



Supporting Information

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**Regio- and Enantioselective *O*-Allylation of Phenol and Alcohol Catalyzed by
Planar-Chiral Cyclopentadienyl-Ruthenium Complex**

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General. All reactions were carried out under Ar atmosphere using Schlenk technique, whereas the workup was performed in air. ^1H , ^{13}C and ^{31}P NMR spectra were recorded in acetone- d_6 or CDCl_3 on JEOL JNM-LA400, -LA600 and Bruker ARX400 spectrometers using SiMe_4 as an internal standard for ^1H and ^{13}C nuclei, and H_3PO_4 as an external standard for ^{31}P nucleus. Mass spectra were obtained with JEOL JMS-600H instrument. Enantiomeric excess was determined with HPLC (JASCO UV-1570 and PU-1580) using DAICEL Chiralcel OD-H and OJ-H columns. Elemental analysis was performed by the Materials Analysis Center, ISIR, Osaka University.

Materials. Anhydrous THF was purchased and deoxygenated with freeze-thaw cycle before use. Ruthenium complexes **1** were prepared as reported previously.¹ *p*-Trifluoromethylcinnamyl chloride **2f** was prepared by the known method.² The other cinnamyl chloride derivatives **2g–2i** were prepared by the similar method to that for analogous bromides,³ and were purified by distillation using glass tube oven. Phenol derivatives were available from commercial source and used without further purification.

Standard method for allylation of phenol derivatives. To a solution of cinnamyl chloride derivative (1.0 mmol) in THF (0.3 mL) was added $\text{Cp}'\text{-Ru}$ catalyst (15 μmol , 3 mol%), and the reaction mixture was stirred at room temperature for 20 min. After potassium carbonate (207 mg, 1.5 mmol) and THF (1 mL) was added, a THF solution (0.7 mL) of phenol derivative (0.5 mmol) was then syringed. After stirring at 30 °C for 24 h, the reaction mixture was diluted with diethyl ether, and the insoluble parts were filtered through Celite. The solvent was evaporated, and diethylamine (*ca.* 1 mL) was added to the resulting brown oil. After stirring at room temperature for 2 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography with hexane to give colorless oil.

The reactions with benzyl alcohol and methanol were performed by using cinnamyl chloride (0.5 mmol), alcohol (5 mmol) and potassium carbonate (5 mmol) with $\text{Cp}'\text{-Ru}$ catalyst (15 μmol) in THF (2 mL). In the workup isolating **4i**, **4j** and **4o**, the crude products were not treated with diethylamine. Resulting allylic ethers were characterized by spectral analyses referred to the reported data except for new compounds **4c** and **4e**. Spectral data and the conditions for HPLC analyses are as follows. Copies of ^1H NMR spectra of **4a–4o** were given in the last part.

(R)-1-Phenyl-1-(*o*-methylphenoxy)prop-2-ene^{4,5} (4a**):** ^1H NMR (CDCl_3 , 400 MHz): δ 7.43–7.40 (m, 2H, Ar), 7.37–7.33 (m, 2H, Ar), 7.30–7.23 (m, 1H, Ar), 7.14 (dd, 1H, J = 7.4, 0.8 Hz, Ar), 7.06–7.01 (m, 1H, Ar), 6.82 (dt, 1H, J = 7.4, 1.1 Hz, Ar), 6.78 (d, 1H, J = 1.2 Hz, Ar),

6.08 (ddd, 1H, J = 17.3, 10.5, 5.8 Hz, CH=), 5.63 (d, 1H, J = 5.8 Hz, CH), 5.37 (dt, 1H, J = 17.3, 1.3 Hz, CH=), 5.23 (dt, 1H, J = 10.5, 1.3 Hz, CH=), 2.32 (s, 3H, Me). ^{13}C NMR (CDCl₃, 151 MHz): δ 156.0, 140.5, 138.4, 130.7, 128.6, 127.7, 127.6, 126.5, 126.4, 120.6, 116.0, 113.4, 80.7, 16.6. $[\alpha]_D^{25} = -8.5$ (c 1.1, CHCl₃) for 89% ee. HPLC analysis: Chiralcel OD-H column, hexane/*i*PrOH = 997/3 (v/v), 0.4 mL/min, 274 nm; major enantiomer t_R = 15.3 min, minor enantiomer t_R = 14.5 min.

1-Phenyl-1-phenoxyprop-2-ene^{5,6} (4b): ^1H NMR (CDCl₃, 400 MHz): δ 7.41 (d, 2H, J = 7.2 Hz, Ar), 7.35 (t, 2H, J = 7.5 Hz, Ar), 7.30–7.20 (m, 3H, Ar), 6.95–6.89 (m, 3H, Ar), 6.10 (ddd, 1H, J = 17.2, 10.4, 6.0 Hz, CH=), 5.63 (d, 1H, J = 6.0 Hz, CH), 5.34 (d, 1H, J = 17.2 Hz, CH=), 5.25 (d, 1H, J = 10.4 Hz, CH=). ^{13}C NMR (CDCl₃, 151 MHz): δ 157.9, 140.1, 138.0, 129.3, 128.6, 127.8, 126.6, 121.0, 116.5, 116.2, 80.8. HPLC analysis: Chiralcel OJ-H column, hexane/*i*PrOH = 997/3 (v/v), 0.8 mL/min, 254 nm; major enantiomer t_R = 35.3 min, minor enantiomer t_R = 38.5 min.

1-Phenyl-1-(*m*-methylphenoxy)prop-2-ene (4c): ^1H NMR (CDCl₃, 400 MHz): δ 7.35–7.32 (m, 2H, Ar), 7.30–7.26 (m, 2H, Ar), 7.23–7.18 (m, 1H, Ar), 7.03 (t, 1H, J = 7.8 Hz, Ar), 6.72 (s, 1H, Ar), 6.67–6.65 (m, 2H, Ar), 6.03 (ddd, 1H, J = 17.2, 10.4, 5.9 Hz, CH=), 5.57 (d, 1H, J = 5.9 Hz, CH), 5.29 (dt, 1H, J = 17.2, 1.3 Hz, CH=), 5.20 (dt, 1H, J = 10.4, 1.3 Hz, CH=), 2.26 (s, 3H, Me). ^{13}C NMR (CDCl₃, 151 MHz): δ 157.9, 140.2, 139.3, 138.0, 129.0, 128.6, 127.7, 126.6, 121.8, 117.1, 116.4, 112.8, 80.6, 21.5. HR-MS (*m/z*): [M + Na]⁺ calcd for C₁₆H₁₆ONa: 247.1099; found: 247.1108. $[\alpha]_D^{20} = -7.3$ (c 1.5, CHCl₃) for 85% ee. HPLC analysis: Chiralcel OD-H column, hexane/*i*PrOH = 997/3 (v/v), 0.4 mL/min, 274 nm; major enantiomer t_R = 14.5 min, minor enantiomer t_R = 15.3 min.

1-Phenyl-1-(*p*-methylphenoxy)prop-2-ene⁵ (4d): ^1H NMR (CDCl₃, 400 MHz): δ 7.35–7.32 (m, 2H, Ar), 7.30–7.25 (m, 2H, Ar), 7.22–7.18 (m, 2H, Ar), 7.95 (d, 2H, J = 8.8 Hz, Ar), 6.76 (d, 2H, J = 8.8 Hz, Ar), 6.03 (ddd, 1H, J = 17.2, 10.4, 6.0 Hz, CH=), 5.53 (d, 1H, J = 6.0 Hz, CH), 5.28 (dt, 1H, J = 17.2, 1.3 Hz, CH=), 5.19 (dt, 1H, J = 10.4, 1.3 Hz, CH=), 2.22 (s, 3H, Me). ^{13}C NMR (CDCl₃, 151 MHz): δ 155.8, 140.3, 138.1, 130.2, 129.8, 128.6, 127.8, 126.6, 116.4, 116.1, 81.0, 20.5. HPLC analysis: Chiralcel OD-H column, hexane/*i*PrOH = 999/1 (v/v), 0.4 mL/min, 274 nm; major enantiomer t_R = 23.2 min, minor enantiomer t_R = 25.8 min.

1-Phenyl-1-(*o*-*tert*-butylphenoxy)prop-2-ene (4e): ^1H NMR (CDCl₃, 400 MHz): δ 7.43–7.26 (m, 6H, Ar), 7.07–7.03 (m, 1H, Ar), 6.85 (dt, 1H, J = 7.6, 1.3 Hz, Ar), 6.78 (d, 1H, J = 8.2 Hz, Ar), 6.14 (ddd, 1H, J = 17.2, 10.5, 6.0 Hz, CH=), 5.69 (d, 1H, J = 6.0 Hz, CH), 5.34 (dt, 1H, J = 17.2, 1.2 Hz, CH=), 5.23 (dt, 1H, J = 10.5, 1.2 Hz, CH=), 1.44 (s, 9H, ³Bu). ^{13}C NMR

(CDCl₃, 151 MHz): δ 156.4, 140.4, 138.2, 138.1, 128.7, 127.7, 126.8, 126.7, 126.6, 120.2, 116.2, 113.5, 81.0, 34.9, 29.8. HR-MS (*m/z*): [M + Na]⁺ calcd for C₁₉H₂₂ONa: 289.1568; found: 289.1567. $[\alpha]_D^{20} = -29.8$ (*c* 1.3, CHCl₃) for 90% ee. HPLC analysis: Chiralcel OD-H column, hexane/ⁱPrOH = 999/1 (v/v), 0.4 mL/min, 274 nm; major enantiomer *t*_R = 16.9 min, minor enantiomer *t*_R = 15.1 min.

1-Phenyl-1-(*o*-phenylphenoxy)prop-2-ene⁵ (4f): ¹H NMR (CDCl₃, 400 MHz): δ 7.52–7.49 (m, 2H, Ar), 7.36–7.31 (m, 2H, Ar), 7.29–7.10 (m, 8H, Ar), 6.93 (dt, 1H, *J* = 7.4, 1.2 Hz, Ar), 6.86 (dd, 1H, *J* = 8.3, 1.2 Hz, Ar), 5.89 (ddd, 1H, *J* = 17.2, 10.4, 5.9 Hz, CH=), 5.53 (d, 1H, *J* = 5.9 Hz, CH), 5.18 (dt, 1H, *J* = 17.2, 1.3 Hz, CH=), 5.07 (dt, 1H, *J* = 10.4, 1.3 Hz, CH=). ¹³C NMR (CDCl₃, 151 MHz): δ 154.6, 140.2, 138.7, 138.1, 132.0, 130.9, 129.7, 128.5, 128.3, 127.8, 127.6, 126.8, 126.5, 121.4, 115.9, 115.4, 81.7. HPLC analysis: Chiralcel OJ-H column, hexane/ⁱPrOH = 999/1 (v/v), 0.1 mL/min, 274 nm; major enantiomer *t*_R = 120 min, minor enantiomer *t*_R = 140 min.

(R)-1-Phenyl-1-(*p*-trifluoromethylphenoxy)prop-2-ene^{4,5} (4g): ¹H NMR (CDCl₃, 400 MHz): δ 7.41 (dd, 2H, *J* = 9.0, 0.6 Hz, Ar), 7.34–7.21 (m, 5H, Ar), 6.94 (dd, 2H, *J* = 9.0, 0.6 Hz, Ar), 6.03 (ddd, 1H, *J* = 17.2, 10.4, 5.9 Hz, CH=), 5.62 (d, 1H, *J* = 5.9 Hz, CH), 5.30 (dt, 1H, *J* = 17.2, 1.2 Hz, CH=), 5.24 (dt, 1H, *J* = 10.4, 1.2 Hz, CH=). ¹³C NMR (CDCl₃, 151 MHz): δ 160.4, 139.4, 137.3, 128.9, 128.2, 126.8 (q, *J*_{C-F} = 4 Hz), 126.6, 124.5 (q, *J*_{C-F} = 271 Hz), 123.1 (q, *J*_{C-F} = 33 Hz), 117.0, 116.1, 81.0. $[\alpha]_D^{24} = -7.5$ (*c* 0.96, CHCl₃) for 93% ee. HPLC analysis: Chiralcel OJ-H column, hexane/ⁱPrOH = 997/3 (v/v), 0.7 mL/min, 274 nm; major enantiomer *t*_R = 19.4 min, minor enantiomer *t*_R = 16.1 min.

1-Phenyl-1-(*p*-chlorophenoxy)prop-2-ene⁵ (4h): ¹H NMR (CDCl₃, 400 MHz): δ 7.33–7.20 (m, 5H, Ar), 7.10 (d, 2H, *J* = 9.0 Hz, Ar), 6.79 (d, 2H, *J* = 9.0 Hz, Ar), 6.02 (ddd, 1H, *J* = 17.2, 10.5, 6.0 Hz, CH=), 5.52 (d, 1H, *J* = 6.0 Hz, CH), 5.28 (dt, 1H, *J* = 17.2, 1.3 Hz, CH=), 5.21 (dt, 1H, *J* = 10.5, 1.3 Hz, CH=). ¹³C NMR (CDCl₃, 151 MHz): δ 156.4, 139.6, 137.6, 129.2, 128.7, 128.0, 126.6, 125.9, 117.5, 116.7, 81.2. HPLC analysis: Chiralcel OJ-H column, hexane/ⁱPrOH = 997/3 (v/v), 0.8 mL/min, 274 nm; major enantiomer *t*_R = 36.3 min, minor enantiomer *t*_R = 32.2 min.

(R)-1-Phenyl-1-benzyloxyprop-2-ene⁷ (4i): ¹H NMR (CDCl₃, 400 MHz): δ 7.39–7.25 (m, 10H, Ar), 5.92 (ddd, 1H, *J* = 17.2, 10.3, 6.7 Hz, CH=), 5.30 (dt, 1H, *J* = 17.2, 1.5 Hz, CH=), 5.23 (ddd, 1H, *J* = 10.3, 1.5, 1.1 Hz, CH=), 4.79 (dt, 1H, *J* = 6.7, 1.1 Hz, CH), 4.48 (s, 2H, CH₂). ¹³C NMR (CDCl₃, 151 MHz): δ 141.0, 138.9, 138.5, 128.5, 128.4, 127.7, 127.5, 127.0, 116.5, 82.0, 70.1. $[\alpha]_D^{23} = + 11.7$ (*c* 1.0, CHCl₃) for 72% ee. HPLC analysis: Chiralcel OJ-H column,

hexane/*i*PrOH = 997/3 (v/v), 0.4 mL/min, 254 nm; major enantiomer t_R = 68 min, minor enantiomer t_R = 61 min.

1-Phenyl-1-methoxyprop-2-ene⁸ (4j): ¹H NMR (CDCl₃, 400 MHz): δ 7.38–7.25 (m, 5H, Ar), 5.93 (ddd, 1H, J = 17.2, 10.3, 6.8 Hz, CH=), 5.27 (dt, 1H, J = 17.2, 1.5 Hz, CH=), 5.21 (ddd, 1H, J = 10.2, 1.5, 1.1 Hz, CH=), 4.62 (dt, 1H, J = 6.8, 1.1 Hz, CH), 3.33 (s, 3H, Me). ¹³C NMR (CDCl₃, 151 MHz): δ 140.9, 138.8, 128.5, 127.7, 126.8, 116.4, 84.7, 56.4. HPLC analysis: Chiralcel OD-H column, hexane/*i*PrOH = 997/3 (v/v), 0.4 mL/min, 254 nm; major enantiomer t_R = 12.0 min, minor enantiomer t_R = 14.5 min.

1-(*p*-Trifluoromethylphenyl)-1-phenoxyprop-2-ene⁶ (4k): ¹H NMR (CDCl₃, 400 MHz): δ 7.62 (d, 2H, J = 8.1 Hz, Ar), 7.54 (d, 2H, J = 8.1 Hz, Ar), 7.27–7.22 (m, 2H, Ar), 6.96–6.91 (m, 3H, Ar), 6.07 (ddd, 1H, J = 17.2, 10.4, 6.0 Hz, CH=), 5.69 (d, 1H, J = 6.0 Hz, CH), 5.38 (dt, 1H, J = 17.2, 1.2 Hz, CH=), 5.29 (dt, 1H, J = 10.4, 1.2 Hz, CH=). ¹³C NMR (CDCl₃, 151 MHz): δ 157.6, 144.2, 137.3, 130.1 (q, J_{C-F} = 32 Hz), 129.5, 126.9, 125.7 (q, J_{C-F} = 4 Hz), 124.1 (q, J_{C-F} = 272 Hz), 121.4, 117.3, 116.2, 80.2. HPLC analysis: Chiralcel OD-H column, hexane/*i*PrOH = 997/3 (v/v), 0.4 mL/min, 274 nm; major enantiomer t_R = 19.7 min, minor enantiomer t_R = 21.2 min.

1-(*p*-Chlorophenyl)-1-phenoxyprop-2-ene⁶ (4l): ¹H NMR (CDCl₃, 400 MHz): δ 7.36–7.30 (m, 4H, Ar), 7.26–7.20 (m, 2H, Ar), 6.97–6.89 (m, 3H, Ar), 6.04 (ddd, 1H, J = 17.2, 10.4, 5.9 Hz, CH=), 5.61 (d, 1H, J = 5.9 Hz, CH), 5.34 (dt, 1H, J = 17.2, 1.3 Hz, CH=), 5.27 (dt, 1H, J = 10.4, 1.3 Hz, CH=). ¹³C NMR (CDCl₃, 151 MHz): δ 157.7, 138.7, 137.6, 133.6, 129.4, 128.8, 128.0, 121.2, 116.9, 116.2, 80.1. HPLC analysis: Chiralcel OJ-H column, hexane/*i*PrOH = 99/1 (v/v), 1.2 mL/min, 254 nm; major enantiomer t_R = 18.4 min, minor enantiomer t_R = 24.3 min.

1-(*o*-Methoxyphenyl)-1-phenoxyprop-2-ene⁵ (4m): ¹H NMR (CDCl₃, 400 MHz): δ 7.43 (dd, J = 7.5, 1.7 Hz, 1H, Ar), 7.26–7.18 (m, 3H, Ar), 6.96–6.85 (m, 5H, Ar), 6.14–6.05 (m, 2H, CH and CH=), 5.37–5.31 (m, 1H, CH=), 5.18 (dd, 1H, J = 9.3, 1.6 Hz, CH=), 5.27 (dt, 1H, J = 10.4, 1.3 Hz, CH=), 3.88 (s, 3H, Me). ¹³C NMR (CDCl₃, 151 MHz): δ 157.9, 156.2, 137.2, 129.3, 128.7, 128.2, 127.1, 121.0, 120.6, 115.8, 115.4, 110.5, 73.9, 55.5. HPLC analysis: Chiralcel OD-H column, hexane/*i*PrOH = 998/2 (v/v), 0.8 mL/min, 254 nm; major enantiomer t_R = 32.7 min, minor enantiomer t_R = 37.8 min.

1-(1'-Naphthyl)-1-phenoxyprop-2-ene⁶ (4n): ¹H NMR (CDCl₃, 400 MHz): δ 8.14 (d, 1H, J = 8.2 Hz, Ar), 7.89 (dd, 1H, J = 7.5, 2.2 Hz, Ar), 7.80 (d, 1H, J = 8.2 Hz, Ar), 7.65 (d, 1H, J =

6.5 Hz, Ar), 7.56–7.43 (m, 3H, Ar), 7.21–7.17 (m, 2H, Ar), 6.95–6.87 (m, 2H, Ar), 6.34–6.25 (m, 2H, CH and CH=), 5.43–5.29 (m, 2H, CH=). ^{13}C NMR (CDCl₃, 151 MHz): δ 157.9, 137.0, 135.4, 134.0, 130.6, 129.4, 129.0, 128.6, 126.3, 125.7, 125.6, 124.8, 123.4, 121.0, 117.2, 115.9, 77.9. HPLC analysis: Chiralcel OJ-H column, hexane/*i*PrOH = 99/1 (v/v), 1.2 mL/min, 254 nm; major enantiomer $t_{\text{R}} = 41.3$ min, minor enantiomer $t_{\text{R}} = 27.3$ min.

2-Phenoxybut-3-ene⁹ (4o): ^1H NMR (CDCl₃, 400 MHz): δ 7.25 (t, 2H, $J = 8.1$ Hz, Ar), 6.94–6.89 (m, 3H, Ar), 5.92 (ddd, 1H, $J = 17.3, 10.6, 5.8$ Hz, CH=), 5.27 (dt, 1H, $J = 17.3, 1.3$ Hz, CH), 5.16 (dt, 1H, $J = 10.6, 1.3$ Hz, CH=), 4.80 (tq, 1H, $J = 6.3, 1.3$ Hz, CH=), 1.43 (d, 3H, $J = 6.3$ Hz, Me). ^{13}C NMR (CDCl₃, 151 MHz): δ 158.0, 139.2, 129.3, 120.7, 116.0, 115.6, 74.5, 21.3. HPLC analysis: Chiralcel OD-H column, hexane/*i*PrOH = 997/3 (v/v), 0.3 mL/min, 282 nm; major enantiomer $t_{\text{R}} = 17.5$ min, minor enantiomer $t_{\text{R}} = 22.1$ min.

3-Phenyl-1-(*o*-methylphenoxy)prop-2-ene⁷ (5a): White solid. ^1H NMR (CDCl₃, 270 MHz): δ 7.43–7.12 (m, 7H, Ar), 6.89–6.77 (m, 2H, Ar), 6.74 (d, 1H, $J = 16.0$ Hz, CH=), 6.43 (dt, 1H, $J = 16.0, 5.5$ Hz, CH=), 4.71 (dd, 2H, $J = 5.5, 1.2$ Hz, CH₂), 2.28 (s, 3H, Me). ^{13}C NMR (CDCl₃, 151 MHz): δ 156.8, 136.6, 132.3, 130.8, 128.6, 127.8, 127.0, 126.8, 126.6, 125.0, 120.6, 111.4, 68.6, 16.4.

Reaction of (S)-1a with cinnamyl chloride. To a THF solution (0.2 mL) of (S)-1a (150 mg, 0.21 mmol) was added cinnamyl chloride 2a (323 mg, 2.1 mmol), and the reaction mixture was allowed to stand overnight at room temperature. The resulting orange precipitate was filtered and washed with diethyl ether several times. Drying in vacuo gave orange powder of (S_{Cp},R_{Ru},R_{allyl})-6a (126 mg, 80%). ^1H NMR (acetone-*d*₆, 400 MHz): δ 8.00–7.31 (m, 15H, Ph), 7.07 (s, 1H, Cp'), 6.61 (s, 1H, Cp'), 6.55 (dd, 1H, $J = 12.4, 2.0$ Hz, allyl), 5.12–5.02 (m, 1H, OCH₂), 4.35–4.30 (m, 1H, OCH₂), 3.63–3.34 (m, 3H, allyl and CH₂P), 3.02–2.93 (m, 1H, CH₂P), 2.86–2.83 (m, 1H, allyl), 2.10 (s, 3H, CpCH₃), 1.27 (s, 9H, CMe₃). ^{13}C NMR (acetone-*d*₆, 150 MHz): δ 166.6 (C=O), 140.8–127.1 (Ph and Cp'), 112.4, 106.5, 100.0, 93.5, 86.3, 84.2, 61.9 (d, $J = 4$ Hz), 60.7 (d, $J = 4$ Hz), 36.1 (CMe₃), 30.3 (CMe₃), 21.7 (d, $J = 32$ Hz, CH₂P), 11.7 (CpMe). ^{31}P NMR (acetone-*d*₆, 160 MHz): δ 27.4. IR (cm⁻¹, KBr): 1745 (v_{C=O}). FAB-MS (*m/z*): 644 [M-PF₆-1]⁺. Anal. Calcd for C₃₄H₃₇ClF₆O₂P₂Ru: C, 51.68; H, 4.72. Found: C, 51.61; H, 4.74.

Reaction of 1b with cinnamyl chloride. This reaction was performed by a similar manner to that for (S)-1a to give (S^{*}_{Cp},S^{*}_{Ru},S^{*}_{allyl})-6b in 84% yield. ^1H NMR (acetone-*d*₆, 600 MHz): δ 7.84–7.25 (m, 15H, Ph), 6.78 (dd, 1H, $J = 2.3, 12.4$ Hz, allyl), 6.39 (s, 1H, Cp'), 6.14 (s, 1H, Cp'), 4.96 (ddd, 1H, $J = 7.4, 11.5, 24.2$ Hz, OCH₂), 4.46–4.43 (m, 1H, allyl), 3.87–3.82 (m, 1H, OCH₂), 3.63–3.54 (m, 2H, CH₂P and allyl), 2.88 (d, 1H, $J = 10.2$ Hz, allyl), 2.79–2.73 (m, 1H, CH₂P),

2.10 (s, 3H, CpCH_3), 1.80 (s, 3H, CpCH_3). ^{13}C NMR (acetone- d_6 , 150 MHz): δ 164.7 (C=O), 133.6–126.6 (Ph), 124.6, 109.4, 105.9 (d, J = 6.2 Hz), 102.5, 90.5, 90.3, 88.1, 61.6 (d, J = 5.0 Hz), 58.4 (d, J = 5.0 Hz), 21.0 (d, J = 40.9 Hz, CH_2P), 12.9 (CpMe), 12.0 (CpMe). ^{31}P NMR (acetone- d_6 , 160 MHz): δ 39.1. IR (cm^{-1} , KBr): 1747 ($\nu_{\text{C=O}}$). FAB-MS (m/z): 603 $[\text{M}-\text{PF}_6]^{+}$. Anal. Calcd for $\text{C}_{31}\text{H}_{31}\text{ClF}_6\text{O}_2\text{P}_2\text{Ru}$: C, 49.78; H, 4.18. Found: C, 50.12; H, 4.31.

Reaction of 1c with cinnamyl chloride. This reaction was performed by a similar manner to that for (S)-**1a** to give ($S^*\text{Cp}, S^*\text{Ru}, S^*\text{allyl}$)-**6c** in 86% yield. ^1H NMR (acetone- d_6 , 600 MHz): δ 8.04 (d, 2H, J = 7.3 Hz, Ph), 7.86–7.70 (m, 8H, Ph), 7.62–7.55 (m, 2H, Ph), 7.48–7.37 (m, 8H, Ph), 7.23 (s, 1H, Cp'), 6.79 (s, 1H, Cp'), 6.68 (dd, 1H, J = 1.9, 12.5 Hz, allyl), 5.06 (ddd, 1H, J = 8.1, 11.4, 24.3 Hz, OCH_2), 4.41–4.38 (m, 1H, allyl), 3.97 (ddt, 1H, J = 1.5, 4.9, 12.1 Hz, OCH_2), 3.71–3.64 (m, 1H, allyl), 3.61–3.56 (m, 1H, CH_2P), 2.83 (dt, 1H, J = 6.0, 15.4 Hz, CH_2P), 1.98 (d, 3H, J = 1.5 Hz, CpCH_3), 1.78 (d, 1H, J = 10.6 Hz, allyl). ^{13}C NMR (CD_3NO_2 , 150 MHz): δ 164.5 (C=O), 135.4–126.4 (Ph), 124.6 (Cp'), 110.0 (Cp'), 102.9 (allyl), 101.2 (Cp'), 91.0 (Cp'), 90.8 (Cp'), 84.6 (allyl), 63.8 (allyl), 61.6 (d, J = 5.0 Hz, CH_2O), 20.8 (d, J = 41.0 Hz, CH_2P), 12.1 (CpMe). ^{31}P NMR (acetone- d_6 , 160 MHz): δ 40.8. IR (cm^{-1} , KBr): 1745 ($\nu_{\text{C=O}}$). FAB-MS (m/z): 664 $[\text{M}-\text{PF}_6-1]^{+}$. Anal. Calcd for $\text{C}_{36}\text{H}_{33}\text{ClF}_6\text{O}_2\text{P}_2\text{Ru}$: C, 53.37; H, 4.11. Found: C, 53.13; H, 4.27.

Reaction of ($S_{\text{Cp}}, R_{\text{Ru}}, R_{\text{allyl}}$)-2a with lithium *o*-methylphenoxide. To a THF solution (0.2 mL) of *o*-cresol (4.8 mg, 44 μmol) was added 2.7 M hexane solution of *n*-BuLi (15 μL , 40 μmol) at room temperature. After stirring for 10 min, evaporation of the solvent gave white powdery lithium *o*-methylphenoxide, which was then dissolved in THF (0.7 mL). This solution was added into a THF suspension (0.3 mL) of ($S_{\text{Cp}}, R_{\text{Ru}}, R_{\text{allyl}}$)-**2a** (15.8 mg, 20 μmol) at room temperature. The orange reaction mixture immediately turned to a dark red solution, which was stirred for 1 h. After addition of diethyl ether, the solution was passed through a SiO_2 short column with diethyl ether. Concentration of the eluent gave crude brownish orange oil, of which the ^1H NMR spectrum was measured to determine yield using hydroquinone dimethyl ether as an internal standard. Then, the crude oil was purified by column chromatography on silica gel with hexane-diethyl ether (v/v = 95/5) to give a clear solution of the products, which was analyzed by HPLC to determine the enantioselectivity.

Reaction of ($S_{\text{Cp}}, S_{\text{Ru}}, S_{\text{allyl}}$)-2c with lithium *o*-methylphenoxide. The title reaction was performed by a similar manner to that for ($S_{\text{Cp}}, R_{\text{Ru}}, R_{\text{allyl}}$)-**2a**, and the resulting ether was analyzed by ^1H NMR and HPLC equipped with chiral stationary phase column.

Crystal data for ($S^*\text{Cp}, R^*\text{Ru}, R^*\text{allyl}$)-6a: $\text{C}_{34}\text{H}_{37}\text{ClF}_6\text{O}_2\text{P}_2\text{Ru}$, M_r = 790.13, monoclinic,

$P2_1/c$ (no. 14), $a = 11.170(5)$, $b = 13.204(9)$, $c = 26.196(5)$ Å, $b = 98.88(3)^\circ$, $V = 3817(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.375$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 6.209$ cm⁻¹, $T = -75$ °C, $2\theta_{\text{max}} = 55^\circ$, 9315 measured reflections, 8863 independent reflections, $R = 0.0905$, $R_w = 0.1711$, GOF = 1.164 ($I > 2s(I)$).

Crystal data for (S*_{Cp},S*_{Ru},S*_{allyl})-6b·CH₃COCH₃: C₃₄H₃₇ClF₆O₃P₂Ru, $M_r = 806.13$, triclinic, $P-1$ (no. 2), $a = 10.784(2)$, $b = 11.351(2)$, $c = 14.880(2)$ Å, $\alpha = 66.07(1)$, $\beta = 96.87(1)$, $\gamma = 92.52(1)^\circ$, $V = 1677.4(5)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.596$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 7.103$ cm⁻¹, $T = -75$ °C, $2\theta_{\text{max}} = 60^\circ$, 10236 measured reflections, 9773 independent reflections, $R = 0.0697$, $R_w = 0.1737$, GOF = 1.305 ($I > 2s(I)$).

Crystal data for (S*_{Cp},S*_{Ru},S*_{allyl})-6c: C₃₆H₃₃ClF₆O₃P₂Ru, $M_r = 810.12$, triclinic, $P-1$ (no. 2), $a = 13.214(3)$, $b = 13.335(3)$, $c = 10.201(3)$ Å, $\alpha = 90.49(2)$, $\beta = 90.49(2)$, $\gamma = 99.38(2)^\circ$, $V = 1773.4(7)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.517$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 6.705$ cm⁻¹, $T = -75$ °C, $2\theta_{\text{max}} = 60^\circ$, 10755 measured reflections, 10337 independent reflections, $R = 0.0746$, $R_w = 0.0822$, GOF = 1.137 ($I > 2s(I)$).

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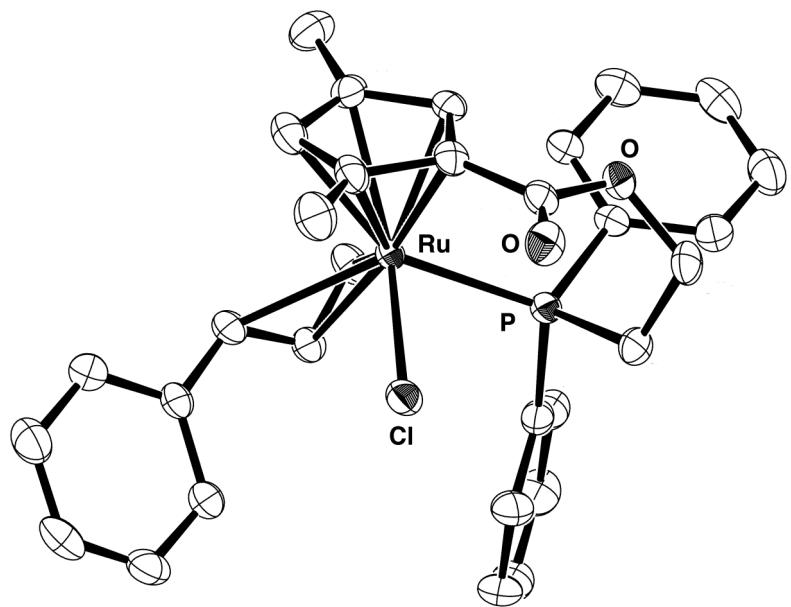


Figure S1. ORTEP drawing of $(S^*_{Cp},S^*_{Ru},S^*_{allyl})\text{-6b}$ (PF_6^- , solvent molecule and hydrogen atoms are omitted for clarity).

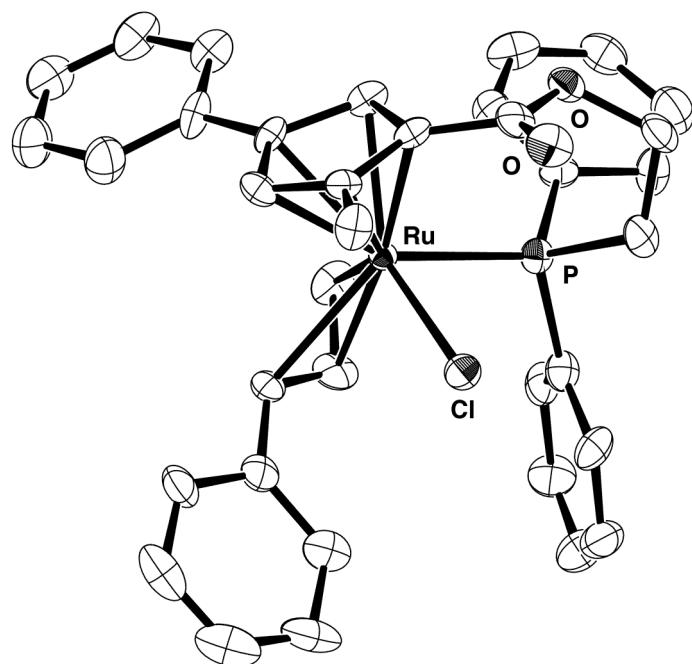
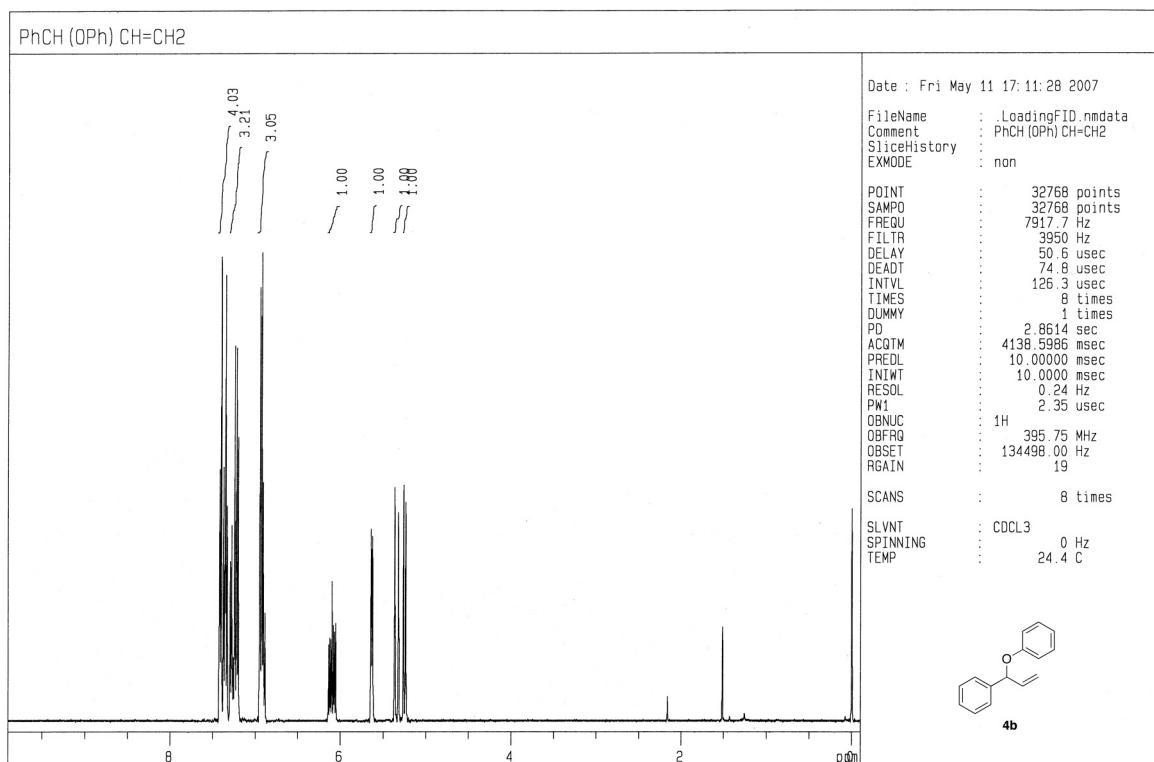
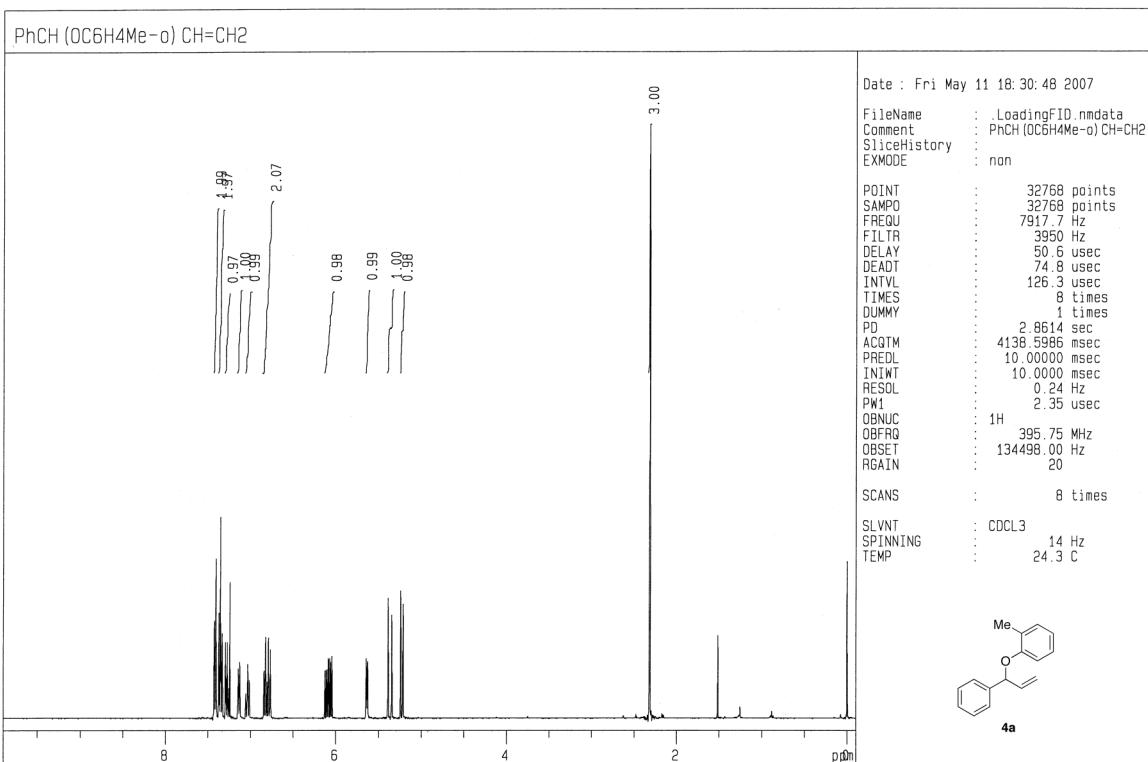
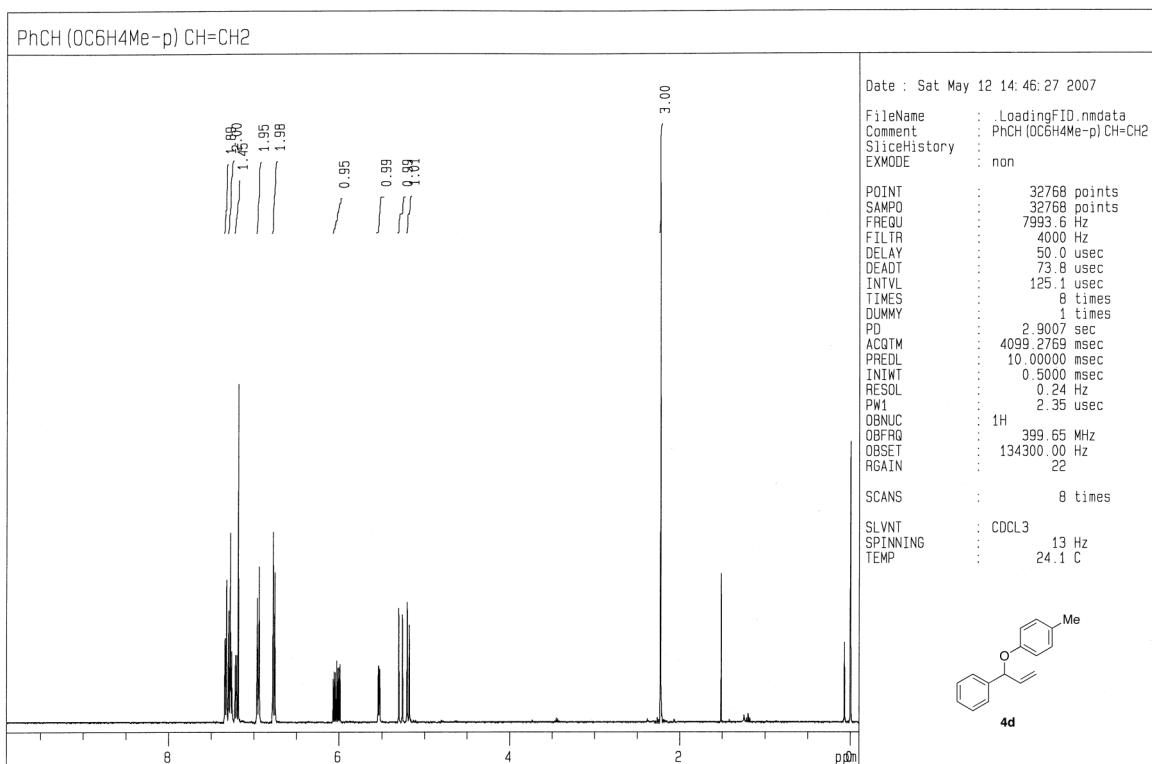
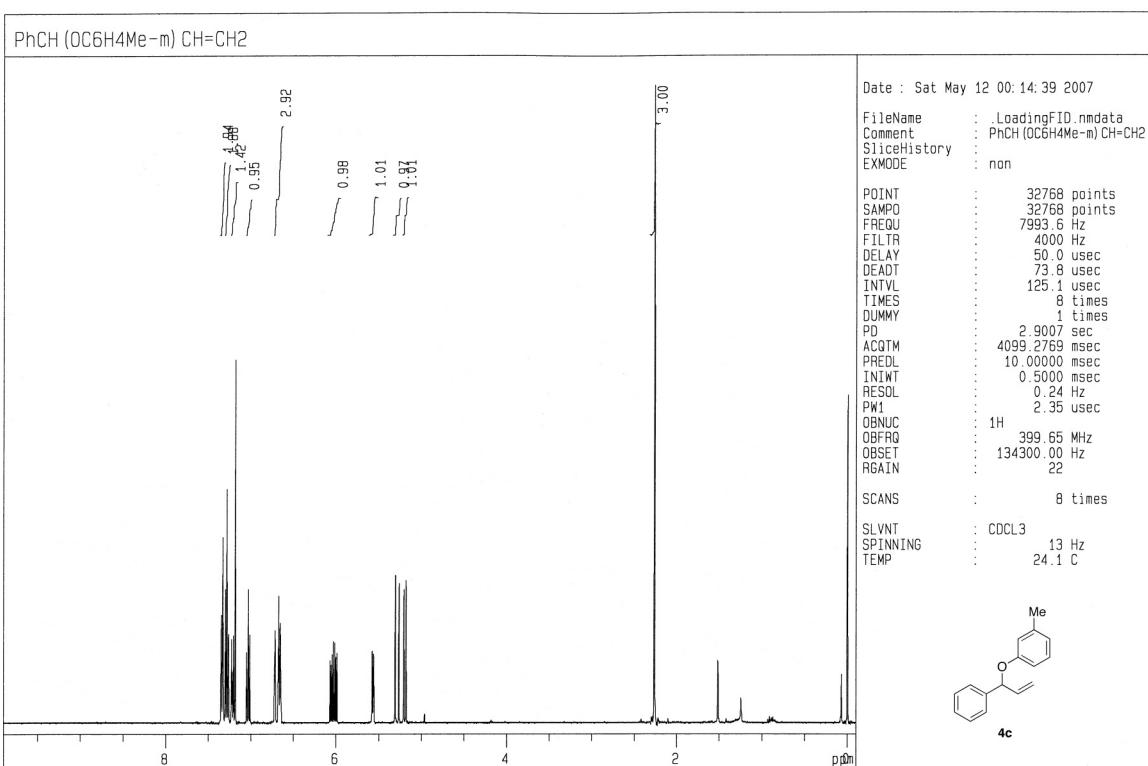
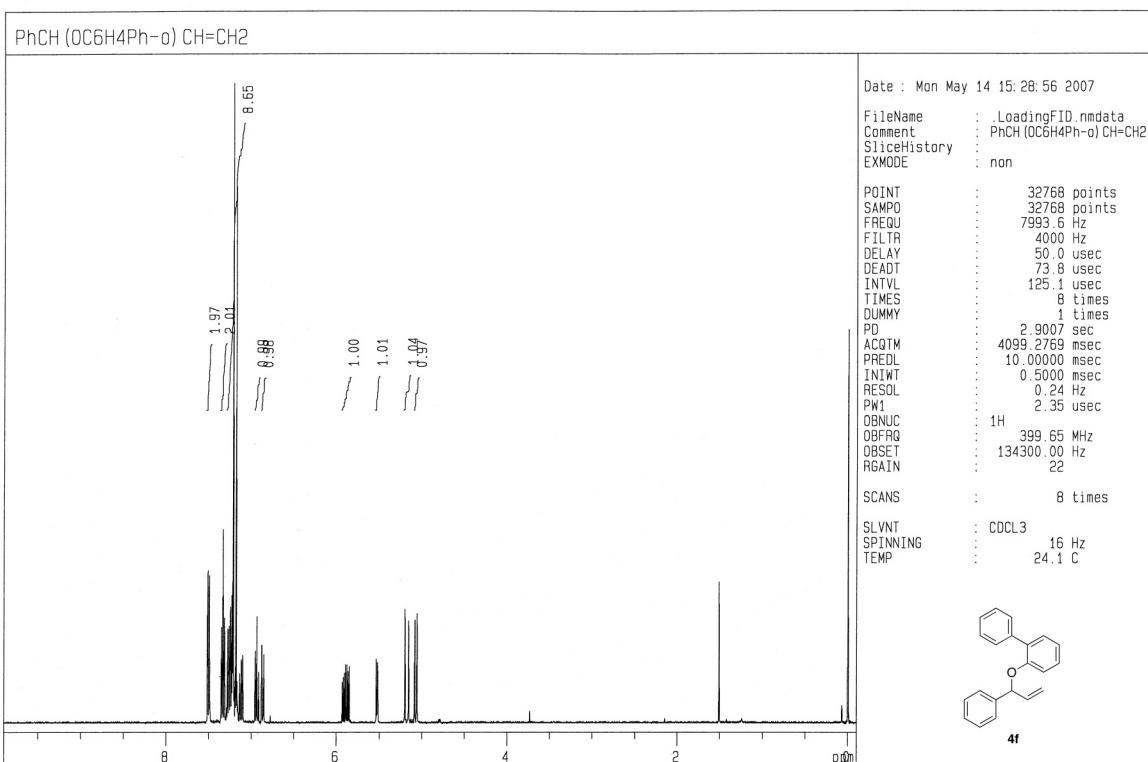
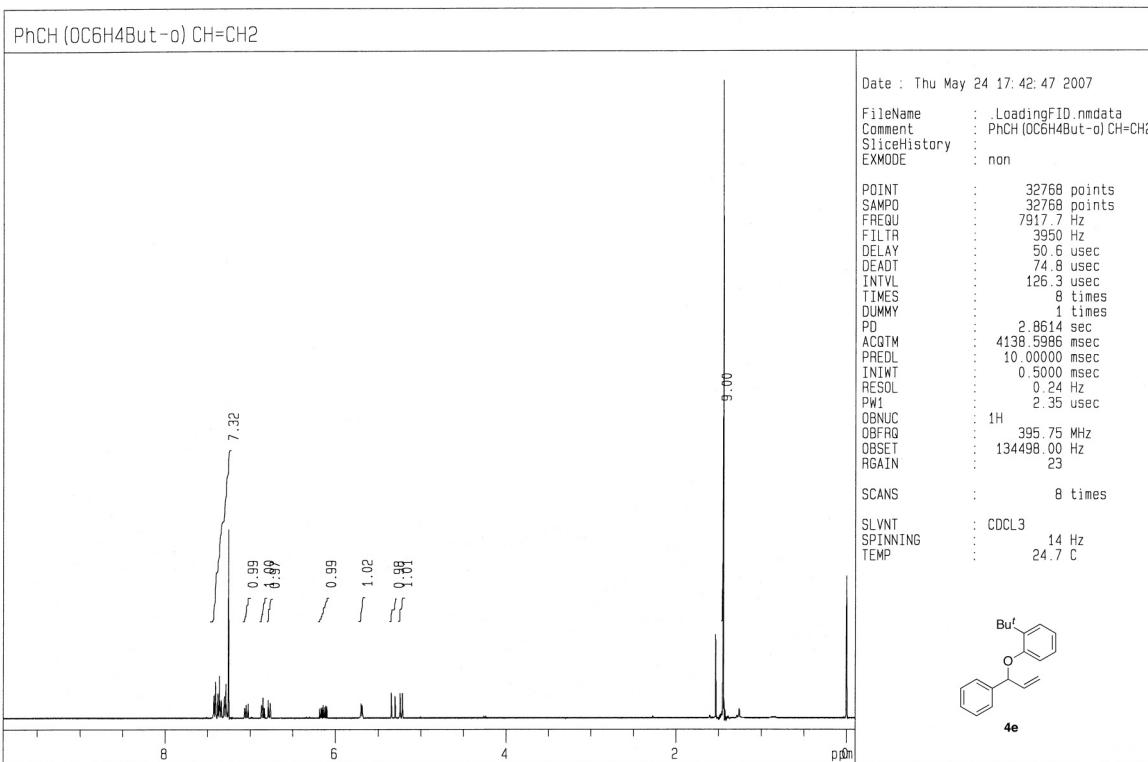
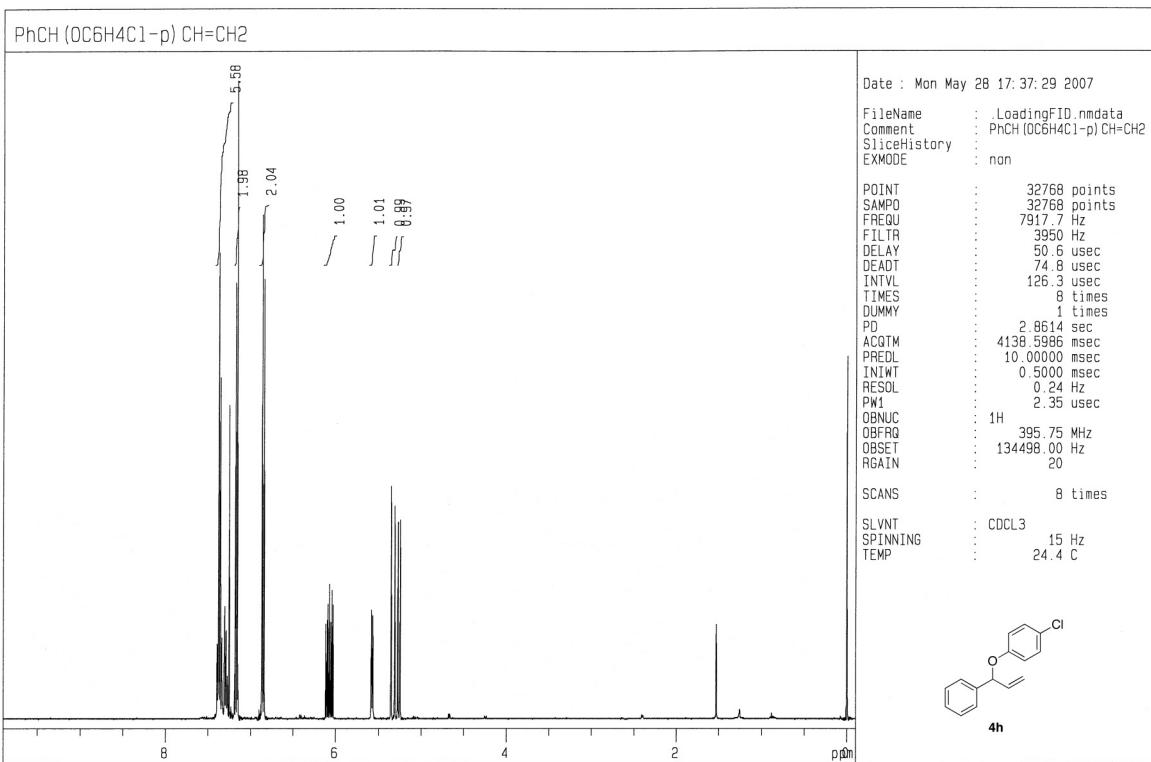
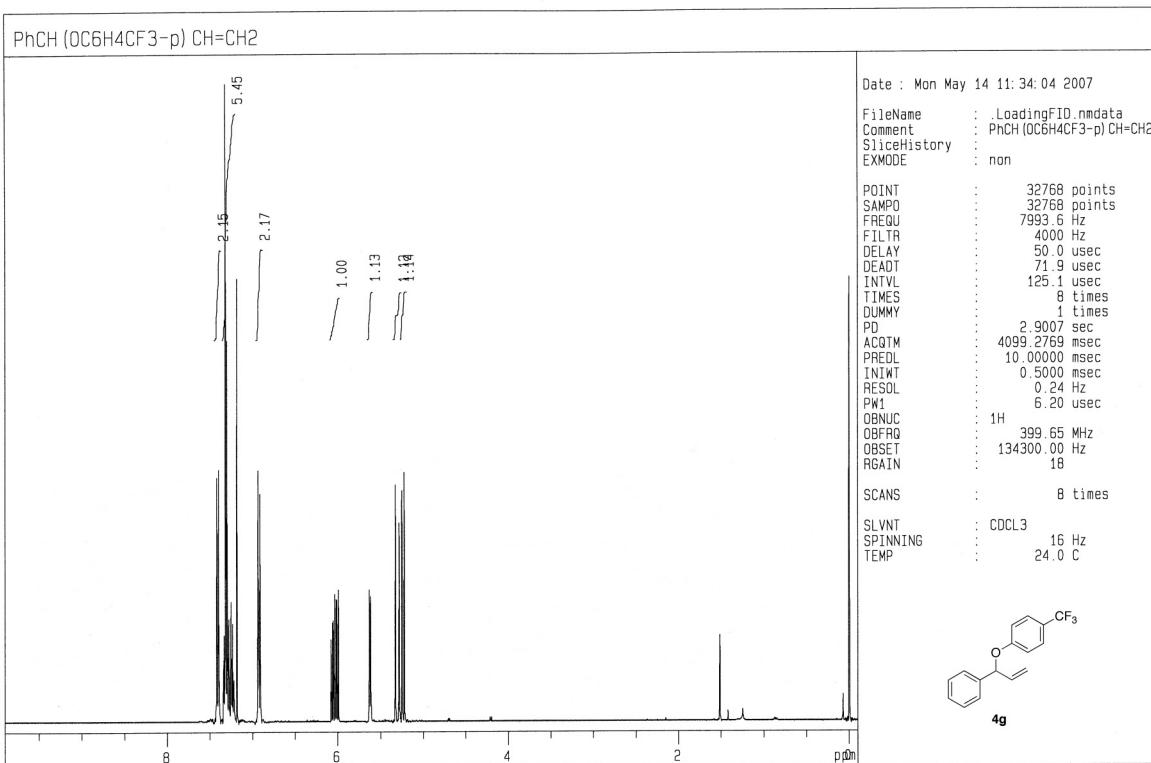


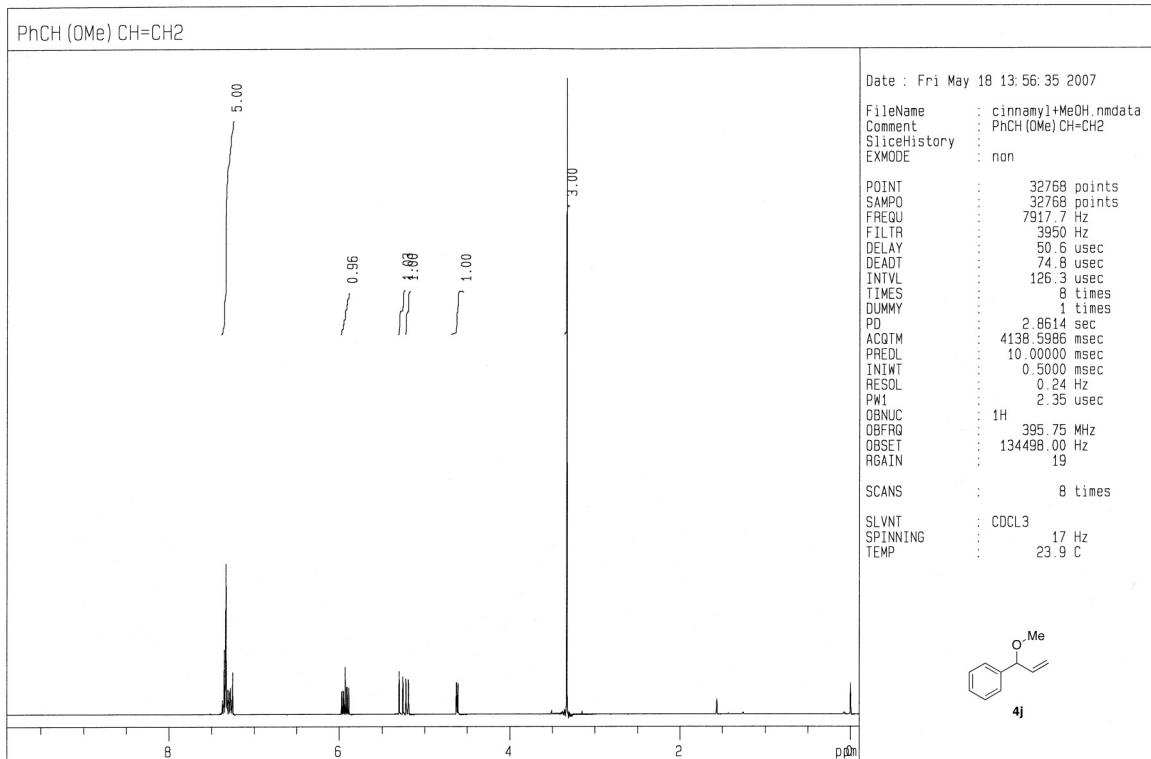
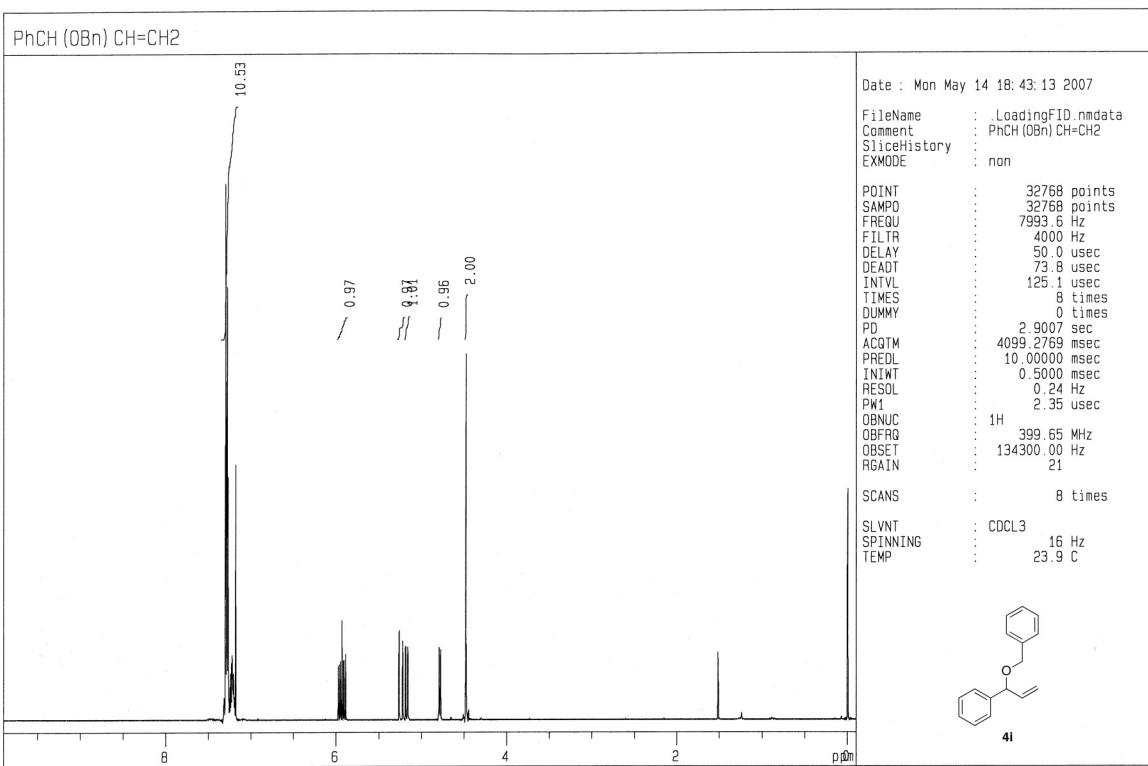
Figure S2. ORTEP drawing of $(S^*_{Cp},S^*_{Ru},S^*_{allyl})\text{-6c}$ (PF_6^- and hydrogen atoms are omitted for clarity).



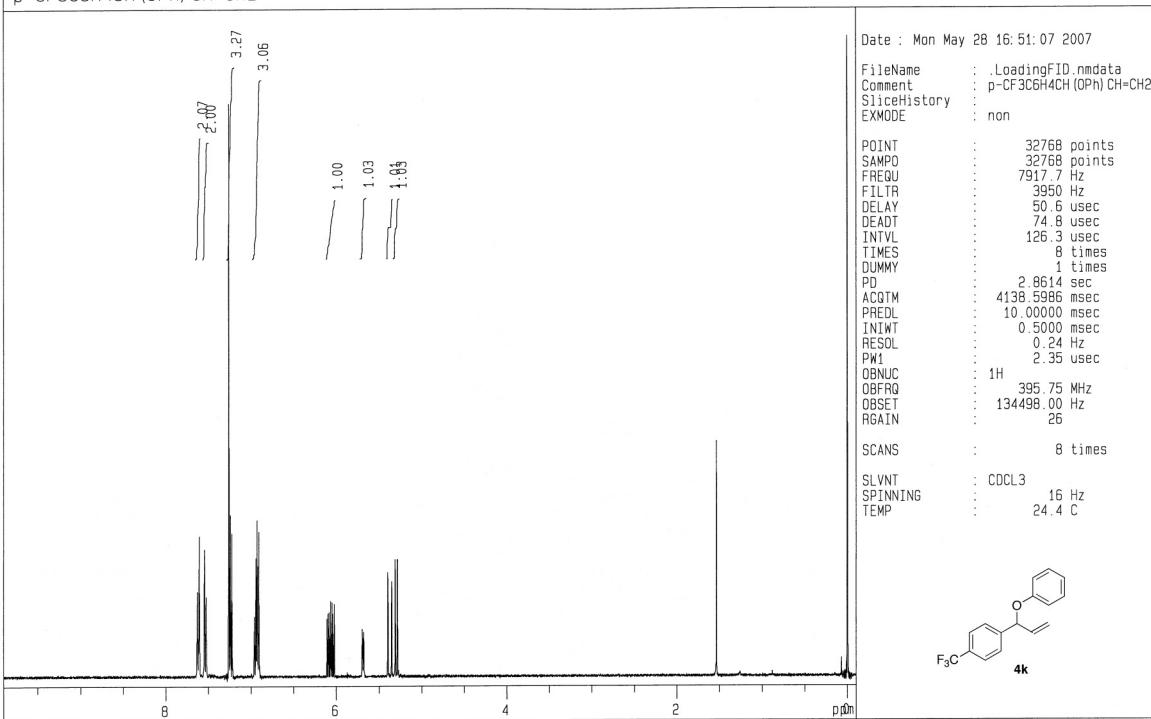








p-CF₃C₆H₄CH (OPh) CH=CH₂



(p-ClC₆H₄)CH (OPh) CH=CH₂

