Iron-Catalyzed Asymmetric Hydrosilylation of Vinylcyclopropanes via Stereospecific C-C Bond Cleavage

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**HIGHLIGHTS**

- Iron-catalyzed 1,5-hydrosilylation of VCPs via C-C bond cleavage was first established.
- Chiral allyl silanes and chiral VCPs were obtained with high enantioselectivity.
- Various chiral allylic derivatives were delivered from chiral Z-allylic silanes.
- A possible mechanism via an iron-silyl species was proposed.

**DATA AND CODE AVAILABILITY**

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Iron-Catalyzed Asymmetric Hydrosilylation of Vinylcyclopropanes via Stereospecific C-C Bond Cleavage

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SUMMARY
An iron-catalyzed highly anti-Markovnikov selective, enantioselective hydrosilylation of vinylcyclopropanes with PhSiH3 was reported for the preparation of valuable chiral allylic silanes via stereospecific C-C bond cleavage. Simultaneously, difficultly prepared chiral VCPs could be also obtained with moderate to excellent enantioselectivity via this kinetic resolution pathway. The chiral Z-allylic silanes could be converted to various chiral allylic derivatives. A possible mechanism via an iron-silyl species was proposed based on experimental and computational studies.

INTRODUCTION
Vinylcyclopropane (VCP) has been widely used in organic synthesis, particularly as a versatile organic synthon in cycloadditions (Lautens et al., 1996; Reissig and Zimmer, 2003; Rubin et al., 2007; Aı¨ss, 2011; Jiao and Yu, 2013; Wang and Yu, 2015; Fumagalli et al., 2017). Although the regio- and stereoselective ring-opening hydrofunctionalization reactions of VCPs could theoretically afford various potentially useful products, poor regioselectivity with eight possible regioisomers extremely limits their utility. Traditionally, in order to control the regioselectivity, gem-substituted electron-deficient groups have to be used to control the 1,4- or 3,4-regioselectivity via the cleavage of more substituted carbon-carbon bond (Crossley et al., 2016; Souillart and Cramer, 2015; Nairoukh et al., 2017; Wu and Zhu, 2019; Shigehisa et al., 2013; Sar- tori et al., 1983; Burgess, 1987; Sebelius et al., 2005; Sumida et al., 2008; Li et al., 2009; Dieskau et al., 2012; Wu et al., 2015; Zell et al., 2016; Meyer et al., 2017; Wang et al., 2019). To the best of our knowledge, asymmetric ring-opening hydrofunctionalization reactions of vinylcyclopropanes are still quite limited. Using donor-acceptor (D-A) vinylcyclopropanes, Krische and co-workers reported the iridium-catalyzed asymmetric allylic alkylation with aldehydes or alcohols as electrophiles, affording the 3,4-regioselective hydrocarboxylation products (Moran et al., 2011). Trost group recently disclosed the palladium-catalyzed asymmetric 1,4-hydrocarboxylation of D-A vinylcyclopropanes with 3-substituted indoles as nucleophiles (Trost et al., 2018) (Figure 1A). Recently, our group reported an iron-catalyzed asymmetric 5,1-hydroboration of non-donor-acceptor (non-D-A) vinylcyclopropanes via iron-hydride intermediate (Chen et al., 2017). However, overstoichiometric amounts of VCPs were used to be converted to chiral boronic esters with less than 90% ee, and the ee values of recovered VCPs were extremely poor. So, the development of various regio- and enantioselective hydrofunctionalizations of vinylcyclopropanes via stereospecific C C bond cleavage for the synthesis of chiral products is highly desirable.

Allylic silane is one of the most useful allylic reagents for organic transformations, such as Hosomi-Sakurai reaction (Masse and Panek, 1995; Fleming et al., 1997; Barbero and Pulido, 2004; Diez-Poza and Barbero, 2017). Chiral allylic silanes were used to be synthesized using stoichiometric chiral reagents via diastereo-selective or stereospecific transformations (Sparks and Panek, 1991; Panek and Clark, 1992; Suginome et al., 1996; Bourque et al., 2007; Binanzer et al., 2010; Aggarwal et al., 2011). It is still a challenge for the catalytic enantioselective synthesis of chiral allylic silanes, which used to focus on the formation of chiral silicon-substituent carbon center (Hayashi et al., 1982; Hofstra et al., 2018; Wu et al., 2010; Ohmura et al., 2006; Da et al., 2018; Shintani et al., 2007; Lee et al., 2012; Kacprzynski et al., 2007; Sang et al., 2018; Wen et al., 2019).

Herein, we reported an iron-catalyzed 1,5-selective asymmetric hydrosilylation of vinylcyclopropanes via stereospecific C C bond cleavage, affording chiral allylic silanes with excellent enantioselectivity and recovering VCPs with moderate to excellent enantioselectivity (Figure 1B).
RESULTS AND DISCUSSION

Initially, we chose the 1-phenyl-2-(1'-phenyl)vinylcyclopropane 1a as a model substrate (Table 1). The reaction of 1a with 1.5 equivalent of PhSiH₃ using 5 mol % of iron precatalyst L₁FeCl₂ and 15 mol % of NaBHEt₃ in a solution of dioxane (0.5 M) at ambient temperature for 24 h was carried out to afford the desired product 2a in 6% yield (entry 1), whereas the reaction with Ph₂SiH₂ did not afford the hydro-silylation product (entry 2). The observation of 2a illustrated the possibility of the generation of iron-silyl species. In our previous studies, free hydroxyl group was found to be tolerated in cobalt-catalyzed alkyne hydrosilylation in which cobalt-silyl species was proposed (Guo and Lu, 2016; Zuo et al., 2016). Ge and coworkers found that the addition of phenol could inhibit the Z/E-isomerization in Co-catalyzed alkyne hydrosilylation (Teo et al., 2017). These examples demonstrated that the addition of free hydroxyl group could promote the formation of cobalt silyl species. However, the proposed iron silyl species has not been reported for the tolerance of free hydroxyl group (Cheng et al., 2018; Hu et al., 2018; Chen et al., 2018; Obligacion and Chirik, 2018). With 15 mol % of water, the reaction afforded 2a in an increasing yield (12%), which indicated that the addition of free hydroxyl group could also promote the formation of iron silyl species (entry 3). Using the phenol as an additive, the reaction was conducted for 2 h to afford 2a in 28% yield with 98% ee, as well as 1a in 65% recovery with 34% ee (entry 4). By further investigation of various phenols, 3-chlorophenol was found to accelerate reaction efficiently (entries 5–8). The reactivities were increased by increasing the steric hindrance of the group on oxazoline (Me, Bn, Cy) (entries 8–10). However, when L₄FeCl₂ was used as a precatalyst, the reaction was inhibited, which might be due to the overlarge steric hindrance (entry 11). When the 4-MeO-phenyl group was introduced into para-position of aniline, the reaction using L₅FeCl₂ as a precatalyst could be further accelerated to access 2a in 48% yield with 13/1 Z/E and 98% ee, simultaneously with 28% recovery of chiral 1a in 86% ee (entry 12). It should be noted that some dienes and hydrogenation products were observed as side products, which decreased the recovery of starting materials (see in Supplemental Information). The standard conditions were identified as 0.5 mmol of racemic vinylcyclopropane, 0.75 mmol of silane, 5 mol % of L₅FeCl₂, 15 mol % of NaBHEt₃, and 15 mol % of 3-chlorophenol in 1 mL of dioxane for 2 h.

With the optimal conditions in hand, the substrate scope was explored in Table 2. The scope of various substituents on alkene was first explored. The allylic silanes 2b-2j with functional groups (methoxyl, methylthio, fluoro, chloro, bromo) at the para-, meta-, or ortho-position on the phenyl ring could be obtained in 39%–47% yields and 92%–98% ee, and chiral VCPs 1b-1j could be observed in 15%–40% recoveries with...
63%–97% ee. 2-Naphthyl substrate 1k was also suitable, providing 2k in 47% yield with 95% ee and 11% recovery of chiral 1k in 99% ee. The reaction of alkyl-substituted VCPs did not occur. The scope of substituents on cyclopropanes was next examined. VCPs bearing electron-donating (1l–1m) or electron-withdrawing (1n–1s) groups at the different positions on the phenyl ring gave the corresponding products in 40%–48% yields with 78%–98% ee, and chiral VCPs 1l–1s were observed in 13%–39% recoveries with 64%–97% ee. Additionally, 1-naphthyl, 2-naphthyl, 2-furyl, and 2-thienyl VCPs 1t–1w were suitable for the catalytic system, affording 2t–2w in 40%–47% yields with 64%–98% ee and chiral 1t–1w in 21%–43% recoveries with 64%–96% ee. Owing to the sterically hindered groups, the selectivities of 1s and 1u were decreased. Notably, the reactions of 1o-, 2o-, 3o-alkyl substrates afforded 2x–2ac in 44%–50% yields with 80%–95% ee and chiral 1x–1ac in 37%–46% recoveries with 74%–96% ee.

To expand the utility of this strategy, a broad range of aryl and alkyl silanes were tested. Various aryl silanes were used in the reaction, affording 2ad–2ag in 38%–45% with 96%–99% ee and chiral 1a in 28%–41% recoveries with 62%–94% ee. When alkyl silanes were employed, the transformation also performed well, affording 2ah–2ak in 37%–42% yields with 87%–98% ee and 12%–31% recoveries with 78%–94% ee. In general, VCPs bearing aryl or alkyl groups proceeded through a kinetic resolution (KR) pathway to deliver the desired chiral allylic silanes in good to excellent yields, moderate to excellent stereoselectivities and

Table 1. Optimization of the Reaction Conditions

| Entry | L | Additives | Yield of 2a (%) | ee of 2a (%) | Recovery of 1a (%) | ee of 1a (%) |
|-------|---|-----------|----------------|-------------|------------------|-------------|
| 1b    | L1 | –         | 6              | –           | 89               | –           |
| 2a,b  | L1 | H2O       | 12             | –           | 86               | –           |
| 3b    | L1 | C6H5OH    | 28             | 98          | 65               | 34          |
| 4     | L1 | 4-MeOC6H4OH | 18            | 97          | 76               | 21          |
| 5     | L1 | 4-CIC6H4OH | 30             | 98          | 62               | 38          |
| 7     | L1 | 3-CIC6H4OH | 35             | 97          | 59               | 41          |
| 8     | L1 | 2-CIC6H4OH | 15             | 98          | 82               | 14          |
| 9     | L2 | 3-CIC6H4OH | 32             | 96          | 60               | 37          |
| 10    | L3 | 3-CIC6H4OH | 41             | 98          | 45               | 63          |
| 11    | L4 | 3-CIC6H4OH | 2              | –           | 90               | –           |
| 12    | L5 | 3-CIC6H4OH | 48             | 98          | 28               | 86          |

Using 1a (0.5 mmol), PhSiH3 (0.75 mmol), L-FeCl2 (5 mol %), NaBHEt3 (15 mol %) and dioxane (0.5 M).

Yields were determined by 1H NMR analysis based on 1a and ee value was determined by chiral HPLC. Unless noted, the ratio of Z/E was around 20/1.

Using Ph2SiH2 instead of PhSiH3, affording 14% yield of dienes without silicon group and 37% yield of hydrogenation products.

Z/E = 13/1.
excellent enantioselectivities, and recover chiral VCPs in moderate to excellent yields with moderate to excellent enantioselectivities (Keith et al., 2001; Vedejs and Jure, 2005; Muller and Schreiner, 2011; Miller and Sarpong, 2011; Gao et al., 2014; Xiao et al., 2016; Hu et al., 2016; Das et al., 2017; Shimoda and Yamamoto, 2017; Jones et al., 2019; Brauns and Cramer, 2019; Zheng et al., 2019; Denget al., 2019; Wu et al., 2019; Rajkumar et al., 2019).

To demonstrate the utility of this method, a gram-scale reaction could be carried out to afford 2ag in 41% yield with 14/1 Z/E, 95% ee and recover chiral 1a in 13% yield with 98% ee (Scheme 1A). The further derivatizations of products were illustrated in Scheme 1B. The Fleming-Tamao oxidation of 2a delivered chiral allylic alcohol 3 in 90% yield with 97% ee (Wen et al., 2019). The absolute configuration was confirmed by X-ray diffraction of 3. Obviously, the Hosomi-Sakurai reaction of 2a with selectfluor and meta-chloroperoxybenzoic acid gave 4 and 5 in 85% and 88% yields with 1.2/1 and 6/1 dr, respectively (Hayashi et al., 1984; Thibaud and Gouverneur, 2003; Tredwell et al., 2008). Moreover, the hydroxylation of n-hexyne with silane 2a accessed a tertiary silane with silicon-stereocenter 6 in 88% yield with 7/1 dr (Cheng et al.,

Table 2. Substrate Scope

| Reaction conditions: 1 (0.5 mmol), PhSiH3 (0.75 mmol), L5: FeCl2 (5 mol %), NaBH4Et3 (15 mol %), 3-CiC6H4OH (15 mol %) and dioxane (0.5 M), r.t. Isolated yield of Z-isomer. The ratio of Z/E and recovery of 1 were determined by 1H NMR analysis and ee value was determined by chiral HPLC. Unless noted, the ratio of Z/E was better than 10/1. |

| Substrate | Z/E | Recovery of 1 | ee |
|-----------|-----|---------------|----|
| 2a        | 8/1 | 95%           | 98% ee |
| 2b        | 10/1| 90%           | 95% ee |
| 2c        | 4/1 | 88%           | 94% ee |
| 2d        | 3/1 | 85%           | 90% ee |
| 2e        | 6/1 | 88%           | 93% ee |
| 2f        | 7/1 | 88%           | 92% ee |
| 2g        | 9/1 | 90%           | 97% ee |
| 2h        | 10/1| 95%           | 98% ee |
| 2i        | 3/1 | 85%           | 91% ee |
| 2j        | 6/1 | 88%           | 92% ee |
| 2k        | 7/1 | 88%           | 93% ee |
| 2l        | 9/1 | 90%           | 97% ee |
| 2m        | 10/1| 95%           | 98% ee |
| 2n        | 3/1 | 85%           | 90% ee |
| 2o        | 6/1 | 88%           | 91% ee |
| 2p        | 7/1 | 88%           | 92% ee |
| 2q        | 9/1 | 90%           | 97% ee |
| 2r        | 10/1| 95%           | 98% ee |
| 2s        | 3/1 | 85%           | 91% ee |
| 2t        | 6/1 | 88%           | 92% ee |
| 2u        | 7/1 | 88%           | 93% ee |
| 2v        | 9/1 | 90%           | 97% ee |
| 2w        | 10/1| 95%           | 98% ee |
| 2x        | 3/1 | 85%           | 91% ee |
| 2y        | 6/1 | 88%           | 92% ee |
| 2z        | 7/1 | 88%           | 93% ee |
| 2A        | 9/1 | 90%           | 97% ee |
| 2B        | 10/1| 95%           | 98% ee |
| 2C        | 3/1 | 85%           | 91% ee |
| 2D        | 6/1 | 88%           | 92% ee |
| 2E        | 7/1 | 88%           | 93% ee |
| 2F        | 9/1 | 90%           | 97% ee |
| 2G        | 10/1| 95%           | 98% ee |
| 2H        | 3/1 | 85%           | 91% ee |
| 2I        | 6/1 | 88%           | 92% ee |
| 2J        | 7/1 | 88%           | 93% ee |
| 2K        | 9/1 | 90%           | 97% ee |
| 2L        | 10/1| 95%           | 98% ee |
| 2M        | 3/1 | 85%           | 91% ee |
| 2N        | 6/1 | 88%           | 92% ee |
| 2O        | 7/1 | 88%           | 93% ee |
| 2P        | 9/1 | 90%           | 97% ee |
| 2Q        | 10/1| 95%           | 98% ee |
| 2R        | 3/1 | 85%           | 91% ee |
| 2S        | 6/1 | 88%           | 92% ee |
| 2T        | 7/1 | 88%           | 93% ee |
| 2U        | 9/1 | 90%           | 97% ee |
| 2V        | 10/1| 95%           | 98% ee |
| 2W        | 3/1 | 85%           | 91% ee |
| 2X        | 6/1 | 88%           | 92% ee |
| 2Y        | 7/1 | 88%           | 93% ee |
| 2Z        | 9/1 | 90%           | 97% ee |

4  iScience 23, 100985, April 24, 2020
The cross-coupling reaction of 2a with phenylmagnesium bromide afforded 7 in 90% yield with 98% ee (Hirone et al., 2010).

Two control experiments were conducted to elucidate the possible reaction pathway (Scheme 2, eq. 1 and 2). The reaction of (S,S)-1a under standard conditions afforded (S,Z)-2a in 94% yield with >99% ee (Scheme 2, eq. 1), whereas the reaction of (S,S)-1a under standard conditions using R-L5·FeCl2 as precatalyst afforded 2a in 12% yield with a 2/3 ratio of Z/E and 46% recovery of (S,S)-1a. The diene (Z,E)-8a was observed as a side product, which also demonstrated the reason of poor recovery (scheme 2, eq. 2). These two control experiments well indicated the phenomenon of “matched and mismatched” between the substrate and iron precatalyst.

Inspired by the control experiments and the previously reported literatures on metal-silyl species (Wei and Darcel, 2019; Randolph and Wrighton, 1986; Lee et al., 2010; Lee and Peters, 2011; Tondreau et al., 2012; Zhang et al., 2014; Jia and Huang, 2016) and hydrosilylation (Chen et al., 2015, 2019; Xi and Lu, 2016; Guo et al., 2017, 2019; Cheng et al., 2019; Sun and Deng, 2016; Du and Huang, 2017; Trost and Ball, 2001; Mo et al., 2014; Ding et al., 2015; Du et al., 2016; Schuster et al., 2016; Pappas et al., 2016; Wang et al., 2017; Gribble et al., 2017; Liu et al., 2018; Wen et al., 2018; Zhan et al., 2018; Hu et al., 2019), we proposed that the iron-silyl species might promote this new 1,5-selective type of hydrosilylation of VCPs, which was different from the hydroboration of VCPs through iron-hydride species. The possible mechanism was proposed (Figure 2). The iron-silyl species is generated from OIP·FeCl2 in the presence of NaBHEt3, 3-chlorophenol, and silanes (Teo et al., 2017). In the matched catalytic
cycle, 1,2-insertion of (S,S)-1a into the iron-silicon bond delivers the tertiary alkyl iron species A. Subsequent β-carbon elimination generates the primary alkyl iron species B. Iron species B undergoes σ-bond metathesis with hydrosilane to access the product and regenerate iron silyl species. The mismatched catalytic cycle was discussed in Supplemental Information.

Figure 2. Proposed Mechanism

Figure 3. Free Energy Diagram for the Most Favorable Reaction Pathway for 1,5-Selective Hydrosilylation of 1a
The proposed mechanism is also supported by density functional theory (DFT) calculations. The computed free energy changes of the most favorable pathway for iron-catalyzed 1,5-selective hydrosilylation of VCP 1a with OIP ligand L2 are shown in Figure 3. From the (OIP)Fe-silyl active species int1, alkene coordinates to allow the subsequent alkene insertion via TS3. This generates the tertiary alkyl-iron intermediate int4, which undergoes the proposed β-carbon elimination through TS5 to give the primary alkyl-iron intermediate int6. From int6, the 1,5-selective hydrosilylation product 2a is produced through a σ-bond metathesis via TS7, accompanied by the regeneration of int1. Based on the free energy changes of the whole catalytic cycle, the irreversible alkene insertion determines the overall regioselectivity of hydrosilylation.

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We next explored the regioselectivity of alkene insertion, and the energies and optimized structures of the competing insertion transition states (TS3 and TS8) are shown in Figure 4. TS3 is 13.8 kcal/mol more favorable than TS8, which is consistent with the experimental observations of the exclusive 1,5-selective hydrosilylation. The distortion/interaction analysis (Bickelhaupt and Houk, 2017) is performed to further elucidate the origins of regioselectivity. The distortion energies $\Delta E_{\text{dist}}$ are the energy penalty associated with the geometric change from the ground state to the corresponding geometry in alkene insertion transition state. $\Delta E_{\text{int}}$ reflects the strength of interaction between the two distorted fragments in the transition state. $\Delta E_{\text{dist-sub}}$ is the leading cause that differentiates the two transition states. This is due to the steric repulsions between the inserting VCP substrate and OIP ligand in TS8. The closest H-H distances between the substrate and ligand are highlighted in Figure 4. Therefore, the sterically demanding OIP ligand forces the anti-Markovnikov insertion of VCP, leading to the excellent regioselectivity of hydrosilylation.

Conclusion
In summary, we have first developed an iron-catalyzed asymmetric anti-Markovnikov-selective hydrosilylation of vinylcyclopropanes via stereospecific C-C bond cleavage. The addition of 3-chlorophenol has been found to promote the formation of proposed iron silyl species to accelerate the reaction. The transformation with a wide range of VCPs and silanes proceeds through a kinetic resolution pathway to generate the
chiral allylic silanes in excellent ee and recover chiral VCPs in moderate to excellent ee. The chiral allylic silanes can be used in the Hosomi-Sakurai reaction, hydrosilylation, and cross-coupling reaction. An iron-silyl species was proposed based on experimental and computational studies. The studies on novel difunctionalization of VCPs are underway in our laboratory.

Limitations of Study
In this study, the scope of substrate is well explored but the vinylcyclopropanes with alkyl-substituents on alkene did not work. It is still a challenge for the highly enantioselective earth abundant metal-catalyzed hydrosilylation of 1,1-disubstituted alkenes with alkyl substituents.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

DATA AND CODE AVAILABILITY
The crystallography data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under accession number CCDC: 1900765 (3) and can be obtained free of charge from www.ccdc.cam.ac.uk/getstructures.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.100985.

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AUTHOR CONTRIBUTIONS
Z.L. conceived and designed the study. X.H. designed the computational studies. Z.L. and C.C. co-wrote the paper. X.H. and H.W. wrote the computational part of the manuscript. C.C. principally performed the experiments. H.W. performed the computational studies. Y.S., J.C., J.X., Y.S., and S.Y. helped to conduct some experiments and collect data.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental Information

Iron-Catalyzed Asymmetric Hydrosilylation of Vinylcyclopropanes via Stereospecific C-C Bond Cleavage

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Transparent Methods

A. General Information

Ether, THF, and dioxane were distilled from sodium benzophenone ketyl prior to use. NaHBEt₃ (1.0 M in THF) and FeCl₂ (99.7%) were purchased from Aldrich and used as received. Pd(OAc)₂ (99%) were purchased from stem and used as received. The other commercially available chemicals were used as received. NMR spectra were recorded on Bruker-400 instrument and WNMR-I 400 instrument. ¹H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), ¹³C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, CDCl₃), ¹⁹F NMR chemical shifts were referenced to the solvent resonance. The following abbreviations (or combinations) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m= multiplet, br = broad, q = quadruplet. HPLC analyses were performed on a Shimadzu SPD-20A. High-resolution mass spectra (HRMS) were recorded on Waters GCT Premier (EI) and Waters XEVO (ESI). IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. The X-ray diffraction data was obtained on Rigaku Gemini A Ultra. Optical rotation data was obtained on PerkinElmer Model 341 Polarimeter. Melting point data was obtained on WRR melting point apparatus.

B. Computational Details

All DFT calculations were performed using Gaussian 09 program (Frisch et al., 2013). Geometry optimizations were carried out using B3LYP (Lee et al., 1988; Becke, 1993; Stephens et al., 1994) -D3 (Becke-Johnson damping function) (Grimme et al., 2010; Grimme et al., 2011) functional, with def2-SVP basis set (Schäfer et al., 1992) for all elements. The vibrational frequency was calculated at the same level of theory to identify each optimized stationary point as an energy minimum or a transition state, and to evaluate the zero-point vibrational energy and thermal corrections at 298 K. Based on the gas-phase optimized structures, the single-point energies and solvent effects of dioxane were calculated using B3LYP-D3 functional and def2-TZVP basis set for all elements, using the SMD solvent model (Marenich et al., 2009). The 3D diagrams of computed species were generated by CYLView (Legault, 2009). In order to adjust the Gibbs free energies from 1 atm to 1 mol/L, a correction of RTln(c_i/c_g) (1.9 kcal/mol) is added to energies of all species. c_i is the standard molar
concentration in solution (1 mol/L), \( c_g \) is standard molar concentration in gas phase (0.040876 mol/L), and \( R \) is the gas constant.

C. Experimental procedures

L1, L2, L3, L4, L5 and L-FeCl2 complexes were prepared according to the previously reported procedure in our group (Chen et al., 2014; Chen et al., 2014; Xi et al., 2015; Guo et al., 2016).

**Synthesis of imine:** 1-(6-bromopyridin-2-yl)ethan-1-one (1.0 equiv.), aniline (1.0 equiv.), \( p \)-toluenesulfonic acid monohydrate (10 mol %) and toluene (0.5 M) was mixed in a 500 mL three-necked round-bottom flask. The reaction mixture was refluxed at 110-130 °C until the starting material disappeared (monitored by TLC with PE/EA (10/1)). The reaction mixture was filtered and washed with petroleum ether. The combined solution was concentrated in vacuo and further purified by crystallized from ethanol.

**Synthesis of oxazoline:** amino alcohol (1.0 equiv.), \( N,N \)-dimethylformamide dimethyl acetal (DMF-DMA, 1.2 equiv.), IR-120 (9 wt %) and toluene (0.4-0.5 M) was mixed in a 500 mL three-necked round-bottom flask. The reaction mixture was refluxed at 110-130 °C until the starting material disappeared. The reaction mixture was washed with saturated NaHCO3, brine, dried over \( \text{Na}_2\text{SO}_4 \), concentrated by rotary evaporation and further purified by distillation.

**Synthesis of OIP ligand:** to a flame-dried Schlenk tube were added oxazoline (1.2 equiv.), \( \text{Pd(OAc)}_2 \) (2.5 mol %), dppe (2.8 mol %) and \( \text{tBuOLi} \) (2.0 equiv.) under \( \text{N}_2 \). The tube was degassed with \( \text{N}_2 \) three times, and imine (1.0 equiv.) and anhydruous 1,4-dioxane (0.2 M) were added in sequence. The reaction mixture was stirred in an oil bath at 100 °C for 24 h until the starting material disappeared (monitored by TLC with PE/EA (10/1)). The reaction mixture was then cooled to room temperature, filtered through a pad of silica gel and washed by dichloromethane (10 mL x 3). The combined solution was concentrated in vacuo and further purified by flash chromatography on silica.
gel (PE/EA/Et₃N).

**Synthesis of iron catalyst:** to a flame-dried Schlenk tube were added OIP ligand (1.02 equiv.), anhydrous FeCl₂ (1.0 equiv.) and THF (0.1 M) under N₂. The reaction mixture was stirred at room temperature for 3 h, then ether (0.1 M) was injected to precipitate the complex and stirred for 30 min. The resulting mixture was filtered, washed with ether and dried in vacuo to give the iron catalyst.

![Chemical reaction diagram]

**1a-1ac** were prepared according to the previously reported procedure in our group (Chen et al., 2017).

**Synthesis of vinylcyclopropanes:** acetophenone (100 mmol) was dissolved in ethanol (150 mL) in a 500 mL round-bottom flask and cooled to 0 °C, a solution of sodium hydroxide (200 mmol) in water (60 mL) was added. Then the solution of alcohol (150 mL) containing benzaldehyde (100 mmol) was added drop wise with stirring over a period of 10 min. The reaction mixture was stirred at room temperature for about 4-12 h until the starting material disappeared (monitored by TLC with PE/EA (10/1)). The reaction mixture was concentrated by rotary evaporation and extracted with DCM (50 mL x 3). The combined organic layers were washed with saturated NaHCO₃ and then brine, dried over Na₂SO₄, concentrated by rotary evaporation and further purified by flash chromatography on silica gel or crystallized from ethanol.

Me₃SOI (1.2 equiv.) and NaH (1.2 equiv., 60% dispersion in mineral oil) was mixed in a 250 mL three-necked flame-dried round-bottom flask under the atmosphere of nitrogen. 150 mL of DMSO were added dropwise and stirred at room temperature for 30 min. Then chalcone was added in portion and stirred at room temperature for about 4-12 h until the starting material disappeared (monitored by TLC with PE/EA (10/1)). The mixture was then treated with water (150 mL) and extracted with DCM (50 mL x 3). The combined organic layers were washed with water (50 mL x 2) and saturated NaHCO₃ (50 mL x 2) and then brine, dried over Na₂SO₄, concentrated by rotary evaporation and further purified by flash chromatography on silica gel or crystallized from ethanol.
A 250 mL of three-necked flame-dried round-bottom flask was cooled at room temperature under the atmosphere of nitrogen, charged with Methyltriphenylphosphonium bromide (1.2 equiv.), NaH (1.3 equiv., 60% dispersion in mineral oil), THF (150 mL). The mixture was refluxed at 80°C for 1 h and then cooled to 0 °C, a solution of cyclopropyl ketone in THF (20 mL) was added dropwise and continued to reflux for about 4-12 h until the starting material disappeared (monitored by TLC with PE). The reaction was quenched by 1.0 mL saturated NH₄Cl, concentrated by rotary evaporation and filtrated on silica gel. The combined filtrates were concentrated by rotary evaporation and further purified by flash chromatography on silica gel.

Synthesis of phenylsilane (S2a): prepared according to the previously reported procedure (Sakurai et al., 1984), a 1000 mL of three-necked flame-dried round-bottom flask was cooled at -20 °C under the atmosphere of nitrogen, charged with lithium aluminum hydride (28.90 g, 750 mmol) and ether (400 mL). Phenyltrichlorosilane (80 mL, 500 mmol) dissolved in 200 mL ether was added dropwise. The mixture was stirred at room temperature for 12 h and then cooled to -20 ºC, quenched with water (100 mL), extracted with ether (50 mL x 3). The organic layers were combined, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The resulting oil was purified via distillation to give 42.27 g (393.4 mmol, 79% yield) of the title compound as a colorless oil.

Synthesis of other silanes: prepared according to the previously reported procedure (Visco et al., 2016), a 250 mL of three-necked flame-dried round-bottom flask was cooled at -20 °C under the atmosphere of nitrogen, charged with magnesium turnings (1.05 equiv.), several iodine crystals and THF (10 mL). bromide (50 mmol, 1.0 equiv.) dissolved in 40 mL THF was added dropwise over 30 min. After completing addition of bromide, the mixture was refluxing for another one hour. The resulting Grignard reagent was cooled to room temperature and added dropwise to a solution of Si(OMe)₄ (3.0 equiv.) and ether (100 mL) at 0 °C. After finishing addition, the mixture was warm to room temperature and stirred overnight. The reaction was quenched with water (10 mL), extracted...
with ether (50 mL x 3). The organic layers were combined, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The mixture (S2-1) was used in next step after removing excess Si(OMe)₄ by distillation.

A 500 mL of three-necked flame-dried round-bottom flask was cooled at 0 °C under the atmosphere of nitrogen, charged with lithium aluminium hydride (1.5 equiv.) and ether (150 mL). S2-1 dissolved in 50 mL ether was added dropwise carefully at 0 °C and stirred at room temperature overnight. The reaction mixture was then diluted with 200 mL of PE, stirred for 30 min, filtered through Celite and concentrated in vacuo. The resulting residue was diluted with an additional 200 mL of PE, filtered through Celite and concentrated in vacuo. The resulting oil was purified via distillation to give the corresponding compound.

Asymmetric hydrosilylation of vinylcyclopropanes: to a 25 mL flame-dried Schlenk flask cooled under nitrogen, [L5-FeCl₂ complex (0.025 mmol, 5 mol%) and vinylcyclopropane (0.5 mmol, 1.0 equiv.)] were added. The mixture was vacuumed and flushed with nitrogen for three times, and then 1.0 mL of dioxane (0.5 M) containing 5 mol% of 3-chlorophenol (0.075 mmol) and silane (0.75 mmol, 1.5 equiv.) were added in sequence. The mixture was injected with NaBHEt₃ (1.0 M in THF, 75 μL, 0.075 mmol) by dropwise. The reaction was run at ambient temperature for 2 h. Then the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity (the ratio of Z/E) was monitored by ¹H NMR analysis. The resulting mixture was purified by flash column chromatography using PE as the eluent to give the corresponding product and recover the chiral vinylcyclopropane.
# Tables and Figures

**Table S1.** Optimization for asymmetric hydrosilylation of vinylecyclopropanes.\(^a\) Related to Table 1.

| entry | ligands | additives | yield of 2a (%)\(^b\) | \(Z/E\)\(^b\) | \(ee\) of 2a (%)\(^b\) | recovery of 2a (%)\(^b\) | yield of \((Z,E)\)-8a (%)\(^b\) | yield of S3a (%)\(^b\) |
|-------|---------|-----------|----------------------|--------------|-----------------|---------------------|-------------------|-------------------|
| 1\(^c\) | L1 \(\cdot\) FeCl2 | - | 6 | - | - | 89 | - | <1 | 3 |
| 2\(^c,d\) | L1 \(\cdot\) FeCl2 | - | 0 | - | - | 48 | - | 0 | 37 |
| 3\(^c\) | L1 | H2O | 12 | - | - | 86 | - | <1 | <1 |
| 4 | L1 | PhOH | 28 | 20/1 | 98 | 65 | 34 | 5 | 3 |
| 5 | L1 | MeOCl\(\cdot\)H2O | 18 | 20/1 | 97 | 76 | 21 | 3 | 3 |
| 6 | L1 | 4-CIC\(\cdot\)H4OH | 30 | >20/1 | 98 | 62 | 38 | 5 | 3 |
| 7 | L1 | 3-CIC\(\cdot\)H4OH | 35 | 19/1 | 97 | 59 | 41 | 6 | 2 |
| 8 | L1 | 2-CIC\(\cdot\)H4OH | 15 | >20/1 | 98 | 82 | 14 | 2 | <1 |
| 9 | L2 | 3-CIC\(\cdot\)H4OH | 32 | 20/1 | 96 | 60 | 37 | 6 | 3 |
| 10 | L3 | 3-CIC\(\cdot\)H4OH | 41 | 19/1 | 98 | 45 | 63 | 11 | 3 |
| 11 | L4 | 3-CIC\(\cdot\)H4OH | 2 | - | - | 90 | - | 0 | 8 |
| 12 | L5 | 3-CIC\(\cdot\)H4OH | 50 | 13/1 | 98 | 28 | 86 | 18 | 4 |

\(^a\) Using 1a (0.5 mmol), PhSiH3 (0.75 mmol), L·FeCl2 (5 mol %), NaBHEt3 (15 mol %), additives
(15 mol %) and dioxane (0.5 M). Yields, recovery and ratio of Z/E were determined by \(^1\)H NMR analysis based on 1a, isolated yield was in the parenthesis and ee value was determined by chiral HPLC. \(^c\) 24 h. \(^d\) Using Ph\(_2\)SiH\(_2\) instead of PhSiH\(_3\), affording 14% yield of dienes without silicon group and 37% yield of hydrogenation products.

Entry 2: using Ph\(_2\)SiH\(_2\) instead of PhSiH\(_3\).
Table S2. Zero-point correction (ZPE), thermal correction to enthalpy (TCH), thermal correction to Gibbs free energy (TCG), energies (E), enthalpies (H), and Gibbs free energies (G) (in Hartree) of the structures for all the figures calculated at the B3LYP-D3(BJ)/def2-TZVP-SMD(dioxane)//B3LYP-D3(BJ)/def2-SVP level of theory. Spin states are shown in parentheses, Related to Figure 3.

| Structures        | ZPE   | TCH   | TCG   | E     | H     | G     | Imaginary Frequency |
|-------------------|-------|-------|-------|-------|-------|-------|---------------------|
| Int1(doublet)     | 0.587657 | 0.623888 | 0.519882 | -2920.263623 | -2919.639735 | -2919.743741 |                      |
| Int1(quadert)     | 0.587119 | 0.623417 | 0.518708 | -2920.259963 | -2919.636546 | -2919.741255 |                      |
| (S,S)-1a          | 0.277168 | 0.292318 | 0.232535 | -657.71446   | -657.422142  | -657.481925  |                      |
| 2a                | 0.39044  | 0.421186 | 0.342902 | -1180.865933 | -1180.444747 | -1180.523031 |                      |
| PhSiH3            | 0.115387 | 0.123326 | 0.083212 | -523.088626  | -522.9653    | -523.005414  |                      |
| Int2(doublet)     | 0.86992  | 0.920396 | 0.788193 | -3578.002525 | -3577.082809 | -3577.218525 |                      |
| Int2(quadert)     | 0.86449  | 0.918559 | 0.780368 | -3578.008611 | -3577.090052 | -3577.228243 |                      |
| TS3(doublet)      | 0.871965 | 0.921265 | 0.791429 | -3577.968384 | -3577.047119 | -3577.176955 | 87.8i               |
| TS3(quadert)      | 0.867333 | 0.918259 | 0.784545 | -3577.95015  | -3577.066756 | -3577.20047  | 153.7i              |
| Int4(doublet)     | 0.868098 | 0.919716 | 0.784   | -3578.002525 | -3577.082809 | -3577.218525 |                      |
| Int4(quadert)     | 0.866381 | 0.918178 | 0.777166 | -3578.012161 | -3577.093983 | -3577.234995 |                      |
| TS5(doublet)      | 0.86955  | 0.919307 | 0.784562 | -3577.971201 | -3577.051894 | -3577.186639 | 289.1i              |
| TS5(quadert)      | 0.865536 | 0.916545 | 0.778204 | -3577.981282 | -3577.064737 | -3577.203078 | 311.2i              |
| Int6(doublet)     | 0.867417 | 0.918593 | 0.781556 | -3578.026051 | -3577.107458 | -3577.244495 |                      |
| Int6(quadert)     | 0.866569 | 0.917983 | 0.779604 | -3578.019383 | -3577.1014   | -3577.239779 |                      |
| TS7(doublet)      | 0.987109 | 1.045466 | 0.894527 | -4101.099158 | -4100.053692 | -4100.204631 | 780.6i              |
| TS7(quadert)      | 0.982705 | 1.041923 | 0.887834 | -4101.100001 | -4100.058078 | -4100.212167 | 863.6i              |
| TS8(doublet)      | 0.86891  | 0.918589 | 0.788132 | -3577.943066 | -3577.024477 | -3577.154934 | 119.4i              |
| TS8(quadert)      | 0.866023 | 0.916803 | 0.783065 | -3577.961626 | -3577.044823 | -3577.178561 | 229.0i              |
The mismatched catalytic cycle: in the mismatched catalytic cycle (Figure S1), the iron-silyl species is generated from OIP·FeCl₂ in the presence of NaBHEt₃, 3-chlorophenol and silanes. Another tertiary alkyl iron species C is formed by 1,2-insertion of (R,R)-1a into the iron-silicon bond. Due to the overlarge steric hindrance, C tends to form iron species and carbon radical intermediate D through iron carbon bond cleavage. Then carbon radical intermediate D is generated through radical ring-opening pathway (Gui et al., 2015), coupling with iron species to deliver iron-silyl species F. β-Hydrogen elimination of iron-silyl species F generates (Z,E)-8a and iron-hydride species. Finally, iron-hydride species regenerates the iron-silyl species with silanes. Moreover, radical-radical coupling reaction between carbon radical intermediate D and iron species affords iron-silyl species C’. Subsequent β-carbon elimination generates the primary alkyl iron species B’. Iron species B’ undergoes δ-bond metathesis with hydrosilane to access R-2a and regenerate iron silyl species.

**Figure S1.** Proposed mechanism of the mismatched catalytic cycle, Related to Figure 2.
Figure S2 shows the protocol of distortion/interaction analysis using TS3 as an example. The optimized structure of TS3 is separated into two fragments: the (OIP)Fe-silyl catalyst fragment (cat) and the VCP substrate fragment (sub). The energies of these distorted fragments were computed at the B3LYP-D3(BJ)/def2-TZVP level, without the inclusion of solvation energy corrections. Comparing the energies of the distorted fragments and those of the corresponding optimized species, we obtained the distortion energies of the catalyst and substrate ($\Delta E_{\text{dist-sub}}$ and $\Delta E_{\text{dist-cat}}$). The interaction energy, $\Delta E_{\text{int}}$, is the difference between the total distortion energy and the electronic reaction barrier, $\Delta E_{\text{int}} = \Delta E^\ddagger - (\Delta E_{\text{dist-sub}} + \Delta E_{\text{dist-cat}})$.

Figure S2. Illustration of distortion/interaction analysis using TS3 as an example, Related to Figure 4.
Figure S3. $^1$H NMR spectra of SL3-1, Related to Table 1
Figure S4. $^{13}$C NMR spectra of SL3-1, Related to Table 1
Figure S5. $^1$H NMR spectra of R-SL5-1, Related to Table 1
Figure S6. $^{13}$C NMR spectra of R-SL5-1, Related to Table 1
Figure S7. $^1$H NMR spectra of L3, Related to Table 1
Figure S8. $^{13}$C NMR spectra of L3, Related to Table 1
Figure S9. $^1$H NMR spectra of SL5-1, Related to Table 1
Figure S10. $^{13}$C NMR spectra of SL5-1, Related to Table 1
Figure S11. $^1$H NMR spectra of L5, Related to Table 1
Figure S12. $^{13}$C NMR spectra of L5, Related to Table 1
Figure S13. $^1$H NMR spectra of $R$-L5, Related to Scheme 2
Figure S14. $^{13}$C NMR spectra of \textit{R-L5}, Related to Scheme 2
Figure S15. $^1$H NMR spectra of S1ab, Related to Table 2
**Figure S16.** $^{13}$C NMR spectra of S1ab, Related to Table 2
Figure S17. $^1$H NMR spectra of 1ab, Related to Table 2
Figure S18. $^{13}$C NMR spectra of 1ab, Related to Table 2
Figure S19. $^1$H NMR spectra of S1ac, Related to Table 2
Figure S20. $^{13}$C NMR spectra of S1ac, Related to Table 2.
Figure S21. $^1$H NMR spectra of 1ac, Related to Table 2
Figure S22. $^{13}$C NMR spectra of 1ac, Related to Table 2
Figure S23. $^1$H NMR spectra of S2a, Related to Table 2
Figure S24. $^1$H NMR spectra of S2b, Related to Table 2
Figure S25. $^1$H NMR spectra of S2c, Related to Table 2
Figure S26. $^1$H NMR spectra of S2d, Related to Table 2
Figure S27. $^1$H NMR spectra of S2e, Related to Table 2
Figure S28. $^1$H NMR spectra of S2f, Related to Table 2
Figure S29. $^1$H NMR spectra of S2g, Related to Table 2
Figure S30. $\text{^1H NMR spectra of S2h, Related to Table 2}$
Figure S31. $^1$H NMR spectra of S2i, Related to Table 2
Figure S32. $^1$H NMR spectra of $2a$, Related to Table 1
Figure S33. $^{13}$C NMR spectra of 2a, Related to Table 1
Figure S34. $^1$H NMR spectra of $2b$, Related to Table 2
Figure S35. $^{13}$C NMR spectra of 2b, Related to Table 2
Figure S36. $^1$H NMR spectra of 2c, Related to Table 2
Figure S37. $^{13}$C NMR spectra of 2c, Related to Table 2
Figure S38. $^1$H NMR spectra of 2d, Related to Table 2
Figure S39. $^{13}$C NMR spectra of 2d, Related to Table 2
Figure S40. $^1$H NMR spectra of 2e, Related to Table 2
Figure S41. $^{13}$C NMR spectra of 2e, Related to Table 2

- 163.154
- 160.712
- 146.299
- 139.270
- 139.236
- 135.176
- 134.407
- 132.256
- 131.829
- 129.788
- 128.462
- 128.124
- 128.047
- 127.982
- 126.971
- 126.008
- 114.980
- 114.768
- 77.318
- 77.000
- 76.682
- 38.921
- 22.556
- 15.262
Figure S42. $^{19}$F NMR spectra of 2e, Related to Table 2
Figure S43. $^1$H NMR spectra of 2f, Related to Table 2
Figure S44. $^{13}$C NMR spectra of 2f, Related to Table 2
Figure S45. $^1$H NMR spectra of 2g, Related to Table 2
Figure S46. $^{13}$C NMR spectra of 2g, Related to Table 2
Figure S47. $^1$H NMR spectra of 2g-ox, Related to Table 2
Figure S48. $^{13}$C NMR spectra of 2g-ox, Related to Table 2
Figure S49. $^1$H NMR spectra of 2h, Related to Table 2
Figure S50. $^{13}$C NMR spectra of 2h, Related to Table 2
Figure S51. $^1$H NMR spectra of 2i, Related to Table 2
Figure S52. $^{13}$C NMR spectra of 2i, Related to Table 2
Figure S53. $^{19}$F NMR spectra of 2i, Related to Table 2
Figure S54. $^1$H NMR spectra of 2j, Related to Table 2
Figure S55. $^{13}$C NMR spectra of 2j, Related to Table 2
Figure S56. $^{19}$F NMR spectra of 2j, Related to Table 2
Figure S57. $^1$H NMR spectra of 2j-ox, Related to Table 2.
Figure S58. $^{13}$C NMR spectra of 2j-ox, Related to Table 2
Figure S59. $^{19}$F NMR spectra of 2j-ox, Related to Table 2
Figure S60. $^1$H NMR spectra of 2k, Related to Table 2
Figure S61. $^{13}$C NMR spectra of 2k, Related to Table 2
Figure S62. $^1$H NMR spectra of 2l, Related to Table 2
Figure S63. $^{13}$C NMR spectra of 2I, Related to Table 2
Figure S64. $^1$H NMR spectra of 2m, Related to Table 2
Figure S65. $^{13}$C NMR spectra of 2m, Related to Table 2
Figure S66. 1H NMR spectra of 2n, Related to Table 2
Figure S67. $^{13}$C NMR spectra of 2n, Related to Table 2
Figure S68. $^{19}$F NMR spectra of 2n, Related to Table 2
Figure S69. $^1$H NMR spectra of 2o, Related to Table 2
Figure S70. $^{13}$C NMR spectra of 2o, Related to Table 2
Figure S71. $^1$H NMR spectra of 2p, Related to Table 2
Figure S72. $^{13}$C NMR spectra of 2p, Related to Table 2
Figure S73. $^1$H NMR spectra of 2q, Related to Table 2
Figure S74. $^{13}$C NMR spectra of $2q$, Related to Table 2
Figure S75. $^{19}$F NMR spectra of 2q, Related to Table 2
Figure S76. $^1$H NMR spectra of 2r, Related to Table 2
Figure S77. $^{13}$C NMR spectra of 2r, Related to Table 2
Figure S78. $^1$H NMR spectra of 2s, Related to Table 2
Figure S79. $^{13}$C NMR spectra of 2s, Related to Table 2
Figure S80. $^1$H NMR spectra of $2t$, Related to Table 2
Figure S81. $^{13}$C NMR spectra of 2t, Related to Table 2
Figure S82. $^1$H NMR spectra of 2u, Related to Table 2
Figure S83. $^{13}$C NMR spectra of 2u, Related to Table 2
Figure S84. $^1$H NMR spectra of 2v, Related to Table 2
Figure S85. $^{13}$C NMR spectra of 2v, Related to Table 2
Figure S86. $^1$H NMR spectra of 2w, Related to Table 2
Figure S87. $^{13}$C NMR spectra of 2w, Related to Table 2
Figure S88. $^1$H NMR spectra of 2x, Related to Table 2
Figure S89. $^{13}$C NMR spectra of 2x, Related to Table 2
Figure S90. $^1$H NMR spectra of 2x-ox, Related to Table 2
Figure S91. $^{13}$C NMR spectra of 2x-ox, Related to Table 2
Figure S92. $^1$H NMR spectra of 2y, Related to Table 2
Figure S93. $^{13}$C NMR spectra of 2y, Related to Table 2
Figure S94. $^1$H NMR spectra of 2y-ox, Related to Table 2
Figure S95. $^{13}$C NMR spectra of 2y-ox, Related to Table 2
Figure S96. $^1$H NMR spectra of 2z, Related to Table 2
Figure S97. $^{13}$C NMR spectra of 2z, Related to Table 2
Figure S98. $^1$H NMR spectra of 2z-ox, Related to Table 2
Figure S99. $^{13}$C NMR spectra of 2z-ox, Related to Table 2
Figure S100. $^1$H NMR spectra of 2aa, Related to Table 2
Figure S101. $^{13}$C NMR spectra of 2aa, Related to Table 2
Figure S102. $^1$H NMR spectra of 2aa-ox, Related to Table 2
Figure S103. $^{13}$C NMR spectra of 2aa-ox, Related to Table 2
Figure S104. $^1$H NMR spectra of 2ab, Related to Table 2
Figure S105. $^{13}$C NMR spectra of 2ab, Related to Table 2
Figure S106. $^1$H NMR spectra of 2ab-ox, Related to Table 2.
Figure S107. $^{13}$C NMR spectra of 2ab-ox, Related to Table 2
Figure S108. $^1$H NMR spectra of 2ac, Related to Table 2
Figure S109. $^{13}$C NMR spectra of 2ac, Related to Table 2
Figure S110. $^1$H NMR spectra of 2ac-ox, Related to Table 2
Figure S11. $^{13}$C NMR spectra of 2ac-ox, Related to Table 2
Figure S112. $^1$H NMR spectra of 2ad, Related to Table 2
Figure S113. $^{13}$C NMR spectra of 2ad, Related to Table 2
Figure S114. $^1$H NMR spectra of 2ae, Related to Table 2
Figure S115. $^{13}$C NMR spectra of 2ae, Related to Table 2
Figure S116. $^1$H NMR spectra of 2af, Related to Table 2
Figure S117. $^{13}$C NMR spectra of 2af, Related to Table 2
Figure S118. $^1$H NMR spectra of 2ag, Related to Table 2
Figure S119. $^{13}$C NMR spectra of 2ag, Related to Table 2
Figure S120. $^1$H NMR spectra of 2ah, Related to Table 2
Figure S121. $^{13}$C NMR spectra of 2ah, Related to Table 2
Figure S12. $^1$H NMR spectra of 2ai, Related to Table 2
Figure S123. $^{13}$C NMR spectra of 2ai, Related to Table 2
Figure S124. $^1$H NMR spectra of 2aj, Related to Table 2
Figure S125. $^{13}$C NMR spectra of $2aj$, Related to Table 2
Figure S126. $^1$H NMR spectra of 2ak, Related to Table 2
Figure S127. $^{13}$C NMR spectra of 2ak, Related to Table 2
Figure S128. $^1$H NMR spectra of 3, Related to Scheme 1
Figure S129. $^{13}$C NMR spectra of 3, Related to Scheme 1
Figure S130. $^1$H NMR spectra of (S,R)-4, Related to Scheme 1
Figure S131. $^{13}$C NMR spectra of (S,R)-4, Related to Scheme 1
Figure S132. $^{19}$F NMR spectra of (S,R)-4, Related to Scheme 1
Figure S133. NOE spectra of (S,R)-4, Related to Scheme 1
Figure S134. $^1$H NMR spectra of (R,R)-4, Related to Scheme 1
Figure S135. $^{13}$C NMR spectra of (R,R)-4, Related to Scheme 1
Figure S136. $^{19}$F NMR spectra of $(R,R)$-4, Related to Scheme 1
Figure S137. NOE spectra of (R,R)-4, Related to Scheme 1
Figure S138. $^1$H NMR spectra of 5, Related to Scheme 1
Figure S139. $^{13}$C NMR spectra of 5, Related to Scheme 1
Figure S140. $^1$H NMR spectra of 6, Related to Scheme 1
Figure S141. $^{13}$C NMR spectra of 6, Related to Scheme 1
Figure S142. $^1$H NMR spectra of 7, Related to Scheme 1
Figure S143. $^{13}$C NMR spectra of 7, Related to Scheme 1
Figure S144. NOE spectra of (S,Z)-2a, Related to Scheme 2
Figure S145. $^1$H NMR spectra of (S,E)-2a, Related to Scheme 2
Figure S146. $^{13}$C NMR spectra of (S,E)-2a, Related to Scheme 2
Figure S147. NOE spectra of (S,E)-2a, Related to Scheme 2
Figure S148. $^1$H NMR spectra of (Z,E)-8a, Related to Scheme 2
Figure S149. $^{13}$C NMR spectra of (Z,E)-8a, Related to Scheme 2
Figure S150. NOE spectra of (Z,E)-8a, Related to Scheme 2
| Chinese characters | English               |
|--------------------|-----------------------|
| 分析日期            | Date of Analysis      |
| 处理日期            | Date of Processing    |
| 描述                | HPLC Condition        |
| 色谱图              | HPLC Spectra          |
| 检测器              | Detector              |
| 峰表                | Area Percent Report   |
| 峰号                | Peak                  |
| 保留时间            | Remaining Time        |
| 面积                | Area                  |
| 高度                | Height                |
| 标记                | Note                  |
| 总计                | Total                 |
Figure S151. HPLC spectra of S-2a, Related to Table 1
Figure S152. HPLC spectra of (R,R)-1a, Related to Table 1
Figure S153. HPLC spectra of S-2b, Related to Table 2
Figure S154. HPLC spectra of (R,R)-1b, Related to Table 2
Figure S155. HPLC spectra of S-2c, Related to Table 2
Figure S156. HPLC spectra of (R,R)-1c, Related to Table 2
Figure S157. HPLC spectra of S-2d, Related to Table 2
Figure S158. HPLC spectra of (R,R)-1d, Related to Table 2
Figure S159. HPLC spectra of S-2e, Related to Table 2
Figure S160. HPLC spectra of (R,R)-1e, Related to Table 2
Figure S161. HPLC spectra of S-2f, Related to Table 2
Figure S162. HPLC spectra of (R,R)-1f, Related to Table 2
Figure S163. HPLC spectra of S-2g, Related to Table 2
Figure S164. HPLC spectra of (R,R)-1g, Related to Table 2
Figure S165. HPLC spectra of S-2h, Related to Table 2
**Figure S166.** HPLC spectra of (R,R)-1h, Related to Table 2
Figure S167. HPLC spectra of S-2i, Related to Table 2
Figure S168. HPLC spectra of (R,R)-1i, Related to Table 2.
Figure S169. HPLC spectra of S-2j, Related to Table 2
Figure S170. HPLC spectra of (R,R)-1j, Related to Table 2
Figure S171. HPLC spectra of S-2k, Related to Table 2
Figure S172. HPLC spectra of (R,R)-1k, Related to Table 2
**Figure S173.** HPLC spectra of S-2l, Related to Table 2
Figure S174. HPLC spectra of (R,R)-11, Related to Table 2
Figure S175. HPLC spectra of S-2m, Related to Table 2
Figure S176. HPLC spectra of (R,R)-1m, Related to Table 2
**Figure S177.** HPLC spectra of S-2n, Related to Table 2
Figure S178. HPLC spectra of (R,R)-1n, Related to Table 2
Figure S179. HPLC spectra of S-2o, Related to Table 2
**Figure S180.** HPLC spectra of (R,R)-10, Related to Table 2
Figure S181. HPLC spectra of S-2p, Related to Table 2
Figure S182. HPLC spectra of (R,R)-1p. Related to Table 2
Figure S183. HPLC spectra of S-2q, Related to Table 2
Figure S184. HPLC spectra of (R,R)-1q. Related to Table 2
**Figure S185.** HPLC spectra of S-2r, Related to Table 2
Figure S186. HPLC spectra of (R,R)-1r, Related to Table 2
Figure S187. HPLC spectra of S-2s, Related to Table 2
Figure S188. HPLC spectra of (R,R)-1s, Related to Table 2
Figure S189. HPLC spectra of S-2t, Related to Table 2
Figure S190. HPLC spectra of (R,R)-1t, Related to Table 2
Figure S191. HPLC spectra of S-2u, Related to Table 2
**Figure S192.** HPLC spectra of (R,R)-1u, Related to Table 2
Figure S193. HPLC spectra of S-2v, Related to Table 2
Figure S194. HPLC spectra of (R,R)-1v, Related to Table 2
Figure S195. HPLC spectra of S-2w, Related to Table 2
**Figure S196.** HPLC spectra of (R,R)-1w, Related to Table 2
Figure S197. HPLC spectra of S-2x, Related to Table 2
Figure S198. HPLC spectra of (R,R)-1x, Related to Table 2
Figure S199. HPLC spectra of S-2y, Related to Table 2
Figure S200. HPLC spectra of (R,R)-1y, Related to Table 2
Figure S201. HPLC spectra of S-2z, Related to Table 2
Figure S202. HPLC spectra of (R,R)-1z, Related to Table 2
Figure S203. HPLC spectra of S-2aa, Related to Table 2
Figure S204. HPLC spectra of (R,R)-1aa, Related to Table 2
Figure S205. HPLC spectra of S-2ab, Related to Table 2
Figure S206. HPLC spectra of (R,R)-1ab, Related to Table 2
Figure S207. HPLC spectra of S-2ac, Related to Table 2
Figure S208. HPLC spectra of (R,R)-1ac, Related to Table 2
**Figure S209.** HPLC spectra of S-2ad, Related to Table 2
Figure S210. HPLC spectra of (R,R)-1a, Related to Table 2
Figure S211. HPLC spectra of S-2ae, Related to Table 2
Figure S212. HPLC spectra of (R,R)-1a, Related to Table 2
Figure S213. HPLC spectra of S-2af, Related to Table 2
**Figure S214.** HPLC spectra of (R,R)-1a, Related to Table 2
Figure S215. HPLC spectra of S-2ag, Related to Table 2
Figure S216. HPLC spectra of \((R,R)-1a\), Related to Table 2
Figure S217. HPLC spectra of S-2ah, Related to Table 2
Figure S218. HPLC spectra of (R,R)-1a, Related to Table 2
Figure S219. HPLC spectra of S-2ai, Related to Table 2
Figure S220. HPLC spectra of (R,R)-1a, Related to Table 2
Figure S221. HPLC spectra of S-2aj. Related to Table 2
Figure S222. HPLC spectra of (R,R)-1a, Related to Table 2
Figure S223. HPLC spectra of S-2ak, Related to Table 2
Figure S224. HPLC spectra of (R,R)-1a, Related to Table 2
Figure S225. HPLC spectra of S-2ag. Related to Scheme 1
Figure S226. HPLC spectra of (R,R)-1a, Related to Scheme 1
Figure S227. HPLC spectra of S-3, Related to Scheme 1
Figure S228. HPLC spectra of (S,R)-4, Related to Scheme 1
Figure S229. HPLC spectra of \((R,R)-4\), Related to Scheme 1
Figure S230. HPLC spectra of S-7, Related to Scheme 1
Figure S231. HPLC spectra of S-2a, Related to Scheme 2
Figure S232. HPLC spectra of (S,S)-1a, Related to Scheme 2
Data S1. Related to Table 1, Table 2, Scheme 1 and Scheme 2.

A. Data of Ligands and Metal Complexes

\((S)-4\text{-cyclohexyloxazoline (SL3-1)}\) Using 16.31 g (114 mmol) of (S)-2-amino-2-cyclohexylethan-1-ol (Podhajsky et al., 2011), 18.2 ml (137 mmol) of \(N,N\)-dimethylformamide dimethyl acetal, 1.47 g of IR-120 and 300 mL of toluene to give 11.52 g (75 mmol, 66% yield) of \(\text{SL3-1}\) as a colorless oil. Optical Rotation: \([\alpha]_{D}^{20} = -120.8\) (c 1.02, CHCl\(_3\)). IR (cm\(^{-1}\)): 2927, 2855, 1635, 1453, 1349. ¹H NMR (CDCl\(_3\), 400 MHz): \(\delta 6.83\) (s, 1H), 4.26-4.17 (m, 1H), 3.99-3.87 (m, 2H), 1.95-1.87 (m, 1H), 1.84-1.75 (m, 2H), 1.74-1.67 (m, 1H), 1.65-1.56 (m, 1H), 1.49-1.38 (m, 1H), 1.34-1.16 (m, 3H), 1.13-0.97 (m, 2H); ¹³C NMR (CDCl\(_3\), 100 MHz): \(\delta 154.0\), 70.5, 69.0, 42.4, 29.3, 29.0, 26.4, 26.0, 25.9. HRMS (EI) calculated for [C\(_9\)H\(_{15}\)NO]\(^+\) requires m/z 153.1154, found m/z 153.1153.

\((R)-4\text{-cyclohexyloxazoline (R-SL5-1)}\) Using 23.53 g (164 mmol) of (R)-2-amino-2-cyclohexylethan-1-ol (Podhajsky et al., 2011), 26.2 ml (197 mmol) of \(N,N\)-dimethylformamide dimethyl acetal, 2.11 g of IR-120 and 300 mL of toluene to give 9.17 g (60 mmol, 36% yield) of \(\text{R-SL5-1}\) as a colorless oil. Optical Rotation: \([\alpha]_{D}^{20} = +118.0\) (c 1.00, CHCl\(_3\)). IR (cm\(^{-1}\)): 2925, 2853, 1633, 1451, 1346. ¹H NMR (CDCl\(_3\), 400 MHz): \(\delta 6.80\) (d, \(J = 1.6\) Hz, 1H), 4.24-4.14 (m, 1H), 3.96-3.84 (m, 2H), 1.92-1.84 (m, 1H), 1.81-1.72 (m, 2H), 1.71-1.64 (m, 1H), 1.62-1.54 (m, 1H), 1.46-1.36 (m, 1H), 1.31-1.14 (m, 3H), 1.10-0.95 (m, 2H); ¹³C NMR (CDCl\(_3\), 100 MHz): \(\delta 153.9\), 70.4, 68.9, 42.3, 29.2, 28.9, 26.3, 25.9, 25.8. HRMS (EI) calculated for [C\(_9\)H\(_{15}\)NO]\(^+\) requires m/z 153.1154, found m/z 153.1152.

\((S,E)-1-(6-(4\text{-cyclohexyl-4,5-dihydrooxazol-2-yl})\text{pyridin-2-yl})\text{-N-(2,6-diisopropylphenyl)ethan-1-imine (L3)}\) Using 1.8209 g (5.1 mmol) of (S,E)-1-(6-bromopyridin-2-yl)-N-(2,6-diisopropylphenyl)ethan-1-imine (Chen et al., 2014), 1.0256 g (6.7 mmol) of \(\text{SL3-1}\), 0.0552
(E)-1-(6-bromopyridin-2-yl)-N-(3,5-diisopropyl-4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-imine (SL5-1)

Using 10.00 g (50 mmol) of 1-(6-bromopyridin-2-yl)ethan-1-one (Chen et al., 2014), 14.17 g (50 mmol) of 3,5-diisopropyl-4'-methoxy-[1,1'-biphenyl]-4-amine (Yoshida et al., 2018), 0.97 g (5.1 mmol) of p-toluenesulfonic acid monohydrate and 100 mL of toluene to give 16.04 g (34 mmol, 69% yield) of SL5-1 as a yellow solid, mp: 151.6-152.9 °C. IR (cm⁻¹): 2960, 1644, 1515, 1439, 1248. ¹H NMR (CDCl₃, 400 MHz): δ 8.33 (d, J = 7.4 Hz, 1H), 7.67 (dd, J = 7.8, 7.6 Hz, 1H), 7.60-7.53 (m, 3H), 7.33 (s, 2H), 7.01-6.95 (m, 2H), 3.86 (s, 3H), 2.79-2.68 (m, 2H), 2.23 (s, 3H), 1.19 (d, J = 4.2 Hz, 6H), 1.17 (d, J = 3.8 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 166.2, 158.7, 157.4, 145.1, 141.0, 138.8, 136.2, 136.0, 134.6, 129.2, 127.9, 121.6, 120.1, 114.1, 55.4, 28.4, 23.2, 22.9, 17.4. HRMS (EI) calculated for [C₂₆H₂₉BrN₂O⁺ requires m/z 464.1463, found m/z 464.1459.

(S,E)-1-(6-(4-cyclohexyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)-N-(3,5-diisopropyl-4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-imine (L5)

Using 2.11 g (4.5 mmol) of SL5-1, 0.8297 g g (0.25 mmol) of Pd(OAc)₂, 0.1225 g (0.31 mmol) of 1,2-bis(diphenylphosphino)ethane, 0.8168 g (10.2 mmol) of tBuOLi and 40 mL of 1,4-dioxane to give 1.6644 g (3.9 mmol, 76% yield) of L3 as a yellow solid, mp: 153.2-154.0 °C. Optical Rotation: [α]₂⁰D = -63.4 (c 1.05, CHCl₃). IR (cm⁻¹): 2962, 2925, 1643, 1573, 1455, 1369. ¹H NMR (CDCl₃, 400 MHz): δ 8.50 (dd, J = 8.0, 1.0 Hz, 1H), 8.18 (dd, J = 7.8, 1.0 Hz, 1H), 7.88 (dd, J = 8.0, 7.8 Hz, 1H), 7.18-7.14 (m, 2H), 7.12-7.07 (m, 1H), 4.54 (dd, J = 9.6, 8.4 Hz, 1H), 4.27 (dd, J = 8.2, 8.4 Hz, 1H), 4.21-4.13 (m, 1H), 2.76-2.67 (m, 2H), 2.28 (s, 3H), 2.08-2.00 (m, 1H), 1.88-1.55 (m, 5H), 1.31-1.07 (m, 17H); ¹³C NMR (CDCl₃, 100 MHz): δ 166.7, 162.5, 156.1, 146.3, 146.1, 136.9, 135.67, 135.66, 125.3, 123.6, 123.0, 122.9, 72.1, 71.1, 42.8, 29.7, 28.9, 28.2, 26.5, 26.0, 23.2, 22.8, 17.2. HRMS (EI) calculated for [C₂₈H₃₇N₃O⁺ requires m/z 431.2937, found m/z 431.2937.
(5.4 mmol) of **SL3-1**, 0.0267 g (0.12 mmol) of Pd(OAc)$_2$, 0.0536 g (0.13 mmol) of 1,2-bis(diphenylphosphino)ethane, 1.2244 g (15.3 mmol) of tBuOLi and 30 mL of 1,4-dioxane to give 1.7582 g (3.3 mmol, 72% yield) of **L5** as a yellow solid, mp: 186.3-187.6 °C. Optical Rotation: $[\alpha]_{20}^D = -55.5$ (c 1.00, CHCl$_3$). IR (cm$^{-1}$): 2960, 2925, 1642, 1572, 1515, 1458, 1368. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.51 (dd, $J = 8.0, 1.0$ Hz, 1H), 8.18 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.89 (dd, $J = 8.0, 7.8$ Hz, 1H), 7.58-7.53 (m, 2H), 7.33 (s, 2H), 7.01-6.96 (m, 2H), 4.54 (dd, $J = 9.8, 8.4$ Hz, 1H), 4.28 (dd, $J = 8.4, 8.6$ Hz, 1H), 4.22-4.14 (m, 1H), 3.86 (s, 3H), 2.81-2.72 (m, 2H), 2.33 (s, 3H), 2.09-2.00 (m, 1H), 1.84-1.55 (m, 4H), 1.35-1.05 (m, 18H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.0, 162.5, 158.7, 156.2, 146.1, 145.3, 136.9, 136.1, 134.6, 127.9, 125.3, 123.1, 121.6, 114.1, 72.1, 71.1, 55.3, 42.8, 29.7, 28.9, 28.3, 26.5, 26.0, 23.3, 22.9, 17.4. HRMS (El) calculated for [C$_{35}$H$_{43}$N$_3$O$_2$]$^+$ requires m/z 537.3355, found m/z 537.3357.

(R,E)-1-(6-(4-cyclohexyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)-N-(3,5-diisopropyl-4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-imine (**R-L5**) Using 0.4659 g (1.0 mmol) of **SL5-1**, 0.2163 g (1.2 mmol) of **R-SL5-1**, 0.0117 g (0.05 mmol) of Pd(OAc)$_2$, 0.0238 g (0.06 mmol) of 1,2-bis(diphenylphosphino)ethane, 0.3551 g (4.0 mmol) of tBuOLi and 6 mL of 1,4-dioxane to give 0.2830 g (0.53mmol, 53% yield) of **R-L5** as a yellow solid. IR (cm$^{-1}$): 2960, 2925, 1645, 1574, 1515, 1454, 1370. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.51 (dd, $J = 8.0, 1.0$ Hz, 1H), 8.19 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.89 (dd, $J = 8.0, 7.8$ Hz, 1H), 7.58-7.53 (m, 2H), 7.33 (s, 2H), 7.01-6.96 (m, 2H), 4.54 (dd, $J = 9.8, 8.4$ Hz, 1H), 4.28 (t, $J = 8.4$ Hz, 1H), 4.22-4.14 (m, 1H), 3.86 (s, 3H), 2.82-2.70 (m, 2H), 2.33 (s, 3H), 2.09-2.00 (m, 1H), 1.84-1.74 (m, 2H), 1.74-1.63 (m, 2H), 1.61-1.54 (m, 1H), 1.35-1.08 (m, 17H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.0, 162.5, 158.7, 156.2, 146.1, 145.3, 136.9, 136.1, 134.6, 127.9, 125.3, 123.1, 121.6, 114.1, 72.1, 71.1, 55.3, 42.8, 29.7, 28.9, 28.4, 26.5, 26.0, 23.3, 22.9, 17.4. HRMS (El) calculated for [C$_{35}$H$_{43}$N$_3$O$_2$]$^+$ requires m/z 537.3355, found m/z 537.3352.

**L3·FeCl$_2$** A 50 mL Schlenk flask was charged with 0.8253 g
(1.91 mmol) of \textbf{L3}, 0.2060 g (1.63 mmol) of \textit{FeCl$_2$} and 10 mL of THF under the atmosphere of nitrogen, then the mixture was stirred at room temperature for 3 h, then 10 mL of ether was injected to precipitate the complex and stirred for 30 min. The resulting mixture was filtered, washed with ether and dried in vacuo to give 0.7111 g (1.27 mmol, 78% yield) of blue powder. Anal. Calcd for C$_{28}$H$_{37}$Cl$_2$FeN$_3$O: C, 60.23; H, 6.68; N, 7.53; Found: C, 59.72; H, 6.90; N, 7.39.

\textit{L5}$ \cdot \textit{FeCl$_2$} \ A 50 \text{ mL} \text{ Schlenk flask was charged with 1.7582 g (3.27 mmol) of } \textbf{L5}, 0.4066 g (3.20 mmol) of \textit{FeCl$_2$} \text{ and } 33 \text{ mL of THF under the atmosphere of nitrogen, then the mixture was stirred at room temperature for 3 h, then 33 mL of ether was injected to precipitate the complex and stirred for 30 min. The resulting mixture was filtered, washed with ether and dried in vacuo to give 1.7111 g (2.58 mmol, 80% yield) of green powder. Anal. Calcd for C$_{35}$H$_{47}$Cl$_2$FeN$_3$O$_4$: C, 63.26; H, 6.52; N, 6.32; Found: C, 60.55; H, 6.48; N, 6.09.}

\textit{R-L5}$ \cdot \textit{FeCl$_2$} \ A 50 \text{ mL} \text{ Schlenk flask was charged with 0.5403 g (1.00 mmol) of } \textbf{R-L5}, 0.0.1261 g (0.99 mmol) of \textit{FeCl$_2$} \text{ and } 10 \text{ mL of THF under the atmosphere of nitrogen, then the mixture was stirred at room temperature for 4 h, then 10 mL of ether was injected to precipitate the complex and stirred for 30 min. The resulting mixture was filtered, washed with ether and dried in vacuo to give 0.5190 g (0.78 mmol, 79% yield) of green powder. Anal. Calcd for C$_{35}$H$_{47}$Cl$_2$FeN$_3$O$_4$: C, 63.26; H, 6.52; N, 6.32; Found: C, 61.82; H, 6.46; N, 6.00.}

\textbf{B. Data of Vinylcyclopropanes}

\textbf{(2-(adamantan-2-yl)cyclopropyl)(phenyl)methanone} \ (\textbf{S1ab}) \ Using 5.03 g (18.9 mmol) of \textit{(E)-3-(adamantan-2-yl)-1-phenylprop-2-en-1-one}
2-(2-(1-phenylvinyl)cyclopropyl)adamantane (1ab) Using 4.03 g (14.4 mmol) of S1ab to give 3.52 g (12.6 mmol, 88% yield) of 1ab. colorless oil; IR (cm⁻¹): 2902, 2849, 1621, 1493, 1451. ¹H NMR (CDCl₃, 400 MHz): δ 7.52 (d, J = 7.8 Hz, 2H), 7.35-7.22 (m, 3H), 5.18 (s, 1H), 4.92 (s, 1H), 2.16-2.00 (m, 2H), 1.97-1.92 (m, 1H), 1.88-1.81 (m, 5H), 1.76-1.72 (m, 2H), 1.70-1.63 (m, 2H), 1.63-1.56 (m, 2H), 1.47-1.40 (m, 1H), 1.40-1.33 (m, 1H), 0.99-0.92 (m, 1H), 0.79-0.73 (m, 1H), 0.67-0.61 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 150.1, 142.2, 128.0, 127.2, 126.2, 108.9, 50.8, 39.20, 39.18, 38.3, 32.8, 32.53, 32.49, 32.3, 28.23, 28.19, 24.0, 23.3, 14.2; HRMS (EI) calculated for [C₂₁H₂₆]⁺ requires m/z 278.2035, found m/z 278.2032.

(2-(adamantan-1-yl)cyclopropyl)(phenyl)methanone (S1ac) Using 22.95 g (86.2 mmol) of (E)-3-(adamantan-1-yl)-1-phenylprop-2-en-1-one (Wang et al., 2017) to give 8.25 g (29.4 mmol, 34% yield) of S1ac. colorless oil; IR (cm⁻¹): 2901, 1667, 1450, 1399, 1333, 1221. ¹H NMR (CDCl₃, 400 MHz): δ 8.03-7.99 (m, 2H), 7.58-7.53 (m, 1H), 7.50-7.44 (m, 2H), 2.65-2.60 (m, 1H), 1.98 (s, 3H), 1.76-1.61 (m, 6H), 1.52-1.48 (m, 6H), 1.46-1.40 (m, 1H), 1.36-1.31 (m, 1H), 1.11-1.06 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 200.7, 138.2, 132.5, 128.5, 127.9, 141.4, 39.6, 37.0, 31.6, 28.4, 19.5, 13.2; HRMS (EI) calculated for [C₂₀H₂₆O]⁺ requires m/z 280.1827, found m/z 280.1831.

1-(2-(1-phenylvinyl)cyclopropyl)adamantane (1ac) Using 8.25 g (29.4
mmol) of S1ac to give 3.80 g (13.7 mmol, 46% yield) of 1ac. colorless oil; IR (cm\(^{-1}\)): 2900, 2846, 1621, 1493, 1449. \(^1\)H NMR: (400 MHz, CDCl\(_3\)) \(\delta\) 7.56-7.51 (m, 2H), 7.35-7.29 (m, 2H), 7.29-7.23 (m, 1H), 5.18 (s, 1H), 4.89 (s, 1H), 1.96 (s, 3H), 1.74-1.58 (m, 7H), 1.53-1.45 (m, 6H), 0.84-0.77 (m, 2H), 0.55-0.48 (m, 1H); \(^1\)C NMR: (100 MHz, CDCl\(_3\)) \(\delta\) 150.3, 142.2, 128.0, 127.2, 126.3, 108.9, 41.6, 37.2, 33.6, 31.3, 28.6, 17.2, 8.6; HRMS (EI) calculated for [C\(_{21}\)H\(_{26}\)]\(^+\) requires m/z 278.2035, found m/z 278.2033.

C. Data of Silanes

**Phenylsilane (S2a)** (Sakurai et al., 1984) colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.61-7.66 (m, 2H), 7.43-7.32 (m, 3H), 4.20 (s, 3H).

**4-Methoxyphenylsilane (S2b)** (Visco et al., 2016) colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.53-7.49 (m, 2H), 6.93-6.89 (m, 2H), 4.18 (s, 3H), 3.81 (s, 3H).

**4-Chlorophenylsilane (S2c)** (Sakurai et al., 1984) colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.57 (d, \(J = 8.0\) Hz, 2H), 7.40 (d, \(J = 8.0\) Hz, 2H), 4.24 (s, 3H).

**\(\alpha\)-Tolylsilane (S2d)** (Banovetz et al., 1993) colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.60-7.55 (m, 1H), 7.35-7.30 (m, 1H), 7.21-7.14 (m, 2H), 4.20 (s, 3H), 2.44 (s, 3H).

**Naphthalen-1-ylsilane (S2e)** (Visco et al., 2016) colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.97-7.89 (m, 2H), 7.87-7.80 (m, 2H), 7.57-7.48 (m, 2H), 7.47-7.41 (m, 1H), 4.47 (s, 3H).

**Benzylsilane (S2f)** (Sakurai et al., 1984) colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.28-7.21 (m, 2H), 7.15-7.09 (m, 3H), 3.66 (t, \(J = 4.0\) Hz, 3H), 2.28 (q, \(J = 4.0\) Hz, 2H).
Phenethylsilane (S2g) (Sakurai et al., 1984) colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.32-7.25 (m, 2H), 7.22-7.15 (m, 3H), 3.55-3.49 (m, 3H), 2.80-2.71 (m, 2H), 1.16-1.07 (m, 2H).

(3-Phenylpropyl)silane (S2h) (Smirnov and Oestreich, 2016) colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.30-7.23 (m, 2H), 7.20-7.13 (m, 3H), 7.52-7.47 (m, 3H), 2.65 (t, $J$ = 8.4 Hz, 2H), 1.79-1.69 (m, 2H), 0.81-0.72 (m, 2H).

Dodecylsilane (S2i) (Rosenberg and Kobus, 2003) colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 3.48 (t, $J$ = 3.8 Hz, 3H), 1.34-1.20 (m, 20H), 0.88 (t, $J$ = 6.4 Hz, 3H), 0.78-0.70 (m, 2H).

D. Iron-Catalyzed Asymmetric Hydrosilylation of Vinylcyclopropanes

$(S,Z$)-(2,4-Diphenylpent-2-en-1-yl)(phenyl)silane (2a) Prepared according to the general procedure, using 0.1117 g (0.5 mmol) of $1a$, 96 µL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of L$_5\cdot$FeCl$_2$, 75 µL (1.0 M in THF, 0.075 mmol) of NaBH$_3$Et, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0795 g (0.24 mmol, 13/1 $E/Z$, 48% yield) of the title compound (Z) and recover chiral $1a$ in 28% NMR yield. $(R,R)$-$1a$: $86.4\%$ $ee$ determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.4 (major), 25.0 (minor). $2a$: colorless oil. Optical Rotation: $[\alpha]_{D}^{20}$ = +28.5 (c 1.03, CHCl$_3$), $98.0\%$ $ee$ determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.4 (minor), 23.0 (major). IR (cm$^{-1}$): 2962, 2144, 1599, 1492, 1428. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.50-7.45 (m, 2H), 7.40-7.33 (m, 3H), 7.33-7.24 (m, 6H), 7.24-7.20 (m, 3H), 7.20-7.14 (m, 1H), 5.76 (d, $J$ = 9.6 Hz, 1H), 4.29-4.21 (m, 2H), 3.72-3.63 (m, 1H), 2.44-2.29 (m, 2H), 1.31 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz):
\[ \delta 146.4, 143.2, 135.3, 135.2, 132.2, 132.1, 129.7, 128.4, 128.1, 128.0, 127.0, 126.9, 126.5, 125.9, 38.9, 22.6, 15.1. \] HRMS (EI) calculated for \([C_{23}H_{24}Si]^+\) requires m/z 328.1647, found m/z 328.1649.

\((S,Z)-(2-(4-Methoxyphenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane\) (2b) Prepared according to the general procedure, using 0.1253 g (0.5 mmol) of 1b, 96 \(\mu\)L (0.75 mmol, 1.5 equiv.) of PhSiH\(_3\), 0.0167 g (0.025 mmol) of \(L_5\cdot FeCl_2\), 75 \(\mu\)L (1.0 M in THF, 0.075 mmol) of NaBHEt\(_3\), and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by \(^1\)H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0741 g (0.21 mmol, 9/1 \(E/Z\), 41% yield) of the title compound (\(Z\)) and recover chiral 1b in 33% NMR yield. \((R,R)-1b\): 75.9% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 11.1 (major), 14.1 (minor). \(2b\): colorless oil. Optical Rotation: \([\alpha]_{D}^{20} = +31.6\) (c 0.98, CHCl\(_3\)), 96.0% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.4 (minor), 25.6 (major). IR (cm\(^{-1}\)): 2957, 2924, 2143, 1511, 1247. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta \) 7.49-7.45 (m, 2H), 7.38-7.32 (m, 3H), 7.32-7.24 (m, 4H), 7.22-7.17 (m, 1H), 7.15-7.10 (m, 2H), 6.84-6.78 (m, 2H), 5.73 (d, \(J = 9.6\) Hz, 1H), 4.30-4.21 (m, 2H), 3.76 (s, 3H), 3.68-3.57 (m, 1H), 2.44-2.28 (m, 2H), 1.28 (d, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta \) 157.8, 143.2, 138.5, 135.2, 135.0, 132.5, 132.1, 129.7, 128.1, 127.9, 127.8, 126.8, 126.5, 113.8, 55.2, 38.0, 22.7, 15.0. HRMS (EI) calculated for \([C_{24}H_{26}OSi]^+\) requires m/z 358.1753, found m/z 358.1756.

\((S,Z)-(2-(4-(Methylthio)phenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane\) (2c) Prepared according to the general procedure, using 0.1343 g (0.5 mmol) of 1c, 96 \(\mu\)L (0.75 mmol, 1.5 equiv.) of PhSiH\(_3\), 0.0166 g (0.025 mmol) of \(L_5\cdot FeCl_2\), 75 \(\mu\)L (1.0 M in THF, 0.075 mmol) of NaBHEt\(_3\), and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by
PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0785 g (0.21 mmol, 11/1 E/Z, 42% yield) of the title compound (Z) and recover chiral 1c in 19% NMR yield. (R,R)-1c: 94.9% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 11.4 (major), 15.7 (minor). 

2c: colorless oil. Optical Rotation: $[\alpha]_20^D = -25.2$ (c 1.03, CHCl$_3$), 98.1% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 12.3 (major), 19.8 (minor). IR (cm$^{-1}$): 2965, 2143, 1596, 1492, 1435. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.49-7.44 (m, 2H), 7.39-7.33 (m, 1H), 7.33-7.24 (m, 6H), 7.23-7.13 (m, 5H), 5.75 (d, 1H), 4.30-4.20 (m, 2H), 3.71-3.61 (m, 1H), 2.46 (s, 3H), 2.41-2.24 (m, 2H), 1.30 (d, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 146.4, 140.1, 136.8, 135.2, 134.7, 132.4, 131.9, 129.7, 128.4, 128.0, 127.0, 126.9, 126.6, 126.0, 38.9, 22.6, 16.0, 14.9. HRMS (ESI) calculated for [C$_{24}$H$_{27}$SSi]$^+$ (M + H$^+$) requires m/z 375.1603, found m/z 375.1603.

[(S,Z)-Phenyl(4-phenyl-2-(p-tolyl)pent-2-en-1-yl)silane] (2d) Prepared according to the general procedure, using 0.1172 g (0.5 mmol) of 1d, 96 µL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of L5·FeCl$_2$, 75 µL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0703 g (0.21 mmol, 17/1 E/Z, 41% yield) of the title compound (Z) and recover chiral 1d in 35% NMR yield. (R,R)-1d: 72.2% ee determined by HPLC, HPLC conditions: Chiralcel AD-H, nhexane/iPrOH = 98/2, 1.0 mL/min, n = 220 nm, tr 4.0 (major), 5.2 (minor). 2d: colorless oil. Optical Rotation: $[\alpha]_20^D = +16.7$ (c 1.04, CHCl$_3$), 97.2% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 8.5 (minor), 11.2 (major). IR (cm$^{-1}$): 2922, 2144, 1511, 1452, 1429. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.50-7.46 (m, 2H), 7.40-7.34 (m, 1H), 7.33-7.20 (m, 8H), 7.19-7.14 (m, 1H), 7.08 (d, $J$ = 7.8 Hz, 2H), 5.74 (d, $J$ = 9.4 Hz, 1H), 4.28-4.20 (m, 2H), 3.70-3.61 (m, 1H), 2.42-2.27 (m, 5H), 1.29 (d, $J$ = 7.2 Hz,
(S,Z)-(2-(4-Fluorophenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2e)
Prepared according to the general procedure, using 0.1192 g (0.5 mmol) of 1e, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH3, 0.0167 g (0.025 mmol) of L5·FeCl2, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by 1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0701 g (0.20 mmol, 11/1 E/Z, 40% yield) of the title compound (Z) and recover chiral 1e in 36% NMR yield. (R,R)-1e: 72.5% ee determined by HPLC, HPLC conditions: Chiralcel AD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 5.8 (major), 6.2 (minor). 2e: colorless oil. Optical Rotation: [α]20D = +28.9 (c 1.00, CHCl3), 96.1% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 9.3 (minor), 10.1 (major). IR (cm⁻¹): 2960, 2924, 2144, 1601, 1507, 1230. 1H NMR (CDCl3, 400 MHz): δ 7.48-7.43 (m, 2H), 7.40-7.34 (m, 1H), 7.33-7.25 (m, 6H), 7.25-7.15 (m, 3H), 6.98-6.90 (m, 2H), 5.69 (d, J = 9.4 Hz, 1H), 4.27-4.19 (m, 2H), 3.71-3.61 (m, 1H), 2.42-2.26 (m, 2H), 1.30 (d, J = 7.0 Hz, 3H); 13C NMR (CDCl3, 100 MHz): δ 162.0 (d, J = 246.4 Hz), 146.3, 139.3 (d, J = 3.4 Hz), 135.2, 134.4, 132.3, 131.8, 129.8, 128.5, 128.1 (d, J = 7.8 Hz), 128.0, 127.0, 126.0, 114.9 (d, J = 21.2 Hz), 38.9, 22.6, 15.3; 19F NMR (CDCl3, 376.5 MHz): δ -116.1. HRMS (EI) calculated for [C23H23FSi]+ requires m/z 346.1553, found m/z 346.1551.

(S,Z)-(2-(4-Chlorophenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2f)
Prepared according to the general procedure, using 0.1272 g (0.5 mmol) of 1f, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH3, 0.0168 g (0.025 mmol) of L5·FeCl2, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 1 h, the resulting solution
was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by \(^1\)H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0857 g (0.24 mmol, 11/1 E/Z, 47% yield) of the title compound (Z) and recover chiral 1f in 15% NMR yield. \((R,R)\)-1f: 97.7% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 10.5 (major), 15.0 (minor). 2f: colorless oil. Optical Rotation: \([\alpha]_D^20 = -2.1 (c 1.01, \text{CHCl}_3), 96.2% ee\) determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 21.8 (minor), 26.2 (major). IR (cm\(^{-1}\)): 2963, 2924, 2144, 1491, 1428. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta 7.46-7.41 (m, 2H), 7.39-7.33 (m, 1H), 7.31-7.14 (m, 11H), 5.73 (d, \text{J} = 9.4 \text{Hz}, 1H), 4.28-4.20 (m, 2H), 3.70-3.61 (m, 1H), 2.40-2.25 (m, 2H), 1.30 (d, \text{J} = 7.0 \text{Hz}, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 146.1, 141.6, 135.2, 134.3, 132.7, 132.6, 131.7, 129.8, 128.5, 128.2, 128.0, 127.8, 126.9, 126.0, 38.9, 22.5, 15.0. \) HRMS (EI) calculated for [C\(_{23}H_{23}ClSi\)]\(^+\) requires m/z 362.1258, found m/z 362.1259.

**(S,Z)**-\(2-(4\)-Bromophenyl\)-4-phenylpent-2-en-1-yl)(phenyl)silane

\((2g)\) Prepared according to the general procedure, using 0.1510 g (0.5 mmol) of 1g, 96 \(\mu\)L (0.75 mmol, 1.5 equiv.) of PhSiH\(_3\), 0.0168 g (0.025 mmol) of L\(_5\)-FeCl\(_2\), 75 \(\mu\)L (1.0 M in THF, 0.075 mmol) of NaBHEt\(_3\), and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by \(^1\)H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0956 g (0.23 mmol, 18/1 E/Z, 47% yield) of the title compound (Z) and recover chiral 1g in 18% NMR yield. \((R,R)\)-1g: 95.5% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 9.0 (major), 12.8 (minor). 2g: colorless oil. Optical Rotation: \([\alpha]_D^20 = -5.5 (c 1.04, \text{CHCl}_3), 97.2% ee\) determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 7.4 (major), 9.6 (minor). IR (cm\(^{-1}\)): 3022, 2964, 2143, 1488, 1439. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta 7.47-7.42 (m, 2H), \)
7.41-7.34 (m, 3H), 7.33-7.25 (m, 4H), 7.22-7.15 (m, 5H), 5.74 (d, J = 9.6 Hz, 1H), 4.27-4.20 (m, 2H), 3.71-3.61 (m, 1H), 2.41-2.25 (m, 2H), 1.30 (d, J = 6.8 Hz, 3H); 13C NMR (CDCl₃, 100 MHz): δ 146.1, 142.1, 135.2, 134.4, 132.8, 131.7, 131.2, 129.8, 128.5, 128.2, 128.0, 127.0, 126.0, 120.7, 38.9, 22.5, 15.0. HRMS (EI) calculated for [C₂₃H₂₃BrSi]⁺ requires m/z 406.0752, found m/z 406.0750.

(S,Z)-2-(4-Bromophenyl)-4-phenylpent-2-en-1-ol (2g-ox)

Colorless oil. IR (cm⁻¹): 3360, 2973, 2908, 1486, 1394. ¹H NMR (CDCl₃, 400 MHz): δ 7.46-7.41 (m, 2H), 7.35-7.25 (m, 6H), 7.24-7.18 (m, 1H), 6.01 (d, J = 9.8 Hz, 1H), 4.58 (d, J = 2.8 Hz, 2H), 4.01-3.91 (m, 1H), 1.45 (d, J = 7.0 Hz, 3H), 1.30 (brs, 1H); 13C NMR (CDCl₃, 100 MHz): δ 145.8, 139.7, 137.7, 136.7, 131.5, 128.8, 128.1, 126.8, 126.4, 121.2, 59.9, 38.3, 22.7. HRMS (EI) calculated for [C₁₇H₁₇BrO]⁺ requires m/z 316.0463, found m/z 316.0460.

(S,Z)-Phenyl(4-phenyl-2-(m-tolyl)pent-2-en-1-yl)silane (2h)

Prepared according to the general procedure, using 0.1173 g (0.5 mmol) of 1h, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0165 g (0.025 mmol) of L₅·FeCl₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0688 g (0.20 mmol, 14/1 E/Z, 40% yield) of the title compound (Z) and recover chiral 1h in 34% NMR yield. ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0688 g (0.20 mmol, 14/1 E/Z, 40% yield) of the title compound (Z) and recover chiral 1h in 34% NMR yield. (R,R)-1h: 80.3% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 8.0 (major), 13.3 (minor).

2h: Colorless oil. Optical Rotation: [α]D₂₀ = +26.2 (c 1.03, CHCl₃), 97.9% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 6.0 (minor), 7.4 (major). IR (cm⁻¹): 2958, 2923, 2142, 1601, 1452, 1428. ¹H NMR (CDCl₃, 400 MHz): δ 7.50-7.45 (m, 2H), 7.40-7.35 (m, 1H), 7.34-7.25 (m, 4H), 7.25-7.21 (m, 2H), 7.20-7.12 (m, 4H), 7.05-7.01 (m, 1H), 5.75 (d, J = 9.6 Hz, 1H), 4.28-4.21 (m, 2H), 3.72-3.63 (m, 1H), 2.43-2.30 (m,
(S,Z)-(2-(3-Fluorophenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2i)

Prepared according to the general procedure, using 0.1206 g (0.5 mmol) of 1i, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH3, 0.0167 g (0.025 mmol) of L5·FeCl2, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 1 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by 1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0831 g (0.24 mmol, 12/1 E/Z, 47% yield) of the title compound (Z) and recover chiral 1i in 18% NMR yield. (R,R)-1i: 97.2% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 16.9 (major), 32.2 (minor). 2i: colorless oil. Optical Rotation: [α]D = +19.5 (c 1.04, CHCl3), 96.7% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 7.0 (minor), 8.8 (major). IR (cm⁻¹): 3024, 2964, 2143, 1582, 1488, 1438. 1H NMR (CDCl3, 400 MHz): δ 7.48-7.43 (m, 2H), 7.40-7.34 (m, 1H), 7.33-7.25 (m, 4H), 7.24-7.15 (m, 4H), 7.13-7.11 (m, 1H), 7.06-7.00 (m, 1H), 6.92-6.85 (m, 1H), 5.78 (d, J = 9.6 Hz, 1H), 4.29-4.22 (m, 2H), 3.71-3.62 (m, 1H), 2.41-2.25 (m, 2H), 1.30 (d, J = 7.0 Hz, 3H); 13C NMR (CDCl3, 100 MHz): δ 162.8 (d, J = 245.0 Hz), 146.1, 145.6 (d, J = 7.4 Hz), 135.2, 134.4 (d, J = 2.2 Hz), 133.1, 131.7, 129.8, 129.5 (d, J = 8.2 Hz), 128.5, 128.0, 127.0, 126.1, 122.2 (d, J = 2.2 Hz), 113.7 (d, J = 16.2 Hz), 113.4 (d, J = 17.0 Hz), 38.9, 22.5, 15.0; 19F NMR (CDCl3, 376.5 MHz): δ -113.6. HRMS (ESI) calculated for [C23H24FSi]+ (M + H+) requires m/z 347.1631, found m/z 347.1608.

(S,Z)-(2-(2-Fluorophenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2j)

Prepared according to the general procedure, using 0.1201 g (0.5 mmol) of
1j, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH3, 0.0167 g (0.025 mmol) of L5·FeCl2, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 12 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by 1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0687 g (0.20 mmol, >20/1 E/Z, 39% yield) of the title compound (Z) and recover chiral 1j in 40% NMR yield. (R,R)-1j: 63.5% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 18.2 (major), 28.1 (minor). 2j: colorless oil.

Optical Rotation: \([\alpha]_{20}^D = +38.6\) (c 1.20, CHCl3), 91.9% ee determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.3 (major), 7.9 (minor). IR (cm⁻¹): 3063, 2965, 2143, 1489, 1445, 1212. 1H NMR (CDCl3, 400 MHz): δ 7.46-7.41 (m, 2H), 7.37-7.31 (m, 1H), 7.31-7.25 (m, 4H), 7.25-7.21 (m, 2H), 7.21-7.11 (m, 3H), 7.04-6.93 (m, 2H), 5.61 (d, J = 9.4 Hz, 1H), 4.23-4.15 (m, 2H), 3.76-3.66 (m, 1H), 2.45-2.30 (m, 2H), 1.32 (d, 3H); 13C NMR (CDCl3, 100 MHz): δ 160.0 (d, J = 247.2 Hz), 146.1, 135.1, 131.9, 131.7 (d, J = 13.4 Hz), 131.4, 130.5 (d, J = 3.8 Hz), 129.7, 128.5, 128.43, 128.40, 127.9, 127.0, 126.0, 123.8 (d, J = 3.0 Hz), 115.5 (d, J = 22.8 Hz), 38.5, 22.5, 15.8 (d, J = 3.0 Hz); 19F NMR (CDCl3, 376.5 MHz): δ -114.6. HRMS (ESI) calculated for [C23H23FSiNa]+ (M + Na⁺) requires m/z 369.1451, found m/z 369.1464.

(S,Z)-2-(2-Fluorophenyl)-4-phenylpent-2-en-1-ol (2j-ox) colorless oil.

1H NMR (CDCl3, 400 MHz): δ 7.35-7.28 (m, 4H), 7.28-7.18 (m, 3H), 7.09 (td, J = 7.4, 1.2 Hz, 1H), 7.03 (ddd, J = 11.0, 8.2, 0.8 Hz, 1H), 5.91 (d, J = 9.8 Hz, 1H), 4.55 (d, J = 5.8 Hz, 2H), 4.05-3.96 (m, 1H), 1.57 (t, J = 4.6 Hz, 1H), 1.45 (d, J = 7.0 Hz, 3H); 13C NMR (CDCl3, 100 MHz): δ 160.0 (d, J = 245.7 Hz), 145.6, 140.1 (d, J = 1.5 Hz), 134.3 (d, J = 1.5 Hz), 130.6 (d, J = 4.4 Hz), 129.2 (d, J = 14.7 Hz), 128.9 (d, J = 8.2 Hz), 128.6, 126.9, 126.3, 124.2 (d, J = 3.8 Hz), 115.5 (d, J = 22.7 Hz), 60.8 (d, J = 3.7 Hz), 38.1, 22.5; 19F NMR: (CDCl3, 376.5 MHz) δ -115.6. HRMS (EI) calculated for [C17H17FO]+ requires m/z 256.1263, found m/z 256.1263.
(S,Z)-(2-(Naphthalen-2-yl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2k) Prepared according to the general procedure, using 0.1362 g (0.5 mmol) of 1k, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0166 g (0.025 mmol) of L₅·FeCl₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0903 g (0.24 mmol, 13/1 E/Z, 47% yield) of the title compound (Z) and recover chiral 1k in 11% NMR yield. (R,R)-1k: 99.4% ee determined by HPLC, HPLC conditions: Chiralcel AD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 8.6 (major), 10.4 (minor).

2k: colorless oil. Optical Rotation: [α]₉₀²⁰D = -19.2 (c 1.03, CHCl₃), 95.7% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.9 (minor), 26.1 (major). IR (cm⁻¹): 2958, 2923, 2143, 1597, 1452, 1428. ¹H NMR (CDCl₃, 400 MHz): δ 7.80-7.70 (m, 4H), 7.55-7.51 (m, 1H), 7.50-7.45 (m, 2H), 7.45-7.37 (m, 2H), 7.36-7.31 (m, 1H), 7.31-7.23 (m, 6H), 7.21-7.15 (m, 1H), 5.92 (d, J = 9.4 Hz, 1H), 4.32-4.25 (m, 2H), 3.78-7.69 (m, 1H), 2.55-2.40 (m, 2H), 1.35 (d, J = 7.0 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 146.4, 140.3, 135.2, 133.4, 132.9, 132.5, 132.1, 129.7, 128.5, 128.04, 127.96, 127.6, 127.4, 127.0, 126.0, 125.6, 125.12, 125.05, 39.0, 22.6, 15.0. HRMS (EI) calculated for [C₂₇H₂₆Si]+ requires m/z 378.1804, found m/z 378.1805.

(S,Z)-(4-(4-Methoxyphenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2l) Prepared according to the general procedure, using 0.1251 g (0.5 mmol) of 1l, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0166 g (0.025 mmol) of L₅·FeCl₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the
eluent to give 0.0764 g (0.21 mmol, 16/1 E/Z, 43% yield) of the title compound (Z) and recover chiral 11 in 39% NMR yield. \((R,R)-11\): 77.1% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 16.7 (major), 22.0 (minor). 21: colorless oil. Optical Rotation: \([\alpha]_D^{20} = +39.2\) (c 1.01, CHCl\(_3\)), 97.8% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 254 nm, tr 15.9 (minor), 19.8 (major). IR (cm\(^{-1}\)): 2960, 2143, 1605, 1507, 1247. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.47 (d, \(J = 7.0\) Hz, 2H), 7.40-7.19 (m, 8H), 7.13 (d, \(J = 8.4\) Hz, 2H), 6.82 (d, \(J = 8.4\) Hz, 2H), 5.73 (d, \(J = 9.6\) Hz, 1H), 4.29-4.21 (m, 2H), 3.78 (s, 3H), 3.68-3.58 (m, 1H), 2.44-2.29 (m, 2H), 1.28 (d, \(J = 7.0\) Hz, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 157.8, 143.2, 138.5, 135.2, 135.0, 132.5, 132.1, 129.7, 128.1, 127.95, 127.85, 126.8, 126.5, 113.8, 55.2, 38.0, 22.7, 15.0. HRMS (ESI) calculated for \([\text{C}_{24}\text{H}_{27}\text{OSi}]^+\) (M + H\(^+\)) requires m/z 359.1831, found m/z 359.1842.

\((S,Z)\)-Phenyl(2-phenyl-4-(p-tolyl)pent-2-en-1-yl)silane \((2m)\)

Prepared according to the general procedure, using 0.1175 g (0.5 mmol) of \(1m\), 96 µL (0.75 mmol, 1.5 equiv.) of PhSiH\(_3\), 0.0166 g (0.025 mmol) of L5·FeCl\(_2\), 75 µL (1.0 M in THF, 0.075 mmol) of NaBH\(_3\)Et, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 3 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by \(^1\)H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0694 g (0.20 mmol, 9/1 E/Z, 40% yield) of the title compound (Z) and recover chiral \(1m\) in 23% NMR yield. \((R,R)-1m\): 88.4% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 11.3 (major), 17.5 (minor). 2m: colorless oil. Optical Rotation: \([\alpha]_D^{20} = +40.4\) (c 1.01, CHCl\(_3\)), 96.0% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 8.5 (minor), 9.0 (major). IR (cm\(^{-1}\)): 2963, 2922, 2143, 1504, 1440. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.50-7.45 (m, 2H), 7.39-7.23 (m, 7H), 7.23-7.17 (m, 1H), 7.14-7.06 (m, 4H), 5.75 (d, \(J = 9.6\) Hz, 1H), 4.29-4.22 (m, 2H), 3.69-3.60 (m, 1H), 2.44-2.28 (m, 2H), 2.31 (s, 3H), 1.29 (d, \(J = 7.2\) Hz, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 143.4, 143.3, 135.4, 135.2, 135.1, 132.5, 132.1, 129.7, 129.1, 128.1, 127.9, 126.9, 126.8, 126.6, 38.5, 22.7, 21.0, 15.0. HRMS (EI) calculated for \([\text{C}_{24}\text{H}_{26}\text{Si}]^+\)
requires m/z 342.1804, found m/z 342.1801.

(S,Z)-(4-(4-Fluorophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane

(2n) Prepared according to the general procedure, using 0.1193 g (0.5 mmol) of 1n, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH3, 0.0166 g (0.025 mmol) of L5·FeCl2, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by 1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0704 g (0.20 mmol, 9/1 E/Z, 40% yield) of the title compound (Z) and recover chiral 1n in 20% NMR yield. (R,R)-1n: 95.3% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 10.2 (major), 12.3 (minor). 2n: colorless oil. Optical Rotation: [α]20D = +24.6 (c 1.01, CHCl3), 95.8% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 11.4 (minor), 13.7 (major). IR (cm⁻¹): 2970, 2144, 1601, 1508, 1428, 1226. 1H NMR (CDCl3, 400 MHz): δ 7.50-7.44 (m, 2H), 7.40-7.33 (m, 3H), 7.33-7.25 (m, 4H), 7.33-7.19 (m, 1H), 7.17-7.11 (m, 2H), 6.99-3.91 (m, 2H), 5.71 (d, J = 9.4 Hz, 1H), 4.30-4.20 (m, 2H), 3.69-3.59 (m, 1H), 2.42-2.29 (m, 2H), 1.28 (d, J = 7.0 Hz, 3H); 13C NMR (CDCl3, 100 MHz): δ 161.2 (d, J = 243.6 Hz), 143.1, 142.0 (d, J = 3.0 Hz), 135.6, 135.2, 131.9, 129.8, 128.3 (d, J = 7.8 Hz), 128.2, 128.0, 127.0, 126.5, 115.1 (d, J = 21.2 Hz), 38.1, 22.7, 15.1; 19F NMR (CDCl3, 376.5 MHz): δ -117.5. HRMS (EI) calculated for [C22H22FSi]⁺ requires m/z 346.1553, found m/z 346.1552.

(S,Z)-(4-(4-Chlorophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane

(2o) Prepared according to the general procedure, using 0.1284 g (0.5 mmol) of 1o, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH3, 0.0168 g (0.025 mmol) of L5·FeCl2, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by 1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0704 g (0.20 mmol, 9/1 E/Z, 40% yield) of the title compound (Z) and recover chiral 1o in 20% NMR yield. (R,R)-1o: 95.3% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 10.2 (major), 12.3 (minor). 2o: colorless oil. Optical Rotation: [α]20D = +24.6 (c 1.01, CHCl3), 95.8% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 11.4 (minor), 13.7 (major). IR (cm⁻¹): 2970, 2144, 1601, 1508, 1428, 1226. 1H NMR (CDCl3, 400 MHz): δ 7.50-7.44 (m, 2H), 7.40-7.33 (m, 3H), 7.33-7.25 (m, 4H), 7.33-7.19 (m, 1H), 7.17-7.11 (m, 2H), 6.99-3.91 (m, 2H), 5.71 (d, J = 9.4 Hz, 1H), 4.30-4.20 (m, 2H), 3.69-3.59 (m, 1H), 2.42-2.29 (m, 2H), 1.28 (d, J = 7.0 Hz, 3H); 13C NMR (CDCl3, 100 MHz): δ 161.2 (d, J = 243.6 Hz), 143.1, 142.0 (d, J = 3.0 Hz), 135.6, 135.2, 131.9, 129.8, 128.3 (d, J = 7.8 Hz), 128.2, 128.0, 127.0, 126.5, 115.1 (d, J = 21.2 Hz), 38.1, 22.7, 15.1; 19F NMR (CDCl3, 376.5 MHz): δ -117.5. HRMS (EI) calculated for [C22H22FSi]⁺ requires m/z 346.1553, found m/z 346.1552.
NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0873 g (0.24 mmol, 11/1 E/Z, 48% yield) of the title compound (Z) and recover chiral 1o in 25% NMR yield. (R,R)-1o: 90.1% ee determined by HPLC, HPLC conditions: Chiralcel AD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 7.0 (major), 7.6 (minor). 2o: colorless oil. Optical Rotation: [α]_D^20 = +48.5 (c 1.01, CHCl₃), 93.5% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 10.7 (minor), 11.9 (major). IR (cm⁻¹): 2963, 2923, 2144, 1491, 1428. ¹H NMR (CDCl₃, 400 MHz): δ 7.49-7.44 (m, 2H), 7.40-7.31 (m, 4H), 7.31-7.26 (m, 3H), 7.25-7.20 (m, 3H), 7.14-7.09 (m, 2H), 5.69 (d, J = 9.4 Hz, 1H), 4.28-2.19 (m, 2H), 3.67-3.58 (m, 1H), 2.40-2.29 (m, 2H), 1.27 (d, J = 6.8 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 144.9, 143.0, 135.9, 135.2, 131.9, 131.5, 129.8, 128.5, 128.3, 128.2, 128.0, 127.0, 126.5, 38.3, 22.6, 15.1. HRMS (EI) calculated for [C₂₃H₂₃ClSi]⁺ requires m/z 362.1258, found m/z 362.1259.

(S,Z)-(4-(4-Bromophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane

(2p) Prepared according to the general procedure, using 0.1499 g (0.5 mmol) of 1p, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0166 g (0.025 mmol) of L₅·FeCl₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0927 g (0.23 mmol, 17/1 E/Z, 46% yield) of the title compound (Z) and recover chiral 1p in 33% NMR yield. (R,R)-1p: 82.9% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 9.7 (major), 11.8 (minor). 2p: colorless oil. Optical Rotation: [α]_D^20 = +52.3 (c 1.07, CHCl₃), 97.3% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 13.2 (minor), 14.7 (major). IR (cm⁻¹): 3059, 2964, 2143, 1487, 1438. ¹H NMR (CDCl₃, 400 MHz): δ 7.48-7.43 (m, 2H), 7.40-7.31 (m, 6H), 7.31-7.25 (m, 3H), 7.21-7.20 (m, 1H), 7.08-7.04 (m, 2H), 5.69 (d, J = 9.4 Hz, 1H), 4.28-2.19 (m, 2H), 3.67-3.58 (m, 1H), 2.40-2.29 (m, 2H), 1.27 (d, J = 7.0 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 145.4, 143.0, 136.0, 135.2, 131.9, 131.4, 129.8, 128.8,
HRMS (ESI) calculated for [C_{23}H_{24}BrSi]^+ (M + H^+) requires m/z 407.0831, found m/z 407.0823.

\[(S,Z)-(4-(3-Fluorophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane\] (2q) Prepared according to the general procedure, using 0.1195 g (0.5 mmol) of 1q, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0167 g (0.025 mmol) of L₅·FeCl₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0741 g (0.21 mmol, 12/1 E/Z, 43% yield) of the title compound (Z) and recover chiral 1q in 19% NMR yield. (R,R)-1q: 94.7% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 8.5 (major), 11.6 (minor). 2q: colorless oil. Optical Rotation: [α]_D⁰ = +26.2 (c 1.06, CHCl₃), 98.3% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 7.1 (minor), 9.2 (major). IR (cm⁻¹): 3061, 2965, 2143, 1597, 1490, 1441. ¹H NMR (CDCl₃, 400 MHz): δ 7.50-7.44 (m, 2H), 7.39-7.33 (m, 3H), 7.33-7.25 (m, 4H), 7.25-7.18 (m, 2H), 7.00-6.96 (m, 1H), 6.93-6.82 (m, 2H), 5.70 (d, J = 9.4 Hz, 1H), 4.28-4.20 (m, 2H), 3.70-3.60 (m, 1H), 2.42-2.29 (m, 2H), 1.28 (d, J = 7.0 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 163.5 (d, J = 245.8 Hz), 149.1 (d, J = 6.2 Hz), 143.0, 136.0, 135.2, 131.9, 131.3, 129.8, 128.2, 128.0, 127.9, 127.0, 126.6, 122.7 (d, J = 3.0 Hz), 113.9 (d, J = 21.6 Hz), 112.8 (d, J = 21.6 Hz), 38.6, 22.4, 15.2; ¹⁹F NMR (CDCl₃, 376.5 MHz): δ -113.3. HRMS (ESI) calculated for [C_{23}H_{24}FSi]^+ (M + H^+) requires m/z 347.1631, found m/z 347.1617.

\[(S,Z)-(4-(3-Chlorophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane\] (2r) Prepared according to the general procedure, using 0.1284 g (0.5 mmol) of 1r, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0167 g (0.025 mmol) of L₅·FeCl₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution
was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0740 g (0.20 mmol, 12/1 $E/Z$, 40% yield) of the title compound (Z) and recover chiral 1r in 13% NMR yield. ($R,R$)-1r: 97.2% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 8.9 (major), 12.1 (minor).

2r: colorless oil. Optical Rotation: $[\alpha]_20^D = +39.3$ (c 0.98, CHCl$_3$), 96.8% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 9.9 (minor), 15.8 (major). IR (cm$^{-1}$): 2958, 2924, 2144, 1594, 1461, 1428. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.50-7.43 (m, 2H), 7.39-7.33 (m, 3H), 7.32-7.25 (m, 4H), 7.25-7.21 (m, 1H), 7.21-7.11 (m, 3H), 7.10-7.05 (m, 1H), 5.70 (d, $J = 9.4$ Hz, 1H), 4.28-4.19 (m, 2H), 3.66-3.56 (m, 1H), 2.41-2.28 (m, 2H), 1.27 (d, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 148.5, 142.9, 136.1, 135.2, 134.2, 131.8, 131.2, 129.8, 129.7, 128.2, 128.0, 127.2, 127.1, 126.5, 126.1, 125.2, 38.7, 22.5, 15.2. HRMS (EI) calculated for [C$_{23}$H$_{23}$ClSi]$^+$ requires m/z 362.1258, found m/z 362.1258.

(S,Z)-(4-(2-Chlorophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2s)

Prepared according to the general procedure, using 0.1278 g (0.5 mmol) of 1s, 96 $\mu$L (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of L$_5$·FeCl$_2$, 75 $\mu$L (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0735 g (0.20 mmol, 8/1 $E/Z$, 40% yield) of the title compound (Z) and recover chiral 1s in 33% NMR yield. ($R,R$)-1s: 63.8% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 8.8 (major), 9.5 (minor). 2s: colorless oil. Optical Rotation: $[\alpha]_20^D = -40.0$ (c 1.02, CHCl$_3$), 78.7% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 11.4 (minor), 17.2 (major). IR (cm$^{-1}$): 2957, 2924, 2145, 1470, 1443. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.49-7.43 (m, 2H), 7.39-7.31 (m, 3H), 7.31-7.25 (m, 6H), 7.25-7.21 (m, 1H), 7.21-7.14 (m, 1H), 7.11-7.03 (m, 3H), 7.03-6.97 (m, 1H), 5.67 (d, $J = 9.4$ Hz, 1H), 4.27-4.19 (m, 2H), 3.66-3.56 (m, 1H), 2.41-2.28 (m, 2H), 1.27 (d, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 148.5, 142.9, 136.1, 135.2, 134.2, 131.8, 131.2, 129.8, 129.7, 128.2, 128.0, 127.2, 127.1, 126.5, 126.1, 125.2, 38.7, 22.5, 15.2. HRMS (EI) calculated for [C$_{23}$H$_{23}$ClSi]$^+$ requires m/z 362.1258, found m/z 362.1258.
(S,Z)-(4-(Naphthalen-2-yl)-2-phenylpent-2-en-1-yl)(phenyl)silane

(2t) Prepared according to the general procedure, using 0.1352 g (0.5 mmol) of 1t, 96 µL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0167 g (0.025 mmol) of L₅·FeCl₂, 75 µL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0761 g (0.20 mmol, 14/1 E/Z, 40% yield) of the title compound (Z) and recover chiral 1t in 32% NMR yield. (R,R)-1t: 68.5% ee determined by HPLC, HPLC conditions: Chiralcel AD-H, nhexane/iPrOH = 98/2, 1.0 mL/min, n = 220 nm, tr 4.9 (major), 6.4 (minor). 2t: colorless oil. Optical Rotation: [α]₂₀° = +72.7 (c 1.01, CHCl₃), 97.1% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.0 (minor), 24.2 (major). IR (cm⁻¹): 2960, 2922, 2142, 1599, 1445. ¹H NMR (CDCl₃, 400 MHz): δ 7.80-7.73 (m, 3H), 7.62 (s, 1H), 7.48-7.32 (m, 8H), 7.31-7.25 (m, 4H), 7.24-7.18 (m, 1H), 5.85 (d, J = 9.4 Hz, 1H), 4.31-4.21 (m, 2H), 3.87-3.78 (m, 1H), 2.48-2.32 (m, 2H), 1.39 (d, J = 7.0 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 143.9, 143.2, 135.8, 135.2, 133.6, 132.1, 132.02, 131.98, 129.7, 128.2, 128.0, 127.9, 127.6, 127.5, 126.9, 126.6, 126.1, 125.9, 125.2, 124.8, 39.1, 22.6, 15.2. HRMS (EI) calculated for [C₂₇H₂₆Si]+ requires m/z 378.1804, found m/z 378.1806.

(S,Z)-(4-(Naphthalen-1-yl)-2-phenylpent-2-en-1-yl)(phenyl)silane

(2u) Prepared according to the general procedure, using 0.1353 g (0.5 mmol) of 1u, 96 µL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0166 g (0.025 mmol) of L₅·FeCl₂, 75 µL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was
added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0761 g (0.20 mmol, 8/1 E/Z, 40% yield) of the title compound (Z) and recover chiral 1u in 43% NMR yield. (R,R)-1u: 64.5% ee determined by HPLC, HPLC conditions: Chiralcel AD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 6.9 (minor), 7.4 (major).

2u: colorless oil. Optical Rotation: $[\alpha]_D^{20} = -83.0$ (c 0.98, CHCl$_3$), 64.4% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 32.7 (major), 34.8 (minor). IR (cm$^{-1}$): 2959, 2924, 2143, 1596, 1446, 1428. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.05 (d, $J = 8.0$ Hz, 1H), 7.87-7.83 (m, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.52-7.42 (m, 3H), 7.42-7.35 (m, 5H), 7.32-7.20 (m, 6H), 6.01 (d, $J = 8.6$ Hz, 1H), 4.42-4.33 (m, 1H), 4.26-4.11 (m, 2H), 2.36-2.19 (m, 2H), 1.41 (d, $J = 7.0$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 143.14, 143.11, 136.4, 135.2, 134.0, 132.2, 132.1, 131.3, 129.7, 129.0, 128.2, 127.9, 127.0, 126.6, 126.5, 125.8, 125.7, 125.3, 123.6, 123.4, 34.4, 23.1, 15.5. HRMS (EI) calculated for [C$_{27}$H$_{26}$Si]$^+$ requires m/z 378.1804, found m/z 378.1805.

(5Z)-(4-(Furan-2-yl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2v)

Prepared according to the general procedure, using 0.1053 g (0.5 mmol) of 1v, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of L5·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0645 g (0.20 mmol, 11/1 E/Z, 40% yield) of the title compound (Z) and recover chiral 1v in 21% NMR yield. (R,R)-1v: 70.6% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 7.4 (major), 9.1 (minor). 2v: yellow oil. Optical Rotation: $[\alpha]_D^{20} = +59.3$ (c 0.97, CHCl$_3$), 98.1% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 8.2 (minor), 9.0 (major). IR (cm$^{-1}$): 2971, 2144, 1591, 1498, 1439. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.51-7.47 (m,
(S,Z)-Phenyl(2-phenyl-4-(thiophen-2-yl)pent-2-en-1-yl)silane \( (2w) \)

Prepared according to the general procedure, using 0.1146 g (0.5 mmol) of \( 1w \), 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0168 g (0.025 mmol) of \( L_5 \cdot FeCl_2 \), 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0794 g (0.24 mmol, 10/1 \( E/Z \), 47% yield) of the title compound (Z) and recover chiral \( 1w \) in 26% NMR yield. \( (R,R)-1w \): 96.0% \( ee \) determined by HPLC, HPLC conditions: Chiralcel OJ-H, \( n \)hexane/iPrOH = 99/1, 1.0 mL/min, \( n \) = 220 nm, \( tr \) 8.1 (major), 8.9 (minor). \( 2w \): yellow oil.

Optical Rotation: \([\alpha]_{20}^D = +28.4 \ (c \ 1.33, \ CHCl_3), \ 96.2\% \ ee \ determined \ by \ HPLC, \ HPLC \ conditions: \ Chiralcel \ OJ-H \times 2, \ n \)hexane/iPrOH = 99.5/0.5, 1.0 mL/min, \( n \) = 220 nm, \( tr \) 26.8 (major), 29.9 (minor).

IR (cm⁻¹): 2965, 2144, 1493, 1439. ¹H NMR (CDCl₃, 400 MHz): \( \delta \) 7.51-7.46 (m, 2H), 7.40-7.33 (m, 3H), 7.33-7.26 (m, 4H), 7.25-7.20 (m, 1H), 7.12 (dd, \( J = 5.2, 1.2 \) Hz, 1H), 6.91 (dd, \( J = 5.2, 3.4 \) Hz, 1H), 6.81-6.78 (m, 1H), 5.70 (d, \( J = 9.6 \) Hz, 1H), 4.32-4.25 (m, 2H), 3.98-3.89 (m, 1H), 2.48-2.31 (m, 2H), 1.36 (d, \( J = 7.0 \) Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): \( \delta \) 150.4, 143.0, 135.8, 135.2, 131.9, 131.4, 129.8, 128.2, 128.0, 127.0, 126.6, 123.0, 122.7, 34.5, 22.9, 15.1. HRMS (ESI) calculated for \([C_{21}H_{23}OSi]^+ (M + H^+) \) requires \( m/z \) 319.1518, found \( m/z \) 319.1525.

(R,Z)-(4-Methyl-2-phenylhept-2-en-1-yl)(phenyl)silane \( (2x) \)

Prepared according to the general procedure, using 0.0951 g (0.5 mmol) of \( 1x \), 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0167 g (0.025 mmol) of \( L_5 \cdot FeCl_2 \), 75 μL (1.0 M in THF,
0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by 1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0683 g (0.23 mmol, 4/1 E/Z, 46% yield) of the title compound (Z) and recover chiral 1x in 37% NMR yield. (R,R)-1x: 75.2% ee determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OD-H, n-hexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 5.5 (major), 6.6 (minor). 2x: colorless oil. Optical Rotation: [α]D = -16.2 (c 1.10, CHCl3), 95.2% ee determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, n-hexane/iPrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 6.2 (major), 7.3 (minor). IR (cm⁻¹): 2956, 2925, 2145, 1456, 1429. 1H NMR (CDCl3, 400 MHz): δ 7.52-7.47 (m, 2H), 7.39-7.17 (m, 8H), 5.39 (d, J = 9.8 Hz, 1H), 4.30-4.23 (m, 2H), 2.43-2.25 (m, 3H), 1.34-1.22 (m, 4H), 0.92 (d, J = 6.6 Hz, 3H), 0.90-0.85 (m, 3H); 13C NMR (CDCl3, 100 MHz): δ 143.6, 135.2, 134.2, 132.3, 129.6, 128.1, 127.9, 126.6, 126.5, 40.0, 33.3, 20.8, 20.7, 14.8, 14.4. HRMS (EI) calculated for [C20H26Si]+ requires m/z 294.1804, found m/z 294.1807.

(R,Z)-4-Methyl-2-phenylhept-2-en-1-ol (2x-ox) colorless oil. IR (cm⁻¹): 3378, 2956, 2925, 1493, 1462, 1377. 1H NMR (CDCl3, 400 MHz): δ 7.47-7.42 (m, 2H), 7.37-7.30 (m, 2H), 7.28-7.23 (m, 1H), 5.64 (d, J = 10.0 Hz, 1H), 4.58 (s, 2H), 2.71-2.59 (m, 1H), 1.43-1.28 (m, 4H), 1.26 (brs, 1H), 1.05 (d, J = 6.6 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H); 13C NMR (CDCl3, 100 MHz): δ 140.9, 139.1, 137.3, 128.5, 127.1, 126.3, 60.0, 39.9, 32.8, 21.5, 20.8, 14.2. HRMS (EI) calculated for [C14H20O]+ requires m/z 204.1514, found m/z 204.1514.

(R,Z)-(4,5-Dimethyl-2-phenylhex-2-en-1-yl)(phenyl)silane (2y) Prepared according to the general procedure, using 0.0935 g (0.5 mmol) of 1y, 96 µL (0.75 mmol, 1.5 equiv.) of PhSiH3, 0.0167 g (0.025 mmol) of L5·FeCl2, 75 µL (1.0 M in THF, 0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered.
through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0680 g (0.23 mmol, 9/1 E/Z, 46% yield) of the title compound (Z) and recover chiral 1y in 45% NMR yield. (R,R)-1y: 74.6% ee determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OD-H, $n$hexane/iPrOH = 99/1, 1.0 mL/min, $n$ = 220 nm, tr 5.3 (major), 6.3 (minor). 2y: colorless oil. Optical Rotation: $[\alpha]_D^{20} = -27.9$ (c 0.90, CHCl$_3$), 92.5% ee determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, $n$hexane/iPrOH = 95/5, 1.0 mL/min, $n$ = 220 nm, tr 6.0 (major), 7.1 (minor). IR (cm$^{-1}$): 2957, 2143, 1458, 1428. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.52-7.47 (m, 2H), 7.39-7.25 (m, 7H), 7.23-7.18 (m, 1H), 5.47 (d, $J$ = 10.2 Hz, 1H), 4.31-4.22 (m, 2H), 2.41-2.24 (m, 2H), 2.24-2.15 (m, 1H), 1.56-1.46 (m, 1H), 0.91 (d, $J$ = 4.2 Hz, 3H), 0.90 (d, $J$ = 4.2 Hz, 3H), 0.87 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 143.8, 135.2, 134.6, 132.9, 132.4, 129.6, 128.1, 127.9, 126.6, 126.5, 39.5, 33.7, 20.2, 20.0, 17.9, 14.8. HRMS (EI) calculated for [C$_{20}$H$_{26}$Si]$^+$ requires m/z 294.1804, found m/z 294.1807.

(R,Z)-4,5-Dimethyl-2-phenylhex-2-en-1-ol (2y-ox) colorless oil. IR (cm$^{-1}$): 3398, 2959, 2871, 1493, 1462, 1369. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.48-7.43 (m, 2H), 7.37-7.31 (m, 2H), 7.29-7.23 (m, 1H), 5.72 (d, $J$ = 10.4 Hz, 1H), 4.57 (s, 2H), 2.48-2.37 (m, 1H), 1.63-1.50 (m, 1H), 1.26 (brs, 1H), 1.04 (d, $J$ = 7.0 Hz, 3H), 0.94 (d, $J$ = 6.8 Hz, 3H), 0.91 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 141.3, 137.6, 136.3, 128.5, 127.0, 126.5, 60.0, 42.5, 33.4, 27.4, 16.2. HRMS (EI) calculated for [C$_{14}$H$_{20}$O]$^+$ requires m/z 204.1514, found m/z 204.1511.

(R,Z)-(4-Cyclohexyl-2-phenylpent-2-en-1-yl)(phenyl)silane (2z) Prepared according to the general procedure, using 0.1151 g (0.5 mmol) of 1z, 96 $\mu$L (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0168 g (0.025 mmol) of L5·FeCl$_2$, 75 $\mu$L (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were
concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0836 g (0.25 mmol, 10/1 E/Z, 49% yield) of the title compound (Z) and recover chiral 1z in 46% NMR yield. $(R,R)$-1z: 77.5% ee determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 5.4 (major), 6.5 (minor). 2z: colorless oil. Optical Rotation: $\left[\alpha\right]_D^{19} = -20.4$ (c 1.00, CHCl$_3$), 93.4% ee determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 5.8 (major), 7.4 (minor). IR (cm$^{-1}$): 2922, 2850, 2142, 1448, 1428. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.52-7.46 (m, 2H), 7.39-7.24 (m, 7H), 7.24-7.17 (m, 1H), 5.46 (d, $J = 10.2$ Hz, 1H), 4.30-4.22 (m, 2H), 2.41-2.15 (m, 3H), 1.81-1.58 (m, 5H), 1.26-1.06 (m, 4H), 1.00-0.85 (m, 5H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 143.8, 135.2, 134.4, 133.2, 132.4, 129.6, 128.1, 127.9, 126.6, 126.5, 43.9, 38.8, 30.7, 30.6, 26.71, 26.67, 26.64, 17.9, 14.8. HRMS (EI) calculated for [C$_{23}$H$_{30}$Si]$^+$ requires m/z 334.2117, found m/z 334.2114.

$(R,Z)$-4-Cyclohexyl-2-phenylpent-2-en-1-ol (2z-ox) colorless oil. IR (cm$^{-1}$): 3357, 2972, 2919, 1484, 1450, 1396. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.48-7.43 (m, 2H), 7.38-7.29 (m, 2H), 1.85-1.58 (m, 5H), 1.33-1.09 (m, 5H), 1.04 (d, $J = 6.8$ Hz, 3H), 1.02-0.87 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 141.0, 137.9, 137.3, 128.5, 127.0, 126.3, 60.0, 43.6, 38.4, 30.74, 30.70, 26.54, 26.50, 18.6. HRMS (EI) calculated for [C$_{17}$H$_{24}$O]$^+$ requires m/z 244.1827, found m/z 244.1828.

$(S,Z)$-Phenyl(4,5,5-trimethyl-2-phenylhex-2-en-1-yl)silane (2aa) Prepared according to the general procedure, using 0.1012 g (0.5 mmol) of 1aa, 96 µL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of L$_5$·FeCl$_2$, 75 µL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EtOH (10/1) and filtered through a pad of silica gel, washed by PE/EtOH (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was
purified by flash column chromatography using PE as the eluent to give 0.0682 g (0.22 mmol, 12/1 E/Z, 44% yield) of the title compound (Z) and recover chiral 1aa in 38% NMR yield. 

(R,R)-1aa: 89.7% ee determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OJ-H x 2, n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 14.8 (minor), 15.5 (major). 2aa: colorless oil. Optical Rotation: [α]_D^0 = -30.1 (c 1.02, CHCl₃), 90.3% ee determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, n-hexane/iPrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 5.9 (major), 6.8 (minor). IR (cm⁻¹): 2963, 2145, 1492, 1367. ¹H NMR (CDCl₃, 400 MHz): δ 7.51-7.46 (m, 2H), 7.39-7.24 (m, 7H), 7.22-7.17 (m, 1H), 5.54 (d, J = 10.6 Hz, 1H), 4.31-4.22 (m, 2H), 2.45-2.37 (m, 1H), 2.30-2.19 (m, 2H), 0.90-0.86 (m, 12H); ¹³C NMR (CDCl₃, 100 MHz): δ 144.1, 135.2, 134.7, 132.4, 131.7, 129.6, 128.1, 127.9, 126.6, 43.0, 33.7, 27.4, 15.6, 14.8. HRMS (EI) calculated for [C₂₁H₂₈Si]+ requires m/z 308.1960, found m/z 308.1961.

(S,Z)-4,5,5-Trimethyl-2-phenylhex-2-en-1-ol (2aa-ox) colorless oil. IR (cm⁻¹): 3365, 2961, 2870, 1493, 1470, 1366. ¹H NMR (CDCl₃, 400 MHz): δ 7.47-7.43 (m, 2H), 7.37-7.31 (m, 2H), 7.29-7.23 (m, 1H), 5.79 (d, J = 10.8 Hz, 1H), 4.59 (q, J = 9.8 Hz, 2H), 2.50-2.40 (m, 1H), 1.26 (brs, 1H), 1.01 (d, J = 7.0 Hz, 3H), 0.92 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz): δ 141.1, 137.5, 128.5, 127.0, 126.4, 60.0, 39.1, 33.7, 20.2, 20.1, 18.7. HRMS (EI) calculated for [C₁₅H₂₂O]+ requires m/z 218.1671, found m/z 218.1673.

((R,Z)-4-(Adamantan-2-yl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2ab) Prepared according to the general procedure, using 0.1395 g (0.5 mmol) of 1ab, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH₃, 0.0168 g (0.025 mmol) of L₅·FeCl₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash
column chromatography using PE as the eluent to give 0.0962 g (0.25 mmol, 11/1 E/Z, 49% yield) of the title compound (Z) and recover chiral \textit{1ab} in 42% NMR yield. (\textit{R,R})-\textit{1ab}: 89.0% ee determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 4.4 (major), 4.8 (minor). \textit{2ab}: colorless oil. Optical Rotation: [\alpha]_{D}^{20} = -11.3 (c 1.02, CHCl3), 80.0% ee determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 5.9 (major), 6.9 (minor). IR (cm\(^{-1}\)): 2905, 2849, 2144, 1492, 1450. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.52-7.47 (m, 2H), 7.38-7.23 (m, 7H), 7.22-7.16 (m, 1H), 5.37 (d, J = 9.8 Hz, 1H), 4.31-4.22 (m, 2H), 2.76-2.65 (m, 1H), 2.50-2.25 (m, 2H), 1.95 (s, 1H), 1.90-1.76 (m, 7H), 1.74-1.62 (m, 4H), 1.57-1.46 (m, 2H), 1.41-1.35 (m, 1H), 0.88 (d, J = 6.4 Hz, 3H); \(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 143.7, 135.2, 134.7, 134.3, 132.4, 129.6, 128.1, 127.9, 126.6, 126.5, 50.6, 39.45, 39.36, 38.3, 33.4, 32.8, 31.8, 30.4, 28.8, 28.1, 27.8, 18.5, 14.8. HRMS (EI) calculated for [C\(_{27}\)H\(_{34}\)Si\]+ requires m/z 386.2430, found m/z 386.2431.

\textbf{(R,Z)-4-(Adamantan-2-yl)-2-phenylpent-2-en-1-ol (2ab-ox)} colorless oil. IR (cm\(^{-1}\)): 3365, 2905, 2850, 1493, 1453, 1372. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.48-7.43 (m, 2H), 7.37-7.30 (m, 2H), 7.28-7.22 (m, 1H), 5.64 (d, J = 10.2 Hz, 1H), 4.62 (s, 2H), 3.00-2.88 (m, 1H), 1.99 (s, 1H), 1.93-1.65 (m, 11H), 1.63-1.47 (m, 2H), 1.43 (d, J = 10.6 Hz, 1H), 1.30 (brs, 1H), 1.01 (d, J = 6.6 Hz, 3H); \(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 140.9, 139.1, 137.0, 128.4, 127.0, 126.3, 60.1, 50.1, 39.3, 39.2, 38.2, 33.0, 32.0, 31.7, 30.5, 28.6, 28.0, 27.7, 19.0. HRMS (EI) calculated for [C\(_{21}\)H\(_{28}\)O\(^+\)] requires m/z 296.2140, found m/z 296.2140.

\textbf{((S,Z)-4-(Adamantan-1-yl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2ac)} Prepared according to the general procedure, using 0.1410 g (0.5 mmol) of \textit{1ac}, 96 \(\mu\)L (0.75 mmol, 1.5 equiv.) of PhSiH\(_3\), 0.0168 g (0.025 mmol) of \textit{L5·FeCl\(_2\)}, 75 \(\mu\)L (1.0 M in THF, 0.075 mmol) of NaBHEt\(_3\), and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel,
washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by $^1$H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0976 g (0.25 mmol, 15/1 E/Z, 50% yield) of the title compound (Z) and recover chiral 1ac in 40% NMR yield. (R,R)-1ac: 95.9% ee determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 17.2 (major), 18.5 (minor). 2ac: colorless oil. Optical Rotation: $[\alpha]_D^{20} = -17.2$ (c 1.05, CHCl$_3$), 89.8% ee determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 6.0 (major), 7.6 (minor). IR (cm$^{-1}$): 2902, 2846, 2142, 1491, 1448, 1359. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.52-7.47 (m, 2H), 7.38-7.25 (m, 7H), 7.23-7.18 (m, 1H), 5.56 (d, $J = 10.6$ Hz, 1H), 4.30-4.21 (m, 2H), 2.45-2.22 (m, 2H), 2.10-2.00 (m, 1H), 1.93 (s, 3H), 1.71-1.48 (m, 12H), 0.84 (d, $J = 7.0$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 144.0, 135.2, 134.8, 132.4, 130.8, 129.6, 128.1, 127.9, 126.6, 43.6, 39.7, 37.3, 35.5, 28.7, 14.8, 13.9. HRMS (EI) calculated for [C$_{27}$H$_{34}$Si]+ requires m/z 386.2430, found m/z 386.2431.

(S,Z)-4-(Adamantan-1-yl)-2-phenylpent-2-en-1-ol (2ac-ox) colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.46 (d, $J = 7.4$ Hz, 2H), 7.35 (dd, $J = 7.4$, 7.2 Hz, 2H), 7.26 (t, $J = 7.2$ Hz, 1H), 5.82 (d, $J = 10.8$ Hz, 1H), 4.63-4.52 (m, 2H), 2.31-2.21 (m, 1H), 1.97 (s, 3H), 1.74-1.50 (m, 12H), 1.28 (t, $J = 5.8$ Hz, 1H), 0.98 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 141.2, 137.7, 135.6, 128.5, 127.0, 126.4, 59.9, 43.1, 39.8, 37.2, 35.2, 28.7, 14.4. HRMS (EI) calculated for [C$_{25}$H$_{36}$O]+ requires m/z 296.2140, found m/z 296.2140.

(S,Z)-(2,4-Diphenylpent-2-en-1-yl)(4-methoxyphenyl)silane (2ad) Prepared according to the general procedure, using 0.1107 g (0.5 mmol) of 1a, 0.1145 g (0.75 mmol, 1.5 equiv.) of 4-MeOC$_6$H$_4$SiH$_3$, 0.0164 g (0.025 mmol) of L5·FeCl$_2$, 75 µL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 1 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel,
washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by \(^1\)H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0741 g (0.21 mmol, 11/1 E/Z, 41% yield) of the title compound (Z) and recover chiral 1a in 33% NMR yield. (R,R)-1a: 81.6% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.2 (major), 24.7 (minor). 2ad: colorless oil. Optical Rotation: [\(\alpha\)]\(_{20}^D\) = +30.9 (c 1.07, CHCl\(_3\)), 98.8% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 16.8 (minor), 26.5 (major). IR (cm\(^{-1}\)): 3021, 2960, 2138, 1594, 1498, 1248. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.41-7.33 (m, 4H), 7.30-7.25 (m, 4H), 7.24-7.15 (m, 4H), 6.87-6.83 (m, 2H), 5.76 (d, \(J = 9.6\) Hz, 1H), 4.27-4.19 (m, 2H), 3.80 (s, 3H), 3.72-3.62 (m, 1H), 2.41-2.27 (m, 2H), 1.32 (d, \(J = 7.2\) Hz, 3H); \(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 161.0, 146.5, 143.3, 136.7, 135.4, 132.1, 128.4, 128.1, 127.0, 126.8, 126.5, 125.9, 122.7, 113.8, 55.0, 38.9, 22.6, 15.4. HRMS (ESI) calculated for \([\text{C}_{25}\text{H}_{27}\text{OSi}]+\) (M + H\(^+\)) requires m/z 359.1831, found m/z 359.1823.

\((S,Z)-(4-\text{Chlorophenyl})(2,4-\text{diphenylpent-2-en-1-yl})\text{silane (2ae)}}\) Prepared according to the general procedure, using 0.1110 g (0.5 mmol) of 1a, 0.1190 g (0.75 mmol, 1.5 equiv.) of 4-ClC\(_6\)H\(_4\)SiH\(_3\), 0.0167 g (0.025 mmol) of L\(_5\)·FeCl\(_2\), 75 \(\mu\)L (1.0 M in THF, 0.075 mmol) of NaBH\(_3\)Et, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 5 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by \(^1\)H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0694 g (0.19 mmol, 10/1 E/Z, 38% yield) of the title compound (Z) and recover chiral 1a in 41% NMR yield. (R,R)-1a: 62.5% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.1 (major), 24.4 (minor). 2ae: colorless oil. Optical Rotation: [\(\alpha\)]\(_{20}^D\) = +24.0 (c 0.97, CHCl\(_3\)), 98.0% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 10.1 (minor), 12.6 (major). IR (cm\(^{-1}\)): 3025, 2963, 2147, 1583, 1488, 1449. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.35-7.29 (m, 4H), 7.29-7.24 (m,
5H), 7.24-7.15 (m, 5H), 5.77 (d, J = 9.4 Hz, 1H), 4.26-4.17 (m, 2H), 3.69-3.59 (m, 1H), 2.41-2.29 (m, 2H), 1.31 (d, J = 7.0 Hz, 3H); 13C NMR (CDCl3, 100 MHz): δ 146.3, 143.0, 136.5, 136.1, 135.1, 132.4, 130.2, 128.4, 128.18, 128.16, 126.97, 126.96, 126.5, 126.0, 38.9, 22.7, 14.9. HRMS (ESI) calculated for [C23H24ClSi]+ (M + H+) requires m/z 363.1336, found m/z 363.1301.

(S,Z)-(2,4-Diphenylpent-2-en-1-yl)(o-tolyl)silane (2af) Prepared according to the general procedure, using 0.1109 g (0.5 mmol) of 1a, 0.0923 g (0.75 mmol, 1.5 equiv.) of 2-MeC6H4SiH3, 0.0166 g (0.025 mmol) of L5·FeCl2, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by 1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0718 g (0.21 mmol, >20/1 E/Z, 42% yield) of the title compound (Z) and recover chiral 1a in 31% NMR yield. (R,R)-1a: 87.4% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.7 (major), 24.1 (minor). 2af: colorless oil. Optical Rotation: [α]20D = +33.4 (c 0.97, CHCl3), 97.1% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 7.5 (minor), 9.0 (major). IR (cm⁻¹): 2962, 2924, 2142, 1596, 1490, 1449. 1H NMR (CDCl3, 400 MHz): δ 7.44 (d, J = 6.4 Hz, 1H), 7.37-7.32 (m, 2H), 7.31-7.16 (m, 9H), 7.16-7.09 (m, 2H), 5.76 (d, J = 9.4 Hz, 1H), 4.33-4.24 (m, 2H), 3.74-3.63 (m, 1H), 2.47-2.29 (m, 5H), 1.32 (d, J = 6.6 Hz, 3H); 13C NMR (CDCl3, 100 MHz): δ 146.4, 143.9, 143.2, 136.4, 135.5, 132.2, 131.5, 130.3, 129.4, 128.4, 128.1, 127.0, 126.9, 126.5, 125.9, 125.1, 38.9, 22.6, 22.6, 14.7. HRMS (ESI) calculated for [C24H27Si]+ (M + H+) requires m/z 343.1882, found m/z 343.1897.

(S,Z)-(2,4-Diphenylpent-2-en-1-yl)(naphthalen-1-yl)silane (2ag) Prepared according to the general procedure, using 0.1110 g (0.5 mmol) of 1a, 0.1197 g (0.75 mmol, 1.5 equiv.) of naphthalen-1-ylsilane, 0.0166 g (0.025 mmol) of L5·FeCl2, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 12 h, the resulting
solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by 1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0835 g (0.22 mmol, 13/1 E/Z, 45% yield) of the title compound (Z) and recover chiral 1a in 28% NMR yield. (R,R)-1a: 94.4% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.0 (major), 24.6 (minor). 2ag: colorless oil. Optical Rotation: [α]30D = +36.4 (c 0.96, CHCl3), 96.0% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 9.3 (minor), 14.1 (major). IR (cm⁻¹): 3052, 2963, 2144, 1497, 1449. 1H NMR (CDCl3, 400 MHz): δ 7.97-7.92 (m, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.84-7.80 (m, 1H), 7.68 (dd, J = 6.6, 1.0 Hz, 1H), 7.50-7.45 (m, 2H), 7.39 (dd, J = 8.2, 6.6 Hz, 1H), 7.36-7.32 (m, 2H), 7.27-7.18 (m, 5H), 7.17-7.11 (m, 3H), 5.73 (d, J = 9.6 Hz, 1H), 4.60-4.53 (m, 2H), 3.62-3.52 (m, 1H), 2.56-2.40 (m, 2H), 1.17 (d, J = 6.8 Hz, 3H); 13C NMR (CDCl3, 100 MHz): δ 146.4, 143.1, 137.0, 136.0, 135.5, 133.1, 132.3, 130.9, 130.7, 128.8, 128.4, 128.1, 127.7, 126.93, 126.88, 126.6, 126.2, 125.9, 125.8, 125.1, 38.9, 22.6, 15.1. HRMS (ESI) calculated for [C27H27Si]+ (M + H⁺) requires m/z 379.1882, found m/z 379.1879.

(S,Z)-Benzyl(2,4-diphenylpent-2-en-1-yl)silane (2ah) Prepared according to the general procedure, using 0.1103 g (0.5 mmol) of 1a, 0.0920 g (0.75 mmol, 1.5 equiv.) of BnSiH3, 0.0168 g (0.025 mmol) of L5·FeCl2, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt3, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 1 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by 1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0687 g (0.20 mmol, 9/1 E/Z, 40% yield) of the title compound (Z) and recover chiral 1a in 31% NMR yield. (R,R)-1a: 80.0% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.4 (major), 23.8 (minor). 2ah: colorless oil. Optical Rotation: [α]30D = +12.5 (c 0.96, CHCl3), 98.4% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 49.0 (minor), 60.4 (major). IR (cm⁻¹): 3025,
2963, 2141, 1599, 1493, 1450. °H NMR (CDCl₃, 400 MHz): δ 7.34-7.15 (m, 12H), 7.09 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 7.4 Hz, 2H), 5.76 (d, J = 9.4 Hz, 1H), 3.80-3.72 (m, 2H), 3.68-3.59 (m, 1H), 2.18-2.05 (m, 4H), 1.38 (d, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 146.5, 143.3, 139.3, 135.7, 131.9, 128.5, 128.4, 128.2, 128.1, 127.0, 126.9, 126.4, 126.0, 124.7, 38.9, 29.9, 19.3, 13.5. HRMS (ESI) calculated for [C₂₄H₂₇Si]⁺ (M + H⁺) requires m/z 343.1882, found m/z 343.1880.

\((S,Z)-(2,4\text{-Diphenylpent-2-en-1-yl})(\text{phenethyl})\text{silane} \ (2\text{ai})\) Prepared according to the general procedure, using 0.1104 g (0.5 mmol) of 1a, 0.1035 g (0.75 mmol, 1.5 equiv.) of PhC₂H₄SiH₃, 0.0167 g (0.025 mmol) of L₅·FeCl₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 5 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by °H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0751 g (0.21 mmol, 10/1 E/Z, 42% yield) of the title compound (Z) and recover chiral 1a in 28% NMR yield. \((R,R)-1\text{a}: \) 82.3% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 20.7 (major), 23.0 (minor).\(2\text{ai}:\) colorless oil. Optical Rotation: \([\alpha]_{D}^{20} = +8.5\ (c \ 1.00, \text{CHCl₃})\), 96.9% ee determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.8 (major), 11.2 (minor).

IR (cm⁻¹): 3026, 2923, 2135, 1599, 1493, 1450. °H NMR (CDCl₃, 400 MHz): δ 7.37-7.33 (m, 2H), 7.31-7.25 (m, 6H), 7.24-7.12 (m, 5H), 7.04 (d, J = 7.4 Hz, 2H), 5.75 (d, J = 9.6 Hz, 1H), 3.77-3.65 (m, 3H), 2.60-2.54 (m, 2H), 2.18-2.05 (m, 2H), 1.40 (d, J = 7.0 Hz, 3H), 0.93-0.86 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 146.5, 143.9, 143.5, 136.0, 131.7, 128.4, 128.3, 128.2, 127.8, 127.0, 126.9, 126.0, 125.7, 38.9, 31.3, 22.9, 13.7, 11.5. HRMS (ESI) calculated for [C₂₅H₂₉Si]⁺ (M + H⁺) requires m/z 357.2039, found m/z 357.2044.

\((S,Z)-(2,4\text{-Diphenylpent-2-en-1-yl})(3\text{-phenylpropyl})\text{silane} \ (2\text{aj})\) Prepared according to the general procedure, using 0.1105 g (0.5 mmol) of 1a, 0.1032 g (0.75 mmol, 1.5 equiv.) of PhC₃H₆SiH₃, 0.0167 g (0.025 mmol) of L₅·FeCl₂, 75 μL.
(1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 5 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0763 g (0.21 mmol, 12/1 E/Z, 41% yield) of the title compound (Z) and recover chiral 1a in 28% NMR yield. (R,R)-1a: 78.7% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.0 (major), 23.3 (minor). 2aj: colorless oil. Optical Rotation: [α]²⁰D = +9.5 (c 0.95, CHCl₃), 94.0% ee determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.8 (major), 11.2 (minor). IR (cm⁻¹): 2924, 2131, 1598, 1493, 1450. ¹H NMR (CDCl₃, 400 MHz): δ 7.36-7.32 (m, 2H), 7.30-7.15 (m, 11H), 7.07 (d, J = 7.4 Hz, 2H), 5.74 (d, J = 9.6 Hz, 1H), 3.78-3.70 (m, 1H), 3.70-3.62 (m, 2H), 2.50 (t, J = 7.8 Hz, 2H), 2.19-2.07 (m, 2H), 1.62-1.53 (m, 2H), 1.40 (d, J = 7.2 Hz, 3H), 0.60-0.53 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 146.5, 143.5, 142.1, 136.2, 131.6, 128.4, 128.2, 128.1, 127.0, 126.9, 126.5, 126.0, 125.7, 38.93, 38.87, 27.2, 22.9, 13.7, 9.2. HRMS (ESI) calculated for [C₂₆H₃₀SiNa⁺]⁺ (M + Na⁺) requires m/z 393.2014, found m/z 393.2017.

(5,Z)-(2,4-Diphenylpent-2-en-1-yl)(dodecyl)silane (2ak) Prepared according to the general procedure, using 0.1113 g (0.5 mmol) of 1a, 0.1524 g (0.75 mmol, 1.5 equiv.) of C₁₂H₂₅SiH₃, 0.0166 g (0.025 mmol) of L₅·FeCl₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 5 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0770 g (0.18 mmol, 11/1 E/Z, 37% yield) of the title compound (Z) and recover chiral 1a in 12% NMR yield. (R,R)-1a: 94.7% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.4 (major), 24.7 (minor). 2ak: colorless oil. Optical Rotation: [α]²⁰D = -1.7 (c 1.00, toluene), 87.1% ee determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.8 (major), 11.2 (minor).
Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.9 (major), 11.6 (minor). IR (cm⁻¹): 2923, 2855, 1949, 1455. ¹H NMR (CDCl₃, 400 MHz): δ 7.39-7.34 (m, 2H), 7.32-7.27 (m, 5H), 7.25-7.15 (m, 3H), 5.74 (d, J = 9.6 Hz, 1H), 3.80-3.71 (m, 1H), 3.69-3.61 (m, 2H), 2.20-2.07 (m, 2H), 1.41 (d, J = 7.0 Hz, 3H), 1.31-1.17 (m, 20H), 0.88 (t, J = 6.4 Hz, 3H), 0.58-0.50 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 146.6, 143.6, 136.3, 131.5, 128.4, 128.1, 127.0, 126.8, 126.5, 125.9, 38.9, 32.8, 31.9, 29.7, 29.5, 29.4, 29.2, 25.2, 22.8, 22.7, 14.1, 13.8, 9.5. HRMS (ESI) calculated for [C₂₉H₄₅Si]+ (M + H+) requires m/z 421.3291, found m/z 421.3300.

E. Data of Gram Scale Reaction and Further Transformations

Gram scale reaction (2ag) Prepared according to the general procedure, using 2.2091 g (10.0 mmol) of 1a, 2.3731 g (15.0 mmol, 1.5 equiv.) of naphthalen-1-ylsilane, 0.3333 g (0.5 mmol) of L₅·FeCl₂, 1.5 mL (1.0 M in THF, 1.5 mmol) of NaBHEt₃, and 20 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.1928 g, 1.5 mmol). After 12 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 1.58 g (4.17 mmol, 14/1 E/Z, 41% yield) of the title compound (Z) and recover chiral 1a in 13% NMR yield. 2ag: colorless oil. 96.6% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 11.3 (minor), 19.6 (major). (R,R)-1a: 98.6% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 23.0 (major), 25.4 (minor).

(S,Z)-2,4-Diphenylpent-2-en-1-ol (3): Prepared according to a previously reported procedure.
a 10 mL Schlenk flask was charged with \textbf{2a} (0.0667 g, 0.2 mmol), KHCO$_3$ (0.0205 g, 0.2 mmol) and THF/MeOH (1/1, 4 mL), and then 30\% aqueous H$_2$O$_2$ (0.4 ml, 3.6 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with water (2 mL), extracted with ether (5 mL x 3). The organic layers were combined, washed with brine, dried over Na$_2$SO$_4$ and concentrated in vacuo. The crude product was purified by column chromatography using PE/EA (10/1) as the eluent to give 0.0434 g (0.18 mmol, 90\% yield) of the title compound as a white solid. mp: 75.5-76.3 °C. Optical Rotation: [\alpha]$_{20}^\text{D}$ = -44.8 (c 0.85, CHCl$_3$), 97.0\% ee determined by HPLC, HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 90/10, 1.0 mL/min, n = 220 nm, tR 6.9 (major), 11.5 (minor). IR (cm$^{-1}$): 3358, 2965, 1599, 1491, 1450. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.44 (d, $J$ = 7.6 Hz, 2H), 7.35-7.24 (m, 7H), 7.23-7.17 (m, 1H), 6.01 (d, $J$ = 9.6 Hz, 1H), 4.62 (s, 2H), 4.01-3.93 (m, 1H), 1.45 (d, $J$ = 7.0 Hz, 3H), 1.34-1.27 (brs, 1H); $^{13}$C NMR: (CDCl$_3$, 100 MHz): $\delta$ 146.0, 140.7, 137.7, 137.1, 128.7, 128.5, 127.3, 126.9, 126.4, 126.3, 60.1, 38.3, 22.8. HRMS (ESI) calculated for [C$_{17}$H$_{18}$ONa]$^+$ (M + Na$^+$) requires m/z 261.1255, found m/z 261.1265.

**X-ray diffraction of 3; CCDC 1900765**
((4R)-3-Fluoropent-1-ene-2,4-diyl)dibenzene (4): Prepared according to a previously reported procedure (Thibaudeau and Gouverneur, 2003; Tredwell et al., 2008), a 10 mL flame-dried Schlenk flask cooled under nitrogen was charged with 2a (0.1651 g, 0.5 mmol) and MeCN (5 mL), and then 0.2136 g of selectflour (0.6 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at room temperature for 36 h and at room temperature for 30 min. The reaction was quenched with ether (5 mL) and filtered through a pad of silica gel, washed by ether (5 mL x 3). The organic layers was concentrated in vacuo and purified by column chromatography using PE as the eluent to give 0.0458 g (0.19 mmol, 38% yield) of (S,R)-4 and 0.0566 g (0.24 mmol, 47% yield) of (R,R)-4.

 Optical Rotation: \([\alpha]_{D}^{20} = +68.9 \text{ (c 0.99, CHCl}_3)\), 96.3% ee determined by HPLC, HPLC conditions: Chiralcel OJ-H, nhexane/iPrOH = 99/1, 1.0 mL/min,
n = 220 nm, tr 7.5 (minor), 11.5 (major). IR (cm⁻¹): 2977, 2929, 1496, 1452. ¹H NMR (CDCl₃, 400 MHz): δ 7.36-7.26 (m, 5H), 7.26-7.21 (m, 2H), 7.21-7.16 (m, 1H), 7.13 (d, J = 7.6 Hz, 2H), 5.47 (dd, J = 47.2, 5.2 Hz, 1H), 5.35 (d, J = 2.4 Hz, 1H), 5.32 (s, 1H), 3.01-2.87 (m, 1H), 1.29 (d, J = 7.0 Hz, 3H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 146.2 (d, J = 16.2 Hz), 143.2 (d, J = 3.0 Hz), 138.8 (d, J = 3.8 Hz), 128.5, 128.3, 127.9 (d, J = 4.4 Hz), 127.8, 127.0 (d, J = 1.6 Hz), 126.6, 115.7 (d, J = 11.8 Hz), 97.7 (d, J = 182.8 Hz), 42.3 (d, J = 22.0 Hz), 14.7 (d, J = 6.0 Hz); ¹⁹F NMR (CDCl₃, 376.5 MHz): δ -188.1. HRMS (ESI) calculated for [C₁₇H₁₇FNa⁺] (M + Na⁺) requires m/z 263.1212, found m/z 263.1205.

\[ ((3R,4R)-3-fluoropent-1-ene-2,4-diyl)dibenzene \ (R,R)-4: \] colorless oil.

Optical Rotation: \( [\alpha]_{D}^{20} = +38.3 \) (c 1.03, CHCl₃), 95.7% ee determined by HPLC. HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 9.3 (minor), 10.7 (major). IR (cm⁻¹): 2972, 2926, 1495, 1451. ¹H NMR (CDCl₃, 400 MHz): δ 7.41-7.31 (m, 5H), 7.30-7.20 (m, 3H), 7.16 (d, J = 7.6 Hz, 2H), 5.36 (dd, J = 46.8, 6.6 Hz, 1H), 5.33 (s, 1H), 5.22 (s, 1H), 3.05-2.91 (m, 1H), 1.24 (d, J = 7.2 Hz, 3H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 146.1 (d, J = 17.0 Hz), 141.8, 138.7 (d, J = 2.2 Hz), 128.5, 128.2, 128.1, 127.9, 127.3, 126.6, 117.0 (d, J = 10.4 Hz), 98.5 (d, J = 179.2 Hz), 42.9 (d, J = 22.2 Hz), 18.1 (d, J = 6.0 Hz); ¹⁹F NMR (CDCl₃, 376.5 MHz): δ -178.9. HRMS (ESI) calculated for [C₁₇H₁₈F⁺] (M + H⁺) requires m/z 241.1393, found m/z 241.1388.

\[(3R,4R)-2,4-Diphenylpent-1-en-3-ol (5): \] Prepared according to a previously reported procedure (Hayashi et al., 1984), a 10 mL flame-dried Schlenk flask cooled under nitrogen was charged with 2a (0.0663 g, 0.2 mmol) and DCM (1 mL), and NaHCO₃ (0.0343 g, 0.4 mmol) was added. The reaction mixture was cooled to -78 °C and a solution of mCPBA (0.0663 g, 0.4 mmol in 2 mL DCM) was added dropwise. The reaction mixture was allowed to stir to room temperature and at room temperature for 24 h. Then 2 mL of MeOH and 140 uL of acetic acid were added and stirred at room temperature for 30 min. The reaction was quenched with water (2 mL), extracted with
DCM (5 mL x 3). The organic layers were combined, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography using PE/EA (10/1) as the eluent to give 0.0426 g (0.18 mmol, 88% yield, 6/1 dr) of the title compound as a colorless oil. Optical Rotation: [α]₂₀D = +91.2 (c 0.97, CHCl₃). IR (cm⁻¹): 3456, 2974, 1494, 1450. ¹H NMR (CDCl₃, 400 MHz): δ 7.38-7.24 (m, 7H), 7.23-7.16 (m, 3H), 5.37 (s, 1H), 5.32 (s, 1H), 4.82 (s, 1H), 2.92-2.83 (m, 1H), 1.74 (d, J = 3.4 Hz, 1H), 1.19 (d, J = 7.2 Hz, 3H); ¹³C NMR: (CDCl₃, 100 MHz): δ 150.0, 144.4, 140.3, 128.4, 128.3, 127.8, 127.6, 126.9, 126.4, 113.7, 77.3, 42.2, 12.7. HRMS (ESI) calculated for [C₁₇H₁₉O]+ (M + H⁺) requires m/z 239.1436, found m/z 239.1434.

((S,Z)-2,4-Diphenylpent-2-en-1-yl)((E)-hex-1-en-1-yl)(phenyl)silane (6): Prepared according to a previously reported procedure (Cheng et al., 2017), a 10 mL flame-dried Schlenk flask cooled under nitrogen was charged with 2a (0.0662 g, 0.2 mmol) and xantphos-CoBr₂ (0.0163 g, 10 mol%). The mixture was vacuumed and flushed with nitrogen for three times, and then 1.0 mL of toluene (0.2 M), NaBHEt₃ (1.0 M in THF, 60 μL, 0.06 mmol) and 1-butyne (46 uL, 0.4 mmol) were added in sequence. The reaction was run at room temperature for 12 h. Then the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and purified by flash column chromatography using PE as the eluent to give 0.0726 g (0.18 mmol, 88% yield, 7/1 dr) of the title compound as a colorless oil. Optical Rotation: [α]₂₀D = +40.0 (c 1.03, CHCl₃). IR (cm⁻¹): 2959, 2924, 2126, 1610, 1454. ¹H NMR (CDCl₃, 400 MHz): δ 7.47-7.42 (m, 2H), 7.35-7.13 (m, 13H), 6.16-6.07 (m, 1H), 5.71 (d, J = 9.6 Hz, 1H), 5.57-5.45 (m, 1H), 4.45-4.40 (m, 1H), 3.72-3.58 (m, 1H), 2.43-2.28 (m, 2H), 2.08-1.97 (m, 2H), 1.33-1.20 (m, 7H), 0.90-0.83 (m, 3H). HRMS (ESI) calculated for [C₂₉H₃₅Si]+ (M + H⁺) requires m/z 411.2508, found m/z 411.2520.
(S,Z)-(2,4-Diphenylpent-2-en-1-yl)diphenylsilane (7): Prepared according to a previously reported procedure (Hirone et al., 2010), a 10 mL flame-dried Schlenk flask cooled under nitrogen was charged with 2a (0.1654 g, 0.5 mmol) and THF (1 mL). Lithium chloride (0.0431 g, 1.0 mmol) and phenylmagnesium bromide (5 mL, 1 M in THF) were added in sequence. The reaction mixture was run at room temperature for 24 h and quenched with water (0.5 mL), filtered through a pad of silica gel, washed by ether (5 mL x 3) and concentrated in vacuo. The crude product was purified by column chromatography using PE as the eluent to give 0.1836 g (0.45 mmol, 90% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]_20^D = +42.2$ (c 1.00, CHCl$_3$), 98.4% ee determined by HPLC after oxidation (Cheng et al., 2019), HPLC conditions: Chiralcel OD-H, nhexane/iPrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.7 (major), 10.9 (minor). IR (cm$^{-1}$): 3059, 2964, 2133, 1491, 1438. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.49-7.43 (m, 4H), 7.39-7.30 (m, 3H), 7.30-7.23 (m, 7H), 7.21-7.10 (m, 6H), 5.68 (d, J = 9.6 Hz, 1H), 4.75 (t, J = 3.8 Hz, 1H), 3.61-3.52 (m, 1H), 2.67-2.52 (m, 2H), 1.14 (d, J = 7.0 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 146.4, 143.6, 135.3, 135.2, 135.1, 133.9, 133.7, 132.4, 129.6, 128.3, 128.0, 127.9, 127.8, 127.0, 126.8, 126.7, 125.8, 38.8, 22.4, 17.3. HRMS (ESI) calculated for [C$_{29}$H$_{29}$Si]+ (M + H$^+$) requires m/z 405.2039, found m/z 405.2041.

F. Mechanism Studies

Control experiments

Prepared according to the general procedure, using 0.0445 g (0.2 mmol) of (S,S)-1a, 77 $\mu$L (0.6 mmol, 3.0 equiv.) of PhSiH$_3$, 0.0134 g (0.02 mmol) of L$_5$-FeCl$_2$, 60 $\mu$L (1.0 M in THF, 0.06 mmol) of NaBHEt$_3$, and 0.8 mL (0.25 M) of dioxane containing 5 mol% of 3-chlorophenol (0.06 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated
and stereoselectivity was monitored by \(^1\)H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0623 g (0.19 mmol, 94% yield) of the title compound \((Z)\). \((S,Z)\)-2a: 99.5\% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.0 (minor), 23.7 (major).

Prepared according to the general procedure, using 0.0449 g (0.2 mmol) of \((S,S)\)-1a, 77 μL (0.6 mmol, 3.0 equiv.) of PhSiH3, 0.0134 g (0.02 mmol) of \(R\)-L5•FeCl2, 60 μL (1.0 M in THF, 0.06 mmol) of NaBHET3, and 0.8 mL (0.25 M) of dioxane containing 5 mol% of 3-chlorophenol (0.06 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by \(^1\)H NMR analysis. A mixture of product 2a (12\% yield, 2/3 Z/E), \((Z,E)\)-8a (40\% yield), \((S,S)\)-1a (46\% yield, >99\% ee) and S3a (<2\% yield) was observed. \((S,S)\)-1a: 99.8\% ee determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, nhexane/iPrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 23.3 (minor), 25.2 (major).

\((S,E)\)-(2,4-diphenylpent-2-en-1-yl)(phenyl)silane \((S,E)\)-2a: colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.49-7.45 (m, 2H), 7.40-7.34 (m, 1H), 7.34-7.26 (m, 4H), 7.25-7.21 (m, 3H), 7.18-7.09 (m, 3H), 7.08-7.03 (m, 2H), 5.49 (d, \(J = 10.2\) Hz, 1H), 4.28-4.20 (m, 2H), 3.45-3.35 (m, 1H), 2.21 (td, \(J = 3.6, 0.8\) Hz, 2H), 1.21 (d, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR: (CDCl\(_3\), 100 MHz) : \(\delta\) 146.8, 141.6, 135.7, 135.3, 132.0, 131.8, 129.6, 128.30, 128.29, 128.1, 127.9, 126.8, 126.7, 129.7, 38.7, 22.9, 22.6. HRMS (EI) calculated for \([C_{23}H_{24}Si]+\) requires m/z 328.1647, found m/z 328.1647.

\(((2Z,4E)-2,5-diphenylpenta-2,4-dien-1-yl)(phenyl)silane \((Z,E)\)-8a: colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.58-7.54 (m, 2H), 7.48-7.43 (m, 2H), 7.38-7.26 (m, 10H), 7.24-7.17 (m, 1H), 6.97 (dd, \(J = 15.4, 11.2\) Hz, 1H), 6.57 (d, \(J = 15.4\) Hz, 2H), 4.68 (d, \(J = 10.2\) Hz, 1H), 4.28-4.20 (m, 2H), 3.45-3.35 (m, 1H), 2.21 (td, \(J = 3.6, 0.8\) Hz, 2H), 1.21 (d, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR: (CDCl\(_3\), 100 MHz) : \(\delta\) 146.8, 141.6, 135.7, 135.3, 132.0, 131.8, 129.6, 128.30, 128.29, 128.1, 127.9, 126.8, 126.7, 129.7, 38.7, 22.9, 22.6. HRMS (EI) calculated for \([C_{23}H_{24}Si]+\) requires m/z 328.1647, found m/z 328.1647.
Hz, 1H), 6.50 (d, J = 11.2 Hz, 1H), 4.39 (t, J = 3.8 Hz, 2H), 2.59 (t, J = 3.8 Hz, 2H); $^{13}$C NMR: 
(CDCl$_3$, 100 MHz) : δ 142.6, 138.5, 137.8, 135.3, 132.3, 131.9, 129.9, 128.5, 128.3, 128.0, 127.29, 127.26, 126.3, 126.2, 125.9, 15.8. HRMS (EI) calculated for [C$_{23}$H$_{22}$Si]+ requires m/z 326.1491, found m/z 326.1491.
Data S2. Cartesian coordinates of the calculated species, Related to Figure 3.
Int1(doublet)

C      -3.540691  -0.020772  -0.631331
C      -4.63781   -0.590392  -1.243851
C      -4.440182  -1.83264   -1.910295
C      -3.190764  -2.440414  -1.908762
C      -2.103174  -1.818373  -1.254371
N      -2.31573   -0.602429  -0.653423
H      -5.27946   -2.315068  -2.41398
H      -5.613829  -0.105859  -1.207084
H      -3.050227  -3.402605  -2.40436
C      -3.458027   1.21025   0.153622
O      -4.513574   1.972953   0.41623
C      -2.519442   2.812983   1.424028
C      -4.050103   3.046903   1.280005
H      -4.295655   4.000168   0.789692
N      -2.313162   1.571193   0.656669
H      -4.601189   2.973884   2.22826
C      -1.674909   3.969257   0.906251
H      -1.894681   4.883576   1.480007
H      -0.605003   3.750906   1.011507
H      -1.88777    4.162703  -0.156853
C      -0.75971    -2.270347  -1.069216
C      -0.279772   -3.60142   -1.567411
H      -0.393899   -4.378669  -0.791924
H      -0.845229   -3.925232  -2.452238
H      0.786816   -3.564806  -1.825829
N      0.013872   -1.431248  -0.358899
C      1.347098   -1.801118  -0.025816
C      2.422198   -1.221484  -0.740034
C      1.568608   -2.683594  1.055019
C      3.725588   -1.55583  -0.353208
C      2.891049   -2.984748  1.403406
C      3.962387   -2.431602  0.705708
H      4.572566   -1.119235  -0.882708
H      3.086749   -3.655798  2.241827
H      4.987768   -2.676021  0.993465
C      0.408784   -3.226885  1.880555
C      0.144437   -2.319552  3.092812
C      0.601046   -4.687059  2.306833
H      -0.495429  -3.187685  1.257446
H      -0.08074   -1.294018  2.765428
H      -0.709958  -2.691039  3.682342
H      1.027174   -2.274726  3.750299
H      0.825862   -5.33382   1.443714
H      1.422484   -4.800252  3.031929
H      -0.312409  -5.066529  2.792025
C      2.155158  -0.260015  -1.891138
C      1.70349   -0.99252   -3.166038
C      3.337643   0.657167  -2.21147
H      1.316559   0.37904  -1.566785
H  0.76575  -1.543291  -3.018236
H  1.537683  -0.270888  -3.9824
H  2.473997  -1.707689  -3.498413
H  3.705071  1.178178  -1.317539
H  4.174433  0.096448  -2.659957
H  3.029626  1.423291  -2.937848
Fe  -0.857828  0.214877  0.286231
H  -2.244908  2.612237  2.47166
Si  0.912837  1.216722  1.560903
H  0.418986  2.042093  2.737474
H  1.959439  0.340311  2.193693
C  1.940242  2.467588  0.53162
C  1.429633  3.044236  -0.646254
C  3.246067  2.83204  0.911726
C  2.174107  3.954022  -1.402927
H  0.429537  2.763413  -0.989696
C  4.001908  3.735168  0.158795
H  3.682958  2.392277  1.81281
C  3.465921  4.302738  -1.001647
H  1.749532  4.382492  -2.315141
H  5.015239  3.996356  0.476398
H  4.05603  5.007171  -1.593576

Int1(quartet)
C  -3.532874  -0.059277  -0.657743
C  -4.611385  -0.632142  -1.298263
C  -4.3888  -1.86376  -1.978165
C  -3.133613  -2.45877  -1.963472
C  -2.062215  -1.835943  -1.282748
N  -2.301309  -0.6301  -0.667281
H  -5.214016  -2.346824  -2.503966
H  -5.59284  -0.157627  -1.274558
H  -2.97545  -3.412097  -2.471011
C  -3.478309  1.161635  0.141082
O  -4.54123  1.924004  0.383396
C  -2.572554  2.768857  1.433485
C  -4.108493  2.967313  1.297205
H  -4.382126  3.936045  0.855263
N  -2.345682  1.522486  0.680397
H  -4.655275  2.831844  2.241733
H  -1.756395  3.933285  0.887358
H  -1.981396  4.851381  1.453015
H  -0.681423  3.733463  0.976684
H  -1.991806  4.10964  -0.174341
C  -0.719384  -2.269345  -1.085637
C  -0.211169  -3.595898  -1.5672
H  -0.267766  -4.357603  -0.770204
H  -0.796401  -3.961528  -2.422165
H  0.843497  -3.531838  -1.86745
N  0.039011  -1.411413  -0.369136
C  1.370683  -1.767135  -0.016096
C  2.450774  -1.188221  -0.723656
C  1.586503  -2.637878  1.075486
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | 3.751656  | -1.510908 | -0.318692 |
| C    | 2.906294  | -2.928074 | 1.44253   |
| C    | 3.981865  | -2.37454  | 0.751784  |
| H    | 4.602235  | -1.074572 | -0.842716 |
| H    | 3.096449  | -3.590014 | 2.289548  |
| H    | 5.005492  | -2.608969 | 1.053773  |
| C    | 0.419494  | -3.183969 | 1.888896  |
| C    | 0.141388  | -2.283564 | 3.103257  |
| C    | 0.609957  | -4.645183 | 2.312683  |
| H    | 0.84307   | -5.288674 | 1.449458  |
| H    | 1.425884  | -4.759028 | 3.043905  |
| H    | -0.306862 | -5.027869 | 2.788933  |
| C    | 2.192792  | -0.241499 | -1.889612 |
| C    | 1.769289  | -0.992369 | -3.16379  |
| C    | 3.371606  | 0.68341   | -2.200855 |
| H    | 1.343346  | 0.392499  | -1.587015 |
| H    | 0.831717  | -1.545913 | -3.026528 |
| H    | 1.615638  | -0.281655 | -3.992047 |
| H    | 2.550004  | -1.706981 | -3.472631 |
| H    | 3.720969  | 1.216023  | -1.306645 |
| H    | 4.220056  | 0.126055  | -2.631186 |
| H    | 3.067967  | 1.439508  | -2.939513 |
| Fe   | -0.866381 | 0.188511  | 0.326897  |
| H    | -2.286193 | 2.592578  | 2.481971  |
| Si   | 0.883906  | 1.235352  | 1.563866  |
| H    | 0.366579  | 2.081094  | 2.715352  |
| H    | 1.929463  | 0.382707  | 2.230458  |
| C    | 1.908934  | 2.477069  | 0.523625  |
| C    | 1.392725  | 3.040323  | -0.657814 |
| C    | 3.211025  | 2.85612   | 0.901463  |
| C    | 2.128207  | 3.951661  | -1.421359 |
| H    | 0.393601  | 2.750133  | -0.997176 |
| C    | 3.957671  | 3.761995  | 0.142676  |
| H    | 3.651812  | 2.426487  | 1.805578  |
| C    | 3.416264  | 4.316096  | -1.0218   |
| H    | 1.699525  | 4.369936  | -2.336343 |
| H    | 4.968232  | 4.035694  | 0.458506  |
| H    | 3.999369  | 5.022427  | -1.618342 |

(S,S)-1a

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | 0.000713  | 0.013751  | -0.089807 |
| C    | 1.235472  | 0.240144  | -0.917473 |
| C    | 0.340081  | -0.936803 | -1.216903 |
| H    | 0.191057  | -0.388361 | 0.912518  |
| H    | 1.171243  | 1.060324  | -1.642012 |
| H    | -0.275896 | -0.890125 | -2.118556 |
| H    | 0.695272  | -1.936841 | -0.953868 |
| C    | -1.193507 | 0.917731  | -0.166237 |
| C    | -1.03187  | 2.233477  | -0.392904 |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -1.869059 | 2.932654 | -0.426776 |
| H    | -0.035926  | 2.65643  | -0.538691 |
| C    | -2.526374  | 0.288742  | 0.048689  |
| C    | -2.626014  | -1.03523  | 0.515641  |
| C    | -3.727554  | 0.979511  | -0.208554 |
| C    | -3.867804  | -1.636202 | 0.734665  |
| H    | -1.720421  | -1.608821 | 0.712001  |
| C    | -4.966978  | 0.381045  | 0.00566   |
| H    | -3.695435  | 1.998665  | -0.596447 |
| C    | -5.045736  | -0.931959 | 0.482799  |
| H    | -3.911385  | -2.664377 | 1.102351  |
| H    | -5.880617  | 0.94167   | -0.207153 |
| H    | -6.017999  | -1.401595 | 0.649534  |
| C    | -6.720421  | 0.5727   | -0.32078  |
| C    | -5.97102   | 0.769667  | 0.828996  |
| C    | -3.53505   | -0.80111  | -0.912506 |
| C    | -4.250076  | 0.63017   | 1.372449  |
| H    | 2.244413   | 1.43624   | 1.301277  |
| C    | 4.815529   | -0.943452 | -0.37181  |
| H    | 3.252797   | -1.364026 | -1.805936 |
| C    | 5.177101   | -0.227485 | 0.772772  |
| H    | 4.523831   | 1.190758  | 2.269854  |
| H    | 5.533539   | -1.618317 | -0.844647 |
| H    | 6.177232   | -0.339865 | 1.198368  |

| 2a   |       |       |       |
|------|-------|-------|-------|
| C    | 0.958304 | -3.134296 | 2.359308 |
| C    | 0.498754 | -2.015448 | 1.409256 |
| H    | 0.098058 | -3.683183 | 2.770133 |
| C    | 1.68666 | -1.22185 | 0.905968 |
| H    | -0.143214 | -1.331162 | 1.991845 |
| C    | -0.383283 | -2.593827 | 0.308847 |
| H    | 2.674399 | -1.599071 | 1.187897 |
| C    | 1.630804 | -0.099013 | 0.157374 |
| C    | -1.774992 | -2.638559 | 0.476925 |
| C    | 0.164216 | -3.125592 | -0.867093 |
| C    | 2.881192 | 0.629714 | -0.193068 |
| C    | 0.323377 | 0.486933 | -0.30771 |
| C    | -2.602009 | -3.189675 | -0.505769 |
| H    | -2.215955 | -2.226905 | 1.389578 |
| C    | -0.657914 | -3.678939 | -1.851295 |
| H    | 1.245381 | -3.084806 | -1.01868 |
| C    | 3.068661 | 1.190361 | -1.46976 |
| C    | 3.917292 | 0.776251 | 0.748398 |
| H    | 0.443137 | 1.06854 | -1.23375 |
| H    | -0.411774 | -0.300944 | -0.52604 |
| C    | -2.044781 | -3.111186 | -1.676175 |
| H    | -3.684772 | -3.207339 | -0.357821 |
| H    | -0.213364 | -4.083229 | -2.764259 |
| C    | 4.251979 | 1.853148 | -1.799257 |
| H    | 2.287465 | 1.087569 | -2.225732 |
| C    | 5.099973 | 1.440857 | 0.421664 |
| H    | 3.777015 | 0.381991 | 1.756825 |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -2.687631 | -4.138317 | -2.449488 |
| C    | 5.274192   | 1.981986   | -0.855109  |
| H    | 4.37704    | 2.269563   | -2.801926  |
| H    | 5.885672   | 1.547869   | 1.173781   |
| H    | 6.197658   | 2.507068   | -1.110542  |
| H    | 1.594999   | -3.856783  | 1.823787   |
| H    | 1.540514   | -2.720361  | 3.198088   |
| Si   | -0.467532  | 1.658574   | 0.959957   |
| H    | 0.313203   | 2.924486   | 1.075598   |
| H    | -0.477327  | 0.996446   | 2.298799   |
| C    | -2.222279  | 2.059108   | 0.410599   |
| C    | -2.701056  | 3.38069    | 0.3687     |
| C    | -3.09573   | 1.025012   | 0.020789   |
| C    | -4.006608  | 3.662382   | -0.044294  |
| H    | -2.04405   | 4.20542    | 0.659687   |
| C    | -4.400514  | 1.301885   | -0.392558  |
| H    | -2.756437  | -0.014811  | 0.033845   |
| C    | -4.858754  | 2.622639   | -0.425282  |
| H    | -4.358991  | 4.696673   | -0.071054  |
| H    | -5.061317  | 0.484607   | -0.692631  |
| H    | -5.879171  | 2.841144   | -0.750083  |

PhSiH3

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| Si   | -2.34908   | 0.00002   | 0.006645  |
| H    | -2.864512  | -1.214885  | -0.689684 |
| H    | -2.86378   | 1.223804   | -0.674456 |
| H    | -2.876524  | -0.008862  | 1.404715  |
| C    | -0.467979  | 0.000085   | -0.016165 |
| C    | 0.255411   | -1.206805  | -0.0111   |
| C    | 0.255503   | 1.206853   | -0.0113   |
| C    | 1.652437   | -1.209286  | 0.003552  |
| H    | -0.27756   | -2.162141  | -0.023265 |
| C    | 1.652593   | 1.209189   | 0.003573  |
| H    | -0.277392  | 2.162214   | -0.023271 |
| C    | 2.353397   | -0.000059  | 0.011522  |
| H    | 2.196161   | -2.157306  | 0.005478  |
| H    | 2.196364   | 2.157181   | 0.005504  |
| H    | 3.446197   | -0.000147  | 0.02044   |

Int2(doublet)

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| N    | 0.931797   | -0.336827  | -1.231295 |
| C    | -4.564188  | 2.95829   | 0.561442 |
| C    | 2.701437   | 0.308056  | -3.248612 |
| C    | 1.95856    | 1.308178  | -2.633932 |
| C    | 1.00342    | 0.965262  | -1.65042 |
| H    | -2.226045  | -0.771679  | -1.614015 |
| H    | 3.430029   | 0.568395  | -4.018276 |
| H    | 3.037256   | -1.861411  | -3.385272 |
| H    | 2.100443   | 2.353051  | -2.912158 |
| C    | 1.275459   | -2.601384  | -1.275663 |
| O    | 1.912614   | -3.719965  | -1.608956 |
| C    | 1.419926   | -4.756128  | -0.723416 |
| H    | 1.045012   | -5.581832  | -1.34549  |
| Element | X    | Y    | Z    |
|--------|------|------|------|
| N      | 0.415273 | 2.767723 | 0.37322 |
| H      | 2.229493 | 5.273332 | 0.299272 |
| C      | -1.103316 | 4.730357 | 0.321827 |
| H      | -1.151461 | 5.80897 | 0.102559 |
| Fe     | -0.427337 | 0.725902 | -0.297236 |
| H      | -1.372856 | 4.574046 | 1.37825 |
| C      | 0.10198 | -1.819455 | 1.162334 |
| C      | 0.006773 | -3.235373 | 1.655639 |
| H      | 0.977562 | -3.745893 | 1.562554 |
| H      | -0.278742 | -3.274575 | 2.721322 |
| H      | -0.742724 | -3.802006 | 1.090115 |
| N      | -0.767869 | -1.264497 | 0.303662 |
| C      | -2.006275 | -1.90805 | 0.042313 |
| C      | -3.014597 | -1.885438 | 1.043029 |
| C      | -2.236166 | -2.536851 | -1.200531 |
| C      | -4.240172 | -2.497665 | 0.763114 |
| C      | -3.484058 | -3.130048 | -1.436741 |
| C      | 2.703033 | 1.100137 | 2.736969 |
| H      | -5.031131 | -2.481336 | 1.51327 |
| H      | -3.670328 | -3.623651 | -2.393051 |
| H      | -5.449024 | -3.580537 | -0.663191 |
| C      | -1.121696 | -2.658671 | -2.225379 |
| C      | -1.566689 | -2.313284 | -3.650533 |
| C      | -0.488884 | -4.058637 | -2.162917 |
| H      | -0.346922 | -1.940479 | -1.934131 |
| H      | -2.052486 | -1.326996 | -3.684447 |
| H      | -0.698106 | -2.295972 | -4.328984 |
| H      | -2.276806 | -3.054356 | -4.051279 |
| H      | -0.07735 | -4.267232 | -1.163479 |
| H      | -1.235905 | -4.838313 | -2.383547 |
| H      | 0.32608 | -4.158274 | -2.898187 |
| C      | -2.778741 | -1.178282 | 2.37399 |
| C      | -3.584915 | -1.772043 | 3.533872 |
| C      | -3.036914 | 0.331803 | 2.255026 |
| H      | -1.716766 | -1.298836 | 2.629926 |
| H      | -3.443639 | -2.861525 | 3.613898 |
| H      | -3.269128 | -1.314476 | 4.484675 |
| H      | -4.663541 | -1.576343 | 3.425542 |
| C      | 1.698228 | 1.338279 | 1.810479 |
| H      | -4.095669 | 0.537448 | 2.041297 |
| H      | -2.762032 | 0.846508 | 3.190138 |
| H      | -1.842521 | 4.218968 | -0.307962 |
| C      | 0.29454 | 4.192916 | 0.037048 |
| C      | 1.700888 | 0.522163 | -1.882453 |
| H      | 0.205188 | 1.749895 | -2.829868 |
| H      | -0.042918 | -0.077347 | -2.977988 |
| C      | 0.51265 | 0.746469 | -2.531534 |
| C      | 2.636185 | 1.618388 | -1.544521 |
| C      | 3.593311 | 1.472996 | -0.5211 |
| C      | 2.613022 | 2.841251 | -2.247605 |
| C      | 4.467892 | 2.510439 | -0.197 |
| H      | 3.637347 | 0.545071 | 0.043485 |
| C      | 3.492377 | 3.874542 | -1.92946 |
|   |   |   |   |
|---|---|---|---|
| H | 1.910811 | 2.974158 | -3.071884 |
| C | 4.424971 | 3.717612 | -0.897095 |
| H | 5.182128 | 2.37304 | 0.618156 |
| H | 3.458239 | 4.806292 | -2.499918 |
| H | 5.1149 | 4.526938 | -0.647388 |
| C | 2.10686 | -0.899918 | 1.603833 |
| C | 3.537419 | -1.40131 | 1.674481 |
| C | 2.527242 | -1.834694 | -2.705475 |
| H | 1.539509 | -1.384883 | -0.806548 |
| H | 4.279845 | -0.679863 | -2.023294 |
| H | 2.63994 | -1.411828 | 3.707037 |
| H | 2.154656 | -2.860443 | -2.687405 |
| C | 4.01373 | -2.282384 | -0.571554 |
| C | 5.148255 | -1.915571 | 0.169923 |
| C | 3.319185 | -3.442151 | -0.18993 |
| C | 5.569159 | -2.672641 | 1.265722 |
| H | 5.703521 | -1.018348 | 0.115436 |
| C | 3.741606 | -4.203824 | 0.900988 |
| H | 2.434426 | -3.757395 | 0.746483 |
| C | 4.865645 | -3.820438 | 1.639142 |
| H | 6.453427 | -2.364338 | 1.829124 |
| H | 3.190269 | -5.107158 | 1.174485 |
| H | 5.195136 | -4.417294 | 2.492794 |
| Si | -2.428674 | 1.507278 | -1.618984 |
| H | -2.646756 | 0.670246 | -2.853996 |
| H | -2.233058 | 2.897208 | -2.189012 |
| C | -4.131927 | 1.542533 | -0.77762 |
| C | -4.9539 | 0.401494 | -0.820663 |
| C | -4.574058 | 2.630451 | -0.001033 |
| C | -6.158174 | 0.343282 | -0.115392 |
| H | -4.640851 | -0.466314 | -1.405619 |
| C | -5.777833 | 2.581151 | 0.706238 |
| H | -3.965127 | 3.536995 | 0.06022 |
| C | -6.575015 | 1.432682 | 0.654982 |
| H | -6.76972 | -0.561656 | -0.163716 |
| H | -6.096384 | 3.441429 | 1.301638 |
| H | -7.516072 | 1.389764 | 1.209553 |
| H | 0.517704 | 4.308368 | -1.035679 |

TS3(doublet)

|   |   |   |   |
|---|---|---|---|
| N | -0.831932 | -0.259042 | 1.390762 |
| C | 4.978332 | 2.32154 | -0.416061 |
| C | -2.742913 | 0.6584 | 3.195517 |
| C | -1.858292 | 1.550975 | 2.604651 |
| C | -0.855491 | 1.08091 | 1.730891 |
| H | 1.838109 | -0.738047 | 1.949364 |
| H | -3.515494 | 1.021756 | 3.874989 |
| H | -3.306805 | -1.458575 | 3.358125 |
| H | -1.936477 | 2.620395 | 2.804385 |
| C | -1.509193 | -2.477938 | 1.480615 |
| O | -2.337413 | -3.457145 | 1.858356 |
| C | -2.021579 | -4.605263 | 1.041005 |
| H | -1.797509 | -5.449692 | 1.710026 |
|   |   |   |   |
|---|---|---|---|
| C | -5.279749 | -1.854644 | 0.407551 |
| H | -2.687097 | 3.8695 | -0.561123 |
| C | -4.89717 | 3.472008 | 1.090089 |
| C | -3.015249 | 4.818482 | 0.409059 |
| C | -5.178426 | 1.626235 | 0.005274 |
| H | -1.817133 | 4.037903 | -1.19895 |
| C | -4.118714 | 4.622099 | 1.245626 |
| H | -5.766477 | 3.308338 | 1.732099 |
| H | -2.405144 | 5.719744 | 0.511361 |
| H | -4.374441 | 5.364421 | 2.005424 |
| Si | 1.545928 | -1.892413 | -2.007984 |
| C | 2.135687 | -1.569058 | -3.341926 |
| H | 1.044311 | 3.294922 | -2.066936 |
| C | 4.409024 | -2.753633 | 0.945624 |
| H | 2.359537 | 3.284527 | 0.589576 |
| C | 5.491775 | -1.962824 | 0.553293 |
| H | 6.190423 | -0.4653 | -0.844093 |
| H | 4.501797 | -3.42343 | 1.804347 |
| H | 6.436825 | -2.014264 | 1.099739 |
| H | -1.054637 | -4.168922 | -0.875731 |

**TS3(quartet)**

|   |   |   |   |
|---|---|---|---|
| C | 1.545928 | -1.892413 | -2.007984 |
| H | 2.135687 | -1.569058 | -3.341926 |
| C | 1.044311 | 3.294922 | -2.066936 |
| C | 5.491775 | -1.962824 | 0.553293 |
| H | 6.190423 | -0.4653 | -0.844093 |
| H | 4.501797 | -3.42343 | 1.804347 |
| H | 6.436825 | -2.014264 | 1.099739 |
| H | -1.054637 | -4.168922 | -0.875731 |

**TS3(quartet)**

|   |   |   |   |
|---|---|---|---|
| C | 1.545928 | -1.892413 | -2.007984 |
| H | 2.135687 | -1.569058 | -3.341926 |
| C | 1.044311 | 3.294922 | -2.066936 |
| C | 5.491775 | -1.962824 | 0.553293 |
| H | 6.190423 | -0.4653 | -0.844093 |
| H | 4.501797 | -3.42343 | 1.804347 |
| H | 6.436825 | -2.014264 | 1.099739 |
| H | -1.054637 | -4.168922 | -0.875731 |
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| H       | 5.565 | -1.266 | 2.299 |
| N       | 2.673 | -1.218 | 0.873 |
| H       | 5.562 | 0.591 | 1.066 |
| C       | 3.179 | -0.442 | 3.158 |
| H       | 5.562 | -0.520 | 0.664 |
| C       | 3.850 | 0.187 | 3.762 |
| H       | 2.159 | -0.055 | 2.697 |
| H       | 3.212 | -1.473 | 3.548 |
| N       | 0.934 | -3.361 | 0.827 |
| C       | 2.094 | -4.242 | -1.194 |
| C       | 2.180 | -3.617 | -2.286 |
| H       | 1.969 | -5.248 | -0.766 |
| H       | 3.039 | 3.826 | -0.825 |
| N       | 1.048 | -2.094 | -0.390 |
| C       | 2.341 | -1.543 | 0.163 |
| C       | 2.756 | 1.393 | 1.187 |
| C       | 3.159 | 1.085 | 1.225 |
| C       | 3.974 | 0.757 | 1.447 |
| C       | 4.368 | -0.450 | 0.906 |
| C       | 4.776 | -0.279 | 0.411 |
| H       | 4.305 | -0.619 | 2.477 |
| H       | 4.998 | -0.066 | 1.711 |
| H       | 5.707 | 0.215 | 0.631 |
| C       | 2.790 | 1.252 | 2.697 |
| C       | 2.733 | 0.081 | 3.463 |
| C       | 3.787 | 2.185 | 3.412 |
| H       | 1.789 | 1.706 | 2.744 |
| H       | 2.000 | 0.778 | 3.041 |
| H       | 2.461 | -0.097 | 4.515 |
| H       | 3.711 | 0.588 | 3.455 |
| H       | 3.921 | 3.173 | 2.886 |
| H       | 4.777 | 1.708 | 3.486 |
| H       | 3.447 | -2.402 | 4.438 |
| C       | 1.889 | 1.927 | 2.323 |
| C       | 1.952 | 3.461 | 2.419 |
| C       | 2.208 | 3.178 | 3.692 |
| H       | 0.843 | 1.666 | 2.073 |
| H       | 1.600 | 3.954 | 1.500 |
| H       | 1.320 | 3.820 | 3.248 |
| H       | 2.985 | 3.793 | 2.610 |
| H       | 2.250 | 0.219 | 3.663 |
| H       | 3.174 | 1.679 | 4.079 |
| H       | 1.435 | 1.606 | 4.419 |
| Fe      | 0.736 | 1.228 | 0.170 |
| C       | 1.561 | 1.048 | 1.022 |
| C       | 1.359 | 1.081 | 2.504 |
| C       | 1.816 | 2.345 | 1.817 |
| H       | 2.522 | 0.609 | 0.734 |
| H       | 0.337 | 1.081 | 2.888 |
| H       | 2.070 | 0.551 | 3.145 |
| H       | 1.064 | 3.129 | 1.716 |
| C       | 3.205 | 2.859 | 1.891 |
| C       | 3.469 | 4.199 | 1.560 |
| C       | 4.299 | 2.032 | 2.208 |
C  4.773779  4.696959  -1.54302
H  2.633222  4.856532  -1.306044
C  5.604984  2.527746  -2.190078
H  4.130786  0.986688  -2.477319
C  5.851008  3.862966  -1.856086
H  4.949927  5.743642  -1.281826
H  6.437168  1.866193  -2.445566
H  6.872432  4.250468  -1.843883
C  0.774075  1.491351  1.323016
C  -0.101462  1.301676  2.414526
C  1.871498  2.350207  1.536735
C  0.117965  1.901482  3.652822
H  -0.974475  0.66556  2.278818
C  2.09734  2.952804  2.778717
H  2.550649  2.574395  0.714718
C  1.228699  2.731071  3.849012
H  -0.581568  1.717213  4.472921
H  2.958768  3.615085  2.902301
H   1.406  3.204072  4.817686
C  -0.93077  1.19464  -0.459921
H  -1.663622  0.84475  0.277211
H  -1.179845  0.635339  -1.365991
C  0.478144  0.828685  0.010172
Si -1.445417  3.005577  -0.729332
H  -1.312392  3.424397  -2.160352
H  -0.645364  3.94499  0.109022
C  -3.264513  3.145657  -0.25414
C  -4.287919  3.184225  -1.216673
C  -3.635385  3.116252  1.103234
C  -5.634509  3.196117  -0.840888
H  -4.030233  3.203413  -2.279726
C  -4.978181  3.133252  1.485548
H  -2.860609  3.074823  1.875426
C  -5.982026  3.173286  0.512506
H  -6.415058  3.226886  -1.605763
H  -5.24451  3.112856  2.545628
H  -7.033954  3.186352  0.80948
H   3.586879  0.628271  1.336877

Int4(quartet)
C  2.259039  -3.042282  -1.274303
C  2.635186  -4.123903  -2.048301
C  1.602207  -4.880772  -2.66253
C  0.27446  -4.575143  -2.398275
C  -0.047369  -3.472008  -1.571817
N  0.966938  -2.660977  -1.127827
H  1.853215  -5.733366  -3.296064
H  3.686198  -4.397457  -2.14496
H  -0.521551  -5.199154  -2.808341
C  3.135312  -2.252013  -0.408313
O  4.468617  -2.367879  -0.46152
C  3.747971  -0.847057  1.219367
C  5.000162  -1.508707  0.579784
H 5.093595 4.326001 0.826332
N 3.260469 1.708741 0.482572
H 4.193061 4.257147 -0.731265
C 3.254256 3.227214 2.420884
H 3.198868 4.281164 2.736789
H 2.401816 2.686736 2.856718
H 4.182126 2.788512 2.821324
C 2.538472 -2.669444 0.026851
C 2.412738 -4.165192 -0.00492
H 2.335425 -4.548759 -1.036415
H 3.298687 -4.637825 0.448604
H 1.523899 -4.503315 0.542016
N 1.560918 -1.829342 0.439096
C 0.293414 -2.334081 0.827915
C -0.061842 -2.262178 2.199547
C -0.614554 -2.861536 -0.123293
C -1.307245 -2.757111 2.599115
C -1.85417 -3.33844 0.325561
C -2.196553 -3.302402 1.673696
H -1.589085 -2.717291 3.652237
H -2.572139 -3.735399 -0.394766
H -3.165617 -3.684583 1.999379
C -0.298672 -2.915476 -1.613351
C -1.198304 -1.961235 -2.412773
C -0.416387 -4.339905 -2.179998
H 0.740475 -2.584436 -1.750594
H -1.125698 -0.932719 -2.035434
H -0.911944 -1.951929 -3.476901
H -2.252271 -2.267543 -2.346257
H 0.184413 -5.059926 -1.606452
H -1.46108 -4.688998 -2.160078
H -0.079533 -4.368339 -3.228996
C 0.925198 -1.694884 3.207156
C 1.966528 -2.747437 3.618185
C 0.262917 -1.064023 4.434179
C 1.465025 -0.888902 2.681693
H 2.501084 -3.144254 2.743565
H 2.71428 -2.312691 4.301998
H 1.483505 -3.593394 4.134619
H -0.499835 -0.326603 4.141168
H -0.218601 -1.816872 5.079391
H 1.018537 -0.548727 5.048124
Fe 2.079212 0.084671 0.517222
C -1.39134 2.488738 -0.101787
C -0.376009 1.408611 -0.342736
H -1.003712 3.391467 0.382417
H -0.887806 0.50802 -0.708196
C -3.595675 3.563966 0.073405
C -4.633956 4.042163 -0.747072
C -3.408926 4.184154 1.323391
C -5.438291 5.109855 -0.345332
H -4.801486 3.58748 -1.72585
C -4.212938 5.250619 1.727764
H  -2.636053  3.800474  1.992462
C  -5.231916  5.720857  0.894544
H  -6.230626  5.468763 -1.00722
H  -4.052023  5.708157  2.707373
H  -5.866191  6.551827  1.212528
C  -3.382173  1.248925 -1.003653
H  -4.298844  1.53718  -1.538961
H  -2.723018  0.758454 -1.734796
C  -2.715771  2.443867 -0.360278
C   0.666495  1.76688  -1.398339
C   1.372138  0.728885 -2.038612
C   1.03167  3.087236 -1.69866
C   2.441616  0.998285 -2.896202
H   1.075694 -0.305492 -1.861664
C   2.101604  3.360672 -2.557207
H   0.47276  3.9136  -1.256175
C   2.824171  2.317961 -3.146161
H   2.980641  0.170974 -3.363612
H   2.368008  4.398914 -2.77435
H   3.665118  2.533752 -3.809243
C   0.334735  0.997947  0.980021
H   0.557646  1.91851  1.556575
H  -0.379799  0.412102  1.58185
H   2.295619  3.57304  0.514423
Si  -3.851133 -0.001676  0.345359
H   -4.737259  0.663565  1.346242
H  -2.618317 -0.444798  1.045946
C  -4.753456 -1.491827 -0.380091
C  -4.814687 -1.715883 -1.76606
C  -5.342934 -2.448943  0.466411
C  -5.41654 -2.864972 -2.28943
H  -4.380654 -0.98738 -2.455408
C  -5.94568 -3.598486 -0.047618
H  -5.324395 -2.298083  1.549745
C  -5.97671 -3.812865 -1.429894
H  -5.446377 -3.0204 -3.370925
H  -6.392055 -4.331192  0.629642
H  -6.444169 -4.713804 -1.8351

Int6(quartet)
C   4.868076  -0.147751 -0.461581
C   5.971479  -0.731114 -1.044988
C   5.933953  -2.14842  -1.230572
C   4.817681  -2.878065 -0.860238
C   3.69244  -2.220198 -0.293439
N   3.782637  -0.863077 -0.08555
H   6.791303  -2.654995 -1.677656
H   6.831243  -0.132392 -1.345823
H   4.790293  -3.957805 -1.020569
C   4.636017  1.263675 -0.139958
O   5.509652  2.232893  -0.403842
C   3.586098  3.043793  0.73219
C   4.848261  3.481008 -0.053556
H  -2.461706  3.916937  1.918703
C  -5.153903  5.660015  0.761405
H  -6.242432  5.185502 -1.046224
H  -3.886316  5.859434  2.502666
H  -5.792196  6.507156  1.023774
C  -3.300785  1.09191  -0.854346
H  -3.830486  1.347262 -1.78941 
H  -2.562428  0.326582 -1.124443
C  -2.62307  2.313074 -0.276274
C  0.753955  1.708879 -1.381798
C  1.461839  0.673298 -2.021611
C  1.085598  3.029452 -1.717132
C  2.494822  0.944511 -2.921318
H  1.210017 -0.363736 -1.797578
C  2.117324  3.306648 -2.621312
H  0.533368  3.855186 -1.265228
C  2.837462  2.266876 -3.217013
H  3.036485  0.117421 -3.386157
H  2.356457  4.345622 -2.865186
H  3.647181  2.484984 -3.917439
C  0.568285  1.119517  1.0414
H  0.855446  2.109  1.449216
H  -0.110852  0.655606  1.777057
H  2.687666  3.523474  0.320129
Si  -4.566126  0.281103  0.305424
H  -5.757505  1.164152  0.47596
H  -3.973427  0.048234  1.651623
C  -5.109853 -1.374277 -0.422452
C  -4.940039 -1.666924 -1.787144
C  -5.663167 -2.374576  0.397747
C  -5.283537 -2.917356 -2.310095
H  -4.518533 -0.914768 -2.458496
C  -6.008069 -3.626441 -0.116219
H  -5.814078 -2.179339  1.463733
C  -5.811344 -3.9036 -1.472951
H  -5.131757 -3.123801 -3.372584
H  -6.425438 -4.391338  0.543538
H  -6.072278 -4.885126 -1.87635

TS7(doublet)
C  -0.739871 -2.764047  0.730625
C  -0.901043 -3.638069  1.791282
C  -1.763682 -3.262421  2.845642
C  -2.411705 -2.04008  2.785879
C  -2.172696 -1.157177  1.710802
N  -1.335439 -1.540116  0.682739
H  -1.935391 -3.938532  3.684657
H  -0.394991 -4.602988  1.772811
H  -3.106172 -1.747202  3.573271
C  -0.011546 -3.108444 -0.489362
O  0.490453 -4.350586 -0.639001
C  0.640979 -3.076743 -2.613801
C  1.195814 -4.332917 -1.905717
|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| H | 2.273727  | -4.247086 | -1.692553 |
| N | 0.094479  | -2.304617 | -1.487139 |
| H | 0.98926   | -5.276373 | -2.426695 |
| C | 1.641887  | -2.316962 | -3.466424 |
| H | 1.96258   | -2.932958 | -4.321354 |
| H | 1.180095  | -1.400284 | -3.861036 |
| H | 2.530729  | -2.044284 | -2.882488 |
| C | -2.711268 | 0.162721  | 1.579599  |
| C | -3.778458 | 0.64197   | 2.523668  |
| H | -4.678364 | 0.014679  | 2.411373  |
| H | -3.464894 | 0.57297   | 3.576314  |
| H | -4.056962 | 1.681685  | 2.31662   |
| N | -2.252696 | 0.875492  | 0.543427  |
| C | -2.495716 | 2.278748  | 0.471177  |
| C | -1.848914 | 3.166862  | 1.375974  |
| C | -3.335945 | 2.808271  | -0.54116  |
| C | -2.042401 | 4.54739   | 1.224084  |
| C | -3.485615 | 4.194653  | -0.658023 |
| C | -2.84175  | 5.069589  | 0.212569  |
| H | -1.543757 | 5.229853  | 1.91506   |
| H | -4.134648 | 4.593737  | -1.440092 |
| H | -2.969374 | 6.149643  | 0.109664  |
| C | -4.150681 | 1.899673  | -1.439707 |
| C | -4.052625 | 2.265347  | -2.923354 |
| C | -5.612654 | 1.853056  | -0.970137 |
| H | -3.733142 | 0.89541   | -1.323854 |
| H | -3.004778 | 2.285414  | -3.258781 |
| H | -4.588059 | 1.523023  | -3.534355 |
| H | -4.495263 | 3.251701  | -3.135939 |
| H | -5.681768 | 1.550877  | 0.08637   |
| H | -6.092629 | 2.840999  | -1.064633 |
| H | -6.192794 | 1.134618  | -1.571415 |
| C | -0.952386 | 2.704434  | 2.518814  |
| C | -1.592067 | 2.972423  | 3.892664  |
| C | 0.428096  | 3.375396  | 2.469876  |
| H | -0.810295 | 1.618914  | 2.419087  |
| H | -2.592587 | 2.531784  | 3.980637  |
| H | -0.962493 | 2.560048  | 4.697785  |
| H | -1.690997 | 4.055433  | 4.069754  |
| H | 0.912776  | 3.257695  | 1.493258  |
| H | 0.35502   | 4.455997  | 2.66628   |
| H | 1.088502  | 2.952634  | 3.242858  |
| Fe| -1.183563 | -0.322672 | -0.835307 |
| C | 1.710052  | 0.391251  | -0.896929 |
| C | 0.799727  | 1.589883  | -0.958938 |
| H | 1.947665  | -0.051771 | -1.866416 |
| H | 0.373509  | 1.770775  | 0.038657  |
| C | 3.049774  | -1.433639 | 0.052145  |
| C | 2.871956  | -2.553834 | 0.882522  |
| C | 4.067813  | -1.485412 | -0.915611 |
| C | 3.667866  | -3.691099 | 0.737695  |
| H | 2.082866  | -2.548212 | 1.636245  |
| C | 4.874421  | -2.614312 | -1.053305 |
| Symbol | X       | Y       | Z       |
|--------|---------|---------|---------|
| H      | 4.255966| -0.607497| -1.534064|
| C      | 4.67601 | -3.726657| -0.229805|
| H      | 3.495308| -4.556216| 1.38232|
| H      | 5.675044| -2.617615| -1.796429|
| H      | 5.310186| -4.610286| -0.334636|
| C      | 1.984447| 0.281648 | 1.6048 |
| H      | 1.027965| 0.808444 | 1.713094|
| C      | 1.977704| -0.543486| 2.331625|
| C      | 2.193704| -0.224746| 0.202034|
| C      | 1.504607| 2.882384 | -1.355525|
| C      | 0.818091| 4.100813 | -1.222487|
| C      | 2.818551| 2.905057 | -1.840767|
| C      | 1.431934| 5.307176 | -1.559654|
| H      | -0.203933| 4.102842| -0.837507|
| C      | 3.433951| 4.113004 | -2.185234|
| H      | 3.375115| 1.970863 | -1.931174|
| C      | 2.744215| 5.319029 | -2.044833|
| H      | 0.882727| 6.244393 | -1.438639|
| H      | 4.460949| 4.109779 | -2.560036|
| H      | 3.226256| 6.263535 | -2.308514|
| C      | -0.389746| 1.282158| -1.918299|
| H      | -1.050439| 2.157355| -1.977794|
| H      | 0.014923| 1.104497| -2.928909|
| H      | -0.223262| -3.348603| -3.248815|
| Si     | 3.412793| 1.461564 | 2.06552 |
| H      | 3.419332| 1.663555 | 3.547334|
| H      | 3.238355| 2.767684 | 1.380345|
| C      | 5.041165| 0.730571 | 1.478007|
| C      | 5.712171| 1.303241 | 0.383243|
| C      | 5.567154| -0.448829| 2.035725|
| C      | 6.866697| 0.714555 | -0.141837|
| H      | 5.320256| 2.216162 | -0.073685|
| C      | 6.716409| -1.042569| 1.513443|
| H      | 5.061506| -0.925965| 2.880242|
| C      | 7.368162| -0.46111 | 0.42109 |
| H      | 7.373872| 1.173441 | -0.994571|
| H      | 7.100448| -1.966688| 1.951803|
| H      | 8.266337| -0.927454| 0.008324|
| Si     | -2.854255| -1.411557| -2.116464|
| H      | -3.833979| -0.64464 | -2.950235|
| H      | -2.256353| -2.415601| -3.05744|
| H      | -1.577975| 0.201408 | -2.19995|
| C      | -3.898851| -2.391729| -0.877312|
| C      | -4.937974| -1.769028| -0.160567|
| C      | -3.574253| -3.717491| 0.533659|
| C      | -5.625334| -2.439341| 0.854201|
| H      | -5.217515| -0.741566| -0.398669|
| C      | -4.252746| -4.309522| 0.484435|
| H      | -2.770344| -4.233567| -1.06619|
| C      | -5.279979| -3.752644| 1.185647|
| H      | -6.434467| -1.934204| 1.389372|
| H      | -3.975567| -5.418205| 0.7357 |
| H      | -5.811431| -4.278129| 1.983139|
TS7(quartet)

C  -0.563588  -2.672749  0.766216
C  -0.637816  -3.548266  1.835124
C  -2.180503  -2.009718  2.875809
C  -2.028163  -1.129535  1.776505
N  -1.187921  -1.473045  0.746009
H  -1.570414  -3.86438  3.778731
H  -0.106135  -4.49864  1.795758
H  -2.865047  -1.746914  3.682175
C   0.074716  -2.993753  -0.507615
O   0.661865  -4.189512  -0.689913
C   0.549661  -2.925234  -2.677114
C   1.251872  -4.133283  -2.012671
H   2.334668  -3.969184  -1.890842
N   0.006719  -2.199074  -1.51549
H   1.07161  -5.094351  -2.510911
C   1.443959  -2.087101  -3.575559
H   1.740412  -2.665485  -4.464767
C   0.907595  -1.189159  -3.91377
H   2.355672  -1.77844  -3.046048
C  -2.677651  0.133068  1.629751
C  -3.734713  0.564849  2.607428
H  -4.588927  -0.13105  2.557959
H  -3.372884  0.561841  3.646529
H  -4.101882  1.571676  2.375645
N  -2.341035  0.838595  0.538346
H  -2.614749  2.229865  0.454973
C  -1.990621  3.14609  1.349869
C  -3.452933  2.72474  -0.578385
C  -2.21223  4.518798  1.171465
C  -3.632561  4.105101  -0.717861
C  -3.01558  5.006884  0.145574
H  -1.730588  5.22373  1.852145
H  -4.28005  4.478676  -1.513642
H  -3.164831  6.082167  0.02385
C  -4.22595  1.780048  -1.478196
C  -4.146929  2.145802  -2.962545
C  -5.680909  1.653823  -1.002747
H  -3.766499  0.7918  -1.365563
H  -3.101108  2.227523  -3.296019
H  -4.636162  1.36979  -3.570697
H  -4.6475  3.102647  -3.181348
H  -5.726697  1.349697  0.054555
H  -6.212668  2.615065  -1.095621
H  -6.223277  0.903568  -1.600473
C  -1.08318  2.723461  2.50114
C  -1.708778  3.050873  3.869056
C  0.302976  3.378457  2.414896
H  -0.943121  1.634916  2.444122
H  -2.721236  2.641868  3.975549
H  -1.086539  2.646733  4.683973
|   |          |          |          |          |
|---|----------|----------|----------|----------|
| H | -1.776984| 4.14094  | 4.014556 |
| H | 0.789108 | 3.197385 | 1.449673 |
| H | 0.240724 | 4.469717 | 2.545988 |
| H | 0.958089 | 2.993338 | 3.212076 |
| Fe| -1.363053| -0.310559| -0.92949 |
| C | 1.738886 | 0.406393 | -0.919527|
| C | 0.792449 | 1.571868 | -0.960034|
| H | 2.001335 | 0.003919 | -1.899419|
| H | 0.340272 | 1.705519 | 0.032636 |
| C | 3.12393  | -1.402142| -0.020175|
| C | 3.014301 | -2.537505| 0.800868 |
| C | 4.108824 | -1.410951| -1.024848|
| C | 3.837228 | -3.648609| 0.610012 |
| H | 2.256673 | -2.565524| 1.585018 |
| C | 4.940716 | -2.513937| -1.210447|
| H | 4.250831 | -0.518925| -1.635595|
| C | 4.806468 | -3.643111| -0.396252|
| H | 3.715965 | -4.525801| 1.250027 |
| H | 5.712406 | -2.4836  | -1.983159|
| H | 5.460757 | -4.506638| -0.537415|
| C | 1.977092 | 0.231023 | 1.578338 |
| C | 0.999346 | 0.720127 | 1.684036 |
| H | 1.983975 | -0.614325| 2.281523 |
| C | 2.228947 | -0.22637 | 0.164722 |
| C | 1.472166 | 2.896037 | -1.302916|
| C | 0.741991 | 4.089847 | -1.176468|
| C | 2.801959 | 2.971992 | -1.73729 |
| C | 1.327829 | 5.321723 | -1.467566|
| H | -0.293855| 4.053738 | -0.832173|
| C | 3.389783 | 4.205206 | -2.037768|
| H | 3.392348 | 2.058273 | -1.821339|
| C | 2.656401 | 5.385663 | -1.90192 |
| H | 0.74349  | 6.238055 | -1.350842|
| H | 4.429618 | 4.241745 | -2.373483|
| H | 3.116503 | 6.350196 | -2.129947|
| C | -0.359433| 1.271168 | -1.954228|
| H | -1.077106| 2.104234 | -1.965191|
| H | 0.053317 | 1.186557 | -2.971505|
| H | -0.32171 | -3.263578| -3.267184|
| Si| 3.356832 | 1.443662 | 2.096391 |
| H | 3.337804 | 1.601006 | 3.583945 |
| H | 3.152093 | 2.765788 | 1.451493 |
| C | 5.011703 | 0.777736 | 1.503601 |
| C | 5.680891 | 1.406667 | 0.439147 |
| C | 5.556117 | -0.412496| 2.018821 |
| C | 6.850857 | 0.86145 | -0.098641|
| H | 5.275317 | 2.329937 | 0.016423 |
| C | 6.721013 | -0.963008| 1.483928 |
| H | 5.052354 | -0.933317| 2.838221 |
| C | 7.370055 | -0.326282| 0.421238 |
| H | 7.35604  | 1.363695 | -0.92781 |
| H | 7.119042 | -1.896659| 1.888287 |
| H | 8.279822 | -0.75923 | -0.002371|
TS8(doublet)

N  0.700776   2.524675   -0.315183
C  4.641025  -2.878073   -0.961728
C  1.392573   5.197729    0.001617
C  2.329585   4.200955    0.234591
C  1.986345   2.845444    0.03797
H  1.733739  -2.570476    2.333492
H  1.656118   6.246018    0.150848
H  -0.647639  5.602585   -0.711117
H   3.337498   4.461425    0.561235
C  -1.406772   2.923916   -1.13766
O  -2.3928    3.68163     -1.633793
C  -3.233377   2.768581   -2.382932
H  -4.276717   3.090646   -2.277261
N  -1.546565   1.631884   -1.220741
H  -2.92903    2.821067   -3.441488
C  -3.907898   1.117301   -0.596311
H  -4.884367   0.814678   -1.000662
Fe  0.268952    0.67239    -0.633965
H  -4.047315   2.01864     0.018028
C  2.843335   1.70951     0.076771
C  4.307305   1.876808    0.369407
H  4.727992   2.712136   -0.211313
H  4.475503   2.106955    1.434332
H  4.873589   0.971324    0.125266
N  2.257429   0.541454   -0.246008
C  3.078995   -0.6074    -0.446287
C  3.555621  -1.387619    0.632873
C  3.404342  -0.951658   -1.785575
C  4.335113  -2.51726     0.346202
C  4.176892  -2.094513   -2.018505
C  0.10115   4.849473   -0.465756
H  4.701828  -3.131576    1.170931
H  4.428674  -2.372145   -3.043515
H  5.245136  -3.766714   -1.160363
C  2.971865  -0.062224   -2.943232
C  2.593316  -0.841587   -4.207027
|   | X     | Y     | Z     |
|---|-------|-------|-------|
| C | 4.887816 | 0.872489 | -2.174828 |
| H | 2.817846 | 0.369542 | -2.017872 |
| H | 3.041435 | -1.9589 | -3.039965 |
| H | 3.513458 | -1.612215 | -4.120174 |
| H | 4.758925 | 1.627291 | -1.377202 |
| H | 4.790175 | 1.3965 | -3.139731 |
| C | 2.812968 | -0.297486 | 3.038842 |
| C | 3.894635 | 0.220151 | 4.004069 |
| C | 1.927336 | -1.316497 | 3.774093 |
| H | 2.176555 | 0.551216 | 2.749933 |
| H | 4.573681 | 0.934554 | 3.520932 |
| H | 3.432978 | 0.718642 | 4.871839 |
| H | 4.50853 | -0.610864 | 4.38707 |
| C | -0.079091 | 3.791231 | -0.604804 |
| H | 2.5176 | -2.175123 | 4.132177 |
| H | 1.454439 | -0.849588 | 4.652816 |
| H | -3.787342 | 0.541448 | -0.877216 |
| C | -2.768129 | 1.944154 | -2.209948 |
| C | -0.364125 | -1.332516 | -1.175005 |
| H | 1.063021 | -0.734264 | -2.719246 |
| H | -0.61727 | -0.066661 | -2.947719 |
| C | 0.13249 | -0.428112 | -2.236403 |
| C | 0.557009 | -2.523937 | -0.951405 |
| C | 1.086228 | -2.920047 | 0.283422 |
| C | 0.90209 | -3.30023 | -2.076653 |
| C | 1.893972 | -4.053151 | 0.402302 |
| H | 0.896024 | -2.334054 | 1.176647 |
| C | 1.701728 | -4.437791 | -1.964001 |
| H | 0.547203 | -2.991332 | -3.060441 |
| C | 2.198373 | -4.825871 | -0.717366 |
| H | 2.299378 | -4.31571 | 1.380737 |
| H | 1.94548 | -5.016693 | -2.858466 |
| H | 2.832975 | -5.710298 | -0.624163 |
| C | -1.835372 | -1.699897 | -1.368374 |
| C | -2.486962 | -2.935233 | -0.781064 |
| C | -2.301188 | -2.806727 | -2.274925 |
| H | -2.475099 | -0.815964 | -1.389734 |
| H | -1.787405 | -3.621032 | -0.295595 |
| H | -1.559954 | -3.46413 | -2.730655 |
| H | -3.183442 | -2.620588 | -2.893587 |
| C | -3.815615 | -2.857333 | -0.118321 |
| C | -4.004332 | -3.470476 | 1.130698 |
| C | -4.888296 | -2.137667 | 0.670815 |
| C | -5.215104 | -3.351315 | 1.816661 |
| H | -3.179814 | -4.032388 | 1.576043 |
| C | -6.097596 | -2.012638 | 0.014022 |
| H | -4.776549 | -1.653805 | -1.643287 |
| C | -6.266889 | -2.615223 | 1.264403 |
| H | -5.334394 | -3.830196 | 2.791644 |
| H | -6.913282 | -1.436981 | -0.430416 |
| H | -7.212695 | -2.51485 | 1.801817 |
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| Si      | -0.86 | -0.49 | 1.00  |
| H       | 0.31  | -0.09 | 1.83  |
| H       | -1.26 | -1.84 | 1.47  |
| C       | -2.27 | 0.64  | 1.52  |
| C       | -3.56 | 0.14  | 1.79  |
| C       | -2.05 | 2.02  | 1.72  |
| C       | -4.59 | 0.99  | 2.21  |
| H       | -3.77 | -0.92 | 1.68  |
| C       | -3.06 | 2.86  | 2.14  |
| H       | -1.05 | 2.43  | 1.53  |
| C       | -4.35 | 2.35  | 2.38  |
| H       | -5.58 | 0.57  | 2.41  |
| H       | -2.86 | 3.93  | 2.28  |
| H       | -5.15 | 3.02  | 2.71  |
| H       | -2.63 | 1.22  | -3.03 |
| H       | -2.63 | 1.22  | -3.03 |
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