Sequential Catalytic Isomerization and Allylic Substitution. Conversion of Racemic Branched Allylic Carbonates to Enantioenriched Allylic Substitution Products

Supporting Information

Shashank Shekhar, Brian Trantow, Andreas Leitner and John F. Hartwig*

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

John. Hartwig@yale.edu

Experimental

General: All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. All glassware was oven dried immediately prior to use. THF was degassed by purging with nitrogen for 45 min and dried with a solvent purification system containing a 1 m column containing activated alumina. Isopropylamine was dried over CaH_2 for 12 h at 50° C and distilled under nitrogen. Anhydrous EtOH (99.9 %) and all other reagents were obtained from commercial sources and used without further purification. ^{1}H 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. $[Ir(COD)Cl]_2$, the *O*,*O*'-(*S*)-(1,1'-Dinaphthyl-2,2'-diyl)-*N*,*N*'-di-(*S,S*)-phenylethylphosphoramidite, the *O*,*O*'-(*S*)-(1,1'-Dinaphthyl-2,2'-diyl)-*N*,*N*'-di-(*S,S*)-naphthylethylphosphoramidite, and the *O*,*O*'-(1,1'-Biphenyl-2,2'-diyl)-*N*,*N*'-(*R*)-phenylethylcyclodoceylphosphoramidite were prepared according to published procedures.[1]

Synthesis of allylic carbonates and acetates. All branched allylic carbonates and acetates were prepared by the reaction of the corresponding aldehydes with vinylmagnesium chloride at 0° C in THF to generate the allylic alcohol. The progress of the reaction was monitored by GC-mass spectroscopy. For the synthesis of the carbonates, methyl chloroformate (1.3 equiv) and pyridine (5 equiv) were added to the reaction mixture at 0 °C after complete consumption of aldehyde. For the synthesis of the acetates, acetic anhydride (1.5 equiv) was added to the reaction mixture at 0 °C after complete consumption of aldehyde. The reaction mixtures were stirred for 1 h, at which time conversion of allylic alcohol to allylic carbonate or acetate was complete. The reaction mixtures were washed with 1 N HCl solution utill the pH of the organic layer was 1, and the organic layers were washed with aqueous $NaHCO_3$ solution utill pH of the organic layer was 7. The organic layers were then dried over anhydrous $MgSO_4$, the solvent was evaporated, and the products were purified by column chromatography. The allylic esters **1a-e** were purified by silica gel chromatography and the allylic esters

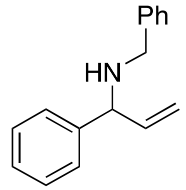
1f-i were purified by chromatography using basic N-H silica gel from Fuji Silysia Chemical Ltd.

General Procedures for the Enantioselective Allylic Substitution Reactions. In a drybox, stock solutions of $Pd(dba)_2$ (8 mM) and PPh_3 (16 mM) were prepared by weighing $Pd(dba)_2$ (4.6 mg, 0.08 μmol) and PPh_3 (4.2 mg, 0.16 μmol) into two vials and adding 1.0 mL THF to each vial. To a reaction vial containing a magnetic stirrer, was added by syringe 0.25-0.50 mL of each stock solution, the appropriate amount of THF to make the final volume of 1 mL, and 1.0 mmol branched allylic ester. The vial was sealed with a cap containing a PTFE septum, and the reaction mixture was removed from the box and stirred at room temperature or 60 °C until the branched carbonate was fully converted to the linear carbonate, as determined by GC.

The Ir-catalyst was prepared by weighing $[Ir(COD)Cl]_2$ (0.015-0.020 mmol) and the phosphoramidite ligand (0.030-0.040 mmol) into a reaction vial and adding 0.2 mL THF and 0.2 mL propylamine. The vial was sealed with a cap containing a PTFE septum. The reaction mixture was removed from the box and was heated at 50 °C for 1 h. The vial was brought back inside the box, and the volatile materials were evaporated. The vial containing the isomerized reaction mixture was also brought back into the box and was filtered through a 10 x 6 mm plug of silica gel (in a 9 mm pipette) into a reaction vial containing the activated Ir-catalyst. The silica gel was washed with 0.2 mL THF, the nucleophile (1.2-2.0 mmol) was added, and the reaction mixture was stirred at room temperature until the linear ester was fully converted to the allylic substitution product, as determined by GC. The ratio of regioisomers (branched to linear b/l) was determined by ^1H NMR spectroscopy of the crude reaction mixture. The crude reaction mixture was purified by flash column chromatography on silica gel (hexanes/ether or hexane/ethyl acetate) to give desired product.

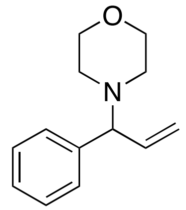
Examples of the enantioselective allylic substitution of branched allylic esters (Table 2).

***N*-(1-phenyl-prop-2-enyl)benzylamine (entry 1).**[2] The general procedure was followed with 0.25 mL of the stock solution of $Pd(dba)_2$, 0.25 mL of the stock solution of PPh_3, **1a** (0.192 g, 1.00 mmol), $[(COD)IrCl]_2$ (0.010 g, 0.015 mmol), **L3** (0.015 g, 0.030 mmol),

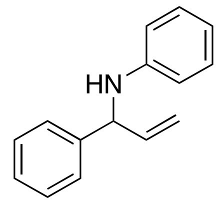


and benzylamine (0.128 g, 1.20 mmol). The isomerization reaction was conducted at room temperature for 4 h, and the allylic substitution was conducted at room temperature for 4 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 98/2. The mixture was purified by flash column chromatography on silica gel (hexanes/ethylacetate 10:1) to give the title compound (0.168 g, 72%). 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 = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 11.9 (major), 13.3 (minor) min]. ^{1}H 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 , *J* = 13.4 Hz, 1H), 3.71 (d , *J* = 13.4 Hz, 1H), 1.64 (brs, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 142.74 (s), 140.90 (s), 140.38 (s), 128.53 (s), 128.37 (s), 128.15, 127.31, 127.21, 126.89, 115.18, 65.09, 51.26.

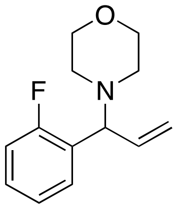
(**1-phenyl)-prop-2-enyl-morpholine (entry 2).**[2] The general procedure was followed with 0.25 mL of the stock solution of $Pd(dba)_2$, 0.25 mL of the stock solution of PPh_3, **1a** (0.192 g, 1.00 mmol), $[(COD)IrCl]_2$ (0.010 g, 0.015 mmol), **L3** (0.015 g, 0.030 mmol), and benzylamine (0.105 g, 1.20 mmol). The isomerization reaction was conducted at room temperature for 4 h, and the allylic substitution was conducted at room temperature for 4 h. ^{1}H 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/ethylacetate 10:1) to give the title compound (0.178 g, 89%). HPLC analysis indicated that the enantiomeric excess of the product was 94% [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]. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.25–7.19 (m, 4H), 7.15–7.11 (m, 1H), 5.81 (ddd, *J* = 17.0, 9.0, 9.0 Hz, 1H), 5.13 (dd, *J* = 17.0, 0.7 Hz, 1H), 5.00 (dd, *J* = 10.0, 1.3 Hz, 1H), 3.59-3.58 (m, 4H), 3.53 (d, *J* = 8.8 Hz, 1H), 2.43–2.55 (m, 2H), 2.29–2.37 (m, 2H). ^{13}C NMR



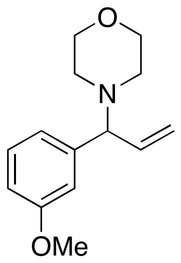
(125.7 MHz, $CDCl_3$) δ 142.05 (s), 140.21 (s), 129.00 (s), 128.39 (s), 127.67 (s), 117.01 (s), 75.88 (s), 67.58 (s), 52.42 (s).



***N*-Phenyl-1-phenyl-prop-2-enylamine (entry 3).**[2] The general procedure was followed with 0.25 mL of the stock solution of $Pd(dba)_2$, 0.25 mL of the stock solution of PPh_3, **1a** (0.192 g, 1.00 mmol), $[(COD)IrCl]_2$ (0.010 g, 0.015 mmol), **L3** (0.015 g, 0.030 mmol), and benzylamine (0.112 g, 1.20 mmol). The isomerization reaction was conducted at room temperature for 4 h, and the allylic substitution was conducted at room temperature for 4 h. ^1H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 98/2. The mixture was purified by flash column chromatography on silica gel (hexanes/ethylacetate 10:0.5) to give the title compound (0.174 g, 83%). HPLC analysis indicated that the enantiomeric excess of the product was 94% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 22.3 (major), 21.2 (minor) min]. ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.52-7.46 (m, 4H), 7.42-7.38 (m, 1H), 7.28-7.25 (m, 2H) 6.84 (t, J = 7.3 Hz, 1H), 6.73 (dd, J = 8.4, 0.8 Hz, 2H), 6.17 (ddd, J = 17.1, 10.3, 5.8 Hz, 1H), 5.41 (dt, J = 17.2, 1.3 Hz, 1 H), 5.36 (dt, J = 10.2, 1.2 Hz, 1 H), 5.07 (d, J = 5.6 Hz, 1 H), 4.15 (brs, 1 H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 147.75 (s), 142.42 (s), 139.46 (s), 129.64 (s), 129.26 (s), 127.89 (s), 127.68 (s), 118.17 (s), 116.56 (s), 114.11 (s), 61.37 (s).

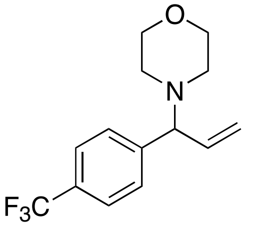


1-(2-Flouro-phenyl)-prop-2-enyl-morpholine (entry 4). The general procedure was followed with 0.25 mL of the stock solution of $Pd(dba)_2$, 0.25 mL of the stock solution of PPh_3, **1b** (0.210 g, 1.00 mmol), $[(COD)IrCl]_2$ (0.013 g, 0.020 mmol), **L2** (0.025 g, 0.040 mmol) or **L3** (0.020 g, 0.040 mmol), and morpholine (0.105 g, 1.20 mmol). The isomerization reaction was conducted at room temperature for 6 h, and the allylic substitution 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 when either **L2** or **L3** was used as ligand. The mixture was purified by flash column chromatography on silica gel (hexanes/ethylacetate 10:0.5) to give the title compound (0.182 g, 82%) when **L2** was used as ligand and (0.140 g, 63%) when **L3** was used as ligand. HPLC analysis indicated that the enantiomeric excess of the product was 82% when either **L2** or **L3** was used as ligand [Diacel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.99/0.1; flow rate = 0.3 mL/min; detection wavelength = 210 nm; TR = 28.7 (major), 33.1 (minor) min]. ^{1}H NMR (499.95 MHz, CDCl$_3$) δ 7.40–7.37 (t, J = 7.4, , 1H), 7.15–7.11 (m, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.97-6.93 (m,1H), 5.80 (ddd, J = 17.4, 7.3, 7.0 Hz, ,1H), 5.22 (d, *J* = 17.0 Hz, 1H), 5.05 (d, *J* = 8.8 Hz, 1H), 4.00 (d, *J* = 8.6 Hz, 1H), 3.61 (t, *J* = 9.2 Hz, 4H), 2.42 (b, 2H), 2.30-2.25 (m, 2H). ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 160.80 (d, *J* = 246 Hz), 138.55 (s), 129.07 (d, *J* = 4.3 Hz), 128.46 (s), 128.14 (d, *J* = 12.9 Hz), 124.20 (d, *J* = 3.4 Hz), 117.14 (s), 115.52 (d, *J* = 22.3 Hz), 67.39 (s), 66.65 (s), 51.86 (s). Anal. Calcd. for $C_{13}H_{16}FNO$: C, 70.56; H, 7.29; N, 6.33; Found: C, 70.65; H, 7.45; N, 6.15.

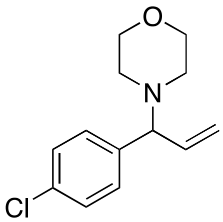


1-(3-methoxy-phenyl)-prop-2-enyl-morpholine (entry 5). The general procedure was followed with 0.25 mL of the stock solution of Pd(dba)$_2$, 0.25 mL of the stock solution of PPh$_3$, **1c** (0.222 g, 1.00 mmol), [(COD)IrCl]$_2$ (0.013 g, 0.020 mmol), **L2** (0.025 g, 0.040 mmol), and morpholine (0.105 g, 1.2 mmol). The isomerization reaction was conducted at room temperature for 4 h, and the allylic substitution was conducted at room temperature for 5 h. ^{1}H 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/ethylacetate 10:1.0) to give the title compound (0.192 g, 82%). HPLC analysis indicated that the enantiomeric excess of the product was 95.5% [Diacel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexanes/2-propanol = 97.5/2.5; flow rate = 0.5 mL/min; detection wavelength = 220 nm; TR = 15.5 (major), 19.2 (minor) min]. ^{1}H NMR (499.95 MHz, C_6D_6) δ 7.22 (b, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12 –7.11(m, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.76 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.89 (ddd, *J* = 17.9, 9.0, 8.9 Hz, 1H), 5.12 (dd, *J*

= 17.1, 1.5 Hz, 1H), 4.98 (dd, *J* = 10.1, 1.7 Hz, 1H), 3.68-3.61 (m, 4H), 3.52 (d, *J* =8.8 Hz, 1H), 3.44 (s, 3H), 2.39 (b, 2H), 2.32-2.27 (m, 2H). ^{13}C NMR (125.7 MHz, C_6D_6) δ 159.22 (s), 142.57 (s), 138.95 (s), 128.44 (s), 118.99 (s), 114.92 (s), 112.67 (s), 111.42 (s), 74.38 (s), 65.86 (s), 53.36 (s), 51.00 (s). Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00; Found: C, 71.74 ; H, 8.28; N, 6.01 .

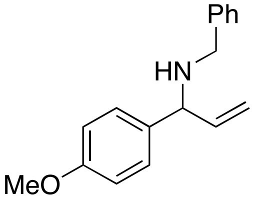


1-(4-trifluoromethyl-phenyl)-prop-2-enyl-morpholine (entry 6). The general procedure was followed with 0.25 mL of the stock solution of Pd(dba)$_2$, 0.25 mL of the stock solution of PPh$_3$, **1d** (0.260 g, 1.00 mmol), [(COD)IrCl]$_2$ (0.013 g, 0.020 mmol), **L2** (0.025 g, 0.040 mmol), and morpholine (0.105 g, 1.20 mmol). The isomerization reaction was conducted at room temperature for 6 h, and the allylic substitution was conducted at room temperature for 5 h. ^{1}H 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/ethylacetate 10:0.1) to give the title compound (0.197 g, 72%). HPLC analysis indicated that the enantiomeric excess of the product was 94% [Diacel CHIRALCEL AD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 220 nm; TR = 17.6 (major), 16.5 (minor) min]. ^{1}H NMR (400.25 MHz, CDCl$_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.69 (ddd, J = 17.9, 8.5, 7.2 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 4.99 (d, *J* = 10.0 Hz, 1H), 3.70-3.66 (m, 4H), 3.46 (d, *J* = 10.1 Hz, 1H), 2.32 (b, 2H), 2.22-2.13 (m, 2H). ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 146.28 (s), 139.28 (s), 130.05 (q, *J* = 97.0 Hz), 128.62 (s), 125.94 (q, *J* = 11.4 Hz), 123.48 (s), 117.92 (s), 75.39 (s), 67.48 (s), 52.28 (s). Anal. Calcd. for $C_{14}H_{16}F_3NO$: C, 61.98; H, 5.94; N, 5.16; Found: C, 62.26; H, 5.98; N, 5.16.

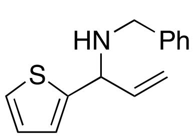


1-(4-chloro-phenyl)-prop-2-enyl-morpholine (entry 7). The general procedure was followed with 0.25 mL of the stock solution of Pd(dba)$_2$, 0.25 mL of the stock solution of PPh$_3$, **1e** (0.226 g, 1.00 mmol), [(COD)IrCl]$_2$ (0.013 g, 0.020 mmol), **L2** (0.025 g, 0.040 mmol), and morpholine (0.105 g, 1.20 mmol). The isomerization reaction was conducted at room temperature for 6 h, and the allylic substitution was conducted at room temperature for 5 h. ^{1}H 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/ethylacetate 10:0.5) to give the title compound (0.194 g, 83%). HPLC analysis indicated that the enantiomeric excess of the product was 96%. After recrystallization from ether a single crop the product was recovered in 52% yield with an enantiomeric excess of 98% [Diacel CHIRALCEL AS-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 220 nm; TR = 14.2 (major), 12.4 (minor) min]. ^{1}H NMR (499.95 MHz, C_6D_6) δ7.24 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 5.74 (ddd, *J* = 18.0, 9.1, 8.9 Hz, 1H), 5.09 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.00 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.53-3.51 (m, 4H), 3.44 (d, *J* = 11.4, 1H), 2.34 (b, 2H), 2.24-2.18 (m, 2H). ^{13}C NMR (125.7 MHz, C_6D_6) δ 140.75 (s), 139.75 (s), 132.84 (s), 129.58 (s), 128.98 (s), 116.86 (s), 74.68 (s), 67.18 (s), 52.14 (s). Anal. Calcd. for $C_{13}H_{16}ClNO$: C, 65.68; H, 6.78; N, 5.89; Found: C, 65.66; H, 6.81; N, 6.64.

1-(4-methoxy-phenyl)-prop-2-enyl-benzylamine (entry 8). The general procedure was followed with 0.25 mL of the stock solution of $Pd(dba)_2$, 0.25 mL of the stock solution of PPh_3, **1f** (0.206 g, 1.00 mmol), $[(COD)IrCl]_2$ (0.013 g, 0.020 mmol), **L1** (0.022 g, 0.040 mmol) or **L2** (0.025 g, 0.040 mmol) or **L3** (0.020 g, 0.040 mmol) and benzylamine (0.210 g, 2.00 mmol). EtOH 0.4 mL was used as a co-solvent. The isomerization reaction was conducted at 60° C for 12 h, and the allylic substitution was conducted at room temperature for 15 h. ^{1}H 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/ethylacetate 10:1.0) to give the title compound (0.190 g, 75%) when **L1** was used as ligand, 0.210 g, (83%) when **L2** was used as ligand, and 0.195 g, (77%) when **L3** was used as ligand. HPLC analysis indicated that the enantiomeric excess of the product was 86.6% when **L1** was used as ligand, 94.4% when **L2** was used as ligand, and 86% when **L3** was used as ligand [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99/1; flow rate = 0.6 mL/min; detection wavelength = 230 nm; TR = 12.7 (minor), 15.8 (major) min]. ^{1}H



NMR (499.95 MHz, C_6D_6) δ 7.27-7.24 (m, 4H), 7.19–7.14 (m, 2H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.88 (ddd, *J* = 17.1, 10.2, 6.9, 1H), 5.12 (dt, *J* =17.1 1.4 Hz, 1H), 4.98 (dt, *J* = 10.1, 1.3 Hz, 1H), 4.08 (d, *J* = 6.9 Hz, 1H), 3.59 (s, 2H), 3.29 (s, 3H). ^{13}C NMR (125.7 MHz, C_6D_6) δ 159.69 (s), 142.87 (s), 141.33 (s), 135.69 (s), 129.27 (s), 128.83 (s), 128.72 (s), 126.99 (s), 114.76 (s), 114.51 (s), 65.08 (s), 55.08 (s), 51.61 (s).



1-(thiophene)-prop-2-enyl-benzylamine (entry 9). The general procedure was followed with 0.25 mL of the stock solution of $Pd(dba)_2$, 0.25 mL of the stock solution of PPh_3, **1g** (0.182 g, 1.00 mmol), $[(COD)IrCl]_2$ (0.013 g, 0.020 mmol), **L3** (0.020 g, 0.040 mmol), and benzylamine (0.210 g, 2.00 mmol). EtOH 0.4 mL was used as a co-solvent. The isomerization reaction was conducted at 60° C for 6 h, and the allylic substitution was conducted at room temperature for 8 h. ^{1}H 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/ethylacetate 10:1.0) to give the title compound (0.180 g, 79%). HPLC analysis indicated that the enantiomeric excess of the product was 93% [Diacel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.75/0.25; flow rate = 0.5 mL/min; detection wavelength = 220 nm; TR = 16.7 (major), 22.8 (minor) min]. ^{1}H NMR (500.13 MHz, C_6D_6) δ 7.27 (d, 2H, *J* = 7.3 Hz), 7.18–7.15 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.9 (dd, *J* = 5.0, 1.1 Hz, 1H), 6.78-6.74 (m, 2H), 5.77 (ddd, *J* = 17.1, 9.8, 7.5 Hz, 1H), 5.03 (d, *J* = 17.0 Hz, 1H), 4.96 (dd, *J* = 10.0, 0.6 Hz, 1H), 4.28 (d, *J* = 7.3 Hz, 1H), 3.61 (s, 2H). ^{13}C NMR (125.7 MHz, C_6D_6) δ 148.36 (s), 141.07 (s), 140.61 (s), 128.65 (s), 128.56 (s), 127.21 (s), 126.54 (s), 124.73 (s), 124.31 (s), 115.82 (s), 60.71 (s), 51.19 (s). Anal. Calcd. for $C_{14}H_{15}NS$: C, 73.32; H, 6.59; N, 6.11; Found: C, 73.32 ; H, 6.63; N, 6.08 .

Sequential reactions of dienyl carbonates.

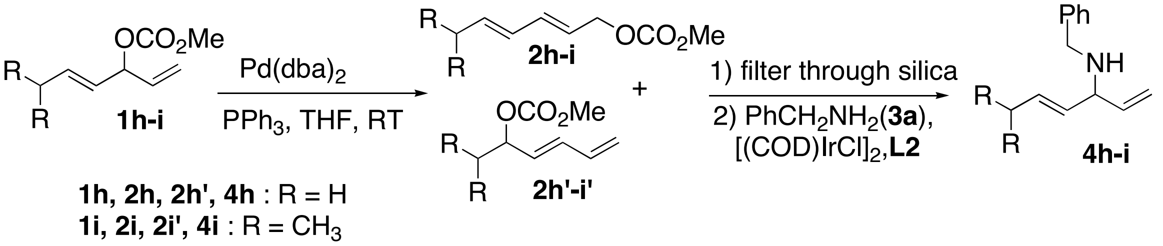
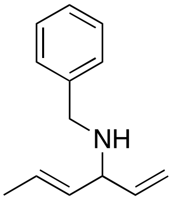


Figure S1. Sequential reaction of dienyl carbonate **1h-I**

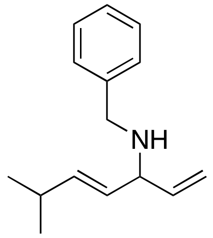
The palladium-catalyzed isomerization of **1h** gave **2h'**, in addition to the expected linear product **2h** (Figure S1). The two linear carbonates **2h** and **2h'** were obtained in 9:1 ratio after 2 h. A decrease in the ratio of **2h** and **2h'** was observed if the isomerization reaction was run for longer times. For example, **2h** and **2h'** were formed in 5:1 ratio after 5 h. Although the Ir-catalyzed amination of both **2h** and **2h'** gave **4h** as the major product, higher ee's were obtained from isomeric mixtures containing larger ratios of **2h** to **2h'** Thus, to obtain **4h** in high enantiomeric excess, the palladium-catalyzed isomerization of **1h** must be run for reaction times that minimize the amount of **2h'**. The isomerization of **1h** for 1.5-2 h, followed by Ir-catalyzed allylic amination, gave the desired product in 57% yield with an enantiomeric excess of 88%.

Palladium-catalyzed isomerization of dienylcarbonate **1i** formed the expected linear product **2i** without significant formation of **2i'**. Subsequent Ir-catalyzed allylic amination of **2i** formed the product in moderate yield and good enantiomeric excess.

Benzyl-(1-vinyl-but-2-enyl)-amine (entry 10). The general procedure was followed with 0.50 mL of the stock solution of Pd(dba)$_2$, 0.50 mL of the stock solution of PPh$_3$, **1h** (0.156 g, 1.00 mmol), [(COD)IrCl]$_2$ (0.013 g, 0.020 mmol), **L2** (0.025 g, 0.040 mmol) or **L3** (0.020 g, 0.040 mmol), and benzylamine (0.112 g, 1.20 mmol). The isomerization reaction was conducted at room temperature for 2 h, and the allylic substitution was conducted at room temperature for 3 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 95/5 when either **L2** or **L3** was used as ligand. The

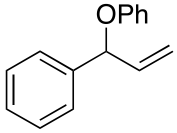


mixture was purified by flash column chromatography on silica gel (hexanes/ethylacetate 10:1-5:1) to give the title compound (0.107 g, 57%) when **L2** was used as ligand and (0.093 g, 50%) when **L3** was used as ligand. HPLC analysis indicated that the enantiomeric excess of the product was 88 % [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 98/2; flow rate = 0.6 mL/min; detection wavelength = 220 nm; TR = 7.4 (minor), 8.6 (major) min]. ^{1}H NMR (500.13 MHz, C_6D_6) δ 7.30 (d, *J* = 4.8 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 5.75 (ddd, *J* = 18.7, 10.0, 3.8 Hz, 1H), 5.45 (dq, *J* = 15.4, 5.8 Hz,1H), 5.35 (ddd, *J* = 15.4, 6.9, 1.3 Hz, 1H), 5.12 (d, *J* = 17.2 Hz, 1H), 4.99 (d, *J* = 17.6, 1H), 3.65 (s, 2H), 3.53 (t, *J* = 6.8 Hz, 1H), 1.43 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (125.7 MHz, C_6D_6) δ 141.77 (s), 141.32 (s), 133.79 (s), 128.90 (s), 128.78 (s), 127.24 (s), 126.57 (s), 114.91 (s), 63.43 (s), 51.52 (s), 18.07 (s).

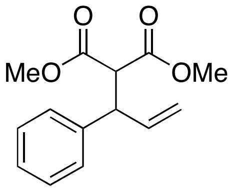


Benzyl-(4-methyl-1-vinyl-pent-2-enyl)-amine (entry 11). The general procedure was followed with 0.38 mL of the stock solution of $Pd(dba)_2$, 0.38 mL of the stock solution of PPh_3 , **1i** (0.184 g, 1.00 mmol), $[(COD)IrCl]_2$ (0.013 g, 0.020 mmol), **L2** (0.025 g, 0.040 mmol), and benzylamine (0.112 g, 1.20 mmol). The isomerization reaction was conducted at room temperature for 12 h, and the allylic substitution was conducted at room temperature for 3 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 94/6. The mixture was purified by flash column chromatography on silica gel (hexanes/ethylacetate 10:0.2) to give the title compound (0.107 g, 70 %). HPLC analysis indicated that the enantiomeric excess of the product was 88 % [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.5/0.5; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 10.2 (minor), 13.4 (major) min]. ^{1}H NMR (500.13 MHz, C_6D_6) δ 7.31 (d, *J* = 7.2 Hz, 2H), 7.19-7.14 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 5.79-5.73 (m, 1H), 5.49 (dd, *J* = 15.5, 6.6 Hz, 1H), 5.33 (ddd, *J* = 15.5, 7.1, 1.0 Hz, 1H), 5.12 (d, *J* = 17.2 Hz, 1H), 5.00 (dd, *J* = 10.3, 0.6 1H), 3.67 (s, 2H), 3.55 (t, *J* = 6.8 Hz, 1H), 2.16 (oct, *J* = 6.7 Hz, 1H), 0.92 (d, *J* = 2.1 Hz, 3H), 0.90 (d, *J* = 2.2 Hz, 3H). ^{13}C NMR (125.7 MHz, C_6D_6) δ 141.54 (s), 141.23 (s), 138.98

(s), 129.35 (s), 128.56 (s), 128.51 (s), 127.02 (s), 114.74 (s), 63.15 (s), 51.19 (s), 31.25 (s), 22.67 (s), 22.63 (s). Anal. Calcd. for $C_{15}H_{21}N$: C, 83.67; H, 9.83; N, 6.50; Found: C, 83.52 ; H, 9.83; N, 6.51 .



1-phenyl-prop-2-enylphenylether (entry 12).[3] The general procedure was followed with 0.25 mL of the stock solution of $Pd(dba)_2$, 0.25 mL of the stock solution of PPh_3, **1a** (0.192 g, 1.00 mmol), $[(COD)IrCl]_2$ (0.010 g, 0.015 mmol), **L1** (0.016 g, 0.030 mmol) or **L3** (0.015 g, 0.030 mmol), and lithium phenoxide (0.210 g, 2.10 mmol). Additional 1 mL THF was added. The isomerization reaction was conducted at room temperature for 4 h, and the allylic substitution was conducted at room temperature for 12 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 90/10 when **L1** was used as ligand and 85/15 when **L3** was used as ligand. The mixture was purified by flash column chromatography on silica gel (hexanes/ethylacetate 10:0.1) to give the title compound (0.159 g, 76%) when **L1** was used as ligand and (0.151 g, 72%) when **L3** was used as ligand. HPLC analysis indicated that the enantiomeric excess of the product was 94% when **L1** was used as ligand and 92% when **L3** was used as ligand [Diacel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.7/0.3; flow rate = 0.8 mL/min; detection wavelength = 220 nm; TR = 30.9 (major), 38.1 (minor) min]. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.34-7.32 (m, 2H), 7.28-7.25 (m, 2H), 7.21-7.19 (m, 1H), 7.16-7.12 (m, 1H), 6.86-6.81 (m, 4H), 6.05-5.98 (m, 1H), 5.55 (d, J = 6.0 Hz, 1H), 5.26 (dq, J = 17.2, 1.0 Hz, 1H), 5.17 (dq, J = 10.4, 1.0 Hz, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 157.93 (s), 140.16 (s), 137.99 (s), 129.33 (s), 128.64 (s), 127.82 (s), 126.62 (s), 120.99 (s), 116.49 (s), 116.21 (s), 80.82 (s).



Dimethyl(1-phenyl-prop-2-enyl)malonate (entry 13).[4] The general procedure was followed with 0.25 mL of the stock solution of $Pd(dba)_2$, 0.25 mL of the stock solution of PPh_3, **1a** (0.192 g, 1.00 mmol), $[(COD)IrCl]_2$ (0.010 g, 0.015 mmol), **L1** (0.016 g, 0.030 mmol) or **L3** (0.015 g, 0.030 mmol), and sodium dimethylmalonate (0.185 g, 1.20 mmol). The isomerization reaction was conducted at room temperature for 4 h, and the allylic substitution was conducted at room temperature for 1.5 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 97/3 when **L1** was used as ligand and 80/20 when **L3** was used as ligand. The mixture was purified by flash column chromatography on silica gel (hexanes/ethylacetate 10:1) to give the title compound (0.19 g, 77%) when **L1** was used as ligand and (0.18 g, 72%) when **L3** was used as ligand. HPLC analysis indicated that the enantiomeric excess of the product was 94.5% when **L1** was used as ligand and 91% when **L3** was used as ligand. [Diacel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexanes/2-propanol = 97/3; flow rate = 0.5 mL/min; detection wavelength = 220 nm; TR = 23.3 (minor), 24.6 (major) min]. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 7.15-7.12 (m, 3H), 5.92(ddd, *J* = 17.6, 9.5, 8.2 Hz, 1H), 5.04 (d, *J* = 17.0 Hz, 1H), 5.00 (d, *J* = 10.3 Hz, 1H), 4.03 (dd, *J* = 10.9, 8.3 Hz, 1H), 3.79 (d, *J* = 11.0, 1H), 3.65 (s, 3H), 3.39 (s, 3H). ^{13}C NMR (125.7 MHz, C_6D_6) δ 168.57 (s), 168.19 (s), 140.58 (s), 138.23 (s), 129.02 (s), 128.32 (s), 127.52 (s), 116.98 (s), 57.75 (s), 52.92 (s), 52.74 (s), 49.94 (s).

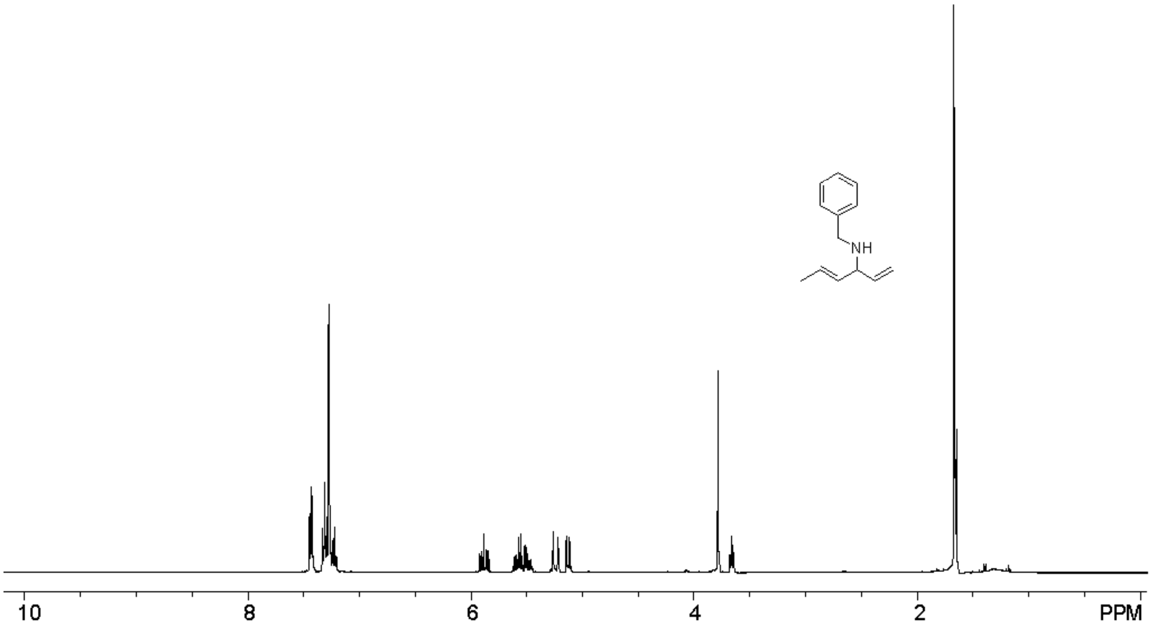


Figure S2. ^{1}H NMR spectra of Benzyl-(1-vinyl-but-2-enyl)-amine.

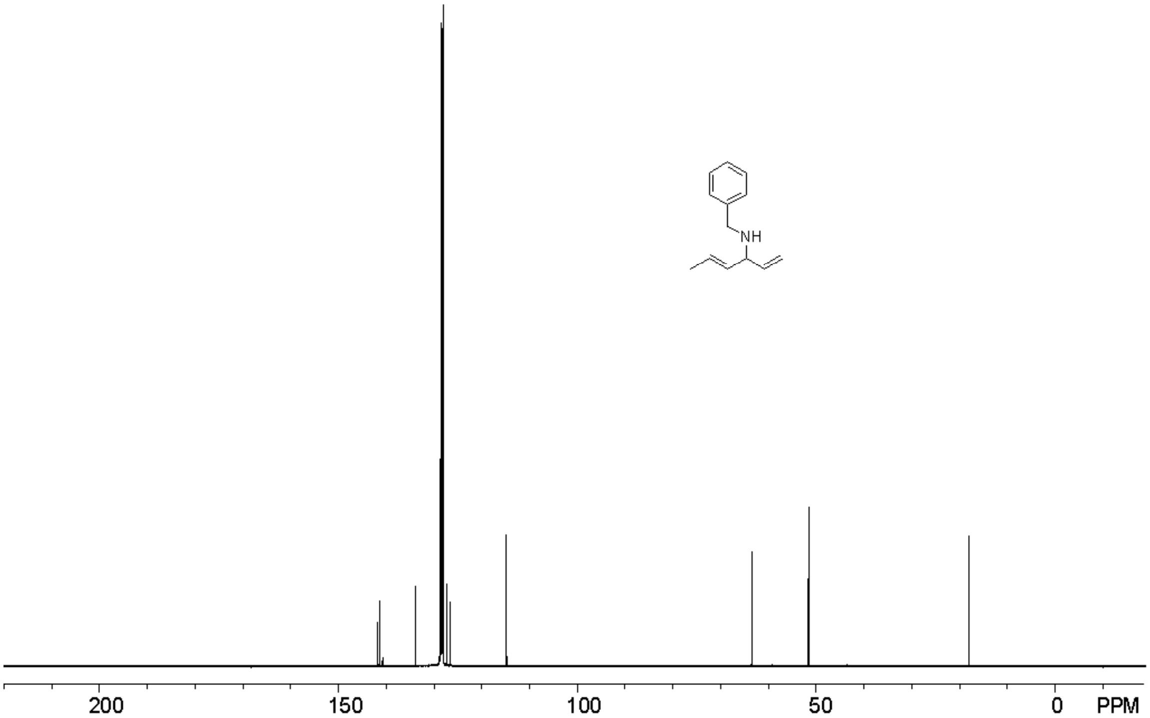


Figure S3. ^{13}C NMR spectra of Benzyl-(1-vinyl-but-2-enyl)-amine.

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