Supporting Information

Highly Stereoselective [2,3]-Sigmatropic Rearrangement of Sulfur Ylide Generated through Cu(I) Carbene and Sulfides

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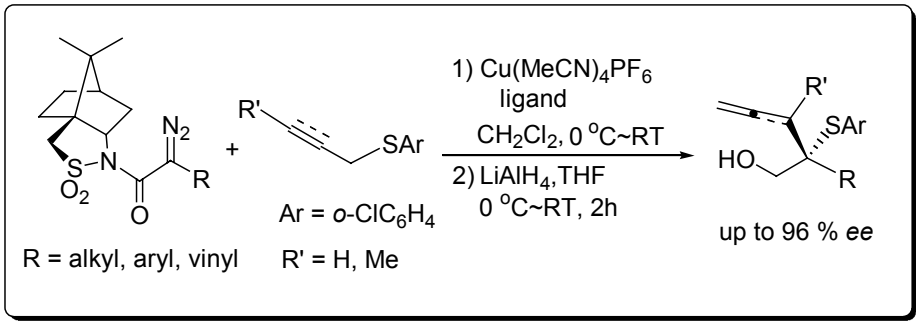


CONTENTS

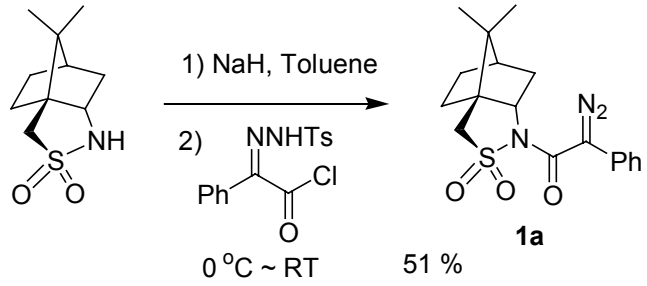
Experimental Section

Caution: All diazo compounds are highly toxic or presumed to be toxic. Diazo compounds are potentially explosive. They should be handled with care in a well-ventilated fumehood.

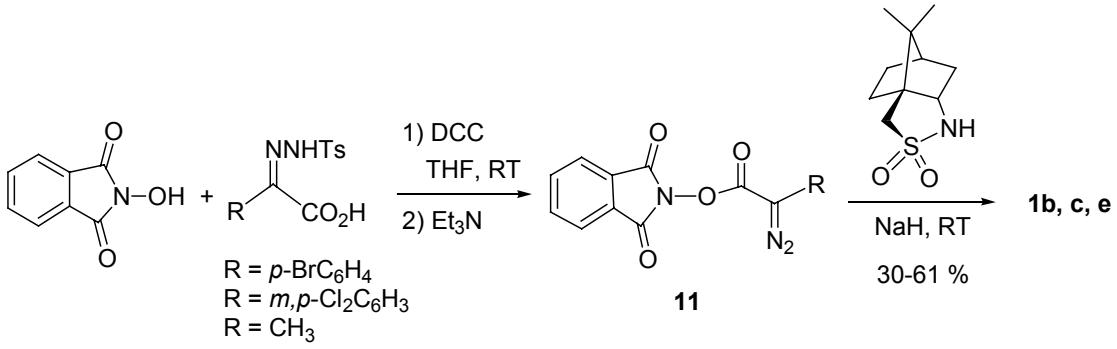
General All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled prior to use. CH_2Cl_2 was distilled over calcium hydroxide, and THF was distilled over sodium. For chromatography, 100-200 mesh silica gel (Qindao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 300 MHz (or 200 MHz) and 75 MHz (or 50 MHz) with Varian Mercury 300 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. HPLC analysis was performed at HP 1100 apparatus with Chiracel column.

The Synthesis of Diazoacetamides 1a-g.

N-Phenyldiazoacety1 camphorsultam **1a** was prepared following the procedure reported by Moody and coworkers.[1] However, for other diazoacetamides the similar approach gave very poor yields.

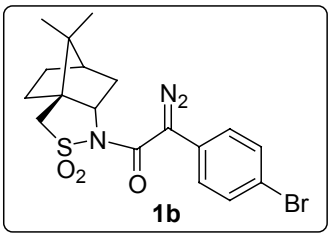


For preparation of **1b**, **c** and **e**, an alternative approach was followed. The nucleophilic substitution approach, originally developed by Badet and coworkers,[2] is modified by using phthalimidyl aryl- or methyldiazoacetate **11** as the diazoacylating reagents instead of succinimidyl diazoacetate.



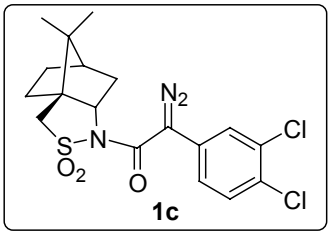
Typical Procedure for the Reaction of 11 with (*1S*)-(-)-2,10-camphorsultam. Under a nitrogen atmosphere, a solution of (*1S*)-(-)-2,10-camphorsultam (1.61 g, 7.5 mmol) in THF (10 mL) was added dropwise to a stirred suspension of NaH (60 % dispersion in mineral oil, 0.3 g, 7.5 mmol) in THF (10 mL) at 0 °C. After 30 min, a solution of **11** (1.93 g, 5 mmol) in THF (10 mL) was added dropwise, and the mixture was stirred at RT for 2 h. Saturated $NaHCO_3$ was added, and the mixture was extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by silica gel column eluted with petroleum ether/ethyl acetate (20 : 1 to 10 : 1) to give pure product **1b** (1.33 g, 61 %).

(*1S*)-(-)-***N*-(*p*-Bromophenyl)diazoacetyl 2,10-camphorsultam (1b)**



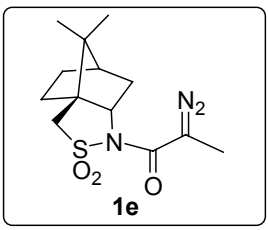
Yield, 61 %; TLC R_f = 0.52 (petroleum : acetone = 5 : 1); $[\alpha]_D^{20}$ = -263.5° (*c* 1.20, $CHCl_3$). IR (neat) 2927, 2117, 1665, 1492, 1320, 1232, 1168, 1130, cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (s, 3H), 1.15 (s, 3H), 1.35~1.58 (m, 2H), 1.88~2.02 (m, 5H), 3.41 (s, 2H), 4.12 (t, *J* = 5.1 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 2 H), 7.51 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.84, 20.33, 26.74, 32.34, 36.78, 44.51, 48.01, 48.47, 52.22, 64.23, 120.13, 124.23, 125.81, 131.99, 162.77; EI-MS (*m/z*, relative intensity): 409 [(M -28)$^+$, 6], 347 (11), 236 (17), 183 (100), 109 (22), 93 (13), 41 (19). Anal. calcd. for $C_{18}H_{20}BrN_3O_3S$: N, 9.59; C, 49.32; H, 4.60. Found: N, 9.48; C, 49.15; H, 4.67.

(*1S*)-(-)-***N*-(*m, p*-Dichlorophenyl)diazoacetyl 2,10-camphorsultam (1c)**



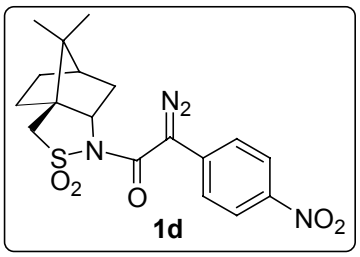
Yield, 30 %; TLC R_f= 0.50 (petroleum : acetone = 5 : 1), $[\alpha]_D^{20}$ = -259.3° (*c* 0.630, $CHCl_3$). IR (neat) 2960, 2099, 1660, 1476, 1336, 1168 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (s, 3H), 1.15 (s, 3H), 1.26~1.45 (m, 1H), 1.55~1.61 (m, 1H), 1.92~2.05 (m, 5H), 3.42 (s, 2H), 4.12 (t, *J* = 4.5 Hz, 1H), 7.23 (dd, *J* = 2.4, 8.7 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.85, 20.36, 26.76, 32.39, 36.84, 44.55, 48.04, 48.52, 52.30, 64.32, 123.20, 125.57, 125.89, 130.22, 130.70, 133.25, 162.57; EI-MS (*m/z*, relative intensity): 399 [(M -28)$^+$, 20], 335 (35), 292 (24), 226 (59), 173 (53), 109 (100), 79 (43), 67 (76), 41 (89). Anal. calcd. for $C_{18}H_{19}Cl_2N_3O_3S$: N, 9.81; C, 50.47; H, 4.71. Found: N, 9.51; C, 50.68; H, 4.68.

(*1S*)-(-)-***N*-(2-Diazo)propionyl 2,10-camphorsultam (1e)**



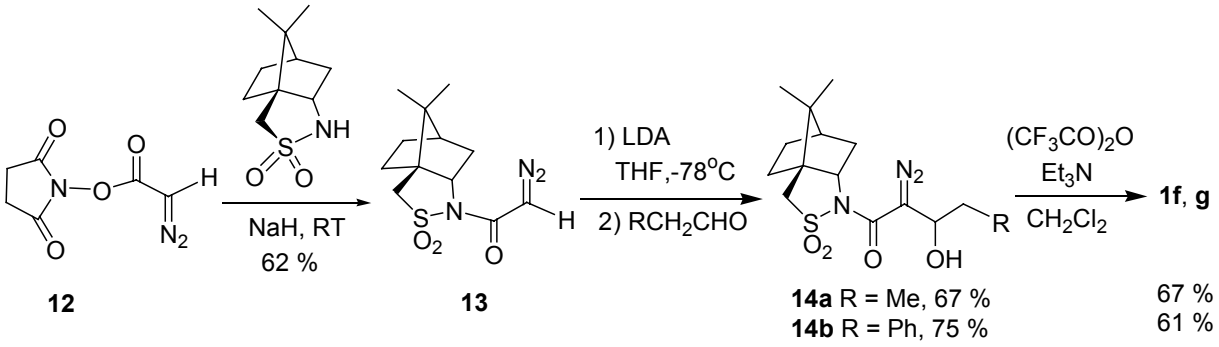
Yield 53 %; TLC R_f = 0.40 (petroleum : acetone = 5 : 1); $[\alpha]_D^{20}$ = -210.0° (*c* 1.02, $CHCl_3$). IR (neat) 2958, 2931, 2097, 1649, 1371, 1338, 1315 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.99 (s, 3H), 1.34 (s, 3H), 1.36~1.38 (m, 1H), 1.49~1.55 (m, 1H), 1.85~1.97 (m, 5H), 2.06 (s, 3H), 3.38 (s, 2H), 4.06 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.80, 20.39, 26.66, 32.33, 36.78, 44.52, 47.86, 48.41, 52.05, 60.03, 64.45, 165.20; EI-MS (*m/z*, relative intensity): 297 (M^+, 3), 226 (2), 135 (38), 121 (49), 107 (36), 93 (86), 79 (34), 67 (23), 55 (32), 43 (100). Anal. calcd. for $C_{13}H_{19}N_3O_3S$: N, 14.13; C, 52.51; H, 6.44. Found: N, 14.01, C, 52.21, H, 6.50.

(*1S*)-***N*-(*p*-Nitrophenyl)diazoacetyl 2,10-camphorsultam (1d)**



This diazo compound was prepared by direct diazo transfer to the corresponding ***N*-(*p*-nitrophenyl)acetyl camphorsultam. This diazo compound was found unstable on silica gel column. IR ($CHCl_3$) 2959, 2104, 1693, 1664, 1596, 1523, 1331 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.94 (s, 3H), 1.13 (s, 3H), 1.17~1.61 (m, 2H), 1.95~2.05 (m, 5H), 3.45 (s, 2H), 4.13~4.16 (m, 1H), 7.59 (d, *J* = 7.2 Hz, 2H), 8,25 (d, *J* = 7.2 Hz, 2H); EI-MS (*m/z*, relative intensity): 404 (M^+, 3), 226 (7), 150 (100), 135 (31), 120 (11), 104 (16), 93 (13), 76 (9).

For the synthesis of **1f** and **1g**, the following procedures were followed.



Under a nitrogen atmosphere, a solution of (*1S*)-(-)-2,10-camphorsultam (2.58 g, 12 mmol) in anhydrous THF (10 mL) was added dropwise at 0 °C to a stirred suspension of NaH (60 % dispersion in mineral oil, 0.48 g, 12 mmol) in anhydrous THF (10 mL). After 30 min, a solution of the succinimidyl diazoacetate **12** (1.83 g, 10 mmol) in anhydrous THF (10 mL) was added dropwise, and the mixture was stirred at RT for 2 h. Saturated $NaHCO_3$ was added, and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by silica gel column eluted with petroleum ether/ethyl acetate (8 : 1) to give pure **13** (1.75 g, 62 %).

(*1S*)-(-)-***N*-Diazoacetyl 2,10-camphorsultam (13).**[3] $[\alpha]_D^{20}$ = -106.3° (*c* 1.245, $CHCl_3$). IR ($CHCl_3$) 3121, 2955, 2876, 2115, 1636, 1325 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.96 (s, 3H), 1.13 (s, 3H), 1.33~1.50 (m, 2H), 1.85~1.96 (m, 3H), 2.05~2.22 (m, 2H), 3.41 (d, *J* = 13.8 Hz, 1H), 3.46 (d, *J* = 13.8 Hz, 1H), 3.91 (dd, *J* = 4.8, 7.5 Hz, 1H), 5.73 (s, 1H).

Preparation of 14a and 14b. Under a nitrogen atmosphere, a solution of *n*-butyllithium in hexane (1.41 mL, 1.8 mol/L, 2.54 mmol) was added with syringe to a solution of diisopropylamine (0.385 mL, 2.76 mmol) in anhydrous THF (5 mL) at –78 °C (dry Ice-acetone bath) and stirred for 0.5 h. Then the solution of *N*-diazoacetyl camphorsultam **13** (600 mg, 2.12 mmol) in anhydrous THF (10 mL) was added dropwise over 30 min. After the mixture was stirred for another 1 h at –78 °C, a solution of propionaldehyde (185 mg, 3.18 mmol) in anhydrous THF (10 mL) was added dropwise. The solution was stirred for 3 h, then saturated NH_4Cl was added and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by silica gel column eluted with petroleum ether/acetone (10 : 1) to give **14a** as a 1 : 1 diastereomeric mixture (482 mg, 67 %). The reaction with phenylacetaldehyde gave similar results.

(*1S*)-(-)-***N*-(2-Diazo-3-hydroxy)pentanoyl 2,10-camphorsultam (14a).** $[\alpha]_D^{20}$ = -159.1° (*c* 0.530, $CHCl_3$). IR ($CHCl_3$) 3479, 2963, 2882, 2099, 1647, 1333 cm^{-1}, ^1H NMR ($CDCl_3$, 300 MHz) δ 0.96 (s, 3H), 1.00 (dt, *J* = 1.2, 7.5 Hz, 3H), 1.14 (s, 3H), 1.33~1.43 (m, 1H), 1.46~1.65 (m, 1H), 1.69~1.83 (m, 2H), 1.86~1.97 (m, 5H), 3.18 (bs, 1H), 3.40 (m, 2H), 4.03~4.06 (m, 1H), 4.58~4.69 (m, 1H).

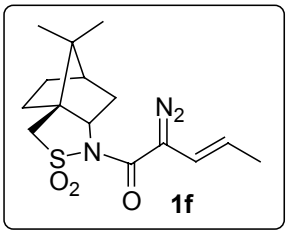
(*1S*)-(-)-***N*-(2-Diazo-3-hydroxy-4-phenyl)butenoyl 2,10-camphorsultam (14b).** Yield 75 %; $[\alpha]_D^{20}$ = -110.5° (*c* 0.750, $CHCl_3$). IR ($CHCl_3$) 3461, 2960, 2101, 1644, 1332 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.94 (s, 3H), 1.09 (s, 3H), 1.24~1.40 (m, 1H), 1.43~1.51 (m, 1H), 1.77~1.87 (m, 5H), 2.89~3.05 (m, 2H), 3.14 (bs, 1H), 3.36 (s, 2H), 3.93~4.03 (m, 1H), 4.88~4.96 (m, 1H), 7.21~7.33 (m, 5H).

General procedure for dehydration of β-hydroxy-α-diazo compounds[4]

Under a nitrogen atmosphere, *N*-(2-diazo-3-hydroxy)pentanoylcamphorsultam **14a** (341 mg, 1 mmol) was dissolved in CH_2Cl_2 (15 mL). Stirring at 0 °C, Et_3N (253 mg, 2.5 mmol) and $(CF_3CO)_2O$ (420 mg, 2

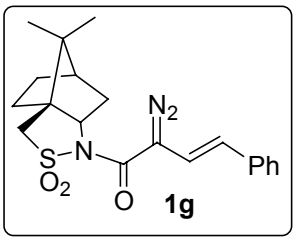
mmol) was added successively with syringe. The mixture was allowed to warmed to room temperature and was stirred over night. Removal of the solvent in vacuo gave a crude residue which was purified by silica gel column eluted with petroleum ether/ethyl acetate (20 : 1 to 15 : 1) to give pure product **1f** (216 mg, 67 %).

(*1S*)-(-)-*N*-(2-Diazo)pent-3-enoyl 2,10-camphorsultam (1f)



TLC R_f = 0.54 (petroleum : acetone = 5 : 1), $[\alpha]_D^{20}$ = -270.3° (*c* 1.075, $CHCl_3$); IR (neat) 2958, 2095, 1656, 1372, 1342, 1167 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.96 (s, 3H), 1.14 (s, 3H), 1.37~1.49 (m, 1H), 1.52~1.55 (m, 1H), 1.85 (dd, *J* = 1.5, 6.6 Hz, 3H), 1.89~1.97 (m, 5H), 3.39 (s, 2H), 4.08 (t, *J* = 7.5 Hz, 1H), 5.32~5.40 (m, 1H), 5.84~5.90 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.02, 19.82, 20.41, 26.67, 32.37, 36.85, 44.53, 47.91, 48.45, 52.22, 64.51, 112.71, 121.31, 162.89; EI-MS (*m/z*, relative intensity): 323 (M^+, 6), 259 (4), 216 (4), 151 (15), 136 (31), 109 (100), 93 (38), 83 (22), 69 (62), 54 (25), 41 (54). Anal. calcd. for $C_{15}H_{21}N_3O_3S$: N, 12.99; C. 55.71; H, 6.54. Found: N, 12.48; C, 55.56; H, 6.68.

(*1S*)-(-)-*N*-(2-Diazo-4-phenyl)but-3-enoyl 2,10-camphorsultam (1g)

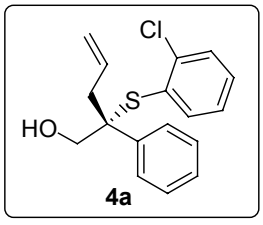


Yield 61 %; TLC R_f = 0.49 (petroleum : acetone = 5 : 1); $[\alpha]_D^{20}$ = -212.9° (*c* 0.635, $CHCl_3$); IR ($CHCl_3$) 2958, 2092, 1790, 1655, 1598 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.96 (s, 3H), 1.16 (s, 3H), 1.30~1.55 (m, 2H), 1.90~1.98 (m., 5H), 3.42 (s, 2H), 4.10~4.14 (m, 1H), 6.19 (d, *J* = 16.2 Hz, 2H), 6.62 (d, *J* = 16.2 Hz, 2H), 7.18~7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.82, 20.48, 26.57, 32.42, 36.97, 44.60, 47.93, 48.51, 52.38, 64.76, 111.39, 123.69, 125.78, 126.03, 127.24, 128.61, 162.88; EI-MS (*m/z*, relative intensity): 385 (M^+, 48), 171 (100), 114 (44), 91 (14), 77 (22), 41 (23); HRMS calcd for $C_{20}H_{23}N_3O_3S$ (M^+) 385.1460, Found: 385.1461.

Typical Procedure for Catalytic Asymmetric [2,3]-Sigmatropic Rearrangement of 1a~g and 2d with Ligand (*S, S*)-7 or 8 and the Removal of the Chiral auxiliary

Under a nitrogen atmosphere, $Cu(MeCN)_4PF_6$ (6.2 mg, 0.017 mmol) and ligand (0.02 mmol) were added to a 25 mL round-bottomed flask. Dry CH_2Cl_2 (2 mL) was introduced and the solution was stirred for 0.5 h at RT. To the slightly yellow-green solution was then added *o*-chlorophenyl allyl sulfide **2d** (17 mg, 0.09 mmol), followed by dropwisely adding *N*-phenyldiazoacetyl camphorsultam **1a** (30 mg, 0.085 mmol,) in dry CH_2Cl_2 (2 mL) at 0 °C . The solution was stirred for an additional 5 h at RT until the yellow solution turned green and **1a** disappeared as judged by TLC. Then to the mixture was added anhydrous THF (2 mL) and $LiAlH_4$ (19 mg, 0.5 mmol) at 0 °C. The mixture was stirred for 20 min. Removal of the solvent in vacuo to give a crude residue which was purified by a silica gel column eluted with petroleum ether / ethyl acetate (20:1) to afford pure product **4a**.

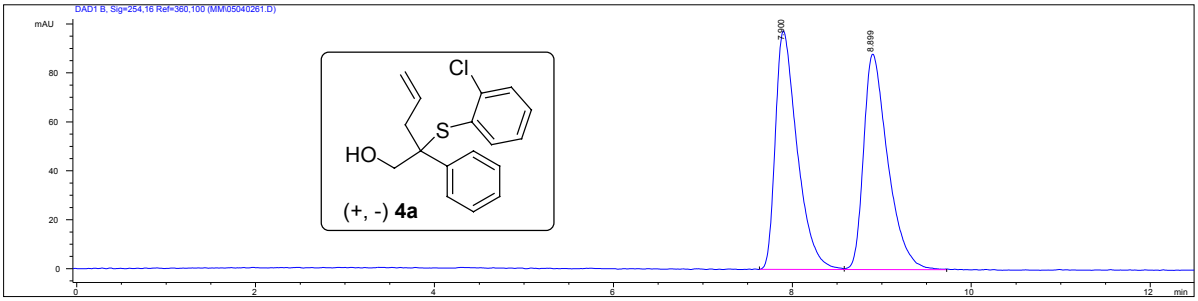
(*2R*)-(+)-(*o*-Chlorophenylsulfanyl)-2-phenylpent-4-en-1-ol (4a)



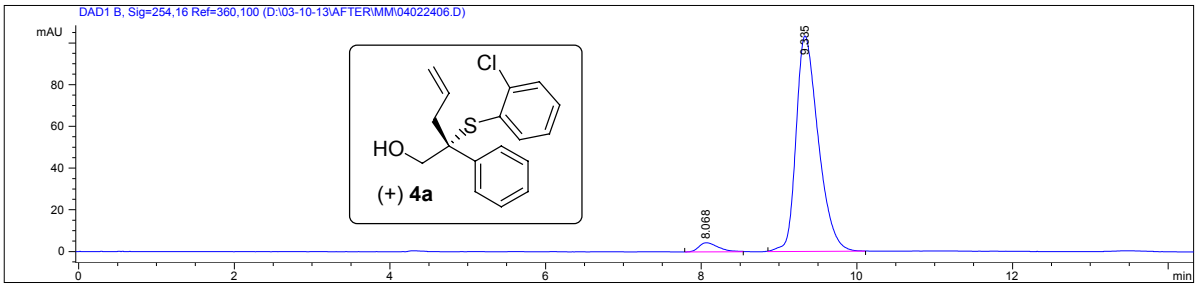
With ligand (*S, S*)-**7,** 90 % *ee*; $[\alpha]_D^{20}$ = +141.0° (*c* 0.985, $CHCl_3$); with ligand **8**, 92 % *ee*, $[\alpha]_D^{20}$ = +144.4° (*c* 1.04, $CHCl_3$); IR ($CHCl_3$) 3498, 1449,1035 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.66 (t, *J* = 7.2 Hz, 1H), 2.80~2.96 (m, 2H), 3.89 (d, *J* = 7.2 Hz, 2H), 4.98~5.12 (m, 2H), 5.45~5.59 (m, 1H), 6.81~6.95 (m, 2H), 7.16~7.43 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 40.73, 62.24, 63.03, 118.93, 126.55, 127.26, 127.59, 128.22, 129.75, 129.91, 130.17, 132.48, 138.31, 139.82,

140.29; EI-MS (*m/z*, relative intensity) 304 (M^+, 24), 161 (34), 144 (35), 105 (19), 91 (100), 77 (14), 41 (13). Anal. calcd. for $C_{17}H_{17}ClOS$: C, 66.98; H, 5.62. Found: C, 66.84; H, 5.68. HPLC condition (254 nm): Chiracel OD; *n*-hexane/*iso*-propanol = 90 : 10, t_R *(S isomer)* = 7.90 min, t_R *(R isomer)* = 8.90 min.

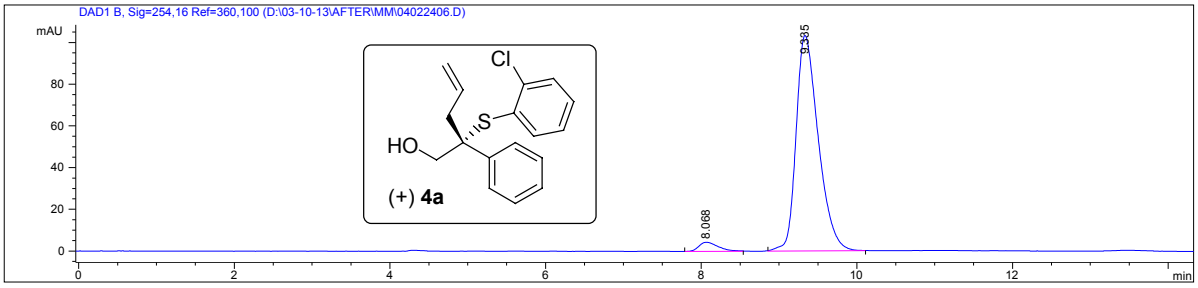
OD , 0.8 min/mL, *n*-hexane : ^{i}PrOH = 90 : 10; racemic.



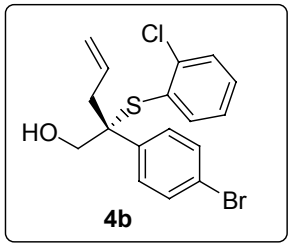
OD , 0.8 min/mL, *n*-hexane : ^{i}PrOH = 90 : 10; with ligand (*S, S*)-**7,** 90 % ee (Table 2, entry 1).



OD , 0.8 min/mL, *n*-hexane: ^{i}PrOH = 90 : 10; with ligand **8**, 92 % ee (Table 2, entry 2).

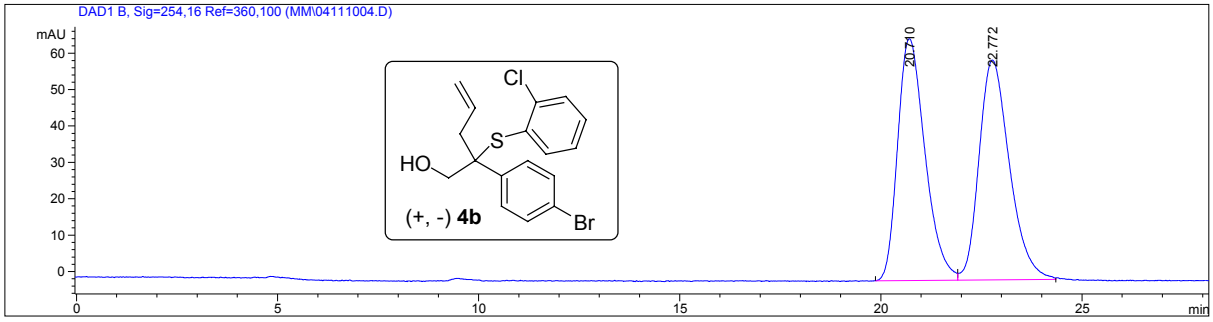


(*2R*)-(+)-(*o*-Chlorophenyl)sulfanyl-2-(*p*-bromophenyl)pent-4-en-1-ol (4b)

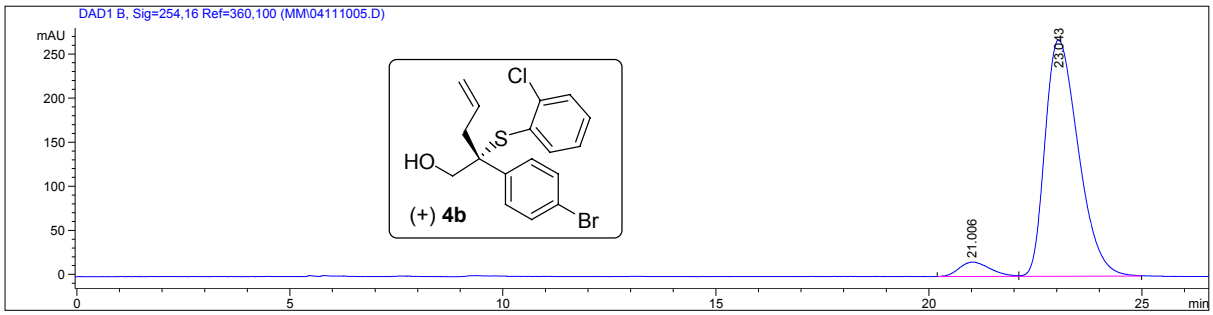


With ligand (*S, S*)-**7,** 90 % *ee*; $[\alpha]_D^{20}$ = +135.7° (*c* 0.98, $CHCl_3$); single recrystallization before removal of the auxiliary, >99 % *ee*, $[\alpha]_D^{20}$ = +150.6 (*c* 0.94, $CHCl_3$). With ligand **8**, 94 % *ee*, $[\alpha]_D^{20}$ = +140.9° (*c* 0.875, $CHCl_3$); IR ($CHCl_3$) 3487, 1490, 1036, 1008 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.71 (t, *J* = 6.9 Hz, 1H), 2.75~2.90 (m, 2H), 3.77~3.89 (m, 2H), 4.50~5.10 (m, 2H), 5.43~5.57 (m, 1H), 6.89~7.01 (m, 3H), 7.18~7.36 (m, 3H), 7.42 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 40.67, 61.61, 62.97, 119.22, 121.15, 126.70, 129.38, 129.48, 129.86, 130.40, 131.21, 132.05, 138.38, 139.46, 139.90; EI-MS (*m/z*, relative intensity) 384 (M^+, 5), 239 (34), 183 (18), 169 (100), 144 (35), 128 (30), 108 (26), 91 (22), 77 (13), 41 (24). Anal. calcd. for $C_{17}H_{16}BrClOS$: C, 55.21; H, 4.20. Found: C, 53.32; H, 4.32. HPLC condition (254 nm): Chiracel ODH; *n*-hexane/*iso*-propanol = 99.3 : 0.7, t_R *(S isomer)* = 20.71 min, t_R *(R isomer)* = 22.77 min.

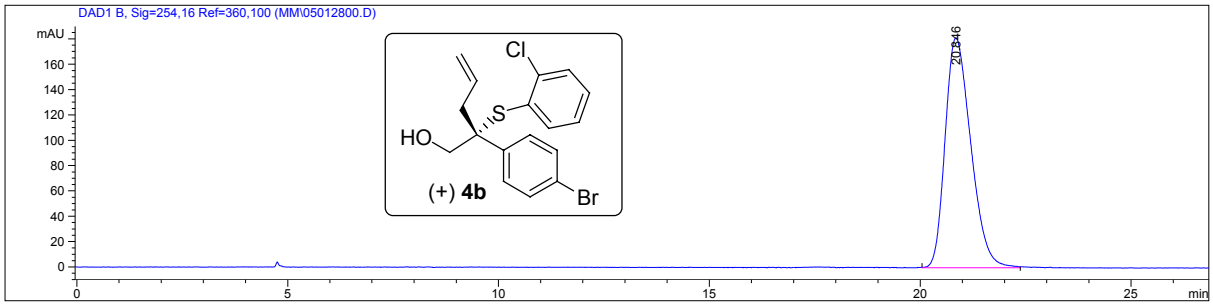
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99.3 : 0.7, racemic.



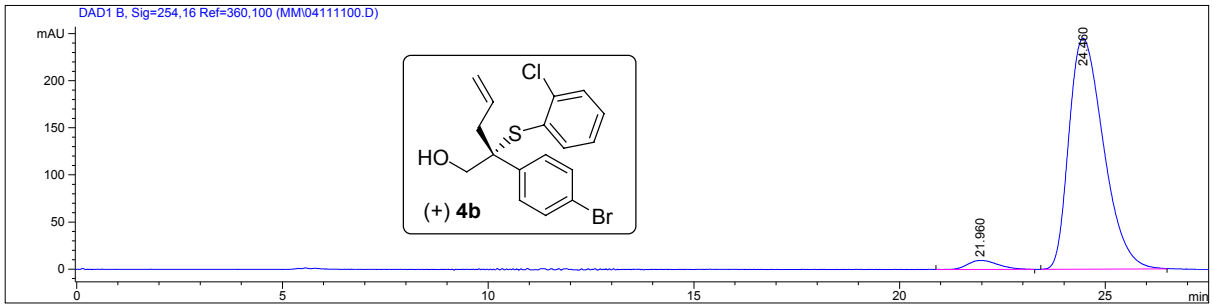
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99.3 : 0.7; with ligand (*S, S*)-**7,** 90 % ee (Table 2, entry 3).



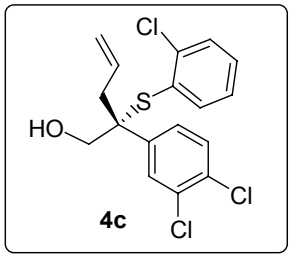
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99.3 : 0.7; single recrystallization before removal of auxiliary, >99 % ee. (Table 2, entry 4).



ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99.3 : 0.7; with ligand **8**, 94 % ee (Table 2, entry 5).

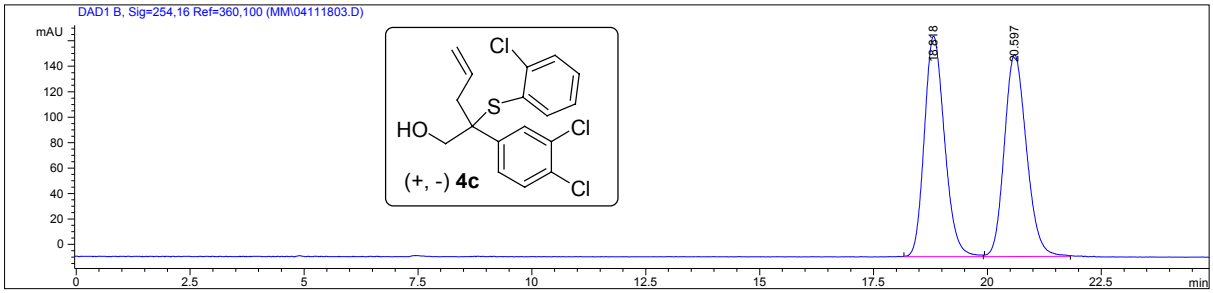


(*2R*)-(+)-(*o*-Chlorophenyl)sulfanyl-2-(*m,p*-dichlorophenyl)pent-4-en-1-ol (4c)

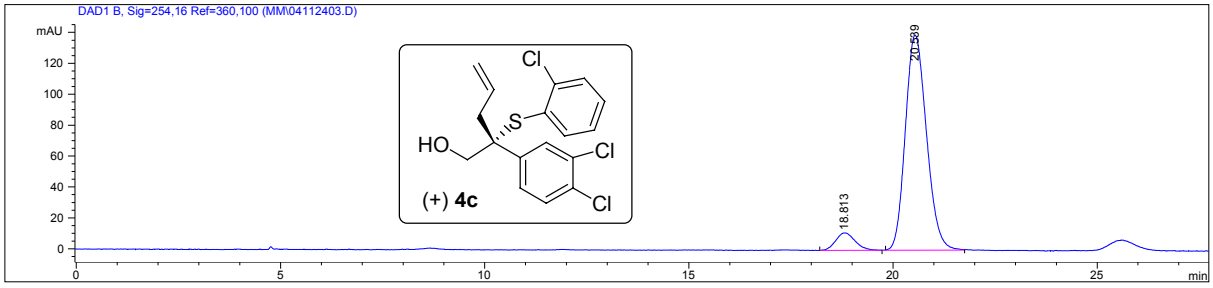


With ligand (*S, S*)-**7,** 86 % *ee*; $[\alpha]_D^{20}$ = +119.8° (*c* 0.80, $CHCl_3$); with ligand **8**, 90 % *ee*, $[\alpha]_D^{20}$ = +126.0° (*c* 0.82, $CHCl_3$); IR ($CHCl_3$) 3471, 1472, 1450, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.67~2.89 (m. 3H), 3.75~3.90 (m, 2H), 5.02~5.12 (m, 2H), 5.45~5.57 (m, 1H), 6.97~7.07 (m, 2H), 7.22~7.36 (m, 2H), 7.37~7.45 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 40.72, 61.15, 63.04, 119.56, 126.85, 127.13, 129.15, 129.78, 129.97, 130.05, 130.74, 131.16, 131.80, 132.29, 138.62, 140.14, 140.87; EI-MS (*m/z*, relative intensity): 372 (M^+, 27), 228 (25), 199 (14), 173 (30), 159 (100), 144 (52), 128 (45), 108 (58), 69 (22), 41 (82). Anal. calcd. for $C_{17}H_{15}Cl_3OS$: C, 54.63; H, 4.05. Found: C, 54.53; H, 4.20. HPLC condition (254 nm): Chiracel ODH; *n*-hexane/*iso*-propanol = 99 : 1, t_R *(S isomer)* = 18.82 min, t_R *(R isomer)* = 20.60 min

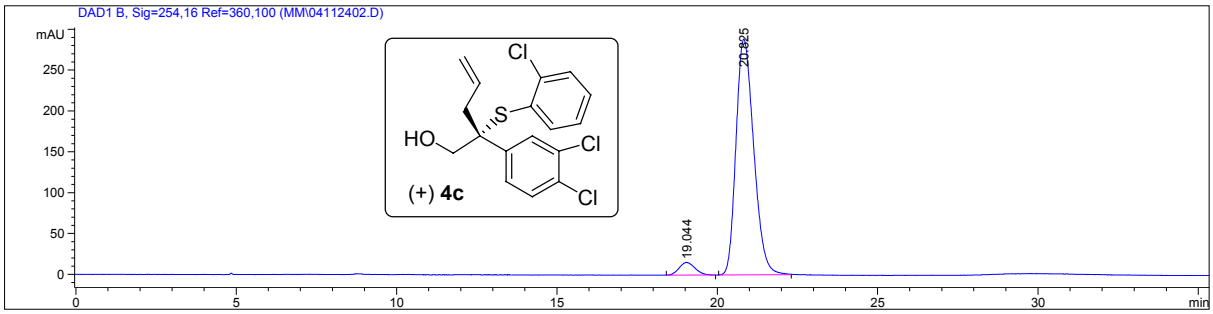
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99 : 1, racemic.



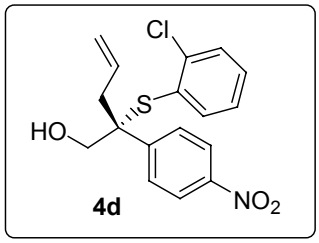
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99 : 1; with ligand (*S, S*)-**7,** 86 % ee (Table 2, entry 6).



ODH , 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99 : 1; with ligand **8**, 90 % ee (Table 2, entry 7).

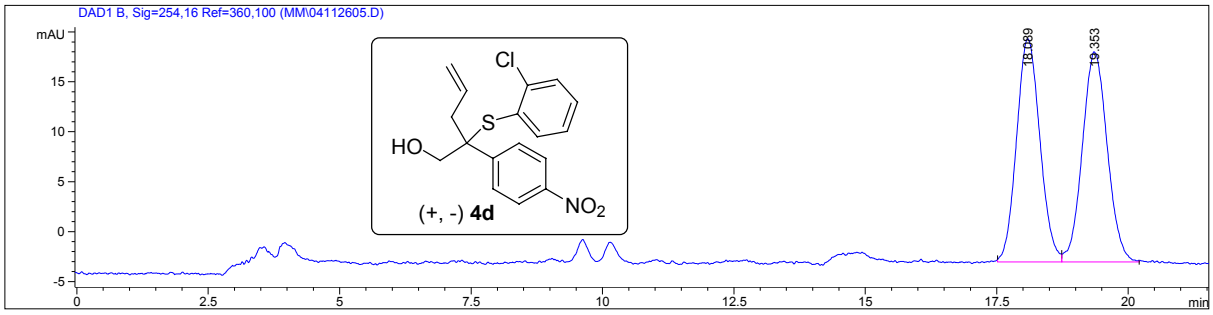


(*2R*)-(+)-(*o*-Chlorophenyl)sulfanyl-2-(*p*-nitrophenyl)pent-4-en-1-ol (4 d)

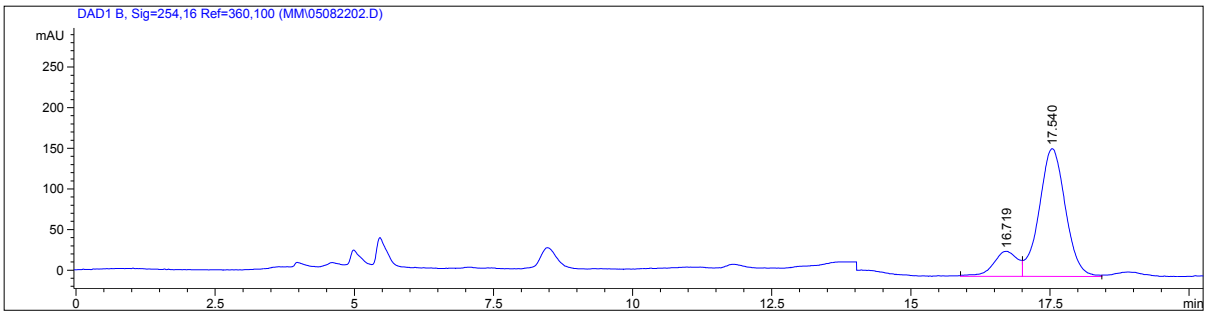


With ligand (*S, S*)-**7,** 85 % ee, $[\alpha]_D^{20}$ = +18.7° (*c* 0.68, $CHCl_3$); with ligand **8**, 70 % ee, $[\alpha]_D^{20}$ = +15.4° (*c* 0.87, $CHCl_3$); IR ($CHCl_3$) 3487, 1519, 1450, 1347, 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.65~2.69 (m, 1H), 2.83~2.96 (m, 2H), 3.87~4.01 (m, 2H), 5.03~5.13 (m, 2H), 5.45~5.58 (m, 1H), 6.92~7.04 (m, 2H), 7.23~7.29 (m, 1H), 7.45 (dd, *J* = 1.2, 8.4 Hz,, 1H), 7.56 (d, *J* = 9 Hz, 2H), 8.16 (d, *J* = 9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 40.81, 61.45, 63.09, 119.86, 123.24, 126.96, 128.77, 128.90, 130.20, 130.95, 131.60, 138.63, 140.31, 146.62, 148.27; EI-MS (*m/z*, relative intensity): 349 (M^+, 4), 205 (44), 144 (100), 128 (19), 108 (26), 41 (35). Anal. calcd. for $C_{17}H_{16}ClNO_3S$: N, 4.00; C, 58.37; H, 4.61. Found: N, 3.95; C, 58.08; H, 4.54. HPLC condition (254 nm): Chiracel ODH; *n*-hexane/*iso*-propanol = 94 : 6, t_R *(S isomer)* = 18.09 min, t_R *(R isomer)* = 19.35 min.

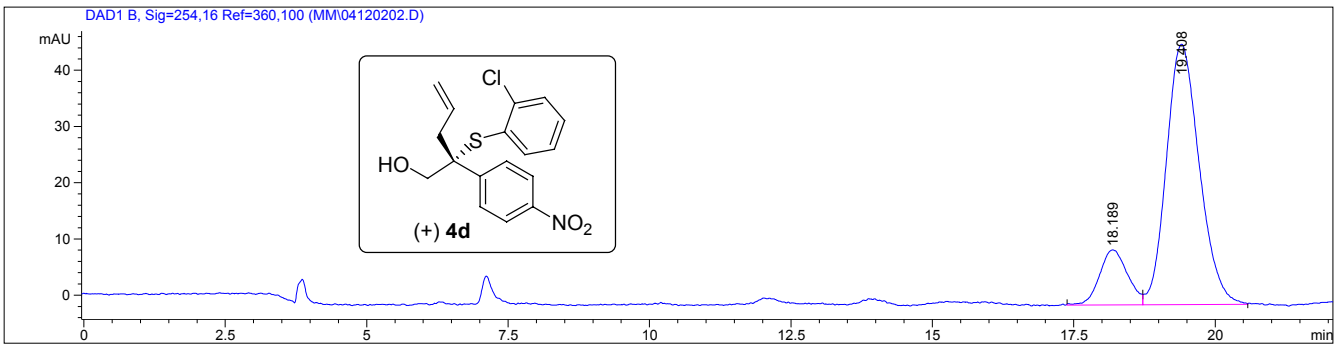
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 94 : 6, racemic.



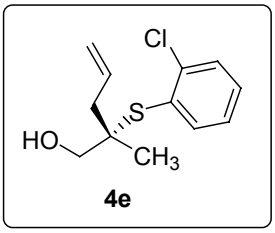
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 94 : 6, with ligand (*S, S*)-**7,** 85 % ee (Table 2, entry 8).



ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 94 : 6, with ligand **8**, 70 % ee (Table 2, entry 9)



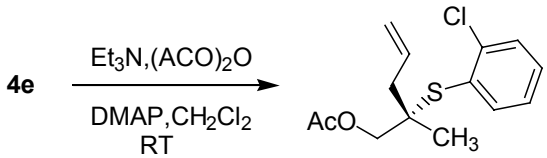
(*2S*)-(-)-(*o*-Chlorophenyl)sulfanyl-2-methylpent-4-en-1-ol (4e)



4e

With ligand (*S, S*)-**7,** 86 % *ee*; $[\alpha]_D^{20}$ = -7.7° (*c* 0.88, $CHCl_3$); with ligand **8**, 82 % *ee*, $[\alpha]_D^{20}$ = -7.3° (*c* 0.91, $CHCl_3$); IR (neat) 3406, 2971, 2926, 1441, 1035 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.16 (s, 3H), 2.34~2.44 (m, 2H), 2.61 (bs, 1H), 3.33 (d, *J* = 4.8 Hz, 2H), 5.11~5.19 (m, 2H), 5.89~6.00 (m, 1H), 7.22~7.37 (m, 2H), 7.51 (dd, *J* = 1.8, 7.5 Hz, 1H), 7.64 (dd, *J* = 1.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.04, 41.76, 56.87, 67.21, 118.73, 126.92, 129.80, 130.18, 130.74, 133.19, 140.27, 140.95; EI-MS (*m/z*, relative intensity): 242 (M^+, 9), 211 (6), 183 (7), 144 (100), 108 (38), 98 (16), 57 (18), 41 (59), 29 (19). Anal. calcd. for $C_{12}H_{15}ClOS$: C, 59.37; H, 6.23. Found: C, 59.13; H, 6.13.

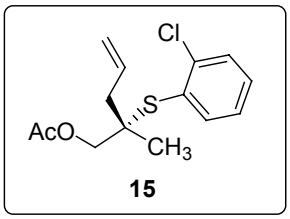
Since the enantiomers of **4e** could not be separated by chiral HPLC, **4e** was transferred to the corresponding acetate **15**.



15

Under N_2, 2-(*o*-chlorophenylsulfanyl)-2-methylpent-4-en-1-ol **4e** (24 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (2 mL). Et_3N (51 mg, 0.5 mmol) and $(AcO)_2O$ (31 mg, 0.3 mmol) was added successively, followed by adding 4-dimethylaminopyridine (2 mg, 0.02 mmol). The mixture was stirred at RT for about 0.5 h. Removal of the solvent in vacuo gave a crude residue which was purified by silica gel column eluted with petroleum ether/ethyl acetate (30 : 1) to afford pure product **15** (27 mg, 95 %).

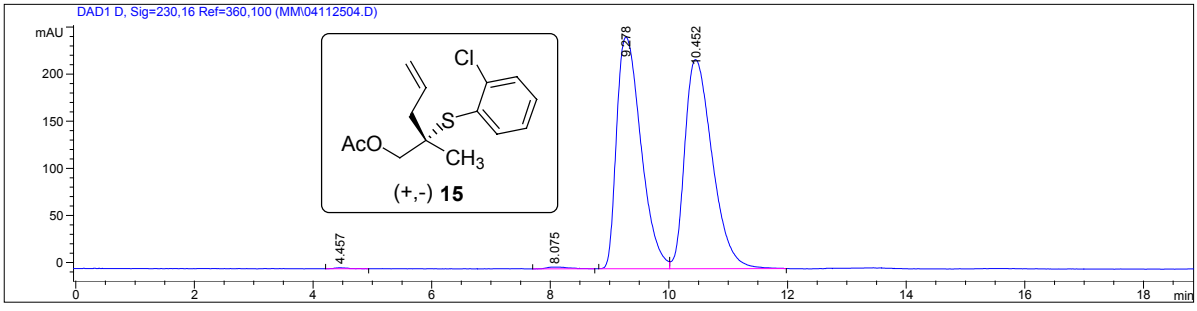
(2*S*)-(-)-2-(*o*-Chlorophenyl)sulfanyl-2-methylpent-4-enyl acetate (15)



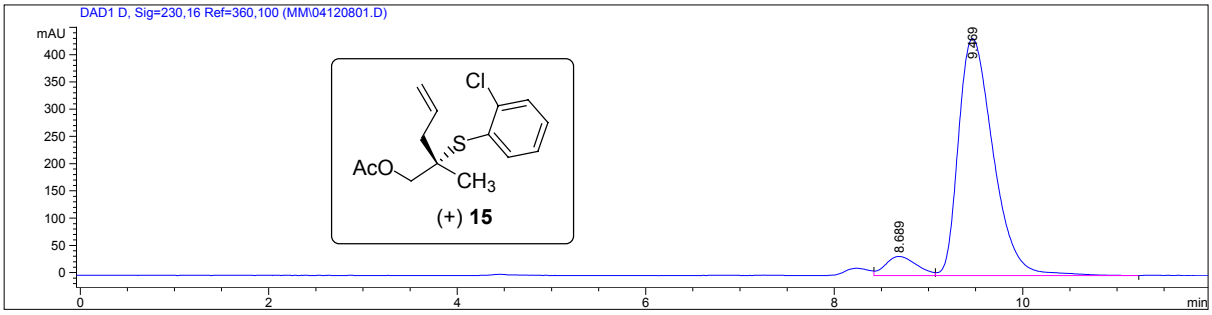
15

96 % *ee*, $[\alpha]_D^{20}$ = -30.6° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 2973, 2927, 1741, 1449, 1245, 1372, 1230, 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (s, 3H), 2.04 (s, 3H), 2.42~2.45 (m, 2H), 4.02 (d, *J* = 11.1 Hz, 1H), 4.11 (d, *J* = 11.1 Hz, 1H), 5.10~5.19 (m, 2H), 5.90~6.04 (m, 1H), 7.21~7.35 (m, 2H), 7.50 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.65 (dd, *J* = 1.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.79, 22.79, 42.24, 52.23, 69.64, 118.84, 126.77, 130.05, 130.22, 130.65, 132.97, 140.19, 141.43, 170.65; EI-MS (*m/z*, relative intensity): 284 (M^+, 8), 243 (8), 201 (7), 141 (33), 108 (17), 81 (78), 43 (100), 32 (3). Anal. calcd. for $C_{14}H_{17}ClO_2S$: C, 59.04; H, 6.02. Found: C, 59.25; H, 6.20. HPLC condition (230 nm): Chiracel OJ; *n*-hexane/*iso*-propanol = 96 : 4, t_R *(R isomer)* = 9.28 min, t_R *(S isomer)* = 10.45 min.

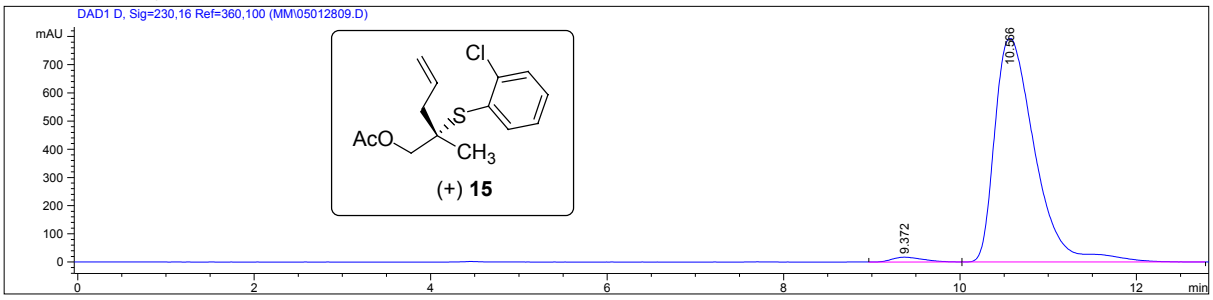
OJ, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 96 : 4, racemic.



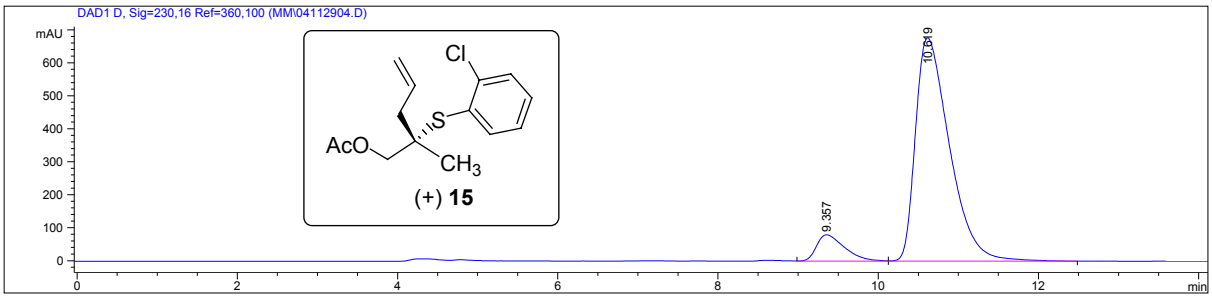
OJ, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 96 : 4, with ligand (*S, S*)-**7,** 86 % ee (Table 2, entry 10).



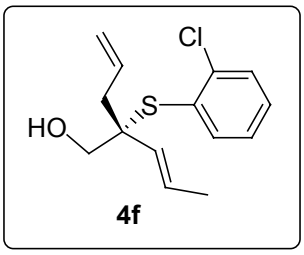
OJ, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 96 : 4, single recrystallization before removal of auxiliary, 96 % ee (Table 2, entry 11).



OJ, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 96 : 4, with ligand **8**, 82 % ee (Table 2, entry 12).

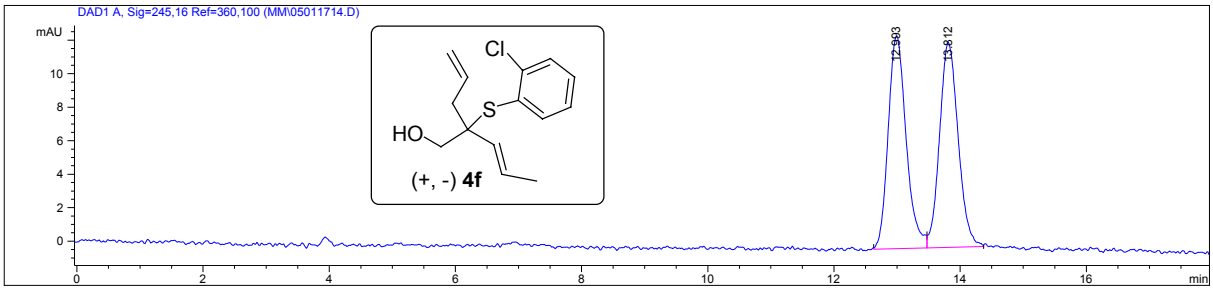


(*2R*)-(-)-(*o*-Chlorophenyl)sulfanyl-2-propenylpent-3-en-1-ol (4f)

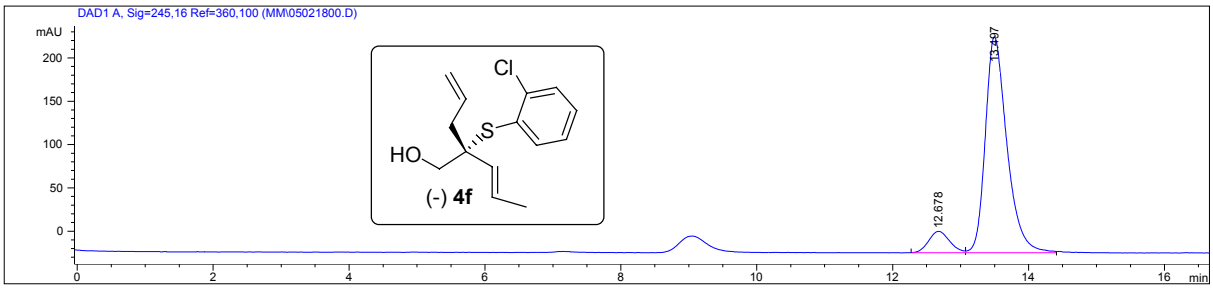


With ligand (*S, S*)-**7,** 82 % *ee*; $[\alpha]_D^{20}$ = -3.6° (*c* 0.93, $CHCl_3$); with ligand **8**, 78 % *ee*, $[\alpha]_D^{20}$ = -3.5° (*c* 0.56, $CHCl_3$); IR ($CHCl_3$) 3467, 1636, 1450, 1216, 1037 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60 (dd, *J* = 1.5, 6.9 Hz, 3H), 2.44 (t, *J* = 6.3 Hz, 1H), 2.51~2.54 (m, 2H), 3.51 (d, *J* = 6.3 Hz, 2H), 5.05~5.19 (m, 3H), 5.53 (dd, *J* = 1.5, 3.3 Hz, 1H), 5.81~5.94 (m, 1H), 7.18~7.33 (m, 2H), 7.45~7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.19, 40.23, 60.84, 63,28, 118.57, 126.40, 126.54, 129.83, 130.11, 130.51, 131.36, 133.17, 140.41, 140.83; EI-MS (*m/z*, relative intensity): 268 (M^+, 10), 237 (5), 144 (60), 124 (76), 108 (26), 83 (74), 69 (83), 55 (100), 41 (96), 29 (19). Anal. calcd. for $C_{14}H_{17}ClOS$: C, 62.56; H, 6.37. Found: C, 62.23; H, 6.41. HPLC condition (245 nm): Chiracel ODH; *n*-hexane/*iso*-propanol = 99.3 : 0.7, t_R *(S isomer)* = 12.99 min, t_R *(R isomer)* = 13.81 min.

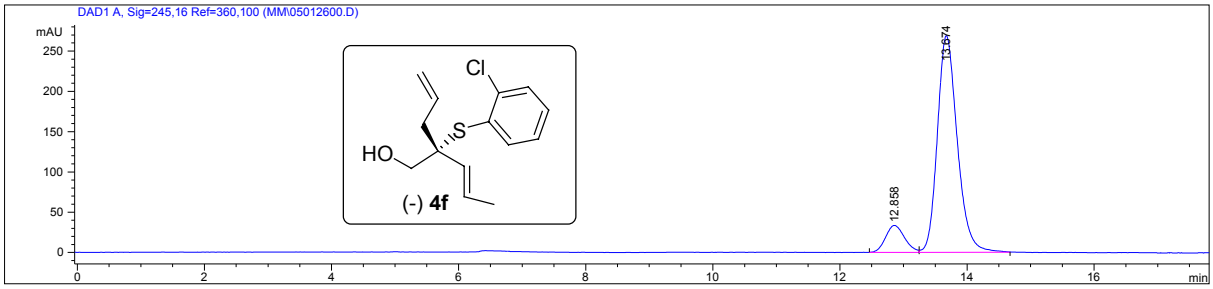
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99.3 : 0.7; racemic.



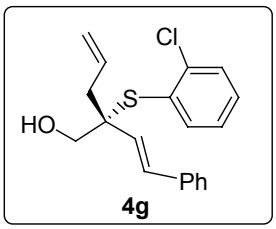
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99.3 : 0.7; with ligand (*S, S*)-**7,** 82 % ee (Table 2, entry 13)



ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99.3 : 0.7; with ligand **8**, 78 % ee (Table 2, entry 14)

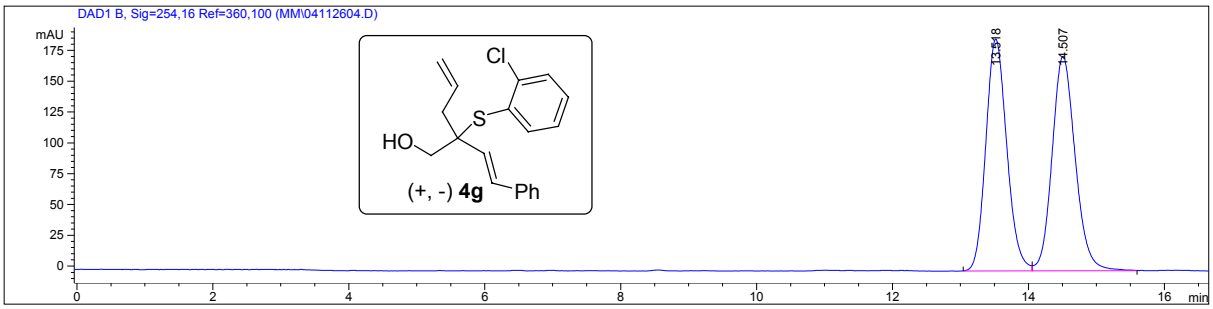


(*2R*)-(+)-(*o*-Chlorophenyl)sulfanyl-2-styrylpent-4-en-1-ol (4g)

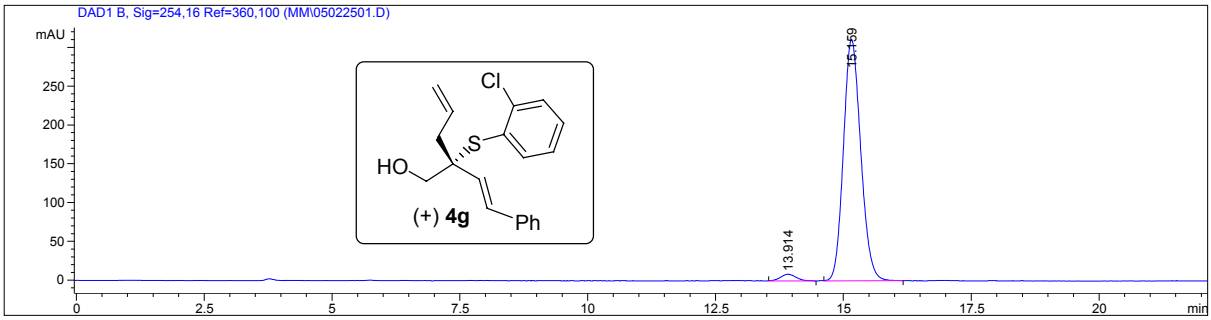


With ligand (*S, S*)-**7,** 95 % *ee*, $[\alpha]_D^{20}$ = +146.9° (*c* 0.83, $CHCl_3$); with ligand **8**, 85 % *ee*, $[\alpha]_D^{20}$ = +131.8° (*c* 0.69, $CHCl_3$); IR ($CHCl_3$) 3467, 1640, 1472, 1378, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.52 (bs, 1H), 2.62~2.72 (m, 2H), 3.58~3.73 (m, 2H), 5.14~5.24 (m, 2H), 5.85~5.99 (m, 2H), 6.26 (d, *J* = 16.5 Hz, 1H), 7.09~7.52 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 40.29, 60.97, 63.86, 118.99, 126.19, 126.62, 127.68, 128.49, 129.76, 129.97, 130.04, 130.18, 130.67, 132.92, 136.53, 140.41; EI-MS (*m/z*, relative intensity): 330 (M^+, 7), 309 (5), 187 (52), 169 (47), 141 (20), 117 (56), 91 (100), 69 (17), 41 (43). Anal. calcd. for $C_{19}H_{19}ClOS$: C, 68.97; H, 5.79. Found: C, 68.89; H, 5.87. HPLC condition (254 nm): Chiracel ODH; *n*-hexane/*iso*-propanol = 97 : 3, t_R *(S isomer)* = 13.55 min, t_R *(R isomer)* = 14.51 min.

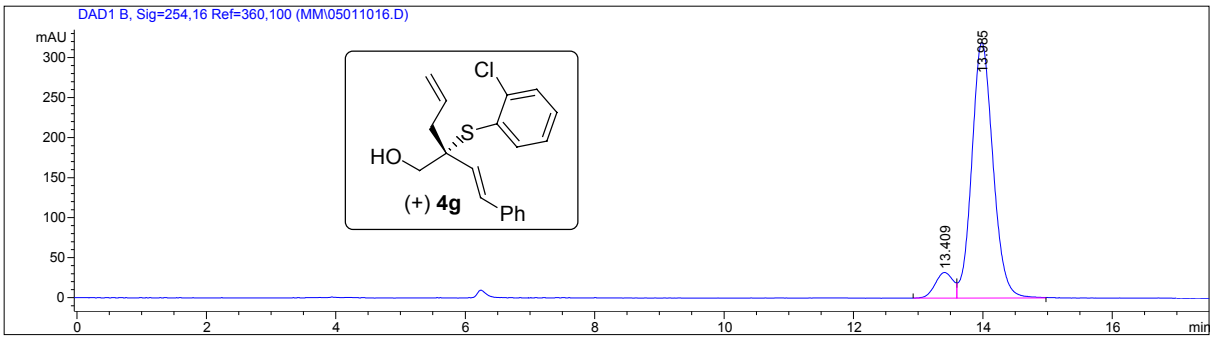
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 97 : 3, racemic.



ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 97 : 3, with ligand (*S, S*)-**7,** 95 % ee (Table 2, entry 15)



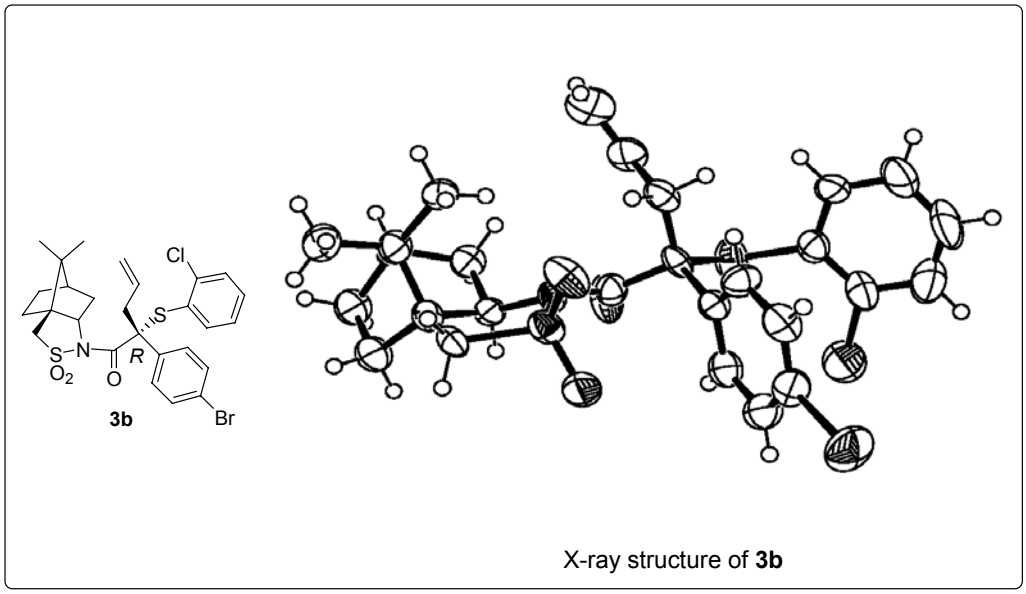
ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 97 : 3, with ligand **8**, 85 % ee (Table 2, entry 16).



Determination of Absolute Configuration of the Products 4b and 4e

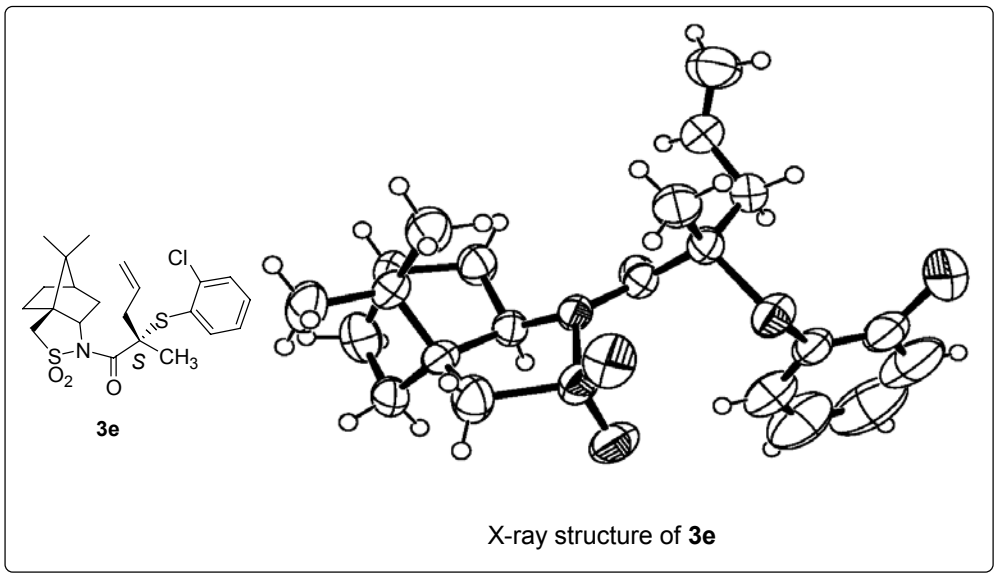
For diazo substrate **1b** and **1e**, the rearrangement products **3b** and **3e** were isolated and recrystallized. The configuration of the newly formed chiral centers were determined by X-ray structures of **3b** and **3e**.

***(1S, 2'R)*-*N*-2'-(*o*-Chlorophenyl)sulfanyl-2'-(*p*-bromophenyl)pent-4'-enoyl 2,10-camphorsultam (3b)**



IR (neat) 2958, 1677, 1330, 1204, 1113 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (s, 3H), 1.03 (s, 3H), 1.31~1.39 (m, 2H), 1.78~1.84 (m, 3H), 1.95~2.07 (m, 2H), 2.66~2.74 (m, 1H), 3.26 (s, 2H), 3.29~3.34 (m, 1H), 3.88 (t, *J* = 6.3 Hz, 1H), 5.01~5.11 (m, 2H), 6.04~6.18 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 7.02 (dt, *J* = 1.2, 7.8 Hz, 1H), 7.16~7.25 (m, 3H), 7.36~7.42 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.94, 20.52, 26.40, 33.01, 38.58, 38.93, 44.10, 47.65, 47.98, 52.91, 67.62, 68.51, 118.91, 122.22, 126.52, 129.42, 129.99, 130.60, 130.69, 131.06, 132.79, 135.40, 139.16, 141.15, 170.94; EI-MS (*m/z*, relative intensity): 595 (M^+, 4), 452 (46), 353 (11), 237 (26), 209 (27), 135 (100), 107 (26), 93 (29). Anal. calcd. for $C_{27}H_{29}BrClNO_3S_2$: N, 2.35; C, 54.50; H, 4.91. Found: N, 2.18; C, 54.07; H, 5.16.

***(1S, 2'S)*-*N*-2'-(*o*-Chlorophenyl)sulfanyl-2'-methylpent-4'-enoyl 2,10-camphorsultam (3e)**



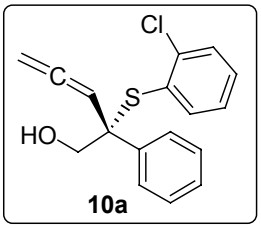
IR (neat) 2958, 1681, 1452 1333, 1211, 1034 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.94 (s, 3H), 1.12 (s, 3H), 1.32~1.38 (m, 1H), 1.51~1.57 (m, 1H), 1.69 (s, 3H), 1.72~2.07 (m, 5H), 2.46 (dd, *J* = 8.1, 13.8 Hz, 1H), 2.63 (dd, *J* = 8.1, 13.8 Hz, 1H), 3.49 (d, *J* = 13.5 Hz, 2H), 4.13 (dd, *J* = 4.8, 7.5 Hz, 1H), 5.04~5.10 (m, 2H), 5.60~5.71 (m, 1H), 7.20 (dt, *J* = 1.8, 7.5 Hz, 1H), 7.27 (dt, *J* = 1.8, 7.5 Hz, 1H), 7.44 (dd, *J* = 1.8, 7.5 Hz, 1H), 7.60 (dd, *J* = 1.8, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.88, 20.45, 22.28, 26.62, 32.52,

38.53, 43.46, 43.95, 47.85, 47.88, 53.44, 56.17, 67.51, 119.26, 126.92, 129.87, 130.17, 130.28, 133.38, 138.57, 139.91, 173.36; EI-MS (*m/z*, relative intensity): 453 (M^+, 4), 310 (4), 211 (100), 169 (9), 135 (21), 67 (47), 41 (22). Anal. calcd. for $C_{22}H_{28}ClNO_3S_2$: N, 3.08; C, 58.20; H, 6.22. Found: N, 2.95; C, 57.86; H, 6.23.

Typical Procedure for Catalytic Asymmetric [2,3]-Sigmatropic Rearrangement of 1a-c, e, f and 9a,b with Ligand (*S, S*)-7 or 8 and the Removal of the Chiral Auxiliary.

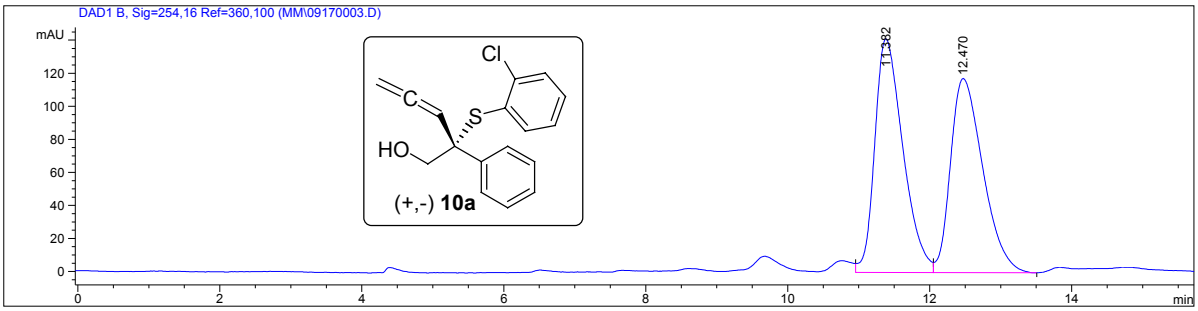
Under a nitrogen atmosphere, $Cu(MeCN)_4PF_6$ (6.25 mg, 0.016 mmol) and (*S, S*)-**7** (8.6 mg, 0.02 mmol) or **8** (7.5 mg, 0.04 mmol)were added to a 25 mL round-bottomed flask. Dry CH_2Cl_2 (2 mL) was introduced and the solution was stirred for 0.5 h at RT. To the solution was then added *o*-chlorophenyl propargyl sulfide **9a** or **9b** (0.09 mmol), followed by dropwisely adding *N*-phenyldiazoacety1 camphorsultam **1a** (30 mg, 0.085 mmol,) in dry CH_2Cl_2 (2 mL) at 0 ^oC. The solution was stirred for an additional 5 h at RT. The yellow solution turned light yellow and **1a** disappeared as judged by TLC. Then anhydrous THF (2 mL) and $LiAlH_4$ (19 mg, 0.5 mmol) was added at 0 ^oC. The mixture was stirred for 20 min. Removal of the solvent in vacuo gave a crude residue which was purified by silica gel column eluted with petroleum ether/ethyl acetate (15 : 1) to afford pure product **10a**.

(+)-2-(*o*-Chlorophenyl)sulfanyl-2-phenylpenta-3,4-dien-1-ol (10a)

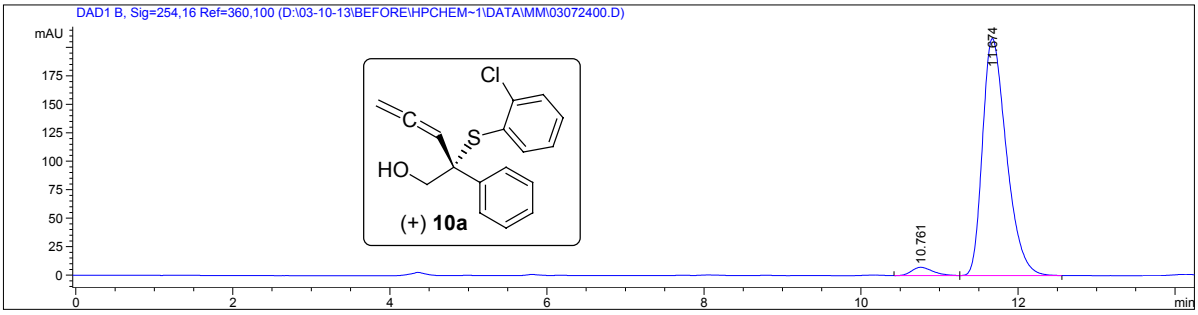


With ligand (*S, S*)-**7,** 94 % ee, $[\alpha]_D^{20}$ = +111.5^o (*c* 0.68, $CHCl_3$); with ligand **8**, 82 % ee, $[\alpha]_D^{20}$ = +97.0^o (*c* 0.85, $CHCl_3$); IR (neat) 3433, 1951, 1448, 1380, 1069 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.37 (t, *J* = 7.2Hz, 1H), 3.90 (d, *J* = 7.2 Hz, 2H), 4.53 (dd, *J* = 6.9, 11.1 Hz, 1H), 4.84 (dd, *J* = 6.9, 11.1 Hz, 1H), 5.71 (t, *J* = 6.9 Hz, 1H), 7.18 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.31~7.44 (m, 5H), 7.51 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.64~7.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 62.07, 66.22, 78.36, 92.77, 126.49, 127.73, 127.85, 128.32, 129.78, 130.45, 130.49, 139.84, 140.14, 140.83, 207.53; EI-MS (*m/z*, relative intensity): 302 (M^+, 11), 191 (13), 159 (50), 141 (100), 128 (55), 115 (42), 91 (54), 77 (32). Anal. calcd. for $C_{17}H_{15}ClOS$: C, 67.43; H, 4.99. Found: C, 67.27; H, 5.06. HPLC condition (254 nm): Chiracel OD; *n*-hexane/*iso*-propanol = 90 : 10, t_R *(S isomer)* = 11.38 min, t_R *(R isomer)* = 12.47 min.

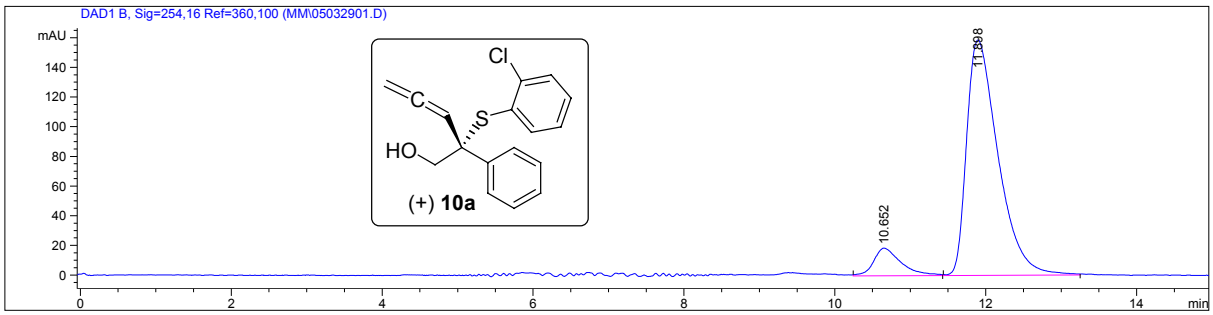
OD, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 90 : 10, racemic.



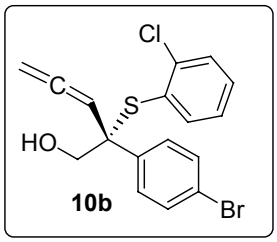
OD, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 90 : 10, with ligand (*S, S*)-**7,** 94 % ee (Table 3, entry 1).



OD, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 90 : 10, with ligand **8,** 82 % ee (Table 3, entry 2).

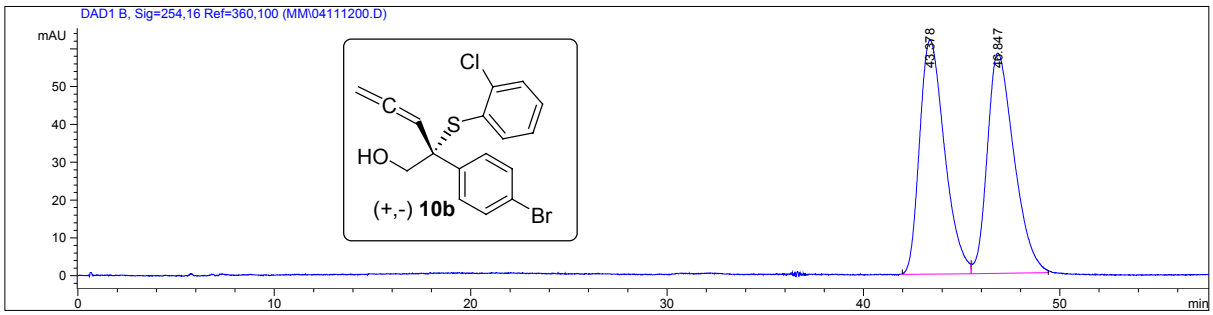


(+)-2-(*o*-Chlorophenyl)sulfanyl-2-(*p*-bromophenyl)penta-3,4-dien-1-ol (10b)

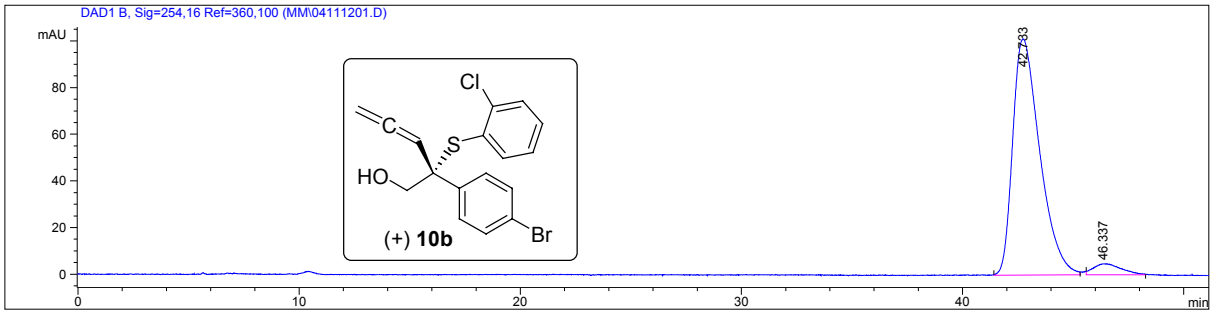


With ligand (*S, S*)-**7,** 91 % ee, $[\alpha]_D^{20}$ = +60.1° (*c* 1.28, $CHCl_3$); with ligand **8**, 88 % ee, $[\alpha]_D^{20}$ = +58.0° (*c* 1.75, $CHCl_3$); IR (neat) 3413, 1951, 1487, 1449, 1394, 1036, 1008 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.36 (t, *J* = 7.2Hz, 1H), 3.82 (d, *J*= 7.2 Hz, 2H), 4.51 (dd, *J*= 6.9, 11.4 Hz, 1H), 4.80 (dd, *J* = 6.9, 11.4 Hz, 1H), 5.60 (t, *J* = 6.9 Hz, 1H), 7.17 (dt, *J* = 1.8, 7.5 Hz, 1H), 7.27~7.39 (m, 3H), 7.42~7.51 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 61.67, 66.09, 78.65, 93.49, 121.85, 126.65, 129.76, 129.91, 130.07, 130.75, 131.35, 139.36, 139.89, 140.88, 207.54; EI-MS (*m/z*, relative intensity): 380 (M^+, 16), 364 (10), 351 (14), 237 (28), 221 (100), 158 (53), 128 (87), 108 (43). Anal. calcd. for $C_{17}H_{14}BrClOS$: C, 53.49; H, 3.70. Found: C, 53.65; H, 3.93. HPLC condition (254 nm): Chiracel OD; *n*-hexane/*iso*-propanol = 99.3 : 0.7, t_R *(S isomer)* = 43.38 min, t_R *(R isomer)* = 48.85 min.

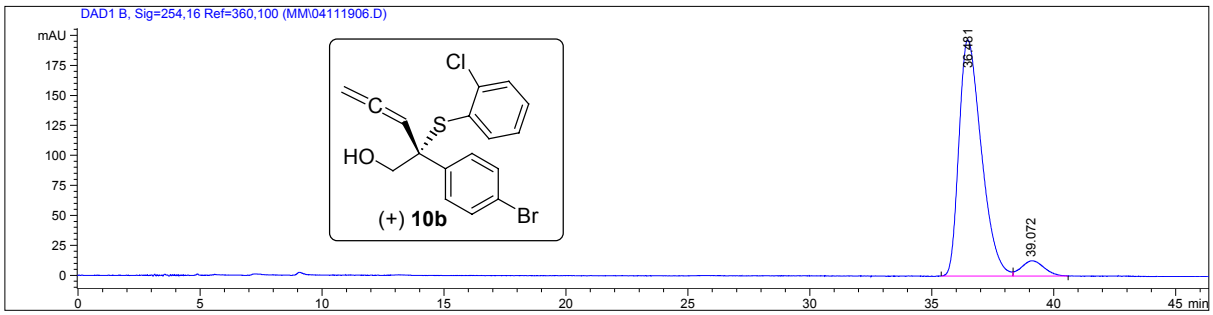
OD, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99.3 : 0.7, racemic.



OD, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99.3 : 0.7, with ligand (*S, S*)-**7,** 91 % ee (Table 3, entry 3).

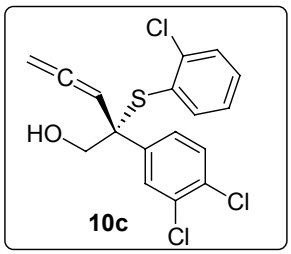


ODH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99.3 : 0.7, with ligand **8,** 88 % ee (Table 3, entry 4).



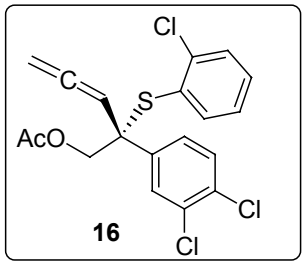
Since the enantiomers of products **10c**~**f** could not be separated by chiral HPLC, they were transferred to acetates by the similar procedure for **4e**.

(+)-2-(*o*-Chlorophenyl)sulfanyl-2-(*m,p*-dichlorophenyl)penta-3,4-dien-1-ol (10c)



With ligand (*S, S*)-**7,** 84 % ee, $[\alpha]_D^{20}$ = +46.1° (*c* 1.08, $CHCl_3$); with ligand **8**, 50 % ee, $[\alpha]_D^{20}$ = +27.1° (*c* 0.96, $CHCl_3$); IR ($CHCl_3$) 3452, 1951, 1469, 1376, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.40 (bs,1H), 3.81(d, *J* = 3.3 Hz, 2H), 4.53 (dd, *J* = 6.6, 11.4 Hz, 1H), 4.82 (dd, *J* = 6.6, 11.4 Hz, 1H), 5.57 (t, *J* = 6.6 Hz, 1H), 7.19 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.34 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.38~7.45 (m, 3H), 7.50 (dd, *J*= 1.8, 8.1 Hz, 1H), 7.69 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 61.19, 66.04, 78.86, 93.20, 126.72, 127.46, 129.71, 129.99, 130.04, 130.15, 130.96, 131.79, 132.32, 139.99, 140.67, 140.95, 207.56; EI-MS (*m/z*, relative intensity): 370 (M^+, 4), 341 (35), 206 (26), 209 (100), 183 (30), 159 (26), 143 (27), 128 (25), 108 (45). Anal. calcd. for $C_{17}H_{13}Cl_3OS$: C, 54.93; H, 3.53. Found: C, 54.46; H, 3.56.

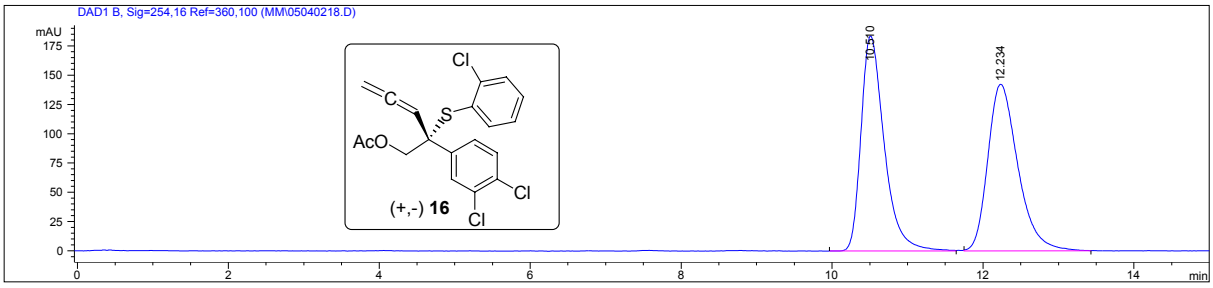
(+)-2-(2-chlorophenyl)sulfanyl-2-(3,4-dichlorophenyl)penta-3,4-dienyl acetate (16)



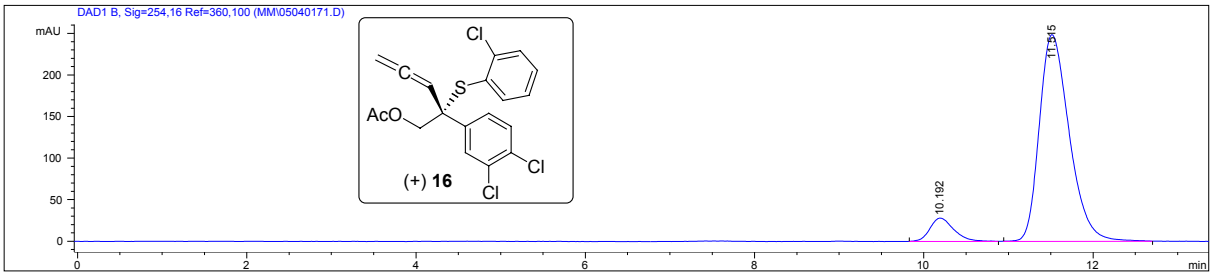
84 % ee, $[\alpha]_D^{20}$ = +77.6° (*c* 0.95, $CHCl_3$); IR (neat) 1954, 1743, 1227, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.95 (s, 3H), 4.35 (d, *J* = 11.7 Hz, 1H), 4.51 (d, *J* = 11.7 Hz, 1H), 4.58 (dd, *J* = 6.6, 11.4 Hz, 1H), 4.83 (dd, *J* = 6.6, 11.4 Hz, 1H), 5.60 (t, *J* = 6.6 Hz, 1H), 7.18 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.33 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.38~7.42 (m, 3H), 7.48 (dd, *J* = 1.2, 7.8 Hz, 1H), 7.57 (t, *J* = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.73, 57.77, 67.52, 79.14, 92.62, 126.71, 127.19, 129.83, 130.03, 130.18, 131.02, 131.91, 132.30, 139.73, 140.30, 141.35, 170.25, 207.71; EI-MS (*m/z*, relative intensity): 412 (M^+, 4), 269 (9), 227 (16), 209 (100), 139 (14), 108 (20), 43 (100). Anal. calcd. for $C_{19}H_{15}Cl_3O_2S$: C, 55.16; H, 3.65. Found: C, 55.02; H, 3.79. HPLC condition (254 nm): Chiracel OJH; *n*-hexane/*iso*-propanol = 94 : 6, t_R *(S isomer)* = 10.54 min,

t_R *(R isomer)* = 12.23 min.

OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 94 : 6, racemic.

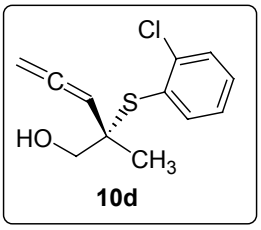


OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 94 : 6, with ligand (*S, S*)-**7,** 84 % ee (Table 3, entry 5).



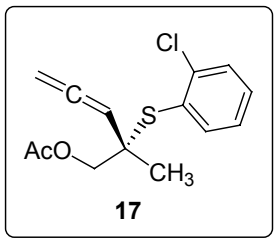
OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 94 : 6, with ligand **8,** 50 % ee (Table 3, entry 6).

(+)-2-(*o*-Chlorophenyl)sulfanyl-2-methylpenta-3,4-dien-1-ol (10d)



With ligand (*S, S*)-**7,** 93 % ee, $[\alpha]_D^{20}$ = +12.6° (*c* 1.24, $CHCl_3$); with ligand **8,** 92 % ee, $[\alpha]_D^{20}$ = +12.4° (*c* 1.36, $CHCl_3$); IR (neat) 3394, 2924, 1952, 1449, 1036, cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42 (s, 3H), 2.52 (t, *J* = 6.9 Hz, 1H), 3.46 (d, *J* = 6.9Hz, 2H), 4.57 (dd, *J* = 6.6, 11.1 Hz, 1H), 4.73 (dd, *J* = 6.6, 11.1 Hz, 1H), 5.32 (t, *J* = 6.6 Hz, 1H), 7.24 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.34 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.49 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.62 (dd, *J* = 1.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.16, 55.87, 67.46, 77.83, 94.35, 126.62, 129.84, 130.18, 130.64, 140.37, 140.87, 207.38; EI-MS (*m/z*, relative intensity): 240 (M^+, 4), 174 (22), 144 (67), 129 (48), 108 (41), 96 (68), 43 (100), 27 (19). Anal. calcd. for $C_{12}H_{13}ClOS$: C, 59.87; H, 5.44. Found: C, 59.74; H, 5.57.

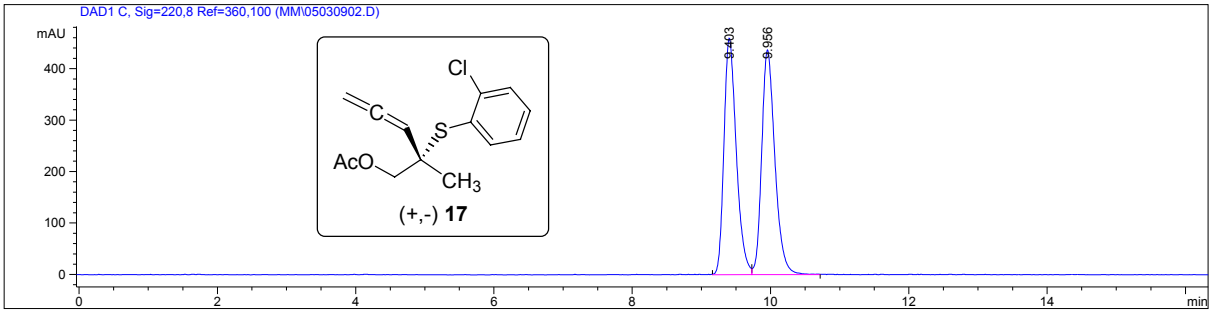
(+)-2-(*o*-Chlorophenyl)sulfanyl-2-methylpenta-3,4-dienyl acetate (17)



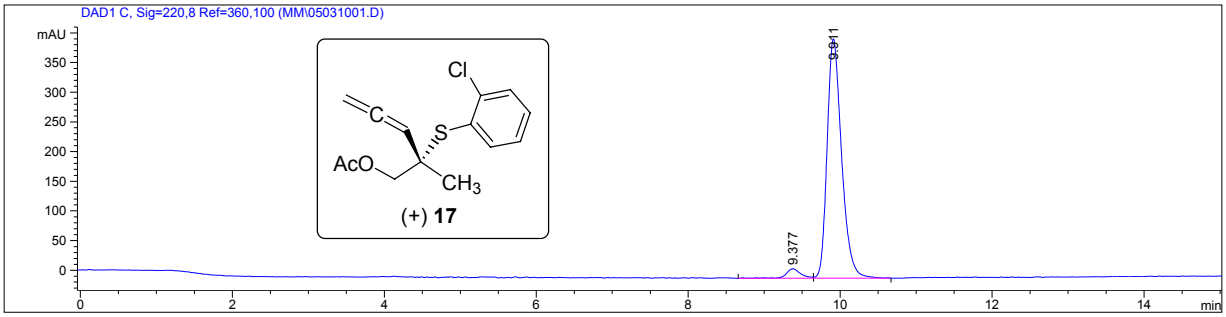
17

93 % ee, $[\alpha]_D^{20}$ = +20.2° (*c* 1.030, $CHCl_3$); IR (neat) 2973, 1953, 1742, 1449, 1383, 1035 cm^{-1} ^1H NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 3H), 2.08 (s, 3H), 4.15 (d, *J* = 11.1 Hz, 2H), 4.62 (dd, *J* = 6.6, 11.1 Hz, 1H), 4.70 (dd, *J* = 6.6, 11.1 Hz, 1H), 5.29 (t, *J* = 6.6 Hz, 1H), 7.23 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.33 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.49 (dd, *J* = 1.5, 8.1 Hz, 1H), 7.62 (dd, *J* = 1.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.81, 23.41, 52.05, 69.33, 78.15, 94.43, 126.55, 130.03, 130.28, 130.64, 140.13, 141.29, 170.62, 207.52; EI-MS (*m/z*, relative intensity): 282 (M^+, 4), 240 (6), 171 (5), 139 (14), 97 (78), 43 (100). Anal. calcd. for $C_{14}H_{15}ClO_2S$: C, 59.46; H, 5.35. Found: C, 59.69; H, 5.41. HPLC condition (220 nm): Chiracel OJH; *n*-hexane/*iso*-propanol = 95 : 5, t_R *(R isomer)* = 9.40 min, t_R *(S isomer)* = 9.97 min.

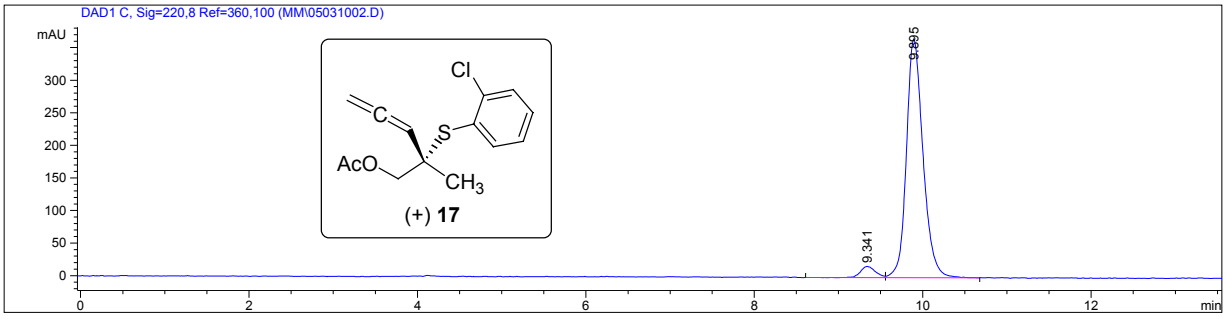
OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 95 : 5, racemic.



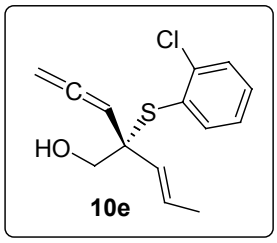
OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 95 : 5, with ligand (*S, S*)-**7,** 93 % ee (Table 3, entry 7).



OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 95 : 5, with ligand **8,** 92 % ee (Table 3, entry 8).

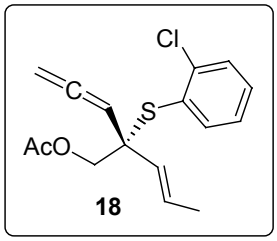


(+)-2-(*o*-Chlorophenyl)sulfanyl-2-propenylpenta-3,4-dien-1-ol (10e)



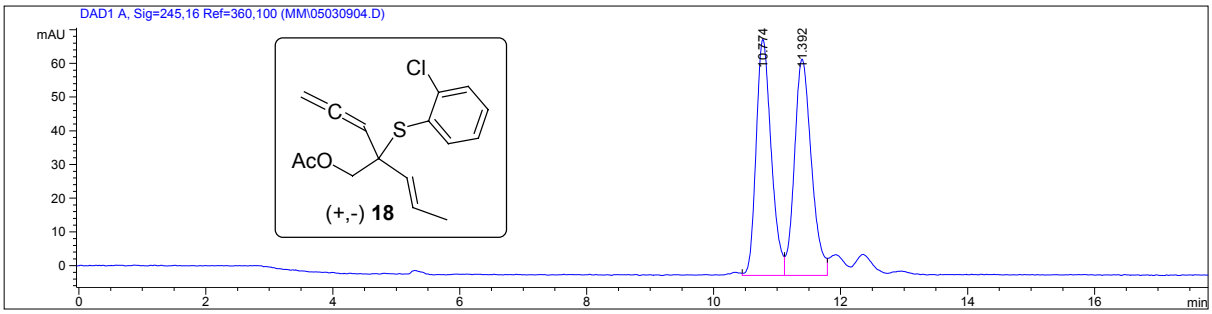
With ligand (*S, S*)-**7,** 91 % ee, $[\alpha]_D^{20}$ = +87.2° (*c* 0.95, $CHCl_3$); with ligand **8**, 90 % ee, $[\alpha]_D^{20}$ = +88.6° (*c* 1.10, $CHCl_3$); IR ($CHCl_3$) 3425, 1951, 1449, 1377, 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.73 (dd, *J* = 2.1, 2.7 Hz, 3H), 2.34 (t, *J* = 7.2 Hz, 1H), 3.58 (d, *J* = 7.2 Hz, 2H), 4.59 (dd, *J* = 6.6, 11.1 Hz, 1H), 4.80 (dd, *J* = 6.6, 11.1 Hz, 1H), 5.44 (t, *J* = 6.6 Hz, 1H), 5.66~5.70 (m, 2H), 7.23 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.33 (dt, *J* = 1.8, 7.5 Hz, 1H), 7.48 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.57 (dd, *J* = 1.8, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.19, 59.93, 65.64, 78.17, 92.78, 126.48, 128.34, 129.81, 130.30, 130.36, 130.56, 140.30, 140.76, 207.53; EI-MS (*m/z*, relative intensity): 266 (M^+, 4), 235 (6), 143 (10), 123 (18), 105 (100), 91 (20). Anal. calcd. for $C_{14}H_{15}ClOS$: C, 63.03; H, 5.67. Found: C, 62.64; H, 5.70.

(+)-2-(*o*-Chlorophenyl)sulfanyl-2-propenylpenta-3,4-dienyl acetate (18)

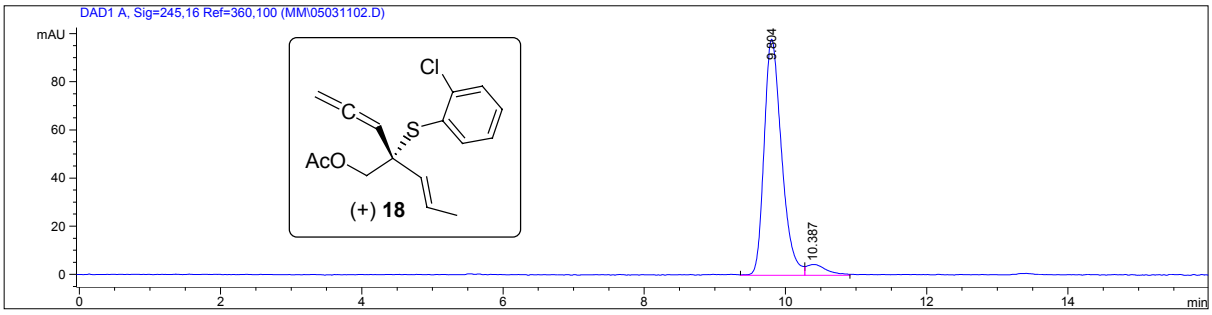


91 % ee, $[\alpha]_D^{20}$ = +62.2° (*c* 1.25, $CHCl_3$); IR ($CHCl_3$) 2916, 1953, 1741, 1228, 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.71 (dd, *J* = 1.8, 3.3 Hz, 3H), 2.05 (s, 3H), 4.19 (d, *J* = 11.4 Hz, 1H), 4.30 (d, *J* = 11.4 Hz, 1H), 4.63 (dd, *J* = 6.9,11.4 Hz, 1H), 4.80 (dd, *J* = 6.9, 11.4 Hz, 1H), 5.40 (t, *J* = 6.9 Hz, 1H), 5.59~5.63 (m, 2H), 7.22 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.31 (dt, *J* = 1.8, 7.5 Hz, 1H), 7.47 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.57 (dd, *J* = 1.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.11, 20.91, 56.33, 67.16, 78.43, 92.70, 126.46, 127.96, 129.83, 129.99, 130.33, 130.55, 139.96, 141.10, 170.70, 207.59; EI-MS (*m/z*, relative intensity): 308 (M^+, 4), 248 (8), 143 (12), 105 (100), 91 (16), 79 (29), 43 (98). Anal. calcd. for $C_{16}H_{17}ClO_2S$: C, 62.23; H, 5.55. Found: C, 62.04; H, 5.59. HPLC condition (254 nm): Chiracel OJH; *n*-hexane/*iso*-propanol = 99 : 1, t_R *(S isomer)* = 10.77 min, t_R *(R isomer)* = 11.39 min.

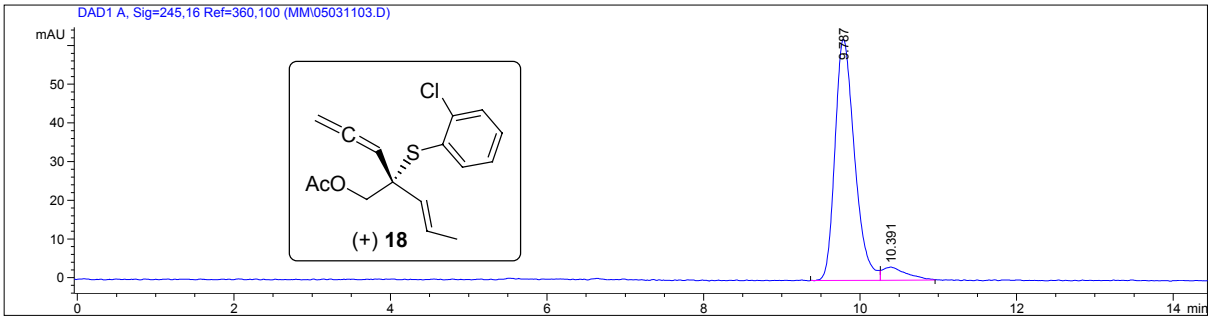
OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99 : 1, racemic.



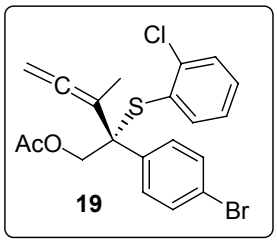
OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99 : 1, with ligand (*S, S*)-**7,** 91 % ee (Table 3, entry 9).



OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99 : 1, with ligand **8,** 90 % ee (Table 3, entry 10).

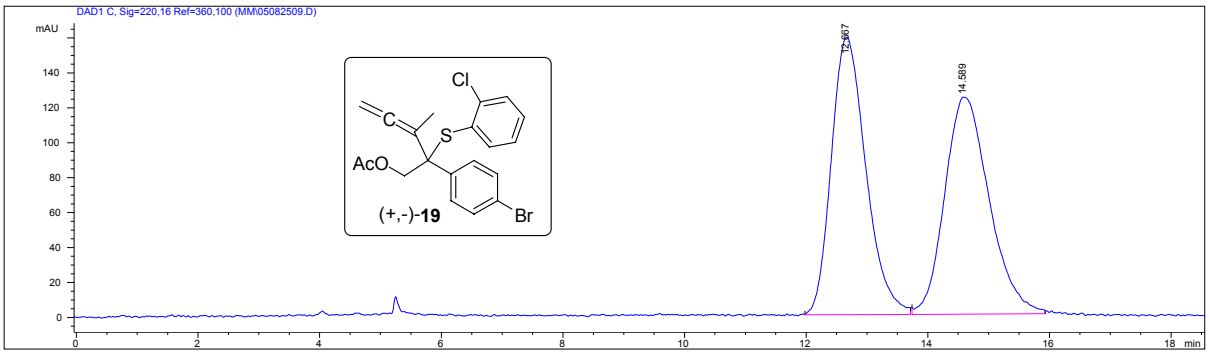


(+)-2-(2-Chlorophenyl)sulfanyl-2-(*p*-bromophenyl)penta-3-methyl-3,4-dienyl acetate (19)

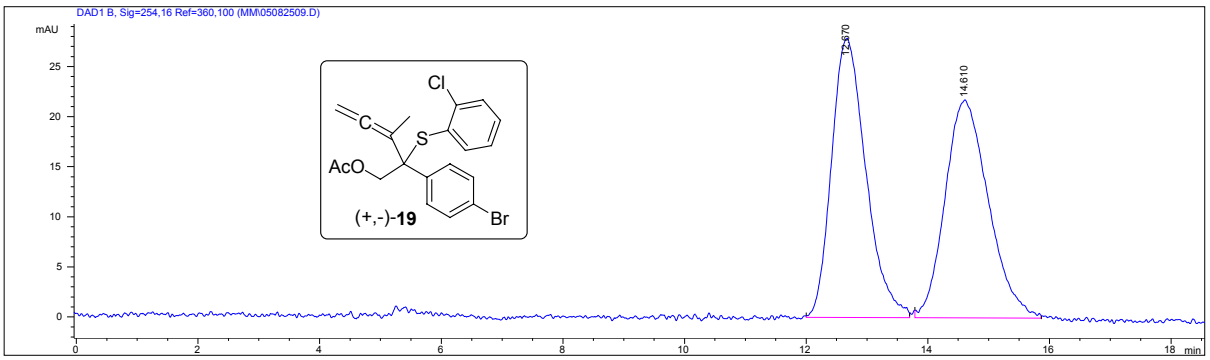


With ligand (*S, S*)-**7,** 93 % *ee*; $[\alpha]_D^{20}$ = +99.5° (*c* = 0. 54, $CHCl_3$); with ligand **8**, 90 % ee, $[\alpha]_D^{20}$ = +95.9° (*c* = 0.58, $CHCl_3$); IR ($CHCl_3$) 1952, 1742, 1450, 1229, 1036 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.74 (t, *J* = 3 Hz, 3H), 1.92 (s, 3H), 4.17 (dd, *J* = 11.7, 26.7 Hz, 2H), 4.36~4.43 (m, 1H), 4.69~4.75 (m, 1H), 7.17~7.22 (m, 1H), 7.30~7.36 (m, 1H), 7.38~7.50 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.85, 20.82, 62.39, 67.93, 77.21, 98.71, 121.63, 126.48, 130.00, 130.72, 131.18, 138.10, 139.40, 141.26, 170.38, 207.33; EI-MS (*m/z*, relative intensity): 436 (M^+, 8), 378 (9), 253 (13), 235 (100), 154 (70), 115 (13), 43 (100). Anal. calcd. for $C_{20}H_{18}BrClO_2S$: C, 54.87; H, 4.14. Found: C, 54.91; H, 4.27. HPLC condition (220 nm): Chiracel OJH; hexane/*iso*-propanol = 99 : 1, t_R *(S isomer)* = 12.67 min, t_R *(R isomer)* = 14.59 min; (254 nm): Chiracel OJH; *n*-hexane/*iso*-propanol = 99 : 1, t_R *(S isomer)* = 12.67 min, t_R *(R isomer)* = 14.61min.

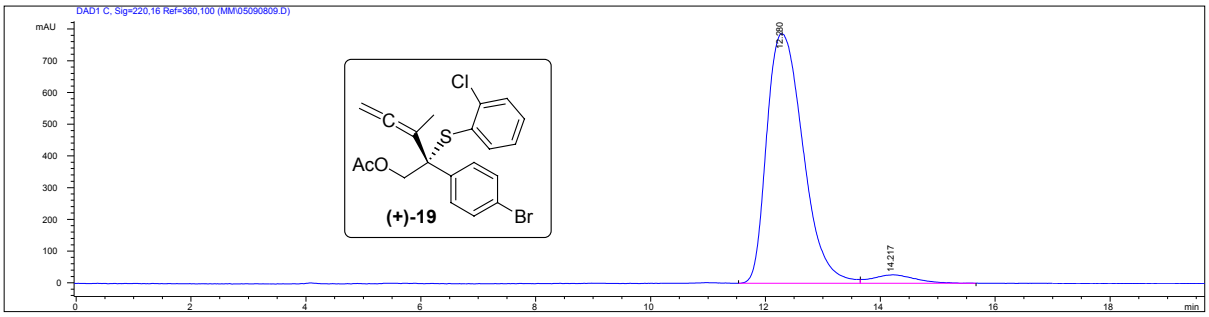
OJH, 220 nm; 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99 : 1, racemic.



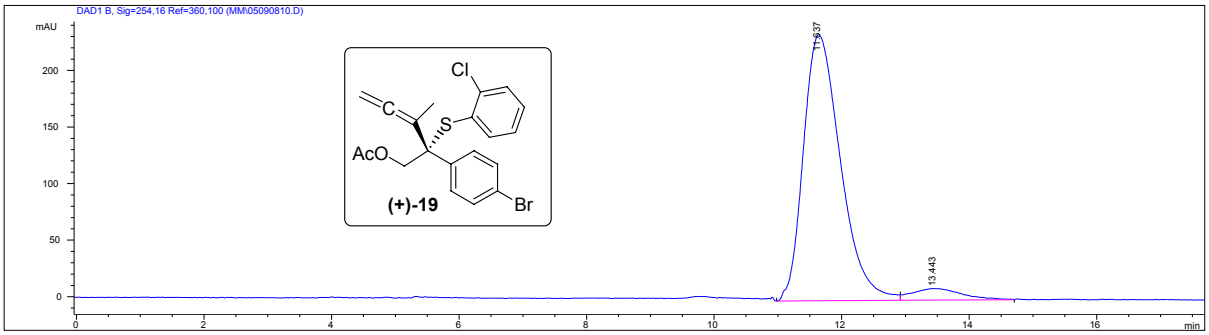
OJH, 254 nm; 0.8 min/mL, *n*-hexane : ^{i}PrOH = 99 : 1, racemic.



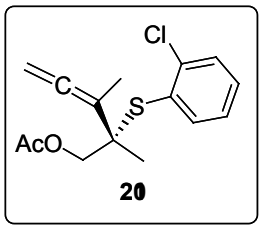
OJH, 220 nm; 0.8 min/L, *n*-hexane : ^{i}PrOH = 99 : 1; with ligand (*S, S*)-**7,** 93 % ee (Table 3, entry 11).



OJH, 254 nm; 0.8 min/L, *n*-hexane : ^{i}PrOH = 99 : 1; with ligand **8**, 90 % ee (Table 3, entry 12).

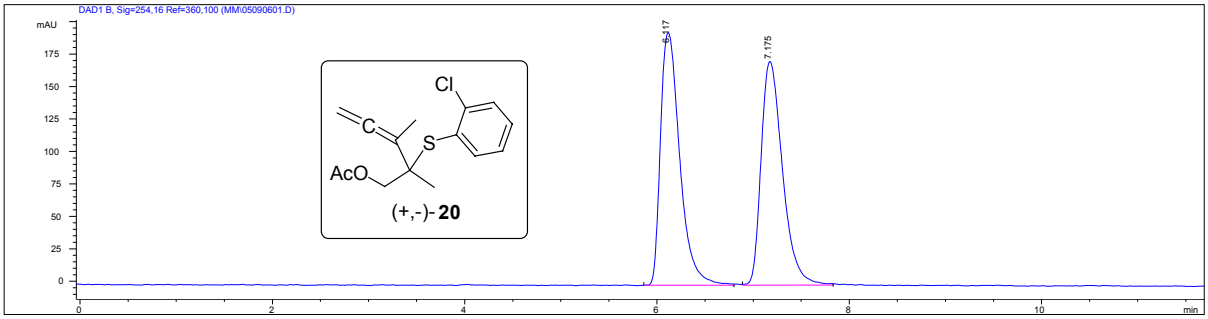


(+)-2-(*o*-Chlorophenyl)sulfanyl-2-propenylpenta-3,4-dienyl acetate (20)

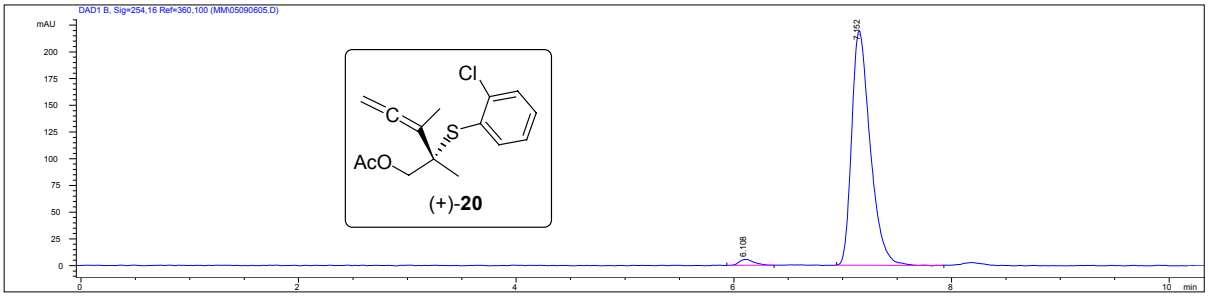


With ligand (*S, S*)-**7,** 96 % *ee*; $[\alpha]_D^{20}$ = +107.8° (*c* = 0.58, $CHCl_3$); with ligand **8**, 94 % *ee*, $[\alpha]_D^{20}$ = +106.1° (*c* = 0.53, $CHCl_3$); IR ($CHCl_3$) 1951, 1742, 1425, 1372 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.41 (s, 3H), 1.90 (t, *J* = 3 Hz, 3H), 2.06 (s, 3H), 4.14 (dd, *J* = 11.7, 12.6 Hz, 2H), 4.27~4.34 (m, 1H), 4.46~4.53 (m, 1H), 7.18~7.23 (m, 1H), 7.28~7.34 (m, 1H), 7.45~7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.44, 20.89, 21.97, 54.85, 68.66, 76.04, 89.50, 126.42, 129.89, 130.39, 139.47, 141.02, 143.56, 170.67, 206.80; EI-MS (*m/z*, relative intensity): 296 (M^+, 4), 185 (18), 152 (20), 111 (100), 43 (100). Anal. calcd. for $C_{15}H_{17}ClO_2S$: C, 60.07; H, 5.77. Found: C, 60.75; H, 5.97. HPLC condition (254 nm): Chiracel OJH; *n*-hexane / *iso*-propanol = 90 : 10, t_R *(S isomer)* = 6.12 min, t_R *(R isomer)* = 7.18 min.

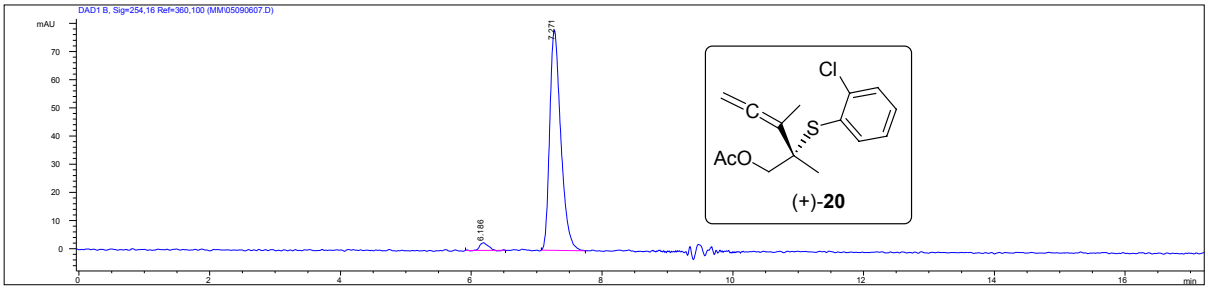
OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 90 : 10, racemic.



OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 90 : 10; with ligand (*S, S*)-**7,** 96 % ee (Table 3, entry 13).

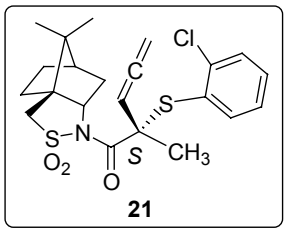


OJH, 0.8 min/mL, *n*-hexane : ^{i}PrOH = 90 : 10; with ligand **8**, 94 % ee (Table 3, entry 14).

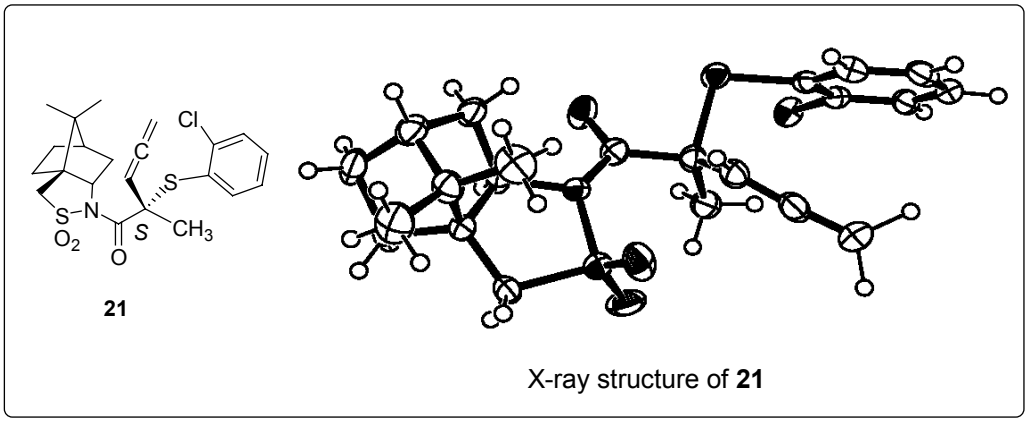


Determination of Absolute Configuration of the Product (10d)

For diazo substrate **1e**, the rearrangement product **21** was isolated and recrystallized. The configuration of the newly formed chiral center was determined by X-ray structures of **21**.

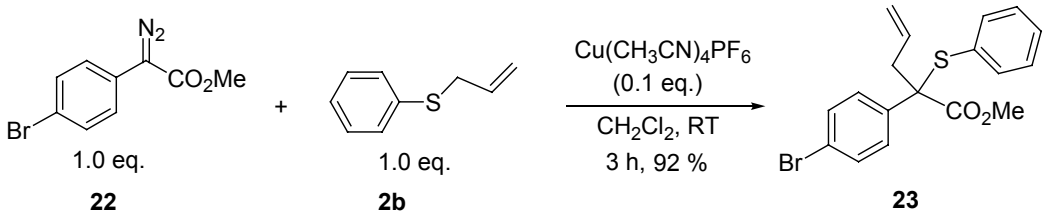


IR ($CHCl_3$) 2962, 1676, 1449, 1340, 1267, 1236, 1141, 1036 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (s, 3H), 1.93 (s, 3H), 1.26~1.49 (m, 2H), 1.73 (s, 3H), 1.83~2.10 (m, 5H), 3.43~3.53 (m, 2H), 4.13 (dd, J_1 = 4.8 Hz, J_2 = 7.5 Hz,, 1H), 4.65 (dd, J = 6.6, 11.4 Hz,, 1H), 4.87 (dd, J = 6.6, 11.4 Hz,, 1H), 5.65 (t, J = 6.6 Hz, 1H), 7.21 (dt, J = 1.5, 7.5 Hz,, 1H), 7.30 (dt, J = 1.8, 7.5 Hz,, 1H), 7.46 (dd, J = 1.5, 7.8 Hz,, 1H), 7.58 (dd, J = 1.8, 7.5 Hz,, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.87, 20.82, 23.17, 26.40, 33.02, 38.75, 44.54, 47.73, 47.99, 53.83, 58.39, 67.77, 78.82, 93.48, 126.41, 129.95, 130.48, 130.85, 139.18, 140.75, 173.06, 208.27; EI-MS (*m/z*, relative intensity): 451 (M^+, 24), 387 (5), 308 (62), 209 (100), 135 (54), 93 (31), 41 (20). Anal. calcd. for $C_{22}H_{26}ClNO_3S_2$: N, 3.10; C, 58.46; H, 5.80. Found: N, 2.89; C, 58.59; H, 6.05.

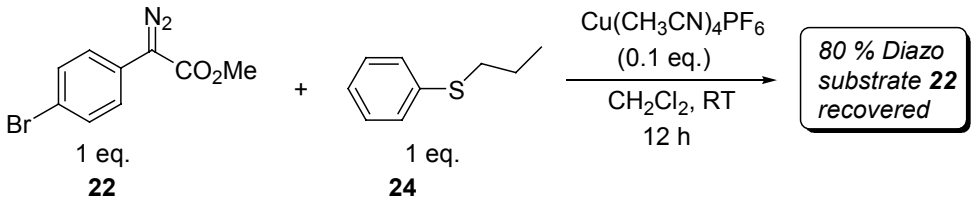


Experiments for Mechanistic Study.

(1) Reaction of Methyl (p-Bromophenyl)diazoacetate 22 with Allyl Sulfide 2b and n-Propyl Phenyl Sulfide 24.

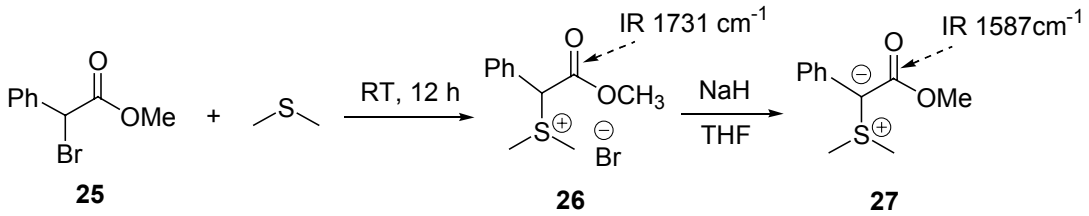


Under a nitrogen atmosphere, $Cu(MeCN)_4PF_6$ (13.2 mg, 0.035 mmol) were added to a 25 mL round-bottomed flask. Dry CH_2Cl_2 (2 mL) was introduced and the solution was stirred at RT. To the colorless solution was then added phenyl ally sulfide **2b** (53 mg, 0.35 mmol), then methyl (*p*-bormophenyl)diazoacete **22** (90 mg, 0.35 mmol,) in dry CH_2Cl_2 (2 mL) was added dropwise at 0 ^{0}C . The solution was stirred for additional 3 h at RT and diazo substrate **22** completely disappeared as judged by TLC. Removal of the solvent in vacuo gave a crude residue which was purified by silica gel column eluted with petroleum ether/ethyl acetate (30 : 1) to afford pure product **23** (122 mg, 92 %).



Under similar condition, the solution was stirred for 12 h at RT, and most diazo substrate **22** still remained. Removal of the solvent in vacuo gave a residue which was purified by silica gel column eluted with petroleum ether / ethyl acetate (30 : 1) to recover the diazo substrate **22** (72 mg, 80 %)**.** In addition to the recovered **22**, there were some very polar products formed. The polar products, presumably to be sulfur ylide and Cu(I) associated ylide, were unstable in silica gel column.

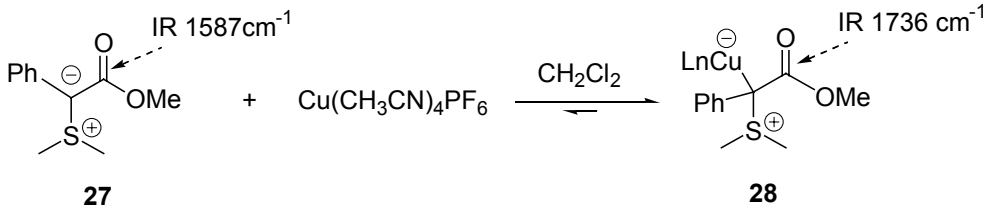
(2) Preparation of Free Ylide.[5]



A mixture of methyl 2-bromo-2-phenylacetate **25** (500 mg, 2.18 mmol) and dimethyl sulfide (205 mg, 2.18 mmol) was stirred overnight. The crude product **26** was formed as white solid. After recrystallization from ethanol, pure salt **26** was obtained (656 mg, 93 %). The IR spectrum of the **26** in ethanol shows that ν(C=O) is 1731 cm^{-1}. Sodium hydride (60 % mineral oil dispersion, 24 mg, 1 mmol) was introduced into a 25 mL round-bottomed flask. Anhydrous THF (3 mL) was added under nitrogen. With stirring, the salt **26** (200 mg, 0.62 mmol) in anhydrous THF (2 mL) added to the mixture by a funnel. After 30 min, the clear solution turned white turbid. The mixture was centrifuged and the supernatant was analyzed with IR.

Compared with the salt **26,** the IR spectra of the free ylide **27** showed that ν(C=O) (in THF) is 1587 cm^{-1}. Removal of the solvent from the supernatant afford the ylide **27** as light yellow oil (143 mg, 95 %).

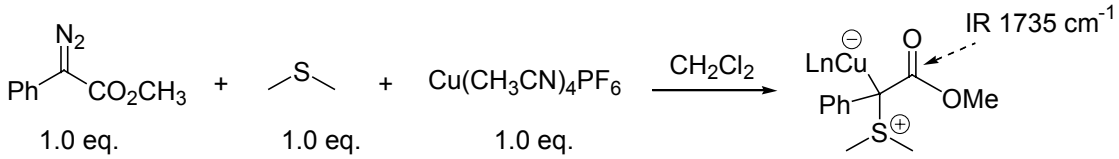
(3) Interaction of Ylide 27 with Cu(MeCN)$_4$•PF$_6$



27 **28**

To the solution of ylide **27** (100 mg, 0.41 mmol) in anhydrous CH_2Cl_2 (2 mL) was added $Cu(CH_3CN)_4$ •PF_6 (92 mg, 0.25 mmol). The clear solution turned turbid after stirring for 30 min. The mixture was centrifuged and the supernatant was analyzed with IR. The IR spectra showed that ν(C=O) (CH_2Cl_2) was 1736 cm^{-1}.

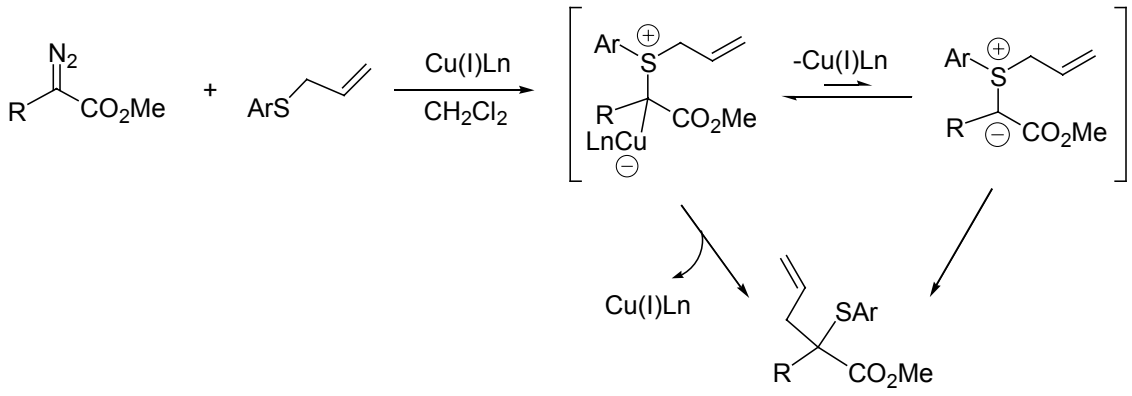
(4) Metal Complexed Ylide from the Reaction of Methyl Phenyldiazoacetate 29 and Dimethyl Sulfide in the Presence of Cu(MeCN)$_4$•PF$_6$



29

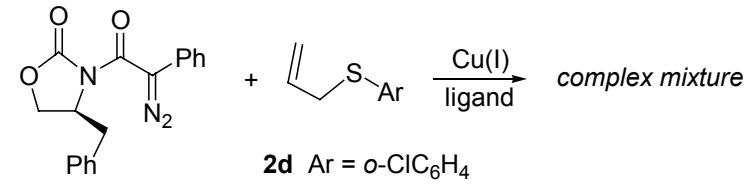
Under nitrogen atmosphere, diazo substrate **29** (30 mg, 0.17 mmol), dimethyl sulfide (16 mg, 0.17mmol) and $Cu(CH_3CN)_4$•PF_6 (64 mg, 0.17 mmol) were mixed and stirred. After 1 h, **29** completely disappeared as judged by TLC. The mixture was centrifuged and the supernatant was analyzed with IR. The IR spectra showed that ν(C=O) (CH_2Cl_2) was 1735 cm^{-1}.

The conclusion that can be drew from the above observations is that the ylide is strongly complexed with the Cu(I) complex.[6] It is possible that [2,3]-sigmatropic rearrangement occurs from the Cu(I)-complexed ylide. However, because the rearrangement is a facile process,[7] the possibility can not be ruled out that the reaction proceeds from the fractional free ylide that is in equilibrium with the Cu(I)-complexed ylide (Curtin-Hammett principle).

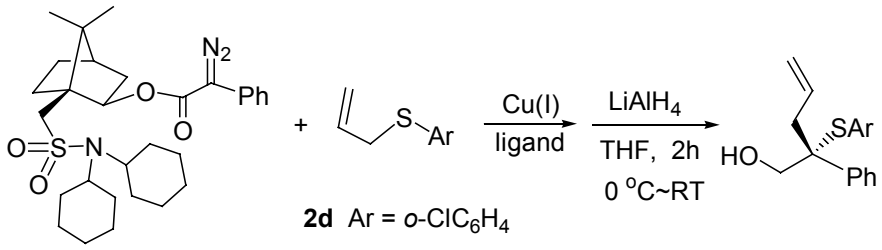


Study with Other Chiral Auxiliary.

Diazo compounds **30** and **31** were examined to study the effect of chiral auxiliary on the selectivity. In both cases, the reaction gave very poor selectivities.



30



31

With (*S*, *S*)-**7** as the ligand: 22 % ee
With **8** as the ligand: 24 %ee

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(6) For complexation of sulfonium ylide with Ru and Rh, see: Gandelman, M.; Rybtchinski, B.; Ashkenazi, N.; Gauvin, R. M.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 5372.

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