Nickel-Catalyzed Remote Hydrosilylation of Unconjugated Enones with Bulky Triphenylsilane

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Table of Contents

1. General Information S2
2. Preparation of Unconjugated Enones S3
3. Nickel-Catalyzed Remote Hydrosilylation of Unconjugated Enones with Bulky Triphenylsilane S6
   3.1 Optimization of reaction conditions S6
   3.2 Experimental details and characterization of products S7
   3.3 Mechanistic experiments S15
      3.3.1 Radical trapping experiments S15
      3.3.2 Deuterium-labelling experiment S16
   3.4 Synthetic applications S17
      3.4.1 Preparation of silyl enol ether 3x S17
      3.4.2 Reaction of mixed isomers 1a, 1v, and 1w with 2a S17
4. References S19
5. ¹H and ¹³C NMR Spectra S20
1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. All commercially available reagents were obtained from chemical suppliers and used after proper purification if necessary. Flash column chromatography was performed on silica gel (200-300 mesh) with the indicated solvent mixtures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light.

The $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker 400 AV or 500 AV spectrometers. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad, h = sextet and all combinations thereof can be explained by their integral parts. Coupling constant (J) was reported in hertz unit (Hz). The high resolution mass spectra (HRMS) were recorded on an Agilent 6210 LC/TOF spectrometer.
2. Preparation of Unconjugated Enones

General procedure:

According to the known literature, aldehyde (5 mmol) was dissolved in 10 mL of dried THF in 50 mL Schlenk tube under N₂. The mixture was cooled to 0 °C and Grignard reagent (1.2 equiv) was added dropwise with stirring under ice bath. Then it was allowed to warm to room temperature and stirred for 5 h. After completion, the mixture was quenched with NH₄Cl (aq.). The aqueous layer was extracted with ethyl acetate (3×25 mL). The combined organic layers were
dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to give the desired products A.

Products A (3 mmol) was dissolved in 10 mL DCM in round bottom flask, PCC (1.2 equiv) was added into solution in batches with stirring under ice bath. Then it was allowed to warm to room temperature and stirred for 5 h. After completion, the aqueous layer was extracted with DCM (3×25 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to give the desired products. Substrates 1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o, 1p, 1q, 1r, 1s, 1t, 1u, and 1x were prepared according to the general procedure.

**Procedure for the preparation of 1v.**

![chemical structure](image)

According to the known literature$^2$, aldehyde (5 mmol) was dissolved in 10 mL of dried THF in 50 mL Schlenk tube under N$_2$. The mixture was cooled to 0 °C and Grignard reagent (1.2 equiv) was added dropwise with stirring under ice bath. Then it was allowed to warm to room temperature and stirred for 5 h. After completion, the mixture was quenched with NH$_4$Cl (aq.). The aqueous layer was extracted with ethyl acetate (3×25 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to give the desired product B.

Product B (3 mmol) was dissolved in 10 mL DCM in round bottom flask, PCC (1.2 equiv) was added into solution in batches with stirring under ice bath. Then it was allowed to warm to room temperature and stirred for 5 h. After completion, the aqueous layer was extracted with DCM (3×25 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to give the product 1v.

**Procedure for the preparation of 1w.**
According to the known literature\(^3\), To a solution of \(\alpha\)-bromoacetophenone (990 mg, 5 mmol) in \(\text{CH}_2\text{Cl}_2\) (10 ml) was added triphenylphosphine (1.31 g, 5 mmol) slowly at room temperature. The solution was allowed to stir for 4 h, and the resulting mixture was concentrated under reduced pressure. The residue was dissolved in \(\text{CH}_2\text{Cl}_2 : \text{H}_2\text{O}\) (12 mL, 4:6) and NaOH (400 mg, 10 mmol) was added. Then the mixture was stirred at room temperature for 1 h before being extracted with \(\text{CH}_2\text{Cl}_2\) (3 x 15 mL). The combine organic extracts were washed with brine (3 x 25 mL), dried, filtered and concentrated under vacuum to give the crude mixture, which was used without further purification. To a solution of propionaldehyde (290 mg, 5 mmol) in CHCl\(_3\) (10 mL) at room temperature was added the above mixture and the solution was allowed to stir for 12 h. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to provide the product \(1\text{w}\).
## 3. Nickel-Catalyzed Remote Hydrosilylation of Unconjugated Enones with Bulky Triphenylsilane

### 3.1 Optimization of reaction conditions

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst/mol%</th>
<th>Ligand/equiv</th>
<th>Solvent/mL</th>
<th>T/°C</th>
<th>Time/h</th>
<th>1e:2a</th>
<th>Yield(^\text{a})/%</th>
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<td>1:1:5</td>
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<sup>a</sup>Reaction was conducted on a 0.4 mmol scale. <sup>b</sup>Isolated yield. <sup>c</sup>No catalyst. <sup>d</sup>No ligand. Ad = Admantyl. Dmbpy = 4,4’-Dimethyl-2,2'-bipyridine. Tpy = 2,2':6',2''-Terpyridine.

In addition to triphenylsilane 2a, other hydrosilanes were examined under the optimized reaction conditions. However, they cannot proceed this reaction at all and the starting material was recovered.

**Inviable hydrosilanes:**

Et₃SiH  PhMe₂SiH  (EtO)₂MeSiH  (EtO)₃SiH  Ph₂SiH₂  PhSiH₃

### 3.2 Experimental details and characterization of products
To a 25 ml flame-dried Schlenk tube containing a stirring bar was added NiCl₂ (10 mol%, 0.04 mmol, 5.2 mg), Ph₃SiH (0.6 mmol, 156 mg), xylene (1 mL), t-BuNC (0.2 mmol, 16.6 mg), and 1-(naphthalen-2-yl)pent-4-en-1-one (0.4 mmol, 84 mg) sequentially under nitrogen. The tube was sealed and stirred at 120 °C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product 3e in 79% yield.

(Z)-triphenyl((1-phenylpent-1-en-1-yl)oxy)silane (3a)

Purified by silica gel column chromatography as colorless oil (121 mg, 72% yield).

^1H NMR (400 MHz, CDCl₃) δ 7.64 – 7.55 (m, 6H), 7.42 – 7.35 (m, 3H), 7.34 – 7.28 (m, 8H), 7.11 – 7.03 (m, 3H), 5.12 (t, J = 7.3 Hz, 1H), 1.99 (q, J = 7.2 Hz, 2H), 1.23 -1.13 (m, 2H), 0.73 (t, J = 7.3 Hz, 3H).


(Z)-triphenyl((1-(p-tolyl)pent-1-en-1-yl)oxy)silane (3b)

Purified by silica gel column chromatography as colorless oil (132 mg, 76% yield).

^1H NMR (500 MHz, CDCl₃) δ 7.63 – 7.55 (m, 6H), 7.42 – 7.37 (m, 3H), 7.35 – 7.29 (m, 6H), 7.20 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 7.9 Hz, 2H), 5.07 (t, J = 7.3 Hz, 1H), 2.24 (s, 3H), 2.01 – 1.93 (m, 2H), 1.23 – 1.11 (m, 2H), 0.72 (t, J = 7.4 Hz, 3H). ^13C NMR (125 MHz, CDCl₃) δ 149.2, 136.8, 136.0, 135.6, 134.2, 129.9, 128.4, 127.6, 126.1, 111.3, 28.5, 22.7, 21.0, 13.8. HRMS(ESI) Calculated for C₃₀H₃₁OSi⁺ ([M+H]⁺): 435.2144, found: 435.2131.

(Z)-triphenyl((1-(o-tolyl)pent-1-en-1-yl)oxy)silane (3c)
Purified by silica gel column chromatography as white solid (78 mg, 45% yield). mp: 74-76 °C.

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\] δ 7.48 – 7.42 (m, 6H), 7.39 – 7.33 (m, 3H), 7.29 – 7.24 (m, 6H), 7.05 – 6.99 (m, 1H), 6.88 – 6.82 (m, 3H). 4.70 (t, \( J = 7.2 \text{ Hz, 1H} \)), 2.21 (q, \( J = 7.3 \text{ Hz, 2H} \)), 2.08 (s, 3H).

\[ ^13C\text{ NMR (100 MHz, CDCl}_3\] δ 149.2, 139.1, 136.9, 135.5, 134.1, 129.9, 129.8, 129.4, 127.7, 127.6, 125.0, 113.6, 28.0, 22.9, 19.9, 14.0. HRMS(ESI) Calculated for C\text{30}H\text{31}OSi ([M+H]^+): 435.2144, found: 435.2130.

\((Z)\)-triphenyl((1-(m-tolyl)pent-1-en-1-yl)oxy)silane (3d)

Purified by silica gel column chromatography as white solid (108 mg, 62% yield, Z/E = 97:3).

\[ ^1H\text{ NMR (500 MHz, CDCl}_3\] δ 7.61 – 7.58 (m, 6H), 7.41 – 7.36 (m, 3H), 7.34 – 7.29 (m, 6H), 7.14 – 7.08 (m, 2H), 6.98 (t, \( J = 7.6 \text{ Hz, 1H} \)), 6.89 (d, \( J = 7.5 \text{ Hz, 1H} \)), 5.11 (t, \( J = 7.3 \text{ Hz, 1H} \)), 2.08 (s, 3H), 2.01 (q, \( J = 7.5 \text{ Hz, 2H} \)), 1.23 – 1.15 (m, 2H), 0.75 (t, \( J = 7.4 \text{ Hz, 3H} \)).

\[ ^13C\text{ NMR (125 MHz, CDCl}_3\] δ 149.3, 138.6, 137.1, 135.6, 134.1, 129.9, 127.9, 127.6, 127.2, 123.2, 111.9, 28.5, 22.7, 21.2, 13.8. HRMS(ESI) Calculated for C\text{30}H\text{31}OSi ([M+H]^+): 435.2144, found: 435.2133.

\((Z)\)-((1-(naphthalen-2-yl)pent-1-en-1-yl)oxy)triphenylsilane (3e)

Purified by silica gel column chromatography as white solid (147 mg, 79% yield). mp: 84-86 °C.

\[ ^1H\text{ NMR (500 MHz, CDCl}_3\] δ 7.73 (s, 1H), 7.70 (d, \( J = 7.6 \text{ Hz, 1H} \)), 7.67 – 7.59 (m, 6H), 7.58 (d, \( J = 8.6 \text{ Hz, 1H} \)), 7.49 – 7.46 (m, 1H), 7.42 – 7.37 (m, 4H), 7.36 – 7.27 (m, 8H), 5.32 (t, \( J = 7.3 \text{ Hz, 1H} \)), 2.06 (q, \( J = 7 \text{ Hz, 2H} \)), 1.21 (h, \( J = 7.5 \text{ Hz, 2H} \)), 0.76 (t, \( J = 7.3 \text{ Hz, 3H} \)).

\[ ^13C\text{ NMR (125 MHz, CDCl}_3\] δ 149.1, 135.8, 135.6, 134.0, 133.0, 132.7, 130.0, 128.2, 127.7, 127.3, 127.2, 125.8, 125.6, 125.0, 124.1, 112.7, 28.7, 22.7, 13.8. HRMS(ESI) Calculated for C\text{33}H\text{31}OSi ([M+H]^+): 471.2144, found: 471.2133.

\((Z)\)-((1-(naphthalen-1-yl)pent-1-en-1-yl)oxy)triphenylsilane (3f)

Purified by silica gel column chromatography as colorless oil (85 mg, 45% yield).

S9
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.14 – 8.10 (m, 1H), 7.66 – 7.60 (m, 1H), 7.55 (d, \(J = 8.0\) Hz, 1H), 7.41 – 7.35 (m, 6H), 7.33 – 7.24 (m, 5H), 7.20 – 7.13 (m, 6H), 7.11 – 7.03 (m, 2H), 4.95 (t, \(J = 7.2\) Hz, 1H), 2.31 (q, \(J = 7.3\) Hz, 2H), 1.47 – 1.36 (m, 2H), 0.94 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.6, 137.3, 135.4, 133.9, 133.4, 131.9, 129.8, 128.3, 127.8, 127.5, 126.7, 126.7, 125.8, 125.5, 124.8, 115.1, 28.2, 22.9, 14.1. HRMS(ESI) Calculated for C\(_{33}\)H\(_{31}\)OSi ([M+H]\(^+\)): 471.2144, found: 471.2132.

(Z)-((1-(4-isopropylphenyl)pent-1-en-1-yl)oxy)triphenylsilane (3g)

Purified by silica gel column chromatography as colorless oil (133 mg, 72% yield).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.61 – 7.58 (m, 6H), 7.39 – 7.34 (m, 3H), 7.31 – 7.27 (m, 6H), 7.22 (d, \(J = 8.2\) Hz, 2H), 6.91 (d, \(J = 8.2\) Hz, 2H), 5.07 (t, \(J = 7.3\) Hz, 1H), 2.82 – 2.72 (m, 1H), 2.00 (q, \(J = 7.5\) Hz, 2H), 1.21 – 1.14 (m, 8H), 0.74 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 149.3, 147.8, 136.4, 135.6, 134.2, 129.9, 127.6, 126.2 125.7, 111.3, 33.7, 28.5, 23.9, 22.7, 13.8. HRMS(ESI) Calculated for C\(_{32}\)H\(_{35}\)OSi ([M+H]\(^+\)): 473.2457, found: 473.2445.

(Z)-((1-[1,1'-biphenyl]-4-yl)pent-1-en-1-yl)oxy)triphenylsilane (3h)

Purified by silica gel column chromatography as white solid (139 mg, 70% yield). mp: 88-90 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.65 – 7.59 (m, 6H), 7.50 (d, \(J = 7.9\) Hz, 2H), 7.41 – 7.35 (m, 7H), 7.34 – 7.28 (m, 9H), 5.18 (t, \(J = 7.3\) Hz, 1H), 2.03 (q, \(J = 7.4\) Hz, 2H), 1.25 – 1.17 (m, 2H), 0.75 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 149.0, 140.9, 139.9, 137.8, 135.7, 134.1, 130.1, 128.8, 127.8, 127.2, 127.0, 126.6, 126.5, 112.3, 28.7, 22.7, 13.9. HRMS(ESI) Calculated for C\(_{35}\)H\(_{33}\)OSi ([M+H]\(^+\)): 497.2301, found: 497.2291.

(Z)-((1-(4-methoxyphenyl)pent-1-en-1-yl)oxy)triphenylsilane (3i)

Purified by silica gel column chromatography as colorless oil (130 mg, 73% yield, Z/E = 80:20).
**1H NMR (400 MHz, CDCl₃)** δ 7.67 – 7.63 (m, 1H), 7.62 – 7.57 (m, 5H), 7.43 – 7.35 (m, 3H), 7.31 (t, J = 7.3 Hz, 6H), 7.26 – 7.20 (m, 2H), 6.64 – 6.58 (m, 2H), 5.04 – 4.95 (m, 1H), 3.69 (s, 3H), 2.02 – 1.91 (m, 2H), 1.22 – 1.10 (m, 2H), 0.73 (t, J = 7.3 Hz, 3H).

**13C NMR (125 MHz, CDCl₃)** δ 158.9, 148.9, 135.6, 135.0, 134.1, 129.9, 127.9, 127.6, 113.1, 110.7, 55.2, 28.5, 22.7, 13.8.


(Z)-4-(1-((triphenylsilyl)oxy)pent-1-en-1-yl)phenyl 4-methylbenzenesulfonate (3j)

![Diagram](OSiPh₃TsO) 3j

Purified by silica gel column chromatography as colorless oil (130 mg, 55% yield, Z/E = 93:7).

**1H NMR (500 MHz, CDCl₃)** δ 7.71 – 7.60 (m, 2H), 7.60 – 7.49 (m, 6H), 7.44 – 7.37 (m, 3H), 7.35 – 7.27 (m, 6H), 7.23 (d, J = 8.1 Hz, 2H), 7.21 – 7.17 (m, 2H), 6.73 – 6.63 (m, 2H), 5.11 – 5.03 (m, 1H), 2.41 (s, 3H), 2.00 – 1.93 (m, 2H), 1.20 – 1.12 (m, 2H), 0.76 – 0.69 (m, 3H).

**13C NMR (125 MHz, CDCl₃)** δ 148.6, 148.0, 145.1, 137.8, 135.5, 135.6, 132.4, 130.1, 129.6, 128.4, 127.7, 127.2, 121.5, 113.1, 28.5, 22.5, 21.6, 13.7. **HRMS(ESI)** Calculated for C₃₆H₃₃O₄SSi ([M-H]⁻): 589.1869, found: 589.1871.

(Z)-tert-butyldimethyl(4-(1-((triphenylsilyl)oxy)pent-1-en-1-yl)phenoxy)silane (3k)

![Diagram](OSiPh₃TBSO) 3k

Purified by silica gel column chromatography as colorless oil (152 mg, 69% yield, Z/E = 91:9).

**1H NMR (500 MHz, CDCl₃)** 7.59 (d, J = 6.8 Hz, 5H), 7.47 (d, J = 6.8 Hz, 1H), 7.38 (t, J = 7.3 Hz, 3H), 7.33 – 7.29 (m, 5H), 7.24 (s, 1H), 7.16 (d, J = 8.6 Hz, 2H), 6.54 (d, J = 8.6 Hz, 2H), 5.04 – 4.94 (m, 1H), 2.03 – 1.90 (m, 2H), 1.22 – 1.13 (m, 2H), 0.97 (s, 9H), 0.73 (t, J = 7.3 Hz, 3H), 0.13 (s, 6H). **13C NMR (125 MHz, CDCl₃)** δ 159.4, 153.5, 140.1, 139.6, 138.6, 134.4, 132.1, 131.9, 123.7, 115.3, 32.9, 30.1, 27.2, 22.6, 18.2, 0.00. **HRMS(ESI)** Calculated for C₃₅H₄₃O₂Si₂ ([M+H]^+): 551.2802, found: 551.2788.

(Z)-4-(1-((triphenylsilyl)oxy)pent-1-en-1-yl)phenyl acetate (3l)

![Diagram](OSiPh₃AcO) 3l

Purified by silica gel column chromatography as colorless oil (86 mg, 45% yield, Z/E = 90:10).

S11
**1H NMR (500 MHz, CDCl₃)** δ 7.62 – 7.56 (m, 6H), 7.40 (t, J = 7.4 Hz, 3H), 7.34 – 7.27 (m, 8H), 6.79 (d, J = 8.6 Hz, 2H), 5.08 (t, J = 7.3 Hz, 1H), 2.24 (s, 3H), 2.02 – 1.96 (m, 2H), 1.21 – 1.14 (m, 2H), 0.73 (t, J = 7.3 Hz, 3H). **13C NMR** (125 MHz, CDCl₃) δ 169.3, 149.8, 148.4, 136.6, 135.5, 133.9, 130.0, 127.7, 127.2, 120.7, 112.3, 28.5, 22.6, 21.1, 13.7. **HRMS(ESI)** Calculated for C₃₁H₃₁O₃Si ([M+H]+): 479.2042, found: 479.2031.

(Z)-((1-(4-chlorophenyl)pent-1-en-1-yl)oxy)triphenylsilane (3m)

Purified by silica gel column chromatography as colorless oil (44 mg, 24% yield).

**1H NMR (500 MHz, CDCl₃)** δ 7.61 – 7.56 (m, 6H), 7.42 – 7.38 (m, 3H), 7.34 – 7.30 (m, 6H), 7.22 – 7.19 (m, 2H), 7.04 – 7.00 (m, 2H), 5.09 (t, J = 7.3 Hz, 1H), 1.99 (q, J = 7.5 Hz, 2H), 1.22 – 1.14 (m, 2H), 0.73 (t, J = 7.4 Hz, 3H). **13C NMR** (125 MHz, CDCl₃) δ 148.2, 137.3, 135.5, 133.8, 132.8, 130.1, 127.8, 127.4, 112.7, 28.5, 22.6, 13.8. **HRMS(ESI)** Calculated for C₂₉H₂₈ClOSi ([M+H]+): 479.2042, found: 479.2031.

(Z)-((1-(4-fluorophenyl)pent-1-en-1-yl)oxy)triphenylsilane (3n)

Purified by silica gel column chromatography as colorless oil (124 mg, 71% yield).

**1H NMR (500 MHz, CDCl₃)** δ 7.60 – 7.56 (m, 6H), 7.42 – 7.38 (m, 3H), 7.34 – 7.30 (m, 6H), 7.25 – 7.21 (m, 2H), 6.76 – 6.69 (m, 2H), 5.03 (t, J = 7.3 Hz, 1H), 2.02 – 1.97 (m, 2H), 1.22 – 1.15 (m, 2H), 0.74 (t, J = 7.3 Hz, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 162.0 (d, J_{C,F} = 246.1 Hz), 148.3, 135.5, 135.0 (d, J_{C,F} = 3.1 Hz), 133.8, 130.0, 127.8 (d, J_{C,F} = 8.0 Hz), 127.7, 114.4 (d, J_{C,F} = 21.5 Hz), 112.1, 28.5, 22.6, 13.8. **HRMS(ESI)** Calculated for C₂₉H₂₈FOSi ([M+H]+): 439.1893, found: 439.1881.

(Z)-triphenyl((1-(4-(trifluoromethyl)phenyl)pent-1-en-1-yl)oxy)silane (3o)

Purified by silica gel column chromatography as colorless oil (110 mg, 57% yield).

**1H NMR (500 MHz, CDCl₃)** δ 7.63 – 7.55 (m, 6H), 7.43 –
7.36 (m, 5H), 7.34 – 7.27 (m, 8H), 5.20 (t, \(J = 7.3\) Hz, 1H), 2.06 – 1.99 (m, 2H), 1.24 – 1.16 (m, 2H), 0.75 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.1, 142.3, 135.6, 133.6, 130.5, 129.0 (q, \(J\), \(C-F\) = 32.3 Hz), 127.8, 126.2, 124.71 (q, \(J\), \(C-F\) = 3.7 Hz), 124.2 (q, \(J\), \(C-F\) = 270.2 Hz), 114.3, 28.6, 22.6, 13.8. HRMS(ESI) Calculated for C\(_{30}\)H\(_{28}\)F\(_3\)O\(_2\)Si ([M+H]\(^+\)): 489.1862, found: 489.1848.

(Z)-((1-(furan-2-yl)pent-1-en-1-yl)oxy)triphenylsilane (3p)

\[
\begin{array}{c}
\text{OSiPh}_3 \\
\text{O}
\end{array}
\]

Purified by silica gel column chromatography as colorless oil (93 mg, 57% yield, Z/E = 88:12).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 – 7.63 (m, 6H), 7.43 – 7.39 (m, 3H), 7.38 – 7.34 (m, 6H), 7.14 (d, \(J = 1.0\) Hz, 1H), 6.14 – 6.10 (m, 1H), 5.98 (d, \(J = 3.3\) Hz, 1H), 5.31 (t, \(J = 7.5\) Hz, 1H), 1.94 (q, \(J = 7.6\) Hz, 2H), 1.18 – 1.10 (m, 2H), 0.74 – 0.68 (m, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 152.2, 141.2, 140.7, 135.6, 133.9, 130.2, 127.8, 110.9, 110.8, 106.3, 27.8, 22.6, 13.8. HRMS(ESI) Calculated for C\(_{27}\)H\(_{27}\)O\(_2\)Si ([M+H]\(^+\)): 411.1780, found: 411.1767.

(Z)-tri phenyl((1-phenylhept-3-en-3-yl)oxy)silane (3q)

\[
\begin{array}{c}
\text{OSiPh}_3 \\
\text{O}
\end{array}
\]

Purified by silica gel column chromatography as colorless oil (127 mg, 69% yield, Z/E = 71:29).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.72 – 7.62 (m, 6H), 7.46 – 7.39 (m, 3H), 7.39 – 7.33 (m, 6H), 7.24 – 7.13 (m, 2.79H), 7.13 – 7.07 (m, 1.77H), 6.93 – 6.84 (m, 0.56H), 4.65 (t, \(J = 7.7\) Hz, 0.69H), 4.48 (t, \(J = 7.1\) Hz, 0.28H), 2.85 – 2.80 (m, 1.42H), 2.70 – 2.62 (m, 0.58H), 2.44 – 2.36 (m, 1.43H), 2.27 – 2.20 (m, 0.58H), 1.92 (q, \(J = 7.5\) Hz, 0.57H), 1.69 (q, \(J = 7.5\) Hz, 1.43H), 1.19 – 1.09 (m, 0.59H), 1.01 (h, \(J = 7.5\) Hz, 1.44H), 0.73 (t, \(J = 7.4\) Hz, 0.87H), 0.62 (t, \(J = 7.4\) Hz, 2.14H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 150.0, 149.6, 142.0, 141.7, 135.5, 135.5, 134.5, 134.3, 130.0, 130.0, 128.5, 128.3, 128.2, 128.1, 127.8, 127.8, 125.7, 125.6, 109.6, 109.5, 38.5, 34.0, 33.5, 33.4, 28.8, 27.6, 23.3, 22.7, 13.8, 13.4. HRMS(ESI) Calculated for C\(_{31}\)H\(_{33}\)O\(_2\)Si ([M+H]\(^+\)): 449.2301, found: 449.2290.

(Z)-((1-(naphthalen-2-yl)prop-1-en-1-yl)oxy)triphenylsilane (3r)
Purified by silica gel column chromatography as white solid (134 mg, 76% yield, Z/E = 98:2). mp: 80-82 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 (s, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.67 – 7.61 (m, 6H), 7.57 (d, J = 8.6 Hz, 1H), 7.45 (d, J = 8.6 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.36 – 7.28 (m, 8H), 5.43 – 5.33 (m, 1H), 1.59 (d, J = 6.8 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 150.2, 135.7, 135.3, 134.1, 133.1, 132.7, 130.1, 128.2, 127.8, 127.4, 127.3, 125.9, 125.7, 125.0, 124.1, 106.8, 12.3. HRMS(ESI) Calculated for C$_{31}$H$_{27}$OSi ([M+H]$^+$): 443.1831, found: 443.1818.

$(Z)$-(2-methyl-1-(naphthalen-1-yl)prop-1-en-1-yl)oxy)triphenylsilane (3s)

Purified by silica gel column chromatography as white solid (84 mg, 46% yield). mp: 73-75 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, J = 7.9 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.42 – 7.39 (m, 7H), 7.38 – 7.31 (m, 4H), 7.26 – 7.20 (m, 6H), 7.17 (dd, $J_1 = 8.1, J_2 = 7.2$ Hz, 1H), 7.02 – 6.97 (m, 1H), 2.08 (s, 3H), 1.51 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.8, 135.6, 135.1, 134.2, 133.4, 132.1, 129.5, 128.0, 127.8, 127.7, 127.3, 126.5, 125.7, 125.3, 124.7, 114.5, 19.6, 17.9. HRMS(ESI) Calculated for C$_{32}$H$_{28}$OSi ([M]$^+$): 456.1909, found: 456.1893.

$(Z)$-((1-(naphthalen-2-yl)but-1-en-1-yl)oxy)triphenylsilane (3t)

Purified by silica gel column chromatography as white solid (127 mg, 70% yield, Z/E = 98:2). mp: 97-99 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (s, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.66 – 7.60 (m, 6H), 7.57 (d, J = 8.6 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.38 (m, 4H), 7.36 – 7.27 (m, 8H), 5.29 (t, J = 7.2 Hz, 1H), 2.11 (m, 2H), 0.78 (t, J = 7.5 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 148.5, 135.6, 134.0, 133.0, 132.7, 130.0, 128.2, 127.7, 127.3, 127.3, 125.8, 125.6, 125.0, 124.1, 114.5, 20.0, 13.9. HRMS(ESI) Calculated for C$_{32}$H$_{28}$OSi ([M]$^+$): 457.1988, found: 457.1973.

$(Z)$-((1-(naphthalen-2-yl)hept-1-en-1-yl)oxy)triphenylsilane (3u)

Purified by silica gel column chromatography as white solid (134 mg, 76% yield, Z/E = 98:2). mp: 80-82 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 (s, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.67 – 7.61 (m, 6H), 7.57 (d, J = 8.6 Hz, 1H), 7.45 (d, J = 8.6 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.36 – 7.28 (m, 8H), 5.43 – 5.33 (m, 1H), 1.59 (d, J = 6.8 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 150.2, 135.7, 135.3, 134.1, 133.1, 132.7, 130.1, 128.2, 127.8, 127.4, 127.3, 125.9, 125.7, 125.0, 124.1, 106.8, 12.3. HRMS(ESI) Calculated for C$_{31}$H$_{27}$OSi ([M+H]$^+$): 443.1831, found: 443.1818.
Purified by silica gel column chromatography as colorless oil (106 mg, 53\% yield, Z/E = 98:2).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.83 (s, 1H), 7.80 – 7.76 (m, 1H), 7.75 – 7.70 (m, 6H), 7.67 (d, $J = 8.7$ Hz, 1H), 7.57 (dd, $J_1 = 8.6$, $J_2 = 1.8$ Hz, 1H), 7.51 – 7.46 (m, 4H), 7.45 – 7.38 (m, 8H), 5.41 (t, $J = 7.2$ Hz, 1H), 2.17 (q, $J = 7.5$ Hz, 2H), 1.33 – 1.18 (m, 6H), 0.92 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 148.9, 136.5, 135.6, 134.0, 133.1, 132.7, 130.0, 128.2, 127.7, 127.3, 127.2, 125.8, 125.6, 125.0, 124.1, 113.0, 31.6, 29.2, 26.7, 22.5, 14.1. HRMS(ESI) Calculated for C$_{35}$H$_{35}$OSi ([M+H]$^+$): 499.2452, found: 499.2448.

(Z)-triphenyl((1-phenylhex-2-en-2-yl)oxy)silane (3x)

Purified by silica gel column chromatography as colorless oil (124 mg, 72\% yield, Z/E = 92:8).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.54 – 7.46 (m, 6H), 7.42 – 7.34 (m, 4H), 7.33 – 7.29 (m, 5H), 7.24 – 7.19 (m, 3H), 7.18 – 7.15 (m, 2H), 4.75 (t, $J = 7.6$ Hz, 1H), 3.43 (s, 2H), 1.93 (q, $J = 7.4$ Hz, 2H), 1.21 – 1.13 (m, 2H), 0.71 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 149.3, 138.8, 135.6, 134.1, 129.9, 129.0, 128.2, 127.6, 126.0, 110.1, 37.6, 29.2, 23.5, 13.5. HRMS(ESI) Calculated for C$_{30}$H$_{31}$OSi ([M+H]$^+$): 435.2139, found: 435.2136.

### 3.3 Mechanistic experiments

#### 3.3.1 Radical trapping experiments

<table>
<thead>
<tr>
<th>Radical scavenger</th>
<th>yield of 3e</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPO</td>
<td>NR</td>
</tr>
<tr>
<td>BHT</td>
<td>56%</td>
</tr>
<tr>
<td>1,1'-diphenylethene</td>
<td>78%</td>
</tr>
</tbody>
</table>
Experimental procedure:
To a 25 ml flame-dried Schlenk tube containing a stirring bar was added NiCl$_2$ (10 mol%, 0.04 mmol, 5.2 mg), Ph$_3$SiH (0.6 mmol, 156 mg), xylene (1 mL), t-BuNC (0.2 mmol, 16.6 mg), 1-(naphthalen-2-yl)pent-4-en-1-one (0.4 mmol, 84 mg) and radical scavenger (1 equiv.), sequentially under nitrogen. The tube was sealed and stirred at 120 °C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product 3e.

3.3.2 Deuterium-labelling experiment
Ph$_3$SiD (>99% D) was synthesized according to the known literature$^4$.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.60 – 7.55 (m, 6H), 7.43 – 7.39 (m, 3H), 7.38 – 7.34 (m, 6H).

![NMR spectrum](image)

Experimental procedure:
To a 25 ml flame-dried Schlenk tube containing a stirring bar was added NiCl$_2$ (10 mol%, 0.04 mmol, 5.2 mg), Ph$_3$SiD (0.6 mmol, 156.6 mg), xylene (1 mL), t-BuNC (0.2 mmol, 16.6 mg), and...
1-(naphthalen-2-yl)pent-4-en-1-one (0.4 mmol, 84 mg) sequentially under nitrogen. The tube was sealed and stirred at 120 °C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the deuterated product 3e-d in 76% yield.

3.4 Synthetic applications

3.4.1 Preparation of silyl enol ether 3x

Following the general procedure, see Section 3.2.

3.4.2 Reaction of mixed isomers 1a, 1v, and 1w with 2a
**Experimental procedure:**

To a 25 ml flame-dried Schlenk tube containing a stirring bar was added NiCl₂ (10 mol%, 0.03 mmol, 3.9 mg), Ph₃SiH (0.45 mmol, 117 mg), xylene (1 mL), t-BuNC (0.15 mmol, 12.5 mg), 1a (0.1 mmol, 16 mg), 1v (0.1 mmol, 16 mg) and 1w (0.1 mmol, 16 mg) sequentially under nitrogen. The tube was sealed and stirred at 120 °C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the same product 3a in 37% yield.
4. References


5. $^1$H and $^{13}$C NMR Spectra

![Diagram of molecule 3a with NMR peaks]
$\text{OSiPh}_3$

$3h$

Chemical Shifts:
- 7.625, 7.612, 7.609
- 7.984, 7.949, 7.891
- 7.804, 7.785, 7.749
- 7.788, 7.771, 7.734
- 7.348, 7.308, 7.283
- 7.229, 7.030, 6.864
- 2.003, 1.978, 0.740
- 2.033, 2.018, 1.978
- 2.048, 2.043, 0.740
\[ 3i \]

\[ \text{OSiPh}_3 \]

\[ \text{MeO} \]

\[ \delta (\text{ppm}) \]

1.28 \text{ ppm}, 1.43 \text{ ppm}, 2.40 \text{ ppm}, 2.02 \text{ ppm}, 2.05 \text{ ppm}, 2.35 \text{ ppm}, 0.05 \text{ ppm}
$3j$

![NMR spectrum](image-url)
OSiPh₃

3n

δ (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 0.5
OSiPh$_3$