# **ELECTRONIC SUPPLEMENTARY INFORMATION**

# Anti-Markovnikov Terminal and *Gem*-Olefin Hydrosilylation Using a κ<sup>4</sup>-Diimine Nickel Catalyst: Selectivity for Alkene Hydrosilylation over Ether C-O Bond Cleavage

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## **Experimental**

Hydrosilylation of allyl phenyl ether using 1.0 mol% 1. Under an inert atmosphere, allyl phenyl ether (85.3  $\mu$ L, 0.621 mmol) and PhSiH<sub>3</sub> (76.5  $\mu$ L, 0.621 mmol) were combined in a 20 mL scintillation vial and added to a vial containing 1 (3.7 mg, 0.00621 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. Gas evolution was observed and <sup>1</sup>H NMR spectroscopic analysis after 24 h at ambient temperature revealed 39.4% conversion to (3-phenoxypropyl)phenylsilane along with the formation of propylene.



**Figure S1.** <sup>1</sup>H NMR spectrum for the **1**-mediated reduction of allyl phenyl ether (**C**) with PhSiH<sub>3</sub> (s at 4.23 ppm) showing (3-phenoxypropyl)phenylsilane (**A**) and propylene (**B**).

**Hydrosilylation of 1-hexene using 1.0 mol% 1.** Under an inert atmosphere, 1-hexene (105.0 μL, 0.840 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (155.9 μL, 0.840 mmol) were combined in a 20 mL scintillation vial and added to a second vial containing **1** (5.0 mg, 0.00840 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenylhexylsilane in 82% yield (184.7 mg, 0.688 mmol). Diphenylhexylsilane was isolated in similar yield (84%) and quality when a mixture of 1-hexene (92.4 μL, 0.739 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (137.2 μL, 0.739 mmol), **1** (4.4 mg, 0.00739 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.58 – 7.45 (m, 4H, *Ar*), 7.19 – 7.05 (m, 6H, *Ar*), 5.08 (t, *J* = 3.7 Hz, 1H, Si-*H*), 1.50 – 1.39 (m, 2H, - C*H*<sub>2</sub>-), 1.33-1.25 (m, 2H, -C*H*<sub>2</sub>-), 1.23 – 1.10 (m, 4H, -C*H*<sub>2</sub>-), 1.09-1.04 (s, 2H, -C*H*<sub>2</sub>-), 0.82 (t, *J* = 7.1 Hz, 3H, -C*H*<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 135.89 (*Ar*), 135.35 (*Ar*), 130.15 (*Ar*), 128.69 (*Ar*), 33.60 (-*C*H<sub>2</sub>-), 32.14 (-*C*H<sub>2</sub>-), 25.16 (-*C*H<sub>2</sub>-), 23.30 (-*C*H<sub>2</sub>-), 14.67 (-*C*H<sub>2</sub>-), 12.95 (-*C*H<sub>3</sub>). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -13.71.



**Figure S2.** <sup>1</sup>H NMR spectrum of diphenylhexylsilane in benzene-*d*<sub>6</sub>.



Figure S3. <sup>13</sup>C NMR spectrum of diphenylhexylsilane in benzene- $d_6$ .



Figure S4. DEPT135 <sup>29</sup>Si NMR spectrum of diphenylhexylsilane in benzene- $d_6$ .

**Hydrosilylation of 1-hexene using 0.1 mol% 1.** Under an inert atmosphere, 1-hexene (6.3 mL, 5.04 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (9.35 mL, 5.04 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (3.0 mg, 0.00504 mmol). The resulting red solution was then stirred for 24 h at ambient temperature, after which >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenylhexylsilane in 92% yield (1.245 g, 4.64 mmol). Diphenylhexylsilane was isolated in similar yield (90%) and quality when a mixture of 1-hexene (1.58 mL, 12.6 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (2.35 mL, 12.6 mmol), and **1** (7.5 mg, 0.0126 mmol) was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.58 (dd, *J* = 6.2, 3.0 Hz, 4H, *Ar*), 7.20 – 7.17 (m, 6H, *Ar*), 5.12 (t, *J* = 3.6 Hz, 1H, Si-*H*), 1.52 – 1.42 (m, 2H, -CH<sub>2</sub>-), 1.30 (dt, *J* = 14.5, 7.4 Hz, 2H, -CH<sub>2</sub>-), 1.26 – 1.13 (m, 4H, -CH<sub>2</sub>-), 1.12 – 1.06 (m, 2H, -CH<sub>2</sub>-), 0.85 (t, *J* = 7.1 Hz, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 135.90 (*Ar*), 135.36 (*Ar*), 130.15 (*Ar*), 128.69 (*Ar*), 33.61 (-CH<sub>2</sub>-), 32.14 (-CH<sub>2</sub>-), 25.17 (-CH<sub>2</sub>-), 23.31 (-CH<sub>2</sub>-), 14.67 (-CH<sub>2</sub>-), 12.95 (-CH<sub>3</sub>).



**Figure S5.** <sup>1</sup>H NMR spectrum of diphenylhexylsilane in benzene- $d_6$ .



Figure S6. <sup>13</sup>C NMR spectrum of diphenylhexylsilane in benzene- $d_6$ .

**Hydrosilylation of 1-hexene using 0.01 mol% 1.** Under an inert atmosphere, 1-hexene (7.17 mL, 57.1 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (10.6 mL, 57.1 mmol) were added to a 100 mL round bottom flask containing **1** (3.4 mg, 0.00571 mmol). The resulting red solution was then stirred for 72 h at ambient temperature, after which 89% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. Alternatively, 58% conversion was observed when a mixture of 1-hexene (10.3 mL, 82.3 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (15.3 mL, 82.3 mmol), and **1** (4.9 mg, 0.00823) was heated to 60 °C for 6 h.



**Figure S7.** <sup>1</sup>H NMR spectrum showing 89% conversion of 1-hexene to diphenylhexylsilane in benzene- $d_6$  at ambient temperature.



**Figure S8.** <sup>1</sup>H NMR spectrum showing 58% conversion of 1-hexene to diphenylhexylsilane in benzene- $d_6$  at 60 °C.

Hydrosilvlation of 4-methylpent-1-ene using 1.0 mol% 1. Under an inert atmosphere, 4methylpent-1-ene (80.8 µL, 0.655 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (121.6 µL, 0.655 mmol) were combined in a 20 mL scintillation vial and added to a vial containing 1 (3.9 mg, 0.00655 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (4methylpentyl)diphenylsilane in 79% yield (139.1 mg, 0.518 mmol). (4-Methylpentyl)diphenylsilane was isolated in similar yield (74%) and quality when a mixture of 4-methylpent-1-ene (64.3 µL, 0.521 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (96.7 µL, 0.521 mmol), **1** (3.1 mg, 0.00521 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene- $d_6$ ): 7.62 – 7.55 (m, 4H, Ar), 7.22 – 7.14 (m, 6H, Ar), 5.13 (t, J = 3.2 Hz, 1H, SiH), 1.56 – 1.37 (m, 3H, -CH<sub>2</sub>-, -CH-), 1.23 (dd, J = 14.9, 7.2 Hz, 2H, -CH<sub>2</sub>-), 1.13 – 1.05 (m, 2H, -CH<sub>2</sub>-), 0.82 (d, J = 6.6 Hz, 6H, -CH<sub>3</sub>). <sup>13</sup>C NMR (benzene-d<sub>6</sub>): 135.88 (Ar), 135.16 (Ar), 130.17 (Ar), 128.70 (Ar), 43.20 (-CH<sub>2</sub>-), 28.20(-CH-), 23.09 (-CH<sub>3</sub>), 22.96 (-CH<sub>2</sub>-), 13.04 (-CH<sub>2</sub>-). DEPT 135 <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): -13.74.



Figure S9. <sup>1</sup>H NMR spectrum of (4-methylpentyl)diphenylsilane in benzene- $d_6$ .



Figure S10. <sup>13</sup>C NMR spectrum of (4-methylpentyl)diphenylsilane in benzene- $d_6$ .



Figure S11. DEPT135 <sup>29</sup>Si NMR spectrum of (4-methylpentyl)diphenylsilane in benzene-*d*<sub>6</sub>.

Hydrosilvlation of 1-tridecene using 1.0 mol% 1. Under an inert atmosphere, 1-tridecene  $(104.0 \ \mu\text{L}, 0.437 \ \text{mmol})$  and Ph<sub>2</sub>SiH<sub>2</sub> (81.1 \ \mu\text{L}, 0.437 \ \text{mmol}) were combined in a 20 \ \text{mL} scintillation vial and added to a vial containing 1 (2.6 mg, 0.00437 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed via <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenyltridecylsilane in 87% yield (123.6 mg, 0.337 mmol). Diphenyltridecylsilane was isolated in similar yield (90%) and quality when a mixture of 1-tridecene (91.9 µL, 0.386 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (71.7 µL, 0.386 mmol), 1 (2.3 mg, 0.00386 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene- $d_6$ ): 7.61 – 7.53 (m, 4H, Ar), 7.21 – 7.14 (m, 6H, Ar), 5.10 (t, J = 3.7 Hz, 1H, SiH), 1.55 – 1.45 (m, 2H, - $CH_{2}$ -), 1.41 – 1.19 (m, 20H, multiple - $CH_{2}$ -), 1.15 – 1.08 (m, 2H, - $CH_{2}$ -), 0.91 (t, J = 6.8 Hz, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (benzene-d<sub>6</sub>): 135.90 (Ar), 135.35 (Ar), 130.15 (Ar), 128.69 (Ar), 34.00 (-CH<sub>2</sub>-), 32.73 (-CH<sub>2</sub>-), 30.55 (multiple -CH<sub>2</sub>-), 30.52 (-CH<sub>2</sub>-), 30.40 (-CH<sub>2</sub>-), 30.21 (-CH<sub>2</sub>-), 30.05 (-CH2-), 25.26 (-CH2-), 23.50 (-CH2-), 14.76 (-CH2-), 13.00 (-CH3). DEPT135 <sup>29</sup>Si NMR  $(\text{benzene-}d_6): -13.72.$ 



Figure S12. <sup>1</sup>H NMR spectrum of diphenyltridecylsilane in benzene- $d_6$ .



Figure S13. <sup>13</sup>C NMR spectrum of diphenyltridecylsilane in benzene- $d_6$ .



Figure S14. DEPT135<sup>29</sup>Si NMR spectrum of diphenyltridecylsilane in benzene-*d*<sub>6</sub>.

Hydrosilylation of allyl trimethylsilane using 1.0 mol% 1. Under an inert atmosphere, allyl trimethylsilane (109.0 µL, 0.689 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (127.9 µL, 0.689 mmol) were combined in a 20 mL scintillation vial and added to a vial containing 1 (4.1 mg, 0.00689 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed via <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (3-(diphenylsilyl)propyl)trimethylsilane in 81% yield (166.6 mg, 0.558 mmol). (3-(Diphenylsilyl)propyl)trimethylsilane was isolated in similar yield (78%) and quality when a mixture of allyl trimethylsilane (109.0 µL, 0.689 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (127.9 µL, 0.689 mmol), **1** (4.1 mg, 0.00689 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene- $d_6$ ): 7.56 – 7.50 (m, 4H, Ar), 7.17 - 7.01 (m, 6H, Ar), 5.09 (t, J = 3.3 Hz, 1H, Si-H), 1.62 - 1.42 (m, 2H, - $CH_{2}$ -), 1.16 (td, J = 7.9, 3.9 Hz, 2H, - $CH_{2}$ -), 0.62 – 0.52 (m, 2H, - $CH_{2}$ -), -0.12 (s, 9H, Si( $CH_{3}$ )<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>) 135.89 (*Ar*), 135.29 (*Ar*), 130.17 (*Ar*), 128.92 (*Ar*), 128.70 (*Ar*), 21.33 (-CH<sub>2</sub>-), 19.88 (-CH<sub>2</sub>-), 17.28 (-CH<sub>2</sub>-), -1.15 (Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): 0.23 (Si(CH<sub>3</sub>)<sub>3</sub>), -14.59 (Si-H).



**Figure S15.** <sup>1</sup>H NMR spectrum of (3-(diphenylsilyl)propyl)trimethylsilane in benzene- $d_6$ .



Figure S16. <sup>13</sup>C NMR spectrum of (3-(diphenylsilyl)propyl)trimethylsilane in benzene-*d*<sub>6</sub>.



Figure S17. <sup>29</sup>Si NMR spectrum of (3-(diphenylsilyl)propyl)trimethylsilane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of vinyl cyclohexane using 1.0 mol% 1.** Under an inert atmosphere, vinyl cyclohexane (75.7 μL, 0.537 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (99.7 μL, 0.537 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (3.2 mg, 0.00537 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenyl-(2-cyclohexyl)ethylsilane in 86% yield (136.2 mg, 0.462 mmol). Diphenyl-(2-cyclohexyl)ethylsilane was isolated in similar yield (85%) and quality when a mixture of vinyl cyclohexane (75.6 μL, 0.537 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (99.8 μL, 0.537 mmol), **1** (3.2 mg, 0.00537 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.62 – 7.54 (m, 4H, *Ar*), 7.23 – 7.18 (m, 6H, *Ar*), 5.10 (t, *J* = 3.6 Hz, 1H, Si-*H*), 1.73 – 1.58 (m, 5H, -C*H*<sub>2</sub>-, -C*H*-), 1.43 – 1.35 (m, 2H, -C*H*<sub>2</sub>-), 1.24 – 1.04 (m, 6H, -C*H*<sub>2</sub>-), 0.85 – 0.70 (m, 2H, -C*H*<sub>2</sub>-). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 135.89 (*Ar*), 135.36 (*Ar*), 130.16 (*Ar*), 128.69 (*Ar*), 41.11 (-CH<sub>2</sub>-), 33.51 (-CH<sub>2</sub>-), 32.63 (-CH-), 27.45 (-CH<sub>2</sub>-), 27.14 (-CH<sub>2</sub>-), 10.02 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -13.03.



**Figure S18.** <sup>1</sup>H NMR spectrum of diphenyl(2-cyclohexylethyl)silane in benzene- $d_6$ .



Figure S19. <sup>13</sup>C NMR spectrum of diphenyl(2-cyclohexylethyl)silane in benzene- $d_6$ .



Figure S20. DEPT135<sup>29</sup>Si NMR spectrum of diphenyl(2-cyclohexylethyl)silane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of allyl benzene using 1.0 mol% 1.** Under an inert atmosphere, allyl benzene (75.7 μL, 0.571 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (106.0 μL, 0.571 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (3.4 mg, 0.00571 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenyl(3-phenyl)propylsilane in 78% yield (135.2 mg, 0447 mmol). Diphenyl(3-phenyl)propylsilane was isolated in similar yield (80%) and quality when a mixture of allyl benzene (73.4 μL, 0.554 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (103.0 μL, 0.554 mmol), **1** (3.3 mg, 0.00554 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.51 (d, *J* = 5.1 Hz, 4H, *Ar*), 7.21 – 7.09 (m, 8H, *Ar*), 7.08 – 6.96 (m, 3H, *Ar*), 5.08 (t, *J* = 3.3 Hz, 1H, Si-*H*), 2.52 (t, *J* = 7.5 Hz, 2H, -CH<sub>2</sub>-), 1.76 (pseudo p, *J* = 7.8 Hz, 2H, -CH<sub>2</sub>-), 1.13 – 1.04 (m, 2H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 142.66 (*Ar*), 135.87 (*Ar*), 135.03 (*Ar*), 130.19 (*Ar*), 129.20 (*Ar*), 128.95 (*Ar*), 128.70 (*Ar*), 126.44 (*Ar*), 39.89 (-CH<sub>2</sub>-), 27.06 (-CH<sub>2</sub>-), 12.48 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -13.87.



**Figure S21.** <sup>1</sup>H NMR spectrum of diphenyl(3-phenylpropyl)silane in benzene- $d_6$ .



Figure S22. <sup>13</sup>C NMR spectrum of diphenyl(3-phenylpropyl)silane in benzene- $d_6$ .



Figure S23. DEPT135<sup>29</sup>Si NMR spectrum of diphenyl(3-phenylpropyl)silane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of styrene using 1.0 mol% 1.** Under an inert atmosphere, styrene (57.7 μL, 0.504 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (93.5 μL, 0.504 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (3.0 mg, 0.00504 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 3 h at 60 °C, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenyl(2-phenyl)ethylsilane in 85% yield (125.9 mg, 0.430 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.55 – 7.44 (m, 4H, *Ar*), 7.19 – 7.08 (m, 7H, *Ar*), 7.08 – 6.93 (m, 4H, *Ar*), 5.05 (t, *J* = 3.7 Hz, 1H, Si-*H*), 2.73 – 2.64 (m, 2H, -C*H*<sub>2</sub>-), 1.42 – 1.33 (m, 2H, -C*H*<sub>2</sub>-). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 144.87 (*Ar*), 136.39 (*Ar*), 135.89 (*Ar*), 134.81 (*Ar*), 130.26 (*Ar*), 128.98 (*Ar*), 128.74 (*Ar*), 128.57 (*Ar*), 126.39 (*Ar*), 31.18 (-CH<sub>2</sub>-), 15.04 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -14.48.



**Figure S24.** <sup>1</sup>H NMR spectrum of diphenyl(2-phenyl)ethylsilane in benzene- $d_6$ .



Figure S25. <sup>13</sup>C NMR spectrum of diphenyl(2-phenyl)ethylsilane in benzene- $d_6$ .



Figure S26. DEPT135<sup>29</sup>Si NMR spectrum of diphenyl(2-phenyl)ethylsilane in benzene-*d*<sub>6</sub>.

#### Hydrosilylation of 4-fluorostyrene using 1.0 mol% 1. Under an inert atmosphere,

4-fluorostyrene (64.0 µL, 0.537 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (99.6 µL, 0.537 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (3.2 mg, 0.00537 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 3 h at 60 °C, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenyl((4-fluoro)phenyl)ethylsilane in 71% yield (116.3 mg, 0.380 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.59 – 7.42 (m, 4H, *Ar*), 7.21 – 7.10 (m, 6H, *Ar*), 6.81 – 6.64 (m, 4H, *Ar*), 5.01 (t, *J* = 3.6 Hz, 1H, Si*H*), 2.61 – 2.45 (m, 2H, -CH<sub>2</sub>-), 1.32 – 1.17 (m, 2H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 162.06 (d, *J* = 243.0 Hz, *Ar*), 140.38 (d, *J* = 3.3 Hz, *Ar*), 135.85 (*Ar*), 134.66 (*Ar*), 130.33 (*Ar*), 129.91 (d, *J* = 7.7 Hz, *Ar*), 128.76 (*Ar*), 115.57 (d, *J* = 21.0 Hz, *Ar*), 30.28 (-CH<sub>2</sub>-), 15.03 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -13.70.



Figure S27. <sup>1</sup>H NMR spectrum of diphenyl((4-fluoro)phenyl)ethylsilane in benzene- $d_6$ .



Figure S28. <sup>13</sup>C NMR spectrum of diphenyl((4-fluoro)phenyl)ethylsilane in benzene-*d*<sub>6</sub>.



**Figure S29.** DEPT135 <sup>29</sup>Si NMR spectrum of diphenyl((4-fluoro)phenyl)ethylsilane in benzene $d_6$ .

Hydrosilylation of 4-chlorostyrene using 1.0 mol% 1. Under an inert atmosphere,

4-chlorostyrene (62.9 mg, 0.454 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (84.2 µL, 0.454 mmol) were combined in a 20 mL scintillation vial, dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub> and added to a vial containing **1** (2.7 mg, 0.00454 mmol). The resulting red solution was then transferred into a J. Young NMR tube. After 3 h at 60 °C, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenyl((4-chloro)phenyl)ethylsilane in 48% yield (70.4 mg, 0.218 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.52 – 7.42 (m, 4H, *Ar*), 7.20 - 7.10 (m, 6H, *Ar*), 7.05 (d, *J* = 8.3 Hz, 2H, *Ar*), 6.63 (d, *J* = 8.3 Hz, 2H, *Ar*), 4.99 (t, *J* = 3.6 Hz, 1H, SiH), 2.55 – 2.42 (m, 2H, -CH<sub>2</sub>-), 1.26 – 1.17 (m, 2H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 143.21 (*Ar*), 135.85 (*Ar*), 134.58 (*Ar*), 132.11 (*Ar*), 130.36 (*Ar*), 129.93 (*Ar*), 129.00 (*Ar*), 128.78 (*Ar*), 30.42 (-CH<sub>2</sub>-), 14.80 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -14.21.



Figure S30. <sup>1</sup>H NMR spectrum of diphenyl((4-chloro)phenyl)ethylsilane in benzene- $d_6$ .



Figure S31. <sup>13</sup>C NMR spectrum of diphenyl((4-chloro)phenyl)ethylsilane in benzene-*d*<sub>6</sub>.



**Figure S32.** DEPT135 <sup>29</sup>Si NMR spectrum of diphenyl((4-fluoro)phenyl)ethylsilane in benzene $d_6$ .

Hydrosilylation of 4-methylstyrene using 1.0 mol% 1. Under an inert atmosphere, 4methylstyrene (73.0  $\mu$ L, 0.554 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (102.9  $\mu$ L, 0.554 mmol) were combined in a 20 mL scintillation vial and added to a vial containing 1 (3.3 mg, 0.00554 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenyl((4-

methyl)phenyl)ethylsilane in 92% yield (154.0 mg, 0.509 mmol). <sup>1</sup>H NMR (benzene- $d_6$ ): 7.58 – 7.47 (m, 4H, Ar), 7.23 – 7.12 (m, 6H, Ar), 7.00 – 6.95 (m, 4H, Ar), 5.08 (dd, J = 6.9, 3.3 Hz, 1H, Si-H), 2.79 – 2.66 (m, 2H, -C $H_2$ -), 2.15 (s, 3H, -C $H_3$ ), 1.43 (m, J = 12.0, 5.2, 3.7 Hz, 2H, -C $H_2$ -). <sup>13</sup>C NMR (benzene- $d_6$ ): 141.87 (Ar), 135.91 (Ar), 135.49 (Ar), 134.91 (Ar), 130.22 (Ar), 129.68 (Ar), 128.73 (Ar), 128.53 (Ar), 30.80, (-C $H_2$ -), 21.42 (-C $H_3$ ), 15.17 (-C $H_2$ -). DEPT135 <sup>29</sup>Si NMR (benzene- $d_6$ ): -14.11.



Figure S33. <sup>1</sup>H NMR spectrum of diphenyl((4-methyl)phenyl)ethylsilane in benzene-*d*<sub>6</sub>.



Figure S34. <sup>13</sup>C NMR spectrum of diphenyl((4-methyl)phenyl)ethylsilane in benzene- $d_6$ .



**Figure S35.** DEPT135 <sup>29</sup>Si NMR spectrum of diphenyl((4-methyl)phenyl)ethylsilane in benzene- $d_6$ .

**Hydrosilylation of 4***-tert*-**butylstyrene using 1.0 mol% 1.** Under an inert atmosphere, 4-*tert*-butylstyrene (113.8 µL, 0.621 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (115.3 µL, 0.621 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (3.7 mg, 0.00621 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 3 h at 60 °C, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenyl((4-*t*-butyl)phenyl)ethylsilane in 75% yield (160.5 mg, 0.466 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.54 – 7.47 (m, 4H, *Ar*), 7.23 (d, *J* = 8.2 Hz, 2H, *Ar*), 7.19 – 7.12 (m, 6H, *Ar*), 7.03 (d, *J* = 8.2 Hz, 2H, *Ar*), 5.08 (t, *J* = 3.5 Hz, 1H, SiH), 2.77 – 2.70 (m, 2H, -CH<sub>2</sub>-), 1.46 – 1.40 (m, 2H, -CH<sub>2</sub>-), 1.23 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 148.88 (*Ar*), 141.88 (*Ar*), 135.91 (*Ar*), 134.90 (*Ar*), 130.22 (*Ar*), 128.73 (*Ar*), 128.35 (*Ar*), 125.86 (*Ar*), 34.74 (-C(CH<sub>3</sub>)<sub>3</sub>), 31.98 (-C(CH<sub>3</sub>)<sub>3</sub>), 30.73 (-CH<sub>2</sub>-), 15.20 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -14.07.



Figure S36. <sup>1</sup>H NMR spectrum of diphenyl((4-t-butyl)phenyl)ethylsilane in benzene- $d_6$ .



**Figure S37.** <sup>13</sup>C NMR spectrum of diphenyl((4-*t*-butyl)phenyl)ethylsilane in benzene-*d*<sub>6</sub>.

![](_page_26_Figure_2.jpeg)

**Figure S38.** DEPT135 <sup>29</sup>Si NMR spectrum of diphenyl((4-*t*-butyl)phenyl)ethylsilane in benzene $d_6$ .

Hydrosilylation of allyl benzyl ether using 1.0 mol% 1. Under an inert atmosphere, allyl benzyl ether (86.0  $\mu$ L, 0.554 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (103.0  $\mu$ L, 0.554 mmol) were combined in a 20 mL scintillation vial and added to a vial containing 1 (3.3 mg, 0.00554 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed via <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (3-(benzyloxy)propyl)diphenylsilane in 84% yield (107.8 mg, 0.324 mmol). (3-(Benzyloxy)propyl)diphenylsilane was isolated in similar yield (81%) and quality when a mixture of allyl benzyl ether (101.6 µL, 0.655 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (121.6 µL, 0.655 mmol), **1** (3.9 mg, 0.00655 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene- $d_6$ ): 7.51 (dt, J = 10.3, 4.8 Hz, 4H, Ar), 7.29 – 7.23 (m, 2H, Ar), 7.18 – 7.11 (m, 8H, Ar), 7.07 (t, J = 7.3 Hz, 1H, Ar), 5.07 (t, J = 3.6 Hz, 1H, Si-H), 4.27 (s, 2H,  $CH_{2}$ -), 3.26 (t, J = 6.4 Hz, 2H,  $CH_{2}$ -), 1.81 – 1.68 (m, 2H,  $CH_{2}$ -), 1.19 – 1.11 (m, 2H,  $CH_{2}$ -). <sup>13</sup>C NMR (benzene-d<sub>6</sub>): 139.80 (Ar), 135.88 (Ar), 135.03 (Ar), 130.19 (Ar), 128.87 (Ar), 128.70 (Ar), 128.08 (Ar), 127.90 (Ar), 73.22 (-CH<sub>2</sub>-), 72.91 (-CH<sub>2</sub>-), 25.53 (-CH<sub>2</sub>-), 9.29 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene- $d_6$ ): -13.52.

![](_page_27_Figure_1.jpeg)

Figure S39. <sup>1</sup>H NMR spectrum of (3-(benzyloxy)propyl)diphenylsilane in benzene- $d_6$ .

![](_page_28_Figure_0.jpeg)

Figure S40. <sup>13</sup>C NMR spectrum of (3-(benzyloxy)propyl)diphenylsilane in benzene- $d_6$ .

![](_page_28_Figure_2.jpeg)

**Figure S41.** DEPT135 <sup>29</sup>Si NMR spectrum of (3-(benzyloxy)propyl)diphenylsilane in benzene $d_6$ .

Hydrosilylation of allyl (2-bromophenyl)methyl ether using 1.0 mol% 1. Under an inert atmosphere, allyl (2-bromophenyl)methyl ether (97.7 µL, 0.571 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (106.0 µL, 0.571 mmol) were combined in a 20 mL scintillation vial and added to a vial containing 1 (3.4 mg, 0.00571 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed via<sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (3-((2-bromobenzyl)oxy)propyl)diphenylsilane in 65% yield (151.9 mg, 0.369 mmol). (3-((2-Bromobenzyl)oxy)propyl)diphenylsilane was isolated in similar yield (76%) and quality when a mixture of allyl (2-bromophenyl)methyl ether (89.2 µL, 0.521 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (96.7 µL, 0.521 mmol), 1 (3.1 mg, 0.00521 mmol), and 0.6 mL  $C_6D_6$  was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene- $d_6$ ): 7.57 – 7.52 (m, 4H, Ar), 7.48 (d, J = 7.5 Hz, 1H, Ar), 7.34 (d, J = 7.9 Hz, 1H, Ar), 7.17 (s, 6H, Ar), 6.98 (t, J = 7.4 Hz, 1H, Ar), 6.72 (t, J = 7.3 Hz, 1H, Ar), 5.08 (t, J = 3.5 Hz, 1H, Si-*H*), 4.43 (s, 2H, -C*H*<sub>2</sub>-), 3.28 (t, *J* = 6.4 Hz, 2H, -C*H*<sub>2</sub>-), 1.75 (p, *J* = 6.4 Hz, 2H, -C*H*<sub>2</sub>-), 1.22 -1.11 (m, 2H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (benzene-d<sub>6</sub>): 138.38 (Ar), 135.17 (Ar), 134.27 (Ar), 132.18 (Ar), 129.51 (Ar), 128.69 (Ar), 128.43 (Ar), 128.01 (Ar), 127.13 (Ar), 122.22 (Ar), 72.70 (-CH<sub>2</sub>-), 71.80 (-CH<sub>2</sub>-), 24.75 (-CH<sub>2</sub>-), 8.54 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): -13.51.

![](_page_30_Figure_0.jpeg)

Figure S42. <sup>1</sup>H NMR spectrum of (3-((2-bromobenzyl)oxy)propyl)diphenylsilane in benzene-*d*<sub>6</sub>.

![](_page_30_Figure_2.jpeg)

**Figure S43.** <sup>13</sup>C NMR spectrum of (3-((2-bromobenzyl)oxy)propyl)diphenylsilane in benzene-*d*<sub>6</sub>.

![](_page_31_Figure_0.jpeg)

**Figure S44.** DEPT135 <sup>29</sup>Si NMR spectrum of (3-((2-bromobenzyl)oxy)propyl)diphenylsilane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of allyl methyl ether using 1.0 mol% 1.** Under an inert atmosphere, allyl methyl ether (39.4 μL, 0.420 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (78.0 μL, 0.420 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (2.5 mg, 0.00420 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (3-methoxypropyl)diphenylsilane in 74% yield (79.9 mg, 0.312 mmol). (3-Methoxypropyl)diphenylsilane was isolated in similar yield (77%) and quality when a mixture of allyl methyl ether (39.4 μL, 0.420 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (78.0 μL, 0.420 mmol), **1** (2.5 mg, 0.00420 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.57 – 7.51 (m, 4H, *Ar*), 7.16 (m, 6H, *Ar*), 5.08 (t, *J* = 3.6 Hz, 1H, Si-*H*), 3.15 (t, *J* = 6.3 Hz, 2H, -OCH<sub>2</sub>-), 3.07 (s, 3H, -OCH<sub>3</sub>), 1.76 – 1.66 (m, 2H, -CH<sub>2</sub>-), 1.19 – 1.12 (m, 2H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 135.87 (*Ar*), 135.13 (*Ar*), 130.16 (*Ar*), 128.68 (*Ar*), 75.15 (-OCH<sub>2</sub>-), 58.51 (-OCH<sub>3</sub>), 25.36 (-CH<sub>2</sub>-), 9.28 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -13.51.

![](_page_32_Figure_0.jpeg)

**Figure S45.** <sup>1</sup>H NMR spectrum of (3-methoxypropyl)diphenylsilane in benzene-*d*<sub>6</sub>.

![](_page_32_Figure_2.jpeg)

Figure S46. <sup>13</sup>C NMR spectrum of (3-methoxypropyl)diphenylsilane in benzene- $d_6$ .

![](_page_33_Figure_0.jpeg)

Figure S47. DEPT135 <sup>29</sup>Si NMR spectrum of (3-methoxypropyl)diphenylsilane in benzene- $d_6$ .

**Hydrosilylation of allyl ethyl ether using 1.0 mol% 1.** Under an inert atmosphere, allyl ethyl ether (62.8 μL, 0.554 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (103.0 μL, 0.554 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (3.3 mg, 0.00554 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (3-ethoxypropyl)diphenylsilane in 63% yield (93.6 mg, 0.346 mmol). (3-Ethoxypropyl)diphenylsilane was isolated in similar yield (69%) and quality when a mixture of allyl ethyl ether (59.0 μL, 0.521 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (96.7 μL, 0.521 mmol), **1** (3.1 mg, 0.00521 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.55-7.50 (m, 4H, *Ar*), 7.18 – 7.11 (m, 6H, *Ar*), 5.06 (t, *J* = 3.8 Hz, 1H, Si-*H*), 3.25-3.18 (m, 4H, -*CH*<sub>2</sub>-), 1.75-1.67 (m, 2H, -*CH*<sub>2</sub>-), 1.18-1.12 (m, 2H, -*CH*<sub>2</sub>-), 1.07 (t, *J* = 7.0 Hz, 3H, -*CH*<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 135.89 (*Ar*), 135.15 (*Ar*), 130.16 (*Ar*), 128.68 (*Ar*), 73.18 (-*C*H<sub>2</sub>-), 66.46 (-*C*H<sub>2</sub>-), 25.63 (-*C*H<sub>2</sub>-), 15.91 (-*C*H<sub>2</sub>-), 9.40 (-*C*H<sub>3</sub>). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -13.49.

![](_page_34_Figure_0.jpeg)

**Figure S48.** <sup>1</sup>H NMR spectrum of (3-ethoxypropyl)diphenylsilane in benzene-*d*<sub>6</sub>.

![](_page_34_Figure_2.jpeg)

**Figure S49.** <sup>13</sup>C NMR spectrum of (3-ethoxypropyl)diphenylsilane in benzene- $d_6$ .

![](_page_35_Figure_0.jpeg)

Figure S50. DEPT135<sup>29</sup>Si NMR spectrum of (3-ethoxypropyl)diphenylsilane in benzene-*d*<sub>6</sub>.

Hydrosilylation of allyl glycidyl ether using 1.0 mol% 1. Under an inert atmosphere, allyl glycidyl ether (71.7  $\mu$ L, 0.605 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (112.0  $\mu$ L, 0.605 mmol) were combined in a 20 mL scintillation vial and added to a vial containing 1 (3.6 mg, 0.00605 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed via <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (3-(oxiran-2ylmethoxy)propyl)diphenylsilane in 78% yield (141.5 mg, 0473 mmol). (3-(Oxiran-2ylmethoxy)propyl)diphenylsilane was isolated in similar yield (77%) and quality when a mixture of allyl glycidyl ether (77.7  $\mu$ L, 0.0.655 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (121.6  $\mu$ L, 0.655 mmol), **1** (3.9 mg, 0.00655 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene- $d_6$ ): 7.53 – 7.48 (m, 4H, Ar), 7.14 (m, 6H, Ar), 5.03 (t, J = 3.6 Hz, 1H, Si-H), 3.32 - 3.24 (m, 2H, -CH<sub>2</sub>-), 3.21 (dt, J = 9.1, 6.4 Hz, 1H, -CH<sub>2</sub>-), 3.01 (dd, J = 11.4, 5.9 Hz, 1H, -CH<sub>2</sub>-), 2.79 (ddt, J = 5.9, 3.9, 2.9 Hz, 1H, -CH-), 2.26 (dd, J = 5.1, 4.3 Hz, 1H, -CH<sub>2</sub>-), 2.13 (dd, J = 5.2, 2.5 Hz, 1H, -CH<sub>2</sub>-), 1.67 (tt, J = 12.6, 6.4 Hz, 2H, -CH<sub>2</sub>-), 1.17 – 1.06 (m, 2H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (benzene- $d_6$ ): 135.86 (Ar), 135.02 (Ar), 130.20 (Ar), 128.71 (Ar), 73.86 (-CH<sub>2</sub>-), 72.21 (-CH<sub>2</sub>-), 51.07(-CH-), 43.96 (-CH<sub>2</sub>-), 25.47 (-CH<sub>2</sub>-), 9.18 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): -13.50.

![](_page_36_Figure_1.jpeg)

Figure S51. <sup>1</sup>H NMR spectrum of (3-(xiran-2-ylmethoxy)propyl)diphenylsilane in benzene-d<sub>6</sub>.

![](_page_37_Figure_0.jpeg)

Figure S52. <sup>13</sup>C NMR spectrum of (3-(oxiran-2-ylmethoxy)propyl)diphenylsilane in benzene-*d*<sub>6</sub>.

![](_page_37_Figure_2.jpeg)

**Figure S53.** DEPT135 <sup>29</sup>Si NMR spectrum of (3-(oxiran-2-ylmethoxy)propyl)diphenylsilane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of allyl trimethylsilyl ether using 1.0 mol% 1.** Under an inert atmosphere, allyl trimethylsilyl ether (96.6 μL, 0.588 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (109.1 μL, 0.588 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (3.5 mg, 0.00588 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (2-(diphenylsilyl)ethoxy)trimethylsilane in 88% yield (163.1 mg, 0.512 mmol). (2-(Diphenylsilyl)ethoxy)trimethylsilane was isolated in similar yield (84%) and quality when a mixture of allyl trimethylsilyl ether (121.7 μL, 0.722 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (134.0 μL, 0.722 mmol), **1** (4.3 mg, 0.00722 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.61 – 7.42 (m, 4H, *Ar*), 7.20 – 7.05 (m, 6H, *Ar*), 5.06 (t, *J* = 3.6 Hz, 1H, Si-*H*), 3.45 (t, *J* = 6.4 Hz, 2H, -CH<sub>2</sub>-), 1.69 (tt, *J* = 13.0, 6.5 Hz, 2H, -CH<sub>2</sub>-), 1.15 – 1.09 (m, 2H, -CH<sub>2</sub>-), 0.06 (s, 9H, -Si(CH<sub>3</sub>)a). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 135.89 (*Ar*), 135.09 (*Ar*), 130.18 (*Ar*), 128.69 (*Ar*), 65.20 (-

(*Si*(CH<sub>3</sub>)<sub>3</sub>), -13.48 (*Si*-H).

![](_page_38_Figure_2.jpeg)

CH2-), 28.41 (-CH2-), 8.92 (-CH2-), 0.07 (-Si(CH3)3). <sup>29</sup>Si NMR (benzene-d6): 15.49

Figure S54. <sup>1</sup>H NMR spectrum of (3-(diphenylsilyl)propoxy)trimethylsilane in benzene- $d_6$ .

![](_page_39_Figure_0.jpeg)

**Figure S55.** <sup>13</sup>C NMR spectrum of (3-(diphenylsilyl)propoxy)trimethylsilane in benzene-*d*<sub>6</sub>.

![](_page_39_Figure_2.jpeg)

Figure S56. <sup>29</sup>Si NMR spectrum of (3-(diphenylsilyl)propoxy)trimethylsilane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of vinyl phenyl ether using 1.0 mol% 1.** Under an inert atmosphere, vinyl phenyl ether (81.0  $\mu$ L, 0.454 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (84.2  $\mu$ L, 0.454 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (2.7 mg, 0.00454 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (2-phenoxyethyl)diphenylsilane in 74% yield (102.4 mg, 0.336 mmol). (2-Phenoxyethyl)diphenylsilane was isolated in similar yield (71%) and quality when a mixture of vinyl phenyl ether (45.5  $\mu$ L, 0.370 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (68.7  $\mu$ L, 0.370 mmol), **1** (2.2 mg, 0.00370 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.50 – 7.43 (m, 4H, *Ar*), 7.14 – 7.06 (m, 6H, *Ar*), 7.06 – 7.00 (m, 2H, *Ar*), 6.76 (dd, *J* = 10.6, 4.1 Hz, 1H, *Ar*), 6.71 (dt, *J* = 3.3, 1.8 Hz, 2H, *Ar*), 5.08 (t, *J* = 3.6 Hz, 1H, Si*H*), 3.88 (t, *J* = 7.8 Hz, 2H, -C*H*<sub>2</sub>-), 1.55 (dt, *J* = 8.1, 3.6 Hz, 2H, -C*H*<sub>2</sub>-). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 159.64 (*Ar*), 135.87 (*Ar*), 130.38 (*Ar*), 130.04 (*Ar*), 128.76 (*Ar*), 121.17 (*Ar*), 115.25 (*Ar*), 65.16 (-CH<sub>2</sub>-), 14.41 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -17.09.

![](_page_40_Figure_1.jpeg)

Figure S57. <sup>1</sup>H NMR spectrum of (2-phenoxyethyl)diphenylsilane in benzene- $d_6$ .

![](_page_41_Figure_0.jpeg)

Figure S58. <sup>13</sup>C NMR spectrum of (2-phenoxyethyl)diphenylsilane in benzene-*d*<sub>6</sub>.

![](_page_41_Figure_2.jpeg)

Figure S59. DEPT135<sup>29</sup>Si NMR spectrum of (2-phenoxyethyl)diphenylsilane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of vinyl isobutyl ether using 1.0 mol% 1.** Under an inert atmosphere, vinyl isobutyl ether (59.1 μL, 0.454 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (84.3 μL, 0.454 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (2.7 mg, 0.00621 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (2-isobutoxyethyl)diphenylsilane in 76% yield (98.1 mg, 0.345 mmol). (2-Isobutoxyethyl)diphenylsilane was isolated in similar yield (73%) and quality when a mixture of isobutyl vinyl ether (59.1 μL, 0.454 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (84.3 μL, 0.454 mmol), **1** (2.7 mg, 0.00454 mmol), and 0.6 mL C<sub>6</sub>D<sub>6</sub> was heated to 60 °C for 1 h. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.60 – 7.55 (m, 4H, *Ar*), 7.20 – 7.16 (m, 6H, *Ar*), 5.15 (t, *J* = 3.6 Hz, 1H, Si-*H*), 3.52 (t, *J* = 7.6 Hz, 2H, -CH<sub>2</sub>-), 2.97 (d, *J* = 6.5 Hz, 2H, -CH<sub>2</sub>-), 1.79 (sep, *J* = 6.8 Hz, 1H, - CH-), 1.53 (td, *J* = 15.9, 8.0 Hz, 2H, -CH<sub>2</sub>-), 0.88 (d, *J* = 6.8 Hz, 6H, -CH<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 135.95 (*Ar*), 134.90 (*Ar*), 130.17 (*Ar*), 128.65 (*Ar*), 77.97 (-CH<sub>2</sub>-), 68.13 (-CH<sub>2</sub>-), 29.33 (-CH-), 20.04 (-CH<sub>3</sub>), 15.00 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -16.34.

![](_page_42_Figure_1.jpeg)

**Figure S60.** <sup>1</sup>H NMR spectrum of (2-isobutoxyethyl)diphenylsilane in benzene-*d*<sub>6</sub>.

![](_page_43_Figure_0.jpeg)

Figure S61. <sup>13</sup>C NMR spectrum of (2-isobutoxyethyl)diphenylsilane in benzene- $d_6$ .

![](_page_43_Figure_2.jpeg)

Figure S62. DEPT135<sup>29</sup>Si NMR spectrum of (2-isobutoxyethyl)diphenylsilane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of vinyl acetate using 1.0 mol% 1.** Under an inert atmosphere, vinyl acetate (48.2  $\mu$ L, 0.521 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (96.6  $\mu$ L, 0.521 mmol) were combined in a 20 mL scintillation vial and added to a vial containing **1** (3.1 mg, 0.00521 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. After 24 h at ambient temperature, 86% conversion was observed via <sup>1</sup>H NMR spectroscopy to a mixture of 2-(diphenylsilyl)ethyl acetate, diphenyl silyl diacetate, and diphenyl silyl acetate.

![](_page_44_Figure_1.jpeg)

**Figure S63.** <sup>1</sup>H NMR spectrum showing the hydrosilylation of vinyl acetate with  $Ph_2SiH_2$  in benzene- $d_6$ .

Hydrosilylation of α-methylstyrene using 1.0 mol% 1: Under an inert atmosphere, αmethylstyrene (74.3 µL, 0.571 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (132.5 µL, 0.714 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing 1 (3.4 mg, 0.00571 mmol) dissolved in 0.6 mL C<sub>6</sub>D<sub>6</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenyl(2-phenylpropyl)silane as a mixture of enantiomers in 85% yield (147.1 mg, 0.486 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.50 – 7.43 (m, 4H, *Ar*), 7.17 – 7.09 (m, 7H, *Ar*), 7.06 – 7.00 (m, 4H, *Ar*), 4.98 (t, *J* = 4.0 Hz, 1H, Si*H*), 2.96 – 2.86 (m, 1H, -C*H*-), 1.54 – 1.36 (m, 2H, -C*H*<sub>2</sub>-), 1.23 (d, *J* = 6.9 Hz, 3H, -C*H*<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 149.53 (*Ar*), 136.57 (*Ar*), 135.87 (*Ar*), 135.80 (*Ar*), 130.43 (*Ar*), 130.15 (*Ar*), 130.11 (*Ar*), 129.03 (*Ar*), 128.77 (*Ar*), 128.67 (*Ar*), 128.66 (*Ar*), 127.30 (*Ar*), 126.63 (*Ar*), 36.99 (-CH-), 25.87 (-CH<sub>3</sub>), 23.27 (-CH<sub>2</sub>). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -15.93.

![](_page_45_Figure_1.jpeg)

**Figure S64.** <sup>1</sup>H NMR spectrum of diphenyl(2-phenylpropyl)silane in benzene- $d_6$ .

![](_page_46_Figure_0.jpeg)

Figure S65. <sup>13</sup>C NMR spectrum of diphenyl(2-phenylpropyl)silane in benzene- $d_6$ .

![](_page_46_Figure_2.jpeg)

Figure S66. DEPT135<sup>29</sup>Si NMR spectrum of diphenyl(2-phenylpropyl)silane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of \alpha-methylstyrene using 0.1 mol% 1**: Under an inert atmosphere,  $\alpha$ methylstyrene (0.7 mL, 5.37 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (1.25 mL, 6.71 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing **1** (3.2 mg, 0.00537 mmol). The resulting red solution was transferred into a 100 mL thick walled glass bomb and heated to 70 °C for 7 d, after which 74% conversion was observed *via* <sup>1</sup>H NMR spectroscopy.

![](_page_47_Figure_1.jpeg)

**Figure S67.** <sup>1</sup>H NMR spectrum showing partial hydrosilylation of  $\alpha$ -methyl-styrene in benzene*d*<sub>6</sub>.

**Hydrosilylation of 4-fluoro-α-methylstyrene using 1.0 mol% 1**: Under an inert atmosphere, 4-fluoro-α-methylstyrene (84.4 µL, 0.605 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (140.3 µL, 0.765 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing **1** (3.6 mg, 0.00605 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which >99% conversion was observed via <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain 2-(4-fluorophenylpropyl)diphenylsilane as a mixture of enantiomers in 91% yield (177.0 mg, 0.552 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.50 – 7.41 (m, 4H, *Ar*), 7.22 – 7.08 (m, 6H, *Ar*), 6.80 – 6.75 (m, 4H, *Ar*), 4.93 (t, *J* = 4.0 Hz, 1H, Si*H*), 2.89 – 2.74 (m, 1H, -C*H*-), 1.45 – 1.28 (m, 2H, -C*H*<sub>2</sub>-), 1.16 (d, *J* = 6.9 Hz, 3H, -C*H*<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 162.06 (d, *J* = 243.2 Hz, *Ar*), 145.01 (d, *J* = 3.1 Hz, *Ar*), 136.56 (*Ar*), 135.82 (*Ar*), 135.75 (*Ar*), 130.22 (*Ar*), 130.17 (*Ar*), 128.72 (*Ar*), 128.72 (*Ar*), 128.67 (*Ar*), 128.64 (*Ar*), 115.63 (d, *J* = 20.9, *Ar*), 36.26 (-CH-), 25.99 (-CH<sub>3</sub>), 23.31 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -15.73.

![](_page_48_Figure_1.jpeg)

**Figure S68.** <sup>1</sup>H NMR spectrum of 2-(4-fluorophenylpropyl)diphenylsilane in benzene-*d*<sub>6</sub>.

![](_page_49_Figure_0.jpeg)

Figure S69. <sup>13</sup>C NMR spectrum of 2-(4-fluorophenylpropyl)diphenylsilane in benzene- $d_6$ .

![](_page_49_Figure_2.jpeg)

**Figure S70.** DEPT135 <sup>29</sup>Si NMR spectrum of 2-(4-fluorophenylpropyl)diphenylsilane in benzene- $d_6$ .

Hydrosilylation of 4-chloro-α-methylstyrene using 1.0 mol% 1: Under an inert atmosphere, 4-chloro-α-methylstyrene (76.3 µL, 0.537 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (124.6 µL, 0.671 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing 1 (3.2 mg, 0.00537 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting green solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which 69% olefin hydrosilylation was observed *via* <sup>1</sup>H NMR spectroscopy. Additionally, dechlorination of the aromatic ring and consumption of Ph<sub>2</sub>SiH<sub>2</sub> to form Ph<sub>2</sub>HSiCl was observed. The ratio of products is 3:2 (2phenylpropyl)diphenylsilane:(2-(4-chlorophenyl)propyl)diphenylsilane.

![](_page_50_Figure_1.jpeg)

**Figure S71.** <sup>1</sup>H NMR spectrum showing the conversion of 4-chloro- $\alpha$ -methylstyrene in benzene- $d_6$ .

Hydrosilylation of 4,*α*-dimethylstyrene using 1.0 mol% 1: Under an inert atmosphere, 4,*α*-dimethylstyrene (63.7 µL, 0.437 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (101.4 µL, 0.546 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing 1 (2.6 mg, 0.00437 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (2-(4methylphenyl)propyl)diphenylsilane as a mixture of enantiomers in 98% yield (125.4 mg, 0.396 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.63 – 7.53 (m, 1H, *Ar*), 7.51 – 7.43 (m, 3H, *Ar*), 7.18 – 7.02 (m, 7H, *Ar*), 6.99 – 6.93 (m, 3H, *Ar*), 4.98 (t, *J* = 3.9 Hz, 1H, -Si*H*), 2.92 (sextet, *J* = 7.0 Hz, 1H, -*CH*-), 2.12 (s, 3H, -*CH*<sub>3</sub>)), 1.56 – 1.38 (m, 2H, -*CH*<sub>2</sub>-), 1.25 (d, *J* = 6.9 Hz, 3H, -*CH*<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): δ 146.54 (*Ar*), 136.58 (*Ar*), 135.90 (*Ar*), 135.82 (*Ar*), 135.72 (*Ar*), 135.43 (*Ar*), 135.26 (*Ar*), 135.09 (*Ar*), 130.89 (*Ar*), 130.42 (*Ar*), 130.11 (*Ar*), 130.04 (*Ar*), 129.69 (*Ar*), 128.77 (*Ar*), 128.65 (*Ar*), 128.62 (*Ar*), 127.25 (*Ar*), 36.64 (-*C*H<sub>3</sub>), 26.09 (-*C*H-), 23.39 (-*C*H<sub>3</sub>), 21.42 (-*C*H<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -15.63.

![](_page_51_Figure_1.jpeg)

**Figure S72.** <sup>1</sup>H NMR spectrum of diphenyl(2-(4-methylphenyl)propyl)silane in benzene-*d*<sub>6</sub>.

![](_page_52_Figure_0.jpeg)

Figure S73. <sup>13</sup>C NMR spectrum of diphenyl(2-(4-methylphenyl)propyl)silane in benzene- $d_6$ .

![](_page_52_Figure_2.jpeg)

**Figure S74.** DEPT135 <sup>29</sup>Si NMR spectrum of diphenyl(2-(4-methylphenyl)propyl)silane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of 4-methoxy-α-methylstyrene using 1.0 mol% 1**: Under an inert atmosphere, 4-methoxy-α-methylstyrene (67.2 mg, 0.454 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (105.3 µL, 0.568 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing **1** (2.7 mg, 0.00454 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain diphenyl(2-(4-methoxyphenyl)propyl)silane as a mixture of enantiomers in 85% yield (127.7 mg, 0.384 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.51 – 7.45 (m, 4H, *Ar*), 7.18 – 7.07 (m, 6H, *Ar*), 6.97 – 6.92 (m, 2H, *Ar*), 6.76 – 6.72 (m, 2H, *Ar*), 4.98 (t, *J* = 3.9 Hz, 1H, Si*H*), 3.32 (s, 3H, -OC*H*<sub>3</sub>), 2.91 (sextet, *J* = 7.1 Hz, 1H, -C*H*-), 1.54 – 1.38 (m, 2H, -C*H*<sub>2</sub>-), 1.25 (d, *J* = 6.9 Hz, 3H, -C*H*<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 158.89 (*Ar*), 141.45 (*Ar*), 136.57 (*Ar*), 135.90 (*Ar*), 135.81 (*Ar*), 130.12 (*Ar*), 130.06 (*Ar*), 128.67 (*Ar*), 128.63 (*Ar*), 128.19 (*Ar*), 114.50 (*Ar*), 55.16 (-OCH<sub>3</sub>), 36.25 (-CH-), 26.33 (-CH<sub>3</sub>), 23.54 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -15.91.

![](_page_53_Figure_1.jpeg)

**Figure S75.** <sup>1</sup>H NMR spectrum of diphenyl(2-(4-methoxyphenyl)propyl)silane in benzene-*d*<sub>6</sub>.

![](_page_54_Figure_0.jpeg)

Figure S76. <sup>13</sup>C NMR spectrum of diphenyl(2-(4-methoxyphenyl)propyl)silane in benzene- $d_6$ .

![](_page_54_Figure_2.jpeg)

**Figure S77.** DEPT135 <sup>29</sup>Si NMR spectrum of diphenyl(2-(4-methoxyphenyl)propyl)silane in benzene-*d*<sub>6</sub>.

**Hydrosilylation of 4-**(*N*,*N*-dimethylamino)-α-methylstyrene using 1.0 mol% 1: Under an inert atmosphere, 4-(*N*,*N*-dimethylamino)-α-methylstyrene (78.5 mg, 0.487 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (113.0 µL, 0.609 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing **1** (2.9 mg, 0.00487 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds removed under reduced pressure to obtain diphenyl(2-(4-(*N*,*N*-dimethylamino))phenyl)propyl)silane as a mixture of enantiomers in 60% yield (100.5 mg, 0.290 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.60 – 7.48 (m, 4H, *Ar*), 7.20 – 7.12 (m, 6H, *Ar*), 7.09 – 7.04 (m, 2H, *Ar*), 6.65 – 6.58 (m, 2H, *Ar*), 5.05 (t, *J* = 4.0 Hz, 1H, Si*H*), 3.07 – 2.93 (m, 1H, -C*H*-), 2.55 (s, 6H, -N(C*H*<sub>3</sub>)<sub>2</sub>), 1.66 – 1.46 (m, 2H, -C*H*<sub>2</sub>-), 1.34 (d, *J* = 6.9 Hz, 3H, -C*H*<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 149.99 (*Ar*), 137.72 (*Ar*), 136.57 (*Ar*), 135.95 (*Ar*), 135.86 (*Ar*), 130.04 (*Ar*), 129.97 (*Ar*), 128.64 (*Ar*), 127.87 (*Ar*), 113.79 (*Ar*), 41.03 (N(CH<sub>3</sub>)<sub>2</sub>), 36.16 (-CH-), 26.49 (-CH<sub>3</sub>), 23.68 (-CH<sub>2</sub>-). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): - 15.87.

![](_page_55_Figure_1.jpeg)

**Figure S78.** <sup>1</sup>H NMR spectrum of diphenyl(2-(4-(N,N-dimethylamino)phenyl)propyl)silane in benzene- $d_6$ .

![](_page_56_Figure_0.jpeg)

**Figure S79.** <sup>13</sup>C NMR spectrum of diphenyl(2-(4-(N,N-dimethylamino)phenyl)propyl)silane in benzene- $d_6$ .

![](_page_56_Figure_2.jpeg)

**Figure S80.** DEPT135 <sup>29</sup>Si NMR spectrum of diphenyl(2-(4-(*N*,*N*-dimethylamino)phenyl)propyl)silane in benzene-*d*<sub>6</sub>.

### Hydrosilylation of 2-methyloctene using 1.0 mol% 1: Under an inert atmosphere,

2-methyloctene (61.5 µL, 0.386 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (89.6 µL, 0.483 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing **1** (2.3 mg, 0.00386 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain (2-methyloctyl)diphenylsilane as a mixture of enantiomers in 78% yield (93.1 mg, 0.300 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.72 – 7.40 (m, 4H, *Ar*), 7.27 – 6.99 (m, 6H, *Ar*), 5.19 (t, *J* = 4.2 Hz, 1H, Si-*H*), 1.74 (m, *J* = 12.0, 8.1, 6.5 Hz, 1H, -C*H*-), 1.49 – 1.12 (m, 10H, -C*H*<sub>2</sub>-), 0.99 (d, *J* = 6.6 Hz, 3H, -C*H*<sub>3</sub>), 0.89 (t, *J* = 7.0 Hz, 3H, -C*H*<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 136.80 (*Ar*), 135.88 (*Ar*), 135.85 (*Ar*), 130.11 (*Ar*), 130.09 (*Ar*), 128.69 (*Ar*), 128.67 (*Ar*), 40.83 (-CH<sub>2</sub>-), 21.47 (-CH<sub>2</sub>-), 30.44 (-CH<sub>2</sub>-), 30.25 (-CH<sub>2</sub>-), 27.72 (-CH<sub>2</sub>-), 23.45 (-CH<sub>3</sub>), 23.28 (-CH<sub>2</sub>-), 21.47 (-CH<sub>2</sub>-), 14.74 (-CH<sub>3</sub>). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -15.56.

![](_page_57_Figure_2.jpeg)

Figure S81. <sup>1</sup>H NMR spectrum of (2-methyloctyl)diphenylsilane in benzene- $d_6$ .

![](_page_58_Figure_0.jpeg)

Figure S82. <sup>13</sup>C NMR spectrum of (2-methyloctyl)diphenylsilane in benzene- $d_6$ .

![](_page_58_Figure_2.jpeg)

Figure S83. DEPT135<sup>29</sup>Si NMR spectrum of (2-methyloctyl)diphenylsilane in benzene-*d*<sub>6</sub>.

Hydrosilylation of D-limonene using 1.0 mol% 1: Under an inert atmosphere, D-limonene (76.1 µL, 0.470 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (109.0 µL, 0.588 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing 1 (2.8 mg, 0.00470 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which >99% conversion was observed via <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain ((rac)-2-((R)-4-methylcyclohex-3en-1-yl)propyl)diphenylsilane as a mixture of diastereomers in 76% yield (114.9 mg, 0.358 mmol). <sup>1</sup>H NMR (benzene- $d_6$ ): 7.58 – 7.51 (m, 4H, Ar), 7.18 – 7.09 (m, 6H, Ar), 5.38 (s, 1H, =CH), 5.15 (m, 1H, SiH), 1.93 – 1.79 (m, 3H, -CH-, -CH<sub>2</sub>-), 1.79 – 1.62 (m, 3H, -CH-, -CH<sub>2</sub>-), 1.61 (s, 3H), 1.59 – 1.50 (m, 1H, -CH-), 1.43 – 1.33 (m, 1H, -CH-), 1.32 – 1.24 (m, 1H, -CH-), 1.22 - 1.10 (m, 1H, -CH-), 0.98 - 0.93 (m, 1H, -CH-), 0.91 (d, J = 2.5 Hz, 3H, -CH<sub>3</sub>), 0.90 (d, J $= 2.5 \text{ Hz}, 3\text{H}, -CH_3$ . <sup>13</sup>C NMR (benzene- $d_6$ ): 136.58 (Ar), 135.91 (Ar), 135.90 (Ar), 135.82 (Ar), 135.80 (Ar), 135.48 (Ar), 133.96 (Ar), 133.95 (Ar), 130.42 (Ar), 130.15 (Ar), 130.10 (Ar), 130.09 (Ar), 128.71 (Ar), 128.67 (Ar), 128.67 (Ar), 121.86 (=CH), 121.82 (=CH), 41.62 (-CH-), 41.56 (-CH-), 34.69 (-CH<sub>2</sub>-), 34.53 (-CH<sub>2</sub>-), 31.58 (-CH<sub>2</sub>-), 31.50 (-CH<sub>2</sub>-), 29.44 (-CH<sub>2</sub>-), 28.63 (-CH<sub>2</sub>-), 27.38 (-CH<sub>2</sub>-), 26.21 (-CH<sub>2</sub>-), 24.10 (-CH<sub>3</sub>), 24.09 (-CH<sub>3</sub>), 19.76 (=CCH<sub>3</sub>), 19.36 (=CCH<sub>3</sub>), 18.33 (-CH<sub>2</sub>Si-), 17.83 (-CH<sub>2</sub>Si-). DEPT135 <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): -14.64, -14.93.

![](_page_60_Figure_0.jpeg)

**Figure S84.** <sup>1</sup>H NMR spectrum of ((rac)-2-((R)-4-methylcyclohex-3-en-1-yl)propyl)diphenylsilane in benzene-*d*<sub>6</sub>.

![](_page_60_Figure_2.jpeg)

**Figure S85.** <sup>13</sup>C NMR spectrum of ((*rac*)-2-((R)-4-methylcyclohex-3-en-1-yl)propyl)diphenylsilane in benzene- $d_6$ .

![](_page_61_Figure_0.jpeg)

**Figure S86.** DEPT135 <sup>29</sup>Si NMR spectrum of ((*rac*)-2-((R)-4-methylcyclohex-3-en-1-yl)propyl)diphenylsilane in benzene- $d_6$ .

**Hydrosilylation of methyl methacrylate using 1.0 mol% 1**: Under an inert atmosphere, methyl methacrylate (66.2 µL, 0.621 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (144.0 µL, 0.776 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing **1** (3.7 mg, 0.00621 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which >99% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure to obtain methyl 3-(diphenylsilyl)-2-methylpropanoate in 64% yield (113.2 mg, 0.378 mmol). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.51 – 7.46 (m, 4H, *Ar*), 7.16 – 7.05 (m, 6H, *Ar*), 5.05 (t, *J* = 3.9 Hz, 1H, Si*H*), 3.21 (s, 3H, -OC*H*<sub>3</sub>), 2.59 (h, *J* = 7.1 Hz, 1H, -C*H*-), 1.65 – 1.57 (m, 1H, -C*H*-), 1.23 – 1.18 (m, 1H, -C*H*-), 1.11 (d, *J* = 7.0 Hz, 3H, -C*H*<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 176.92 (*C*=O), 135.90 (*Ar*), 135.83 (*Ar*), 130.29 (*Ar*), 130.26 (*Ar*), 128.72 (*Ar*), 128.70 (*Ar*), 51.39 (-OCH<sub>3</sub>), 36.33 (-CH-), 20.49 (-CH<sub>2</sub>-), 18.13 (-CH<sub>3</sub>). DEPT135 <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>): -15.85.

![](_page_62_Figure_0.jpeg)

Figure S87. <sup>1</sup>H NMR spectrum of methyl 3-(diphenylsilyl)-2-methylpropanoate in benzene-*d*<sub>6</sub>.

![](_page_62_Figure_2.jpeg)

Figure S88. <sup>13</sup>C NMR spectrum of methyl 3-(diphenylsilyl)-2-methylpropanoate in benzene-*d*<sub>6</sub>.

![](_page_63_Figure_0.jpeg)

**Figure S89.** DEPT135 <sup>29</sup>Si NMR spectrum of methyl 3-(diphenylsilyl)-2-methylpropanoate in benzene- $d_6$ .

**Hydrosilylation of 1,1-diphenylethene using 1.0 mol% 1**: Under an inert atmosphere, 1,1diphenylethene (73.9  $\mu$ L, 0.420 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (97.4  $\mu$ L, 0.525 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing **1** (2.5 mg, 0.00420 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which 38% conversion was observed *via* <sup>1</sup>H NMR spectroscopy.

![](_page_64_Figure_1.jpeg)

**Figure S90.** <sup>1</sup>H NMR spectrum showing partial hydrosilylation of 1,1-diphenyl ethene in benzene-*d*<sub>6</sub>.

Attempted hydrosilylation of 1,1-dicyclohexylethene using 1.0 mol% 1: Under an inert atmosphere, 1,1-dicyclohexylethene (86.5  $\mu$ L, 0.403 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (93.5  $\mu$ L, 0.504 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing 1 (2.4 mg, 0.00403 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which no conversion was observed *via* <sup>1</sup>H NMR spectroscopy.

**Dechlorination of chlorobenzene with 1.0 mol% 1.** Under an inert atmosphere, chlorobenzene (49.4  $\mu$ L, 0.487 mmol) and Ph<sub>2</sub>SiH<sub>2</sub> (113.0  $\mu$ L, 0.609 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing **1** (2.9 mg, 0.00487 mmol) dissolved in 0.6 mL toluene-*d*<sub>8</sub>. The resulting red solution was transferred into a J. Young NMR tube and heated to 70 °C for 7 d, after which time 67% conversion was observed *via* <sup>1</sup>H NMR spectroscopy. Products were identified as benzene and Ph<sub>2</sub>SiHCl.

![](_page_65_Figure_2.jpeg)

Figure S91. <sup>1</sup>H NMR showing partial dechlorination of chlorobenzene in toluene- $d_8$ .

![](_page_66_Figure_0.jpeg)

Figure S92. <sup>31</sup>P NMR spectrum of 1 with 100 equivalents of PhSiH<sub>3</sub> after 24 h at 25 °C.

![](_page_66_Figure_2.jpeg)

Figure S93. <sup>31</sup>P NMR spectrum of 1 with 100 equivalents of Ph<sub>2</sub>SiH<sub>2</sub> after 24 h at 25 °C.

![](_page_67_Figure_0.jpeg)

**Figure S94.** <sup>31</sup>P NMR spectra of **1**-mediated 1-hexene hydrosilylation with Ph<sub>2</sub>SiH<sub>2</sub> after 1 h (top), 5 h (middle), and 24 h (bottom).