrofuran (3 ml) were successively added into the pressure resistant reaction tube under the protection of nitrogen atmosphere. White solid was precipitated after reaction at 120 °C for 24 hours. After the reaction, the solvent was removed under reduced pressure and dried in vacuum for 6 hours. Finally, 1.8 g of white polymer POL-PPh$_3$ was obtained.

The synthesis of POL-dppe



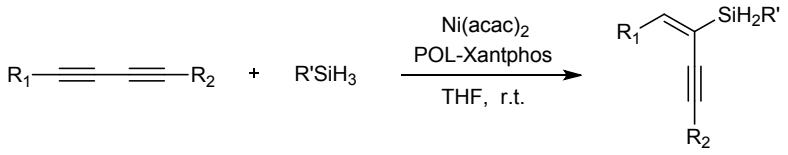
Under the protection of nitrogen atmosphere, magnesium chips (2.40g, 100 mmol) were added into the round bottom bottle, and then a particle of iodine and a small amount of 1-bromo-4-vinylbenzene were added to activate the magnesium chips. After heating until the reaction refluxed, the THF solution (80 ml) of 1-bromo-4-vinylbenzene (14.64g, 80 mmol) was added. After dropping, the mixture was refluxed and stirred for 1 h. Then the reaction was cooled to 0 °C, then 1,2-bis (dichlorophosphino)-ethane (4.2g, 18 mmol) was slowly added into the reaction solution with a syringe, stirred at 0 °C for 30 minutes, then slowly raised to room temperature, and stirred for 4 h. The reaction was quenched with saturated ammonium chloride aqueous solution (20 ml), and extracted with ethyl acetate twice (20 ml*2). 4V-dppe (4.5g, 50%) was obtained by silica gel column chromatography.



POL-dppe

Under the protection of nitrogen atmosphere, 2 g monomer 4V-dppe, 0.2 g AIBN and anhydrous tetrahydrofuran (4 ml) were successively added into the pressure resistant reaction tube under the protection of nitrogen atmosphere. White solid was precipitated in the reaction at 120 °C for 24 hours. After the reaction, the solvent was removed under reduced pressure and dried in vacuum for 6 hours. Finally, 1.8 g of white polymer POL-dppe was obtained.

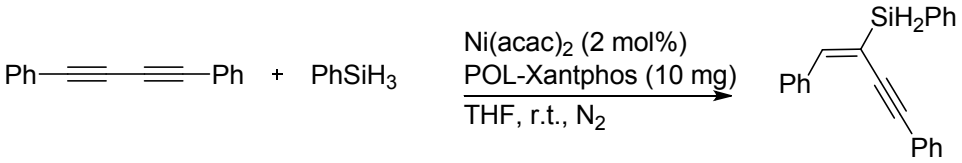
S3. General procedure for 1,3-diyne hydrosilylation



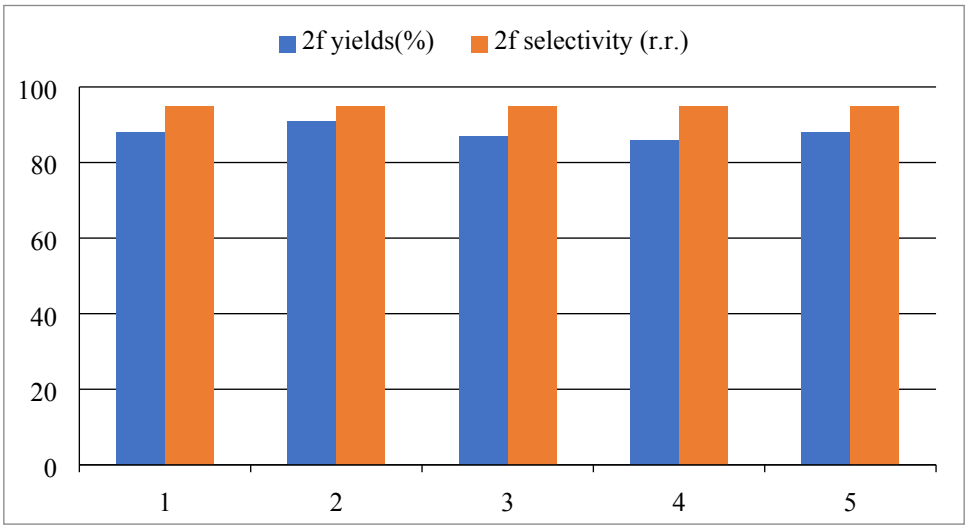
In a nitrogen filled schlenk tube, $Ni(acac)_2$ (1 mg, 0.005 mmol) and POL-xantphos (10 mg) were added to THF (1 mL), followed by 1,3-diyne (0.25 mmol) and $PhSiH_3$ (33 mg, 0.3 mmol), and stirred at room temperature under N_2 atmosphere. When the reaction was completed, the solvent was removed in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product.

A small number of samples of crude products were used for NMR detection to obtain the selectivity of the reaction.

Studies on recycling of POL-Xantphos for the Hydrosilylation of 1,4-diphenylbuta-1,3-diyne and $PhSiH_3$



In a nitrogen filled schlenk tube, $Ni(acac)_2$ (2 mol%) and 10 mg POL-xantphos were added in 2mL THF in the first run. And then 1,4-diphenylbuta-1,3-diyne (50.5 mg, 0.25 mmol) and $PhSiH_3$ (32.4 mg, 0.3 mmol) were added. The reaction mixture was stirred at room temperature for 3 h. Upon completion, centrifuge and pour out the supernatant, POL-xantphos 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 analyzed 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 POL-xantphos was added, then the additional $Ni(acac)_2$ (2 mol%) was added. Then 1,4-diphenylbuta-1,3-diyne (50.5 mg, 0.25 mmol) and $PhSiH_3$ (32.4 mg, 0.3 mmol) were added. After reaction, analyze by ^1H NMR again. 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 S1. recycling of POL-xantphos for the hydrosilylation of 1,4-diphenylbuta-1,3-diyne and $PhSiH_3$

In order to test the leak of nickel, we conducted a series of reaction and subjected to ICP-MS to test the amount of nickel. Detailed operation was depicted as following:

In a nitrogen filled schlenk tube, $Ni(acac)_2$ (1.5 mg, 0.006 mmol, 2 mol%) and 10 mg POL-xantphos were added in 2mL THF, stirring in room temperature for 2h. After the reaction, the solid catalyst was isolated by centrifugal, dried over and digestion by 5mL H_2SO_4, then took 0.1 mL solution dissolved by 10 mL ultrapure water and this solution was subjected to ICP-MS as Sample 1.

The full amount of the added nickel:

60×0.006=0.36 mg.

The amount of nickel coordinated to 10 mg POL-xantphos:

316.85 ppb×100×10^{-6}=0.0316 mg/mL 0.0316 mg/mL×5mL=0.158 mg.

The amount of nickel in the extract:

0.36 mg-158 mg=0.202 mg.

In a nitrogen filled schlenk tube, $Ni(acac)_2$ (1.5 mg, 0.006 mmol) and POL-xantphos (10 mg) were added to THF (1 mL), followed by 1,3-diyne (0.3 mmol) and $PhSiH_3$ (39 mg, 0.36 mmol), and stirred at room temperature under N_2 atmosphere. When the reaction was completed, the solid catalyst and supernatant were isolated by centrifugal. The solid catalyst was dried over and digestion by 5mL H_2SO_4, then took 0.1 mL solution dissolved by 10 mL ultrapure water and this solution was subjected to ICP-MS as Sample 2.

The amount of nickel coordinated to 10 mg POL-xantphos after each reaction:

127.11 ppb×100×10^{-6}=0.0127 mg/mL 0.0127 mg/mL×5mL=0.0635 mg.

While the supernatant was dissolved in THF to get a 6 mL solution. Taking 0.1 mL solution dissolved by 10 mL ultrapure water and then 1mL diluted into 10 mL ultrapure water and this solution was subjected to ICP-MS as Sample 3.

The leak of nickel after each reaction:

24.007 ppb×6000×10^{-6}=0.144 mg/mL 0.144 mg/mL×2mL=0.288 mg.

This shows the weak coordination of nickel to POL-xantphos and the large leak of nickel after every reaction. As a result, we need to complement $Ni(acac)_2$ for every run of the recycling experiments in order to process the recycling.

Analytic report

【 Method information 】

Method name	20210531-4.exp	Time	2021/5/31 22:00:25
Element	58Ni, 60Ni, 61Ni, 62Ni, 64Ni		

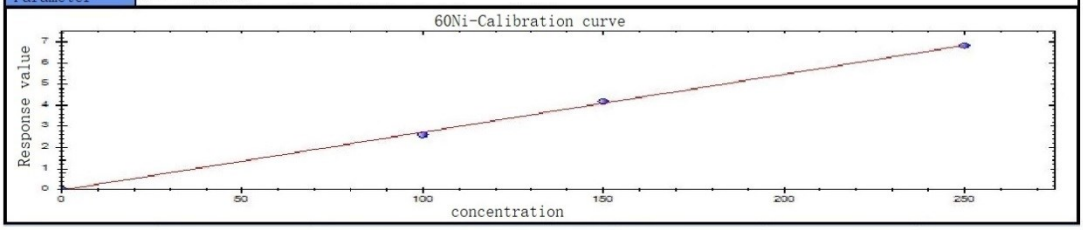
【 Quality calibration 】

Standard curve	V = 0.03446 * amu -0.04813
High scale curve	V = 0.03446 * amu -0.04359

【 Cross correction information 】

Cross curve	K = -0.000124 * amu^4 + 0.0656 * amu^3 -12.87 * amu^2 + 1339 * amu + 6.474E+04

Curve name	Total quantitative curve-60Ni
Equation	CPS = 0.02743 * C-0.01535
Parameter	R^2 = 0.9993



【 Results 】

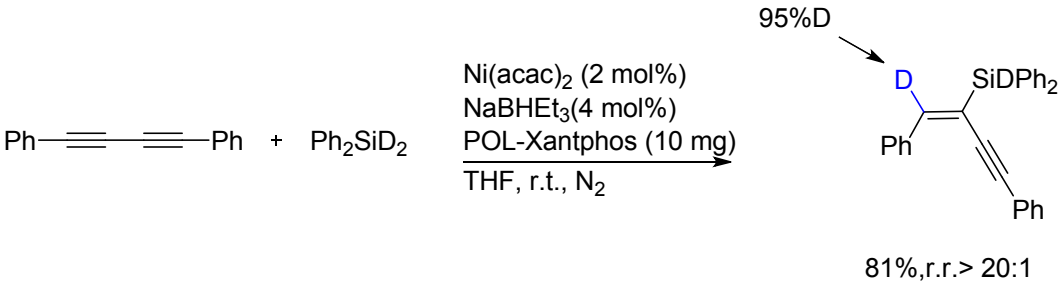
concentration

Name	Acquisition time	45Sc	58Ni	60Ni	61Ni	62Ni	64Ni
Sample1	2021-05-31 21:55:29-AVG	111.96	310.45	316.85	314.04	315.81	144.81
	SD	5.0726	33.201	38.337	37.557	33.799	8.6695
	RSD(%)	4.53	10.7	12.1	12	10.7	5.99
Sample2	2021-05-31 21:56:05-AVG	17.957	128	127.11	113.88	112.22	<0.0000
	SD	3.7191	6.855	7.9122	6.4632	6.3643	0.7068
	RSD(%)	20.7	5.36	6.22	5.68	5.67	111
Sample3	2021-05-31 21:58:57-AVG	27.414	23.513	24.007	22.733	21.213	<0.0000
	SD	7.6652	2.3133	2.7084	2.6973	2.2107	0.4682
	RSD(%)	28	9.84	11.3	11.9	10.4	8.63

Instrument model: SUPEC 7000

Software version: 7000.P004.V2.2

S4. Procedure for deuterium-labeling experiments



81%,r.r.> 20:1

In a nitrogen filled schlenk tube, $Ni(acac)_2$ (1 mg, 0.5 mmol%), POL-xantphos (10 mg), $NaBHEt_3$ (4 mol %) were added to THF (1 mL), followed by the addition of 1,3-diyne (0.25 mmol) and Ph_2SiD_2 (0.3 mmol) in THF (1 mL) under nitrogen. The reaction mixture was stirred at room temperature for 12h and the resulting suspension was concentrated in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate, to afford the corresponding product as a colorless oil (78 mg, 81%).

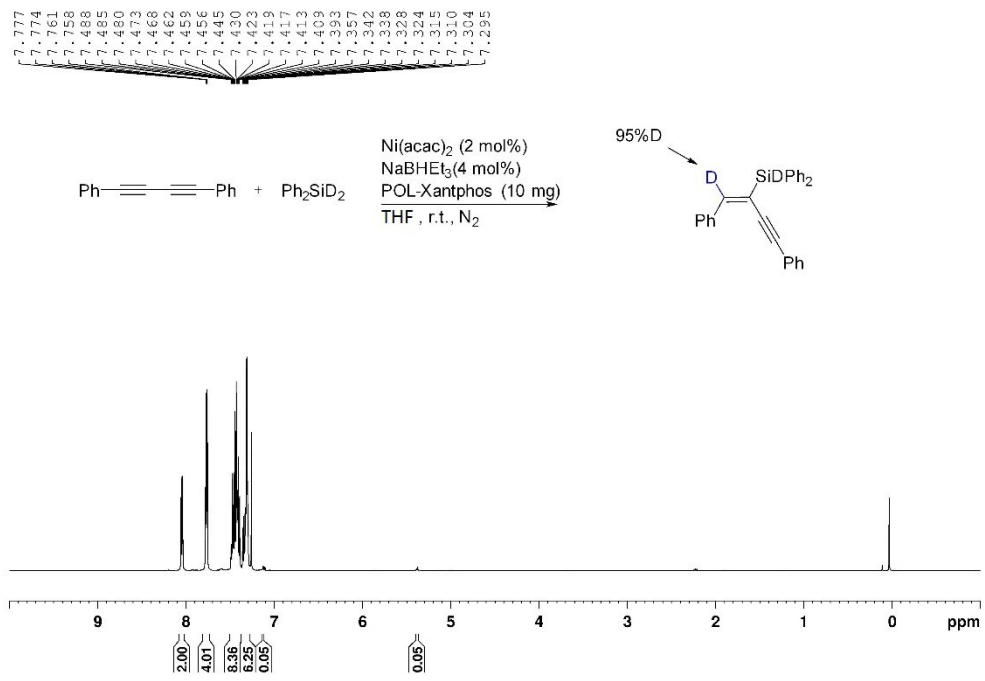
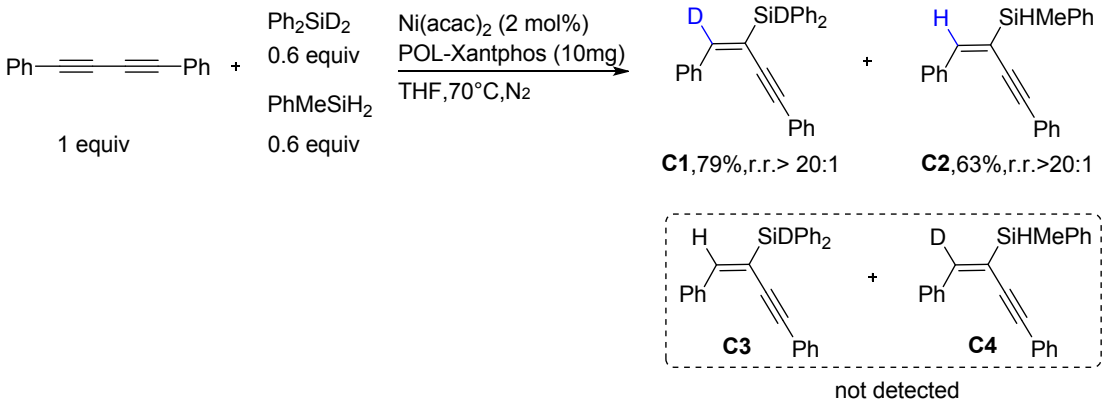


Figure S1. ^1H NMR spectra for deuterated **2p**

S5. Crossover experiments related to operable mechanism:

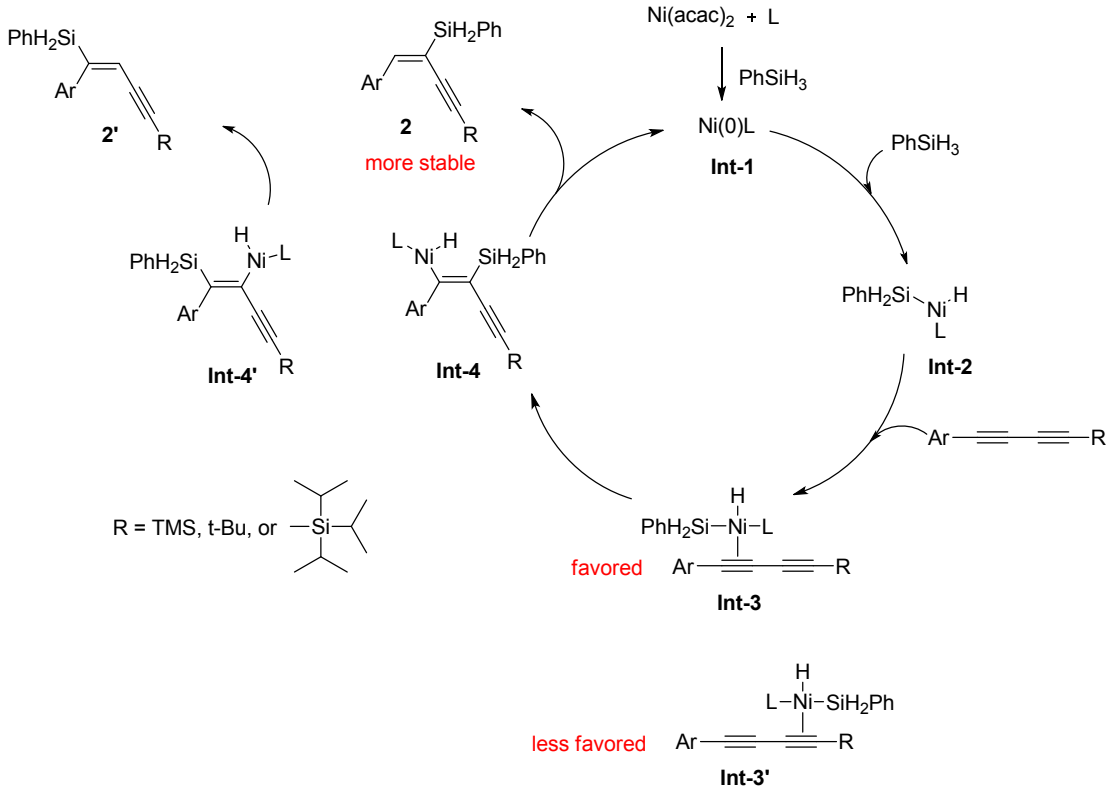
Control experiment: Into two separate nitrogen filled schlenk tube, $Ni(acac)_2$ (1 mg, 0.005 mmol), POL-xantphos (10 mg) were added to THF (1 mL), followed by addition of Ph_2SiD_2 (0.3 mmol) to the first schlenk tube and $PhMeSiH_2$ (0.3 mmol) to the second one. No 1,3-diyne was added and the contents of the two schlenk tubes were immediately mixed. After 12 hours, the mixture was observed by ^1H NMR spectroscopy. No H/D exchange was observed.

Crossover experiment: Into two separate nitrogen filled schlenk tube, $Ni(acac)_2$ (1 mg, 0.005 mmol), POL-xantphos (10 mg) were added to THF (1 mL), followed by addition of Ph_2SiD_2 (0.15 mmol) to the first schlenk tube and $PhMeSiH_2$ (0.15 mmol) to the second one. To each of these, 1,3-diyne (0.25 mmol) was added and the contents of the two schlenk tubes were immediately mixed. After 12 hours, reaction completion monitored by TLC. The resultant ^1H NMR showed that no crossover products were observed (see Scheme S2 and spectra below), thus ruling out the mechanism of nickel hydrides (Scheme S3).



Scheme S2. Products formed in crossover experiment

We propose a hydrometalation pathway with a Ni(0) intermediate for this Ni-catalyzed hydrosilylation of 1,3-diynes (Scheme S3). In such a mechanism, nickel precursor is *in situ* reduced by phenylsilane to form Ni(0) Int-1, then a silane oxidative addition of it generates the Int-2, the favored Int-3 generates alkenyl nickel intermediate Int-4 after insertion of the alkyne into the Ni-Si bond, and the final product is obtained by C-H reductive elimination with the return of the Ni(0) active species Int-1 into the catalytic cycle. Note that the insertion of the alkyne into the Ni-Si bond to selectively give Int-4 not Int-4', because Int-4 gives a more thermodynamic stable product 2 and Int-4' gives a less thermodynamic stable product 2'.



Scheme S3. [Ni-H] involved mechanism

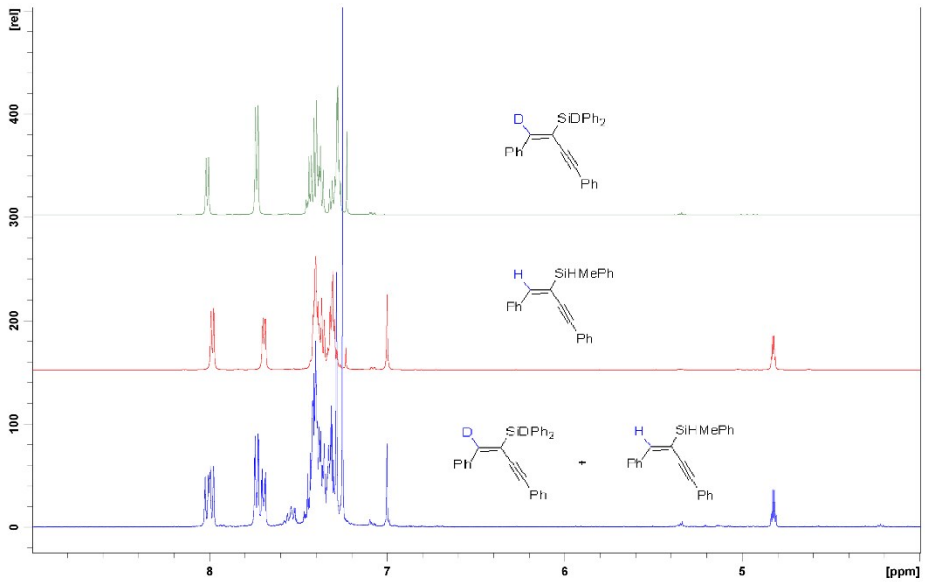


Figure S2. Green: pure product C1 in 400M ^{1}NMR; Red: pure product C2 in 400M ^{1}NMR; Blue: crude reaction mixture in 400M ^{1}NMR

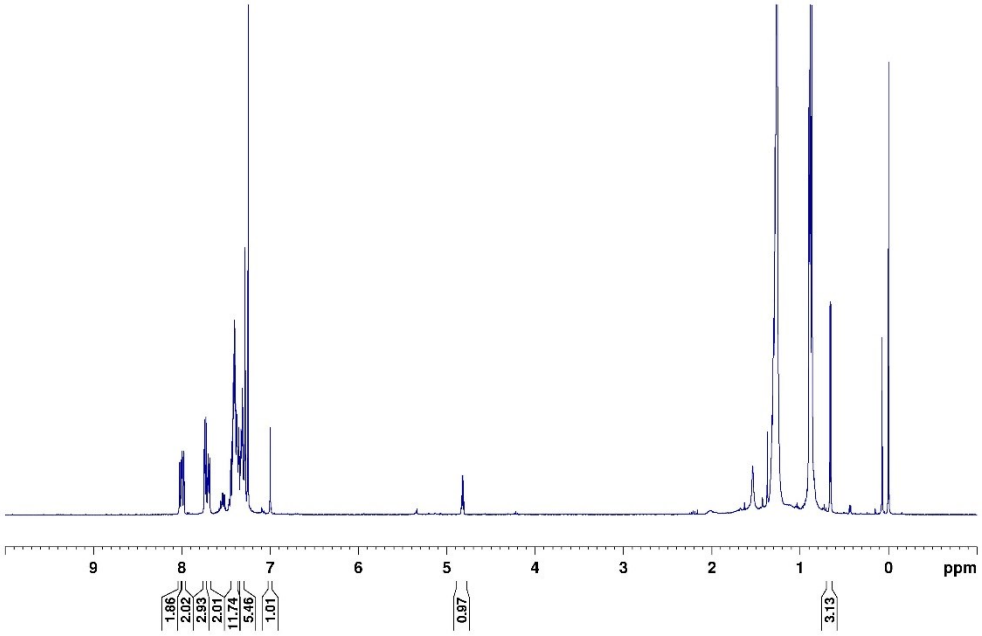
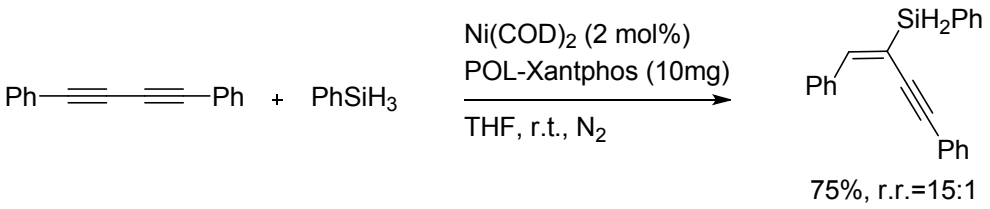


Figure S3. 400M ^{1}NMR spectrum of crude reaction mixture from crossover experiment

S6. Procedure for control experiment with $Ni(COD)_2$



In the glove box, $Ni(COD)_2$ (1.5 mg, 2 mol%), POL-xantphos (10 mg) were added to THF (1 mL), and stirred for 5 mins. then 1,3-diyne (0.25 mmol) and $PhSiH_3$ (0.3 mmol) in THF (1 mL) was added. The reaction mixture was stirred at 25 ^{o}C and monitored by TLC. the reaction was complete within 15 mins. Resulting suspension was concentrated in vacuum. The crude product was purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate, to afford the corresponding product as a colorless oil (58 mg, 75%).

S7. Characterization of polymer

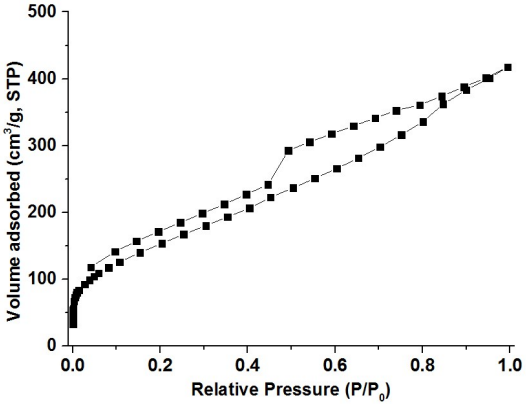


Figure S4. Nitrogen sorption isotherms of POL-xantphos

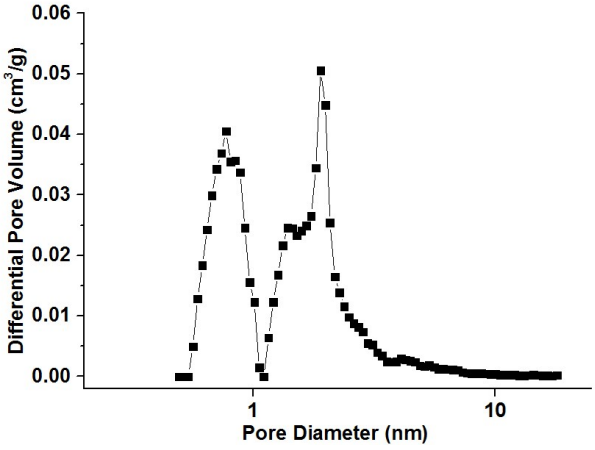


Figure S5. Pore size distribution of POL-xantphos, calculated from non-local density functional theory (NLDFT).

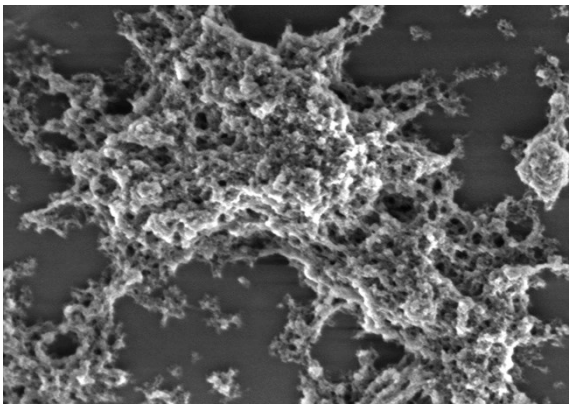


Figure S6. Scanning electron microscopy (SEM) of POL-xantphos

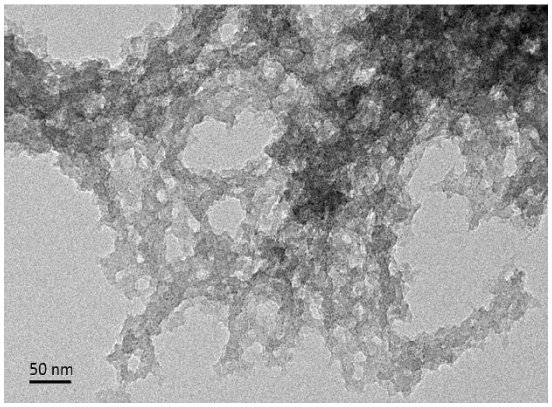


Figure S7. Transmission electron microscope (TEM) images of POL-xantphos

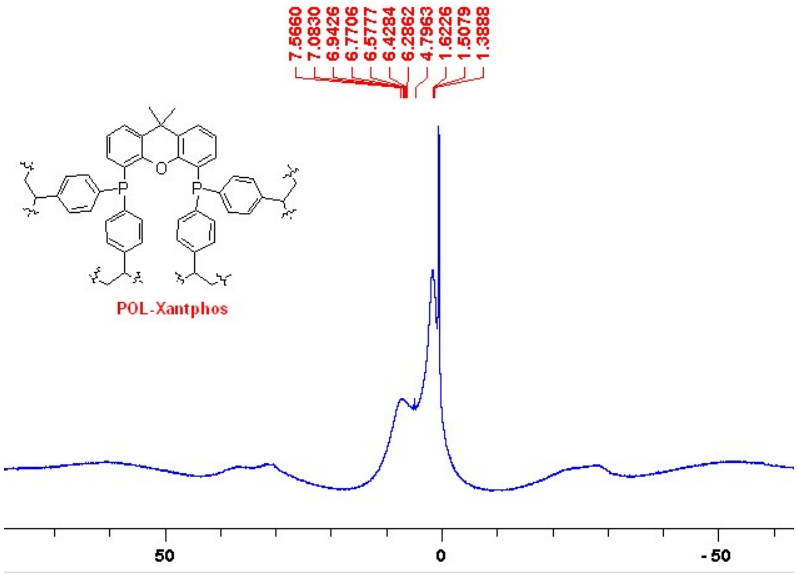


Figure S8. ^{1}H CP/MAS (400 MHz) of POL-xantphos δ 1.39-7.57

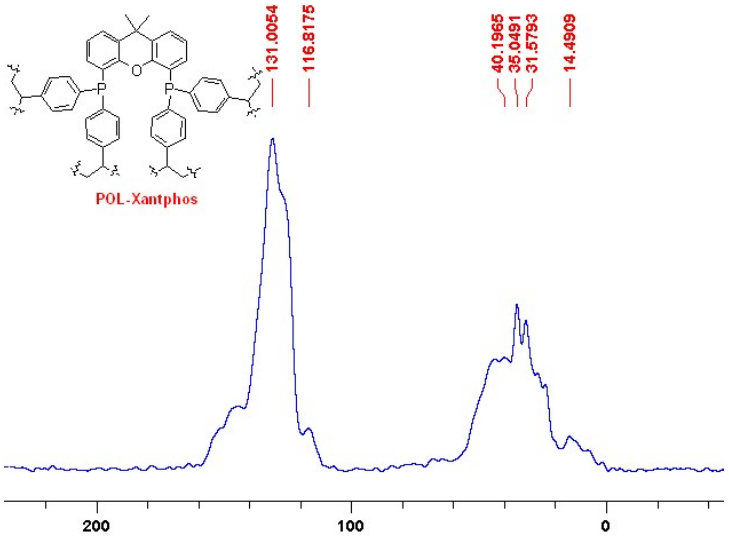


Figure S9. ^{13}C CP/MAS (100 MHz) of POL-xantphos δ 14.5, 31.6, 35.0, 40.2, 116.8, 131.0.

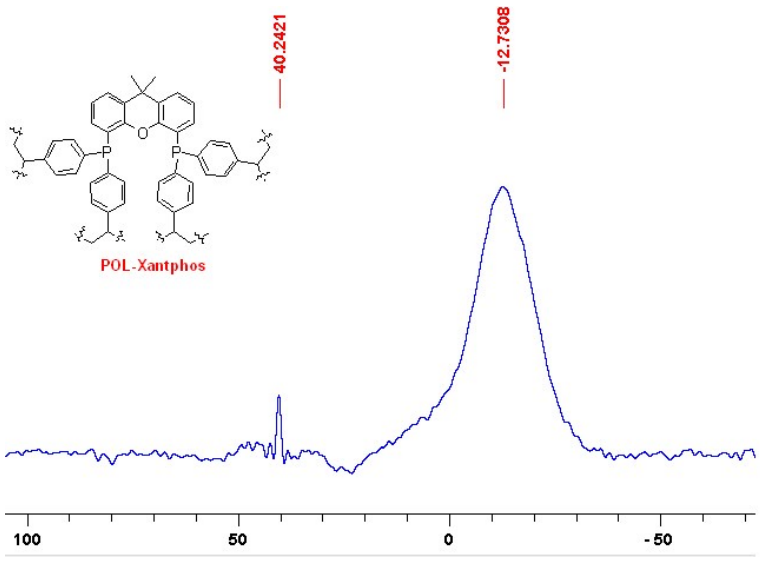
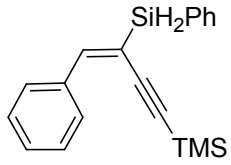


Figure S10. ^{31}P CP/MAS (100 MHz) of POL-xantphos δ -12.7.

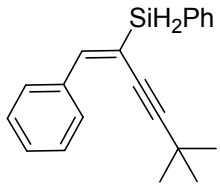
S8. Analytical data for compounds

(*E*)-trimethyl(4-phenyl-3-(phenylsilyl)but-3-en-1-yn-1-yl)silane (2a)



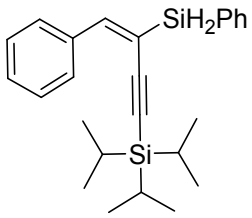
colorless liquid (85%, 65 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 2H), 7.71 (dd, J_1 = 7.9 Hz, J_2 = 1.4 Hz, 2H), 7.48-7.38 (m, 3H), 7.38-7.29 (m, 3H), 7.04 (s, 1H), 4.77 (s, 2H), 0.22 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.4, 137.2, 135.7, 130.6, 130.1, 129.2, 129.0, 128.1, 128.0, 115.4, 107.7, 105.1, -0.2. **HRMS** (ESI) m/z Calculated for $C_{19}H_{22}NaSi_2^+$ $[M+Na]^+$: 329.1158, found: 329.1152.

(*E*)-(5,5-dimethyl-1-phenylhex-1-en-3-yn-2-yl)(phenyl)silane (2b)



colorless liquid (60%, 44 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 2H), 7.73 (dd, J_1 = 7.9 Hz, J_2= 1.4 Hz, 2H), 7.46-7.39 (m, 3H), 7.39-7.34 (m, 2H), 7.34-7.28 (m, 1H), 6.99 (s, 1H), 4.77 (s, 2H), 1.29 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.8, 137.5, 135.8, 131.1, 130.0, 128.7, 128.1, 128.0, 116.3, 111.7, 79.4, 30.8, 28.8. **HRMS** (ESI) m/z Calculated for $C_{20}H_{22}NaSi^+$ $[M+Na]^+$: 313.1388, found: 313.1383.

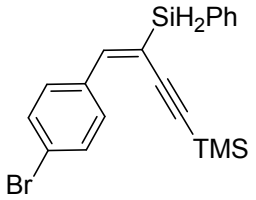
(*E*)-triisopropyl(4-phenyl-3-(phenylsilyl)but-3-en-1-yn-1-yl)silane (2c)



colorless liquid (91%, 89 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.5 Hz, 2H), 7.69 (dd, J_1 = 8.0 Hz, J_2= 1.3 Hz, 2H), 7.43-7.27 (m, 6H), 7.04 (s, 1H), 4.78 (s, 2H), 1.06 (s, 21H); **^{13}C**

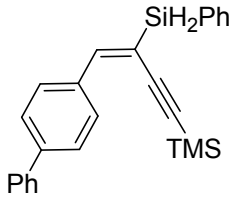
NMR (125 MHz, $CDCl_3$) δ 148.9, 137.3, 135.7, 130.6, 130.1, 129.13, 129.06, 128.17, 128.02, 115.9, 106.6, 105.0, 18.6, 11.4. **HRMS** (ESI) m/z Calculated for $C_{25}H_{34}NaSi_2^+$ $[M+Na]^+$: 413.2097, found: 413.2091.

(*E*)-(4-(4-bromophenyl)-3-(phenylsilyl)but-3-en-1-yn-1-yl)trimethylsilane (2d)



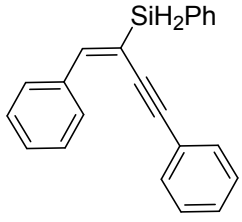
colorless liquid (71%, 68 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 2H), 7.70 (dd, J_1 = 8.0 Hz, J_2= 1.4 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.46-7.38 (m, 3H), 6.96 (s, 1H), 4.76 (s, 2H), 0.22 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.8, 136.0, 135.7, 131.3, 130.4, 130.3, 130.2, 128.1, 123.1, 116.6, 108.9, 104.7, -0.2. **HRMS** (ESI) m/z Calculated for $C_{19}H_{21}BrNaSi_2^+$ $[M+Na]^+$: 407.0263, found: 407.0257.

(*E*)-(4-([1,1'-biphenyl]-4-yl)-3-(phenylsilyl)but-3-en-1-yn-1-yl)trimethylsilane (2e)



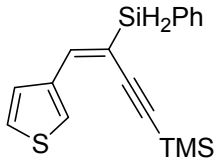
colorless liquid (60%, 57 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.74 (dd, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 2H), 7.67-7.59 (m, 4H), 7.50-7.34 (m, 6H), 7.09 (s, 1H), 4.81 (s, 2H), 0.25 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.9, 141.8, 140.5, 136.2, 135.7, 130.6, 130.1, 129.5, 128.8, 128.0, 127.6, 127.0, 126.8, 115.3, 108.0, 105.2, 0.16. **HRMS** (ESI) m/z Calculated for $C_{25}H_{26}NaSi_2^+$ $[M+Na]^+$: 405.1471, found: 405.1465.

(*E*)-(1,4-diphenylbut-1-en-3-yn-2-yl)(phenyl)silane (2f)



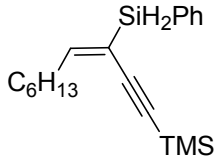
colorless liquid (75%, 58 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.78 (d, *J* = 7.0 Hz, 2H), 7.50-7.38 (m, 7H), 7.38-7.30 (m, 4H), 7.12 (s, 1H), 4.88 (d, *J* = 1.8 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.3, 137.3, 135.7, 131.4, 130.6, 130.1, 129.1, 129.0, 128.3, 128.2, 128.1, 123.8, 115.0, 101.3, 89.7. **^{29}Si NMR** (79.5 MHz, $CDCl_3$) δ -28.2. **HRMS** (ESI) m/z Calculated for $C_{22}H_{18}NaSi^+$ $[M+Na]^+$: 333.1075, found: 333.1079.

(*E*)-trimethyl(3-(phenylsilyl)-4-(thiophen-3-yl)but-3-en-1-yn-1-yl)silane (2g)



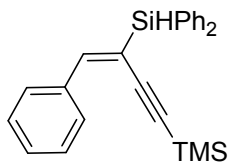
colorless liquid (78%, 61 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.5 Hz, 1H), 7.73 (d, *J* = 5.1 Hz, 1H), 7.69 (d, J = 7.5 Hz, 2H), 7.47-7.38 (m, 3H), 7.28-7.27 (m, 1H), 7.05 (s, 1H), 4.75 (s, 2H), 0.22 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.9, 140.0, 135.7, 130.6, 130.1, 128.0, 126.9, 125.0, 113.4, 107.0, 105.7, -0.15. **HRMS** (ESI) m/z Calculated for $C_{17}H_{20}NaSSi_2^+$ $[M+Na]^+$: 335.0722, found: 335.0717.

(*E*)-trimethyl(3-(phenylsilyl)dec-3-en-1-yn-1-yl)silane (2h)



colorless liquid (65%, 51 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 6.5 Hz, 2H), 7.43-7.36 (m, 3H), 6.39 (t, *J* = 7.1 Hz, 1H), 4.61 (s, 2H), 2.41 (q, *J* = 7.2 Hz, 2H), 1.44-1.41 (m, 2H), 1.31-1.29 (m, 6H), 0.89 (t, *J* = 6.4 Hz, 3H), 0.17 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.2, 135.6, 130.8, 129.9, 127.9, 116.3, 103.5, 102.6, 32.9, 31.6, 28.9, 28.3, 22.6, 14.1, 0.05. **HRMS** (ESI) m/z Calculated for $C_{19}H_{30}NaSi_2^+$ $[M+Na]^+$: 337.1784, found: 337.1778.

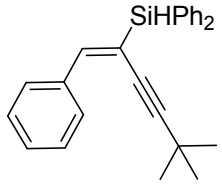
(*E*)-(3-(diphenylsilyl)-4-phenylbut-3-en-1-yn-1-yl)trimethylsilane (2i)



colorless liquid (64%, 61 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.1 Hz, 2H), 7.73 (dd,

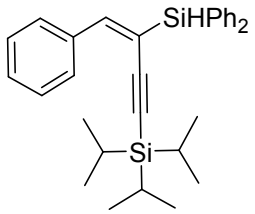
J_1 = 8.0 Hz, J_2 = 1.3 Hz, 4H), 7.47-7.31 (m, 9H), 7.08 (s, 1H), 5.28 (s, 1H), 0.16 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.6, 137.3, 135.8, 132.5, 129.97, 129.16, 129.12, 128.1, 127.9, 117.5, 108.4, 105.5, -0.3. **HRMS** (ESI) m/z Calculated for $C_{25}H_{26}NaSi_2^+$ $[M+Na]^+$: 405.1471, found: 405.1477. Characterization data matched with those reported in the literature.[3]

(*E*)-(5,5-dimethyl-1-phenylhex-1-en-3-yn-2-yl)diphenylsilane (2j)



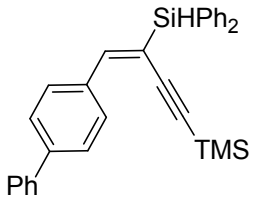
colorless liquid (75%, 68 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.2 Hz, 4H), 7.48-7.32 (m, 9H), 7.01 (s, 1H), 5.26 (s, 1H), 1.21 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.1, 137.6, 135.8, 133.0, 129.9, 128.8, 128.7, 128.1, 127.9, 118.2, 112.2, 79.9, 30.6, 28.8. **HRMS** (ESI) m/z Calculated for $C_{26}H_{26}NaSi^+$ $[M+Na]^+$: 389.1701, found: 389.1695.

(*E*)-(3-(diphenylsilyl)-4-phenylbut-3-en-1-yn-1-yl)triisopropylsilane (2k)



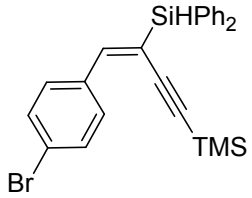
colorless liquid (88%, 102 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 2H), 7.75 (dd, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 4H), 7.49-7.44 (m, 2H), 7.44-7.39 (m, 4H), 7.39-7.33 (m, 3H), 7.12 (s, 1H), 5.33 (s, 1H), 1.07-1.03 (m, 21H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.5, 137.3, 135.8, 132.4, 129.94, 129.19, 129.09, 128.1, 128.0, 118.0, 107.0, 105.3, 18.6, 11.4. **HRMS** (ESI) m/z Calculated for $C_{31}H_{38}NaSi_2^+$ $[M+Na]^+$: 489.2410, found: 489.2401.

(*E*)-(4-([1,1'-biphenyl]-4-yl)-3-(diphenylsilyl)but-3-en-1-yn-1-yl)trimethylsilane (2l)



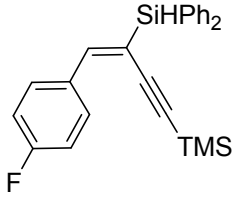
colorless liquid (91%, 104 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 2H), 7.82 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 4H), 7.73-7.66 (m, 4H), 7.55-7.46 (m, 8H), 7.45-7.38 (m, 1H), 7.20 (s, 1H), 5.40 (s, 1H), 0.26 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.1, 141.8, 140.5, 136.3, 135.8, 132.5, 129.98, 129.60, 128.8, 127.94, 127.54, 127.0, 126.8, 117.5, 108.7, 105.8, -0.27. **HRMS** (ESI) m/z Calculated for $C_{31}H_{30}NaSi_2^+$ $[M+Na]^+$: 481.1784, found: 481.1778.

(*E*)-(4-(4-bromophenyl)-3-(diphenylsilyl)but-3-en-1-yn-1-yl)trimethylsilane (2m)



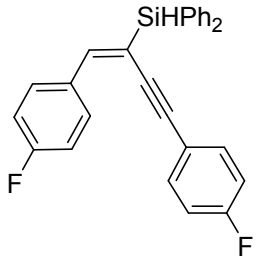
colorless liquid (78%, 90 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.70 (dd, J_1 = 7.9 Hz, J_2 = 1.4 Hz, 4H), 7.50-7.43 (m, 4H), 7.43-7.37 (m, 4H), 6.98 (s, 1H), 5.25 (s, 1H), 0.15 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.0, 136.1, 135.7, 132.2, 131.3, 130.5, 130.1, 128.0, 123.0, 118.7, 109.5, 105.2, -0.4. **HRMS** (ESI) m/z Calculated for $C_{25}H_{25}BrNaSi_2^+$ $[M+Na]^+$: 483.0576, found: 483.0581. Characterization data matched with those reported in the literature.[3]

(*E*)-(3-(diphenylsilyl)-4-(4-fluorophenyl)but-3-en-1-yn-1-yl)trimethylsilane (2n)



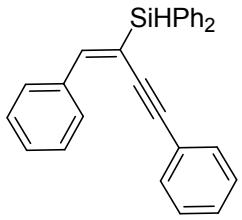
colorless liquid (89%, 89 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08-8.03 (m, 2H), 7.75 (dd, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 4H), 7.51-7.40 (m, 6H), 7.09-7.04 (m, 3H), 5.31 (s, 1H), 0.20 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 250.5 Hz), 148.1, 135.7, 133.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 132.4, 131.0 (d, $J_{C\text{-}F}$ = 8.3 Hz), 130.0, 128.0, 117.0 (d, $J_{C\text{-}F}$ = 2.0 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.3 Hz), 108.4, 105.4, -0.3. **HRMS** (ESI) m/z Calculated for $C_{25}H_{25}FNaSi_2^+$ $[M+Na]^+$: 423.1377, found: 423.1371. Characterization data matched with those reported in the literature.[3]

(*E*)-(1,4-bis(4-fluorophenyl)but-1-en-3-yn-2-yl)diphenylsilane (2o)



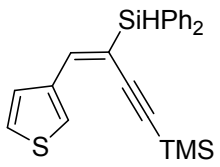
colorless liquid (92%, 97 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00-7.94 (m, 2H), 7.71 (dd, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 4H), 7.46-7.36 (m, 6H), 7.24-7.19 (m, 2H), 7.08-7.01 (m, 3H), 6.96 (t, J = 8.6 Hz, 2H), 5.33 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.9 (d, J_{C-F} = 250.3 Hz), 162.6 (d, J_{C-F} = 250.3 Hz), 147.2, 135.8, 133.8 (d, J = 3.2 Hz), 133.2 (d, J_{C-F} = 8.2 Hz), 132.4, 130.9 (d, J_{C-F} = 8.0 Hz), 130.1, 128.1, 119.9 (d, J_{C-F} = 3.3 Hz), 116.5 (d, J_{C-F} = 1.9 Hz), 115.6 (d, J_{C-F} = 21.8 Hz), 115.2 (d, J_{C-F} = 21.4 Hz), 100.6, 89.7. **HRMS** (ESI) m/z Calculated for $C_{28}H_{20}F_2NaSi^+$ $[M+Na]^+$: 445.1200, found: 445.1192. Characterization data matched with those reported in the literature.[3]

(*E*)-(1,4-diphenylbut-1-en-3-yn-2-yl)diphenylsilane (2p)



colorless liquid (83%, 80 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 2H), 7.77 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 2H), 7.50-7.38 (m, 8H), 7.37-7.27 (m, 6H), 7.13 (s, 1H), 5.38 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.7, 137.5, 135.8, 132.6, 131.4, 130.1, 129.1, 128.34, 128.32, 128.19, 128.09, 124.0, 117.1, 101.8, 90.3. **HRMS** (ESI) m/z Calculated for $C_{28}H_{22}NaSi^+$ $[M+Na]^+$: 409.1388, found: 409.1395. Characterization data matched with those reported in the literature.[3]

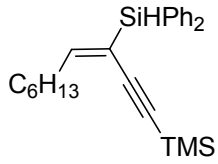
(*E*)-(3-(diphenylsilyl)-4-(thiophen-3-yl)but-3-en-1-yn-1-yl)trimethylsilane (2q)



colorless liquid (80%, 77 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, J = 2.5 Hz, 1H), 7.76 (d, J

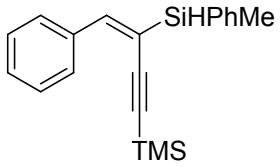
= 5.0 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 4H), 7.47-7.38 (m, 6H), 7.29-7.27 (m, 1H), 7.09 (s, 1H), 5.26 (s, 1H), 0.17 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.1, 140.1, 135.7, 132.5, 129.9, 128.1, 127.9, 126.9, 124.9, 115.4, 107.7, 106.2, -0.3. **HRMS** (ESI) m/z Calculated for $C_{23}H_{24}NaSSi_2^+$ $[M+Na]^+$: 411.1035, found: 411.1039. Characterization data matched with those reported in the literature.[3]

(*E*)-(3-(diphenylsilyl)dec-3-en-1-yn-1-yl)trimethylsilane (2r)



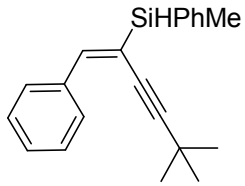
colorless liquid (80%, 78 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.6 Hz, 4H), 7.43-7.37 (m, 6H), 6.41 (t, *J* = 7.1 Hz, 1H), 5.12 (s, 1H), 2.47 (q, *J* = 7.16 Hz, 2H), 1.45-1.43 (m, 2H), 1.34-1.31 (m, 6H), 0.90 (t, *J* = 14.9, 3H), 0.13 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.4, 135.6, 132.8, 129.8, 127.8, 118.3, 104.1, 103.2, 32.8, 31.5, 28.9, 28.4, 22.6, 14.1, -0.04. **^{29}Si NMR** (799.4 MHz, $CDCl_3$) δ -18.4, -18.8. **HRMS** (ESI) m/z Calculated for $C_{25}H_{34}NaSi_2^+$ $[M+Na]^+$: 413.2097, found: 413.2091.

(*E*)-trimethyl(3-(methyl(phenyl)silyl)-4-phenylbut-3-en-1-yn-1-yl)silane (2s)



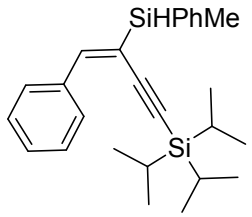
colorless liquid (83%, 66 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 7.0 Hz, 2H), 7.47-7.29 (m, 6H), 6.97 (s, 1H), 4.78 (q, *J* = 3.6 Hz, 1H), 0.63 (d, *J* = 3.6 Hz, 3H), 0.25 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.0, 137.3, 134.8, 134.3, 129.7, 128.98, 128.96, 128.10, 127.9, 119.2, 107.7, 105.3, -0.2, -5.7. **HRMS** (ESI) m/z Calculated for $C_{20}H_{24}NaSi_2^+$ $[M+Na]^+$: 343.1314, found: 343.1318.

(*E*)-(5,5-dimethyl-1-phenylhex-1-en-3-yn-2-yl)(methyl)(phenyl)silane (2t)



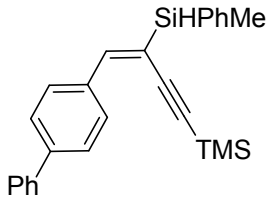
colorless liquid (63%, 48 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.65 (dd, J_1 = 7.5 Hz, J_2 = 1.4 Hz, 2H), 7.41-7.22 (m, 6H), 6.87 (s, 1H), 4.72 (q, J = 3.6 Hz, 1H), 1.27 (s, 9H), 0.57 (d, J = 3.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.3, 137.6, 134.8, 129.6, 128.7, 128.4, 128.0, 127.8, 120.0, 111.7, 79.5, 30.8, 28.8, -5.7. **HRMS** (ESI) m/z Calculated for $C_{21}H_{24}NaSi^+$ $[M+Na]^+$: 327.1545, found: 327.1539.

(*E*)-triisopropyl(3-(methyl(phenyl)silyl)-4-phenylbut-3-en-1-yn-1-yl)silane (2v)



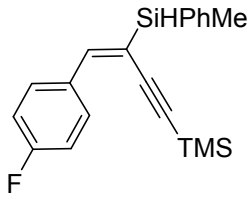
colorless liquid (93%, 94 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, J = 7.8 Hz, 2H), 7.69 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 2H), 7.45-7.37 (m, 3H), 7.37-7.30 (m, 3H), 7.01 (s, 1H), 4.80 (q, J = 3.6 Hz, 1H), 1.11 (s, 21H), 0.63 (d, J = 3.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.7, 137.4, 134.8, 134.3, 129.7, 129.1, 128.9, 128.1, 127.9, 119.6, 106.8, 104.6, 18.7, 11.4, -5.6. **HRMS** (ESI) m/z Calculated for $C_{26}H_{36}NaSi_2^+$ $[M+Na]^+$: 427.2253, found: 427.2248.

(*E*)-(4-([1,1'-biphenyl]-4-yl)-3-(methyl(phenyl)silyl)but-3-en-1-yn-1-yl)trimethylsilane (2w)



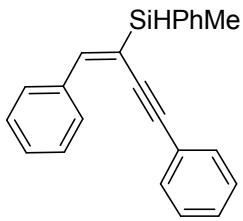
colorless liquid (79%, 78.3 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 7.5 Hz, 2H), 7.68-7.59 (m, 4H), 7.50-7.35 (m, 6H), 7.02 (s, 1H), 4.81 (q, J = 3.6 Hz, 1H), 0.65 (d, J = 3.6 Hz, 3H), 0.28 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.5, 141.6, 140.6, 136.4, 134.8, 134.3, 129.8, 129.5, 128.8, 127.9, 127.5, 127.0, 126.7, 119.2, 108.1, 105.5, -0.1, -5.7. **HRMS** (ESI) m/z Calculated for $C_{26}H_{28}NaSi_2^+$ $[M+Na]^+$: 419.1627, found: 419.1621.

(E)-(4-(4-fluorophenyl)-3-(methyl(phenyl)silyl)but-3-en-1-yn-1-yl)trimethylsilane(2x)



colorless liquid (85%, 72 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03-7.98 (m, 2H), 7.68 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 2H), 7.47-7.39 (m, 3H), 7.07-7.02 (m, 2H), 6.92 (s, 1H), 4.77 (q, J = 3.6 Hz, 1H), 0.63 (d, J = 3.6 Hz, 3H), 0.25 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 250.4 Hz), 146.5, 134.8, 134.2, 133.7 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.8 (d, $J_{C\text{-}F}$ = 8.1 Hz), 129.8, 127.9, 118.7 (d, $J_{C\text{-}F}$ = 2.3 Hz), 115.0 (d, $J_{C\text{-}F}$ = 21.6 Hz), 107.7, 105.1, -0.2, -5.8. **HRMS** (ESI) m/z Calculated for $C_{20}H_{23}FNaSi_2^+$ $[M+Na]^+$: 361.1220, found: 361.1213.

(*E*)-(1,4-diphenylbut-1-en-3-yn-2-yl)(methyl)(phenyl)silane (2y)



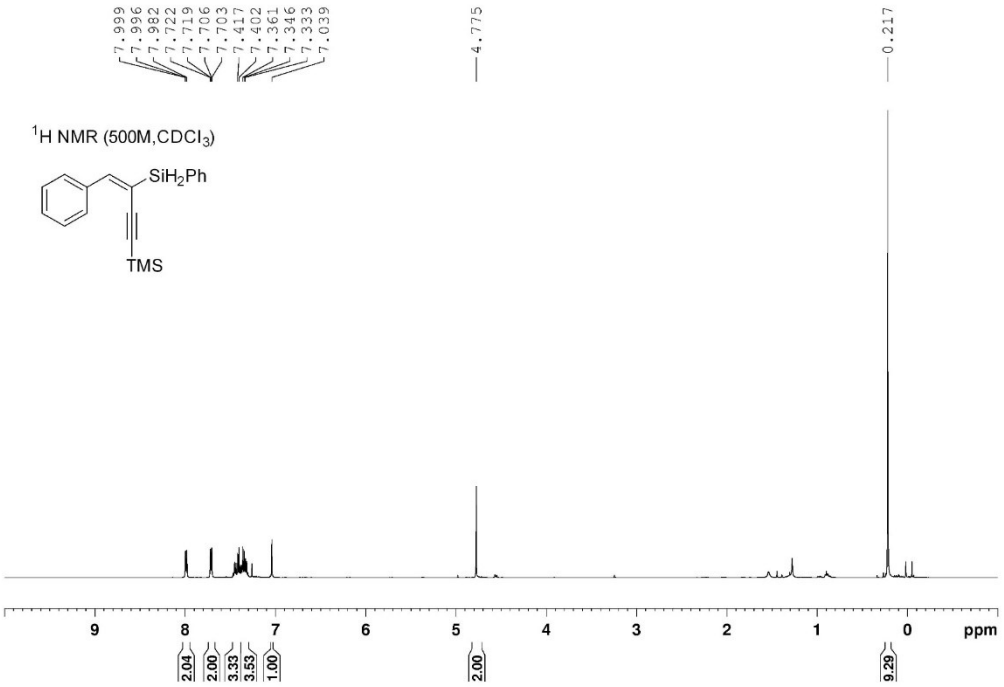
colorless liquid (77%, 62 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, J = 7.9 Hz, 2H), 7.72 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 2H), 7.47-7.37 (m, 7H), 7.37-7.30 (m, 4H), 7.03 (s, 1H), 4.85 (q, J = 3.6 Hz, 1H), 0.69 (d, J = 3.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.0, 137.5, 134.9, 134.4, 131.4, 129.8, 128.96, 128.88, 128.37, 128.31, 128.15, 128.01, 124.1, 118.9, 89.94, -5.5. **HRMS** (ESI) m/z Calculated for $C_{23}H_{20}NaSi^+$ $[M+Na]^+$: 347.1232, found: 347.1228. Characterization data matched with those reported in the literature.[3]

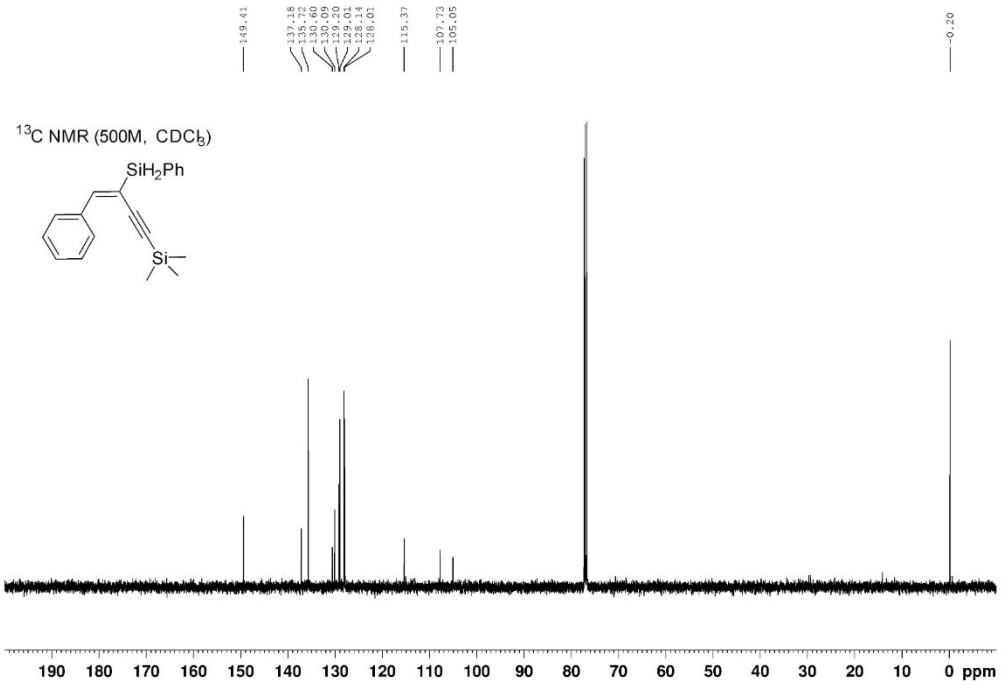
reference:

[3] Sang, H.; Hu, Y.; Ge, S. *Org. Lett.* **2019**, *21*, 5234-5237.

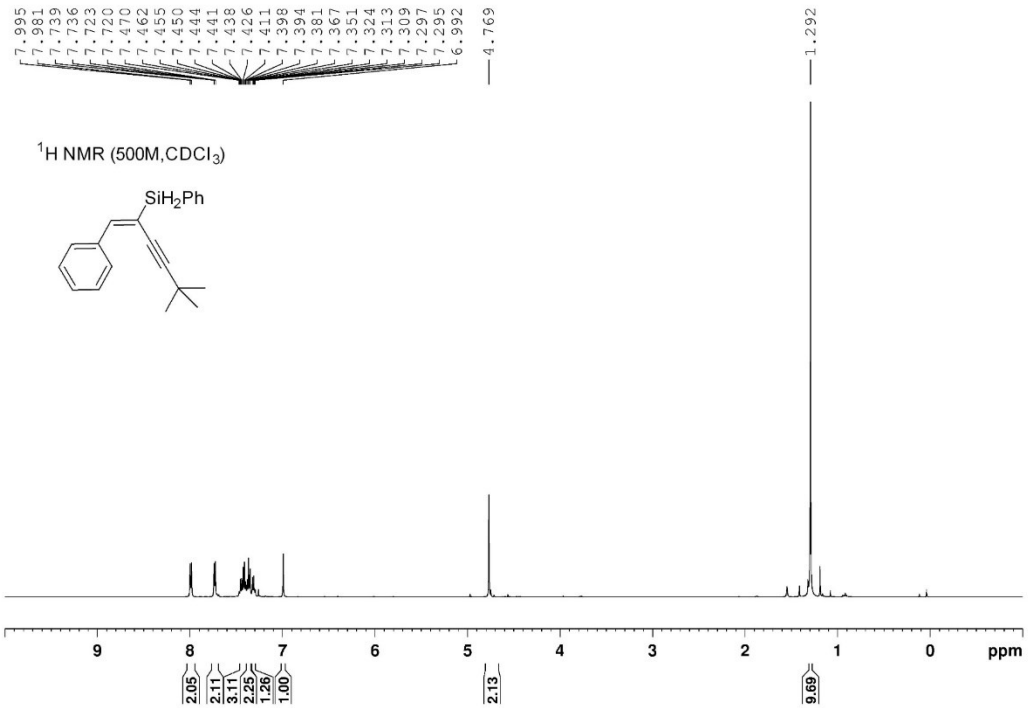
S9. NMR spectra

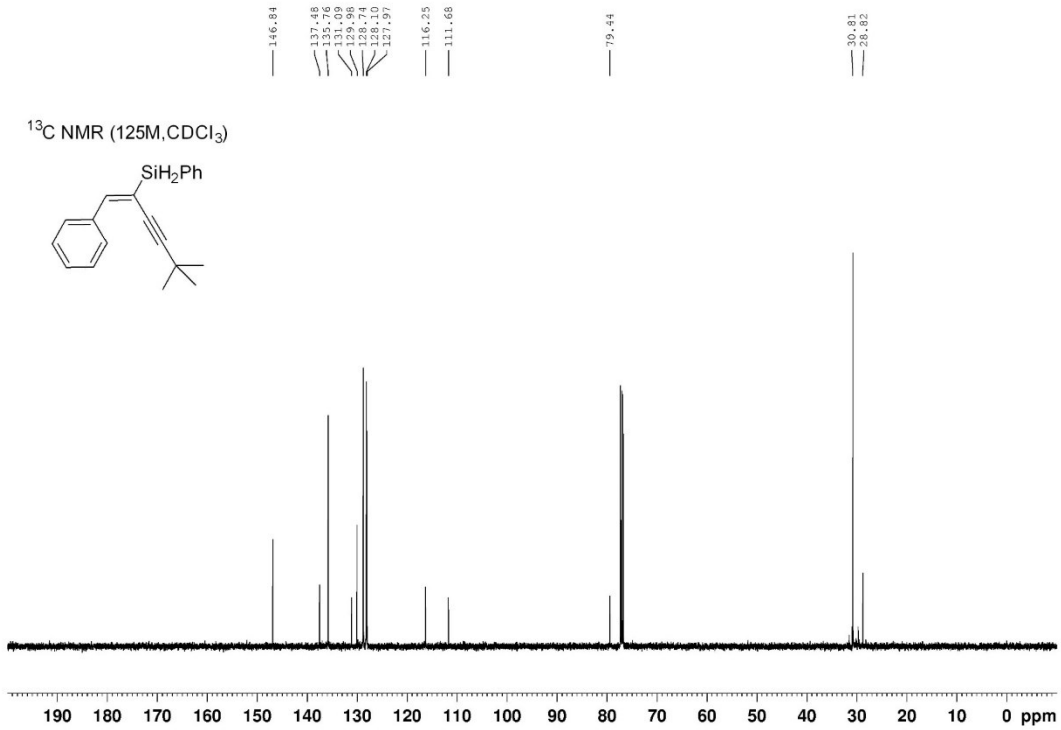
(*E*)-trimethyl(4-phenyl-3-(phenylsilyl)but-3-en-1-yn-1-yl)silane (2a)



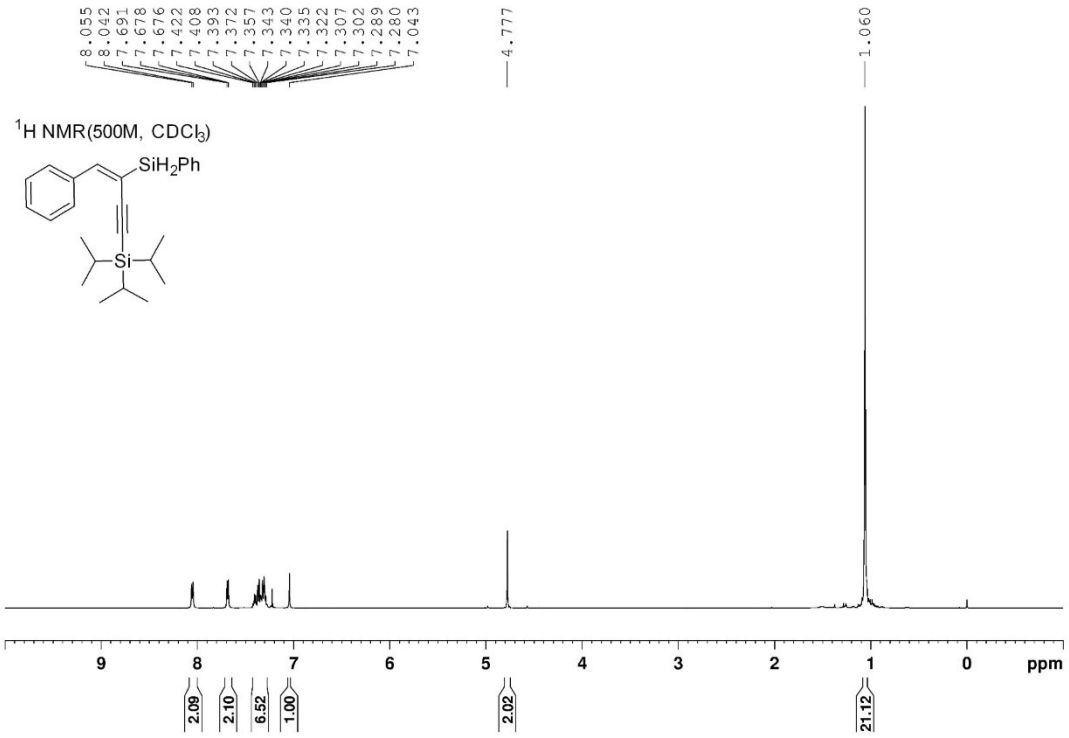


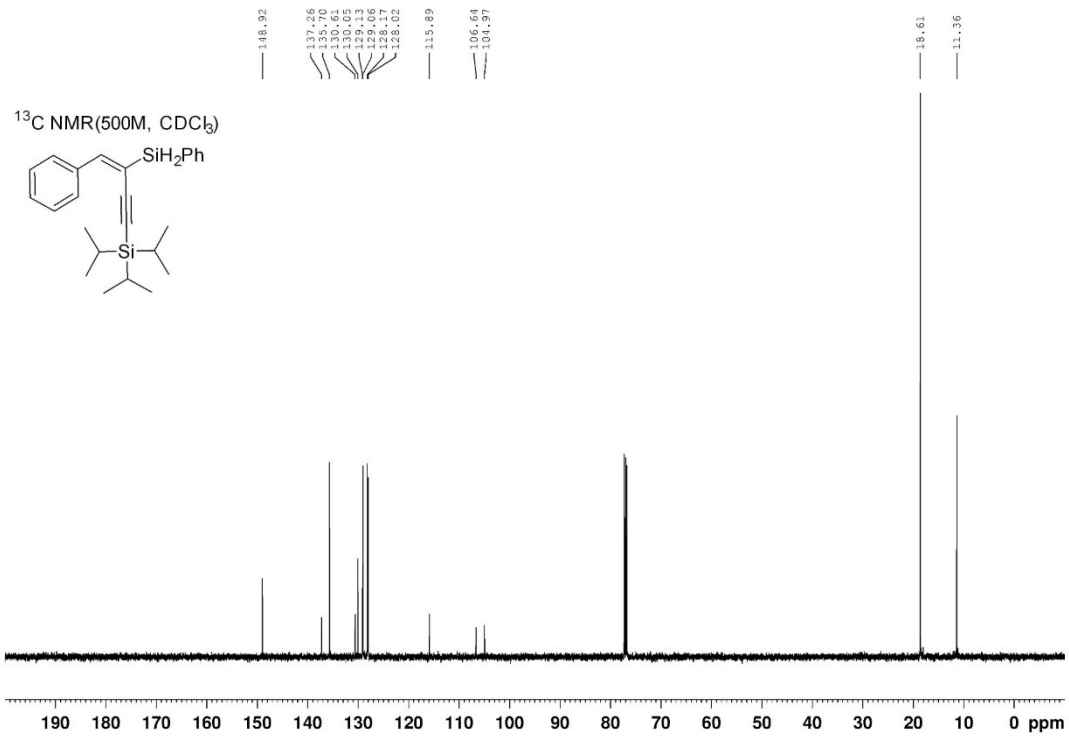
(*E*)-(5,5-dimethyl-1-phenylhex-1-en-3-yn-2-yl)(phenyl)silane (2b)



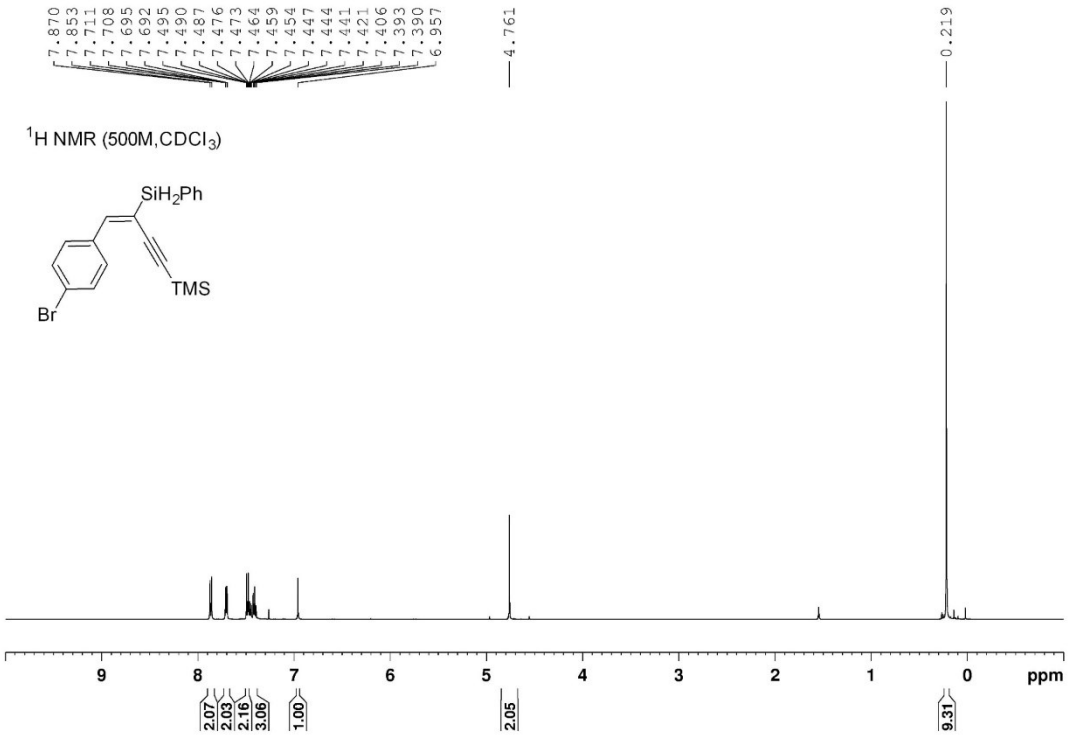


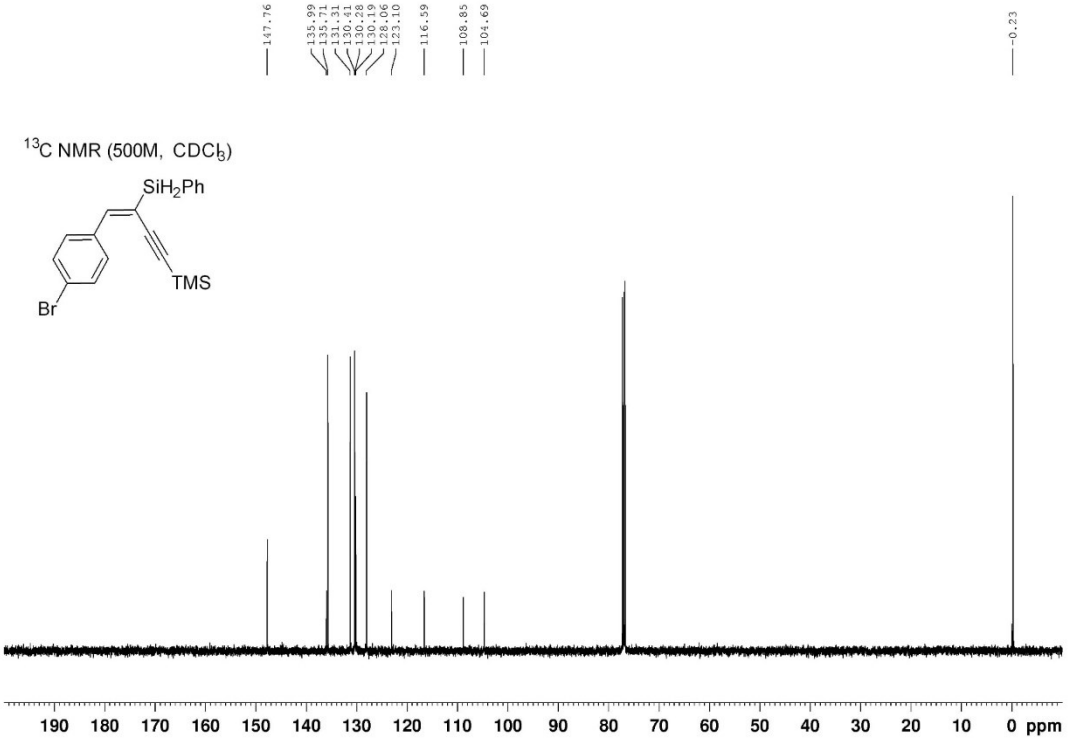
(*E*)-triisopropyl(4-phenyl-3-(phenylsilyl)but-3-en-1-yn-1-yl)silane (2c)



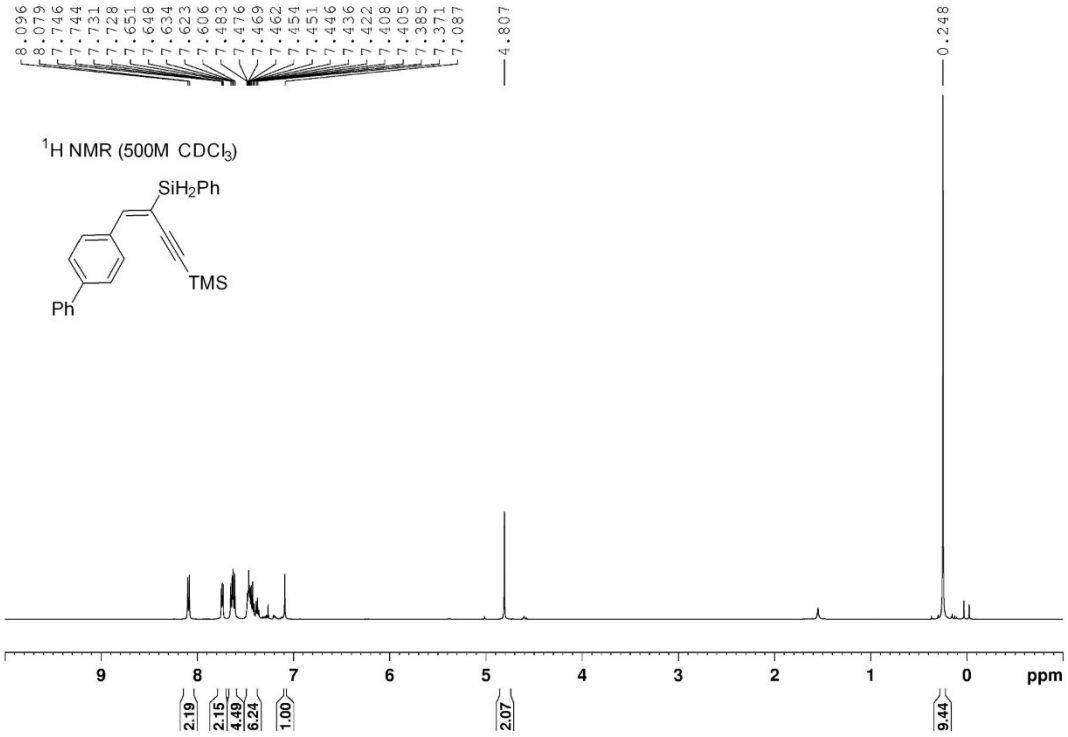


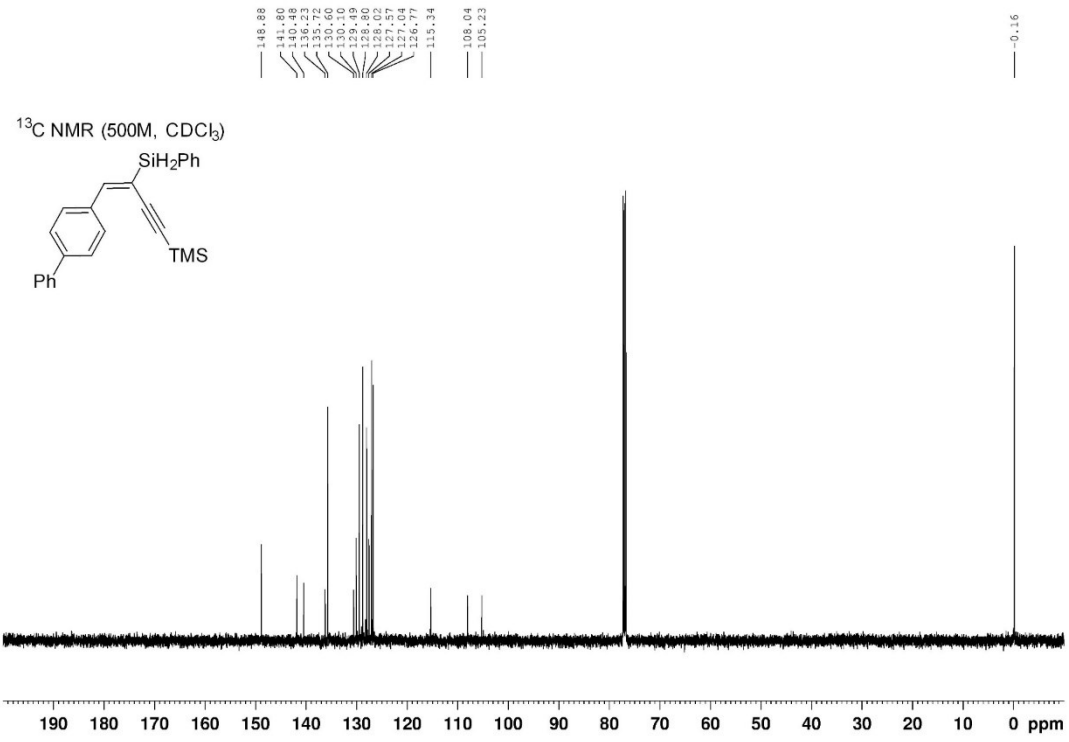
(*E*)-(4-(4-bromophenyl)-3-(phenylsilyl)but-3-en-1-yn-1-yl)trimethylsilane (2d)



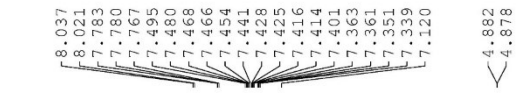


(*E*)-(4-([1,1'-biphenyl]-4-yl)-3-(phenylsilyl)but-3-en-1-yn-1-yl)trimethylsilane (2e)

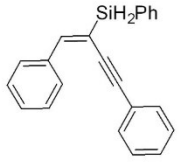


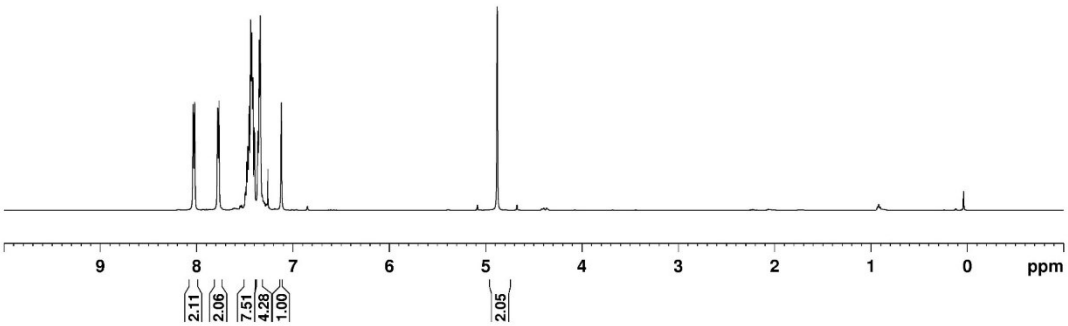


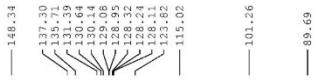
(*E*)-(1,4-diphenylbut-1-en-3-yn-2-yl)(phenyl)silane (2f)



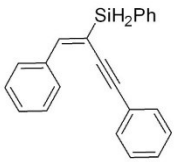
^{1}H NMR (500M,$CDCl_3$)





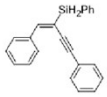


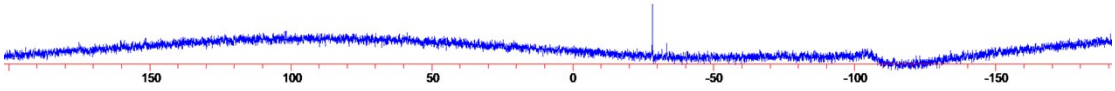
^{13}C NMR (500M, $CDCl_3$)



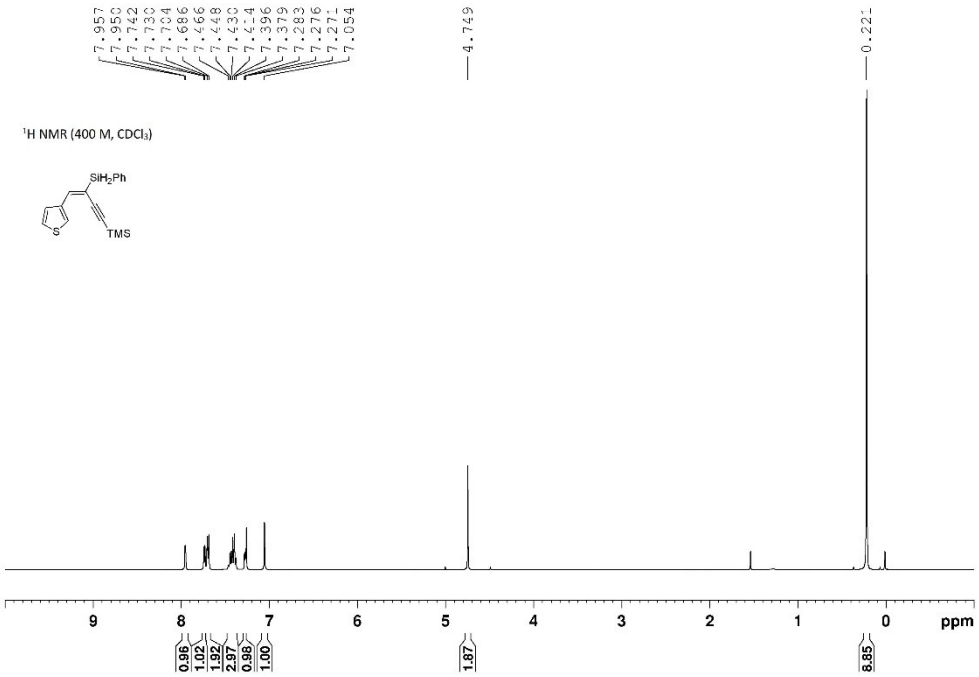
^{29}Si NMR 79.5 MHz decoupling $CDCl_3$

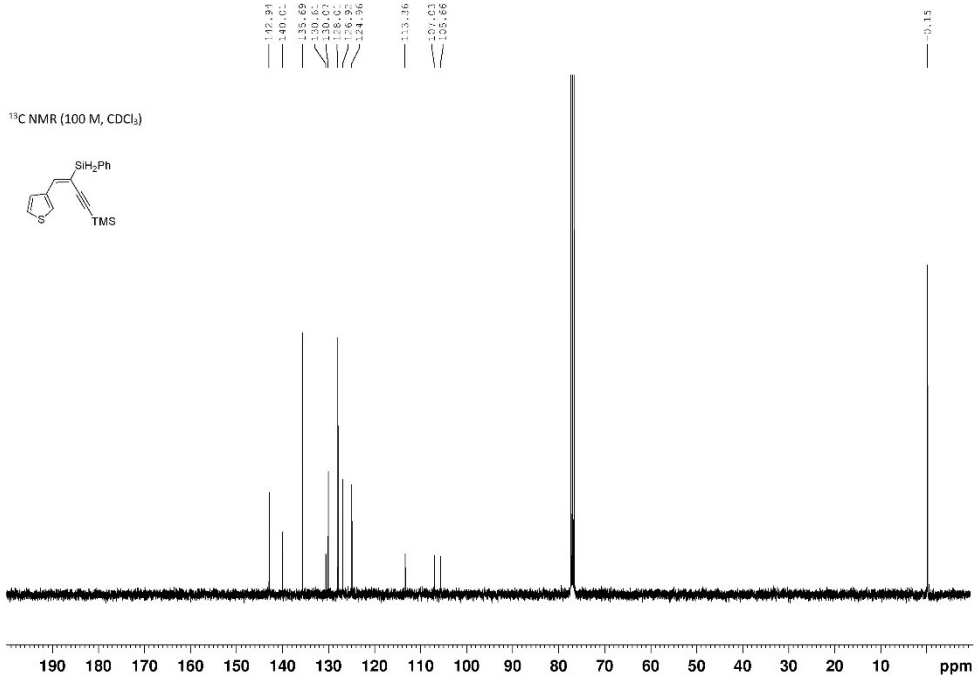
-28.247



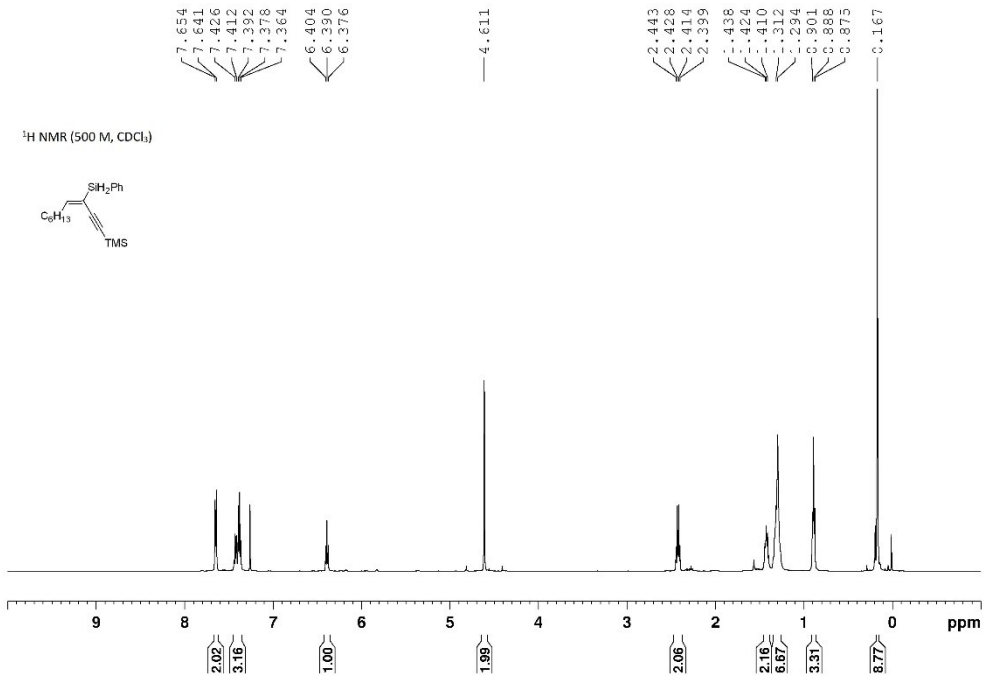


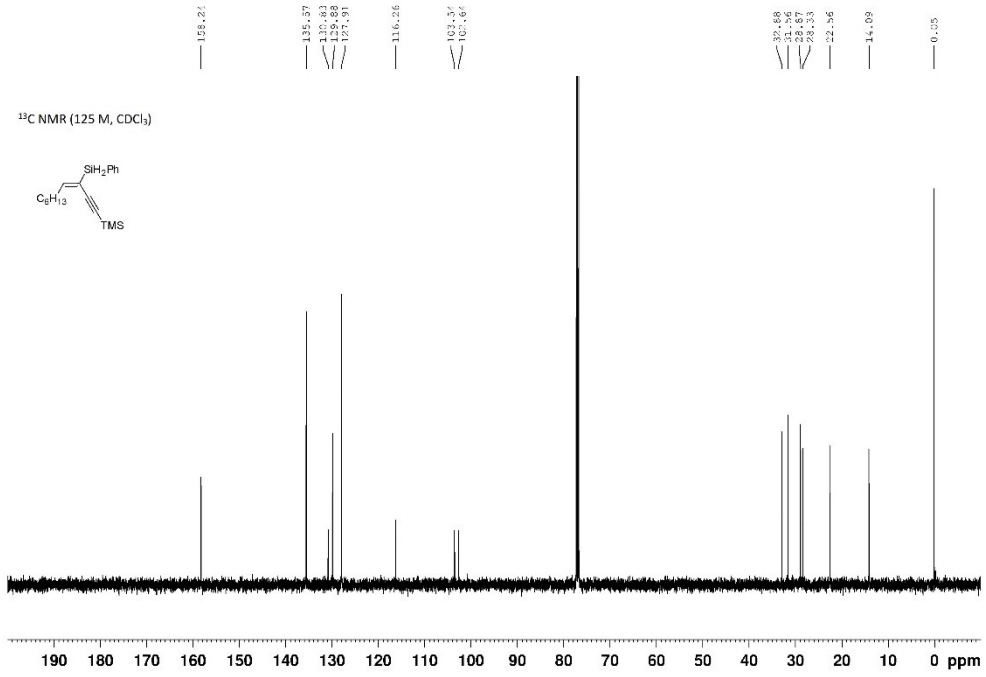
(*E*)-trimethyl(3-(phenylsilyl)-4-(thiophen-3-yl)but-3-en-1-yn-1-yl)silane (2g)



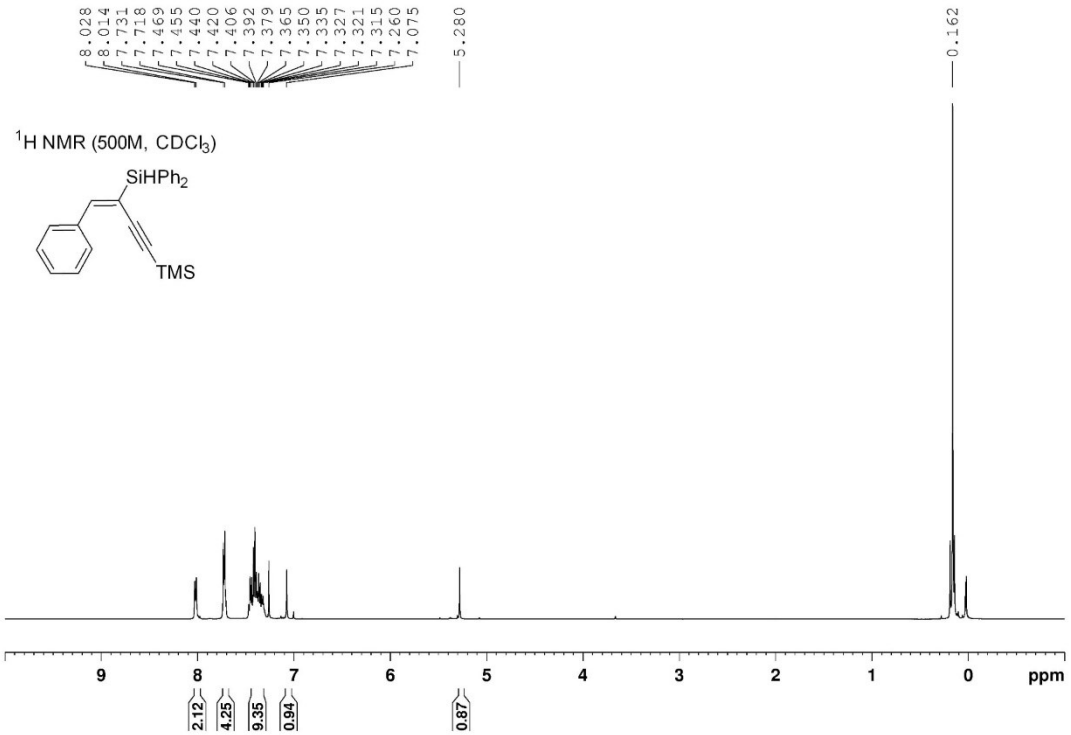


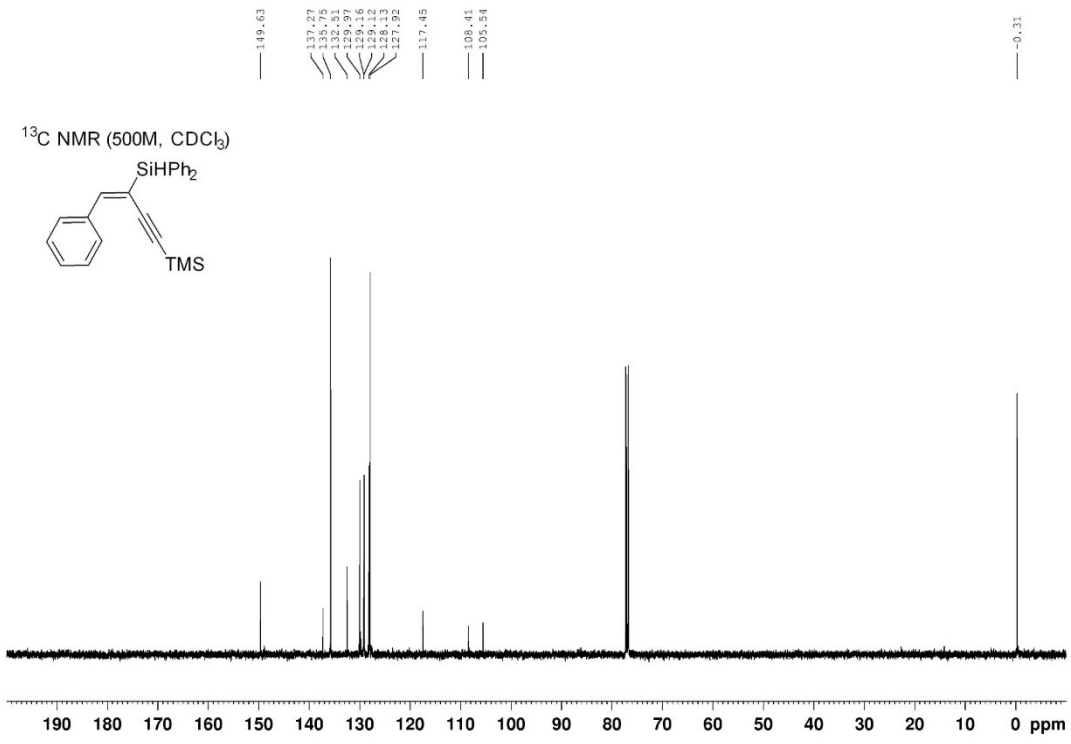
(*E*)-trimethyl(3-(phenylsilyl)dec-3-en-1-yn-1-yl)silane (2h)



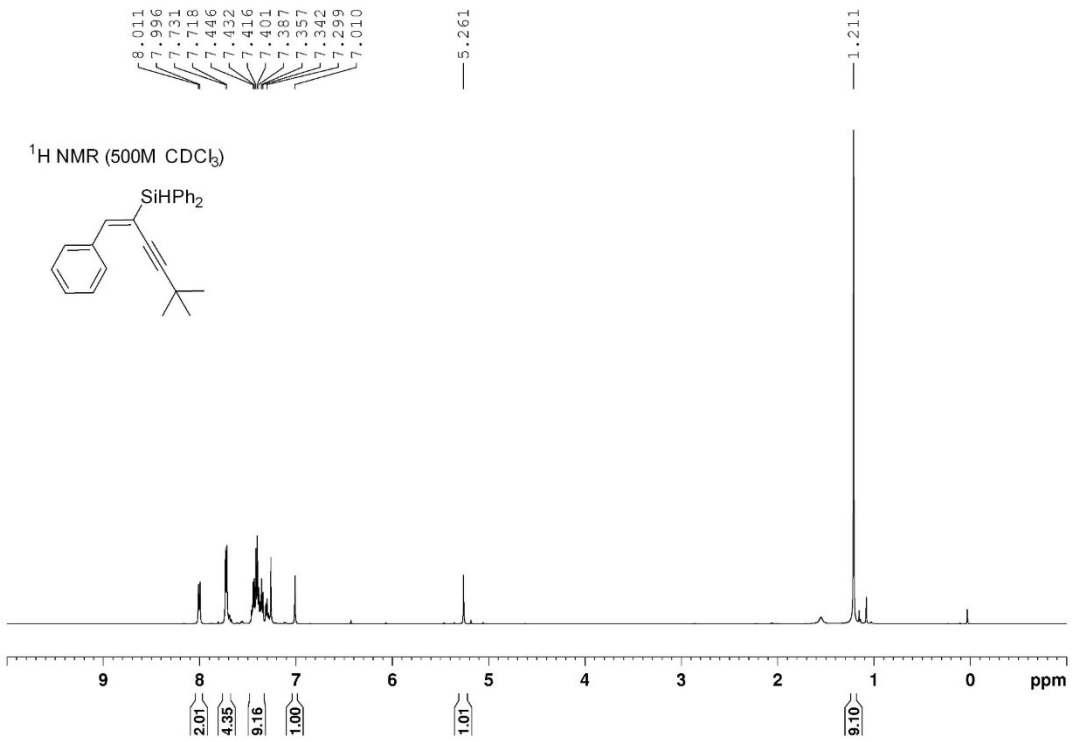


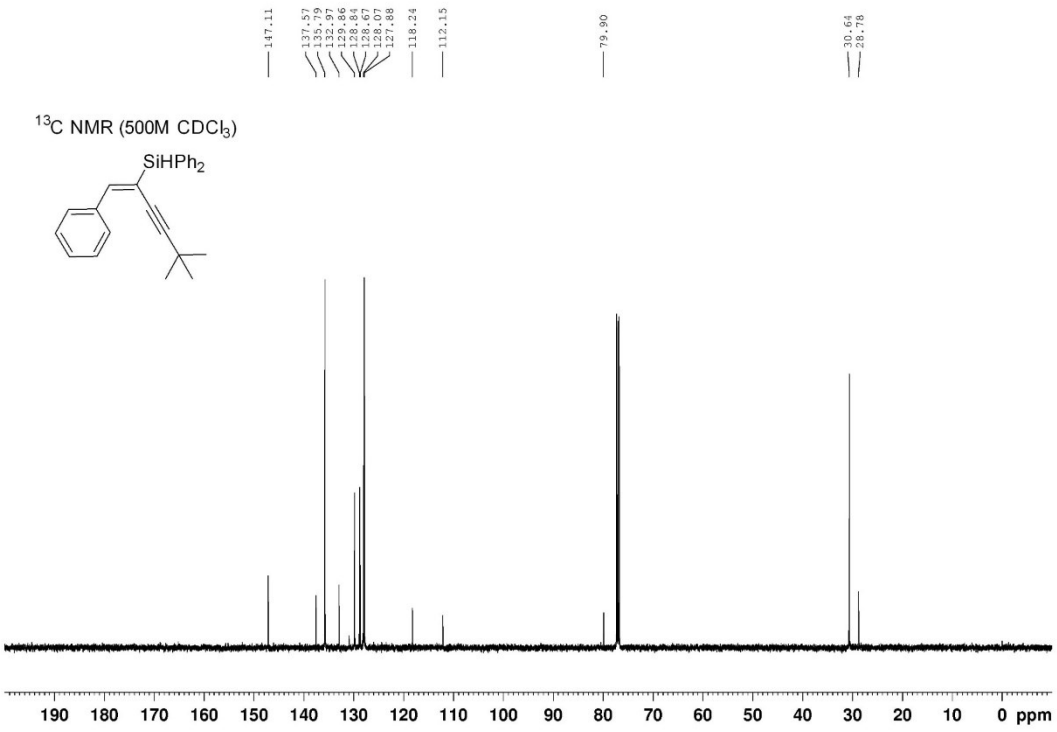
(*E*)-(3-(diphenylsilyl)-4-phenylbut-3-en-1-yn-1-yl)trimethylsilane (2i)



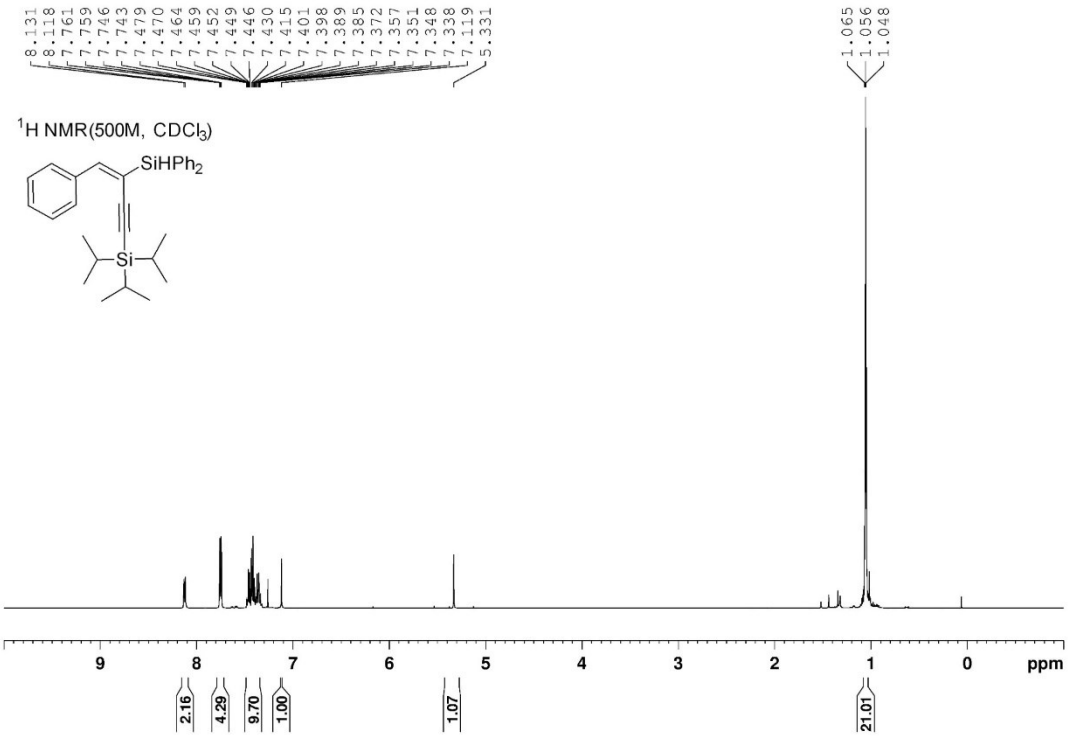


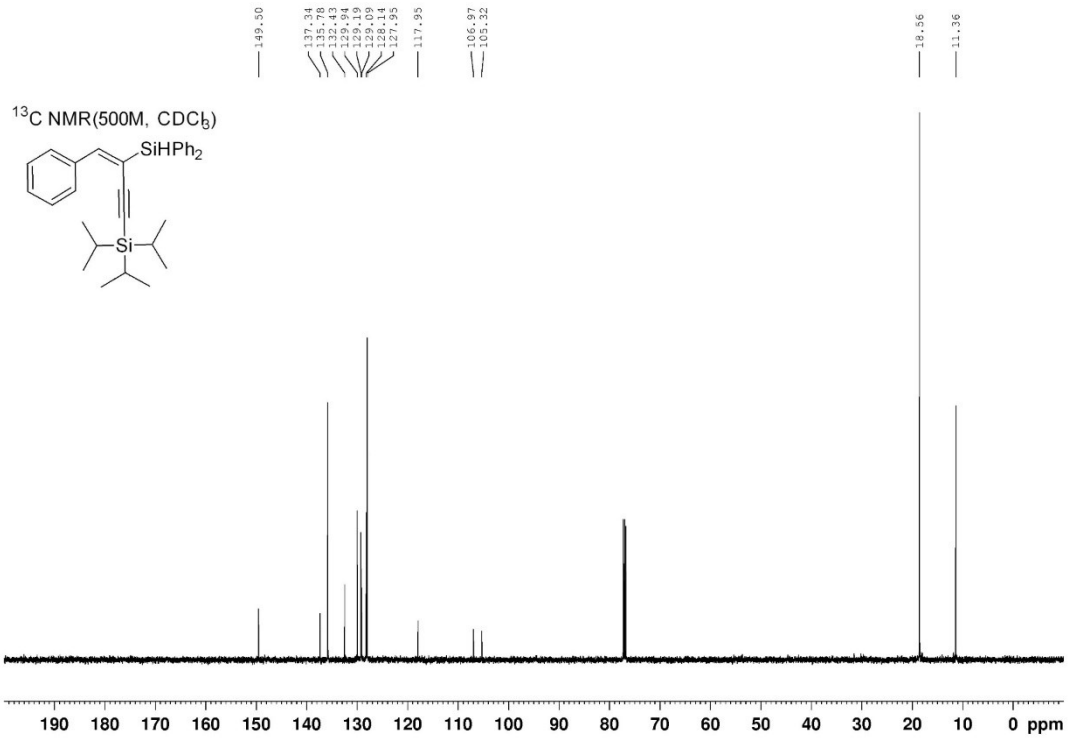
(*E*)-(5,5-dimethyl-1-phenylhex-1-en-3-yn-2-yl)diphenylsilane (2j)



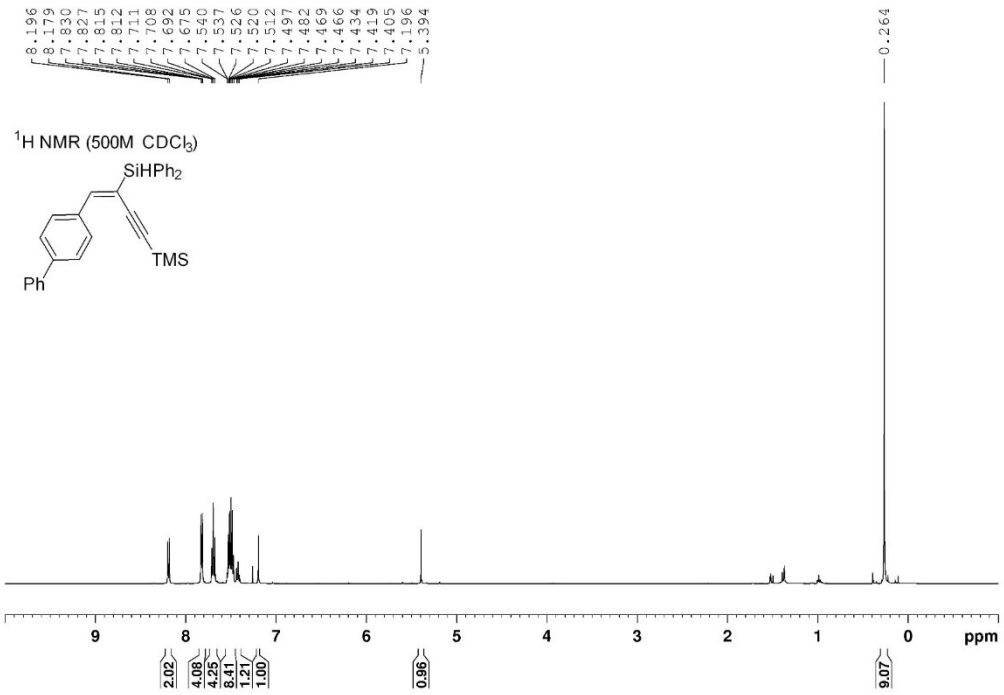


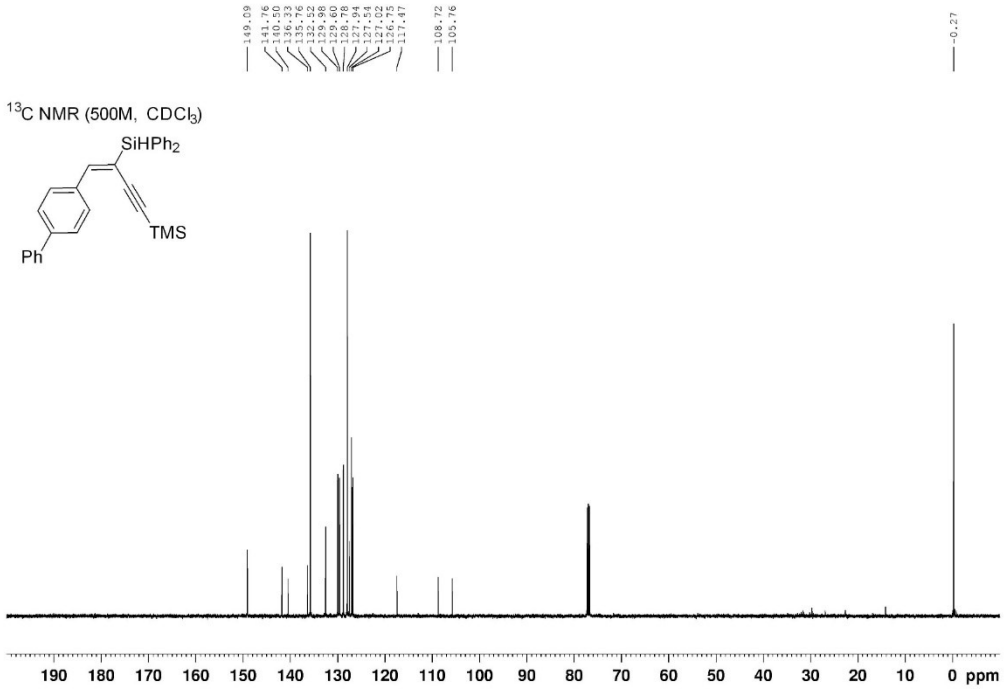
(*E*)-(3-(diphenylsilyl)-4-phenylbut-3-en-1-yn-1-yl)triisopropylsilane (2k)



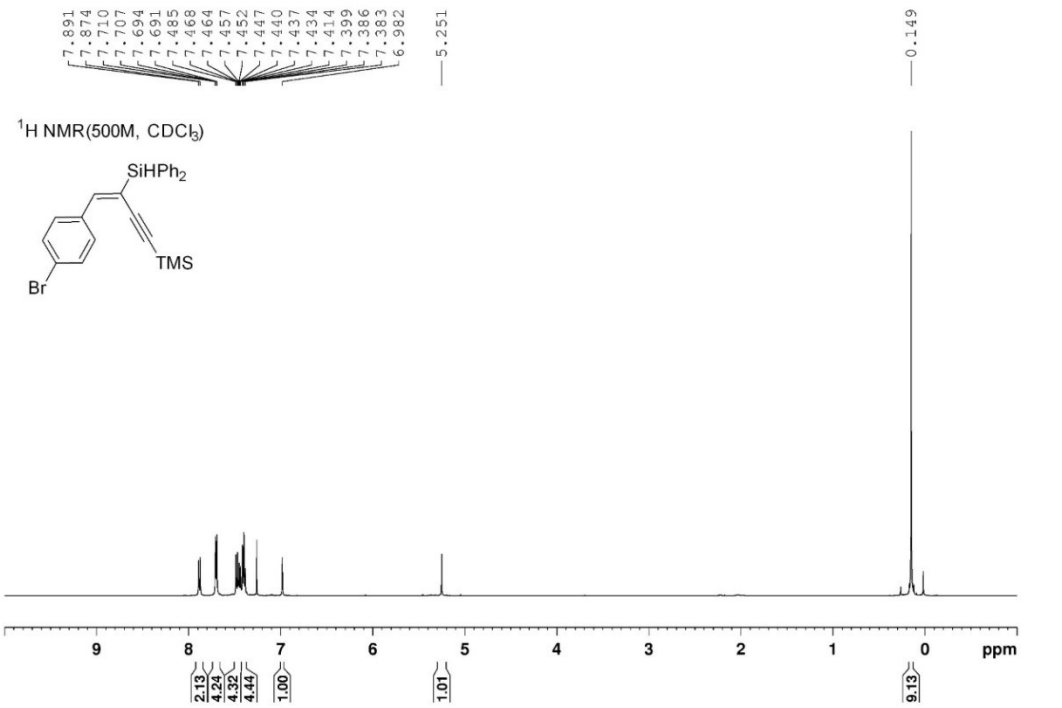


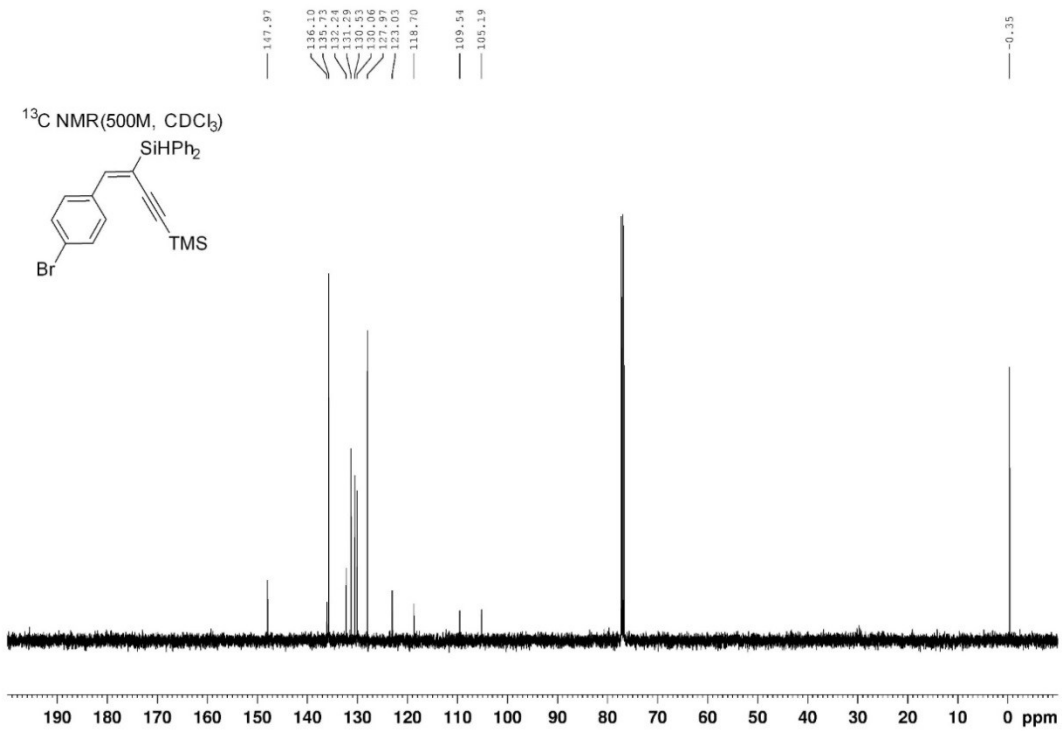
(*E*)-(4-([1,1'-biphenyl]-4-yl)-3-(diphenylsilyl)but-3-en-1-yn-1-yl)trimethylsilane (2l)



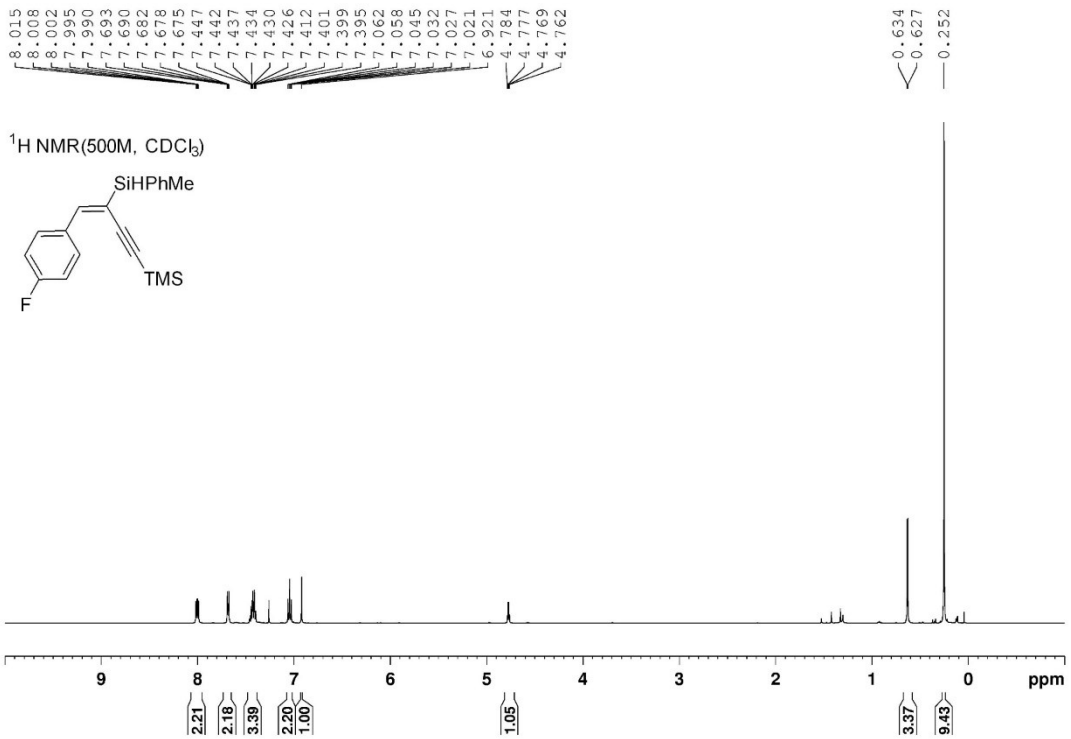


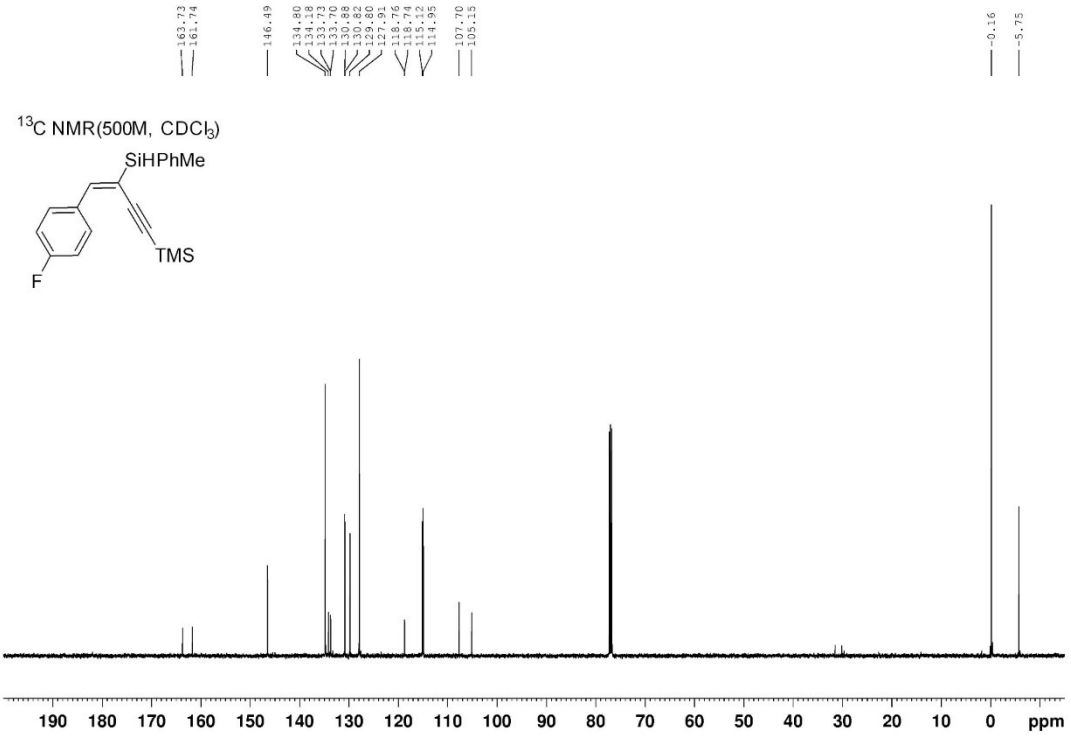
(*E*)-(4-(4-bromophenyl)-3-(diphenylsilyl)but-3-en-1-yn-1-yl)trimethylsilane (2m)



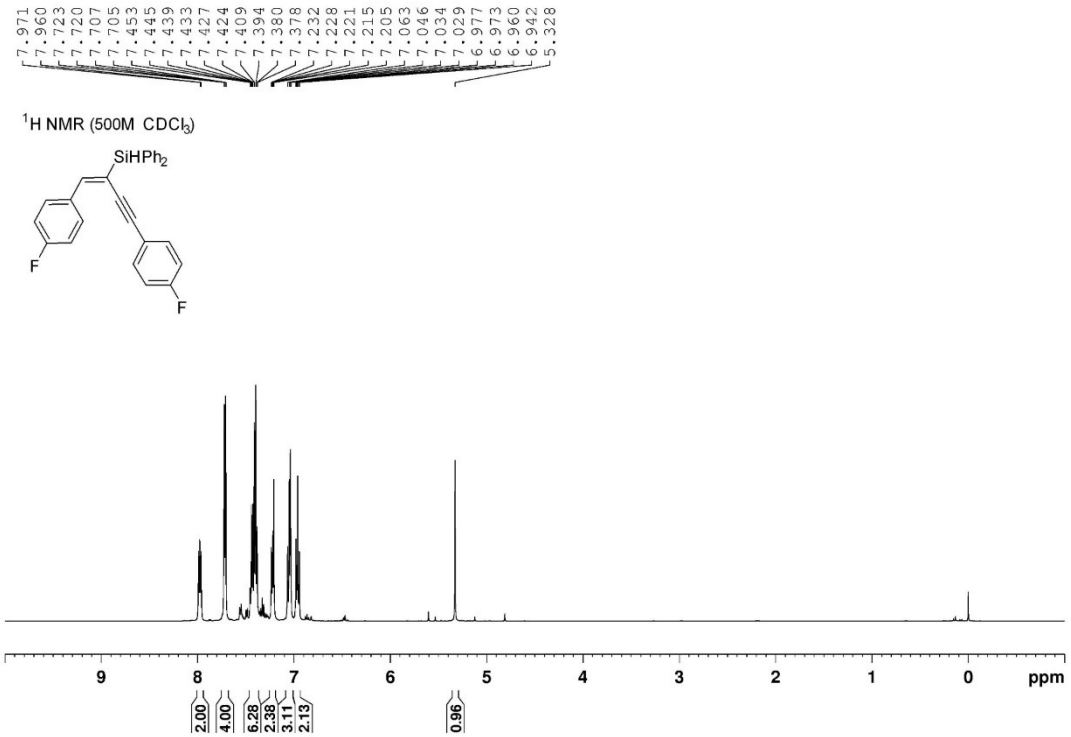


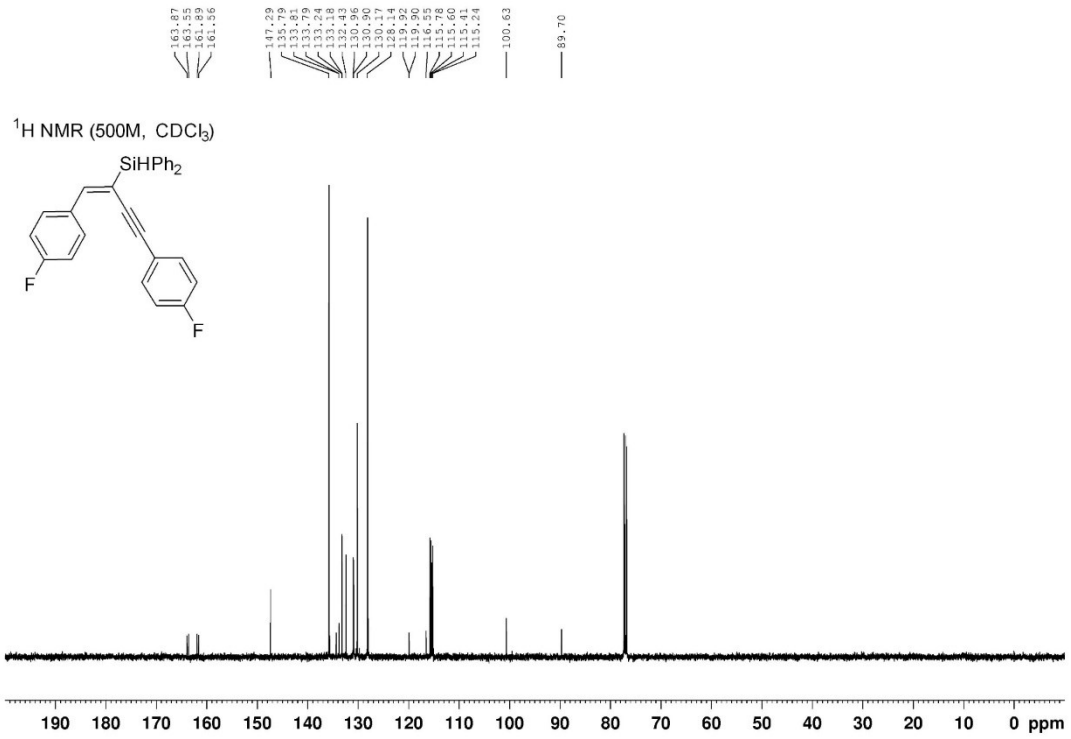
(*E*)-(3-(diphenylsilyl)-4-(4-fluorophenyl)but-3-en-1-yn-1-yl)trimethylsilane (2n)



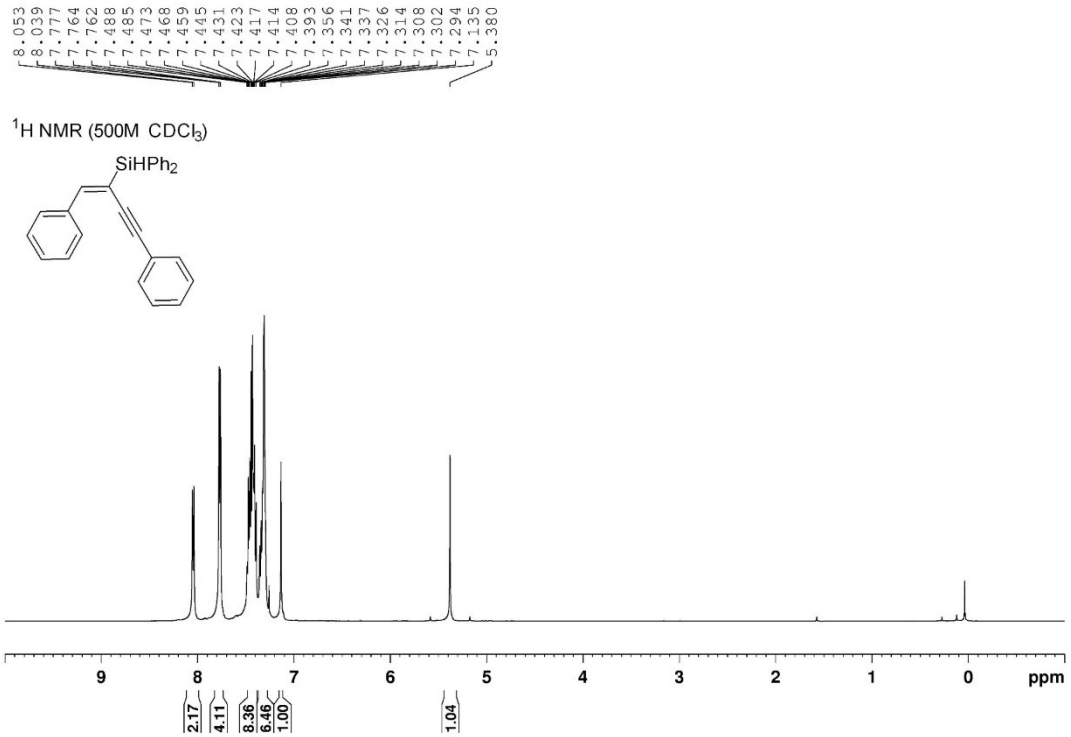


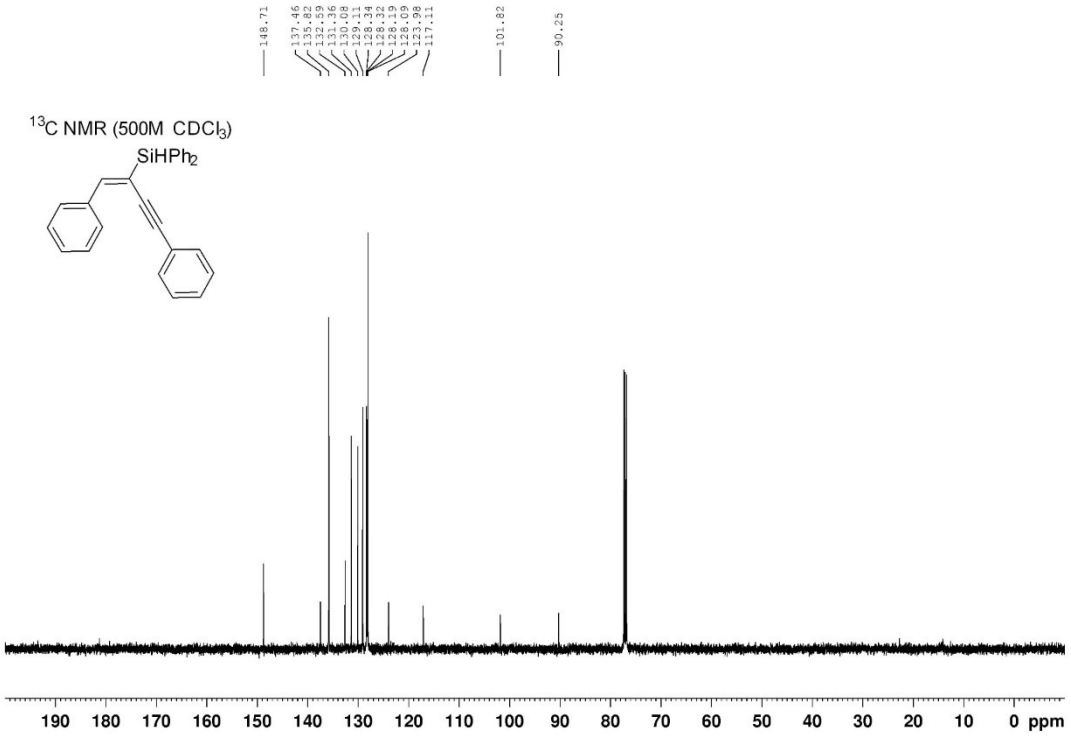
(*E*)-(1,4-bis(4-fluorophenyl)but-1-en-3-yn-2-yl)diphenylsilane (2o)



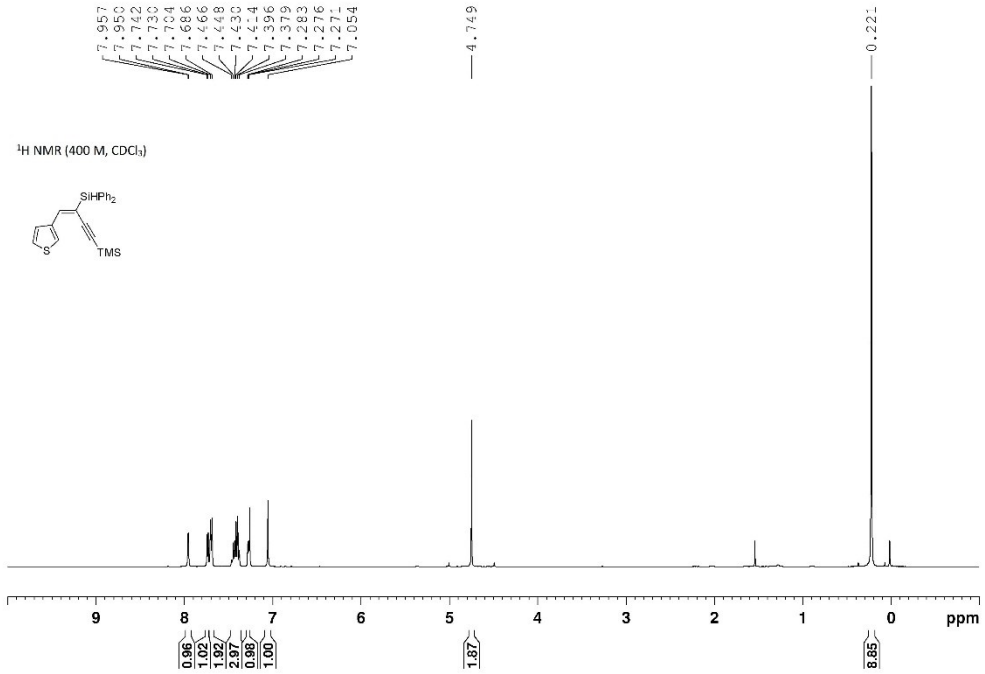


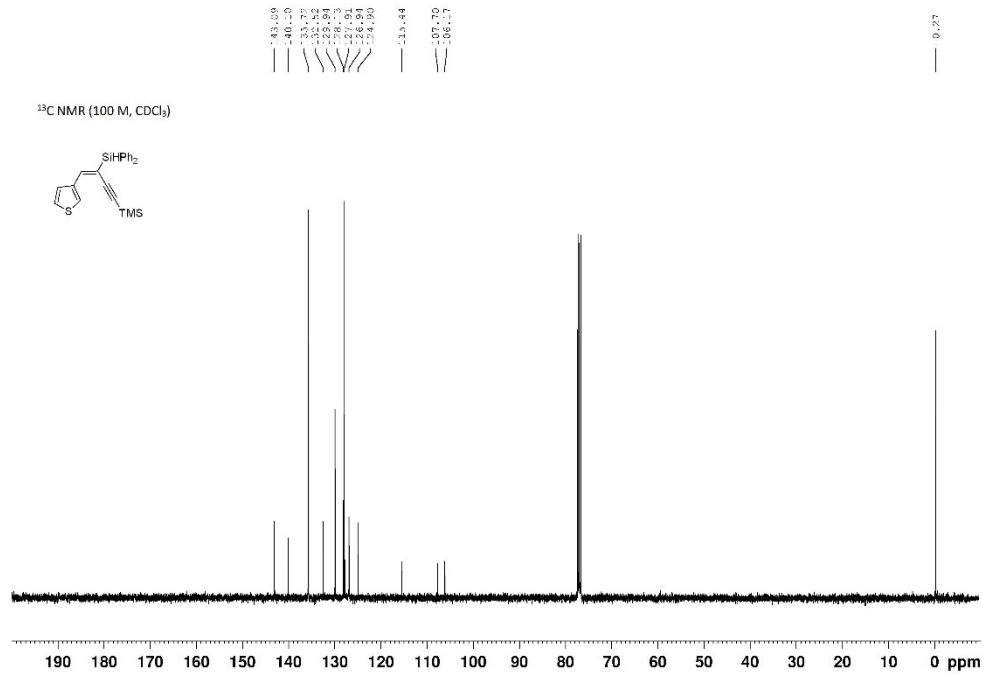
(*E*)-(1,4-diphenylbut-1-en-3-yn-2-yl)diphenylsilane (2p)



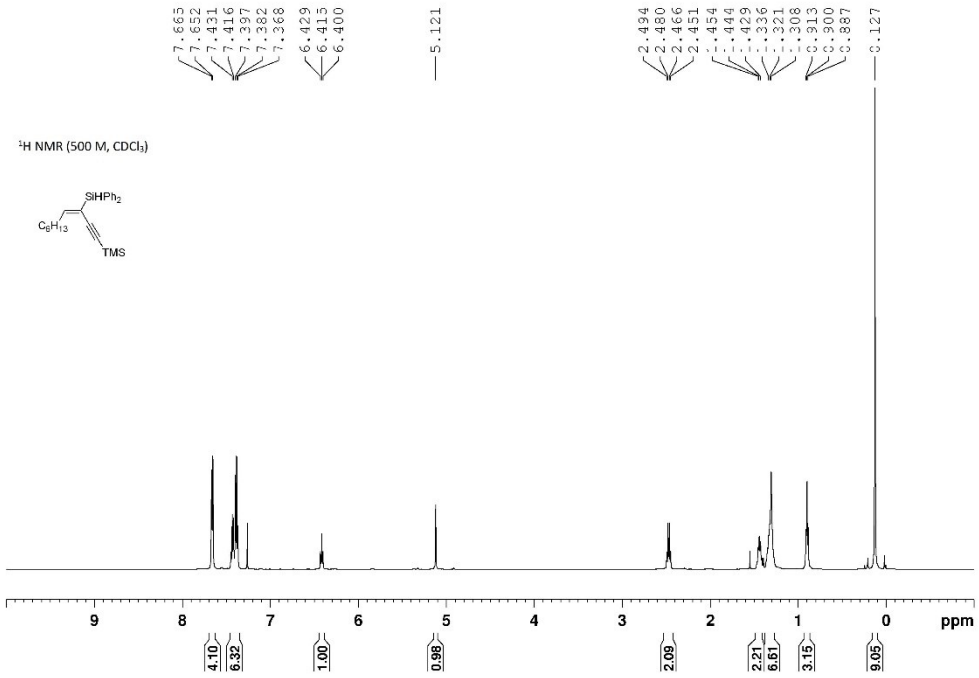


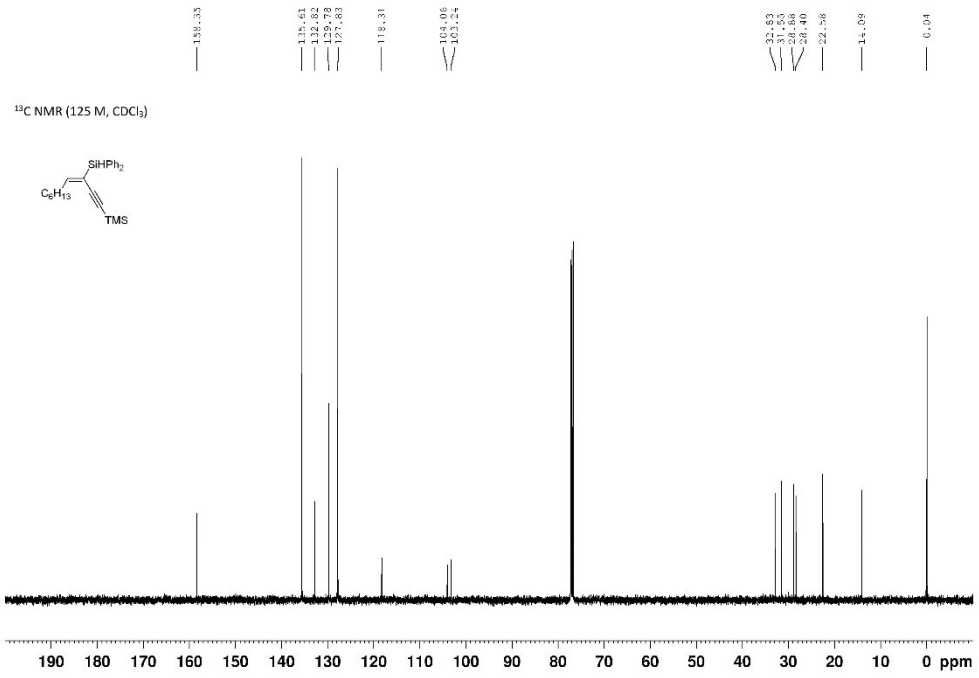
(*E*)-(3-(diphenylsilyl)-4-(thiophen-3-yl)but-3-en-1-yn-1-yl)trimethylsilane (2q)


7.957
7.950
7.742
7.730
7.704
7.686
7.466
7.448
7.430
7.414
7.396
7.379
7.283
7.276
7.271
7.054
4.749
0.222
1H NMR (400 M, CDCl3)
SiHPh2
TMS
S
9
8
7
6
5
4
3
2
1
0
ppm
0.96
1.02
1.92
2.97
0.98
1.00
1.87
8.85

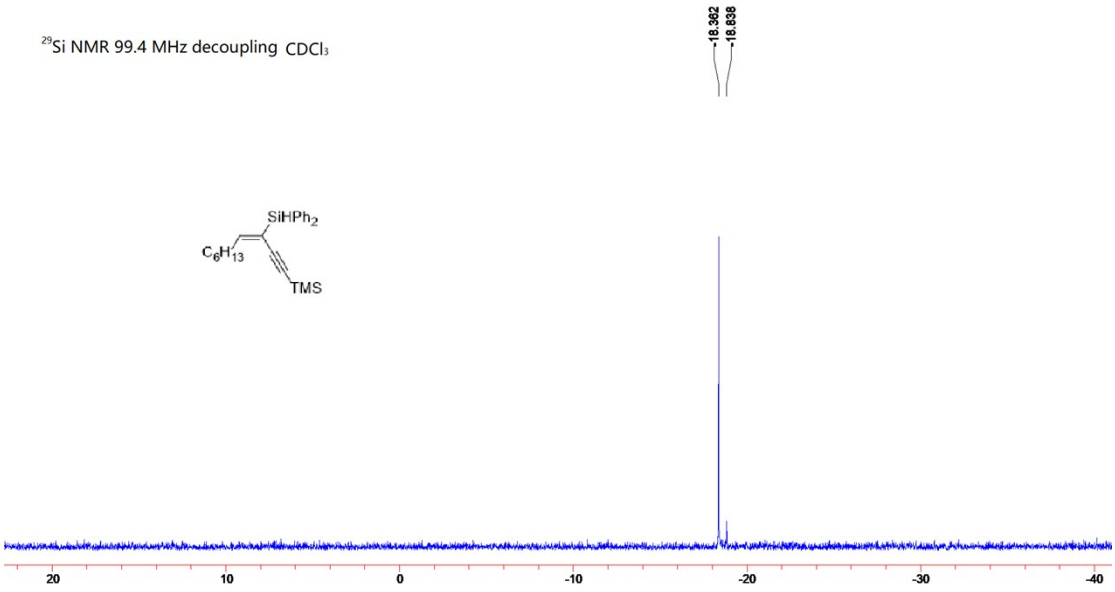

143.09
140.16
133.72
133.52
128.94
128.73
127.91
126.94
124.90
113.44
107.70
106.17
0.07
13C NMR (100 M, CDCl3)
SiHPh2
TMS
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

(*E*)-(3-(diphenylsilyl)dec-3-en-1-yn-1-yl)trimethylsilane (2r)

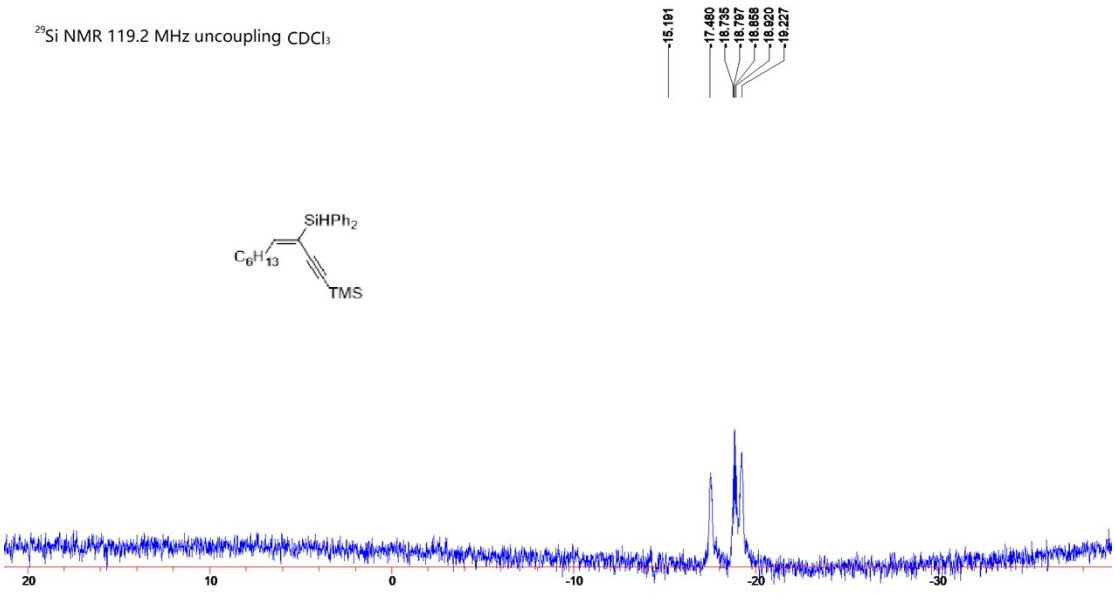




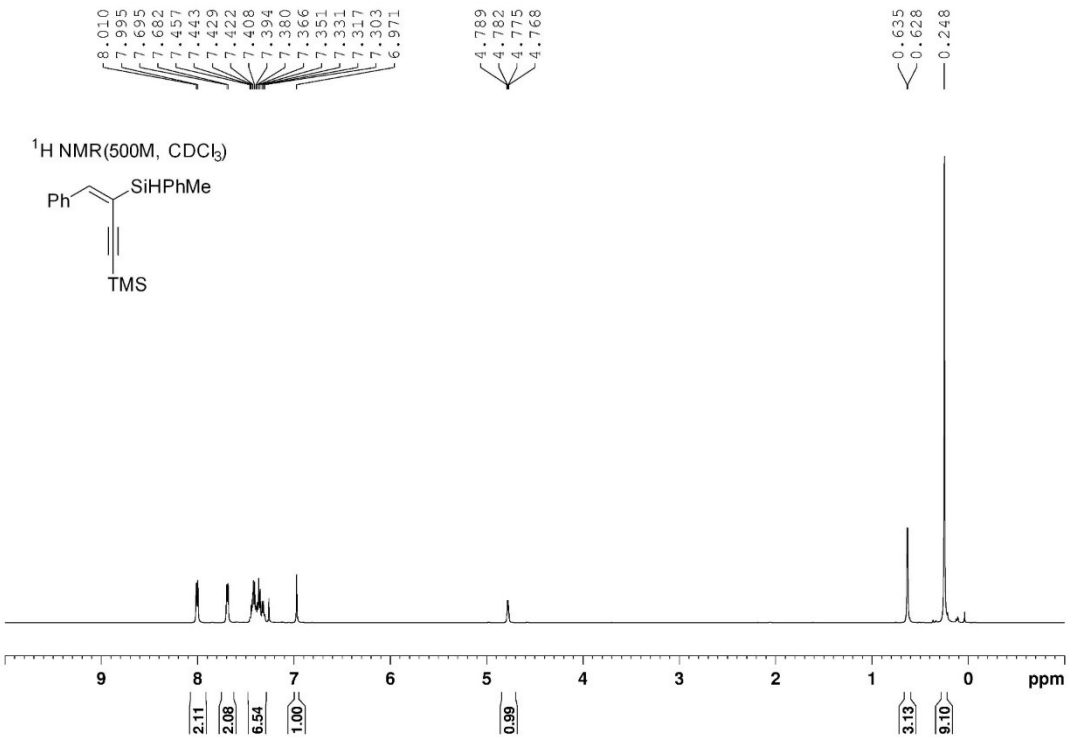
^{29}Si NMR 99.4 MHz decoupling $CDCl_3$

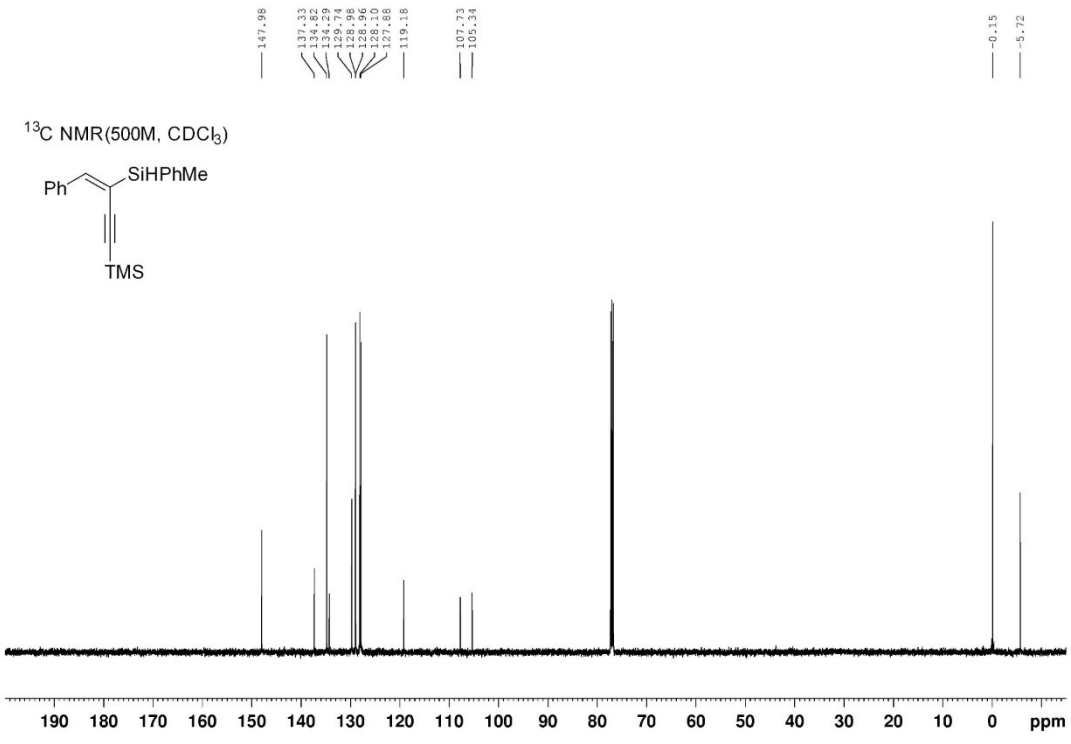


^{29}Si NMR 119.2 MHz uncoupling $CDCl_3$

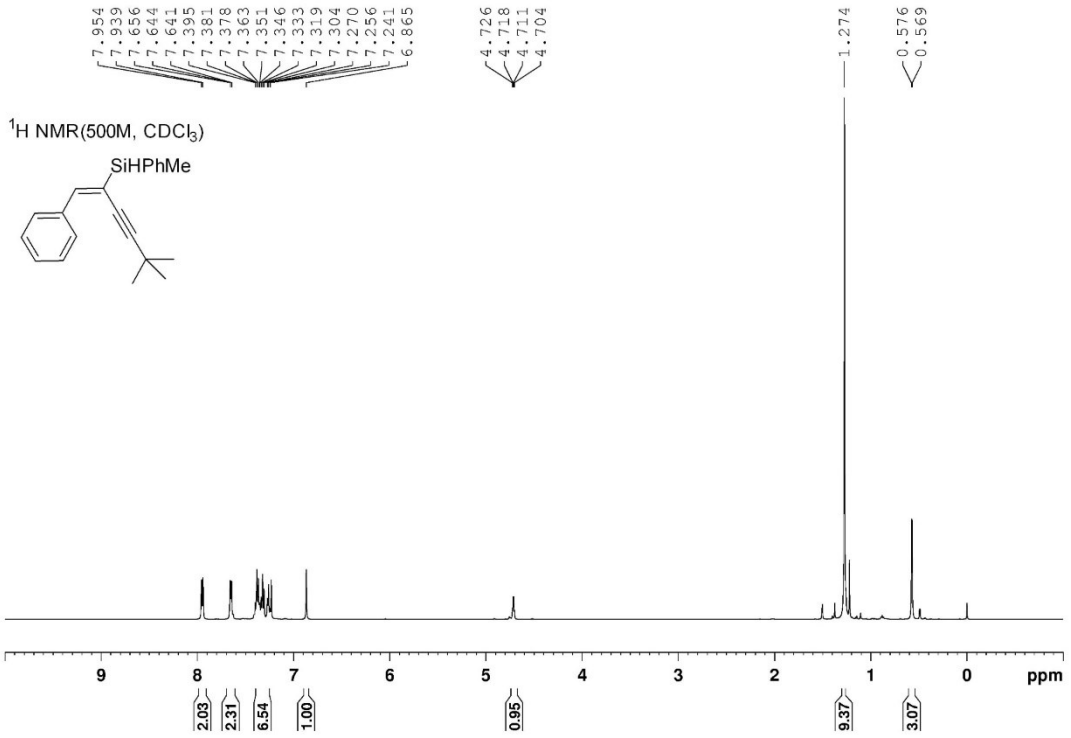


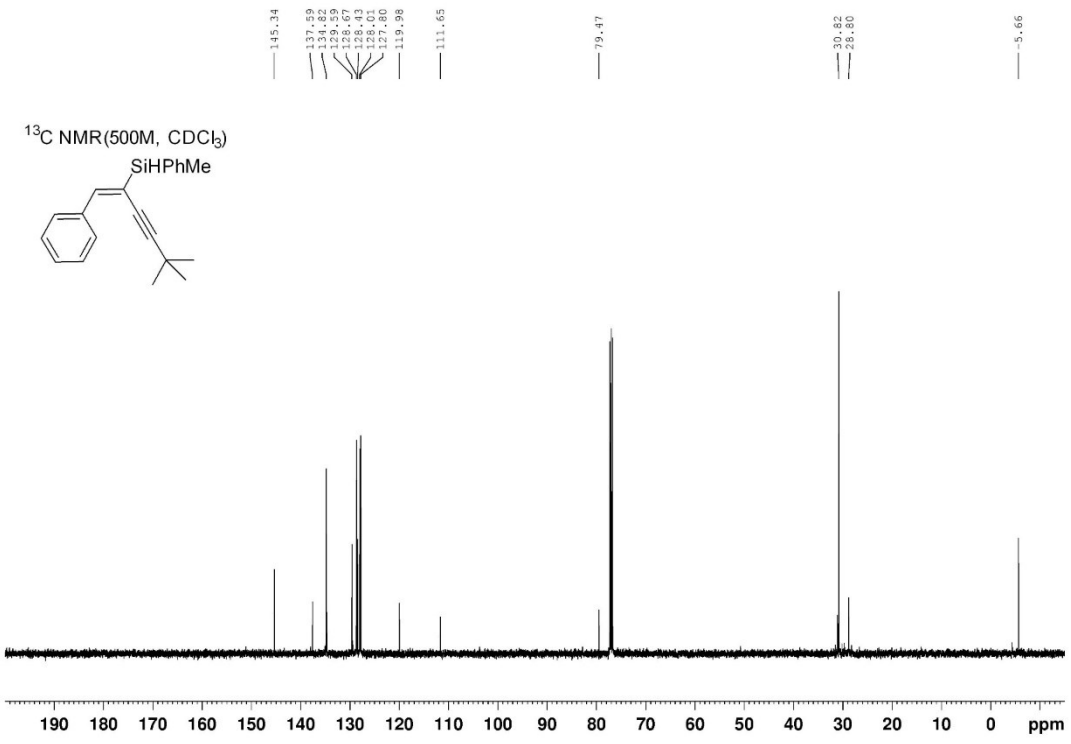
(*E*)-trimethyl(3-(methyl(phenyl)silyl)-4-phenylbut-3-en-1-yn-1-yl)silane (2s)



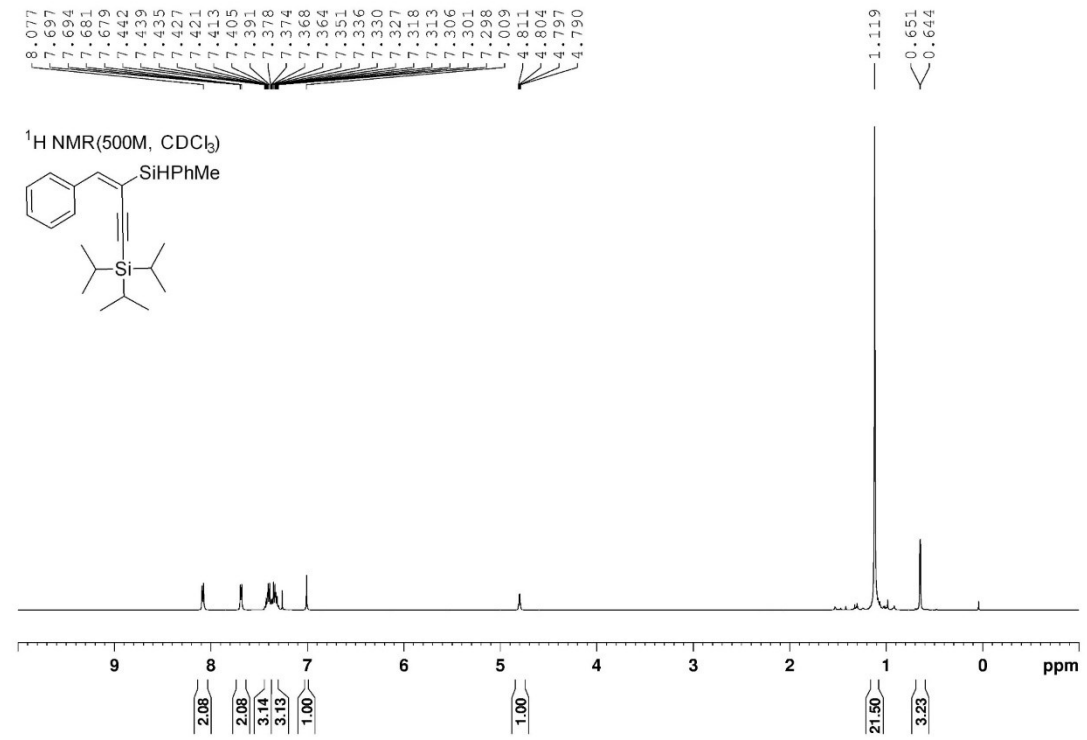


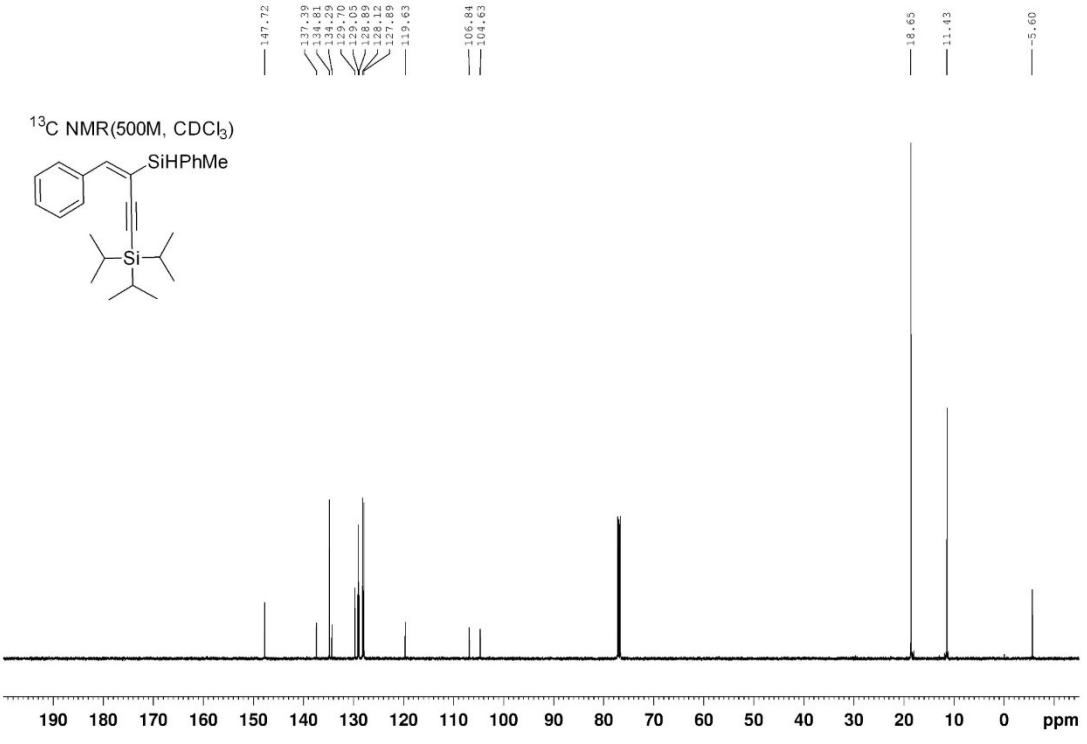
(*E*)-(5,5-dimethyl-1-phenylhex-1-en-3-yn-2-yl)(methyl)(phenyl)silane (2t)



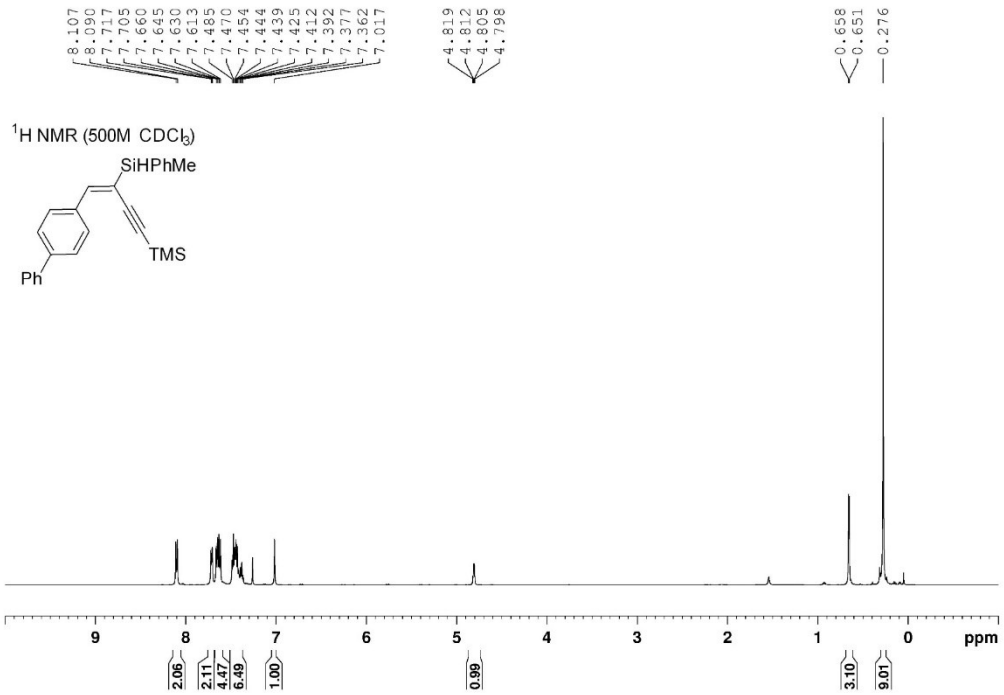


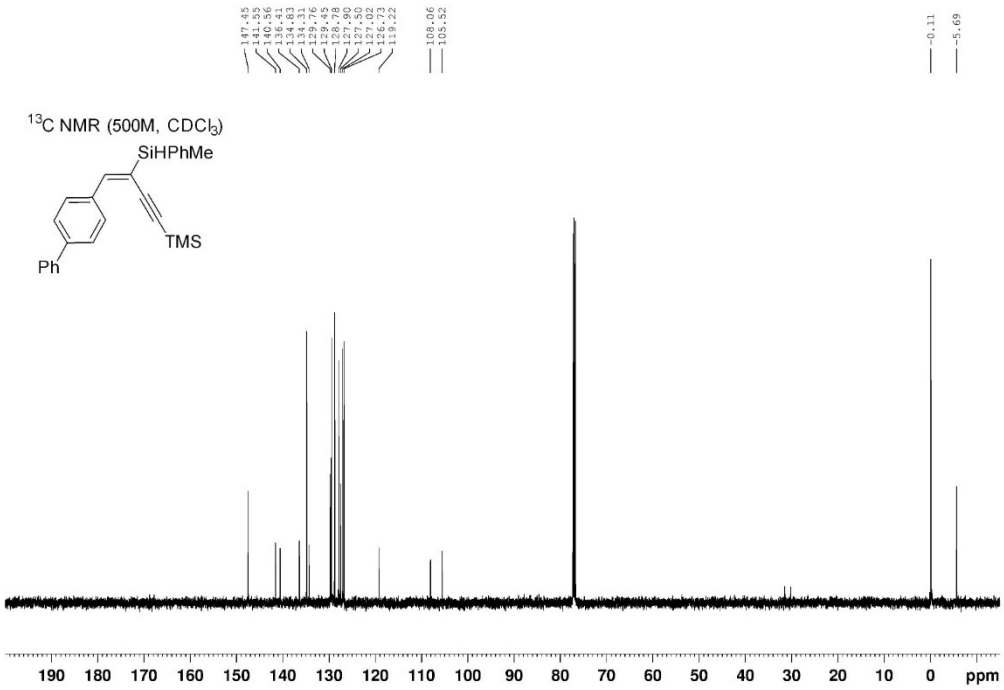
(*E*)-triisopropyl(3-(methyl(phenyl)silyl)-4-phenylbut-3-en-1-yn-1-yl)silane (2v)



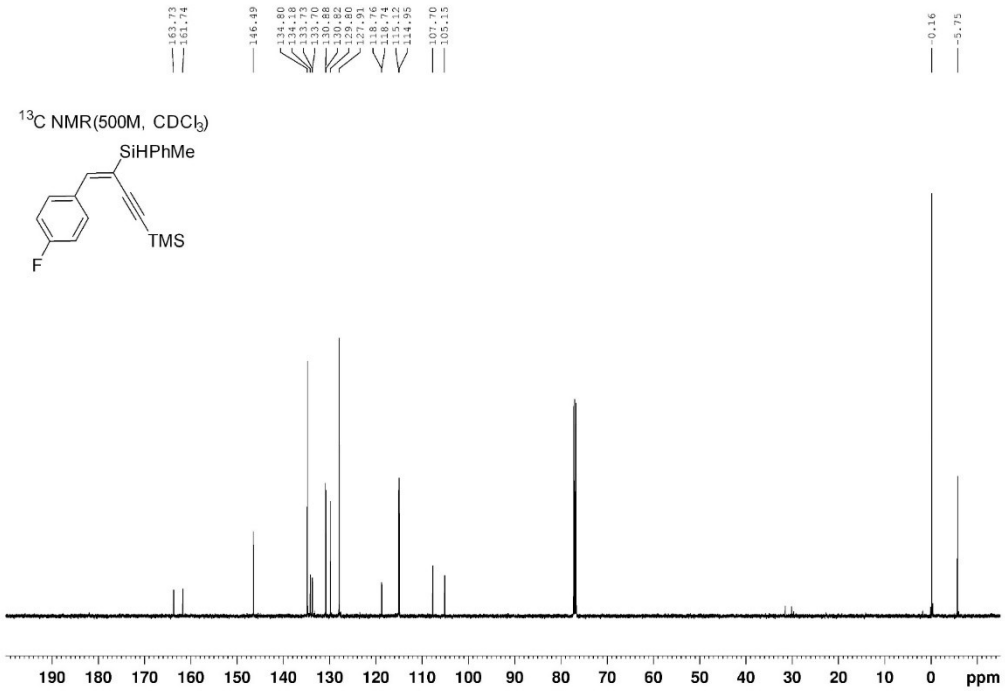


(*E*)-(4-([1,1'-biphenyl]-4-yl)-3-(methyl(phenyl)silyl)but-3-en-1-yn-1-yl)trimethylsilane (2w)





(*E*)-(4-(4-fluorophenyl)-3-(methyl(phenyl)silyl)but-3-en-1-yn-1-yl)trimethylsilane(2x)



(*E*)-(1,4-diphenylbut-1-en-3-yn-2-yl)(methyl)(phenyl)silane (2y)