Shuffle off the Classic β-Si Elimination by Ni-NHC Cooperation: Implication for C-C Forming Reactions Involving Ni-Alkyl-β-Silanes.

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ESI

Experimental Procedures, Analytical and Spectroscopic Data for New Compounds.

Table of Content:

General Aspects:

Unless otherwise indicated, all reactions were performed under a nitrogen or argon atmosphere from which oxygen and moisture were rigidly excluded from reagents and glassware. Bis(cyclooctadienyl)nickel(0) ($Ni(cod)_2$) was purchased from ACROS or IL, stored under nitrogen atmosphere and used without further purification. IPr [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene] was purchased from Aldrich or Strem. Triethylsilyl trifluoromethanesulfonate (TESOTf), p-anisaldehyde and triethylamine (NEt_3) were distilled before use. Vinylsilane and alkenes were filtered through a short plug of silica gel and dried before use. Toluene was distilled over sodium before use.

Analytical thin layer chromatography (TLC) was performed using EM Science silica gel 60 F254 plates. The developed chromatogram was analyzed by UV lamp (254 nm), ethanolic phosphomolybdic acid (PMA) or potassium permanganate ($KMnO_4$). Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on Merck Silica Gel (230–400 mesh, 0.040-0.063 mm) using a coarse fritted glass column. Desired hydroalkenylation products can be isolated by flash column chromatography on silica gel.

^1H and ^{13}C spectra were recorded on Bruker 400 spectrometers in $CDCl_3$ (400 MHz for ^1H and 100 MHz for ^{13}C). Chemical shifts in ^1H NMR spectra are reported in ppm on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in hertz (Hz), and integration. Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of $CDCl_3$ (77.16 ppm) on the δ scale. Vinylsilane conversion and products ratio was determined by integration of areas of selected peaks in crude ^1H NMR with relaxation time d1 = 10 seconds and nitromethane as standard where specified. Several entries in Table 1 were confirmed further by GC-MS analysis, the spectra were recorded on a HP G1530A GC / 5973N MS equipped with a column (HP-5ms 30m x 0.25mm x 0.25µm, + 5m x 0.25mm x 0.25µm guard column [(5%-Phenyl)-methylpolysiloxane, length, internal diameter, film thickness]). Yield and ratio were determined by integration of areas of selected peaks in crude GC with hexamethylbenzene as standard unless otherwise indicated.

High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95XL GC Mass Spectrometer by Miss. Hau Yan Ng of the Chinese University of Hong Kong, Department of Chemistry.

General Procedure for Group 14 Vinylmetalloid-α-Olefin h-t Hydroalkenylation

$Ni(cod)_2$ and IPr [0.05 mmol, 10 mol% each, IPr = 1,3-Bis(2,6-di-isopropylphenyl)imidazol-2-ylidene] were added to an oven-dried test tube equipped with a stir bar in glove box. After sealed with a septum and brought out of the glove box, it was connected to a N_2 line. The mixture was dissolved in 2 mL dried degassed toluene and stirred at rt for 1 h. 1-Octene (20 mol%, or 100 mol% for reaction carried out at 0 ^oC later on), NEt_3 (0.6 mmol), *p*-anisaldehyde (10 mol%), TESOTf (20 mol%) were then added sequentially, stirred 45 mins at rt to generate the catalyst. Group 14 vinylmetalloid **1** and α-olefin **2** (0.5 and 2.0 mmol, respectively or indicated amount in Table 1) were added to the above mixture together at rt. After stirring for 24 h, the mixture was diluted with 4 mL hexane and was allowed to stir 30 mins in open air. The mixture was then filtered through a short plug of silica gel and rinsed with 75 mL 50% ether/hexane. Solvent was removed, purification via column chromatography afforded product **3**.

Important Notes for the Catalyst Generation and Product Purification:

- Catalytic amount of in situ generated Ni-H complex was presumably obtained by modifying a previously-described procedure[ESI Ref 1]: Oxidative cyclization of *p*-anisaldehyde and 1-octene by $Ni(cod)_2$, IPr, in TESOTf/NEt_3/toluene under rt without $P(OPh)_3$ additive, followed by a *β*-hydride elimination to generate the corresponding $[IPr\text{-}NiH(OTf)]L_n$.

- The reaction is highly oxygen and moisture sensitive, please use pre-dried solvent, reagents and substrates (CaH_2, rt and filter) before use.

- In case of reactions carried out at 0 °C, as stated in the general procedure, required to use extra amount of 1-octene at the beginning. This modification help us to force all the IPr-Ni(0) to the catalyst before cooling. No 1-octene was left before substrate addition after 45 mins by NMR.

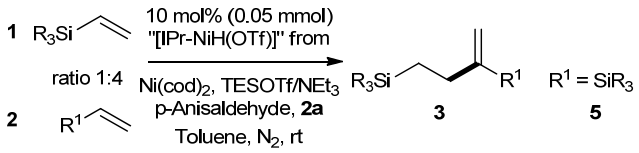
- While products **3** are stable on typical silica gel column chromatography, the vinylsilane products **5** in many cases were found not. The **3**:**5** ratios in Table 1 were therefore determined by crude ^1H NMR (d1 = 10 second) in order to avoid over estimation of the selectivity. The identification and isolation of **5** was done by using a short NEt_3 buffered silica gel column and by comparing with similar literature compounds ^1H NMR Data[ESI Ref 2]: ~ 1.5 inch long, packed with 0.25% NEt_3/Hex before loading, elute out in less than 3 mins. Please also note that the use of florisil or neutral/basic alumina as stationary phase did not provide improvement or positive results in our hand.

Estimation of the Amount of Minor Products in Table 1 *H.A.* by GC Analysis

To demonstrate the amount of minor products present in the *H.A.* reaction in Table 1, we have also tried to analyze the results by GCMS, but not many attempts were successful.

We found that the GC analysis data quality was subjected significantly to the spectrometer separation efficiency and the stability of both desired and minor products at a higher analyzing temperature, especially in case of **5** which will decompose gradually upon isolation at rt. Therefore, in this regards, we chose NMR and isolation as the method for yield determination. Some examples with marginal GC separation were shown below for comparison only.

The yields of the desired products determined here were found only similar to that obtained Table 1. The discrepancies observed between those analytical techniques can be the results of practical experimental errors, in both imperfect peaks separation of crude mixture in GC and NMR or by isolation.



				By GC Analysis		By NMR & Isolation (From Table 1)	
Entry[a]	**1**, R_3 =	**2**, R^1 =	**3**	% Yield	**3:5**	% Yield	**3:5**
1	Et_3	*n*-Hexyl	**3c**	91[b]		93[b]	
2	$(i\text{-PrO})_3$		**3f**	83	85:15	85	85:15
3	$Ph_2(EtO)$		**3k**	46	76:24	56	87:13
4	Me_2Ph	CH_2Ph	**3o**	94		95	
5		*p*-CH_2(veratrole)	**3q**	90		95	
6	Me_3	CH_2OCH_2Ph	**3u**	71		75	
7	$Ph_2(EtO)$		**3w**	94[b]	87:13	95[b]	85:15

[a] Reaction condition as in Table 1. Yields are based on **1**. [b] 40 hrs.

GC analysis conditions:

GC-MS: HP G1530A GC / 5973N MS
Carrier gas: He
Column: HP-5ms 30m x 0.25mm x 0.25µm, + 5m guard column.
Method HLS3: Initial 50°C for 3 mins; increase 40°C/min to 160°C; increase 10°C/min to 200°C; increase 40°C/min to 300°C and hold for 10 mins;
Method HLS6: Initial 50°C for 3 mins; increase 40°C/min to 160°C; increase 10°C/min to 185°C; increase 80°C/min to 300°C and hold for 10 mins.
Flow rate = 1.0 mL/min
Standard: Hexamethylbenzene

We would like to thank also the CUHK Environmental Science Department for providing the GCMS instrument and help associated.

3c

Yield (**3c**) = peak (5) = 91%
With other isomers, peak (2+3+4+6) = 8%

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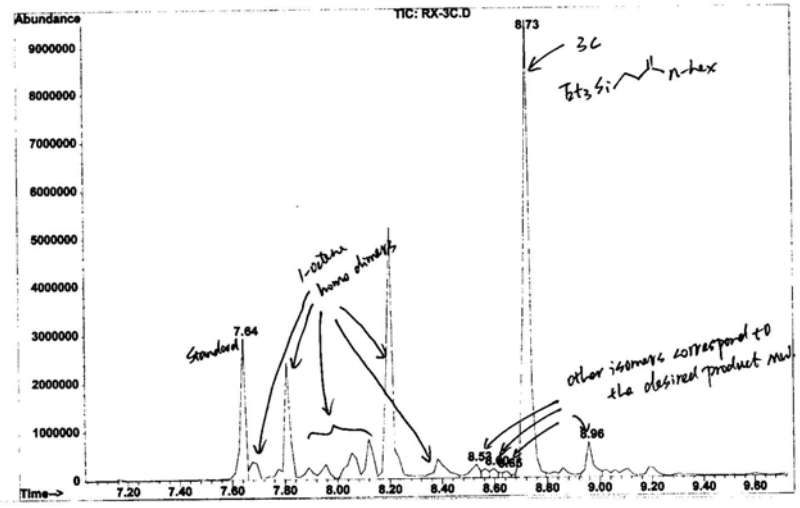

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hls-2-rx-3c-s

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	7.644	rm	0.099	4177561	7.578	7.676
2	8.531	rm	0.082	386571	8.465	8.547
3	8.596	rm	0.033	64601	8.580	8.613
4	8.646	rm	0.033	47945	8.629	8.662
5	8.728	rm	0.115	15770262	8.679	8.794
6	8.958	rm	0.082	956504	8.925	9.007

3f

Yield (**3f**) = peak (5) = 61%
Yield (**5f**) = peak (8) = 11%
With other isomers, peak (3+4+6+7) = 2%
1f remained, peak (1) = 13%

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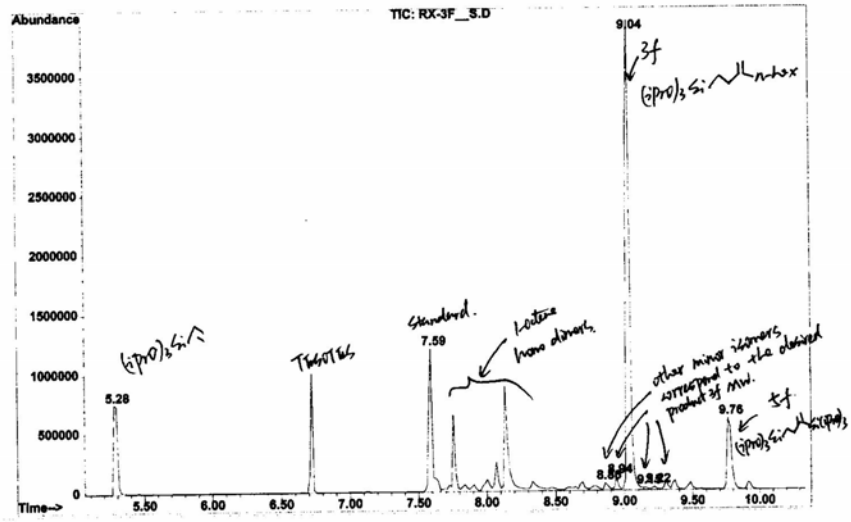

TIC: RX-3F__S.D
hls-2-rx-3f-s

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.277	rm	0.148	1582220	5.261	5.408
2	7.594	rm	0.148	2265212	7.528	7.676
3	8.859	rm	0.082	95934	8.826	8.908
4	8.941	rm	0.066	137518	8.908	8.974
5	9.039	rm	0.164	7673214	8.974	9.138
6	9.154	rm	0.049	4041	9.138	9.187
7	9.220	rm	0.066	38276	9.187	9.253
8	9.762	rm	0.181	1383380	9.713	9.894

3k

Yield (**3k**) = peak (6) =28%
Yield (**5k**) = peak (8) = 9%
With other isomers, peak (3+4+5+7) = 5%
1k remained, peak (2) = 49%

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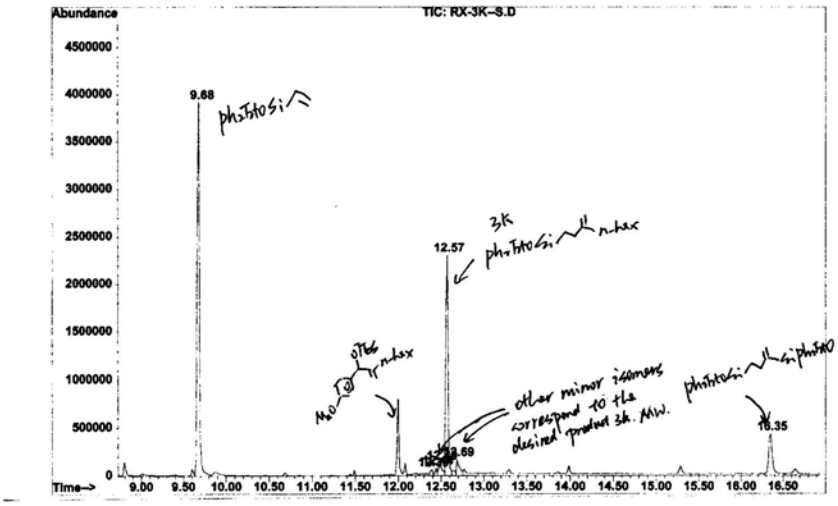

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hls-2-rx-3k-s

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	7.694	rm	0.016	3730688	7.678	7.694
2	9.682	rm	0.197	7754530	9.633	9.830
3	12.393	rm	0.049	135779	12.360	12.409
4	12.442	rm	0.049	137831	12.409	12.459
5	12.492	rm	0.082	380960	12.459	12.541
6	12.574	rm	0.082	4365366	12.541	12.623
7	12.689	rm	0.082	453761	12.672	12.755
8	16.353	rm	0.246	1526581	16.271	16.517

3o

Yield (**3o**) = peak (4) = 94%
With other isomers, peak (2+3+5+6) = 3%

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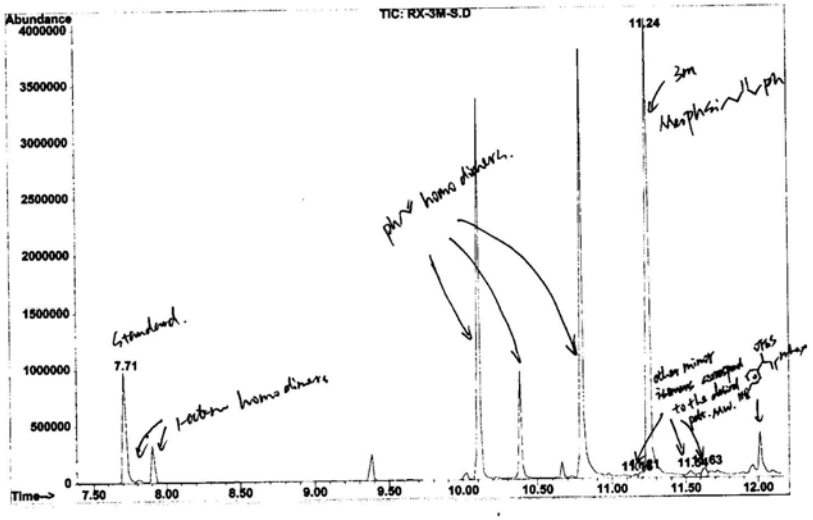

TIC: RX-3M-S.D
hls-2-rx-3m-s

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	7.707	rm	0.131	1663194	7.658	7.790
2	11.158	rm	0.049	17802	11.125	11.174
3	11.207	rm	0.033	54342	11.174	11.207
4	11.240	rm	0.279	6552102	11.207	11.486
5	11.536	rm	0.066	82533	11.486	11.552
6	11.634	rm	0.049	105126	11.601	11.651

3q

Yield (**3q**) = peak (2) = 90%
With other isomers, peak (3+4) = 4%

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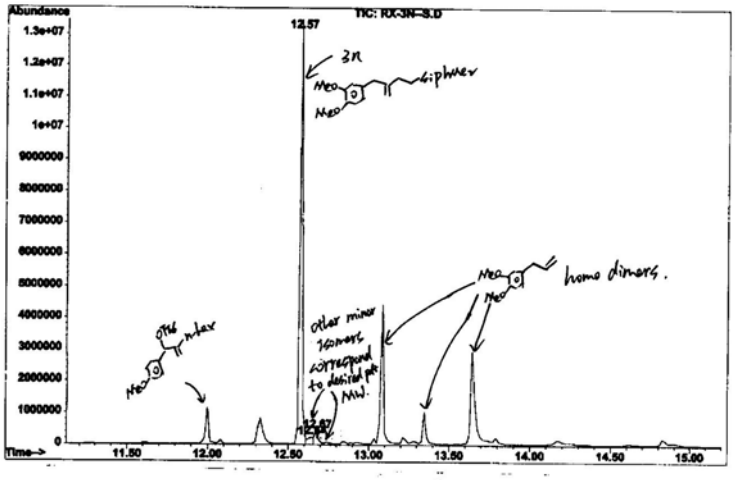

TIC: RX-3N--S.D
hls-2-rx-3n-s

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	7.694	rm	0.049	4037762	7.662	7.711
2	12.574	rm	0.066	15095459	12.541	12.607
3	12.640	rm	0.049	272524	12.607	12.656
4	12.673	rm	0.066	444990	12.656	12.722

3u

Yield (**3u**) = peak (2) = 71%
With other isomers, peak (3+4) = 3%

```
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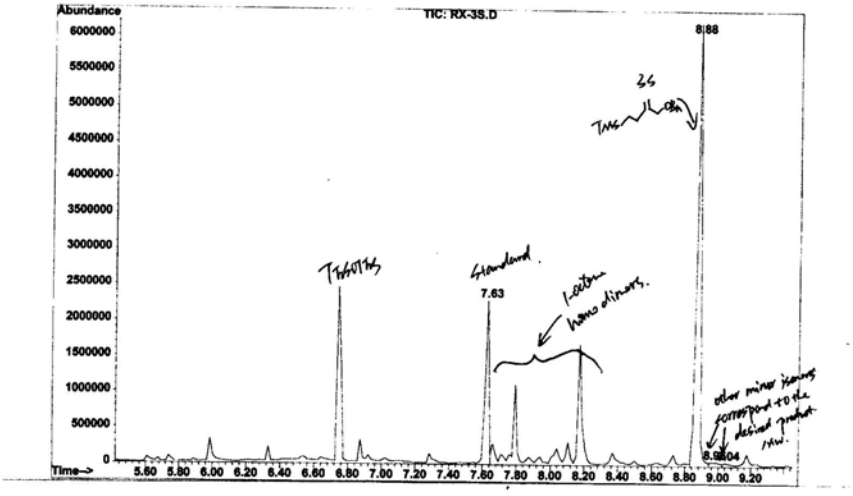

TIC: RX-3S.D
hls-2-rx-3s-s

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	7.629	rm	0.082	3506294	7.563	7.645
2	8.877	rm	0.115	10315928	8.828	8.943
3	8.960	rm	0.082	251093	8.943	9.025
4	9.042	rm	0.082	177356	9.025	9.107

3w

```
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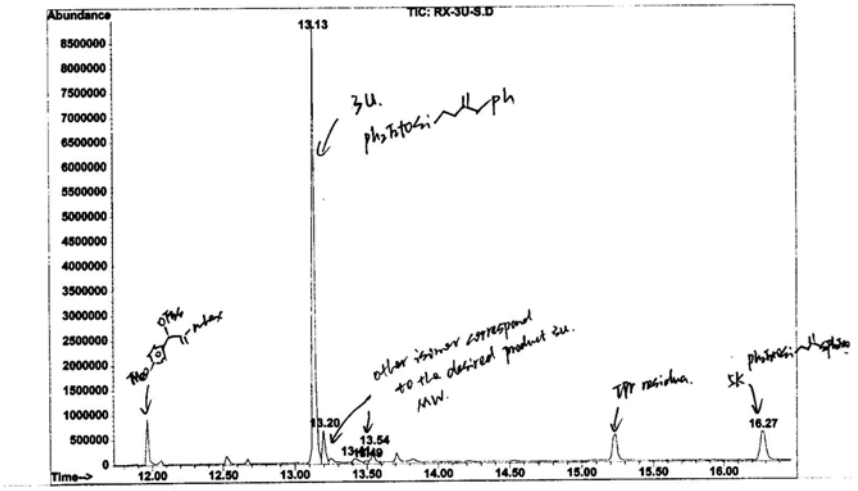


TIC: RX-3U-S.D
hls-2-rx-3u-s

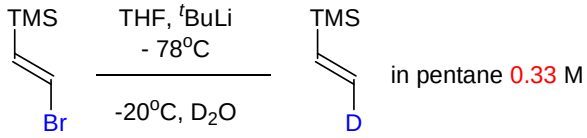
Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	7.645	rm	0.181	3670363	7.563	7.744
2	13.133	rm	0.099	11186246	13.084	13.182
3	13.199	rm	0.049	724319	13.182	13.232
4	13.412	rm	0.082	152412	13.396	13.478
5	13.494	rm	0.033	37291	13.478	13.511
6	13.544	rm	0.082	328521	13.511	13.593
7	16.271	rm	0.181	1927121	16.205	16.386

Yield (**3w**) = peak (2) = 72%
Yield (**5**) = peak (8) = 11%
With other isomers, peak (2+3+4+6) = 6%

The Labeling Experiment Procedure and the Estimation of the Extent of *β*-Silyl Elimination in the Absence of α-Olefin

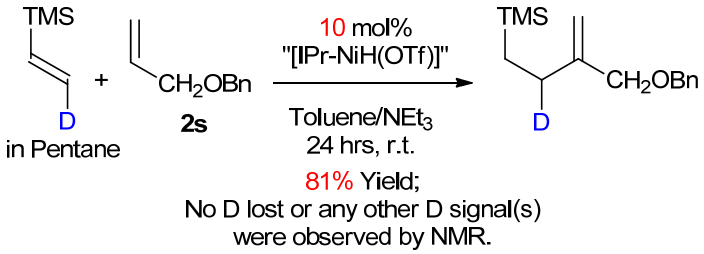
A/ Labeling Experiment

The TMS-(2-D-ethenyl) was prepared according to a literature procedure: [ESI ref 3]



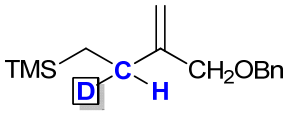
Its cross-H.A. with **2s** was carried out according to the general procedure, except the TMS-(2-D-ethenyl) prepared above was added as a stock solution in pentane (at 0.33 M), only 2 equivalent of α-olefin **2s** was added and using 10 mol% of catalyst.

The yield of the desired *h-t* product is comparable with the case that using non-labeled vinylTMS run in parallel. The result was further analyzed by ^{2}H NMR and GC as shown on following pages in this section.



**Despite the material imbalance can be a result of the vinylsilane high volatility, it is important to note we cannot completely exclude the possibility that it can be a result of incomplete β-Si elimination suppression or subsequent side reactions in minority which we did not observed.

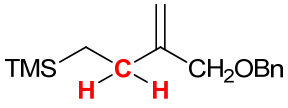
Compound Characterization data:



^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.34 (m, 4H), 7.31-7.27 (m, 1H), 5.02 (s, 1H), 4.97 (s, 1H), 4.50 (s, 2H), 3.99 (s, 2H), **2.08-2.04 (m, 1H)**, 0.66-0.64 (m, 2H), 0.01 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.9, 138.7, 128.5, 127.9, 127.7, 110.6, 73.1, 72.0, **27.1 (t, *J* = 20 Hz)**, 14.5, -1.6.

HRMS–EI (m/z): $[M+H]^+$ calcd for **D**$C_{15}H_{24}OSi$, 250.1737; found, 250.1738.



3u

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.33 (m, 4H), 7.33-7.27 (m, 1H), 5.02 (s, 1H), 4.97 (s, 1H), 4.50 (s, 2H), 3.99 (s, 2H), **2.10-2.05 (m, 2H)**, 0.68-0.64 (m, 2H), 0.01 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.9, 138.6, 128.5, 127.9, 127.7, 110.6, 73.1, 72.0, **27.5**, 14.5, -1.6.

HRMS–EI (m/z): $[M+H]^+$ calcd for $C_{15}H_{25}OSi$, 249.1675; found, 249.1664.

GC Analysis and the NMR of the Labelling Experiments

<u>GC Analysis</u>
for comparison

Yield (Deuterio **3u**) =
peak (2) = 78%
(vs 81% NMR yield)

With other isomers,
peak (3+4) = 4%

Not separated completely.
As additional information only

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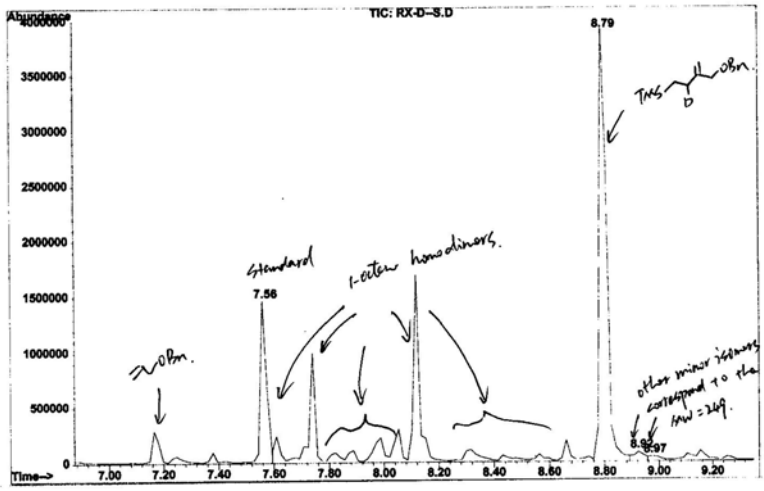

TIC: RX-D--S.D
hls-2-rx-labelling-s

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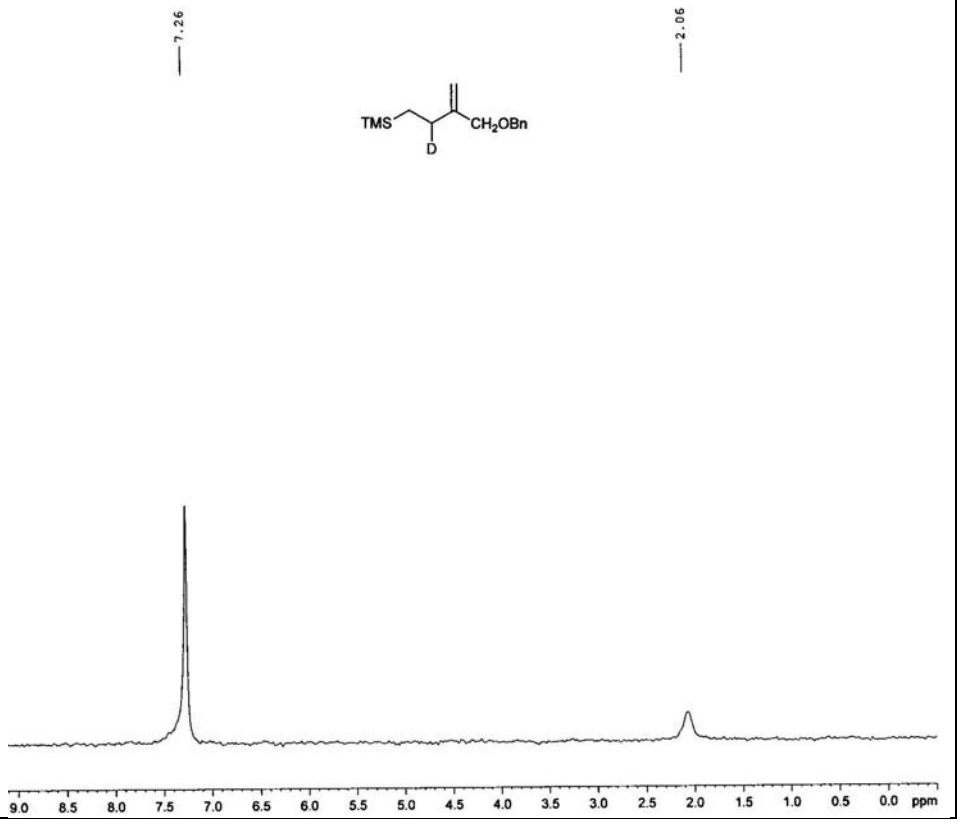
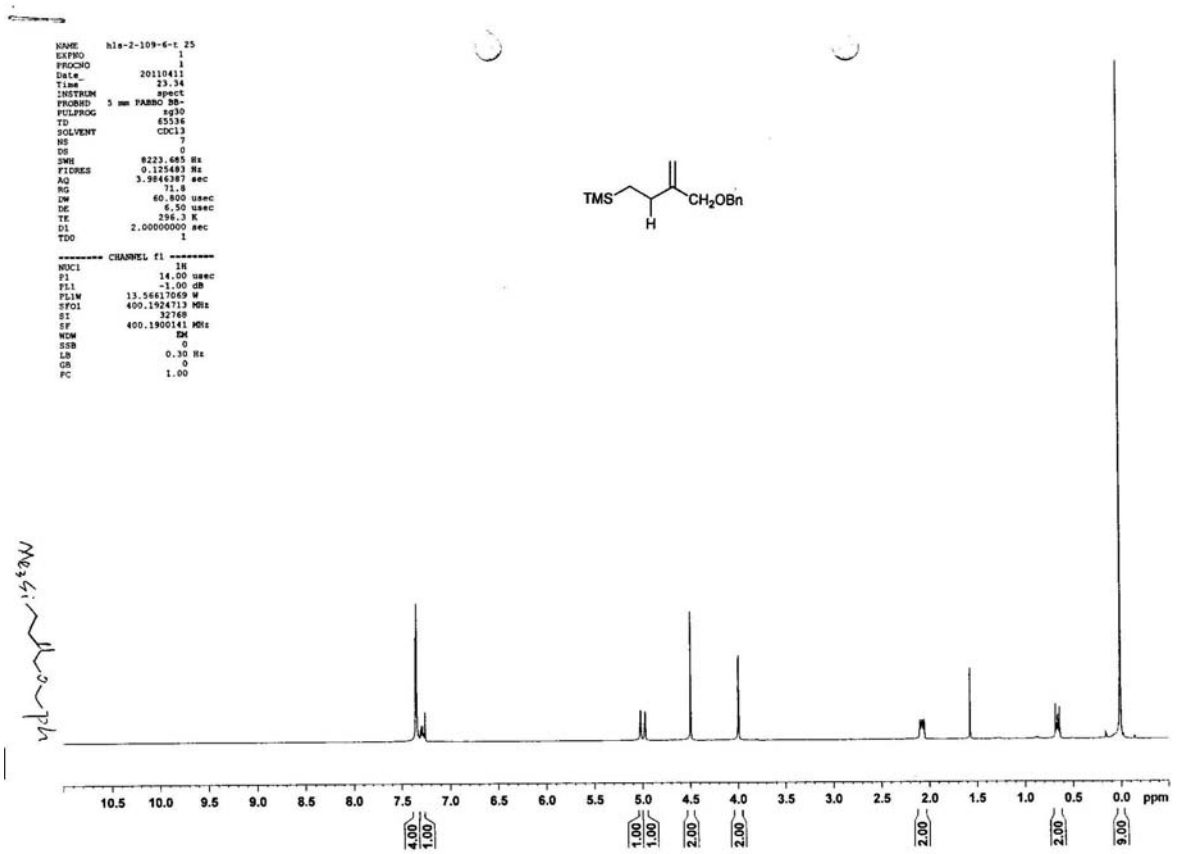
2	8.793	rm	0.131	7432820	8.760	8.891
3	8.924	rm	0.066	218937	8.891	8.957
4	8.973	rm	0.066	115573	8.957	9.023

<u>^{2}H NMR</u>



^{1}H NMR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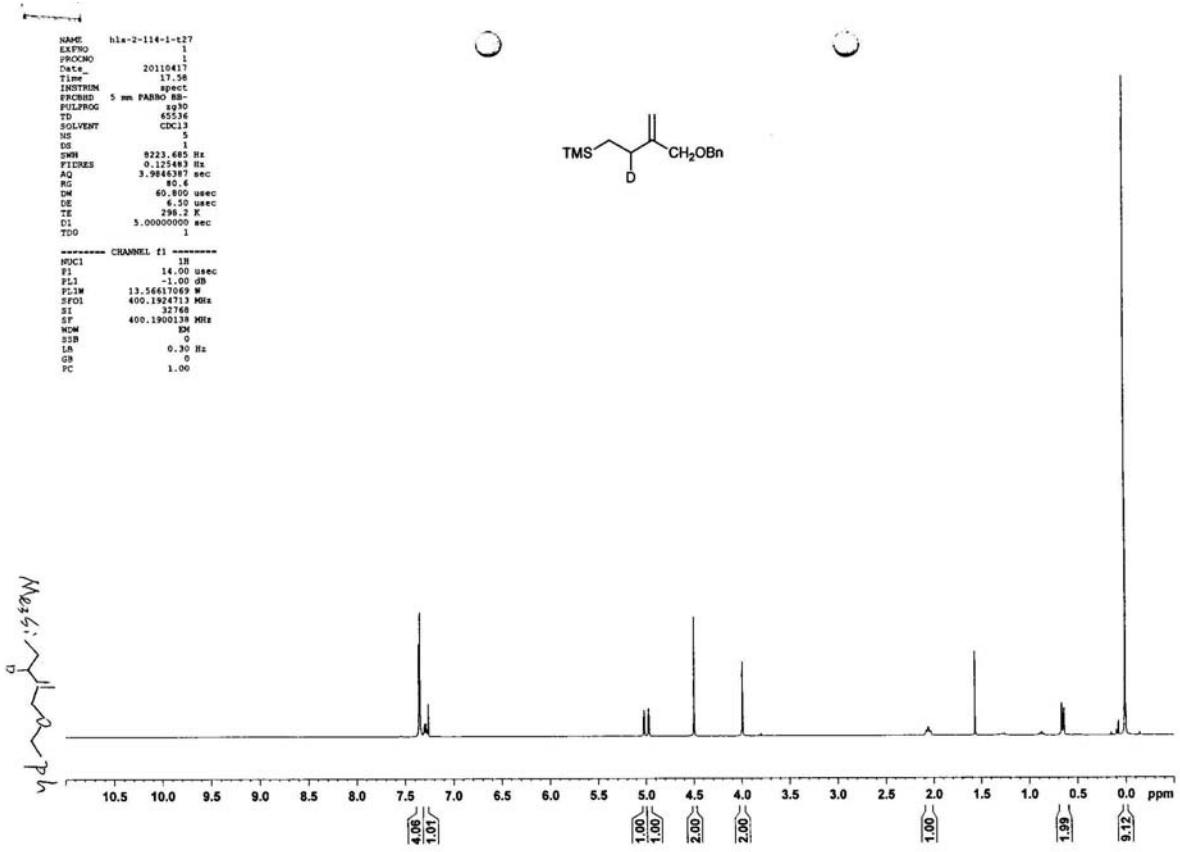
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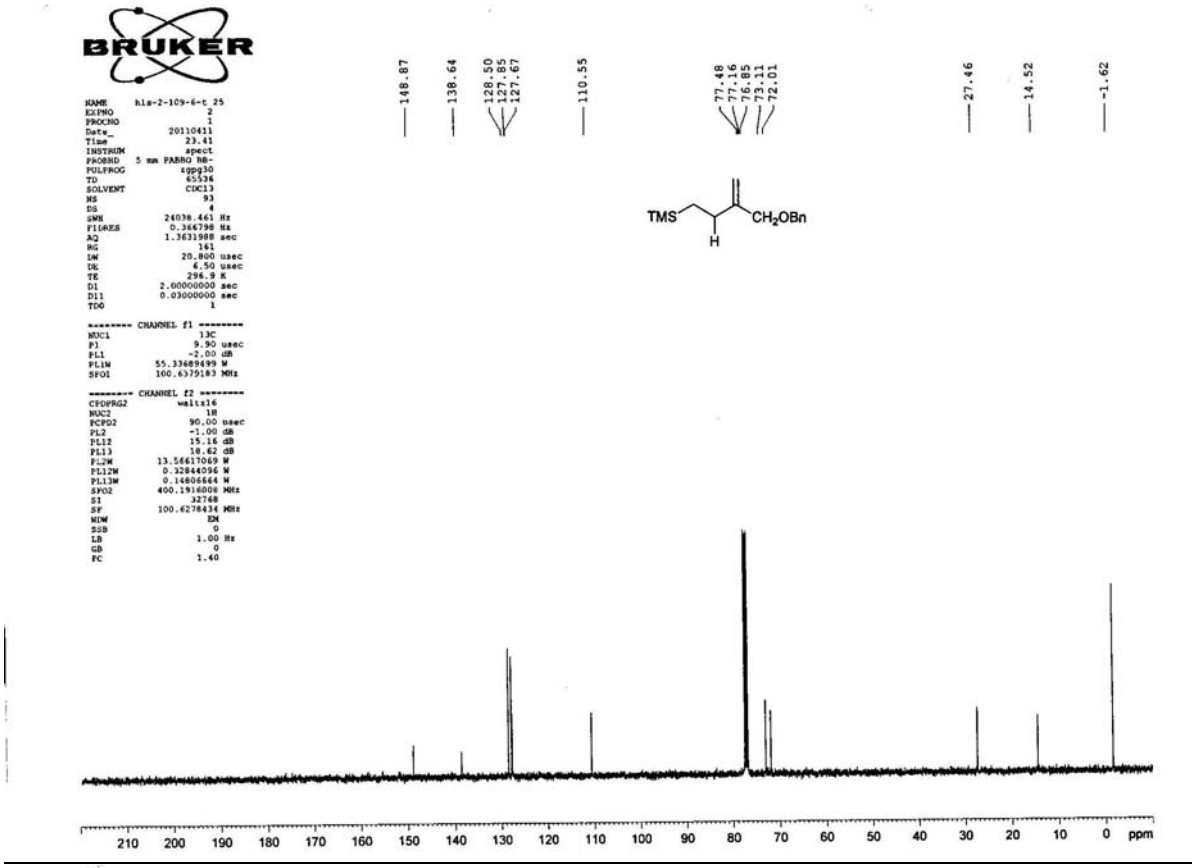
^{13}C NMR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128.50
127.85
127.67
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77.16
76.85
73.11
72.01
27.46
14.52
-1.62
TMS
CH2OBn
H
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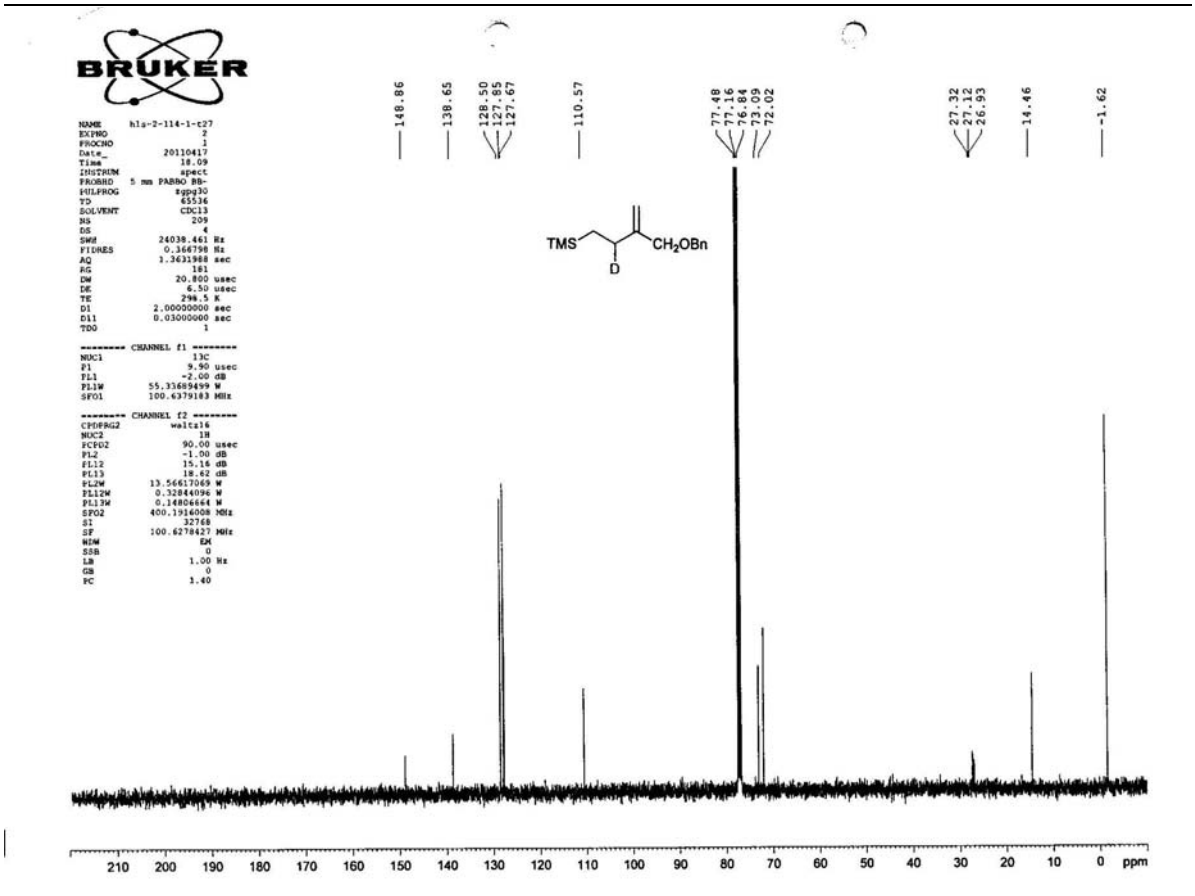
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27.12
26.93
14.46
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TMS
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D
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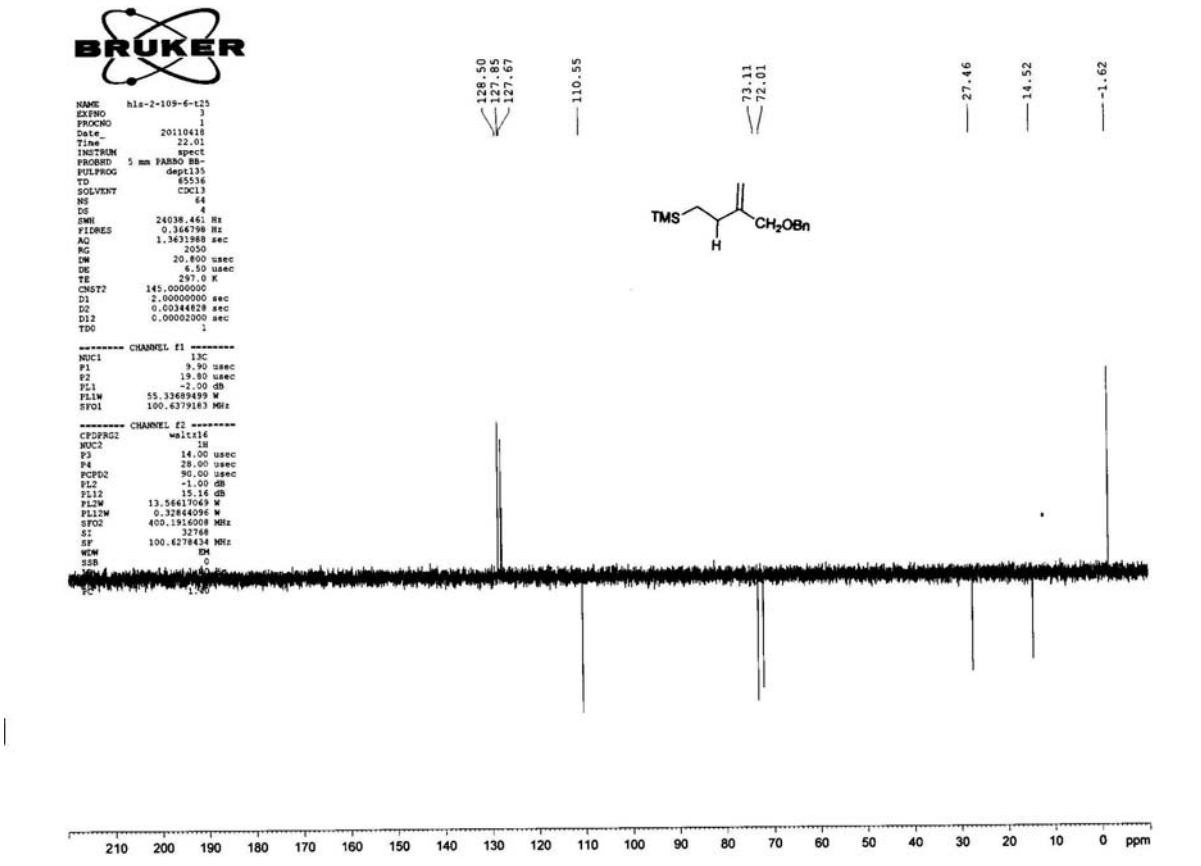
DEPT 135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DE 6.50 usec
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CNST2 145.0000000
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D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
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P2 19.80 usec
PL1 -2.00 dB
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CHANNEL f2
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PL12W 0.32864096 W
SFO2 400.1916008 MHz
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WDW EM
SSB 0
128.50
127.85
127.67
110.55
73.11
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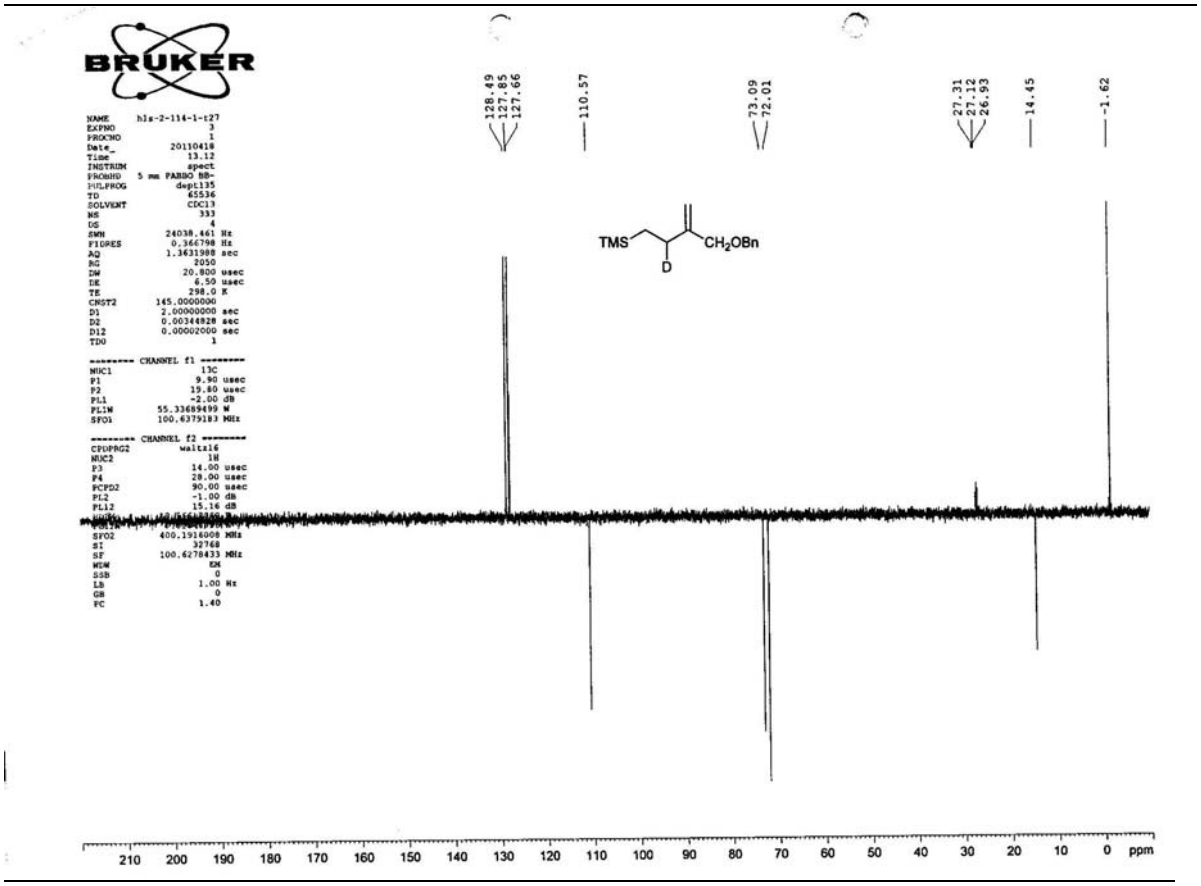
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TE 298.0 K
CNST2 145.0000000
D1 2.00000000 sec
D2 0.00344828 sec
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TD0 1
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P2 19.80 usec
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PL1W 55.33689499 W
SFO1 100.6379183 MHz
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NUC2 1H
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P4 28.00 usec
PCPD2 90.00 usec
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PL12 15.16 dB
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SSB 0
LB 1.00 Hz
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PC 1.40
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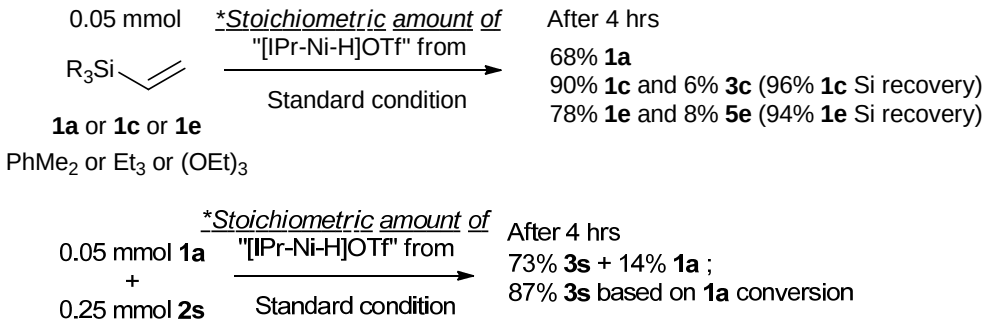
110.57
73.09
72.01
27.31
27.12
26.93
14.45
-1.62
TMS
CH2OBn
D
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

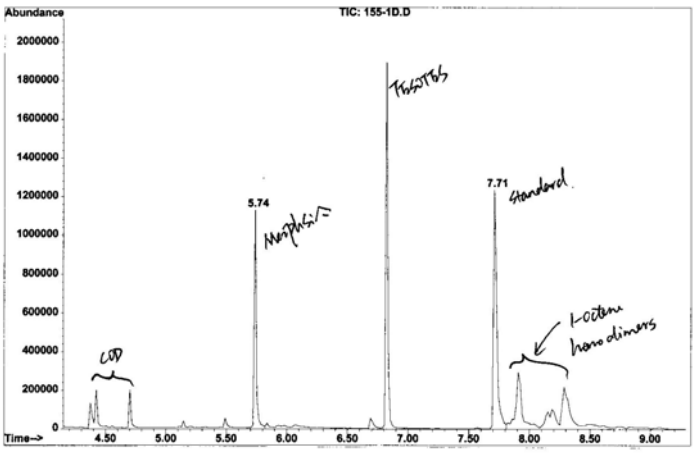
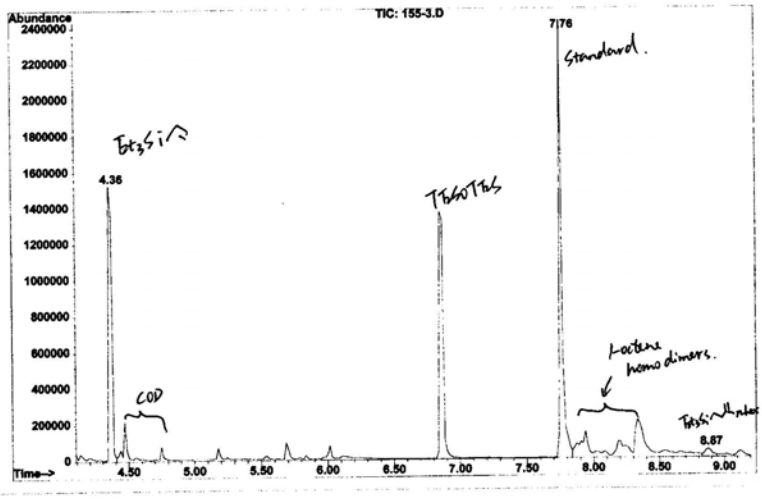
B/ Estimation of the Extent of *β*-Silyl Elimination in the Absence of α-Olefin

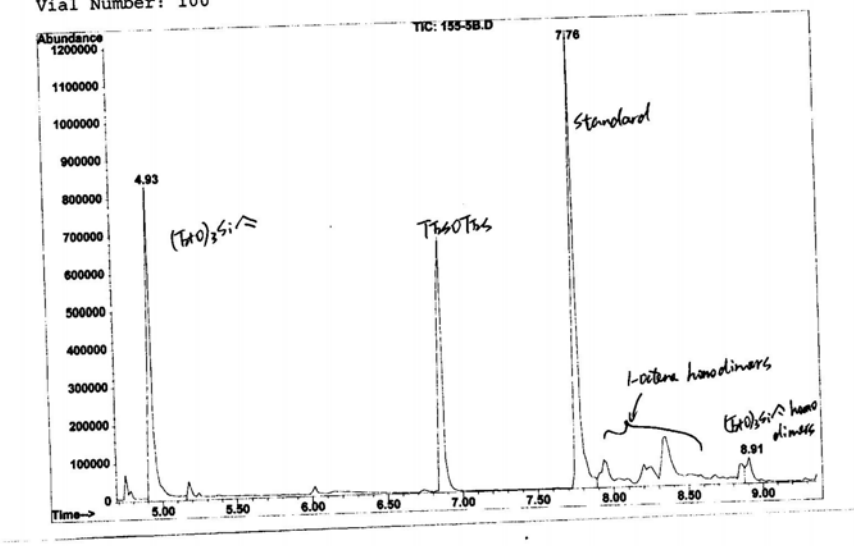
Analyzing the vinylsilane Si material balance after running stoichiometric reactions in the absence of **2** should provide a relevant estimation of the extent of [IPr-Ni(σ-SiR_3)(OTf)] that could be formed via the possible *β*-silyl elimination from the hydrometallated vinylsilane (**1**: "[IPrNiH(OTf)]" = 1:1). Sterically fair vinylsilanes with different electronic properties and with practicable boiling point, **1a**, **1c** and **1e** [vinylSi(Me_2Ph)/$(Et)_3$/$(OEt)_3$], were therefore selected as representative examples for the above study, and monitored by GCMS. We found that, within 4 h reaction time, most of the vinylsilanes remained as starting materials except some **3** and **5** was observed. This suggested that the extent of *β*-silyl elimination is rather limited even in a condition *free* of intermolecular cross-*H.A.* competition and the efficiency/amount of stoichiometric vinylsilane conversion to [IPr-Ni(σ-SiR_3)(OTf)] is again relatively low, which are consistent with the labelling experiment.



In addition, a parallel run with the α-olefin **2s** (which was employed in the labelling study) added to the above reaction with **1a** can provide 87% **3s** based on conversion within the same period of time (by NMR**). Thus, on the basis of the results mentioned above and the maximum extent of *β*-silyl eliminated to Ni that can be done in the period, we surmised that the most plausible pathway to yield **3** (and **5**) selectively from **1** and **2** should be the catalytic cycle depicted in main text Scheme 1, having a [IPr-NiH(OTf)] catalyst. However, the reason for a higher lost in **1a** in the above stoichiometric run than **1c** and **1e** remains unclear. One of the possible explanations is that aryl substituted vinylsilane **1a** is more susceptible for acid catalyzed *β*-effect accelerated decomposition in the absence of α-olefin for cross-H.A.. Alternative explanation is that this medium sized silyl group ($PhMe_2Si$) undergo *β*-silyl elimination relatively more efficient than larger **1c** ($SiEt_3$) and smaller **1e** [$Si(OEt)_3$].[ESI ref 4]

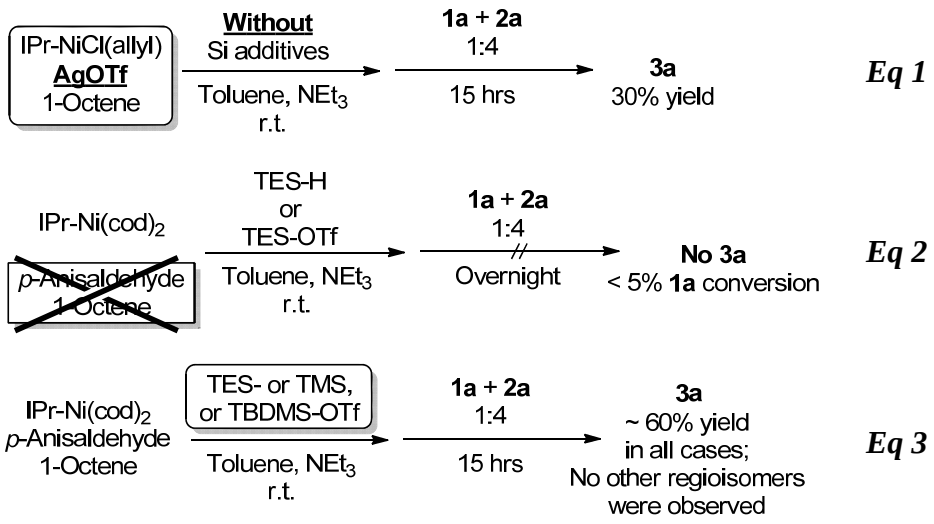
**(N.B. We have also tried to analyze this cross-H.A. by GCMS but unsuccessful)

GC spectrum from reaction of Eq 1, **1a** $VinylSiPhMe_2$ **1a** remained, peak (1) = 68%	File : D:\DATA\HLS\155-1D.D Operator : Acquired : 16 Jul 11 2:19 pm using AcqMethod HLS3 Instrument : GC/MS Ins Sample Name: hls-2-155-1d Misc Info : Vial Number: 100  TIC: 155-1D.D hls-2-155-1d Peak# Ret Time Type Width Area Start Time End Time 1 5.738 rm 0.164 1394021 5.656 5.820 2 7.709 rm 0.131 2190542 7.677 7.808
GC spectrum from reaction of Eq 1, **1c** $VinylSiEt_3$ **1c** remained, peak (1) = 90% Yield (**3c**) = peak (3) = 6% (96% **1c** Si recovery)	File : D:\data\hls\155-3.D Operator : Acquired : 15 Jul 11 10:18 pm using AcqMethod HLS3 Instrument : GC/MS Ins Sample Name: hls-2-155-3 Misc Info : Vial Number: 100  TIC: 155-3.D hls-2-155-3 Peak# Ret Time Type Width Area Start Time End Time 1 4.357 rm 0.082 2924762 4.324 4.406 2 7.758 rm 0.115 3476370 7.725 7.840 3 8.875 rm 0.115 189611 8.826 8.941

GC spectrum from reaction of Eq 1, **1e** $VinylSi(OEt)_3$ **1e** remained, peak (1) = 78% Yield (**5e**) = peak (3) = 8% (94% **1e** Si recovery)	File : D:\DATA\HLS\155-5B.D Operator : Acquired : 15 Jul 11 9:57 pm using AcqMethod HLS6 Instrument : GC/MS Ins Sample Name: hls-2-155-5b Misc Info : Vial Number: 100  TIC: 155-5B.D hls-2-155-5b Peak# Ret Time Type Width Area Start Time End Time 1 4.932 rm 0.263 1609447 4.899 5.162 2 7.758 rm 0.164 2225703 7.725 7.889 3 8.908 rm 0.099 177946 8.875 8.974

Studies on Silyl Additive Effects and Procedure for Silyl Additive Free Cross-H.A.

The following supplementary experiments were performed in hope to gain further insight of the mechanism, and the results were summarized below. The results strongly suggested that the selectivities/products obtained in this work are unlikely a result of the mechanism directed by IPr-NiH(σ-TES) catalyst as mentioned in the main text Scheme 4. [ESI ref 5]



A/ Cross-H.A. by "silyl triflate additive free" condition (Equation 1):

Procedure: In a glove box, analogous to other commonly used NiH catalyst generation methods,[ESI ref 6a] the AgOTf (0.055 mmol) was added to the preformed [IPr-Ni(allyl)Cl] complex[ESI ref 6b] (0.05 mmol) in 2 mL toluene and stirred at r.t. for 1 hr. 1-Octene (0.25 mmol) was added to the mixture outside the box and stirred under N_2 for additional 30 mins. NEt_3, **1a** and **2a** (1:4) were then added finally. After a further 15 hrs, the reaction was quenched as usual.

For a better reproducibility in this additional experiment, Tf_2O (0.075 mmol) can be added right after the substrates addition to remove the moisture in the system. Filtering off the Ag salt with celite after 1 hr stirring or lengthen the anion exchange time in this case did not make further improvement in our hands.

B/ Additional experiments by using TES-H/OTf with IPr-Ni(0) (Equation 2)

Procedure: Similar to the H.A. general procedure, except no aldehyde was added.

In spite of the catalytic alkyne hydrosilylation by NHC-Ni(0) with hydrosilane is a well-precedented procedure for unsaturated organosilane preparation,[ESI ref 7] we found that the treatment of TESH with IPr-Ni(0) did not result any **3a** at a physical condition comparable with our general procedure and it showed no alkene (de)hydrosilylation activity as well. It should be important to note that the ligand choice (P vs NHC) also has a significant impact on alkyne hydrosilylation mechanism.

In case of using NHC-Ni(0) catalysts, alkyne hydrometallation was found not being the first step account for the production of hydrosilylation products.[ESI ref 7a] We also found that *no NHC-Ni(0) catalyzed alkene (de)hydrosilylation* was reported in the literature. One of the possible explanations is the use of NHC may exert significant impacts on both (σ-SiR_3)Ni-H bonds & alkene coordination efficiency.

In addition to the above, it should be also interesting to note that an experiment mimic an unintended TESOTf addition to IPr-Ni(0) in NEt_3/toluene also resulted < 5% **1a** conversion for 15 hrs at r.t. and no **3a** was observed. This experiment suggested that a catalytic cycle for **3a** production based on that unintended direct addition(s) resulted species "[IPr-Ni(TES)(OTf)L_n]" may not be operative as well.

C/ Effect of the size of silyl triflate additive (Equation 3):

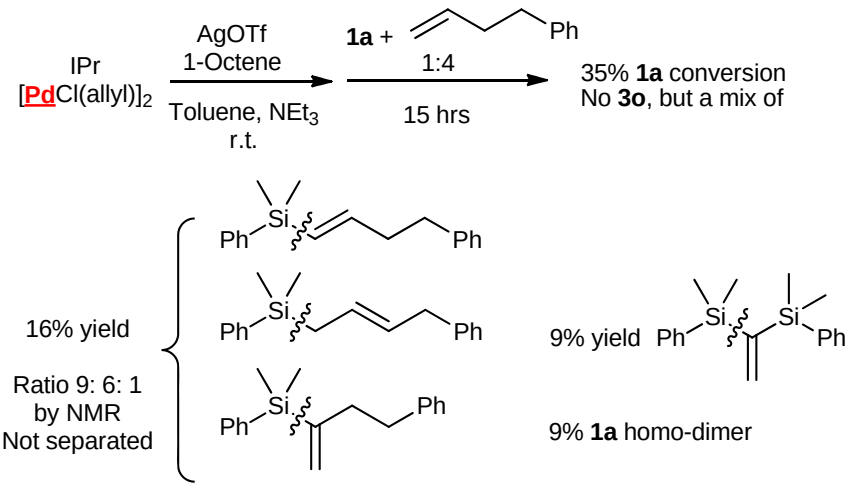
Procedure: Similar to the H.A. general procedure, except using TMS/TBDMS-OTf.

Experimental results obtained by quenching the parallel reactions which employed silyl triflates with different sizes at a shorter reaction time than usual (TES/TMS/TBDMS-OTf; from 24 hrs to 15 hrs) may provide evidence further supporting that the silyl additives plays no crucial role for the reaction (all cases examined are comparable, providing 60% yield of the desired product, Eq 3).

It would be ideal if we can obtain an active isolated complex or crystal structure in the form of [IPrNi$(CH_2)_2SiR_3$(OTf/X)]L_n and carry out a stoichiometric run with α-olefin yielding **3 successfully so as to support the mechanism further, however, the attempts were summarily failed. We surmised that the highly reversible nature of alkene hydrometallation by using NiH catalyst avoided us to do so. Similarly, attempts to trap the hydrometallated vinylsilane in situ with O_2 or MeOH both didn't yield the corresponding products versus the case involving an oxanickellacycle.[ESI ref 8]

Preliminary Results on using [(Allyl)PdCl]$_2$, IPr, AgOTf with **1** and **2**

The following results revealed that the choice of the ligand-metal combination was very critical.



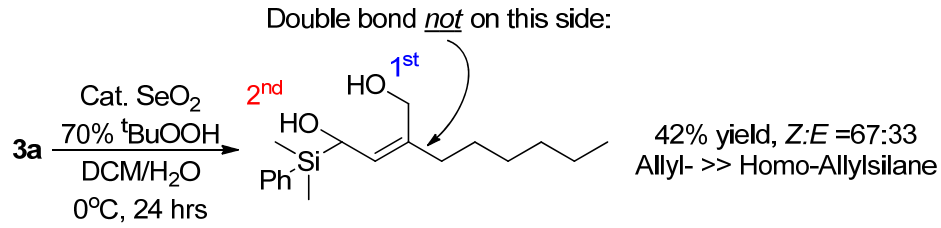
Procedure: Similar to the "silyl additive free cross-H.A.", except allowing the IPr to stir with the commercially available [(Allyl)PdCl]$_2$ for 1 hr before substrate addition according to literature procedure.

The IPr-Pd reaction did not result cross-H.A. as the IPr-Ni did, but contrarily yielded vinylsilane-olefin coupling products. These remarkable changes can be illustrated more clearly by using homoallylbenzene as α-olefin than **2a**. The products obtained and their substitution patterns were confirmed by comparing the spectroscopic data provided in the literature.[ESI ref 9]

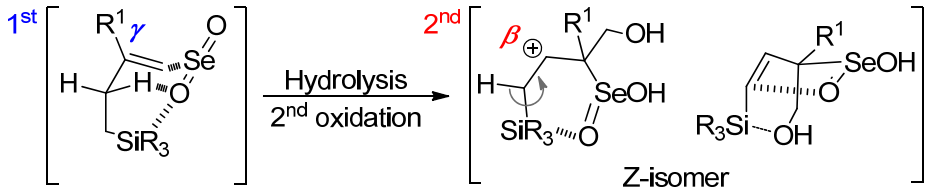
Also, it is worthwhile to mention again that replacing the IPr with smaller ligands of choice, e.g. IMes or PCy_3 for Ni have also resulted adverse effect on the desire reaction and will become quite difficult to control. The yield of **3a** dropped to 6-11%, and with up to 10% **1a** homo-dimers mixture observed within 15 hrs rx time (**1a** conversion ranged from 25-40%).

Novel Si Directed Highly Regioselective Riley Oxidation Example

3a was subjected to typical Riley oxidation,[ESI ref 10] the yield and the stereoselectivity is only moderate here but the high regioselectivity observed is noteworthy.[ESI ref 11]



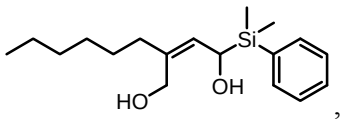
One of the possible rationale for the major product selectivity



Experimental procedure:

A mixture of selenium dioxide (9.0 mg, 0.08 mmol, 0.55 equiv) and 0.2 ml 70% tert-butyl hydroperoxide solution in 2 ml dichloromethane was stirred for 30 min at 0 °C. **3a** (40 mg, 0.146 mmol, 1.0 equiv) was then added to the above mixture. After stirring for 24 hours at 0 °C, the reaction mixture was diluted with 2 ml dichloromethane and dried over $MgSO_4$. Filtered and concentrated, purification via silica gel column chromatography (Ethyl acetate:hexane, 70:30) afforded the product. The Z:E selectivity was determined by NOESY.

Characterization data:



, a mixture of Z/E products, *Z:E* = 67:33, Z/E ratio was determined by NOESY.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.53 (m, 2H), 7.37-7.35 (m, 3H), 5.57-5.51 (m, 1H), 5.25-5.22 (m, 0.67H), 4.99-4.96 (m, 0.33H), 4.06 (d, 0.67H, *J* = 13.7 Hz), 4.05 (d, 0.33H, *J* = 13.4 Hz), 3.69 (d, 0.33H, *J* = 13.4 Hz), 3.48 (d, 0.67H, *J* = 13.7 Hz), 2.05-1.98 (m, 2H), 1.38-1.21 (m, 8H), 0.88 (t, 3H, *J* = 6.7 Hz), 0.40 (s, 1H), 0.38 (s, 4H), 0.35 (s, 1H).

For interesting potential uses of homoallylsilanes other than in the subsequent olefin cross-metathesis, Fleming-Tamao oxidation, cross-coupling and Riley oxidation, *such as* the preparation of cyclopropylmethyl ketones and *β*-Si carbonyls, regiospecific Baeyer-Villiger reaction and cross-coupling, please kindly look up the ESI reference section.[ESI ref 12,13]

For general outcomes and exceptional examples on silylation of alkynes and 2-substituted dienes, please kindly look up the ESI reference section. [ESI ref 16-18]

ESI Reference Section [ESI Ref]:

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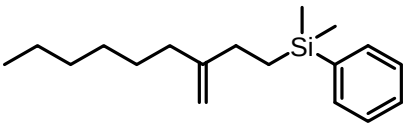
(18) α-Selective vinylsilane synthesis from alkyne: (*a*) B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* 2005, **127**, 17644; (*b*) S. Nakamura, M. Uchiyama, T. Ohwada, *J. Am. Chem. Soc.* 2004, **126**, 11146.

Compound Characterization Data

1/ Products 3a- 3n (Scope of Vinylmetalloids, Table 1, Entries 1-8)):

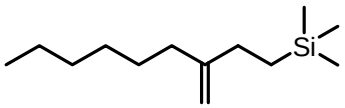


Entry 1, **3a**:

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.50 (m, 2H), 7.35-7.34 (m, 3H), 4.73 (s, 1H), 4.66 (s, 1H), 2.02-1.98 (m, 4H), 1.39-1.26 (m, 8H), 0.91-0.86 (m, 5H), 0.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.7, 139.4, 133.7, 129.0, 127.9, 107.5, 36.0, 31.9, 30.2, 29.3, 27.9, 22.8, 14.3, 13.9, -3.0.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{18}H_{30}Si$, 274.2117; found, 274.2109.

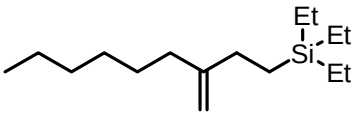


Entry 3, **3b**:

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.73 (s, 1H), 4.66 (s, 1H), 2.02-1.96 (m, 4H), 1.42-1.28 (m, 8H), 0.88 (t, 3H, J = 6.7 Hz), 0.65-0.61 (m, 2H), 0.0 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.0, 107.3, 36.0, 32.0, 30.3, 29.3, 28.0, 22.8, 14.9, 14.3, -1.6.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{13}H_{28}Si$, 212.1960; found, 212.1958.



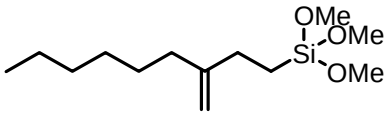
Entry 3, **3c**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.73 (s, 1H), 4.66 (s, 1H), 2.05-1.96 (m, 4H), 1.43-1.28 (m, 8H), 0.96-0.87 (m, 12H), 0.67-0.63 (m, 2H), 0.55-0.50 (q, 6H, J = 7.9 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3, 107.3, 35.9, 32.0, 29.3, 28.0, 22.8, 14.3, 9.8, 7.6, 3.4.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{16}H_{34}Si$, 254.2430; found, 254.2425

.



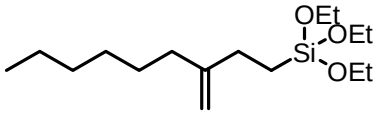
Entry 4, **3d**:

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.74 (s, 1H), 4.70 (s, 1H), 3.58 (s, 9H), 2.12-2.08 (m, 2H), 2.02 (t, 2H, J = 7.6 Hz), 1.60-1.25 (m, 8H), 0.88 (t, 3H, J = 6.7 Hz), 0.80-0.77 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.0, 107.6, 50.7, 36.1, 31.9, 29.3, 28.7, 27.9, 22.8, 14.3, 7.6.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{13}H_{28}O_3Si$, 260.1808; found, 260.1799.

Entry 4, **3e**:

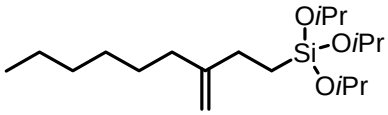


^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.74 (s, 1H), 4.68 (s, 1H), 3.83 (q, 6H, *J* = 7.0 Hz), 2.11-2.08 (m, 2H), 2.02 (t, 2H, *J* = 7.6 Hz), 1.43-1.20 (m, 8H), 1.24 (t, 9H, *J* = 7.0 Hz), 0.88 (t, 3H, *J* = 6.7 Hz), 0.80-0.75 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 107.5, 58.5, 36.1, 31.9, 29.3, 28.9, 27.9, 22.8, 18.4, 14.3, 8.8.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{16}H_{34}O_3Si$, 302.2277; found, 302.2276.

Entry 4, **3f**:

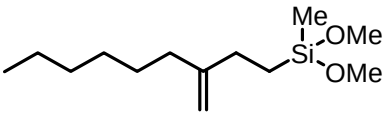


^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.72 (s, 1H), 4.66 (s, 1H), 4.22 (septet, 3H, *J* = 6.1 Hz), 2.11-2.06 (m, 2H), 2.02 (t, 2H, *J* = 7.6 Hz), 1.42-1.27 (m, 8H), 1.20 (d, 18H, *J* = 6.1 Hz), 0.88 (t, 3H, *J* = 6.7 Hz), 0.74-0.70 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.6, 107.4, 65.0, 36.0, 31.9, 29.3, 28.0, 25.7, 22.8, 14.3, 10.4.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{19}H_{40}O_3Si$, 344.2747; found, 344.2742.

Entry 5, **3g**:

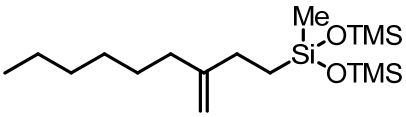


^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.74 (s, 1H), 4.69 (s, 1H), 3.52 (s, 6H), 2.08-2.00 (m, 4H), 1.43-1.28 (m, 8H), 0.88 (t, 3H, *J* = 6.7 Hz), 0.79-0.75 (m, 2H), 0.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.1, 107.7, 50.3, 36.0, 31.9, 29.3, 28.9, 28.0, 22.8, 14.2, 11.4, -5.7.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{13}H_{28}O_2Si$, 244.1859; found, 244.1856.

Entry 5, **3h:**

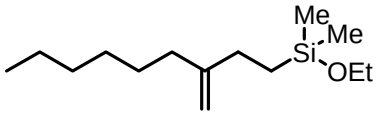


^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.72 (s, 1H), 4.66 (s, 1H), 2.04-1.98 (m, 4H), 1.45-1.28 (m, 8H), 0.89 (t, 3H, *J* = 6.7 Hz), 0.61-0.57 (m, 2H), 0.09 (s, 18H), 0.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.7, 107.4, 36.0, 32.0, 29.4, 29.3, 28.0, 22.8, 16.0, 14.3, 2.0, -0.2.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{17}H_{40}O_2Si_3$ 360.2336; found, 360.2338.

Entry 6, **3i:**

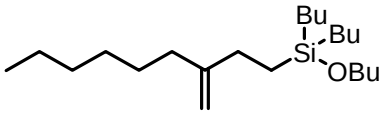


^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.74 (s, 1H), 4.68 (s, 1H), 3.67 (q, 2H, *J* = 7.0 Hz), 2.05-2.01 (m, 4H), 1.43-1.19 (m, 8H), 1.20 (t, 3H, *J* = 7.0 Hz), 0.89 (t, 3H, *J* = 6.7 Hz), 0.76-0.72 (m, 2H), 0.12 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.6, 107.5, 58.4, 36.0, 31.9, 29.5, 29.3, 28.0, 22.8, 18.7, 14.6, 14.2, -2.0.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{14}H_{30}OSi$, 242.2066; found, 242.2067.

Entry 6, **3j:**

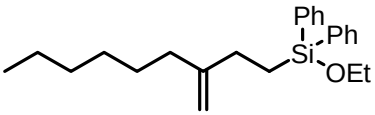


^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.74 (s, 1H), 4.67 (s, 1H), 3.60 (t, 2H, *J* = 6.6 Hz), 2.05-2.00 (m, 4H), 1.54-1.47 (m, 2H), 1.43-1.29 (m, 20H), 0.93-0.87 (m, 12H), 0.75-0.71 (m, 2H), 0.63-0.59 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 107.4, 62.8, 36.0, 35.2, 32.0, 29.5, 29.3, 28.0, 26.8, 25.6, 22.8, 19.2, 14.3, 14.1, 13.9, 13.4, 12.0.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{22}H_{46}OSi$, 354.3318; found, 354.3309.

Entry 6, **3k:**

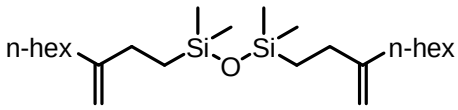


^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60-7.58 (m, 4H), 7.42-7.35 (m, 6H), 4.75 (s, 1H), 4.68 (s, 1H), 3.77 (q, 2H, *J* = 7.0 Hz), 2.12-2.07 (m, 2H), 2.00 (t, 2H, *J* = 7.5 Hz), 1.39-1.19 (m, 13H), 0.87 (t, 3H, *J* = 6.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.5, 135.2, 134.8, 129.9, 128.0, 127.9, 107.6, 59.5, 36.0, 31.9, 29.3, 29.2, 27.9, 22.8, 18.6, 14.2, 12.3.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{24}H_{34}OSi$, 366.2379; found, 366.2376.

Entry 6, **3l:**

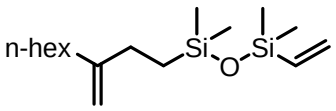


^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.73 (s, 1H), 4.67 (s, 1H), 2.04-1.99 (m, 8H), 1.43-1.29 (m, 16H), 0.89 (t, 6H, *J* = 6.7 Hz), 0.68-0.63 (m, 4H), 0.07 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.8, 107.4, 36.0, 32.0, 29.6, 29.3, 28.0, 22.8, 16.6, 14.3, 0.5.

HRMS–EI (m/z): $[M]^+$ calcd for 410.3400; found 410.3403.

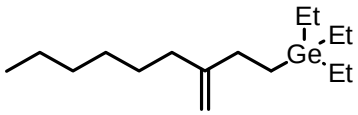
Significant amount of vinylsilane h-t homo-product (**5l**) and other h-t cross-product (**reacted with 1-Octene at one side, 3l′**) in a total of 25% yield on top of **3l** 70% yield.

3l′: 

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.12 (dd, 2H, *J* = 14.8 Hz), 5.92 (dd, 2H, *J* = 14.8, 4.0 Hz), 5.72 (dd, 2H, *J* = 14.8, 4.0 Hz), 4.72 (s, 1H), 4.67 (s, 1H), 2.04-1.99 (m, 4H), 1.43-1.28 (m, 8H), 0.89 (t, 3H, *J* = 6.7 Hz), 0.68-0.63 (m, 2H), 0.14 (s, 6H), 0.07 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.8, 139.8, 131.7, 107.4, 36.0, 32.0, 29.7, 29.6, 29.3, 28.0, 22.8, 16.7, 16.6, 14.3, 0.6, 0.5, 0.4.

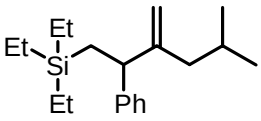
HRMS–EI (m/z): $[M]^+$ calcd for $C_{16}H_{34}OSi_2$, 298.2148; found, 298.2141.

Entry 7, **3m:** 

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.74 (s, 1H), 4.67 (s, 1H), 2.05-1.97 (m, 4H), 1.42-1.28 (m, 8H), 1.01 (t, 9H, *J* = 7.9 Hz), 0.90-0.80 (m, 5H), 0.75-0.69 (m, 6H).

(100 MHz, $CDCl_3$) δ: 153.2, 107.4, 35.9, 32.0, 31.5, 29.3, 28.0, 22.8, 14.3, 9.8, 9.1, 4.0.

HRMS–EI (m/z): $[M\text{-}C_2H_5]^+$ calcd for $C_{14}H_{29}Ge$, 271.1481; found, 271.1474.

Entry 8, **3n:** 

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.08 (s, 1H), 4.80 (s, 1H), 3.30 (t, 1H, *J* = 7.6 Hz), 1.86-1.67 (m, 3H), 1.09 (d, 2H, *J* = 7.6 Hz), 0.89-0.79 (m, 15H), 0.42-0.25 (m, 6H).

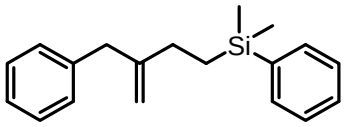
^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.7, 145.9, 128.2, 128.1, 126.2, 109.3, 46.9, 45.0, 26.4, 23.1, 22.3, 17.4, 7.5, 3.7.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{20}H_{34}Si$, 302.2430; found, 302.2413.

The *cis*-TES-styrene **1n** was prepared according to a literature procedure.[ESI ref 14]

Compound Characterization Data

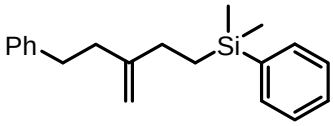
2/ Products 3o- 3x (Scope of α-Olefins, Table 1, Entries 9-18):

Entry 9, **3o:** 

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.45 (m, 2H), 7.34-7.32 (m, 3H), 7.28-7.13 (m, 5H), 4.84 (s, 1H), 4.66 (s, 1H), 3.33 (s, 2H), 2.01-1.96 (m, 2H), 0.93-0.89 (m, 2H), 0.23 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.7, 140.0, 133.7, 129.2, 129.0, 128.4, 127.9, 126.1, 110.1, 42.7, 29.8, 13.9, -3.0.

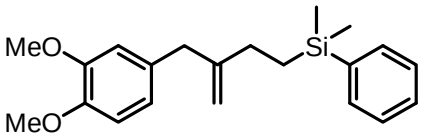
HRMS–EI (m/z): $[M]^+$ calcd for $C_{19}H_{24}Si$, 280.1647; found, 280.1642.

Entry 10, **3p:** 

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.49 (m, 2H), 7.36-7.34 (m, 3H), 7.28-7.15 (m, 5H), 4.79 (s, 1H), 4.73 (s, 1H), 2.71 (t, 2H, *J* = 8.1 Hz), 2.31 (t, 2H, *J* = 8.1 Hz), 2.06-2.02 (m, 2H), 0.92-0.88 (m, 2H), 0.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.8, 142.4, 139.3, 133.7, 129.0, 128.5, 128.4, 127.9, 125.9, 108.1, 37.7, 34.5, 30.5, 13.9, -3.0.

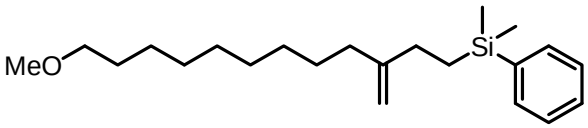
HRMS–EI (m/z): $[M]^+$ calcd for $C_{20}H_{26}Si$, 294.1804; found, 294.1795.

Entry 11, **3q:** 

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.46 (m, 2H), 7.34-7.33 (m, 3H), 6.77 (d, 1H, *J* = 7.9 Hz), 6.67 (d, 1H, *J* = 7.9 Hz), 6.67 (s, 1H), 4.83 (s, 1H), 4.68 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.27 (s, 2H), 2.01-1.96 (m, 2H), 0.93-0.89 (m, 2H), 0.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.9, 148.9, 147.5, 139.3, 133.7, 132.6, 129.0, 127.9, 121.1, 112.4, 111.2, 109.9, 56.1, 55.9, 42.4, 29.7, 14.0, -3.0.

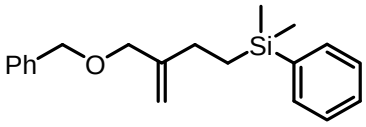
HRMS–EI (m/z): $[M]^+$ calcd for 340.1859; found 340.1852.

Entry 12, **3r:** 

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.51 (m, 2H), 7.36-7.35 (m, 3H), 4.72 (s, 1H), 4.66 (s, 1H), 3.36 (t, 2H, *J* = 6.7 Hz), 3.33 (s, 3H), 2.01-1.97 (m, 4H), 1.37-1.27 (m, 14H), 0.91-0.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.7, 139.4, 133.7, 129.0, 127.9, 107.5, 73.1, 58.7, 35.9, 30.2, 29.8, 29.7, 29.6, 29.6, 27.9, 26.3, 13.9, -3.0.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{22}H_{38}OSi$, 346.2686; found, 346.2676.

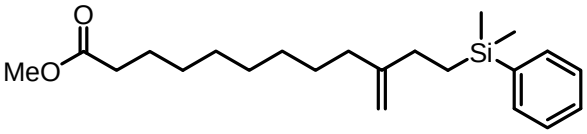


Entry 13, **3s:**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.50 (m, 2H), 7.35-7.27 (m, 8H), 5.01 (s, 1H), 4.96 (s, 1H), 4.46 (s, 2H), 3.96 (s, 2H), 2.11-2.07 (m, 2H), 0.93-0.89 (m, 2H), 0.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.6, 139.2, 138.6, 133.7, 129.0, 128.5, 127.9, 127.9, 127.7, 110.7, 73.1, 72.0, 27.4, 13.6, -3.0.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{20}H_{26}OSiNa$, 333.1651; found 333.1650.

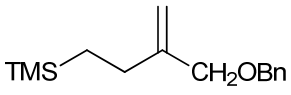


Entry 14, **3t:**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.50 (m, 2H), 7.37-7.34 (m, 3H), 4.72 (s, 1H), 4.66 (s, 1H), 3.67 (s, 3H), 2.30 (t, 2H, *J* = 7.6 Hz), 2.02-1.97 (m, 4H), 1.63-1.59 (m, 2H), 1.38-1.28 (m, 10H), 0.90-0.86 (m, 2H), 0.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 152.6, 139.4, 133.7, 129.0, 127.9, 107.5, 51.6, 35.9, 34.3, 30.2, 29.5, 29.5, 29.4, 29.3, 27.9, 25.1, 13.9, -3.0.

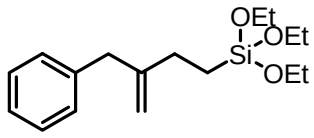
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{22}H_{36}O_2SiNa$, 383.2382; found, 383.2382.

Entry 15, **3u:** 

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.33 (m, 4H), 7.33-7.27 (m, 1H), 5.02 (s, 1H), 4.97 (s, 1H), 4.50 (s, 2H), 3.99 (s, 2H), 2.10-2.05 (m, 2H), 0.68-0.64 (m, 2H), 0.01 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.9, 138.6, 128.5, 127.9, 127.7, 110.6, 73.1, 72.0, 27.5, 14.5, -1.6.

HRMS–EI (m/z): $[M+H]^+$ calcd for $C_{15}H_{25}OSi$, 249.1675; found, 249.1664.

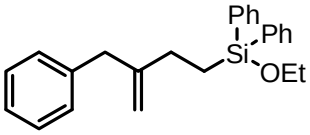


Entry 16, **3v:**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29-7.25 (m, 2H), 7.20-7.17 (m, 3H), 4.86 (s, 1H), 4.71 (s, 1H), 3.77 (q, 6H, *J* = 7.0 Hz), 3.36 (s, 2H), 2.09-2.05 (m, 2H), 1.19 (t, 9H, *J* = 7.0 Hz), 0.81-0.76 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.2, 139.9, 129.2, 128.4, 126.1, 110.1, 58.5, 42.9, 28.5, 18.4, 8.8.

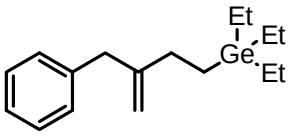
HRMS–EI (m/z): $[M]^+$ calcd for $C_{17}H_{28}O_3Si$, 308.1808; found, 308.1801.

Entry 17, **3w:** 

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, 4H, *J* = 6.5 Hz), 7.40-7.33 (m, 6H), 7.24-7.11 (m, 5H), 4.87 (s, 1H), 4.68 (s, 1H), 3.71 (q, 2H, *J* = 7.0 Hz), 3.34 (s, 2H), 2.11-2.07 (m, 2H), 1.32-1.27 (m, 2H), 1.64 (t, 3H, *J* = 7.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.4, 139.9, 135.1, 134.8, 129.9, 129.2, 128.4, 128.0, 126.1, 110.2, 59.4, 42.7, 28.9, 18.5, 12.3.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{25}H_{28}OSi$, 372.1909; found, 372.1906.

Entry 18, **3x:** 

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 4.86 (s, 1H), 4.68 (s, 1H), 3.36 (s, 2H), 2.03-1.99 (m, 2H), 0.98 (t, 9H, *J* = 7.9 Hz), 0.88-0.83 (m, 2H), 0.68 (q, 6H, *J* = 7.9 Hz).

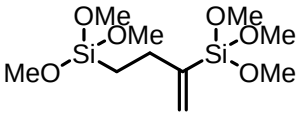
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 140.1, 129.2, 128.4, 126.1, 110.0, 42.7, 31.1, 9.8, 9.1, 4.0.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{17}H_{28}Ge$, 306.1403; found, 306.1387.

Compound Characterization Data

3/ Products 5 (Homo-dimerization of 1, Table 1)

Some of the product **5** was found unstable on typical silica gel column chromatography, please refer to the Important Notes on ESI p3 for purification detail. Oxidized IPr ligand and alkene-aldehyde coupling product was also identified in the mixture in some cases.[ESI Ref 1,15]

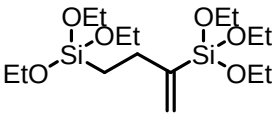


Entry 4, **5d:**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.79-5.78 (m, 1H), 5.61-5.60 (m, 1H), 3.58 (s, 9H), 3.57 (s, 9H), 2.28-2.23 (m, 2H), 0.85-0.80 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2, 128.5, 50.8, 50.7, 28.6, 8.4.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{10}H_{24}O_6Si_2$, 290.1111; found, 296.1112.

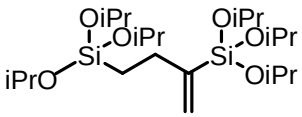


Entry 4, **5e:**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.76-5.75 (m, 1H), 5.62-5.61 (m, 1H), 3.83 (q, 6H, *J* = 7.0 Hz), 3.82 (q, 6H, *J* = 7.0 Hz), 2.28-2.24 (m, 2H), 1.26-1.21 (m, 18H), 0.84-0.80 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7, 127.9, 58.6, 58.5, 28.7, 18.4, 18.4, 9.6.

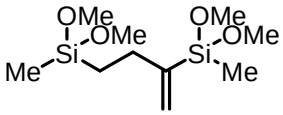
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{16}H_{36}O_6Si_2Na$, 403.1948; found, 403.1943.



Entry 4, **5f:**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.71-5.70 (m, 1H), 5.62-5.61(m, 1H), 4.30-4.15 (m, 6H), 2.28-2.24 (m, 2H), 1.21-1.16 (m, 36H), 0.79-0.74 (m, 2H).

HRMS–EI (m/z): $[M]^+$ calcd for $C_{22}H_{48}O_6Si_2$, 464.2989; found, 464.2987.

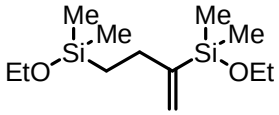


Entry 5, **5g:**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.74-5.73 (m, 1H), 5.53-5.52 (m, 1H), 3.53 (s, 6H), 3.52 (s, 6H), 2.23-2.18 (m, 2H), 0.81-0.77 (m, 2H), 0.20 (s, 3H), 0.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.5, 126.5, 50.5, 50.3, 28.1, 12.0, -5.4, -5.7.

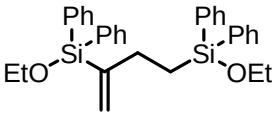
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{10}H_{24}O_4Si_2Na$, 287.1111; found, 287.1107.



Entry 6, **5i:**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.67-5.66 (m, 1H), 5.41-5.40 (m, 1H), 3.70-3.62 (m, 4H), 2.21-2.16 (m, 2H), 1.19-1.17 (m, 6H), 0.76-0.72 (m, 2H), 0.19 (s, 6H), 0.11 (s, 6H).

This compound was found particularly unstable for unknown reason(s), we are not able to get a spectra of **5i** with satisfactory quality even after several attempts. We are able to identify it on the crude ^{1}H NMR, but it decomposed ready on purification.

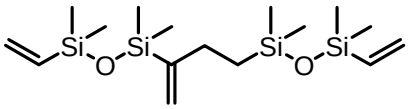


Entry 6, **5k:**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59-7.57 (m, 5H), 7.49-7.47 (m, 5H), 7.40-7.30 (m, 10H), 5.93 (d, 1H, *J* = 1.4 Hz), 5.56 (d, 1H, *J* = 1.4 Hz), 3.76 (q, 2H, *J* = 7.0 Hz), 3.66 (q, 2H, *J* = 7.0 Hz), 2.35-2.31 (m, 2H), 1.28-1.24 (m, 2H), 1.19-1.12 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 135.3, 135.2, 134.9, 134.8, 134.6, 130.0, 129.9, 129.8, 129.6, 128.5, 128.0, 127.9, 127.8, 59.7, 59.3, 29.1, 18.5, 13.4.

HRMS–EI (m/z): $[M]^+$ calcd for $C_{32}H_{36}O_2Si_2$, 508.2254; found, 508.2247.



Entry 6, **5l:**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.12 (dd, 2H, *J* = 14.8 Hz), 5.92 (dd, 2H, *J* = 14.8, 4.0 Hz), 5.72 (dd, 2H, *J* = 14.8, 4.0 Hz), 5.57 (m, 1H), 5.34 (m, 1H), 2.17-2.12 (m, 2H), 0.69-0.64 (m, 2H), 0.15 (s, 6H), 0.14 (s, 6H), 0.13 (s, 6H), 0.07 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.5, 139.8, 139.7, 131.7, 131.7, 122.8, 28.5, 17.3, 0.7, 0.6, 0.5, 0.5.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{16}H_{36}O_2Si_4Na$, 395.1690; found, 395.1682.