Regio- and Enantioselective Allylic Amination of Achiral Allylic Esters Catalyzed by An Iridium–Phosphoramidite Complex

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Supporting Information

General Procedures. ^1H NMR spectra were recorded at 400.13 MHz with CDCl_3 as the solvent and tetramethylsilane as the internal standard. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained at 100.59 MHz or 125.77 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 with in a 10 cm cell (concentration c given as g/100 mL). 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 reagents and used without further purification. $[\text{Ir}(\text{cod})\text{Cl}]_2$ ¹, O,O' -(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-*N,N'*-di-(*R,R*)-1-phenylethylphosphoramidite² [(*R_a*,*R_C*,*R_C*)-**6**], O,O' -(*S*)-(1,1'-Dinaphthyl-2,2'-diyl)-*N,N'*-di-(*R,R*)-1-phenylethylphosphoramidite² [(*S_a*,*R_C*,*R_C*)-**6**], O,O' -(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-*N,N'*-diisopropylphosphoramidite² [(*R*)-**8**], and O,O' -(1,1'-Diphenyl-2,2'-diyl)-*N,N'*-di-(*R,R*)-1-phenylethylphosphoramidite² [(*R,R*)-**9**] were prepared according to published procedures. O,O' -(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-*N,N'*-dimethylphosphoramidite [(*R*)-**7**] was purchased from Strem Chemicals. All allylic carbonates (**1a** – **1f**) were synthesized by the reaction of corresponding allylic alcohols with methyl chloroformate in the presence of pyridine. (*E*)-4-Methoxycinnamyl alcohol, (*E*)-2-methoxycinnamyl alcohol, and (*E*)-3-(2-furanyl)-2-propen-1-ol were prepared by the DIBAH reduction of corresponding aldehydes. All amines (**2a** – **2h**), (*E*)-cinnamyl alcohol, (*E*)-2-hexen-1-ol, 2-methoxycinnamaldehyde, (*E*)-3-(2-furyl)acrolein, cinnamyl acetate (**1g**) (Aldrich Chemicals Co.), (*E*)-4-methoxycinnamaldehyde (TCI), and 4-nitrocinnamyl alcohol (Alfa Aesar) were purchased and used without further purification.

General Procedure for the Enantioselective Allylic Amination Catalyzed by Iridium–Phosphoramidite Complex: A typical procedure is given for the reaction of entry 1 in Table 1. In a drybox, $[\text{Ir}(\text{cod})\text{Cl}]_2$ (6.5 mg, 0.010 mmol) and (*R_a*,*R_C*,*R_C*)-**6** (10.8 mg, 0.0200 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. Benzylamine (**2a**, 135 mg, 1.26 mmol) and cinnamyl methycarbonate (**1a**, 188 mg, 0.979 mmol) were added to the reaction mixture by syringe. The reaction mixture was stirred at room temperature for 10 h and monitored by GC. After the reaction was complete, the volatile materials were evaporated. ¹H NMR analysis of the residual crude mixture indicated the ratio of regioisomers **3/4** and diallylation product **5** to be 98/1/1. The mixture was then purified by flash column chromatography on silica gel (2.5% ethyl acetate in hexane) to give (*R*)-*N*-(1-phenyl-2-propenyl)benzylamine (184 mg, 84%). HPLC analysis indicated that the enantiomeric excess of product was 95% [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol/diethylamine = 99.74/0.25/0.01; flow rate = 0.6 mL/min; detection wave length = 220 nm; T_R = 15.1 (major), 17.4 (minor) min].

(*R*)-*N*-(1-Phenyl-2-propenyl)benzylamine:³ ¹H NMR (400.13 MHz, CDCl₃) δ 7.30–7.39 (m, 8H), 7.22–7.28 (m, 2H), 5.95 (ddd, *J* = 16.8, 10.0, 7.2 Hz, 1H), 5.23 (dt, *J* = 16.8, 1.6 Hz, 1H), 5.12 (dq, *J* = 10.0, 0.8 Hz, 1H), 4.23 (d, *J* = 7.2 Hz, 1H), 3.75 (d of AB pattern, *J* = 13.4 Hz, 1H), 3.71 (d of AB pattern, *J* = 13.4 Hz, 1H), 1.64 (brs, 1H). ¹³C NMR (100.59 MHz, CDCl₃) δ 142.74, 140.90, 140.38, 128.53, 128.37, 128.15, 127.31, 127.21, 126.89, 115.18, 65.09, 51.26. The absolute configuration was determined by comparison of the optical rotation with literature data: [α]_D^{RT} = −7.0 (*c* 3.1, CHCl₃), lit.⁴ [α]_D²⁵ = +3.6 (*c* 0.5, CHCl₃) for (*S*)-enantiomer of 86% ee.

***N*-(1-Phenyl-2-propenyl)-4-methoxybenzylamine**⁴ (Table 2, entry 1): The general procedure was followed with 4-methoxybenzylamine (**2b**, 186 mg, 1.35 mmol) and **1a** (199 mg, 1.04 mmol). The reaction was conducted at room temperature for 18 h. ¹H NMR analysis of the crude mixture indicated the ratio of regioisomers **3/4** and diallylation product **5** to be 98/0/2. The mixture was purified by flash column chromatography on silica gel (5% ethyl acetate in hexane) to give the title compound (210 mg, 80%). HPLC analysis indicated that the enantiomeric excess of product was 94% [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 99.75/0.25; flow rate = 0.5 mL/min; detection wave length = 230 nm; T_R = 26.2 (major), 29.3 (minor) min]: [α]_D^{RT} = −1.8 (*c* 5.5, CHCl₃). ¹H NMR (400.13 MHz, CDCl₃) δ 7.21–7.38 (m, 7H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.94 (ddd, *J* = 17.2, 10.0, 7.6 Hz, 1H), 5.22 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.11 (ddd, *J* = 10.0, 1.6, 1.2 Hz, 1H), 4.21 (d, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.68 (d of AB pattern, *J* = 13.0 Hz, 1H), 3.64 (d of AB pattern, *J* = 13.0 Hz, 1H), 1.58 (brs, 1H). ¹³C NMR (125.77 MHz, CDCl₃) δ 158.54, 142.84, 141.01, 132.56, 129.29, 128.49, 127.30, 127.14, 115.05, 113.72, 64.99, 55.24, 50.65.

(*R*)-*N*-(1-Phenyl-2-propenyl)-*n*-hexylamine⁵ (Table 2, entry 2): The general procedure was followed with *n*-hexylamine (**2c**, 129 mg, 1.27 mmol) and **1a** (193 mg, 1.00 mmol). The reaction was conducted at room temperature for 9 h. ¹H NMR analysis of the crude mixture indicated the ratio of regioisomers **3/4** and diallylation product **5** to be 98/2/0. The mixture was

purified by flash column chromatography on silica gel (2.5% ethyl acetate in hexane) to give the title compound (192 mg, 88%). The HPLC analysis indicated that the enantiomeric excess of product was 96% [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/diethylamine = 99.98/0.02; flow rate = 0.4 mL/min; detection wave length = 210 nm; T_R = 19.8 (major), 20.9 (minor) min]. The absolute configuration was determined by comparison of the optical rotation with literature data: $[\alpha]_D^{RT} = -19$ (c 1.1, CHCl_3), lit.⁴ $[\alpha]_D^{25} = +18.5$ (c 0.5, CHCl_3) for (*S*)-enantiomer of 90% ee. ^1H NMR (400.13 MHz, CDCl_3) δ 7.30–7.35 (m, 4H), 7.21–7.27 (m, 1H), 5.93 (ddd, J = 17.2, 10.0, 6.8 Hz, 1H), 5.20 (dt, J = 17.2, 1.4 Hz, 1H), 5.08 (ddd, J = 10.0, 1.6, 1.2 Hz, 1H), 4.17 (d, J = 6.8 Hz, 1H), 2.58 (dt, J = 11.2, 7.2 Hz, 1H), 2.48 (dt, J = 11.2, 7.2 Hz, 1H), 1.20–1.53 (m, 9H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100.59 MHz, CDCl_3) δ 143.07, 141.23, 128.46, 127.17, 127.07, 114.77, 66.28, 47.72, 31.77, 30.14, 27.04, 22.61, 14.06.

***N*-(1-Phenyl-2-propenyl)allylamine (Table 2, entry 3):** The general procedure was followed with allyl amine (**2d**, 75.5 mg, 1.32 mmol) and **1a** (204 mg, 1.06 mmol). The reaction was conducted at room temperature for 12 h. The mixture was purified by flash column chromatography on silica gel (10% ethyl acetate in hexane) to give the title compound (140 mg, 76%). The HPLC analysis indicated that the enantiomeric excess of product was 97% [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/diethylamine = 99.99/0.01; flow rate = 0.5 mL/min; detection wave length = 210 nm; T_R = 17.9 (major), 19.2 (minor) min]: $[\alpha]_D^{RT} = -14$ (c 3.1, CHCl_3). ^1H NMR (400.13 MHz, CDCl_3) δ 7.30–7.35 (m, 4H), 7.22–7.28 (m, 1H), 5.83–5.88 (m, 2H), 5.21 (dt, J = 17.2, 1.2 Hz, 1H), 5.16 (dq, J = 17.2, 1.6 Hz, 1H), 5.11 (dt, J = 10.0, 1.2 Hz, 1H), 5.09 (dq, J = 10.0, 1.6 Hz, 1H), 4.23 (d, J = 7.2 Hz, 1H), 3.21 (ddt of AB pattern, J = 14.2, 6.0, 1.4 Hz, 1H), 3.16 (ddt of AB pattern, J = 14.2, 6.0, 1.4 Hz, 1H), 1.41 (brs, 1H). ^{13}C NMR (100.59 MHz, CDCl_3) δ 142.69, 140.82, 136.72, 128.50, 127.24, 127.18, 115.90, 115.09, 65.17, 49.88. Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{N}$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.06; H, 8.61; N, 8.06.

1-(1-Phenyl-2-propenyl)pyrrolidine⁶ (Table 2, entry 4): The general procedure was followed with pyrrolidine (**2e**, 86.9 mg, 1.22 mmol) and **1a** (185 mg, 0.96 mmol). The reaction was conducted at room temperature for 2 h. ^1H NMR analysis of the crude mixture indicated the ratio of regioisomers **3/4** to be 98/2. The mixture was purified by flash column chromatography on silica gel (5% ethyl acetate in hexane) to give the title compound (135 mg, 75%). HPLC analysis indicated that the enantiomeric excess of product was 97% [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/diethylamine = 99.99/0.01; flow rate = 0.6 mL/min; detection wave length = 210 nm; T_R = 11.2 (major), 12.5 (minor) min]: $[\alpha]_D^{RT} = -85$ (c 3.2, CHCl_3). ^1H NMR (400.13 MHz, CDCl_3) δ 7.28–7.37 (m, 4H), 7.20–7.25 (m, 1H), 6.04 (ddd, J = 17.2, 10.0, 8.8 Hz, 1H), 5.20 (dd, J = 17.2, 1.2 Hz, 1H), 5.00 (dd, J = 10.0, 1.2 Hz, 1H), 3.58 (d, J = 8.8 Hz, 1H),

2.45–2.54 (m, 2H), 2.33–2.42 (m, 2H), 1.76 (m, 4H). ^{13}C NMR (100.59 MHz, CDCl_3) δ 142.73, 141.02, 128.48, 127.57, 127.12, 115.09, 75.20, 52.97, 23.27.

1-(1-Phenyl-2-propenyl)piperidine⁷ (Table 2, entry 5): The general procedure was followed with piperidine (**2f**, 114 mg, 1.33 mmol) and **1a** (194 mg, 1.01 mmol). The reaction was conducted at room temperature for 10 h. ^1H NMR analysis of the crude mixture indicated the ratio of regioisomers **3/4** to be 97/3. The mixture was purified by flash column chromatography on silica gel (2.5% ethyl acetate in hexane) to give the title compound (185 mg, 91%). HPLC analysis indicated that the enantiomeric excess of product was 96% [Daicel CHIRALCEL OJ (0.46 cm x 25 cm); hexane/2-propanol/diethylamine = 99.97/0.02/0.01; flow rate = 0.6 mL/min; detection wave length = 210 nm; T_R = 9.3 (minor), 13.1 (major) min]: $[\alpha]_D^{RT} = -99$ (*c* 3.2, CHCl_3). ^1H NMR (400.13 MHz, CDCl_3) δ 7.28–7.35 (m, 4H), 7.20–7.24 (m, 1H), 5.94 (ddd, J = 17.2, 10.4, 8.5 Hz, 1H), 5.18 (dd, J = 17.2, 1.6 Hz, 1H), 5.07 (dd, J = 10.4, 1.6 Hz, 1H), 3.65 (d, J = 8.5 Hz, 1H), 2.35–2.48 (m, 2H), 2.22–2.34 (m, 2H), 1.50–1.59 (m, 4H), 1.36–1.45 (m, 2H). ^{13}C NMR (125.77 MHz, CDCl_3) δ 142.41, 140.39, 128.34, 127.95, 126.87, 115.82, 75.42, 52.46, 26.15, 24.65.

1-(1-Phenyl-2-propenyl)morpholine⁸ (Table 2, entry 6): The general procedure was followed with morpholine (**2g**, 113 mg, 1.30 mmol) and **1a** (187 mg, 0.974 mmol). The reaction was conducted at room temperature for 24 h. ^1H NMR analysis of the crude mixture indicated the ratio of regioisomers **3/4** to be 99/1. The mixture was purified by flash column chromatography on silica gel (2.5% ethyl acetate in hexane) to give the title compound (183 mg, 92%). HPLC analysis indicated that the enantiomeric excess of product was 97% [Daicel CHIRALCEL OJ (0.46 cm x 25 cm); hexane/2-propanol/diethylamine = 98.99/1/0.01; flow rate = 0.5 mL/min; detection wave length = 210 nm; T_R = 12.4 (minor), 13.7 (major) min]: $[\alpha]_D^{RT} = -98$ (*c* 5.2, CHCl_3). ^1H NMR (400.13 MHz, CDCl_3) δ 7.29–7.36 (m, 4H), 7.22–7.26 (m, 1H), 5.90 (ddd, J = 17.2, 10.0, 8.8 Hz, 1H), 5.23 (dd, J = 17.2, 1.6 Hz, 1H), 5.10 (dd, J = 10.0, 1.6 Hz, 1H), 3.69 (t, J = 4.0 Hz, 4H), 3.62 (d, J = 8.8 Hz, 1H), 2.43–2.55 (m, 2H), 2.29–2.37 (m, 2H). ^{13}C NMR (100.59 MHz, CDCl_3) δ 141.54, 139.70, 128.57, 127.92, 127.24, 116.64, 75.51, 67.12, 51.96.

(1-Phenyl-2-propenyl)diethylamine³ (Table 2, entry 7): The general procedure was followed with diethylamine (**2h**, 91.1 mg, 1.25 mmol) and **1a** (193 mg, 1.01 mmol). The reaction was conducted at 50 °C for 16 h. ^1H NMR analysis of the crude mixture indicated the ratio of regioisomer **3/4** to be 98/2. The mixture was purified by flash column chromatography on silica gel (2.5% ethyl acetate in hexane) to give the title compound (158 mg, 83%). HPLC analysis indicated that the enantiomeric excess of product was 97% [Daicel CHIRALCEL OJ (0.46 cm x 25 cm); hexane/diethylamine = 99.99/0.01; flow rate = 0.4 mL/min; detection wave length = 210 nm; T_R = 12.6 (minor), 13.6 (major) min]: $[\alpha]_D^{RT} = -106$ (*c* 3.1, CHCl_3). ^1H NMR (400.13 MHz, CDCl_3) δ 7.19–7.40 (m, 5H), 5.95 (ddd, J = 17.2, 10.0, 8.8 Hz, 1H), 5.19 (dd, J = 17.2, 1.6 Hz,

1H), 5.12 (dd, $J = 10.0, 1.6$ Hz, 1H), 4.13 (d, $J = 8.8$ Hz, 1H), 2.49–2.63 (m, 4H), 0.98 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100.59 MHz, CDCl_3) δ 142.96, 139.50, 128.29, 127.82, 126.79, 116.06, 69.46, 42.82, 11.44.

***N*-[1-(4-Methoxyphenyl)-2-propenyl]benzylamine⁹ (Table 2, entry 8):** The general procedure was followed with **2a** (129 mg, 1.20 mmol) and 4-methoxycinnamyl methylcarbonate (**1b**, 222 mg, 1.00 mmol). The reaction was conducted at room temperature for 9 h. ^1H NMR analysis of the crude mixture indicated the ratio of regioisomers **3/4** and diallylation product **5** to be 99/1/0. The mixture was purified by flash column chromatography on silica gel (5% ethyl acetate in hexane) to give the title compound (223 mg, 88%). HPLC analysis indicated that the enantiomeric excess of product was 96% [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2; flow rate = 0.6 mL/min; detection wave length = 230 nm; $T_R = 10.5$ (major), 12.0 (minor) min]: $[\alpha]_D^{RT} = -0.43$ (c 5.1, CHCl_3). ^1H NMR (400.13 MHz, CDCl_3) δ 7.21–7.33 (m, 7H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.93 (ddd, $J = 17.2, 10.0, 7.6$ Hz, 1H), 5.20 (dt, $J = 17.2, 1.6$ Hz, 1H), 5.10 (dt, $J = 10.0, 1.6$ Hz, 1H), 4.18 (d, $J = 7.6$ Hz, 1H), 3.80 (s, 3H), 3.74 (d of AB pattern, $J = 13.4$ Hz, 1H), 3.70 (d of AB pattern, $J = 13.4$ Hz, 1H), 1.59 (brs, 1H). ^{13}C NMR (100.59 MHz, CDCl_3) δ 158.71, 141.12, 140.42, 134.84, 128.35, 128.33, 128.13, 126.85, 114.84, 113.86, 64.39, 55.24, 51.19.

***N*-[1-(4-Nitrophenyl)-2-propenyl]benzylamine (Table 2, entry 9):** The general procedure was followed with $[\text{Ir}(\text{cod})\text{Cl}]_2$ (3.3 mg, 0.0050 mmol), (R_a, R_C, R_C)-**6** (5.4 mg, 0.010 mmol), THF (0.25 mL), **2a** (111 mg, 1.03 mmol) and 4-nitrocinnamyl methylcarbonate (**1c**, 103 mg, 0.43 mmol). The reaction was conducted at room temperature for 12 h. ^1H NMR analysis of the crude mixture indicated the ratio of regioisomers **3/4** and diallylation product **5** to be 83/13/4. The mixture was purified by flash column chromatography on silica gel (50% CH_2Cl_2 in hexane) to give the title compound (78.1 mg, 67%). HPLC analysis indicated that the enantiomeric excess of product was 86% [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol/diethylamine = 99.4/0.5/0.1; flow rate = 0.6 mL/min; detection wave length = 270 nm; $T_R = 45.2$ (minor), 51.1 (major) min]: $[\alpha]_D^{RT} = -12$ (c 0.74, CHCl_3). ^1H NMR (400.13 MHz, CDCl_3) δ 8.19 (d, $J = 7.2$ Hz, 2H), 7.57 (d, $J = 7.2$ Hz, 2H), 7.24–7.35 (m, 5H), 5.87 (ddd, $J = 17.2, 10.4, 7.2$ Hz, 1H), 5.26 (d, $J = 17.2$ Hz, 1H), 5.19 (d, $J = 10.4$ Hz, 1H), 4.33 (d, $J = 7.2$ Hz, 1H), 3.74 (d of AB pattern, $J = 13.2$ Hz, 1H), 3.69 (d of AB pattern, $J = 13.2$, 1H), 1.67 (brs, 1H). ^{13}C NMR (125.77 MHz, CDCl_3) δ 150.35, 147.14, 139.77, 139.51, 128.45, 128.14, 128.06, 127.12, 123.74, 116.56, 64.58, 51.26. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.39; H, 5.99; N, 10.31.

***N*-[1-(2-Methoxyphenyl)-2-propenyl]benzylamine (Table 2, entry 10):** The general procedure was followed with **2a** (139 mg, 1.30 mmol) and 2-methoxycinnamyl methylcarbonate (**1d**, 254 mg, 1.00 mmol). The reaction was conducted at room temperature for 16 h. ^1H NMR

analysis of the crude mixture indicated the ratio of regioisomers **3/4** and diallylation product **5** to be 95/4/1. The mixture was purified by flash column chromatography on silica gel (5% ethyl acetate in hexane) to give the title compound (196 mg, 77%). HPLC analysis indicated that the enantiomeric excess of product was 76% [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol/diethylamine = 99.49/0.5/0.01; flow rate = 0.5 mL/min; detection wave length = 220 nm; T_R = 23.3 (major), 25.1 (minor) min]: $[\alpha]_D^{RT} = -4.6$ (*c* 5.2, CHCl_3). ^1H NMR (400.13 MHz, CDCl_3) δ 7.28–7.36 (m, 5H), 7.21–7.26 (m, 2H), 6.96 (dt, J = 7.6, 0.8 Hz, 1H), 6.88 (dd, J = 8.4, 0.8 Hz, 1H), 6.03 (ddd, J = 17.2, 10.4, 6.8 Hz, 1H), 5.21 (dt, J = 17.2, 1.6 Hz, 1H), 5.11 (ddd, J = 10.4, 1.6, 1.0 Hz, 1H), 4.58 (d, J = 6.8 Hz, 1H), 3.81 (s, 3H), 3.74 (d of AB pattern, J = 13.2, 1H), 3.69 (d of AB pattern, J = 13.2 Hz, 1H), 1.83 (brs, 1H). ^{13}C NMR (100.59 MHz, CDCl_3) δ 157.10, 140.63, 139.90, 130.66, 128.25, 128.22, 128.10, 128.05, 126.74, 120.78, 114.95, 110.71, 59.57, 55.32, 51.47. Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.68; H, 7.55; N, 5.72.

***N*-[1-(2-Furyl)-2-propenyl]benzylamine¹⁰ (Table 2, entry 11):** The general procedure was followed with **2a** (130 mg, 1.21 mmol) and 3-(2-furanyl)-2-propenyl methylcarbonate (**1e**, 182 mg, 1.00 mmol). The reaction was conducted at room temperature for 10 h. ^1H NMR analysis of the crude mixture indicated the ratio of regioisomers **3/4** and diallylation product **5** to be 96/2/2. The mixture was purified by flash column chromatography on silica gel (2.5% ethyl acetate in hexane) to give the title compound (125 mg, 58%). HPLC analysis indicated that the enantiomeric excess of product was 97% [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2; flow rate = 0.5 mL/min; detection wave length = 230 nm; T_R = 10.3 (major), 11.2 (minor) min]: $[\alpha]_D^{RT} = +9.0$ (*c* 3.0, CHCl_3). ^1H NMR (400.13 MHz, CDCl_3) δ 7.38 (dd, J = 1.8, 0.6 Hz, 1H), 7.29–7.34 (m, 4H), 7.22–7.28 (m, 1H), 6.33 (dd, J = 3.2, 1.8 Hz, 1H), 6.20 (d, J = 3.2 Hz, 1H), 5.98 (ddd, J = 17.2, 10.0, 7.2 Hz, 1H), 5.26 (dt, J = 17.2, 1.2 Hz, 1H), 5.23 (dt, J = 10.0, 1.2 Hz, 1H), 4.31 (d, J = 7.2 Hz, 1H), 3.77 (s, 2H), 1.68 (brs, 1H). ^{13}C NMR (125.77 MHz, CDCl_3) δ 155.31, 141.82, 140.01, 137.50, 128.39, 128.22, 126.97, 116.87, 110.08, 106.37, 58.31, 50.98.

***N*-[1-(*n*-Propyl)-2-propenyl]benzylamine⁴ (Table 2, entry 12):** The general procedure was followed with **2a** (145 mg, 1.35 mmol) and 2-hexenyl methylcarbonate (**1f**, 160 mg, 1.01 mmol). The reaction was conducted at room temperature for 10 h. ^1H NMR analysis of the crude mixture indicated the ratio of regioisomers **3/4** and diallylation product **5** to be 88/8/4. The mixture was purified by flash column chromatography on silica gel (2.5% ethyl acetate in hexane) to give the title compound (127 mg, 66%). HPLC analysis indicated that the enantiomeric excess of product was 95% [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol/diethylamine = 99.49/0.5/0.01; flow rate = 0.6 mL/min; detection wave length = 210 nm; T_R = 8.9 (major), 11.6 (minor) min]: $[\alpha]_D^{RT} = +1.1$ (*c* 5.1, CHCl_3). ^1H NMR

(400.13 MHz, CDCl₃) 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). ¹³C NMR (125.77 MHz, CDCl₃) δ 141.37, 140.72, 128.34, 128.16, 126.76, 115.92, 61.00, 51.22, 37.93, 19.08, 14.06.

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