## Access to branched allylsilanes by nickel-catalyzed

# regioselective hydrosilylation of allenes

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## 1. General Methods and Materials

The liquid-state NMR was recorded on a 400 or 500 MHz spectrometer. Chemical shifts were reported in ppm. <sup>1</sup>H NMR spectra were referenced to CDCl<sub>3</sub> (7.28 ppm), and <sup>13</sup>C-NMR spectra were referenced to CDCl<sub>3</sub> (77.0 ppm). All <sup>13</sup>C NMR spectra were measured with complete proton decoupling. Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. The solid-state <sup>13</sup>C CP/MAS NMR was performed on a VARIAN Infinity-plus spectrometer. Mass spectroscopy: We were grateful to the assistance of the Department of Chemistry, Xiamen University in obtaining the MS data.

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. The allenes<sup>[1,2,3]</sup> were prepared according to corresponding literature procedures. Reference:

[1] J. Kuang and S. Ma, An Efficient Synthesis of Terminal Allenes from Terminal 1-Alkynes, J. Org. Chem., 2009, 74, 1763.

[2] J. Kuang and S. Ma, One-Pot Synthesis of 1,3-Disubstituted Allenes from 1-Alkynes, Aldehydes, and Morpholine, *J. Am. Chem. Soc.*, 2010, **132**, 1786.

[3] X. Tang, Y. Han and S. Ma, Cadmium Iodide Mediated Allenylation of Terminal Alkynes for the Synthesis of Methyl-Substituted Allenes, *Org. Lett.*, 2015, **17**, 1176.

## 2. General procedure for hydrosilylation of allenes

$$\begin{array}{c} \mathsf{R}'_{} \\ \mathsf{R}^{} \\ \mathsf{R}^{} \end{array} + \operatorname{PhSiH}_{3} \xrightarrow{\begin{array}{c} \mathsf{Ni}(\mathsf{acac})_{2} (\mathsf{1mol}\%) \\ \mathsf{xantphos} (\mathsf{1mol}\%) \\ \mathsf{THF.} 25 \, {}^{\circ}\mathsf{C}, \, \mathsf{N}_{2} \end{array}} \xrightarrow{\begin{array}{c} \mathsf{SiH}_{2}\mathsf{Ph} \\ \mathsf{R}^{\prime}_{} \\ \mathsf{R}^{\prime}_{} \end{array}}$$

In a nitrogen filled schlenk tube, Ni(acac)<sub>2</sub> (1.5 mg, 1 mmol%), Xantphos (3.5 mg, 1 mol%) were added to THF (1 mL), followed by the addition of allenes (0.5 mmol) and PhSiH<sub>3</sub> (0.6 mmol) in THF (1 mL) under nitrogen. The reaction mixture was stirred at 25 °C. When the reaction was completed (0.5-5 h, monitored by TLC), the solvent was removed in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product.

## 3. Procedure for Deuterium-labeling Experiments



In a nitrogen filled schlenk tube, Ni(acac)<sub>2</sub> (1.5 mg, 1 mmol%), Xantphos (3.5 mg, 1 mol%) were added to THF (1 mL), followed by the addition of octa-6,7-dien-1-ol (0.5 mmol) and Ph<sub>2</sub>SiD<sub>2</sub> (0.6 mmol) in THF (1 mL) under nitrogen. The reaction mixture was stirred at 30 °C for 12h and the resulting solution was concentrated in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate, to afford the corresponding product as a colorless oil (125 mg, 80%).



Figure S1. <sup>1</sup>H NMR spectra for deuterated 3d

## 4. Crossover experiments related to operable mechanism:

Control experiment: Into two separate nitrogen filled schlenk tube,  $Ni(acac)_2$  (1.5 mg), Xantphos (3.5mg, ) were added to THF (1 mL), followed by addition of  $Ph_2SiD_2$  (0.25 mmol) to the first schlenk tube and PhMeSiH<sub>2</sub> (0.25 mmol) to the second one. No cyclohexylallene was added and the contents of the two schlenk tubes were immediately mixed. After 12 hours, the mixture was observed by 1H NMR spectroscopy. No H/D exchange was observed.

Crossover experiment: Into two separate nitrogen filled schlenk tube, Ni(acac)<sub>2</sub> (1.5 mg), Xantphos (3.5 mg) were added to THF (1 mL), followed by addition of Ph<sub>2</sub>SiD<sub>2</sub> (0.3 mmol) to the first schlenk tube and PhMeSiH<sub>2</sub> (0.3 mmol) to the second one. To each of these, cyclohexylallene (0.25 mmol) was added and the contents of the two schlenk tubes were immediately mixed. After 12 hours, reaction completion monitored by TLC. Comparing the resultant <sup>1</sup>H NMR spectrum with spectra of 3k and deuterated 3c, there was no new characteristic peak appeared in the spectra of crossover experiment, and the integral value of characteristic peaks revealed the 3:4 mixture of Ph<sub>2</sub>SiDCH(Cy)CD=CH<sub>2</sub> and PhMeSiHCH(Cy)CH=CH<sub>2</sub>, no crossover products were observed (see Scheme S1 and spectra below), thus ruling out the mechanism of Nickel hydrides(Scheme S2).



Scheme S1. Products formed in crossover experiment



Scheme S2. [Ni-H] involved mechanism



Figure S2: 500M <sup>1</sup>H NMR spectra for 3K



Figure S3: .Internal vinylic hydrogen region from <sup>1</sup>H NMR spectrum of 3k



Figure S4: External vinylic hydrogen region from <sup>1</sup>H NMR spectrum of 3k



Figure S5: 400M  $^{1}$ H NMR spectra for deuterated 3c



Figure S6. 400M <sup>1</sup>H NMR spectrum of crude reaction mixture from crossover experiment:



Figure S7.Internal vinylic hydrogen region from <sup>1</sup>H NMR spectrum of crossover experiment:



Figure S8. External vinylic hydrogen region from <sup>1</sup>H NMR spectrum of crossover experiment



Figure S9: the sum of three <sup>1</sup>H NMR spectrum. green: deuterated 3c; red: 3k; blue: crossover experiment.

## 5. Procedure for control Experiment with Ni(cod)<sub>2</sub>



In the glove box, Ni(COD)<sub>2</sub> (1.5 mg, 1 mmol%), Xantphos (3.5 mg, 1 mol%) were added to THF (1 mL), and stirred for 5 mins. then undeca-1,2-diene (0.5 mmol) and PhSiH<sub>3</sub>(0.6 mmol) in THF (1 mL) was added. The reaction mixture was stirred at 25 °C and monitored by TLC. the reaction was complete within 15 mins. Resulting solution was concentrated in vacuum. The crude product was purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate, to afford the corresponding product as a colorless oil (110 mg, 85%).

#### 6. Analytical data for compounds

#### (undec-1-en-3-yl)(phenyl)silane (2a)



colorless liquid (2h, 90%, 116 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59-7.53 (m, 2H), 7.41-7.31 (m, 3H), 5.73 (ddd,  $J_1 = 17.1$  Hz,  $J_2 = 10.3$  Hz,  $J_3 = 9.0$  Hz, 1H), 4.96-4.85 (m, 2H), 4.27-4.21 (m, 2H), 2.06-1.96 (m, 1H), 1.57-1.48 (m, 1H), 1.46-1.36 (m, 1H), 1.32-1.20 (m, 12H), 0.87 (t, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.6, 135.8, 131.5, 129.7, 127.9, 113.2, 32.0, 30.19, 30.15, 29.54, 29.51, 29.4, 29.1, 22.7, 14.2. HRMS (ESI) m/z Calculated for C<sub>17</sub>H<sub>28</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>: 283.1852, found:\_283.1856.

#### (heptadec-1-en-3-yl)(phenyl)silane (2b)



colorless liquid (3h, 80%, 138 mg); <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59-7.53 (m, 2H), 7.42-7.31 (m, 3H), 5.75 (ddd,  $J_1 = 17.1$  Hz,  $J_2 = 10.3$  Hz,  $J_3 = 9.1$  Hz, 1H), 4.96-4.85 (m, 2H), 4.27-4.20 (m, 2H), 2.05-1.96 (m, 1H), 1.57-1.47 (m, 1H), 1.45-1.36 (m, 1H), 1.32-1.20 (m, 24H), 0.88 (t, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  139.6, 135.7, 131.4, 129.7, 127.9, 113.2, 31.9, 30.13, 30.08, 29.71, 29.68, 29.67, 29.64, 29.51, 29.44, 29.38, 29.1, 22.7, 14.1. HRMS (ESI) m/z Calculated for C<sub>23</sub>H<sub>40</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>: 367.2791, found: 367.2786.

#### (1-cyclohexylallyl)(phenyl)silane (2c)



colorless liquid (0.5h, 80%, 92 mg); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.60-7.55 (m, 2H), 7.42-7.32 (m, 3H), 5.77 (dt,  $J_1 = 17.1$  Hz,  $J_2 = 10.3$  Hz, 1H), 4.95 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 1.8$ Hz, 1H), 4.86 (apparent dt,  $J_1 = 17.0$  Hz,  $J_2 = 1.0$  Hz, 1H), 4.36 (dd,  $J_1 = 6.4$  Hz,  $J_2 = 2.4$  Hz, 1H), 4.31 (dd,  $J_1 = 6.4$  Hz,  $J_2 = 3.6$  Hz, 1H), 1.98-1.91 (m, 1H), 1.86-1.77 (m, 2H), 1.75-1.68 (m, 2H), 1.66-1.60 (m, 1H), 1.58-1.50 (m, 1H), 1.30-1.00 (m, 5H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.0, 135.8, 131.9, 129.5, 127.8, 114.3, 39.1, 38.0, 33.4, 32.1, 26.60, 26.55, 26.4. HRMS (ESI) m/z Calculated for C<sub>15</sub>H<sub>22</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>:253.1383, found: 253.1385

#### phenyl(5-phenylpent-1-en-3-yl)silane (2d)



colorless liquid (1h, 73%, 92 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.58-7.50 (m, 2H), 7.42-7.36 (m, 1H), 7.36-7.31 (m, 2H), 7.28-7.22 (m, 2H), 7.20-7.10 (m, 3H), 5.78 (ddd,  $J_1 = 17.2$  Hz,  $J_2 = 10.3$  Hz,  $J_3 = 9.0$  Hz, 1H), 5.02 (dd,  $J_1 = 10.3$  Hz,  $J_2 = 0.7$  Hz,1H), 4.95 (dt,  $J_1 = 17.2$  Hz,  $J_2 = 1.3$  Hz, 1H), 4.30-4.22 (m, 2H), 2.80-2.70 (m, 1H), 2.61-2.51 (m, 1H), 2.10-2.01 (m, 1H), 1.94-1.77 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  142.2, 139.1, 135.8, 131.0, 129.8, 128.5, 128.3, 127.9, 125.8, 113.9, 35.1, 31.9, 29.6. HRMS (ESI) m/z Calculated for C<sub>17</sub>H<sub>20</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>: 275.1226, found: 275.1227.

#### 6-(phenylsilyl)oct-7-en-1-ol (2e)

colorless liquid (0.5h, 87%, 102 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59-7.53 (m, 2H), 7.43-7.32 (m, 3H), 5.73 (ddd, *J*<sub>1</sub> = 17.1 Hz, *J*<sub>2</sub> = 10.2 Hz, *J*<sub>3</sub> = 9.1 Hz, 1H), 4.98-4.86 (m, 2H), 4.28-4.22 (m, 2H), 3.61 (t, *J* = 6.6 Hz, 2H), 2.07-1.96 (m, 1H), 1.61-1.42 (m, 5H), 1.38-1.25 (m, 3H); <sup>13</sup>C NMR

(125 MHz, CDCl<sub>3</sub>) δ 139.4, 135.7, 131.3, 129.7, 127.9, 113.3, 62.9, 32.6, 30.1, 30.0, 28.8, 25.5. HRMS (ESI) m/z Calculated for C<sub>14</sub>H<sub>22</sub>NaOSi<sup>+</sup> [M+Na]<sup>+</sup>: 257.1332, found: 257.1336.

#### tert-butyldimethyl((6-(phenylsilyl)oct-7-en-1-yl)oxy)silane (2f)

colorless liquid (0.5h, 81%, 141 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.60-7.53 (m, 2H), 7.43-7.32 (m, 3H), 5.73 (ddd, *J*<sub>1</sub> = 17.1 Hz, *J*<sub>2</sub> = 10.2 Hz, *J*<sub>3</sub> = 9.0 Hz, 1H), 4.97-4.86 (m, 2H), 4.27-4.21 (m, 2H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.05-1.95 (m, 1H), 1.58-1.42 (m, 4H), 1.35-1.25 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 139.5, 135.7, 131.4, 129.7, 127.9, 113.2, 63.2, 32.7, 30.08, 30.05, 28.8, 26.0, 25.6, 18.4, -5.3. HRMS (ESI) m/z Calculated for C<sub>20</sub>H<sub>36</sub>NaOSi<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 371.2197, found: 371.2193.

#### 6-(phenylsilyl)oct-7-en-1-yl acetate (2g)



colorless liquid (0.5h, 85%, 117 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.60-7.53 (m, 2H), 7.43-7.32 (m, 3H), 5.72 (ddd,  $J_1 = 17.1$  Hz,  $J_2 = 10.2$  Hz,  $J_3 = 9.0$  Hz, 1H),4.98-4.86 (m, 2H), 4.27-4.21 (m, 2H), 4.02 (t, J = 6.7 Hz, 2H), 2.03 (s, 3H), 2.02-1.97 (m, 1H), 1.62-1.42 (m, 4H), 1.38-1.24 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  171.2, 139.3, 135.7, 131.2, 129.7, 127.9, 113.4, 64.5, 30.1, 29.9, 28.7, 28.5, 25.7, 21.0. HRMS (ESI) m/z Calculated for C<sub>16</sub>H<sub>24</sub>NaO<sub>2</sub>Si<sup>+</sup> [M+Na]<sup>+</sup>: 299.1438, found: 299.1442.

#### 6-(phenylsilyl)oct-7-en-1-yl 4-methylbenzenesulfonate (2h)

SiH<sub>2</sub>Ph

colorless liquid (0.5h, 88%, 171 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.80-7.75 (m, 2H), 7.57-7.51 (m, 2H), 7.42-7.37 (m, 1H), 7.36-7.30 (m, 4H), 5.68 (ddd, *J*<sub>1</sub> = 17.1 Hz, *J*<sub>2</sub> = 10.2 Hz, *J*<sub>3</sub> = 9.2 Hz, 1H), 4.93 (d, *J* = 10.2 Hz, 1H), 4.87 (d, *J* = 17.1 Hz, 1H), 4.25-4.19 (m, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 2.44 (s, 3H), 1.90-2.00 (m, 1H), 1.63-1.56 (m, 2H), 1.53-1.4 (m, 2H), 1.38-1.18 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 144.6, 139.2, 135.7, 133.3, 131.1, 129.81, 129.78, 127.92, 127.88, 113.4,

70.6, 30.0, 29.8, 28.7, 28.3, 25.1, 21.6. **HRMS** (ESI) m/z Calculated for C<sub>21</sub>H<sub>28</sub>NaO<sub>3</sub>SSi<sup>+</sup> [M+Na]<sup>+</sup>: 411.1421, found: 411.1427.

#### (7-chlorohept-1-en-3-yl)(phenyl)silane (2i)



colorless liquid (0.5h, 87%, 104 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.60-7.51 (m, 2H), 7.45-7.32 (m, 3H), 5.73 (ddd,  $J_1 = 17.2$  Hz,  $J_2 = 10.2$  Hz,  $J_3 = 9.2$  Hz, 1H), 4.97 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 0.7$  Hz, 1H), 4.92 (dt,  $J_1 = 17.1$  Hz,  $J_2 = 1.2$  Hz, 1H), 4.30-4.22 (m, 2H), 3.50 (t, J = 6.8 Hz, 2H), 2.06-1.97 (m, 1H), 1.82-1.67 (m, 2H), 1.62-1.52 (m, 3H),1.47-1.39 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  139.0, 135.7, 131.1, 129.8, 127.9, 113.6, 44.9, 32.4, 30.0, 29.3, 26.3. HRMS (ESI) m/z Calculated for C<sub>13</sub>H<sub>19</sub>ClNaSi<sup>+</sup> [M+Na]<sup>+</sup>: 261.0837, found: 261.0839.

#### (8-bromooct-1-en-3-yl)(phenyl)silane (2j)

colorless liquid (0.5h, 89%, 131 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.60-7.53 (m, 2H), 7.44-7.33 (m, 3H), 5.72 (ddd,  $J_1 = 17.1$  Hz,  $J_2 = 10.2$  Hz,  $J_3 = 9.2$  Hz, 1H), 4.95 (d, J = 10.2 Hz, 1H), 4.90 (d, J = 17.1 Hz, 1H), 4.29-4.21 (m, 2H), 3.37 (t, J = 6.9 Hz, 2H), 2.06-1.97 (m, 1H), 1.85-1.78 (m, 2H), 1.59-1.50 (m, 2H), 1.49-1.25 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  139.3, 135.7, 131.2, 129.8, 127.9, 113.4, 33.9, 32.7, 30.0, 29.8, 28.2, 27.9. HRMS (ESI) m/z Calculated for C<sub>14</sub>H<sub>21</sub>BrNaSi<sup>+</sup> [M+Na]<sup>+</sup>: 319.0488, found: 319.0491.

## 2-(6-(phenylsilyl)oct-7-en-1-yl)isoindoline-1,3-dione (2k)

colorless liquid (1h, 78%, 142 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87-7.80 (m, 2H), 7.74-7.67 (m, 2H), 7.58-7.52 (m, 2H), 7.41-7.30 (m, 3H), 5.70 (apparent dt, *J*<sub>1</sub> = 17.4 Hz, *J*<sub>2</sub> = 9.4 Hz, 1H), 4.98-4.81 (m, 2H), 4.28-4.18 (m, 2H), 3.65 (t, *J* = 7.3 Hz, 2H), 2.04-1.94 (m, 1H), 1.70-1.60 (m,

2H), 1.58-1.42 (m, 2H), 1.39-1.22 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 168.4, 139.3, 135.7, 133.8, 132.2, 131.2, 129.7, 127.9, 123.2, 113.4, 38.0, 30.0, 29.9, 28.6, 28.5, 26.7. HRMS (ESI) m/z Calculated for C<sub>22</sub>H<sub>25</sub>NNaO<sub>2</sub>Si<sup>+</sup> [M+Na]<sup>+</sup>: 386.1547, found: 386.1552.

#### 2-((2-(phenylsilyl)but-3-en-1-yl)oxy)ethanol (2l)

colorless liquid (1h, 55%, 61 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62-7.55 (m, 2H), 7.45-7.33 (m, 3H), 5.85 (ddd,  $J_1 = 17.2$  Hz,  $J_2 = 10.5$  Hz,  $J_3 = 8.7$  Hz, 1H), 5.05-4.95 (m, 2H), 4.30 (d, J = 3.0 Hz, 2H), 3.73-3.62 (m, 4H), 3.55-3.44 (m, 2H), 2.54-2.44 (m, 1H), 1.90 (t, J = 6.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.7, 135.7, 130.8, 129.9, 128.0, 114.5, 71.7, 71.6, 61.8, 31.9. HRMS (ESI) m/z Calculated for C<sub>12</sub>H<sub>18</sub>NaO<sub>2</sub>Si<sup>+</sup> [M+Na]<sup>+</sup>:245.0968 , found: 245.0970

#### (8-(benzyloxy)oct-1-en-3-yl)(phenyl)silane (2m)



colorless liquid (1h, 71%, 115 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.58-7.52 (m, 2H), 7.40-7.30 (m, 7H), 7.30-7.25 (m, 1H), 5.71 (ddd,  $J_1 = 17.2$  Hz,  $J_2 = 10.2$  Hz,  $J_3 = 9.2$  Hz, 1H), 4.93 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 0.6$  Hz, 1H), 4.89 (d, J = 17.1 Hz, 1H), 4.48 (s, 2H), 4.26-4.21 (m, 2H), 3.43 (t, J = 6.6 Hz, 2H), 2.04-1.96 (m, 1H), 1.60-1.50 (m, 4H), 1.35-1.27 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  139.5, 138.7, 135.7, 131.3, 129.7, 128.4, 127.9, 127.6, 127.5, 113.3, 72.9, 70.4, 30.1, 30.0, 29.6, 28.9, 26.0. HRMS (ESI) m/z Calculated for C<sub>21</sub>H<sub>28</sub>NaOSi<sup>+</sup> [M+Na]<sup>+</sup>: 347.1802 , found: 347.1809

#### 6-(phenylsilyl)oct-7-en-1-yl 4-methylbenzoate (2n)

$$\operatorname{SiH}_2\operatorname{Ph}$$

colorless liquid (1h, 93%, 164 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96-7.88 (m, 2H), 7.59-7.51 (m, 2H), 7.43-7.31 (m, 3H), 7.25-7.20 (m, 2H), 5.72 (ddd,  $J_1 = 17.1$  Hz,  $J_2 = 10.2$  Hz,  $J_3 = 9.2$  Hz, 1H), 4.97-4.86 (m, 2H), 4.30-4.20 (m, 4H), 2.40 (s, 3H), 2.06-1.97 (m, 1H), 1.78-1.68 (m, 2H), 1.60-1.30 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.8, 143.4, 139.3, 135.7, 131.2, 129.7, 129.6, 129.0, 127.9, 127.8, 113.4, 64.8, 30.1, 30.0, 28.7, 28.6, 25.9, 21.7. HRMS (ESI) m/z Calculated for C<sub>22</sub>H<sub>28</sub>NaO<sub>2</sub>Si<sup>+</sup> [M+Na]<sup>+</sup>: 375.1751, found: 375.17527.

#### phenyl(1-phenylallyl)silane (20)



colorless liquid (0.5h, 76%, 85 mg); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.42-7.34 (m, 3H), 7.32-7.23 (m, 4H), 7.17-7.10 (m, 3H), 6.16 (ddd,  $J_1 = 17.0$  Hz,  $J_2 = 10.3$  Hz,  $J_3 = 8.6$  Hz, 1H), 5.08-4.98 (m, 2H), 4.43 (dd,  $J_1 = 7.1$  Hz,  $J_2 = 3.4$  Hz, 1H), 4.40 (dd,  $J_1 = 7.1$  Hz,  $J_2 = 3.3$  Hz, 1H) , 3.47-3.39 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  141.0, 137.7, 135.8, 130.8, 129.9, 128.6, 127.8, 127.7, 125.5, 114.4, 38.8. **HRMS** (ESI) m/z Calculated for C<sub>15</sub>H<sub>16</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>: 247.0913, found: 247.0910

#### phenyl(1-(p-tolyl)allyl)silane (2p)



colorless liquid (0.5h, 80%, 95 mg); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.45-7.40 (m, 2H), 7.40-7.35 (m, 1H), 7.32-7.27 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.13 (ddd, *J*<sub>1</sub> = 17.0 Hz, *J*<sub>2</sub> = 10.2 Hz, *J*<sub>3</sub> = 8.5 Hz, 1H), 5.05-4.95 (m, 2H), 4.45-4.35 (m, 2H), 3.42-3.36 (m, 1H), 2.30 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.0, 137.9, 135.8, 134.9, 131.0, 130.0, 129.3, 127.8, 127.6, 114.2, 38.2, 21.0. **HRMS** (ESI) m/z Calculated for C<sub>16</sub>H<sub>18</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>: 261.1070 , found: 261.1074

(1-(4-(*tert*-butyl)phenyl)allyl)(phenyl)silane (2q)



colorless liquid (0.5h, 74%, 104 mg); <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44-7.34 (m, 3H), 7.32-7.25 (m, 4H), 7.09-7.03 (m, 2H), 6.15 (ddd,  $J_1 = 17.0$  Hz,  $J_2 = 10.2$  Hz,  $J_3 = 8.8$  Hz, 1H), 5.05-4.96 (m, 2H), 4.44-4.37 (m, 2H), 3.44-3.37 (m, 1H), 1.30 (s, 9H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.3, 137.90, 137.88, 135.8, 131.0, 129.9, 127.8, 127.4, 125.5, 114.2, 38.1, 34.4, 31.4. **HRMS** (ESI) m/z Calculated for C<sub>19</sub>H<sub>24</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>: 303.1539, found: 303.1542.

#### (1-(4-methoxyphenyl)allyl)(phenyl)silane (2r)



colorless liquid (0.5h, 70%, 89 mg); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.44-7.35 (m, 3H), 7.32-7.26 (m, 2H), 7.04 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 6.12 (ddd,  $J_1 = 17.0$  Hz,  $J_2 = 10.2$  Hz,  $J_3 = 8.4$  Hz, 1H), 5.05-4.96 (m, 2H), 4.44-4.36 (m, 2H), 3.78 (s, 3H), 3.41-3.34 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  157.5, 138.1, 135.8, 132.9, 130.9, 129.9, 128.8, 127.8, 114.11, 114.09, 55.3, 37.5. **HRMS** (ESI) m/z Calculated for C<sub>16</sub>H<sub>18</sub>NaOSi<sup>+</sup> [M+Na]<sup>+</sup>: 277.1019, found: 277.1022.

#### (1-(2-methoxyphenyl)allyl)(phenyl)silane (2s)



colorless liquid (0.5h, 74%, 94 mg); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.46-7.41 (m, 2H), 7.38-7.32 (m, 1H), 7.31-7.26 (m, 2H), 7.17-7.10 (m, 2H), 6.93-6.86 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.24-6.14 (m, 1H), 5.05-4.96 (m, 2H), 4.39 (dd, *J*<sub>1</sub> = 7.3 Hz, *J*<sub>2</sub> = 3.4 Hz, 1H), 4.32 (dd, *J*<sub>1</sub> = 7.3 Hz, *J*<sub>2</sub> = 2.8 Hz, 1H), 3.84-3.76 (m, 1H), 3.68 (s, 3H); <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$  156.0, 137.6, 135.6, 132.1, 129.9, 129.6, 128.1, 127.7, 126.4, 120.7, 114.1, 110.5, 55.1, 31.9. **HRMS** (ESI) m/z

Calculated for C<sub>16</sub>H<sub>18</sub>NaOSi<sup>+</sup> [M+Na]<sup>+</sup>: 277.1019, found: 277.1023.

#### (1-(4-fluorophenyl)allyl)(phenyl)silane (2t)



colorless liquid (0.5h, 60%, 73 mg); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.41-7.35 (m, 3H), 7.32-7.28 (m, 2H), 7.08-7.03 (m, 2H), 6.98-6.92 (m, 2H), 6.11 (ddd,  $J_1 = 17.0$  Hz,  $J_2 = 10.3$  Hz,  $J_3 = 8.4$  Hz, 1H), 5.06 (apparent dt,  $J_1 = 10.2$  Hz,  $J_2 = 1.2$  Hz, 1H), 5.02 (apparent dt,  $J_1 = 17.0$  Hz,  $J_2 = 1.3$  Hz, 1H), 4.42 (dd,  $J_1 = 7.1$  Hz,  $J_2 = 3.2$  Hz, 1H), 4.38 (dd,  $J_1 = 7.1$  Hz,  $J_2 = 3.3$  Hz, 1H), 3.45-3.37 (m, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.0 (d, J = 243.9 Hz), 137.6, 136.6 (d, J = 3.1 Hz), 135.8, 130.5, 130.1, 129.0 (d, J = 7.6 Hz), 127.9, 115.4 (d, J = 21.3 Hz), 114.6, 37.9. **HRMS** (ESI) m/z Calculated for C<sub>15</sub>H<sub>15</sub>FNaSi<sup>+</sup> [M+Na]<sup>+</sup>: 265.0819, found: 265.0825.

#### phenyl(2-phenylbut-3-en-2-yl)silane (2u)



colorless liquid (0.5h, 75%, 90 mg); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.38-7.33 (m, 1H), 7.32-7.23 (m, 8H), 7.18-7.13 (m, 1H), 6.35 (dd,  $J_1 = 17.3$  Hz,  $J_2 = 10.7$  Hz, 1H), 5.14 (dd,  $J_1 = 10.7$  Hz,  $J_2 = 1.0$  Hz, 1H), 5.02 (dd,  $J_1 = 17.3$  Hz,  $J_2 = 0.8$  Hz, 1H), 4.42 (d, J = 7.3 Hz, 1H), 4.37 (d, J = 7.3 Hz, 1H), 1.55 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  145.1, 143.3, 136.2, 130.9, 129.9, 128.4, 127.7, 126.8, 125.4, 112.7, 36.0, 21.2. **HRMS** (ESI) m/z Calculated for C<sub>16</sub>H<sub>18</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>: 261.1070, found: 261.1075.

#### phenyl(1-(thiophen-3-yl)allyl)silane (2v)



colorless liquid (0.5h, 84%, 97mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.43-7.35 (m, 3H), 7.32-7.27 (m, 2H), 7.25-7.22 (m, 1H), 6.88 (dd, *J*<sub>1</sub> = 4.9 Hz, *J*<sub>2</sub> = 1.1 Hz, 1H), 6.85-6.81 (m, 1H), 6.08 (ddd,

*J*<sub>1</sub> = 17.0 Hz, *J*<sub>2</sub> = 10.2 Hz, *J*<sub>3</sub> = 8.6 Hz, 1H), 5.06-4.97 (m, 2H), 4.44-4.38 (m, 2H), 3.59-3.52 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.7, 137.4, 135.8, 130.7, 130.0, 127.9, 127.7, 125.5, 119.3, 114.3, 33.9. HRMS (ESI) m/z Calculated for C<sub>13</sub>H<sub>14</sub>NaSSi<sup>+</sup> [M+Na]<sup>+</sup>: 253.0478, found: 253.0482.

#### pent-1-en-3-yldiphenylsilane (3a)

$$\overbrace{}^{\text{SiHPh}_2}_{7}$$

colorless liquid (24h, 90%, 90 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.62-7.54 (m, 4H), 7.42-7.30 (m, 6H), 5.70 (ddd,  $J_1 = 17.1$  Hz,  $J_2 = 10.2$  Hz,  $J_3 = 9.3$  Hz, 1H), 4.95-4.84 (m, 2H), 4.76 (d, J = 2.8 Hz, 1H), 2.27-2.19 (m, 1H), 1.64-1.55 (m, 1H), 1.53-1.40 (m, 2H), 1.30-1.15 (m, 11H), 0.87 (t, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  139.1, 135.7, 135.6, 133.5, 133.2, 129.61, 129.60, 127.9, 127.8, 113.7, 31.9, 31.6, 29.5, 29.4, 29.3, 29.0, 22.7, 14.1. HRMS (ESI) m/z Calculated for C<sub>23</sub>H<sub>32</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>: 359.2165, found: 359.2160.

#### heptadec-1-en-3-yldiphenylsilane (3b)



colorless liquid (24h, 80%, 101 mg); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.64-7.58 (m, 4H), 7.43-7.31 (m, 6H), 5.70 (dt,  $J_1 = 17.2$  Hz,  $J_2 = 10.1$  Hz, 1H), 4.92 (d, J = 10.2 Hz, 1H), 4.87 (d, J = 17.2 Hz, 1H), 4.76 (d, J = 2.6 Hz, 1H), 2.27-2.17 (m, 1H), 1.65-1.55 (m, 1H), 1.50-1.40 (m, 1H), 1.32-1.15 (m, 24H), 0.88 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  139.1, 135.7, 135.6, 133.5, 133.2, 129.60, 129.58, 127.9, 127.8, 113.7, 32.0, 31.6, 29.72, 29.70, 29.68, 29.65, 29.54, 29.49, 29.39, 29.37, 29.0, 22.7, 14.1. HRMS (ESI) m/z Calculated for C<sub>29</sub>H<sub>44</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>: 443.3104, found: 443.3110.

#### (1-cyclohexylallyl)diphenylsilane (3c)



colorless liquid (12h, 80%, 73 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62-7.54 (m, 4H), 7.40-7.29 (m, 6H), 5.76 (dt,  $J_1 = 17.0$  Hz,  $J_2 = 10.3$  Hz, 1H), 4.96-4.88 (m, 2H), 4.80 (apparent dt,  $J_1 = 17.0$  Hz,  $J_2 = 1.0$  Hz, 1H), 2.20-2.10 (m, 1H), 1.85-1.52 (m, 6H), 1.22-0.98 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.2, 135.9, 135.6, 134.2, 133.8, 129.5, 127.9, 127.8, 115.1, 39.6, 38.9, 33.8, 31.8,

26.7, 26.6, 26.4. HRMS (ESI) m/z Calculated for C<sub>21</sub>H<sub>26</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>:329.1696, found:329.1700

#### 6-(diphenylsilyl)oct-7-en-1-ol (3d)

colorless liquid (12h, 86%, 80 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61-7.54 (m, 4H), 7.42-7.30 (m, 6H), 5.70 (dt,  $J_1 = 17.1$  Hz,  $J_2 = 10.1$  Hz, 1H), 4.93 (d, J = 10.3 Hz, 1H), 4.88 (d, J = 17.1 Hz, 1H), 4.77 (d, J = 2.8 Hz, 1H), 3.55 (t, J = 6.6 Hz, 2H), 2.28-2.18 (m, 1H), 1.67-1.56 (m, 1H), 1.55-1.44 (m, 3H), 1.35-1.22 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.0, 135.7, 135.6, 133.4, 133.1, 129.69, 129.68, 128.0, 127.9, 113.9, 62.9, 32.6, 31.6, 29.5, 28.8, 25.5. HRMS (ESI) m/z Calculated for C<sub>20</sub>H<sub>26</sub>NaOSi<sup>+</sup> [M+Na]<sup>+</sup>: 333.1645, found: 333.1649.

#### tert-butyl((6-(diphenylsilyl)oct-7-en-1-yl)oxy)dimethylsilane (3e)

SiHPh<sub>2</sub> TBSO

colorless liquid (12h, 90%, 114 mg); <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65-7.58 (m, 4H), 7.45-7.35 (m, 6H), 5.80-5.66 (m, 1H), 5.00-4.86 (m, 2H), 4.80 (d, *J* = 2.7 Hz, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.33-2.21 (m, 1H), 1.70-1.60 (m, 1H), 1.58-1.40 (m, 4H), 1.38-1.22 (m, 3H), 0.92 (s, 9H), 0.06 (s, 6H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.0, 135.7, 135.6, 134.4, 133.4, 133.1, 129.6, 127.9, 127.8, 113.7, 63.3, 32.7, 31.5, 29.5, 28.8, 26.0, 25.5, 18.3, -5.3. **HRMS** (ESI) m/z Calculated for C<sub>26</sub>H<sub>40</sub>NaOSi<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 447.2510, found: 447.2517.

#### 6-(diphenylsilyl)oct-7-en-1-yl acetate (3f)

$$\mathsf{AcO}_{\texttt{1}} \mathsf{CO}_{\texttt{1}} \mathsf{CO}_{\texttt{1}} \mathsf{CO}_{\texttt{2}} \mathsf{$$

colorless liquid (12h, 76%, 80 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63-7.55 (m, 4H), 7.42-7.32 (m, 6H), 5.69 (ddd, *J*<sub>1</sub> = 17.1 Hz, *J*<sub>2</sub> = 10.2 Hz, *J*<sub>3</sub> = 9.4 Hz, 1H), 4.93 (dd, *J*<sub>1</sub> = 10.3 Hz, *J*<sub>2</sub> = 1.2 Hz, 1H), 4.88 (dd, *J*<sub>1</sub> = 17.1 Hz, *J*<sub>2</sub> = 1.2 Hz ,1H), 4.76 (d, *J* = 2.7 Hz, 1H), 4.00 (t, *J* = 6.8 Hz, 2H), 2.29-2.17 (m, 1H), 2.02 (s, 3H), 1.65-1.40 (m, 5H), 1.35-1.23 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.2, 138.9, 135.7, 135.6, 134.4, 133.3, 133.0, 129.7, 127.93, 127.85, 113.9, 64.6, 31.5, 29.4,

28.7, 28.5, 25.7, 21.0. **HRMS** (ESI) m/z Calculated for C<sub>22</sub>H<sub>28</sub>NaO<sub>2</sub>Si<sup>+</sup> [M+Na]<sup>+</sup>: 375.1751, found: 375.1756.

#### (7-chlorohept-1-en-3-yl)diphenylsilane (3g)

colorless liquid (12h, 72%, 68 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.62-7.54 (m, 4H), 7.43-7.32 (m, 6H), 5.69 (ddd,  $J_1 = 17.2$  Hz,  $J_2 = 10.2$  Hz,  $J_3 = 9.4$  Hz, 1H), 4.95 (dd,  $J_1 = 10.3$  Hz,  $J_2 = 1.1$  Hz, 1H), 4.89 (dd,  $J_1 = 17.1$  Hz,  $J_2 = 1.1$  Hz, 1H), 4.77 (d, J = 2.8 Hz, 1H), 3.45 (t, J = 6.8 Hz, 2H), 2.27-2.19 (m, 1H), 1.80-1.48 (m, 5H), 1.42-1.34 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.6, 135.7, 135.6, 133.1, 132.9, 129.74, 129.73, 128.0, 127.9, 114.1, 45.0, 32.4, 31.5, 28.8, 26.4. HRMS (ESI) m/z Calculated for C<sub>19</sub>H<sub>23</sub>ClNaSi<sup>+</sup> [M+Na]<sup>+</sup>: 337.1150, found: 337.1155.

#### (8-bromooct-1-en-3-yl)diphenylsilane (3h)

colorless liquid (12h, 70%, 78 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.63-7.53 (m, 4H), 7.42-7.31 (m, 6H), 5.69 (ddd,  $J_1 = 17.1$  Hz,  $J_2 = 10.1$  Hz,  $J_3 = 9.5$  Hz, 1H), 4.94 (dd, J = 10.2 Hz,  $J_2 = 1.0$  Hz, 1H), 4.88 (d, J = 17.1 Hz, 1H), 4.76 (d, J = 2.7 Hz, 1H), 3.34 (t, J = 6.8 Hz, 2H), 2.27-2.18 (m, 1H), 1.83-1.73 (m, 2H), 1.65-1.56 (m, 1H), 1.55-1.40 (m, 3H), 1.35-1.25 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.9, 135.7, 135.6, 133.3, 133.0, 129.70, 129.68, 128.0, 127.9, 114.0, 34.0, 32.7, 31.5, 29.3, 28.1, 27.9. HRMS (ESI) m/z Calculated for C<sub>20</sub>H<sub>25</sub>BrNaSi<sup>+</sup> [M+Na]<sup>+</sup>: 395.0801, found: 395.0806.

#### (1-(2-methoxyphenyl)allyl)diphenylsilane (3i)

O SiHPh<sub>2</sub>

colorless liquid (6h, 63%, 62mg); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.59-7.53 (m, 2H), 7.41-7.31 (m, 5H), 7.30-7.26 (m, 1H), 7.24-7.19 (m, 2H), 7.12-7.05 (m, 2H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 6.23-6.13(m, 1H), 5.01-4.92 (m, 2H), 4.85 (d, *J* = 3.2 Hz, 1H), 4.09 (dd, *J*<sub>1</sub> = 9.0 Hz,

 $J_2$ = 2.8 Hz, 1H), 3.52 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  156.0, 137.5, 135.8, 135.4, 133.63, 133.57, 129.7, 129.6, 129.4, 128.4, 127.8, 127.5, 126.2, 120.5, 114.3, 110.4, 55.0, 33.3. HRMS (ESI) m/z Calculated for C<sub>22</sub>H<sub>22</sub>NaOSi<sup>+</sup> [M+Na]<sup>+</sup>: 353.1332, found: 353.1337.

# 6-(methyl(phenyl)silyl)oct-7-en-1-ol as 50/50 mixture of diastereomers (3j)

colorless liquid (12h, 81%, 60 mg); Diastereomer A: <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.54-7.48 (m, 2H), 7.39-7.31 (m, 3H), 5.6-5.63 (m, 1H), 4.91 (dd, *J*<sub>1</sub> = 10.3 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 4.85 (ddd, *J*<sub>1</sub> = 17.1 Hz, *J*<sub>2</sub> = 1.1 Hz, *J*<sub>3</sub> = 1.2 Hz 1H), 4.30-4.27 (m, 1H), 3.56 (t, *J* = 6.6 Hz, 2H), 1.89-1.82 (m, 1H), 1.76-1.70 (m, 1H), 1.55-1.40 (m, 4H), 1.35-1.20 (m, 3H), 0.33 (d, *J* = 3.7 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.45, 134.9, 129.4, 127.81, 113.0, 62.9, 32.63, 32.56, 29.4, 28.91, 25.5, -7.51.

Diastereomer B: <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.54-7.48 (m, 2H), 7.39-7.31 (m, 3H), 5.63-5.57 (m, 1H), 4.91 (dd,  $J_1 = 10.3$  Hz,  $J_2 = 1.0$  Hz, 1H), 4.84 (ddd,  $J_1 = 17.1$  Hz,  $J_2 = 1.1$  Hz,  $J_3 = 1.2$  Hz 1H), 4.27-4.23 (m, 1H), 3.56 (t, J = 6.6 Hz, 2H), 1.89-1.82 (m, 1H), 1.76-1.70 (m, 1H), 1.55-1.40 (m, 4H), 1.35-1.20 (m, 3H), 0.31 (d, J = 3.7 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.44, 134.8, 129.4, 127.77, 112.9, 62.9, 32.63, 32.50, 29.2, 28.88, 25.5, -7.57. HRMS (ESI) m/z Calculated for C<sub>15</sub>H<sub>24</sub>NaOSi<sup>+</sup> [M+Na]<sup>+</sup>:271.1489, found: 271.1493

## (1-cyclohexylallyl)(methyl)(phenyl)silane as 45/55 mixture of diastereomers (3k) SiHMePh

colorless liquid (12h, 80%, 59 mg); Diastereomer A: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.54-7.49 (m, 2H), 7.38-7.30 (m, 3H), 5.71 (dt, *J*<sub>1</sub> = 17.0 Hz, *J*<sub>2</sub> = 10.3 Hz, 1H), 4.91 (dt, *J*<sub>1</sub> = 10.1 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H ), 4.81 (dd, *J*<sub>1</sub> = 17.0 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 4.45-4.40 (m, 1H), 1.82-1.56 (m, 6H), 1.52-1.42 (m, 1H), 1.20-0.90 (m, 5H), 0.33 (d, *J* = 3.7 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.9, 136.1, 135.0, 129.21, 127.73, 114.1, 40.8, 38.8, 33.7, 32.3, 26.70, 26.6, 26.43, -6.27.

Diastereomer B: <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.54-7.49 (m, 2H), 7.38-7.30 (m, 3H), 5.63 (dt,  $J_1$ = 17.0 Hz,  $J_2$  = 10.4 Hz, 1H), 4.91 (dt,  $J_1$  = 10.1 Hz,  $J_2$  = 2.4 Hz, 1H), 4.76 (dd,  $J_1$  = 17.0 Hz,  $J_2$  = 1.4 Hz, 1H), 4.45-4.40 (m, 1H), 1.82-1.56 (m, 6H), 1.52-1.42 (m, 1H), 1.20-0.90 (m, 5H), 0.31 (d, J = 3.7 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.5, 135.5, 134.8, 129.20, 127.70, 113.9, 40.4, 38.5, 33.6, 31.8, 26.68, 26.58, 26.41, -6.75. HRMS (ESI) m/z Calculated for C<sub>16</sub>H<sub>24</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>:267.1539, found:267.1546

(E)-(9-methylnonadec-10-en-9-yl)(phenyl)silane (4a)

colorless liquid (18h, 70%, 81 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.55-7.51 (m, 2H), 7.37-7.30 (m, 3H), 5.43 (d, *J* = 15.5 Hz, 1H), 5.15 (dt, *J*<sub>1</sub> = 15.6 Hz, *J*<sub>2</sub> = 6.8 Hz, 1H), 4.14 (s, 2H), 2.04-1.98 (m, 2H), 1.48-1.40 (m, 2H), 1.34-1.20 (m, 24H), 1.09 (s, 3H), 0.90-0.85 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.2, 136.0, 131.8, 129.5, 127.8, 127.7, 37.9, 33.1, 31.95, 31.92, 30.4, 30.0, 29.6, 29.5, 29.4, 29.1, 28.2, 24.2, 22.72, 22.70, 20.0, 14.1. HRMS (ESI) m/z Calculated for C<sub>26</sub>H<sub>46</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>:409.3261, found:409.3269

#### (E)-(7-methylpentadec-8-en-7-yl)(phenyl)silane (4b)



colorless liquid (12h, 73%, 72 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.55-7.51 (m, 2H), 7.37-7.30 (m, 3H), 5.43 (d, *J* = 15.5 Hz, 1H), 5.15 (dt, *J*<sub>1</sub> = 15.6 Hz, *J*<sub>2</sub> = 6.8 Hz, 1H), 4.14 (s, 2H), 2.06-1.98 (m, 2H), 1.47-1.40 (m, 2H), 1.35-1.20 (m, 16H), 1.09 (s, 3H), 0.91-0.84 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.2, 136.0, 131.8, 129.5, 127.8, 127.7, 37.9, 33.1, 31.9, 31.84, 31.80, 30.1, 29.9, 28.8, 28.2, 24.2, 22.7, 20.0, 14.14, 14.10. HRMS (ESI) m/z Calculated for C<sub>22</sub>H<sub>38</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>:353.2635, found:353.2627

#### (E)-(7-methylpentadec-8-en-7-yl)diphenylsilane (4c)

colorless liquid (24h, 70%, 85 mg); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.67-7.60 (m, 4H), 7.40-7.29 (m, 6H), 5.49 (d, *J* = 15.6 Hz, 1H), 5.17-5.08 (m, 1H), 4.64 (s, 1H), 2.07-2.00 (m, 2H), 1.53-1.48 (m, 1H), 1.35-1.15 (m, 17H), 1.13 (s, 3H), 0.89 (t, *J* = 6.6 Hz, 3H), 0.84 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>**C** 

NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.1, 136.0, 135.8, 133.8, 129.43, 129.38, 128.1, 127.7, 37.6, 33.2, 31.93, 31.87, 30.1, 30.0, 29.6, 28.9, 23.6, 22.73, 22.70, 19.6, 14.2, 14.1. HRMS (ESI) m/z Calculated for C<sub>28</sub>H<sub>42</sub>NaSi<sup>+</sup> [M+Na]<sup>+</sup>:429.2948, found:429.2940

#### (E)-(1-(4-chlorophenyl)undec-1-en-3-yl)(phenyl)silane (4d)



colorless liquid (0.5h, 83%, 92 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.56-7.52 (m, 2H), 7.42-7.37 (m, 1H), 7.36-7.32 (m, 2H), 7.25-7.21 (m, 2H), 7.21-7.17 (m, 2H), 6.19 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J*<sub>1</sub> = 15.9 Hz, *J*<sub>2</sub> = 9.0 Hz, 1H), 4.33-4.27 (m, 2H), 2.20-2.11 (m, 1H), 1.68-1.54 (m, 2H), 1.33-1.19 (m, 12H), 0.86 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.5, 135.8, 132.9, 132.1, 131.1, 129.8, 128.6, 128.0, 127.5, 126.9, 31.9, 30.6, 29.8, 29.5, 29.4, 29.3, 22.7, 14.1. HRMS (ESI) m/z Calculated for C<sub>23</sub>H<sub>31</sub>NaClSi<sup>+</sup> [M+Na]<sup>+</sup>:393.1776, found:393.1770.

#### (E)-(1-(4-chlorophenyl)undec-1-en-3-yl)diphenylsilane (4e)



colorless liquid (6h, 76%, 102 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.62-7.58 (m, 2H), 7.57-7.54 (m, 2H), 7.43-7.30 (m, 6H), 7.20 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.14 (d, J = 15.9 Hz, 1H), 6.07 (dd,  $J_1 = 15.9$  Hz,  $J_2 = 9.0$  Hz, 1H), 4.82 (d, J = 2.3 Hz, 1H), 2.41-2.34 (m, 1H), 1.74-1.65 (m, 1H), 1.62-1.55 (m, 1H), 1.48-1.39 (m, 1H), 1.30-1.17 (m, 11H), 0.85 (t, J = 6.7 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.7, 135.7, 135.6, 133.1, 132.9, 132.7, 132.0, 129.8, 129.7, 128.6, 128.0, 127.9, 127.8, 126.9, 31.9, 31.3, 30.1, 29.5, 29.41, 29.40, 29.3, 22.7, 14.1. HRMS (ESI) m/z Calculated for C<sub>29</sub>H<sub>35</sub>NaClSi<sup>+</sup> [M+Na]<sup>+</sup>:469.2089, found:469.2081.

#### (E)-(1-(4-methoxyphenyl)undec-1-en-3-yl)diphenylsilane (4f)



colorless liquid (6h, 82%, 109 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.64-7.55 (m, 4H), 7.40-7.30

(m, 6H), 7.16 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 6.17 (d, J = 15.9 Hz, 1H), 5.95 (dd,  $J_1 = 15.8$  Hz,  $J_2 = 9.4$  Hz, 1H), 4.82 (d, J = 2.4 Hz, 1H), 3.77 (s, 3H), 2.40-2.30 (m, 1H), 1.74-1.64 (m, 1H), 1.62-1.54 (m, 1H), 1.50-1.40 (m, 1H), 1.32-1.16 (m, 11H), 0.86 (t, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.5, 135.8, 135.7, 133.5, 133.2, 131.2, 129.7, 129.6, 129.5, 128.4, 128.0, 127.9, 126.8, 113.9, 55.3, 31.9, 30.9, 30.2, 29.5, 29.4, 29.3, 22.7, 14.2. **HRMS** (ESI) m/z Calculated for C<sub>30</sub>H<sub>38</sub>NaOSi<sup>+</sup> [M+Na]<sup>+</sup>:465.2584, found:465.2589

# 7. NMR spectra















































































