Supporting Information

Toward Vanadium-Mediated Alkyne Metathesis

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General Experimental Details

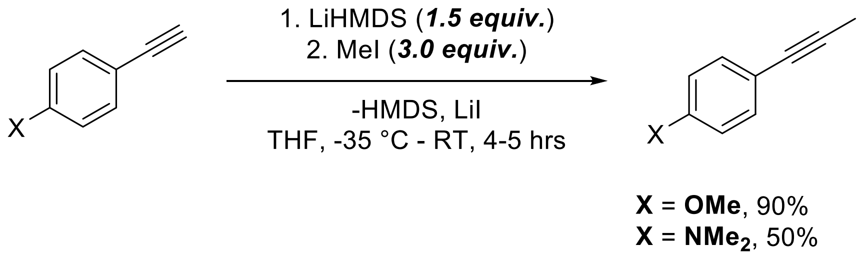
All reactions involving air and moisture-sensitive materials were performed in a nitrogen-filled MBraun glovebox or otherwise in a fumehood with a Schlenk line. All glassware was oven-dried prior to use (160-200 °C). Solvents used, such as diethyl ether (Et_2O), n-Hexane, pentane, etc. were dried using Na/benzophenone system and stored in the glovebox under inert atmosphere over 3 Å molecular sieves (which were also oven-dried beforehand). C_6D_6 was stored in the glovebox under 3 Å molecular sieves as well. ^{1}HNMR and ^{51}VNMR spectra were obtained with a Bruker 400 MHz spectrometer, while ^{13}CNMR was obtained on a Bruker 600 MHz machine. Chemical shifts for ^{1}H, ^{51}V, and ^{13}C spectra are reported in parts per million (ppm) and use the residual ^{1}H and ^{13}C resonances of the deuterated solvent as reference (^{1}H δ: C_6D_6 7.16 ppm, ^{13}C δ: C_6D_6 128.06 ppm). All NMR data shown have the following format: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad), coupling constants (Hz), and integration. Elemental analysis (C, H, and N) was done by Atlantic Microlab.

Starting Materials

Reagents were purchased at the highest commercial quality and utilized without further purification unless otherwise stated. 2,6-Dimethoxyphenol, and Iodomethane were purchased from **Thermo Scientific Chemicals**. 2-Methoxybenzenethiol, Guaiacol, 4-Ethynyl-N,N-dimethylaniline, 4-Ethynylanisole, Iodoethane, and 1-Iodopropane were also purchased from **TCI America**. 1,10-Phenanthroline was purchased from **Acros Organics**.

Experimental Details

Synthesis of Alkyne Substrates



The reactions were performed using a modified version of the procedure by Hou *et al.*[1] The reaction itself was performed in the glovebox, but the purification steps were performed in a fumehood. 1.0 g of each starting material ethyne was dissolved in THF (5 mL for every 4.30 mmol of SM). The reaction mixture was cooled to -35 °C for 30-60 min. and LiHMDS (1.50 equiv.) was added slowly while the solution was still cold. The solution was stirred for 1 h and then cooled again. Cold MeI (3.0 equiv.) was then added to the solution dropwise to the cold reaction mixture. The solution was allowed to warm up to RT and stir for 4-5 hrs. (reaction progress was monitored by ^{1}H NMR). Upon completion, the reaction mixture was taken out from the glovebox and quenched with saturated NH_4Cl and extracted 2-3 times with ethyl acetate. The combined organic layers were washed with brine ($NaCl_{(aq)}$), dried over Na_2SO_4, filtered, and the EtOAc was removed via rotavap to yield red-orange oil (1-(4-Methoxyphenyl)propyne), and/or a red-brown flaky solid (N,N-Dimethyl-4-(prop-1-yn-1-yl)aniline).

1-Methoxy-4-(1-propyn-1-yl)benzene

The product appears as a red-orange oil. If impure, the product can be purified using column chromatography (100:1 hexane:ethyl acetate) (Yield: 0.992 g, 90%). ^{1}H NMR spectrum in $CDCl_3$ is consistent with reported values.[2] ^{1}H NMR spectrum in C_6D_6 is provided below for convenience.

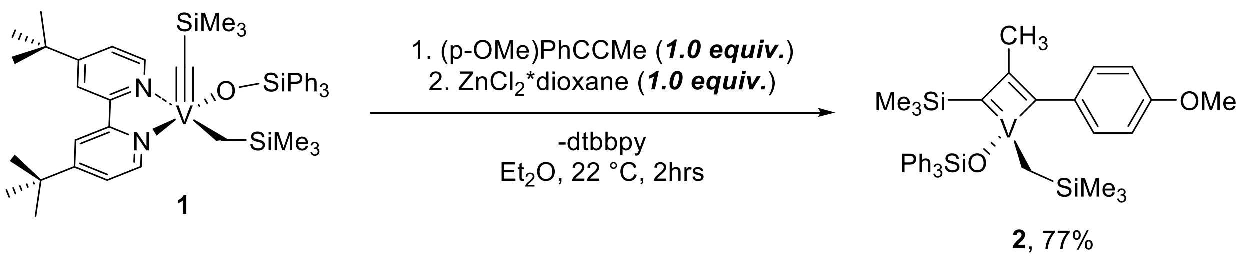
^{1}H NMR: (C_6D_6, 400 MHz) δ 7.42 (d, J = 8.9 Hz, 2H), 6.60 (d, J = 8.9 Hz, 2H), 3.19 (s, 3H), 1.72 (s, 3H).

N,*N*-Dimethyl-4-(prop-1-yn-1-yl)aniline

The product appears as a red-brown solid. If impure, the product can be purified using column chromatography (100:1 hexane:ethyl acetate). (Yield: 0.553 g, 50%). ^{1}H NMR spectrum in $CDCl_3$ is consistent with reported values.[2] ^{1}H NMR spectrum in C_6D_6 is provided below for convenience.

^{1}H NMR: (C_6D_6, 400 MHz) δ 7.54 (d, J = 9.0 Hz, 2H), 6.39 (d, J = 9.0 Hz, 2H), 2.39 (s, 6H), 1.80 (s, 3H).

MCBD 2



V(CHSiMe$_3$)(dtbbipy)(CH$_2$SiMe$_3$)(OSiPh$_3$) (**1**) (0.312 g, 0.407 mmol, 1.0 equiv.) was weighed out and dissolved in diethyl ether and the 1-Methoxy-4-(1-propyn-1-yl)benzene (0.059 mL, 0.407 mmol, 1.0 equiv.) was added all at once to the stirred solution. The reaction mixture was stirred for 2 hours, upon which all of **1** should have all completely reacted with the alkyne, before the ZnCl$_2$*dioxane (white solid, 0.091 g, 0.407 mmol, 1.0 equiv.) was added to scavenge the dtbbpy that dissociates from **1** as cycloaddition occurs. The reaction mixture was allowed to stir for another hour at RT before the ether was removed via vacuum, the residue was suspended in pentane, and filtered (to remove ZnCl$_2$*dtbbpy). Product **2** can be acquired as a dark green-black oil upon removal of all solvents. All attempts to find a proper recrystallization system for **2** were unsuccessful. (Yield: 0.214 g, 77%)

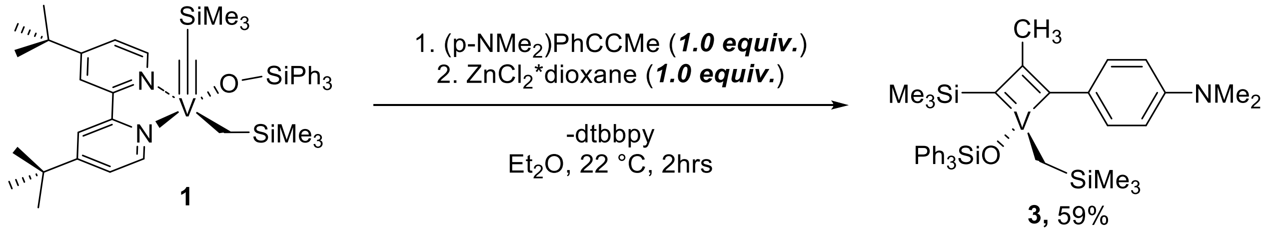
^{1}H NMR: (C_6D_6, 400 MHz) δ 7.76-7.79 (m, 6H), 7.18-7.20 (m, 9H), 7.13 (d, 2H, J = 8.8 Hz), 6.83 (d, 2H, J = 8.8 Hz), 3.33 (s, 3H), 3.15 (s, 3H), 1.61 (br. s, 1H), 1.53 (br. s, 1H), 0.37 (s, 9H), 0.11 (s, 9H)

^{13}C NMR: (C_6D_6, 151 MHz) δ 299.3 (br., Ar-$\underline{C}$-V), 257.0 (br., TMS-$\underline{C}$-V), 163.2, 159.0, 137.7, 135.5, 133.2, 129.93, 129.73, 128.10, 114.1, 60.2 (br., TMS-$\underline{CH_2}$-V), 54.9, 20.8, 2.3, 0.6

^{51}V NMR: (C_6D_6, 105 MHz) δ 466.

Anal. Calcd for $C_{36}H_{45}O_2Si_3V$: C, 67.04%; H, 7.03%. Found: C, 66.80%; H, 7.32%.

MCBD 3



Complex **1** (1.92 g, 2.50 mmol, 1.0 equiv.) was weighed out dissolved in diethyl ether and the *N*,*N*-Dimethyl-4-(prop-1-yn-1-yl)aniline (0.399 g, 2.50 mmol, 1.0 equiv.) was weighed out and added all at once to the stirred solution. The reaction mixture was stirred for 2 hours, upon which all of **1** should have all completely reacted with the alkyne, before the $ZnCl_2$*dioxane (white solid, 0.562 g, 2.50 mmol, 1.0 equiv.) was added to scavenge the dtbbpy that dissociates from **1** as cycloaddition occurs. The reaction mixture was allowed to stir for another hour at RT before the ether was removed via vacuum, the residue was suspended in pentane, filtered (to remove $ZnCl_2$*dtbbpy), and placed in the freezer for recrystallization. Product MCBD **3** can be acquired as dark rod-shaped crystals.

Recrystallized from *n*-pentane at −35 °C. (Yield: 0.967 g, 59%)

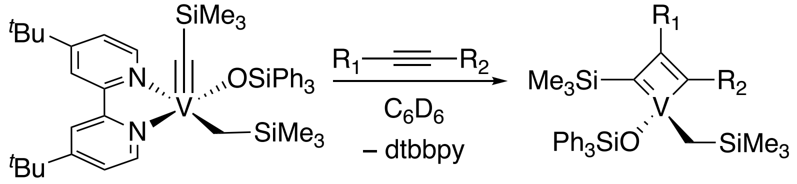
^{1}H NMR: (C_6D_6, 600 MHz) δ 7.83-7.81 (m, 6H), 7.28 (d, *J* = 8.9 Hz, 2H), 7.22-7.17 (m, 9H), 6.59 (d, *J* = 8.9 Hz, 2H), 3.28 (s, 3H), 2.53 (s, 6H), 1.59 (dd, *J* = 60.0, 10.2 Hz, 2H), 0.38 (s, 9H), -0.08 (s, 9H).

^{13}C NMR: (C_6D_6, 151 MHz) δ 298.7 (br., Ar-*C*-V), 259.4 (br., TMS-*C*-V), 163.6, 149.4, 137.9, 135.5, 133.5, 129.83, 129.71, 128.6, 112.1, 59.1 (br., TMS-*C*H_2-V), 40.0, 21.2, 2.3, 0.6.

^{51}V NMR: (C_6D_6, 105 MHz) δ 478.

Anal. Calcd for $C_{37}H_{48}NOSi_3V$: C, 67.54%; H, 7.35%; N, 2.13%. Found: C, 67.68%; H, 7.53%; N, 2.14%.

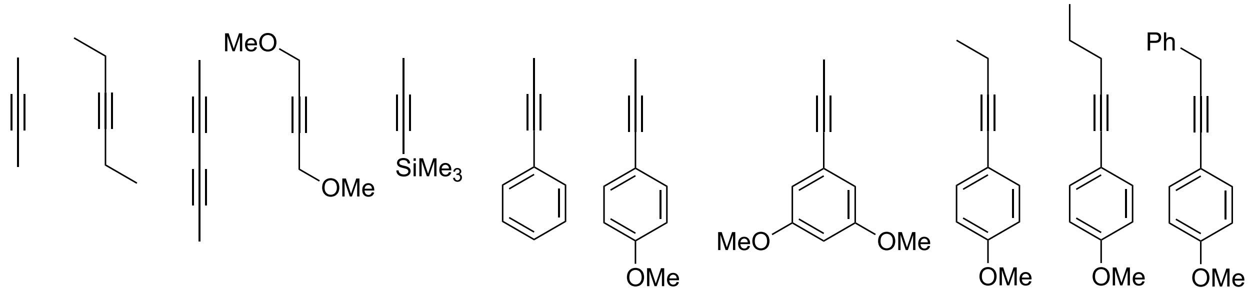
Tested Alkynes with Alkylidyne 1



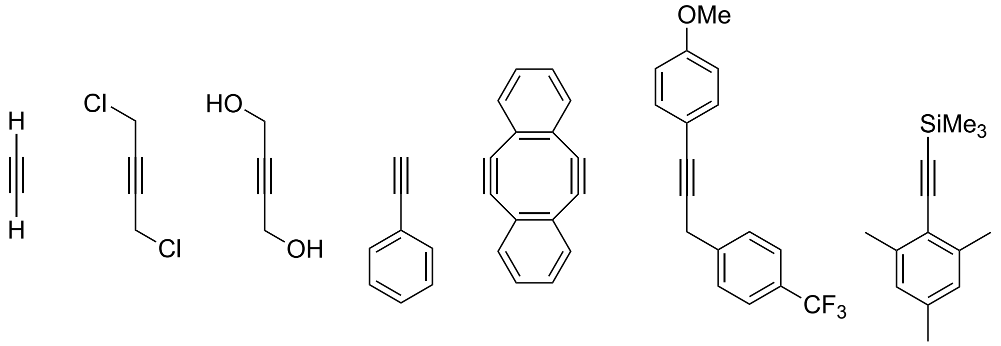
1

General procedure: In a nitrogen-filled glovebox, complex **1** (10 mg, 13.0 µmol, 1 eq.) and alkyne (13.0 µmol, 1 eq.) are weighed and dissolved in 0.6 mL of C_6D_6. The solution is transferred into a J. Young NMR tube. The ^{1}H NMR spectrum was checked for product signals after 1 hour and again after 16 hours. If no MCBD is observed and a complex **1** remains, the reaction mixture is heated at 60 °C for 1 hour and analyzed by ^{1}H NMR spectroscopy.

Alkynes that form MCBD at 22 °C by ^{1}H NMR spectroscopy, but are not crystalline



Alkynes that do not form MCBD and decompose complex 1 at RT by ^{1}H NMR spectroscopy



Alkynes that do not form MCBD and decompose complex 1 at 60 °C by ^{1}H NMR spectroscopy

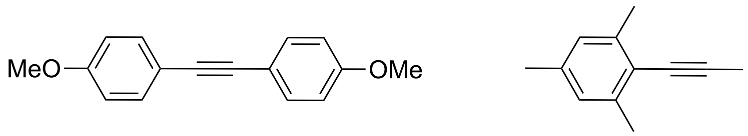
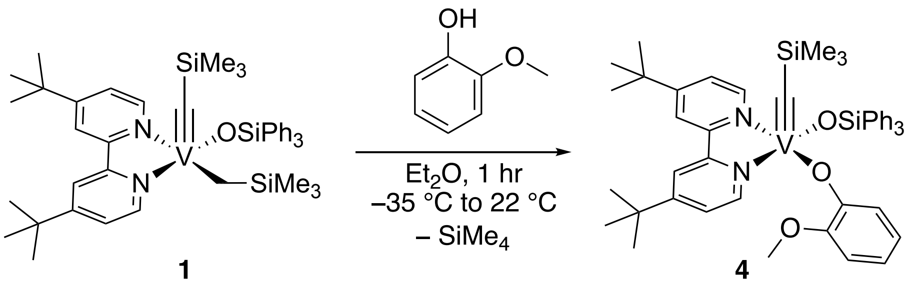


Figure S1. Tested alkynes in reaction with **1** to form MCBD products.

Alkylidyne 4



Compound **1** (500 mg, 0.65 mmol, 1.0 equiv.) was dissolved in 10 ml of diethyl ether and placed in the freezer to cool to -35 °C for 30 minutes. Afterwards, it was taken out and the phenol (81 mg, 0.65 mmol, 1.0 equiv.) was weighed out and added all at once. The reaction mixture was allowed to warm to RT (22 °C) and stir for 1 hour (during which the product can be observed partially precipitating out of the ether solution) before the ether was removed via vacuum. The semi-solid residue was filtered, washed with pentane, and dried under vacuum to yield the product as a yellow-brown powder (290 mg, 56%).

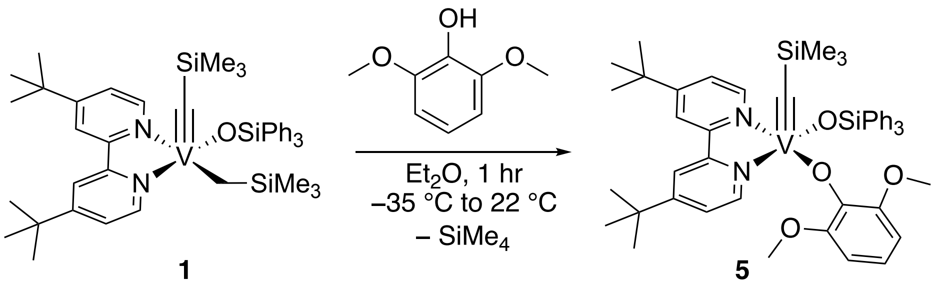
^{1}H NMR: (C_6D_6, 400 MHz) δ 10.08 (d, *J* = 4.8 Hz, 2H), 8.41-8.39 (m, 6H), 7.87 (d, *J* = 1.8 Hz, 2H), 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.39-7.35 (m, 6H), 7.31-7.27 (m, 3H), 7.09 (td, *J* = 7.7, 1.6 Hz, 1H), 6.76 (d, *J* = 18.2 Hz, 2H), 6.59 (td, *J* = 7.7, 1.7 Hz, 1H), 6.20 (dd, *J* = 8.0, 1.5 Hz, 1H), 2.38 (s, 3H), 0.94 (s, 18H), -0.28 (s, 9H).

^{13}C NMR: (C_6D_6, 151 MHz) δ 416.9 (br., V≡C), 163.6, 162.7, 157.8, 153.2, 152.6, 151.5, 147.7, 141.8, 136.7, 128.8, 127.7, 123.2, 121.9, 118.7, 117.5, 117.0, 112.2, 54.7, 34.9, 30.1, 0.3.

^{51}V NMR: (C_6D_6, 105 MHz) δ 350.

Anal. Calcd for $C_{47}H_{55}N_2O_3Si_2V$: C, 70.29%; H, 6.90%; N, 3.49%. Found: C, 70.29%; H, 6.74%; N, 3.35%.

Alkylidyne 5



Compound **1** (0.988 g, 1.29 mmol, 1.0 equiv.) was dissolved in 20 ml of diethyl ether and placed in the freezer to cool to -35 °C for 60 minutes. Afterwards, it was taken out and the phenol (0.198 g, 1.29 mmol, 1.0 equiv.) was weighed out and added all at once. The reaction mixture was allowed to warm to RT (22 °C) and stir for ~1 hour (during which the product can be observed partially precipitating out of the ether solution) before the ether was removed via vacuum and the semi-solid residue was filtered and washed with pentane and dried under vacuum to yield the product as a pale, brown powder. The product was recrystallized from diethyl ether at –35° C (0.656 g, 61%).

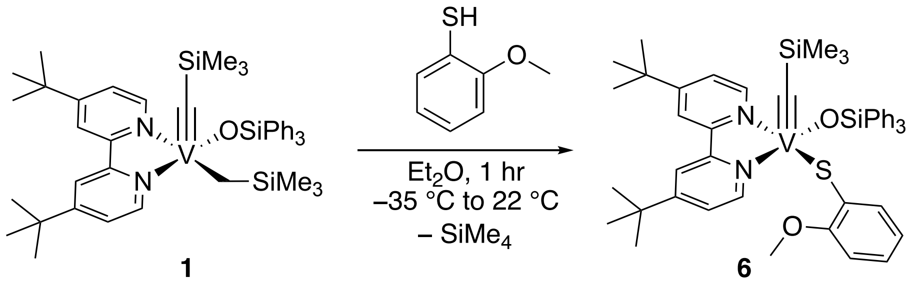
^{1}H NMR: (C_6D_6, 400 MHz) δ 10.09 (s, 2H), 8.42 (d, J = 6.6 Hz, 6H), 7.88 (s, 2H), 7.37 (t, J = 7.2 Hz, 6H), 7.29 (t, J = 7.3 Hz, 3H), 6.79 (s, 1H), 6.65 (s, 1H), 6.46 (d, J = 15.8 Hz, 1H), 6.41-6.38 (m, 2H), 3.27 (s, 6H), 0.93 (s, 18H), -0.25 (s, 9H).

^{13}C NMR: (C_6D_6, 151 MHz) δ 418.2 (br., V≡C), 163.8, 162.7, 153.5, 152.6, 151.6, 151.2, 148.7, 141.9, 136.7, 128.8, 127.7, 122.7, 121.8, 117.2, 116.1, 109.1, 56.7, 34.9, 30.2, 0.4.

^{51}V NMR: (C_6D_6, 105 MHz) δ 365.

Anal. Calcd for $C_{48}H_{57}N_2O_4Si_2V$: C, 69.20%; H, 6.90%; N, 3.36%. Found: C, 68.90%; H, 6.86%; N, 3.27%.

Alkylidyne 6



Compound **1** (0.413 g, 0.538 mmol, 1.0 equiv.) was dissolved in 10 ml of diethyl ether and placed in the freezer to cool to -35 °C for 30 minutes. Afterwards, it was taken out and the thiolphenol (0.075 mg, 0.538 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was allowed to warm to RT (22 °C) and stir for ~1 hour (during which the product can be observed partially precipitating out of the ether solution) before the ether was removed via vacuum, and the semi-solid residue was filtered and washed with pentane and dried under vacuum to yield the products as brown powder. The product was recrystallized from diethyl ether at –35° C (0.330 g, 75%).

^{1}H NMR: (C_6D_6, 600 MHz) δ 10.58 (d, J = 6.0 Hz, 1H), 10.14 (d, J = 5.9 Hz, 1H), 8.31 (dd, J = 8.0, 1.5 Hz, 6H), 7.99 (dd, J = 7.7, 1.7 Hz, 1H), 7.82 (s, 2H), 7.33-7.30 (m, 6H), 7.28-7.26 (m, 3H), 6.90 (td, J = 7.5, 1.1 Hz, 1H), 6.81 (dd, J = 5.8, 1.6 Hz, 1H), 6.67 (td, J = 7.7, 1.7 Hz, 1H), 6.54 (dd, J = 6.0, 1.7 Hz, 1H), 6.03 (dd, J = 8.1, 0.9 Hz, 1H), 2.49 (s, 3H), 0.95 (s, 11H), 0.90 (s, 10H), -0.04 (s, 9H).

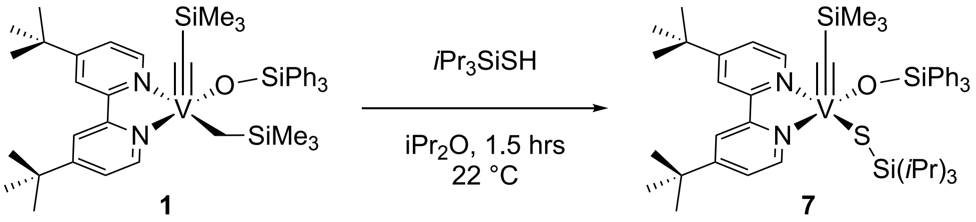
^{13}C NMR: (C_6D_6, 151 MHz) δ 411.2, 163.8, 162.7, 155.5, 155.0, 153.4, 152.0, 141.6, 137.8, 136.8, 130.5, 128.8, 123.5, 122.5, 122.2, 117.0, 116.7, 110.8, 54.9, 34.92, 34.76, 30.0, 0.6.

^{51}V NMR: (C_6D_6, 105 MHz) δ 457.

Anal. Calcd for $C_{47}H_{55}N_2O_2SSi_2V$: C, 68.92%; H, 6.77%; N, 3.42%. Found: C, 61.81%; H, 6.42%; N, 2.98%.

Multiple attempts to obtain an EA for sulfur-containing alkylidynes consistently yielded low carbon content.

Alkylidyne 7



Compound **1** (300 mg, 0.39 mmol, 1.0 equiv.) was dissolved in 9.0 ml of *i*-Pr_2O, and *i*-Pr_3SiSH (92 µL, 0.43 mmol, 1.1 equiv.) was added while stirring. The reaction mixture was stirred at RT (22 °C) for 1.5 hours before *i*-Pr_2O was removed under vacuum. The resulting powder was washed with a cold (-35 °C) mixture of *i*-Pr_2O/*n*-hexane (1:1, 3×2 mL) to obtain the product as a light-brown powder (170 mg, 50%).

^{1}H NMR: (C_6D_6, 600 MHz) δ 8.47 (d, *J* = 6.7 Hz, 6H), 7.71 (s, 2H), 7.40 (t, *J* = 7.3 Hz, 6H), 7.30 (t, *J* = 7.4 Hz, 3H), 6.82 (s, 4H), 1.30-1.21 (m, 4H), 1.05 (d, *J* = 7.4 Hz, 11H), 0.93 (d, *J* = 7.4 Hz, 24H), -0.20 (s, 9H).

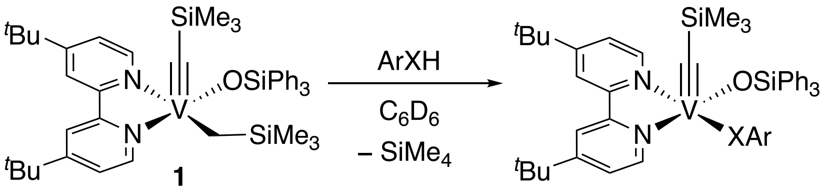
^{13}C NMR: (C_6D_6, 151 MHz) δ 431.6, 141.0, 137.1, 129.1, 128.1, 117.1, 30.0, 19.5, 0.2.

^{51}V NMR: (C_6D_6, 105 MHz) δ 490.

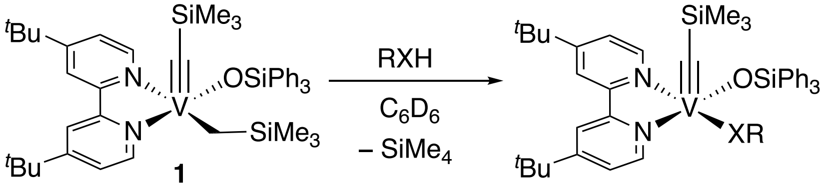
Anal. Calcd for $C_{49}H_{69}N_2OSSi_3V$: C, 67.70%; H, 8.00%; N, 3.22%. Found: C, 59.97%; H, 7.43%; N, 2.80%.

Multiple attempts to obtain an EA for sulfur-containing alkylidynes consistently yielded low carbon content.

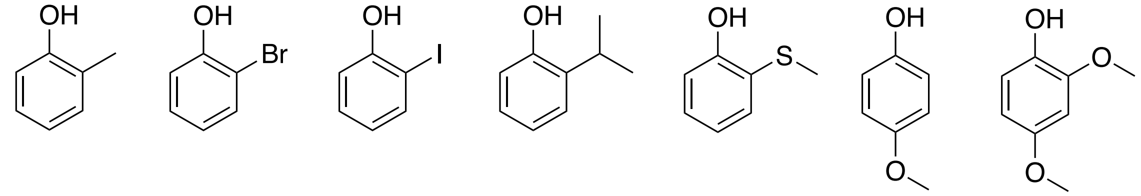
Tested Phenols, Alcohol, and Anilines



General procedure: In a nitrogen-filled glovebox, complex **1** (10 mg, 13.0 µmol, 1 eq.) and phenol, alcohol, or aniline (13.0 µmol, 1 eq.) are weighed and dissolved in 0.6 mL of C_6D_6. The solution is transferred into a J. Young NMR tube. The ^1H NMR spectrum was checked for product signals after 1 hour and again after 16 hours.



Phenols that form new alkylidynes at 22 °C by ^1H NMR spectroscopy



Compounds that do not form new alkylidynes and decompose complex 1 at RT by ^1H NMR spectroscopy

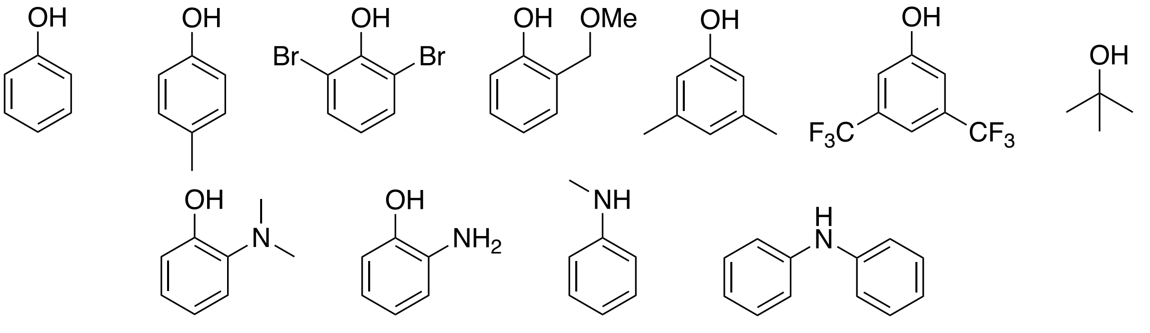
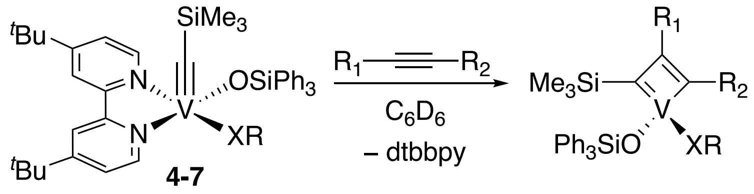


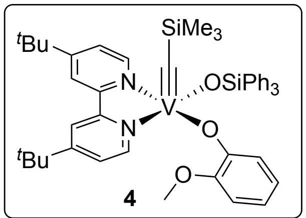
Figure S2. Tested phenols and anilines in reaction with **1** to form new alkylidynes.

Tested Alkynes with Alkylidynes 4-7

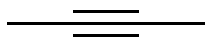


General procedure: In a nitrogen-filled glovebox, complexes **4-7** (13.0 µmol, 1 eq.) and alkyne (13.0 µmol, 1 eq.) are weighed and dissolved in 0.6 mL of C_6D_6. The solution is transferred into a J. Young NMR tube. The ^{1}H NMR spectrum was checked for product signals after 1 hour and again after 16 hours. If no MCBD is observed and complexes **4-7** remain, the reaction mixture is heated at 60 °C for 1 hour and analyzed by ^{1}H NMR spectroscopy.

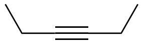
Alkylidyne 4



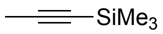
4



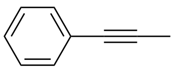
traces of cycloreversion product (TMSC≡CMe)



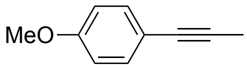
reaction observed, presumably MCBD formation



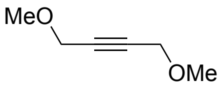
reaction observed, presumably MCBD formation



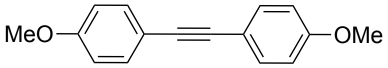
traces of cycloreversion product (TMSC≡CMe)



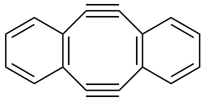
traces of cycloreversion product (TMSC≡CMe)



decomposition

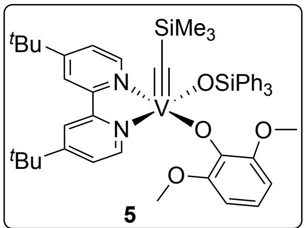


no reaction



decomposition

Alkylidyne 5



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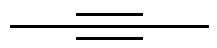
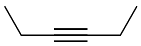
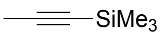


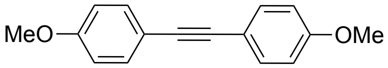
no reaction



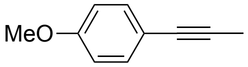
no reaction



no reaction

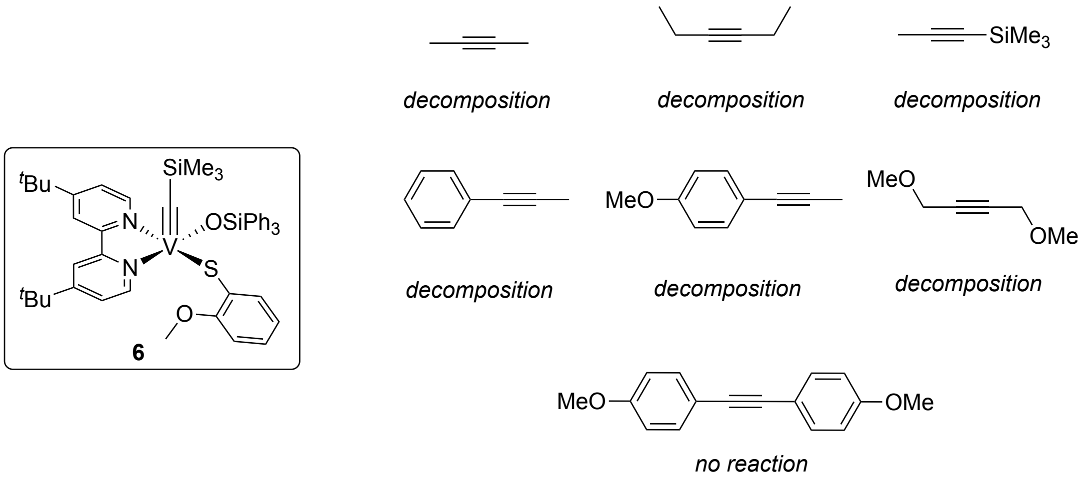


no reaction



no reaction

Alkylidyne 6



Alkylidyne 7

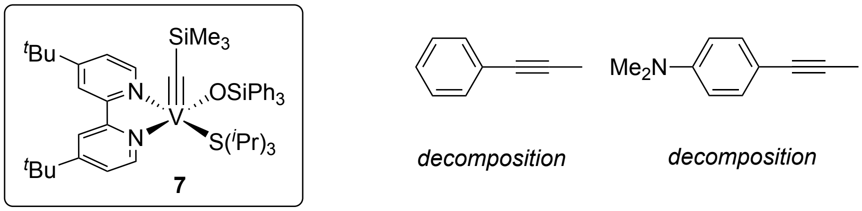
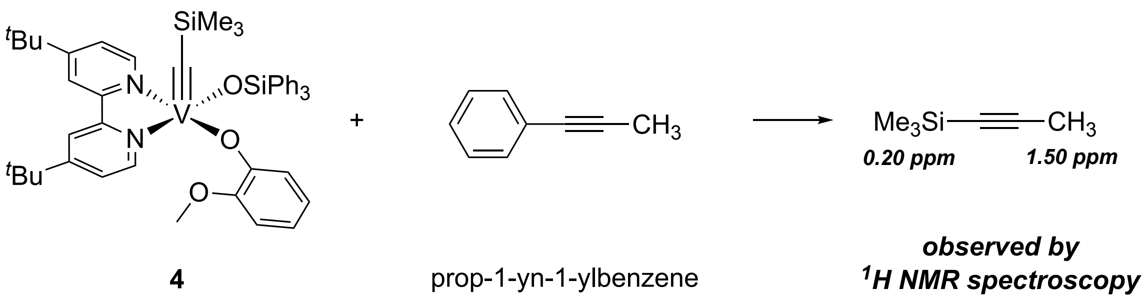


Figure S3. Tested alkynes in reaction with alkylidynes **4**-**7**.

Selected Reactivity of Complex 4 with Alkynes



In a nitrogen-filled glovebox, complex **4** (20 mg, 24.9 µmol, 1 eq.) and prop-1-yn-1-ylbenzene (5.8 mg, 49.8 µmol, 2.0 equiv.) are weighed and dissolved in 0.6 mL of C_6D_6. The solution is transferred into a J. Young NMR tube. The ^{1}H NMR spectrum was checked immediately (Figure S4, top). The reaction mixture is heated at 60 °C for 1 hour and analyzed by ^{1}H spectroscopy (Figure S4, bottom). The ^{1}H NMR spectrum indicated that complex **4** was consumed, along with 63% of prop-1-yn-1-ylbenzene (based on the residual benzene peak as an internal standard), corresponding to 1.26 equiv. of prop-1-yn-1-ylbenzene with respect to complex **4**.

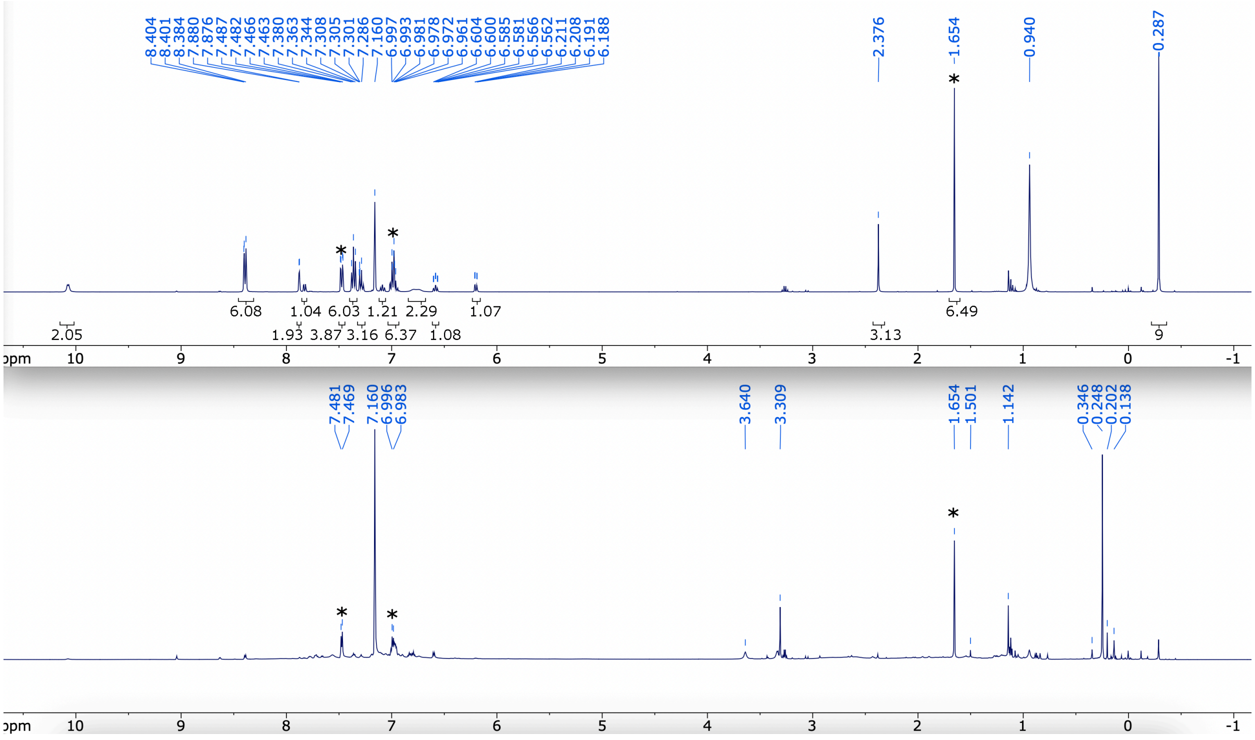
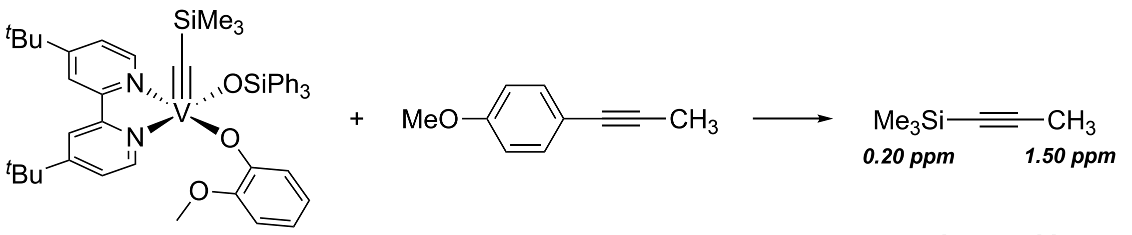


Figure S4. ^{1}H NMR spectra (C_6D_6, 400 MHz, 22 °C) of the reaction between **4** and prop-1-yn-1-ylbenzene: before heating (top) and after 1 hour at 60 °C (bottom). Signals of prop-1-yn-1-ylbenzene are indicated by *. Signals at 1.501 ppm and 0.202 ppm are assigned to 1-(trimethylsilyl)-1-propyne.



4

1-methoxy-4-(prop-1-yn-1-yl)benzene

observed by
^{1}H NMR spectroscopy

In a nitrogen-filled glovebox, complex **4** (20 mg, 24.9 µmol, 1 eq.) and 1-methoxy-4-(prop-1-yn-1-yl)benzene (6 mg, 41.1 µmol, 1.65 eq.) are weighed and dissolved in 0.6 mL of C_6D_6. The solution is transferred into a J. Young NMR tube. The ^{1}H NMR spectrum was checked immediately (Figure S5, top). The reaction mixture is heated at 60 °C for 1 hour and analyzed by ^{1}H NMR spectroscopy (Figure S5, bottom). The ^{1}H NMR spectrum indicated that 97% of complex **4** was consumed, along with 72% of 1-methoxy-4-(prop-1-yn-1-yl)benzene (based on the residual benzene peak as an internal standard), corresponding to 1.19 equiv. of alkyne with respect to complex **4**.

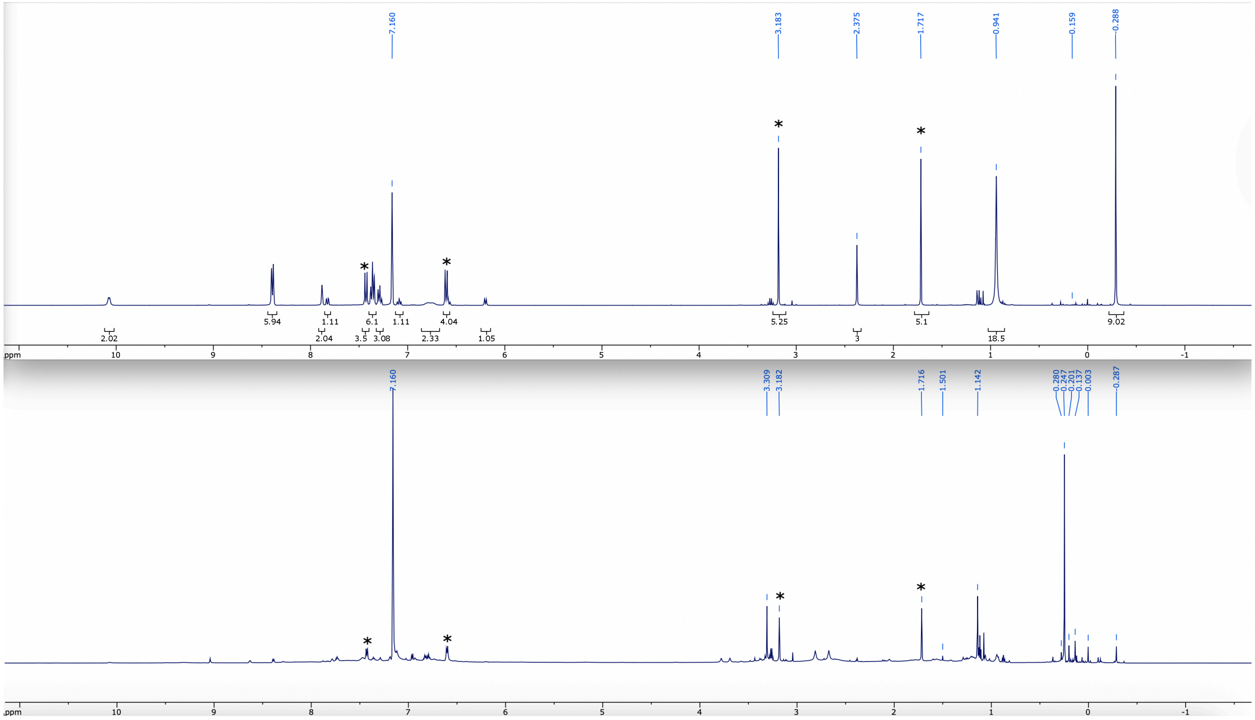


Figure S5. ^{1}H NMR spectra (C_6D_6, 400 MHz, 22 °C) of the reaction between **4** and 1-methoxy-4-(prop-1-yn-1-yl)benzene: before heating (top) and after 1 hour at 60 °C (bottom). Signals of 1-methoxy-4-(prop-1-yn-1-yl)benzene are indicated by *. Signals at 1.501 ppm and 0.201 ppm are assigned to 1-(trimethylsilyl)-1-propyne.

X-Ray Structures

MCBD 3

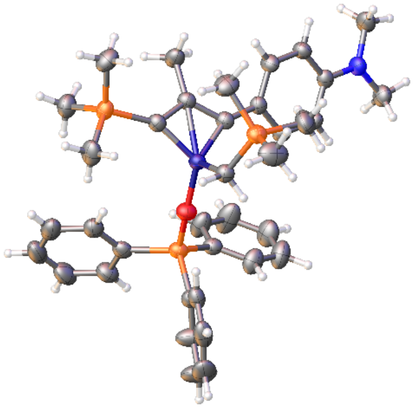


Figure S5. ORTEP representation of compound **MCBD (3)** (thermal ellipsoids are shown at 50% probability).

Single crystals of $C_{37}H_{48}NOSi_3V$ **MCBD (3)** were obtained from pentanes at –35°C. Data collection: **Bruker D8 Quest Photon II** diffractometer. The crystal was kept at 172(2) K during data collection. Using Olex2[3], the structure was solved with the SHELXT[4] structure solution program using Intrinsic Phasing and refined with the SHELXL[5] refinement package using Least Squares minimization.

Table S1. Crystal data and structure refinement for **MCBD (3)**.

CCDC	**2493563**
Empirical formula	$C_{37}H_{48}NOSi_3V$
Formula weight	657.97
Temperature/K	172(2)
Crystal system	monoclinic
Space group	P2/c
a/Å	11.8811(7)
b/Å	14.3289(9)
c/Å	22.4754(14)
α/°	90
β/°	100.0810(10)
γ/°	90
Volume/Å^3	3767.2(4)
Z	4
ρ_{calc}g/cm^3	1.16
μ/mm^{-1}	0.386
F(000)	1400
Crystal size/mm^3	0.2 × 0.19 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.62 to 50.126

Index ranges	$-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-26 \leq l \leq 26$
Reflections collected	40057
Independent reflections	6662 [R_{int} = 0.0542, R_{sigma} = 0.0271]
Data/restraints/parameters	6662/0/397
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.0899
Final R indexes [all data]	R_1 = 0.0522, wR_2 = 0.1000
Largest diff. peak/hole / e Å^{-3}	0.35/-0.27

Alkylidyne 4

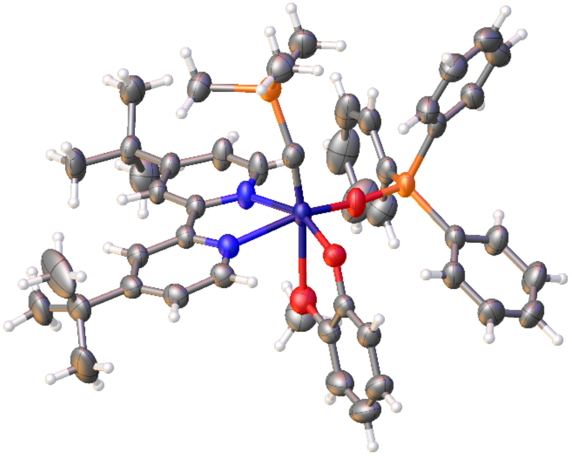


Figure S6. ORTEP representation of compound **Alkylidyne (4)** (thermal ellipsoids are shown at 50% probability).

Single crystals of $C_{47}H_{55}N_2O_3Si_2V$ **Alkylidyne (5)** were obtained from Et_2O/pentane (2:1 ratio) at –35°C. Data collection: **XtaLAB Synergy, Dualflex, HyPix** diffractometer. The crystal was kept at 150(2) K during data collection. Using Olex2,[3] the structure was solved with the SHELXT[4] structure solution program using Intrinsic Phasing and refined with the SHELXL[5] refinement package using Least Squares minimization. A solvent mask was calculated with Olex2[3] 1.5 to address the solvent disorder issue. The implementation of solvent masking in Olex2 is based on the BYPASS paper.[6]

Table S2. Crystal data and structure refinement for **Alkylidyne (4)**.

CCDC	**2499223**
Empirical formula	$C_{47}H_{55}N_2O_3Si_2V$
Formula weight	803.05
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.1091(10)
b/Å	10.5060(2)
c/Å	36.0901(17)
α/°	90

β/°	142.997(10)
γ/°	90
Volume/Å^3	4817.1(8)
Z	4
ρ_{calc}g/cm^3	1.107
μ/mm^{-1}	2.488
F(000)	1704.0
Crystal size/mm^3	0.129 × 0.066 × 0.042
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.958 to 131.988
Index ranges	$-25 \leq h \leq 25$, $-12 \leq k \leq 12$, $-42 \leq l \leq 42$
Reflections collected	45063
Independent reflections	8382 [R_{int} = 0.0430, R_{sigma} = 0.0300]
Data/restraints/parameters	8382/0/500
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1012
Final R indexes [all data]	R_1 = 0.0515, wR_2 = 0.1071
Largest diff. peak/hole / e Å^{-3}	0.36/-0.35

Alkylidyne 5

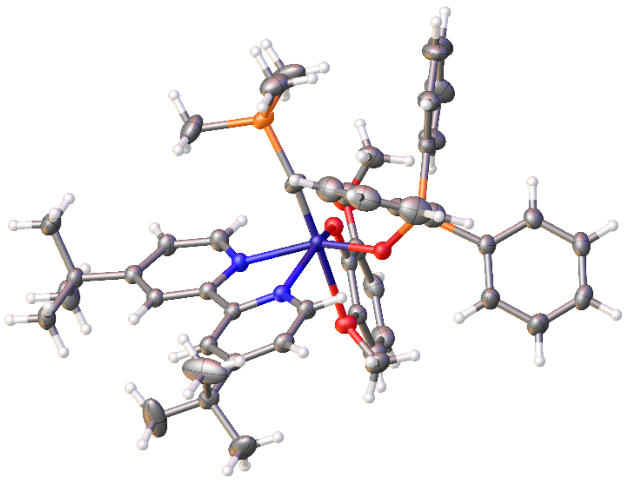


Figure S7. ORTEP representation of compound **Alkylidyne (5)** (thermal ellipsoids are shown at 50% probability).

Single crystals of $C_{48}H_{57}N_2O_4Si_2V$ **Alkylidyne (5)** were obtained from Et_2O at –35°C. Data collection: **XtaLAB Synergy, Dualflex, HyPix** diffractometer. The crystal was kept at 150(2) K during data collection. Using Olex2[3], the structure was solved with the SHELXT[4] structure solution program using Intrinsic Phasing and refined with the SHELXL[5] refinement package using Least Squares minimization.

Table S3. Crystal data and structure refinement for **Alkylidyne (5)**.

CCDC	**2493564**
Empirical formula	$C_{48}H_{57}N_2O_4Si_2V$
Formula weight	833.07
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	22.2210(2)
b/Å	10.89970(10)
c/Å	20.6591(2)
α/°	90
β/°	114.0650(10)
γ/°	90
Volume/Å^3	4568.78(8)
Z	4
ρ_{calc}g/cm^3	1.211
μ/mm^{-1}	2.658
F(000)	1768.0
Crystal size/mm^3	0.067 × 0.05 × 0.036
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.356 to 152
Index ranges	$-27 \leq h \leq 27$, $-13 \leq k \leq 12$, $-25 \leq l \leq 21$
Reflections collected	45261
Independent reflections	9299 [R_{int} = 0.0303, R_{sigma} = 0.0247]
Data/restraints/parameters	9299/0/519
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0850
Final R indexes [all data]	R_1 = 0.0394, wR_2 = 0.0874
Largest diff. peak/hole / e Å^{-3}	0.52/-0.27

Alkylidyne 6

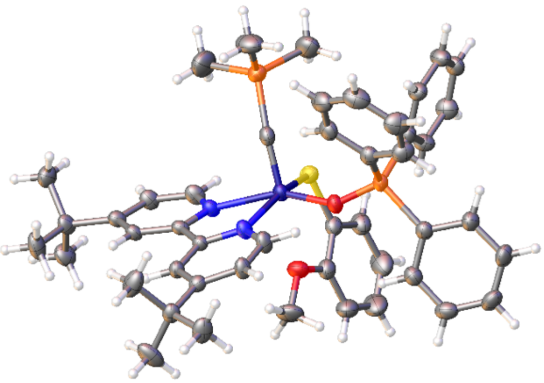


Figure S8. ORTEP representation of compound **Alkylidyne (6)** (thermal ellipsoids are shown at 50% probability).

Single crystals of $C_{47}H_{55}N_2O_2Si_2SV$ **Alkylidyne (6)** were obtained from Et_2O at –35°C. Data collection: **Bruker D8 Quest Photon II** diffractometer. The crystal was kept at 172(2) K during data collection. Using Olex2[3], the structure was solved with the SHELXT[4] structure solution program using Intrinsic Phasing and refined with the SHELXL[5] refinement package using Least Squares minimization.

Table S4. Crystal data and structure refinement for **Alkylidyne (6)**.

CCDC	**2493565**
Empirical formula	$C_{47}H_{55}N_2O_2Si_2SV$
Formula weight	819.11
Temperature/K	172(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.1289(11)
b/Å	30.044(3)
c/Å	13.4314(14)
α/°	90
β/°	99.874(2)
γ/°	90
Volume/Å^3	4424.3(8)
Z	4
ρ_{calc}g/cm^3	1.230
μ/mm^{-1}	0.364
F(000)	1736.0
Crystal size/mm^3	0.13 × 0.12 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.6 to 50.15
Index ranges	$-13 \leq h \leq 13$, $-35 \leq k \leq 35$, $-15 \leq l \leq 15$
Reflections collected	46652
Independent reflections	7811 [R_{int} = 0.0981, R_{sigma} = 0.0649]
Data/restraints/parameters	7811/0/506
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0481, wR_2 = 0.0935
Final R indexes [all data]	R_1 = 0.0894, wR_2 = 0.1116
Largest diff. peak/hole / e Å^{-3}	0.27/-0.32

Alkylidyne 7

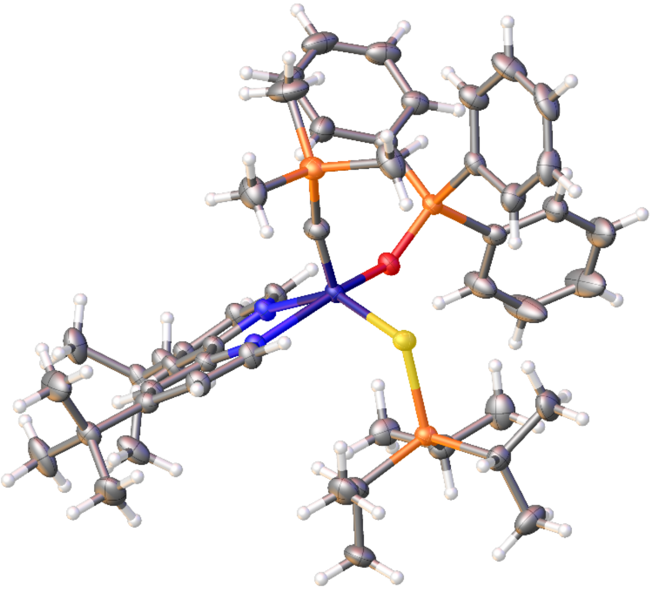


Figure S9. ORTEP representation of compound **Alkylidyne (7)** (thermal ellipsoids are shown at 50% probability).

Single crystals of $C_{48}H_{57}N_2O_4Si_2V$ **Alkylidyne (7)** were obtained from Et_2O at –35°C. Data collection: **XtaLAB Synergy, Dualflex, HyPix** diffractometer. The crystal was kept at 150(2) K during data collection. Using Olex2[3], the structure was solved with the SHELXT[4] structure solution program using Intrinsic Phasing and refined with the SHELXL[5] refinement package using Least Squares minimization.

Table S5. Crystal data and structure refinement for **Alkylidyne (7)**.

CCDC	**2493566**
Empirical formula	$C_{49}H_{69}N_2OSSi_3V$
Formula weight	869.33
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.33270(10)
b/Å	13.7549(3)
c/Å	16.4917(3)
α/°	79.778(2)
β/°	77.4170(10)
γ/°	80.9740(10)
Volume/Å^3	2450.39(8)
Z	2
ρ_{calc}g/cm^3	1.178
μ/mm^{-1}	3.059
F(000)	932.0
Crystal size/mm^3	0.139 × 0.073 × 0.054

Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.58 to 158.446
Index ranges	$-14 \le h \le 13$, $-17 \le k \le 16$, $-20 \le l \le 15$
Reflections collected	46608
Independent reflections	10103 [R_{int} = 0.0357, R_{sigma} = 0.0293]
Data/restraints/parameters	10103/0/523
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0911
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.0932
Largest diff. peak/hole / e Å^{-3}	0.50/-0.26

Computational Details

Density functional theory (DFT) based calculations are performed to propose a reaction mechanism for the metallacyclobutadiene formation. Energies are computed at the B3LYP-D3 level of theory[7-9] as implemented in Gaussian16.[10] During geometry optimizations, the main group elements are represented with the all-electron Pople's 6-31+G(d,p),[11, 12] and Vanadium is described with the Wachters-Hay 6-311+G(d,p)[13, 14] basis sets. Energy refinement is performed with single-point calculations in which main group elements are described with the 6-311+G(d,p)[15] basis sets. At this stage, solvent effects are included with the SMD continuum model[16] and using benzene as solvent. The nature of the stationary points is verified by vibrational analysis. Thermal corrections are computed at 298.15 K and 1 atm in the gas phase with the basis sets employed in the geometry optimizations. This methodology is equivalent to that used in our previous contributions on vanadium-based olefin metathesis, and its suitability was verified by ensuring that trends are not functionally dependent.[17, 18] The experimentally used 1-phenyl-1-propyne was considered as the reacting alkyne for most of the explored pathways. However, to ensure that conclusions do not depend on the considered alkyne, the reactivity and selectivity for the observed metallacyclobutadiene of V1 with (4-methoxy-phenyl-)1-propyne were also analyzed. The comparison of the two reagents is summarized in Figure S9 and shows that energetics with the two alkynes are extremely similar (differing less than 1.3 kcal mol-1) and trends are conserved.

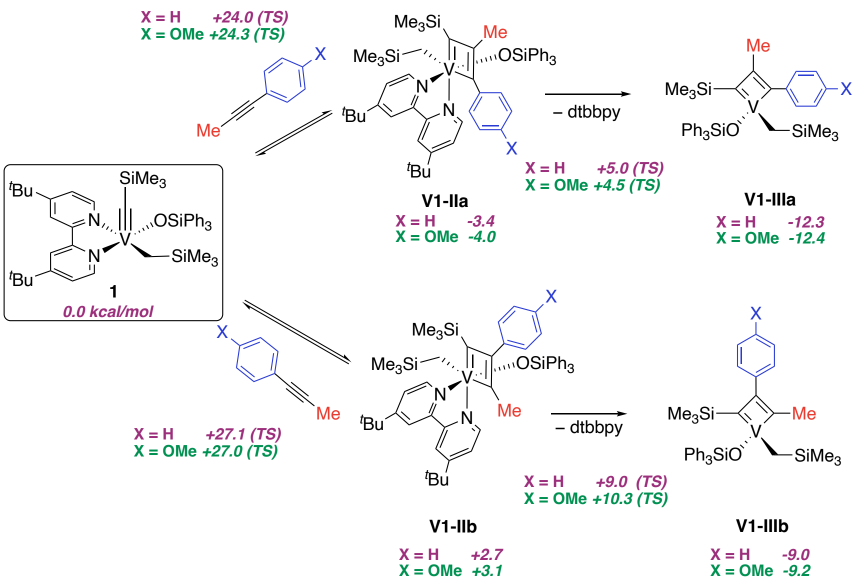
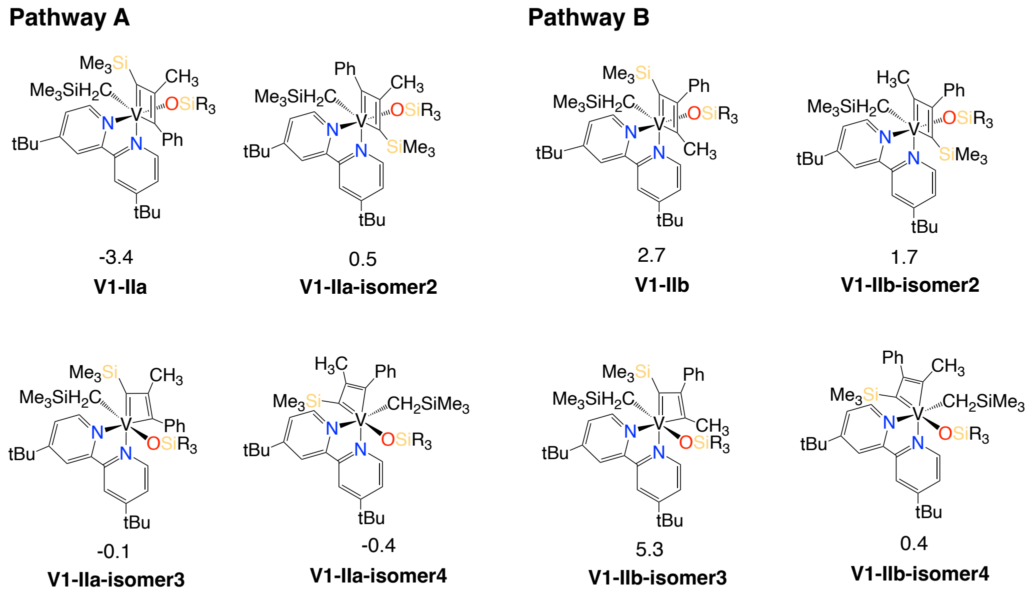


Figure S10. Comparison of the Gibbs energies (in kcal mol^{-1}) for the tetracoordinated metallacyclobutadiene formation by reaction of 1-phenyl-1-propyne and (4-methoxy-phenyl)-1-propyne with 1. **V1** and the reacting alkyne is taken as asymptote.



Pathway A

-3.4 **V1-IIa**

0.5 **V1-IIa-isomer2**

-0.1 **V1-IIa-isomer3**

-0.4 **V1-IIa-isomer4**

Pathway B

2.7 **V1-IIb**

1.7 **V1-IIb-isomer2**

5.3 **V1-IIb-isomer3**

0.4 **V1-IIb-isomer4**

Figure S11. Gibbs energies (in kcal mol^{-1}) with respect to **V1** and prop-1-yn-1-ylbenzene of the considered six coordinated metallacyclobutadiene intermediates.

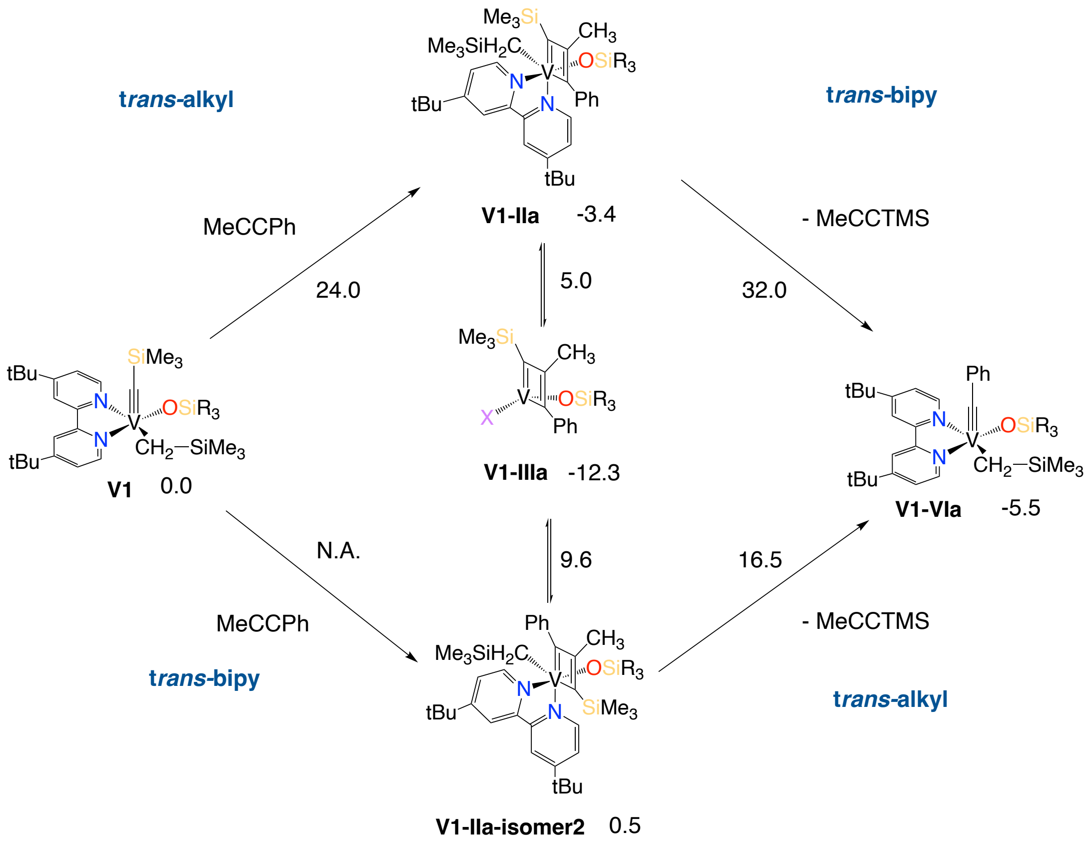


Figure S12. Gibbs energies (in kcal mol^{-1}) with respect to **V1** and prop-1-yn-1-ylbenzene of the alkyne metathesis process leading to trimethyl(prop-1-yn-1-yl)silane through two pathways differing in the metallacyclobutadiene intermediate isomer involved.

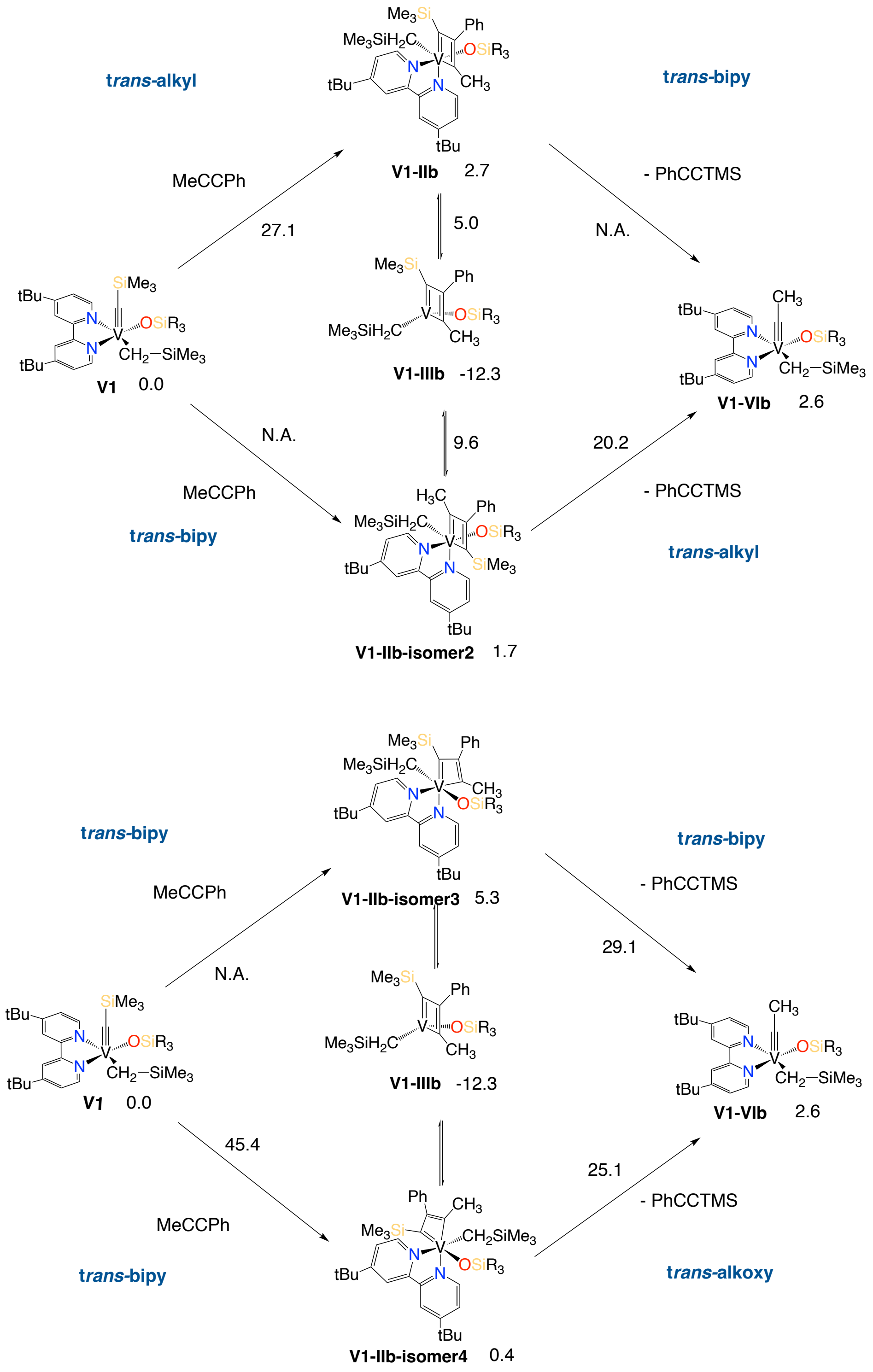


Figure S13. Gibbs energies (in kcal mol^{-1}) with respect to **V1** and prop-1-yn-1-ylbenzene of the alkyne metathesis process leading to trimethyl(phenylethynyl)silane through four pathways differing on on the metallacyclobutadiene intermediate isomer involved.

Table S6. Natural population charges at the α-carbon and the metal. Atomic contribution to the metal-alkylidyne bond according to the NBO scheme.

	V1	MoCTMS(OR$_{F6}$)$_3$
q_M	+0.44	+1.02
q_C	-0.51	-0.33
σ-bond	M=39%; C =61%	M=40%; C =60%
π_1-bond	M=49%; M=51%	M=58%; M=42%
π_2-bond	M=53%; M=47%	M=57%; M=43%

Table S7. Selected V-L Wiberg bond indexes.

Complex	Bond	1	TSN-IIa	IIa	IIIa
V1	V≡C	2.49	2.40	1.51	1.43
	V-O$_{SiPh3}$	0.83	0.81	0.86	0.94
	O-Si	0.60	0.60	0.60	0.58
	V-C	0.80	0.76	0.83	0.88
V4	V≡C	2.53	2.49	1.54	1.51
	V-O$_{SiPh3}$	0.83	0.76	0.82	0.93
	O-Si	0.62	0.62	0.63	0.59
	V-O$_{Ph}$	0.70	0.71	0.88	0.88
	O-C	1.09	1.10	1.07	1.03

NMR Spectra

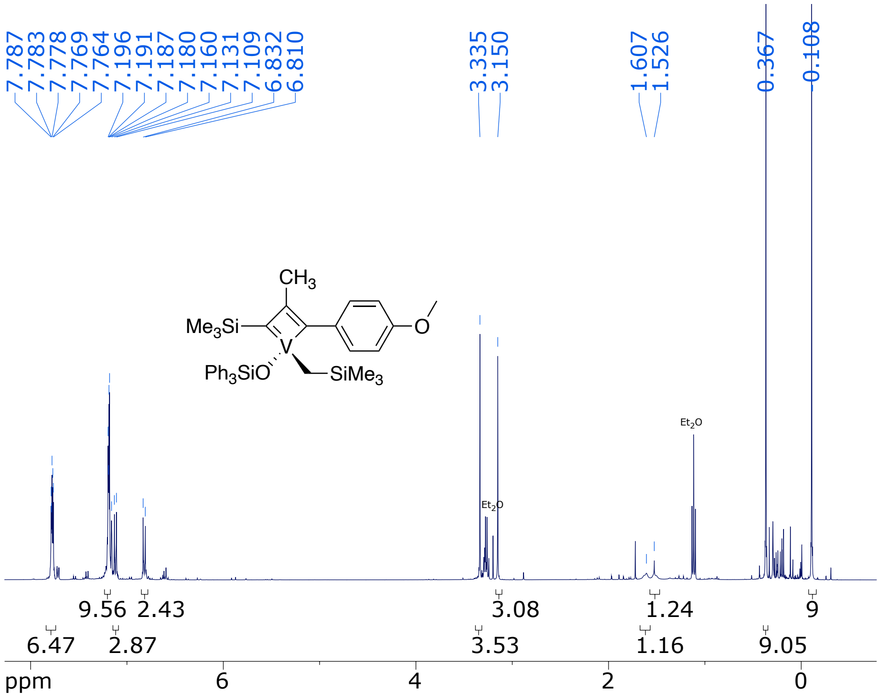


Figure S14. ^{1}H NMR spectrum of **2** (C_6D_6, 400 MHz, 22 °C). *Complex **2** is an oil that hinders its purification.*

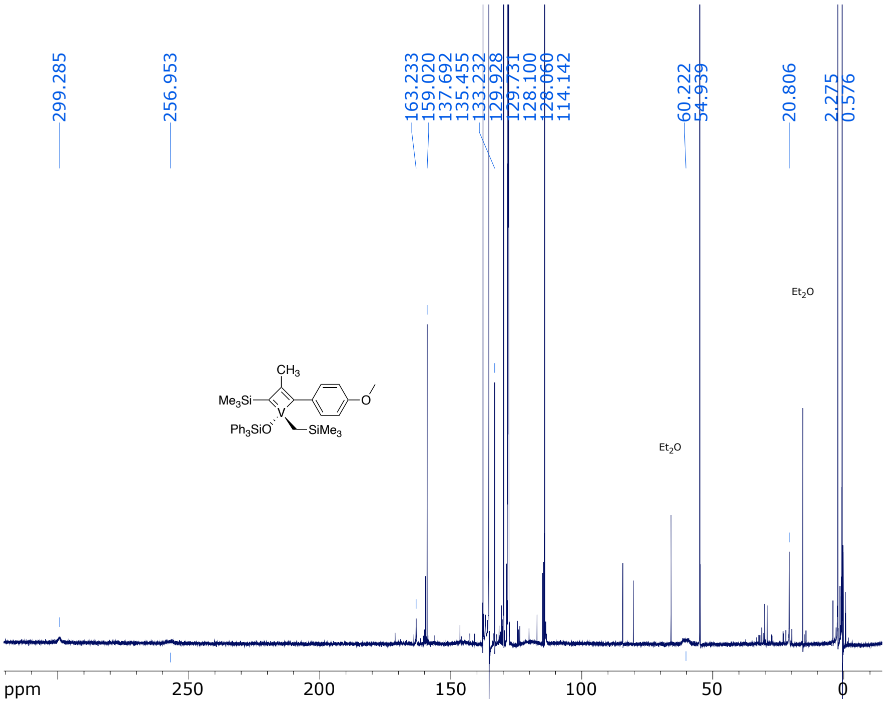


Figure S15. ^{13}C NMR spectrum of **2** (C_6D_6, 151 MHz, 22 °C). *Complex **2** is an oil that hinders its purification*

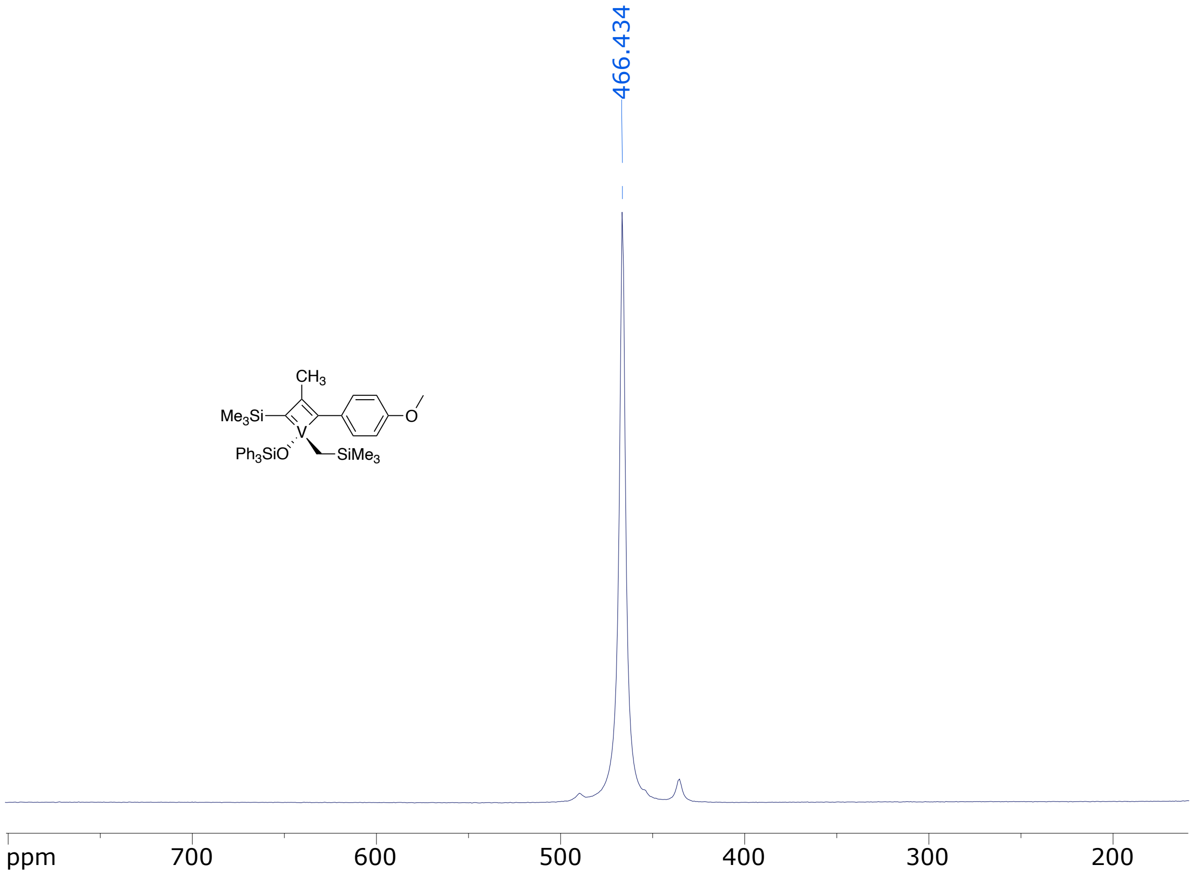


Figure S16. ^{51}V NMR spectrum of **2** (C_6D_6, 105 MHz, 22 °C).

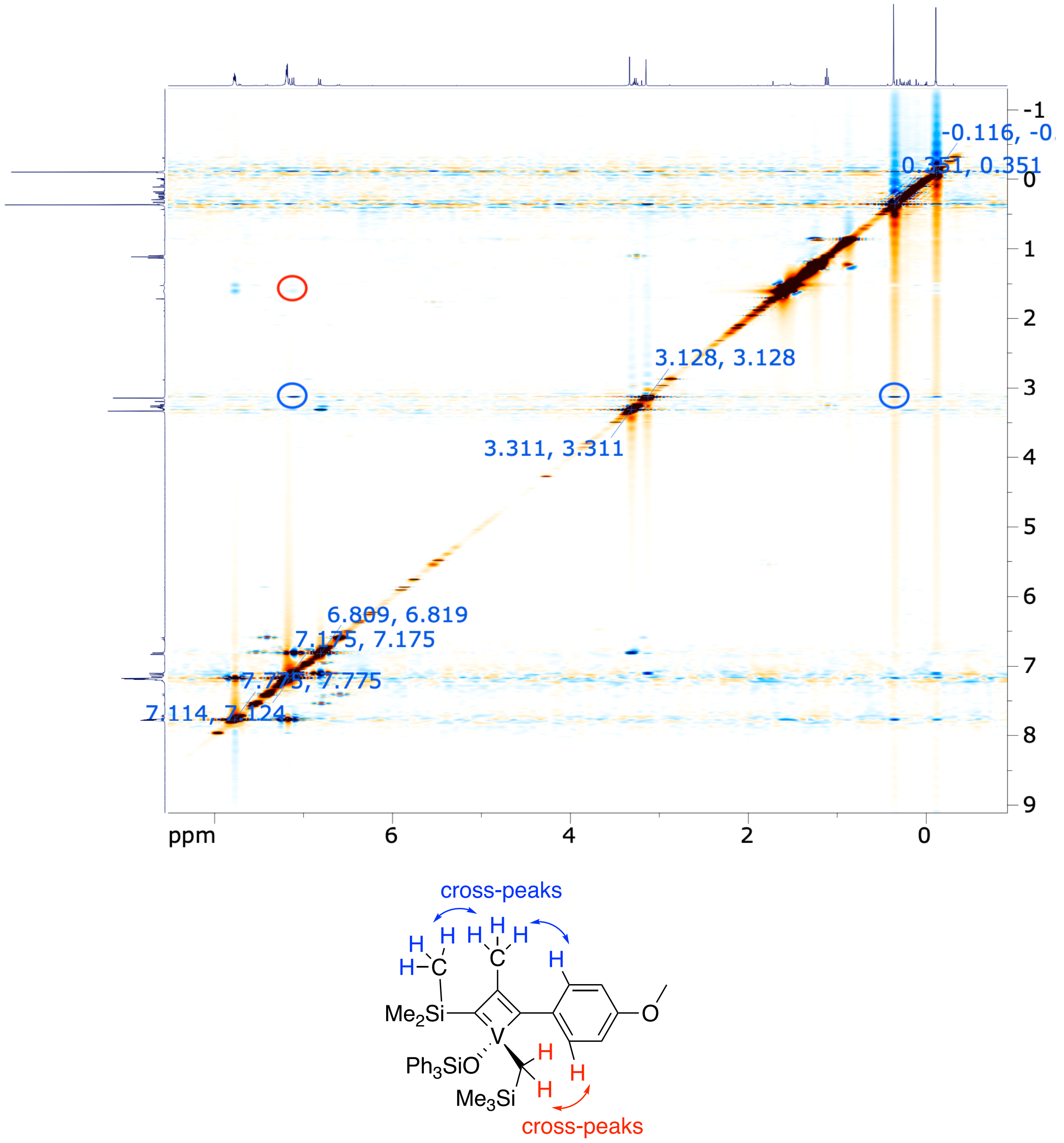


Figure S17. NOESY NMR spectrum of **2** (C_6D_6, 400 MHz, 22 °C).

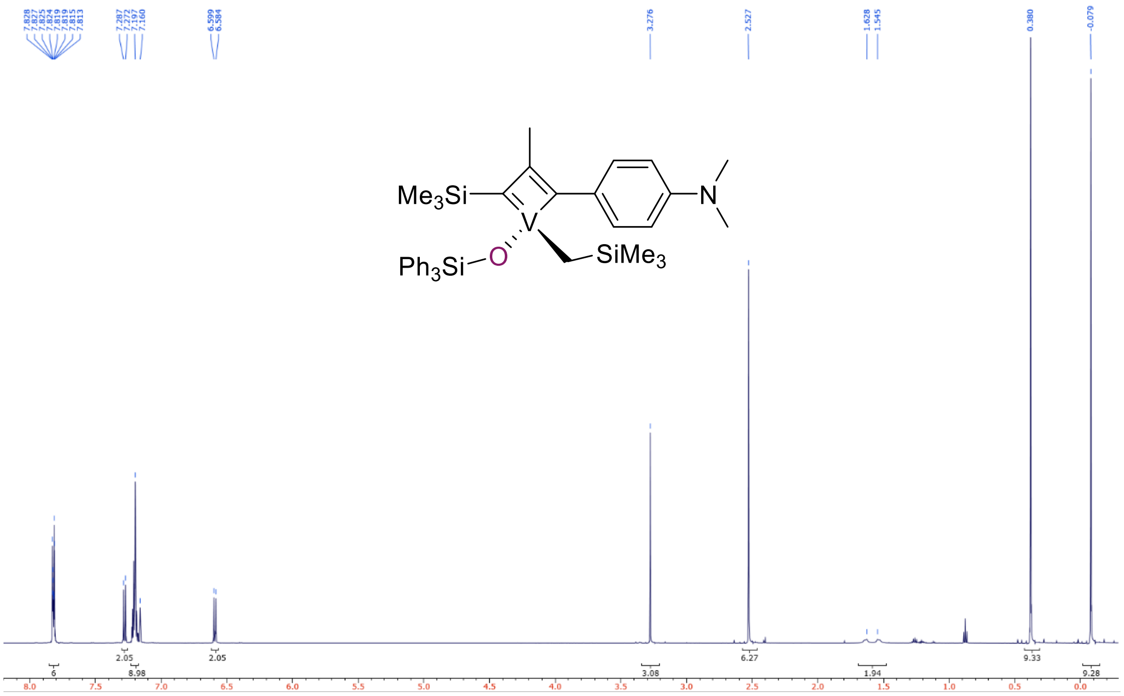


Figure S18. ^{1}H NMR spectrum of **3** (C_6D_6, 600 MHz, 22 °C).

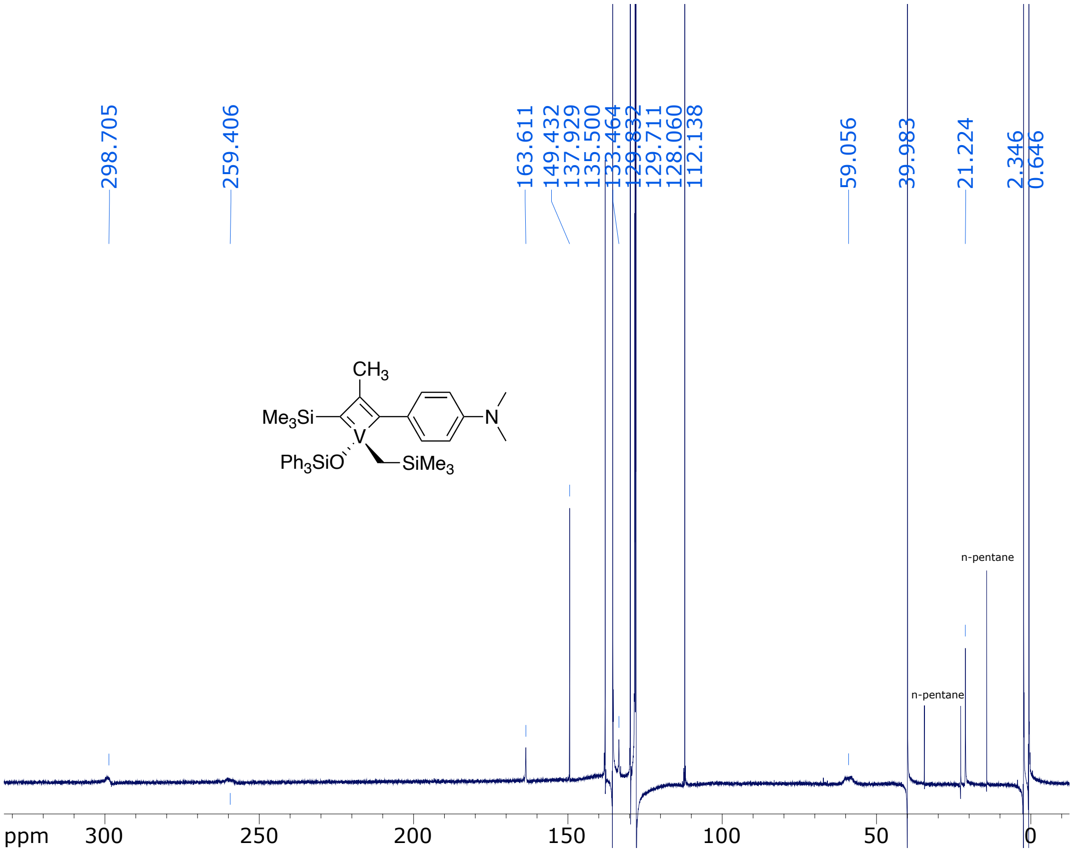


Figure S19. ^{13}C NMR spectrum of **3** (C_6D_6, 151 MHz, 22 °C).

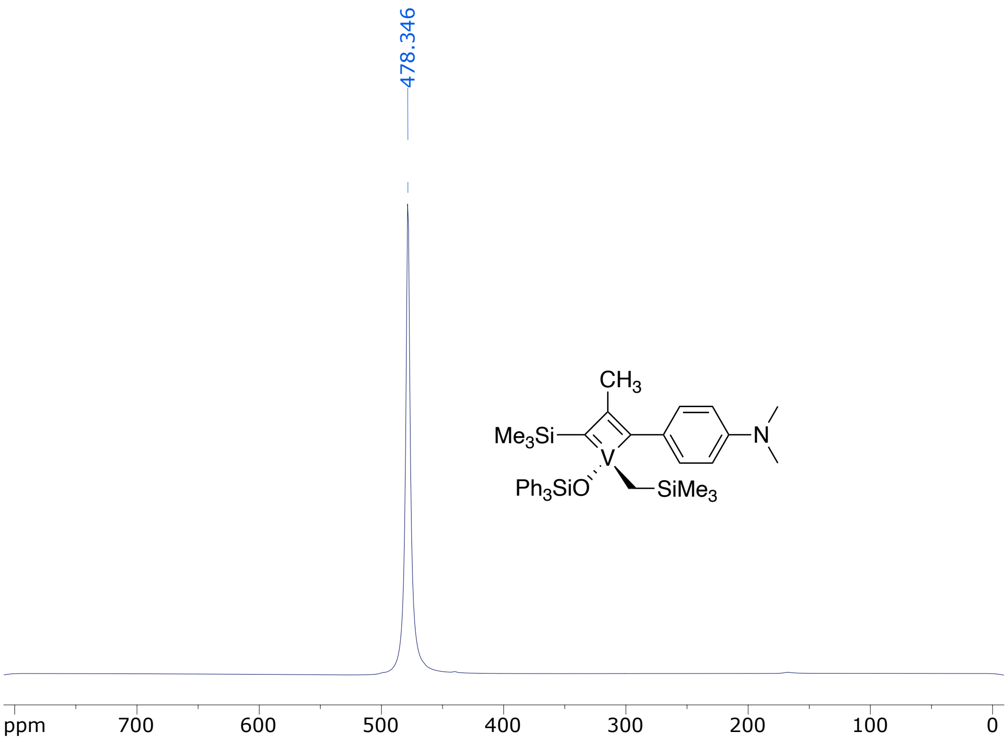


Figure S20. ^{51}V NMR spectrum of **3** (C_6D_6, 105 MHz, 22 °C).

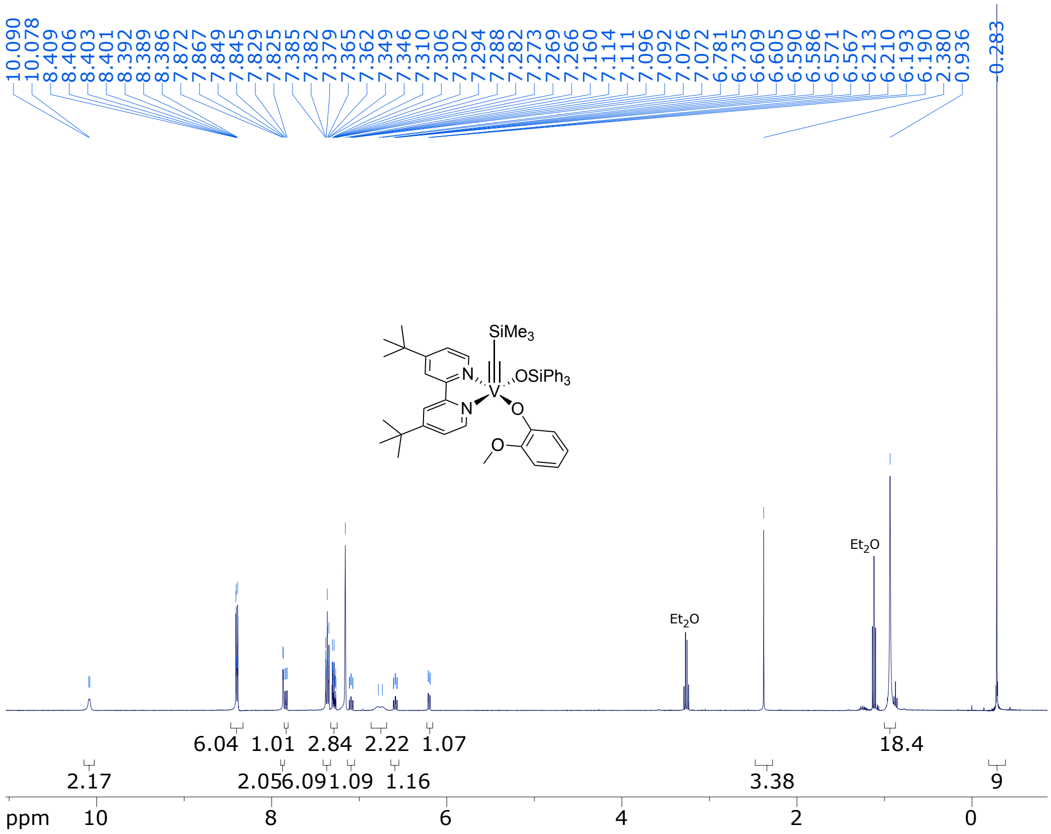


Figure S21. ^{1}H NMR spectrum of **4** (C_6D_6, 400 MHz, 22 °C).

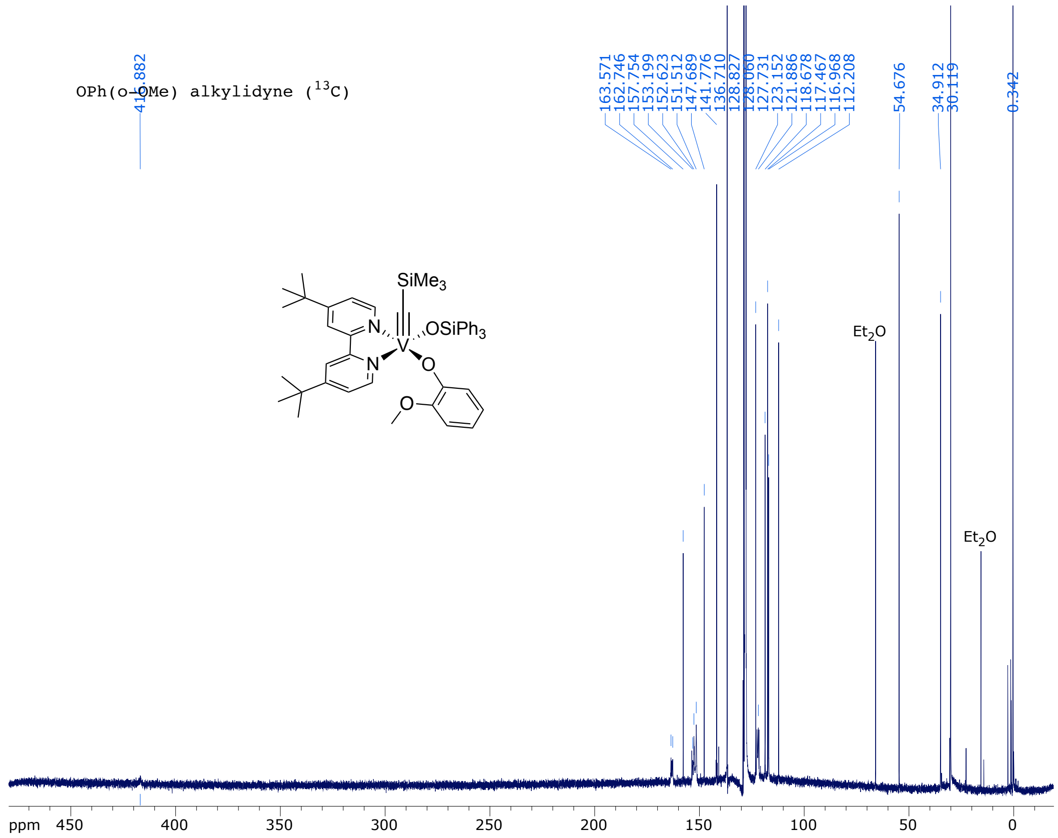


Figure S22. ^{13}C NMR spectrum of **4** (C_6D_6, 151 MHz, 22 °C).

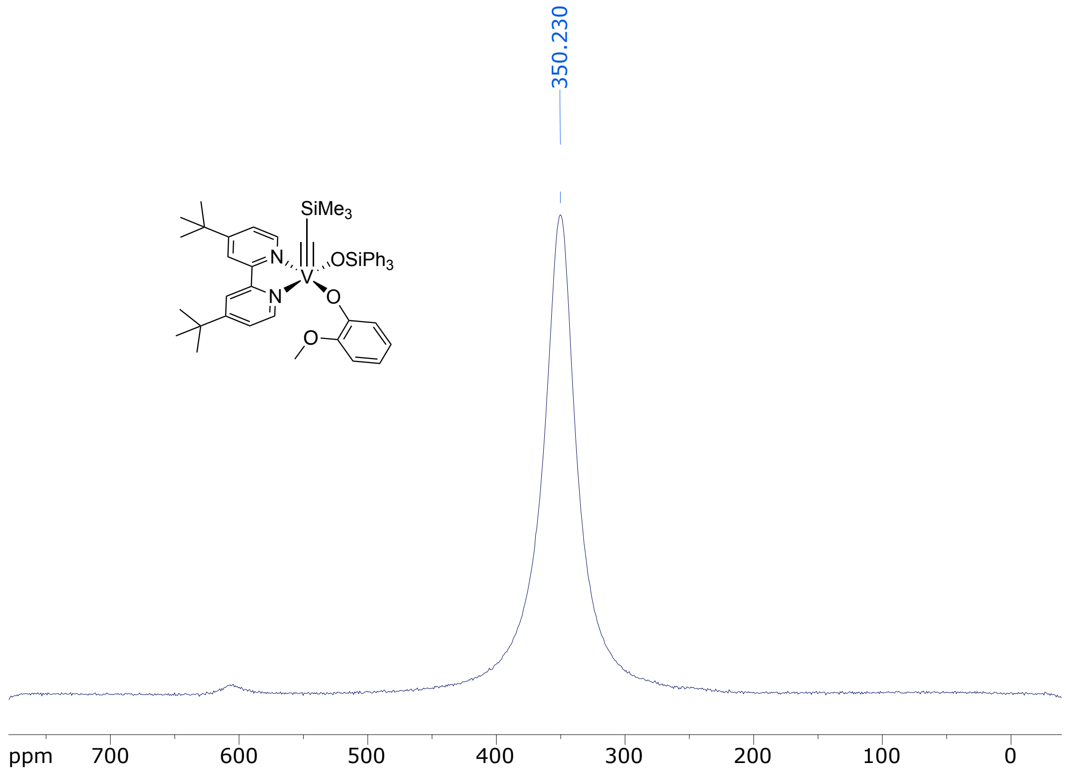


Figure S23. ^{51}V NMR spectrum of **4** (C_6D_6, 105 MHz, 22 °C).

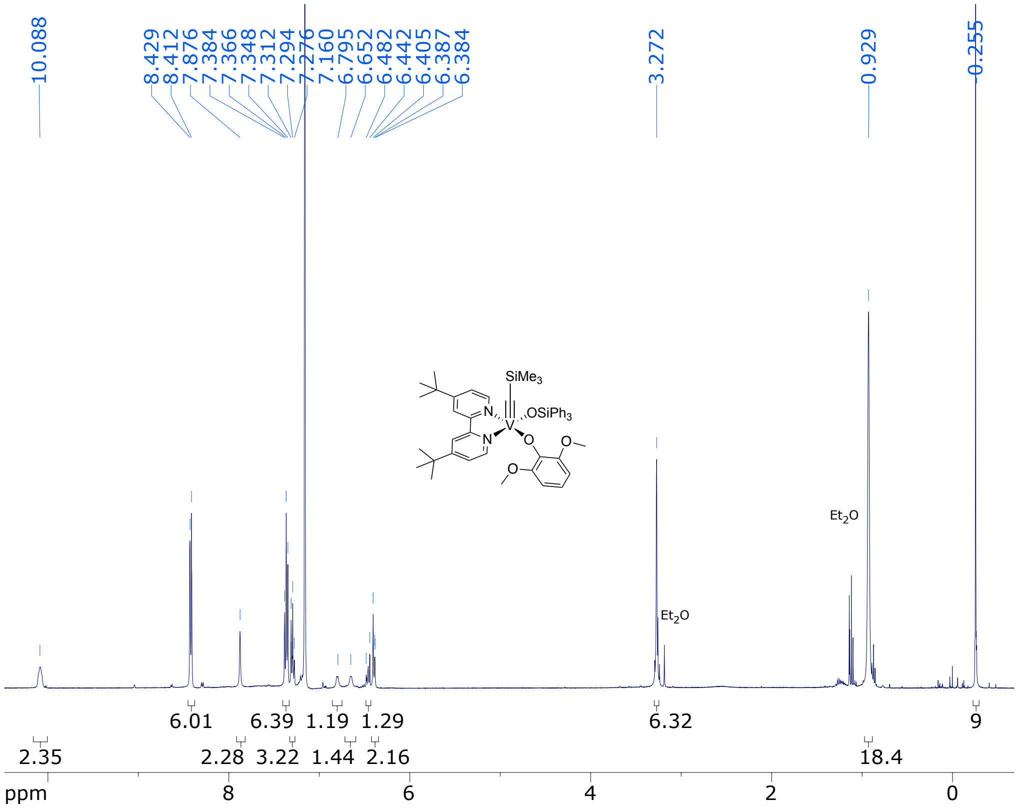


Figure S24. ^{1}H NMR spectrum of **5** (C_6D_6, 400 MHz, 22 °C).

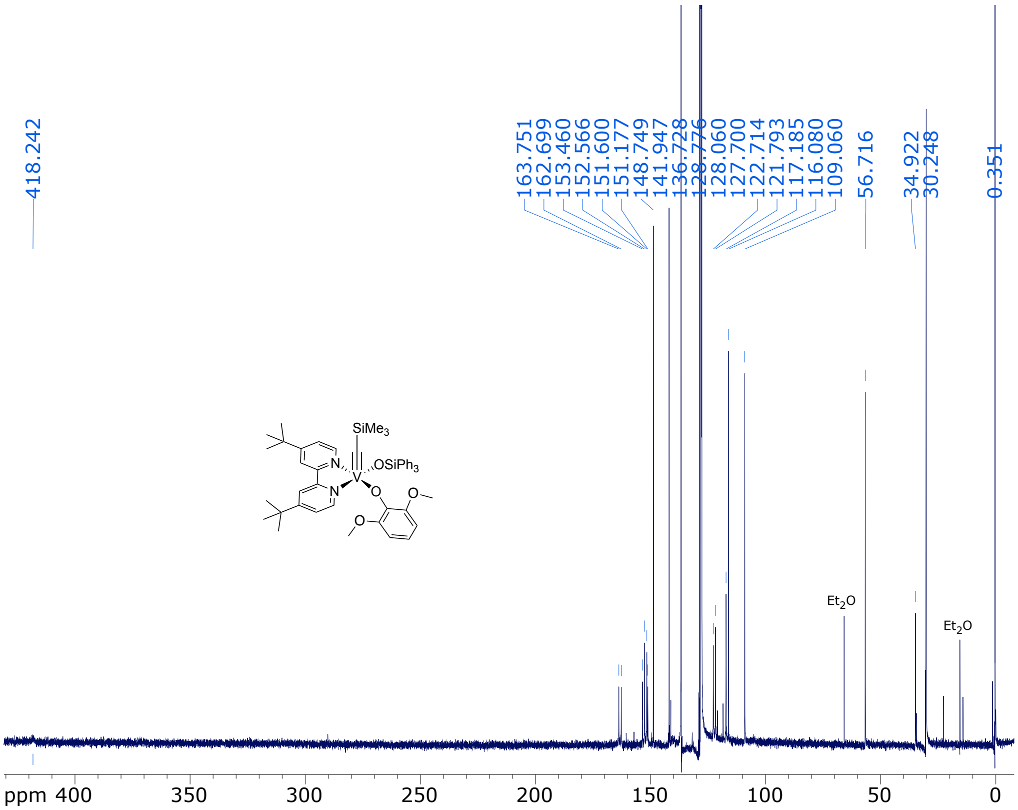


Figure S25. ^{13}C NMR spectrum of **5** (C_6D_6, 151 MHz, 22 °C).

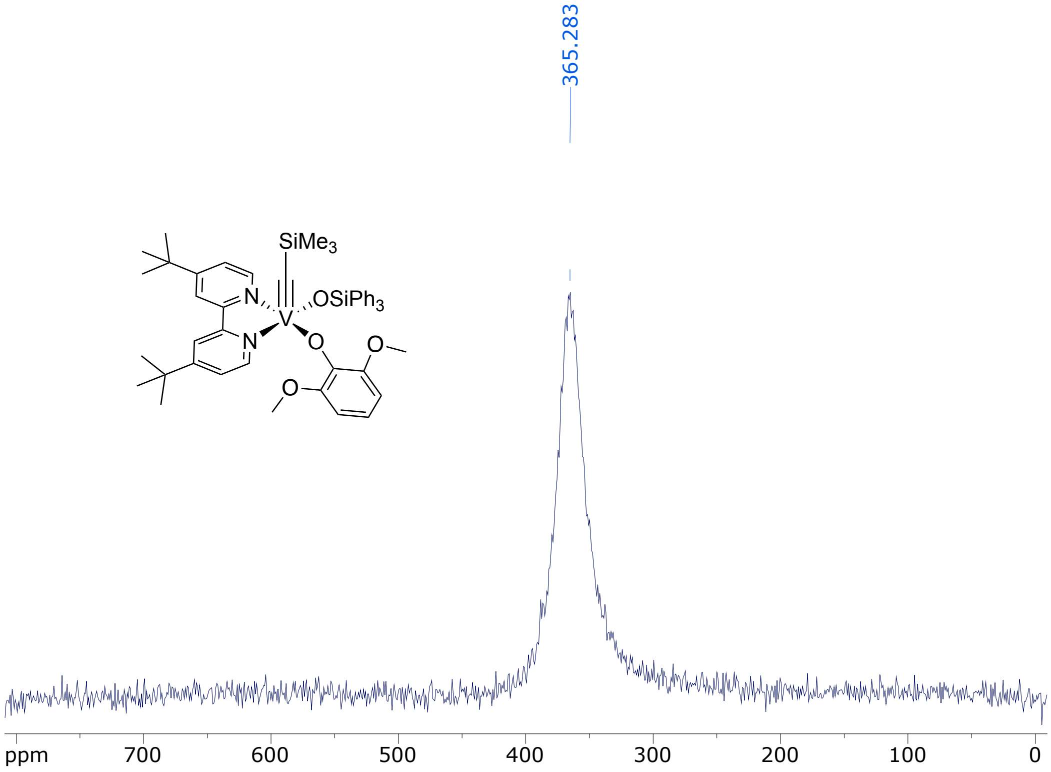


Figure S26. ^{51}V NMR spectrum of **5** (C_6D_6, 105 MHz, 22 °C).

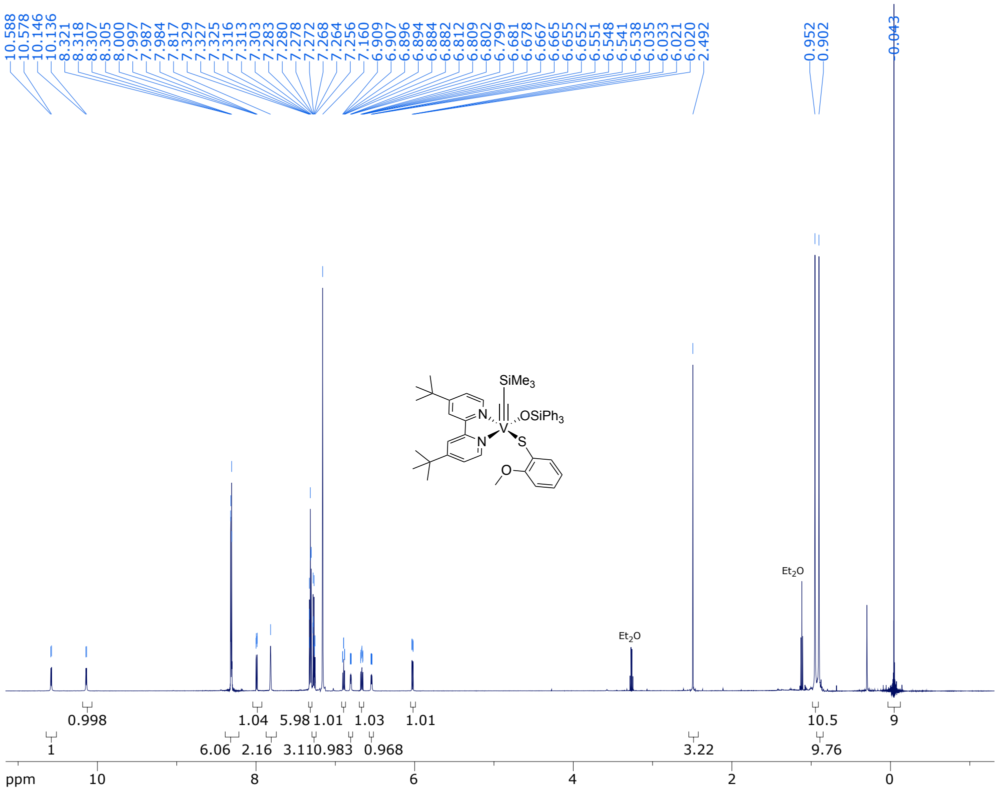


Figure S27. ^{1}H NMR spectrum of **6** (C_6D_6, 600 MHz, 22 °C).

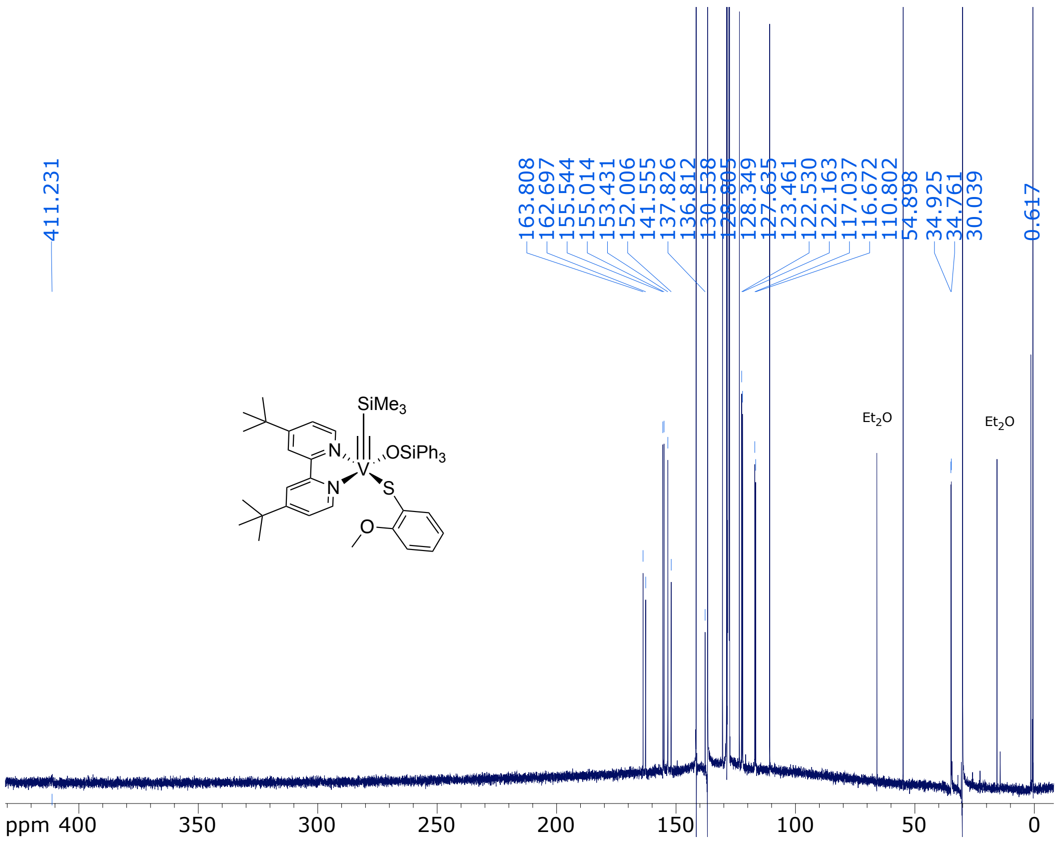


Figure S28. ^{13}C NMR spectrum of **6** (C_6D_6, 151 MHz, 22 °C).

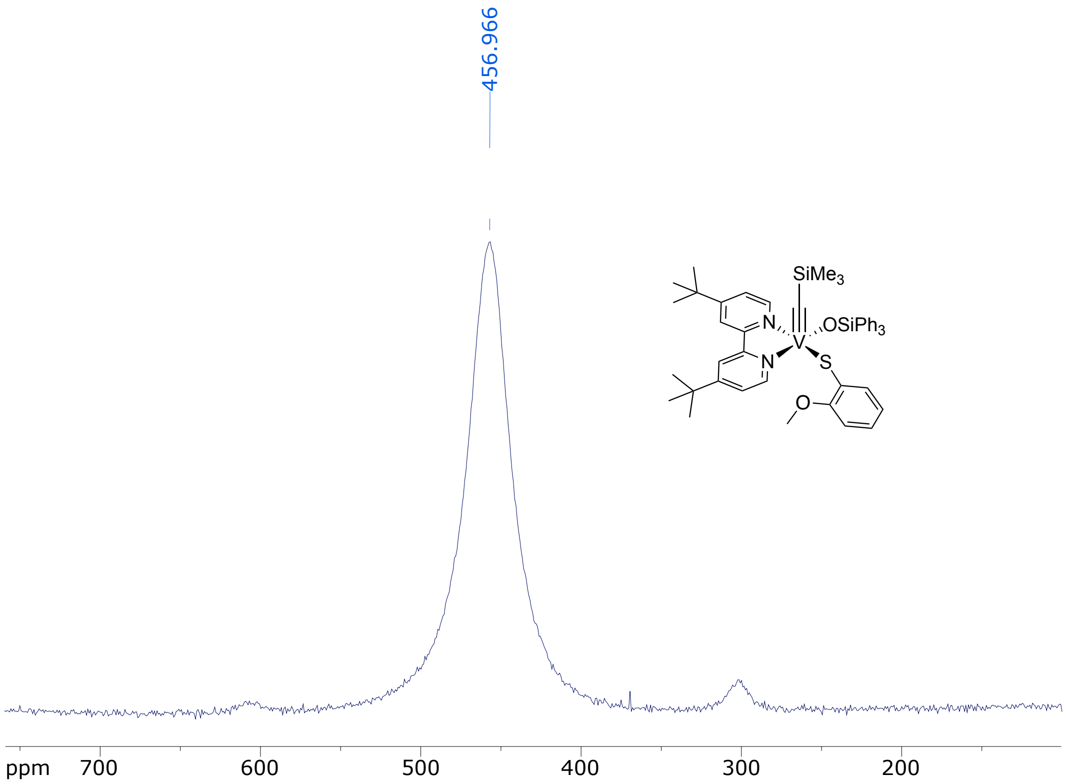


Figure S29. ^{51}VNMR spectrum of **6** (C_6D_6, 105 MHz, 22 °C).

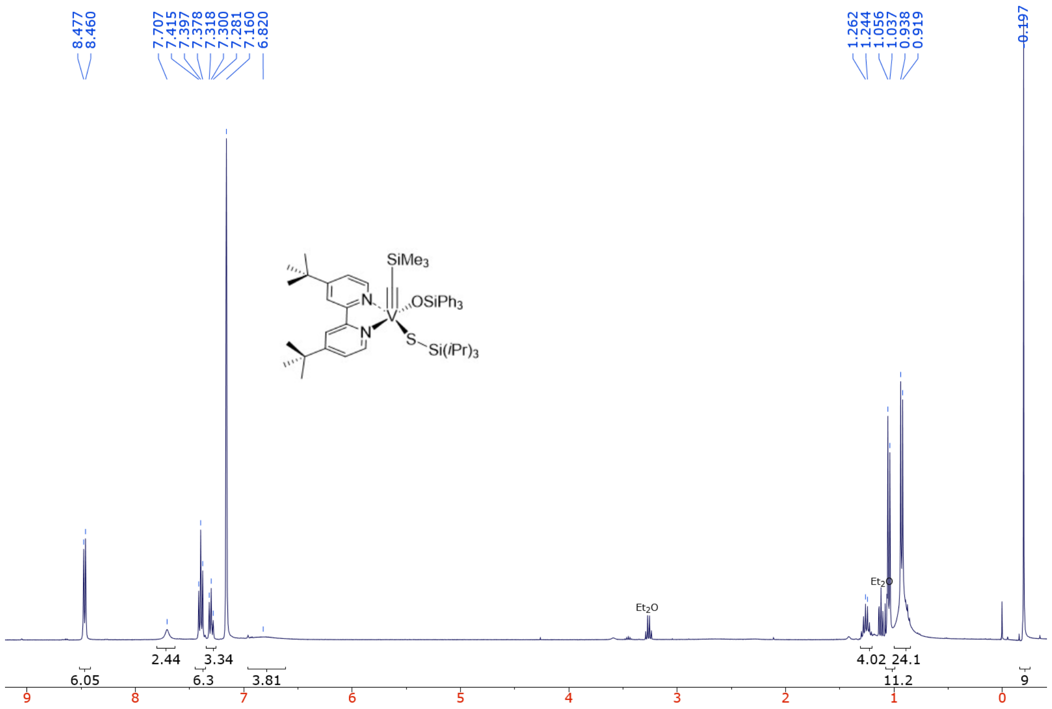


Figure S30. ^{1}H NMR spectrum of **7** (C_6D_6, 400 MHz, 22 °C).

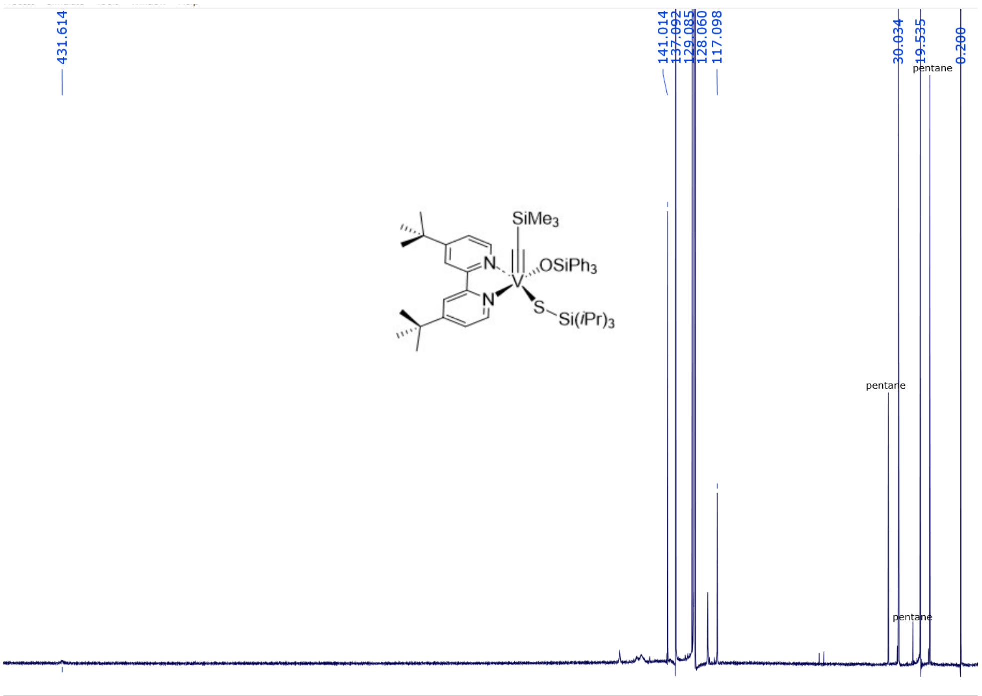


Figure S31. ^{13}C NMR spectrum of **7** (C_6D_6, 151 MHz, 22 °C).

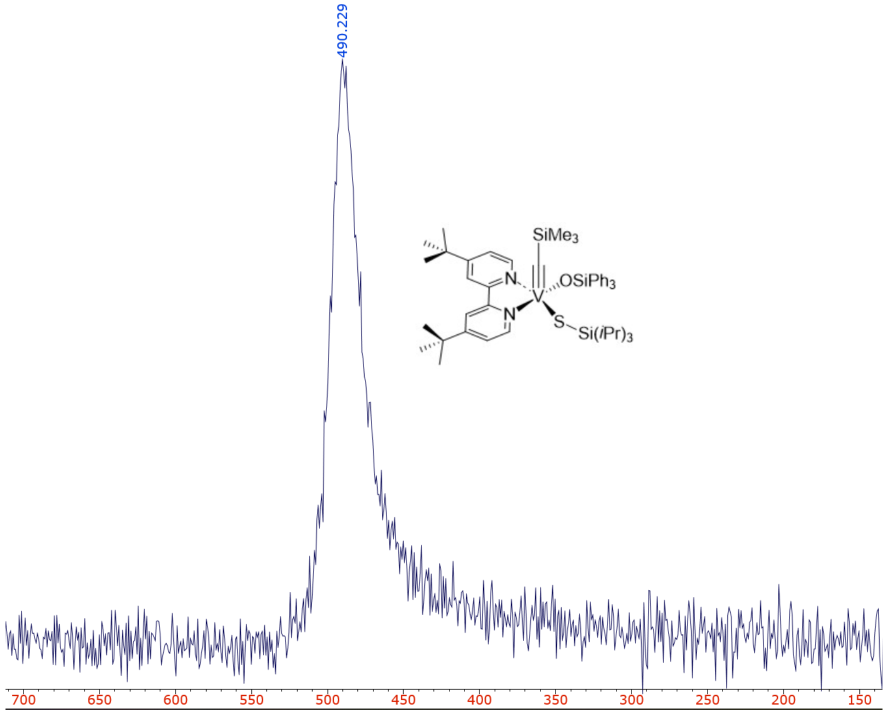


Figure S32. ^{51}V NMR spectrum of **7** (C_6D_6, 105 MHz, 22 °C).

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