Supporting Information

Enantioselective Carbonyl Reverse Prenylation from the Alcohol or Aldehyde Oxidation Level Employing 1,1-Dimethylallene as the Prenyl Donor

Soo Bong Han, In Su Kim, Hoon Han and Michael J. Krische*

University of Texas at Austin, Department of Chemistry and Biochemistry,
Austin, TX 78712, USA

Table of Contents

General Experimental Methods -- S2

Procedure for the Preparation of (*S*)-Ir-Complex I ---------------------------- S3

Procedure for the Enantioselective Reverse Prenylation of Aldehydes 2a-2i and Spectral Data for Adducts 4a-4i -- S4–S30

Procedure for the Enantioselective Reverse Prenylation of Alcohols 3a-3i and Spectral Data for Adducts 4a-4i --S31–S48

Procedures for Mechanistic Studies ------------------------------------ S49–S54

General Methods

All reactions were run under an atmosphere of nitrogen. Tetrahydrofuran (THF) and toluene were obtained from Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Anhydrous solvents were transferred by an oven-dried syringe. Sealed tubes (13x100 mm^2) were purchased from Fischer Scientific and were dried in an oven overnight and cooled under a stream of nitrogen prior to use. Commercially available alcohols and aldehydes were purified by distillation or recrystallisation prior to use. Cesium carbonate was purchased from Alfa Aesar and was used directly without further purification. Isopropanol (Fisher) was purified by distillation prior to use. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F_{254}). 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 or M-H) or a suitable fragment ion. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) spectra were recorded with a Varian Gemini (400 MHz) spectrometer for $CDCl_3$ solutions and chemical shifts are reported as parts per million (ppm) relative to residual $CHCl_3$ δ_H (7.26 ppm) and $CDCl_3$ δ_C (77.0 ppm), respectively, as internal standards. Coupling constants are reported in Hertz (Hz).

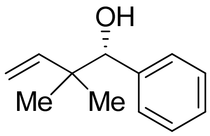
Preparation of (*S*)-Ir-Complex I

To a mixture of $[Ir(cod)Cl]_2$ (100 mg, 0.15 mmol, 100 mol%), (*S*)-SEGPHOS (183 mg, 0.3 mmol, 200 mol%), Cs_2CO_3 (195 mg, 0.6 mmol, 400 mol%) and *m*-nitrobenzoic acid (100 mg, 0.6 mmol, 400 mol%) in a sealed tube under N_2 atmosphere was added THF (3 mL, 0.05 M). The reaction mixture was heated at 80 ^{o}C for 30 min and was then allowed to cool to ambient temperature. Allyl acetate (75 mg, 0.75 mmol, 500 mol%) was added and the reaction mixture was allowed to stir for an additional 90 min at 80 ºC, at which point the reaction mixture was allowed to cool to the ambient temperature. The reaction mixture was filtered and washed with THF (15 mL) until all yellow residue was dissolved. 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 (233 mg, 0.231 mmol, 77% yield).

The yellow solid was dissolved in THF and diethyl ether was allowed to diffuse into the THF solution at the ambient temperature, resulting in the formation of crystals. Single crystal X-ray diffraction data for (*S*)-Ir-Complex I has been deposited in the CCDB.

Detailed Procedure and Spectral Data for Enantioselective Carbonyl Reverse Prenylation from Aldehydes (4a-4i)

(*S*)-2,2-Dimethyl-1-phenylbut-3-en-1-ol (4a)



4a

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). Benzaldehyde **2a** (53 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and isopropanol (60 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 40 ^{o}C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:50) provides **4a** (83 mg, 0.471 mmol) as a colorless oil in 94% yield.

TLC (SiO_2): R_f = 0.26 (ethyl acetate:hexanes, 1:20).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.23 (m, 5H), 5.90 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 5.06 (d, *J* = 17.6 Hz, 1H), 4.39 (s, 1H), 2.10 (s, 1H), 1.00 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 140.7, 127.7, 127.4, 127.3, 113.8, 80.5, 42.2, 24.4, 21.0.

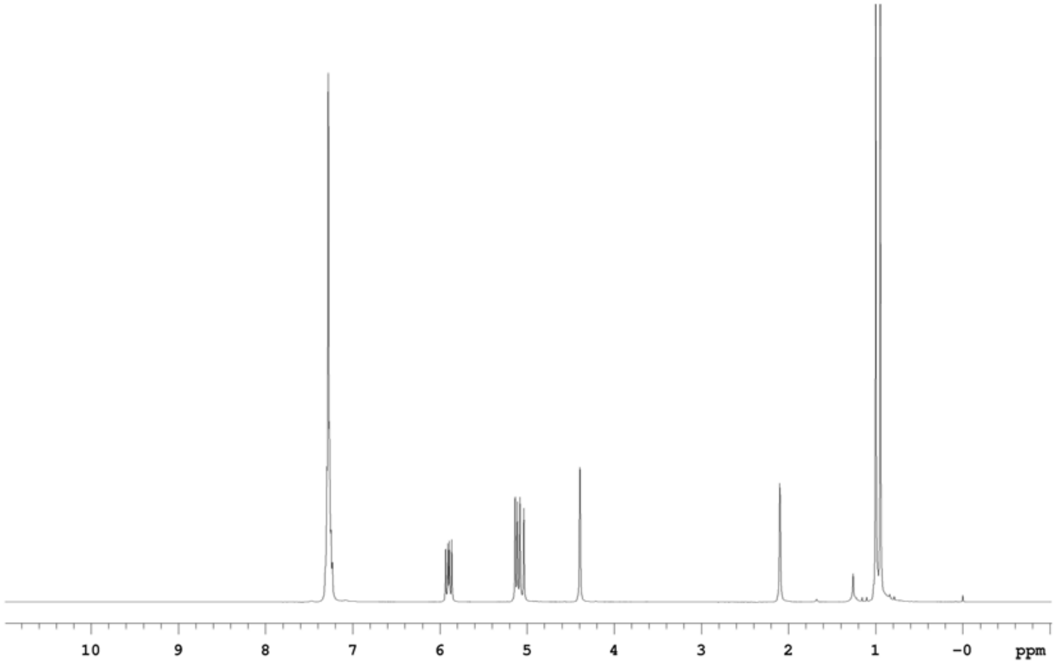
HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1 mL/min, 210 nm), t_{minor} = 9.1 min, t_{major} = 11.4 min; ee = 89%.[1]

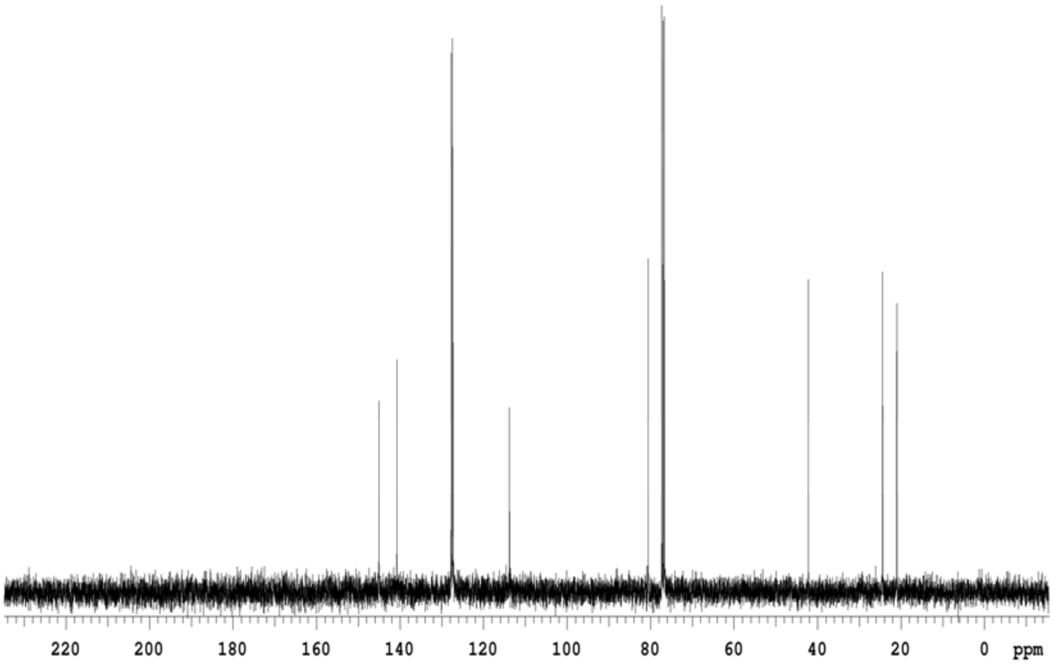
The spectroscopic properties of this compound were consistent with the data available in the literature.[2]

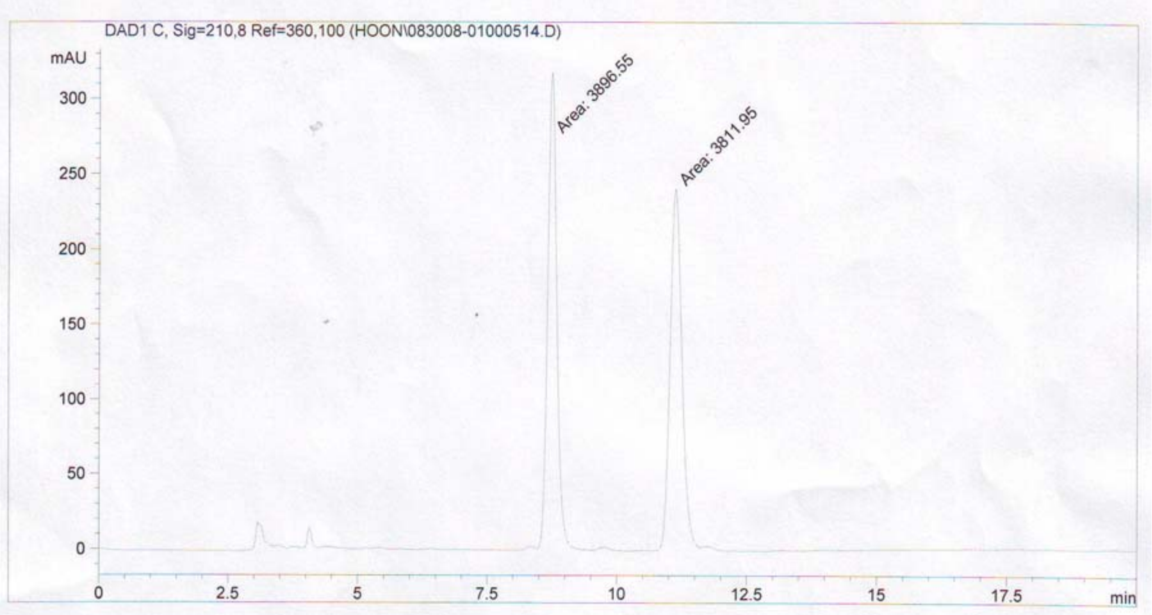
---

[1] Kotani, S.; Hashimoto, S.; Nakajima, M. *Tetrahedron* **2007**, *63*, 3122.

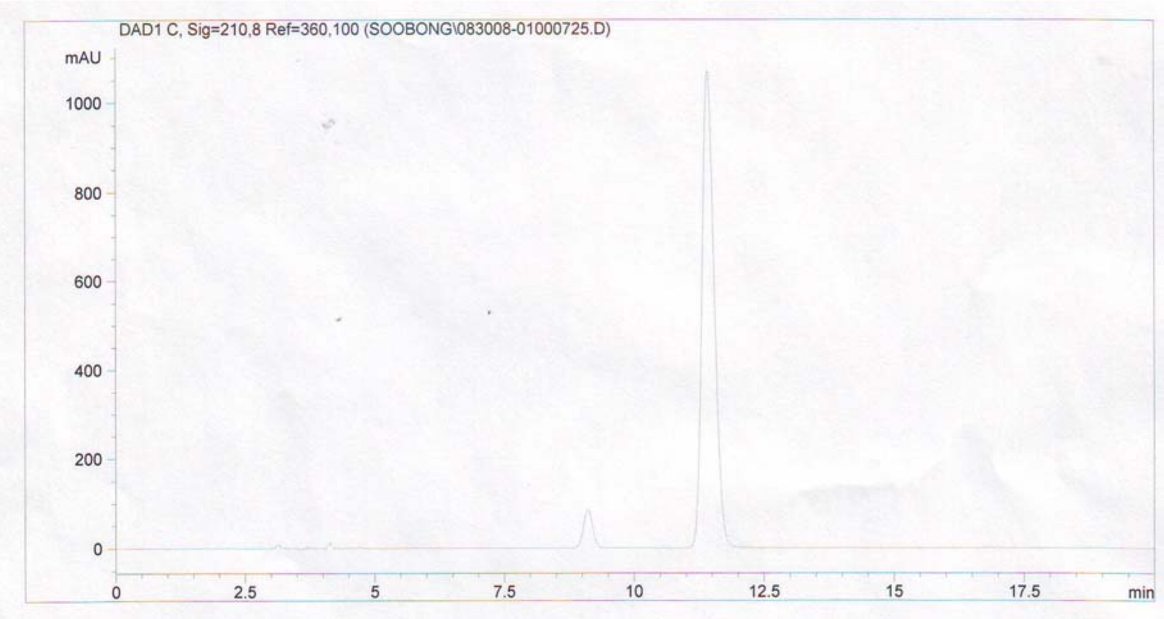
[2] Bower, J.; Skucas, E.; Patman, R. L.; Krische, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 15134.


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

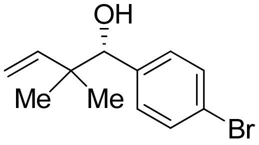


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.738 MM    0.2045 3896.54614  317.60913  50.5487
   2  11.122 MM    0.2641 3811.95020  240.54678  49.4513
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.110 BB    0.1880 1048.25378   86.15184   5.6675
   2  11.416 BB    0.2544 1.74475e4  1069.30750  94.3325
```

(*S*)-1-(4-Bromophenyl)-2,2-dimethylbut-3-en-1-ol (4b)



4b

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). 4-Bromobenzaldehyde **2b** (93 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and isopropanol (60 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 40 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:20) provided **4b** (123 mg, 0.482 mmol) as a colorless oil in 96% yield.

TLC (SiO_2): R_f = 0.25 (ethyl acetate:hexanes, 1:10).

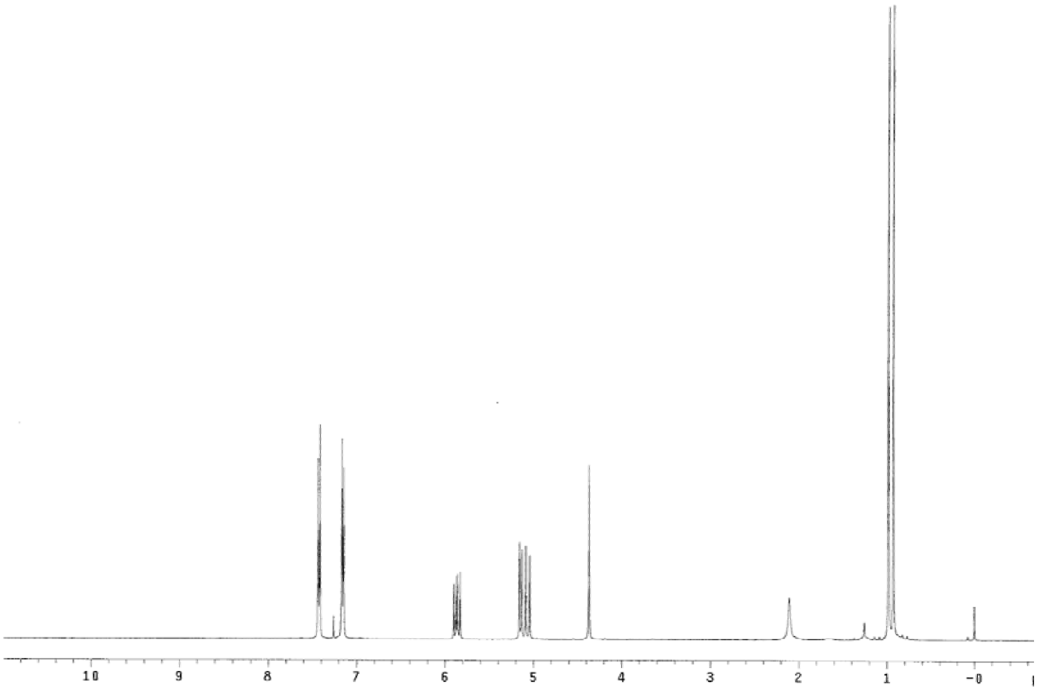
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.88 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.15 (d, *J* = 10.8 Hz, 1H), 5.07 (d, *J* = 17.6 Hz, 1H), 4.37 (s, 1H), 2.07 (d, *J* = 2.4 Hz, 1H), 0.99 (s, 3H), 0.93 (s, 3H).

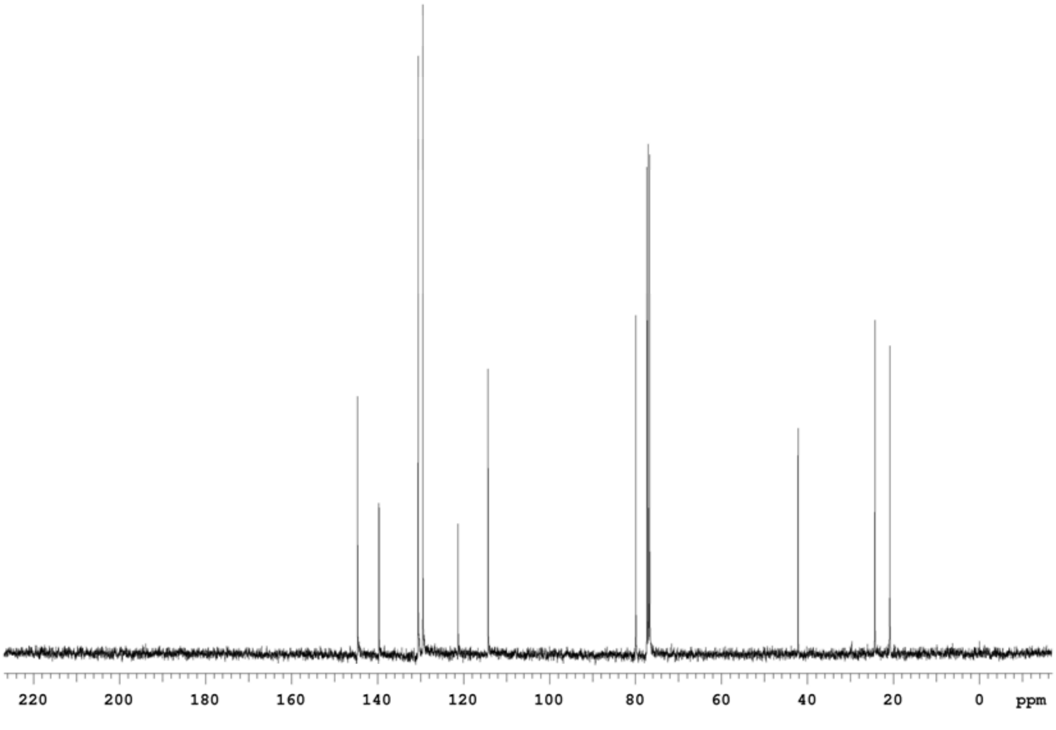
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 139.6, 130.5, 129.4, 121.2, 114.3, 79.9, 42.2, 24.3, 20.8.

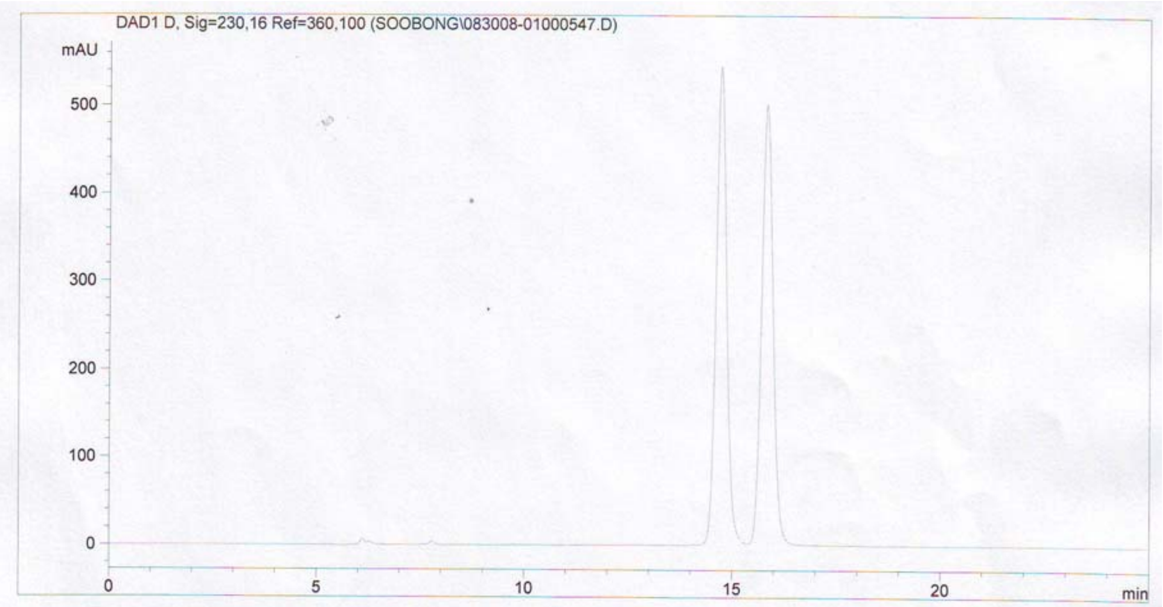
HRMS (CI) Calcd. for $C_{12}H_{16}OBr$ $(M+H)^+$: 255.0385 Found: 255.0381.

FTIR (neat): 3447, 2968, 2871, 1637, 1591, 1487, 1378, 1362, 1284, 1183, 1104, 1070, 1052, 1030, 1009, 915, 884, 836, 817, 754, 694, 670 cm^{-1}.

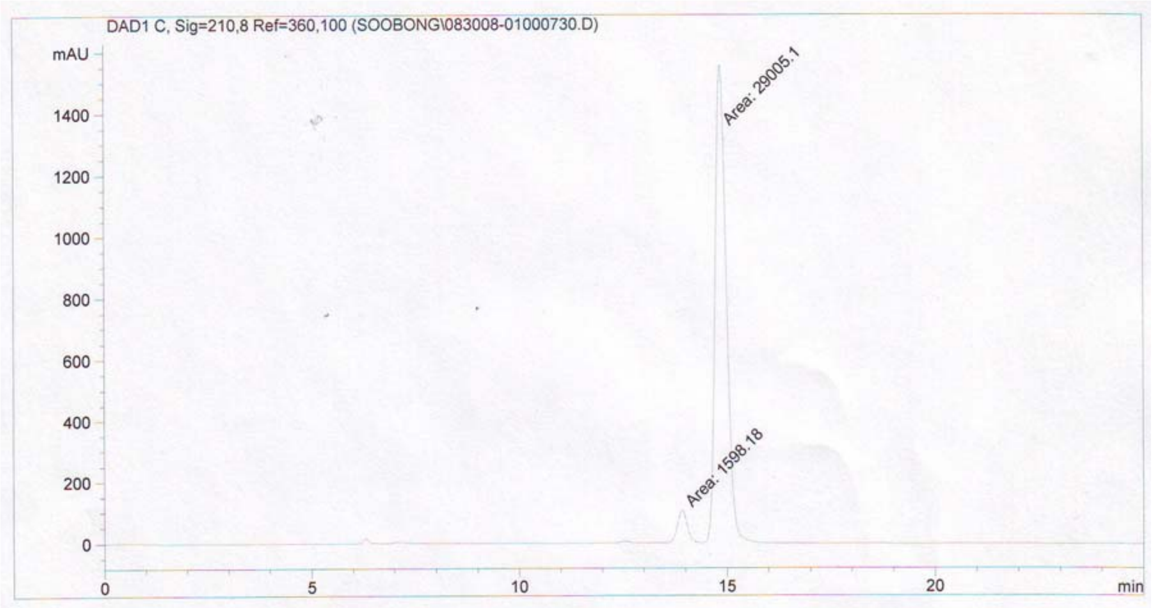
HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 210 nm), t_{minor} = 13.9 min, t_{major} = 14.9 min; ee = 90%.


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


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

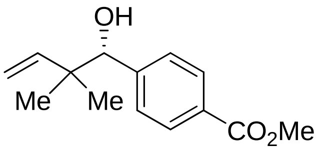


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.709 BV    0.2742 9612.62598  543.87854  50.1557
   2  15.815 VB    0.2947 9552.92969  500.55899  49.8443
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.918 MM    0.2623 1598.17664  101.53664   5.2222
   2  14.853 MM    0.3115 2.90051e4  1551.81067  94.7778
```

(*S*)-Methyl 4-(1-hydroxy-2,2-dimethylbut-3-enyl)benzoate (4c)



4c

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). Methyl 4-formylbenzoate **2c** (82 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and isopropanol (60 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 40 °C for 20 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:15) provided **4c** (103 mg, 0.440 mmol) as a colorless oil in 88% yield.

TLC (SiO_2): $R_f = 0.25$ (ethyl acetate:hexanes, 1:10).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.88 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.14 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.05 (dd, *J* = 17.6, 1.2 Hz, 1H), 4.46 (s, 1H), 3.90 (s, 3H), 2.34(br, 1H), 1.00 (s, 3H), 0.95 (s, 3H).

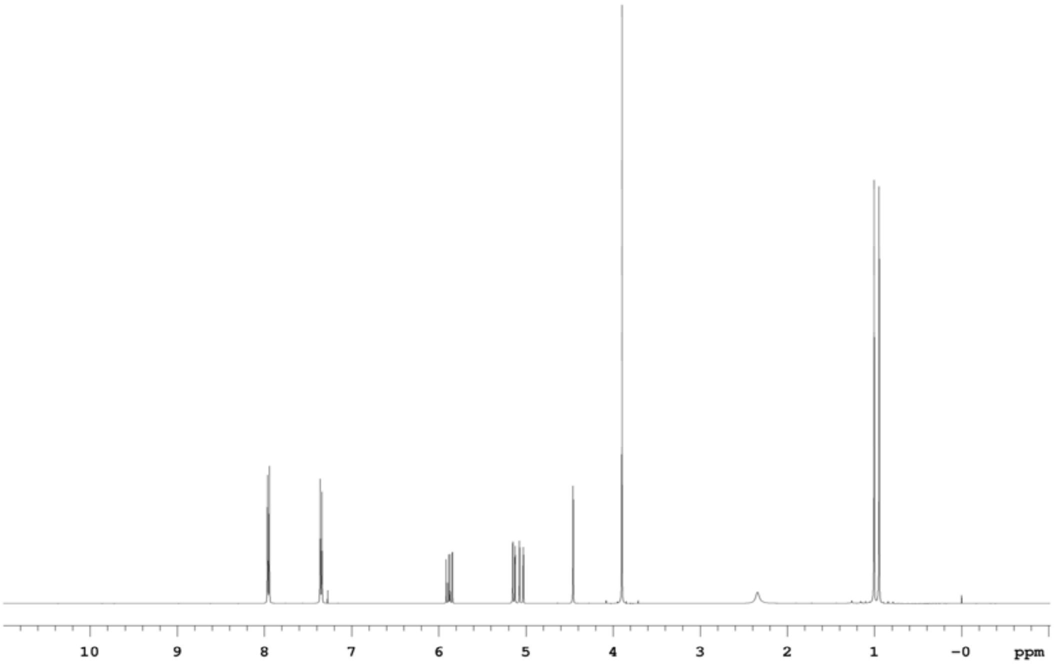
^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 146.0, 144.5, 129.1, 128.7, 127.7, 114.2, 80.1, 52.0, 42.2, 24.2, 21.0.

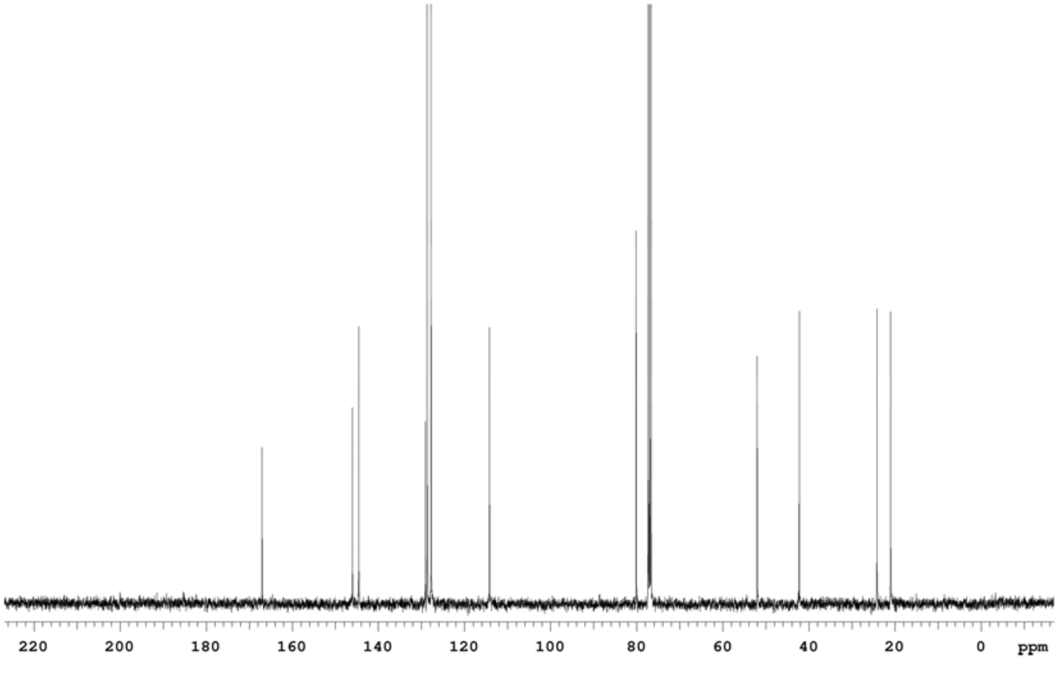
HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 254 nm), t_{minor} = 12.7 min, t_{major} = 17.9 min; ee = 89%.

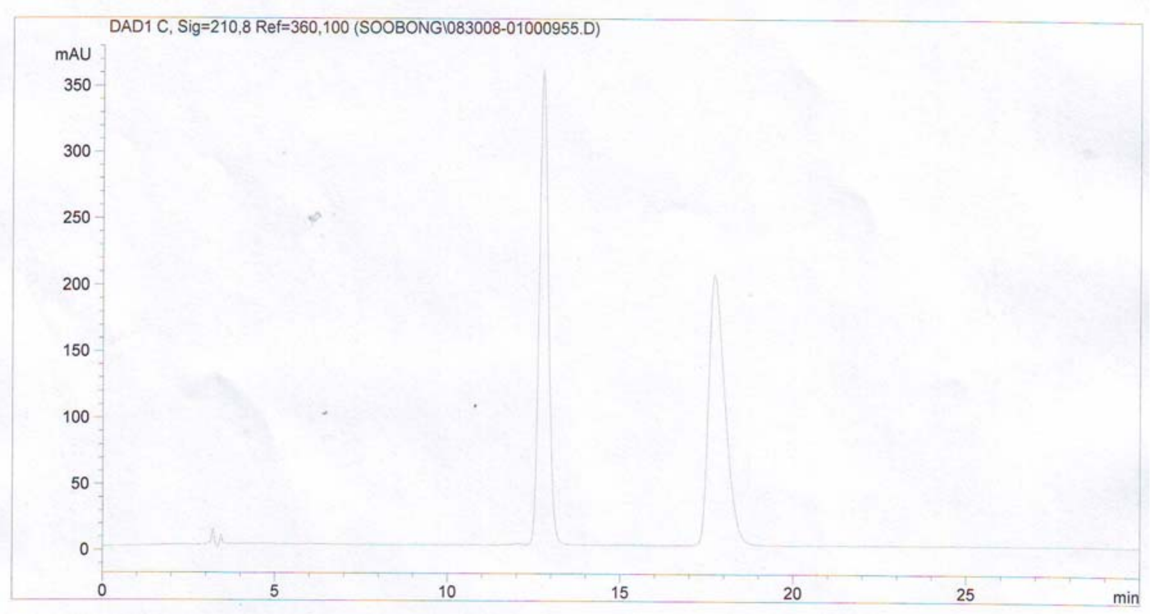
The spectroscopic properties of this compound were consistent with the data available in the literature.[3]

---

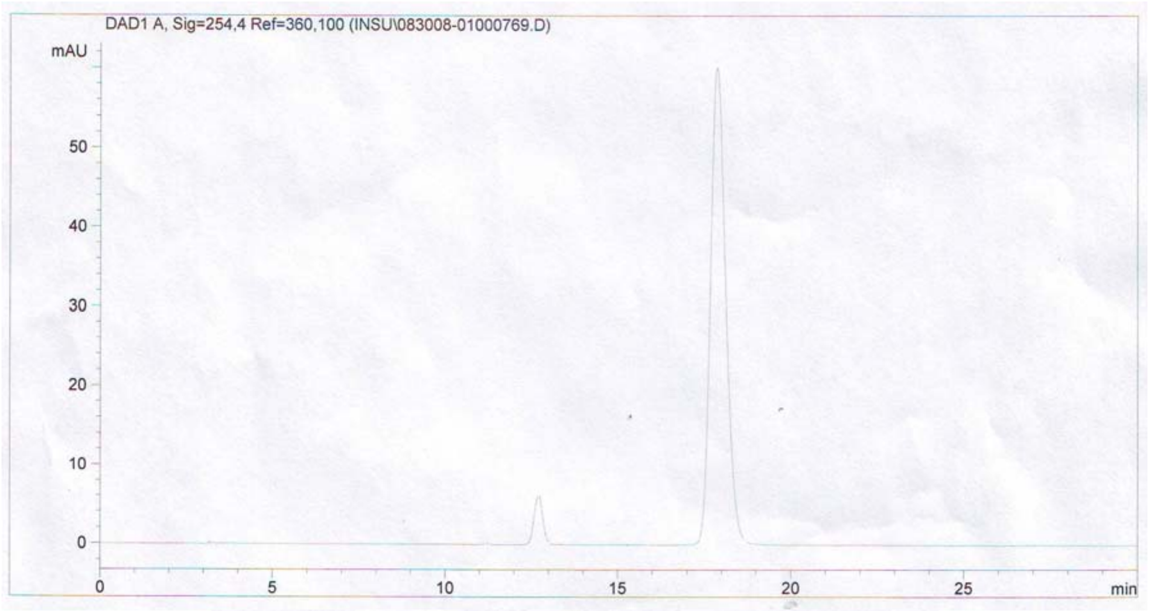
[3] Skucas, E.; Bower, J.; Krische, M. J. *J. Am. Chem. Soc*. **2007**, *129*, 12678.


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

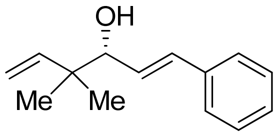


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.744 VB    0.2853 6596.89648  357.39426  49.4977
   2  17.707 BB    0.4970 6730.79150  203.95091  50.5023
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.701 BB    0.2718  109.17606    6.18954   5.5456
   2  17.857 BB    0.4758 1859.52771   60.29585  94.4544
```

(*R*,*E*)-4,4-Dimethyl-1-phenylhexa-1,5-dien-3-ol (4d)



4d

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). Cinnamaldehyde **2d** (66 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and isopropanol (60 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 40 ^{o}C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:30) provided **4d** (82 mg, 0.404 mmol) as a colorless oil in 81% yield.

TLC (SiO_2): R_f = 0.25 (ethyl acetate:hexanes, 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.21 (m, 5H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.91 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.14 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.11 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.97 (dd, *J* = 6.8, 1.2 Hz, 1H), 1.08 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 136.8, 132.0, 128.6, 128.5, 127.5, 126.4, 113.8, 79.2, 41.9, 23.8, 21.8.

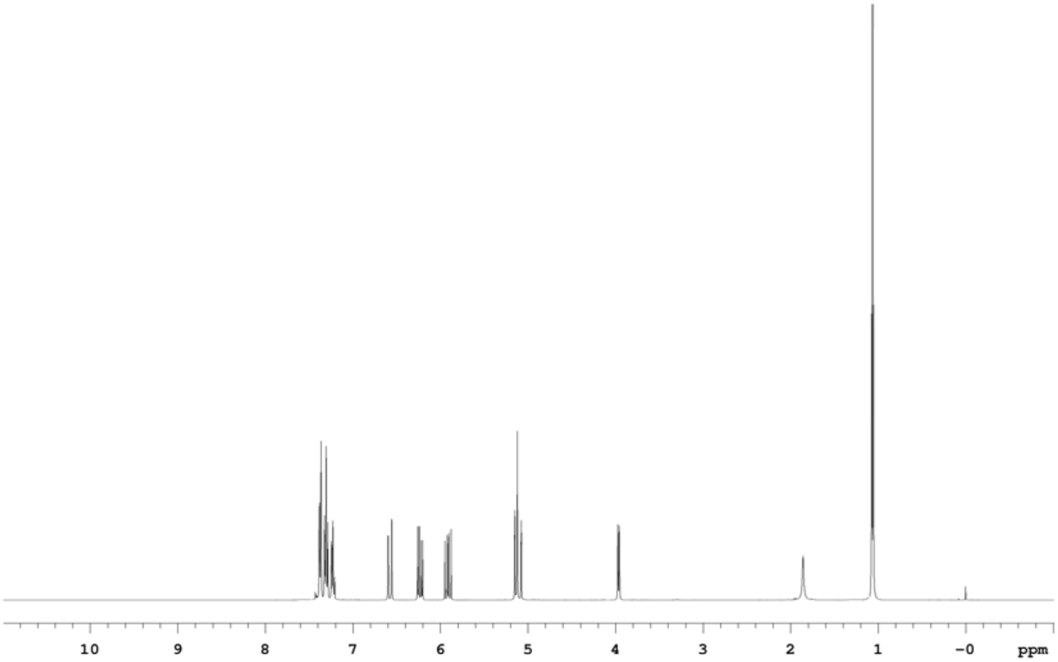
HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm), t_{major} = 13.5 min, t_{minor} = 20.3 min; ee = 93%.[4]

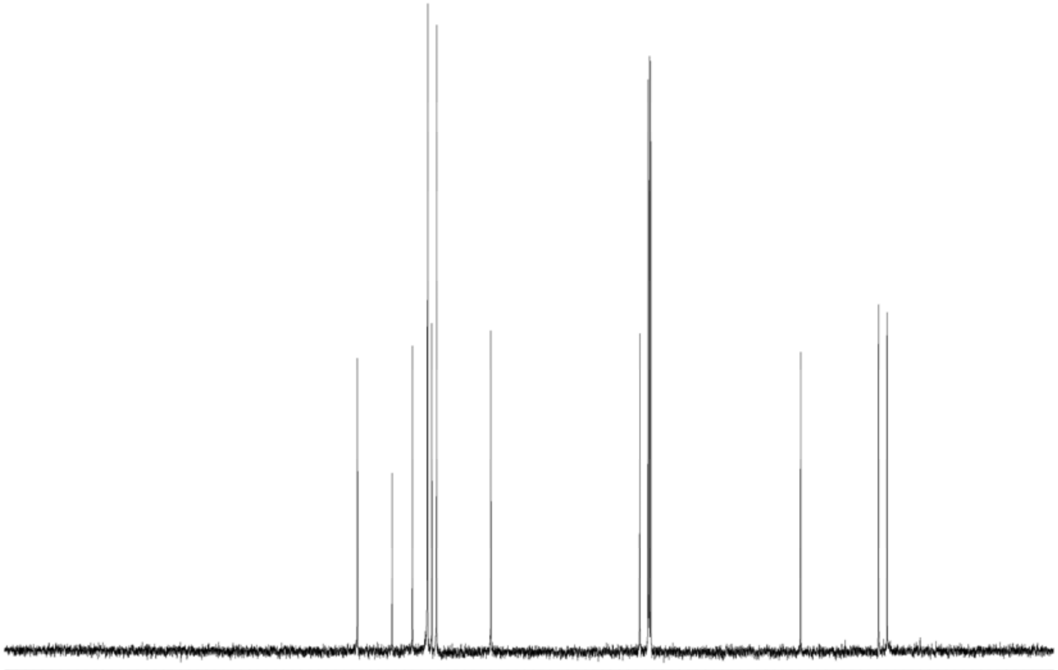
The spectroscopic properties of this compound were consistent with the data available in the literature.[5]

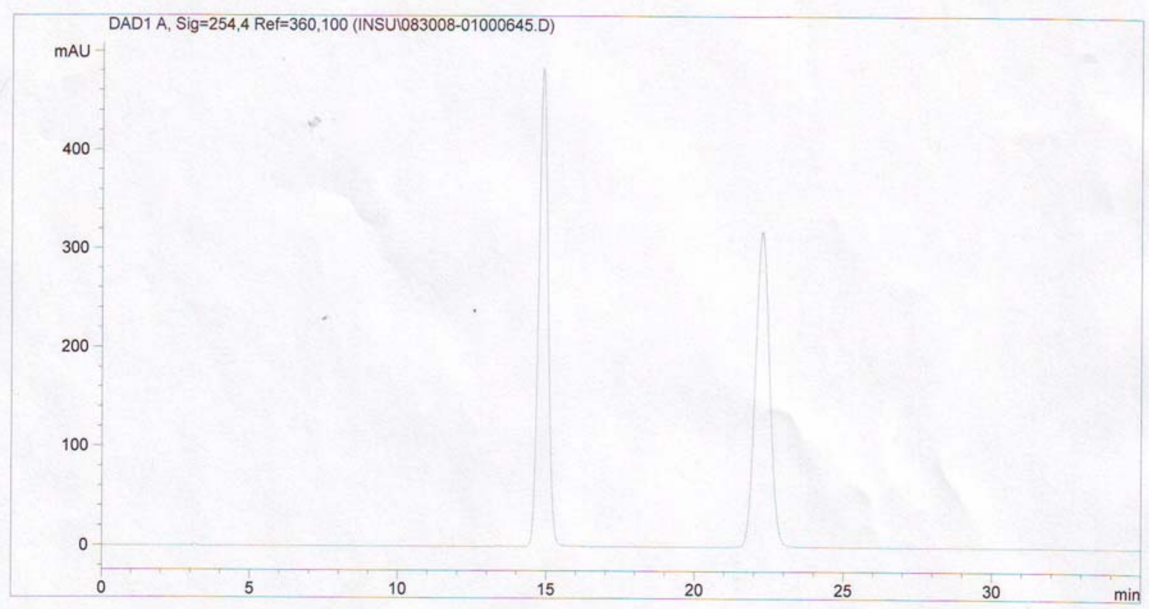
---

[4] Loh, T.-P.; Zhou, J.-R.; Yin, Z. *Org. Lett.* **1999**, *1*, 1855.

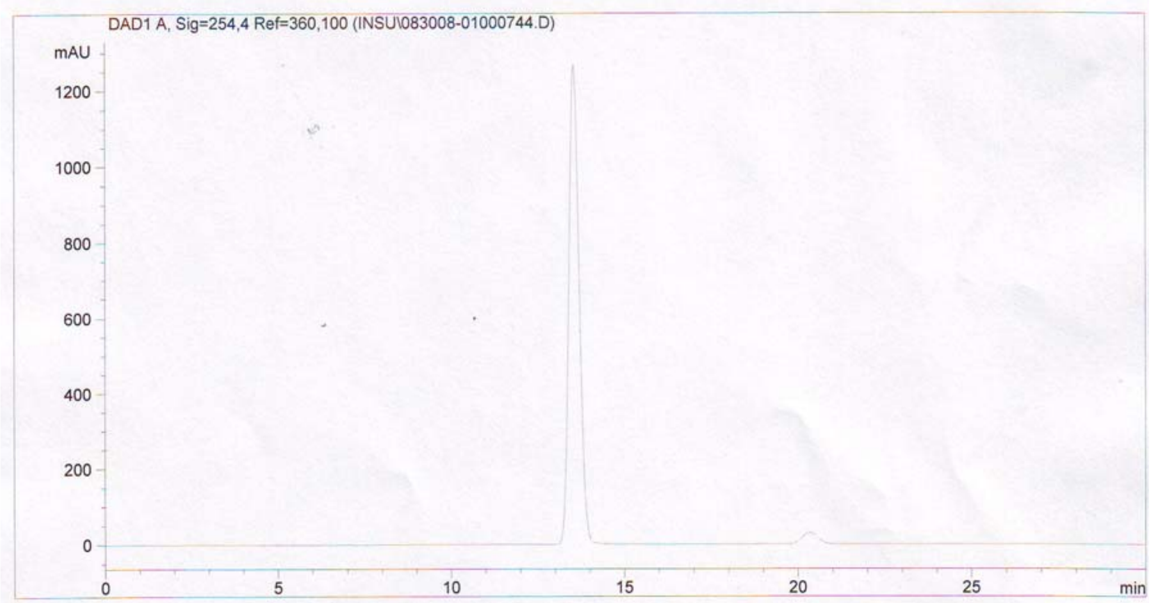
[5] Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2001**, *123*, 9488.


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

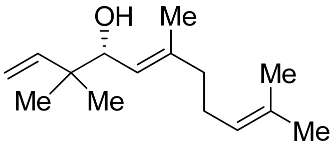


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  14.869 BB    0.3390 1.05802e4  484.03745 50.0335
   2  22.259 BB    0.5173 1.05660e4  318.27399 49.9665
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  13.542 BV    0.3237 2.62352e4 1266.37024 96.4505
   2  20.331 VB    0.4992  965.50189  30.34915  3.5495
```

(*R*,*E*)-3,3,6,10-Tetramethylundeca-1,5,9-trien-4-ol (4e)



4e

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). Geranial **2e** (76 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and isopropanol (60 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 50 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:30) provided **4e** (94 mg, 0.423 mmol) as a colorless oil in 85% yield.

TLC (SiO_2): $R_f = 0.37$ (ethyl acetate:hexanes, 1:20).

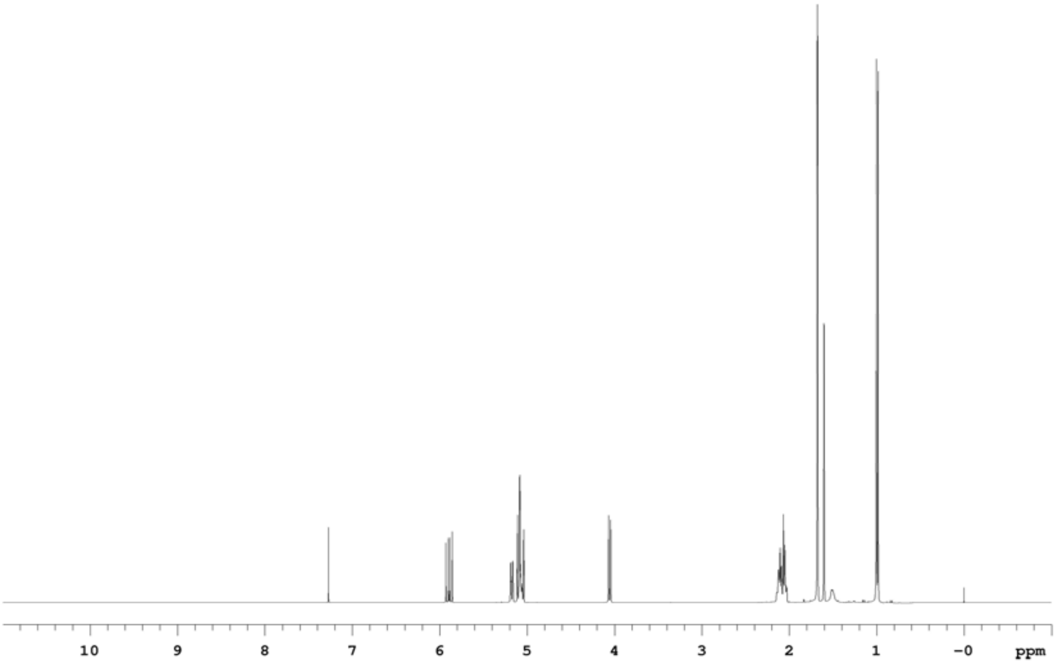
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.19-5.16 (m, 1H), 5.11-5.04 (m, 1H), 4.06 (d, *J* = 9.6 Hz, 1H), 2.14-2.03 (m, 4H), 1.68 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 1.52 (br, 1H), 1.00 (s, 3H), 0.98 (s, 3H).

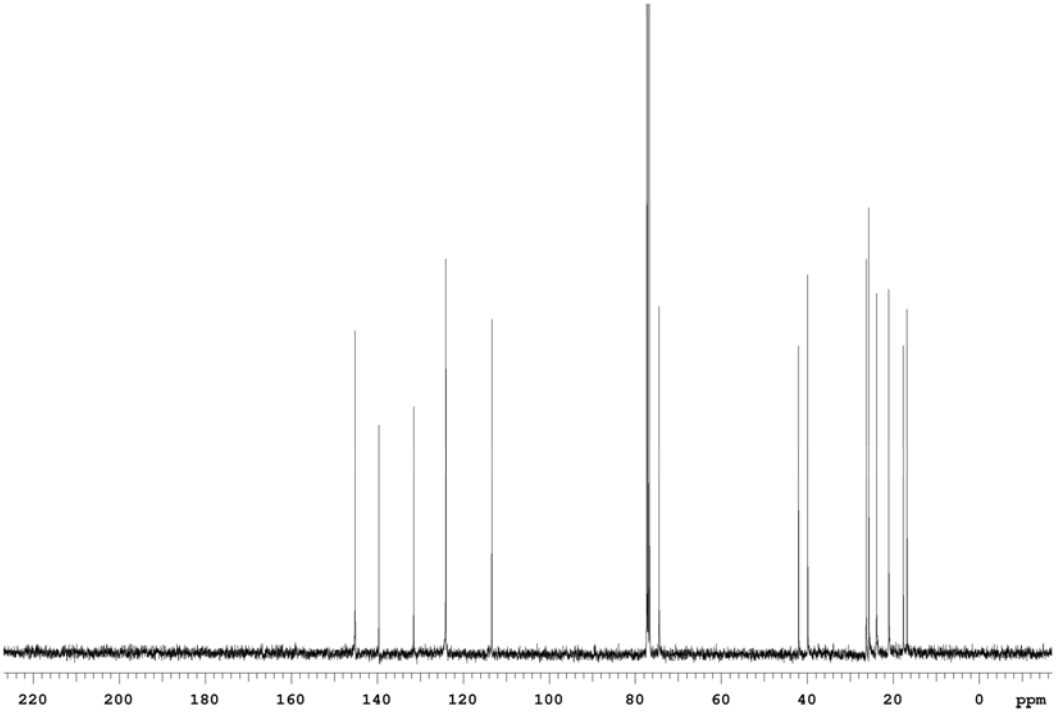
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 139.6, 131.5, 124.1, 124.0, 113.3, 74.4, 42.0, 39.9, 26.3, 25.7, 23.9, 21.0, 17.6, 16.8.

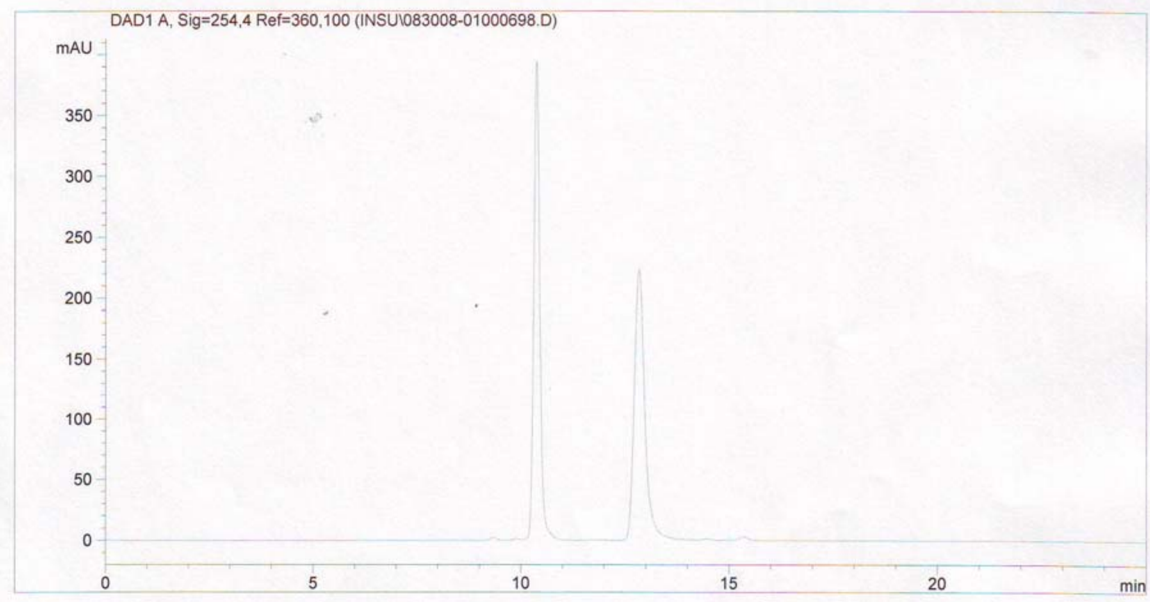
HRMS (CI) Calcd. for $C_{15}H_{27}O$ $(M+H)^+$: 223.2062, Found: 223.2057.

FTIR (neat): 3415, 2965, 2915, 1667, 1638, 1445, 1414, 1377, 1360, 1266, 1182, 1099, 1009, 990, 909, 817, 741, 691 cm^{-1}.

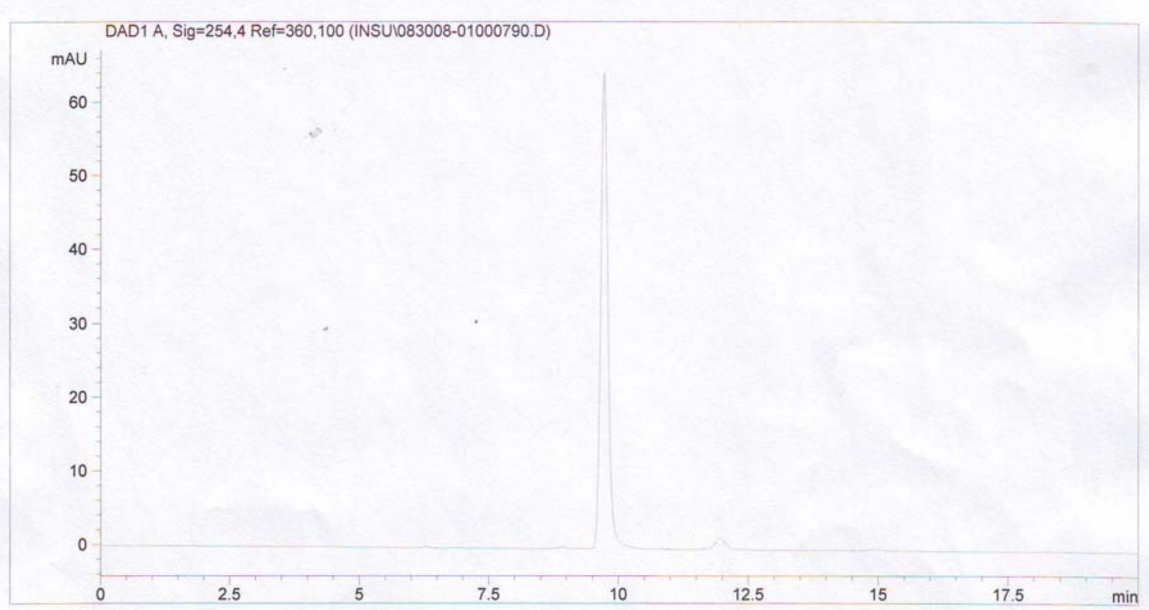
HPLC: Enantiomeric excess was determined by HPLC analysis of the 3,5-nitrobenzoate derivative of the product (Chiralcel AD-H column, hexanes:*i*-PrOH = 99.5:0.5, 0.5 mL/min, 254 nm), $t_{major} = 9.7$ min, $t_{minor} = 12.0$ min; ee = 93%.


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

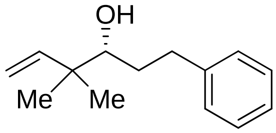


```
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.371 VB    0.1573 4027.62817  393.84918  50.1950
   2  12.838 VV    0.2722 3996.32739  223.94914  49.8050
```



```
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.720 BB    0.1533  637.96912   64.57761  96.4024
   2  11.956 BB    0.2363   23.80840    1.50687   3.5976
```

(*R*)-4,4-Dimethyl-1-phenylhex-5-en-3-ol (4f)



4f

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). 3-Phenylpropanal **2f** (67 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and isopropanol (60 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 °C for 72 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:30) provided **4f** (86 mg, 0.420 mmol) as a colorless oil in 84% yield.

TLC (SiO_2): $R_f = 0.25$ (ethyl acetate:hexanes, 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.17 (m, 5H), 5.79 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.09 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.05 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.28 (dd, *J* = 10.8, 1.6 Hz, 1H), 2.96-2.89 (m, 1H), 2.65-2.58 (m, 1H), 1.89-1.79 (m, 1H), 1.62-1.52 (m, 1H), 1.00 (s, 6H).

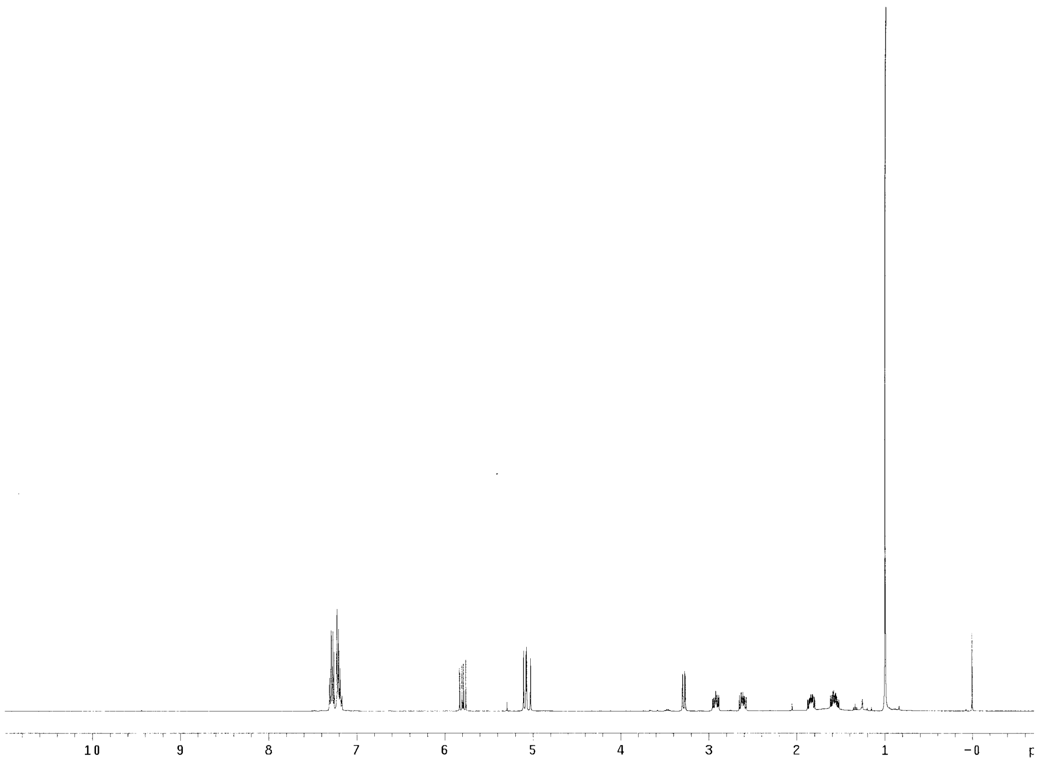
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 142.4, 128.5, 128.4, 125.8, 113.6, 77.5, 41.7, 33.3, 33.2, 23.1, 21.9.

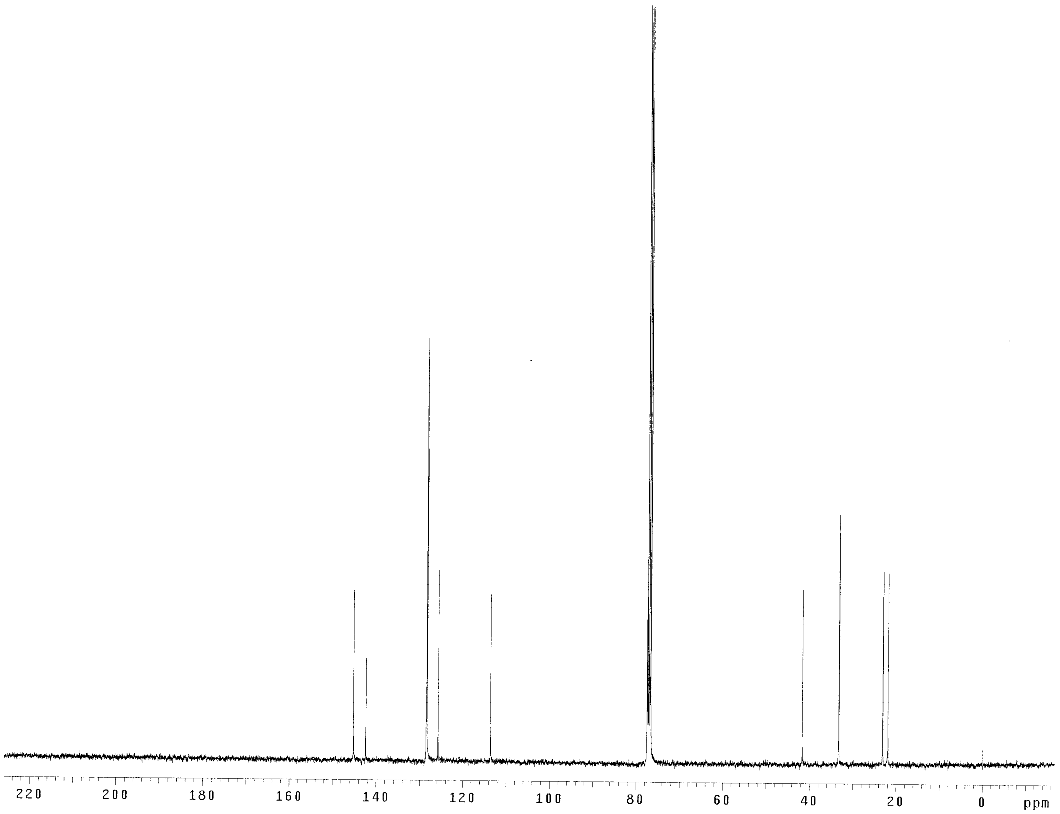
HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 97:3, 0.5 mL/min, 254 nm), t_{minor} = 11.6 min, t_{major} = 12.6 min; ee = 87%.

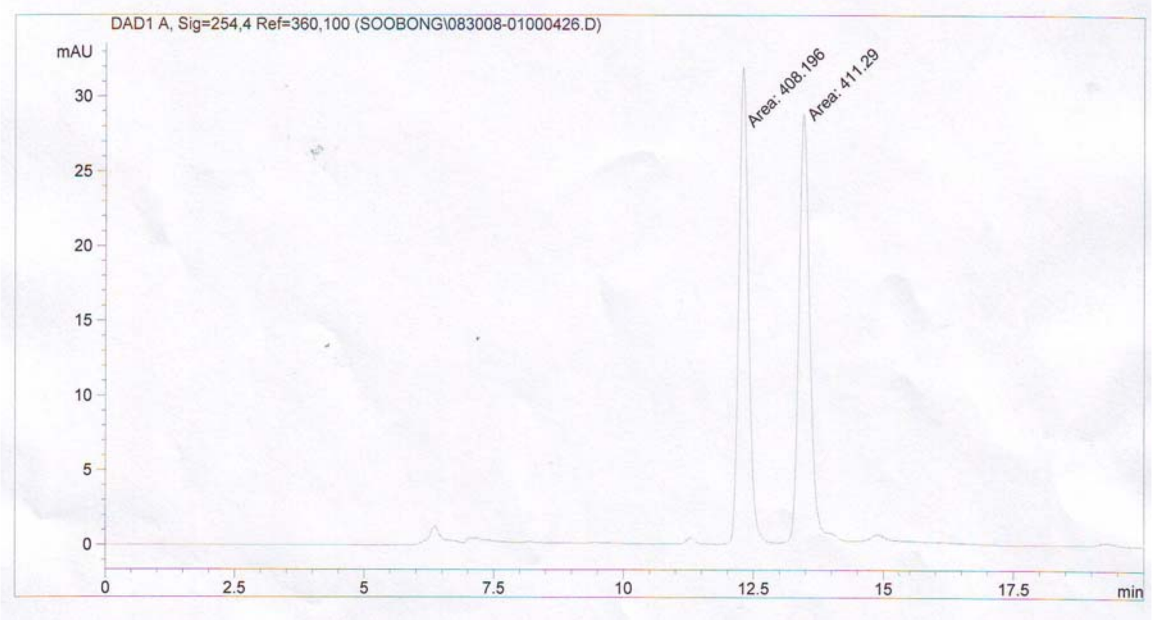
The spectroscopic properties of this compound were consistent with the data available in the literature.[6]

---

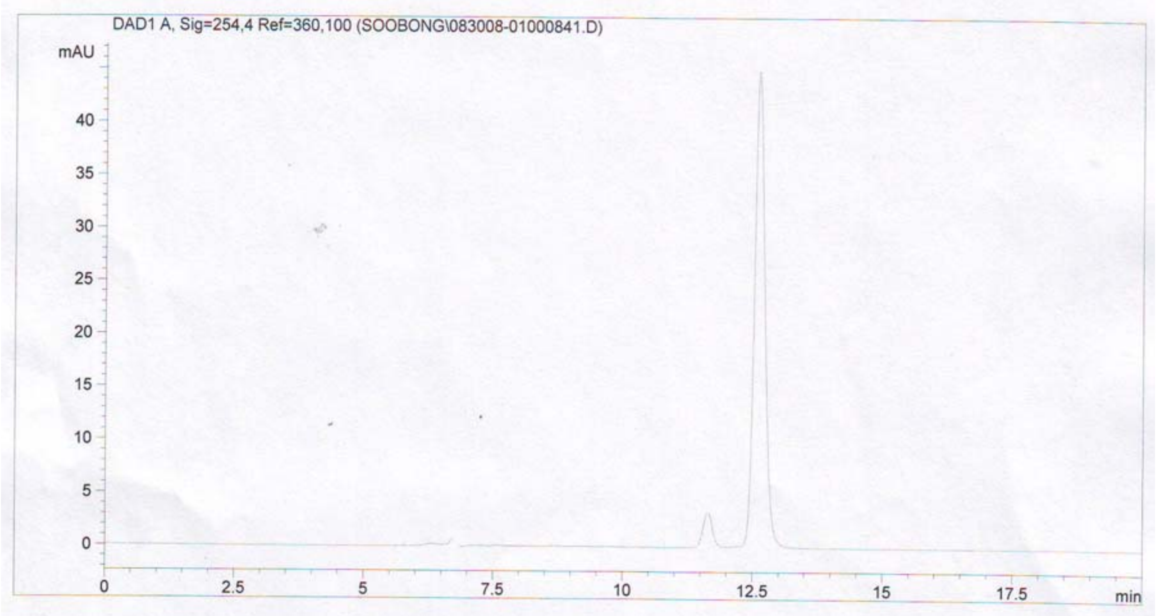
[6] Holt, D. A.; Leuengo, J. I.; Yamashita, D. S.; Oh, H.-J.; Konialian, A. L.; Yen, H.-K.; Rozamus, L. W.; Brandt, M.; Bossard, M. J.; Levy, M. A.; Eggleston, D. S.; Liang, J.; Schultz, L. W.; Stout, T. J.; Clardy, J. *J. Am. Chem. Soc.* **1993**, *115*, 9925.


10
9
8
7
6
5
4
3
2
1
-0
p


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

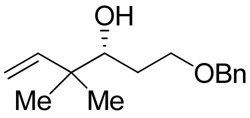


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  12.294 MM    0.2136  408.19638   31.84447  49.8112
   2  13.456 MM    0.2401  411.29044   28.54853  50.1888
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.638 BV    0.1941   43.29736    3.41057   6.3906
   2  12.607 VB    0.2161  634.22131   45.07738  93.6094
```

(*R*)-1-(Benzyloxy)-4,4-dimethylhex-5-en-3-ol (4g)



4g

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and chlorobenzene (1.0 M, 0.5 mL). 3-(Benzyloxy)propanal **2g** (82 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and isopropanol (60 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 °C for 72 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:20) provided **4g** (76 mg, 0.325 mmol) as a colorless oil in 65% yield.

TLC (SiO_2): $R_f = 0.35$ (ethyl acetate:hexanes, 1:7).

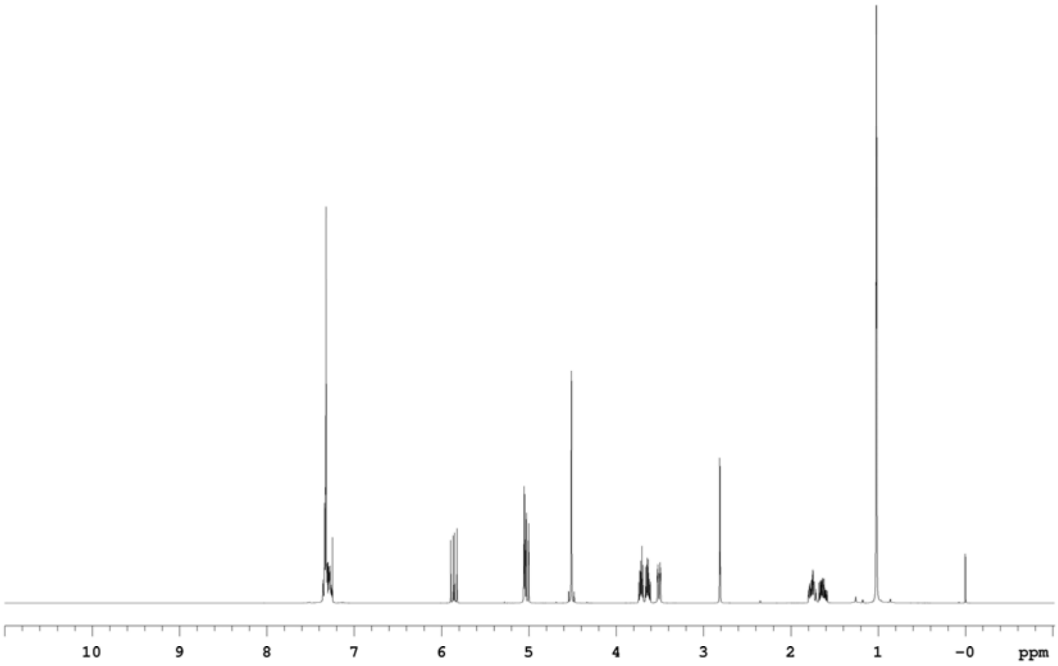
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 5H), 5.86 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.04 (dd, *J* = 10.8, 1.6 Hz, 1H), 5.02 (dd, *J* = 17.6, 1.6 Hz, 1H), 4.51 (d, *J* = 1.2 Hz, 2H), 3.74-3.49 (m, 2H), 3.51 (dt, *J* = 10.4, 2.4 Hz, 1H), 2.81(d, *J* = 2.8 Hz, 1H), 1.80-1.73 (m, 1H), 1.68- 1.58 (m, 1H), 1.02 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 137.9, 128.4, 127.7, 112.6, 77.7, 73.3, 69.9, 41.2, 31.2, 22.7, 22.5.

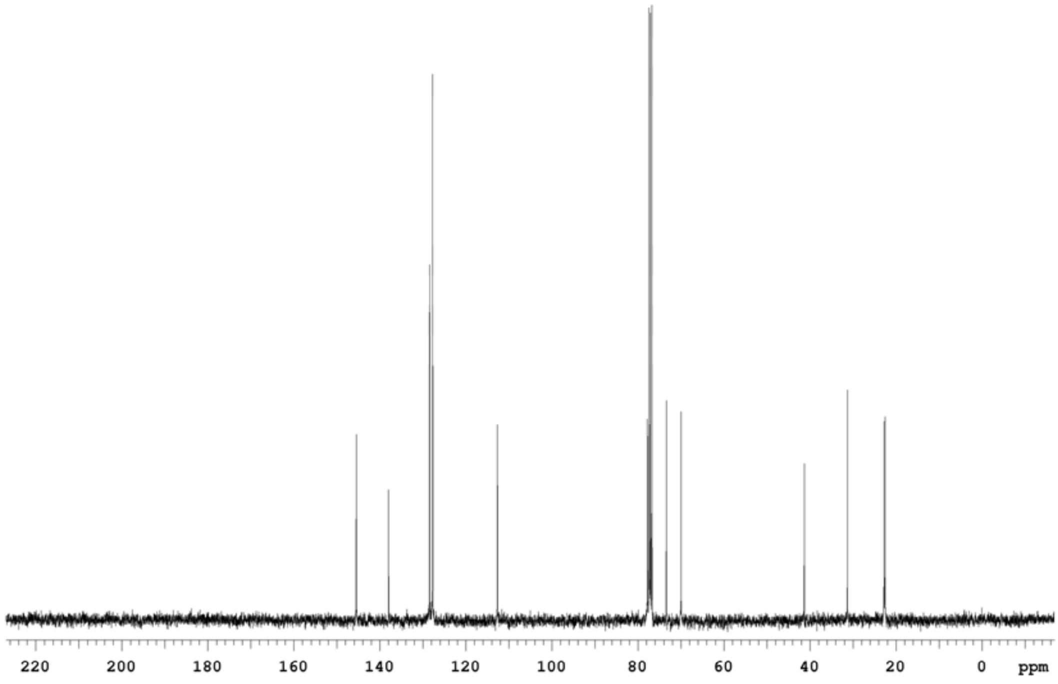
HRMS (CI) Calcd. for $C_{15}H_{23}O_2$ $(M+H)^+$: 235.1698, Found: 235.1696.

FTIR (neat): 3480, 2962, 2864, 1638, 1496, 1454, 1415, 1362, 1309, 1205, 1078, 1028, 1005, 970, 911, 735, 696 cm^{-1}.

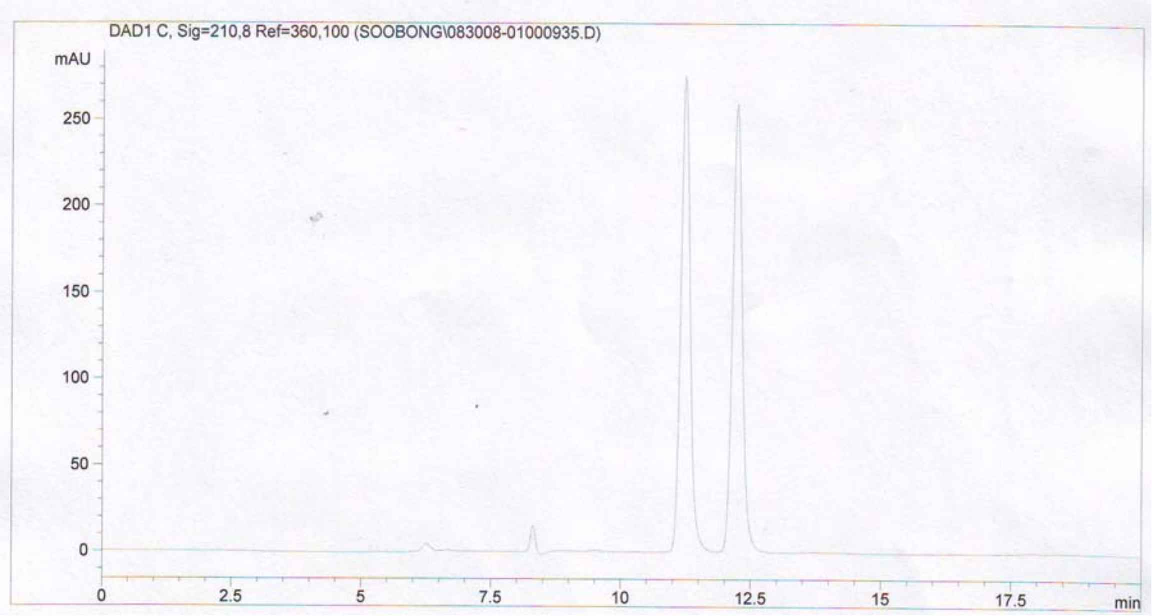
HPLC: (Chiralcel AS-H column, hexanes:*i*-PrOH = 99:1, 0.5 mL/min, 210 nm), t_{minor} = 11.4 min , t_{major} = 12.5 min; ee = 89%.



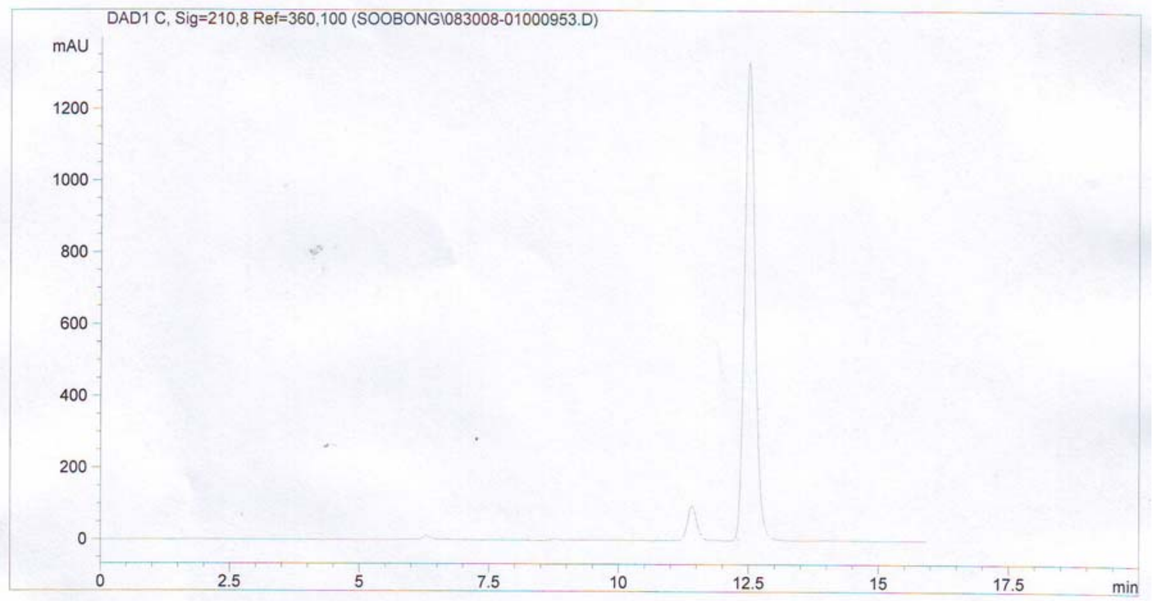
10
9
8
7
6
5
4
3
2
1
-0
ppm



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

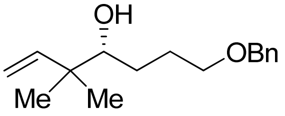


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.225	BB	0.1915	3434.01050	275.37466	49.9179
2	12.225	BB	0.2050	3445.30688	259.36694	50.0821



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.390	BB	0.1849	132.03104	11.09047	5.6993
2	12.497	BB	0.2059	2184.58325	163.44003	94.3007

(*R*)-7-(Benzyloxy)-3,3-dimethylhept-1-en-4-ol (4h)



4h

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). 4-(Benzyloxy)butanal **2h** (89 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and isopropanol (60 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 50 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:10) provided **4h** (107 mg, 0.431 mmol) as a colorless oil in 86% yield.

TLC (SiO_2): R_f = 0.35 (ethyl acetate:hexanes, 1:5).

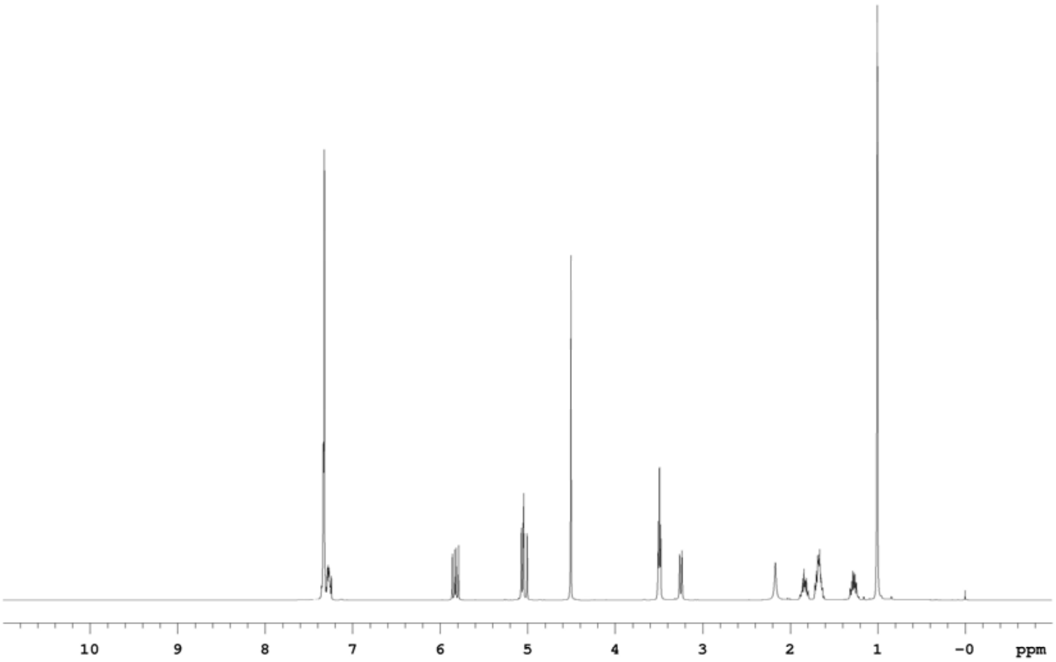
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.24 (m, 5H), 5.82 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.06 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.03 (dd, *J* = 17.6, 1.2 Hz, 1H), 4.51 (s, 1H), 3.49 (t, *J* = 6.0 Hz, 2H), 3.25 (dd, *J* = 10.8, 1.2 Hz, 1H), 2.17 (br, 1H), 1.86-1.81 (m, 1H), 1.72- 1.63 (m, 2H), 1.32-1.24 (m, 1H), 1.00 (s, 6H).

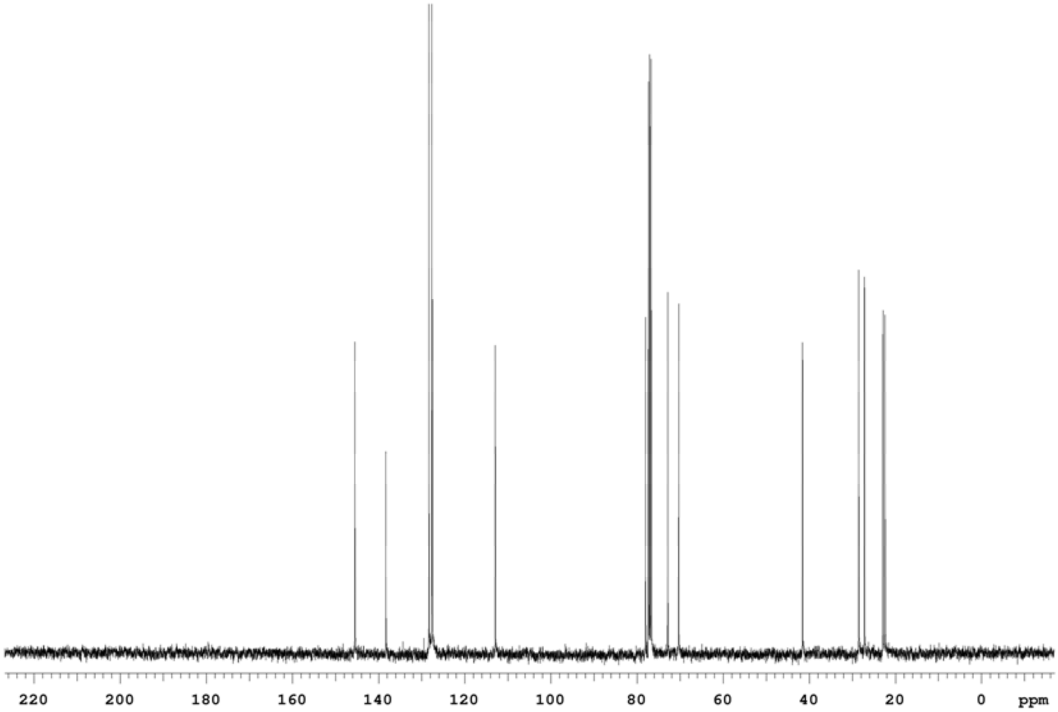
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 138.3, 128.3, 127.6, 127.5, 112.9, 78.0, 72.8, 70.3, 41.5, 28.5, 27.2, 22.8, 22.4.

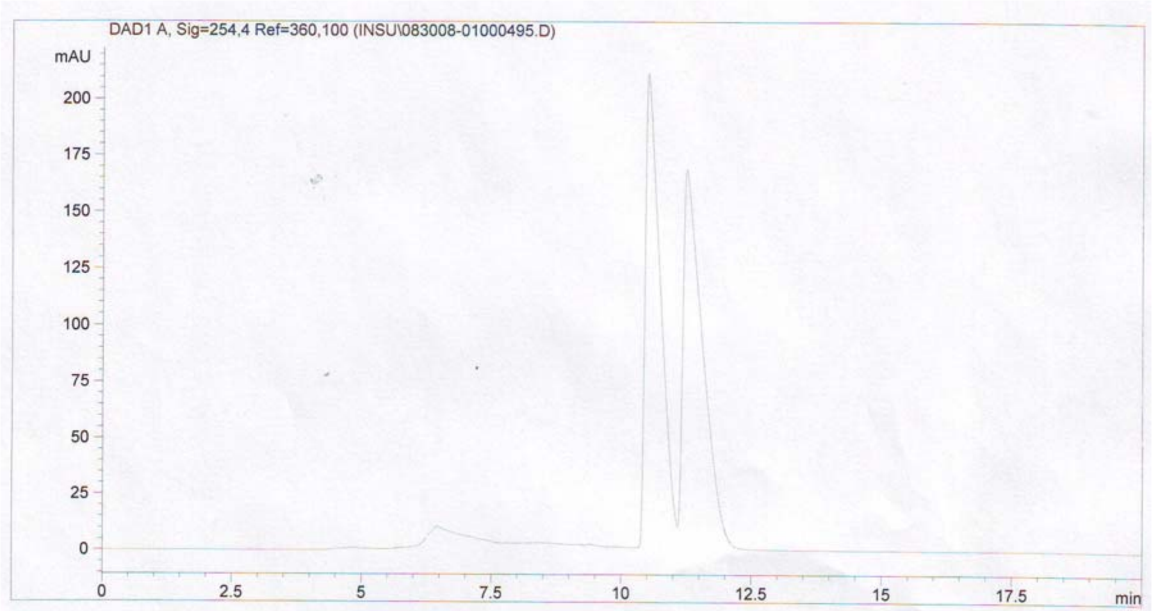
HRMS (CI) Calcd. for $C_{16}H_{25}O_2$ $(M+H)^+$: 249.1855, Found: 249.1857.

FTIR (neat): 3478, 2959, 2862, 1637, 1496, 1454, 1414, 1361, 1274, 1204, 1091, 1028, 1005, 972, 910, 734, 696 cm^{-1}.

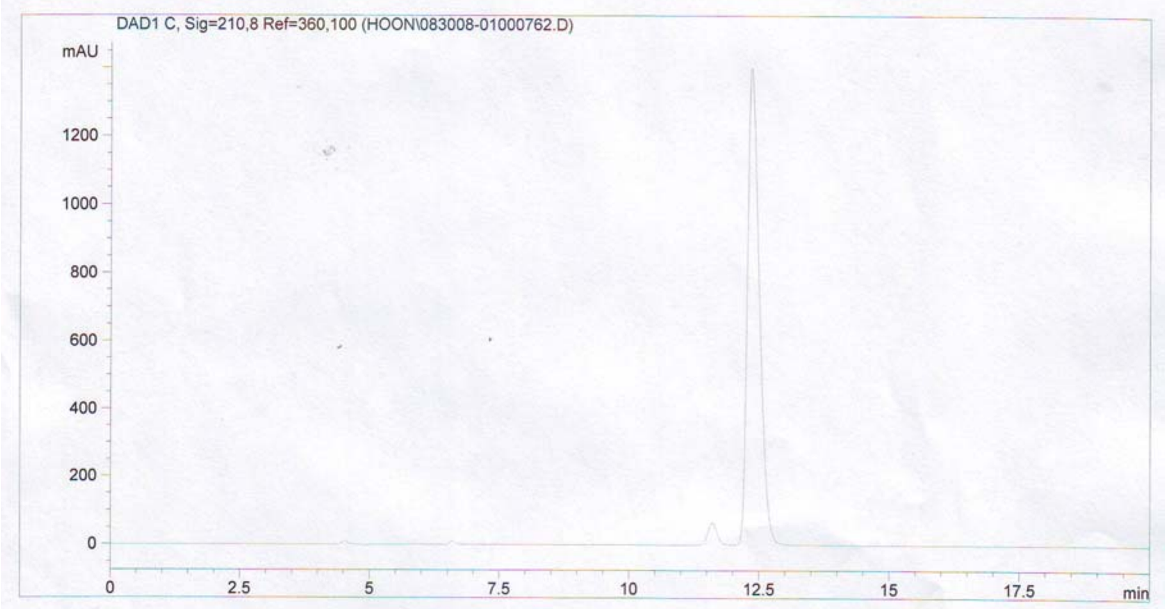
HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 97:3, 0.7 mL/min, 210 nm), t_{minor} = 11.6 min , t_{major} = 12.3 min; ee = 93%.


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

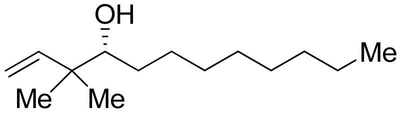


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.504 VV    0.3083 4360.97510  211.71979  49.2840
  2  11.245 VB    0.3876 4487.68359  169.08885  50.7160
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  11.602 VV    0.1978  821.55951   64.86417   3.5421
  2  12.347 VB    0.2441 2.23726e4  1402.40833  96.4579
```

(*R*)-3,3-Dimethyldodec-1-en-4-ol (4i)



4i

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and chlorobenzene (1.0 M, 0.5 mL). Nonanal **2i** (71 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and isopropanol (60 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 50 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:30) provided **4i** (75 mg, 0.353 mmol) as a colorless oil in 71% yield.

TLC (SiO_2): $R_f = 0.39$ (ethyl acetate:hexanes, 1:20).

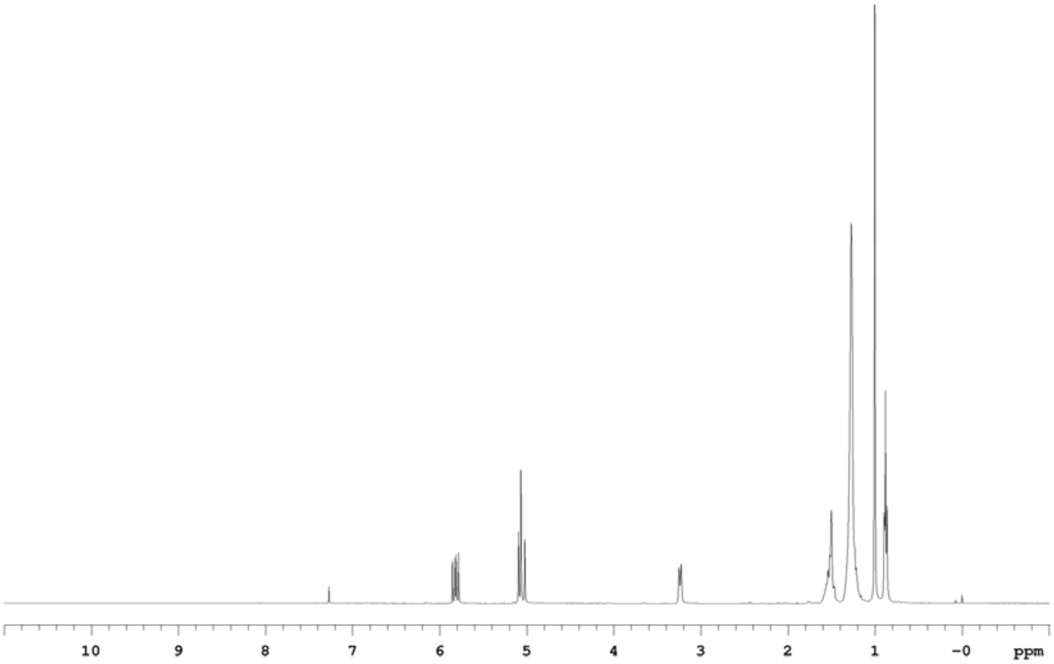
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.08 (d, *J* = 10.8 Hz, 1H), 5.04 (d, *J* = 17.6 Hz, 1H), 3.24 (d, *J* = 9.2 Hz, 1H), 1.56-1.46 (m, 2H), 1.34-1.22 (m,12H), 1.00 (s, 6H), 0.88 (t, *J* = 6.4 Hz, 3H).

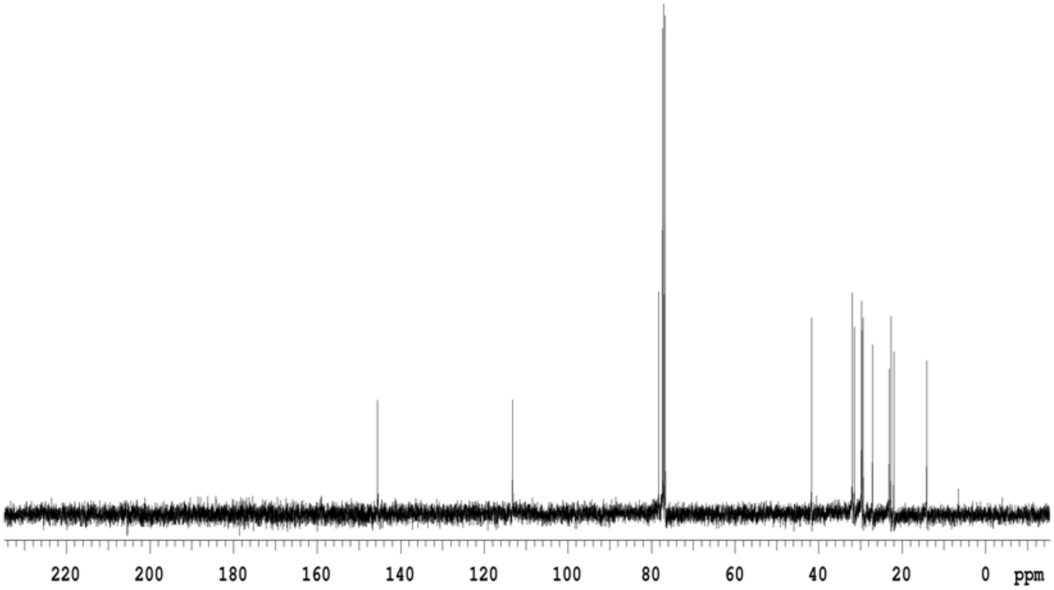
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 113.2, 78.2, 41.6, 31.9, 31.4, 29.7, 29.6, 29.3, 27.1, 23.1, 22.7, 22.0, 14.1.

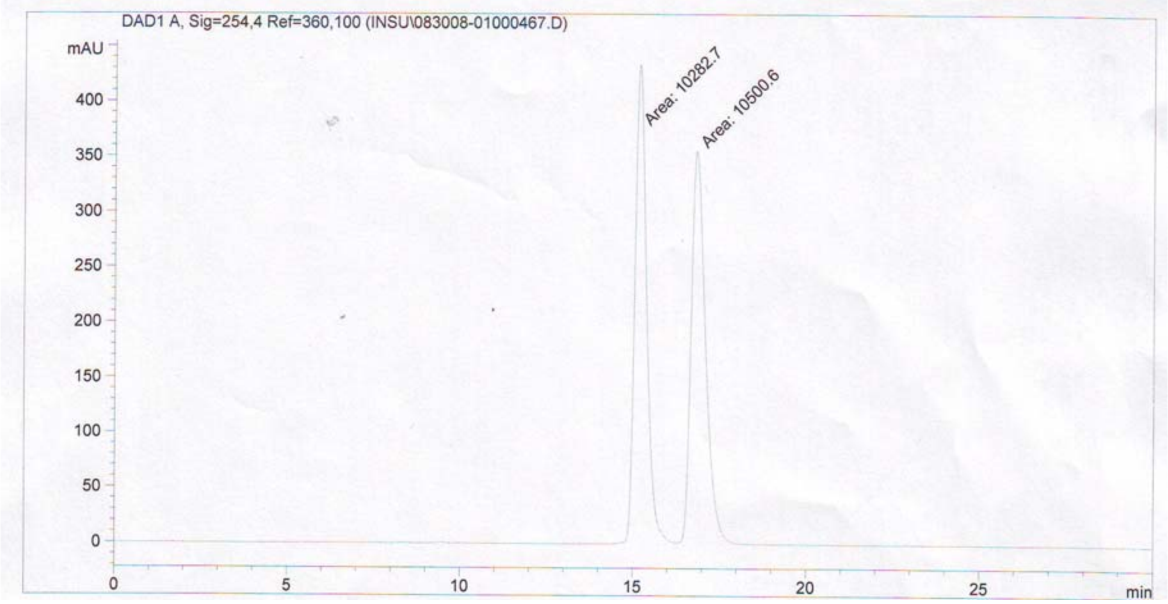
HPLC: Enantiomeric excess was determined by HPLC analysis of the 3,5-nitrobenzoate derivative of the product (Chiralcel OD-H column, hexanes:*i*-PrOH = 99:1, 0.5 mL/min, 230 nm), t_{major} = 16.7 min, t_{minor} = 19.1 min; ee = 92%.[7]

---

[7] Loh, T.-P.; Zhou, J.-R.; Yin, Z. *Org. Lett.* **1999**, *1*, 1855.

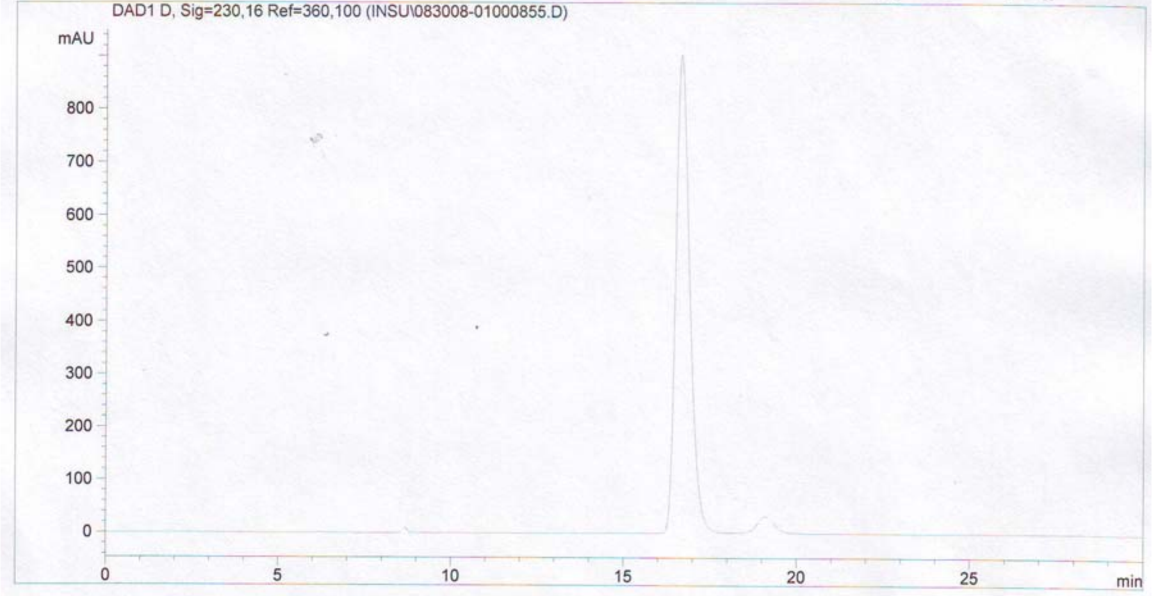

10
9
8
7
6
5
4
3
2
1
-0
ppm


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



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.166	MM	0.3951	1.02827e4	433.81290	49.4757
2	16.816	MM	0.4893	1.05006e4	357.65274	50.5243

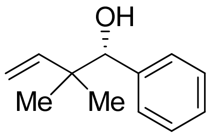
(from [illegible])



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.651	BB	0.4276	2.52431e4	904.37537	95.9538
2	19.095	BB	0.5216	1064.45813	31.23492	4.0462

Detailed Procedure and Spectral Data for Enantioselective Carbonyl Reverse Prenylation from Alcohols (4a-4i)

(*S*)-2,2-Dimethyl-1-phenylbut-3-en-1-ol (4a)

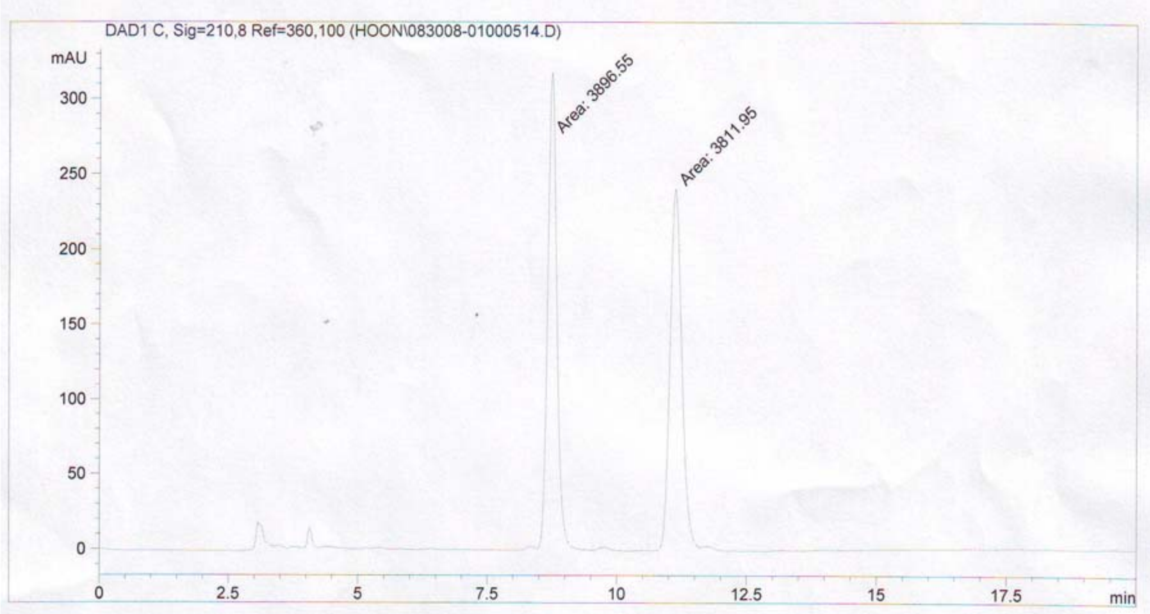


4a

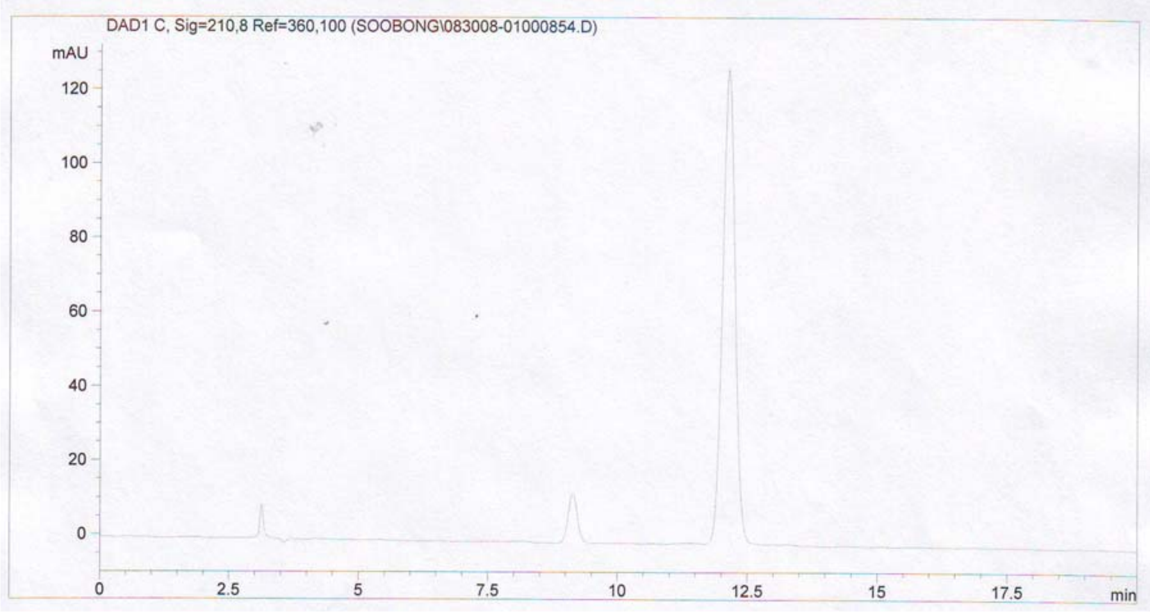
An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). Benzyl alcohol **3a** (54 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and propionaldehyde (1.5 mg, 0.025 mmol, 5 mol%) were added and the reaction mixture was allowed to stir at 40 ^{o}C for 15 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:50) provided **4a** (75 mg, 0.426 mmol) as a colorless oil in 85% yield.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1 mL/min, 210 nm), t_{minor} = 9.1 min, t_{major} = 12.1min; ee = 86%.[1]

The spectroscopic properties of this compound were consistent with the data available in the literature.[2]

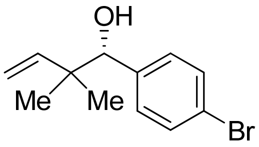


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.738 MM    0.2045 3896.54614  317.60913  50.5487
   2  11.122 MM    0.2641 3811.95020  240.54678  49.4513
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.136 BB    0.1907  164.87082   13.29160   7.1039
   2  12.128 BB    0.2627 2155.96851  127.90440  92.8961
```

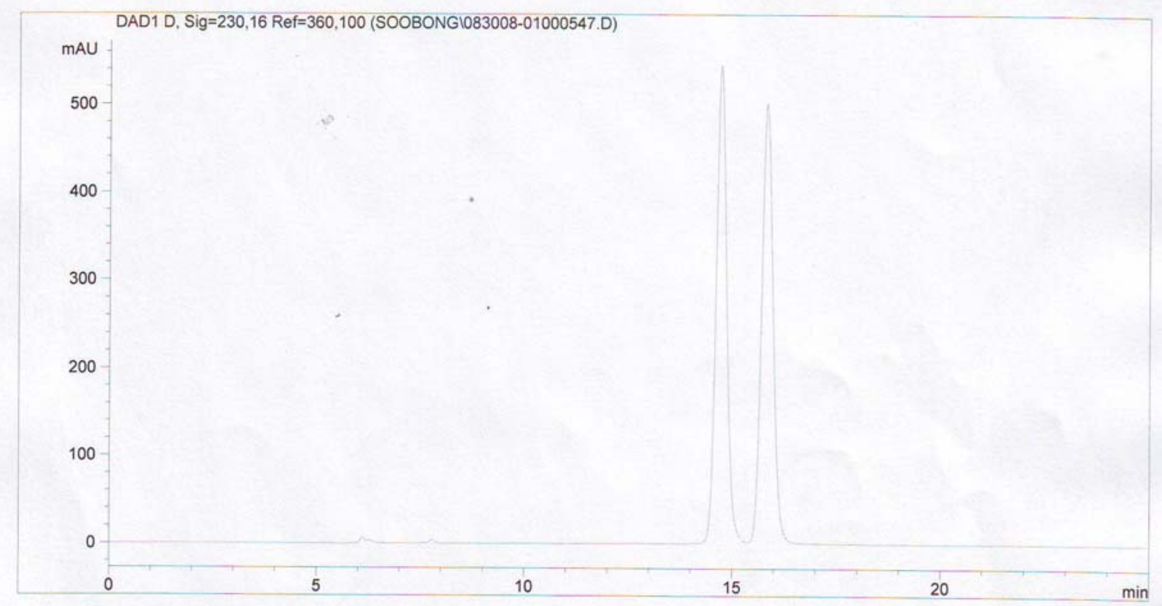
(*S*)-1-(4-Bromophenyl)-2,2-dimethylbut-3-en-1-ol (4b)



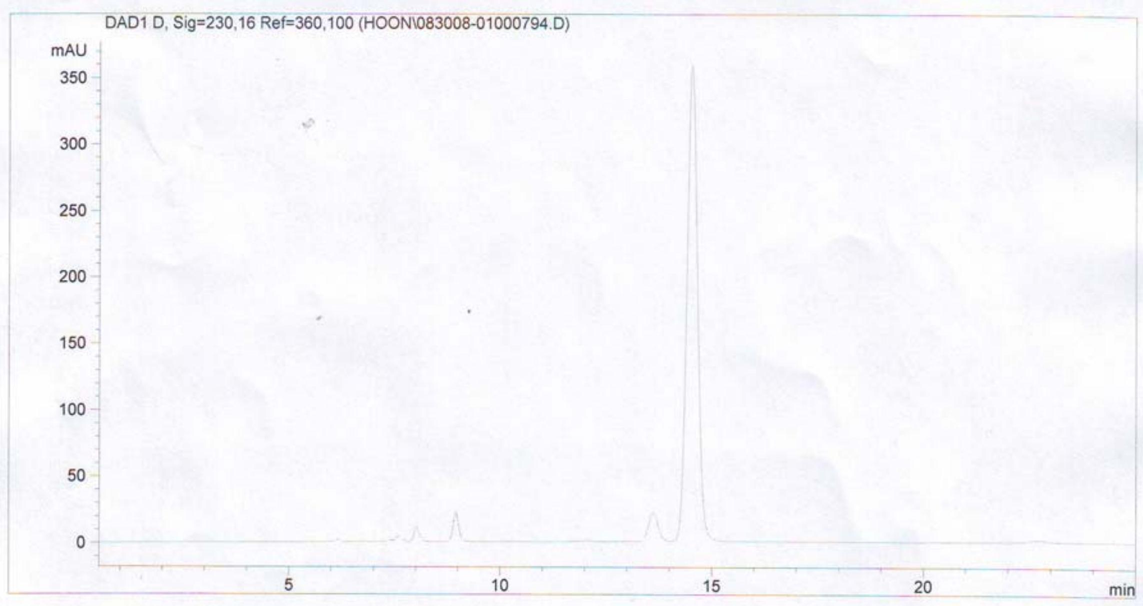
4b

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). 4-Bromobenzyl alcohol **3b** (94 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and propionaldehyde (1.5 mg, 0.025 mmol, 5 mol%) were added and the reaction mixture was allowed to stir at 40 ^{o}C for 9 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:20) provided **4b** (102 mg, 0.400 mmol) as a colorless oil in 80% yield.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 230 nm), t_{minor} = 13.6 min, t_{major} = 14.5 min; ee = 90%.

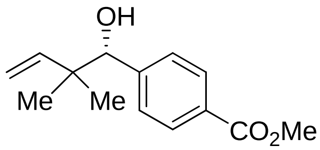


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.709 BV    0.2742 9612.62598  543.87854  50.1557
   2  15.815 VB    0.2947 9552.92969  500.55899  49.8443
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.621 BB    0.2457  336.33322   21.35495   5.1396
   2  14.522 BB    0.2705 6207.58154  357.62726  94.8604
```

(*S*)-Methyl 4-(1-hydroxy-2,2-dimethylbut-3-enyl)benzoate (4c)

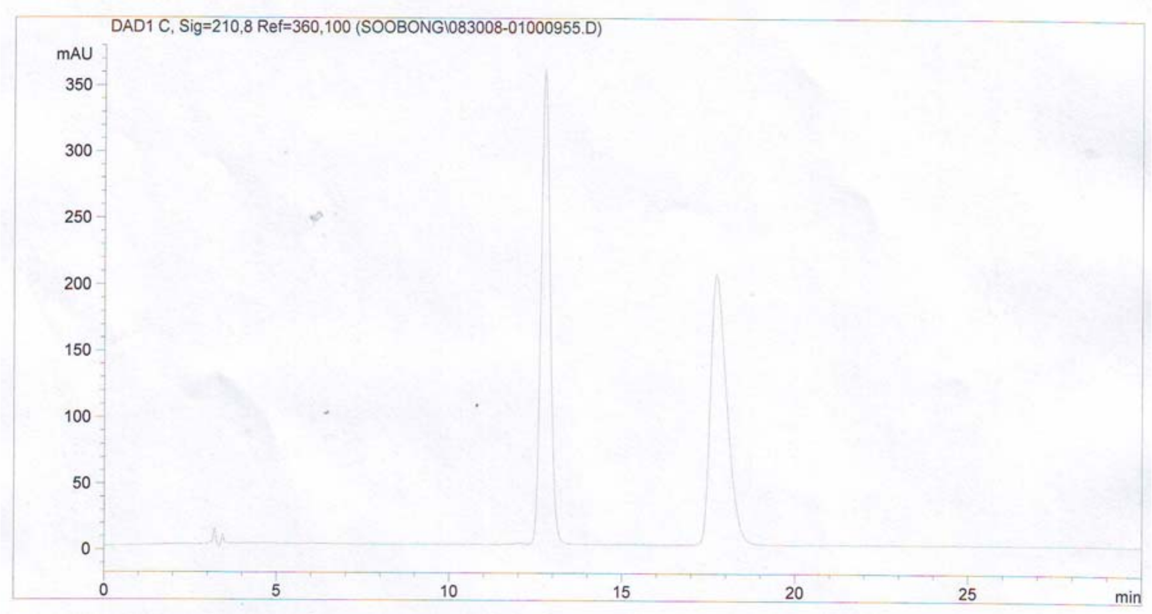


4c

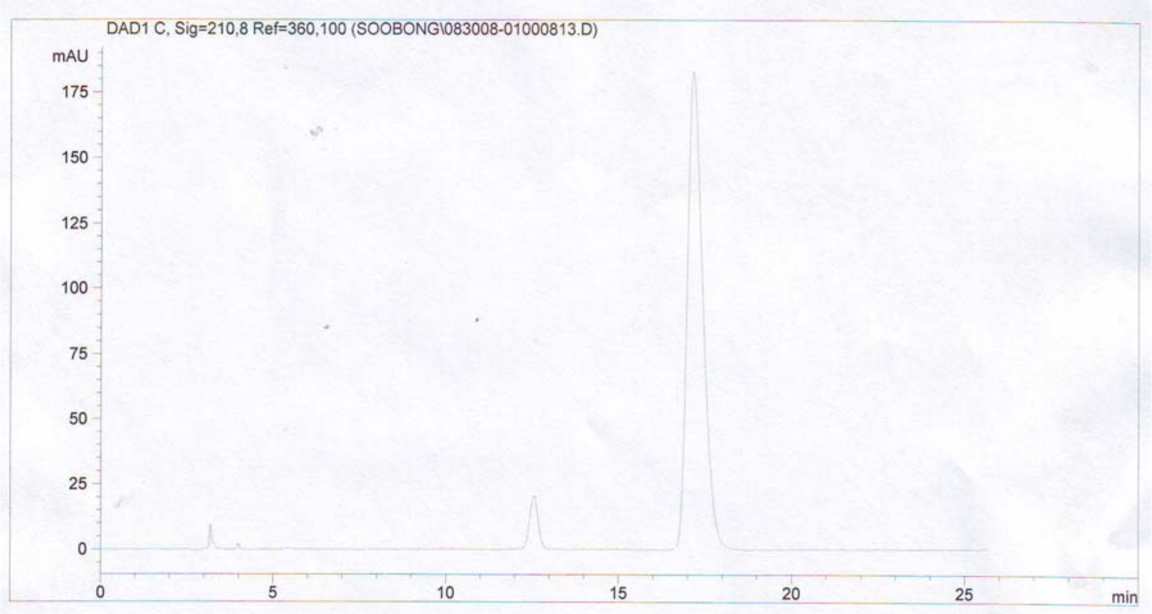
An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). Methyl 4-(hydroxymethyl)benzoate **3c** (83 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and propionaldehyde (1.5 mg, 0.025 mmol, 5 mol%) were added and the reaction mixture was allowed to stir at 40 ^{o}C for 27 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:15) provided **4c** (86 mg, 0.365 mmol) as a colorless oil in 73% yield.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 210 nm), t_{minor} = 12.5 min, t_{major} = 17.1 min; ee = 89%.

The spectroscopic properties of this compound were consistent with the data available in the literature.[3]

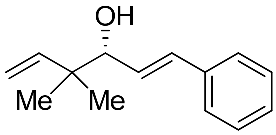


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  12.744 VB    0.2853 6596.89648  357.39426  49.4977
  2  17.707 BB    0.4970 6730.79150  203.95091  50.5023
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  12.548 BB    0.2685  345.19196   20.08661   5.7079
  2  17.140 BB    0.4738 5702.43896  182.89044  94.2921
```

(*R*,*E*)-4,4-Dimethyl-1-phenylhexa-1,5-dien-3-ol (4d)

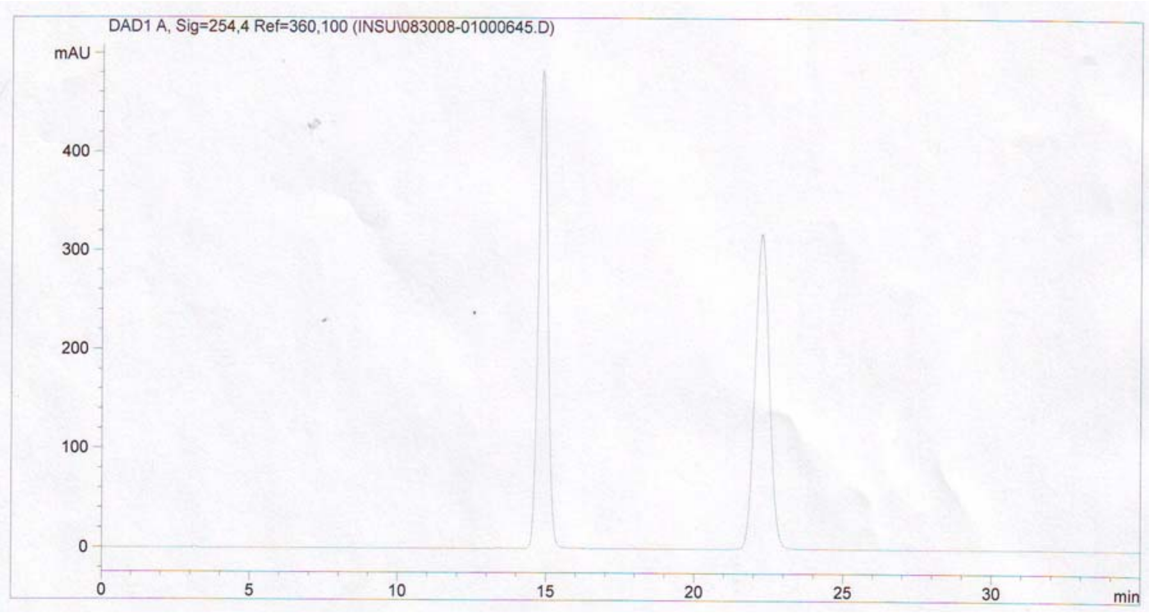


4d

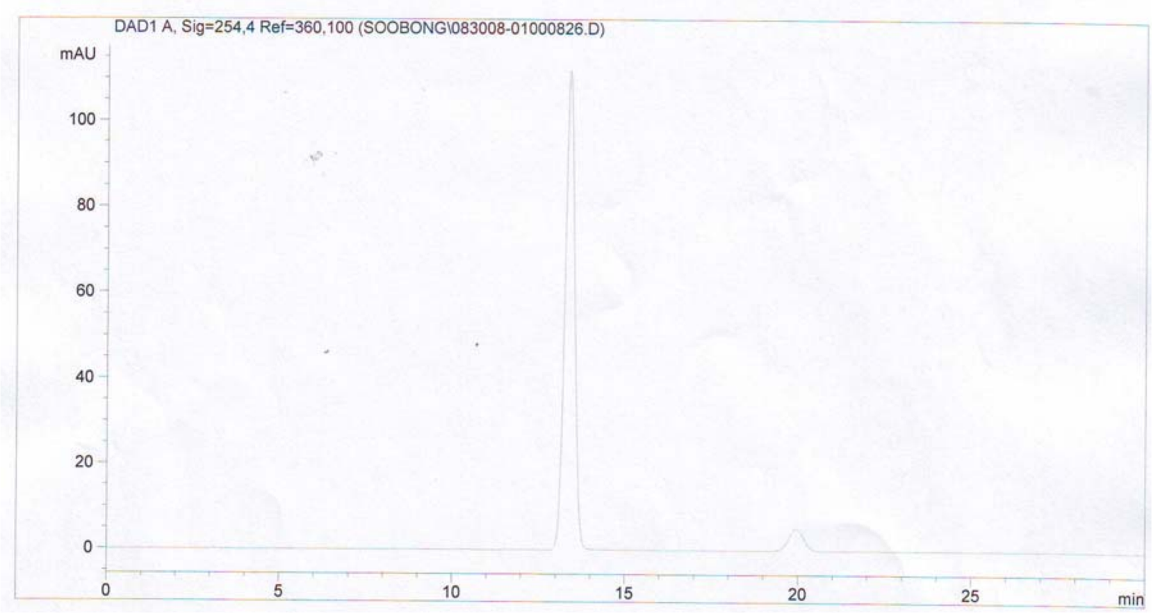
An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). Cinnamyl alcohol **3d** (67 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and propionaldehyde (1.5 mg, 0.025 mmol, 5 mol%) were added and the reaction mixture was allowed to stir at 30 ^{o}C for 28 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:30) provided **4d** (85 mg, 0.420 mmol) as a colorless oil in 84% yield.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm), t_{major} = 13.4 min, t_{minor} = 20.0 min; ee = 87%.[4]

The spectroscopic properties of this compound were consistent with the data available in the literature.[5]

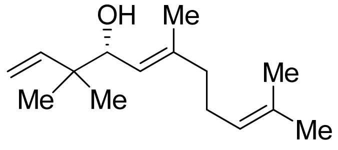


```
Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  14.869 BB    0.3390 1.05802e4  484.03745  50.0335
   2  22.259 BB    0.5173 1.05660e4  318.27399  49.9665
```



```
Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  13.374 BB    0.3115 2221.55737  111.95267  93.3313
   2  19.952 BB    0.4814  158.73332    5.15226   6.6687
```

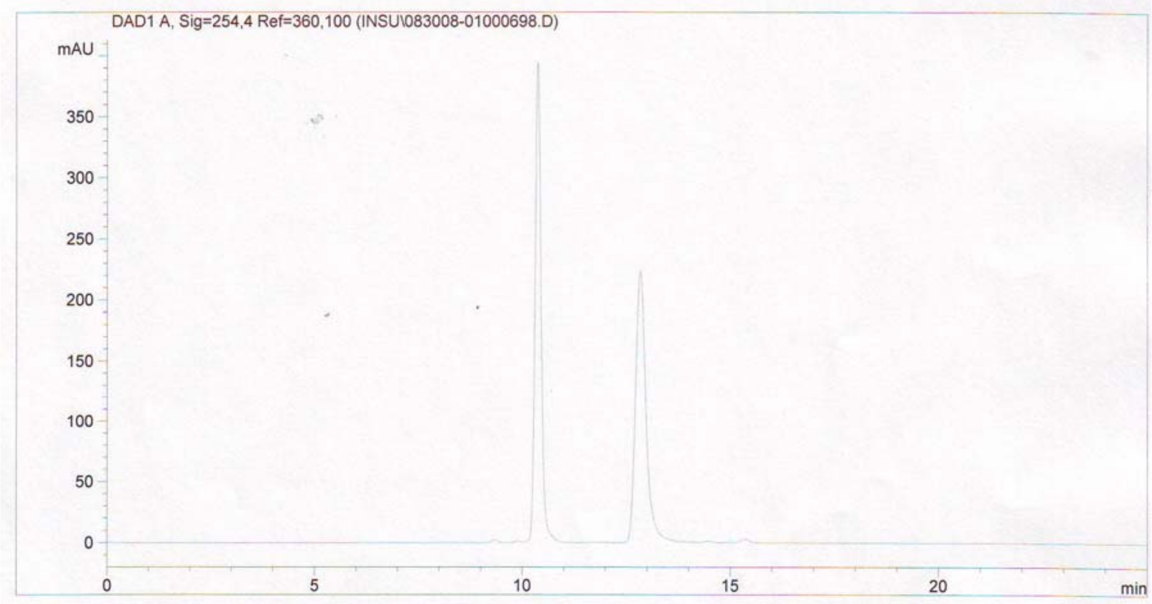
(*R,E*)-3,3,6,10-Tetramethylundeca-1,5,9-trien-4-ol (4e)



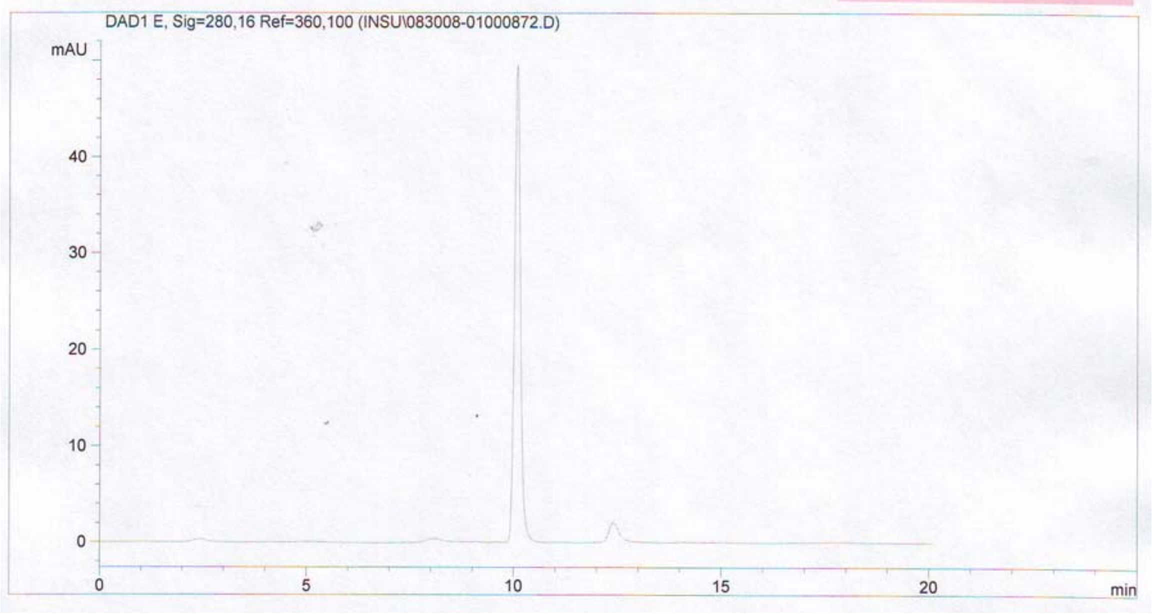
4e

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and chlorobenzene (1.0 M, 0.5 mL). Geraniol **3e** (77 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and propionaldehyde (1.5 mg, 0.025 mmol, 5 mol%) were added and the reaction mixture was allowed to stir at 30 ^{o}C for 40 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:30) provided **4e** (79 mg, 0.355 mmol) as a colorless oil in 71% yield.

HPLC: Enantiomeric excess was determined by HPLC analysis of the 3,5-nitrobenzoate derivative of the product (Chiralcel AD-H column, hexanes:*i*-PrOH = 99.5:0.5, 0.5 mL/min, 254 nm), t_{major} = 10.1 min, t_{minor} = 12.4 min; ee = 87%.

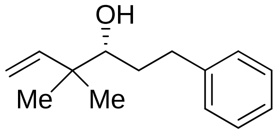


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.371 VB    0.1573 4027.62817  393.84918  50.1950
   2  12.838 VV    0.2722 3996.32739  223.94914  49.8050
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.076 BB    0.1552  497.48169   49.52344  93.4697
   2  12.404 BB    0.2581   34.75699    2.04694   6.5303
```

(*R*)-4,4-Dimethyl-1-phenylhex-5-en-3-ol (4f)

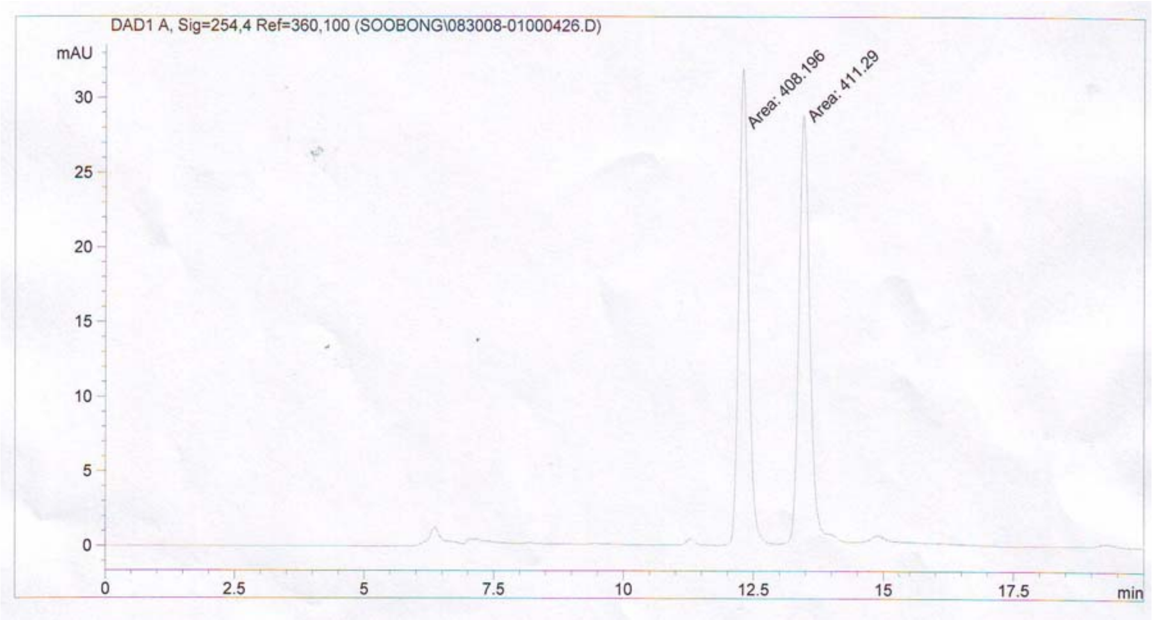


4f

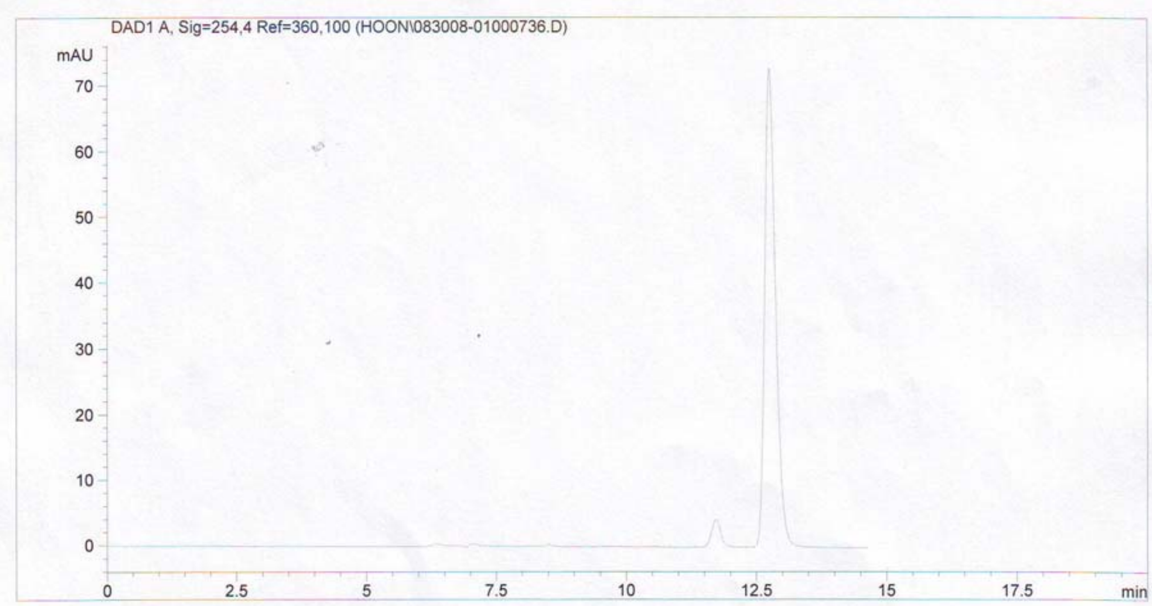
An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). 3-Phenylpropan-1-ol **3f** (68 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and propionaldehyde (1.5 mg, 0.025 mmol, 5 mol%) were added and the reaction mixture was allowed to stir at 50 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:30) provided **4f** (92 mg, 0.450 mmol) as a colorless oil in 90% yield.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 97:3, 0.5 mL/min, 254 nm), t_{minor} = 11.7 min, t_{major} = 12.7 min; ee = 91%.

The spectroscopic properties of this compound were consistent with the data available in the literature.[6]

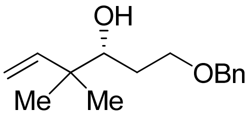


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  12.294 MM     0.2136  408.19638   31.84447  49.8112
   2  13.456 MM     0.2401  411.29044   28.54853  50.1888
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.719 BB     0.1906   52.52541    4.23711   4.7540
   2  12.745 BB     0.2204 1052.33191   72.90183  95.2460
```

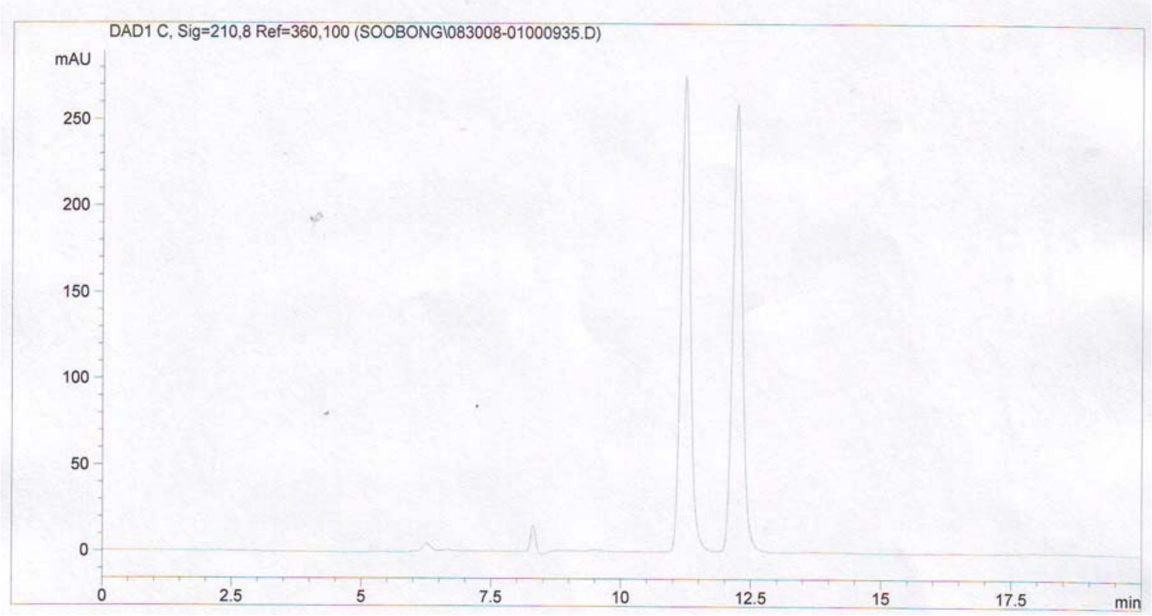
(*R*)-1-(Benzyloxy)-4,4-dimethylhex-5-en-3-ol (4g)



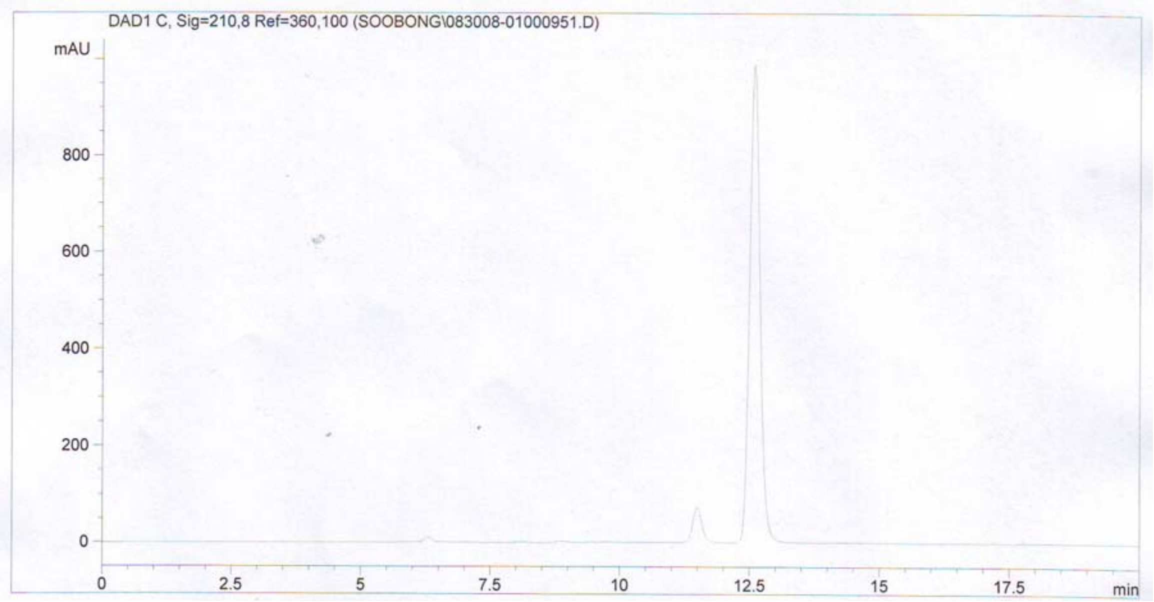
4g

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and chlorobenzene (1.0 M, 0.5 mL). 3-(Benzyloxy)propan-1-ol **3g** (82 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and isopropanol (60 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 50 °C for 72 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:20) provided **4g** (80 mg, 0.341 mmol) as a colorless oil in 68% yield.

HPLC: (Chiralcel AS-H column, hexanes:*i*-PrOH = 99:1, 0.5 mL/min, 210 nm), t_{minor} = 11.5 min , t_{major} = 12.6 min; ee = 88%.

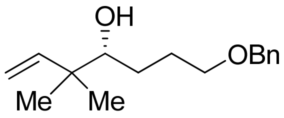


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.225 BB    0.1915 3434.01050  275.37466  49.9179
   2  12.225 BB    0.2050 3445.30688  259.36694  50.0821
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.489 BB    0.1921  892.74121   72.27936   6.1113
   2  12.580 BB    0.2139 1.37153e4   988.35419  93.8887
```

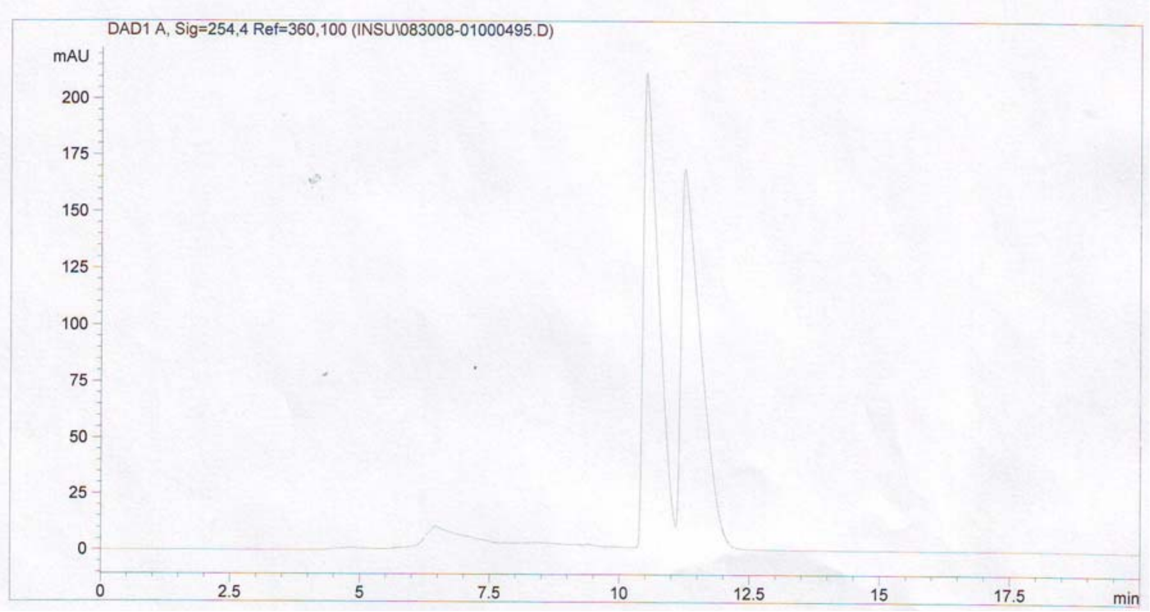
(*R*)-7-(Benzyloxy)-3,3-dimethylhept-1-en-4-ol (4h)



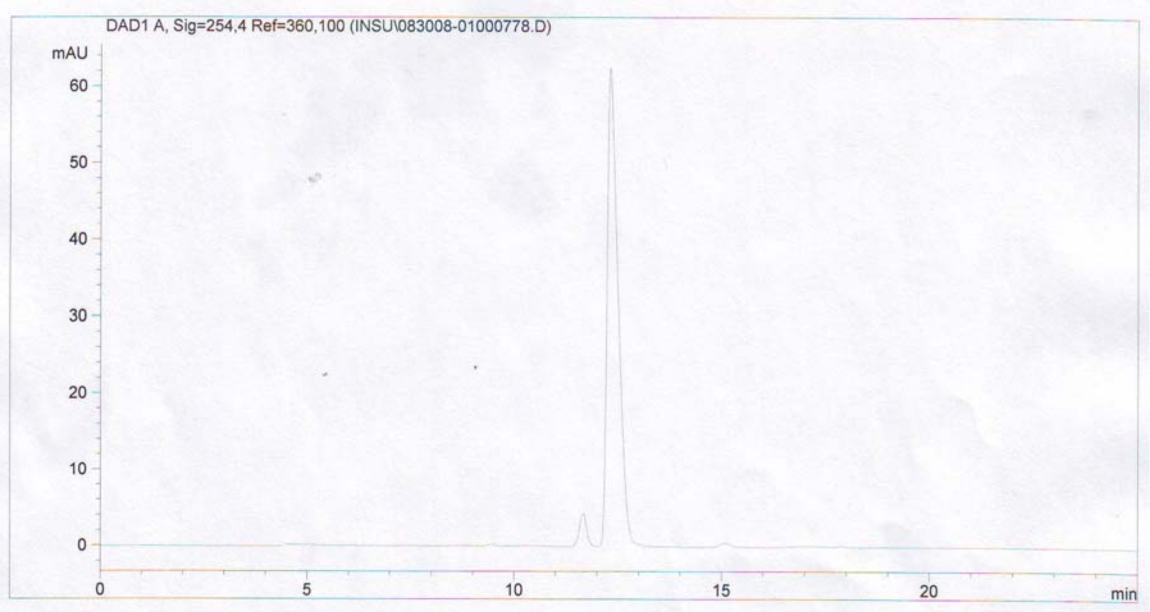
4h

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). 4-(Benzyloxy)butan-1-ol **3h** (90 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and propionaldehyde (1.5 mg, 0.025 mmol, 5 mol%) were added and the reaction mixture was allowed to stir at 50 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:10) provided **4h** (108 mg, 0.435 mmol) as a colorless oil in 87% yield.

<u>HPLC</u>: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 97:3, 0.7 mL/min, 210 nm), t_{minor} = 11.7 min , t_{major} = 12.3 min; ee = 91%.

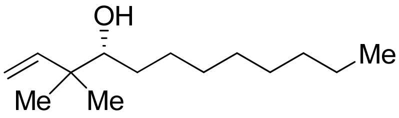


```
Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.504 VV    0.3083 4360.97510  211.71979  49.2840
   2  11.245 VB    0.3876 4487.68359  169.08885  50.7160
```



```
Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.656 BV    0.1905   53.42230    4.31202   4.4440
   2  12.299 VB    0.2827 1148.70837   62.41932  95.5560
```

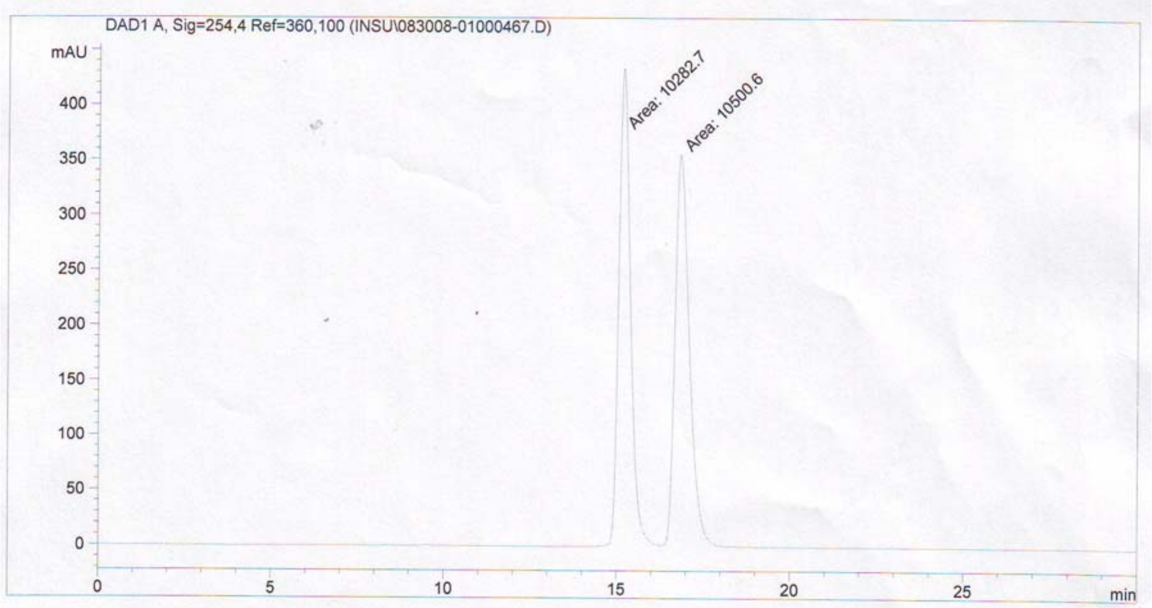
(*R*)-3,3-Dimethyldodec-1-en-4-ol (4i)



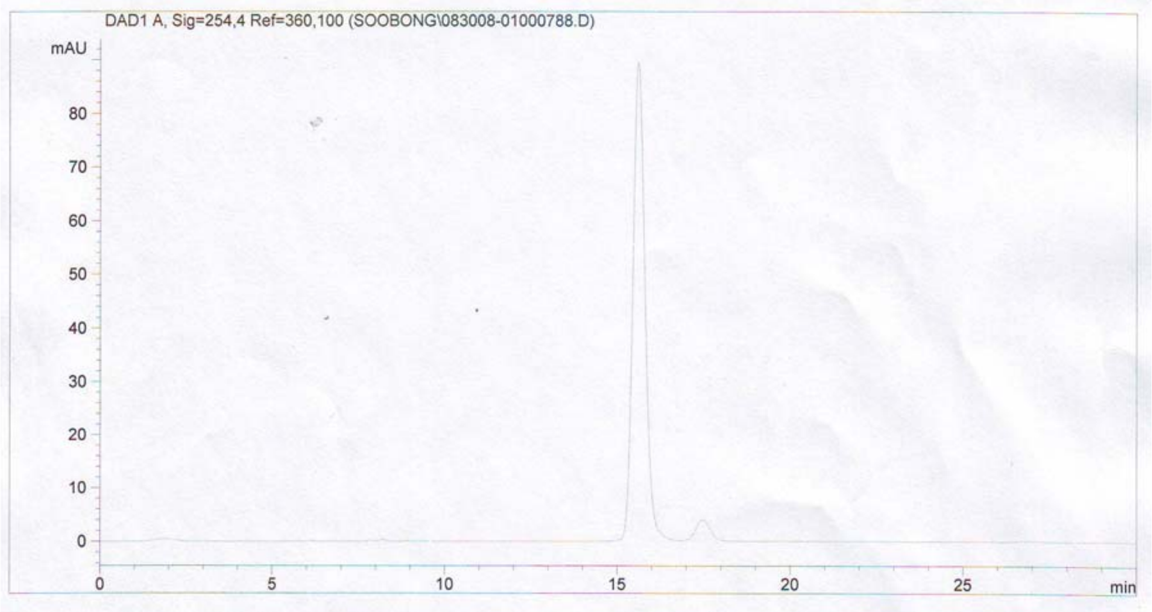
4i

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with (*S*)-Ir-complex I (25 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). Nonan-1-ol **3i** (72 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and propionaldehyde (1.5 mg, 0.025 mmol, 5 mol%) were added and the reaction mixture was allowed to stir at 50 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:30) provided **4i** (100 mg, 0.470 mmol) as a colorless oil in 94% yield.

HPLC: Enantiomeric excess was determined by HPLC analysis of the 3,5-nitrobenzoate derivative of the product (Chiralcel OD-H column, hexanes:*i*-PrOH = 99:1, 0.5 mL/min, 254 nm), t_{major} = 15.6 min, t_{minor} = 17.5 min; ee = 90%.[7]



```
Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  15.166 MM    0.3951 1.02827e4  433.81290  49.4757
  2  16.816 MM    0.4893 1.05006e4  357.65274  50.5243
```



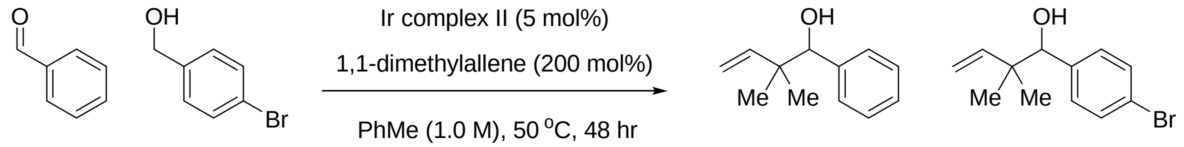
```
Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  15.606 BB    0.3802 2192.81152   89.40071  94.7650
  2  17.476 BB    0.4677  121.13474    3.99556   5.2350
```

Experimental Details for Mechanistic Studies

Procedure for the Preparation of Ir-Complex II

To a mixture of $[Ir(cod)Cl]_2$ (100 mg, 0.15 mmol, 100 mol%), BIPHEP (157 mg, 0.3 mmol, 200 mol%), Cs_2CO_3 (195 mg, 0.6 mmol, 400 mol%) and *m*-nitrobenzoic acid (100 mg, 0.6 mmol, 400 mol%) in a sealed tube under N_2 atmosphere was added THF (3 mL, 0.05 M). The reaction mixture was heated at 80 ^{o}C for 30 min and was then allowed to cool to the ambient temperature. Allyl acetate (75 mg, 0.75 mmol, 500 mol%) was added and the reaction mixture was allowed to stir for an additional 90 min at 80 ºC, at which point the reaction mixture was allowed to cool to the ambient temperature. The reaction mixture was filtered and washed with THF (15 mL) until all yellow residue was dissolved. 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 (213 mg, 0.231 mmol, 77% yield).

Competition Experiments

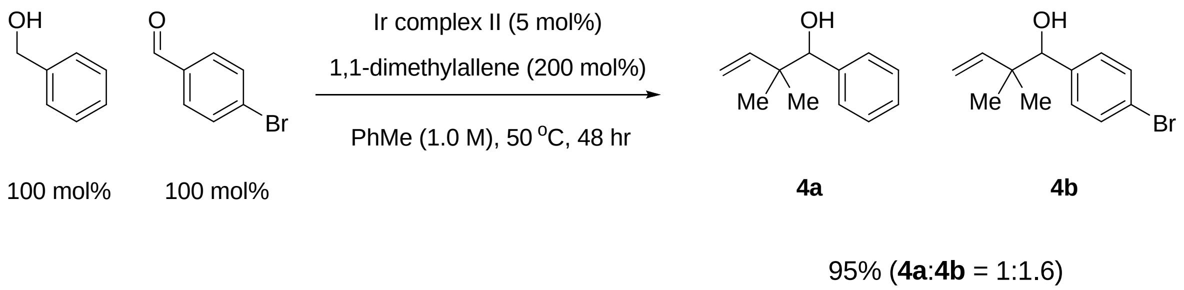


100 mol% 100 mol%

4a **4b**

87% (**4a**:**4b** = 1:1.2)

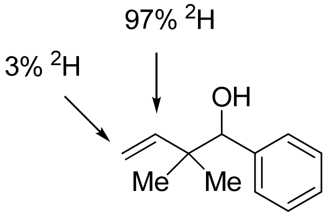
An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with Ir-complex II (23 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). Benzaldehyde **2a** (53 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and 4-bromobenzyl alcohol **3b** (94 mg, 0.5 mmol, 100 mol%) were added and the reaction mixture was allowed to stir at 50 ^{o}C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:50) provided a 1:1.2 mixture of **4a** and **4b** (95 mg, *ca.* 87%) as a colorless oil. (*N.B.* yield is based upon 100 mol% of alcohol as the limiting reagent and is calculated based upon product stoichiometry).



An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with Ir-complex II (23 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). 4-Bromobenzaldehyde **2b** (93 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and benzyl alcohol **3a** (54 mg, 0.5 mmol, 100 mol%) were added and the action mixture was allowed to stir at 50 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:50) provided a 1:1.6 mixture of **4a** and **4b** (107 mg, *ca.* 95%) as a colorless oil. (*N.B.* yield is based upon 100 mol% of alcohol as the limiting reagent and is calculated based upon product stoichiometry).

Isotopic Labeling Experiments

3-*Deuterio*-2,2-dimethyl-1-phenylbut-3-en-1-ol (*deuterio*-4a)



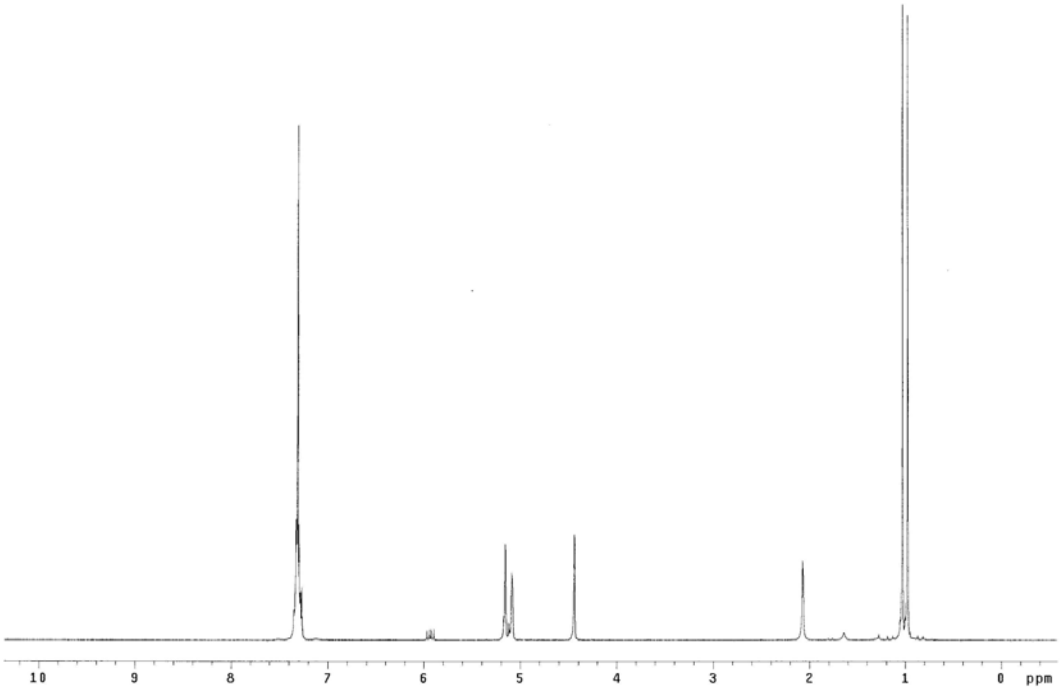
***deuterio*-4a**

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with Ir-complex II (23 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). Benzaldehyde **2a** (53 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and d_8-isopropanol (68 mg, 1.0 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 50 ^{o}C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2; ethyl acetate:hexanes, 1:50) provided *deuterio*-**4a** (65 mg, 0.365 mmol) as a colorless oil in 73% yield.

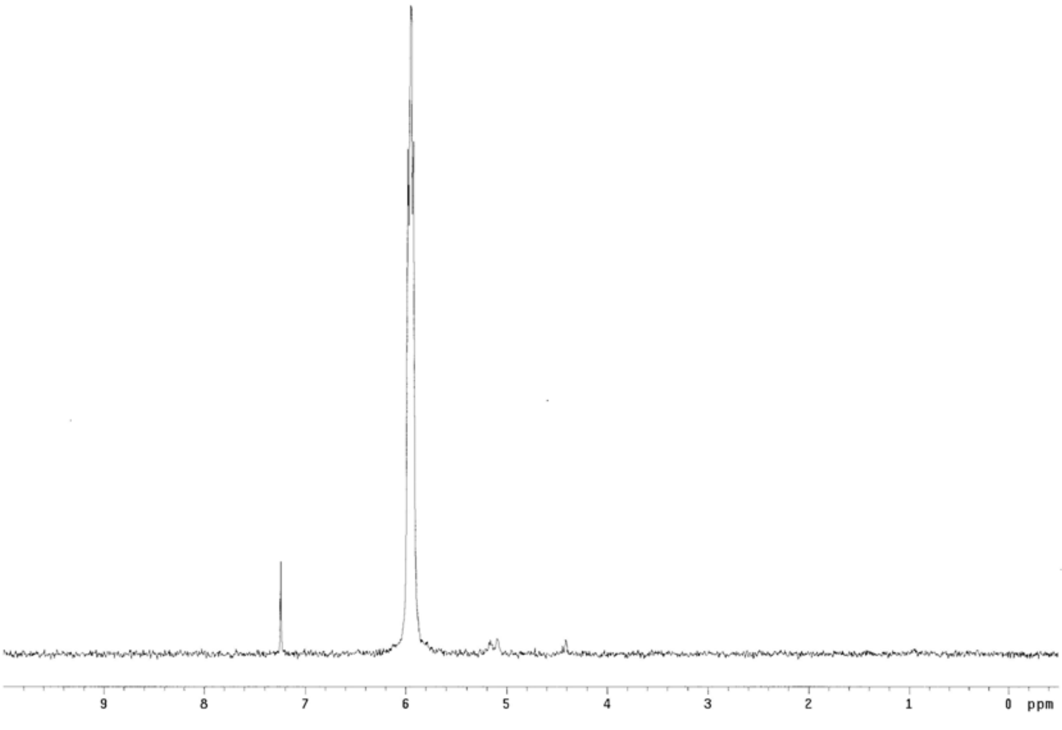
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.23 (m, 5H), 5.90 (dd, *J* = 17.6, 10.8 Hz, 0.18H), 5.18-5.09(m, 1.96H), 4.44 (s, 1H), 2.10 (s, 1H), 1.00 (s, 3H), 0.95 (s, 3H).

^{2}H NMR (77 MHz, $CHCl_3$): δ 5.95 (s, 0.97^{2}H), 5.18-5.07 (m, 0.03^{2}H)*. *(this signal corresponds to 3% total ^{2}H incorporation in the terminal vinylic protons)

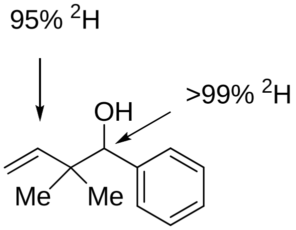
^{1}H NMR



^{2}H NMR



1,3-*Deuterio*-2,2-dimethyl-1-phenylbut-3-en-1-ol (*deuterio*-4a')



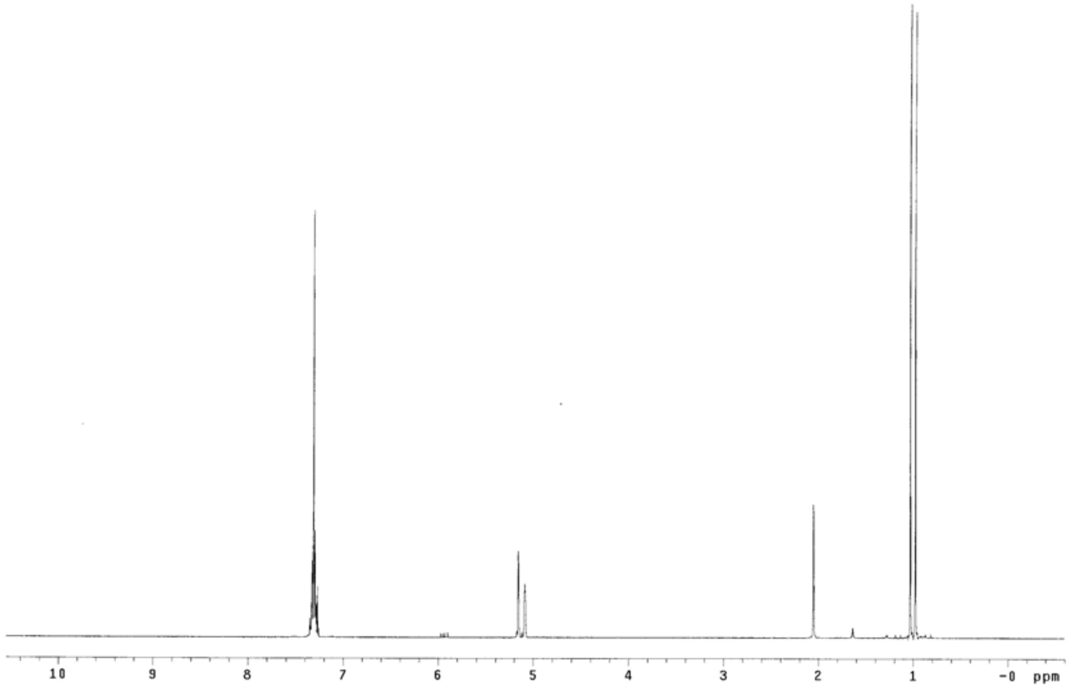
***deuterio*-4a'**

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with Ir-complex II (23 mg, 0.025 mmol, 5 mol%) and toluene (1.0 M, 0.5 mL). d_2-Benzyl alcohol (56 mg, 0.5 mmol, 100 mol%), 1,1-dimethylallene (68 mg, 1.0 mmol, 200 mol%) and propionaldehyde (1.5 mg, 0.025 mmol, 5 mol%) were added and the reaction mixture was allowed to stir at 50 ^{o}C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:50) provided *deuterio*-**4a'** (70 mg, 0.392 mmol) as a colorless oil in 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.23 (m, 5H), 5.90 (dd, *J* = 17.6, 10.8 Hz, 0.09H), 5.12 (d, *J* = 10.8 Hz, 1H), 5.06 (d, *J* = 17.6 Hz, 1H), 4.39 (s, 1H), 2.10 (s, 1H), 1.00 (s, 3H), 0.95 (s, 3H).

^{2}H NMR (77 MHz, $CHCl_3$): δ 5.95 (m, 0.95^{2}H), 4.40 (s, 1.0^{2}H).

^{1}H NMR



^{2}H NMR