**Effects of Catalyst Activation and Ligand Steric Properties on
the Enantioselective Allylation of Amines and Phenoxides**

Supporting Information

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General: All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. THF was obtained as HPLC grade without inhibitors; benzene, toluene, dichloromethane, and pentane were obtained as ACS reagent grade. THF, diethyl ether, benzene, toluene, dichloromethane, and pentane were degassed by purging with nitrogen for 45 min and dried with a solvent purification system containing a 1 m column containing activated alumina. All reagents were obtained from commercial sources and used without further purification. ^1H NMR spectra were obtained at 400 or 500-MHz and recorded relative to residual protio-solvent. ^{13}C NMR spectra were obtained at 101 or 126 MHz, and chemical shifts were recorded relative to the solvent resonance. $[\text{Ir}(\text{COD})\text{Cl}]_2$, O,O'-(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-N,N'-di-(*R,R*)-phenylethylphosphoramidite,¹ and O,O'-(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-N,N'-di-(*R,R*)-naphthylethylphosphoramidite² were prepared according to published procedures. All allylic carbonates were prepared by the reaction of the corresponding allylic alcohol with methyl chloroformate in the presence of pyridine. (*E*)-4-methoxycinnamyl alcohol, (*E*)-2-methoxycinnamyl alcohol, (*E*)-3-(2-furanyl)-2-propen-1-ol, and (*E*)-4-methyl-2-penten-1-ol were prepared by reduction of the corresponding aldehyde with $\text{NaBH}_4/\text{CeCl}_3$.

General Procedures for the Enantioselective Allylic Amination.

Method A: Catalyst activation with propylamine. $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.070 mmol), phosphoramidite ligand (**L1** or **L2**) (0.140 mmol) were diluted in 0.3 mL of THF and 0.3 mL propylamine and heated at 50 °C for 20 min. After this time, all volatile materials were evaporated. The yellow solid was diluted in 3.5 mL of THF to generate a stock solution of the activated catalyst. In a drybox, amine (1.20 mmol) was added to 0.5 mL of the stock solution of the catalyst (0.020 mmol) in a screw capped vial containing a stirring bar. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Carbonate (1.00 mmol) was added with a syringe, and the reaction was stirred at room temperature until the carbonate was fully converted, as determined by GC and TLC. The volatile materials were evaporated. The ratio of regioisomers (branched to linear b/l) was determined by ^1H NMR or gas chromatographic analysis of the crude mixture. The crude reaction mixture was purified by flash column chromatography on silica gel (hexanes/ether) to give desired product.

Method B: Catalyst activation with DABCO. In a drybox, DABCO (0.100 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.010 mmol) and phosphoramidite ligand (**L1** or **L2**) (0.020 mmol) were dissolved in 0.5 mL of THF in a screw-capped vial. A small magnetic stirbar was added, and the vial was sealed with a cap containing a PTFE septum. The vial was removed from the drybox. Amine (1.20 mmol) and methyl carbonate (1.00 mmol) were added by syringe, and the reaction was stirred at room temperature until the carbonate was fully converted, as determined by GC and TLC. The volatile materials were evaporated. The ratio of regioisomers (branched to linear b/l) was determined by ^1H NMR or gas chromatographic analysis of the crude mixture. The crude reaction mixture then was purified by flash column chromatography on silica gel (hexanes/ether) to give desired product.

Allylic Alkylation conducted with O,O'-(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-N,N'-di-(*R,R*)-naphthylethylphosphoramidite (L2**):**

***N*-[1-(*n*-Propyl)-2-propenyl]benzylamine.**³ The general procedure of method A was followed with methyl carbonate derived from (*E*)-2-hexen-1-ol (0.152 g, 0.94 mmol) and benzylamine (0.140 mL, 1.28 mmol). The reaction was conducted at room temperature for 0.5 h. ^1H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 94/6. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1 to 5:1) to give the title compound (0.122 g, 67%). HPLC analysis indicated that the enantiomeric excess of the product was 98% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 98.0/2.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 11.2 (major), 9.10 (minor) min]. ^1H NMR (500.13 MHz, CDCl_3) δ = 7.22–7.32 (m, 5H), 5.62 (ddd, J = 16.8, 10.4, 7.6 Hz, 1H), 5.14 (dd, J = 10.4, 1.6 Hz, 1H), 5.10 (dd, J = 16.8, 1.6 Hz, 1H), 3.83 (d, J = 13.2 Hz, 1H), 3.64, (d, J = 13.2 Hz, 1H), 3.03 (dt, J = 7.6, 6.0 Hz, 1H), 1.25–1.52 (m, 5H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125.7 MHz, CDCl_3) δ = 141.3, 140.7, 128.3, 128.1, 126.7, 115.9, 61.0, 51.2, 37.9, 19.1, 14.0.

***N*-Phenyl-1-*n*-propyl-2-propenylamine.**³ The general procedure was followed with the methyl carbonate derived from (*E*)-2-hexen-1-ol (0.149 g, 0.94 mmol) and aniline (109 mL, 1.20 mmol). ^1H NMR analysis of the residue crude mixture indicated that the ratio of regioisomers (b/l) was 92/8. The crude reaction mixture was purified by flash column chromatography on silica gel (hexanes/ether 20:1) to give desired product (0.161 g, 93%) as colourless liquid. HPLC

analysis indicated that the enantiomeric excess of the product was 92% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.95/0.05; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 14.3 (major), 18.3 (minor) min]. $[\alpha]_D^{25} = -8.30$ (*c* 0.995, CHCl₃).

¹H NMR (400.13 MHz, CDCl₃) δ = 7.22-7.14 (m, 2H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.63 (dd, *J* = 8.0, 0.8 Hz, 2H), 5.77 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1 H), 3.85 (q, *J* = 6.4 Hz, 1H), 3.65 (br s, 1 H), 1.65-1.55 (m, 2H), 1.53-1.43 (m, 2H), 0.99 (d, *J* = 7.4 Hz, 3H). ¹³C NMR (100.59 MHz, CDCl₃) δ = 147.6, 140.1, 129.1, 117.0, 114.9, 113.2, 55.6, 38.0, 19.1, 14.0.

***N*-(furan-2-ylmethyl)hex-1-en-3-amine.** The general procedure of method A was followed with the methyl carbonate derived from (*E*)-2-hexen-1-ol (0.157 g, 0.99 mmol) and furfurylamine (0.111 mL, 1.20 mmol). The reaction was conducted at room temperature for 1 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 94/6. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.138 g, 85%). HPLC analysis indicated that the enantiomeric excess of the product was 98% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99/1.0; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 10.2 (major), 7.04 (minor) min]. $[\alpha]_D^{25} = +26.7$ (*c* 1.050, CHCl₃). ¹H NMR (CDCl₃, 500.13 MHz) δ = 7.40 (m, 1H), 6.37 (m, 1H), 6.17 (m, 1H), 5.61 (m, 1H), 5.18 (m, 2H), 3.86 (d, *J* = 14.6 Hz, 1H), 3.71 (d, *J* = 14.3 Hz, 1H), 3.05 (m, 1H), 1.58-1.30 (m, 5H), 0.90 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (125.7 MHz, CDCl₃) δ = 154.0, 141.6, 140.9, 116.4, 110.0, 106.7, 60.7, 43.5, 37.7, 19.0, 14.0.

***N*-(thiophen-2-ylmethyl)hex-1-en-3-amine.** The general procedure of method A was followed with the methyl carbonate derived from (*E*)-2-hexen-1-ol (0.147 g, 0.95 mmol) and 2-thiophenemethanamine (0.138 mL, 1.30 mmol). The reaction was conducted at room temperature for 1 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 93/7. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.144 g, 86%). HPLC analysis indicated that the enantiomeric excess of the product was 98% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 11.6 (minor), 10.6 (major) min]. $[\alpha]_D^{25} = +14.8$ (*c* 1.39, CHCl₃). ¹H NMR (500.13 MHz, CDCl₃) δ = 7.22 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.94 (m, 1H), 6.92 (m, 1H), 5.60 (m, 1H), 5.14 (m, 2H), 4.05 (d, *J* = 14.2 Hz, 1H), 3.87 (d, *J* = 14.2 Hz, 1H), 3.06 (m, 1H), 1.52-1.27 (m, 4H), 0.89 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (125.7 MHz, CDCl₃) δ = 144.6, 141.0, 126.5, 124.6, 124.1, 116.2, 60.5, 45.6, 37.9, 19.0, 14.0.

***N*-(hex-1-en-3-yl)-4-(methylthio)benzenamine.** The general procedure of method A was followed with the methyl carbonate derived from (*E*)-2-hexen-1-ol (0.148 g, 0.93 mmol) and 4-aminothioanisole (0.146 mL, 1.20 mmol). The reaction was conducted at room temperature for 1 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be >99/1. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1) to give the title compound (0.198 g, 92%). HPLC analysis indicated that the enantiomeric excess of the product was 98% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 18.1 (major), 19.0 (minor) min]. $[\alpha]_D^{25} = -4.1$ (*c* 0.82, CHCl₃). ¹H NMR (500.13 MHz, CDCl₃) δ = 7.19 (d, *J* = 8.5 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 5.72 (ddd, *J* = 16.9, 10.5, 6.4 Hz, 1H), 5.19 (dt, *J* = 16.9, 1.4 Hz, 1H), 5.12 (dt, *J* = 10.3, 1.1 Hz, 1H), 3.78 (m, 2H), 2.40 (s, 3H), 1.60-1.54 (m, 2H), 1.46-1.38 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (125.7 MHz, CDCl₃) δ = 146.4, 139.8, 131.5, 123.9, 115.1, 113.9, 55.8, 37.9, 19.2, 19.1, 13.9. Anal. Calcd. for C₁₃H₁₉NS: C, 70.54; H, 8.65; N, 6.33; S, 14.49. Found: C, 70.34; H, 9.26; N, 6.30.

***(E)*-N-(furan-2-ylmethyl)hexa-1,4-dien-3-amine.** The general procedure of method B was followed with methyl (2*E*, 4*E*)-hexa-2,4-dienylcarbonate (0.149 g, 0.95 mmol), furfurylamine (0.140 mL, 1.58 mmol), [Ir(COD)Cl]₂ (6.7 mg, 0.010 mmol), **L2** (12.7 mg, 0.02 mmol) and DABCO (10 mg, 0.09 mmol). The reaction was conducted at room temperature for 1 h. GC analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 91/9. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.128 g, 76%). 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 = 99.9/0.1; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 8.72 (major), 7.85 (minor) min]. $[\alpha]_D^{25} = +13.2$ (*c* 1.42, CHCl₃). ¹H NMR (500.13 MHz, CDCl₃) δ = 7.35 (m, 1H), 6.30 (m, 1H), 6.15 (m, 1H), 5.76 (ddd, *J* = 17.3, 10.3, 7.2 Hz, 1H), 5.61 (dq, *J* = 15.2, 6.6, 1H), 5.39 (ddq, *J* = 15.2, 7.6, 1.6 Hz, 1H), 5.16 (dt, *J* = 16.6, 1.6 Hz, 1H), 5.10 (dm, *J* = 10.0 Hz, 1H), 3.74 (s, 2H), 3.59 (t, *J* = 7.4 Hz, 1H), 1.70 (dd, *J* = 6.7, 1.6 Hz, 3H), 1.65-1.50 (br s, 1H). ¹³C NMR (125.7 MHz, CDCl₃) δ = 153.9, 141.7, 139.8, 132.1, 127.3, 115.5, 110.0, 106.8, 62.7, 43.3,

17.8. Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90; O, 9.03. Found: C, 74.29; H, 8.76; N, 8.01.

(*E*)-*N*-(thiophen-2-ylmethyl)hexa-1,4-dien-3-amine. The general procedure of method B was followed with methyl (*2E*, *4E*)-hexa-2,4-dienylcarbonate (0.157 g, 1.00 mmol), 2-thiophenemethanamine (0.138 mL, 1.35 mmol), $[Ir(COD)Cl]_2$ (6.7 mg, 0.010 mmol), **L2** (12.7 mg, 0.02 mmol) and DABCO (10 mg, 0.09 mmol). The reaction was conducted at room temperature for 2 h. 1H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 92/8. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.143 g, 71%). HPLC analysis indicated that the enantiomeric excess of the product was 98% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.0 /1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 10.13 (major), 11.01 (minor) min]. $[\alpha]_D^{25} = +13.6$ (*c* 1.33, $CHCl_3$). 1H NMR (500.13 MHz, $CDCl_3$) δ = 7.15 (dd, *J* = 5.06, 1.4 Hz, 1H), 6.96-6.90 (m, 2H), 5.77 (ddd, *J* = 17.4, 10.0, 6.9 Hz, 1H), 5.63 (dq, *J* = 12.3, 6.7, 1H), 5.40 (ddq, *J* = 15.3, 7.5, 1.6 Hz, 1H), 5.17 (dt, *J* = 17.4, 1.3 Hz, 1H), 5.10 (dm, *J* = 9.74 Hz, 1H), 3.94 (s, 2H), 3.67 (t, *J* = 7.2 Hz, 1H), 1.71 (dd, *J* = 6.7, 1.3 Hz, 3H), 1.58-1.41 (br s, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ = 144.2, 139.9, 132.2, 127.3, 126.6, 124.8, 124.2, 115.5, 62.5, 45.4, 17.8. Anal. Calcd. for $C_{11}H_{15}NS$: C, 68.35; H, 7.82; N, 7.25; S, 16.59. Found: C, 68.08; H, 7.53; N, 7.31.

(*E*)-*N*-(hexa-1,4-dien-3-yl)-4-(methylthio)benzenamine. The general procedure of method B was followed with methyl (*2E*, *4E*)-hexa-2,4-dienylcarbonate (0.153 g, 0.98 mmol), 4-aminothioanisole (0.146 mL, 1.50 mmol), $[Ir(COD)Cl]_2$ (6.7 mg, 0.010 mmol), **L2** (12.7 mg, 0.02 mmol) and DABCO (10 mg, 0.09 mmol). The reaction was conducted at room temperature for 2 h. GC analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 99/1. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.199 g, 93%). HPLC analysis indicated that the enantiomeric excess of the product was 98% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 15.3 (major), 16.0 (minor) min]. $[\alpha]_D^{25} = +40.4$ (*c* 0.935, $CHCl_3$). 1H NMR (500.13 MHz, $CDCl_3$) δ = 7.19 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 5.85 (ddd, *J* = 17.4, 10.4, 5.7 Hz,

1H), 5.71 (dq, $J = 15.5, 6.5, 1.1$ Hz, 1H), 5.48 (ddq, $J = 15.5, 6.3, 1.6$ Hz, 1H), 5.24 (dt, $J = 17.4, 1.3$ Hz, 1H), 5.16 (dt, $J = 10.1, 1.3$ Hz, 1H), 4.33 (t, $J = 6.1$ Hz, 1H), 4.10-3.80 (br s, 1H), 2.40 (s, 3H), 1.72 (dm, $J = 6.6$ Hz, 3H). ^{13}C NMR (125.7 MHz, CDCl_3) $\delta = 145.9, 138.5, 131.2, 130.7, 127.6, 124.4, 115.5, 114.3, 57.7, 19.1, 17.8$. Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{NS}$: C, 71.18; H, 7.81; N, 6.39; S, 14.62. Found: C, 71.15; H, 7.67; N, 6.23.

***N*-Phenyl-1-vinyl-2-butenylamine.**⁴ The general procedure of method B was followed with methyl (2*E*, 4*E*)-hexa-2,4-dienylcarbonate (0.136, 0.87 mmol), aniline (0.116 mL, 1.27 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (6.7 mg, 0.010 mmol), **L2** (12.7 mg, 0.02 mmol) and DABCO (10 mg, 0.09 mmol). The reaction was conducted at room temperature for 3 h. ^1H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 97/3. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.122 g, 81%). 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 = 98.0/2.0; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 11.5 (major), 12.2 (minor) min]. $[\alpha]_{\text{D}}^{25} = -15.2$ (c 0.97, CHCl_3). ^1H NMR (400.13 MHz, CDCl_3) $\delta = 7.11\text{--}7.02$ (m, 2H), 6.61 (td, $J = 7.2, 0.8$ Hz, 1H), 6.64 (d, $J = 8.8$ Hz, 2H), 5.77 (ddd, $J = 17.2, 10.4, 6.0$ Hz, 1H), 5.63 (dq, $J = 15.2, 6.6$ Hz, 1H), 5.41 (ddq, $J = 15.2, 6.2, 0.8$ Hz, 1H), 5.17 (dd, $J = 17.2, 1.4$ Hz, 1H), 5.08 (dd, $J = 10.2, 1.2$ Hz, 1H), 4.27 (t, $J = 6.4$ Hz, 1H), 3.63 (br s, 1H), 1.63 (dd, $J = 6.4, 0.8$ Hz, 3H). ^{13}C NMR (100.59 MHz, CDCl_3) $\delta = 147.2, 138.8, 131.0, 129.0, 127.3, 117.4, 115.3, 113.5, 57.6, 17.8$.

***N*-benzyl-1-(furan-2-yl)prop-2-en-1-amine.**³ The general procedure of method A was followed with methyl (*E*)-3-(furan-2-yl)allylcarbonate (0.211 g, 1.16 mmol) and benzylamine (0.140 mL, 1.28 mmol). The reaction was conducted at room temperature for 0.5 h. ^1H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 91/9. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.200 g, 81%). HPLC analysis indicated that the enantiomeric excess of the product was 98% [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 = 230 nm; TR = 14.6 (major), 19.2 (minor) min]. $[\alpha]_{\text{D}}^{25} = +9.0$ (c 1.065, CHCl_3). ^1H NMR (500.13 MHz, CDCl_3) $\delta = 7.38$ (m, 1H), 7.34-7.31 (m, 4H), 7.28-7.24 (m, 1H), 6.34 (dd, $J = 3.4, 1.7$ Hz, 1H), 6.21 (dm, $J = 3.4$ Hz, 1H),

5.98 (ddd, $J = 16.9, 10.1, 7.3$ Hz, 1H), 5.27 (dt, $J = 17.1, 1.3$ Hz, 1H), 5.24 (dt, $J = 10.1, 1.0$ Hz, 1H), 4.32 (d, $J = 7.3$ Hz, 1H), 3.77 (s, 2H), 2.00 (br s, 1H). ^{13}C NMR (125.7 MHz, CDCl_3) $\delta = 155.2, 141.8, 140.0, 137.5, 128.4, 128.3, 127.0, 116.9, 110.0, 106.3, 58.3, 50.9$.

***N*-benzyl-4-methylpent-1-en-3-amine.** The general procedure of method A was followed with (*E*)-methyl-4-methylpent-2-enylcarbonate (0.147 g, 0.93 mmol) and benzylamine (0.140 mL, 1.28 mmol). ^1H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 95/5. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.158 g, 90%). 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 = 99.9/0.1; flow rate = 0.5 mL/min; detection wavelength = 220 nm; TR = 6.79 (major), 5.67 (minor) min]. ^1H NMR (500.13 MHz, CDCl_3) $\delta = 7.35\text{--}7.20$ (m, 5H), 5.63 (ddd, $J = 18.7, 10.4, 8.6$ Hz, 1H), 5.26 (dd, $J = 10.3, 2.0$ Hz, 1H), 5.10 (dq, $J = 17.2, 2.0, 0.8$ Hz, 1H), 3.85 (d, $J = 13.5$ Hz, 1H), 3.62 (d, $J = 13.5$ Hz, 1H), 2.77 (dd, $J = 8.2, 5.7$ Hz, 1H), 1.70 (m, 1H), 1.30 (br s, 1H), 0.92 (d, $J = 6.5$ Hz, 3H), 0.89 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (125.7 MHz, CDCl_3) $\delta = 140.9, 139.0, 128.3, 128.1, 126.7, 116.9, 66.8, 51.3, 32.2, 19.4, 18.4$. Anal. Calcd. for $\text{C}_{13}\text{H}_{19}\text{N}$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.21; H, 10.30; N, 7.50.

***N*-benzyl-1-(4-nitrophenyl)prop-2-en-1-amine.**³ The general procedure of method A was followed with methyl 4-nitrocinnamylcarbonate (0.116 g, 0.49 mmol) and benzylamine (0.140 mL, 1.28 mmol). The reaction was conducted at room temperature for 4 h. ^1H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 94/6. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 2/1) to give the title compound (0.108 g, 82%). HPLC analysis indicated that the enantiomeric excess of the product was 96% [Diacel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexanes/2-propanol = 95.0/5.0; flow rate = 0.6 mL/min; detection wavelength = 220 nm; TR = 28.5 (major), 31.0 (minor) min]. $[\alpha]_{\text{D}}^{25} = -15.2$ (c 0.5, CHCl_3). ^1H NMR (500 MHz, CDCl_3) $\delta = 8.20$ (dm, $J = 8.5$ Hz, 2H), 7.58 (dm, $J = 8.5$ Hz, 2H), 7.37–7.24 (m, 6H), 5.88 (ddd, $J = 16.9, 10.1, 7.6$ Hz, 1H), 5.26 (dt, $J = 17.1, 1.3$ Hz, 1H), 5.20 (dm, $J = 10.1$ Hz, 1H), 4.35 (d, $J = 7.3$ Hz, 1H), 3.50 (d, $J = 3.8$ Hz, 2H), 1.70 (br s, 1H). ^{13}C NMR (125.7 MHz, CDCl_3) $\delta = 150.3, 147.1, 139.7, 139.5, 128.5, 128.2, 128.1, 127.2, 123.8, 116.6, 64.6, 51.2$. Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$: C, 71.62; H, 6.01; N, 10.44; O, 11.93. Found: C, 71.39; H, 6.00; N, 10.24.

1-Methyl-2-(1-propylallyloxy)benzene.⁴ The general procedure of method A was followed with lithium 2-methylphenoxide (0.228 g, 2.00 mmol) and (*E*)-2-hexenyl methylcarbonate (147 mg, 0.93 mmol) in THF (2 mL). The reaction was conducted at room temperature for 2 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 94/6. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1) to give the title compound (0.158 g, 90%). HPLC analysis indicated that the enantiomeric excess of the product was 98% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 8.97 (major), 8.38 (minor) min]. ¹H NMR (500.13 MHz, CDCl₃) 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). ¹³C NMR (125.7 MHz, CDCl₃) δ = 156.5, 138.5, 130.6, 127.4, 126.4, 120.2, 115, 113.1, 78.6, 37.9, 18.5, 16.4, 14.0.

1-Methoxy-4-(1-propylallyloxy)benzene.⁵ The general procedure A was followed with lithium 4-methoxyphenoxide (0.130 g, 1.00 mmol) and 2-hexenyl methylcarbonate (0.085, 0.53 mmol) in THF (1 mL). The reaction was conducted at room temperature for 2 h. ¹H NMR analysis of the mixture indicated the ratio of regioisomers (b/l) to be 95/5. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1) to give the title compound (0.104 g, 94%). 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 = 254 nm; TR = 18.4 (major), 20.7 (minor) min]. ¹H NMR (500.13 MHz, CDCl₃) 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). ¹³C NMR (125.7 MHz, CDCl₃) δ = 153.8, 152.5, 138.5, 117.3, 116.2, 114.4, 79.9, 55.6, 37.7, 18.5, 13.9.

Allylic Alkylation conducted with O,O'-(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-N,N'-di-(*R,R*)-phenylethylphosphoramidite (L1):

***N*-[1-(*n*-Propyl)-2-propenyl]benzylamine.** The general procedure of method A was followed with the 2-hexenyl methylcarbonate (0.143 g, 0.90 mmol) and benzylamine (0.140 mL, 1.28 mmol). The reaction was conducted at room temperature for 3 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 94/6. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1 to 5:1) to give the title compound (0.108 g, 58%). 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 = 98/2; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 11.3 (major), 9.12 (minor) min].

***N*-Phenyl-1-*n*-propyl-2-propenylamine.** The general procedure A was followed with the 2-hexenyl methylcarbonate (0.149 g, 0.94 mmol) and aniline (109 mL, 1.20 mmol). ¹H NMR analysis of the residue crude mixture indicated that the ratio of regioisomers (b/l) was 92/8. The crude reaction mixture was purified by flash column chromatography on silica gel (hexanes/ether 20:1) to give desired product (0.161 g, 93%) as a colorless liquid. HPLC analysis indicated that the enantiomeric excess of the product was 92% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.95/0.05; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 14.3 (major), 18.3 (minor) min].

***N*-(furan-2-ylmethyl)hex-1-en-3-amine.** The general procedure of method A was followed with the 2-hexenyl methylcarbonate (0.149 g, 0.94 mmol) and furfurylamine (0.111 mL, 1.20 mmol). The reaction was conducted at room temperature for 3 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 92/8. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.107 g, 69%). 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 = 99.0 /1.0; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 10.6 (major), 7.3 (minor) min].

***N*-(thiophen-2-ylmethyl)hex-1-en-3-amine.** The general procedure of method A was followed with 2-hexenyl methylcarbonate (0.150 g, 0.95 mmol) and 2-thiophenemethanamine (0.138 mL, 1.30 mmol). The reaction was conducted at room temperature for 3 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 91/9. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.130 g, 76%). 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 = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 11.4 (major), 10.3 (minor) min].

***N*-(hex-1-en-3-yl)-4-(methylthio)benzenamine.** The general procedure of method A was followed with 2-hexenyl methylcarbonate (0.153 g, 0.96 mmol) and 4-aminothioanisole (0.146 mL, 1.20 mmol). The reaction was conducted at room temperature for 3 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 99/1. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1) to give the title compound (0.195 g, 94%). HPLC analysis indicated that the enantiomeric excess of the product was 92% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 18.6 (major), 17.9 (minor) min].

***(E)*-N-(furan-2-ylmethyl)hexa-1,4-dien-3-amine.** The general procedure of method B was followed with (2*E*, 4*E*)-hexa-2,4-dienylmethylcarbonate (0.145 g, 0.92 mmol), furfurylamine (0.140 mL, 1.58 mmol), [Ir(COD)Cl]₂ (6.7 mg, 0.010 mmol), L1 (12.7 mg, 0.02 mmol) and DABCO (10 mg, 0.09 mmol). The reaction was conducted at room temperature for 18 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 80/20. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.079 g, 48%). HPLC analysis indicated that the enantiomeric excess of the product was 96% [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 = 230 nm; TR = 8.72 (major), 7.85 (minor) min].

(*E*)-*N*-(thiophen-2-ylmethyl)hexa-1,4-dien-3-amine. The general procedure of method B was followed with (*2E*, *4E*)-hexa-2,4-dienylmethylcarbonate (0.157 g, 1.00 mmol), thiophenemethanamine (0.138 mL, 1.34 mmol), [Ir(COD)Cl]₂ (6.7 mg, 0.010 mmol), L1 (12.7 mg, 0.02 mmol) and DABCO (10 mg, 0.09 mmol). The reaction was conducted at room temperature for 18 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 82/18. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.094 g, 49%). HPLC analysis indicated that the enantiomeric excess of the product was 92% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 11.04 (major), 10.12 (minor) min].

(*E*)-*N*-(hexa-1,4-dien-3-yl)-4-(methylthio)benzenamine. The general procedure of method B was followed with (*2E*, *4E*)-hexa-2,4-dienylmethylcarbonate (0.153 g, 0.97 mmol), 4-aminothioanisole (0.146 mL, 1.50 mmol), [Ir(COD)Cl]₂ (6.7 mg, 0.010 mmol), L1 (12.7 mg, 0.02 mmol) and DABCO (10 mg, 0.09 mmol). The reaction was conducted at room temperature for 18 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 93/7. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1) to give the title compound (0.161 g, 73%). 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 = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 16.0 (major), 15.3 (minor) min].

***N*-Phenyl-1-vinyl-2-butenylamine.** The general procedure of method B was followed with (*2E*, *4E*)-hexa-2,4-dienylmethylcarbonate (0.144 g, 0.91 mmol), aniline (0.116 mL, 1.27 mmol), [Ir(COD)Cl]₂ (6.7 mg, 0.010 mmol), L1 (10.7 mg, 0.02 mmol) and DABCO (10 mg, 0.09 mmol). ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 71/29. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1) to give the title compound (0.124 g, 78%). 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 = 98.0/2.0; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 12.2 (major), 11.5 (minor) min].

***N*-benzyl-1-(furan-2-yl)prop-2-en-1-amine.** The general procedure of method A was followed with (*E*)-3-(furan-2-yl)allylmethylcarbonate (0.174 g, 0.96 mmol), benzylamine (0.140 mL, 1.28 mmol). The reaction was conducted at room temperature for 1 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 84/16. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.083 g, 41%). 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 = 99.9/0.1; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 15.2 (major), 20.8 (minor) min].

***N*-benzyl-4-methylpent-1-en-3-amine.** The general procedure of method A was followed with (*E*)-methyl-4-methylpent-2-enylcarbonate (0.150 g, 0.95 mmol), benzylamine (0.140 mL, 1.28 mmol). The reaction was conducted at room temperature for 14 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 92/8. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.119 g, 66%). HPLC analysis indicated that the enantiomeric excess of the product was 89% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 98/2; flow rate = 0.5 mL/min; detection wavelength = 220 nm; TR = 6.81 (major), 5.68 (minor) min].

***N*-benzyl-1-(4-nitrophenyl)prop-2-en-1-amine.** The general procedure of method A was followed with 4-nitrocinnamylmethylcarbonate (0.116 g, 0.49 mmol), benzylamine (0.140 mL, 1.28 mmol). The reaction was conducted at room temperature for 14 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 83/17. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1 to 5/1) to give the title compound (0.098 g, 75%). HPLC analysis indicated that the enantiomeric excess of the product was 96% [Diacel CHIRALCEL OJH (0.46 cm x 25 cm); hexanes/2-propanol = 99.9/0.1; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 30.4 (major), 28.8 (minor) min].

1-Methyl-2-(1-propylallyloxy)benzene. The general procedure of method A was followed with lithium 2-methylphenoxide (114 mg, 1.0 mmol) and 2-hexenyl methylcarbonate (70 mg, 0.48 mmol) in THF (1 mL). The reaction was conducted at RT for 14 h. ¹H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 92/8. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1) to give the title compound (0.066 g, 79%). 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 = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 8.38 (major), 8.96 (minor) min].

1-Methoxy-4-(1-propylallyloxy)benzene. The general procedure of method A was followed with lithium 4-methoxyphenoxide (130 mg, 1.0 mmol) and 2-hexenyl methylcarbonate (85 mg, 0.53 mmol) in THF (1 mL). The reaction was conducted at RT for 2 h. ¹H NMR analysis of the crude mixture indicated the ratio of regioisomers (b/l) 95/5. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10/1) to give the title compound (0.106 g, 95%). 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 = 99.5/0.5; flow rate = 0.6 mL/min; detection wavelength = 254 nm; TR = 20.5 (major), 18.6 (minor) min].

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