Supplementary Information for:

# Phenanthroline-Imine Ligands for Iron-Catalyzed Alkene

## **Hydrosilylation**

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## 1. Materials and methods

All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques. THF, Et<sub>2</sub>O, 1,4-dioxane, and toluene were distilled from sodium benzophenone ketyl prior to use. Iron(II) chloride (99.99%) was purchased from Sigma-Aldrich and used as received. The conjugated dienes **1a**, **1c**, **1d**, **1e**, **1g**, **1h**, **1k**, **1n**, **1p**, **1w**, **1y**, **1z** and **1aa** used for hydrosilylation were synthesized according to reported procedures.<sup>1</sup> The conjugated dienes **1b**, **1f**, **1i**, **1j** and **1q** were synthesized according to reported procedures.<sup>1.2</sup> The conjugated dienes **1l**, <sup>3</sup> **1m**, <sup>4</sup> **1o**, <sup>1.5</sup> **1t**, <sup>6</sup> **1u**, <sup>7</sup> and **1x**<sup>8</sup> were synthesized according to corresponding literatures. The silanes **2a**, **2j**, **2k** conjugated diene **1r**, **1s**, and alkenes **7a**-**7h**, **7k**-**7o** were purchased from Sigma-Aldrich, Alfa Aesar, Acros, TCI and other reagent companies. Alkenes **7i** and **7j** were synthesized according to reported procedures.<sup>10</sup> Conjugated dienes, alkenes, and silanes were dried over LiAlH<sub>4</sub> or CaH<sub>2</sub> and distilled prior to use. 2,9-dichloro-1,10-phenanthroline was prepared according to reported procedures.<sup>11</sup>

Melting points were measured on a RY-I apparatus and uncorrected. Infrared spectra were recorded on a Bruker Fourier transform spectrometric (FT-IR) and reported in wave number. High resolution mass spectrometric (HRMS) were determined on an IonSpec FT-ICR mass spectrometer or a Waters GCT Premier mass spectrometer. The molar masses and their distribution for the polymer samples were determined by GPC on a Waters system equipped with a set of three Ultrastyragel columns HT2 30 cm x 7.8 mm; 10 µm particles; exclusion limits: 100-10000 g/mol, respectively), THF was used as the mobile phase (1 mL/min), and polystyrene samples as the standards in the calibration of the molar masses. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra were recorded with a Bruker AV 400 spectrometer at 400 MHz (<sup>1</sup>H NMR), 101 MHz (<sup>13</sup>C NMR) and 376 MHz (<sup>19</sup>F NMR), respectively in CDCl<sub>3</sub>. <sup>2</sup>H NMR spectra was recorded with a Bruker AV 600 spectrometer at 92 MHz in DCM. Chemical shifts were reported in ppm down field from internal Me4Si (<sup>1</sup>H NMR) and CDCl<sub>3</sub> (<sup>13</sup>C NMR).

## 2. Synthesis of new ligands and catalysts

#### 2.1. Synthesis of 2-chloro-9-aryl-1,10-phenanthrolines



To a 100 mL three-necked round-bottom flask fitted with a reflux condenser tube, 2,9dichloro-1,10-phenanthroline (1.24 g, 5 mmol), 2,4,6-trimethylphenylboronic acid (0.9 g, 5.5 mmol, 1.1 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (577 mg, 0.5 mmol, 10 mol%), K<sub>3</sub>PO<sub>4</sub>•3H<sub>2</sub>O (6.65 g, 25 mmol, 5 equiv), DME (50 mL), and water (5 mL) were introduced. The resulted reaction mixture was degassed three times through freeze degassing, replaced with an argon atmosphere, and placed in an oil bath, and heated to 95 °C until the reaction was finished. After cooling to room temperature, the reaction mixture was neutralized with saturated NH<sub>4</sub>Cl (aq., 50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL × 3). The combined organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography with petroleum ether/ethyl acetate (PE/EA) = 10:1 (v/v) as eluent to give 2-chloro-9-(2,4,6- trimethylphenyl)-1,10-phenanthroline (**2a**) as a white solid (1.1 g, 66% yield), melting point: 231.2 – 233.0 °C.

- <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 8.28 (d, J = 8.2 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.89 7.84 (m, 1H), 7.82 7.77 (m, 1H), 7.63 7.55 (m, 2H), 6.97 (s, 2H), 2.35 (s, 3H), 2.14 (s, 6H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.7 (1C), 151.2 (1C), 146.3 (1C), 145.0 (1C), 138.6 (2C),
  137.9 (1C), 137.5 (1C), 136.1 (1C), 135.8 (1C), 128.4 (2C), 127.5 (1C), 127.3 (1C),
  126.8 (1C), 125.4 (2C), 124.1 (1C), 21.1 (1C), 20.6 (2C).

<u>HRMS (ESI)</u> calcd for [M+H, C<sub>21</sub>H<sub>18</sub>ClN<sub>2</sub>]<sup>+</sup>: 333.1153, found: 333.1156.

2-chloro-9-(2,4,6-triisopropylphenyl)-1,10-phenanthroline (2b)



White solid, 83% yield, melting point: 248.0 - 250.0 °C.

 $\frac{^{1}\text{H NMR}}{^{1}\text{H NMR}} (400 \text{ MHz, CDC1}_{3}) \delta 8.26 (d, J = 8.1 \text{ Hz}, 1\text{H}), 8.17 (d, J = 8.4 \text{ Hz}, 1\text{H}), 7.86 (d, J = 8.7 \text{ Hz}, 1\text{H}), 7.65 (d, J = 8.2 \text{ Hz}, 1\text{H}), 7.58 (d, J = 8.4 \text{ Hz}, 1\text{H}), 7.12 (s, 2\text{H}), 2.96 (hept, J = 6.9 \text{ Hz}, 1\text{H}), 2.59 (hept, J = 6.9 \text{ Hz}, 2\text{H}), 1.32 (d, J = 6.9 \text{ Hz}, 6\text{H}), 1.19 (d, J = 6.8 \text{ Hz}, 6\text{H}), 1.12 (d, J = 6.9 \text{ Hz}, 6\text{H}).$ 

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.1 (1C), 151.2 (1C), 148.9 (1C), 146.5 (1C), 146.4 (2C), 144.9 (1C), 138.4 (1C), 137.0 (1C), 135.2 (1C), 127.6 (1C), 127.4 (1C), 126.8 (1C), 125.6 (1C), 125.4 (1C), 124.2 (1C), 120.8 (2C), 34.5 (1C), 30.5 (2C), 24.2 (6C).
 <u>HRMS (ESI)</u> calcd for [M+H, C<sub>27</sub>H<sub>30</sub>ClN<sub>2</sub>]<sup>+</sup>: 417.2092, found 417.2093.

2-chloro-9-(3,5-di-*tert*-butylphenyl)-1,10-phenanthroline (2c)



White solid, 95% yield, melting point: 285.5 – 287.9 °C.

 $\frac{^{1}\text{H NMR}}{^{1}\text{H NMR}} (400 \text{ MHz, CDCl}_{3}) \delta 8.33 (d, J = 8.4 \text{ Hz}, 1\text{H}), 8.20 (d, J = 8.4 \text{ Hz}, 1\text{H}), 8.15 - 8.06 (m, 3\text{H}), 7.86 (d, J = 8.7 \text{ Hz}, 1\text{H}), 7.77 (d, J = 8.7 \text{ Hz}, 1\text{H}), 7.63 (d, J = 8.3 \text{ Hz}, 1\text{H}), 7.58 (t, J = 1.8 \text{ Hz}, 1\text{H}), 1.45 (s, 18\text{H}).$ 

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.3 (1C), 151.4 (1C), 151.2 (2C), 146.3 (1C), 144.9 (1C),
 139.2 (1C), 138.6 (1C), 136.6 (1C), 127.7 (1C), 127.6 (1C), 126.7 (1C), 125.1 (1C),

# 124.1 (1C), 123.8 (1C), 122.4 (2C), 121.6 (1C), 35.1 (2C), 31.6 (6C). <u>HRMS (ESI)</u> calcd for [M+H, C<sub>26</sub>H<sub>28</sub>ClN<sub>2</sub>]<sup>+</sup>: 403.1936, found 403.1938.

## 2.2. Synthesis of 2-acetyl-9-aryl-1,10-phenanthrolines



Compound 2a (0.8 g, 2.4 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (277 mg, 0.24 mmol, 10 mol%) were introduced into a 100 mL three-necked round-bottom flask fitted with a reflux condenser tube. The reaction system was replaced with an argon atmosphere, followed by the addition of 1ethoxyvinyltri-n-butylstannane (1.04 g, 2.88 mmol, 1.2 equiv) and anhydrous DMF (30 ml) using a syringe, respectively, and then stirred at 100 °C for 24 h until the reaction was finished. After cooling to room temperature, the reaction mixture was quenched with saturated KF (aq., 50 mL) and extracted with Et<sub>2</sub>O (100 mL  $\times$  3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was dissolved in acetone (30 mL), and was added dropwise concentrated hydrochloric acid (6 mL) with stirring overnight. Complete consumption of the reactants was determined by TLC. The reaction mixture was neutralized with aqueous NaHCO3 solution, the acetone was removed under reduced pressure, extracted with DCM, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography with PE/EA = 10:1 (v/v) as eluent to give the target product 1-(9-mesityl-1,10-phenanthrolin-2yl)ethan-1-one (**3a**) as a white solid (628 mg, 76% yield), melting point: 237.5 - 238.2 °C.  $^{1}$ <u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.41 – 8.26 (m, 3H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.8

Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.02 (s, 2H), 2.97 (s, 3H), 2.37 (s, 3H), 2.27 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 201.2 (1C), 160.3 (1C), 153.0 (1C), 145.9 (1C), 145.4 (1C), 137.7 (1C), 137.6 (1C), 136.8 (1C), 136.4 (1C), 135.6 (1C), 130.6 (1C), 128.8 (3C), 128.6 (1C), 127.0 (1C), 125.8 (1C), 125.6 (1C), 120.0 (1C), 25.9 (1C), 21.1 (1C), 20.9 (2C).

<u>HRMS (ESI)</u> calcd for [M+H, C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O]<sup>+</sup>: 341.1648, found 341.1652.

1-(9-(2,4,6-triisopropylphenyl)-1,10-phenanthrolin-2-yl)ethan-1-one (3b)



White solid, 98% yield, melting point: 185.7 – 186.1 °C.

- <sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (q, J = 8.3 Hz, 2H), 8.28 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.7 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.18 (s, 2H), 3.07 2.96 (m, 1H), 2.94 (s, 3H), 2.69 (hept, J = 6.0 Hz, 2H), 1.36 (d, J = 6.8 Hz, 6H), 1.26 (d, J = 6.7 Hz, 6H), 1.19 (d, J = 6.8 Hz, 6H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 201.5 (1C), 160.6 (1C), 153.0 (1C), 148.8 (1C), 146.7 (2C), 145.9 (1C), 145.6 (1C), 136.7 (1C), 136.6 (1C), 135.2 (1C), 130.7 (1C), 128.6 (1C), 127.1 (1C), 125.8 (1C), 125.5 (1C), 120.9 (2C), 119.9 (1C), 34.4 (1C), 30.7 (2C), 26.2 (1C), 24.9 (2C), 24.1 (4C).

<u>HRMS (ESI)</u> calcd for [M+H, C<sub>29</sub>H<sub>33</sub>N<sub>2</sub>O]<sup>+</sup>: 425.2587, found 425.2589.

1-(9-(3,5-di-*tert*-butylphenyl)-1,10-phenanthrolin-2-yl)ethan-1-one (3c)



White solid, 67% yield, melting point: 160.2 - 162.1 °C.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.40 – 8.31 (m, 5H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.58 (m, 1H), 3.14 (s, 3H), 1.47 (s, 18H). <sup>13</sup><u>C NMR</u> (101 MHz, CDCl<sub>3</sub>)  $\delta$  200.9 (1C), 158.2 (1C), 152.7 (1C), 151.3 (2C), 145.9 (1C), 145.4 (1C), 138.4 (1C), 136.9 (1C), 136.8 (1C), 130.9 (1C), 128.6 (1C), 127.6 (1C), 125.5 (1C), 124.1 (1C), 122.0 (2C), 120.3 (1C), 120.0 (1C), 35.1 (2C), 31.5 (6C), 25.4 (1C).

<u>HRMS (ESI)</u> calcd for  $[M+H, C_{28}H_{31}N_2O]^+$ : 411.2431, found 411.2433.

#### 2.3 Synthesis of 2-imino-9-aryl-1,10-phenanthrolines ligands



To a 100 mL three-necked round-bottom flask fitted with a reflux condenser tube, was added the compound **3a** (342 mg, 1.0 mmol) and the catalyst TsOH (17.2 mg, 0.1 mmol, 10 mol%). The resulted mixture was replaced with an argon atmosphere, added 2,6-dimethylaniline (242 mg, 2.0 mmol, 2.0 equiv) and anhydrous ethanol (10 mL), and stirred in an oil bath at 85 °C for 48 h until the reaction was finished. The reaction mixture was

concentrated under reduced pressure, and the residue was purified by silica-gel column chromatography with PE/EA/Et<sub>3</sub>N= 50:10:1 (v/v/v) as eluent to give the target product (*E*)-N-(2,6-dimethylphenyl)-1-(9-mesityl-1,10-phenanthrolin-2-yl)ethan-1-imine (**L1a**) as a yellow solid (330 mg, 74% yield), melting point: 236.0 - 237.0 °C.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.76 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 7.88-7.80 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.99 (s, 2H), 6.97-6.90 (m, 1H), 2.44 (s, 3H), 2.34 (s, 3H), 2.27 (s, 6H), 2.04 (s, 6H). <sup>13</sup><u>C NMR</u> (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.3 (1C), 159.9 (1C), 155.9 (1C), 149.0 (1C), 146.0 (1C), 145.4 (1C), 137.7 (1C), 137.6 (1C), 136.5 (2C), 136.3 (1C), 135.7 (1C), 129.6 (1C), 128.8 (2C), 127.9 (2C), 127.4 (1C), 127.0 (1C), 126.1 (1C), 125.3 (3C), 123.0 (1C), 120.6 (1C), 21.2 (1C), 21.1 (2C), 18.1 (2C), 16.8 (1C).

<u>HRMS (ESI)</u> calculated for  $[M+H, C_{31}H_{30}N_3]^+$ : 444.2434, found: 444.2438.

(*E*)-N-(2,6-dimethylphenyl)-1-(9-(2,4,6-triisopropylphenyl)-1,10-phenanthrolin-2yl)ethan-1-imine (L1b)



Yellow solid, 64% yield, melting point: 211.2 – 213.4 °C.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.73 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.2 Hz, 1H), 7.92 – 7.84 (m, 2H), 7.65 (d, J = 8.1 Hz, 1H), 7.15 (s, 2H), 7.09 – 7.04 (m, 2H), 6.97 – 6.91 (m, 1H), 2.99 (hept, J = 6.9 Hz, 1H), 2.73 (p, J = 6.8 Hz, 2H), 2.39 (s, 3H), 2.05 (s, 6H), 1.34 (d, J = 6.9 Hz, 6H), 1.24 (d, J = 6.7 Hz, 6H), 1.17 (d, J = 6.9 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.6 (1C), 160.2 (1C), 155.9 (1C), 149.0 (1C), 148.7 (1C),

146.8 (2C), 145.9 (1C), 145.6 (1C), 136.7 (1C), 136.1 (1C), 135.1 (1C), 129.6 (1C), 127.8 (2C), 127.3 (1C), 127.0 (2C), 126.0 (1C), 125.4 (1C), 125.2 (1C), 122.9 (1C), 120.9 (2C), 120.4 (1C), 34.3 (1C), 30.6 (2C), 24.9 (2C), 24.2 (2C), 24.1 (2C), 18.0 (2C), 17.0 (1C).

<u>HRMS (ESI)</u> calcd for [M+H, C<sub>37</sub>H<sub>42</sub>N<sub>3</sub>]<sup>+</sup>: 528.3373, found: 528.3375.

(*E*)-N-(2,6-diethylphenyl)-1-(9-(2,4,6-triisopropylphenyl)-1,10-phenanthrolin-2-yl)ethan-1-imine (L1c)



Yellow solid, 67% yield, melting point: 204.9 – 206.2 °C.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.72 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.82 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.15 (s, 2H), 7.13 – 7.08 (m, 2H), 7.06 – 7.00 (m, 1H), 2.99 (hept, *J* = 6.9 Hz, 1H), 2.73 (hept, *J* = 6.8 Hz, 2H), 2.50 – 2.29 (m, 7H), 1.34 (d, *J* = 6.9 Hz, 6H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.19 – 1.11 (m, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.3 (1C), 160.2 (1C), 156.0 (1C), 148.7 (1C), 148.0 (1C), 146.8 (2C), 146.0 (1C), 145.6 (1C), 136.8 (1C), 136.1 (1C), 135.1 (1C), 131.2 (2C), 129.6 (1C), 127.3 (1C), 127.0 (1C), 126.0 (1C), 125.9 (2C), 125.2 (1C), 123.2 (1C), 120.9 (2C), 120.3 (1C), 34.4 (1C), 30.6 (2C), 24.9 (2C), 24.6 (2C), 24.1 (4C), 17.3 (1C), 13.7 (2C).

<u>HRMS (ESI)</u> calcd for [M+H, C<sub>39</sub>H<sub>46</sub>N<sub>3</sub>]<sup>+</sup>: 556.3686, found: 556.3689.

(*E*)-N-(2,6-diisopropylphenyl)-1-(9-(2,4,6-triisopropylphenyl)-1,10-phenanthrolin-2yl)ethan-1-imine (L1d)



Yellow solid, 90% yield, melting point: 249.0 – 251.2 °C.

- <sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 8.72 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 8.1 Hz, 1H), 7.93 7.83 (m, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.19 7.14 (m, 4H), 7.13 7.06 (m, 1H), 2.99 (hept, J = 6.9 Hz, 1H), 2.77 (dp, J = 24.9, 6.8 Hz, 4H), 2.42 (s, 3H), 1.34 (d, J = 6.9 Hz, 6H), 1.24 (d, J = 6.8 Hz, 6H), 1.19 1.11 (m, 18H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.3 (1C), 160.1 (1C), 155.9 (1C), 148.6 (1C), 146.8 (2C), 146.7 (1C), 146.0 (1C), 145.6 (1C), 136.8 (1C), 136.1 (1C), 135.7 (2C), 135.1 (1C), 129.6 (1C), 127.3 (1C), 127.0 (1C), 126.0 (1C), 125.2 (1C), 123.5 (1C), 122.9 (2C), 120.9 (2C), 120.4 (1C), 34.3 (1C), 30.6 (2C), 28.2 (2C), 24.9 (2C), 24.2 (2C), 24.1 (2C), 23.2 (2C), 22.9 (2C), 17.6 (1C).

<u>HRMS (ESI)</u> calcd for  $[M+H, C_{41}H_{50}N_3]^+$ : 584.3999, found 584.4003.

(E) - N - (2,6 - dibenzhydryl - 4 - methoxyphenyl) - 1 - (9 - (2,4,6 - triisopropylphenyl) - 1,10 - phenanthrolin - 2 - yl) ethan - 1 - imine (L1e)



Yellow solid, 66% yield, melting point: 127.1 - 129.0 °C. The amount of arylamine is 1.2 equivalents.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (q, *J* = 9.0, 8.5 Hz, 3H), 7.85 (q, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.24 – 6.92 (m, 22H), 6.46 (s, 2H), 5.33 (s, 2H), 3.56 (s, 3H), 3.02 (p, *J* = 7.0 Hz, 1H), 2.62 (p, *J* = 6.9 Hz, 2H), 1.38 (d, *J* = 6.9 Hz, 6H), 1.32 (s, 3H), 1.15 (dd, *J* = 16.5, 6.8 Hz, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.0 (1C), 159.2 (1C), 155.0 (1C), 154.0 (1C), 147.6 (1C), 145.7 (2C), 145.0 (1C), 144.5 (1C), 142.5 (2C), 141.3 (1C), 141.1 (2C), 136.0 (1C), 134.7 (1C), 134.0 (1C), 132.6 (2C), 128.7 (4C), 128.4 (4C), 128.3 (1C), 127.4 (4C), 126.9 (4C), 126.1 (1C), 125.9 (1C), 125.2 (2C), 125.0 (3C), 123.8 (1C), 119.7 (2C), 119.3 (1C), 112.7 (2C), 54.1 (1C), 51.1 (2C), 33.4 (1C), 29.7 (2C), 23.9 (2C), 23.2 (2C), 22.8 (2C), 16.3 (1C).

<u>HRMS (ESI)</u> calcd for [M+H, C<sub>62</sub>H<sub>60</sub>N<sub>3</sub>O]<sup>+</sup>: 862.4731, found: 862.4735.

(*E*)-1-(9-(3,5-di-*tert*-butylphenyl)-1,10-phenanthrolin-2-yl)-N-(2,6-dimethylphenyl)ethan-1-imine (L1f)



Yellow solid, 48% yield, melting point: 202.8 – 203.3 °C.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 8.80 (d, J = 8.4 Hz, 1H), 8.37 – 8.31 (m, 4H), 8.21 (d, J = 8.4 Hz, 1H), 7.91 – 7.81 (m, 2H), 7.59 – 7.54 (m, 1H), 7.12 (d, J = 7.5 Hz, 2H), 7.02 – 6.95 (m, 1H), 2.64 (s, 3H), 2.10 (s, 6H), 1.43 (s, 18H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.0 (1C), 157.8 (1C), 155.5 (1C), 151.1 (2C), 149.1 (1C), 145.9 (1C), 145.2 (1C), 138.5 (1C), 136.8 (1C), 136.3 (1C), 129.7 (1C), 127.9 (2C),

127.5 (1C), 127.3 (1C), 125.7 (1C), 125.3 (2C), 123.9 (1C), 123.0 (1C), 121.9 (2C), 120.3 (1C), 119.9 (1C), 35.0 (2C), 31.5 (6C), 18.0 (2C), 16.4 (1C). <u>HRMS (ESI)</u> calcd for [M+H, C<sub>36</sub>H<sub>40</sub>N<sub>3</sub>]<sup>+</sup>: 514.3217, found: 514.3220.

(E)-1-(9-(3,5-di-tert-butylphenyl)-1,10-phenanthrolin-2-yl)-N-(2,6-

diisopropylphenyl)ethan-1-imine (L1g)



Yellow solid, 98% yield, melting point: 281.5 – 282.9 °C.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.79 (d, *J* = 8.4 Hz, 1H), 8.40 – 8.28 (m, 4H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.86 (q, *J* = 8.7 Hz, 2H), 7.55 (s, 1H), 7.24 – 7.18 (m, 2H), 7.18 – 7.09 (m, 1H), 2.85 (p, *J* = 6.9 Hz, 2H), 2.66 (s, 3H), 1.42 (s, 18H), 1.17 (d, *J* = 6.8 Hz, 12H). <sup>13</sup><u>C NMR</u> (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.8 (1C), 157.8 (1C), 155.6 (1C), 151.2 (2C), 146.8 (1C), 145.9 (1C), 145.2 (1C), 138.5 (1C), 136.8 (1C), 136.3 (1C), 135.8 (2C), 129.7 (1C), 127.5 (1C), 127.2 (1C), 125.7 (1C), 123.9 (1C), 123.6 (1C), 123.0 (2C), 121.9 (2C), 120.3 (1C), 119.9 (1C), 35.1 (2C), 31.5 (6C), 28.3 (2C), 23.3 (2C), 22.9 (2C), 17.1 (1C).

<u>HRMS (ESI)</u> calcd for [M+H, C<sub>40</sub>H<sub>48</sub>N<sub>3</sub>]<sup>+</sup>: 570.3843, found: 570.3846.

#### 2.4 Preparation of iron complexes with 2-imino-9-aryl-1,10-phenanthroline ligands



In an argon-filled glovebox, a tube with branch seal (125 mL) was charged with L1a (90 mg, 0.2 mmol), FeCl<sub>2</sub> (25.3 mg, 1 equiv) and dry THF (20 mL). The reaction mixture was stirred at 70 °C for 24 h until the free ligand was fully consumed according to <sup>1</sup>H NMR analysis. The solvent was partially removed under vacuum (about 5 mL left), then dry *n*-hexane (15 mL) was added, and solids precipitated. The product was collected by filtration, washed with 20 mL *n*-hexane, and dried under vacuum to give dark blue solid C1a (110 mg, 96% yield), decomposition temperature: 270 °C

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 70.82, 47.63, 30.79, 28.78, 18.25, 9.08, 7.84, 4.21, 3.77, 2.78, 2.04, 1.86, 1.26, 0.88, -3.47, -5.90, -20.93.

IR (neat): 2912w, 1617m, 1558m, 1500m, 1435m, 1371m, 1295m, 1255m, 1204m, 1158m, 1140m, 1112m, 1091m, 1066m, 1034m, 989w, 912w, 898w, 866s, 846m, 789m, 777m, 764m, 752w, 734m, 652w, 619m cm<sup>-1</sup>.



C1b, gray-green solid, 96% yield, decomposition temperature: 260 °C.

 $\frac{1}{1} \underline{\text{H NMR}} (400 \text{ MHz}, \text{CDCl}_3) \delta 69.70, 46.31, 39.20, 32.23, 31.79, 19.29, 6.03, 5.82, 5.48, 4.20, 6.03, 5.82, 5.48,$ 

1.75, 1.41, 1.37, 1.34, 1.25, 1.19, 0.87, -3.49, -6.23, -28.34, -48.96.

<u>IR (KBr)</u>: 3053w, 2959s, 2926m, 2868m, 1611m, 1499m, 1465m, 1442m, 1376m, 1304m, 1266m, 1206m, 1149w, 867m, 792w, 765s, 742s, 703w cm<sup>-1</sup>.



C1c, green solid, 94% yield, decomposition temperature: 236 °C.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 69.47, 46.22, 39.59, 34.02, 31.55, 19.33, 6.12, 5.88, 5.68,

4.17, 2.04, -2.61, -4.24, -6.39, -13.52, -28.93, -48.95.

<u>IR (KBr)</u>: 2959s, 2930m, 2868m, 2361s, 2342s, 1609m, 1575m, 1507s, 1458s, 1374s, 1299s,

1267s, 1245s, 1192s, 1059m, 865s, 785s, 735m cm<sup>-1</sup>.



C1d, dark blue solid, 96% yield, decomposition temperature: 290 °C.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 69.49, 53.02, 47.24, 45.42, 32.26, 19.67, 7.52, 6.16, 5.62,

5.42, 2.51, -0.58, -2.10, -8.17, -9.74, -17.41, -33.98, -36.73, -62.40.

<u>IR (KBr):</u> 2959s, 2927m, 2867m, 2359w, 2333w, 1609m, 1559m, 1497m, 1461m, 1382m, 1303m, 1189m, 1139w, 1109w, 1057w, 864m, 783m, 735w cm<sup>-1</sup>.



C1e, dark green solid, 96% yield, decomposition temperature: >320 °C.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 63.39, 56.47, 51.54, 49.42, 33.93, 21.38, 11.52, 10.71, 8.67,

7.99, 7.30, 6.11, 3.84, 1.72, 0.88, -9.20, -11.60, -23.81, -38.84, -65.42.

IR (KBr): 3547m, 3478s, 3414s, 3240w, 2958w, 2360w, 2341w, 1638m, 1617m, 1495w, 1436w,

1373w, 1305w, 1205w, 864w, 703m, 624m, 605m, 484w cm<sup>-1</sup>.



C1f, green solid, 94% yield, decomposition temperature: 220 °C.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 79.50, 44.28, 31.28, 27.29, 15.77, 15.00, 10.21, 4.02, 1.92, -1.58, -5.02, -6.13, -22.41, -27.33.

<u>IR (KBr)</u>: 3062w, 2958s, 2907m, 2867m, 1615m, 1597m, 1557m, 1500s, 1470m, 1420m, 1371m, 1297w, 1267w, 1203m, 1140w, 1094w, 862s, 799w, 768s, 709m, 629w cm<sup>-1</sup>.



C1g, dark green solid, 92% yield, decomposition temperature: 248 °C.

 $\underline{^{1}H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  82.81, 42.19, 34.99, 27.35, 13.57, 10.43, 7.28, 4.08, 3.46, -

5.84, -6.55, -6.70, -9.97, -26.40, -37.71, -39.22.

<u>IR (KBr)</u>: 3060w, 2962s, 2867m, 2360s, 2341s, 1605m, 1557m, 1498m, 1458m, 1371s, 1298s, 1244m, 1188m, 1057w, 934w, 863s, 809m, 794m, 779m, 731w cm<sup>-1</sup>.

## 3. Additional optimization of reaction conditions

### 3.1 Effect of additives and solvents



General procedure: In an argon-filled glovebox, a vial (10 mL) was charged with C1d (3.6 mg, 0.005 mmol, 1 mol%) and solvent (1 mL). The reaction mixture was stirred at room temperature for 1 min, then was added the conjugated diene 1a (65 mg, 0.5 mmol), PhSiH<sub>3</sub> (59.4 mg, 0.55 mmol) and additive (0.01 mmol, 2 mol%). After stirring for 2 h at room temperature, the vial was removed from the glovebox and the reaction mixture was concentrated by rotary evaporation. Iron species were removed by flash column chromatography with DCM as eluent. The raw product was detected by <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene as internal standard. The results were listed as following.

entry	[Fe]	reductant	solvent	conv. (%)	yield (%)	<b>3aa/4aa/5aa/6aa</b>
1	C1d	EtMgBr	THF	>95	99	99:1:0:0
2	C1d	MeMgBr	THF	>95	98	98:2:0:0
3	C1d	MeMgCl	THF	>95	97	98.5:1.5:0:0
4	C1d	PhMgBr	THF	>95	99	98:2:0:0
5	C1d	ZnEt <sub>2</sub>	THF	<5	$ND^a$	$\mathbf{NA}^b$
6	C1d	LiAlH <sub>4</sub>	THF	<5	ND	NA
7	C1d	NaHBEt <sub>3</sub>	THF	56	22	88:12:0:0
8	C1d	<sup>t</sup> BuOK	THF	75	38	91:9:0:0
9	C1d	LDA	THF	>95	20	93:7:0:0

Table S1	Effect of	of	additives	and	solvents

10	C1d	none	THF	<5	ND	NA
11	C1d	EtMgBr	Et <sub>2</sub> O	59	45	98:2:0:0
12	C1d	EtMgBr	dioxane	<5	ND	NA
13	C1d	EtMgBr	toluene	62	40	98:2:0:0
14	C1d	EtMgBr	hexane	67	57	98:2:0:0

<sup>*a*</sup> ND, not detected. <sup>*b*</sup> NA, not applicable.

#### 3.2 Effect of metal salts



**General procedure:** In an argon-filled glovebox, a vial (10 mL) was charged with metal salt (0.005 mmol, 1 mol%), **L1d** (2.9 mg, 0.005 mmol, 1 mol%) and THF (1 mL). The reaction mixture was stirred at 70 °C for 12 h, and then cooled to room temperature. The conjugated diene **1a** (65 mg, 0.5 mmol), PhSiH<sub>3</sub> (59.4 mg, 0.55 mmol, 1.1 equiv) and EtMgBr (10  $\mu$ L, 0.01 mmol, 2 mol%) was added and the mixture was stirred for 2 h at room temperature. The vial was removed from the glovebox and the reaction mixture was concentrated by rotary evaporation. Metal species were removed by flash column chromatography with DCM as eluent. The raw product was detected by <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene as internal standard. The results were listed as following.

entry	metal salt	conv. (%)	yield (%)	<b>3</b> aa/4aa/5aa/6aa
1	FeCl <sub>2</sub>	>95	98	98:2:0:0
2	Fe(acac) <sub>2</sub>	<5	$ND^{a}$	$\mathrm{NA}^b$

Table S2 Effect of metal salt	S
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3	CoCl <sub>2</sub>	<5	ND	NA
4	NiCl <sub>2</sub>	<5	ND	NA
5	MnCl <sub>2</sub>	<5	ND	NA
6	CuCl <sub>2</sub>	<5	ND	NA
7	ZnCl <sub>2</sub>	<5	ND	NA
8	none	<5	ND	NA

<sup>*a*</sup> ND, not detected. <sup>*b*</sup> NA, not applicable.

## 4. Typical procedures for hydrosilylation reactions

#### 4.1. Hydrosilylation of conjugated dienes



In an argon-filled glovebox, a vial (10 mL) was charged with complexes C1d (5.0 mg, 0.007 mmol), dry anhydrous THF (1 mL), conjugated dienes 1 (0.7 mmol) and silanes 2 (0.77 mmol, 1.1 equiv) successively. The vial was removed from the glovebox after EtMgBr (1 M in THF, 14  $\mu$ L, 0.014 mmol, 2.0 mol%) was added and the reaction mixture was stirred at room temperature for 2 h. When the reaction was finished, the mixture was concentrated by rotating evaporation. The residue was purified by column chromatography to afford the desired products **3**.

## 4.2 Hydrosilylation of terminal alkenes



In an argon-filled glovebox, a vial (10 mL) was charged with complexes C1b (4.6 mg, 0.007 mmol), dry anhydrous THF (1 mL), alkene 7 (0.7 mmol) and phenylsilane (0.77 mmol, 1.1 equiv) successivelly. The vial was removed from the glovebox after EtMgBr (1 M in THF, 14  $\mu$ L, 0.014 mmol, 2.0 mol%) was added and the reaction mixture was stirred at room temperature for 2 h. When the reaction was finished, the mixture was concentrated by rotating evaporation. The residue was purified by column chromatography to afford the desired product **8**.

## 5. Analytical data of hydrosilylation products

(E)-phenyl(4-phenylbut-3-en-1-yl)silane (3aa)<sup>12</sup>

Serial number: sw-2-76, 162.6 mg, 98% yield, >98:2 r.r., colorless oil,  $R_f = 0.52$  (PE)

<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.55 (m, 2H), 7.43 – 7.26 (m, 7H), 7.23 – 7.15 (m, 1H),
6.37 (d, J = 15.8 Hz, 1H), 6.25 (dt, J = 15.7, 6.5 Hz, 1H), 4.34 (t, J = 3.6 Hz, 2H),
2.41 – 2.32 (m, 2H), 1.18 – 1.10 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.7 (1C), 135.3 (2C), 132.2 (2C), 129.6 (1C), 129.2 (1C), 128.4 (2C), 128.0 (2C), 126.9 (1C), 126.0 (2C), 28.4 (1C), 9.9 (1C).

#### (E)-(4-phenylbut-3-en-1-yl)(o-tolyl)silane (3ab)



Serial number: sw-3-43, 167.0 mg, 95% yield, 94:6 r.r., colorless oil. *R*<sub>f</sub> = 0.59 (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.50 (m, 1H), 7.34 – 7.25 (m, 5H), 7.22 – 7.14 (m, 3H),

6.37 (d, *J* = 15.7 Hz, 1H), 6.25 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.37 (t, *J* = 3.7 Hz, 2H), 2.45 (s, 3H), 2.40 – 2.32 (m, 2H), 1.19 – 1.09 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.0 (1C), 137.7 (1C), 136.4 (1C), 132.2 (1C), 131.6 (1C), 130.1 (1C), 129.4 (1C), 129.2 (1C), 128.4 (2C), 126.8 (1C), 126.0 (2C), 125.2 (1C), 28.6 (1C), 22.6 (1C), 9.6 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>20</sub>Si]<sup>+</sup>:252.1334, found: 252.1328.

## (E)-(4-phenylbut-3-en-1-yl)(m-tolyl)silane (3ac)



Serial number: sw-3-44, 163.6 mg, 93% yield, >98:2 r.r., colorless oil.  $R_f = 0.50$  (PE).

 $^{1}$ <u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.35 (m, 2H), 7.33 – 7.24 (m, 5H), 7.23 – 7.15 (m, 2H),

- 6.37 (d, *J* = 15.7 Hz, 1H), 6.25 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.32 (t, *J* = 3.7 Hz, 2H), 2.42 2.29 (m, 5H), 1.18 1.05 (m, 2H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.8 (1C), 137.5 (1C), 136.0 (1C), 132.3 (3C), 130.5 (1C), 129.3 (1C), 128.5 (2C), 128.0 (1C), 126.9 (1C), 126.0 (2C), 28.5 (1C), 21.5 (1C), 10.0 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>20</sub>Si]<sup>+</sup>: 252.1334, found: 252.1328.

## (E)-(4-methoxyphenyl)(4-phenylbut-3-en-1-yl)silane (3ad)



Serial number: sw-2-144, 178.0 mg, 95% yield, >98:2 r.r., colorless oil. *R<sub>f</sub>*= 0.30 (PE). <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.45 (m, 2H), 7.32 – 7.25 (m, 4H), 7.23 – 7.14 (m, 1H), 6.95 – 6.86 (m, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.7, 6.5 Hz, 1H), 4.32 (t, *J* = 3.6 Hz, 2H), 3.81 (s, 3H), 2.40 – 2.31 (m, 2H), 1.15 – 1.07 (m, 2H). <u><sup>13</sup>C NMR</u> (101 MHz, CDCl<sub>3</sub>) δ 160.9 (1C), 137.7 (2C), 136.7 (1C), 132.3 (1C), 129.2 (1C), 128.4 (2C), 126.8 (1C), 126.0 (2C), 122.8 (1C), 113.9 (2C), 55.0 (1C), 28.4 (1C), 10.2 (1C).

HRMS (EI) calculated for [M, C<sub>17</sub>H<sub>20</sub>OSi]<sup>+</sup>: 268.1283, found: 268.1278.

## (E)-(4-(*tert*-butyl)phenyl)(4-phenylbut-3-en-1-yl)silane (3ae)



Serial number: sw-2-194, 204 mg, 99% yield, >98:2 r.r., colorless oil. *R*<sub>f</sub> = 0.48 (PE). <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) 7.56 – 7.49 (m, 2H), 7.43 – 7.37 (m, 2H), 7.33 – 7.25 (m, 4H), 7.21 – 7.15 (m, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 6.24 (dt, *J* = 15.7, 6.5 Hz, 1H), 4.33 (t, *J* = 3.6 Hz, 2H), 2.42 – 2.32 (m, 2H), 1.32 (s, 9H), 1.18 – 1.08 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.7 (1C), 137.7 (1C), 135.2 (2C), 132.3 (1C), 129.2 (1C), 128.6 (1C), 128.4 (2C), 126.8 (1C), 126.0 (2C), 125.0 (2C), 34.7 (1C), 31.2 (3C), 28.5 (1C), 10.0 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>20</sub>H<sub>26</sub>Si]<sup>+</sup>: 294.1804, found: 294.1796.

(E)-(4-fluorophenyl)(4-phenylbut-3-en-1-yl)silane (3af)



Serial number: sw-4-126, 169.4 mg, 94% yield, >98:2 r.r., colorless oil. *R<sub>f</sub>*= 0.78 (PE).
<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ7.59 – 7.51 (m, 2H), 7.33 – 7.26 (m, 4H), 7.23 – 7.16 (m, 1H), 7.10 – 7.02 (m, 2H), 6.36 (d, *J* = 17.2 Hz, 1H), 6.23 (dt, *J* = 15.7, 6.6 Hz, 1H), 4.33 (t, *J* = 3.6 Hz, 2H), 2.41 – 2.30 (m, 2H), 1.17 – 1.07 (m, 2H).
<u><sup>13</sup>C NMR</u> (101 MHz, CDCl<sub>3</sub>) δ 164.0 (*J* = 250.5 Hz, 1C), 162.8 (1C), 137.6 (1C), 137.2 (1C), 137.2 (1C), 137.2 (1C), 129.4 (1C), 128.5 (2C), 127.6 (1C), 126.9 (1C), 126.0 (2C), 115.4 (1C), 115.2 (1C), 28.3 (1C), 10.0 (1C).

 $\frac{19}{\text{F NMR}}$  (376 MHz, CDCl<sub>3</sub>)  $\delta$  -110.83.

<u>HRMS (EI)</u> calculated for [M, C<sub>16</sub>H<sub>17</sub>FSi]<sup>+</sup>: 256.1084, found: 256.1078.

(E)-(4-chlorophenyl)(4-phenylbut-3-en-1-yl)silane (3ag)



Serial number: sw-4-118, 185.2 mg, 97% yield, >98:2 r.r., colorless oil.  $R_f = 0.81$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.25

(m, 4H), 7.22 - 7.16 (m, 1H), 6.36 (d, J = 15.7 Hz, 1H), 6.21 (dt, J = 15.8, 6.6 Hz,

1H), 4.32 (t, *J* = 3.6 Hz, 2H), 2.41 – 2.27 (m, 2H), 1.18 – 1.06 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.5 (1C), 136.6 (2C), 136.0 (1C), 131.8 (1C), 130.5 (1C),

129.4 (1C), 128.5 (2C), 128.3 (2C), 126.9 (1C), 125.9 (2C), 28.3 (1C), 9.8 (1C). <u>HRMS (EI)</u> calculated for [M, C<sub>16</sub>H<sub>17</sub>ClSi]<sup>+</sup>: 272.0788, found: 272.0783.

## (E)-(4-methylbenzyl)(4-phenylbut-3-en-1-yl)silane (3ah)



Serial number: sw-2-146, 178.8 mg, 96% yield, >98:2 r.r., colorless oil. *R<sub>f</sub>*= 0.55 (PE). <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.27 (m, 4H), 7.23 – 7.14 (m, 1H), 7.09 – 6.94 (m, 4H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.83 (p, *J* = 3.6 Hz, 2H), 2.32 – 2.24 (m, 5H), 2.22 (t, *J* = 3.7 Hz, 2H), 0.91 – 0.80 (m, 2H). <u><sup>13</sup>C NMR</u> (101 MHz, CDCl<sub>3</sub>) δ 137.7 (1C), 136.4 (1C), 134.0 (1C), 132.2 (1C), 129.2 (2C), 129.1 (1C), 128.5 (2C), 128.0 (2C), 126.9 (1C), 126.0 (2C), 28.5 (1C), 20.9 (1C),

18.4 (1C), 8.7 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>18</sub>H<sub>22</sub>Si]<sup>+</sup>: 266.1491, found: 266.1486.

### (E)-octyl(4-phenylbut-3-en-1-yl)silane (3ai)

SiH<sub>2</sub>C<sub>8</sub>H<sub>17</sub>

Serial number: sw-4-179, 175.3 mg, 91% yield, 98:2 r.r., colorless oil.  $R_f = 0.72$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.27 (m, 4H), 7.22 – 7.16 (m, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.26 (dt, J = 15.7, 6.5 Hz, 1H), 3.70 (p, J = 3.6 Hz, 2H), 2.37 – 2.25 (m, 2H), 1.42 – 1.25 (m, 12H), 0.92 – 0.85 (m, 5H), 0.76 – 0.67 (m, 2H).
<sup>13</sup><u>C NMR</u> (101 MHz, CDCl<sub>3</sub>) δ 137.8 (1C), 132.6 (1C), 129.0 (1C), 128.5 (2C), 126.8 (1C),

126.0 (2C), 32.9 (1C), 31.9 (1C), 29.3 (1C), 29.2 (1C), 28.8 (1C), 25.4 (1C), 22.7 (1C), 14.1 (1C), 9.1 (1C), 9.0 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>18</sub>H<sub>30</sub>Si]<sup>+</sup>: 274.2117, found: 274.2112.

(E)-phenyl(4-(o-tolyl)but-3-en-1-yl)silane (3ba)

Serial number: sw-2-107, 170.4 mg, 96% yield, 98:2 r.r., colorless oil.  $R_f = 0.52$  (PE).

 $\frac{^{1}\text{H NMR}}{^{1}\text{H NMR}} (400 \text{ MHz, CDCl}_{3}) \delta 7.63 - 7.54 \text{ (m, 2H)}, 7.43 - 7.32 \text{ (m, 4H)}, 7.16 - 7.08 \text{ (m, 3H)}, 6.57 \text{ (d, } J = 15.6 \text{ Hz}, 1\text{H}), 6.11 \text{ (dt, } J = 15.6, 6.7 \text{ Hz}, 1\text{H}), 4.35 \text{ (t, } J = 3.7 \text{ Hz}, 2\text{H}), 2.44 - 2.35 \text{ (m, 2H)}, 2.31 \text{ (s, 3H)}, 1.19 - 1.11 \text{ (m, 2H)}.$ 

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.8 (1C), 135.3 (2C), 135.0 (1C), 133.5 (1C), 132.3 (1C), 130.1 (1C), 129.6 (1C), 128.0 (2C), 127.1 (1C), 126.8 (1C), 126.0 (1C), 125.5 (1C), 28.7 (1C), 19.8 (1C), 10.0 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>20</sub>Si]<sup>+</sup>: 252.1334, found: 252.1327.

(E)-phenyl(4-(3-(trifluoromethyl)phenyl)but-3-en-1-yl)silane (3ca)



Serial number: sw-2-138, 196.8 mg, 92% yield, 98:2 r.r., colorless oil.  $R_f = 0.48$  (PE).

<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.49 (m, 3H), 7.48 – 7.31 (m, 6H), 6.39 (d, J = 15.9 Hz,

1H), 6.30 (dt, *J* = 15.7, 6.2 Hz, 1H), 4.35 (t, *J* = 3.6 Hz, 2H), 2.39 (q, *J* = 7.1 Hz, 2H), 1.21 – 1.07 (m, 2H).

 $\frac{^{13}\text{C NMR}}{^{13}\text{C NMR}} (101 \text{ MHz, CDCl}_3) \delta 138.4 (1C), 135.2 (2C), 134.2 (1C), 132.1 (1C), 130.9 (q, J = 32.1 \text{ Hz}, 1C)., 129.7 (1C), 129.1 (d, J = 1.4 \text{ Hz}, 1C), 128.8 (1C), 128.1 (3C), 124.2 (q, J = 270 \text{ Hz}, 1C), 123.4 (q, J = 3.8 \text{ Hz}, 1C), 122.6 (q, J = 4.0 \text{ Hz}, 1C), 28.4 (1C), 9.7 (1C).$ 

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.73.

<u>HRMS (ESI)</u> calculated for [M-H, C<sub>17</sub>H<sub>16</sub>F<sub>3</sub>Si]<sup>-</sup>: 305.0979, found: 305.0965.

#### (E)-phenyl(4-(p-tolyl)but-3-en-1-yl)silane (3da)

Serial number: sw-2-108, 172.1 mg, 98% yield, >98:2 r.r., colorless oil. *R<sub>f</sub>*= 0.52 (PE).
<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.54 (m, 2H), 7.44 – 7.31 (m, 3H), 7.23 – 7.18 (m, 2H), 7.12 – 7.06 (m, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.19 (dt, *J* = 15.7, 6.6 Hz, 1H), 4.34 (t, *J* = 3.6 Hz, 2H), 2.39 – 2.33 (m, 2H), 2.32 (s, 3H), 1.17 – 1.07 (m, 2H).
<sup>13</sup><u>C NMR</u> (101 MHz, CDCl<sub>3</sub>) δ 136.6 (1C), 135.3 (2C), 134.9 (1C), 132.3 (1C), 131.2 (1C), 129.6 (1C), 129.2 (2C), 129.1 (1C), 128.1 (2C), 125.9 (2C), 28.4 (1C), 21.2 (1C),

10.0 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>20</sub>Si]<sup>+</sup>: 252.1334, found: 252.1327.

## (E)-(4-(4-methoxyphenyl)but-3-en-1-yl)(phenyl)silane (3ea)



Serial number: sw-2-86, 178.2 mg, 95% yield, >98:2 r.r., colorless oil.  $R_f = 0.53$  (PE/EA = 20:1, v/v).

 $\frac{^{1}\text{H NMR}}{^{1}\text{H NMR}} (400 \text{ MHz, CDCl}_{3}) \delta 7.64 - 7.52 \text{ (m, 2H)}, 7.43 - 7.32 \text{ (m, 3H)}, 7.26 - 7.22 \text{ (m, 2H)}, 6.88 - 6.76 \text{ (m, 2H)}, 6.31 \text{ (d, } J = 15.6, 1\text{H}), 6.10 \text{ (dt, } J = 15.7, 6.7 \text{ Hz}, 1\text{H}), 4.33 \text{ (t, } J = 3.6 \text{ Hz}, 2\text{H}), 3.79 \text{ (d, } J = 1.4 \text{ Hz}, 3\text{H}), 2.35 \text{ (dtd, } J = 7.8, 6.4, 1.4 \text{ Hz}, 2\text{H}), 1.18 - 1.05 \text{ (m, 2H)}.$ 

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.6 (1C), 135.2 (2C), 132.3 (1C), 130.5 (1C), 130.0 (1C), 129.6 (1C), 128.6 (1C), 128.0 (2C), 127.0 (2C), 113.9 (2C), 55.2 (1C), 28.3 (1C), 10.0 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>20</sub>OSi]<sup>+</sup>: 268.1283, found 268.1278.

(E)-N,N-dimethyl-4-(4-(phenylsilyl)but-1-en-1-yl)aniline (3fa)

\_SiH<sub>2</sub>Ph Me<sub>2</sub>N<sup>2</sup>

Serial number: sw-2-160, 193 mg, 98% yield, >98:2 r.r., yellow oil.  $R_f = 0.24$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.52 (m, 2H), 7.42 – 7.31 (m, 3H), 7.24 – 7.15 (m, 2H),

6.70 – 6.62 (m, 2H), 6.28 (d, J = 15.7 Hz, 1H), 6.04 (dt, J = 15.9, 6.7 Hz, 1H), 4.33

(t, J = 3.5 Hz, 2H), 2.92 (s, 6H), 2.39 – 2.28 (m, 2H), 1.16 – 1.07 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.7 (1C), 135.3 (2C), 132.5 (1C), 129.5 (1C), 129.0 (1C),

128.0 (3C), 126.8 (2C), 126.4 (1C), 112.6 (2C), 40.6 (2C), 28.4 (1C), 10.2 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>18</sub>H<sub>23</sub>NSi]<sup>+</sup>: 281.1600, found: 281.1592.

(E)-(4-(4-fluorophenyl)but-3-en-1-yl)(phenyl)silane (3ga)

F SiH<sub>2</sub>Ph

Serial number: sw-2-99, 177.2 mg, 99% yield, >98:2 r.r., colorless oil.  $R_f = 0.59$  (PE).

 $\frac{1}{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 – 7.53 (m, 2H), 7.46 – 7.30 (m, 3H), 7.29 – 7.21 (m, 2H), 7.03 – 6.88 (m, 2H), 6.32 (d, *J* = 15.7 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.34 (t, *J* = 3.6 Hz, 2H), 2.41 – 2.30 (m, 2H), 1.18 – 1.07 (m, 2H).

 $\frac{^{13}\text{C NMR}}{^{13}\text{C NMR}}$  (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.9 (J = 244.1 Hz, 1C), 135.2 (2C), 133.8 (1C), 132.2 (1C), 131.9 (1C), 129.6 (1C), 128.1 (1C), 128.0 (2C), 127.4 (1C), 127.3 (1C), 115.4 (1C), 115.2 (1C), 28.3 (1C), 9.9 (1C).

 $^{19}$ F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -115.71.

HRMS (EI) calculated for [M, C<sub>16</sub>H<sub>17</sub>FSi]<sup>+</sup>: 256.1084, found: 256.1078.

## (E)-(4-(4-chlorophenyl)but-3-en-1-yl)(phenyl)silane (3ha)

CI SiH<sub>2</sub>Ph

Serial number: sw-2-126, 186.9 mg, 98% yield, >98:2 r.r., colorless oil. *R<sub>f</sub>*= 0.63 (PE). <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.52 (m, 2H), 7.45 – 7.31 (m, 3H), 7.25 – 7.18 (m, 4H), 6.32 (d, *J* = 15.8, 1H), 6.21 (dt, *J* = 15.8, 6.4 Hz, 1H), 4.34 (t, *J* = 3.6 Hz, 2H), 2.44

- 2.29 (m, 2H), 1.18 - 1.08 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.2 (1C), 135.2 (2C), 132.9 (1C), 132.4(1C), 132.1 (1C), 129.6 (1C), 128.6 (2C), 128.1 (1C), 128.0 (2C), 127.2 (2C), 28.4 (1C), 9.8 (1C).
 <u>HRMS (EI)</u> calculated for [M, C<sub>16</sub>H<sub>17</sub>ClSi]<sup>+</sup>: 272.0788, found: 272.0783.

## (E)-(4-(naphthalen-2-yl)but-3-en-1-yl)(phenyl)silane (3ia)

SiH<sub>2</sub>Ph

Serial number: sw-2-148, 199 mg, 99% yield, 98:2 r.r., colorless oil.  $R_f = 0.50$  (PE).

- <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.81 7.71 (m, 3H), 7.66 7.57 (m, 3H), 7.53 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.47 7.32 (m, 5H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.37 (dt, *J* = 15.7, 6.6 Hz, 1H), 4.37 (t, *J* = 3.6 Hz, 2H), 2.49 2.35 (m, 2H), 1.23 1.11 (m, 2H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.3 (2C), 135.1 (1C), 133.7 (1C), 132.7 (1C), 132.6 (1C), 132.2 (1C), 129.6 (1C), 129.4 (1C), 128.0 (3C), 127.8 (1C), 127.6 (1C), 126.1 (1C), 125.4 (2C), 123.6 (1C), 28.5 (1C), 9.9 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>20</sub>H<sub>20</sub>Si]<sup>+</sup>: 288.1334, found: 288.1329.

## (E)-(4-(benzo[d][1,3]dioxol-5-yl)but-3-en-1-yl)(phenyl)silane (3ja)

O SiH<sub>2</sub>Ph

Serial number: sw-3-8, 196.2 mg, 99% yield, 98:2 r.r., colorless oil.  $R_f = 0.53$  (PE/EA = 10:1, v/v).

- <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.63 7.52 (m, 2H), 7.45 7.31 (m, 3H), 6.88 6.82 (m, 1H),
  6.76 6.68 (m, 2H), 6.28 (d, J = 15.7, 1H), 6.07 (dt, J = 15.8, 6.8 Hz, 1H), 5.93 (s, 2H), 4.38 4.29 (m, 2H), 2.39 2.27 (m, 2H), 1.17 1.06 (m, 2H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.9 (1C), 146.6 (1C), 135.2 (2C), 132.2 (2C), 130.4 (1C), 129.6 (1C), 128.8 (1C), 128.0 (2C), 120.3 (1C), 108.2 (1C), 105.4 (1C), 100.9 (1C), 28.3 (1C), 10.0 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>Si]<sup>+</sup>: 282.1076, found: 282.1069.

(E)-(4-(furan-2-yl)but-3-en-1-yl)(phenyl)silane (3ka)

SiH<sub>2</sub>Ph

Serial number: sw-2-161, 148 mg, 93% yield, 97:3 r.r., colorless oil.  $R_f = 0.73$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.52 (m, 2H), 7.43 – 7.27 (m, 4H), 6.35 – 6.30 (m, 1H),
6.22 – 6.17 (m, 2H), 6.14 – 6.09 (m, 1H), 4.33 (t, J = 3.7 Hz, 2H), 2.39 – 2.27 (m, 2H), 1.17 – 1.05 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.2 (1C), 141.3 (1C), 135.2 (2C), 132.2 (1C), 131.2 (1C), 129.6 (1C), 128.0 (2C), 118.0 (1C), 111.1 (1C), 106.2 (1C), 28.1 (1C), 9.7 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>14</sub>H<sub>16</sub>OSi]<sup>+</sup>: 228.0970, found 228.0966.

#### (*E*)-phenyl(4-phenylpent-3-en-1-yl)silane (3la)



Serial number: sw-2-202, 167.0 mg, 95% yield, >98:2 r.r., colorless oil.  $R_f = 0.61$  (PE).

- <sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.62 7.55 (m, 2H), 7.43 7.27 (m, 7H), 7.24 7.18 (m, 1H),
   5.83 5.74 (m, 1H), 4.34 (t, J = 3.6, 2H), 2.42 2.30 (m, 2H), 1.98 (s, 3H), 1.18 1.07 (m, 2H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.8 (1C), 135.2 (2C), 134.3 (1C), 132.4 (1C), 129.9 (1C),
  129.6 (1C), 128.1 (2C), 128.0 (2C), 126.5 (1C), 125.6 (2C), 24.1 (1C), 15.8 (1C),
  10.3 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>20</sub>Si]<sup>+</sup>: 252.1334, found: 252.1329.

#### (4,4-diphenylbut-3-en-1-yl)(phenyl)silane (3ma)

Ph SiH<sub>2</sub>Ph

Serial number: sw-3-190, 191.7 mg, 87% yield, >98:2 r.r., colorless oil. Complex C1b was used as the catalyst.  $R_f$ = 0.29 (PE).

 $\frac{^{1}\text{H NMR}}{^{1}\text{H NMR}}$  (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 – 7.46 (m, 2H), 7.40 – 7.11 (m, 13H), 6.08 (t, *J* = 7.4 Hz, 1H), 4.28 (t, *J* = 3.7 Hz, 2H), 2.29 (q, *J* = 7.7 Hz, 2H), 1.15 – 1.03 (m, 2H).

 $\frac{13}{C}$  NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.7 (1C), 141.1 (1C), 140.0 (1C), 135.2 (2C), 132.3 (1C),

131.3 (1C), 129.9 (2C), 129.6 (1C), 128.2 (2C), 128.1 (2C), 128.0 (2C), 127.3 (2C), 126.9 (1C), 126.9 (1C), 25.2 (1C), 10.7 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>22</sub>H<sub>22</sub>Si]<sup>+</sup>: 314.1491, found: 314.1481.

(E)-(3-methyl-4-phenylbut-3-en-1-yl)(phenyl)silane (3na)<sup>13</sup>

SiH<sub>2</sub>Ph Me

Serial number: sw-2-162, 176.2 mg, 99% yield, >98:2 r.r., colorless oil.  $R_f = 0.69$  (PE).

<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.55 (m, 2H), 7.43 – 7.25 (m, 5H), 7.24 – 7.13 (m, 3H),
6.29 (s, 1H), 4.34 (t, J = 3.6 Hz, 2H), 2.36 – 2.26 (m, 2H), 1.84 (s, 3H), 1.24 – 1.12 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.2 (1C), 138.5 (1C), 135.3 (2C), 132.4 (1C), 129.6 (1C), 128.8 (2C), 128.0 (4C), 125.9 (1C), 124.4 (1C), 35.8 (1C), 17.5 (1C), 8.7 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>20</sub>Si]<sup>+</sup>: 252.1334, found: 252.1328.

### (Z)-phenyl(3-phenylpent-3-en-1-yl)silane (3oa)

Me SiH<sub>2</sub>Ph

Serial number: llj-1-106, 172.9 mg, 98% yield, 98:2 r.r., colorless oil. Complex C1b (2 mol%) was used as the catalyst.  $R_f = 0.59$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) 7.56 – 7.48 (m, 2H), 7.43 – 7.28 (m, 5H), 7.22 (d, *J* = 7.3 Hz, 1H),
7.15 – 7.08 (m, 2H), 5.59 – 5.51 (m, 1H), 4.26 (t, *J* = 3.7 Hz, 2H), 2.53 – 2.43 (m, 2H), 1.54 (d, *J* = 6.9 Hz, 3H), 1.04 – 0.90 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.8 (1C), 140.6 (1C), 135.2 (1C), 132.4 (1C), 129.5 (1C), 128.6 (1C), 128.0 (1C), 127.9 (1C), 126.4 (1C), 120.6 (1C), 34.4 (1C), 14.6 (1C), 8.9

(1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>20</sub>Si]<sup>+</sup>: 252.1334, found: 252.1328.

## (E)-non-3-en-1-yl(phenyl)silane (3pa)<sup>13</sup>

C<sub>5</sub>H<sub>11</sub> SiH<sub>2</sub>Ph

Serial number: sw-4-79A, 156.7 mg, 96% yield, 1,2/1,4 > 98:2 (the 1,2/1,4 refers to the ratio of 1,2- and 1,4-*anti*-Markovnikov hydrosilylation product), colorless oil. Complex **C1e** was used as the catalyst; EtMgBr (4 mol%) was added at -30 °C, and then the mixture was stirred at 0 °C for 10 h.  $R_f$ = 0.85 (PE).

- <sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.60 7.52 (m, 2H), 7.43 7.31 (m, 3H), 5.50 5.34 (m, 2H),
  4.29 (t, J = 3.7 Hz, 2H ), 2.15 (td, J = 7.6, 5.3 Hz, 2H), 1.96 (q, J = 6.6 Hz, 2H), 1.37 1.20 (m, 6H), 1.07 0.97 (m, 2H), 0.88 (t, J = 6.8 Hz, 3H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.3 (2C), 132.6 (1C), 131.5 (1C), 130.1 (1C), 129.5 (1C), 128.0 (2C), 32.4 (1C), 31.4 (1C), 29.3 (1C), 27.9 (1C), 22.6 (1C), 14.1 (1C), 10.1 (1C).

## (*E*)-(4-cyclohexylbut-3-en-1-yl)(phenyl)silane (3qa)<sup>13</sup>

SiH<sub>2</sub>Ph

Serial number: sw-4-79B, 164.0 mg, 96% yield, 1,2/1,4 > 98:2 (the 1,2/1,4 refers to the ratio of 1,2- and 1,4-*anti*-Markovnikov hydrosilylation product), colorless oil. Complex **C1e** was used as the catalyst; EtMgBr (4 mol%) was added at -30 °C, and then the mixture was stirred at 0 °C for 10 h.  $R_f = 0.86$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.51 (m, 2H), 7.42 – 7.30 (m, 3H), 5.46 – 5.29 (m, 2H),
4.28 (t, J = 3.7 Hz, 2H), 2.18 – 2.09 (m, 2H), 1.94 – 1.81 (m, 1H), 1.74 – 1.58 (m, 5H), 1.29 – 0.98 (m, 7H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.0 (1C), 135.3 (2C), 132.6 (1C), 129.5 (1C), 128.9 (1C), 128.0 (2C), 40.6 (1C), 33.2 (2C), 28.0 (1C), 26.3 (1C), 26.1 (2C), 10.1 (1C).

## (4-(*tert*-butyl)phenyl)(3-methylbut-3-en-1-yl)silane (3re)



Serial number: sw-3-167, 154.1 mg, 95% yield, 1,2/1,4 = 94:6 (the 1,2/1,4 refers to the ratio of 1,2- and 1,4-*anti*-Markovnikov hydrosilylation product), colorless oil. Silane **2e** was used instead of **2a**.  $R_f = 0.56$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ7.54 – 7.49 (m, 2H), 7.42 – 7.37 (m, 2H), 4.75 – 4.68 (m, 2H),
4.29 (t, J = 3.7 Hz, 2H), 2.20 – 2.10 (m, 2H), 1.73 (s, 3H), 1.32 (s, 9H), 1.13 – 1.02 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.7 (1C), 147.4 (1C), 135.2 (2C), 128.8 (1C), 125.0 (2C), 109.1 (1C), 34.7 (1C), 33.0 (1C), 31.2 (3C), 22.2 (1C), 8.3 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>15</sub>H<sub>24</sub>Si]<sup>+</sup>: 232.1647, found: 232.1641.

(7-methyl-3-methyleneoct-6-en-1-yl)(phenyl)silane (3sa)<sup>13</sup>



Serial number: sw-4-79C, 153.7 mg, 90% yield, 1,2/1,4 = 93:7 (the 1,2/1,4 refers to the ratio of 1,2- and 1,4-*anti*-Markovnikov hydrosilylation product), colorless oil. Complex **C1d** was used as the catalyst; EtMgBr (4 mol%) was added at -30 °C, and then the mixture was stirred at 0 °C for 10 h.  $R_f$ = 0.61 (PE).

- <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.61 7.54 (m, 2H), 7.43 7.32 (m, 3H), 5.14 5.04 (m, 1H),
  4.77 (s, 1H), 4.73 (s, 1H), 4.30 (t, *J* = 3.6 Hz, 2H), 2.18 2.00 (m, 6H), 1.68 (s, 3H),
  1.60 (s, 3H), 1.14 1.03 (m, 2H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.0 (1C), 135.2 (2C), 132.4 (1C), 131.6 (1C), 129.6 (1C), 128.0 (2C), 124.1 (1C), 108.3 (1C), 35.8 (1C), 31.4 (1C), 26.4 (1C), 25.7 (1C), 17.7 (1C), 8.3 (1C).

(3-cyclohexylidenepropyl)(phenyl)silane (3ta)

SiH<sub>2</sub>Ph

Serial number: sw-3-147, 155.7 mg, 97% yield, 1,2/1,4 = 92:8 (the 1,2/1,4 refers to the ratio of 1,2- and 1,4-*anti*-Markovnikov hydrosilylation product), colorless oil.  $R_f = 0.64$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.52 (m, 2H), 7.42 – 7.30 (m, 3H), 5.10 (t, J = 7.1 Hz, 1H), 4.28 (t, J = 3.7 Hz, 2H), 2.15 (q, J = 7.5 Hz, 2H), 2.11 – 1.99 (m, 4H), 1.58 – 1.41 (m, 6H), 1.06 – 0.94 (m, 2H).

<u>1<sup>3</sup>C NMR</u> (101 MHz, CDCl<sub>3</sub>) δ 139.2 (1C), 135.2 (2C), 132.7 (1C) 129.5 (1C), 127.9 (2C),
122.9 (1C), 37.1 (1C), 28.7 (1C), 28.6 (1C), 27.7 (1C), 27.0 (1C), 22.5 (1C), 10.9 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>15</sub>H<sub>22</sub>Si]<sup>+</sup>: 230.1491, found: 230.1488.

## (E)-(4,8-dimethylnona-3,7-dien-1-yl)(phenyl)silane (3ua)

Me Me SiH<sub>2</sub>Ph

Serial number: sw-3-75, 172.3 mg, 95% yield, 1,2/1,4 = 97:3 (the 1,2/1,4 refers to the ratio of 1,2- and 1,4-*anti*-Markovnikov hydrosilylation product), colorless oil.  $R_f = 0.81$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ7.60 – 7.53 (m, 2H), 7.42 – 7.31 (m, 3H), 5.16 (tq, J = 7.1, 1.4 Hz, 1H), 5.10 (dtd, J = 6.7, 5.2, 4.1, 2.6 Hz, 1H), 4.29 (t, J = 3.7 Hz, 2H), 2.15 (q, J = 7.5 Hz, 2H), 2.09 – 2.00 (m, 2H), 1.99 – 1.92 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.56 (s, 3H), 1.05 – 0.96 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.2 (2C), 134.7 (1C), 132.7 (1C), 131.3 (1C), 129.5 (1C), 128.0 (2C), 126.1 (1C), 124.4 (1C), 39.7 (1C), 26.7 (1C), 25.7 (1C), 23.2 (1C), 17.7 (1C), 16.0 (1C), 10.5 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>26</sub>Si]<sup>+</sup>: 258.1804, found: 258.1793.

### ((3E,5E)-4-methyl-6-(2,6,6-trimethylcyclohex-1-en-1-yl)hexa-3,5-dien-1-

#### yl)(phenyl)silane (3va)



Serial number: llj-1-19, 182.0 mg, 80% yield, 1,2/1,4 > 98:2 (the 1,2/1,4 refers to the ratio of 1,2- and 1,4-*anti*-Markovnikov hydrosilylation product), colorless oil.  $R_f = 0.44$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ7.60 – 7.53 (m, 2H), 7.43 – 7.31 (m, 3H), 5.97 (s, 2H), 5.43 (td,

*J* = 7.3, 1.4 Hz, 1H), 4.31 (t, *J* = 3.7 Hz, 2H), 2.30 (q, *J* = 7.6 Hz, 2H), 1.99 (t, *J* = 6.3 Hz, 2H), 1.74 (s, 3H), 1.68 (s, 3H), 1.64 – 1.57 (m, 2H), 1.48 – 1.43 (m, 2H), 1.11 – 1.02 (m, 2H), 1.00 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.9 (1C), 137.8 (1C), 135.3 (2C), 133.6 (1C), 132.6 (1C), 132.4 (1C), 129.6 (1C), 128.3 (1C), 128.0 (2C), 124.5 (1C), 39.6 (1C), 34.2 (1C), 32.9 (1C), 28.9 (2C), 23.6 (1C), 21.7 (1C), 19.3 (1C), 12.3 (1C), 10.4 (1C).
 <u>HRMS (EI)</u> calculated for [M, C<sub>22</sub>H<sub>32</sub>Si]<sup>+</sup>: 324.2273, found: 324.2266.

## (S)-phenyl(2-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)ethyl)silane (3wa)<sup>13</sup>



Serial number: sw-3-10, 170.0 mg, 95% yield, 1,2/1,4 > 98:2 (the 1,2/1,4 refers to the ratio of 1,2- and 1,4-*anti*-Markovnikov hydrosilylation product), colorless oil.  $R_f = 0.78$  (PE).

- <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.61 7.51 (m, 2H), 7.43 7.30 (m, 3H), 5.43 (s, 1H), 4.74 4.65 (m, 2H), 4.28 (t, J = 3.6 Hz, 2H), 2.13 1.75 (m, 8H), 1.72 (s, 3H), 1.47 1.33 (m, 1H), 1.12 1.01 (m, 2H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.3 (1C), 138.6 (1C), 135.2 (2C), 132.6 (1C), 129.5 (1C), 128.0 (2C), 120.0 (1C), 108.4 (1C), 41.2 (1C), 32.7 (1C), 30.7 (1C), 28.6 (1C), 27.8 (1C), 20.8 (1C), 8.2 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>17</sub>H<sub>24</sub>Si]<sup>+</sup>: 256.1647, found: 256.1653.

## (2-(cyclohept-1-en-1-yl)ethyl)(phenyl)silane (3xa)<sup>13</sup>

SiH<sub>2</sub>Ph

Serial number: sw-4-60, 156.1 mg, 97% yield, 1,2/1,4 = 96:4 (the 1,2/1,4 refers to the ratio of 1,2- and 1,4-*anti*-Markovnikov hydrosilylation product), colorless oil. *R<sub>f</sub>*= 0.68 (PE).
<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.50 (m, 2H), 7.44 – 7.31 (m, 3H), 5.55 (t, *J* = 6.5 Hz, 1H), 4.28 (t, *J* = 3.7 Hz, 2H), 2.14 – 2.01 (m, 6H), 1.71 (p, *J* = 5.9 Hz, 2H), 1.50 – 1.40 (m, 4H), 1.09 – 0.98 (m, 2H).
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.9 (1C), 135.2 (2C), 132.7 (1C), 129.5 (1C), 127.9 (2C),

<u>C NMR</u> (101 MHz, CDCl<sub>3</sub>) 8 145.9 (1C), 155.2 (2C), 152.7 (1C), 129.5 (1C), 127.9 (2C), 125.1 (1C), 35.2 (1C), 32.6 (2C), 28.2 (1C), 27.3 (1C), 26.9 (1C), 8.6 (1C).

## phenethyl(phenyl)silane (8aa)<sup>14</sup>



Serial number: lmp-1-109, 147 mg, 99% yield, colorless oil.  $R_f = 0.64$  (PE).

 $^{1}$ <u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 – 7.52 (m, 2H), 7.43 – 7.31 (m, 3H), 7.30 – 7.23 (m, 2H),

7.22 – 7.13 (m, 3H), 4.32 (t, *J* = 3.6 Hz, 2H), 2.80 – 2.72 (m, 2H), 1.33 – 1.25 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.9 (1C), 135.2 (2C), 132.1 (1C), 129.6 (1C), 128.3 (2C), 128.0 (2C), 127.9 (2C), 125.8 (1C), 31.1 (1C), 12.1 (1C).

## (3-methylphenethyl)(phenyl)silane (8ba)<sup>3</sup>

```
Me_____SiH<sub>2</sub>Ph
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Serial number: sw-3-183, 150.0 mg, 95% yield, colorless oil.  $R_f = 0.32$  (PE).

 $^{1}$ <u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 – 7.52 (m, 2H), 7.44 – 7.31 (m, 3H), 7.21 – 7.12 (m, 1H),

7.02 – 6.95 (m, 3H), 4.31 (t, J = 3.6 Hz, 2H), 2.77 – 2.68 (m, 2H), 2.31 (s, 3H), 1.33

– 1.24 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.9 (1C), 137.9 (1C), 135.2 (2C), 132.2 (1C), 129.6 (1C), 128.7 (1C), 128.2 (1C), 128.0 (2C), 126.5 (1C), 124.9 (1C), 31.0 (1C), 21.4 (1C), 12.1 (1C).

## (4-fluorophenethyl)(phenyl)silane (8ca)<sup>14</sup>

F SiH<sub>2</sub>Ph

Serial number: lmp-2-99, 159 mg, 99% yield, colorless oil.  $R_f = 0.75$  (PE)

<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.51 (m, 2H), 7.44 – 7.31 (m, 3H), 7.16 – 7.06 (m, 2H),
7.00 – 6.89 (m, 2H), 4.30 (t, J = 3.6 Hz, 2H), 2.78 – 2.68 (m, 2H), 1.32 – 1.22 (m, 2H).

 $\frac{^{13}\text{C NMR}}{^{12}\text{C NMR}} (101 \text{ MHz, CDCl}_3) \delta 161.2 (J = 242.4 \text{ Hz, 1C}), 139.5 (1C), 135.2 (2C), 132.0 (1C), 129.7 (1C), 129.2 (2C), 128.0 (2C), 115.1 (1C), 114.9 (1C), 30.3 (1C), 12.3 (1C).$ 

#### (4-methoxyphenethyl)(phenyl)silane(8da)<sup>14</sup>

MeO SiH<sub>2</sub>Ph

Serial number: lmp-4-87, 163.0 mg, 96% yield, colorless oil. *R<sub>f</sub>*= 0.61 (PE/EA = 20:1, *ν/ν*). <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.54 (m, 2H), 7.41 – 7.33 (m, 3H), 7.13 – 7.08 (m, 2H), 6.84 – 6.79 (m, 2H), 4.30 (t, *J* = 3.6 Hz, 2H), 3.79 (s, 3H), 2.75 – 2.68 (m, 2H), 1.31 – 1.23 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.7 (1C), 136.0 (1C), 135.2 (2C), 132.2 (1C), 129.6 (1C),
 128.8 (2C), 128.0 (2C), 113.7 (2C), 55.2 (1C), 30.2 (1C), 12.3 (1C).

## (4-(*tert*-butyl)phenethyl)(phenyl)silane (8ea)<sup>15</sup>

SiH<sub>2</sub>Ph

Serial number: sw-3-175, 178.6 mg, 95% yield, colorless oil.  $R_f = 0.45$  (PE).
<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.51 (m, 2H), 7.42 – 7.32 (m, 3H), 7.32 – 7.27 (m, 2H),
7.15 – 7.09 (m, 2H), 4.32 (t, J = 3.6 Hz, 2H), 2.78 – 2.69 (m, 2H), 1.33 – 1.26 (m, 11H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.6 (1C), 141.0 (1C), 135.3 (2C), 132.3 (1C), 129.7 (1C), 128.1 (2C), 127.6 (2C), 125.3 (2C), 34.4 (1C), 31.5 (3C), 30.6 (1C), 12.0 (1C).

#### (2-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)silane (8fa)

SiH<sub>2</sub>Ph

Serial number: sw-3-176, 194.2 mg, 96% yield, colorless oil.  $R_f = 0.50$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ7.62 – 7.54 (m, 4H), 7.53 – 7.47 (m, 2H), 7.46 – 7.29 (m, 6H),
7.28 – 7.23 (m, 2H), 4.35 (t, J = 3.6 Hz, 2H), 2.87 – 2.74 (m, 2H), 1.39 – 1.29(m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.2 (1C), 141.2 (1C), 138.9 (1C), 135.3 (2C), 132.2 (1C),
 129.7 (1C), 128.8 (2C), 128.4 (2C), 128.1 (2C), 127.2 (2C), 127.1 (3C), 30.8 (1C),
 12.2 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>20</sub>H<sub>20</sub>Si]<sup>+</sup>: 288.1334, found: 288.1329.

#### phenyl(6-phenylhexyl)silane (8ga)

Ph SiH<sub>2</sub>Ph

Serial number: lmp-4-68, 176.3 mg, 94% yield, colorless oil.  $R_f = 0.41$  (PE).

<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.53 (m, 2H), 7.42 – 7.32 (m, 3H), 7.30 – 7.24 (m, 2H),
 7.17 (m, 3H), 4.28 (t, J = 3.7 Hz, 2H), 2.63 – 2.54 (m, 2H), 1.65 – 1.55 (m, 2H), 1.51 – 1.28 (m, 6H), 0.97 – 0.88 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.8 (1C), 135.2 (2C), 132.7 (1C), 129.5 (1C), 128.4 (2C),
 128.2 (2C), 127.9 (2C), 125.5 (1C), 35.9 (1C), 32.6 (1C), 31.3 (1C), 28.9 (1C),
 25.0 (1C), 10.0 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>18</sub>H<sub>24</sub>Si]<sup>+</sup>: 268.1647, found: 268.1642.

#### (6-chlorohexyl)(phenyl)silane (8ha)<sup>3</sup>

CI SiH<sub>2</sub>Ph

Serial number: lmp-4-6, 133.3 mg, 84% yield, colorless oil.  $R_f = 0.72$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.52 (m, 2H), 7.43 – 7.33 (m, 3H), 4.29 (t, J = 3.7 Hz, 2H), 3.52 (t, J = 6.7 Hz, 2H), 1.75 (p, J = 6.7 Hz, 2H), 1.53 – 1.34 (m, 6H), 0.98 – 0.91 (m, 2H).
 <sup>13</sup><u>C NMR</u> (101 MHz, CDCl<sub>3</sub>) δ 135.2 (2C), 132.6 (1C), 129.5 (1C), 127.9 (2C), 45.1 (1C),

32.5 (1C), 32.0 (1C), 26.5 (1C), 24.9 (1C), 9.9 (1C).

#### 1-(6-(phenylsilyl)hexyl)piperidine (8ia)

SiH<sub>2</sub>Ph

Serial number: lmp-4-1, 162.0 mg, 84% yield, colorless oil.  $R_f = 0.15$  (PE/EA = 1:1, v/v).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.53 (m, 2H), 7.41 – 7.31 (m, 3H), 4.27 (t, J = 3.7 Hz, 2H), 2.34 (br, 4H), 2.28 – 2.21 (m, 2H), 1.58 (p, J = 5.7 Hz, 4H), 1.50 – 1.34 (m, 8H), 1.30 – 1.23 (m, 2H), 0.96 – 0.89 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.1 (2C), 132.6 (1C), 129.4 (1C), 127.9 (2C), 59.6 (1C),
 54.6 (2C), 32.7 (1C), 27.3 (1C), 26.8 (1C), 26.0 (2C), 24.9 (1C), 24.5 (1C), 9.9 (1C).

<u>HRMS (EI)</u> calcd for [M, C<sub>17</sub>H<sub>29</sub>NSi]<sup>+</sup>: 275.2069, found: 275.2063.

#### 4-(6-(phenylsilyl)hexyl)morpholine (8ja)<sup>3</sup>

Serial number: lmp-4-22, 169 mg, 87% yield, yellow oil.  $R_f = 0.33$  (PE/EA = 1:1, v/v)

 $^{1}$ <u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 – 7.50 (m, 2H), 7.42 – 7.32 (m, 3H), 4.28 (t, *J* = 3.7 Hz,

2H), 3.71 (t, *J* = 4.7 Hz, 4H), 2.48 – 2.26 (m, 6H), 1.50 – 1.24 (m, 8H), 0.99 – 0.87

(m, 2H).

# <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.2 (2C), 132.7 (1C), 129.5 (1C), 127.9 (2C), 67.0 (2C), 59.2 (1C), 53.8 (2C), 32.7 (1C), 27.1 (1C), 26.4 (1C), 25.0 (1C), 9.9 (1C).

## N,N-dimethyl-3-(phenylsilyl)propan-1-amine (8ka)<sup>16</sup>

 $Me_2N$  SiH<sub>2</sub>Ph

Serial number: sw-4-80, 108.1 mg, 80% yield, colorless oil. The reaction mixture was directly desolvated by vacuum under reduced pressure, and the resulting crude product was distilled under reduced pressure using a high vacuum pump, and the fraction was collected as the pure product.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.53 (m, 2H), 7.42 – 7.31 (m, 3H), 4.31 (t, J = 3.7 Hz, 2H), 2.31 – 2.25 (m, 2H), 2.19 (s, 6H), 1.67 – 1.57 (m, 2H), 0.98 – 0.91 (m, 2H).
 <sup>13</sup><u>C NMR</u> (101 MHz, CDCl<sub>3</sub>) δ 135.1 (2C), 133.0 (1C), 129.4 (1C), 127.9 (2C), 62.2 (1C), 45.4 (2C), 23.2 (1C), 7.8 (1C).

#### (2-phenoxyethyl)(phenyl)silane (8la)



Serial number: sw-4-55, 153.2 mg, 96% yield, colorless oil.  $R_f = 0.61$  (PE/EA = 20:1, v/v).

<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.54 (m, 2H), 7.44 – 7.32 (m, 3H), 7.29 – 7.20 (m, 2H), 6.97 – 6.90 (m, 1H), 6.89 – 6.82 (m, 2H), 4.40 (t, *J* = 3.6 Hz, 2H), 4.13 (t, *J* = 7.7 Hz, 2H), 1.59 – 1.49 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.6 (1C), 135.3 (2C), 131.4 (1C), 129.8 (1C), 129.4 (2C),
 128.1 (2C), 120.7 (1C), 114.6 (2C), 65.1 (1C), 11.7 (1C).

<u>HRMS (EI)</u> calcd for [M, C<sub>14</sub>H<sub>16</sub>OSi]<sup>+</sup>: 228.0970, found: 228.0966.

(2-butoxyethyl)(phenyl)silane (8ma)

Me O SiH<sub>2</sub>Ph

Serial number: lmp-3-144, 137.0 mg, 94% yield, colorless oil. Amount of EtMgBr, 5 mol%.  $R_f$  = 0.63 (PE/EA = 20:1, v/v).

<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.56 (m, 2H), 7.42 – 7.32 (m, 3H), 4.31 (t, J = 3.6 Hz, 2H), 3.55 (t, J = 7.8 Hz, 2H), 3.39 (t, J = 6.6 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.41 – 1.31 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.2 (2C), 132.0 (1C), 129.6 (1C), 128.0 (2C), 70.3 (1C), 67.7 (1C), 31.8 (1C), 19.4 (1C), 13.9 (1C), 12.1 (1C).

<u>HRMS (EI)</u> calcd for [M, C<sub>12</sub>H<sub>20</sub>OSi]<sup>+</sup>: 208.1283, found: 208.1288.

#### trimethyl(2-(phenylsilyl)ethyl)silane (8na)<sup>17</sup>

TMS SiH<sub>2</sub>Ph

Serial number: sw-4-52, 136.8 mg, 94% yield, colorless oil. Complex C1d was used as the catalyst.  $R_f = 0.76$  (PE).

<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.55 (m, 2H), 7.43 – 7.32 (m, 3H), 4.31 (t, J = 3.6 Hz, 2H), 0.91 – 0.82 (m, 2H), 0.62 – 0.53 (m, 2H), -0.02 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.2 (2C), 132.9 (1C), 129.5 (1C), 127.9 (2C), 10.6 (1C),
 2.7 (1C), -2.1 (3C).

#### dimethyl(phenyl)(2-(phenylsilyl)ethyl)silane (80a)



Serial number: sw-3-180, 176.0 mg, 93% yield, colorless oil.  $R_f = 0.45$  (PE).

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 – 7.46 (m, 4H), 7.42 – 7.30 (m, 6H), 4.27 (t, *J* = 3.3 Hz, 2H), 0.89 – 0.77 (m, 4H), 0.26 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.0 (1C), 135.3 (2C), 133.7 (2C), 132.7 (1C), 129.6 (1C), 128.9 (1C), 128.0 (2C), 127.8 (2C), 9.8 (1C), 2.8 (1C), -3.5 (2C).

<u>HRMS (ESI)</u> calculated for [M-H, C<sub>16</sub>H<sub>21</sub>Si<sub>2</sub>]<sup>-</sup>: 269.1187, found: 269.1176.

#### 6. Gram-scale experiment and product transformations

#### 6.1 Gram-scale experiment



In an argon-filled glovebox, a vial (125 mL) was charged with complexes C1d (14.2 mg, 0.02 mmol), dry anhydrous THF (20 mL), conjugated diene 1a (1.3 g, 10 mmol, 1.0 equiv) and phenylsilane 2a (1.2 g, 11 mmol, 1.1 equiv) successively. The vial was removed from the glovebox after EtMgBr (1 M in THF, 200  $\mu$ L, 0.2 mmol, 2.0 mol%) was added and the reaction mixture was stirred at room temperature for 12 h. When the reaction was finished, the mixture was concentrated by rotating evaporation. The residue was purified by column chromatography to afford the desired products 3aa as a colorless oil (2.3 g, 97% yield, >98:2 r.r.).

#### 6.2 Synthesis of (E)-dimethoxy(phenyl)(4-phenylbut-3-en-1-yl)silane (9)<sup>3</sup>

Ph 
$$SiH_2Ph$$
  $[RuCl_2(p-cymene)]_2 (0.5 mol\%)$  Ph  $Si(OMe)_2Ph$   
**3aa**  $9$   
98% yield

To a Schlenk tube (15 mL) was charged with  $[RuCl_2(p-cymene)]_2$  (1 mg, 0.0016 mmol), the tube was replaced with argon and anhydrous methanol (2 mL) was added throuth syringe. Then **3aa** (76.2 mg, 0.32 mmol) was added dropwise at 0 °C and stirred for 10 min. When the reaction was finished, the mixture was concentrated by rotating evaporation. The residue was purified by chromatography to afford the desired products **9** as a colorless oil (93.6 mg, 98% yield).

#### (*E*)-dimethoxy(phenyl)(4-phenylbut-3-en-1-yl)silane (9)

# Ph Si(OMe)<sub>2</sub>Ph

Serial number: sw-4-145, 93.6 mg, 98% yield, colorless oil. *R<sub>f</sub>*= 0.5 (PE/EA = 20:1, *v*:*v*). <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.51 (m, 2H), 7.40 – 7.27 (m, 3H), 7.24 – 7.15 (m, 4H), 7.13 – 7.06 (m, 1H), 6.26 (d, *J* = 15.8 Hz, 1H), 6.15 (dt, *J* = 15.7, 6.4 Hz, 1H), 3.53 (s, 6H), 2.28 – 2.14 (m, 2H), 1.03 – 0.91 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.8 (1C), 134.3 (2C), 132.8 (1C), 130.2 (1C), 128.7 (1C), 128.4 (2C), 128.0 (2C), 126.7 (2C), 125.9 (2C), 50.7 (2C), 26.0 (1C), 12.0 (1C).
 <u>HRMS (EI)</u> calculated for [M, C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>Si]<sup>+</sup>: 298.1389, found: 298.1383.

6.3 Synthesis of (*E*)-difluoro(phenyl)(4-phenylbut-3-en-1-yl)silane (10)<sup>3</sup>



To a Schlenk tube (15 mL) was charged with CuI (2.9 mg, 0.015 mmol, 5 mol%), CuCl<sub>2</sub> (168.8 mg, 1.26 mmol, 4.2 equiv) and CsF (115.5 mg, 0.76 mmol, 2.5 equiv), the tube was replaced with argon and anhydrous THF (2 mL) was added. Then **3aa** (71.4 mg, 0.3 mmol) was added dropwise at room temperature and stirred for 18 h. When the reaction was finished, the mixture was concentrated by rotating evaporation. The resulting crude product was distilled under reduced pressure using a high vacuum pump, and the fraction was collected as **10** as a colorless oil (62.5 mg, 76% yield).

(E)-difluoro(phenyl)(4-phenylbut-3-en-1-yl)silane (10)

Ph SiF<sub>2</sub>Ph

Serial number: sw-4-162, 62.5 mg, 76% yield, colorless oil.

- $\frac{^{1}\text{H NMR}}{^{7}\text{MR}} (400 \text{ MHz, CDCl}_{3}) \delta 7.71 7.61 \text{ (m, 2H)}, 7.58 7.50 \text{ (m, 1H)}, 7.48 7.40 \text{ (m, 2H)}, 7.34 7.26 \text{ (m, 4H)}, 7.24 7.16 \text{ (m, 1H)}, 6.39 \text{ (d, } J = 16.1 \text{ Hz}, 1\text{H}), 6.22 \text{ (dt, } J = 15.6, 6.6 \text{ Hz}, 1\text{H}), 2.50 2.37 \text{ (m, 2H)}, 1.30 1.22 \text{ (m, 2H)}.$
- $\frac{^{13}\text{C NMR}}{^{12}\text{MR}} (101 \text{ MHz, CDCl}_3) \delta 137.4 (1C), 133.7 (1C), 131.9 (1C), 130.9 (1C), 129.9 (1C), 129.0 (J = 20.2 \text{ Hz}, 1C), 128.5 (2C), 128.3 (2C), 127.1 (2C), 126.0 (2C), 24.9 (1C), 12.0 (J = 20.2 \text{ Hz}, 1C).$

<u>HRMS (EI)</u> calculated for [M, C<sub>16</sub>H<sub>16</sub>F<sub>2</sub>Si]<sup>+</sup>: 274.0989, found: 274.0985.

#### 6.4 Synthesis of (*E*)-4-phenylbut-3-en-1-ol $(11)^3$



To a solution of **3aa** (71.4 mg, 0.3 mmol, 1.0 equiv) in MeOH and THF (3 mL, MeOH/THF = 1:1, v/v), K<sub>2</sub>CO<sub>3</sub> (207 mg, 1.5 mmol, 5.0 equiv) and hydrogen peroxide (0.18 mL, 5 equiv, 30% aqueous solution) were added insequencely. Then the mixture was stirred at 50°C. After 8 h, the mixture was etracted with EtOAc and then the organic layer was separated and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography to afford the desired products **11** as a colorless oil (42.5 mg, 96% yield).

#### (*E*)-4-phenylbut-3-en-1-ol (11)

Ph

Serial number: sw-4-131, 42.5 mg, 96% yield, colorless oil.  $R_f = 0.35$  (PE/EA = 5:1, v:v).

 $\frac{^{1}\text{H NMR}}{^{1}\text{H NMR}}$  (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 – 7.28 (m, 4H), 7.25 – 7.18 (m, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 7.1 Hz, 1H), 3.76 (t, *J* = 6.3 Hz, 2H), 2.54 – 2.43 (m, 2H), 1.64 – 1.54 (br, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.2 (1C), 132.8 (1C), 128.5 (2C), 127.2 (1C), 126.3 (1C), 126.1 (2C), 62.0 (1C), 36.4 (1C).

6.5 Synthesis of phenyl((*E*)-4-phenylbut-3-en-1-yl)((*E*)-styryl)silane (12)<sup>18</sup>



In an argon-filled glovebox, a vial (10 ml) was charged with  $CoBr_2$  (1.3 mg, 0.006 mmol, 2 mol%), Xantphos (3.8 mg, 0.0066 mmol, 2.2 mol%) and anhydrous THF (2 mL), the mixture was stirred at room temperature for 2 h. Then **3aa** (71.4 mg, 0.3 mmol, 1.0 equiv) and phenylacetylene (30.6 mg, 0.3 mmol, 1.0 equiv) were added. The vial was removed from the glovebox after NaBHEt<sub>3</sub> (1 M in THF, 18  $\mu$ L, 0.018 mmol, 6.0 mol%) was added and the

reaction mixture was stirred at room temperature for 3 h. When the reaction was finished, the mixture was concentrated by rotating evaporation. The residue was purified by chromatography to afford the desired products **12** as a colorless oil (86.3 mg, 85% yield, 96:4 r.r.).

#### phenyl((E)-4-phenylbut-3-en-1-yl)((E)-styryl)silane (12)



Serial number: sw-4-170, 86.3 mg, 85% yield, 96:4 r.r., colorless oil.  $R_f = 0.54$  (PE).

- <sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 7.57 (m, 2H), 7.44 7.25 (m, 12H), 7.21 7.16 (m, 1H), 7.08 (d, *J* = 19.1 Hz, 1H), 6.56 (dd, *J* = 19.1, 3.4 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.8, 6.3 Hz, 1H), 4.70 (q, *J* = 3.5 Hz, 1H), 2.39 (dt, *J* = 9.7, 6.5 Hz, 2H), 1.26 – 1.19 (m, 2H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.9 (1C), 137.9 (1C), 137.7 (1C), 134.9 (2C), 134.4 (1C),
   132.7 (1C), 129.6 (1C), 129.0 (1C), 128.6 (2C), 128.4 (3C), 128.0 (2C), 126.8 (1C),
   126.6 (2C), 125.9 (2C), 122.3 (1C), 27.8 (1C), 12.1 (1C).

<u>HRMS (EI)</u> calculated for [M, C<sub>24</sub>H<sub>24</sub>Si]<sup>+</sup>: 340.1647, found: 340.1640.

### 6.6 Synthesis of polyorganosiloxane 13



In an argon-filled glovebox, a Schlenk tube (25 mL) was charged with 1,4cyclohexanediol (116 mg, 1 mmol, 1 equiv),  $B(C_6F_5)_3$  (2.6 mg, 0.005 mmol, 0.5 mol%), anhydrous toluene (3 mL) and **3aa** (238 mg, 1 mmol, 1.0 equiv) successively. The tube was removed from the glovebox, connected to an argon filled balloon and stirred at room temperature for 48 h. When the reaction was finished, the mixture was concentrated by rotating evaporation. The residue was dissolved in THF (1 mL), which was added dropwise to hexane (50 mL). The emulsion formed was centrifuged, and the residue obtained after removing the supernatant was re-precipitated and centrifuged twice more according to the above method. The final residue was collected and dried under vacuum as the target product **13** as solid-liquid mixtures (213.5 mg, 61% yield). The M<sub>n</sub> and M<sub>w</sub>/M<sub>n</sub> values were determined by GPC with THF solvent and polystyrene standards, M<sub>n</sub> = 5551, M<sub>w</sub>/M<sub>n</sub> = 1.4.



Serial number: sw-5-19B, 213.5 mg, 61% yield, solid-liquid mixtures.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.6 - 77.53 (m, 2H), 7.43 - 7.29 (m, 3H), 7.28 - 7.18 (m, 4H),
 7.17 - 7.09 (m, 1H), 6.40 - 6.06 (m, 2H), 3.97 - 3.68 (m, 2H), 2.35 - 2.15 (m, 2H),
 1.99 - 1.73 (m, 4H), 1.46 - 1.30 (m, 4H), 1.07 - 0.92 (m, 2H).



Scheme S1 GPC Spectra of Polymer13

#### 6.7 Synthesis of polyorganosiloxane 14<sup>19</sup>



In an argon-filled glovebox, a vial (10 mL) was charged with [Co] (11.5 mg, 0.025 mmol, 5 mol%), anhydrous toluene (3 mL), **3aa** (119 mg, 0.5 mmol) and terephthalaldehyde (67 mg, 0.5 mmol, 1.0 equiv) successively. The vial was removed from the glovebox after NaBEt<sub>3</sub>H (1.0 M in THF, 75  $\mu$ L, 0.075 mmol, 15 mol%) was added and stirred at room temperature for 48 h. When the reaction was finished, the mixture was concentrated by rotating evaporation. The residue was dissolved in THF (1 mL), which was added dropwise to hexane (50 mL). The emulsion formed was centrifuged, and the residue obtained after removing the supernatant was re-precipitated and centrifuged twice more according to the above method. The final residue was collected and dried under vacuum as the target product **14** as brown viscous liquid (91.2 mg, 49% yield). The M<sub>n</sub> and M<sub>w</sub>/M<sub>n</sub> values were determined by GPC with THF solvent and polystyrene standards, M<sub>n</sub> = 5197, M<sub>w</sub>/M<sub>n</sub> = 1.7.



Serial number: sw-4-190, 91.2 mg, 49% yield, brown viscous liquid. <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.73 – 7.19 (m, 14H), 6.50-5.95 (m, 2H), 5.00 – 4.55 (m, 4H), 2.50 – 2.00 (m, 2H), 1.22 – 0.98 (m, 2H).



Scheme S2 GPC Spectra of Polymer 14

### 7. Mechanistic studies

#### 7.1 Hydrosilylation of an *E*/*Z* mixture of 1,3-diene 1a'



In an argon-filled glovebox, a vial (10 mL) was charged with complexes C1d (3.6 mg, 0.005 mmol), dry anhydrous THF (1 mL), 1,3-dienes 1a' (65 mg, 0.5 mmol, E/Z = 38:62) and silanes 2a (59.4 mg, 0.55 mmol, 1.1 equiv) successively. The reaction mixture was stirred at room temperature for 2 h after EtMgBr (1 M in THF, 10 µL, 0.01 mmol, 2.0 mol%) was added. The vial was removed from the glovebox and the reaction mixture was concentrated by rotating evaporation. The residue was purified by column chromatography to afford the products 3aa' as a colorless oil (117 mg, 98% yield, >98:2 r.r., E/Z = 38:62).

(*E*)-phenyl(4-phenylbut-3-en-1-yl)silane (*E*-3aa)<sup>12</sup>

Ph SiH<sub>2</sub>Ph

 $\frac{^{1}\text{H NMR}}{^{1}\text{H NMR}} (400 \text{ MHz, CDCl}_{3}) \delta 7.62 - 7.56 \text{ (m, 2H)}, 7.44 - 7.15 \text{ (m, 8H)}, 6.43 - 6.33 \text{ (m, 1H)}, 6.25 \text{ (dt, } J = 15.6, 6.5 \text{ Hz}, 1\text{H}), 4.34 \text{ (t, } J = 3.3 \text{ Hz}, 2\text{H}), 2.37 \text{ (q, } J = 7.4 \text{ Hz}, 2\text{H}), 1.19 - 1.03 \text{ (m, 2H)}.$ 

(Z)-phenyl(4-phenylbut-3-en-1-yl)silane (Z-3aa)<sup>20</sup>

Ph

<u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.49 (m, 2H), 7.44 – 7.15 (m, 8H), 6.43 – 6.33 (m, 1H),
5.70 (dt, J = 11.5, 7.3 Hz, 1H), 4.31 (q, J = 3.3 Hz, 2H), 2.48 (q, J = 7.7 Hz, 2H),
1.19 – 1.03 (m, 2H).

#### 7.2 Deuterium labelling experiments



In an argon-filled glovebox, a vial (10 mL) was charged with complexes C1d (1.42 mg, 0.002 mmol), dry anhydrous THF (1 mL), 1i (72 mg, 0.4 mmol, 2 equiv) and silane 2e-*d* (33.4 mg, 0.20 mmol) successively. The reaction mixture was stirred at room temperature for 2 h after EtMgBr (1 M in THF, 4  $\mu$ L, 0.004 mmol, 2.0 mol%) was added. The vial was removed from the glovebox and the reaction mixture was concentrated by rotating evaporation. The residue was purified by column chromatography to afford the products **3ie**-*d* (65.8 mg, 95% yield, >98:2 r.r.) and **1i**-*d* (35.3 mg, 98% recovery). The <sup>2</sup>H NMR spectroscopy was measured with CDCl<sub>3</sub> as an internal standard, and the 1,3,5-trimethoxybenzene was used as an internal standard to determine the ratio of product and CDCl<sub>3</sub> by <sup>1</sup>H NMR.



**3ie-d**, 65.8 mg, 95% yield, >98:2 r.r., colorless oil, R<sub>f</sub>= 0.22 (PE).
<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.79 – 7.70 (m, 3H), 7.64 (s, 1H), 7.57 – 7.49 (m, 3H), 7.47 – 7.35 (m, 4H), 6.53 (d, J = 15.7 Hz, 1H), 6.37 (dt, J = 15.7, 6.3 Hz, 1H), 4.35 (q, J = 3.8 Hz, 0.36 H), 2.47 – 2.36 (m, 0.95 H), 1.32 (s, 9H), 1.14 (d, J = 8.0 Hz, 2H).
<sup>13</sup><u>C NMR</u> (101 MHz, CDCl<sub>3</sub>) δ 152.8 (1C), 135.3 (2C), 135.2 (1C), 133.7 (1C), 132.8 (1C), 132.7 (1C), 129.4 (1C), 128.6 (1C), 128.1 (1C), 127.9 (1C), 127.7 (1C), 126.2 (1C), 125.5 (2C), 125.1 (2C), 123.6 (1C), 34.8 (1C), 31.3 (3C), 28.3 (1C), 9.9 (1C).

The <sup>2</sup>H NMR analysis is well consistent with the <sup>1</sup>H NMR analysis. See followed spectrum:



Figure S1. <sup>2</sup>H NMR of the product **3ie-***d*. CDCl<sub>3</sub> (1.20 equiv) was used as an internal standard.



1i-d, 35.3 mg, 0.2 mmol, white solid.

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<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.82 – 7.71 (m, 4H), 7.65 – 7.58 (m, 1H), 7.48 – 7.38 (m, 2H),
6.96 – 6.86 (m, 1H), 6.72 (d, J = 15.6 Hz, 1H), 6.56 (dt, J = 16.9, 10.2 Hz, 0.77 H),
5.38 (dd, J = 16.8, 1.4 Hz, 1H), 5.20 (dd, J = 9.9, 1.5 Hz, 1H).
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.3 (1C), 134.6 (1C), 133.7 (1C), 133.0 (1C), 132.9 (1C)
```

130.0 (1C), 128.3 (1C), 128.0 (1C), 127.7 (1C), 126.6 (1C), 126.3 (1C), 125.9 (1C), 123.5 (1C), 117.8 (1C).

The <sup>2</sup>H NMR analysis is well consistent with the <sup>1</sup>H NMR analysis. See followed spectrum:





#### 7.3 Mixture silanes experiment



In an argon-filled glovebox, a vial (10 mL) was charged with complexes C1d (2.8 mg, 0.004 mmol), dry anhydrous THF (1 mL), conjugated diene 1a (57.2 mg, 0.44 mmol, 2.2 equiv), silanes 2e-*d* (33.4 mg, 0.2 mmol, 1.0 equiv) and 2d (27.6 mg, 0.2 mmol, 1 equiv) successively. The reaction mixture was stirred at room temperature for 5 min after EtMgBr (1 M in THF, 8  $\mu$ L, 0.004 mmol, 2.0 mol%) was added. The vial was removed from the glovebox and quenched with 2 drops water, the reaction mixture was concentrated by rotating evaporation. The residue was purified by column chromatography to afford the products **3ae-***d* (20 mg, 17% yield, >98:2 r.r.) and **3ad-***d* (14 mg, 13% yield, >98:2 r.r.). The <sup>2</sup>H NMR spectroscopy was measured with CDCl<sub>3</sub> as an internal standard, and the 1,3,5-trimethoxybenzene was used as an internal standard to determine the ratio of product and CDCl<sub>3</sub> by <sup>1</sup>H NMR.



**3ae-***d*, 20 mg, 17% yield, >98:2 r.r., colorless oil.

<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 – 7.50 (m, 2H), 7.43 – 7.37 (m, 2H), 7.33 – 7.26 (m, 4H), 7.22 – 7.16 (m, 1H), 6.38 (d, *J* = 16.4, 1H), 6.24 (dd, *J* = 15.8, 6.4 Hz, 1H), 4.32 (q, *J* = 3.8 Hz, 0.24 H), 2.42 – 2.31 (m, 0.98 H), 1.32 (s, 9H), 1.11 (d, *J* = 8.0 Hz, 2H). <sup>13</sup><u>C NMR</u> (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.7 (1C), 137.7 (1C), 135.2 (2C), 132.3 (1C), 129.2 (1C), 128.6 (1C), 128.4 (2C), 126.8 (1C), 126.0 (2C), 125.0 (2C), 34.7 (1C), 31.2 (3C), 28.1 (1C), 9.8 (1C). The <sup>2</sup>H NMR analysis is well consistent with the <sup>1</sup>H NMR analysis. See followed spectrum:



Figure S3. <sup>2</sup>H NMR of the product **3ae-***d*. CDCl<sub>3</sub> (2.22 equiv) was used as an internal standard.



**3ad-d**, 14 mg, 13% yield, >98:2 r.r., colorless oil.
<sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.47 (m, 2H), 7.33 – 7.27 (m, 4H), 7.22 – 7.15 (m, 1H), 6.95 – 6.88 (m, 2H), 6.37 (d, J = 15.8, 1H), 6.24 (dt, J = 15.7, 6.5 Hz, 1H), 4.32 (t, J = 3.6 Hz, 1.87 H), 3.82 (s, 3H), 2.40 – 2.31 (m, 1.94 H), 1.14 – 1.07 (m, 2H).
<sup>13</sup><u>C NMR</u> (101 MHz, CDCl<sub>3</sub>) δ 160.9 (1C), 137.7 (1C), 136.7 (2C), 132.3 (1C), 129.2 (1C), 128.4 (2C), 126.8 (1C), 125.9 (2C), 122.8 (1C), 113.9 (2C), 55.0 (1C), 28.4 (1C), 10.2 (1C).

The <sup>2</sup>H NMR analysis is well consistent with the <sup>1</sup>H NMR analysis. See followed spectrum:



Figure S4. <sup>2</sup>H NMR of the product **3ad-***d*. CDCl<sub>3</sub> (4.69 equiv) was used as an internal standard

#### 7.4 Parallel kinetic isotope effect experiment



In an argon-filled glovebox, a vial (10 mL) was charged with complexes C1d (1.4 mg, 0.002 mmol), dry anhydrous THF (1 mL), conjugated diene 1a (26.0 mg, 0.2 mmol), silane 2e (36.1 mg, 0.22 mmol, 1.1 equiv) or 2e-*d* (36.7 mg, 0.22 mmol, 1.1 equiv) successively. The reaction mixture was stirred at room temperature for 2 min after EtMgBr (1 M in THF, 5  $\mu$ L, 0.005 mmol, 2.5 mol%) was added. The vial was removed from the glovebox and quenched with 2 drops water. Iron species were removed by flash column chromatography with DCM as eluent. The raw product was detected by <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene as internal standard. We repeated the experiments for four times, respectively. The average of *k*<sub>H</sub>/*k*<sub>D</sub> is 0.46. The results were listed as following.

entry	% yield ( <b>3ae</b> )	% yield ( <b>3ae-</b> <i>d</i> )
1	6.4	14.6
2	6.3	12.1
3	7.6	16.1
4	6.0	15.2
Average yield	6.6	14.5
$k_{ m H}/k_{ m D}$	0.46	

 Table S3 Parallel kinetic isotope effect experiments

# 8 NMR spectra of all products

# 2-chloro-9-mesityl-1,10-phenanthroline (2a)





## 2-chloro-9-(2,4,6-triisopropylphenyl)-1,10-phenanthroline (2b)







# 1-(9-(2,4,6-triisopropylphenyl)-1,10-phenanthrolin-2-yl)ethan-1-one (3b)





# (E)-N-(2,6-dimethylphenyl)-1-(9-mesityl-1,10-phenanthrolin-2-yl)ethan-1-imine (L1a) -8.766 -8.745 -8.745 -8.245 -8.295 -8.268 -8.268 -8.268 -7.861 -7.833 -7.861 -7.833 -7.733 -7.833 -7.733 -7.833 -7.735 -7.735 -7.735 -7.735 -7.735 -6.635 -7.755 -7.7555 -7.7555 -7.7555 -7.7555 -7.7555 -7.7555 -7.7555 -7.7555 -

(*E*)-N-(2,6-dimethylphenyl)-1-(9-(2,4,6-triisopropylphenyl)-1,10-phenanthrolin-2-yl)ethan-1-imine (L1b)





(*E*)-N-(2,6-diethylphenyl)-1-(9-(2,4,6-triisopropylphenyl)-1,10-phenanthrolin-2-yl)ethan-1-imine (L1c)



(*E*)-N-(2,6-diisopropylphenyl)-1-(9-(2,4,6-triisopropylphenyl)-1,10-phenanthrolin-2-yl)ethan-1-imine (L1d)



(E)-N-(2,6-dibenzhydryl-4-methoxyphenyl)-1-(9-(2,4,6-triisopropylphenyl)-1,10-



# (E)-1-(9-(3,5-di-tert-butylphenyl)-1,10-phenanthrolin-2-yl)-N-(2,6-





# (E)-phenyl(4-phenylbut-3-en-1-yl)silane (3aa)

7,596 7,592 7,582 7,573 7,573 7,573 7,573 7,573 7,582 7,583 7,583 7,583 7,583 7,583 7,583 7,583 7,583 7,583 7,583 7,586 7,382 7,732 7,382 7,732 7,382 7,732 7,382 7,732 7,382 7,732 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,382 7,773 7,773 7,273 7,773 7,273 7,773 7,273 7,773 7,273 7,773 7,273



# (E)-(4-phenylbut-3-en-1-yl)(o-tolyl)silane (3ab)



#### (*E*)-(4-phenylbut-3-en-1-yl)(m-tolyl)silane (3ac) (*E*)-



#### (*E*)-(4-methoxyphenyl)(4-phenylbut-3-en-1-yl)silane (3ad) <sup>2122</sup> <sup>2</sup>


# (E)-(4-(tert-butyl)phenyl)(4-phenylbut-3-en-1-yl)silane (3ae)



### (E)-(4-fluorophenyl)(4-phenylbut-3-en-1-yl)silane (3af)









### (*E*)-(4-methylbenzyl)(4-phenylbut-3-en-1-yl)silane (3ah)

#### 7,329 7,7326 7,7327 7,7327 7,7327 7,7327 7,7327 1,747 1,275 1,275 1,275 1,275 1,191 1,275 1,191 1,275 1,191 1,275 1,191 1,275 1,191 1,275 1,191 1,275 1,191 1,275 1,191 1,275 1,191 1,275 1,191 1,275 1,191 1,275 1,215



### (E)-octyl(4-phenylbut-3-en-1-yl)silane (3ai)



# (E)-phenyl(4-(o-tolyl)but-3-en-1-yl)silane (3ba)

7,602 7,7598





# (E)-phenyl(4-(3-(trifluoromethyl)phenyl)but-3-en-1-yl)silane (3ca)



### (E)-phenyl(4-(p-tolyl)but-3-en-1-yl)silane (3da)

7,592 7,575 7,575 7,575 7,575 7,575 7,575 7,575 7,575 7,539 7,539 7,539 7,537 7,337 7,337 7,337 7,337 7,337 7,337 7,337 7,337 7,337 7,335 7,337 7,337 7,337 7,335 7,337 7,337 7,335 7,337 7,335 7,337 7,335 7,337 7,337 7,335 7,337 7,337 7,335 7,337 7,337 7,335 7,337 7,337 7,335 7,337 7,335 7,337 7,335 7,337 7,335 7,335 7,337 7,3357 7,3357 7,3357 7,3357 7,3357 7,3357 7,3357 7,3357 7,3357 7,3



### (E)-(4-(4-methoxyphenyl)but-3-en-1-yl)(phenyl)silane (3ea)





# (E)-(4-(4-fluorophenyl)but-3-en-1-yl)(phenyl)silane (3ga)

7,558 7,7569 7,7574 7,7574 7,7569 7,7586 7,7586 7,7587 7,7375 7,7375 7,7375 7,7375 7,7375 7,7375 7,7375 7,7375 7,7375 7,7375 7,7375 7,7375 6,698 6,534 6,533 6,5356 6,5356 6,5356 6,5556 6,5556 6,5556 6,5556 6,5556 6,5556 6,5556 6,55566 6,555





100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -31



# (E)-(4-(naphthalen-2-yl)but-3-en-1-yl)(phenyl)silane (3ia)

7,7,77 7,7,77 7,7,75 7,7,56 1,



#### (*E*)-(4-(benzo[d][1,3]dioxol-5-yl)but-3-en-1-yl)(phenyl)silane (3ja) (*E*)-(4-(benzo[d][1,3]dioxol-5-yl)but-3-en-1-yl)(phenyl)silane (3ja) (*E*)-(2-(benzo[d][1,3]dioxol-5-yl)(but-3-en-1-yl)(phenyl)silane (3ja) (*E*)-(2-(benzo[d][1,3]dioxol-5-yl)(but-3-en-1-yl)(but-3-en-1-yl)(but-3-en-1-yl)(but-3-en-1-yl)(but-3-en



#### (*E*)-(4-(furan-2-yl)but-3-en-1-yl)(phenyl)silane (3ka) (*E*)-

SiH<sub>2</sub>Ph





# (E)-phenyl(4-phenylpent-3-en-1-yl)silane (3la)



(4,4-diphenylbut-3-en-1-yl)(phenyl)silane (3ma) (8,4-diphenylbut-3-en-1-yl)(phenyl)silane (3ma) (9,6-1) (10,0-1



# (E)-(3-methyl-4-phenylbut-3-en-1-yl)(phenyl)silane (3na)

7,259 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,593 7,594 7,594 7,219 7,719





### (E)-non-3-en-1-yl(phenyl)silane (3pa)





# (E)-(4-cyclohexylbut-3-en-1-yl)(phenyl)silane (3qa)



# (4-(*tert*-butyl)phenyl)(3-methylbut-3-en-1-yl)silane (3re)



# (7-methyl-3-methyleneoct-6-en-1-yl)(phenyl)silane (3sa)

7,558 7,558 7,558 7,559 7,559 7,559 7,559 7,559 7,738 7,739 7,738 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749 7,749



# (3-cyclohexylidenepropyl)(phenyl)silane (3ta)

7.579 7.5655 7.5655 7.5665 7.560 7.560 7.560 7.560 7.530 7.330 7.332 7.332 7.335 7.3377 7.335 7.3377 7.335 7.3377 7.3357 7.3377 7.3377 7.3377 7.33777 7.33777 7.337777 7.3377777777	<u>5.119</u> 5.101 5.083	4.300 4.294 4.284 4.275	2.181 2.162 2.142 2.1123 2.105 2.015 2.075 2.075 2.075 2.032 2.032 2.032	1.534 1.526 1.528 1.517 1.518 1.504 1.1.504 1.1.455 1.1.055 1.1.455 1.1.455 1.1.0555 1.1.0555 1.1.05555 1.1.05555555555
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# (2-(cyclohept-1-en-1-yl)ethyl)(phenyl)silane (3xa)





S104

# (3-methylphenethyl)(phenyl)silane (8ba) 7,574 7,555 7,555 7,555 7,555 7,555 7,555 7,417 7,417 7,417 7,417 7,413 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,390 7,310 -4.324 -4.315 -4.306 2.749 2.735 2.721 2.721 2.721 2.721 2.721 2.721 2.314 1.321 1.321 1.321 1.307 1.307 1.307 1.302 1.209 1.209 1.2011 SiH<sub>2</sub>Ph Me 2.00J 3.05J 1.08y 3.03y 1.95-2.20H 3.22H 2.45H 8.5 8.0 , 7.5 7.0 6.5 4.5 3.5 3.0 2.5 1.5 6.0 5.5 5.0 4.0 2.0 1.0 0.5 0.0 -0.5 143.9 137.9 135.2 135.2 135.2 135.2 128.7 128.7 128.2 128.0 128.0 128.0 128.0 — 31.0 - 21.4 — 12.1 SiH<sub>2</sub>Ph Me

# (4-fluorophenethyl)(phenyl)silane (8ca)

7,573 7,564 7,564 7,556 7,556 7,556 7,556 7,556 7,556 7,556 7,556 7,556 7,556 7,556 7,536 7,339 7,339 7,336 7,346 7,347 7,447



### (4-methoxyphenethyl)(phenyl)silane (8da)

#### 7.572 7.568 7.7.568 7.7.568 7.7.568 7.7.568 7.7.5378 7.7.5378 7.7.5378 7.7.3378 7.7.3378 7.7.3378 7.7.3378 7.7.3338 7.7.3338 7.7.3338 7.7.099







# (4-(*tert*-butyl)phenethyl)(phenyl)silane (8ea)


(2-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)silane (8fa) (2-([1,1'-biphenyl]-4-yl)ethyl)(



phenyl(6-phenylhexyl)silane (8ga)









## 1-(6-(phenylsilyl)hexyl)piperidine (8ia)







# **N,N-dimethyl-3-(phenylsilyl)propan-1-amine (8ka)**

Me<sub>2</sub>N SiH<sub>2</sub>Ph







### (2-phenoxyethyl)(phenyl)silane(8la)





## trimethyl(2-(phenylsilyl)ethyl)silane (8na)



## dimethyl(phenyl)(2-(phenylsilyl)ethyl)silane (80a)

7,545 7,557 7,557 7,557 7,557 7,551 7,551 7,551 7,551 7,551 7,551 7,551 7,551 7,551 7,551 7,551 7,558 7,748 7,748 7,748 7,748 7,748 7,735



### (E)-dimethoxy(phenyl)(4-phenylbut-3-en-1-yl)silane (9)

### 7.575 7.575 7.556 7.556 7.556 7.556 7.358 7.338 7.338 7.338 7.335 7.3349 7.335 7.3349 7.335 7.3349 7.3349 7.335 7.3349 7.3349 7.335 7.3349 7.3349 7.335 7.3349 7.7308 6.287 7.710 7.710 7.7208 6.287 7.710 7.7208 6.287 7.7108 6.287 7.7108 6.287 7.7108 6.281 7.7108 6.281 7.7108 6.281 7.7108 6.281 7.7108 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.281 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.2217 7.7208 6.22217 7.7208 7.72008 7.7208 7.7208 7.7208 7.7208 7.72008 7.7208 7.7208 7.7



### (*E*)-difluoro(phenyl)(4-phenylbut-3-en-1-yl)silane (10) (*E*)-difluoro(phenylbut-3-en-1-yl)silane (10) (*E*)-difluoro(p







, 70 . 50 . 40 

### phenyl((*E*)-4-phenylbut-3-en-1-yl)((*E*)-styryl)silane (12)

7,611 7,611 7,611 7,611 7,611 7,611 7,611 7,447 7,447 7,447 7,447 7,447 7,441 7,447 7,447 7,339 7,349 7,349 7,349 7,349 7,349 7,349 7,349 7,349 7,349 7,349 7,449 7,449 7,449 7,449 7,449





## Phenyl(4-phenylbut-3-en-1-yl)silane (3aa')

7,596 7,577 7,577 7,573 7,579 7,579 7,574 7,574 7,525 7,525 7,528 7,528 7,339 7,336 7,236 7,247













### 9. References

- R. J. Maza, E. Davenport, N. Miralles, J. J. Carbo and E. Fernandez, *Org. Lett.*, 2019, 21, 2251.
- (2) N. T. Patil and V. Singh, Chem. Commun., 2011, 47, 11116.
- (3) M.-Y. Hu, Q. He, S.-J. Fan, Z.-C. Wang, L.-Y. Liu, Y.-J. Mu, Q. Peng and S.-F. Zhu, Nat. Commun., 2018, 9, 221.
- (4) T.-Q. Wang, Y.-Y. Hu and S.-L. Zhang, Org. Biomol. Chem., 2010, 8, 2312.
- (5) K. Clinch, C. J. Marquez, M. J. Parrott and R. Ramage, Tetrahedron, 1989, 45, 239.
- (6) L. T. Kliman, S. N. Mlynarski, G. E. Ferris and J. P. Morken, *Angew. Chem. Int. Ed.* 2012, 51, 521.
- (7) L.-H. Liao, R.-Z. Guo and X.-D. Zhao, Angew. Chem. Int. Ed., 2017, 56, 3201.
- (8) W. Herz and R. R. Juo, J. Org. Chem., 1985, 50, 618.
- (9) A. M. Schmidt and P. Eilbracht, J. Org. Chem., 2005, 70, 5528.
- (10) M. D. Visco, J. M. Wieting and A. E. Mattson, Org. Lett., 2016, 18, 2883.
- (11) M. Kuritani, S. Tashiro and M. Shionoya, Inorg. Chem., 2012, 51, 1508.
- (12) M. D. Greenhalgh, D. J. Frank and S. P. Thomas, Adv. Synth. Catal., 2014, 356, 584.
- (13) B. Raya, S. Jing, V. Balasanthiran and T. V. RajanBabu, ACS Catal., 2017, 7, 2275.
- (14) D.-J. Peng, Y.-L. Zhang, X.-Y. Du, L. Zhang, X.-B. Leng, M. D. Walter and Z. Huang, J. Am. Chem. Soc., 2013, 135, 19154.
- (15) A. J. Challinor, M. Calin, G. S. Nichol, N. B. Carter and S. P. Thomas, *Adv. Synth. Catal.*, 2016, **358**, 2404.
- (16) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix and P. L. Holland, J. Am. Chem. Soc., 2015, 137, 13244.
- (17) P.-F. Fu, J. Mol. Catal. A-Chem., 2006, 243, 253.
- (18) C.-Z. Wu, W. J. Teo and S.-Z. Ge, ACS Catal., 2018, 8, 5896.
- (19) M.-Y. Hu, P. He, T.-Z. Qiao, W. Sun, W.-T. Li, J. Lian, J.-H. Li and S.-F. Zhu, J. Am. Chem. Soc., 2020, 142, 16894.
- (20) R. Y. Kong and M. R. Crimmin, J. Am. Chem. Soc., 2020, 142, 11967.