



## Supporting Information

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**An Iridium-Catalyzed Regio-, Enantio-, and Diastereoselective  
Intermolecular Allylic Etherification with Aliphatic Alkoxides:  
Asymmetric Synthesis of Dihydropyrans and Dihydrofurans**

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**General Comments.**  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  solvent at 400.13 MHz with residual  $\text{CHCl}_3$  as the internal standard (7.26 ppm).  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded in  $\text{CDCl}_3$  solvent at 100.59 MHz with residual  $\text{CDCl}_3$  as the internal standard (77.0 ppm).  $^{31}\text{P}$  NMR spectra were recorded at 121.65 MHz, and the chemical shifts are recorded relative to  $\text{H}_3\text{PO}_4$  (0.0 ppm) as the external standard. Optical rotations were measured with a 1 cm cell (concentration  $c$  given as g / 100 mL). All reactions were conducted using standard Schlenk and drybox techniques. THF and benzene were distilled from sodium-benzophenone ketyl under nitrogen. Thin-layer chromatography (TLC) was performed on silica gel plates, and components were visualized by observation under UV lights or by treating the plates with phosphomolybdic acid followed by heating. Flash chromatography was performed either manually or with a Flashmaster II instrument from Argonaut Technology.

All allylic carbonates were prepared by the reaction of the corresponding allylic alcohol with di-*tert*-butyl carbonate catalyzed by Bu<sub>4</sub>N<sup>+</sup>HSO<sub>4</sub><sup>-</sup> as phase transfer reagent<sup>i</sup>. (*E*)-4-Methoxycinnamyl alcohol and (*E*)-2-buten-1-ol were prepared by reduction of the corresponding aldehyde with NaBH<sub>4</sub>/CeCl<sub>3</sub>. Bis[(*R*)-(-)-(1-naphthyl)ethyl]amine hydrochloride, CuI, BuLi, alcohols, bis[tricyclohexylphosphine]benzylidene ruthenium dichloride (Grubbs's catalyst),<sup>ii</sup> and (*R*), (*S*)-BINOL were purchased from commercial suppliers and used without purification.

***O,O'*-(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-*N,N'*-di-(*R,R*)-1-naphthylethylphosphoramidite ((*Ra,Rc,Rc*)-L2):** To a Schlenk flask containing a solution of bis[(*R*)-(-)-(1-naphthyl)ethyl]amine hydrochloride (0.90 g, 2.5 mmol) in THF (3.0 mL) was added under an N<sub>2</sub> atmosphere a 2.5 M solution of BuLi in hexane (2.0 mL, 5.0 mmol, 2.0 equiv) at -78 °C. The reaction mixture was slowly warmed to 0 °C over 30 min and transferred to a second Schlenk flask at -78 °C containing a solution of PCl<sub>3</sub> (0.22 mL, 2.5 mmol, 1.0 equiv) in THF (3.0 mL) at -78 °C. The reaction mixture was slowly warmed to 0 °C over 30 min. To this flask was added Et<sub>3</sub>N (1.1 mL, 7.5 mmol, 3.0 equiv) followed by a solution (*R*)-BINOL (0.71 g, 2.5 mmol, 1.0 equiv) at 0 °C. The reaction was allowed to warm to room temperature overnight and was passed through a pad of Celite. The solution was concentrated, and the crude

mixture was purified by column chromatography (SiO<sub>2</sub>, 5% EtOAc in hexanes) to afford the desired ligand as a white solid (1.11 g, 70%).  $[\alpha]_D = +214.0$  ( $c = 7.58$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>)  $\delta$  8.11 (d,  $J = 8.8$  Hz, 1 H), 8.01 (d,  $J = 8.4$  Hz, 1 H), 7.86–7.70 (m, 8 H), 7.56 (d,  $J = 8.8$  Hz, 1 H), 7.54–7.36 (m, 8 H), 7.36–7.25 (m, 5 H), 7.15 (t,  $J = 7.6$  Hz, 2 H), 5.60 (q,  $J = 7.2$  Hz, 1 H), 5.58 (q,  $J = 7.2$  Hz, 1 H), 1.81 (d,  $J = 7.2$  Hz, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.8 (d,  $J = 9.0$  Hz), 149.5, 139.0 (d,  $J = 4.2$  Hz), 133.1, 132.9 (d,  $J = 1.4$  Hz), 132.7 (d,  $J = 1.5$  Hz), 131.4, 130.6, 130.3 (d,  $J = 24.4$  Hz), 129.6, 128.4, 128.3, 128.1, 127.1, 126.9, 126.1, 125.8, 125.4, 124.9 (d,  $J = 7.4$  Hz), 124.8, 124.5 (d,  $J = 4.5$  Hz), 124.42, 124.37, 124.24, 123.0 (d,  $J = 1.6$  Hz), 122.3 (d,  $J = 1.7$  Hz), 122.0, 121.5 (d,  $J = 2.2$  Hz), 52.9 (d,  $J = 11.7$  Hz), 23.27 (d,  $J = 13.4$  Hz). <sup>31</sup>P NMR (121.65 MHz, CDCl<sub>3</sub>)  $\delta$  154.5.

**General Procedure for reaction between *tert*-butyl carbonates and alkoxides:** In a drybox, lithium alkoxides (1.00 mmol) and CuI (200 mg, 1.05 mmol) were added to a screw-capped vial. THF (1.0 mL) was added, and the suspension was stirred for 30 min. To this suspension was added a solution of [Ir(COD)Cl]<sub>2</sub> (3.4 mg, 0.005 mmol for reactions of primary alkoxides; 6.7 mg, 0.010 mmol for reactions of secondary and tertiary alkoxides) and (*Ra,Rc,Rc*)-**L2** (6.4 mg, 0.010 mmol for reactions of primary

alkoxides; 12.8 mg, 0.020 mmol for reactions of secondary and tertiary alkoxides) in THF (0.5 mL for primary alkoxides; 1.0 mL for secondary and tertiary alkoxides). A small magnetic stir bar was added, and the vial was sealed with a cap containing a PTFE septum and removed from the drybox. The vial was placed into an ice-water bath, and *tert*-butyl carbonate (0.50 mmol) was added to the reaction mixture by syringe. The reaction mixture was slowly warmed to room temperature over 4 h. After the reaction was complete, as determined by GC and TLC (the reaction time is considerable longer for tertiary alkoxide nucleophiles (48 h) than that with common secondary alkoxides (12 h)), the crude mixture was passed through a pad of silica gel, eluting with 10% EtOAc in hexanes, and the resulting solutions were concentrated. The ratio of regioisomers was determined by  $^1\text{H}$  NMR analysis of the crude sample. The mixture was then purified by flash column chromatography (1% ethyl acetate in hexanes for manual chromatography or 0-2% ethyl acetate in hexanes for automated chromatography) on silica gel to give the desired product.

**(*R*)-(+) -1-Benzyloxy-1-phenyl-2-propene<sup>iii</sup> (3a):** Following the general procedure, the desired product was obtained as colorless oil using manual chromatography (102.6 mg, 91%).  $^1\text{H}$  NMR analysis of the crude mixture showed a branched to linear ratio of 99/1. HPLC analysis indicated that the enantiomeric excess of the product was 94% [Diacel CHIRALPAK OJ (0.46 cm x 25 cm);

hexanes/2-propanol = 99.8/0.2; flow rate = 0.5 mL/min; detection wavelength = 220 nm; Tr = 36.8 (major), 41.9 (minor) min].  $[\alpha]_D = +13.4$  (c = 10.7, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>)  $\delta$  7.44–7.28 (m, 10 H), 6.04 (ddd, *J* = 17.0, 10.2, 6.4 Hz, 1 H), 5.34 (dt, *J* = 16.8, 1.4 Hz, 1 H), 5.27 (dt, *J* = 10.0, 1.4 Hz, 1 H), 4.89 (d, *J* = 6.8 Hz, 1 H), 4.57 (s, 2 H).

**(-)-2-Benzoyloxy-3-butene<sup>iii</sup> (3b):** Following the general procedure (Table 2, entry 1), the desired product was obtained as colorless oil using automated chromatography (64.4 mg, 80%). <sup>1</sup>H NMR analysis of the crude mixture showed a branched to linear ratio of 95/5. HPLC analysis indicated that the enantiomeric excess of the product was 97% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.5/0.5; flow rate = 0.6 mL/min; detection wavelength = 220 nm; Tr = 13.9 (major), 26.3 (minor) min].  $[\alpha]_D = -22.0$  (c = 0.65, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>)  $\delta$  7.40–7.22 (m, 5 H), 5.80 (ddd, *J* = 17.0, 10.2, 6.4 Hz, 1 H), 5.22 (dt, *J* = 16.8, 1.4 Hz, 1 H), 5.18 (dt, *J* = 10.0, 1.4 Hz, 1 H), 4.58 (d, *J* = 11.6 Hz, 1 H), 4.40 (d, *J* = 12.0 Hz, 1 H), 3.93 (dq, *J* = 6.8, 6.8 Hz, 1 H), 1.30 (d, *J* = 6.4 Hz, 3 H).

**(-)-1-[2-Methyl-1-(1-methylethyl)propyloxy]-1-phenyl-2-propene<sup>iv</sup> (3c):** Following the general procedure (Table1, entry 2), the desired product was obtained as colorless oil using manual chromatography (99.8 mg, 86%). <sup>1</sup>H NMR analysis of the

crude mixture showed a branched to linear ratio of 99/1.  $[\alpha]_D = -45.7$  ( $c = 2.35$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32–7.15 (m, 5 H), 5.83 (ddd,  $J = 17.2, 10.0, 6.0$  Hz, 1 H), 5.18 (dt,  $J = 17.2, 1.2$  Hz, 1 H), 5.10 (dt,  $J = 10.4, 1.3$  Hz, 1 H), 4.74 (d,  $J = 7.6$  Hz, 1 H), 2.95 (t,  $J = 5.2$  Hz, 1 H), 1.85–1.73 (m, 2 H), 0.90 (d,  $J = 4.4$  Hz, 3 H), 0.88 (d,  $J = 4.4$  Hz, 3 H), 0.77 (d,  $J = 6.8$  Hz, 3 H), 0.74 (d,  $J = 6.8$  Hz, 3 H). Anal. Calcd. For  $\text{C}_{16}\text{H}_{24}\text{O}$ : C, 82.70; H, 10.41. Found: C, 82.49; H, 10.47. To measure the ee of the product, it was converted to the corresponding terminal alcohol by hydroboration. A portion of the product (46 mg, 0.20 mmol) was dissolved in THF (0.5 mL), cooled to 0 °C, and treated with  $\text{BH}_3\cdot\text{THF}$  (1.0 M, 0.15 mL, 0.30 mmol). After 1 h,  $\text{H}_2\text{O}$  (0.10 mL) was added, and the reaction was stirred for another 30 min before adding aqueous NaOH (20 wt%, 0.2 mL) and  $\text{H}_2\text{O}_2$  (30 wt%, 0.1 mL). The reaction was then warmed to room temperature over 1 h, saturated with  $\text{K}_2\text{CO}_3$ , and washed with  $\text{CH}_2\text{Cl}_2$  (3 x 5 mL). The combined organic layer was washed with brine (2 x 10 mL), dried over  $\text{Na}_2\text{CO}_3$ , concentrated, and purified by manual chromatography ( $\text{SiO}_2$ , 12% EtOAc in hexanes) to give the alcohol. HPLC analysis indicated that the enantiomeric excess of the alcohol was 96% [Diacel CHIRALPAK OJ (0.46 cm x 25 cm); hexanes/2-propanol = 90/10; flow rate = 0.5 mL/min; detection wavelength = 210 nm; Tr = 7.7 (major), 8.7 (minor) min].

**(+)-1-Cyclohexyloxy-1-phenyl-2-propene (3d):** Following the general procedure (Table 2, entry 3), the branched product was obtained as colorless oil using automated plastic columns (85.4 mg, 79%).  $^1\text{H}$  NMR analysis of the crude mixture showed a branched to linear ratio of 97/3.  $[\alpha]_{\text{D}} = +6.2$  ( $c = 1.67$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32–7.15 (m, 5 H), 5.86 (ddd,  $J = 17.2$ , 10.0, 6.0 Hz, 1 H), 5.15 (dt,  $J = 17.2$ , 1.2 Hz, 1 H), 5.06 (dt,  $J = 10.4$ , 1.2 Hz, 1 H), 4.84 (d,  $J = 6.4$  Hz, 1 H), 3.26 (tt,  $J = 9.6$ , 4.0 Hz, 1 H), 1.90–1.82 (br, 1 H), 1.80–1.72 (br, 1 H), 1.72–1.58 (m, 2 H), 1.48–1.36 (m, 1 H), 1.36–1.20 (m, 2 H), 1.20–1.05 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.9, 139.8, 128.2, 127.2, 126.7, 115.5, 79.4, 74.6, 32.5, 32.3, 25.8, 24.13, 24.12. Anal. Calcd. For  $\text{C}_{15}\text{H}_{20}\text{O}$ : C, 83.28; H, 9.32. Found: C, 83.05; H, 9.29. To measure the ee of the product, it was converted to the corresponding terminal alcohol using the same procedure as that was used to convert **3c** to the terminal alcohol. HPLC analysis indicated that the enantiomeric excess of the alcohol was 94% [Diacel CHIRALPAK OJ (0.46 cm x 25 cm); hexanes/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 210 nm; Tr = 4.4 (major), 5.6 (minor) min].

**(+)-1-(N-*tert*-Butoxycarbonyl-4-piperidinyloxy)-1-phenyl-2-propene (3e):** Following the general procedure (Table 2, entry 4), the branched ether was obtained as colorless oil using



manual chromatography eluting with 4% ethyl acetate in hexanes (111.0 mg, 70%).  $^1\text{H}$  NMR analysis of the crude mixture showed a branched to linear ratio of 98/2. HPLC analysis indicated that the enantiomeric excess of the product was 95% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 97/3; flow rate = 0.6 mL/min; detection wavelength = 220 nm; Tr = 9.5 (major), 10.3 (minor) min].  $[\alpha]_{\text{D}} = +7.1$  (c = 2.09,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.24 (m, 5 H), 5.93 (ddd,  $J = 17.0, 10.0, 6.0$  Hz, 1 H), 5.25 (dt,  $J = 17.2, 1.4$  Hz, 1 H), 5.17 (dt,  $J = 10.4, 1.2$  Hz, 1 H), 4.91 (d,  $J = 6.4$  Hz, 1 H), 3.82-3.66 (br, 2 H), 3.58 (tt,  $J = 7.6, 4.0$  Hz, 1 H), 3.16-3.03 (m, 2 H), 1.88-1.79 (br, 1 H), 1.79-1.69 (br, 1 H), 1.66-1.50 (m, 2 H), 1.45 (s, 9 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.8, 141.4, 139.3, 128.4, 127.5, 126.7, 115.8, 79.6, 79.3, 71.6, 41.5, 40.8, 31.2, 31.1, 28.4. Anal. Calcd. For  $\text{C}_{19}\text{H}_{27}\text{O}_3\text{N}$ : C, 71.89; H, 8.57; N, 4.41. Found: C, 71.67; H, 8.71; N, 4.39.

**(-)-2-(N-*t*-Butoxycarbonyl-4-piperidinyloxy)-3-butene (3f):**

Following the general procedure (Table 2, entry 5), the branched ether was obtained as colorless oil using manual chromatography eluting with 3% ethyl acetate in hexanes (71.5 mg, 56%).  $^1\text{H}$  NMR analysis of the crude mixture showed a branched to linear ratio of 97/3. HPLC analysis indicated that the enantiomeric excess of the product was 94% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm);

hexanes/2-propanol = 99.75/0.25; flow rate = 0.6 mL/min; detection wavelength = 210 nm; Tr = 14.2 (major), 14.9 (minor) min].  $[\alpha]_D = -3.4$  ( $c = 2.92$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  5.74 (ddd,  $J = 17.0, 10.4, 7.2$  Hz, 1 H), 5.15 (d,  $J = 17.2$  Hz, 1 H), 5.08 (d,  $J = 10.4$  Hz, 1 H), 3.98 (quintet,  $J = 6.6$  Hz, 1 H), 3.85-3.69 (br, 2 H), 3.50 (tt,  $J = 8.6, 4.0$  Hz, 1 H), 3.08-2.97 (m, 2 H), 1.83-1.70 (br, 2 H), 1.54-1.39 (m, 2 H), 1.44 (s, 9 H), 1.21 (d,  $J = 6.4$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.8, 140.8, 115.1, 79.3, 73.7, 71.6, 41.6, 41.2, 32.2, 30.8, 28.4, 21.8. Anal. Calcd. For  $\text{C}_{14}\text{H}_{25}\text{O}_3\text{N}$ : C, 65.85; H, 9.87; N, 5.49. Found: C, 65.87; H, 9.80; N, 5.30.

**(-)-3-(N-*t*-Butoxycarbonyl-4-piperidinyloxy)-1-hexene (3f):**

Following the general procedure (Table 2, entry 6), the desired product was obtained as colorless oil using manual chromatography eluting with 3% ethyl acetate in hexanes (93.5 mg, 66%).  $^1\text{H}$  NMR analysis of the crude mixture showed a branched to linear ratio of 92/8. HPLC analysis indicated that the enantiomeric excess of the product was 93% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.75/0.25; flow rate = 0.6 mL/min; detection wavelength = 210 nm; Tr = 11.9 (major), 12.9 (minor) min].  $[\alpha]_D = -18.4$  ( $c = 2.49$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  5.67 (ddd,  $J = 17.2, 10.2, 7.2$  Hz, 1 H), 5.13 (d,  $J = 16.0$  Hz, 1 H), 5.10 (d,  $J = 8.8$  Hz, 1 H), 3.80-3.63 (m, 3 H),

3.48 (tt,  $J = 8.0, 4.0$  Hz, 1 H), 3.10–2.99 (m, 2 H), 1.80–1.67 (br, 2 H), 1.56–1.25 (m, 6 H), 1.43 (s, 9 H), 0.88 (t,  $J = 7.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.8, 140.0, 115.7, 79.3, 78.0, 71.4, 41.6, 41.0, 38.0, 32.4, 30.4, 28.4, 18.7, 14.0. Anal. Calcd. For  $\text{C}_{14}\text{H}_{25}\text{O}_3\text{N}$ : C, 65.85; H, 9.87; N, 5.49. Found: C, 65.87; H, 9.80; N, 5.30.

**(-)-1-Cyclohexyloxy-1-(4'-nitro)phenyl-2-propene (3g):**

Following the general procedure (Table 2, entry 7), the desired product was obtained as light yellow oil using automated chromatography (77.1 mg, 59%).  $^1\text{H}$  NMR analysis of the crude mixture showed a branched to linear ratio of 94/6. HPLC analysis indicated that the enantiomeric excess of the product was 86% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.9/0.1; flow rate = 0.5 mL/min; detection wavelength = 254 nm; Tr = 20.5 (major), 21.8 (minor) min].  $[\alpha]_{\text{D}} = -21.7$  (c = 1.75,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (dt,  $J = 8.8, 2.0$  Hz, 2 H), 7.53 (dt,  $J = 8.4, 2.0$  Hz, 2 H), 5.85 (ddd,  $J = 17.2, 10.0, 6.0$  Hz, 1 H), 5.29 (dt,  $J = 17.2, 1.2$  Hz, 1 H), 5.22 (dt,  $J = 10.4, 1.2$  Hz, 1 H), 5.00 (d,  $J = 6.4$  Hz, 1 H), 3.37 (tt,  $J = 9.0, 4.0$  Hz, 1 H), 1.95–1.87 (br, 1 H), 1.87–1.78 (br, 1 H), 1.78–1.66 (m, 2 H), 1.54–1.46 (m, 1 H), 1.46–1.30 (m, 2 H), 1.27–1.15 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6, 147.1, 138.4, 127.4, 123.5, 117.0, 78.7, 75.3, 32.4, 32.2, 25.6, 23.98, 23.94.

Anal. Calcd. For  $C_{15}H_{19}O_3N$ : C, 68.94; H, 7.33; N, 5.36. Found: C, 69.01; H, 7.56; N, 5.23.

**(-)-1-Cyclohexyloxy-1-(4'-methoxy)phenyl-2-propene (3h):**

Following the general procedure (Table 2, entry 8), the desired product was obtained as light yellow oil using automated chromatography (105.9 mg, 86%).  $^1H$  NMR analysis of the crude mixture showed a branched to linear ratio of 99/1. HPLC analysis indicated that the enantiomeric excess of the product was 95% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.8/0.2; flow rate = 0.5 mL/min; detection wavelength = 220 nm; Tr = 22.7 (minor), 27.0 (major) min].  $[\alpha]_D = -11.1$  (c = 2.57,  $CHCl_3$ );  $^1H$  NMR (400.13 MHz,  $CDCl_3$ )  $\delta$  7.18 (dt,  $J = 8.8, 2.4$  Hz, 2 H), 6.79 (dt,  $J = 8.4, 2.4$  Hz, 2 H), 5.86 (ddd,  $J = 17.2, 10.0, 6.0$  Hz, 1 H), 5.12 (d,  $J = 17.2, 1$  H), 5.05 (d,  $J = 10.4, 1$  H), 4.80 (d,  $J = 6.8$  Hz, 1 H), 3.71 (s, 3 H), 3.24 (tt,  $J = 9.6, 4.0$  Hz, 1 H), 1.89-1.79 (br, 1 H), 1.79-1.70 (br, 1 H), 1.70-1.55 (m, 2 H), 1.44-1.36 (m, 1 H), 1.34-1.20 (m, 2 H), 1.20-1.05 (m, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  158.8, 140.0, 134.1, 128.0, 115.2, 113.7, 78.9, 74.5, 55.2, 32.6, 32.3, 25.8, 24.20, 24.17. Anal. Calcd. For  $C_{16}H_{22}O_2$ : C, 78.01; H, 9.00. Found: C, 77.71; H, 9.02.

**(+)-1-(tert-Butyl)oxy-1-phenyl-2-propene (3i):** Following the general procedure (Table1, entry 9), the desired product was obtained as colorless oil using manual chromatography (75.8 mg,

80%).  $^1\text{H}$  NMR analysis of the crude mixture showed a branched to linear ratio of 96/4.  $[\alpha]_{\text{D}} = +14.4$  ( $c = 0.32$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.20 (m, 5 H), 5.97 (ddd,  $J = 17.2$ , 10.4, 6.0 Hz, 1 H), 5.17 (dt,  $J = 17.2$ , 1.6 Hz, 1 H), 5.08 (dt,  $J = 10.4$ , 1.2 Hz, 1 H), 5.02 (d,  $J = 5.6$  Hz, 1 H), 1.22 (s, 9 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 141.6, 128.1, 126.8, 126.4, 114.1, 74.85, 74.77, 28.6. To measure its ee, it was converted to the corresponding terminal alcohol using the same procedure as that was used to convert **3c** to the terminal alcohol. HPLC analysis indicated that the enantiomeric excess of the alcohol was 64% [Diacel CHIRALPAK OJ (0.46 cm x 25 cm); hexanes/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 210 nm; Tr = 5.8 (major), 10.2 (minor) min].

**(-)-(1R)-[(S)-1-(2'-Np)ethyl]oxy-1-phenyl-2-propene (3j):**

Following the general procedure (Table1, entry 10), the desired product was obtained as colorless oil using manual chromatography (130.0 mg, 90%).  $^1\text{H}$  NMR analysis of the crude mixture showed a branched to linear ratio of 99/1 and d.e. of 95%.  $[\alpha]_{\text{D}} = -209.3$  ( $c = 2.49$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93–7.79 (m, 4 H), 7.60–7.48 (m, 3 H), 7.48–7.28 (m, 5 H), 6.03 (ddd,  $J = 17.2$ , 10.0, 7.2 Hz, 1 H), 5.39 (d,  $J = 11.2$  Hz, 1 H), 5.35 (d,  $J = 16.8$  Hz, 1 H), 4.93 (q,  $J = 6.4$  Hz, 1 H), 4.78 (d,  $J = 7.6$  Hz, 1 H), 1.66 (d,  $J = 6.4$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,

CDCl<sub>3</sub>)  $\delta$  141.3, 141.2, 138.4, 133.2, 133.0, 128.4, 128.3, 127.8, 127.7, 127.3, 126.8, 126.0, 125.7, 125.3, 124.4, 117.2, 79.6, 74.6, 24.1. Anal. Calcd. For C<sub>21</sub>H<sub>20</sub>O: C, 87.46; H, 6.99. Found: C, 87.19; H, 7.04.

**(-)-(1S)-[(S)-1-(2'-Np)ethyl]oxy-1-phenyl-2-propene (3k):**

Following the general procedure (Table1, entry 11), the desired product was obtained as colorless oil using manual chromatography (131.0 mg, 91%). <sup>1</sup>H NMR analysis of the crude mixture showed a branched to linear ratio of 99/1 and d.e. of 93%. [ $\alpha$ ]<sub>D</sub> = -35.6 (c = 1.91, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>)  $\delta$  7.93-7.83 (m, 3 H), 7.73 (br s, 1 H), 7.57-7.48 (m, 3 H), 7.45-7.32 (m, 5 H), 6.03 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1 H), 5.18 (dt, *J* = 16.8, 1.6 Hz, 1 H), 5.14 (dt, *J* = 10.4, 1.4 Hz, 1 H), 4.74 (d, *J* = 5.6 Hz, 1 H), 4.58 (q, *J* = 6.4 Hz, 1 H), 1.54 (d, *J* = 6.4 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.1, 141.0, 139.4, 133.2, 133.0, 128.6, 128.5, 127.8, 127.65, 127.62, 127.2, 126.0, 125.7, 125.2, 124.3, 115.3, 79.5, 74.6, 24.3. Anal. Calcd. For C<sub>21</sub>H<sub>20</sub>O: C, 87.46; H, 6.99. Found: C, 87.17; H, 6.93.

**(-)-(3R)-[(S)-1-(2'-Np)ethyl]oxy-1,4-hexadiene (3l):**

Following the general procedure (Table,1 entry 12), the desired product was obtained as colorless oil using manual chromatography (113.6 mg, 90%). <sup>1</sup>H NMR and GC analysis of the crude mixture showed a branched to linear ratio of 98/2 and d.e.

of 96%, respectively.  $[\alpha]_D = -79.2$  ( $c = 2.10$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.84 (m, 3 H), 7.77 (br s, 1 H), 7.57-7.47 (m, 3 H), 5.86 (ddd,  $J = 17.2, 10.0, 7.2$  Hz, 1 H), 5.70-5.50 (m, 2 H), 5.28 (dd,  $J = 10.0, 0.8$  Hz, 1 H), 5.19 (dt,  $J = 17.2, 1.2$  Hz, 1 H), 4.78 (q,  $J = 6.4$  Hz, 1 H), 4.14 (t,  $J = 6.6$  Hz, 1 H), 1.72 (d,  $J = 6.0$  Hz, 3 H), 1.56 (d,  $J = 6.4$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.4, 137.8, 133.2, 132.9, 131.0, 128.2, 127.8, 127.66, 127.62, 125.9, 125.6, 125.1, 124.4, 116.9, 78.4, 74.2, 24.2, 17.8. Anal. Calcd. For  $\text{C}_{18}\text{H}_{20}\text{O}$ : C, 85.67; H, 7.99. Found: C, 85.55; H, 8.07.

**(-)-(3S)-[(S)-1-(2'-Np)ethyloxy]-1,4-hexadiene (3m):**

Following the general procedure (Table1, entry 13), the desired product was obtained as colorless oil using manual chromatography (111.0 mg, 88%).  $^1\text{H}$  NMR and GC analysis of the crude mixture showed a branched to linear ratio of 98/2 and d.e. of 96%, respectively.  $[\alpha]_D = -181.2$  ( $c = 1.725$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.84 (m, 3 H), 7.78 (br s, 1 H), 7.57-7.47 (m, 3 H), 5.92 (ddd,  $J = 17.2, 10.0, 7.2$  Hz, 1 H), 5.68-5.59 (m, 1 H), 5.50 (ddq,  $J = 16.0, 6.8, 1.4$  Hz, 1 H), 5.24 (dt,  $J = 17.2, 1.5$  Hz, 1 H), 5.15 (dt,  $J = 10.4, 1.6$  Hz, 1 H), 4.82 (q,  $J = 6.4$  Hz, 1 H), 4.16 (t,  $J = 6.6$  Hz, 1 H), 1.83 (dd,  $J = 6.2, 1.4$  Hz, 3 H), 1.57 (d,  $J = 6.4$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 138.6, 133.2, 132.9, 130.3, 129.1, 128.2, 127.8,

127.6, 125.9, 125.6, 125.0, 124.4, 115.2, 78.2, 73.9, 24.3, 17.8. Anal. Calcd. For  $C_{18}H_{20}O$ : C, 85.67; H, 7.99. Found: C, 85.43; H, 8.09.

**(+) - (1R) - ((R) -1' -Vinyl)hexyloxy-1-phenyl-2-propene (5) :**

Following the general procedure, the desired product was obtained as colorless oil using automated chromatography eluting with 0-1% ethyl acetate in hexanes (104.7 mg, 86%).  $^1H$  NMR and GC analysis of the crude mixture showed a branched to linear ratio of 98/2 and d.e. of 93%, respectively.  $[\alpha]_D = +32.2$  ( $c = 0.93$ ,  $CHCl_3$ );  $^1H$  NMR (400.13 MHz,  $CDCl_3$ )  $\delta$  7.30-7.18 (m, 5 H), 5.91 (ddd,  $J = 16.8, 10.4, 6.0$  Hz, 1 H), 5.64 (ddd,  $J = 17.4, 10.0, 7.0$  Hz, 1 H), 5.11 (dt,  $J = 9.0, 1.2$  Hz, 1 H), 5.10 (dt,  $J = 18.0, 1.2$  Hz, 1 H), 5.02 (dt,  $J = 10.4, 1.2$  Hz, 1 H), 5.01 (dt,  $J = 15.2, 1.2$  Hz, 1 H), 4.80 (d,  $J = 6.0$  Hz, 1 H), 3.52 (q,  $J = 6.8$  Hz, 1 H), 1.60-1.50 (m, 1 H), 1.40-1.05 (m, 7 H), 0.76 (t,  $J = 7.2$  Hz, 3 H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  141.2, 139.7, 139.2, 128.4, 121.5, 127.4, 116.9, 115.1, 79.2, 77.8, 35.6, 31.7, 24.9, 22.6, 14.0. Anal. Calcd. For  $C_{17}H_{24}O$ : C, 83.55; H, 9.90. Found: C, 83.55; H, 9.77.

**(+) - (1S) - ((R) -1' -Vinyl)hexyloxy-1-phenyl-2-propene (5') :**

Following the general procedure, the desired product was obtained as colorless oil using automated chromatography eluting with 0-1% ethyl acetate in hexanes (102.6 mg, 84%).  $^1H$  NMR and GC



analysis of the crude mixture showed a branched to linear ratio of 98/2 and d.e. of 94%, respectively.  $[\alpha]_D = +23.4$  ( $c = 1.58$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.30 (m, 4 H), 7.28-7.23 (m, 1 H), 5.86 (ddd,  $J = 17.2, 10.0, 7.2$  Hz, 1 H), 5.70 (ddd,  $J = 16.8, 11.0, 7.6$  Hz, 1 H), 5.29 (dt,  $J = 16.8, 1.2$  Hz, 1 H), 5.25 (dt,  $J = 9.2, 1.2$  Hz, 1 H), 5.18 (dt,  $J = 10.4, 1.2$  Hz, 1 H), 5.17 (dt,  $J = 18.4, 1.2$  Hz, 1 H), 4.86 (d,  $J = 8.0$  Hz, 1 H), 3.93 (q,  $J = 6.8$  Hz, 1 H), 1.74-1.64 (m, 1 H), 1.58-1.25 (m, 7 H), 0.91 (t,  $J = 7.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.9, 139.3, 139.0, 128.3, 127.3, 126.6, 116.8, 116.7, 79.4, 78.1, 35.5, 31.8, 25.0, 22.6, 14.1. Anal. Calcd. For  $\text{C}_{17}\text{H}_{24}\text{O}$ : C, 83.55; H, 9.90. Found: C, 83.45; H, 9.80.

**(+)-(1R)-((S)-1'-Methyl-3-butenyl)oxy-1-(p-methoxy)phenyl-2-propene (6):** Following the general procedure, the desired product was obtained as colorless oil using automated chromatography eluting with 0-3% ethyl acetate in hexanes (87.1 mg, 75%).  $^1\text{H}$  NMR and GC analysis of the crude mixture showed a branched to linear ratio of 98/2 and d.e. of 94%, respectively.  $[\alpha]_D = +2.0$  ( $c = 1.08$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (dt,  $J = 8.8, 2.6$  Hz, 2 H), 6.90 (dt,  $J = 8.8, 2.4$  Hz, 2 H), 5.98 (ddd,  $J = 17.2, 10.0, 6.0$  Hz, 1 H), 5.79 (ddt,  $J = 17.2, 10.0, 6.8$  Hz, 1 H), 5.25 (dt,  $J = 17.2, 1.2$  Hz, 1 H), 5.17 (dt,  $J = 10.0, 1.2$  Hz, 1 H), 5.08-5.01 (m, 2 H), 4.87 (d,  $J = 6.8$  Hz,

1 H), 3.81 (s, 3 H), 3.57 (sextet,  $J = 6.0$  Hz, 1 H), 2.40-2.30 (m, 1 H), 2.27-2.17 (m, 1 H), 1.20 (d,  $J = 6.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 139.8, 135.1, 133.5, 128.1, 116.6, 115.2, 113.6, 79.6, 71.8, 55.1, 41.2, 19.5. Anal. Calcd. For  $\text{C}_{14}\text{H}_{18}\text{O}$ : C, 77.55; H, 8.68. Found: C, 77.15; H, 8.82.

**(+)-(1S)-((S)-1'-Methyl-3-butenyl)oxy-1-(p-methoxy)phenyl-2-propene (6')**: Following the general procedure, the desired product was obtained as colorless oil using automated chromatography eluting with 0-3% ethyl acetate in hexanes (83.6 mg, 72%).  $^1\text{H}$  NMR and GC analysis of the crude mixture showed a branched to linear ratio of 98/2 and d.e. of 93%, respectively.  $[\alpha]_{\text{D}} = +10.9$  ( $c = 0.76$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (dt,  $J = 8.8, 2.2$  Hz, 2 H), 6.89 (dt,  $J = 8.8, 2.4$  Hz, 2 H), 5.93 (ddd,  $J = 17.2, 10.0, 6.0$  Hz, 1 H), 5.86 (ddt,  $J = 17.2, 10.4, 7.2$  Hz, 1 H), 5.22 (dt,  $J = 17.2, 1.2$  Hz, 1 H), 5.16 (dt,  $J = 10.0, 1.2$  Hz, 1 H), 5.14-5.04 (m, 2 H), 4.85 (d,  $J = 7.2$  Hz, 1 H), 3.81 (s, 3 H), 3.61 (sextet,  $J = 6.0$  Hz, 1 H), 2.42-2.34 (m, 1 H), 2.30-2.20 (m, 1 H), 1.13 (d,  $J = 6.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 139.7, 135.1, 133.9, 128.0, 116.7, 115.6, 113.7, 79.9, 71.9, 55.2, 40.9, 19.8. Anal. Calcd. For  $\text{C}_{14}\text{H}_{18}\text{O}$ : C, 77.55; H, 8.68. Found: C, 77.46; H, 8.84.

**General Procedure for Ring Closing Metathesis of 5, 5', 6, and 6'**: To a flask containing Grubbs' catalyst **7** (8.0 mg, 0.050

equiv) in benzene (2 mL) under a nitrogen atmosphere was added the appropriate allyl ether (0.20 mmol, 1.0 equiv) by syringe at room temperature. The reaction mixture was stirred at either 70 °C (**5** and **5'**) or room temperature (**6** and **6'**) for 12 h and monitored by GC. Upon completion, the crude mixture was directly purified by column chromatography to afford the desired product as colorless oil. Residual ruthenium catalyst appeared to induce oxidation and aromatization of the products. Thus, care was taken to ensure removal of the catalyst during the chromatography.

**(+) - (2*R*,5*R*)-2-Phenyl-5-*n*-pentyl-2,5-dihydrofuran (8) :**

Following the general procedure, the desired product was obtained as colorless oil using automated chromatography eluting with 0-1% ethyl acetate in hexanes (34.2 mg, 79%).  $[\alpha]_D = +71.4$  ( $c = 1.03$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.26 (m, 5 H), 5.95 (ddd,  $J = 6.0, 2.0, 0.4$  Hz, 1 H), 5.85 (dt,  $J = 6.0, 2.0$  Hz, 1 H), 5.76 (dt,  $J = 4.0, 2.0$  Hz, 1 H), 4.95-4.88 (m, 1 H), 1.77-1.60 (m, 2 H), 1.56-1.39 (m, 2 H), 1.39-1.28 (m, 4 H), 0.90 (t,  $J = 7.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.1, 130.6, 130.0, 128.4, 127.7, 126.7, 87.6, 86.6, 36.8, 31.9, 25.4, 22.6, 14.0.

**(-) - (2*S*,5*R*)-2-Phenyl-5-*n*-pentyl-2,5-dihydrofuran (8') :**

Following the general procedure, the desired product was

obtained as colorless oil using automated chromatography eluting with 0-1% ethyl acetate in hexanes (36.4 mg, 84%).  $[\alpha]_D = -267.8$  ( $c = 3.98$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.27 (m, 5 H), 5.97 (ddd,  $J = 6.0, 2.0, 0.4$  Hz, 1 H), 5.91 (dt,  $J = 6.0, 2.0$  Hz, 1 H), 5.84 (dt,  $J = 6.0, 2.0$  Hz, 1 H), 5.12 (qt,  $J = 6.0, 2.0$  Hz, 1 H), 1.71-1.65 (m, 2 H), 1.57-1.30 (m, 6 H), 0.95 (t,  $J = 7.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.1, 130.2, 129.9, 128.4, 127.6, 126.4, 87.4, 86.6, 36.1, 31.9, 25.0, 22.6, 14.0.

**(+) - (2*R*, 6*S*) -2- (p-Methoxy)phenyl-6-methyl-2,5-dihydropyran**

**(9):** Following the general procedure, the desired product was obtained as light yellow oil using automated chromatography eluting with 0-3% ethyl acetate in hexanes (35.5 mg, 87%).  $[\alpha]_D = +138.5$  ( $c = 0.60$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (dt,  $J = 8.8, 2.4$  Hz 1 H), 6.89 (dt,  $J = 8.8, 2.6$  Hz, 1 H), 6.02 (ddt,  $J = 10.4, 4.4, 2.2$  Hz, 1 H), 5.96 (ddt,  $J = 10.4, 3.4, 2.2$  Hz, 1 H), 5.21 (br, 1 H), 3.81 (s, 3 H), 3.74-3.65 (m, 1 H), 2.07-2.01 (m, 2 H), 1.17 (d,  $J = 6.4$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 133.4, 129.4, 127.5, 125.6, 113.5, 73.7, 63.3, 55.2, 32.5, 21.3.

**(-) - (2*S*, 6*S*) -2- (p-Methoxy)phenyl-6-methyl-2,5-dihydropyran**

**(9'):** Following the general procedure, the desired product was obtained as light yellow oil using automated chromatography

eluting with 0-3% ethyl acetate in hexanes (31.8 mg, 78%).  $[\alpha]_D = -104.5$  ( $c = 0.65$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J = 8.8$  Hz, 1 H), 6.88 (d,  $J = 8.4$  Hz, 1 H), 5.94-5.87 (m, 1 H), 5.71 (dd,  $J = 10.0, 0.8$  Hz, 1 H), 5.13 (br, 1 H), 3.92-3.84 (m, 1 H), 3.79 (s, 3 H), 2.16-1.98 (m, 2 H), 1.28 (d,  $J = 6.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 139.9, 130.2, 128.6, 124.7, 113.9, 77.3, 70.5, 56.3, 32.6, 21.8.

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