**A Simple Iridium Catalyst with a Single Resolved Stereocenter
for Enantioselective Allylic Amination Deduced from
Mechanistic Studies**

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. $[\text{Ir}(\text{COD})\text{Cl}]_2$, $\text{O},\text{O}'\text{-(R)}\text{-(1,1'-Dinaphthyl-2,2'-diyl)-N,N'-di-(R,R)-phenylethylphosphoramidite}$,^{1,2} and $\text{O},\text{O}'\text{-(R)}\text{-(1,1'-Dinaphthyl-2,2'-diyl)-N,N'-di-(R,R)-naphthylethylphosphoramidite}$ ^{1,3,4} 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.

General Procedures for the Enantioselective Allylic Amination.

Catalyst activation with propylamine. $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.020 mmol), phosphoramidite ligand (0.040 mmol) were diluted in 0.2 mL of THF and 0.2 mL propylamine and heated at 50 °C for 20 min. After this time, all volatile materials were evaporated. The yellow solid was diluted in 1.0 mL of THF to generate a stock solution of the activated catalyst.

Catalytic Reaction. 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.

Yields and selectivities from reactions of diastereomeric versions of L6.

Amination reaction with (*R_aR_c*)-L6: The general procedure was followed with cinnamyl methylcarbonate (0.179 g, 0.93 mmol) and 4-methoxybenzylamine (0.173 mL, 1.30 mmol). The reaction was conducted at room temperature for 1.5 h. 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 give the title compound (0.245 g, 98%). 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 = 0.5 mL/min; detection wavelength = 230 nm; TR = 26.3 min (major), 29.3 min (minor)].

Amination reaction with (*S_aR_c*)-L6: The general procedure was followed with cinnamyl methylcarbonate (0.179 g, 0.93 mmol) and 4-methoxybenzylamine (0.173 mL, 1.30 mmol). GC analysis of the reaction mixture after 14 h showed that the conversion was ~50%. All solvents were evaporated, and the crude mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1). HPLC analysis of the allylic amine product indicated that the enantiomeric excess was 59% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.75/0.25; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 26.3 min (minor), 29.3 min (major)].

Amination reaction with (*R_aS_c*)-L6: The general procedure was followed with cinnamyl methylcarbonate (0.190 g, 0.99 mmol) and 4-methoxybenzylamine (0.175 mL, 1.30 mmol). GC analysis of the reactions mixture after 60 h showed that the conversion was about 70%. All solvents were evaporated, and the crude mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1) to get the product. HPLC analysis indicated that the enantiomeric excess of the product was 64% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.75/0.25; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 26.3 min (minor), 29.3 min (major)].

Amination reaction with (*rac_aR_c*)-L6: The general procedure was followed with cinnamyl methylcarbonate (0.170 g, 0.93 mmol) and 4-methoxybenzylamine (0.175 mL, 1.30 mmol). The reaction was conducted at room temperature for 2.0 h. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1) to give the title compound (0.211 g, 90%).

HPLC analysis indicated that the enantiomeric excess of the product was 91% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.75/0.25; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 26.3 min (major), 29.3 min (minor)].

Amination reaction with (*R_wrac*)-L6: The general procedure was followed with cinnamyl methylcarbonate (0.202 g, 1.05 mmol) and 4-methoxy benzylamine (0.175 mL, 1.30 mmol). The reaction was conducted at room temperature for 1.5 h. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1) to give the title compound (0.226 g, 85%). HPLC analysis indicated that the enantiomeric excess of the product was 81% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.75/0.25; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 26.3 min (major), 29.3 min (minor)].

Relative rates of reaction of catalysts derived from diastereomeric ligands.

Amination catalyzed by complexes of (*R_wR_c*)-L6 (Figure 4). [Ir(COD)Cl]₂ (13.6 mg, 0.020 mmol) and the phosphoramidite ligand (*R_wR_c*)-L6 (23.3 mg, 0.039 mmol) were dissolved in 0.2 mL of THF and 0.2 mL propylamine. The resulting solution was heated at 50 °C for 20 min. After this time, all volatile materials were evaporated, and the residue dried for 5 h under vacuum. The yellow solid was dissolved in 1.0 mL of THF-*d*₈. To 0.5 ml of this solution was added mesitylene (16.9 mg, 0.14 mmol) as internal standard and cinnamyl methylcarbonate (0.197 g, 1.03 mmol). Aniline (0.120 ml, 1.31 mmol) was then added, at which point the sample was placed in the NMR spectrometer probe that had been equilibrated at 25 °C. The reaction was monitored by ¹H-NMR spectroscopy using an automated data acquisition program.

Amination with (*S_wR_c*)-L6 (Figure 4). [Ir(COD)Cl]₂ (6.7 mg, 0.010 mmol) and phosphoramidite ligand (*S_wR_c*)-L6 (12.1 mg, 0.020 mmol) were dissolved in 0.2 mL of THF and 0.2 mL propylamine. The resulting solution was heated at 50 °C for 20 min. After this time, all volatile materials were evaporated, and the residue was dried for 5 h under vacuum. The yellow solid was dissolved in 0.5 mL of THF-*d*₈. To this solution was added mesitylene (16.9 mg, 0.14 mmol) as an internal standard and cinnamyl methylcarbonate (0.193 g, 1.01 mmol). Aniline (0.120 ml, 1.31 mmol) was then added, at which point the sample was placed in the NMR

spectrometer probe that had been equilibrated at 25 °C. The reaction was monitored by ^1H -NMR spectroscopy using an automated data acquisition program.

Amination with (*rac*,*R*_c)-L6 (Figure 4). $[\text{Ir}(\text{COD})\text{Cl}]_2$ (6.7 mg, 0.010 mmol) and phosphoramidite ligand (*rac*,*R*_c)-L6 (12.1 mg, 0.020 mmol) were dissolved in 0.2 mL of THF and 0.2 mL propylamine. The resulting solution was heated at 50 °C for 20 min. After this time, all volatile materials were evaporated, and the residue was dried for 5 h under vacuum. The yellow solid was dissolved in 0.5 mL of THF-*d*₈. To this solution was added mesitylene (15.1 mg, 0.13 mmol) as an internal standard and cinnamyl methylcarbonate (0.191 g, 1.01 mmol). Aniline (0.120 mL, 1.31 mmol) was then added, at which point the sample was placed in the NMR spectrometer probe that had been equilibrated at 25 °C. The reaction was monitored by ^1H -NMR spectroscopy using an automated data acquisition program.

Relative rates of the Cyclometallation.

Rate of cyclometalation of $[(\text{COD})\text{IrClL6}]$ derived from (*R*,*R*_c)-L6 (Figure 5). $[(\text{COD})\text{IrCl}]_2$ (40 mg, 5.9×10^{-5} mol) and (*R*,*R*_c)-L6 (71.5 mg, 1.18×10^{-4} mol) were dissolved in 0.1 mL propyl amine and 0.3 mL THF. The resulting solution was transferred into an NMR tube, and the tube was placed in the NMR spectrometer probe that had been equilibrated at 25 °C. The reaction was monitored by ^{31}P -NMR spectroscopy using an automated data acquisition program.

Rate of cyclometalation of $[(\text{COD})\text{IrClL6}]$ derived from (*S*,*R*_c)-L6 (Figure 5). $[(\text{COD})\text{IrCl}]_2$ (40 mg, 5.9×10^{-5} mol) and (*S*,*R*_c)-L6 (71.5 mg, 1.18×10^{-4} mol) were dissolved in 0.1 mL propyl amine and 0.3 mL THF. The resulting solution was transferred into an NMR tube, and the tube was placed in the NMR spectrometer probe that had been equilibrated at 25 °C. The reaction was monitored by ^{31}P -NMR spectroscopy using an automated data acquisition program.

Allylic Alkylation conducted with O,O'-(*R*)-(1,1'-Dinaphthyl-2,2'-diyl)-N-cylcododecyl-N'-(*R*)-phenylethylphosphoramidite (L6) (Table 2)

***N*-(1-Phenyl-2-propenyl)benzylamine: (entry 1)⁵** The general procedure was followed with cinnamyl methylcarbonate (0.186 g, 0.97 mmol) and benzylamine (0.130 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 (0.201 g, 93%). 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 = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 11.9 (major), 13.3 (minor) min]. ^1H NMR (500.13 MHz, CDCl_3) 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). ^{13}C NMR (125.7 MHz, CDCl_3) 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.

1-Phenyl-*N*-(thiophen-2-ylmethyl)prop-2-en-1-amine. (entry 2) The general procedure was followed with cinnamyl methylcarbonate (0.192 g, 1.00 mmol) and thiophenemethylamine

(0.138 mL, 1.34 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 give the title compound (0.178 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 = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 11.9 (major), 11.3 (minor) min]. ^1H NMR (500.13 MHz, CDCl_3) δ 7.41–7.33 (m, 5H), 7.32–7.26 (m, 1H), 6.34 (dd, J = 3.2, 1.9 Hz, 1H), 6.16 (d, J = 3.2, 1H), 5.96 (ddd, J = 17.1, 10.1, 7.1 Hz, 1H), 5.25 (dt, J = 17.1, 1.24 Hz, 1H), 5.15 (dq, J = 10.4, 1.2, 0.7 Hz, 1H), 4.22 (d, J = 7.3 Hz, 1H), 3.75 (s, 2H), 1.79 (brs, 1H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 153.8, 142.3, 141.7, 140.6, 128.4, 127.3, 127.2, 115.3, 110.0, 106.9, 64.7, 43.6. Anal. Calcd. for $\text{C}_{14}\text{H}_{15}\text{NS}$: C, 73.32; H, 6.59; N, 6.11; S, 13.98 Found: C, 73.02; H, 6.36; N, 5.88.

***N*-(Furan-2-ylmethyl)-1-phenylprop-2-en-1-amine. (entry 3)** The general procedure was followed with cinnamyl methylcarbonate (0.188 g, 0.98 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 96/4. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1) to give the title compound (0.179 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 = 11.3 (major), 11.9 (minor) min]. ^1H NMR (500.13 MHz, CDCl_3) δ 7.41–7.31 (m, 5H), 7.30–7.26 (m, 2H), 6.33 (m, 1H), 6.17 (m, 1H), 5.96 (ddd, J = 17.2, 10.4, 7.3 Hz, 1H), 5.25 (dm, J = 17.2, 1H), 5.15 (dm, J = 10.2, 1H), 4.22 (d, J = 7.0 Hz, 2H), 3.75 (s, 2H), 2.20 (brs, 1H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 153.7, 142.2, 141.6, 140.5, 128.4, 127.3, 127.2, 115.3, 106.9, 64.6, 43.5. Anal. Calcd. for $\text{C}_{14}\text{H}_{15}\text{NO}$: C, 78.84; H, 7.09; N, 6.57; O, 7.50 Found: C, 78.60; H, 6.86; N, 6.57.

(1-Phenyl-2-propenyl)diethylamine. (entry 4)⁵ The general procedure was followed with cinnamyl methylcarbonate (0.204 g, 1.06 mmol) and diethylamine (0.134 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 98/2. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1 to 3:1) to give the title compound (0.166 g, 83%). HPLC analysis indicated that the enantiomeric excess of the product was 98% [Diacel CHIRALCEL OJ (0.46 cm x 25 cm); hexanes/diethylamine = 99.99/0.01; flow rate = 0.4 mL/min; detection wavelength = 210 nm; TR = 12.6 (minor), 13.6 (major) min]. ^1H NMR (500.13 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 (125.7 MHz, CDCl_3) δ 142.96, 139.50, 128.29, 127.82, 126.79, 116.06, 69.46, 42.82, 11.44.

(1-Phenyl-2-propenyl)morpholine. (entry 5)⁵ The general procedure was followed with cinnamyl methylcarbonate (0.196 g, 1.02 mmol) and morpholine (0.114 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 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 (0.192 g, 93%). HPLC

analysis indicated that the enantiomeric excess of the product was 96% [Diacel CHIRALCEL OJ (0.46 cm x 25 cm); hexanes/2-propanol/diethylamine = 98.99/1/0.01; flow rate = 0.5 mL/min; detection wavelength = 210 nm; TR = 12.4 (minor), 13.7 (major) min]. ^1H NMR (500.13 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 (125.7 MHz, CDCl_3) δ 141.54, 139.70, 128.57, 127.92, 127.24, 116.64, 75.51, 67.12, 51.96.

***N*-Phenyl-1-phenyl-2-propenylamine. (entry 6)**⁵ The general procedure was followed with cinnamyl methylcarbonate (0.205 g, 1.06 mmol) and aniline (0.118 mL, 1.24 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 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 (0.205 g, 92%). HPLC analysis indicated that the enantiomeric excess of the product was 97% [Diacel CHIRALCEL ODH (0.46 cm x 25 cm); hexanes/2-propanol = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 22.3 (major), 21.2 (minor) min]. ^1H NMR (500.13 MHz, CDCl_3) δ 7.44–7.24 (m, 5H), 7.20–7.10 (m, 2H), 6.69 (t, J = 7.2 Hz, 1H), 6.60 (d, J = 8.0 Hz, 2H), 6.04 (ddd, J = 16.8, 10.4, 6.4 Hz, 1H), 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 (125.7 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

4-(Methylthio)-*N*-(1-phenylallyl)benzenamine. (entry 7) The general procedure was followed with cinnamyl methylcarbonate (0.201 g, 1.05 mmol) and aniline (0.159 mL, 1.56 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 98/2. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1 to 5:1) to give the title compound (0.251 g, 94%). HPLC analysis indicated that the enantiomeric excess of the product was 97% [Diacel CHIRALCEL ODH (0.46 cm x 25 cm); hexanes/2-propanol = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 254 nm; TR = 23.7 (major), 30.2 (minor) min]. ^1H NMR

(500.13 MHz, CDCl_3) δ 7.42–7.27 (m, 6H), 7.19 (d, J = 8.9 Hz, 2H), 6.58 (d, J = 8.6 Hz, 2H), 6.01 (ddd, J = 17.1, 10.5, 5.9 Hz, 1H), 5.32–5.24 (m, 2H), 4.92 (d, J = 5.7 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 145.7, 141.3, 138.6, 130.9, 128.5, 127.3, 126.9, 124.3, 115.9, 114.0, 60.5, 18.6. Anal. Calcd. for $\text{C}_{16}\text{H}_{17}\text{NS}$: C, 75.25; H, 6.71; N, 5.48; S, 12.56. Found: C, 75.56; H, 6.95; N, 5.32.

***N*-(hex-1-en-3-yl)benzenamine. (entry 8)**⁶ The general procedure was followed with the methylcarbonate derived from (*E*)-2-hexen-1-ol (0.164 g, 1.04 mmol) and aniline (0.118 mL, 1.30 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 98/2. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1 to 5:1) to give the title compound (0.146 g, 80%). HPLC analysis indicated that the enantiomeric excess of the product was 97% [Diacel CHIRALCEL ODH (0.46 cm x 25 cm); hexanes/2-propanol = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 23.7 (major), 30.2 (minor) min]. ^1H NMR (400.13 MHz, CDCl_3) 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, 1H), 3.85 (q, J = 6.4 Hz, 1H), 3.65 (br s, 1H), 1.65–1.55 (m, 2H), 1.53–1.43 (m, 2H), 0.99 (d, J = 7.4 Hz, 3H). ^{13}C NMR (100.59 MHz, CDCl_3) δ 147.6, 140.1, 129.1, 117.0, 114.9, 113.2, 55.6, 38.0, 19.1, 14.0.

***N*-(hex-1-ene-3-yl)benzylamine. (entry 9)**⁵ The general procedure was followed with the methylcarbonate derived from (*E*)-2-hexen-1-ol (0.164 g, 1.04 mmol) and benzylamine (0.131 mL, 1.20 mmol). The reaction was conducted at room temperature for 5 h. ^1H

NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 96/4. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1 to 5:1) to give the title compound (0.146 g, 76%). HPLC analysis indicated that the enantiomeric excess of the product was 96% [Diacel CHIRALCEL ODH (0.46 cm x 25 cm); hexanes/2-propanol/diethylamine = 99.74/0.25/0.01; flow rate = 0.6 mL/min; detection wavelength = 210 nm; TR = 12.3 (major), 20.9 (minor) min]. ^1H NMR (400.13 MHz, CDCl_3) δ 7.32–7.22 (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), 1.52-1.25 (m, 5H), 0.89 (t, J = 7.2 Hz 3H). ^{13}C NMR (125.77 MHz, CDCl_3) δ 141.4, 140.7, 128.3, 128.2, 126.8, 115.9, 61.0, 51.2, 37.9, 19.1, 14.0.

Allylic Alkylation conducted with O,O'-(1,1'-phenyl-2,2'-diyl)-N-cylcododecyl-N'-(R)-phenylethylphosphoramidite (L17) (Table 3). For data on characterization and separation of enantiomers, see the information for entries of Table 2.

***N*-(1-Phenyl-2-propenyl)benzylamine: (entry 1)**⁵ The general procedure was followed with cinnamyl methylcarbonate (0.186 g, 0.97 mmol) and benzylamine (0.130 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 98/2. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1) to give the title compound (0.186 g, 86%). HPLC analysis indicated that the enantiomeric excess of the product was 94%.

***1*-Phenyl-*N*-(thiophen-2-ylmethyl)prop-2-en-1-amine. (entry 2)** The general procedure was followed with cinnamyl methylcarbonate (0.192 g, 1.00 mmol) and thiophenemethylamine (0.138 mL, 1.34 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 give the title compound (0.189 g, 83%). HPLC analysis indicated that the enantiomeric excess of the product was 94%.

***N*-(Furan-2-ylmethyl)-1-phenylprop-2-en-1-amine. (entry 3)** The general procedure was followed with cinnamyl methylcarbonate (0.188 g, 0.98 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 99/1. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1) to give the title

compound (0.175 g, 84%). HPLC analysis indicated that the enantiomeric excess of the product was 93%.

(1-Phenyl-2-propenyl)diethylamine. (entry 4) The general procedure was followed with cinnamyl methylcarbonate (0.204 g, 1.06 mmol) and diethylamine (0.134 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 98/2. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1 to 3:1) to give the title compound (0.146 g, 72%). HPLC analysis indicated that the enantiomeric excess of the product was 97%.

(1-Phenyl-2-propenyl)morpholine. (entry 5) The general procedure was followed with cinnamyl methylcarbonate (0.196 g, 1.02 mmol) and morpholine (0.114 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 98/2. The mixture was purified by flash column chromatography on silica gel (hexanes/ether 10:1 to 5:1) to give the title compound (0.175 g, 85%). HPLC analysis indicated that the enantiomeric excess of the product was 95%.

N-Phenyl-1-phenyl-2-propenylamine. (entry 6) The general procedure was followed with cinnamyl methylcarbonate (0.205 g, 1.06 mmol) and aniline (0.118 mL, 1.24 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 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 (0.207 g, 93%). HPLC analysis indicated that the enantiomeric excess of the product was 94%.

4-(Methylthio)-N-(1-phenylallyl)benzenamine. (entry 7) The general procedure was followed with cinnamyl methylcarbonate (0.201 g, 1.05 mmol) and aniline (0.159 mL, 1.56 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 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 (0.216 g, 81%). HPLC analysis indicated that the enantiomeric excess of the product was 94%.

***N*-(hex-1-en-3-yl)benzenamine. (entry 8)** The general procedure was followed with the methylcarbonate derived from (*E*)-2-hexen-1-ol (0.164 g, 1.04 mmol) and aniline (0.118 mL, 1.30 mmol). The reaction was conducted at room temperature for 5 h. 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 (0.137 g, 75%). HPLC analysis indicated that the enantiomeric excess of the product was 95%.

***N*-(hex-1-ene-3-yl)benzylamine. (entry 9)** The general procedure was followed with the methylcarbonate derived from (*E*)-2-hexen-1-ol (0.164 g, 1.04 mmol) and benzylamine (0.131 mL, 1.20 mmol). The reaction was conducted at room temperature for 5 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 5:1) to give the title compound (0.138 g, 72%). HPLC analysis indicated that the enantiomeric excess of the product was 94%.

Preparation of *C*₁-symmetric phosphoramidites

General procedure. The procedure is based on the procedure of Alexakis.² To a solution of PCl₃ (3.0 mmol) in THF (2 ml) at 0 °C were added 5 ml of triethylamine (3.5 mmol) and a solution of the secondary chiral amine (3.0 mmol) in THF (3 ml). This suspension was stirred at RT for 3 h and cooled to 0 °C. A solution of BINOL (3.0 mmol) in 6 ml THF was added, and the reaction mixture stirred at room temperature for 18 h. The reaction was diluted with ethyl acetate and filtered through Celite. After removal of the solvent, the resulting white foam was purified by column chromatography (hexanes/ether = 10:1). ¹H NMR (500.13 MHz, CDCl₃) δ 7.97 (d, *J* = 8.5 Hz,

1H), 7.91 (d, $J = 8.2$ Hz, 1H), 7.85 (d, $J = 8.2$ Hz, 1H), 7.76 (d, $J = 8.5$ Hz, 1H), 7.58 (d, $J = 7.5$ Hz, 1H), 7.53 (d, $J = 8.8$ Hz, 1H), 7.43-7.20 (m, 11 H), 4.53 (m, 1H), 2.73 (m, 1H), 1.83 (m, 1H), 1.68 (d, $J = 6.9$ Hz, 3H), 1.60-1.20 (m, 6H), 0.90 (m, 1H), 0.77 (m, 1H), 0.52 (m, 1H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 150.43, 150.35, 149.94, 145.5, 132.8 (d, $J_{P-C} = 1.5$ Hz, 1C), 132.6 (d, $J_{P-C} = 1.5$ Hz, 1C), 131.2, 130.3, 130.2, 129.4, 128.2, 128.1, 128.05, 127.04, 127.01, 126.5, 125.9, 125.8, 124.6, 124.3, 124.1, 124.0, 122.4 (d, $J_{P-C} = 2.5$ Hz, 1C), 122.0, 121.6 d, ($J_{P-C} = 2.3$ Hz, 1C), 55.5 (d, $J_{P-C} = 4.6$ Hz, 1C), 53.8, 53.6, 33.8 (d, $J_{P-C} = 5.5$ Hz, 1C), 26.1, 25.3, 24.5, 24.4. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 151.7 (s). $[\alpha]_{\text{D}}^{25} = -178.4$ (c 0.790, CHCl_3). Anal. Calcd. for $\text{C}_{34}\text{H}_{32}\text{NO}_2\text{P}$: C, 78.90; H, 6.23; N, 2.71; O, 6.18; P, 5.98. Found: C, 78.72; H, 5.98; N, 2.59.

^1H NMR (500.13 MHz, CDCl_3) δ 8.01 (d, $J = 8.9$ Hz, 1H), 7.95 (d, $J = 8.2$ Hz, 1H), 7.88 (d, $J = 8.2$ Hz, 1H), 7.79 (d, $J = 8.9$ Hz, 1H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.58 (d, $J = 8.5$ Hz, 1H), 7.50-7.20 (m, 11 H), 4.57 (m, 1H), 3.00 (m, 1H), 1.98 (m, 1H), 1.79 (m, 1H), 1.72 (d, $J = 7.2$ Hz, 3H), 1.70-1.00 (m, 9H), 0.70 (m, 1H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 150.3, 150.2, 149.9, 132.8 (d, $J_{P-C} = 1.5$ Hz, 1C), 132.6, 131.2 (d, $J_{P-C} = 1.5$ Hz, 1C), 130.4, 130.2, 129.5, 128.2, 128.1, 128.0, 127.0, 126.98, 126.95, 126.5, 125.9, 125.8, 124.6, 124.3, 124.0, 123.9, 122.35, 122.34, 122.0, 121.64, 121.62, 57.3 (d, $J_{P-C} = 4.4$ Hz, 1C), 54.5, 54.3, 37.0, 35.3, 27.2, 26.8, 25.1, 24.9. ^{31}P -NMR (161.9 MHz, CDCl_2) δ 150.7 (s). $[\alpha]_{\text{D}}^{25} = -142.9$ (c 1.055, CHCl_3). Anal. Calcd. for $\text{C}_{34}\text{H}_{32}\text{NO}_2\text{P}$: C, 79.07; H, 6.45; N, 2.63; O, 6.02; P, 5.83. Found: C, 78.82; H, 6.12; N, 2.57.

^1H NMR (500.13 MHz, CDCl_3) δ 8.01 (d, $J = 8.7$ Hz, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.81 (d, $J = 8.9$ Hz, 1H), 7.61 (d, $J = 7.6$ Hz, 1H), 7.58 (d, $J = 8.5$ Hz, 1H), 7.48-7.24 (m, 11 H), 4.52 (m, 1H), 3.19 (m, 1H), 1.93-1.77 (m, 2H), 1.72 (d, $J = 7.0$ Hz, 3H), 1.62-0.86 (m, 10H), 0.60 (m, 1H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 150.31, 150.3, 150.0, 132.83, 132.82, 132.79, 131.25, 130.5, 130.2, 129.7, 128.4, 128.2, 127.9, 127.0, 126.95, 126.91, 126.88, 126.5, 125.9, 125.8, 124.6, 124.3, 123.9, 123.8, 122.4 (d, $J_{P-C} = 2.4$ Hz, 1C), 122.1, 121.7 (d, $J_{P-C} = 2.4$ Hz, 1C), 55.3 (d, $J_{P-C} = 3.6$ Hz, 1C), 54.8, 54.6, 35.95, 35.98, 26.0, 25.7, 25.6, 24.9, 23.7. ^{31}P -NMR (161.9 MHz, CDCl_2) δ

150.9 (s). $[\alpha]_D^{25} = -169.1$ (c 0.725, CHCl_3). Anal. Calcd. for $\text{C}_{36}\text{H}_{36}\text{NO}_2\text{P}$: C, 79.24; H, 6.65; N, 2.57; O, 5.86; P, 5.68. Found: C, 79.14; H, 6.38; N, 2.52.

^1H NMR (500.13 MHz, CDCl_3) δ 7.96 (d, $J = 8.9$ Hz, 1H), 7.89 (d, $J = 8.3$ Hz, 1H), 7.82 (d, $J = 8.3$ Hz, 1H), 7.77 (d, $J = 8.9$ Hz, 1H), 7.57 (d, $J = 7.7$ Hz, 1H), 7.51 (d, $J = 8.5$ Hz, 1H), 7.45-7.15 (m, 11 H), 4.54 (m, 1H), 3.30 (m, 1H), 1.64 (d, $J = 7.0$ Hz, 3H) 1.38-0.60 (m, 21H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 150.2, 150.1, 149.8, 132.9, 132.8 (d, $J_{P-C} = 1.8$ Hz, 1C), 131.3, 130.6, 130.2, 129.9, 128.2, 128.1, 127.9, 127.8, 126.9, 126.7, 125.8, 125.7, 124.6, 124.2, 123.95, 123.91, 122.3, 122.2 (d, $J_{P-C} = 1.9$ Hz, 1C), 121.6, 53.8, 53.7, 50.9 (d, $J_{P-C} = 5.7$ Hz, 1C), 34.6, 32.8, 23.3, 23.2, 22.9, 22.8, 22.7, 22.6 (d, $J_{P-C} = 3.7$ Hz, 1C), 22.1. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 151.6 (s). $[\alpha]_D^{25} = -69.8$ (c 0.895, CHCl_3). Anal. Calcd. for $\text{C}_{40}\text{H}_{44}\text{NO}_2\text{P}$: C, 79.84; H, 7.37; N, 2.33; O, 5.32; P, 5.15. Found: C, 79.90; H, 7.15; N, 2.27.

^1H NMR (500.13 MHz, CDCl_3) δ 8.32 (m, 1H), 8.16 (d, $J = 8.3$ Hz, 1H), 8.02 (d, $J = 8.9$ Hz, 1H), 7.95 (d, $J = 7.8$ Hz, 1H), 7.85 (d, $J = 8.2$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.74 (d, $J = 8.6$ Hz, 1H), 7.70-7.60 (m, 1H), 7.61-7.50 (m, 3H), 7.45-7.34 (m, 4H), 7.30-7.20 (m, 4H), 5.48 (m, 1H), 3.52 (m, 1H), 1.86 (d, $J = 7.2$ Hz, 3H), 1.70-0.60 (m, 18H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 150.3, 150.2, 149.7, 133.8, 132.9, 132.8, 131.3, 130.6, 130.3, 130.2, 129.1, 128.4, 127.9, 127.3, 127.1, 126.9, 126.1, 125.9, 125.8, 125.5, 125.4, 124.6, 124.3, 124.2, 123.9, 123.8, 122.2 (d, $J = 2.38$ Hz, 1C), 121.9, 51.6, 50.8, 50.5, 34.6, 31.95 (d, $J = 2.6$ Hz, 1C), 25.3, 24.9, 24.6, 23.3, 23.0, 22.9, 22.8, 22.7, 21.5. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 151.4 (s). $[\alpha]_D^{25} = -133.3$ (c 0.135, CHCl_3). Anal. Calcd. for $\text{C}_{44}\text{H}_{46}\text{NO}_2\text{P}$: C, 81.08; H, 7.11; N, 2.15; O, 4.91; P, 4.75. Found: C, 80.97; H, 6.97; N, 2.08.

^1H NMR (500.13 MHz, CDCl_3) δ 8.05-7.75 (m, 9H), 7.60-7.50 (m, 3H), 7.45-7.18 (m, 7H), 4.74 (m, 1H), 3.37 (m, 1H), 1.76 (d, $J = 7.1$ Hz, 3H), 1.78-0.60 (m, 22H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 150.2, 150.18, 149.8, 133.3, 132.9, 132.81, 132.80, 132.5, 131.3, 1230.6, 130.2, 130.0,

128.2, 128.0, 127.9, 127.7, 127.5, 127.1, 127.0, 126.7, 126.0, 125.97, 125.9, 125.8, 125.7, 124.6, 124.3, 123.96, 123.93, 122.3, 122.2, 121.6, 54.1, 54.0, 51.1, 51.0, 32.9, 32.7, 24.3, 23.3, 23.2, 22.8, 22.6, 22.5. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 151.3 (s). $[\alpha]_{\text{D}}^{25} = +26.7$ (c 1.050, CHCl_3).

Anal. Calcd. for $\text{C}_{44}\text{H}_{46}\text{NO}_2\text{P}$: C, 81.08; H, 7.11; N, 2.15;

O, 4.91; P, 4.75. Found: C, 80.80; H, 6.86; N, 2.00.

^1H NMR (500.13 MHz, CDCl_3) δ 7.98 (d, $J = 8.6$ Hz, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.85 (d, $J = 7.6$ Hz, 1H), 7.80 (d, $J = 8.9$ Hz, 1H), 7.57-7.49 (m, 3H), 7.43-7.33 (m, 3H), 7.27-7.18 (m, 4H), 7.13-7.06 (m, 2H), 4.54 (m, 1H), 3.30 (m, 1H), 1.74-1.67 (m, 1H), 1.64 (d, $J = 6.96$ Hz, 3H), 1.60-1.51 (m, 2H), 1.37-0.92 (m, 14H), 0.80-0.40 (m, 5H). ^{13}C NMR

(125.7 MHz, CDCl_3) δ 162.7, 160.8, 150.1, 150.05, 149.7, 132.95 (d, $J = 2.0$ Hz, 1C), 132.8, 131.3, 130.6, 130.3, 129.9, 129.5 (d, $J = 2.0$ Hz, 1C), 129.4, 128.2, 128.0, 127.1, 127.02, 125.9, 125.8, 124.6, 124.3, 123.9, 123.8, 122.14, 122.13 (d, $J = 2.0$ Hz, 1C), 121.6 (d, $J = 3.1$ Hz, 1C), 114.9, 114.8, 53.2, 53.0, 50.9 (d, $J = 6.7$ Hz, 1C), 32.8, 32.7, 24.4, 23.3, 23.2, 22.9, 22.8, 22.6, 22.5, 22.2. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 151.5 (s). $[\alpha]_{\text{D}}^{25} = -92.5$ (c 0.845, CHCl_3). Anal. Calcd. for $\text{C}_{40}\text{H}_{43}\text{FNO}_2\text{P}$: C, 77.52; H, 6.99; F, 3.07; N, 2.26; O, 5.16; P, 5.00. Found: C, 77.31; H, 6.72; N, 2.19.

^1H NMR (500.13 MHz, CDCl_3) δ 8.25 (d, $J = 8.5$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.57 (d, $J = 8.8$ Hz, 1H), 7.48 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.45-7.37 (m, 4H), 7.25-7.22 (m, 4H), 4.98 (m, 1H), 3.50 (m, 1H), 1.72 (m, 1H), 1.48 (m, 2H), 1.40-1.20 (m, 4H), 1.11-0.74 (m, 11H), 0.62

(m, 1H), 0.53 (m, 1H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 149.7, 149.6, 149.4, 143.8, 132.9 (d, $J = 1.5$ Hz, 1C), 132.7 (d, $J = 1.5$ Hz, 1C), 132.0, 131.3, 130.7, 130.5, 130.2, 129.5, 129.4, 129.1, 128.2, 127.9, 127.5, 127.0, 126.8, 125.9, 124.7, 124.5, 123.8, 123.7, 121.9 (d, $J = 2.3$ Hz, 1C), 121.8 (d, $J = 2.3$ Hz, 1C), 121.5, 51.5 (d, $J = 4.6$ Hz, 1C), 51.3, 51.1, 31.8, 27.1, 25.1, 24.7, 23.0,

22.9, 22.8, 22.7, 22.4, 21.5. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 149.2 (s). $[\alpha]_{\text{D}}^{25} = -73.4$ (c 1.030, CHCl_3). Anal. Calcd. for $\text{C}_{40}\text{H}_{42}\text{Cl}_2\text{NO}_2\text{P}$: C, 71.64; H, 6.31; Cl, 10.57; N, 2.09; O, 4.77; P, 4.62. Found: C, 71.82; H, 6.03; N, 1.95.

^1H NMR (500.13 MHz, CDCl_3) δ 8.10 (d, $J = 7.6$ Hz, 1H), 8.00 (d, $J = 8.5$ Hz, 1H), 7.94 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 1H), 7.78 (d, $J = 8.5$ Hz, 1H), 7.45-7.15 (m, 10H), 6.91 (d, $J = 8.2$ Hz, 1H), 5.07 (m, 1H), 3.88 (m, 1H), 3.49 (m, 1H), 1.71 (d, $J = 7.3$ Hz, 3H), 1.50 (m, 2H), 1.40-0.80 (m, 16H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 155.3, 150.2, 150.1, 149.8, 135.6, 132.9,

132.8 (d, $J = 1.6$ Hz, 1C), 131.3, 130.6, 130.2, 130.1, 128.2, 128.0, 127.5, 127.0, 126.9, 125.8, 125.7, 124.5, 124.2, 123.9, 123.8, 122.2 (d, $J = 1.5$ Hz, 1C), 122.0, 121.8 (d, $J = 2.3$ Hz, 1C), 120.5, 110.1, 55.2, 51.2 (d, $J = 3.9$ Hz, 1C), 47.8, 47.6, 31.5, 25.1, 24.8, 23.0, 22.97 (d, $J = 2.2$ Hz, 1C), 22.8, 22.7, 22.5, 21.6. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 151.2 (s). $[\alpha]_{\text{D}, 22}^{25} = -108.1$ (c 1.000, CHCl_3). Anal. Calcd. for $\text{C}_{41}\text{H}_{46}\text{NO}_3\text{P}$: C, 77.94; H, 7.34; N, 2.22; O, 7.60; P, 4.90. Found: C, 77.99; H, 7.60; N, 2.18.

^1H NMR (500.13 MHz, CDCl_3) δ 7.53 (m, 4H), 7.44-7.20 (m, 9H), 4.82 (m, 1H), 3.19 (m, 1H), 1.89 (m, 2H), 1.71-1.63 (m, 1H), 1.59 (d, $J = 6.87$, 3H), 1.49 (m, 17H), 0.71 (m, 2H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 151.95, 151.89, 151.32, 151.30, 131.26, 131.22, 130.16, 130.13, 129.9, 129.8, 129.1, 128.9 (d, $J = 1.9$ Hz, 1C), 128.4, 127.9, 126.8, 124.45, 124.44, 123.88, 122.44 (d, $J = 1.9$ Hz, 1C), 122.0, 51.8, 50.6, 50.5, 24.1,

23.8, 23.6, 23.5, 23.4, 22.8 (d, $J = 1.9$ Hz, 1C), 22.7, 22.5. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 148.3 (s). $[\alpha]_{\text{D}, 22}^{25} = +111.0$ (c 0.810, CHCl_3). Anal. Calcd. for $\text{C}_{32}\text{H}_{40}\text{NO}_2\text{P}$: C, 76.62; H, 8.04; N, 2.79; O, 6.38; P, 6.17. Found: C, 76.53; H, 7.78; N, 2.81.

^1H NMR (500.13 MHz, CDCl_3) δ 8.03 (d, $J = 8.7$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.67 (d, $J = 8.8$ Hz, 1H), 7.60-7.53 (m, 3H), 7.47-7.21 (m, 10H), 4.82 (m, 1H), 3.16

(d, $J = 20.5$ Hz, 1H), 2.66 (m, 2H), 2.13 (brs, 1H), 1.99 (brs, 1H), 1.85-1.53 (m, 9H), 1.50 (d, $J = 6.8$ Hz, 1H), 1.40 (m, 1H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 151.3, 151.2, 149.8, 142.4, 132.9 (d, $J = 1.6$ Hz, 1C), 132.7, 131.2 (d, $J = 1.6$ Hz, 1C), 130.4 (d, $J = 1.6$ Hz, 1C), 130.1, 129.6, 128.2, 127.97, 127.90, 127.6, 127.2, 127.1, 126.6, 125.9, 125.7, 124.7, 124.3, 124.2, 124.1, 122.5, 122.4, 122.2, 120.5, 120.4, 61.9, 61.8, 53.8, 39.7, 38.9 (d, $J = 1.5$ Hz, 1C), 38.5, 38.4, 35.3, 35.28, 34.26, 34.22, 32.4, 32.1, 31.6, 31.4, 27.5, 27.4, 20.4. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 146.0 (s). $[\alpha]_{\text{D}, 22}^{25} = +26.7$ (c 1.050, CHCl_3). Anal. Calcd. for $\text{C}_{38}\text{H}_{36}\text{NO}_2\text{P}$: C, 80.12; H, 6.37; N, 2.46; O, 5.62; P, 5.44. Found: C, 79.71; H, 6.60; N, 2.46.

 (R_a, S_c)

^1H NMR (500.13 MHz, CDCl_3) δ 8.01 (d, $J = 8.6$ Hz, 1H), 7.94 (d, $J = 8.9$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.61 (d, $J = 8.9$ Hz, 1H), 7.55 (d, $J = 8.9$ Hz, 1H), 7.50-7.35 (m, 5H), 7.33-7.16 (m, 7H), 4.61 (m, 1H), 3.13 (m, 1H), 1.89 (m, 2H), 1.80-1.54 (m, 3H), 1.50 (d, $J = 6.8$ Hz, 3H), 1.40 – 0.94 (m, 2H), 0.73 (m, 1H).

^{13}C NMR (125.7 MHz, CDCl_3) δ 150.0, 149.9, 149.7, 142.3, 132.8, 131.3, 130.4, 130.2, 129.4, 128.3, 128.2, 128.0, 127.7, 127.0, 126.7, 125.9, 125.8, 124.6, 124.3, 124.0, 123.9, 122.5, 122.3 (d, $J = 1.53$ Hz, 1C), 121.7 (d, $J = 2.23$ Hz, 1C), 51.4, 50.4, 50.2, 34.4 (d, $J = 10.7$ Hz, 1C), 31.6, 25.2, 24.3, 24.0, 23.5, 23.2, 22.8, 22.6, 20.7.

^{31}P -NMR (161.9 MHz, CDCl_3) δ 146.9 (s). $[\alpha]_{\text{D}}^{25} = -248.7$ (c 1.245, CHCl_3). Anal. Calcd. for $\text{C}_{41}\text{H}_{46}\text{NO}_3\text{P}$: C, 79.97; H, 6.88; N, 2.39; O, 5.46; P, 5.29. Found: C, 79.71; H, 6.60; N, 2.46.

(*R_a*, *rac_c*)

¹H NMR (500.13 MHz, CDCl₃) δ 8.04-7.76 (m, 6H), 7.63-7.50 (m, 4H), 7.50-7.34 (m, 8H), 7.32-7.15 (m, 16H), 4.59 (m, 2H), 3.34 (m, 1H), 3.15 (m, 1H), 1.88 (m, 2H), 1.77-0.85 (m, 41H), 0.78-0.60 (m, 5H), 0.47 (m, 1H), 0.10 (m, 1H). ¹³C NMR (125.7 MHz, CDCl₃) δ 150.2, 150.1, 150.0, 149.97, 149.8, 149.7, 132.9, 132.8, 131.3, 131.2, 130.5, 130.4, 130.2, 129.9, 129.4, 128.3, 128.2, 128.18, 128.1, 128.0, 127.9, 127.8, 127.0, 126.9, 126.8, 126.7, 125.9, 125.85, 125.85, 125.73, 124.6, 124.5, 124.3, 124.2, 123.96, 123.91, 123.86, 122.5, 122.35, 122.25, 122.1, 121.8, 121.7, 121.5, 53.8, 53.7, 51.4, 50.8, 50.5, 50.2, 32.8, 32.7, 31.6.

25.2, 24.4, 24.3, 24.0, 23.5, 23.3, 23.25, 23.2, 23.1, 22.86, 22.78, 22.72, 22.61, 22.55, 22.52, 22.0. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 151.0 (s), 146.9 (s). $[\alpha]_{\text{D}, 22}^{25} = -152.0$ (c 0.665, CHCl_3). Anal. Calcd. for $\text{C}_{41}\text{H}_{46}\text{NO}_3\text{P}$: C, 79.97; H, 6.88; N, 2.39; O, 5.46; P, 5.29. Found: C, 79.71; H, 6.60; N, 2.46.

(rac_a, R)

^1H NMR (500.13 MHz, CDCl_3) δ 8.04-7.79 (m, 8H), 7.64-7.50 (m, 5H), 7.49-7.34 (m, 10H), 7.33-7.15 (m, 11H), 4.59 (m, 2H), 3.34 (m, 1H), 3.13 (m, 1H), 1.88 (m, 2H), 1.77-1.43 (m, 14H), 1.37-0.89 (m, 32H), 0.79-0.60 (m, 4H), 0.45 (m, 1H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 150.1, 150.08, 149.8, 149.79, 132.9, 132.8, 131.3, 131.3, 130.5, 130.2, 129.9, 129.4, 128.3, 128.2, 128.18, 128.1, 128.0, 127.99, 127.88, 127.80, 127.1, 127.0, 126.8, 126.7, 125.9, 125.89, 125.86, 125.86, 125.76, 124.65,

124.58, 124.34, 124.25, 124.08, 123.92, 122.5, 122.4 (d, $J = 1.9\text{Hz}$, 1C), 122.3, 122.2 (d, $J = 1.9\text{Hz}$, 1C), 121.8 (d, $J = 1.9\text{Hz}$, 1C), 53.8, 53.7, 51.4, 51.0, 50.6, 50.4, 34.7, 32.8, 32.7, 31.6, 25.3, 24.7, 24.5, 24.3, 24.0, 23.6, 23.4, 23.3, 23.2, 23.1, 22.9, 22.8, 22.7, 22.6, 22.5, 22.4. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 151.0 (s), 146.9 (s). $[\alpha]_{\text{D}, 22}^{25} = +116.3$ (c 0.760, CHCl_3). Anal. Calcd. for $\text{C}_{41}\text{H}_{46}\text{NO}_3\text{P}$: C, 79.97; H, 6.88; N, 2.39; O, 5.46; P, 5.29. Found: C, 79.71; H, 6.60; N, 2.46.

(S_a, R)

^1H NMR (500.13 MHz, CDCl_3) δ 8.01 (d, $J = 8.2\text{ Hz}$, 1H), 7.94 (d, $J = 8.7\text{ Hz}$, 1H), 7.90 (d, $J = 8.2\text{ Hz}$, 1H), 7.61 (d, $J = 8.6\text{ Hz}$, 1H), 7.55 (d, $J = 8.6\text{ Hz}$, 1H), 7.60-7.30 (m, 5H), 7.32-7.15 (m, 7H), 4.61 (m, 1H), 3.13 (m, 1H), 1.89 (m, 2H), 1.77-1.54 (m, 3H), 1.50 (d, $J = 7.1\text{Hz}$, 3H), 1.41-0.89 (m, 15H), 0.71 (m, 2H).

^{13}C NMR (125.7 MHz, CDCl_3) δ 150.0, 149.9, 149.7, 132.3, 132.8, 131.3, 130.4, 130.2, 129.4, 128.3, 128.2, 128.0, 127.8,

127.1, 126.7, 125.9, 125.8, 124.6, 124.3, 124.0, 123.9, 122.5, 122.3, 121.7, 51.4, 50.5, 50.3, 34.6, 34.4, 31.6, 24.3, 23.9, 23.5, 23.4, 23.3, 22.8, 22.6, 22.5. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 146.9 (s). $[\alpha]_{\text{D}}^{25} = +330.2$ (c 1.525, CHCl_3). Anal. Calcd. for $\text{C}_{41}\text{H}_{46}\text{NO}_3\text{P}$: C, 79.97; H, 6.88; N, 2.39; O, 5.46; P, 5.29. Found: C, 79.71; H, 6.60; N, 2.46.

^1H NMR (500.13 MHz, CDCl_3) δ 8.10 (d, $J = 8.4$ Hz, 1H), 7.97 (m, 2H), 7.77 (m, 3H), 7.63 (m, 3H), 7.46 (t, $J = 7.3$ Hz, 1H), 7.40-7.10 (m, 14H), 5.32 (m, 1H) 3.40 (m, 1H), 1.57 (m, 3H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 150.0, 149.9, 149.7, 132.3, 132.8, 131.3, 130.4, 130.2, 129.4, 128.3, 128.2, 128.0, 127.8, 127.1, 126.7, 125.9, 125.8, 124.6, 124.3, 124.0, 123.9, 122.5, 122.3, 121.7, 51.4, 50.5, 50.3, 34.6, 34.4, 31.6, 24.3, 23.9, 23.5, 23.4, 23.3, 22.8, 22.6, 22.5. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 145.7 (s). $[\alpha]_{\text{D}}^{25} = +56.2$ (c 0.240, CHCl_3). Anal. Calcd. for $\text{C}_{41}\text{H}_{30}\text{NO}_2\text{P}$: C, 82.12; H, 5.04; N, 2.34; O, 5.34; P, 5.17. Found: C, 81.86; H, 5.05; N, 2.17.

Preparation of $[(\text{COD})\text{Ir}(\kappa^2\text{-L5})(\text{PPh}_3)]$. $[(\text{COD})\text{IrCl}]_2$ (50 mg, 7.5×10^{-5} mol) and **L5** (66 mg,

1.5 $\times 10^{-4}$ mol) were weighed into a screw capped vial. Propylamine (0.5 mL) and THF (2.0 mL) were added to the vial, and the reaction mixture was heated at 50 °C for 1 h. PPh_3 (39 mg, 1.5×10^{-4} mol) was added to the above solution, and the reaction mixture was stirred for 6 h at room temperature. ^{31}P NMR spectra of the crude reaction mixture revealed a 1:0.4 mixture of two isomers, δ 1.91 (d, $J = 37$ Hz), δ 8.08 (d, $J = 40$ Hz), δ 149.5 (d, $J = 40$ Hz), δ 153.4 (d, $J = 37$ Hz). The solvent was evaporated, and the resulting solid was suspended in 1 mL of ether and 2 mL of benzene. The resulting suspension was filtered, and the solvent was evaporated. The resulting residue was washed three times with 3 mL pentane. The residue was dissolved in dichloromethane to make a saturated solution, and the resulting suspension was filtered, layered with 2 mL pentane, and stored in a freezer at -35 °C for 14 h. The solvent was decanted and the precipitate was dried under high vacuum for 2 h to obtain 74 mg (44%) yield of a single isomer of the $[(\text{COD})\text{Ir}(\kappa^2\text{-L5})\text{PMe}_3]$ complex. ^1H NMR (500.13 MHz, CDCl_3) δ 8.10 (d, $J = 8.4$ Hz, 1H), 7.97 (m, 2H), 7.77 (m, 3H), 7.63 (m, 3H), 7.46 (t, $J = 7.3$ Hz, 1H), 7.40-7.10 (m, 14H), 5.32 (m, 1H) 3.40 (m, 1H), 1.57 (m, 3H). ^{13}C NMR (125.7 MHz, CDCl_3) δ 150.0, 149.9, 149.7, 132.3, 132.8, 131.3, 130.4, 130.2, 129.4, 128.3, 128.2, 128.0, 127.8, 127.1, 126.7, 125.9, 125.8, 124.6, 124.3, 124.0, 123.9, 122.5, 122.3, 121.7, 51.4, 50.5, 50.3, 34.6, 34.4, 31.6, 24.3, 23.9, 23.5, 23.4, 23.3, 22.8, 22.6, 22.5. ^{31}P -NMR (161.9 MHz, CDCl_3) δ 149.0 (d, $J = 54$

Hz), δ 3.18 (d, J = 54 Hz). Anal. Calcd. for $C_{41}H_{30}NO_2P$: C, 82.12; H, 5.04; N, 2.34; O, 5.34; P, 5.17. Found: C, 81.86; H, 5.05; N, 2.17.

Preparation of $[(COD)Ir(\kappa^2\text{-L17})(PMe_3)] \cdot [(COD)IrCl]_2$ (100 mg, 1.5×10^{-4} mol) and **L17** (300 mg, 5.9×10^{-4} mol) were weighed into a screw capped vial. Propylamine (1.5 mL) and THF (2.0

mL) were added to the vial, and the reaction mixture was heated at 50 °C for 1 h. PMe_3 (22.7 mg, 3.0×10^{-4} mol) was added to the above solution, and the reaction mixture was stirred for 2 h at room temperature. The solvent was evaporated and the resulting solid was suspended

in 2 mL ether and 4 mL benzene. The resulting suspension was filtered and the solvent was evaporated. The resulting residue was washed three times with 3 mL pentane. The residue was dissolved in toluene to make a saturated solution, and the resulting suspension was filtered, layered with 2 mL pentane, and stored in a freezer at -35 °C for 14 h. The solvent was decanted and the precipitate was dried under high vacuum for 2 h to obtain 160 mg (60%) yield of $[(COD)Ir(\kappa^2\text{-L17})PMe_3]$ complex. 1H NMR (400.13 MHz, C_6D_6) δ 7.78 (d, J = 8.0 Hz, 1H), 7.47 (m, 3H), 7.33 (m, 2H), 7.28 (m, 3H), 7.20-7.04 (m, 4H), 4.88 (d, J = 8.8 Hz, 1H) 4.78 (d, J = 8.4 Hz, 1H), 4.36 (m, 2H), 3.79 (m, 2H), 3.63 (m, 2H), 2.71 (m, 1H), 2.57 (m, 2H), 2.41-2.27 (m, 5H), 2.03-1.93 (m, 4H), 1.68 (m, 2H), 1.53-1.23 (m, 25H). ^{13}C NMR (100.6 MHz, C_6D_6) δ 153.8, 152.0, 151.3, 132.2, 130.9, 130.6, 129.9, 127.6, 126.2, 124.8, 122.7, 122.3, 122.0, 77.5, 71.7, 63.7, 63.2, 55.6, 55.3, 52.5, 51.7, 50.7, 50.2, 36.8, 36.3, 34.8, 34.1, 31.5, 29.0, 25.7, 25.4, 24.5, 24.3, 24.1, 23.7, 23.6, 18.9, 18.8, 18.7, 17.9, 17.6. ^{31}P -NMR (161.9 MHz, C_6D_6) δ 149.7 (d, J = 40 Hz), δ -57.0 (d, J = 41 Hz). Anal. Calcd. for $C_{43}H_{60}NO_2P$: C, 58.88; H, 6.89; N, 1.60. Found: C, 58.96; H, 6.65; N, 1.54.

Variable Temperature NMR data

Figure S1. Variable temperature NMR data of ligand **L17** in THF.

Figure S2. Variable temperature NMR data of $[\text{Ir}(\text{COD})(\kappa^1\text{-L17})\text{Cl}]$ in THF.

Figure S3. Variable temperature NMR data of $[\text{Ir}(\text{COD})(\kappa^2\text{-L17})(\text{PMe}_3)]$ in THF.

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