Supporting Information

Regio- and Enantioselective Iridium-Catalyzed Intermolecular Allylic Etherification of Achiral Allylic Carbonates with Phenoxides

Fernando López, Toshimichi Ohmura and John F. Hartwig*

Department of Chemistry, Yale University, P.P. Box 208107, New Haven, Connecticut 06520-8107.

General Procedures : ^{1}H NMR spectra were recorded at 400 or 500 MHz with $CDCl_3$ as solvent. $^{13}C\{^1H\}$ NMR spectra were obtained at 100.59 MHz in $CDCl_3$. Carbon types were determined from DEPT ^{13}C NMR experiments. The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Optical rotations were measured with a 10 cm cell (concentration *c* given in g/100 mL) Absolute configuration of the products was determined by correlation with compounds published previously. Elemental Analyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ 07940. All reactions were conducted using standard Schlenk and drybox techniques. THF, Et_2O, and toluene were distilled from sodium-benzophenone ketyl under nitrogen. All other solvents were purchased as anhydrous grade and were used without further purification. Thin-layer chromatography (TLC) was performed on silica gel plates, and components were visualized by observation under UV light or by treating the plates with phosphomolybdic reagent followed by heating. Flash chromatography was performed on silica gel, unless otherwise stated. Drying of solutions was performed with anhydrous Na_2SO_4. Concentrations of solutions were conducted with a rotary evaporator.

$[Ir(cod)Cl]_2$[1], *O*, *O'*-(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-*N*,*N'*-di-(*R*,*R*)-phenylethylphosphoramidite [(R_a, R_c, R_c)-**3**] was prepared according to published procedures.[2] Lithium aryloxides were prepared by reaction of the corresponding phenols with *n*-BuLi in THF at 0 °C. After being stirred for 10 min at room temperature, the solution was concentrated under vacuum to afford the corresponding lithium aryloxides as white powders, which were stored under inert atmosphere. All allylic carbonates were synthesized by the reaction of the corresponding allylic alcohols with the corresponding alkylchloroformate in the presence of pyridine. (*E*)-4-Methoxycinnamamyl alcohol[3] and (*E*)-2-methoxycinnamyl alcohol[3] were prepared by the reduction of the corresponding aldehydes with DIBAL-H. Phenols, (*E*)-4-methoxycinnamaldehyde, and (*E*)-2-methoxycinnamaldehyde were purchased from Aldrich Chemicals Co. and used without further purification.

General Procedure for the Enantioselective Allylic Etherification Catalyzed by Iridium-Phosphoramidite Complex .

(–)-1-phenyl-1-phenoxy-2-propene: The reaction of **2a** with cinnamyl methylcarbonate **1a** is used as example. In a drybox, $[Ir(cod)Cl]_2$ (6.7 mg, 0.010 mmol), (R_a,R_c,R_c)-**3** (10.8 mg, 0.020 mmol) and lithium phenoxide (**2a**, 200 mg, 2.0 mmol) were dissolved in THF (2 mL) in a screw-capped vial containing a small stirbar. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Cinnamyl methylcarbonate (**1a**, 192 mg, 1.0 mmol) was added to the reaction mixture by syringe. After being stirred at 50 ºC for 20 h, the reaction mixture was poured into brine, extracted with Et_2O, dried, filtered, and concentrated. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 96/4. The residue was purified by flash

chromatographyy on silica gel (1% Et_2O/Hexanes) to afford 182 mg of **4** as a viscous oil.[86%, R_f 0.85 (5% Et_2O/Hexanes)]. $[\alpha]_D^{20}$ = -8.9 (c 1.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ7.48-7.27 (m, 8H), 7.01-6.96 (m, 2H), 6.15 (ddd, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.70 (d, *J* = 5.9 Hz, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 157.9 (C), 140.1 (C), 137.9 (CH), 129.3 (CH), 128.6 (CH), 127.8 (CH), 126.6 (CH), 121.0 (CH), 116.5 (CH_2), 116.2 (CH), 80.8 (CH). Anal. Calc. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.86; H, 7.00. HPLC analysis indicated an enantiomeric excess of 96% [Chiralcel® OJ-H column, eluting with 99.7:0.3 hexane/*i*-PrOH, 0.8 mL/min, 220 nm; minor enantiomer t_R, 39.1, major enantiomer t_R 47.1 min].

(*R*)-(–)-1-phenyl-1-(2-methylphenoxy)-2-propene[4] **(Table 2, entry 1)**: The general procedure was followed with lithium 2-methylphenoxide (**2c,** 228 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 14 h. ^1H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 96/4. The residue was purified by flash chromatography on silica gel (1-2% Et_2O/Hexanes) to afford 196 mg of the title compound as a viscous oil. [87%, R_f 0.88 (5% Et_2O/Hexanes)]. The absolute configuration was determined by comparison of the optical rotation with the literature data: $[\alpha]_D^{20}$ = -7.3 (c 0.84, $CHCl_3$), lit.[3] $[\alpha]_D^{23}$ = -6.9 (c 1.0, $CHCl_3$) ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.46 (m, 2H), 7.38 (m, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.13 (m, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.20 (ddd, *J* = 17.1, 10.4, 5.8 Hz, 1H), 5.74 (d, *J* = 5.8 Hz, 1H), 5.48 (d, *J* = 17.1 Hz, 1H), 5.34 (d, *J* = 10.4 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 155.9 (C), 140.5 (C), 138.3 (CH), 130.7 (CH), 128.6 (CH), 127.7 (CH), 127.5 (C), 126.5 (CH), 126.4 (CH), 120.6 (CH), 115.9 (CH_2), 113.4 (CH), 80.6 (CH), 16.6 (CH_3); Anal. Calc. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.47; H, 7.10. HPLC analysis indicated an enantiomeric excess of 95% [Chiralcel® OD-H column, eluting with 99.85:0.15 hexane/*i*-PrOH, 0.7 mL/min, 220 nm; (*S*) enantiomer t_R, 16.6, (*R*) enantiomer t_R 19.4 min].

(+)-1-phenyl-1-(4-methylphenoxy)-2-propene (Table 2, entry 2): The general procedure was followed with lithium 4-methylphenoxide (**2d**, 228 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 22 h. ^1H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 98/2. The residue was purified by flash chromatography on silica gel (1-2% Et_2O/Hexanes) to afford 203 mg of the title compound as a viscous oil. [91%, R_f 0.85 (5% Et_2O/Hexanes)].$[\alpha]_D^{20}$ = + 5.0 (c 1.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.34 (m, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.16 (ddd, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.66 (d, *J* = 5.9 Hz, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 155.8 (C), 140.3 (C), 138.1 (CH), 130.2 (C), 129.8 (CH), 128.6 (CH), 127.7 (CH), 126.6 (CH), 116.4 (CH_2), 116.1 (CH), 81.0 (CH), 20.5 (CH_3); Anal. Calc. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.91; H, 7.48. HPLC analysis

indicated an enantiomeric excess of 95% [Chiralcel® OD-H column, eluting with 99.85:0.15 hexane/*i*-PrOH, 0.6 mL/min, 220 nm; minor enantiomer t_R, 18.1, major enantiomer t_R 19.4 min].

(+)-1-phenyl-1-(4-methoxyphenoxy)-2-propene (Table 2, entry 3): The general procedure was followed with lithium 4-methoxyphenoxide (**2e,** 260 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 8 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4**/**5** to be 98/2. The residue was purified by flash chromatography on silica gel (1-4% Et_2O/Hexanes) to afford 210 mg of the title compound as a viscous oil. [88%, R_f 0.65 (5% Et_2O/Hexanes)].$[\alpha]_D^{20}$ = +6.6 (c 1.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 4H), 7.35 (m, 1H), 6.95(d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.17 (ddd, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.60 (d, *J* = 5.2 Hz, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 154.0 (C), 152.0 (C), 140.3 (C), 138.2 (CH), 128.5 (CH), 127.7 (CH), 126.6 (CH), 117.4 (CH), 116.4 (CH_3), 114.4 (CH), 81.8 (CH), 55.5 (CH_3); Anal. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.22; H, 6.72. HPLC analysis indicated an enantiomeric excess of 97% [Chiralcel® OD-H column, eluting with 97:3 hexane/*i*-PrOH, 0.8 mL/min, 220 nm; minor enantiomer t_R, 17.9, major enantiomer t_R 16.3 min].

(–)-1-phenyl-1-(3-methoxyphenoxy)-2-propene (Table 2, entry 4): The general procedure was followed with lithium 3-methoxyphenoxide (**2f**, 260 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 17 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 95/5. The residue was purified by flash chromatography on silica gel (1-4% Et_2O/Hexanes) to afford 218 mg of the title compound as a viscous oil. [84%, R_f 0.65 (5% Et_2O/Hexanes)].$[\alpha]_D^{20}$ = -15.3 (c 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.3 Hz, 2H), 7.48 (m, 2H), 7.40 (m, 1H), 7.25 (t, *J* = 8.5 Hz, 1H), 6.68 (m, 2H), 6.61 (m, 1H), 6.23 (ddd, *J* = 17.1, 10.4, 5.9, 1H), 5.76 (d, *J* = 5.9 Hz, 1H), 5.48 (d, *J* = 17.1 Hz, 1H), 5.38 (d, *J* = 10.4 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 161.3 (C), 159.7 (C), 140.7 (C), 138.5 (CH), 103.3 (CH), 129.2 (CH), 128.4 (CH), 127.2 (CH), 117.1 (CH_2), 108.9 (CH), 107.2 (CH), 103.2 (CH), 81.4 (CH), 55.7 (CH_3); Anal. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.25; H, 6.47. HPLC analysis indicated an enantiomeric excess of 96% [Chiralcel® OJ-H column, eluting with 97:3 hexane/*i*-PrOH, 0.7 mL/min, 220 nm; minor enantiomer t_R, 68.2, major enantiomer t_R 89.0 min].

(–)-1-phenyl-1-(3-phenylphenoxy)-2-propene (Table 2, entry 5): The general procedure was followed with lithium 3-phenylphenoxide (**2g**, 352 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 13 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 96/4. The residue was purified by flash chromatography on silica gel (1-2% Et_2O/Hexanes) to afford 218 mg of the title compound as a viscous

oil. [76%, R_f 0.76 (5% Et_2O/Hexanes)]. $[\alpha]_D^{20}$ = -2.5 (c 1.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.66-7.26 (m, 14H), 6.24 (ddd, *J* = 17.1, 10.4, 5.9 Hz, 1H), 5.82 (d, *J* = 5.9 Hz, 1H), 5.50 (d, *J* = 17.1 Hz, 1H), 5.39 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 158.2 (C), 142.5 (C), 140.9 (C), 140.0 (C), 137.8 (CH), 129.6 (CH), 128.7 (CH), 128.6 (CH), 127.8 (CH), 127.3 (CH), 127.1 (CH), 126.6 (CH), 119.9 (CH), 116.6 (CH_2), 115.2 (CH), 114.7 (CH), 80.9 (CH); Anal. Calc. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.85; H, 6.37. HPLC analysis indicated an enantiomeric excess of 95% [Chiralcel® OJ-H column, eluting with 98:2 hexane/*i*-PrOH, 0.6 mL/min, 220 nm; minor enantiomer t_R, 45.5, major enantiomer t_R 55.4 min].

(–)-1-phenyl-1-(2-phenylphenoxy)-2-propene (Table 2, entry 6): The general procedure was followed with lithium 2-phenylphenoxide (**2h**, 352 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 10 h. ^1H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 96/4. The residue was purified by flash chromatography on silica gel (1-2% Et_2O/Hexanes) to afford 187 mg of the title compound as a viscous oil. [65%, R_f 0.76 (5% Et_2O/Hexanes)]. $[\alpha]_D^{20}$ = -42 (c 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70-7.02 (m, 14H), 6.08 (m, 1H), 5.71 (d, *J* = 5.6 Hz, 1H), 5.35 (d, *J* = 17.1 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 154.5 (C), 140.1 (C), 138.7 (C), 138.1 (CH), 131.9 (C), 130.9 (CH), 129.7 (CH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 127.6 (CH), 126.8 (CH), 126.4 (CH), 121.3 (CH), 115.9 (CH_2), 115.3 (CH), 81.6 (CH); Anal. Calc. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.79; H, 6.15. HPLC analysis indicated an enantiomeric excess of 93% [Chiralcel® OJ-H column, eluting with 99.9:0.01 heptane/*i*-PrOH, 0.6 mL/min, 220 nm; minor enantiomer t_R, 29.6, major enantiomer t_R 34.2 min].

(–)-1-phenyl-1-(3-dimethylaminophenoxy)-2-propene (Table 2, entry 7): The general procedure was followed with lithium 3-dimethylaminophenoxide (**2i**, 274 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 14 h. ^1H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 99/1. The residue was purified by flash chromatography on silica gel (1-5% Et_2O/Hexanes) to afford 142 mg of the title compound as a viscous oil. [56%, R_f 0.45 (5% Et_2O/Hexanes)]. $[\alpha]_D^{20}$ = -13.9 (c 0.82, $CHCl_3$) ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 1H), 7.38 (m, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 8.2 Hz, 2H), 6.40 (s, 1H), 6.36 (m, 2H), 6.15 (ddd, *J* = 17.1, 10.4, 5.9 Hz, 1H), 5.68 (d, *J* = 5.9 Hz, 1H), 5.38 (d, *J* = 17.1 Hz, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 2.93 (s, 6H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 159.0 (C), 151.8 (C), 140.5 (C), 138.2 (CH), 129.5 (CH), 128.6 (CH), 127.7 (CH), 126.6 (CH), 116.4 (CH_2), 105.9 (CH), 103.8 (CH), 101.2 (CH), 80.7 (CH), 40.5 (CH_3); Anal. Calc. for $C_{17}H_{19}NO$: C, 80.60; H, 7.56, N, 5.53. Found: C, 80.74; H, 7.63; N, 5.28. HPLC analysis indicated an enantiomeric excess of 97% [Chiralcel® OJ-H column, eluting with 96:4 hexane/*i*-PrOH, 0.8 mL/min, 220 nm; minor enantiomer t_R 29.1, major enantiomer t_R 35.5 min].

(–)-1-phenyl-1-[(3,4-methyenedioxy)phenoxy)]-2-propene (Table 2, entry 8): The general procedure was followed with lithium (3,4-methyenedioxy)phenoxide (**2j**, 288 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 18 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 99/1. The residue was purified by flash chromatography on silica gel (1-5% Et_2O/Hexanes) to afford 165 mg of the title compound as a viscous oil. [65% , R_f 0.60 (5% Et_2O/Hexanes)].$[\alpha]_D^{RT}$ = -24.3 (c 1.1, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.28 (m, 5H), 6.66 (d, *J* = 8.5 Hz, 1H), 6.55 (d, *J* = 2.5 Hz, 1H), 6.38 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.10 (ddd, *J* = 17.2, 10.3, 6.1 Hz, 1H), 5.9 (s, 2H), 5.51 (d, *J* = 6.1Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.27 (d, J = 10.3 Hz, 1H); ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 153.3 (C), 148.1 (C), 141.9 (C), 140.2 (C), 138.0 (CH), 128.7 (CH), 127.9 (CH), 126.6 (CH), 116.6 (CH_2), 108.1 (CH), 108.0 (CH), 106.1 (CH), 101.2 (CH_2), 82.3 (CH). Anal. Calc. for $C_{16}H_{14}O_3$: C, 75.57, H, 5.55. Found: C, 75.55; H, 5.51. HPLC analysis indicated an enantiomeric excess of 94% [Chiralcel® OJ-H column, eluting with 98:2 hexane/*i*-PrOH, 0.7 mL/min, 220 nm; minor enantiomer t_R, 71.8, major enantiomer t_R 79.1 min].

(+)-1-phenyl-1-(2,4-dimethylphenoxy)-2-propene (Table 2, entry 9): The general procedure was followed with lithium 2,4-dimethylphenoxide (**2k**, 256 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 11 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 98/2. The residue was purified by flash chromatography on silica gel (1-2% Et_2O/Hexanes) to afford 202 mg of the title compound as a viscous oil. [85%, R_f 0.89 (4% Et_2O/Hexanes)].$[\alpha]_D^{20}$ = +4.4 (c 1.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.41 (m, 2H), 7.33 (m, 1H), 7.02 (s, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.14 (ddd, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.64 (d, *J* = 5.8 Hz, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 153.8 (C), 140.7 (C), 138.5 (CH), 131.5 (CH), 129.8 (C), 128.5 (CH), 127.6 (CH), 127.3 (C), 126.6 (CH), 126.4 (CH), 115.9 (CH_2), 113.6 (CH), 80.9 (CH), 20.4 (CH_3), 16.5 (CH_3); Anal. Calc. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.69; H, 7.56. HPLC analysis indicated an enantiomeric excess of 95% [Chiralcel® OJ-H column, eluting with 99.9:0.1 hexane/*i*-PrOH, 0.6 mL/min, 220 nm; minor enantiomer t_R, 27.4, major enantiomer t_R 29.2 min].

(–)-1-phenyl-1-(2,4,6-trimethylphenoxy)-2-propene (Table 2, entry 10): The general procedure was followed with lithium 2,4,6-trimethylphenoxide (**2l**, 284 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 22 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 93/7. The residue was purified by flash chromatography on silica gel (1-2% Et_2O/Hexanes) to afford 207 mg of the title compound as a viscous oil. [82%, R_f 0.90 (5% Et_2O/Hexanes)].$[\alpha]_D^{20}$ = -8.8 (c 1.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.44-7.38 (m, 3H), 6.85 (s, 2H),

6.21 (m, 1H), 5.32 (d, *J* = 16.1 Hz, 1H), 5.30-5.24 (m, 2H), 2.30 (s, 3H), 2.19 (s, 6H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 152.6 (C), 140.8 (C), 138.0 (CH), 132.7 (C), 130.9 (C), 129.4 (CH), 128.3 (CH), 127.8 (CH), 127.2 (CH), 116.9 (CH_2), 85.5 (CH), 20.6 (CH_3), 17.2 (CH_3); Anal. Calc. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.77; H, 7.86. HPLC analysis indicated an enantiomeric excess of 93% [Chiralcel® OD-H column, eluting with 99.9:0.1 hexane/*i*-PrOH, 0.6 mL/min, 220 nm; minor enantiomer t_R, 20.4, major enantiomer t_R 25.6 min].

(+)-1-phenyl-1-(4-bromophenoxy)-2-propene (Table 2, entry 11): The general procedure was followed with sodium 4-bromophenoxide (**2m**, 390 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 8 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 96/4. The residue was purified by flash chromatography on silica gel (1-4% Et_2O/Hexanes) to afford 262 mg of the title compound as a viscous oil. [91%, R_f 0.75 (5% Et_2O/Hexanes)]. $[\alpha]_D^{20}$ = +12.7 (c 1.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.33 (m, 7H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.13 (ddd, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.63 (d, *J* = 5.9 Hz, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 156.9 (C), 139.6 (C), 137.5 (CH), 132.1 (CH), 128.6 (CH), 128.0 (CH), 126.5 (CH), 118.0 (CH), 116.7 (CH_2), 113.2 (C), 81.1 (CH); Anal. Calc. for $C_{15}H_{13}BrO$: C, 62.30, H, 4.53. Found: C, 62.58; H, 4.70. HPLC analysis indicated an enantiomeric excess of 90% [Chiralcel® OJ-H column, eluting with 99.7: 0.3 hexane/*i*-PrOH, 0.8 mL/min, 220 nm; minor enantiomer t_R, 31.2, major enantiomer t_R 35.7 min].

(+)-1-phenyl-1-(4-chlorophenoxy)-2-propene (Table 2, entry 12): The general procedure was followed with sodium 4-chlorophenoxide (**2n**, 300 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 20 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 93/7. The residue was purified by flash chromatography on silica gel (1-3% Et_2O/Hexanes) to afford 210 mg of the title compound as a viscous oil. [86%, R_f 0.72 (5% Et_2O/Hexanes)]. $[\alpha]_D^{20}$ = +10.1 (c 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.24 (m, 7H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.15 (ddd, *J* = 17.3, 10.4, 5.8 Hz, 1H), 5.65 (d, *J* = 5.8 Hz, 1H), 5.41 (d, *J* = 17.3 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 156.9 (C), 140.1 (C), 138.1 (CH), 129.7 (CH), 129.2 (CH), 128.5 (CH), 127.1 (CH), 126.4 (C), 118.0 (CH), 117.2 (CH_2), 81.8 (CH); Anal. Calc. for $C_{15}H_{13}ClO$: C, 73.62; H, 5.35. Found: C, 73.61; H, 5.08. HPLC analysis indicated an enantiomeric excess of 92% [Chiralcel® OJ-H column, eluting with 99.7: 0.3 hexane/*i*-PrOH, 0.8 mL/min, 220 nm; minor enantiomer t_R, 30.7, major enantiomer t_R 36.5 min].

(–)-1-phenyl-1-(3-methyl,4-bromophenoxy)-2-propene (Table 2, entry 13): The general procedure was followed with sodium 3-methyl,4-bromophenoxide (**2o**, 418

mg, 2.0 mmol). The reaction was conducted at 50 ºC for 8 h.^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 95/5. [89%, R_f 0.79 (7% Et_2O/Hexanes))]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.33 (m, 6H), 6.92 (s, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 6.13 (ddd, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.64 (d, *J* = 5.8 Hz, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 157.0 (C), 139.7 (C), 138.7 (C), 137.6 (CH), 132.7 (CH), 128.6 (CH), 127.9 (CH), 126.5 (CH), 118.9 (CH), 116.6 (CH_2), 115.8 (C), 115.0 (CH), 81.0 (CH), 23.1 (CH3); Anal. Calc. for $C_{16}H_{15}BrO$: C, 63.38, H, 4.99. Found: C, 63.72; H, 5.24. HPLC analysis indicated an enantiomeric excess of 87%. [Chiralcel® OJ-H column, eluting with 99.9: 0.1 hexane/*i*-PrOH, 0.6 mL/min, 220 nm; minor enantiomer t_R, 72, major enantiomer t_R 79 min].

(*R*)-(–)-1-phenyl-1-(4-trifluoromethylphenoxy)-2-propene[4] **(Table 2, entry 14)**: The general procedure was followed with sodium 4-trifluoromethylphenoxide (**2p**, 368 mg, 2.0 mmol). The reaction was conducted at 50 ºC for 10 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 90/10. The residue was purified by flash chromatography on silica gel (1-2% Et_2O/Hexanes) to afford 256 mg of the title compound as a viscous oil. [92%, R_f 0.69 (5% Et_2O/Hexanes)]. The absolute configuration was determined by comparison of the optical rotation with the literature data: $[\alpha]_D^{20}$ = -6.7 (c 1.3, $CHCl_3$), lit.[3] $[\alpha]_D^{23}$ = -7.4 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.23 (m, 7H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.14 (ddd, *J* = 17.1, 10.5, 5.8 Hz, 1H), 5.72 (d, *J* = 5.8 Hz, 1H), 5.41 (d, *J* = 17.1 Hz, 1H), 5.32 (d, J = 10.4 Hz, 1H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 160.3, 139.3, 137.3, 128.8, 128.2, 126.7 (q, *J* = 10.9 Hz), 126.6, 123.3 (q, *J* = 33 Hz), 116.9, 116.0, 81.0; The cuaternary carbon of CF_3 could not be detected. Anal. Calc. for $C_{16}H_{13}F_3O$: C, 69.06; H, 4.71. Found: C, 69.03; H, 4.71. HPLC analysis indicated an enantiomeric excess of 80% [Chiralcel® OJ-H column, eluting with 99.7: 0.3 hexane/*i*-PrOH, 0.7 mL/min, 220 nm; (*S*) enantiomer t_R, 21.5, (*R*) enantiomer t_R 26.2 min].

(–)-1-(2-Methoxyphenyl)-1-phenoxy-2-propene (Table 2, entry 15): The general procedure was followed with lithium phenoxide (**2a**, 300 mg, 3.0 mmol) and 2-methoxycinnamyl methylcarbonate (**1c**, 222 mg, 1.0 mmol) in THF (2 mL). The reaction was conducted at 50 ºC for 41 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 98/2. The residue was purified by flash chromatography on silica gel (1-3% Et_2O/Hexanes) to afford 190 mg of the title compound as a viscous oil. [79%, R_f 0.60 (5% Et_2O/Hexanes)].$[\alpha]_D^{20}$ = -31.0 (c 0.82, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.32 (m, 3H), 7.05-6.96 (m, 5H), 6.21 (m, 2H), 5.45 (dt, *J* = 15.9, 1.2 Hz, 1H), 5.28 (d, *J* = 9.3 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 157.9 (C), 156.1 (C), 137.2 (CH), 129.2 (CH), 128.7 (CH), 128.4 (C), 127.1 (CH), 121.0 (CH), 120.6 (CH), 115.8 (CH), 115.4 (CH_2), 110.5 (CH), 73.9 (CH), 55.5

(CH_3); Anal. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.07; H, 6.52. HPLC analysis indicated an enantiomeric excess of 75% [Chiralcel® OD-H column, eluting with 99.9: 0.1 hexane/*i*-PrOH, 0.6 mL/min, 254 nm; major enantiomer t_R, 29.6, minor enantiomer t_R 35.0 min].

(+)-1-(4-Methoxyphenyl)-1-phenoxy-2-propene (Table 2, entry 16): The general procedure was followed with lithium phenoxide (**2a**, 300 mg, 3.0 mmol) and 4-methoxycinnamyl methylcarbonate (**1d**, 222 mg, 1.0 mmol) in THF (1 mL). The reaction was conducted at 50 ºC for 13 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 97/3. The residue was purified by flash chromatography on silica gel (pre-coated with 1% Et_3N/hexanes) (1-3% Et_2O/Hexanes) to afford 169 mg of the title compound as a viscous oil. [70%, R_f 0.62 (5% Et_2O/Hexanes)].$[\alpha]_D^{20}$ = +9.4 (c 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.27 (m, 2H), 6.94 (m, 5H), 6.14 (ddd, *J* = 17.3, 10.4, 5.8, 1H), 5.64 (d, *J* = 5.8 Hz, 1H), 5.36 (dt, *J* = 17.3, 1.2 Hz, 1H), 5.29 (dt, *J* = 10.4, 1.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 159.2 (C), 157.9 (C), 138.1 (CH), 132.2 (C), 129.3 (CH), 128.0 (CH), 120.9 (CH), 116.2 (CH_2), 116.2 (CH), 114.0 (CH), 80.4 (CH), 55.3 (CH_3); Anal. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.78; H, 6.92. HPLC analysis indicated an enantiomeric excess of 86% [Chiralcel® OD-H column, eluting with 99.9: 0.1 hexane/*i*-PrOH, 0.6 mL/min, 254 nm; major enantiomer t_R, 44.8, minor enantiomer t_R 48.1 min].

(–)-1-Propyl allyloxybenzene[5] **(Table 2, entry 17)**: The general procedure was followed with lithium phenoxide (**2a**, 200 mg, 2.0 mmol) and 2-hexenyl methylcarbonate (**1e**, 160 mg, 1.0 mmol) in THF (2 mL). The reaction was conducted at 50 ºC for 14 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 92/8. The residue was purified by flash chromatography on silica gel (0-1% Et_2O/Hexanes) to afford 162 mg of the title compound as an oil. [93%, R_f 0.90 (5% Et_2O/Hexanes)]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (m, 2H), 6.91 (m, 3H), 5.84 (ddd, *J* = 17.3, 10.6, 6.2 Hz, 1H), 5.25 (d, *J* = 17.4 Hz, 1H), 5.20 (d, *J* = 10.6 Hz, 1H), 4.59 (dt, *J* = 6.8, 6.0 Hz, 1H), 1.83-1.74 (m, 1H), 1.68-1.61 (m, 1H), 1.58-1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 158.4, 138.2, 129.3, 120.6, 116.2, 116.0, 78.6, 37.7, 18.6, 14.0. HPLC analysis indicated an enantiomeric excess of 92% [Chiralcel® OD-H column, eluting with 99.9: 0.1 hexane/*i*-PrOH, 0.6 mL/min, 220 nm; major enantiomer t_R, 13.3, minor enantiomer t_R 15.8 min].

(–)-1-Methyl-2-(1-propylallyloxy)benzene[5] **(Table 2, entry 18)**: The general procedure was followed with lithium 2-methylphenoxide (**2c**, 228 mg, 2.0 mmol) and 2-hexenyl methylcarbonate (**1e**,160 mg, 1.0 mmol) in THF (2 mL). The reaction was conducted at 50 ºC for 20 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 87/13. The residue was purified by flash chromatography on silica

gel (0-1% Et_2O/Hexanes) to afford 165 mg of the title compound as an oil. [86%, R_f 0.92 (5% Et_2O/Hexanes)].$[\alpha]_D^{20}$ = -3.0 (c 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (m, 2H), 6.88 (m, 2H), 5.92 (ddd, *J* = 17.4, 10.5, 6.1 Hz, 1H), 5.28 (dt, *J* = 17.4, 1.2 Hz, 1H), 5.22 (dt, *J* = 10.5, 1.0 Hz, 1H), 4.67 (dt, *J* = 6.4, 6.1 Hz, 1H), 2.31 (s, 3H), 1.89-1.83 (m, 1H), 1.76-1.69 (m, 1H), 1.60-1.47 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ156.5 (C), 138.5 (CH), 130.6 (CH), 127.4 (C), 126.4 (CH), 120.2 (CH), 115.9 (CH_2), 113.1 (CH), 78.6 (CH), 37.9 (CH_2), 18.5 (CH_2), 16.4 (CH_3), 14.0 (CH_3); HPLC analysis indicated an enantiomeric excess of 90% [Chiralcel® OD-H column, eluting with 99.9: 0.1 hexane/*i*-PrOH, 0.6 mL/min, 220 nm; major enantiomer t_R, 12.2, minor enantiomer t_R 13.7 min].

(–)-1-Methoxy-4-(1-propylallyloxy)benzene (Table 2, entry 19): The general procedure was followed with lithium 4-methoxyphenoxide (**2e**, 260 mg, 2.0 mmol) and 2-hexenyl methylcarbonate (**1e**, 160 mg, 1.0 mmol) in THF (2 mL). The reaction was conducted at 50 ºC for 14 h. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 90/ 10. The residue was purified by flash chromatography on silica gel (1% Et_2O/Hexanes) to afford 155 mg of the title compound as an oil. [73%, R_f 0.82 (5% Et_2O/Hexanes)].$[\alpha]_D^{20}$ = -8.2 (c 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (d, *J* = 9.3 Hz, 2H), 6.84 (d, *J* = 9.2 Hz, 2H), 5.87 (ddd, *J* = 17.3, 10.6, 6.3 Hz, 1H), 5.25 (d, *J* = 17.3 Hz, 1H), 5.21 (d, *J* = 10.6 Hz, 1H), 4.51 (q, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 1.81 (m, 1H), 1.66 (m, 1H), 1.56-1.46 (m. 2H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 153.8 (C), 152.5 (C), 138.5 (CH), 117.3 (CH), 116.2 (CH_2), 114.4 (CH), 79.9 (CH), 55.6 (CH_3), 37.7 (CH_2), 18.5 (CH_2), 13.9 (CH_3); Anal. Calc. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.90, H, 9.07. HPLC analysis indicated an enantiomeric excess of 85% [Chiralcel® OD-H column, eluting with 99.9: 0.1 hexane/*i*-PrOH, 0.6 mL/min, 220 nm; major enantiomer t_R, 24.5, minor enantiomer t_R 27.6 min].

General Procedure for the Enantioselective Allylic Etherification with lithium aryloxides generated in situ.

(–)-1-phenyl-1-phenoxy-2-propene: The reaction of phenol with cinnamyl methylcarbonate **1a** is provided as a representative example. To a solution of phenol (188 mg, 2.0 mmol) in THF (1 mL), a solution of *n*-Buli (2.58M in hexanes, 0.78 mL, 2.0 mmol,) was added dropwise at 23 ºC. After 10 min this solution was added by syringe to a round bottom flask containing $[Ir(cod)Cl]_2$ (6.7 mg, 0.010 mmol), (R_a,R_c,R_c)-**3** (10.8 mg, 0.020 mmol) and a small stirbar. After the mixture was stirred for 5 min, cinnamyl methylcarbonate (**1a**, 192 mg, 1.0 mmol) was added to the reaction mixture by syringe. After this final mixture was stirred at 50 ºC for 20 h, the reaction mixture was poured into brine, extracted with Et_2O, dried, filtered, and concentrated. ^{1}H NMR analysis of the mixture indicated the ratio of regioisomers **4/5** to be 96/4. The residue was purified by flash chromatography on silica gel (1% Et_2O/Hexanes) to afford 182 mg of the title

compound as a viscous oil.[86%, 96% ee, R_f 0.85 (5% Et_2O/Hexanes)]. The same procedure was followed when Cy_2NLi (1.0 M in THF) was used instead of *n*-BuLi.

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