Supplementary Materials for

Enantioselective C-H Crotylation of Primary Alcohols via Hydrohydroxyalkylation of Butadiene

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Published 22 March 2012 on Science Express
DOI: 10.1126/science.1219274

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Materials and Methods

General Information

All reactions were run under an atmosphere of argon. Tetrahydrofuran (THF) and toluene were obtained from Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Anhydrous solvents were transferred by oven-dried syringe. Sealed tubes (13×100 mm²) were purchased from Fisher Scientific (catalog number 14-959-35C) and were dried in an oven overnight and cooled under a stream of argon prior to use. RuH₂(CO)(PPh₃)₃ were prepared according to literature procedure (34). All ligands were used as received from Strem Chemicals Inc. Alcohols and aldehydes were purified by distillation or recrystallization immediately prior to use. Preparative column chromatography employing silica gel was performed according to the method of Still (35). Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Dynamic Adsorbents F₂₅₄). Visualization was accomplished with UV light followed by dipping in a p-anisaldehyde solution and heating. Purification of reaction products was carried out by flash column chromatography using Silicycle silica gel (40-63 μm).

Spectroscopy and Spectrometry

Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. Low-resolution mass spectra (LRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+H, M or M-H) or a suitable fragment ion. ¹H NMR spectra were recorded on a Varian Gemini (400 MHz) spectrometer at ambient temperature unless otherwise noted. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant(s) in Hz. ¹³C NMR spectra were recorded on a Varian Gemini (100 MHz) spectrometer and were routinely run with broadband decoupling. Chemical shifts are reported in ppm from tetramethylsilane, with the residual solvent resonance employed as the internal standard (CDCl₃ at 77.0 ppm).
Experimental Details and Characterization Data

(1R,2R)-2-methyl-1-phenylbut-3-en-1-ol (3a)

From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH₂(CO)(PPh₃)₃ (13.8 mg, 0.015 mmol, 5 mol%), dpff (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A₉ (15.1 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Alcohol 1a (0.031 mL, 0.30 mmol, 100 mol%) and tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) were added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography (SiO₂; 0-10% EtOAc/hexanes) to furnish the title compound (41.8 mg, 0.26 mmol, anti:syn = 8:1, 95:5 er) as a colorless oil in 86% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH₂(CO)(PPh₃)₃ (13.8 mg, 0.015 mmol, 5 mol%), dpff (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A₉ (15.1 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Aldehyde 2a (0.031 mL, 0.30 mmol, 100 mol%), tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) and 1,4-butanediol (0.053 mL, 0.60 mmol, 200 mol%) were added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography (SiO₂; 0-10% EtOAc/hexanes) to furnish the title compound (36.2 mg, 0.22 mmol, anti:syn = 8:1, 94:6 er) as a colorless oil in 74% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.26-7.38 (m, 5H), 5.86-5.76 (m, 1H), 5.24-5.17 (m, 2H), 4.35 (d, J = 8.0 Hz, 1H), 2.52-2.45 (m, 1H), 2.07 (br s, 1H), 0.87 (d, J = 6.8 Hz, 3H)

¹³C NMR (100 MHz, CDCl₃): δ 142.6, 140.9, 128.5, 127.9, 127.1, 117.1, 78.1, 46.6, 16.8.

LRMS (Cl⁺) m/z 145 [M-OH]⁺

[ α ]₂⁵ = +51 (c =1.0, CH₂Cl₂).

FTIR (neat): 3411, 3064, 3029, 2964, 2927, 2356, 1940, 1638, 1493, 1453, 1416, 1372, 1261, 1195, 1075, 1018, 912, 800, 759, 700, 680 cm⁻¹.

GC: Cyclosil-B: Initial temperature: 50 °C (5 min hold); 50-100 °C, rate: 0.5 °C/min (20 min hold); 100-135 °C, rate: 0.5 °C/min) t_major = 128.5 min, t_minor=129.5 min.

The spectroscopic properties of this compound were consistent with the data available in the literature (36).
Racemic:

Alcohol:
Aldehyde:

![Graph showing FID1 A, Front Signal]

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Methyl 4-((1R,2R)-1-hydroxy-2-methylbut-3-en-1-yl)benzoate (3b)

**From Alcohol Oxidation Level:** To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH₂(CO)(PPh₃)₃ (13.8 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A⁹ (15.1 mg, 0.03 mmol, 10 mol%) and alcohol 1b (49.9 mg, 0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) was added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO₂; 0-20% EtOAc/hexanes) to furnish the title compound (52.9 mg, 0.24 mmol, *anti*:syn = 7:1, 94:6 er) as a colorless oil in 80% yield.

**From Aldehyde Oxidation Level:** To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH₂(CO)(PPh₃)₃ (13.8 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A⁹ (15.1 mg, 0.03 mmol, 10 mol%) and aldehyde 2b (49.2 mg, 0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) and 1,4-butanediol (0.053 mL, 0.60 mmol, 200 mol%) were added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO₂; 0-20% EtOAc/hexanes) to furnish the title compound (52.9 mg, 0.24 mmol, *anti*:syn = 6:1, 93:7 er) as a colorless oil in 80% yield.

**¹H NMR** (400 MHz, CDCl₃): δ 7.97 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 5.79-5.69 (m, 1H), 5.17-5.12 (m, 2H), 4.40 (d, J = 7.2 Hz, 1H), 3.88 (s, 3H), 2.49-2.36 (m, 2H), 0.86 (d, J = 6.8 Hz, 3H).

**¹³C NMR** (100 MHz, CDCl₃): δ 147.9, 140.1, 129.7, 129.6, 127.0, 117.5, 77.3, 52.3, 46.5, 16.6.

**LRMS** (Cl+) *m/z* 221 [M+H]⁺

\[ [\alpha]_D^{25} = +41.4 \text{ (c} = 1.0, \text{ CHCl}_3) \]

**FTIR** (neat): 3467, 2953, 1719, 1435, 1276, 1177, 1110, 1017, 915, 810, 709 cm⁻¹.

**HPLC** (Chiralcel AD-H column, hexanes:i-PrOH = 95:5, 0.5 mL/min, 230 nm), *t*_major = 27.9 min, *t*_minor = 33.2 min.

The spectroscopic properties of this compound were consistent with the data available in the literature (37).
Racemic:

Signal 1: DAD1 D, Sig=230,16 Ref=360,100

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Signal 1: DAD1 D, Sig=230,16 Ref=360,100

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From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH\(_2\)(CO)(PPh\(_3\))\(_3\) (13.8 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid \(\text{H}_{3}\) (15.1 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Alcohol 1c (0.041 mL, 0.30 mmol, 100 mol%) and tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) were added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated \textit{in vacuo} and purified by flash column chromatography (SiO\(_2\); 0-20% EtOAc/hexanes) to furnish the title compound (57.3 mg, 0.25 mmol, \textit{anti:syn} = 7:1, 96:4 er) as a colorless oil in 83% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH\(_2\)(CO)(PPh\(_3\))\(_3\) (13.8 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid \(\text{H}_{3}\) (15.1 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Aldehyde 3a (0.041 mL, 0.30 mmol, 100 mol%), tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) and 1,4-butanediol (0.053 mL, 0.60 mmol, 200 mol%) were added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated \textit{in vacuo} and purified by flash column chromatography (SiO\(_2\); 0-10% EtOAc/hexanes) to furnish the title compound (43.6 mg, 0.19 mmol, \textit{anti:syn} = 6:1, 94:6 er) as a colorless oil in 63% yield.

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 7.60 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 5.81-5.72 (m, 1H), 5.23-5.18 (m, 1H), 4.43 (dd, J = 7.2 Hz, 2.6Hz, 1H), 2.51-2.42 (m, 1H), 2.26 (d, J = 2.6Hz, 1H) 0.89 (d, J = 6.8 Hz, 3H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 146.3, 139.8, 129.7 (q, J = 32 Hz), 127.1, 125.2 (q, J = 3.7 Hz), 124.0 (q, J = 271 Hz), 117.6, 77.2, 46.4, 16.4 ppm.

LRMS (Cl+) \(m/z\) 213 [M-OH]\(^+\)

\([\alpha\rceil^D_{25} = +52\) (c =1.0, CHCl\(_3\)) reported for 92% ee of the (R,R) compound \([\alpha\rceil^D_{25} = +55\) (c =1.0, CHCl\(_3\)).

FTIR (neat): 3380, 2976, 1620, 1458, 1418, 1323, 1162, 1120, 1066, 1016, 917, 831, 763, 741, 684 cm\(^{-1}\)

HPLC (Compound 3c was converted to the 4-nitro-benzoate for analysis, Chiralcel OD-H/OD-H/OD-H column, hexanes:i-ProOH = 97:3, 0.3 mL/min, 254 nm), \(t_{\text{major}} = 71.5\) min, \(t_{\text{minor}} = 75.9\) min

The spectroscopic properties of this compound were consistent with the data available in the literature (38).
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(1R,2R)-1-(4-bromophenyl)-2-methylbut-3-en-1-ol (3d)

From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH₂(CO)(PPh₃)₃ (13.8 mg, 0.015 mmol, 5 mol%), dpff (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A₀ (15.1 mg, 0.03 mmol, 10 mol%) and alcohol 1d (56.1 mg, 0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) was added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography (SiO₂; 0-20% EtOAc/hexanes) to furnish the title compound (70.2 mg, 0.29 mmol, anti: syn = 5:1, 93:7 er) as a colorless oil in 83% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH₂(CO)(PPh₃)₃ (13.8 mg, 0.015 mmol, 5 mol%), dpff (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A₀ (15.1 mg, 0.03 mmol, 10 mol%) and aldehyde 2d (55.5 mg, 0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) and 1,4-butanediol (0.053 mL, 0.60 mmol, 200 mol%) were added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography (SiO₂; 0-20% EtOAc/hexanes) to furnish the title compound (58.7 mg, 0.24 mmol, anti: syn = 5:1, 93:7 er) as a colorless oil in 81% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.46 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 5.81-5.71 (m, 1H), 5.22-5.16 (m, 2H), 4.32 (d, J = 7.6 Hz, 1H), 2.45-2.37 (m, 1H), 2.20 (s, 1H), 0.87 (d, J = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 141.4, 140.1, 131.3, 128.6, 121.4, 117.3, 77.1, 46.4, 16.4 ppm.

LRMS (Cl+). m/z 223 [M-OH]⁺

[ α ]D²⁵ = +53 (c =1.0, CHCl₃).

FTIR (neat): 3404, 2972, 2928, 1486, 1070, 1009, 916, 817, 755, 666 cm⁻¹.

HPLC (Chiralcel AS-H/AS-H column, hexanes:i-PrOH = 98.5:1.5, 0.5 mL/min, 230 nm), t_major = 36.1 min, t_minor = 42.1 min.

The spectroscopic properties of this compound were consistent with the data available in the literature (37).
Racemic:

Alcohol:
Aldehyde:

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Signal 1: DAD1 D, Sig=230,16 Ref=360,100
(1R,2R)-1-(4-fluorophenyl)-2-methylbut-3-en-1-ol (3e)

From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH₂(CO)(PPh₃)₃ (13.8 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A₉ (15.1 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Alcohol 1e (0.033 mL, 0.30 mmol, 100 mol%) and tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) were added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography (SiO₂; 0-20% EtOAc/hexanes) to furnish the title compound (45.8 mg, 0.26 mmol, \textit{anti:syn} = 6:1, 93:7 er) as a colorless oil in 85% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH₂(CO)(PPh₃)₃ (13.8 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A₉ (15.1 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Aldehyde 2e (0.032 mL, 0.30 mmol, 100 mol%), tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) and 1,4-butanediol (0.053 mL, 0.60 mmol, 200 mol%) were added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography (SiO₂; 0-20% EtOAc/hexanes) to furnish the title compound (43.2 mg, 0.24 mmol, \textit{anti:syn} = 5:1, 94:6 er) as a colorless oil in 80% yield.

\textbf{¹H NMR} (400 MHz, CDCl₃): δ 7.31-7.26 (m, 2H), 7.05-7.00 (m, 2H), 5.82-5.73 (m, 1H), 5.22-5.17 (m, 2H), 4.33 (dd, \textit{J} = 7.6 Hz, 2.4 Hz, 1H), 2.47-2.38 (m, 1H), 2.24 (d, \textit{J} = 2.4 Hz, 1H), 0.85 (d, \textit{J} = 6.8 Hz, 3H).

\textbf{¹³C NMR} (100 MHz, CDCl₃): δ 162.3 (d, 244.0 Hz), 140.4, 138.1 (d, 3.0 Hz), 128.4 (d, 8.2 Hz), 117.1, 115.0 (d, 21.6 Hz), 77.1, 46.5, 16.5 ppm.

\textbf{LRMS} (CI+). \textit{m/z} 181 [M+H]+

[\alpha]_D^{25} = +56.6 (c =1.0, CHCl₃).

\textbf{FTIR} (neat): 3411 3412, 2975, 1634, 1603, 1509, 1417, 1220, 1157, 1012, 829, 676 cm⁻¹.

\textbf{GC}: Cyclosil-B: Initial temperature: 50 °C (5 min hold); 50-100 °C, rate: 0.4 °C/min (25 min hold); 100-150 °C, rate: 0.4 °C/min) \textit{t}_\text{major} = 153.2 min, \textit{t}_\text{minor}=159.1 min.
Racemic:

Alcohol:
Aldehyde:

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(1R,2R)-1-(4-methoxyphenyl)-2-methylbut-3-en-1-ol

**From Alcohol Oxidation Level:** To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH2(CO)(PPh3)3 (13.8 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A9 (15.1 mg, 0.03 mmol, 10 mol%) and alcohol 1f (37.2 µL, 0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) was added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography (SiO2; 0-20% EtOAc/hexanes) to furnish the title compound (41.7 mg, 0.22 mmol, anti:syn = 6:1, 93:7 er) as a colorless oil in 72% yield.

**From Aldehyde Oxidation Level:** To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH2(CO)(PPh3)3 (13.8 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A9 (15.1 mg, 0.03 mmol, 10 mol%) and aldehyde 2f (36.5 µL, 0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) and 1,4-butanediol (0.053 mL, 0.60 mmol, 200 mol%) were added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography (SiO2; 0-20% EtOAc/hexanes) to furnish the title compound (38.1 mg, 0.20 mmol, anti:syn = 6:1, 94:6 er) as a colorless oil in 66% yield.

**1H NMR** (400 MHz, CDCl3): δ 7.25 (d, J = 7.8 Hz, 2H), 6.88 (d, J = 7.8 Hz, 2H), 5.86-5.77 (m, 1H), 5.29-5.16 (m, 2H), 4.30 (d, J = 8.0 Hz, 1H), 3.80 (s, 3H), 2.50-2.41 (m, 1H), 2.15 (s, 1H), 0.85 (d, J = 6.8 Hz, 3H).

**13C NMR** (100 MHz, CDCl3): δ 159.1, 141.0, 134.6, 128.0, 116.7, 113.6, 77.5, 55.3, 46.4, 16.6 ppm.

**LRMS** (Cl+). m/z 193 [M+H]+

[ α ]D25 = +51.8 (c =1.0, CHCl3).

**FTIR** (neat): 2961, 1611, 1510, 1458, 1302, 1260, 1173, 1032, 911, 731 cm⁻¹.

**GC** Cyclosil-B: Initial temperature: 50 °C (5 min hold); 50-115 °C rate: 0.5 C/min (20 min hold); 115-165°C, rate: 0.475 C/min t_major = 184.9 min, t_minor = 187.3 min.

The spectroscopic properties of this compound were consistent with the data available in the literature (39).
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![Graph of Racemic](image)

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(1R,2R)-2-methyl-1-(naphthalen-2-yl)but-3-en-1-ol (3g)

**From Alcohol Oxidation Level:** To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH₂(CO)(PPh₃)₃ (13.8 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A₉ (15.1 mg, 0.03 mmol, 10 mol%) and alcohol 1f (47.2 mg, 0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) was added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO₂; 0-20% EtOAc/hexanes) to furnish the title compound (60.4 mg, 0.29 mmol, *anti*:syn = 9:1, 94:6 er) as a colorless oil in 95% yield.

**From Aldehyde Oxidation Level:** To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added RuH₂(CO)(PPh₃)₃ (13.8 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), (R)-phosphoric acid A₉ (15.1 mg, 0.03 mmol, 10 mol%) and aldehyde 2f (46.8 mg, 0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Tetrahydrofuran (0.15 mL, 2.0 M concentration with respect to alcohol) and 1,4-butandiol (0.053 mL, 0.60 mmol, 200 mol%) were added and the solution was cooled to -78°C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO₂; 0-20% EtOAc/hexanes) to furnish the title compound (50.0 mg, 0.24 mmol, *anti*:syn = 4:1, 93:7 er) as a colorless oil in 79% yield.

**1H NMR** (400 MHz, CDCl₃): δ 7.85-7.83 (m, 3H), 7.78 (s, 1H), 7.51-7.46 (m, 3H), 5.91-5.82 (m, 1H), 5.27-5.20 (m, 2H), 4.53 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 2.65-2.56 (m, 1H), 2.32 (d, J = 2.0 Hz, 1H), 0.92 (d, J = 6.8 Hz, 3H).

**13C NMR** (100 MHz, CDCl₃): δ 140.6, 139.9, 133.2, 133.1, 128.1, 128.0, 127.7, 126.1, 126.0, 125.8, 124.7, 117.0, 78.0, 46.2, 16.6 ppm.

**LRMS** (Cl+). m/z 213 [M+H]⁺

[ α ]D²⁵ = +57 (c =1.0, CHCl₃).

**FTIR** (neat): 3411, 3056, 2972, 2869, 2359, 1932, 1636, 1507, 1371, 1270, 1159, 1123, 1018, 908, 817, 731 cm⁻¹

**HPLC** (Chiralcel AS-H/AS-H column, hexanes:i-PrOH = 95:5, 0.5 mL/min, 230 nm), tₘₐₗ₉₉ = 74.2 min, tₘ₂₉₉ = 92.3 min.

The spectroscopic properties of this compound were consistent with the data available in the literature (40).
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Figure S1: Chiral Phosphoric Acid A$_9$ Synthetic Approach

(i) Pd(PPh$_3$)$_4$ (5 mol%), 2-bromomesitylene (300 mol%), NaOH (350 mol%), THF, H$_2$O, 95 ºC, 18hr.
(ii) $n$-BuLi (150 mol%), iodoethane (150 mol%), THF, 18 hr. (iii) conc. HCl, EtOH, 18 hr. (vi) POCl$_3$ (130 mol%), pyridine, 115 ºC, 18 hr then H$_2$O, 115 ºC, 3h.
(R)-3-mesityl-2,2'-bis(methoxymethoxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene (B)

To a flame dried resealable pressure tube equipped with a magnetic stir bar was added compound A (3.72 g, 9.2 mmol, 100 mol%), Pd(PPh₃)₄ (0.53 g, 0.46 mmol, 5 mol%), and NaOH (1.3 g, 32.2 mmol, 350 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Tetrahydrofuran (46 mL, 0.2 M concentration with respect to compound A), water (18.4 mL, 0.5 M concentration with respect to compound A) and bromomesitylene (4.2 mL, 27.6 mmol, 300 mol%) were added. The solution was then vigourously degassed and the rubber septum quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 18 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was transferred to separatory funnel and extracted with CH₂Cl₂ (3x100 mL). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (SiO₂; ethyl acetate:hexanes, 1:15) to furnish the title compound (3.50 g, 7.2 mmol) as a white solid in 78% yield (41).

m.p.: 64-65 ºC

¹H NMR (400 MHz, CDCl₃): δ 7.04 (d, J = 8.6 Hz, 1H), 6.99 (d, J = 8.6 Hz, 1H), 6.93 (s, 2H), 6.83 (s, 1H), 5.12 (d, J = 6.7 Hz, 1H), 5.06 (d, J = 6.7 Hz, 1H), 4.36 (d, J = 5.5 Hz, 1H), 4.24 (d, J = 5.5 Hz, 1H), 3.37 (s, 3H), 2.84-2.78 (m, 4H), 2.54 (s, 3H), 2.47-2.38 (m, 2H), 2.33 (s, 3H), 2.26-2.20 (m, 2H), 2.16 (s, 3H), 2.14 (s, 3H), 1.81-1.63 (m, 8H).

¹³C NMR (100 MHz, CDCl₃): δ 152.5, 149.7, 137.1, 136.8, 136.7, 136.2, 136.0, 135.7, 132.9, 131.5, 131.3, 130.8, 130.7, 128.8, 127.9, 127.8, 127.1, 112.1, 97.7, 94.7, 55.6, 55.6, 29.6, 29.4, 27.5, 27.3, 23.3, 23.2, 23.1, 23.1, 21.1, 20.9, 20.8 ppm.

LRMS (CI+) m/z 500 [M]+.

FTIR (neat): 2922, 1478, 1244, 1206, 1060, 1016, 984, 922, 849, 807 cm⁻¹.
(R)-3-ethyl-3'-mesityl-2,2'-bis(methoxymethoxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene (C)

To a flame dried 100 mL round bottom flask compound B (1.70g, 3.4 mmol, 100 mol%) is added. The flask is sealed with a rubber septum and purged with nitrogen. Tetrahydrofuran (11 mL, 0.3 M concentration with respect to compound B) is added and the solution is cooled to 0°C. A solution of 2.5M n-BuLi in hexanes (2.0 mL, 5.1 mmol, 150 mol%) is added dropwise and stirred for 10 minutes. The reaction mixture is then allowed to warm to RT and stir for an additional 3 hrs. Iodoethane (0.4 mL, 5.1mmol, 150 mol%) is added dropwise and the mixture is stirred for 18 hrs. Upon complete consumption of starting material, as determined by TLC analysis, ammonium chloride (15 mL, sat. aq. sol.) was added. The organic layer was extracted with CH$_2$Cl$_2$ (3x50 mL) and the combined organic extracts were dried (MgSO$_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography (SiO$_2$; diethylether:hexanes, 1:20) to provide the title compound (1.12 g, 2.1 mmol) as a white solid in 63% yield.

m.p.: 63-66 °C

$^1$H NMR (400 MHz, CDCl$_3$): δ 6.93 (s, 3H), 6.90 (s, 3H), 6.79 (s, 3H), 4.75 (d, $J = 5.5$ Hz, 1H), 4.67 (d, $J = 5.5$ Hz, 1H), 4.29 (d, $J = 5.7$ Hz, 1H), 4.27 (d, $J = 5.7$ Hz, 1H), 3.15 (s, 3H), 2.78-2.75 (m, 2H), 2.67 (q, $J = 7.5$ Hz, 2H), 2.52 (s, 3H), 2.48-2.39 (m, 2H), 2.30 (s, 3H), 2.30-2.18 (m, 2H), 2.11 (s, 3H), 2.09 (s, 3H), 1.78-1.69 (m, 8H), 1.23 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 150.8, 149.8, 136.7, 136.5, 136.4, 136.1, 135.9, 134.6, 134.0, 132.9, 131.1, 131.0, 130.9, 128.9, 128.0, 127.9, 98.5, 97.3, 56.5, 55.5, 31.6, 29.6, 29.6, 27.7, 27.4, 23.3, 23.2, 23.1, 22.9, 21.1, 20.9, 20.8, 14.9 ppm.

LRMS (Cl+) $m/z$ 528 [M]$^+$. 

FTIR (neat): 2926, 1711, 1437, 1359, 1280, 1095, 909 cm$^{-1}$.

42
(R)-3-ethyl-3'-mesityl-5,5',6,6',7,7',8,8'-octahydro-[1,1'-binaphthalene]-2,2'-diol (D)

To a 250 mL round bottom flask compound C (1.12 g, 2.1 mmol, 100 mol%) is added. Ethanol (70 mL, 0.03 M concentration with respect to compound C) and conc. hydrochloric acid (7 mL, 0.3 M concentration with respect to compound C) were added sequentially. The reaction mixture is stirred at room temperature overnight. Upon complete consumption of starting material, as determined by TLC analysis, the reaction mixture is concentrated in vacuo. The residue was purified by column chromatography (SiO2; DCM:hexanes, 1:1) to provide the title compound (0.88 g, 2.0 mmol) as a white solid in 95% yield.

**m.p.:** 89-92 °C

**$^1$H NMR** (400 MHz, CDCl3): $\delta$ 7.07 (s, 2H), 7.06 (s, 1H), 6.97 (s, 1H), 4.77 (s, 1H), 4.65 (s, 1H), 2.88 (q, $J = 7.4$ Hz, 2H), 2.81-2.75 (m, 4H), 2.52-2.31 (m, 7H), 2.20 (s, 3H), 2.19 (s, 3H), 1.91-1.73 (m, 8H), 1.37 (t, $J = 7.4$ Hz, 3H).

**$^{13}$C NMR** (100 MHz, CDCl3): $\delta$ 148.8, 148.6, 137.2, 137.1, 137.0, 136.5, 133.8, 133.5, 131.7, 130.1, 130.0, 129.3, 128.5, 128.4, 127.7, 125.0, 119.9, 119.5, 31.7, 29.4, 27.2, 27.0, 23.4, 23.3, 23.2, 23.2, 22.8, 21.2, 20.7, 20.6, 14.2 ppm.

**LRMS** (CI+) $m/z$ 440 [M]$^+$.  

**FTIR** (neat): 2926, 1450, 1264, 1154, 982, 736 cm$^{-1}$.  

45
To a 100 mL round bottom flask equipped with a reflux condenser is added compound D (0.44g, 1 mmol, 100 mol%). Pyridine (2 mL, 0.5 M concentration with respect to compound D) and POCl₃ (0.170 mL, 1.8 mmol, 180 mol%) were added to the reaction mixture. The mixture was heated at 115°C (oil bath temperature) for 18 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. Water (1 mL, 1.0 M concentration with respect to compound D) was added dropwise and then heated to 115°C for an additional 3 hrs. Upon complete consumption of starting material, as determined by TLC analysis, the reaction mixture was cooled to ambient temperature and a solution of hydrochloric acid (10 mL, 3M aq. sol.) was added. The organic layer was extracted with CH₂Cl₂ (3x50 mL) and the combined organic extracts were dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography (SiO₂; 0-20% IPA:CH₂Cl₂) and concentrated in vacuo. The residue was diluted with CH₂Cl₂ then washed with a solution of hydrochloric acid (10 mL, 3M aq. sol.) and concentrated in vacuo to provide the title compound (0.46 g, 0.92 mmol) as a white solid in 92% yield.

m.p.: 228-230 °C

¹H NMR (400 MHz, CDCl₃): δ 8.17 (brs, 1H), 6.90 (s, 1H), 6.84 (s, 1H), 6.76 (s, 1H), 2.81-2.69 (m, 4H), 2.66-2.55 (m, 3H), 2.49-2.42 (m, 1H), 2.27-2.12 (m, 2H), 2.10 (s, 3H), 2.05 (s, 3H), 1.88 (s, 3H), 1.79-1.66 (m, 8H), 1.11 (t, J = 7.5 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 144.1, 144.0, 143.5, 143.4, 136.9, 136.8, 136.5, 135.1, 135.0, 133.3, 132.8, 131.6, 130.2, 129.7, 128.5, 127.6, 126.2, 29.3, 29.2, 27.8, 27.7, 22.8, 22.7, 22.7, 22.6, 22.3, 21.0, 20.8, 20.2, 14.0 ppm.

³¹P NMR (162 MHz, CDCl₃): 2.5 ppm.

LRMS (Cl⁺) m/z 502 [M⁺].

FTIR (neat): 2931, 1612, 1434, 1245, 1202, 1017, 905, 728 cm⁻¹.
Optimization of (R)-BINOL phosphoric acids.

Table S1.
Evaluation of 3,3’-disubstituted (R)-BINOL phosphoric acids

\[
\begin{align*}
\text{RuH}_2\text{CO(PPh}_3)_3 & \quad (5 \text{ mol\%}) \\
dppf & \quad (5 \text{ mol\%}) \\
\text{ac} & \quad (5 \text{ mol\%}) \\
\text{THF} & \quad 2\text{M}, 19 \text{ h}, 95 ^\circ \text{C}
\end{align*}
\]
Table S2.
Evaluation of mono-substituted (R)-BINOL phosphoric acids

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Conditions: RuH₂CO(PPh₃)₃ (5 mol%), dpff (5 mol%), acid (5 mol%), THF 2M, 19 h, 95 °C
Table S3.
Evaluation of acid loading of various 3’-substituted,3-mesityl-(R)-BINOL phosphoric acids

5 mol% acid

- 15% Yield
  - 6:1 dr
  - 71% ee

10 mol% acid

- 23% Yield
  - 6:1 dr
  - 78% ee

- 33% Yield
  - 8:1 dr
  - 84% ee

- 41% Yield
  - 4:1 dr
  - 72% ee

- 33% Yield
  - 7:1 dr
  - 76% ee
Table S4.
Evaluation of different substituent of (R)-3,3’-disubstituted (R)-H₈-BINOL phosphoric acids derivatives.

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<td>87% ee</td>
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References and Notes


36. I. Kim, S. B. Han, M. J. Krische, anti-Diastereo- and enantioselective carbonyl crotylation from the alcohol or aldehyde oxidation level employing a cyclometallated iridium catalyst: α-Methyl allyl acetate as a surrogate to preformed crotylmetal reagents. J. Am. Chem. Soc. 131, 2514 (2009). doi:10.1021/ja808857w


