Highly enantioselective Hiyama cross-coupling reactions have been achieved through rhodium(I)-catalyzed dynamic kinetic asymmetric transformations between aryl siloxanes and racemic allyl halides. This process affords valuable enantiomerically enriched allyl arenes and is compatible with heterocyclic allyl chloride electrophiles.
Highly Enantioselective Hiyama Cross-Coupling via Rh-Catalyzed Allylic Arylation of Racemic Allyl Chlorides

Jesús González, Philipp Schäfer and Stephen P. Fletcher

Abstract: Highly enantioselective Hiyama cross-coupling reactions have been achieved through rhodium(I)-catalyzed dynamic kinetic asymmetric transformations between aryl siloxanes and racemic allyl halides. This process affords valuable enantiomerically enriched allyl arenes and is compatible with heterocyclic allyl chloride electrophiles.

Cross-coupling reactions occupy a privileged place among the tools to assemble carbon-based frameworks and Suzuki, Negishi, Heck and related reactions are established routine procedures. In general, the development of C–C bond forming cross-coupling reactions has mainly focused on the construction of Csp²–Csp² bonds, while the formation of Csp³–Csp³ bonds is more elusive.

Hiyama cross-coupling procedures have been gaining in popularity as the use of organosilicon coupling partners is attractive. Non-toxicity, stability and ease of handling are features that promise to make organosilanes useful in an array of synthetic applications. Moreover, along with studies of their reactivity and applications, novel approaches for the preparation of organosilanes is an area of active research.

In the context of asymmetric transformations, most processes involving organosilanes are Hosomi-Sakurai-type allylation reactions. Oi and Inoue have reported Rh-catalyzed asymmetric 1,4-addition of siloxanes to α,β-unsaturated compounds (Scheme 1a). In cross-coupling processes enantiospecific Hiyama couplings have been reported. However, to the best of our knowledge, only one example of enantioselective Hiyama-type coupling has been reported. In that work, Fu and coworkers developed a Ni-catalyzed coupling between α-bromosteres and allyl- or vinylsiloxanes to prepare highly enantioenriched α-functionalized esters (Scheme 1b). Within our research group we became interested in the development of new dynamic kinetic asymmetric transformations (DYKATS), and have reported Rh-catalyzed Suzuki-Miyaura type procedures where boronic acids are coupled to racemic cyclic allyl halides. In this work we extend catalytic asymmetric Csp²–Csp³ bond forming cross-coupling procedures to Hiyama-type process, employing arylsilanes as coupling partners (Scheme 1c). These reactions use racemic allyl halides as starting materials and appear to induce enantioselectivity through a DYKAT type mechanism.

Scheme 1. Enantioselective transformations with organosilanes

We first evaluated racemic 3-chlorocyclohex-1-ene 1a in combination with typical silicon based coupling partners that have been previously used in other Hiyama couplings (Table 1). In these initial studies we used the cationic rhodium(I) complex [Rh(COD)(MeCN)₂][BF₄] (5 mol%) and (S)-BINAP (6 mol%) as the ligand in THF at 60 °C. Under these conditions the Hiyama-Denmark protocol involving a silanol and a bulky base did not give rise to desired product (entry 1). The use of trisiloxane was also unsuccessful (entries 2 and 3) but fortunately we found that phenyl triethoxysilane in combination with TBAF afforded the desired product in low yield but good enantioselectivity (entry 4). The use of trisiloxane was also unsuccessful (entries 2 and 3) but fortunately we found that phenyl triethoxysilane in combination with TBAF afforded the desired product in low yield but good enantioselectivity (entry 4).

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were tested. However, none of them proved superior to the yield (entry 6). Carrying out the reaction in 1,4 ratio up to 1:1.5. Thus, 7.5 mol% of (able to slightly improve the yield by increasing the metal/ligand was tested, no trace of enantioselectivity (entries 3 and 4). When diene diminised yields, although maintaining complete whereas the employment of other bisphosphine ligands led to Using SEGP

TBAF (2 equiv.) gave 3a in 55% yield with 99% ee (entry 1).

\[
\text{[Rh(COD)(MeCN)]BF}_4 \quad \text{[Rh(COD)(MeCN)]BF}_4 \quad \text{[Rh(COD)(MeCN)]BF}_4
\]

HOS as ligand afforded similar results (entry 2),

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

- BINAP (6 mol%), Additive (2 equiv.)

Additive (2 equiv.), 2 equiv. siloxane in THF heated to reflux} we explored the scope of this transformation. Pleasingly, we found that the enantioselective Rh(I)-catalyzed Hiyama cross-coupling with racemic allyl chlorides could be accomplished with several aryl siloxanes (Scheme 2). Different aromatic motifs such as naphthyl or biphenyl are also compatible, giving rise to the corresponding products 3b-c in moderate yields and excellent enantioselectivity. Para- and meta- alkyl substituted arenes were tolerated, providing 3d-f with similar results in terms of both yield and enantioselectivity. In contrast, the use of an ortho-methyl substituted substrate only afforded traces of the desired product (not shown, <5% yield). A para-methoxy group slightly diminished the yield, although maintaining great enantioselectivity (98%) (3g). A similar effect was observed for the thioanisole derivative, leading to 34% yield and 95% ee (3h).

However, with a methoxy group in the meta position, the desired product can be obtained in 51% yield and 96% ee (3i). Further, a 1,3-dioxole moiety can be used to prepare 3j with high

| Entry | [Si] | Additive | Yield % (%ee) |
|-------|------|----------|---------------|
| 1     | Si(Me)$_2$OH | TMSOK     | -             |
| 2*    | Si(OTMS)$_2$Me | TBAF    | -             |
| 3*    | Si(OTMS)$_2$Me | TMSOK     | -             |
| 4     | Si(OEt)$_3$ | TBAF | 25 (92) |
| 5     | Si(OH)$_3$ | TBAF | 45 (99) |
| 6*    | Si(OH)$_3$ | TBAF | 55 (99) |
| 7*    | Si(OH)$_3$:Ph | TBAF | 21 (99) |
| 8*    | Si(OH)$_3$ | - | - |
| 9     | Si(OH)$_3$ | CsF | - |
| 10    | Si(OH)$_3$ | AgF | - |

Table 1. Organosilane screening for the Rh-catalyzed allylic arylation.

We then proceeded to further optimize the conditions with the aim of improving the reaction yield (Table 2). As above, heating the reaction mixture to reflux in THF in the presence of [Rh(COD)(MeCN)]$_2$BF$_4$ (5 mol%), (S)-BINAP (6 mol%) and TBAF (2 equiv.) gave 3a in 55% yield with 99% ee (entry 1).

Using SEGPhos as ligand afforded similar results (entry 2), whereas the employment of other bisphosphine ligands led to diminished yields, although maintaining complete enantioselectivity (entries 3 and 4). When diene-type ligand L3 was tested, no trace of 3a was detected (entry 5). We were able to slightly improve the yield by increasing the metal/ligand ratio up to 1:1.5. Thus, 7.5 mol% of (S)-BINAP gave 3a in 65% yield (entry 6). Carrying out the reaction in 1,4-dioxane at 90 °C resulted in 11% yield (entry 7). Finally, other Rh(I) complexes were tested. However, none of them proved superior to the tetrafluoroborate salt (entries 8-11).

Table 2. Effect of varying reaction conditions in the enantioselective cross-coupling of 1a and 2a.

| Entry | [Rh] | Ligand | Yield % (%ee) |
|-------|------|--------|---------------|
| 1     | [Rh(COD)(MeCN)]$_2$BF$_4$ | (S)-BINAP | 55 (99) |
| 2     | [Rh(COD)(MeCN)]$_2$BF$_4$ | (R)-SEGPHOS | 56 (-99) |
| 3     | [Rh(COD)(MeCN)]$_2$BF$_4$ | L1 | 17 (99) |
| 4     | [Rh(COD)(MeCN)]$_2$BF$_4$ | L2 | 45 (99) |
| 5     | [Rh(COD)(MeCN)]$_2$BF$_4$ | L3 | - |
| 6*    | [Rh(COD)(MeCN)]$_2$BF$_4$ | (S)-BINAP | 65 (99) |
| 7*    | [Rh(COD)(MeCN)]$_2$BF$_4$ | (S)-BINAP | 14 (99) |
| 8*    | [Rh(COD)(OH)$_2$] | (S)-BINAP | 34 (90) |
| 9*    | [Rh(COD)Cl]$_2$ | (S)-BINAP | 34 (84) |
| 10*   | [Rh(COD)Cl]$_2$ | (S)-BINAP | 25 (95) |
| 11*   | [Rh(COD)Cl]$_2$ | (S)-BINAP | 13 (99) |

Isolated yields after purification by chromatographic column. Enantioselectivity determined by HPLC. * 1 equivalent of organosilane and 3 equivalents of additive were used. ** Reaction carried out at reflux. *** Reaction carried out with 7.5 mol% of ligand. + Reaction carried out in 1,4-dioxane/H$_2$O at 90 °C.

Using the reaction conditions described in entry 6, Table 2 ([Rh(COD)(MeCN)]$_2$BF$_4$ (5 mol%), S-BINAP (7.5 mol%), TBAF (2 equiv.), 2 equiv. siloxane in THF heated to reflux) we explored the scope of this transformation. Pleasingly, we found that the enantioselective Rh(I)-catalyzed Hiyama cross-coupling with racemic allyl chlorides could be accomplished with several aryl siloxanes (Scheme 2). Different aromatic motifs such as naphthyl or biphenyl are also compatible, giving rise to the corresponding products 3b-c in moderate yields and excellent enantioselectivity. Para- and meta- alkyl substituted arenes were tolerated, providing 3d-f with similar results in terms of both yield and enantioselectivity. In contrast, the use of an ortho-methyl substituted substrate only afforded traces of the desired product (not shown, <5% yield). A para-methoxy group slightly diminished the yield, although maintaining great enantioselectivity (98%) (3g). A similar effect was observed for the thioanisole derivative, leading to 34% yield and 95% ee (3h). However, with a methoxy group in the meta position, the desired product can be obtained in 51% yield and 96% ee (3i). Further, a 1,3-dioxole moiety can be used to prepare 3j with high
enantioselectivity (99% ee). In addition, halogen-substituted aryl siloxanes were suitable coupling partners, affording the products 3k–n with near complete enantioselectivity (97–99% ee).

Regarding heteroaryl siloxanes, commercially available triethoxy(thiophen-2-yl)silane was tested under these reaction conditions but no product was detected. Additionally, some vinyl siloxanes were also tried and only traces of product were observed in some cases.

Despite the promise of organosilicon coupling partners in synthesis, a limitation of this method is that there are currently few general robust procedures for the synthesis of aryl-tri- methoxysilanes, preventing the use of more elaborately functionalized silane coupling partners. However, we anticipate that if such aryl species were available, many of them would be tolerated in this reaction and hope researchers in the field will develop methods to prepare such silanes.

Next, we examined if this protocol is applicable to heterocyclic allyl chloride coupling partners (Scheme 3). Using 3-chloro-3,6-dihydro-2H-pyran 1b with the conditions described above allowed us to prepare compound 3m with high enantioselectivity (98%), albeit with only 34% yield. The synthesis of piperidine derivatives holds a significant importance within chemistry as it is present in numerous natural alkaloids, pharmaceuticals and various synthetic substances with important properties.15 Therefore, we decided to apply this asymmetric Hiyama cross-coupling in the synthesis of enantioenriched dihydroperipin derivatives using racemic N-Boc protected allyl chloride 1c in combination with different arylsiloxanes. We were pleased to find that this process gave rise to compounds 3n–q with high levels of enantiomeric excess.

Scheme 2. Rhodium-catalyzed enantioselective synthesis of tetrahydrobiphenyls 3a–e. Reactions conditions: 1a (0.4 mmol), 2 (2 equiv.), TBAF (2 equiv.), [Rh(cod)(MeCN)2][BF4] (5 mol%), (S)-BINAP (7.5 mol%), THF (0.2 M) at reflux. Yields correspond to isolated products. Enantioselectivity was determined by HPLC or SFC. [a] Contains minor impurities inseparable by flash column chromatography.

![Scheme 2](image)

Scheme 3. Rhodium-catalyzed enantioselective Hiyama coupling with heterocyclic racemic chlorides. Reactions conditions: 1 (0.4 mmol), 2 (2 equiv.), TBAF (2 equiv.), [Rh(cod)(MeCN)2][BF4] (5 mol%), (S)-BINAP (7.5 mol%), THF (0.2 M) at reflux. Yields correspond to isolated products. Enantioselectivity was determined by HPLC or SFC.

![Scheme 3](image)

Regarding the reaction mechanism, we tentatively hypothesize the catalytic cycle operates as outlined in Scheme 4. In contrast to our work with boronic acid nucleophiles13c the use of a cationic Rh source with a BF4- counterion gave the best results. We suggest that initial activation of silicon by fluoride sets the stage for Si to Rh transmetallation. Then, oxidative addition to the allyl chloride likely takes place to provide a Rh(III) species. This intermediate could equilibrate between diastereomeric Rh-allyl species through suprafacial 1,3-isomerization.16 If reductive elimination takes place preferentially in one of the isomers this would lead to the enantioenriched cross-coupling products 3.

Scheme 4. Proposed mechanism.

In summary, we have reported highly enantioselective Rh-catalyzed cross-couplings between arylsiloxanes and racemic cyclic allyl chlorides. This process represents a rare example of asymmetric Hiyama coupling. The method enables the preparation of valuable allyl arenes with uniformly high enantioselectivity (92–99% ee). Important heterocyclic scaffolds are compatible with this transformation, leading to highly enantioenriched dihydropyran and piperidine derivatives. At this stage, it is proposed that diastereoselective 1,3-isomerization between two competing Rh-α-allyl species accounts for enantioselection.
Experimental Section

Representative procedure for the synthesis of 3a: In a 10 mL round bottomed flask [Rh(cod)(MeCN)]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of phenyltrimethoxysilane (173.0 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 m in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then refluxed for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (-)-(S)-cyclohex-2-enylbenzene in 65% yield (39.5 mg, 0.26 mmol) as a colorless oil.

Acknowledgements

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Keywords: Hiyama coupling • DYKAT • Rhodium allyl species

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Highly Enantioselective Hiyama Cross-Coupling via Rh-Catalyzed Allylic Arylation of Racemic Allyl Chlorides

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Supporting Information
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General Information

Procedures using oxygen- and/or moisture-sensitive materials were performed with anhydrous solvents (vide infra) under an atmosphere of anhydrous argon in flame-dried flasks, using standard Schlenk techniques. Analytical thin-layer chromatography was performed on precoated glass-backed plates (Silica Gel 60 F254; Merck) and visualised using a combination of UV light (254 nm) and aqueous ceric ammonium molybdate (CAM) or aqueous basic potassium permanganate stains. Flash column chromatography was carried out using Apollo Scientific silica gel 60 (0.040 – 0.063 nm), Merck 60 Å silica gel, VWR (40-63 μm) silica gel and Sigma Aldrich silica gel. Pressure was applied at the column head via a flow of nitrogen with the solvent system used in parentheses.

Unless stated otherwise, solution NMR spectra were recorded at room temperature; $^1$H and $^{13}$C NMR experiments were carried out using Bruker AVG-400 (400/100 MHz), AVH-400 (400/100 MHz), AVB-400 (400/100 MHz) or AVC-500 (500/125 MHz) spectrometers. Chemical shifts are reported in ppm from the residual solvent peak. Chemical shifts (δ) are given in ppm and coupling constants (J) are quoted in hertz (Hz). Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet).

Chiral HPLC separations were achieved using an Agilent 1230 Infinity series normal phase HPLC unit and HP Chemstation software. Chiralpak® columns (250 × 4.6 mm), fitted with matching Chiralpak® Guard Cartridges (10 × 4 mm), were used as specified in the text. Solvents used were of HPLC grade (Fisher Scientific, Sigma Aldrich or Rathburn); all eluent systems were isocratic.

Chiral SFC (supercritical fluid chromatography) separations were conducted on a Waters Acquity UPC² system using Waters Empower software. Chiralpak® columns (150 × 3 mm, particle size 3 μm) were used as specified in the text. Solvents used were of HPLC grade (Fisher Scientific, Sigma Aldrich or Rathburn).

Low-resolution mass spectra were recorded using a Walters LCT premier XE. High Resolution Mass spectra were carried out by internal service at the university of Oxford. (1) Electron spray ionisation (ESI+) were recorded on a Fisons Platform II. (2) Electron ionisation (EI)/Chemical ionisation (CI): Analyses were performed on an Agilent 7200 quadrupole time of flight (Q-ToF) instrument equipped with a direct insertion probe supplied by Scientific instrument Manufacturer (SIM) GmbH. Instrument control and data processing were performed using Agilent MassHunter software. The system was calibrated on the day of the analysis and its mass accuracy with external calibration (as used for these experiments) is better than 5ppm for 24 hours following calibration. Source conditions for both EI and CI were adjusted to maximise sensitivity, the reagent gas used in CI was either methane or ammonia (and should be apparent in the metadata associated with the data). (3) Atmospheric pressure chemical ionisation (APCI+): Analyses were performed using a Thermo Exactive mass spectrometer equipped with Waters Acquity liquid chromatography system. Instrument control and data processing were performed using Thermo Xcalibur Software. The system was calibrated on the day of the analysis and its mass accuracy with external calibration (as used for these experiments) is better than 5ppm for 24 hours following calibration. The mass spect was operated using the APCI probe and resolution was set to 50,000. APCI source conditions were adjusted to maximise sensitivity. A mixture of 10% water, 89.9% methanol and 0.1% formic acid was used to transport samples to the mass spectrometer at a flow rate of 0.2 mL/min.

Infrared measurements (neat, thin film) were carried out using a Bruker Tensor 27 FT-IR with internal calibration in the range 600-4000 cm⁻¹.
Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 20 °C in a 10 cm cell in the stated solvent; [α]D values are given in 10–1 deg.cm2 g–1 (concentration c given as g/100 mL).

**General chemicals**

Dry THF and 1,4-dioxane were collected fresh from an mBraun SPS-800 solvent purification system having been passed through anhydrous alumina columns.

Unless stated otherwise, commercially available reagents were purchased from Sigma-Aldrich, Fisher Scientific, Apollo Scientific, Acros Organics, Strem Chemicals, Alfa Aesar or TCI UK and were used without purification. Deuterated solvents were purchased from Sigma-Aldrich.

The cyclic allylic chlorides 1a-c, 3-chlorocyclohex-1-ene (1a), 3-chloro-3,6-dihydro-2H-pyran (1b), N-tert- butoxycarbonyl-5-chloro-3-piperidine (3c) were prepared according to reported methods.

Siloxanes 2a and 2d were purchased from Sigma-Aldrich and Fluorochem respectively and used without further purification. The rest of the siloxanes were prepared from the corresponding organolithium or Grignard reagent, according to the methodology described by DeShong et al.4

![Chemical Structures](image)

**Figure S1.** Starting materials used in this work

**Characterisation data for new siloxanes**

**Trimethoxy(naphthalen-2-yl)silane 2b**

The described procedure4 through the corresponding Grignard reagent (10 mmol) afforded 2b in 51% yield (1.27 g, 5.12 mmol) after Kugelrohr distillation (1 mbar, 210 °C) as a colourless liquid.

**1H-NMR** (400 MHz, CDCl3) δ 3.68 (9 H, s), 7.46 – 7.57 (2 H, m), 7.69 (1 H, d, J = 8.0 Hz), 7.81 – 7.92 (3 H, m), 8.21 (1 H, s); **13C-NMR** (101 MHz, CDCl3) δ 51.1 (3 x CH3), 126.2 (CH), 126.9 (CH), 127.1 (C), 127.5 (CH), 127.9 (CH), 128.6 (CH), 130.3 (CH), 132.9 (C), 134.6 (C), 136.5 (CH); **IR** (ATR) \( \nu_{\text{max}} / \text{cm}^{-1} \) = 2943, 2841, 2361, 1191, 1081, 859, 811, 744, 713; **HRMS** (EI) \( m/z \) calc. for C14H16O3Si [M]: 248.0863, found: 248.0864
3-Tolytrimethoxysilane 2e

The described procedure through the corresponding Grignard reagent (10 mmol) afforded 2e in 38% yield (811 mg, 3.82 mmol) after column chromatography eluted with petrol ether/EtOAc (97:3) as a colourless liquid.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 2.39 (3 H, s), 3.66 (9 H, s), 7.26 – 7.35 (2 H, m), 7.44 – 7.53 (2 H, m); $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ 21.6 (CH$_3$), 51.0 (CH$_3$), 128.1 (CH), 129.3 (CH), 131.6 (CH), 131.9 (C), 135.5 (CH), 137.6 (C); IR (ATR) $\nu_{max}/cm^{-1}$ = 2943, 2841, 1190, 1074, 867, 809, 778, 722, 700, 658 HRMS (EI) $m/z$ calc. for C$_{10}$H$_{16}$O$_3$Si [M]: 212.0863, found: 212.0861.

(3,5-Dimethylphenyl)trimethoxysilane 2f

The described procedure through the corresponding Grignard reagent (10 mmol) afforded 2f in 32% yield (738 mg, 3.26 mmol) after distillation (1 mbar, 120 °C) as a colourless liquid.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 2.35 (6 H, d, $J$ = 0.6 Hz), 3.65 (9 H, s), 7.08 (1 H, m), 7.28 (2 H, s); $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ 21.5 (2 x CH$_3$), 51.0 (3 x CH$_3$), 129.1 (C), 132.5 (2 x CH), 132.58 (CH), 137.52 (2 x C); IR (ATR) $\nu_{max}/cm^{-1}$ = 2944, 2841, 2362, 2337, 1992, 1144, 1085, 872, 810, 696; HRMS (CI) $m/z$ calc. for C$_{11}$H$_{19}$O$_3$Si [M + H]: 227.1098, found: 227.1090.

Benzo[d][1,3]dioxol-5-yltrimethoxysilane 2j

The described procedure through the corresponding Grignard reagent (10 mmol) afforded 2j in 47% yield (1.14 g, 4.74 mmol) after distillation (1 mbar, 180 °C) as a colourless liquid.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.61 (9 H, s), 5.96 (2 H, s), 6.87 (1 H, dd, $J$ = 7.7, 0.5 Hz), 7.08 (1 H, dd, $J$ = 1.1, 0.5 Hz), 7.16 (1 H, dd, $J$ = 7.7, 1.1 Hz); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 50.8 (3 x CH$_3$), 100.7 (CH$_2$), 108.8 (CH), 113.9 (CH), 122.2 (C), 129.4 (CH), 147.5 (C), 149.7 (C); IR (ATR) $\nu_{max}/cm^{-1}$ = 2945, 2842, 2361, 1484, 1420, 1237, 1192, 1073, 1041, 935, 900, 805, 736; HRMS (EI) $m/z$ calc. for C$_{10}$H$_{14}$O$_5$Si [M]: 242.0605, found: 242.0609.

(3-Fluorophenyl)trimethoxysilane 2m

The described procedure through the corresponding Grignard reagent (10 mmol) afforded 2m in 57% yield (1.24 g, 5.74 mmol) after distillation (1 mbar, 120 °C) as a colourless liquid.
\(^{1}\text{H-NMR}\ (400 \text{ MHz, CDCl}_3) \ \delta \ 3.63 \ (8 \ H, \ s), \ 7.13 \ (1 \ H, \ m), \ 7.30 - 7.45 \ (3 \ H, \ m); \ \text{\(^{13}\text{C-NMR}\)} \ (101 \text{ MHz, CDCl}_3) \ \delta \ 51.1 \ (3 \ x \ \text{CH}_3), \ 117.8 \ (\text{CH, d, } J = 20.8 \text{ Hz}), \ 121.3 \ (\text{CH, d, } J = 19.5 \text{ Hz}), \ 130.0 \ (\text{CH, d, } J = 7.1 \text{ Hz}), \ 130.4 \ (\text{CH, d, } J = 3.2 \text{ Hz}), \ 132.5 \ (\text{C, d, } J = 4.8 \text{ Hz}), \ 162.8 \ (\text{C, d, } J = 248.8 \text{ Hz}); \ \text{\(^{19}\text{F-NMR}\)} \ (376 \text{ MHz, CDCl}_3) \ \delta \ -117.66; \ \text{IR} \ (\text{ATR}) \ \nu_{\text{max}} / \text{cm}^{-1} = 2047, \ 2843, \ 2361, \ 2337, \ 1221, \ 1192, \ 1085, \ 817, \ 790, \ 724, \ 692; \ \text{HRMS} \ (\text{APCI}) \ m/z \ \text{calc. for C\textsubscript{9}H\textsubscript{14}O\textsubscript{3}FSi [M+H\textsuperscript{+}]: 217.06908, found: 217.06926.}

\((3\text{-Chlorophenyl})\text{trimethoxysilane 2n}

\[\text{Cl} - \text{Si(OMe)}_3\]

The described procedure\(^d\) through the corresponding Grignard reagent (10 mmol) afforded 2l in 63\% yield (1.46 g, 6.27 mmol) after Kugelrohr distillation (1 mbar, 170 °C) as a colourless liquid.

\(^{1}\text{H-NMR}\ (400 \text{ MHz, CDCl}_3) \ \delta \ 3.63 \ (9 \ H, \ s), \ 7.33 \ (1 \ H, \ ddd, \ J = 7.9, 7.2, 0.6 \text{ Hz}), \ 7.42 \ (1 \ H, \ ddd, \ J = 8.0, 2.2, 1.2 \text{ Hz}), \ 7.51 \ (1 \ H, \ dt, \ J = 7.2, 1.1, 1.1 \text{ Hz}), \ 7.61 \ (1 \ H, \ ddd, \ J = 2.2, 1.0, 0.5 \text{ Hz}); \ \text{\(^{13}\text{C-NMR}\)} \ (101 \text{ MHz, CDCl}_3) \ \delta \ 51.1 \ (3 \ x \ \text{CH}_3), \ 129.7 \ (\text{CH}), \ 130.9 \ (\text{CH}), \ 132.3 \ (\text{C}), \ 132.8 \ (\text{CH}), \ 134.6 \ (\text{C}), \ 134.7 \ (\text{CH}); \ \text{IR} \ (\text{ATR}) \ \nu_{\text{max}} / \text{cm}^{-1} = 2944, \ 2843, \ 1467, \ 1391, \ 1190, \ 1137, \ 1074l, \ 784, \ 693l; \ \text{HRMS} \ (\text{EI}) \ not \ found.
Rh-catalyzed asymmetric synthesis of allyl arenes 3a-s

\[
\begin{align*}
\text{[Rh(cod)(MeCN)_2]BF}_4 (7.6 \text{ mg, 0.02 mmol, 0.05 eq}) & \quad \text{(S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq)} \\
\text{THF, reflux} & \quad \text{3-chlorocyclohex-1-ene (45 \mu L, 0.40 mmol, 1.00 eq)}
\end{align*}
\]

\(-\)-(S)-Cyclohex-2-enylbenzene 3a

In a 10 mL round bottomed flask \([\text{[Rh(cod)(MeCN)_2]BF}_4 (7.6 \text{ mg, 0.02 mmol, 0.05 eq}) \text{ and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq}) \text{ were stirred in THF (0.7 mL) at reflux for 30 min. A solution of phenyltrimethoxysilane (173.0 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 mL in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 \mu L, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain \(-\)-(S)-cyclohex-2-enylbenzene in 65\% yield (39.5 mg, 0.26 mmol) as a colorless oil.}

HPLC analysis indicated an enantiomeric excess of 99\% \([\text{Chiralpak}® \text{ID; flow: 0.6 mL/min; hexane/i-PrOH 99.9:0.1; \lambda = 210 nm; major enantiomer } t_R = 6.7 \text{ min; minor enantiomer } t_R = 7.3 \text{ min}].

\(^1\)H-NMR (400 MHz, CDCl\textsubscript{3}): \delta 1.60 – 1.80 (2H, m), 1.82 (1H, m), 2.06 (1H, m), 2.16 (2H, m), 3.46 (1H, m), 5.79 (1H, m), 5.95 (1H, ddd, J = 9.9, 6.1, 3.4 Hz), 7.25 – 7.29 (3H, m), 7.35 (2H, m).

\(^1\)C-NMR (101 MHz, CDCl\textsubscript{3}): \delta 21.4 (CH\textsubscript{2}), 25.2 (CH\textsubscript{2}), 32.8 (CH\textsubscript{2}), 42.0 (CH), 126.1 (C-4), 127.9 (2 x CH), 128.4 (2 x CH), 128.5 (CH), 130.3 (CH), 146.8 (C). The spectral data are according to those previously reported.\(^5\) \([\alpha]^{25}_{589} = -74.6° \text{ (c 1.0, CHCl}_3)\), \text{ [Lit: } [\alpha]^{20}_{589} = -134.6° \text{ (c 0.55 CHCl}_3) \text{ for 99\% ee}].\(^5\) \text{ HRMS (El/Fl): } m/z \text{ calc. for C}_{12}H_{14}^+ [M]^+ : 158.1094, \text{ found: 158.1096.}

HPLC traces:
(-)-(S)-2-(Cyclohex-2-en-1-yl)naphthalene 3b

In a 10 mL round bottomed flask [Rh(cod)(MeCN)₂]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of trimethoxy(naphthalen-2-yl)silane (198.7 mg, 0.80 mmol, 2.00 eq), tetrabutyl-ammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (-)-(S)-2-(cyclohex-2-en-1-yl)naphthalene in 52% yield (43.4 mg, 0.21 mmol) as a colorless oil.

Enantiomeric excess of 99% was determined by HPLC [Chiralpak® IA; flow: 0.6 mL/min; hexane; λ = 210 nm; minor enantiomer tᵣ = 11.0 min; major enantiomer tᵣ = 11.4 min].

^1H-NMR (400 MHz, CDCl₃) δ 1.60 – 1.72 (2 H, m), 1.78 (1 H, m), 2.04 – 2.17 (3 H, m), 3.57 (1 H, m), 5.81 (1 H, m), 5.96 (1 H, m), 7.37 (1 H, dd, J = 8.5, 1.8 Hz), 7.40 – 7.48 (2 H, m), 7.62 – 7.68 (1 H, m), 7.80 (3 H, m); ^13C-NMR (101 MHz, CDCl₃) δ 21.3 (CH₂), 25.3 (CH₂), 32.6 (CH₂), 42.1 (CH), 125.3 (CH), 125.9 (CH), 126.0 (CH), 126.9 (CH), 127.7 (CH), 127.7 (CH), 128.0 (CH), 128.8 (CH), 130.2 (CH), 132.3 (CH), 133.7 (CH), 144.2 (C). The spectral data are according to those previously reported.^[5] [α]²⁵⁰⁵₈⁹ = −74.5° (c 0.4, CHCl₃). [Lit: [α]²⁰⁵₈⁹ = −221.1° (c 0.91 CHCl₃ for 89% ee)]^⁵; HRMS (El) m/z calc. for C₁₆H₁₆ [M]: 208.1247, found: 208.1239.

HPLC traces:
(-)-(S)-4-(Cyclohex-2-en-1-yl)biphenyl 3c

In a 10 mL round bottomed flask [Rh(cod)(MeCN)₂]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of [1,1'-biphenyl]-4-yltrimethoxysilane (219.5 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 mL in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (-)-(S)-4-(cyclohex-2-en-1-yl)biphenyl in 40% yield (37.5 mg, 0.21 mmol) as a pale yellow solid (m.p.: 46-48 °C). (The NMR spectra contains a small amount of pentane).

Enantiomeric excess of 98% was determined by SFC [Chiralpak® ID-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; \( \lambda = 210 \) nm; major enantiomer \( t_R = 2.9 \) min; minor enantiomer \( t_R = 2.6 \) min].

\(^1\)H NMR (400 MHz, CDCl₃) δ 1.54 – 1.76 (2 H, m), 1.80 (1 H, m), 2.01 – 2.19 (3 H, m), 3.47 (1 H, m), 5.72 – 5.82 (1 H, m), 5.94 (1 H, m), 7.27 – 7.44 (3 H, m), 7.40 – 7.52 (2 H, m), 7.49 – 7.66 (4 H, m). \(^{13}\)C-NMR (101 MHz, CDCl₃) δ 21.22 (CH₂), 25.07 (CH₂), 32.62 (CH₂), 41.54 (CH), 127.02 (CH), 127.07 (4 x CH), 128.19 (2 x CH), 128.52 (CH), 128.72 (2 x CH), 130.09 (CH), 138.98 (C), 141.16 (C), 145.82 (C). \([\alpha]_{D}^{25}\) = −143.9° (c 0.87, CHCl₃); IR (ATR) \( \nu_{\text{max}} /\text{cm}^{-1} \): 3022 (w), 2929 (m), 2856 (s), 2361 (s), 1485 (m), 763 (s), 721 (s); HRMS (CI) m/z calc. for C₁₈H₁₉ [M + H]: 235.1481, found: 235.1474.

SFC traces:
(-)-(S)-3-(4-Methylphenyl)cyclohexene 3d

In a 10 mL round bottomed flask [Rh(cod)(MeCN)$_2$]BF$_4$ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of p-tolytrimethoxysilane (164 µL, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (-)-(S)-3-(4-methylphenyl)cyclohexene in 53% yield (36.8 mg, 0.21 mmol) as a colorless oil.

Enantiomeric excess of 98% was determined by HPLC [Chiralpak® IC; flow: 0.7 mL/min; hexane; λ = 210 nm; major enantiomer $t_R$ = 6.3 min; minor enantiomer $t_R$ = 6.7 min].

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 1.51 – 1.70 (2 H, m), 1.78 (1 H, m), 2.03 (1 H, m), 2.11 (2 H, m), 2.35 (3 H, s), 3.40 (1 H, m), 5.74 (1 H, m), 5.90 (1 H, m), 7.14 (4 H, s); $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ 21.2 (CH$_3$), 21.4 (CH$_2$), 25.2 (CH$_2$), 32.8 (CH$_2$), 41.6 (CH), 127.8 (2 x CH), 128.3 (CH), 129.1 (2 x CH), 130.6 (CH), 135.6 (C-), 143.8 (C). The spectral data are according to those previously reported.$^5$ [$\alpha$]$^{25}$$_{589}$ = $-143.9^\circ$ (c 1.0, CHCl$_3$), [Lit: [$\alpha$]$^{20}$$_{589}$ = $-128.0^\circ$ (c 0.47 CHCl$_3$) for >94% ee]$^5$ HRMS (EI) m/z calc. for C$_{14}$H$_{16}$ [M]: 172.1247, found: 172.1248.

HPLC traces:
(--)(S)-3-(3-Methylphenyl)cyclohexene 3e

In a 10 mL round bottomed flask [Rh(cod)(MeCN)$_2$]BF$_4$ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of 3-tolyltrimethoxysilane (170 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 m in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (--)(S)-3-(3-methylphenyl)cyclohexene in 48% yield (32.9 mg, 0.19 mmol) as a colorless oil.

Enantiomeric excess of 98% was determined by HPLC [Chiralpak® IB; flow: 0.5 mL/min; hexane; λ = 210 nm; minor enantiomer $t_R = 8.9$ min; major enantiomer $t_R = 9.2$ min].

$^{1}$H-NMR (400 MHz, CDCl$_3$) δ 1.56 – 1.74 (2 H, m), 1.83 (1 H, m), 2.06 (1 H, m), 2.11 – 2.20 (2 H, m), 2.41 (3 H, s), 3.43 (1 H, m), 5.80 (1 H, m), 5.95 (1 H, m), 7.05 – 7.14 (3 H, m), 7.21 – 7.28 (1 H, m); $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 21.4 (CH$_2$), 21.6 (CH$_3$), 25.2 (CH$_2$), 32.8 (CH$_2$), 42.0 (CH), 124.9 (CH), 126.9 (CH), 128.3 (CH), 128.6 (CH), 130.48 (CH), 137.9 (C), 146.8 (C). The spectral data are according to those previously reported.$^{5}$ [α]$^{25}_{589} = -73.5^o$ (c 1.0, CHCl$_3$), [Lit: [α]$^{20}_{589} = -117.0^o$ (c 0.96 CHCl$_3$ for 97% ee)];$^{5}$ HRMS (EI) m/z calc. for C$_{14}$H$_{16}$ [M]: 172.1247, found: 172.1250.

HPLC traces:
(-)-(S)-3-(3,5-diMethylphenyl)cyclohexene 3f

In a 10 mL round bottomed flask [Rh(cod)(MeCN)₂]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of (3,5-dimethylphenyl)trimethoxysilane (226.3 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to afford the product in 42% yield (31.3 mg, 0.17 mmol) as a colorless oil.

Enantiomeric excess of >99% was determined by SFC [Chiralpak® ID-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; λ = 210 nm; major enantiomer $t_R = 0.84$ min; minor enantiomer $t_R = 0.96$ min].

$^1$H-NMR (400 MHz, CDCl₃) δ 1.52 – 1.74 (3 H, m), 1.98 – 2.09 (3 H, m), 2.30 (6 H, s), 3.33 (1 H, m), 5.71 (1 H, m), 5.88 (1 H, m), 6.81 – 6.88 (3 H, m). $^{13}$C-NMR (101 MHz, CDCl₃) δ 21.34 (2 x CH₃), 21.39 (CH₂), 25.05 (CH₂), 32.66 (CH₂), 41.81 (CH), 125.56 (CH), 127.66 (CH), 128.08 (CH), 130.50 (CH), 137.75 (CH), 146.67 (C); $[\alpha]^{25}_{D}$ = –25.3° (c 0.2, CHCl₃); IR ν max/cm$^{-1}$: 2926 (m), 2857 (w), 2361 (s), 2338 (m), 1604 (w), 845 (w), 772 (w); HRMS (CI) m/z calc. for C₁₄H₁₉ [M + H]: 187.1481, found: 187.1477.
(−)-(S)-3-(4-Methoxyphenyl)cyclohexene 3g

In a 10 mL round bottomed flask [Rh(cod)(MeCN)₂]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of 4-(trimethoxysilyl)anisole (183.0 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 m in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane/diethyl ether (95:5) to afford the product in 32% yield (24 mg, 0.13 mmol) as a colorless oil.

Enantiomeric excess of 98% was determined by SFC [Chiralpak® ID-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; λ = 210 nm; major enantiomer tᵣ = 1.35 min; minor enantiomer tᵣ = 1.26 min].

¹H-NMR (400 MHz, CDCl₃) δ 1.47 – 1.80 (3 H, m), 1.94 – 2.04 (1 H, m), 2.04 – 2.13 (2 H, m), 3.37 (1 H, m), 3.80 (3 H, s), 5.70 (1 H, m), 5.88 (1 H, m), 6.81 – 6.88 (2 H, m), 7.11 – 7.18 (2 H, m);

¹³C-NMR (101 MHz, CDCl₃) δ 21.3 (CH₂), 25.2 (CH₂), 32.9 (CH₂), 41.1 (CH₂), 55.4 (CH₃), 113.8 (2 x CH), 128.28 (CH), 128.8 (2 x CH), 130.6 (CH), 138.9 (C), 158.0 (C). The spectral data are according to those previously reported.⁵ [α]²⁵₅₈⁹ = −143.5° (c 1.4, CHCl₃), [Lit: [α]²⁰₅₈⁹ = −134.6° (c 1.4 CHCl₃) for 97% ee)].⁵ HRMS (EI) m/z calc. for C₁₃H₁₆O [M]: 188.1196, found: 188.1194.

SFC traces:
In a 10 mL round bottomed flask [Rh(cod)(MeCN)$_2$]BF$_4$ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of 4-(trimethoxysilyl)thioanisole (195.5 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane/diethyl ether (40:1) to obtain (−)-(S)-3-(4-methylthiophenyl)cyclohexene in 34% yield (27.8 mg, 0.14 mmol) as colorless oil.

Enantiomeric excess of 95% was determined by SFC [Chiralpak® IA-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; λ = 210 nm; major enantiomer $t_R = 2.07$ min; minor enantiomer $t_R = 1.95$ min].

$^1$H-NMR (400 MHz CDCl$_3$) δ 1.41 – 1.68 (2 H, m), 1.68 – 1.82 (1 H, m), 1.96 – 2.01 (1 H, m), 2.05-2.11 (2 H, m), 2.47 (3 H, s), 3.37 (1 H, m), 5.64 – 5.72 (1 H, m), 5.89 (1 H, m), 7.15 (2 H, d, $J = 8.3$ Hz), 7.22 (1 H, d, $J = 8.3$ Hz); $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 16.5 (CH$_3$), 21.2 (CH$_2$), 25.1 (CH$_2$), 32.7 (CH$_2$), 41.5 (CH$_2$), 127.2 (2 x CH), 128.4 (2 x CH), 128.7 (CH), 130.1 (CH), 135.6 (C), 144.0 (C).

[α]$^{25}_{	ext{D}}$ = −50.9° (c 0.5, CHCl$_3$), IR $\nu_{\text{max}}$/cm$^{-1}$: 3019 (w), 2925 (s), 2858 (w), 2361 (w), 2338 (m), 1492 (m), 1439 (m), 1095 (w), 817 (m). [HRMS (El) $m/z$ calc. for C$_{13}$H$_{16}$S [M]: 204.0967, found: 204.0971.

SFC traces:
In a 10 mL round bottomed flask [Rh(cod)(MeCN)₂]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-
BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of
3-(trimethoxysilyl)anisole (183 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 mL in THF,
0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL)
was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then
heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was
directly loaded onto a chromatographic column and eluted with pentane to obtain (−)-(S)-3-(3-
methoxyphenyl)cyclohexene in 51% yield as a pale yellow oil.

Enantiomeric excess of 96% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane; λ = 210 nm; major enantiomer tᵣ = 11.2 min; minor enantiomer tᵣ = 16.0 min].

¹H-NMR (400 MHz, CDCl₃) δ 1.52 – 1.81 (3 H, m), 1.96 – 2.13 (3 H m), 3.39 (1 H, m), 3.81 (3 H,
d, J = 3.9 Hz), 5.72 (1 H, m), 5.90 (1 H, m), 6.72 – 6.85 (3 H, m), 7.23 (1 H, t, J = 7.8 Hz); ¹³C-NMR
(101 MHz, CDCl₃) δ 21.34 (CH₂), 25.2 (CH₂), 32.6 (CH₂), 42.0 (CH), 55.3 (CH₃), 111.3 (CH), 113.7
(CH), 120.4 (CH), 128.6 (CH), 129.3 (CH), 130.2 (CH), 148.5 (C), 159.7 (C). The spectral data are
similar to those previously reported for the racemic compound.⁶ [α]²⁵°₅₈₉ = −9.3° (c 0.4, CHCl₃); HRMS
(El) m/z calc. for C₁₃H₁₆[M⁺]: 188.120, found: 188.117.

HPLC traces:
In a 10 mL round bottomed flask [Rh(cod)(MeCN)$_2$]BF$_4$ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of benzo[d][1,3]dioxol-5-yltrimethoxysilane (194 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (–)-(S)-5-(cyclohex-2-en-1-yl)benzo[d][1,3]dioxole in 48% yield (38.8 mg, 0.19 mmol) as a colorless oil.

Enantiomeric excess of 98% was determined by SFC [Chiralpak® IF-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; λ = 210 nm; major enantiomer $t_R = 2.01$ min; minor enantiomer $t_R = 2.20$ min].

$^1$H-NMR (400 MHz, CDCl$_3$) δ 1.44 – 1.68 (3 H, m), 1.73 (1 H, m), 1.97 (1 H, m), 2.07 (2 H, m), 3.33 (1 H, m), 5.67 (1 H, dd, $J = 10.1$, 2.5 Hz), 5.87 (1 H, m), 5.92 (2 H, s), 6.67 (1 H, dd, $J = 7.9$, 1.7 Hz), 6.69 – 6.78 (2 H, m); $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 21.20 (CH$_2$), 25.12 (CH$_2$), 32.92 (CH$_2$), 41.67 (CH), 100.89 (CH$_2$), 108.13 (CH), 108.40 (CH), 120.66 (CH), 128.51 (CH), 130.39 (CH), 140.86 (C), 145.78 (C), 147.61 (C); [α]$_{25}^{D}$ = –180º (c 1.3, CHCl$_3$); IR (ATR) $\nu_{max}$/cm$^{-1}$: 2928 (w), 1503 (m), 1484 (s), 1439 (w), 1247 (m), 1232 (m), 1040 (m); HRMS (APCI) m/z calc. for C$_{13}$H$_{15}$O$_2$ [M+H$^+$]: 203.1067, found: 203.1067.

SFC traces:
(-)-(S)-3-(4-Fluorophenyl)cyclohexene 3k

In a 10 mL round bottomed flask [Rh(cod)(MeCN)₂]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of (4-fluorophenyl)trimethoxysilane (173.0 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (-)-(S)-3-(4-fluorophenyl)cyclohexene in 51% yield (35.6 mg, 0.20 mmol) as a colorless oil.

Enantiomeric excess of 97% was determined by SFC [Chiralpak® IG-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; λ = 210 nm; major enantiomer tᵣ = 1.10 min; minor enantiomer tᵣ = 1.05 min].

¹H-NMR (400 MHz, CDCl₃) δ 1.47 – 1.57 (1 H, m), 1.62 (1 H, m), 1.73 (1 H, m), 2.00 (1 H, m), 2.11 (m, 2 H), 3.40 (1 H, m), 5.68 (1 H, m), 5.90 (1 H, m), 6.98 (2 H, m), 7.18 (2 H, m); ¹³C-NMR (101 MHz, CDCl₃) δ 21.2 (CH₂), 25.1 (CH₂), 32.9 (CH₂), 41.2 (CH), 115.1 (2x CH, d, J = 21.3 Hz), 128.7 (CH), 129.2 (2 x CH, d, J = 7.9 Hz), 130.1 (CH), 142.4 (C, d, J = 3.2 Hz), 161.5 (C, d, J = 243.4 Hz); ¹⁹F-NMR (376 MHz, CDCl₃) δ −117.66. The spectral data are according to those previously reported.⁵ [α]₂⁰ sub = −108° (c 1.0, CHCl₃), [Lit: [α]₂⁰ sub = −112° (c 1.09 CHCl₃) for 99% ee]⁵; HRMS (EI) m/z calc. for C₁₂H₁₃F [M]: 176.0996, found: 176.1001.

SFC traces:
In a 10 mL round bottomed flask [Rh(cod)(MeCN)₂]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of (4-bromophenyl)trimethoxysilane (189.7 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (−)-(S)-3-(4-bromophenyl)cyclohexene in 34% yield (32.3 mg, 0.14 mmol) as a colorless oil.

Enantiomeric excess of 99% was determined by SFC [Chiralpak® IG-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; λ = 210 nm; major enantiomer tᵣ = 2.20 min; minor enantiomer tᵣ =1.94 min].

¹H-NMR (400 MHz, CDCl₃) δ 1.46 – 1.66 (2 H, m), 1.69 – 1.74 (1 H, m), 1.98 (1 H, m), 2.08 (m, 2 H), 3.36 (1 H, m), 5.66 (1 H, m), 5.90 (1 H, m), 7.09 (2 H, d, J = 8.4 Hz), 7.41 (2 H, d, J = 8.4 Hz);

¹³C-NMR (101 MHz, CDCl₃) δ 21.1 (CH₂), 25.1 (CH₂), 32.7 (CH₂), 41.4 (CH), 119.8 (C), 129.0 (CH), 129.6 (CH), 129.7 (2x CH), 131.4 (2x CH), 145.8 (C); [α]²⁰⁵₈³ = –144.6° (c 1.4, CHCl₃); IR (ATR) νmax /cm⁻¹: 3020 (w), 2929 (s), 2857 (w), 2361 (w), 1503 (m), 1487 (s), 1011 (m), 819 (s); HRMS (EI) m/z calc. for C₁₂H₁₃Br [M]: 236.0195, found: 236.0190.

**SFC traces:**
\(-\)-(S)-3-(3-Fluorophenyl)cyclohexene 3m

\[
\text{\begin{tikzpicture}[scale=0.8]
  \node[anchor=west] {\includegraphics[width=0.2\textwidth]{image}};
\end{tikzpicture}}
\]

In a 10 mL round bottomed flask \([\text{Rh(cod)(MeCN)}_2]BF_4\) (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of (3-fluorophenyl)trimethoxysilane (173.0 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain \(-\)-(S)-3-(3-fluorophenyl)cyclohexene in 55% yield (38.8 mg, 0.20 mmol) as a colorless oil.

Enantiomeric excess of >99% was determined by SFC [Chiralpak® ID-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; \(\lambda = 210\) nm; major enantiomer \(t_R = 0.83\) min; minor enantiomer \(t_R = 0.93\) min].

\textbf{\(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\):} 1.45 – 1.68 (2 H, m), 1.73 (1 H, m), 2.01 (1 H, m), 2.09 (2 H, m), 3.41 (1 H, m), 5.69 (1 H, m), 5.91 (1 H, m), 6.84 – 6.97 (2 H, m), 7.00 (1 H, dd, \(J = 7.7, 1.4\) Hz), 7.25 (1 H, m); \textbf{\(^{13}\text{C-NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\):} 21.1 (CH\(_2\)), 25.1 (CH\(_2\)), 32.5 (CH\(_2\)), 41.7 (CH), 112.9 (CH, d, \(J = 20.8\) Hz), 114.7 (CH, d, \(J = 21.4\) Hz), 123.5 (CH, d, \(J = 2.7\) Hz), 129.0 (CH), 129.6 (CH), 129.7 (CH, d, \(J = 8.2\) Hz), 149.5 (C, d, \(J = 6.7\) Hz), 163.0 (C, d, \(J = 245.8\) Hz); \textbf{\(^{19}\text{F-NMR}\) (376 MHz, CDCl\(_3\)) \(\delta\):} –113.84; \([\alpha]_{2589}^{20} = \text{–124° (c 1.1, CHCl\(_3\))}; \text{\(\text{IR (ATR)} \nu_{max} /\text{cm}^{-1}:\) } 2931 (m), 1614 (m), 1589 (s), 1485 (m), 1446 (m), 783 (s); \textbf{\(\text{HRMS (CI)}\) m/z calc. for C\(_{12}\)H\(_{14}\)F [M + H]}: 177.1074, found: 177.1067.

\textbf{SFC traces:}
(−)-(S)-3-(3-Chlorophenyl)cyclohexene 3n

In a 10 mL round bottomed flask [Rh(cod)(MeCN)₂]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of (3-chlorophenyl)trimethoxysilane (186.2 mg, 0.80 mmol, 2.00 eq), tetrabutyl-ammonium fluoride (1 m in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chlorocyclohex-1-ene (45 µL, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (−)-(S)-3-(3-chlorophenyl)cyclohexene in 54% yield (41.8 mg, 0.22 mmol) as a colorless oil.

Enantiomeric excess of 99% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane; λ = 210 nm; major enantiomer \( t_R = 4.6 \) min; major enantiomer \( t_R = 6.9 \) min].

\(^1\)H-NMR (400 MHz, CDCl₃) δ 1.49 – 1.59 (1 H, m), 1.59 – 1.68 (1 H, m), 1.69 – 1.79 (1 H, m), 1.97 – 2.06 (1 H, m), 2.06 – 2.14 (2 H, m), 3.38 (1 H, m), 5.69 (1 H, m), 5.93 (1 H, m), 7.11 (1 H, dt, \( J = 7.6, 1.5, 1.5 \) Hz), 7.15 – 7.27 (3 H, m); \(^{13}\)C-NMR (101 MHz, CDCl₃) δ 21.1 (CH₂), 25.1 (CH₂), 32.6 (CH₂), 41.7 (CH), 126.1 (CH), 126.3 (CH), 128.0 (CH), 129.1 (CH), 129.4 (CH), 129.6 (CH), 134.2 (C), 148.9 (C). The spectral data are according to those previously reported.\(^5\) \([\alpha]^{20}_{589} = −131° \) (c 1.00, CHCl₃), [Lit: \([\alpha]^{20}_{589} = −132° \) (c 1.18 CHCl₃) for 99% ee\(^5\)]; HRMS (El/FI) m/z calc. for C₁₂H₁₅Cl [M]+: 192.0706, found: 192.0708.

HPLC traces:
(-)-(S)-5-(3,6-dihydro-2H-pyran-3-yl)benzo[d][1,3]dioxole 3o

In a 10 mL round bottomed flask [Rh(cod)(MeCN)$_2$]BF$_4$ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of benzo[d][1,3]dioxol-5-yltrimethoxysilane (194 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and 3-chloro-3,6-dihydro-2H-pyran (47.4 mg, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux for 3 h. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (-)-(S)-5-(3,6-dihydro-2H-pyran-3-yl)benzo[d][1,3]dioxole in 34% yield (27.8 mg, 0.14 mmol) as a colorless oil.

Enantiomeric excess of 98% was determined by SFC [Chiralpak® IA-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; $\lambda$ = 210 nm; major enantiomer $t_R$ = 1.86 min; minor enantiomer $t_R$ = 2.06 min].

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.5 (1 H, m), 3.5 (1 H, dd, $J$ = 10.9, 6.9 Hz), 4.0 (1 H, ddd, $J$ = 10.9, 4.9, 0.6 Hz), 4.2 (2 H, m), 5.8 – 6.0 (4 H, m, signals overlapped), 6.7 (1 H, dd, $J$ = 8, 1.8 Hz), 6.7 – 6.8 (2 H, m); $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ 41.2 (CH), 65.5 (CH$_2$), 71.4 (CH$_2$), 101.1 (CH$_2$), 108.4 (CH), 108.6 (CH), 121.2 (CH), 127.1 (CH), 128.1 (CH), 136.0 (C), 146.5 (C), 147.9 (C); [α]$^{25}$$_{sS}$ = $-$55.5° (c 0.5, CHCl$_3$); IR (ATR) $\nu_{max}$/cm$^{-1}$: 2981 (m), 2886 (w), 1503 (m), 1486 (s), 1441 (w), 1248 (m), 1232 (m), 1038 (m); HRMS (APCI): m/z calc. for C$_{12}$H$_{13}$O$_3$ [M+H$^+$]: 205.0859, found: 205.0860.

SFC traces:
(--)-tert-butyl (S)-3-phenyl-3,6-dihydropyridine-1(2H)-carboxylate 3p

In a 10 mL round bottomed flask [Rh(cod)(MeCN)₂]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of phenyltrimethoxysilane (173.0 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 m in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and tert-butyl 3-chloro-3,6-dihydropyridine-1(2H)-carboxylate (87.1 mg, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux overnight. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (--)-tert-butyl (S)-3-phenyl-3,6-dihydropyridine-1(2H)-carboxylate in 42% yield (43.6 mg, 0.17 mmol) as a yellow oil.

Enantiomeric excess of 95% was determined by HPLC [Chiralpak® IA; flow: 1.0 mL/min; hexane/i-PrOH: 99.4: 0.6; λ = 210 nm; major enantiomer t_R = 5.7 min; major enantiomer t_R = 6.1 min].

¹H-NMR (400 MHz, CDCl₃) δ 1.19 – 1.63 (9 H, m), 3.01, 3.33 – 3.46, 3.70 – 3.79 and 4.07 (2 H, rotameric, m), 3.46 – 3.62 (m, 1H), 3.82 and 4.07 (2 H, rotameric, m), 5.89 (br s, 2H), 7.19 – 7.27 (m, 3H), 7.31 (m, 2H); ¹³C-NMR (101 MHz, CDCl₃) δ 28.3 (3 x CH₃), 41.5, 42.9 and 43.6 (rotameric, 1C), 47.3 and 48.5 (rotameric, 1C), 79.5 (C), 125.9 (CH), 126.7 (CH), 127.9 (2 x CH), 128.2 (CH), 128.5 (2 x CH), 142.2 (C), 154.7 (C). The spectral data are according to those previously reported [¹] [α]²⁵ Nagar = – 44° (c 0.5, CHCl₃), [Lit: [α]²⁰ Nagar = +112° (c 1.00 CHCl₃) for –96% ee]³; HRMS (ESI): m/z calc. for C₁₆H₂₁O₂NNa⁺ [M+Na]⁺: 282.1465, found: 282.1466.

HPLC traces:
(-)-tert-butyl (S)-3-(p-tolyl)-3,6-dihydropyridine-1(2H)-carboxylate 3q

In a 10 mL round bottomed flask [Rh(cod)(MeCN)$_2$]BF$_4$ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of p-tolyltrimethoxysilane (164 µL, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and tert-butyl 3-chloro-3,6-dihydropyridine-1(2H)-carboxylate (87.1 mg, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux overnight. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (-)-tert-butyl (S)-3-(p-tolyl)-3,6-dihydropyridine-1(2H)-carboxylate in 40% yield (43.7 mg, 0.16 mmol) as a pale yellow solid (m.p.: 66-68 °C).

Enantiomeric excess of 92% was determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane/i-PrOH: 99: 1; λ = 210 nm; major enantiomer $t_R = 9.2$ min; major enantiomer $t_R = 9.1$ min].

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 1.26 – 1.54 (9 H, m), 2.33 (3 H, s), 2.97, 3.31, 3.78 and 4.06 (2 H, rotameric), 3.49 (1 H, m), 3.78 and 4.06 (2 H, rotameric, m), 5.88 (2 H, br s), 7.08 – 7.15 (4 H, m). $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ 21.2 (CH$_3$), 28.3 (3 x CH$_3$), 41.1, 42.9 and 43.6 (rotameric, 1C), 47.4 and 48.6 (rotameric, 1C), 79.4 (C), 124.8 and 125.6 (CH, rotameric), 127.7 (2 x CH), 128.6 and 129.5 (CH, rotameric), 129.2 (2 x CH), 136.2 (C), 139.2 (C), 154.7 (C). The spectral data are consistent with those previously reported.$^3$ $[^{[\alpha]}]_{25}^{D} = -78^\circ$ (c 0.7, CHCl$_3$), [Lit: $[^{[\alpha]}]_{25}^{D} = +122^\circ$ (c 1.0 CHCl$_3$) for -92% ee].$^5$

HPLC traces:
(-)-tert-butyl (S)-3-(3-fluorophenyl)-3,6-dihydropyridine-1(2H)-carboxylate 3r

In a 10 mL round bottomed flask [Rh(cod)(MeCN)₂]BF₄ (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of (3-fluorophenyl)trimethoxysilane (173.0 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 mL in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and tert-butyl 3-chloro-3,6-dihydropyridine-1(2H)-carboxylate (87.1 mg, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux overnight. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with pentane to obtain (-)-tert-butyl (S)-3-phenyl-3,6-dihydropyridine-1(2H)-carboxylate in 52% yield (57.7 mg, 0.21 mmol) as a colorless oil.

Enantiomeric excess of 94% was determined by SFC [Chiralpak® IG-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; λ = 210 nm; major enantiomer tᵣ = 2.1 min; minor enantiomer tᵣ = 2.4 min].

¹H-NMR (400 MHz, CDCl₃) δ 1.25 – 1.50 (9 H, m), 3.10, 3.54 – 3.68, 3.87 – 4.14 (4 H, rotamer, m, signals overlapped), 3.50 (1 H, m), 5.87 (2 H, br s), 6.89 – 6.95 (2 H, m), 6.99 (2 H, d, J = 7.7 Hz), 7.24 – 7.29 (1 H, m); ¹³C-NMR (101 MHz, CDCl₃) δ 28.4 (3 x CH₃), 41.3, 43.0 and 43.7 (rotamer, 1C), 47.1 and 48.3 (rotamer, 1C), 79.7 (C), 113.7 (CH, d, J = 20.6 Hz), 114.8 (CH, m), 123.7 (CH, d, J = 2.9 Hz), 125.6 and 126.6 (CH, rotamer), 127.5 and 128.5 (CH), 129.9 (CH, d, J = 8.8 Hz), 144.9 (CH, d, J = 7.1 Hz), 154.7 (C), 163.1 (C, d, J = 246.5 Hz); IR (ATR) νmax /cm⁻¹: 2976 (w), 2361 (w), 1693 (s), 1420 (m), 1238 (m), 1168 (m); [α]²⁵backup = -162° (c 1.5, CHCl₃), HRMS (ESI): m/z calc. for C₁₆H₂₀O₂NFNa⁺ [M+Na]⁺: 300.1370, found: 300.1370.

SFC traces:
(--)-tert-butyl (S)-3-(benzo[d][1,3]dioxol-5-yl)-3,6-dihydropyridine-1(2H)-carboxylate 3s

In a 10 mL round bottomed flask \([\text{Rh(cod)(MeCN)}_2]\text{BF}_4\) (7.6 mg, 0.02 mmol, 0.05 eq) and (S)-BINAP (18.7 mg, 0.03 mmol, 0.075 eq) were stirred in THF (0.7 mL) at reflux for 30 min. A solution of benzo[d][1,3]dioxol-5-yltrimethoxysilane (193.6 mg, 0.80 mmol, 2.00 eq), tetrabutylammonium fluoride (1 M in THF, 0.8 mL, 0.8 mmol, 2.00 eq) and tert-butyl 3-chloro-3,6-dihydropyridine-1(2H)-carboxylate (87.1 mg, 0.40 mmol, 1.00 eq) in THF (0.3 mL) was then added via syringe and the flask rinsed with THF (0.2 mL). The resulting mixture was then heated to reflux overnight. The solvent was then carefully evaporated and the resulting mixture was directly loaded onto a chromatographic column and eluted with hexane/EtOAc (10 : 1) to obtain (--)-tert-butyl (S)-3-(benzo[d][1,3]dioxol-5-yl)-3,6-dihydropyridine-1(2H)-carboxylate in 43% yield (52.2 mg, 0.17 mmol).

Enantiomeric excess of 92% was determined by SFC [Chiralpak® IC-3, 1500 psi, 30 °C; flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; \(\lambda = 210\) nm; major enantiomer \(t_R = 2.7\) min; minor enantiomer \(t_R = 2.8\) min].

\(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 1.33 – 1.49 (9 H, m), 3.00, 3.35, and 3.65 – 3.72 (2 H, rotameric, m), 3.42 (1 H, m), 4.00 (2 H, m), 5.84 (2 H, br s), 5.91 (1 H, d, \(J = 1.5\) Hz), 5.92 (1 H, d, \(J = 1.5\) Hz), 6.67 (2 H, m), 6.74 (1 H, d, \(J = 7.9\) Hz); \(^{13}\text{C-NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 28.5 (3 x CH\(_3\)), 41.4, 43.0 and 43.7 (rotameric, 1C), 47.5 and 48.9 (rotameric, 1C), 79.8 (C), 101.0 (CH\(_2\)) 108.3 (2 x CH), 121.0 (CH), 123.7 (CH, d, \(J = 2.9\) Hz), 125.0 and 126.0 (CH, rotameric), 128.5 and 129.4 (CH, rotameric), 136.3 (C), 146.4 (C), 147.8 (C), 154.8 (C); \(\text{IR (ATR)}\) \(\nu_{\text{max}}/\text{cm}^{-1}\): 2980 (w), 1693 (s), 1487 (m), 1441 (m), 1241 (m), 1170 (s), 1039 (w); \([\alpha]_{25}^{25}\) = \(-60.2\)° HRMS (ESI): \(m/z\) calc. for C\(_{17}\)H\(_{21}\)O\(_4\)Na\(^+\) [M+Na\(^+\)]: 326.1363, found: 326.1362.

SFC traces:
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