Copper-Catalyzed Enantioselective
1,2-Borylation of 1,3-Dienes

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1. General information

All reactions were carried out under an inert atmosphere of nitrogen using either two-manifold vacuum/inert nitrogen lines or a M.Braun glove-box. Solvents were dried over activated alumina columns and further degassed by three successive “freeze-pump-thaw” cycles if necessary. NMR spectra were recorded on AMX–300, AMX–400 and AMX–500 Bruker Avance spectrometers at 298 K. \(^1\)H and \(^{13}\)C(\(^1\)H) NMR chemical shifts are given in ppm relative to SiMe\(_4\), with the solvent resonance used as internal reference. \(^1\)H NMR spectra were referenced to CDCl\(_3\) (7.26 ppm) and \(^{13}\)C(\(^1\)H) NMR spectra were referenced to CDCl\(_3\) (77.16 ppm). Infrared spectra were obtained on a Perkin–Elmer 1650 FT-IR spectrometer using neat samples on a diamond ATR Golden Gate sampler. The mass spectrometric data were obtained at the mass spectrometry facility of the University of Geneva (http://www.unige.ch/sciences/sms/). GC-MS analyses were performed on GC–HP 6890, column Agilent–HP1 (30 m–ID 0.32 mm, Film 0.25 μm) coupled with MS–HP 5973. The enantiomeric excesses (ee’s) were determined by HPLC, SFC and GC analyses.

HPLC analyses performed on a Shimadzu CTO-20AA with column DAICEL OD-H, OJ-H, AD-H and IC. GC analyses were performed on HP–6890, column HYDRODEX DiMOM and HYDRODEX TBDM, 50 m. SFC analyses were performed on a Waters Acquity UPC2 with columns OD-3, OJ-3, OZ-3, OB-H, AZ-3, AD, AS-3, AY-H. Retention times \((t_R)\) are given in minutes. Thin layer chromatography (TLC) was performed on plates of silica precoated with 0.25 mm Kieselgel 60 F\(_{254}\) from Merck. Flash chromatography was performed using silica gel SiliaFlash® P60 (230-400 mesh) from Silicycle. Commercial reagents, precatalysts and ligands were purchased from Aldrich, Fluka, Acros or Strem and used without purification unless otherwise noted. Liquid reagents were transferred with stainless steel syringes or cannula. All the dienes were prepared following reports from the literature.\(^1\) Copper complexes and ligands were stored and weighted inside a M. Braun glove-box. CuO\(_2\)Bu was prepared as described in the literature.\(^2\) Simplephos ligands L\(_8\)-\(9\) were prepared following reports from the literature.\(^3\)
2. Reaction optimization

**Table S1**: Ligand screening

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Reaction conditions: Unless otherwise noted, all reactions were performed with diene (0.12 mmol), ligand/CuCl (1:1, 10 mol%), B$_2$pin$_2$ (0.1 mmol), KOtBu (40 mol%), MeOH (0.2 mmol) in THF (0.3 mL) at 0 °C. Conversion and regioselectivity are for the boronic ester detected by $^1$H NMR. Enantioselectivity determined by HPLC analysis on a chiral stationary phase after oxidation to the alcohol. CuCl (10 mol%), ligand (20 mol%).
Table S2: Solvent optimization\(^a\)

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\(^a\) Reaction conditions: all reactions were performed with diene (0.12 mmol), (S,S)-L9/CuCl (2:1, 10 mol%), B\(_2\)pin\(_2\) (0.1 mmol), KOtBu (40 mol%), MeOH (0.2 mmol) in THF (1.0 mL) at 0 °C. \(^b\) At room temperature. \(^c\) Ligand/CuCl (1:1, 10 mol%). \(^d\) At –40 °C for 40 h.
Table S3: Base survey

Table S3: Base survey

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<sup>a</sup> Reaction conditions: all reactions were performed with diene (0.12 mmol), (S,S)-L9/CuCl (1:1, 10 mol%), B<sub>2</sub>(pin<sub>2</sub>) (0.1 mmol), Base (x mol%), MeOH (0.2 mmol) in n-pentane (1.0 mL) at −40 °C. <sup>b</sup>CuOtBu (10 mol%) was used without extra base, 0.15 M.
3. General procedure for the borylation/oxidation sequence

CuO{sub}Bu (0.03 mmol, 10 mol%), (R,R)-Simplephos-naph L9 (0.03 mmol, 10 mol%) and B{sub}2pin{sub}2 (0.3 mmol, 1.0 equiv.) were introduced into a Schlenk tube in a glove-box and dissolved in anhydrous and degassed n-pentane (2.0 mL, 0.15 M). After stirring at room temperature for 20 min, the reaction mixture was cooled to −40 °C. Diene 1 (0.36 mmol, 1.2 equiv.) and MeOH (0.6 mmol, 2.0 equiv.) were added next. After stirring at −40 °C for 40 h, the reaction was filtered through a short pad of Celite®, washed with diethyl ether (10 mL) and the solvent was removed under vacuum. The conversion and isomeric ratio of boronic ester were determined by {sup}1{sub}H NMR analysis of the crude reaction mixture.

To a solution of boronic ester in THF (3.0 mL) was added 30% H{sub}2{sub}O{sub}2 (1.5 mL) and 4 M NaOH (1.5 mL). The reaction mixture was stirred vigorously for 30 min at room temperature. The mixture was diluted with water and extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na{sub}2SO{sub}4, and concentrated. The residue was purified by column chromatography (pentane/ethyl acetate 6:1 to 3:1) to afford the corresponding alcohol 2'. This compound was used for determination of the enantiomeric excess.

Note: All racemates were prepared according to a similar procedure using DrewPhos (L10) as ligand (THF, rt, 24 h).
4. Substrate scope

Figure S1. Sequential borylation/oxidation of 2-(hetero)aryl substituted 1,3-dienes. Reaction conditions: 1 (0.36 mmol), B₂(pin)₂ (0.30 mmol). Chemoselectivity assessed by ¹H NMR after borylation. Yields of isolated alcohols 2'. Enantioselectivity determined by HPLC, GC or SFC using a chiral stationary phase after oxidation. a The minor isomer is 4'n. b Isolated as a 5:1 mixture.
**Figure S2.** Sequential borylation/oxidation of 2-alkyl substituted 1,3-dienes. Reaction conditions: 1u-x (0.18-0.36 mmol), B₂(pin)₂ (0.15-0.30 mmol). Chemoselectivity assessed by ¹H NMR after borylation. Isolated yields for alcohols 2v-x. Enantioselectivity determined by HPLC, GC, SFC using a chiral stationary phase after oxidation. "Conversion determined by ¹H NMR. At 0 °C for 24 h."
Figure S3. Catalyst-controlled diastereoselective borylation of (S)-1y. Reaction conditions: (S)-1y (0.24 mmol), B$_2$(pin)$_2$ (0.20 mmol). Chemoselectivity >20:1 in all cases was assessed by $^1$H NMR after borylation. Diastereoselectivity assessed by $^1$H and $^{13}$C{$^1$H} NMR after borylation and oxidation. Isolated yields after oxidation. (B) borylation of bis-diene 1z (0.36 mmol scale). $^a$ 1,2-/4,3-selectivity = 10:1. $^b$ Inseparable mixture.
**Figure S4.** Sequential borylation/oxidation of other substituted 1,3-dienes.
Following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl 1a (74 mg, 0.36 mmol, 1.2 equiv.), CuO/tBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.).

Conversion: 89%, 2a:3a > 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’a as a colorless oil (55 mg, 82% yield, 2’a:3’a > 20:1, 90% ee).

**TLC:** Rf = 0.5 (pentane/ethyl acetate 2:1).

**1H NMR** (300 MHz, CDCl3) δ (ppm) = 7.54 – 7.44 (m, 4H), 7.40 – 7.30 (m, 2H), 7.29 – 7.18 (m, 3H), 5.95 (ddd, JHH = 16.8, 10.7, 7.3 Hz, 1H, H-3), 5.23 – 5.05 (m, 2H, H-4), 3.77 (dd, JHH = 7.4, JHH = 3.1 Hz, 2H, H-1), 3.49 (dt, JHH = 7.3, 7.2 Hz, 1H, H-2), 1.52 (s, 1H, OH).

**13C{1H} NMR** (75 MHz, CDCl3) δ (ppm) = 140.8 (C-Ar), 139.9 (C-Ar), 139.7 (C-Ar), 138.2 (CH-3), 128.8 (CH-Ar), 128.4 (CH-Ar), 127.5 (CH-Ar), 127.3 (CH-Ar), 127.1 (CH-Ar), 117.2 (CH2-4), 66.1 (CH2-1), 52.2.


**IR** (neat) ν (cm⁻¹): 3354, 3029, 2923, 2855, 1637, 1601, 1519, 1486, 1463, 1407, 1261, 1181, 1027, 917, 836, 763, 696.

**HPLC:** 90% ee, chiral stationary column: IC, mobile phase: hexane/iPrOH = 99/1, 1.0 mL/min, 254 nm, 30 °C, tR (major) = 28.1 min, tR (minor) = 26.5 min.

[α]D²⁵ = +69.2 (c 1.03, CH₂Cl₂).
(S)-2-phenylbut-3-en-1-ol 2′b

Following the general procedure using buta-1,3-dien-2-ylbenzene 1b (47 mg, 0.36 mmol, 1.2 equiv.), CuOtBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 μL, 0.6 mmol, 2.0 equiv.). Conversions: 84%, 2b:3b = 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2′b as a colorless oil (29 mg, 65% yield, 2′b:3′b > 20:1, 90% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.4

HPLC: 90% ee, chiral stationary column: AD-H, mobile phase: hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm, 30 °C, tR (major) = 33.2 min, tR (minor) = 39.1 min.

[α]D = +51.2 (c 0.24, CH2Cl2).
(S)-2-(4-(dimethylamino)phenyl)but-3-en-1-ol 2’c

Following the general procedure using 4-(buta-1,3-dien-2-yl)-N,N-dimethylaniline 1c (62 mg, 0.36 mmol, 1.2 equiv.), CuOtBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 70%, 2c:3c = 12:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’c as a colorless oil (36 mg, 63% yield, 2’c:3’c = 14:1, 88% ee).

**TLC:** Rf = 0.3 (pentane/ethyl acetate 2:1).

**1H NMR** (300 MHz, CDCl3) δ (ppm) = 7.16 – 7.06 (m, 2H), 6.78 – 6.68 (m, 2H), 5.98 (ddd, 3 JHH = 16.6, 10.8, 7.6 Hz, 1H, H-3), 5.24 – 5.08 (m, 2H, H-4), 3.78 (d, 3 JHH = 7.2 Hz, 2H, H-1), 3.44 (dt, 3 JHH = 7.3, 7.2 Hz, 1H, H-2), 2.94 (s, 6H, H-5), 1.5 (s, 1H, O-H).

**13C{1H} NMR** (75 MHz, CDCl3) δ (ppm) = 149.7 (C-Ar), 138.9 (CH-3), 128.6 (CH-Ar), 128.2 (C-Ar), 116.3 (CH2-4), 113.1 (CH-Ar), 66.2 (CH2-1), 51.5 (CH-2), 40.7 (CH3-5).


**IR** (neat) ν (cm⁻¹): 3366, 3077, 2922, 2875, 2800, 1613, 1565, 1519, 1478, 1445, 1345, 1223, 1163, 1134, 1055, 1027, 946, 913, 814, 745, 646.

**HPLC:** 88% ee, chiral stationary column: AD-H, mobile phase: hexane/iPrOH = 97/3, 1.0 mL/min, 254 nm, 30 °C, tR (major) = 20.4 min, tR (minor) = 17.9 min.

[α]20D = +63.2 (c 0.65, CH2Cl2).
Supporting Information
(S)-2-(4-methoxyphenyl)but-3-en-1-ol 2’d

Following the general procedure using 1-(buta-1,3-dien-2-yl)-4-methoxybenzene 1d (58 mg, 0.36 mmol, 1.2 equiv.), CuOtfBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.).

Conversions: 87%, 2d:3d = 9:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’d as a colorless oil (37 mg, 70% yield, 2’d:3’d > 20:1, 90% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.4

**HPLC:** 90% ee, chiral stationary column: AD-H, mobile phase: hexane/iPrOH = 98/2, 1.0 mL/min, 220 nm, 30 °C, tR (major) = 26.3 min, tR (minor) = 23.6 min.

[α]D25 = +68.2 (c 0.56, CH2Cl2).
Supporting Information

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(S)-2-(4-isobutylphenyl)but-3-en-1-ol 2’e

Following the general procedure using 1-(buta-1,3-dien-2-yl)-4-isobutylbenzene 1e (74 mg, 0.3 mmol, 1.0 equiv.), CuOtfBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (91 mg, 0.36 mmol, 1.2 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 84%, 2e:3e = 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’e as a colorless oil (45 mg, 73% yield, 2’e:3’e > 20:1, 91% ee).

TLC: Rf = 0.6 (pentane/ethyl acetate 2:1).

1H NMR (400 MHz, CDCl3) δ (ppm) = 7.18 – 7.10 (m, 4H), 6.01 (ddd, 3JHH = 16.8, 10.6, 7.7 Hz, 1H, H-3), 5.23 – 5.16 (m, 2H, H-4), 3.85 – 3.77 (m, 2H, H-1), 3.51 (dt, 3JHH = 7.3, 7.2 Hz, 1H, H-2), 2.46 (d, 3JHH = 7.1 Hz, 2H, H-5), 1.85 (dt, 3JHH = 13.5, 6.8 Hz, 1H, H-6), 1.50 (s, 1H, H-O), 0.90 (d, 3JHH = 6.6 Hz, 6H, H-7).

13C{1H} NMR (100 MHz, CDCl3) δ (ppm) = 140.4 (C-Ar), 138.4 (C-3), 137.7 (C-Ar), 129.5 (CH-Ar), 127.6 (CH-Ar), 116.9 (CH2-4), 66.1 (CH2-1), 52.2 (CH-2), 45.0 (CH2-5), 30.2 (CH-6), 22.4 (CH3-7).


IR (neat) ν (cm⁻¹): 3351, 3082, 2954, 2923, 2869, 1638, 1512, 1465, 1415, 1383, 1367, 1168, 1117, 1054, 1031, 917, 844, 794.

HPLC: 91% ee, chiral stationary column: AD-H, mobile phase: hexane/iPrOH = 99/1, 1.0 mL/min, 220 nm, 30 °C, tR (major) = 16.9 min, tR (minor) = 15.2 min.

[a]D²⁵ = +55.5 (c 0.84, CH₂Cl₂).
(S)-2-(4-(trifluoromethyl)phenyl)but-3-en-1-ol 2’f

Following the general procedure using 1-(buta-1,3-dien-2-yl)-4-(trifluoromethyl)benzene 1f (48 mg, 0.24 mmol, 1.2 equiv.), CuOttBu (2.7 mg, 0.02 mmol, 10 mol%), (R,R)-L9 (15 mg, 0.02 mmol, 10 mol%), B2pin2 (51 mg, 0.2 mmol, 1.0 equiv.) and MeOH (16 µL, 0.4 mmol, 2.0 equiv.). Conversions: 70%, 2f:3f = 50:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’f as a colorless oil (24 mg, 56% yield, 2’f:3’f > 50:1, 86% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.4

HPLC: 86% ee, chiral stationary column: OJ-H, mobile phase: hexane/PrOH = 99/1, 1.0 mL/min, 220 nm, 30 °C, tR (major) = 16.5 min, tR (minor) = 19.7 min.

$[\alpha]_{D}^{20} = +34.6$ (c 0.80, CHCl3).
(S)-2-(4-fluorophenyl)but-3-en-1-ol 2’g

Following the general procedure using 1-(buta-1,3-dien-2-yl)-4-fluorobenzene 1g (54 mg, 0.36 mmol, 1.2 equiv.), CuOtBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 76%, 2g:3g = 8:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’g as a colorless oil (28 mg, 56% yield, 2’g:3’g > 20:1, 89% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.

**HPLC**: 89% ee, chiral stationary column: AD-H, mobile phase: hexane/iPrOH = 99/1, 1.0 mL/min, 220 nm, 30 °C, tR (major) = 26.6 min, tR (minor) = 24.6 min.

[α]D = +61.0 (c 0.26, CH2Cl2).
(S)-2-(4-chlorophenyl)but-3-en-1-ol 2'h

Following the general procedure using 1-((buta-1,3-dien-2-yl))-4-chlorobenzene 1h (60 mg, 0.36 mmol, 1.2 equiv.), CuOttBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 95%, 2h:3h = 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2'h as a colorless oil (44 mg, 80% yield, 2'h:3'h > 50:1, 89% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.$^4$

**HPLC:** 89% ee, chiral stationary column: AD-H, mobile phase: hexane/iPrOH = 99/1, 1.0 mL/min, 221 nm, 30 °C, $t_R$(major) = 30.8 min, $t_R$(minor) = 28.1 min.

$[\alpha]^{20}_D = +55.9$ (c 0.60, CHCl$_3$).
(S)-2-(benzo[d][1,3]dioxol-5-yl)but-3-en-1-ol 2'i

Following the general procedure using 5-(buta-1,3-dien-2-yl)benzo[d][1,3]dioxole 1i (63 mg, 0.36 mmol, 1.2 equiv.), CuOtfBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.).

Conversions: 93%, 2'i:3'i:4'i = 20:4:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2'i as a colorless oil (45 mg, 77% yield, 2'i:3'i:4'i = 50:1:1.6, 90% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.$^5$

**HPLC:** 90% ee, chiral stationary column: AD-H, mobile phase: hexane/iPrOH = 98/2, 1.0 mL/min, 220 nm, 30 °C, $t_R$ (major) = 40.6 min, $t_R$ (minor) = 44.1 min.

$^9$H$_2$Cl$_2$: $\alpha_{D}^{20} = +52.8$ (c 0.72, CH$_2$Cl$_2$).
(S)-2-(naphthalen-2-yl)but-3-en-1-ol 2‘j

Following the general procedure using 2-(buta-1,3-dien-2-yl)naphthalene 1j (65 mg, 0.36 mmol, 1.2 equiv.), CuOttBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 90%, 2j:3j > 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’j as a colorless oil (48 mg, 81% yield, 2’j:3’j > 20:1, 90% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.4

**HPLC**: 90% ee, chiral stationary column: AD-H, mobile phase: hexane/iPrOH = 99/1, 1.0 mL/min, 254 nm, 30 °C, tR (major) = 52.9 min, tR (minor) = 45.7 min.

[α]D20 = +73.4 (c 0.96, CH2Cl2).
(S)-2-(3-methoxyphenyl)but-3-en-1-ol 2'k

Following the general procedure using 1-(buta-1,3-dien-2-yl)-3-methoxybenzene 1k (49 mg, 0.3 mmol, 1.0 equiv.), CuOtfBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (91 mg, 0.36 mmol, 1.2 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.).

Conversions: 85%, 2k:3k = 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2'k as a colorless oil (43 mg, 73% yield, 2'k:3'k > 20:1, 91% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.6

HPLC: 91% ee, chiral stationary column: OD-H, mobile phase: hexane/iPrOH = 98/2, 1.0 mL/min, 220 nm, 30 °C, tR (major) = 23.3 min, tR (minor) = 21.6 min.

[α]25D = +56.2 (c 0.70, CH2Cl2).
(S)-2-(o-tolyl)but-3-en-1-ol 2’I

Following the general procedure using 1-(buta-1,3-dien-2-yl)-2-methylbenzene 1I (35 mg, 0.24 mmol, 1.2 equiv.), CuOtBu (2.7 mg, 0.02 mmol, 10 mol%), (R,R)-L9 (14.7 mg, 0.02 mmol, 10 mol%), B2pin2 (50.8 mg, 0.2 mmol, 1.0 equiv.) and MeOH (18 µL, 0.4 mmol, 2.0 equiv.) at −40 °C for 60 h. Conversions: 90%, 2I:3I = 2.6:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’I as a colorless oil (18 mg, 56% yield, 2’I:3’I > 20:1, 88% ee).

TLC: Rf = 0.6 (pentane/ethyl acetate 3:1).

1H NMR (400 MHz, CDCl3) δ (ppm) = 7.22 – 7.12 (m, 4H), 5.96 (dd, 3 JH-H = 17.1, 10.3, 6.8 Hz, 1H, H-3), 5.26 – 5.06 (m, 2H, H-4), 3.88 – 3.74 (m, 3H, H-1 and H-2), 2.37 (s, 3H, H-5), 1.56 (s, 1H, H-O).

13C(1H) NMR (100 MHz, CDCl3) δ (ppm) = 138.6 (C-Ar), 138.2 (CH-3), 136.7 (C-Ar), 130.8 (CH-Ar), 126.7 (CH-Ar), 126.4 (CH-Ar), 126.3 (CH-Ar), 117.0 (CH2-4), 65.3 (CH2-1), 47.9 (CH-2), 19.6 (CH3-5).


IR (neat) ν (cm⁻¹): 3355, 3075, 3020, 2927, 2876, 1726, 1637, 1604, 1490, 1462, 1413, 1380, 1295, 1261, 1028, 994, 916, 869, 753, 726, 665.

GC: 88% ee, HYDRODEX G-DiMOM, 100°C-1°C/min-170°C, 45 cm/s, H2, tR (major) = 44.1 min, tR (minor) = 43.1 min.

[α]D²⁰ = +52.4 (c 0.25, CH2Cl2).
### Supporting Information

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(S)-2-(2-fluorophenyl)but-3-en-1-ol 2’m

Following the general procedure using 1-(buta-1,3-dien-2-yl)-2-fluorobenzene 1m (54 mg, 0.36 mmol, 1.2 equiv.), CuOtBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 81%, 2m:3m = 15:1.

The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’m as a colorless oil (35 mg, 70% yield, 2’m:3’m > 20:1, 87% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.7

**HPLC:** 87% ee, chiral stationary column: IC, mobile phase: hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm, 30 °C, tR (major) = 24.5 min, tR (minor) = 23.6 min.

\[ \alpha \]D = +55.8 (c 0.45, CH2Cl2).
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(S)-4-(1-hydroxybut-3-en-2-yl)benzonitrile 2’n

Following the general procedure using 4-(buta-1,3-dien-2-yl)benzonitrile 1n (56 mg, 0.36 mmol, 1.2 equiv.), CuOtfBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 26%, 2n:4n = 13:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’n as a colorless oil (13 mg, 24% yield, 2’n:4’n = 18:1, 85% ee).

**TLC:** Rf = 0.3 (pentane/ethyl acetate 2:1).

**1H NMR** (400 MHz, CDCl3) δ (ppm) = 7.66 – 7.58 (m, 2H), 7.40 – 7.30 (m, 2H), 5.97 (ddd, 3JHH = 17.2, 10.4, 7.6 Hz, 1H, H-3), 5.33 – 5.11 (m, 2H, H-4), 3.86 (d, 3JHH = 6.8 Hz, 2H, H-1), 3.60 (dt, 3JHH = 7.1, 7.0 Hz, 1H, H-2), 1.55 (br, 1H, H-O).

**13C{1H} NMR** (75 MHz, CDCl3) δ (ppm) = 146.5 (C-Ar), 136.8 (CH-3), 132.5 (CH-Ar), 128.9 (CH-Ar), 118.8 (C-5), 118.3 (CH2-4), 110.8 (C-Ar), 65.6 (CH2-1), 52.4 (CH-2).


**IR** (neat) ν (cm⁻¹): 3437, 2926, 2228,1741, 1643, 1604, 1504, 1377, 1266, 1022, 984, 825, 733.

**HPLC:** 85% ee, chiral stationary column: AD-H, mobile phase: hexane/iPrOH = 97/3, 1.0 mL/min, 220 nm, 30 °C, tR (major) = 44.9 min, tR (minor) = 41.5 min.

[α]D²⁰ = +71.9 (c 0.15, CH2Cl2).
Supporting Information
(S)-2-(4-((trimethylsilyl)ethynyl)phenyl)but-3-en-1-ol 2’o

Following the general procedure using ((4-(buta-1,3-dien-2-yl)phenyl)ethynyl)trimethylsilane 10 (82 mg, 0.36 mmol, 1.2 equiv.), CuO-tBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 75%, 2'o:3'o > 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’o as a colorless oil (47 mg, 65% yield, 2’o:3’o > 20:1, 89% ee).

**TLC:** $R_f = 0.5$ (pentane/ethyl acetate 2:1).

**$^1$H NMR** (400 MHz, CDCl$_3$) δ (ppm) = 7.43 (d, $^3$J$_{HH} = 8.2$ Hz, 2H), 7.17 (d, $^3$J$_{HH} = 8.2$ Hz, 2H), 5.97 (ddd, $^3$J$_{HH} = 17.6$, 10.4, 7.6 Hz, 1H, **H-3**), 5.27 – 5.11 (m, 2H, **H-4**), 3.80 (d, $^3$J$_{HH} = 7.0$ Hz, 2H, **H-1**), 3.51 (dt, $^3$J$_{HH} = 7.2$ Hz, 7.2 Hz, 1H, **H-2**), 1.51 (br, 1H, **H-O**), 0.24 (s, 9H, **H-5**).

**$^{13}$C($^1$H) NMR** (100 MHz, CDCl$_3$) δ (ppm) = 141.2 (**C-Ar**), 137.7 (**CH-3**), 132.3 (**CH-Ar**), 127.9 (**CH-Ar**), 121.8 (**C-Ar**), 117.4 (**CH$_2$-4**), 104.9 (**C-7**), 94.2 (**C-6**), 65.9 (**CH$_2$-1**), 52.3 (**CH-2**), 0.0 (**CH$_3$-5**).

**LRMS** (ESI+): calculated for C$_{15}$H$_{20}$OSi [M]$: 244.13; found: 262.15 [M+NH$_4$]$^+$. 

**IR** (neat) ν (cm$^{-1}$): 3347, 3081, 2959, 2926, 2158, 1639, 1503, 1409, 1249, 1223, 1107, 1057, 1020, 995, 912, 861, 837, 758, 667.

**HPLC:** 89% ee, chiral stationary column: AD-H, mobile phase: hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 254 nm, 30 °C, $t_R$(major) = 20.9 min, $t_R$(minor) = 19.5 min. 

$[\alpha]^{20}_D = +66.3$ (c 0.54, CH$_2$Cl$_2$).
(S)-2-(1-methyl-1H-pyrrol-2-yl)but-3-en-1-ol 2’p

Following the general procedure using 2-(buta-1,3-dien-2-yl)-1-methyl-1H-pyrrole 1p (48 mg, 0.36 mmol, 1.2 equiv.), CuOtfBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 60%, 2p:3p = 1.3:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’p as a colorless oil (13 mg, 28% yield).

**TLC**: R$_f$ = 0.4 (pentane/ethyl acetate 2:1).

$^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) = 6.59 (dd, $^3$J$_{HH}$ = 2.7, 1.8 Hz, 1H, H-8), 6.11 (dd, $^3$J$_{HH}$ = 3.6, 2.7 Hz, 1H, H-9), 5.97 (dd, $^3$J$_{HH}$ = 3.6, 1.8 Hz, 1H, H-7), 5.82 (ddd, $^3$J$_{HH}$ = 17.1, 10.2, 7.5 Hz, 1H, H-3), 5.21 – 5.15 (m, 1H, H-4), 5.13 – 5.05 (m, 1H, H-4), 3.89 – 3.74 (m, 2H, H-1), 3.60 (t, $^3$J$_{HH}$ = 7.2 Hz, 1H, H-2), 3.55 (s, 3H, H-5), 1.69 (br, 1H, H-0).

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ (ppm) = 137.5 (CH-3), 131.0 (C-6), 122.3 (CH-8), 117.2 (CH$_2$-4), 107.0 (CH-9), 105.1 (CH-7), 64.6 (CH$_2$-1), 44.5 (CH-2), 33.7 (CH$_3$-5).

**LRMS (ESI+):** calculated for C$_9$H$_{13}$NO [M$^+$]: 151.10; found: 134.45 [M-OH]$^+$. 

**IR** (neat) ν (cm$^{-1}$): 3358, 2958, 2925, 2864, 1731, 1637, 1592, 1464, 1422, 1395, 1364, 1300, 1248, 1176, 1148, 1057, 1032, 996, 917, 870, 792, 608.

**HPLC**: 86% ee, chiral stationary column: OD-H, mobile phase: hexane/PrOH = 99/1, 1.0 mL/min, 220 nm, 30 °C, t$_R$ (major) = 28.3 min, t$_R$ (minor) = 37.2 min.

[$\alpha$]$^{20}_D$ = +74.7 (c 0.12, CH$_2$Cl$_2$).
**tert-butyl (S)-3-(1-hydroxybut-3-en-2-yl)-1H-indole-1-carboxylate 2′q**

Following the general procedure using tert-butyl 3-(buta-1,3-dien-2-yl)-1H-indole-1-carboxylate 1q (97 mg, 0.36 mmol, 1.2 equiv.), CuOtBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 84%, 2q:3q = 3.8:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2′q as a colorless oil (55 mg, 64% yield, 2′q:4′q = 20:1, 60% ee).

**TLC**: R$_f$ = 0.4 (pentane/ethyl acetate 2:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) = 8.15 (d, $^3$J$_{HH}$ = 8.4 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.47 (s, 1H, H-5), 7.36 – 7.30 (m, 1H), 7.25 – 7.19 (m, 1H), 6.06 (ddd, $^3$J$_{HH}$ = 17.4, 10.3, 7.3 Hz, 1H, H-3), 5.31 – 5.25 (m, 2H, H-4), 4.02 – 3.94 (m, 1H, H-1), 3.80 (td, $^3$J$_{HH}$ = 7.1, 6.1, Hz, 1H, H-2), 3.83 – 3.73 (m, 1H, H-1), 1.68 (br, 10H, H-O and H-8).

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ (ppm) = 149.7 (C-6), 137.1 (C-3), 135.6 (C-Ar), 129.7 (C-Ar), 124.5 (CH-Ar), 122.8 (CH-Ar), 122.4 (CH-Ar), 119.5 (C-Ar), 119.4 (CH-5), 117.5 (CH$_2$-4), 115.4 (CH-Ar), 83.7 (C-7), 64.8 (CH$_2$-1), 43.7 (CH-2), 28.2 (CH$_3$-8).

LRMS (ESI +): calculated for C$_{17}$H$_{21}$NO$_3$ [M]$^+$: 287.15; found: 288.05 [M+H]$^+$; 305.35 [M+NH$_4$]$^+$.

IR (neat) ν (cm$^{-1}$): 3405, 3055, 2978, 2930, 1728, 1639, 1608, 1567, 1452, 1369, 1308, 1255, 1068, 1020, 919, 856, 765, 739, 704, 636.

**HPLC**: 60% ee, chiral stationary column: OD-H, mobile phase: hexane/iPrOH = 98/2, 1.0 mL/min, 254 nm, 30 °C, $t_r$ (major) = 16.1 min, $t_r$ (minor) = 21.3 min.

$[\alpha]_{D}^{20} = +36.6$ (c 0.96, CH$_2$Cl$_2$).
Following the general procedure using 5-(buta-1,3-dien-2-yl)-2-methoxypyridine 1r (65 mg, 0.36 mmol, 1.2 equiv.), CuOtBu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.).

Conversions: 46%, 2r:3r:4r = 50:10:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2r as a colorless oil (24 mg, 45% yield, 2r:3r:4r = 50:10:1, 80% ee).

**TLC:** R$_f$ = 0.2 (pentane/acetone 2:1).

**$^1$H NMR** (400 MHz, CDCl$_3$) δ (ppm) = 8.02 (d, $^3$J$_{HH}$ = 2.4 Hz, 1H), 7.45 (dd, $^3$J$_{HH}$ = 8.5, 2.5 Hz, 1H), 6.72 (dd, $^3$J$_{HH}$ = 8.5, 0.7 Hz, 1H), 5.96 (ddd, $^3$J$_{HH}$ = 17.5, 10.4, 7.4 Hz, 1H, H-3), 5.26 – 5.11 (m, 2H, H-4), 3.91 (s, 3H, H-5), 3.83 – 3.77 (m, 2H, H-1), 3.48 (dt, $^3$J$_{HH}$ = 7.1 Hz, 7.1 Hz, 1H, H-2), 1.70 – 1.64 (m, 1H, H-O).

**$^{13}$C{H} NMR** (100 MHz, CDCl$_3$) δ (ppm) = 163.3 (C-Ar), 146.2 (CH-Ar), 138.2 (CH-Ar), 137.6 (CH-3), 128.8 (CH-Ar), 117.5 (CH$_2$-4), 110.9 (CH-Ar), 65.8 (CH$_2$-1), 53.4 (CH$_3$-5), 48.9 (CH-2).

**LRMS (ESI +):** calculated for C$_{10}$H$_{13}$NO$_2$ [M$^+$]: 179.09; found: 180.05 [M+H$^+$]; 162.25 [M-OH$^+$].

**IR** (neat) ν (cm$^{-1}$): 3328, 3080, 2980, 2946, 2871, 2816, 1844, 1639, 1605, 1572, 1492, 1391, 1312, 1286, 1130, 1055, 1023, 996, 919, 878, 827, 762, 662.

**HPLC:** 80% ee, chiral stationary column: OD-H, mobile phase: hexane/iPrOH = 99/1, 1.0 mL/min, 220 nm, 30 ºC, t$_R$ (major) = 55.2 min, t$_R$ (minor) = 59.3 min.

[$\alpha$]$^{20}$ D = +44.8 (c 0.36, CH$_2$Cl$_2$).
Following the general procedure using 1-(buta-1,3-dien-2-yl)cyclohex-1-ene (1S (48 mg, 0.36 mmol, 1.2 equiv.), CuOtBu (4 mg, 0.03 mmol, 10 mol%), \((R,R)-L9\) (22 mg, 0.03 mmol, 10 mol%), \(\text{B}_{2}\text{pin}_{2}\) (76 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 \(\mu\)L, 0.6 mmol, 2.0 equiv.). Conversions: 99\%, \(2s:4s = 25:1\). The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol \((S)-2's\) as a colorless oil (40 mg, 88\% yield, \(2's:4's = 25:1, 89\% \text{ ee}\)).

**TLC:** \(R_f = 0.2\) (pentane/ diethyl ether 9:1).

\(\text{H NMR}\) (400 MHz, CDCl\(3\)) \(\delta\) (ppm) = 5.75 (m, 1H, \(H-9\)), 5.55 (m, 1H, \(H-4\)), 5.12 (d, \(^3J_{HH} = 10.9\) Hz, 1H, \(H-10\)), 5.11 (d, \(^3J_{HH} = 16.4\) Hz, 1H, \(H-10\)), 3.60 (m, 2H, \(H-1\)) 2.81 (m, 1H, \(H-2\)), 2.03 (m, 2H, \(H-5\)), 1.94 (m, 2H, \(H-8\)), 1.58 (m, 4H, \(H-6 + H-7\)), 1.45 (t, \(^3J_{HH} = 6.1\) Hz, 1H, \(O\)H).

\(\text{C}^{1}\text{H NMR}\) (100 MHz, CDCl\(3\)) \(\delta\) (ppm) = 137.8 (\(CH-9\)), 136.5 (\(C-3\)), 124.1 (\(CH-4\)), 116.7 (\(CH_{2}-10\)), 63.4 (\(CH_{2}-1\)), 54.2 (\(CH-2\)), 26.6 (\(CH_{2}-8\)), 25.4 (\(CH_{2}-5\)), 23.0 (\(CH_{2}-6\) or \(CH_{2}-7\)), 22.6 (\(CH_{2}-6\) or \(CH_{2}-7\)).

**GC-MS (EI)** (C\(_{10}\)H\(_{16}\)O): 152.1 (3, \(M^+\)), 134.1 (5, \(M^+–18\)), 121.1 (53, \(M^+–31\)), 105.1 (53, \(M^+–47\)), 105.1 (12, \(M^+–47\)), 93.1 (49, \(M^+–49\)), 91.1 (63, \(M^+–61\)), 79.1 (100, \(M^+–73\)), 77.1 (48, \(M^+–75\)), 67.1 (39, \(M^+–85\)).

**IR** (neat) \(\nu\) (cm\(^{-1}\)): 3347, 2925, 2858, 2837, 1635, 1438, 1341, 1207, 1138, 1054, 102, 994, 913, 838, 801.

**HPLC:** 89\% ee, chiral stationary column: AD-H, mobile phase: hexane/PrOH = 99/1, 1.0 mL/min, 208 nm, 30 °C, \(t_{R}\) (major) = 14.5 min, \(t_{R}\) (minor) = 16.1 min.

\([\alpha]^{25}_{D} = +38.3\) (c 0.30, CH\(_2\)Cl\(_2\)).
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(S,E)-4-(2,6,6-trimethylcyclohex-1-en-1-yl)-2-vinylbut-3-en-1-ol 2’t

Following the general procedure using (E)-1,3,3-trimethyl-2-(3-methylene-penta-1,4-dien-1-yl)cyclohex-1-ene 1t (73 mg, 0.36 mmol, 1.2 equiv.), CuOfBu (4 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (76 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 99%, 2t:3t = 50:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S,E)-2’t as a colorless oil (40 mg, 60% yield, 2’t:3’t = 50:1, 80% ee).

**TLC**: Rf = 0.3 (pentane/ diethyl ether 4:1).

**1H NMR** (400 MHz, CDCl3) δ (ppm) = 5.98 (d, 3J_HH = 16.0 Hz, 1H, H-4), 5.80 (ddd, 3J_HH = 17.4, 10.5, 7.1 Hz, 1H, H-13), 5.29 (dd, 3J_HH = 16.0, 7.9 Hz, 1H, H-3), 5.18 (m, 2H, H-14), 3.58 (m, 2H, H-1), 3.03 (m, 1H, H-2), 1.97 (m, 2H, H-9), 1.67 (s, 3H, H-11), 1.60 (s, 1H, H-8), 1.46 (m, 1H, H-7), 0.99 (s, 3H, H-12), 0.98 (s, 3H, H-12).

**13C{1H} NMR** (100 MHz, CDCl3) δ (ppm) = 138.1 (CH-13), 137.4 (C-10), 132.3 (CH-3), 130.7 (CH-13), 128.7 (C-5), 116.8 (CH2-14), 65.5 (CH2-1), 50.6 (CH2-2), 39.5 (CH2-7), 34.0 (C-6), 32.8 (CH2-9), 29.0 (CH2-12), 28.9 (CH2-12), 21.7 (CH2-11), 19.4 (CH2-8).


**IR** (neat ν (cm⁻¹)): 3344, 2927, 2865, 1638, 1457, 1360, 1205, 1039, 973, 916.

**SFC**: 80% ee; chiral stationary phase: AZ column; 2% MeOH; tr (major) = 8.4 min, tr (minor) = 7.4 min.

[α]D^25 = +30.0 (c 0.55, CH2Cl2)
Supporting Information

Sample Name Q61; Vial 1:1; Injection 1; Channel PDA Ch1 210nm@4.8nm; Date Acquired 1/24/2018 3:02:45 PM CET

Sample Name DP9-18ox; Vial 1:2; Injection 1; Channel PDA Ch1 210nm@4.8nm; Date Acquired 1/24/2018 3:19:00 PM CET
(R)-6-methyl-2-vinylhept-5-en-1-ol 2’u

Following the general procedure using myrcene 1u (25 mg, 0.18 mmol, 1.2 equiv.), CuOtfBu (2.1 mg, 0.015 mmol, 10 mol%), (R,R)-L9 (11 mg, 0.0015 mmol, 10 mol%), B3pin2 (38 mg, 0.15 mmol, 1.0 equiv.) and MeOH (12 µL, 0.3 mmol, 2.0 equiv.). Reaction temperature: 0°C. Reaction time: 24 h. Conversions: 94%, 2u:3u = 1:5.7. Then it was oxidized under basic condition following the general procedure to afford mixture of alcohols 2'u:3'u, whose ratio was determined by 1H NMR 2'u:3'u = 1:5.7. All spectroscopic and spectrometric analyses of 2'u and 3'u were in agreement with the literature. Determination of enantiomeric excess was carried out on the crude mixture of homoallylic boronates 2u and 3u.

**GC:** HYDRODEX TBDM, 160°C-1°C/min-180°C, 45 cm/s, H2, \( t_R \) (major) = 67.98 min, \( t_R \) (minor) = 67.74 min.
(R)-2-phenethylbut-3-en-1-ol 2’v

Following the general procedure using (3-methylenepent-4-en-1-yl)benzene 1v (57 mg, 0.36 mmol, 1.2 equiv.), CuO–Bu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B2pin2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.).

Reaction temperature: 0°C. Reaction time: 24 h. Conversions: 84%, 2v:3v = 1:3. Then it was oxidized under basic condition following the general procedure to afford the alcohol (R)-2’v as a colorless oil (7.6 mg, 14% yield, 2’v:3’v > 20:1, 35% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.9

SFC: 35% ee; chiral stationary phase: AY column, 2% MeOH, 3 ml/min, 210 nm, tR (major) = 3.6 min, tR (minor) = 3.9 min.

[α]D = +3.5 (c 0.10, CH2Cl2).

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(S)-2-cyclohexylbut-3-en-1-ol 2′w

Following the general procedure using buta-1,3-dien-2-ylcyclohexane 1w (49 mg, 0.36 mmol, 1.2 equiv.), CuO·Bu (4.1 mg, 0.03 mmol, 10 mol%), (R,R)-L9 (22 mg, 0.03 mmol, 10 mol%), B₂pin₂ (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 77%, 2w:3w:4w = 10:12:1. Then it was oxidized under basic condition following the general procedure to afford the alcohol (S)-2′w as a yellow oil (11 mg, 23% yield, 2′w:3′w:4′w = 20:1:4, 87% ee). All spectroscopic and spectrometric analyses were in agreement with the literature.⁷

**GC**: HYDRODEX G-DiMOM, 100°C-1°C/min-170°C, 45 cm/s, H₂, tₗ (major) = 35.4 min, tₗ (minor) = 34.4 min.

[α]̂D = +11.5 (c 0.10, CH₂Cl₂).
(S)-2-((3r,5r,7r)-adamantan-1-yl)but-3-en-1-ol 2’x

Following the general procedure using (3r,5r,7r)-1-(buta-1,3-dien-2-yl)adamantane 1x (34 mg, 0.18 mmol, 1.2 equiv.), CuOtfBu (2.1 mg, 0.015 mmol, 10 mol%), (R,R)-L9 (11 mg, 0.015 mmol, 10 mol%), B$_2$pin$_2$ (38 mg, 0.15 mmol, 1.0 equiv.) and MeOH (13 µL, 0.3 mmol, 2.0 equiv.). Conversions: 87%, 2x:3x:4x = 14:2:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (S)-2’x as a colorless oil (24 mg, 78% yield, 2’x:4’x = 25:1, 94% ee).

TLC: R$_f$ = 0.4 (pentane/ethyl acetate 9:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) = 5.73 (ddd, 3J$_{HH}$ = 17.0, 10.1 Hz, 1H, H-3), 5.25 (dd, 3J$_{HH}$ = 10.1 Hz, 2J$_{HH}$ = 2.2 Hz, 1H, H-4), 3.80 (m, 1H, H-1), 3.42 (t, 3J$_{HH}$ = 10.3 Hz, 1H, H-1), 1.95 (m, 3H, CH$_2$-adamantyl), 1.82 (dt, 3J$_{HH}$ = 10.1, 5.0 Hz, 1H, H-2), 1.71 – 1.50 (m, 12H, CH$_2$-adamantyl), 1.30 (bs, 1H, OH).

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ (ppm) = 137.1 (CH-3), 119.4 (CH$_2$-4), 60.5 (CH$_2$-1), 58.9 (CH-2), 40.7 (CH$_2$-adamantyl), 37.3 (CH$_2$-adamantyl), 34.1 (C-5), 28.8 (CH$_2$-adamantyl).

LRMS (ESI +): calculated for C$_{14}$H$_{22}$O [M$^+$]: 206.17; found: 224.6 [M+NH$_4$]$^+$; 229.1 [M+Na]$^+$.

IR (neat) ν (cm$^{-1}$): 3338, 1902, 2849, 1447, 1344, 1260, 1024, 913, 797.

GC: 94% ee; chiral stationary phase: Hydrodex DiMOM, method: 100 °C for 120 minutes then 100–170 °C in 70 minutes, t$_R$ (major) = 56.3 min, t$_R$ (minor) = 55.7 min.

[α]$^2$$^0_D$ = +27.1 (c 0.25, CH$_2$Cl$_2$).
### Supporting Information

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**Note:** The images contain chemical structures and GC chromatograms. The tables show peak retention times, widths, areas, heights, and percentages.
(S)-2-((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)but-3-en-1-ol 2'y
Following the general procedure using (S)-1-(buta-1,3-dien-2-yl)-4-(prop-
1-en-2-yl)cyclohex-1-ene 1y (41 mg, 0.24 mmol, 1.0 equiv.), CuOBF₄ (2.8
mg, 0.020 mmol, 10 mol%), DrewPhos-L10 (12 mg, 0.020 mmol, 10
mol%), B₂pin₂ (51 mg, 0.2 mmol, 1.0 equiv.) and MeOH (16 µL, 0.4 mmol,
2.0 equiv.). Conversions: 80%, 2y:4y = 20:1, dr 1.8:1. The reaction mix-
ture was then oxidized under basic conditions following the general procedure and purified
by column chromatography to afford alcohol (S,S)-2'y as a colorless oil (22 mg, 57% yield,
2'y:4'y = 20:1, dr 1.8:1). TLC: Rf = 0.3 (pentane/diethyl ether 4:1).
[α]²⁵d = −68.3 (c 0.55, CH₂Cl₂).

(S)-2-((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)but-3-en-1-ol 2'y
Following the general procedure using (S)-1-(buta-1,3-dien-2-yl)-4-
(prop-1-en-2-yl)cyclohex-1-ene 1y (41 mg, 0.24 mmol, 1.0 equiv.), CuOBF₄ (2.8
mg, 0.020 mmol, 10 mol%), (R,R)-L9 (14.6 mg, 0.020
mmol, 10 mol%), B₂pin₂ (51 mg, 0.2 mmol, 1.0 equiv.) and MeOH (16
µL, 0.4 mmol, 2.0 equiv.). Conversions: 99%, 2y:3y = 50:1, dr >20:1.
The reaction mixture was then oxidized under basic conditions following the general pro-
cedure and purified by column chromatography to afford alcohol (S,S)-2'y as a colorless oil (34
mg, 86% yield, 2'y:4'y > 50:1, dr >20:1). Diastereomeric ratio (dr) calculated by integration
of non isochronic signals by ¹³C[¹H] NMR.
TLC: Rf = 0.3 (pentane/diethyl ether 4:1).
¹H NMR (500 MHz, CDCl₃) δ (ppm) = 5.75 (ddd, 3JHH = 16.9, 10.7, 7.8 Hz, 1H, H-12), 5.58
(m, 1H, H-4), 5.12 (m, 2H, H-13), 4.71 (m, 2H, H-11), 3.62 (m, 2H, H-1), 2.84 (m, 1H, H-2),
2.14 (m, 3H, H-6 + H-5), 2.02 (m, 2H, H-8), 1.98 (m, 1H, H-5), 1.83 (m, 1H, H-7), 1.73 (s,
3H, H-10), 1.47 (m, 2H, H-7 + H-10).
¹³C[¹H] NMR (126 MHz, CDCl₃) δ (ppm) = 149.9 (C-9), 137.8 (CH-12), 136.3 (C-3), 123.7
(CH-4), 116.7 (CH₂-13), 108.8 (CH₂-11), 63.4 (CH₂-1), 53.8 (CH-2), 41.2 (CH-6), 30.9 (CH₂-
5), 27.8 (CH₂-7), 26.9 (CH₂-8), 20.9 (CH₂-10).
LRMS (ESI +): calculated for C₁₃H₂₀O [M⁺]: 192.15; found: 210.4 [M+NH₄⁺].
GC-MS (EI) (C₁₃H₂₀O): 161.2 (19, M⁺-31), 131.1 (19, M⁺-61), 121.1 (13, M⁺-71), 117.1 (23,
M⁺-75), 105.1 (52, M⁺-87), 91.1 (100, M⁺-101), 79.1 (58, M⁺-113), 67.1 (34, M⁺-125), 53.1
(23, M⁺-139).
IR (neat) v (cm⁻¹): 3352, 3078, 2920, 1642, 1643, 1436, 1375, 1292, 1202, 1146, 1055,
1027, 994, 914, 886.
[α]²⁵d = −37.9 (c 0.80, CH₂Cl₂).
(R)-2-((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)but-3-en-1-ol 2’y

Following the general procedure using (S)-1-(buta-1,3-dien-2-yl)-4-(prop-1-en-2-yl)cyclohex-1-ene 1y (41 mg, 0.24 mmol, 1.0 equiv.), CuOtfBu (2.8 mg, 0.020 mmol, 10 mol%), (S,S)-L9 (14.6 mg, 0.020 mmol, 10 mol%), B2pin2 (51 mg, 0.2 mmol, 1.0 equiv.) and MeOH (16 µL, 0.4 mmol, 2.0 equiv.). Conversions: 99%, 2y:3y:4y = 20:1:1, dr 1:7.

The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (R,S)-2’y as a colorless oil (33 mg, 85% yield, 2’y:4’y = 20:1, dr 1:7).

Diastereoisomeric ratio (dr) calculated by integration of non isochronic signals by $^{13}$C($^1$H) NMR.

**TLC:** Rf = 0.3 (pentane/diethyl ether 4:1).

**$^1$H NMR** (500 MHz, CDCl$_3$) δ (ppm) = 5.74 (m, 1H, H-12), 5.57 (m, 1H, H-4), 5.13 (m, 2H, H-13), 4.71 (m, 2H, H-11), 3.61 (m, 2H, H-1), 2.84 (m, 1H, H-2), 2.16 (m, 3H, H-6 + H-5), 2.03 (m, 2H, H-8), 1.98 (m, 1H, H-5), 1.83 (m, 1H, H-7), 1.73 (s, 3H, H-10), 1.46 (m, 2H, H-7 + H-10).

**$^{13}$C($^1$H) NMR** (126 MHz, CDCl$_3$) δ (ppm) = 149.9 (C-9), 137.6 (CH-12), 136.2 (C-3), 123.4 (CH-4), 117.0 (CH$_2$-13), 108.8 (CH$_2$-11), 63.6 (CH$_2$-1), 53.8 (CH-2), 41.2 (CH-6), 30.9 (CH$_2$-5), 27.9 (CH$_2$-7), 27.1 (CH$_2$-8), 20.9 (CH$_3$-10).

**LRMS** (ESI +): calculated for C$_{13}$H$_{20}$O [M$^+$]: 192.15; found: 210.4 [M+NH$_4$]$^+$.

**GC-MS** (EI) (C$_{13}$H$_{20}$O): 161.2 (19, M$^+$-31), 131.1 (19, M$^+$-61), 121.1 (13, M$^+$-71), 117.1 (23, M$^+$-75), 105.1 (52, M$^+$-87), 91.1 (100, M$^+$-101), 79.1 (58, M$^+$-113), 67.1 (34, M$^+$-125), 53.1 (23, M$^+$-139).

**IR** (neat) ν (cm$^{-1}$): 3357, 3079, 2920, 1726, 1642, 1436, 1375, 1291, 1203, 1145, 1055, 1027, 994, 914, 886.

[α]$^{25}_D = -94.6$ (c 0.80, CH$_2$Cl$_2$).
(2S,2'S)-2,2'-((1,4-phenylene)bis(but-3-en-1-ol) 2'z

Following the general procedure using 1,4-di(buta-1,3-dien-2-y1)benzene 1z (65.6 mg, 0.36 mmol, 1.2 equiv.), CuOtBu (6.2 mg, 0.045 mmol, 15 mol%), (R,R)-L9 (33 mg, 0.045 mmol, 15 mol%), B3pin2 (152.4 mg, 0.6 mmol, 2.0 equiv.) and MeOH (54 µL, 1.2 mmol, 4.0 equiv.). Conversion: 79%, 2z:3z:4z = 24:2:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford the isomers of alcohol as a colorless oil (45 mg, 68% yield, 2'z:3'z:4'z = 10:1:0.3).

For the alcohol (S,S)-2'z (8:1 dr, 99% ee). Diastereoisomeric ratio (dr) estimated by integration of the HPLC chromatogram.

TLC: Rf = 0.4 (pentane/acetone 1:1).

1H NMR (400 MHz, CDCl3) δ (ppm) = 7.21 (s, 4H, H-6), 5.99 (ddd, 3JHH = 17.1, 10.4, 7.8 Hz, 2H, H-3), 5.10 – 5.26 (m, 4H, H-4), 3.81 (d, 3JHH = 7.1 Hz, 4H, H-1), 3.60 – 3.43 (m, 2H, H-2), 1.56 (s, 2H, H-O).

13C{1H} NMR (100 MHz, CDCl3) δ (ppm) = 139.3 (C-5), 138.2 (C-3), 128.3 (C-6), 117.1 (C-2), 66.0 (C-1), 52.2 (CH-2).


IR (neat) ν (cm⁻¹): 3334, 3080, 2928, 2878, 1638, 1511, 1412, 1300, 1189, 1111, 1051, 1025, 994, 915, 829, 732, 641.

HPLC: 99% ee, chiral stationary column: OD-H, mobile phase: hexane/iPrOH = 95/5, 1.0 mL/min, 220 nm, 30 °C, tR (major) = 24.7 min, tR (minor) = 21.5 min.

[α]D²⁵ = +89.3 (c 0.90, CH2Cl2).
5. Non-linear effect

Table S4

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a Reaction conditions: all reactions were performed with 1a (0.12 mmol), (R,R)-L9/CuOtBu (1:1, 10 mol%), B2pin2 (0.10 mmol), MeOH (0.20 mmol) in n-pentane (0.7 mL, 0.15 M) at –40 °C for 40 h. Average of two experiments.
6. References

7. NMR spectra of new compounds
(S)-2’a

$^1$H NMR (300 MHz, CDCl$_3$)
(S)-2'a

$^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$)
(S)-2'c
(S)-2'c:3'c = 14:1

$^1$H NMR (300 MHz, CDCl$_3$)

* = 3'c
(S)-2′c
(S)-2′c:3′c = 14:1

$^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$)
(S)-2'e

$^1$H NMR (400 MHz, CDCl$_3$)
(S)-2'e

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)
(S)-2'1

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C\(^{1}{\text{H}}\) NMR (100 MHz, CDCl\(_3\))
(S)-2'\text{n}
(S)-2'\text{n}:4'\text{n} = 18:1

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C$^1$H NMR (75 MHz, CDCl$_3$)

(S)-2'n
(S)-2'n:4'n = 18:1
$^1$H NMR (300 MHz, CDCl$_3$)
(S)-2°

$^{13}\text{C}[^1\text{H}]$ NMR (75 MHz, CDCl$_3$)
$\text{HO}$

$\text{Me}$

(S)-2'p

$^1\text{H}$ NMR (300 MHz, CDCl$_3$)

OH of (S)-2'p + H$_2$O
(S)-2\textsuperscript{p}

\(^{13}\text{C}\{^1\text{H}\}\text{ NMR}\ (100\text{ MHz}, \text{CDCl}_3)\)
(S)-2'q
(S)-2'q : 4'q = 20:1

$^1$H NMR (400 MHz, CDCl$_3$)
(S)-2'q
(S)-2'q : 4'q = 20:1
$^{13}$C\text{[H]}$\text{NMR (100 MHz, CDCl}_3$}
(S)-2'R
(S)-2'R : 3'R = 5:1
$^1$H NMR (400 MHz, CDCl$_3$)

* = 3'R
(S)-2'r
(S)-2'r : 3'r = 5:1

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)
(S)-2's
(S)-2's : 4's = 25:1
$^1$H NMR (400 MHz, CDCl$_3$)
(S)-2's
(S)-2's : 4's = 25:1

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)
(S,E)-2't

$^1$H NMR (400 MHz, CDCl$_3$)
(S,E)-$2^t$

$^{13}\text{C}^{1\text{H}}$ NMR (100 MHz, CDCl$_3$)
(S)-2'x
(S)-2'x : 4'x = 25:1

$^1$H NMR (400 MHz, CDCl$_3$)

* = 4'x
(S)-2':x
(S)-2':x : 4':x = 25:1

$^{13}\text{C}^{[1]}\text{H}$ NMR (100 MHz, CDCl$_3$)
(S,S)-2'y (dr = 20:1)

$^1$H NMR (500 MHz, CDCl$_3$)
(S,S)-2'y (dr = 20:1)

$^{13}$C$^1$H NMR (126 MHz, CDCl$_3$)
(R,S)-2'y (dr = 1:7)
(R,S)-2'y : 4'y = 20:1

$^1$H NMR (500 MHz, CDCl$_3$)

* = 4'y
(R,S)-2'y (dr = 1:7)
(R,S)-2'y : 4'y = 20:1

$^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$)
(S,S)-2'y (dr = 1.8:1)
$^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$)

(S,S)-2'y (dr = 20:1)
$^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$)

(R,S)-2'y (dr = 1:7)
$^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$)
(S,S)-2*z (dr = 8:1)
(S,S)-2*z: 3*z: 4*z = 10: 1: 0.3

$^1$H NMR (400 MHz, CDCl$_3$)

* = 3*z
# = 4*z
(S,S)-2'z (dr = 8:1)
(S,S)-2'z : 3'z : 4'z = 10 : 1 : 0.3

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)