Supporting Information

anti-Diastereo- and Enantioselective Carbonyl Crotylation from the Alcohol or Aldehyde Oxidation Level Employing a Cyclometallated Iridium Catalyst: α-Methyl Allyl Acetate as a Surrogate to Preformed Crotylmetal Reagents

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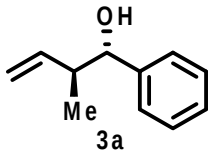
General Methods

All reactions were run under an atmosphere of nitrogen. Tetrahydrofuran (THF) was purifed using the Pure-Solv MD-5 Solvent Purification System. Anhydrous solvents were transferred using an oven-dried syringe. Sealed tubes (13x100 mL) were purchased from Fischer Scientific and were dried in an oven overnight and cooled under a stream of nitrogen prior to use. Commercially available α-methyl allyl acetate (acetic acid 3-buten-2-yl ester, TCI), alcohols and aldehydes were purified by distillation or recrystallisation prior to use. Cesium carbonate was purchased from Alfa Aesar and used directly without further purification. Isopropanol was purchased from 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+1, M or M-1) or a suitable fragment ion. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) spectra were recorded on a Varian Gemini (400 MHz) spectrometer in $CDCl_3$ solution. 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).

Detailed Procedure and Spectral Data for *anti*-Diastereo- and Enantioselective Crotylation Adducts (3a-3j) from Alcohols (1a-1j)

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



3a

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Benzyl alcohol **1a** (43.3 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:20) provides **3a** (42.4 mg, 0.261 mmol, *anti*:*syn* = 6:1) as a colorless oil in 65% yield.

TLC (SiO_2): R_f = 0.26 (ethyl acetate:hexanes, 1:15).

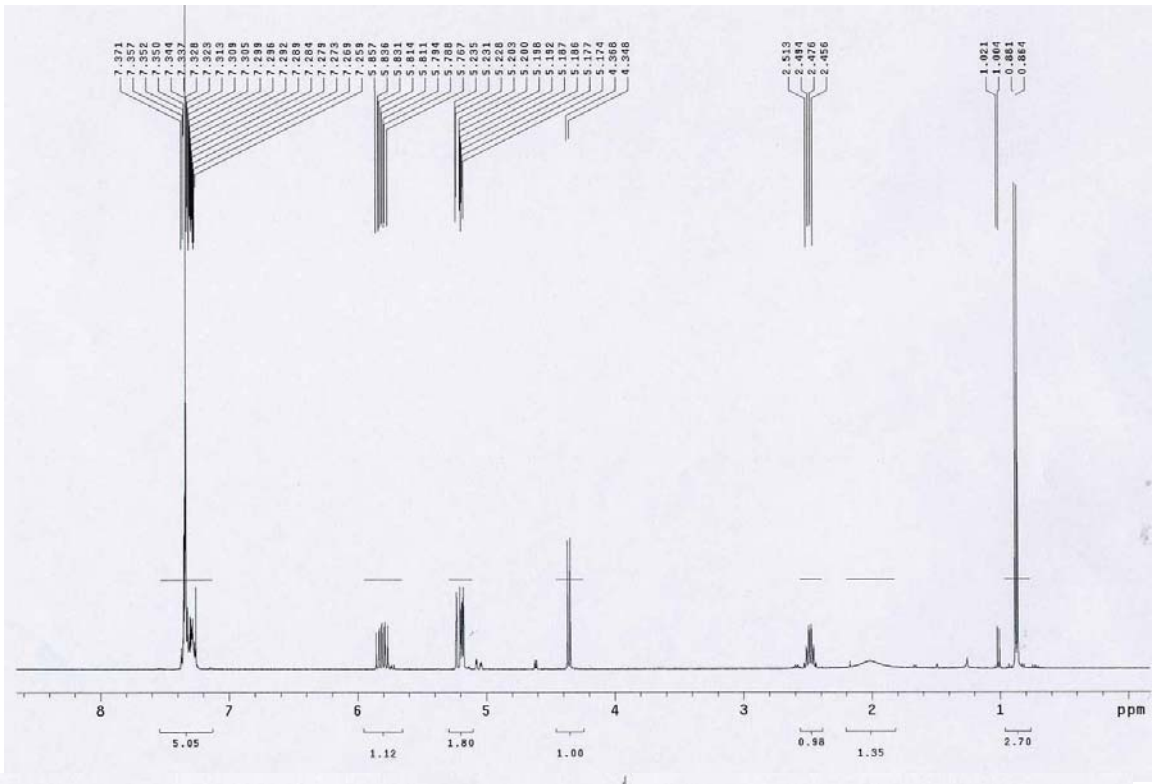
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.38 (m, 5H), 5.86-5.76 (m, 1H), 5.24-5.17 (m, 2H), 4.35 (d, *J* = 8.0 Hz, 1H), 2.52-2.45 (m, 1H), 2.07 (br s, 1H), 0.87 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 140.9, 128.5, 127.9, 127.1, 117.1, 78.1, 46.6, 16.8.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 99:1, 0.5 mL/min, 210 nm), t_{major} = 27.5 min, t_{minor} = 30.8 min; ee = 95%.[1]

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

[1] Nemoto, T.; Hitomi, T.; Nakamura, H.; Jin, L.; Hatano, K.; Hamada, Y. *Tetrahedron: Asymmetry* **2007**, *18*, 1844–1849.
[2] Jiang, S.; Agoston, E. G.; Chen, T.; Cabal, M.-P.; Turos, E. *Organometallics* **1995**, *14*, 4697–4709.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7.269
7.259
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5.811
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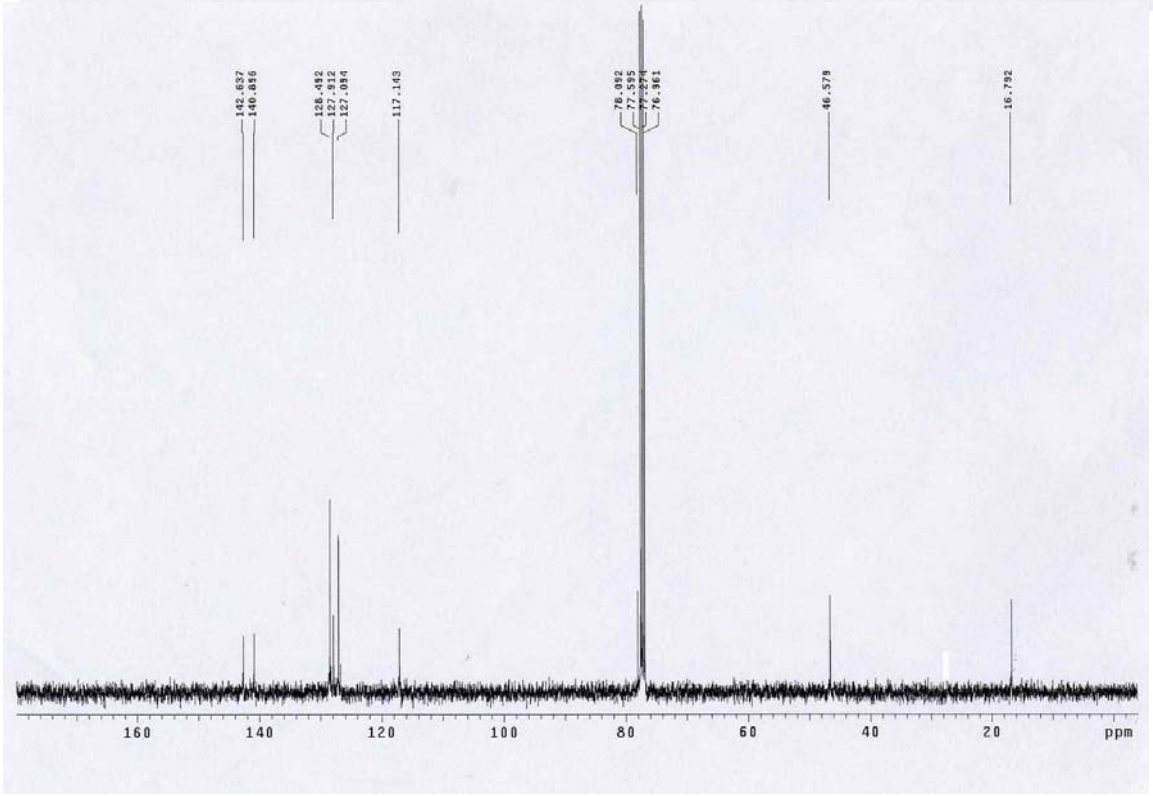
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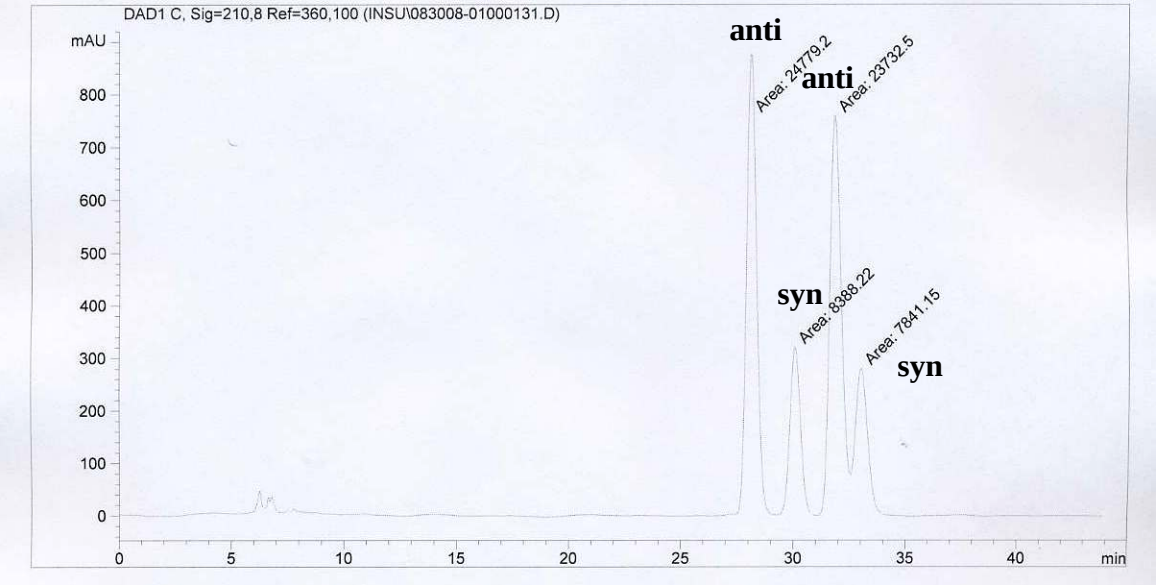

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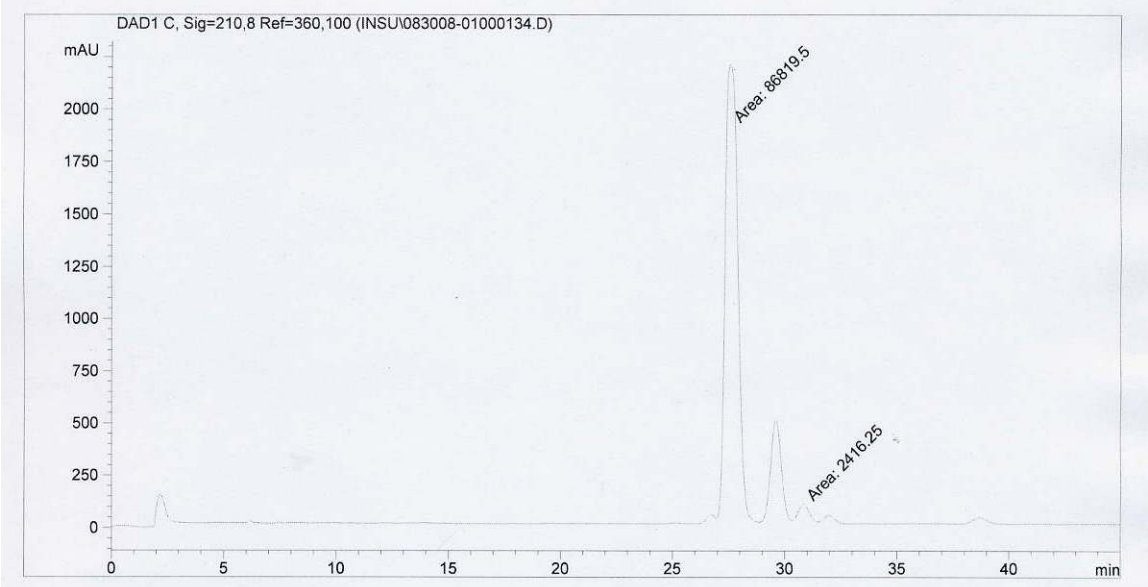

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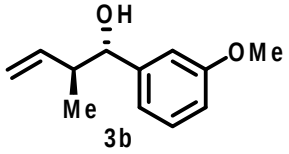
(1*S*,2*S*)-1-(3-Methoxyphenyl)-2-methylbut-3-en-1-ol (3b)



3b

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. 3-Methoxybenzyl alcohol **1b** (55.3 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:15) provides **3b** (53.9 mg, 0.280 mmol, *anti*:*syn* = 6:1) as a colorless oil in 70% yield.

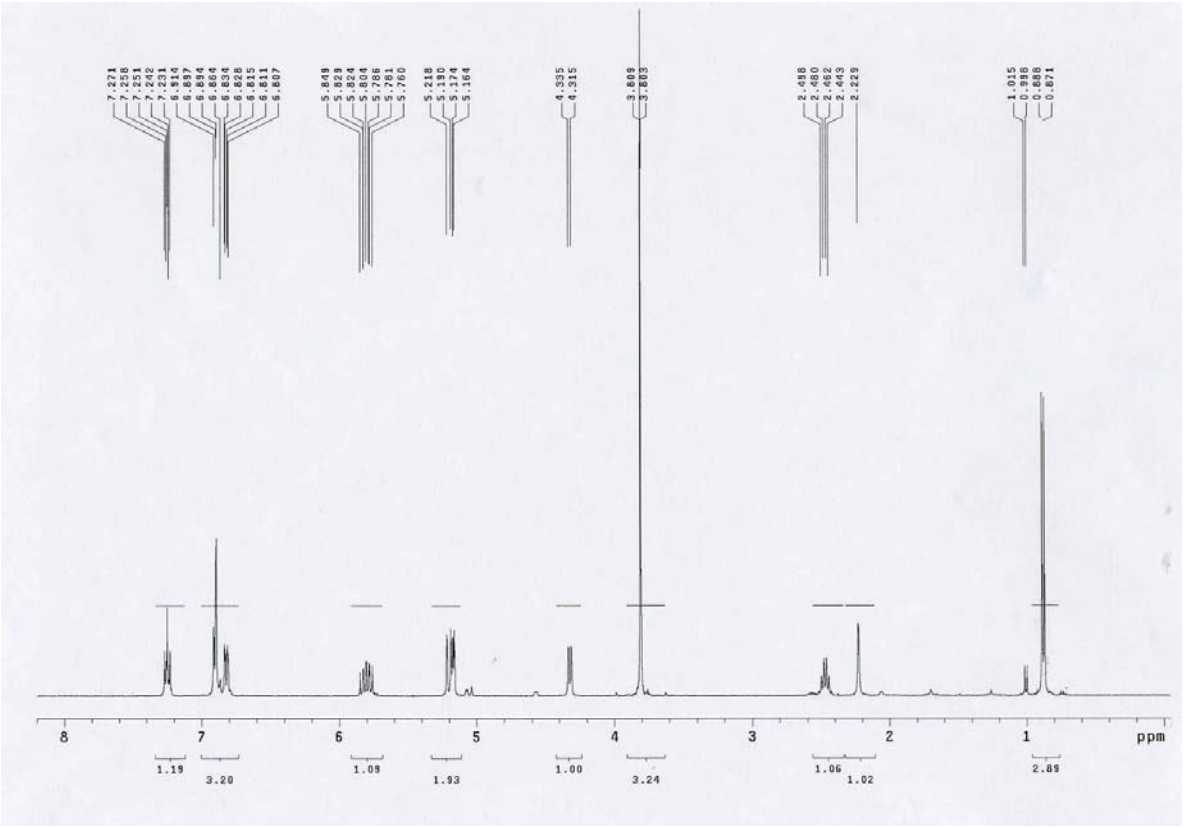
TLC (SiO_2): R_f = 0.30 (ethyl acetate:hexanes, 1:10).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.23 (m, 1H), 6.92-6.80 (m, 3H), 5.85-5.76 (m, 1H), 5.22-5.16 (m, 2H), 4.32 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 2.50-2.44 (m, 1H), 2.22 (br s, 1H), 0.87 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 144.4, 140.9, 129.4, 119.5, 117.0, 113.3, 112.5, 78.0, 55.5, 46.4, 16.8.

HPLC: (Chiralpak AD-H column, hexanes:*i*-PrOH = 96:4, 0.5 mL/min, 254 nm), t_{minor} = 24.5 min, t_{major} = 28.0 min; ee = 95%.

The spectroscopic properties of this compound were consistent with the data available in the literature.[2]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5.760
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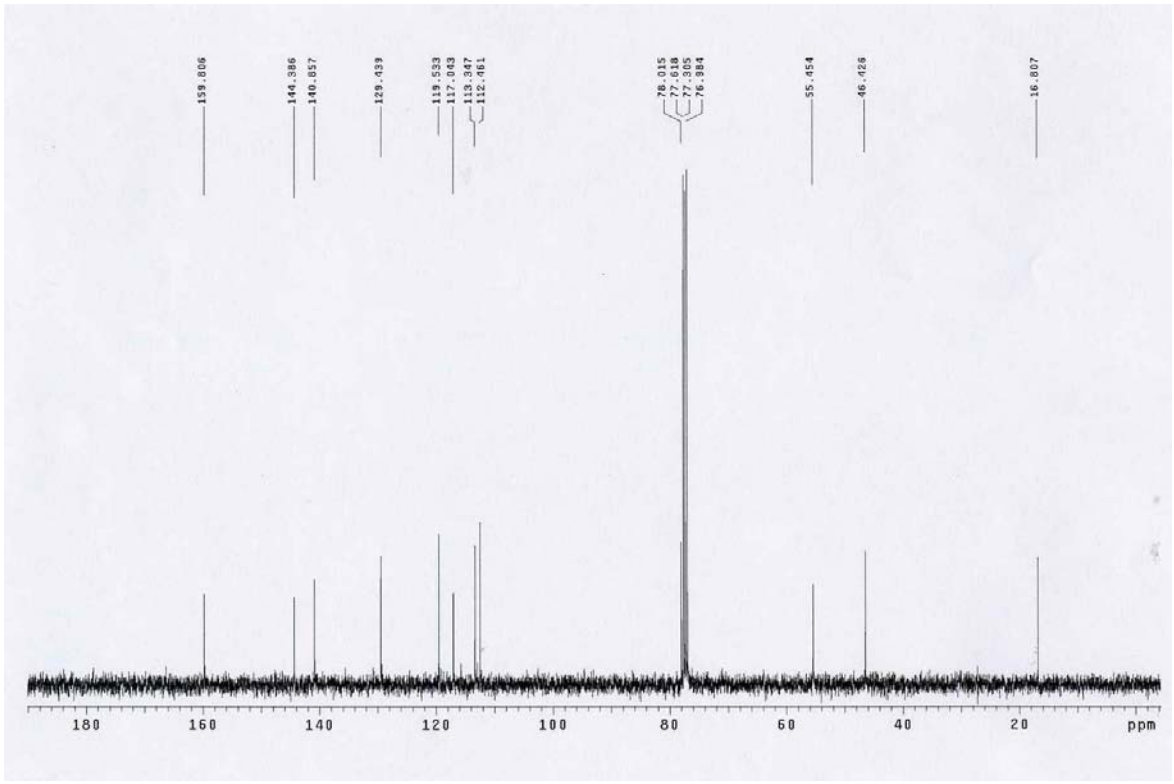
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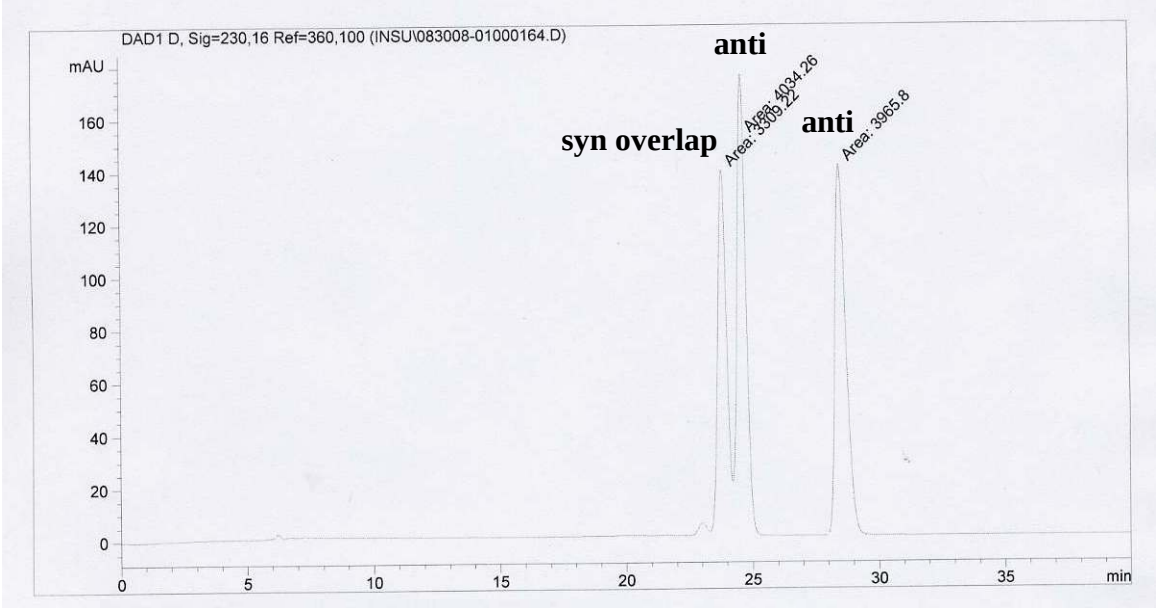

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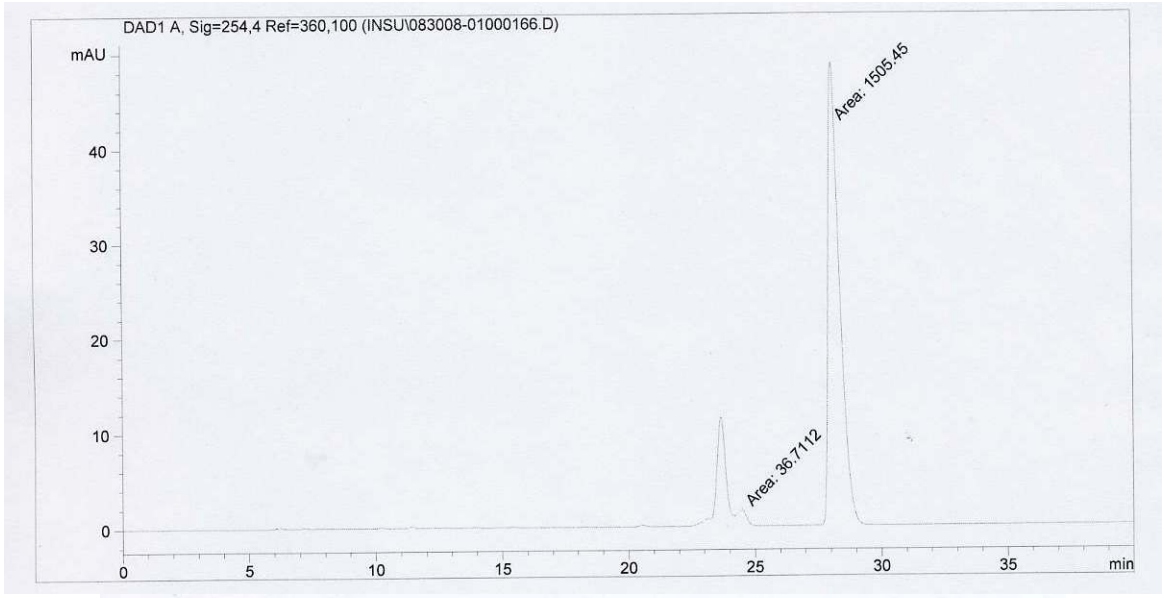
2	24.613	MM	0.3870	4034.26050	173.73439	35.6721
3	28.466	MM	0.4754	3965.80420	139.04333	35.0668



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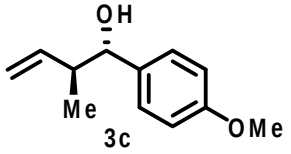
1	24.501	MM	0.4529	36.71121	1.35110	2.3805
2	28.083	MM	0.5211	1505.44727	48.15324	97.6195

(1*S*,2*S*)-1-(4-Methoxyphenyl)-2-methylbut-3-en-1-ol (3c)



3c

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. 4-Methoxybenzyl alcohol **1c** (55.3 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 80 ^oC for 72 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes:triethylamine, 1:20:0.01) provides **3c** (51.8 mg, 0.269 mmol, *anti*:*syn* = 5:1) as a colorless oil in 67% yield.

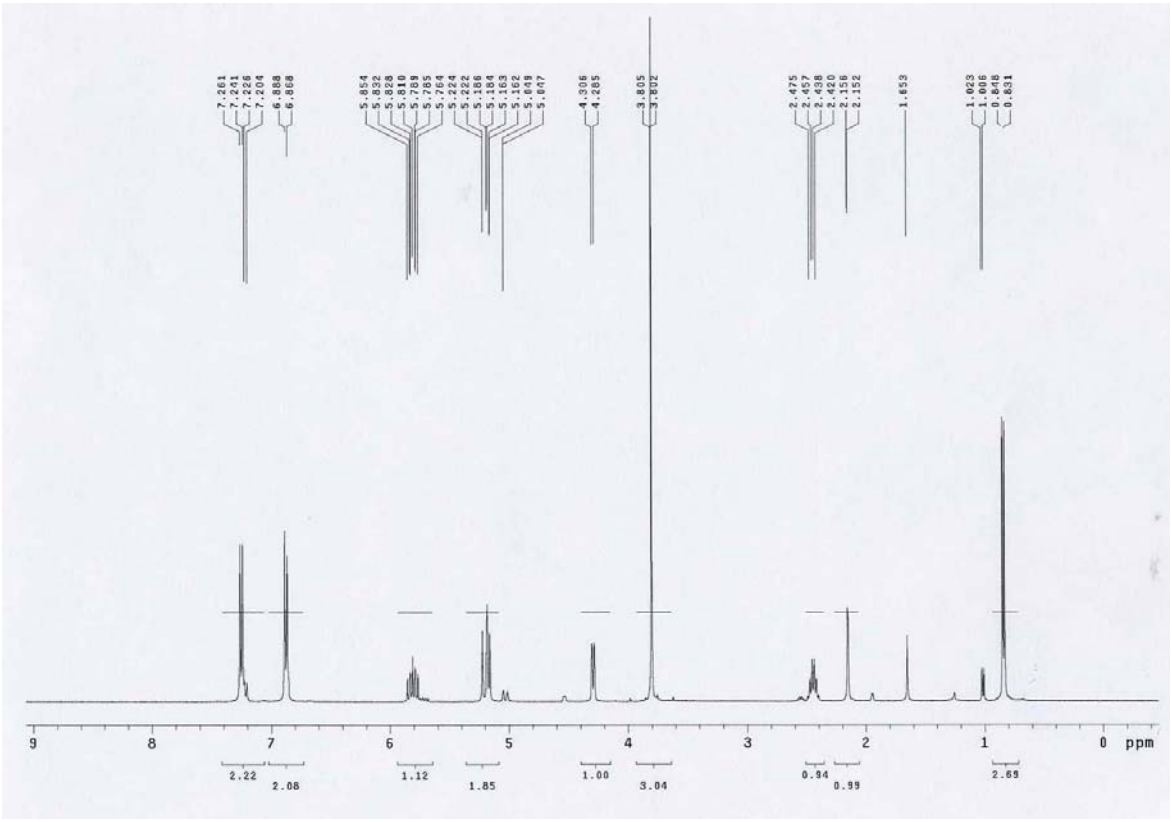
TLC (SiO_2): R_f = 0.28 (ethyl acetate:hexanes, 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 5.86-5.76 (m, 1H), 5.23-5.16 (m, 2H), 4.29 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 2.48-2.42 (m, 1H), 2.15 (br s, 1H), 0.83 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 141.2, 134.8, 128.2, 117.0, 113.9, 77.7, 55.5, 46.7, 16.8.

HPLC: (Chiralpak AD-H/AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 230 nm), t_{minor} = 41.2 min, t_{major} = 48.9 min; ee = 90%.

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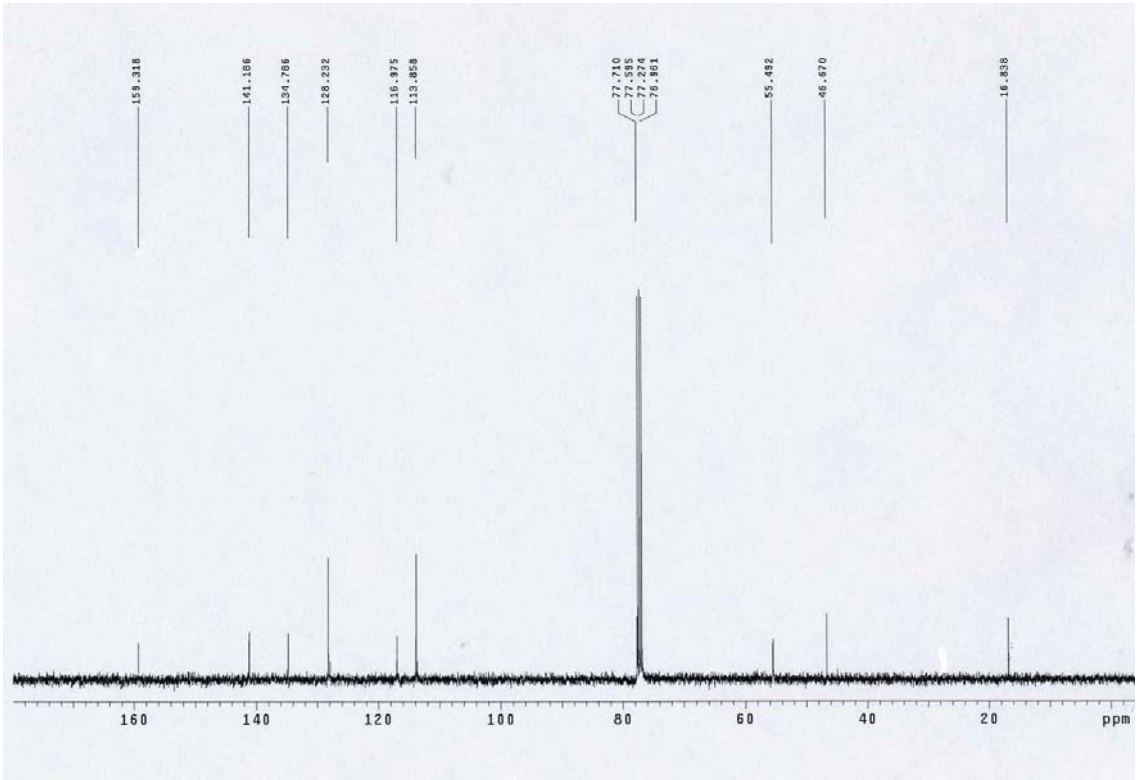
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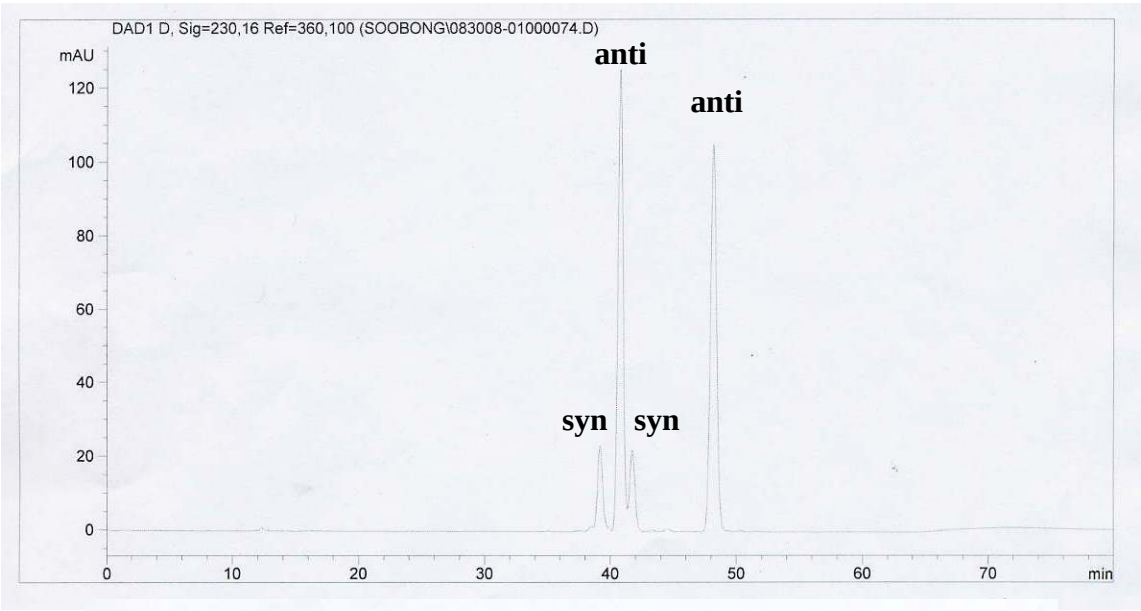

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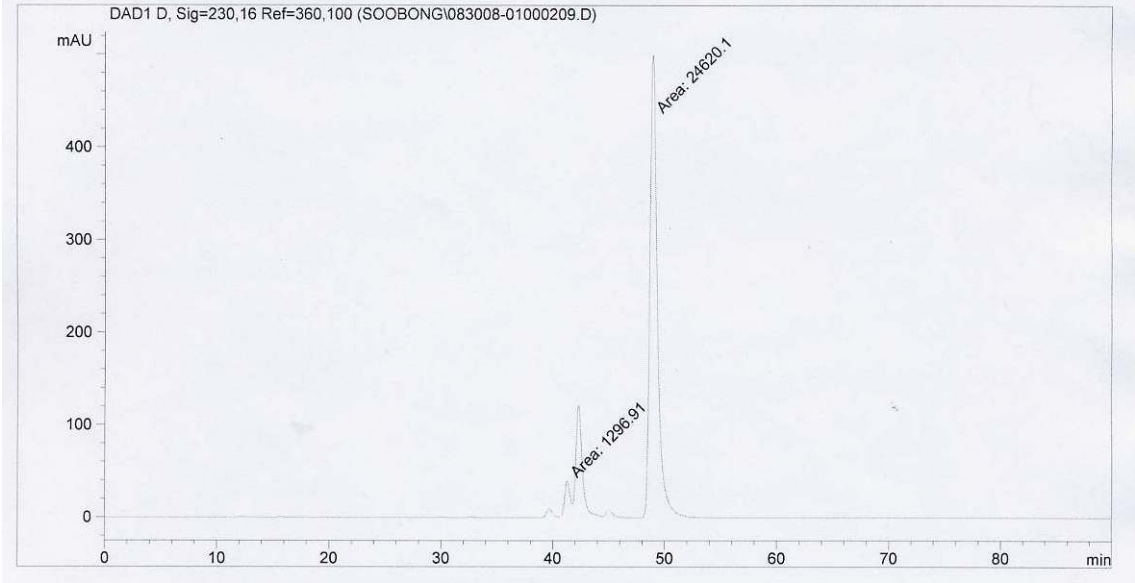

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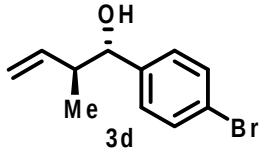
(1*S*,2*S*)-1-(4-Bromophenyl)-2-methylbut-3-en-1-ol (3d)



3d

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. 4-Bromobenzyl alcohol **1d** (74.8 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes:triethylamine, 1:15:0.01) provides **3d** (70.5 mg, 0.292 mmol, *anti*:*syn* = 8:1) as a colorless oil in 73% yield.

TLC (SiO_2): R_f = 0.26 (ethyl acetate:hexanes, 1:15).

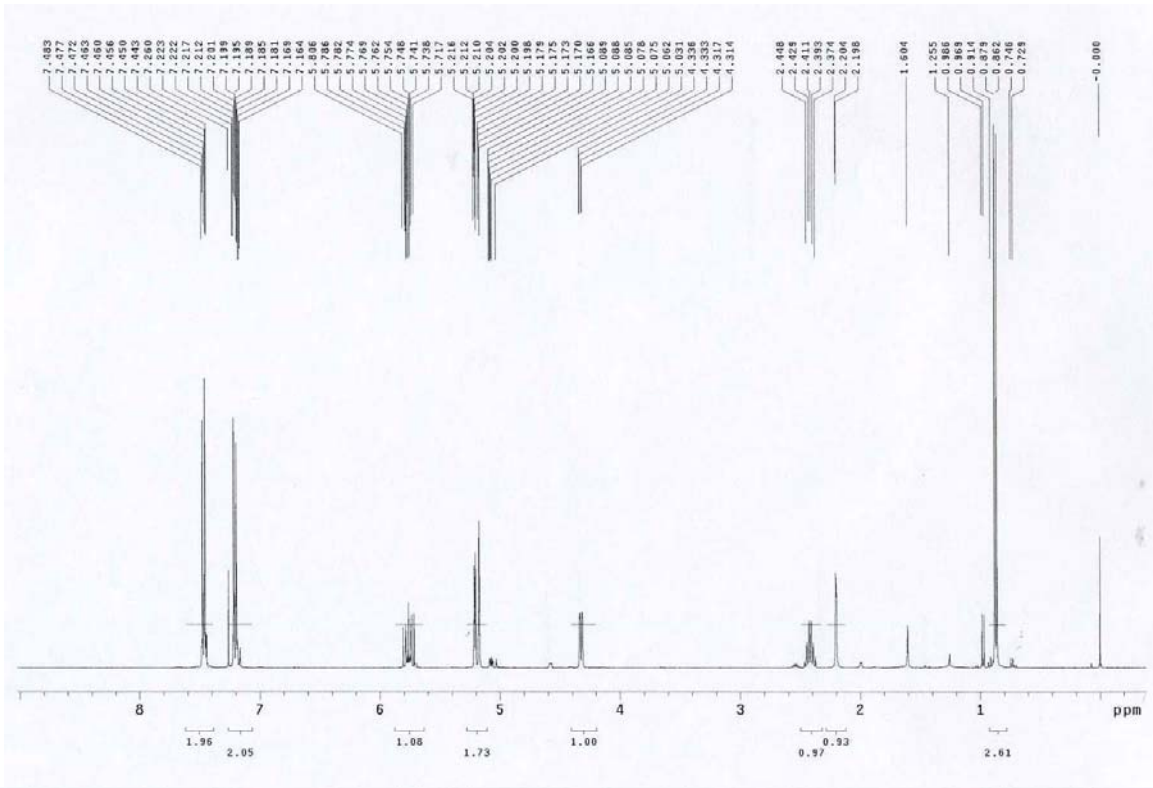
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.81-5.71 (m, 1H), 5.22-5.16 (m, 2H), 4.32 (d, *J* = 7.6 Hz, 1H), 2.45-2.37 (m, 1H), 2.20 (br s, 1H), 0.87 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 140.1, 131.3, 128.6, 121.4, 117.3, 77.1, 46.4, 16.4.

HPLC: (Chiralpak AS-H/AS-H column, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm), t_{minor} = 30.0 min, t_{major} = 34.4 min; ee = 95%.

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

[3] Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. *Tetrahedron* **2001**, *57*, 835–843.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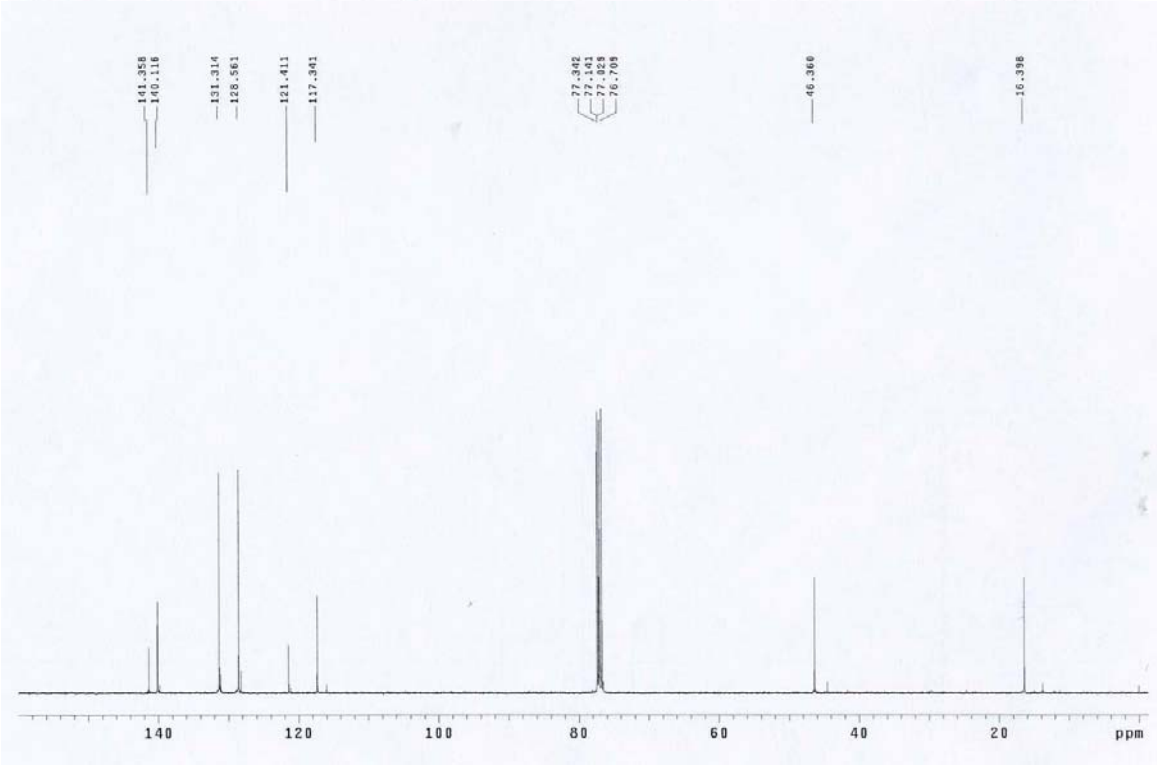
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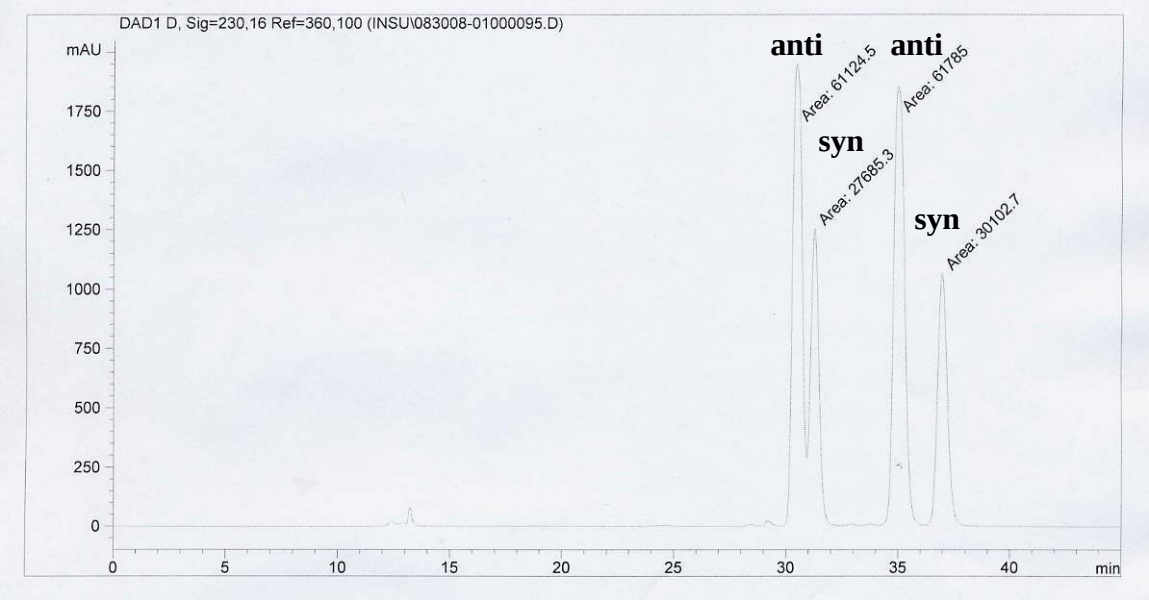

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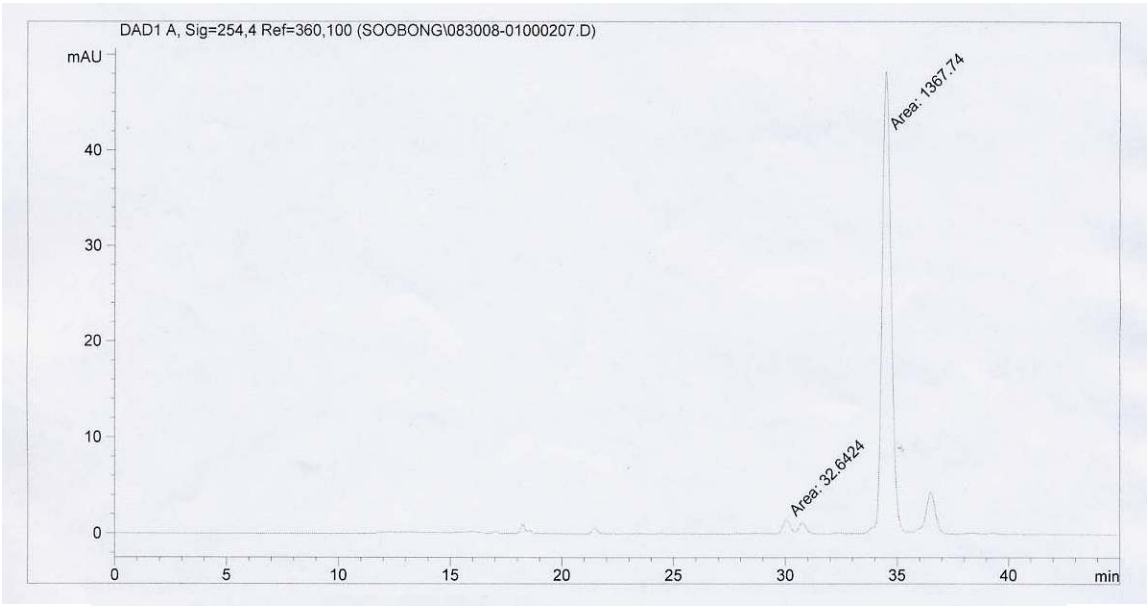
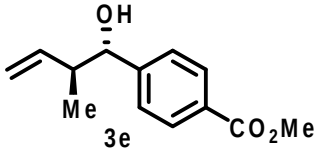
2	31.244	MM	0.3686	2.76853e4	1251.77246	15.3213
3	34.965	MM	0.5588	6.17850e4	1842.82361	34.1925
4	36.940	MM	0.4762	3.01027e4	1053.47668	16.6592



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.030	MM	0.3707	32.64238	1.46759	2.3310
2	34.475	MM	0.4723	1367.74329	48.26240	97.6690

Methyl 4-((1*S*,2*S*)-1-hydroxy-2-methylbut-3-enyl)benzoate (3e)



To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-C3-TUNEPHOS (11.9 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Methyl 4-(hydroxymethyl)benzoate **1e** (66.5 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:8) provides **3e** (67.7 mg, 0.307 mmol, *anti*:*syn* = 8:1) as a pale yellow oil in 77% yield.

TLC (SiO_2): R_f = 0.30 (ethyl acetate:hexanes, 1:6).

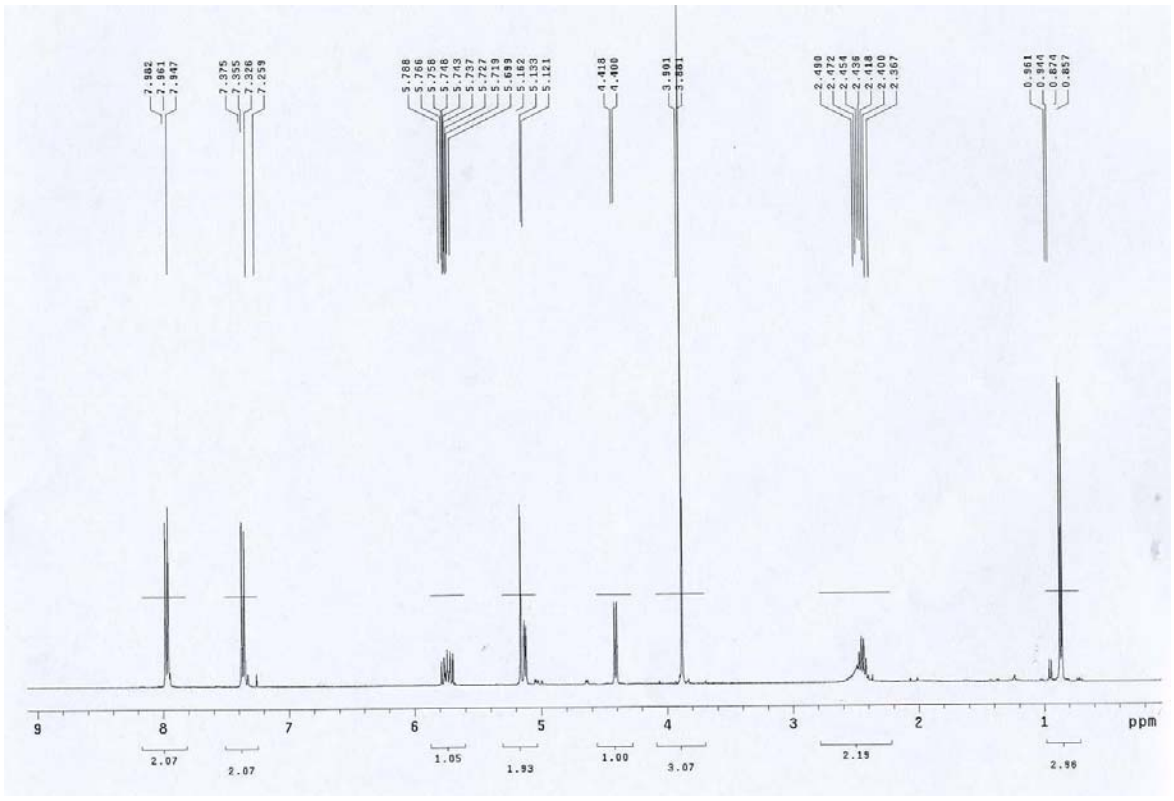
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.79-5.69 (m, 1H), 5.17-5.12 (m, 2H), 4.40 (d, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 2.49-2.36 (m, 2H), 0.86 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 147.9, 140.1, 129.7, 129.6, 127.0, 117.5, 77.3, 52.3, 46.5, 16.6.

HPLC: (Chiralpak AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 254 nm), t_{minor} = 25.3 min, t_{major} = 30.3 min; ee = 97%.

The spectroscopic properties of this compound were consistent with the data available in the literature.[4]

[4] Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2005**, *7*, 3577–3579.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5.121
4.418
4.400
3.901
3.881
2.480
2.472
2.454
2.436
2.418
2.400
2.367
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0.944
0.874
0.857
9
8
7
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1.05
1.93
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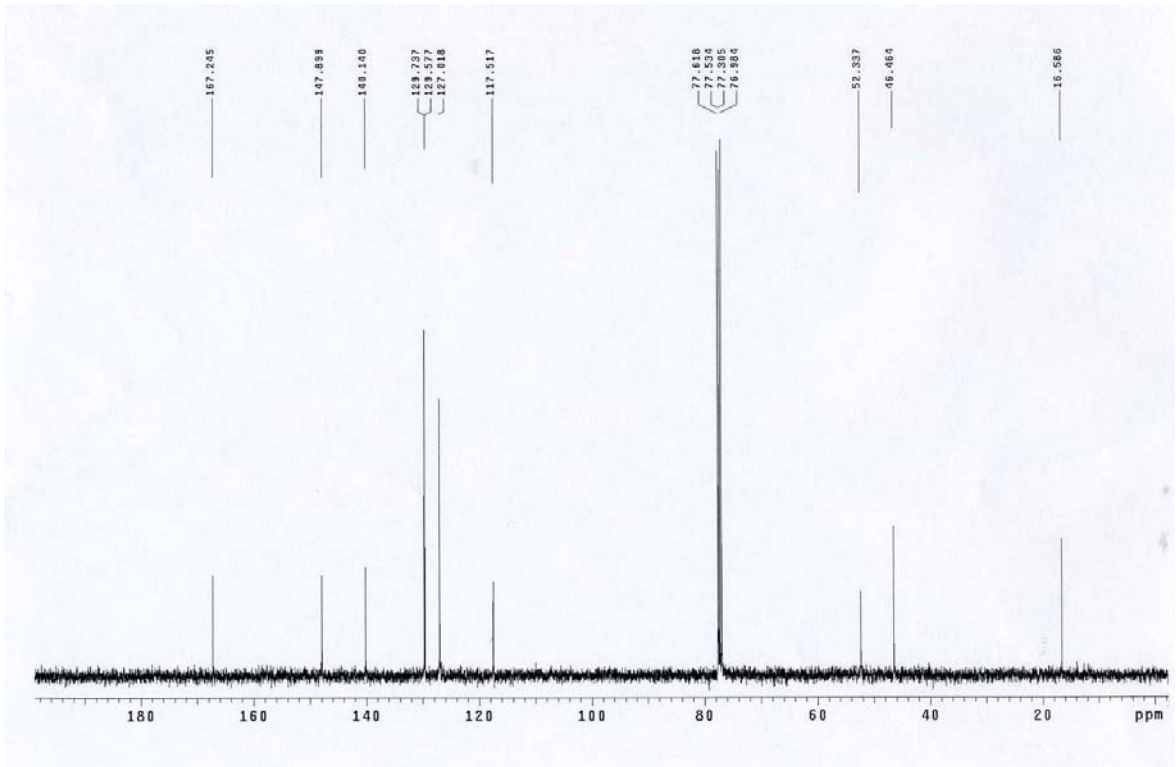
2.15
2.98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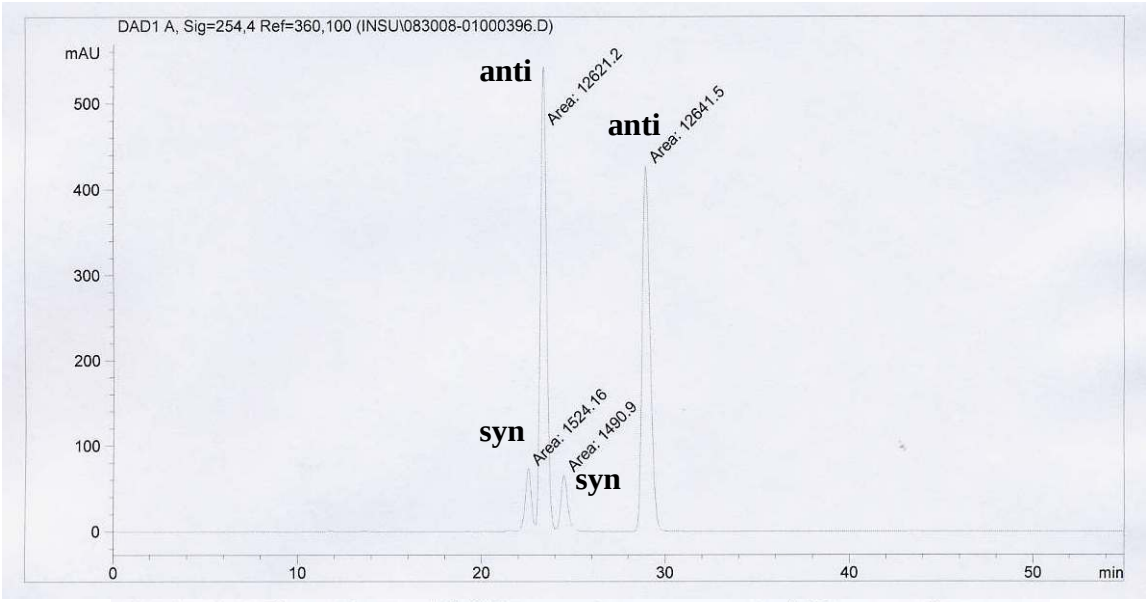
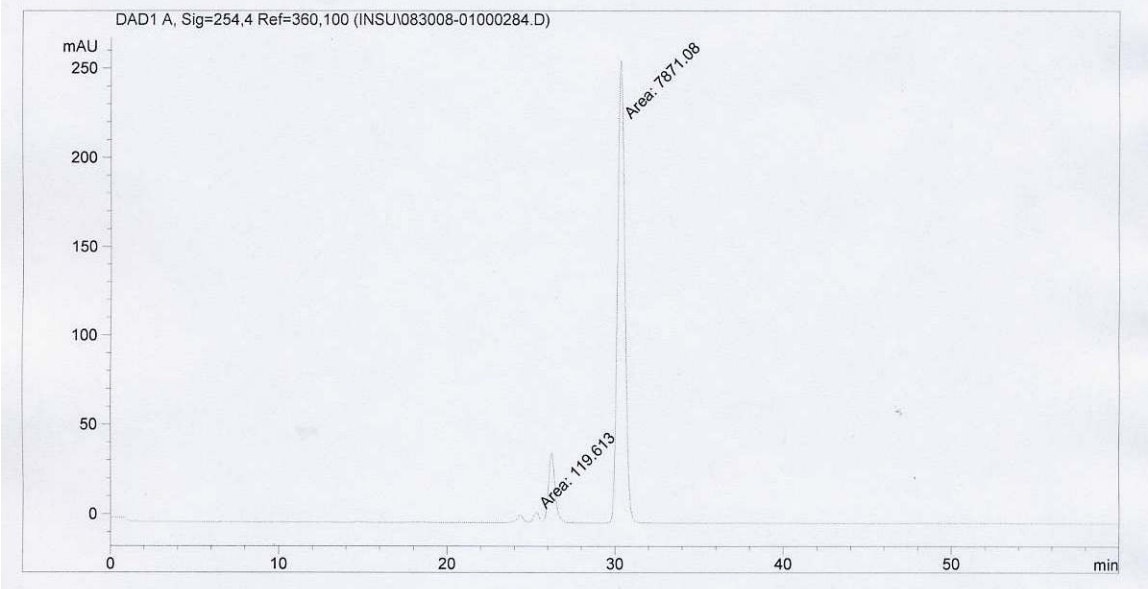
ppm

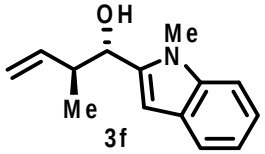


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.551	MM	0.3655	1524.15723	69.50020	5.3899
2	23.345	MM	0.3897	1.26212e4	539.76276	44.6329
3	24.492	MM	0.3972	1490.89722	62.56374	5.2723
4	28.911	MM	0.4964	1.26415e4	424.43793	44.7048



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.309	MM	0.3685	119.61345	5.40966	1.4969
2	30.307	MM	0.5063	7871.08057	259.11520	98.5031

(1*S*,2*S*)-2-Methyl-1-(1-methyl-1*H*-indol-2-yl)but-3-en-1-ol (3f)



To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. (1-Methyl-1*H*-indol-2-yl)methanol **1f** (64.5 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 80 ^oC for 72 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes:triethylamine, 1:12:0.01) provides **3f** (63.2 mg, 0.294 mmol, *anti*:*syn* = 5:1) as yellow solid in 73% yield.

TLC (SiO_2): R_f = 0.26 (ethyl acetate:hexanes, 1:10).

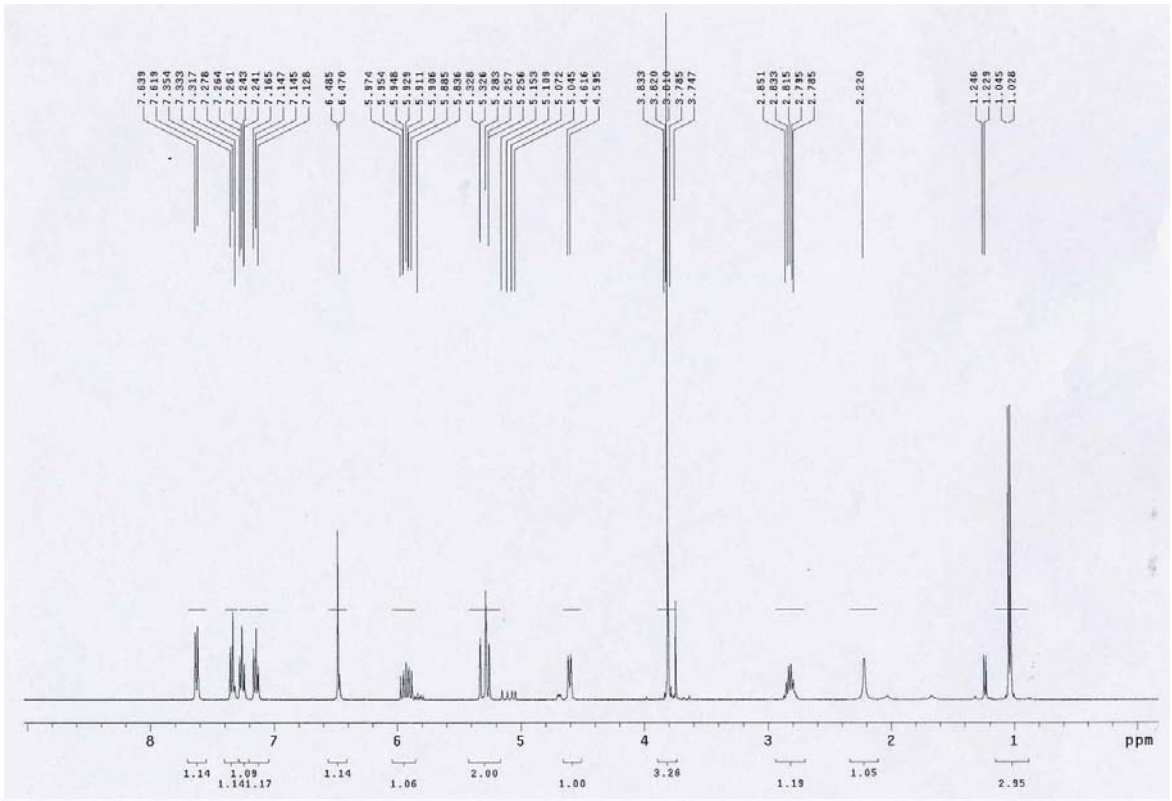
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.48 (s, 1H), 5.98-5.88 (m, 1H), 5.33-5.25 (m, 2H), 4.60 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 2.86-2.78 (m, 1H), 2.22 (br s, 1H), 1.03 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 140.3, 138.2, 127.5, 121.9, 120.9, 119.8, 117.4, 109.4, 100.8, 71.4, 44.3, 30.7, 17.5.

FTIR (neat): υ 3512, 3415, 3052, 2972, 2929, 1638, 1611, 1540, 1468, 1416, 1316, 1233, 1138, 1102, 1010, 918, 842, 785, 750, 735, 672 cm^{-1}.

HRMS (CI) Calcd. for $C_{14}H_{18}NO$ (M+1): 202.1388, Found: 202.1389.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 93:7, 0.5 mL/min, 254 nm), t_{major} = 62.8 min, t_{minor} = 78.9 min; ee = 95%.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7.128
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6.470
5.974
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5.948
5.911
5.886
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5.836
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5.283
5.257
5.256
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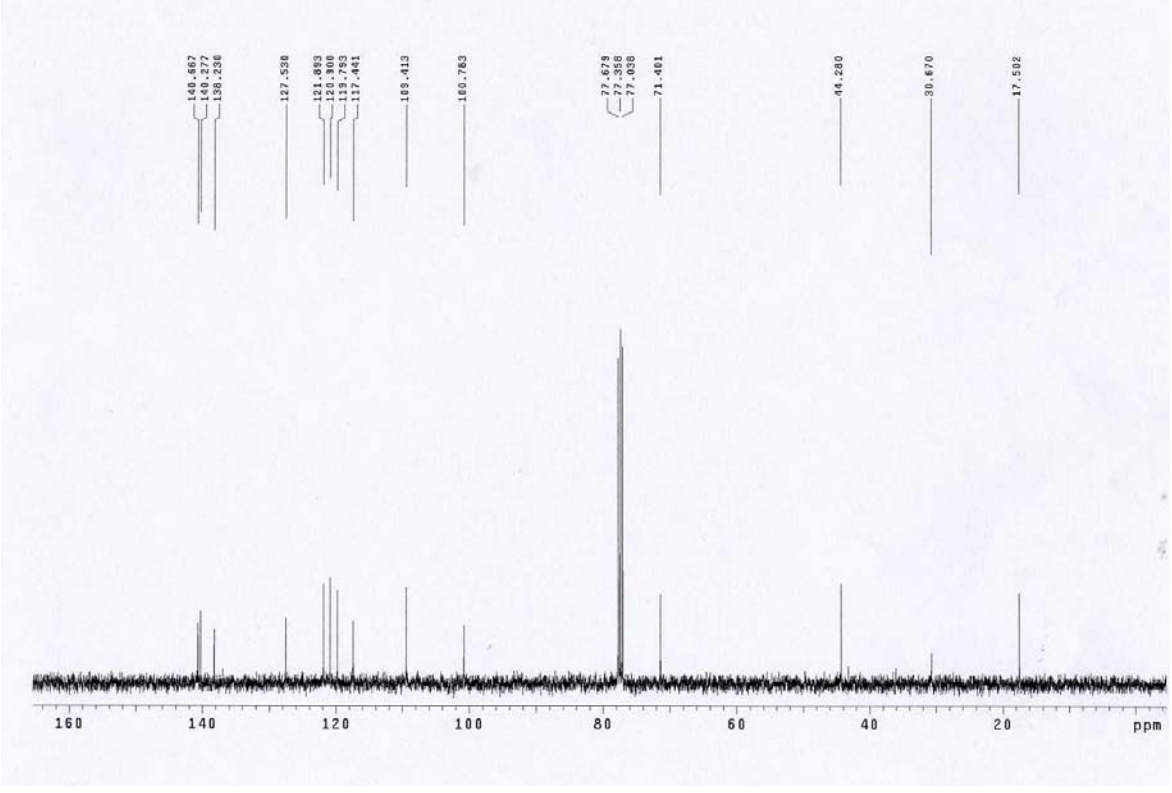
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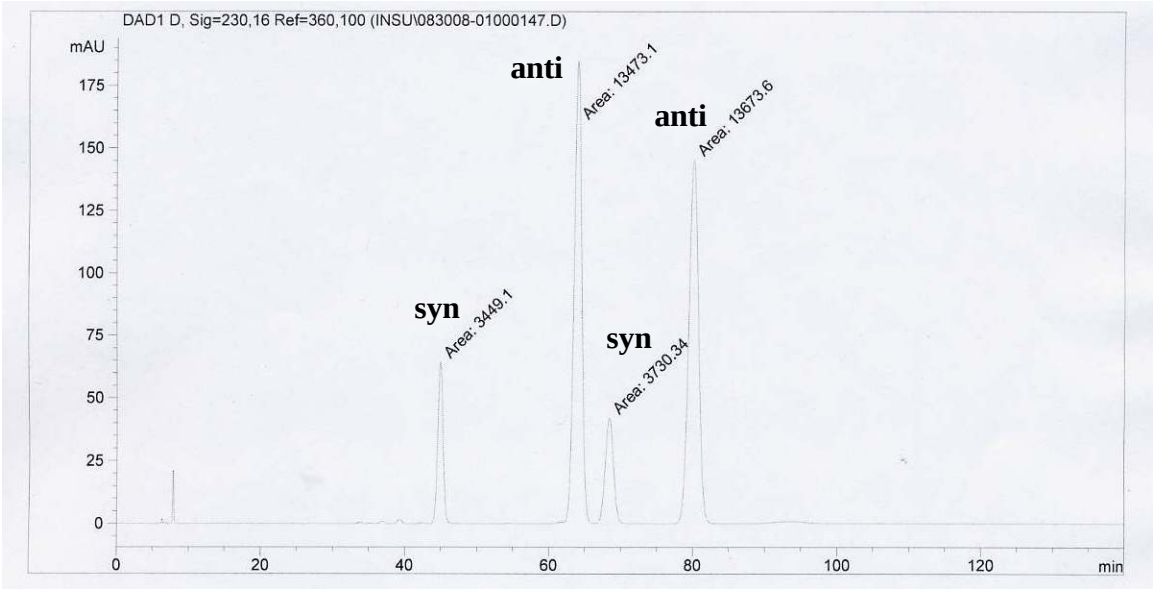
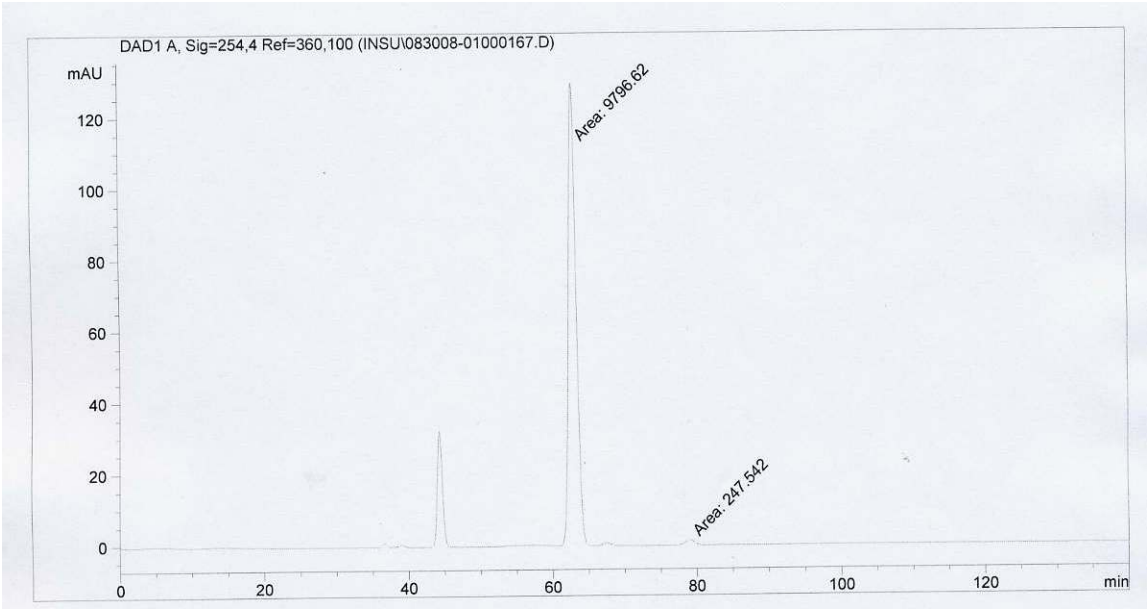
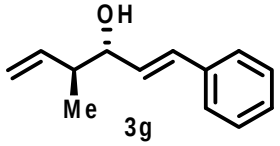


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.899	MM	0.8836	3449.09595	65.05764	10.0480
2	63.934	MM	1.2225	1.34731e4	183.68874	39.2502
3	68.404	MM	1.4447	3730.33984	43.03532	10.8673
4	80.037	MM	1.5674	1.36736e4	145.39421	39.8344



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	62.882	MM	1.2557	9796.61719	130.02975	97.5355
2	78.981	MM	2.2175	247.54234	1.86049	2.4645

(3*R*,4*S*)-4-Methyl-1-phenylhexa-(1*E*,5)-dien-3-ol (3g)



3g

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-C3-TUNEPHOS (11.9 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Cinnamyl alcohol **1g** (53.7 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes:triethylamine, 1:15:0.01) provides **3g** (47.5 mg, 0.252 mmol, *anti*:*syn* = 6:1) as a pale yellow oil in 63% yield.

TLC (SiO_2): R_f = 0.30 (ethyl acetate:hexanes, 1:10).

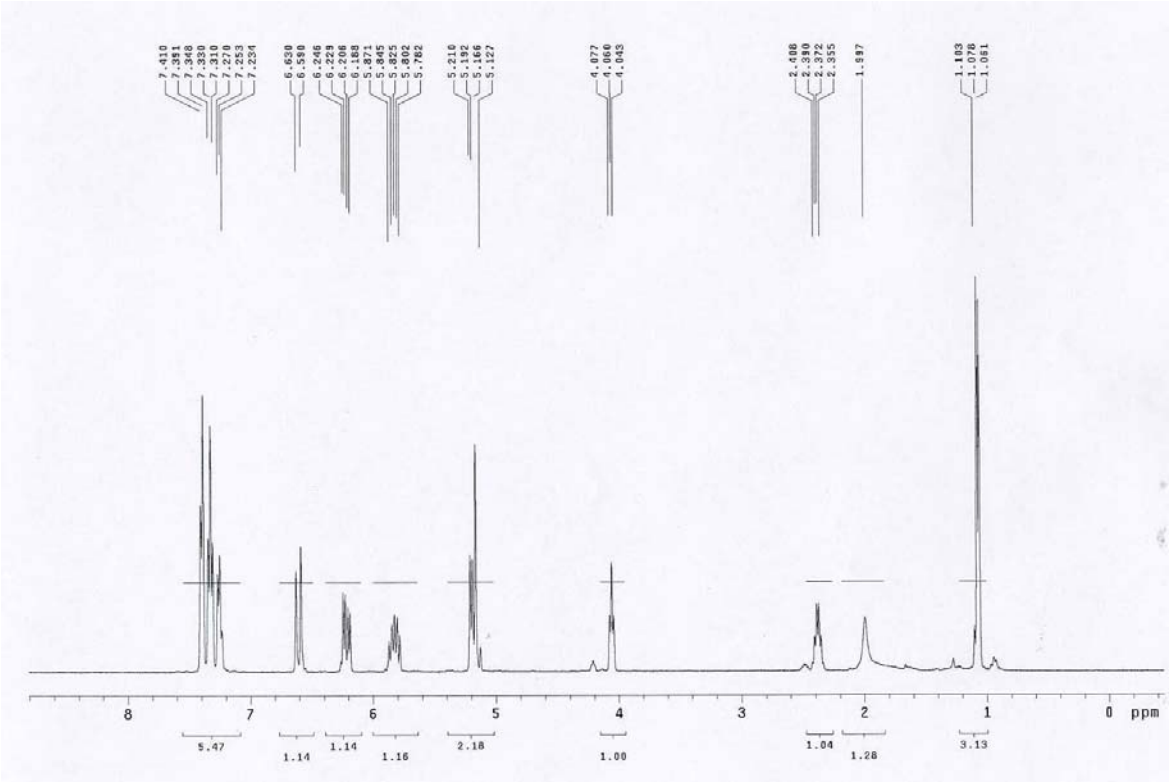
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.23 (m, 5H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.88-5.78 (m, 1H), 5.21-5.16 (m, 2H), 4.06 (t, *J* = 6.8 Hz, 1H), 2.41-2.35 (m, 1H), 1.99 (br s, 1H), 1.06 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 136.9, 132.0, 130.4, 128.8, 127.9, 126.8, 117.0, 76.4, 44.9, 16.3.

HPLC: (Chiralpak AS-H/AS-H column, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm), t_{minor} = 29.2 min, t_{major} = 35.4 min; ee = 90%.

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

[5] Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620-6628.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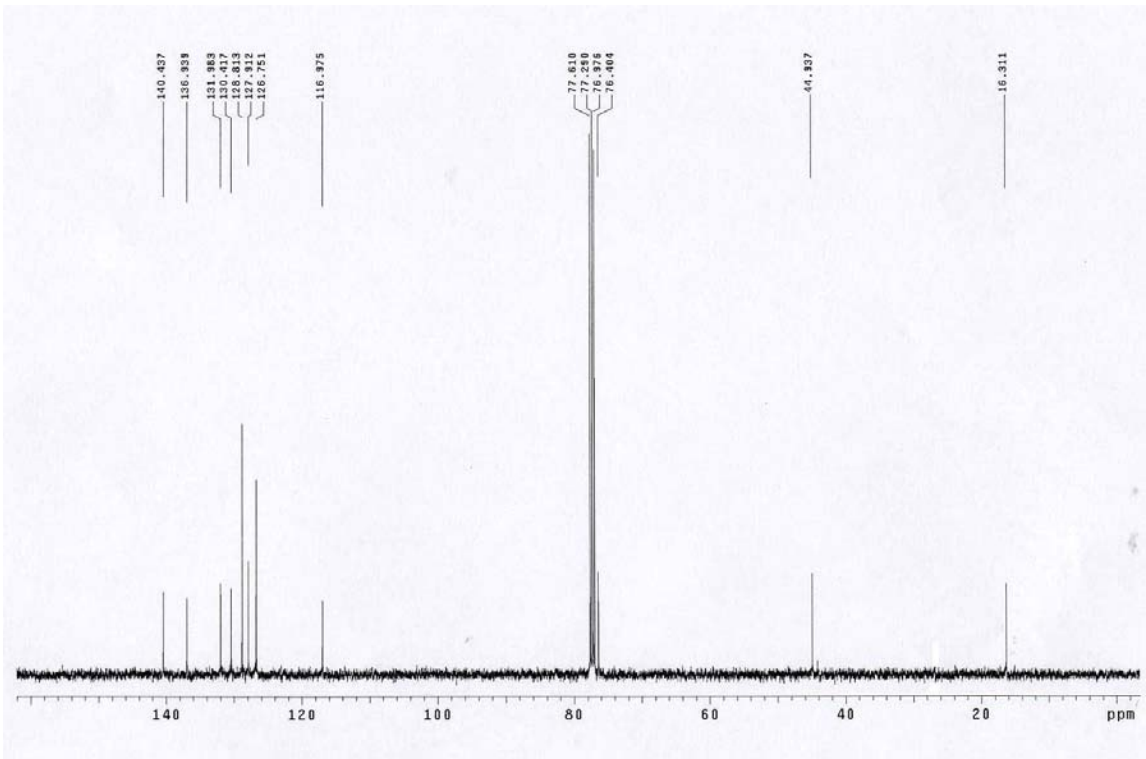
3.13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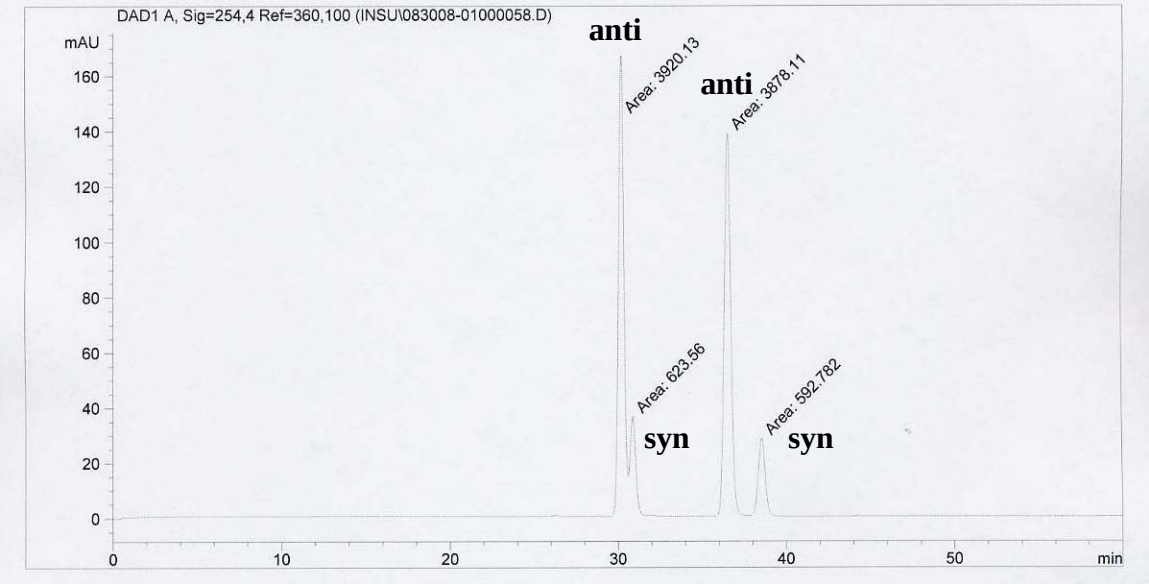
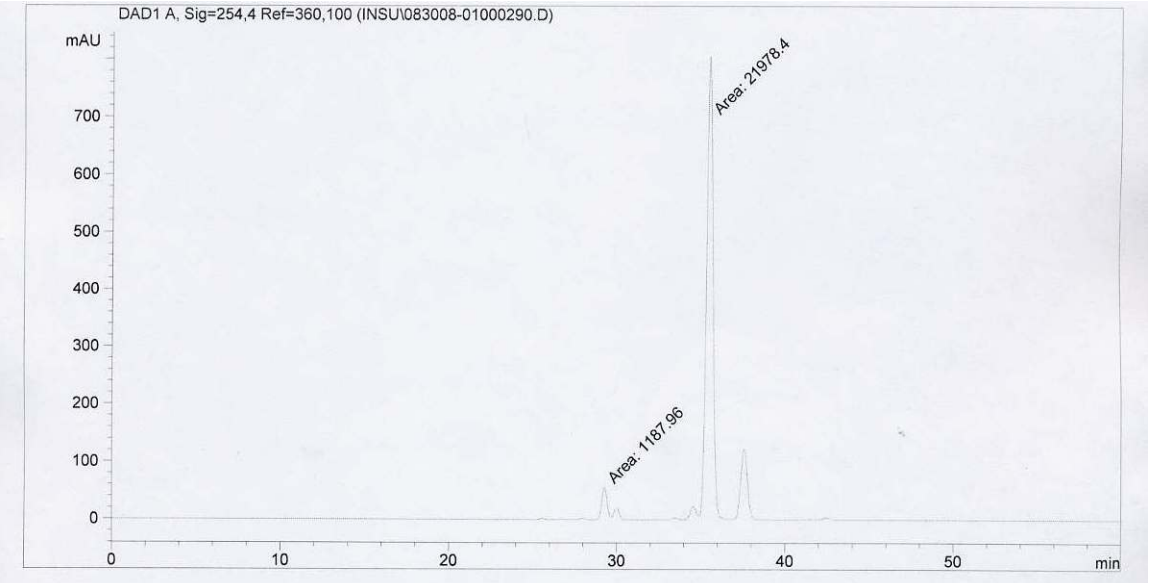
ppm

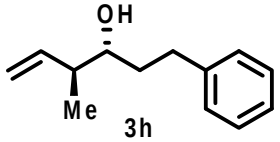


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.156	MM	0.3938	3920.13306	165.92987	43.4866
2	30.846	MM	0.2934	623.55994	35.42169	6.9172
3	36.477	MM	0.4653	3878.10742	138.90073	43.0204
4	38.499	MM	0.3667	592.78198	26.94354	6.5758



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.261	MM	0.3545	1187.95825	55.85067	5.1279
2	35.460	MM	0.4518	2.19784e4	810.71771	94.8721

(3*R*,4*S*)-4-Methyl-1-phenylhex-5-en-3-ol (3h)



To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. 3-Phenylpropan-1-ol **1h** (54.5 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:15) provides **3h** (52.6 mg, 0.276 mmol, *anti*:*syn* = 7:1) as a colorless oil in 69% yield.

TLC (SiO_2): R_f = 0.31 (ethyl acetate:hexanes, 1:10).

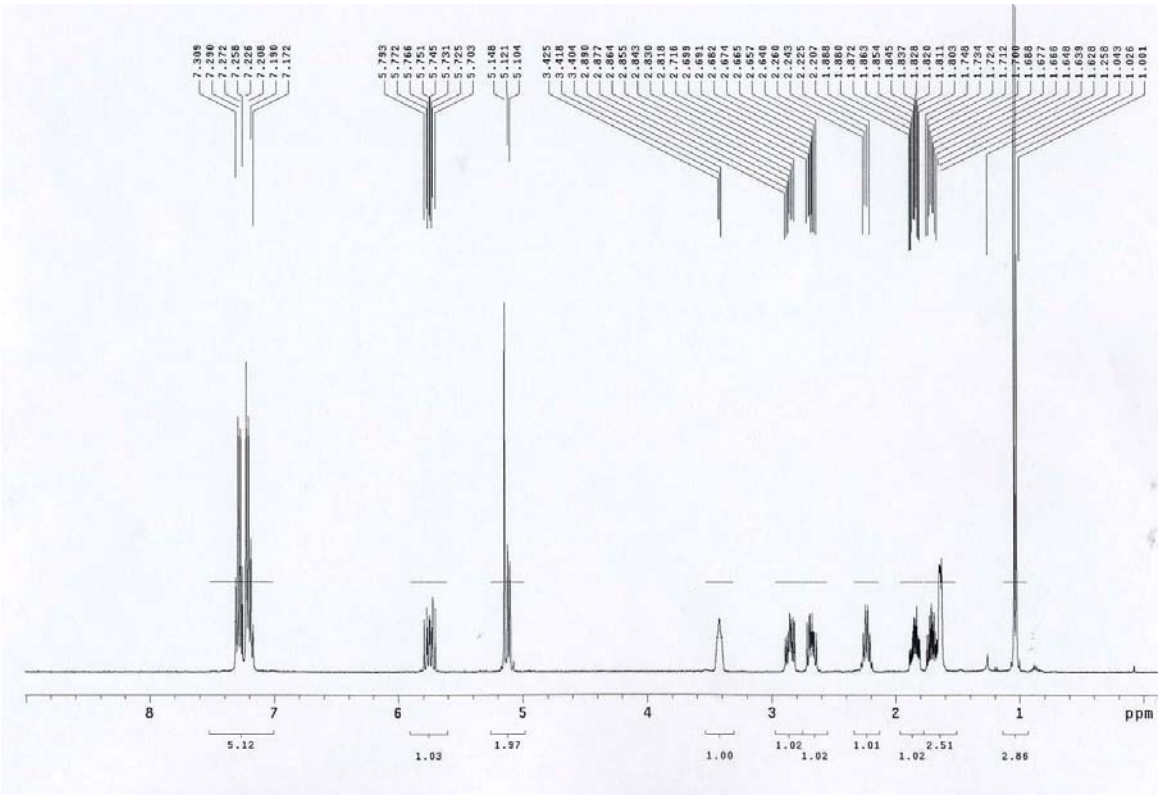
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.17 (m, 5H), 5.80-5.70 (m, 1H), 5.15-5.10 (m, 2H), 3.43-3.40 (m, 1H), 2.89-2.81 (m, 1H), 2.72-2.64 (m, 1H), 2.26-2.20 (m, 1H), 1.89-1.80 (m, 1H), 1.75-1.62 (m, 2H), 1.03 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 140.4, 128.7, 128.6, 126.0, 116.8, 74.2, 44.6, 36.4, 32.4, 16.5.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 97:3, 0.7 mL/min, 254 nm), t_{minor} = 11.2 min, t_{major} = 17.4 min; ee = 97%.[6]

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

[6] (a) McManus, H. A.; Cozzi, P. G.; Guiry, P. J. *Adv. Synth. Catal.* **2006**, *348*, 551–558.
(b) Hackman, B. M.; Lombardi, P. J.; Leighton, J. L. *Org. Lett.* **2004**, *6*, 4375–4377.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5.731
5.725
5.703
5.148
5.121
5.104
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3.404
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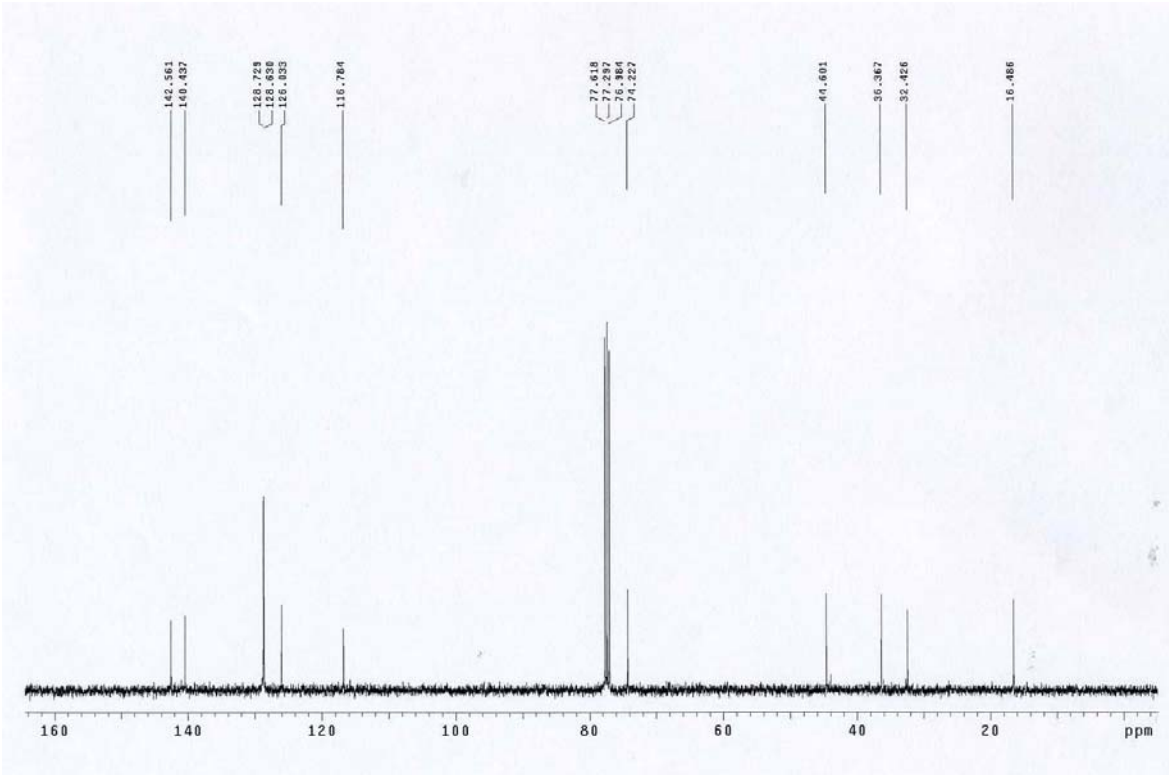
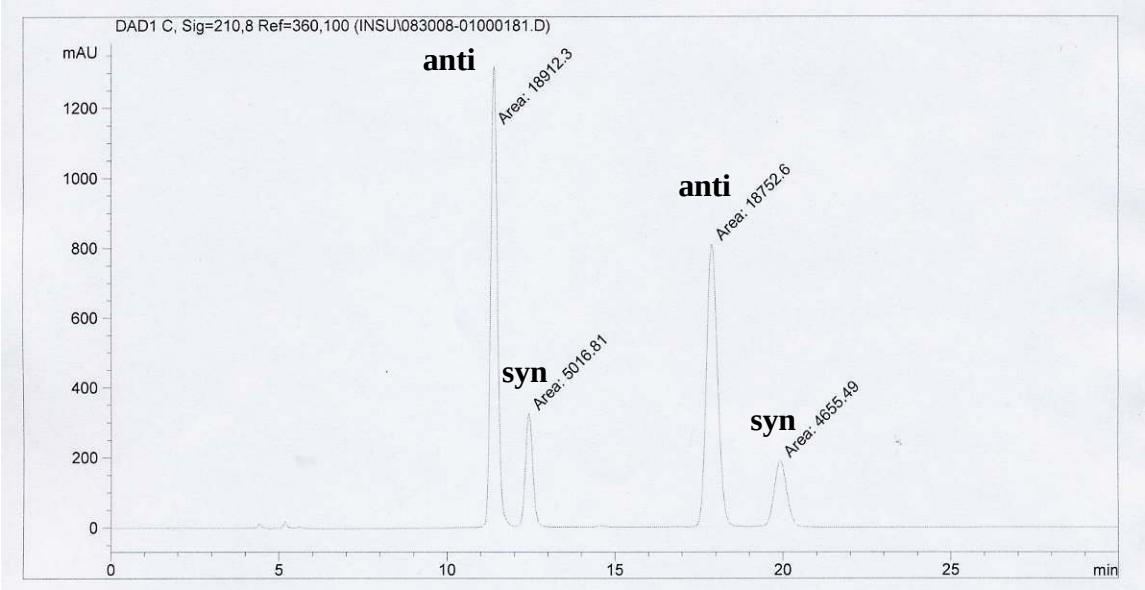
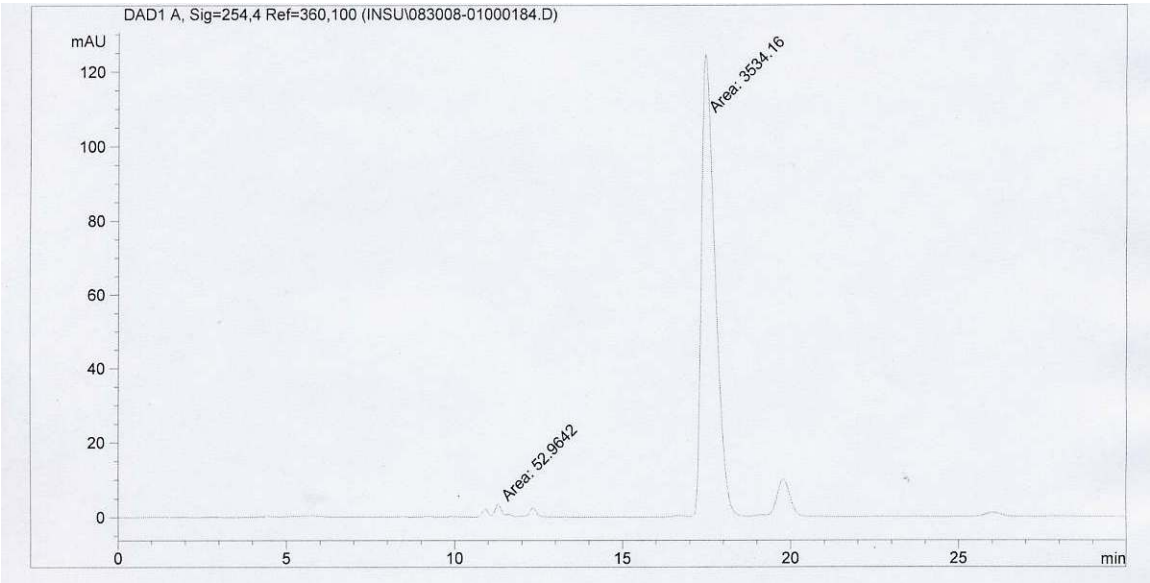
2.51
2.86


142.561
140.437
128.724
128.630
126.033
116.764
77.618
77.287
76.964
74.227
44.601
36.367
32.426
16.486
160
140
120
100
80
60
40
20
ppm

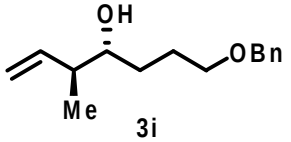


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.381	MM	0.2384	1.89123e4	1322.16956	39.9523
2	12.431	MM	0.2570	5016.80615	325.38425	10.5980
3	17.868	MM	0.3856	1.87526e4	810.45520	39.6150
4	19.911	MM	0.4220	4655.49316	183.85841	9.8347



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.290	MM	0.2474	52.96424	3.56858	1.4765
2	17.446	MM	0.4725	3534.16113	124.65968	98.5235

(3*S*,4*R*)-7-(Benzyloxy)-3-methylhept-1-en-4-ol (3i)



3i

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. 4-(Benzyloxy)butan-1-ol **1i** (72.1 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:12) provides **3i** (63.9 mg, 0.273 mmol, *anti*:*syn* = 7:1) as a colorless oil in 68% yield.

TLC (SiO_2): R_f = 0.26 (ethyl acetate:hexanes, 1:12).

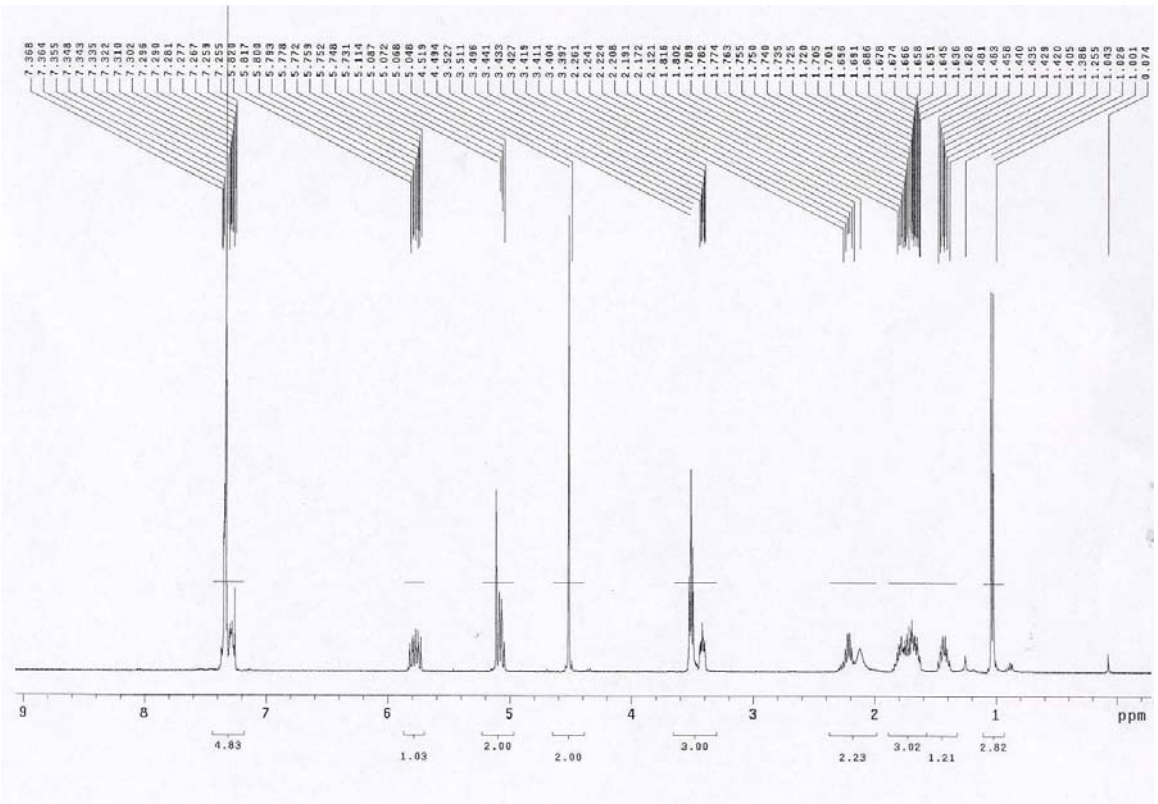
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.25 (m, 5H), 5.82-5.73 (m, 1H), 5.12-5.06 (m, 2H), 4.51 (s, 2H), 3.51 (t, *J* = 6.4 Hz, 2H), 3.45-3.39 (m, 1H), 2.27-2.17 (m, 1H), 2.12 (br s, 1H), 1.82-1.62 (m, 3H), 1.49-1.38 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H).

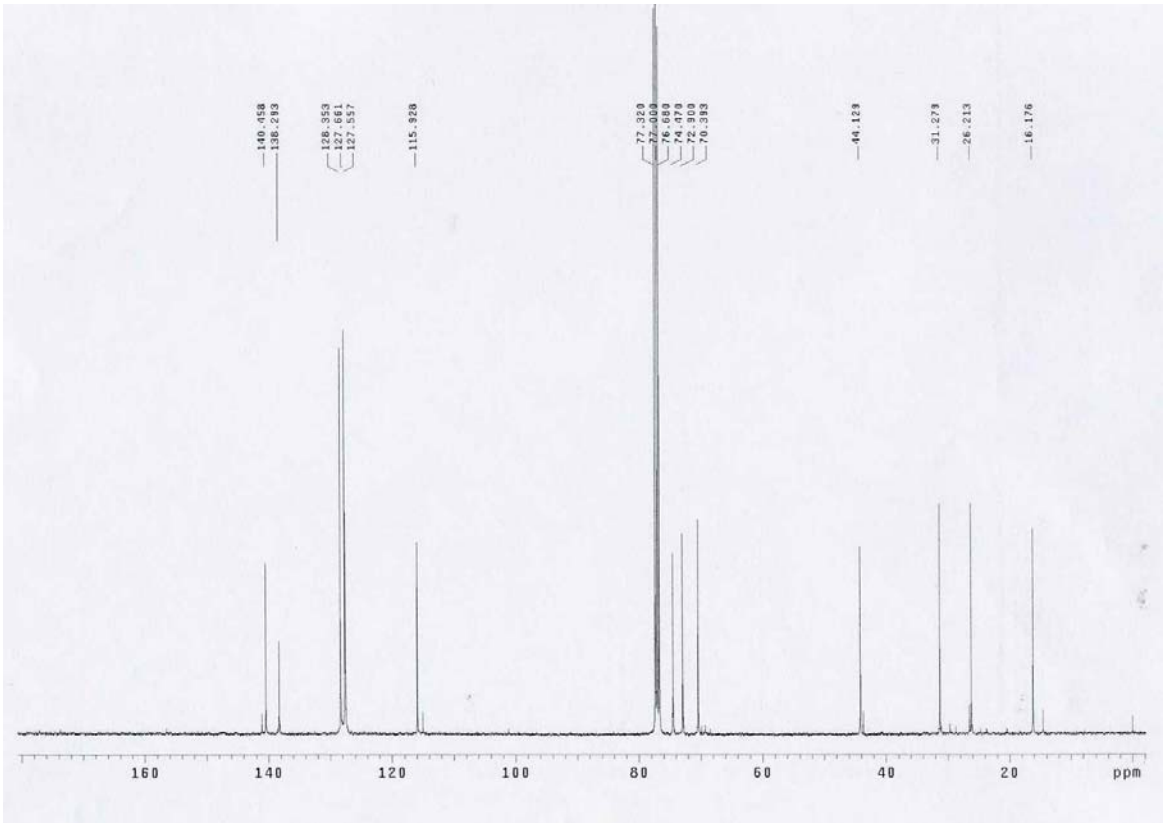
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 138.3, 128.4, 127.7, 127.6, 115.9, 74.5, 72.9, 70.4, 44.1, 31.3, 26.2, 16.2.

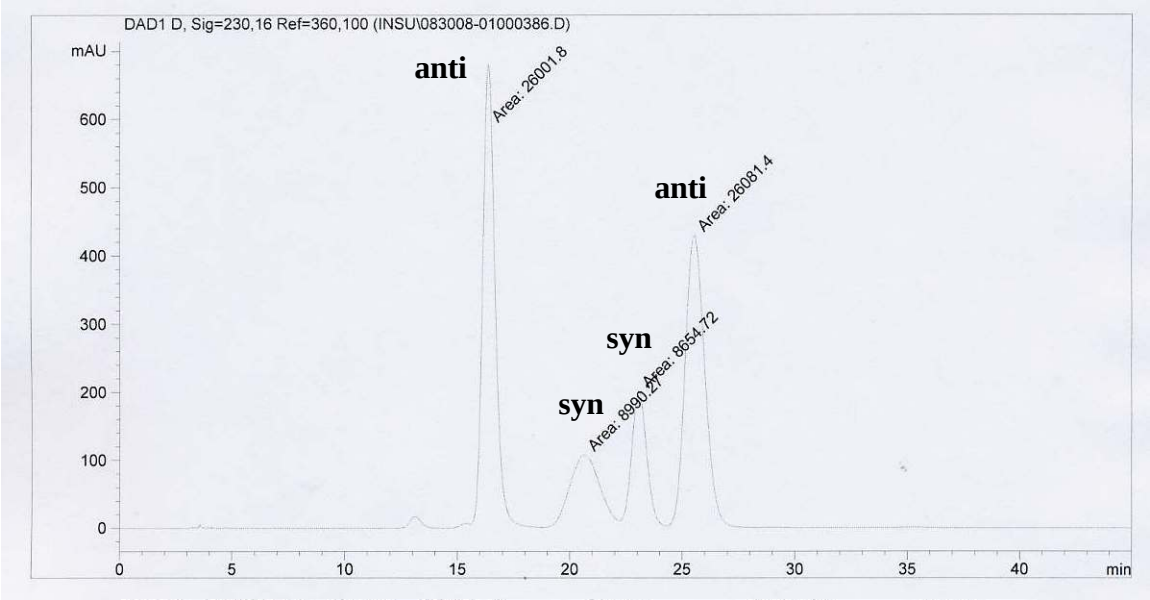
HPLC: Enantiomeric excess was determined by HPLC analysis of the 2-naphthoate derivative of the product (Chiralcel OJ-H column, hexanes:*i*-PrOH = 98.5:1.5, 1.0 mL/min, 230 nm), t_{major} = 16.4 min, t_{minor} = 25.8 min; ee = 97%.

The spectroscopic properties of this compound were consistent with the data available in the literature.[7]

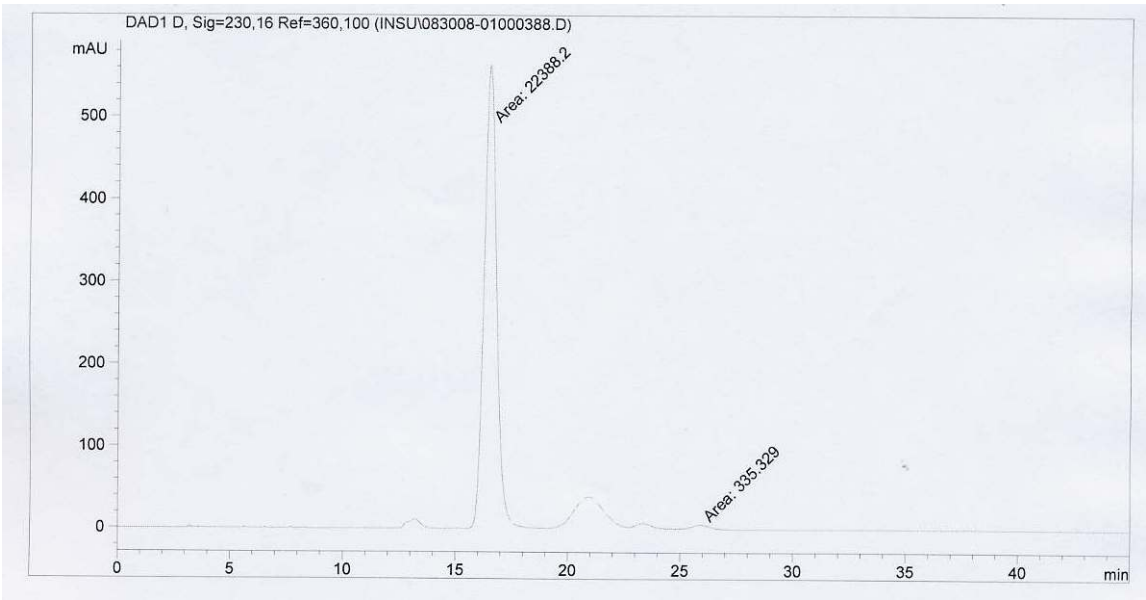
[7] Kobayashi, Y.; Tan, C.-H.; Kishi, Y. *J. Am. Chem. Soc.* **2001**, *123*, 2076–2078.





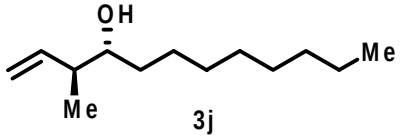


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.343	MM	0.6395	2.60018e4	677.66370	37.2902
2	20.654	MM	1.4762	8990.26855	101.50465	12.8933
3	23.061	MM	0.7472	8654.72070	193.04347	12.4121
4	25.511	MM	1.0137	2.60814e4	428.80423	37.4044



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.440	MM	0.6585	2.23882e4	566.62378	98.5243
2	25.887	MM	1.0217	335.32941	5.47016	1.4757

(3*S*,4*R*)-3-Methyldodec-1-en-4-ol (3j)



3j

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Nonan-1-ol **1j** (57.7 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:30) provides **3j** (54.8 mg, 0.276 mmol, *anti*:*syn* = 7:1) as a colorless oil in 69% yield.

TLC (SiO_2): R_f = 0.30 (ethyl acetate:hexanes, 1:20).

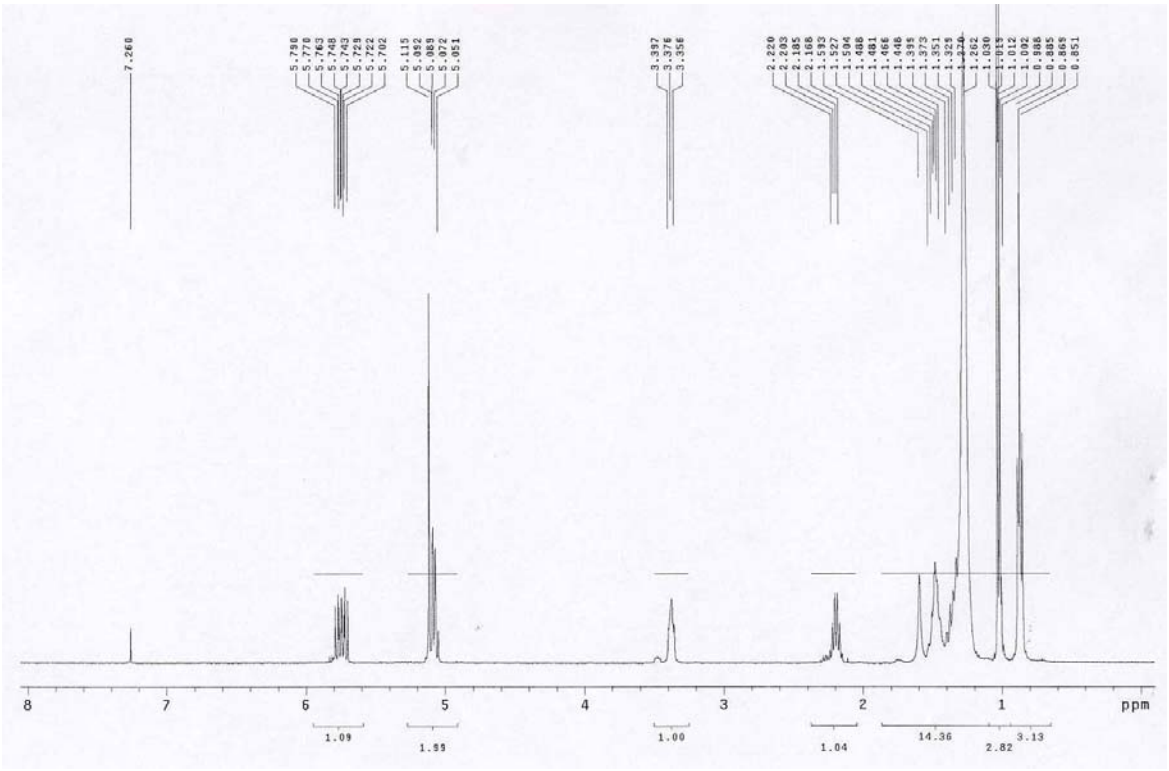
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.79-5.70 (m, 1H), 5.12-5.07 (m, 2H), 3.40-3.35 (m, 1H), 2.20-2.16 (m, 1H), 1.59 (br s, 1H), 1.53-1.26 (m, 14H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 116.4, 74.9, 44.3, 34.5, 32.1, 30.0, 29.8, 29.5, 26.0, 22.9, 16.5, 14.3.

HPLC: Enantiomeric excess was determined by HPLC analysis of the 2-naphthoate derivative of the product (Chiralpak AD-H column, hexanes:*i*-PrOH = 99.5:0.5, 0.4 mL/min, 254 nm), t_{minor} = 12.9 min, t_{major} = 18.3 min; ee = 97%.

The spectroscopic properties of this compound were consistent with the data available in the literature.[8]

[8] Takai, K.; Toratsu, C. *J. Org. Chem.* **1998**, *63*, 6450–6451.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5.722
5.702
5.115
5.082
5.069
5.072
5.051
3.397
3.376
3.356
2.220
2.203
2.185
2.168
1.593
1.527
1.504
1.488
1.481
1.466
1.446
1.375
1.373
1.351
1.325
1.324
1.262
1.030
1.019
1.012
1.092
0.986
0.885
0.865
0.851
8
7
6
5
4
3
2
1
ppm
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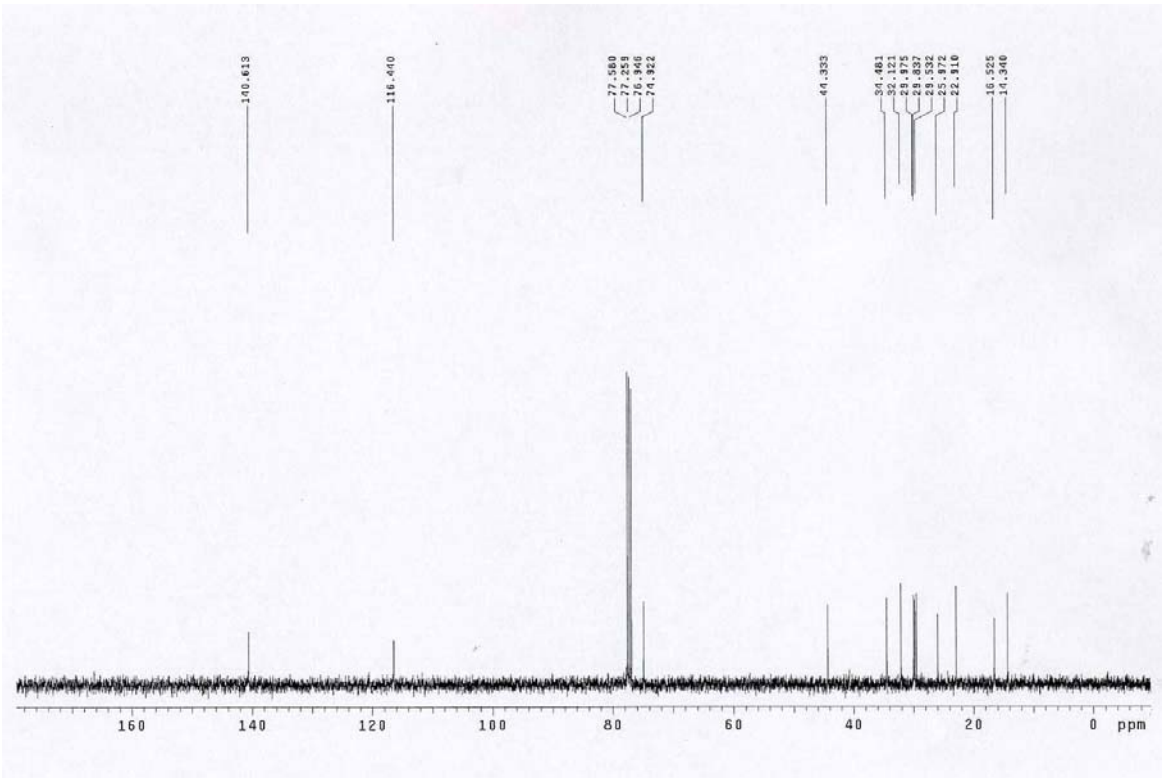
1.99
1.00
1.04
14.36
2.82
3.13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74.922
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29.532
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22.910
16.525
14.340
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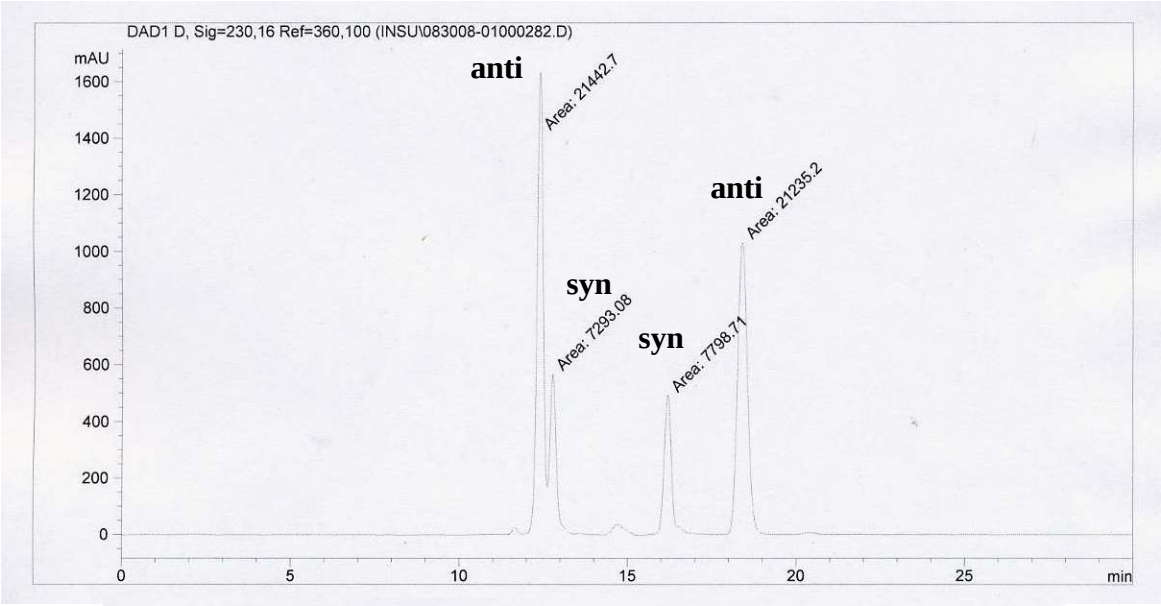
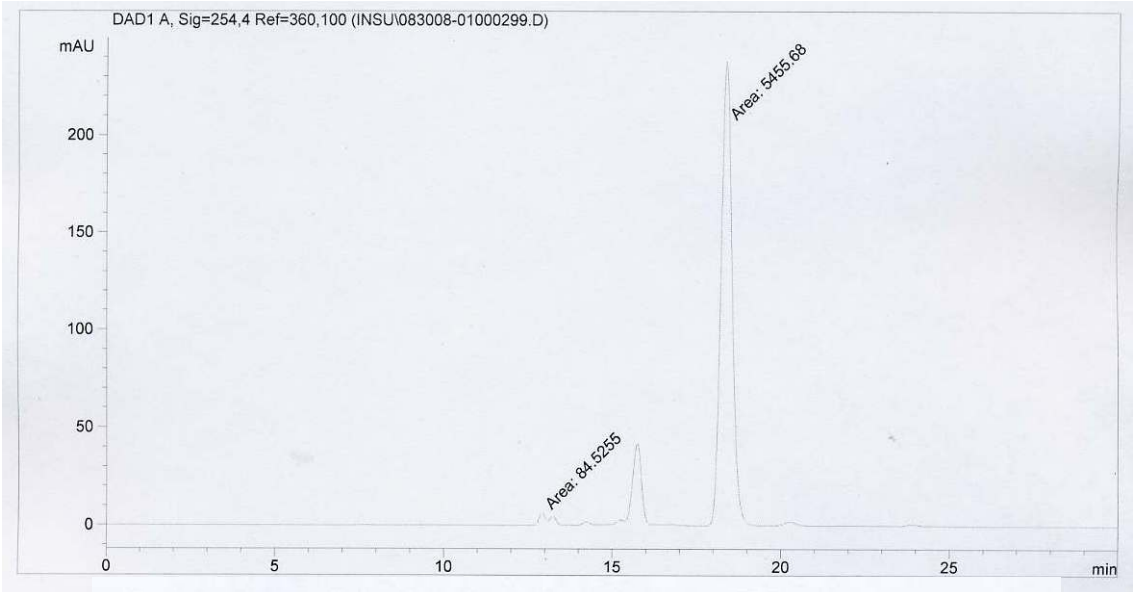
120
100
80
60
40
20
0
ppm



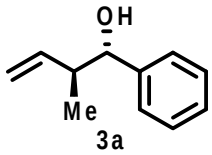
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.383	MM	0.2184	2.14427e4	1636.01721	37.1176
2	12.774	MM	0.2136	7293.07861	569.18518	12.6244
3	16.191	MM	0.2622	7798.70605	495.73898	13.4997
4	18.390	MM	0.3426	2.12352e4	1033.06030	36.7583



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.919	MM	0.2199	84.52553	6.40736	1.5257
2	18.340	MM	0.3824	5455.67578	237.80714	98.4743

Detailed Procedure and Spectral Data for *anti*-Diastereo- and Enantioselective Crotylation Adducts (3a-3j) from Aldehydes (2a-2j)

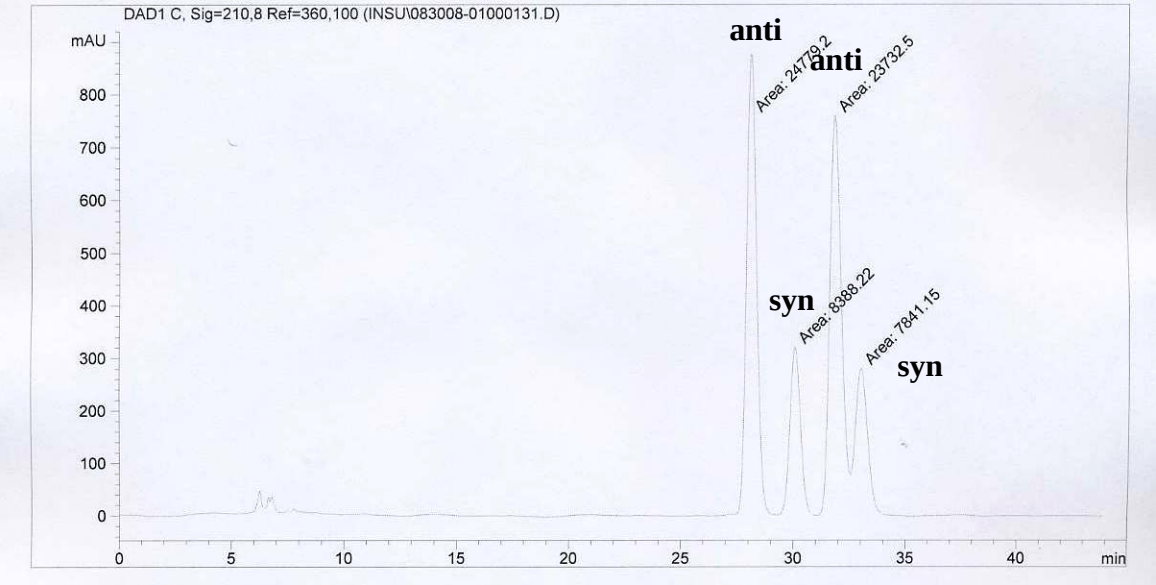
(1*S*,2*S*)-2-Methyl-1-phenylbut-3-en-1-ol (3a)



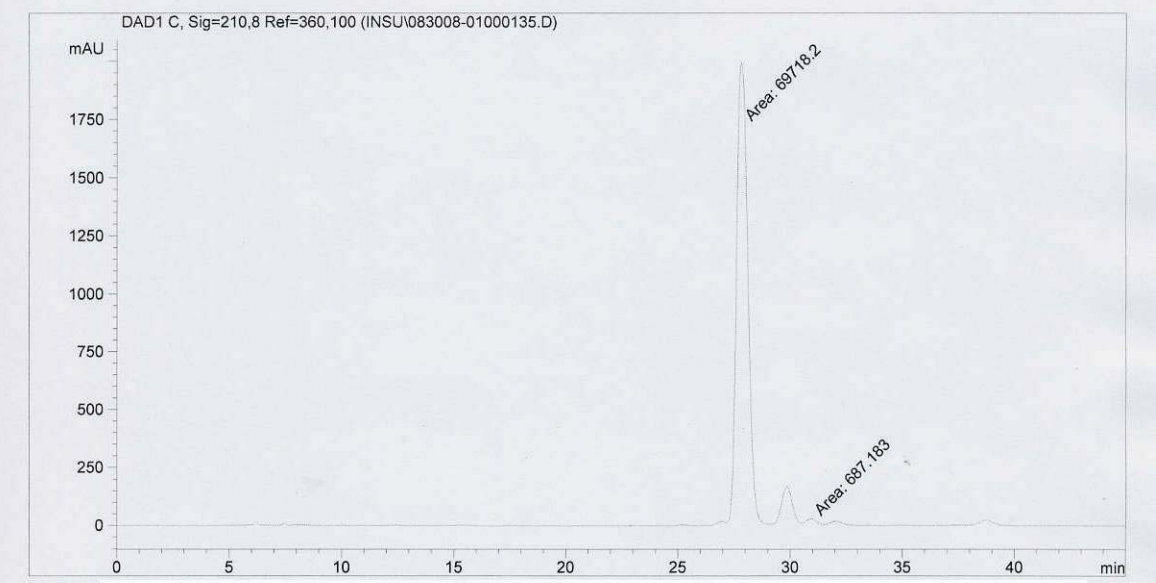
3a

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Benzaldehyde **2a** (42.4 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) and isopropanol (59.8 μL, 0.8 mmol, 200 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:20) provides **3a** (50.0 mg, 0.308 mmol, *anti*:*syn* = 9:1) as a colorless oil in 77% yield.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 99:1, 0.5 mL/min, 210 nm), t_{major} = 27.8 min, t_{minor} = 30.9 min; ee = 98%.

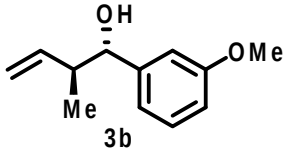


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.147	MM	0.4698	2.47792e4	878.99377	38.2743
2	30.093	MM	0.4400	8388.22266	317.70355	12.9566
3	31.852	MM	0.5530	2.37325e4	715.23456	36.6576
4	33.036	MM	0.5618	7841.14746	232.62761	12.1115



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.813	MM	0.5844	6.97182e4	1988.25208	99.0240
2	30.937	MM	0.5007	687.18292	22.87475	0.9760

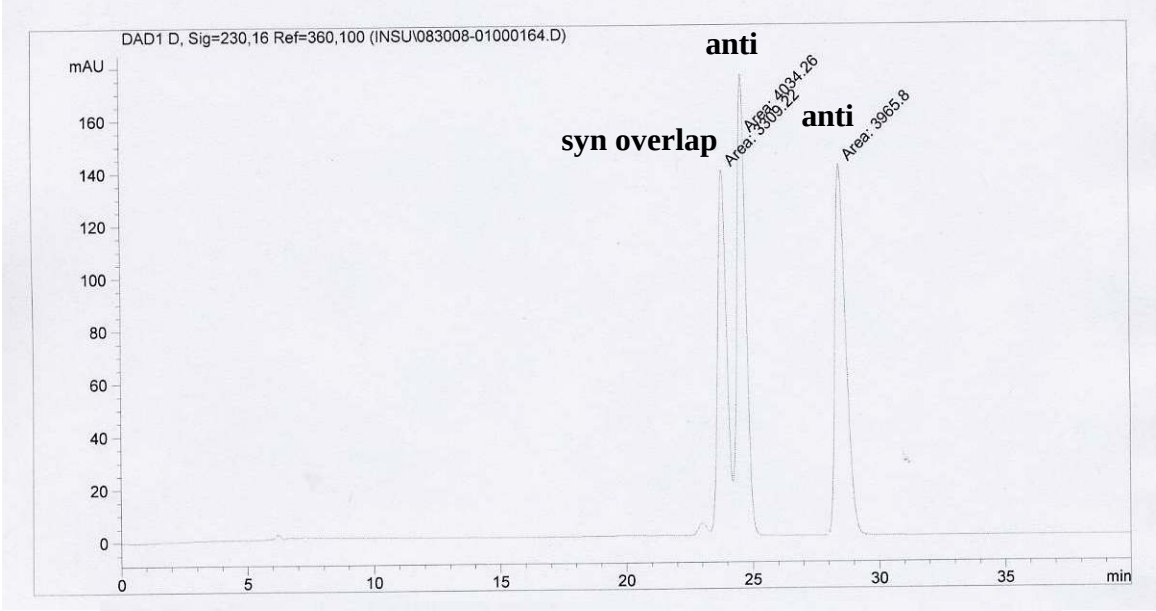
(1*S*,2*S*)-1-(3-Methoxyphenyl)-2-methylbut-3-en-1-ol (3b)



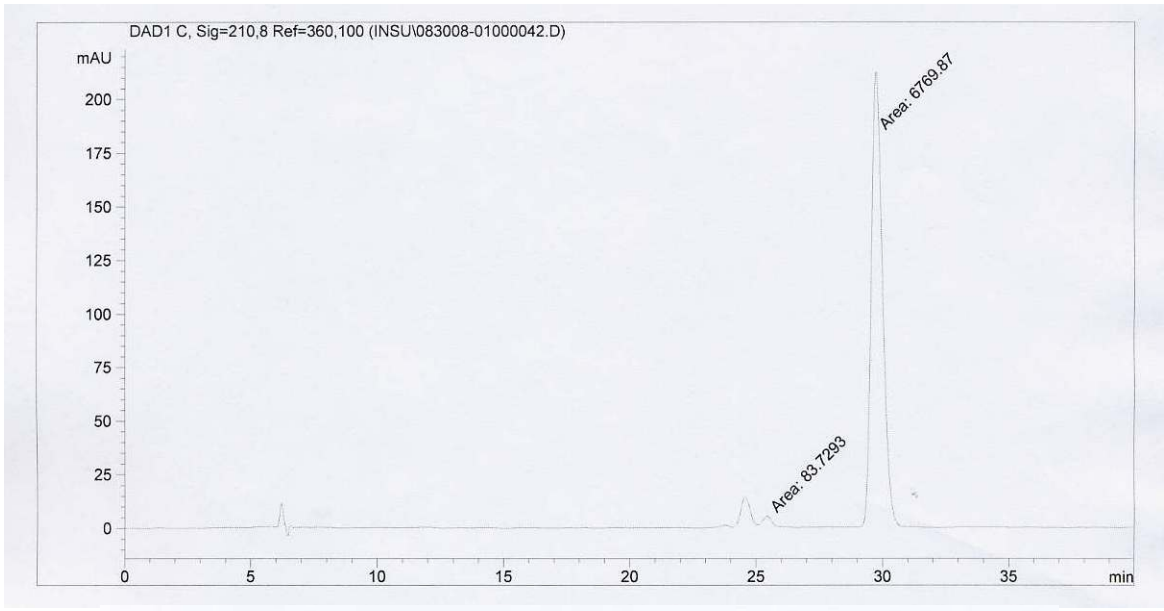
3b

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. 3-Methoxybenzaldehyde **2b** (54.5 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) and isopropanol (59.8 μL, 0.8 mmol, 200 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:15) provides **3b** (56.8 mg, 0.295 mmol, *anti*:*syn* = 9:1) as a colorless oil in 74% yield.

HPLC: (Chiralpak AD-H column, hexanes:*i*-PrOH = 96:4, 0.5 mL/min, 210 nm), t_{minor} = 25.4 min, t_{major} = 29.7 min; ee = 98%.

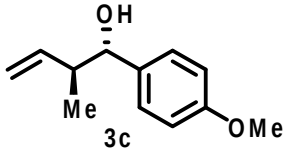


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.834	MM	0.4056	3309.22461	135.98813	29.2611
2	24.613	MM	0.3870	4034.26050	173.73439	35.6721
3	28.466	MM	0.4754	3965.80420	139.04333	35.0668



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.432	MM	0.3354	83.72932	4.16100	1.2217
2	29.711	MM	0.5281	6769.87207	213.67189	98.7783

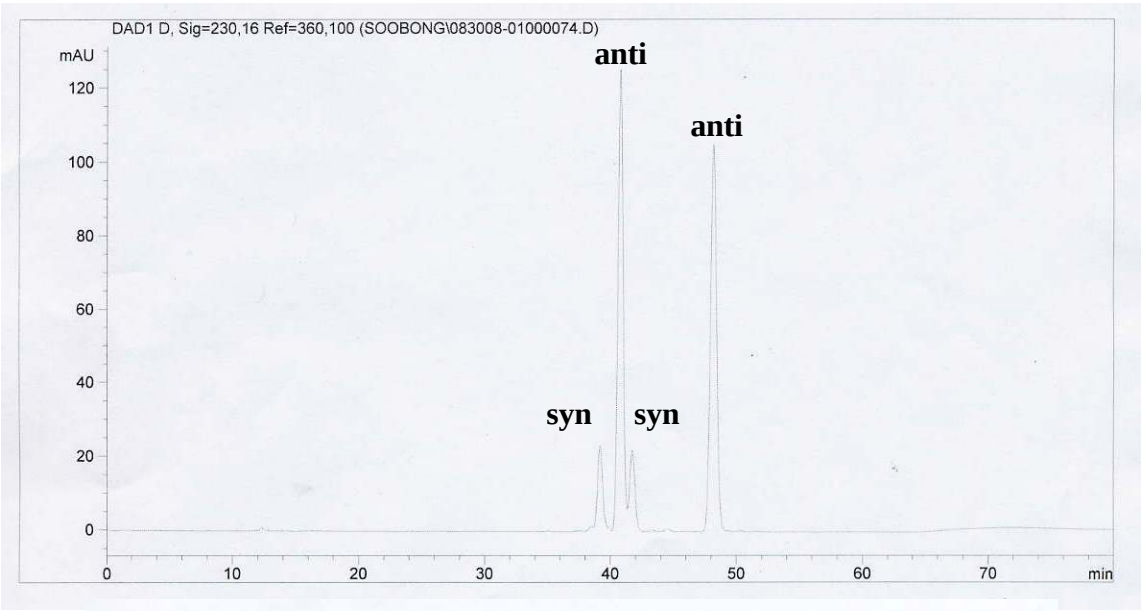
(1*S*,2*S*)-1-(4-Methoxyphenyl)-2-methylbut-3-en-1-ol (3c)



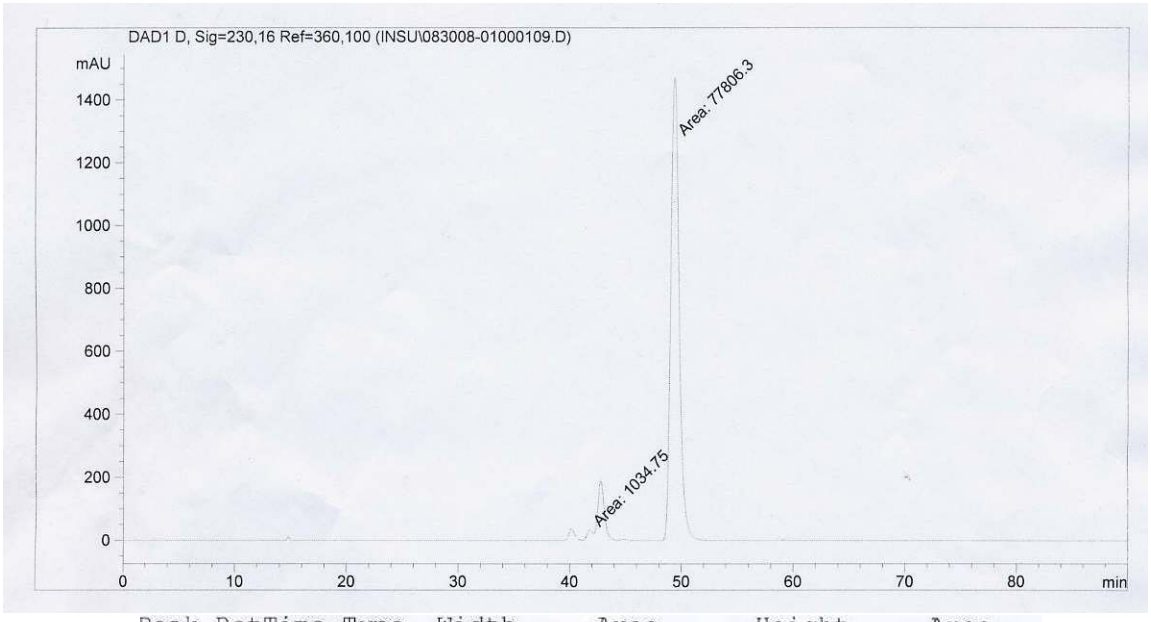
3c

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. *p*-Anisaldehyde **2c** (54.5 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) and isopropanol (59.8 μL, 0.8 mmol, 200 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir at 80 ^oC for 72 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes:triethylamine, 1:20:0.01) provides **3c** (57.7 mg, 0.300 mmol, *anti*:*syn* = 7:1) as a colorless oil in 75% yield.

HPLC: (Chiralpak AD-H/AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 230 nm), t_{minor} = 41.8 min, t_{major} = 49.2 min; ee = 97%.

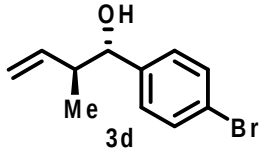


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.161	BB	0.4261	616.05029	22.45514	7.3246
2	40.757	BV	0.4466	3590.92212	125.20443	42.6946
3	41.716	VB	0.4583	646.22864	21.76813	7.6834
4	48.145	BB	0.5281	3557.50903	104.78043	42.2974



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.810	MM	0.5498	1034.74670	31.36497	1.3124
2	49.271	MM	0.8821	7.78063e4	1470.14929	98.6876

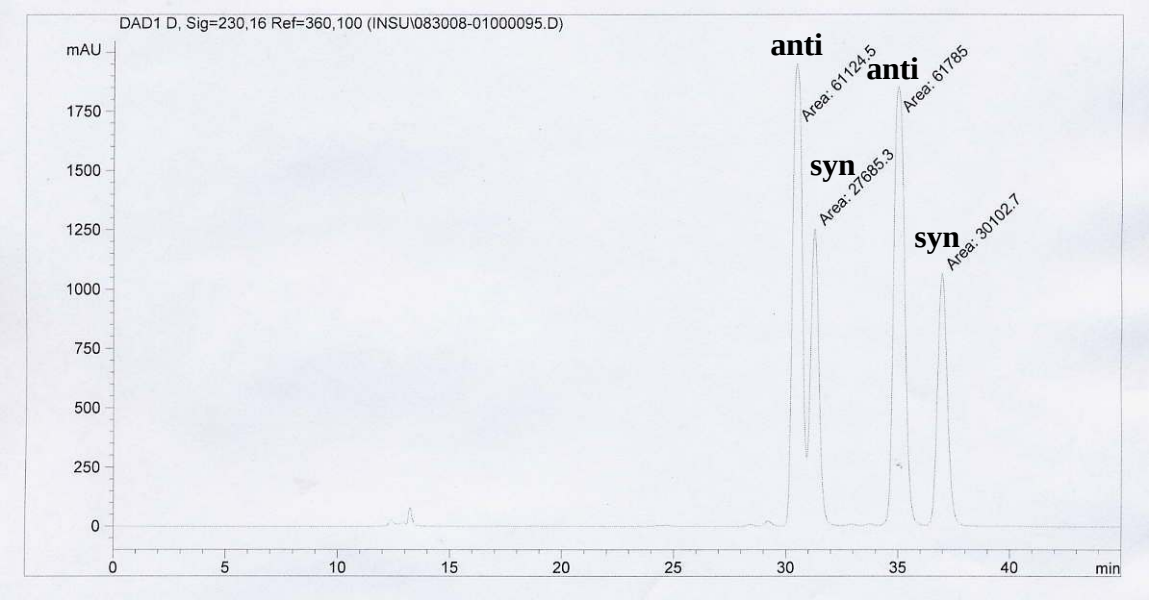
(1*S*,2*S*)-1-(4-Bromophenyl)-2-methylbut-3-en-1-ol (3d)



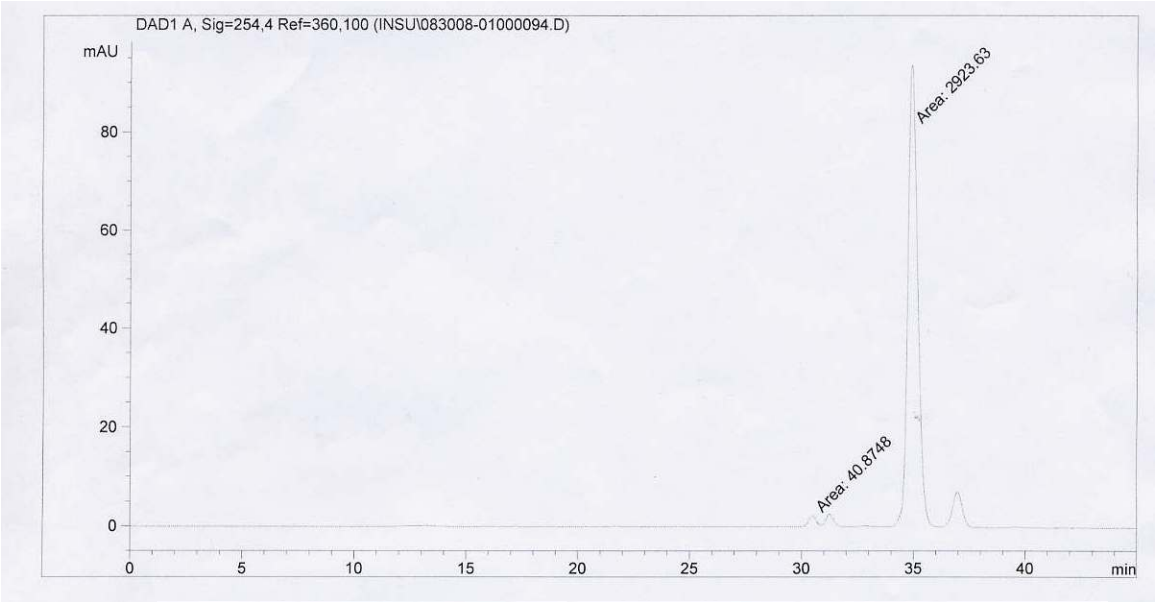
3d

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. 4-Bromobenzaldehyde **2d** (74.0 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) and isopropanol (59.8 μL, 0.8 mmol, 200 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes:triethylamine, 1:15:0.01) provides **3d** (75.5 mg, 0.313 mmol, *anti*:*syn* = 11:1) as a colorless oil in 78% yield.

HPLC: (Chiralpak AS-H/AS-H column, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm), t_{minor} = 30.4 min, t_{major} = 34.8 min; ee = 97%.

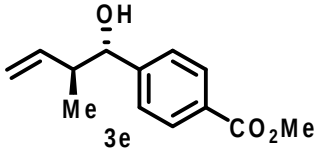


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.439	MM	0.5210	6.11245e4	1955.34973	33.8270
2	31.244	MM	0.3686	2.76853e4	1251.77246	15.3213
3	34.965	MM	0.5588	6.17850e4	1842.82361	34.1925
4	36.940	MM	0.4762	3.01027e4	1053.47668	16.6592



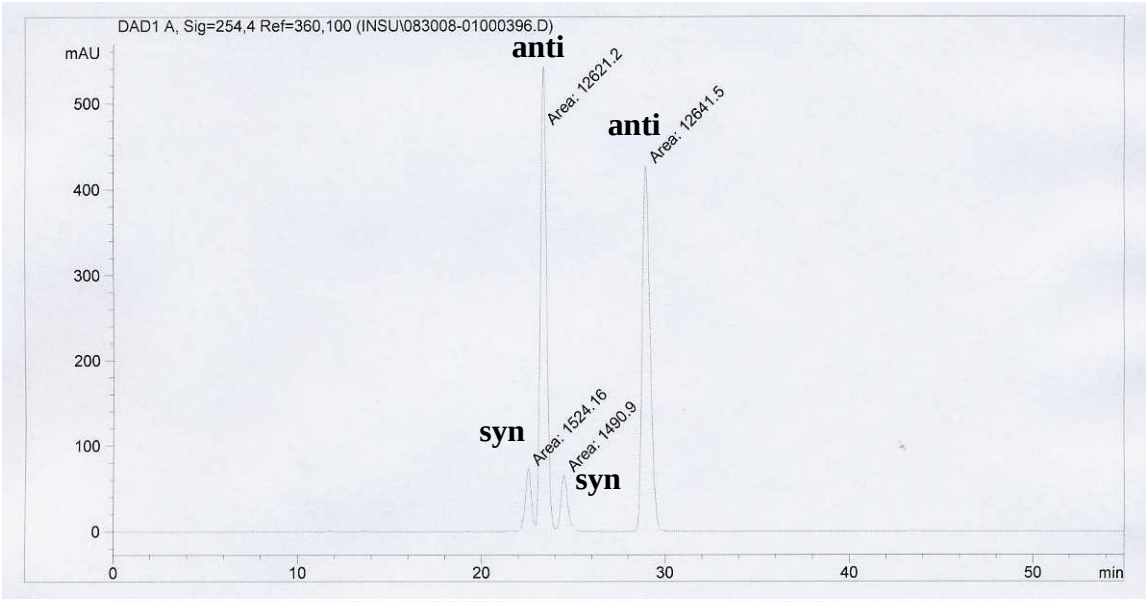
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.483	MM	0.3222	40.87479	2.11448	1.3788
2	34.878	MM	0.5190	2923.62842	93.88819	98.6212

Methyl 4-((1*S*,2*S*)-1-hydroxy-2-methylbut-3-enyl)benzoate (3e)

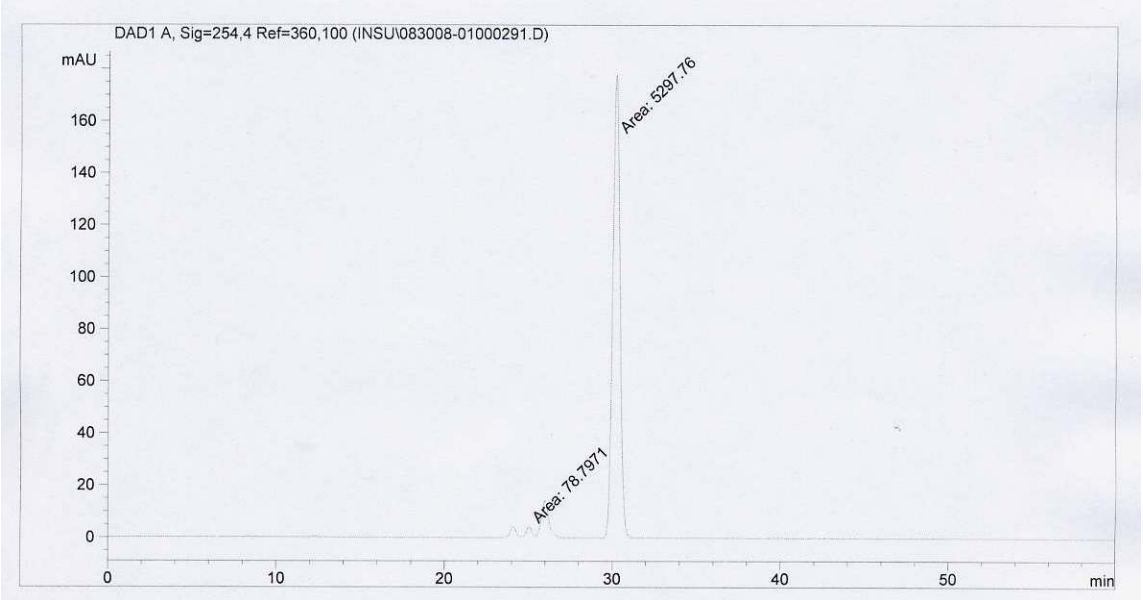


To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-C3-TUNEPHOS (11.9 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Methyl 4-formylbenzoate **2e** (65.7 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) and isopropanol (59.8 μL, 0.8 mmol, 200 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:8) provides **3e** (72.2 mg, 0.328 mmol, *anti*:*syn* = 13:1) as a pale yellow oil in 82% yield.

HPLC: (Chiralpak AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 254 nm), t_{minor} = 25.0 min, t_{major} = 30.1 min; ee = 97%.

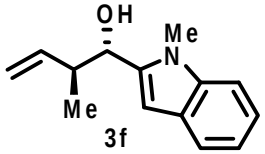


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.551	MM	0.3655	1524.15723	69.50020	5.3899
2	23.345	MM	0.3897	1.26212e4	539.76276	44.6329
3	24.492	MM	0.3972	1490.89722	62.56374	5.2723
4	28.911	MM	0.4964	1.26415e4	424.43793	44.7048



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.038	MM	0.3544	78.79714	3.70601	1.4656
2	30.166	MM	0.4978	5297.75879	177.38268	98.5344

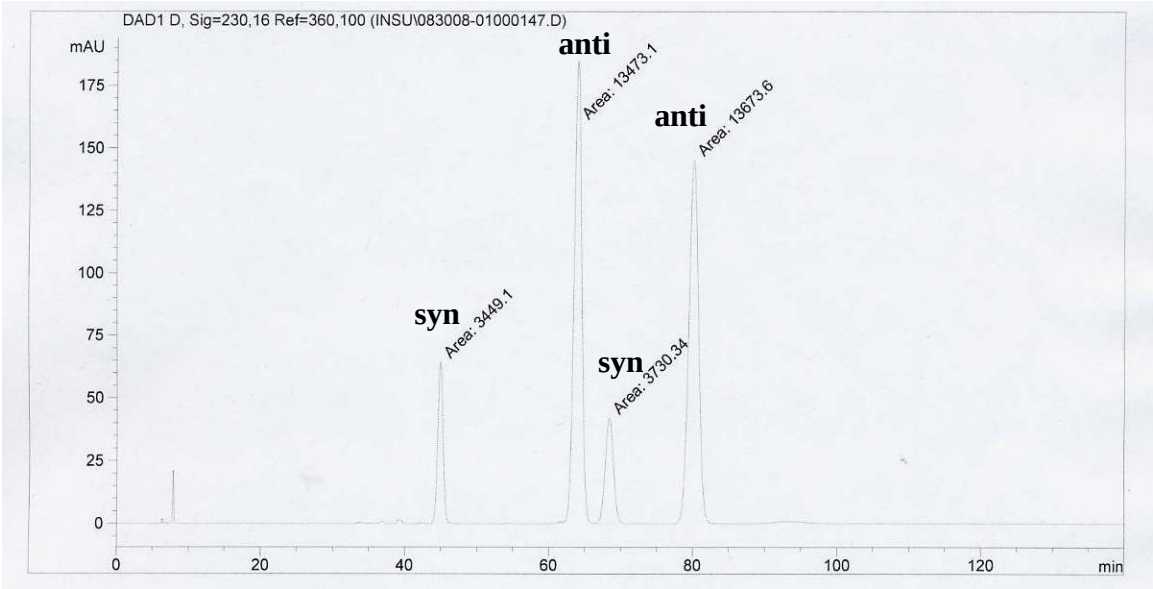
(1*S*,2*S*)-2-Methyl-1-(1-methyl-1*H*-indol-2-yl)but-3-en-1-ol (3f)



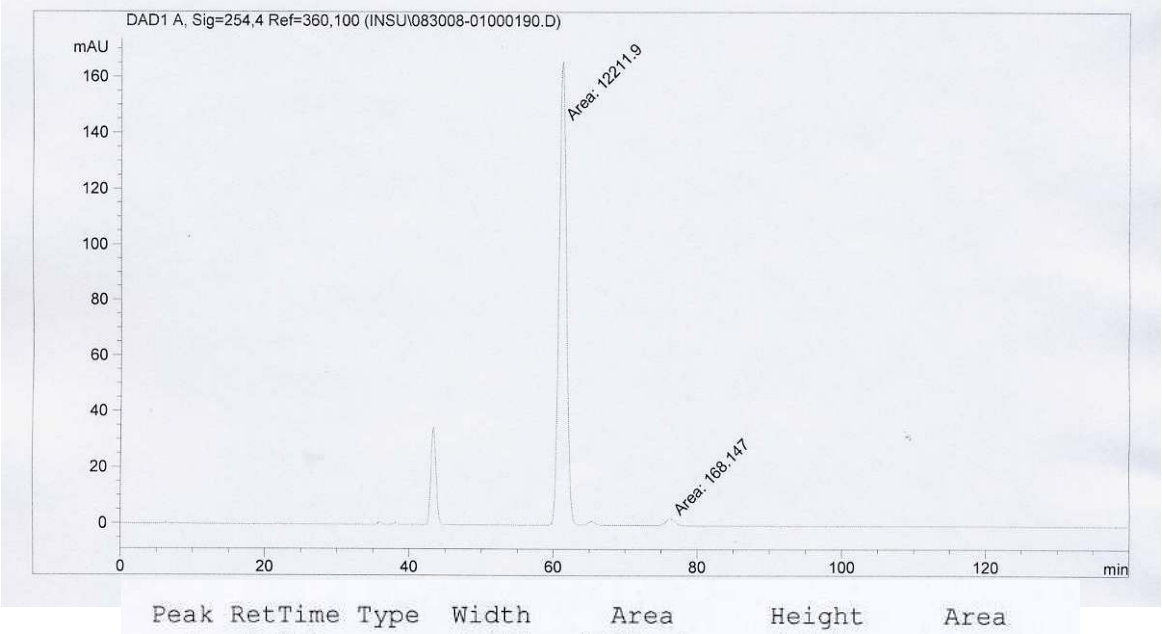
3f

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. 1-Methylindole-2-carboxaldehyde **2f** (63.7 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) and isopropanol (59.8 μL, 0.8 mmol, 200 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir at 80 ^oC for 72 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes:triethylamine, 1:12:0.01) provides **3f** (67.3 mg, 0.312 mmol, *anti*:*syn* = 6:1) as yellow solid in 78% yield.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 93:7, 0.5 mL/min, 254 nm), t_{major} = 61.1 min, t_{minor} = 76.2 min; ee = 97%.

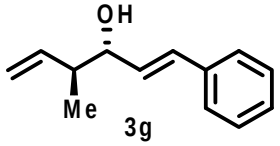


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.899	MM	0.8836	3449.09595	65.05764	10.0480
2	63.934	MM	1.2225	1.34731e4	183.68874	39.2502
3	68.404	MM	1.4447	3730.33984	43.03532	10.8673
4	80.037	MM	1.5674	1.36736e4	145.39421	39.8344



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	61.171	MM	1.2205	1.22119e4	166.76016	98.6418
2	76.248	MM	1.2490	168.14716	2.24382	1.3582

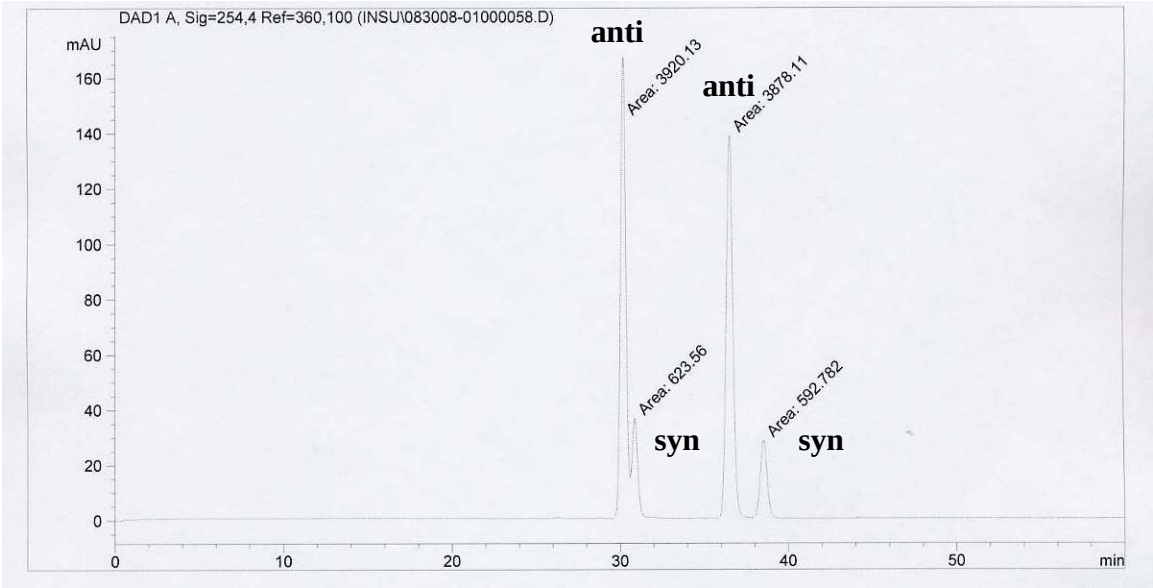
(3*R*,4*S*)-4-Methyl-1-phenylhexa-(1*E*,5)-dien-3-ol (3g)



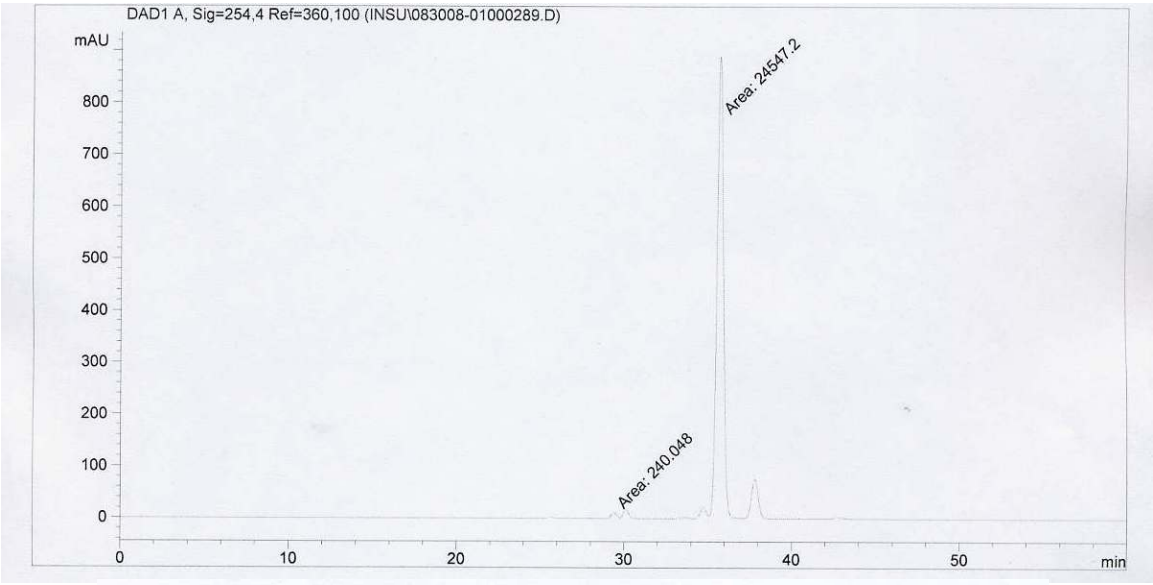
3g

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-C3-TUNEPHOS (11.9 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Cinnamaldehyde **2g** (52.9 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) and isopropanol (59.8 μL, 0.8 mmol, 200 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes:triethylamine, 1:15:0.01) provides **3g** (51.2 mg, 0.272 mmol, *anti*:*syn* = 8:1) as a pale yellow oil in 68% yield.

HPLC: (Chiralpak AS-H/AS-H column, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm), t_{minor} = 29.3 min, t_{major} = 35.6 min; ee = 98%.

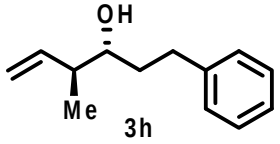


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.156	MM	0.3938	3920.13306	165.92987	43.4866
2	30.846	MM	0.2934	623.55994	35.42169	6.9172
3	36.477	MM	0.4653	3878.10742	138.90073	43.0204
4	38.499	MM	0.3667	592.78198	26.94354	6.5758



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.398	MM	0.3308	240.04750	12.09306	0.9684
2	35.673	MM	0.4574	2.45472e4	894.35132	99.0316

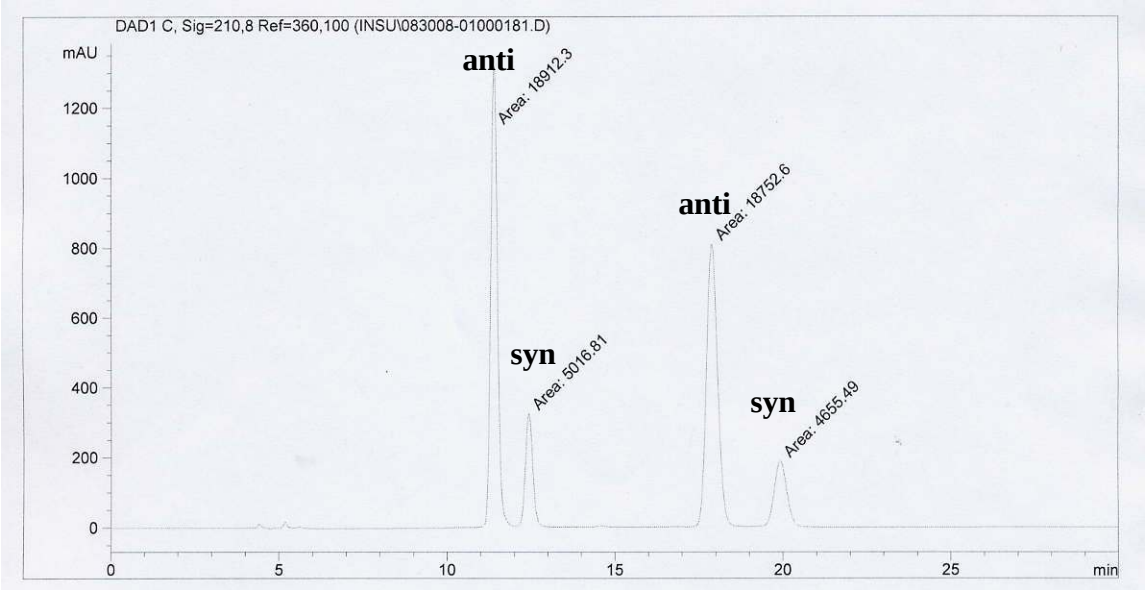
(3*R*,4*S*)-4-Methyl-1-phenylhex-5-en-3-ol (3h)



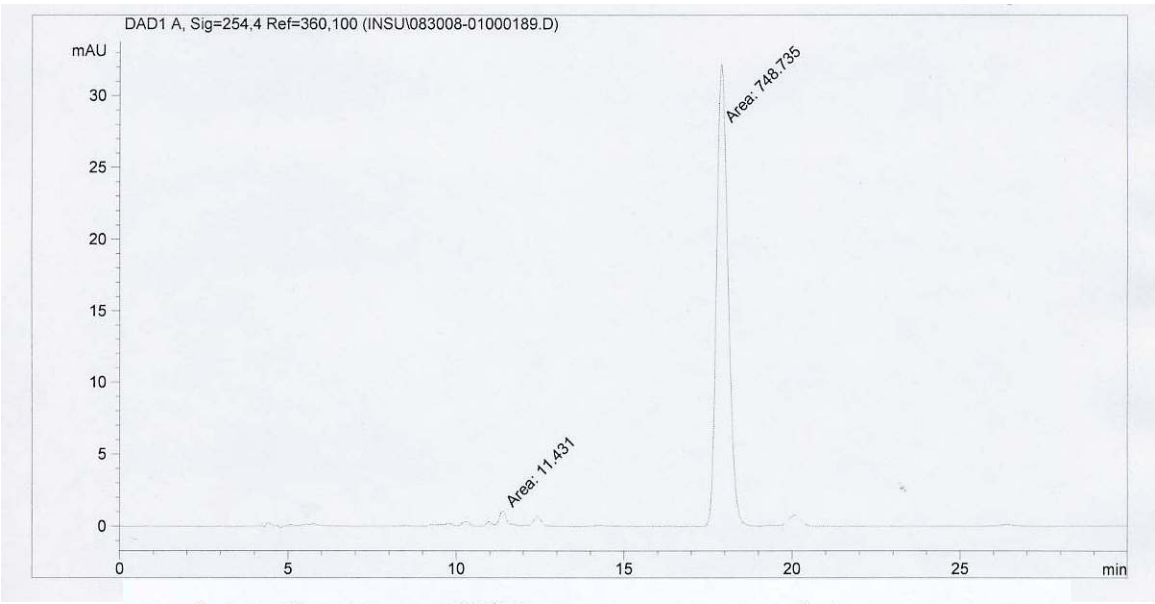
3h

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^{o}C for 0.5 hr and was then cooled to room temperature. 3-Phenylpropionaldehyde **2h** (53.7 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) and isopropanol (59.8 μL, 0.8 mmol, 200 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^{o}C for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:15) provides **3h** (54.1 mg, 0.284 mmol, *anti*:*syn* = 11:1) as a colorless oil in 71% yield.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 97:3, 0.7 mL/min, 254 nm), t_{minor} = 11.3 min, t_{major} = 17.8 min; ee = 97%.

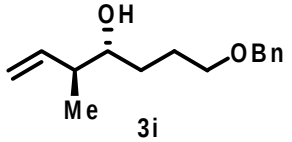


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.381	MM	0.2384	1.89123e4	1322.16956	39.9523
2	12.431	MM	0.2570	5016.80615	325.38425	10.5980
3	17.868	MM	0.3856	1.87526e4	810.45520	39.6150
4	19.911	MM	0.4220	4655.49316	183.85841	9.8347



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.380	MM	0.1971	11.43095	9.66435e-1	1.5037
2	17.890	MM	0.3911	748.73468	31.90515	98.4963

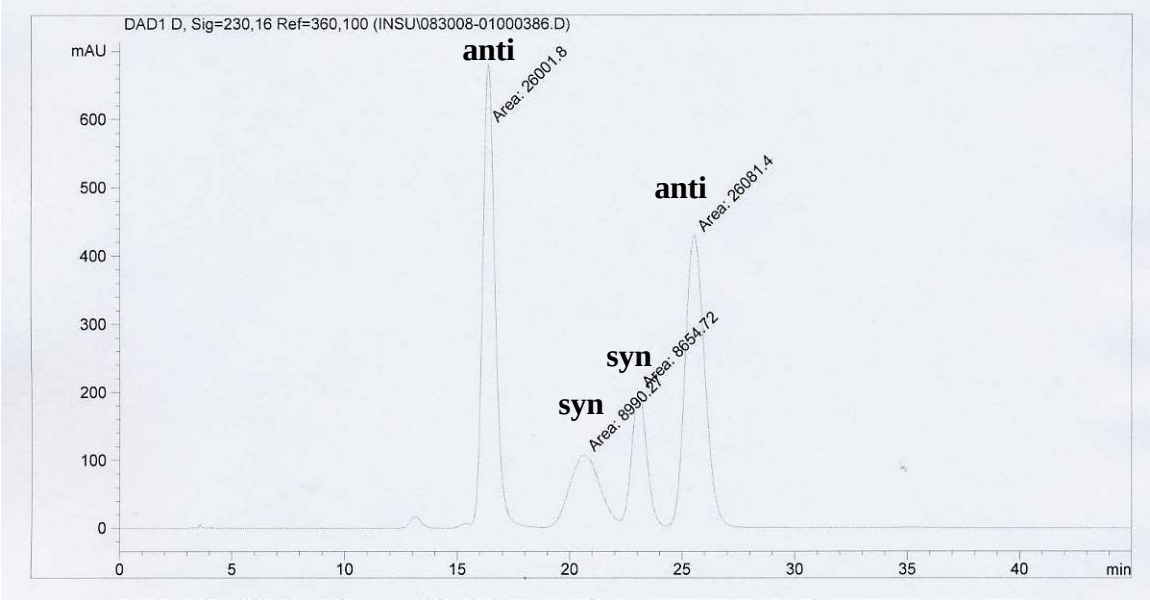
(3*S*,4*R*)-7-(Benzyloxy)-3-methylhept-1-en-4-ol (3i)



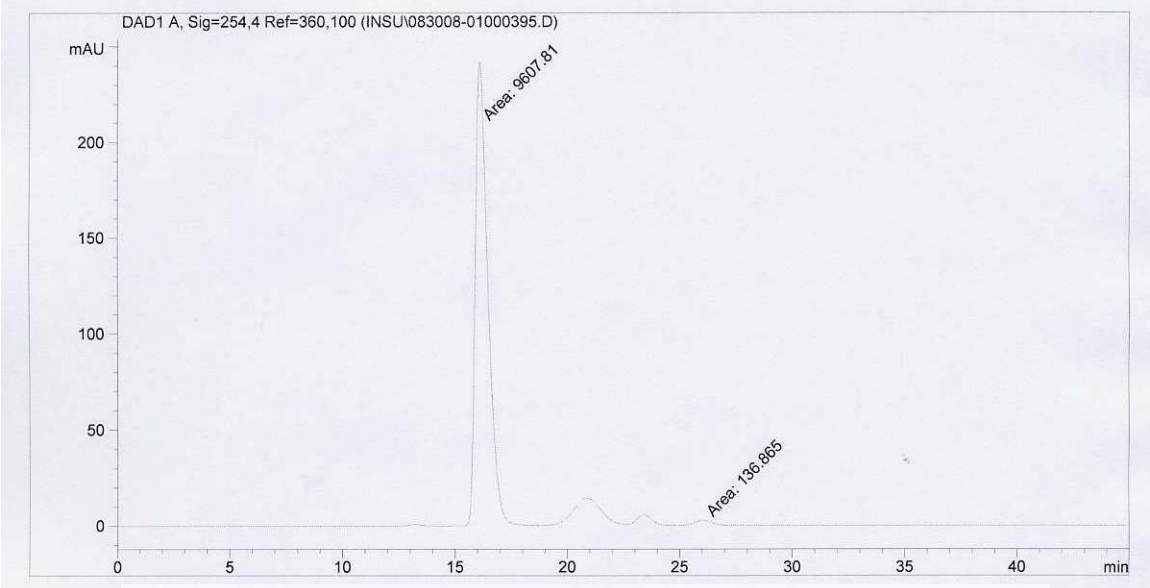
3i

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. 4-(Benzyloxy)butanal **2i** (71.3 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) and isopropanol (59.8 μL, 0.8 mmol, 200 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:12) provides **3i** (63.8 mg, 0.272 mmol, *anti*:*syn* = 11:1) as a colorless oil in 68% yield.

HPLC: Enantiomeric excess was determined by HPLC analysis of the 2-naphthoate derivative of the product (Chiralcel OJ-H column, hexanes:*i*-PrOH = 98.5:1.5, 1.0 mL/min, 254 nm), t_{major} = 16.0 min, t_{minor} = 26.0 min; ee = 97%.

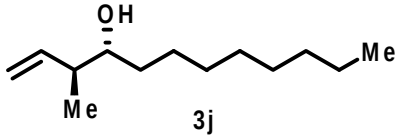


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.343	MM	0.6395	2.60018e4	677.66370	37.2902
2	20.654	MM	1.4762	8990.26855	101.50465	12.8933
3	23.061	MM	0.7472	8654.72070	193.04347	12.4121
4	25.511	MM	1.0137	2.60814e4	428.80423	37.4044



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.060	MM	0.6610	9607.80762	242.24773	98.5955
2	26.041	MM	0.8548	136.86462	2.66843	1.4045

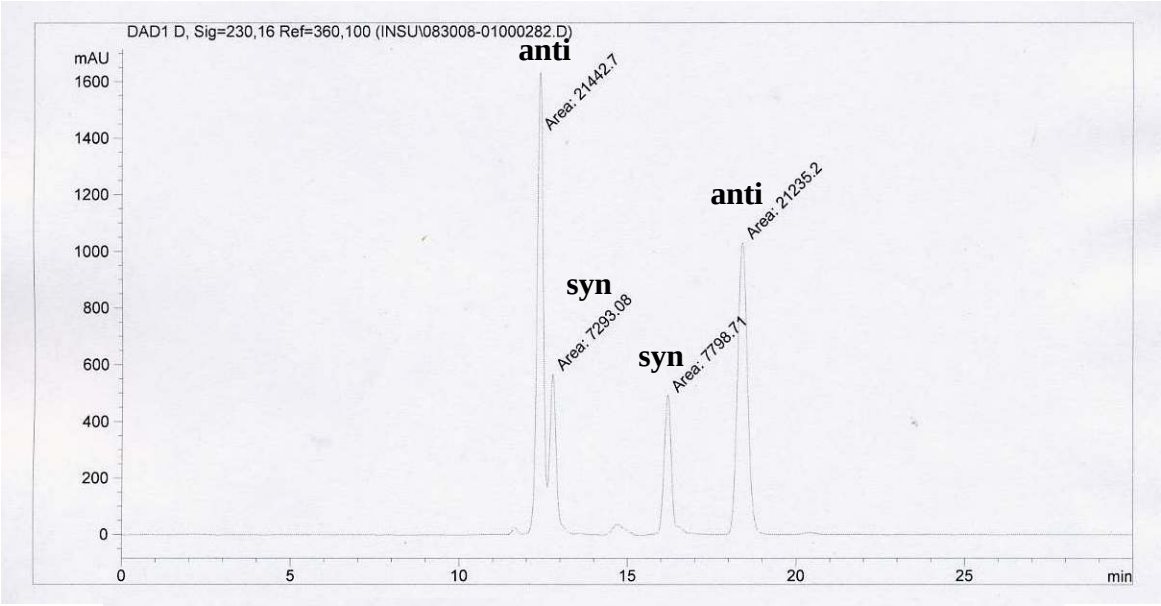
(3*S*,4*R*)-3-Methyldodec-1-en-4-ol (3j)



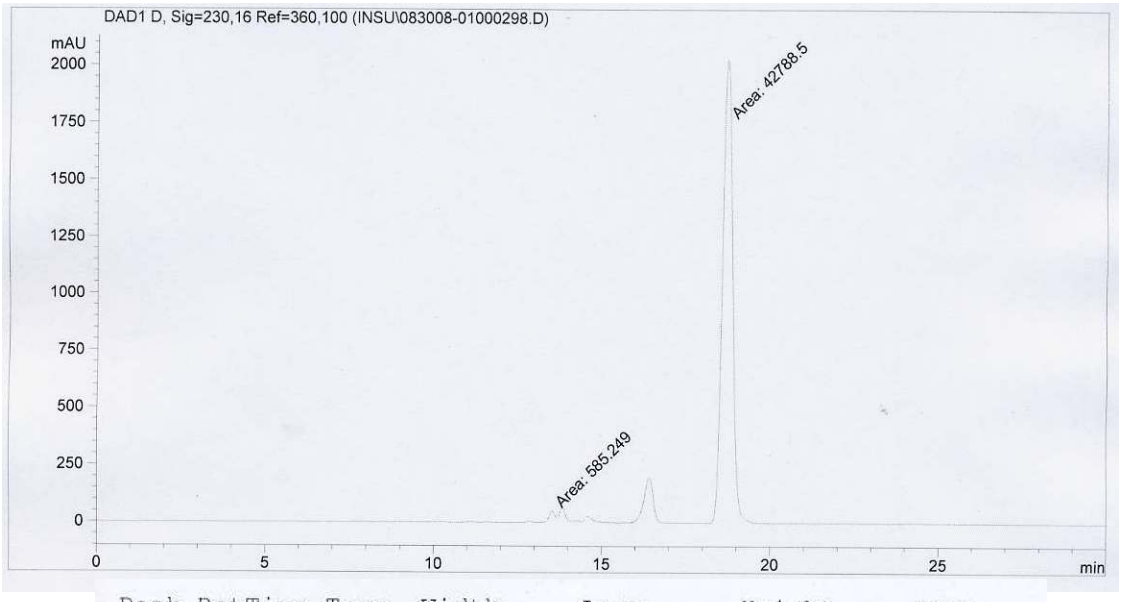
3j

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Nonanal **2j** (56.9 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) and isopropanol (59.8 μL, 0.8 mmol, 200 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:30) provides **3j** (59.4 mg, 0.299 mmol, *anti*:*syn* = 11:1) as a colorless oil in 75% yield.

HPLC: Enantiomeric excess was determined by HPLC analysis of the 2-naphthoate derivative of the product (Chiralpak AD-H column, hexanes:*i*-PrOH = 99.5:0.5, 0.4 mL/min, 230 nm), t_{minor} = 13.5 min, t_{major} = 18.6 min; ee = 97%.



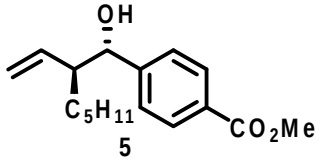
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.383	MM	0.2184	2.14427e4	1636.01721	37.1176
2	12.774	MM	0.2136	7293.07861	569.18518	12.6244
3	16.191	MM	0.2622	7798.70605	495.73898	13.4997
4	18.390	MM	0.3426	2.12352e4	1033.06030	36.7583



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.525	MM	0.2034	585.24896	47.95393	1.3493
2	18.681	MM	0.3517	4.27885e4	2027.82654	98.6507

Detailed Procedure and Spectral Data for Experiments Aimed at Probing the Origins of Stereoselection

Methyl 4-((1*S*,2*S*)-1-hydroxy-2-vinylheptyl)benzoate (5)



5

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), BIPHEP (10.5 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by (*R*)-oct-1-en-3-yl acetate[9] (**4**) (136 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Methyl 4-(hydroxymethyl)benzoate **1e** (66.5 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:10) provides **5** (53.1 mg, 0.192 mmol, *anti*:*syn* = 9:1) as a pale yellow oil in 48% yield.

TLC (SiO_2): R_f = 0.26 (ethyl acetate:hexanes, 1:10).

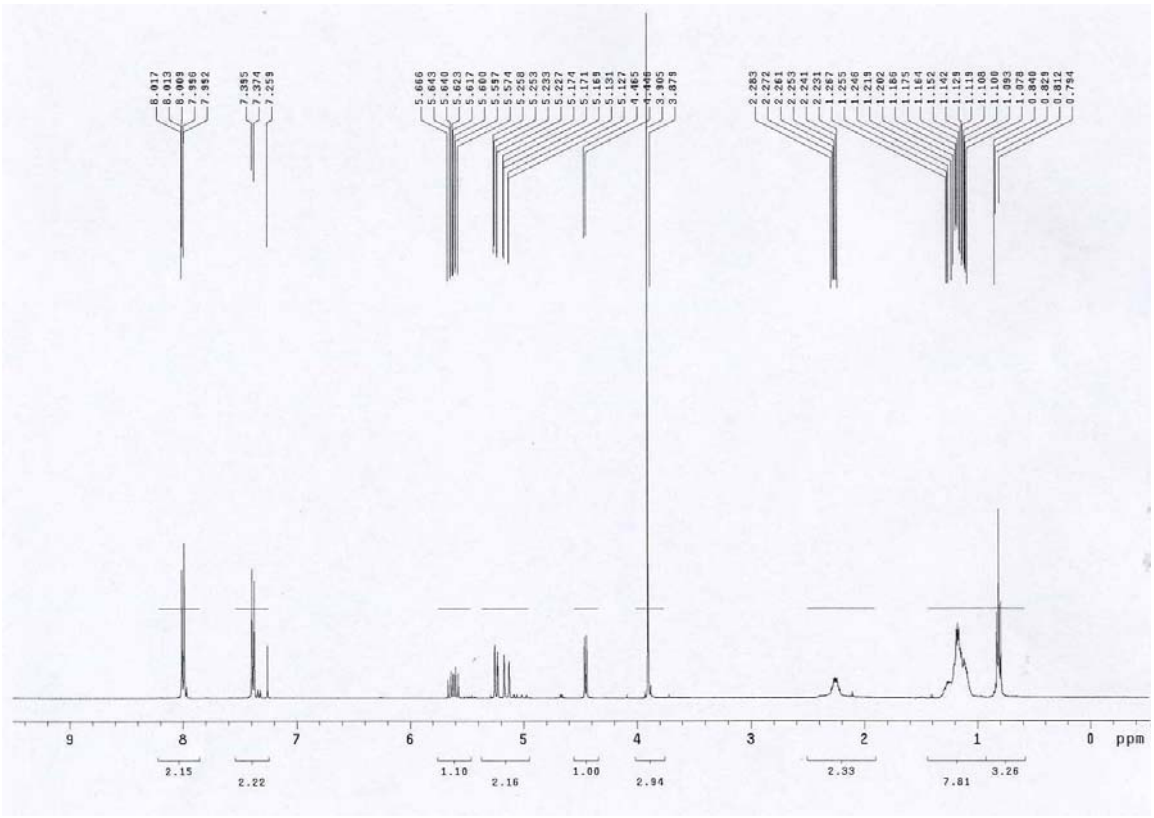
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 5.62 (ddd, *J* = 16.0, 10.0, 7.6 Hz, 1H), 5.24 (d, *J* = 10.0, 7.6 Hz, 1H), 5.17 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.45 (d, *J* = 7.6 Hz, 1H), 3.90 (s, 3H), 2.29-2.23 (m, 2H), 1.27-1.07 (m, 8H), 0.81 (t, *J* = 7.2 Hz, 3H).

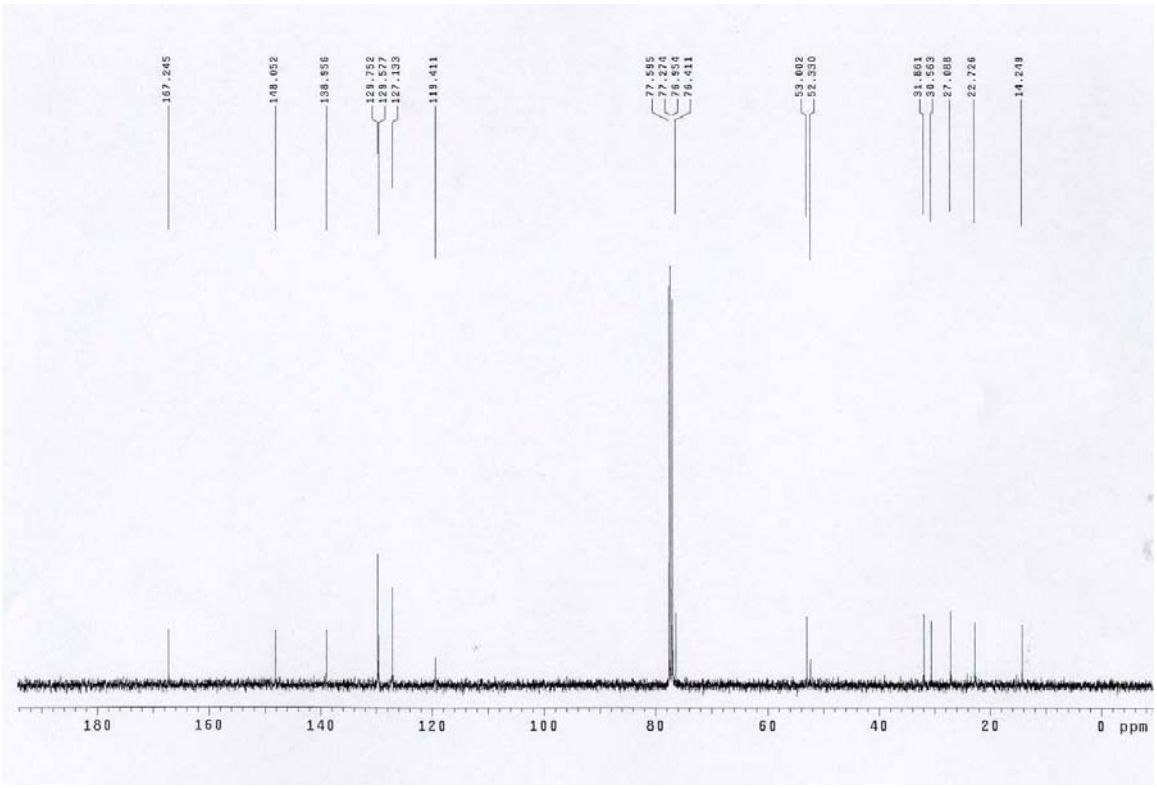
^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 148.1, 139.0, 129.8, 129.6, 127.1, 119.4, 76.4, 53.0, 52.3, 31.9, 30.6, 27.1, 22.7, 14.2.

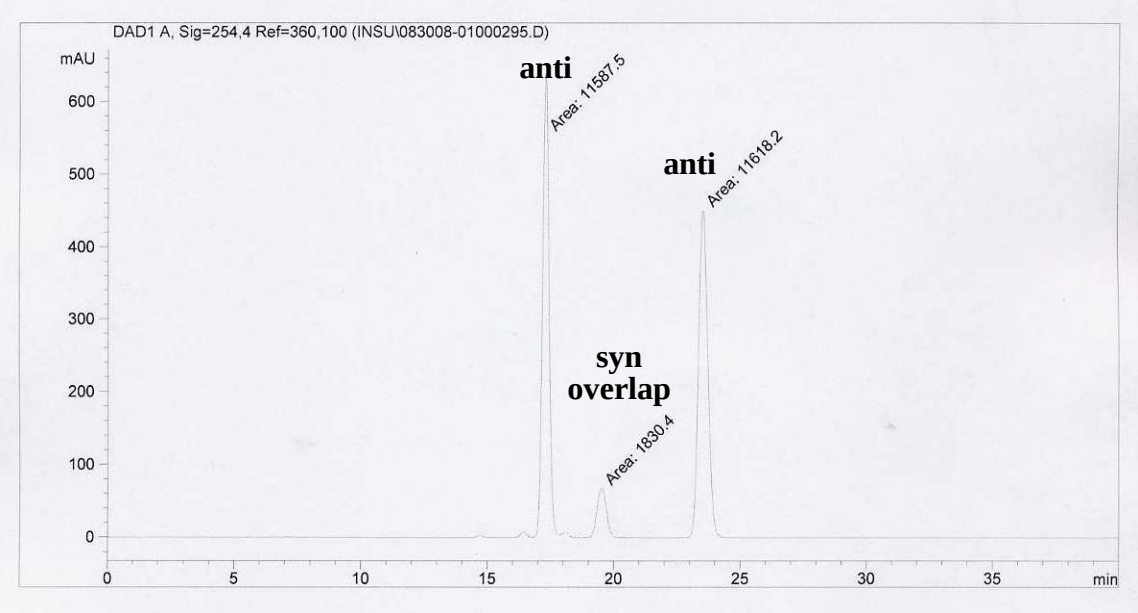
FTIR (neat): υ 3481, 2953, 2928, 2857, 2161, 1979, 1722, 1638, 1611, 1576, 1435, 1416, 1275, 1191, 1176, 1109, 1050, 1018, 999, 967, 913, 859, 809, 774, 736, 721, 709, 667 cm^{-1}.

HPLC: (Chiralpak AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 254 nm), t_{minor} = 17.2 min, t_{major} = 23.4 min; ee = 14%.

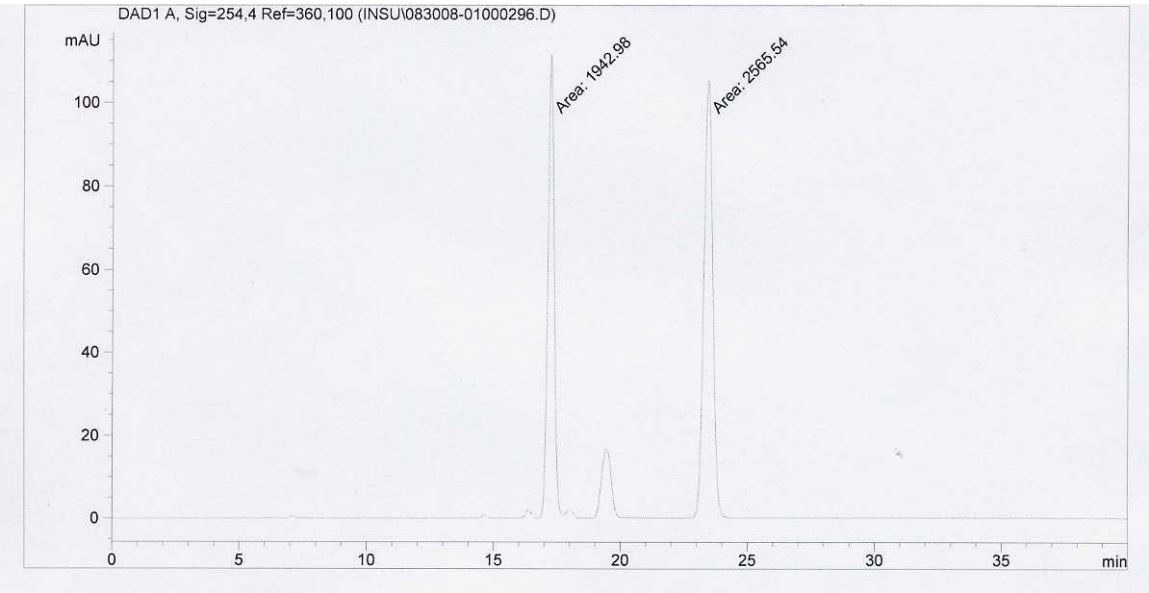
[9] The optically active (*R*)-oct-1-en-3-yl acetate (98%ee) was prepared from commercially available (*R*)-oct-en-3-ol (ACROS) by acetylation with Ac_2O.







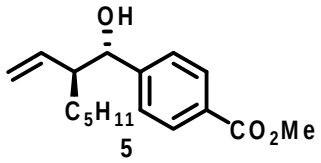
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.273	MM	0.3012	1.15875e4	641.20361	46.2831
2	19.520	MM	0.4501	1830.40491	67.77759	7.3110
3	23.497	MM	0.4290	1.16182e4	451.32141	46.4059



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.232	MM	0.2904	1942.98035	111.49592	43.0957
2	23.431	MM	0.4066	2565.54126	105.14960	56.9043

Matched Case

Methyl 4-((1*S*,2*S*)-1-hydroxy-2-vinylheptyl)benzoate (5)



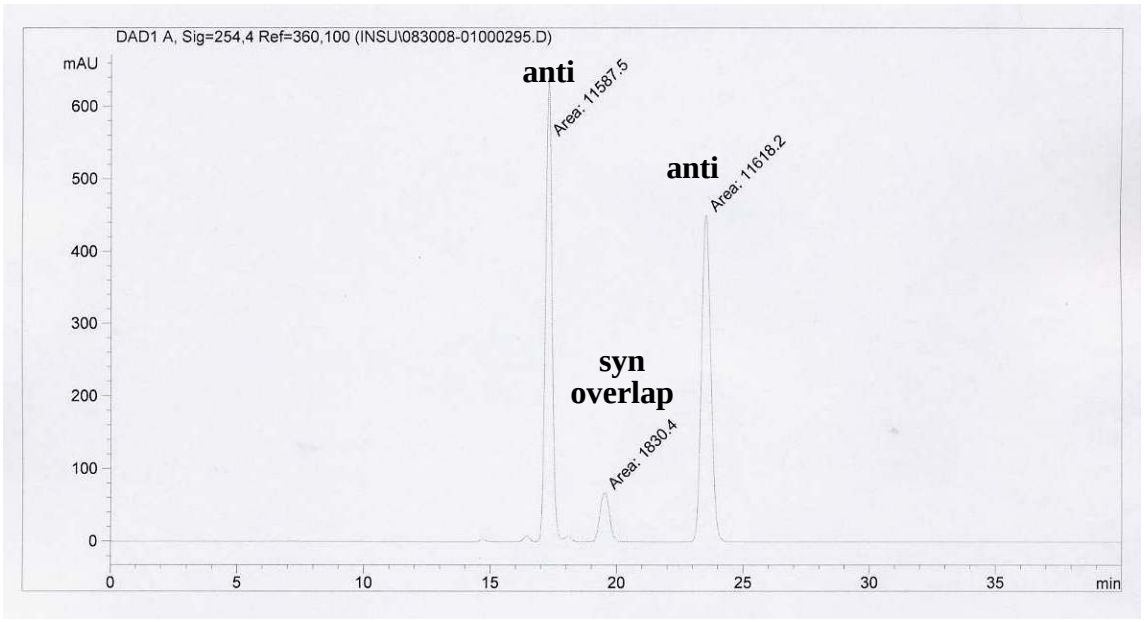
5

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*S*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by (*R*)-oct-1-en-3-yl acetate[9] (**4**) (136 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Methyl 4-(hydroxymethyl)benzoate **1e** (66.5 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:30-1:10) provides **5** (68.3 mg, 0.247 mmol, 62% yield, *anti*:*syn* = 11.9:1) and **4** (62.5 mg, 0.367 mmol, 46% recovered yield), respectively.

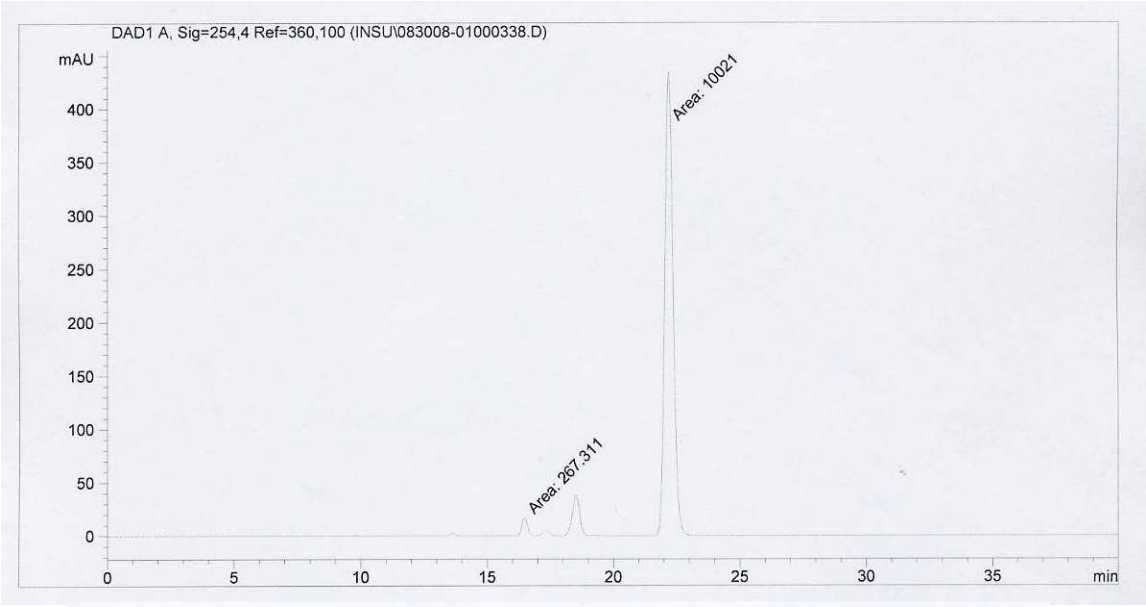
HPLC for 5: (Chiralpak AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 254 nm), t_{minor} = 16.4 min, t_{major} = 22.1 min; ee = 95%.

HPLC for 4: Enantiomeric excess was determined by HPLC analysis of the 3,5-dinitrobenzoate derivative of the alcohol obtained from deacetylation of **4** (Chiralcel OJ-H column, hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 254 nm), t_{major} = 10.3 min, t_{minor} = 11.3 min; ee = 39%.

HPLC for 5

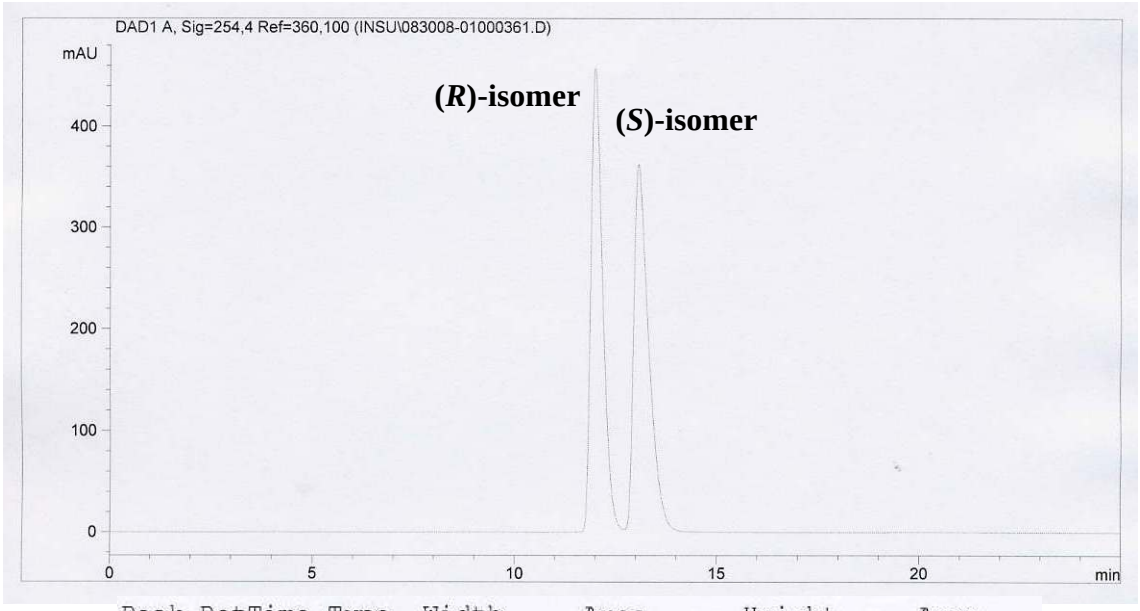


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.273	MM	0.3012	1.15875e4	641.20361	46.2831
2	19.520	MM	0.4501	1830.40491	67.77759	7.3110
3	23.497	MM	0.4290	1.16182e4	451.32141	46.4059

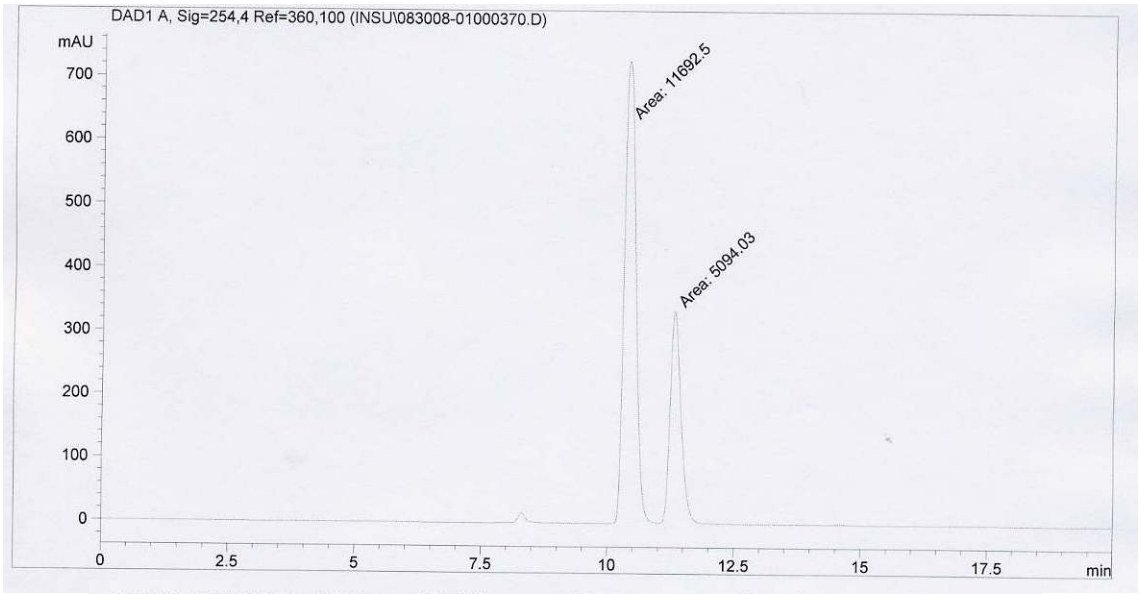


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.473	MM	0.2612	267.31143	17.05376	2.5982
2	22.181	MM	0.3840	1.00210e4	434.92172	97.4018

HPLC for 4



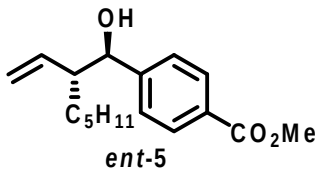
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.968	VV	0.3079	9332.04590	457.56354	49.8522
2	13.046	VB	0.3822	9387.37695	362.42276	50.1478



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.374	MM	0.2674	1.16925e4	728.79681	69.6540
2	11.305	MM	0.2516	5094.02734	337.42206	30.3460

Mismatched Case

Methyl 4-((1*R*,2*R*)-1-hydroxy-2-vinylheptyl)benzoate (*ent*-5)



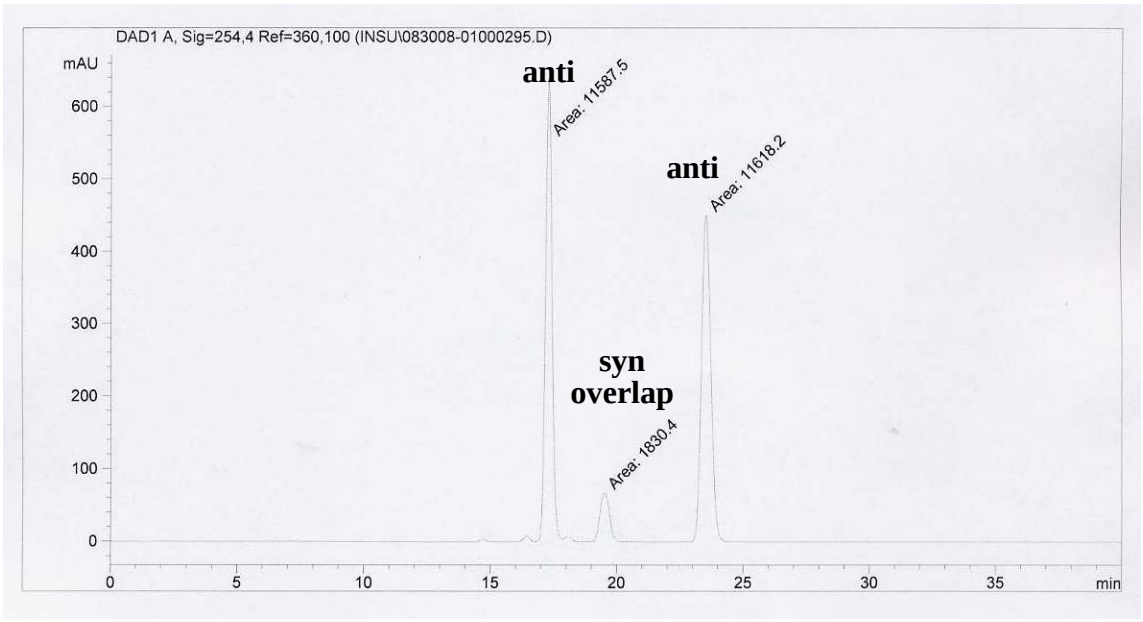
ent-5

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), (*R*)-SEGPHOS (12.2 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by (*R*)-oct-1-en-3-yl acetate[9] (**4**) (136 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Methyl 4-(hydroxymethyl)benzoate **1e** (66.5 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) was added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:30-1:10) provides ***ent*-5** (37.8 mg, 0.137 mmol, 34% yield, *anti*:*syn* = 4.6:1) and **4** (80.3 mg, 0.472 mmol, 59% recovered yield), respectively.

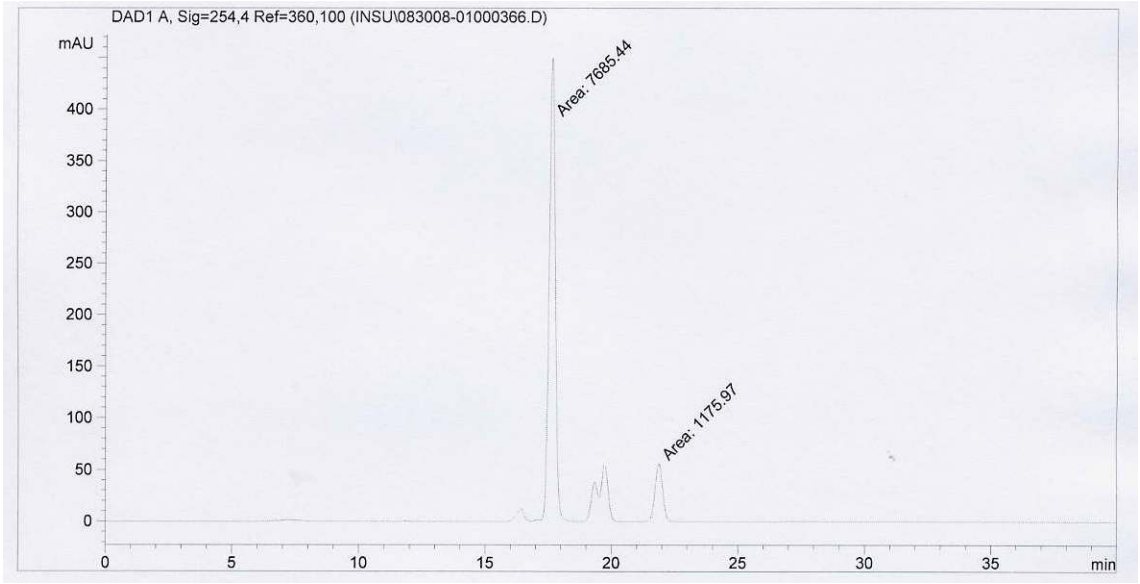
HPLC for *ent*-5: (Chiralpak AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 254 nm), t_{major} = 17.6 min, t_{minor} = 21.8 min; ee = 73%.

HPLC for 4: Enantiomeric excess was determined by HPLC analysis of the 3,5-dinitrobenzoate derivative of the alcohol obtained from deacetylation of **4** (Chiralcel OJ-H column, hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 254 nm), t_{major} = 10.0 min, t_{minor} = 11.0 min; ee = 30%.

HPLC for *ent*-5

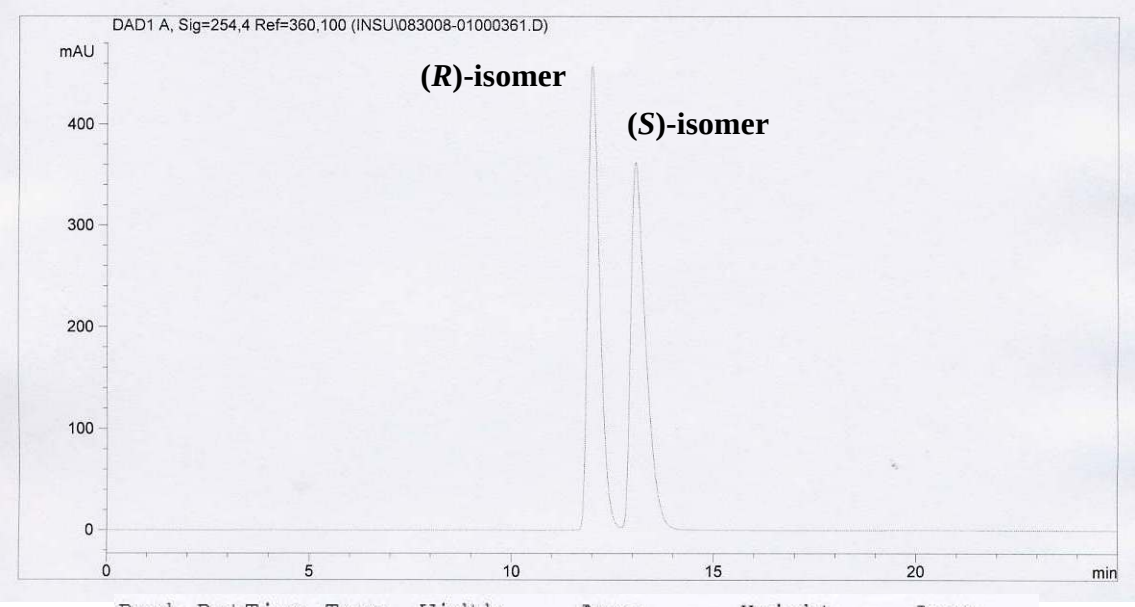


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.273	MM	0.3012	1.15875e4	641.20361	46.2831
2	19.520	MM	0.4501	1830.40491	67.77759	7.3110
3	23.497	MM	0.4290	1.16182e4	451.32141	46.4059

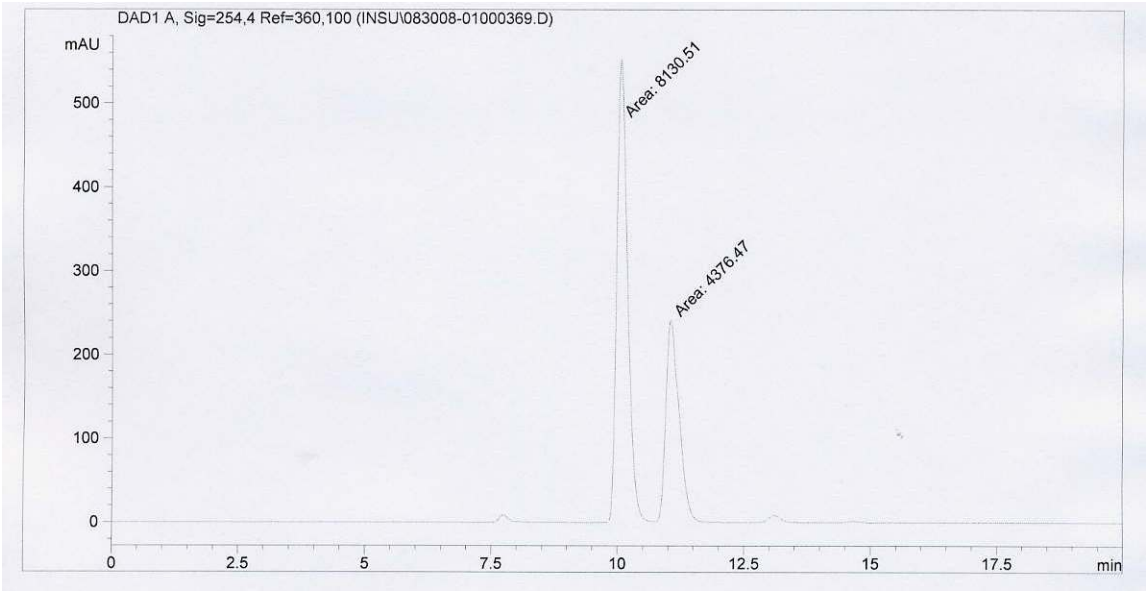


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.616	MM	0.2850	7685.44141	449.39328	86.7293
2	21.871	MM	0.3516	1175.97424	55.74825	13.2707

HPLC for 4



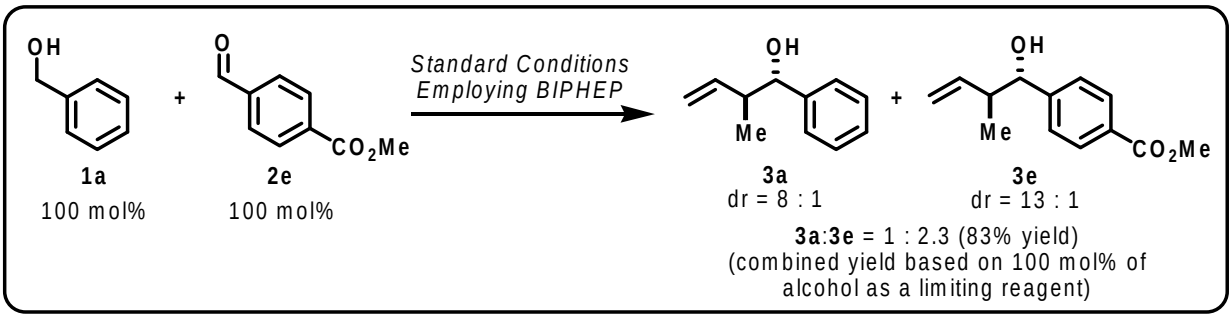
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.968	VV	0.3079	9332.04590	457.56354	49.8522
2	13.046	VB	0.3822	9387.37695	362.42276	50.1478



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.048	MM	0.2463	8130.51074	550.11261	65.0078
2	11.045	MM	0.3037	4376.46777	240.19214	34.9922

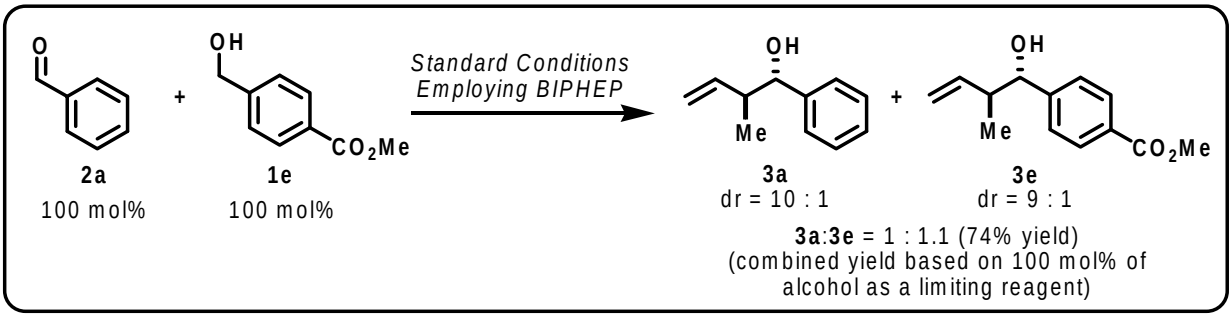
Competition Experiment Establishing Rapid Redox Equilibration

Reaction between Alcohol (1a) and Aldehyde (2e)



To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), BIPHEP (10.5 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^oC for 0.5 hr and was then cooled to room temperature. Benzyl alcohol **1a** (43.3 mg, 0.4 mmol, 100 mol%) and methyl 4-formylbenzoate **2e** (65.7 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) were added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^oC for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:20-1:10) provides **3a** (22.1 mg, 0.136 mmol, 34% yield, *anti*:*syn* = 8:1) and **3e** (42.8 mg, 0.194 mmol, 49% yield, *anti*:*syn* = 13:1).

Reaction between Aldehyde (2a) and Alcohol (1e)



To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol, 2.5 mol%), BIPHEP (10.5 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.1 mg, 0.08 mmol, 20 mol%) and 4-cyano-3-nitrobenzoic acid (7.7 mg, 0.04 mmol, 10 mol%) was added THF (0.2 mL) followed by acetic acid 3-buten-2-yl ester (91.3 mg, 0.8 mmol, 200 mol%). The reaction mixture was allowed to stir at 90 ^{o}C for 0.5 hr and was then cooled to room temperature. Benzaldehyde **2a** (42.4 mg, 0.4 mmol, 100 mol%) and methyl 4-(hydroxymethyl)benzoate **1e** (66.5 mg, 0.4 mmol, 100 mol%) in THF (0.2 mL) were added to the reaction mixture and the reaction mixture was allowed to stir at 90 ^{o}C for 48 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:20-1:10) provides **3a** (22.7 mg, 0.140 mmol, 35% yield, *anti*:*syn* = 10:1) and **3e** (34.1 mg, 0.155 mmol, 39% yield, *anti*:*syn* = 9:1).