Highly *Z*- and Enantioselective Ring-Opening/Cross-Metathesis Reactions Catalyzed by Stereogenic-at-Mo Adamantylimido Complexes

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SUPPORTING INFORMATION, PART A

General. Infrared (IR) spectra were recorded on a Bruker FTIR Alpha (ATR Mode) spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), or weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard ($CDCl_3$: δ 7.26 ppm, C_6D_6: δ 7.16 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.26 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS (positive mode) at the Boston College Mass Spectrometry Facility. Enantiomer ratios were determined by HPLC (Chiral Technologies Chiralpak OD, OJ-H, AS column or Chiralcel OD-R column Boston College (4.6 mm x 250 mm)) in comparison with authentic racemic materials. Optical rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter. A CIF file of the X-ray structure on page is SI-21 attached.

Unless otherwise noted, all reactions were performed with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 ºC) or flame-dried glassware with standard dry box or vacuum line techniques. Oxabicycles were prepared according to previously published procedures[1] and dried by azeotropic distillation with C_6H_6 prior to use in reactions with Mo-based complexes. Styrene (Aldrich), *p*-methoxystyrene (Acros), *p*-trifluoromethylstyrene (Aldrich), *o*-methylstyrene (Fluka) and *o*-bromostyrene (Aldrich), were dried by distillation from CaH_2 under N_2 prior to use.

Solvents: Solvents were purged with argon and purified under a positive pressure of dry Ar by a modified Innovative Technologies purification system. Toluene (Doe & Ingalls), and benzene (Aldrich) were passed successively through activated copper and alumina columns. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl immediately prior to use. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Doe & Ingalls) under air atmosphere.

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(1) Hoffman, H. M. R.; Kim, H. *Eur. J. Org. Chem.* **2000**, 2195–2201

Metal-based Complexes: Mo bispyrrolide complexes **1a**-**1b**[2] and Mo monoaryloxides **3a, 3b, 3c** were synthesized according to previously disclosed procedures.[3] Alkylidenes **5a, 5b, 5c** and **5d** were synthesized based on the general protocols described below (procedure A). All Mo complexes were handled under an inert atmosphere of N_2 in a dry box.

***d_6*-Benzene** was purchased from Cambridge Isotope Laboratories and distilled over Na into activated 4 Å molecular sieves prior to use.

Tetrabutylammonium fluoride, 1.0 M solution in tetrahydrofuran was purchased from Aldrich and used as received.

Preparation of Monoaryloxide Mo Complexes

General Precedure: In an N_2-filled glovebox, a 4-mL vial with magnetic stir bar was charged with **1b** (8.6 mg, 15.2 μmol), **2a** (7.2 mg, 15.2 μmol), and C_6D_6 (760 μL). The vial was tightly capped and the mixture was allowed to stir for 1 hour, at which time it was transferred to an NMR tube (screw cap NMR) by a pipette. The NMR tube was capped and sealed with Teflon tape. (Please note that for *in situ*-generated complexes, only the diagnostic signals of the α-carbon of the *syn*-alkylidenes are reported. ^{1}H NMR (400 MHz, C_6D_6): δ 12.94 (1H, s), 12.74 (1H, s), 12.46 (1H, s), 12.38 (1H, s); dr = 3:1 (entry 1, Table 1). ^{1}H NMR data are summarized in Table 1 (see manuscript text).

Representative procedure for preparation of Mo complex 5b (used *in situ*): In an N_2-filled glovebox, a 4-mL vial containing a magnetic stir bar was charged with **1b** (6.0 mg, 10.5 μmol), **2b** (6.0 mg, 10.5 μmol), and C_6H_6 (500 μL, 0.02 M), causing the mixture to turn orange. The vial was capped and the mixture was allowed to stir for 1 hour at 22 ºC, after which the catalyst solution was transferred to the reaction mixture by a syringe (dried at 65 ºC under vacuum).

General Procedure for Catalytic Enantioselective Ring-Opening/Cross-Metathesis (ROCM) Reactions with *in situ*-Generated Catalyst: In an N_2-filled glovebox, an oven-dried 4-mL vial with a magnetic stir bar was charged with the appropriate amount of the chiral complex in C_6H_6 (or toluene), prepared as mentioned above, and the cross partner. The resulting mixture was allowed to stir for 3-4 min, and added by syringe to a solution of the oxabicycle in C_6H_6 (or toluene) in an over-dried 4-mL vial. The resulting solution was allowed to stir for the required period of time. The reaction was then quenched by exposure to air and concentrated *in vacuo* (percent conversion determined by 400 MHz ^{1}H NMR analysis). Purification was performed by silica gel chromatography. Enantiomeric purity of the product was determined by HPLC analysis.

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(2) (a) Hock, A. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373–16375. (b) Singh, R.; Czekelius, C.; Schrock, R. R.; Müller, P. M.; Hoveyda, A. H. *Organometallics* **2007**, *26*, 2528–2539.

(3) Malcolmson, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2008**, *456*, 933–937. (b) Sattely, S. E.; Meek, S. J.; Malcolmson, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.*, ASAP.

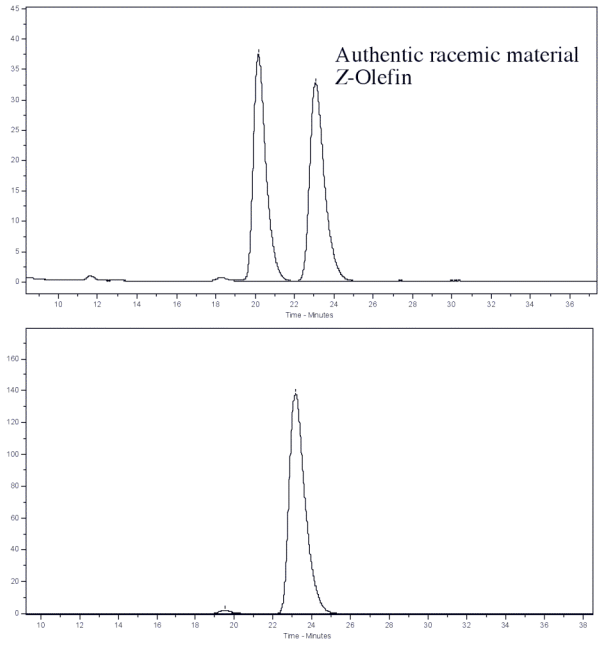
Representative Procedure for Desilylation with *n*-Tetrabutylammonium Fluoride (TBAF): Silyl ether **6a** (0.035 mmol, 12.0 mg) was dissolved in 2.0 mL distilled THF. 1.0 M TBAF in THF (20.0 equiv. 0.7 mmol, 200 μL) was added and the mixture was allowed to stir at 22 ºC for 6-8 h. The mixture was concentrated *in vacuo* and the residue purified by silica gel chromatography (1:1 hexanes:diethyl ether).

Representative Procedure for Catalytic Enantioselective Ring-Opening/Cross-Metathesis Reactions with *in situ*-Generated Catalyst: In an N_2-filled glovebox, an oven-dried 4-mL vial with a magnetic stir bar was charged with (1 mol %) of *in situ*-generated complex **5b** (20.0 μL, 0.02 M, 0.40 μmol in C_6H_6), prepared as mentioned above, and 2.0 equivalent of styrene (10 μl, 0.0832 mmol). The resulting mixture was allowed to stir for 3-4 min, and added by syringe to a solution of the oxabicycle **4** (10.0 mg, 41.6 μmol) in C_6H_6 (190 μL) in a 4-mL vial, (final substrate concentration = 0.2 M). The resulting solution was allowed to stir for 1 hour, after which the reaction was quenched through exposure of the solution to air. The mixture was concentrated *in vacuo* and conversion determined by 400 MHz ^{1}H NMR analysis. Purification of the resulting oil residue (typically light yellow) was performed by silica gel chromatography. Enantiomeric purity of **6a** was determined by HPLC analysis of the derived secondary alcohol in comparison with authentic racemic material.

***tert*-Butyldimethyl((*2S,4R,6R*)-2-*Z*-styryl-6-vinyltetrahydro-2*H*-pyran-4-yloxy)silane (6a) (Table 1, entry 2).** Following the aforementioned procedure, oxabicycle **4** (10.0 mg, 41.6 μmol) dissolved in C_6H_6 (190 μL) was treated with (1 mol %) of *in situ*-generated **5b** (20.0 μL, 0.02 M, 0.40 μmol) and styrene (10 μL, 83.2 μmol, 2.0 equiv; final substrate concentration = 0.2 M); the mixture was allowed to stir for 1 hour. The resulting brown oil was purified by silica gel chromatography (50:1 hexanes:diethyl ether) to afford **6a** (11.70 mg, 0.0340 mmol, 85.0% yield) as a colorless oil. **IR (neat)**: 2949 (s), 2927 (s), 2855 (s), 1471 (m), 1376 (m), 1252 (m), 1064 (s), 909 (m), 834 (m), 773 (m), 733(m), 701 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37-7.28 (m, 5H), 6.60 (d, *J* = 11.7 Hz, 1H), 5.92 (ddd, *J* = 17.3, 10.5, 5.7 Hz, 1H), 5.71 (dd, *J* = 11.6, 8.7 Hz, 1H), 5.30 (ddd, *J* = 17.2, 1.4, 1.4 Hz, 1H), 5.13 (ddd, *J* = 10.5, 1.3, 1.3 Hz, 1H), 4.26-4.19 (m, 1H), 3.92-3.86 (m, 1H), 3.82 (ddd, *J* = 15.5, 10.7, 4.5 Hz, 1H), 1.93-1.85 (m, 2H), 1.49 (m, 1H), 1.40 (m, 1H), 0.90 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.7, 137.1, 132.1, 132.0, 129.0, 128.5, 127.5, 115.6, 76.3, 72.3, 68.6, 41.8, 41.3, 26.1, 18.4, -4.3; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{21}H_{33}O_2Si$: 345.2250, found: 345.2254; $[\alpha]_D^{20}$ +51.2 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 98.5:1.5 er (97% ee). Enantiomeric purity was determined by analysis of HPLC of the corresponding alcohol (after removal of the silyl group) in comparison with authentic racemic material.

(*2S,4R,6R*)-2-*Z*-Styryl-6-vinyltetrahydro-2*H*-pyran-4-ol. Following the aforementioned procedure, pyran **6a** was desilylated. **IR (neat)**: 3374 (br), 3081 (w), 3018 (w), 2942 (m), 2918 (m), 2849 (m), 1647 (m), 1493 (w), 1447 (w), 1362 (m), 1303 (m), 1061(s), 988 (s), 773 (s), 693 (s); **^{1}H NMR (400 MHz, $CDCl_3$):** δ7.36-7.20 (m, 5H), 6.60 (d, *J* = 11.7 Hz, 1H), 5.91(ddd, *J* =

17.3, 10.6, 5.6 Hz, 1H), 5.72 (dd, *J* = 11.6, 8.7 Hz, 1H), 5.29 (ddd, *J* = 17.4, 1.5, 1.5 Hz, 1H), 5.15 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 4.31-4.25 (m, 1H), 3.93-3.83 (m, 2H), 2.08-2.01 (m, 2H), 1.56 (br s, 1H), 1.50-1.30 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.4, 137.0, 132.2, 131.8, 129.0, 128.5, 127.6, 115.8, 76.0, 72.3, 68.0, 41.2, 40.8; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{15}H_{19}O_2$: 231.1385, found: 231.1391; $[\alpha]_D^{20}$ +76.12 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 98.5:1.5 er (97% ee). Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (OD column, 98/2 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 23.16 min, t_r (minor enantiomer) = 19.51 min.



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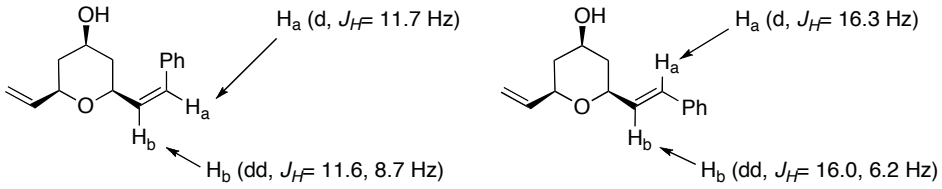
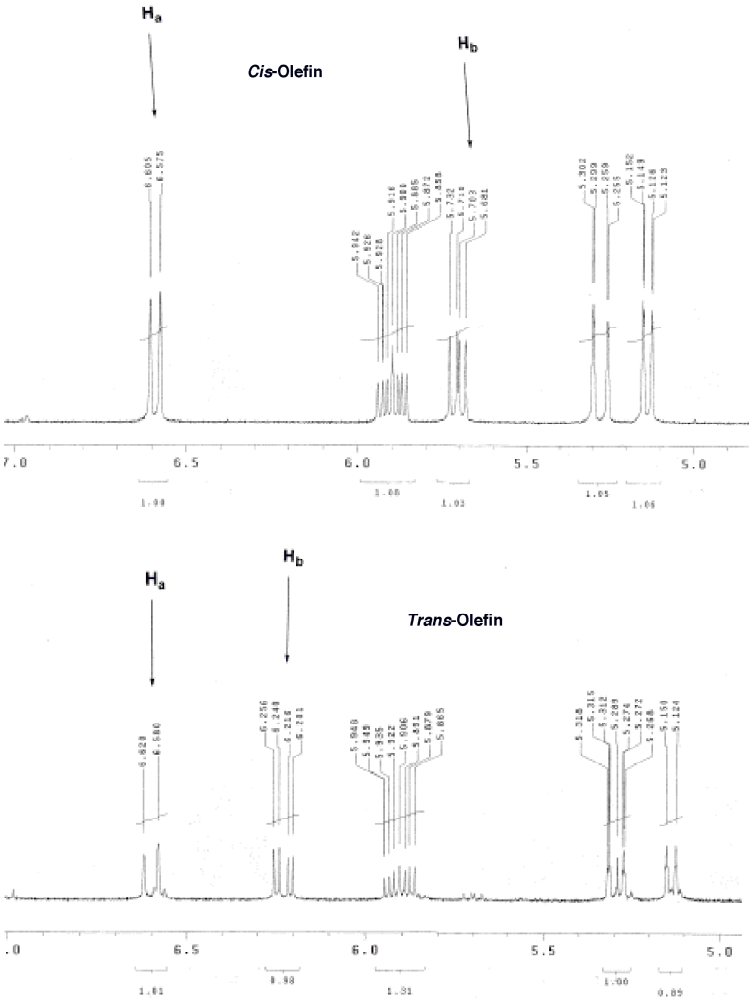
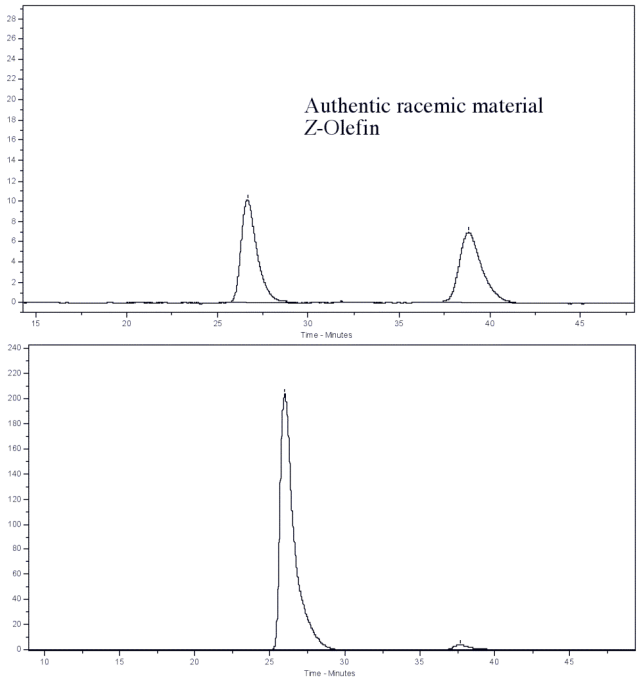




***tert*-Butyl((*2S,4R,6R*)-2-*Z*-(4-methoxystyryl)-6-vinyltetrahydro-2*H*-pyran-4-yloxy)dimethylsilane (6b) (Table 2, entry 1).** Following the aforementioned procedure, oxabicycle **4** (10.0 mg, 41.6 μmol) was treated with *in situ*-generated **5b** (20.0 μL, 0.02 M, 0.40 μmol, neat) and *p*-methoxystyrene (11.0 μL, 83.2 μmol, 2.0 equiv); the mixture was allowed to stir for 0.5 h. The resulting oil was purified by silica gel chromatography (50:1 hexanes:diethyl ether) to afford **6b** (12.5 mg, 33.3 μmol, 80.0% yield) as colorless oil. **IR (neat)**: 2951 (s), 2929 (s), 2856 (s), 1462 (m), 1376 (m), 1250 (m), 1069 (s), 910 (m), 837 (m), 775 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.53 (d, *J* = 11.5 Hz, 1H), 5.91 (ddd, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.62 (dd, *J* = 11.6, 8.6 Hz, 1H), 5.29 (ddd, *J* = 17.2, 1.4, 1.4 Hz, 1H), 5.14 (ddd, *J* = 10.5, 1.3, 1.3 Hz, 1H), 4.25-4.18 (m, 1H), 3.93-3.88 (m, 1H), 3.87-3.84 (m, 1H), 3.82 (s, 3H), 1.94-1.86 (m, 2H), 1.49-1.40 (m, 2H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.1, 138.8, 132.0, 130.5, 130.4, 129.7, 115.6, 114.0, 76.3, 72.4, 68.6, 55.5, 41.8, 41.3, 26.1, 18.4, –4.3; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{22}H_{35}O_3Si$: 375.2355, found: 375.2339; $[\alpha]_D^{20}$ +60.8 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er (94% ee). Enantiomeric purity was determined by analysis of HPLC of the

corresponding alcohol after removal of the silyl group, in comparison with authentic racemic material.

(*2S,4R,6R*)-2-*Z*-(4-Methoxystyryl)-6-vinyltetrahydro-2*H*-pyran-4-ol. Following the aforementioned procedure, pyran **6b** was desilylated. **IR (neat)**: 3386 (br), 3012 (m), 2920 (m), 1607 (s), 1510 (s), 1301 (m), 1247 (s), 1175 (m), 1061 (m), 1033 (m), 989 (m), 842 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.23 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.54 (d, *J* = 11.6 Hz, 1H), 5.92 (ddd, *J* = 18.0, 10.5, 5.6 Hz, 1H), 5.63 (dd, *J* = 11.6, 8.7 Hz, 1H), 5.30 (ddd, *J* = 17.4, 1.5, 1.5 Hz, 1H), 5.15 (ddd, *J* = 10.5, 1.5, 1.5 Hz, 1H), 4.30-4.23 (m, 1H), 3.94-3.84 (m, 2H), 3.82 (s, 3H), 2.10-2.00 (m, 2H), 1.57 (br s, 1H), 1.44-1.35 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.1, 138.4, 132.0, 130.3, 130.1, 129.5, 115.8, 114.0, 76.0, 72.3, 68.0, 55.5, 41.3, 40.8; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{16}H_{21}O_3$: 261.1490, found: 261.1498; $[\alpha]_D^{20}$ = + 71.1 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er (94% ee). Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (OD column, 98/2 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 26.01 min, t_r (minor enantiomer) = 37.67 min.



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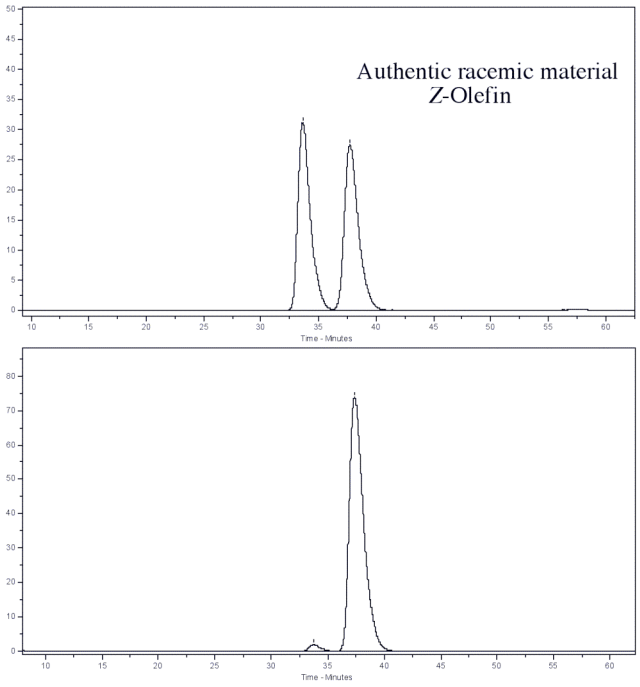
2	38.82	597167	49.339	2	37.67	589118	2.681

***tert*-Butyldimethyl((*2S,4R,6R*)-2-*Z*-(4-(trifluoromethyl)styryl)-6-vinyltetrahydro-2*H*-pyran-4-yloxy)silane (6c) (Table 2, entry 2).** Following the previously mentioned procedure, oxabicycle **4** (10.0 mg, 41.6 μmol) was treated with (1 mol %) of *in situ*-generated **5b** (20.0 μL, 0.02 M, 0.40 μmol, neat) and *p*-trifluoromethylstyrene (12.0 μL, 83.2 μmol, 2.0 equiv); the mixture was allowed to stir for 1.0 h. The resulting oil was purified by silica gel chromatography

(50:1 hexanes:diethyl ether) to afford **6c** (11.2 mg, 30.0 μmol, 67.0% yield) as colorless oil. **IR (neat):** 2951 (s), 2928 (s), 2856 (s), 1471 (m), 1377 (m), 1254 (m), 1069 (s), 910 (m), 837 (m), 775 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 11.6 Hz, 1H), 5.90 (ddd, *J* = 17.2, 10.6, 5.8 Hz, 1H), 5.82 (dd, *J* = 11.7, 8.6 Hz, 1H), 5.29 (ddd, *J* = 17.3, 1.4, 1.4 Hz, 1H), 5.15 (ddd, *J* = 10.6, 1.3, 1.3 Hz, 1H), 4.19-4.11 (m, 1H), 3.92-3.86 (m, 1H), 3.81-3.75 (m, 1H), 1.92-1.84 (m, 2H), 1.50-1.40 (m, 2H), 0.90 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 140.6, 138.5, 134.0, 131.0, 129.4 (q, J_{CF} = 33.2 Hz), 129.2, 126.1 (q, J_{CF} = 271.9 Hz), 125.5 (q, J_{CF} = 3.7 Hz), 115.8, 76.4, 72.1, 68.4, 41.6, 41.3, 26.1, 18.3, –4.29, –4.32; **^{19}F NMR (376 MHz,$CDCl_3$):** δ –63.00; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{22}H_{32}F_3O_2Si$: 413.2123, found: 413.2121; $[\alpha]_D^{20}$ +32.8 (c = 0.5, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er (96% ee). Enantiomeric purity was determined by analysis of HPLC of the corresponding alcohol after removal of the silyl group, in comparison with authentic racemic material.

(*2S,4R,6R*)-2-*Z*-(4-(Trifluoromethyl)styryl)-6-vinyltetrahydro-2*H*-pyran-4-ol. Following the aforementioned procedure, pyran **6c** was desilylated. **IR (neat)**: 3378 (br), 3019 (m), 2921 (m), 1616 (m), 1427 (m), 1323 (s), 1163 (s), 1122 (s), 1065 (s), 988 (m), 854 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 8.2 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.30-7.25 (m, 1H), 7.17-7.12 (m, 1H), 6.63 (d, *J* = 11.8 Hz, 1H), 5.91 (ddd, *J* = 17.2, 10.6, 5.6 Hz, 1H), 5.82 (dd, *J* = 11.7, 8.6 Hz, 1H), 5.30 (ddd, *J* = 17.2, 1.5, 1.5 Hz, 1H), 5.16 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 4.10-4.00 (m, 1H), 3.90-3.80 (m, 1H), 3.78-3.72 (m, 1H), 1.88-1.83 (m, 2H), 1.48-1.43 (m, 1H), 1.40-1.35 (m, 1H), 0.87 (s, 9H), 0.04 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 140.5, 138.2, 133.7, 131.1, 129.4 (q, J_{CF} = 32.5 Hz), 129.2, 125.5 (q, J_{CF} = 271.9 Hz), 123.0 (q, J_{CF} = 3.8 Hz), 116.0, 76.2, 72.1, 68.0, 41.1, 40.8; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{16}H_{18}F_3O_2$: 299.1258, found: 299.1248; $[\alpha]_D^{20}$ +64.5 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er (96% ee). Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (OD column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 37.36 min, t_r (minor enantiomer) = 33.76 min.



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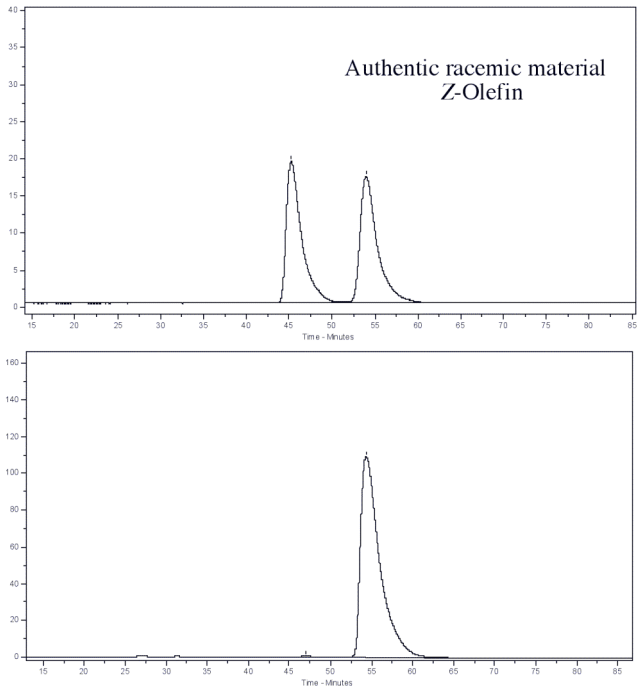
2	37.71	2339704	49.946	2	37.36	6505922	97.908

((*2S,4R,6R*)-2-*Z*-(2-Bromostyryl)-6-vinyltetrahydro-2*H*-pyran-4-yloxy)(*tert*-butyl)dimethylsilane (6d) (Table 2, entry 3). Following the general procedure described previously, oxabicycle **4** (10.0 mg, 41.6 μmol) was treated with *in situ*-generated complex **5b** (40.0 μL, 0.02 M, 0.80 μmol, neat) and *o*-bromostyrene (52.0 μL, 416 μmol, 10.0 equiv); the mixture was allowed to stir for 1.0 hour. The resulting oil was purified by silica gel chromatography (50:1 hexanes:diethyl ether) to afford **6d** (8.9 mg, 21.0 μmol, 50.0% yield) as colorless oil. **IR (neat):** 3019 (s), 2927 (s), 2856 (s), 1470 (m), 1376 (m), 1254 (m), 1070 (s), 910 (m), 837 (m), 773 (m), 746(m), 730 (m) **^{1}H NMR (400 MHz $CDCl_3$):** δ 7.60 (d, *J* = 8.2 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.30-7.25 (m, 1H), 7.17-7.12 (m, 1H), 6.63 (d, *J* = 11.5 Hz, 1H), 5.90 (ddd, *J* = 17.2, 10.6, 5.6 Hz, 1H), 5.80 (dd, *J* = 11.5, 8.6 Hz, 1H), 5.30 (ddd, *J* = 17.2, 1.4, 1.4 Hz, 1H), 5.14 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 4.10- 4.00 (m, 1H), 3.86-3.80 (m, 1H), 3.78-3.72 (m, 1H), 1.88-1.83 (m, 2H), 1.47-1.43 (m, 1H), 1.40-1.36 (m, 1H), 0.87 (s, 9H), 0.04 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: 138.7, 137.2, 133.0, 132.8, 131.6, 131.0, 129.1, 127.3, 124.2, 115.6, 76.3, 72.3, 68.5, 41.6, 41.3, 26.1, 18.3, –4.3; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{21}H_{32}$ Br O_2Si: 423.1353, found: 423.1349; $[\alpha]_D^{20}$ +43.7 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of >98:<2 er (>98% ee). Enantiomeric purity was determined by analysis of HPLC of the corresponding alcohol after removal of the silyl group, in comparison with authentic racemic material.

(*2S,4R,6R*)-2-*Z*-(2-Bromostyryl)-6-vinyltetrahydro-2*H*-pyran-4-ol. Following the aforementioned procedure, pyran **6d** was desilylated. **IR (neat)**: 3360 (br), 3019 (m), 2920 (m),

2853 (m), 1468 (m), 1362 (m), 1302 (m), 1065 (m), 988 (m), 926 (m), 768 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.39 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.30-7.24 (m, 1H), 7.17-7.12 (m, 1H), 6.63 (d, *J* = 11.5 Hz, 1H), 5.91 (ddd, *J* = 17.3, 10.6, 5.6 Hz, 1H), 5.82 (dd, *J* = 11.4, 8.8 Hz, 1H), 5.29 (ddd, *J* = 17.2, 1.5, 1.5 Hz, 1H), 5.16 (ddd, *J* = 10.6, 1.4, 1.4 Hz, 1H), 4.12-4.05 (m, 1H), 3.88-3.76 (m, 2H), 1.99-1.85 (m, 2H), 1.55 (br s, 1H), 1.42-1.32 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** 138.4, 137.1, 133.0, 132.7, 131.7, 130.7, 129.2, 127.3, 124.1, 115.8, 76.0, 72.2, 68.0, 41.1, 40.7; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{15}H_{18}BrO_2$: 309.0490, found: 309.0496; $[\alpha]_D^{20}$ +45.9 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of >98:<2 er (>98% ee). Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (OD column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 53.35 min, t_r (minor enantiomer) = 46.14 min.

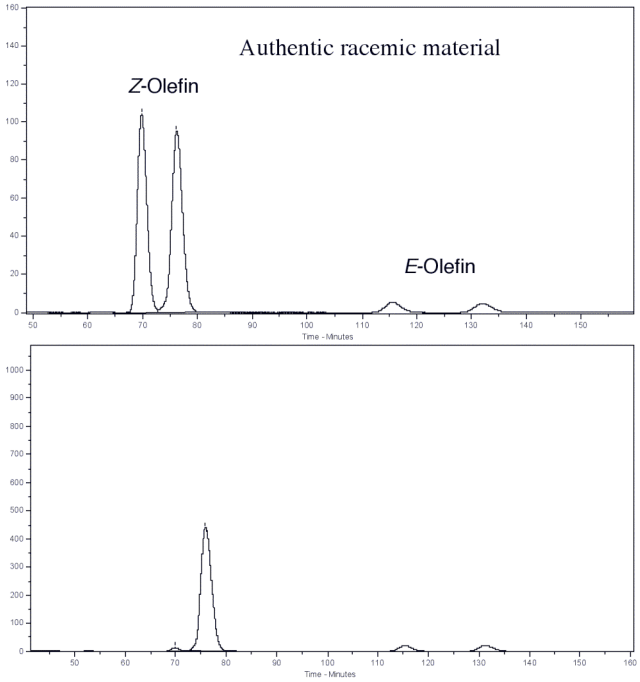


#	time (min)	area	area %	#	time (min)	area	area %
1	45.27	2391163	49.785	1	46.14	34040	0.484
2	53.93	2411786	50.215	2	53.35	6993783	99.516

***tert*-butyldimethyl((*2S,4R,6R*)-2-*Z*-(2-methylstyryl)-6-vinyltetrahydro-2*H*-pyran-4-yloxy)silane (6e) (Table 2, entry 4).** Following the general procedure described previously, oxabicycle **4** (10.0 mg, 41.6 μmol) was treated with *in situ*-generated complex **5b** (40.0 μL, 0.02 M, 0.80 μmol, neat) and *o*-methylstyrene (54.0 μL, 416 μmol, 10.0 equiv), the mixture was allowed to stir for 1.0 h. The resulting oil was purified by silica gel chromatography (50:1 hexanes:diethyl ether) to afford **6e** (8.2 mg, 23.0 μmol, 54.0% yield) as colorless oil. **IR (neat)**: 2950 (s), 2927 (s), 2856 (s), 1471 (m), 1377 (m), 1253 (m), 1069 (s), 910 (m), 836 (m), 774 (m), 740(m), 715 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.24-7.12 (m, 4H), 6.60 (d, *J* = 11.6 Hz, 1H), 5.90 (ddd, *J* = 17.1, 10.5, 5.8 Hz, 1H), 5.74 (dd, *J* = 11.5, 8.8 Hz, 1H), 5.30 (ddd, *J* = 17.2, 1.4,

1.4 Hz, 1H), 5.11 (ddd, *J* = 10.6, 1.3, 1.3 Hz, 1H), 4.10-4.01 (m, 1H), 3.82-3.77 (m, 1H), 3.73 (ddd, *J* = 15.4, 10.8, 4.6 Hz, 1H), 2.26 (s, 3H), 1.81-1.75 (m, 2H), 1.44-1.35 (m, 2H), 0.85 (s, 9H), 0.02 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 139.0, 136.7, 136.3, 132.2, 131.0, 130.1, 129.2, 127.7, 125.7, 115.6, 76.2, 72.5, 68.5, 41.8, 41.3, 26.1, 20.2, 18.3, –4.3; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{22}H_{35}O_2Si$: 359.2406, found: 359.2393; $[\alpha]_D^{20}$ +40.1 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er (98% ee). Enantiomeric purity was determined by HPLC analysis of the corresponding alcohol after removal of the silyl group, in comparison with authentic racemic material.

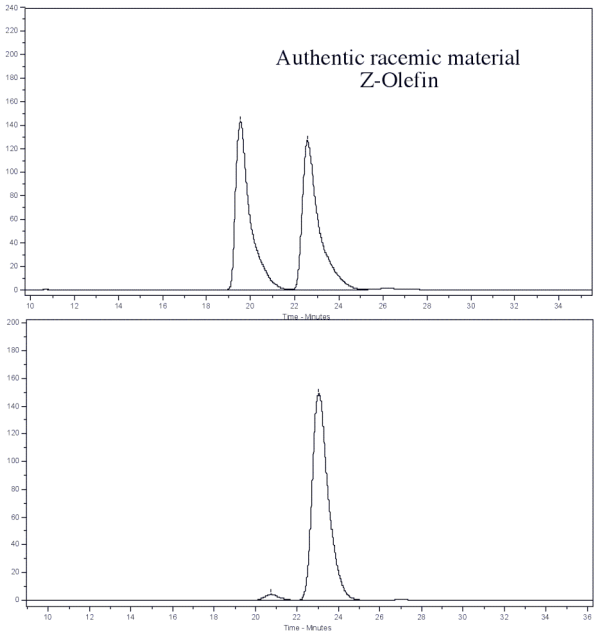
(*2S,4R,6R*)-2-*Z*-(2-Methylstyryl)-6-vinyltetrahydro-2*H*-pyran-4-ol. Following the previous procedure, pyran **6e** was desilylated. **IR (neat)**: 3380 (br), 2941 (m), 2920 (m), 2854 (m), 1486 (m), 1361 (m), 1301 (m), 1063 (m), 988 (m), 925 (m), 793 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.23-7.12 (m, 4H), 6.60 (d, *J* = 11.5 Hz, 1H), 5.90 (ddd, *J* = 17.3, 10.7, 5.7 Hz, 1H), 5.75 (dd, *J* = 11.6, 8.9 Hz, 1H), 5.26 (ddd, *J* = 17.2, 1.4, 1.4 Hz, 1H), 5.13 (ddd, *J* = 10.5, 1.4, 1.4 Hz, 1H), 4.13-4.06 (m, 1H), 3.85-3.74 (m, 2H), 2.26 (s, 3H), 1.98-1.88 (m, 2H), 1.58 (br s, 1H), 1.39-1.30 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: 138.5, 137.0, 136.1, 132.0, 131.0, 130.1, 129.1, 127.7, 125.8, 115.7, 76.0, 72.4, 68.0, 41.3, 40.7, 20.1; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{16}H_{21}O_2$: 245.1542, found: 245.1537; $[\alpha]_D^{20}$ +45.9 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er (98% ee). Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (OD column, 97/3 hexanes/*i*-PrOH, 0.2 mL/min, 254 nm; t_r (major enantiomer) = 75.93 min, t_r (minor enantiomer) = 69.90 min.



#	time (min)	area	area (%)	#	time (min)	area	area %
1	69.81	12734510	48.795	1	69.90	283472	1.046
2	76.22	13363450	51.205	2	75.93	26811780	98.954

(*tert*-Butyldimethyl((*2S,4S,6R*)-2-*Z*-styryl-6-vinyltetrahydro-2*H*-pyran-4-yloxy)silane (7a) (Table 3, entry 1). Following the general procedure described before, oxabicycle **7** (10.0 mg, 41.6 μmol) in C_6H_6 (380 μL) was treated with *in situ*-generated complex **5b** (40.0 μL, 0.02 M, 0.80 μmol; final substrate concentration = 0.1 M) and styrene (48.0 μL, 416 μmol, 10.0 equiv.); the mixture was allowed to stir for 1.0 hour. The resulting oil was purified by silica gel chromatography (50:1 hexanes:diethyl ether) to afford **7a** (12.0 mg, 35.0 μmol, 83.0% yield) as colorless oil. **IR (neat)**: 3016 (w), 2950 (s), 2927 (s), 2855 (s), 1252 (m), 1092 (s), 1053 (s), 910 (m), 828 (s), 772 (m), 690 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34-7.23 (m, 5H), 6.48 (d, *J* = 12.0 Hz, 1H), 5.87 (ddd, *J* = 17.3, 10.6, 5.8 Hz, 1H), 5.70 (dd, *J* = 11.9, 8.8 Hz, 1H), 5.24 (ddd, *J* = 17.4, 1.6, 1.6 Hz, 1H), 5.10 (ddd, *J* = 10.6, 1.6, 1.6 Hz, 1H), 5.00-4.94 (m, 1H), 4.39-4.32 (m, 1H), 4.28-4.24 (m, 1H), 1.76-1.52 (m, 4H), 0.90 (s, 9H), 0.06 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 139.5, 137.1, 133.2, 130.2, 129.1, 128.4, 127.3, 115.1, 72.3, 68.8, 65.2, 39.0, 38.9, 26.1, 18.3, –4.6, –4.7; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{21}H_{33}O_2Si$: 345.2249, found: 345.2260; $[\alpha]_D^{20}$ –1.6 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er (94% ee). Enantiomeric purity was determined by analysis of HPLC of the corresponding alcohol after removal of the silyl group, in comparison with authentic racemic material.

(*2S,4S,6R*)-2-*Z*-Styryl-6-vinyltetrahydro-2*H*-pyran-4-ol. Following the procedure described above, pyran **7a** was desilylated. **IR (neat)**: 3419 (br), 3016 (w), 2917 (m), 1415 (w), 1308 (m), 1053 (s), 962 (s), 775 (s), 699 (s); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36-7.23 (m, 5H), 6.57 (d, *J* = 11.8 Hz, 1H), 5.90 (ddd, *J* = 17.2, 10.6, 5.7 Hz, 1H), 5.67 (dd, *J* = 11.7, 8.8 Hz, 1H), 5.29 (ddd, *J* = 17.4, 1.5, 1.5 Hz, 1H), 5.13 (ddd, *J* = 10.5, 1.3, 1.3 Hz, 1H), 4.90-4.80 (m, 1H), 4.42-4.35 (m, 1H), 4.34-4.30 (m, 1H), 1.78-1.72 (m, 2H), 1.71-1.61 (m, 2H), 1.42 (br s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 139.2, 137.0, 132.4, 132.1, 129.1, 128.5, 127.5, 115.5, 72.1, 68.4, 64.8, 38.6, 38.2; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{15}H_{19}O_2$: 231.1385, found: 231.1395; $[\alpha]_D^{20}$ +52.8 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 94% ee. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (OD column, 98/2 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 23.04 min, t_r (minor enantiomer) = 20.74 min.



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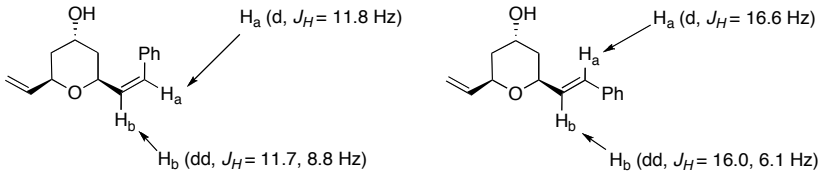
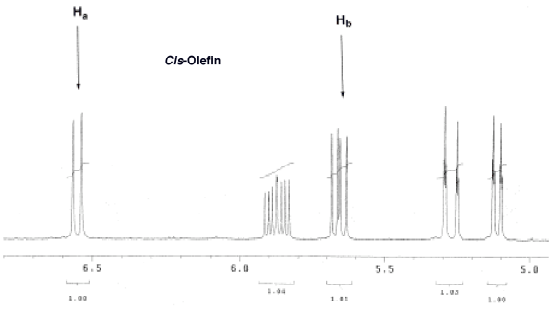
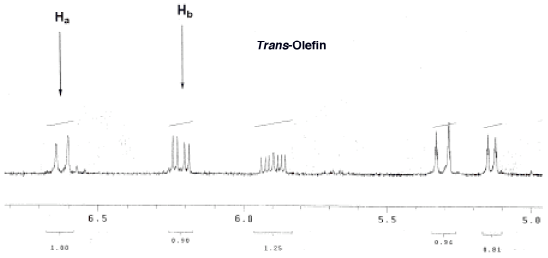
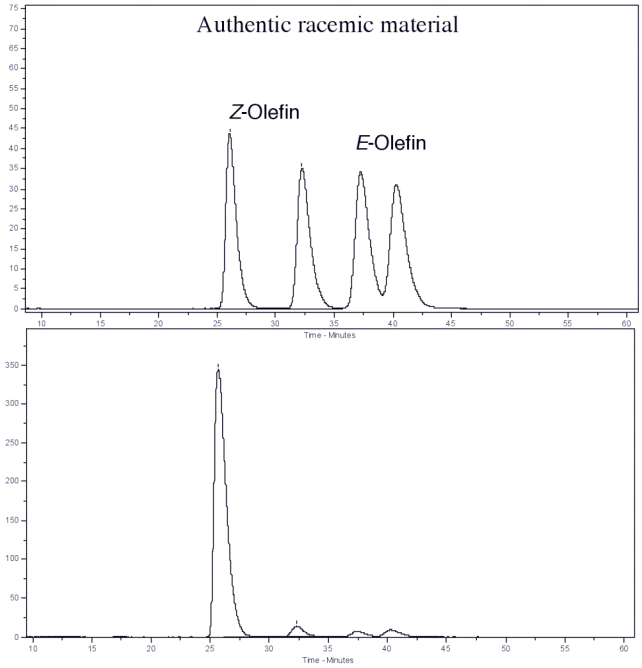






***tert*-Butyl((*2S,4S,6R*)-2-*Z*-(4-methoxystyryl)-6-vinyltetrahydro-2*H*-pyran-4-yloxy)dimethylsilane (7b) (Table 3, entry 2).** Following the aforementioned procedure, oxabicycle **7** (10.0 mg, 41.6 μmol) in C_6H_6 (150 μL) was treated with *in situ*-generated **5b** (60.0 μL, 0.02 M, 1.20 μmol, final substrate concentration = 0.2 M) and *p*-methoxystyrene (60.0 μL, 416 μmol, 10.0 equiv), and the mixture was allowed to stir for 1.0 hour. The resulting oil was purified by silica gel chromatography (50:1 hexanes:diethyl ether) to afford **7b** (12.5 mg, 33.4 μmol, 80.0% yield) as colorless oil. **IR (neat)**: 2951 (s), 2928 (s), 2855 (s), 1463 (m), 1360 (m), 1249 (m), 1092 (s), 912 (m), 836 (m), 774 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.23 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 12.0 Hz, 1H), 5.90 (ddd, *J* = 17.2, 10.6, 5.6 Hz, 1H), 5.60 (dd, *J* = 11.8, 8.6 Hz, 1H), 5.24 (ddd, *J* = 17.4, 1.5, 1.5 Hz, 1H), 5.10 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 5.00-4.93 (m, 1H), 4.40-4.33 (m, 1H), 4.30-4.24 (m, 1H), 3.81 (s, 3H), 1.76-1.55 (m, 4H), 0.92 (s, 9H), 0.07 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.0, 139.6, 132.0, 130.4, 130.0, 129.8, 115.1, 114.0, 72.3, 69.0, 65.2, 55.5, 39.0, 39.0, 26.0, 18.3, –4.6, –4.7; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{22}H_{35}O_3Si$: 375.2355, found: 375.2370; $[\alpha]_D^{20}$ + 33.2 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 92% ee. Enantiomeric purity was determined by analysis of HPLC of the corresponding alcohol after removal of the silyl group, in comparison with authentic racemic material.

(*2S,4S,6R*)-2-*Z*-(4-Methoxystyryl)-6-vinyltetrahydro-2*H*-pyran-4-ol. Following the procedure described before, oxabicycle **7b** was desilylated. **IR (neat)**: 3427 (br), 3081 (w), 3012 (m), 2921 (m), 1607 (s), 1511 (s), 1303 (m), 1250 (s), 1176 (m), 1091 (m), 1034 (m), 963 (m), 840 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 11.5 Hz, 1H), 5.90 (ddd, *J* = 17.3, 10.6, 5.8 Hz, 1H), 5.60 (dd, *J* = 11.6, 8.6 Hz, 1H), 5.30 (ddd, *J* = 17.2, 1.5, 1.5 Hz, 1H), 5.13 (ddd, *J* = 10.6, 1.4, 1.4 Hz, 1H), 4.80-4.71 (m, 1H), 4.43-4.36 (m, 1H), 4.34-4.30 (m, 1H), 3.81 (s, 3H), 1.78-1.72 (m, 2H), 1.70-1.61 (m, 2H), 1.56 (br s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.1, 139.2, 131.8, 130.7, 130.4, 129.7, 115.5, 114.0, 72.1, 68.5, 65.0, 55.5, 38.6, 38.2; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{16}H_{21}O_3$: 261.1490, found: 261.1490; $[\alpha]_D^{20}$ +73.3 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 96:4 er (92% ee). Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (OD column, 98/2 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 26.00 min, t_r (minor enantiomer) = 32.34 min.

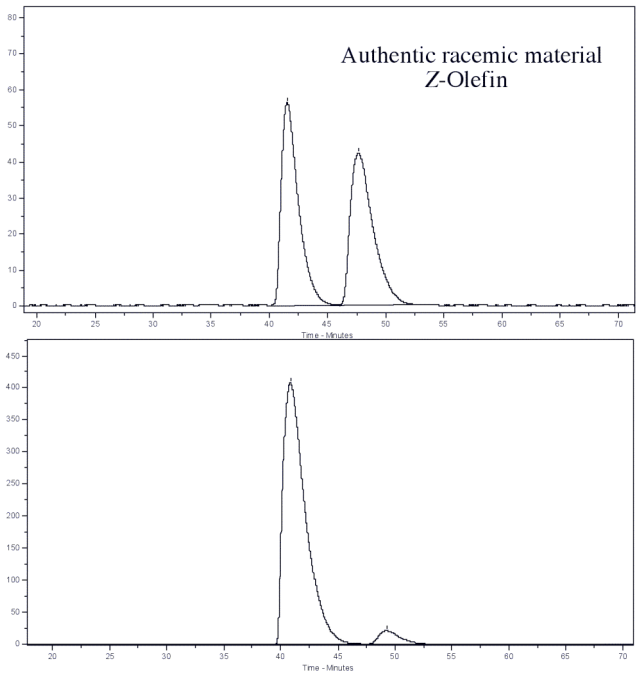


#	time (min)	area	area %	#	time (min)	area	area %
1	26.07	2750359	50.155	1	26.00	24555790	96.095
2	32.26	2733389	49.845	2	32.34	997822	3.905

***tert*-Butyldimethyl((*2S,4S,6R*)-2-*Z*-(4-(trifluoromethyl)styryl)-6-vinyltetrahydro-2*H*-pyran-4-yloxy)silane (7c) (Table 3, entry 3).** Following the general procedure **B**, oxabicycle **7** (10.0 mg, 41.6 μmol) was treated with *in situ*-generated complex **5b** (40.0 μL, 0.02 M, 0.80 μmol, neat) and *p*-trifluoromethylstyrene (61.0 μL, 416 μmol, 10.0 equiv); the mixture was allowed to stir for 1.0 hour. The resulting oil was purified by silica gel chromatography (50:1 hexanes:diethyl ether) to afford **7c** (14.0 mg, 34.0 μmol, 81.0% yield) as a colorless oil. **IR (neat)**: 2952 (s), 2928 (s), 2857 (s), 1463 (m), 1361 (m), 1165 (s), 1126 (s), 1064 (s), 853 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 6.51 (d, *J* = 12.0 Hz, 1H), 5.90 (ddd, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.80 (dd, *J* = 11.8, 8.8 Hz, 1H), 5.24 (ddd, *J* = 17.3, 1.5, 1.5 Hz, 1H), 5.10 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 4.92-4.82 (m, 1H), 4.38-4.31 (m, 1H), 4.26-4.22 (m, 1H), 1.67-1.62 (m, 2H), 1.61-1.51 (m, 2H), 0.90 (s, 9H), 0.036 (s, 3H), 0.034 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 140.6, 139.3, 135.2, 129.4 (q, J_{CF} = 32.73 Hz), 129.2, 129.1, 124.4 (q, J_{CF} = 271.9 Hz), 125.3 (q, J_{CF} = 3.60 Hz), 115.2, 72.3, 69.0, 65.0, 39.0, 38.8, 26.0, 18.1, –4.6, –4.8. **^{19}F NMR (376 MHz, $CDCl_3$):** δ –63.01; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{22}H_{32}F_3O_2Si$: 413.2123, found: 413.2120; $[\alpha]_D^{20}$ +23.6 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er (96% ee). Enantiomeric purity was determined by analysis of HPLC of the corresponding alcohol after removal of the silyl group, in comparison with authentic racemic material.

(*2S,4S,6R*)-2-*Z*-(4-(Trifluoromethyl)styryl)-6-vinyltetrahydro-2*H*-pyran-4-ol. Following the procedure **C**, pyran **7c** was desilylated. **IR (neat)**: 3385 (br), 2953 (m), 2923 (m), 1616 (m),

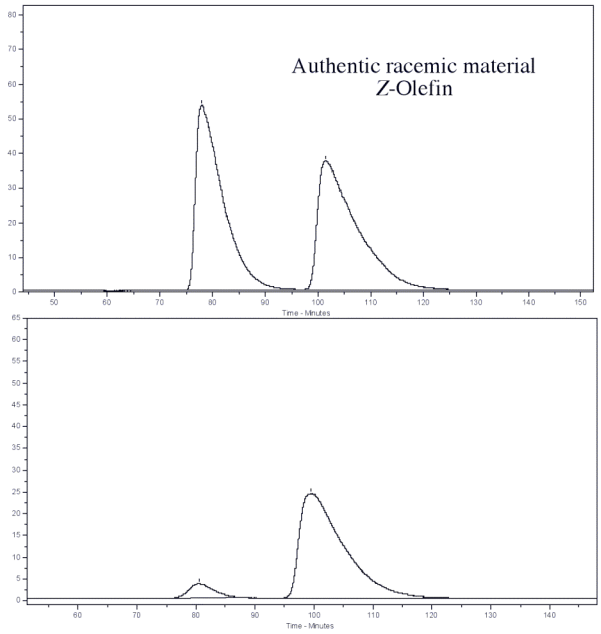
1402 (m), 1324 (s), 1164 (s), 1123 (s), 1064 (s), 989 (m), 862 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 11.8 Hz, 1H), 5.90 (ddd, *J* = 17.2, 10.6, 5.6 Hz, 1H), 5.80 (dd, *J* = 11.7, 8.7 Hz, 1H), 5.30 (ddd, *J* = 17.3, 1.5, 1.5 Hz, 1H), 5.14 (ddd, *J* = 10.5, 1.3, 1.3 Hz, 1H), 4.80-4.70 (m, 1H), 4.41-4.35 (m, 1H), 4.33-4.30 (m, 1H), 1.80-1.72 (m, 2H), 1.70-162 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 140.4, 139.0, 134.3, 131.0, 129.6 (q, J_{CF} = 32.30 Hz), 129.2, 125.8 (q, J_{CF} = 271.9 Hz), 125.5 (q, J_{CF} = 3.6 Hz), 116.0, 72.1, 68.2, 64.6, 38.4, 38.2; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{16}H_{18}F_3O_2$: 299.1258, found: 299.1245; $[\alpha]_D^{20}$ +96.2 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er (96% ee). Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (OD column, 99.5/0.5 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 40.87 min, t_r (minor enantiomer) = 49.27 min.



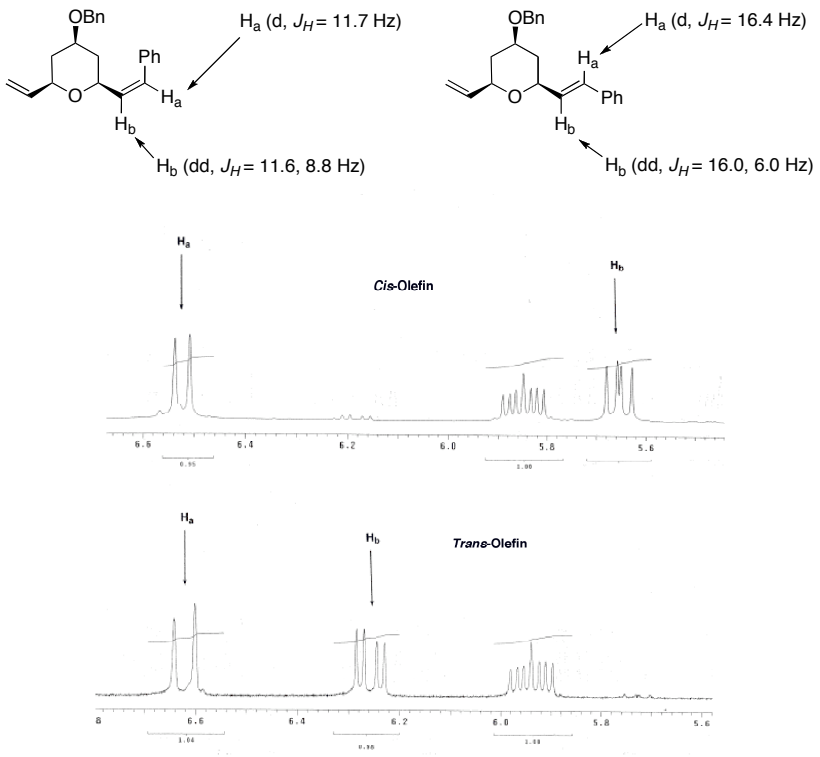
#	time (h)	area	area %	#	time (h)	area	area %
1	41.58	5815648	50.116	1	40.87	24201800	98.368
2	47.61	5788734	49.884	2	49.27	401629	1.632

(*2S,4R,6R*)-4-(Benzyloxy)-2-*Z*-styryl-6-vinyltetrahydro-2*H*-pyran (8) (Table 3, entry 4). Following the general procedure described above, oxabicycle **10** (10.0 mg, 46.0 μmol) in C_6H_6 (360 μL) was treated with *in situ*-generated complex **5b** (100.0 μL, 0.02 M, 2.10 μmol, final substrate concentration = 0.1 M) and styrene (53.0 μL, 0.460 mmol, 10.0 equiv), the mixture was allowed to stir for 1.0 hour at 60 ºC. The resulting oil was purified by silica gel chromatography (30:1 hexanes:diethyl ether) to afford **8a** (11.2 mg, 34.4 μmol, 75.0% yield) as colorless oil. **IR (neat)**: 2944 (m), 2855 (m), 1494 (w), 1452 (w), 1358 (m), 1066 (s), 986 (m), 736(s), 697 (s); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37-7.24 (m, 10H), 6.60 (d, *J* = 11.6 Hz, 1H), 5.93 (ddd, *J* = 17.2, 10.7, 5.7 Hz, 1H), 5.73 (dd, *J* = 11.5, 8.7 Hz, 1H), 5.29 (ddd, *J* = 17.2, 1.5, 1.5 Hz, 1H), 5.15

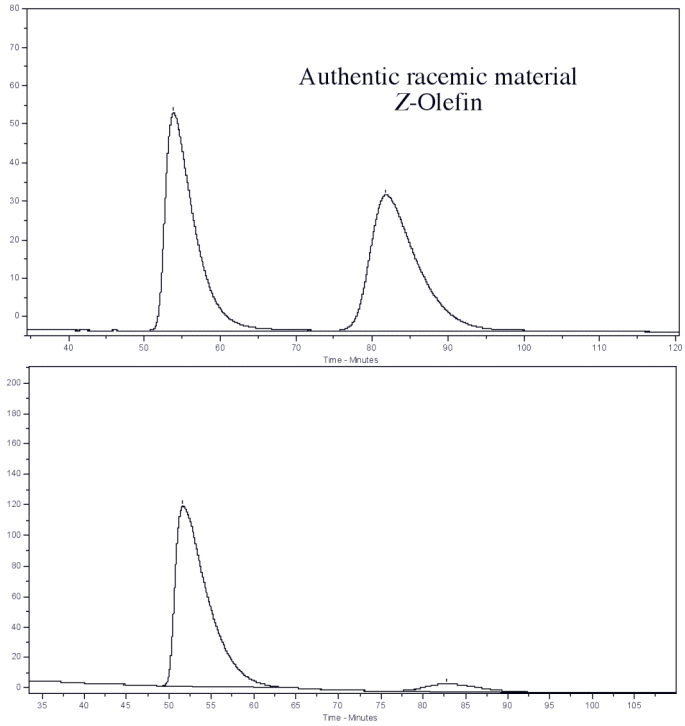
(ddd, *J* = 10.6, 1.3, 1.3 Hz, 1H), 4.58 (s, 2H), 4.28-4.21 (m, 1H), 3.92-3.85 (m, 1H), 3.62-3.48 (m, 1H), 2.15-2.10 (m, 2H), 1.51-1.42 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.7, 138.6, 137.0, 132.2, 131.9, 129.0, 128.7, 128.5, 127.8, 127.5, 127.2, 115.7, 76.2, 74.2, 72.3, 69.8, 38.2, 37.8; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{22}H_{25}O_2$: 321.1854, found: 321.1847; $[\alpha]_D^{20}$ +12.1 (c = 0.5, $CHCl_3$) for an enantiomerically enriched sample of 92:8 er (84% ee). Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (OJ-H column, 99.8/0.2 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 99.57 min, t_r (minor enantiomer) = 80.51 min.



#	time (min)	area	area %	#	time (min)	area	area %
1	77.93	19191690	49.926	1	80.51	1050521	7.695
2	101.38	19248600	50.074	2	99.57	12601580	92.305



(*2S,4S,6R*)-4-(Benzyloxy)-2-*Z*-styryl-6-vinyltetrahydro-2*H*-pyran (9) (Table 3, entry 9). Following the general procedure described before, oxabicycle (10.0 mg, 46.0 μmol) in C_6H_6 (420 μL) was treated with *in situ*-generated **5b** (40.0 μL, 0.02 M, 0.80 μmol, final substrate concentration = 0.1 M) and styrene (53.0 μL, 0.460 mmol, 10.0 equiv); the mixture was allowed to stir for 1.0 hour. The resulting oil was purified by silica gel chromatography (30:1 hexanes:diethyl ether) to afford **9a** (12.0 mg, 37.5 μmol, 80.0% yield) as colorless oil. **IR (neat)**: 3061 (w), 3025 (w), 2919 (w), 2855 (w), 1494 (w), 1452 (w), 1337 (m), 1052(s), 989 (m), 695 (s); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.36-7.23 (m, 10H), 6.52 (d, *J* = 11.7 Hz, 1H), 5.86 (ddd, *J* = 17.0, 10.7, 5.7 Hz, 1H), 5.69 (dd, *J* = 11.8, 8.6 Hz, 1H), 5.25 (ddd, *J* = 17.4, 1.4, 1.4 Hz, 1H), 5.10 (ddd, *J* = 10.7, 1.5, 1.5 Hz, 1H), 4.92-4.86 (m, 1H), 4.53 (dd, *J* = 15.5, 11.9 Hz, 2H), 4.38-4.32 (m, 1H), 3.94-3.90 (m, 1H), 2.01-1.91 (m, 2H), 1.62-1.54 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 139.3, 139.0, 137.1, 132.8, 131.3, 129.1, 128.6, 128.5, 127.7, 127.4, 126.4, 115.4, 72.7, 71.5, 70.3, 69.1, 35.5, 35.3; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{22}H_{25}O_2$: 321.1854, found: 321.1863; $[\alpha]_D^{20}$ +52.8 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 86 % ee. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (OJ-H column, 99.8/0.2 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 51.69 min, t_r (minor enantiomer) = 82.77 min.

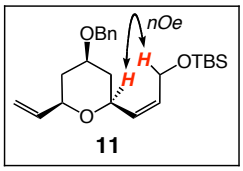


#	time (min)	area	area %	#	time (min)	area	area %
1	53.90	15189940	49.649	1	51.69	31343360	94.147
2	81.78	15404440	50.351	2	82.77	1948478	5.853

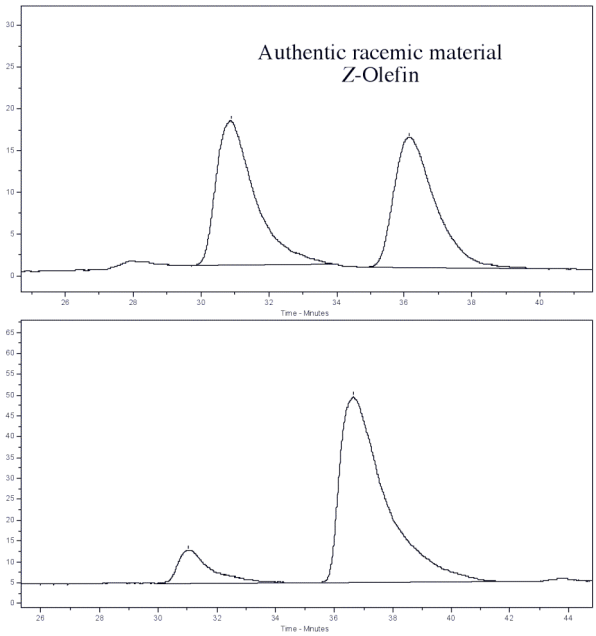
((*Z*)-3-((*2S,4R,6R*)-4-(Benzyloxy)-6-vinyltetrahydro-2*H*-pyran-2-*Z*-yl)allyloxy)(*tert*-butyl)dimethylsilane (11) (eq 2). Following the previously described procedure, oxabicycle **10** (10.0 mg, 46.0 μmol) in C_6H_6 (360 μL) was treated with *in situ*-generated complex **5b** (100.0 μL, 0.02 M, 2.10 μmol, final substrate concentration = 0.1 M) and allylsilyl ether (80.0 mg, 460 μmol, 10.0 equiv.), the mixture was allowed to stir for 1.0 hour. The resulting oil was purified by silica gel chromatography (50:1 hexanes:diethyl ether) to afford **11** (8.1 mg, 21.0 μmol, 45.0% yield) as colorless oil. **IR (neat)**: 2951 (m), 2928 (m), 2883 (m), 2856 (m), 1496 (w), 1462 (w), 1408 (w), 1356 (m), 1254 (m), 1072 (s), 986 (m), 735 (s), 697 (s); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38-7.24 (m, 5H), 5.86 (ddd, *J* = 18.8, 10.6, 5.4 Hz, 1H), 5.63-5.56 (m, 1H), 5.51-5.45 (m, 1H), 5.24 (ddd, *J* = 17.3, 1.4, 1.4 Hz, 1H), 5.11 (ddd, *J* = 10.6, 1.4, 1.4 Hz, 1H), 4.57 (s, 2H), 4.25 (ddd, *J* = 5.9, 1.4, 1.4 Hz, 2H), 4.21-4.14 (m, 1H), 3.90-3.81 (m, 1H), 3.62-3.55 (m, 1H), 2.12-2.06 (m, 1H), 2.04-1.97 (m, 1H), 1.42-1.29 (m, 2H), 0.88 (s, 9H), 0.05 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 139.1, 138.5, 132.0, 131.0, 128.7, 127.8, 127.6, 115.6, 76.4, 74.5, 72.5, 69.8, 60.1, 38.3, 37.7, 26.2, 18.3, –4.90, –4.97; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{23}H_{37}O_3Si$: 389.2512, found: 389.2506; $[\alpha]_D^{20}$ –3.2 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 88:12 er (76% ee). Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material of the corresponding alcohol.

(*Z*)-3-((*2S,4R,6R*)-4-(Benzyloxy)-6-vinyltetrahydro-2*H*-pyran-2-yl)prop-2-en-1-ol. Following the procedure described before, pyran **10** was desilylated. **IR (neat)**: 3405 (br), 3026 (m), 2920 (m), 2851 (m), 1454 (m), 1356 (m), 1302 (m), 1069 (m), 1009 (m), 926 (m), 737 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37-7.23 (m, 5H), 5.86 (ddd, *J* = 20.8, 10.6, 5.7 Hz, 1H), 5.80-5.73 (m, 1H), 5.61-5.55 (m, 1H), 5.25 (ddd, *J* = 17.3, 1.3, 1.3 Hz, 1H), 5.13 (ddd, *J* = 10.6, 1.3, 1.3 Hz, 1H), 4.57 (s, 2H), 4.27-4.11 (m, 3H), 3.92-3.85 (m, 1H), 3.63 (ddd, *J* = 20.0, 11.1, 4.6 Hz, 1H), 2.14-2.10 (m, 1H), 2.07-2.04 (m, 1H), 2.03-2.00 (m, 1H), 1.46-1.32 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.6, 138.2, 132.4, 132.0, 128.7, 128.0, 127.8, 116.0, 76.7, 74.3, 72.5, 70.0, 59.3, 38.3, 37.7; **HRMS (ESI$^+$) [M+H]$^+$** calcd for $C_{17}H_{23}O_3$: 275.1647, found: 275.1654; $[\alpha]_D^{20}$ +7.5 (c = 0.375, $CHCl_3$) for an enantiomerically enriched sample of 88:12 er (76% ee). Enantiomeric purity was determined by chiral HPLC analysis in comparison with authentic racemic material (OD column, 98.0/2.0 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm; t_r (major enantiomer) = 36.66 min, t_r (minor enantiomer) = 31.03 min

Proof of *Z*-selectivity: The stereochemistry of the product olefin was established through NOESY experiments, as summarized below. For the complete spectrum, see page 42–43 of Supporting Information Part B.



11



#	time (min)	area	area %	#	time (min)	area	area %
1	30.88	1406152	51.407	1	31.03	640265	11.734
2	36.15	1329180	48.593	2	36.66	4816096	88.266

■ **For additional examples of previously reported *Z*-selective olefin metathesis processes**, see: (a) Randall, M. L.; Tallarico, J. A.; Snapper, M. L. *J. Am. Chem. Soc*. **1995**, *117*, 9610–9611. (b) Tallarico, J. A.; Randall, M. L.; Snapper, M. L. *Tetrahedron*, **1997**, *vol. 53*, 16511–16520. (c) Kang, B.; Kim, D.; Do, Y.; Chang, S. *Organic Letters*, **2003**, *vol. 5*, 3041–3043. (d) Kang, B.; Lee, J. M.; Kwak, J.; Lee, Y. S.; Chang, S. *J. Org. Chem.* **2004**, *69*, 7661–7664. (e) Sashuk, V.; Samojlowicz, C.; Szadkowska, A.; Grela, K. *Chem. Commun.*, **2008**, 2468–2470.

■ **Proof of Absolute Stereochemistry.** The identity of the major enantiomer from Mo-catalyzed enantioselective ROCM was established through X-ray crystallography (see below). The stereochemical assignments for other pyran products obtained in this study are by inference.

X-ray structure obtained for *p*-bromobenzoate derived from ROCM product **7a** Table 3)

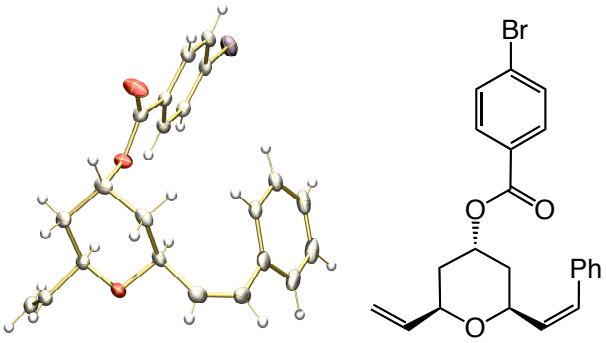


Table 1. Crystal data and structure refinement

Identification code	$C_{22}H_{21}BrO_3$	
Empirical formula	$C_{22}H_{21}BrO_3$	
Formula weight	413.30	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 5.916(4) ≈	α= 90∞.
	b = 7.695(5) ≈	β= 92.434(8)∞.
	c = 21.225(13) ≈	γ = 90∞.
Volume	965.4(10) ≈^{3}	
Z	2	
Density (calculated)	1.422 Mg/m^3	
Absorption coefficient	2.147 mm^{-1}	
F(000)	424	
Crystal size	0.10 x 0.05 x 0.02 mm^3	
Theta range for data collection	2.88 to 28.27∞.	
Index ranges	-7<=h<=7, -10<=k<=10, -27<=l<=28	
Reflections collected	11087	
Independent reflections	4556 [R(int) = 0.0441]	
Completeness to theta = 28.27∞	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9583 and 0.8139	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	4556 / 22 / 298
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0899
R indices (all data)	R1 = 0.0438, wR2 = 0.0931
Absolute structure parameter	0.019(9)
Extinction coefficient	0
Largest diff. peak and hole	0.940 and -0.453 e.$\approx^{-3}$

Table 2. **Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor**

	x	y	z	U(eq)
Br(1)	718(1)	4254(1)	9901(1)	33(1)
O(1)	-1394(3)	1162(3)	6940(1)	22(1)
O(2)	-4850(4)	740(4)	7317(1)	36(1)
O(3)	2232(3)	-861(4)	5917(1)	20(1)
C(1)	-347(5)	3244(4)	9131(1)	22(1)
C(2)	1010(5)	3322(4)	8616(2)	22(1)
C(3)	226(5)	2634(4)	8049(1)	21(1)
C(4)	-1930(5)	1886(4)	7998(1)	18(1)
C(5)	-3269(6)	1826(5)	8520(2)	22(1)
C(6)	-2476(5)	2497(4)	9094(1)	24(1)
C(7)	-2914(5)	1195(4)	7393(1)	21(1)
C(8)	-2048(6)	254(5)	6354(2)	23(1)
C(9)	-889(5)	1196(5)	5831(1)	23(1)
C(10)	1673(5)	942(4)	5874(1)	20(1)
C(11)	1350(5)	-1654(4)	6473(1)	20(1)
C(12)	-1227(6)	-1596(5)	6423(2)	24(1)
C(13)	2742(5)	1610(4)	5296(1)	23(1)
C(14)	4140(5)	2921(5)	5280(2)	27(1)
C(15)	2299(6)	-3451(4)	6504(2)	27(1)
C(16)	3280(6)	-4208(4)	7002(2)	29(1)
C(17)	3576(6)	-3494(4)	7647(2)	26(1)
C(18)	5589(6)	-3791(5)	7998(2)	32(1)
C(19)	5930(7)	-3144(6)	8603(2)	34(1)
C(20)	4220(6)	-2222(5)	8879(2)	33(1)
C(21)	2208(6)	-1928(5)	8541(2)	28(1)
C(22)	1884(5)	-2550(4)	7938(2)	23(1)

Table 3. Bond lengths [≈] and angles [∞]

Br(1)-C(1)	1.893(3)
O(1)-C(7)	1.344(3)
O(1)-C(8)	1.464(4)
O(2)-C(7)	1.202(4)
O(3)-C(10)	1.428(4)
O(3)-C(11)	1.446(3)
C(1)-C(6)	1.384(5)
C(1)-C(2)	1.384(4)
C(2)-C(3)	1.377(4)
C(2)-H(2)	0.916(18)
C(3)-C(4)	1.399(4)
C(3)-H(3)	0.944(18)
C(4)-C(5)	1.391(4)
C(4)-C(7)	1.485(4)
C(5)-C(6)	1.385(5)
C(5)-H(5)	0.940(19)
C(6)-H(6)	0.941(18)
C(8)-C(12)	1.509(5)
C(8)-C(9)	1.514(5)
C(8)-H(8)	0.964(18)
C(9)-C(10)	1.527(4)
C(9)-H(9A)	0.980(19)
C(9)-H(9B)	0.978(18)
C(10)-C(13)	1.496(4)
C(10)-H(10)	0.987(18)
C(11)-C(15)	1.493(5)
C(11)-C(12)	1.525(5)
C(11)-H(11)	0.994(18)
C(12)-H(12A)	0.982(18)
C(12)-H(12B)	0.974(18)
C(13)-C(14)	1.306(5)
C(13)-H(13)	0.945(18)
C(14)-H(14A)	0.951(18)
C(14)-H(14B)	0.949(19)

C(15)-C(16)	1.319(5)
C(15)-H(15)	0.925(18)
C(16)-C(17)	1.480(5)
C(16)-H(16)	0.918(18)
C(17)-C(18)	1.396(5)
C(17)-C(22)	1.401(5)
C(18)-C(19)	1.385(6)
C(18)-H(18)	0.965(19)
C(19)-C(20)	1.385(6)
C(19)-H(19)	0.957(19)
C(20)-C(21)	1.382(5)
C(20)-H(20)	0.949(19)
C(21)-C(22)	1.373(5)
C(21)-H(21)	0.969(18)
C(22)-H(22)	0.959(18)

C(7)-O(1)-C(8)	117.1(2)
C(10)-O(3)-C(11)	111.8(2)
C(6)-C(1)-C(2)	122.0(3)
C(6)-C(1)-Br(1)	119.3(2)
C(2)-C(1)-Br(1)	118.7(2)
C(3)-C(2)-C(1)	119.2(3)
C(3)-C(2)-H(2)	116(2)
C(1)-C(2)-H(2)	125(2)
C(2)-C(3)-C(4)	119.9(3)
C(2)-C(3)-H(3)	124(2)
C(4)-C(3)-H(3)	116(2)
C(5)-C(4)-C(3)	120.0(3)
C(5)-C(4)-C(7)	117.5(3)
C(3)-C(4)-C(7)	122.5(3)
C(6)-C(5)-C(4)	120.3(3)
C(6)-C(5)-H(5)	123(2)
C(4)-C(5)-H(5)	117(2)
C(1)-C(6)-C(5)	118.6(3)
C(1)-C(6)-H(6)	117(2)
C(5)-C(6)-H(6)	124(2)

O(2)-C(7)-O(1)	124.1(3)
O(2)-C(7)-C(4)	123.9(3)
O(1)-C(7)-C(4)	112.0(2)
O(1)-C(8)-C(12)	107.2(3)
O(1)-C(8)-C(9)	106.5(3)
C(12)-C(8)-C(9)	111.6(3)
O(1)-C(8)-H(8)	109(2)
C(12)-C(8)-H(8)	109(2)
C(9)-C(8)-H(8)	114(2)
C(8)-C(9)-C(10)	112.0(3)
C(8)-C(9)-H(9A)	109(2)
C(10)-C(9)-H(9A)	109(2)
C(8)-C(9)-H(9B)	107(2)
C(10)-C(9)-H(9B)	110(2)
H(9A)-C(9)-H(9B)	110(3)
O(3)-C(10)-C(13)	106.3(2)
O(3)-C(10)-C(9)	110.8(3)
C(13)-C(10)-C(9)	111.1(2)
O(3)-C(10)-H(10)	113(2)
C(13)-C(10)-H(10)	109(2)
C(9)-C(10)-H(10)	107(2)
O(3)-C(11)-C(15)	106.2(2)
O(3)-C(11)-C(12)	109.0(2)
C(15)-C(11)-C(12)	113.8(3)
O(3)-C(11)-H(11)	107(2)
C(15)-C(11)-H(11)	112(2)
C(12)-C(11)-H(11)	108.2(17)
C(8)-C(12)-C(11)	110.5(3)
C(8)-C(12)-H(12A)	113(2)
C(11)-C(12)-H(12A)	106(2)
C(8)-C(12)-H(12B)	110(2)
C(11)-C(12)-H(12B)	111(2)
H(12A)-C(12)-H(12B)	106(3)
C(14)-C(13)-C(10)	125.2(3)
C(14)-C(13)-H(13)	121(2)
C(10)-C(13)-H(13)	114(2)

C(13)-C(14)-H(14A)	124(2)
C(13)-C(14)-H(14B)	125(2)
H(14A)-C(14)-H(14B)	111(3)
C(16)-C(15)-C(11)	126.6(3)
C(16)-C(15)-H(15)	116(3)
C(11)-C(15)-H(15)	117(3)
C(15)-C(16)-C(17)	127.5(3)
C(15)-C(16)-H(16)	120(2)
C(17)-C(16)-H(16)	113(2)
C(18)-C(17)-C(22)	117.4(3)
C(18)-C(17)-C(16)	119.8(3)
C(22)-C(17)-C(16)	122.8(3)
C(19)-C(18)-C(17)	121.5(4)
C(19)-C(18)-H(18)	119(2)
C(17)-C(18)-H(18)	120(2)
C(18)-C(19)-C(20)	119.7(4)
C(18)-C(19)-H(19)	117(3)
C(20)-C(19)-H(19)	123(3)
C(21)-C(20)-C(19)	119.6(4)
C(21)-C(20)-H(20)	117(2)
C(19)-C(20)-H(20)	123(2)
C(22)-C(21)-C(20)	120.6(3)
C(22)-C(21)-H(21)	117(2)
C(20)-C(21)-H(21)	121(2)
C(21)-C(22)-C(17)	121.1(3)
C(21)-C(22)-H(22)	118(2)
C(17)-C(22)-H(22)	121(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. **Anisotropic displacement parameters ($\approx^2$x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	44(1)	36(1)	18(1)	-4(1)	-3(1)	-9(1)
O(1)	15(1)	33(1)	19(1)	-7(1)	0(1)	-3(1)
O(2)	19(1)	66(2)	24(1)	-9(1)	2(1)	-13(1)
O(3)	22(1)	23(1)	16(1)	0(1)	4(1)	1(1)
C(1)	29(2)	22(2)	15(1)	-1(1)	-5(1)	2(1)
C(2)	20(2)	20(2)	25(2)	0(1)	-2(1)	0(1)
C(3)	20(2)	23(2)	20(2)	3(1)	3(1)	2(1)
C(4)	17(1)	20(2)	19(1)	0(1)	-1(1)	2(1)
C(5)	24(2)	20(2)	22(2)	2(1)	3(1)	0(1)
C(6)	26(2)	26(2)	19(1)	4(1)	5(1)	1(1)
C(7)	20(2)	24(2)	21(2)	0(1)	0(1)	3(1)
C(8)	18(2)	33(2)	16(2)	-6(1)	-2(1)	-2(1)
C(9)	19(2)	33(2)	18(1)	1(1)	-3(1)	4(1)
C(10)	19(1)	24(2)	15(1)	0(1)	0(1)	2(1)
C(11)	23(2)	24(2)	13(1)	1(1)	2(1)	-2(1)
C(12)	25(2)	31(2)	15(2)	-3(1)	1(1)	-8(1)
C(13)	22(2)	30(2)	17(1)	2(1)	2(1)	5(1)
C(14)	23(2)	31(2)	27(2)	8(1)	2(1)	6(1)
C(15)	31(2)	24(2)	26(2)	-4(1)	7(1)	-2(1)
C(16)	36(2)	18(2)	33(2)	3(1)	12(2)	3(1)
C(17)	28(2)	21(2)	30(2)	11(1)	4(1)	-3(1)
C(18)	25(2)	27(2)	46(2)	16(2)	2(2)	2(1)
C(19)	31(2)	30(2)	41(2)	15(2)	-11(2)	-6(2)
C(20)	36(2)	33(2)	28(2)	13(2)	-7(2)	-11(2)
C(21)	31(2)	30(2)	22(2)	8(1)	2(1)	-1(1)
C(22)	20(2)	26(2)	24(2)	8(1)	0(1)	-1(1)

Table 5. **Hydrogen coordinates (x10^4) and isotropic displacement parameters (≈^{2}x 10 ^{3})**

	x	y	z	U(eq)
H(2)	2410(40)	3840(40)	8618(15)	26
H(3)	1070(50)	2620(50)	7682(12)	25
H(5)	-4630(40)	1200(50)	8474(18)	27
H(6)	-3340(50)	2570(50)	9454(12)	28
H(8)	-3670(30)	240(50)	6305(17)	27
H(9A)	-1240(60)	2440(30)	5853(17)	28
H(9B)	-1510(50)	720(50)	5433(11)	28
H(10)	2250(60)	1610(40)	6243(13)	23
H(11)	1870(50)	-940(50)	6842(11)	24
H(12A)	-1680(60)	-2320(40)	6059(13)	28
H(12B)	-1880(60)	-2140(50)	6786(13)	28
H(13)	2360(60)	960(40)	4928(12)	27
H(14A)	4550(60)	3620(40)	5637(13)	32
H(14B)	4860(60)	3320(50)	4917(13)	32
H(15)	2180(60)	-4110(50)	6139(13)	33
H(16)	3970(50)	-5270(30)	6958(17)	34
H(18)	6790(50)	-4440(50)	7813(18)	39
H(19)	7330(50)	-3430(60)	8821(18)	41
H(20)	4410(60)	-1640(50)	9272(12)	40
H(21)	1060(50)	-1160(40)	8699(16)	33
H(22)	440(40)	-2340(50)	7728(15)	28

Table 6. **Torsion angles [∞]**

C(6)-C(1)-C(2)-C(3)	-0.1(5)
Br(1)-C(1)-C(2)-C(3)	-178.2(2)
C(1)-C(2)-C(3)-C(4)	0.7(5)
C(2)-C(3)-C(4)-C(5)	-0.5(5)
C(2)-C(3)-C(4)-C(7)	177.1(3)
C(3)-C(4)-C(5)-C(6)	-0.3(5)
C(7)-C(4)-C(5)-C(6)	-178.1(3)
C(2)-C(1)-C(6)-C(5)	-0.7(5)
Br(1)-C(1)-C(6)-C(5)	177.4(3)
C(4)-C(5)-C(6)-C(1)	0.9(5)
C(8)-O(1)-C(7)-O(2)	-10.4(5)
C(8)-O(1)-C(7)-C(4)	170.5(3)
C(5)-C(4)-C(7)-O(2)	7.0(5)
C(3)-C(4)-C(7)-O(2)	-170.7(3)
C(5)-C(4)-C(7)-O(1)	-173.8(3)
C(3)-C(4)-C(7)-O(1)	8.5(4)
C(7)-O(1)-C(8)-C(12)	-92.4(3)
C(7)-O(1)-C(8)-C(9)	148.0(3)
O(1)-C(8)-C(9)-C(10)	68.8(3)
C(12)-C(8)-C(9)-C(10)	-47.8(4)
C(11)-O(3)-C(10)-C(13)	178.1(2)
C(11)-O(3)-C(10)-C(9)	-61.0(3)
C(8)-C(9)-C(10)-O(3)	52.1(3)
C(8)-C(9)-C(10)-C(13)	170.0(3)
C(10)-O(3)-C(11)-C(15)	-172.8(2)
C(10)-O(3)-C(11)-C(12)	64.2(3)
O(1)-C(8)-C(12)-C(11)	-65.2(3)
C(9)-C(8)-C(12)-C(11)	51.1(3)
O(3)-C(11)-C(12)-C(8)	-58.3(3)
C(15)-C(11)-C(12)-C(8)	-176.6(3)
O(3)-C(10)-C(13)-C(14)	-124.5(3)
C(9)-C(10)-C(13)-C(14)	114.9(4)
O(3)-C(11)-C(15)-C(16)	131.6(3)
C(12)-C(11)-C(15)-C(16)	-108.5(4)

C(11)-C(15)-C(16)-C(17)	3.0(6)
C(15)-C(16)-C(17)-C(18)	-140.7(4)
C(15)-C(16)-C(17)-C(22)	40.9(5)
C(22)-C(17)-C(18)-C(19)	-1.6(5)
C(16)-C(17)-C(18)-C(19)	180.0(3)
C(17)-C(18)-C(19)-C(20)	1.9(5)
C(18)-C(19)-C(20)-C(21)	-1.3(5)
C(19)-C(20)-C(21)-C(22)	0.4(5)
C(20)-C(21)-C(22)-C(17)	-0.1(5)
C(18)-C(17)-C(22)-C(21)	0.7(5)
C(16)-C(17)-C(22)-C(21)	179.1(3)

Symmetry transformations used to generate equivalent atoms: