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Supporting Information

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A Highly Practical and Enantioselective Reagent for the Allylation of Aldehydes

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General Information. All reactions were carried out under an atmosphere of nitrogen in flame- or oven-dried glassware with magnetic stirring unless otherwise indicated. Degassed solvents were purified by passage through an activated alumina column. ^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) spectrometer and are reported in ppm from $CDCl_3$ internal standard (7.26 ppm). Data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of doublets; coupling constant(s) in Hz; integration; assignment). Proton decoupled ^{13}C NMR spectra were recorded on a Bruker DPX-300 (75 MHz) and are reported in ppm from $CDCl_3$ internal standard (77.0 ppm). Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer.

Preparation of (*R*,*R*)-*N*,*N*'-bis-(4-bromo-benzyl)-cyclohexane-1,2-diamine: To a suspension of (1*R*,2*R*)-(+)-1,2-diaminocyclohexane•L-tartrate (11.43 g, 43.2 mmol) in water (200 ml) was added potassium carbonate (11.96 g, 86.5 mmol). Ethanol (100 ml) was added to the resulting solution, followed by a solution of methanesulfonic acid (0.50 g, 5.2 mmol) and 4-bromobenzaldehyde (16.0 g, 86.5 mmol) in CH_2Cl_2 (200 ml). The reaction mixture was stirred for 12 h, then was heated at reflux for 1 h. The reaction mixture was concentrated, diluted with water, and filtered. The collected solid was suspended in methanol (50 ml), and the suspension was cooled to 0 °C. $NaBH_4$ (3.62 g, 96.7 mmol) was added, and after the gas evolution subsided, the solution was heated at reflux for 1 h. The reaction mixture was cooled to room temperature and concentrated. To the residue was added 1N aq. NaOH, EtOAc, hexane. The layers were separated and the aqueous layer was extracted with EtOAc and hexane two times. The combined organics were washed with brine, dried ($MgSO_4$), filtered, and concentrated. The residue was chromatographed on silica gel (1:4 EtOAc:hexanes, and then 1:1:0.1 EtOAc:hexanes:Et_3N) to obtain the diamine as a slightly yellow paste (16.27 g, 83%). ^{1}H NMR (300 MHz, C_6D_6) δ 7.43 (d, 4H, J = 8.3 Hz, Ar-**H**), 7.19 (d, 4H, J = 8.3 Hz, Ar-**H**), 3.85 (d, 1H, J = 13.4 Hz, two of

NC**H**$_2$Ar), 3.61 (d, 1H, *J* = 13.4 Hz, two of NC**H**$_2$Ar), 2.07-2.27 (m, 4H, two of C**H**NSiBn and two of Cy), 1.68-1.98 (m, 4H, two of Cy and N**H**), 1.00-1.32 (m, 4H, four of Cy); ^{13}C NMR (75MHz, C_6D_6) δ 139.2, 130.5, 128.9, 119.6, 60.0, 49.4, 30.7, 24.1; IR (neat) ν 3298, 3023, 2927, 2854, 1896, 1736, 1592, 1487, 1457, 1404, 1358, 1241, 1116, 1070, 1011, 797 cm^{-1}; LRMS (FAB+) calcd for $C_{20}H_{24}Br_2N_2$ 450.0, found 451.0, 453.1 $(M+H)^+$.

Preparation of Reagent (*R*,*R*)-3: To a cooled (0 °C) solution of allyltrichlorosilane (2.05 ml, 14.1 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (4.24 ml, 28.4 mmol) in dichloromethane (50 ml) was added (*R*,*R*)-*N*,*N'*-bis-(4-bromo-benzyl)-cyclohexane-1,2-diamine (5.37 g, 11.9 mmol) in dichloromethane (20 ml) over 50 min. After 2 h, the mixture was warmed to room temperature, and was stirred for 13 h. The reaction mixture was concentrated. Diethylether (60 ml) was added, and the mixture was stirred for 1 h. The mixture was filtrated through a pad of celite with ether washes (2 x 10 ml). The filtrate was concentrated. Benzene (10 ml) was added, and the solution was concentrated. This procedure was repeated to give the product as an oil (5.37 g, 88%). Upon standing in a freezer, the oil solidified to a white solid that may be stored in a freezer and used as needed. ^{1}H NMR (300 MHz, C_6D_6) δ 7.43 (d, 2H, *J* = 8.4 Hz, Ar-**H**), 7.42 (d, 2H, *J* = 8.4 Hz, Ar-**H**),), 7.18 (d, 2H, *J* = 8.5 Hz, Ar-**H**),), 7.17 (d, 2H, *J* = 8.5 Hz, Ar-**H**), 5.72 (m, 1H, C**H**=CH$_2$), 5.00-4.92 (m, 2H, CH=C**H**$_2$), 3.98 (d, 1H, *J* = 16.2 Hz, one of NC**H**$_2$Ar), 3.95 (d, 1H, *J* = 15.1 Hz, one of NC**H**$_2$Ar), 3.65 (d, 1H, *J* = 15.1 Hz, one of NC**H**$_2$Ar), 3.64 (d, 1H, *J* = 16.2 Hz, one of NC**H**$_2$Ar), 2.63-2.75 (m, 2H, two of C**H**N), 1.42-1.79 (m, 6H, four of Cy and SiC**H**$_2$CH=CH$_2$), 0.83-1.05 (m, 4H, four of Cy); ^{13}C NMR (75 MHz, C_6D_6) δ 141.7, 140.7, 131.7, 131.4, 130.3, 129.5, 128.7, 121.2, 120.9, 116.6, 66.8, 65.8, 48.3, 47.5, 31.1, 30.7, 25.1, 25.0; ^{29}Si NMR (60 MHz, C_6D_6) δ -4.4; IR (neat) ν 3078, 3035, 2934, 2860, 2690, 1958, 1899, 1814, 1633, 1592, 1487, 1445, 1405 cm^{-1}. LRMS (EI+) calcd for $C_{23}H_{27}Br_2ClN_2Si$, 552.0, found 449.7, 451.7 $(M-Si(C_3H_5)Cl)$. (**Note:** Several other methods were attempted, but in no case could the molecular ion be found.)

General procedure for the enantioselective allylation of aldehydes with (*R*,*R*)-3: To a cooled (–10 °C) solution of **(*R*,*R*)-3** in CH_2Cl_2 (0.2 M) is added the aldehyde (1.0 equiv). The reaction mixture is transferred to a freezer (-10 °C) and maintained at that temperature for 20 h. To this cooled solution is added 1N HCl and EtOAc, and the mixture is vigorously stirred at room temperature for 15 min. The layers are separated and the aqueous layer is extracted with EtOAc 3 times. The combined organic layers are diluted with hexane, dried (MgSO4), filtered, and concentrated. Sufficiently pure for many uses, the homoallylic alcohol product may be purified further by chromatography on silica gel. All yields listed in Tables 1-3 are for chromatographed, analytically pure material.

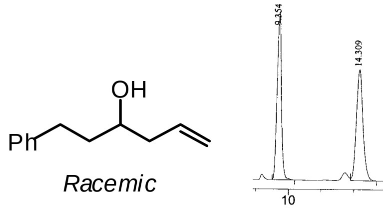
Alternative work up procedure for volatile products: The reactions of isovaleraldehyde (Table 2, entry 2) and 1-hexenal (Table 3, entry 5) give volatile products and low yields were obtained using the above procedure. In these cases toluene was used instead of EtOAc for extractions. The combined toluene layers were poured onto a column of silica gel and the toluene was eluted with pentane. The products were then eluted with 5% Et_2O/pentane and 20% Et_2O/pentane. The solutions were concentrated by distillation through a vigreaux column to give the pure products in the yields quoted in the Tables.

Alcohol **5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.40 (m, 10 H, Ar-**H**), 5.89 (m, 1 H, C**H**=CH_2), 5.14-5.19 (m, 2 H, CH=C$\mathbf{H}_2$), 4.68 (d, 1H, *J* = 11.3 Hz, OC$\mathbf{H}_2$Ph), 4.51 (d, 1H, *J* = 11.3 Hz, OC$\mathbf{H}_2$Ph), 3.77-3.92 (m, 2 H, C**H**OBn and C**H**OH), 3.47 (s, 1 H, O**H**), 2.67-2.82 (m, 2 H, C$\mathbf{H}_2$CH=CH_2), 2.26-2.31 (m, 2 H, C$\mathbf{H}_2$Ph), 1.73-2.05 (m, 4 H, four of methylene); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 137.8, 134.7, 128.3 (4C), 128.1 (2C), 127.8 (2C), 127.6, 125.7, 78.5, 70.5, 70.2, 42.0, 40.0, 36.0. 30.7; IR (NaCl) ν 3443, 3064, 3028, 2938, 2864, 1949, 1870, 1710, 1641, 1603, 1496, 1454, 1350, 1067 cm^{-1}. LRMS (FAB+) calcd for $C_{21}H_{26}O_2$ 310.2, found 311.3 $(M+H)^+$.

Alcohol **6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21-7.40 (m, 10 H, Ar-**H**), 5.88 (m, 1 H, C**H**=CH_2), 5.14-5.19 (m, 2 H, CH=C$\mathbf{H}_2$), 4.62 (d, 1H, *J* = 12.6 Hz, one of OC$\mathbf{H}_2$Ph), 4.59 (d, 1H, *J* = 12.6 Hz, one of OC$\mathbf{H}_2$Ph), 3.97-4.08 (m, 1 H, C**H**OH), 3.77-3.84 (m, 1 H, C**H**OBn), 2.67-2.82 (m, 3 H, O**H** and C$\mathbf{H}_2$CH=CH_2), 2.28 (t, 2 H, *J* = 6.5 Hz, C$\mathbf{H}_2$Ph), 1.68-2.16 (m, 4 H, four of methylene); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9, 138.1, 134.8, 128.3 (6C), 127.9 (2C), 127.7, 125.8, 117.5, 76.2, 71.2, 67.6, 42.1, 39.4, 35.3, 31.6; IR (NaCl) ν 3447, 3064, 3028, 2939, 2863, 1947, 1810, 1718, 1641, 1603, 1496, 1454, 1353, 1067 cm^{-1}. LRMS (FAB+) calcd for $C_{21}H_{26}O_2$ 310.2, found 311.3 $(M+H)^+$.

Determination of enantioselectivity of the homoallylic alcohol products:

Dihydrocinnamaldehyde (Table 2, entry 1): The ee was determined by chiral HPLC analysis using a chiralcel OD column. It has been established that the (*S*) enantiomer elutes first.[1]



Racemic

HPLC Conditions:
Chiralcel OD, Hex:*i*-PrOH 95:5, 1mL/min.

```
Peak RetTime  Type   Width     Area       Area
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----|-------|------|-------|----------|--------|
  1    9.354 BP      0.2732  622.39453  49.4276
  2   14.309 VB      0.4280  636.80902  50.5724
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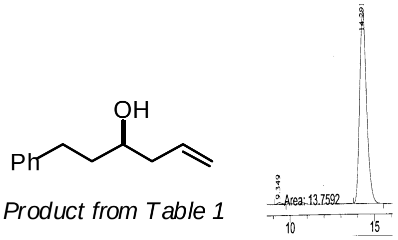
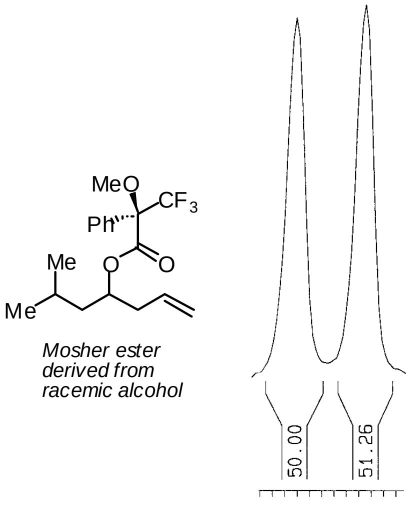


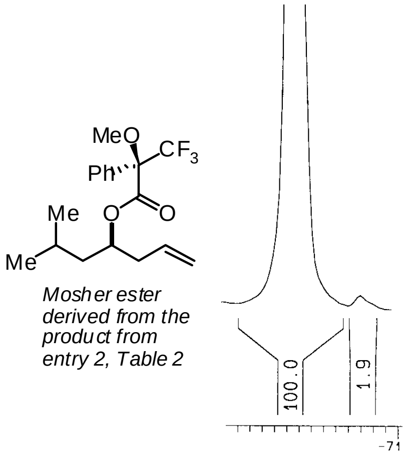
Product from Table 1

```
Peak RetTime  Type   Width     Area       Area
  #   [min]          [min]   mAU   *s      %
----|-------|------|-------|----------|--------|
  1    9.349 MM      0.3861   13.75921   0.8198
  2   14.291 BB      0.4375 1664.57983  99.1802
```

Isovaleraldehyde (Table 2, entry 2): The ee was determined by ^{19}F NMR (C_6D_6, 282 MHz) analysis of the derived Mosher ester.[2] We have previously correlated the absolute configuration of the alcohol to the peaks in the ^{19}F NMR spectrum.[3]



Mosher ester derived from racemic alcohol



Mosher ester derived from the product from entry 2, Table 2

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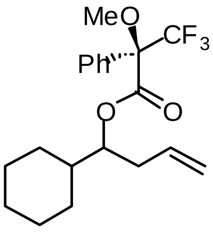
[1] Nakajima, M.; Saito, M.; Shiro, M. and Hashimoto, S. J. Am. Chem. Soc. 1998, 120, 6419-6420.

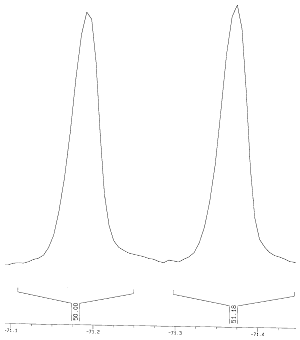
[2] Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543-2549.

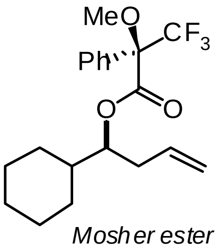
[3] Kinnaird, J. W. A.; Ng, P. Y.; Kubota, K.; Wang, X.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7920-7921. See the supporting information.

Cyclohexanecarboxaldehyde (Table 2, entry 3): The ee was determined by ^{19}F NMR (C_6D_6, 282 MHz) analysis of the derived Mosher ester.[2] We have previously correlated the absolute configuration of the alcohol to the peaks in the ^{19}F NMR spectrum.[3]

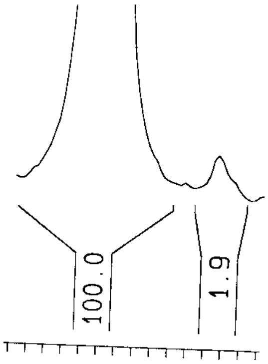


Mosher ester derived from racemic alcohol

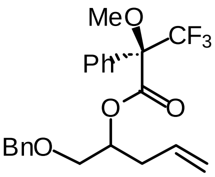




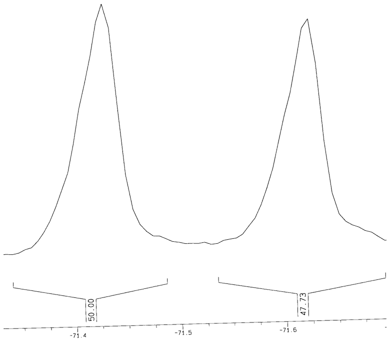
Mosher ester derived from the product from entry 3, Table 2

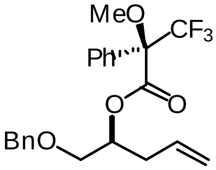


Benzyloxyacetaldehyde (Table 2, entry 4): The ee was determined by ^{19}F NMR (C_6D_6, 282 MHz) analysis of the derived Mosher ester.[2] We have previously correlated the absolute configuration of the alcohol to the peaks in the ^{19}F NMR spectrum.[3]

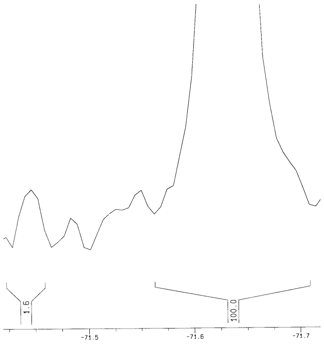


Mosher ester derived from racemic alcohol



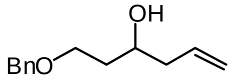


Mosher ester derived from the product from entry 4, Table 2

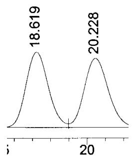


3-(Benzyloxy)propionaldehyde (Table 2, entry 5): The ee was determined by chiral HPLC analysis using a chiralcel OD column.

HPLC Conditions:
Chiralcel OD, Hex:*i*-PrOH 99:1, 1mL/min.



Racemic



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Peak RetTime Type  Width     Area       Height      Area
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----|-------|----|-------|----------|----------|--------|
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  2  20.228 VB    0.7154  441.57849    9.57983  49.8861
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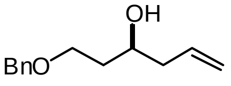
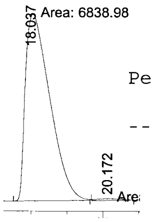


Product from Table 2



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 #   [min]        [min]   mAU    *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1  18.037 MM    0.7916 6838.98291  143.99869  99.2300
  2  20.172 MM    0.7433   53.06953    1.19002   0.7700
```
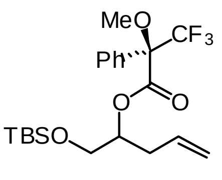
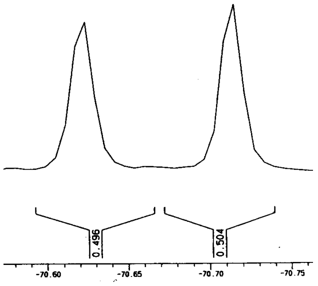
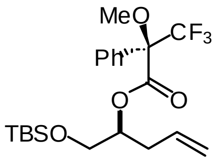

***tert*-Butyldimethylsilyloxyacetaldehyde (Table 2, entry 6):** The ee was determined by ^{19}F NMR (C_6D_6, 282 MHz) analysis of the derived Mosher ester.[2] We have previously correlated the absolute configuration of the alcohol to the peaks in the ^{19}F NMR spectrum.[3]

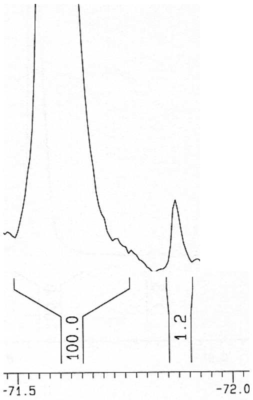


Mosher ester derived from racemic alcohol

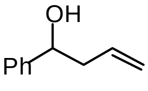




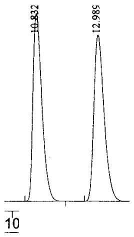
Mosher ester derived from the product from entry 6, Table 2



Benzaldehyde (Table 3, entry 1): The ee was determined by chiral HPLC analysis using a chiralcel OD column. It has been established that the (*R*) enantiomer elutes first.[1]



Racemic



HPLC Conditions:
Chiralcel OD, Hex:*i*-PrOH 97:3, 1mL/min.

```
Peak RetTime  Type   Width     Area       Area
 #   [min]          [min]   mAU    *s      %
----|-------|------|-------|----------|--------|
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  2   12.989 BB     0.3823 2648.83618  50.2865
```
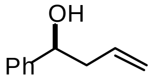
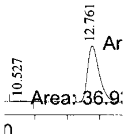



Product from Table 3



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Peak RetTime  Type   Width     Area       Area
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----|-------|------|-------|----------|--------|
  1   10.527 MM     0.3060   36.93769   1.1811
  2   12.761 MM     0.4205 3090.33057  98.8189
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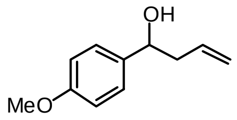
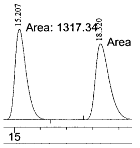
***p*-Anisaldehyde (Table 3, entry 2):** The ee was determined by chiral HPLC analysis using a chiralcel OD column. It has been established that the (*R*) enantiomer elutes first.[1]



Racemic



HPLC Conditions:
Chiralcel OD, Hex:*i*-PrOH 95:5, 1mL/min.

```
Peak RetTime  Type   Width     Area       Area
  #   [min]          [min]   mAU   *s       %
----|-------|------|-------|----------|--------|
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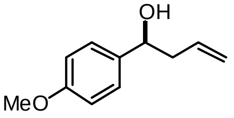
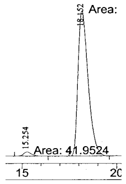


Product from Table 3



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Peak RetTime  Type   Width     Area       Area
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----|-------|------|-------|----------|--------|
   1  15.254 MM       0.4889   41.95237   2.2314
   2  18.152 MM       0.6129 1838.15210  97.7686
```
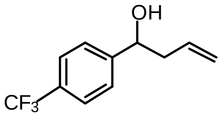
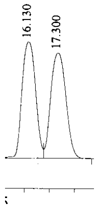

***p*-CF$_3$-Benzaldehyde (Table 3, entry 3):** The ee was determined by chiral HPLC analysis using a chiralcel OJ-H column. It has been established that the (*S*) enantiomer elutes first.[1]

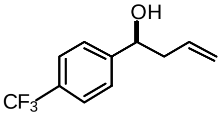


Racemic

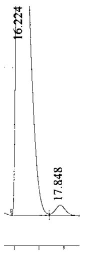


HPLC Conditions:
Chiralcel OJ-H, Hex:*i*-PrOH 99:1, 1mL/min.

```
Peak RetTime  Type   Width     Area       Area
  #   [min]          [min]   mAU   *s       %
----|-------|------|-------|----------|--------|
   1  16.130 BV      0.6094 1102.86060  49.7204
   2  17.300 VP      0.6773 1115.26526  50.2796
```

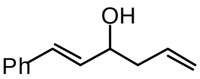


Product from Table 3

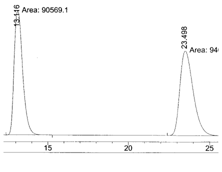


```
Peak RetTime  Type   Width     Area       Area
  #   [min]          [min]   mAU   *s       %
----|-------|------|-------|----------|--------|
   1  16.224 VV      0.4941 3744.86133  97.9859
   2  17.848 VP      0.4451   76.97663   2.0141
```

***trans*-Cinnamaldehyde (Table 3, entry 4):** The ee was determined by chiral HPLC analysis using a chiralcel OD column. It has been established that the (*R*) enantiomer elutes first.[1]

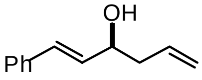


Racemic

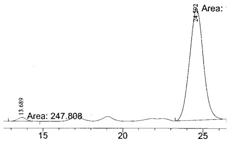


HPLC Conditions:
Chiralcel OD, Hex:*i*-PrOH 95:5, 1mL/min.

```
Peak RetTime Type  Width     Area      Height
  #   [min]        [min]   mAU   *s    [mAU   ]
----|-------|----|-------|----------|----------|
   1  13.116 MM    0.6152 9.05691e4  2453.79102
   2  23.498 MM    0.9438 9.46904e4  1672.20422
```

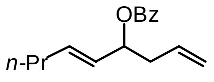


Product from Table 3

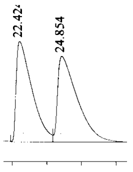


```
Peak RetTime  Type   Width     Area       Area
  #   [min]          [min]   mAU   *s       %
----|-------|------|-------|----------|--------|
   1  13.689 MM       0.6134  247.80823   2.1178
   2  24.592 MM       1.0043 1.14532e4   97.8822
```

***trans*-2-Hexenal (Table 3, entry 5):** The ee was determined by chiral HPLC analysis of the derived benzoate using a chiralcel AD-H column.

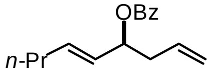


Racemic

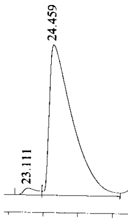


HPLC Conditions:
Chiralcel AD-H, Hex:*i*-PrOH 500:1, 0.5mL/min.

```
Peak RetTime  Type   Width      Area       Area
  #   [min]          [min]  mAU    *s        %
----|-------|------|-------|----------|--------|
   1  22.424 VV     0.9291 4312.36816  48.4575
   2  24.854 VB     1.1471 4586.90430  51.5425
```



Product from Table 3



```
Peak RetTime  Type   Width      Area       Area
  #   [min]          [min]  mAU    *s        %
----|-------|------|-------|----------|--------|
   1  23.111 PV     0.7682  331.80750   2.5414
   2  24.459 VV     1.3333 1.27243e4   97.4586
```

^{1}H NMR spectrum of reagent (*R*,*R*)-**3**: