Supporting Information

**Synthesis of Allylsilanes via Nickel-Catalyzed Cross-Coupling of Silicon Nucleophiles with Allyl Alcohols**

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Experimental details and characterization data

1. General

2. Preparation of allyl alcohols

Method A

Characterization data

(1) \((E)-3-(3\text{-phenoxyphenyl})\text{prop-2-en-1-ol (1o)}\)

(2) \((E)-3-([1,1'\text{-biphenyl}]-2-yl)\text{prop-2-en-1-ol (1q)}\)

(3) \((E)-3-(2\text{-fluorophenyl})\text{prop-2-en-1-ol (1r)}\)

(4) \((E)-3-(1\text{-methyl-1H-indol-5-yl})\text{prop-2-en-1-ol (1zf)}\)

Method B

Method C

Method D

Characterization data

(5) \((E)-3-(\text{benzo[b]thiophen-3-yl})\text{prop-2-en-1-ol (1ze)}\)

Method E

Method F

Method G

Method H

3. Experimental procedure for the catalytic coupling

(i) General procedure for the catalytic coupling

(ii) Reaction of \((E)-3\text{-phenylprop-2-en-1-ol with PhMe}_2\text{SiZnCl (2 mmol scale)}\)

Characterization data

(1) \(\text{cinnamyl(dimethyl(phenyl)silane (3a)}\)

(2) \((E)-(3-(4\text{-}(\text{tert-butyl)phenyl})\text{allyl(dimethyl(phenyl)silane (3b)}\)

(3) \((E)-(3-(4\text{-methoxyphenyl})\text{allyl(dimethyl(phenyl)silane (3c)}\)

(4) \((E)-4\text{-((dimethyl(phenyl)silyl)prop-1-en-1-yl)-N,N-dimethyl aniline (3d)}\)

(5) \((E)\text{-dimethyl(3-(4-(methylthio)phenyl)allyl(phenyl)silane (3e)}\)

(6) \((E)\text{-dimethyl(phenyl)(3-(4-(trifluoromethyl)phenyl)allyl)silane (3f)}\)

(7) \((E)\text{-dimethyl(phenyl)(3-(4-(trifluoromethoxy)phenyl)allyl)silane (3g)}\)

(8) \((E)-(3-(4\text{-((difluoromethoxy)phenyl})\text{allyl(dimethyl(phenyl)silane (3h)}\)

(9) \((E)-(3-(4\text{-fluorophenyl})\text{allyl(dimethyl(phenyl)silane (3i)}\)

(10) \((E)-(3-(4\text{-chlorophenyl})\text{allyl(dimethyl(phenyl)silane (3j)}\)

(11) \((E)-3-(4\text{-dimethyl(phenyl)silyl})\text{phenyl)prop-2-en-1-ol (3k)}\)

(12) \((E)-(3-(4\text{-dimethyl(phenyl)silyl})\text{phenyl)allyl(dimethyl(phenyl) silane (3ka)}\)

(13) \(\text{methyl (E)-4-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)benzoate (3l)}\)

(14) \((E)-4-(3\text{-dimethyl(phenyl)silyl)prop-1-en-1-yl)-N,N-diethyl benzamide (3m)}\)

(15) \((E)-(3-(3\text{-methoxyphenyl})\text{allyl(dimethyl(phenyl)silane (3n)}\)

(16) \((E)-\text{dimethyl(3-(3-phenoxyphenyl)allyl)(phenyl)silane (3o)}\)
(17) \((E)\)-dimethyl(phenyl)(3-(3-(trifluoromethyl)phenyl)allyl)silane \((3p)\)
(18) \((E)\)-(3-[[1,1'-biphenyl]-2-yl]allyl)dimethyl(phenyl)silane \((3q)\)
(19) \((E)\)-(3-(2-fluorophenyl)allyl)dimethyl(phenyl)silane \((3r)\)
(20) \((E)\)-(3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)allyl)dimethyl(phenyl)silane \((3s)\)
(21) \((E)\)-(3-(benzo[d][1,3]dioxol-5-yl)allyl)dimethyl(phenyl)silane \((3t)\)
(22) \((E)\)-dimethyl(3-(naphthalen-2-yl)allyl)(phenyl)silane \((3u)\)
(23) \((E)\)-dimethyl(3-(naphthalen-1-yl)allyl)(phenyl)silane \((3v)\)
(24) \((E)\)-dimethyl(phenyl)(4-phenylbut-3-en-2-yl)silane \((3w)\)
(25) \((E)\)-(1,3-diphenylallyl)dimethyl(phenyl)silane \((3x)\)
(26) \((E)\)- and \((Z)\)-dimethyl(2-methyl-3-phenylallyl)(phenyl)silane \((3y)\)
(27) \((E)\)-(6-(4-methoxyphenyl)hex-2-en-1-yl)dimethyl(phenyl)silane and \((E)\)-(6-(4-methoxyphenyl)hex-1-en-3-yl)dimethyl(phenyl)silane \((3z)\)
(28) \((E)\)-dimethyl(phenyl)(3-(tetrahydro-2H-pyran-4-yl)allyl)silane and dimethyl(phenyl)(1-(tetrahydro-2H-pyran-4-yl)allyl)silane \((3za)\)
(29) \((E)\)-(3-(furan-2-yl)allyl)dimethyl(phenyl)silane \((3zb)\)
(30) \((E)\)-dimethyl(phenyl)(3-(thiophen-2-yl)allyl)silane and \((Z)\)-dimethyl(phenyl)(3-(thiophen-2-yl)allyl)silane \((3zc)\)
(31) \((E)\)-2-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)pyridine \((3zd)\)
(32) \((E)\)-(3-(benzo[b]thiophen-3-yl)allyl)dimethyl(phenyl)silane \((3ze)\)
(33) \((E)\)-5-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-1-methyl-1H-indole \((3zf)\)
(34) \((E)\)-dimethyl(phenyl)(3-(p-tolyl)allyl)silane \((3zh)\)
(35) cinnamyl(methyl)diphenylsilane \((3zm)\)
(36) Cinnamyltriphenylsilane \((3zn)\)
(37) \((R,E)\)-dimethyl(phenyl)(1-phenylpent-1-en-3-yl)silane \((3zo)\)

4. Catalytic coupling of cinnamyl(dimethyl(phenyl)silane with Ph₂CHOH

5. Mechanism studies

- Nickel-catalyzed reaction of cinnamyl alcohol with \(\text{PhMe}_2\text{SiZnCl}\) in the presence of \((1\text{-cyclopropylvinyl})\)benzene
- Reaction of cinnamyl alcohol with \(\text{PhMe}_2\text{SiZnCl}\) catalyzed by \(\text{Ni(COD)}_2/\text{PMe}_3\)
- Reaction of \(\text{rac-}(E)\)-1-phenylpent-1-en-3-ol with \(\text{PhMe}_2\text{SiZnCl}\) under the catalysis of \(\text{NiCl}_2(\text{PMe}_3)_2\)
- Reaction of \((S,E)\)-1-phenylpent-1-en-3-ol with \(\text{PhMe}_2\text{SiZnCl}\) under the catalysis of \(\text{NiCl}_2(\text{PMe}_3)_2\)
- Isolation and identification of \(\text{PhMe}_2\text{Si-SiMe}_2\text{Ph}\) in the \(\text{NiCl}_2(\text{PMe}_3)_2\)-catalyzed reaction of cinnamyl alcohol with \(\text{PhMe}_2\text{SiZnCl}\)

References

6. Copied of NMR spectra of the unreported allylic alcohols, the cross-coupling products, and 1,1,2,2-tetramethyl-1,2-diphenyl-disilane

I. NMR spectral copies of the unknown allyl alcohols
II. NMR spectral copies of the cross-coupling products
III. NMR spectral copies of 1,1,2,2-tetramethyl-1,2-diphenyl-disilane
Experimental details and characterization data

1. General

All reactions were performed under a nitrogen atmosphere using standard Schlenk and vacuum line techniques. All chemicals were purchased as reagent grade and used without further purification unless otherwise noted. Toluene and tetrahydrofuran were purified by JC Meyer Phoenix Solvent Systems. Butyl ether (nBu₂O) was distilled under nitrogen over sodium and degassed prior to use. ZnCl₂ and LiCl were purchased from commercial vendors and dried under vacuum at 140 °C for 12 h prior to use. MeMgCl was purchased from commercial vendors and used as received. MeZnCl was prepared from ZnCl₂ and 1.0 equiv of MeMgCl in the presence of 1.0 equiv of LiCl. PhMe₂SiZnCl, Ph₂MeSiZnCl and Ph₃SiZnCl were prepared according to reported procedure.[1] Concentration of MeZnCl, PhMe₂SiZnCl, Ph₂MeSiZnCl and Ph₃SiZnCl were titrated using Knoechel’s method.[2] NMR spectra were recorded on a Bruker av400 spectrometer at 25 °C. The chemical shifts of the ¹H NMR spectra were referenced to TMS and the chemical shifts of the ¹³C NMR spectra were referenced to internal solvent resonances. The chemical shifts of the ¹⁹F NMR spectra were referenced to external CF₃COOH. High-resolution mass spectra (HR-MS) were acquired in the ESI or EI mode using an Orbitrap mass analyzer.

2. Preparation of allyl alcohols

Method A: To a stirred suspension of NaH (60% disp. in mineral oil, 240 mg, 6.0 mmol) in THF (15 mL) was added triethyl phosphonoacetate (1.2 mL, 6.0 mmol) at 0 °C and stirred for 20 min. Then appropriate aldehyde (5.0 mmol) was added and the resultant mixture was stirred at room temperature until full conversion of the aldehyde detected by TLC. After cooling to 0 °C, the reaction was quenched with H₂O (10 mL) and the mixture was extracted with EtOAc (3 × 25 mL). The combined organic phases were washed with brine (20 mL), dried over Na₂SO₄ and concentrated by rotary evaporation. The residue was purified by column chromatography to give corresponding allylic ester. DIBAL-H (10.5 mL, 1.0 M in hexane, 10.5 mmol) was added dropwise to a stirred solution of the allylic ester in CH₂Cl₂ (10 mL) at −78 °C. The resultant solution was allowed to warm to room temperature and stirred for 3-5 h. The reaction was quenched by slow addition of sat. aq. Na-,K-tartrate solution at 0 °C (20 mL) and H₂O (10 mL) successively. The resulting mixture was diluted with CH₂Cl₂ (20 mL). Organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic phases were washed with brine (30 mL), dried
over Na₂SO₄, concentrated by rotary evaporation, and purified by column chromatography (Scheme S1).

Scheme S1. Preparation of allyl alcohols (Method A).

Characterization data

(1) \((E)\)-3-(3-phenoxyphenyl)prop-2-en-1-ol (1o)
Eluent: petroleum ether / ethyl acetate = 8:1. Colorless oil, 1.01 g (90%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38–7.30 (m, 2H), 7.26 (d, $J = 8.0$ Hz, 1H), 7.16–7.07 (m, 2H), 7.06–6.96 (m, 3H), 6.93–6.86 (m, 1H), 6.56 (d, $J = 15.9$ Hz, 1H), 6.32 (dt, $J = 15.9$, 5.6 Hz, 1H), 4.30 (dd, $J = 5.6$, 1.3 Hz, 2H), 1.62 (br, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 157.66, 157.19, 138.70, 130.49, 130.00, 129.90, 129.44, 123.45, 121.66, 119.04, 118.25, 116.71, 63.66. HR-MS (ESI): m/z 227.1064 [M+H]$^+$, calcd for C$_{15}$H$_{15}$O$_2$ 227.1067.

(2) (E)-3-([1,1'-biphenyl]-2-yl)prop-2-en-1-ol (1q)

Eluent: petroleum ether / ethyl acetate = 10:1. Colorless oil, 0.98 g (93%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.66–7.57 (m, 1H), 7.46–7.26 (m, 8H), 6.60 (d, $J = 15.8$ Hz, 1H), 6.30 (dt, $J = 15.8$, 5.9 Hz, 1H), 4.21 (dd, $J = 5.9$, 1.2 Hz, 2H), 1.52 (br, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 141.09, 140.94, 134.72, 130.37, 130.22, 129.87, 129.48, 128.22, 127.72, 127.63, 127.19, 126.18, 64.01. HR-MS (ESI): m/z 211.1115 [M+H]$^+$, calcd for C$_{15}$H$_{15}$O 211.1117.

(3) (E)-3-(2-fluorophenyl)prop-2-en-1-ol (1r)

Eluent: petroleum ether / ethyl acetate = 10:1. Colorless oil, 0.68 g (89%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.44 (t, $J = 7.7$ Hz, 1H), 7.25–7.16 (m, 1H), 7.13–6.98 (m, 2H), 6.77 (d, $J = 16.1$ Hz, 1H), 6.51–6.39 (m, 1H), 4.34 (s, 2H), 1.99–1.58 (br, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 160.41 (d, $J = 249.3$ Hz), 131.34 (d, $J = 4.8$ Hz), 129.04 (d, $J = 8.4$ Hz), 127.64 (d, $J = 3.8$ Hz), 124.60 (d, $J = 12.2$ Hz), 124.23 (d, $J = 3.6$ Hz), 123.53 (d, $J = 3.5$ Hz), 115.85 (d, $J = 22.1$ Hz), 63.91. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –118.10. HR-MS (ESI): m/z 153.0697 [M+H]$^+$, calcd for C$_9$H$_{10}$OF 153.0710.

(4) (E)-3-(1-methyl-1H-indol-5-yl)prop-2-en-1-ol (1zf)
Eluent: petroleum ether / ethyl acetate = 5:1. White solid, 0.83 g (89%), mp: 96–98°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.59 (d, $J = 1.4$ Hz, 1H), 7.33 (dd, $J = 8.5$, 1.6 Hz, 1H), 7.27–7.21 (m, 1H), 7.01 (d, $J = 3.1$ Hz, 1H), 6.70 (d, $J = 15.8$ Hz, 1H), 6.45 (dd, $J = 3.1$, 0.7 Hz, 1H), 6.31 (dt, $J = 15.8$, 6.1 Hz, 1H), 4.30 (dd, $J = 6.1$, 1.3 Hz, 2H), 3.75 (s, 3H), 1.62 (br, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 136.62, 133.06, 129.49, 128.72, 128.28, 125.48, 120.16, 119.71, 109.48, 101.35, 64.32, 33.00. HR-MS (ESI): m/z 188.1067 [M+H]$^+$, caleed for C$_{12}$H$_{14}$ON 188.1070.

**Method B**: Cinnamaldehyde (5 mmol) and THF (10 mL) were successively added to a Schlenk tube. To the stirred solution was added MeMgCl or PhMgBr (6 mmol, 1.2 equiv) at 0 °C. Then the mixture was stirred for 3 h at room temperature. Hydrochloric acid (5% aq., 10 mL) was added with stirring. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, concentrated by rotary evaporation, and purified by column chromatography to give the corresponding allylic alcohol (Scheme S2).

![Scheme S2. Preparation of allyl alcohols (Method B).](image)

**Method C**: allylic aldehydes (10 mmol) and MeOH (30 mL) were successively added to a round bottom flask. The resulting solution was cooled to 0 °C and NaBH$_4$ (575 mg, 15 mmol) was added. The mixture was warmed to room temperature and stirred until the reaction was complete (TLC detection). MeOH was removed by rotary evaporation, and H$_2$O (15 mL) was added. The resulting mixture was extracted with EtOAc (2 × 20 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, concentrated by rotary evaporation, and purified by column chromatography to give the corresponding allylic alcohol (Scheme S3).
Method D: A solution of arylcarbaldehydes (5 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (2.45 g, 7.0 mmol) in THF (10 mL) was heated at 80 °C for 12 h. The reaction mixture was cooled to ambient temperature, quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na₂SO₄, concentrated by rotary evaporation, and purified by column chromatography to give the corresponding allylic esters.

DIBAL-H (10.5 mL, 1.0 M in hexane, 10.5 mmol) was added dropwise to a stirred solution of the allylic esters in CH₂Cl₂ (10 mL) at −78 °C. The resulting solution was allowed to warm to room temperature and stirred for 3-5 h. The reaction was quenched by slow addition of sat. aq. Na-, K-tartrate solution at 0 °C (20 mL) and H₂O (10 mL) successively. The resulting mixture was diluted with CH₂Cl₂ (20 mL). Organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic phases were washed with brine (30 mL), dried over Na₂SO₄, concentrated by rotary evaporation and purified by column chromatography (Scheme S4).
Eluent: petroleum ether / ethyl acetate = 8:1. Pale yellow oil, 0.81 g (85%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95–7.88 (m, 1H), 7.88–7.81 (m, 1H), 7.46–7.31 (m, 3H), 6.89 (dd, $J = 15.9$, 0.4 Hz, 1H), 6.44 (dt, $J = 15.9$, 5.7 Hz, 1H), 4.38 (d, $J = 5.2$ Hz, 2H), 1.69 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 140.57, 137.76, 133.50, 130.34, 124.63, 124.42, 123.46, 123.04, 122.39, 122.02, 64.00. HR-MS (ESI): m/z 191.0523 [M+H]$^+$, calcd for C$_{11}$H$_{11}$OS 191.0525.

**Method E**: In a round bottom flask a solution of substituted benzaldehydes (10 mmol) and (triphenylphosphoranyldiene)acetaldehyde (5 mmol) in toluene was stirred at 50 °C for 12 h. The crude mixture was purified by column chromatography to give allylic aldehydes. The allylic aldehydes and MeOH (20 mL) were successively added to a round bottom flask. The resulting solution was cooled to 0 °C and NaBH$_4$ (1.5 equiv) was added. The reaction mixture was warmed to room temperature and stirred until the aldehydes were completely converted (TLC detection). The MeOH was removed by rotary evaporation, and H$_2$O (15 mL) was added. The mixture was extracted with EtOAc (2 × 20 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, concentrated by rotary evaporation, and purified by column chromatography to give corresponding allylic alcohols (Scheme S5).

![Scheme S5. Preparation of allyl alcohols (Method E).](image1)

**Method F**: 4-Bromobenzoic acid (2.01 g, 10 mmol), DMAP (244 mg, 2 mmol), EDC·HCl (3.83 g, 20 mmol), CH$_2$Cl$_2$ (30 mL) and Et$_2$NH (1.58 mL, 15 mmol) were successively added to a round bottom flask. The solution was stirred at room temperature for 12 h. The mixture was purified by column chromatography to give 4-bromo-$N,N$-diethylbenzamide. To a solution of 4-bromo-$N,N$-diethylbenzamide (3.0 mmol) in DMF (15 mL) was successively
added acrolein diethyl acetal (1.37 mL, 9 mmol), nBu4NOAc (1.81 g, 6.0 mmol), K2CO3 (0.62 g, 4.5 mmol), KCl (0.22 g, 3.0 mmol) and Pd(OAc)2 (33.7 mg, 0.15 mmol). The mixture was stirred at 90 °C for 3 h. After cooling to room temperature, 10% hydrochloric acid was slowly added and the mixture was stirred for 10 min. Then, it was diluted with H2O and extracted with EtOAc (3 × 25 mL). The organic phase was washed with saturated NaCl solution, dried over Na2SO4, concentrated under reduced pressure and purified by column chromatography to give (E)-N,N-diethyl-4-(3-oxoprop-1-en-1-yl)benzamide 0.303 g (44%) as a white solid. Then the allylic aldehyde (0.303 g, 1.31 mmol) and MeOH (15 mL) were successively added to a round bottom flask. The solution was cooled to 0 °C and NaBH4 (1.5 equiv) was added. The mixture was warmed to room temperature and stirred until the reaction was complete (TLC detection). Solvent was removed by rotary evaporation, and H2O (15 mL) was added. The mixture was extracted with EtOAc (2 × 25 mL). The combined organic phases were dried over anhydrous Na2SO4, concentrated by rotary evaporation, and purified by column chromatography (eluent: petroleum ether / ethyl acetate = 2:1) to give (E)-N,N-diethyl-4-(3-hydroxyprop-1-en-1-yl)benzamide (Scheme S6) as a white solid, 0.29 g, mp 55–57 °C. 1H NMR (400 MHz, CDCl3): δ 7.36 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 16.0 Hz, 1H), 6.34 (dt, J = 15.9, 5.4 Hz, 1H), 4.30 (dd, J = 5.4, 1.2 Hz, 2H), 3.54 (b, 2H), 3.27 (b, 2H), 2.43 (b, 1H), 1.24 (b, 3H), 1.11 (b, 3H). 13C NMR (101 MHz, CDCl3) δ 171.33, 137.88, 136.10, 130.21, 129.74, 126.79, 126.47, 63.41, 43.46, 39.45, 14.31, 13.00. HR-MS (ESI): m/z 234.1486 [M+H]+, calcd for C14H20O2N 234.1489.

Method G: To a stirred solution of argoncarbalddehydes (5.0 mmol) in THF (10 mL) was added vinylmagnesium bromide (6.0 mL, 1.0 M in THF, 6.0 mmol) at 0 °C. Then the mixture was stirred at room temperature for 3 h. Hydrochloric acid (5% aq., 10 mL) was added with
stirring. The mixture was extracted with ethyl acetate \((3 \times 10 \text{ mL})\). The combined organic phases were dried over anhydrous \(\text{Na}_2\text{SO}_4\), concentrated by rotary evaporation, and purified by column chromatography to give the corresponding allylic alcohols (Scheme S7).

\[
\begin{align*}
\text{Ar} & \quad + \quad 
\begin{array}{c}
\text{MgBr} \\
\text{THF}
\end{array}
\quad \text{0 °C-rt} \\
\quad \longrightarrow \\
\begin{array}{c}
\text{OH} \\
\text{Ar}
\end{array}
\end{align*}
\]

\[
\begin{array}{c}
\text{OH} \\
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{Me} \\
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{OH} \\
\text{MeO}
\end{array}
\]

\[
\begin{array}{c}
\text{Me}_2\text{N} \\
\text{F}
\end{array}
\]

\[
\begin{array}{c}
\text{F} \\
\text{F}_3\text{C}
\end{array}
\]

\[
\begin{array}{c}
1\text{zg}^{[22]} \\
1\text{zh}^{[23]} \\
1\text{zi}^{[22]} \\
1\text{zj}^{[24]} \\
1\text{zk}^{[22]} \\
1\text{zl}^{[25]}
\end{array}
\]

Scheme S7. Preparation of allyl alcohols (Method G)

**Method H.**\(^{[26]}\) Diol A \((0.467 \text{ g}, 1.0 \text{ mmol})\), toluene \((10 \text{ mL})\) and \(\text{Ti}(\text{OCHMe}_2)_4\) \((0.36 \text{ mL}, 1.2 \text{ mmol})\) were charged to a Schlenk tube. After the mixture was stirred at room temperature for 5 h, volatiles were removed in vacuo. The residue was combined with toluene \((15 \text{ mL})\), \(\text{Ti}(\text{OCHMe}_2)_4\) \((1.78 \text{ mL}, 6.0 \text{ mmol})\) and cinnamaldehyde \((0.63 \text{ mL}, 5 \text{ mmol})\). The solution was cooled to \(-27 \text{ °C}\) and \(\text{Et}_2\text{Zn} (3 \text{ mL}, 2.0 \text{ M in hexane}, 6.0 \text{ mmol})\) was added dropwise. After stirring at \(-27 \text{ °C}\) for 24 h, the reaction mixture was quenched with saturated aq. \(\text{NH}_4\text{Cl} (10 \text{ mL})\), and extracted with ethyl acetate \((3 \times 10 \text{ mL})\). The combined organic phases were dried over anhydrous \(\text{Na}_2\text{SO}_4\), concentrated by rotary evaporation, and purified by column chromatography (eluent: petroleum ether / ethyl acetate = 10:1) to give \((S,E)-1\text{-phenylpent-1-en-3-ol (}(S)-1\text{zo})\) as a colorless oil \(0.75 \text{ g} \text{ (92% yield, 96% ee) (Scheme S8). Optical purity was determined by HPLC with a ChiralCel OD-H column: 25 °C; hexane/i-PrOH = 95/5; flow rate = 1.0 \text{ mL/min}; t_{\text{major}} = 22.25 \text{ min}, t_{\text{minor}} = 13.13 \text{ min}, \lambda = 254 \text{ nm; ee = 96%;} \quad [\alpha]_{D}^{20} = -20.85 \text{ (c = 1.05, CHCl}_3) \text{ (ref.(26): [}\alpha]_{D}^{20} = -6.18 \text{ (c = 1.65, CHCl}_3)\text{ for the (S)-form).}^{1}\text{H NMR (400 MHz, CDCl}_3): \delta 7.42–7.36 \text{ (m, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.27–7.20 (m, 1H), 6.57 (d, J = 15.9 Hz, 1H), 6.21 (dd, J = 15.9, 6.8 Hz, 1H), 4.21 (q, J = 6.4 Hz, 1H), 1.77–1.57 (m, 3H), 0.97 (t, J = 7.5 Hz, 3H).}^{13}\text{C NMR (101 MHz, CDCl}_3): \delta 136.86, 132.39, 130.56, 128.70, 127.75, 126.57, 74.54, 30.34, 9.88.\)
3. Experimental procedure for the catalytic coupling

(i) General procedure for the catalytic coupling
NiCl$_2$(PMe$_3$)$_2$ (5.6 mg, 10 mol %) and allyl alcohol (1.0 mL, 0.2 M in THF, 0.2 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeZnCl (0.55 mL, 0.44 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of silicon-based zinc reagent (0.6 mL, 0.4 M solution in THF, 0.24 mmol) was added, and the solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (2 mL) was added. The resultant mixture was stirred at room temperature for 5 h, diluted with EtOAc (5 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and purified by silica gel chromatography to give the desired products.

(ii) Reaction (E)-3-phenylprop-2-en-1-ol with PhMe$_2$SiZnCl (2 mmol scale)
NiCl$_2$(PMe$_3$)$_2$ (56.0 mg, 10 mol %), (E)-3-phenylprop-2-en-1-ol (268.4 mg, 2.0 mmol) and THF (4 mL) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeZnCl (3.70 mL, 0.65 M solution in THF, 2.4 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of PhMe$_2$SiZnCl (5.2 mL, 0.46 M solution in THF, 2.4 mmol) was added, and the solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (15 mL) was added. The resultant mixture was stirred at room temperature for 5 h, diluted with EtOAc (20 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (50 mL). The filtrate was concentrated and purified by silica gel chromatography to give the desired product 3a as a pale yellow oil (453.6 mg, 90%).
Characterization data

(1) cinnamyldimethyl(phenyl)silane (3a)[27]

\[
\text{Me}_2\text{Si} + \text{Ph} \\
\text{Me}_2\text{Si} + \text{Ph}
\]

Eluent: petroleum ether. pale yellow oil, 49.1 mg (97%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.57–7.49 (m, 2H), 7.40–7.33 (m, 3H), 7.29–7.22 (m, 4H), 7.18–7.10 (m, 1H), 6.29–6.14 (m, 2H), 1.89 (d, \(J = 6.8\) Hz, 2H), 0.31 (s, 6H). \(^13\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 138.67, 138.52, 133.76, 129.23, 129.09, 128.58, 127.94, 127.26, 126.44, 125.70, 23.16, –3.17.

(2) \((E)-(3-(4-(\text{tert}-\text{butyl})\text{phenyl})\text{allyl})\text{dimethyl(phenyl)silane (3b)}\)

\[
\text{Bu} + \text{Me}_2\text{Si} + \text{Ph}
\]

Eluent: petroleum ether. Colorless oil, 55.7 mg (90%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.56–7.50 (m, 2H), 7.38–7.32 (m, 3H), 7.21 (d, \(J = 8.4\) Hz, 2H), 6.28–6.11 (m, 2H), 1.88 (d, \(J = 7.0\) Hz, 2H), 1.30 (s, 9H), 0.30 (s, 6H). \(^13\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 149.37, 138.75, 135.75, 133.76, 129.19, 128.77, 127.93, 126.37, 125.48, 125.40, 34.58, 31.48, 23.06, –3.19. HR-MS (EI): m/z 308.1958 [M]^+, calcd for C\(_{21}\)H\(_{28}\)Si 308.1955.

(3) \((E)-(3-(4-\text{methoxyphenyl})\text{allyl})\text{dimethyl(phenyl)silane (3c)}[28]\)

\[
\text{MeO} + \text{Me}_2\text{Si} + \text{Ph}
\]

Eluent: petroleum ether. Colorless oil, 51.4 mg (91%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.57–7.49 (m, 2H), 7.39–7.32 (m, 3H), 7.20 (d, \(J = 8.7\) Hz, 2H), 6.81 (d, \(J = 8.7\) Hz, 2H), 6.19 (d, \(J = 15.7\) Hz, 1H), 6.05 (dt, \(J = 15.8, 8.0\) Hz, 1H), 3.77 (s, 3H), 1.86 (dd, \(J = 8.0, 0.8\) Hz, 2H), 0.31 (s, 6H). \(^13\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 158.39, 138.78, 133.75, 131.39, 129.17, 128.41, 127.90, 126.71, 124.93, 114.00, 55.39, 22.88, –3.20.

(4) \((E)-\text{4-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-N,N-dimethylaniline (3d)}\)

\[
\text{Me}_2\text{N} + \text{Me}_2\text{Si} + \text{Ph}
\]

Eluent: petroleum ether/ethyl acetate = 100:1. Pale yellow oil, 53.4 mg (90%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.56–7.49 (m, 2H), 7.39–7.32 (m, 3H), 7.17 (d, \(J = 8.8\) Hz, 2H), 6.66 (d, \(J = 8.8\) Hz, 2H), 6.17 (d, \(J = 15.7\) Hz, 1H), 6.00 (dt, \(J = 15.8, 8.1\) Hz, 1H), 2.91 (s, 6H), 1.85 (dd,
$J = 8.1, 1.1 \text{ Hz, } 2\text{H}$, 0.30 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 149.50, 139.01, 133.78, 129.09, 128.83, 127.87, 127.47, 126.50, 122.82, 112.87, 40.85, 22.77, −3.20. HR-MS (ESI): m/z 296.1827 [M+H]$^+$, calcd for C$_{19}$H$_{26}$NSi 296.1829.

5) $(E)$-dimethyl(3-(4-(methylthio)phenyl)allyl)(phenyl)silane (3e)

![Structure](Image)

Eluent: petroleum ether. Colorless oil, 56.8 mg (95%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55–7.48 (m, 2H), 7.40–7.33 (m, 3H), 7.21–7.14 (m, 4H), 6.21–6.14 (m, 2H), 2.45 (s, 3H), 1.92–1.85 (m, 2H), 0.31 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 138.58, 136.01, 135.67, 133.73, 129.22, 128.35, 127.92, 127.16, 126.89, 126.09, 23.15, 16.33, −3.20. HR-MS (EI): m/z 298.1201 [M]$^+$, calcd for C$_{18}$H$_{22}$SSi 298.1206.

6) $(E)$-dimethyl(phenyl)(3-(4-(trifluoromethyl)phenyl)allyl) silane (3f)

![Structure](Image)

Eluent: petroleum ether. Colorless oil, 63.5 mg (99%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56–7.46 (m, 4H), 7.40–7.34 (m, 3H), 7.32 (d, $J = 8.2$ Hz, 2H), 6.32 (dt, $J = 15.7, 7.9$ Hz, 1H), 6.23 (d, $J = 15.8$ Hz, 1H), 1.93 (d, $J = 7.8$ Hz, 2H), 0.33 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 141.89 (d, $J = 1.2$ Hz), 138.25, 133.73, 130.49, 129.37, 128.01, 127.76, 125.70, 125.54 (q, $J = 3.8$ Hz), 124.51 (q, $J = 271.5$ Hz), 23.60, −3.20. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −62.23. HR-MS (EI): m/z 320.1198 [M]$^+$, calcd for C$_{18}$H$_{19}$F$_3$Si 320.1203.

7) $(E)$-dimethyl(phenyl)(3-(4-(trifluoromethoxy)phenyl)allyl) silane (3g)

![Structure](Image)

Eluent: petroleum ether. Colorless oil, 66.5 mg (99%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55–7.49 (m, 2H), 7.40–7.34 (m, 3H), 7.27–7.22 (m, 2H), 7.10 (dd, $J = 8.8, 0.9$ Hz, 2H), 6.24–6.14 (m, 2H), 1.94–1.87 (m, 2H), 0.32 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 147.68 (d, $J = 1.8$ Hz), 138.43, 137.29, 133.74, 129.31, 128.55, 127.98, 127.57, 126.74, 121.20, 120.64 (q, $J = 256.7$ Hz), 23.27, −3.20. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −57.90. HR-MS (EI): m/z 336.1152 [M]$^+$, calcd for C$_{18}$H$_{19}$OF$_3$Si 336.1152.
(8) (E)-(3-(4-(difluoromethoxy)phenyl)allyl)dimethyl(phenyl)silane (3h)

Eluent: petroleum ether. Colorless oil, 59.4 mg (93%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55–7.48 (m, 2H), 7.40–7.32 (m, 3H), 7.23 (d, $J$ = 8.7 Hz, 2H), 7.01 (d, $J$ = 8.7 Hz, 2H), 6.45 (t, $J$ = 74.2 Hz, 1H), 6.23–6.09 (m, 2H), 1.89 (d, $J$ = 6.9 Hz, 2H), 0.32 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 149.71 (t, $J$ = 2.8 Hz), 138.49, 135.99, 133.74, 129.28, 127.96, 127.75, 127.73, 126.85, 119.79, 116.17 (d, $J$ = 259.3 Hz), 23.17, –3.20. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –80.40. HR-MS (ESI): m/z 319.1320 [M+H]$^+$, calcd for C$_{18}$H$_{21}$OF$_2$Si 319.1324.

(9) (E)-(3-(4-fluorophenyl)allyl)dimethyl(phenyl)silane (3i)

Eluent: petroleum ether. Pale yellow oil, 50.4 mg (93%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55–7.49 (m, 2H), 7.39–7.32 (m, 3H), 7.23–7.16 (m, 2H), 6.94 (t, $J$ = 8.7 Hz, 2H), 6.19 (d, $J$ = 15.8 Hz, 1H), 6.10 (dt, $J$ = 15.6, 7.7 Hz, 1H), 1.88 (d, $J$ = 7.6 Hz, 2H), 0.31 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.71 (d, $J$ = 245.0 Hz), 138.57, 134.63 (d, $J$ = 3.1 Hz), 133.75, 129.26, 127.95, 127.87, 127.02 (d, $J$ = 5.1 Hz), 126.97, 115.37 (d, $J$ = 21.4 Hz), 23.05, –3.19. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –116.44. HR-MS (EI): m/z 270.1236 [M]$^+$, calcd for C$_{17}$H$_{19}$FSi 270.1235.

(10) (E)-(3-(4-chlorophenyl)allyl)dimethyl(phenyl)silane (3j)

Eluent: petroleum ether. Colorless oil, 54.7 mg (95%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55–7.47 (m, 2H), 7.39–7.32 (m, 3H), 7.21 (d, $J$ = 8.4 Hz, 2H), 7.16 (d, $J$ = 8.4 Hz, 2H), 6.23–6.12 (m, 2H), 1.94–1.83 (m, 2H), 0.31 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 138.43, 136.93, 133.73, 131.87, 129.28, 128.66, 128.12, 127.96, 127.80, 126.84, 23.24, –3.19. HR-MS (EI): m/z 286.0938 [M]$^+$, calcd for C$_{17}$H$_{19}$ClSi 286.0939.

(11) (E)-3-(4-(dimethyl(phenyl)silyl)phenyl)prop-2-en-1-ol (3k)
Eluent: petroleum ether/ethyl acetate = 10:1. Colorless oil, 38.7 mg (72%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55–7.49 (m, 2H), 7.48 (d, $J$ = 8.0 Hz, 2H), 7.41–7.30 (m, 5H), 6.60 (d, $J$ = 15.9 Hz, 1H), 6.38 (dt, $J$ = 15.9, 5.7 Hz, 1H), 4.31 (dd, $J$ = 5.6, 1.2 Hz, 2H), 1.66 (s, 1H), 0.54 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 138.25, 137.87, 137.47, 134.63, 134.27, 131.08, 129.25, 129.12, 127.95, 125.96, 63.81, –2.28. HR-MS (ESI): m/z 269.1354 [M+H$^+$], calcd for C$_{17}$H$_{21}$OSi 269.1356.

(12) (E)-(3-(4-(dimethyl(phenyl)silyl)phenyl)allyl)dimethyl(phenyl)silane (3ka)

Eluent: petroleum ether. Colorless oil, 76.6 mg (99%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56–7.48 (m, 4H), 7.42 (d, $J$ = 7.6 Hz, 2H), 7.39–7.30 (m, 6H), 7.25 (d, $J$ = 7.7 Hz, 2H), 6.31–6.16 (m, 2H), 1.89 (d, $J$ = 6.6 Hz, 2H), 0.53 (s, 6H), 0.31 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 139.23, 138.58, 138.51, 135.97, 134.54, 134.29, 133.74, 129.24, 129.18, 128.96, 127.95, 127.92, 125.14, 23.30, –2.21, –3.19. HR-MS (EI): m/z 386.1886 [M$^+$], calcd for C$_{25}$H$_{30}$Si$_2$ 386.1881.

(13) methyl (E)-4-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)benzoate (3l)

Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 61.6 mg (99%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.93 (d, $J$ = 8.4 Hz, 2H), 7.56–7.48 (m, 2H), 7.40–7.34 (m, 3H), 7.29 (d, $J$ = 8.4 Hz, 2H), 6.36 (dt, $J$ = 16.0, 8.0 Hz, 1H), 6.24 (d, $J$ = 15.8 Hz, 1H), 3.88 (s, 3H), 1.93 (dd, $J$ = 8.0, 0.6 Hz, 2H), 0.33 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 167.13, 142.95, 138.23, 133.69, 130.66, 129.99, 129.31, 128.20, 127.96, 127.81, 125.41, 52.05, 23.68, –3.21. HR-MS (ESI): m/z 311.1461 [M+H$^+$], calcd for C$_{19}$H$_{23}$O$_2$Si 311.1462.

(14) (E)-4-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-N,N-diethylbenzamide (3m)
Eluent: petroleum ether/ethyl acetate = 4:1. Colorless oil, 60.0 mg (85%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60–7.51 (m, 2H), 7.44–7.35 (m, 3H), 7.30 (s, 4H), 6.36–6.19 (m, 2H), 3.55 (b, 2H), 3.31 (b, 2H), 1.94 (d, $J = 6.7$ Hz, 2H), 1.19 (b, 6H), 0.35 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 171.39, 139.31, 138.38, 134.99, 133.68, 129.23, 128.61, 128.29, 127.91, 126.74, 125.47, 43.35, 39.38, 23.30, 14.30, 12.99, –3.22. HR-MS (ESI): m/z 352.2089 [M+H]$^+$, calcd for C$_{22}$H$_{30}$ONSi 352.2091.

(15) ($E$)-(3-(3-methoxyphenyl)allyl)dimethyl(phenyl)silane (3n)$^{[29]}$

Eluent: petroleum ether. Colorless oil, 54.1 mg (96%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56–7.48 (m, 2H), 7.39–7.32 (m, 3H), 7.17 (t, $J = 8.0$ Hz, 1H), 6.87 (d, $J = 7.7$ Hz, 1H), 6.81 (t, $J = 2.0$ Hz, 1H), 6.71 (dd, $J = 7.6$, 2.5 Hz, 1H), 6.27–6.15 (m, 2H), 3.78 (s, 3H), 1.95–1.83 (m, 2H), 0.31 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 159.86, 139.97, 138.59, 133.74, 129.51, 129.22, 128.89, 127.93, 127.69, 118.38, 111.87, 111.18, 55.25, 23.13, –3.20.

(16) ($E$)-dimethyl(3-(3-phenoxyphenyl)allyl)(phenyl)silane (3o)

Eluent: petroleum ether. Colorless oil, 68.0 mg (99%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.54–7.48 (m, 2H), 7.37–7.28 (m, 3H), 7.20 (t, $J = 7.9$ Hz, 1H), 7.11–7.04 (m, 1H), 7.00 (dd, $J = 8.6$, 1.0 Hz, 3H), 6.94 (t, $J = 2.0$ Hz, 1H), 6.78 (ddd, $J = 8.1$, 2.4, 0.9 Hz, 1H), 6.26–6.13 (m, 2H), 1.93–1.80 (m, 2H), 0.31 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 157.46, 157.43, 140.44, 138.48, 133.72, 129.82, 129.78, 129.25, 128.43, 128.27, 127.94, 123.20, 120.79, 118.88, 116.90, 116.14, 23.21, –3.19. HR-MS (ESI): m/z 345.1666 [M+H]$^+$, calcd for C$_{23}$H$_{25}$OSi 345.1669.

(17) ($E$)-dimethyl(phenyl)(3-(3-(trifluoromethyl)phenyl)allyl)silane (3p)

Eluent: petroleum ether. Colorless oil, 63.3 mg (99%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$
7.55–7.50 (m, 2H), 7.47 (s, 1H), 7.43–7.34 (m, 6H), 6.34–6.20 (m, 2H), 1.93 (d, J = 6.9 Hz, 2H), 0.33 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 139.16, 138.31, 133.73, 130.92 (q, J = 32.0 Hz), 129.60, 129.35, 128.96, 128.71, 128.70, 127.99, 127.68, 126.77 (q, J = 212.9 Hz), 122.93 (q, J = 3.8 Hz), 122.31 (q, J = 3.8 Hz), 23.41, –3.18. $^{19}$F NMR (376 MHz, CDCl$_3$): δ –62.71. HR-MS (EI): m/z 320.1198 [M]$^+$, calcd for C$_{18}$H$_{19}$F$_3$Si 320.1203.

(18) (E)-(3-([1,1'-biphenyl]-2-yl)allyl)dimethyl(phenyl)silane (3q)

![Chemical structure](image1)

Eluent: petroleum ether. Colorless oil, 60.5 mg (92%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.53–7.46 (m, 3H), 7.40–7.21 (m, 11H), 6.22 (d, J = 15.7 Hz, 1H), 6.19–6.09 (m, 1H), 1.82 (d, J = 7.2 Hz, 2H), 0.29 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 141.40, 139.95, 138.69, 136.49, 133.72, 130.22, 129.96, 129.20, 128.08, 128.06, 127.94, 127.51, 126.89, 126.47, 125.76, 23.43, –3.06. HR-MS (EI): m/z 328.1642 [M]$^+$, calcd for C$_{23}$H$_{24}$Si 328.1642.

(19) (E)-(3-(2-fluorophenyl)allyl)dimethyl(phenyl)silane (3r)

![Chemical structure](image2)

Eluent: petroleum ether. Pale yellow oil, 49.1 mg (91%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.56–7.50 (m, 2H), 7.39–7.30 (m, 4H), 7.14–7.06 (m, 1H), 7.05–6.94 (m, 2H), 6.39 (d, J = 15.9 Hz, 1H), 6.28 (dt, J = 15.9, 7.9 Hz, 1H), 1.93 (d, J = 7.9 Hz, 2H), 0.32 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 159.78 (d, J = 248.6 Hz), 138.51, 133.74, 130.21 (d, J = 4.5 Hz), 129.27, 127.96, 127.51 (d, J = 8.3 Hz), 126.84 (d, J = 4.2 Hz), 124.05 (d, J = 3.5 Hz), 121.27 (d, J = 3.5 Hz), 115.67 (d, J = 22.3 Hz), 23.78, –3.21. $^{19}$F NMR (376 MHz, CDCl$_3$): δ –119.13. HR-MS (EI): m/z 270.1236 [M]$^+$, calcd for C$_{17}$H$_{19}$FSi 270.1235.

(20) (E)-(3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)allyl)dimethyl(phenyl)silane (3s)

![Chemical structure](image3)

Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 56.0 mg (90%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.55–7.47 (m, 2H), 7.38–7.31 (m, 3H), 6.83–6.71 (m, 3H), 6.12 (d, J = 15.7 Hz, 1H), 6.04 (dt, J = 15.6, 7.4 Hz, 1H), 4.20 (s, 4H), 1.85 (d, J = 7.4 Hz, 2H), 0.30 (s, 6H).
\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3\): } \delta 143.51, 142.36, 138.69, 133.72, 132.42, 129.17, 128.27, 127.90, 125.57, 119.06, 117.26, 114.03, 64.49, 22.87, -3.23. \text{HR-MS (ESI): m/z 311.1463 [M+H]^+, calcd for C}_{19}H_{23}O_{2}Si 311.1462.} \\

\( (21) \) (\( E \)-\( (3\)-(benzo[\( d \][1,3]dioxol-5-yl)allyl)dimethyl(phenyl)silane (3t) \\

\begin{align*}
\text{Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 53.8 mg (91%). } ^{1}H \text{ NMR (400 MHz, CDCl}_3\): } \delta 7.56–7.47 (m, 2H), 7.40–7.31 (m, 3H), 6.82 (d, } J = 1.4 \text{ Hz, 1H}), 6.74–6.64 (m, 2H), 6.15 (d, } J = 15.7 \text{ Hz, 1H}), 6.02 (dt, } J = 15.6, 8.0 \text{ Hz, 1H}), 5.90 (s, 2H), 1.85 (dd, } J = 8.0, 0.7 \text{ Hz, 2H}), 0.31 (s, 6H). ^{13}C \text{ NMR (101 MHz, CDCl}_3\): } \delta 147.98, 146.28, 138.66, 133.73, 133.07, 129.20, 128.58, 127.92, 125.44, 119.82, 108.32, 105.21, 100.96, 22.86, -3.21. \text{HR-MS (ESI): m/z 297.1303 [M+H]^+, calcd for C}_{18}H_{21}O_{2}Si 297.1305. \\

\( (22) \) (\( E \)-dimethyl(3-(naphthalen-2-yl)allyl)(phenyl)silane (3u)\textsuperscript{[29]} \\

\begin{align*}
\text{Eluent: petroleum ether. Pale yellow oil, 59.5 mg (98%). } ^{1}H \text{ NMR (400 MHz, CDCl}_3\): } \delta 7.77–7.68 (m, 3H), 7.58 (s, 1H), 7.56–7.52 (m, 2H), 7.49 (dd, } J = 8.5, 1.7 \text{ Hz, 1H}), 7.43–7.33 (m, 5H), 6.39 (d, } J = 15.7 \text{ Hz, 1H}), 6.33 (dt, } J = 15.6, 6.8 \text{ Hz, 1H}), 1.94 (d, } J = 7.0 \text{ Hz, 2H}), 0.34 (s, 6H). ^{13}C \text{ NMR (101 MHz, CDCl}_3\): } \delta 138.61, 135.91, 133.89, 133.77, 132.52, 129.25, 129.17, 128.11, 127.96, 127.83, 127.80, 127.73, 126.22, 125.35, 124.76, 123.57, 23.37, -3.15. \text{HR-MS (EI): m/z 302.1485 [M]^+, calcd for C}_{21}H_{22}Si 302.1485. \\

\( (23) \) (\( E \)-dimethyl(3-(naphthalen-1-yl)allyl)(phenyl)silane (3v) \\

\begin{align*}
\text{Eluent: petroleum ether. Pale yellow oil, 59.8 mg (99%). } ^{1}H \text{ NMR (400 MHz, CDCl}_3\): } \delta 7.99–7.93 (m, 1H), 7.82–7.77 (m, 1H), 7.69 (d, } J = 8.1 \text{ Hz, 1H}), 7.59–7.53 (m, 2H), 7.47–7.41 (m, 3H), 7.41–7.33 (m, 4H), 6.92 (d, } J = 15.4 \text{ Hz, 1H}), 6.21 (dt, } J = 15.5, 8.3 \text{ Hz, 1H}), 2.02 (dd, } J = 8.3, 1.3 \text{ Hz, 2H}), 0.37 (s, 6H). ^{13}C \text{ NMR (101 MHz, CDCl}_3\): } \delta 138.56,
136.37, 133.84, 133.70, 131.14, 130.42, 129.25, 128.49, 127.99, 126.95, 126.34, 125.82, 125.79, 125.70, 124.22, 123.32, 23.71, -3.10. HR-MS (EI): m/z 302.1485 [M]⁺, calcd for C₂₁H₂₂Si 302.1485.

(24) (E)-dimethyl(phenyl)(4-phenylbut-3-en-2-yl)silane (3w)\(^{[30]}\)

Eluent: petroleum ether. Colorless oil, 50.8 mg (95%). \(^{1}\)H NMR (400 MHz, CDCl₃): δ 7.54–7.47 (m, 2H), 7.39–7.32 (m, 3H), 7.31–7.22 (m, 4H), 7.19–7.10 (m, 1H), 6.23 (dd, \(J = 15.6, 7.2 \) Hz, 1H), 6.17 (d, \(J = 16.0 \) Hz, 1H), 2.08–1.93 (m, 1H), 1.15 (d, \(J = 7.2 \) Hz, 3H), 0.31 (s, 3H), 0.30 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl₃): δ 138.60, 137.68, 134.16, 134.08, 129.19, 128.59, 127.83, 126.40, 126.33, 125.74, 26.98, 13.82, −4.66, −5.12. HR-MS (EI): m/z 266.1486 [M]⁺, calcd for C₁₈H₂₂Si 266.1485.

(25) (E)-(1,3-diphenylallyl)dimethyl(phenyl)silane (3x)

Eluent: petroleum ether. Colorless oil, 64.8 mg (99%). \(^{1}\)H NMR (400 MHz, CDCl₃): δ 7.39–7.33 (m, 3H), 7.33–7.23 (m, 6H), 7.23–7.12 (m, 3H), 7.12–7.05 (m, 1H), 7.01–6.94 (m, 2H), 6.49 (dd, \(J = 15.6, 9.8 \) Hz, 1H), 6.26 (d, \(J = 15.7 \) Hz, 1H), 3.29 (d, \(J = 9.8 \) Hz, 1H), 0.29 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl₃): δ 141.75, 138.21, 136.68, 134.51, 130.34, 129.37, 128.59, 128.49, 128.38, 127.68, 127.57, 126.73, 125.98, 124.99, 43.65, −4.01, −4.54. HR-MS (EI): m/z 328.1641 [M]⁺, calcd for C₂₃H₂₄Si 328.1642.

(26) (E)- and (Z)-dimethyl(2-methyl-3-phenylallyl)(phenyl)silane (3y)

Eluent: petroleum ether. Colorless oil, 30.0 mg, (56%). A mixture of \(E\) and \(Z\) isomers (72/28). \(^{1}\)H NMR (400 MHz, CDCl₃): δ 7.57–7.44 (m, 3H), 7.39–7.20 (m, 7.5H), 7.19–7.11 (m, 3.5H), 6.17 (s, 0.38H), 6.07 (s, 1H), 2.09 (s, 0.77H), 1.91 (d, \(J = 0.5 \) Hz, 2H), 1.78 (d, \(J = 1.3 \) Hz, 1.2H), 1.74 (d, \(J = 1.2 \) Hz, 3H), 0.36 (s, 6H), 0.26 (s, 2.3H). \(^{13}\)C NMR (101 MHz, CDCl₃): δ
139.16, 139.09, 137.16, 136.97, 134.31, 134.00, 133.78, 133.64, 129.16, 129.12, 128.81, 128.66, 128.19, 128.11, 127.91, 127.84, 125.65, 125.55, 123.86, 123.47, 30.86, 27.52, 23.17, 20.69, –2.01, –2.62. HR-MS (EI): m/z 266.1486 [M]+, calcd for C_{18}H_{22}Si 266.1485.

(27) (E)-(6-(4-methoxyphenyl)hex-2-en-1-yl)dimethyl(phenyl)silane and (6-(4-methoxyphenyl)hex-1-en-3-yl)dimethyl(phenyl)silane (3z)

Eluent: petroleum ether. Colorless oil, 56.0 mg (86%). A mixture of linear and branched isomers (33:67). $^1$H NMR (400 MHz, CDCl$_3$): \(\delta\ 7.54–7.44\) (m, 3H), 7.38–7.29 (m, 4.5H), 7.06 (d, \(J = 8.6\) Hz, 1H), 7.01 (d, \(J = 8.6\) Hz, 2H), 6.81 (d, \(J = 8.6\) Hz, 1H), 6.78 (d, \(J = 8.6\) Hz, 2H), 5.57 (dt, \(J = 17.0, 9.9\) Hz, 1H), 5.39 (dt, \(J = 15.3, 7.7\) Hz, 0.5H), 5.27 (dt, \(J = 14.1, 6.6\) Hz, 0.5H), 4.88 (dd, \(J = 10.3, 1.8\) Hz, 1H), 4.80 (ddd, \(J = 17.1, 1.8, 0.9\) Hz, 1H), 3.77 (s, 1.5H), 3.76 (s, 3H), 2.58–2.45 (m, 2H), 2.44–2.32 (m, 1H), 1.98 (dd, \(J = 14.1, 7.0\) Hz, 1H), 1.77 (t, \(J = 10.1\) Hz, 1H), 1.70–1.56 (m, 3H), 1.52–1.33 (m, 3H), 0.26 (s, 3H), 0.254 (s, 3H), 0.249 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): \(\delta\ 157.75, 157.69, 139.73, 139.10, 137.96, 134.95, 134.92, 134.18, 133.77, 129.46, 129.43, 129.32, 129.04, 127.84, 127.75, 125.99, 113.78, 113.75, 112.80, 55.36, 34.72, 34.49, 34.31, 32.41, 32.04, 31.40, 28.12, 21.78, −3.21, −4.29, −5.11. HR-MS (ESI): m/z 325.1983 [M+H]+, calcd for C$_{21}$H$_{29}$OSi 325.1982.

(28) (E)-dimethyl(phenyl)(3-(tetrahydro-2H-pyran-4-yl)allyl)silane and dimethyl (phenyl)(1-(tetrahydro-2H-pyran-4-yl)allyl)silane (3za)

Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 41.8 mg (80%). A mixture of linear and branched isomers (39:61). $^1$H NMR (400 MHz, CDCl$_3$): \(\delta\ 7.53–7.44\) (m, 3.2H), 7.39–7.29 (m, 4.8H), 5.67 (dt, \(J = 16.8, 10.2\) Hz, 1H), 5.38 (dt, \(J = 15.7, 7.9\) Hz, 0.6H), 5.20 (dd, \(J = 15.2, 6.8\) Hz, 0.6H), 4.95 (dd, \(J = 10.2, 1.9\) Hz, 1H), 4.88–4.78 (m, 1H), 3.98–3.79 (m, 3.2H), 3.38 (dt, \(J = 11.6, 1.9\) Hz, 1.2H), 3.30–3.15 (m, 2H), 1.75–1.62 (m, 3.2H), 1.62–1.49 (m, 3.7H), 1.45–1.23 (m, 5.1H), 0.31 (s, 3H), 0.29 (s, 3H), 0.26 (s, 3.6H). $^{13}$C NMR (101 MHz, CDCl$_3$): \(\delta\ 138.91, 138.58, 137.16, 134.05, 134.02, 133.77, 129.07, 127.85,
127.83, 124.22, 114.67, 68.46, 68.29, 67.95, 41.75, 38.20, 35.86, 33.82, 33.28, 31.89, 21.80, -2.54, -3.32, -3.51. HR-MS (ESI): m/z 261.1666 [M+H]+, calcd for C_{16}H_{25}OSi 261.1669.

(29) \((E)-(3-(furan-2-yl)allyl)dimethyl(phenyl)silane (3zb)\)

Eluent: petroleum ether. Pale yellow oil, 44.0 mg (91%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.55–7.50 (m, 2H), 7.40–7.32 (m, 3H), 7.26 (d, \(J = 1.6\) Hz, 1H), 6.31 (dd, \(J = 3.2, 1.8\) Hz, 1H), 6.18 (dt, \(J = 15.7, 8.1\) Hz, 1H), 6.06 (d, \(J = 15.8\) Hz, 1H), 6.03 (d, \(J = 3.3\) Hz, 1H), 1.87 (dd, \(J = 8.2, 0.8\) Hz, 2H), 0.31 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 153.86, 140.91, 138.58, 133.73, 129.24, 127.94, 126.50, 117.86, 111.14, 104.94, 23.08, –3.20. HR-MS (ESI): m/z 243.1193 [M+H]+, calcd for C\(_{15}\)H\(_{19}\)OSi 243.1200.

(30) \((E)\)-dimethyl(phenyl)(3-(thiophen-2-yl)allyl)silane and \((Z)\)-dimethyl(phenyl)(3-(thiophen-2-yl)allyl)silane (3zc)

Eluent: petroleum ether. Pale yellow oil, 43.8 mg (85%). A mixture of \(E\) and \(Z\) isomers (91/9). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.55–7.49 (m, 2.2H), 7.39–7.33 (m, 3.6H), 7.02 (d, \(J = 5.1\) Hz, 1H), 6.91 (dd, \(J = 5.1, 3.5\) Hz, 1H), 6.78 (d, \(J = 3.4\) Hz, 0.98H), 6.48 (d, \(J = 11.5\) Hz, 0.1H), 6.36 (d, \(J = 15.5\) Hz, 1H), 6.06 (dt, \(J = 15.5, 8.3\) Hz, 1H), 5.60 (dt, \(J = 11.4, 9.3\) Hz, 0.1H), 2.20 (dd, \(J = 9.3, 1.3\) Hz, 0.2H), 1.85 (dd, \(J = 8.3, 1.1\) Hz, 2H), 0.32 (s, 6.8H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 143.80, 138.49, 133.75, 129.27, 127.95, 127.51, 127.31, 123.34, 122.50, 122.27, 23.02, –3.20. HR-MS (EI): m/z 258.0893 [M]+, calcd for C\(_{15}\)H\(_{18}\)SSi 258.0893.

(31) \((E)-2-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)pyridine (3zd)\)

Eluent: petroleum ether/ethyl acetate = 10:1. Colorless oil, 44.6 mg (88%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.52–8.46 (m, 1H), 7.59–7.50 (m, 3H), 7.40–7.31 (m, 3H), 7.15 (d, \(J = 7.9\) Hz, 1H), 7.03 (d, \(J = 7.6\) Hz, 1H), 6.34 (d, \(J = 15.9\) Hz, 1H), 5.96 (dt, \(J = 15.9, 8.2\) Hz, 1H), 5.66 (dd, \(J = 8.2, 1.9\) Hz, 1H), 4.93 (dd, \(J = 8.2, 1.9\) Hz, 1H), 1.84 (dd, \(J = 8.2, 1.9\) Hz, 1H), 0.31 (s, 6H). HR-MS (ESI): m/z 257.1261 [M+H]+, calcd for C\(_{16}\)H\(_{20}\)OSi 257.1259.
Hz, 1H), 7.03 (ddd, J = 7.4, 4.9, 1.0 Hz, 1H), 6.75 (dt, J = 15.6, 8.5 Hz, 1H), 6.34 (d, J = 15.6 Hz, 1H), 1.98 (dd, J = 8.5, 1.3 Hz, 2H), 0.34 (s, 6H). 13C NMR (101 MHz, CDCl3): δ 156.52, 149.39, 138.44, 136.39, 133.70, 132.54, 129.26, 129.21, 127.94, 121.15, 120.47, 23.48, −3.13. HR-MS (ESI): m/z 254.1358 [M+H]+, calcd for C16H20NSi 254.1360.

(32) (E)-(3-(benzo[b]thiophen-3-yl)allyl)dimethyl(phenyl)silane (3ze)

![Structure of 3ze](image)

Eluent: petroleum ether. Pale yellow oil, 53.9 mg (87%). 1H NMR (400 MHz, CDCl3): δ 7.84–7.79 (m, 1H), 7.77–7.72 (m, 1H), 7.58–7.51 (m, 2H), 7.40–7.30 (m, 5H), 7.19 (s, 1H), 6.47 (dd, J = 15.7, 0.8 Hz, 1H), 6.23 (dt, J = 15.7, 8.2 Hz, 1H), 1.95 (dd, J = 8.2, 1.2 Hz, 2H), 0.35 (s, 6H). 13C NMR (101 MHz, CDCl3): δ 140.46, 138.49, 137.99, 135.16, 133.81, 129.36, 129.27, 127.97, 124.35, 124.11, 122.93, 121.12, 121.32, 119.68, 23.45, −3.17. HR-MS (EI): m/z 308.1049 [M]+, calcd for C19H20SSi 308.1050.

(33) (E)-5-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-1-methyl-1H-indole (3zf)

![Structure of 3zf](image)

Eluent: petroleum ether/ethyl acetate = 100:1. Pale yellow oil, 52.7 mg (86%). 1H NMR (400 MHz, CDCl3): δ 7.51–7.43 (m, 2H), 7.40 (s, 1H), 7.33–7.22 (m, 3H), 7.17–7.08 (m, 2H), 6.89 (d, J = 2.8 Hz, 1H), 6.33 (d, J = 2.7 Hz, 1H), 6.28 (d, J = 15.6 Hz, 1H), 6.06 (dt, J = 15.6, 8.1 Hz, 1H), 3.64 (s, 3H), 1.82 (d, J = 8.1 Hz, 2H), 0.24 (s, 6H). 13C NMR (101 MHz, CDCl3): δ 139.01, 135.96, 133.80, 130.22, 130.12, 129.22, 129.11, 128.79, 127.88, 123.91, 119.75, 118.13, 109.27, 101.07, 32.96, 22.86, −3.16. HR-MS (ESI): m/z 306.1671 [M+H]+, calcd for C20H24NSi 306.1673.

(34) (E)-dimethyl(phenyl)(3-((p-tolyl)allyl)silane (3zh)

![Structure of 3zh](image)

Eluent: petroleum ether. Colorless oil, 44.8 mg (84%). 1H NMR (400 MHz, CDCl3): δ 7.56–7.49 (m, 2H), 7.39–7.33 (m, 3H), 7.17 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.21 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.7, 7.5 Hz, 1H), 2.31 (s, 3H), 1.88 (d, J = 7.1 Hz,
2H), 0.31 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 138.74, 136.08, 135.72, 133.76, 129.27, 129.19, 128.88, 127.92, 126.13, 125.58, 23.02, 21.24, –3.20. HR-MS (EI): m/z 266.1486 [M]$^+$, calc'd for C$_{18}$H$_{22}$Si 266.1485.

(35) cinnamyl(methyl)diphenylsilane (3zm)

Eluent: petroleum ether. Colorless oil, 66.9 mg (99%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57–7.49 (m, 4H), 7.40–7.31 (m, 6H), 7.28–7.19 (m, 4H), 7.16–7.10 (m, 1H), 6.27 (d, $J =$ 15.8 Hz, 1H), 6.20 (dt, $J =$ 15.7, 6.8 Hz, 1H), 2.21 (d, $J =$ 7.0 Hz, 2H), 0.58 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 138.34, 136.53, 134.69, 129.76, 129.50, 128.55, 128.01, 126.64, 126.51, 125.73, 21.58, –4.48. HR-MS (EI): m/z 314.1485 [M]$^+$, calc'd for C$_{22}$H$_{22}$Si 314.1485.

(36) Cinnamyltriphenylsilane (3zn)$^{[31]}

Eluent: petroleum ether. Colorless oil, 68.4 mg (91%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57–7.50 (m, 6H), 7.44–7.31 (m, 9H), 7.26–7.10 (m, 5H), 6.32–6.19 (m, 2H), 2.59–2.47 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 138.32, 135.90, 134.53, 130.44, 129.75, 128.53, 128.03, 126.55, 126.31, 125.77, 20.52.

(37) ($R,E$)-dimethyl(phenyl)(1-phenylpent-1-en-3-yl)silane (3zo)$^{[32]}

Eluent: petroleum ether. Colorless oil, 51.8 mg (92% yield, 94% ee). Optical purity was determined by HPLC with Daicel ChiralCel OJ-RH column coupled with Daicel ChiralCel OD-RH column: 30 °C, H$_2$O/MeCN = 30/70, flow rate = 0.8 mL/min, $t_{major} = 28.06$ min, $t_{minor} = 25.35$ min, $\lambda = 254$ nm, ee = 94%. $[\alpha]_D^{20} = +61.85$ (c = 1.0, CHCl$_3$) (ref.32: $[\alpha]_D^{20} = +30.5$ (c = 1.05, CHCl$_3$) for the ($R$)-form). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.53–7.47 (m, 2H), 7.38–7.32 (m, 3H), 7.31–7.24 (m, 4H), 7.20–7.12 (m, 1H), 6.20 (d, $J =$ 15.8 Hz, 1H), 6.02 (dd, $J =$ 15.8, 9.7 Hz, 1H), 1.84–1.73 (m, 1H), 1.67–1.54 (m, 1H), 1.49–1.36 (m, 1H), 0.89 (t, $J =$ 7.3 Hz, 3H), 0.31 (s, 3H), 0.30 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 138.57, 137.92,
134.21, 132.67, 129.12, 128.59, 128.28, 127.79, 126.40, 125.74, 36.28, 22.36, 14.63, –4.07, –4.85.

4. Catalytic coupling of cinnamyldimethyl(phenyl)silane with Ph$_2$CHOH

To a mixture of InCl$_3$ (8.8 mg, 0.04 mmol) and Ph$_2$CHOH (36.8 mg, 0.2 mmol) in 1,2-dichloroethane (2 mL) was added cinnamyldimethyl(phenyl)silane (101.0 mg, 0.4 mmol) under nitrogen. The reaction mixture was stirred at 80 °C for 3 h, diluted with EtOAc (5 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (15 mL). The filtrate was concentrated and purified by silica gel chromatography to give compound 4 as a white solid (48.4 mg, 85%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.36 (d, $J$ = 7.3 Hz, 2H), 7.28 (t, $J$ = 7.6 Hz, 2H), 7.20-7.09 (m, 7H), 7.09-7.01 (m, 3H), 6.97 (t, $J$ = 7.2 Hz, 1H), 5.98-5.85 (m, 1H), 4.90 (d, $J$ = 10.2 Hz, 1H), 4.86 (d, $J$ = 17.2 Hz, 1H), 4.30 (d, $J$ = 11.6 Hz, 1H), 4.17 (dd, $J$ = 11.4, 7.7 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 143.58, 143.29, 142.80, 141.02, 128.76, 128.53, 128.50, 128.44, 128.34, 128.21, 126.39, 126.19, 125.95, 116.07, 57.12, 54.54.

5. Mechanism studies
Mechanistic experiments

(1) Nickel-catalyzed reaction of cinnamyl alcohol with PhMe₂SiZnCl in the presence of (1-cyclopropylvinyl)benzene

NiCl₂(PMe₃)₂ (5.6 mg, 0.02 mmol) and cinnamyl alcohol (1.0 mL, 0.2 M in THF, 0.2 mmol) were charged to a Schlenk tube. To the stirred mixture was added MeZnCl (0.55 mL, 0.44 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of PhMe₂SiZnCl (2a) (0.6 mL, 0.4 M solution in THF, 0.24 mmol) was added, and the solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (2 mL) and (1-cyclopropylvinyl)benzene (29 mg, 0.2 mmol) were added. The resultant mixture was stirred at room temperature for 5 h, diluted with EtOAc (5 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and purified by silica gel chromatography (eluent: petroleum ether) to give cinnamyldimethyl(phenyl)silane (3a) as pale yellow oil (48.9 mg, 97% yield) and (1-cyclopropylvinyl)benzene as colorless oil (27.1 mg, 94% recovered yield) (Scheme S9a).

(2) Reaction of cinnamyl alcohol with PhMe₂SiZnCl catalyzed by Ni(COD)₂/PMe₃
Cinnamyl alcohol (1.0 mL, 0.2 M in THF, 0.2 mmol) was charged to a Schlenk tube. To the stirred mixture was added MeZnCl (0.55 mL, 0.44 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of PhMe₂SiZnCl (2a) (0.6 mL, 0.4 M solution in THF, 0.24 mmol) was added, and the solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (2 mL), Ni(COD)₂ (5.5 mg, 0.02 mmol) and PMe₃ (3.0 mg, 0.04 mmol) were successively added. The resultant mixture was stirred at room temperature for 5 h, diluted with EtOAc (5 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and purified by silica gel chromatography (eluent: petroleum ether) to give cinnamyldimethyl(phenyl) silane (3a) as pale yellow oil (48.6 mg, 96% yield) (Scheme S9b).

(3) Reaction of rac-(E)-1-phenylpent-1-en-3-ol with PhMe₂SiZnCl under the catalysis of NiCl₂(PMe₃)₂
NiCl₂(PMe₃)₂ (5.6 mg, 0.02 mmol), rac-(E)-1-phenylpent-1-en-3-ol (32.5 mg, 0.2 mmol) and THF (1 mL) were charged to a Schlenk tube. To the stirred mixture was added MeZnCl (0.55 mL, 0.44 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of PhMe₂SiZnCl (2a) (0.6 mL, 0.4 M solution in THF, 0.24 mmol) was added, and the solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (2 mL) was added. The resultant mixture was stirred at room temperature for 24 h, diluted with EtOAc (5 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and purified by silica gel chromatography (eluent: petroleum ether) to give rac-(E)-dimethyl(phenyl)(1-phenylpent-1-en-3-yl)silane (rac-3zo) as colorless oil (51.2 mg, 91% yield) (Scheme S9c).

(4) Reaction of (S, E)-1-phenylpent-1-en-3-ol with PhMe₂SiZnCl under the catalysis of NiCl₂(PMe₃)₂
NiCl₂(PMe₃)₂ (5.6 mg, 0.02 mmol), (S,E)-1-phenylpent-1-en-3-ol (32.5 mg, 0.2 mmol, 96% ee) and THF (1 mL) were charged to a Schlenk tube. To the stirred mixture was added MeZnCl (0.55 mL, 0.44 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of PhMe₂SiZnCl (2a) (0.6 mL, 0.4 M solution in THF, 0.24 mmol) was added, and the solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (2 mL) was added. The resultant mixture was stirred at room temperature for 24 h, diluted with EtOAc (5 mL) and filtered through a plug of silica
gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and purified by silica gel chromatography (eluent: petroleum ether.) to give \((R,E)\)-dimethyl(phenyl)(1-phenylpent-1-en-3-yl)silane \((/R/-3zo)\) as colorless oil (51.8 mg, 92% yield, 94% ee) (Scheme S9d).

(5) Isolation and identification of PhMe₂Si-SiMe₂Ph in the NiCl₂(PMe₃)₂-catalyzed reaction of cinnamyl alcohol with PhMe₂SiZnCl

Cinnamyl alcohol (67.1 mg, 0.5 mmol) and THF (1 mL) were charged to a Schlenk tube. To the stirred solution was added MeZnCl (0.77 mL, 0.65 M solution in THF, 0.5 mmol) at room temperature. After the mixture was stirred for 5 min, NiCl₂(PMe₃)₂ (14.0 mg, 10 mol %) and a solution of PhMe₂SiZnCl (1.3 mL, 0.46 M solution in THF, 0.6 mmol) was added. The solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (5 mL) was added. The resultant mixture was stirred at room temperature for 5 h, diluted with EtOAc (10 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (30 mL). The filtrate was concentrated and purified by silica gel chromatography to give \((PhMe₂Si)₂\) as a white solid (6.9 mg, 5.1% based cinnamyl alcohol, 51% based on NiCl₂(PMe₃)₂). 1H NMR (400 MHz, CDCl₃): δ 7.42-7.34 (m, 4H), 7.33-7.24 (m, 6H), 0.32 (s, 12H). 13C NMR (101 MHz, CDCl₃): δ 139.13, 134.00, 128.56, 127.84, −3.78.

References

2008, 10, 1767.


6. Copied of NMR spectra of the unreported allylic alcohols, the cross-coupling products, and 1,1,2,2-tetramethyl-1,2-diphenyldisilane
I. NMR spectral copies of the unknown allyl alcohols

(1) \((E)-3-(3\text{-}\text{phenoxyphenyl})\text{prop-2-en-1-ol (1o)}\)
(2) (E)-3-([1,1'-biphenyl]-2-yl)prop-2-en-1-ol (1q)

1H NMR
Solvent: CDCl₃

13C NMR
Solvent: CDCl₃
(3) (E)-3-(2-fluorophenyl)prop-2-en-1-ol (1r)

$^1$H NMR
Solvent: CDCl$_3$

$^{13}$C NMR
Solvent: CDCl$_3$
$^{19}$F NMR
Solvent: CDCl$_3$
(4) (E)-3-(1-methyl-1H-indol-5-yl)prop-2-en-1-ol (1zf)
(5) (E)-3-(benzo[b]thiophen-3-yl)prop-2-en-1-ol (1ze)

$^1$H NMR
Solvent: CDCl$_3$

$^{13}$C NMR
Solvent: CDCl$_3$
(6) (E)-N,N-diethyl-4-(3-hydroxyprop-1-en-1-yl)benzamide (1m)
(7) (S,E)-1-phenylpent-1-en-3-ol ((S)-1zo))

1H NMR (CDCl₃)

13C NMR (CDCl₃)
II. NMR spectral copies of the cross-coupling products

(1) cinnamyldimethyl(phenyl)silane (3a)
(2) \((E)-(3-(4-(\text{tert-butyl})\text{phenyl})\text{allyl})\text{dimethyl(phenyl)silane} \ (3b)\)
(3) (E)-(3-(4-methoxyphenyl)allyl)dimethyl(phenyl)silane (3c)

1H NMR
Solvent: CDCl₃

13C NMR
Solvent: CDCl₃
(4) (E)-4-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-N,N-dimethylaniline (3d)

**1H NMR**
Solvent: CDCl₃

**13C NMR**
Solvent: CDCl₃
(5) (E)-dimethyl(3-(4-(methylthio)phenyl)allyl)(phenyl)silane (3e)
(6) (E)-dimethyl(phenyl)(3-(4-(trifluoromethyl)phenyl)allyl)silane (3f)
(7) (E)-dimethyl(phenyl)(3-(4-(trifluoromethoxy)phenyl)allyl)silane (3g)
19F NMR
Solvent: CDCl$_3$
(8) (E)-(3-(4-(difluoromethoxy)phenyl)allyl)dimethyl(phenyl)silane (3h)
(9) (E)-(3-(4-fluorophenyl)allyl)dimethyl(phenyl)silane (3i)
(10) (E)-(3-(4-chlorophenyl)allyl)dimethyl(phenyl)silane (3j)

1H NMR
Solvent: CDCl₃

13C NMR
Solvent: CDCl₃
(11) \((E)-3-\text{(4-(dimethyl(phenyl)silyl)phenyl)prop-2-en-1-ol (3k)}\)
(12) (E)-(3-(4-(dimethyl(phenyl)silyl)phenyl)allyl)dimethyl(phenyl)silane (3ka)
(13) methyl (E)-4-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)benzoate (3l)
(14) \((E)-4-(3-(\text{dimethyl(phenyl)silyl})\text{prop-1-en-1-yl})-\text{N,N-diethylbenzamide (3m)}\)
(15) \((E)-(3-(3\text{-}methoxyphenyl)\text{allyl})\text{dimethyl(phenyl)silane (3n)}\)
(16) (E)-dimethyl(3-(3-phenoxyphenyl)allyl)(phenyl)silane (3o)
(17) (E)-dimethyl(phenyl)(3-(3-(trifluoromethyl)phenyl)allyl)silane (3p)
$^{19}F$ NMR
Solvent: CDCl$_3$
(18) \((E)-(3-([1,1^\prime\text{-biphenyl}]-2-yl)allyl)\)dimethyl(phenyl)silane (3q)

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\end{center}}
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\text{\begin{center}
\includegraphics[width=\textwidth]{image2.png}
\end{center}}
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\includegraphics[width=\textwidth]{image3.png}
\end{center}}
\]
(19) \((E)-(3-(2\text{-}fluorophenyl)allyl)\text{dimethyl(phenyl)silane}\ (3r)\)
19F NMR
Solvent: CDCl₃
(20) (E)-(3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)allyl)dimethyl(phenyl)silane (3s)

1H NMR
Solvent: CDCl$_3$

13C NMR
Solvent: CDCl$_3$
(21) \((E)-(3\text{-}(\text{benzo}[d][1,3]\text{dioxol-5-yl})\text{allyl})\text{dimethyl(phenyl)silane} \ (3t)\)
(22) \((E)\)-dimethyl(3-(naphthalen-2-yl)allyl)(phenyl)silane (3u)
(23) (E)-dimethyl(3-(naphthalen-1-yl)allyl)(phenyl)silane (3v)
(24) \((E)\)-dimethyl(phenyl)(4-phenylbut-3-en-2-yl)silane (3w)
(25) \((E)-(1,3\text{-diphenylallyl})\text{dimethyl(phenyl)silane (3x)}\)

\(^1H\) NMR
Solvent: CDCl\(_3\)

\(^13C\) NMR
Solvent: CDCl\(_3\)
(26) \((E)-\) and \((Z)-\)dimethyl(2-methyl-3-phenylallyl)(phenyl)silane \((3y)\)

**1H NMR**

Solvent: CDCl₃

(E/Z \(\sim 72/28\))

**13C NMR**

Solvent: CDCl₃
(27) (E)-(6-(4-methoxyphenyl)hex-2-en-1-yl)dimethyl(phenyl)silane and (6-(4-methoxyphenyl)hex-1-en-3-yl)dimethyl(phenyl)silane (3z)
(28) \((E)\)-dimethyl(phenyl)(3-(tetrahydro-2H-pyran-4-yl)allyl)silane and dimethyl (phenyl)(1-(tetrahydro-2H-pyran-4-yl)allyl)silane (3za)

\[ \text{\textsuperscript{1}H NMR} \]
Solvent: CDCl\textsubscript{3}

\[ \text{\textsuperscript{13}C NMR} \]
Solvent: CDCl\textsubscript{3}
(29) (E)-(3-(furan-2-yl)allyl)dimethyl(phenyl)silane (3zb)

1H NMR
Solvent: CDCl$_3$

13C NMR
Solvent: CDCl$_3$
(30) (E)-dimethyl(phenyl)(3-(thiophen-2-yl)allyl)silane and (Z)-dimethyl(phenyl)(3-(thiophen-2-yl)allyl)silane (3zc)
(31) (E)-2-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)pyridine (3zd)

1H NMR
Solvent: CDCl₃

13C NMR
Solvent: CDCl₃
(32) \((E)-(3-(benzo[b]thiophen-3-yl)allyl)dimethyl(phenyl)silane (3ze)\)
(33) (E)-5-(3-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-1-methyl-1H-indole (3zf)

\[ \text{\textsuperscript{1}H NMR} \]
Solvent: CDCl\textsubscript{3}

\[ \text{\textsuperscript{13}C NMR} \]
Solvent: CDCl\textsubscript{3}
(34) \( (E) \)-dimethyl(phenyl)(3-(p-tolyl)allyl)silane (3zh)
(35) cinnamyl(methyl)diphenylsilane (3zm)
(36) Cinnamyltriphenylsilane (3zn)

\[ \text{Cinnamyltriphenylsilane (3zn)} \]

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\begin{align*}
\text{^1H NMR} \\
\text{Solvent: CDCl}_3
\end{align*}
\]

\[
\begin{align*}
\text{^13C NMR} \\
\text{Solvent: CDCl}_3
\end{align*}
\]
(37) (R,E)-dimethyl(phenyl)(1-phenylpent-1-en-3-yl)silane (3zo)
but-3-ene-1,1,2-triyltribenzene (4)
III. NMR spectral copies of 1,1,2,2-tetramethyl-1,2-diphenyldisilane