Supporting Information

Enantioselective Iridium Catalyzed Carbonyl Allylation from the Alcohol or Aldehyde Oxidation Level Using Allyl Acetate as an Allyl Metal Surrogate

In Su Kim, Ming-Yu Ngai and Michael J. Krische*

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

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General Methods

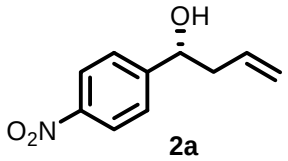
All reactions were run under an atmosphere of nitrogen. Tetrahydrofuran (THF) was obtained from Pure-Solv MD-5 Solvent Purification System (Innovative Technology, inc). Anhydrous solvents were transferred by an oven-dried syringe. Sealed tubes were purchased from Fischer Scientific and dried in oven for overnight and cooled under a stream of nitrogen prior to use. Commercially available allyl acetate (Acros), acetic acid 2-methyl-2-propenyl ester (3-acetoxy-1-butene, TCI), alcohols and aldehydes were purified by distillation or recrystallisation prior to use. $[Ir(cod)_2Cl]$ was used as received from Strem Chemicals. Cesium carbonate and 3-nitrobenzoic acid were purchased from Alfa Aesar and used directly without further purification. Isopropanol was used as received from Acros. 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. Melting points were obtained on a Thomas-Hoover Unimelt apparatus. 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).

General Procedure for Enantioselective *C*-Allylation of Alcohols Using Allyl Acetate

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with alcohols **1a**-**1i** (0.20 mmol, 100 mol%), $[Ir(cod)Cl]_2$ (0.005 mmol, 2.5 mol%), (*R*)-BINAP (0.010 mmol, 5 mol%), Cs_2CO_3 (0.040 mmol, 20 mol%) and 3-nitrobenzoic acid (0.020 mmol, 10 mol%) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (2.0 mmol, 1000 mol%). The reaction mixture was allowed to stir at 100 ^oC for 20 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes) provided **2a**-**2i**.

Detailed Procedure and Spectral Data for Enantioselective *C*-Allylation Adducts (2a-2i) from Alcohols (1a-1i)

(*R*)-1-(4-Nitrophenyl)but-3-en-1-ol (2a)



2a

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 4-nitrobenzyl alcohol **1a** (30.6 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (*R*)-BINAP (6.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:6) provided **2a** (27.9 mg, 0.144 mmol) as a yellow oil in 72% yield.

TLC (SiO_2): R_f = 0.26 (ethyl acetate:hexanes, 1:4).

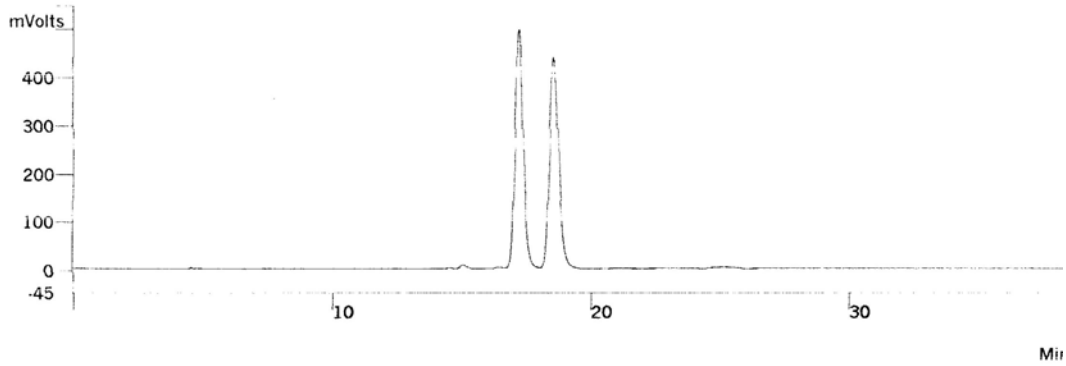
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 5.83-5.72 (m, 1H), 5.21-5.14 (m, 2H), 4.85 (dd, *J* = 8.0, 4.8 Hz, 1H), 2.59-2.52 (m, 1H), 2.49-2.40 (m, 1H), 2.32 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 147.4, 133.4, 126.7, 123.8, 119.9, 72.3, 44.1.

HPLC: (Chiralpak AS-H column, hexanes:*i*-PrOH = 93:7, 0.7 mL/min, 254 nm), t_{major} = 17.8 min, t_{minor} = 19.1 min; ee = 91%.

The spectroscopic properties of this compound were consistent with the data available in the literature.[1]

[1] Bower, J. F.; Skucas, E.; Patman, R.; Krische, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 15134–15135.



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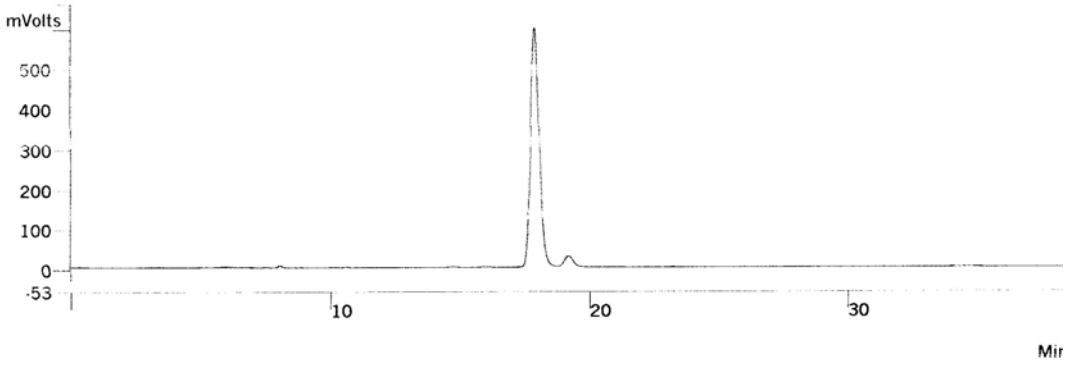

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2		4.3007	19.182	0.000	616756	0.00	BB	21.5		0
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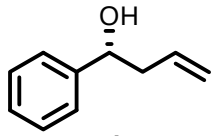
(*R*)-1-Phenylbut-3-en-1-ol (2b)



2b

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with benzyl alcohol **1b** (21.6 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (*R*)-BINAP (6.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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) provided **2b** (18.4 mg, 0.124 mmol) as a colorless oil in 62% yield.

TLC (SiO_2): R_f = 0.28 (ethyl acetate:hexanes, 1:10).

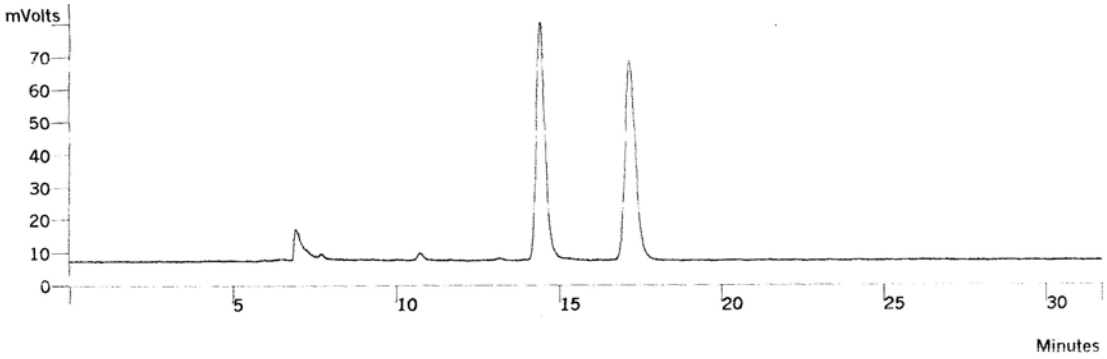
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.17 (m, 5H), 5.79-5.68 (m, 1H), 5.12-5.06 (m, 2H), 4.65 (dd, *J* = 7.6, 5.6 Hz, 1H), 2.47-2.39 (m, 2H), 1.93 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 134.4, 128.3, 127.5, 125.7, 118.4, 73.2, 43.8.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 254 nm), t_{major} = 14.4 min, t_{minor} = 17.2 min; ee = 93%.

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

[2] Yao, Q.; Sheets, M. *J. Org. Chem.* **2006**, *71*, 5384–5387.



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1		50.2320	14.411	0.000	1383682	0.00	BB	16.9		0
2		49.7680	17.172	0.000	1370899	0.00	BB	20.4		0
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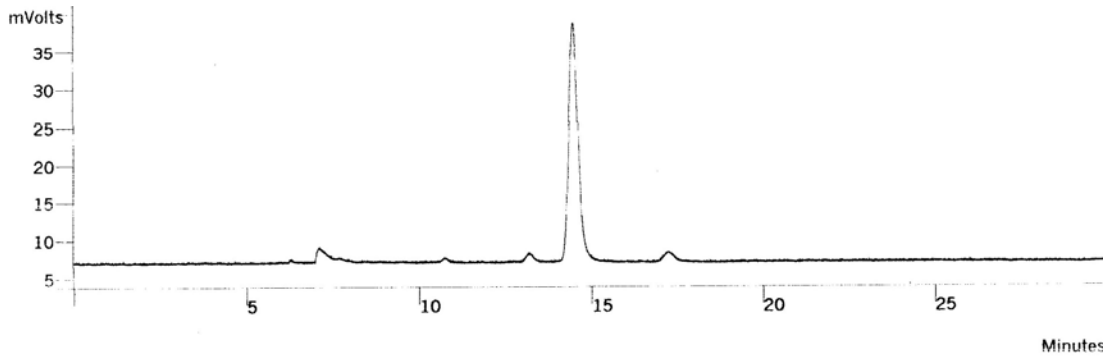

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2		3.5464	17.226	0.000	21831	0.00	BB	16.9		0
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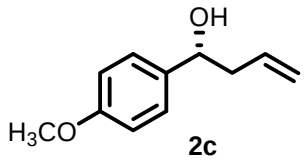
(*R*)-1-(4-Methoxyphenyl)but-3-en-1-ol (2c)



2c

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 4-methoxybenzyl alcohol **1c** (27.6 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (*R*)-BINAP (6.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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, 1:15:0.1) provided **2c** (26.0 mg, 0.146 mmol) as a colorless oil in 73% yield.

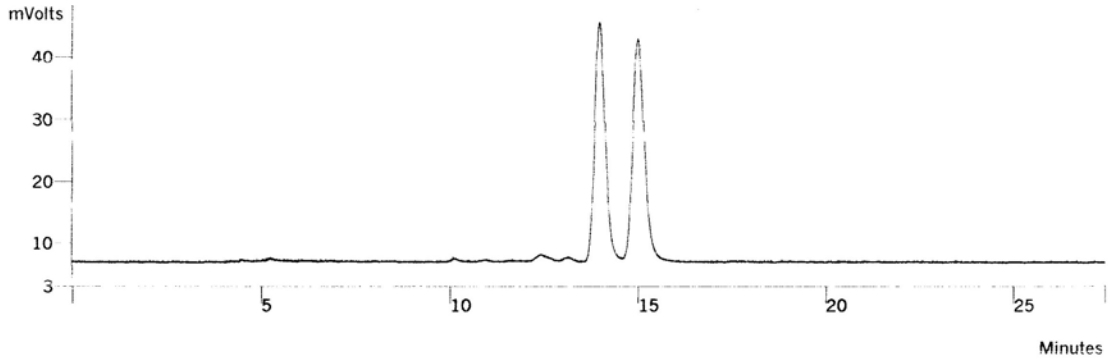
TLC (SiO_2): R_f = 0.27 (ethyl acetate:hexanes, 1:8).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.86-5.75 (m, 1H), 5.19-5.12 (m, 2H), 4.69 (t, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 2.50 (t, *J* = 6.8 Hz, 2H), 2.07 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 136.2, 134.8, 127.3, 118.4, 114.0, 73.2, 55.5, 43.9.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 0.7 mL/min, 254 nm), t_{major} = 13.9 min, t_{minor} = 15.0 min; ee = 93%.

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



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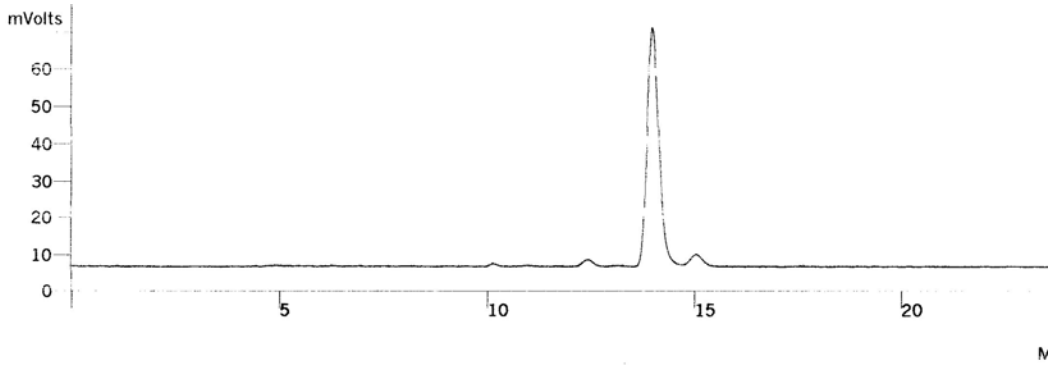

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1		96.3082	13.964	0.000	1256931	0.00	BB	18.2		0
2		3.6918	15.030	0.000	48182	0.00	BB	16.1		0
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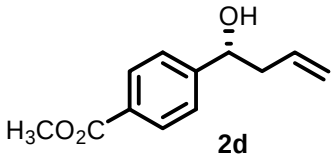
(*R*)-Methyl 4-(1-hydroxybut-3-enyl)benzoate (2d)



2d

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 4-hydroxymethylbenzoic acid methyl ester **1d** (33.2 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (*R*)-BINAP (6.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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) provided **2d** (31.8 mg, 0.154 mmol) as a colorless oil in 77% yield.

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

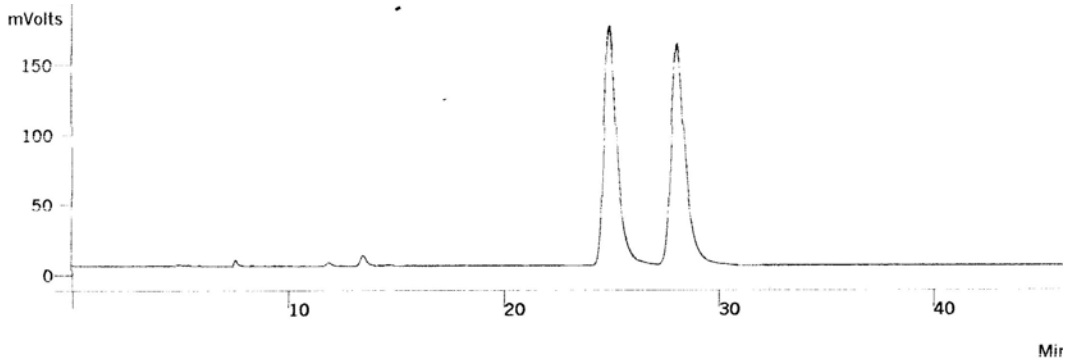
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.83-5.72 (m, 1H), 5.17-5.12 (m, 2H), 4.78 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.89 (s, 3H), 2.56-2.41 (m, 2H), 2.27 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 149.2, 134.0, 129.9, 129.4, 125.9, 119.1, 72.9, 52.3, 44.0.

HPLC: (Chiralpak AD-H column, hexanes:*i*-PrOH = 95:5, 0.6 mL/min, 254 nm), t_{major} = 24.8 min, t_{minor} = 28.0 min; ee = 93%.

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

[3] Thadani, A. N.; Batey, R. A. *Org. Lett.* **2002**, *4*, 3827–3830.



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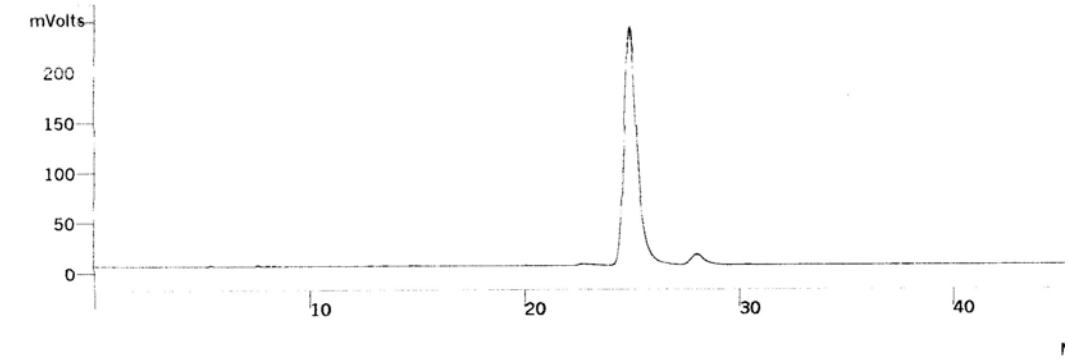

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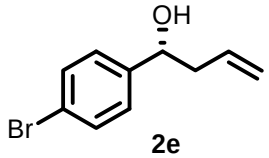
1		96.5879	24.879	0.000	9767664	0.00	BB	36.7		0
2		3.4121	28.062	0.000	345059	0.00	BB	34.5		0
	Totals	**100.0000**		**0.000**	**10112723**					

(*R*)-1-(4-Bromophenyl)but-3-en-1-ol (2e)



2e

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 4-bromobenzyl alcohol **1e** (37.4 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (*R*)-BINAP (6.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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, 1:20:0.1) provided **2e** (33.6 mg, 0.148 mmol) as a colorless oil in 74% yield.

TLC (SiO_2): R_f = 0.25 (ethyl acetate:hexanes, 1:12).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.83-5.71 (m, 1H), 5.18-5.13 (m, 2H), 4.69 (dd, *J* = 7.6, 4.8 Hz, 1H), 2.52-2.39 (m, 2H), 2.13 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 134.1, 131.7, 127.7, 121.4, 119.1, 72.7, 44.0.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 0.4 mL/min, 254 nm), t_{minor} = 22.9 min, t_{major} = 24.1 min; ee = 93%.

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

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
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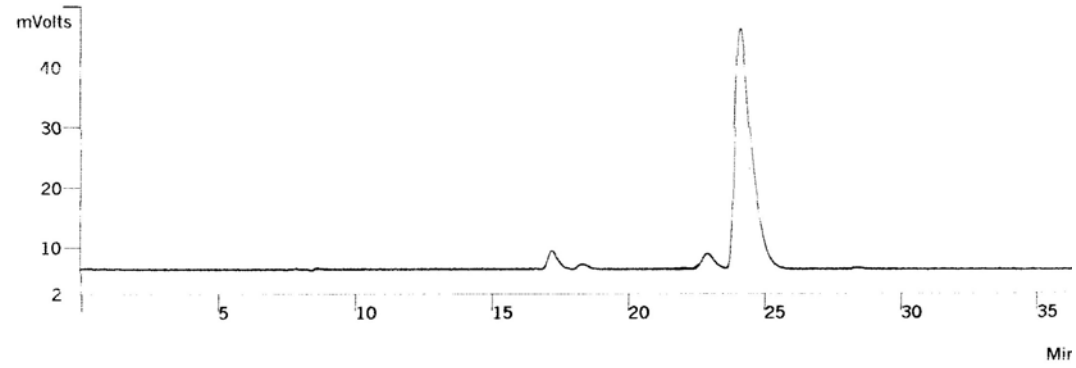
2		50.2334	24.048	0.000	1938018	0.00	BB	36.4		0
	Totals	**100.0000**		**0.000**	**3858028**					



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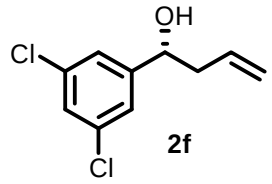
1		3.5155	22.910	0.000	58924	0.00	BB	23.6		0
2		96.4845	24.134	0.000	1617188	0.00	BB	37.1		0
	Totals	**100.0000**		**0.000**	**1676112**					

(*R*)-1-(3,5-Dichlorophenyl)but-3-en-1-ol (2f)



2f

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 3,5-dichlorobenzyl alcohol **1f** (35.4 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (*R*)-BINAP (6.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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, 1:15:0.1) provided **2f** (26.5 mg, 0.122 mmol) as a colorless oil in 61% yield.

TLC (SiO_2): R_f = 0.31 (ethyl acetate:hexanes, 1:8).

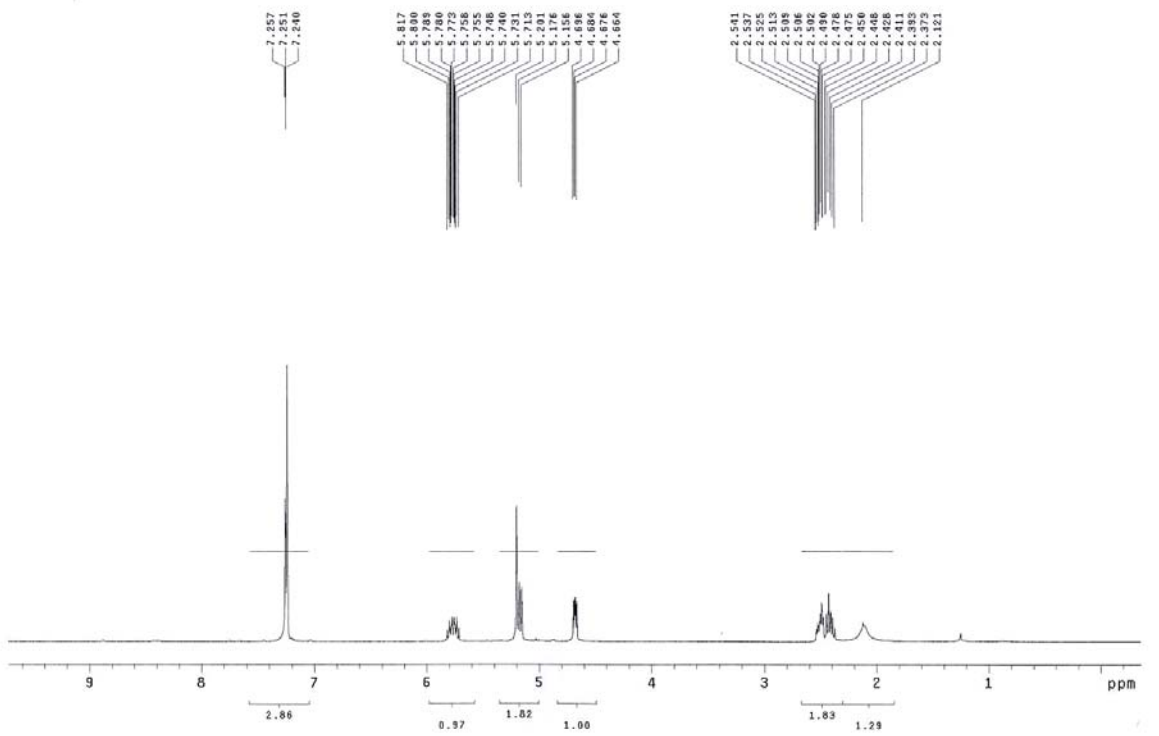
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.26 (m, 3H), 5.82-5.71 (m, 1H), 5.21-5.15 (m, 2H), 4.68 (dd, *J* = 8.0, 4.8 Hz, 1H), 2.55-2.37 (m, 2H), 2.12 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 135.1, 133.5, 127.7, 124.5, 119.7, 72.1, 44.0.

FTIR (neat): υ 3393, 3332, 1716, 1642, 1588, 1569, 1539, 1432, 1386, 1339, 1200, 1095, 1055, 994, 920, 858, 798, 689, 632 cm^{-1}.

HRMS (CI) Calcd. for $C_{10}H_{11}Cl_2O$ (M+1): 217.0187, Found: 217.0188.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 0.8 mL/min, 254 nm), t_{minor} = 6.6 min, t_{major} = 7.3 min; ee = 92%.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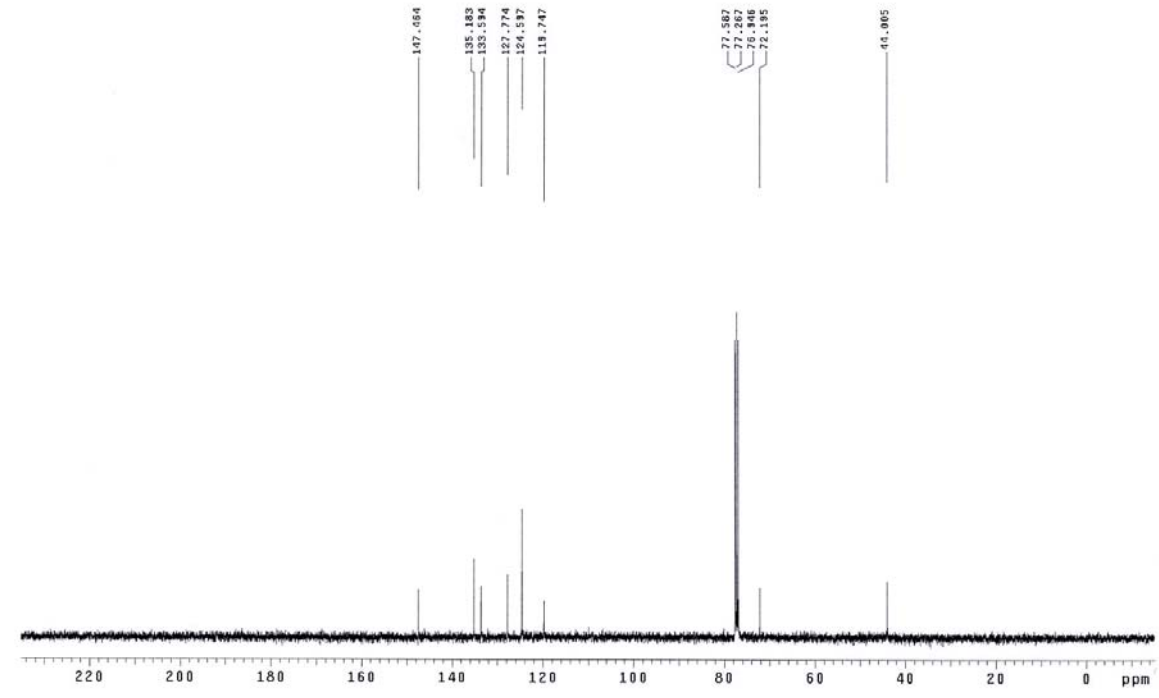
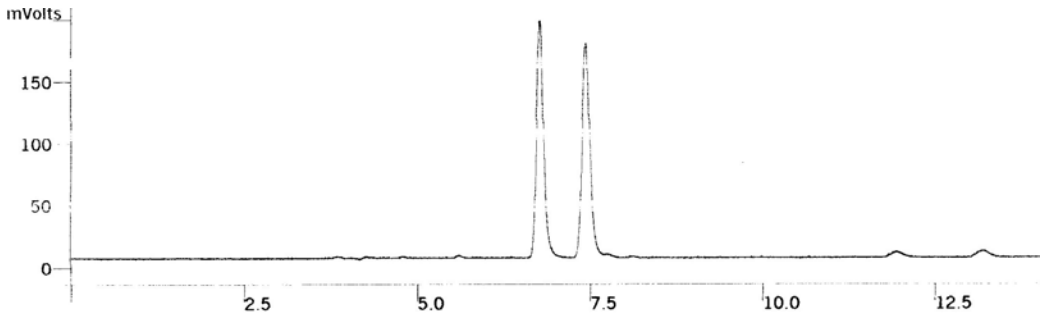
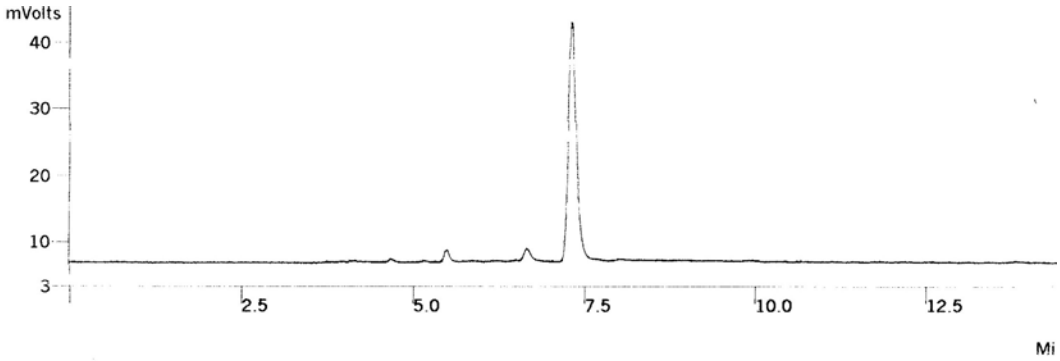
1.83
1.29


147.464
135.183
133.594
127.774
124.597
118.747
77.587
77.267
76.946
72.195
44.005
220
200
180
160
140
120
100
80
60
40
20
0
ppm

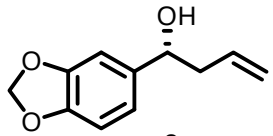


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.0744	6.768	0.000	1366093	0.00	BB	6.3		0
2		49.9256	7.435	0.000	1362033	0.00	BB	7.1		0
	Totals	**100.0000**		**0.000**	**2728126**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		3.8686	6.656	0.000	11647	0.00	BB	5.6		0
2		96.1314	7.309	0.000	289408	0.00	BB	7.2		0
	Totals	**100.0000**		**0.000**	**301055**					

(*R*)-1-(Benzo[d][1,3]dioxol-5-yl)but-3-en-1-ol (2g)



2g

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with piperonyl alcohol **1g** (30.4 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (*R*)-BINAP (6.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^{o}C for 20 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, 1:15:0.1) provided **2g** (31.2 mg, 0.151 mmol) as a colorless oil in 76% yield.

TLC (SiO_2): R_f = 0.22 (ethyl acetate:hexanes, 1:10).

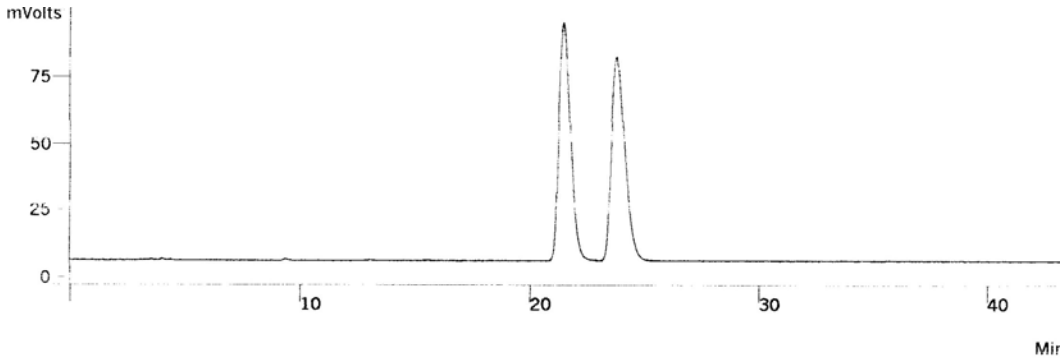
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 1H), 6.81-6.75 (m, 2H), 5.93 (s, 2H), 5.84-5.72 (m, 1H), 5.17-5.11 (m, 2H), 4.63 (t, *J* = 6.8 Hz, 1H), 2.46 (t, *J* = 6.4 Hz, 2H), 2.12 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 147.1, 138.2, 134.6, 119.4, 118.5, 108.2, 106.6, 101.2, 73.4, 44.0.

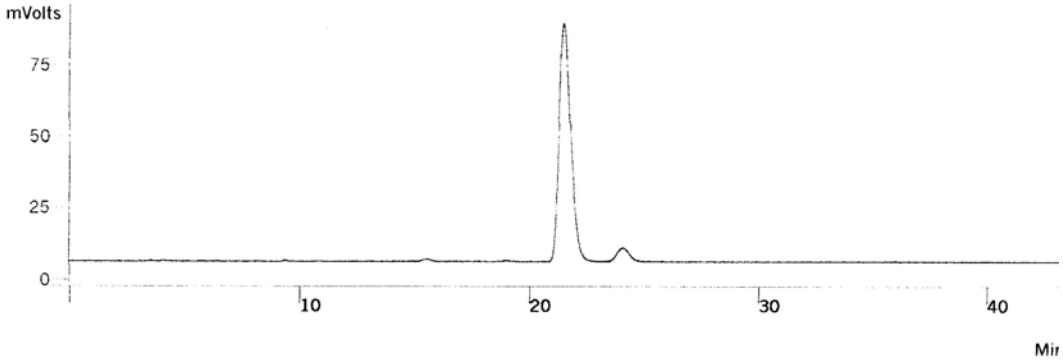
HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm), t_{major} = 21.4 min, t_{minor} = 24.0 min; ee = 91%.

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

[4] Zha, Z.; Hui, A.; Zhou, Y.; Miao, Q.; Wang, Z.; Zhang, H. *Org. Lett.* **2005**, *7*, 1903–1905.

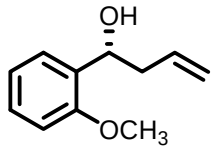


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.0174	21.429	0.000	3103757	0.00	BB	32.7		0
2		49.9826	23.784	0.000	3101601	0.00	BB	38.0		0
	Totals	**100.0000**		**0.000**	**6205358**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		95.3213	21.465	0.000	2942144	0.00	BB	32.9		0
2		4.6787	24.067	0.000	144410	0.00	BB	31.3		0
	Totals	**100.0000**		**0.000**	**3086554**					

(*R*)-1-(2-Methoxyphenyl)but-3-en-1-ol (2h)



2h

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 2-methoxybenzyl alcohol **1h** (27.6 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (*R*)-BINAP (6.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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, 1:15:0.1) provided **2h** (28.5 mg, 0.160 mmol) as a colorless oil in 80% yield.

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

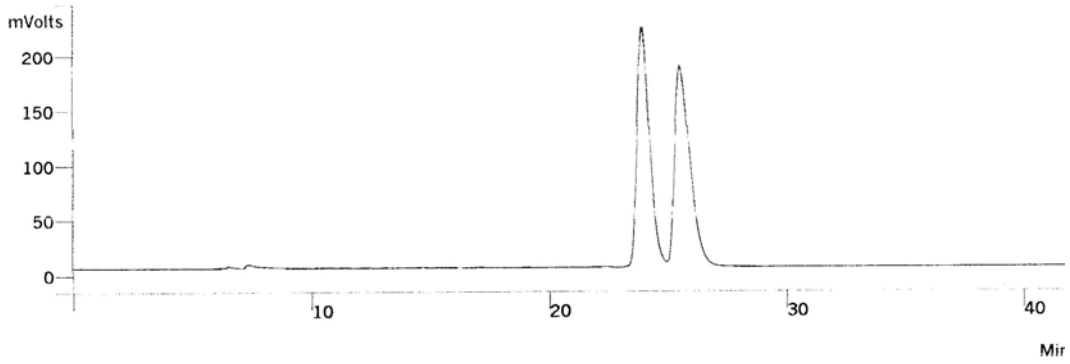
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.28-7.23 (m, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 5.91-5.80 (m, 1H), 5.17-5.09 (m, 2H), 4.96 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.85 (s, 3H), 2.63-2.46 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 135.4, 131.9, 128.5, 127.0, 120.9, 117.8, 110.6, 69.9, 55.4, 42.0.

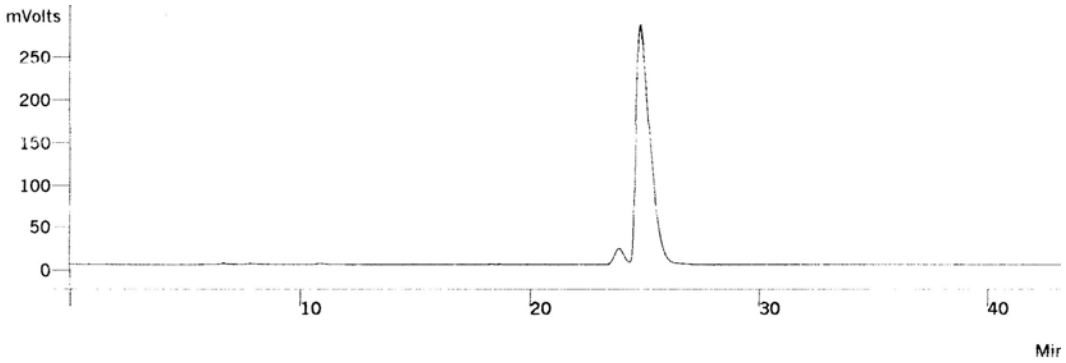
HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm), t_{minor} = 23.8 min, t_{major} = 24.8 min; ee = 92%.

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

[5] Malkov. A. V.; Bell, M.; Castelluzzo, F.; Kočovoský, P. *Org. Lett.* **2005**, *7*, 3219–3222.

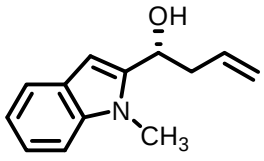


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.3683	23.895	0.000	7744330	0.00	BB	33.8		0
2		49.6317	25.488	0.000	7631090	0.00	BB	39.8		0
	Totals	**100.0000**		**0.000**	**15375420**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		3.8352	23.874	0.000	459631	0.00	BB	27.8		0
2		96.1648	24.809	0.000	11524981	0.00	BB	38.5		0
	Totals	**100.0000**		**0.000**	**11984612**					

(*R*)-1-(1-Methyl-1*H*-indol-2-yl)but-3-en-1-ol (2i)



2i

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with (1-methyl-1*H*-indol-2-yl)methanol **1i** (32.2 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (*R*)-BINAP (6.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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, 1:6:0.1) provided **2i** (22.1 mg, 0.110 mmol) as pale yellow solid in 55% yield.

TLC (SiO_2): R_f = 0.28 (ethyl acetate:hexanes, 1:4).

mp: 80–81 ^oC

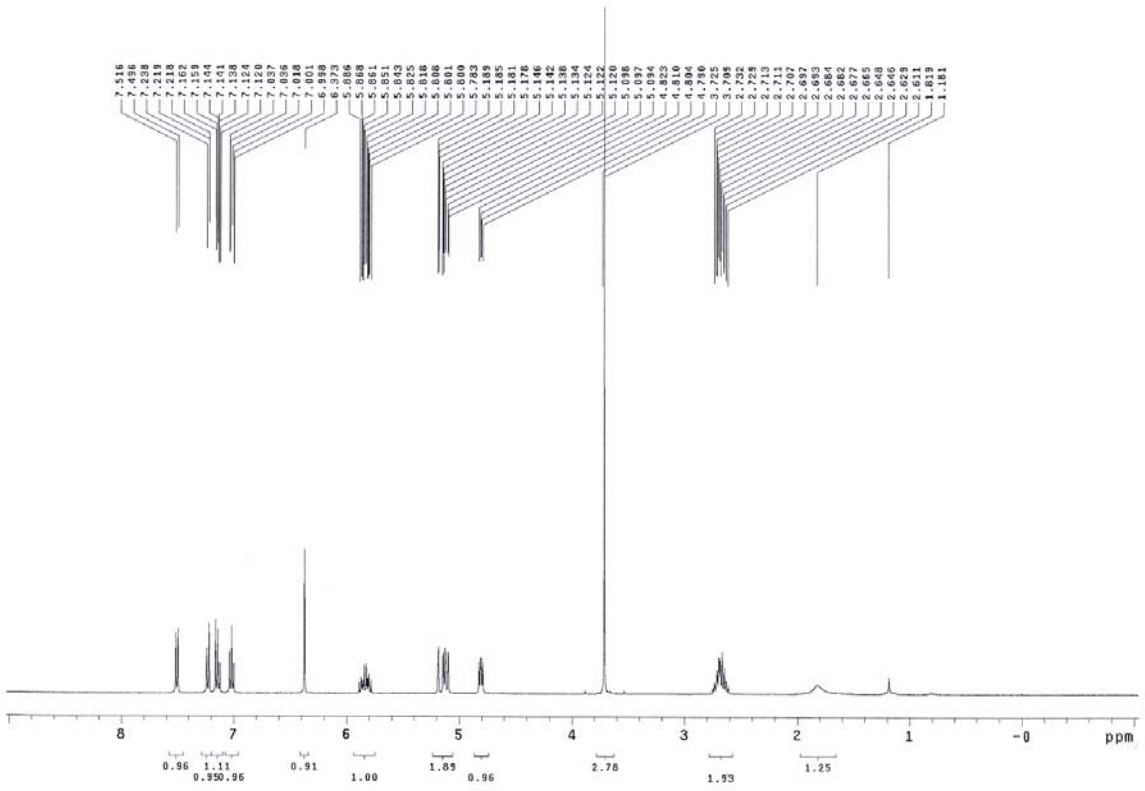
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 5.89-5.78 (m, 1H), 5.19-5.09 (m, 2H), 4.80 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.70 (s, 3H), 2.74-2.61 (m, 2H), 1.81 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 138.1, 134.4, 127.3, 122.0, 120.9, 119.8, 118.8, 109.3, 99.3, 66.5, 40.9, 30.3.

FTIR (neat): υ 3361, 3051, 2975, 2930, 1640, 1558, 1540, 1521, 1506, 1468, 1418, 1314, 1233, 1171, 1141, 1100, 987, 917, 870, 784, 749, 734, 662, 610 cm^{-1}.

HRMS (CI) Calcd. for $C_{13}H_{16}NO$ (M+1): 202.1232, Found: 202.1231.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 90:10, 0.8 mL/min, 254 nm), t_{major} = 33.8 min, t_{minor} = 36.2 min; ee = 90%.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7.219
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7.144
7.141
7.138
7.124
7.120
7.037
7.036
7.018
7.001
6.998
6.373
5.866
5.858
5.851
5.843
5.825
5.818
5.806
5.801
5.800
5.783
5.189
5.185
5.181
5.176
5.146
5.142
5.136
5.134
5.124
5.122
5.120
5.106
5.097
5.094
4.823
4.810
4.804
4.796
3.725
3.708
2.732
2.723
2.715
2.711
2.707
2.697
2.693
2.684
2.682
2.677
2.665
2.648
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1.619
1.181
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7
6
5
4
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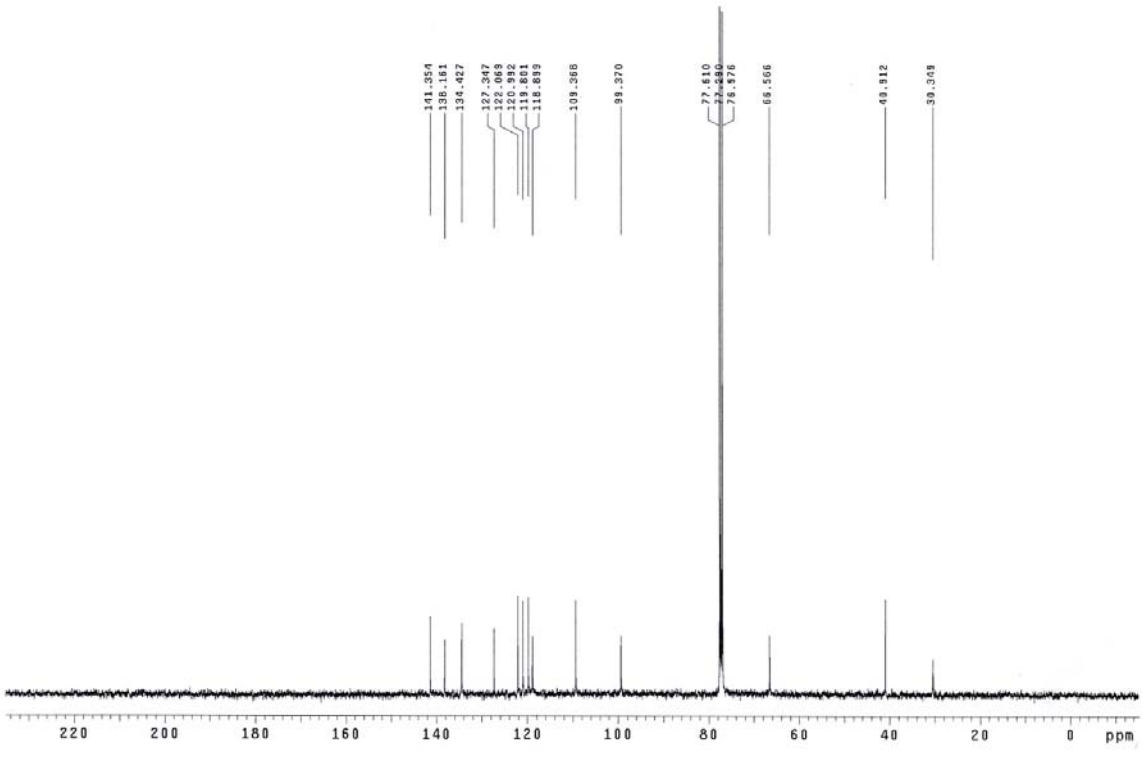
0.91
1.00
1.85
0.96
2.78
1.93
1.25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66.566
49.812
39.349
220
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140
120
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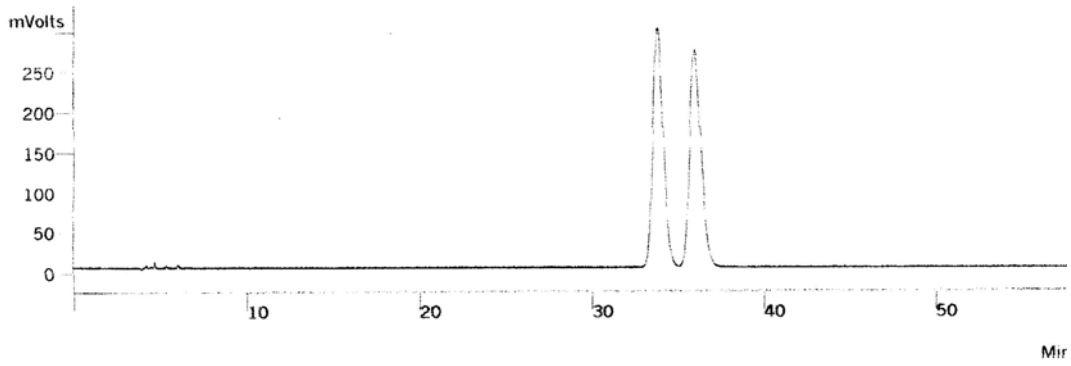
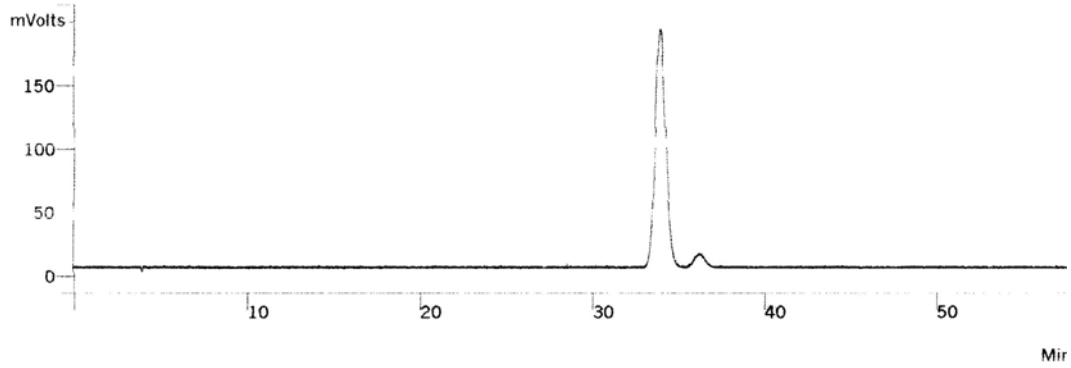
40
20
0
ppm



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.2086	33.821	0.000	12345802	0.00	BB	38.8		0
2		49.7914	35.931	0.000	12243240	0.00	BB	42.4		0
	Totals	**100.0000**		**0.000**	**24589042**					



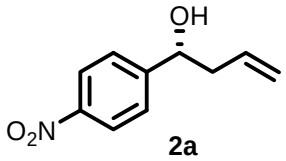
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		95.0462	33.894	0.000	7929205	0.00	BB	39.3		0
2		4.9539	36.200	0.000	413274	0.00	BB	37.0		0
	Totals	**100.0001**		**0.000**	**8342479**					

General Procedure for Enantioselective *C*-Allylation of Aldehydes Using Allyl Acetate

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with aldehydes **3a**-**3i** (0.20 mmol, 100 mol%), $[Ir(cod)Cl]_2$ (0.005 mmol, 2.5 mol%), (–)-TMBTP (0.010 mmol, 5 mol%), Cs_2CO_3 (0.040 mmol, 20 mol%) and 3-nitrobenzoic acid (0.020 mmol, 10 mol%) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (2.0 mmol, 1000 mol%) and isopropanol (0.40 mmol, 200 mol%). The reaction mixture was allowed to stir at 100 ^{o}C for 20 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes) provided **2a**-**2i**.

Detailed Procedure and Spectral Data for Enantioselective *C*-Allylation Adducts (2a-2i) from Aldehydes (3a-3i)

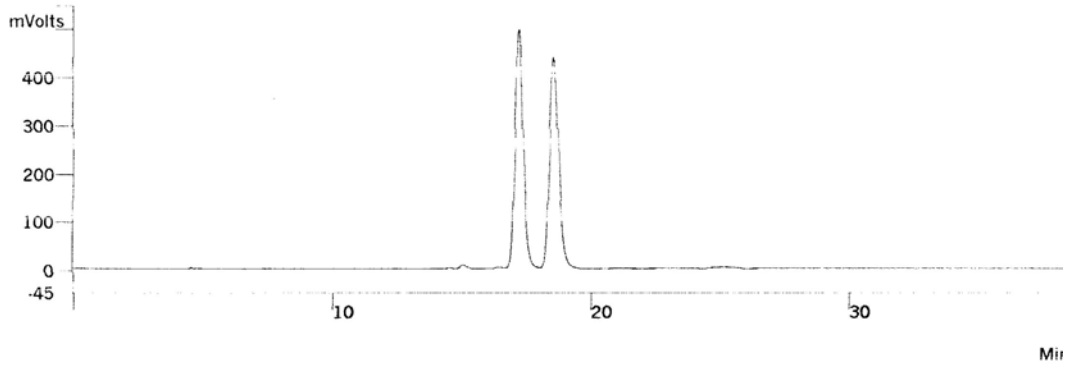
(*R*)-1-(4-Nitrophenyl)but-3-en-1-ol (2a)



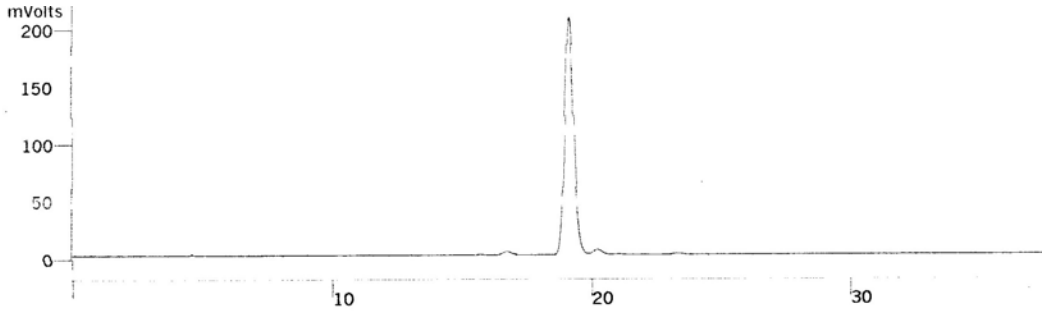
2a

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 4-nitrobenzaldehyde **3a** (30.2 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (–)-TMBTP (5.9 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol) and isopropanol (29.9 μL, 0.40 mmol). The reaction mixture was allowed to stir at 100 ^{o}C for 20 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:6) provided **2a** (30.1 mg, 0.156 mmol) as a yellow oil in 78% yield.

HPLC: (Chiralpak AS-H column, hexanes:*i*-PrOH = 93:7, 0.7 mL/min, 254 nm), t_{major} = 19.1 min, t_{minor} = 20.2 min; ee = 97%.

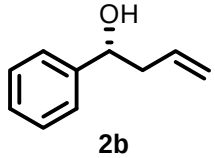


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.8825	17.200	0.000	10670740	0.00	BB	19.8		0
2		50.1175	18.552	0.000	10721031	0.00	BB	22.7		0
	Totals	**100.0000**		**0.000**	**21391772**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		98.4350	19.129	0.000	4978573	0.00	BB	22.4		0
2		1.5650	20.255	0.000	79153	0.00	BB	19.0		0
	Totals	**100.0000**		**0.000**	**5057726**					

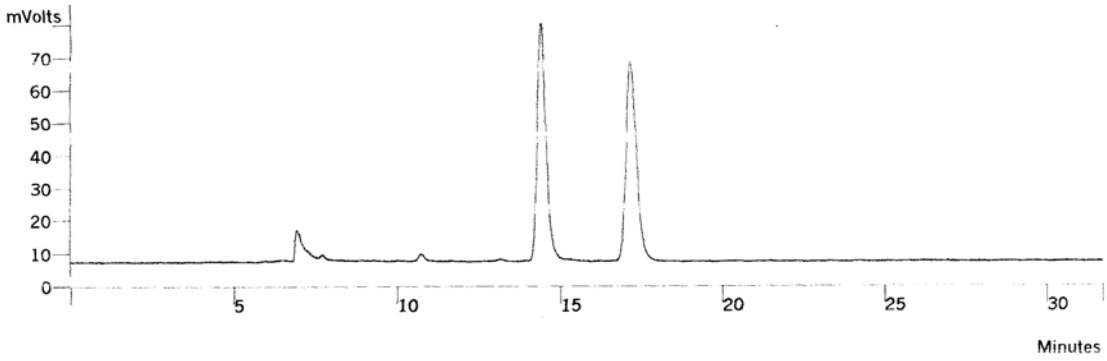
(*R*)-1-Phenylbut-3-en-1-ol (2b)



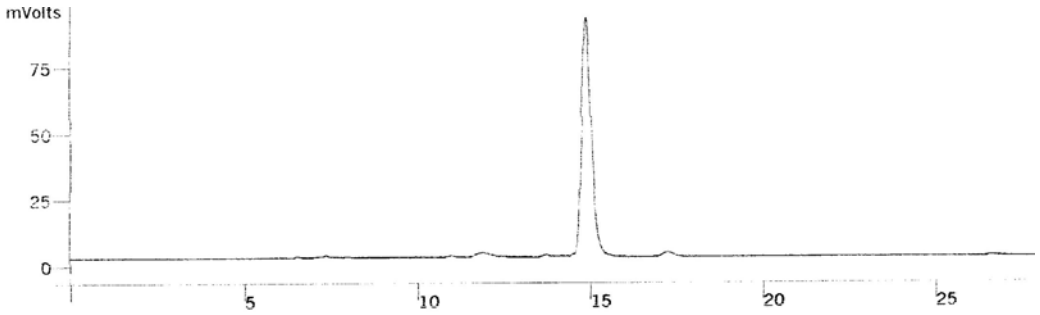
2b

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with benzaldehyde **3b** (21.2 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (–)-TMBTP (5.9 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol) and isopropanol (29.9 μL, 0.40 mmol). The reaction mixture was allowed to stir at 100 ^{o}C for 20 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) provided **2b** (22.5 mg, 0.152 mmol) as a colorless oil in 76% yield.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 254 nm), t_{major} = 14.8 min, t_{minor} = 17.2 min; ee = 96%.

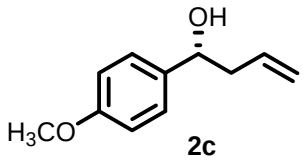


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.2320	14.411	0.000	1383682	0.00	BB	16.9		0
2		49.7680	17.172	0.000	1370899	0.00	BB	20.4		0
	Totals	**100.0000**		**0.000**	**2754581**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		97.9818	14.856	0.000	1710883	0.00	BB	17.6		0
2		2.0182	17.238	0.000	35240	0.00	BB	17.5		0
	Totals	**100.0000**		**0.000**	**1746123**					

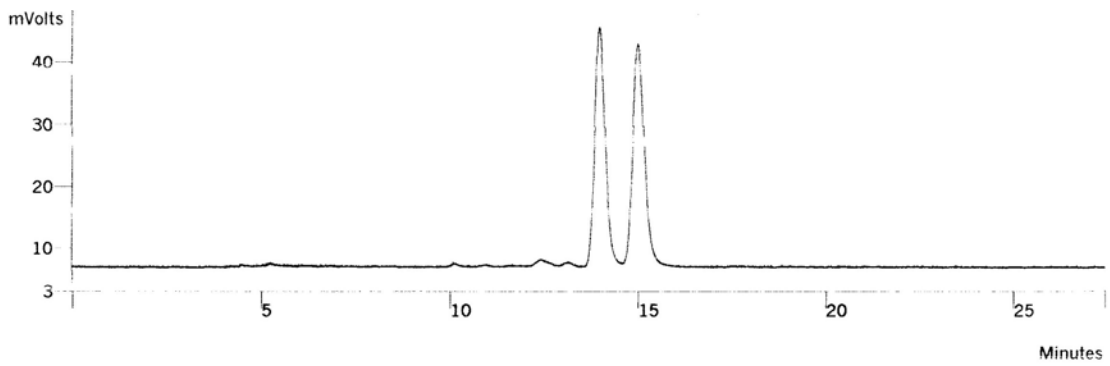
(*R*)-1-(4-Methoxyphenyl)but-3-en-1-ol (2c)



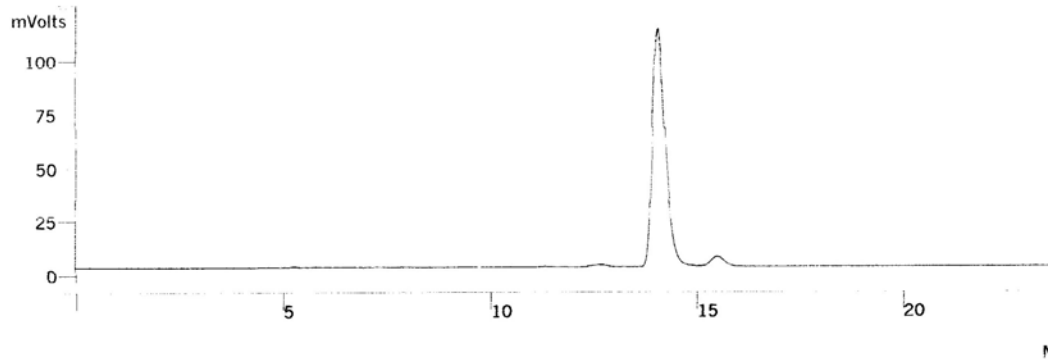
2c

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with *p*-anisaldehyde **3c** (27.2 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (–)-TMBTP (5.9 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol) and isopropanol (29.9 μL, 0.40 mmol). The reaction mixture was allowed to stir at 100 ^{o}C for 20 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, 1:15:0.1) provided **2c** (26.8 mg, 0.150 mmol) as a colorless oil in 75% yield.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 0.7 mL/min, 254 nm), t_{major} = 14.0 min, t_{minor} = 15.4 min; ee = 94%.

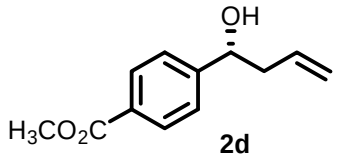


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.0846	13.963	0.000	737817	0.00	BB	18.0		0
2		49.9154	14.986	0.000	735326	0.00	BB	19.5		0
	Totals	**100.0000**		**0.000**	**1473143**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		96.9602	14.055	0.000	2382967	0.00	BB	19.8		0
2		3.0398	15.492	0.000	74709	0.00	BB	17.7		0
	Totals	**100.0000**		**0.000**	**2457676**					

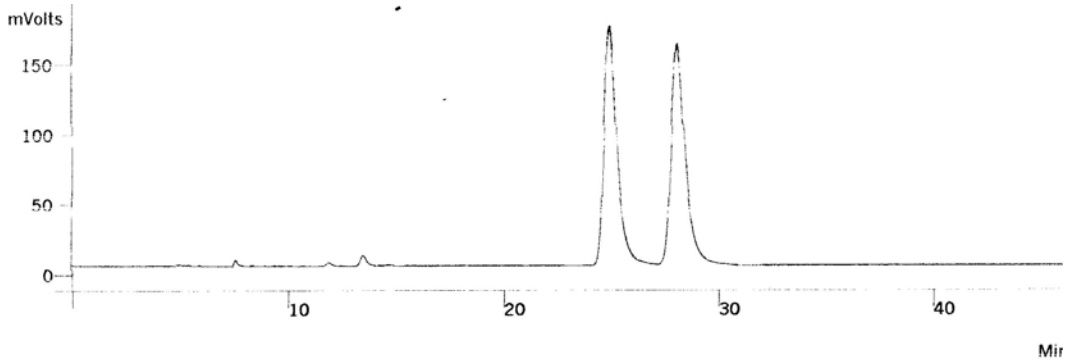
(*R*)-Methyl 4-(1-hydroxybut-3-enyl)benzoate (2d)



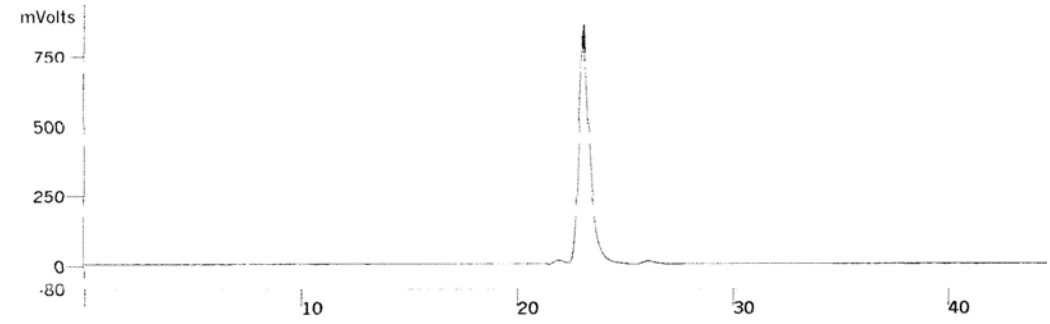
2d

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with methyl 4-formylbenzoate **3d** (32.8 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (–)-TMBTP (5.9 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol) and isopropanol (29.9 μL, 0.40 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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) provided **2d** (35.1 mg, 0.170 mmol) as a colorless oil in 85% yield.

HPLC: (Chiralpak AD-H column, hexanes:*i*-PrOH = 95:5, 0.6 mL/min, 225 nm), t_{major} = 23.0 min, t_{minor} = 26.1 min; ee = 98%.

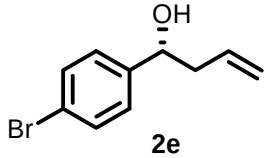


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.0614	24.908	0.000	7100910	0.00	BB	36.9		0
2		49.9386	28.089	0.000	7083503	0.00	BB	39.5		0
	Totals	**100.0000**		**0.000**	**14184413**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		98.7299	23.083	0.000	28407220	0.00	BB	29.2		0
2		1.2701	26.125	0.000	365444	0.00	BB	30.5		0
	Totals	**100.0000**		**0.000**	**28772664**					

(*R*)-1-(4-Bromophenyl)but-3-en-1-ol (2e)

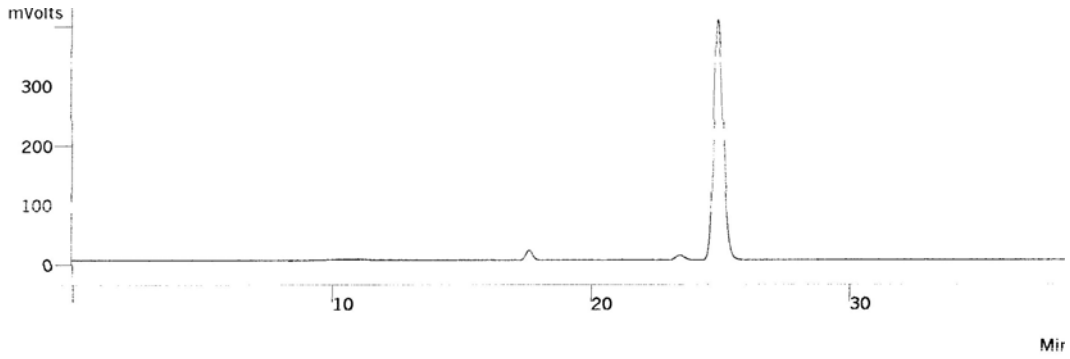


2e

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 4-bromobenzaldehyde **3e** (37.0 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (–)-TMBTP (5.9 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol) and isopropanol (29.9 μL, 0.40 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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, 1:20:0.1) provided **2e** (34.9 mg, 0.154 mmol) as a colorless oil in 77% yield.

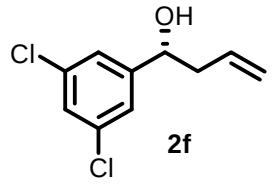
HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 0.4 mL/min, 225 nm), t_{minor} = 23.3 min, t_{major} = 24.8 min; ee = 97%.

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.7666	22.695	0.000	1920010	0.00	BB	34.9		0
2		50.2334	24.048	0.000	1938018	0.00	BB	36.4		0
	Totals	**100.0000**		**0.000**	**3858028**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.4711	23.485	0.000	153522	0.00	BB	18.6		0
2		98.5289	24.940	0.000	10282486	0.00	BB	23.6		0
	Totals	**100.0000**		**0.000**	**10436008**					

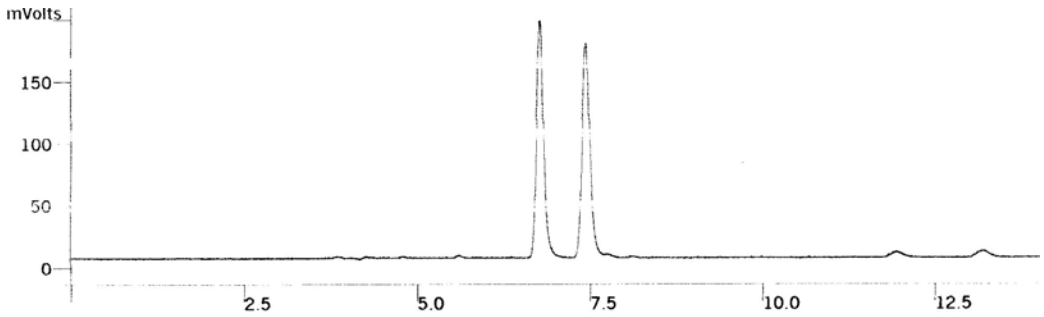
(*R*)-1-(3,5-Dichlorophenyl)but-3-en-1-ol (2f)



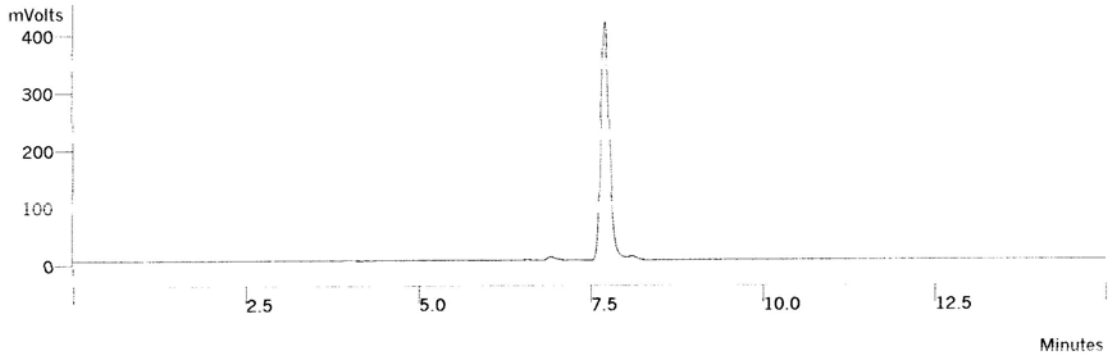
2f

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 3,5-dichlorobenzaldehyde **3f** (35.0 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (–)-TMBTP (5.9 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol) and isopropanol (29.9 μL, 0.40 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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, 1:15:0.1) provided **2f** (33.5 mg, 0.154 mmol) as a colorless oil in 77% yield.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 0.8 mL/min, 225 nm), t_{minor} = 6.9 min, t_{major} = 7.7 min; ee = 98%.

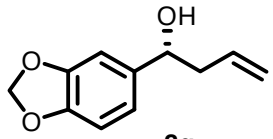


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.0744	6.768	0.000	1366093	0.00	BB	6.3		0
2		49.9256	7.435	0.000	1362033	0.00	BB	7.1		0
	Totals	**100.0000**		**0.000**	**2728126**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.8277	6.928	0.000	28881	0.00	BB	4.8		0
2		99.1723	7.706	0.000	3460514	0.00	BB	7.7		0
	Totals	**100.0000**		**0.000**	**3489395**					

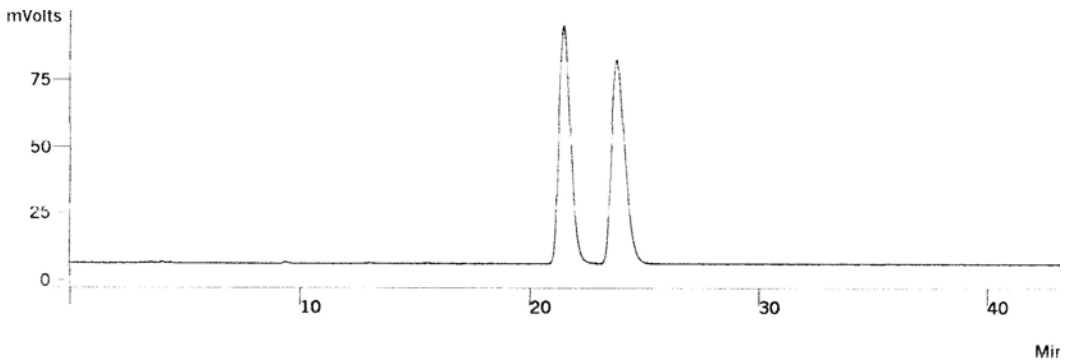
(*R*)-1-(Benzo[d][1,3]dioxol-5-yl)but-3-en-1-ol (2g)



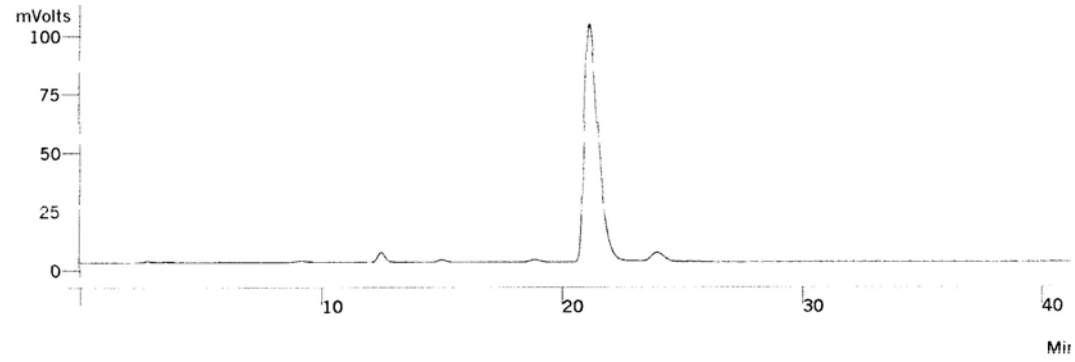
2g

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with piperonal **3g** (30.0 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (–)-TMBTP (5.9 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol) and isopropanol (29.9 μL, 0.40 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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, 1:15:0.1) provided **2g** (34.2 mg, 0.166 mmol) as a colorless oil in 83% yield.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm), t_{major} = 21.1 min, t_{minor} = 23.9 min; ee = 94%.

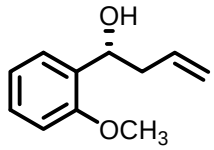


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.0174	21.429	0.000	3103757	0.00	BB	32.7		0
2		49.9826	23.784	0.000	3101601	0.00	BB	38.0		0
	Totals	**100.0000**		**0.000**	**6205358**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		97.2356	21.131	0.000	4075048	0.00	BB	37.0		0
2		2.7644	23.977	0.000	115853	0.00	BB	29.8		0
	Totals	**100.0000**		**0.000**	**4190901**					

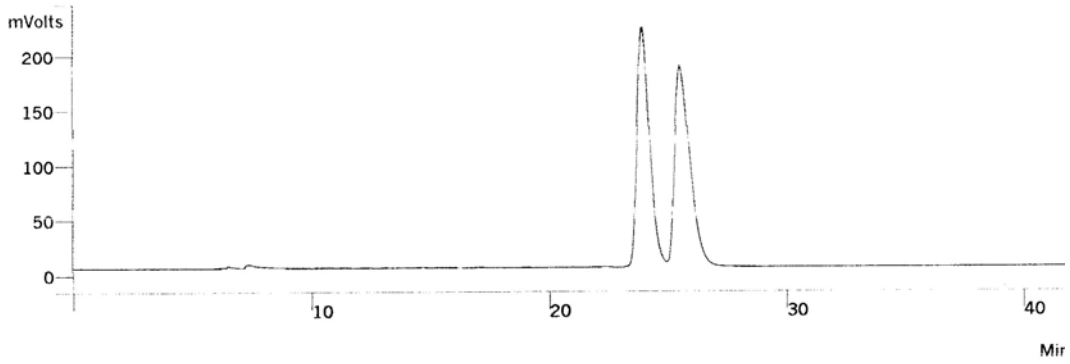
(*R*)-1-(2-Methoxyphenyl)but-3-en-1-ol (2h)



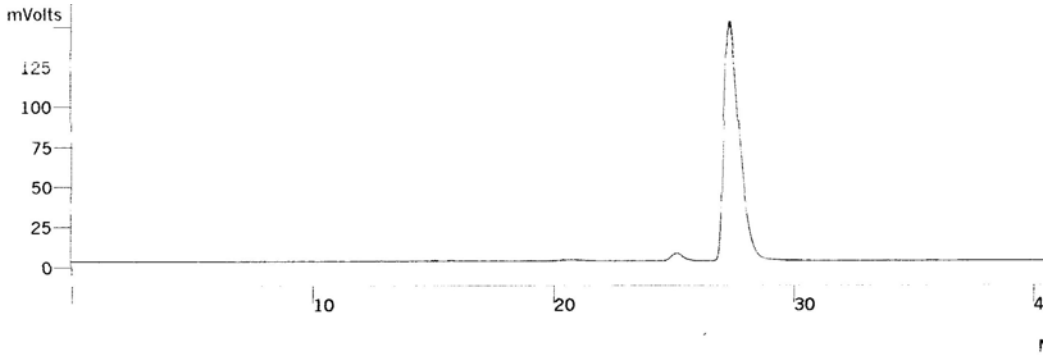
2h

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with *o*-anisaldehyde **3h** (27.2 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (–)-TMBTP (5.9 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol) and isopropanol (29.9 μL, 0.40 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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, 1:15:0.1) provided **2h** (30.6 mg, 0.172 mmol) as a colorless oil in 86% yield.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm), t_{minor} = 25.1 min, t_{major} = 27.3 min; ee = 95%.

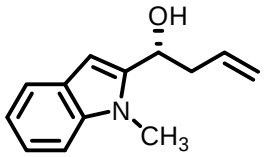


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.3683	23.895	0.000	7744330	0.00	BB	33.8		0
2		49.6317	25.488	0.000	7631090	0.00	BB	39.8		0
	Totals	**100.0000**		**0.000**	**15375420**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.3244	25.129	0.000	157011	0.00	BB	31.5		0
2		97.6756	27.308	0.000	6597769	0.00	BB	40.6		0
	Totals	**100.0000**		**0.000**	**6754780**					

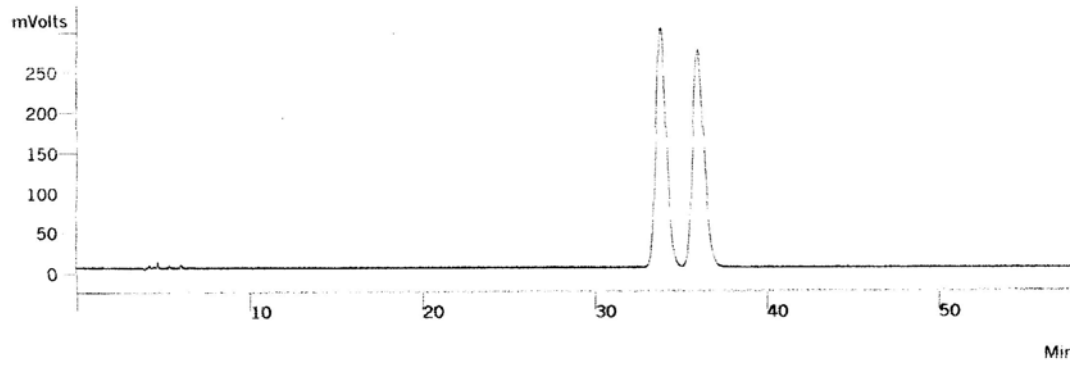
(*R*)-1-(1-Methyl-1*H*-indol-2-yl)but-3-en-1-ol (2i)



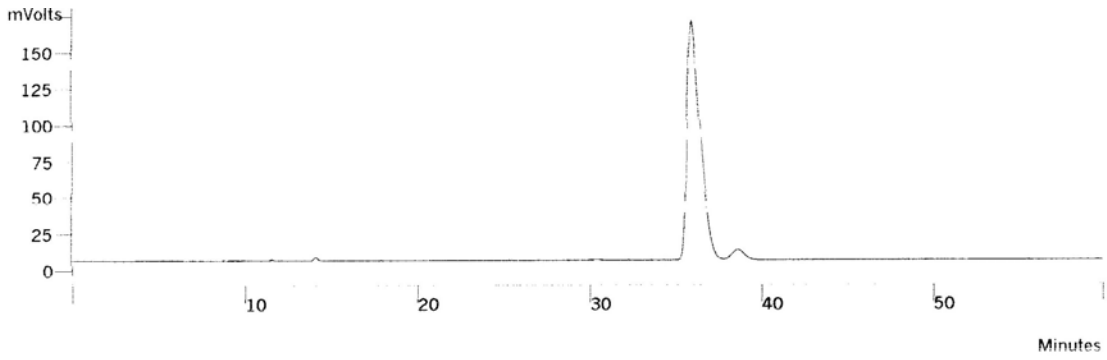
2i

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 1-methylindole-2-carboxaldehyde **3i** (31.8 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (–)-TMBTP (5.9 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by allyl acetate (0.2 g, 2.0 mmol) and isopropanol (29.9 μL, 0.40 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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, 1:6:0.1) provided **2i** (33.0 mg, 0.164 mmol) as pale yellow solid in 82% yield.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 90:10, 0.8 mL/min, 254 nm), t_{major} = 35.9 min, t_{minor} = 38.6 min; ee = 94%.



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.2086	33.821	0.000	12345802	0.00	BB	38.8		0
2		49.7914	35.931	0.000	12243240	0.00	BB	42.4		0
	Totals	**100.0000**		**0.000**	**24589042**					



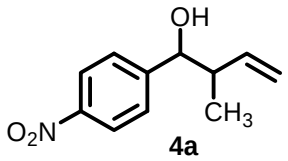
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		96.9781	35.900	0.000	8598938	0.00	BB	49.0		0
2		3.0219	38.618	0.000	267951	0.00	BB	40.4		0
	Totals	**100.0000**		**0.000**	**8866889**					

General Procedure for Crotylation of Alcohols (1a-1c) Using 3-Acetoxy-1-butene

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with alcohols **1a-1c** (0.20 mmol, 100 mol%), $[Ir(cod)Cl]_2$ (0.005 mmol, 2.5 mol%), BIPHEP (0.010 mmol, 5 mol%), Cs_2CO_3 (0.040 mmol, 20 mol%) and 3-nitrobenzoic acid (0.020 mmol, 10 mol%) was added THF (1.0 mL, 0.2 M) followed by 3-acetoxy-1-butene (2.0 mmol, 1000 mol%). The reaction mixture was allowed to stir at 100 ^{o}C for 20 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes) provided **4a-4c**.

Detailed Procedure and Spectral Data for Crotylation Adducts (4a–4c)

2-Methyl-1-(4-nitrophenyl)but-3-en-1-ol (4a)



4a

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 4-nitrobenzyl alcohol **1a** (30.6 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), BIPHEP (5.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by 3-acetoxy-1-butene (0.228 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 hr, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: ethyl acetate:hexanes, 1:6) provided **4a** (32.4 mg, 0.156 mmol, *anti*:*syn* = 2:1) as a yellow oil in 78% yield.

TLC (SiO_2): R_f = 0.27 (ethyl acetate:hexanes, 1:4).

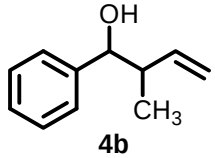
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.17 (m, 4H), 7.52-7.46 (m, 4H), 5.82-5.69 (m, 2H), 5.22-5.05 (m, 4H), 4.76 (d, *J* = 4.8 Hz, 1H, *syn*), 4.51 (d, *J* = 5.6 Hz, 1H, *anti*), 2.62-2.57 (m, 1H, *syn*), 2.49-2.41 (m, 1H, *anti*), 2.34 (br s, 1H, *anti*), 2.19 (br s, 1H, *syn*), 0.96 (d, *J* = 6.8 Hz, 3H, *syn*), 0.92 (d, *J* = 6.8 Hz, 3H, *anti*)..

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 150.1, 147.5, 147.3, 139.6, 139.3, 127.8, 127.4, 123.6, 123.4, 118.0, 116.6, 76.9, 76.2, 46.5, 44.8, 16.4, 13.6.

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

[6] Jiang, S.; Agoston, E. G.; Chen, T.; Cabal, M.-P.; Turos, E. *Organometallics* **1995**, *14*, 4697–4709.

2-Methyl-1-phenylbut-3-en-1-ol (4b)



4b

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with benzyl alcohol **1b** (21.6 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), BIPHEP (5.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by 3-acetoxy-1-butene (0.228 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^oC for 20 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) provided **4b** (23.3 mg, 0.144 mmol, *anti*:*syn* = 2:1) as a colorless oil in 72% yield.

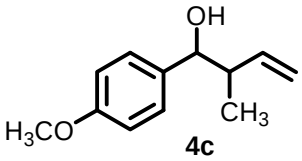
TLC (SiO_2): R_f = 0.26 (ethyl acetate:hexanes, 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.25 (m, 10H), 5.86-5.72 (m, 2H), 5.24-5.17 (m, 2H, *anti*), 5.08-4.35 (m, 2H, *syn*), 4.61 (d, *J* = 5.6 Hz, 1H, *syn*), 4.36 (d, *J* = 7.6 Hz, 1H, *anti*), 2.62-2.56 (m, 1H, *syn*), 2.50-2.46 (m, 1H, *anti*), 2.07 (br s, 2H), 1.01 (d, *J* = 6.8 Hz, 3H, *syn*), 0.87 (d, *J* = 6.8 Hz, 3H, *anti*).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 142.6, 140.8, 140.5, 128.4, 128.3, 127.9, 127.5, 127.0, 126.7, 117.1, 115.8, 78.0, 77.5, 46.5, 44.8, 16.7, 14.2.

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

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



4c

To an oven-dried sealed tube under one atmosphere of nitrogen gas charged with 4-methoxybenzyl alcohol **1c** (27.6 mg, 0.20 mmol), $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), BIPHEP (5.2 mg, 0.010 mmol), Cs_2CO_3 (13.0 mg, 0.040 mmol) and 3-nitrobenzoic acid (3.3 mg, 0.020 mmol) was added THF (1.0 mL, 0.2 M) followed by 3-acetoxy-1-butene (0.228 g, 2.0 mmol). The reaction mixture was allowed to stir at 100 ^{o}C for 20 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, 1:20:0.1) provided **4c** (27.4 mg, 0.142 mmol, *anti*:*syn* = 2:1) as a colorless oil in 71% yield.

TLC (SiO_2): R_f = 0.28 (ethyl acetate:hexanes, 1:10).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.19 (m, 4H), 6.90-6.84 (m, 4H), 5.86-5.76 (m, 1H, *anti*), 5.75-5.67 (m, 1H, *syn*), 5.22-5.15 (m, 2H, *anti*), 5.05-4.99 (m, 2H, *syn*), 4.52 (d, *J* = 6.0 Hz, 1H, *syn*), 4.29 (d, *J* = 7.6 Hz, 1H, *anti*), 3.79 (s, 6H), 2.56-2.53 (m, 1H, *syn*), 2.48-2.41 (m, 1H, *anti*), 2.20 (br s, 2H), 1.01 (d, *J* = 6.8 Hz, 3H, *syn*), 0.83 (d, *J* = 6.8 Hz, 3H, *anti*).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 159.0, 140.1, 140.5, 135.0, 134.8, 128.2, 127.9, 116.9, 115.6, 113.8, 113.6, 77.6, 76.9, 55.4 (2 signals), 46.6, 44.9, 16.8, 14.6.

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