Carbonyl and Ester C-O Bond Hydrosilylation Using κ4-Diimine Nickel Catalysts

Electronic Supplementary Information

Christopher L. Rock, Thomas L. Groy, and Ryan J. Trovitch*

School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287

ryan.trovitch@asu.edu
Table S1. Crystallographic Data for (\textsuperscript{iPr}PPr\textsubscript{DI})Ni (2) and (\textsuperscript{Bu}PPr\textsubscript{DI})Ni (3).

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Figure S1. The molecular structure of (iPr$_2$PP-DI)Ni (2) shown at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.
Table S2. Metrical parameters for \((\text{iPr}^2\text{PPrDI})\text{Ni}\) (2).

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Figure S2. The molecular structure of (tBu₂PPrDI)Ni (3) shown at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.
Table S3. Metrical parameters for (Bu2PrDi)Ni (3). 

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Characterization of Newly Prepared Complexes:

Figure S3. $^1$H NMR spectrum of tBu2PPrDI in benzene-$d_6$.

Figure S4. $^{13}$C NMR spectrum of tBu2PPrDI in benzene-$d_6$. 
Figure S5. $^{31}$P NMR spectrum of $^{t}$Bu$_2$PPr-DI in benzene-$d_6$. 

Figure S6. $^1$H NMR spectrum of (iPr$_2$PP-DI)Ni (2) in benzene-$d_6$. 
Figure S7. $^{13}$C NMR spectrum of (iPr$_2$PPrDI)Ni (2) in benzene-$d_6$.

Figure S8. $^{31}$P NMR spectrum of (iPr$_2$PPrDI)Ni (2) in benzene-$d_6$. 
Figure S9. $^1$H NMR spectrum of (tBu$_2$PPrDI)Ni (3) in benzene-$d_6$.

Figure S10. $^{13}$C NMR spectrum of (tBu$_2$PPrDI)Ni (3) in benzene-$d_6$. 
Aldehyde Hydrosilylation:

Hydrosilylation of Benzaldehyde Using 0.1 mol% 1: In a glove box, benzaldehyde (478 μL, 3.88 mmol) and PhSiH₃ (395 μL, 3.88 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (2.3 mg, 0.00388 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH (aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as benzyl alcohol (337.8 mg, 3.12 mmol, 80.5%). ¹H NMR (benzene-ᵈ sext): δ 7.10 (m, 2H), 7.06 (m, 2H), 7.03 (m, 1H), 5.12 (s, 1H), 4.34 (s, 2H). ¹³C NMR (benzene-ᵈ sext): δ 141.83, 128.95, 127.85, 127.81, 64.88.

Figure S11. ³¹P NMR spectrum of (tBu₂PPrDI)Ni (3) in benzene-ᵈ₆.
Figure S12. $^1$H NMR spectrum of benzyl alcohol in benzene-$d_6$.

Figure S13. $^{13}$C NMR spectrum of benzyl alcohol in benzene-$d_6$. 
Hydrosilylation of 4-Fluorobenzaldehyde Using 0.1 mol% 1: In a glove box, 4-fluorobenzaldehyde (378 μL, 3.53 mmol) and PhSiH₃ (435 μL, 3.53 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (2.1 mg, 0.00353 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH (aq) and the organic product was extracted using Et₂O (2x3 mL) and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 4-fluorobenzyl alcohol (408.8 mg, 3.24 mmol, 91.9%). ¹H NMR (benzene-d₆): δ 6.93 (m, 2H), 6.79 (m, 2H), 4.18 (s, 2H), 2.37 (bs, 1H). ¹³C NMR (benzene-d₆): δ 162.88 (d, J = 244.7 Hz), 137.47 (d, J = 5.4 Hz), 129.23 (d, J = 7.5 Hz), 115.67 (d, J = 11.6 Hz), 64.24.

Figure S14. ¹H NMR spectrum of 4-fluorobenzyl alcohol in benzene-d₆.
Hydrosilylation of 4-Chlorobenzaldehyde Using 0.1 mol% 1: In a glove box, 4-chlorobenzaldehyde (371 μL, 2.64 mmol) and PhSiH₃ (326 μL, 2.64 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (1.5 mg, 0.00264 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 4-chlorobenzyl alcohol (273.0 mg, 1.91 mmol, 72.5%). ¹H NMR (benzene-d₆): δ 7.09 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.11 (s, 2H), 1.83 (s, 1H). ¹³C NMR (benzene-d₆): δ 140.41, 133.58, 129.03, 128.62, 64.38.

Figure S15. ¹³C NMR spectrum of 4-fluorobenzyl alcohol in benzene-d₆.
Figure S16. $^1$H NMR spectrum of 4-chlorobenzyl alcohol in benzene-$d_6$.

Figure S17. $^{13}$C NMR spectrum of 4-chlorobenzyl alcohol in benzene-$d_6$. 
Hydrosilylation of 4-Methylbenzaldehyde Using 0.1 mol% 1: In a glove box, 4-methylbenzaldehyde (911 μL, 7.73 mmol) and PhSiH₃ (952 μL, 7.73 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (4.6 mg, 0.00773 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 4-methylbenzyl alcohol (762.5 mg, 6.24 mmol, 85.3%). ¹H NMR (benzene-d₆): δ 7.14 (d, J = 7.8 Hz, 2H), 6.98 (d, J = 7.8 Hz, 2H), 4.38 (s, 2H), 2.58 (bs, 1H), 2.09 (s, 3H). ¹³C NMR (benzene-d₆): δ 139.29, 137.17, 129.62, 127.61, 65.17, 21.45.

Figure S18. ¹H NMR spectrum of 4-methylbenzyl alcohol in benzene-d₆.
Hydrosilylation of 4-Methoxybenzaldehyde Using 0.1 mol% 1: In a glove box, 4-methoxybenzaldehyde (515 μL, 4.23 mmol) and PhSiH₃ (521 μL, 4.23 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (2.4 mg, 0.00423 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 4-methoxybenzyl alcohol (437.5 mg, 3.17 mmol, 74.9%). ¹H NMR (benzene-d₆): δ 7.17 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 4.44 (s, 2H), 4.39 (s, 1H), 3.35 (s, 3H). ¹³C NMR (benzene-d₆): δ 159.7, 134.2, 129.2, 114.4, 64.7, 55.2.

Figure S19. ¹³C NMR spectrum of 4-methylbenzyl alcohol in benzene-d₆.
Figure S20. $^1$H NMR spectrum of 4-methoxybenzyl alcohol in benzene-$d_6$.

Figure S21. $^{13}$C NMR spectrum of 4-methoxybenzyl alcohol in benzene-$d_6$. 
Hydrosilylation of 4-Cyanobenzaldehyde Using 0.1 mol% 1: In a glove box, 4-cyanobenzaldehyde (859 mg, 6.55 mmol) and PhSiH$_3$ (807 μL, 6.55 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (3.9 mg, 0.00655 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via $^1$H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH$_{(aq)}$ and the organic product was extracted using Et$_2$O and dried over Na$_2$SO$_4$. The solvent was removed in vacuo and the product was identified as 4-cyanobenzyl alcohol (413.4 mg, 3.10 mmol, 47.4%).

$^1$H NMR (benzene-$d_6$): δ 7.12 (d, $J = 8.2$ Hz, 2H), 7.03 (d, $J = 8.2$ Hz, 2H), 4.38 (s, 2H), 4.20 (s, 1H). $^{13}$C NMR (benzene-$d_6$): δ 147.62, 132.57, 127.40, 119.63, 110.80, 63.91.

Figure S22. $^1$H NMR spectrum of 4-cyanobenzyl alcohol in benzene-$d_6$. 
Hydrosilylation of Furfural Using 0.1 mol% 1: In a glove box, furfural (292 μL, 3.52 mmol) and PhSiH₃ (435 μL, 3.52 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (2.1 mg, 0.00352 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as furfuryl alcohol (178.2 mg, 1.81 mmol, 51.6%). ¹H NMR (benzene-d₆): δ 7.10 (m, 1H), 6.06 (m, 2H), 4.36 (s, 2H), 3.92 (s, 1H). ¹³C NMR (benzene-d₆): δ 155.35, 142.72, 110.89, 108.02, 57.38.

Figure S23. ¹³C NMR spectrum of 4-cyanobenzyl alcohol in benzene-d₆.
Figure S24. $^1$H NMR spectrum of furfuryl alcohol in benzene-$d_6$.

Figure S25. $^{13}$C NMR spectrum of furfuryl alcohol in benzene-$d_6$. 
Hydrosilylation of Cyclohexanecarboxaldehyde Using 0.1 mol% 1: In a glove box, cyclohexanecarboxaldehyde (726 μL, 5.99 mmol) and PhSiH₃ (739 μL, 5.99 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (3.6 mg, 0.00599 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH (aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as cyclohexanemethanol (499.3 mg, 4.37 mmol, 73.0%). ¹H NMR (benzene-d₆): δ 3.18 (s, 2H), 1.64 (s, 5H), 1.25 (m, 1H), 1.11 (m, 3H), 0.80 (s, 2H), 0.69 (m, 1H). ¹³C NMR (benzene-d₆): δ 68.70, 41.26, 30.54, 27.50, 26.77.

Figure S26. ¹H NMR spectrum of cyclohexanemethanol in benzene-d₆.
Hydrosilylation of 3-Cyclohexencarboxaldehyde Using 0.1 mol% 1: In a glove box, 3-cyclohexencarboxaldehyde (541 μL, 4.76 mmol) and PhSiH₃ (586 μL, 4.76 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (2.8 mg, 0.00476 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOHₐq and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 3-cyclohexene-1-methanol (431.4 mg, 3.84 mmol, 80.1%). ¹H NMR (benzene-d₆): δ 5.65 (s, 2H), 3.21 (s, 2H), 1.94 (m, 3H), 1.62 (m, 3H), 1.14 (m, 1H), 0.75 (s, 1H). ¹³C NMR (benzene-d₆): δ 127.64, 126.76, 67.84, 37.05, 28.98, 26.07, 25.44.

Figure S27. ¹³C NMR spectrum of cyclohexanemethanol in benzene-d₆.
Figure S28. $^1$H NMR spectrum of 3-cyclohexene-1-methanol in benzene-$d_6$.

Figure S29. $^{13}$C NMR spectrum of 3-cyclohexene-1-methanol in benzene-$d_6$. 
**Hydrosilylation of Hexanal Using 0.1 mol% 1:** In a glove box, hexanal (682 μL, 5.54 mmol) and PhSiH₃ (683 μL, 5.54 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (3.3 mg, 0.00554 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed *in vacuo* and the product was identified as hexanol (459.6 mg, 4.50 mmol, 81.2%). ¹H NMR (benzene-<em>d</em>₆): δ 4.04 (s, 1H), 3.55 (t, <em>J</em> = 6.7 Hz, 2H), 1.52 (pseudo p, <em>J</em> = 7.0 Hz, 2H), 1.25 (m, 6H), 0.87 (t, <em>J</em> = 7.0 Hz, 3H). ¹³C NMR (benzene-<em>d</em>₆): δ 63.04, 33.49, 32.43, 26.26, 23.41, 14.64.

**Figure S30.** ¹H NMR spectrum of hexanol in benzene-<em>d</em>₆.
Hydrosilylation of Decanal Using 0.1 mol% 1: In a glove box, decanal (948 μL, 5.04 mmol) and PhSiH₃ (621 μL, 5.04 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (3.0 mg, 0.00504 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as decanol (716 mg, 4.52 mmol, 89.8%). ¹H NMR (benzene-d₆): δ 4.29 (s, 1H), 3.46 (s, 2H), 1.49 (d, 2H), 1.24 (s, 16H), 0.87 (s, 3H). ¹³C NMR (benzene-d₆): δ 62.93, 33.66, 32.86, 30.70, 30.65, 30.54, 30.34, 26.86, 23.58, 14.80.
Figure S32. $^1$H NMR spectrum of decanol in benzene-$d_6$.

Figure S33. $^{13}$C NMR spectrum of decanol in benzene-$d_6$. 
Ketone Hydrosilylation:

**Hydrosilylation of Acetophenone with 1.0 mol% 1:** In a glove box, acetophenone (80.3 μL, 0.689 mmol) and PhSiH₃ (84.8 μL, 0.689 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (4.1 mg, 0.00689 mmol). The resulting red solution was dissolved in benzene-

\( d_6 \) and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed via \(^1\)H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% \( \text{NaOH(aq)} \) and the organic product was extracted using Et₂O and dried over \( \text{Na}_2\text{SO}_4 \). The solvent was removed in vacuo and the product was identified as 1-phenylethanol (56.8 mg, 0.465 mmol, 67.5%). \(^1\)H NMR (benzene-

\( d_6 \)): \( \delta \) 7.23 (d, \( J = 7.5 \) Hz, 2H), 7.14 (t, \( J = 7.5 \) Hz, 2H), 7.06 (t, \( J = 7.3 \) Hz, 1H), 4.57 (q, \( J = 6.5 \) Hz, 1H), 2.52 (s, 1H), 1.29 (d, \( J = 6.5 \) Hz, 3H). \(^{13}\)C NMR (benzene-

\( d_6 \)): \( \delta \) 147.17, 128.88, 127.66, 126.08, 70.50, 25.97.

**Figure S34.** \(^1\)H NMR spectrum of 1-phenylethanol in benzene-

\( d_6 \).
Hydrosilylation of 4-Fluoroacetophenone with 1.0 mol% 1: In a glove box, 4-fluoroacetophenone (116 μL, 0.957 mmol) and PhSiH₃ (117 μL, 0.957 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (5.7 mg, 0.00957 mmol). The resulting red solution was dissolved in benzene-d6 and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 1-(4-fluorophenyl)ethanol (120.9 mg, 0.863 mmol, 90.1%). ¹H NMR (benzene-d6): δ 7.00 (m, 2H), 6.81 (m, 2H), 4.44 (q, J = 6.5 Hz, 1H), 2.15 (s, 1H), 1.20 (d, J = 6.5 Hz, 3H). ¹³C NMR (benzene-d6): δ 162.02 (d, J = 244.2 Hz), 142.02 (d, J = 3.3 Hz), 126.92 (d, J = 7.9 Hz), 114.83 (d, J = 21.4 Hz), 69.06, 25.15.

Figure S35. ¹³C NMR spectrum of 1-phenylethanol in benzene-d6.
Figure S36. $^1$H NMR spectrum of 1-(4-fluorophenyl)ethanol in benzene-$d_6$.

Figure S37. $^{13}$C NMR spectrum of 1-(4-fluorophenyl)ethanol in benzene-$d_6$. 
Hydrosilylation of 4-Chloroacetophenone with 1.0 mol% 1: In a glove box, 4-chloroacetophenone (94.0 μL, 0.723 mmol) and PhSiH₃ (89.0 μL, 0.723 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (4.3 mg, 0.00723 mmol). The resulting red solution was dissolved in benzene-­d₆ and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 1-(4-chlorophenyl)ethanol (97.8 mg, 0.624 mmol, 86.5%). ¹H NMR (benzene-d₆): δ 7.11 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 4.39 (q, J = 6.5 Hz, 1H), 2.48 (s, 1H), 1.16 (d, J = 6.5 Hz, 3H). ¹³C NMR (benzene-d₆): δ 145.34, 133.39, 129.01, 127.44, 69.77, 25.74.

Figure S38. ¹H NMR spectrum of 1-(4-chlorophenyl)ethanol in benzene-d₆.
Hydrosilylation of 2,4,6-Trimethylacetophenone with 1.0 mol% 1: In a glove box, 2,4,6-trimethylacetophenone (109.0 μL, 0.655 mmol) and PhSiH₃ (80.7 μL, 0.655 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (3.9 mg, 0.00655 mmol). The resulting red solution was dissolved in benzene-d₆ and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 1-mesitylethanol (89.7 mg, 0.546 mmol, 83.3%). ¹H NMR (benzene-d₆): δ 6.70 (s, 2H), 5.10 (q, J = 6.7 Hz, 1H), 2.45 (s, 1H), 2.32 (s, 6H), 2.12 (s, 3H), 1.37 (d, J = 6.7 Hz, 3H). ¹³C NMR (benzene-d₆): δ 138.86, 136.20, 135.95, 130.75, 130.68, 67.69, 67.56, 22.22, 22.17, 21.18, 21.13, 21.08, 21.00.

Figure S39. ¹³C NMR spectrum of 1-(4-chlorophenyl)ethanol in benzene-d₆.
Figure S40. $^1$H NMR spectrum of 1-mesitylethanol in benzene-$d_6$.

Figure S41. $^{13}$C NMR spectrum of 1-mesitylethanol in benzene-$d_6$. 
Hydrosilylation of 4-Methoxyacetophenone with 1.0 mol% 1: In a glove box, 4-methoxyacetophenone (75.7 mg, 0.504 mmol) and PhSiH₃ (62.1 μL, 0.504 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (3.0 mg, 0.00504 mmol). The resulting red solution was dissolved in benzene-ᵈ⁶ and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% NaOHₐq and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 1-(4-methoxyphenyl)ethanol (64.1 mg, 0.421 mmol, 83.6%). ¹H NMR (benzene-ᵈ⁶): δ 7.19 (d, J = 8.3 Hz, 2H), 6.78 (d, J = 8.3 Hz, 2H), 4.65 (q, J = 6.1 Hz, 1H), 3.34 (s, 3H), 2.78 (s, 1H), 1.36 (d, J = 6.3 Hz, 3H). ¹³C NMR (benzene-ᵈ⁶): δ 159.66, 139.36, 127.36, 114.36, 70.17, 70.09, 55.21, 55.17, 26.02, 25.97.

Figure S42. ¹H NMR spectrum of 1-(4-methoxyphenyl)ethanol in benzene-ᵈ⁶.
**Figure S43.** $^{13}$C NMR spectrum of 1-(4-methoxyphenyl)ethanol in benzene-$d_6$.

**Hydrosilylation of Dicyclohexyl Ketone with 1.0 mol% 1:** In a glove box, dicyclohexylketone (125.8 μL, 0.638 mmol) and PhSiH$_3$ (78.7 μL, 0.638 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (3.8 mg, 0.00638 mmol). The resulting red solution was dissolved in benzene-$d_6$ and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed via $^1$H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% NaOH$_{(aq)}$ and the organic product was extracted using Et$_2$O and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the product was identified as dicyclohexylmethanol (111.5 mg, 0.568 mmol, 89.0%). $^1$H NMR (benzene-$d_6$): δ 2.91 (t, $J = 5.5$ Hz, 1H), 1.84 (d, $J = 12.6$ Hz, 2H), 1.74 (dd, $J = 16.7$, 7.1 Hz, 4H), 1.64 (dd, $J = 6.8$, 3.5 Hz, 2H), 1.49 (d, $J = 12.5$ Hz, 2H), 1.36 (m, 3H), 1.10 (m, 9H). $^{13}$C NMR (benzene-$d_6$): δ 80.51, 40.67, 30.72, 28.11, 27.40, 27.31, 27.03.
Figure S44. $^1$H NMR spectrum of dicyclohexylmethanol in benzene-$d_6$.

Figure S45. $^{13}$C NMR spectrum of dicyclohexylmethanol in benzene-$d_6$. 
Hydrosilylation of Cyclohexanone with 1.0 mol% 1: In a glove box, cyclohexanone (78.3 μL, 0.756 mmol) and PhSiH\(_3\) (93.2 μL, 0.756 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (4.5 mg, 0.00756 mmol). The resulting red solution was dissolved in benzene-\(d_6\) and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed via \(^1\)H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% NaOH\(_{aq}\) and the organic product was extracted using Et\(_2\)O and dried over Na\(_2\)SO\(_4\). The solvent was removed in vacuo and the product was identified as cyclohexanol (42.6 mg, 0.425 mmol, 56.3%). \(^1\)H NMR (benzene-\(d_6\)): δ 3.43 (m, 1H), 1.84 (bs, 1H), 1.75 (m, 2H), 1.59 (m, 2H), 1.35 (m, 1H), 1.21 (m, 2H), 1.09 (m, 3H). \(^{13}\)C NMR (benzene-\(d_6\)): 30.37, 36.18, 26.33, 24.89.

Figure S46. \(^1\)H NMR spectrum of cyclohexanol in benzene-\(d_6\).
Hydrosilylation of 2,4-dimethyl-3-pentanone with 1.0 mol% 1: In a glove box, 2,4-dimethyl-3-pentanone (85.6 μL, 0.605 mmol) and PhSiH₃ (74.5 μL, 0.605 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (3.6 mg, 0.00605 mmol). The resulting red solution was dissolved in benzene-ᴅ₆ and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 2,4-dimethyl-3-pentanol (0.01458 mg, 0.125 mmol, 20.7%). ¹H NMR (benzene-ᴅ₆): δ 2.78 (t, J = 5.8 Hz, 1H), 1.60 (dh, J = 13.2, 6.7 Hz, 2H), 0.89 (d, J = 6.7 Hz, 6H), 0.81 (d, J = 6.8 Hz, 6H). ¹³C NMR (benzene-ᴅ₆): δ 31.21, 20.37, 17.51.
Figure S48. $^1$H NMR spectrum of 2,4-dimethyl-3-pentanol in benzene-$d_6$.

Figure S49. $^{13}$C NMR spectrum of 2,4-dimethyl-3-pentanol in benzene-$d_6$. 
Hydrosilylation of 2-Hexanone with 1.0 mol% 1: In a glove box, 2-hexanone (89.1 μL, 0.722 mmol) and PhSiH₃ (89.0 μL, 0.722 mmol) were added sequentially to a 20 mL scintillation vial containing 1 (4.3 mg, 0.00722 mmol). The resulting red solution was dissolved in benzene-d₆ and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% NaOH(aq) and the organic product was extracted using Et₂O and dried over Na₂SO₄. The solvent was removed in vacuo and the product was identified as 2-hexanol (35.7 mg, 0.349 mmol, 63.1%). ¹H NMR (benzene-d₆): δ 3.54 (h, J = 5.7 Hz, 1H), 1.23 (m, 7H), 1.02 (d, J = 6.2 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H). ¹³C NMR (benzene-d₆): δ 68.12, 68.03, 39.83, 28.75, 24.12, 24.07, 23.51, 14.70.

**Figure S50.** ¹H NMR spectrum of 2-hexanol in benzene-d₆.
Figure S51. $^{13}$C NMR spectrum of 2-hexanol in benzene-$d_6$. 
Ester Hydrosilylation:

**Dihydrosilylation of Ethyl Acetate with 1.0 mol% 1:** In a glove box, 90.7 µL of ethyl acetate (0.924 mmol) and 342.0 µL PhSiH₃ (2.77 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing 5.5 mg 1 (0.00924 mmol) in 0.5 mL benzene-ᵈₒ. The red solution was then transferred into a J. Young NMR tube, sealed, and heated to 60 °C for 24 h. Analysis by ¹H NMR spectroscopy revealed 80% conversion of ethyl acetate to a mixture of silyl ethers.

**Figure S52.** ¹H NMR spectrum of silyl ether mixture collected at 24 h in benzene-ᵈₒ.
Cleavage of Allyl Acetate Using 1.0 mol% 1: Under an inert atmosphere, allyl acetate (83.4 µL, 0.773 mmol) and PhSiH₃ (95.2 µL, 0.773 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing 1 (4.6 mg, 0.00773 mmol) in 0.5 mL benzene-ᵈ₆. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 30 min, the solution returned to red and greater than 99% conversion was observed by ¹H NMR spectroscopy. The solution was diluted with benzene and a benzene solution containing 1 equivalent of I₂ (relative to Ni, 31.2 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl triacetate (55.9 mg, 0.198 mmol, 76.8%) as a dark yellow oil. ¹H NMR (benzene-ᵈ₆): δ 8.02 – 7.99 (m, J = 3.5 Hz, 2H), 7.19 – 7.08 (m, 3H), 1.67 (s, 9H). ¹³C NMR (benzene-ᵈ₆): δ 169.11, 135.62, 132.70, 128.78, 127.19, 22.22.

Figure S53. ¹H NMR spectrum of phenylsilanetriyl triacetate in benzene-ᵈ₆.
Atom Efficient Cleavage of Allyl Acetate Using 1.0 mol% 1: Under an inert atmosphere, allyl acetate (90.6 µL, 0.840 mmol) and PhSiH₃ (34.5 µL, 0.280 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing 1 (5.0 mg, 0.00840 mmol) in 0.5 mL benzene-$_d$_6. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 3 h, the solution returned to red and greater than 99% conversion was observed via $^1$H NMR spectroscopy.

Cleavage of Allyl Acetate Using 0.1 mol% 1: Under an inert atmosphere, allyl acetate (0.94 mL, 8.73 mmol) and PhSiH₃ (1.08 mL, 8.73 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing 1 (5.2 mg, 0.00521 mmol). A color change to pale yellow and vigorous bubbling was quickly observed. The vial was left loosely capped and after 1 h, the solution returned to red. Greater than 99% conversion was observed via $^1$H NMR spectroscopy.
**Figure S5.** $^1$H NMR spectrum of phenylsilanetriyl triacetate and propylene obtained following allyl acetate cleavage using 0.33 equivalents of PhSiH$_3$ in benzene-$d_6$.

**Figure S6.** $^1$H NMR spectrum of the silyl esters obtained following allyl acetate cleavage using 0.1 mol% 1 in benzene-$d_6$. 
Cleavage of Allyl Benzoate Using 1.0 mol% 1: Under an inert atmosphere, allyl benzoate (93.1 µL, 0.605 mmol) and PhSiH$_3$ (75.6 µL, 0.605 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing 1 (3.6 mg, 0.00605 mmol) in 0.5 mL benzene-$d_6$. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 30 min, the solution returned to red and greater than 99% conversion was observed via $^1$H NMR spectroscopy. The solution was diluted with benzene and 1 equivalent of I$_2$ in benzene (relative to Ni, 24.4 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl triabenzoate (80.4 mg, 0.172 mmol, 85.1%) as a dark yellow oil. $^1$H NMR (benzene-$d_6$): 8.27 (dd, $J = 4.8$, 2.3 Hz, 2H), 8.21 (d, $J = 7.3$ Hz, 6H), 7.14 (d, $J = 6.6$ Hz, 4H), 7.04 (t, $J = 7.4$ Hz, 3H), 6.93 (t, $J = 7.7$ Hz, 6H). $^{13}$C NMR (benzene-$d_6$): δ 164.95, 135.89, 134.16, 132.83, 131.51, 131.42, 130.47, 129.06, 128.99.

Figure S57. $^1$H NMR spectrum of phenylsilanetriyl tribenzoate in benzene-$d_6$. 
Cleavage of Allyl Phenylacetate Using 1.0 mol% 1: Under an inert atmosphere, allyl phenylacetate (111.3 µL, 0.655 mmol) and PhSiH₃ (80.7 µL, 0.655 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing 1 (3.9 mg, 0.00655 mmol) in 0.5 mL benzene-d₆. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 30 min, the solution returned to red and greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was diluted with benzene and 1 equivalent of I₂ in benzene (relative to Ni, 24.4 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl tris(2-phenylacetate) (94.1 mg, 0.184 mmol, 84.4%) as an off white solid. ¹H NMR (benzene-d₆): δ 7.80 (d, J = 6.7 Hz, 2H), 7.16 – 6.99 (m, 18H), 3.41 (s, 6H). ¹³C NMR (benzene-d₆): δ 169.66, 135.55, 134.06, 132.71, 130.18, 129.04, 128.72, 127.64, 126.58, 42.69.

**Figure S58.** ¹³C NMR spectrum of phenylsilanetriyl tribenzoate in benzene-d₆.
Figure S59. $^1$H NMR spectrum of phenylsilanetriyl tris(2-phenylacetate) in benzene-$d_6$.

Figure S60. $^{13}$C NMR spectrum of phenylsilanetriyl tris(2-phenylacetate) in benzene-$d_6$. 
Cleavage of Allyl Phenoxyacetate Using 1.0 mol% 1: Under an inert atmosphere, allyl phenoxyacetate (101.8 µL, 0.588 mmol) and PhSiH₃ (72.5 µL, 0.588 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing 1 (3.5 mg, 0.00588 mmol) in 0.5 mL benzene-d₆. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 30 min, the solution returned to red and greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was diluted with benzene and 1 equivalent of I₂ in benzene (relative to Ni, 23.7 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl tris(2-phenoxyacetate) (98.1 mg, 0.176 mmol, 90%) as an off white solid. ¹H NMR (benzene-d₆): δ 7.81 (d, J = 6.8 Hz, 2H), 7.17 – 7.04 (m, 4H), 7.00 (t, J = 7.9 Hz, 6H), 6.75 (dd, J = 10.3, 4.5 Hz, 8H), 4.20 (s, 6H). ¹³C NMR (benzene-d₆): δ 167.15, 158.38, 135.54, 133.35, 130.16, 129.01, 125.11, 122.27, 115.33, 65.59.

Figure S61. ¹H NMR spectrum of phenylsilanetriyl tris(2-phenoxyacetate) in benzene-d₆.
Cleavage of Allyl Hexanoate Using 1.0 mol% 1: Under an inert atmosphere, allyl hexanoate (118.0 µL, 0.672 mmol) and PhSiH3 (83.0 µL, 0.672 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing 1 (4.0 mg, 0.672 mmol) in 0.5 mL benzene-d6. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 3 h, the solution returned to red and greater than 99% conversion was observed via ¹H NMR spectroscopy. The solution was diluted with benzene and 1 equivalent of I2 in benzene (relative to Ni, 27.1 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl trihexanoate (94.8 mg, 0.210 mmol, 93.9%) as a dark yellow oil. ¹H NMR (benzene-d6): δ 8.33 – 8.00 (m, 2H), 7.18 (m, 3H), 2.28 – 2.08 (m, 6H), 1.58 – 1.43 (m, 6H), 1.10 (m, 12H), 0.76 (m, 9H). ¹³C NMR (benzene-d6): δ 171.94, 135.68, 132.65, 128.80, 127.69, 35.98, 31.61, 24.95, 22.92, 14.37.

Figure S62. ¹³C NMR spectrum of phenylsilanetriyl tris(2-phenoxyacetate) in benzene-d6.
Figure S63. $^{1}$H NMR spectrum of phenylsilanetriyl trihexanoate in benzene-$d_6$.

Figure S64. $^{13}$C NMR spectrum of phenylsilanetriyl trihexanoate in benzene-$d_6$. 
Cleavage of Allyl Cyclohexylpropanoate using 1.0 mol% 1: Under an inert atmosphere, allyl cyclohexylpropanoate (100.1 µL, 0.487 mmol) and PhSiH$_3$ (60.0 µL, 0.487 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing 1 (2.9 mg, 0.00621 mmol) in 0.5 mL benzene-$d_6$. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 3 h, the solution returned to red and greater than 99% conversion was observed via $^1$H NMR spectroscopy. The solution was diluted with benzene and 1 equivalent of I$_2$ in benzene (relative to Ni, 19.6 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl tris(3-cyclohexylpropanoate) (86.3 mg, 0.151, 93.0%) as a dark yellow oil. $^1$H NMR (benzene-$d_6$): δ 8.37 – 8.10 (m, 2H), 7.33 – 7.16 (m, 3H), 2.33 – 2.26 (m, 6H), 1.63 – 1.41 (m, 21H), 1.16 – 0.96 (m, 12H), 0.69 (m, 6H). $^{13}$C NMR (benzene-$d_6$): δ 172.25, 135.71, 132.65, 128.80, 127.72, 37.50, 33.70, 33.43, 32.60, 27.17, 26.88.

Figure S65. $^1$H NMR spectrum of phenylsilanetriyl tris(3-cyclohexylpropanoate) in benzene-$d_6$. 
Cleavage of Allyl Cinnamate Using 1.0 mol% 1: Under an inert atmosphere, allyl cinnamate (75.9 mg, 0.403 mmol) and PhSiH₃ (49.7 µL, 0.403 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing 1 (2.4 mg, 0.00403 mmol) in 0.5 mL benzene-d₆. The red solution was transferred into a J. Young NMR tube and sealed. After 3 h, greater than 99% conversion was observed via ¹H NMR spectroscopy. Since I₂ addition was found to result in product alteration, this tricarboxyphenylsilane could not be isolated.
Figure S67. $^1$H NMR spectrum showing the conversion of allyl cinnamate to phenylsilanetriyl tris(3-phenylacrylate) and propylene in benzene-$d_6$.

Figure S68. $^{13}$C NMR spectrum showing the conversion of allyl cinnamate to phenylsilanetriyl tris(3-phenylacrylate) and propylene in benzene-$d_6$. 
Hydrosilylation of 5-(acetoxymethyl)furfural with 1.0 mol% 1: Under inert atmosphere, 5-(acetoxymethyl)furfural (107.3 mg, 0.638 mmol) and PhSiH\(_3\) (157.3 µL, 1.28 mmol) were added to a 20 mL scintillation vial containing 1 (3.8 mg, 0.00639 mmol) dissolved in benzene-\(d_6\). After 3 h, greater than 99% conversion of the aldehyde to a mixture of silyl ethers was observed by \(^1\)H NMR. Additional time and heating did not result in ester C-O bond hydrosilylation.

Dehydrogenative coupling of PhSiH\(_3\) using 1.0 mol% 1: Under inert atmosphere, PhSiH\(_3\) (72.5 µL, 0.588 mmol) was added to a 20 mL scintillation vial containing 1 (3.5 mg, 0.00588 mmol) dissolved in benzene-\(d_6\). After 24 h, several coupled silane products were observed by \(^1\)H NMR, indicating approximately 35% conversion of PhSiH\(_3\). \(^{29}\)Si NMR revealed the presence of two coupled silanes in appreciable quantity [(PhSiH\(_2\))\(_2\) (-61.50 ppm), (PhSiH\(_2\))\(_2\)SiHPh (-58.85 ppm)] and a small amount of (PhSiH\(_2\))\(_3\)SiPh (-56.12 ppm). Quaternary silane resonances not located.

Figure S69. \(^1\)H NMR spectrum collected following the hydrosilylation of 5-(acetoxymethyl)furfural with PhSiH\(_3\) using 1.0 mol% 1 in benzene-\(d_6\).
**Figure S70.** $^1$H NMR spectrum of PhSiH$_3$ coupling using 1.0 mol% 1 in benzene-$d_6$.

**Figure S71.** $^{29}$Si NMR spectrum of PhSiH$_3$ coupling using 1.0 mol% 1 in benzene-$d_6$. 
Hydrosilylation of Benzaldehyde with 1.0 mol% 1 and 20 mol% PMe₃: Under an inert atmosphere, benzaldehyde (66.8 µL, 0.655 mmol) and PhSiH₃ (80.7 µL, 0.655 mmol) were combined in a 20 mL scintillation vial before transferring to another vial containing PMe₃ (13.6 µL, 0.13 mmol) and 1 (3.9 mg, 0.00655 mmol) dissolved in benzene-d₆. The resulting yellow solution was transferred to a J. Young NMR tube and allowed to stand for 3 h at 25 °C. Only 3% conversion was observed by ¹H NMR spectroscopy. ³¹P NMR spectroscopy indicates the displacement of the pendant phosphine arms by PMe₃.

![Figure S72](image.png)

Figure S72. ¹H NMR spectrum of attempted benzaldehyde hydrosilylation using PhSiH₃ and 1.0 mol% 1 in the presence of 20 mol% PMe₃ in benzene-d₆.
Figure S73. $^{31}$P NMR spectrum collected during the catalytic hydrosilylation of benzaldehyde using PhSiH$_3$ and 1.0 mol% 1 in the presence of 20 mol% PMe$_3$ in benzene-$d_6$. 
Addition of PMe₃ to 1: Under inert atmosphere, PMe₃ (7.5 µL, 0.0729 mmol) was added to a vial containing 1 (21.7 mg, 0.0364 mmol) dissolved in benzene-ｄ₆. After 1 h, ³¹P NMR spectroscopy revealed partial displacement of the diphenylphosphine arms by PMe₃.

**Figure S74.** ³¹P NMR spectrum collected upon adding two equivalents of PMe₃ to 1 in benzene-ｄ₆. The resonance at 39.03 ppm is unreacted 1. Partial conversion to two new compounds is observed: one that exhibits a singlet at -21.81 ppm [Ni(PMe₃)₄]¹ and a second possessing resonances at 25.88 (q) and -24.69 (d) ppm [proposed to be (κ¹-P₂-Ph₂PPrDI)Ni(PMe₃)₃].

Hydrosilylation of Allyl Acetate with 1.0 mol% 1 and 20 mol% PMe₃: Under an inert atmosphere, allyl acetate (49.0 µL, 0.454 mmol) and PhSiH₃ (56.0 µL, 0.454 mmol) were combined in a 20 mL scintillation vial before transferring to another vial containing PMe₃ (9.4 µL, 0.09 mmol) and 1 (2.7 mg, 0.00454 mmol) dissolved in benzene-ｄ₆. The resulting yellow solution was transferred to a J. Young NMR tube and allowed to stand for 30 min. Only 12% conversion was observed by ¹H NMR spectroscopy. ³¹P NMR spectroscopy reveals the formation of (κ²-N,N-Ph₂PPrDI)Ni(PMe₃)₂.
Figure S75. $^{31}$P NMR spectrum collected during the catalytic hydrosilylation of allyl acetate using PhSiH$_3$ and 1.0 mol% 1 in the presence of 20 mol% PMe$_3$ in benzene-$d_6$.

References: