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Enantioselective Allylation of Aromatic Amines after *in situ* Generation of an Activated Cyclometalated Iridium Catalyst

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General Procedure: ^{1}H NMR spectra were recorded at 400.13 MHz with $CDCl_3$ and residue $CHCl_3$ as the internal standard (7.26 ppm). $^{13}C\{^{1}H\}$ NMR spectra were obtained at 100.59 MHz with $CDCl_3$ as the solvent. Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.0 ppm). Optical rotations were measured within a 10 cm cell (concentration c given as g/100 mL). Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA and Robertson Microlab Inc., Madison, NJ. All reactions were conducted using standard Schlenk and drybox techniques. THF and Et_2O were distilled from sodium-benzophenone ketyl under nitrogen. All other solvents were purchased as anhydrous grade reagents and used without further purification. 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 phosphormolybdic acid followed by heating. *O*,*O*'-(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-*N*,*N*'-di-(*R*,*R*)-phenylethylphosphoramidite (**L1**) and

O,*O*'-(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-*N*,*N*'-di-(*R*,*R*)-naphthylethylphosphoramidite (**L2**) were prepared according to published procedures.[1] 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 $NaBH_4/CeCl_3$.

General Procedures for the Enantioselective Allylic Amination.

Method A: $[Ir(COD)Cl]_2$ (46.9 mg, 0.070 mmol), **L1** (75.5 mg, 0.140 mmol) were diluted in 0.3 ml THF and 0.3 ml propylamine and heated to 50°C for 20 min. Afterwards all volatiles were removed. The yellow solid was diluted in 3.5 ml THF to get a stock solution.

In a dry box, aniline **3** (1.20 mmol)was added to 0.5 mL of the stock solution of the catalyst (0.010 mmol) in a screw capped vial equipped with a stirring bar. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Carbonate **2** (1.00 mmol) was added with a syringe and the reaction 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 was determined by ^1H NMR analysis of the residue crude mixture. The crude reaction mixture was purified by flash column chromatography on silica gel (hexanes/ether 20:1) to give desired product **4**.

Method **B**: In a drybox, DABCO (11.2 mg, 0.100 mmol for cinnamyl methyl carbonate **2a**, 5.6 mg, 0.050 mmol for other aromatic and aliphatic methyl carbonates), $[Ir(COD)Cl]_2$ (3.4 mg, 0.005 mmol) and (*Ra*,*Rc*,*Rc*)-**L2** (6.4 mg, 0.010 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 and removed from the drybox. Aniline **3** (1.20 mmol) and methyl carbonate **2** (1.00 mmol) were added by syringe and the reaction was continued at room temperature for the specified time. After the reaction was completed as monitored by GC and TLC, the volatile materials were evaporated. The ratio of regioisomers was determined by ^{1}H NMR analysis of the residue crude mixture. The mixture was then purified by flash column chromatography on silica gel to give desired **4**.

***N*-Phenyl-1-phenyl-2-propenylamine (4a).**[2] The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and aniline (0.125 g, 1.34 mmol). The reaction was conducted at room temperature for 10 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be > 99/1. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.164 g, 80%). 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 = 99.75/0.25; flow rate = 0.6 mL/min; detection wavelength = 254 nm; Tr = 28.8 (minor), 30.3 (major) min]: $[\alpha]_D$ = +12.0 (c = 2.10, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.44-7.24 (m, 5 H), 7.20-7.10 (m, 2 H), 6.69 (t, *J* = 7.2 Hz, 1 H), 6.60 (d, *J* = 8.0 Hz, 2 H), 6.04 (ddd, *J* = 16.8, 10.4, 6.4 Hz, 1 H), 5.28 (dt, *J* = 17.2, 1.2 Hz, 1 H), 5.22 (dt, *J* = 10.0, 1.2 Hz, 1 H), 4.94 (t, *J* = 4.4 Hz, 1 H), 4.04 (br s, 1 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 147.8, 142.4, 139.6, 129.6, 129.1, 127.8, 127.7, 118.2, 115.9, 114.2, 61.1.

***N*-(*p*-Tolyl)-1-phenyl-2-propenylamine (4b).** The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and *p*-toludine (0.160 g, 1.50 mmol). The reaction was conducted at room temperature for 6 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be > 99/1. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.166 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 = 99.75/0.25; flow rate = 0.6 mL/min; detection wavelength = 254 nm; T_R = 24.2 (minor), 32.2 (major) min]: $[\alpha]_D$ = -13.7 (c = 0.41, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.44-7.32 (m, 4 H), 7.28 (dt, *J* = 7.2, 2.0 Hz, 1 H), 7.06 (d, *J* = 7.6 Hz, 1 H), 7.03 (t, *J* = 7.2 Hz, 1 H), 6.65 (t, *J* = 7.2 Hz, 1 H), 6.52 (d, *J* = 8.0 Hz, 1 H), 6.08 (ddd, *J* = 16.8, 10.4, 6.0 Hz, 1 H), 5.27 (dt, *J* = 17.2, 1.2 Hz, 1 H), 5.23 (dt, *J* = 10.4, 1.2 Hz, 1 H), 4.99 (t, *J* = 4.4 Hz, 1 H), 3.88 (br s, 1 H), 2.20 (s, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 144.9, 142.0, 139.2, 129.6, 128.7, 127.4, 127.1, 126.8, 115.9, 113.6, 61.1, 20.4. Anal. Calcd. for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.89; H, 7.62; N, 6.41.

***N*-(*p*-Methylphenyl)-1-propyl-2-propenylamine (4c).** The general procedure of method **A** was followed with carbonate **2e** (0.163 g, 1.03 mmol) derived from (*E*)-2-hexen-1-ol and *p*-toluidine (0.128 g, 1.20 mmol). The reaction was conducted at room temperature for 2 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 96:4. The mixture was purified by flash column chromatography on silica gel (hexanes) to give the title compound (0.183 g, 94%). 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; T_R = 13.2 (major), 14.8 (minor) min]: $[\alpha]_D$ = -0.1 (c = 1.090, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 6.95 (dd, *J* = 8.6, 0.8 Hz, 2 H), 6.53 (d, *J* = 8.7 Hz, 2 H), 5.72 (ddd, *J* = 17.1, 10.1, 6.4 Hz, 1H), 5.19 (td, *J* = 17.2, 1.6 Hz, 1H), 5.10 (td, *J* = 10.3, 1.1 Hz, 1H), 3.75-3.82 (m, 1H), 3.54 (br s, 1H), 2.22 (s, 3H), 1.52-1.60 (m, 2H), 1.37-1.47 (m, 2H), 0.94 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 145.7, 140.8, 130.0, 126.7, 115.3, 113.9, 56.4, 38.4, 20.8, 19.5, 14.4. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.29; H, 10.24; N, 7.44.

***N*-(*p*-Anisyl)-1-phenyl-2-propenylamine (4d).** The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and *p*-anisidine (0.150 g, 1.22 mmol). The reaction was conducted at room temperature for 4 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 98/2. The mixture was purified by flash column chromatography on silica gel (3% ethyl acetate in hexanes) to give the title compound (0.214 g, 91%). 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 = 99.75/0.25; flow rate = 0.6 mL/min; detection wavelength = 254 nm; T_R = 38.9 (major), 58.4 (minor) min]: $[\alpha]_D$ = +23.0 (c = 1.16, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.44-7.24 (m, 5 H), 6.73 (dt, *J* = 8.8, 2.8 Hz, 1 H), 6.56 (dt, *J* = 8.8, 2.8 Hz, 1 H), 6.03 (ddd, *J* = 16.8, 10.0, 6.0 Hz, 1 H), 5.26 (dt, *J* = 17.2, 1.2 Hz, 1 H), 5.20 (dt, *J* = 10.0, 1.3 Hz, 1 H), 4.85 (d, *J* = 6.0 Hz, 1 H), 3.79 (br s, 1 H), 3.72 (s, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 152.1, 142.0, 141.4, 139.4,

128.6, 127.3, 127.0, 115.8, 114.8, 114.6, 61.7, 55.7. Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.05; H, 7.06; N, 5.97.

***N*-(*p*-Methoxyphenyl)-1-*n*-propyl-2-propenylamine (4e).** Method **A**: The general procedure was followed with carbonate **2b** (0.161 g, 1.02 mmol) and *p*-toluidine (148 mg, 1.20 mmol). The reaction was conducted at room temperature for 2 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 95:5. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1) to give the title compound (0.201 g, 96%). HPLC analysis indicated that the enantiomeric excess of the product was 95% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 254 nm; T_R = 21.4 (major), 22.8 (minor) min]: [□]$_D$ = +31.2 (c = 1.30, $CHCl_3$). Method **B**: Following the general procedure, the amount of catalyst, additive, and reagents was changed: DABCO (3.4 mg, 0.030 mmol), [Ir(COD)Cl]$_2$ (0.034 mg, 0.0005 mmol) and (*Ra*,*Rc*,*Rc*)-**L2** (0.64 mg, 0.001 mmol), methyl carbonate **2e** (0.158 g, 1.00 mmol) derived from (*E*)-2-hexenol, and *p*-methoxyaniline (0.160 g, 1.30 mmol). The reaction was conducted at 50 °C for 8 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 98/2. The mixture was purified by flash column chromatography on silica gel (3% ethyl acetate in hexanes) to give the title compound (0.175 g, 85%). HPLC analysis indicated that the enantiomeric excess of the product was 94%. ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 6.78 (d, *J* = 8.8 Hz, 2 H), 6.59 (d, *J* = 9.2 Hz, 2 H), 5.73 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.20 (dt, *J* = 17.2, 1.4 Hz, 1 H), 5.12 (dd, *J* = 10.0, 1.0 Hz, 1 H), 3.75 (s, 3 H), 1.64-1.52 (m, 2 H), 1.52-1.40 (m, 2 H),

0.96 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 151.8, 141.8, 140.5, 114.9, 114.70, 114.66, 56.7, 55.7, 38.0, 19.1, 14.0. Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.19; H, 9.32; N, 6.89.

***N*-(*m*-Anisyl)-1-phenyl-2-propenylamine (4f)**. The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and *m*-anisidine (0.150 g, 1.22 mmol). The reaction was conducted at room temperature for 4 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 98/2. The mixture was purified by flash column chromatography on silica gel (4% ethyl acetate in hexanes) to give the title compound (0.192 g, 82%). 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 = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; T_R = 7.5 (minor), 10.1 (major) min]: $[\alpha]_D$ = +15.2 (c = 1.17, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.50-7.40 (m, 4 H), 7.36 (tt, *J* = 6.8, 2.0 Hz, 1 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 6.37 (dd, *J* = 8.0, 2.4 Hz, 1 H), 6.32 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.12 (ddd, *J* = 16.8, 10.0, 6.0 Hz, 1 H), 5.37 (dt, *J* = 16.8, 1.4 Hz, 1 H), 5.32 (dt, *J* = 10.4, 1.4 Hz, 1 H), 5.03 (br s, 1 H), 4.18 (br s, 1 H), 3.79 (s, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 160.5, 148.5, 141.7, 138.8, 129.7, 128.6, 127.4, 127.0, 116.0, 106.5, 102.6, 99.5, 60.7, 54.9. Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.17; H, 7.24; N, 5.78.

***N*-(*m*-Ethoxyphenyl)-1-phenyl-2-propenylamine (4g)**. The general procedure of method **A** was followed with cinnamyl methyl carbonate **2a** (0.195 g, 1.02 mmol) and *m*-phenetidine (0.158 g, 1.16 mmol). The reaction was conducted at room temperature for 2.5 h. ^{1}H NMR analysis of the crude reaction

mixture indicated the ratio of regioisomers to be 97:3. The mixture was purified by flash column chromatography on silica gel (Hexanes/Ether 10:1) to give the title compound (0.210 g, 86%). 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 = 90/10; flow rate = 0.5 mL/min; detection wavelength = 254 nm; T_R = 29.1 (minor), 50.9 (major) min]: $[\alpha]_D$ = +18.5 (c = 0.970, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.42-7.24 (m, 5 H), 7.02 (t, *J* = 8.1 Hz, 1 H), 6.25 (dd, *J* = 8.1, 2.3 Hz, 1 H), 6.21 (dd, *J* = 7.82, 1.85 Hz, 1 H), 6.16 (t, *J* = 2.3 Hz, 1 H), 6.03 (ddd, *J* = 17.2, 10.2, 5.8 Hz, 1 H), 5.28 (td, *J* = 16.9 ,1.5 Hz, 1 H), 5.22 (td, *J* = 10.1, 1.2 Hz, 1 H), 4.92 (d, *J* = 5.8 Hz, 1 H), 4.04 (broad s, 1 H), 3.95 (m, 2 H), 1.36 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 160.0, 138.9, 129.8, 128.7, 127.4, 127.1, 116.1, 106.5, 103.4, 100.0, 63.1, 60.8, 14.84. Anal. Calcd for $C_{17}H_{19}NO$: C, 86.60; H, 7.56; N, 5.53; O, 6.32. Found: C, 80.82; H, 7.28; N, 5.29.

***N*-(*p*-Fluorophenyl)-1-phenyl-2-propenylamine (4h).** The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and *p*-fluoroaniline (0.130 g, 1.17 mmol). The reaction was conducted at room temperature for 10 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 98/2. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.200 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 = 99.75/0.25; flow rate = 0.6 mL/min; detection wavelength = 254 nm; T_R = 22.5 (major), 29.4

(minor) min]: $[\alpha]_D$ = -1.2 (c = 1.06, $CHCl_3$). ^1H NMR (400.13 MHz, $CDCl_3$) δ 7.48-7.41 (m, 4 H), 7.39-7.34 (m, 1 H), 6.96-6.89 (m, 2 H), 6.63-6.56 (m, 2 H), 6.11 (ddd, *J* = 16.8, 10.4, 6.0 Hz, 1 H), 5.36 (dt, *J* = 17.2, 1.2 Hz, 1 H), 5.31 (dt, *J* = 10.0, 1.2 Hz, 1 H), 4.95 (d, *J* = 5.6 Hz, 1 H), 4.02 (br s, 1 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 155.8 (d. *J* = 234 Hz), 143.4 (d, *J* = 2.3 Hz), 141.6, 138.4, 128.7, 127.5, 127.0, 116.0, 115.4 (d, *J* = 22.1 Hz), 114.3 (d, J = 8.4 Hz), 61.4. Anal. Calcd. for $C_{15}H_{14}NF$: C, 79.27; H, 6.21; N, 6.16; F, 8.36. Found: C, 79.16; H, 6.24; N, 6.24; F, 8.46.

***N*-(*p*-Chlorophenyl)-1-phenyl-2-propenylamine (4i).** Method **A**: The general procedure was followed with cinnamyl methyl carbonate **2a** (0.175 g, 0.911 mmol) and *p*-chloroaniline (0.152 g, 1.19 mmol). The reaction was conducted at room temperature for 2.5 h. ^1H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 95:5. The mixture was purified by flash column chromatography on silica gel (Hexanes/Ether 15:1) to give the title compound (0.170 g, 80%). 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 = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 254 nm; T_R = 26.0 (major), 37.8 (minor) min]: $[\alpha]_D$ = + 25.6 (c = 0.860, $CHCl_3$). Method **B**: The general procedure was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and *p*-chloroaniline (0.150 g, 1.18 mmol). The reaction was conducted at room temperature for 10 h. ^1H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 98/2. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.212 g, 89%). HPLC analysis indicated that the

enantiomeric excess of the product was 96%. ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.48-7.36 (m, 5 H), 7.17 (dt, *J* = 8.8, 2.0 Hz, 2 H), 6.59 (dt, *J* = 8.8, 2.4 Hz, 2 H), 6.10 (ddd, *J* = 16.8, 10.4, 6.0 Hz, 1 H), 5.36 (dt, *J* = 14.8, 1.3 Hz, 1 H), 5.33 (dt, *J* = 8.0, 1.2 Hz, 1 H), 4.98 (d, *J* = 6.0 Hz, 1 H), 4.14 (br s, 1 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 145.6, 141.3, 138.5, 128.8, 128.7, 127.5, 127.0, 122.0, 116.2, 114.6, 60.8. Anal. Calcd. for $C_{15}H_{14}NCl$: C, 73.92; H, 5.79; N, 5.75; Cl, 14.55. Found: C, 73.94; H, 5.83; N, 5.83; Cl, 14.67.

***N*-(*p*-Iodophenyl)-1-phenyl-2-propenylamine (4j).** The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and *p*-iodoaniline (0.220 g, 1.04 mmol). The reaction was conducted at room temperature for 10 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 98/2. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.303 g, 92%). HPLC analysis indicated that the enantiomeric excess of the product was 96% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 99/1; flow rate = 0.6 mL/min; detection wavelength = 254 nm; T_R = 18.4 (major), 23.1 (minor) min]: [□]$_D$ = +4.8 (c = 0.084, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.48-7.40 (m, 6 H), 7.36 (s, *J* = 4.6 Hz, 1 H), 6.43 (dt, *J* = 8.8, 2.4 Hz, 2 H), 6.09 (ddd, *J* = 16.8, 10.4, 6.0 Hz, 1 H), 5.34 (dt, *J* = 12.0, 1.3 Hz, 1 H), 5.31 (dt, *J* = 5.2, 1.2 Hz, 1 H), 4.97 (d, *J* = 5.6 Hz, 1 H), 4.15 (br s, 1 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 146.5, 141.1, 138.4, 137.5, 128.7, 127.5, 127.0, 116.3, 115.7, 78.3, 60.5. Anal. Calcd. for $C_{15}H_{14}NI$: C, 53.75; H, 4.21; N, 4.18; I, 37.86. Found: C, 53.59; H, 4.27; N, 4.17; I, 38.04.

***N*-(1-Naphthyl)-1-phenyl-2-propenylamine (4k).** The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and 1-naphthylamine (0.170 g, 1.18 mmol). The reaction was conducted at room temperature for 10 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 97/3. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.210 g, 83%). 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 = 99/1; flow rate = 0.6 mL/min; detection wavelength = 254 nm; T_R = 29.3 (minor), 40.3 (major) min]: $[\alpha]_D$ = -50.7 (c = 0.14, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.62 (dd, *J* = 7.6, 2.0 Hz, 1 H), 7.30-7.03 (m, 9 H), 6.39 (dd, *J* = 6.6, 1.8 Hz, 1 H), 5.97 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.18 (dt, *J* = 16.8, 1.2 Hz, 1 H), 5.10 (dt, *J* = 10.0, 1.2 hz, 1 H), 4.95 (d, *J* = 6.0 Hz, 1 H), 4.57 (br s, 1 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 142.0, 141.6, 138.9, 134.2, 128.74, 128.67, 127.5, 127.1, 126.4, 125.6, 124.7, 123.4, 119.8, 117.6, 116.3, 106.20, 60.86. Anal. Calcd. for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 88.07; H, 6.53; N, 5.49.

***N*-(2-Naphthyl)-1-phenyl-2-propenylamine (4l).** The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and 2-naphthylamine (0.170 g, 1.18 mmol). The reaction was conducted at room temperature for 10 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 99/1. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.225 g, 89%). 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 = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; T_R = 6.6 (major), 7.6 (minor) min]: [□]$_D$ = +92.8 (c = 1.45, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.53 (d, *J* = 8.0 Hz, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.31-7.11 (m, 6 H), 7.06 (t, *J* = 7.6 Hz, 1 H), 6.76 (dd, *J* = 9.0, 2.2 Hz, 1 H), 6.64 (d, *J* = 2.0 Hz, 1 H), 5.95 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.20 (d, *J* = 17.6 Hz, 1 H), 5.13 (d, *J* = 9.6 Hz, 1 H), 4.94 (d, *J* = 5.6 Hz, 1 H), 4.06 (br s, 1 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 144.7, 141.5, 138.6, 134.9, 128.74, 128.73, 127.53, 127.48, 127.45, 127.1, 126.2, 126.0, 122.0, 118.0, 116.2, 105.8, 60.2. Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 88.16; H, 6.58; N, 5.41.

***N*-(*p*-Trifluoromethylphenyl)-1-phenyl-2-propenylamine (4m).** The amount of the additive and catalyst was twice that described in the general procedure of method **B**: DABCO (22.4 mg, 0.200 mmol), $[Ir(COD)Cl]_2$ (6.7 mg, 0.010 mmol) and (*Ra*,*Rc*,*Rc*)-**L2** (12.8 mg, 0.020 mmol). After adding cinnamyl methyl carbonate **2a** (0.188 g, 0.980 mmol) and *p*-trifluoromethylaniline (0.200 g, 1.24 mmol), the reaction was continued at room temperature for 16 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 94/6. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.196 g, 72%). 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 = 99.75/0.25; flow rate = 0.6 mL/min; detection wavelength = 254 nm; T_R = 29.8 (major), 34.9 (minor) min]: [□]$_D$ = 17.3 (c = 0.79, $CHCl_3$). ^{1}H NMR (400.13

MHz, $CDCl_3$) δ 7.50-7.35 (m, 7 H), 6.64 (d, *J* = 8.4 Hz, 2 H), 6.08 (ddd, *J* = 16.8, 10.4, 6.0 Hz, 1 H), 5.33 (dt, *J* = 7.2, 1.2 Hz, 1 H), 5.30 (d, *J* = 1.2 Hz, 1 H), 5.02 (t, *J* = 5.6 Hz, 1 H), 4.40 (d, *J* = 4.8 Hz, 1 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 149.5, 140.9, 138.0, 128.9, 127.8, 127.1, 126.4 (q, *J* = 3.8 Hz), 124.9 (*J* = 264.3 Hz), 119.0 (q, *J* = 32.5 Hz), 116.6, 112.6, 60.3. Anal. Calcd. for $C_{16}H_{14}NF_3$: C, 69.31; H, 5.09; N, 5.05; F, 20.55. Found: C, 69.46; H, 5.12; N, 5.09; F, 20.37.

***N*-(*o*-Bromophenyl)-1-phenyl-2-propenylamine (4n).** The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and *o*-bromoaniline (0.215 g, 1.25 mmol). The reaction was conducted at room temperature for 16 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 93/7. The mixture was purified by flash column chromatography on silica gel (1.5% ethyl acetate in hexanes) to give the title compound (0.185 g, 66%). 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 = 254 nm; T_R = 14.8 (minor), 23.9 (major) min]: $[\alpha]_D$ = -15.1 (c = 0.59, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.46-7.25 (m, 5 H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1 H), 6.55 (t, *J* = 7.6 Hz, 2 H), 6.07 (ddd, *J* = 16.8, 10.4, 6.0 Hz, 1 H), 5.27 (d, *J* = 10.0 Hz, 1 H), 5.24 (t, *J* = 1.2 Hz, 1 H), 4.98 (t, *J* = 5.6 Hz, 1 H), 4.75 (d, *J* = 5.2 Hz, 1 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 143.8, 141.1, 138.6, 132.3, 128.8, 128.3, 127.5, 126.9, 118.1, 116.3, 112.7, 109.9, 60.5. Anal. Calcd. for $C_{15}H_{14}NBr$: C, 62.52; H, 4.90; N, 4.86; Br, 27.73. Found: C, 62.77; H, 4.92; N, 4.87; Br, 27.46.

***N*-(2,4,6-Trimethylphenyl)-1-phenyl-2-propenylamine (4o).** The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and 2,4,6-trimethylaniline (0.170 g, 1.25 mmol). The reaction was conducted at room temperature for 2 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 97/3. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.207 g, 85%). 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 = 99.75/0.25; flow rate = 0.6 mL/min; detection wavelength = 254 nm; T_R = 17.0 (major), 19.5 (minor) min]: $[\alpha]_D$ = +137.4 (c = 1.225, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.38-7.23 (m, 5 H), 6.78 (s, 2 H), 6.05 (ddd, *J* = 17.2, 10.0, 6.4 Hz, 1 H), 5.25 (dt, *J* = 16.8, 1.6 Hz, 1 H), 5.17 (dt, *J* = 10.4, 1.6 Hz, 1 H), 4.61 (t, *J* = 6.4 Hz, 1 H), 3.12 (br s, 1 H), 2.22 (s, 3 H), 2.11 (s, 6 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 142.9, 141.9, 139.3, 130.9, 129.8, 129.3, 128.4, 127.1, 126.9, 115.5, 64.2, 20.6, 18.6. Anal. Calcd. for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 86.18; H, 8.49; N, 5.62.

***N*-(*p*-Methylthiophenyl)-1-phenyl-2-propenylamine (4p).** The general procedure of method **A** was followed with cinnamyl methyl carbonate **2a** (0.183 g, 0.953 mmol) and 4-(methylthio)aniline (160 mg, 1.15 mmol). The reaction was conducted at room temperature for 2.5 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 97:3. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1) to give the title compound (0.206 g, 80%). HPLC analysis indicated that the enantiomeric excess of the product was

96% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 254 nm; T_R = 38.8 (major), 52.1 (minor) min]: [□]$_D$ = +27.8 (c = 0.845, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.43-7.33 (m, 6 H), 7.33-7.25 (m, 2 H), 6.55 (d, *J* = 8.8 Hz, 2 H), 6.03 (ddd, *J* = 17.35, 10.1, 5.7 Hz, 1 H), 5.27 (td, *J* = 17.1, 1.2 Hz, 1 H), 5.24 (td, *J* = 10.2, 1.3 Hz, 1 H)), 4.92 (d, *J* = 5.7 Hz, 1 H) 4.09 (broad s, 1 H), 2.39 (s, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 146.4, 142.1, 139.3, 131.6, 129.3, 128.0, 127.6, 125.0, 116.7, 114.7, 61.3, 19.4. Anal. Calcd for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.48; S, 12.56. Found: C, 75.52; H, 6.98; N, 5.34.

1-(1-Phenyl-2-propenyl)-1,2,3,4-tetrahydroquinoline (4q). The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and 1,2,3,4-tetrahydroquinoline (0.160 g, 1.20 mmol). The reaction was conducted at room temperature for 2 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 97/3. The mixture was purified by flash column chromatography on silica gel (0.5% ethyl acetate in hexanes) to give the title compound and its regioisomer as a mixture (0.212 g, 89%). 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 = 0.6 mL/min; detection wavelength = 254 nm; T_R = 20.7 (major), 25.6 (minor) min]: [□]$_D$ = +45.0 (c = 0.72, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.52-7.30 (m, 5 H), 7.20-7.08 (m, 2 H), 6.77 (dd, *J* = 8.0, 3.6 Hz, 1 H), 6.73 (t, *J* = 3.2 Hz, 1 H), 6.29 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.61 (d, *J* = 4.8 Hz, 1 H), 5.52 (dd, *J* = 10.4, 1.2 Hz, 1 H), 5.41 (dd, *J* = 17.2, 1.6 Hz, 1 H), 3.36 (quintet, *J* = 5.6 Hz, 1 H), 3.22 (quintet, *J* = 5.2

Hz, 1 H), 2.93 (d, *J* = 4.8 Hz, 2 H), 2.04 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 145.3, 140.05, 135.1, 129.0, 128.3, 127.9, 127.0, 126.9, 122.8, 118.0, 115.7, 111.2, 63.5, 44.5, 28.4, 22.3. Anal. Calcd. for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.48; H, 7.66; N, 5.50.

1-(1-Phenyl-2-propenyl)-2,3-dihydroindoline (4r).[3] The general procedure of method **B** was followed with cinnamyl methyl carbonate **2a** (0.188 g, 0.979 mmol) and 2,3-dihydroindoline (0.145 g, 1.22 mmol). The reaction was conducted at room temperature for 2 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 98/2. The mixture was purified by flash column chromatography on silica gel (0.5% ethyl acetate in hexanes) to give the title compound and its regioisomer as a mixture (0.214 g, 90%). 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 = 99/1; flow rate = 0.6 mL/min; detection wavelength = 254 nm; T_R = 16.5 (major), 18.1 (minor) min]: [□]$_D$ = +11.5 (c = 0.26, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.32 (d, *J* = 7.6 Hz, 2 H), 7.24 (t, *J* = 7.6 Hz, 2 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 6.96 (d, *J* = 7.2 Hz, 1 H), 6.85 (t, *J* = 7.2 Hz, 1 H), 6.52 (t, *J* = 7.2 Hz, 1 H), 6.21 (d, *J* = 8.0 Hz, 1 H), 6.00 (ddd, *J* = 17.2, 10.0, 6.0 Hz, 1 H), 5.21 (dd, *J* = 11.6, 0.8 Hz, 1 H), 5.20 (dd, *J* = 15.6, 0.8 Hz, 1 H), 4.87 (d, *J* = 7.2 Hz, 1 H), 3.25 (t, *J* = 8.8 Hz, 1 H), 3.24 (t, *J* = 8.2 Hz, 1 H), 2.84 (t, *J* = 8.2 Hz, 2 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 151.2, 140.4, 135.7, 130.4, 128.4, 127.7, 127.2, 126.9, 124.3, 118.0, 117.4, 108.2, 64.3, 50.2, 28.3. Anal. Calcd. for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.56; H, 7.20; N, 5.97.

***N*-Phenyl-1-(*o*-methoxyphenyl)-2-propenylamine (4s).** The general procedure of method **B** was followed with *p*-methoxycinnamyl methyl carbonate **2c** (0.222 g, 1.00 mmol) and aniline (0.125 g, 1.34 mmol). The reaction was conducted at room temperature for 10 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 97/3. The mixture was purified by flash column chromatography on silica gel (3% ethyl acetate in hexanes) to give the title compound (0.210 g, 88%). 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 = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; T_R = 49.1 (major), 61.2 (minor) min]: $[\alpha]_D$ = +27.0 (c = 0.30, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.32 (dt, *J* = 8.4, 1.6 Hz, 2 H), 7.17 (dt, *J* = 7.6, 1.6 Hz, 1 H), 7.15 (dt, *J* = 7.2, 1.6 Hz, 1 H), 6.90 (dt, *J* = 7.2, 2.2 Hz, 2 H), 6.71 (tt, *J* = 7.2, 1.2 Hz, 1 H), 6.62 (dd, *J* = 8.6, 1.0 Hz, 2 H), 6.04 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.28 (dt, *J* = 17.2, 1.2 Hz, 1 H), 5.23 (dd, *J* = 10.0, 1.2 Hz, 1 H), 4.91 (d, *J* = 5.6 Hz, 1 H), 4.01 (br s, 1 H), 3.82 (s, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 158.8, 147.2, 139.1, 133.8, 129.0, 128.2, 117.4, 115.6, 114.0, 113.4, 60.1, 55.1.

***N*-Phenyl-1-(2-furyl)-2-propenylamine (4t).** The general procedure of method **B** was followed with the methyl carbonate **2d** derived from (*E*)-1-(2-furyl)-1-propen-3-ol (0.180 g, 0.989 mmol) and aniline (0.125 g, 1.34 mmol). The reaction was conducted at room temperature for 10 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 94/6. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.156 g, 81%). 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 = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; T_R = 5.1 (minor), 5.6 (major) min]: [□]$_D$ = +48.9 (c = 2.06, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.27 (s, 1 H), 7.06 (t, *J* = 7.6 Hz, 2 H), 6.63 (t, *J* = 7.4 Hz, 1 H), 6.54 (d, *J* = 8.0 Hz, 2 H), 6.22 (dd, *J* = 3.0, 1.8 Hz, 1 H), 6.12 (d, *J* = 2.6 Hz, 1 H), 5.94 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.24 (dd, *J* = 17.2, 0.8 Hz, 1 H), 5.17 (dd, *J* = 10.4, 1.0 Hz, 1 H), 4.98 (br s, 1 H), 3.94 (br s, 1 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 154.2, 146.7, 142.0, 136.1, 129.1, 117.9, 116.8, 113.5, 110.2, 106.7, 54.3. Anal. Calcd. for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.44; H, 6.81; N, 7.07.

***N*-Phenyl-1-(*o*-methoxyphenyl)-2-propenylamine (4u).** The general procedure of method **B** was followed with *o*-methoxycinnamyl methyl carbonate **2e** (0.222 g, 1.00 mmol) and aniline (0.125 g, 1.34 mmol). The reaction was conducted at room temperature for 10 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 99/1. The mixture was purified by flash column chromatography on silica gel (3% ethyl acetate in hexanes) to give the title compound (0.226 g, 91%). HPLC analysis indicated that the enantiomeric excess of the product was 74% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99/1; flow rate = 1.0 mL/min; detection wavelength = 254 nm; T_R = 24.6 (major), 37.7 (minor) min]: [□]$_D$ = +14.1 (c = 1.40, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.31 (dd, *J* = 7.4, 1.8 Hz, 1 H), 7.23 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.13 (dt, *J* = 7.2, 2.0 Hz, 1 H), 7.11 (dt, *J* = 7.2, 2.0 Hz, 1 H), 6.92 (t, *J* = 7.2 Hz, 1 H), 6.91 (d, *J* = 8.4 Hz, 1 H), 6.66 (t, *J* = 7.2 Hz, 1 H),

6.10 (d, *J* = 8.0 Hz, 2 H), 6.07 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.34 (d, *J* = 5.2 Hz, 1 H), 5.21 (dt, *J* = 16.8, 1.4 Hz, 1 H), 5.16 (dd, *J* = 10.0, 1.4 Hz, 1 H), 4.22 (br s, 1 H), 3.87 (s, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 156.8, 147.3, 138.6, 129.7, 129.0, 128.3, 127.7, 120.8, 117.3, 115.1, 113.4, 110.7, 55.4, 54.6. Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.58; H, 7.23; N, 6.05.

***N*-Phenyl-1-*n*-propyl-2-propenylamine (4v).** Method **A**: The general procedure was followed with the methyl carbonate **2b** (0.149 g, 0.942 mmol) derived from (*E*)-2-hexen-1-ol and aniline (109 □l, 1.20 mmol). ^{1}H NMR analysis of the residue crude mixture indicated that the ratio of regioisomers 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 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]: [□]$_D$ = -8.30 (c = 0.995, $CHCl_3$). Method **B**: The general procedure was followed with the methyl carbonate **2e** (0.158 g, 1.00 mmol) derived from (*E*)-2-hexen-1-ol and aniline (0.125 g, 1.34 mmol). The reaction was conducted at room temperature for 3 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 98/2. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.152 g, 87%). HPLC analysis indicated that the enantiomeric excess of the product was 95%. ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.22-7.14 (m, 2 H), 6.71 (t, *J* = 7.4 Hz, 1 H), 6.63 (dd, *J*

= 8.0, 0.8 Hz, 2 H), 5.77 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.24 (d, *J* = 17.2 Hz, 1 H), 5.15 (d, *J* = 10.2 Hz, 1 H), 3.85 (q, *J* = 6.4 Hz, 1 H), 3.65 (br s, 1 H), 1.65-1.55 (m, 2 H), 1.53-1.43 (m, 2 H), 0.99 (d, *J* = 7.4 Hz, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 147.6, 140.1, 129.1, 117.0, 114.9, 113.2, 55.6, 38.0, 19.1, 14.0. Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.40; H, 9.85; N, 8.04.

***N*-Phenyl-1-methyl-2-propenylamine (4w).**[4] The general procedure of method **B** was followed with the methyl carbonate **2f** (0.130 g, 1.00 mmol) derived from (*E*)-2-buten-1-ol and aniline (0.125 g, 1.34 mmol). The reaction was conducted at room temperature for 3 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 97/3. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.106 g, 72%). 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 = 0.6 mL/min; detection wavelength = 254 nm; T_R = 20.0 (major), 22.9 (minor) min]: [□]$_D$ = -4.1 (c = 2.68, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.20-7.06 (m, 2 H), 6.59 (tt, *J* = 7.4, 1.2 Hz, 1 H), 6.51 (dd, *J* = 8.2, 1.0 Hz, 2 H), 5.73 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.12 (dd, *J* = 17.6, 1.4 Hz, 1 H), 4.99 (dd, *J* = 10.4, 1.4 Hz, 1 H), 3.88 (quintet, *J* = 6.4 Hz, 1 H), 3.50 (br s, 1 H), 1.21 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 147.3, 141.2, 129.1, 117.2, 114.0, 113.3, 51.0, 21.5.

***N*-Phenyl-1-vinyl-2-butenylamine (4x).** The general procedure of method **B** was followed with the methyl carbonate **2g** (0.156 g, 1.00 mmol) derived from (*E*,*E*)-2,4-hexadien-1-ol and aniline (0.125 g, 1.34 mmol). The

reaction was conducted at room temperature for 3 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 98/1/1. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.150 g, 87%). 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 = 0.6 mL/min; detection wavelength = 254 nm; T_R = 17.9 (major), 19.2 (minor) min]: [□]$_D$ = +25.3 (c = 0.97, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) □ 7.11-7.02 (m, 2 H), 6.61 (td, J = 7.2, 0.8 Hz, 1 H), 6.64 (d, J = 8.8 Hz, 2 H), 5.77 (ddd, J = 17.2, 10.4, 6.0 Hz, 1 H), 5.63 (dq, J = 15.2, 6.6 Hz, 1 H), 5.41 (ddq, J = 15.2, 6.2, 0.8 Hz, 1 H), 5.17 (dd, J = 17.2, 1.4 Hz, 1 H), 5.08 (dd, J = 10.2, 1.2 Hz, 1 H), 4.27 (t, J = 6.4 Hz, 1 H), 3.63 (br s, 1 H), 1.63 (dd, J = 6.4, 0.8 Hz, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) □ 147.2, 138.8, 131.0, 129.0, 127.3, 117.4, 115.3, 113.5, 57.6, 17.8. Anal. Calcd. for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.06; H, 8.58; N, 8.04.

***N*-Phenyl-1-*i*-propyl-2-propenylamine (4y).** The general procedure of method **B** was followed with the methyl carbonate **2h** (0.158 g, 1.00 mmol) derived from (*E*)-4-methyl-2-pentenol and aniline (0.125 g, 1.34 mmol) and 3.4 mg (0.030 mmol) DABCO additive. The reaction was conducted at room temperature for 16 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers to be 97/3. The mixture was purified by flash column chromatography on silica gel (1% ethyl acetate in hexanes) to give the title compound (0.145 g, 83%). 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 = 0.6 mL/min; detection

wavelength = 254 nm; T_R = 13.0 (major), 14.1 (minor) min]: $[\alpha]_D$ = -12.1 (c = 0.52, $CHCl_3$). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.18-7.08 (m, 2 H), 6.66 (tt, *J* = 7.6, 1.0 Hz, 1 H), 6.62-6.54 (m, 2 H), 5.73 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.20 (dd, *J* = 16.0, 1.6 Hz, 1 H), 5.16 (dd, *J* = 10.2, 1.6 Hz, 1 H), 3.66 (br s, 2 H), 1.92-1.80 (m, 1 H), 1.00 (d, *J* = 6.8 Hz, 3 H), 0.97 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100.59 MHz, $CDCl_3$) δ 147.8, 137.8, 129.0, 116.9, 116.0, 113.2, 61.3, 32.4, 18.8, 18.5. Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.06; H, 9.93; N, 7.83.

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