Supporting Information

Selective Hydrosilylation of Alkynes and Ketones: Contrasting Reactivity Between Cationic 3-Iminophosphine Palladium and Nickel Complexes

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1) General methods and instrumentation: All NMR-scale reactions were set up in a nitrogen-filled glovebox. CDCl₃ and C₆D₆ were purchased from Cambridge Isotope Laboratories and for air-sensitive usage, dried over calcium hydride and sodium, respectively, freeze-pump-thawed three times, vacuum-transferred, and stored over molecular sieves in a nitrogen-filled glovebox. Precatalysts 1a and 1b were synthesized via the previously reported procedure.¹⁻² Hydrosilanes for catalytic hydrosilylation reactions were purchased from Gelest, AK Scientific, or Acros, dried neat over calcium hydride and distilled under nitrogen, freeze-pump-thawed, and transferred to the glovebox. All aromatic aldehydes and ketones were supplied from Alfa Aesar, AK Scientific, Sigma-Aldrich, and Acros. Alkynes were purchased from either Sigma-Aldrich or AK Scientific. ¹H and ¹³C NMR data were obtained either on a 400 MHz Varian VXRS NMR spectrometer at 399.95 MHz for ¹H and 100.56 MHz for ¹³C NMR spectroscopy or on a 600 MHz Bruker Avance III at 599.9 MHz for ¹H and 150.8 MHz for ¹³C NMR spectroscopy. High resolution mass spectrometry data were determined by the University of Illinois Mass Spectrometry Laboratory, Urbana, IL, USA.

2) Catalytic reactions and isolation of hydrosilylation products: For the hydrosilylation reactions of alkynes, unless otherwise noted, 1a or 1b was suspended in CDCl₃ or C₆D₆, followed by addition of hydrosilane (1 eq.) and alkyne (1 eq.). In the case of carbonyl hydrosilylation, the carbonyl derivative was added before the hydrosilane. Then, the resulting solution was transferred to an NMR tube, sealed and reaction progress was monitored by acquiring ¹H NMR data frequently. Gram scale reactions were set up in 20 ml vials, sealed with gentle stirring, and reaction completion was monitored by TLC analysis of the reaction mixture. After detection of reaction completion by ¹H NMR spectroscopy (based on diminishing starting material peaks), all volatiles were removed under vacuum, and the crude reaction mixture was extracted with hexanes and passed through a short plug of silica gel to remove inorganics. This mixture was concentrated and purified by flash chromatography (hexanes for vinylsilane products and 90:10 hexanes:ethylacetate for silylether products) as a colorless oily liquid. Isolated yields are calculated based on unsaturated substrate (alkyne or carbonyl derivative). For silylether products, due to partial hydrolysis of the product on silica gel, yields are based on total of
silyl ether and corresponding alcohol. All vinylsilanes were characterized by $^1$H and $^{13}$C NMR spectroscopy and high resolution mass spectrometry. Silyl ether products were characterized only by $^1$H and $^{13}$C NMR spectroscopy. Hydrosilylation products $3a$, $3b$, $3d$, $3i$, $3j$, $3k$, $3l$, $3m$, $4a$, $4b$, and $4c$ were identified by comparison to previously reported NMR spectral data. Nonetheless, their observed spectra are included below.

3) Characterization of hydrosilylation products:

\[ \text{Methyl 2-(phenylsilyl)acrylate (2a): 86\% isolated yield (83 mg), } ^1\text{H NMR (CDCl}_3, 400 \text{ MHz): 7.64-7.61 (m, 2H), 7.44-7.37 (m, 3H), 7.03 (d, } ^2\text{J=2.0 Hz, 1H), 6.26 (d, } ^2\text{J=2.0 Hz, 1H), 4.69 (s, 2H), 3.76 (s, 3H); } ^{13}\text{C}^{[1]}\text{H} \text{ NMR (CDCl}_3, 400 \text{ MHz): 168.5, 144.6, 137.2, 135.7, 130.5, 130.2, 128.2, 52.1; HRMS (EI) (m/z): [M-H]\text{+ calc for C}_{10}H_{11}O_2Si, 191.0528; found, 191.0530.} \]

\[ \text{Methyl 2-(diphenylsilyl)acrylate (2b): 91\% isolated yield (122 mg), } ^1\text{H NMR (CDCl}_3, 400 \text{ MHz): 7.66-7.63 (m, 4H), 7.47-7.41 (m, 6H), 7.15 (d, } ^2\text{J=2.8 Hz, 1H), 6.25 (d, } ^2\text{J=2.8 Hz, 1H), 5.31 (s, 1H), 3.73 (s, 3H); } ^{13}\text{C}^{[1]}\text{H} \text{ NMR (CDCl}_3, 400 \text{ MHz): 168.9, 145.0, 138.9, 135.7, 132.4, 130.1, 128.2, 52.0; HRMS (EI) (m/z): [M-H]\text{+ calc for C}_{16}H_{15}O_2Si, 267.0841; found, 267.0841.} \]

\[ \text{Methyl 2-(methyl(phenyl)silyl)acrylate (2c): 80\% isolated yield (83 mg), } ^1\text{H NMR (CDCl}_3, 400 \text{ MHz): 7.60-7.58 (m, 2H), 7.42-7.37 (m, 3H), 6.96 (d, } ^2\text{J=2.8 Hz, 1H), 6.16 (d, } ^2\text{J=2.8 Hz, 1H), 4.72 (q, } ^3\text{J= 4.0 Hz, 1H), 3.75 (s, 3H), 0.57 (d, } ^3\text{J=4.0 Hz, 3H); } ^{13}\text{C}^{[1]}\text{H} \text{ NMR (CDCl}_3, 400 \text{ MHz): 169.0, 142.9, 140.3, 134.8, 133.5, 129.8, 128.0, 51.9, -5.3; HRMS (EI) (m/z): [M-H]\text{+ calc for C}_{11}H_{13}O_2Si, 205.0685; found, 205.0684.} \]
Methyl 2-(diisopropylsilyl)acrylate (2d): 64% isolated yield (64 mg), $^1$H NMR (CDCl$_3$, 600 MHz): 6.92 (d, $^2$J=3.6 Hz, 1H), 6.17 (d, $^2$J=3.6 Hz, 1H), 3.75 (s, 3H), 3.65 (t, $^3$J=3.6 Hz, 1H), 1.20-1.15 (m, 2H), 1.05 (d, $^3$J=7.2 Hz, 6H), 0.98 (d, $^3$J=7.2 Hz, 6H); $^{13}$C($^1$H) NMR (CDCl$_3$, 600 MHz): 169.6, 143.3, 139.0, 51.8, 18.9, 18.8, 10.7; HRMS (CI) (m/z): [M+H]$^+$ calc for C$_{10}$H$_{21}$O$_2$Si, 201.1311; found, 201.1313.

Methyl (E)-2-(phenylsilyl)hex-2-enoate (2e): 93% isolated yield (109 mg), $^1$H NMR (CDCl$_3$, 400 MHz): 7.62-7.60 (m, 2H), 7.42-7.36 (m, 3H), 6.68 (t, $^3$J=6.8 Hz, 1H), 4.66 (s, 2H), 3.70 (s, 3H), 2.62 (q, $^3$J=6.8 Hz, 2H), 1.53-1.47 (m, 2H), 0.95 (t, $^3$J=7.2 Hz, 3H); $^{13}$C($^1$H) NMR (CDCl$_3$, 400 MHz): 168.7, 162.9, 135.6, 131.5, 129.9, 128.1, 127.5, 51.4, 33.9, 22.2, 13.9; HRMS (ELI) (m/z): [M-H]$^+$ calc for C$_{13}$H$_{17}$O$_2$Si, 233.0998; found, 233.0990.

Methyl (E)-2-(diphenylsilyl)hex-2-enoate (2f): (same regio- and stereoisomers from either 1a or 1b) 88% isolated yield (137 mg), $^1$H NMR (CDCl$_3$, 400 MHz): 7.64-7.62 (m, 2H), 7.45-7.39 (m, 6H), 6.60 (t, $^3$J=7.2 Hz, 1H), 5.23 (s, 1H), 3.63 (s, 3H), 2.62 (q, $^3$J=7.2 Hz, 2H), 1.55-1.49 (m, 2H), 0.97 (t, $^3$J=7.2 Hz, 3H); $^{13}$C($^1$H) NMR (CDCl$_3$, 400 MHz): 169.3, 161.7, 135.6, 133.1, 129.9, 129.5, 128.0, 51.3, 33.9, 22.3, 13.9; HRMS (ELI) (m/z): [M-H]$^+$ calc for C$_{19}$H$_{21}$O$_2$Si, 309.1311; found, 309.1306.

Methyl (E)-2-(methyl(phenyl)silyl)hex-2-enoate (2g): 85% isolated yield (106 mg), $^1$H NMR (CDCl$_3$, 400 MHz): 7.60-7.57 (m, 2H), 7.41-7.38 (m, 3H), 6.52 (t, $^3$J= 7.2 Hz, 1H), 4.67 (q, $^3$J=4.0 Hz, 1H), 3.69 (s, 3H), 2.54 (q, $^3$J= 7.2 Hz, 2H), 1.49 (sext, $^3$J=7.2 Hz, 2H), 0.95 (t, $^3$J=7.2 Hz, 3H), 0.54 (d, $^3$J=4.0 Hz, 3H); $^{13}$C($^1$H) NMR (CDCl$_3$, 400 MHz): 169.5, 159.2, 134.9, 134.7, 131.0, 129.6, 127.9, 51.2, 33.8, 22.3, 13.9, -5.0; HRMS (ELI) (m/z): [M-H]$^+$ calc for C$_{14}$H$_{19}$O$_2$Si, 247.1154; found, 247.1153.
Methyl (E)-2-(diisopropylsilyl)hex-2-enoate (2h): 83% isolated yield (101 mg). $^1$H NMR (CDCl$_3$, 400 MHz): 6.38 (t, $^3$J=7.6 Hz, 1H), 3.68 (s, 3H), 3.56 (t, $^3$J=3.2 Hz, 1H), 2.42 (q, $^3$J=7.6 Hz, 2H), 1.50-1.41 (m, 2H), 1.13-1.05 (m, 2H), 1.01 (d, $^3$J=6.8 Hz, 6H), 0.97 (d, $^3$J=6.8 Hz, 6H), 0.90 (t, $^3$J=7.6 Hz, 3H); $^{13}$C($^1$H) NMR (CDCl$_3$, 400 MHz): 170.4, 158.1, 129.9, 51.1, 33.8, 22.4, 18.8, 18.7, 13.8, 11.0. HRMS (EI) (m/z): [M-H]$^+$ calc for C$_{13}$H$_{25}$O$_2$Si, 241.1624; found, 241.1624.

Methyl (E)-2-(diphenylsilyl)-3-phenylacrylate (2j): 93% isolated yield (160 mg). $^1$H NMR (CDCl$_3$, 600 MHz): 7.69-7.68 (m, 4H), 7.48-7.45 (m, 2H), 7.43-7.41 (m, 4H), 7.38-7.32 (m, 5H), 7.10 (s, 1H), 5.34 (s, 1H), 3.58 (s, 3H); $^{13}$C($^1$H) NMR (CDCl$_3$, 600 MHz): 171.2, 148.8, 136.2, 135.8, 132.0, 131.7, 130.3, 129.3, 128.7, 128.5, 128.2, 51.8; HRMS (EI) (m/z): [M]$^+$ calc for C$_{22}$H$_{20}$O$_2$Si, 344.1233; found, 344.1238.

Methyl (E)-2-(methyl(phenyl)silyl)-3-phenylacrylate (2k): 79% isolated yield (112 mg). $^1$H NMR (CDCl$_3$, 400 MHz): 7.66-7.64 (m, 2H), 7.44-7.31 (m, 8H), 7.03 (s, 1H), 4.81 (q, $^3$J=3.6 Hz, 1H), 3.67 (s, 3H), 2.62 (d, $^3$J=3.6 Hz, 3H); $^{13}$C($^1$H) NMR (CDCl$_3$, 400 MHz): 171.5, 146.6, 136.3, 134.9, 133.4, 130.8, 130.1, 129.0, 128.53, 128.50, 128.2, 51.8, -5.3; HRMS (EI) (m/z): [M]$^+$ calc for C$_{17}$H$_{18}$O$_2$Si, 282.1076; found, 282.1079.

Methyl (E)-2-(diisopropylsilyl)-3-phenylacrylate (2l): 68% isolated yield (94 mg). $^1$H NMR (CDCl$_3$, 600 MHz): 7.33-7.24 (m, 5H), 7.05 (s, 1H), 3.77-3.75 (m, 1H), 3.69 (s, 3H), 1.24-1.19 (m, 2H), 1.12 (d, $^3$J=7.6 Hz, 6H), 1.10 (d, $^3$J=7.6 Hz, 6H); $^{13}$C($^1$H) NMR (CDCl$_3$, 600 MHz): 172.3, 158.8,
146.4, 136.5, 128.8, 128.5, 128.4, 51.7, 18.61, 18.56, 11.1; HRMS (EI) (m/z): [M-H]^+ calc for C_{16}H_{23}O_2Si, 275.1467; found, 275.1471.

Ph_2HSi

(3-Methylbuta-1,3-dien-1-yl)diphenylsilane (2m): 92% isolated yield (115 mg), ^1H NMR (CDCl_3, 400 MHz): 7.60-7.58 (m, 4H), 7.43-7.37 (m, 6H), 6.83 (d, ^4J=18.8 Hz, 1H), 6.09 (dd, ^4J=18.8 Hz, ^2J=3.2 Hz, 1H), 5.17 (d, ^3J=3.2 Hz, 1H), 5.14 (s, 1H), 5.06 (s, 1H), 1.92 (s, 3H); ^13C{^1H} NMR (CDCl_3, 400 MHz): 152.1, 143.3, 135.6, 133.9, 129.8, 128.2, 121.4, 119.0, 18.1; HRMS (EI) (m/z): [M]^+ calc for C_{17}H_{18}Si, 250.1178; found, 250.1172.

Ph

Si

(E)-(2-Methylhexa-1,3-dien-3-yl)diphenylsilane (2n): (same regio- and stereoisomers from either 1a or 1b) 81% isolated yield (113 mg), ^1H NMR (CDCl_3, 600 MHz): 7.60 (dd, ^3J=7.8 Hz, ^4J=1.4 Hz, 4H), 7.42-7.26 (m, 6H), 5.89 (t, ^3J=7.1 Hz, 1H), 5.09 (s, 1H), 4.86 (d, ^2J=1.3 Hz, 1H), 4.53 (d, ^3J=1.3 Hz, 1H), 2.20 (quint, ^3J=7.1 Hz, 2H), 1.71 (s, 3H), 0.99 (t, ^3J=7.1 Hz, 3H); ^13C{^1H} NMR (CDCl_3, 600 MHz): 147.5, 145.4, 139.2, 135.9, 133.9, 129.7, 128.0, 112.2, 24.5, 23.8, 14.4; HRMS (EI) (m/z): [M]^+ calc for C_{19}H_{22}Si, 278.1491; found, 278.1491.

O

SiPh_2

Diphenyl(1-phenylethoxy)silane (3a): 94% isolated yield (143 mg), ^1H NMR (CDCl_3, 400 MHz): 7.71 (dd, ^3J=7.6 Hz, ^4J=1.6 Hz, 2H), 7.66 (d, ^3J=2.0 Hz, 2H), 7.52-7.36 (m, 11H), 5.51 (s, 1H), 5.09 (q, ^3J=6.4 Hz, 1H), 1.60 (d, ^3J=6.4 Hz, 3H); ^13C{^1H} NMR (CDCl_3, 400 MHz): 145.4, 134.83, 134.79, 134.4, 134.3, 130.5, 130.4, 128.4, 128.13, 128.06, 127.3, 125.7, 72.8, 26.4.

O

SiPh_2

Diphenyl(1-phenylpropoxy)silane (3b): 85% isolated yield (135 mg), ^1H NMR (CDCl_3, 400 MHz): 7.71-7.62 (m, 4H), 7.51-7.36 (m, 11H), 5.47 (s, 1H), 4.81 (t, ^3J=6.0 Hz, 1H), 2.01-1.91 (m, 1H),
1.91-1.82 (m, 1H), 0.96 (t, \( ^3J=7.2\) Hz, 3H); \(^{13}\)C\(^{(1)H}\) NMR (CDCl\(_3\), 400 MHz): 143.9, 135.9, 135.8, 134.9, 134.8, 134.4, 134.2, 130.4, 130.3, 130.0, 129.9, 128.2, 128.1, 128.0, 127.3, 126.4, 78.2, 32.9, 10.1.

![O-SiHPh\(_2\)]

**Diphenyl(1-(p-tolyl)ethoxy)silane (3c):** 71% isolated yield (113 mg), \(^1\)H NMR (CDCl\(_3\), 400 MHz): 7.72 (d, \( ^3J=7.6\) Hz, 2H), 7.67 (d, \( ^3J=7.2\) Hz, 2H), 7.52-7.41 (m, 6H), 7.33 (d, \( ^3J=8.0\) Hz, 2H), 7.21 (d, \( ^3J=8.0\) Hz, 2H), 5.51 (s, 1H), 5.07 (q, \( ^3J=6.0\) Hz, 1H), 2.42 (s, 3H), 1.59 (d, \( ^3J=6.0\) Hz, 3H); \(^{13}\)C\(^{(1)H}\) NMR (CDCl\(_3\), 400 MHz): 142.4, 136.8, 135.9, 134.83, 134.79, 134.4, 130.41, 130.36, 129.0, 128.1, 128.0, 125.6, 72.7, 26.4, 21.4.

![O-SiHPh\(_2\)]

**1-(4-Methoxyphenyl)ethoxy)diphenylsilane (3d):** 86% isolated yield (144 mg), \(^1\)H NMR (CDCl\(_3\), 400 MHz): 7.63 (dd, \( ^3J=8.0\) Hz, \( ^4J=1.6\) Hz, 2H), 7.57 (dd, \( ^3J=8.0\) Hz, \( ^4J=1.6\) Hz, 2H), 7.46-7.33 (m, 6H), 7.26 (d, \( ^3J=8.8\) Hz, 2H), 6.85 (d, \( ^3J=8.8\) Hz, 2H), 5.39 (s, 1H), 4.97 (q, \( ^3J=6.4\) Hz, 1H), 3.81 (s, 3H), 1.50 (d, \( ^3J=6.4\) Hz, 3H); \(^{13}\)C\(^{(1)H}\) NMR (CDCl\(_3\), 400 MHz): 158.8, 137.6, 134.84, 134.79, 134.4, 134.3, 130.4, 130.3, 128.1, 128.0, 127.0, 113.7, 72.5, 55.4, 26.3.

![O-SiHPh\(_2\)]

**1-(4-Chlorophenyl)ethoxy)diphenylsilane (3e):** 66% isolated yield (112 mg), \(^1\)H NMR (CDCl\(_3\), 400 MHz): 7.62 (dd, \( ^3J=8.0\) Hz, \( ^4J=1.6\) Hz, 2H), 7.57 (dd, \( ^3J=8.0\) Hz, \( ^4J=1.6\) Hz, 2H), 7.46-7.33 (m, 6H), 7.27 (s, 4H), 5.40 (s, 1H), 4.96 (q, \( ^3J=6.4\) Hz, 1H), 1.48 (d, \( ^3J=6.4\) Hz, 3H); \(^{13}\)C\(^{(1)H}\) NMR (CDCl\(_3\), 400 MHz): 143.9, 134.81, 134.76, 134.1, 133.9, 132.9, 130.6, 130.5, 128.5, 128.2, 128.1, 127.1, 72.2, 26.4.
(1-(2-Methoxyphenyl)ethoxy)diphenylsilane (3g): 77% isolated yield (129 mg), $^1$H NMR (CDCl$_3$, 400 MHz): 7.64 (dd, $^3$J=8.0 Hz, $^4$J=1.6 Hz, 2H), 7.59 (dd, $^3$J=8.0 Hz, $^4$J=1.6 Hz, 2H), 7.45-7.34 (m, 6H), 7.23 (t, $^3$J=8.4 Hz, 1H), 6.93-6.90 (m, 2H), 6.79 (dm, $^3$J=8.4 Hz, 1H), 5.42 (s, 1H), 4.99 (q, $^3$J=6.4 Hz, 1H), 3.77 (s, 3H), 1.51 (d, $^3$J=6.4 Hz, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 400 MHz): 159.7, 147.1, 134.84, 134.82, 134.3, 134.1, 130.5, 130.4, 129.4, 128.14, 128.07, 118.1, 112.8, 111.1, 72.7, 55.3, 26.4.

(Cyclohexyloxy)diphenylsilane (3i): 89% isolated yield (126 mg), $^1$H NMR (CDCl$_3$, 400 MHz): 7.69 (dd, $^3$J=8.0 Hz, $^4$J=1.6 Hz, 4H), 7.49-7.41 (m, 6H), 5.53 (s, 1H), 3.90-3.83 (m, 1H), 1.94-1.91 (m, 2H), 1.81-1.76 (m, 2H), 1.56-1.45 (m, 3H), 1.33-1.24 (m, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 400 MHz): 134.9, 134.7, 130.3, 128.1, 73.1, 35.4, 25.6, 24.2.

(Cyclopentyloxy)diphenylsilane (3j): 82% isolated yield (110 mg), $^1$H NMR (CDCl$_3$, 600 MHz): 7.65 (dd, $^3$J=7.1 Hz, $^4$J=1.2 Hz, 4H), 7.47-7.39 (m, 6H), 5.46 (s, 1H), 4.44 (quint, $^3$J=4.6 Hz, 1H), 1.81-1.78 (m, 2H), 1.77-1.71 (m, 4H), 1.57-1.51 (m, 2H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 600 MHz): 134.8, 134.7, 130.3, 128.1, 76.7, 35.4, 23.2.

(Pentan-3-ylloxy)diphenylsilane (3k): 76% isolated yield (103 mg), $^1$H NMR (CDCl$_3$, 600 MHz): 7.65 (dd, $^3$J=7.8 Hz, $^4$J=1.4 Hz, 4H), 7.44-7.38 (m, 6H), 5.49 (s, 1H), 3.70 (quint, $^3$J=5.8 Hz, 1H), 1.58-1.53 (m, 4H), 0.90 (t, $^3$J=7.4 Hz, 6H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 600 MHz): 134.8, 134.4, 128.2, 128.0, 77.4, 29.2, 10.0.
**O-SiHPh₂**

(Pentan-2-yloxy)diphenylsilane (3l): 83% isolated yield (112 mg), ¹H NMR (CDCl₃, 400 MHz): 7.66-7.58 (m, 4H), 7.45-7.35 (m, 6H), 5.46 (s, 1H), 4.01-3.95 (m, 1H), 1.62-1.55 (m, 1H), 1.47-1.32 (m, 3H), 1.21 (d, ³J=6.0 Hz, 3H), 0.87 (t, ³J=7.2 Hz, 3H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 134.82, 134.79, 130.3, 128.1, 70.9, 41.6, 23.4, 19.0, 14.2.

4-Phenylbutan-2-one (3m): 79% isolated yield (58 mg), ¹H NMR (CDCl₃, 400 MHz): 7.31-7.26 (m, 2H), 7.22-7.18 (m, 3H), 2.91 (t, ³J=7.2 Hz, 2H), 2.77 (t, ³J=7.2 Hz, 2H), 2.15 (s, 3H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 208.1, 134.4, 128.6, 128.4, 126.2, 45.3, 30.2, 29.8.

(E)-Oct-4-en-4-yldiphenylsilane (4a): 84% isolated yield (124 mg), ¹H NMR (CDCl₃, 400 MHz): 7.57 (d, ³J=6.6 Hz, 4H), 7.41-7.36 (m, 6H), 5.92 (t, ³J=7.2 Hz, 1H), 5.09 (s, 1H), 2.22 (t, ³J=7.8 Hz, 2H), 2.18 (q, ³J=7.2 Hz, 2H), 1.45-1.37 (m, 2H), 1.36-1.30 (m, 2H), 0.93 (t, ³J=7.2 Hz, 3H), 0.84 (t, ³J=7.2 Hz, 3H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 146.8, 135.8, 134.4, 129.6, 128.3, 128.0, 32.8, 31.0, 23.2, 22.7, 14.4, 14.1; HRMS (El) (m/z): [M]⁺ calc for C₂₀H₂₆Si, 294.1804; found, 294.1811.

(E)-(1,2-Diphenylnvinyl)diphenylsilane (4b): 77% isolated yield (140 mg), ¹H NMR (CDCl₃, 400 MHz): 7.58 (dd, ³J=7.6 Hz, 4H), 7.45-7.35 (m, 6H), 7.23-7.16 (m, 3H), 7.13-7.10 (m, 3H), 7.04-7.00 (m, 5H), 5.30 (s, 1H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 143.0, 141.7, 140.3, 137.1, 136.0, 133.1, 129.9, 129.8, 128.8, 128.2, 128.14, 128.09, 127.7, 126.3; HRMS (El) (m/z): [M]⁺ calc for C₂₆H₂₂Si, 362.1491; found, 362.1479.
(E)-Diphenyl(1-phenylprop-1-en-1-yl)silane (4c):^10 80% isolated yield (120 mg), ^1H NMR (CDCl$_3$, 600 MHz): 7.53 (dd, ^3$J$=7.8 Hz, ^4$J$=1.8 Hz, 4H), 7.42-7.39 (m, 2H), 7.36-7.34 (m, 4H), 7.25 (t, ^3$J$=7.8 Hz, 2H), 7.17-7.15 (m, 1H), 7.03 (dd, ^3$J$=7.2 Hz, ^4$J$=1.2 Hz, 2H), 6.31 (q, ^3$J$=6.6 Hz, 1H), 5.21 (s, 1H), 1.74 (d, ^3$J$=6.6 Hz, 3H); ^13C{^1H} NMR (CDCl$_3$, 600 MHz): 142.2, 141.2, 139.1, 135.9, 133.7, 129.7, 128.6, 128.2, 128.0, 126.0, 16.5; HRMS (EI) (m/z): [M]$^+$ calc for C$_{21}$H$_{20}$Si, 300.1334; found, 300.1340.

(E)-(2-Butyl-3-methylenehept-1-en-1-yl)diphenylsilane (4e): 86% isolated yield (150 mg, 2,3-di$n$-butyl/2,4-di$n$-butyl isomer : 1/0.27 from crude mixture), ^1H NMR (CDCl$_3$, 600 MHz): 7.56-7.54 (dd, ^3$J$=7.6 Hz, ^4$J$=1.6 Hz, 4H), 7.37-7.33 (m, 6H), 5.64 (d, ^3$J$=5.7 Hz, 1H), 5.14 (d, ^3$J$=5.7 Hz, 1H), 4.80 (d, ^3$J$=2.0 Hz, 1H), 4.77 (d, ^3$J$=2.0 Hz, 1H), 2.28 (t, ^3$J$=7.6 Hz, 2H), 2.05 (t, ^3$J$=7.1 Hz, 2H), 1.44-1.24 (m, 8H), 0.92 (t, ^3$J$=7.3 Hz, 3H), 0.86 (t, ^3$J$=6.9 Hz, 3H); ^13C{^1H} NMR (CDCl$_3$, 600 MHz): 166.3, 150.9, 136.3, 135.1, 128.0, 127.9, 118.1, 113.1, 38.8, 34.6, 30.4, 29.6, 22.8, 22.4, 14.11, 14.08; HRMS (EI) (m/z): [M]$^+$ calc for C$_{24}$H$_{32}$Si, 348.2273; found, 348.2269.

4) Crystallography: A summary of crystal data and collection parameters for the crystal structure of 1b is provided in Table S1. Detailed descriptions of data collection, as well as data solution, are provided below. A suitable crystal was mounted on a polymer loop using Paratone-N hydrocarbon oil. The crystal was transferred to an Apex2 diffractometer with a CCD area detector, centered in the X-ray beam, and cooled to 150 K using a nitrogen-flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. An arbitrary hemisphere of data was collected using 0.3° ω scans, and the data were integrated by the program SAINT. The final unit cell parameters were determined by a least-squares refinement of the reflections with I > 2σ(I). Data analysis using Siemens XPREP and the successful solution and refinement of the structure determined the space group. Equivalent reflections were averaged, and the structure was solved by direct methods using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically. X-ray quality crystals of 1b were grown from a pentane layered tetrahydrofuran solution at room temperature.
Table S1. Crystallographic data for compound 1b.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1b</th>
</tr>
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<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{26}$H$</em>{31}$F$<em>{3}$NNiO$</em>{3}$PS</td>
</tr>
<tr>
<td>Formula weight</td>
<td>584.26</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbc$ar{a}$</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150(2)</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>16.472(2)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>17.510(2)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>18.549(2)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90.00</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>90.00</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>90.00</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>5350.2(9)</td>
</tr>
<tr>
<td>$Z$</td>
<td>8</td>
</tr>
<tr>
<td>Density$_{calc}$ (g/cm$^3$)</td>
<td>1.451</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>Bruker APEX2</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo-K$_\alpha$ (λ = 0.71073 Å)</td>
</tr>
<tr>
<td>Monochromator</td>
<td>Graphite</td>
</tr>
<tr>
<td>Detector</td>
<td>CCD detector</td>
</tr>
<tr>
<td>Scan type, width</td>
<td>$\Omega$, 0.3°</td>
</tr>
<tr>
<td>Scan speed (s)</td>
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</tr>
<tr>
<td>Reflections measured</td>
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<tr>
<td>2θ range (°)</td>
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<tr>
<td>Crystal dimensions (mm)</td>
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<td>Reflections measured</td>
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<tr>
<td>Unique reflections</td>
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<tr>
<td>Observations (I &gt; 2σ(I))</td>
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<tr>
<td>$R_{int}$</td>
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<tr>
<td>Parameters</td>
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</tr>
<tr>
<td>$R_{obs}$, $R_w$, $R_{all}$</td>
<td>0.0325, 0.0925, 0.0467</td>
</tr>
<tr>
<td>GoF</td>
<td>1.070</td>
</tr>
</tbody>
</table>
5) NMR spectra of hydrosilylation products:

\[ \text{SiH}_2\text{Ph} \]

**2a**

$\text{H}^1$ NMR, CDCl$_3$, 400 MHz

\[ \text{SiH}_2\text{Ph} \]

**2a**

$\text{C}^{13}$ NMR, CDCl$_3$, 400 MHz
2b

$^1$H NMR, CDCl$_3$, 400 MHz

2b

$^{13}$C NMR, CDCl$_3$, 400 MHz
$\text{SiHMePh}$

2c

$^1\text{H NMR, CDCl}_3, 400 \text{ MHz}$

$\text{SiHMePh}$

2c

$^{13}\text{C NMR, CDCl}_3, 400 \text{ MHz}$


**1H NMR, CDCl₃, 600 MHz**

![1H NMR Spectrum](image)

**13C NMR, CDCl₃, 600 MHz**

![13C NMR Spectrum](image)
2e

$^1$H NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 400 MHz
$2f$

$^1H$ NMR, CDCl$_3$, 400 MHz

$1^3C$ NMR, CDCl$_3$, 400 MHz
$^{1}H$ NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 400 MHz
$\text{SiHPr}_2$ $\text{SiHPr}_2$

$\text{2h}$

$^1\text{H NMR, CDCl}_3, 400 \text{ MHz}$

$\text{SiHPr}_2$ $\text{SiHPr}_2$

$\text{13C NMR, CDCl}_3, 400 \text{ MHz}$
\textbf{STANDARD PROTON PARAMETERS}

\[ 2j \]
\textbf{\textsuperscript{1}H NMR, CDCl\textsubscript{3}, 600 MHz}

\textbf{STANDARD CARBON PARAMETERS}

\[ 2j \]
\textbf{\textsuperscript{13}C NMR, CDCl\textsubscript{3}, 600 MHz}
$\text{H NMR, CDCl}_3, 400 \text{ MHz}$

$\text{C NMR, CDCl}_3, 400 \text{ MHz}$
$\text{H NMR, CDCl}_3, 600 \text{ MHz}$

$\text{C NMR, CDCl}_3, 600 \text{ MHz}$
$^1$H NMR, CDCl$_3$, 400 MHz

$^1$H NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 400 MHz
$\text{SiHPh}_2$

$2n$

$^1\text{H NMR, CDCl}_3, 600 \text{ MHz}$

$\text{SiHPh}_2$

$2n$

$^{13}\text{C NMR, CDCl}_3, 600 \text{ MHz}$
$\begin{align*}
&\text{O} \quad \text{SiHPh}_2 \\
&\text{3a} \\
&^1\text{H NMR, CDCl}_3, 400 \text{ MHz}
\end{align*}$

$\begin{align*}
&\text{O} \quad \text{SiHPh}_2 \\
&\text{3a} \\
&^{13}\text{C NMR, CDCl}_3, 400 \text{ MHz}
\end{align*}$
$^1$H NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 400 MHz
$\text{O-SiHPh}_2$

$3c$

$^1\text{H NMR, CDCl}_3, 400 \text{ MHz}$

$\text{O-SiHPh}_2$

$3c$

$^{13}\text{C NMR, CDCl}_3, 400 \text{ MHz}$
$\text{O} \text{SiHPh}_2$

$3d$

$^1H$ NMR, CDCl$_3$, 400 MHz

$\text{O} \text{SiHPh}_2$

$3d$

$^{13}C$ NMR, CDCl$_3$, 400 MHz
$\text{O-SiHPh}_2$

3e

$^1\text{H NMR, CDCl}_3, 400 \text{ MHz}$

$\text{O-SiHPh}_2$

3e

$^{13}\text{C NMR, CDCl}_3, 400 \text{ MHz}$
$^{1}H$ NMR, CDCl$_3$, 400 MHz

$^{13}C$ NMR, CDCl$_3$, 400 MHz
$^1$H NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 400 MHz
**3j**

$^{1}H$ NMR, CDCl$_3$, 600 MHz

$^{13}$C NMR, CDCl$_3$, 600 MHz
$^{1}{H}$ NMR, CDCl$_3$, 600 MHz

$^{13}{C}$ NMR, CDCl$_3$, 600 MHz
3I
$^1$H NMR, CDCl$_3$, 400 MHz

3I
$^{13}$C NMR, CDCl$_3$, 400 MHz
$^1$H NMR spectra of 3m as crude mixture after reaction completion

STANDARD PROTON PARAMETERS

![NMR Spectrum](image)

$^1$H NMR, C$_6$D$_6$, 600 MHz
$^1$H NMR, $\text{CDCl}_3$, 400 MHz

$^{13}$C NMR, $\text{CDCl}_3$, 400 MHz
$^{1}H$ NMR, CDCl$_3$, 600 MHz

STANDARD PROTON PARAMETERS

STANDARD CARBON PARAMETERS

$^{1}H$ NMR, CDCl$_3$, 600 MHz

S37
4b
$^1$H NMR, CDCl$_3$, 400 MHz

4b
$^{13}$C NMR, CDCl$_3$, 400 MHz
$^{1}H$ NMR, CDCl$_3$, 600 MHz

$^{13}$C NMR, CDCl$_3$, 600 MHz
$^1$H NMR, CDCl$_3$, 600 MHz

$^{13}$C NMR, CDCl$_3$, 600 MHz
Time-resolved $^1$H NMR analysis of reaction of 1a and diphenylsilane (recorded every 15 minutes)

$^2J_{H-P} = 92.4$ Hz
Time-resolved $^{31}$P NMR analysis of reaction of 1a and diphenylsilane (recorded every 15 minutes)

1a $^{31}$P resonance
$^1$H NMR spectra of catalytic reaction of methyl phenylpropiolate and diphenylsilane at room temperature (forming mixture of $E$ and $Z$ isomer)

$^1$H NMR spectra of catalytic reaction of methylphenylpropiolate and methylphenylsilane at room temperature (forming mixture of $E$ and $Z$ isomer)
Representative SELNOE experiments to determine between stereoisomers

N500.1.fid