# Supplementary Information

## *anti*-Diastereo and Enantioselective Carbonyl (Hydroxymethyl)allylation from the Alcohol or Aldehyde Oxidation Level: Allyl Carbonates as Allylmetal Surrogates

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[†]*University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX 78712, and* [‡]*School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

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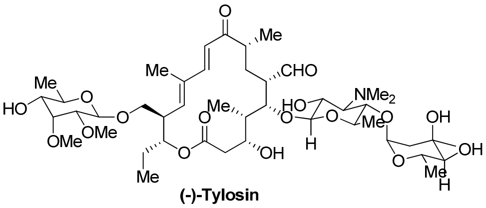
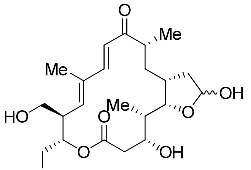


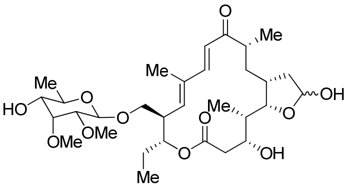
**(-)-Tylosin**

**Tatsuta**, *TL* **1982**, *23*, 3375



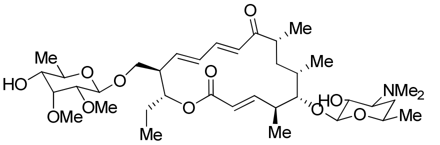
**(+)-Tylonolide**

**Tatsuta**, *TL*, **1981**, *22*, 3997.
**Masamune**, *JACS*, **1982**, *104*, 5523.
**Grieco**, *JACS*, **1982**, *104*, 5781.
**Yonemitsu**, *CPB*, **1987**, *35*, 2219.



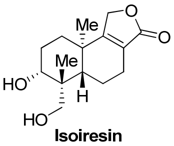
**O-Mycinosyltylonolide**

**Nicolaou**, *JACS*, **1982**, *104*, 2027, 2030.



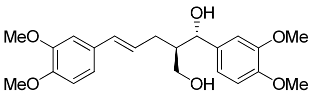
**Mycinamicin IV**

**Suzuki**, *CL*, **1987**, 113
**Suzuki**, *TL*, **1988**, *29*, 3575



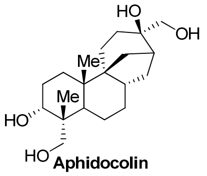
**Isoiresin**

**Pelletier**, *JACS*, **1968**, *90*, 5318.



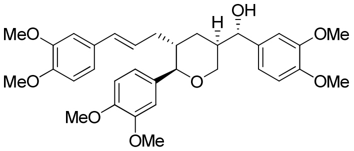
**morinol D**

**Yamauchi**, *OBC*, **2003**, *1*, 1329



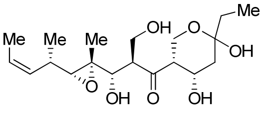
**Aphidocolin**

**Trost**, *JACS*, **1979**, *101*, 1328.
**McMurry**, *JACS*, **1979**, *101*, 1330.
**Corey**, *JACS*, **1980**, *102*, 1742.
**Ireland**, *JACS*, **1981**, *103*, 2446.
**Van Tamelen**, *JACS*, **1983**, *105*, 142.
**Bettolo & Lupi**, *HCA*, **1983**, *66*, 1922.
**Holton**, *JACS*, **1987**, *109*, 1597.



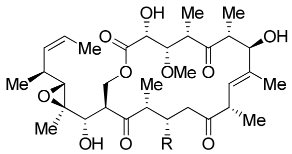
**morinol A**

**Yamauchi**, *JNP*, **2007**, *70*, 549



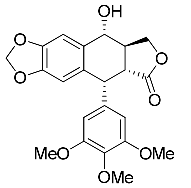
**Myriaporone 3**

**Echavarren & Cuevas**, *ACIE*, **2004**, *43*, 1724
**Taylor**, *ACIE*, **2004**, *43*, 1728.



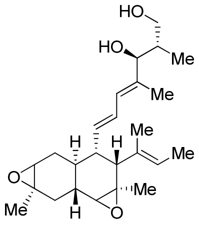
**(+)-Tedanolide (R = OH)**
**(+)-13-Deoxytedanolide (R = H)**

**Rush**, *JACS*, **2005**, *127*, 6186.
**Kalesse**, *JACS*, **2006**, *128*, 14038.
**Smith**, *JACS*, **2007**, *129*, 10957.



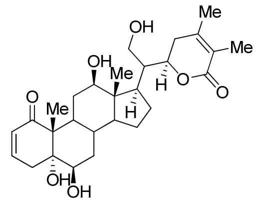
**podophyllotoxin**

**Gensler**, *JOC*, **1966**, *31*, 3224, 4004.
**Curran**, *JOC*, **1981**, *46*, 2826.
**Rodrigo**, *JACS*, **1981**, *103*, 6208.
**Durst**, *JOC*, **1986**, *51*, 4749.
**Doyle**, *TL*, **1986**, 27, 3099.
**Wong**, *TL*, **1987**, *28*, 517.
**Thompson**, *CC*, **1987**, 1797.
**Meyers**, *JACS*, **1988**, *110*, 7854.
**Bush & Jones**, *CC*, **1993**, 1200.
**Bhat**, *TL*, **1996**, *37*, 4791.
**Casey**, *CC*, **2004**, 184.
**Zhang**, *OL*, **2007**, *9*, 1199.
**Bach**, *ACIE*, **2008**, *47*, 7557.



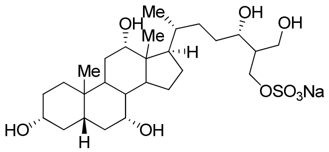
**Fusarielin A**

Isolation: **Son**, *JNP*, **2007**, *70*, 1188.



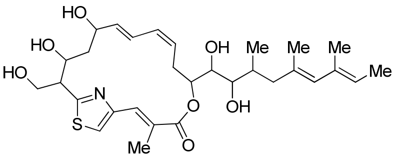
**Baimantuoluolines F**

Isolation: **Kuang**, *HCA*, **2008**, *91*, 964



**Sodium Scymnol Sulfate**

**Macrides**, *Steroids*, **2008**, *73*, 424.



**Thuggacin variant**

Isolation: **Jansen**, *ECJ*, **2007**, *13*, 5822

**Figure S1.** Natural Products containing $\alpha$-hydromethylated alcohol

**General Experimental Details.** All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred *via* oven-dried syringe. Reaction tubes were oven-dried and cooled under a stream of argon. Reactions tubes were purchased from Fischer Scientific (catalog number 14-959-35C). Tetrahydrofuran was obtained from solvent delivery system (Innovative Technology Inc. Ps-MD-5). Commercially available alcohols and aldehydes were purified by distillation or recrystallization prior to use. 4-Vinyl-1,3-oxolan-2-one was purchased from Aldrich and used after distillation. Allyl benzyl carbonate (**1b**) was prepared according to the literature report.[1] Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 $F_{254}$). Preparative column chromatography employing silica gel was performed according to the method of Still.[2] Solvents for chromatography are listed as volume/volume ratios. Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+H]^+$, $[M-H]^+$ or a suitable fragment ion. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded with a Varian Gemini 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. $^{13}$C NMR spectra were routinely run with broadband decoupling.

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[1] Guibe, F.; M'leux, S. *Tetrahedron Lett.* **1981**, *22*, 3591.

[2] Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

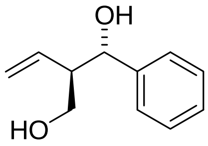
**Preparation of (*S*)-I:** To a mixture of $[Ir(cod)Cl]_2$ (87.3 mg, 0.13 mmol, 100 mol%), (*S*)-SEGPHOS (159 mg, 0.26 mmol, 200 mol%), $Cs_2CO_3$ (169 mg, 0.52 mmol, 400 mol%), 4-CN-3-$NO_2$BzOH (100 mg, 0.52 mmol, 400 mol%) and allyl acetate (65 mg, 0.65 mmol, 500 mol%) in a sealed tube under $N_2$ atmosphere was added THF (2.6 mL, 0.05 M). The reaction mixture was stirred for 30 min at ambient temperature and heated for 1.5 hr at 80 $^{o}$C, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered and washed with THF (10 mL). The filtrate was concentrated *in vacuo* and hexanes (50 mL) was added. A yellow precipitate formed, which was collected by filtration and dried under vacuum (101 mg, 0.098 mmol, 75% yield).

**Preparation of BIPHEP-I:** To a mixture of $[Ir(cod)Cl]_2$ (87.3 mg, 0.13 mmol, 100 mol%), BIPHEP (136 mg, 0.26 mmol, 200 mol%), $Cs_2CO_3$ (169 mg, 0.52 mmol, 400 mol%), 4-CN-3-$NO_2$BzOH (100 mg, 0.52 mmol, 400 mol%) and allyl acetate (65 mg, 0.65 mmol, 500 mol%) in a sealed tube under $N_2$ atmosphere was added THF (2.6 mL, 0.05 M). The reaction mixture was stirred for 30 min at ambient temperature and heated for 1.5 hr at 80 $^{o}$C, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered and washed with THF (10 mL). The filtrate was concentrated *in vacuo* and hexanes (50 mL) was added. A yellow precipitate formed, which was collected by filtration and dried under vacuum (108 mg, 0.11 mmol, 88% yield).

**General Procedure for the Carbonyl (Hydroxymethyl)allylation from Alcohols:** To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added (*S*)-I (10.3 mg, 0.01 mmol, 5 mol%), alcohol (0.2 mmol, 100 mol%). The tube was evacuated and backfilled with nitrogen (3 times). 4-Vinyl-1,3-dioxolan-2-one (38 μL, 0.4 mmol, 200 mol%) and THF (0.2 mL, 1.0 M concentration with respect to alcohol) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 90 $^{o}$C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$) under the conditions noted to furnish the corresponding product.

**General Procedure for the Carbonyl (Hydroxymethyl)allylation from Aldehydes:** To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added (*S*)-I (10.3 mg, 0.01 mmol, 5 mol%), aldehyde (0.2 mmol, 100 mol%). The tube was evacuated and backfilled with nitrogen (3 times). 4-Vinyl-1,3-dioxolan-2-one (38 μL, 0.4 mmol, 200 mol%), isopropanol (31 μL, 0.4 mmol, 200 mol%) and THF (0.2 mL, 1.0 M concentration with respect to aldehyde) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 90 $^{o}$C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$) under the conditions noted to furnish the corresponding product.

**(1*S*,2*R*)-1-Phenyl-2-vinylpropane-1,3-diol (4a)**



**4a**

In accordance with the general procedure, the product was isolated by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:2). The reaction from benzyl alcohol gave the title compound (23.6 mg, *anti*:*syn* = 6:1) as a colorless oil in 67% yield, and the reaction from benzaldehyde gave the product (22.5 mg, *anti*:*syn* = 5:1) in 63% yield.

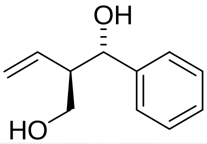
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.26 – 7.37 (m, 5H), 5.82 (ddd, *J* = 8.8, 10.4, 17.2 Hz, 1H), 5.26 (ddd, *J* = 0.4, 2.0, 10.0 Hz, 1H), 5.17 (ddd, *J* = 0.8, 1.6, 17.2 Hz, 1H), 4.83 (dd, *J* = 3.2, 6.0 Hz, 1H), 3.58 – 3.68 (m, 2H), 2.58 – 2.64 (m, 1H), 2.56 (d, *J* = 3.2 Hz, 1H), 1.87 (t, *J* = 5.2 Hz, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 142.0, 135.2, 128.3, 127.7, 126.4, 119.7, 75.0, 63.7, 53.4.

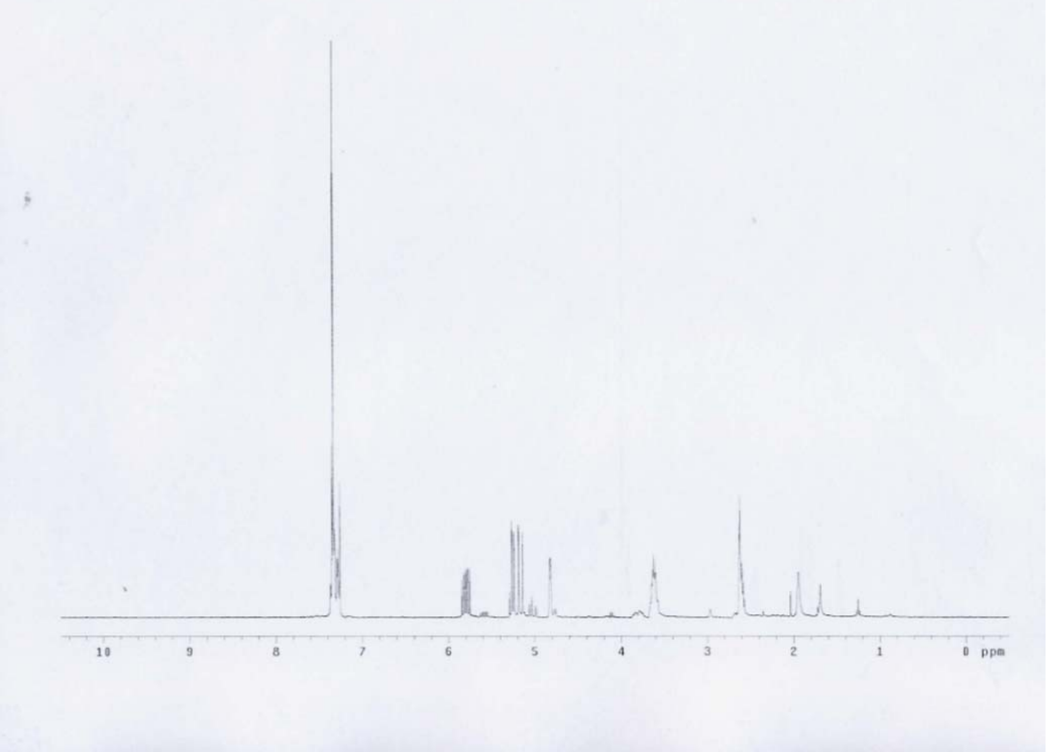
**HRMS** (ESI-MS): Calcd. for $C_{11}H_{14}O_2$+Na (M+Na): 201.0891, Found: 201.0885.

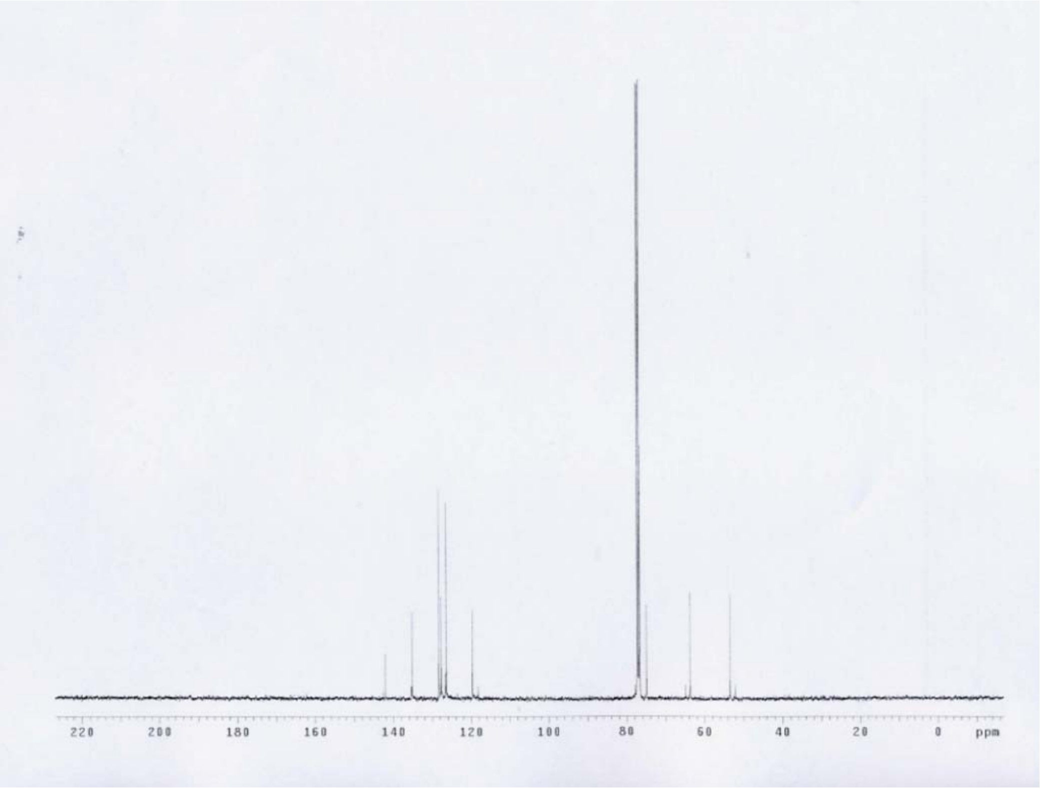
**FTIR** (neat): 3384, 3055, 1264, 733 cm$^{-1}$.

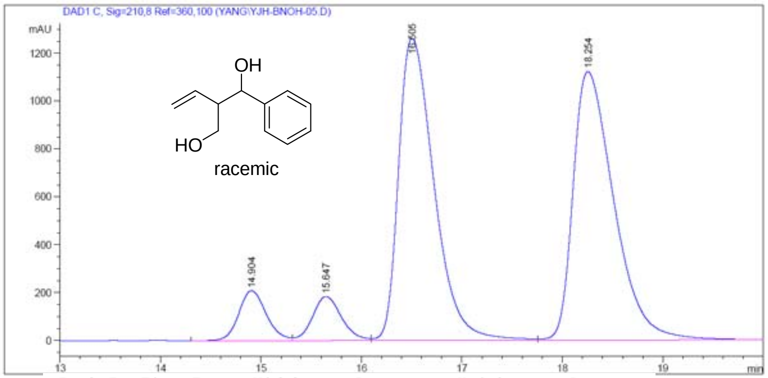
**HPLC** (Chiralcel OB-H column, hexanes:*i*-PrOH = 93:7, 0.5 mL/min, 210 nm), ee = 94% from benzyl alcohol, ee = 99% from benzaldehyde.



**4a**







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   1  14.904 VV     0.2960 4026.30981  209.69662   5.6952
   2  15.647 VV     0.3118 3724.62646  184.27658   5.2685
   3  16.505 VV     0.3830 3.10874e4  1263.67078  43.9730
   4  18.254 VB     0.4383 3.18582e4  1125.30078  45.0633
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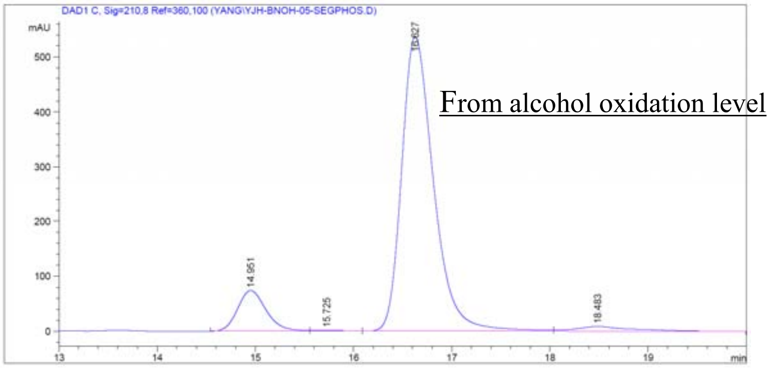

From alcohol oxidation level

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   1  14.951 BV     0.3086 1511.87122   74.56531  10.7373
   2  15.725 VV     0.3271   46.87523    2.07822   0.3329
   3  16.627 VV     0.3481 1.21558e4   536.95856  86.3304
   4  18.483 VB     0.5708  366.01489    8.84497   2.5994
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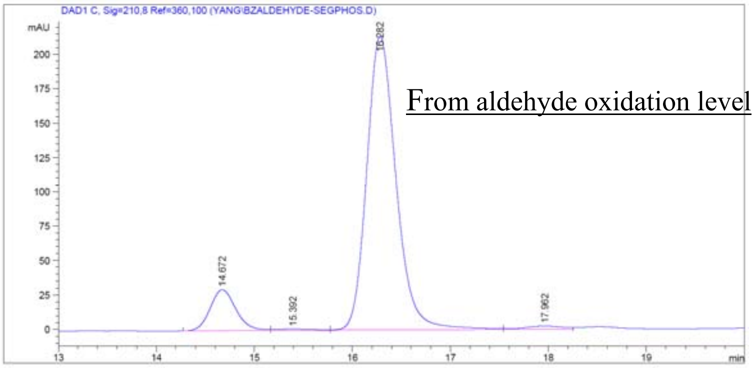

From aldehyde oxidation level

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   2  15.392 VV     0.3555   29.73244    1.14289   0.5833
   3  16.282 VB     0.3231 4449.84717  213.54999  87.3010
   4  17.962 BV     0.3855   66.96167    2.46070   1.3137
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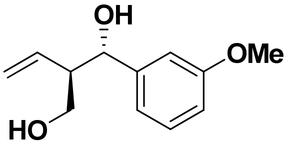
### (1*S*,2*R*)-1-(3-Methoxyphenyl)-2-vinylpropane-1,3-diol (4b)



**4b**

In accordance with the general procedure, the product was isolated by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:2). The reaction from 3-methoxybenzyl alcohol gave the title compound (30.0 mg, *anti*:*syn* = 7:1) as a colorless oil in 72% yield, and the reaction from 3-methoxybenzaldehyde gave the product (30.8 mg, *anti*:*syn* = 6:1) in 74% yield.

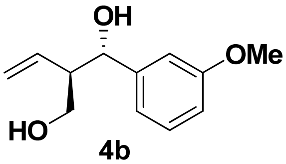
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.28 – 7.24 (m, 1H), 6.93 – 6.90 (m, 2H), 6.84 – 6.81 (m, 1H), 5.78 (ddd, *J* = 8.8, 10.4, 17.6 Hz, 1H), 5.28 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.20 (ddd, *J* = 1.6, 1.6, 17.6 Hz, 1H), 4.81 (dd, *J* = 3.2, 6.0 Hz, 1H), 3.82 (s, 3H), 3.70 – 3.60 (m, 2H), 2.64 – 2.58 (m, 1H), 2.43 (d, *J* = 3.6 Hz, 1H), 1.72 (dd, *J* = 4.8, 6.0 Hz, 1H)

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 159.6, 143.8, 135.2, 129.3, 119.6, 118.7, 113.1, 111.9, 74.8, 63.7, 55.2, 53.4

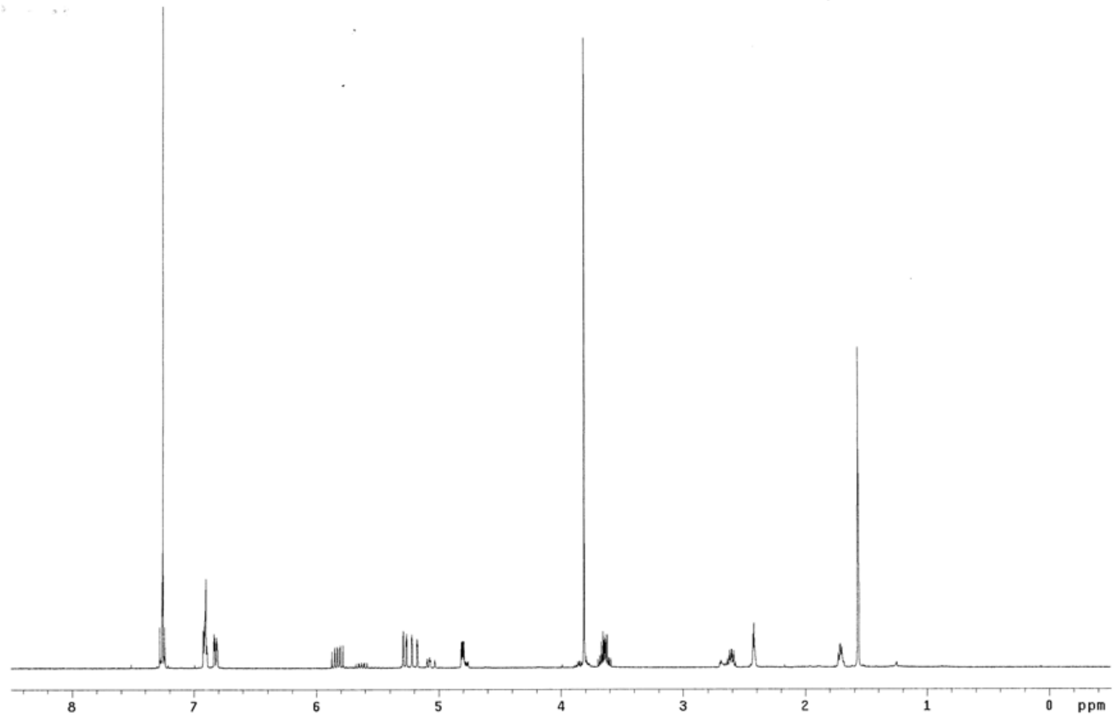
**HRMS** (CI): Calcd. for $C_{12}H_{15}O_3$ (M-H): 207.1021, Found: 207.1020

**FTIR** (neat): 3384, 2924, 1601, 1436, 1260, 1043, 764cm$^{-1}$

**HPLC** (Connecting Chiralcel OD-H column and AD-H column, hexanes:*i*-PrOH = 87:13, 1.0 mL/min, 220 nm), ee = 97% from 3-methoxybenzyl alcohol, ee = 98% from 3-methoxybenzaldehyde.


OH
OMe
HO

**4b**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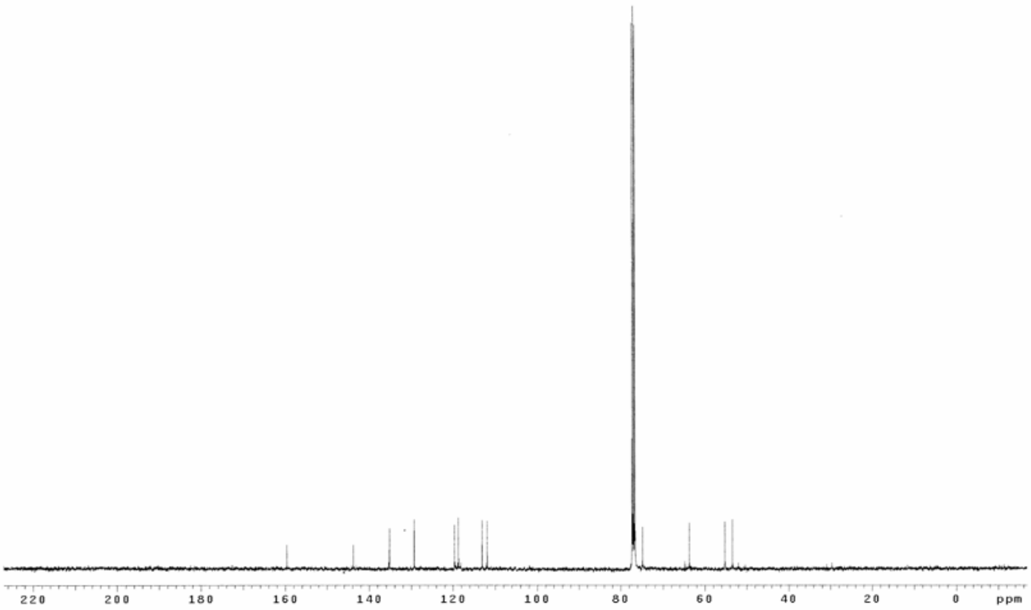
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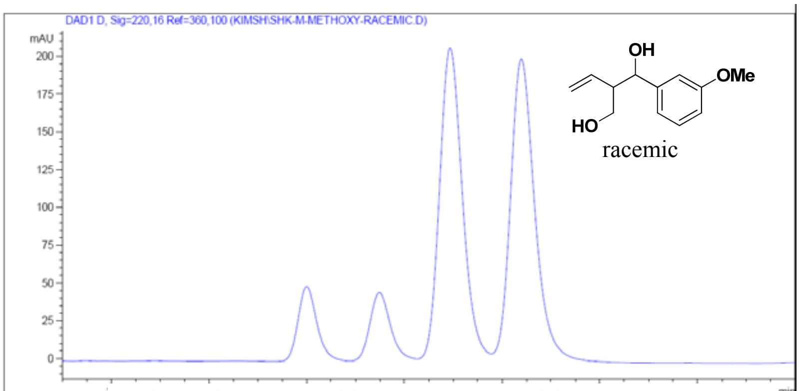

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   2  21.486 BB    0.4525 1342.05884   45.45400   8.2413
   3  22.934 BV    0.5048 6760.89746  207.16138  41.5174
   4  24.392 VB    0.5242 6850.31006  199.71408  42.0664
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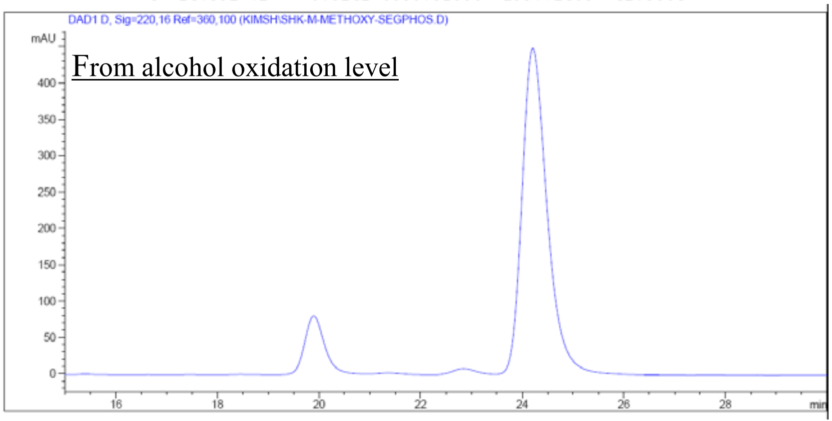

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   2  21.360 BB    0.3282   46.08250    1.79090   0.2586
   3  22.843 BV    0.4633  255.94115    8.31030   1.4364
   4  24.206 VB    0.5230 1.53518e4   448.83963  86.1599
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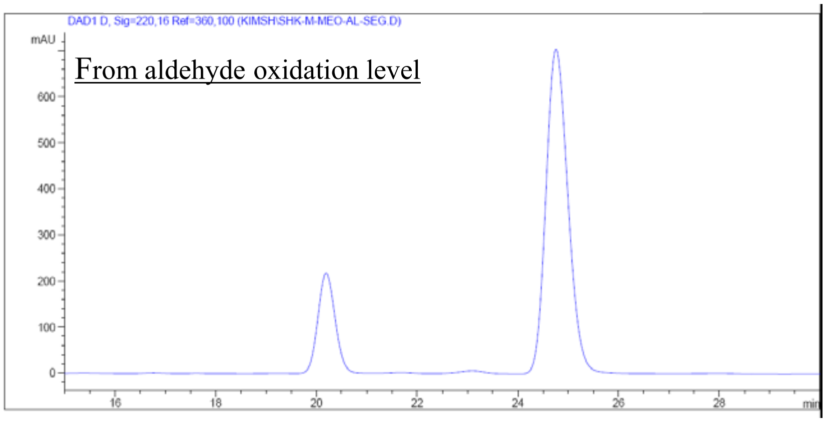

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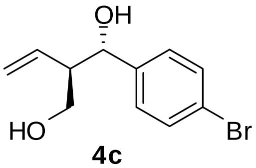
   1  20.189 BB    0.3696 5183.15771  217.79654  19.3052
   2  21.670 BB    0.3532   46.86443    1.93040   0.1746
   3  23.093 BB    0.5044  226.53180    6.73529   0.8437
   4  24.753 BB    0.4741 2.13920e4   704.85583  79.6765
```

### (1*S*,2*R*)-1-(4-Bromophenyl)-2-vinylpropane-1,3-diol (4c)



**4c**

In accordance with the general procedure, the product was isolated by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:2). The reaction from 4-bromobenzyl alcohol gave the title compound (35.0 mg, *anti*:*syn* = 5:1) as a colorless oil in 68% yield, and the reaction from 4-bromobenzaldehyde gave the product (33.0 mg, *anti*:*syn* = 5:1) in 64% yield.

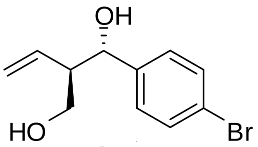
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.78 (ddd, *J* = 8.4, 10.8, 17.2 Hz, 1H), 5.24 (dd, *J* = 1.6, 10.8 Hz, 1H), 5.13 (dd, *J* = 1.6, 17.2 Hz, 1H), 4.84 (d, *J* = 5.2 Hz, 1H), 3.66 (m, 2H), 2.73 (bs, 1H), 2.58 – 2.51 (m, 1H), 1.90 (bs, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 141.1, 134.5, 131.3, 128.1, 121.4, 119.9, 74.3, 63.8, 53.1.

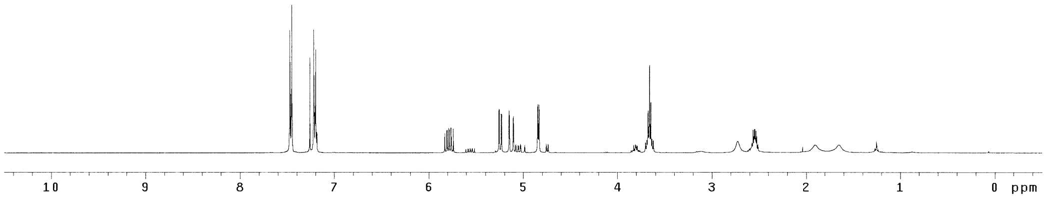
**HRMS** (CI): Calcd. for $C_{11}H_{12}BrO_2$ (M–H): 255.0021, Found: 255.0019.

**FTIR** (neat): 3356, 3076, 2884, 1639, 1487, 1402, 1070, 1010, 832 $cm^{-1}$.

**HPLC** (connecting two Chiralcel AS-H columns, hexanes:*i*-PrOH = 90:10, 1.0 mL/min, 220 nm), ee = 95% from 4-bromobenzyl alcohol, ee = 95% from 4-bromobenzaldehyde.


OH
HO
Br

**4c**


10
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6
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4
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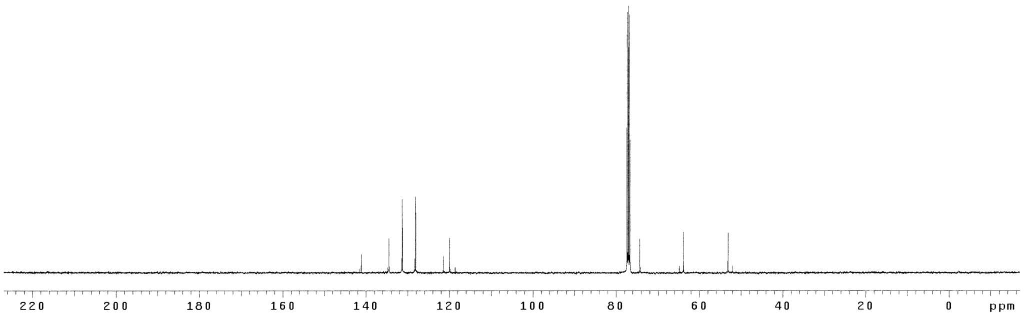
2
1
0 ppm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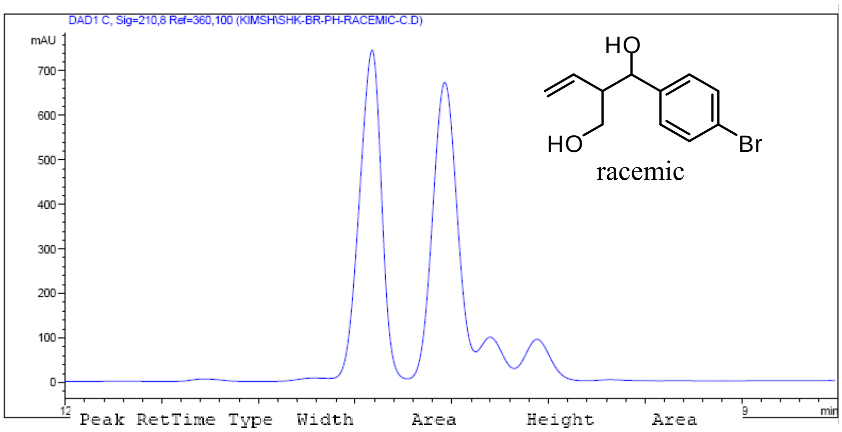
ppm



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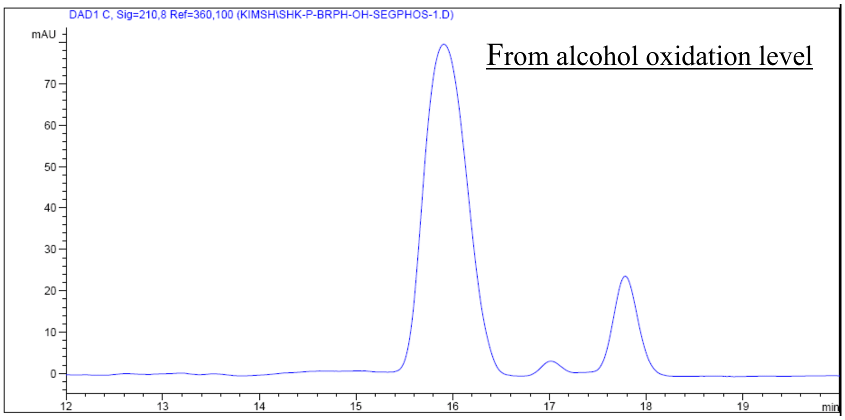
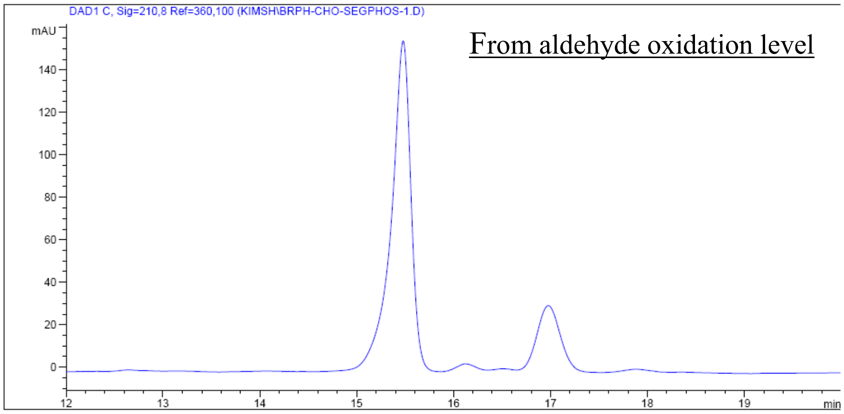
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]   [mAU*s]    [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  15.171 VV    0.2518 1.19662e4  743.56537  43.5833
  2  15.926 VV    0.2813 1.20435e4  671.46277  43.8651
  3  16.395 VV    0.2573 1671.50452  98.81628   6.0880
  4  16.880 VV    0.2885 1774.65417  93.90662   6.4637
```


From alcohol oxidation level

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]   [mAU*s]    [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  15.906 BV    0.5055 2482.26709   80.11668  82.9558
  2  17.014 VV    0.2472   57.71053    3.59747   1.9286
  3  17.782 VB    0.2903  452.29956   24.16989  15.1156
```


From aldehyde oxidation level

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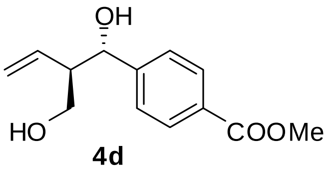
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]   [mAU*s]    [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  15.476 BV    0.2106 2223.83887  155.71327  78.0572
  2  16.122 VV    0.2385   59.58075    3.89469   2.0913
  3  16.510 VV    0.2115   24.31493    1.69375   0.8535
  4  16.976 VB    0.2644  541.25012   31.51503  18.9980
```

### Methyl 4-((1*S*,2*R*)-1-hydroxy-2-(hydroxymethyl)but-3-enyl)benzoate (4d)



**4d**

In accordance with the general procedure, the product was isolated by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:2). The reaction from methyl 4-(hydroxymethyl)benzoate gave the title compound (33.0 mg, *anti*:*syn* = 5:1) as a colorless oil in 70% yield, and the reaction from methyl 4-formylbenzoate gave the product (32.8 mg, *anti*:*syn* = 4:1) in 70% yield.

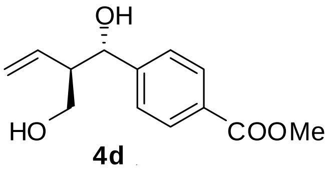
**<u>$^1$H NMR</u>** (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 5.78 (ddd, *J* = 8.8, 10.4, 17.2 Hz, 1H), 5.21 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.08 (dd, *J* = 1.6, 17.2 Hz, 1H), 4.96 (d, *J* = 5.2 Hz, 1H), 3.90 (s, 3H), 3.73 – 3.66 (m, 2H), 2.94 (bs, 1H), 2.63 – 2.55 (m, 1H), 2.07 (bs, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 167.0, 147.5, 134.2, 129.6, 129.5, 126.3, 119.8, 74.5, 63.9, 53.0, 52.1.

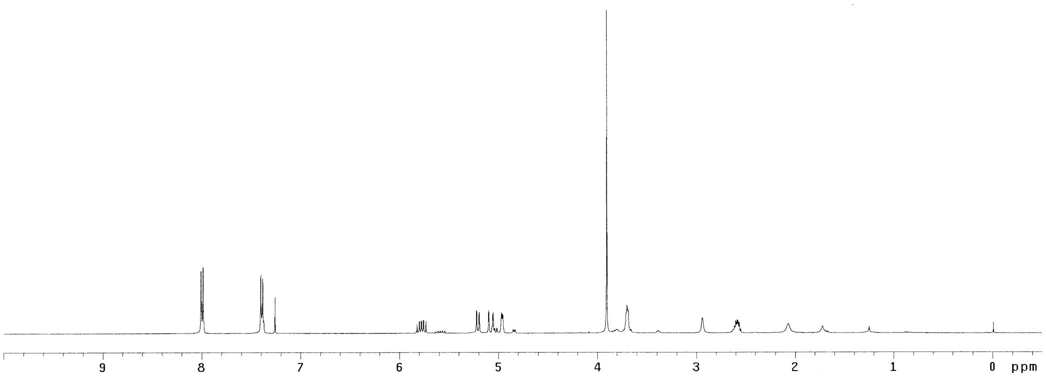
**HRMS** (CI): Calcd. for $C_{13}H_{17}O_4$ (M+H): 237.1127, Found: 237.1126.

**FTIR** (neat): 3392, 2952, 1703, 1640, 1436, 1279, 1018, 810, 735 $cm^{-1}$.

**HPLC** (connecting two Chiralcel OJ-H columns and one Chiralcel AD-H column, hexanes:*i*-PrOH = 85:15, 0.8 mL/min, 254 nm), ee = 98% from methyl 4-(hydroxymethyl)benzoate, ee = 98% from methyl 4-formylbenzoate.


OH
HO
COOMe

**4d**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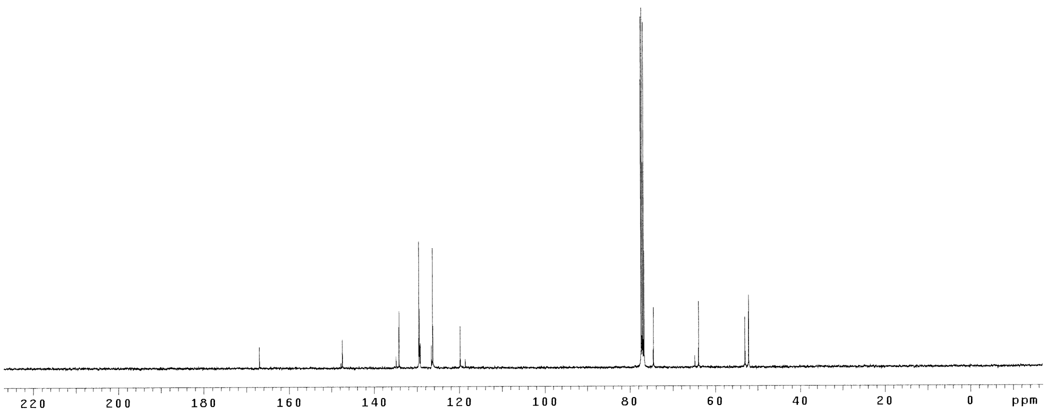
0
ppm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140
120
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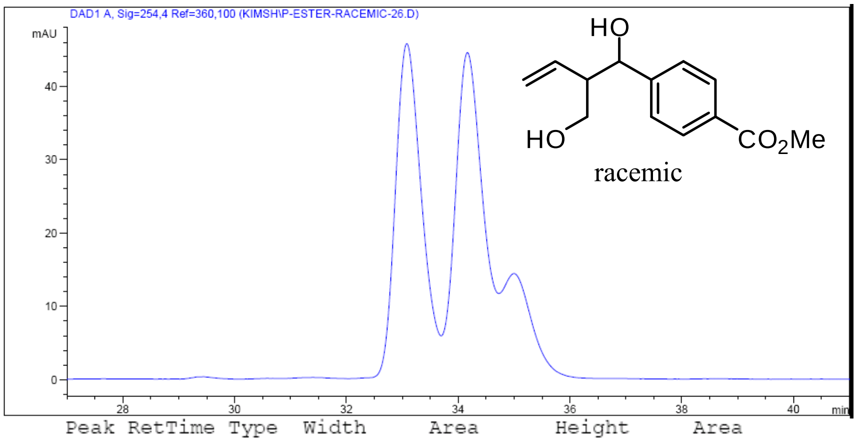
80
60
40
20
0
ppm



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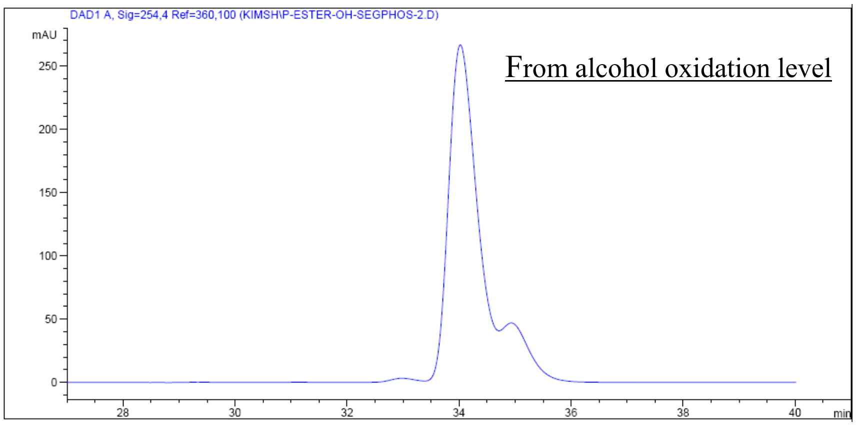
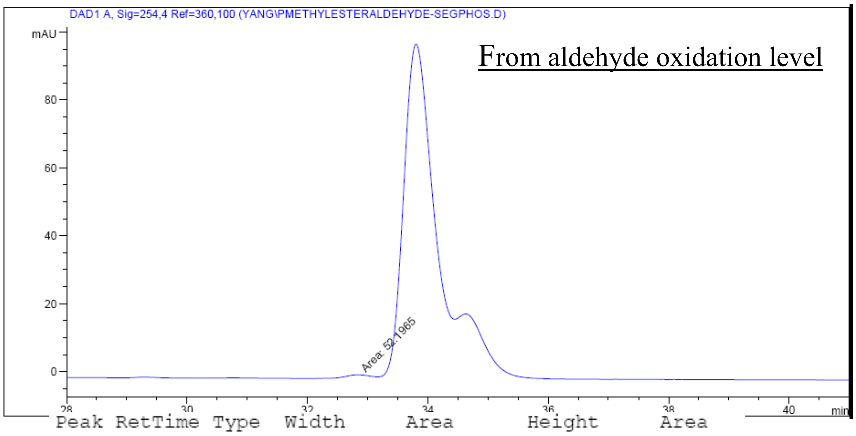
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  33.077 BV    0.4955 1471.16809   45.46518  41.9791
  2  34.161 VV    0.5200 1522.37134   44.18516  43.4402
  3  34.994 VB    0.5331  510.98178   14.02446  14.5806
```



From alcohol oxidation level

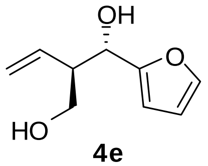
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  32.976 BV    0.3707   86.62597    3.01985   0.7838
  2  34.018 VV    0.5396 9348.05371  266.29123  84.5842
  3  34.927 VB    0.5193 1617.09045   46.55301  14.6320
```



From aldehyde oxidation level

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  32.848 MM    0.4239   52.19654    1.49107   1.3148
  2  33.802 BV    0.5182 3313.97998   98.08543  83.4763
  3  34.628 VB    0.4698  603.78870   18.74553  15.2089
```

**(1*S*,2*R*)-1-(Furan-2-yl)-2-vinylpropane-1,3-diol (4e)**



**4e**

In accordance with the general procedure, the product was isolated by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:2). The reaction from furfuryl alcohol gave the title compound (24.4 mg, *anti*:*syn* = 9:1) as a colorless oil in 72% yield, and the reaction from 2-furaldehyde gave the product (22.5 mg, *anti*:*syn* = 5:1) in 67% yield.

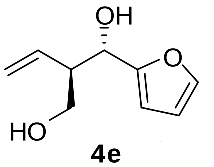
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.39 (m, 1H), 6.35 – 6.34 (m, 1H), 6.30 – 6.29 (m, 1H), 5.83 (ddd, *J* = 8.4, 10.4, 17.6 Hz, 1H), 5.29 (ddd, *J* = 0.8, 1.6, 10.4 Hz, 1H), 5.25 (ddd, *J* = 1.2, 1.6, 17.2 Hz, 1H), 4.87 (d, *J* = 5.6 Hz, 1H), 3.74 (dd, *J* = 6.0, 10.8 Hz, 1H), 3.66 (dd, *J* = 6.0, 10.8 Hz, 1H), 2.85 – 2.78 (m, 1H), 2.55 (bs, 1H), 1.81 (bs, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 154.8, 142.0, 134.8, 119.6, 110.2, 107.1, 68.8, 63.6, 50.9.

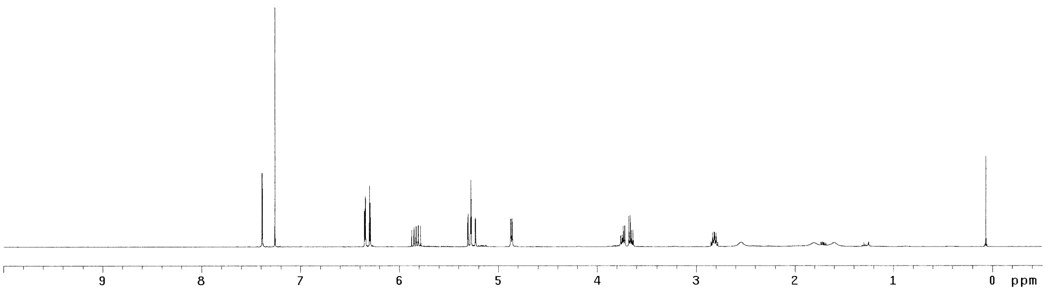
**HRMS** (CI): Calcd. for $C_9H_{11}O_3$ (M–H): 167.0708, Found: 167.0708.

**FTIR** (neat): 3354, 3079, 2886, 1640, 1505, 1422, 1148, 1010, 922, 738 cm$^{-1}$.

**HPLC** (Chiralcel AD-H column, hexane:*i*-PrOH = 92:8, 1.0 mL/min, 210 nm), ee = 99% from furfuryl alcohol, ee = 97% from 2-furaldehyde.


OH
O
HO

**4e**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4
3
2
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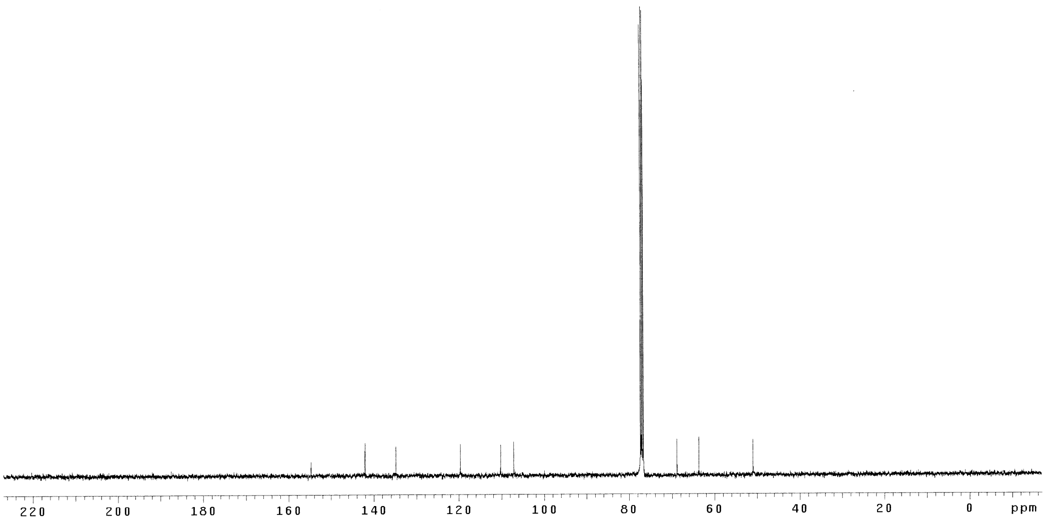
0 ppm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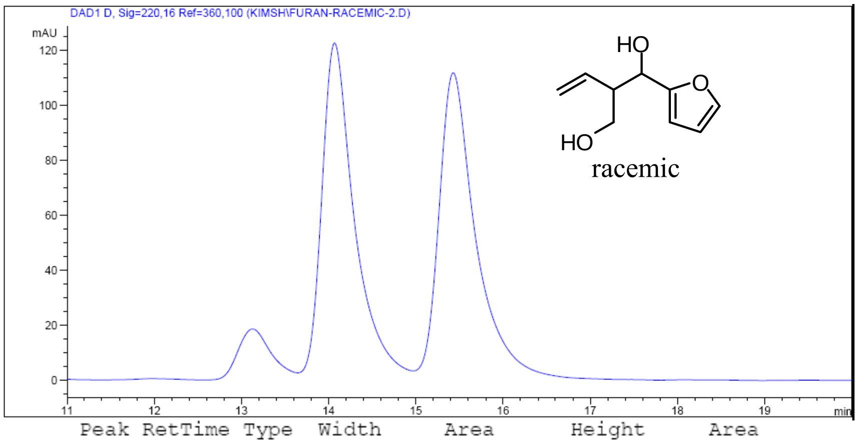
0
ppm



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  13.126 BV    0.4059  488.47025   18.39135   7.0743
   2  14.066 VV    0.3849 3191.95215  122.14404  46.2274
   3  15.426 VB    0.4268 3224.47046  111.03874  46.6983
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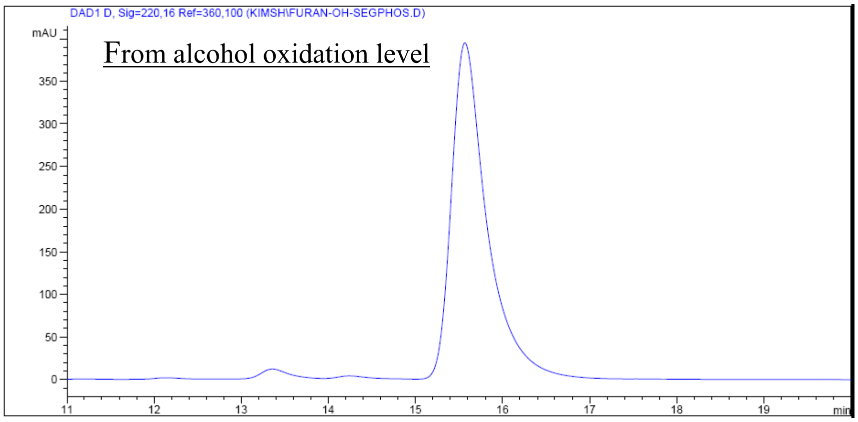

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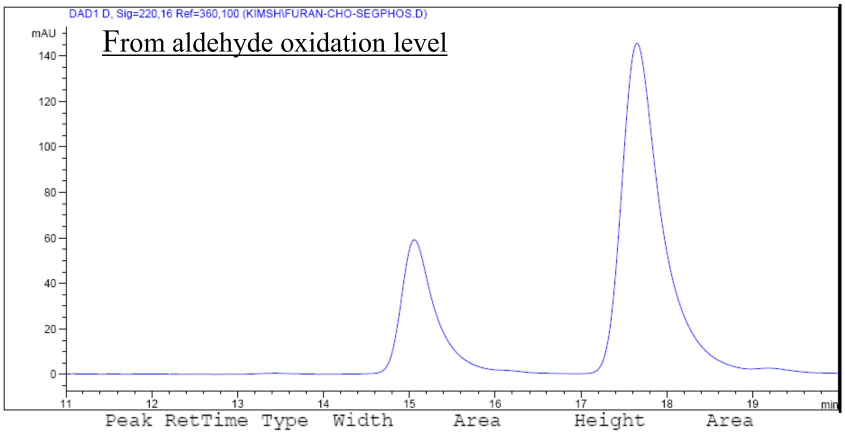
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  13.356 BB    0.3371  263.57352   11.68803   2.2814
   2  14.238 BB    0.3434   82.08502    3.58071   0.7105
   3  15.566 BB    0.4175 1.12076e4   394.40692  97.0081
```



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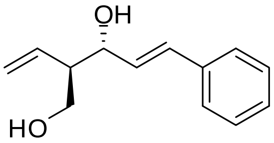
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.056 BB    0.3965 1562.52380   58.33337  25.2634
   2  17.649 BB    0.4729 4622.40625  144.60069  74.7366
```

### (2*R*,3*R*,*E*)-5-Phenyl-2-vinylpent-4-ene-1,3-diol (4f)



**4f**

In accordance with the general procedure, the product was isolated by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:2). The reaction from *trans*-cinnamyl alcohol gave the title compound (30.0 mg, *anti*:*syn* = 7:1) as a colorless oil in 74% yield, and the reaction from *trans*-cinnamaldehyde gave the product (27.8 mg, *anti*:*syn* = 7:1) in 68% yield.

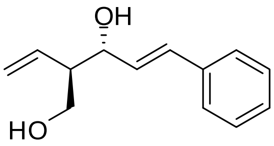
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.40 – 7.37 (m, 2H), 7.34 – 7.31 (m, 2H), 7.27 – 7.24 (m, 1H), 6.64 (d, J = 16.0 Hz, 1H), 6.27 (dd, *J* = 6.8, 16 Hz, 1H), 5.85 (ddd, *J* = 8.4, 10.4, 17.2 Hz, 1H), 5.30 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.25 (dd, *J* = 1.6, 17.2 Hz, 1H), 4.48 (dd, *J* = 5.6, 6.0 Hz, 1H), 3.87 (dd, *J* = 6.4, 10.8 Hz, 1H), 3.76 (dd, *J* = 6.0, 10.8 Hz, 1H), 2.60 – 2.53 (m, 1H), 2.29 (bs, 1H), 1.94 (bs, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 136.5, 134.8, 131.6, 129.6, 128.6, 127.8, 126.5, 119.4, 74.0, 63.9, 51.6.

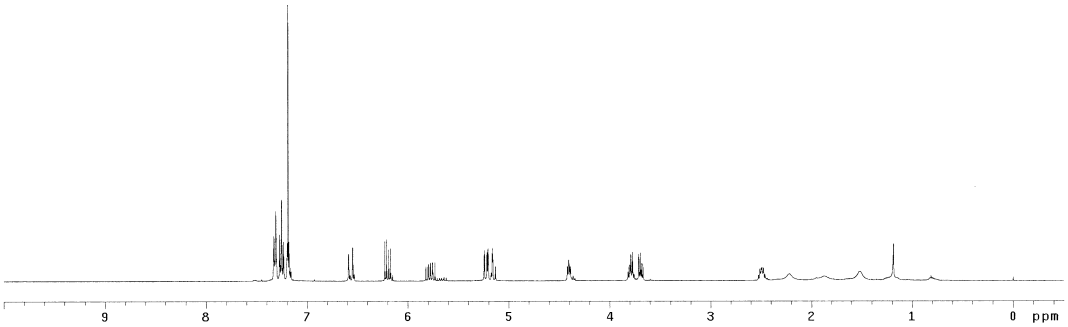
**HRMS** (CI): Calcd. for $C_{13}H_{15}O_2$ (M–H): 203.1072, Found: 203.1074.

**FTIR** (neat): 3342, 3078, 2282, 1739, 1639, 1599, 1448, 1229, 966, 751, 692 $cm^{-1}$.

**HPLC** (connecting two Chiralcel AD-H columns and one Chiralcel OD-H column, hexanes:*i*-PrOH = 92:8, 1.0 mL/min, 254 nm), ee = 93% from *trans*-cinnamyl alcohol, ee = 99% from *trans*-cinnamaldehyde.


OH
HO

**4f**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4
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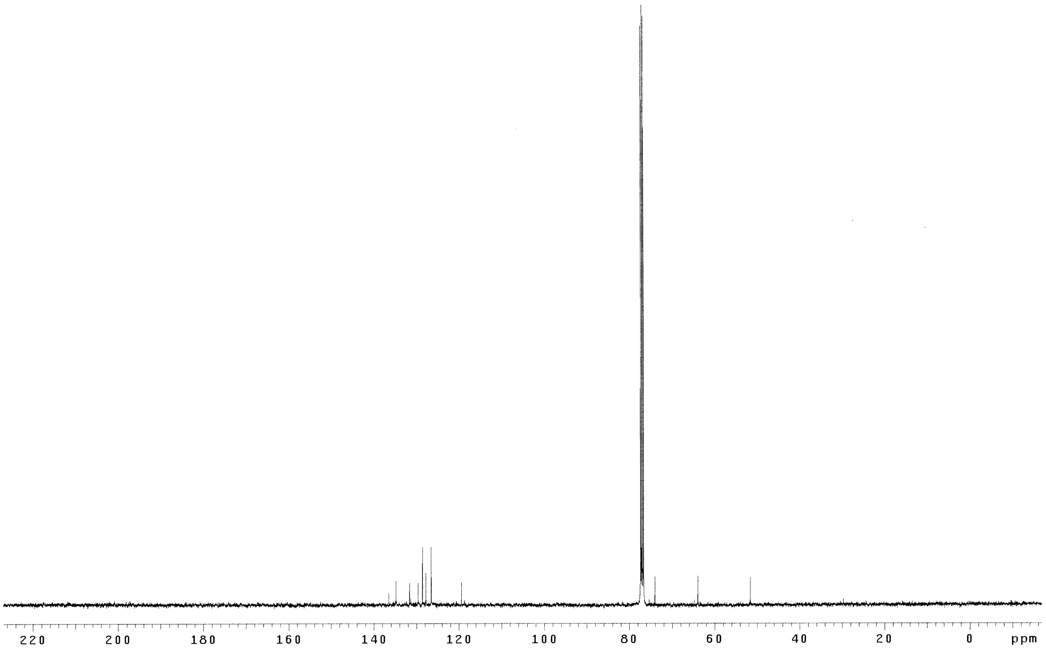
0 ppm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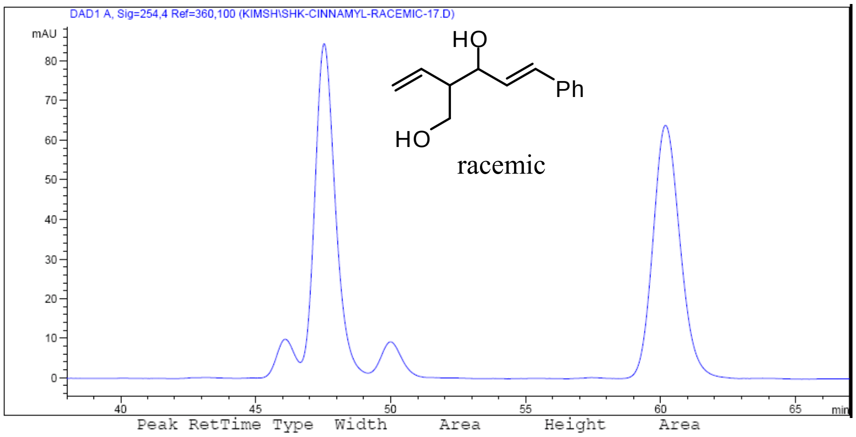

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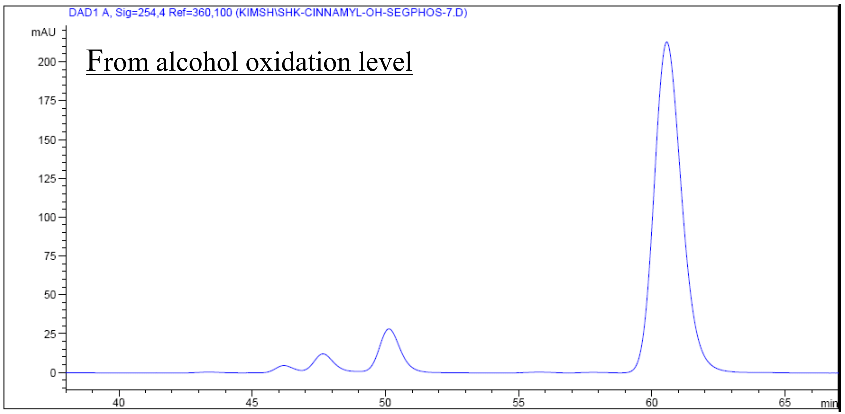
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  46.090 BV    0.6289  415.97379    9.38859   4.3546
   2  47.531 VB    0.7925 4356.57227   83.53457  45.6065
   3  49.984 BB    0.6551  412.03314    8.24414   4.3133
   4  60.176 BB    1.0442 4367.94775   63.52284  45.7256
```



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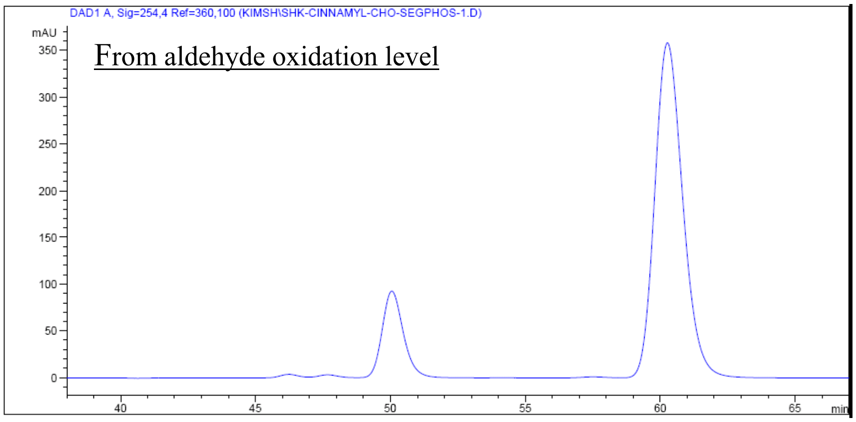
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  46.189 BV    0.5673  193.10158    4.27214   1.1027
   2  47.654 VB    0.7344  588.72607   11.55478   3.3620
   3  50.125 BB    0.8017 1486.36902   27.53917   8.4880
   4  60.555 BB    1.1054 1.52432e4   212.36853  87.0473
```



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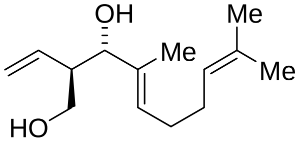
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  46.233 BB    0.5418  152.56747    3.35956   0.4949
   2  47.670 BB    0.5385  132.51459    2.94766   0.4299
   3  50.045 BB    0.8298 4946.44434   92.22185  16.0468
   4  60.261 BB    1.1148 2.55937e4   357.66116  83.0284
```

**(2*R*,3*S*,*E*)-4,9-Dimethyl-2-vinyldeca-4,8-diene-1,3-diol (4g)**



**4g**

In accordance with the general procedure, the product was isolated by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:2). The reaction from geraniol gave the title compound (27.7 mg, *anti*:*syn* = 10:1) as a colorless oil in 66% yield, and the reaction from (*E*)-3,7-dimethyl-2,6-octadienal gave the product (26.4 mg, *anti*:*syn* = 14:1) in 63% yield.

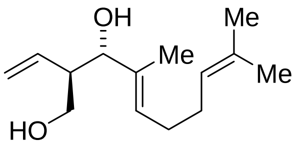
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 5.76 (ddd, *J* = 8.8, 10.4, 17.2 Hz, 1H), 5.21 – 5.28 (m, 3H), 5.06 (dt, *J* = 0.4, 6.4 Hz, 1H), 4.47 (dd, *J* = 5.6, 8.8 Hz, 1H), 3.75 (dd, *J* = 6.4, 10.8 Hz, 1H), 3.60 (dd, *J* = 6.4, 10.8 Hz, 1H), 2.37 – 2.41 (m, 1H), 2.02 – 2.11 (m, 6H), 1.68 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 140.0, 135.7, 131.9, 125.0, 123.8, 119.4, 69.3, 63.7, 52.5, 39.7, 26.3, 25.7, 17.7, 16.7.

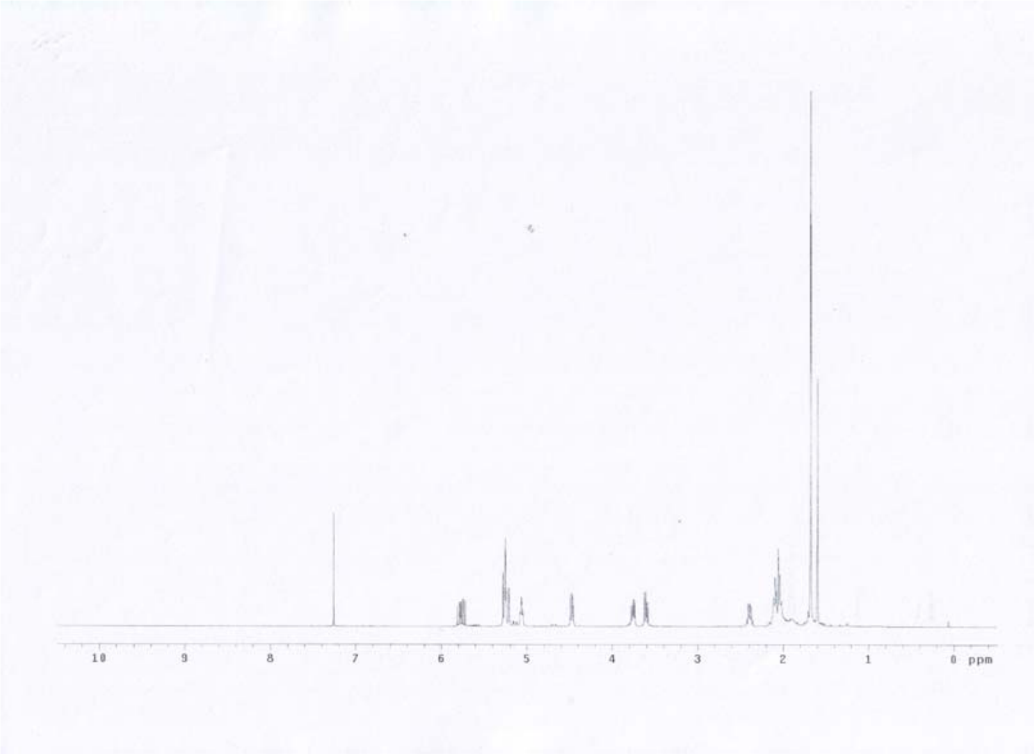
**HRMS** (ESI-MS): Calcd. for $C_{14}H_{24}O_{2+}Na$ (M+Na): 247.1674, Found: 247.1668.

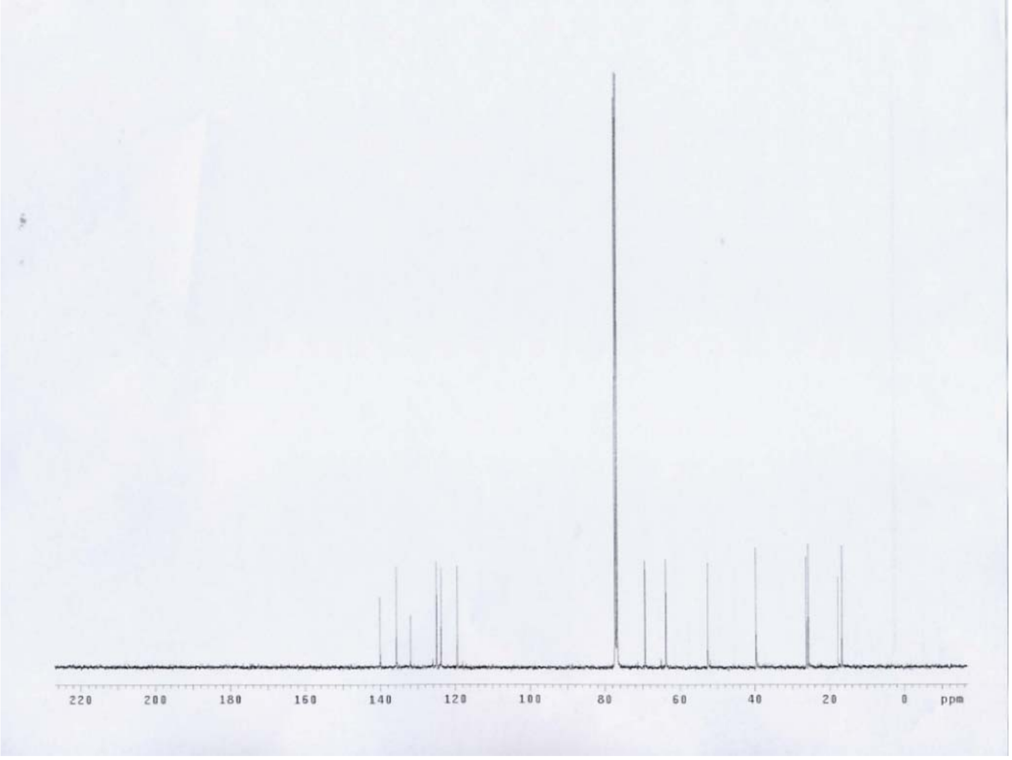
**FTIR** (neat): 3350, 2966, 2917, 1666, 1290, 915 cm$^{-1}$.

**HPLC** The enantioselectivity was determined by transformation of **4g** to corresponding dibenzoate. (connecting Chiralcel AD-H and OD-H column, hexanes:*i*-PrOH = 97:3, 0.5 mL/min, 210 nm), ee = 95% from geraniol, ee = 97% from geranial.


OH
Me
Me
Me
HO

**4g**


10
9
8
7
6
5
4
3
2
1
0 ppm


220
200
180
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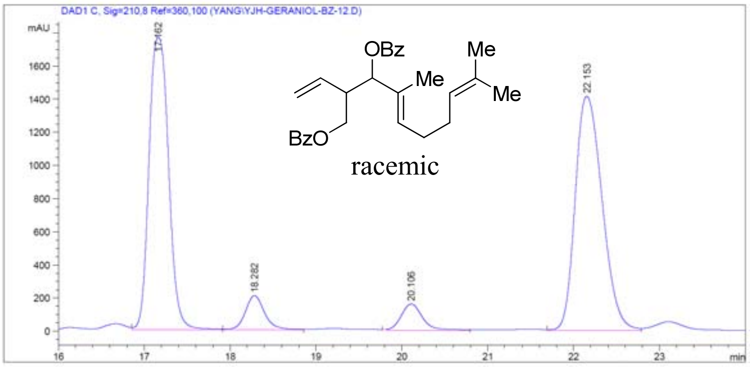
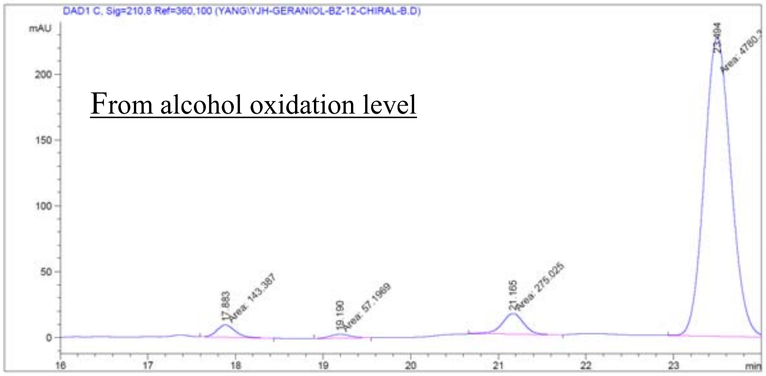
140
120
100
80
60
40
20
0
ppm



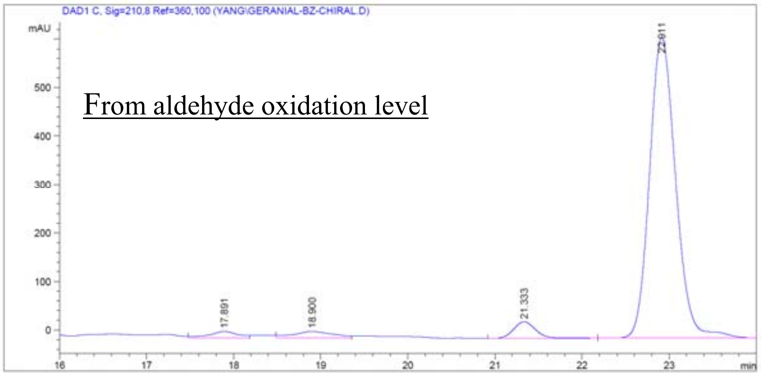
racemic

```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]   [mAU*s]     [mAU]        %
 ----|-------|----|-------|----------|----------|--------|
    1  17.162 VV    0.2535 2.81415e4  1769.80334  43.1889
    2  18.282 VV    0.2438 3367.86450  209.25429   5.1687
    3  20.106 VV    0.2676 2785.43359  159.60603   4.2748
    4  22.153 VV    0.3465 3.08643e4  1414.86780  47.3676
```



From alcohol oxidation level

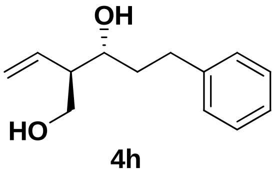
```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]   [mAU*s]     [mAU]        %
 ----|-------|----|-------|----------|----------|--------|
    1  17.883 MM    0.2510  143.38678    9.52284   2.7281
    2  19.190 MM    0.2938   57.19692    3.24419   1.0882
    3  21.165 MM    0.2899  275.02454   15.81079   5.2326
    4  23.494 MM    0.3506 4780.39160  227.21985  90.9511
```



From aldehyde oxidation level

```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]   [mAU*s]     [mAU]        %
 ----|-------|----|-------|----------|----------|--------|
    1  17.891 VV    0.3257  316.58041   13.69504   2.2016
    2  18.900 VV    0.4368  454.50034   14.22511   3.1608
    3  21.333 VV    0.2801  620.56354   34.13235   4.3156
    4  22.911 VB    0.3243 1.29877e4   620.21704  90.3219
```

**(2*R*,3*R*)-5-Phenyl-2-vinylpentane-1,3-diol (4h)**



**4h**

In accordance with the general procedure, the product was isolated by flash column chromatography ($SiO_2$: ethyl acetate:toluene, 1:3). The reaction from 3-phenylpropan-1-ol gave the title compound (27.6 mg, *anti*:*syn* = 9:1) as a colorless oil in 67% yield, and the reaction from 3-phenylpropanal gave the product (25 mg, *anti*:*syn* = 8:1) in 61% yield.

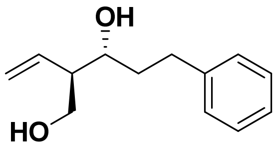
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 5.87 (ddd, *J* = 8.8, 10.0, 17.6 Hz, 1H), 5.28 (dd, *J* = 1.6, 10.0 Hz, 1H), 5.20 (ddd, *J* = 1.6, 1.6, 17.6 Hz, 1H), 3.86 – 3.75 (m, 3H), 2.85 – 2.77 (m, 1H), 2.71 – 2.63 (m, 1H), 2.35 – 2.32 (m, 1H), 2.03 (d, *J* = 4.8 Hz, 1H), 1.83 – 1.75 (m, 3H)

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 141.9, 134.6, 128.4, 128.4, 125.9, 119.3, 72.3, 64.8, 51.0, 36.7, 32.2

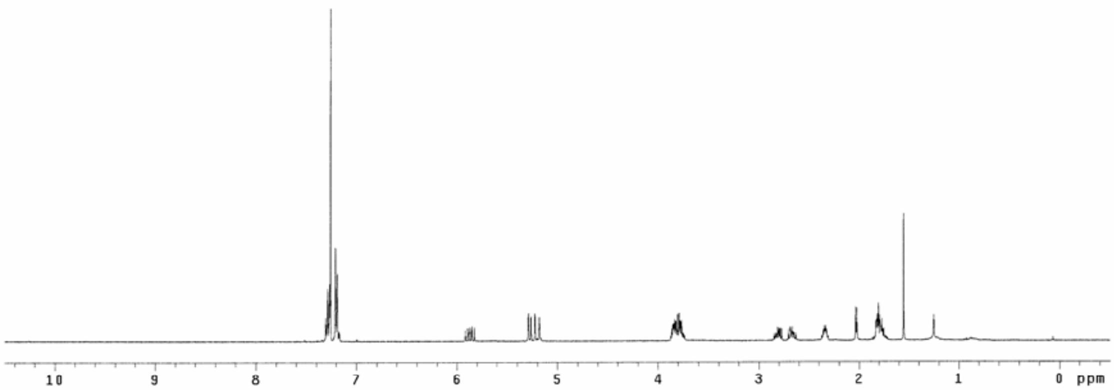
**HRMS** (CI): Calcd. for $C_{13}H_{19}O_2$ (M+H): 207.1385, Found: 207.1383

**FTIR** (neat): 3354, 2921, 1455, 1085, 1055, 1028, 919, 699 $cm^{-1}$

**HPLC** (Chiralcel OB-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 210 nm), ee = 97% from 3-phenylpropan-1-ol, ee = 99% from 3-phenylpropanal.


OH
HO

**4h**


10
9
8
7
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5
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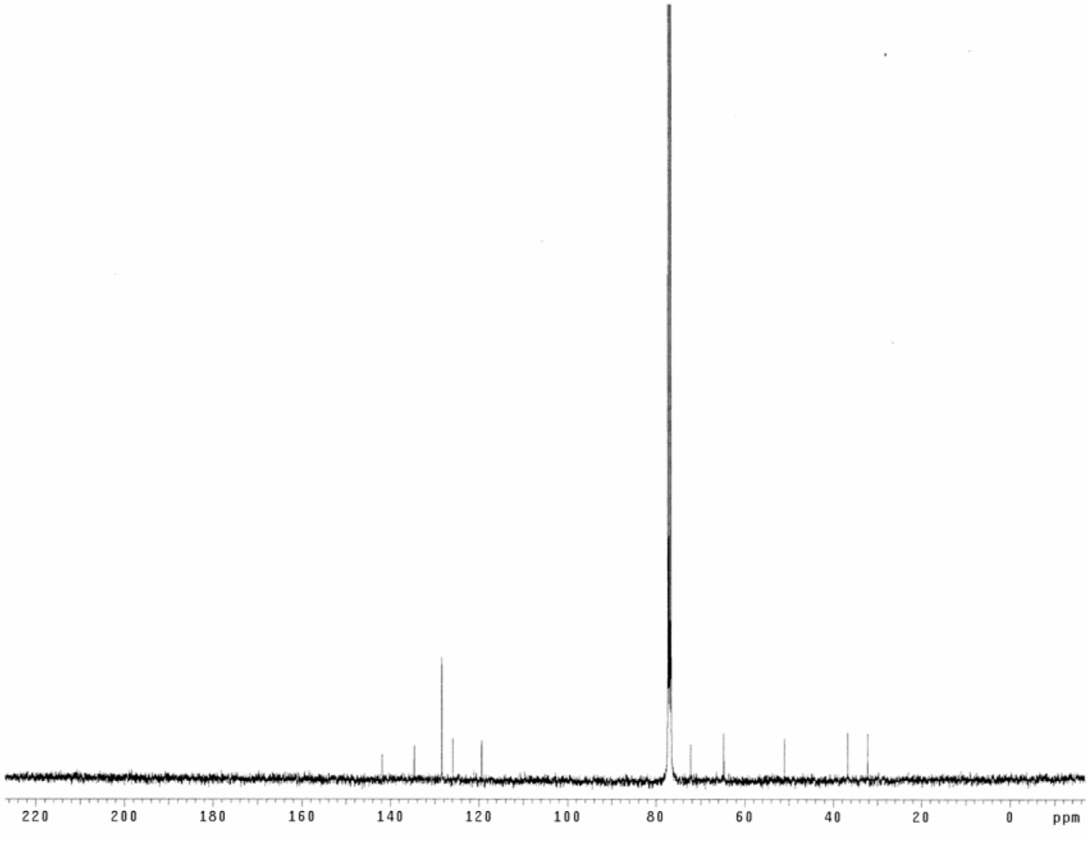
3
2
1
0
ppm


220
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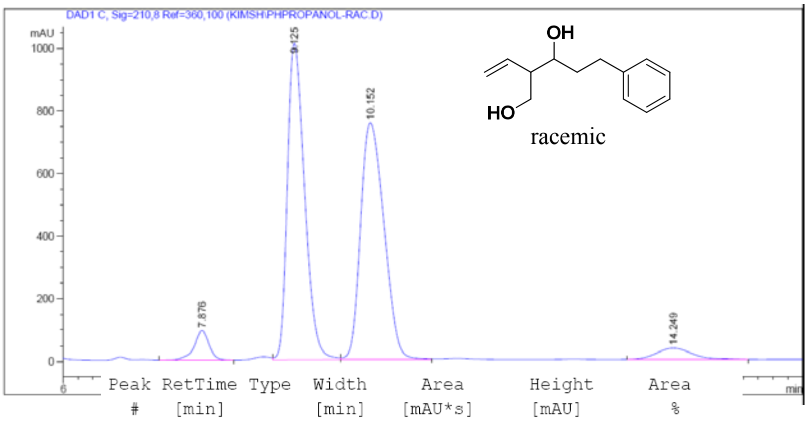
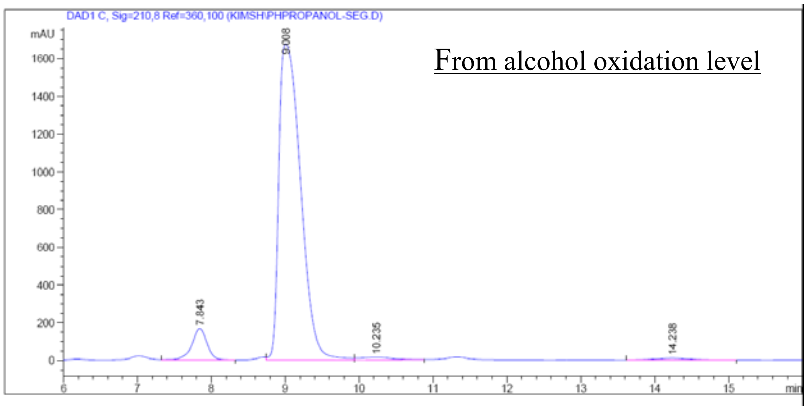
140
120
100
80
60
40
20
0
ppm



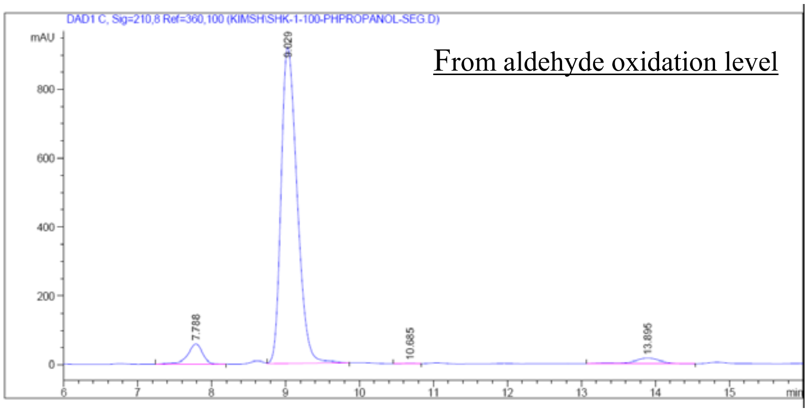
racemic

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.876 VB    0.2140 1348.08264   94.71818   3.7648
   2   9.125 VV    0.2511 1.64274e4  1013.42743  45.8776
   3  10.152 VB    0.3539 1.67562e4   758.10400  46.7958
   4  14.249 BB    0.5168 1275.37598   37.69189   3.5618
```



From alcohol oxidation level

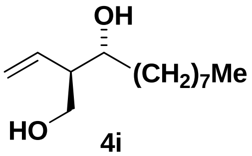
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.843 VB    0.2174 2450.70728  168.73413   6.5351
   2   9.008 VB    0.3265 3.42556e4  1675.72290  91.3465
   3  10.235 BV    0.4739  488.30756   14.91590   1.3021
   4  14.238 BB    0.4566  306.09937   10.07142   0.8162
```



From aldehyde oxidation level

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.788 BB    0.2123  839.03009   58.86872   5.5748
   2   9.029 VB    0.2332 1.37965e4   918.86267  91.6690
   3  10.685 BV    0.1819   14.71610    1.28252   0.0978
   4  13.895 BB    0.3773  400.10629   15.69943   2.6584
```

### **(2*R*,3*R*)-2-Vinylundecane-1,3-diol (4i)**



**4i**

In accordance with the general procedure, the product was isolated by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:3). The reaction from nonan-1-ol gave the title compound (25.7 mg, *anti*:*syn* = 9:1) as a colorless oil in 60% yield, and the reaction from nonanal gave the product (24.8 mg, *anti*:*syn* = 8:1) in 58% yield.

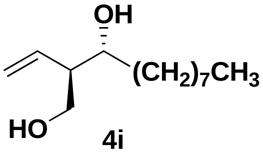
**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 5.87 (ddd, *J* = 8.8, 10.4, 17.6 Hz, 1H), 5.55 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.20 (dd, *J* = 1.6, 17.6 Hz, 1H), 3.85 – 3.72 (m, 3H), 2.35 – 2.29 (m, 1H), 1.93 (bs, 2H), 1.50 – 1.20 (m, 14H), 0.88 (t, *J* = 7.2 Hz).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 134.8, 119.1, 72.9, 64.9, 50.8, 35.0, 31.9, 29.6, 29.5, 29.3, 25.8, 22.7, 14.1

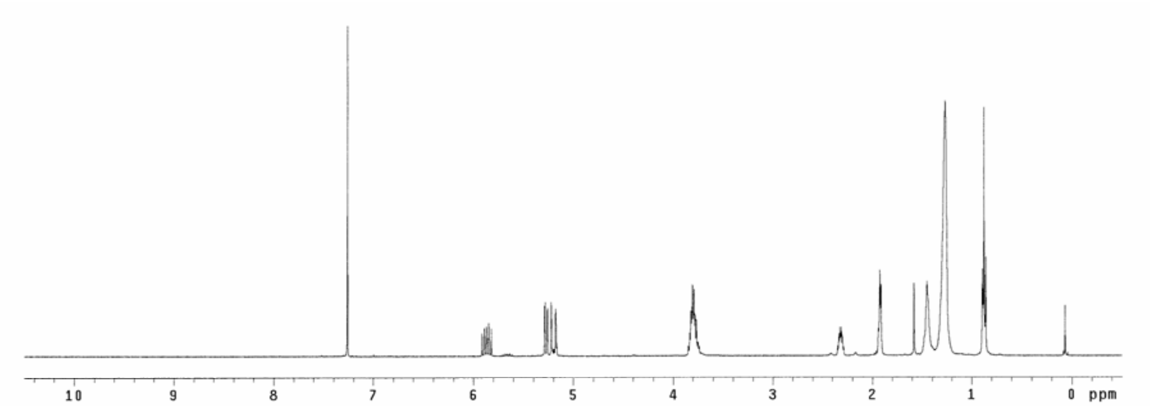
**HRMS** (CI): Calcd. for $C_{13}H_{27}O_2$ (M+H): 215.2011, Found: 215.2010.

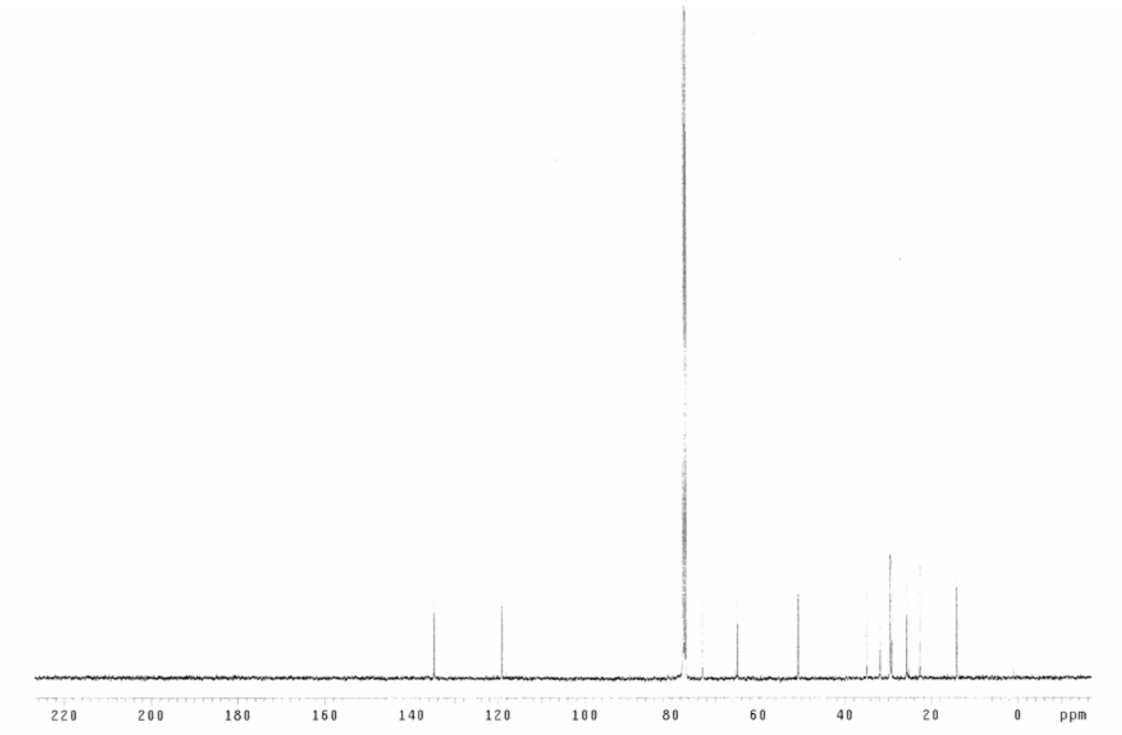
**FTIR** (neat): 3339, 2924, 2854, 1465, 1276, 1036, 916, 750 cm$^{-1}$.

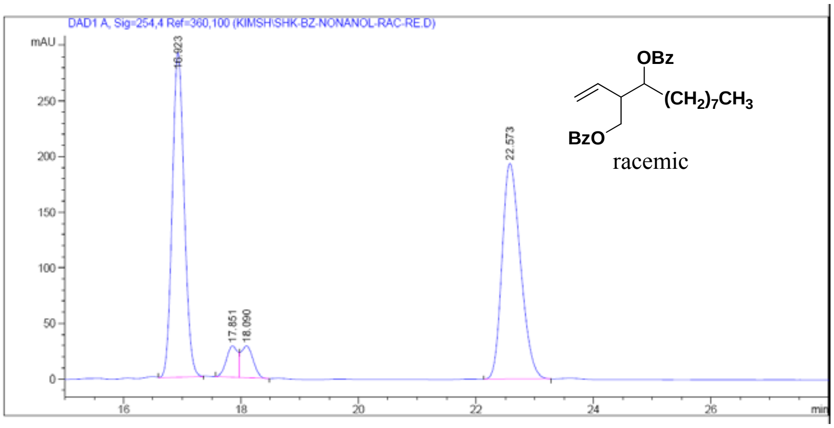
**HPLC** The enantioselectivity was determined by transformation of **4i** to corresponding dibenzoate. (Connecting Chiralcel AD-H column and OD-H column, hexanes:*i*-PrOH = 97:3, 0.5 mL/min, 254 nm), ee = 98% from nonan-1-ol, ee = 97% from nonanal.


OH
(CH2)7CH3
HO

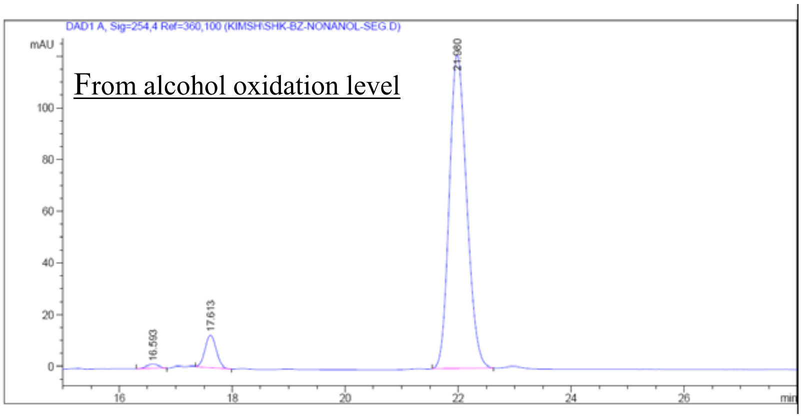
**4i**


10
9
8
7
6
5
4
3
2
1
0 ppm

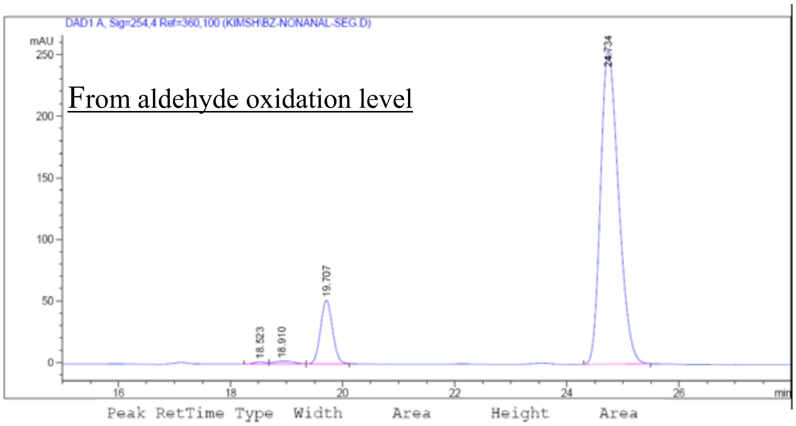

220
200
180
160
140
120
100
80
60
40
20
0
ppm



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  16.923 VB    0.2185 4123.70508  292.38681  45.0539
  2  17.851 BV    0.2038  377.12216   27.87433   4.1203
  3  18.090 VB    0.2181  409.87469   28.44050   4.4781
  4  22.573 BB    0.3389 4242.13232  194.16255  46.3477
```

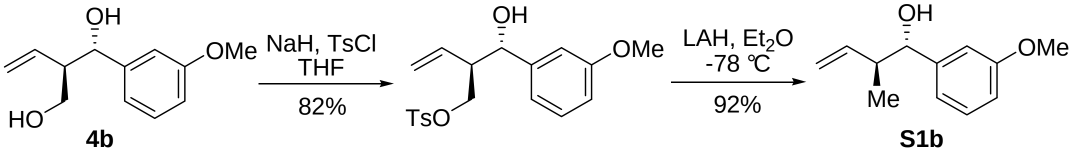


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  16.593 BV    0.2481   24.04416    1.55752   0.8611
  2  17.613 BB    0.2161  172.92590   12.59985   6.1932
  3  21.980 BB    0.3333 2595.21973  121.45881  92.9457
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  18.523 BV    0.2129   27.63643    1.97922   0.4220
  2  18.910 VV    0.3506   59.65333    2.28498   0.9109
  3  19.707 VB    0.2302  773.62268   51.82526  11.8138
  4  24.734 BB    0.3466 5687.56787  254.66058  86.8532
```

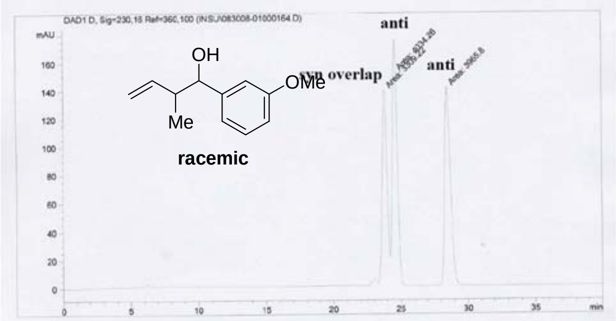
## Confirmation of the Absolute Configuration of (1*S*,2*R*)-1-(3-methoxyphenyl)-2-vinylpropane-1,3-diol (4b)



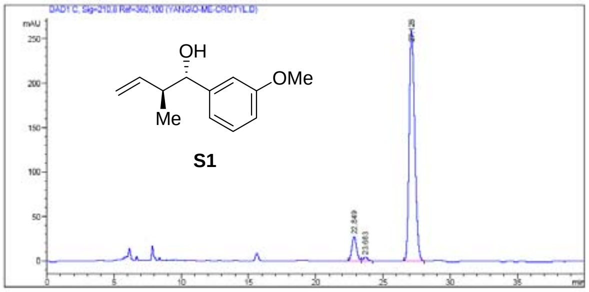
**Scheme S1**

The absolute configuration of **4b** was confirmed by transformation of **4b** to corresponding crotylated compound **S1b**. The mono-tosylation of primary alcohol of **4b** in the presence of NaH with *p*-toluenesulfonyl chloride in THF followed by reduction with LAH in diethyl ether furnished **S1b** in 75% overall yield (Scheme S1).[3] The (1*S*,2*R*) configuration of compound **4b** was deduced by chiral HPLC analysis in comparison with our previous report.[4]

**<u>HPLC</u>** (Chiralcel AD-H column, hexane:*i*-PrOH = 96:4, 0.5 mL/min, 210 nm), ee = 97%.



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.834 MM    0.4056 3309.22461  135.98813  29.2611
   2  24.613 MM    0.3870 4034.26050  173.73439  35.6721
   3  28.466 MM    0.4754 3965.80420  139.04333  35.0668
```



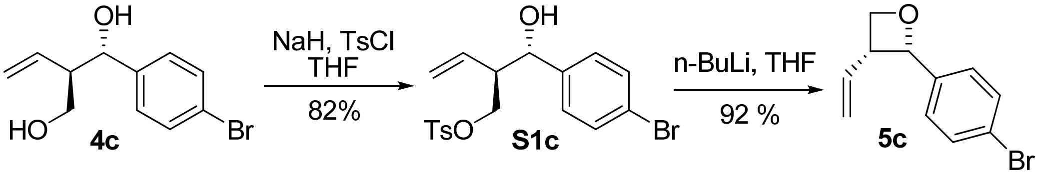
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  22.849 BV    0.3708  667.38037   27.53378   8.0741
   2  23.683 VB    0.3529   98.37540    4.20512   1.1902
   3  27.126 BB    0.4492 7499.97559  259.48309  90.7358
```

---

[3] Roush, W. R.; Bannister, T. D.; Wendt, M. D.; Jablonowski, J. A.; Schedit, K. A. *J. Org. Chem.* **2002**, *67*, 4275

[4] Kim, I. S.; Han, S. B.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 2514

**Synthesis of 2-(4-bromophenyl)-3-vinyloxetane (5c)**



**(4-Bromophenyl)(hydroxy)methyl)but-3-enyl 4-methylbenzenesulfonate (S2c).** To a suspension of NaH (14.4 mg of 60% dispersion in mineral oil, 0.36 mmol, 200 mol%) in THF (1.0 mL) was added dropwise a solution of **4c** (40.6 mg, 0.18 mmol, 100 mol%) in THF (0.2 mL, 0.15 M) at 0 ºC. The mixture was stirred for 30 min at ambient temperature and then *p*-toluenesulfonyl chloride (37.6 mg, 0.19 mmol, 105 mol%) was added. The reaction mixture was stirred at ambient temperature for 2 hr, at which point the reaction was quenched with water and extracted with diethyl ether (2 mL ×3). The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The obtained residue was purified by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:3) to furnish **S2c** (59.8 mg, 82%) as a colorless oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.67 (ddd, *J* = 8.4, 10.4, 17.2 Hz, 1H), 5.18 (dd, *J* = 0.8, 10.4 Hz, 1H), 5.03 (dd, *J* = 0.4, 17.2 Hz, 1H), 4.81 (t, *J* = 4.4 Hz, 1H), 4.15 (dd, *J* = 7.2, 10.0 Hz, 1H), 3.87 (dd, *J* = 5.2, 9.6 Hz, 1H), 2.61 (m, 1H), 2.47 (s, 3H), 2.16 (dd, *J* = 10.4 Hz, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 145.1, 140.5, 132.6, 132.1, 131.4, 129.9, 128.0, 127.9, 121.5, 120.8, 71.4, 70.0, 50.7, 21.7.

**HRMS** (CI): Calcd. for $C_{18}H_{18}BrO_2S$ (M-H): 409.0109, Found: 409.0107.

**FTIR** (neat): 3535, 2922, 1355, 1172 cm$^{-1}$.

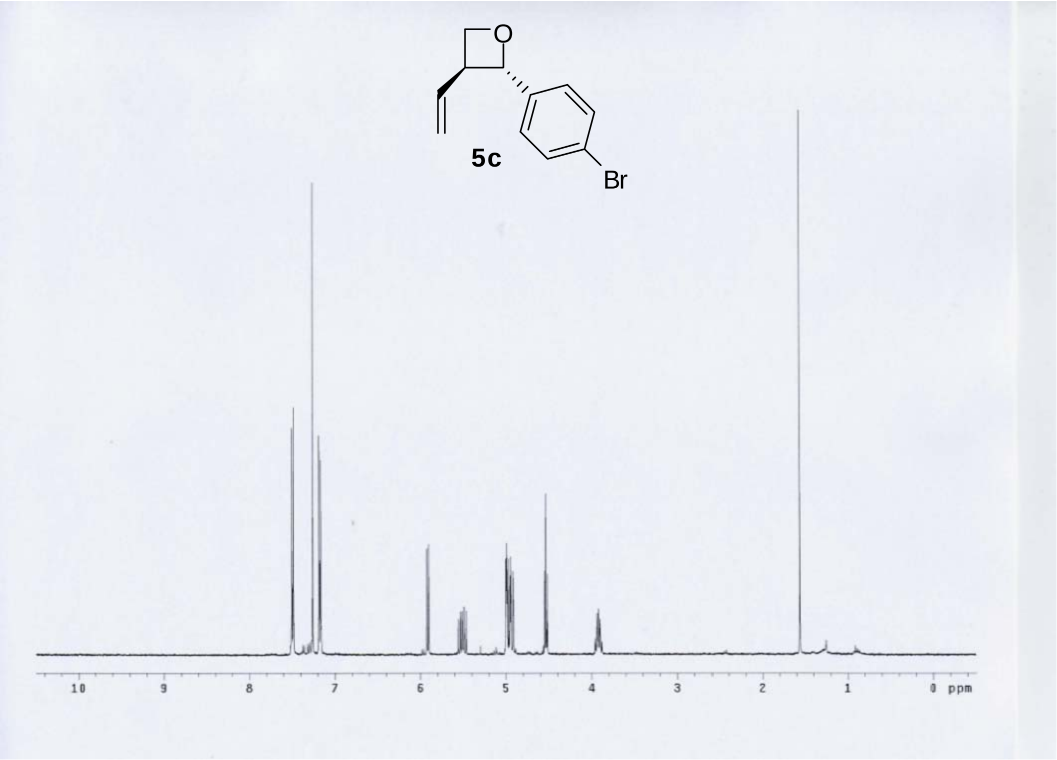
**2-(4-Bromophenyl)-3-vinyloxetane (5c).** To a solution of **S2c** (59.8 mg, 0.15 mmol, 100 mol%) in THF (1.5 mL, 0.1 M) was added dropwise *n*-BuLi (75.0 µL of 2.0 M solution in THF, 0.15 mmol, 100 mol%) at 0 ºC. The mixture was stirred for 30 min at ambient temperature and refluxed for 8 hr, at which point the reaction was allowed to cool to 0 ºC, quenched with water, and extracted with diethyl ether (2 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The obtained residue was purified by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:10) to furnish **5c** (32.5 mg, 92%) as a colorless oil.

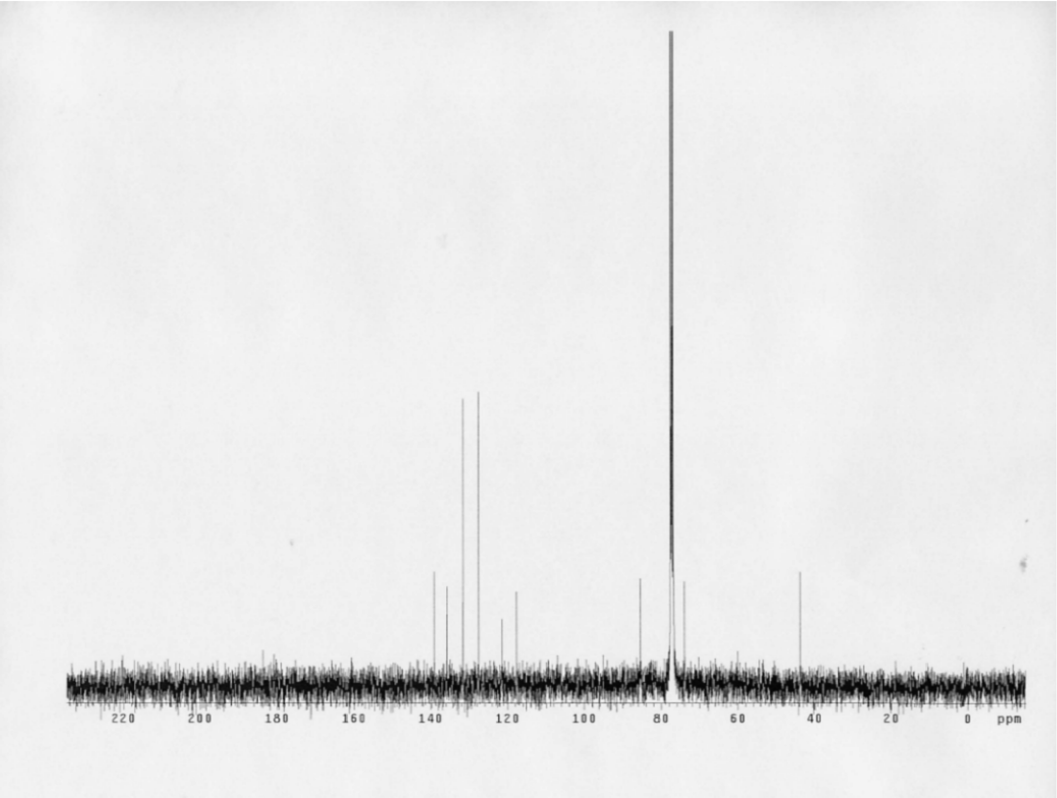
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.91 (d, *J* = 8.4 Hz, 1H), 5.51 (ddd, *J* = 8.8, 10.0, 12.8 Hz, 1H), 4.91 – 5.00 (m, 3H), 4.54 (t, *J* = 8.4 Hz, 1H), 3.92 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 139.1, 135.7, 131.6, 127.5, 121.5, 117.6, 85.4, 73.9, 43.7.

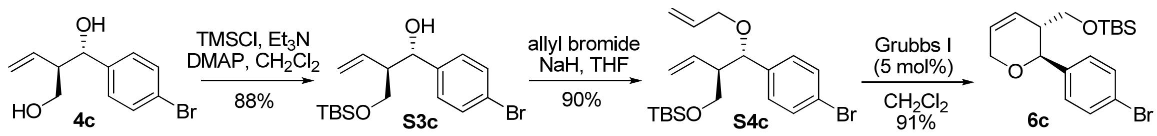
**HRMS** (CI): Calcd. for $C_{11}H_{12}BrO$ (M+H): 239.0072, Found: 239.0065.

**FTIR** (neat): 2857, 1485, 988, 920 $cm^{-1}$.


O
5c
Br
10
9
8
7
6
5
4
3
2
1
0 ppm


220
200
180
160
140
120
100
80
60
40
20
0 ppm

**Synthesis of 2-(4-bromophenyl)-3-(*tert*-butyldimethylsilyloxy)methyl-3,6-dihydro-2H-pyran-3-yl (6c)**



**1-(4-Bromophenyl)-2-(*tert*-butyldimethylsilyloxy)methyl-3-buten-1-ol (S3c).** To a solution of **4c** (40.0 mg, 0.16 mmol, 100 mol%), triethylamine (26.4 µL, 0.19 mmol, 120 mol), and DMAP (2.0 mg, 0.02 mmol, 10 mol%) in $CH_2Cl_2$ (1 mL, 0.16 M) was added TBSCl (29.0 mg, 0.19 mmol, 120 mol%) at 0 °C. The reaction mixture was stirred overnight at ambient temperature, and then quenched with saturated aqueous $NaHCO_3$ (1 mL), and extracted with $CH_2Cl_2$ (1 mL × 3). The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The obtained residue was purified by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:10) to furnish **S3c** (52 mg, 88%) as a colorless oil.

**$^1$H NMR** (400 MHz, $CDCl_3$): 7.45 (d, $J$ = 8.4 Hz, 2H), 7.21 (d, $J$ = 8.4 Hz, 2H), 5.82 (ddd, $J$ = 8.8, 10.4, 17.6 Hz, 1H), 5.15 (dd, $J$ = 2.0, 10.4 Hz, 1H), 5.01 (ddd, $J$ = 1.2, 2.0, 17.6 Hz, 1H), 4.94 (dd, $J$ = 3.6, 3.6 Hz, 1H), 3.76 – 3.69 (m, 2H), 3.43 (d, $J$ = 3.6 Hz, 1H), 2.52 – 2.41 (m, 1H), 0.93 (s, 9H), 0.07 (s, 6H)

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 141.5, 134.5, 131.0, 128.2, 120.9, 118.7, 74.8, 65.4, 52.4, 25.8, 18.2, -5.6

**HRMS** (CI): Calcd. for $C_{17}H_{26}BrO_2Si$ (M-H): 369.0885, Found: 369.0889

**FTIR** (neat): 3446, 2954, 1640, 1487, 1255, 1084, 834, 777 cm$^{-1}$

**(2-(Allyloxy(4-bromophenyl)methyl)but-3-enyloxy)(*tert*-butyl)dimethylsilane (S4c).** To a suspension of NaH (8.0 mg of 60% dispersion in mineral oil, 0.20 mmol, 150 mol%) in THF (1 mL) was added dropwise a solution of **S3c** (50 mg, 0.13 mmol, 100 mol%) in THF (0.3 mL) at 0 ºC. The mixture was stirred for 30 min at ambient temperature and then allyl bromide (17.3 µL, 0.20 mL, 150 mol%) was added dropwise at 0 ºC. The reaction mixture was refluxed for 8 hr, at which point the reaction was allowed to cool to 0 ºC, and quenched with water and extracted with diethyl ether (1 mL ×3). The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The obtained residue was purified by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:50) to furnish **S4c** (48.0 mg, 90%) as a colorless oil.

**$^1$H NMR** (400 MHz, $CDCl_3$): 7.44 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.92 – 5.77 (m, 2H), 5.22 (ddd, *J* = 1.6, 3.6, 17.2 Hz, 1H), 5.13 (ddd, *J* = 1.6, 3.6, 10.4 Hz, 1H), 5.05 (dd, *J* = 2.0, 10.4 Hz, 1H), 4.89 (ddd, *J* = 0.8, 2.0, 17.6 Hz, 1H), 4.61 (d, *J* = 4.8 Hz, 1H), 3.95 – 3.90 (m, 1H), 3.77 – 3.71 (m, 1H) 3.71 (dd, *J* = 7.2, 10.0 Hz, 1H), 3.43 (dd, *J* = 5.2, 10.0 Hz, 1H), 2.38 – 2.31 (m, 1H), 0.91 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H)

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 140.4, 135.2, 134.9, 131.1, 128.9, 120.9, 117.9, 116.5, 79.1, 70.0, 63.5, 53.9, 25.9, 18.3, -5.4, -5.5

**HRMS** (CI): Calcd. for $C_{20}H_{30}BrO_2Si$ (M-H): 409.1198, Found: 409.1208

**FTIR** (neat): 3078, 2954, 1487, 1255, 1090, 836, 776 $cm^{-1}$

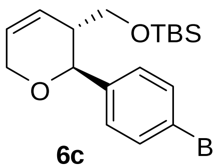
**2-(4-bromophenyl)-3-(*tert*-butyldimethylsilyloxy)methyl-3,6-dihydro-2H-pyran-3-yl (6c).** A solution of **S4c** (45 mg, 0.11 mmol, 100 mol%) and Grubbs I (4.5 mg, 5.5 µmol, 5 mol%) in $CH_2Cl_2$ (1.1 mL, 0.1 M) was stirred at ambient temperature for 8 hr, at which point the reaction solvent was removed *in vacuo*. The obtained residue was purified by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:30) to furnish **6c** (38.4 mg, 91%) as a colorless oil.

**$^1$H NMR** (400 MHz, $CDCl_3$): 7.48 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 5.91 – 5.84 (m, 2H), 4.38 (d, *J* = 8.4 Hz, 1H), 4.25 – 4.23 (m, 2H), 3.49 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.36 (dd, *J* = 5.6, 10.0 Hz, 1H), 2.42 – 2.49 (m, 1H), 0.86 (s, 9H), -0.02 (s, 3H), -0.02 (s, 3H)

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 140.0, 131.4, 129.0, 127.1, 126.9, 121.7, 77.2, 65.7, 63.0, 43.6, 25.8, 18.2, -5.5

**HRMS** (CI): Calcd. for $C_{18}H_{28}BrO_2Si$ (M+H): 383.1042, Found: 383.1043

**FTIR** (neat): 2953, 1651, 1471, 1252, 1072, 833, 775 cm$^{-1}$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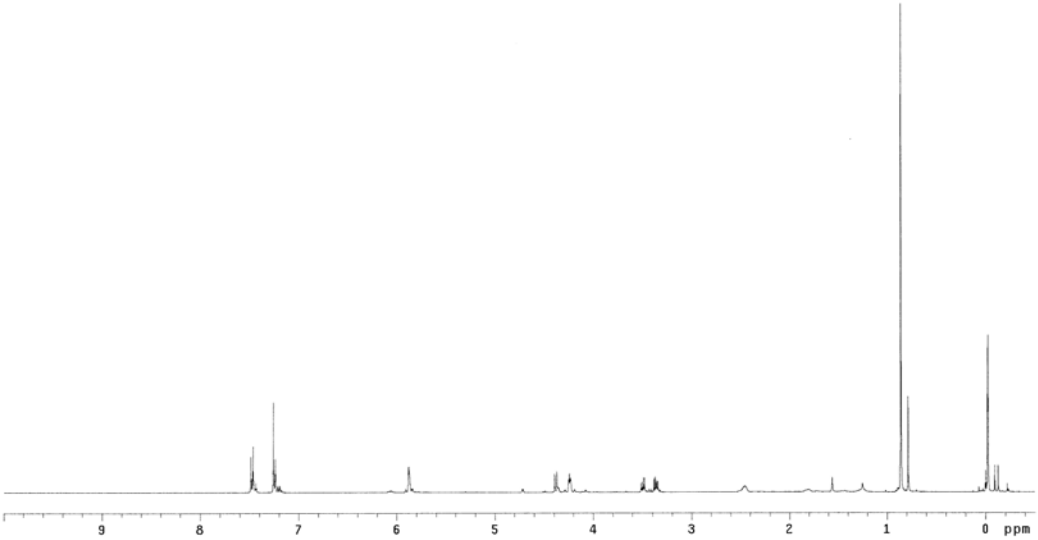
O
Br

**6c**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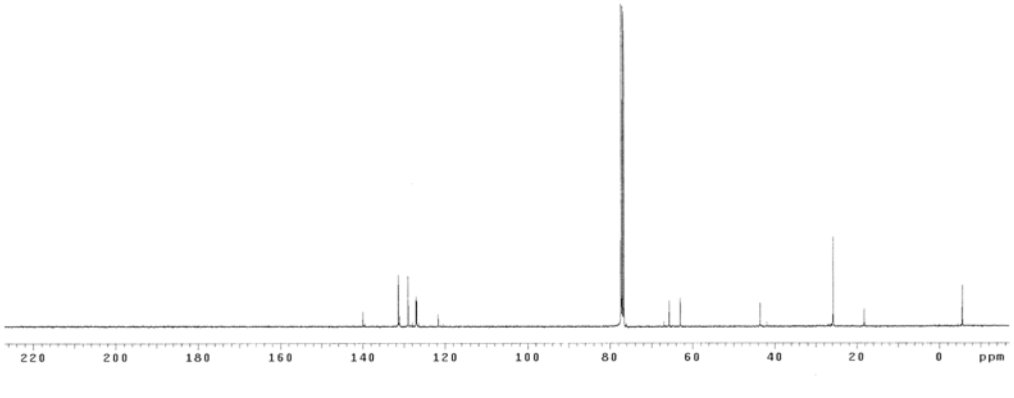
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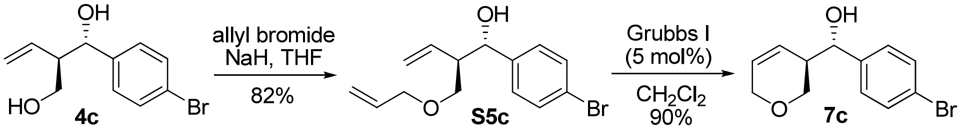
## Synthesis of (4-bromophenyl)(3,6-dihydro-2H-pyran-3-yl)methanol (7c)



**2-(Allyloxymethyl)-1-(4-bromophenyl)but-3-en-1-ol (S5c).** To a suspension of NaH (14.6 mg of 60% dispersion in mineral oil, 0.36 mmol, 200 mol%) in THF (1.2 mL) was added dropwise a solution of **4c** (47.0 mg, 0.18 mmol, 100 mol%) in THF (0.6 mL, 0.1 M) at 0 ºC. The mixture was stirred for 30 min at ambient temperature and then allyl bromide (17.3 µL, 0.20 mmol, 110 mol%) was added dropwise at 0 ºC. The reaction mixture was stirred for 4 hr at ambient temperature, at which point the reaction was quenched with water and extracted with diethyl ether (1 mL ×3). The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The obtained residue was purified by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:3) to furnish **S5c** (44.3 mg, 82%) as a colorless oil.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.86 (m, 1H), 5.74 (ddd , *J* = 8.8, 10.0, 17.2 Hz, 1H), 5.13 – 5.25 (m, 3H), 5.01 (dd, *J* = 1.2, 17.6 Hz, 1H), 4.52 (d, *J* = 5.2 Hz, 1H), 3.65 – 3.76 (m, 2H), 3.56 (m, 1H), 2.55 (m, 1H), 2.01 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 138.8, 134.8, 134.3, 131.4, 128.9, 121.5, 118.9, 117.2, 81.4, 69.8, 63.5, 52.8.

**HRMS** (CI): Calcd. for $C_{14}H_{18}BrO_2$ (M+H): 297.0490, Found: 297.0497

**FTIR** (neat): 3398, 3077, 2923, 1486, 1070, 1010, 919 cm$^{-1}$.

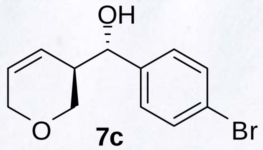
**(4-Bromophenyl)(3,6-dihydro-2H-pyran-3-yl)methanol (7c).** A solution of **S5c** (44.3 mg, 0.15 mmol, 100 mol%) and Grubbs I (6.2 mg, 7.5 μmol, 5 mol%) in $CH_2Cl_2$ (1.5 mL, 0.1 M) was stirred at ambient temperature for 8 hr, at which point the reaction solvent was removed *in vacuo*. The obtained residue was purified by flash column chromatography ($SiO_2$: ethyl acetate:hexanes, 1:3) to furnish **7c** (36.4 mg, 90%) as a colorless oil.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.99 (ddd, *J* = 2.4, 2.4, 10.0 Hz, 1H), 5.91 (ddd, *J* = 2.0, 2.0, 10.0 Hz, 1H), 4.50 (d, *J* = 8.4, 1H), 4.27 (m, 2H), 3.62 (m, 1H), 3.45 (m, 1H), 2.51 (m, 1H), 1.26 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 139.7, 131.6, 129.0, 128.7, 126.0, 121.9, 77.2, 65.6, 62.9, 43.6.

**HRMS** (CI): Calcd. for $C_{12}H_{14}BrO_2$ (M+H): 269.0177, Found: 269.0178.

**FTIR** (neat): 3396, 2927, 2881, 1489, 1024, 1011, 818 $cm^{-1}$.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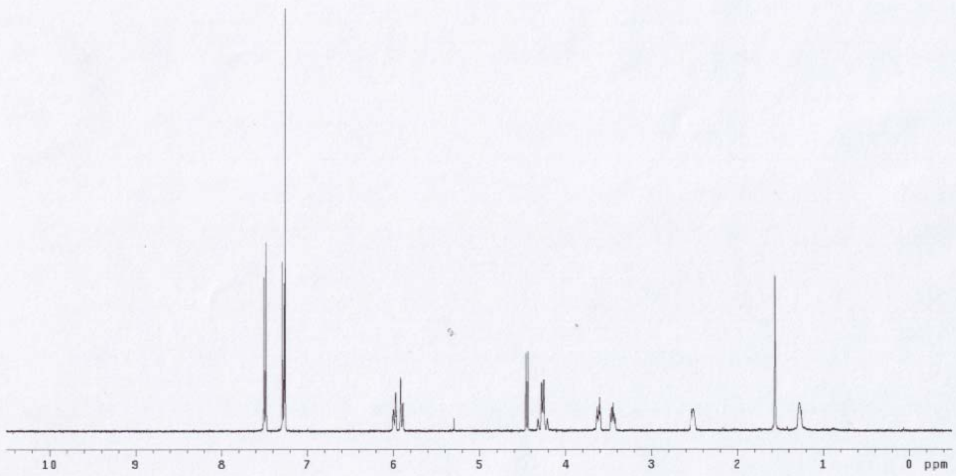
O
Br

**7c**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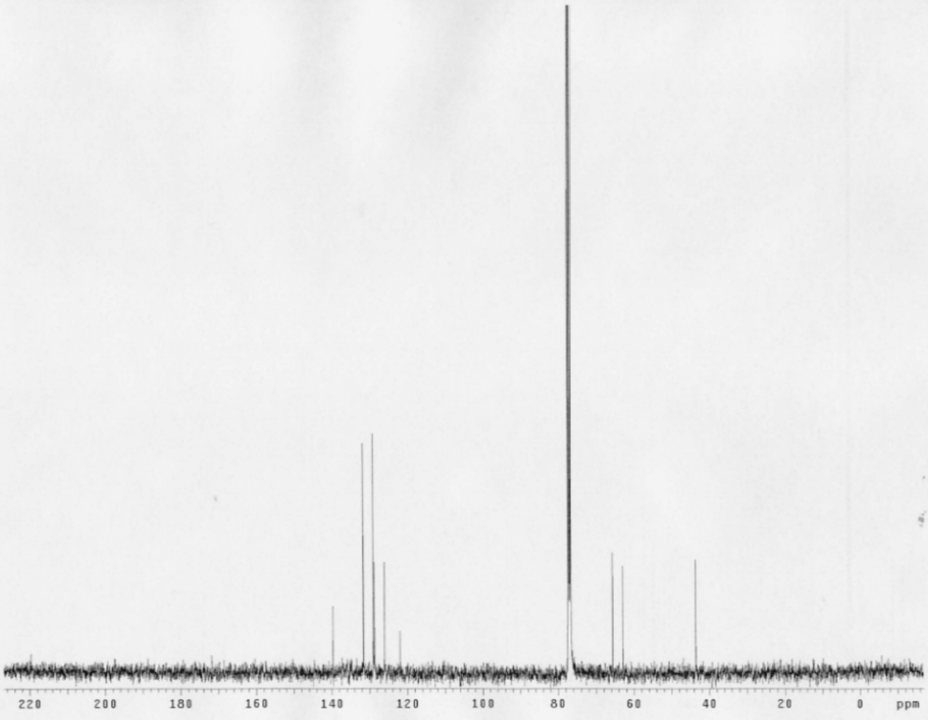
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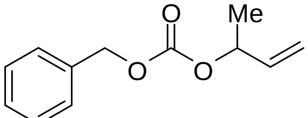
**Preparation of Benzyl But-3-en-2-yl Carbonate (1c)**



**1c**

To a solution of but-3-en-2-ol (2.0 g, 28.0 mmol, 100 mol%) and pyridine (2.2 mL, 28.0 mmol, 100 mol%) in diethyl ether (28.0 mL, 1.0 M) was added dropwise benzyl carbonochloridate (4.8 g, 28.0 mmol, 100 mol%) at 0 °C. The reaction mixture was stirred overnight at ambient temperature, at which point the reaction was quenched with saturated aqueous $NH_4Cl$ (20.0 mL) and extracted with diethyl ether (20.0 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo.* The obtained residue was purified by flash column chromatography ($SiO_2$; ethyl acetate:hexanes, 1:20) to furnish **1c** (5.2 g, 91%) as a colorless oil.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.41 – 7.31 (m, 5H), 5.87 (ddd, *J* = 6.0, 10.4, 17.2 Hz, 1H), 5.30 (ddd, *J* = 1.2, 1.2, 17.2 Hz, 1H), 5.25 – 5.16 (m, 4H), 1.38 (d, *J* = 6.4 Hz, 3H)

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 154.4, 137.0, 135.3, 128.5, 128.5, 128.3, 116.6, 75.3, 69.4, 20.0

**HRMS** (CI) Calcd. for $C_{12}H_{15}O_3$ $[M+H]^+$: 207.1021, Found: 207.1021

**FTIR** (neat): 2984, 1738, 1455, 1246, 1040, 789, 696 $cm^{-1}$

**<u>The Procedure</u> for Intramolecular Decarboxylative C-C Bond Forming Transfor Hydrogenation of 1b:** To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar was added (*S*)-BIPHEP-I (9.5 mg, 0.01 mmol, 5 mol%). The tube was evacuated and backfilled with nitrogen (3 times). **1b** (38.4 mg, 0.2 mmol, 100 mol%) and THF (0.2 mL, 1.0 M concentration with respect to **1b**) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 70 °C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$, ethyl acetate:hexanes, 1:10) to furnish desired product (8.9 mg, 30%) as a colorless oil.

**<u>The Procedure</u> for Intramolecular decarboxylative C-C Bond Forming Transfor Hydrogenation of 1c:** To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar was added (*S*)-BIPHEP-I (9.5 mg, 0.01 mmol, 5 mol%). The tube was evacuated and backfilled with nitrogen (3 times). **1c** (41.2 mg, 0.2 mmol, 100 mol%) and THF (0.2 mL, 1.0 M concentration with respect to **1c**) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 50 °C (oil bath temperature) for 48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$, ethyl acetate:hexanes, 1:10) to furnish desired product (13.6 mg, 42%, *anti*:*syn*, 5:1) as a colorless oil.