## Supporting Information

# Construction of highly sterically hindered geminal disilylated terminal alkenes 

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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 SigmaAldrich ${ }^{\circledR}$ and $\mathrm{J} \& \mathrm{~K}^{\circledR}$ Scientific Ltd., and used as received. $\left[\mathrm{CpRu}(\mathrm{MeCN})_{3}\right] \mathrm{PF}_{6}$ and $\left[\mathrm{Cp} * \mathrm{Ru}(\mathrm{MeCN})_{3}\right] \mathrm{PF}_{6}$ were purchased from Strem ${ }^{\circledR}$ Chemicals, Inc. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were collected on a Bruker AV 400 MHz NMR spectrometer using residue solvent peaks as an internal standard ( ${ }^{1} \mathrm{H}$ NMR: $\mathrm{CDCl}_{3}$ at $7.26 \mathrm{ppm},{ }^{13} \mathrm{C}$ NMR: $\mathrm{CDCl}_{3}$ at 77.0 ppm ). Mass spectra were collected on an Thermo Scientific GC/MS ISQ7000 system, or a Xevo G2 Qtof mass spectrometer.

## II. Ru-Catalyzed Hydrosilylation of 1-Silyl Terminal Alkynes

## General Procedure.

In a glove box, to an oven-dried $5-\mathrm{mL}$ vial was added the alkyne ( 0.40 mmol ), the silane $(0.60 \mathrm{mmol}),\left[\mathrm{CpRu}(\mathrm{MeCN})_{3}\right] \mathrm{PF}_{6}(0.008 \mathrm{mmol})$, and $\mathrm{DCM}(2.0 \mathrm{~mL})$. The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 4 h , and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: $0 \rightarrow 10 \%$ EtOAc in hexanes) to give the desired product.


Triethoxy(1-(trimethylsilyl)vinyl)silane (3a) was prepared as colorless oil from ethynyltrimethylsilane ( $0.40 \mathrm{mmol}, 40.0 \mathrm{mg}$ ) and ( EtO$)_{3} \mathrm{SiH}(0.60 \mathrm{mmol}, 100.6 \mathrm{mg})$, according to the General Procedure in $78 \%$ yield ( $81.9 \mathrm{mg}, 78 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.56(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.41(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.78$ (q, $J=6.8 \mathrm{~Hz}, 6 \mathrm{H}), 1.20(\mathrm{t}, J=6.8 \mathrm{~Hz}, 9 \mathrm{H}), 0.10(\mathrm{~s}, 9 \mathrm{H})$.
${ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 146.4,144.9,58.3,18.1,-1.2$.
MS (ESI) m/z (relative intensity) 247.11(100) [M-15( $\left.\left.\mathrm{CH}_{3}\right)\right]^{+}$.


Triethoxy(1-(triethylsilyl)vinyl)silane (3b) was prepared as colorless oil from triethyl(ethynyl)silane ( $0.40 \mathrm{mmol}, 56.2 \mathrm{mg}$ ) and ( EtO$)_{3} \mathrm{SiH}(0.60 \mathrm{mmol}, 100.6 \mathrm{mg})$, according to the General Procedure in $96 \%$ yield ( $117.0 \mathrm{mg}, 96 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.65(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.41(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.79$ (q, $J=6.8 \mathrm{~Hz}, 6 \mathrm{H}$ ), $1.20(\mathrm{t}, J=6.8 \mathrm{~Hz}, 9 \mathrm{H}), 0.90(\mathrm{t}, J=8.0 \mathrm{~Hz}, 9 \mathrm{H}), 0.63(\mathrm{q}, J=8.0$ $\mathrm{Hz}, 6 \mathrm{H})$.
${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 146.3,143.2,58.3,18.1,7.2,3.1$.
MS (ESI) $m / z$ (relative intensity) 275.21 (100) $\left[\mathrm{M}-29\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)\right]^{+}$.

3c


Triethoxy(1-(triisopropylsilyl)vinyl)silane (3c) was prepared as colorless oil from ethynyltriisopropylsilane ( $0.40 \mathrm{mmol}, 73.0 \mathrm{mg}$ ) and ( EtO$)_{3} \mathrm{SiH}(0.60 \mathrm{mmol}, 100.6 \mathrm{mg})$ according to the General Procedure in $89 \%$ yield ( $123.4 \mathrm{mg}, 89 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.74(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.47(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.80$ (q, $J=6.8 \mathrm{~Hz}, 6 \mathrm{H}$ ), 1.32-1.23 (m, 3 H ), 1.22 (t, $J=6.8 \mathrm{~Hz}, 9 \mathrm{H}), 1.05(\mathrm{~d}, J=7.6 \mathrm{~Hz}$, $18 \mathrm{H})$.
${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 147.7,141.3,58.4,18.7,18.1,11.3$.
MS (ESI) $m / z$ (relative intensity) $303.21(100)\left[\mathrm{M}-43\left(\mathrm{C}_{3} \mathrm{H}_{7}\right)\right]^{+}$.

(1-(Dimethyl(phenyl)silyl)vinyl)triethoxysilane (3d) was prepared as colorless oil from ethynyldimethyl(phenyl)silane ( $0.40 \mathrm{mmol}, 64.1 \mathrm{mg}$ ) and ( EtO$)_{3} \mathrm{SiH}(0.60 \mathrm{mmol}$, 100.6 mg ) according to the General Procedure in $87 \%$ yield ( $112.8 \mathrm{mg}, 87 \%, \alpha / \beta>$ 50:1)
${ }^{\mathbf{1}} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.56-7.53(\mathrm{~m}, 2 \mathrm{H}), 7.35-7.33(\mathrm{~m}, 3 \mathrm{H}), 6.67(\mathrm{~d}, J=5.6$ $\mathrm{Hz}, 1 \mathrm{H}), 6.40(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.73(\mathrm{q}, J=7.2 \mathrm{~Hz}, 6 \mathrm{H}), 1.17(\mathrm{t}, J=7.2 \mathrm{~Hz}, 9 \mathrm{H})$, 0.43 (s, 6 H).
${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 146.9,144.5,138.4,134.2,128.7,127.5,58.3,18.1$, 2.5 .

HRMS $m / z(\mathrm{CI})$ calcd. for $\mathrm{C}_{16} \mathrm{H}_{29} \mathrm{O}_{3} \mathrm{Si}_{2}(\mathrm{M}+\mathrm{H})^{+} 325.1655$, found 325.1641.


Triethyl(1-(trimethylsilyl)vinyl)silane (3e) was prepared as colorless oil from ethynyltrimethylsilane ( $0.40 \mathrm{mmol}, 40.0 \mathrm{mg}$ ) and $\mathrm{Et}_{3} \mathrm{SiH}(0.60 \mathrm{mmol}, 69.8 \mathrm{mg}$ ) according to the General Procedure in $84 \%$ yield ( $72.1 \mathrm{mg}, 84 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.38(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.28(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}), 0.90$ (t, $J=7.6 \mathrm{~Hz}, 9 \mathrm{H}), 0.62(\mathrm{q}, J=7.6 \mathrm{~Hz}, 6 \mathrm{H}), 0.09(\mathrm{~s}, 9 \mathrm{H})$.
${ }^{13} \mathbf{C}$ NMR (100MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 151.0,141.6,7.4,3.6,0.2$.

MS (ESI) $m / z$ (relative intensity) $214.28(0.5), 87.12(100)[\mathrm{M}]^{+}$.

(1-(Dimethyl(phenyl)silyl)vinyl)trimethylsilane (3f) was prepared as colorless oil from ethynyltrimethylsilane ( $0.40 \mathrm{mmol}, 40.0 \mathrm{mg}$ ) and $\mathrm{PhMe}_{2} \mathrm{SiH}(0.60 \mathrm{mmol}, 81.8$ mg ) according to the General Procedure in $84 \%$ yield ( $78.8 \mathrm{mg}, 84 \%, \alpha / \beta>50: 1$ ).
${ }^{\mathbf{1}} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50-7.46(\mathrm{~m}, 2 \mathrm{H}), 7.36-7.33(\mathrm{~m}, 3 \mathrm{H}), 6.41(\mathrm{~d}, J=4.8$ $\mathrm{Hz}, 1 \mathrm{H}), 6.31(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 1 \mathrm{H}), 0.39(\mathrm{~s}, 6 \mathrm{H}), 0.00(\mathrm{~s}, 9 \mathrm{H})$.
${ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 152.9,141.9,139.1,134.1,128.8,127.6,-0.3,-1.8$. MS (ESI) $m / z$ (relative intensity) 234.32(12), 135.14(100) [M] ${ }^{+}$.


Benzyldimethyl(1-(trimethylsilyl)vinyl)silane (3g) was prepared as colorless oil from ethynyltrimethylsilane ( $0.40 \mathrm{mmol}, 40.0 \mathrm{mg}$ ) and $\mathrm{BnMe}_{2} \mathrm{SiH}(0.60 \mathrm{mmol}, 90.2 \mathrm{mg}$ ) according to the General Procedure in $85 \%$ yield ( $84.5 \mathrm{mg}, 85 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.24-7.18(\mathrm{~m}, 2 \mathrm{H}), 7.10-7.15(\mathrm{~m}, 1 \mathrm{H}), 7.01-6.98(\mathrm{~m}, 2$ H), 6.36 (d, $J=5.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 6.29 (d, $J=5.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 2.18 ( $\mathrm{s}, 2 \mathrm{H}$ ), 0.13 ( $\mathrm{s}, 9 \mathrm{H}), 0.07$ ( $\mathrm{s}, 6 \mathrm{H}$ ).
${ }^{13} \mathbf{C}$ NMR (100MHz, $\mathrm{CDCl}_{3}$ ) $\delta 153.0,141.2,140.1,128.3,128.0,123.9,26.4,-0.3,-$ 2.5.

HRMS $m / z(\mathrm{CI})$ calcd. for $\mathrm{C}_{14} \mathrm{H}_{25} \mathrm{Si}_{2}(\mathrm{M}+\mathrm{H})^{+}$249.1496, found 249.1507.

3h


Triethyl(1-(trimethoxysilyl)vinyl)silane (3h) was prepared as colorless oil from triethyl(ethynyl)silane ( $0.40 \mathrm{mmol}, 56.2 \mathrm{mg}$ ) and ( MeO$)_{3} \mathrm{SiH}(0.60 \mathrm{mmol}, 73.3 \mathrm{mg})$ according to the General Procedure in $88 \%$ yield ( $92.4 \mathrm{mg}, 88 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.66(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.46(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.55$ (s, 9 H ), 0.92 (t, $J=8.0 \mathrm{~Hz}, 9 \mathrm{H}$ ), 0.65 (q, $J=8.0 \mathrm{~Hz}, 6 \mathrm{H}$ ).
${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 147.0,141.7,50.5,7.2,3.0$.

HRMS $m / z(\mathrm{CI})$ calcd. for $\mathrm{C}_{11} \mathrm{H}_{27} \mathrm{O}_{3} \mathrm{Si}_{2}(\mathrm{M}+\mathrm{H})^{+}$263.1499, found 263.1469.

(1-(Diethoxy(methyl)silyl)vinyl)triethylsilane (3i) was prepared as colorless oil from triethyl(ethynyl)silane ( $0.40 \mathrm{mmol}, 56.2 \mathrm{mg}$ ) and ( EtO$)_{2} \mathrm{MeSiH}(0.60 \mathrm{mmol}, 80.6 \mathrm{mg})$ according to the General Procedure in $88 \%$ yield ( $96.6 \mathrm{mg}, 88 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.56(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}), \delta 6.38(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H})$, $3.74(\mathrm{q}, J=7.2 \mathrm{~Hz}, 4 \mathrm{H}), 1.21(\mathrm{t}, J=7.2 \mathrm{~Hz}, 6 \mathrm{H}), 0.92(\mathrm{t}, J=7.6 \mathrm{~Hz}, 9 \mathrm{H}), 0.65(\mathrm{t}, J=$ $7.6 \mathrm{~Hz}, 6 \mathrm{H}), 0.17$ (s, 3 H ).
${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 147.3,144.7,58.0,18.3,7.3,3.2,-3.9$.
HRMS $m / z$ (CI) calcd. for $\mathrm{C}_{13} \mathrm{H}_{29} \mathrm{O}_{2} \mathrm{Si}_{2}(\mathrm{M}-\mathrm{H})^{+} 273.1705$, found 273.1700.

(1-(Dimethyl(phenyl)silyl)vinyl)triethylsilane (3j) was prepared as colorless oil from triethyl(ethynyl)silane ( $0.40 \mathrm{mmol}, 56.2 \mathrm{mg}$ ) and $\mathrm{PhMe}_{2} \mathrm{SiH}(0.60 \mathrm{mmol}, 81.8 \mathrm{mg})$ according to the General Procedure in $93 \%$ yield ( $102.9 \mathrm{mg}, 93 \%, \alpha / \beta>50: 1$ ).
${ }^{1}$ H NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.55-7.52 (m, 2 H ), 7.39-7.36 (m, 3 H ), 6.46 (d, $J=$ $5.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.44(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}), 0.88(\mathrm{t}, J=8.0 \mathrm{~Hz}, 9 \mathrm{H}), 0.56(\mathrm{q}, J=8.0 \mathrm{~Hz}, 6$ H), 0.43 ( $\mathrm{s}, 6 \mathrm{H}$ ).
${ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 149.4,143.6,139.1,134.0,128.7,127.6,7.3,3.5,-1.7$. MS (ESI) $m / z$ (relative intensity) 276.52 (0.6), 247.30 (100) [M] ${ }^{+}$.

3k


Benzyldimethyl(1-(triethylsilyl)vinyl)silane (3k) was prepared as colorless oil from triethyl(ethynyl)silane ( $0.40 \mathrm{mmol}, 56.2 \mathrm{mg}$ ) and $\mathrm{BnMe}_{2} \mathrm{SiH}(0.60 \mathrm{mmol}, 90.2 \mathrm{mg})$ according to the General Procedure in $97 \%$ yield ( $112.8 \mathrm{mg}, 97 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.26-7.22(\mathrm{~m}, 2 \mathrm{H}), 7.12-7.02(\mathrm{~m}, 3 \mathrm{H}), 6.43(\mathrm{~d}, J=4.8$ $\mathrm{Hz}, 1 \mathrm{H}), 6.39(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.2(\mathrm{~s}, 2 \mathrm{H}), 0.96(\mathrm{t}, J=7.6 \mathrm{~Hz}, 9 \mathrm{H}), 0.68(\mathrm{q}, J=7.6$ $\mathrm{Hz}, 6 \mathrm{H}), 0.09(\mathrm{~s}, 6 \mathrm{H})$.
${ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 149.3,142.8,140.2,128.4,128.0,123.9,26.3,7.4,3.7$, -2.5.

HRMS $m / z(\mathrm{CI})$ calcd. for $\mathrm{C}_{17} \mathrm{H}_{34} \mathrm{NSi}_{2}\left(\mathrm{M}+\mathrm{NH}_{4}{ }^{+}\right)^{+}$308.2230, found 308.2241.


Ethene-1,1-diylbis(triethylsilane) (31) was prepared as colorless oil from triethyl(ethynyl)silane ( $0.40 \mathrm{mmol}, 56.2 \mathrm{mg}$ ) and $\mathrm{Et}_{3} \mathrm{SiH}(0.60 \mathrm{mmol}, 69.8 \mathrm{mg}$ ) according to the General Procedure in $93 \%$ yield ( $95.5 \mathrm{mg}, 93 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.39(\mathrm{~s}, 2 \mathrm{H}), 0.91(\mathrm{t}, J=7.6 \mathrm{~Hz}, 18 \mathrm{H}), 3.78(\mathrm{q}, J=7.6$ $\mathrm{Hz}, 12 \mathrm{H}$ ).
${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 147.4,143.1,7.3,3.6$.
MS (ESI) $m / z$ (relative intensity) 256.61 (1.0), 115.16 (100) $[\mathrm{M}]^{+}$.


Triisopropyl(1-(trimethoxysilyl)vinyl)silane (3m) was prepared as colorless oil from ethynyltriisopropylsilane ( $0.40 \mathrm{mmol}, 73.0 \mathrm{mg}$ ) and ( MeO$)_{3} \mathrm{SiH}(0.60 \mathrm{mmol}, 73.3 \mathrm{mg})$ according to the General Procedure in $84 \%$ yield ( $102.3 \mathrm{mg}, 84 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.75(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.51(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.54$ (s, 9 H ), 1.18-1.29 (m, 3 H ), 1.04 (d, $J=4.4 \mathrm{~Hz}, 18 \mathrm{H}$ ).
${ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 148.4,139.9,50.5,18.6,11.2$.
HRMS $m / z(\mathrm{CI})$ calcd. for $\mathrm{C}_{14} \mathrm{H}_{31} \mathrm{O}_{3} \mathrm{Si}_{2}(\mathrm{M}-\mathrm{H})^{+}$303.1811, found 303.1850.

3n


Triethyl(1-(triisopropylsilyl)vinyl)silane (3n) was prepared as colorless oil from ethynyltriisopropylsilane ( $0.40 \mathrm{mmol}, 73.0 \mathrm{mg}$ ) and $\mathrm{Et}_{3} \mathrm{SiH}(0.60 \mathrm{mmol}, 69.8 \mathrm{mg}$ ) according to the General Procedure in $42 \%$ yield ( $50.2 \mathrm{mg}, 42 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.50(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.46(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.15-$ 1.23 (m, 3 H ), 1.05 (d, $J=7.2 \mathrm{~Hz}, 18 \mathrm{H}), 0.92(\mathrm{t}, J=8.0 \mathrm{~Hz}, 9 \mathrm{H}) .0 .86(\mathrm{q}, \mathrm{J}=8.0 \mathrm{~Hz}$, 6 H ).
${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 145.2, 145.1, 19.3, 11.6, 7.4, 4.1.
MS (ESI) $m / z$ (relative intensity) 298.24 (0.1), 59.09 (100) [M] ${ }^{+}$.


Ethene-1,1-diylbis(dimethyl(phenyl)silane) (30) was prepared as colorless oil from ethynyldimethyl(phenyl)silane ( $0.40 \mathrm{mmol}, 64.1 \mathrm{mg}$ ) and $\mathrm{PhMe}_{2} \mathrm{SiH}(0.60 \mathrm{mmol}, 81.8$ mg ) according to the General Procedure in $94 \%$ yield ( $111.5 \mathrm{mg}, 94 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.60-7.55$ (m, 4 H ), 7.49-7.42 (m, 6 H$), 6.58$ ( $\mathrm{s}, 2 \mathrm{H}$ ), 0.42 (s, 12 H ).
${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 150.9,143.9,138.8,134.0,128.8,127.6,-1.8$.
HRMS $m / z(C I)$ calcd. for $\mathrm{C}_{18} \mathrm{H}_{25} \mathrm{Si}_{2}(\mathrm{M}+\mathrm{H})^{+}$297.1495, found 297.1506.

3p


Trimethyl(1-(triphenylsilyl)vinyl)silane (3p) was prepared as colorless oil from ethynyltrimethylsilane ( $0.40 \mathrm{mmol}, 40.0 \mathrm{mg}$ ) and $\mathrm{Ph}_{3} \mathrm{SiH}(0.60 \mathrm{mmol}, 156.2 \mathrm{mg})$, according to the General Procedure in $62 \%$ yield ( $88.9 \mathrm{mg}, 62 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.60-7.55(\mathrm{~m}, 6 \mathrm{H}), 7.44-7.33(\mathrm{~m}, 9 \mathrm{H}), 6.74(\mathrm{~d}, J=4.8$ $\mathrm{Hz}, 1 \mathrm{H}), 6.40(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 1 \mathrm{H}),-0.10(\mathrm{~s}, 9 \mathrm{H})$.
${ }^{13}$ C NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 149.1,147.3,136.5,135.0,129.4,127.8,0.0$.
MS (ESI) m/z (relative intensity) 358.16(4.0), 259.32(100) [M] ${ }^{+}$.


1,4-Bis(dimethyl(1-(trimethylsilyl)vinyl)silyl)benzene (3q) was prepared as colorless oil from ethynyltrimethylsilane ( $1.20 \mathrm{mmol}, 120.0 \mathrm{mg}$ ) and $1,4-$ bis(dimethylsilyl)benzene ( $0.40 \mathrm{mmol}, 77.7 \mathrm{mg}$ ) according to the General Procedure in $84 \%$ yield ( $131.3 \mathrm{mg}, 84 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.51(\mathrm{~s}, 4 \mathrm{H}), 6.45(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.37(\mathrm{~d}, J=5.2$ $\mathrm{Hz}, 2 \mathrm{H}), 0.4$ (s, 12 H$), 0.04$ (s, 18 H ).
${ }^{13}$ C NMR (100MHz, $\mathrm{CDCl}_{3}$ ) $\delta 152.8,141.8,139.5,133.2,-0.3,-1.8$.
HRMS $m / z(\mathrm{CI})$ calcd. for $\mathrm{C}_{20} \mathrm{H}_{39} \mathrm{Si}_{4}(\mathrm{M}+\mathrm{H})^{+}$391.2130, found 391.2182.

3r


1,1,3,3-Tetramethyl-1,3-bis(1-(triethylsilyl)vinyl)disiloxane (3r) was prepared as colorless oil from triethyl(ethynyl)silane ( $1.20 \mathrm{mmol}, 168.6 \mathrm{mg}$ ) and $1,1,3,3-$ tetramethyldisiloxane ( $0.40 \mathrm{mmol}, 54.0 \mathrm{mg}$ ) according to the General Procedure in $70 \%$ yield ( $116.2 \mathrm{mg}, 70 \%, \alpha / \beta>50: 1$ ).
${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.50(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.33(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 2 \mathrm{H}), 0.95$ (t, $J=8.0 \mathrm{~Hz}, 18 \mathrm{H}$ ), $0.67(\mathrm{q}, J=8.0 \mathrm{~Hz}, 12 \mathrm{H}), 0.2(\mathrm{~s}, 12 \mathrm{H})$.
${ }^{13}$ C NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 150.8,142.2,7.1,3.8,1.6$.
HRMS $m / z(\mathrm{CI})$ calcd. for $\mathrm{C}_{20} \mathrm{H}_{47} \mathrm{OSi}_{4}(\mathrm{M}+\mathrm{H})^{+} 415.2704$, found 415.2668.


3,3,10,10-Tetramethoxy-5,5,8,8-tetramethyl-4,9-dimethylene-2,11-dioxa-3,5,8,10tetrasiladodecane (3s) was prepared as colorless oil from 1,2bis(ethynyldimethylsilyl)ethane ( $0.40 \mathrm{mmol}, 77.8 \mathrm{mg}$ ) and ( MeO$)_{3} \mathrm{SiH}(1.20 \mathrm{mmol}$, 146.6 mg ) according to the General Procedure in $58 \%$ yield ( $101.8 \mathrm{mg}, 58 \%, \alpha / \beta>$ 50:1).
${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.58(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.43(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 2 \mathrm{H}), 3.52$ (s, 18 H ), 0.5 ( $\mathrm{s}, 4 \mathrm{H}$ ), 0.07 ( $\mathrm{s}, 12 \mathrm{H}$ ).
${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 146.0,144.1,50.4,37.2,3.7$.
HRMS $m / z(\mathrm{CI})$ calcd. for $\mathrm{C}_{16} \mathrm{H}_{38} \mathrm{KO}_{6} \mathrm{Si}_{4}(\mathrm{M}+\mathrm{K})^{+} 477.1383$, found 477.1380.

## III. Derivatizations of the Hydrosilylation Products



3a


4

Triethoxy(1-iodovinyl)silane (4). To an oven-dried $5-\mathrm{mL}$ vial was added $\mathbf{3 a}$ ( 54 mg , 0.20 mmol ), 2,6-lutidine ( $12 \mu \mathrm{~L}, 0.10 \mathrm{mmol}$ ), and ( $\left.\mathrm{CF}_{3}\right)_{2} \mathrm{CHOH}(1.0 \mathrm{~mL})$. The reaction mixture was cooled to $0^{\circ} \mathrm{C}$, and N -iodosuccinimide ( 0.25 mmol ) was added in one portion. The reaction mixture was stirred for 1 h under air, and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: hexanes) to give the desired product $\mathbf{4}$ as pale yellow oil ( $38.0 \mathrm{mg}, 60 \%$ ).
${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.13-7.12(\mathrm{~m}, 1 \mathrm{H}), 6.89-6.87(\mathrm{~m}, 1 \mathrm{H}), 3.89(\mathrm{q}, J=7.2$ $\mathrm{Hz}, 6 \mathrm{H}), 1.25(\mathrm{t}, J=7.2 \mathrm{~Hz}, 9 \mathrm{H})$.
${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 143.7,102.9,60.2,18.7$.
HRMS $m / z(\mathrm{CI})$ calcd. for $\mathrm{C}_{8} \mathrm{H}_{18} \mathrm{IO}_{3} \mathrm{Si}(\mathrm{M}+\mathrm{H})^{+}$317.0071, found 317.0065.

$3 a$
6
4,4',4"-(ethene-1,1,2-triyl)tris(methoxybenzene) (6). To an oven-dried $5-\mathrm{mL}$ vial was added $\mathbf{3 a}$ ( $104 \mathrm{mg}, 0.40 \mathrm{mmol}$ ), 4-methoxybenzenediazonium tetrafluoroborate ( $\mathbf{5}$, $320 \mathrm{mg}, 1.44 \mathrm{mmol}), \mathrm{Pd}(\mathrm{OAc})_{2}(9.0 \mathrm{mg}, 0.04 \mathrm{mmol})$, and EtOH $(2.0 \mathrm{~mL})$. The reaction mixture was stirred at $40^{\circ} \mathrm{C}$ for 4 h , and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: 2\% EtOAc in hexanes) to give the desired product $\mathbf{6}$ as colorless oil ( $54.4 \mathrm{mg}, 40 \%$ ).
${ }^{\mathbf{1}} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.16(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.05(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.89$ (t, $J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.81-6.74(\mathrm{~m}, 4 \mathrm{H}), 6.70(\mathrm{~s}, 1 \mathrm{H}), 6.60(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 3.76(\mathrm{~s}$, $3 \mathrm{H}), 3.73$ (s, 3 H$), 3.67$ (s, 3 H ).
${ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 159.0,158.8,158.1,139.8,136.6,133.0,131.6,130.6$, $128.6,125.8,114.0,113.5,113.4,55.3,55.2,55.1$.

MS (ESI) $m / z$ (relative intensity) 346.31 (100) $[\mathrm{M}]^{+}$.

## IV. Deuterium Labeling Experiment



Triethyl(1-(trimethylsilyl)vinyl)silane (3e-D) was prepared as colorless oil from ethynyltrimethylsilane $(0.40 \mathrm{mmol})$ and $\mathrm{Et}_{3} \mathrm{SiD}(0.60 \mathrm{mmol})$ according to the General Procedure.





## V. ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR Spectra

## 3a <br> TMS

${ }^{1} \mathrm{H}$ NMR

${ }^{13}$ C NMR


## 3 3ato $_{3} \mathrm{si}^{2}=\mathrm{C}_{\mathrm{H}}^{\mathrm{H}}$

DEPT 135

${ }^{1} \mathrm{H}$ NMR


WV|l|

${ }^{13}$ C NMR


DEPT 135


${ }^{1} \mathrm{H}$ NMR

${ }^{13}$ C NMR


## DEPT 135


$\qquad$
${ }^{1} \mathrm{H}$ NMR

${ }^{13}$ C NMR


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DEPT 135

${ }^{1} \mathrm{H}$ NMR

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| :---: | :---: |
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${ }^{13}$ C NMR

${ }^{1} \mathrm{H}$ NMR

${ }^{13} \mathrm{C}$ NMR

${ }^{1} \mathrm{H}$ NMR

${ }^{13}$ C NMR

${ }^{1} \mathrm{H}$ NMR

${ }^{13}$ C NMR


${ }^{1} \mathrm{H}$ NMR


${ }^{13} \mathrm{C}$ NMR

${ }^{1}$ H NMR





${ }^{13}$ C NMR


${ }^{1} \mathrm{H}$ NMR


${ }^{13}$ C NMR

${ }^{1} \mathrm{H}$ NMR

${ }^{13}$ C NMR

${ }^{1} \mathrm{H}$ NMR

${ }^{13}$ C NMR

${ }^{1} \mathrm{H}$ NMR


${ }^{13} \mathrm{C}$ NMR

${ }^{1} \mathrm{H}$ NMR

${ }^{13}$ C NMR


DEPT135


3p
${ }^{1} \mathrm{H}$ NMR

${ }^{13} \mathrm{C}$ NMR

${ }^{1} \mathrm{H}$ NMR

${ }^{13}$ C NMR


${ }^{1} \mathrm{H}$ NMR


${ }^{13} \mathrm{C}$ NMR

${ }^{1} \mathrm{H}$ NMR

${ }^{13}$ C NMR


${ }^{1} \mathrm{H}$ NMR

$4 \underset{\left.(\mathrm{EtO})_{3} \mathrm{si}^{\mathrm{I}}\right\rangle}{>} \mathrm{C}_{\mathrm{H}}^{\mathrm{H}}$
${ }^{13} \mathrm{C}$ NMR


${ }^{1} \mathrm{H}$ NMR


${ }^{13} \mathrm{C}$ NMR


