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SUPPLEMENTARY INFORMATION

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# Rhodium-catalysed asymmetric allylic arylation of racemic halides with arylboronic acids

Mireia Sidera and Stephen P. Fletcher*

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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), aqueous basic potassium permanganate stains or vanillin solution. 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.

Reactions at 0 °C were performed using an ice-water bath, which was covered with cotton and foil if overnight stirring is required. Other temperatures were obtained using a Julabo FT902 immersion cooler or the heating plate of the stirrer.

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), AVF-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). Labels H and H' refer to diastereotopic protons attached to the same carbon and impart no stereochemical information. Assignments were made with the assistance of gCOSY, gHSQC, gHMBC or NOESY NMR spectra.

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 GC measurements were conducted on a HP6890 ($H_2$ as vector gas) or HP6850 ($H_2$ as vector gas) with the stated column in the characterization. Temperature programs are described as follows: initial temperature (°C) - initial time (min) - temperature gradient (°C/min) –[certain temperature – holding time - temperature gradient (°C/min)]- final temperature (°C) – holding time. Retention times ($R_T$) are given in min.

Low-resolution mass spectra were recorded using a Walters LCT premier XE. High-resolution mass spectra (EI and ESI) were recorded using a Bruker MicroTOF spectrometer by the internal service at the University of Oxford.

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; $[\alpha]_D$ values are given in $10^{-1}$ deg.$cm^2$ $g^{-1}$ (concentration c given as g/100 mL).

## Chemicals

### General chemicals:

Dry THF and $CH_2Cl_2$ were collected fresh from an mBraun SPS-800 solvent purification system having been passed through anhydrous alumina columns. Dry 1,2-dichloroethane ether was purchased from Acros with an AcroSeal® respectively.

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 ($CD_2Cl_2$, $CDCl_3$).

The cyclic allylic chlorides (*1*), 3-chloro-3,6-dihydro-2*H*-pyran (*2*) and 3-chloro-5-phenylcyclohex-1-ene were prepared according to reported methods. 3-bromocyclohex-1-ene was purchased from ACROS and used without further purification.

### General procedure for the preparation of racemates of compounds 2–12 and 14:

In a 10 mL round bottomed flask $Rh(acac)(C_2H_4)_2$ (10.3 mg, 0.04 mmol, 0.10 eq), (±)-BINAP (29.9mg, 0.048 mmol, 0.12 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of boronic acid (0.80 mmol, 2.00 eq) and allyl bromide (0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto a chromatography column eluting with pentane to obtain the pure product.

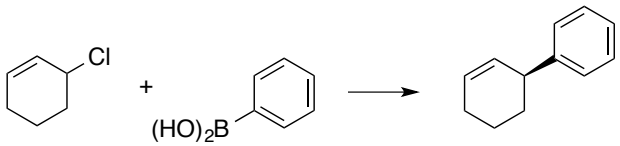
### General procedure for the preparation of racemates of compounds 13, 15–25 and 27:

In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (9.1 mg, 0.012 mmol, 0.03 eq), (*R*)-Xyl-P-PHOS **A** (9.1 mg, 0.012 mmol, 0.03 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of boronic acid (0.80 mmol, 2.00 eq) and the corresponding allyl chloride (0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto a flash chromatography column to obtain the purified product.

### General procedure for the asymmetric allylic alkylation of allyl halides with boronic acids:

In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (S)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of the boronic acid (0.80 mmol, 2.00 eq) and the allyl halide (0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto a flash chromatography column to obtain the purified product.

**(–)-(*S*)-Cyclohex-2-enylbenzene 2**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of phenylboronic acid (97.5 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 99% yield (62.0 mg, 0.39 mmol) as a colorless oil.

Enantiomeric excess of 99% was determined by HPLC [Chiralpak® ID; flow: 0.6 mL/min; hexane/i-PrOH: 99.9: 0.1; λ = 210 nm; major enantiomer $t_R$ = 8.3 min; minor enantiomer $t_R$ = 8.9 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.31 (m, 3H), 7.27 – 7.17 (m, 2H), 5.90 (dq, *J* = 9.8, 3.4 Hz, 1H), 5.73 (dq, *J* = 10.0, 2.4 Hz, 1H), 3.42 (m, 1H), 2.15 – 1.95 (m, 3H), 1.85 – 1.70 (m, 1H), 1.70 – 1.51 (m, 2H).

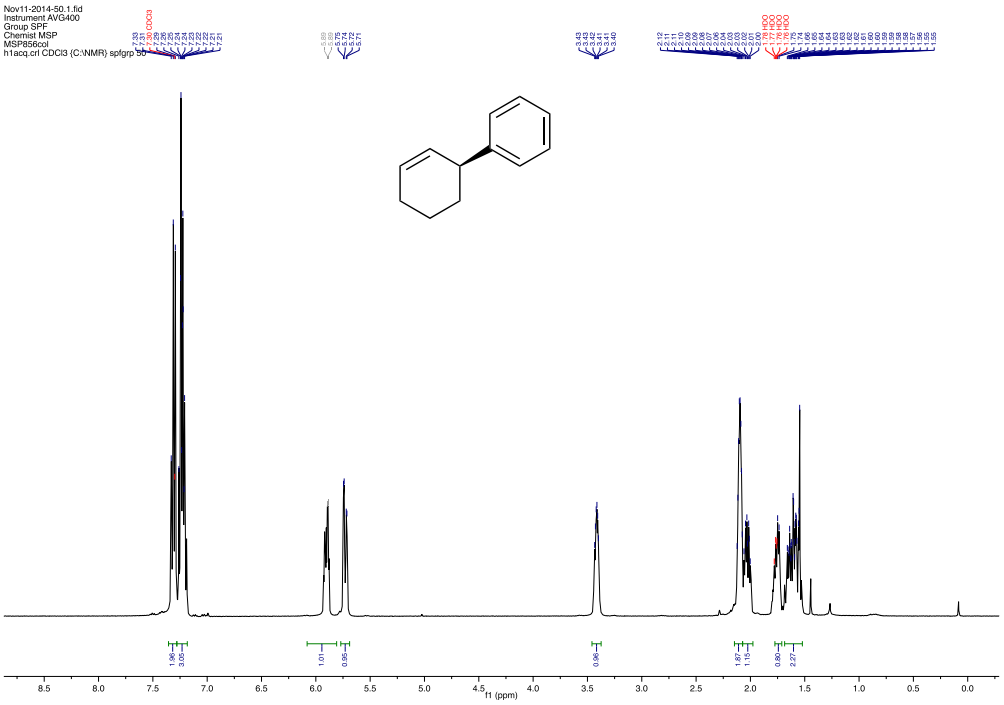
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 146.8, 130.3, 128.5, 128.4 (2C), 127.9 (2C), 126.1, 42.0, 32.8, 25.2, 21.3.

**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{14}[M]^+$: 158.1094, found: 158.1096.

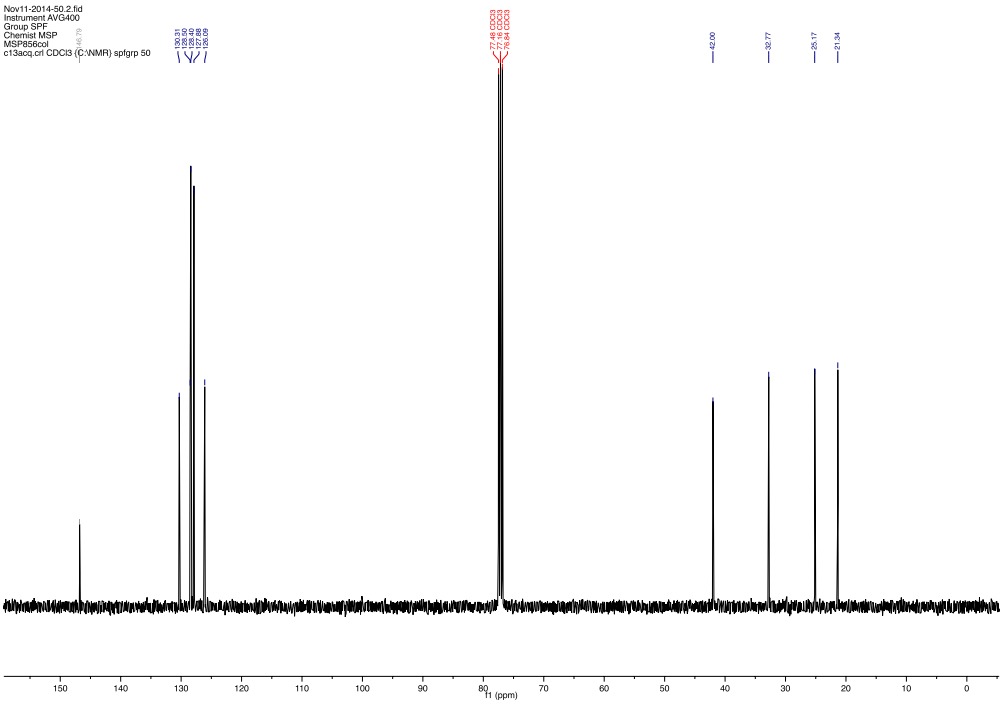
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1233, 1748, 2117, 2857, 2930, 3022.

**$[\alpha]^{20}_{589}$** = –134.6 (c 0.55 $CHCl_3$) for 99% ee [lit. **$[\alpha]^{20}_{589}$** = –121.9 (c 1.00 $CHCl_3$) for 96% ee].(*3*)

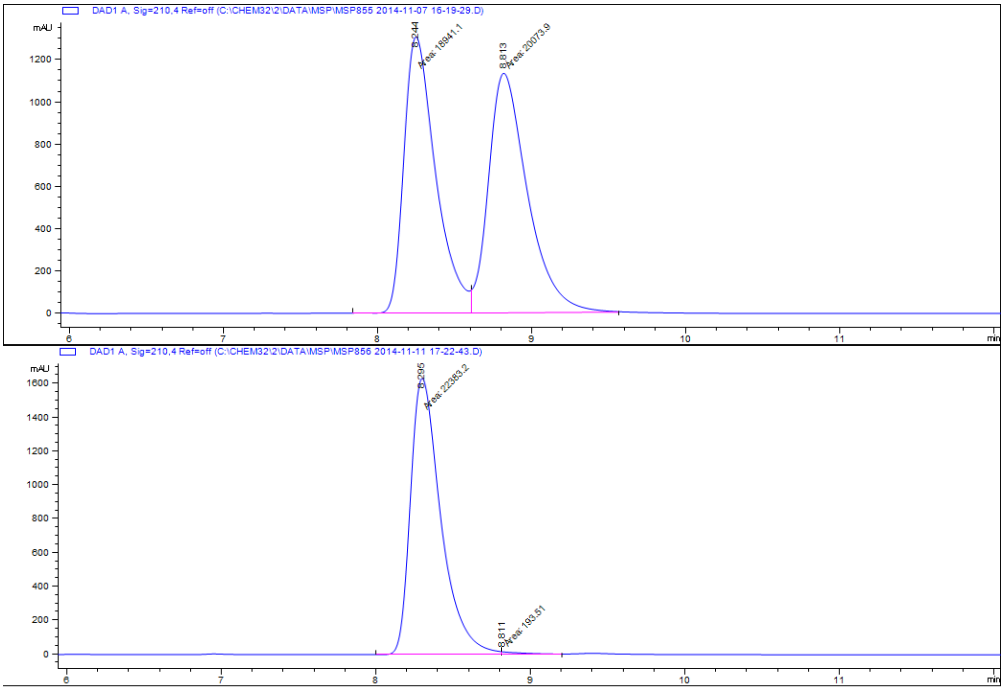
**$^1$H NMR:**



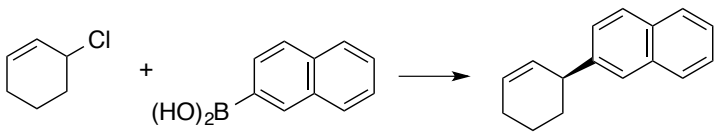

**$^{13}$C NMR:**



**HPLC traces:**




**(–)-(*S*)-2-(Cyclohex-2-en-1-yl)naphthalene 3**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 2-naphtaleneboronic acid (137.6 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain (–)-(S)-2-(cyclohex-2-en-1-yl)naphthalene in 96% yield (79.8 mg, 0.38 mmol) as a white solid.

Enantiomeric excess of 89% was determined by HPLC [Chiralpak® IA; flow: 0.6 mL/min; hexane 100; λ = 210 nm; minor enantiomer $t_R$ = 10.8 min; major enantiomer $t_R$ = 11.4 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.81 (m, 3H), 7.67 (m, 1H), 7.57 – 7.35 (m, 3H), 5.98 (m, 1H), 5.84 (dq, *J* = 10.1, 2.4 Hz, 1H), 3.60 (m, 1H), 2.27 – 1.99 (m, 3H), 1.80 (s, 1H), 1.68 (m, 2H).

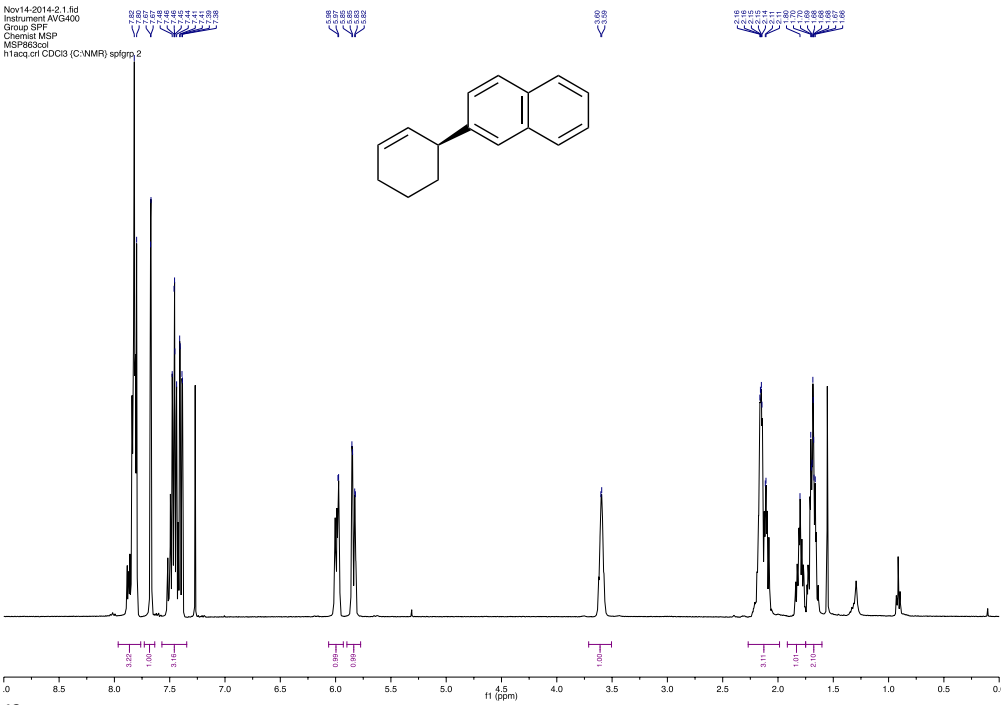
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 144.1, 133.6, 132.2, 130.1, 128.7, 127.9, 127.6, 127.6, 126.8, 125.9, 125.8, 125.2, 42.0, 32.5, 25.1, 21.2.

**HRMS** (EI/FI) *m*/z calcd for $C_{16}H_{16}[M]^+$: 208.1252, found: 208.1254.

**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1235, 1748, 2120, 2860, 2935, 3017, 3052.

**$[\alpha]^{20}_{589}$** = –221.1 (c 0.91 $CHCl_3$) for 89% ee.

**$^1$H NMR:**

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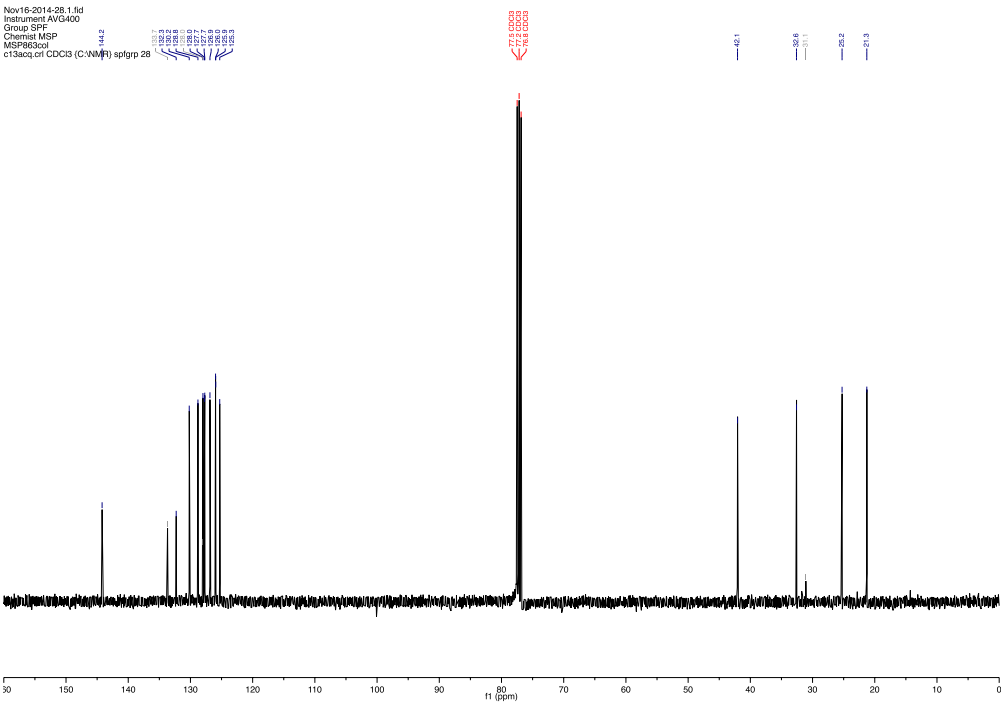
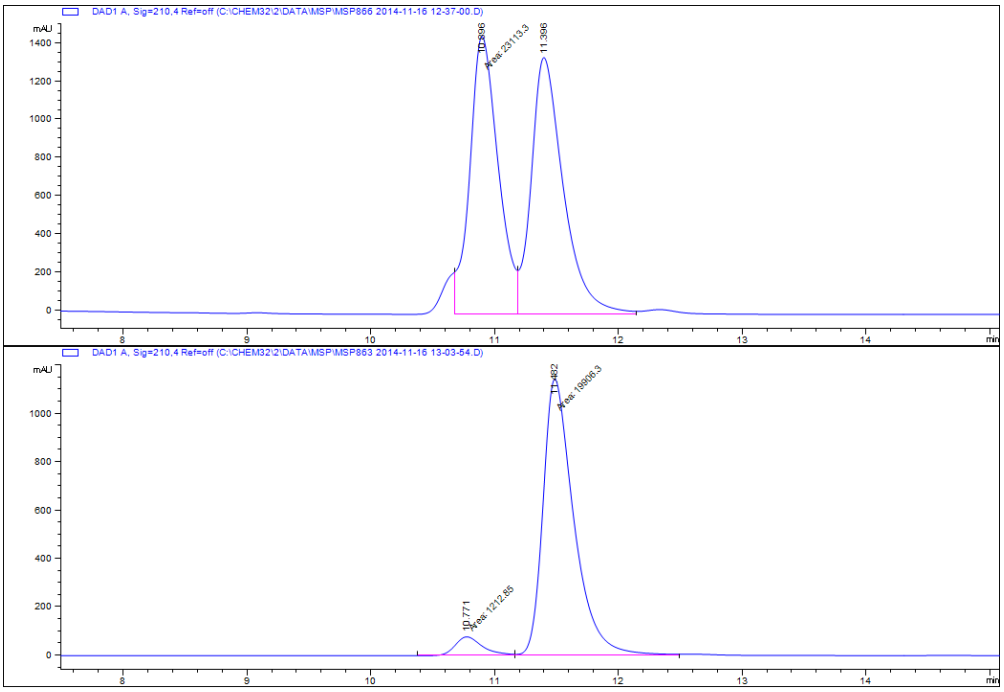
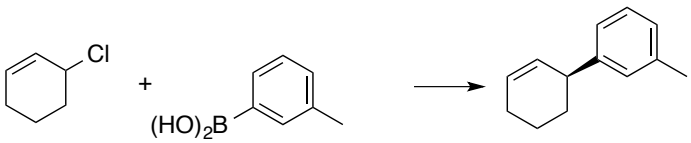


**HPLC traces:**




**(–)-(*S*)-3-(3-Methylphenyl)cyclohexene 4**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 3-methylphenylboronic acid (108.8 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 96% yield (65.9 mg, 0.38 mmol) as a colorless oil.

Enantiomeric excess of 97% was determined by HPLC [Chiralpak® IB; flow: 0.5 mL/min; hexane 100; λ = 210 nm; minor enantiomer $t_R$ = 9.1 min; major enantiomer $t_R$ = 9.4 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.24 – 7.15 (m, 1H), 7.03 (d, *J* = 7.7 Hz, 3H), 5.94 – 5.84 (m, 1H), 5.71 (dq, *J* = 10.0, 2.4 Hz, 1H), 3.37 (m, 1H), 2.35 (s, 3H), 2.19 – 2.03 (m, 2H), 2.03 – 1.95 (m, 1H), 1.82 – 1.72 (m, 1H), 1.60 (m, 2H).

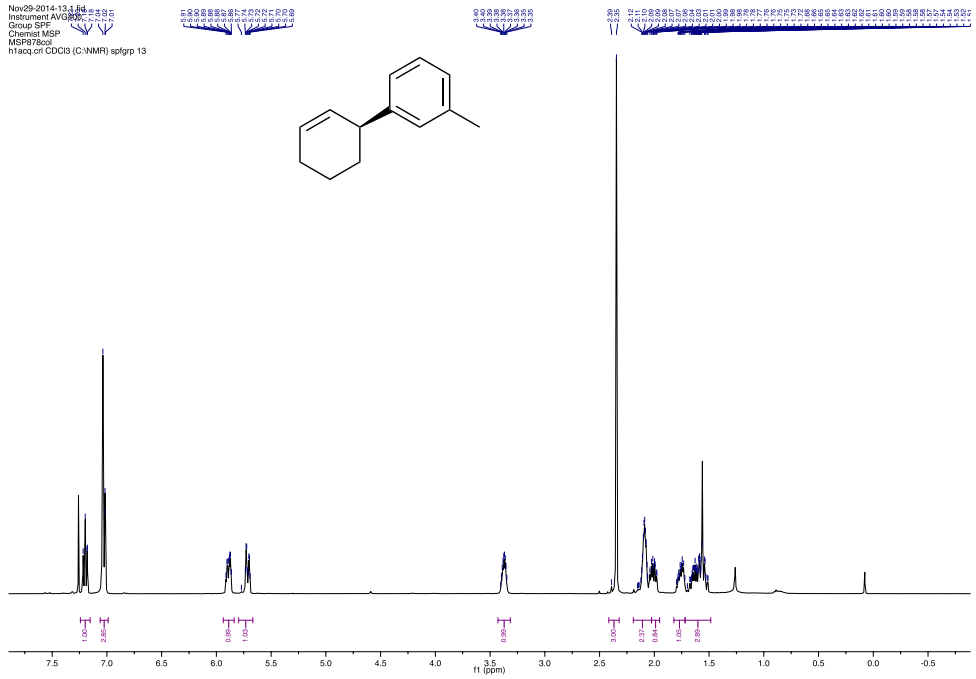
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 146.8, 138.0, 130.5, 128.6, 128.4, 128.3, 126.9, 124.9, 42.0, 32.8, 25.2, 21.6, 21.4.

**HRMS** (EI/FI) *m*/z calcd for $C_{13}H_{16}$ $[M]^+$: 172.1252, found: 172.1255.

**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1446, 1488, 1607, 2836, 2857, 2928, 3020.

**$[\alpha]^{20}_{589}$** = –117.0 (c 0.96 $CHCl_3$) for 97% ee.

**$^1$H NMR:**

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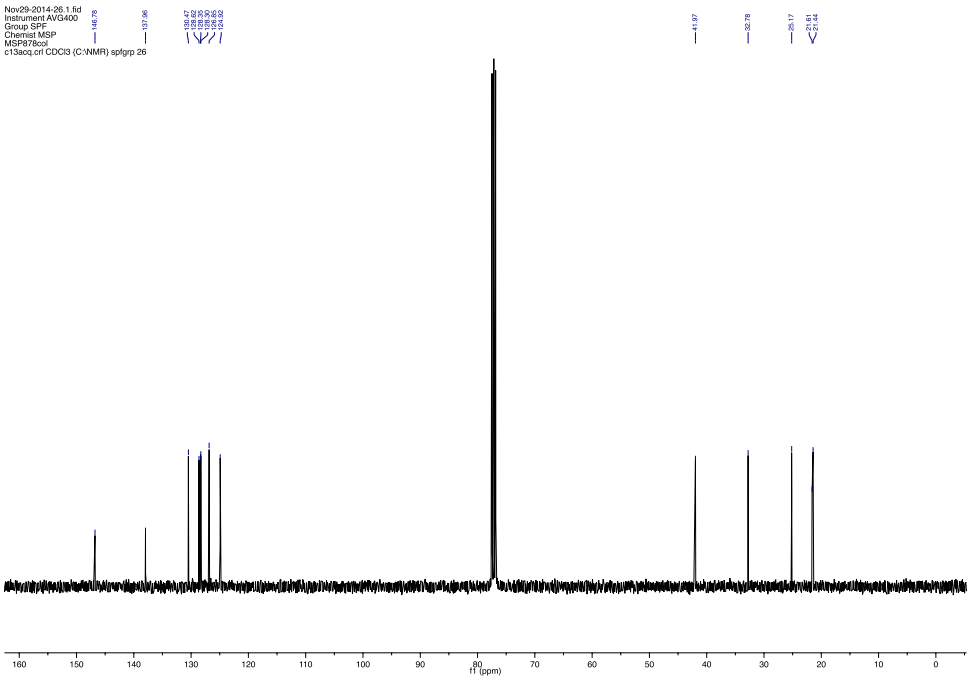
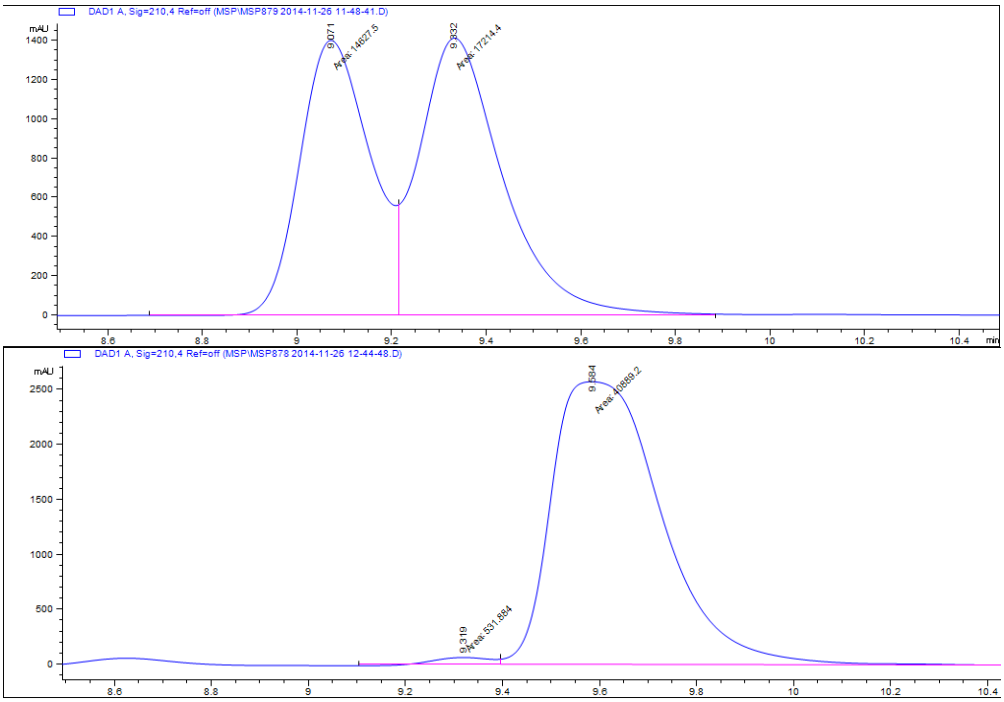
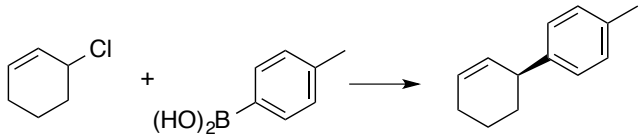



**HPLC traces:**



**(–)-(*S*)-3-( 4-Methylphenyl)cyclohexene 5**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 4-methylphenylboronic acid (108.8 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 58% yield (40.0 mg, 0.23 mmol) as a colorless oil.

Enantiomeric excess of >94% was determined by HPLC [Chiralpak® IC; flow: 0.7 mL/min; hexane 100; λ = 210 nm; minor enantiomer $t_R$ = 6.4 min; major enantiomer $t_R$ = 6.8 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.13 (s, 4H), 5.89 (dq, *J* = 9.8, 2.5 Hz, 1H), 5.71 (dq, *J* = 10.2, 2.5 Hz, 1H), 3.38 (m, 1H), 2.34 (s, 3H), 2.09 (s, 2H), 2.01 (m, 1H), 1.75 (m, 1H), 1.71 – 1.48 (m, 2H).

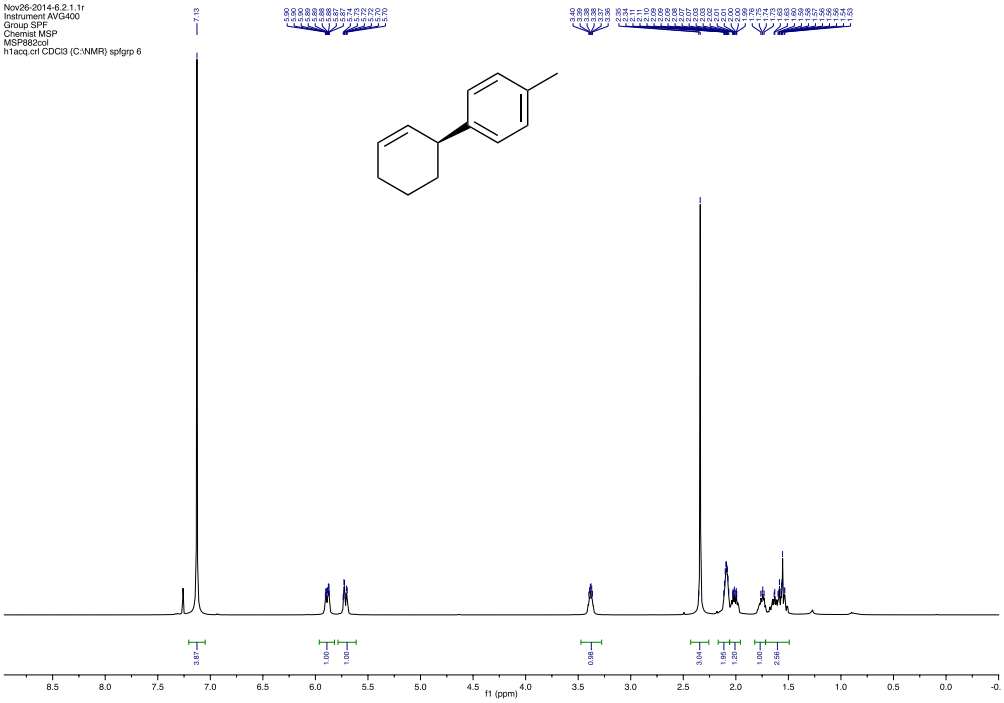
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 143.8, 135.6, 130.5, 129.1 (2C), 128.3, 127.8 (2C), 41.6, 32.8, 25.2, 21.4, 21.2.

**HRMS** (EI/FI) *m*/z calcd for $C_{13}H_{16}[M]^+$: 172.1252, found: 172.1254.

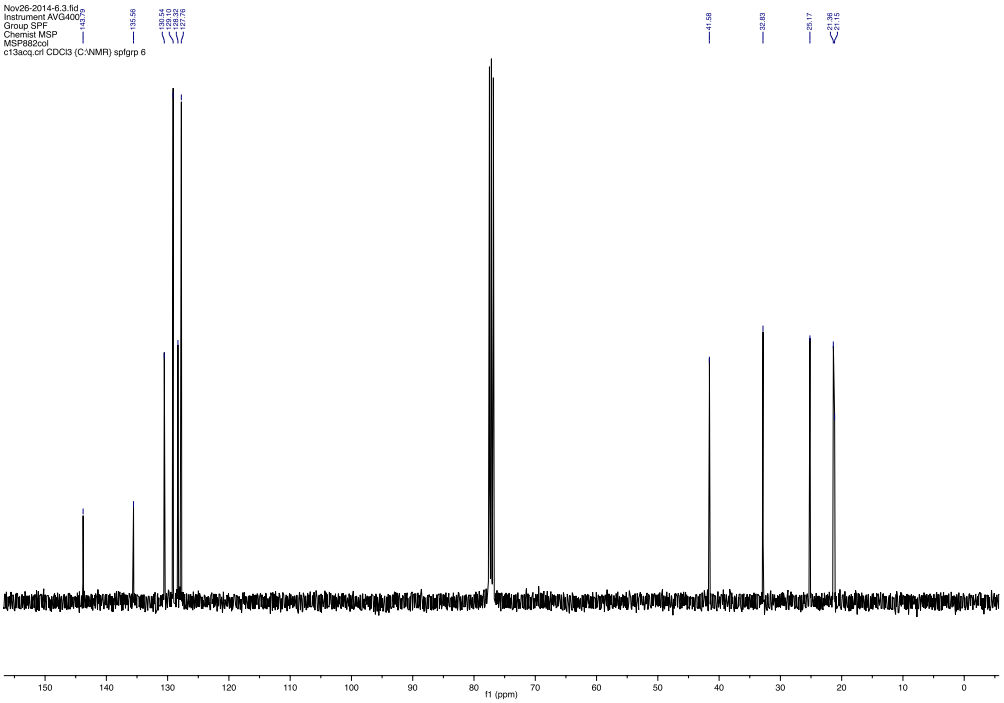
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 766, 1445, 1511, 2857, 2928, 3019.

**$[\alpha]^{20}_{589}$** = –128.0 (c 0.47 $CHCl_3$) for >94% ee [lit. $[\alpha]^{20}_{589}$ = –129.3 (c 1.10 $CHCl_3$) for 94% ee].(*3*)

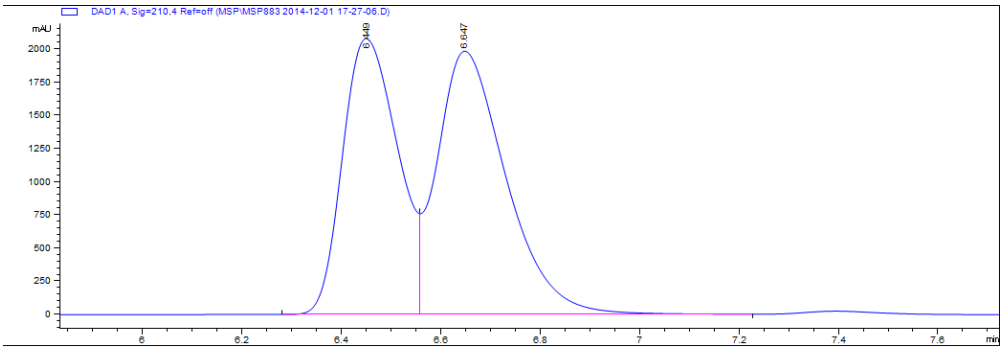
**$^{1}$H NMR:**

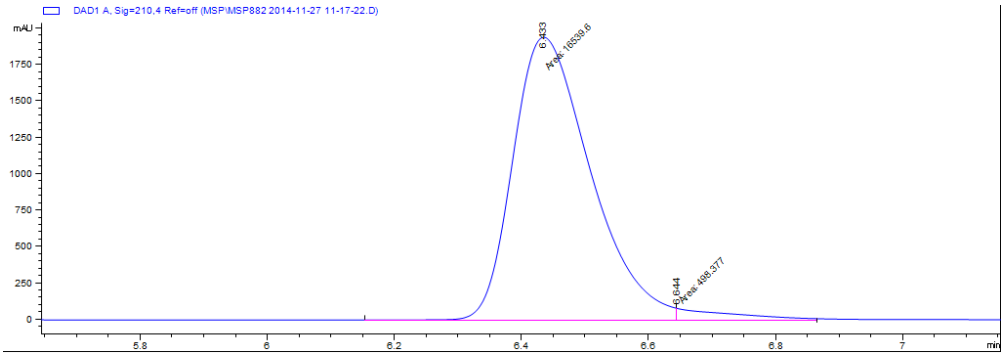



**$^{13}$C NMR:**

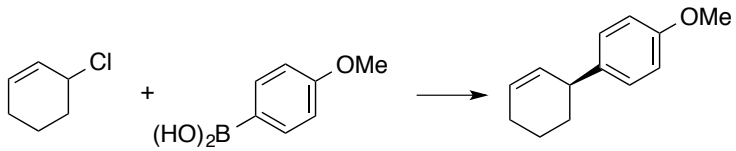


**HPLC traces:**




**(–)-(*S*)-3-(4-Methoxyphenyl)cyclohexene 6**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 4-methoxyphenylboronic acid (121.6 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 77% yield (58.0 mg, 0.31 mmol) as a colorless oil.

Enantiomeric excess of 97% was determined by HPLC [Chiralpak® IB; flow: 0.6 mL/min; hexane 100; λ = 210 nm; minor enantiomer $t_R$ = 8.8 min; major enantiomer $t_R$ = 8.3 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.15 (dd, *J* = 7.8, 1.4 Hz, 2H), 6.93 – 6.76 (m, 2H), 5.88 (dt, *J* = 10.2, 3.2 Hz, 1H), 5.78 – 5.61 (m, 1H), 3.80 (s, 3H), 3.37 (m, 1H), 2.14 – 2.05 (m, 2H), 2.05 – 1.95 (m, 1H), 1.74 (m, 1H), 1.69 – 1.45 (m, 2H).

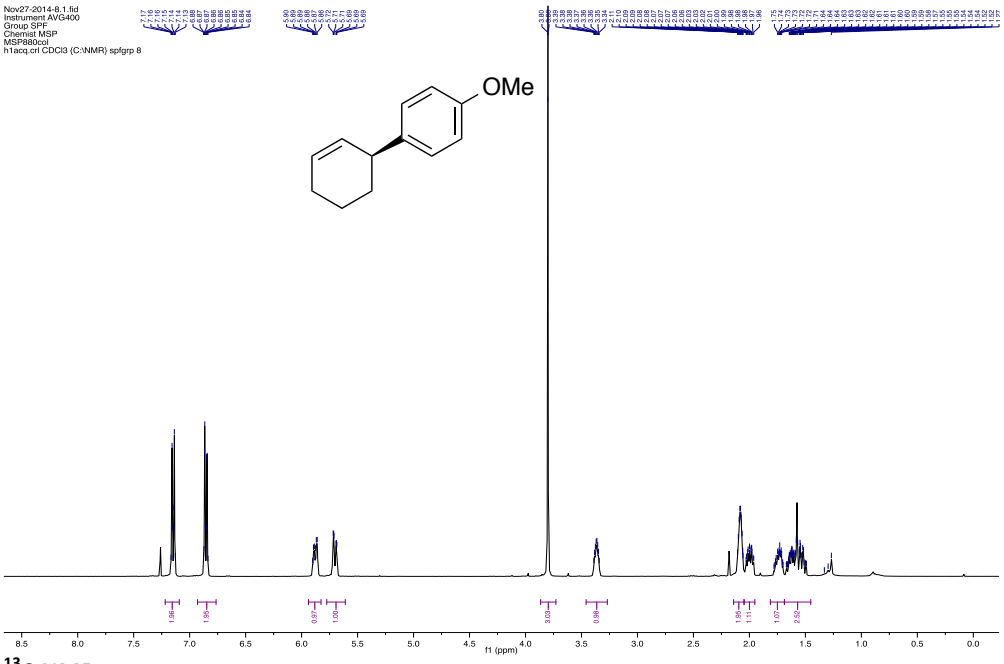
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 158.0, 138.9, 130.6, 128.8 (2C), 128.3, 113.8 (2C), 55.4, 41.1, 32.9, 25.2, 21.3.

**HRMS** (EI/FI) *m*/z calcd for $C_{13}H_{16}O[M]^+$: 188.1201, found: 188.1204.

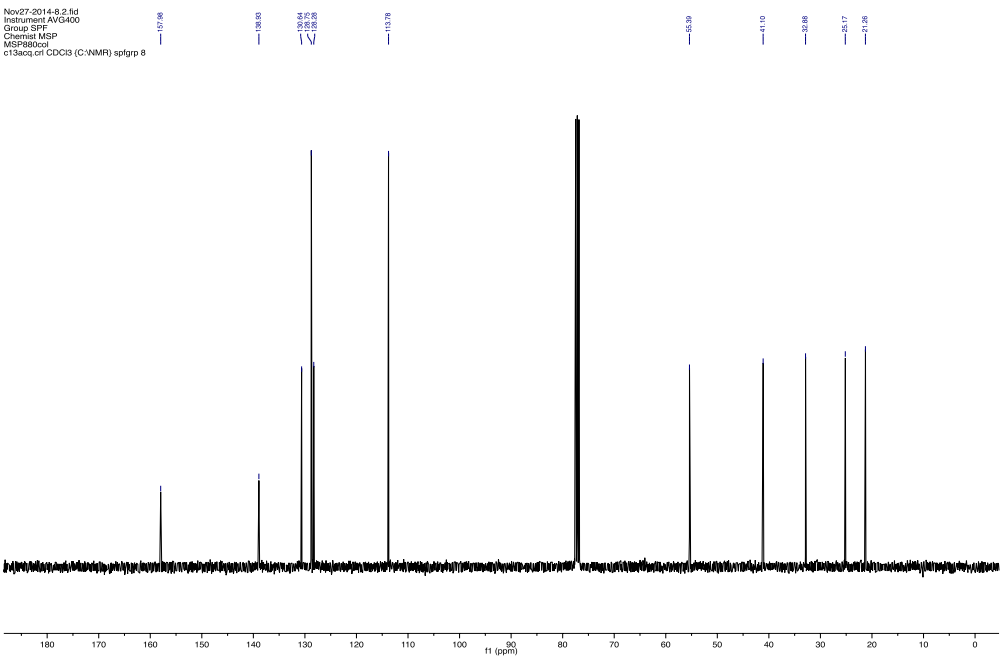
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1243, 1444, 1509, 2834, 2929, 3019.

**$[\alpha]^{20}_{589}$** = –134.6 (c 1.40 $CHCl_3$) for 97% ee [lit. *ent*. $[\alpha]^{20}_{589}$ = +145.8 (c 1.00 Benzene) for >99% ee].(*4*)

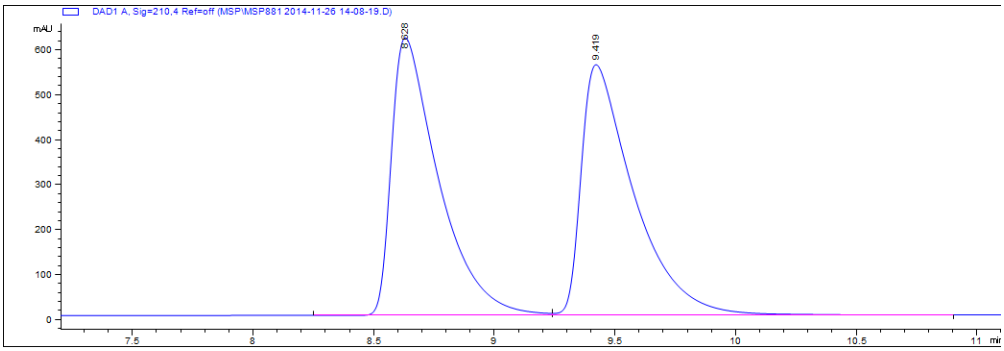
**$^1$H NMR:**

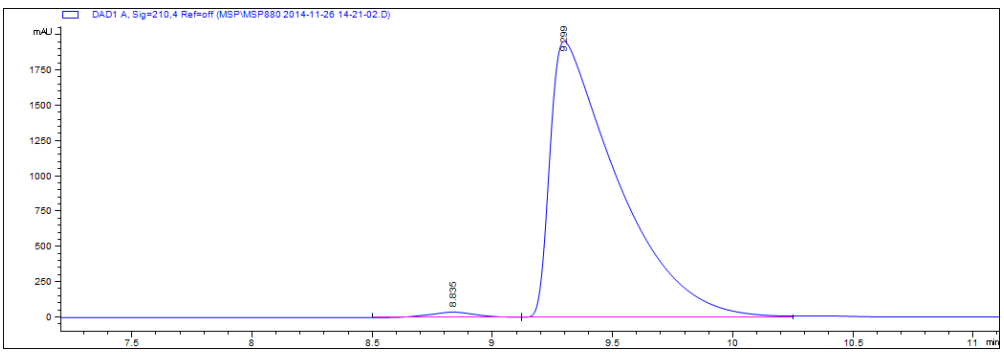



**$^{13}$C NMR:**

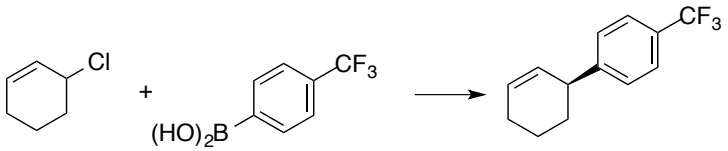



**HPLC traces:**




**(–)-(*S*)-3-(4-Trifluoromethylphenyl)cyclohexene 7**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 4-trifluoromethylphenylboronic acid (151.9 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 60% yield (54.0 mg, 0.24 mmol) as a colorless oil.

Enantiomeric excess of 96% was determined by HPLC [Chiralpak® IA; flow: 0.6 mL/min; hexane 100; λ = 210 nm; minor enantiomer $t_R$ = 6.2 min; major enantiomer $t_R$ = 6.5 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.55 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.94 (dq, *J* = 9.9, 2.3 Hz, 1H), 5.68 (dq, *J* = 9.9, 2.3 Hz, 1H), 3.47 (m, 1H), 2.16 – 1.91 (m, 3H), 1.81 – 1.66 (m, 1H), 1.67 – 1.59 (m, 1H), 1.59 – 1.41 (m, 1H).

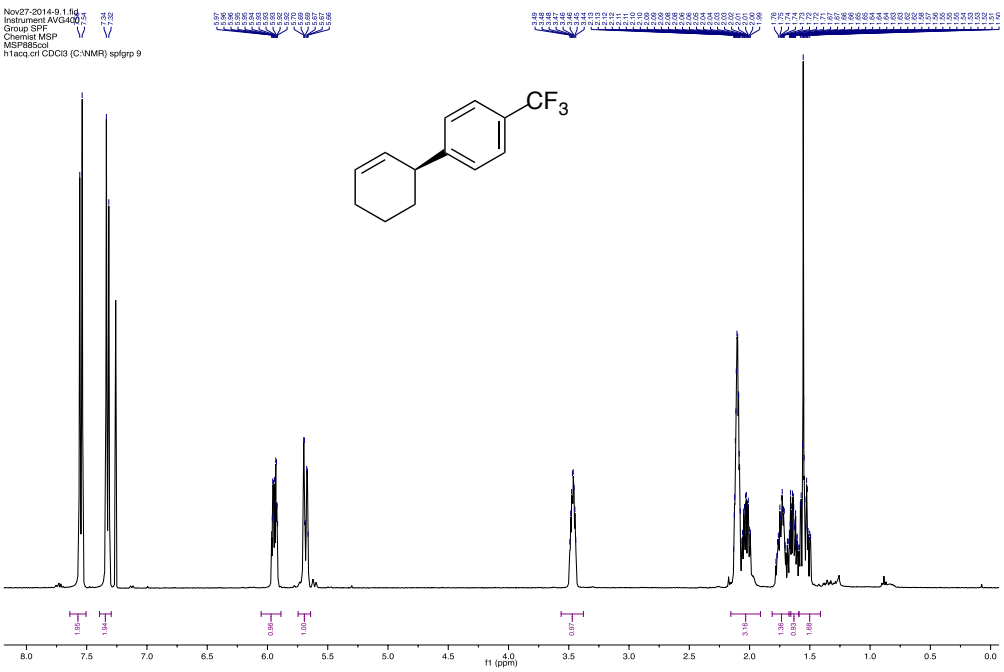
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 150.9, 129.3, 129.2, 128.2 (2C), 125.4, 125.4, 125.3, 125.2 (q, *J* = 3.8 Hz, 1C), 41.8, 32.6, 25.1, 21.1.

**HRMS** (EI/FI) *m*/z calcd for $C_{13}H_{13}F_3$ $[M]^+$: 226.0969, found: 226.0970.

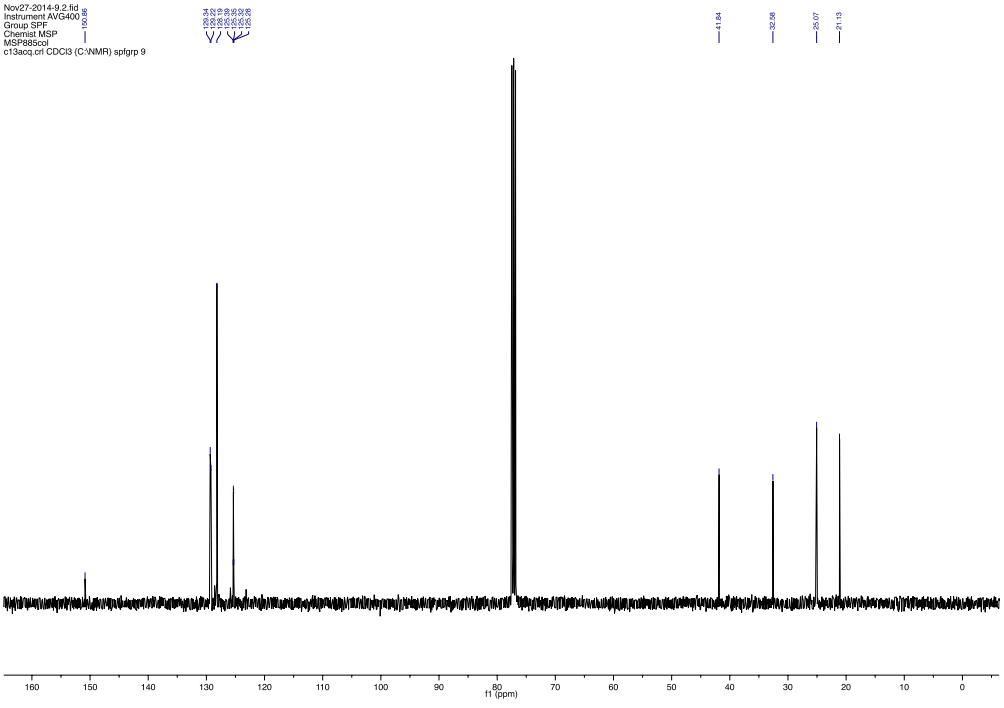
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1122, 1324, 1619, 2834, 2932, 3019.

**$[\alpha]^{20}_{589}$** = –98.9 (c 1.60 $CHCl_3$) for 96% ee.

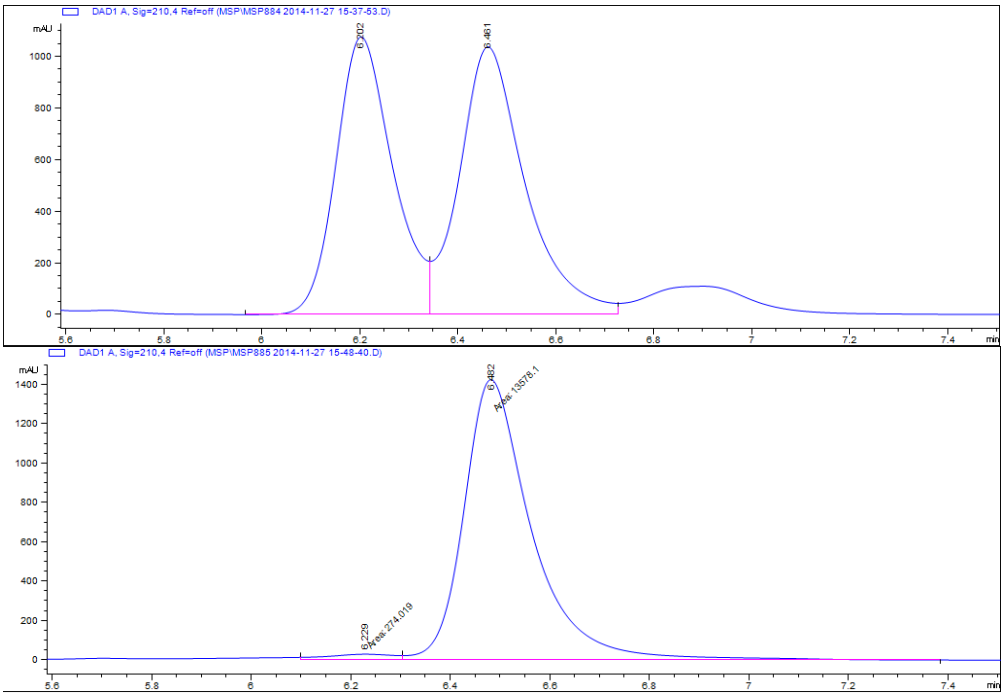
**$^1$H NMR:**



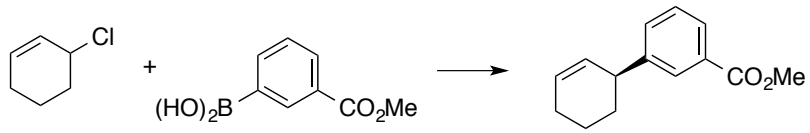

**$^{13}$C NMR:**




**HPLC traces:**




**(–)-(*S*)-3-(3-Methoxycarbonylphenyl)cyclohexene 8**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 3-methoxycarbonylphenylboronic acid (144.0 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with hexane:EtOAc (92:8) to obtain the pure product in 86% yield (74.0 mg, 0.34 mmol) as a colorless oil.

Enantiomeric excess of >99% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 99:1 100; λ = 210 nm; major enantiomer $t_R$ = 5.6 min; minor enantiomer $t_R$ = 6.1 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.93 – 7.84 (m, 2H), 7.47 – 7.32 (m, 2H), 5.98 – 5.88 (m, 1H), 5.70 (m, 1H), 3.91 (s, 3H), 3.46 (m, 1H), 2.10 (m, 2H), 2.06 – 1.97 (m, 1H), 1.81 – 1.48 (m, 3H).

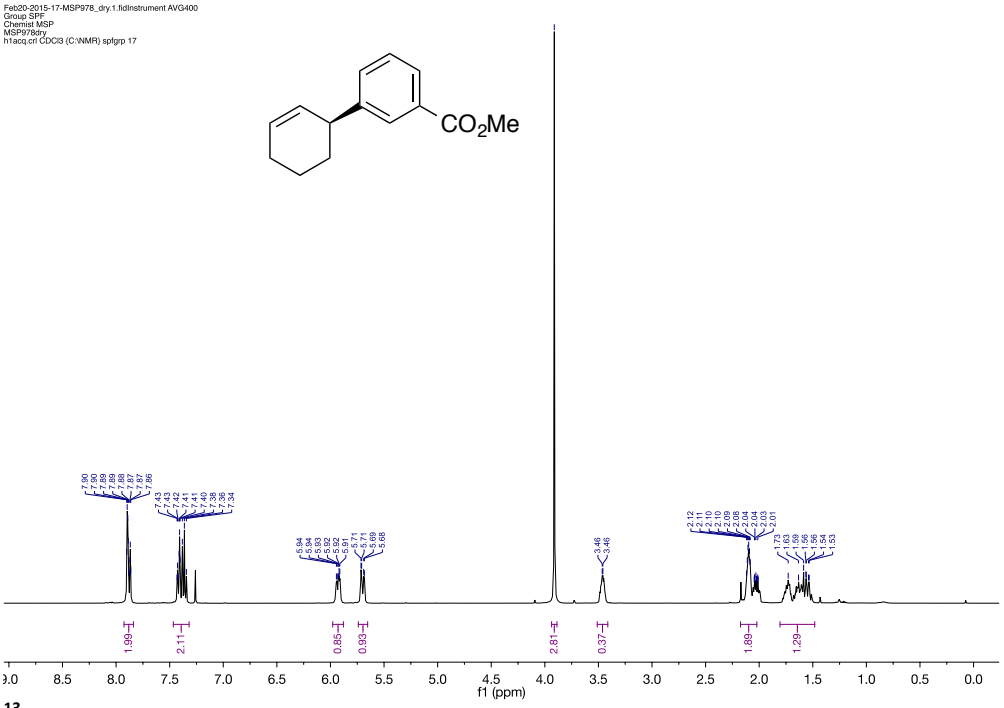
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 167.5, 147.2, 132.6, 130.3, 129.6, 129.1, 129.0, 128.4, 127.4, 5.20, 41.8, 32.7, 25.1, 21.2.

**HRMS** (EI/FI) *m*/z calcd for $C_{14}H_{16}O_2$ $[M]^+$: 216.1150, found: 216.1148.

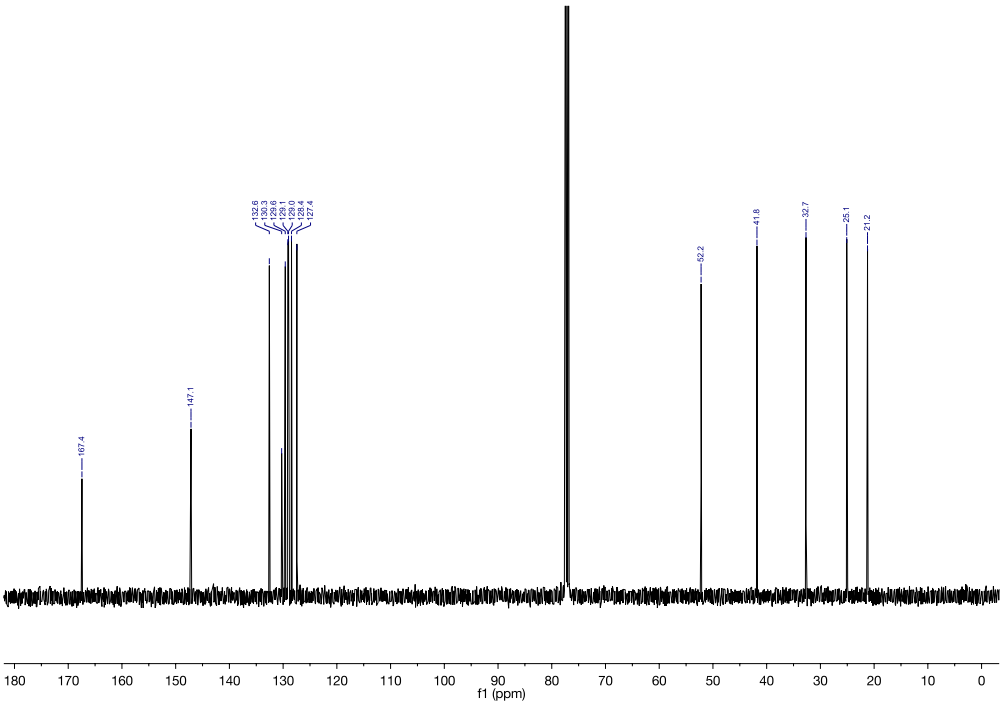
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 3020, 2930, 2857, 1721.

**$[\alpha]^{20}_{589}$** = –101.0 (c 1.12 $CHCl_3$) for >99% ee.

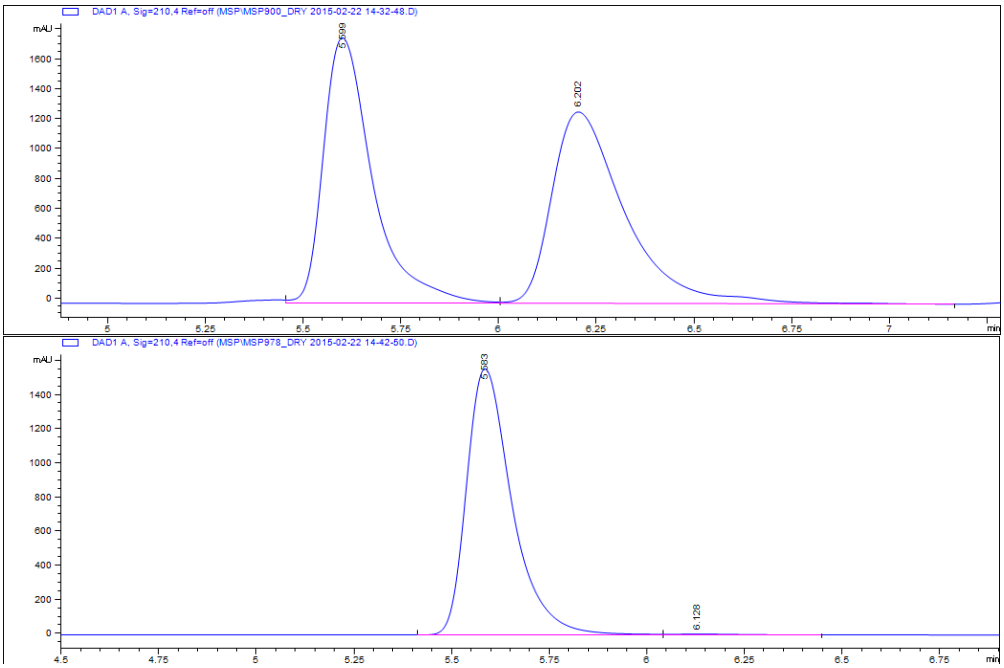
**$^1$H NMR:**



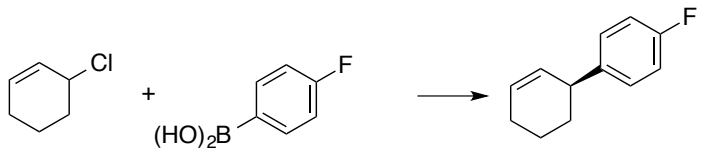

**$^{13}$C NMR:**




**HPLC traces:**



**(–)-(*S*)-3-(4-Fluorophenyl)cyclohexene 9**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 4-fluorophenylboronic acid (111.9 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 54% yield (38.4 mg, 0.22 mmol) as a colorless oil.

Enantiomeric excess of >99% was determined by HPLC [Chiralpak® ID; flow: 0.4 mL/min; hexane 100; λ = 210 nm; minor enantiomer $t_R$ = 11.4 min; major enantiomer $t_R$ = 11.8 min].

**$^1$H NMR** (500 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.17 (dd, *J* = 8.3, 5.5 Hz, 2H), 6.98 (t, *J* = 8.5 Hz, 2H), 5.89 (dq, *J* = 9.9, 3.4 Hz, 1H), 5.68 (dd, *J* = 10.1, 2.5 Hz, 1H), 3.39 (m, 1H), 2.08 (m, 2H), 2.00 (m, 1H), 1.79 – 1.44 (m, 3H).

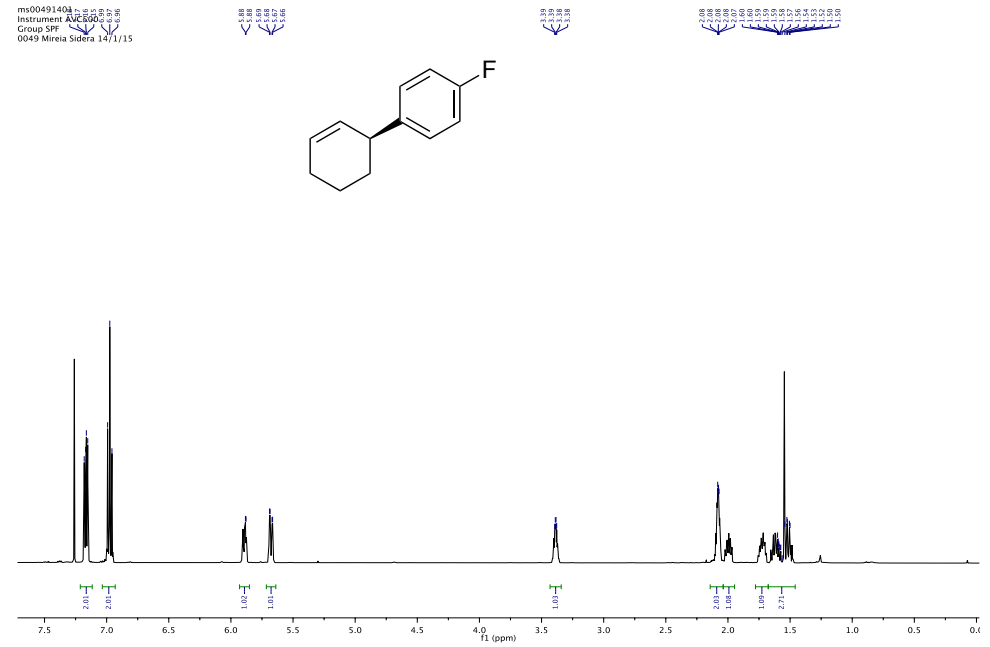
**$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta_C$ /ppm: 161.3 (d, *J* = 243.3 Hz, 1C), 142.4 (d, *J* = 3.2 Hz, 1C), 130.1, 129.2 (d, *J* = 7.8 Hz, 2C), 128.7, 115.0 (d, *J* = 21.0 Hz, 2C), 41.2, 32.9, 25.1, 21.2.

**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{13}F$ $[M]^+$: 176.1001, found: 176.1003.

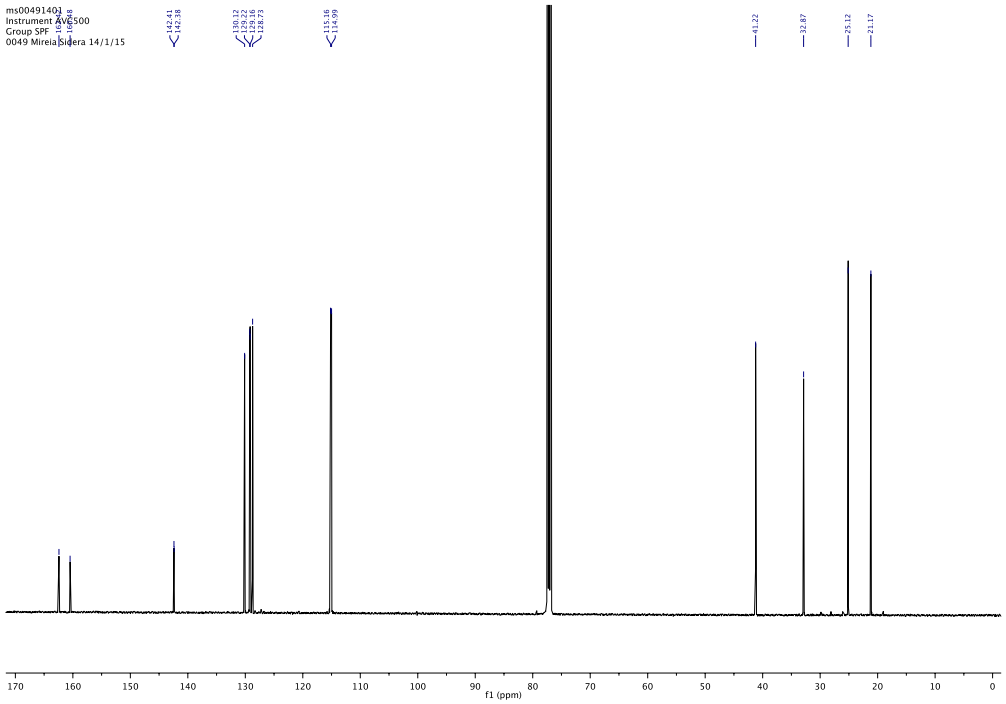
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1220, 1507, 1601, 2856, 2930, 3020.

**$[\alpha]^{20}_{589}$** = –112.4 (c 1.09 $CHCl_3$) for >99% ee.

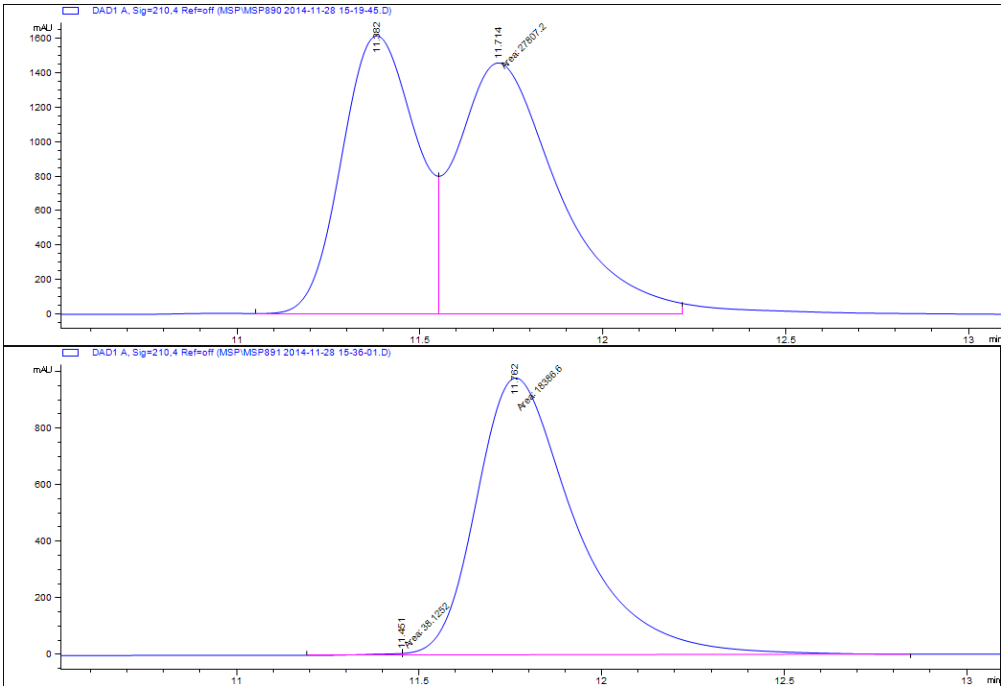
**$^{1}$H NMR:**



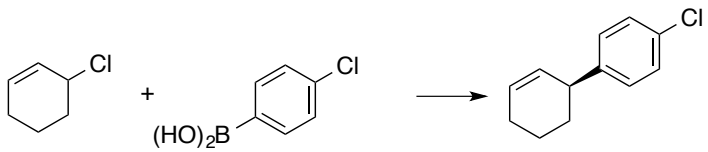

**$^{13}$C NMR:**



**HPLC traces:**




**(–)-(*S*)-3-(4-Chlorophenyl)cyclohexene 10**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 4-chlorophenylboronic acid (111.9 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 81% yield (62.7 mg, 0.32 mmol) as a colorless oil.

Enantiomeric excess of >99% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane 100; λ = 210 nm; minor enantiomer $t_R$ = 4.7 min; major enantiomer $t_R$ = 5.4 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.23 – 7.14 (m, 2H), 7.14 – 7.04 (m, 2H), 5.83 (dq, *J* = 9.9, 2.3 Hz, 1H), 5.59 (dq, *J* = 10.0, 2.3 Hz, 1H), 3.30 (m, 1H), 2.01 (m, *J* = 3.5, 1.7 Hz, 2H), 1.97 – 1.87 (m, 1H), 1.64 (m, 1H), 1.59 – 1.50 (m, 1H), 1.43 (m, 1H).

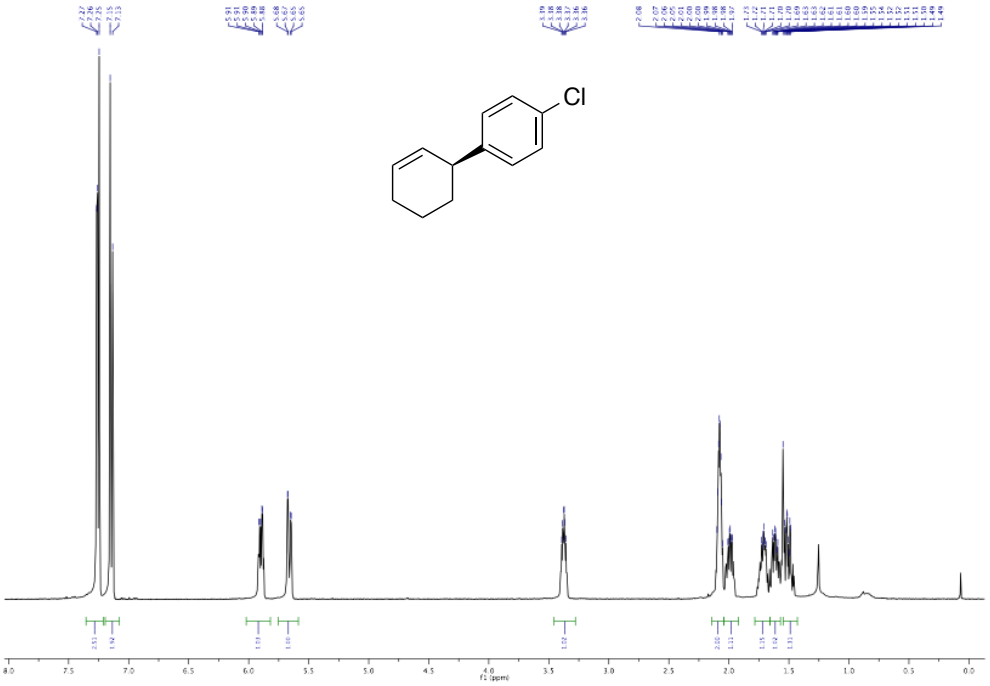
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 145.3, 131.8, 129.8, 129.3 (2C), 129.0, 128.6 (2C), 41.4, 32.8, 25.2, 21.2.

**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{13}Cl$ $[M]^+$: 192.0706, found: 192.0708.

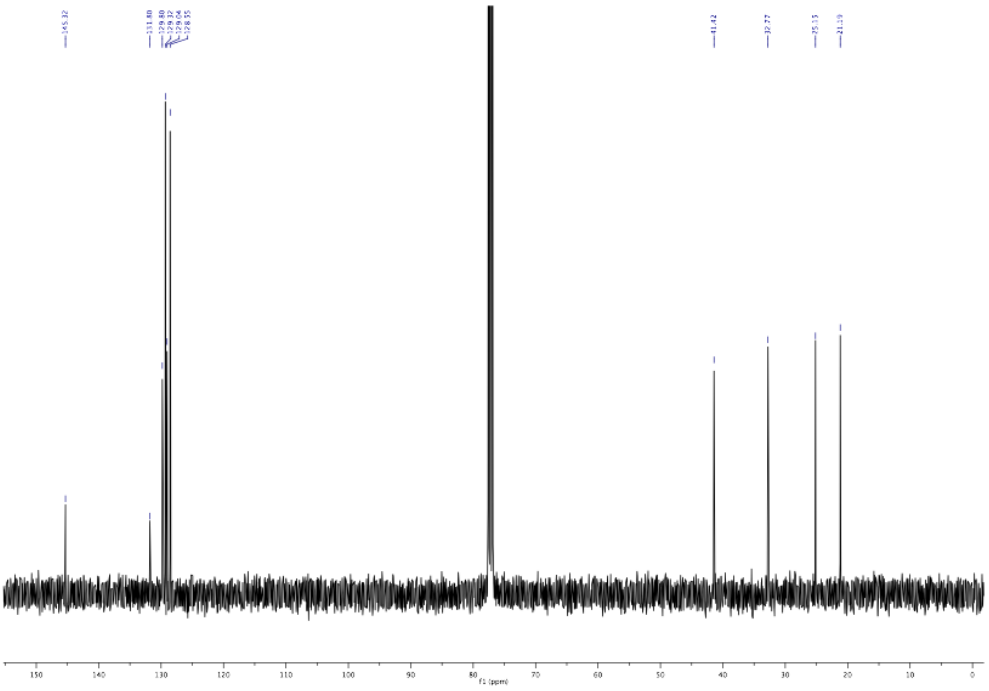
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1091, 1489, 2836, 2858, 2930, 3020.

**$[\alpha]^{20}_{589}$** = –139.0 (c 1.45 $CHCl_3$) for >99% ee.

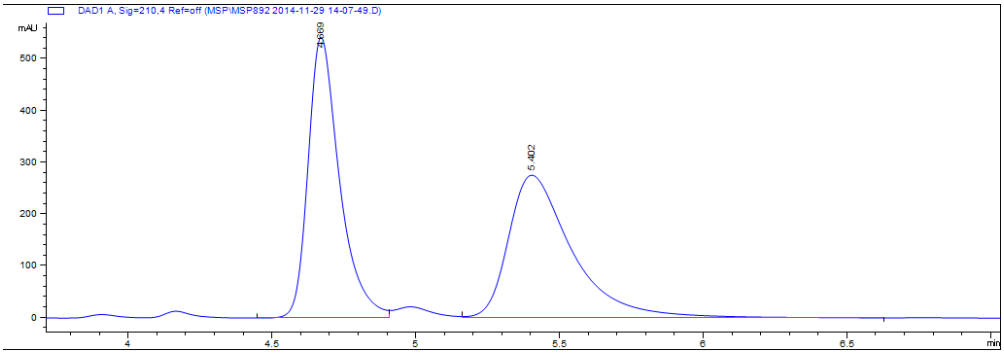
**$^1$H NMR:**

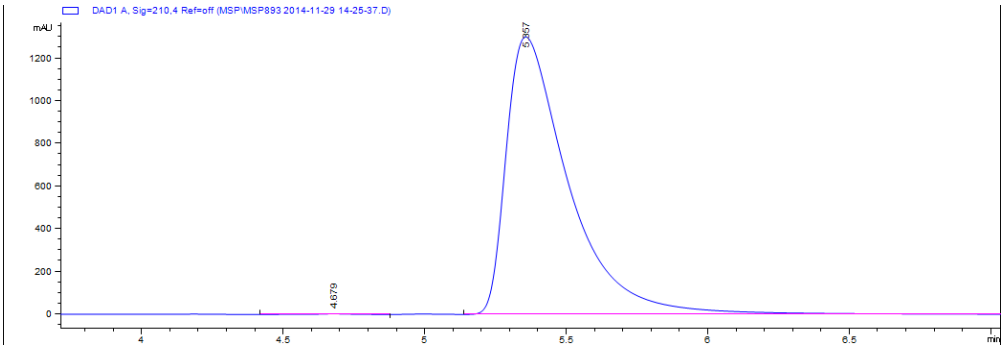



**$^{13}$C NMR:**

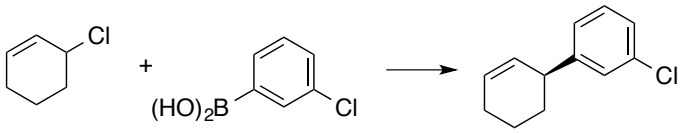


**HPLC traces:**




**(–)-(*S*)-3-(3-Chlorophenyl)cyclohexene 11**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 3-chlorophenylboronic acid (125.1 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 70% yield (54.0 mg, 0.28 mmol) as a colorless oil.

Enantiomeric excess of 99% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane 100; λ = 210 nm; major enantiomer $t_R$ = 4.9 min; minor enantiomer $t_R$ = 6.6 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.25 – 7.14 (m, 3H), 7.10 (dt, *J* = 7.2, 1.6 Hz, 1H), 5.92 (dq, *J* = 9.8, 2.3 Hz, 1H), 5.76 – 5.54 (m, 1H), 3.38 (m, 1H), 2.18 – 1.94 (m, 3H), 1.73 (m, 1H), 1.68 – 1.45 (m, 2H).

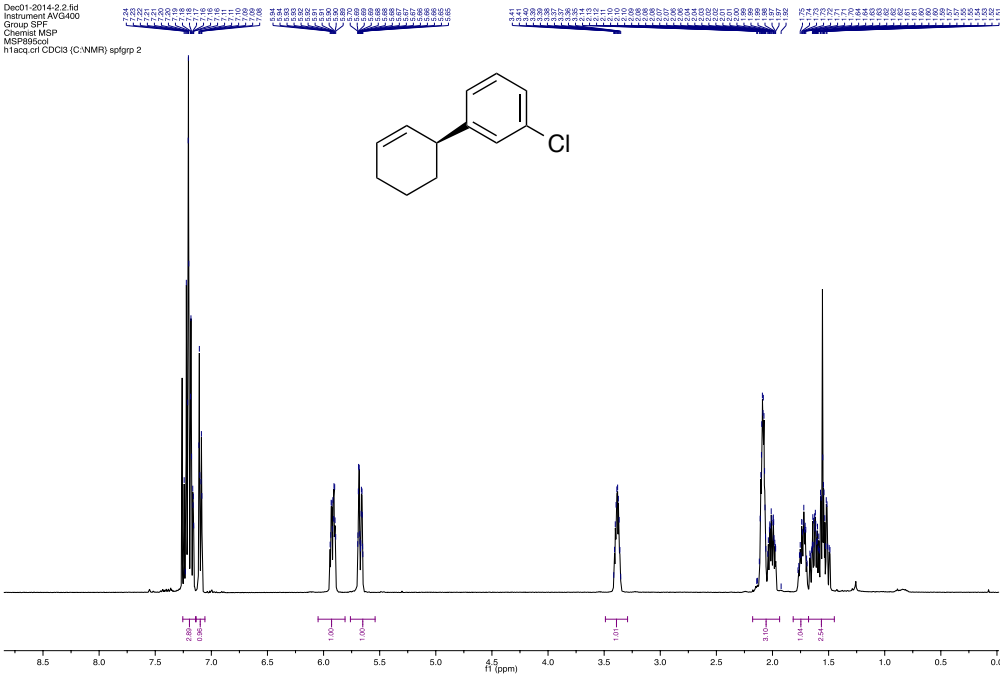
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 148.9, 134.2, 129.6, 129.4, 129.2, 128.0, 126.3, 126.1, 41.7, 32.6, 25.1, 21.1.

**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{13}Cl$ $[M]^+$: 192.0706, found: 192.0708.

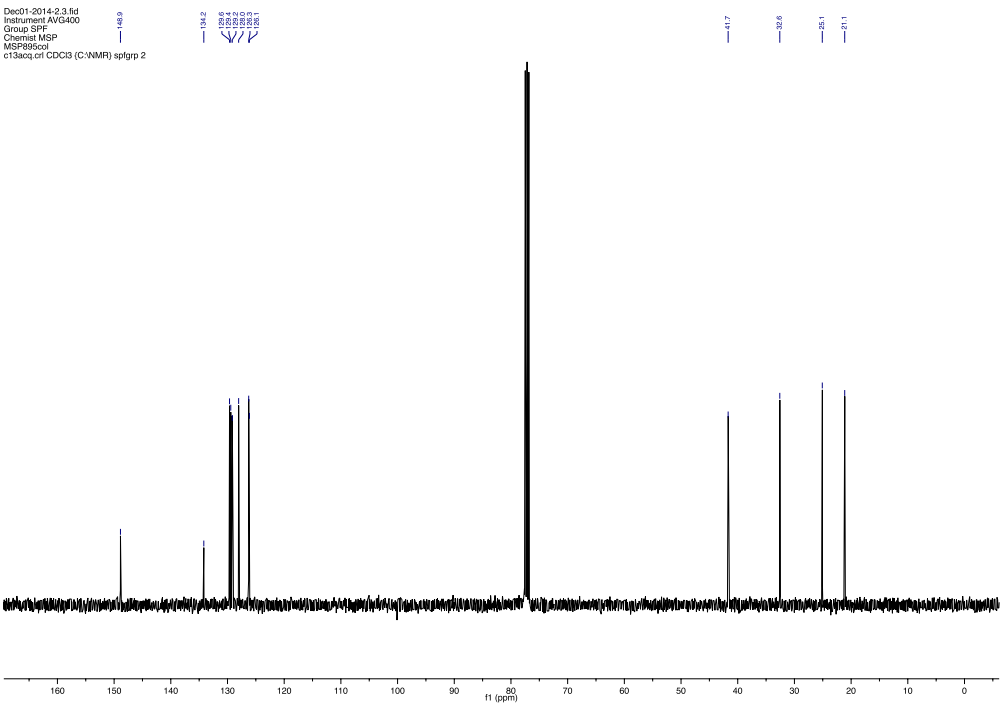
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1096, 1475, 1650, 2836, 2857, 2930, 3020, 3059.

**$[\alpha]^{20}_{589}$** = −132.2 (c 1.18 $CHCl_3$) for 99% ee.

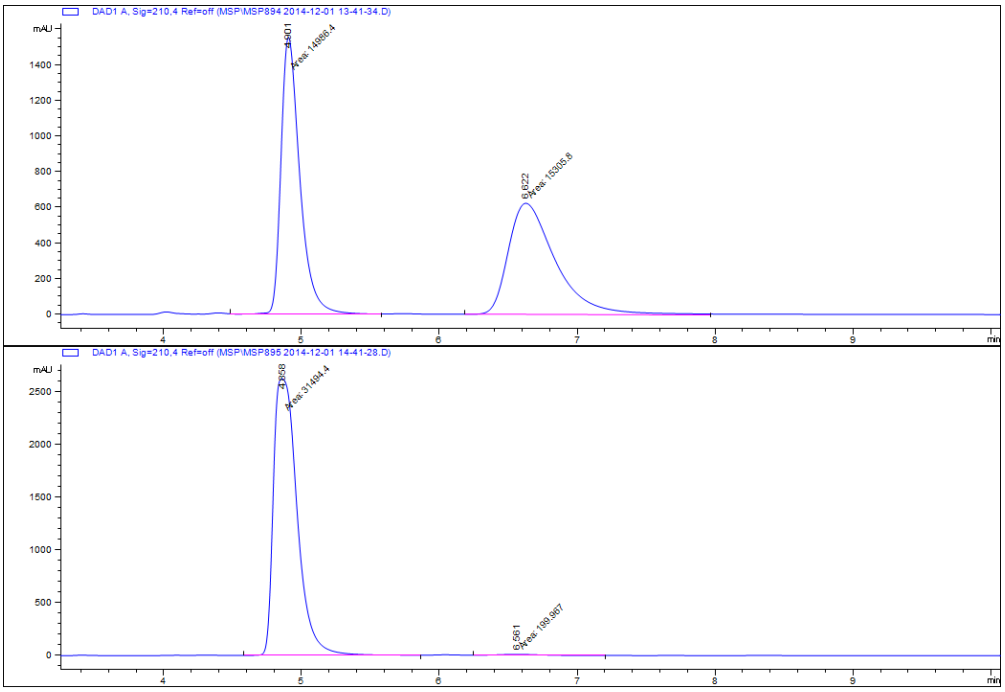
**$^1$H NMR:**



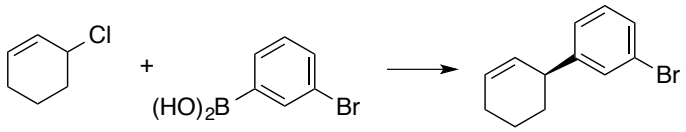

**$^{13}$C NMR:**



**HPLC traces:**



**(–)-(*S*)-3-(3-Bromophenyl)cyclohexene 12**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 3-bromophenylboronic acid (125.1 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded into a chromatographic column eluting with hexane to obtain the pure product in 56% yield (53.0 mg, 0.22 mmol) as a colorless oil.

Enantiomeric excess of 96% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane 100; λ = 210 nm; major enantiomer $t_R$ = 5.1min; minor enantiomer $t_R$ = 7.6 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.25 – 7.15 (m, 3H), 7.10 (dt, *J* = 7.2, 1.6 Hz, 1H), 5.92 (dq, *J* = 9.8, 2.3 Hz, 1H), 5.76 – 5.59 (m, 1H), 3.38 (m, 1H), 2.20 – 1.94 (m, 3H), 1.73 (m, 1H), 1.69 – 1.45 (m, 2H).

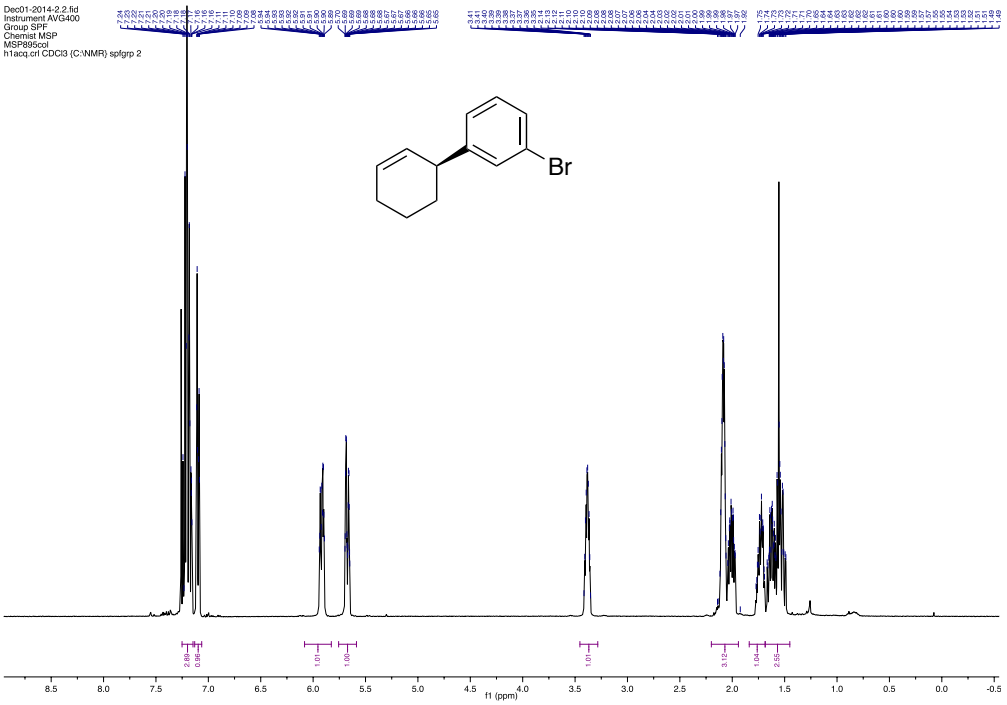
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 149.2, 131.0, 130.0, 129.4, 129.2 (2C), 126.6, 122.5, 41.7, 32.6, 25.1, 21.1.

**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{13}Br$ $[M]^+$: 236.0208, found: 236.0203.

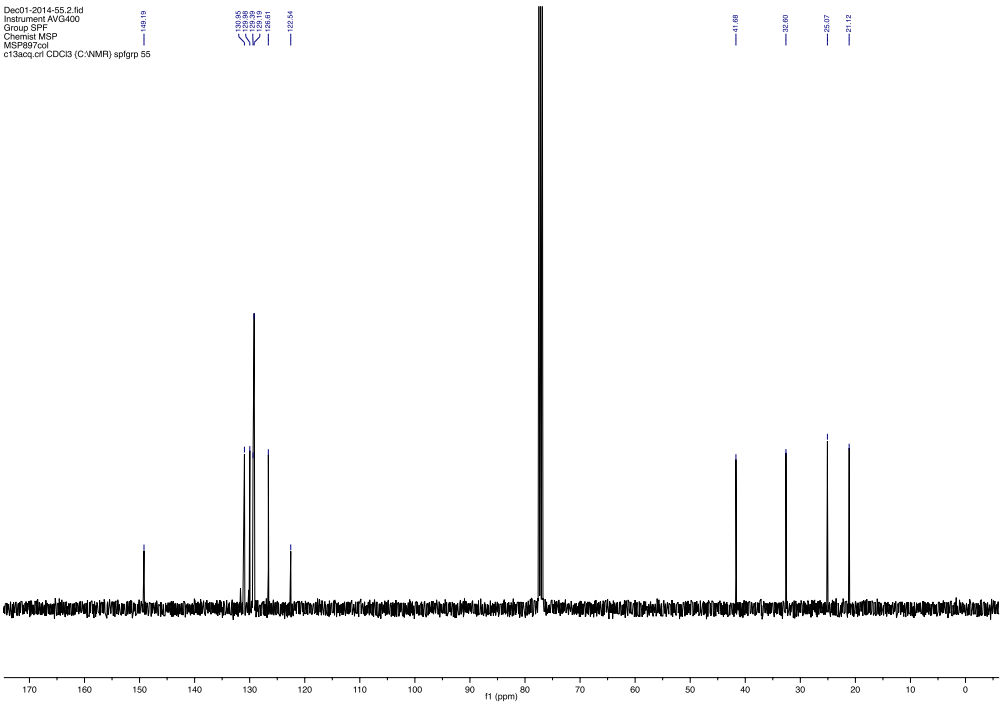
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1096, 1477, 1651, 2835, 2857, 2930, 3020, 3057.

**$[\alpha]^{20}_{589}$** = –104.5 (c 1.17 $CHCl_3$) for 96% ee.

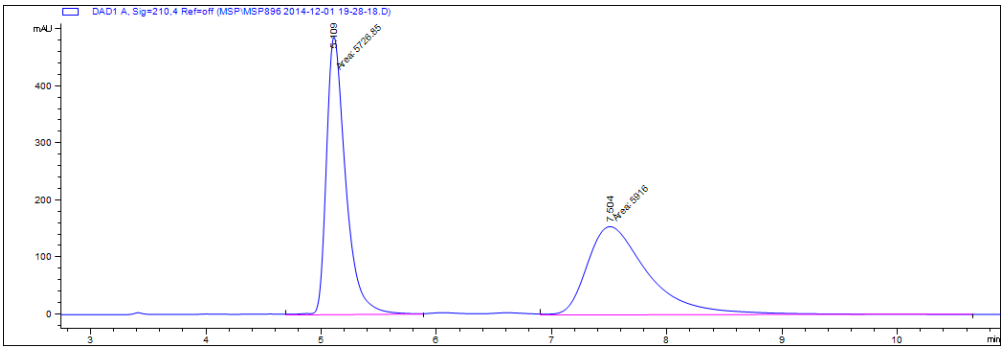
**$^{1}$H NMR:**

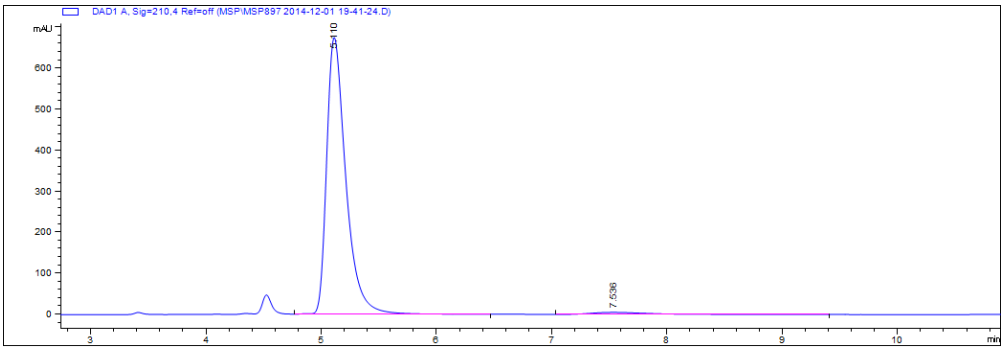



**$^{13}$C NMR:**

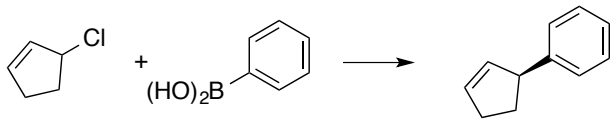


**HPLC traces:**




**(–)-(*S*)-Cyclopent-2-enylbenzene 13**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of phenylboronic acid (97.5 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclopentene (52 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 4 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 67% yield (38.0 mg, 0.27 mmol) as a colorless oil.

Enantiomeric excess of >99% was determined by HPLC [Chiralpak® ID; flow: 0.6 mL/min; hexane 100; λ = 210 nm; major enantiomer $t_R$ = 8.0 min; minor enantiomer $t_R$ = 8.5 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.36 – 7.24 (m, 3H), 7.24 – 7.12 (m, 2H), 5.94 (m, 1H), 5.79 (m, 1H), 4.02 – 3.79 (m, 1H), 2.61 – 2.28 (m, 3H), 1.81 – 1.65 (m, 1H).

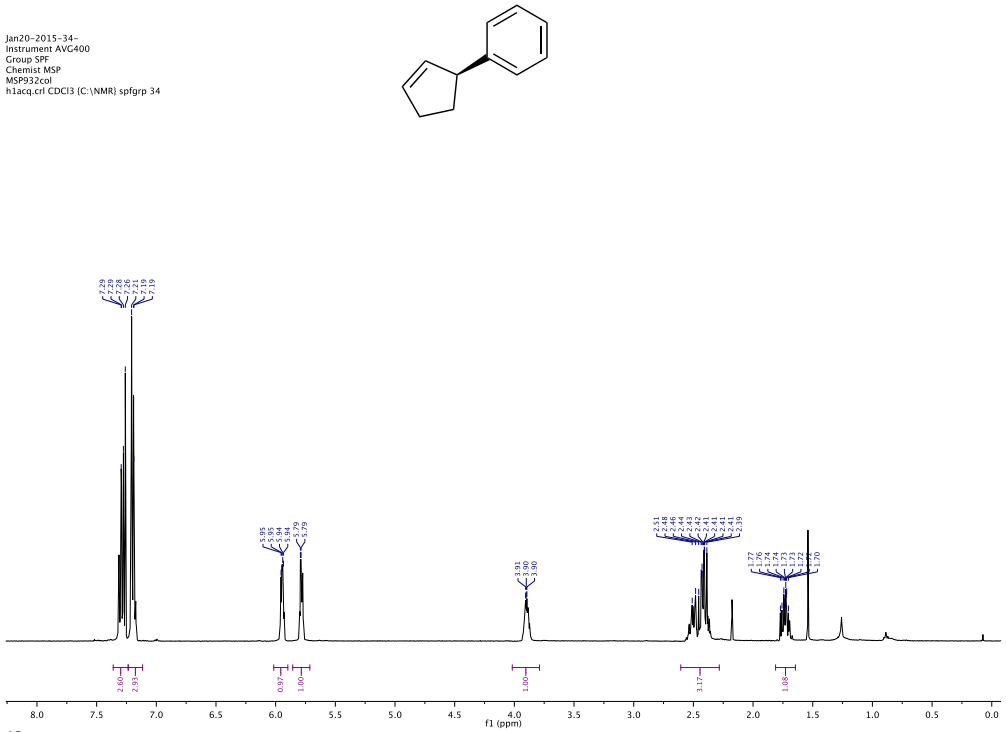
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 146.7, 134.4, 132.1, 128.5 (2C), 127.4 (2C), 126.1, 51.5, 34.0, 32.7.

**HRMS** (EI/FI) *m*/z calcd for $C_{11}H_{12}$ $[M]^+$: 144.0939, found: 144.0932.

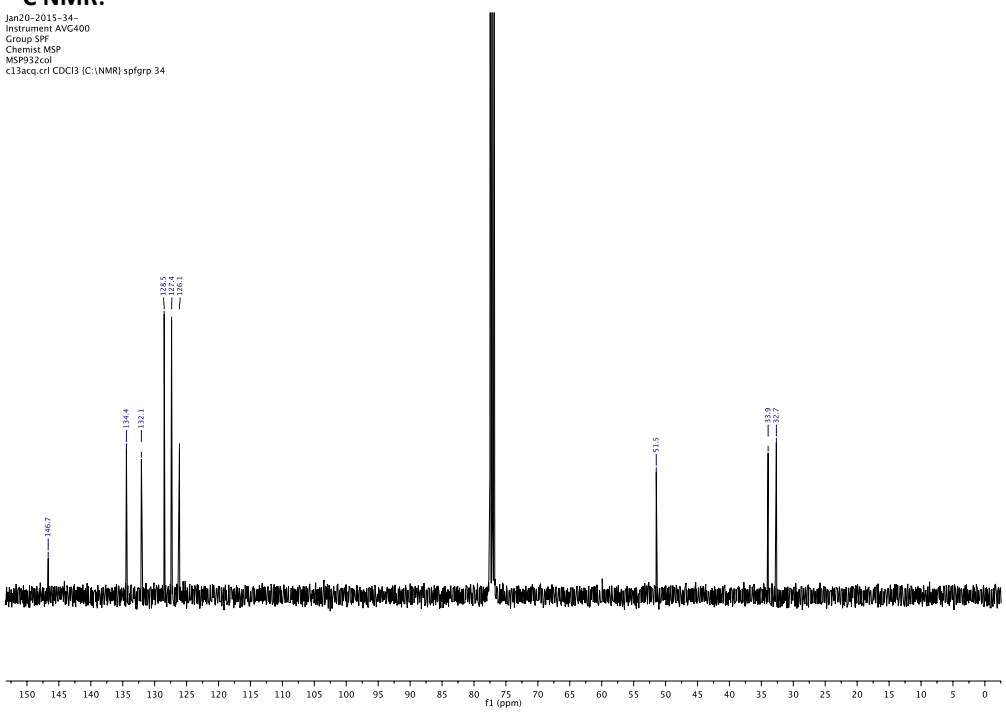
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1376, 1735, 2856, 2926.

**$[\alpha]^{20}_{589}$** = –35.0 (c 1.0 $CHCl_3$) for 80% ee.

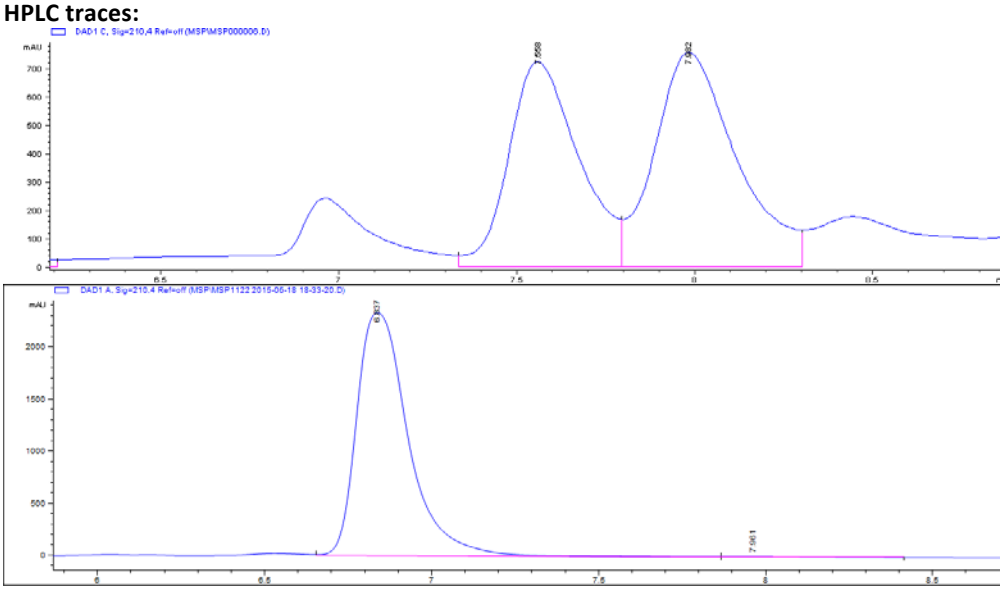
**$^1$H NMR:**



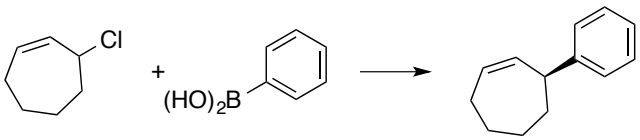

**$^{13}$C NMR:**



**HPLC traces:**



**(–)-(*S*)-Cyclohept-2-enylbenzene 14**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of phenylboronic acid (97.5 mg, 0.80 mmol, 2.00 eq) and 3-chlorocycloheptene (52 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 62% yield (43.0 mg, 0.25 mmol) as a colorless oil.

Enantiomeric excess of 97% was determined by HPLC [Chiralpak® ID; flow: 0.6 mL/min; hexane 100; λ = 210 nm; major enantiomer $t_R$ = 8.6 min; minor enantiomer $t_R$ = 9.3 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.38 – 7.14 (m, 5H), 5.88 (m, 1H), 5.79 (m, 1H), 3.55 (m, 1H), 2.36 – 2.18 (m, 2H), 1.97 (m, 1H), 1.90 – 1.62 (m, 4H), 1.48 (m, 1H).

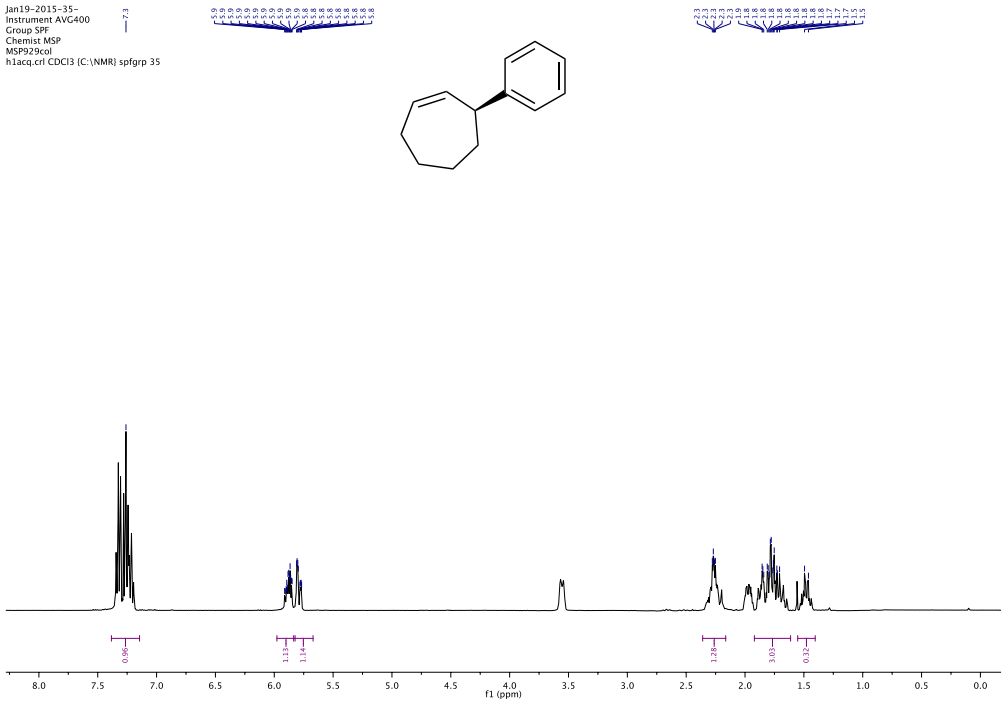
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 148.1, 137.2, 131.8, 128.6 (2C), 127.4 (2C), 125.9, 47.3, 36.4, 30.4, 29.0, 27.2.

**HRMS** (EI/FI) *m*/z calcd for $C_{13}H_{16}$ $[M]^+$: 172.1252, found: 172.1253.

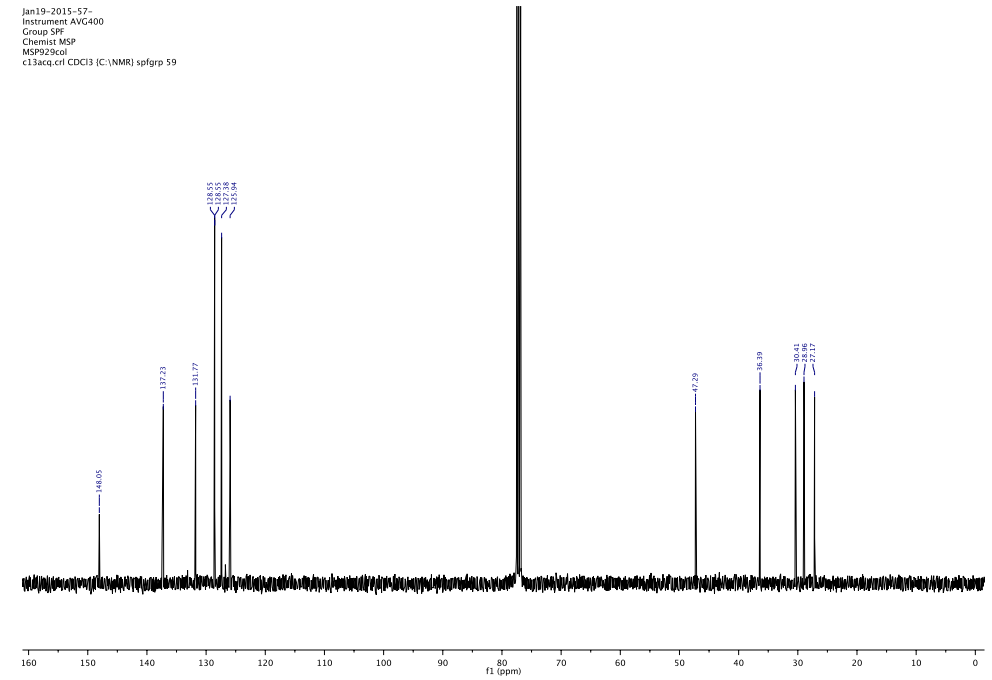
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1445, 1492, 2852, 2920, 3024.

**$[\alpha]^{20}_{589}$** = –26.7 (c 0.82 $CHCl_3$) for 80% ee.

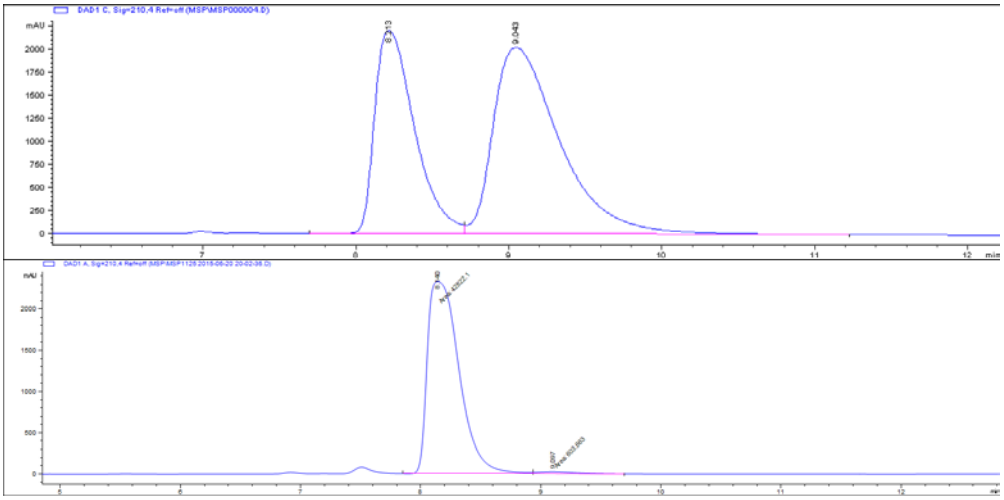
**$^{1}$H NMR:**



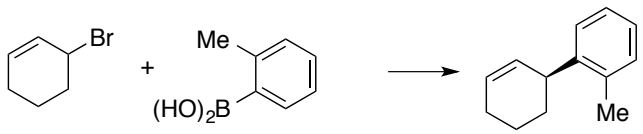

**$^{13}$C NMR:**



**HLC traces:**



**(–)-(*S*)-3-(2-Methylphenyl)cyclohexene 15**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 2-methylphenylboronic acid (108.8 mg, 0.80 mmol, 2.00 eq) and 3-bromocyclohexene (46 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 45% yield (30.3 mg, 0.18 mmol) as a colorless oil.

Enantiomeric excess of >99% was determined by HPLC [Chiralpak® ID; flow: 0.7 mL/min; hexane 100; λ = 210 nm; minor enantiomer $t_R$ = 6.1 min; major enantiomer $t_R$ = 6.5 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.26 – 7.00 (m, 4H), 5.93 (dq, *J* = 9.9, 2.4 Hz, 1H), 5.68 (dd, *J* = 10.1, 2.5 Hz, 1H), 3.63 (m, 1H), 2.36 (s, 3H), 2.16 – 2.05 (m, 2H), 2.05 – 1.94 (m, 1H), 1.75 (m, 1H), 1.69 – 1.58 (m, 1H), 1.48 (m, 1H).

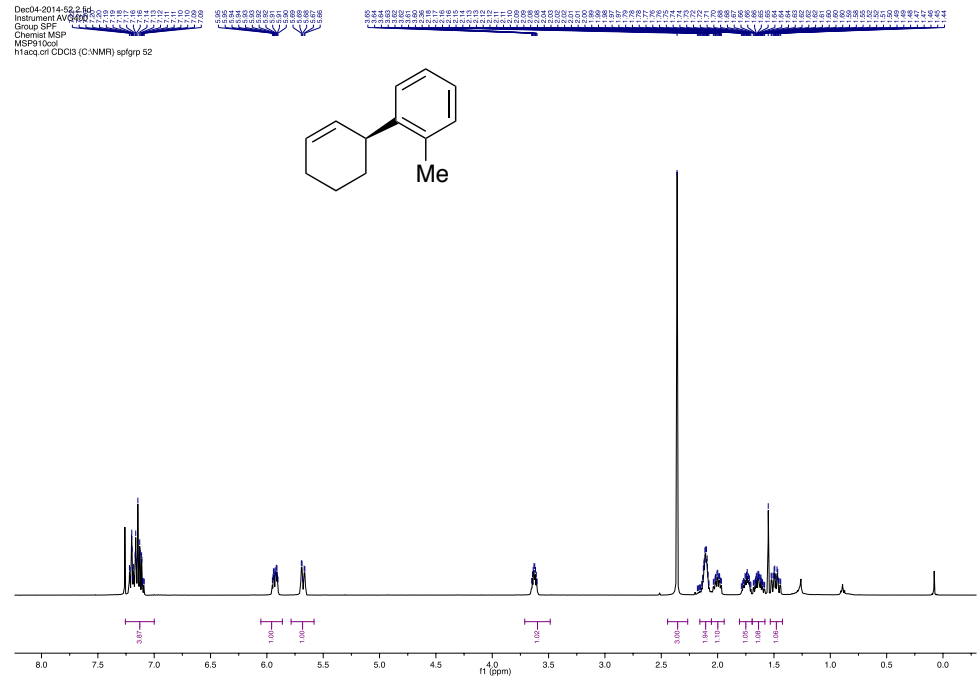
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 144.5, 135.6, 130.6, 130.4, 128.5, 127.7, 126.1, 126.0, 37.9, 30.7, 25.2, 21.3, 19.4.

**HRMS** (ESI) *m*/z calcd for $C_{13}H_{16}$ $[M]^+$: 172.1252, found: 172.1255.

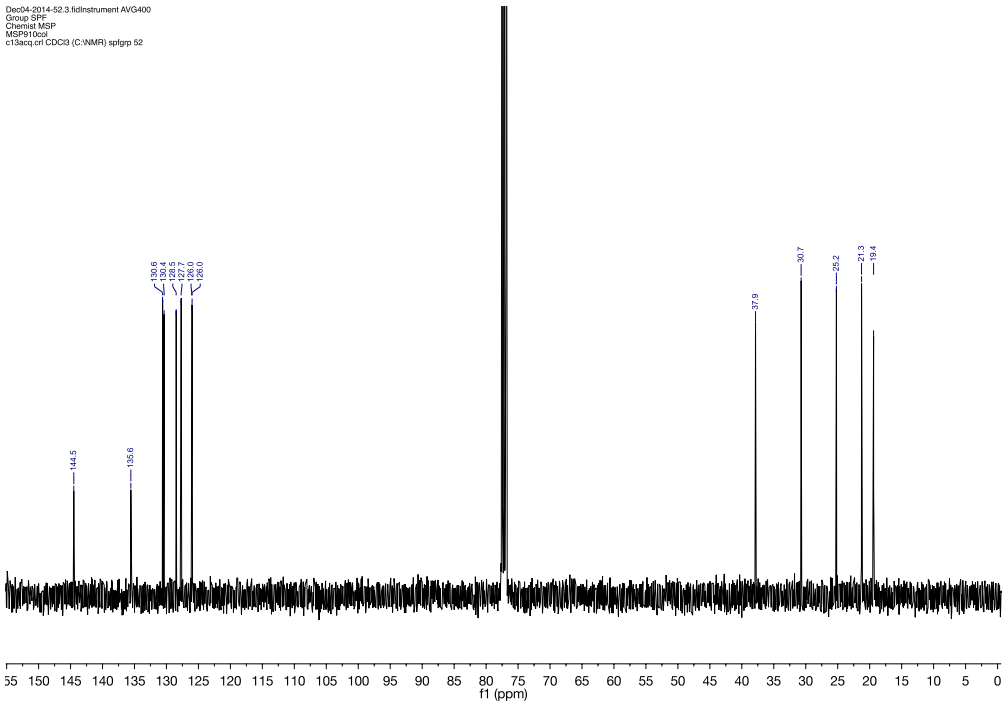
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1487, 2856, 2929, 3019, 3061.

**$[\alpha]^{20}_{589}$** = –47.5 (c 0.97 $CHCl_3$) for >99% ee.

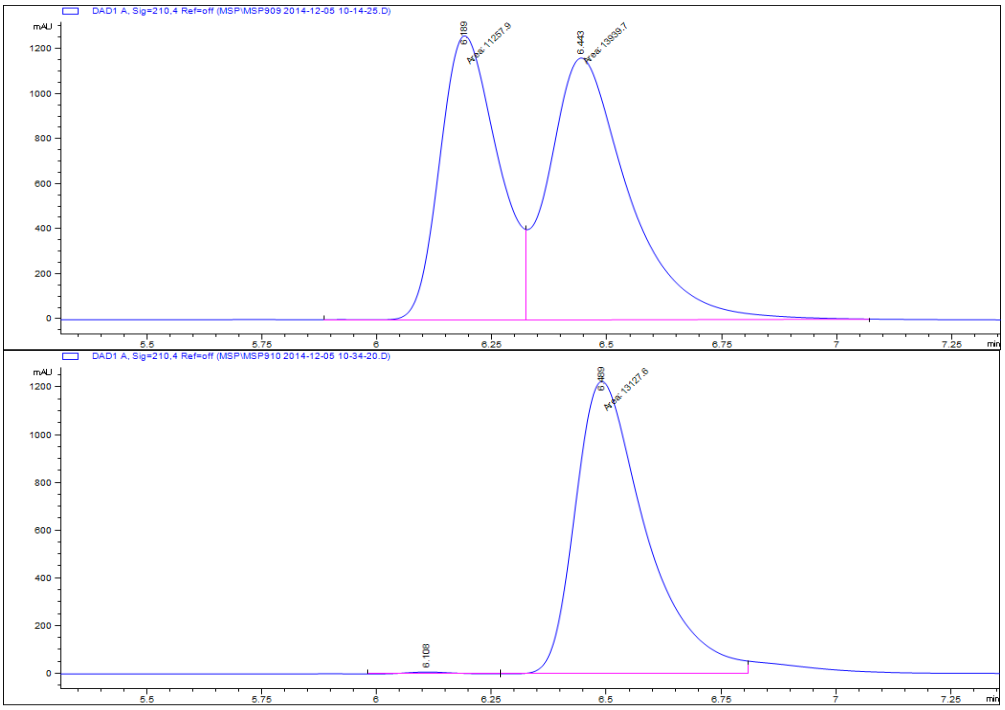
**$^1$H NMR:**



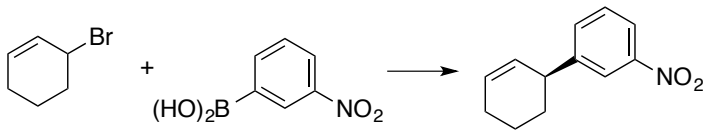

**$^{13}$C NMR:**




**HPLC traces:**




**(–)-(*S*)-3-(3-Nitrophenyl)cyclohexene 16**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 3-nitrophenylboronic acid (125.1 mg, 0.80 mmol, 2.00 eq) and 3-bromocyclohexene (46 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with hexane:EtOAc (92:8) to obtain the pure product in 51% yield (41.4 mg, 0.20 mmol) as a colorless oil.

Enantiomeric excess of 96% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 99:1 100; λ = 210 nm; major enantiomer $t_R$ = 5.5 min; minor enantiomer $t_R$ = 5.8 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 8.11 – 7.99 (m, 2H), 7.55 (m, 1H), 7.45 (m, 1H), 5.98 (dq, *J* = 9.9, 2.3 Hz, 1H), 5.68 (dq, *J* = 10.1, 2.4 Hz, 1H), 3.52 (m, 1H), 2.16 – 2.00 (m, 3H), 1.79 – 1.47 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 148.8, 148.5, 134.3, 130.1, 129.3, 128.6, 122.8, 121.3, 41.6, 32.6, 25.0, 20.9.

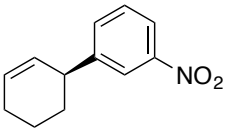
**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{13}NO_2$ $[M]^+$: 203.0946, found: 203.0947.

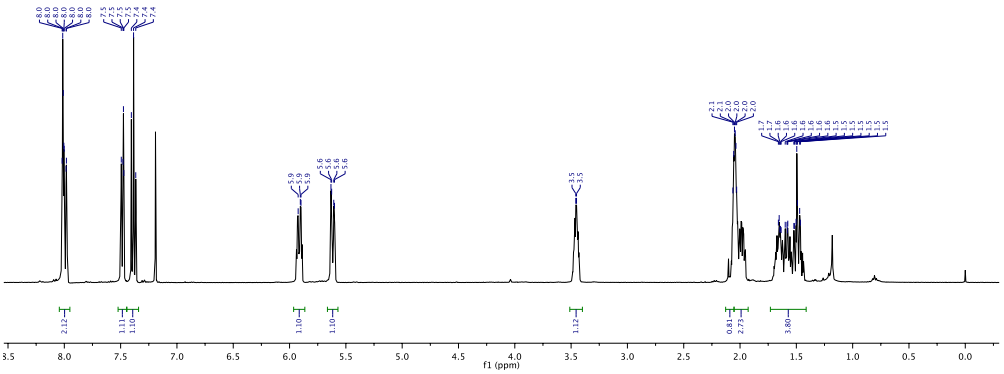
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1350, 1529, 2930, 3054.

**[α]$^{20}_{589}$** = –78.1 (c 0.24 $CHCl_3$) for 96% ee.

**$^1$H NMR:**

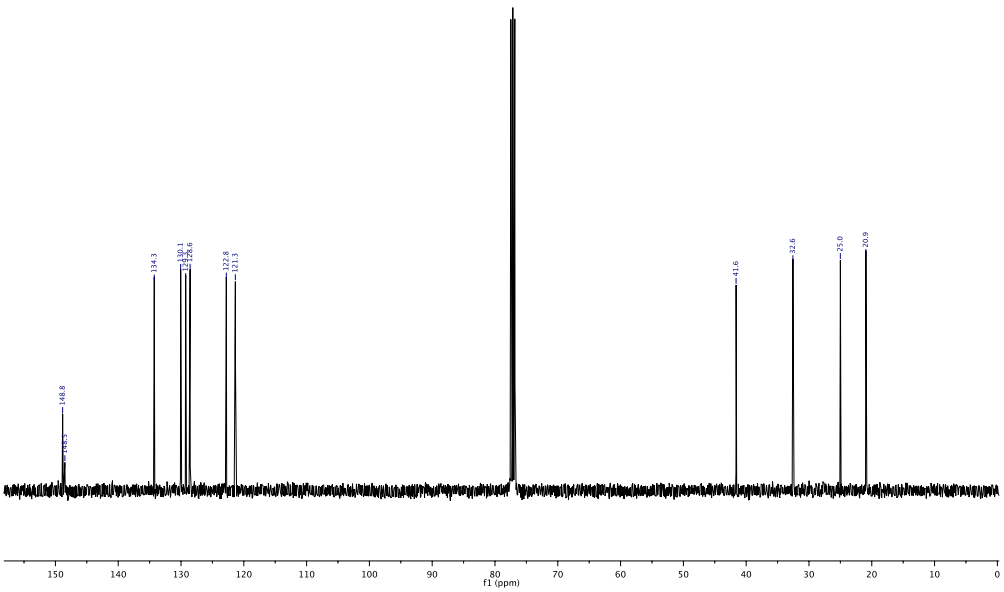
Jan16-2015-59-
Instrument AVG400
Group SPF
Chemist MSP
MSP898col3
h1acq.crl CDCl3 {C:\NMR} spfgrp 59



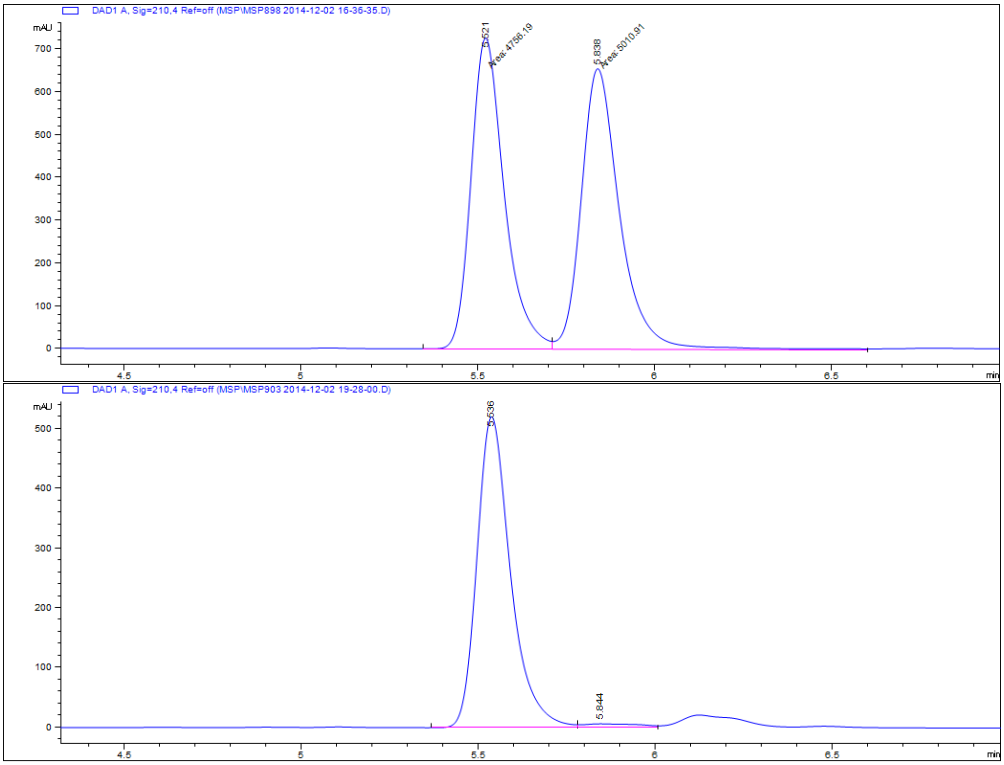




**$^{13}$C NMR:**

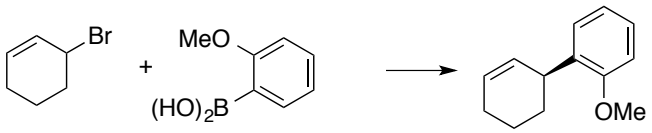
Jan16-2015-59-
Instrument AVG400
Group SPF
Chemist MSP
MSP898col3
c13acq.crl CDCl3 {C:\NMR} spfgrp 59



**HPLC traces:**




**(–)-(*S*)-3-(2-Methoxyphenyl)cyclohexene 17**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 2-methoxyphenylboronic acid (150.6 mg, 0.80 mmol, 2.00 eq) and 3-bromocyclohexene (46 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 80% yield (60.2 mg, 0.32 mmol) as a colorless oil.

Enantiomeric excess of 74% was determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane 100; λ = 210 nm; minor enantiomer $t_R$ = 6.2 min; major enantiomer $t_R$ = 6.9 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.25 – 7.02 (m, 4H), 5.93 (dq, *J* = 9.9, 2.4 Hz, 1H), 5.68 (dd, *J* = 10.1, 2.5 Hz, 1H), 3.63 (m, 1H), 2.36 (s, 3H), 2.19 – 2.07 (m, 2H), 2.07 – 1.90 (m, 1H), 1.75 (m, 1H), 1.70 – 1.57 (m, 1H), 1.48 (m, 1H).

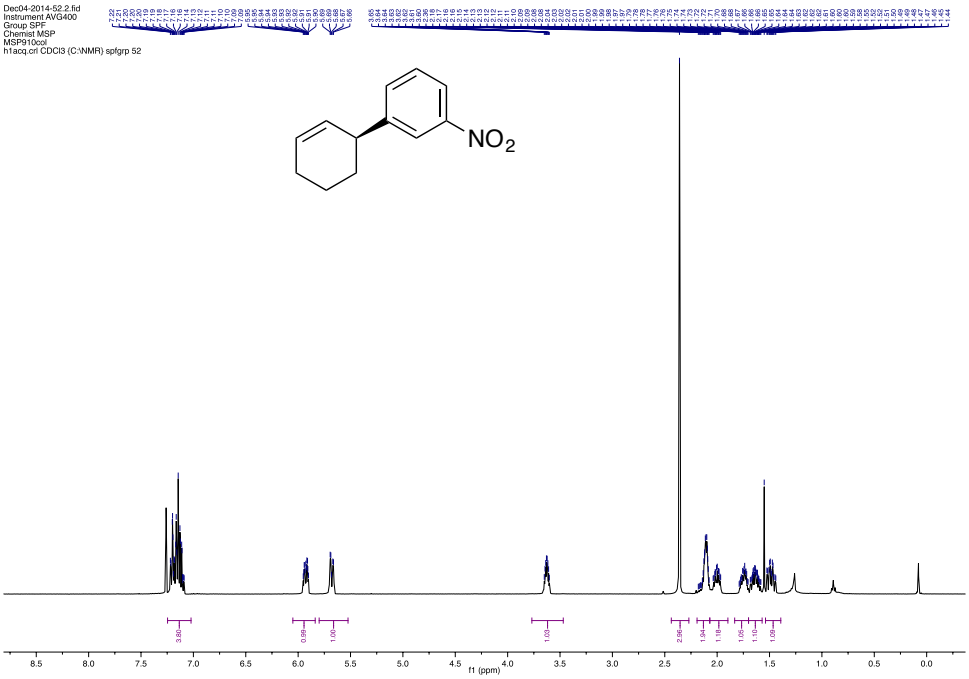
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta_C$ /ppm: 144.4, 135.6, 130.6, 130.4, 128.5, 127.7, 126.1, 126.0, 37.9, 30.7, 25.2, 21.3, 19.4.

**HRMS** (EI/FI) *m*/z calcd for $C_{13}H_{16}O$ $[M]^+$: 188.1201, found:188.1204.

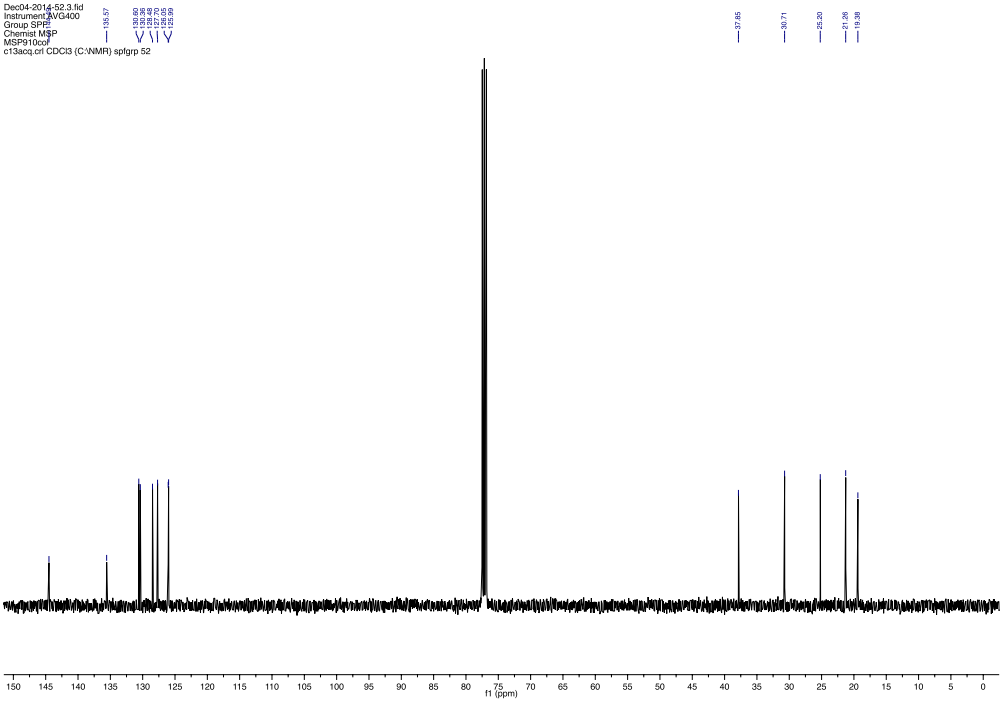
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1238, 1490, 2857, 2929, 3019.

**$[\alpha]^{20}_{589}$** = –41.2 (c 1.88 $CHCl_3$) for 74% ee.

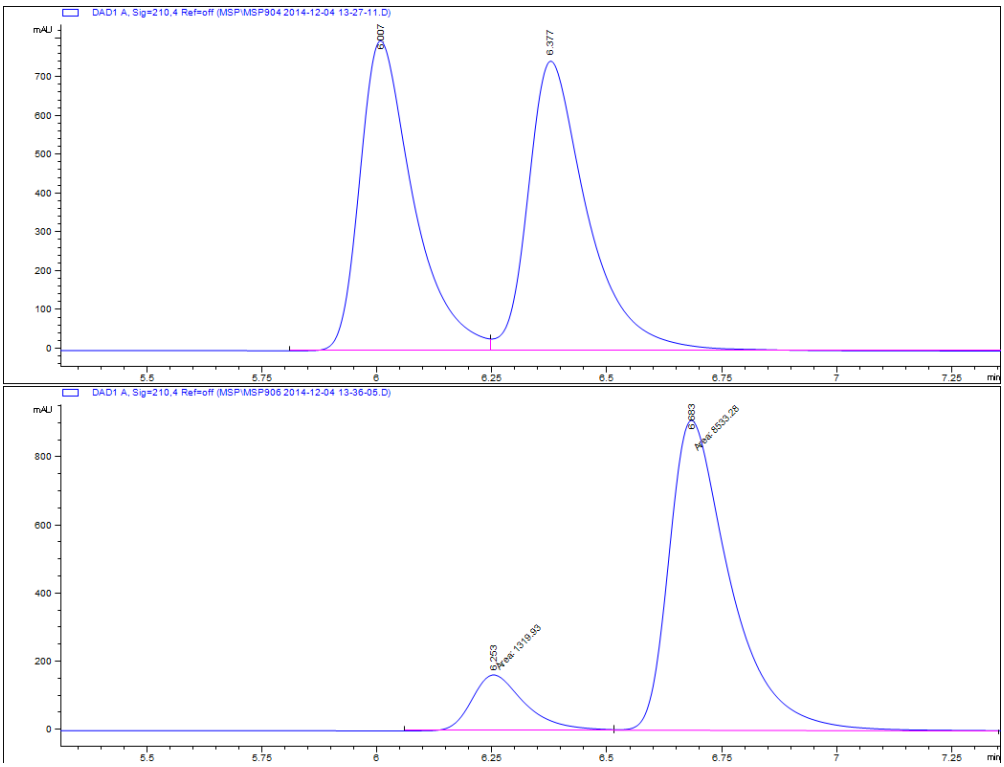
**$^1$H NMR:**



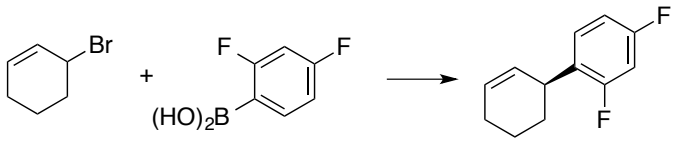
**$^{13}$C NMR:**




**HPLC traces:**



**(–)-(*S*)-3-(2,4-Difluorophenyl)cyclohexene 18**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 2,4-difluorophenylboronic acid (126.3 mg, 0.80 mmol, 2.00 eq) and 3-bromocyclohexene (46 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded into onto the top of a flash chromatography column. The column was eluted with pentane to obtain the pure product in 53% yield (41.2 mg, 0.21 mmol) as a colorless oil.

Enantiomeric excess of 92% was determined by HPLC [Chiralpak® ID; flow: 0.7 mL/min; hexane 100; λ = 210 nm; major enantiomer $t_R$ = 6.4 min; minor enantiomer $t_R$ = 6.8 min].

**$^1$H NMR** (500 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.18 (m, 1H), 6.89 – 6.72 (m, 2H), 5.94 (dq, *J* = 9.9, 3.4 Hz, 1H), 5.61 (dq, *J* = 10.1, 2.5 Hz, 1H), 3.71 (m, 1H), 2.15 – 1.91 (m, 3H), 1.77 – 1.45 (m, 3H).

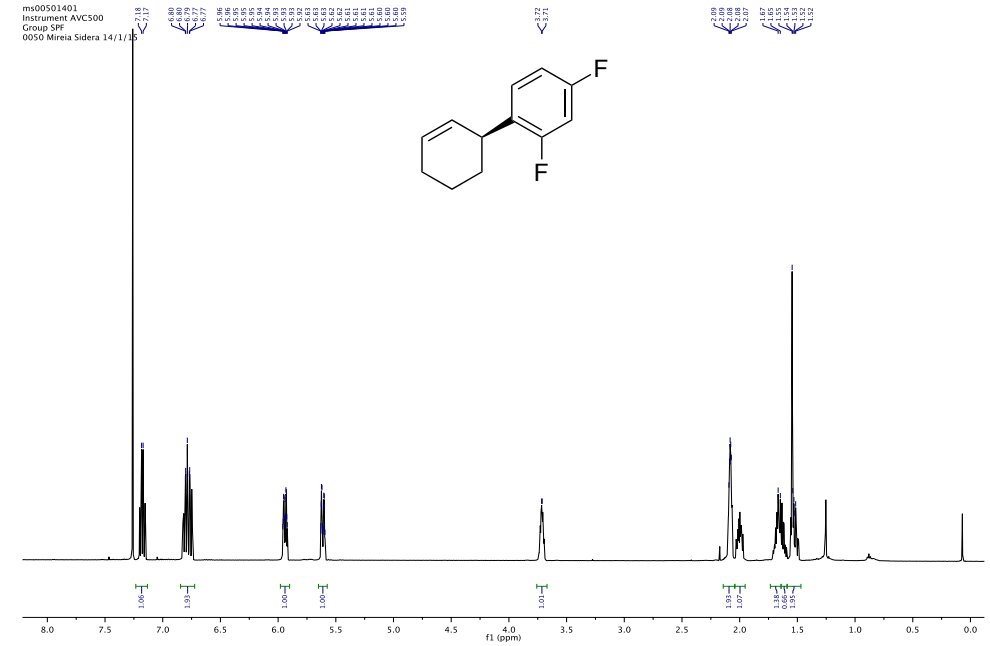
**$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta_C$ /ppm: 161.3 (dd, *J* = 246.1, 12.2 Hz), 160.5 (dd, *J* = 247.8, 11.7 Hz), 129.9 (dd, *J* = 9.4, 6.5 Hz), 129.4, 128.83 (dd, *J* = 14.8, 3.8 Hz), 128.6, 110.7 (dd, *J* = 20.6, 3.7 Hz), 103.5 (dd, *J* = 26.0, 25.3 Hz), 33.7 (d, *J* = 2.3 Hz), 30.6, 24.9, 20.7.

**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{12}F_2$ $[M]^+$: 194.0907, found: 194.0909.

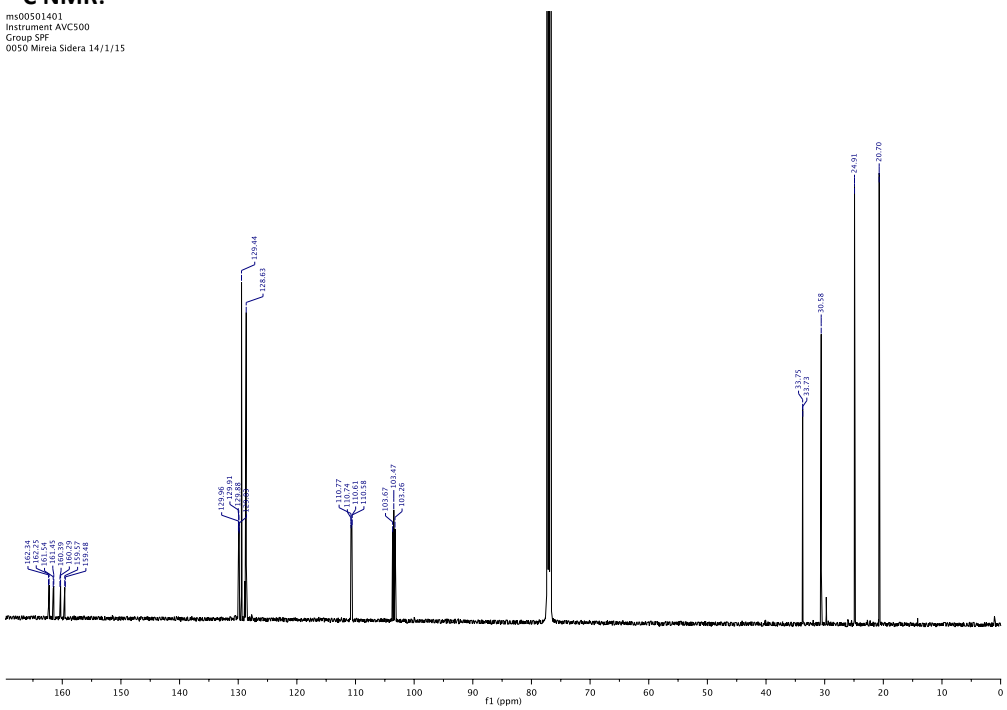
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1500, 2861, 2930, 3022.

**$[\alpha]^{20}_{589}$** = –73.5 (c 0.89 $CHCl_3$) for 92% ee.

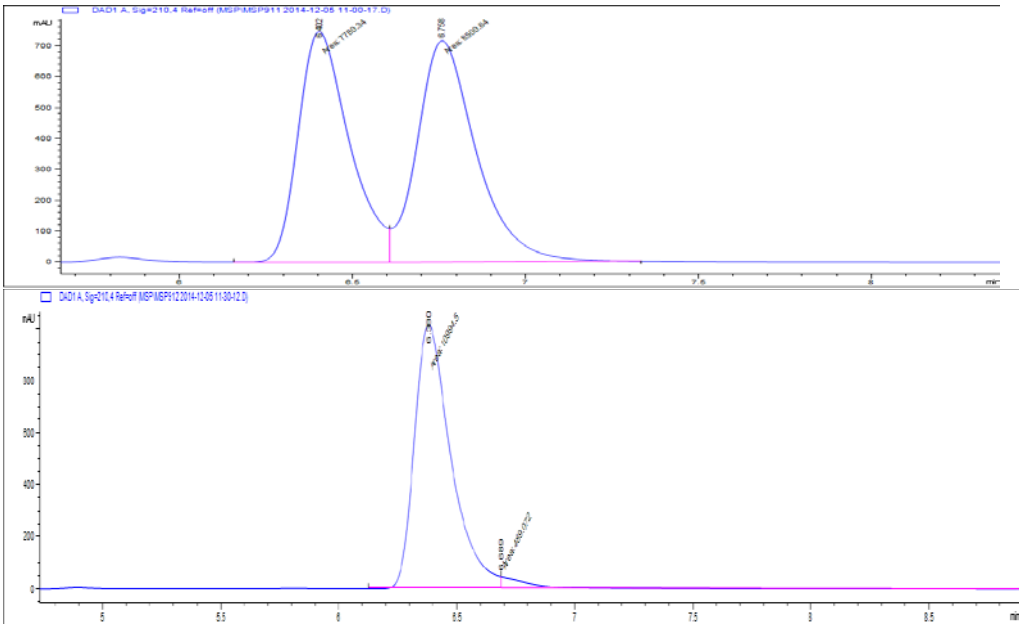
**$^{1}$H NMR:**



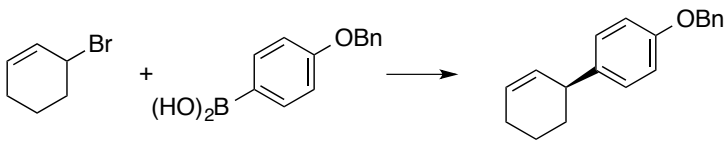

**$^{13}$C NMR:**



**HPLC traces:**



**(–)-(*S*)-3-(4-Benzyloxyphenyl)cyclohexene 19**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 4-benzyloxyphenylboronic acid (182.4 mg, 0.80 mmol, 2.00 eq) and 3-bromocyclohexene (46 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane 100% to obtain the pure product in 61% yield (64.8 mg, 0.24 mmol) as a colorless oil.

Enantiomeric excess of 84% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 99:1 100; λ = 210 nm; minor enantiomer $t_R$ = 4.4 min; major enantiomer $t_R$ = 5.0 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.50 – 7.40 (m, 4H), 7.30 (s, 1H), 7.19 (s, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.95 – 5.86 (m, 1H), 5.73 (m, 1H), 5.08 (s, 2H), 3.39 (m, 1H), 2.15 – 2.07 (m, 2H), 2.07 – 1.99 (m, 1H), 1.76 (m, 1H), 1.70 – 1.52 (m, 2H).

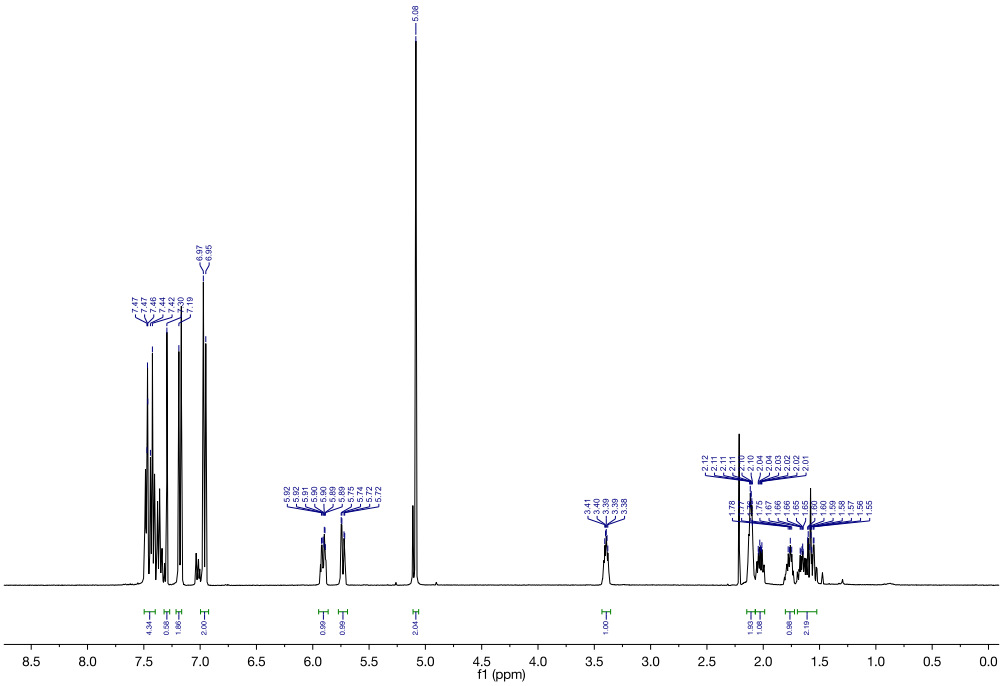
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 157.3, 139.2, 137.4, 130.6, 128.8 (2C), 128.7 (2C), 128.3, 128.0, 127.6 (2C), 114.7 (2C), 70.2, 41.1, 32.9, 25.2, 21.3.

**HRMS** (EI/FI) *m*/z calcd for $C_{19}H_{20}O$ $[M]^+$: 264.1514, found: 264.1518.

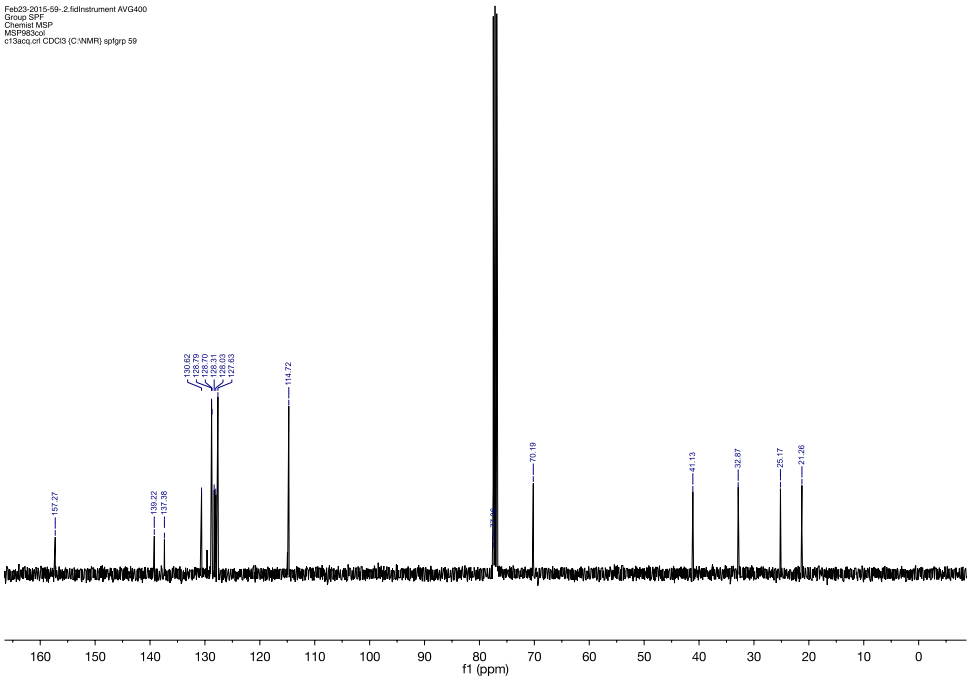
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 3020, 2929, 2857, 1509, 1238.

**$[\alpha]^{20}_{589}$** = – 103.1 (c 1.96 $CHCl_3$) for 84% ee.

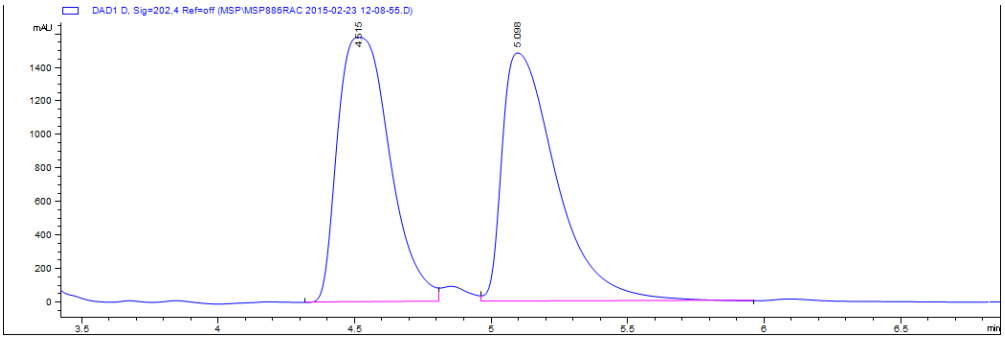
**$^1$H NMR:**

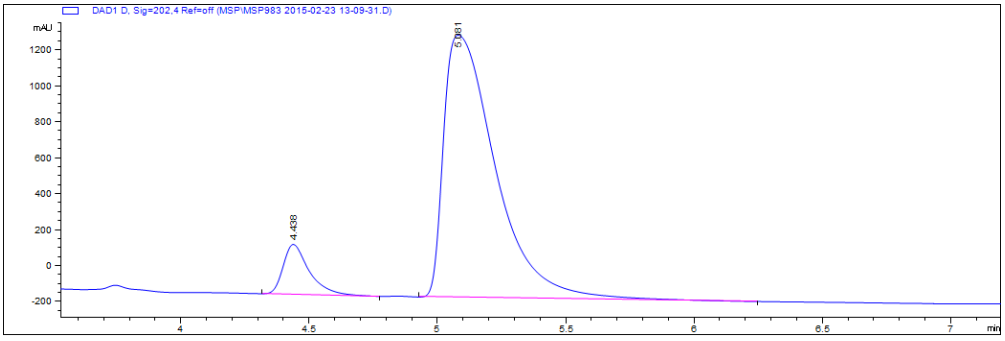



**$^{13}$C NMR:**

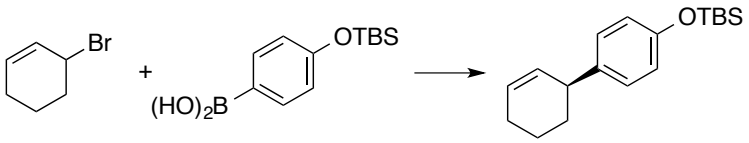



**HPLC traces:**



**(–)-(*S*)-3-(4-*tert*-Butyldimethylsilyloxyphenyl)cyclohexene 20**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of 4-*tert*-butyldimethylsilyloxyphenylboronic acid (201.8 mg, 0.80 mmol, 2.00 eq) and 3-bromocyclohexene (46 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto the top of a flash chromatography column. The column was eluted with pentane 100% to obtain the pure product in 40% yield (46.2 mg, 0.16 mmol) as a colorless oil.

Enantiomeric excess of 99% was determined by HPLC [Chiralpak® ID; flow: 1.0 mL/min; hexane:IPA 99.9:0.1 100; λ = 210 nm; minor enantiomer $t_R$ = 4.6 min; major enantiomer $t_R$ = 5.1 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.05 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 5.90 – 5.81 (m, 1H), 5.69 (m, 1H), 3.33 (m, 1H), 2.06 (m, 2H), 2.02 – 1.92 (m, 1H), 1.72 (m, 1H), 1.64 – 1.45 (m, 2H), 0.98 (s, 9H), 0.19 (s, 6H).

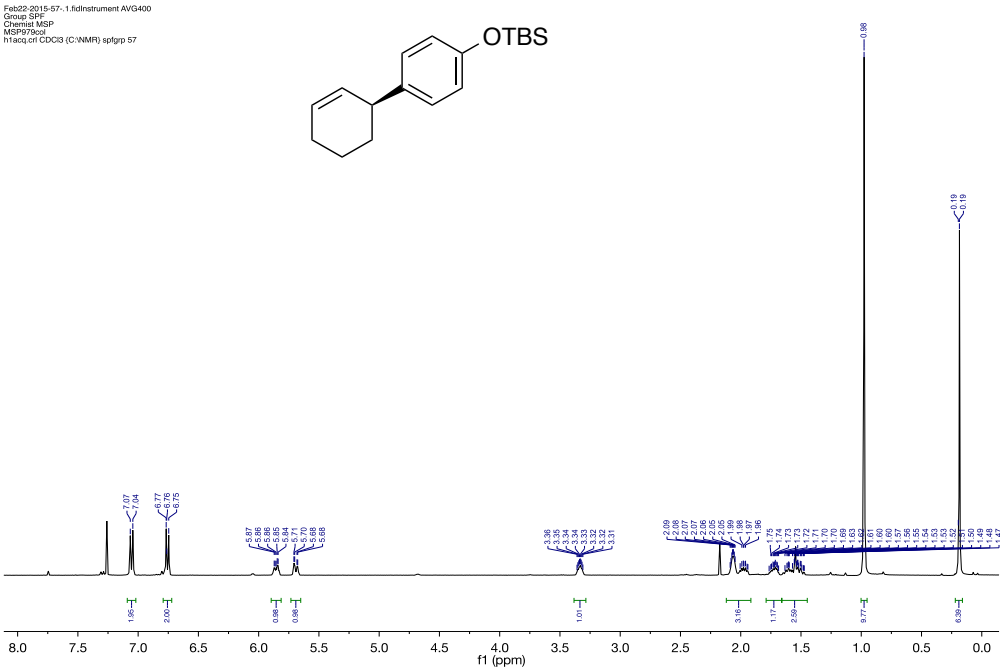
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 153.9, 139.4, 130.8, 128.7 (2C), 128.2, 119.8 (2C), 41.2, 32.9, 25.9 (3C), 25.2, 21.3, 18.3, -4.3 (2C).

**HRMS** (EI/FI) *m*/z calcd for $C_{18}H_{28}OSi$ $[M]^+$: 288.1909, found: 288.1909.

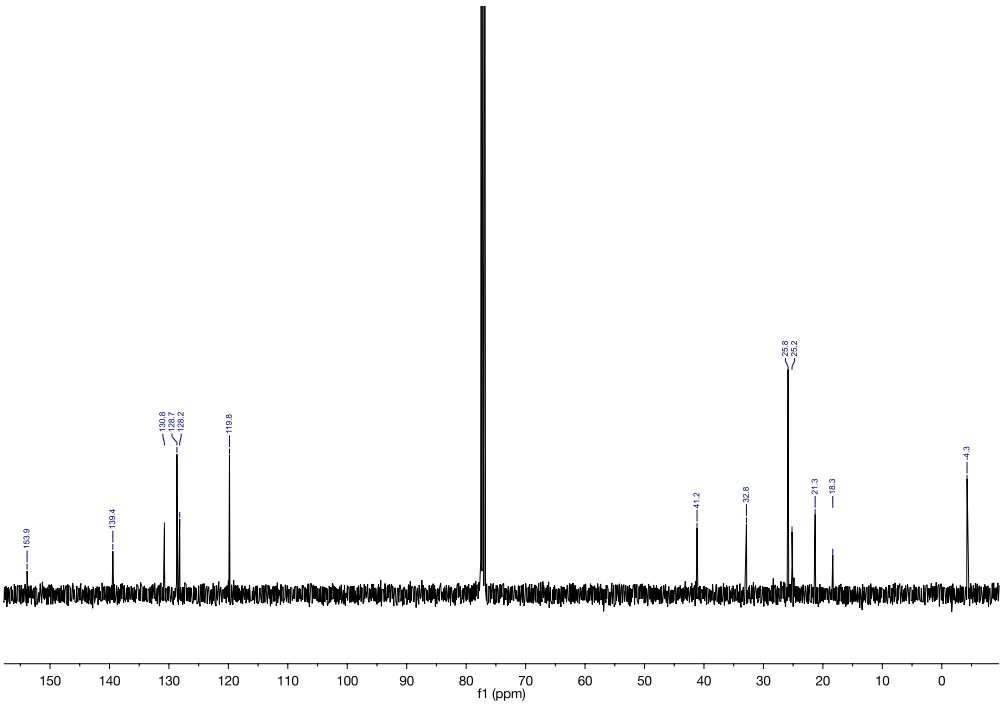
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 2955, 2930, 2858, 1509, 1256.

**$[\alpha]^{20}_{589}$** = – 17.6 (c 1.54 $CHCl_3$) for 99% ee.

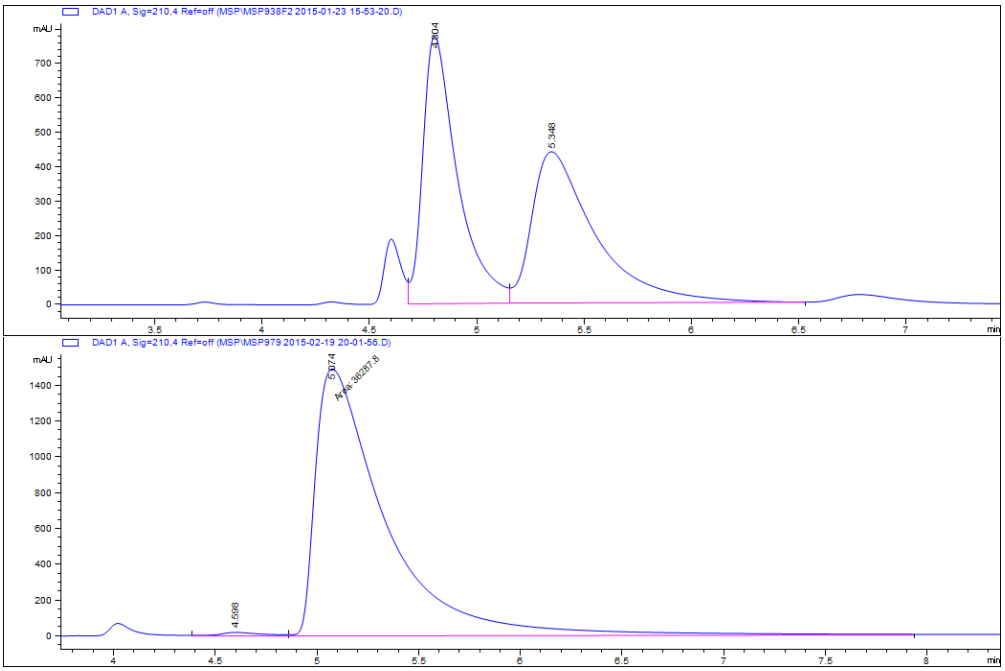
**$^{1}$H NMR:**



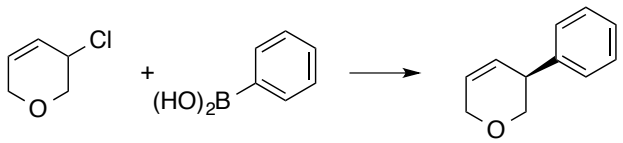

**$^{13}$C NMR:**



**HPLC traces:**




**(–)-(*S*)-3-Phenyl-3,6-dihydro-2*H*-pyran 21**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (6.8 mg, 0.015 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (27.2 mg, 0.036 mmol, 0.06 eq) and $Cs_2CO_3$ (195.5 mg, 0.60 mmol, 1.00 eq) were stirred in THF (3 mL) at 60 °C for 30 min. A solution of phenylboronic acid (146.3 mg, 1.20 mmol, 2.00 eq) and 3-chloro-3,6-dihydro-2*H*-pyran (71.1 mg, 0.60 mmol, 1.00 eq) in THF (2.0 mL) was then added *via* syringe and the flask rinsed with THF (1.0 mL). The resulting mixture was then stirred for 3 h at 60 °C before the addition of NaOH 2M (0.2 mL). The aqueous phase was extracted with $Et_2O$ (2 x 0.2 mL). The combined organic extracts were washed with water (0.4 mL), dried with $MgSO_4$, and filtered before adding $SiO_2$ (20 mg) and carefully concentrated under vacuum. The resulting solid was directly loaded into a column containing silica gel, and flash column chromatography (eluting with pentane:$Et_2O$ (95:5)) was used to obtain the pure product in 99% yield (92.0 mg, 0.59 mmol) as a colorless oil.

Enantiomeric excess of 96% was determined by HPLC [Chiralpak® ID; flow: 0.8 mL/min; hexane:iPA 98:2; λ = 210 nm; major enantiomer $t_R$ = 7.1 min; minor enantiomer $t_R$ = 7.5 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.38 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 5.94 (s, 2H), 4.23 (d, *J* = 2.1 Hz, 2H), 4.10 – 3.99 (m, 1H), 3.62 – 3.50 (m, 2H).

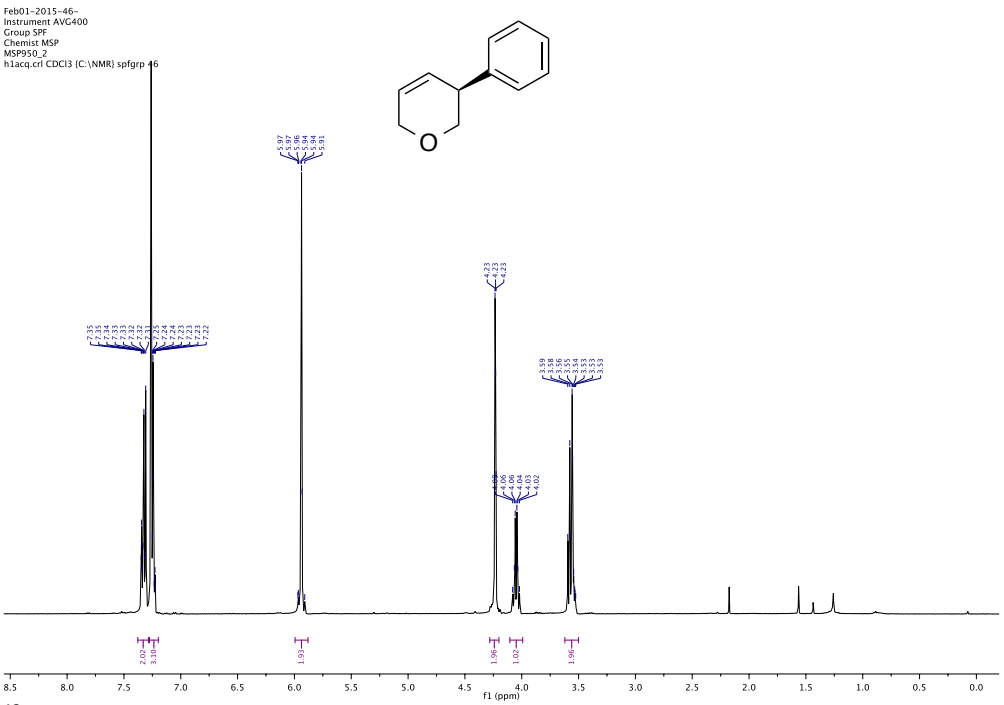
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 141.9, 128.6 (2C), 128.2 (2C), 128.0, 127.1, 126.9, 71.3, 65.5, 41.5.

**HRMS** (EI/FI) *m*/z calcd for $C_{11}H_{12}O$ $[M]^+$: 160.0888, found: 160.0884.

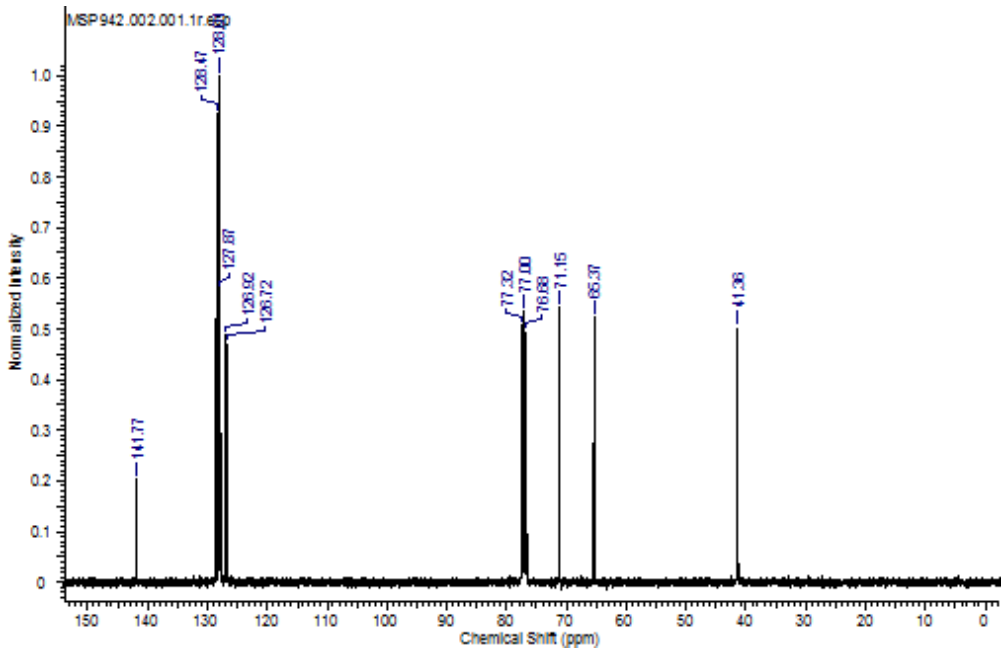
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1453, 1492, 2845, 2956, 3061.

**$[\alpha]^{20}_{589}$** = –115.3 (c 0.76 $CHCl_3$) for 96% ee.

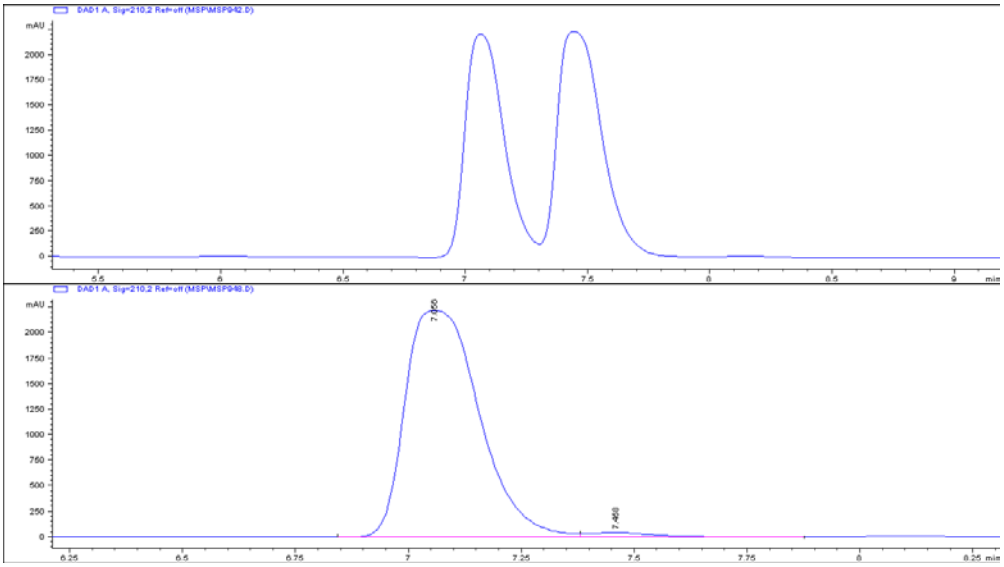
**$^1$H NMR:**



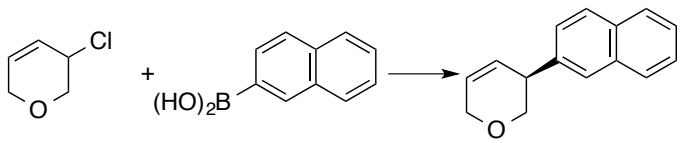

**$^{13}$C NMR:**



**HPLC traces:**



**(–)-(*S*)-3-(Naphthalen-2-yl)-3,6-dihydro-2*H*-pyran 22**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (5.7 mg, 0.013 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (22.7 mg, 0.03 mmol, 0.06 eq) and $Cs_2CO_3$ (162.9 mg, 0.50 mmol, 1.00 eq) were stirred in THF (3 mL) at 60 °C for 30 min. A solution of 2-naphthylboronic acid (172.0 mg, 1.00 mmol, 2.00 eq) and 3-chloro-3,6-dihydro-2*H*-pyran (59.3 mg, 0.50 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (1.0 mL). The resulting mixture was then stirred for 3 h at 60 °C before the addition of NaOH 2M (0.2 mL). The aqueous phase was extracted with $Et_2O$ (2 x 0.2 mL). The combined organic extracts were washed with water (0.4 mL), dried with $MgSO_4$, and filtered before adding $SiO_2$ (20 mg) and carefully evaporated. The resulting solid was directly loaded onto the top of a flash chromatography column, and eluting with pentane: $Et_2O$ (95:5) to obtain the pure product in 90% yield (93.9 mg, 0.45 mmol) as a colorless oil.

Enantiomeric excess of 98% was determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane:iPA 98:2; λ = 210 nm; minor enantiomer $t_R$ = 6.2 min; major enantiomer $t_R$ = 6.6 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.89 – 7.79 (m, 3H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.54 – 7.38 (m, 3H), 6.03 (m, 2H), 4.30 (m, 2H), 4.15 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.78 – 3.65 (m, 2H).

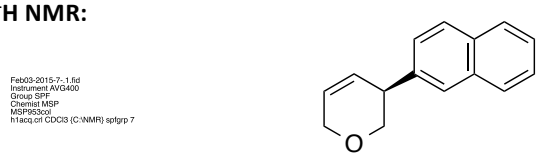
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 139.4, 133.6, 132.6, 128.3, 128.0, 127.8, 127.7, 127.3, 126.6, 126.6, 126.2, 125.7, 71.2, 65.6, 41.6.

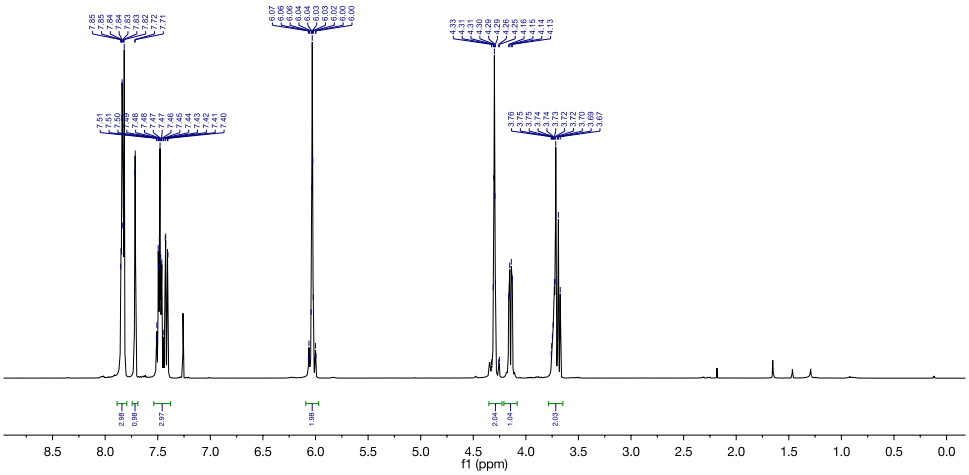
**HRMS** (EI/FI) *m*/z calcd for $C_{15}H_{14}O$ $[M]^+$: 210.1045, found: 210.1051.

**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1456, 1507, 2846, 2929, 3052.

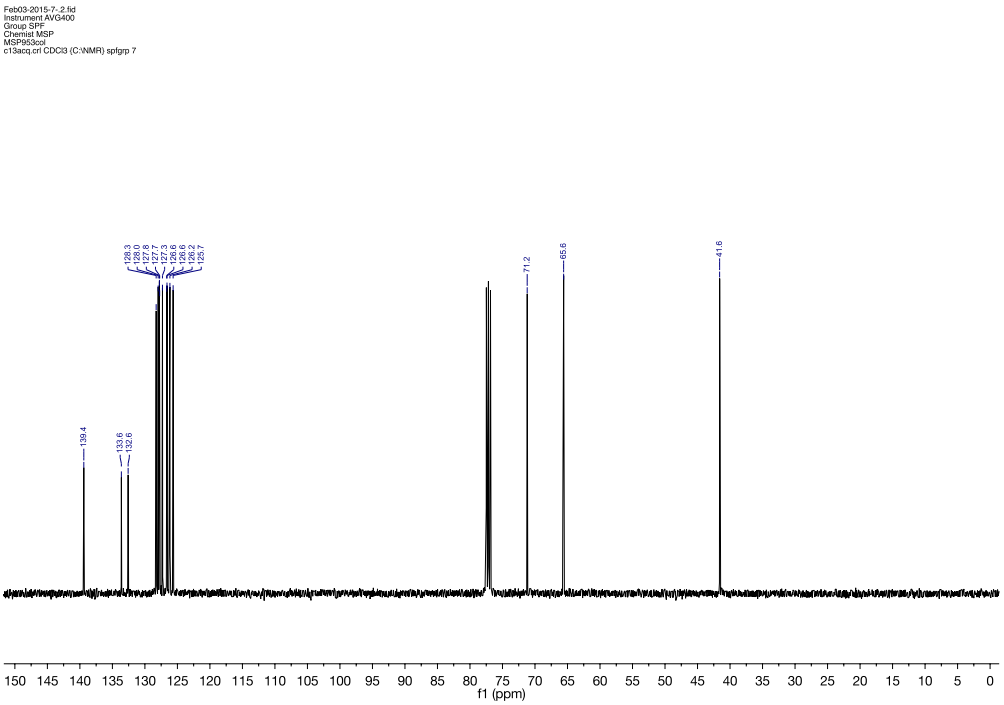
**[α]$^{20}_{589}$** = –171.4 (c 0.83 $CHCl_3$) for 98% ee.

**$^1$H NMR:**

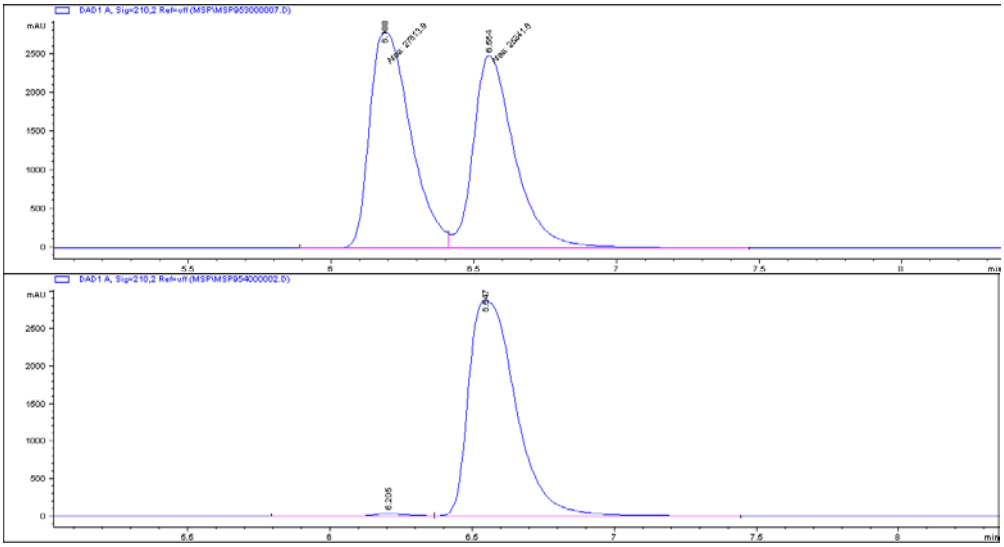


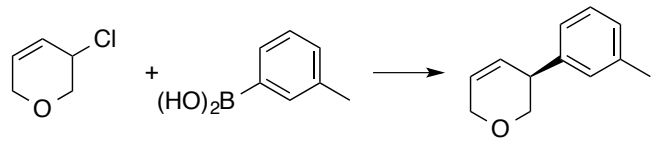

**$^{13}$C NMR:**



**HPLC traces:**



**(–)-(*S*)-3-(*m*-Tolyl)-3,6-dihydro-2*H*-pyran 23**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (5.7 mg, 0.013 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (22.7 mg, 0.03 mmol, 0.06 eq) and $Cs_2CO_3$ (162.9 mg, 0.50 mmol, 1.00 eq) were stirred in THF (2.5 mL) at 60 °C for 30 min. A solution of *m*-tolylboronic acid (136.0 mg, 1.00 mmol, 2.00 eq) and 3-chloro-3,6-dihydro-2*H*-pyran (59.3 mg, 0.50 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (1.0 mL). The resulting mixture was then stirred for 3 h at 60 °C before the addition of NaOH 2M (0.2 mL). The aqueous phase was extracted with $Et_2O$ (2x0.2 mL). The combined organic extracts were washed with water (0.4 mL), dried with $MgSO_4$, and filtered before adding $SiO_2$ (20 mg) and and carefully concentrated under vacuum. The resulting solid was directly loaded into a column containing silica gel, and flash column chromatography (eluting with pentane:$Et_2O$ (95:5)) was used to obtain the pure product in 99% yield (85.7 mg, 0.49 mmol) as a colorless oil.

Enantiomeric excess of >99% was determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane:iPA 98:2; λ = 210 nm; minor enantiomer $t_R$ = 4.5 min; major enantiomer $t_R$ = 4.9 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.29 – 7.17 (m, 1H), 7.10 – 7.01 (m, 3H), 5.93 (m, 2H), 4.23 (m, 2H), 4.04 (dd, *J* = 10.1, 4.3 Hz, 1H), 3.61 – 3.47 (m, 2H), 2.35 (s, 3H).

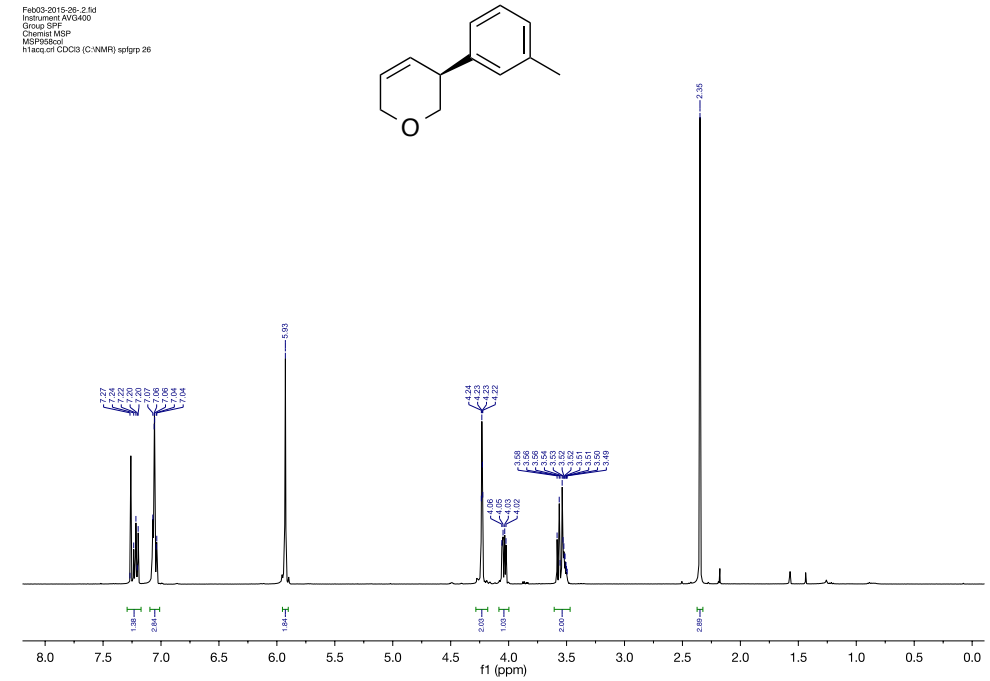
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 141.9, 138.3, 128.9, 128.5, 128.2, 127.7, 127.0, 125.2, 71.4, 65.6, 41.5, 21.6.

**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{14}O$ $[M]^+$: 174.1045, found: 174.1046.

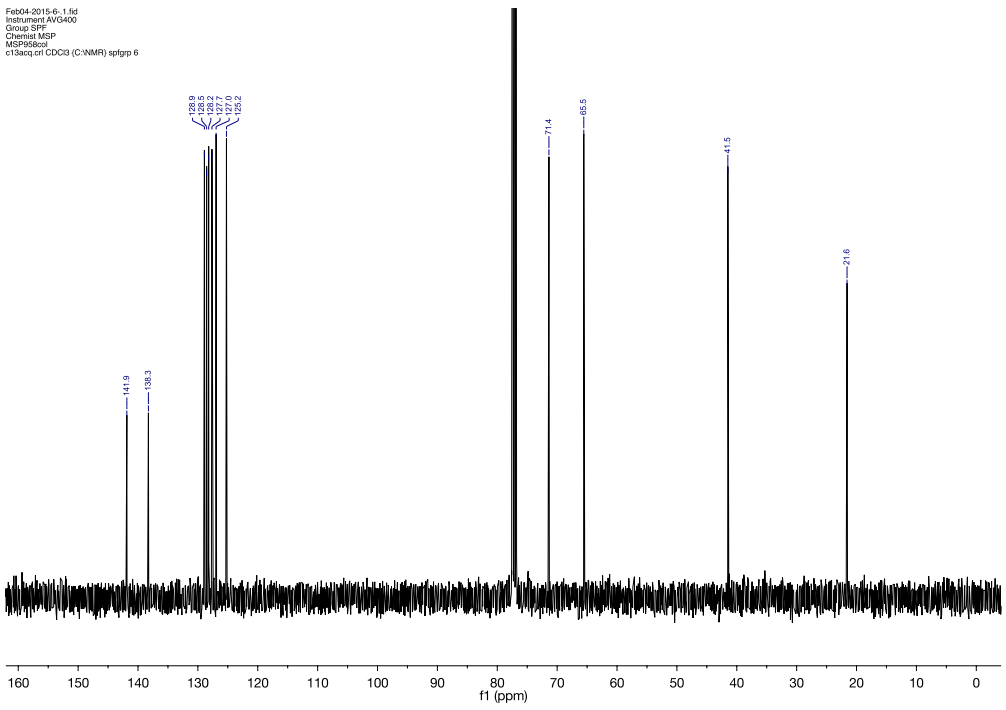
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1487, 1607, 2844, 2917, 3030.

**$[\alpha]^{20}_{589}$** = –118.3 (c 0.68 $CHCl_3$) for >99% ee.

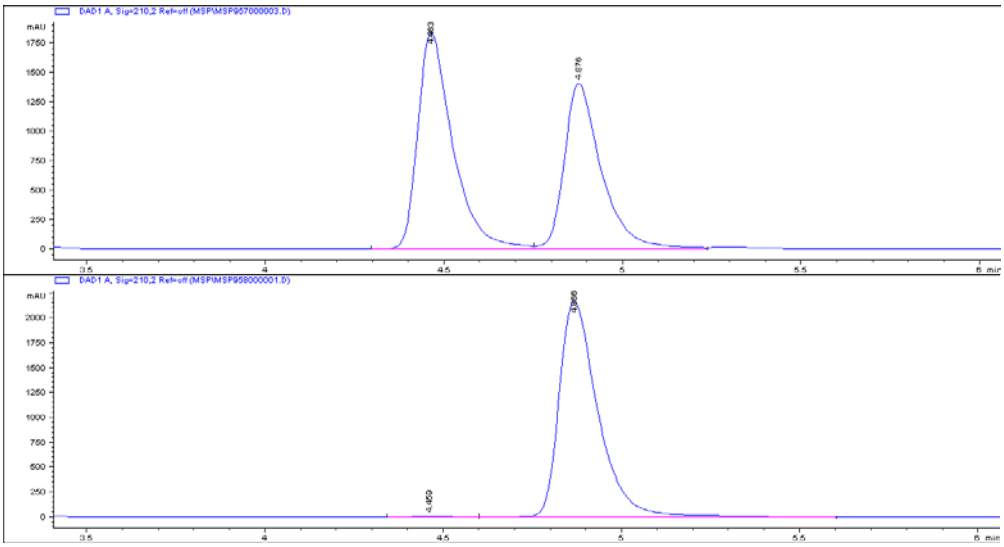
**$^1$H NMR:**



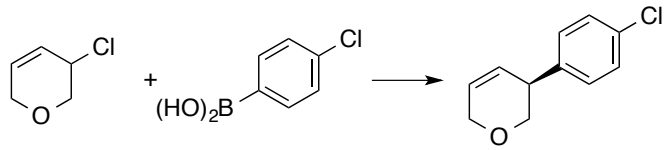

**$^{13}$C NMR:**



**HPLC traces:**



**(–)-(*S*)-3-(4-Chlorophenyl)-3,6-dihydro-2*H*-pyran 24**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (5.7 mg, 0.013 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (22.7 mg, 0.03 mmol, 0.06 eq) and $Cs_2CO_3$ (162.9 mg, 0.50 mmol, 1.00 eq) were stirred in THF (2.5 mL) at 60 °C for 30 min. A solution of (4-chlorophenyl)boronic acid (156.4 mg, 1.00 mmol, 2.00 eq) and 3-chloro-3,6-dihydro-2*H*-pyran (59.3 mg, 0.50 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (1.0 mL). The resulting mixture was then stirred for 3 h at 60 °C before the addition of NaOH 2M (0.2 mL). The aqueous phase was extracted with $Et_2O$ (2x0.2 mL). The combined organic extracts were washed with water (0.4 mL), dried with $MgSO_4$, and filtered before adding $SiO_2$ (20 mg) and carefully concentrated under vacuum. The resulting solid was directly loaded into a column containing silica gel, and flash column chromatography (eluting with pentane:$Et_2O$ (95:5)) was used to obtain the pure product in 83% yield (80.5 mg, 0.42 mmol) as a colorless oil.

Enantiomeric excess of 99% was determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane:iPA 98:2; λ = 210 nm; major enantiomer $t_R$ = 6.0 min; minor enantiomer $t_R$ = 7.4 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.33 – 7.24 (m, 2H), 7.23 – 7.14 (m, 2H), 5.95 (dq, *J* = 10.3, 2.4 Hz, 1H), 5.92 – 5.84 (m, 1H), 4.22 (q, *J* = 2.5 Hz, 2H), 4.01 (dd, *J* = 10.7, 4.7 Hz, 1H), 3.60 – 3.44 (m, 2H).

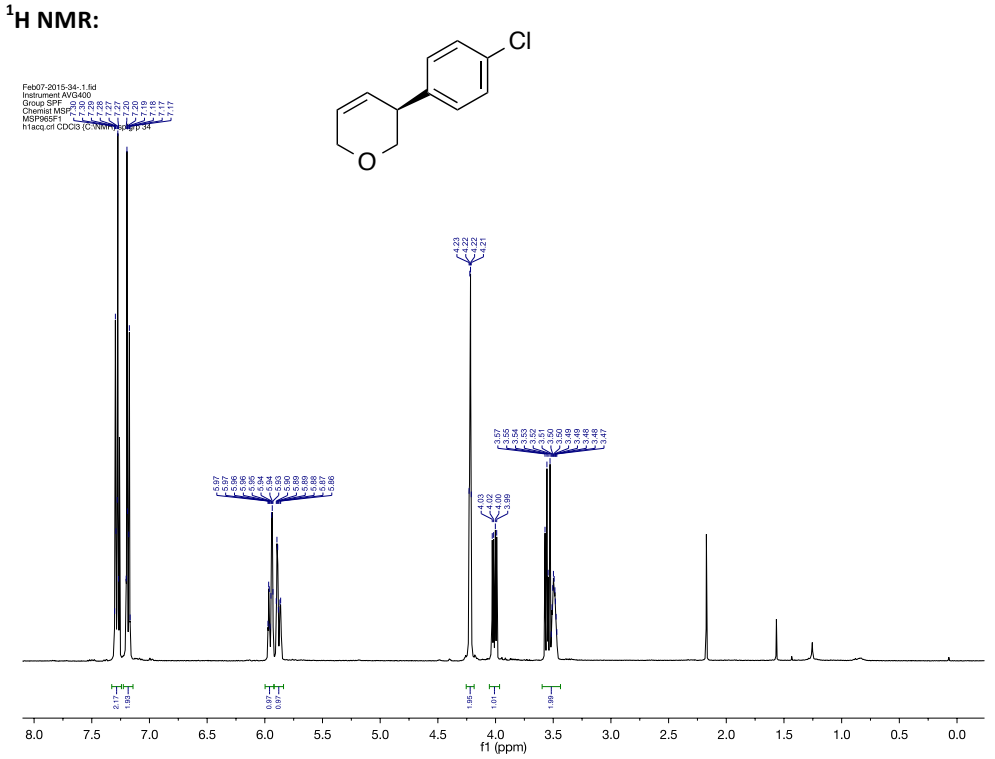
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 140.5, 132.7, 129.6 (2C), 128.8 (2C), 127.5, 127.5, 71.1, 65.5, 40.9.

**HRMS** (EI/FI) *m*/z calcd for $C_{11}H_{11}ClO$ $[M]^+$: 194.0498, found: 190.0499.

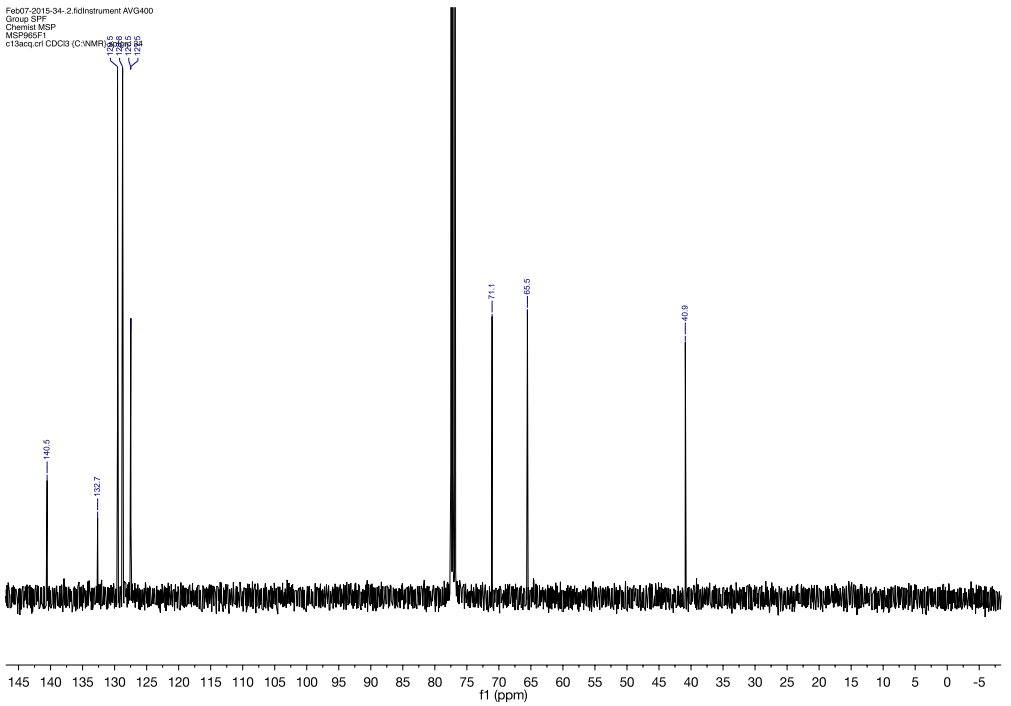
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1086, 1490, 2843, 2925, 3030.

**$[\alpha]^{20}_{589}$** = –113.4 (c 2.80 $CHCl_3$) for 99% ee.

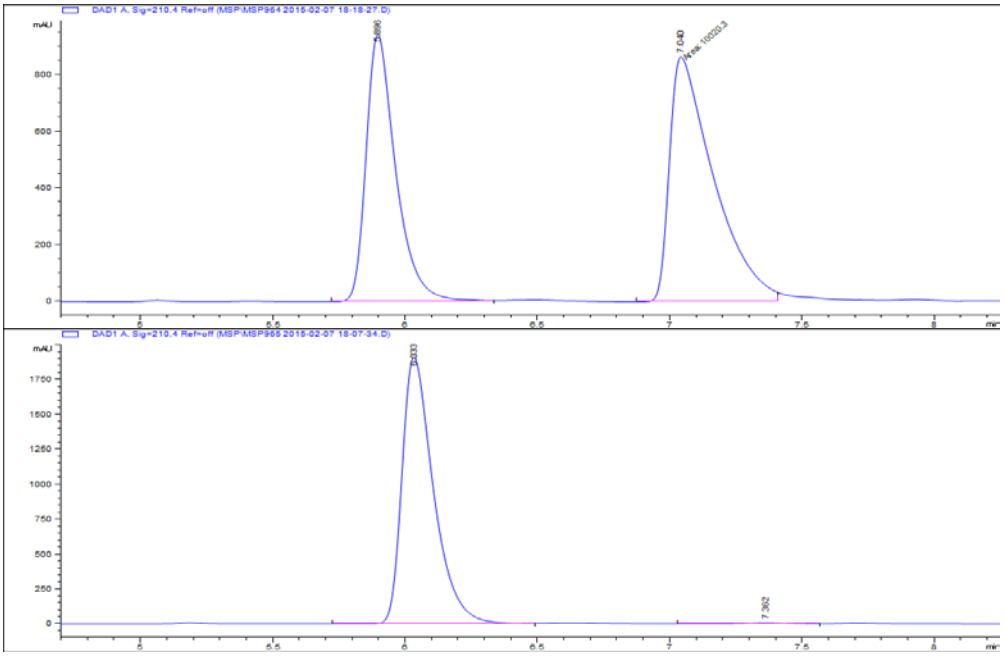
**$^1$H NMR:**



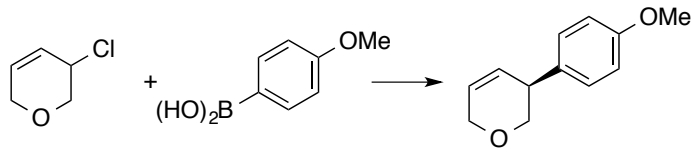

**$^{13}$C NMR:**



**HPLC traces:**



**(–)-(*S*)-3-(4-Methoxyphenyl)-3,6-dihydro-2*H*-pyran 25**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (5.7 mg, 0.013 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (22.7 mg, 0.03 mmol, 0.06 eq) and $Cs_2CO_3$ (162.9 mg, 0.50 mmol, 1.00 eq) were stirred in THF (2.5 mL) at 60 °C for 30 min. A solution of (4-methoxyphenyl)boronic acid (152.0 mg, 1.00 mmol, 2.00 eq) and 3-chloro-3,6-dihydro-2*H*-pyran (59.3 mg, 0.50 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (1.0 mL). The resulting mixture was then stirred for 3 h at 60 °C before the addition of NaOH 2M (0.2 mL). The aqueous phase was extracted with $Et_2O$ (2x0.2 mL). The combined organic extracts were washed with water (0.4 mL), dried with $MgSO_4$, and filtered before adding $SiO_2$ (20 mg) and carefully concentrated under vacuum. The resulting solid was directly loaded into a column containing silica gel, and flash column chromatography (eluting with pentane:$Et_2O$ (95:5)) was used to obtain the pure product in 81% yield (77.3 mg, 0.41 mmol) as a white solid.

Enantiomeric excess of >99% was determined by HPLC [Chiralpak® IB; flow: 1.0 mL/min; hexane:iPA 98:2; λ = 210 nm; major enantiomer $t_R$ = 9.0 min; minor enantiomer $t_R$ = 10.8 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.21 – 7.13 (m, 2H), 6.92 – 6.82 (m, 2H), 5.91 (m, 2H), 4.22 (m, 2H), 4.08 – 3.96 (m, 1H), 3.80 (s, 3H), 3.61 – 3.45 (m, 2H).

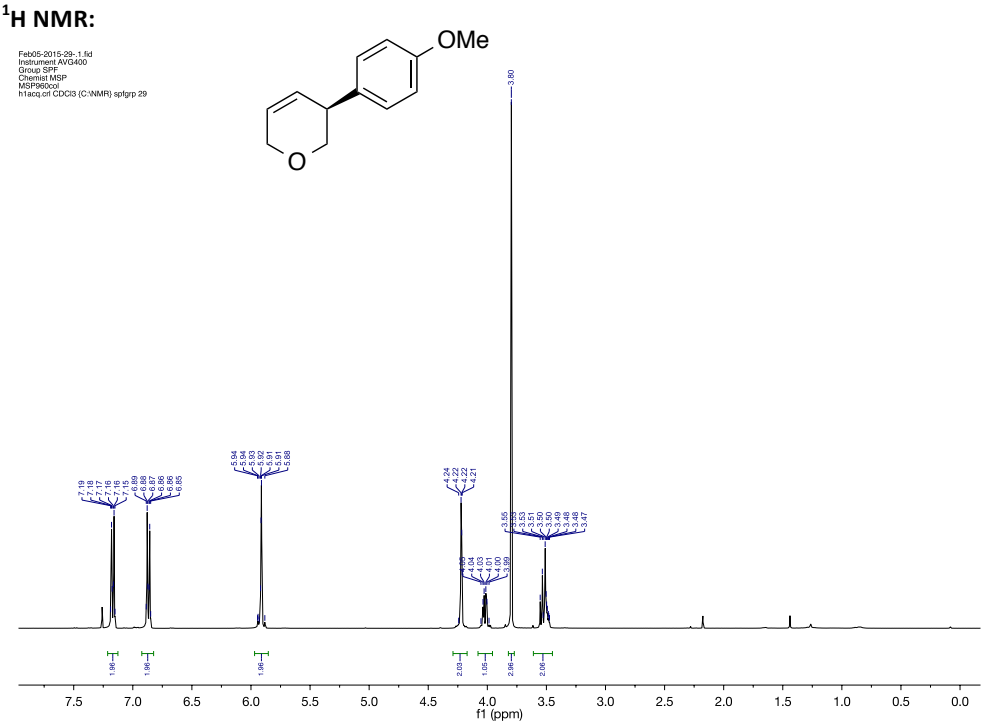
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 158.6, 134.0, 129.1 (2C), 128.4, 126.9, 114.0 (2C), 71.5, 65.5, 55.4, 40.7.

**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{14}O_2$ $[M]^+$: 190.0994, found: 190.0998.

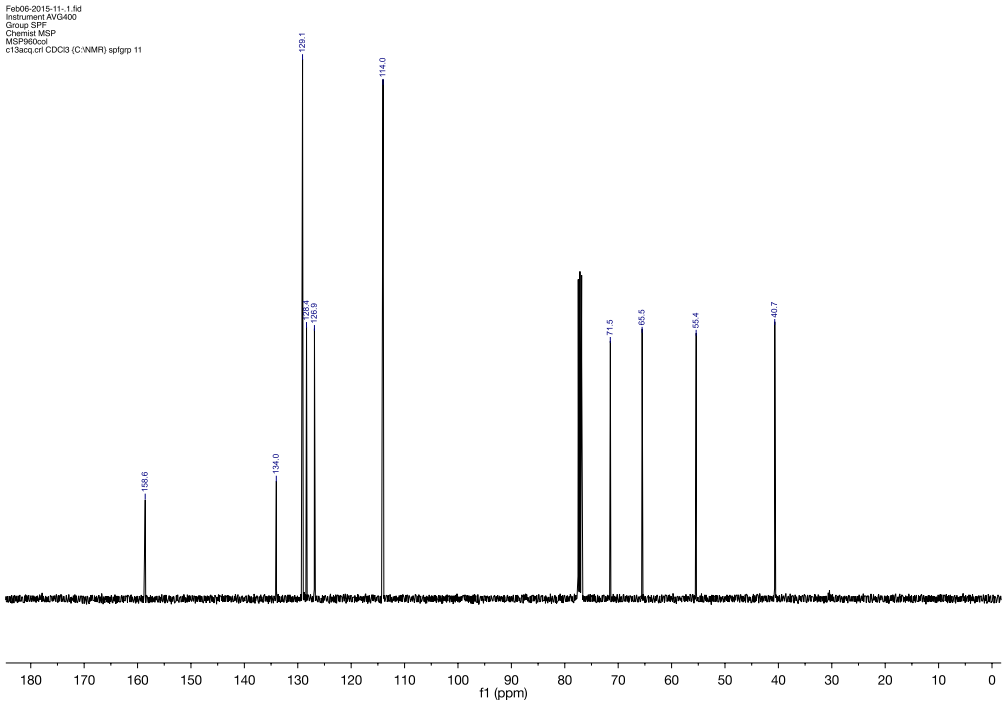
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1512, 1611, 2844, 2926, 3029.

**$[\alpha]^{20}_{589}$** = –94.2 (c 1.96 $CHCl_3$) for >99% ee.

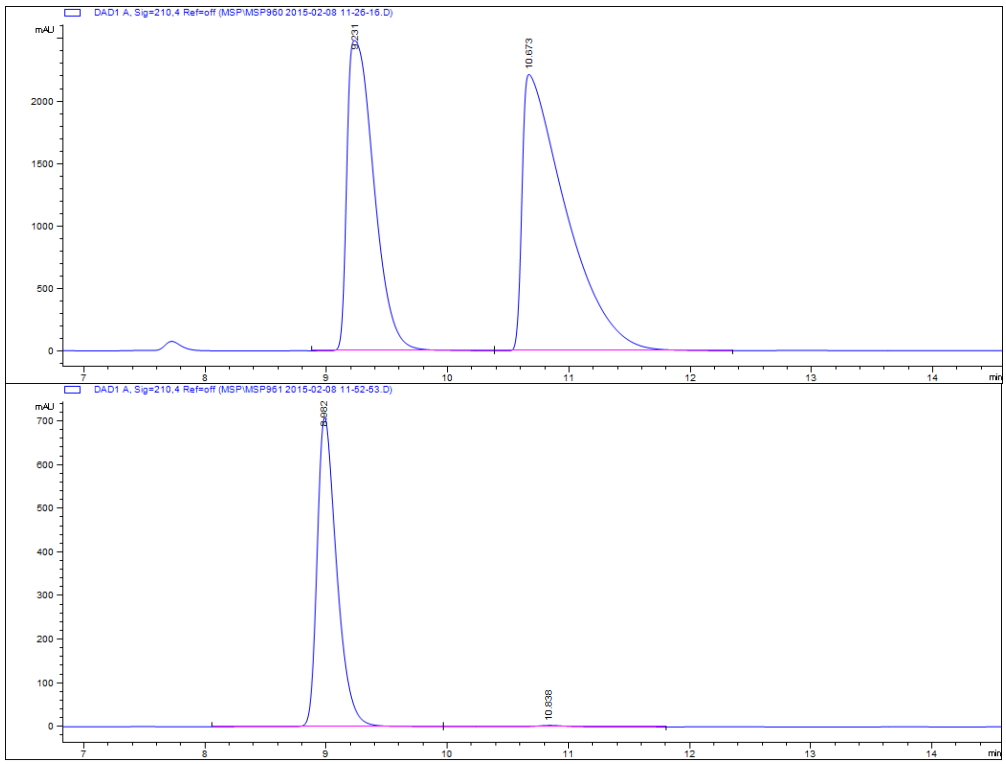
**$^1$H NMR:**



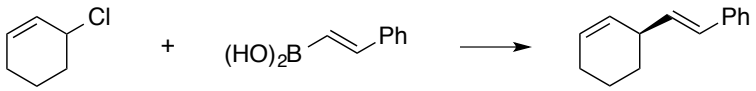

**$^{13}$C NMR:**




**HPLC traces:**



**(–)-(*S*,*E*)-(2-(Cyclohex-2-en-1-yl)vinyl)benzene 26**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of (*E*)-styrylboronic acid (118.4 mg, 0.80 mmol, 2.00 eq) and the allyl chloride (45µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 4 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto a flash chromatography column and eluted with pentane to obtain (*S*,*E*)-(2-(cyclohex-2-en-1-yl)vinyl)benzene in 67% yield (53.0 mg, 0.34 mmol).

Enantiomeric excess of 96% was determined by HPLC [Chiralpak® IE; flow: 0.7 mL/min; hexane; λ = 210 nm; minor enantiomer $t_R$ = 10.4 min; major enantiomer $t_R$ = 11.2 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 1.6 Hz, 1H), 7.28 (s, 1H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.16 – 7.07 (m, 1H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.8, 7.4 Hz, 1H), 5.78 – 5.68 (m, 1H), 5.57 (m, 1H), 2.89 (m, 1H), 1.95 (m, 2H), 1.81 (m, 1H), 1.74 – 1.61 (m, 1H), 1.59 – 1.46 (m, 2H).

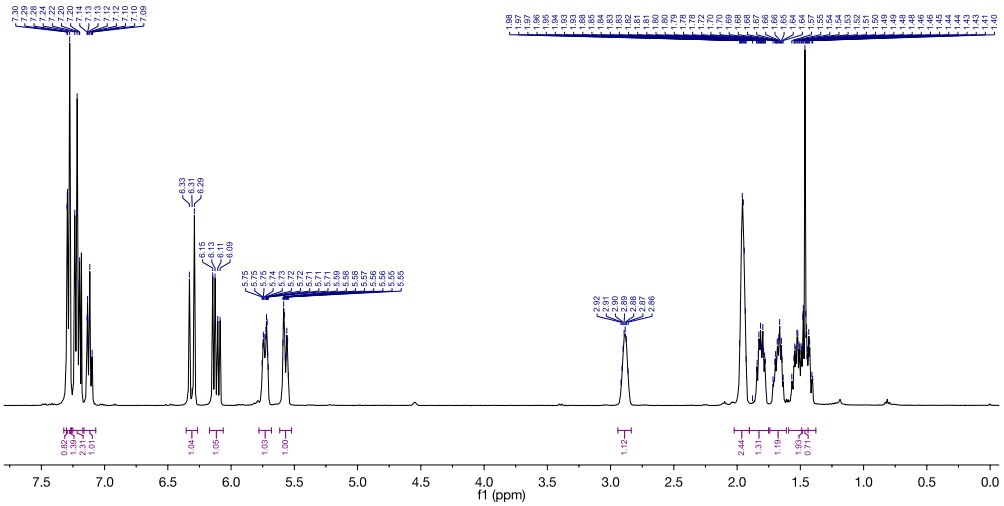
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.9, 134.8, 129.6, 129.2, 128.6 (2C), 128.2, 127.0, 126.2 (2C), 38.8, 29.4, 25.2, 20.7.

**HRMS** (EI) *m/z* calcd for $C_{14}H_{16}$ $[M]^+$: 184.1252, found: 184.1261.

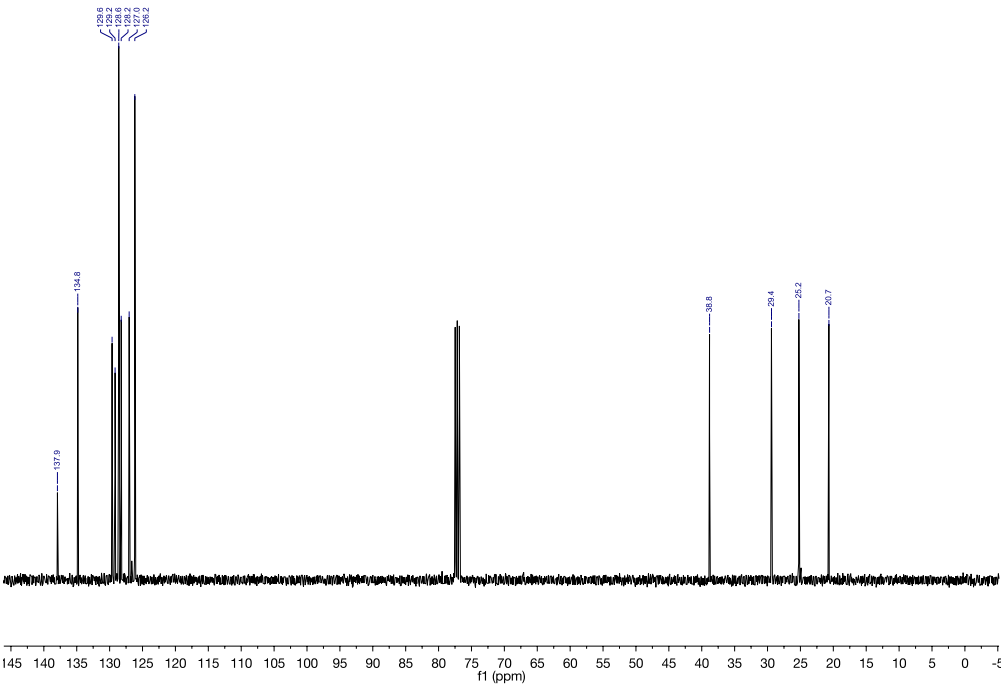
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 1171, 1542, 2867, 3058.

**$[\alpha]^{20}_{589}$** = –78.8 (c 0.65 $CHCl_3$) for 96% ee.

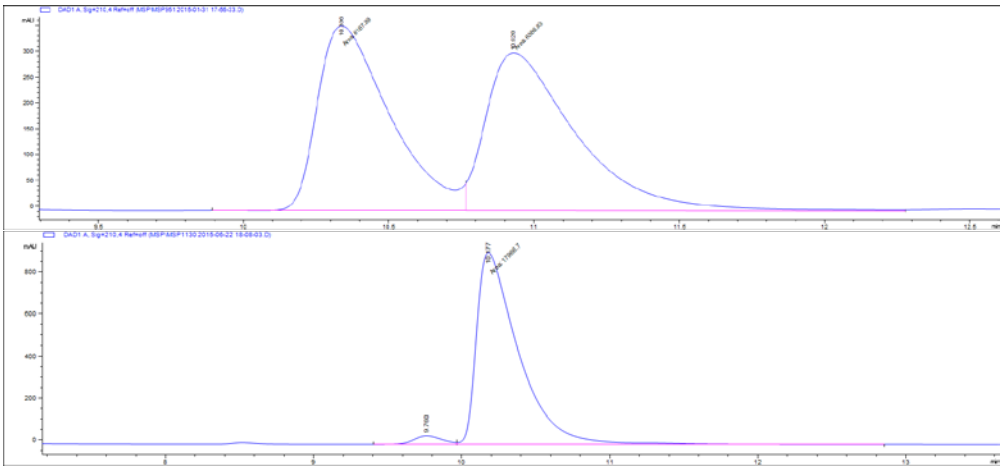
**$^1$H NMR:**



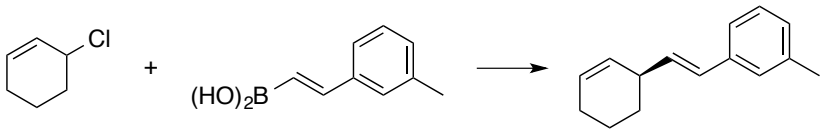

**$^{13}$C NMR:**




**HPLC traces:**



**(–)-(*S*,*E*)-1-(2-(Cyclohex-2-en-1-yl)vinyl)-3-methylbenzene 27**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2.0 mL) at 60 °C for 30 min. A solution of (*E*)-(3-methylstyryl)boronic acid (129.6 mg, 0.80 mmol, 2.00 eq) and the allyl chloride (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 4 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto a flash chromatography column and eluted with pentane to obtain (*R*,*E*)-1-(2-(Cyclohex-2-en-1-yl)vinyl)-3-methylbenzene in 52% yield (41.1 mg, 0.21 mmol).

Enantiomeric excess of 94% was determined by HPLC [Chiralpak® IA; flow: 0.3 mL/min; hexane; λ = 210 nm; minor enantiomer $t_R$ = 17.8 min; major enantiomer $t_R$ = 19.1 min].

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm 7.26 – 7.13 (m, 3H), 7.08 – 6.99 (m, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.19 (dd, *J* = 15.9, 7.4 Hz, 1H), 5.81 (m, 1H), 5.70 – 5.60 (m, 1H), 2.96 (m, 1H), 2.35 (s, 3H), 2.04 (m, 3H), 1.95 – 1.70 (m, 1H), 1.68 – 1.46 (m, 2H).

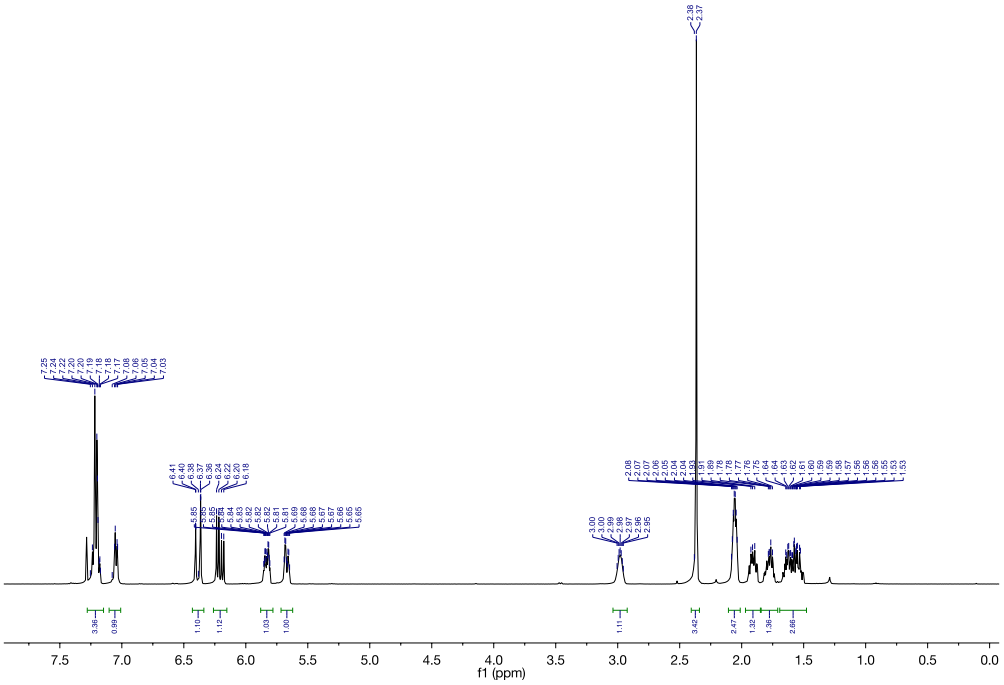
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm 138.1, 137.9, 134.7, 129.7, 129.2, 128.5, 128.2, 127.8, 126.9, 123.4, 38.8, 29.4, 25.3, 21.6, 20.7.

**HRMS** (EI) *m*/*z* calcd for $C_{15}H_{18}$ $[M]^+$: 198.1409, found: 198.1412.

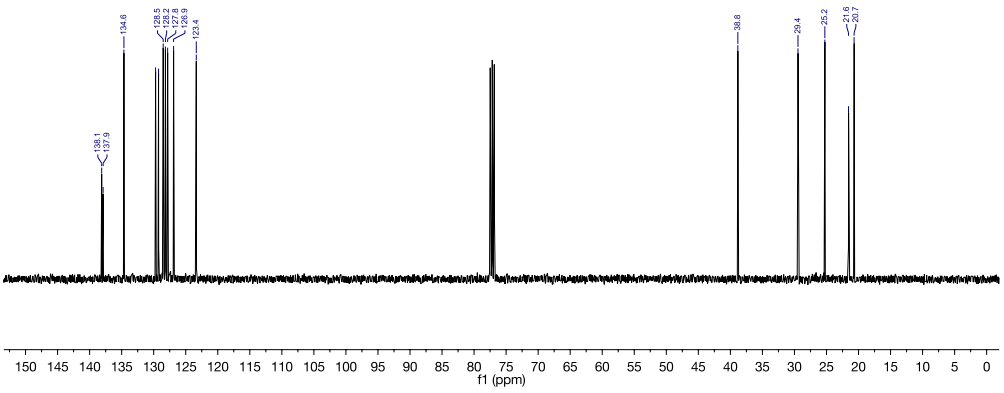
**IR** ($\nu_{max}$/cm$^{-1}$): 1510, 2859, 2926, 3036.

**$[\alpha]^{20}_{589}$** = –115.4 (c 0.6 $CHCl_3$) for 94% ee.

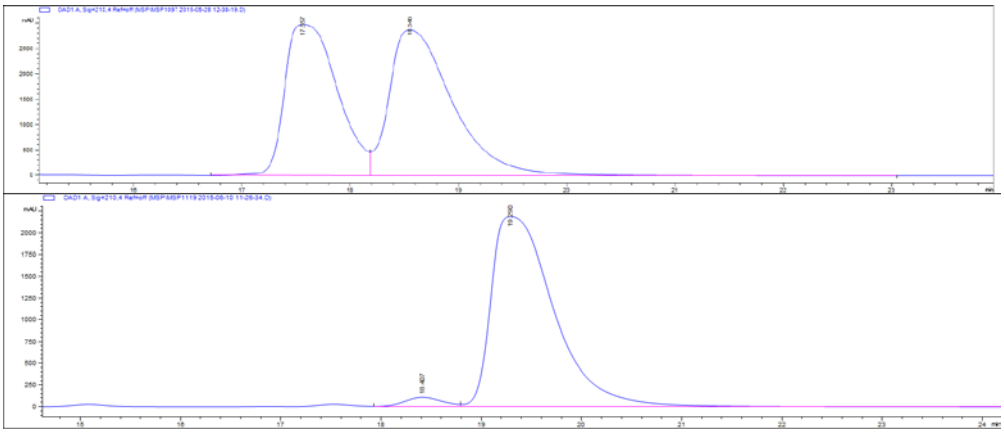
**$^1$H NMR:**



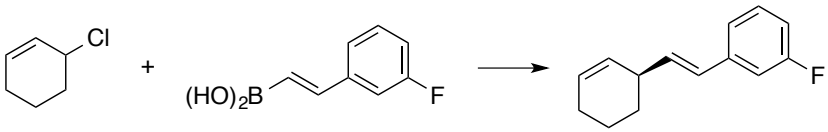

**$^{13}$C NMR:**




**HPLC traces:**



**(–)-(*S*,*E*)-1-(2-(Cyclohex-2-en-1-yl)vinyl)-3-fluorobenzene 28**




In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2.0 mL) at 60 °C for 30 min. A solution of (*E*)-(3-fluorostyryl)boronic acid (132.8 mg, 0.80 mmol, 2.00 eq) and the allyl chloride (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 4 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly loaded onto a flash chromatography column and eluted with pentane to obtain (*S*,*E*)-1-(2-(cyclohex-2-en-1-yl)vinyl)-3-fluorobenzene in 44% yield (35 mg, 0.17 mmol).

Enantiomeric excess of 92% was determined by HPLC [Chiralpak® ID; flow: 0.5 mL/min; hexane; λ = 210 nm; minor enantiomer $t_R$ = 15.6 min; major enantiomer $t_R$ = 17.9 min].

**$^1$H NMR** (500 MHz, $CDCl_3$) $\delta_H$ /ppm 7.17 (td, *J* = 7.9, 6.0 Hz, 1H), 7.06 – 6.95 (m, 2H), 6.81 (td, *J* = 8.4, 2.5 Hz, 1H), 6.27 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.9, 7.3 Hz, 1H), 5.74 (m, 1H), 5.55 (m, 1H), 2.88 (m, 1H), 1.96 (m, 2H), 1.81 (m, 1H), 1.66 (m, 1H), 1.58 – 1.38 (m, 2H).

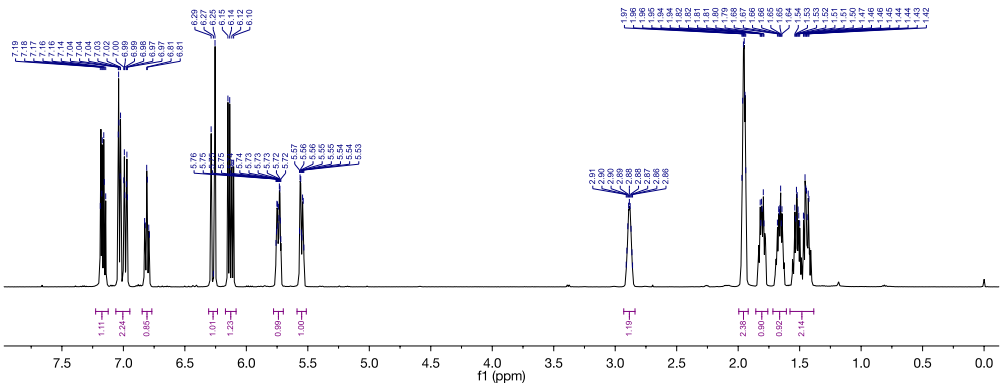
**$^{13}$C NMR** (126 MHz, $CDCl_3$) 163.3 (d, *J* = 244.8 Hz), 140.4 (d, *J* = 7.7 Hz), 136.3, 130.0 (d, *J* = 8.6 Hz), 129.2, 128.5, 128.2 (d, *J* = 2.6 Hz), 122.1 (d, *J* = 2.7 Hz), 113.8 (d, *J* = 21.4 Hz), 112.6 (d, *J* = 21.7 Hz), 38.7, 29.3, 25.2, 20.6.

**HRMS** (EI) *m*/*z* calcd for $C_{14}H_{15}F$ $[M]^+$: 202.1158, found: 202.1151.

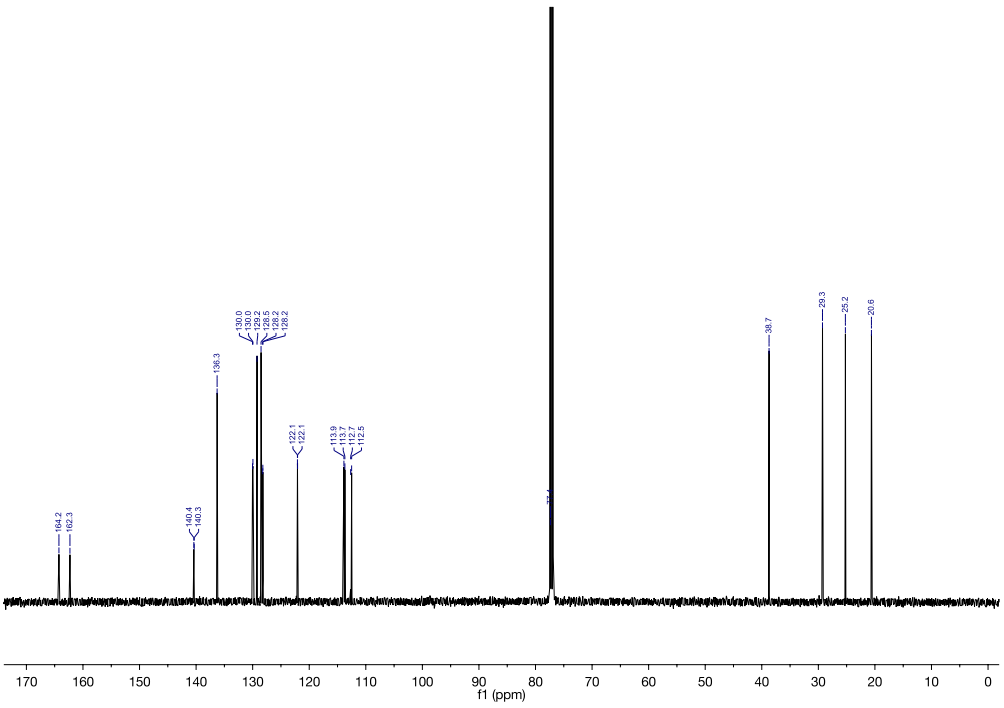
**IR** ($\nu_{max}$/cm$^{-1}$): 1584, 2860, 2927, 3018.

**$[\alpha]^{20}_{589}$** = –103.0 (c 1.24 $CHCl_3$) for 92% ee.

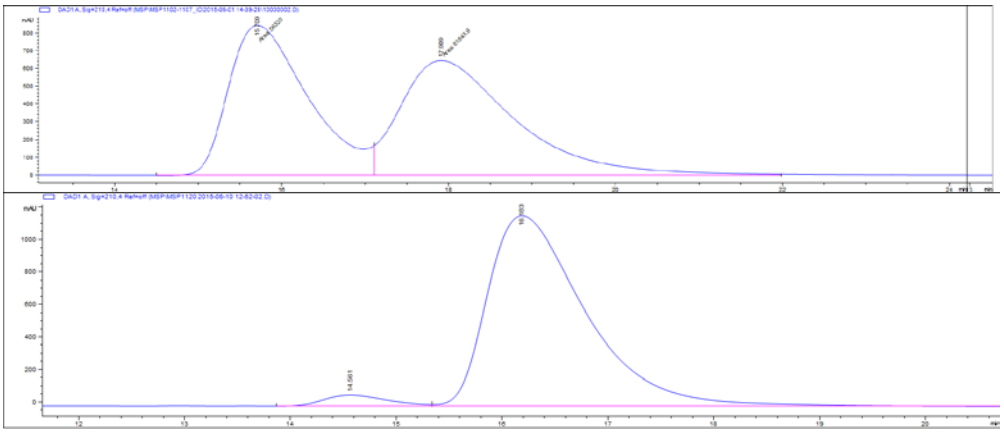
**$^1$H NMR:**




**$^{13}$C NMR:**




**HPLC traces:**



**Non-Linear effects**

A set of reactions was performed where the enantiomeric ratio of chiral ligand **A** was varied. *Common procedure:* In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), a mixture of (*R*) and (*S*)-Xyl-P-PHOS (18.2 mg in total, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.3 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of phenylboronic acid (97.5 mg, 0.80 mmol, 2.00 eq) and 3-chlorocyclohexene (45 µL, 0.40 mmol, 1.00 eq) in THF (1.5 mL) was then added *via* syringe and the flask rinsed with THF (0.5 mL). The resulting mixture was then stirred for 1 h at 60 °C before the addition of $SiO_2$ (20 mg). The solvent was then carefully evaporated and the solid directly analysed by HPLC.

Enantiomeric excess was determined by HPLC [Chiralpak® ID; flow: 0.6 mL/min; hexane/i-PrOH: 99.9: 0.1; λ = 210 nm; major enantiomer $t_R$ = 8.3 min; minor enantiomer $t_R$ = 8.9 min].

The relationship between the ee of ligand **A** and product **2** is shown in the graphic below:

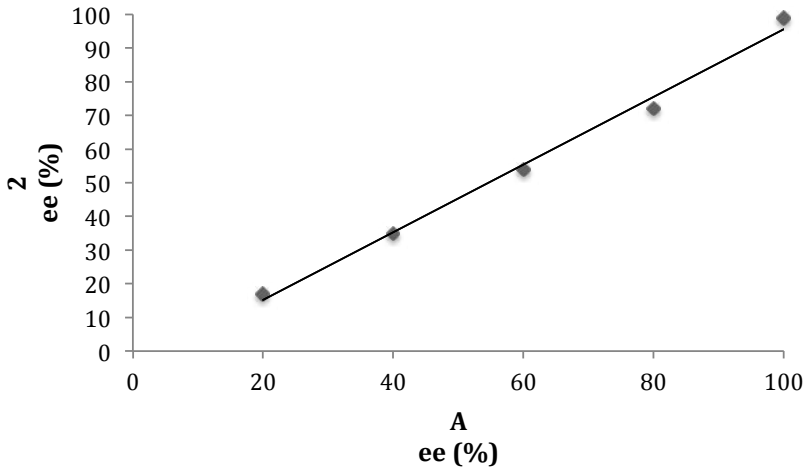
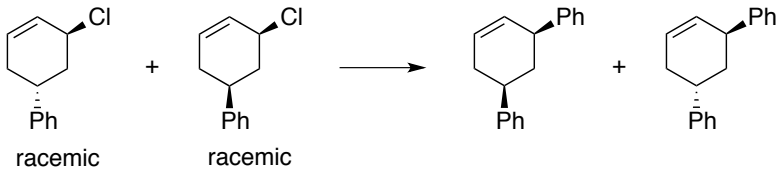



**Figure S1. Non-Linear effects.**

**(–)-(*S*,*S*)-3,5-Diphenylcyclohex-1-ene 30**




*Starting from a 1:5.3 mixture of cis:trans 3-chloro-5-phenylcyclohex-1-ene:*

In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (4.6 mg, 0.01 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (18.2 mg, 0.024 mmol, 0.06 eq) and $Cs_2CO_3$ (130.1 mg, 0.40 mmol, 1.00 eq) were stirred in THF (2 mL) at 60 °C for 30 min. A solution of phenylboronic acid (97.5 mg, 0.80 mmol, 2.00 eq) and 3-chloro-5-phenylcyclohex-1-ene (77.0 mg, 0.40 mmol, 1.00 eq) in THF (1 mL) was then added *via* syringe and the flask rinsed with THF (1 mL). The resulting mixture was then stirred for 18 h at 60 °C. $SiO_2$ was then added to the reaction mixture and the solvent was carefully concentrated under vacuum. The resulting solid was directly loaded into a silica pad and eluted with pentane to obtain the pure product as a mixture of diastereomers in 98% yield (91.8 mg, 0.39 mmol) as a colorless oil.

The product was isolated as a 5.3:1 mixture of *cis*:*trans* isomers in favour of the *cis* isomer. The stereochemistry of the isomers was determined by NOESY NMR spectroscopy.

Enantiomeric excess of >99% of both *cis* and *trans* products was determined by HPLC [Chiralpak® IA; flow: 1.0 mL/min; hexane:iPA 99.9:0.1; λ = 210 nm; minor enantiomers (*trans*) $t_R$ = 6.2, 7.2 min; major enantiomers (*cis*) $t_R$ = 9.0, 10.3 min].

**$^1$H NMR** (500 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.27 – 7.05 (m, 13H), 6.02 – 5.95 (m, 0.2H$_{cis}$), 5.90 – 5.84 (m, 1H), 5.81 – 5.75 (m, 0.2H$_{cis}$), 5.74 – 5.69 (m, 1H), 3.58 – 3.49 (m, 1H), 3.49 – 3.45 (m, 0.2H$_{cis}$), 2.99 – 2.88 (m, 1H), 2.84 – 2.75 (m, 0.2H$_{cis}$), 2.39 – 2.35 (m, 0.1H$_{cis}$), 2.30 (m, 1H), 2.21 – 2.09 (m, 2H+0.2 H$_{cis}$), 1.94 – 1.86 (m, 0.2H$_{cis}$), 1.69 (td, *J* = 12.7, 11.3 Hz, 1H).

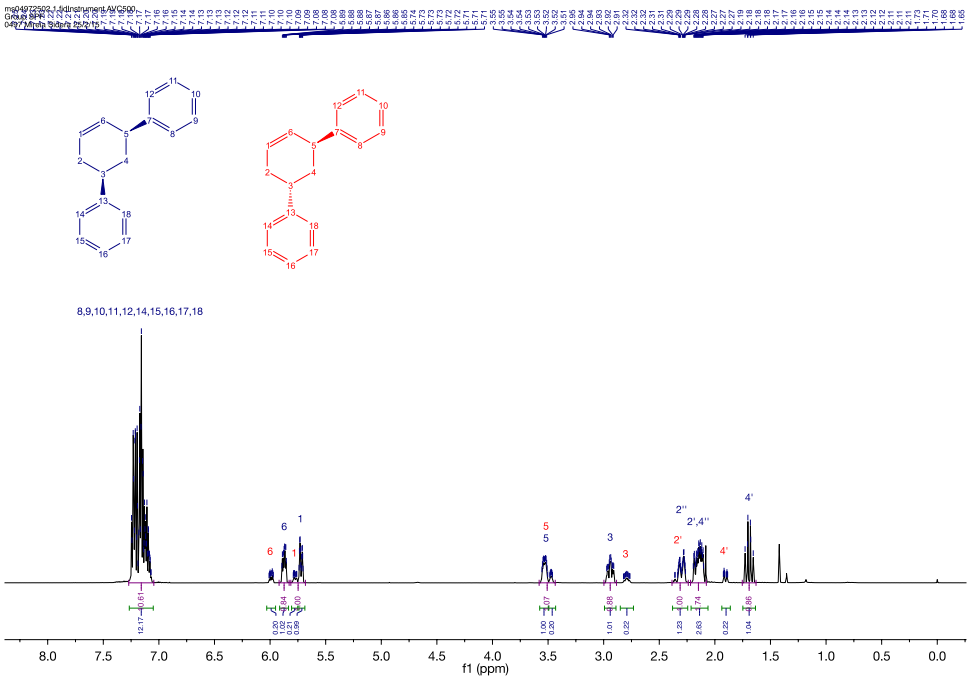
**$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta_C$ /ppm: 146.8, 146.7 (*cis*), 146.3, 145.6 (*cis*), 130.7, 128.9 (*cis*), 128.6 (2C), 128.6 (2C), 128.5 (2C, *cis*), 128.4 (2C, *cis*), 128.4 (*cis*), 128.3 (*cis*), 127.9, 127.5 (2C), 127.1 (*cis*), 126.9 (2C), 126.3, 126.3, 126.2 (2C, *cis*), 126.1 (2C, *cis*), 44.2, 41.1, 40.5, 40.4 (*cis*), 38.1 (*cis*), 35.0 (*cis*), 34.0, 33.1 (*cis*).

**HRMS** (EI/FI) *m*/z calcd for $C_{18}H_{18}$ $[M]^+$: 234.1409, found: 234.1410.

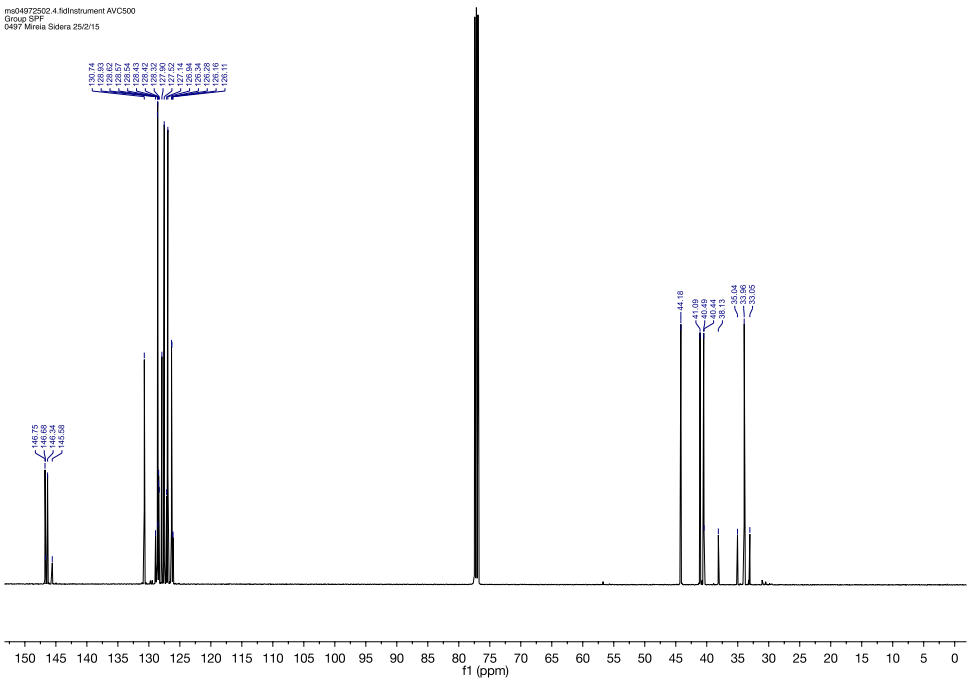
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 3060, 3025, 2913, 1717, 1602, 1506.

**$[\alpha]^{20}_{589}$** = –54.8 (c 1.17 $CHCl_3$) for >99% ee.

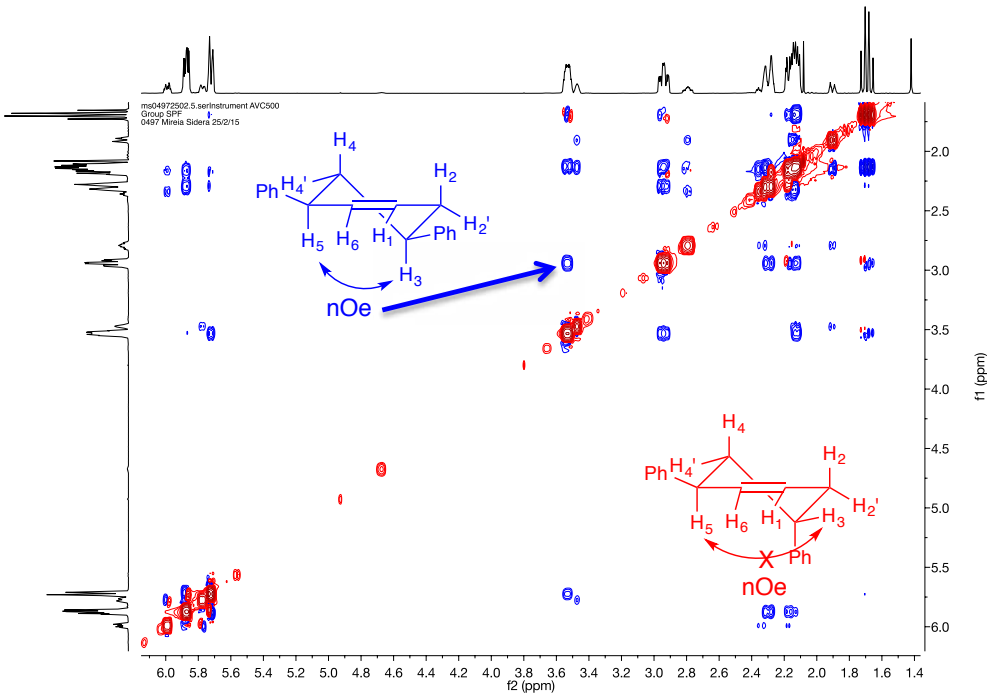
**$^{1}$H NMR:**



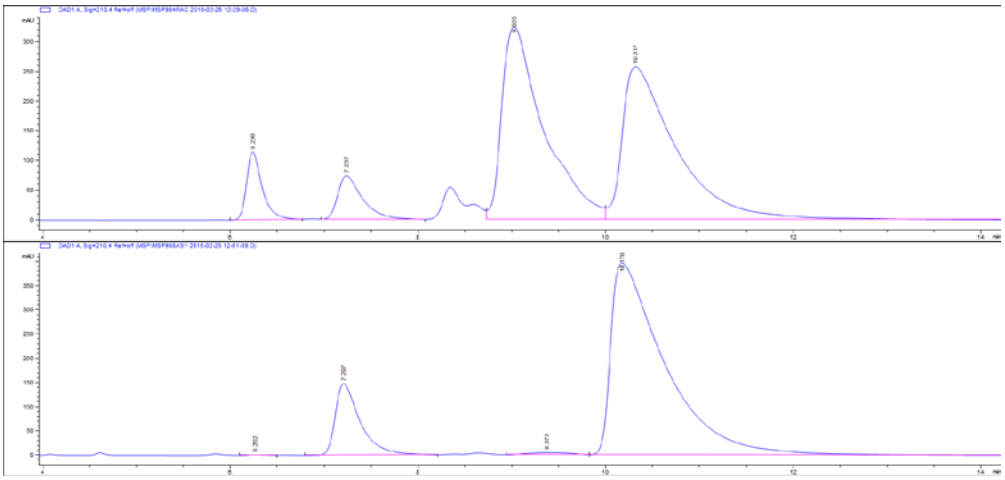

**$^{13}$C NMR:**



**NOESY:**




**HPLC traces:**

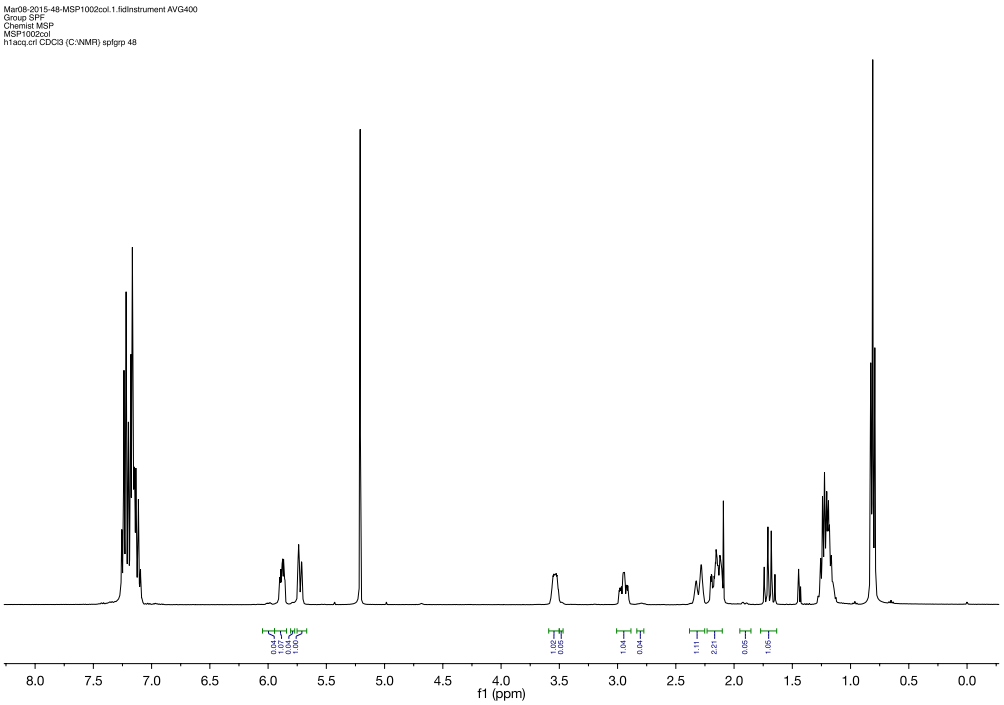


*Starting from a cis:trans mixture 1:25 of 3-chloro-5-phenylcyclohex-1-ene:*

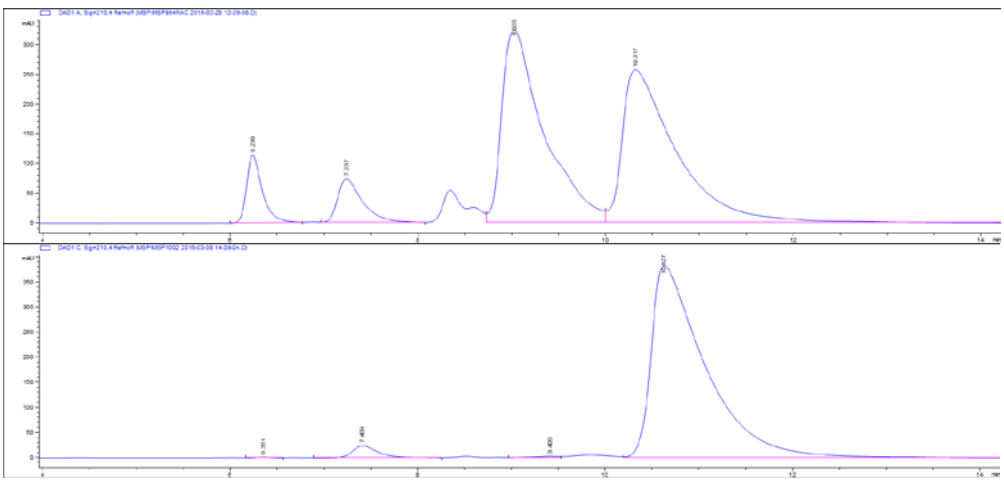
In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (1.5 mg, 0.003 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (5.9 mg, 0.008 mmol, 0.06 eq) and $Cs_2CO_3$ (42.4mg, 0.13 mmol, 1.00 eq) were stirred in THF (0.65 mL) at 60 °C for 30 min. A solution of phenylboronic acid (30.8 mg, 0.25 mmol, 2.00 eq) and 3-chloro-5-phenylcyclohex-1-ene (24.3 mg, 0.13 mmol, 1.00 eq) in THF (0.35 mL) was then added *via* syringe and the flask rinsed with THF (0.3 mL). The resulting mixture was

then stirred at 60 °C for 18 h. $SiO_2$ was then added to the reaction mixture and the solvent was carefully concentrated under vacuum. The resulting solid was directly loaded into a silica pad and eluted with pentane to obtain the pure product as a mixture of diastereomers in 95% yield (29.0 mg, 0.12 mmol) as a colorless oil. The product was isolated as a cis:trans mixture 25:1.

**$^1$H NMR:**




**HPLC traces:**

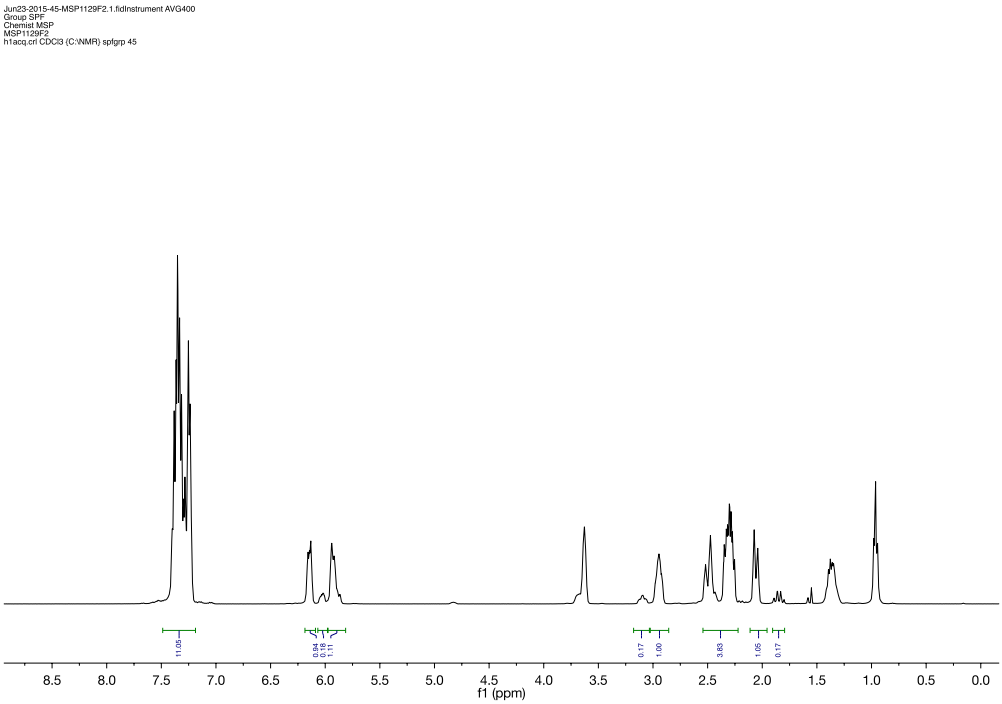


*Starting from a cis:trans mixture 6.1:1 of 3-chloro-5-phenylcyclohex-1-ene:*

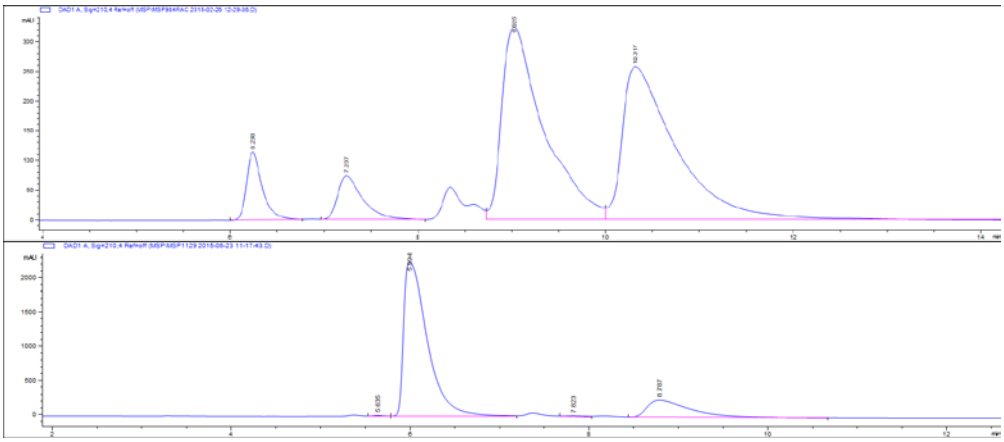
In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (1.5 mg, 0.003 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (5.9 mg, 0.008 mmol, 0.06 eq) and $Cs_2CO_3$ (42.4mg, 0.13 mmol, 1.00 eq) were stirred in THF (0.65 mL) at 60 °C for 30 min. A solution of phenylboronic acid (30.8 mg, 0.25 mmol,

2.00 eq) and 3-chloro-5-phenylcyclohex-1-ene (24.3 mg, 0.13 mmol, 1.00 eq) in THF (0.35 mL) was then added *via* syringe and the flask rinsed with THF (0.3 mL). The resulting mixture was then stirred at 60 °C for 18 h. $SiO_2$ was then added to the reaction mixture and the solvent was carefully concentrated under vacuum. The resulting solid was directly loaded into a column containing silica gel, and flash column chromatography (eluting with pentane) was used to obtain the pure product as a mixture of diastereomers in 97% yield (31.0 mg, 0.13 mmol) as a colorless oil. The product was isolated as a cis:trans mixture 1:5.3.

**$^1$H NMR:**




**HPLC traces:**

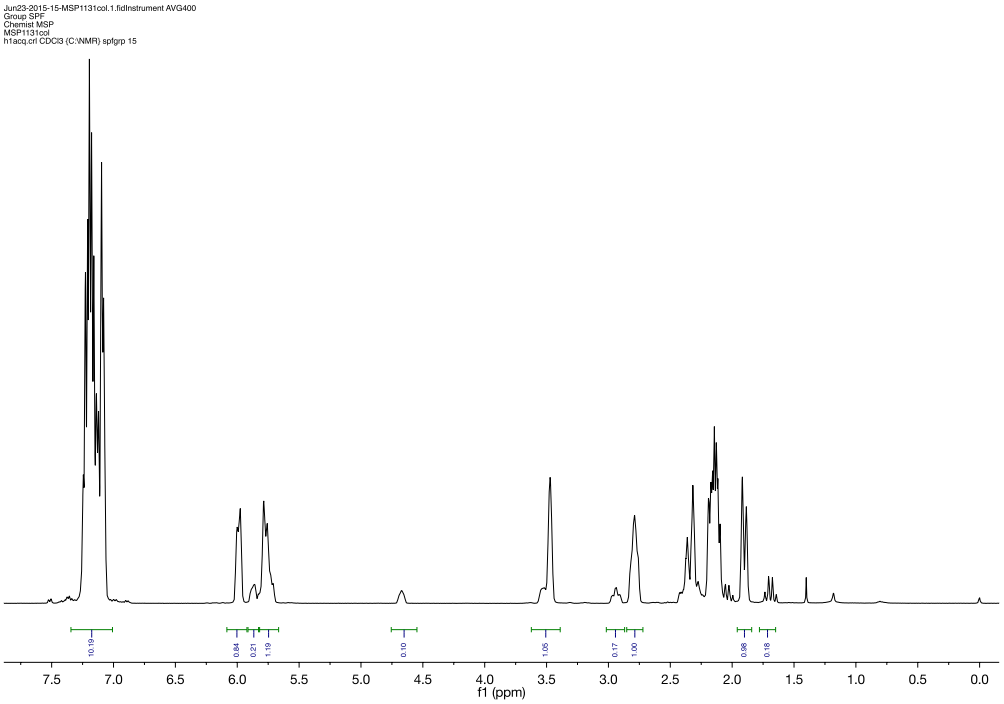


*Starting from a cis:trans mixture 6.1:1 of 3-chloro-5-phenylcyclohex-1-ene, stopping the reaction in 3 h:*

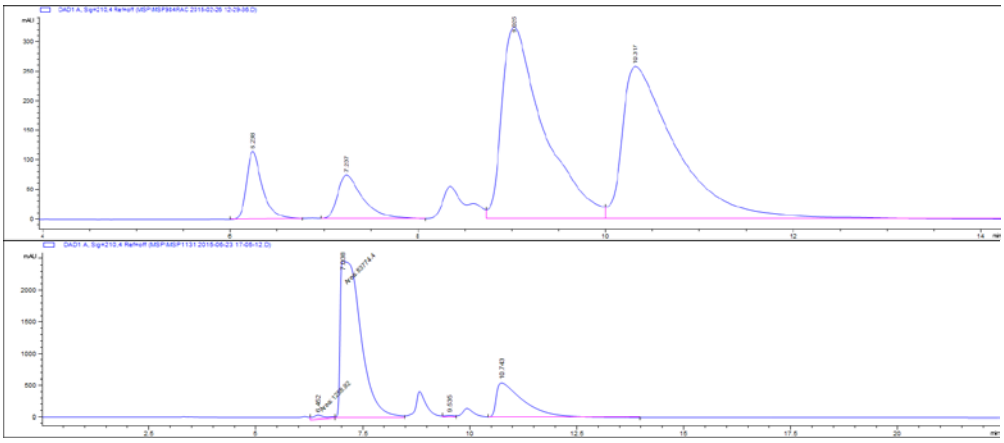
In a 10 mL round bottomed flask $[Rh(cod)(OH)]_2$ (1.5 mg, 0.003 mmol, 0.025 eq), (*S*)-Xyl-P-PHOS **A** (5.9 mg, 0.008 mmol, 0.06 eq) and $Cs_2CO_3$ (42.4mg, 0.13 mmol, 1.00 eq) were stirred in THF (0.65 mL) at 60 °C for 30 min. A solution of phenylboronic acid (30.8 mg, 0.25 mmol,

2.00 eq) and 3-chloro-5-phenylcyclohex-1-ene (24.3 mg, 0.13 mmol, 1.00 eq) in THF (0.35 mL) was then added *via* syringe and the flask rinsed with THF (0.3 mL). The resulting mixture was then stirred at 60 °C for 18 h. $SiO_2$ was then added to the reaction mixture and the solvent was carefully concentrated under vacuum. The resulting solid was directly loaded into a silica pad and eluted with pentane to obtain the pure product as a mixture of diastereomers in 95% yield (28.0 mg, 0.12 mmol) as a colorless oil. The product **30** was isolated as a cis:trans mixture 1:4.5. The remaining starting material **29** was a diastereomeric mixture >50:1 *cis*:*trans*.

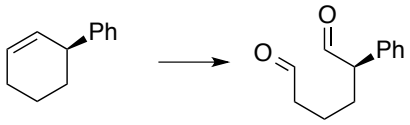
**$^1$H NMR:**




**HPLC traces:**



**(–)-(*R*)-2-Phenylhexanedial 31**




(*S*)-3-Phenylcyclohex-1-ene (102.7 mg, 0.65 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (0.9 mL) and MeOH (0.9 mL). The reaction flask was cooled to –78 °C before $O_2$ was bubbled trough the solution for 10 min, and then $O_3$ was bubbled through at –78 °C for 10 min (the starting material was completely consumed by TLC). $PPh_3$ (306.4 mg, 1.17 mmol, 1.80 eq) was added and the mixture was then allowed to warm to room temperature. After stirring for 20 additional min at room temperature the solvent was removed under reduced pressure and the crude reaction mixture purified by flash column chromatography (pentane: $Et_2O$, 8:2). (–)-(*R*)-2-Phenylhexanedial was obtained in 84% yield (103.4 mg, 0.54 mmol).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 9.74 (s, 1H), 9.69 (s, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.29 (m, 1H), 7.21 (d, *J* = 7.0 Hz, 2H), 3.55 (t, *J* = 8.1, 1H), 2.52 – 2.43 (m, 2H), 2.21 – 2.05 (m, 1H), 1.85 – 1.74 (m, 1H), 1.74 – 1.50 (m, 2H).

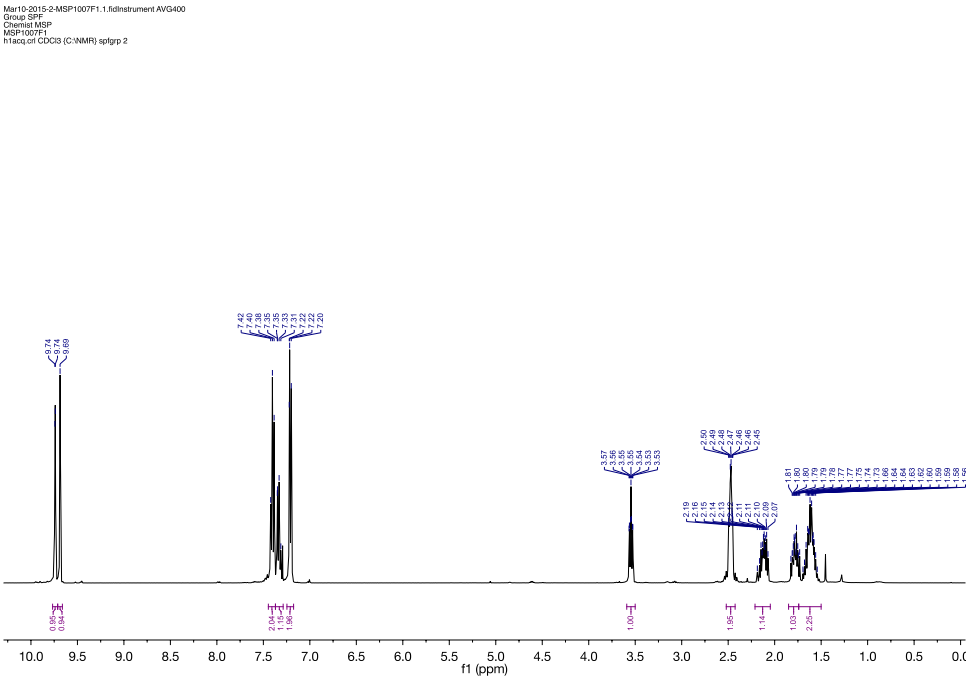
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 201.9, 200.3, 135.8, 129.3, 128.9, 127.8, 59.1, 43.7, 29.1, 19.7.

**HRMS** (ESI) *m*/z calcd for $C_{12}H_{14}O_2Na$ $[M+Na]^+$: 213.0886, found: 213.0887.

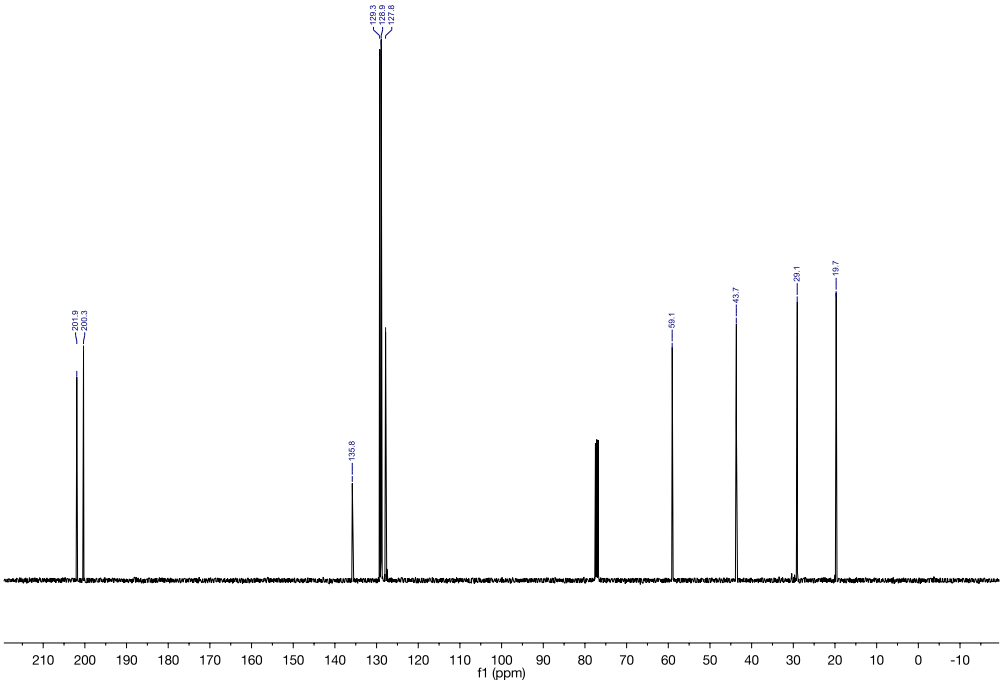
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 2941, 2822, 2723, 1719.

**$[\alpha]^{20}_{589}$** = –98.7 (c 1.91 $CHCl_3$).

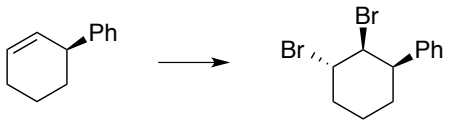
**$^1$H NMR:**




**$^{13}$C NMR:**




**(–)-((1*R*,2*S*,3*S*)-2,3-Dibromocyclohexyl)benzene 32**




In a flame dried flask purged with argon, $Br_2$ (1 µL, 0.02 mmol, 0.03 eq) and tetrabutylammonium tribromide (455.7 mg, 0.95 mmol, 1.50 eq) were dissolved in DCE (2.1 mL). The resulting mixture was then slowly added (dropwise, by syringe over 15 min) to a second flask containing (–)-(*S*)-cyclohex-2-enylbenzene (100 mg, 0.63 mmol, 1.0 eq) in DCE (0.5 mL). The resulting mixture was stirred at room temperature for 2 h (TLC control for the complete consumption of the starting material) before water (2 mL) was added. The mixture was partition and the aqueous phase extracted with $CH_2Cl_2$ (2 x 1 mL). The combined organic phase was washed with water (2 mL) and brine (2 mL), dried over $MgSO_4$, filtered and then concentrated under reduced pressure. The crude was purified by flash column chromatography (eluting with pentane) to afford the desired product in 70% yield (140.0 mg, 0.44 mmol).

**$^1$H NMR** (500 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.38 – 7.29 (m, 2H), 7.34 – 7.19 (m, 3H), 4.89 (m, 1H), 4.70 (m, 1H), 3.62 (dt, *J* = 12.2, 3.0 Hz, 1H), 2.53 (m, 1H), 2.23 – 2.08 (m, 1H), 2.10 – 1.93 (m, 2H), 1.88 – 1.75 (m, 2H).

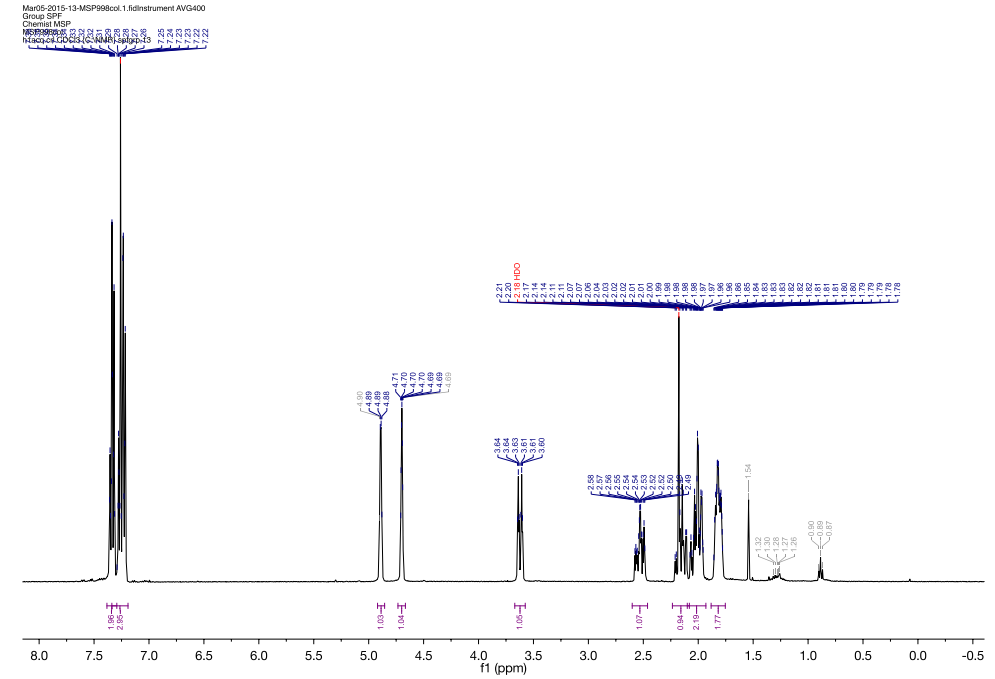
**$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta_C$ /ppm: 142.7, 128.4 (2C), 127.7 (2C), 127.0, 62.3, 54.7, 40.8, 28.0, 24.6, 20.8.

**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{14}Br_2$ $[M]^+$: 315.9462, found: 315.9463.

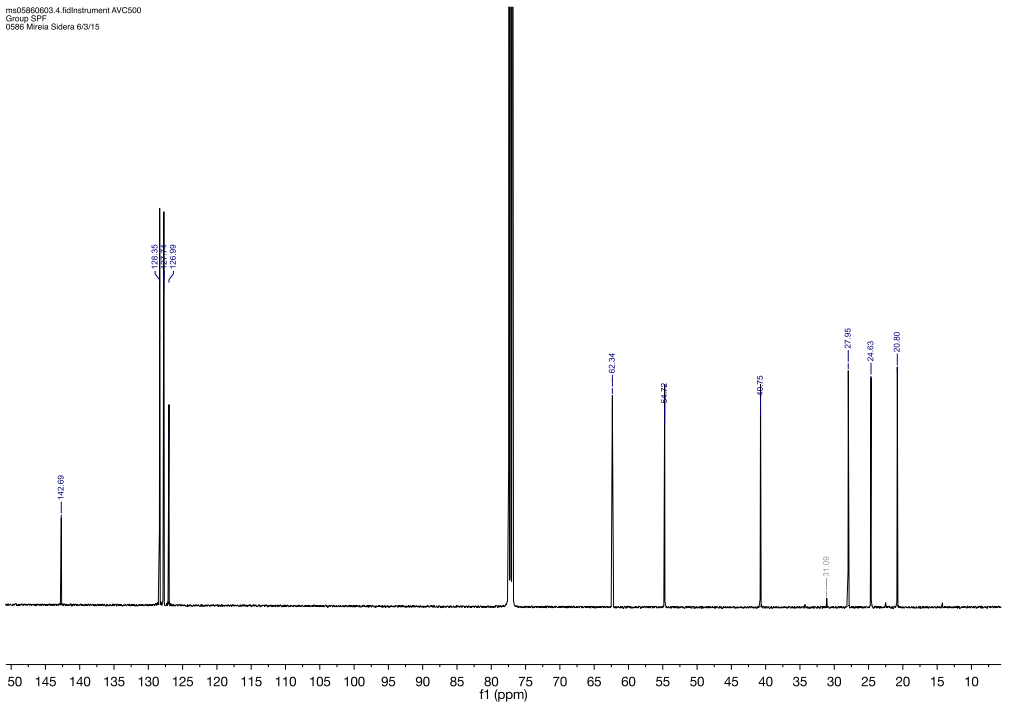
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 3061, 2939, 2836, 1603.

$[\alpha]^{20}_{589}$ = +58.2 (c 1.52 $CHCl_3$).

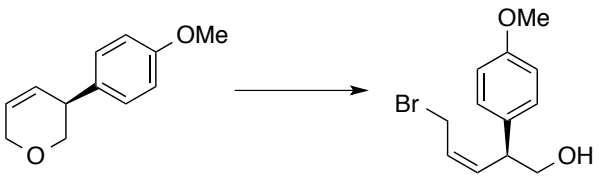
**$^1$H NMR:**




**$^{13}$C NMR:**



**(–)-(*S*,*Z*)-5-Bromo-2-(4-methoxyphenyl)pent-3-en-1-ol 33**




(–)-(*S*)-3-(4-methoxyphenyl)-3,6-dihydro-2*H*-pyran (39.5 mg, 0.20 mmol, 1.0 eq) was added to a flame dried flask, under argon, dissolved in $CH_2Cl_2$ (0.3 mL) and cooled to 0 °C. $BBr_3$ (60 µL, 0.62 mmol, 3.00 eq) was then slowly added dropwise via syringe over 15 min and the reaction mixture was allowed to warm to room temperature and stirring was continued overnight. Water (2 mL) was then added, the phases were partitioned and the aqueous phase extracted with $CH_2Cl_2$ (3 x 1 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified by flash column chromatography (hexane:EtOAc 9:1) to obtain the pure product in ~100 % yield (56.9 mg, 0.20 mmol).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta_H$ /ppm: 7.15 – 6.98 (m, 2H), 6.86 – 6.73 (m, 2H), 5.93 – 5.81 (m, 1H), 5.79 – 5.64 (m, 1H), 4.04 – 3.98 (m, 1H), 3.98 – 3.86 (m, 1H), 3.86 – 3.62 (m, 6H).

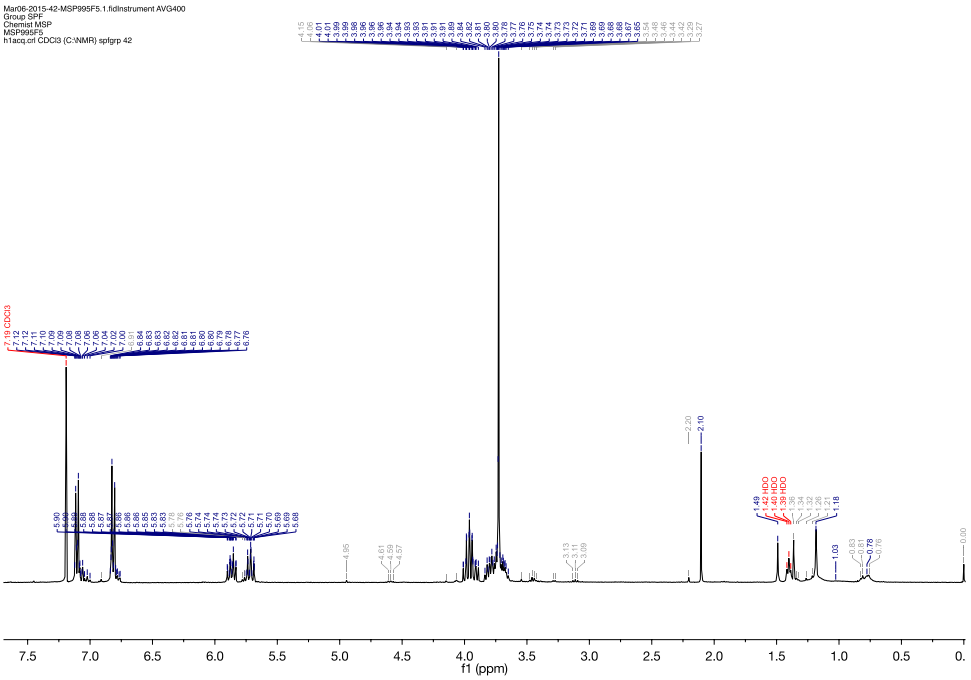
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta_C$ /ppm: 158.7, 135.0, 132.1, 128.7 (2C), 127.7, 114.4 (2C), 66.6, 55.3, 45.4, 26.8.

**HRMS** (EI/FI) *m*/z calcd for $C_{12}H_{15}BrO_2$ $[M]^+$: 270.0235, found: 270.0226.

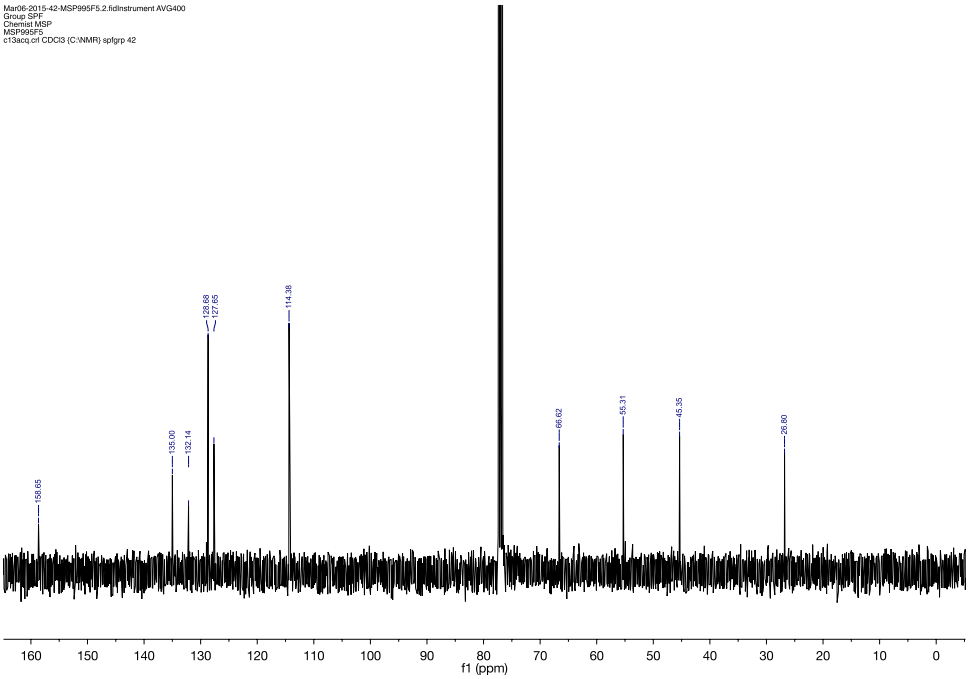
**IR** (ATR) ν ($cm^{-1}$, $CHCl_3$): 3421 (br.), 2919, 2836, 1512, 1248.

**$[\alpha]^{20}_{589}$** = –42.4 (c 1.39 $CHCl_3$).

**$^{1}$H NMR:**




**$^{13}$C NMR:**



1. H. You, E. Rideau, M. Sidera, S. P. Fletcher, Non-stabilized nucleophiles in Cu-catalysed dynamic kinetic asymmetric allylic alkylation. *Nature*. **517**, 351–355 (2015).
2. M. H. Katcher, A. G. Doyle, Palladium-Catalyzed Asymmetric Synthesis of Allylic Fluorides.pdf, 17402–17404 (2010).
3. K. Tissot-Croset, D. Polet, A. Alexakis, A highly effective phosphoramidite ligand for asymmetric allylic substitution. *Angew. Chem. Int. Ed.* **43**, 2426–2428 (2004).
4. T. Hayashi, A. Okada, T. Suzuka, M. Kawatsura, High enantioselectivity in rhodium-catalyzed allylic alkylation of 1-substituted 2-propenyl acetates. *Org. Lett.* **5**, 1713–1715 (2003).