Supporting Information

Iridium-catalyzed regioselective hydrosilylation of internal alkynes facilitated by directing and steric effect

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I. General information

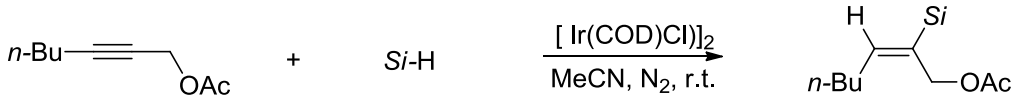
All air or moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere using dry solvents. Flash column chromatography was performed over silica gel (200-300 mesh) purchased from Qingdao Puke Co., China. Silanes and common organic chemicals were purchased from commercial suppliers, such as Sigma-Aldrich® and J&K® Scientific Ltd., and used as received. Iridium complexes were purchased from Strem® Chemicals, Inc. ^{1}H and ^{13}C NMR spectra were collected on a Bruker AV 400 MHz NMR spectrometer using residue solvent peaks as an internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm, ^{13}C NMR: $CDCl_3$ at 77.0 ppm). Mass spectra were collected on a Thermo Scientific GC/MS ISQ7000 system, or a Xevo G2 Qtof mass spectrometer.

II. Iridium-catalyzed regioselective hydrosilylation of internal alkynes

General Procedure.

In a glove box, to an oven-dried 5-mL vial were added the alkene (0.50 mmol), the silane (0.75 mmol), $[Ir(COD)Cl]_2$ (0.01 mmol, 2 mol %), and MeCN (1.0 mL). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 9 h, and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: 0→20% EtOAc in petroleum ether) to give the desired product.

Table S1. Screening of hydrosiliane.

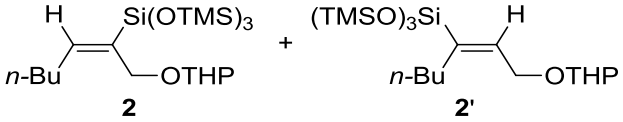


Entry	*Si*-H	Conv (%)	Yield (%)[b]	α/β[c]
1	$HSi(OEt)_3$	50	46	91 : 9
2	$HSi(OMe)_3$	50	29	89 : 11
3	$HSiMe(OEt)_2$	50	23	91 : 9
4	$HSiEt_3$	100	35	87: 13
5	$HSiPh_3$	99	35	86 : 14
6	$HSiPh_2Me$	99	29	91 : 9
7	$HSiPhMe_2$	99	30	97: 3
8	$HSiBnMe_2$	99	30	93 : 7

[a] Reaction conditions: internal alkyne (0.20 mmol, 1.0 eq.), hydrosilane (0.30 mmol, 1.5 eq.) and $[Ir(COD)Cl]_2$ (0.004 mmol, 2 mol%) in MeCN (0.40 mL, 0.5 M) under N_2 for 9 h at room temperature.

[b] ^1H NMR yield using dimethylsulfone as an internal standard.

[c] α/β ratio of the crude product determined by ^1H NMR analysis.



2 **2'**

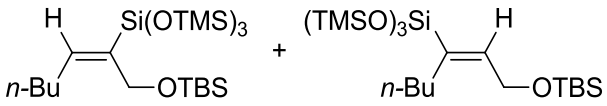
Compounds **2** and **2'** were prepared as a mixture according to the General Procedure in a total yield of 84% (207.0 mg) with an α/β ratio of 83:17.

(*E*)-1,1,1,5,5,5-hexamethyl-3-(1-((tetrahydro-2*H*-pyran-2-yl)oxy)hept-2-en-2-yl)-3-((trimethylsilyl)oxy)trisiloxane (2).

^1H NMR (400 MHz, $CDCl_3$) δ 6.12 (t, *J* = 7.2 Hz, 1 H), 4.60 (t, *J* = 3.2 Hz, 1 H), 4.31 (d, *J* = 12.0 Hz, 1 H), 4.01 (d, *J* = 11.6 Hz, 1 H), 3.92-3.85 (m, 1 H), 3.53-3.46 (m, 1 H), 2.18 (q, *J* = 7.2 Hz, 2 H), 1.69-1.46 (m, 6 H), 1.39-1.29 (m, 4 H), 0.90 (t, *J* = 7.2 Hz, 3 H), 0.10 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 132.9, 97.8, 63.9, 61.8, 31.5, 30.6, 28.6, 25.6, 22.4, 19.4, 13.9, 1.8.

HRMS *m/z* (CI) calcd. for $C_{21}H_{49}O_5Si_4$ $(M+H)^+$ 493.2658, found 493.2643.



3 **3'**

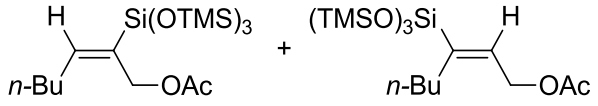
Compounds **3** and **3'** were prepared as a mixture according to the General Procedure in a total yield of 96% (251.1 mg) with an α/β ratio of 81:19.

(*E*)-3-(1-((tert-butyldimethylsilyl)oxy)hept-2-en-2-yl)-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (t, *J* = 7.2 Hz, 1 H), 4.20 (s, 2 H), 2.20 (q, *J* = 7.2 Hz, 2 H), 1.39-1.28 (m, 4 H), 0.90 (s, 12 H), 0.10 (s, 27 H), 0.06 (d, *J* = 0.4 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 135.2, 60.1, 31.5, 28.9, 26.1, 25.9, 22.5, 14.0, 1.8, -5.3.

HRMS *m/z* (CI) calcd. for $C_{22}H_{55}O_4Si_5$ $(M+H)^+$ 523.2947, found 523.2968.



4 **4'**

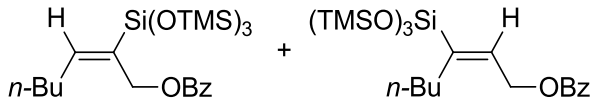
Compounds **4** and **4'** were prepared as a mixture according to the General Procedure in a total yield of 95% (214.2 mg) with an α/β ratio of 90:10.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)hept-2-en-1-yl acetate (4).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (t, *J* = 7.2 Hz, 1 H), 4.66 (s, 2 H), 2.14 (q, *J* = 6.8 Hz, 2 H), 2.04 (d, *J* = 0.8 Hz, 3 H), 1.38-1.31 (m, 4 H), 0.90 (t, *J* = 7.2 Hz, 3 H), 0.10 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 148.2, 130.8, 61.9, 31.2, 28.5, 22.3, 21.2, 13.9, 1.7.

HRMS *m/z* (CI) calcd. for $C_{18}H_{43}O_5Si_4$ $(M+H)^+$ 450.2188, found 450.2164.



5 **5'**

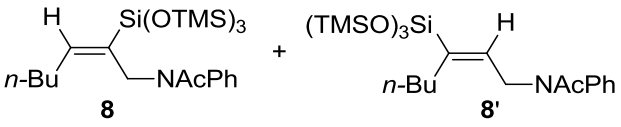
Compounds **5** and **5'** were prepared as a mixture according to the General Procedure in a total yield of 90% (230.8 mg) with an α/β ratio of 91:9.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)hept-2-en-1-yl benzoate (5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 1.2, 8.4 Hz, 2 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 2 H), 6.21 (t, *J* = 7.2 Hz, 1 H), 4.92 (s, 2 H), 2.21 (q, *J* = 6.8 Hz, 2 H), 1.43-1.32 (m, 4 H), 0.90 (t, *J* = 7.2 Hz, 3 H), 0.09 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 148.1, 132.7, 131.0, 130.5, 129.8, 128.2, 62.6, 31.3, 28.7, 22.4, 13.9, 1.8.

HRMS *m/z* (CI) calcd. for $C_{23}H_{45}O_5Si_4$ $(M+H)^+$ 513.2345, found 513.2356.



8 **8'**

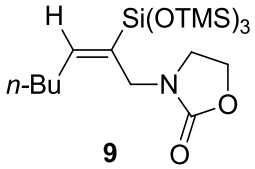
Compounds **8** and **8'** were prepared as a mixture according to the General Procedure in a total yield of 63% (165.7 mg) with an α/β ratio of 85:15.

(*E*)-N-(2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)hept-2-en-1-yl)-N-phenylacetamide (8).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 3 H), 7.15 (d, *J* = 6.4 Hz, 2 H), 5.97 (t, *J* = 7.2 Hz, 1 H), 4.49 (s, 2 H), 1.76 (s, 3 H), 1.65 (q, *J* = 7.2 Hz, 2 H), 1.14-1.06 (m, 2 H), 1.00-0.92 (m, 2 H), 0.77 (t, *J* = 7.2 Hz, 3 H), 0.10 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 148.9, 142.3, 130.5, 129.2, 128.9, 127.5, 44.2, 30.8, 27.8, 23.0, 22.2, 13.8, 1.7.

HRMS *m/z* (CI) calcd. for $C_{24}H_{48}NO_4Si_4$ $(M+H)^+$ 526.2661, found 526.2650.



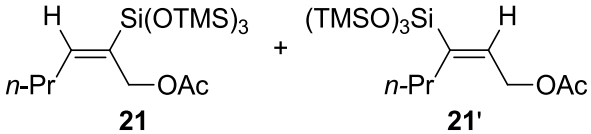
9

(*E*)-2-(2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)hept-2-en-1-yl)isoxazolidin-3-one (9) was prepared as colorless oil according to the General Procedure in a yield of 73% (174.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (t, *J* = 7.2 Hz, 1 H), 4.24 (t, *J* = 8.0 Hz, 2 H), 3.94 (s, 2 H), 3.41 (t, *J* = 8.4 Hz, 2 H), 2.17 (q, *J* = 6.8 Hz, 2 H), 1.38-1.26 (m, 4 H), 0.90 (t, *J* = 6.8 Hz, 3 H), 0.12 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 149.2, 130.4, 61.7, 43.9, 31.2, 28.3, 22.3, 13.9, 1.7.

HRMS *m/z* (CI) calcd. for $C_{19}H_{44}NO_5Si_4$ $(M+H)^+$ 478.2297, found 478.2283.



21 **21'**

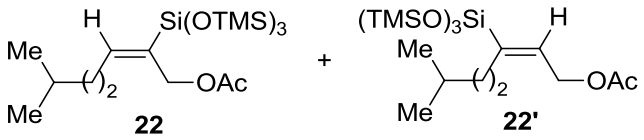
Compounds **21** and **21'** were prepared as a mixture according to the General Procedure in a total yield of 92% (200.9 mg) with an α/β ratio of 90:10.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)hex-2-en-1-yl acetate (21).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (t, *J* = 7.2 Hz, 1 H), 4.7 (s, 2 H), 2.13 (q, *J* = 7.2 Hz, 2 H), 2.0 (s, 3 H), 1.42 (q, *J* = 7.2 Hz, 2 H), 0.91 (t, *J* = 7.2 Hz, 3 H), 0.10 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 148.0, 131.0, 61.9, 30.8, 22.3, 21.2, 13.7, 1.7.

HRMS *m/z* (CI) calcd. for $C_{17}H_{41}O_5Si_4$ $(M+H)^+$ 437.2032, found 437.2045.



22 **22'**

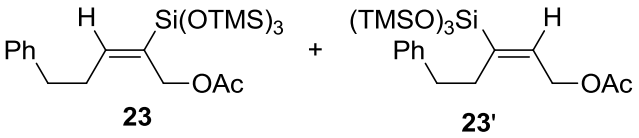
Compounds **22** and **22'** were prepared as a mixture according to the General Procedure in a total yield of 92% (213.9 mg) with an α/β ratio of 89:11.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-6-methylhept-2-en-1-yl acetate (22).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (t, *J* = 7.2 Hz, 1 H) , 4.66 (s, 2 H), 2.14 (q, *J* = 7.2 Hz, 2 H), 2.04 (s, 3 H), 1.61-1.51 (m, 1 H), 1.27 (q, *J* = 6.8 Hz, 2 H), 0.90 (s, 3 H), 0.88 (s, 3 H), 0.11 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 148.4, 130.6, 61.9, 38.2, 27.7, 26.8, 22.4, 21.1, 1.7.

HRMS *m/z* (CI) calcd. for $C_{19}H_{45}O_5Si_4$ $(M+H)^+$ 465.2345, found 465.2338.



23 **23'**

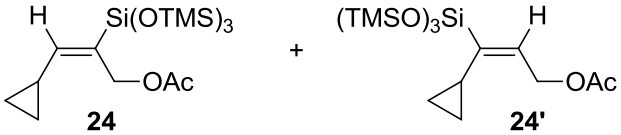
Compounds **23** and **23'** were prepared as a mixture according to the General Procedure in a total yield of 91% (227.0 mg) with an α/β ratio of 88:12.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-5-phenylpent-2-en-1-yl acetate(23).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 5 H), 6.20 (t, *J* = 7.2 Hz, 1 H), 4.64 (s, 2 H), 2.73 (t, *J* = 7.6 Hz, 2 H), 2.51 (t, *J* = 7.6 Hz, 2 H), 2.05 (s, 3 H), 0.12 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 146.6, 141.3, 131.7, 128.4, 128.4, 125.9, 61.8, 35.2, 30.5, 21.1, 1.7.

HRMS *m/z* (CI) calcd. for $C_{22}H_{43}O_5Si_4$ $(M+H)^+$ 498.2188, found 498.2176.



24 **24'**

Compounds **24** and **24'** were prepared as a mixture according to the General Procedure in a total yield of 99% (215.2 mg) with an α/β ratio of 75:25.

(*E*)-3-cyclopropyl-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)allyl acetate (24).

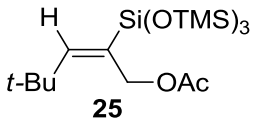
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (d, *J* = 10.0 Hz, 1 H), 4.79 (d, *J* = 0.8 Hz, 2 H), 2.06 (s, 3 H), 1.26 (t, *J* = 6.8 Hz, 1 H), 0.87-0.81 (m, 2 H), 0.46-0.41(m, 2 H), 0.10 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 152.5, 128.1, 62.3, 21.2, 11.2, 7.7, 1.7.

HRMS *m/z* (CI) calcd. for $C_{17}H_{39}O_5Si_4$ $(M+H)^+$ 435.1875, found 435.1879.

(*E*)-3-cyclopropyl-3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)allyl acetate (24').

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (td, *J* = 1.2, 5.6 Hz, 1 H), 4.83 (d, *J* = 5.6 Hz, 2 H), 2.08 (s, 3 H), 1.43-1.35 (m, 1 H), 0.70-0.64 (m, 2 H), 0.62-0.57 (m, 2 H), 0.11 (s, 27 H).

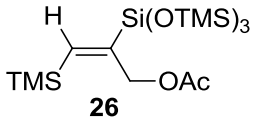


25

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-4,4-dimethylpent-2-en-1-yl acetate (25) was prepared as colorless oil according to the General Procedure in a yield of 89% (200.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.12 (t, *J* = 1.6 Hz, 1 H), 4.80 (d, *J* = 1.2 Hz, 2 H), 2.04 (s, 3 H), 1.13 (s, 9 H), 0.10 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 156.3, 129.7, 61.8, 34.8, 30.7, 21.3, 1.7.

HRMS *m/z* (CI) calcd. for $C_{18}H_{43}O_5Si_4$ $(M+H)^+$ 450.2188, found 450.2197.



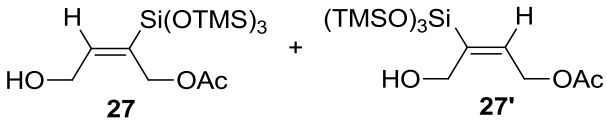
26

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-3-(trimethylsilyl)allyl acetate (26) was prepared as colorless oil according to the General Procedure in a yield of 85% yield (198.5 m g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (s, 1 H), 4.69 (s, 2 H), 2.06 (s, 3 H), 0.14 (s, 9 H), 0.10 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 152.4, 149.6, 66.4, 21.2, 1.70, -0.13.

HRMS *m/z* (CI) calcd. for $C_{17}H_{43}O_5Si_5$ $(M+H)^+$ 467.1958, found 467.1942.



27 **27'**

Compounds **27** and **27'** were prepared as a mixture according to the General Procedure in a total yield of 90% (191.2 mg) with an α/β ratio of 67:33.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-4-hydroxybut-2-en-1-yl acetate (27).

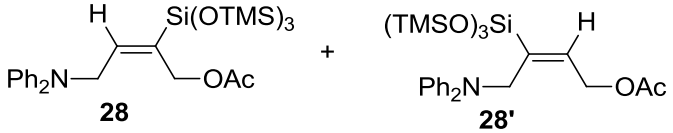
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (tt, *J* = 1.2, 6.0 Hz, 1 H), 4.67 (s, 2 H), 4.26 (d, *J* = 4.4 Hz, 2 H), 2.03 (d, *J* = 1.6 Hz, 3 H), 0.10 (d, *J* = 1.6 Hz, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 145.2, 133.1, 61.8, 59.5, 21.1, 1.7.

HRMS *m/z* (CI) calcd. for $C_{15}H_{37}O_6Si_4$ $(M+H)^+$ 425.1688, found 425.1673.

(*E*)-3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-4-hydroxybut-2-en-1-yl acetate (27').

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (t, *J* = 6.0 Hz, 1 H), 4.72 (d, *J* = 6.4 Hz, 2 H), 4.29 (s, 2 H), 2.05 (d, *J* = 1.2 Hz, 3 H), 0.11 (d, *J* = 0.8 Hz, 27 H).



28 **28'**

Compounds **28** and **28'** were prepared as a mixture according to the General Procedure in a total yield of 92% (265.0 mg) with an α/β ratio of 50:50.

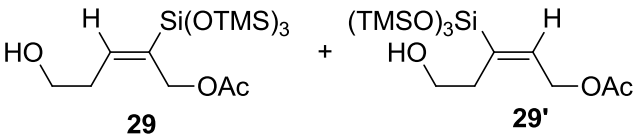
(*E*)-4-(diphenylamino)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)but-2-en-1-yl acetate (28).

(*E*)-4-(diphenylamino)-3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)but-2-en-1-yl acetate (28').

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 8 H), 7.10-6.90 (m, 12 H), 6.31 (tt, *J* = 1.2, 5.6 Hz, 1 H), 5.96 (tt, *J* = 1.6, 5.6 Hz, 1 H), 4.71 (s, 2 H), 4.67 (d, *J* = 5.6 Hz, 2 H), 4.51 (d, *J* = 5.6 Hz, 2 H), 4.41 (d, *J* = 1.6 Hz, 2 H), 2.09 (s, 3 H), 2.01 (s, 3 H), 0.13 (s, 27 H), 0.08 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.7, 148.4, 147.8, 144.7, 137.7, 136.5, 133.2, 129.2, 129.0, 121.6, 121.4, 121.3, 121.0, 62.7, 61.7, 53.1, 51.0, 21.1, 20.8, 1.7, 1.6.

HRMS m/z (CI) calcd. for $C_{27}H_{46}NO_5Si_4$ $(M+H)^+$ 575.2375, found 575.2369.



29 **29'**

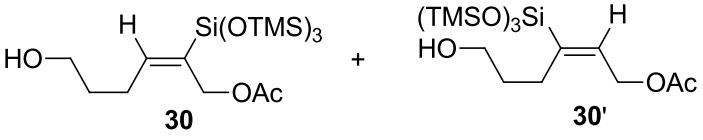
Compounds **29** and **29'** were prepared as a mixture according to the General Procedure in a total yield of 86% (189.6 mg) with an α/β ratio of 86:14.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-5-hydroxypent-2-en-1-yl acetate (29).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (t, *J* = 7.2 Hz, 1 H), 4.69 (s, 2 H), 3.69 (t, *J* = 6.4 Hz, 2 H), 2.45 (q, *J* = 6.8 Hz, 2 H), 2.04 (s, 3 H), 0.11 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 143.4, 134.3, 61.8, 61.7, 32.4, 21.2, 1.7.

HRMS *m/z* (CI) calcd. for $C_{16}H_{39}O_6Si_4$ $(M+H)^+$ 439.1824, found 439.1810.



30 **30'**

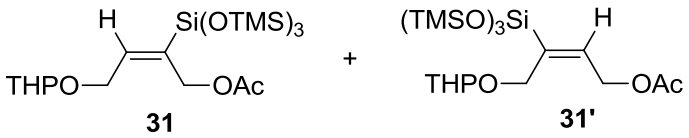
Compounds **30** and **30'** were prepared as a mixture according to the General Procedure in a total yield of 90% (203.8 mg) with an α/β ratio of 88:12.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-6-hydroxyhex-2-en-1-yl acetate (30).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (t, *J* = 7.2 Hz, 1 H), 4.68 (s, 2 H), 3.63 (t, *J* = 6.0 Hz, 2 H), 2.27 (q, *J* = 7.2 Hz, 2 H), 2.03 (s, 3 H), 1.71-1.63 (m, 2 H), 0.1 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 147.0, 131.9, 61.9, 61.8, 31.9, 25.0, 21.2, 1.7.

HRMS *m/z* (CI) calcd. for $C_{17}H_{41}O_6Si_4$ $(M+H)^+$ 453.1981, found 453.1995.



31 **31'**

Compounds **31** and **31'** were prepared as a mixture according to the General Procedure in a total yield of 93% (236.6 mg) with an α/β ratio of 75:25.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-4-((tetrahydro-2*H*-pyran-2-yl)oxy)but-2-en-1-yl acetate (31).

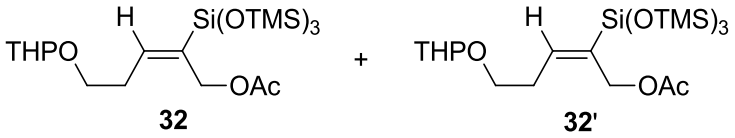
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (t, *J* = 4.8 Hz, 1 H), 4.65 (d, *J* = 3.2 Hz, 2 H), 4.61 (d, *J* = 3.6 Hz, 1 H), 3.88-3.81 (m, 2 H), 3.53-3.3.45 (m, 2 H), 2.03 (s, 3 H), 1.62-1.52 (m, 6 H), 0.10 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 143.5, 133.3, 98.0, 64.4, 63.8, 62.2, 30.6, 25.4, 21.1, 19.4, 1.7.

HRMS *m/z* (CI) calcd. for $C_{20}H_{45}O_7Si_4$ $(M+H)^+$ 508.2164 , found 508.2152.

(*E*)-3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-4-((tetrahydro-2H-pyran-2-yl)oxy)but-2-en-1-yl acetate (31').

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (t, *J* = 5.6 Hz, 1 H), 4.81-4.78 (m, 2 H), 4.59 (d, *J* = 5.6 Hz, 1 H), 3.88-3.81 (m, 2 H), 3.53-3.3.45 (m, 2 H), 2.05 (s, 3 H), 1.62-1.52 (m, 6 H), 0.10 (s, 27 H).



32 **32'**

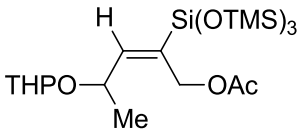
Compounds **32** and **32'** were prepared as a mixture according to the General Procedure in a total yield of 99% (258.8 mg) with an α/β ratio of 88:12.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-5-((tetrahydro-2*H*-pyran-2-yl)oxy)pent-2-en-1-yl acetate (32).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (t, *J* = 7.2 Hz, 1 H), 4.68 (s, 2 H), 4.60 (t, *J* = 3.6 Hz, 1 H), 3.88-3.75 (m, 2 H), 3.53-3.38 (m, 2 H), 2.46 (q, *J* = 6.8 Hz, 2 H), 2.04 (s, 3 H), 1.72-1.47 (m, 6 H), 0.10 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 143.9, 132.9, 98.6, 66.3, 62.0, 30.6, 29.5, 25.5, 21.1, 19.3, 1.7.

HRMS *m/z* (CI) calcd. for $C_{21}H_{47}O_7Si_4$ $(M+H)^+$ 522.2321, found 522.2337.

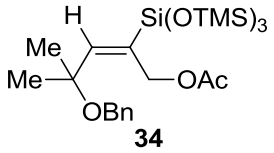


33

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-4-((tetrahydro-2*H*-pyran-2-yl)oxy)pent-2-en-1-yl acetate (33) was prepared as colorless oil according to the General Procedure in a yiel d of 85% (222.2 mg).

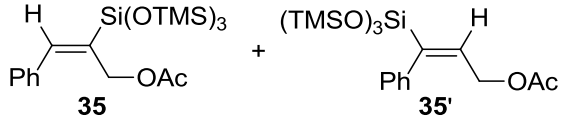
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (d, *J* = 8.8 Hz, 1 H), 4.75-4.62 (m, 3 H), 4.50-4.47 (m, 1 H), 3.92-3.85 (m, 1 H), 3.49-3.43 (m, 1 H), 2.04 (s, 3 H), 1.86-1.50 (m, 6 H), 1.26 (d, *J* = 6.4 Hz, 3 H), 0.11 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 148.1, 133.8, 96.1, 66.9, 62.9, 61.8, 30.9, 25.5, 21.1, 20.9, 20.0, 1.7.
HRMS *m/z* (CI) calcd. for $C_{21}H_{47}O_7Si_4$ $(M+H)^+$ 523.2400, found 523.2408.



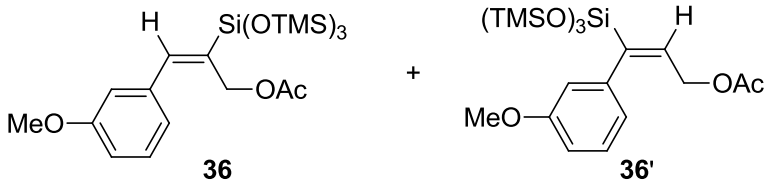
34

(*E*)-4-(benzyloxy)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-4-methylpent-2-en-1-yl acetate (34) was prepared as colorless oil according to the General Procedure in a yield of 92% (249.8 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 4.4 Hz, 4 H), 7.25-7.21 (m, 1 H), 6.08 (s, 1 H), 4.97 (d, *J* = 1.2 Hz, 2 H), 4.42 (s, 2 H), 1.91 (s, 3 H), 1.44 (s, 6 H), 0.12 (s, 27 H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 148.9, 139.3, 134.7, 128.2, 127.1, 127.0, 76.6, 64.9, 62.2, 27.9, 21.1, 1.8.
HRMS *m/z* (CI) calcd. for $C_{24}H_{47}O_6Si_4$ $(M+H)^+$ 543.2450, found 543.2463.



35 **35'**

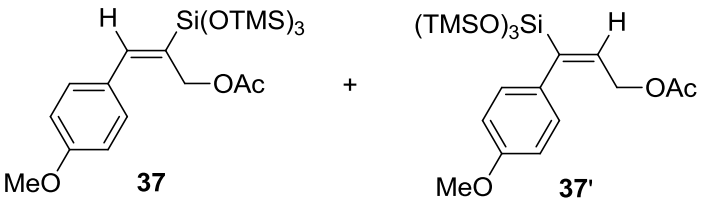
Compounds **35** and **35'** were prepared as a mixture according to the General Procedure in a total yield of 90% (211.9 mg) with an α/β ratio of 89:11.
(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-3-phenylallyl acetate (35).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 3 H), 7.30-7.27 (m, 2 H), 7.14 (s, 1 H), 7.30 (d, *J* = 1.6 Hz, 2 H), 2.06 (s, 3 H), 0.15 (s, 27 H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 144.1, 136.9, 133.7, 128.7, 128.3, 127.6, 63.1, 21.2, 1.8.
HRMS *m/z* (CI) calcd. for $C_{20}H_{39}O_5Si_4$ $(M+H)^+$ 470.1875, found 470.1893.



36 **36'**

Compounds **36** and **36'** were prepared as a mixture according to the General Procedure in a total yield of 83% (207.9 mg) with an α/β ratio of 86:14.
(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-3-(3-methoxyphenyl)allyl acetate (36).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 8.0 Hz, 1 H), 7.12 (s, 1 H), 6.85-6.79 (m, 2 H), 6.78 (t, *J* = 2.0 Hz, 1 H), 4.83 (d, *J* = 1,2 Hz, 2 H), 3.81 (s, 3 H), 2.06 (s, 3 H), 0.15 (s, 27 H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 159.4, 144.1, 138.3, 133.9, 129.3, 121.2, 114.2, 113.2, 63.1, 55.2, 21.2, 1.8.

HRMS *m/z* (CI) calcd. for $C_{21}H_{41}O_6Si_4$ $(M+H)^+$ 501.1981, found 501.1975.



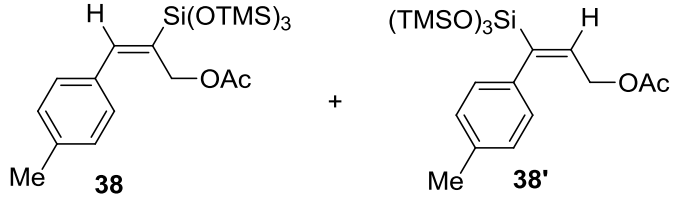
Compounds **37** and **37'** were prepared as a mixture according to the General Procedure in a total yield of 77% (192.8 mg) with an α/β ratio of 81:19.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-3-(4-methoxyphenyl)allyl acetate (37).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1 H), 7.17 (s, 1 H), 7.08 (s, 1 H), 6.90 (s, 1 H), 6.87 (s, 1 H), 4.84 (s, 2 H), 3.82 (s, 3 H), 2.07 (s, 3 H), 0.15 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 159.2, 143.8, 130.3, 129.5, 129.3, 113.7, 63.2, 55.3, 21.2, 1.8.

HRMS *m/z* (CI) calcd. for $C_{21}H_{41}O_6Si_4$ $(M+H)^+$ 501.1981, found 501.2001.



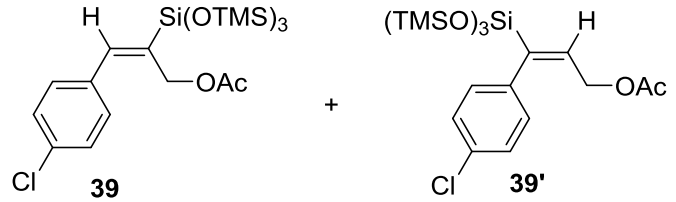
Compounds **38** and **38'** were prepared as a mixture according to the General Procedure in a total yield of 90% (218.2 mg) with an α/β ratio of 86:14.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-3-(p-tolyl)allyl acetate (38).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.07 (m, 5 H), 4.84 (s, 2 H), 2.35 (s, 3 H), 2.06 (s, 3 H), 0.15 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 144.1, 137.6, 134.0, 132.8, 129.0, 128.8, 63.2, 21.2, 1.8.

HRMS *m/z* (CI) calcd. for $C_{21}H_{41}O_5Si_4$ $(M+H)^+$ 485.1672, found 485.1664.



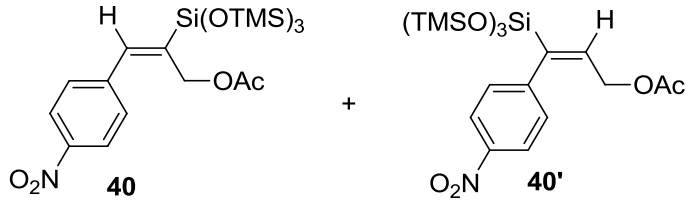
Compounds **39** and **39'** were prepared as a mixture according to the General Procedure in a total yield of 75% (189.5 mg) with an α/β ratio of 88:12.

(*E*)-3-(4-chlorophenyl)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)allyl acetate (39).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 7.07 (s, 1 H), 4.80 (s, 2 H), 2.06 (s, 3 H), 0.15 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 142.6, 135.3, 134.7, 133.6, 130.0, 128.5, 62.8, 21.1, 1.8.

HRMS *m/z* (CI) calcd. for $C_{20}H_{38}ClO_5Si_4$ $(M+H)^+$ 505.1486, found 505.1501.



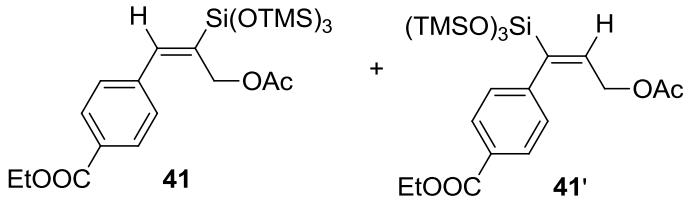
Compounds **40** and **40'** were prepared as a mixture according to the General Procedure in a total yield of 58% (149.6 mg) with an α/β ratio of 95:5.

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-3-(4-nitrophenyl)allyl acetate (40).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2 H), 7.37 (d, *J* = 8.8 Hz, 2 H), 7.12 (s, 1 H), 4.78 (d, *J* = 1.2 Hz, 2 H), 2.04 (s, 3 H), 0.16 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 166.2, 142.8, 141.3, 136.0, 129.5, 128.5, 62.8, 60.9, 21.1, 14.3, 1.7.

HRMS *m/z* (CI) calcd. for $C_{20}H_{38}NO_7Si_4$ $(M+H)^+$ 516.1726, found 516.1720.



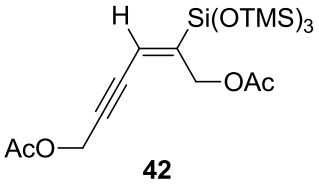
Compounds **41** and **41'** were prepared as a mixture according to the General Procedure in a total yield of 60% (162.9 mg) with an α/β ratio of 91:9.

Ethyl(*E*)-4-(3-acetoxy-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)prop-1-en-1-yl)benzoate (41).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz， 2 H), 7.24 (s, 1 H), 4.90 (d, *J* = 1.6 Hz, 2 H), 4.48 (q, *J* = 7.2 Hz, 2 H)， 2.15 (s, 3 H)， 1.49 (t, *J* = 7.2 Hz, 3 H), 0.26 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 166.2, 142.8, 141.3, 136.0, 129.5, 128.5, 62.8, 60.9, 21.1, 14.3, 1.7.

HRMS *m/z* (CI) calcd. for $C_{23}H_{43}O_7Si_4$ $(M+H)^+$ 543.2087, found 543.2090.

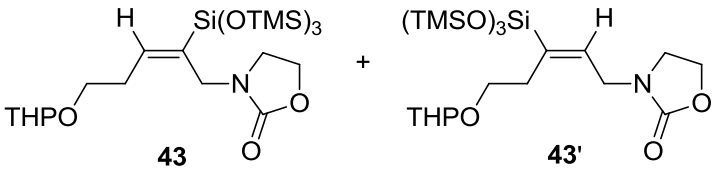


(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)hex-2-en-4-yne-1,6-diyl diacetate (42) was prepared as pale yellow oil according to the General Procedure in a yield of 84% (206.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (t, *J* = 6.0 Hz, 1 H), 4.84 (s, 2 H), 4.83 (d, *J* = 6.0 Hz, 2 H), 2.07 (d, *J* = 2.0 Hz, 6 H), 0.12 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.2, 146.6, 122.2, 92.4, 83.9, 63.7, 52.9, .20.8, 20.6, 1.54.

HRMS *m/z* (CI) calcd. for $C_{19}H_{39}O_7Si_4$ $(M+H)^+$ 491.1774, found 491.1768.



43 **43'**

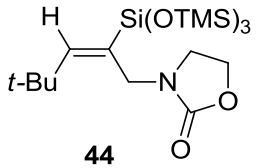
Compounds **43** and **43'** were prepared as a mixture according to the General Procedure in a total yield of 77% (211.7 mg) with an α/β ratio of 88:12.

(*E*)-3-(2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-5-((tetrahydro-2H-pyran-2-yl)oxy)pent-2-en-1-yl)oxazolidin-2-one (43).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29 (t, *J* = 6.8 Hz, 1 H), 4.59 (t, *J* = 3.6 Hz, 1 H), 4.24 (t, *J* = 8.0 Hz, 2 H), 3.96 (s, 2 H), 3.83-3.78 (m, 2 H), 3.52-3.46 (m, 2 H), 3.43 (t, *J* = 8.0 Hz, 2 H), 2.47 (q, *J* = 6.4 Hz, 2 H), 1.79-1.52 (m, 6 H), 0.12 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 145.2, 132.3, 98.7, 66.3, 62.0, 61.7, 43.9, 41.7, 30.6, 29.3, 25.4, 19.3, 1.7.

HRMS *m/z* (CI) calcd. for $C_{22}H_{48}NO_7Si_4$ $(M+H)^+$ 550.2509, found 550.2497.



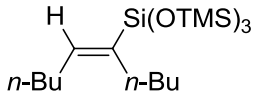
44

(*E*)-3-(2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)-4,4-dimethylpent-2-en-1-yl)oxazolidin-2-one (44) was prepared as white solid according to the General Procedure in a yield of 81% (193.5mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (t, *J* = 1.2 Hz, 1 H), 4.24 (t, *J* = 7.6 Hz, 2 H), 4.13 (d, *J* = 1.2 Hz, 2 H), 3.48 (t, *J* = 7.6 Hz, 2 H), 1.16 (s, 9 H), 0.12 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 156.9, 130.4, 61.8, 44.1, 42.2, 34.7, 31.1, 1.7.

HRMS *m/z* (CI) calcd. for $C_{19}H_{44}NO_5Si_4$ $(M+H)^+$ 478.2297, found 478.2308.



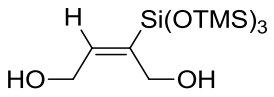
45

(*E*)-3-(dec-5-en-5-yl)-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (45) was prepared as col orless oil according to the General Procedure in a yield of 40% (87.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (t, *J* = 7.2 Hz, 1 H), 2.11-2.04 (m, 4 H), 1.36-1.29 (m, 8 H), 0.91 (t, *J* = 6.4 Hz, 6 H), 0.10 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 136.3, 32.2, 31.6, 29.0, 27.8, 23.1, 22.5, 14.1, 14.0, 1.8.

HRMS *m/z* (CI) calcd. for $C_{19}H_{47}O_3Si_4$ $(M+H)^+$ 435.2603, found 435.2599.



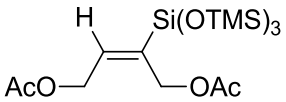
47

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)but-2-ene-1,4-diol (47) was prepared as white solid according to the General Procedure in a yield of 93% (178.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (t, *J* = 6.0 Hz, 1 H), 4.28 (d, *J* = 6 Hz, 2 H), 4.25 (s, 2 H), 2.18 (s, 2 H), 0.127 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 105.0, 60.0, 59.7, 1.9, 1.7.

HRMS *m/z* (CI) calcd. for $C_{13}H_{35}O_5Si_4$ $(M+H)^+$ 383.1562, found 383.1546.



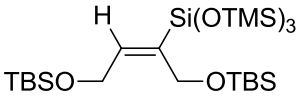
48

(*E*)-2-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)but-2-ene-1,4-diyl diacetate (48) was prepared as colorless oil according to the General Procedure in a yield of 95% (221.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (tt, *J* = 0.8, 6.0 Hz, 1 H), 4.72 (d, *J* = 6.0 Hz, 2H), 4.67 (s, 2 H), 2.07 (s, 3 H), 2.04 (s, 3 H), 0.11 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 139.8, 135.0, 61.7, 61.3, 21.0, 20.8, 1.7.

HRMS *m/z* (CI) calcd. for $C_{17}H_{39}O_7Si_4$ $(M+H)^+$ 467.1774, found 467.1783.



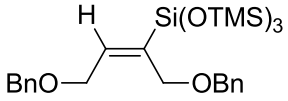
49

(*E*)-1,1,1,5,5,5-hexamethyl-3-(2,2,3,3,10,10,11,11-octamethyl-4,9-dioxa-3,10-disiladodec-6-en-6-yl)-3-((trimethylsilyl)oxy)trisiloxane (49) was prepared as colorless oil according to the General Procedure in a yield of 90% (275.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (t, *J* = 4.8 Hz, 1 H), 4.45 (d, *J* = 4.8 Hz, 2 H), 4.18 (d, *J* = 1.2 Hz, 2 H), 0.09 (d, *J* = 2.0 Hz, 18 H), 0.11 (s, 27 H), 0.06 (d, *J* = 1.2 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 134.2, 62.0, 61.2, 26.0, 25.9, 18.3, 1.8, -5.2, -5.5.

HRMS *m/z* (CI) calcd. for $C_{25}H_{63}O_5Si_6$ $(M+H)^+$ 611.3292, found 611.3276.



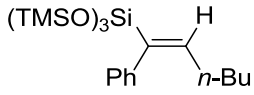
50

(*E*)-3-(1,4-bis(benzyloxy)but-2-en-2-yl)-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (50) was prepared as colorless oil according to the General Procedure in a yield of 90% (253.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 10 H), 6.30 (t, *J* = 5.2 Hz, 1 H), 4.50 (s, 2 H), 4.45 (s, 2 H), 4.20 (d, *J* = 5.2 Hz, 2 H)，4.06 (s, 2 H), 0.13 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.5, 138.3, 135.8, 128.3, 128.2, 127.7, 127.7, 127.5, 127.4, 72.3, 72.2, 67.6, 67.6, 1.8.

HRMS *m/z* (CI) calcd. for $C_{27}H_{47}O_5Si_4$ $(M+H)^+$ 563.2501, found 563.2523.



52'

(*E*)-1,1,1,5,5,5-hexamethyl-3-(1-phenylhex-1-en-1-yl)-3-((trimethylsilyl)oxy)trisiloxane (52') was prepared as colorless oil according to the General Procedure in a yield of 50% (113.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2 H), 7.18-7.14 (m, 1 H), 7.06-7.04 (s, 2 H), 6.17 (t, *J* = 7.2 Hz, 1 H), 2.01 (q, *J* = 7.2 Hz, 2 H), 1.36-1.23 (m, 4 H), 0.84 (t, *J* = 7.2 Hz, 3 H), 0.04 (s, 27 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 141.1, 139.0, 128.6, 127.6, 125.4, 31.6, 29.3, 22.3, 13.9, 1.6.

HRMS *m/z* (CI) calcd. for $C_{21}H_{43}O_3Si_4$ $(M+H)^+$ 455.2290, found 455.2301.

III. ^{1}H NMR and ^{13}C NMR Spectra

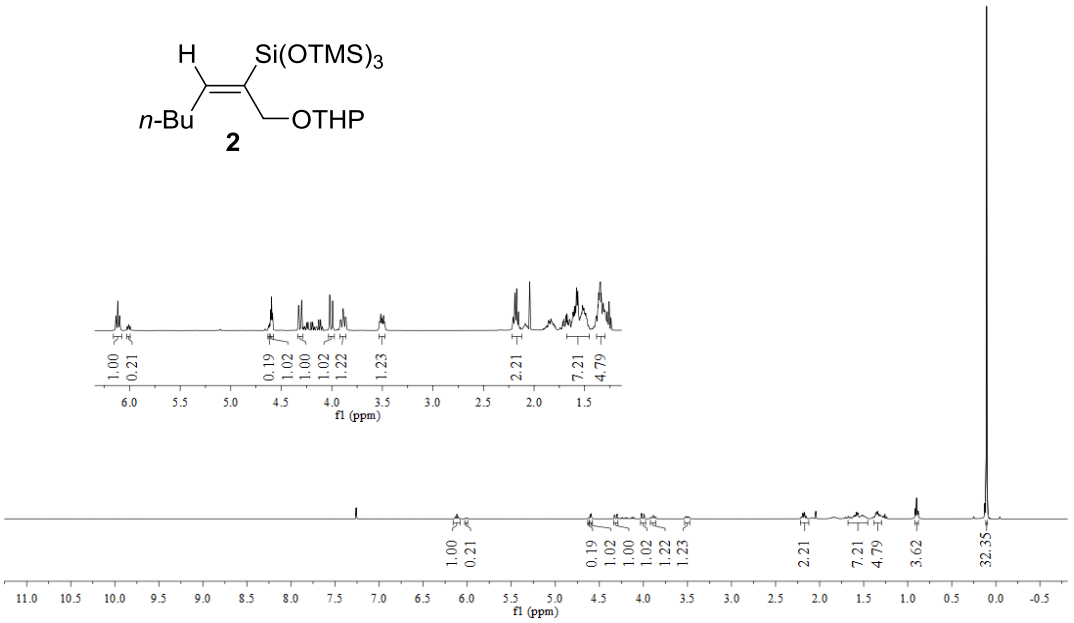


Figure S1. ^{1}H NMR spectra of **2**. (83:17 *α/β*)

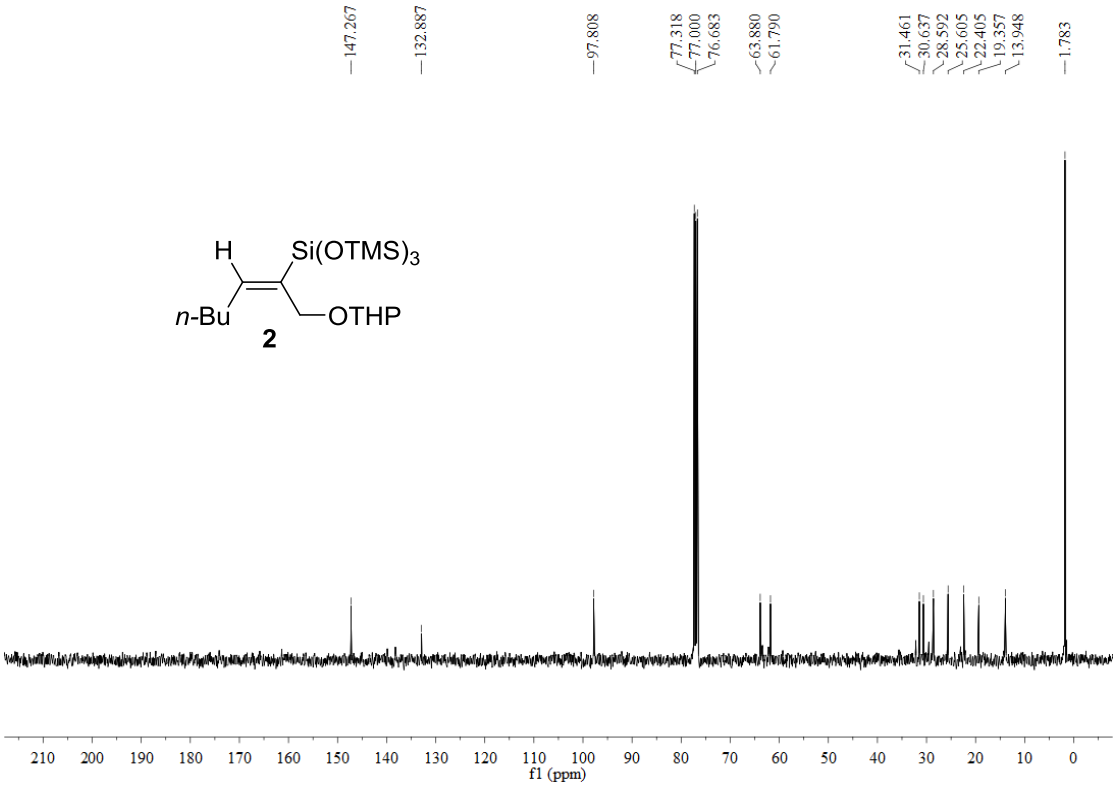


Figure S2. ^{13}C NMR spectra of **2**.

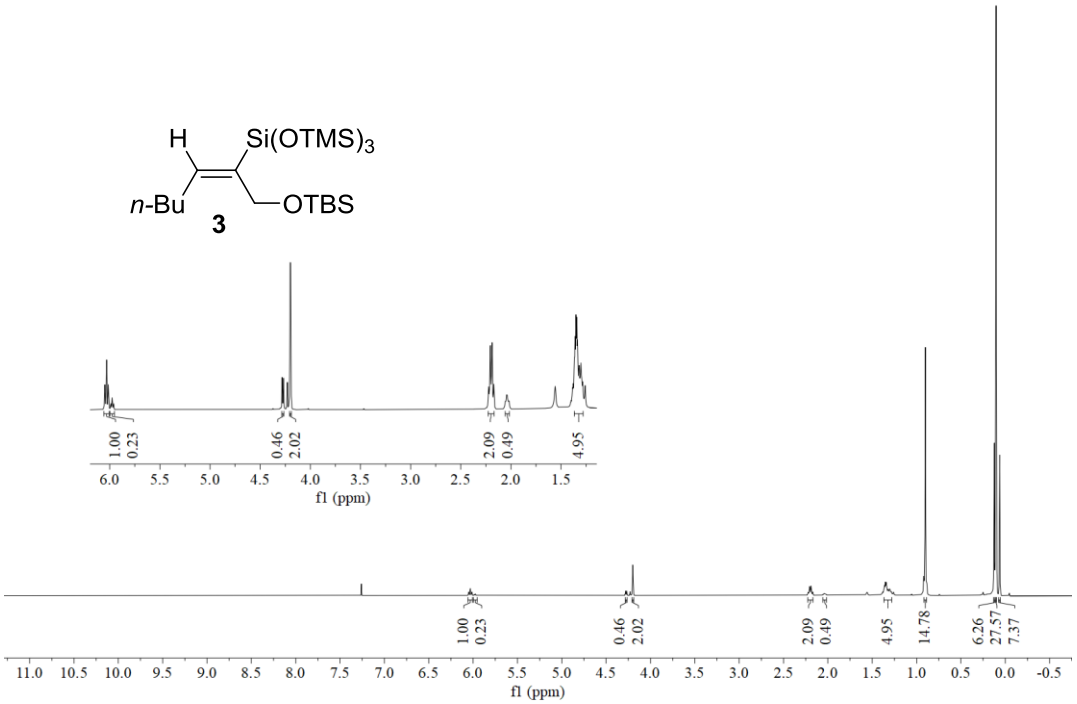


Figure S3. ^{1}H NMR spectra of **3**. **(**81:19 *α/β*).

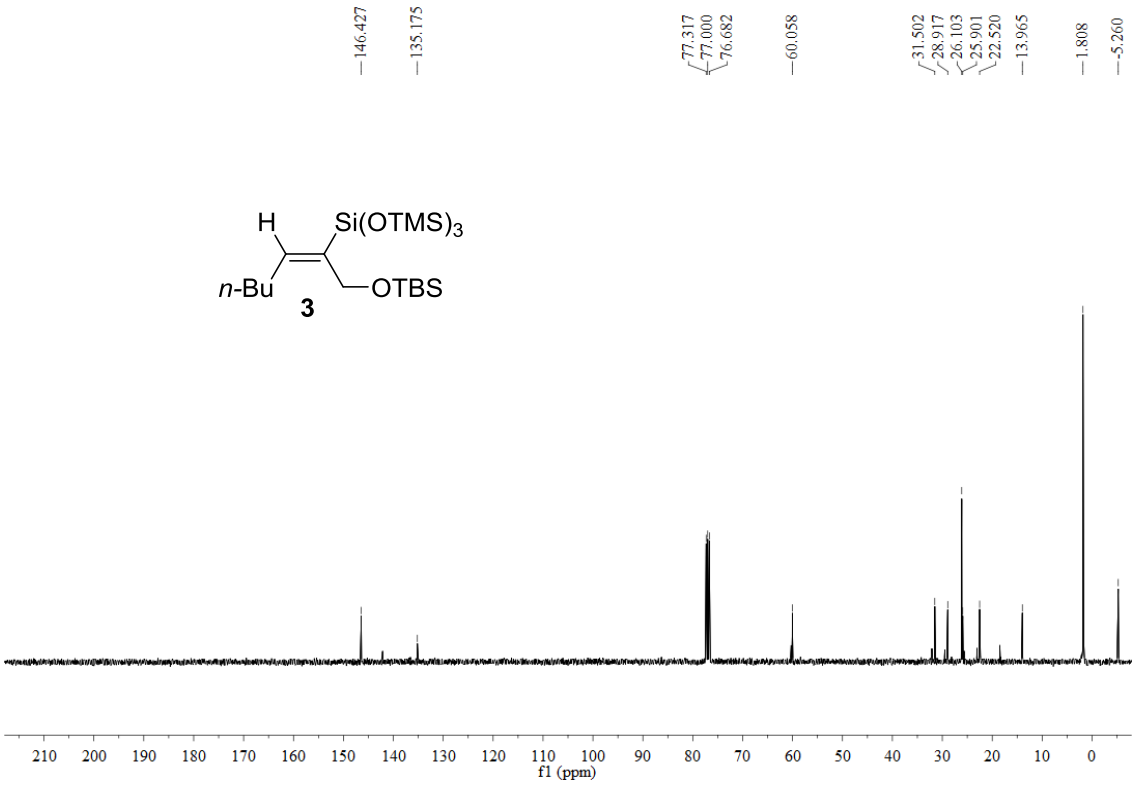


Figure S4. ^{13}C NMR spectra of **3**.

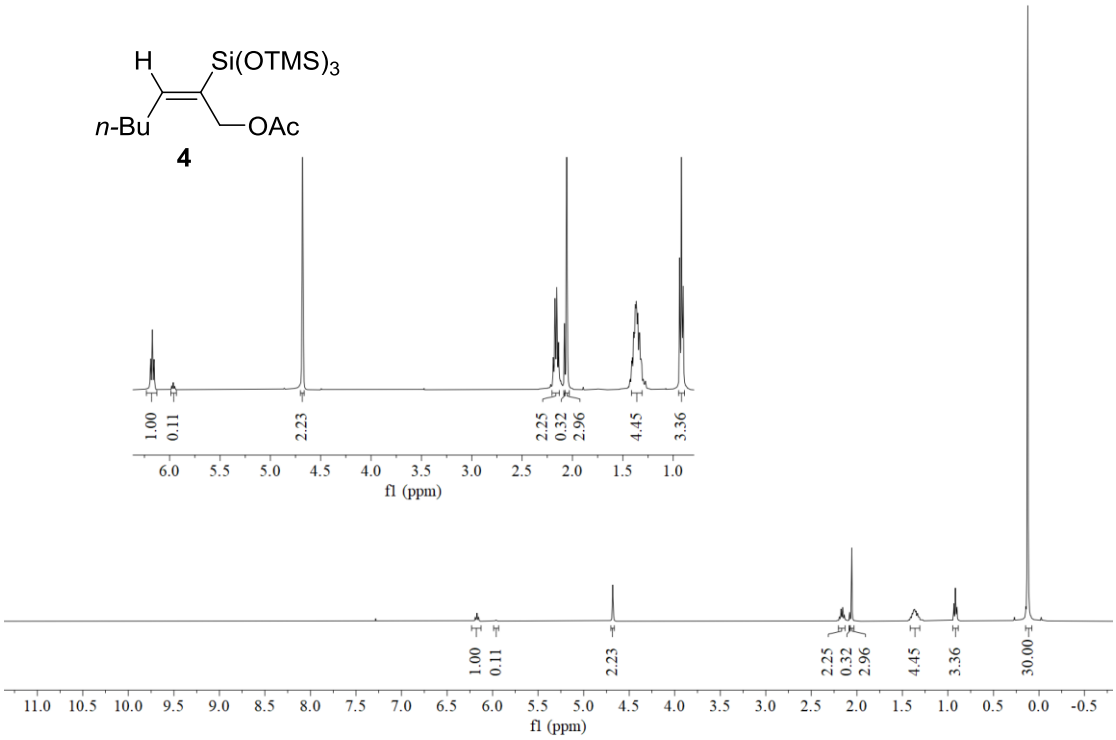


Figure S5. ^{1}H NMR spectra of **4**. (90:10 *α/β*)

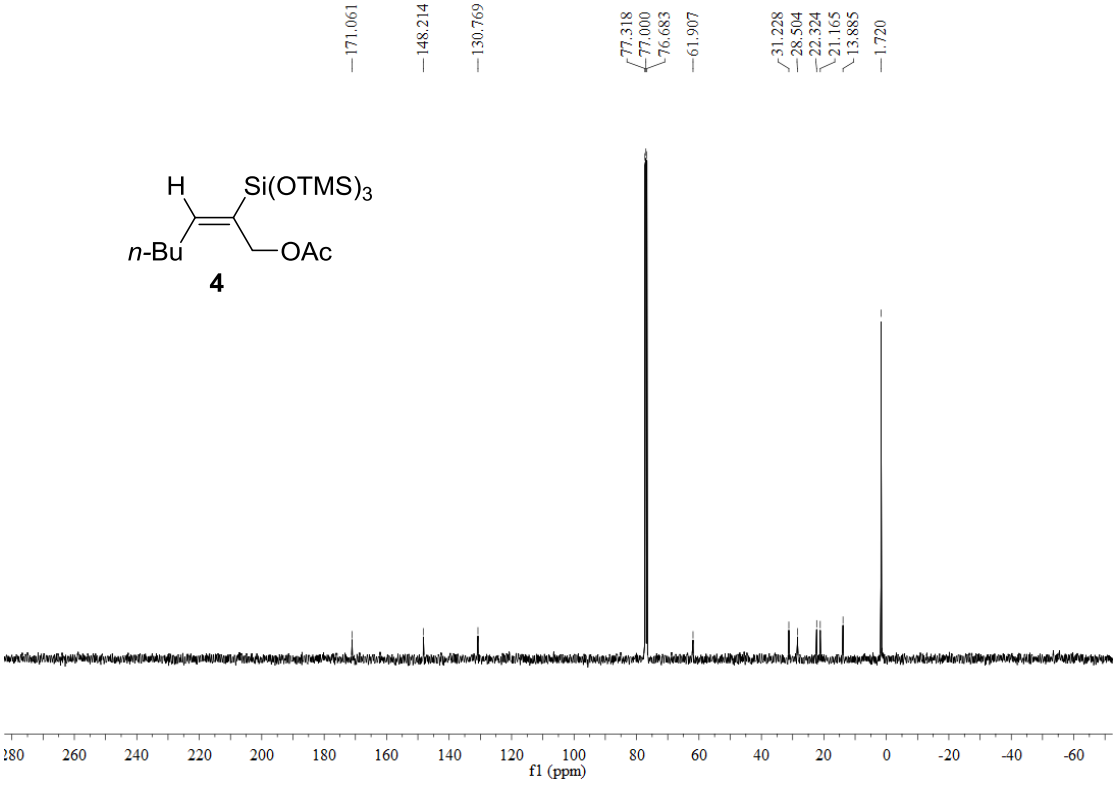


Figure S6. ^{13}C NMR spectra of **4**.

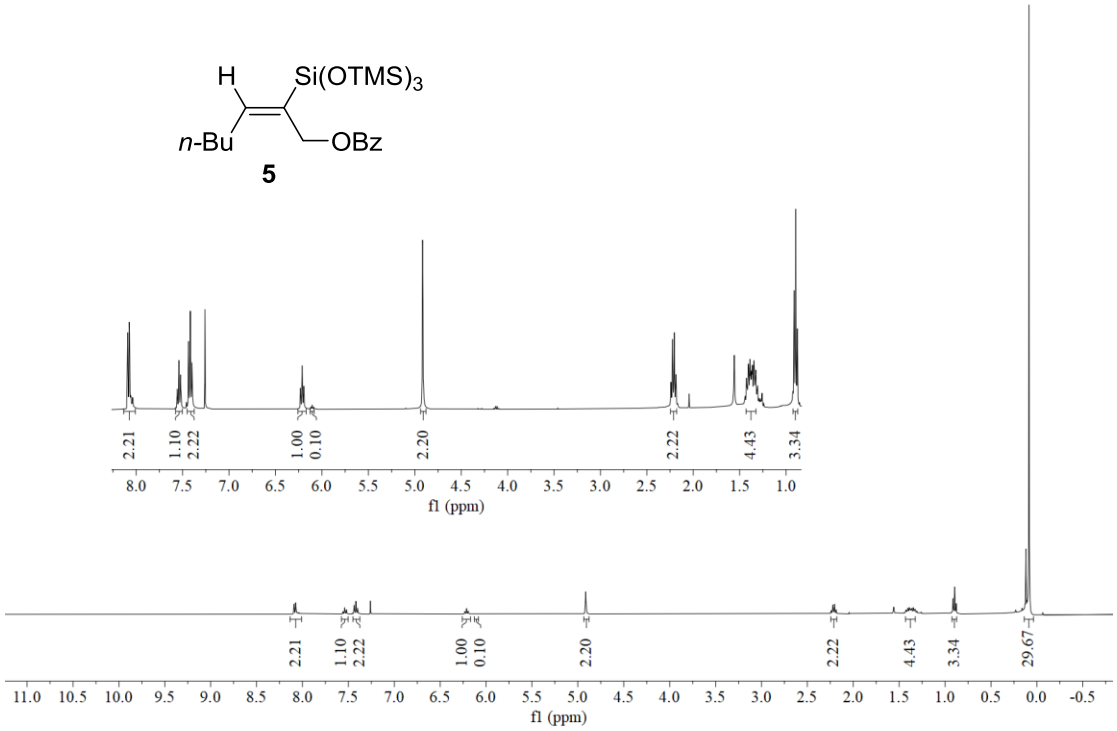


Figure S7. ^{1}H NMR spectra of **5**. (91:9 *α/β*)

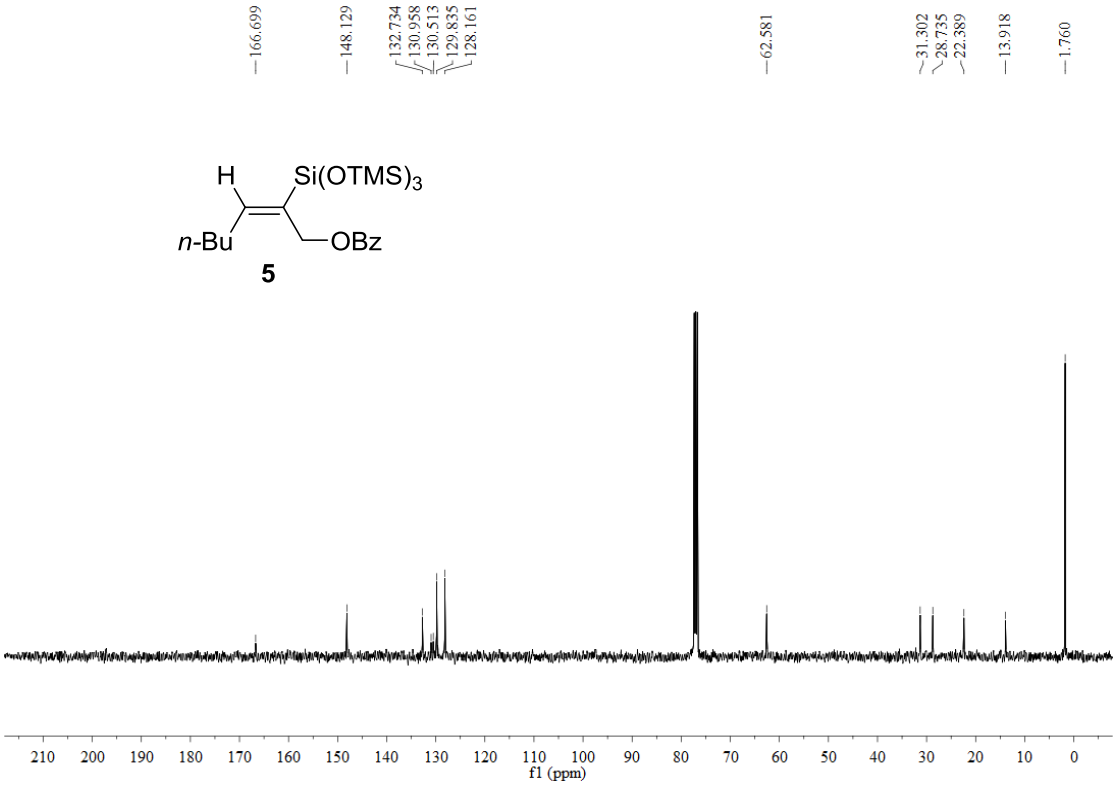


Figure S8. ^{13}C NMR spectra of **5**.

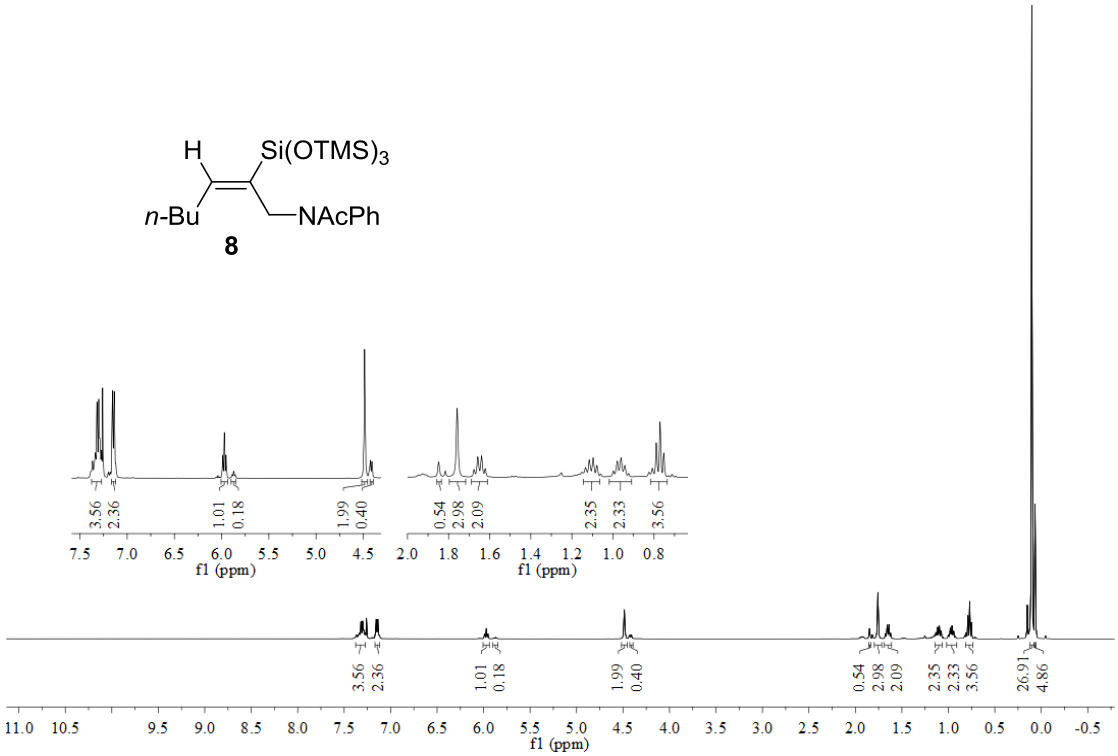


Figure S9. ^{1}H NMR spectra of **8**. (85:15 *α/β*)

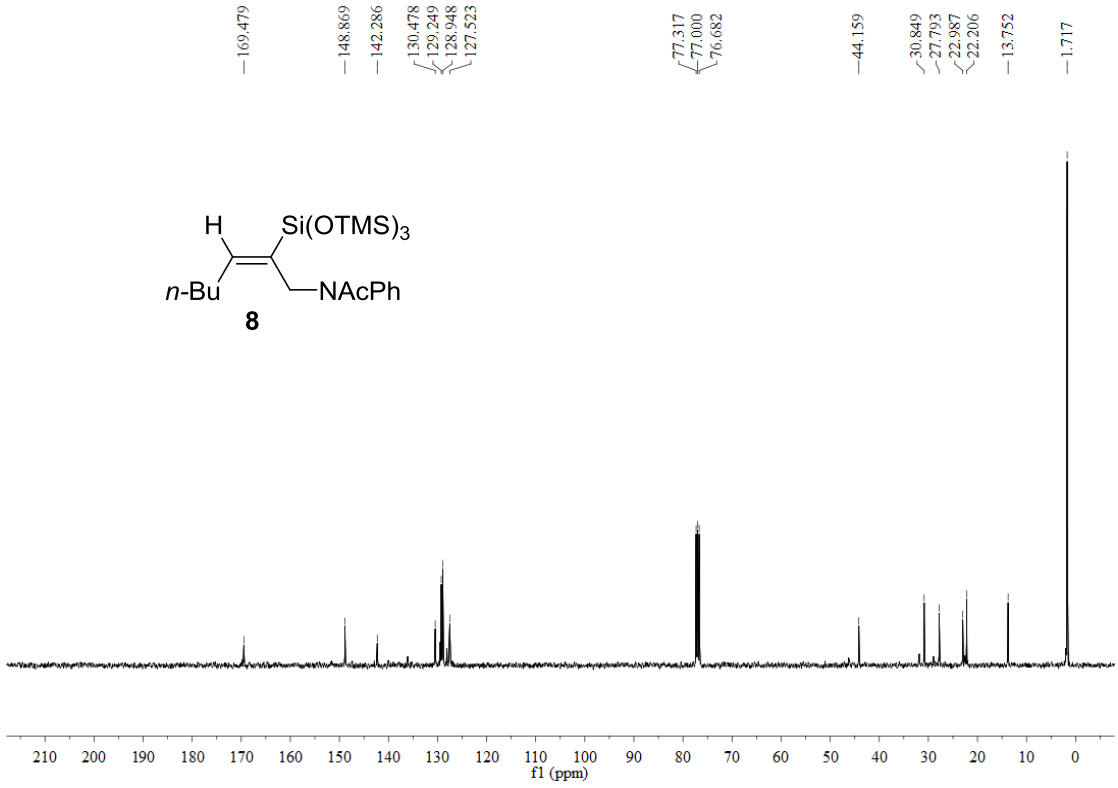


Figure S10. ^{13}C NMR spectra of **8**.

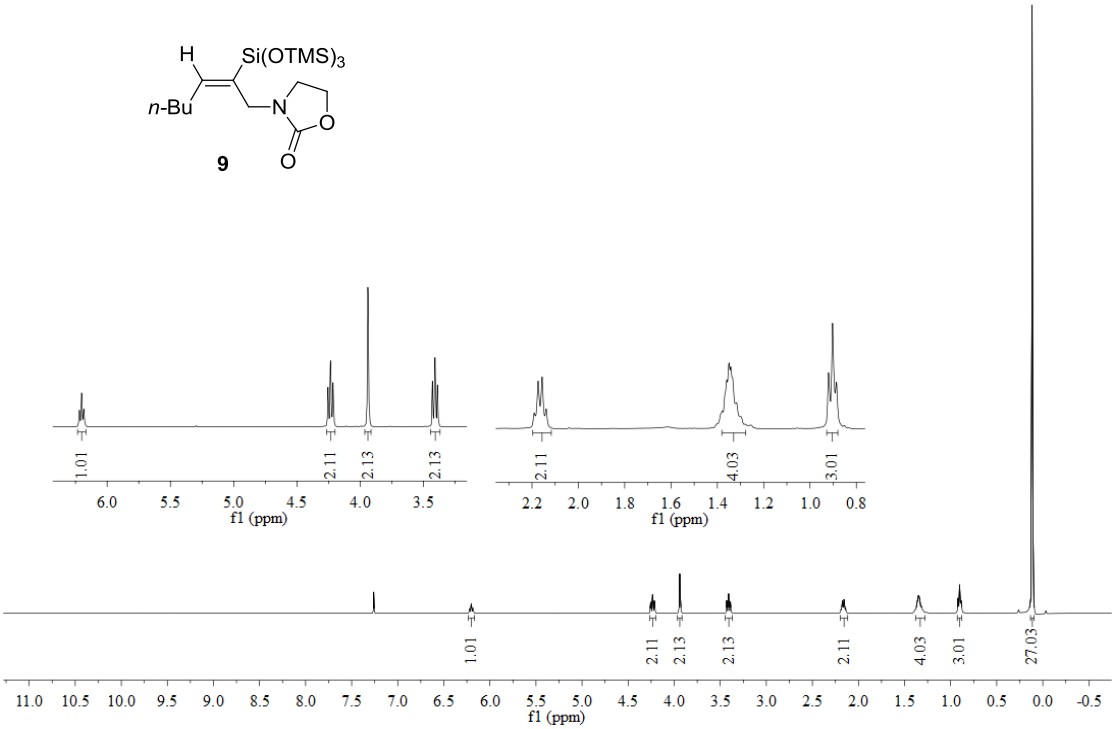


Figure S11. ^{1}H NMR spectra of **9**. (89:11 *α/β*).

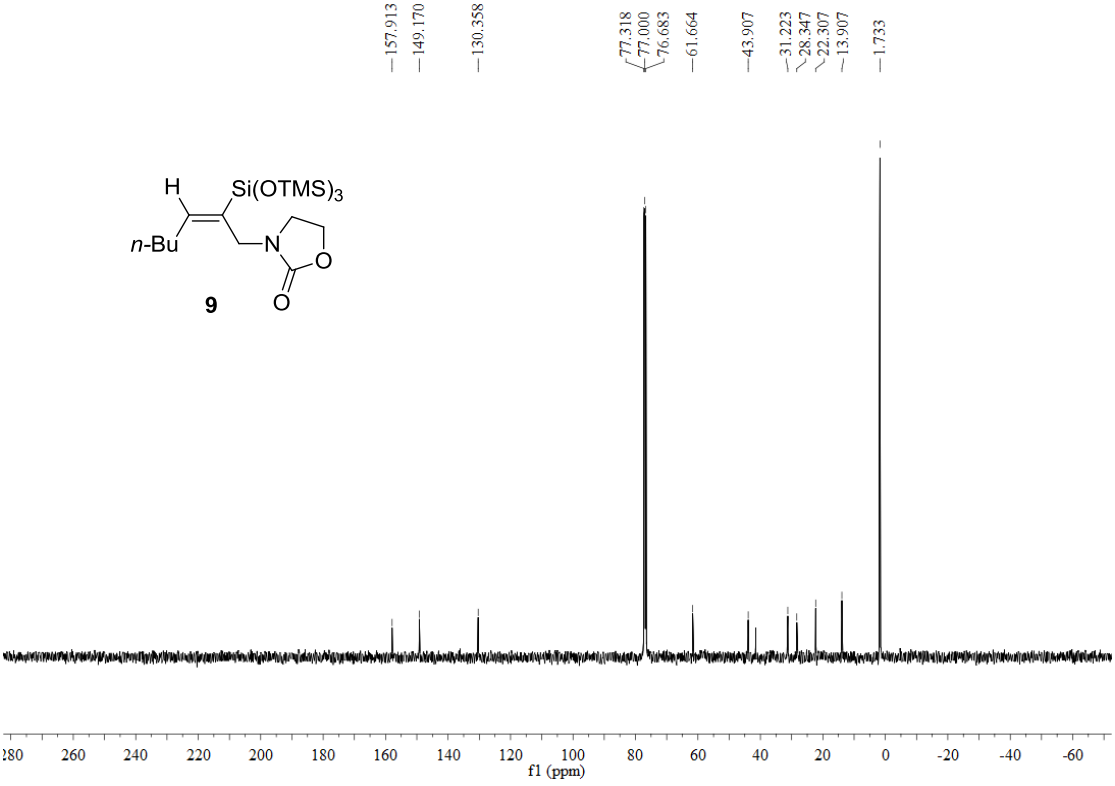


Figure S12. ^{13}C NMR spectra of **9**.

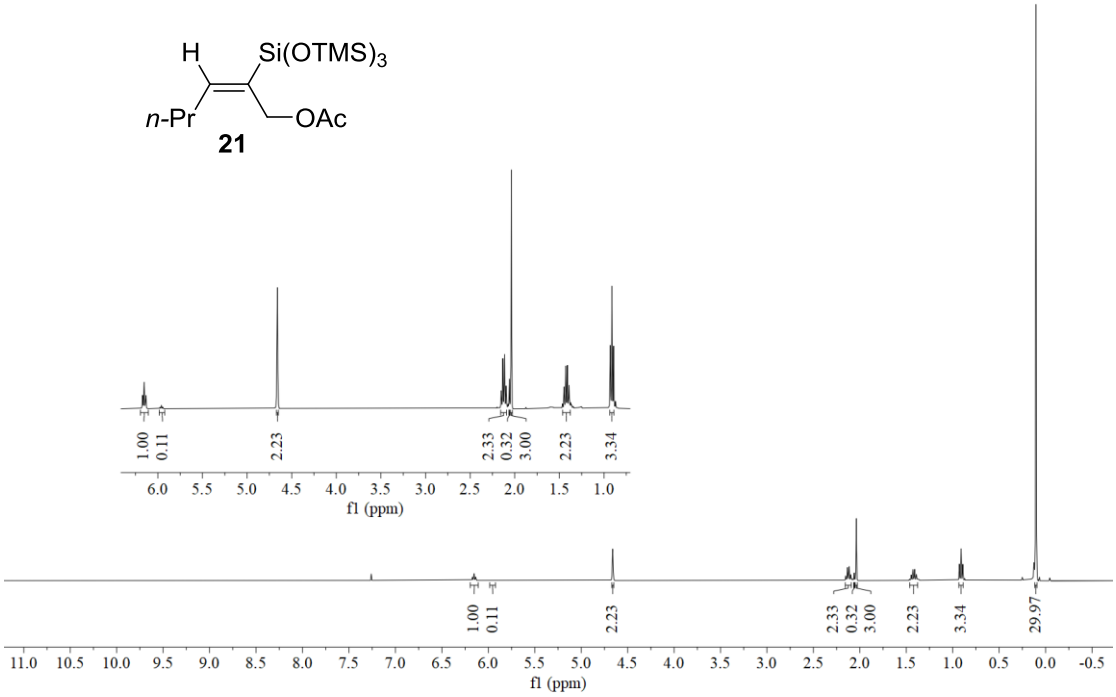


Figure S13. ^{1}H NMR spectra of **21**. **(**90:10 *α/β***)**.

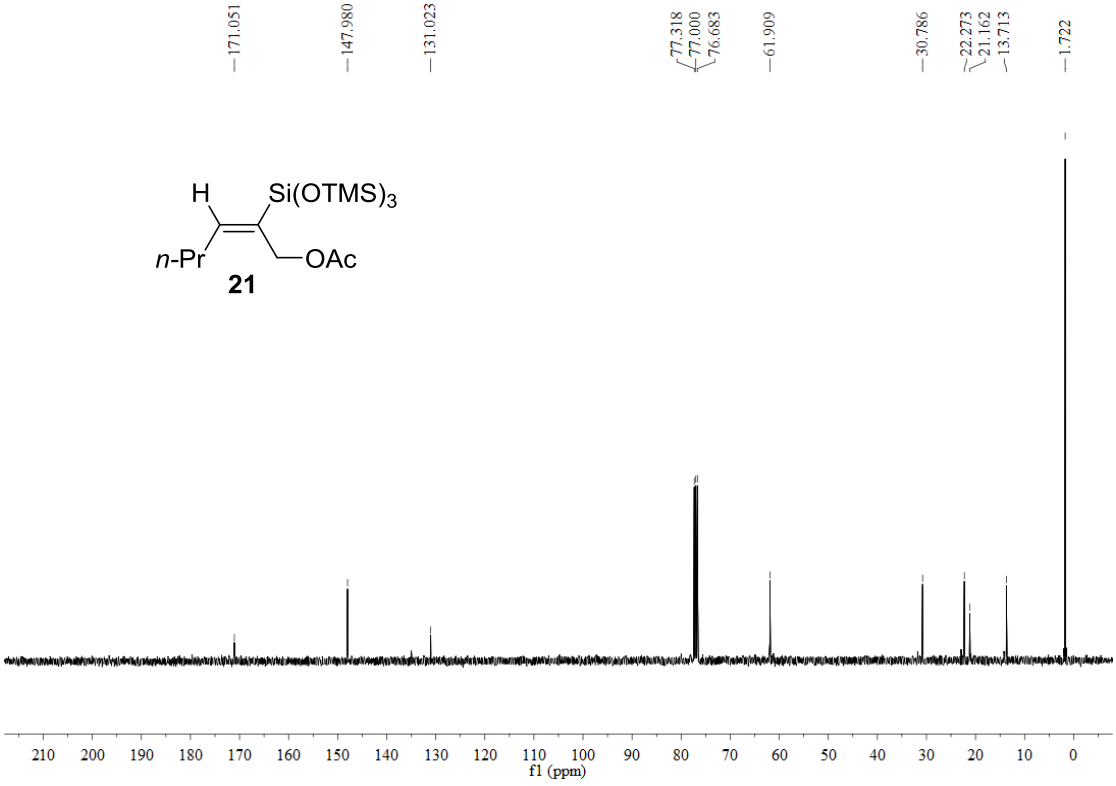


Figure S14. ^{13}C NMR spectra of **21**.

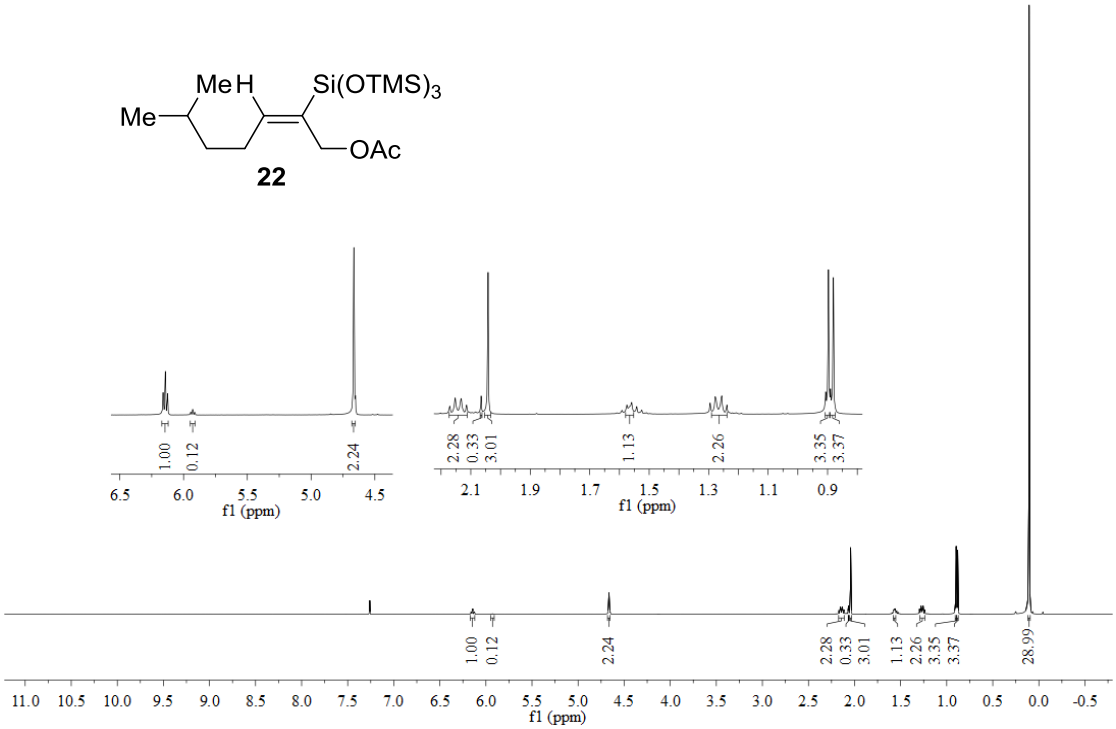


Figure S15. ^{1}H NMR spectra of **22**. (89:11 *α/β*)

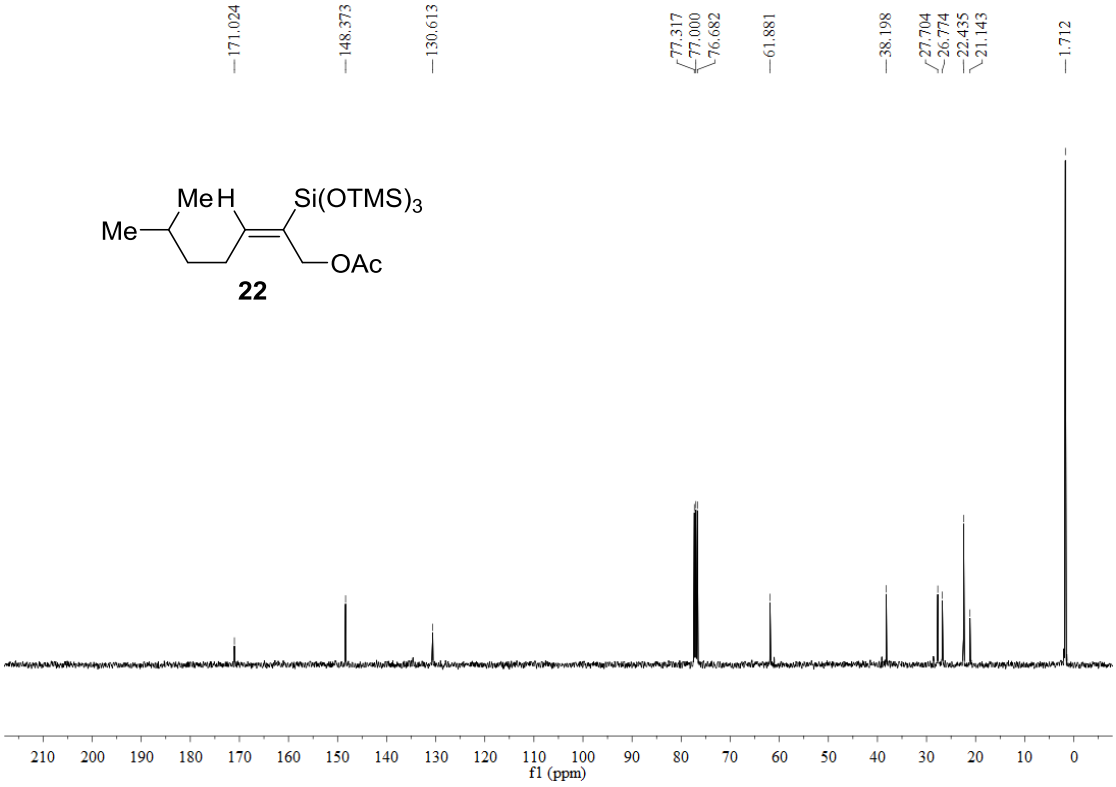


Figure S16. ^{13}C NMR spectra of **22**.

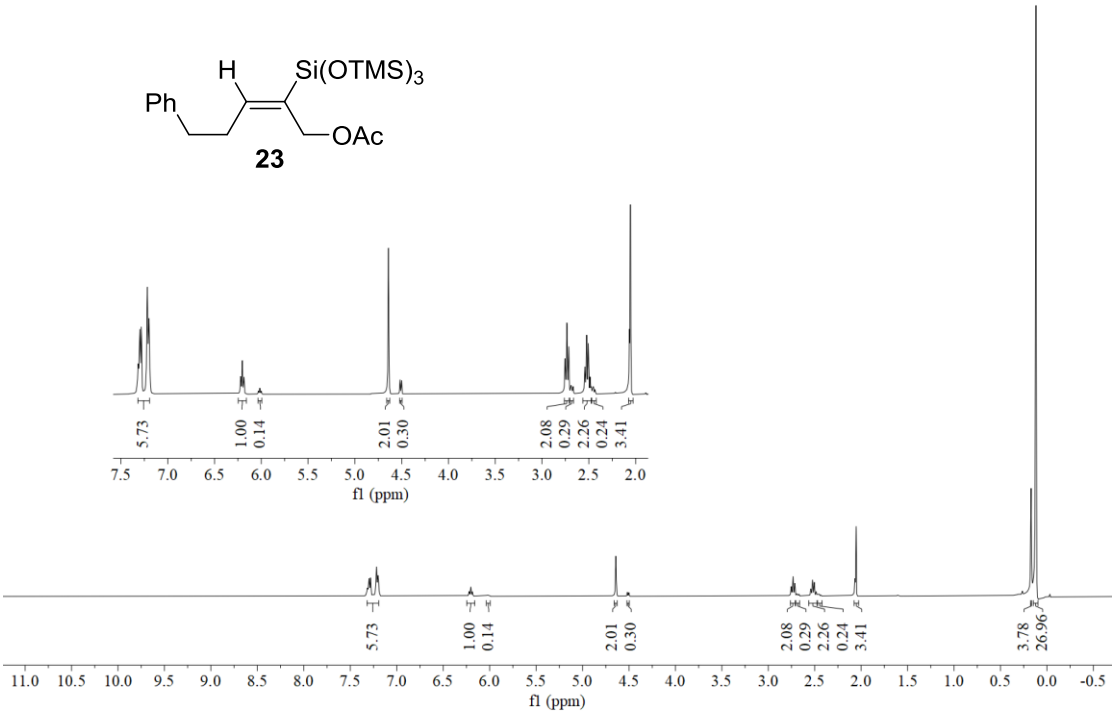


Figure S17. ^{1}H NMR spectra of **23**. (88:12 *α/β*)

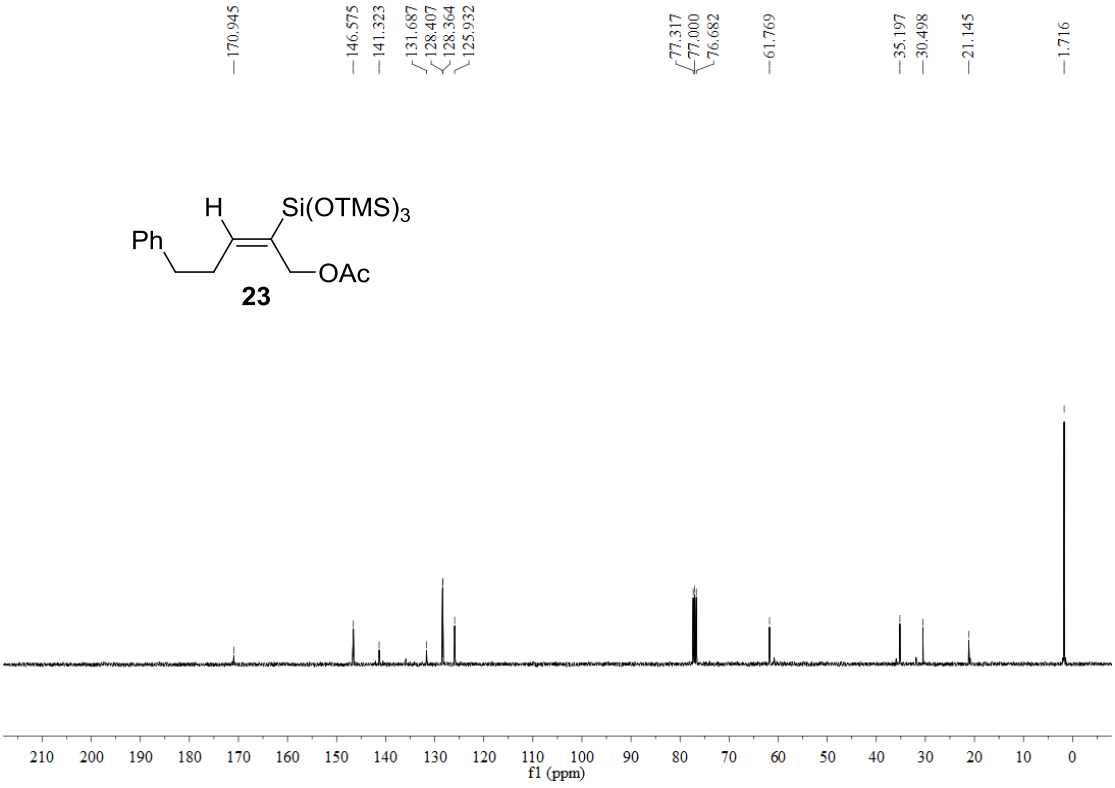


Figure S18. ^{13}C NMR spectra of **23**.

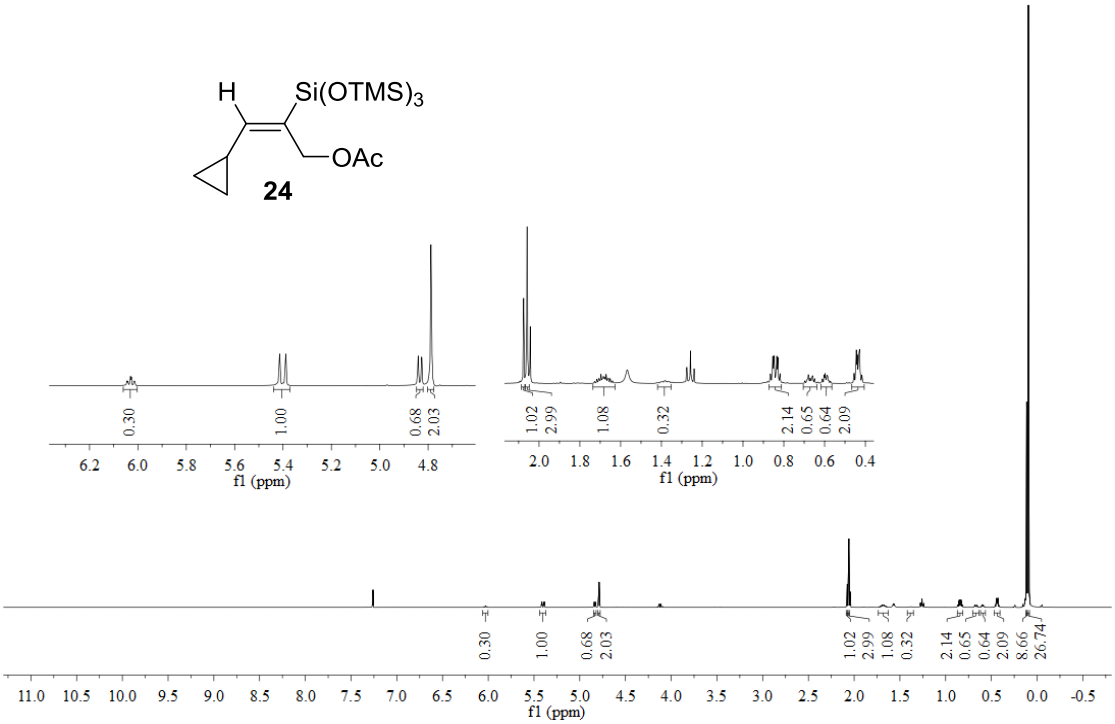


Figure S19. ^{1}H NMR spectra of **24**. (75:25 *α/β*)

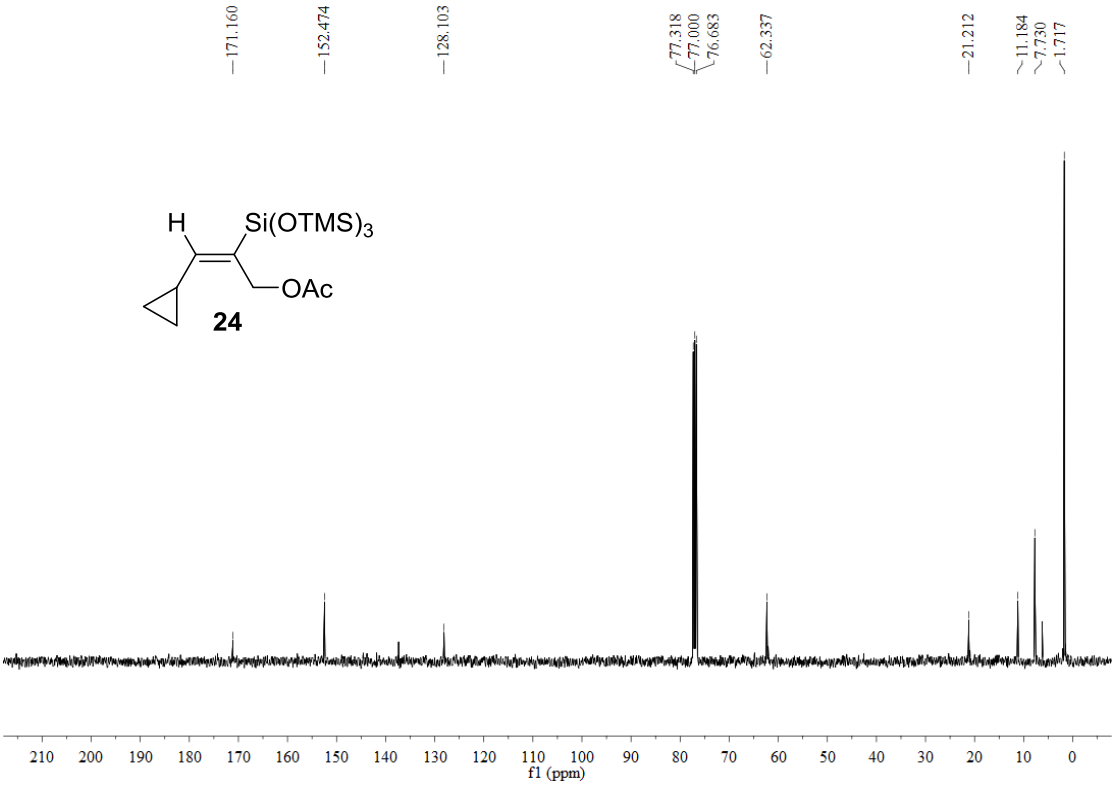


Figure S20. ^{13}C NMR spectra of **24**.

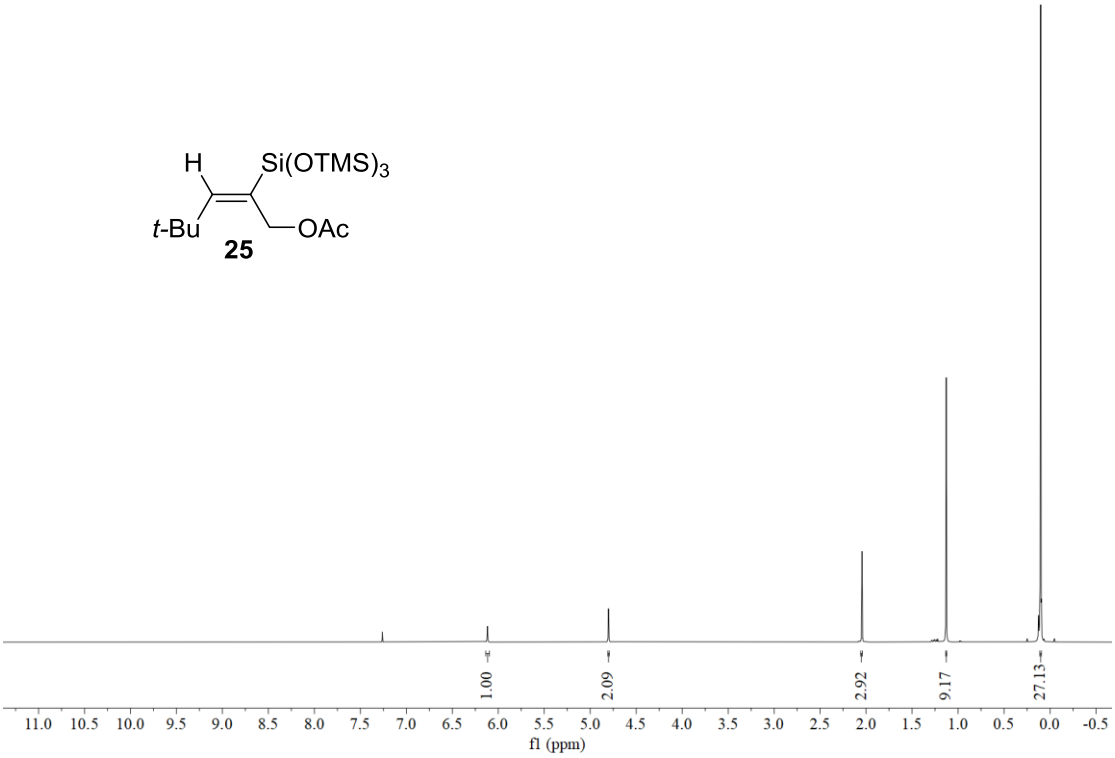


Figure S21. ^{1}H NMR spectra of **25**. (100:0 *α/β*)

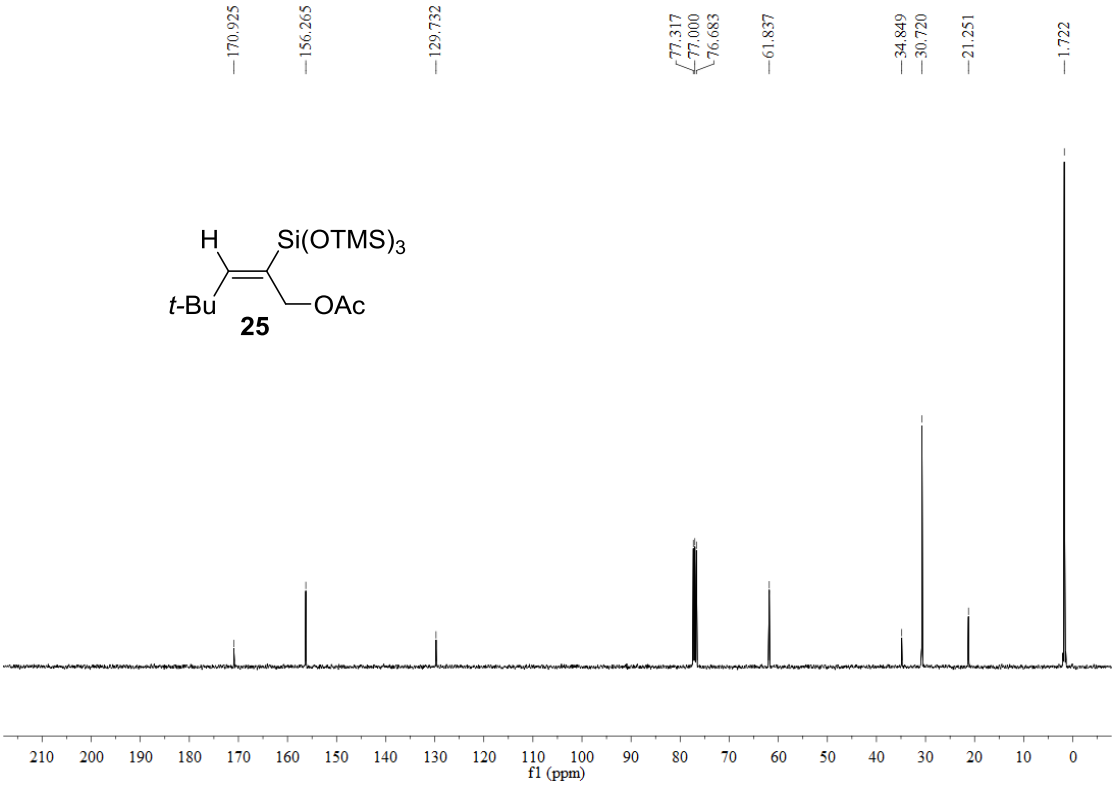


Figure S22. ^{13}C NMR spectra of **25**.

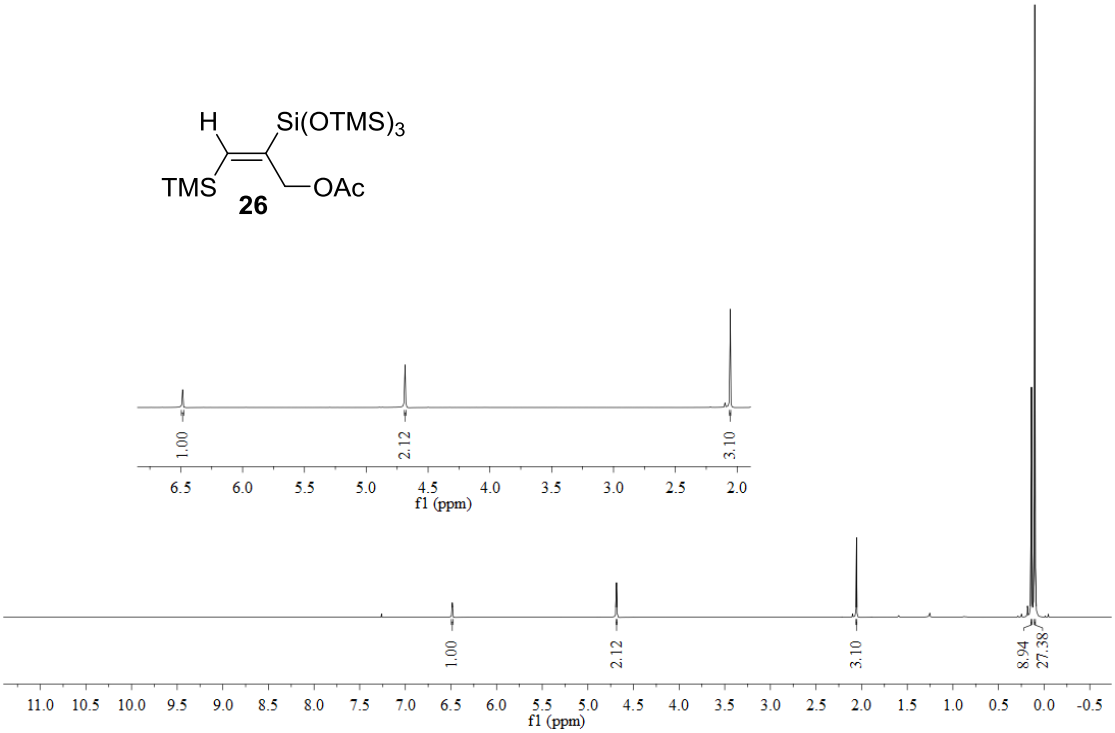


Figure S23. ^{1}H NMR spectra of **26**. (100:0 *α/β*)

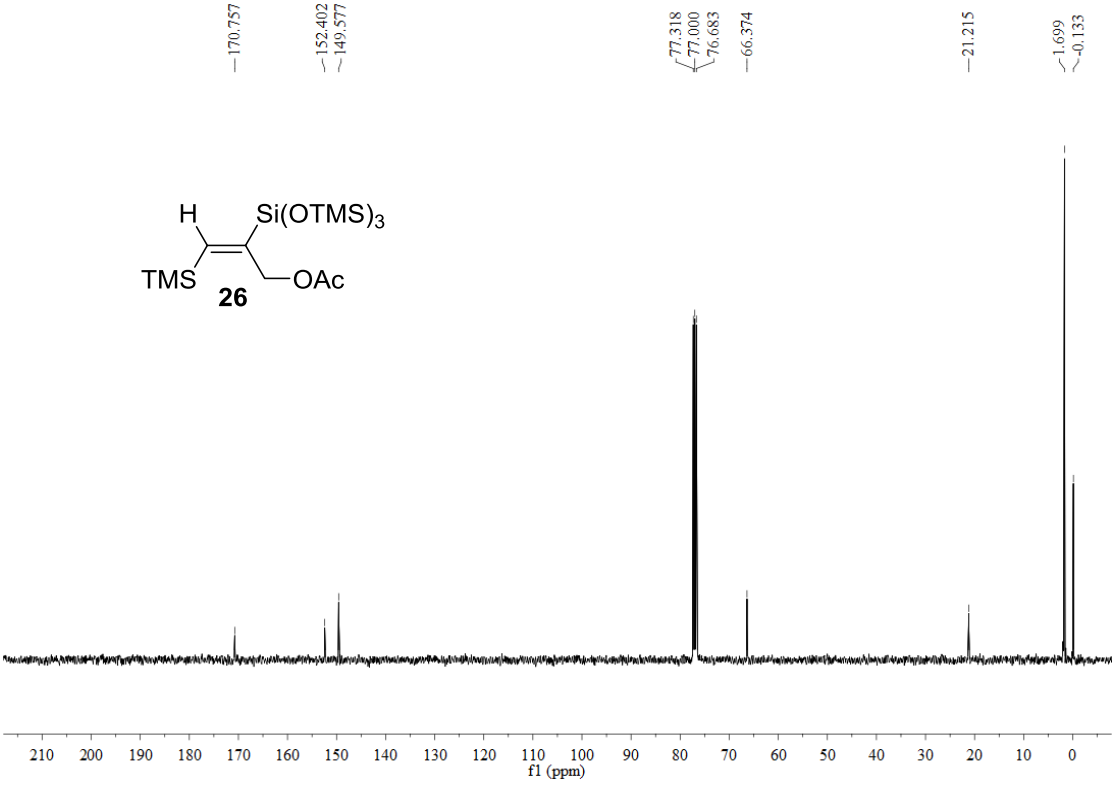


Figure S24. ^{13}C NMR spectra of **26**.

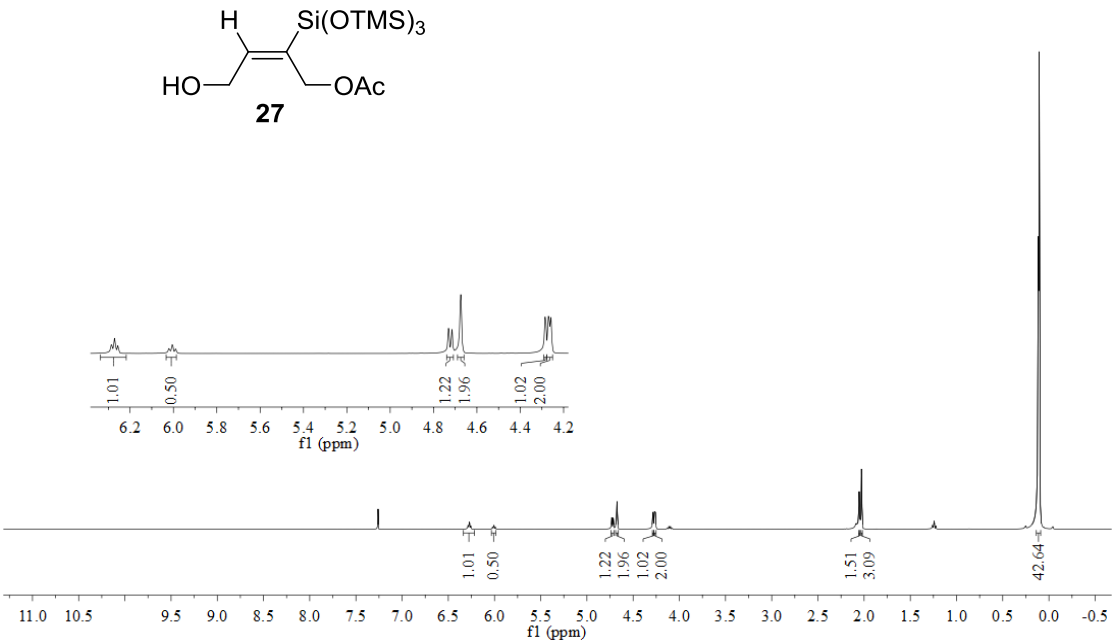


Figure S25. ^{1}H NMR spectra of **27**. (67:33 *α/β*)

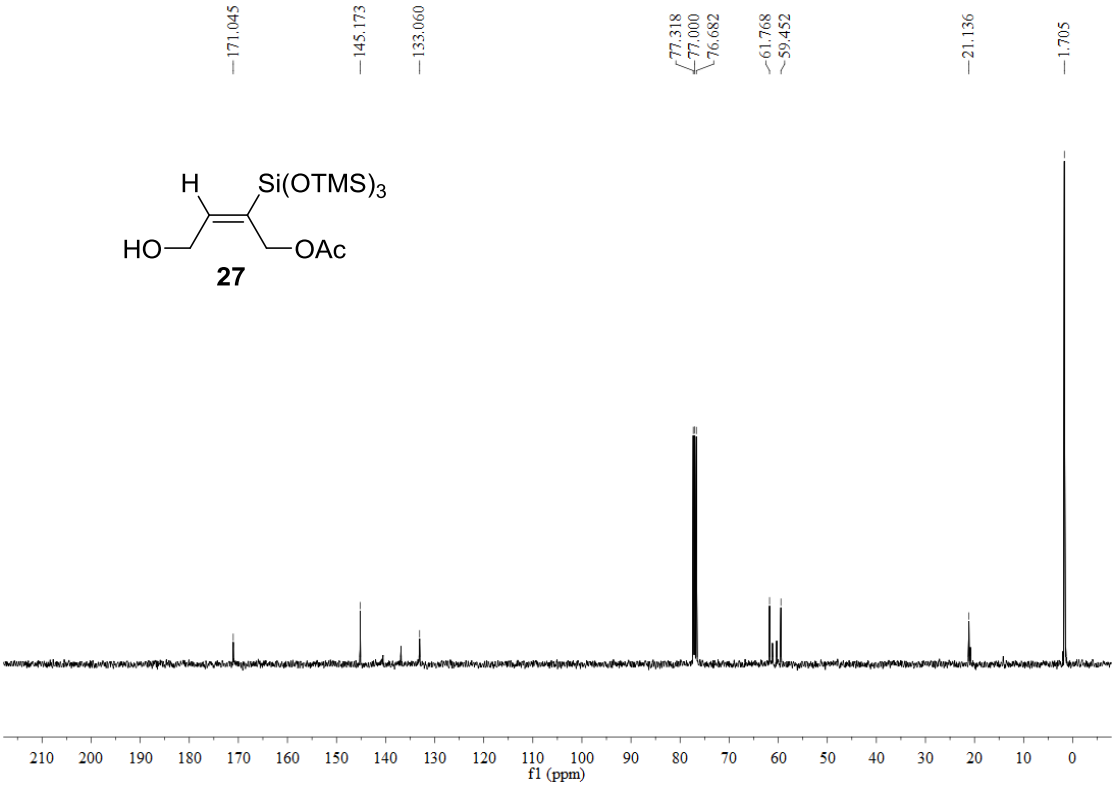


Figure S26. ^{13}C NMR spectra of **27**.

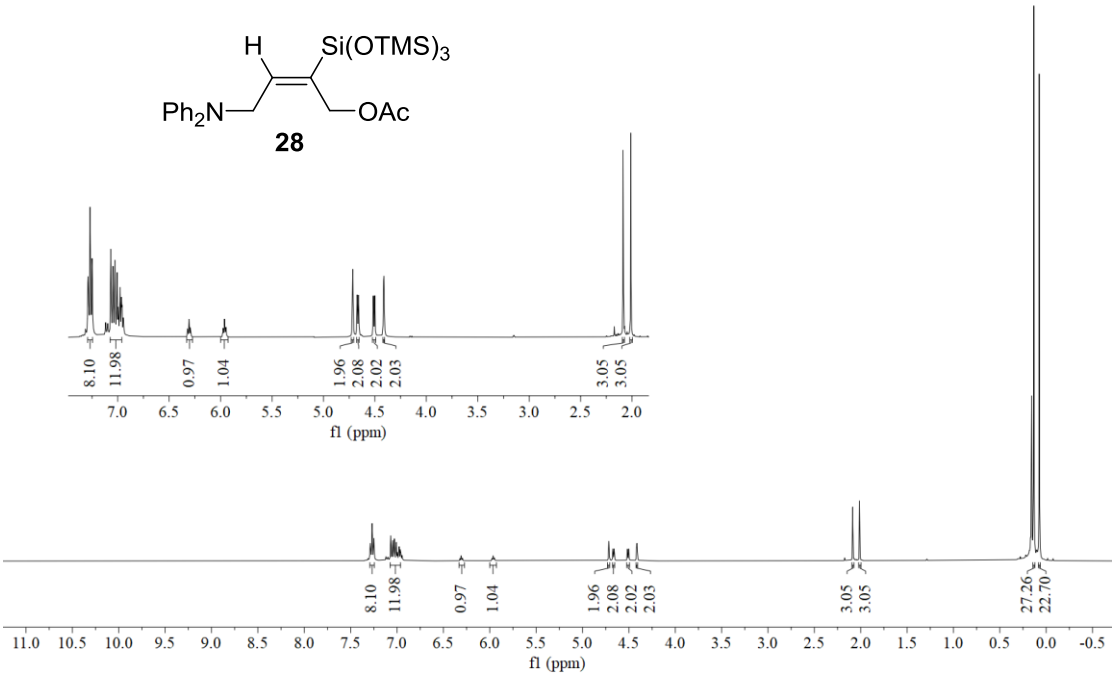


Figure S27. ^{1}H NMR spectra of **28**. (50:50 *α/β*)

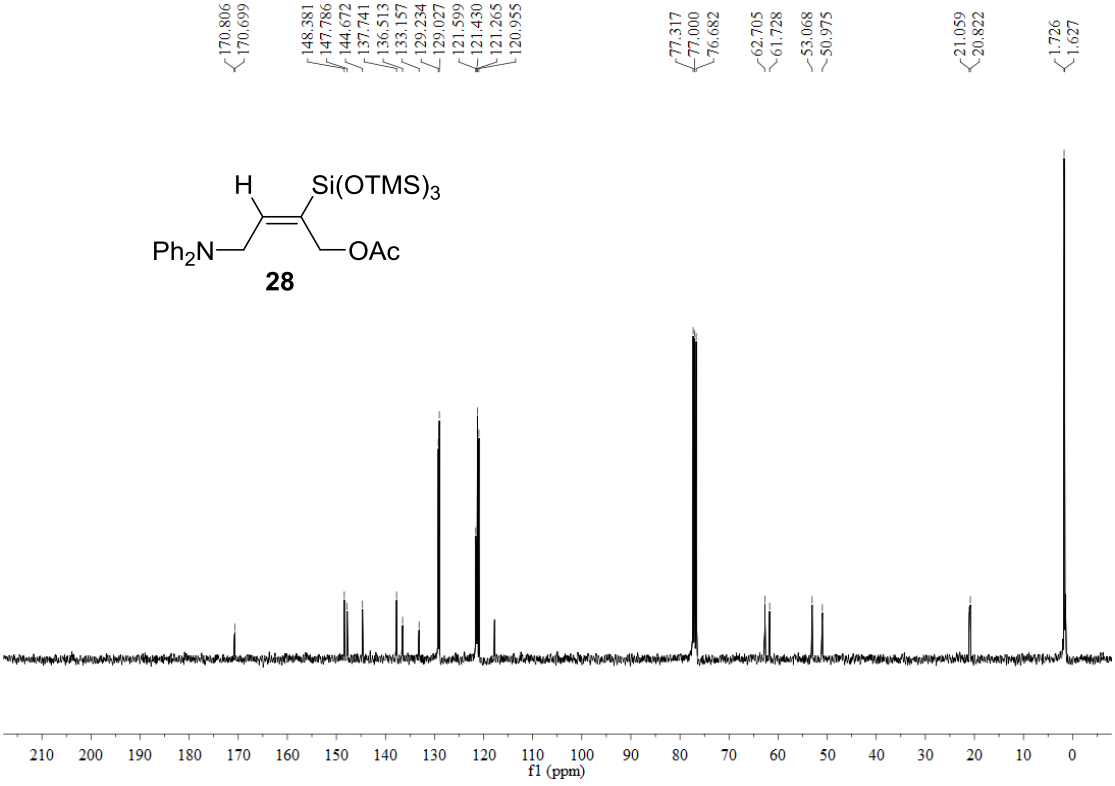


Figure S28. ^{13}C NMR spectra of **28**.

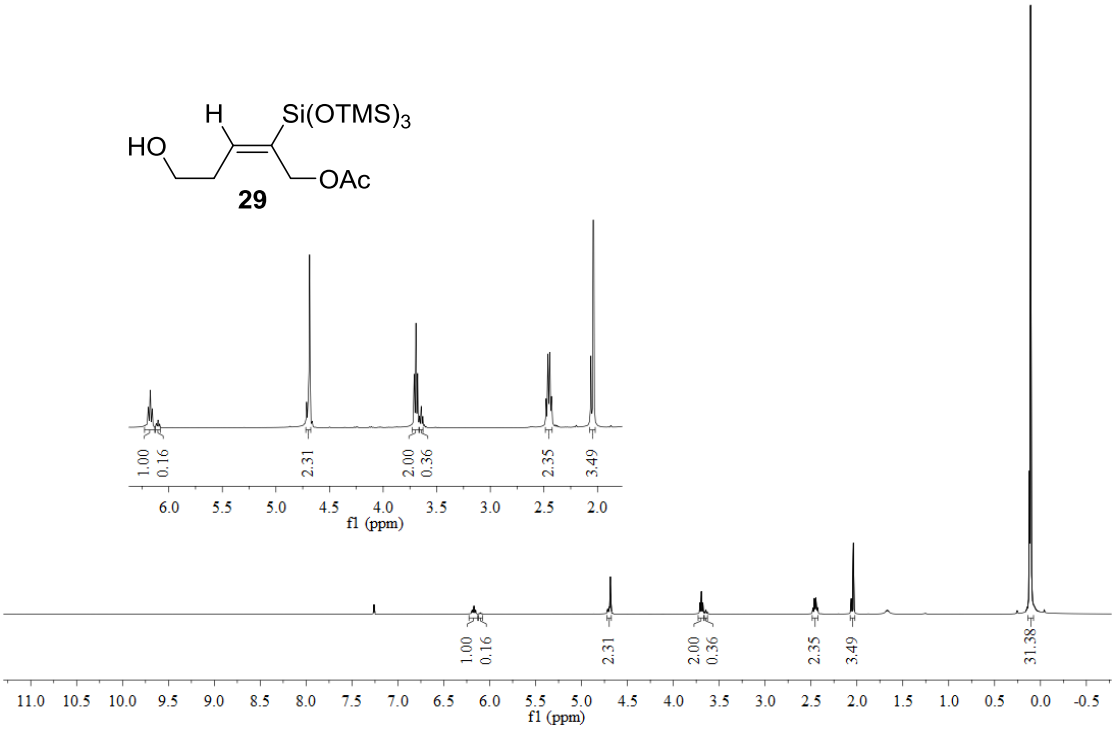


Figure S29. ^{1}H NMR spectra of **29**. (86:14 *α/β*)

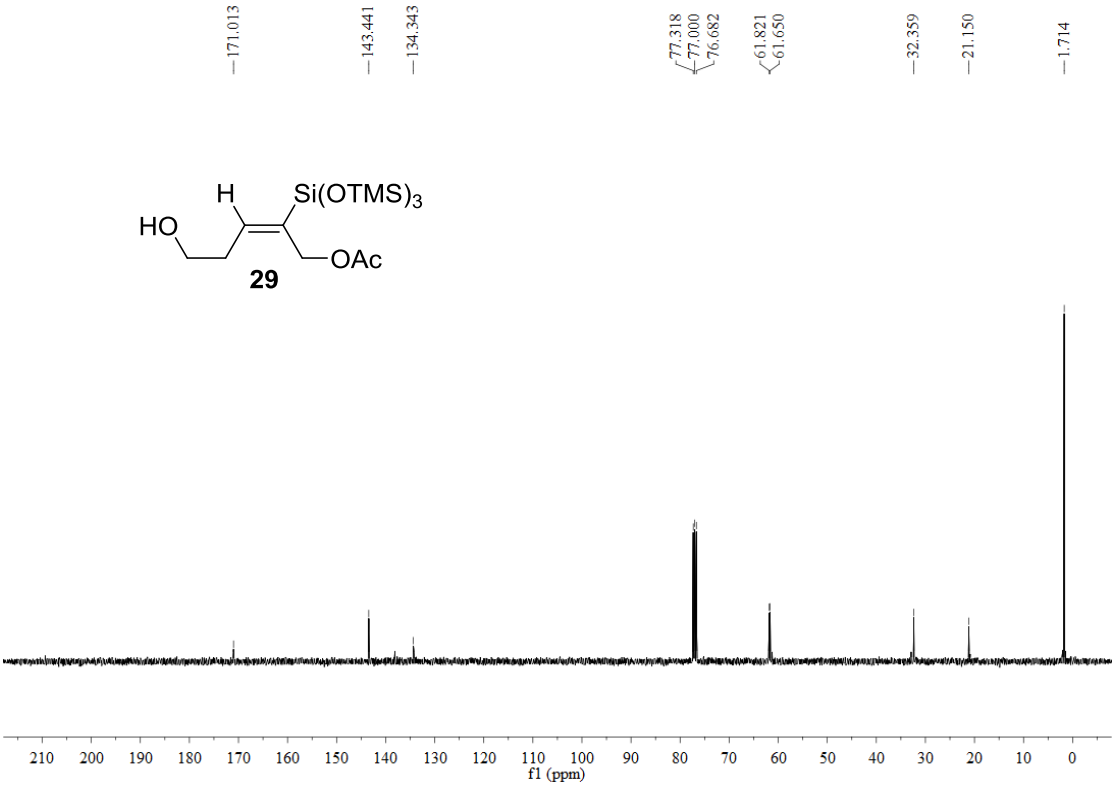


Figure S30. ^{13}C NMR spectra of **29**.

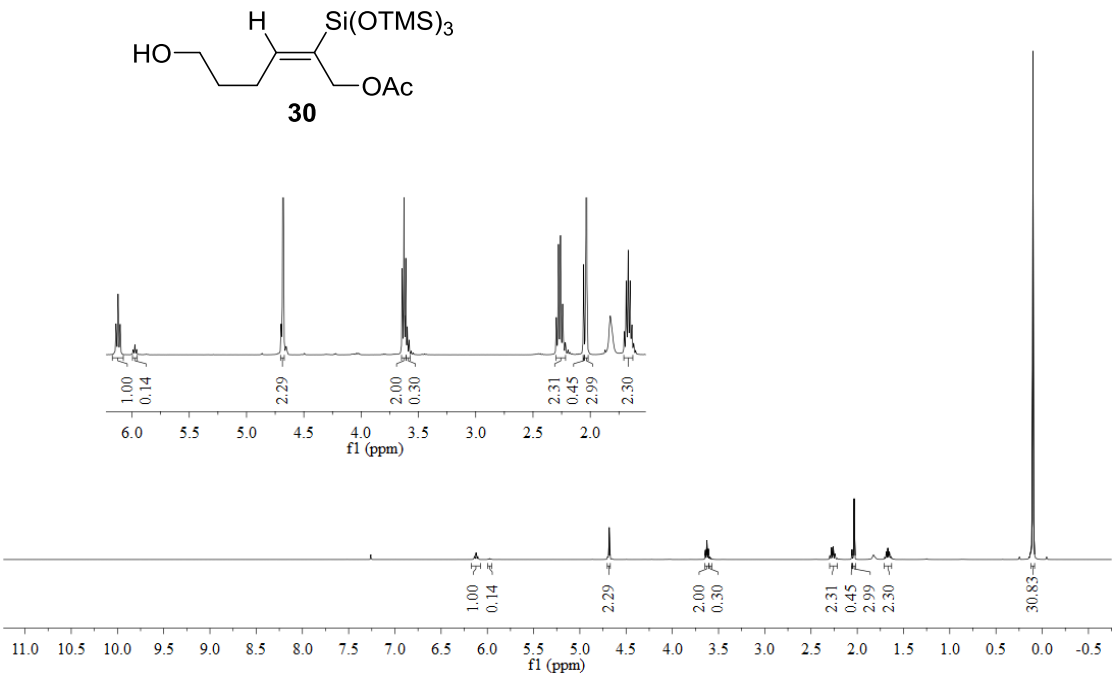


Figure S31. ^{1}H NMR spectra of **30**. (88:12 *α/β*)

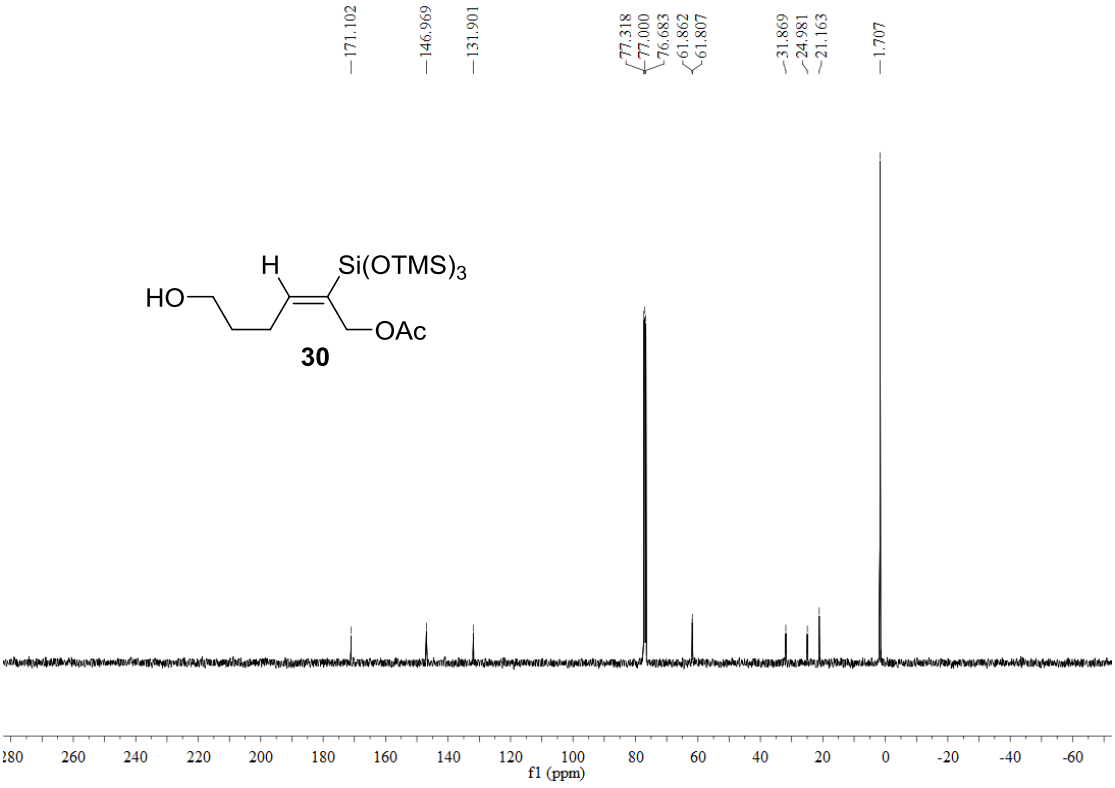


Figure S32. ^{13}C NMR spectra of **30**.

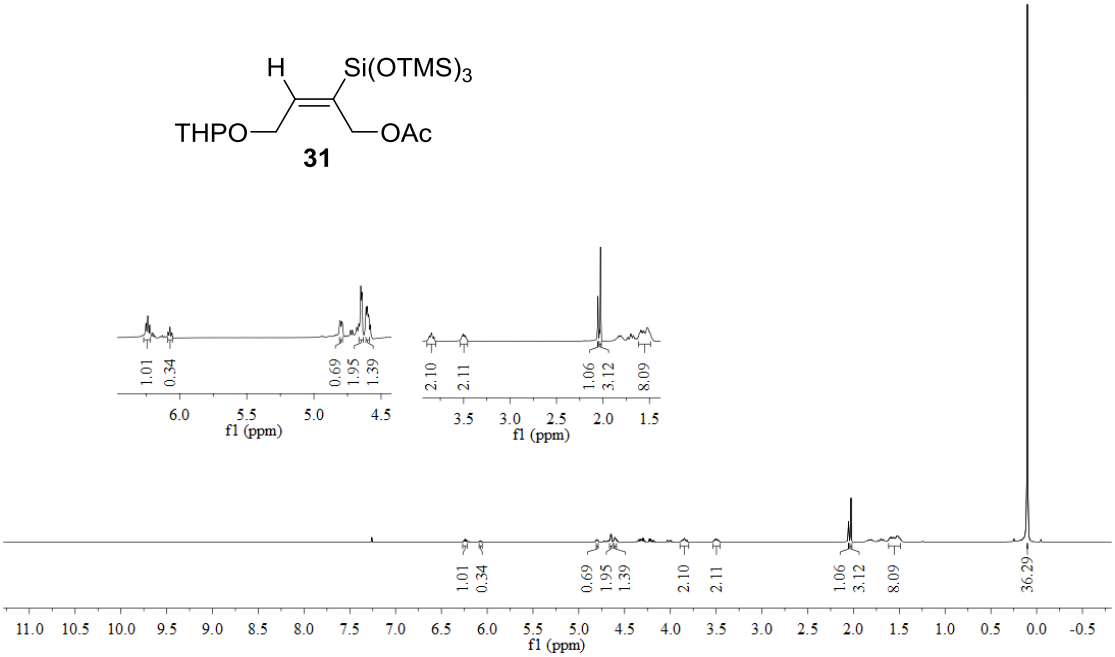


Figure S33. ^{1}H NMR spectra of **31**. (75:25 *α/β*)

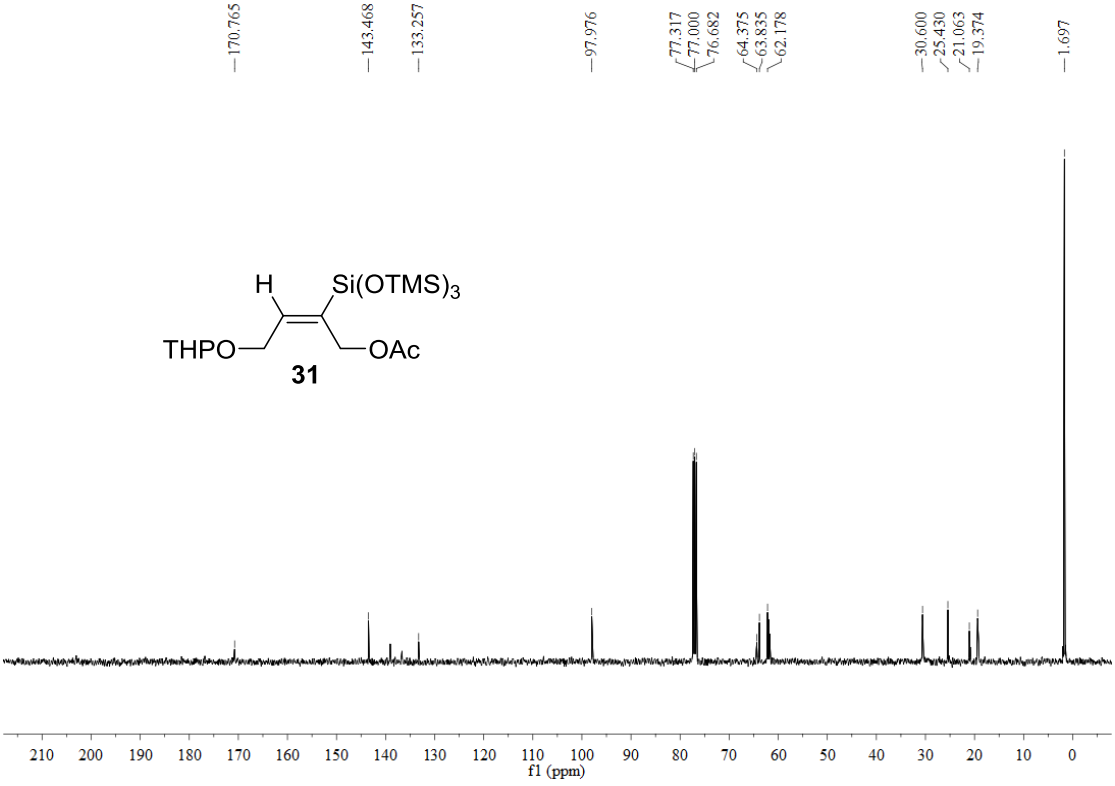


Figure S34. ^{13}C NMR spectra of **31**.

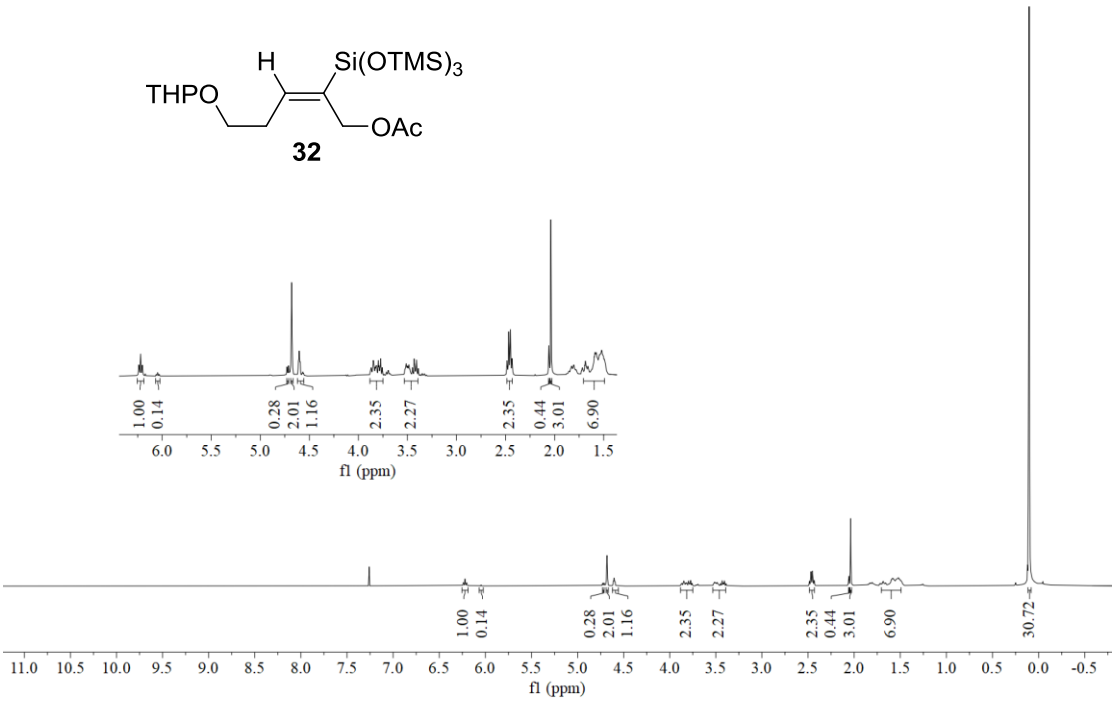


Figure S35. ^{1}H NMR spectra of **32**. (88:12 *α/β*)

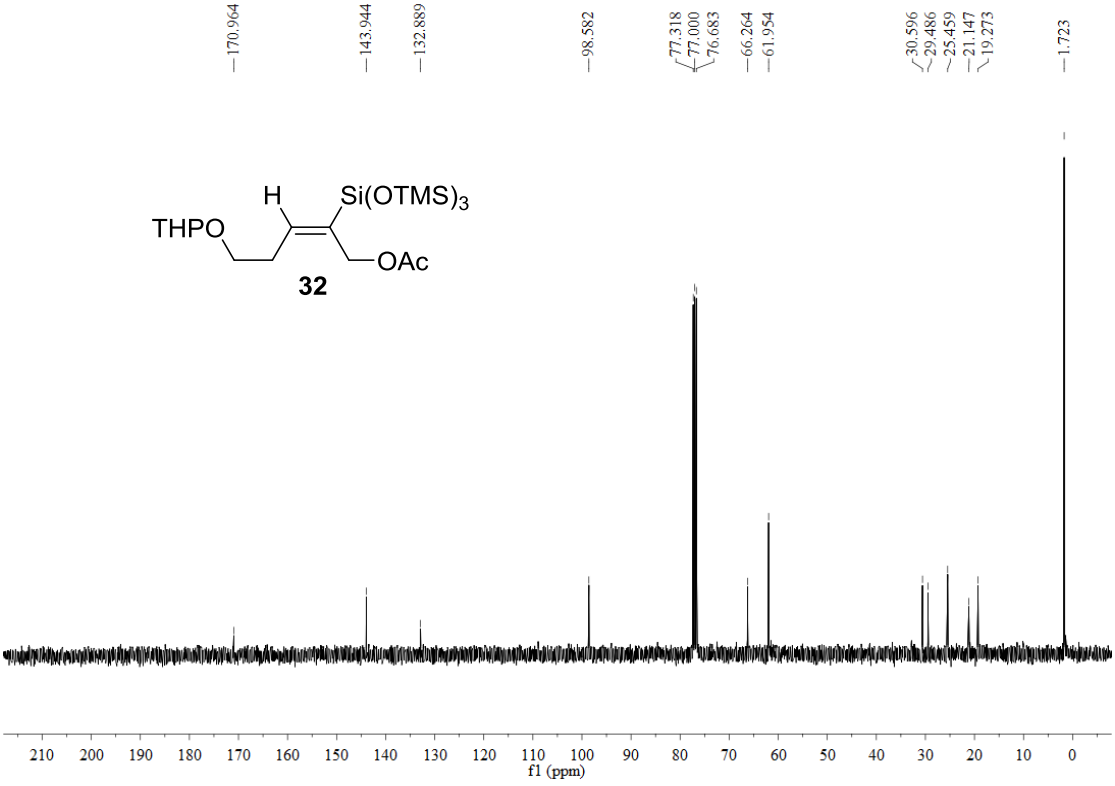


Figure S36. ^{13}C NMR spectra of **32**.

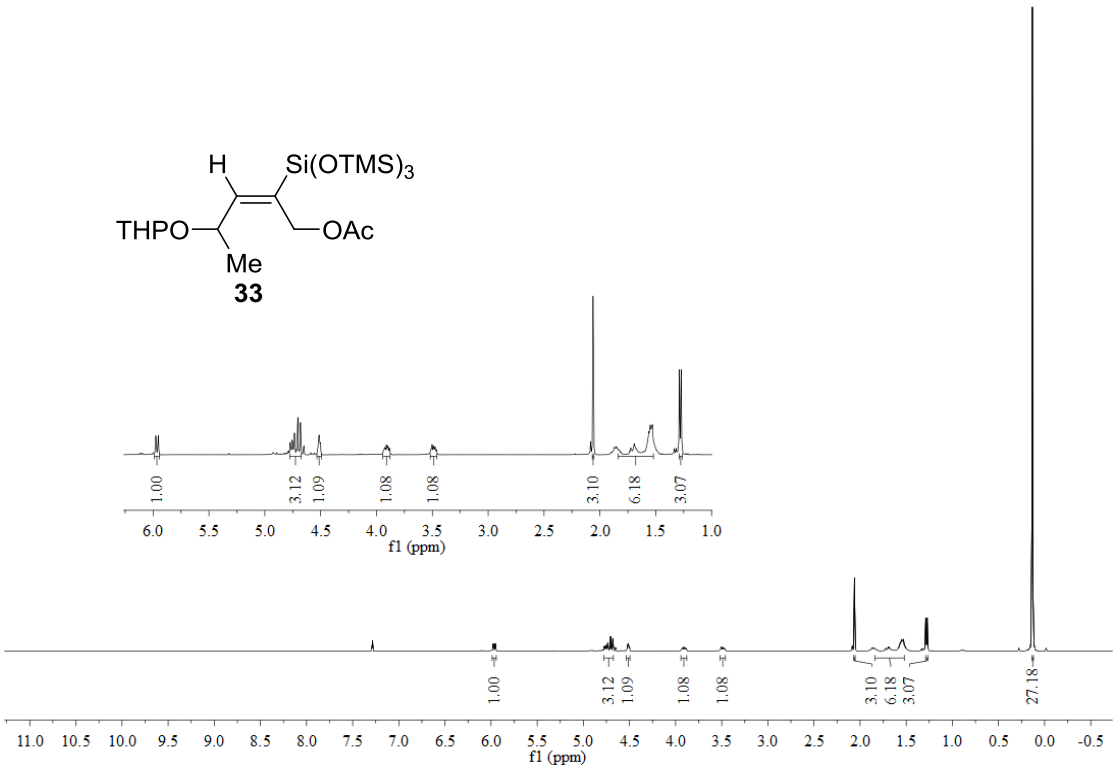


Figure S37. ^{1}H NMR spectra of **33**. (100:0 *α/β*)

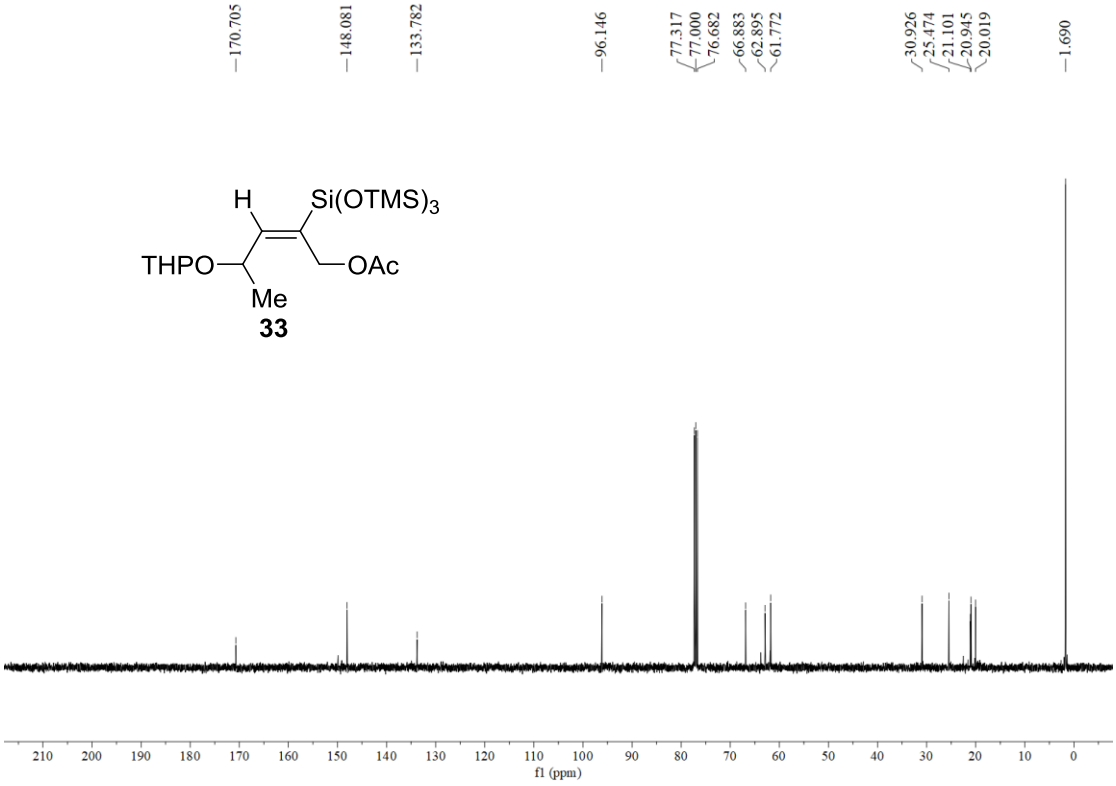


Figure S38. ^{13}C NMR spectra of **33**.

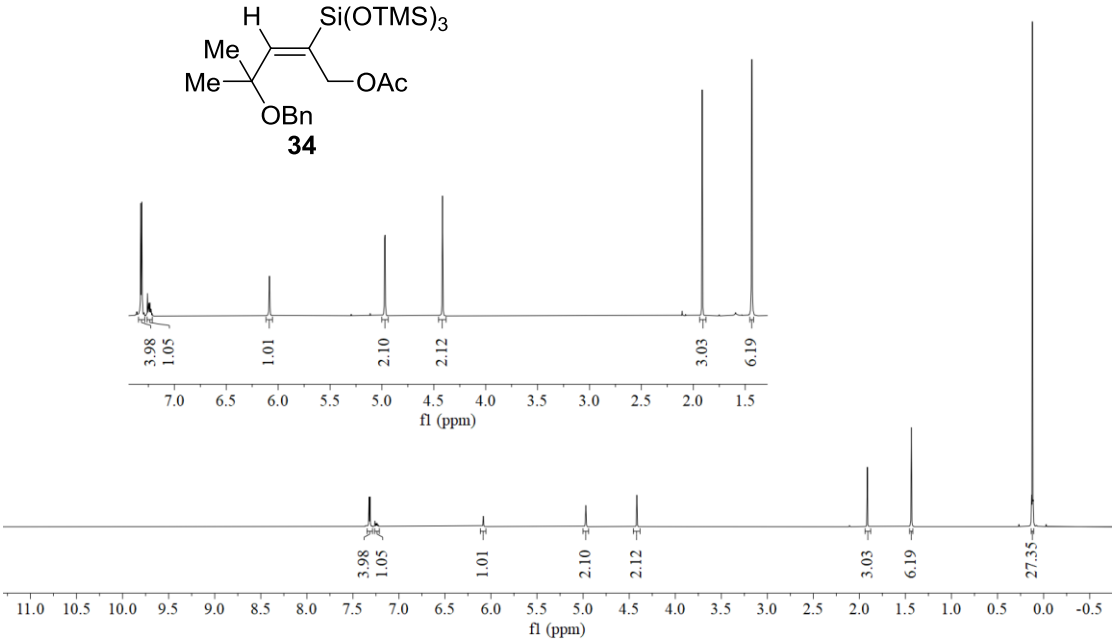


Figure S39. ^{1}H NMR spectra of **34**. (100:0 *α/β*)

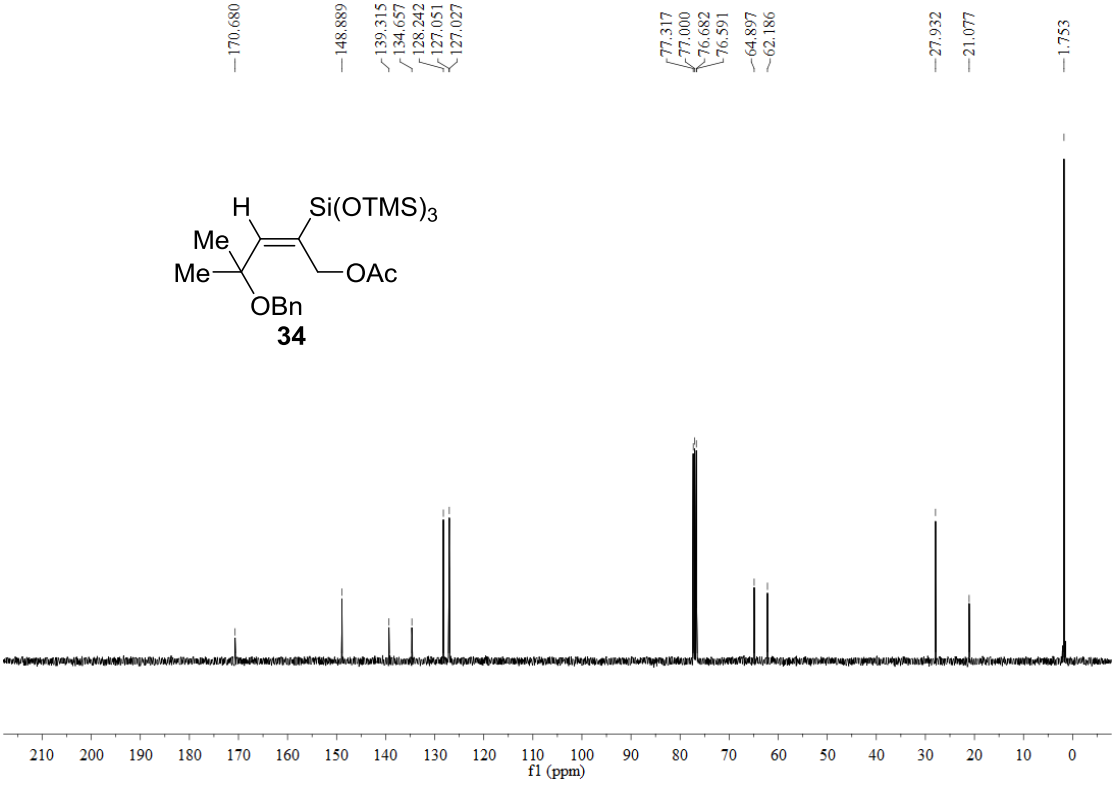


Figure S40. ^{13}C NMR spectra of **34**.

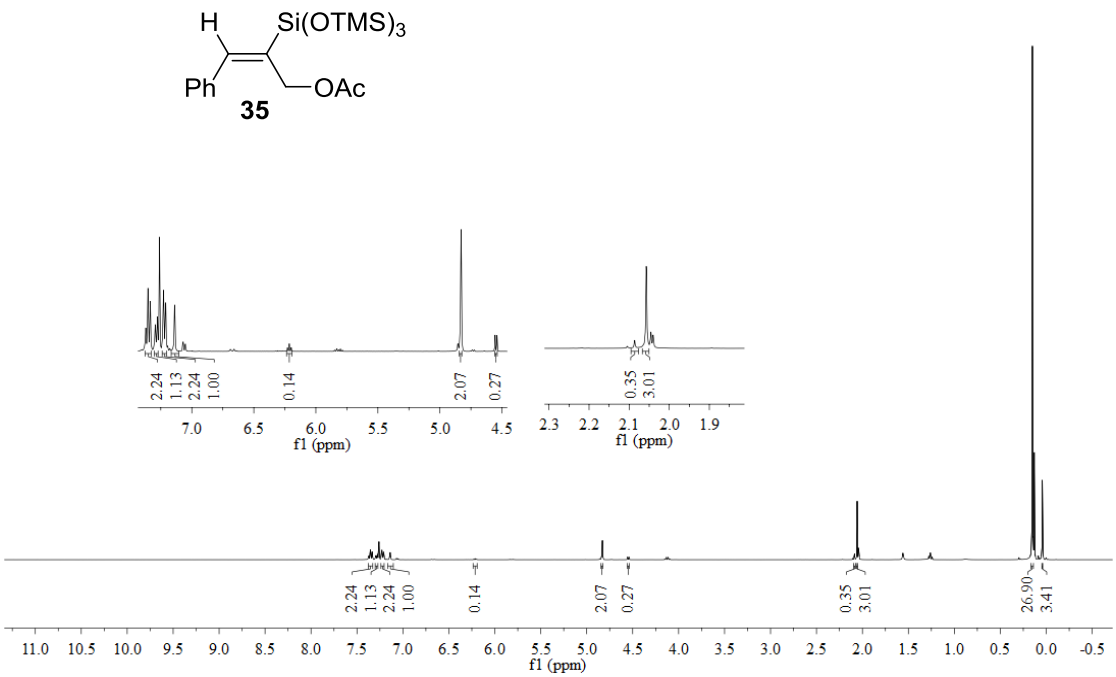


Figure S41. ^{1}H NMR spectra of **35**. (89:11 *α/β*)

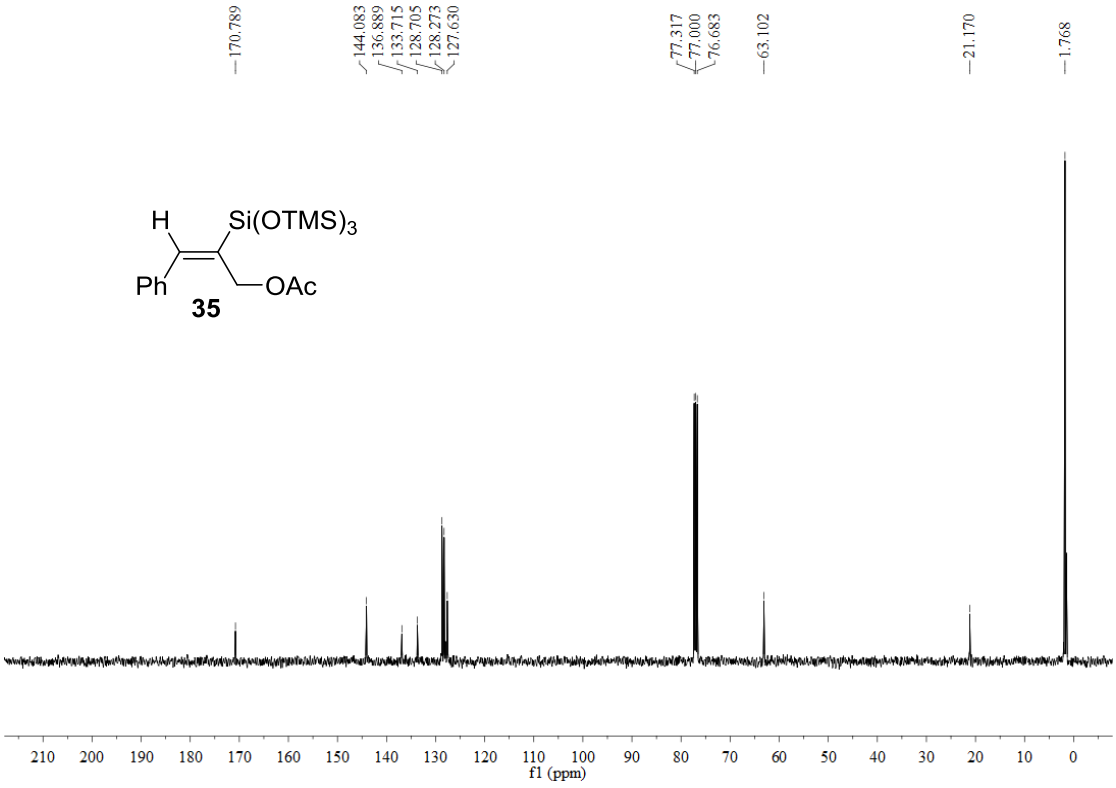


Figure S42. ^{13}C NMR spectra of **35**.

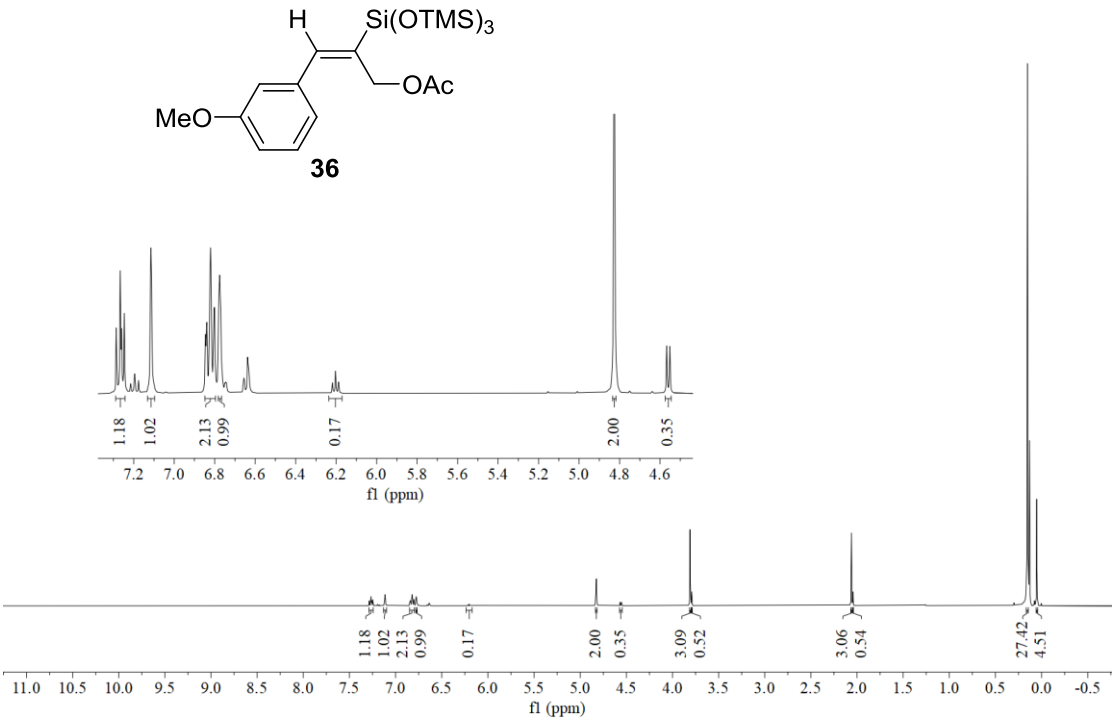


Figure S43. ^{1}H NMR spectra of **36**. (86:14 *α/β*)

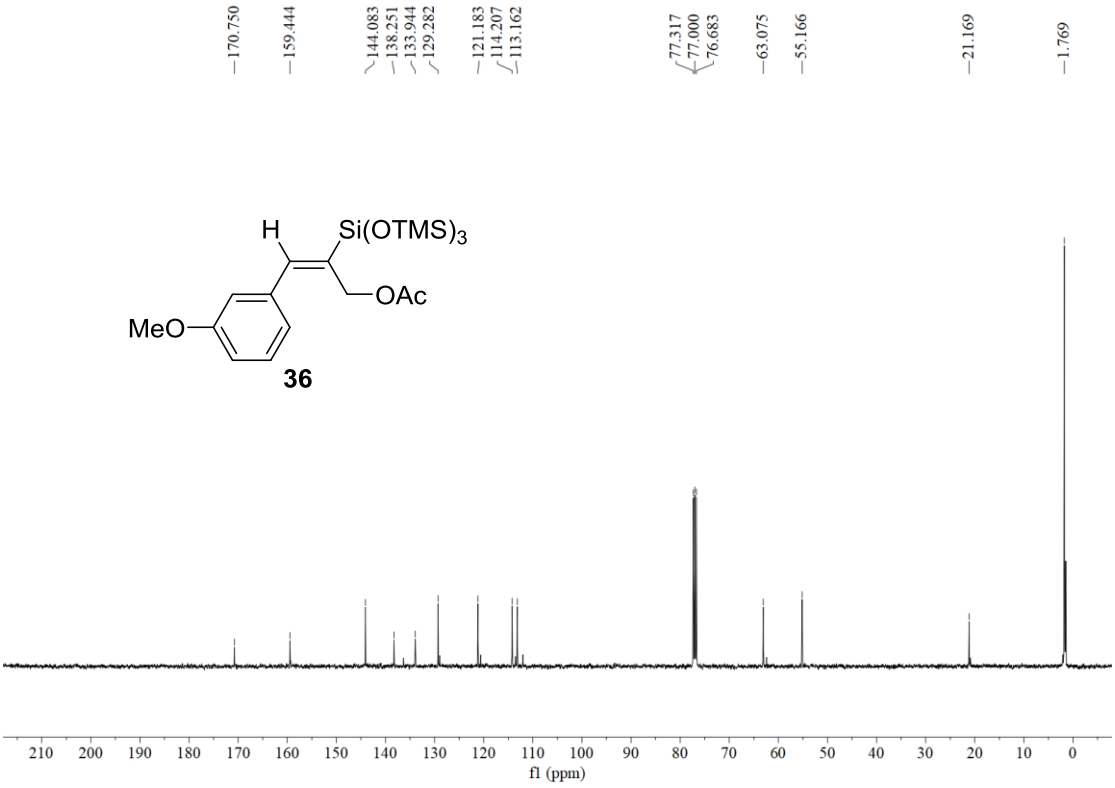


Figure S44. ^{13}C NMR spectra of **36**.

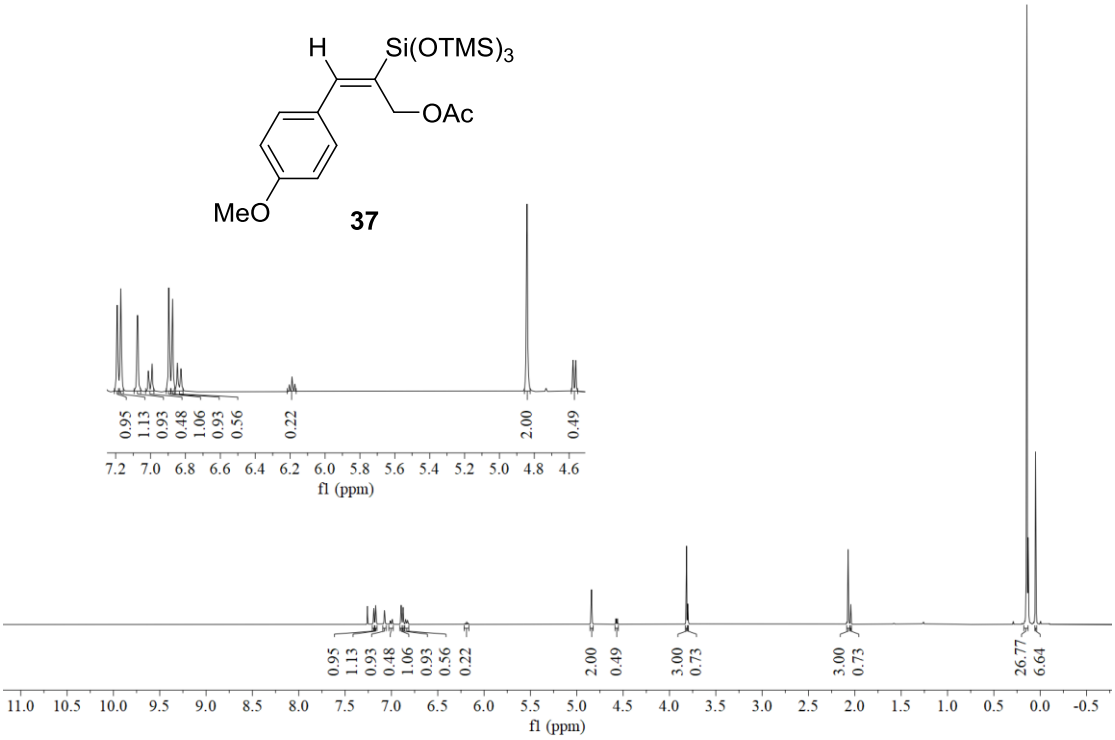


Figure S45. ^{1}H NMR spectra of **37**. (81:19 *α/β*)

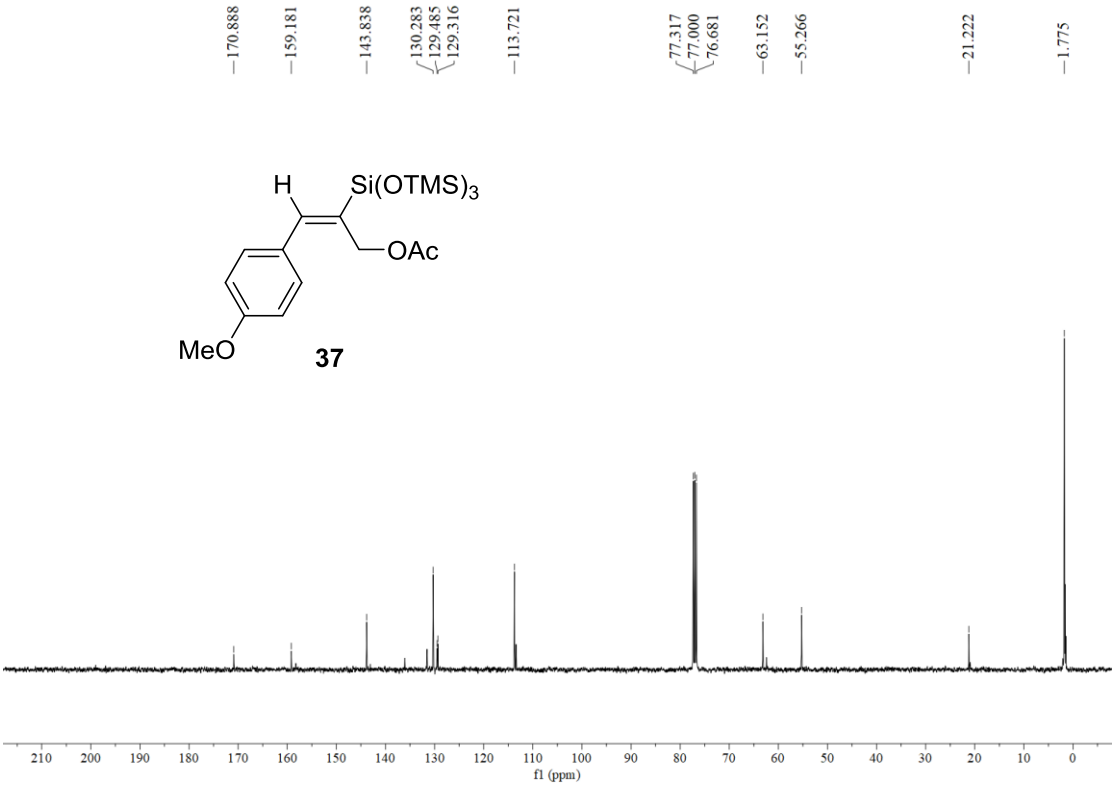


Figure S46. ^{13}C NMR spectra of **37**.

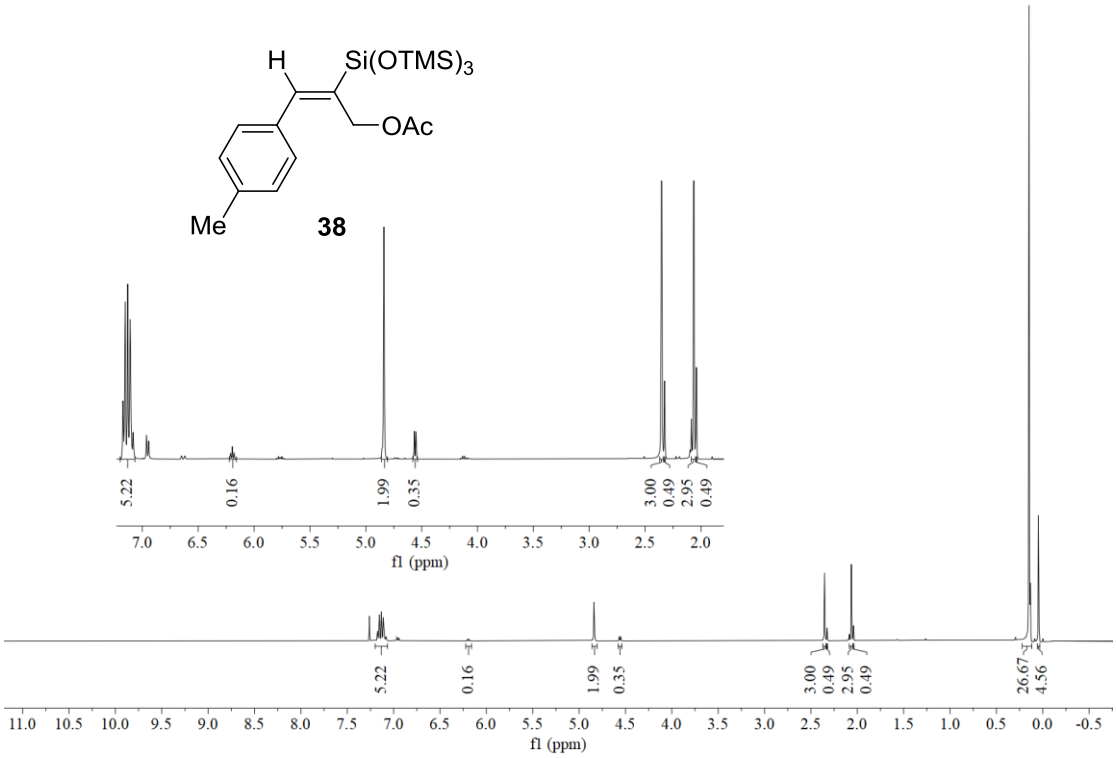


Figure S47. ^{1}H NMR spectra of **38**. (86:14 *α/β*)

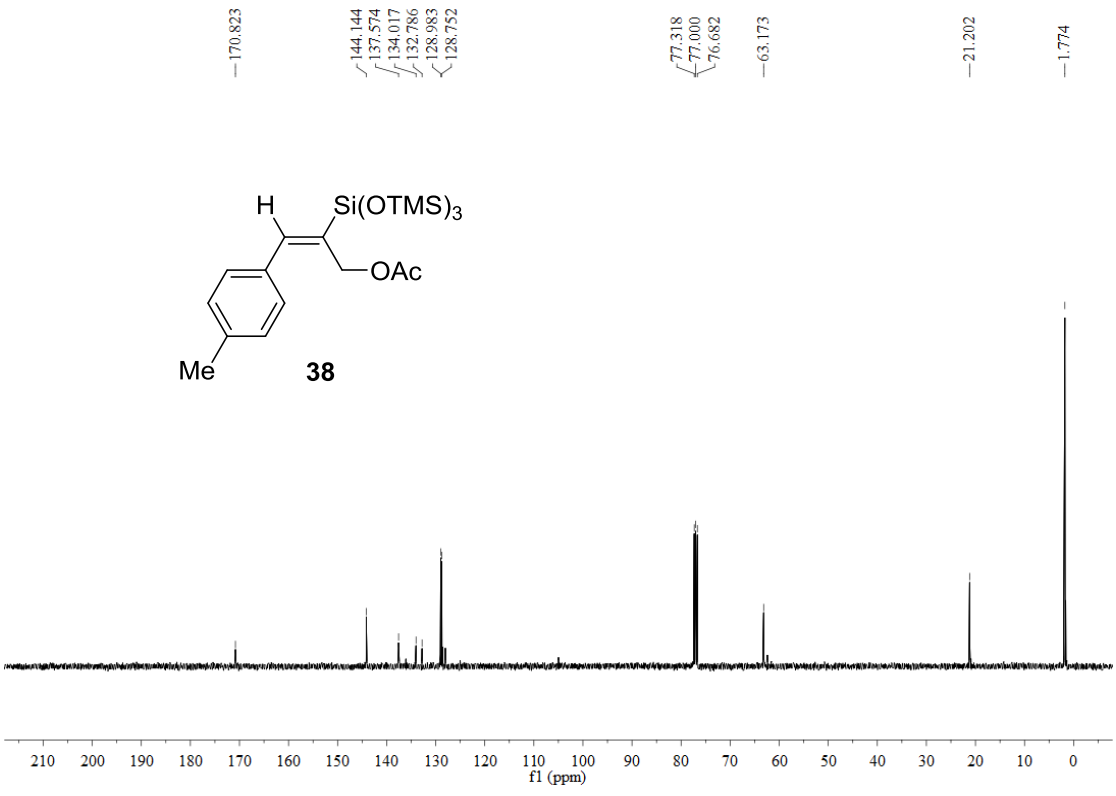


Figure S48. ^{13}C NMR spectra of **38**.

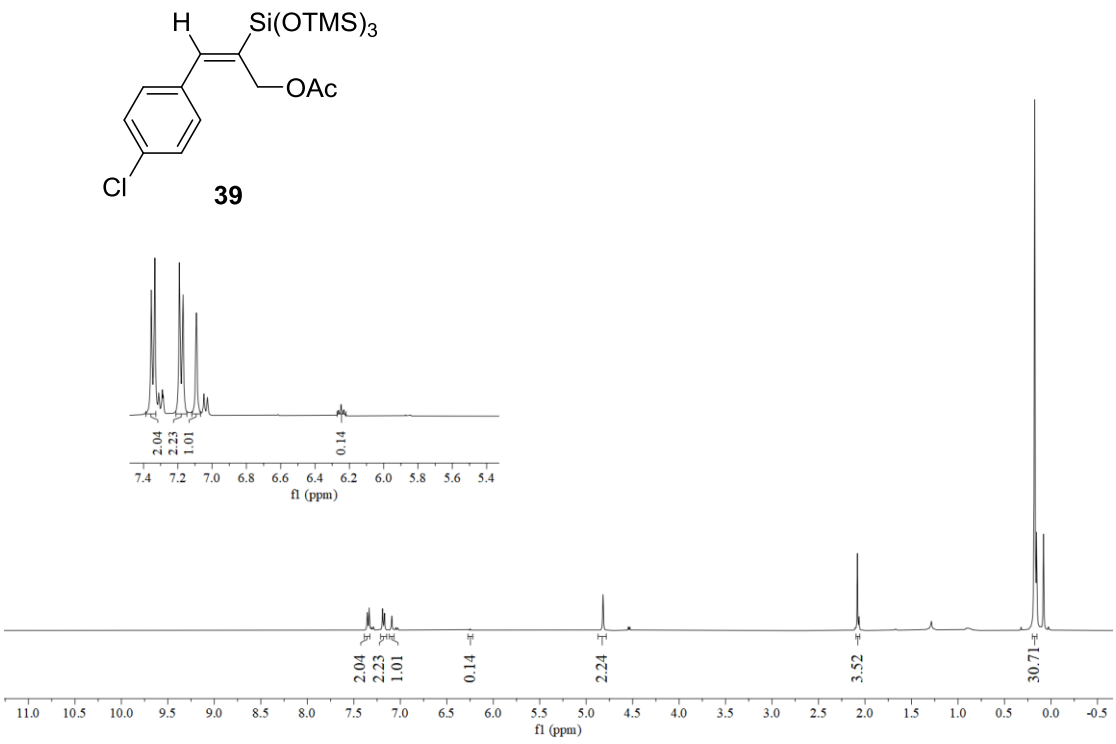


Figure S49. ^{1}H NMR spectra of **39**. (88:12 *α/β*)

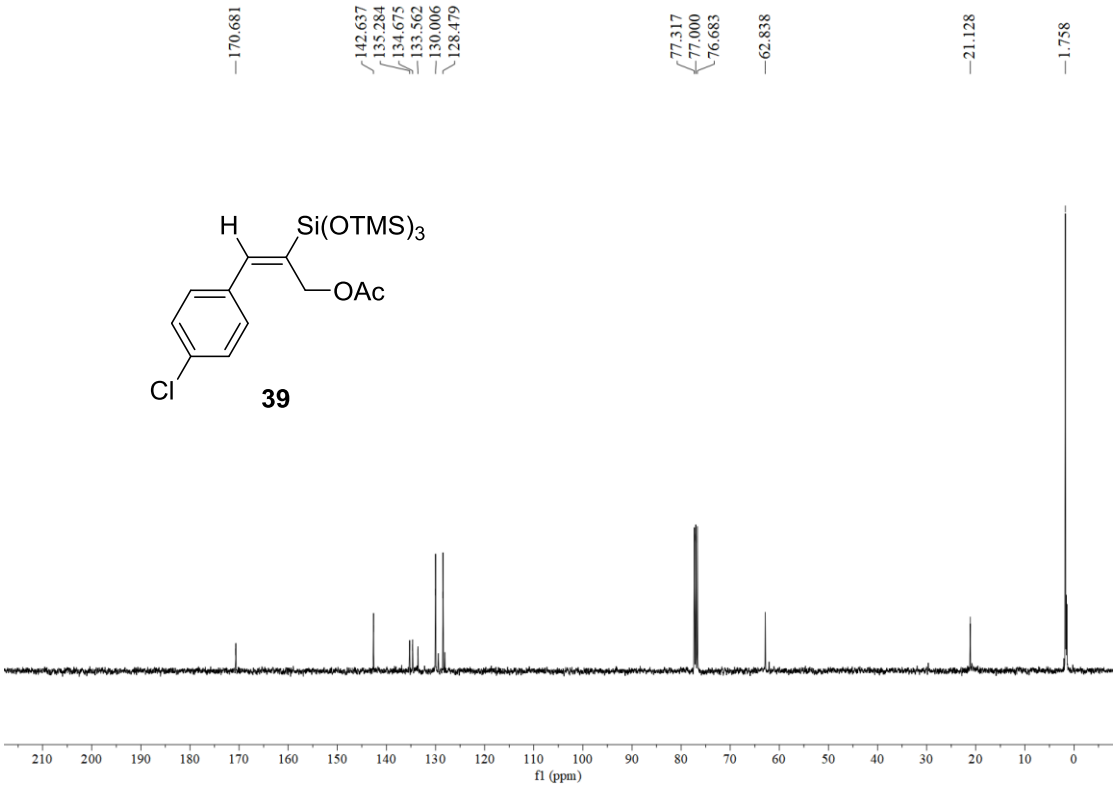


Figure S50. ^{13}C NMR spectra of **39**.

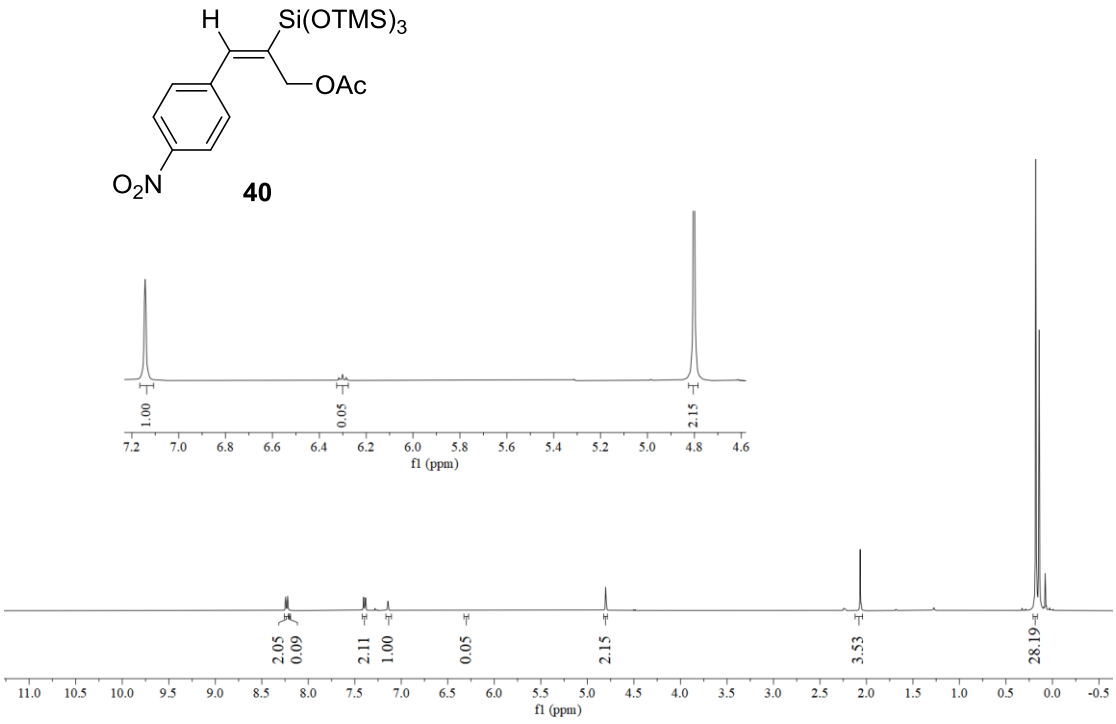


Figure S51. ^{1}H NMR spectra of **40**. (95:5 *α/β*)

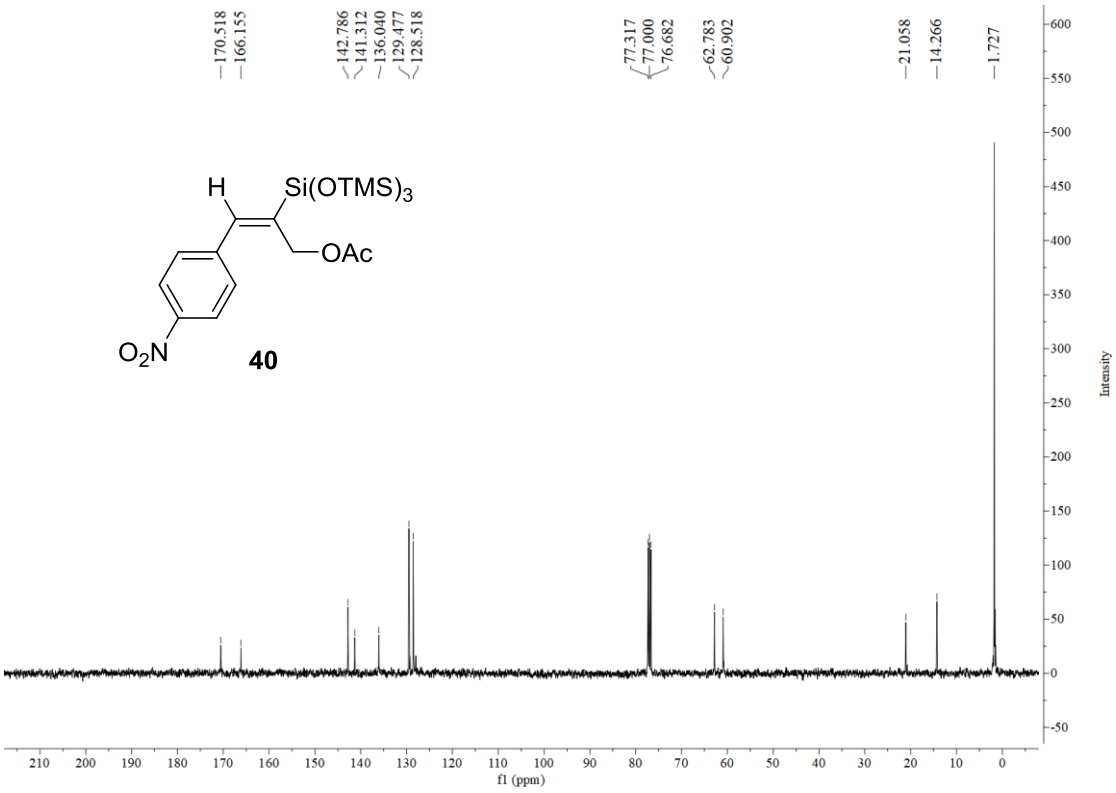


Figure S52. ^{13}C NMR spectra of **40**.

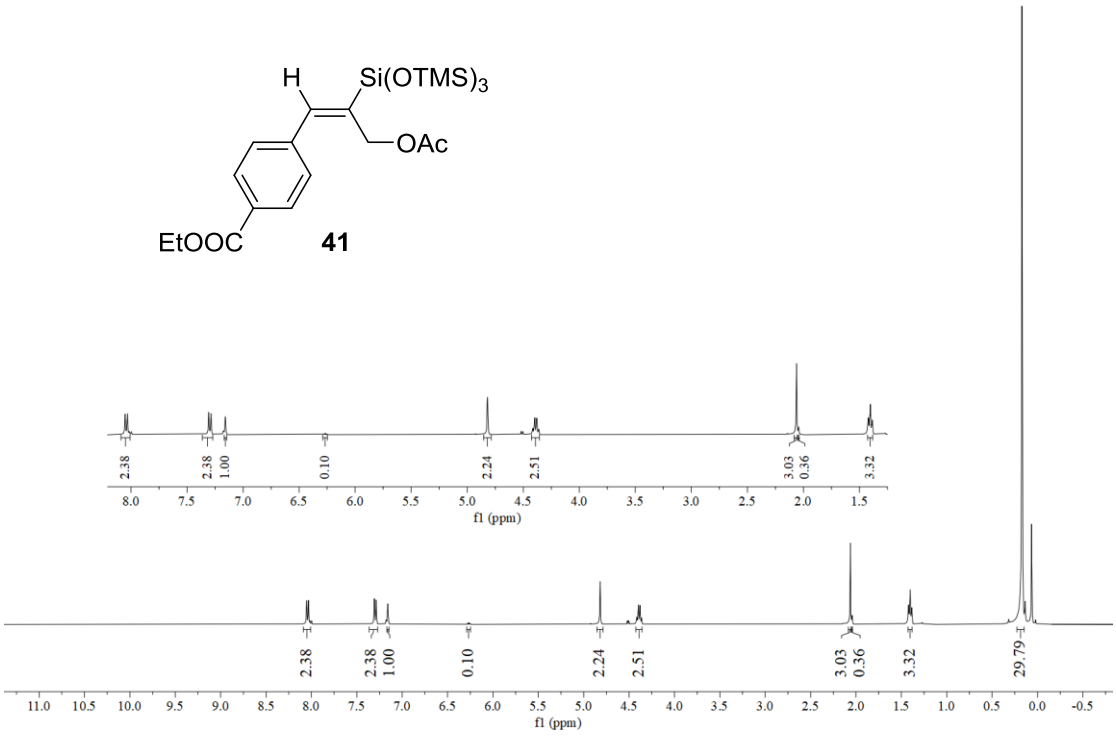


Figure S53. ^{13}C NMR spectra of **41**. (91:9 *α/β*)

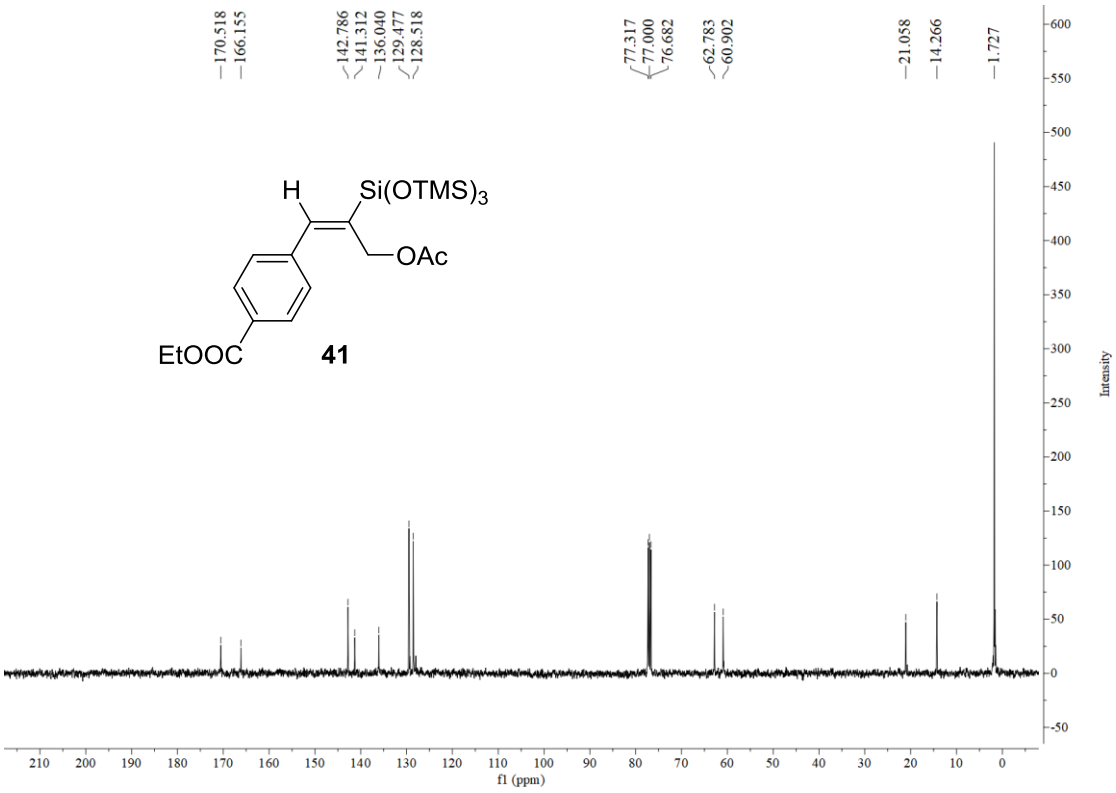


Figure S54. ^{13}C NMR spectra of **41**.

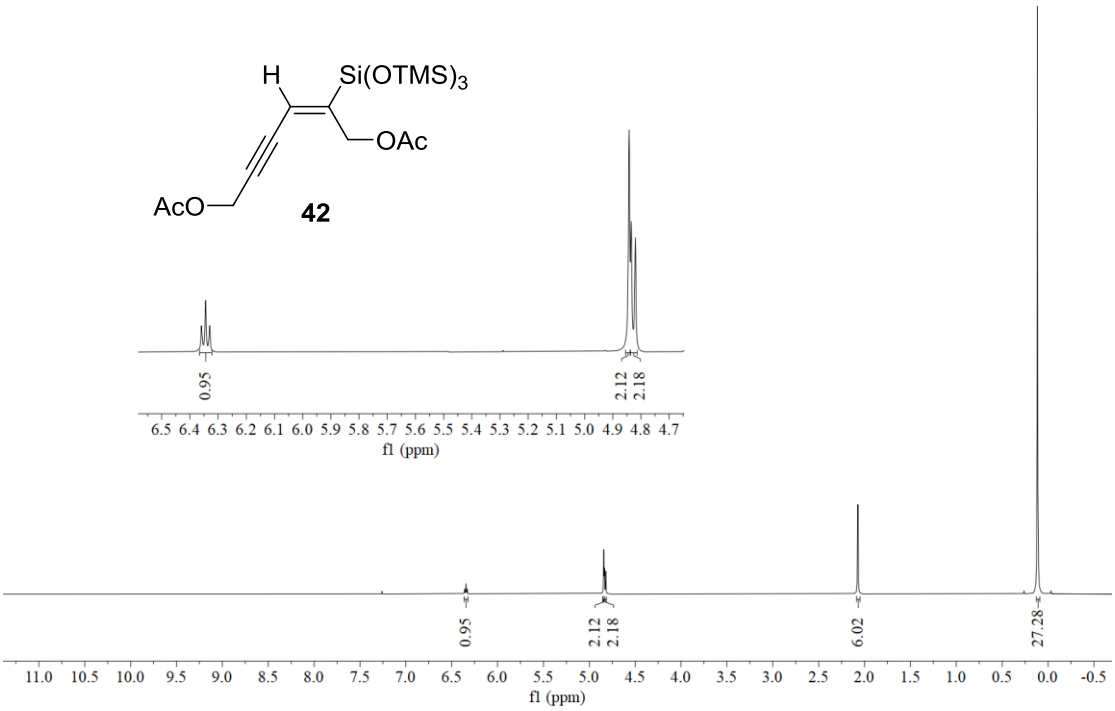


Figure S55. ^{1}H NMR spectra of **42**. (100:0 *α/β*)

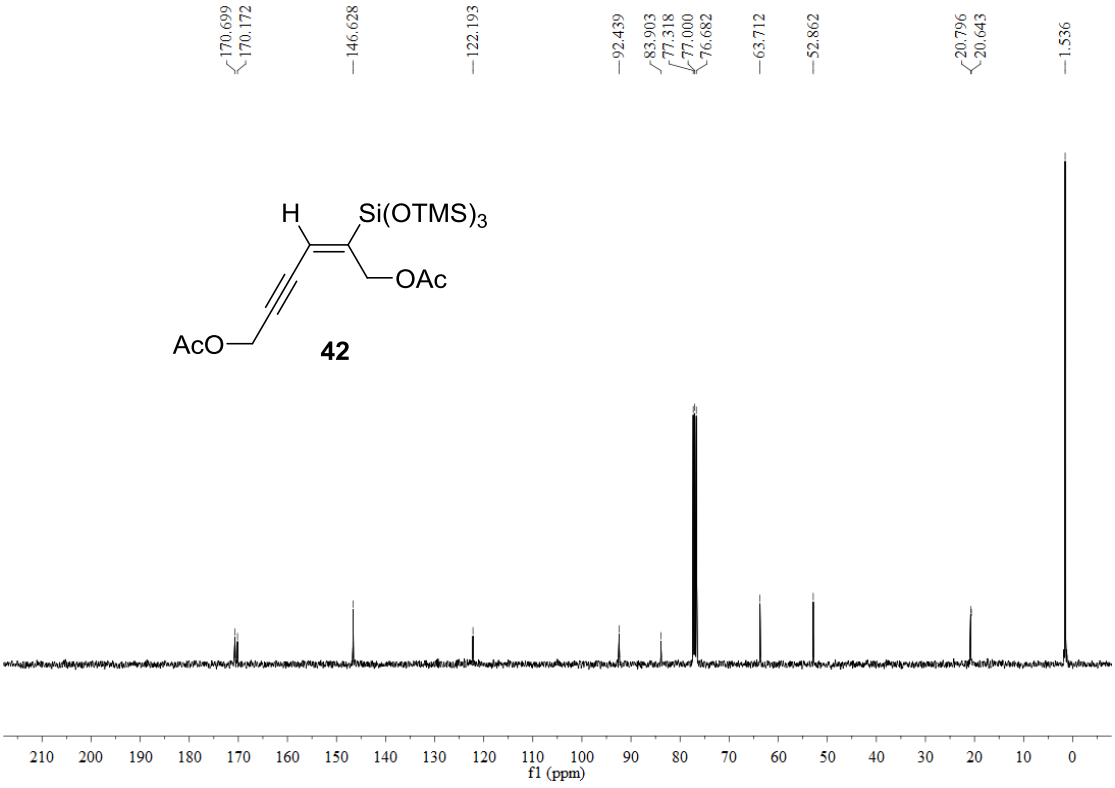


Figure S56. ^{13}C NMR spectra of **42**.

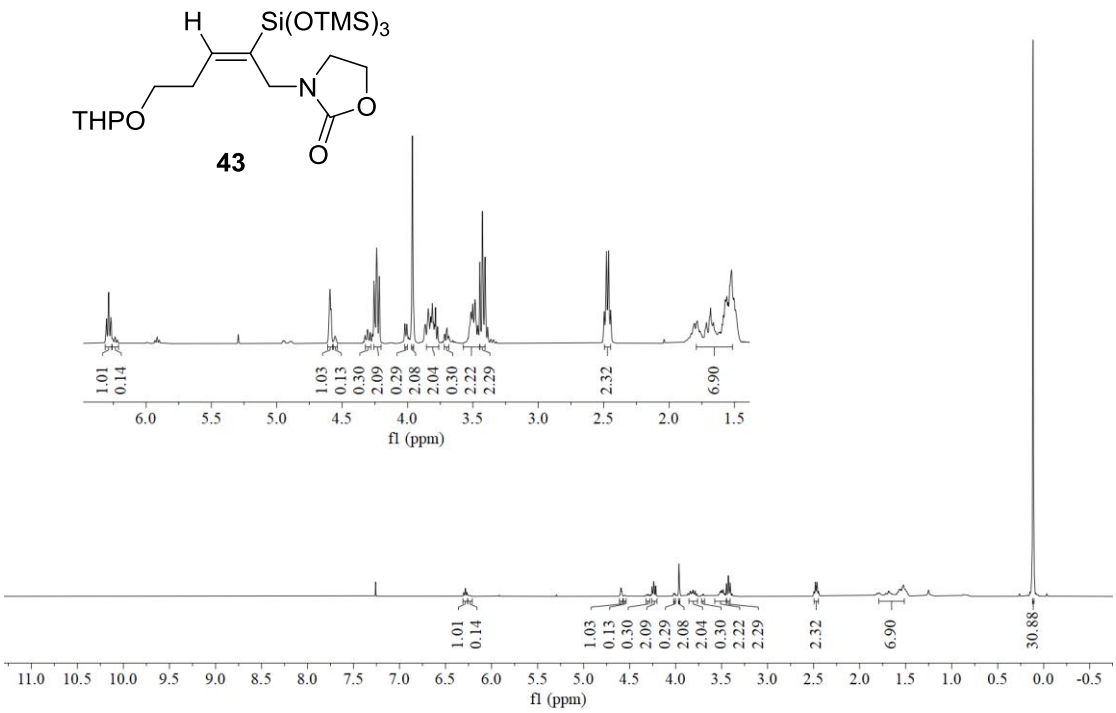


Figure S57. ^{1}H NMR spectra of **43**. (88:12 *α/β*)

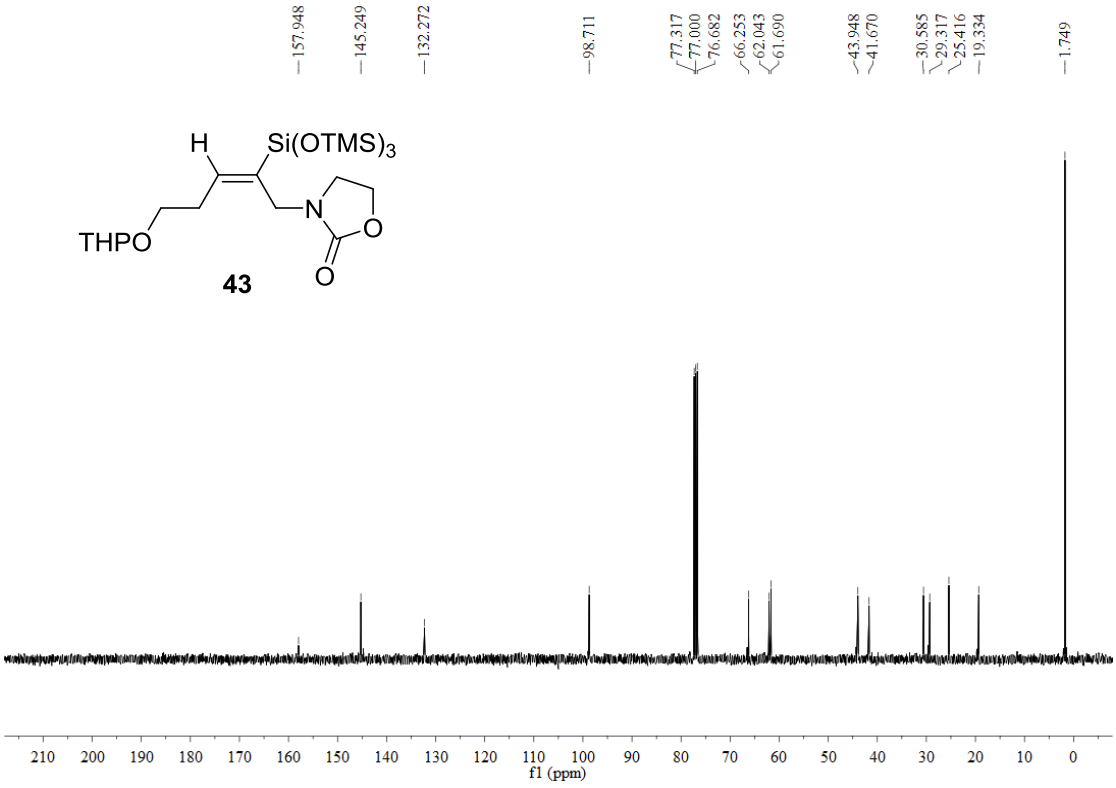


Figure S58. ^{13}C NMR spectra of **43**.

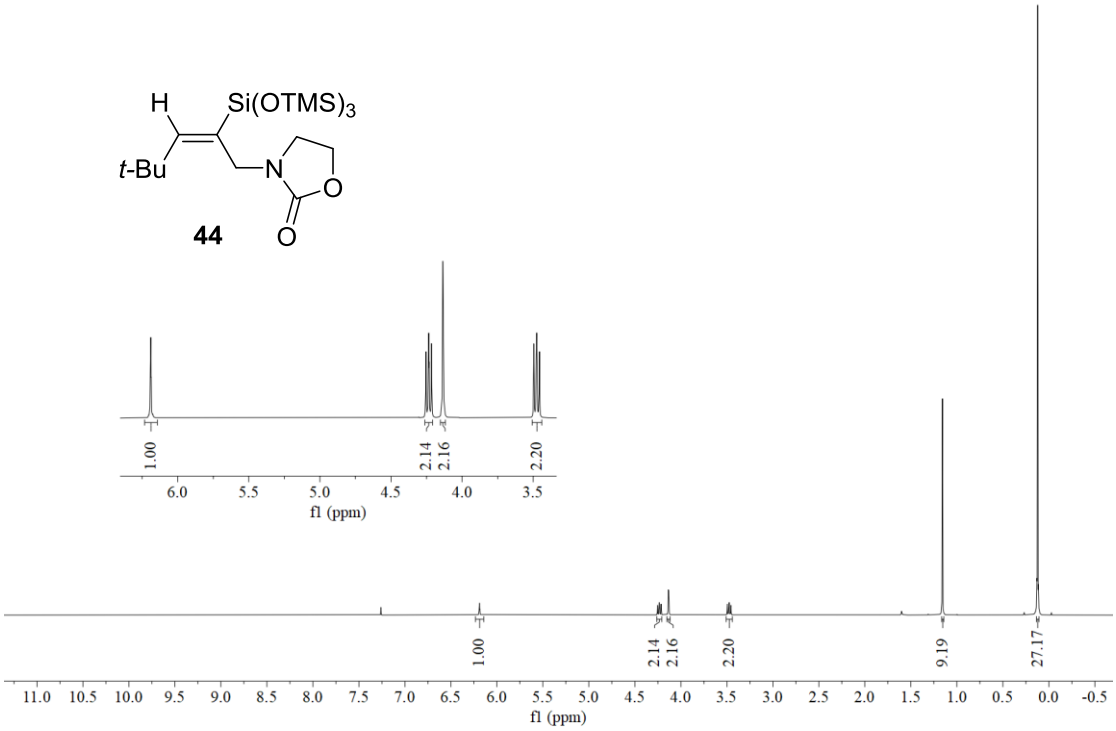


Figure S59. ^{1}H NMR spectra of **44**. (100:0 *α/β*)

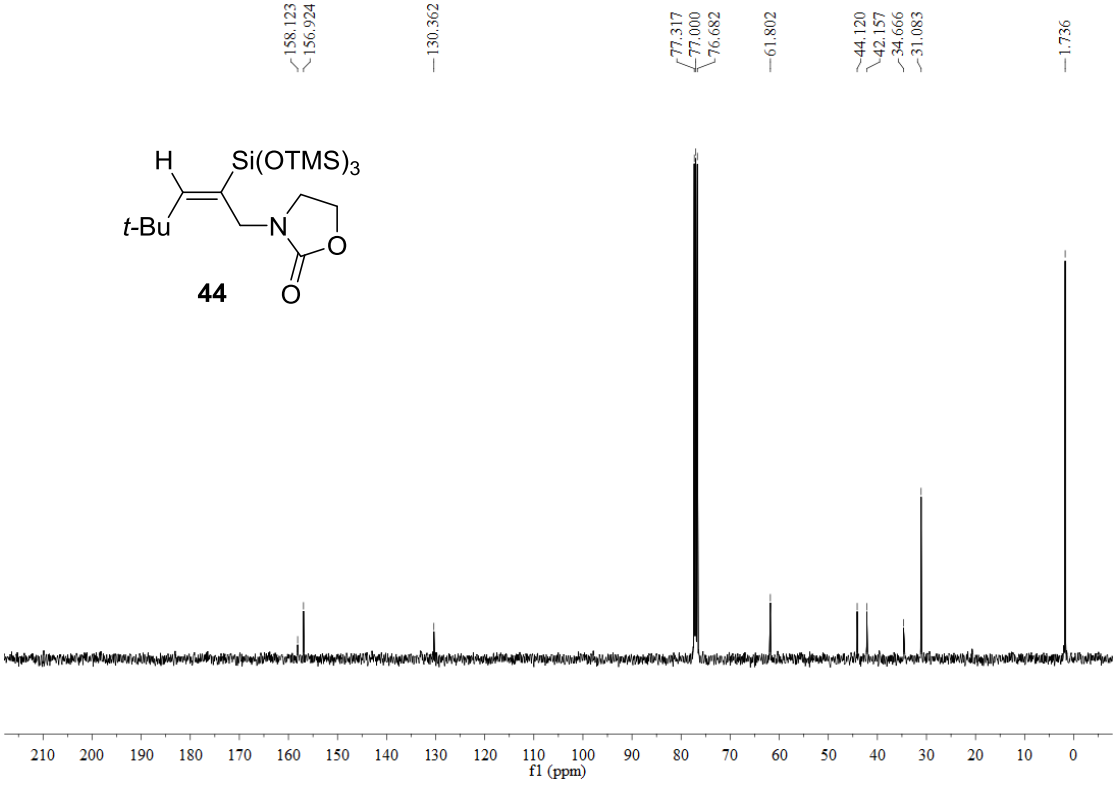


Figure S60. ^{13}C NMR spectra of **44**.

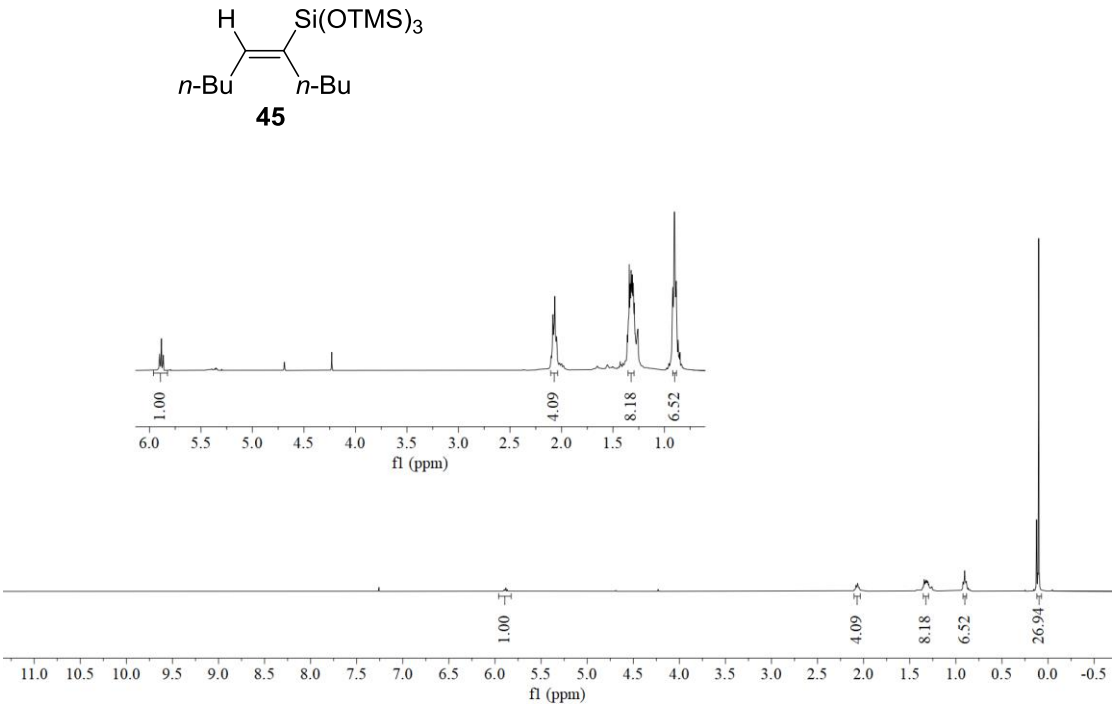


Figure S61. ^{1}H NMR spectra of **45**.

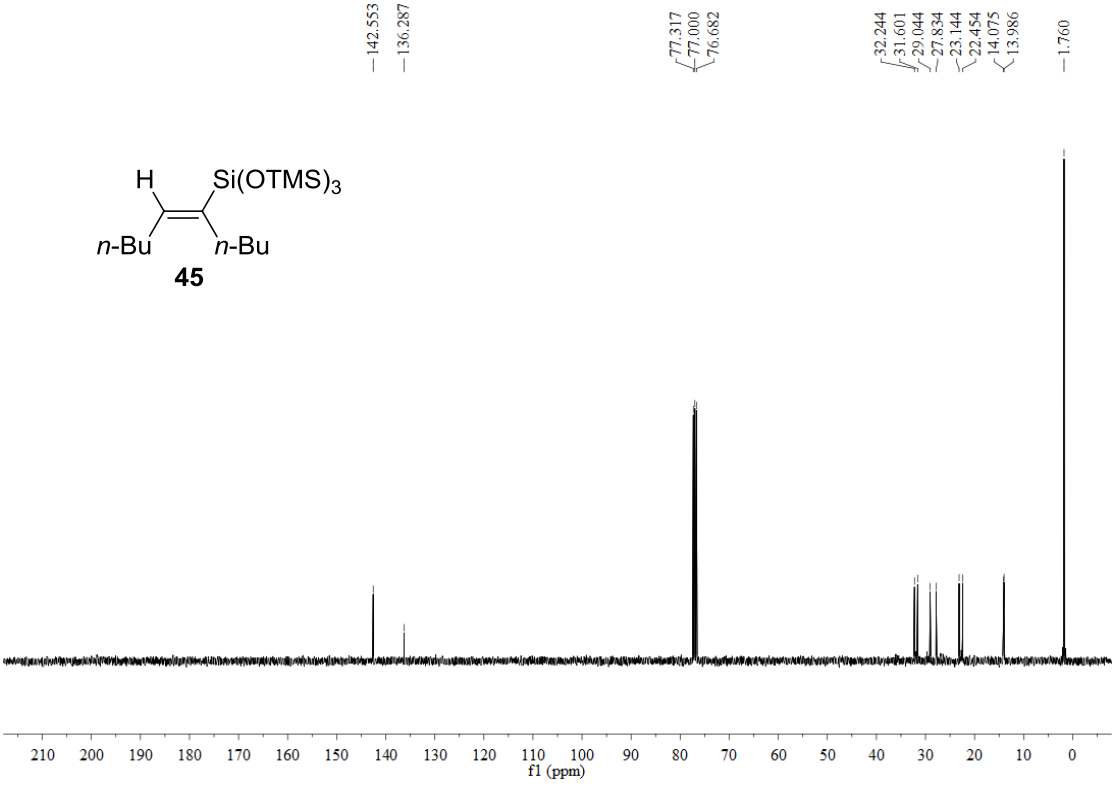


Figure S62. ^{13}C NMR spectra of **45**.

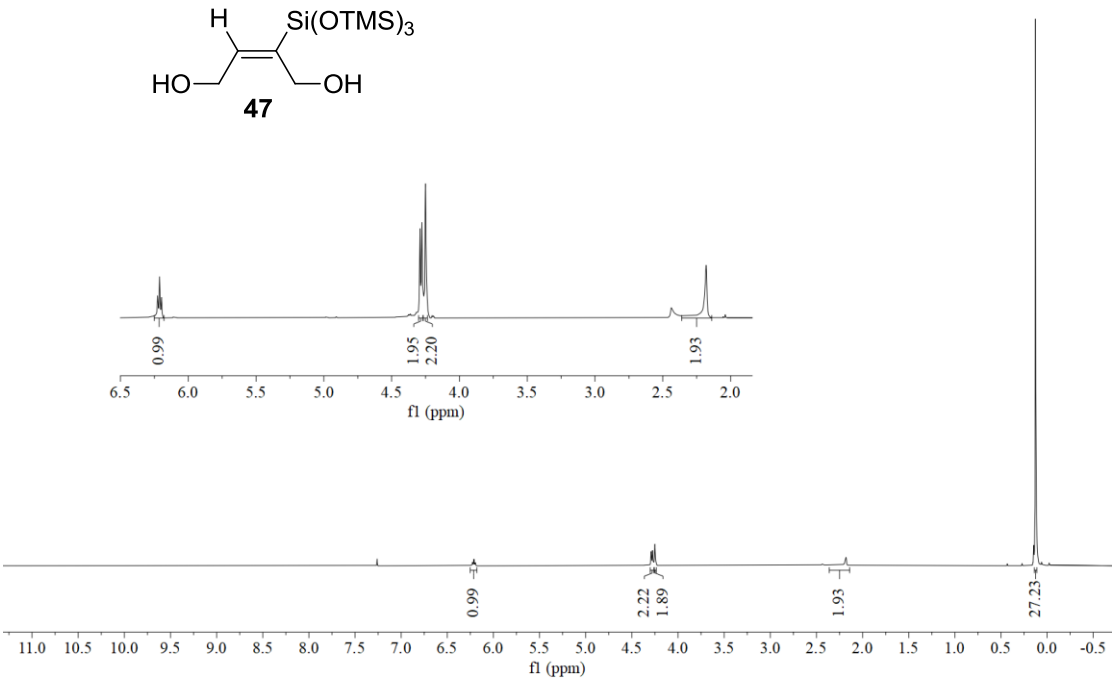


Figure S63. ^{1}H NMR spectra of **47**.

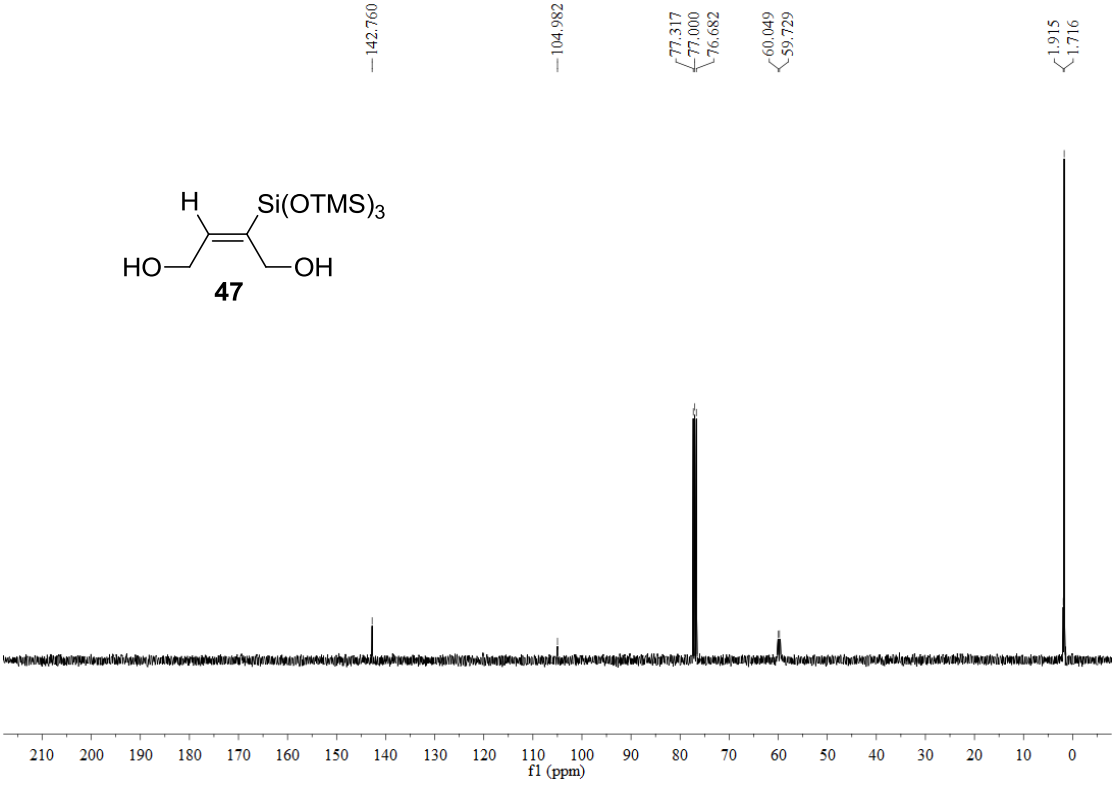


Figure S64. ^{13}C NMR spectra of **47**.

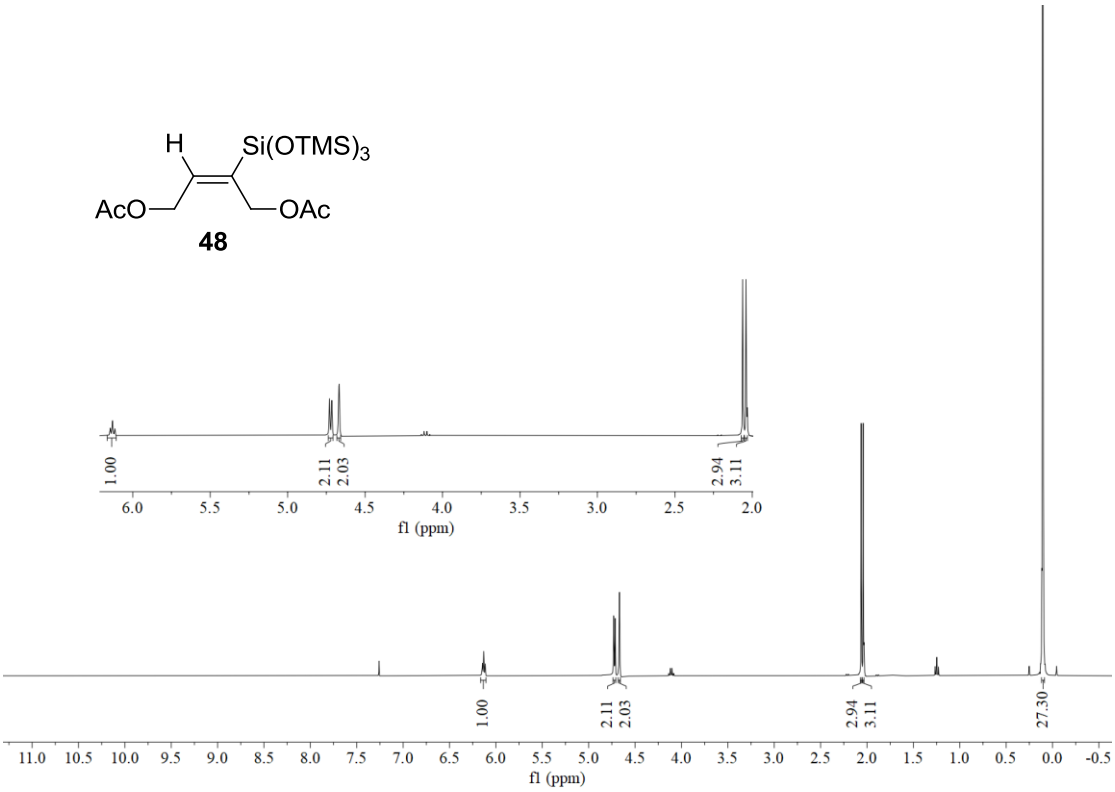


Figure S65. ^{1}H NMR spectra of **48**.

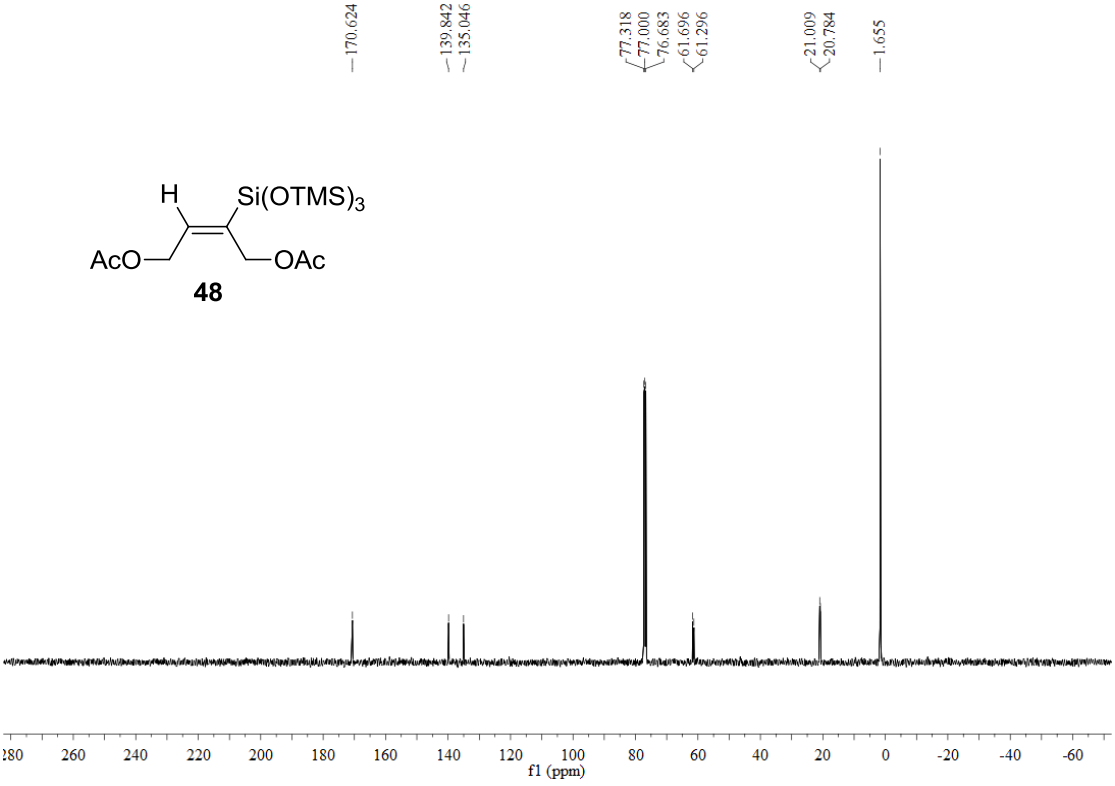


Figure S66. ^{13}C NMR spectra of **48**.

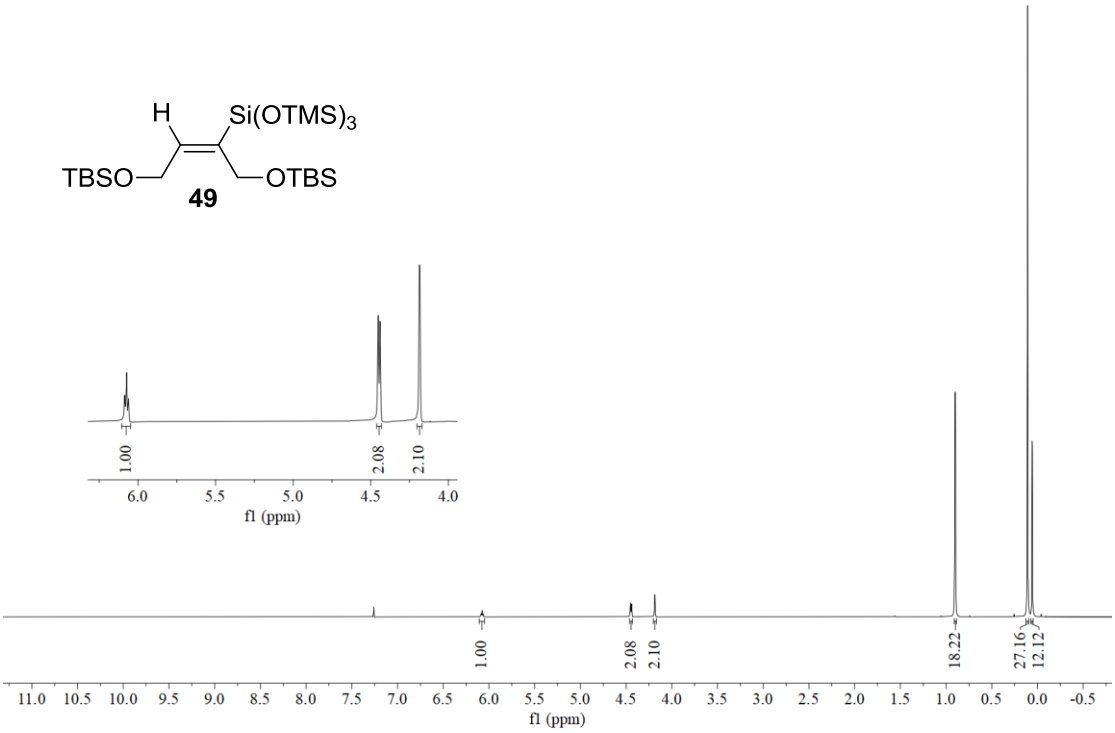


Figure S67. ^{1}H NMR spectra of **49**.

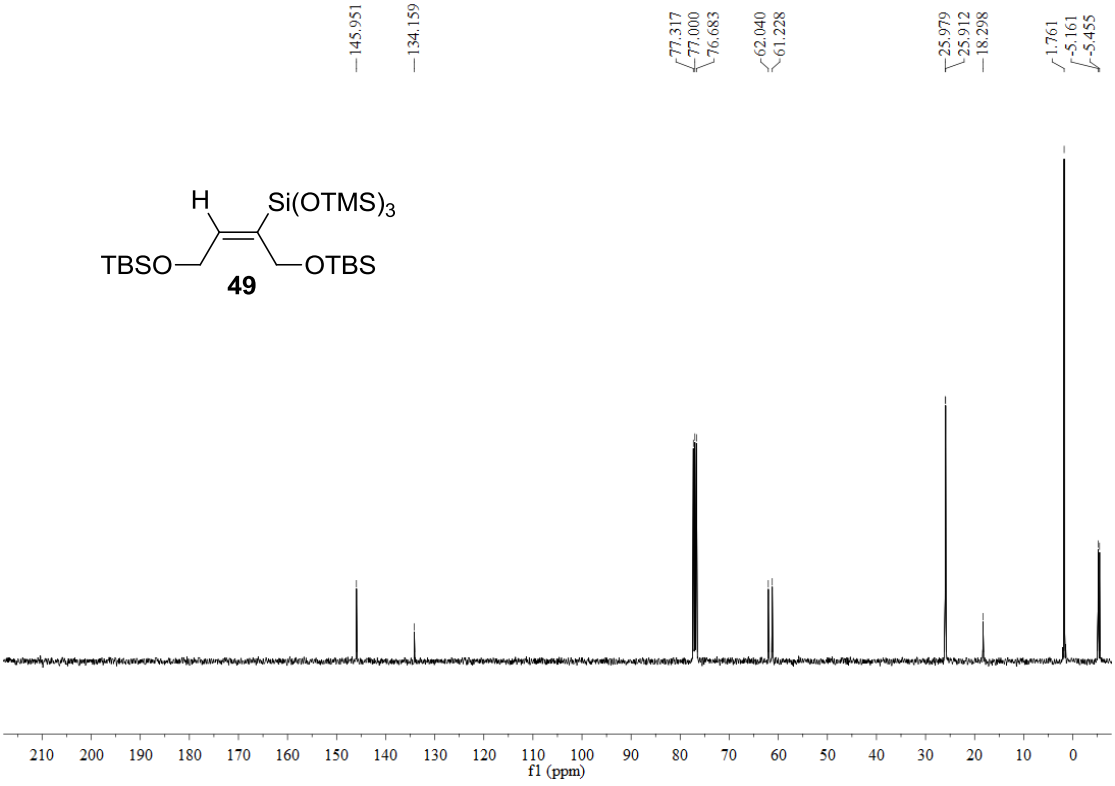


Figure S68. ^{13}C NMR spectra of **49**.

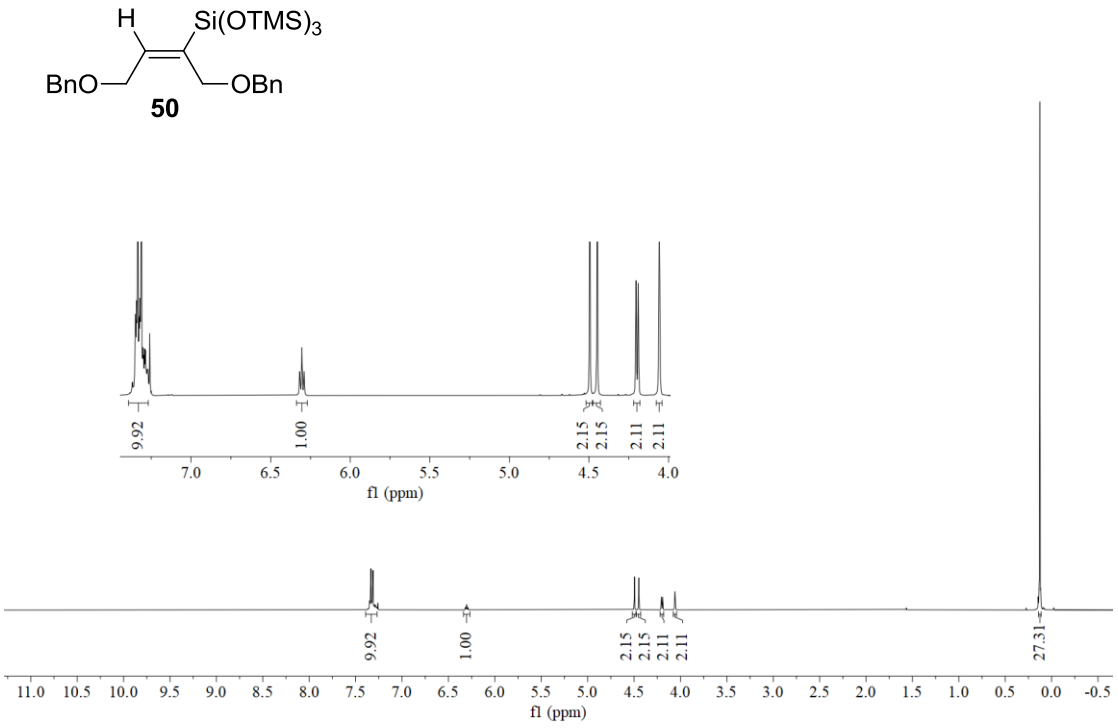


Figure S69. [1]H NMR spectra of **50**.

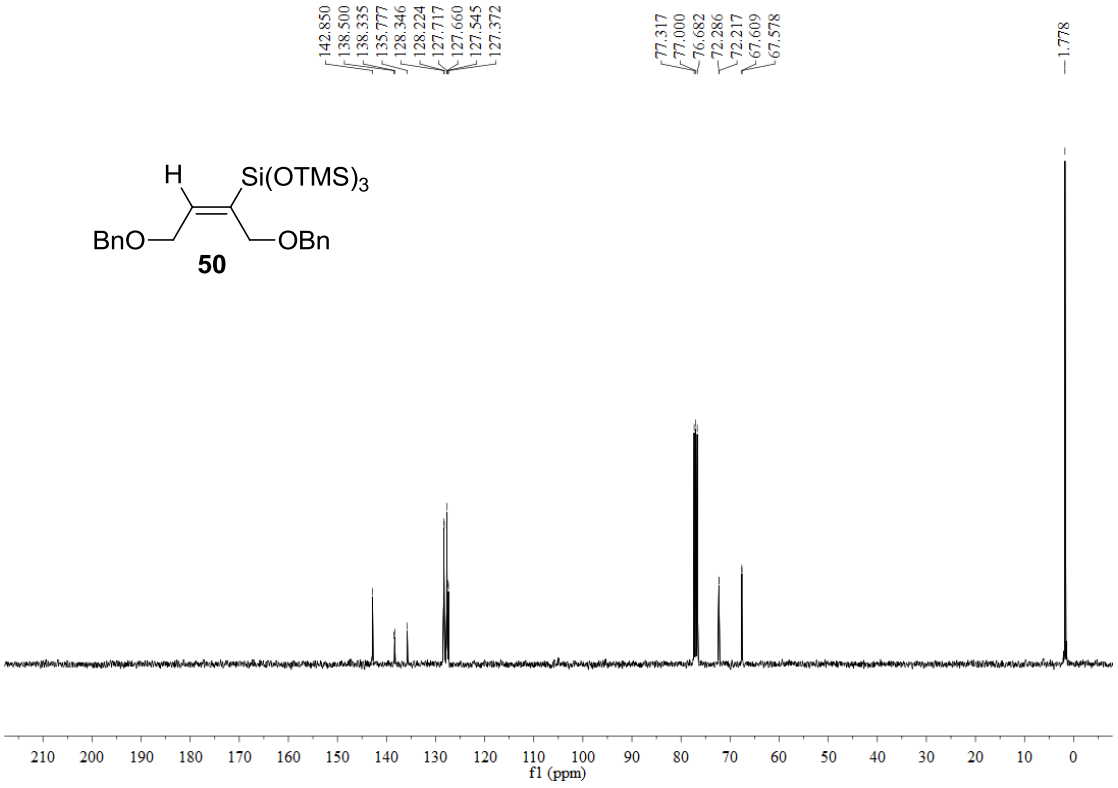


Figure S70. [13]C NMR spectra of **50**.

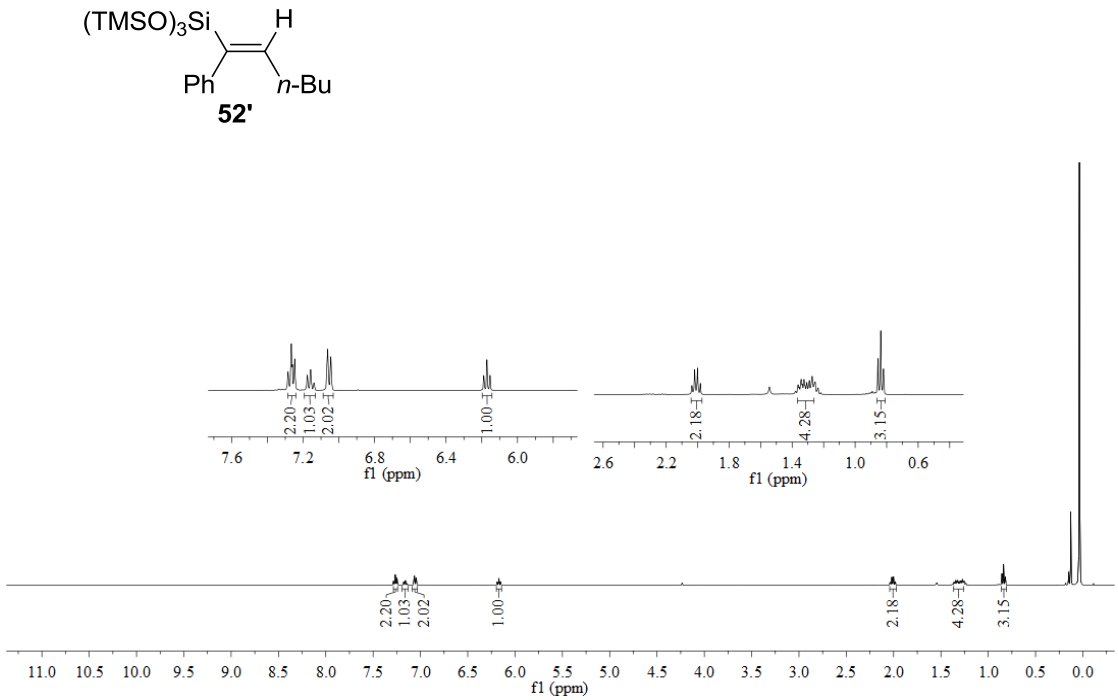


Figure S71. ^{1}H NMR spectra of **52'**.

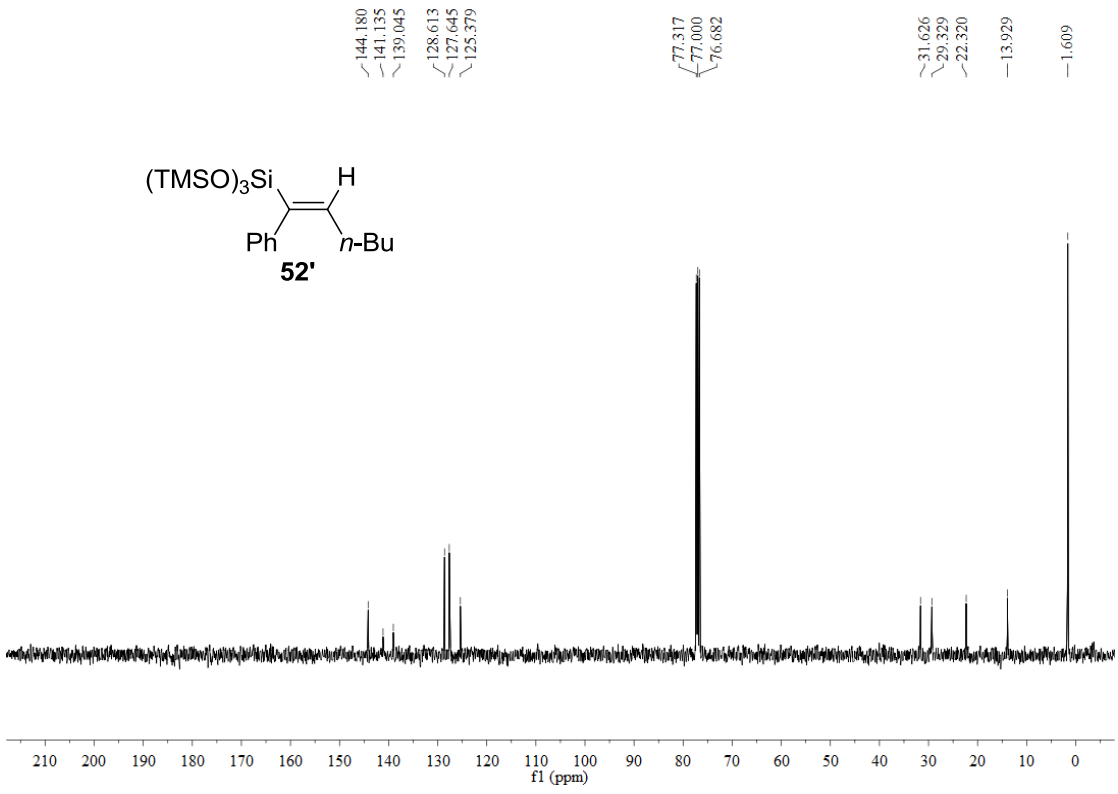


Figure S72. ^{13}C NMR spectra of **52'**.