Iridium-Catalyzed Kinetic Asymmetric Transformations of Racemic Allylic Benzoates

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Supporting Information

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General Experimental Details

All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. THF was degassed by purging with argon for 45 minutes and dried with a solvent purification system containing a one-meter column of activated alumina. Hydrocinnamaldehyde, butyraldehyde, isobutyraldehyde, cyclohexanecarboxaldehyde, trimethylacetaldehyde, benzaldehyde, 4-methoxybenzaldehyde, 4-(trifluoromethyl)benzaldehyde, 4-bromobenzaldehyde, 3-bromobenzaldehyde, 2-fluorobenzaldehyde, *o*-tolualdehyde, and 3-pyridinecarboxaldehyde were purchased from Sigma-Aldrich and used without further purification. Vinylmagnesium chloride was purchased as a 1.6 M solution in THF from Sigma-Aldrich. Phenol, di-*tert*-butyliminodicarboxylate, trifluoroacetamide, benzimidazole, dimethyl malonate, and malononitrile were purchased from Aldrich and used without further purification. Sodium *p*-toluenesulfinate (NaTs) was purchased from TCI and used without further purification. Sodium phenoxide (NaOPh) and sodium benzimidazolate (NaBzIm) were prepared by reaction of either phenol or benzimidazole with

NaH in THF at room temperature. After stirring for 1 h at room temperature, the solvent was evaporated to afford either sodium phenoxide or sodium benzimidazolate as a white powder. The lithium salt of di-*tert*-butyliminodicarboxylate [$LiN(Boc)_2$] was prepared by reaction of di-*tert*-butyliminodicarboxylate with *n*-BuLi in THF at -78 °C. After warming the reaction to room temperature and stirring for 1 h at room temperature, the solvent was evaporated to afford the lithium salt of di-*tert*-butyliminodicarboxylate as a white powder. Potassium trifluoroacetamide [$KNC(O)CF_3$] was prepared by reaction of trifluoroacetamide with KH in THF at 0 °C After stirring for 1 h at room temperature, the solvent was evaporated to afford potassium trifluoroacetamide as a white powder.

$[Ir(COD)Cl]_2$ was synthesized from $IrCl_3 \cdot xH_2O$ and 1,5-cyclooctadiene according to a literature procedure[1] or was obtained from Johnson-Matthey and used without further purification. Phosphoramidite ligands **L1** and **L2** were synthesized according to literature procedures.[2] [Ir(COD)(κ^2-**L1**)(ethylene) (**1a**)[3] and [Ir(COD)(κ^2-**L2**)(ethylene) (**1b**)[4] were prepared according to literature procedures.

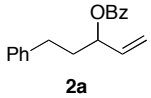
Elemental analyses were performed by the University of Illinois at Urbana-Champaign Microanalysis Laboratory and by Robertson Microlit Laboratories, Inc. (Madison, NJ). GC analyses were obtained on an Agilent 6890 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μm film) and an FID detector. HPLC analyses were carried out on a Waters chromatography system (1525 binary pump, 717+ autosampler, 2487 dual wavelength detector). Optical rotations were measured on a Rudolph Instruments (Denville, NJ) Autopol IV polarimeter. NMR spectra were acquired on a 400 MHz Varian Unity instrument or on 500 MHz Varian Unity or Inova instruments at the University of Illionis VOICE NMR facility. Chemical shifts are reported in ppm relative to a residual solvent peak ($CDCl_3$ = 7.26 ppm for ^1H and 77.23 ppm for ^{13}C) or to an external standard ($CFCl_3$ = 0 for ^{19}F). Coupling constants are reported in hertz. Note: Relatively broad signals prevent observation of the allylic ^4J coupling between the terminal alkene protons and the allylic proton for the allylic resonance in the branched allylic benzoate substrates and branched allylic substitution products. However, the allylic ^4J coupling is typically observed for the terminal alkene resonances.

Flash column chromatography was performed on Silicylce Siala-P silica gel or on a Teledyne Isco CombiFlash Rf automated chromatography system with RediSep Rf Gold normal-phase silica columns. Products were visualized on TLC plates by UV or by staining with $KMnO_4$, phosphomolybdic acid, or ceric ammonium molybdate.

General Procedure for the Synthesis of Allylic Benzoates 2a-2m

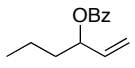
The appropriate aldehyde (1.0 equiv) and THF (2.5 mL/mmol of aldehyde) were added to a round-bottom flask and cooled to 0 °C under a positive pressure of nitrogen. Vinylmagnesium chloride (1.0 equiv as 1.6 M solution in THF) was then added. This solution was stirred at 0 °C for 1.5 h. Then, pyridine (2.0 equiv) and benzoyl chloride (1.3 equiv) were added. The reaction mixture was warmed to room temperature and stirred for an additional 1.5 h. The crude reaction mixture was quenched with 1 M HCl. The organic layer was separated and washed with saturated aqueous $NaHCO_3$ and brine, then dried over $MgSO_4$, filtered, and concentrated. The

crude reaction mixtures were purified by flash column silica gel chromatography (eluting with hexanes:EtOAc) to yield allylic benzoates **2a**-**2m**.



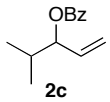
2a

5-phenylpent-1-en-3-yl benzoate (2a):[5] Prepared according to the general procedure from hydrocinnamaldehyde (2.55 g, 19.0 mmol). Purified by flash column chromatography (98:2 to 90:10 hexanes:EtOAc) to give **2a** as a colorless oil in 87% yield (4.39 g, 16.5 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.06-2.12 (m, 1H), 2.13-2.23 (m, 1H), 2.74-2.84 (m, 2H), 5.28 (ddd, J = 10.5, 1.5, 1.0 Hz, 1H), 5.39 (dddd, J = 17.0, 1.5, 1.0 Hz, 1H), 5.58 (ddd, J = 7.0, 7.0, 6.0 Hz, 1H), 5.97 (ddd, J = 17.0, 10.5, 6.0 Hz, 1H), 7.21-7.24 (m, 3H), 7.31 (t, J = 8.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.60 (tt, J = 7.5, 1.5 Hz, 1H), 8.07-8.20 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 31.6, 36.1, 74.9, 117.1, 126.2, 128.5, 128.6, 129.7, 129.8, 130.6, 133.1, 136.5, 141.5, 165.9.



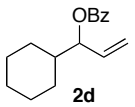
2b

hex-1-en-3-yl benzoate (2b):[6] Prepared according to the general procedure from butyraldehyde (1.29 g, 17.9 mmol). Purified by flash column chromatography (95:5 hexanes:EtOAc) to give **2b** as a colorless oil in 94% yield (3.42 g, 16.7 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.96 (t, J = 7.5 Hz, 3H), 1.37-1.52 (m, 2H), 1.64-1.74 (m, 1H), 1.76-1.83 (m, 1H), 5.20 (ddd, J = 11.0, 1.0, 1.0 Hz, 1H), 5.34 (ddd, J = 17.5, 1.0, 1.0 Hz, 1H), 5.52 (ddd, J = 7.0, 7.0, 6.0 Hz, 1H), 5.90 (ddd, J = 17.5, 11.0, 6.0 Hz, 1H), 7.43-7.47 (m 2H), 7.56 (t, J = 8.0 Hz, 1H), 8.06-8.09 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.9, 18.4, 36.4, 75.1, 116.5, 128.3, 129.6, 130.6, 132.8, 136.6, 165.9.



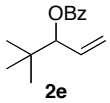
2c

4-methylpent-1-en-3-yl benzoate (2c):[7] Prepared according to the general procedure from isobutyraldehyde (2.37 g, 32.9 mmol). Purified by flash column chromatography (95:5 hexanes:EtOAc) to give **2c** as a colorless oil in 62% yield (4.15 g, 20.3 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.00 (d, J = 7.0 Hz, 3H), 1.04 (d, J = 7.0 Hz, 3H), 1.98-2.12 (m, 1H), 5.25 (ddd, J = 10.5, 1.0, 1.0 Hz, 1H), 5.30-5.34 (m, 2H), 5.88 (ddd, J = 18.0, 10.5, 6.0 Hz, 1H), 7.43-7.47 (m, 2H), 7.56 (tt, J = 7.5, 1.5 Hz, 1H), 8.07-8.10 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.9, 18.2, 32.0, 79.8 117.5, 128.3, 129.5, 130.6, 132.8, 134.7, 165.8. Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; N, 0.00; found: C, 76.41; H, 7.97; N, <0.02.



2d

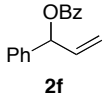
1-cyclohexylallyl benzoate (2d):[8] Prepared according to the general procedure from cyclohexanecarboxaldehyde (2.04 g, 18.2 mmol). Purified by flash column chromatography (98:2 to 90:10 hexanes:EtOAc) to give **2d** as a colorless oil in 86% yield (3.83 g, 15.7 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.04-1.28 (m, 5H), 1.62-1.89 (6H), 5.23 (ddd, J = 10.5, 1.5, 1.0 Hz, 1H), 5.30 (ddd, J = 17.0, 1.5, 1.0 Hz, 1H), 5.32 (dd, J = 6.5, 6.5 Hz, 1H), 5.88 (ddd, J = 17.0, 10.5, 6.5 Hz, 1H), 7.42-7.46 (m, 2H), 7.55 (ddt, J = 1.5, 1.0, 7.0 Hz, 1H), 8.06-8.09 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.9, 26.2, 26.6, 28.6, 28.9, 42.0, 79.5, 117.6, 128.5, 129.7, 130.9, 133.0, 135.2, 166.0.



2e

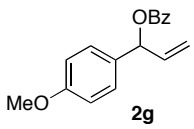
4,4-dimethylpent-1-en-3-yl benzoate (2e): Prepared according to the general procedure from trimethylacetaldehyde (2.78 g, 32.2 mmol). Purified by flash column chromatography (95:5 hexanes:EtOAc) to give **2e** as a colorless oil in 70% yield (4.93 g, 22.6 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.03 (s, 9H), 5.23-5.28 (m, 2H), 5.32 (ddd, J = 17.0, 1.5, 1.0 Hz, 1H), 5.92 (ddd, J = 17.5, 10.5, 6.5 Hz, 1H), 7.56 (tt, J = 7.0, 1.5 Hz, 1H), 7.45 (dd, J = 8.0, 7.0 Hz, 2H), 8.09 (dd, J = 8.0, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz)

δ 25.9, 34.5, 82.3, 118.2, 128.3, 129.5, 130.6, 132.8, 133.5, 165.7. Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31; N, 0.00; found: C, 76.78; H, 8.48; N, <0.02.



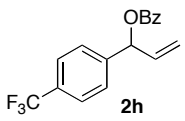
2f

1-phenylallyl benzoate (2f):[9] Prepared according to the general procedure from benzaldehyde (3.14 g, 29.6 mmol). Purified by flash column chromatography (98:2 to 90:10 hexanes:EtOAc) to give **2f** as a colorless oil in 93% yield (6.55 g, 27.5 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.34 (ddd, *J* = 10.5, 1.5, 1.0 Hz, 1H), 5.45 (ddd, *J* = 17.0, 1.0, 1.0 Hz, 1H), 6.18 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 6.58 (d, *J* = 6.0 Hz, 1H), 7.34-7.38 (m, 1H), 7.40-7.52 (m, 6H), 7.59 (tt, *J* = 7.5, 1.5 Hz, 1H), 8.14-8.17 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.8, 117.2, 127.3, 128.4, 128.5, 128.8, 129.9, 130.5, 133.2, 136.5, 139.1, 165.6.



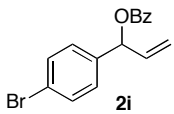
2g

1-(4-methoxyphenyl)allyl benzoate (2g): Prepared according to the general procedure from 4-methoxybenzaldehyde (2.50 g, 18.4 mmol). Purified by flash column chromatography (98:2 to 90:10 hexanes:EtOAc) to give **2g** as a colorless oil in 88% yield (4.36 g, 16.2 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.81 (s, 3H), 5.30 (ddd, *J* = 10.5, 1.5, 1.0 Hz, 1H), 5.40 (ddd, *J* = 17.0, 1.5, 1.0 Hz, 1H), 6.14 (ddd, *J* = 17.0, 10.5, 5.5 Hz, 1H), 6.50 (d, *J* = 5.5 Hz, 1H), 6.92 (m, 2H), 7.39-7.47 (m, 4H), 7.56 (app tt, *J* = 8.0, 1.5 Hz, 1H), 8.09-8.13 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.4, 76.5, 114.2, 116.8, 128.5, 128.9, 129.9, 130.6, 131.2, 133.2, 136.6, 159.7, 165.7. Anal. Calcd. for $C_{17}H_{13}O_2F_3$: C, 76.10; H, 6.01; N, 0.00; found: C, 76.38; H, 6.29; N, <0.02.



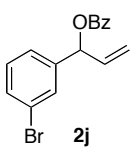
2h

1-(4-(trifluoromethyl)phenyl)allyl benzoate (2h):[10] Prepared according to the general procedure from 4-(trifluoromethyl)benzaldehyde (3.18 g, 18.3 mmol). Purified by flash column chromatography (98:2 to 90:10 hexanes:EtOAc) to give **2h** as a white amorphous solid in 80% yield (4.46 g, 14.6 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.37 (ddd, *J* = 10.5, 1.0, 1.0 Hz, 1H), 5.45 (d, *J* = 17.0, 1.5, 1.0 Hz, 1H), 6.13 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 6.57 (d, *J* = 6.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.58-7.62 (m, 3H), 7.66 (d, *J* = 8.0 Hz, 2H), 8.12-8.15 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.4, 118.4, 124.5 (q, *J* = 271.2 Hz), 126.1 (q, 4.0 Hz), 127.8, 129.0, 130.2, 130.4, 130.8 (q, 32.1 Hz), 133.7, 136.1, 143.4, 165.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -63.0.



2i

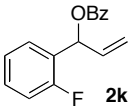
1-(4-bromophenyl)allyl benzoate (2i): Prepared according to the general procedure from 4-bromobenzaldehyde (3.00 g, 16.2 mmol). Purified by flash column chromatography (98:2 to 90:10 hexanes:EtOAc) to give **2i** as a colorless oil in 77% yield (3.95 g, 12.5 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.33 (ddd, *J* = 10.5, 1.5, 1.0, 1H), 5.42 (ddd, *J* = 17.0, 1.5, 1.5 Hz, 1H), 6.11 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 6.48 (d, *J* = 6.0 Hz, 1H), 7.33-7.36 (m, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.52 (m, 2H), 7.58 (ddd, *J* = 7.5, 1.5, 1.0, 1H), 8.11 (dd, *J* = 8.0, 1.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.1, 117.7, 122.4, 128.6, 129.1, 129.9, 130.2, 131.9, 133.4, 136.0, 138.2, 165.5. Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.59; H, 4.13; N, 0.00; found: C, 60.51; H, 3.97; N, <0.02.



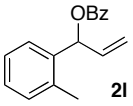
2j

1-(3-bromophenyl)allyl benzoate (2j): Prepared according to the general procedure from 3-bromobenzaldehyde (3.97 g, 21.5 mmol). Purified by flash column chromatography (98:2 to 90:10 hexanes:EtOAc) to give **2j** as a colorless oil in 80% yield (5.43 g, 17.1 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.34 (d, *J* = 10.5 Hz, 1H), 5.34 (d, *J* = 17.0 Hz, 1H), 6.10 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 6.49 (d, *J* = 6.0 Hz,

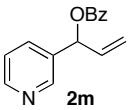
1H), 7.25 (t, J = 8.0 Hz, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.44-7.49 (m, 3H), 7.59 (t, J = 8.0 Hz, 1H), 7.61 (d, 1.5 Hz, 1H), 8.12 (dd, J = 8.0, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.0, 117.9, 122.9, 126.0, 128.6, 129.9, 130.2, 130.3, 130.4, 131.5, 133.4, 135.9, 141.4, 165.5. Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.59; H, 4.13; N, 0.00; found: C, 60.39; H, 4.14; N, <0.02.



1-(2-fluorophenyl)allyl benzoate (2k): Prepared according to the general procedure from 2-fluorobenzaldehyde (2.36 g, 19.0 mmol). Purified by flash column chromatography (98:2 to 90:10 hexanes:EtOAc) to give **2k** as a colorless oil in 84% yield (4.09 g, 16.0 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.33 (d, J = 10.5, 1.5, 1.0 Hz, 1H), 5.42 (ddd, J = 17.0, 1.5, 1.0 Hz, 1H), 6.19 (ddd, J = 17.0, 10.5, 5.5 Hz, 1H), 6.81 (d, 5.5 Hz, 1H), 7.10 (ddd, J = 8.5, 8.0, 1.0 Hz, 1H), 7.18 (dt, J = 1.0, 8.0 Hz, 1H), 7.29-7.34 (m, 1H), 7.44-7.50 (m, 2H), 7.51 (dt, J = 1.5, 7.5 Hz, 1H), 7.58 (tt, J = 7.5, 1.5 Hz, 1H), 8.12-8.15 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 71.3 (d, J = 3.0 Hz), 115.9 (d, J = 21.4 Hz), 117.5, 124.5 (d, J = 3.9 Hz), 126.6 (d, J = 13.6 Hz), 128.5 (d, J = 3.9 Hz), 128.6, 129.9, 130.0 (d, J = 7.8 Hz), 130.3, 133.3, 135.3, 160.3 (d, J = 247.9 Hz), 165.4. Anal. Calcd. for $C_{16}H_{13}O_2F$: C, 74.99; H, 5.11; N, 0.00; found: C, 74.87; H, 5.08; N, <0.02. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -117.8.



1-(*o*-tolyl)allyl benzoate (2l): Prepared according to the general procedure from *o*-tolualdehyde (2.50 g, 20.8 mmol). Purified by flash column chromatography (98:2 to 90:10 hexanes:EtOAc) to give **2l** as a colorless oil in 89% yield (4.66 g, 18.4 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.45 (s, 3H), 5.29 (d, J = 16.5 Hz, 1H), 5.32 (d, J = 12.0 Hz, 1H), 6.12 (ddd, J = 16.5, 10.0, 5.5 Hz, 1H), 6.69 (d, J = 5.5 Hz, 1H), 7.18-7.26 (m, 3H), 7.43-7.51 (m, 3H), 7.57 (t, J = 7.5 Hz, 1H), 8.11 (dd, J = 8.5, 1.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.5, 74.2, 117.2, 126.4, 127.1, 128.2, 128.5, 129.8, 129.9, 130.7, 133.2, 135.8, 136.0, 137.2, 165.6. Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39; N, 0.00; found: C, 80.81; H, 6.66; N, <0.02.



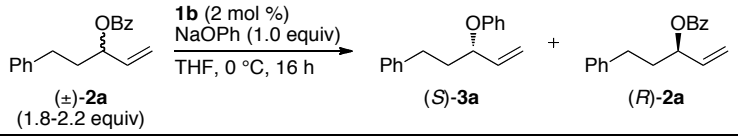
1-(pyridin-3-yl)allyl benzoate (2m): Prepared according to the general procedure from 3-pyridinecarboxaldehyde (2.27 g, 21.2 mmol). Purified by flash column chromatography (75:25 hexanes:EtOAc) to give **2m** as a yellow oil in 89% yield (4.51 g, 18.9 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.34 (ddd, J = 10.5, 1.0, 1.0 Hz, 1H), 5.41 (ddd, J = 17.0, 1.0, 1.0 Hz, 1H), 6.10 (ddd, J = 17.0, 10.5, 5.5 Hz, 1H), 6.53 (d, J = 5.5 Hz, 1H), 7.27 (dd, J = 8.0, 5.0 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.53 (tt, J = 7.5, 1.5, 1.0 Hz, 1H), 7.74 (ddd, J = 8.0, 2.0, 1.5 Hz, 1H), 8.05-8.08 (m, 2H), 8.55 (dd, J = 8.0, 1.5 Hz, 1H), 8.72 (d, J = 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 74.5, 118.5, 123.5, 128.5, 129.7, 129.9, 133.3, 134.6, 134.9, 135.4, 148.9, 149.6, 165.3. Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85; found: C, 75.09; H, 5.45; N, 5.74.

Iridium-Catalyzed Allylic Substitution and Kinetic Resolution of 5-phenylpent-1-en-3-yl benzoate (2a) with NaOPh

In a nitrogen-filled dry-box, the catalyst precursor **1b** (0.0046 g, 0.0050 mmol), NaOPh (0.0290 g, 0.250 mmol, 1.00 equiv), and THF (2 mL) were added to a 1-dram vial. The vial was sealed with a PTFE/silicone lined septum cap, removed from the dry-box, and cooled to 0 °C. Then, a pre-cooled (0 °C), degassed solution of allylic benzoate **2a** (0.120-0.146 g, 0.450-0.550 mol, 1.80-2.20 equiv) in THF (1 mL) was added to the solution containing the catalyst precursor and

NaOPh. The reaction mixture was stirred at 0 °C for 16 h. The vial was removed from the cold bath, and the reaction mixture was filtered through a 0.5 inch plug of silica gel (eluting with Et_2O). The crude reaction mixture was concentrated under reduced pressure. $CDCl_3$ (0.7-0.8 mL) was added to dissolve the crude reaction mixture, and mesitylene (11 μL) was added as an internal standard. The branched-to-linear ratio of **3a** (>95:5) and conversion were determined by ^{1}H NMR spectroscopy. After this analysis, the crude reaction mixture was dry-loaded onto silica gel (approximately 1 g) and purified by flash column silica gel chromatography (100:0 to 95:5 hexanes:EtOAc) on a Teledyne Isco CombiFlash Rf automated chromatography system with a RediSep Rf Gold (12 g) normal-phase silica column to give allylic substitution product **3a** in 81-86% yield (based on 1.0 equiv of NaOPh) and branched allylic benzoate **2a** in 42-53% yield (based on 1.80-2.20 equiv **2a**). The enantiomeric excess of **3a** was determined by HPLC analysis (254 nm, 25 °C) t_R 11.0 min (major); t_R 11.8 min (minor) [Chiralcel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.75:0.25, 0.5 mL/min] to be 75-95%. The enantiomeric excess of **2a** was determined by HPLC analysis (254 nm, 25 °C) t_R 10.9 min (minor); t_R 12.0 min (major) [Chiralcel OJ-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 78-97%. See Table S1 for specific data corresponding to the various quantities of allylic benzoate **2a** and the following section for spectroscopic data for **3a**.

***Table S1*: Ir-Catalyzed Allylic Substitution and Kinetic Resolution of 2a with NaOPh**



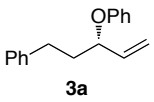
entry	equiv (±)-**2a**	conversion (%)[a]	yield **3a** (%)[b]	ee **3a** (%)[c]	yield **2a** (%)[d]	ee **2a** (%)[c]	*s*[e]
1	2.2	45	83	95	52	78	99
2	2.0	50	86	93	48	94	115
3	1.8	54	81	75	42	97	43

[a] Conversion of (±)-**2** determined by ^{1}H NMR spectroscopy. [b] Isolated yield of **3a** based on 1.0 equiv NaOPh. [c] Enantiomeric excess determined by HPLC methods. [d] Isolated yield of **2a** based on 1.8-2.2 equiv **2a**. [e] Selectivity factor (s) = ln{(1-c)(1-ee)}/ln{(1-c)(1+ee)} where c is the conversion of the branched allylic benzoate (±)-**2a** and ee is the enantiomeric excess of the remaining branched allylic benzoate **2a**.

General Procedure for Iridium-Catalyzed Allylic Substitution of Racemic Aliphatic Allylic Benzoates

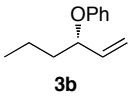
In a nitrogen-filled dry-box, the catalyst precursor **1b** (0.0046 g, 0.0050 mmol, 0.020 equiv), nucleophile (0.250 mmol, 1.00 equiv), and THF (2 mL) were added to a 1-dram vial. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and cooled to 0 °C. Then, a pre-cooled (0 °C), degassed solution of allylic benzoate (**2a**-**2e**, 0.550 mmol, 2.20 equiv) in THF (1 mL) was added to the solution containing the catalyst precursor and nucleophile. The reaction mixture was stirred at 0 °C for 12-16 h. The vial was removed from the cold bath, and the reaction mixture was filtered through a 0.5 inch plug of silica gel (eluting with Et_2O or EtOAc). The crude reaction mixture was concentrated under reduced pressure.

$CDCl_3$ (0.7-0.8 mL) was added to dissolve the crude reaction mixture, and mesitylene (11 μL) was added as an internal standard. The branched-to-linear ratio was then determined by ^1H NMR spectroscopy to be >95:5 for each reaction. After this analysis, the crude reaction mixture was dry-loaded onto silica gel (approximately 1 g) and purified by flash column silica gel chromatography (eluting with hexanes:EtOAc) on a Teledyne Isco CombiFlash Rf automated chromatography system with a RediSep Rf Gold (12 g) normal-phase silica column to yield product **3a**-**3e** or **4a**-**9a**.



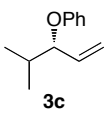
3a

(*S*)-(3-phenoxypent-4-en-1-yl)benzene (3a):[11] Prepared according to the general procedure from **2a** (0.146 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol) (reaction time = 16 h). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **3a** as a colorless oil in 83% yield (0.0493 g, 0.207 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 11.0 min (major); t_R 11.8 min (minor) [Chiralcel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.75:0.25, 0.5 mL/min] to be 95%. $[\alpha]_D^{24}$ = -30.4° (c 0.51, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 1.97-2.05 (m, 1H), 2.13-2.20 (m, 1H), 2.76-2.90 (m, 2H), 4.64 (app q, *J* = 6.0 Hz, 1H), 5.25 (ddd, *J* = 10.5, 1.5, 1.0 Hz, 1H), 5.30 (ddd, *J* = 17.5, 1.5, 1.0 Hz, 1H), 5.91 (ddd, *J* = 17.5, 10.5, 6.0 Hz, 1H), 6.92-6.98 (m, 3H), 7.21-7.26 (m, 3H), 7.27-7.33 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 31.7, 37.5, 78.0, 116.2, 116.8, 121.0, 126.1, 128.6, 128.7, 129.5, 138.1, 141.9, 158.5.



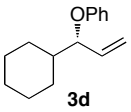
3b

(*S*)-(hex-1-en-3-yloxy)benzene (3b):[11,12] Prepared according to the general procedure from **2b** (0.112 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol) (reaction time = 16 h). The crude mixture was purified by flash column chromatography (99:1 pentanes:Et_2O) to give **3b** as a colorless oil in 86% yield (0.0380 g, 0.216 mmol) The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 11.7 min (major); t_R 14.1 min (minor) [Chiralcel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.1:0.1, 0.5 mL/min] to be 92%. $[\alpha]_D^{25}$ = -24.7° (c 1.05, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 0.99 (t, *J* = 7.0 Hz, 3H), 1.44-1.59 (m, 2H), 1.65-1.71 (m, 1H), 1.79-1.86 (m, 1H), 4.64 (ddddd, *J* = 6.0. 6.0, 6.0, 1.5, 1.5 Hz, 1H), 5.22 (ddd, *J* = 10.5, 1.5, 1.5 Hz, 1H), 5.28 (ddd, *J* = 17.5, 1.5, 1.5 Hz, 1H), 5.89 (ddd, *J* = 17.5, 10.5, 6.0 Hz, 1H), 6.93-6.96 (m, 3H), 7.26-7.30 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.9, 18.5, 37.7, 78.7, 116.0, 116.2, 120.6, 129.2, 138.2, 158.4.

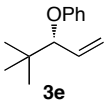


3c

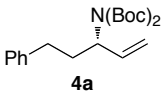
(*S*)-((4-methylpent-1-en-3-yl)oxy)benzene (3c): Prepared according to the general procedure from **2c** (0.112 g, 0.550 mmol) and NaOPh (0.290 g, 0.250 mmol) (reaction time = 16 h). The crude mixture was purified by flash column chromatography (99:1 pentanes:Et_2O) to give **3c** as a colorless oil in 76% yield (0.0333 g, 0.189 mmol) The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 9.7 min (major); t_R 11.3 min (minor) [Chiralcel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.9:0.1, 0.5 mL/min] to be 98%. $[\alpha]_D^{25}$ = -26.2° (c 0.66, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 1.00 (d, *J* = 7.0 Hz, 3H), 1.04 (d, *J* = 7.0 Hz, 3H), 1.95-2.04 (m, 1H), 4.36 (dddd, *J* = 6.0, 6.0, 1.5, 1.0 Hz, 1H), 5.23-5.28 (m, 2H), 5.84 (ddd, *J* =17.0, 11.0, 6.0 Hz, 1H), 6.90-6.94 (m, 3H), 7.24-7.28 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.1, 18.2, 32.9, 83.9, 116.1, 117.4, 120.5, 129.2, 136.3, 158.7. Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15; N, 0.00; found: C, 81.69; H, 9.12; N, <0.02.



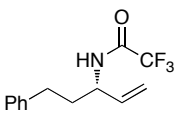
(*R*)-((1-cyclohexylallyl)oxy)benzene (3d):[13] Prepared according to the general procedure from **2d** (0.134 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol) (reaction time = 16 h). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **3d** as a colorless oil in 86% yield (0.0465 g, 0.215 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 10.7 min (minor); t_R 12.3 min (major) [Chiralcel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.9:0.1, 0.5 mL/min] to be 96%. $[\alpha]_D^{25}$ = -13.5° (c 0.88, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.09-1.34 (m, 5H), 1.64-1.82 (m, 5H), 1.96-2.01 (m, 1H), 4.37 (t, *J* = 6.5 Hz, 1H), 5.21-5.28 (m, 2H), 5.84 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 6.91-6.95 (m, 3H), 7.24-7.30 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.33, 26.36, 26.7, 28.9, 29.0, 42.9, 83.7, 116.3, 117.4, 120.7, 129.4, 136.8, 159.0.



(*R*)-((4,4-dimethylpent-1-en-3-yl)oxy)benzene (3e): Prepared according to a modified version of the general procedure from **2e** (0.120 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol). The reaction was run with 4 mol % of the catalyst precursor **1b** (0.0093 g, 0.010 mmol, 0.040 equiv) for 24 h at 50 °C. The crude mixture was purified by flash column chromatography (99:1 pentanes:Et_2O) to give **3e** as a colorless oil in 88% yield (0.0421 g, 0.221 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 9.0 min (minor); t_R 9.8 min (major) [Chiralcel OJ-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.9:0.1, 0.4 mL/min] to be 96%. $[\alpha]_D^{25}$ = -18.1° (c 0.74, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.03 (s, 9H), 4.21 (ddd, *J* = 6.5, 1.0, 1.0, 1H), 5.24 (ddd, *J* = 17.5, 1.0, 1.0 Hz, 1H), 5.29 (ddd, *J* = 11.0, 1.0, 1.0 Hz, 1H), 5.87 (ddd, *J* = 17.5, 11.0, 6.5 Hz, 1H), 6.90-6.93 (m, 3H), 7.24-7.27 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.0, 35.2, 86.8, 116.0, 118.2, 120.4, 129.2, 135.0, 159.0. Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53; N, 0.00; found: C, 82.34; H, 9.73; N, <0.02.

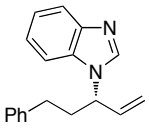


(*S*)-*N,N*-bis-Boc-5-phenylpent-1-en-3-amine (4a): Prepared according to the general procedure from **2a** (0.146 g, 0.250 mmol) and $LiN(Boc)_2$ (0.0558 g, 0.250 mmol) (reaction time = 16 h). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **4a** as a colorless oil in 96% yield (0.0866 g, 0.240 mmol) The enantiomeric excess was determined after monodeprotection with trifluoroacetic acid by HPLC analysis (220 nm, 25 °C) t_R 5.6 min (minor); t_R 7.4 min (major) [Chiralcel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 93%. $[\alpha]^{25}_{405}$ = -0.5° (c 1.09, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.51 (s, 18H), 2.01-2.09 (m, 1H), 2.19-2.27 (m, 1H), 2.64 (app t, *J* = 7.5 Hz, 2H), 4.70 (ddd, *J* = 7.0, 6.5, 6.5 Hz, 1H), 5.15 (ddd, *J* = 10.5, 1.0, 1.0 Hz, 1H), 5.20 (ddd, *J* = 17.5, 1.5, 1.0 Hz, 1H), 6.06 (ddd, *J* = 17.5, 10.5, 6.5 Hz, 1H), 7.18-7.21 (m, 3H), 7.27-7.31 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.2, 32.9, 34.6, 59.0, 82.4, 116.7, 126.0, 128.56, 128.58, 137.8, 141.9, 153.2. Anal. Calcd. for $C_{21}H_{31}NO_4$: C, 69.78; H, 8.64; N, 3.87; found: C, 69.74; H, 8.43; N, 3.79.



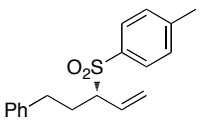
5a

(*S*)-2,2,2-trifluoro-*N*-(5-phenylpent-1-en-3-yl)acetamide (5a):[14] Prepared according to the general procedure from **2a** (0.146 g, 0.250 mmol) and $KNHC(O)CF_3$ (0.0558 g, 0.250 mmol) (reaction time = 16 h). The crude mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to give **5a** as a white amorphous solid in 74% yield (0.0479 g, 0.186 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 12.1 min (minor); t_R 13.0 min (major) [Chiralcel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 98%. $[\alpha]_D^{25}$ = 21.9° (c 0.91, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.90-2.02 (m, 2H), 2.68 (app t, *J* = 7.5 Hz, 2H), 4.52 (ddd, *J* = 7.0, 7.0, 6.0 Hz, 1H), 5.23 (d, *J* = 17.0 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.80 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 6.23 (br s, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.30 (dd, *J* = 8.0, 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.1, 36.0, 52.4, 116.0 (q, 291.6 Hz), 117.2, 126.5, 128.5, 128.9, 136.2, 140.8, 156.7 (q, $J_{C\text{-}F}$ = 37.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ -76.3.



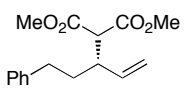
6a

(*S*)-1-(5-phenylpent-1-en-3-yl)-1*H*-benzo[*d*]imidazole (6a): Prepared according to the general procedure from **2a** (0.146 g, 0.250 mmol) and NaBzIm (0.0350 g, 0.250 mmol) (reaction time = 14 h). The crude mixture was purified by flash column chromatography (100:0 to 20:80 hexanes:EtOAc) to give **6a** as a tan oil in 84% yield (0.0552 g, 0.210 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 10.2 min (minor); t_R 11.1 min (major) [Chiralcel AS-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 97%. $[\alpha]_D^{25}$ = 22.2° (c 1.01, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.35-2.43 (m, 1H), 2.44-2.52 (m, 1H), 2.54-2.66 (m, 2H), 4.81-4.86 (m, 1H), 5.14 (d, *J* = 17.0 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 6.08 (ddd, *J* = 17.0, 10.5, 5.5 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.27-7.35 (m, 5H), 7.85 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.96 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.2, 35.2, 57.7, 110.8, 117.8, 120.7, 122.4, 123.0, 126.6, 128.6, 128.8, 133.5, 136.3, 140.3, 141.8, 144.2. Anal. Calcd. for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68; found: C, 82.16; H, 6.99; N, 10.32.



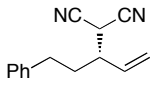
7a

(*S*)-1-methyl-4-((5-phenylpent-1-en-3-yl)sulfonyl)benzene (7a):[15] Prepared according to the general procedure from **2a** (0.146 g, 0.250 mmol) and NaTs (0.0445 g, 0.250 mmol) (reaction time = 16 h). The crude mixture was purified by flash column chromatography (100:0 to 75:25 hexanes:EtOAc) to give **7a** as a white amorphous solid in 80% yield (0.0600 g, 0.200 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 9.2 min (minor); t_R 10.2 min (major) [Chiralcel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 94%. $[\alpha]_D^{25}$ = +61.0° (c 0.99, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.93-2.01 (m, 1H), 2.40-2.47 (two overlapping resonances: m, 1H; s, 3H), 2.54 (ddd, *J* = 14.0, 8.5, 8.5 Hz, 1H), 2.79 (ddd, *J* = 14.0, 9.0, 5.0 Hz, 1H), 3.49 (ddd, *J* = 10.0, 10.0, 3.0 Hz, 1H), 5.10 (d, *J* = 17.0 Hz, 1H), 5.38 (d, *J* = 10.0 Hz, 1H), 5.68 (ddd, *J* = 17.0, 10.0, 10.0 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.26-7.32 (m, 4H), 7.69 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.8, 28.6, 32.5, 69.2, 124.1, 126.5, 128.6, 128.7, 129.4, 129.6, 130.4, 134.6, 140.3, 144.7.



8a

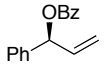
(*S*)-dimethyl 2-(5-phenylpent-1-en-3-yl)malonate (8a):[16] Prepared according to a modified version of the general procedure from **2a** (0.146 g, 0.550 mmol) and sodium dimethyl malonate (0.250 mmol) (reaction time = 16 h). A solution of sodium dimethyl malonate in THF (1 mL) was prepared from dimethyl malonate (0.0330 g, 0.250 mmol) and NaH (0.0060 g, 0.25 mmol). To the solution of sodium dimethyl malonate was added catalyst precursor **1b** (0.0046 g, 0.0050 mmol) as a solution in THF (1 mL). Allylic benzoate **2a** was added as described in the general procedure. The crude mixture was purified by flash column chromatography (100:0 to 90:10 hexanes:EtOAc) to give **8a** as a colorless oil in 82% yield (0.0479 g, 0.186 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 27.2 min (minor); t_R 33.4 min (major) [Chiralcel OJ-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 0.5 mL/min] to be 94%. $[\alpha]_D^{25}$ = -9.3° (c 0.64, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.60-1.68 (m, 1H), 1.86-1.79 (m, 1H), 2.50-2.57 (m, 1H), 2.66-2.75 (m, 1H), 2.85 (dddd, J = 9.5, 9.5, 9.0, 3.5 Hz, 1H), 3.44 (d, J = 9.0 Hz, 1H), 3.70 (s, 3H), 3.72 (s, 3H), 5.16 (ddd, J = 17.0, 1.5, 1.0 Hz, 1H), 5.18 (dd, J = 10.0, 1.5 Hz, 1H), 5.73 (ddd, J = 17.0, 10.5, 9.5 Hz, 1H), 7.15-7.22 (m, 3H), 7.26-7.31 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 33.3, 34.0, 43.8, 52.2, 52.4, 56.8, 118.1, 125.8, 128.3, 128.3, 137.6, 141.6, 168.4, 168.5.



9a

(*S*)-2-(5-phenylpent-1-en-3-yl)malononitrile (9a): Prepared according to a modified version of the general procedure from **2a** (0.146 g, 0.550 mmol) and the sodium salt of malononitrile (0.250 mmol) (reaction time = 16 h). A solution of the sodium salt of malononitrile in THF (1 mL) was prepared from malononitrile (0.0165 g, 0.250 mmol) and NaH (0.0060 g, 0.25 mmol). To the solution of the sodium salt of malononitrile was added catalyst precursor **1b** (0.0046 g, 0.0050 mmol) as a solution in THF (1 mL). Allylic benzoate **2a** was added as described in the general procedure. The crude mixture was purified by flash column chromatography (100:0 to 90:10 hexanes:EtOAc) to give **9a** as a colorless oil in 77% yield (0.0406 g, 0.193 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 10.5 min (minor); t_R 11.4 min (major) [Chiralcel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 97:3, 1.0 mL/min] to be 88%. $[\alpha]_D^{25}$ = +21.7° (c 1.28, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.91-1.99 (m, 1H), 2.00-2.07 (m, 1H), 2.55-2.68 (m, 2H), 2.79 (ddd, *J* = 13.5, 8.5, 5.0 Hz, 1H), 3.68 (d, *J* = 5.5 Hz, 1H), 5.41 (d, *J* = 17.0 Hz, 1H), 5.49 (d, *J* = 10.0 Hz, 1H), 5.74 (ddd, *J* = 17.0, 10.0, 9.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.9, 32.8, 33.3, 44.5, 111.6, 111.8, 122.4, 126.7, 128.5, 128.9, 133.9, 140.1. Anal. Calcd. for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32; found: C, 79.71; H, 6.65; N, 13.07.

Kinetic Resolution of 1-Phenylallyl Benzoate (2f)

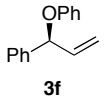


(*S*)-**2f**

In a nitrogen-filled dry-box, allylic benzoate (±)-**2f** (0.119 g, 0.500 mmol, 1.00 equiv) and THF (2 mL) were added to a 1-dram vial. To a separate 1-dram vial were added the catalyst precursor **1b** (0.0023 g, 0.0025 mmol, 0.0050 equiv) and THF (1 mL). Both vials were sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and cooled to 0 °C. Then, the pre-cooled (0 °C) solution of catalyst precursor **1b** was added to the solution of allylic benzoate **2f**. The reaction mixture was stirred at 0 °C for 16 h. The vial was removed from the cold bath, and the reaction mixture was filtered through a 0.5 inch plug of silica gel (eluting with Et_2O). The crude reaction mixture was concentrated under reduced

pressure. $CDCl_3$ (0.7-0.8 mL) was added to dissolve the crude reaction mixture, and mesitylene (11 μL) was added as an internal standard. The conversion was determined to be 54% and the branched-to-linear ratio was determined to be >95:5 by ^1H NMR spectroscopy. After this analysis, the crude reaction mixture was purified by flash column silica gel chromatography (90:10 pentane:Et_2O) to give (*S*)-**2f** as a colorless oil in 45% yield (0.0536 g, 0.225 mmol) and the linear cinnamyl benzoate **10a** as a colorless oil in 49% yield (0.0583 g, 0.245 mmol). The enantiomeric excess of (*S*)-**2f** was determined by HPLC analysis (220 nm, 25 °C) t_R 11.6 min (minor); t_R 14.7 min (major) [Chiralcel OJ-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 98%. $[\alpha]_D^{26}$ = -3.4° (c 1.00, $CHCl_3$).

Iridium-Catalyzed Allylic Etherification of 1-Phenylallyl Benzoate (*S*)-2f



3f

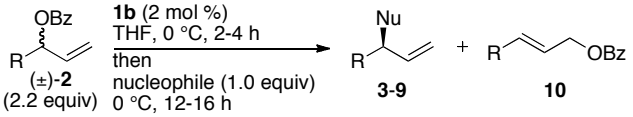
In a nitrogen-filled dry-box, allylic benzoate (*S*)-**2f** (0.0525 g, 0.220 mmol, 98% ee) and THF (2 mL) were added to a 1-dram vial. To a separate 1-dram vial were added the catalyst precursor **1b** (0.0041 g, 0.0044 mol), NaOPh (0.0281 g, 0.242 mmol), and THF (1 mL). Both vials were sealed with a PTFE/silcone-lined septum cap, removed from the dry-box, and cooled to 0 °C. Then, the pre-cooled (0 °C) solution of allylic benzoate (*S*)-**2f** was added to the solution of catalyst precursor **1b** and NaOPh. The reaction mixture was stirred at 0 °C for 6 h. The vial was removed from the cold bath, and the reaction mixture was filtered through a 0.5 inch plug of silica gel (eluting with Et_2O). The crude reaction mixture was concentrated under reduced pressure. $CDCl_3$ (0.7 mL) was added to dissolve the crude reaction mixture, and mesitylene (11 μL) was added as an internal standard. The conversion was determined to be >98% and the branched-to-linear ratio was determined to be >95:5 by ^1H NMR spectroscopy. After this analysis, the crude reaction mixture was purified by flash column silica gel chromatography (97:3 hexanes:EtOAc) to give product (*S*)-**3f** in 91% yield (0.0420 g, 0.200 mmol).[17] The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 33.7 min (major); t_R 39.4 min (minor) [Chiralcel OJ-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.7:0.3, 0.8 mL/min] to be 98%. $[\alpha]_D^{25}$ = +8.2° (c 1.11, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 5.30 (ddd, *J* = 10.0, 1.5, 1.0 Hz, 1H), 5.39 (ddd, *J* = 17.5, 1.5, 1.0 Hz, 1H), 5.68 (d, *J* = 6.0 Hz, 1H), 6.15 (ddd, *J* = 17.5, 10.0, 6.0 Hz, 1H), 6.94-7.00 (m, 3H), 7.25-7.29 (m, 2H), 7.31-7.42 (m, 1H), 7.40 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.46 (d, *J* = 7.5, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 81.0, 116.4, 116.7, 121.2, 126.8, 128.0, 128.8, 129.5, 138.2, 140.4, 158.1.

General Procedure for Iridium-Catalyzed Allylic Substitution of Racemic Aromatic Allylic Benzoates

In a nitrogen-filled dry-box, the catalyst precursor **1b** (0.0046 g, 0.0050 mmol, 0.020 equiv) and THF (1 mL) were added to a 1-dram vial. To a separate 1-dram vial were added the appropriate nucleophile (0.250 mmol, 1.00 equiv) and THF (1 mL). The vials were sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and cooled to 0 °C. Then, a pre-cooled (0 °C), degassed solution of the appropriate branched aromatic allylic benzoate (**2f-2m**, 0.550 mmol, 2.20 equiv) in THF (1 mL) was added to the solution containing the catalyst precursor. This mixture was stirred at 0 °C for 2-4 h to isomerize the faster reacting enantiomer of the branched allylic benzoate to the linear isomer. Then, the resulting mixture of the allylic benzoate isomers and the catalyst was added to the solution or suspension containing the

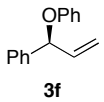
nucleophile. The reaction mixture was stirred an additional 12-16 h at 0 °C. The vial was removed from the cold bath, and the reaction mixture was filtered through a 0.5 inch plug of silica gel (eluting with Et_2O). The crude reaction mixture was concentrated under reduced pressure. $CDCl_3$ (0.7-0.8 mL) was added to dissolve the crude reaction mixture, and mesitylene (11 μL) was added as an internal standard. The branched-to-linear ratio of products **3-9** (>95:5) and yield of linear allylic benzoate **10** were then determined by ^{1}H NMR spectroscopy. After this analysis, the crude reaction mixture was dry-loaded onto silica gel (approximately 1 g) and purified by flash column silica gel chromatography (eluting with hexanes:EtOAc) on a Teledyne Isco CombiFlash Rf automated chromatography system with a RediSep Rf Gold (12 g) normal-phase silica column to yield product **3f-3m** or **4b**, **5b**, **7b**, **7c**, **8b**, or **9b**.

Table S2. Ir-Catalyzed Allylic Substitution of Racemic Aromatic Allylic Benzoates



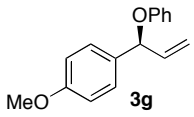
entry	R (**2**)	nucleophile	product **3-9**	yield **3-9** (%)[a]	ee **3-9** (%)[b]	**10**	yield **10** (%)[c]
1	Ph (**2f**)	NaOPh	**3f**	81	96	**10f**	50
2	4-MeO-C_6H_4 (**2g**)	NaOPh	**3g**	90	95	**10g**	49
3	4-F_3C-C_6H_4 (**2h**)	NaOPh	**3h**	86	95	**10h**	51
4	4-Br-C_6H_4 (**2i**)	NaOPh	**3i**	84	98	**10i**	51
5	3-Br-C_6H_4 (**2j**)	NaOPh	**3j**	95	98	**10j**	50
6	2-F-C_6H_4 (**2k**)	NaOPh	**3k**	87	94	**10k**	51
7[d]	2-Me-C_6H_4 (**2l**)	NaOPh	**3l**	83	-84	**10l**	8
8	3-pyridyl (**2m**)	NaOPh	**3m**	86	92	**10m**	48
9	Ph (**2f**)	$LiN(Boc)_2$	**4b**	92	93	**10f**	52
10[f]	Ph (**2f**)	$KNHC(O)CF_3$	**5b**	76	92	**10f**	52
11	Ph (**2f**)	NaTs	**7b**	75	96	**10f**	51
12[d]	2-Me-C_6H_4 (**2l**)	NaTs	**7c**	93	-94	**10f**	5
13	Ph (**2f**)	$NaCH(CO_2Me)_2$	**8b**	87	98	**10f**	51
14	Ph (**2f**)	$NaCH(CN)_2$	**9b**	83	91	**10f**	52

[a] Isolated yield of **3-9**. [b] Enantiomeric excess of **3-9** determined by chiral HPLC methods. [c] Yield of **10** (based on **2**) determined by ^{1}H NMR spectroscopy with mesitylene as the internal standard. [d] Nucleophile was added prior to isomerization. [e] Allylic substitution was run at 0 °C to rt in the presence of 4 mol % **1b**.

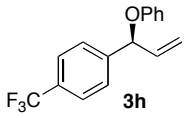


3f

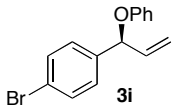
(*S*)-(1-phenoxyallyl)benzene (3f):[17] Prepared according to the general procedure from **2f** (0.131 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol). Isomerization occurred over 2 h prior to addition of the nucleophile (total reaction time = 16 h). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **3f** as a colorless oil in 81% yield (0.0428 g, 0.204 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 33.7 min (major); t_R 39.4 min (minor) [Chiralcel OJ-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.7:0.3, 0.8 mL/min] to be 96%.



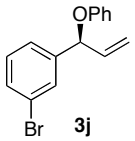
(*S*)-1-methoxy-4-(1-phenoxyallyl)benzene (3g):[17] Prepared according to the general procedure from **2g** (0.148 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol). Isomerization occurred over 4 h prior to addition of the nucleophile (total reaction time = 18 h). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **3f** as a colorless oil in 90% yield (0.0542 g, 0.226 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 12.2 min (minor); t_R 14.8 min (major) [Chiralcel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.5:0.5, 0.6 mL/min] to be 95%. $[\alpha]_D^{26}$ = -10.5° (c 0.98, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.82 (s, 3H), 5.28 (ddd, *J* = 10.5, 1.5, 1.5 Hz, 1H), 5.36 (ddd, *J* = 17.5, 1.5, 1.5 Hz, 1H), 5.65 (d, *J* = 6.0 Hz, 1H), 6.13 (ddd, *J* = 17.5, 10.5, 6.0 Hz, 1H), 6.91-6.95 (m, 3H), 6.95-6.99 (m, 2H), 7.24-7.28 (m, 2H), 7.37 (ddd, *J* = 8.5, 2.5, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.4, 80.6, 114.2, 116.4 (aromatic *C*H), 116.4 (=*C*H$_2$), 121.1, 128.2, 129.5, 132.4, 138.3, 158.1, 159.4.



(*S*)-1-(1-phenoxyallyl)-4-(trifluoromethyl)benzene (3h):[13] Prepared according to the general procedure from **2h** (0.168 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol). Isomerization occurred over 4 h prior to addition of the nucleophile (total reaction time = 20 h). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **3h** as a colorless oil in 86% yield (0.0596 g, 0.214 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 7.6 min (minor); t_R 8.4 min (major) [Chiralcel OJ-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 95%. $[\alpha]_D^{26}$ = +16.5° (c 0.63, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.32 (ddd, *J* = 10.5, 1.5, 1.0 Hz, 1H), 5.40 (ddd, *J* = 17.5, 1.5, 1.0 Hz, 1H), 5.71 (d, *J* = 6.0 Hz, 1H), 6.09 (ddd, *J* = 17.5, 10.5, 6.0 Hz, 1H), 6.93-6.99 (m, 3H), 7.25-7.29 (m, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 80.4, 116.3, 117.6, 121.6, 124.3 (q, *J* = 271.3 Hz), 125.9 (q, *J* = 3.9 Hz), 127.1, 129.7, 130.2 (q, *J* = 32.1 Hz), 137.5, 144.4, 157.7. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -63.0.

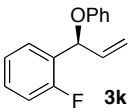


(*S*)-1-bromo-4-(1-phenoxyallyl)benzene (3i):[13] Prepared according to the general procedure from **2i** (0.174 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol). Isomerization occurred over 4 h prior to addition of the nucleophile (total reaction time = 16 h). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **3i** as a colorless oil in 84% yield (0.0605 g, 0.209 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 18.5 min (minor); t_R 22.2 min (major) [Chiralcel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.7:0.3, 0.6 mL/min] to be 98%. $[\alpha]_D^{26}$ = +1.5° (c 1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.30 (ddd, *J* = 10.5, 1.5, 1.0 Hz, 1H), 5.37 (ddd, *J* = 17.0, 1.5, 1.0 Hz, 1H), 5.63 (d, *J* = 6.0 Hz, 1H), 6.09 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 6.93-6.98 (m, 3H), 7.24-7.29 (m, 2H), 7.31-7.33 (m, 2H), 7.50-7.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 80.4, 116.4, 117.2, 121.5, 122.0, 128.6, 129.7, 132.0, 137.8, 139.5, 157.9.



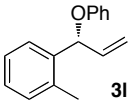
(*S*)-1-bromo-3-(1-phenoxyallyl)benzene (3j):[13] Prepared according to the general procedure from **2j** (0.174 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol). Isomerization occurred over 4 h prior to addition of the nucleophile (total reaction time = 20 h). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **3j** as a colorless oil in 95% yield (0.0684 g,

0.237 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 10.9 min (major); t_R 13.0 min (minor) [Chiralcel OJ-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 98%. $[\alpha]_D^{26}$ = +10.9° (c 1.23, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 5.31 (ddd, *J* = 10.5, 1.5, 1.0, 1H), 5.39 (ddd, *J* = 17.0, 1.5, 1.0 Hz, 1H), 5.62 (d, *J* = 6.0 Hz, 1H), 6.08 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 6.95-6.99 (m, 3H), 7.25-7.29 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.45 (ddd, 8.0, 2.0, 2.0 Hz, 1H), 7.61 (dd, *J* = 2.0, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 80.3, 116.4, 117.3, 121.5, 123.0, 125.4, 129.6, 129.9, 130.4, 131.1, 137.5, 142.7, 157.8.



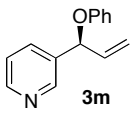
3k

(*S*)-1-fluoro-2-(1-phenoxyallyl)benzene (3k): Prepared according to the general procedure from **2k** (0.141 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol). Isomerization occurred over 2 h prior to addition of the nucleophile (total reaction time = 18 h). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **3j** as a colorless oil in 87% yield (0.0494 g, 0.216 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 5.8 min (major); t_R 10.4 min (minor) [Chiralcel OB-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 94%. $[\alpha]_D^{25}$ = +15.5° (c 0.52, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 5.30 (d, *J* = 10.5 Hz, 1H), 5.42 (d, *J* = 17.5 Hz, 1H), 6.04 (d, *J* = 5.5 Hz, 1H), 6.15 (ddd, *J* = 17.5, 10.5, 5.5 Hz, 1H), 6.93-6.99 (m, 3H), 7.10 (ddd, *J* = 8.0, 7.5, 1.0 Hz, 1H), 7.16 (app dt, 1.0, 7.5 Hz, 1H), 7.24-7.32 (m, 3H), 7.52 (app dt, *J* = 1.5, 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 74.0, 115.6 (d, *J* = 21.4 Hz), 116.1, 116.8, 121.4, 124.8 (d, *J* = 2.9 Hz), 127.6 (d, *J* = 13.6 Hz, 1H), 128.2 (d, *J* = 3.9 Hz), 129.57, 129.61, 136.8, 158.4 (d, *J* = 167.1 Hz), 161.0. Anal. Calcd. for $C_{15}H_{13}FO$: C, 78.93; H, 5.74; N, 0.00; found: C, 78.87; H, 5.80; N, <0.02. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -119.6.



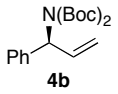
3l

(*R*)-1-methyl-2-(1-phenoxyallyl)benzene (3l): Prepared according to a modified version of the general procedure from **2l** (0.139 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol). In a nitrogen-filled dry-box, the catalyst precursor **1b** (0.0046 g, 0.0050 mmol, 0.020 equiv), NaOPh (0.0290 g, 0.250 mmol), and THF (2 mL) were added to a 1-dram vial. The vial was sealed with a PTFE/silicone-line septum cap, removed from the dry-box, and cooled to 0 °C. Then, a pre-cooled (0 °C), degassed solution of the branched aromatic allylic benzoate **2l** (0.139 g, 0.550 mmol, 2.20 equiv) in THF (1 mL) was added to the solution containing the catalyst precursor and nucleophile. The reaction mixture was stirred for 16 h at 0 °C. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **3l** as a colorless oil in 83% yield (0.0463 g, 0.206 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 5.8 min (minor); t_R 9.3 min (major) [Chiralcel OB-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 84%. $[\alpha]_D^{25}$ = -39.8° (c 1.08, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 2.43 (s, 3H), 5.29-5.34 (m, 2H), 5.82 (d, *J* = 5.5 Hz, 1H), 6.14 (ddd, *J* = 17.5, 10.5, 5.5 Hz, 1H), 6.90-6.96 (m, 3H), 7.20-7.28 (m, 5H), 7.48-7.52 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.5, 78.0, 116.0, 117.0, 121.1, 126.6, 126.8, 128.0, 129.5, 130.8, 135.4, 136.8, 138.0, 158.1. Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19; N, 0.00; found: C, 85.42; H, 7.22; N, <0.02.



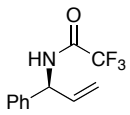
3m

(*S*)-3-(1-phenoxyallyl)pyridine (3m): Prepared according to the general procedure from **2m** (0.131 g, 0.550 mmol) and NaOPh (0.0290 g, 0.250 mmol). Isomerization occurred over 4 h prior to addition of the nucleophile (total reaction time = 20 h). The crude mixture was purified by flash column chromatography (100:0 to 75:25 hexanes:EtOAc) to give **3m** as a yellow oil in 86% yield (0.0455 g, 0.215 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 6.0 min (major); t_R 11.4 min (minor) [Chiralcel AS-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 92%. $[\alpha]_D^{25}$ = +3.1° (c 0.32, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.34 (d, *J* = 10.5 Hz, 1H), 5.40 (d, *J* = 17.5 Hz, 1H), 5.71 (d, *J* = 6.0 Hz, 1H), 6.09 (ddd, *J* = 17.5, 10.5, 6.0 Hz, 1H), 6.93-6.98 (m, 3H), 7.24-7.28 (m, 2H), 7.31 (dd, *J* = 8.0, 5.0 Hz 1H), 7.76 (ddd, *J* = 8.0, 2.0, 1.5 Hz, 1H), 8.55 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.68 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 78.8, 116.4, 117.8, 121.6, 123.8, 129.7, 134.5, 135.9, 137.2, 148.7, 149.5, 157.6. Anal. Calcd. for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63; found: C, 79.28; H, 6.01; N, 6.26.



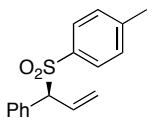
4b

(*S*)-*N*,*N*-bis-Boc-1-phenylprop-2-en-1-amine (4b):[18] Prepared according to the general procedure from **2f** (0.131 g, 0.550 mmol) and $LiN(Boc)_2$ (0.0558 g, 0.250 mmol). Isomerization occurred over 3 h prior to addition of the nucleophile (total reaction time = 19 h). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give **4b** as a white amorphous solid in 92% yield (0.0769 g, 0.231 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 4.8 min (minor); t_R 5.8 min (major) [Chiralcel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.5:0.5, 1.0 mL/min] to be 93%. $[\alpha]_D^{25}$ = -37.0° (c 1.30, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.31 (s, 18H), 5.27-5.32 (m, 2H), 5.86 (d, *J* = 8.0 Hz, 1H), 6.33 (ddd, *J* = 18.0, 10.0, 8.0 Hz, 1H), 7.15-7.31 (m, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.8, 61.8, 82.3, 119.2, 126.4, 126.8, 128.1, 135.4, 140.3, 152.3.



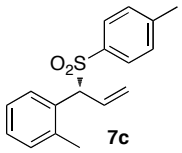
5b

(*S*)-2,2,2-trifluoro-*N*-(1-phenylallyl)acetamide (5b):[18] Prepared according a modified version of the general procedure from **2f** (0.131 g, 0.550 mmol) and $KNHC(O)CF_3$ (0.0378 g, 0.250 mmol) in the presence of 4 mol % of the catalyst precursor **1b** (0.0093 g, 0.010 mmol, 0.040 equiv). Isomerization occurred at 0 °C over 2 h prior to addition of the nucleophile. The reaction was stirred at 0 °C for 10 h after addition of the nucleophile, then allowed to warm to room temperature and stir for an additional 6 h. The crude mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to give **5b** as a white amorphous solid in 76% yield (0.0437 g, 0.191 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 10.4 min (minor); t_R 11.2 min (major) [Chiralcel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 92%. $[\alpha]_D^{25}$ = -108.6° (c 0.71, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.27 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.35 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.63 (br t, *J* = 7.0 Hz, 1H), 6.03 (ddd, *J* = 17.0, 10.5, 5.0 Hz, 1H), 6.61 (br s, 1H), 7.29-7.42 (m, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 56.0, 116.0 (q, 287.6 Hz), 117.5, 127.4, 128.7, 129.3, 135.5, 138.6, 156.5 (q, 37.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ -75.9.



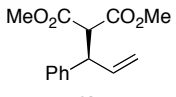
7b

(*S*)-1-methyl-4-((1-phenylallyl)sulfonyl)benzene (7b):[14] Prepared according to the general procedure from **2f** (0.131 g, 0.550 mmol) and NaTs (0.0445 g, 0.250 mmol). Isomerization occurred over 2 h prior to addition of the nucleophile (total reaction time = 14 h). The crude mixture was purified by flash column chromatography (100:0 to 75:25 hexanes:EtOAc) to give **7b** as a white amorphous solid in 75% yield (0.0510 g, 0.187 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 13.9 min (minor); t_R 15.6 min (major) [Chiralcel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 96%. $[\alpha]_D^{25}$ = -56.6° (c 0.58, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.41 (s, 3H), 4.69 (d, *J* = 9.0 Hz, 1H), 5.31 (d, *J* = 17.5 Hz, 1H), 5.45 (d, *J* = 10.5 Hz, 1H), 6.31 (ddd, *J* = 17.5, 10.5, 9.0 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.24-7.33 (m, 5H), 7.52 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.8, 75.8, 123.6, 128.7, 129.0, 129.4, 129.5, 129.6, 129.9, 132.4, 134.5, 144.7.



7c

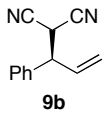
(*R*)-1-methyl-2-(1-tosylallyl)benzene (7c): Prepared according to a modified version of the general procedure from **2l** (0.139 g, 0.550 mmol) and NaTs (0.0445 g, 0.250 mmol). In a nitrogen-filled dry-box, the catalyst precursor **1b** (0.0046 g, 0.0050 mmol, 0.020 equiv), NaTs (0.0445 g, 0.250 mmol), and THF (2 mL) were added to a 1-dram vial. The vial was sealed with a PTFE/silicone-line septum cap, removed from the dry-box, and cooled to 0 °C. Then, a pre-cooled (0 °C), degassed solution of the branched aromatic allylic benzoate **2l** (0.139 g, 0.550 mmol, 2.20 equiv) in THF (1 mL) was added to the solution containing the catalyst precursor and nucleophile. The reaction mixture was stirred for 12 h at 0 °C. The crude mixture was purified by flash column chromatography (100:0 to 75:25 hexanes:EtOAc) to give **7c** as a white amorphous solid in 93% yield (0.0667 g, 0.233 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 15.5 min (minor); t_R 17.3 min (major) [Chiralcel AS-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 94%. $[\alpha]_D^{26}$ = +37.3° (c 1.08, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.12 (s, 3H), 2.40 (s, 3H), 5.02 (d, *J* = 8.5 Hz, 1H), 5.26 (d, *J* = 17.0 Hz, 1H), 5.42 (d, *J* = 10.5 Hz, 1H), 6.29 (ddd, *J* = 17.0, 10.5, 8.5 Hz, 1H), 7.09 (dd, *J* = 6.5, 2.5 Hz, 1H), 7.19-7.25 (m, 4H), 7.50-7.53 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.7, 21.7, 70.8, 123.4, 126.4, 128.7, 129.0, 129.3, 129.4, 130.1, 130.7 (2 carbons), 134.8, 137.5, 144.7. Anal. Calcd. for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34; N, 0.00; found: C, 71.34; H, 6.56; N, <0.02.



8b

(*R*)-dimethyl 2-(1-phenylallyl)malonate (8b):[19] Prepared according to a modified version of the general procedure from **2f** (0.131 g, 0.550 mmol) and sodium dimethyl malonate (0.250 mmol). A solution of sodium dimethyl malonate in THF (1 mL) was prepared from dimethyl malonate (0.0330 g, 0.250 mmol) and NaH (0.0060 g, 0.25 mmol). The catalyst and nucleophile were added as described in the general procedure. Isomerization occurred over 3 h prior to addition of the nucleophile (total reaction time = 17 h). The crude mixture was purified by flash column chromatography (100:0 to 90:10 hexanes:EtOAc) to give **8b** as a white amorphous solid in 87% yield (0.0541 g, 0.218 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 30.8 min (minor); t_R 32.8 min (major) [Chiralcel OJ-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 0.5 mL/min] to be 98%. $[\alpha]_D^{26}$ = +94.9° (c 0.88, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.49 (s, 3H), 3.74 (s, 3H), 3.87 (d, *J* = 11.0 Hz, 1H), 4.11 (dd, *J* = 11.0, 8.5 Hz, 1H), 5.08 (d, *J* = 10.5 Hz, 1H), 5.12 (d, *J* = 17.0 Hz, 1H), 5.99 (ddd, *J* = 17.0, 10.5, 8.5 Hz,

1H), 7.20-7.24 (m, 3H), 7.28-7.32 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 49.9, 52.6, 52.8, 57.5, 116.8, 127.3, 128.1, 128.8, 138.0, 140.1, 168.0, 168.4.



9b

(*R*)-2-(1-phenylallyl)malononitrile (9b):[20] Prepared according to a modified version of the general procedure from **2f** (0.131 g, 0.550 mmol) and the sodium salt of malononitrile (0.250 mmol). A solution of the sodium salt of malononitrile in THF (1 mL) was prepared from malononitrile (0.0165 g, 0.250 mmol) and NaH (0.0060 g, 0.25 mmol). The catalyst and nucleophile were added as described in the general procedure. Isomerization occurred over 2 h prior to addition of the nucleophile (total reaction time = 18 h). The crude mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to give **9b** as a colorless oil in 83% yield (0.0378 g, 0.207 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 17.3 min (major); t_R 19.4 min (minor) [Chiralcel AS-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 91%. $[\alpha]_D^{24}$ = +41.4° (c 0.54, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.94 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.01 (d, *J* = 7.0 Hz, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.49 (d, *J* = 10.5 Hz, 1H), 6.17 (ddd, *J* = 17.0, 10.5, 7.5 Hz, 1H), 7.32-7.35 (m, 2H), 7.34-7.45 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.9, 50.3, 111.7, 111.8, 121.2, 128.0, 129.2, 129.6, 133.3, 136.3. Anal. Calcd. for $C_{12}H_{10}N_2$: C, 79.10; H, 5.53; N, 15.37; found: C, 78.88; H, 5.80; N, 15.34.

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