Supplementary Information

The Silicon–Hydrogen Exchange Reaction: A Catalytic σ-Bond Metathesis Approach to the Enantioselective Synthesis of Enol Silanes

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1. General considerations

Chemicals

Unless otherwise indicated, starting materials were obtained from Sigma-Aldrich, ABCR-GmbH, TCI, or Acros Co. Ltd. Moreover, commercially available reagents were used without additional purification. Ketone 1a was obtained from commercial suppliers and used after chromatographic purification and recrystallization. Ketones 1c–1o, 1s, 1u, 1v, 1w and 1ac were synthesized according to literature procedure. The allyl(tert-butyl)dimethylsilane 2a was obtained from commercial suppliers, and used after distillation. Triethyl(2-methylallyl)silane 2b was synthesized according to literature procedures. The chiral imidodiphosphorimidate acids (IDPis) 4a–4f were synthesized according to literature procedures.

Solvents

Solvents (Et₂O, THF, 1,4-Dioxane, Cyclohexane, CH₂Cl₂, CHCl₃, Benzene and Toluene) were dried by distillation from an appropriate drying agent in the technical department of the Max-Planck-Institut für Kohlenforschung and received in Schlenk flasks under argon. In addition, more solvents (MTBE, CH₃CN and Mesitylene) were purchased from commercial suppliers and dried over molecular sieves.

Inert Gas

Dry argon was purchased from Air Liquide with >99.5% purity.

Thin Layer Chromatography

Thin-layer chromatography (TLC) was performed using silica gel pre-coated plastic sheets (Polygram SIL G/UV₂₅₄, 0.2 mm, with fluorescent indicator; Macherey-Nagel) which was visualized with a UV lamp (254 nm) and/or phosphomolybdic acid (PMA). PMA stain: PMA (20 g) in EtOH (200 mL).

Column Chromatography

Column chromatography (CC) was carried out using Merck silica gel (60 Å, 230–400 mesh, particle size 0.040–0.063 mm) using technical grade solvents. Elution was accelerated using compressed argon. All reported yields, unless otherwise specified, refer to spectroscopically and chromatographically pure compounds.

Nomenclature

Nomenclature follows the suggestions proposed by the computer program ChemBioDraw (12.0.3.1216) of CBD/cambridgesoft.

Nuclear Magnetic Resonance Spectroscopy

¹H, ¹³C, ¹⁹F, ³¹P Nuclear magnetic resonance (NMR) spectra for compound characterization were recorded on Bruker AVIII-500 MHz, NMR spectrometer in a suitable deuterated solvent. The solvent employed and the respective measuring frequency are indicated for each experiment. Chemical shifts are reported with tetramethylsilane (TMS) serving as a universal reference of all nuclides. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and b (broad). All spectra were recorded at 298 K, processed with MestReNova 10.0.2 suits of program, and coupling constants are reported as observed. The residual deuterated solvent signal relative to tetramethylsilane was used as the internal reference in ¹H NMR spectra (e.g. CDCl₃ = 7.26 ppm,
CD$_2$Cl$_2$ = 5.32 ppm. Signals are reported as follows: chemical shift $\delta$ in ppm (multiplicity, coupling constant $J$ in Hz, number of protons). All X-nuclei spectra were acquired proton decoupled unless otherwise noted.

Kinetic NMR measurements were performed at a Bruker AVIII- 300MHz WB NMR spectrometer. The temperature of low temperature experiments was calibrated against a 4% MeOH in MeOD-$d_4$ sample. Further details are mentioned in the corresponding section.

**Mass Spectrometry**

Electrospray ionization (ESI) mass spectrometry was conducted on a Bruker ESQ 3000 spectrometer. High resolution mass spectra were determined on a Bruker APEX III FTMS (7 T magnet). The ionization method and mode of detection employed is indicated for the respective experiment and all masses are reported in atomic units per elementary charge ($m/z$) with an intensity normalized to the most intense peak.

**Specific Rotations**

Specific rotations ([alpha]$_D^T$) were measured with a Rudolph RA Autopol IV Automatic Polarimeter at the indicated temperature with a sodium lamp (sodium D line, $\lambda$ = 589 nm). Measurements were performed in an acid resistant 1 mL cell (50 mm length) with concentrations (g/(100 mL)) reported in the corresponding solvent.

**High Performance Liquid Chromatography**

High performance liquid chromatography (HPLC) was performed on a Shimadzu LC-20AD liquid chromatograph SIL-20AC autosampler, CMB-20A using Daicel columns with a chiral stationary phase. All solvents used were HPLC-grade solvents purchased from Sigma-Aldrich. The column employed and the respective solvent mixture are indicated for each experiment.

**Gas Chromatography**

Gas chromatography (GC) analyses on a chiral stationary phase were performed on HP 6890 and 5890 series instruments (split-mode capillary injection system, flame ionization detector (FID), hydrogen carrier gas). The conditions employed are described in detail for the individual experiments.

**Abbreviations**

e.r. = enantiomeric ratio, TLC = thin layer chromatography, THF = tetrahydrofuran, MTBE = methyl tert-butyl ether, CH$_3$CN = acetonitrile, Mesitylene = 1,3,5-trimethylbenzene, TBS = SiMe$_2$Bu, TMS = SiMe$_3$, TES = triethylsilyl, Tf = SO$_2$CF$_3$, MOM = methoxymethyl ether.
2. Preparation and characterization of imidodiphosphorimidates (IDPis)

Representative procedure for 3,3'-disubstituted BINOL synthesis by Suzuki coupling and the subsequent hydrolysis:

(S)-3,3'-bis(9,9-diethyl-9H-fluoren-3-yl)-[1,1'-binaphthalene]-2,2'-diphenyl

In a flame dried 2-neck round-bottom flask with a condenser, (S)-2,2'-bis(2,2'-bis(methoxymethoxy)-1,1'-binaphthyl-3,3'-dihydroxide(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (500 mg, 0.8 mmol, 1.0 equiv.), 2'-bromospiro[cyclobutane-1,9'-fluorene] (524 mg, 2.3 equiv.), and tetrakis(triphenylphosphine)palladium (92 mg, 0.08 mmol, 0.1 equiv.) were dissolved in 1,4-dioxane (10 mL). After degassing the reaction mixture with argon for 10–15 min, a degassed aqueous solution of K₂CO₃ (2.0 M, 3 mL) was added. The resultant mixture was then transferred into a microwave reactor and stirred at 90 °C for 2 h. After cooling the reaction system to room temperature, the mixture was further purified by column chromatography to afford (S)-3,3'-bis(2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-dihydroxide(1,9'-fluorene). A solution of this material and Amberlyst®-15 (Hydrogen form) in THF/MeOH (1:1) was then stirred at 90 °C for 12 h. After completion of the reaction (as monitored by TLC analysis), Amberlyst®-15 was removed by filtration, and the mixture was concentrated under reduced pressure. Finally, the crude mixture was purified by column chromatography (Ethyl acetate/hexanes 1:20 to 1:4) to afford the title compound as a white/off white solid (overall yield of the two steps: 75%).

1H NMR (501 MHz, CD₂Cl₂) δ 8.13 (s, 1H), 7.99 (dd, J = 8.2, 1.2 Hz, 1H), 7.89–7.83 (m, 1H), 7.81–7.77 (m, 1H), 7.76–7.71 (m, 2H), 7.43 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.40–7.32 (m, 4H), 7.25 (dd, J = 8.5, 1.1 Hz, 1H), 5.55 (s, 1H), 2.17–2.01 (m, 4H), 0.38 (td, J = 7.4, 1.5 Hz, 6H).

13C NMR (126 MHz, CD₂Cl₂) δ 153.1, 153.0, 150.7, 139.3, 139.2, 137.2, 133.5, 131.6, 131.5, 130.0, 128.9, 128.8, 128.1, 127.5, 127.4, 124.6, 124.6, 124.5, 123.1, 119.9, 119.8, 113.2, 52.4, 33.7, 33.6, 17.3.

Rf = 0.28 (Ethyl acetate/hexanes = 1:9).

ESI-HRMS (m/z): calculated for C₅₅H₄₅O₂ ([M-H]⁻): 725.3425, found: 725.3424.

m.p. = 220.2–224.8°C.

[α]D²⁵ = 85.2 (c 0.14, CHCl₃).

(S)-3,3'-di(triphenyl-2-yl)-[1,1'-binaphthalene]-2,2'-diphenyl
In a flame dried 2-neck round-bottom flask with a condenser, (S)-2,2’-(2,2’-bis(methoxymethoxy)-1,1’-binapthyl-3,3’-diyl)bis(4,4’,5,5’-tetramethyl-1,3,2-dioxaborolane) (1.1 g, 1.8 mmol, 1.0 equiv.), 2-bromophenanthrene (1.1 g, 2.3 equiv.), and tetrakis(triphenylphosphine)palladium (208 mg, 0.08 mmol, 0.1 equiv.) were dissolved in 1.4-dioxane (22 mL). After degassing the reaction mixture with argon for 10–15 min, a degassed aqueous solution of K$_2$CO$_3$ (2.0 M, 6.8 mL) was added. The resultant mixture was then transferred into a microwave reactor and stirred at 90 °C for 2 h. After cooling the reaction to room temperature, the mixture was further purified by column chromatography to afford (S)- 2,2’-(2,2’-bis(methoxymethoxy)-1,1’-binaphthalene)-3,3’-diyl)diphenylene. A solution of this material and Amberlyst®-15 (Hydrogen form) in THF/MeOH (1:1) was then stirred at 90 °C for 12 h. After the completion of the reaction (as monitored by TLC analysis), Amberlyst®-15 was removed by filtration, and the mixture was concentrated under reduced pressure. Finally, the crude mixture was purified by column chromatography (Ethyl acetate/hexanes 1:20 to 1:4) to afford the title compound as a white/off white solid (overall yield of the two steps: 85 %).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 9.08 (d, $J$ = 1.7 Hz, 2H), 8.81–8.76 (m, 4H), 8.72 (ddd, $J$ = 9.5, 7.5, 3.2 Hz, 6H), 8.28 (s, 2H), 8.09 (dd, $J$ = 8.5, 1.8 Hz, 2H), 8.05 (dd, $J$ = 8.2, 1.2 Hz, 2H), 7.70 (m, $J$ = 8H), 7.47 (ddd, $J$ = 8.1, 6.7, 1.3 Hz, 2H), 7.41 (ddd, $J$ = 8.3, 6.8, 1.4 Hz, 2H), 7.34 (dd, $J$ = 8.4, 1.1 Hz, 2H), 5.69 (s, 2H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 151.0, 136.9, 133.7, 132.2, 131.0, 130.4, 130.3, 130.2, 130.1, 129.9, 129.5, 129.2, 129.0, 127.9, 127.8, 124.9, 124.8, 124.7, 123.8, 123.8, 123.8, 113.1.

R$_f$ = 0.23 (Ethyl acetate/hexanes = 1:4).

ESI-HRMS (m/z): calculated for C$_{58}$H$_{33}$O$_2$ ([M-H]): 737.2486, found: 737.2497.

m.p. = 286.3–288.1°C.

$[\alpha]_D^{25}$ = 88.3 (c 0.29, CHCl$_3$).

(S)-3,3’-bis(3’5’-di-tert-butyl-[1,1’-biphenyl]-4-yl)-[1,1’-binaphthalene]-2,2’-diol

In a flame dried 2-neck round-bottom flask with a condenser, (S)-2,2’-(2,2’-bis(methoxymethoxy)-1,1’-binapthyl-3,3’-diyl)bis(4,4’,5,5’-tetramethyl-1,3,2-dioxaborolane) (500 mg, 0.8 mmol, 1.0 equiv.), 4’-bromo-3,5-di-tert-butyl-1,1’-biphenyl (635 mg, 2.3 equiv.), and tetrakis(triphenylphosphine)palladium (92 mg, 0.08 mmol, 0.1 equiv.) were dissolved in 1.4-dioxane (10 mL). After degassing the reaction mixture under argon for 10–15 min, a degassed aqueous solution of K$_2$CO$_3$ (2.0 M, 3 mL) was added. The resultant mixture was then transferred into a microwave reactor and stirred at 90 °C for 2 h. After cooling the reaction to room temperature, the mixture was further purified by column chromatography to afford (S)-3,3’-bis(3’5’-di-tert-butyl-[1,1’-biphenyl]-4-yl)-2,2’-bis(methoxymethoxy)-1,1’-binaphthalene. A solution of this material and Amberlyst®-15 (Hydrogen form) in THF/MeOH (1:1) was then stirred at 90 °C for 12 h. After the completion of the reaction (as monitored by TLC analysis), Amberlyst®-15 was removed by filtration, and the mixture was concentrated under reduced pressure. Finally, the crude mixture was purified by column chromatography (ethyl acetate/hexanes 1:20 to 1:4) to afford the title compound as a white/off white solid (overall yield of theses two steps: 75 %).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 8.02 (s, 2H), 7.90 (d, $J$ = 8.1 Hz, 2H), 7.77–7.73 (m, 4H), 7.68–7.64 (m, 4H), 7.43 (d, $J$ = 1.8 Hz, 4H), 7.39 (t, $J$ = 1.8 Hz, 2H), 7.34 (d, $J$ = 1.4 Hz, 2H), 7.26 (d, $J$ = 1.5 Hz, 2H), 7.15 (dd, $J$ = 8.4, 1.1 Hz, 2H), 5.42 (s, 2H), 1.31 (s, 36H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 151.4, 150.4, 141.8, 140.1, 136.3, 133.1, 131.3, 130.5, 129.9, 129.6, 128.5, 127.4, 127.3, 124.3, 124.2, 121.7, 121.6, 112.5, 34.9, 31.3.
Rf = 0.49 (Ethyl acetate/hexanes = 1:9).

ESI-HRMS (m/z): calculated for C$_{60}$H$_{61}$O$_2$ ([M-H]$: 813.4677, found: 813.4682.

m.p. = 175.3–178.5 °C.

[$\alpha$]$^D_{25}$ = 40.0 (c 0.17, CHCl$_3$).

The synthesis of phosphorimidoyl trichlorides R$_f$-1–5.

The syntheses of ((trifluoromethyl)sulfonyl)phosphorimidoyl trichloride$^{10}$ R$_f$-1, ((perfluoroethyl)sulfonyl)phosphorimidoyl trichloride$^{11}$ R$_f$-2 have been described previously. ((perfluorohexyl)sulfonyl)phosphorimidoyl trichloride R$_f$-3 and ((perfluoroctyl)sulfonyl)phosphorimidoyl trichloride R$_f$-4 were synthesized as reported in the literature$^6$. ((perfluoronaphthalen-2-yl)sulfonyl)phosphorimidoyl trichloride R$_f$-5 was synthesized according to the procedure reported in the literature$^{12}$.

The synthesis of ((perfluoronaphthalen-2-yl)sulfonyl)phosphorimidoyl trichloride R$_f$-6

Step 1. According to a known procedure$^{13}$: octafluoronaphthalene (5.4 g, 20 mmol, 1 equiv.) was dispersed in a mixture of ethylene glycol (15 mL) and anhydrous N,N dimethylformamide (30 mL). A yellow solution of sodium hydrosulphide hydrate (2.2 g, 40 mmol, 2 equiv.) in ethylene glycol (15 ml) and anhydrous N,N-dimethylformamide (30 ml) was slowly added over 10 min keeping the reaction temperature below 5 °C. The reaction temperature was raised to 20 °C and the reaction were monitored by TLC (hexanes as eluent). After complete consumption of the starting material (~90 min), the orange mixture was acidified (2 M H$_2$SO$_4$) extracted with ether, dried over anhydrous Na$_2$SO$_4$ and the crude brown solid (3.6 g, 12.5 mmol, 63% crude yield) was used without purification for the next step.

Step 2. According to a known procedure$^{14}$: N-chlorosuccinimide (5.6 g, 42 mmol, 4 equiv.) was added to a mixture of HCl:MeCN (2 M, 1:5, 12 mL) and then the mixture was cooled to 0 °C. The 1,3,4,5,6,7,8-heptafluoronaphthalene-2-thiol (3 g, 10.5 mmol, 1 equiv.) was added portion wise using a spatula into the mixture. Temperature of the reaction mixture was kept below 15 °C for 30 min. The cooling bath was removed and it was allowed to warm up to room temperature. Once the reaction mixture became orange homogeneous solution (~15 min, consumption of starting materials was confirmed by TLC: 20% EtOAc in hexanes), it was diluted with ethyl acetate (100 mL). The organic layer was washed with copious amount of aq. NaCl (5 x 50 mL) to remove excess NCS and dried over anhydrous Na$_2$SO$_4$, concentrated in vacuo to get the desired product as brown solid (3.2 g, 9.1 mmol, 86% crude yield). The crude product was used for the next step without purification.
Step 3. According to a known procedure\textsuperscript{15}: 1,3,4,5,6,7,8-Heptafluoronaphthalene-2-sulfonyl chloride (3.2 g, 9.1 mmol, 1 equiv.) was dissolved in newly-distilled THF and then the mixture was cooled to −10 °C. 0.5 M ammonia solution in dioxane (−30 mL, 14.6 mmol, 1.6 equiv.) was added dropwise to get a dark brown solution. The cooling bath was removed and it was allowed to attain room temperature. The reaction mixture was stirred for another 3 h (consumption of starting materials was confirmed by TLC: 30% EtOAc in hexanes). The volatiles were removed via vacuum and the crude product was directly subjected to silica gel flash column chromatography using 25% EtOAc in hexanes as eluents. The pure desired product was isolated as yellow solid (1.8 g, 5.4 mmol, 59% yield). Yield over three steps were 32% from octafluoronaphthalene.

Step 4. In a flame dried pre-weighed Schlenk flask (25 mL) under Ar equipped with a magnetic stirring bar, solid PCl\textsubscript{3} (0.951 g, 4.57 mmol, 1.3 equiv.) was added and weighed directly inside the Schlenk flask. 1,3,4,5,6,7,8-heptafluoronaphthalene-2-sulphonamide (1.17 g, 3.15 mmol, 1.0 equiv.) were placed. 0.5 mL of dry toluene was added and the mixture was heated to 110 °C under Ar. The yellow solution was stirred for 30 min and then volatiles were carefully removed at 300 mbar until bubbling disappeared. The liquid mixture was then heated to 130 °C for 1 h at 10 mbar to remove the excess amount of PCl\textsubscript{3} by sublimation. PCl\textsubscript{3} that condensed in the top part of the Schlenk flask was removed by heating with hot gun (100 °C for 15 min). The mixture was then cooled to room temperature and the remaining traces of HCl were removed in vacuo to afford the desired product R\textsubscript{f}-6 as a light brown solid (1.61 g, 98%).

Note: \textsuperscript{13}C NMR spectrum could not be obtained due to very low signal intensity.

\textbf{((perfluoronaphthalen-2-yl)sulfonyl)phosphorimidoyl trichloride R\textsubscript{f}-6}

\textbf{General procedure for the preparation of compounds 4a-4f}. To a mixture of the 3,3'-disubstituted BINOL (2.1 equiv.) and various (substituted sulfonyl)phosphorimidoyl trichlorides (2.1 equiv.) in toluene (0.1 M) was added diisopropylethylamine (16 equiv.) at room temperature under an argon atmosphere. After stirring for 10–30 min, HMDPS (1.0 equiv.) was added. After an additional 10 min at room temperature, the reaction mixture was sealed and heated to 120 °C for 2–3 d. The mixture was diluted with ethyl acetate and insoluble solid was filtered off through a short pad of Celite. Then the solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel using ethyl acetate/hexanes mixtures. After evaporation of solvent, the collected solid was stirred in a biphasic solution (DCM/6 N HCl) for 15 min and extracted with DCM. Azeotropic removal of water using toluene gave catalysts 4a-4f as white solids in their acidic form (yield: 50–65%).

\textbf{(S,S)-IDPi-4a}:

\textbf{1H NMR (501 MHz, CDCl\textsubscript{3})} δ 8.16 (s, 2H), 8.10 (dd, J = 12.3, 8.3 Hz, 4H), 7.91 (ddd, J = 8.1, 6.7, 1.1 Hz, 2H), 7.89–7.84 (m, 4H), 7.81 (d, J = 7.5 Hz, 2H), 7.75 (ddd, J = 8.3, 6.8, 1.3 Hz, 2H), 7.67 (dt, J = 7.7, 0.9 Hz, 2H), 7.63 (ddd, J = 8.2, 6.4, 1.5 Hz, 2H), 7.59–7.53 (m, 4H), 7.49–7.39 (m, 6H), 7.35–7.17 (m, 11H), 6.54 (d, J = 8.0 Hz, 2H), 6.47 (dd, J = 7.9, 1.6 Hz, 2H), 6.34 (dd, J = 8.0, 1.7 Hz, 2H), 2.83–2.73 (m, 2H), 2.70–2.53 (m, 9H), 2.44–2.20 (m, 13H), 2.20–2.10 (m, 2H).

\textbf{13C NMR (126 MHz, CDCl\textsubscript{3})} δ 153.0, 152.6, 152.4, 151.9, 143.8 (t, J = 5.2 Hz), 142.8 (t, J = 4.7 Hz), 139.5, 138.7, 138.6, 138.5, 135.1, 134.5, 134.4, 133.7, 132.2, 131.8, 131.8, 131.7, 131.6, 131.4, 129.3, 129.0, 128.7, 128.6, 127.9, 127.6, 127.3, 127.0, 126.9, 126.8, 126.7, 126.6, 126.6, 123.7, 123.4, 122.5, 122.4, 121.9, 119.6, 119.0, 118.6, 118.0, 52.0, 51.9, 33.2, 32.9, 32.8, 32.5, 16.8, 16.7.
$^{19}$F NMR (471 MHz, CD$_2$Cl$_2$) $\delta$ –79.3, –115.8, –116.1.

$^{31}$P NMR (203 MHz, CD$_2$Cl$_2$) $\delta$ –17.8.

R$_f$ = 0.27 (Ethyl acetate/hexanes = 1:4).

ESI-HRMS (m/z): calculated for C$_{10}$H$_{12}$F$_{10}$N$_2$O$_8$P$_2$S$_2$ ([M-H]): 1854.4082, found: 1854.4098.

m.p. = 284.4–289.5 °C.

$[\alpha]_{D}^{25}$ = 205.0 (c 0.12, CHCl$_3$).

(S,S)-IDPi-4b:

$^{1}$H NMR (501 MHz, CD$_2$Cl$_2$) $\delta$ 8.16 (s, 2H), 8.10 (d, $J$ = 8.3 Hz, 2H), 8.07–8.02 (m, 2H), 7.92 (ddd, $J$ = 8.1, 6.7, 1.1 Hz, 2H), 7.89–7.84 (m, 4H), 7.79–7.74 (m, 4H), 7.67–7.59 (m, 5H), 7.56 (d, $J$ = 7.3 Hz, 2H), 7.51 (d, $J$ = 1.6 Hz, 2H), 7.47 (d, $J$ = 7.9 Hz, 2H), 7.42–7.37 (m, 2H), 7.33–7.14 (m, 11H), 7.11 (s, 2H), 6.75 (dd, $J$ = 7.9, 1.7 Hz, 2H), 6.63 (d, $J$ = 8.0 Hz, 2H), 6.32 (dd, $J$ = 8.0, 1.7 Hz, 2H), 5.21–4.88 (m, 1H), 2.81–2.71 (m, 2H), 2.65 (dd, $J$ = 11.2, 9.5, 7.2 Hz, 2H), 2.62–2.50 (m, 7H), 2.41–2.25 (m, 10H), 2.25–2.03 (m, 7H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ 153.0, 152.6, 152.4, 152.0, 143.9, 142.8, 139.5, 138.7, 138.7, 138.5, 135.1, 134.3, 134.2, 133.4, 132.2, 131.9, 131.8, 131.6, 131.5, 131.3, 129.5, 129.1, 128.7, 128.4, 127.9, 127.5, 127.3, 127.0, 126.8, 126.7, 126.5, 126.4, 123.7, 123.4, 123.3, 122.4, 122.4, 122.0, 119.4, 119.0, 118.5, 118.0, 51.9, 51.9, 33.2, 33.0, 32.7, 32.4, 16.7, 16.6.

$^{19}$F NMR (471 MHz, CD$_2$Cl$_2$) $\delta$ –81.1 (t, $J$ = 9.9 Hz), –111.7 (dt, $J$ = 129.3 Hz, $J$ = 15.0 Hz), –120.3 (dd, $J$ = 23.3, 13.6 Hz), –121.7–122.0 (m), –123.0 (q, $J$ = 13.8 Hz), –126.4 (t, $J$ = 14.8 Hz).

$^{31}$P NMR (203 MHz, CD$_2$Cl$_2$) $\delta$ –17.2.

R$_f$ = 0.42 (Ethyl acetate/hexanes = 1:4).

ESI-HRMS (m/z): calculated for C$_{116}$H$_{152}$N$_{3}$O$_{3}$P$_{2}$S$_{2}$F$_{26}$ ([M-H]): 2254.3826, found: 2254.3813.

m.p. = 228.7–233.1 °C.

$[\alpha]_{D}^{25}$ = 168.0 (c 0.10, CHCl$_3$).

(S,S)-IDPi-4c:

$^{1}$H NMR (501 MHz, CD$_2$Cl$_2$) $\delta$ 8.07 (s, 2H), 8.01 (d, $J$ = 8.2 Hz, 2H), 7.95 (dd, $J$ = 8.3, 1.2 Hz, 2H), 7.82 (ddd, $J$ = 8.1, 6.7, 1.2 Hz, 2H), 7.79–7.73 (m, 4H), 7.70–7.63 (m, 4H), 7.58–7.50 (m, 4H), 7.47 (dd, $J$ = 7.5, 1.0 Hz, 2H), 7.43 (d, $J$ = 1.6 Hz, 2H), 7.38 (d, $J$ = 8.0 Hz, 2H), 7.32–7.29 (m, 4H), 7.22 (d, $J$ = 7.4 Hz, 2H), 7.13 (ddt, $J$ = 35.5, 18.1, 7.5, 1.2 Hz, 9H), 7.02 (s, 2H), 6.66 (dd, $J$ = 7.9, 1.6 Hz, 2H), 6.54 (d, $J$ = 8.0 Hz, 2H), 6.24 (dd, $J$ = 8.0, 1.7 Hz, 2H), 2.67 (q, $J$ = 9.8 Hz, 2H), 2.60–2.42 (m, 8H), 2.31–1.98 (m, 14H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ 153.0, 152.6, 152.4, 152.1, 143.9 (t, $J$ = 4.7 Hz), 142.8 (t, $J$ = 4.7 Hz), 139.5, 138.7, 138.7, 138.5, 135.1, 134.3, 134.2, 133.4, 132.2, 131.9, 131.8, 131.6, 131.5, 131.2, 129.5, 129.1, 128.7, 128.4, 127.9, 127.5, 127.3, 127.0, 126.8, 126.7, 126.5, 126.4, 123.7, 123.4, 123.3, 122.4, 122.3, 122.0, 119.4, 119.0, 118.5, 118.1, 53.8, 53.6, 53.4, 53.2, 53.0, 51.9, 51.9, 33.2, 33.0, 32.7, 32.4, 16.7, 16.6.

$^{19}$F NMR (471 MHz, CD$_2$Cl$_2$) $\delta$ –81.1 (t, $J$ = 10.0 Hz), –111.7 (qt, $J$ = 16.0 Hz, $J$ = 14.4 Hz), –120.3, –121.6, –122.1, –122.9, –126.3.
$^{31}$P NMR (203 MHz, CD$_2$Cl$_2$) δ −17.2.
Rf = 0.51 (Ethyl acetate/hexanes = 1:4).

ESI-HRMS (m/z): calculated for C$_{120}$H$_{72}$F$_{34}$N$_{10}$O$_{8}$P$_{2}$S$_{2}$ ([M-H]): 2454.3699, found: 2454.3705.
m.p. = 242.3–243.3 °C.
$[\alpha]_D^{25} = 147.7$ (c 0.13, CHCl$_3$).

LC-MS (50 mm YMC TriArt Bio C4, 3.0 mm i.D., 0.1% TFA/MeCN 15:85, 1.0 mL/min, 5.0 MPa, 308 K): 254 nm: $t_R = 5.63$ min, 98% ([M – H]): 2454.

(S,S)-IDPi-4d:

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 8.17 (s, 2H), 8.08 (d, J = 8.2 Hz, 2H), 8.03 (d, J = 8.2 Hz, 2H), 7.84–7.79 (m, 4H), 7.74 (d, J = 7.5 Hz, 2H), 7.70 (d, J = 1.7 Hz, 2H), 7.68–7.58 (m, 8H), 7.45 (dt, J = 7.2, 1.6 Hz, 4H), 7.37 (ddd, J = 8.1, 6.7, 1.3 Hz, 2H), 7.33–7.21 (m, 10H), 7.21–7.13 (m, 4H), 6.95 (d, J = 8.0 Hz, 2H), 6.73 (dd, J = 8.0, 1.7 Hz, 2H), 6.56 (dd, J = 8.0, 1.6 Hz, 2H), 4.02 (d, J = 29.6 Hz, 1H), 3.62 (d, J = 24.7 Hz, 2H), 2.99–2.86 (m, 2H), 2.66 (dd, J = 7.2, 4.1 Hz, 2H), 2.53 (q, J = 8.3 Hz, 4H), 2.40–2.11 (m, 5H), 1.61 (s, 3H), 1.40 (s, 2H), 1.28 (s, 4H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 152.9, 152.3, 152.1, 152.1, 143.9 (t, J = 4.5 Hz), 143.0 (t, J = 4.5 Hz), 139.1, 138.6, 138.6, 138.4, 135.0, 134.6, 133.9, 133.7, 131.9, 131.7, 131.7, 131.5, 131.4, 131.1, 129.2, 128.7, 128.4, 127.7, 127.4, 127.3, 126.9, 126.8, 126.7, 126.7, 126.6, 124.0, 123.2, 123.1, 122.4, 122.4, 119.5, 119.3, 118.9, 118.3, 51.9, 51.6, 33.3, 33.2, 32.9, 32.6, 16.7, 16.7.

$^{19}$F NMR (471 MHz, CD$_2$Cl$_2$) δ −136.4 (d, J = 22.2 Hz), −146.7, −160.0 (t, J = 20.3 Hz).

$^{31}$P NMR (203 MHz, CD$_2$Cl$_2$) δ −15.6.

Rf = 0.54 (Ethyl acetate/hexanes = 1:4).

EI-HRMS (m/z): calculated for C$_{119}$H$_{72}$F$_{34}$N$_{10}$O$_{8}$P$_{2}$S$_{2}$ ([M-H]): 1950.4082, found: 1950.4082.
m.p. = 288.9–291.6 °C.
$[\alpha]_D^{25} = 382.0$ (c 0.10, CHCl$_3$).

LC-MS (50 mm Zorbax SB300-C8, 3.5 μm, 4.6 mm i.D., 0.1% TFA/MeCN 15:85, 1.0 mL/min, 5.0 MPa, 308 K): 254 nm: $t_R = 3.78$ min, 96% ([M – H]): 1950.

(S,S)-IDPi-4e:

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 8.95 (d, J = 1.7 Hz, 2H), 8.78 (dd, J = 8.4, 4.8 Hz, 4H), 8.61–8.56 (m, 2H), 8.50–8.40 (m, 10H), 8.19 (dd, J = 8.4, 1.4 Hz, 2H), 8.11–8.06 (m, 4H), 8.06–8.00 (m, 6H), 8.00–7.91 (m, 4H), 7.82 (ddd, J = 8.4, 7.0, 1.1 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.72–7.66 (m, 6H), 7.63 (d, J = 8.6 Hz, 6H), 7.58–7.41 (m, 16H), 6.58 (d, J = 8.7 Hz, 2H), 6.15 (ddd, J = 8.5, 1.8 Hz, 2H), 5.69 (d, J = 8.5 Hz, 2H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 143.5, 143.1, 134.6, 132.3, 132.3, 132.1, 131.7, 131.6, 130.2, 129.9, 129.7, 129.4, 129.4, 129.3, 129.3, 129.2, 129.1, 129.1, 128.8, 128.5, 128.0, 127.7, 127.6, 127.4, 127.3, 127.2, 127.2, 127.04, 126.8, 126.8, 126.8, 126.6, 126.4, 124.9, 124.4, 123.7, 123.6, 123.4, 123.4, 123.3, 123.2, 123.2, 122.9, 122.8, 122.80, 122.4, 122.0.
19F NMR (471 MHz, CD2Cl2) δ −79.3.

31P NMR (203 MHz, CD2Cl2) δ −14.5.

Rf = 0.35 (Ethyl acetate/hexanes = 2:3).

ESI-HRMS (m/z): calculated for C114H66F36N3O3P5S2 ([M-H]): 1842.3520; found: 1842.3538.

m.p. = 389.4–395.5 °C.

[α]D 25 197.3 (c 0.22, CHCl3).

The data were in accordance with the reported literature.

(S,S)-IDPi-4f:

\[
\text{[M-H]}^- = 2362.7775.
\]

\[
\text{[M-H]}^- = 2362.7774.
\]

1H NMR (501 MHz, CD2Cl2) δ 8.17–8.11 (m, 2H), 7.89 (s, 2H), 7.80 (d, J = 7.0 Hz, 4H), 7.65 (ddd, J = 8.1, 6.5, 1.5 Hz, 2H), 7.44–7.35 (m, 7H), 7.22 (d, J = 6.4 Hz, 10H), 7.19 (t, J = 1.8 Hz, 2H), 7.16 (d, J = 1.8 Hz, 6H), 7.12 (t, J = 1.8 Hz, 2H), 6.95 (d, J = 1.8 Hz, 4H), 6.93–6.86 (m, 4H), 6.73 (d, J = 8.4 Hz, 4H), 4.89 (s, 1H), 1.13 (s, 36H), 0.99 (s, 36H).

13C NMR (126 MHz, CD2Cl2) δ 150.9, 150.8, 143.7, 143.7 (t, J = 5.0 Hz), 143.4 (t, J = 5.0 Hz), 141.5, 141.5, 141.1, 140.0, 139.6, 134.4, 133.9, 133.7, 133.4, 132.4, 131.8, 131.7, 131.2, 131.0, 131.0, 129.5, 129.5, 129.0, 128.2, 127.1, 127.1, 126.8, 126.7, 126.4, 126.3, 123.4, 122.3, 121.3, 121.2, 121.1, 34.7, 34.6, 31.0, 29.7.

19F NMR (471 MHz, CD2Cl2) δ −112.2 (dd, J = 76.0, 17.8 Hz), −133.7 (d, J = 18.5 Hz), −140.8 (dt, J = 77.3, 17.3 Hz), −145.2 (dt, J = 59.0, 16.5 Hz), −146.8 (dt, J = 58.6, 18.7 Hz), −149.8 (t, J = 18.7 Hz), −154.5 (d, J = 20.0 Hz).

31P NMR (203 MHz, CD2Cl2) δ −10.1.

Rf = 0.8 (Ethyl acetate/hexanes = 1:4).

ESI-HRMS (m/z): calculated for C130H128F16N3O3P5S2 ([M-H]): 2362.77774, found: 2362.7775.

m.p. = 193.8–195.2 °C.

[α]D 25 241.8 (c 0.11, CHCl3).

The data were in accordance with the reported literature.

3. Development of suitable reaction conditions and catalyst identification.

General procedure for the optimization of the catalytic silylation of ketones with allylsilanes.

Allyl silane 2a or 2b (0.05 mmol, 2.0 equiv.) was placed in a flame-dried Schlenk flask, which was equipped with a teflon-coated magnetic stirring bar. IDPi 4a–4f (0.01 equiv.) and solvent (0.08 M, 0.3 mL) were added, and the resultant solution was stirred for 5 min at 25 °C. Ketone 1a (4.4 mg, 0.025 mmol, 1.0 equiv.) was slowly added and the reaction mixture was stirred for an additional 12 h. After the ketone was fully consumed, as monitored by TLC, the reaction mixture was treated with triethylamine. Volatiles were removed in vacuo and the yield of 3a was determined by NMR analysis with nitrobenzene as internal standard. The enantiomeric ratio was determined by HPLC after purification by prep. TLC.

Table S1. Initial screening with commonly used Brønsted acid catalysts:

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Table S2. Screening of different IDPi catalysts:

| entry | catalyst | yield (%) | e.r. |
|-------|----------|-----------|------|
| 1     | 4a       | 95        | 82:18|
| 2     | 4b       | 99        | 85.5:14.5 |
| 3     | 4c       | 99        | 88:12|
| 4     | 4d       | 99        | 80:20|
| 5     | 4e       | 80        | 80:20|
| 6     | 4f       | 99        | 75:25|

*a*Reactions were conducted with ketone 1a (0.025 mmol), allyl silane 2a (2.0 equiv.), and catalyst 4a–4f (1.0 mol%) in toluene at rt. *b*All yields were determined by crude 1H NMR analysis with nitrobenzene as internal standard. *c*The enantiomeric ratio (e.r.) was determined by HPLC analysis.

Table S3. Screening of different solvents:
Reactions were conducted with ketone 1a (0.025 mmol), silane source 2a (2.0 equiv.), and catalyst 4a (1.0 mol%) at 25 °C. All yields were determined by crude 1H NMR analysis with nitrobenzene as internal standard. The enantiomeric ratio (e.r.) was determined by HPLC analysis.

**Table S4.** Screening of different silicon sources:

| entry<sup>b</sup> | solvent      | yield (%)<sup>b</sup> | e.r.<sup>c</sup> |
|-------------------|--------------|------------------------|------------------|
| 1                 | Et<sub>2</sub>O | 99                     | 60:40            |
| 2                 | THF          | NR                     | --               |
| 3                 | MTBE         | NR                     | --               |
| 4                 | CH<sub>3</sub>CN | NR                   | --               |
| 5                 | CH<sub>2</sub>Cl<sub>2</sub> | 99                 | 68:32            |
| 6                 | CHCl<sub>3</sub> | 99                     | 70:30            |
| 7                 | Cyclohexane  | 99                     | 70:30            |
| 8                 | Benzene      | 99                     | 80:20            |
| 9                 | Mesitylene   | 99                     | 78:22            |
| 10                | Toluene      | 99                     | 82:18            |
| 11                | 1,4-Dioxane  | 99                     | 87:13            |

<sup>a</sup>Reactions were conducted with ketone 1a (0.025 mmol), silane source 2a (2.0 equiv.), and catalyst 4a (1.0 mol%) at 25 °C. <sup>b</sup>All yields were determined by crude 1H NMR analysis with nitrobenzene as internal standard. <sup>c</sup>The enantiomeric ratio (e.r.) was determined by HPLC analysis.

**Notes:** 1. the reaction time with 2b was 7 h. 2. compared to 2c, silicon source 2a was commercially available, thus it was chosen as optimal agent for the next screening.

**Table S5.** Screening of the reaction temperature:

| solvent      | yield (%) | e.r. |
|--------------|-----------|------|
| 1,4-Dioxane  | 99%       | 87:13|
| 1,4-Dioxane  | 77%       | 64:36|
| 1,4-Dioxane  | 99%       | 87:13|
| 1,4-Dioxane  | 10%       | 53.5:46.5 |
| 1,4-Dioxane  | No Reaction |

only Mukaiyama aldol product was observed

Notes: 1. the reaction time with 2b was 7 h. 2. compared to 2c, silicon source 2a was commercially available, thus it was chosen as optimal agent for the next screening.
Reactions were conducted with ketone 1a (0.025 mmol), 2a (2.0 equiv.), and catalyst 4c (1.0 mol%) in combined solvent (toluene/dioxane = 2:1) at 25 °C. All yields were determined from crude NMR analysis with newly distilled nitrobenzene as internal standard. The enantiomeric ratio (e.r.) was determined by HPLC analysis. 4 with sole dioxane as solvent.

4. The preparation and characterization of cyclic ketones

The 4-aryl substituted ketones were prepared according to the methods reported in the literature with minor modifications. 1c, 1e, 1j, 1k and 1n are known compounds and the spectra are in accordance with the reported structures.1

Step 1: To a flame dried two-neck round-bottom flask with a condenser, magnesium turnings (0.60 g, 49.6 mmol) and a small portion of iodine as initiator was added. After the first 5 mL of R1-Br (23.5 mmol) solution in THF (40 mL) was added in one portion, the suspension was heated till the color changed from dark brown to clear (which indicates the formation of the Grignard reagent). Then the remaining solution of R1-Br was slowly added via a funnel and the reaction mixture was heated to reflux for 2 h. After the flask was cooled to room temperature, a solution of 1,4-cyclohexanedione monoethylene ketal (3.50 g, 22.4 mmol) in THF (40 mL) was added dropwise, and the reaction mixture was heated to reflux for 12 h. The mixture was treated with a saturated aqueous NH4Cl solution (50 mL), and the resultant mixture was extracted with ethyl acetate (3 x 50 mL). The organic layers were dried (MgSO4), filtered, and concentrated under reduced pressure to give the crude product. This material was purified directly by column chromatography on silica gel to afford the desired alcohols.

Step 2: To a solution of alcohols (15.0 mmol) in pyridine (85 mL) at 0 °C was added DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (4.5 mL, 30.0 mmol) followed by POCl3 (2.7 mL, 29.5 mmol) dropwise. The resultant orange solution was stirred at room temperature for 1 h and at 80 °C for 90 min during which time the orange color darkened. The solution was cooled to 0 °C and carefully treated with ethyl acetate (100 mL) and H2O (100 mL). The organic phase was washed with H2O and brine, dried (MgSO4), and evaporated in vacuo to give the alkenes as orange-brown oil. The crude products were purified by column chromatography on silica gel to afford the desired pure alkenes.

Step 3: The pure alkenes from the above reactions were dissolved in 1:1 MeOH/ethyl acetate (25 mL) and Palladium (10% on carbon, 0.3 g) was added. The mixture was stirred for 5 h under hydrogen (4 MPa) and filtered through a pad of Celite®. The solvent was
removed under reduced pressure to afford the crude ketals. The crude products were purified directly by column chromatography on silica gel to afford the desired pure ketals.

Step 4: The ketals were dissolved in a mixture of THF, water, and concentrated sulfuric acid (4:2:1, 70 mL). The mixture was stirred for 90 min, diluted with brine (50 mL), and extracted with ethyl acetate (3 x 50 mL). The combined organic extracts were dried (MgSO4), filtered, and concentrated. Column chromatography of the residue over silica gel gave the desired pure 4-substituted cyclohexanones.

4-(4-chlorophenyl)cyclohexan-1-one (1d)

\[ \text{1H NMR (501 MHz, CDCl}_3 \] \( \delta \) 7.22 (d, \( J = 8.4 \) Hz, 2H), 7.10 (d, \( J = 8.4 \) Hz, 2H), 2.94 (tt, \( J = 12.1, 3.4 \) Hz, 1H), 2.46–2.39 (m, 4H), 2.18–2.06 (m, 2H), 1.91–1.79 (m, 2H).

\[ \text{13C NMR (126 MHz, CDCl}_3 \] \( \delta \) 210.6, 143.2, 128.7, 128.0, 42.2, 41.2, 33.9.

Rf = 0.35 (Ethyl acetate/hexanes = 1:4).

EI-HRMS (m/z): calculated for C12H13O1Cl [M\textsuperscript{+}]: 208.0649, found: 208.0651.

m.p. = 66.2–68.4 °C.

4-(4-(trifluoromethyl)phenyl)cyclohexan-1-one (1f)

\[ \text{1H NMR (501 MHz, CDCl}_3 \] \( \delta \) 7.51 (d, \( J = 8.1 \) Hz, 2H), 7.29 (d, \( J = 8.0 \) Hz, 2H), 3.03 (tt, \( J = 12.1, 3.4 \) Hz, 1H), 2.51–2.40 (m, 4H), 2.21–2.10 (m, 2H), 1.95–1.81 (m, 2H).

\[ \text{13C NMR (126 MHz, CDCl}_3 \] \( \delta \) 210.3, 148.7, 128.9 (q, \( J = 32.6 \) Hz), 127.0, 125.5 (q, \( J = 3.8 \) Hz), 124.1 (app d, \( J = 271.8 \) Hz), 42.6, 41.1, 33.7.

\[ \text{19F NMR (471 MHz, CDCl}_3 \] \( \delta \) –64.4.

Rf = 0.29 (Ethyl acetate/hexanes = 1:4).

EI-HRMS (m/z): calculated for C13H13O1F3 [M\textsuperscript{+}]: 242.0913, found: 242.0915.

m.p. = 45.6–46.9 °C.

4-(3-(tert-butyl)phenyl)cyclohexan-1-one (1g)

\[ \text{1H NMR (501 MHz, CDCl}_3 \] \( \delta \) 7.20–7.18 (m, 3H), 7.01–6.96 (m, 1H), 3.00–2.90 (m, 1H), 2.51–2.39 (m, 4H), 2.17 (ddt, \( J = 14.7, 5.9, 2.4 \) Hz, 2H), 1.96–1.83 (m, 2H), 1.26 (s, 9H).

\[ \text{13C NMR (126 MHz, CDCl}_3 \] \( \delta \) 211.3, 151.4, 144.4, 128.2, 123.8, 123.5, 123.5, 43.1, 41.4, 34.7, 34.1, 31.4.

Rf = 0.50 (Ethyl acetate/hexanes = 1:4).

EI-HRMS (m/z): calculated for C16H23O1 [M\textsuperscript{+}]: 230.1665, found: 230.1667.

m.p. = 52.2–53.8 °C.

4-(3-chlorophenyl)cyclohexan-1-one (1h)
H NMR (501 MHz, CDCl\textsubscript{3}) \(\delta\) 7.07 (s, 4H), 2.92 (tt, \(J = 12.1, 3.5\) Hz, 1H), 2.45 (d, \(J = 1.0\) Hz, 4H), 2.13 (dddd, \(J = 13.7, 6.4, 5.2, 3.2\) Hz, 2H), 1.96–1.77 (m, 2H).

\(\text{C NMR (126 MHz, CDCl}_3\text{)} \delta 211.3, 151.4, 144.4, 128.2, 123.9, 123.6, 123.5, 43.1, 41.5, 34.7, 34.1, 31.4.

\(\text{Rf} = 0.36\) (Ethyl acetate/hexanes = 1:4).

ESI-HRMS (\(m/z\)): calculated for C\textsubscript{13}H\textsubscript{16}O\textsubscript{1}Na\textsubscript{1} ([M+Na]\textsuperscript{+}): 211.1093, found: 211.1095.

\(\text{m.p.} = 58.9–62.3\) °C.

4-(3-(trifluoromethyl)phenyl)cyclohexan-1-one (1i)

\H NMR (501 MHz, CDCl\textsubscript{3}) \(\delta\) 7.43 (dt, \(J = 3.8, 2.5\) Hz, 2H), 7.40–7.33 (m, 2H), 3.08–2.98 (m, 1H), 2.49–2.42 (m, 4H), 2.23–2.12 (m, 2H), 1.96–1.83 (m, 2H).

\(\text{C NMR (126 MHz, CDCl}_3\text{)} \delta 210.3, 145.6, 130.8 (app d, \(J = 33.2\) Hz), 130.0, 129.0, 124.1 (app d, \(J = 275.1\) Hz), 123.5 (q, \(J = 3.1\) Hz), 42.6, 41.1, 33.7.

\(\text{F NMR (471 MHz, CDCl}_3\text{)} \delta -64.5.

\(\text{Rf} = 0.30\) (Ethyl acetate/hexanes = 1:4).

EI-HRMS (\(m/z\)): calculated for C\textsubscript{13}H\textsubscript{17}O\textsubscript{1}F\textsubscript{3} [M\textsuperscript{+}]: 242.0913, found: 242.0916.

\(\text{m.p.} = 71.5–72.5\) °C.

4-(3,5-difluorophenyl)cyclohexan-1-one (1l)

\H NMR (501 MHz, CDCl\textsubscript{3}) \(\delta\) 6.73–6.65 (m, 2H), 6.61 (tt, \(J = 8.9, 2.3\) Hz, 1H), 2.95 (tt, \(J = 12.1, 3.4\) Hz, 1H), 2.49–2.40 (m, 4H), 2.21–2.09 (m, 2H), 1.89–1.75 (m, 2H).

\(\text{C NMR (126 MHz, CDCl}_3\text{)} \delta 210.1, 164.1–162.2 (d d, \(J = 248.5\) Hz, \(J = 12.6\) Hz), 148.7 (t, \(J = 8.6\) Hz), 109.6–109.5 (d d, \(J = 19.6\) Hz, \(J = 5.5\) Hz), 102.0 (t, \(J = 37.9\) Hz), 42.4 (t, \(J = 2.1\) Hz), 41.0, 33.5.

\(\text{F NMR (471 MHz, CDCl}_3\text{)} \delta -109.8.

\(\text{Rf} = 0.36\) (Ethyl acetate/hexanes = 1:4).

EI-HRMS (\(m/z\)): calculated for C\textsubscript{12}H\textsubscript{13}O\textsubscript{1}F\textsubscript{2} [M\textsuperscript{+}]: 210.0851, found: 210.0853.

\(\text{m.p.} = 76.8–80.6\) °C.

4-(naphthalen-1-yl)cyclohexan-1-one (1m)

\H NMR (501 MHz, CDCl\textsubscript{3}) \(\delta\) 8.08 (d, \(J = 8.5\) Hz, 1H), 7.85–7.78 (m, 1H), 7.68 (dt, \(J = 8.2, 1.1\) Hz, 1H), 7.49 (ddd, \(J = 8.5, 6.8, 1.5\) Hz, 1H), 7.44 (dd d, \(J = 8.1, 6.8, 1.2\) Hz, 1H), 7.38 (d d, \(J = 8.2, 7.2\) Hz, 1H), 7.31 (d d, \(J = 7.2, 1.2\) Hz, 1H), 3.77 (tt, \(J = 12.0, 3.2\) Hz, 1H), 2.67–2.43 (m, 4H), 2.32 (ddq, \(J = 13.6, 6.0, 3.1\) Hz, 2H), 1.99 (dd d, \(J = 13.3, 12.0, 4.6\) Hz, 2H).

\(\text{C NMR (126 MHz, CDCl}_3\text{)} \delta 211.0, 140.5, 134.0, 131.2, 129.2, 127.1, 126.1, 125.6, 125.6, 122.7, 122.2, 41.7, 37.6, 33.4.

\(\text{Rf} = 0.39\) (Ethyl acetate/hexanes = 1:4).

EI-HRMS (\(m/z\)): calculated for C\textsubscript{16}H\textsubscript{17}O\textsubscript{1} [M\textsuperscript{+}]: 224.1196, found: 224.1200.

\(\text{m.p.} = 71.1–73.8\) °C.
4,4'-disubstituted cyclohexanone 1s was prepared according to a literature report with minor revisions\textsuperscript{2}

\[
\text{O} \quad \text{Ph} + \text{CH}_2=\text{CH} \quad \xrightarrow{\text{PTSA}+\text{H}_2\text{O}} \quad \xrightarrow{\text{Pd/C}, \text{H}_2, 0.8 \text{MPa}} \quad \text{Ph}
\]

Step 1: To a 25 mL round-bottom flask with a condenser, 2-phenylpropanal (20 mmol, 2 g, 1.0 equiv.), but-3-en-2-one (30 mmol, 2.4 mL, 1.5 equiv.), p-toluenesulfonic acid monohydrate (4 mmol, 0.76 g, 0.2 equiv.), and toluene (6 mL) were added subsequently. Then the reaction mixture was stirred in an oil bath at 80 °C for 12 h till completion (as monitored by TLC). After the reaction mixture cooled down to room temperature, the solvent was removed in vacuo. Then 1M aqueous sodium hydroxide solution was added to the residue and the mixture extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed by brine, dried over NaSO\textsubscript{4}, and filtered. The crude product was purified by column chromatography on silica gel to afford the desired pure unsaturated ketone.

Step 2: To a solution of the aforementioned unsaturated ketone (9.1 mmol, 1.7 g) in ethyl acetate (17 mL) at rt was added Palladium (10% on carbon, 0.3 g). The resultant suspension was stirred for 5 h under hydrogen (8 bar) and filtered through a pad of Celite\textsuperscript{®}. The crude products were purified by column chromatography on silica gel to afford the desired pure ketone 1s.

4-methyl-4-phenylcyclohexan-1-one 1s

\text{^1H NMR (501 MHz, CDCl}_3\text{) }\delta\text{ 7.47–7.42 (m, 2H), 7.41–7.36 (m, 2H), 7.27–7.23 (m, 1H), 2.54–2.45 (m, 2H), 2.42–2.27 (m, 4H), 2.01–1.89 (m, 2H), 1.33 (s, 3H).}

\text{^13C NMR (126 MHz, CDCl}_3\text{) }\delta\text{ 211.6, 145.9, 128.7, 126.1, 125.5, 38.3, 37.6, 37.1, 31.0.}

Rf = 0.50 (Ethyl acetate/hexanes = 1:4).

El-HRMS (m/z): calculated for C\textsubscript{13}H\textsubscript{16}O\textsubscript{1} [M\textsuperscript{+}]: 188.1195, found: 188.1199.

m.p. = 43.7–44.2 °C.

Biscyclopentanone 1u and 1w were prepared according to reported methods\textsuperscript{3}

Step 1. To a solution of cis-bicyclo [3.3.0]octan-3,7-dione (25 g, 181.06 mmol) in toluene (300 mL) was added 2,2-dimethyl-1-propanediol (18.9 g, 181.06 mmol) and p-toluenesulfonic acid monohydrate (5%). The resultant solution was stirred at room temperature

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overnight. After completion of the reaction (as monitored by TLC), the mixture was evaporated in vacuo and the crude residue was subjected to column chromatography to give the mono-protected ketone 1w.

Step 2. The aforementioned mono-protected ketone (5.19 g, 23.1 mmol) was dissolved in dry MeOH (80 mL) and treated with NaBH₄ portion wise (1.73 g, 45.8 mmol, 2.0 equiv.) at 0 °C. The mixture was stirred for 4 h and then 0.1 M NaOH (100 mL) was added while keeping the temperature in between 0-10 °C. The aqueous layer was extracted with diethyl ether and the combined organic layers were dried over sodium sulfate, filtered, and concentrated to give 5',5'-dimethylhexahydro-1H-spiro[pentalene-2,2'-[1,3]dioxan]-5-ol as colorless crystals.

Step 3. To a solution of 5',5'-dimethylhexahydro-1H-spiro[pentalene-2,2'-[1,3]dioxan]-5-ol (5.83 g, 25.8 mmol), pyridine (4.62 mL, 45.6 g, 58.0 mmol) and DMAP (90 mg, 0.720 mmol) in CH₂Cl₂ (50 mL) was added O-phenyl chloroformate (5.00 g, 22.9 mmol) and the reaction mixture was stirred for 4 h. The mixture was then filtered through SiO₂ with hexanes/ethyl acetate (3 : 1) and the filtrate was concentrated under reduced pressure to give O-(5,5-dimethylhexahydro-1'H-spiro[1,3-dioxane-2,2'-pentalen]-5'-yl)-O-phenyl thiocarbonate as a yellow solid, which was used without further purification.

Step 4. To a solution of O-(5,5-dimethylhexahydro-1'H-spiro[1,3-dioxane-2,2'-pentalen]-5'-yl) O-phenylthiocarbonate (25.8 mmol) in absolute toluene (100 mL), AIBN (50 mg, 0.3 mmol) and Bu₃SnH (7.69 mL, 8.46 mg, 29.0 mmol) were added. The mixture was degassed by passing a stream of dry Argon for 10 min through the stirred solution and stirred at 130 °C for 16 h. The desired product 5,5-dimethylhexahydro-1'H-spiro[1,3-dioxane-2,2'-pentalene] was obtained after column chromatography with silica gel.

Step 5. p-Toluenesulfonic acid (219 mg, 1.15 mmol) was added to a solution of 5,5-dimethylhexahydro-1'H-spiro[1,3-dioxane-2,2'-pentalene] (19.0 mmol) in acetone (300 mL). The resultant reaction mixture was stirred at rt for 60 h. After the reaction was completed, the solvent was removed through evaporation and the reaction residue was purified by column chromatography to give the desired ketone 1u.

**(3aR,6aS)**-hexahypentalen-2(1H)-one 1u

![结构式](image)

$^{1}$$H$ NMR (501 MHz, CD₂Cl₂) δ 2.78–2.64 (m, 2H), 2.54–2.38 (m, 2H), 2.06–1.90 (m, 4H), 1.79 (tdd, J = 13.6, 7.6, 6.1 Hz, 1H), 1.71–1.60 (m, 1H), 1.43 (dt, J = 12.6, 7.3, 4.9 Hz, 2H).

$^{13}$$C$ NMR (126 MHz, CDCl₃) δ 220.4, 44.6, 39.7, 33.4, 22.5.

Rf = 0.19 (Ethyl acetate/hexanes = 1:9).

EI-HRMS (m/z): calculated for C₈H₁₄O₂ [M⁺]: 124.0883, found: 124.0885.

**(3aR,6aS)-5',5'-dimethyltetrahydro-1H-spiro[pentalene-2,2'-[1,3]dioxan]-5(3H)-one 1w**

![结构式](image)

$^{1}$$H$ NMR (501 MHz, CDCl₃) δ 3.42 (d, J = 1.0 Hz, 2H), 3.38 (d, J = 1.0 Hz, 2H), 2.82–2.71 (m, 2H), 2.45–2.35 (m, 2H), 2.26–2.18 (m, 2H), 2.14–2.06 (m, 2H), 1.79–1.71 (m, 2H), 0.89 (s, 6H).

$^{13}$$C$ NMR (126 MHz, CDCl₃) δ 220.1, 109.5, 72.2, 72.1, 44.5, 41.2, 36.8, 30.1, 22.4.

Rf = 0.11 (Ethyl acetate/hexanes = 1:9).

EI-HRMS (m/z): calculated for C₁₃H₂₀O₃ [M⁺]: 224.1407, found: 224.1407.

m.p. = 38.4–42.5 °C.

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Cyclobutanone 1v was prepared according to a literature method with minor modification.4

\[
\begin{align*}
\text{Ph} & \quad + \quad \text{Cl}_3\text{CCOCl} \quad \text{Zn-Cu} \quad \text{POCl}_3, \text{Et}_2\text{O} \quad \text{Zn, AcOH} \\
\end{align*}
\]

Step 1. To a stirred suspension of freshly-prepared Zn-Cu couple (1.60 g, 25 mmol) and styrene (10 mmol) in dry Et\(_2\)O (20 mL) was added a solution of trichloroacetic chloride (2.2 mL, 20 mmol) and phosphorus oxychloride (1.9 mL, 20 mmol) in Et\(_2\)O (10 mL) dropwise through an addition funnel, after 2 h at reflux. The mixture was cooled to room temperature and then filtered through a pad of Celite. The residue was extracted with Et\(_2\)O (3 × 15 mL). The organic phase was concentrated under reduced pressure to give a crude product, which was carefully purified through column chromatography with silica gel.

Step 2. The solution of the obtained product from the above-mentioned step in acetic acid (10 mL) was added dropwise to a vigorously stirred suspension of zinc dust (2.6 g, 40 mmol) in acetic acid (8 mL) at 0 °C. After the addition, the reaction mixture was heated to 70 °C for 2 h. The mixture was allowed to cool to room temperature and then evacuated to remove most of the acetic acid. The residue was dissolved in Et\(_2\)O (20 mL) and then poured into a separation funnel containing water (20 mL) and Et\(_2\)O (20 mL). The organic layer was washed with water (3 × 10 mL), saturated sodium bicarbonate solution (2 × 10 mL), brine (50 mL) and dried over MgSO\(_4\). The solution was then filtered and concentrated, followed by purification by flash chromatography to afford the desired pure cyclobutanone 1v as a light yellow liquid. (Notes: the mono-chlorine substituted 3-ph cyclobutanone byproduct from the first step, which is inseparable from the desired product, can be further reduced with fine Zn powder, thus furnishing the desired product that can be used without purification)

3-phenylcyclobutan-1-one 1v

\[
\begin{align*}
\text{H NMR (501 MHz, CDCl}_3) & \delta 7.43–7.32 (m, 4H), 7.31–7.25 (m, 1H), 3.72 (ddd, J = 16.4, 9.1, 7.5 Hz, 1H), 3.55–3.45 (m, 2H), 3.32–3.22 (m, 2H). \\
\text{C NMR (126 MHz, CDCl}_3) & \delta 206.2, 143.9, 128.6, 126.5, 126.4, 54.6, 28.4. \\
\end{align*}
\]

Rf = 0.22 (Ethyl acetate/hexanes = 1:9).

EI-HRMS (m/z): calculated for C\(_{10}\)H\(_{10}\)O\(_1\) [M\(^+\)]: 146.0726, found: 146.0726.

3-phenyl cyclopentanone 1ac was prepared according to a literature method.5

\[
\begin{align*}
\text{O} & \quad + \quad \text{PhB(OH)}_2 \quad \text{[Rh(cod)Cl]}_2, \text{Et}_3\text{N} \quad 1,4\text{-dioxane, H}_2\text{O, 50 °C, 6 h} \\
\end{align*}
\]

To a stirred solution of [Rh(cod)Cl]\(_2\) (1 mol%) and PhB(OH)\(_2\) (1.37 g, 11.3 mmol) in degassed aqueous 1,4-dioxane was added a solution of 2-cyclopentene-1-one (0.63 mL, 7.5 mmol) in aqueous 1,4-dioxane and degassed Et\(_3\)N (1.0 equiv.). The resulting solution was stirred at 50 °C for 6 h, then cooled to rt and concentrated under reduced pressure. The crude product was purified via column chromatography and the desired brown oil 1ac was obtained.

rac-3-phenylcyclohexan-1-one (1ac)

\[
\begin{align*}
\text{H NMR (501 MHz, CDCl}_3) & \delta 7.28 (dd, J = 8.3, 6.9 Hz, 2H), 7.21–7.14 (m, 3H), 3.36 (tt, J = 11.0, 6.5 Hz, 1H), 2.65–2.55 (m, 1H), 2.45–2.33 (m, 2H), 2.33–2.17 (m, 2H), 1.92 (dtd, J = 12.5, 11.0, 10.5, 8.7 Hz, 1H). \\
\text{C NMR (126 MHz, CDCl}_3) & \delta 218.4, 143.0, 128.6, 126.7, 45.8, 42.2, 38.8, 31.2. \\
\end{align*}
\]

Rf = 0.16 (Ethyl acetate/hexanes = 1:9).
EI-HRMS (m/z): calculated for C_{11}H_{12}O [M^+]: 160.0883, found: 160.0884.

5. Substrate scope for the deprotosilylation of ketones 1 with allylsilane reagents 2a or 2b

General procedure for the catalytic desymmetrization of ketones with allylsilanes.

Allyl silane 2a or 2b (80 μL, 0.4 mmol, 2.0 equiv.) was placed in a flame-dried Schlenk flask, equipped with a teflon-coated magnetic stirring bar. IDPi 4a–4f (0.01 equiv.) and a solvent mixture of toluene with 1,4-dioxane (2:1 v/v 0.08 M, 2.4 mL) were added at 25 °C and stirred for 30 min. The resultant mixture was cooled to −20 °C for 10 min, and ketones 1a–1w (0.2 mmol, 1.0 equiv.) were slowly added. The reaction was stirred for 1–5 d at −20 °C. After the ketone was fully consumed as monitored by TLC, the reaction was treated with one drop of triethylamine. All volatiles were removed in vacuo and the crude residue was purified by column chromatography with silica gel to afford the desired enol silanes 3a–3w.

Analytical data of products

(R)-tert-butyldimethyl(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane 3a

The reaction was performed according to the general procedure and catalyzed by IDPi 4c.

The titled product was purified by column chromatography with hexanes as eluent to afford 3a as a colorless oil (57.1 mg, 99% yield).

1H NMR (501 MHz, CDCl₃) δ 7.31–7.22 (m, 4H), 7.20–7.15 (m, 1H), 4.96–4.91 (m, 1H), 2.75 (ddt, J = 16.5, 8.2, 3.1 Hz, 1H), 2.31–2.12 (m, 3H), 2.09–2.00 (m, 1H), 1.93 (dddt, J = 8.9, 4.2, 2.9, 1.6 Hz, 1H), 1.90–1.79 (m, 1H), 0.93 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H).

13C NMR (126 MHz, CDCl₃) δ 151.3, 147.7, 129.0, 127.6, 126.7, 104.3, 40.8, 32.8, 31.0, 31.0, 26.3, 18.7, –3.8, –4.0.

Rf = 0.36 (Hexanes).

EI-HRMS (m/z): calculated for C_{18}H_{28}O_{1}Si [M^+]: 288.1904, found: 288.1903.

HPLC (OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 224 nm): tᵣ₁ = 24.1 min, tᵣ₂ = 22.9 min, e.r. = 97:3.

[α]_{D}^{25} = 29.0 (c 0.49, CHCl₃).

(R)-tert-butyldimethyl(4'-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane 3b

The reaction was performed according to the general procedure and catalyzed by IDPi 4c.

The titled product was purified by column chromatography with hexanes as eluent to afford 3b as a white solid (54.4 mg, 90% yield).

1H NMR (501 MHz, CDCl₃) δ 6.99–6.91 (m, 4H), 4.80–4.73 (m, 1H), 2.59–2.51 (m, 1H), 2.15 (s, 3H), 2.08 (ddd, J = 13.0, 9.9, 4.4, 2.1 Hz, 2H), 2.03–1.95 (m, 1H), 1.93–1.84 (m, 1H), 1.79–1.72 (m, 1H), 1.72–1.61 (m, 1H), 0.78 (s, 9H), 0.16 (s, 3H), 0.16 (s, 3H).

13C NMR (126 MHz, CDCl₃) δ 151.0, 144.4, 136.0, 129.5, 127.3, 104.2, 40.2, 32.7, 30.9, 30.8, 26.1, 21.3, 18.5, –4.0, –4.1.
Rf = 0.61 (Ethyl acetate/hexanes = 1:20).

EI-HRMS (m/z): calculated for \( \text{C}_{19}\text{H}_{30}\text{O}_{1}\text{Si}_{1} [M^+] \): 302.2060, found: 302.2055.

HPLC (OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm): \( t_{R1} = 20.2 \text{ min}, t_{R2} = 18.2 \text{ min}, \text{e.r.} = 97:3 \).

\[ \alpha \text{\textsubscript{D}}^{25} = 31.3 (c 0.53, \text{CH}_3\text{CN}). \]

m.p. = 31.9–35.2 °C.

\((R)-\text{tert-} \text{butyl}([4'-\text{methoxy-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl]}\text{oxy})\text{dimethylsilane 3c}\)

The reaction was performed according to the general procedure and catalyzed by IDPi 4c.

The titled product was purified by column chromatography with hexanes as eluent to afford 3c as a colorless oil (59.9 mg, 94% yield).

\(^1\text{H NMR (501 MHz, CD}_2\text{Cl}_2 ) \delta 7.04 – 6.94 (m, 2H), 6.71 – 6.62 (m, 2H), 4.79 – 4.73 (m, 1H), 3.61 (s, 3H), 2.55 (ddq, } J = 13.0, 8.1, 3.1 \text{ Hz, 1H), 2.14 – 2.02 (m, 2H), 1.98 (dddt, } J = 16.5, 10.2, 3.8, 2.0 \text{ Hz, 1H), 1.93 – 1.84 (m, 1H), 1.75 (dddd, } J = 13.3, 5.8, 4.6, 2.8 \text{ Hz, 1H), 1.70 – 1.59 (m, 1H), 0.78 (s, 9H), 0.00 (s, 3H), 0.00 (s, 3H).

\(^{13}\text{C NMR (126 MHz, CD}_2\text{Cl}_2 ) \delta 157.9, 150.4, 138.9, 127.6, 113.6, 103.6, 55.1, 39.1, 32.1, 30.4, 30.2, 25.5, 17.9, –4.6, –4.7.

Rf = 0.50 (Ethyl acetate/hexanes = 1:20).

EI-HRMS (m/z): calculated for \( \text{C}_{19}\text{H}_{30}\text{O}_{1}\text{Si}_{1} [M^+] \): 318.2010, found: 318.2004.

HPLC (AD-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm): \( t_{R1} = 15.1 \text{ min}, t_{R2} = 14.4 \text{ min}, \text{e.r.} = 96:4 \).

\[ \alpha \text{\textsubscript{D}}^{25} = 27.4 (c 0.46, \text{CH}_3\text{CN}). \]

\((R)-\text{tert-} \text{butyl}([4'-\text{chloro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl]}\text{oxy})\text{dimethylsilane 3d}\)

The reaction was performed according to the general procedure and catalyzed by IDPi 4c.

The titled product was purified by column chromatography with hexanes as eluent to afford 3d as a white solid (63.9 mg, 99% yield).

\(^1\text{H NMR (501 MHz, CD}_2\text{Cl}_2 ) \delta 7.15 – 7.06 (m, 2H), 7.06 – 6.97 (m, 2H), 4.81 – 4.70 (m, 1H), 2.59 (ddq, } J = 14.3, 8.2, 2.9 \text{ Hz, 1H), 2.15 – 2.03 (m, 2H), 2.03 – 1.93 (m, 1H), 1.93 – 1.82 (m, 1H), 1.76 (dddt, } J = 10.6, 5.9, 2.9, 1.5 \text{ Hz, 1H), 1.67 (dddd, } J = 12.8, 11.6, 10.6, 5.6 \text{ Hz, 1H), 0.78 (s, 9H), 0.00 (s, 3H), 0.00 (s, 3H).

\(^{13}\text{C NMR (126 MHz, CD}_2\text{Cl}_2 ) \delta 151.1, 146.0, 131.9, 128.9, 128.8, 103.8, 40.0, 32.4, 30.7, 30.6, 26.1, 18.5, –4.0, –4.2.

Rf = 0.53 (Ethyl acetate/hexanes = 1:20).

EI-HRMS (m/z): calculated for \( \text{C}_{18}\text{H}_{29}\text{O}_{1}\text{Cl}_{1}\text{Si}_{1} [M^+] \): 322.1514, found: 322.1509.

HPLC (OJ-3R, Acetonitrile: Water = 65:35, 1.0 mL/min, 298 K, 220 nm): \( t_{R1} = 25.2 \text{ min}, t_{R2} = 23.9 \text{ min, e.r.} = 94.5:5.5 \).

\[ \alpha \text{\textsubscript{D}}^{25} = 24.7 (c 0.68, \text{CHCl}_3). \]

m.p. = 41.0–41.8 °C.

\((R)-\text{tert-} \text{butyl}([4'-\text{fluoro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl]}\text{oxy})\text{dimethylsilane 3e}\)
The reaction was performed according to the general procedure and catalyzed by IDPi 4c. The titled product was purified by column chromatography with hexanes as eluent to afford 3e as a colorless oil (60.7 mg, 99% yield).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 7.09–7.02 (m, 2H), 6.86–6.79 (m, 2H), 4.80–4.73 (m, 1H), 2.60 (ddt, $J = 14.6, 8.2, 3.0$ Hz, 1H), 2.16–2.03 (m, 2H), 2.03–1.94 (m, 1H), 1.92–1.83 (m, 1H), 1.76 (dddt, $J = 11.8, 5.8, 2.8, 1.7$ Hz, 1H), 1.67 (dddd, $J = 12.7, 11.6, 10.6, 5.6$ Hz, 1H), 0.78 (s, 9H), 0.00 (s, 3H), 0.00 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 162.0 (d, $J = 252.14$ Hz), 151.3, 143.3 (d, $J = 3.2$ Hz), 128.2 (d, $J = 7.7$ Hz), 114.7 (d, $J = 21.1$ Hz), 103.3, 39.2, 32.0, 30.2, 30.0, 25.4, 17.8, –4.6, –4.7.

$^{19}$F NMR (471 MHz, CD$_2$Cl$_2$) δ –118.4.

Rf = 0.53 (Ethyl acetate/hexanes = 1:20).

EI-HRMS (m/z): calculated for C$_{18}$H$_{30}$O$_3$SiF$_3$ [M$^{+}$]: 306.1810, found: 306.1805.

HPLC (OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm): $t_{R1} = 36.8$ min, $t_{R2} = 33.2$ min, e.r. = 94:6.

$[\alpha]_D^{25}$ = 26.7 (c 0.42, CH$_3$CN).

(R)-tert-butyldimethyl(4′-(trifluoromethyl)-1,2,3,6-tetrahydro-[1,1′-biphenyl]-4-yl)oxy)silane 3f

The reaction was performed according to the general procedure and catalyzed by IDPi 4c.

The titled product was purified by column chromatography with hexanes as eluent to afford 3f as a white solid (69.2 mg, 97% yield).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 7.56 (d, $J = 8.1$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 4.93 (dt, $J = 4.6, 1.9$ Hz, 1H), 2.88–2.79 (m, 1H), 2.34–2.14 (m, 3H), 2.09–2.01 (m, 1H), 1.98–1.92 (m, 1H), 1.87 (dddd, $J = 12.8, 11.6, 10.7, 5.7$ Hz, 1H), 0.93 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 151.9, 151.3, 128.7 (app d, $J = 32.0$ Hz), 128.1, 125.9 (q, $J = 3.8$ Hz), 125.2 (app d, $J = 271.4$ Hz), 103.9, 40.6, 32.4, 30.6, 30.6, 26.2, 18.6, –3.8, –4.0.

$^{19}$F NMR (471 MHz, CD$_2$Cl$_2$) δ –62.6.

Rf = 0.64 (Ethyl acetate/hexanes = 1:20).

EI-HRMS (m/z): calculated for C$_{19}$H$_{32}$O$_3$SiF$_3$ [M$^{+}$]: 356.1778, found: 356.1777.

HPLC (AD-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 237 nm): $t_{R1} = 25.1$ min, $t_{R2} = 23.3$ min, e.r. = 96:4.

$[\alpha]_D^{25}$ = 23.4 (c 0.46, CH$_3$CN).

m.p. = 57.4–58.7 °C.

(R)-tert-butyl((3′-(tert-butyl)-1,2,3,6-tetrahydro-[1,1′-biphenyl]-4-yl)oxy)dimethylsilane 3g

The reaction was performed according to the general procedure and catalyzed by IDPi 4c.

The titled product was purified by column chromatography with hexanes as eluent to afford 3g as a colorless oil (68.2 mg, 99% yield).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 7.10 (q, $J = 1.5$ Hz, 1H), 7.08–7.03 (m, 2H), 6.88 (dddd, $J = 7.4, 2.8, 1.7$ Hz, 1H), 4.77 (dd, $J = 4.1, 1.9$ Hz, 1H), 2.56 (dddd, $J = 11.4, 5.1, 3.0$ Hz, 1H), 2.15–1.96 (m, 3H), 1.95–1.84 (m, 1H), 1.81–1.64 (m, 2H), 1.15 (s, 9H), 0.78 (s, 9H), 0.00 (s, 3H), 0.00 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 151.7, 151.1, 147.1, 128.5, 124.6, 124.3, 123.5, 104.2, 41.0, 35.1, 32.8, 31.8, 30.9, 26.1, 18.5, –4.0, –4.1.

Rf = 0.53 (Ethyl acetate/hexanes = 1:20).
El-HRMS (m/z): calculated for C_{22}H_{36}O_5Si [M^+]: 344.2530, found: 344.2525.

HPLC (OD-3R, Acetonitrile: Water = 65:35, 1.0 mL/min, 298 K, 220 nm): t_{R1} = 23.3 min, t_{R2} = 24.7 min, e.r. = 96:4.

[α]_{D}^{25} = 28.1 (c 0.54, CH_3CN).

(R)-tert-butyli((3'-chloro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)dimethylsilane 3h

The reaction was performed according to the general procedure and catalyzed by IDPi 4c. The titled product was purified by column chromatography with hexanes as eluent to afford 3h as a colorless oil (54.9 mg, 85% yield).

^1H NMR (501 MHz, CDCl_3) δ 7.11–7.04 (m, 2H), 7.04–6.95 (m, 2H), 4.77 (dt, J = 4.6, 1.8 Hz, 1H), 2.60 (ddq, J = 14.5, 8.1, 3.0 Hz, 1H), 2.17–1.95 (m, 3H), 1.94–1.85 (m, 1H), 1.78 (dddt, J = 13.6, 5.9, 2.9, 1.8 Hz, 1H), 1.68 (dddd, J = 12.8, 11.7, 10.7, 5.6 Hz, 1H), 0.78 (s, 9H), 0.00 (s, 3H), 0.00 (s, 3H).

^13C NMR (126 MHz, CDCl_3) δ 151.3, 149.8, 134.7, 130.4, 127.8, 126.8, 126.1, 104.0, 40.5, 32.5, 30.8, 30.7, 26.3, 18.7, –3.8, –3.9.

Rf = 0.61 (Ethyl acetate/hexanes = 1:20).

El-HRMS (m/z): calculated for C_{18}H_{27}O_5Cl_3Si [M^+]: 322.1514, found: 322.1509.

HPLC (AD-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm): t_{R1} = 33.3 min, t_{R2} = 30.0 min, e.r. = 98:2.

[α]_{D}^{25} = 25.7 (c 0.42, CH_3CN).

(R)-tert-butyldimethyl((3'-trifluoromethyl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane 3i

The reaction was performed according to the general procedure and catalyzed by IDPi 4c. The titled product was purified by column chromatography with hexanes as eluent to afford 3i as a colorless oil (69.2 mg, 97% yield).

^1H NMR (501 MHz, CDCl_3) δ 7.36 (dq, J = 1.9, 1.0 Hz, 1H), 7.33–7.24 (m, 3H), 4.78 (dt, J = 4.5, 1.8 Hz, 1H), 2.69 (ddt, J = 14.8, 5.1, 3.0 Hz, 1H), 2.21–1.98 (m, 3H), 1.94–1.86 (m, 1H), 1.80 (dddt, J = 12.1, 6.2, 3.0, 2.0 Hz, 1H), 1.72 (dddd, J = 12.8, 11.5, 10.5, 5.6 Hz, 1H), 0.78 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H).

^13C NMR (126 MHz, CDCl_3) δ 151.1, 148.4, 131.1 (q, J = 1.1 Hz), 130.8 (q, J = 31.7 Hz), 129.4, 124.2 (q, J = 273.1 Hz), 123.4 (q, J = 3.7 Hz), 123.3 (q, J = 3.9 Hz), 103.7, 40.4, 32.3, 30.5, 26.1, 18.5, –4.1, –4.2.

^19F NMR (471 MHz, CDCl_3) δ –62.8.

Rf = 0.61 (Ethyl acetate/hexanes = 1:20).

El-HRMS (m/z): calculated for C_{19}H_{27}O_5SiF_3 [M^+]: 356.1778, found: 356.1774.

HPLC (OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 244 nm): t_{R1} = 22.1 min, t_{R2} = 23.9 min, e.r. = 97:3.

[α]_{D}^{25} = 22.4 (c 0.34, CH_3CN).

(R)-tert-butyldimethyl((2'-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane 3j

The reaction was performed according to the general procedure and catalyzed by IDPi 4c. The titled product was purified by column chromatography with hexanes as eluent to afford 3j as a colorless oil (55.7 mg, 92% yield).

^1H NMR (501 MHz, CDCl_3) δ 7.22 (dd, J = 7.8, 1.4 Hz, 1H), 7.18–7.11 (m, 2H), 7.07 (id, J = 7.3, 1.5 Hz, 1H), 4.95 (dt, J = 4.8, 1.9 Hz, 1H), 3.03–2.92 (m, 1H), 2.35 (s, 3H), 2.32–2.18 (m, 2H), 2.17–2.02 (m, 2H), 1.94–1.81 (m, 2H), 0.95 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H).
The reaction was performed according to the general procedure and catalyzed by IDPi. 

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 151.0, 145.4, 136.1, 130.7, 126.7, 126.2, 125.9, 104.3, 36.2, 31.7, 31.1, 30.2, 26.1, 19.7, 18.5, −4.0, −4.1.

R$^f$ = 0.56 (Ethyl acetate/hexanes = 1:20).

EI-MS (m/z): calculated for C$_{18}$H$_{30}$O$_3$Si: [M$^+$]: 302.2060, found: 302.2055.

HPLC (OD-3R, Acetonitrile: Water = 65:35, 1.0 mL/min, 298 K, 220 nm): $t_{R1}$ = 20.8 min, $t_{R2}$ = 19.9 min, e.r. = 96:4.

$[\alpha]_D^{25} = 24.8$ (c 0.42, CH$_3$CN).

**[(R)-tert-butyl(3',5'-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy]dimethylsilane 3k**

The reaction was performed according to the general procedure and catalyzed by IDPi 4c. The titled product was purified by column chromatography with hexanes as eluent to afford 3k as a colorless oil (59.5 mg, 94% yield).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 6.84 (d, J = 9.0 Hz, 3H), 4.93 (dt, J = 4.7, 2.4 Hz, 1H), 2.67 (ddq, J = 10.7, 8.3, 3.1 Hz, 1H), 2.29 (s, 6H), 2.27–2.12 (m, 3H), 2.09–2.00 (m, 1H), 1.93–1.87 (m, 1H), 1.83 (ddt, J = 12.8, 7.0, 5.2 Hz, 1H), 0.95 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 150.4, 146.7, 137.6, 127.5, 124.7, 103.6, 39.9, 32.0, 30.3, 30.2, 25.5, 21.0, 17.9, −4.6, −4.7.

R$^f$ = 0.20 (Hexanes).

EI-MS (m/z): calculated for C$_{20}$H$_{32}$O$_3$Si: [M$^+$]: 316.2217, found: 316.2214.

HPLC (OD-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm): $t_{R1}$ = 11.6 min, $t_{R2}$ = 12.3 min, e.r. = 97:3.

$[\alpha]_D^{25} = 32.8$ (c 0.5, CHCl$_3$).

**[(R)-tert-butyl((3',5'-difluoro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy]dimethylsilane 3l**

The reaction was performed according to the general procedure and catalyzed by IDPi 4c. The titled product was purified by column chromatography with hexanes as eluent to afford 3l as a colorless oil (53.9 mg, 83% yield).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 6.84–6.74 (m, 2H), 6.65 (tt, J = 9.1, 2.4 Hz, 1H), 4.91 (dt, J = 5.1, 2.3 Hz, 1H), 2.82–2.72 (m, 1H), 2.33–2.09 (m, 3H), 2.09–1.99 (m, 1H), 1.94 (dddt, J = 13.6, 6.0, 3.0, 1.9 Hz, 1H), 1.81 (dddd, J = 12.9, 11.5, 10.5, 5.7 Hz, 1H), 0.93 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 164.7–162.8 (dd, J = 247.4 Hz, J = 13.1 Hz), 151.8 (t, J = 8.4 Hz), 151.2, 110.5–110.4 (dd, J = 19.2 Hz, J = 5.4 Hz), 103.7, 101.9 (t, J = 25.6 Hz), 101.7, 40.5 (t, J = 2.0 Hz), 32.2, 30.5, 26.2, 18.7, −3.8, −3.9.

$^{19}$F NMR (471 MHz, CD$_2$Cl$_2$) δ −111.4.

R$^f$ = 0.20 (Hexanes).

EI-MS (m/z): calculated for C$_{18}$H$_{30}$O$_3$SiF$_2$: [M$^+$]: 324.1716, found: 324.1710.

HPLC (OD-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm): $t_{R1}$ = 19.0 min, $t_{R2}$ = 20.7 min, e.r. = 95:5.

$[\alpha]_D^{25} = 29.2$ (c 0.5, CHCl$_3$).

**[(R)-tert-butyl(diethyl(4-(naphthalen-1-yl)cyclohex-1-en-1-yl)oxy]silane 3m**

The reaction was performed according to the general procedure and catalyzed by IDPi 4c.
The titled product was purified by column chromatography with hexanes as eluent to afford 3m as a colorless oil (67.0 mg, 99% yield).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 7.95 (d, J = 8.4 Hz, 1H), 7.67 (dd, J = 8.1, 1.4 Hz, 1H), 7.52 (dd, J = 6.8, 2.5 Hz, 1H), 7.36 –7.20 (m, 4H), 4.84–4.77 (m, 1H), 3.41 (tt, J = 9.5, 4.7 Hz, 1H), 2.31–2.23 (m, 1H), 2.22–2.03 (m, 2H), 1.97–1.80 (m, 3H), 0.79–0.75 (m, 9H), 0.01 (s, 3H), 0.00 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 151.1, 143.1, 134.5, 132.1, 129.4, 126.9, 126.3, 126.2, 125.8, 123.8, 123.0, 104.3, 35.4, 32.1, 31.0, 30.4, 26.1, 18.5, –4.0, –4.1.

Rf = 0.47 (Ethyl acetate/hexanes = 1:20).

EI-HRMS (m/z): calculated for C$_{22}$H$_{30}$O$_3$Si$_1$ [M$^+$]: 338.2060, found: 338.2060.

HPLC (OD-3R, Acetonitrile: Water = 65:35, 1.0 mL/min, 298 K, 220 nm): $t_{R1}$ = 56.9 min, $t_{R2}$ = 60.8 min, e.r. = 96:4.

$[\alpha]_D^{25} = 2.3$ (c 0.44, CH$_3$CN).

(R)-tert-butyldimethyl(4-(naphthalen-2-yl)cyclohex-1-en-1-yl)oxy)silane 3n

The reaction was performed according to the general procedure and catalyzed by IDPi 4c.

The titled product was purified by column chromatography with hexanes as eluent to afford 3n as a white solid (65.7 mg, 97% yield).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 7.81 (tdd, J = 8.9, 8.2, 3.0, 1.8 Hz, 3H), 7.69 (dd, J = 1.7, 0.8 Hz, 1H), 7.50–7.37 (m, 3H), 4.99 (dd, J = 4.0, 2.2 Hz, 1H), 3.00–2.88 (m, 1H), 2.42–2.23 (m, 3H), 2.15–1.90 (m, 3H), 0.96 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 150.5, 144.3, 133.6, 132.2, 127.7, 127.5, 127.4, 126.0, 125.8, 125.1, 124.7, 103.5, 40.0, 31.8, 30.1, 30.1, 25.5, 17.9, –4.6, –4.7.

Rf = 0.47 (Ethyl acetate/hexanes = 1:20).

EI-HRMS (m/z): calculated for C$_{22}$H$_{30}$O$_3$Si$_1$ [M$^+$]: 338.2060, found: 338.2057.

HPLC (OD-3R, Acetonitrile: Water = 90:10, 1.0 mL/min, 323 K, 220 nm): $t_{R1}$ = 8.1 min, $t_{R2}$ = 8.6 min, e.r. = 95.5:4.5.

$[\alpha]_D^{25} = 30.5$ (c 0.40, CH$_3$CN).

m.p. = 42.9–43.1 °C.

(R)-tert-butyldimethyl(1,2,3,6-tetrahydro-[1,1'-:4',1''-terphenyl]-4-yl)oxy)silane 3o

The reaction was performed according to the general procedure and catalyzed by IDPi 4c.

The titled product was purified by column chromatography with hexanes as eluent to afford 3o as a white solid (66.4 mg, 91% yield).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 7.45–7.39 (m, 2H), 7.39–7.34 (m, 2H), 7.26 (dd, J = 8.4, 7.0 Hz, 2H), 7.18–7.12 (m, 3H), 4.81 –4.76 (m, 1H), 2.64 (tdd, J = 11.3, 5.2, 3.0 Hz, 1H), 2.19–2.00 (m, 3H), 1.94–1.86 (m, 1H), 1.84–1.77 (m, 1H), 1.72 (dddd, J = 12.8, 11.7, 10.7, 5.6 Hz, 1H), 0.78 (s, 9H), 0.00 (s, 3H), 0.00 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 150.7, 146.2, 141.1, 138.9, 128.9, 127.5, 127.2, 127.1, 127.0, 103.6, 39.8, 32.1, 30.4, 30.3, 25.6, 18.1, –4.4, –4.6.

Rf = 0.43 (Ethyl acetate/hexanes = 1:20).

EI-HRMS (m/z): calculated for C$_{34}$H$_{33}$O$_3$Si$_1$ [M$^+$]: 364.2217, found: 364.2214.

HPLC (Amycoat RP, Acetonitrile/MeOH/Water = 45:45:10, 1.0 mL/min, 298 K, 220 nm): $t_{R1}$ = 5.3 min, $t_{R2}$ = 4.5 min, e.r. = 96:4.
\[ \alpha_{D}^{25} = 38.2 \text{ (c 0.65, CH}_2\text{CN).} \]

m.p. = 49.6–50.7 °C.

**((R)-**tert-butyl(4-(**tert**-butyl)cyclohex-1-en-1-yl)oxy)dimethylsilane 3p**

The reaction was performed according to the general procedure and catalyzed by IDPi 4d at room temperature. The titled product was purified by column chromatography with hexanes as eluent to afford 3p as a colorless oil (51.6 mg, 96% yield).

\[^1H\text{ NMR (501 MHz, CD}_2\text{Cl}_2) \delta 4.70 \text{ (dt, } J = 5.8, 2.1 \text{ Hz, 1H), 2.03–1.81 (m, 3H), 1.74–1.61 (m, 2H), 1.19–1.02 (m, 2H), 0.77 (d, } J = 21.2 \text{ Hz, 18H), 0.00 (s, 3H), 0.00 (s, 3H).} \]

\[^{13}C\text{ NMR (126 MHz, CD}_2\text{Cl}_2) \delta 151.3, 104.7, 44.9, 32.8, 31.8, 29.7, 26.3, 25.9, 25.2, 18.7, –3.8, –3.9.} \]

Rf = 0.42 (pentane).

EI-**HRMS** (m/z): calculated for C\(_{16}\)H\(_{32}\)O\(_2\)Si\(_{1}\) [M\(^+\)]: 268.2217, found: 268.2215.

HPLC (OJ-3R, MeOH: Water = 75:25, 1.0 mL/min, 298 K, 214 nm): \( t_{R1} = 11.9 \text{ min, } t_{R2} = 12.1 \text{ min, e.r. = 97:3.} \)

\[ \alpha_{D}^{25} = 32.3 \text{ (c 0.60, CHCl}_3). \]

**((R)-**[1,1′-bi(cyclohexan)]-3-en-4-yloxy)**(**tert**-butyl)dimethylsilane 3q**

The reaction was performed according to the general procedure and catalyzed by IDPi 4b for 2 d. The titled product was purified by column chromatography with hexanes as eluent to afford 3q as a colorless oil (51.8 mg, 88% yield).

\[^1H\text{ NMR (501 MHz, CD}_2\text{Cl}_2) \delta 4.70 \text{ (dt, } J = 4.9, 2.1 \text{ Hz, 1H), 2.00–1.78 (m, 3H), 1.72–1.46 (m, 7H), 1.23–0.97 (m, 6H), 0.93 –0.81 (m, 2H), 0.80 (s, 9H), 0.00 (s, 3H), 0.00 (s, 3H).} \]

\[^{13}C\text{ NMR (126 MHz, CD}_2\text{Cl}_2) \delta 151.1, 104.3, 42.8, 39.8, 31.1, 30.9, 30.9, 28.0, 27.4, 27.4, 27.1, 26.1, 18.5, –4.0, –4.2.} \]

Rf = 0.40 (pentane).

EI-**HRMS** (m/z): calculated for C\(_{18}\)H\(_{34}\)O\(_2\)Si\(_{1}\) [M\(^+\)]: 294.2373, found: 294.2369.

HPLC (OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm): \( t_{R1} = 11.7 \text{ min, } t_{R2} = 12.3 \text{ min, e.r. = 92:8.} \)

\[ \alpha_{D}^{25} = 31.6 \text{ (c 0.38, CHCl}_3). \]

**((R)-**4-benzylcyclohex-1-en-1-yl)oxy)**(**tert**-butyl)dimethylsilane 3r**

The reaction was performed according to the general procedure and catalyzed by IDPi 4b. The titled product was purified by column chromatography with hexanes as eluent to afford 3r as a colorless oil (55.7 mg, 92% yield).

\[^1H\text{ NMR (501 MHz, CD}_2\text{Cl}_2) \delta 7.15 \text{ (dd, } J = 8.3, 6.5 \text{ Hz, 2H), 7.09–7.00 (m, 3H), 4.72–4.63 (m, 1H), 2.44 (dd, } J = 6.7, 4.3 \text{ Hz, 2H), 1.99–1.80 (m, 3H), 1.64 (tq, } J = 12.8, 5.6, 4.3 \text{ Hz, 3H), 1.23 (ddd, } J = 9.9, 6.4, 2.5 \text{ Hz, 1H), 0.79 (s, 9H), 0.00 (s, 3H), –0.01 (s, 3H).} \]

\[^{13}C\text{ NMR (126 MHz, CD}_2\text{Cl}_2) \delta 151.2, 142.1, 129.9, 128.9, 128.5, 103.9, 43.1, 36.4, 31.0, 30.3, 29.6, 26.3, 18.7, –3.8, –3.9.} \]

Rf = 0.60 (Hexanes).

EI-**HRMS** (m/z): calculated for C\(_{19}\)H\(_{38}\)O\(_2\)Si\(_{1}\) [M\(^+\)]: 302.2066, found: 302.2068.

HPLC (OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 259 nm): \( t_{R1} = 13.5 \text{ min, } t_{R2} = 12.7 \text{ min, e.r. = 92:8.} \)
[\alpha^D]_{D}^{25} = 6.4 (c 0.50, CHCl_3).

**(R)-tert-butylidimethyl(1-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane 3s**

The reaction was performed according to the general procedure and catalyzed by IDPi 4a. The title product was purified by column chromatography with hexanes as eluent to afford 3s as a colorless oil (50.8 mg, 80% yield).

\[ \text{OTBS} \]

\[ \text{HPLC (AD-3R, Acetonitrile: Water = 50:50, 1.0 mL/min, 298 K, 220 nm): } t_{R1} = 17.0 \text{ min, } t_{R2} = 21.6 \text{ min, e.r. = 94:6.} \]

[\alpha^D]_{D}^{25} = 7.2 (c 0.25, CHCl_3).

**(R)-4-((tert-butylidimethylsilyloxy)cyclohex-3-ene-1-carboxylate 3t**

The reaction was performed according to the general procedure and catalyzed by IDPi 4c. The title product was purified by column chromatography with hexanes as eluent to afford 3t as a colorless oil (52.3 mg, 92% yield).

\[ \text{OTBS} \]

\[ \text{HPLC (AD-3R, Acetonitrile: Water = 50:50, 1.0 mL/min, 298 K, 220 nm): } t_{R1} = 38.5 \text{ min, } t_{R2} = 32.4 \text{ min, e.r. = 98:2.} \]

[\alpha^D]_{D}^{25} = 17.2 (c 0.51, CHCl_3).

**(((3aS,6aS)-1,3a,4,5,6,6a-hexahydropentalen-2-yl)oxy)triethylsilane 3u**

The reaction was performed according to the general procedure and catalyzed by IDPi 4e. The title product was purified by column chromatography with hexanes as eluent to afford 3u as a colorless oil (46.7 mg, 98% yield).

\[ \text{OTES} \]

\[ \text{HPLC (AD-3R, Acetonitrile: Water = 50:50, 1.0 mL/min, 298 K, 215 nm): } t_{R1} = 37.1 \text{ min, } t_{R2} = 39.2 \text{ min, e.r. = 95:5.} \]
\[ [\alpha]_{D}^{25} = -11.1 \ (c \ 0.74, \ CH_3CN). \]

**(R)-tert-butyldimethyl(3-phenyleclobut-1-en-1-yl)oxy)silane 3v**

The reaction was performed according to the general procedure with 8 equiv. \( 2a \) catalyzed by IDPi 4e with sole dioxane as solvent at room temperature for 12 h. The titled product was purified by column chromatography with hexanes as eluent to afford 3v as a colorless oil (50.0 mg, 96% yield).

\(^1\)H NMR (501 MHz, CDCl\(_2\)) \( \delta \) 7.29–7.25 (m, 4H), 7.17 (td, \( J = 5.4, 2.6 \) Hz, 1H), 4.85 (d, \( J = 0.9 \) Hz, 1H), 3.54 (dt, \( J = 4.6, 1.2 \) Hz, 1H), 3.09 (dd, \( J = 12.9, 4.6 \) Hz, 1H), 2.34 (dd, \( J = 12.8, 1.6 \) Hz, 1H), 0.96 (s, 9H), 0.23 (s, 3H), 0.22 (s, 3H).

\(^13\)C NMR (126 MHz, CDCl\(_2\)) \( \delta \) 149.9, 145.0, 128.1, 126.5, 125.9, 106.0, 44.2, 36.9, 25.4, 18.0, –4.9.

Rf = 0.55 (Hexanes).

EI-MS (m/z): calculated for C\(_{16}\)H\(_{24}\)O\(_3\)Si [M\(^+\)]: 260.1588, found: 260.1591.

HPLC (OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm): \( t_{R1} = 24.6 \) min, \( t_{R2} = 18.8 \) min, e.r. = 89:11.

\[ [\alpha]_{D}^{25} = 3.0 \ (c \ 0.41, \ CH_3CN). \]

### 6. Gram scale reaction and derivatizations of the enol silane 3a

**i. Gram scale catalytic deprotonsilylative desymmetrization of ketone 1a with allylsilane 2a.**

Allyl(\( \text{tert}-\)butyl)dimethylsilane 2a (1.4 mL, 7.0 mmol, 2.0 equiv.) was added to a flame-dried Schlenk flask, equipped with a teflon-coated magnetic stirring bar. IDPi 4e (86.0 mg, 0.035 mmol, 0.01 equiv.) in combined solvent (toluene/dioxane = 2:1, 0.08 M, 43.7 mL) was added at 25 °C for 15 min, and ketone 1a (609.8 mg, 3.5 mmol, 1.0 equiv.) was slowly added, then the resultant mixture was stirred at –20 °C. After the ketone 1a was fully consumed which was monitored by TLC, the reaction was quenched by three drops of triethylamine through pipet. Organic volatiles were evaporated in vacuo and the crude mixture was purified by the silica column to afford the desired enol silane 3a (1.06 g, 92% yield, 95.5:4.5 e.r.), and the recycled IDPi catalyst 4e was collected (80 mg, 93%).

**ii. Preparation of ((1R,3S)-3-bromo-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)(\( \text{tert}-\)butyl)dimethylsilane 5**
To a solution of compound 3a (57.7 mg, 0.2 mmol) in THF (0.1 M), N-Bromosuccinimide was added at 0 °C. The reaction mixture was stirred for 1.5 h at this temperature. After the reaction was completed (monitored by TLC), the reaction mixture was quenched with water (1 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined, dried over anhydrous Na₂SO₄ and filtered through celite. The volatile components were removed under reduced pressure, and purified by column chromatography (hexanes) affording the brominated enol silane 5 as a colorless oil (68.3 mg, 93% yield).

\[ {_{1}H} \text{NMR (501 MHz, CD}_2\text{Cl}_2) \delta \, 7.14-7.09 \text{ (m, 2H), 7.08-7.04 \text{ (m, 2H), 7.04-6.99 \text{ (m, 1H), 4.87 \text{ (dd, J = 5.6, 2.6 Hz, 1H), 4.53-4.46 \text{ (m, 1H), 3.18-3.01 \text{ (m, 1H), 2.29-2.21 \text{ (m, 1H), 2.21-2.10 \text{ (m, 3H), 0.77 \text{ (s, 9H), 0.00 \text{ (s, 3H), 0.00 \text{ (s, 3H).}}} \text{H}}) \text{, 3.18 \text{ (ddt, J = 12.4, 6.7, 0.7 Hz, 1H), 3.18 (dtt, J = 12.7, 9.2, 1.9 Hz, 1H), 2.62 (ddt, J = 12.2, 6.5, 4.3, 3.2 Hz, 1H), 2.59-2.51 \text{ (m, 2H), 2.27-2.16 \text{ (m, 1H), 2.10 (qd, J = 12.4, 9.7 Hz, 1H), 1.96-1.80 \text{ (m, 1H).}}} \text{C}}) \text{ NMR (126 MHz, CD}_2\text{Cl}_2) \delta \, 149.3, 145.0, 128.4, 107.1, 51.8, 39.8, 35.2, 32.2, 25.4, 18.0, -4.7, -5.1.} \text{H}}) \text{, 3.18 (ddt, J = 12.4, 6.7, 0.7 Hz, 1H), 3.18 (dtt, J = 12.7, 9.2, 1.9 Hz, 1H), 2.62 (ddt, J = 12.2, 6.5, 4.3, 3.2 Hz, 1H), 2.59-2.51 (m, 2H), 2.27-2.16 (m, 1H), 2.10 (qd, J = 12.4, 9.7 Hz, 1H), 1.96-1.80 (m, 1H).} \text{R} f = 0.24 \text{ (Hexanes).} \text{ESI-HRMS (m/z): calculated for C}_{18}\text{H}_{25}\text{O}_{13}\text{BrSi} \, ([M+H]^+) \div 367.1087, \text{found: 367.1085.} \text{HPLC (OJ-3R, Acetonitrile: Water = 80:20, 1.0 mL/min, 298 K, 254 nm): } t_{R1} = 5.6 \text{ min, } t_{R2} = 8.1 \text{ min, e.r. = 95:5.} \text{[α]}_D^{25} = -12.8 \text{ (c 0.42, CH}_3\text{CN).} \text{iii. Preparation of (2R,4R)-2-fluoro-4-phenylcyclohexan-1-one 6} \text{According to a known procedure with minor modification}^{17} \text{To a solution of compound 3a (57.7 mg, 0.2 mmol) in CH}_3\text{CN (0.06 M), selectfluor (1.1 equiv.) was added at rt. The reaction mixture was stirred for 1 h at this temperature. After the reaction was completed (monitored by TLC), the reaction mixture was quenched with water (1 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined, dried over Na}_2\text{SO}_4 and filtered through celite. The volatile components were removed under reduced pressure, and purified by column chromatography (ethyl acetate/hexanes 1:9) affording the fluorinated cyclic ketone 6 as a colorless oil (31.1 mg, 81% yield). There are two diastereomers formed, d.r. = 1.3:1, for the major product:

\[ {_{1}H} \text{NMR (500 MHz, CD}_2\text{Cl}_2) \delta \, 7.36-7.30 \text{ (m, 2H), 7.30-7.21 \text{ (m, 3H), 5.10 (dddd, J = 48.3, 12.4, 6.7, 0.7 Hz, 1H), 3.18 (dtt, J = 12.7, 9.2, 1.9 Hz, 1H), 2.62 (ddt, J = 12.2, 6.5, 4.3, 3.2 Hz, 1H), 2.59-2.51 \text{ (m, 2H), 2.27-2.16 \text{ (m, 1H), 2.10 (qd, J = 12.4, 9.7 Hz, 1H), 1.96-1.80 \text{ (m, 1H).}}} \text{C}}) \text{ NMR (126 MHz, CD}_2\text{Cl}_2) \delta \, 204.5-204.3 \text{ (d, J = 14.2 Hz), 142.9 \text{ (d, J = 1.2 Hz), 128.6, 126.9, 126.6, 92.6-91.0 \text{ (d, J = 191.2 Hz), 41.2-41.1 \text{ (d, J = 9.1 Hz), 40.7-40.6 \text{ (d, J = 18.3 Hz), 39.4, 34.2-34.2 \text{ (d, J = 1.2 Hz).}}} \text{F}}) \text{ NMR (470 MHz, CD}_2\text{Cl}_2) \delta \, -189.4. \text{R} f = 0.24 \text{ (Ethyl acetate/hexanes = 1:20).} \text{ESI-HRMS (m/z): calculated for C}_{18}\text{H}_{15}\text{O}_{13}\text{F} \, [M^-]^+ \div 192.0945, \text{found: 192.0947.} \text{HPLC (AD-3, n-heptane/i-PrOH = 99:1, 1.0 mL/min, 298 K, 254 nm): for major diastereomer, } t_{R1} = 15.0 \text{ min, } t_{R2} = 18.5 \text{ min, e.r. = 91.5:8.5, for minor diastereomer, } t_{R1} = 9.0 \text{ min, } t_{R2} = 5.9 \text{ min, e.r. = 94.5:5.5.} \text{[α]}_D^{25} = 18.3 \text{ (c 0.48, CH}_3\text{CN).} \text{For the major diastereomer) Optimal rotation data of trans-product was reported. Lit}^{18} \text{[α]}_D = 36.9 \text{ (c 1.04, CHCl}_3). \text{iv. Preparation of (R)-2,3-dihydro-}[1,1'-biphenyl]-4(1H)-one 7}
According to a known procedure with minor modification
To a solution of compound 3a (57.7 mg, 0.2 mmol) in CH$_2$CN (0.1 M), Pd(OAc)$_2$ (49.4 mg, 0.22 mmol, 1.1 equiv.) was slowly added at 0 °C. The reaction mixture was stirred for 12 h at this temperature. After the reaction was completed (monitored by TLC), the reaction mixture was quenched with water (1 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined, dried over Na$_2$SO$_4$ and filtered through celite. The volatile components were removed under reduced pressure, and purified by column chromatography (ethyl acetate/hexanes 1:9) affording the aldehyde 7 as a white solid (29.2 mg, 85% yield).

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 7.33–7.25 (m, 2H), 7.21–7.11 (m, 3H), 6.90 (ddd, $J = 10.2, 2.8, 1.4$ Hz, 1H), 6.02 (dd, $J = 10.2, 2.6$ Hz, 1H), 3.65 (ddt, $J = 9.9, 5.2, 2.7$ Hz, 1H), 2.46–2.32 (m, 2H), 2.26 (dqd, $J = 13.3, 4.9, 1.4$ Hz, 1H), 1.95 (dddd, $J = 13.4, 11.1, 9.5, 5.5$ Hz, 1H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 198.6, 152.7, 143.2, 129.7, 128.7, 127.5, 126.8, 42.6, 36.9, 32.5.

RF = 0.12 (Ethyl acetate/hexanes = 1:9).

ESI-HRMS (m/z): calculated for C$_{12}$H$_{13}$O$_1$ ([M+H]$^+$): 173.0960, found: 173.0963.

HPLC (OJ-3, n-heptane/i-PrOH = 99:1, 1.0 mL/min, 298 K, 220 nm): $t_{R1} = 15.8$ min, $t_{R2} = 12.2$ min, e.r. = 95.5:4.5.

$[\alpha]_{D}^{25} = 179.5$ (c 0.28, CH$_3$OH)

And the absolute configuration of unsaturated ketone 7 was determined to be R by comparing the optical rotation value with the reported value. Lit$^{20}$

$[\alpha]_{D}^{25} = 195.0$ (c 1.0, CH$_3$OH).

The configuration of the enolsilane product 3a could be deduced by analogy to be R.

v. Preparation of methyl (1S,3S,6R,7R)-6-((tert-butyl(dimethyl)silyl)oxy)-3-phenylbicyclo[4.2.0]octane-7-carboxylate 8

According to a known procedure with minor modification
To a solution of compound 3a (57.7 mg, 0.2 mmol) in DCM (0.1 M), methyl acrylate (2 equiv.) and diethylaluminium chloride (0.2 equiv.) was added at -78 °C. The reaction mixture was stirred for 4 h at this temperature. After the reaction completed (monitored by TLC), the reaction mixture was quenched with water (1 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and dried over Na$_2$SO$_4$ and filtered through celite. The volatile components were removed under reduced pressure and purified by column chromatography (ethyl acetate/hexanes 1:20) affording the bridged product 8 as a colorless oil (68.2 mg, 91% yield).

There were three diastereomers formed, d.r. = 25:6:1, for the major product:

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 7.13–7.07 (m, 2H), 7.04–6.97 (m, 3H), 3.49 (s, 3H), 2.80 (dd, $J = 10.1, 8.3$ Hz, 1H), 2.46 (td, $J = 5.5, 3.0$ Hz, 1H), 2.24 (tq, $J = 5.0, 1.9$ Hz, 1H), 1.76–1.55 (m, 4H), 1.52–1.39 (m, 4H), 0.74 (s, 9H), 0.00 (s, 3H), 0.00 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 172.3, 147.4, 128.3, 128.2, 126.8, 125.8, 75.5, 53.8, 53.6, 53.4, 53.1, 52.9, 50.9, 49.5, 41.8, 39.8, 32.5, 32.3, 27.9, 25.4, 19.2, 17.8, -3.1.

RF = 0.45 (Ethyl acetate/hexanes = 1:20).

ESI-HRMS (m/z): calculated for C$_{22}$H$_{33}$O$_2$Si$_1$Na$_1$ ([M+Na]$^+$): 397.2169, found: 397.2167.

HPLC (OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm): $t_{R1} = 21.5$ min, $t_{R2} = 20.2$ min, e.r. = 95:5 (for major diastereomer).

$[\alpha]_{D}^{25} = 39.6$ (c 0.50, CH$_3$CN). (For the major diastereomer)

vi. Preparation of (2S,4R)-2-benzyl-4-phenylcyclohexan-1-one 9
According to a known procedure with minor modification\textsuperscript{22}

To a solution of compound 3a (57.7 mg, 0.2 mmol) in DCM (0.1 M), ZnCl\textsubscript{2} (1.0 equiv.) and BnBr (3 equiv.) was added at rt. The reaction mixture was stirred for 4 h at this temperature. After the reaction completed (monitored by TLC), the reaction mixture quenched with water (1 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and dried over Na\textsubscript{2}SO\textsubscript{4}, then filtered through celite. The volatile components were removed under vacuo and purified by column chromatography (ethyl acetate/hexanes 1:10) affording the ketone 9 as a white solid (29.1 mg, 55% yield).

There are two diastereomers formed, d.r. = 1.7:1, for the major product:

\textsuperscript{1}H NMR (501 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 7.22–7.13 (m, 4H), 7.13–7.05 (m, 6H), 3.52 (s, 1H), 3.18 (dd, J = 14.1, 4.8 Hz, 1H), 3.01–2.91 (m, 1H), 2.69 (d, J = 5.0 Hz, 1H), 2.48 (ddd, J = 13.8, 6.0, 1.2 Hz, 1H), 2.39 (ddd, J = 13.7, 4.4, 2.5 Hz, 1H), 2.31 (dd, J = 14.1, 8.7 Hz, 1H), 2.16–2.08 (m, 1H), 2.05 (dd, J = 13.1, 5.5 Hz, 1H), 1.84 (dd, J = 13.1, 4.4 Hz, 1H).

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 211.5, 144.4, 140.0, 129.0, 128.4, 128.2, 126.6, 126.4, 125.9, 51.7, 43.3, 41.7, 40.4, 35.1, 35.0.

R\textsubscript{f} = 0.22 (Ethyl acetate/hexanes = 1:9).

EI-HRMS (m/z): calculated for C\textsubscript{19}H\textsubscript{20}O\textsubscript{1} [M\textsuperscript{+}]: 264.1508, found: 264.1508.

HPLC (AD-3, n-heptane/i-PrOH = 99:1, 1.0 mL/min, 298 K, 220 nm): for major diastereomer, \( t_R1 = 10.0 \) min, \( t_R2 = 10.9 \) min, e.r. = 94.5:5.5. for minor diastereomer, \( t_R1 = 13.3 \) min, \( t_R2 = 14.7 \) min, e.r. = 94:6.

\( \left[ \alpha \right]_{D}^{25} = 15.5 \) (c 0.21, CHCl\textsubscript{3}). (For the major diastereomer)

For the minor product:

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.34–7.27 (m, 4H), 7.24–7.17 (m, 6H), 3.25 (tt, J = 10.3, 4.0 Hz, 1H), 3.12 (dd, J = 13.0, 5.2 Hz, 1H), 2.84 (dd, J = 13.0, 9.6 Hz, 1H), 2.84–2.75 (m, 1H), 2.66 (ddd, J = 14.9, 11.4, 5.9 Hz, 1H), 2.46 (dt, J = 14.9, 4.8, 1.3 Hz, 1H), 2.27–2.18 (m, 1H), 2.18–2.05 (m, 1H), 2.09 (ddd, J = 13.8, 10.3, 5.2 Hz, 1H), 1.95 (dt, J = 13.8, 4.4, 4.0, 2.2 Hz, 1H).

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 213.3, 144.1, 138.8, 128.9, 128.6, 126.7, 126.5, 50.6, 38.6, 37.1, 36.8, 36.6, 33.0.

Recycling of catalyst 4c recovered from the gram-scale reaction:

Allyl silane 2a (80 μL, 0.4 mmol, 2.0 equiv.) was placed in a flame-dried Schlenk flask, equipped with a Teflon-coated magnetic stirring bar. Recovered IDPi 4c (0.01 equiv.) and solvent mixture toluene with 1,4-dioxane (2:1 v/v 0.08 M, 2.4 mL) were added at 25 °C and stirred for 30 min. The resultant mixture was cooled to −20 °C for 10 min, and ketones 1a (0.2 mmol, 1.0 equiv.) was slowly added. After stirring at −20 °C for 2 d, till the ketone was fully consumed monitored by TLC, the reaction was quenched with one drop of triethylamine added via pipet. Organic volatiles were evaporated in vacuo and the crude residue was purified by column chromatography with silica gel to afford the desired enol silanes 3a (99%, 97:3 e.r.).

7. Formal synthesis of iloprost\textsuperscript{23}
Triethyl(2-methylallyl)silane 2b (79 μL, 0.4 mmol, 2.0 equiv.) was placed in a flame-dried Schlenk flask, equipped with a teflon-coated magnetic stirring bar. IDPi 4f (0.01 equiv.) in solvent mixture toluene (0.08 M, 2.4 mL) was added at 25 °C and stirred for 10 min. The reaction mixture was cooled to −20 °C for 10 min, and ketone 1w (0.2 mmol, 1.0 equiv.) was slowly added. The resultant solution was stirred at −20 °C. After the ketone was fully consumed monitored by TLC, the reaction was quenched by one drop of trimethylamine through pipet. Organic volatiles were evaporated in vacuo and the crude residue was purified by column chromatography with silica gel to afford the desired enol silane 3w as light yellow oil (66.4 mg, 98%, 97:3 e.r).

$({(3aR, 6aS)}$-5',5'-dimethyl-3,3a,4,6a-tetrahydro-1H-spiro[pentalene-2,2',[1,3]dioxan]-5-yl)oxy)trimethylsilane 3w

$^1$H NMR (501 MHz, CD$_2$Cl$_2$) δ 4.51 (q, J = 1.9 Hz, 1H), 3.37 (d, J = 0.9 Hz, 2H), 3.34 (d, J = 0.9 Hz, 2H), 2.95–2.40 (m, 2H), 2.57–2.40 (m, 2H), 2.25–2.13 (m, 2H), 1.95–1.87 (m, 1H), 1.49–1.36 (m, 2H), 0.88 (t, J = 8.0 Hz, 9H), 0.86 (s, 3H), 0.83 (s, 3H), 0.59 (q, J = 7.8 Hz, 6H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 153.0, 108.7, 106.8, 72.5, 71.2, 44.4, 43.2, 41.2, 40.0, 39.8, 36.7, 35.6, 29.9, 22.2, 22.1, 22.0, 6.3, 4.7.

Rf = 0.63 (Ethyl acetate/hexanes = 1:9).

EI-HRMS (m/z): calculated for C$_{19}$H$_{35}$O$_3$Si ($[M+H]^+$): 339.2350, found: 339.2345.

HPLC (OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm): $t_{R1}$ = 7.0 min, $t_{R2}$ = 6.6 min, e.r. = 97:3.

$[\alpha]_{D}^{25}$ = 8.0 (c 0.10, CH$_3$CN), $[\alpha]_{D}^{20}$ = 7.3 (c 0.10, THF).

And the absolute configuration of the titled product was confirmed to be 3aR, 6aS according to the reported data.lit$^{23}$

$[\alpha]_{D}^{20}$ = 2.1 (c 9.8, THF).

8. Development of a catalytic asymmetric protodesilylation of racemic enol silanes.

General procedure for the optimization of catalytic kinetic resolution of racemic silyl enol ethers with different proton sources.

Racemic silyl enol ether 3x (0.2 mmol, 1.0 equiv.) was placed in a flame-dried Schlenk flask with a teflon-coated magnetic stirring bar. IDPi 4c–d (0.01 equiv.) in toluene (0.1 M, 2 mL) was added at 25 °C, after 5 min, the reaction mixture was cooled to a certain temperature for 10 min, then proton source (0.5 equiv., with H$_2$O: 0.25 equiv.) was added. After calibration with triphenylmethane as internal standard, the resultant solution was stirred at this temperature for proper time and monitored by GC or NMR analysis. Then the reaction was quenched by one drop of triethylamine through pipet. Organic volatiles were evaporated under vacuo and the crude residue was purified by prep. TLC, and the enantiomeric ratio (e.r.) was determined by HPLC.
Unless otherwise noted, reactions were performed with racemic silyl enol ether 3x (0.1 mmol), proton source (0.5 equiv., with H₂O: 0.25 equiv.), and catalyst (1 mol%) in toluene (0.2 mL, 0.5 M) under argon at 0 °C for 24 h. Conversion was determined by GC analysis. The enantiomeric ratio (e.r.) was determined by HPLC analysis. The selectivity factor (s) was determined by the equation: 

\[ s = \frac{k_{\text{rel}}}{(\text{fast/slow})} = \frac{\ln(1-C)(1-ee)}{\ln(1-C)(1+ee)} \]

where ee is the enantiomeric excess of the remained starting material 3x and C is the conversion. Reaction at −30 °C for 12–72 h. Reaction at −60 °C for 24 h. TMP = 2,4,6-trimethylphenol. BCA = biphenyl carboxylic acid.

9. Scope of the catalytic asymmetric protodesilylative kinetic resolution of racemic enol silanes.

General procedure for the optimization of catalytic kinetic resolution of racemic silyl enol ethers with different proton sources.

Racemic silyl enol ether (0.2 mmol, 1.0 equiv.) was placed in a flame-dried Schlenk flask equipped with a teflon-coated magnetic stirring bar. IDPi 4d (0.01 equiv.) in toluene (0.1 M, 2 mL) was added at 25 °C and stirred for 5 min. The reaction mixture was cooled to −30 °C or −60 °C for 10 min, then 2-biphenylcarboxylic acid 10 (0.1M solution in toluene) was added. The resultant solution was stirred at −30 °C or −60 °C for proper time and monitored by GC or NMR analysis (GC calibrations for all substrates were conducted with triphenylmethane as internal standard, and NMR yields were determined with triphenylmethane as internal standard). When the conversion of the racemic enol silane was around 50%, the reaction was quenched by one drop of triethylamine through pipet. Organic volatiles were evaporated under reduced pressure and the crude product was purified by column chromatography (starting with sole hexanes with eluent to obtain the recovered silyl enol ethers, then with ethyl acetate : hexanes = 1:20–1:10 as eluent to get the ketone byproducts) or prep. TLC, then the enantiomeric ratio was determined by HPLC analysis.

Analytical data of products

(S)-tert-butyldimethyl[(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy]silane 3a

The titled product was purified by prep. TLC with hexanes as eluent to afford ent-3a as a colorless oil.

HPLC (OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm): \( t_{R1} = 24.1 \text{ min, } t_{R2} = 22.9 \text{ min, e.r. = 94:6.} \)

\[ [\alpha]_{D}^{25} = -32.5 \text{ (c 0.20, CHCl}_3). \]

(S)-tert-butyl[(4-isopropylcyclohex-1-en-1-yl)oxy]dimethylsilane 3x

| entry | catalyst | proton source | conversion / % | er | s |
|-------|----------|---------------|----------------|----|---|
| 1     | 4c       | i-ProOH       | 68             | 64:36 | 2 |
| 2     | 4d       | i-ProOH       | 66             | 87:13 | 5 |
| 3     | 4d       | i-ProOH       | 55             | 91:9 | 12 |
| 4     | 4d       | H₂O           | 49             | 66:34 | 3 |
| 5     | 4d       | TMP           | 62             | 85:15 | 5 |
| 6     | 4d       | BCA           | 52             | 91:9 | 18 |
| 7     | 4d       | BCA           | 51             | 97:3 | 70 |
The titled product was purified by prep. TLC with hexanes as eluent to afford 3x as a colorless oil.

\[
\text{HPLC (OJ3R, Acetonitrile: Water = 30:70, 1.0 mL/min, 298 K, 220 nm): } t_{R1} = 15.3 \text{ min, } t_{R2} = 14.2 \text{ min, e.r. } = 97:3.
\]

\[\alpha_{D}^{25} = -40.7 \text{ (c 0.28, CHCl}_3).\]

\((S)\text{-tert-butyldimethyl(4-ethylcyclohex-1-en-1-yl)oxy)silane 3y}\)

The titled product was purified by column chromatography (sole hexanes to ethyl acetate : hexanes = 1 : 20) to afford 3y as a colorless oil.

\[
\text{HPLC (OJ3R, MeOH: Water = 80:20, 1.0 mL/min, 298 K, 220 nm): } t_{R1} = 14.3 \text{ min, } t_{R2} = 13.4 \text{ min, e.r. } = 98:2.
\]

\[\alpha_{D}^{25} = -46.7 \text{ (c 0.30, CH}_3\text{CN).}\]

\((S)\text{-tert-butyldimethyl(4-methylcyclohex-1-en-1-yl)oxy)silane 3z}\)

The titled product was purified by column chromatography (sole hexanes to ethyl acetate : hexanes = 1 : 20) to afford 3z as a colorless oil.

\[\alpha_{D}^{25} = -10.0 \text{ (c 0.30, CH}_3\text{CN).}\]

\((S)\text{-ethyl-4-((tert-butyldimethylsilyl)oxy)cyclohex-3-ene-1-carboxylate 3t}\)

The titled product was purified by column chromatography (sole hexanes to ethyl acetate : hexanes = 1 : 20) to afford \textit{ent-3t} as a colorless oil.

\[\alpha_{D}^{25} = -10.0 \text{ (c 0.30, CH}_3\text{CN).}\]
(S)-tert-butyl(dimethyl)((3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)silane 3aa

The titled product was purified by column chromatography (sole hexanes to ethyl acetate: hexanes = 1:20) to afford 3aa as a colorless oil.

1H NMR (501 MHz, CD2Cl2) δ 7.28–7.23 (m, 2H), 7.22–7.18 (m, 2H), 7.18–7.13 (m, 1H), 5.04 (td, J = 4.0, 1.2 Hz, 1H), 3.35 (ddd, J = 6.4, 4.5, 2.1 Hz, 1H), 2.21–2.05 (m, 2H), 2.05–1.97 (m, 1H), 1.71–1.63 (m, 1H), 1.62–1.55 (m, 1H), 1.51–1.43 (m, 1H), 0.67 (s, 9H), 0.07 (s, 3H), 0.00 (s, 3H).

13C NMR (126 MHz, CD2Cl2) δ 150.9, 144.6, 128.3, 127.8, 125.7, 105.3, 46.2, 33.2, 25.1, 24.1, 19.7, 17.6, −4.8, −5.1.

RF = 0.41 (Hexanes).

ESI-HRMS (m/z): calculated for C18H25O3Si ([M+H]+): 289.1982, found: 289.1977.

HPLC (OD-3R, Acetonitrile: Water = 50:50, 1.0 mL/min, 298 K, 220 nm): tR1 = 78.7 min, tR2 = 72.8 min, e.r. = 99:1.

[α]D25 = 41.3 (c = 0.16, CH3CN).

(R)-2-phenylcyclohexan-1-one 1aa

HPLC (OD-3, n-heptane/i-PrOH = 98:2, 1.0 mL/min, 298 K, 220 nm): tR1 = 8.1 min, tR2 = 7.3 min, e.r. = 17:83.

(S)-([1,1'-bi(cyclohexan)]-2-en-2-yloxy)(tert-butyl)dimethylsilane 3ab

The titled product was purified by column chromatography (sole hexanes to ethyl acetate: hexanes = 1:20) to afford 3ab as a colorless oil.

1H NMR (501 MHz, CD2Cl2) δ 4.70 (ddd, J = 4.9, 3.4, 1.6 Hz, 1H), 1.94–1.86 (m, 1H), 1.82 (ddd, J = 7.5, 3.5, 1.9 Hz, 2H), 1.70 (d, J = 3.7 Hz, 1H), 1.64–1.54 (m, 2H), 1.53–1.46 (m, 3H), 1.37–1.22 (m, 4H), 1.16–0.96 (m, 4H), 0.87 (ddd, J = 12.2, 3.5 Hz, 1H), 0.79 (s, 9H), 0.00 (s, 3H), 0.00 (s, 3H).

13C NMR (126 MHz, CD2Cl2) δ 152.3, 104.2, 44.2, 38.5, 31.2, 27.6, 27.3, 26.9, 26.8, 25.5, 24.3, 24.1, 21.9, 17.9, −4.7, −5.0.

RF = 0.71 (Hexanes).

ESI-HRMS (m/z): calculated for C18H35O3Si ([M+H]+): 295.2451, found: 295.2452.

HPLC (OJ-3R, MeOH: Water = 80:20, 1.0 mL/min, 298 K, 220 nm): tR1 = 15.2 min, tR2 = 13.7 min, e.r. = 99.9:0.1.

[α]D25 = −30.5 (c 0.28, CH3CN).

(R)-[1,1'-bi(cyclohexan)]-2-one 1ab

GC (30.0 m BGB 176, injection temperature: 220 °C, 120 °C, 0.5 bar H2): tR1 = 54.6 min, tR2 = 52.6 min, e.r. = 15:85.

(S)-tert-butyl(dimethyl)((4-methylcyclohex-1-en-1-yl)oxy)silane 3ac

The titled product was purified by column chromatography (sole hexanes to ethyl acetate: hexanes = 1:20) to afford 3ac as a light yellow liquid. For this compound, s = ln[(1−ee)/(1−ee)]/ln[(1+ee)/(1+ee)] (C = ee3ac/ ee3ac + ee1ac).

1H NMR (501 MHz, CD2Cl2) δ 7.12–7.05 (m, 4H), 7.01–6.96 (m, 1H), 4.49 (p, J = 2.0 Hz, 1H), 3.28 (tt, J = 9.1, 6.9 Hz, 1H), 2.59–2.45 (m, 2H), 2.29–2.12 (m, 2H), 0.76 (s, 9H), 0.00 (s, 3H), 0.00 (s, 3H).

13C NMR (126 MHz, CD2Cl2) δ 153.6, 147.3, 128.2, 126.7, 125.7, 101.4, 41.8, 41.4, 37.5, 25.4, 17.9, −4.8, −4.9.
Rf = 0.35 (Hexanes).

ESI-HRMS (m/z): calculated for C_{17} H_{27} O_{1} Si_{1} ([M+H]^+): 275.1826, found: 275.1826.

HPLC (OJ-3R, Acetonitrile: Water = 80:20, 1.0 mL/min, 298 K, 220 nm): t_{R1} = 6.0 min, t_{R2} = 6.3 min, e.r. = 95:5.

[\alpha]_{D}^{25} = -6.7 (c 0.30, CH3CN).

(S)-3-phenylcyclopentan-1-one 1ac

\[ \text{HPLC (AS-3, n-heptane/i-PrOH = 99:1, 1.0 mL/min, 298 K, 220 nm): } t_{R1} = 21.2 \text{ min, } t_{R2} = 18.6 \text{ min, e.r. = 15:85.} \]

**tert-butyldimethylsilyl [1,1'-biphenyl]-2-carboxylate**

The titled product was purified by prep. TLC with hexanes as eluent:

1\text{H NMR (501 MHz, CD}_{2}\text{Cl}_{2}) \delta 7.64 (dd, J = 7.8, 1.4 Hz, 1H), 7.34 (td, J = 7.5, 1.4 Hz, 1H), 7.26 – 7.11 (m, 8H), 0.59 (s, 9H), 0.00 (s, 6H).

1\text{C NMR (126 MHz, CD}_{2}\text{Cl}_{2}) \delta 168.6, 142.2, 141.7, 132.6, 130.9, 130.8, 130.0, 128.5, 128.1, 127.2, 127.0, 25.2, 17.4, -5.3.

Rf = 0.51 (Ethyl acetate/hexanes = 1:20).

ESI-HRMS (m/z): calculated for ([M+Na]^+): 335.1438, found: 335.1436.

10. Limitations of the method:

11. Mechanistic study

Procedure of reactivity comparison between Tf_2NH (Bistriflimide) and confined IDPi catalysts 4c:
Reaction with IDPi: Allyl(tert-butyl)dimethylsilane 2a (80 μL, 0.4 mmol, 2.0 equiv.) was placed in a flame-dried Schlenk flask, equipped with a teflon-coated magnetic stirring bar. IDPi 4c (0.01 equiv.) and toluene (0.08 M, 2.4 mL) were added at 25 °C and stirred for 5 min, ketone 1a was added afterwards, then the resultant solution was stirred at this temperature for 12 h. After the ketone was fully consumed which was monitored by TLC, the reaction was quenched by one drop of triethylamine through pipet. Organic volatiles were evaporated in vacuo and the crude residue was purified by silica column chromatography to afford the desired enol silane 3a in quantitative yield with 88:12 e.r.

Reaction with Tf₂NH: Allyl(tert-butyl)dimethylsilane 2a (80 μL, 0.4 mmol, 2.0 equiv.) and ketone 1a was placed in a flame-dried Schlenk flask, equipped with a teflon-coated magnetic stirring bar. Tf₂NH (0.01 equiv.) and toluene (0.08 M, 2.4 mL) were added at 25 °C and stirred for 12 h. After the ketone was fully consumed which was monitored by TLC, the reaction was quenched by one drop of triethylamine through pipet. Then the components of the crude reaction solution were verified by GC-MS and HRMS, which was a mixture of homo-aldol adducts 11 in quantitative yield without formation of the enol silane 3a. [see the GC-MS (ESI) spectrum below] (for the reaction at ~20 °C, after 24 h, the total conversion of 1a is ~40%, only ~5% 3a was observed, homo-aldol adducts were still the major products, which indicates the enol silane can be the intermediate for aldol reaction)

Notes: small amount of Hosomi–Sakurai product may also formed as inseparable mixture with homo-aldol products.
**Figure S1.** ESI-MS spectrum of the reaction mixture catalyzed by Tf$_2$NH. **11-5** was isolatable and the structure was confirmed by NMR analysis.

4-(2-oxo-5-phenylcyclohexyl)-1,2,3,6-tetrahydro-1,1'-biphenyl **11-5**

The titled product was purified by column chromatography with ethyl acetate/hexanes = 1:4 as eluent to afford **11-5** as a white solid.

$^1$H NMR (501 MHz, CDCl$_3$) δ 7.27 – 7.14 (m, 10H), 5.53 – 5.43 (m, 1H), 3.11 (tdd, $J = 12.2, 8.8, 3.4$ Hz, 2H), 2.72 (dddt, $J = 25.2, 12.3, 5.2, 2.8$ Hz, 1H), 2.53 – 2.40 (m, 2H), 2.17 (ddtd, $J = 18.3, 11.1, 5.5, 2.7$ Hz, 4H), 2.07 – 1.84 (m, 5H), 1.84 – 1.63 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 210.4, 147.2, 147.1, 144.7, 135.6, 135.4, 128.6, 128.4, 128.4, 128.3, 126.9, 126.8, 126.7, 126.7, 126.6, 126.0, 126.0, 124.1, 123.9, 58.3, 57.8, 43.5, 43.4, 42.0, 41.9, 40.2, 40.0, 39.9, 39.6, 34.5, 34.4, 33.7, 33.4, 30.0, 29.8, 28.1, 27.5.

Rf = 0.31 (Ethyl acetate/hexanes = 1:4).

ESI-HRMS (m/z): calculated for C$_{24}$H$_{27}$O$_1$ ([M+H]$^+$): 331.2056, found: 331.2056.

Reaction with Tf$_2$NH and Et$_3$N: Allyl(tert-butyl)dimethylsilane 2a (60 µL, 0.3 mmol, 1.5 equiv.) and ketone 1a (35 mg, 0.2 mmol, 1.0 equiv.) was placed in a flame-dried Schlenk flask, equipped with a teflon-coated magnetic stirring bar. Tf$_2$NH (0.01 equiv.), Et$_3$N (0.01 equiv.), and toluene (0.1 M, 2.0 mL) were added stepwise at 25 °C and stirred for 1.5 h, then the reaction was quenched by triethylamine and the solvent was removed by vacuum. The yield of the desired racemic enol silane 3a was determined to be 65% with nitrobenzene as internal standard via the $^1$H NMR analysis attached below (Figure S2).
Figure S2. $^1$H NMR studies of the reaction catalyzed by Tf$_2$NH and Et$_3$N. (I). Crude $^1$H NMR analysis of the reaction with nitrobenzene as internal standard in CD$_2$Cl$_2$. (II): $^1$H NMR of the desired product 3a in CD$_2$Cl$_2$; (III). $^1$H NMR of the starting material 1a in CD$_2$Cl$_2$.

Notes: with pre-mixed Tf$_2$NH and Et$_3$N, no reaction was detected. Separate addition of the acid and amine is indispensable for the promotion of enol silylation.

Kinetic studies

When studying the reaction in a toluene-$d_8$/dioxane-$d_8$ = 2:1 mixture, a significant dormant period was observed (Figure S3).

Procedure: allyl(tert-butyl)dimethylsilane 2a (20 μL, 0.1 mmol, 2.0 equiv.) was placed in a flame-dried Schlenk flask, equipped with a teflon-coated magnetic stirring bar. IDPi 4c (0.01 equiv.) and toluene-$d_8$/dioxane-$d_8$ = 2:1 (0.08 M, 0.6 mL) were added at 25 °C and stirred for 5 min. The reaction mixture was cooled to −20 °C for 10 min, ketone 1a (8.7 mg, 0.05 mmol, 1.0 equiv.) was added afterwards, then the resultant solution was transferred to a 5mm NMR tube and reaction was performed at this temperature for 3 d.

Conclusion: during the first 10 h of NMR monitoring of the reaction, no product formation was observed. Instead, only the conversion of TBSOH accompanied by the formation of TBSOTBS. Till all the TBSOH was consumed fully, the formation of the desired product starts to be observed. In sharp contrast, the reaction in toluene-$d_8$ had a ~0.5 h dormant period, which was detected via NMR studies.

Determination of reaction order of IDPi catalyst 4c.

Figure S3. left: Conversion plot showing the initial formation of TBSOH and TBSOTBS; right: $^1$H NMR spectra showing regions of interest taken at different time points during the reaction.

The catalyst order was determined by time normalization analysis reported by the Bures group. When comparing conversion plots normalized to different catalyst orders (Figure S4), the curves were found to overlap nicely when a first order with respect to the catalyst
was used, implying no significant influence from off-cycle equilibria or synergistic effects. The model reaction was conducted with 0.6, 1.2 and 2.4 mol% of catalyst 4c under standard reaction conditions.

**Figure S4.** Conversion plots obtained from NMR measurements with time scales normalized to different catalyst orders: a) zero-order reaction; b) half-order reaction; c) first-order reaction and d) second-order reaction.

**Determination of reaction order of ketone 1a and allylsilane 2a**

The order of the ketone 1a was also determined by variable time normalisation analysis (VTNA). Reaction plots normalized to different reaction order of ketone can be found in Figure S5. By comparing the outcome of different orders, the reactions were found to in accordance with the zeroth order in ketone 1a (Figure S5).

*Note: we have observed this zeroth order dependence of aldehyde in the cyanosilylation of aldehyde catalyzed by disulfonimide.*

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*S39*
Figure S5. Conversion plots obtained from NMR measurements with time scales normalized to the catalyst concentration and different orders of ketone 1a: a) zero-order reaction; b) half-order reaction; c) first-order reaction and d) second-order reaction.

The reaction order with respect to the silane source was also determined by VTNA. Concentration plots obtained from NMR normalized to different orders of silane 2a can be found in Figure S6.
Figure S6. Product concentrations obtained from NMR measurements with time scales normalized to the catalyst concentration and different orders of ketone 1aa: a) zero-order reaction; b) half-order reaction; c) first-order reaction and d) second-order reaction.

The best overlap was found, when a first order dependence in silane concentration was assumed (Figure S6c).

Taking all the measurements into account, this data supports the hypothesis that the silylation of the catalyst is the overall rate determining step of the reaction.

Study of racemization process of unsymmetric ketones

During the substrate screening of the catalytic asymmetric protodesilylative kinetic resolution of racemic enol silanes with 2-biphenyl carboxylic acid, we found that under the reaction conditions the chiral ketone byproducts partially racemize. This may due to the tautomerization between ketone and enol, and also caused by the kinetic equilibrium among enol silane regiomers and the relevant ketone.
In order to verify the tautomerization, reactions of both enantiomers of 2-phenylcyclohexanone with IDPi 4d were conducted, and the ee was checked by HPLC analysis.

![Diagram of tautomerization reaction]

**Figure S7. Study of keto-enol tautomerization**

With the data in hand, we confirmed one reason is tautomerization, which causes ketone racemization. However, under lower temperature, this tautomerization effect could be slower.

Since the rate of tautomerization is quite slow, there may be another reason. In order to verify our hypothesis, the kinetic resolution between racemic enolisilane 3aa and biphenyl carboxylic acid 10 under standard condition were performed in toluene-d8, and the reaction was monitored by reaction progress kinetic analysis (Figure S8).

![Diagram of kinetic resolution reaction]
Figure S8. Reaction progress kinetic analysis of the kinetic resolution of racemic enol silane 3aa and acid 10

From the kinetic plot, the racemic enolsilane 3aa keep decreasing, accompanied by increasing of the ketone 1aa. It is quite clear that there is equilibrium between 3aa and 1aa in the reaction system, which possibly cause the racemization of 1aa. The starting racemic enolsilane 3aa was a mixture of kinetic product and thermodynamic product (isomer) (95:5), and the ratio of isomer remains the same throughout the entire reaction process. To 2-substituted enol silane, there presumed to be no equilibrium between the kinetic product and the thermodynamic product under acidic atmosphere. ArCOOTBS keeps increasing till the conversion was ~ 50%, after that, TBSOTBS starts to be observed from the hydrolysis of 3aa with less reactive adventitious water. Finally, the reaction end up with ~55% conversion.

$^{31}$P NMR analysis of the reaction solution:

The hypothesis that the silylation of the catalyst is the rate-determining step can be further confirmed by $^{31}$P NMR spectra taken at different time points (Figure S9). At the beginning of the reaction, only the protonated form of the catalyst is observed ($\delta_{31P} = -16.9$ ppm). After 12 h, two new signals at –11.3 and –20.0 ppm with a characteristic coupling $^1J_{pp}=134$ Hz appeared. At early stage of the reaction, most of the catalyst remained in the protonated form and when it started to be silylated, the enolsilane product was immediately generated. At a later stage, the amount of ketone presumed to be prominent in terms of rate limiting factors, while the silylated catalyst can also be observed in the reaction mixture. If the silylation of the ketone turned out to be the rate determining step instead of the catalyst silylation, we would expect to observe the only presence of the Cat-TBS in the reaction. In contrary, both of the Cat-TBS (silylated catalyst) and Cat-H (initial protonated catalyst) exist till the end of the reaction.
Figure S9. $^{31}$P NMR spectra taken at different time points showing the different catalyst species present in the entire reaction process.

The ESI-MS spectrum acquired from the mixture of IDPi 4d and BCA showed below:

Figure S10. Detection of catalyst species of the kinetic resolution.
12. Characterization and study of dynamic behavior of catalyst 4c-TBS

$^1$H NMR in Toluene-$d_8$:

$^{31}$P NMR spectrum of the activated catalyst TBS-4c:

$^1$H-$^{31}$P HMBC NMR spectrum of the activated catalyst 4c-TBS showing long range coupling of the protons at position 4 in the BINOL-backbone to the $^{31}$P in the core of the catalyst.
$^{29}$Si INEPT NMR spectrum of the activated catalyst TBS-4c showing multiple species obtained from the activation of the catalyst. The signal attributed to the silylated catalyst appears at 54.9 ppm.

From $^1$H-$^{29}$Si HMBC NMR spectrum of the activated catalyst 4c-TBS, the correlation of the TBS moiety to the $^{29}$Si signal appears at 54.9 ppm. Other signals in the mixture can be assigned to the side products from the silylation process and grease.
$^1$H EASY ROESY NMR spectrum of the activated catalyst 4c-TBS showing only an excerpt of the aromatic region. The red boxes show the chemical exchange between the 4 and 4' positions of both sites of the catalyst. The spectrum was acquired with a spin-lock time of 300 ms.

$^1$H EASY ROESY NMR spectrum of the activated catalyst 4c-TBS showing the signals of the TBS group attached to the catalyst. The red box shows the chemical exchange between the diastereotopic Si-Me groups.
The spectrum was acquired with a spin-lock time of 300 ms. The exchange peaks in the ROESY show that there is an internal silicon transfer within the catalyst observable at a 0.3 s timescale (see the scheme below), which is much quicker than the reaction rates observed during the reaction.
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14. Copies of NMR spectra

(S)-3', 3''-bis(9,9-diethyl-9H-fluoren-3-yl)-[1,1''-binaphthalene]-2,2'-diol:
| Parameter       | Value |
|-----------------|-------|
| Solvent         | CDCl3 |
| Temperature     | 298.0 |
| Spectrometer Frequency | 125.94 |
| Nucleus         | 13C   |
(S)-3,3′-di(triphenyl-2-yl)-[1,1′-binaphthalene]-2,2′-diol:
(S)-3,3'-bis(3',5'-di-tert-butyl-[1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol:
(S,S)-IDPi-4a

Parameter | Value
---|---
Solvent | CDCl3
Temperature | 298.0
Spectrometer Frequency | 125.04
Nucleus | 13C

Parameter | Value
---|---
Solvent | CDCl3
Temperature | 298.0
Spectrometer Frequency | 500.13
Nucleus | 1H
| Parameter      | Value |
|---------------|-------|
| Solvent       | CDCl3 |
| Temperature   | 298.0 |
| Spectrometer Frequency | 471.21 |
| Nucleus       | 31P   |
(S,S)-IDPi-4b:

Parameter | Value
--- | ---
Solvent | CDCl3
Temperature | 297.0
Spectrometer Frequency | 600.11 MHz
Nucleus | 1H

---

Parameter | Value
--- | ---
Solvent | CDCl3
Temperature | 298.0
Spectrometer Frequency | 125.94 MHz
Nucleus | 13C

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S57
(S,S)-IDPi-4c:
(S,S)-IDPI-4d:
$(S,S)$-IDPi-4e:
((perfluoronaphthalen-2-yl)sulfonyl)phosphorimidoyl trichloride $R_f$-6:
(S,S)-IDPi-4f:
4-(4-chlorophenyl)cyclohexan-1-one 1d:
4-(4-(trifluoromethyl)phenyl)cyclohexan-1-one 1f:
4-(3-(tert-butyl)phenyl)cyclohexan-1-one 1g:
4-(3-chlorophenyl)cyclohexan-1-one 1h:
4-(3-(trifluoromethyl)phenyl)cyclohexan-1-one 1i:

Parameter | Value
---|---
Solvant | CDCl3
Temperature | 298.0
Spectrometer Frequency | 500.01
Nucleus | 1H
4-(3,5-difluorophenyl)cyclohexan-1-one 11:
4-(naphthalen-1-yl)cyclohexan-1-one 1m:
4-methyl-4-phenylcyclohexan-1-one 1s:

Parameter | Value
--- | ---
Solvent  | CDCl3
Temperature | 297.8
Spectrometer Frequency | 500.81
Nucleus | 1H
(3aR,6aS)-hexahydropentalen-2(1H)-one 1u:
(3aR,6aS)-5',5'-dimethyltetrahydro-1H-spiro[pentalene-2,2'-[1,3]dioxan]-5(3H)-one 1w:

![Chemical structure of (3aR,6aS)-5',5'-dimethyltetrahydro-1H-spiro[pentalene-2,2'-[1,3]dioxan]-5(3H)-one 1w]
3-phenylcyclobutan-1-one 1v:
rac-3-phenylcyclohexan-1-one 1ac:
(R)-tert-butyldimethyl(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane 3a:
(R)-tert-butyl(dimethyl)silane 3b:
(R)-tert-butyl(4'-methoxy-1,2,3,6-tetrahydro-[1,1′-biphenyl]-4-yl)oxy)dimethylsilane 3c:
(R)-tert-butyl(4′-chloro-1,2,3,6-tetrahydro-[1,1′-biphenyl]-4-yl)oxydimethylsilane 3d:
(R)-tert-butyl((4'-fluoro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)dimethylsilane 3e:
(R)-tert-butyldimethyl((4'-(trifluoromethyl)-1,2,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane 3f:
(R)- tert-butyl((3’-(tert-butyl)-1,2,3,6-tetrahydro-[1,1’-biphenyl]-4-yl)oxy)dimethylsiline 3g:
(R)-tert-butyl((3'-chloro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)dimethylsilane 3h:
(R)-tert-butyldimethyl((3'-(trifluoromethyl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane 3i:

\[
\text{Parameter} \quad \text{Value} \\
\text{Solvent} \quad \text{CD2Cl2} \\
\text{Temperature} \quad 298.0 \\
\text{Spectrometer Frequency} \quad 125.94 \\
\text{Nucleus} \quad 13C
\]
| Parameter       | Value  |
|-----------------|--------|
| Solvent         | CDCl3  |
| Temperature     | 296.0  |
| Spectrometer Frequency | 125.94 |
| Nucleus         | 13C    |

| Parameter       | Value  |
|-----------------|--------|
| Solvent         | CDCl3  |
| Temperature     | 298.0  |
| Spectrometer Frequency | 400.23 |
| Nucleus         | 19F    |
(R)-tert-butyldimethyl(2’-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane 3j:
(R)-tert-butyl(3',5'-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)dimethylsilane 3k:
(R)-tert-butyl(3',5'-difluoro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxydimethylsilane 3l:
(R)-tert-butyl(dimethyl)((4-(naphthalen-1-yl)cyclohex-1-en-1-yl)oxy)silane 3m:
(R)-tert-butyldimethyl((4-(naphthalen-2-yl)cyclohex-1-en-1-yl)oxy)silane 3n:

| Parameter      | Value       |
|----------------|-------------|
| Solvent        | CDCl₃       |
| Temperature    | 298.0       |
| Spectrometer Frequency | 125.94     |
| Nucleus        | 13C         |

![Chemical structure of 3n](image)
(R)-tert-butyl(dimethyl((1,2,3,6-tetrahydro-[1,1’:4’,1’’-terphenyl]-4-yl)oxy)silane 3o:
(R)-tert-butyl((4-(tert-butyl)cyclohex-1-en-1-yl)oxy)dimethylsilane 3p:
\((R)-([1,1']\text{-bi(cyclohexan}])\text{-3-en-4-yloxy})(\text{tert-butyl})\text{dimethylsilane 3q}:
(R)-((4-benzylcyclohex-1-en-1-yl)oxy)(tert-butyl)dimethylsilane 3r

OTBS

3r
(R)-tert-butyldimethyl(1-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yloxoy)silane 3s:

Parameter | Value
--- | ---
Solvent | CDCl₃
Temperature | 298.0
Spectrometer Frequency | 500.13 MHz
Nucleus | 1H
(R)-4-((tert-butyldimethylsilyl)oxy)cyclohex-3-ene-1-carboxylate 3t:
(((3aS,6aS)-1,3a,4,5,6,6a-hexahydropentalen-2-yl)oxy)triethylsilane 3u:

S103
(R)-tert-butyldimethyl((3-phenylcyclobut-1-en-1-yl)oxy)silane 3v:

Parameter Value
1. Solvent CD2Cl2
2. Temperature 297.9 K
3. Spectrometer Frequency 500.13 MHz
4. Nucleus 1H

OTBS

3v
((1R,3S)-3-bromo-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy/(tert-butyl)dimethylsilane 5:
(2R,4R)-2-fluoro-4-phenylcyclohexan-1-one 6:

NMR data support the formation of the 2,4-cis compound.

Important structural evidences are: NOEs between H2, H4 and one proton at C6 (can be distinguished due to similar chemical shifts.) Strong couplings of H3\(^*\) with H2, and H4 (~12.5 Hz) -> both trans-positioned
$^1$H-$^1$H COSY
(R)-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one 7:

- Solvent: CDCl₃
- Temperature: 297.8 K
- Spectrometer Frequency: 500.61 MHz
- Number of H: 1
(1S,3S,6R,7R)-6-((tert-butyldimethylsilyl)oxy)-3 phenylbicyclo[4.2.0]octane-7-carboxylate 8
User Report
ARK-AB-078-02

NMR data support the formation of the 2,4-mono 1,11-oxa compound as
the major diastereomeric compound.

Important structural evidences are:
NOEs between H6/H11 and H2
W-Coupling between H2 and H6’ (~1.8 Hz)
NOE between H11/H2 and H17” (trans-configuration of cyclobutane)

Observed couplings for H11 fit well to reported literature values of similar
compound (10.2, 8.85 Hz) Ref: J. Org. Chem. 2004, 69, 2, 517-521

The sample contains a second diastereomer (probably, 1,11-trans, due to
similar couplings of H11 when compared to literature)

Due to big overlap of H17” and H6’, the sample was also measured in CDCl3
near ARK-AB-078-S3, which gave the same result.

3D Model of Major Component

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 499.87
4 Nucleus 1H

TBOS
MeO₂C
Ph

8
(2S,4R)-2-benzyl-4-phenylcyclohexan-1-one 9:

The data from 1H, 13C and 2D-correlations supports the following structure:

User Report

ZHH-
ZB-324-01

For NMR assignment table please see the next page of this report.

1H NMR (500 MHz, CDCl3) 7.33 – 7.12 (m, 10H), 3.32 (dt, 4.1, 4.6 Hz, 1H), 2.03 (br, 12.4, 3.5 Hz, 1H), 2.85 – 2.71 (m, 1H), 2.59 – 2.51 (m, 2H), 2.42 (dt, 8.9 Hz, 1H), 2.27 – 2.21 (m, 2H), 2.23 – 2.13 (m, 1H), 2.03 – 1.96 (m, 1H), 1.64 (spp, Ag, 12.6 Hz, 1H).

13C NMR (125 MHz, CDCl3) 211.60, 144.57, 140.11, 129.13, 128.56, 128.34, 126.70, 126.59, 126.01, 51.81, 43.41, 70.53, 35.23, 35.15.

Chem3D Model to show important overoDIE connections

H4 has 2 large (12.4 Hz) and 2 small couplings, that suggest it is in the axial position in ring. The coupling constant between H5ax and H4 and H5 are both large (>15 Hz) this supports the fact that both of the H are in the axial position and so cis to eachother.
| Atom | Chemical Shift | J | COSY | HSQC | HMBC | NOESY |
|------|----------------|----|------|------|------|-------|
| C    | 211.596        |    | 2, 3, seq, Saa, seq, 6, 7, 7' |    |      |       |
| C    | 41.777         | 2  | 3ax, 3eq, 4 |    |      |       |
| C    | 35.147         |    | 1, 3, 4, 6, 4, 6 |    |      |       |
| H2   | 2.564          | 3ax, 3eq | 2 | 4 | 4, 6 |       |
| C    | 35.147         | 3ax, 3eq | 2 | 4 | 4, 6 |       |
| Hax  | 1.555          | 12.40(4) | 2, 4 | 3 | 2, 4, 5, 12, 5ax, 13 |       |
| Heq  | 2.237          | 3.50(4) | 2, 4 | 3 | 1, 2, 4, 5, 12 | 4 |
| C    | 43.418         |    | 2, 3ax, seq, 5ax, 13, 13' |    | 6, 7, 7' |       |
| H    | 3.030          | 12.40(5ax), 3.50(3eq), 3.50(5eq), 12.40(3ax) | 4 | 2, 3, 5, 6, 12, 13, 13', 2, 3eq, 5ax, 6, 13 |    |      |       |
| C    | 40.535         |    | 3ax, 3eq, 4, 6, 7, 7' |    |      |       |
| Hax  | 1.643          | 12.40(4), 12.80(6) | 4, 5ax, 6 | 5 | 1, 4, 6, 7, 12 | 3ax, 7, 7', 13 |
| Heq  | 2.194          | 3.50(4) | 4, 5ax, 6 | 5 | 1, 4, 6, 7, 12 | 4, 6 |
| C    | 51.812         |    | 2, 4, 5ax, 7, 7' |    |      |       |
| H    | 2.762          | 12.80(5ax), 4.60(7'), 8.90(7') | 5ax, 7', 7' | 6 | 1, 5, 7, 8 | 2, 4, 5eq, 9, 9' |
| D    | 2.762          | 7', 7' | 5ax, 7', 7' | 6 | 1, 5, 7, 8 | 2, 4, 5eq, 9, 9' |
| H    | 3.322          | 14.10(7'), 4.60(5) | 6, 7' | 7 | 1, 5, 6, 8, 9, 9' | 5ax, 7', 9, 9' |
| H    | 2.419          | 14.10(7'), 8.90(6) | 6, 7' | 7 | 1, 5, 6, 8, 9, 9' | 5ax, 7', 9, 9' |
| C    | 140.112        |    | 6, 7', 10, 10' |    |      |       |
| C    | 129.131        |    | 9, 7', 9', 11 |    |      |       |
| H    | 7.150          |    | 9, 7', 9', 6, 7', 7' |    |      |       |
$^1$H-$^1$H NOESY
(2S,4S)-2-benzyl-4-phenylcyclohexan-1-one

The data from H, $^{13}$C and 2D-correlations supports the following structure:

**User Report**

**ZBH**

**ZB-324-02**

**EFLA**

**F0174**

**Client:** Dr. Hui Zhou

**Group:** LT

**Specrometer:** AV600

**Probes:** 5 mm PABBO 1H/13C-ZAB-2 GRD 194780/0004

**Experiment:** 1H zg30, 13C zg30, [13C, 1H]-ASAP_hgcpctempsp, [13C, 1H]-hmbcsp2dndf, [1H, 1H]-noeypsp, [1H, 1H]-dpnypsp.cdf

For full assignment table please see the next page.

Chem3D Model to show important overvDQE connections.

![Chem3D Model](image)

H4 has 2 large (12.4 Hz) and 2 small couplings, that suggest it is dominantly in the axial position in the ring. H5ax has two different coupling constants to H4 (10.3; larger) and H (5.2; small). This indicates that H4 and H5 attach to each other.

**Table**

| Atom | Chemical Shift | J | COSY | HSQC | HMBC | NOESY |
|------|----------------|----|------|------|------|-------|
| 1C   | 213.39        |    |      |      |      |       |
| 2C   | 59.018        |    |      |      |      |       |
| H1H  | 10.305        | 10 | 0    |      |      |       |
| H2H  | 10.305        | 10 | 0    |      |      |       |
| H3H  | 10.305        | 10 | 0    |      |      |       |
| H4H  | 10.305        | 10 | 0    |      |      |       |
| H5H  | 10.305        | 10 | 0    |      |      |       |
| H6H  | 10.305        | 10 | 0    |      |      |       |

**Notes**

- H4 has 2 large (12.4 Hz) and 2 small couplings, that suggest it is dominantly in the axial position in the ring. H5ax has two different coupling constants to H4 (10.3; larger) and H (5.2; small). This indicates that H4 and H5 attach to each other.

**Reference:** solvent

**Temperature:** 298 K
(((3aR,6aS)-5',5'-dimethyl-3,3a,4,6a-tetrahydro-1H-spiropentalene-2,2'[1,3]dioxan]-5-yl)oxy)trimethylsilane 3w:
(S)-tert-butyl(4-isopropylcyclohex-1-en-1-yl)oxy)dimethylsilane 3x:
(S)-tert-butyldimethyl((4-ethylcyclohex-1-en-1-yl)oxy)silane 3y:
(S)-tert-butyldimethyl(4-methylcyclohex-1-en-1-yl)oxy)silane 3z:
(S)-tert-butyldimethyl(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)silane 3aa:
(S)-[(1,1'-bi(cyclohexan)]-2-en-2-yloxy)(tert-butyl)dimethylsilane 3ab:
(S)-tert-butyldimethyl((4-methylcyclohex-1-en-1-yl)oxy)silane 3ac
From the crude NMR, the remained product 3ac was a mixture of regiomers, the r.r. = 18:1:

**tert-butyldimethylsilyl [1,1'-biphenyl]-2-carboxylate**
Spectra for homo aldol product **11-5** (4-(2-oxo-5-phenylcyclohexyl)-1,2,3,6-tetrahydro-1,1’-biphenyl)
LC-MS spectrum of IDPi 4c

HPLC column: 50 mm YMC TriArt Bio C4, 3.0 mm i.D., 0.1% TFA/MeCN 15:85, 1.0 mL/min, 5.0 MPa, 308 K, \( \lambda = 254 \text{ nm} \)

| \( t_R/\text{min} \) | \( \% \) peak area | m/z found       |
|------------------|-------------------|-----------------|
| 5.63             | 98.1              | 2454 ([M-H])    |
| Total            |                   | Total 100       |
LC-MS spectrum of IDPi 4d

| t<sub>r</sub>/min | % peak area | m/z found |
|------------------|-------------|-----------|
| 3.78             | 96.2        | 1950 ([M-H]<sup>-</sup>) |
| Total            |             | 100       |
15. Copies of HPLC and GC traces

HPLC column: OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 224 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 21.1    | 49.99       |
| 2      | 23.6    | 50.01       |
| Total  |         | 100         |

GC column: Rac-3a, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 224 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 21.9    | 3.05        |
| 2      | 24.1    | 96.95       |
| Total  |         | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t R/min | % peak area |
|--------|---------|-------------|
| 1      | 18.0    | 49.91       |
| 2      | 20.2    | 50.09       |
| Total  |         | 100         |

| Peak # | t R/min | % peak area |
|--------|---------|-------------|
| 1      | 18.2    | 2.62        |
| 2      | 20.2    | 97.38       |
| Total  |         | 100         |
HPLC column: AD-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm.

**Peak #** | t<sub>r</sub>/min | % peak area | Peak # | t<sub>r</sub>/min | % peak area | Total | 100
---|---|---|---|---|---|---|---
1 | 14.4 | 49.46 | 2 | 15.1 | 50.54 | **Total** | **100**

**Peak #** | t<sub>r</sub>/min | % peak area | Peak # | t<sub>r</sub>/min | % peak area | Total | 100
---|---|---|---|---|---|---|---
1 | 14.4 | 3.87 | 2 | 15.1 | 96.13 | **Total** | **100**
HPLC column: OJ-3R, Acetonitrile: Water = 65:35, 1.0 mL/min, 298 K, 220 nm.

| Peak # | tR/min | % peak area |
|--------|--------|-------------|
| 1      | 22.7   | 45.91       |
| 2      | 24.0   | 54.09       |
| Total  |        | 100         |

mAU
HPLC column: OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 33.9    | 49.80       |
| 2      | 38.4    | 50.20       |
| Total  |         | 100         |

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 34.3    | 3.96        |
| 2      | 38.0    | 96.04       |
HPLC column: AD-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 237 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 23.3    | 50.44       |
| 2      | 25.4    | 49.56       |
| Total  |         | 100         |

Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 23.3    | 5.76        |
| 2      | 25.2    | 94.24       |
| Total  |         | 100         |
HPLC column: OD-3R, Acetonitrile: Water = 65:35, 1.0 mL/min, 298 K, 220 nm

Peak # | $t_R$/min | % peak area |
---|---|---|
1 | 4.7 | 49.85 |
2 | 5.2 | 50.15 |
Total | | 100 |

Peak # | $t_R$/min | % peak area |
---|---|---|
1 | 4.5 | 96.24 |
2 | 5.2 | 3.76 |
Total | | 100 |
HPLC column: AD-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 29.8    | 50.11       |
| 2      | 33.3    | 49.89       |
| Total  |         | 100         |

mAU

mAU
HPLC column: OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 244 nm.

| Peak # | t_R/min | % peak area |
|-------|---------|-------------|
| 1     | 22.2    | 49.92       |
| 2     | 24.0    | 50.08       |
| Total |         | 100         |

HPLC column: OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 244 nm.

| Peak # | t_R/min | % peak area |
|-------|---------|-------------|
| 1     | 22.2    | 97.38       |
| 2     | 23.9    | 2.62        |
| Total |         | 100         |
HPLC column: OD-3R, Acetonitrile: Water = 65:35, 1.0 mL/min, 298 K, 220 nm

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 20.0    | 49.40       |
| 2      | 20.9    | 50.60       |
| Total  |         | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm

| Peak # | t_R/min | % peak area |
|-------|---------|-------------|
| 1     | 11.6    | 51.49       |
| 2     | 12.4    | 48.51       |
| Total |         | 100         |

mAU

| Peak # | t_R/min | % peak area |
|-------|---------|-------------|
| 1     | 11.6    | 97.53       |
| 2     | 12.3    | 2.47        |
| Total |         | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 19.5    | 52.80       |
| 2      | 21.1    | 47.20       |
| Total  |         | 100         |

Peak # | t_R/min | % peak area |
--------|---------|-------------|
| 1      | 19.0    | 95.42       |
| 2      | 20.8    | 4.58        |
| Total  |         | 100         |
HPLC column: OD-3R, Acetonitrile: Water = 65:35, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 57.1    | 49.86       |
| 2      | 60.7    | 50.14       |
| Total  |         | 100         |

S149
HPLC column: OJ-3, CO₂/2-Propanol = 90:10, 1.0 mL/min, 323 K, 220 nm.

| Peak # | tᵣ/min | % peak area |
|--------|---------|-------------|
| 1      | 8.1     | 49.87       |
| 2      | 8.6     | 50.13       |
| Total  |         | 100         |
HPLC column: Amycoat RP, Acetonitrile/MeOH/Water = 45:45:10, 1.0 mL/min, 298 K, 220 nm.

Additional Info: Peak(s) manually integrated

| Peak # | $t_R$/min | % peak area |
|--------|-----------|-------------|
| 1      | 4.4       | 49.91       |
| 2      | 5.3       | 50.09       |
| Total  |           | 100         |
HPLC column: OJ-3R, MeOH: Water = 75:25, 1.0 mL/min, 298 K, 214 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 4.5     | 4.11        |
| 2      | 5.3     | 95.89       |
| Total  |         | 100         |

HPLC column: OJ-3R, MeOH: Water = 75:25, 1.0 mL/min, 298 K, 214 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 31.7    | 50.16       |
| 2      | 36.2    | 49.84       |
| Total  |         | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 31.2    | 97.28       |
| 2      | 36.4    | 2.72        |
| Total  |         | 100         |

HPLC column: OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 11.8    | 50.89       |
| 2      | 12.3    | 49.11       |
| Total  |         | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 259 nm.

| Peak # | t_R/min | % peak area |
|-------|---------|-------------|
| 1     | 11.7    | 91.64       |
| 2     | 12.3    | 8.36        |
| Total |         | 100         |

HPLC column: OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 259 nm.

| Peak # | t_R/min | % peak area |
|-------|---------|-------------|
| 1     | 13.1    | 50.13       |
| 2     | 14.1    | 49.87       |
| Total |         | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 12.6    | 8.13        |
| 2      | 13.5    | 91.87       |
| Total  |         | 100         |

mAU
HPLC column: AD-3R, Acetonitrile: Water = 50:50, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 16.4    | 94.25       |
| 2      | 20.5    | 5.75        |
| Total  |         | 100         |

HPLC column: AD-3R, Acetonitrile: Water = 50:50, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 30.8    | 50.09       |
| 2      | 37.5    | 49.91       |
| Total  |         | 100         |
**HPLC column: AD-3R, Acetonitrile: Water = 50:50, 1.0 mL/min, 298 K, 215 nm.**

| Peak # | tR/min | % peak area |
|--------|--------|-------------|
| 1      | 32.4   | 2.07        |
| 2      | 38.5   | 97.93       |
| Total  |        | 100         |

**Peak # | tR/min | % peak area
--------|--------|-------------|
| 1      | 36.8   | 49.75       |
| 2      | 38.8   | 50.25       |
| Total  |        | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t<sub>R</sub>/min | % peak area |
|--------|------------------|-------------|
| 1      | 37.1             | 95.11       |
| 2      | 39.2             | 4.89        |
| Total  |                  | 100         |

HPLC column: OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t<sub>R</sub>/min | % peak area |
|--------|------------------|-------------|
| 1      | 18.6             | 50.54       |
| 2      | 24.5             | 49.46       |
| Total  |                  | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 80:20, 1.0 mL/min, 298 K, 254 nm.

| Peak # | $t_0$/min | % peak area |
|--------|------------|-------------|
| 1      | 18.8       | 11.18       |
| 2      | 24.6       | 88.82       |
| Total  |            | 100         |

HPLC column: OJ-3R, Acetonitrile: Water = 80:20, 1.0 mL/min, 298 K, 254 nm.

| Peak # | $t_0$/min | % peak area |
|--------|------------|-------------|
| 1      | 5.7        | 51.53       |
| 2      | 8.0        | 48.46       |
HPLC column: AD-3, n-heptane/i-PrOH = 99:1, 1.0 mL/min, 298 K, 254 nm.

| Peak # | tR/min | % peak area |
|--------|--------|-------------|
| 1      | 5.6    | 94.94       |
| 2      | 8.1    | 5.06        |
| Total  |        | 100         |

Total 100
| Peak # | $t_r$/min | % peak area |
|-------|-----------|-------------|
| 1     | 5.9       | 7.53        |
| 2     | 9.1       | 7.08        |
| 3     | 15.0      | 43.30       |
| 4     | 18.5      | 42.09       |
| Total |           | 100         |
HPLC column: OJ-3, n-heptane/i-PrOH = 99:1, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 12.1    | 50.08       |
| 2      | 15.9    | 49.92       |
| Total  |         | 100         |

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 12.2    | 4.45        |
| 2      | 15.8    | 95.55       |
| Total  |         | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 60:40, 1.0 mL/min, 298 K, 220 nm.

Peak # | t_R/min | % peak area |
-------|---------|-------------|
1      | 13.6    | 5.13        |
2      | 16.3    | 5.18        |
3      | 20.7    | 1.14        |
4      | 22.9    | 43.40       |
5      | 24.4    | 43.60       |
6      | 25.5    | 1.55        |
Total  |         | 100         

Peak # | t_R/min | % peak area |
-------|---------|-------------|
1      | 13.5    | 0.57        |
2      | 16.2    | 11.92       |
3      | 20.6    | 1.83        |
HPLC column: AD-3, n-heptane/i-PrOH = 99:1, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t<sub>R</sub>/min | % peak area |
|--------|------------------|-------------|
| 1      | 10.3             | 25.51       |
| 2      | 11.2             | 25.04       |
| 3      | 13.6             | 24.90       |
| 4      | 15.0             | 24.55       |
| Total  |                  | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm.

Peak #  | t<sub>R</sub>/min | % peak area
---|---|---
1  | 7.0 | 49.51
2  | 7.6 | 50.49
Total  | 100

Peak #  | t<sub>R</sub>/min | % peak area
---|---|---
1  | 7.1 | 3.31
2  | 7.6 | 96.69
Total  | 100
HPLC column: OJ-3R, Acetonitrile: Water = 70:30, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t<sub>R</sub>/min | % peak area |
|--------|-----------------|-------------|
| 1      | 21.1            | 49.99       |
| 2      | 23.6            | 50.01       |
| Total  |                 | 100         |

mAU

| Peak # | t<sub>R</sub>/min | % peak area |
|--------|-----------------|-------------|
| 1      | 20.2            | 93.87       |
| 2      | 23.7            | 6.13        |
| Total  |                 | 100         |
HPLC column: OJ-3R, MeOH: Water = 80:20, 1.0 mL/min, 298 K, 220 nm.

| Peak # | $t_R$/min | % peak area |
|--------|------------|-------------|
| 1      | 14.2       | 49.81       |
| 2      | 15.5       | 50.19       |
| Total  |            | 100         |

| Peak # | $t_R$/min | % peak area |
|--------|------------|-------------|
| 1      | 14.4       | 3.15        |
| 2      | 15.6       | 96.85       |
| Total  |            | 100         |
The forward asymmetric silylation was conducted with IDPi 4c to afford (R)-3x under standard reaction conditions, and the e.r. of (R)-3x was determined to be 74:26.

Note: because the HPLC traces were acquired at different time, so calibration of racemate needed.
HPLC column: OJ-3R, MeOH: Water = 80:20, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 13.5    | 49.33       |
| 2      | 14.5    | 50.67       |
| Total  |         | 100         |

**Second Chart**

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 13.4    | 2.46        |
| 2      | 14.3    | 97.54       |
| Total  |         | 100         |
HPLC column: OJ-3R, MeOH: Water = 75:25, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 21.7    | 49.73       |
| 2      | 23.5    | 50.27       |
| Total  |         | 100         |

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 21.3    | 8.81        |
| 2      | 23.0    | 91.19       |
| Total  |         | 100         |
HPLC column: AD-3R, Acetonitrile: Water = 50:50, 1.0 mL/min, 298 K, 220 nm.

Note: because the HPLC traces were acquired at different time, so calibration of rac-3t was needed again.
HPLC column: OD-3R, Acetonitrile: Water = 50:50, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 72.7    | 50.06       |
| 2      | 78.7    | 49.94       |
| Total  |         | 100         |

Peak # | t_R/min | % peak area |
--------|---------|-------------|
1       | 72.9    | 99.25       |
2       | 78.3    | 0.75        |
HPLC column: OD-3, n-heptane/i-PrOH = 98:2, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|----------|-------------|
| 1      | 7.3      | 49.99       |
| 2      | 8.1      | 50.01       |
| Total  |          | 100         |

mAU

Peak # | t_R/min | % peak area |
-------|---------|-------------|
1       | 7.1     | 17.45       |
2       | 7.8     | 82.55       |
Total   |         | 100         |

mAU
HPLC column: OJ-3R, MeOH: Water= 80:20, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 13.4    | 49.17       |
| 2      | 15.2    | 50.83       |
| Total  |         | 100         |

![HPLC Chromatogram](image-url)
GC column: 30.0 m BGB 176, injection temperature: 220 °C, 120 °C, 0.5 bar H₂.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 13.7    | 0.03        |
| 2      | 15.2    | 99.97       |
| Total  |         | 100         |

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 52.3    | 49.99       |
| 2      | 54.4    | 50.01       |
| Total  |         | 100         |
HPLC column: OJ-3R, Acetonitrile: Water = 80:20, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 52.6    | 15.43       |
| 2      | 54.6    | 84.57       |
| Total  |         | 100         |

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 5.9     | 47.63       |
| 2      | 6.3     | 52.37       |
| Total  |         | 100         |
HPLC column: AS-3, n-heptane/i-PrOH = 99:1, 1.0 mL/min, 298 K, 220 nm.

| Peak # | tR/min | % peak area |
|--------|--------|-------------|
| 1      | 6.0    | 94.78       |
| 2      | 6.3    | 5.22        |
| Total  |        | 100         |

HPLC column: AS-3, n-heptane/i-PrOH = 99:1, 1.0 mL/min, 298 K, 220 nm.

| Peak # | tR/min | % peak area |
|--------|--------|-------------|
| 1      | 18.7   | 50.17       |
| 2      | 21.3   | 49.83       |
| Total  |        | 100         |
Enantiomers of 1aa was made by prep LC. And the HPLC showed below:

HPLC column: IB-3, n-heptane/i-PrOH = 98:2, 1.0 mL/min, 308 K, 210 nm.

| Peak # | tR/min | % peak area |
|--------|--------|-------------|
| 1      | 18.6   | 15.44       |
| 2      | 21.2   | 84.56       |
| Total  |        | 100         |
| Peak # | t_r/min | % peak area |
|--------|---------|-------------|
| 1      | 4.8     | 50.28       |
| 2      | 5.2     | 49.72       |
| Total  |         | 100         |

For (S)-1aa:

| Peak # | t_r/min | % peak area |
|--------|---------|-------------|
| 1      | 4.8     | 100         |
Starting material of regiomer of racemic 3ac was separated by prep LC. And the HPLC traces are given below:

HPLC column: 3-Amycoat RP, Acetonitrile: Water = 75:25, 1.0 mL/min, 298 K, 220 nm.

| Peak # | t_R/min | % peak area |
|--------|---------|-------------|
| 1      | 4.8     | 2           |
| 2      | 5.2     | 98          |
| Total  |         | 100         |
### Table 1: Peak #, t<sub>r</sub>/min, and % peak area

| Peak # | t<sub>r</sub>/min | % peak area |
|--------|-----------------|-------------|
| 1      | 2.8             | 6.45        |
| 2      | 3.6             | 31.77       |
| 3      | 4.0             | 61.78       |
| Total  |                 | 100         |

### Table 2: Peak #, t<sub>r</sub>/min, and % peak area

| Peak # | t<sub>r</sub>/min | % peak area |
|--------|-----------------|-------------|
| 1      | 3.8             | 1.24        |
| 2      | 4.2             | 98.76       |
| Total  |                 | 100         |

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OTBS

rac-3ac

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