ELECTRONIC SUPPLEMENTARY INFORMATION

Anti-Markovnikov Terminal and *Gem*-Olefin Hydrosilylation Using a κ⁴-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 μ L, 0.621 mmol) and PhSiH₃ (76.5 μ 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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. Gas evolution was observed and ¹H 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. ¹H NMR spectrum for the **1**-mediated reduction of allyl phenyl ether (**C**) with PhSiH₃ (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 Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* ¹H 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), Ph₂SiH₂ (137.2 μL, 0.739 mmol), **1** (4.4 mg, 0.00739 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H NMR (benzene-*d*₆): 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*₂-), 1.33-1.25 (m, 2H, -C*H*₂-), 1.23 – 1.10 (m, 4H, -C*H*₂-), 1.09-1.04 (s, 2H, -C*H*₂-), 0.82 (t, *J* = 7.1 Hz, 3H, -C*H*₃). ¹³C NMR (benzene-*d*₆): 135.89 (*Ar*), 135.35 (*Ar*), 130.15 (*Ar*), 128.69 (*Ar*), 33.60 (-*C*H₂-), 32.14 (-*C*H₂-), 25.16 (-*C*H₂-), 23.30 (-*C*H₂-), 14.67 (-*C*H₂-), 12.95 (-*C*H₃). DEPT135 ²⁹Si NMR (benzene-*d*₆): -13.71.



Figure S2. ¹H NMR spectrum of diphenylhexylsilane in benzene-*d*₆.



Figure S3. ¹³C NMR spectrum of diphenylhexylsilane in benzene- d_6 .



Figure S4. DEPT135 ²⁹Si 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 Ph₂SiH₂ (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* ¹H 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), Ph₂SiH₂ (2.35 mL, 12.6 mmol), and **1** (7.5 mg, 0.0126 mmol) was heated to 60 °C for 1 h. ¹H NMR (benzene-*d*₆): 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, -CH₂-), 1.30 (dt, *J* = 14.5, 7.4 Hz, 2H, -CH₂-), 1.26 – 1.13 (m, 4H, -CH₂-), 1.12 – 1.06 (m, 2H, -CH₂-), 0.85 (t, *J* = 7.1 Hz, 3H, -CH₃). ¹³C NMR (benzene-*d*₆): 135.90 (*Ar*), 135.36 (*Ar*), 130.15 (*Ar*), 128.69 (*Ar*), 33.61 (-CH₂-), 32.14 (-CH₂-), 25.17 (-CH₂-), 23.31 (-CH₂-), 14.67 (-CH₂-), 12.95 (-CH₃).



Figure S5. ¹H NMR spectrum of diphenylhexylsilane in benzene- d_6 .



Figure S6. ¹³C 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 Ph₂SiH₂ (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* ¹H NMR spectroscopy. Alternatively, 58% conversion was observed when a mixture of 1-hexene (10.3 mL, 82.3 mmol), Ph₂SiH₂ (15.3 mL, 82.3 mmol), and **1** (4.9 mg, 0.00823) was heated to 60 °C for 6 h.



Figure S7. ¹H NMR spectrum showing 89% conversion of 1-hexene to diphenylhexylsilane in benzene- d_6 at ambient temperature.



Figure S8. ¹H 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 Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* ¹H 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), Ph₂SiH₂ (96.7 µL, 0.521 mmol), **1** (3.1 mg, 0.00521 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H 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, -CH₂-, -CH-), 1.23 (dd, J = 14.9, 7.2 Hz, 2H, -CH₂-), 1.13 – 1.05 (m, 2H, -CH₂-), 0.82 (d, J = 6.6 Hz, 6H, -CH₃). ¹³C NMR (benzene-d₆): 135.88 (Ar), 135.16 (Ar), 130.17 (Ar), 128.70 (Ar), 43.20 (-CH₂-), 28.20(-CH-), 23.09 (-CH₃), 22.96 (-CH₂-), 13.04 (-CH₂-). DEPT 135 ²⁹Si NMR (benzene-d₆): -13.74.



Figure S9. ¹H NMR spectrum of (4-methylpentyl)diphenylsilane in benzene- d_6 .



Figure S10. ¹³C NMR spectrum of (4-methylpentyl)diphenylsilane in benzene- d_6 .



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

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 Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed via ¹H 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), Ph₂SiH₂ (71.7 µL, 0.386 mmol), 1 (2.3 mg, 0.00386 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H 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, -CH₃). ¹³C NMR (benzene-d₆): 135.90 (Ar), 135.35 (Ar), 130.15 (Ar), 128.69 (Ar), 34.00 (-CH₂-), 32.73 (-CH₂-), 30.55 (multiple -CH₂-), 30.52 (-CH₂-), 30.40 (-CH₂-), 30.21 (-CH₂-), 30.05 (-CH2-), 25.26 (-CH2-), 23.50 (-CH2-), 14.76 (-CH2-), 13.00 (-CH3). DEPT135 ²⁹Si NMR $(\text{benzene-}d_6): -13.72.$



Figure S12. ¹H NMR spectrum of diphenyltridecylsilane in benzene- d_6 .



Figure S13. ¹³C NMR spectrum of diphenyltridecylsilane in benzene- d_6 .



Figure S14. DEPT135²⁹Si NMR spectrum of diphenyltridecylsilane in benzene-*d*₆.

Hydrosilylation of allyl trimethylsilane using 1.0 mol% 1. Under an inert atmosphere, allyl trimethylsilane (109.0 µL, 0.689 mmol) and Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed via ¹H 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), Ph₂SiH₂ (127.9 µL, 0.689 mmol), **1** (4.1 mg, 0.00689 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H 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})₃). ¹³C NMR (benzene-*d*₆) 135.89 (*Ar*), 135.29 (*Ar*), 130.17 (*Ar*), 128.92 (*Ar*), 128.70 (*Ar*), 21.33 (-CH₂-), 19.88 (-CH₂-), 17.28 (-CH₂-), -1.15 (Si(CH₃)₃). ²⁹Si NMR (benzene-d₆): 0.23 (Si(CH₃)₃), -14.59 (Si-H).



Figure S15. ¹H NMR spectrum of (3-(diphenylsilyl)propyl)trimethylsilane in benzene- d_6 .



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



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

Hydrosilylation of vinyl cyclohexane using 1.0 mol% 1. Under an inert atmosphere, vinyl cyclohexane (75.7 μL, 0.537 mmol) and Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* ¹H 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), Ph₂SiH₂ (99.8 μL, 0.537 mmol), **1** (3.2 mg, 0.00537 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H NMR (benzene-*d*₆): 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*₂-, -C*H*-), 1.43 – 1.35 (m, 2H, -C*H*₂-), 1.24 – 1.04 (m, 6H, -C*H*₂-), 0.85 – 0.70 (m, 2H, -C*H*₂-). ¹³C NMR (benzene-*d*₆): 135.89 (*Ar*), 135.36 (*Ar*), 130.16 (*Ar*), 128.69 (*Ar*), 41.11 (-CH₂-), 33.51 (-CH₂-), 32.63 (-CH-), 27.45 (-CH₂-), 27.14 (-CH₂-), 10.02 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -13.03.



Figure S18. ¹H NMR spectrum of diphenyl(2-cyclohexylethyl)silane in benzene- d_6 .



Figure S19. ¹³C NMR spectrum of diphenyl(2-cyclohexylethyl)silane in benzene- d_6 .



Figure S20. DEPT135²⁹Si NMR spectrum of diphenyl(2-cyclohexylethyl)silane in benzene-*d*₆.

Hydrosilylation of allyl benzene using 1.0 mol% 1. Under an inert atmosphere, allyl benzene (75.7 μL, 0.571 mmol) and Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* ¹H 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), Ph₂SiH₂ (103.0 μL, 0.554 mmol), **1** (3.3 mg, 0.00554 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H NMR (benzene-*d*₆): 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, -CH₂-), 1.76 (pseudo p, *J* = 7.8 Hz, 2H, -CH₂-), 1.13 – 1.04 (m, 2H, -CH₂-). ¹³C NMR (benzene-*d*₆): 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 (-CH₂-), 27.06 (-CH₂-), 12.48 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -13.87.



Figure S21. ¹H NMR spectrum of diphenyl(3-phenylpropyl)silane in benzene- d_6 .



Figure S22. ¹³C NMR spectrum of diphenyl(3-phenylpropyl)silane in benzene- d_6 .



Figure S23. DEPT135²⁹Si NMR spectrum of diphenyl(3-phenylpropyl)silane in benzene-*d*₆.

Hydrosilylation of styrene using 1.0 mol% 1. Under an inert atmosphere, styrene (57.7 μL, 0.504 mmol) and Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 3 h at 60 °C, >99% conversion was observed *via* ¹H 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). ¹H NMR (benzene-*d*₆): 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*₂-), 1.42 – 1.33 (m, 2H, -C*H*₂-). ¹³C NMR (benzene-*d*₆): 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 (-CH₂-), 15.04 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -14.48.



Figure S24. ¹H NMR spectrum of diphenyl(2-phenyl)ethylsilane in benzene- d_6 .



Figure S25. ¹³C NMR spectrum of diphenyl(2-phenyl)ethylsilane in benzene- d_6 .



Figure S26. DEPT135²⁹Si NMR spectrum of diphenyl(2-phenyl)ethylsilane in benzene-*d*₆.

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

4-fluorostyrene (64.0 µL, 0.537 mmol) and Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 3 h at 60 °C, >99% conversion was observed *via* ¹H 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). ¹H NMR (benzene-*d*₆): 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, -CH₂-), 1.32 – 1.17 (m, 2H, -CH₂-). ¹³C NMR (benzene-*d*₆): 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 (-CH₂-), 15.03 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -13.70.



Figure S27. ¹H NMR spectrum of diphenyl((4-fluoro)phenyl)ethylsilane in benzene- d_6 .



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



Figure S29. DEPT135 ²⁹Si 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 Ph₂SiH₂ (84.2 µL, 0.454 mmol) were combined in a 20 mL scintillation vial, dissolved in 0.6 mL of C₆D₆ 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* ¹H 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). ¹H NMR (benzene-*d*₆): 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, -CH₂-), 1.26 – 1.17 (m, 2H, -CH₂-). ¹³C NMR (benzene-*d*₆): 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 (-CH₂-), 14.80 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -14.21.



Figure S30. ¹H NMR spectrum of diphenyl((4-chloro)phenyl)ethylsilane in benzene- d_6 .



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



Figure S32. DEPT135 ²⁹Si 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 μ L, 0.554 mmol) and Ph₂SiH₂ (102.9 μ 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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* ¹H 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). ¹H 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 -). ¹³C 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 ²⁹Si NMR (benzene- d_6): -14.11.



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



Figure S34. ¹³C NMR spectrum of diphenyl((4-methyl)phenyl)ethylsilane in benzene- d_6 .



Figure S35. DEPT135 ²⁹Si 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 Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 3 h at 60 °C, >99% conversion was observed *via* ¹H 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). ¹H NMR (benzene-*d*₆): 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, -CH₂-), 1.46 – 1.40 (m, 2H, -CH₂-), 1.23 (s, 9H, -C(CH₃)₃). ¹³C NMR (benzene-*d*₆): 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(CH₃)₃), 31.98 (-C(CH₃)₃), 30.73 (-CH₂-), 15.20 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -14.07.



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



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



Figure S38. DEPT135 ²⁹Si 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 μ L, 0.554 mmol) and Ph₂SiH₂ (103.0 μ 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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed via ¹H 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), Ph₂SiH₂ (121.6 µL, 0.655 mmol), **1** (3.9 mg, 0.00655 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H 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} -). ¹³C NMR (benzene-d₆): 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 (-CH₂-), 72.91 (-CH₂-), 25.53 (-CH₂-), 9.29 (-CH₂-). DEPT135 ²⁹Si NMR (benzene- d_6): -13.52.



Figure S39. ¹H NMR spectrum of (3-(benzyloxy)propyl)diphenylsilane in benzene- d_6 .



Figure S40. ¹³C NMR spectrum of (3-(benzyloxy)propyl)diphenylsilane in benzene- d_6 .



Figure S41. DEPT135 ²⁹Si 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 Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed via¹H 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), Ph₂SiH₂ (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. ¹H 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*₂-), 3.28 (t, *J* = 6.4 Hz, 2H, -C*H*₂-), 1.75 (p, *J* = 6.4 Hz, 2H, -C*H*₂-), 1.22 -1.11 (m, 2H, -CH₂-). ¹³C NMR (benzene-d₆): 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 (-CH₂-), 71.80 (-CH₂-), 24.75 (-CH₂-), 8.54 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-d₆): -13.51.



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



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



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

Hydrosilylation of allyl methyl ether using 1.0 mol% 1. Under an inert atmosphere, allyl methyl ether (39.4 μL, 0.420 mmol) and Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* ¹H 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), Ph₂SiH₂ (78.0 μL, 0.420 mmol), **1** (2.5 mg, 0.00420 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H NMR (benzene-*d*₆): 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, -OCH₂-), 3.07 (s, 3H, -OCH₃), 1.76 – 1.66 (m, 2H, -CH₂-), 1.19 – 1.12 (m, 2H, -CH₂-). ¹³C NMR (benzene-*d*₆): 135.87 (*Ar*), 135.13 (*Ar*), 130.16 (*Ar*), 128.68 (*Ar*), 75.15 (-OCH₂-), 58.51 (-OCH₃), 25.36 (-CH₂-), 9.28 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -13.51.



Figure S45. ¹H NMR spectrum of (3-methoxypropyl)diphenylsilane in benzene-*d*₆.



Figure S46. ¹³C NMR spectrum of (3-methoxypropyl)diphenylsilane in benzene- d_6 .



Figure S47. DEPT135 ²⁹Si 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 Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* ¹H 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), Ph₂SiH₂ (96.7 μL, 0.521 mmol), **1** (3.1 mg, 0.00521 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H NMR (benzene-*d*₆): 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*₂-), 1.75-1.67 (m, 2H, -*CH*₂-), 1.18-1.12 (m, 2H, -*CH*₂-), 1.07 (t, *J* = 7.0 Hz, 3H, -*CH*₃). ¹³C NMR (benzene-*d*₆): 135.89 (*Ar*), 135.15 (*Ar*), 130.16 (*Ar*), 128.68 (*Ar*), 73.18 (-*C*H₂-), 66.46 (-*C*H₂-), 25.63 (-*C*H₂-), 15.91 (-*C*H₂-), 9.40 (-*C*H₃). DEPT135 ²⁹Si NMR (benzene-*d*₆): -13.49.



Figure S48. ¹H NMR spectrum of (3-ethoxypropyl)diphenylsilane in benzene-*d*₆.



Figure S49. ¹³C NMR spectrum of (3-ethoxypropyl)diphenylsilane in benzene- d_6 .



Figure S50. DEPT135²⁹Si NMR spectrum of (3-ethoxypropyl)diphenylsilane in benzene-*d*₆.

Hydrosilylation of allyl glycidyl ether using 1.0 mol% 1. Under an inert atmosphere, allyl glycidyl ether (71.7 μ L, 0.605 mmol) and Ph₂SiH₂ (112.0 μ 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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed via ¹H 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 μ L, 0.0.655 mmol), Ph₂SiH₂ (121.6 μ L, 0.655 mmol), **1** (3.9 mg, 0.00655 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H 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, -CH₂-), 3.21 (dt, J = 9.1, 6.4 Hz, 1H, -CH₂-), 3.01 (dd, J = 11.4, 5.9 Hz, 1H, -CH₂-), 2.79 (ddt, J = 5.9, 3.9, 2.9 Hz, 1H, -CH-), 2.26 (dd, J = 5.1, 4.3 Hz, 1H, -CH₂-), 2.13 (dd, J = 5.2, 2.5 Hz, 1H, -CH₂-), 1.67 (tt, J = 12.6, 6.4 Hz, 2H, -CH₂-), 1.17 – 1.06 (m, 2H, -CH₂-). ¹³C NMR (benzene- d_6): 135.86 (Ar), 135.02 (Ar), 130.20 (Ar), 128.71 (Ar), 73.86 (-CH₂-), 72.21 (-CH₂-), 51.07(-CH-), 43.96 (-CH₂-), 25.47 (-CH₂-), 9.18 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-d₆): -13.50.



Figure S51. ¹H NMR spectrum of (3-(xiran-2-ylmethoxy)propyl)diphenylsilane in benzene-d₆.



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



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

Hydrosilylation of allyl trimethylsilyl ether using 1.0 mol% 1. Under an inert atmosphere, allyl trimethylsilyl ether (96.6 μL, 0.588 mmol) and Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* ¹H 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), Ph₂SiH₂ (134.0 μL, 0.722 mmol), **1** (4.3 mg, 0.00722 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H NMR (benzene-*d*₆): 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, -CH₂-), 1.69 (tt, *J* = 13.0, 6.5 Hz, 2H, -CH₂-), 1.15 – 1.09 (m, 2H, -CH₂-), 0.06 (s, 9H, -Si(CH₃)a). ¹³C NMR (benzene-*d*₆): 135.89 (*Ar*), 135.09 (*Ar*), 130.18 (*Ar*), 128.69 (*Ar*), 65.20 (-

(*Si*(CH₃)₃), -13.48 (*Si*-H).



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

Figure S54. ¹H NMR spectrum of (3-(diphenylsilyl)propoxy)trimethylsilane in benzene- d_6 .



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



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

Hydrosilylation of vinyl phenyl ether using 1.0 mol% 1. Under an inert atmosphere, vinyl phenyl ether (81.0 μ L, 0.454 mmol) and Ph₂SiH₂ (84.2 μ 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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* ¹H 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 μ L, 0.370 mmol), Ph₂SiH₂ (68.7 μ L, 0.370 mmol), **1** (2.2 mg, 0.00370 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H NMR (benzene-*d*₆): 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*₂-), 1.55 (dt, *J* = 8.1, 3.6 Hz, 2H, -C*H*₂-). ¹³C NMR (benzene-*d*₆): 159.64 (*Ar*), 135.87 (*Ar*), 130.38 (*Ar*), 130.04 (*Ar*), 128.76 (*Ar*), 121.17 (*Ar*), 115.25 (*Ar*), 65.16 (-CH₂-), 14.41 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -17.09.



Figure S57. ¹H NMR spectrum of (2-phenoxyethyl)diphenylsilane in benzene- d_6 .



Figure S58. ¹³C NMR spectrum of (2-phenoxyethyl)diphenylsilane in benzene-*d*₆.



Figure S59. DEPT135²⁹Si NMR spectrum of (2-phenoxyethyl)diphenylsilane in benzene-*d*₆.

Hydrosilylation of vinyl isobutyl ether using 1.0 mol% 1. Under an inert atmosphere, vinyl isobutyl ether (59.1 μL, 0.454 mmol) and Ph₂SiH₂ (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 C₆D₆. The resulting red solution was then transferred into a J. Young NMR tube. After 24 h at ambient temperature, >99% conversion was observed *via* ¹H 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), Ph₂SiH₂ (84.3 μL, 0.454 mmol), **1** (2.7 mg, 0.00454 mmol), and 0.6 mL C₆D₆ was heated to 60 °C for 1 h. ¹H NMR (benzene-*d*₆): 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, -CH₂-), 2.97 (d, *J* = 6.5 Hz, 2H, -CH₂-), 1.79 (sep, *J* = 6.8 Hz, 1H, - CH-), 1.53 (td, *J* = 15.9, 8.0 Hz, 2H, -CH₂-), 0.88 (d, *J* = 6.8 Hz, 6H, -CH₃). ¹³C NMR (benzene-*d*₆): 135.95 (*Ar*), 134.90 (*Ar*), 130.17 (*Ar*), 128.65 (*Ar*), 77.97 (-CH₂-), 68.13 (-CH₂-), 29.33 (-CH-), 20.04 (-CH₃), 15.00 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -16.34.



Figure S60. ¹H NMR spectrum of (2-isobutoxyethyl)diphenylsilane in benzene-*d*₆.



Figure S61. ¹³C NMR spectrum of (2-isobutoxyethyl)diphenylsilane in benzene- d_6 .



Figure S62. DEPT135²⁹Si NMR spectrum of (2-isobutoxyethyl)diphenylsilane in benzene-*d*₆.

Hydrosilylation of vinyl acetate using 1.0 mol% 1. Under an inert atmosphere, vinyl acetate (48.2 μ L, 0.521 mmol) and Ph₂SiH₂ (96.6 μ 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 C₆D₆. After 24 h at ambient temperature, 86% conversion was observed via ¹H NMR spectroscopy to a mixture of 2-(diphenylsilyl)ethyl acetate, diphenyl silyl diacetate, and diphenyl silyl acetate.



Figure S63. ¹H 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 Ph₂SiH₂ (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 C₆D₆. 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* ¹H 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). ¹H NMR (benzene-*d*₆): 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*₂-), 1.23 (d, *J* = 6.9 Hz, 3H, -C*H*₃). ¹³C NMR (benzene-*d*₆): 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 (-CH₃), 23.27 (-CH₂). DEPT135 ²⁹Si NMR (benzene-*d*₆): -15.93.



Figure S64. ¹H NMR spectrum of diphenyl(2-phenylpropyl)silane in benzene- d_6 .



Figure S65. ¹³C NMR spectrum of diphenyl(2-phenylpropyl)silane in benzene- d_6 .



Figure S66. DEPT135²⁹Si NMR spectrum of diphenyl(2-phenylpropyl)silane in benzene-*d*₆.

Hydrosilylation of \alpha-methylstyrene using 0.1 mol% 1: Under an inert atmosphere, α methylstyrene (0.7 mL, 5.37 mmol) and Ph₂SiH₂ (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* ¹H NMR spectroscopy.



Figure S67. ¹H NMR spectrum showing partial hydrosilylation of α -methyl-styrene in benzene*d*₆.

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 Ph₂SiH₂ (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 C₆D₆. 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 ¹H 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). ¹H NMR (benzene-*d*₆): 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*₂-), 1.16 (d, *J* = 6.9 Hz, 3H, -C*H*₃). ¹³C NMR (benzene-*d*₆): 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 (-CH₃), 23.31 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -15.73.



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



Figure S69. ¹³C NMR spectrum of 2-(4-fluorophenylpropyl)diphenylsilane in benzene- d_6 .



Figure S70. DEPT135 ²⁹Si 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 Ph₂SiH₂ (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 C₆D₆. 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* ¹H NMR spectroscopy. Additionally, dechlorination of the aromatic ring and consumption of Ph₂SiH₂ to form Ph₂HSiCl was observed. The ratio of products is 3:2 (2phenylpropyl)diphenylsilane:(2-(4-chlorophenyl)propyl)diphenylsilane.



Figure S71. ¹H NMR spectrum showing the conversion of 4-chloro- α -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 Ph₂SiH₂ (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 C₆D₆. 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* ¹H 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). ¹H NMR (benzene-*d*₆): 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*₃)), 1.56 – 1.38 (m, 2H, -*CH*₂-), 1.25 (d, *J* = 6.9 Hz, 3H, -*CH*₃). ¹³C NMR (benzene-*d*₆): 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*H₃), 26.09 (-*C*H-), 23.39 (-*C*H₃), 21.42 (-*C*H₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -15.63.



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



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



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

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 Ph₂SiH₂ (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 C₆D₆. 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* ¹H 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). ¹H NMR (benzene-*d*₆): 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*₃), 2.91 (sextet, *J* = 7.1 Hz, 1H, -C*H*-), 1.54 – 1.38 (m, 2H, -C*H*₂-), 1.25 (d, *J* = 6.9 Hz, 3H, -C*H*₃). ¹³C NMR (benzene-*d*₆): 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 (-OCH₃), 36.25 (-CH-), 26.33 (-CH₃), 23.54 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): -15.91.



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



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



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

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 Ph₂SiH₂ (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 C₆D₆. 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* ¹H 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). ¹H NMR (benzene-*d*₆): 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*₃)₂), 1.66 – 1.46 (m, 2H, -C*H*₂-), 1.34 (d, *J* = 6.9 Hz, 3H, -C*H*₃). ¹³C NMR (benzene-*d*₆): 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(CH₃)₂), 36.16 (-CH-), 26.49 (-CH₃), 23.68 (-CH₂-). DEPT135 ²⁹Si NMR (benzene-*d*₆): - 15.87.



Figure S78. ¹H NMR spectrum of diphenyl(2-(4-(N,N-dimethylamino)phenyl)propyl)silane in benzene- d_6 .



Figure S79. ¹³C NMR spectrum of diphenyl(2-(4-(N,N-dimethylamino)phenyl)propyl)silane in benzene- d_6 .



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

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

2-methyloctene (61.5 µL, 0.386 mmol) and Ph₂SiH₂ (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 C₆D₆. 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* ¹H 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). ¹H NMR (benzene-*d*₆): 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*₂-), 0.99 (d, *J* = 6.6 Hz, 3H, -C*H*₃), 0.89 (t, *J* = 7.0 Hz, 3H, -C*H*₃). ¹³C NMR (benzene-*d*₆): 136.80 (*Ar*), 135.88 (*Ar*), 135.85 (*Ar*), 130.11 (*Ar*), 130.09 (*Ar*), 128.69 (*Ar*), 128.67 (*Ar*), 40.83 (-CH₂-), 21.47 (-CH₂-), 30.44 (-CH₂-), 30.25 (-CH₂-), 27.72 (-CH₂-), 23.45 (-CH₃), 23.28 (-CH₂-), 21.47 (-CH₂-), 14.74 (-CH₃). DEPT135 ²⁹Si NMR (benzene-*d*₆): -15.56.



Figure S81. ¹H NMR spectrum of (2-methyloctyl)diphenylsilane in benzene- d_6 .



Figure S82. ¹³C NMR spectrum of (2-methyloctyl)diphenylsilane in benzene- d_6 .



Figure S83. DEPT135²⁹Si NMR spectrum of (2-methyloctyl)diphenylsilane in benzene-*d*₆.

Hydrosilylation of D-limonene using 1.0 mol% 1: Under an inert atmosphere, D-limonene (76.1 µL, 0.470 mmol) and Ph₂SiH₂ (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 C₆D₆. 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 ¹H 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). ¹H 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-, -CH₂-), 1.79 – 1.62 (m, 3H, -CH-, -CH₂-), 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, -CH₃), 0.90 (d, J $= 2.5 \text{ Hz}, 3\text{H}, -CH_3$. ¹³C 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 (-CH₂-), 34.53 (-CH₂-), 31.58 (-CH₂-), 31.50 (-CH₂-), 29.44 (-CH₂-), 28.63 (-CH₂-), 27.38 (-CH₂-), 26.21 (-CH₂-), 24.10 (-CH₃), 24.09 (-CH₃), 19.76 (=CCH₃), 19.36 (=CCH₃), 18.33 (-CH₂Si-), 17.83 (-CH₂Si-). DEPT135 ²⁹Si NMR (benzene-d₆): -14.64, -14.93.



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



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



Figure S86. DEPT135 ²⁹Si 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 Ph₂SiH₂ (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 C₆D₆. 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* ¹H 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). ¹H NMR (benzene-*d*₆): 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*₃), 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*₃). ¹³C NMR (benzene-*d*₆): 176.92 (*C*=O), 135.90 (*Ar*), 135.83 (*Ar*), 130.29 (*Ar*), 130.26 (*Ar*), 128.72 (*Ar*), 128.70 (*Ar*), 51.39 (-OCH₃), 36.33 (-CH-), 20.49 (-CH₂-), 18.13 (-CH₃). DEPT135 ²⁹Si NMR (benzene-*d*₆): -15.85.



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



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



Figure S89. DEPT135 ²⁹Si 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 μ L, 0.420 mmol) and Ph₂SiH₂ (97.4 μ 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 C₆D₆. 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* ¹H NMR spectroscopy.



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

Attempted hydrosilylation of 1,1-dicyclohexylethene using 1.0 mol% 1: Under an inert atmosphere, 1,1-dicyclohexylethene (86.5 μ L, 0.403 mmol) and Ph₂SiH₂ (93.5 μ 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 C₆D₆. 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* ¹H NMR spectroscopy.

Dechlorination of chlorobenzene with 1.0 mol% 1. Under an inert atmosphere, chlorobenzene (49.4 μ L, 0.487 mmol) and Ph₂SiH₂ (113.0 μ 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*₈. 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* ¹H NMR spectroscopy. Products were identified as benzene and Ph₂SiHCl.



Figure S91. ¹H NMR showing partial dechlorination of chlorobenzene in toluene- d_8 .



Figure S92. ³¹P NMR spectrum of 1 with 100 equivalents of PhSiH₃ after 24 h at 25 °C.



Figure S93. ³¹P NMR spectrum of 1 with 100 equivalents of Ph₂SiH₂ after 24 h at 25 °C.



Figure S94. ³¹P NMR spectra of **1**-mediated 1-hexene hydrosilylation with Ph₂SiH₂ after 1 h (top), 5 h (middle), and 24 h (bottom).