Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Enantioselective Iridium Catalyzed Carbonyl Isoprenylation via Alcohol-Mediated Hydrogen Transfer

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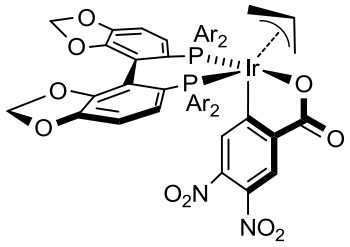
General Information

All reactions were run under an atmosphere of argon. All glassware was oven dried at 120 °C overnight and cooled in a desiccator. All iridium catalyzed isoprenylation reactions were carried in sealed pressure tubes (13 x 100 mm). THF was subjected to distillation from sodium and benzophenone immediately before use. DME was dried by 4Å molecule sieves. $[Ir(COD)Cl]_2$, DM-SEGPHOS, cesium carbonate, potassium phosphate and 3,4-dinitrobenzoic acid were purchased from commercial suppliers and used as received. Isoprenyl *tert*-butoxy carbonate **3a**[1] and compounds **1m**[2], **1q**[3]**,** and **2m**[2] were prepared following literature procedures. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates. Visualization was accomplished with UV light followed by dipping in a cerium ammonium molybdate or potassium permanganate solutions followed by heating. Purification of reaction products was carried out by flash column chromatography using 40-63 μm silica gel.

Spectroscopy, Spectrometry, and Data Collection

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). Specific optical rotations were recorded on an Atago AP-300 automatic polarimeter at the sodium line (589 nm) in $CHCl_3$. Solution concentrations are given in the units of 10^{-2}g mL^{-1}. Accurate masses are reported for the molecular ion (M-H, M, M+H, M-H_2O or M+Na). ^1H nuclear magnetic resonance spectra were recorded on a Varian INOVA (500 MHz) spectrometer. Chemical shifts are reported as parts per million (ppm) relative to residual $CHCl_3$ δ_H (7.26 ppm).^{13}C nuclear magnetic resonance spectra were recorded on a Varian INOVA (125 MHz) spectrometer for $CDCl_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual $CDCl_3$ δ_C (77.0 ppm). Melting points were taken on a Stuart SMP3 melting point apparatus.

Detailed Procedure for Preparation of Preformed Iridium Catalyst (S)-Ir-VII



(*S*)-Ir-VII, Ar = 3,5-Me_2-Ph

To a sealed tube equipped with a magnetic stir bar was added Cs_2CO_3 (652 mg, 2.0 mmol, 200 mol%), 3,4-dinitrobenzoic acid (424.2 mg, 2.0 mmol, 200 mol%), (*S*)-DM-SEGPHOS (723 mg, 1.0 mmol, 100 mol%) and $[Ir(COD)Cl]_2$ (335 mg, 0.5 mmol, 50 mol%). The reaction vessel was purged with argon and THF (10 mL, 0.1 M) was added followed by allyl acetate (0.27 mL, 2.5 mmol, 250 mol%). The reaction mixture was stirred at room temperature for 30 min, and for another 120 min at 80 ˚C. After cooling to ambient temperature the mixture was filtered through a celite plug with the aid of DCM (100 mL). The combined filtrate was concentrated *in vacuo* and subjected to flash column chromatography (SiO_2, DCM:THF = 20:1). The resulting gum-like residue was dissolved in THF (5.0 mL). Addition of HPLC grade hexanes (40 mL) led to formation of a precipitate, which was collected by filtration, washed with a small amount of HPLC grade hexanes, and dried *in vacuo* to furnish the title complex as a yellow powder in 83% yield (968 mg) as a mixture of stereoisomers.

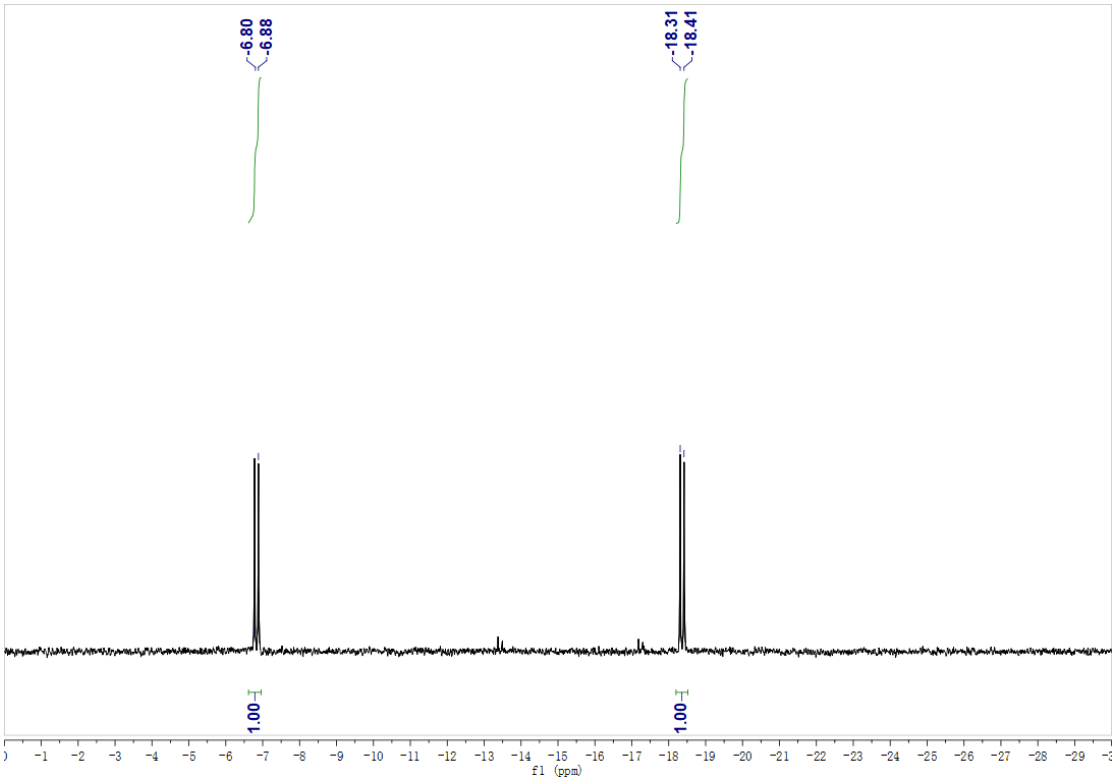
Spectral data is reported for the major isomer.

^{31}P NMR (202 MHz, $CDCl_3$): δ = -6.84 (d, *J*=16.6 Hz), -18.36 (d, *J*=21.0 Hz).

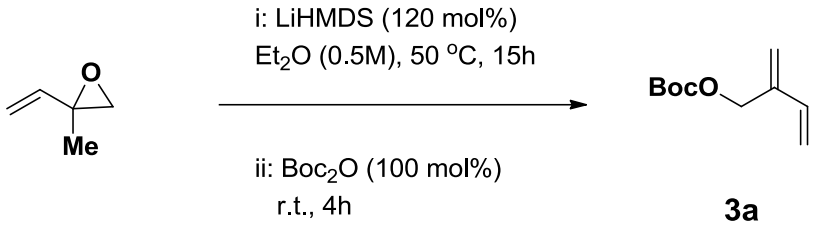
HRMS (ESI) Calculated for $C_{56}H_{51}IrN_2O_{10}P_2$ $[M+H]^+$ = 1167.2725, Found 1167.2718.

$[\alpha]_D^{34}$: 122.0 (*c* = 1.0, $CHCl_3$)

MP: 119-123 ˚C (decomposition)


-6.80
-6.88
-18.31
-18.41
1.00
1.00
f1 (ppm)

***tert*-Butyl (2-methylenebut-3-en-1-yl) carbonate (3a)**[1]



Isoprene monoxide

A resealable pressure tube was charged with lithium bis(trimethylsilyl)amide (LHMDS) (10.2 g, 61.0 mmol, 120 mol%). The reaction vessel was placed under an atmosphere of argon, and Et_2O (100 mL, 0.5 M) was added. Isoprene monoxide (4.28g, 50.9 mmol, 100 mol%) was added dropwise at room temperature and the reaction was allowed to stir at 50 °C overnight. After cooling to room temperature di-*tert*-butyl dicarbonate (11.1g, 50.9 mmol, 100 mol%) was added dropwise and the reaction was stirred at room temperature for 4 hours. Water (50 mL) was added and the reaction mixture was transferred to a separatory funnel. The aqueous layer was extracted with Et_2O (3 x 50 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes : ethyl acetate = 99:1) to furnish the title compound 3a (5.85 g, 31.8 mmol) in 62 % yield as a colorless oil.

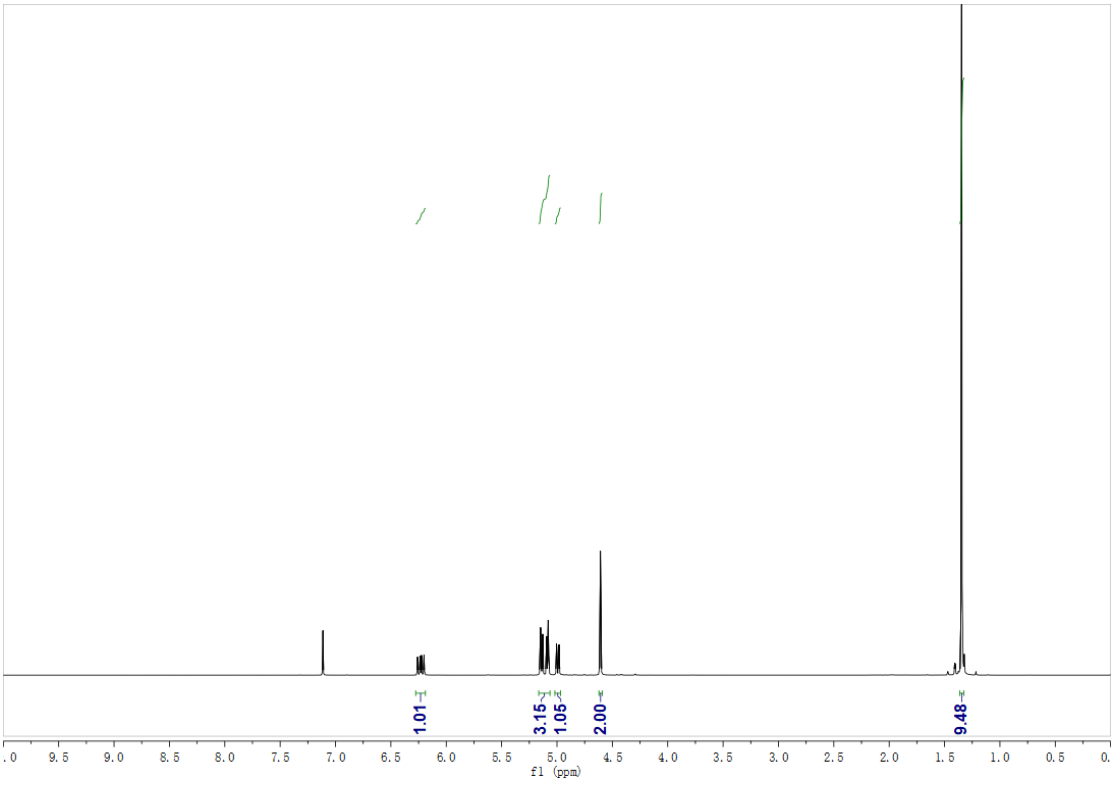
TLC (SiO_2): Rf = 0.5 (hexanes : ethyl acetate = 98:2).

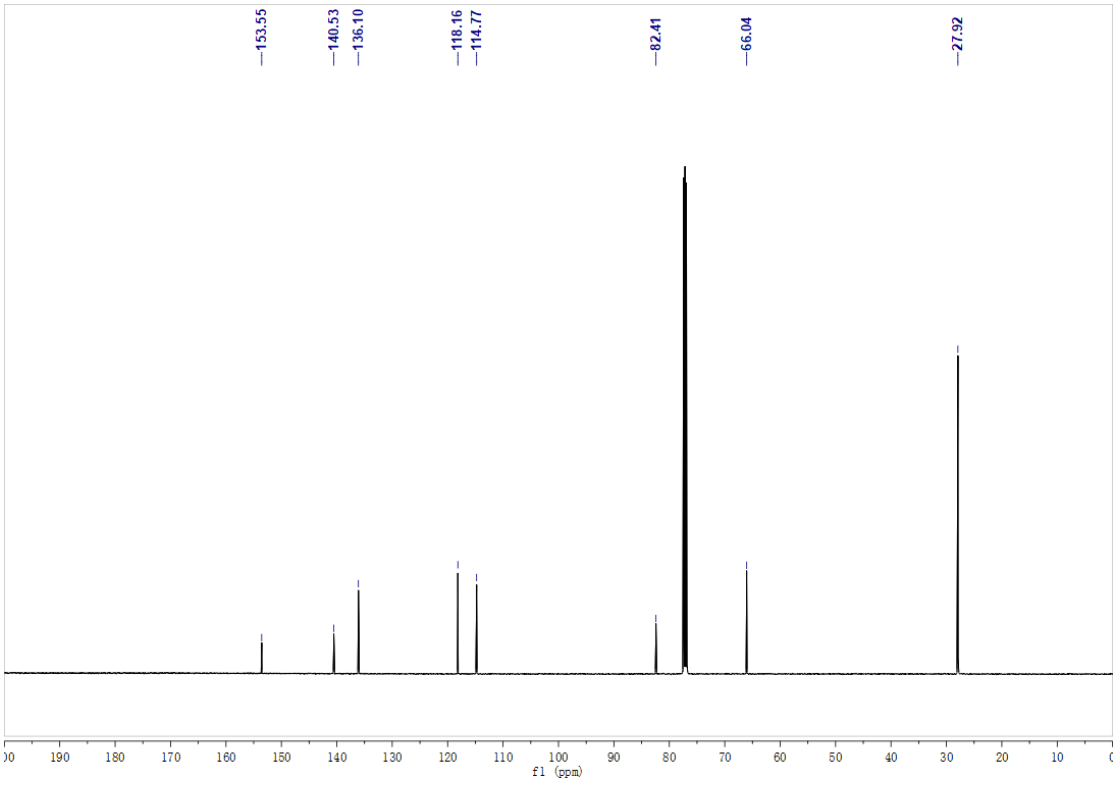
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 6.38 (dd, *J*=17.8, 11.1 Hz, 1H), 5.26 (m, 3H), 5.14 (d, *J*=11.1 Hz, 1H), 4.75 (s, 2H), 1.49 (s, 9H) ppm.

^{13}C NMR: (125 MHz, $CDCl_3$): δ = 153.6, 140.5, 136.1, 118.2, 114.8, 82.4, 66.0, 27.9 ppm.

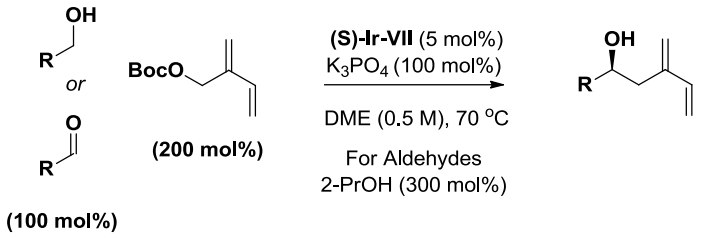
HRMS: (ESI) Calculated for $C_{10}H_{16}O_3$ $[M]^+$ =184.1099, Found 184.1097.

FTIR: (neat): 2982, 1739, 1599, 1369, 1276, 1251, 1158, 862 cm^{-1}.


1.01
3.15
1.05
2.00
9.48
f1 (ppm)


153.55
140.53
136.10
118.16
114.77
82.41
66.04
27.92
f1 (ppm)

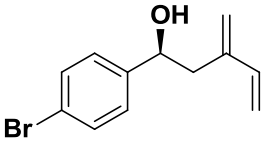
General Procedure and Spectral Data for Iridium Catalyzed Isoprenylation Reactions.



From alcohol oxidation level: A resealable pressure tube equipped with a magnetic stir bar was charged with K_3PO_4 (42.5 mg, 0.20 mmol, 100 mol%), alcohol (0.20 mmol, 100 mol%) and iridium catalyst **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). Under an atmosphere of argon, DME (0.4 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 70 ˚C for 24 h. After cooling to room temperature the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the desired product **4a-4q**.

For aldehyde oxidation level: A resealable pressure tube equipped with a magnetic stir bar was charged with K_3PO_4 (42.5 mg, 0.20 mmol, 100 mol%), aldehyde (0.20 mmol, 100 mol%), and iridium catalyst **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). Under an atmosphere of argon, DME (0.4 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%) and isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 70 ˚C for 24 h. After cooling to room temperature the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the desired product **4a-4q**.

(*S*)-1-(4-bromophenyl)-3-methylenepent-4-en-1-ol (4a)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 4-bromobenzyl alcohol (**1a**, 37.4 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4a** as a colorless oil in 80% yield with 95% ee (40.5 mg, 0.16 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 4-bromobenzaldehyde (**2a**, 37 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4a** as a colorless oil in 84% yield with 96% ee (42.5 mg, 0.168 mmol).

TLC (SiO_2) R_f = 0.43 (hexanes/ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, *J*=8.3 Hz, 2H), 7.27 – 7.22 (m, 2H), 6.40 (dd, *J*=17.6, 10.8 Hz, 1H), 5.30 (d, *J*=17.6 Hz, 1H), 5.19 – 5.13 (m, 2H), 5.07 (s, 1H), 4.84 – 4.76 (m, 1H), 2.66 (dd, *J*=14.1, 4.0 Hz, 1H), 2.51 (dd, *J*=14.1, 9.2 Hz, 1H), 2.06 (d, *J*=2.0 Hz, 1H) ppm.

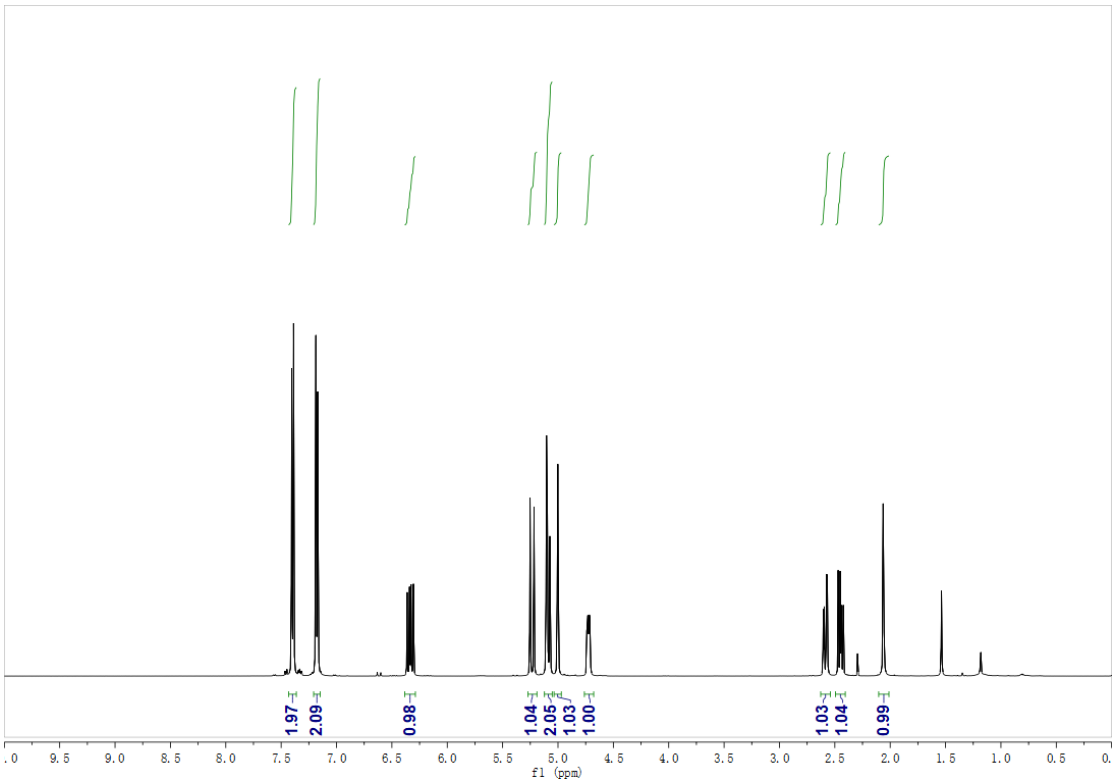
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 142.5, 138.3, 131.7, 127.7, 121.4, 119.4, 114.6, 71.7, 42.4 ppm.

HRMS (ESI) Calculated for $C_{12}H_{13}BrO$ $[M]^+$ = 252.0150, Found 252.0148.

FTIR (neat) 3393, 3086, 2926, 1593, 1487, 1103, 1009, 824 cm^{-1}.

$[\alpha]_D^{34}$: –149.8 (*c* = 1.05, $CHCl_3$)

HPLC: (Two connected chiralcel AD-H columns, hexanes:*i*-PrOH = 98:2, 0.50 mL/min, 230 nm).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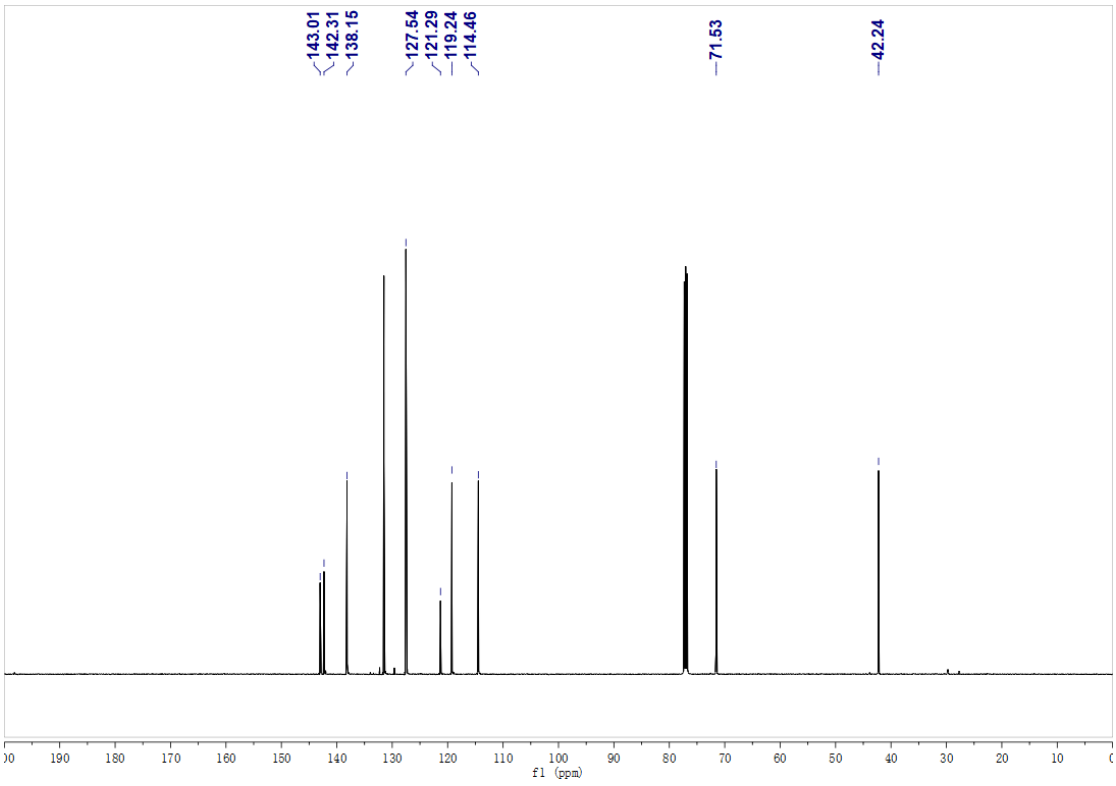
0.98
1.04
2.05
1.03
1.00
1.03
1.04
0.99
f1 (ppm)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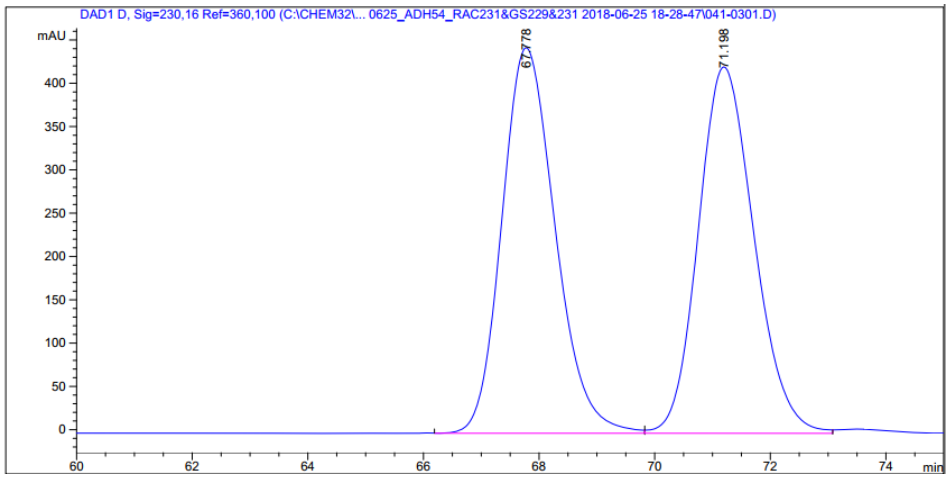
114.46
71.53
42.24
f1 (ppm)



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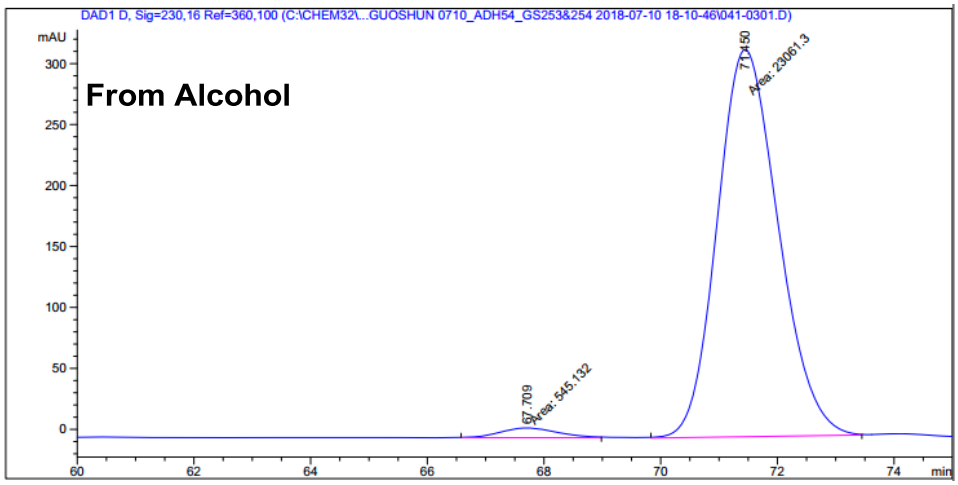

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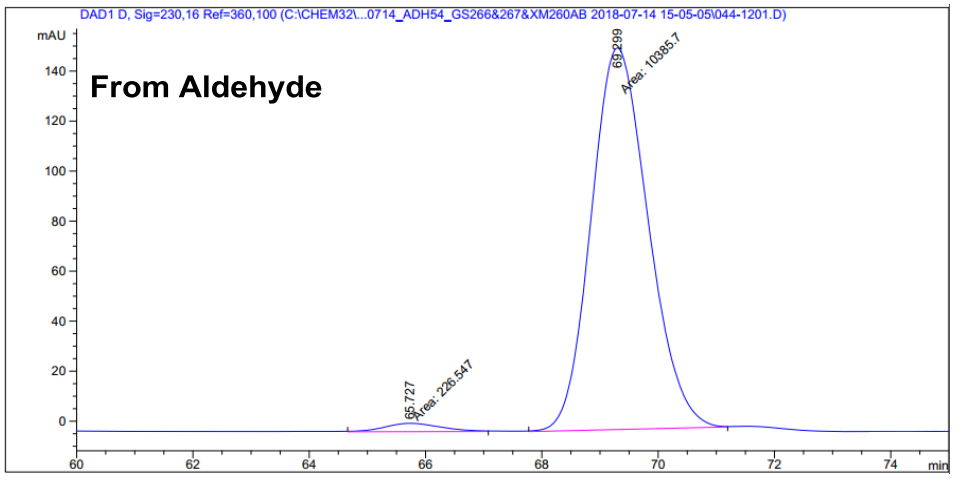

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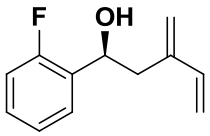
1	65.727	MM	1.1276	226.54732	3.34860	2.1348
2	69.299	MM	1.1345	1.03857e4	152.57021	97.8652

(S)-1-(2-fluorophenyl)-3-methylenepent-4-en-1-ol (4b)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 2-fluorobenzyl alcohol (**1b**, 25.2 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4b** as a colorless oil in 83% yield with 96% ee (31.9 mg, 0.166 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 2-fluorobenzaldehyde (**2b**, 24.8 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. Volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4b** as a colorless oil in 75% yield with 96% ee (28.8 mg, 0.15 mmol).

TLC (SiO_2) R_f = 0.5 (hexanes/ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.20–7.15 (m, 1H), 7.12–7.07 (m, 1H), 6.96 (ddd, *J* = 13.6, 6.8, 2.7 Hz, 1H), 6.35 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.35 (d, *J* = 17.7 Hz, 1H), 5.15–5.05 (m, 4H), 2.76 (dd, *J* = 14.0, 3.4 Hz, 1H), 2.40 (dd, *J* = 14.0, 9.6 Hz, 1H), 2.04 (d, *J* = 2.5 Hz, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7 (d, *J* = 245.1 Hz), 142.6, 137.9, 131.0 (d, *J* = 13.1 Hz), 128.8 (d, *J* = 8.3 Hz), 127.0 (d, *J* = 4.5 Hz), 124.3 (d, *J* = 3.4 Hz), 119.2, 115.2 (d, *J* = 21.7 Hz), 114.7, 66.2, 66.1, 41.2.

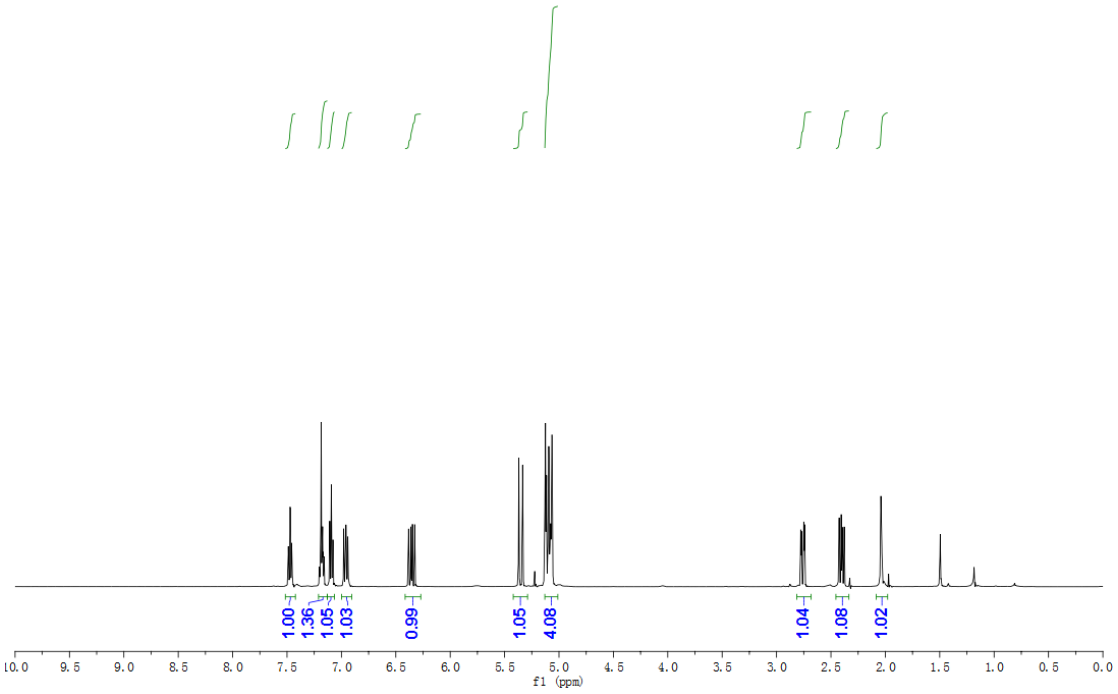
^{19}F NMR (471 MHz, $CDCl_3$): δ (-119.35) – (-119.45) (m, 1F).

HRMS (ESI) Calculated for $C_{12}H_{13}OF$ $[M]^+$ = 192.0950, Found 192.0946.

FTIR (neat) 3392, 2923, 1593, 1455, 1221, 1056, 1031, 992, 941, 817, 754 cm^{-1}.

$[\alpha]_D^{34}$: –49.5 (*c* = 1.0, $CHCl_3$)

HPLC: (Two connected chiralcel OD-H columns, hexanes:*i*-PrOH = 99:1, 0.50 mL/min, 230 nm).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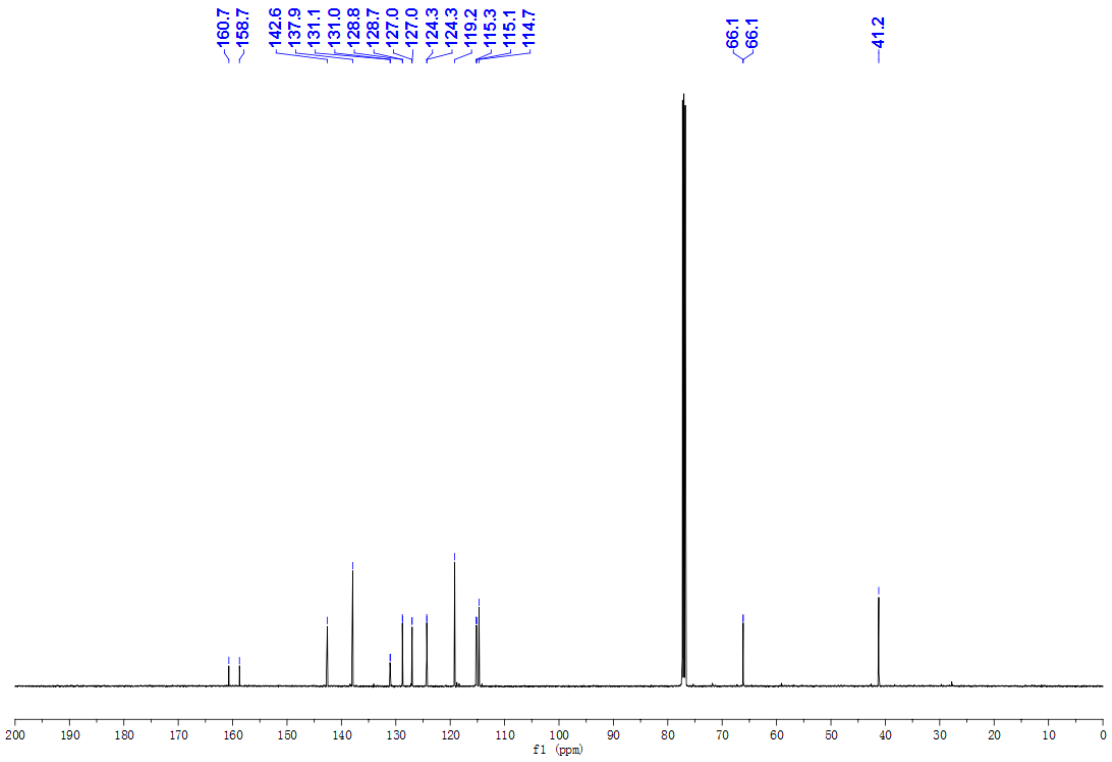
0.99
1.05
4.08
1.04
1.08
1.02
f1 (ppm)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158.7
142.6
137.9
131.1
131.0
128.8
128.7
127.0
127.0
124.3
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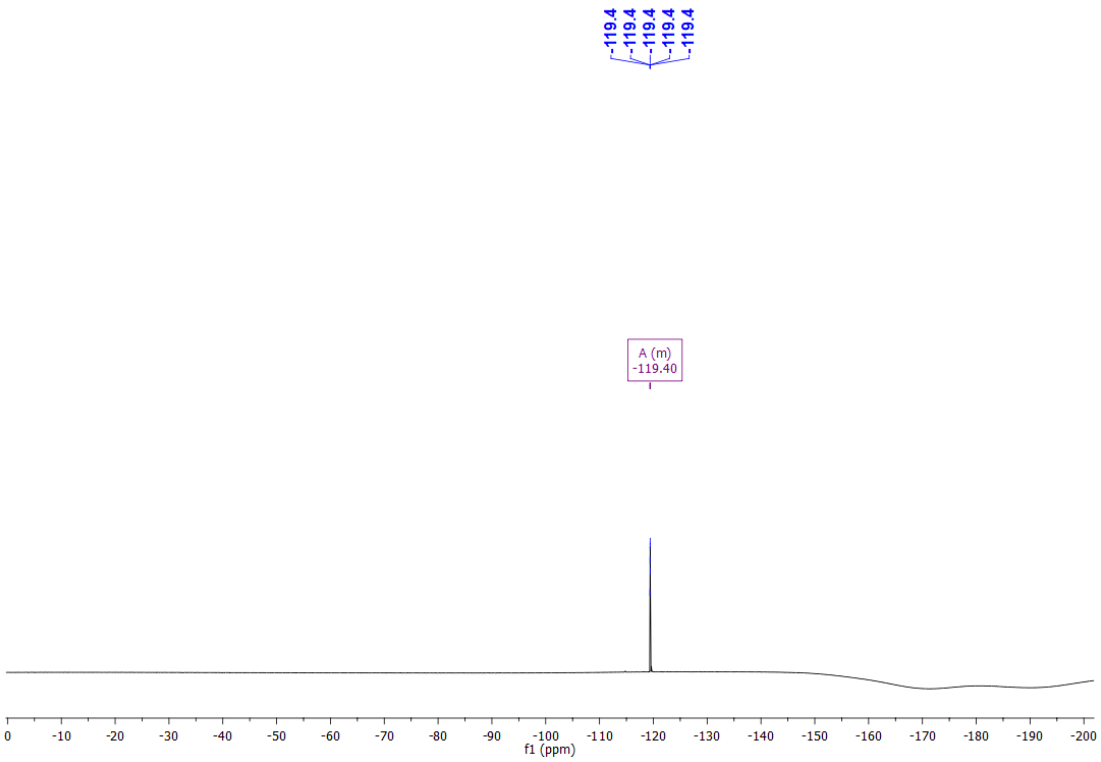
115.1
114.7
66.1
66.1
41.2
f1 (ppm)


-119.4
-119.4
-119.4
-119.4
-119.4
A (m)
-119.40
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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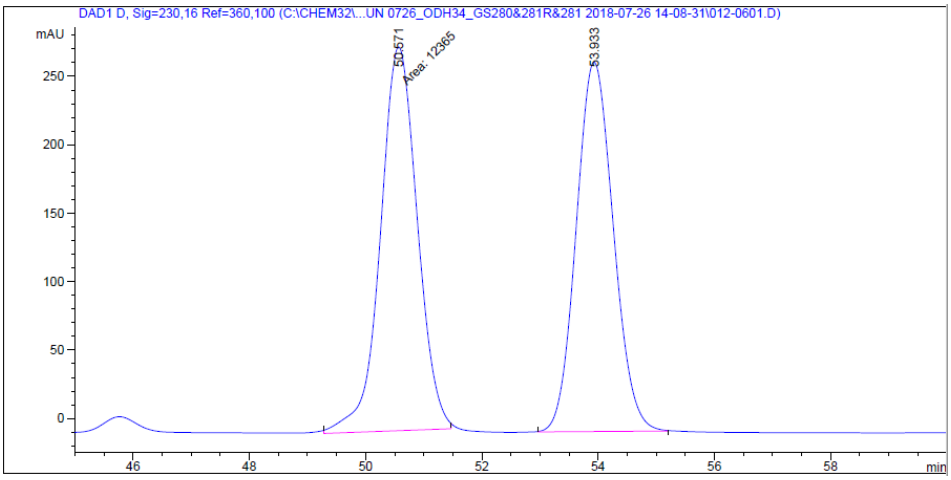
-180
-190
-200
f1 (ppm)



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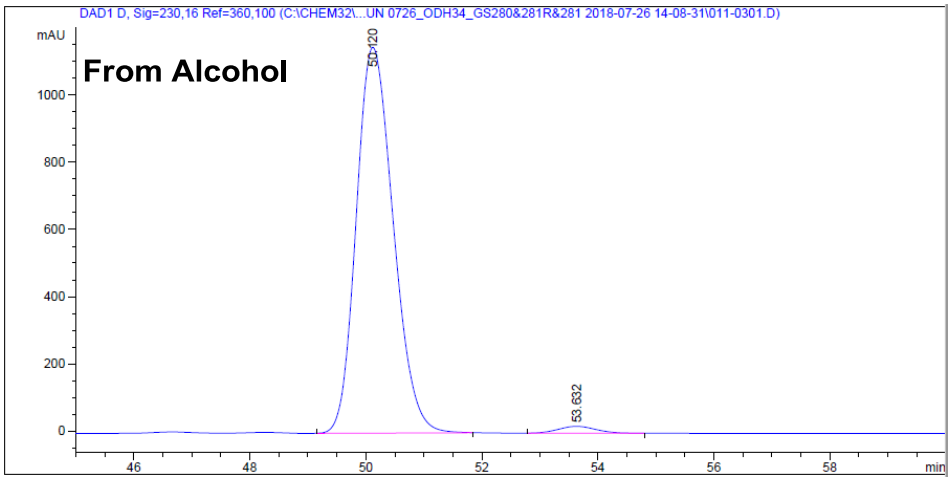

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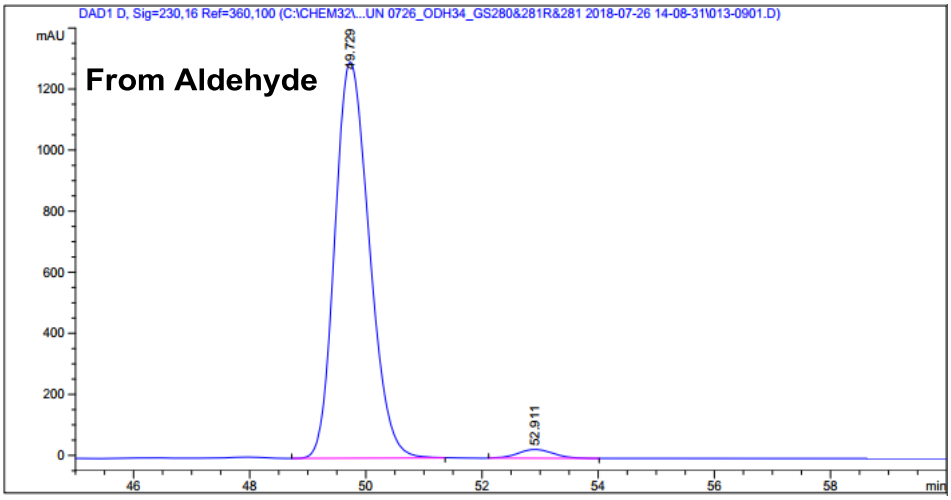

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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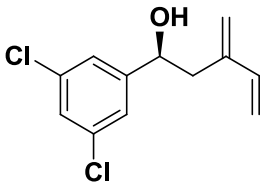
2	52.911	BB	0.6559	1217.99036	28.88548	2.2349

(*S*)-1-(3, 5-dichlorophenyl)-3-methylenepent-4-en-1-ol (4c)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 3, 5-dichlorobenzyl alcohol (**1c**, 35.1 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4c** as a colorless solid in 81% yield with 94% ee (39.2 mg, 0.162 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 3, 5-dichlorobenzaldehyde (**2c**, 34.6 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (1.0 mL, 0.2 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4c** as a colorless solid in 64% yield with 95% ee (30.97 mg, 0.127 mmol).

TLC (SiO_2) R_f = 0.45 (hexanes/ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (dq, *J* = 3.2, 1.6, 3H), 6.41 (dd, *J* = 17.6, 10.9, 1H), 5.35–5.25 (m, 1H), 5.25–5.12 (m, 2H), 5.09 (s, 1H), 4.77 (dd, *J* = 9.4, 3.8, 1H), 2.71–2.41 (m, 2H), 2.10 (s, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.4, 141.9, 137.9, 134.9, 127.6, 124.4, 119.6, 114.7, 71.0, 42.3 ppm.

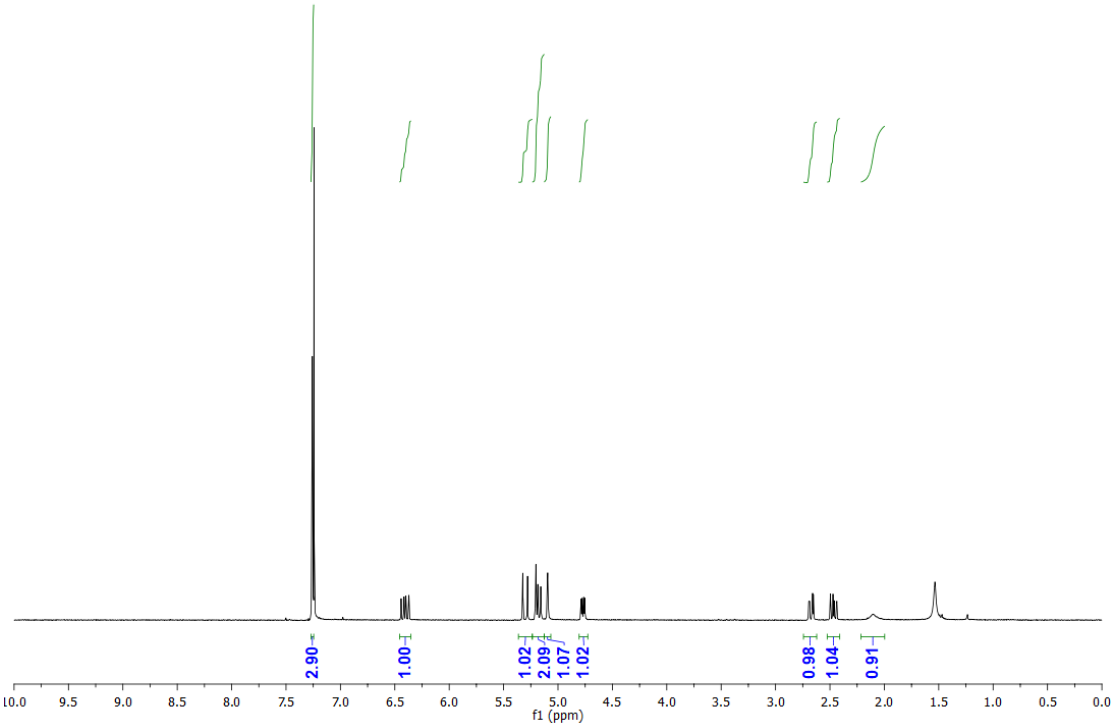
HRMS (ESI) Calculated for $C_{12}H_{12}Cl_2O$ $[M]^+$ = 242.0265, Found 242.0264.

FTIR (neat) 3328, 2931, 1592, 1568, 1428, 1230, 1044, 923, 882, 749, 682 cm^{-1}.

$[\alpha]_D^{34}$: –38.5 (*c* = 0.5, $CHCl_3$)

HPLC: (Two connected chiralcel OD-H columns, hexanes:*i*-PrOH = 99:1, 0.50 mL/min, 230 nm).

MP: 87.5–88.5 °C.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1.02
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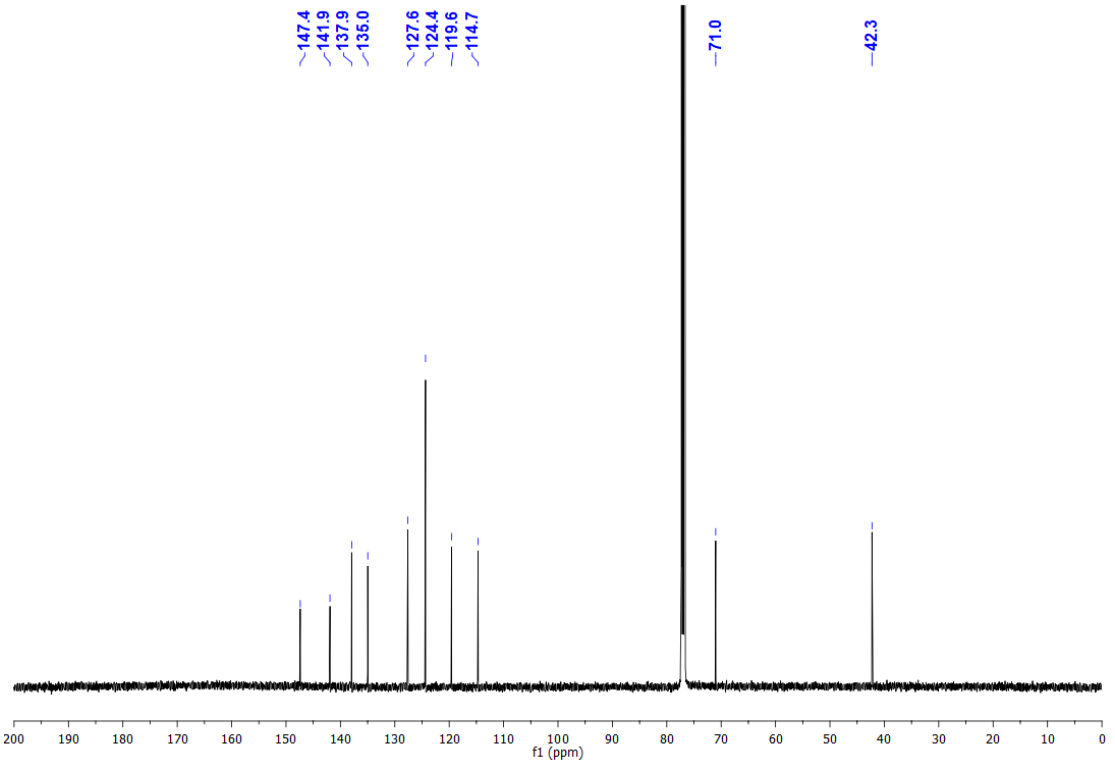
0.91
f1 (ppm)


147.4
141.9
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114.7
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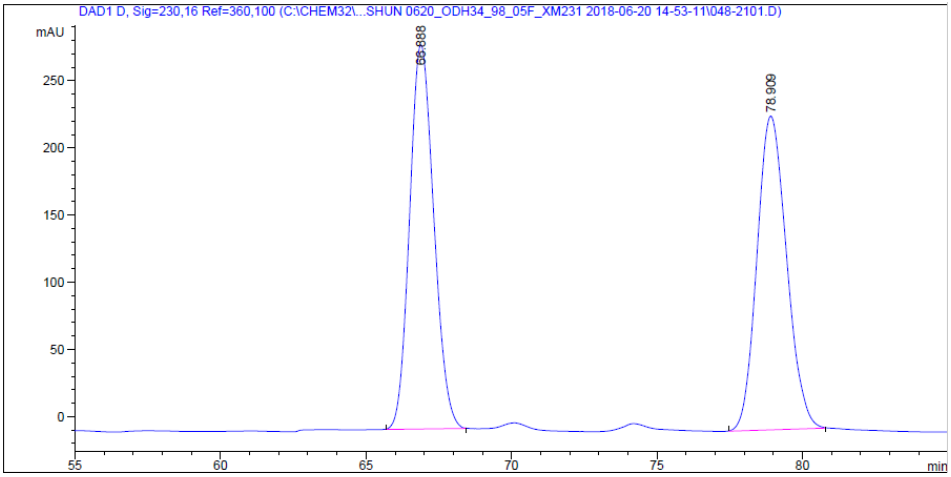
42.3
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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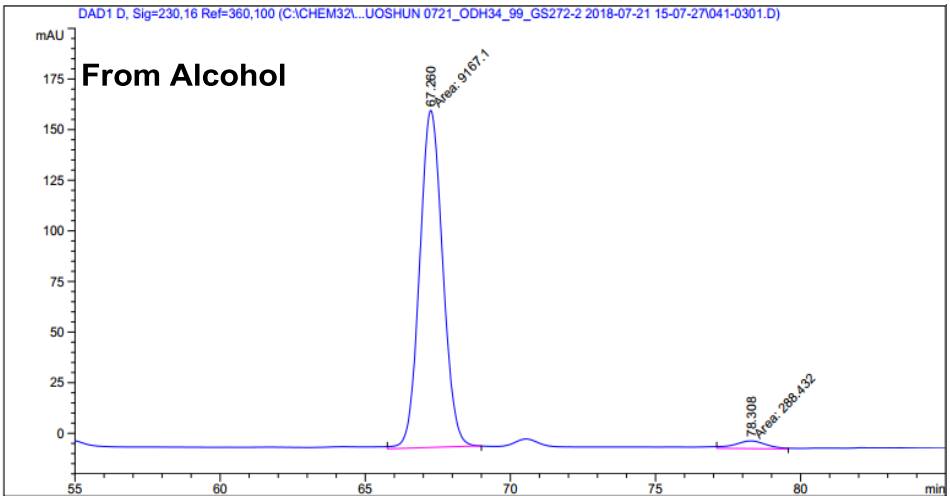
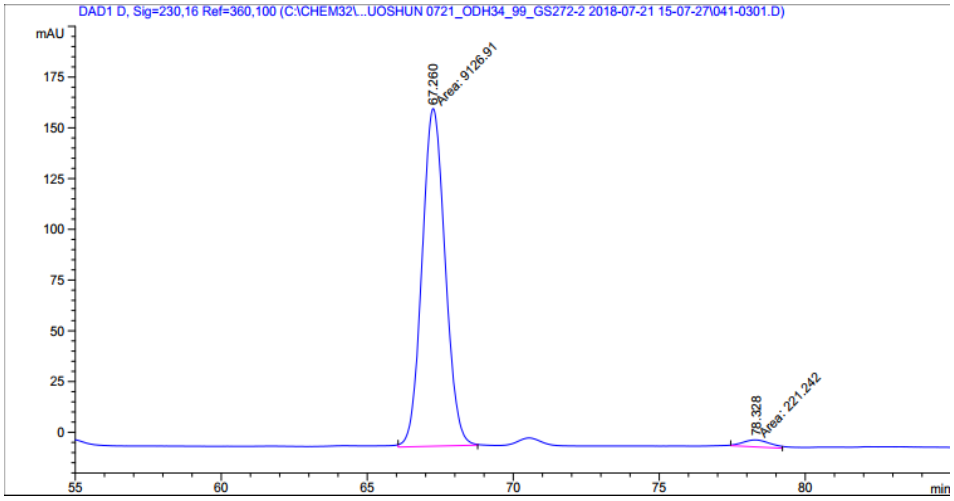
2	78.909	BB	1.1058	1.65282e4	233.51842	49.9946

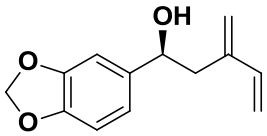


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	67.260	MM	0.9179	9167.10059	166.44281	96.9496
2	78.308	MM	1.2675	288.43243	3.79252	3.0504



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	67.260	MM	0.9146	9126.90723	166.31177	97.6333
2	78.328	MM	1.0742	221.24164	3.43279	2.3667

(S)-1-(benzo[d][1,3]dioxol-5-yl)-3-methylenepent-4-en-1-ol (4d)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with piperonyl alcohol (**1d**, 30.4 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4d** as a colorless oil in 77% yield with 96% ee (33.6 mg, 0.154 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with piperonal (**2d**, 30.0 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4d** as a colorless oil in 77% yield with 96% ee (33.5 mg, 0.154 mmol).

TLC (SiO_2) R_f = 0.43 (hexanes/ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.91 (s, 1H), 6.82 (dd, *J* = 8.0, 1.1 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.41 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.95 (s, 2H), 5.31 (d, *J* = 17.6 Hz, 1H), 5.14 (m, 3H), 4.77 (dd, *J* = 8.8, 3.3 Hz, 1H), 2.66 (dd, *J* = 14.1, 3.6 Hz, 1H), 2.55 (dd, *J* = 14.1, 9.1 Hz, 1H), 2.02 (s, 1H) ppm.

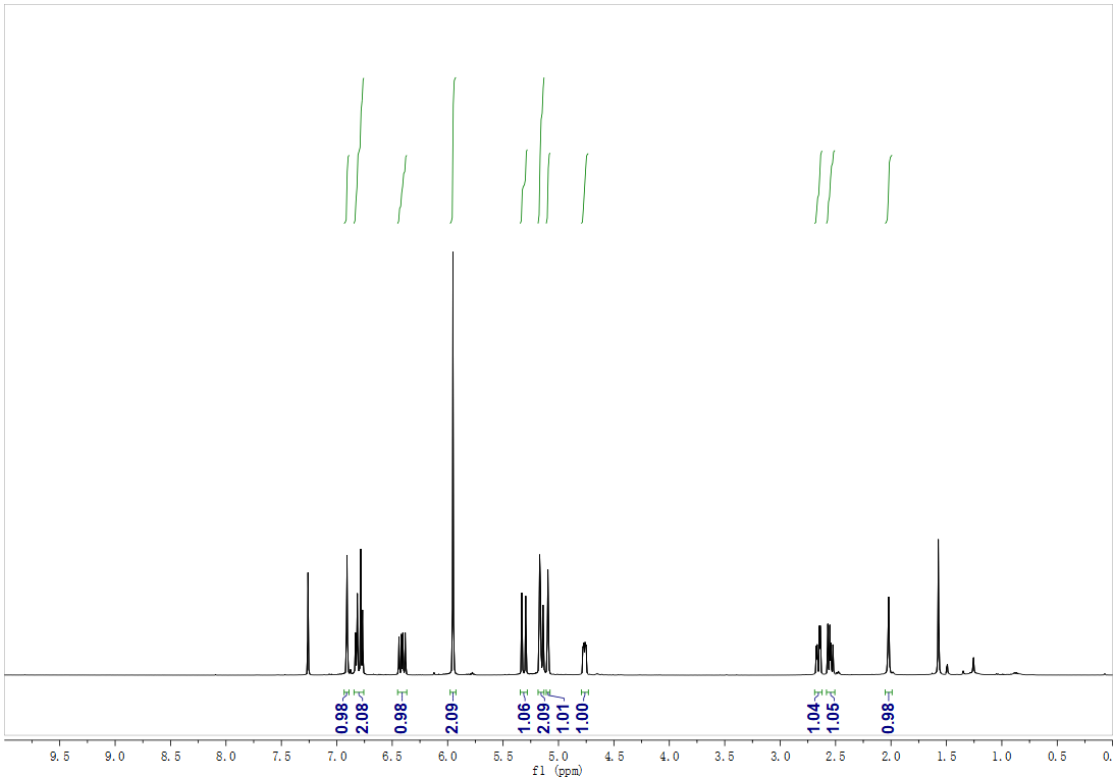
^{13}C NMR (125 MHz, $CDCl_3$): δ 147.9, 147.1, 142.8, 138.4, 138.3, 119.3, 119.1, 114.5, 108.2, 106.5, 101.1, 72.2, 42.4 ppm.

HRMS (ESI) Calculated for $C_{13}H_{14}O_3$ $[M+H]^+$ = 218.0943, Found 218.0938.

FTIR (neat) 3409, 3005, 1502, 1486, 1275, 1259, 1037, 764 cm^{-1}.

$[\alpha]_D^{34}$: –42.8 (*c* = 0.76, $CHCl_3$)

HPLC: (Two connected chiralcel OD-H columns, hexanes:*i*-PrOH = 99:1, 0.50 mL/min, 230 nm).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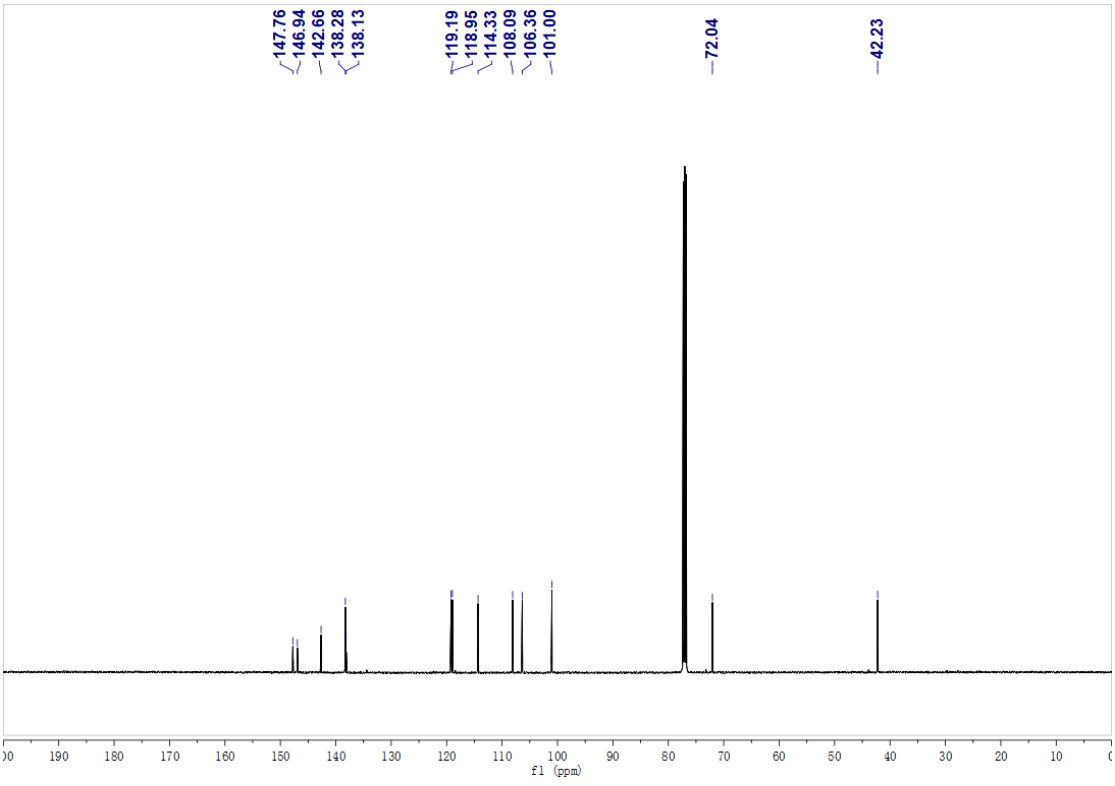
1.06
2.09
1.01
1.00
1.04
1.05
0.98
f1 (ppm)


147.76
146.94
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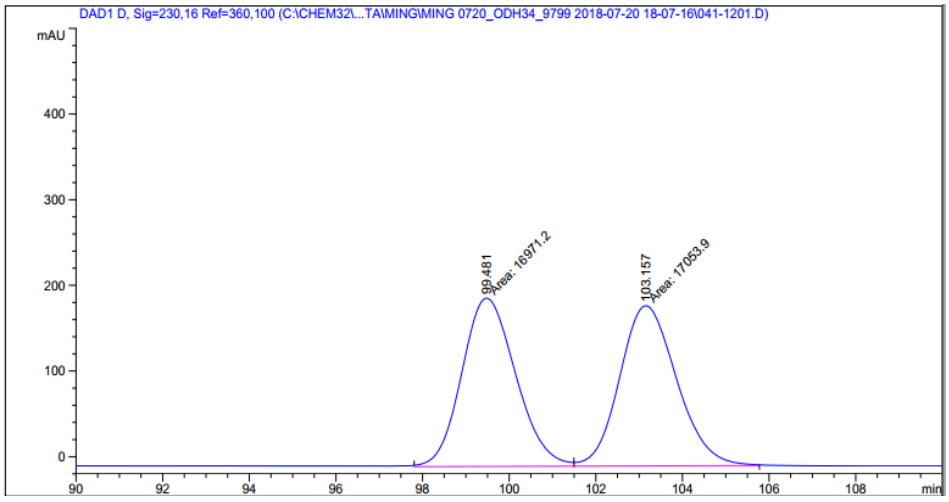
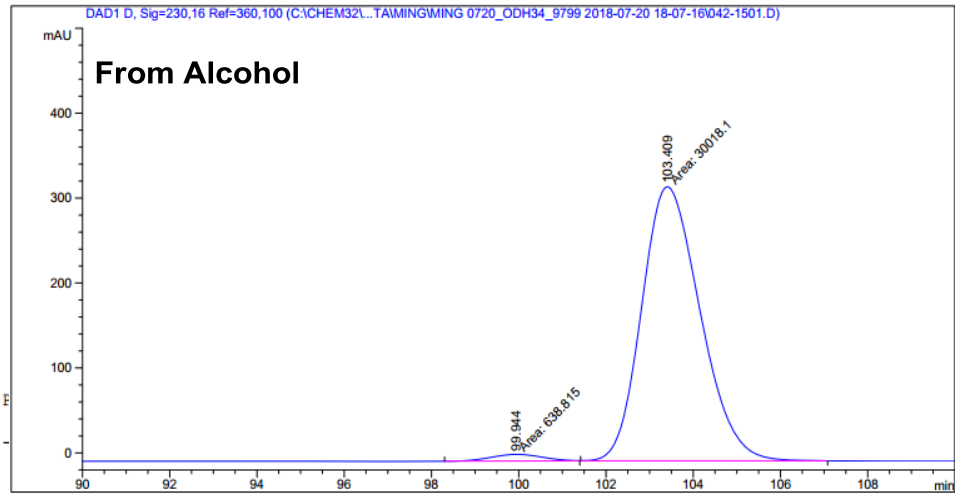
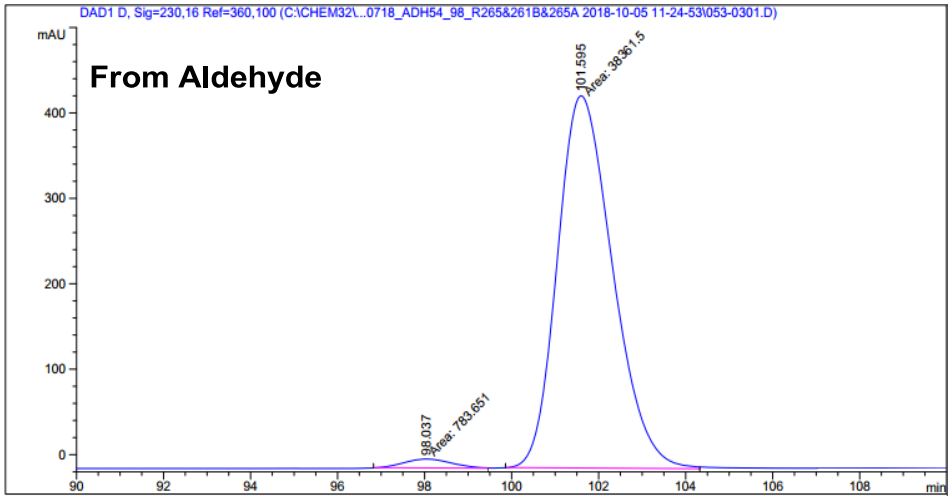
138.28
138.13
119.19
118.95
114.33
108.09
106.36
101.00
72.04
42.23
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	99.481	MF	1.4395	1.69712e4	196.49550	49.8785
2	103.157	FM	1.5204	1.70539e4	186.94481	50.1215

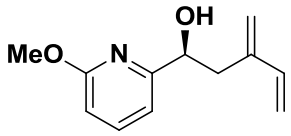


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	99.944	MM	1.3568	638.81500	7.84722	2.0838
2	103.409	MM	1.5506	3.00181e4	322.65732	97.9162



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	98.037	MM	1.2574	783.65094	10.38707	2.0019
2	101.595	MM	1.4675	3.83615e4	435.68677	97.9981

(S)-1-(6-methoxypyridin-2-yl)-3-methylenepent-4-en-1-ol (4e)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with (6-methoxypyridin-2-yl)methanol (**1e**, 27.8 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 10:1) to furnish the title compound **4e** as a yellow oil in 66% yield with 96% ee (27.1 mg, 0.132 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 6-methoxypicolinaldehyde (**2e**, 27.4 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.4 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 10:1) to furnish the title compound **4e** as a yellow oil in 71% yield with 96% ee (29.1 mg, 0.142 mmol).

TLC (SiO_2) R_f = 0.6 (hexanes/ethyl acetate = 2:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dt, *J* = 8.2, 6.9 Hz, 1H), 6.86–6.77 (m, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 6.40 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.38–5.23 (m, 1H), 5.16–5.01 (m, 3H), 4.81 (dt, *J* = 8.1, 5.3 Hz, 1H), 3.93 (d, *J* = 2.6 Hz, 3H), 3.52 (d, *J* = 5.9 Hz, 1H), 2.76 (ddd, *J* = 14.1, 4.8, 1.1 Hz, 1H), 2.60–2.47 (m, 1H).

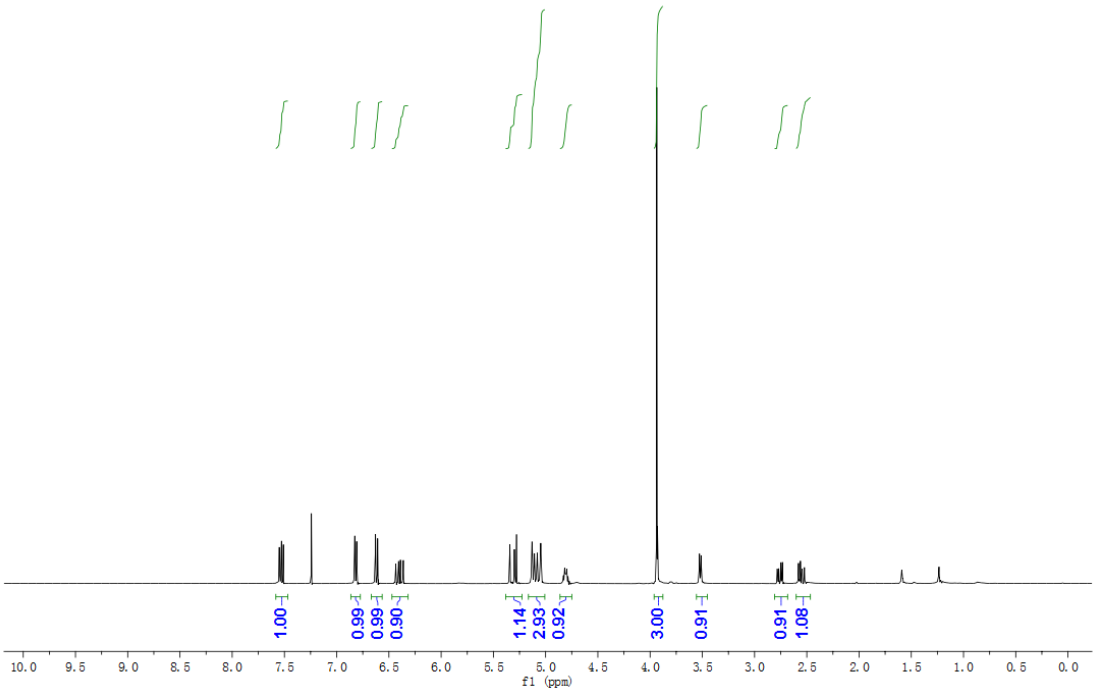
^{13}C NMR (125 MHz, $CDCl_3$): δ 163.4, 159.4, 142.5, 139.1, 138.5, 118.7, 113.9, 112.9, 109.2, 71.4, 53.3, 41.1.

HRMS (ESI) Calculated for $C_{12}H_{15}NO_2$ $[M+H]^+$ = 206.1176, Found 206.1178.

FTIR (neat) 3425, 2948, 1595, 1578, 1466, 1413, 1264, 1031, 900, 832, 796 cm^{-1}.

$[\alpha]_D^{34}$: –29.5 (*c* = 1.0, $CHCl_3$)

HPLC: (Chiralcel AD-H column, hexanes:*i*-PrOH = 95:5, 0.50 mL/min, 230 nm).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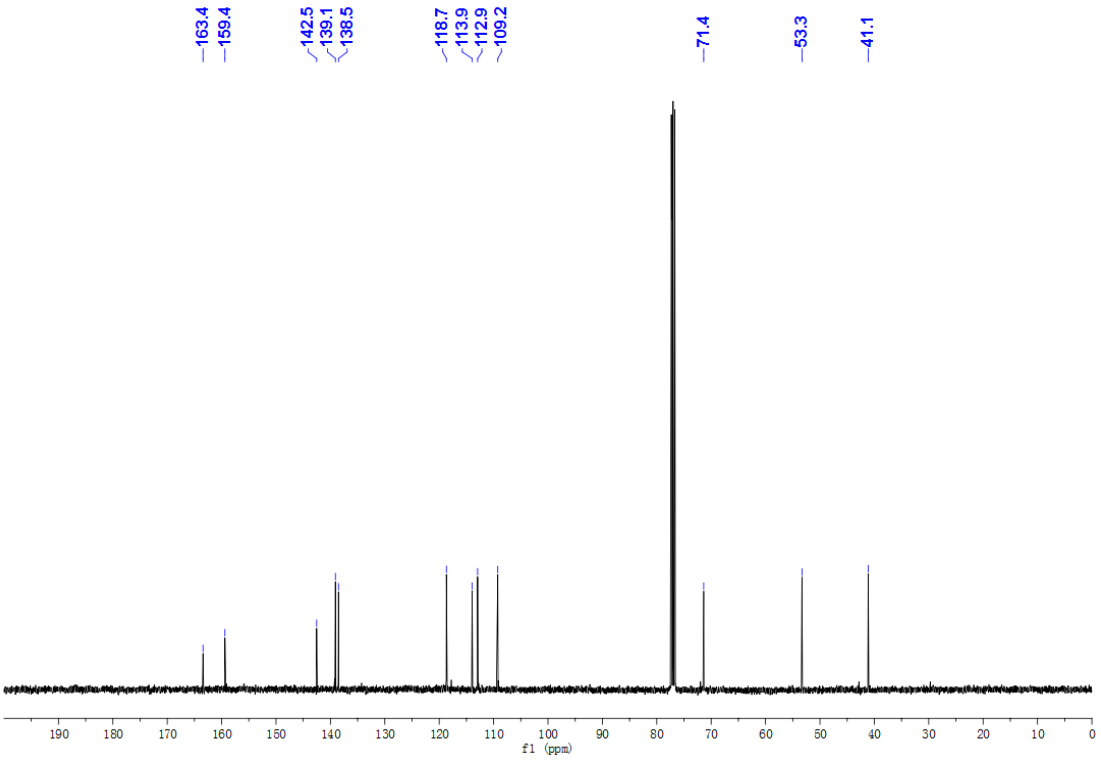
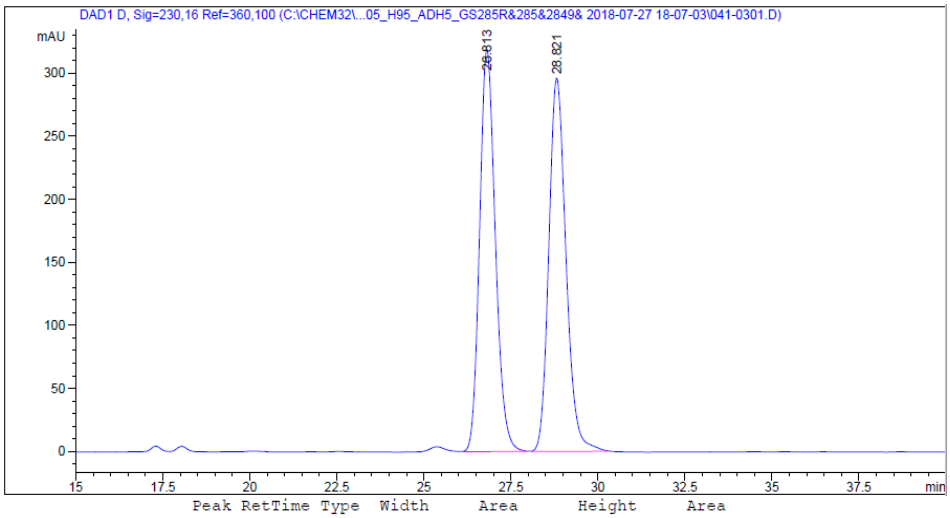
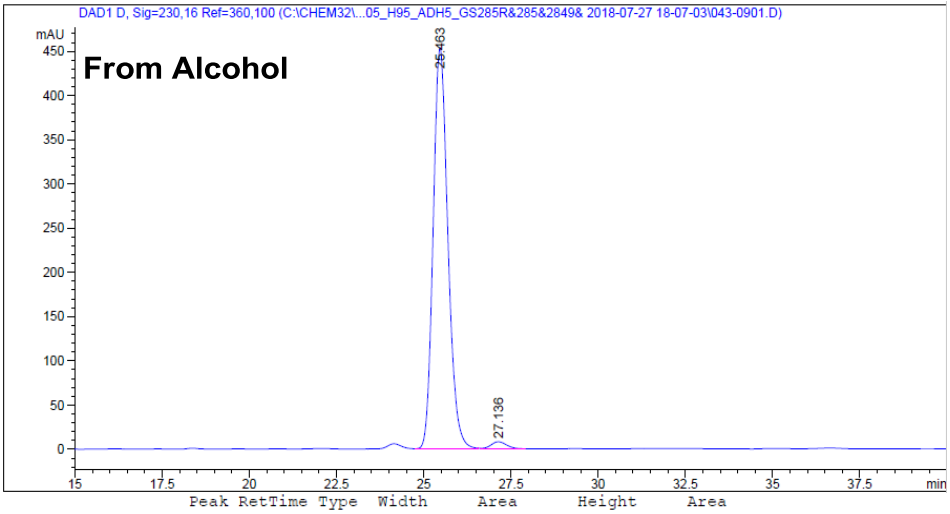
2.93
0.92
3.00
0.91
0.91
1.08
f1 (ppm)

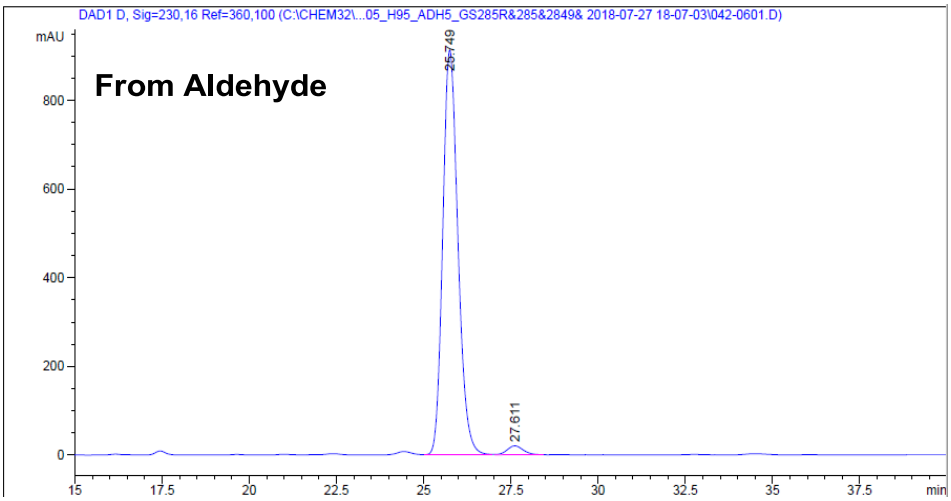

163.4
159.4
142.5
139.1
138.5
118.7
113.9
112.9
109.2
71.4
53.3
41.1
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.813	BB	0.4831	1.00323e4	318.85431	49.7183
2	28.821	BB	0.5178	1.01460e4	296.08566	50.2817

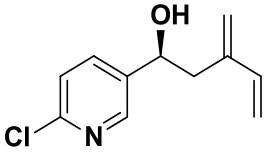


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.463	VB	0.4548	1.33303e4	453.70190	98.1682
2	27.136	BB	0.4783	248.73775	8.01067	1.8318



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.749	VB	0.4607	2.75955e4	912.83411	97.7313
2	27.611	BB	0.4935	640.59406	20.11963	2.2687

(*S*)-1-(6-chloropyridin-3-yl)-3-methylenepent-4-en-1-ol (4f)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with (6-chloropyridin-3-yl)methanol (**1f**, 28.6 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 8:1) to furnish the title compound **4f** as a colorless oil in 65% yield with 94% ee (27.2 mg, 0.13 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 6-chloronicotinaldehyde (**2f**, 28.2 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (1.0 mL, 0.2 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 8:1) to furnish the title compound **4f** as a colorless oil in 72% yield with 94% ee (30.1 mg, 0.144 mmol).

TLC (SiO_2) R_f = 0.3 (hexanes/ethyl acetate = 2:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* = 2.5 Hz, 1H), 7.69 (ddd, *J* = 8.2, 2.5, 0.5 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 6.39 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.28 (d, *J* = 17.7 Hz, 1H), 5.22–5.12 (m, 2H), 5.06 (s, 1H), 4.87 (ddd, *J* = 8.8, 4.4, 2.3 Hz, 1H), 2.66 (ddd, *J* = 14.0, 4.5, 1.0 Hz, 1H), 2.55 (ddd, *J* = 14.0, 9.0, 0.7 Hz, 1H), 2.22 (d, *J* = 2.5 Hz, 1H) ppm.

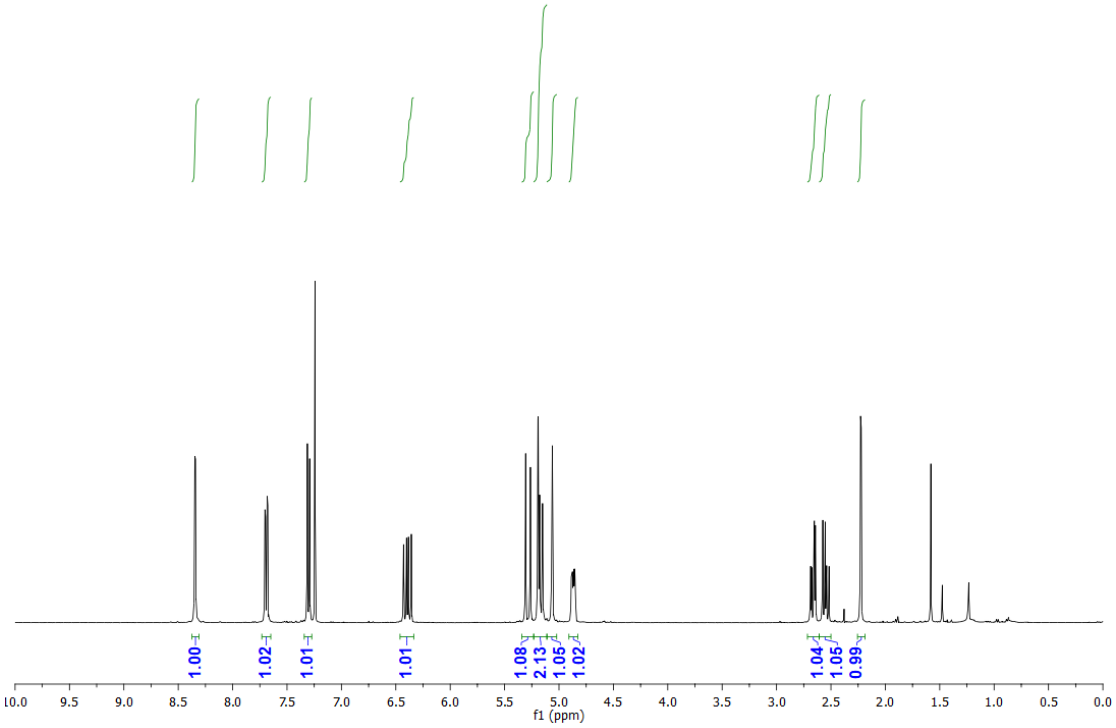
^{13}C NMR (125 MHz, $CDCl_3$): δ 150.6, 147.6, 141.7, 138.1, 137.9, 136.4, 124.1, 119.7, 114.7, 69.4, 42.2 ppm.

HRMS (ESI) Calculated for $C_{11}H_{12}ClNO$ $[M+H]^+$ = 210.0680, Found 210.0686.

FTIR (neat) 3424, 2921, 1587, 1459, 1275, 1260, 1104, 764, 748 cm^{-1}.

$[\alpha]_D^{34}$: –35 (*c* = 0.5, $CHCl_3$)

HPLC: (Chiralcel AD-H column, hexanes:*i*-PrOH = 97:3, 0.50 mL/min, 230 nm).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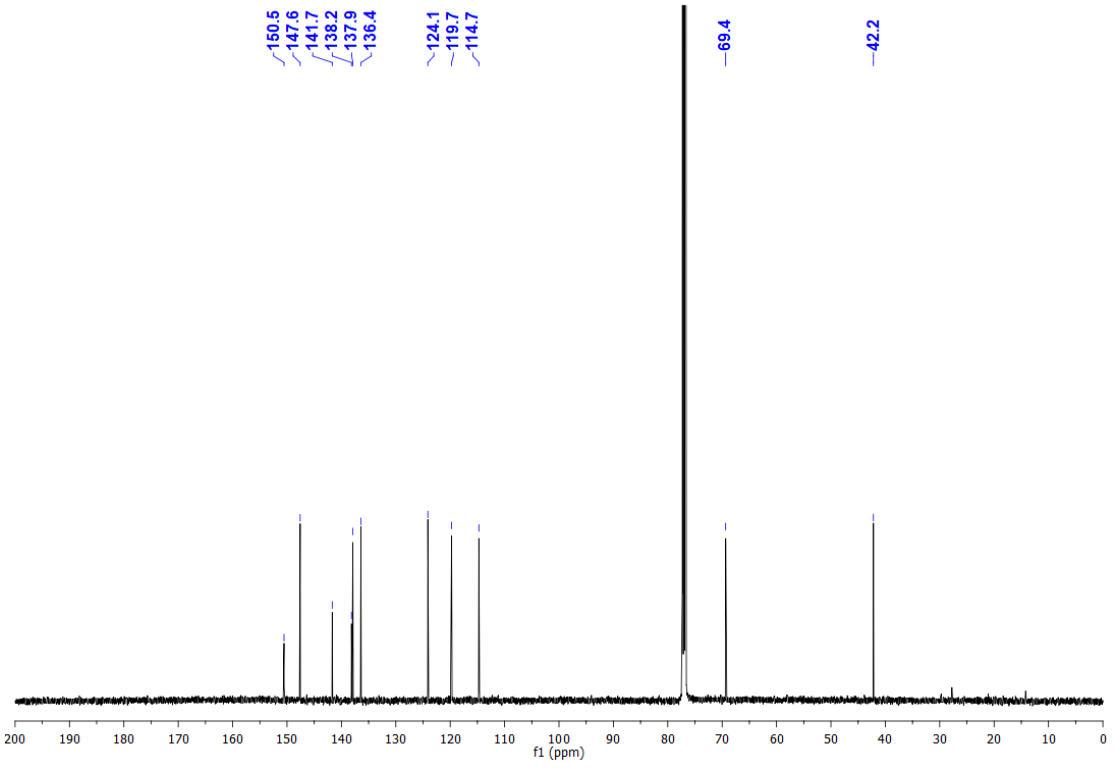
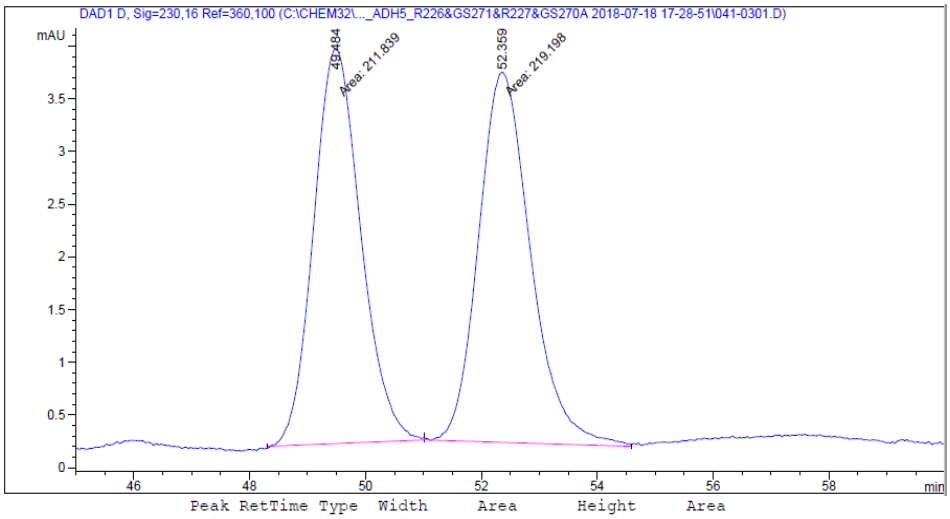
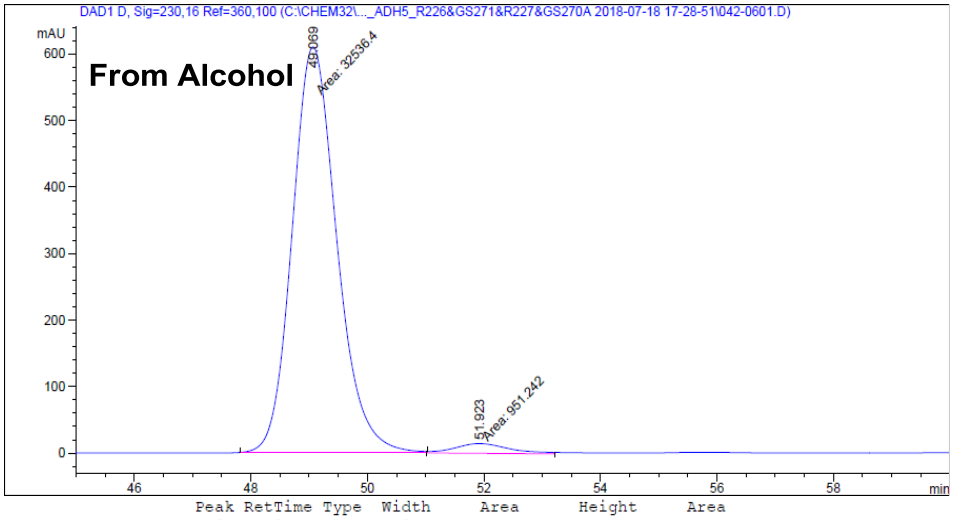
1.05
1.02
1.04
1.05
0.99
f1 (ppm)

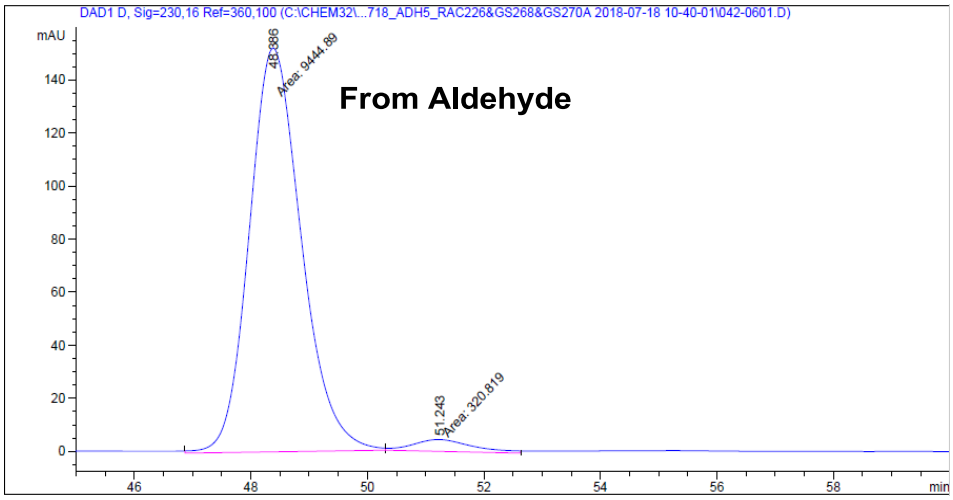

150.5
147.6
141.7
138.2
137.9
136.4
124.1
119.7
114.7
69.4
42.2
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.484	MM	0.9421	211.83945	3.74754	49.1465
2	52.359	MM	1.0396	219.19757	3.51414	50.8535

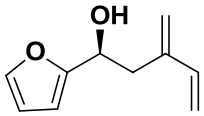


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.069	MM	0.8882	3.25364e4	610.54425	97.1594
2	51.923	MM	1.0785	951.24225	14.70058	2.8406



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.386	MM	1.0342	9444.89063	152.21178	96.7148
2	51.243	MM	1.1923	320.81924	4.48445	3.2852

(S)-1-(furan-2-yl)-3-methylenepent-4-en-1-ol (4g)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with furfuryl alcohol (**1g**, 19.6 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4g** as a colorless oil in 64% yield with 95% ee (21.0 mg, 0.128 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with furfural (**2g**, 19.2 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4g** as a colorless oil in 72% yield with 95% ee (23.6 mg, 0.144 mmol).

TLC (SiO_2) R_f = 0.38 (hexanes/ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 0.9 Hz, 1H), 6.40 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.33 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 5.29 (d, *J* = 17.6 Hz, 1H), 5.19 – 5.10 (m, 3H), 4.88 (dt, *J* = 8.4, 4.1 Hz, 1H), 2.86 (dd, *J* = 14.2, 4.7 Hz, 1H), 2.71 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.07 (s, 1H) ppm.

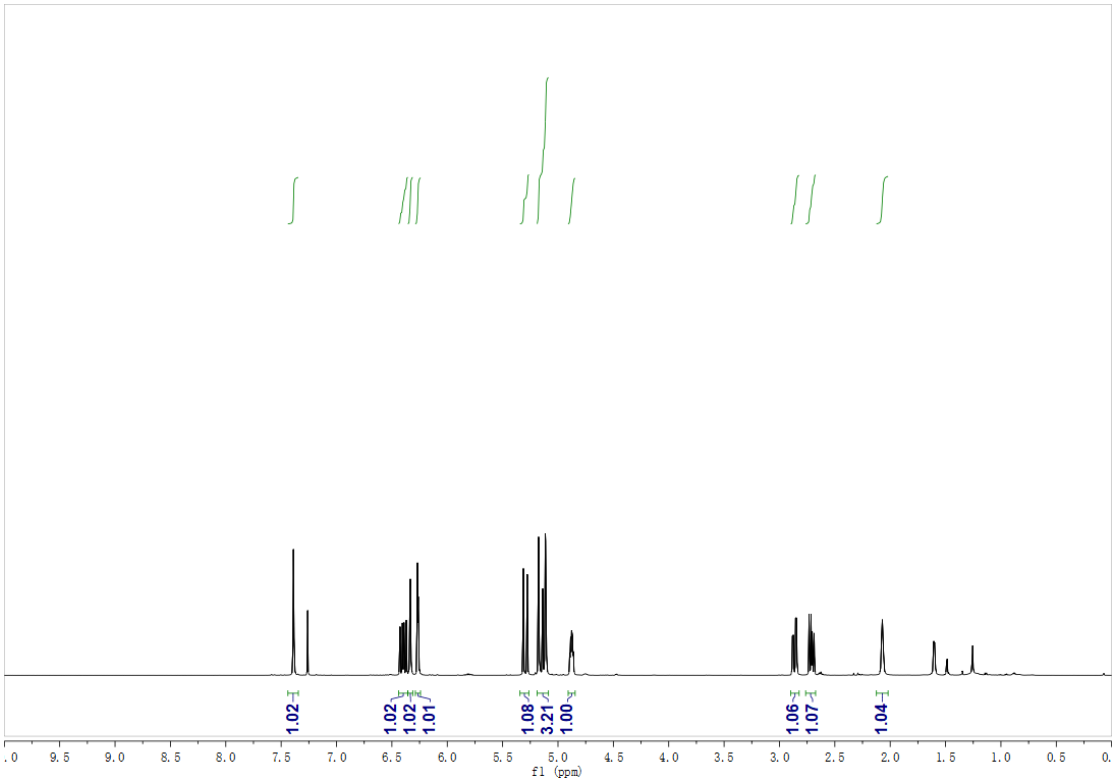
^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 142.1, 138.3, 119.2, 114.4, 110.3, 106.3, 66.1, 38.3 ppm.

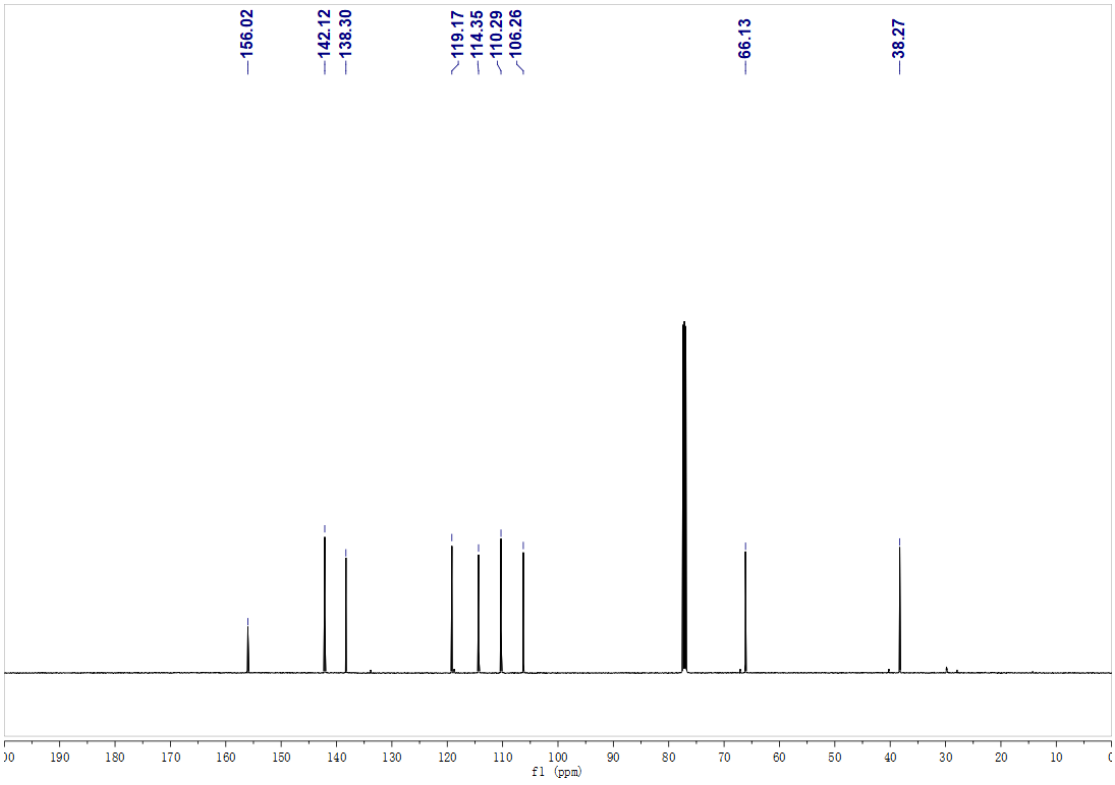
HRMS (ESI) Calculated for $C_{10}H_{12}O_2$ $[M]^+$ = 164.0837, Found 164.0833.

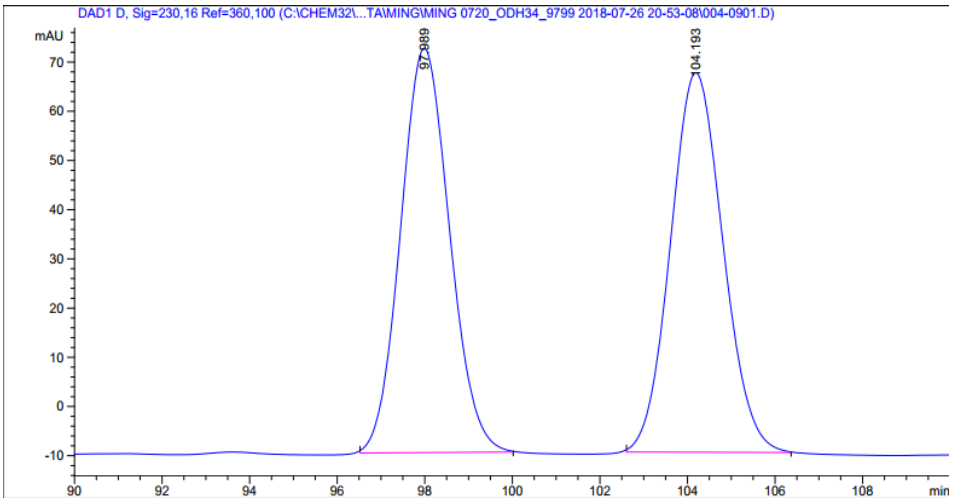
FTIR (neat) 3361, 3006, 1595, 1276, 1261, 1145, 1010, 750 cm^{-1}.

$[\alpha]_D^{34}$: –265.7 (*c* = 0.5, $CHCl_3$)

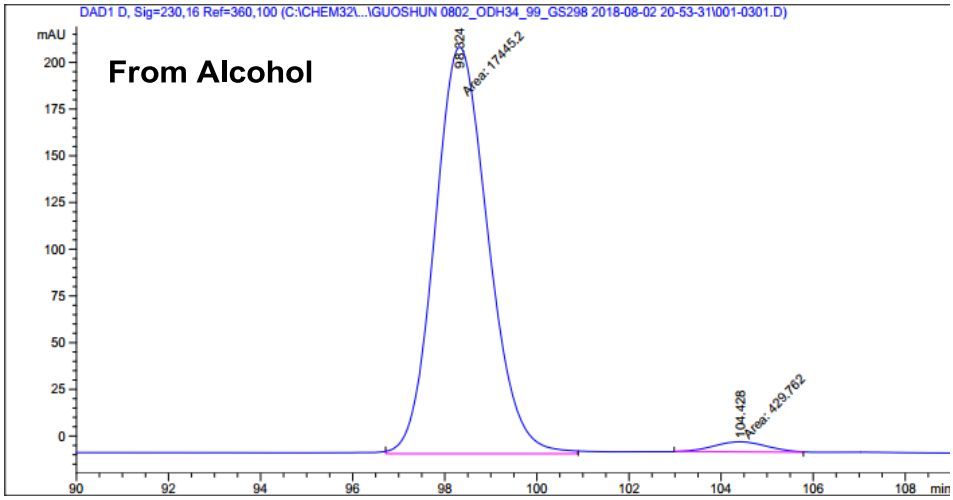
HPLC: (Two connected chiralcel OD-H columns, hexanes:*i*-PrOH = 99:1, 0.50 mL/min, 230 nm).


1.02
1.02
1.02
1.01
1.08
3.21
1.00
1.06
1.07
1.04
f1 (ppm)

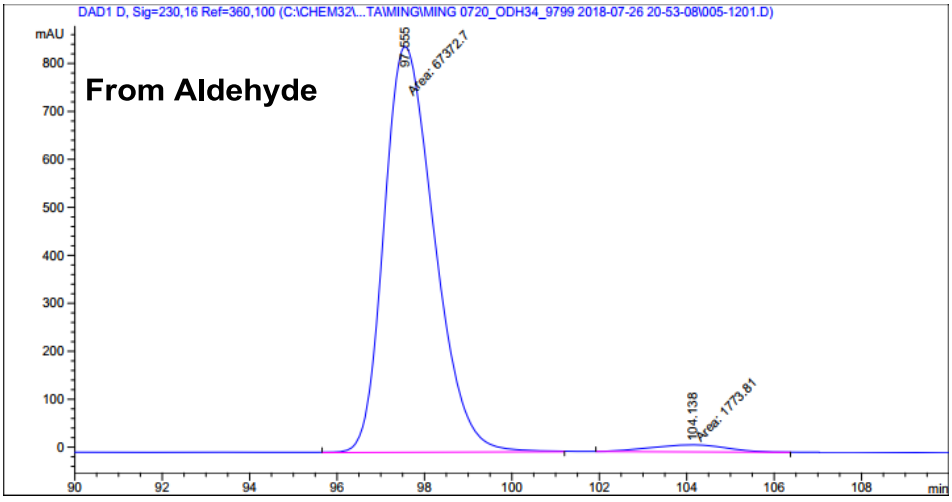

156.02
142.12
138.30
119.17
114.35
110.29
106.26
66.13
38.27
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	97.989	BB	1.1852	6374.65234	82.15516	49.8366
2	104.193	BB	1.2802	6416.45215	77.15578	50.1634

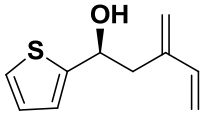


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	98.324	MM	1.3360	1.74452e4	217.63118	97.5957
2	104.428	MM	1.3260	429.76154	5.40163	2.4043



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	97.555	MM	1.3276	6.73727e4	845.78369	97.4347
2	104.138	MM	1.9934	1773.81384	14.83067	2.5653

(S)-3-methylene-1-(thiophen-2-yl)pent-4-en-1-ol (4h)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 2-thiophenemethanol (**1h**, 22.8 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4h** as a colorless oil in 80% yield with 95% ee (28.8 mg, 0.16 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with thiophene-2-carbaldehyde (**2h**, 22.4 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4h** as a colorless oil in 83% yield with 95% ee (29.9 mg, 0.166 mmol).

TLC (SiO_2) R_f = 0.35 (hexanes/ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, *J*=4.6 Hz, 1H), 6.98 (dt, *J*=4.7, 3.3 Hz, 2H), 6.42 (dd, *J*=17.6, 10.7 Hz, 1H), 5.32 (d, *J*=17.7 Hz, 1H), 5.20 – 5.13 (m, 3H), 5.11 (dd, *J*=8.7, 3.9 Hz, 1H), 2.84 (dd, *J*=14.1, 4.3 Hz, 1H), 2.70 (dd, *J*=14.1, 9.0 Hz, 1H), 2.20 (d, *J*=3.0 Hz, 1H) ppm.

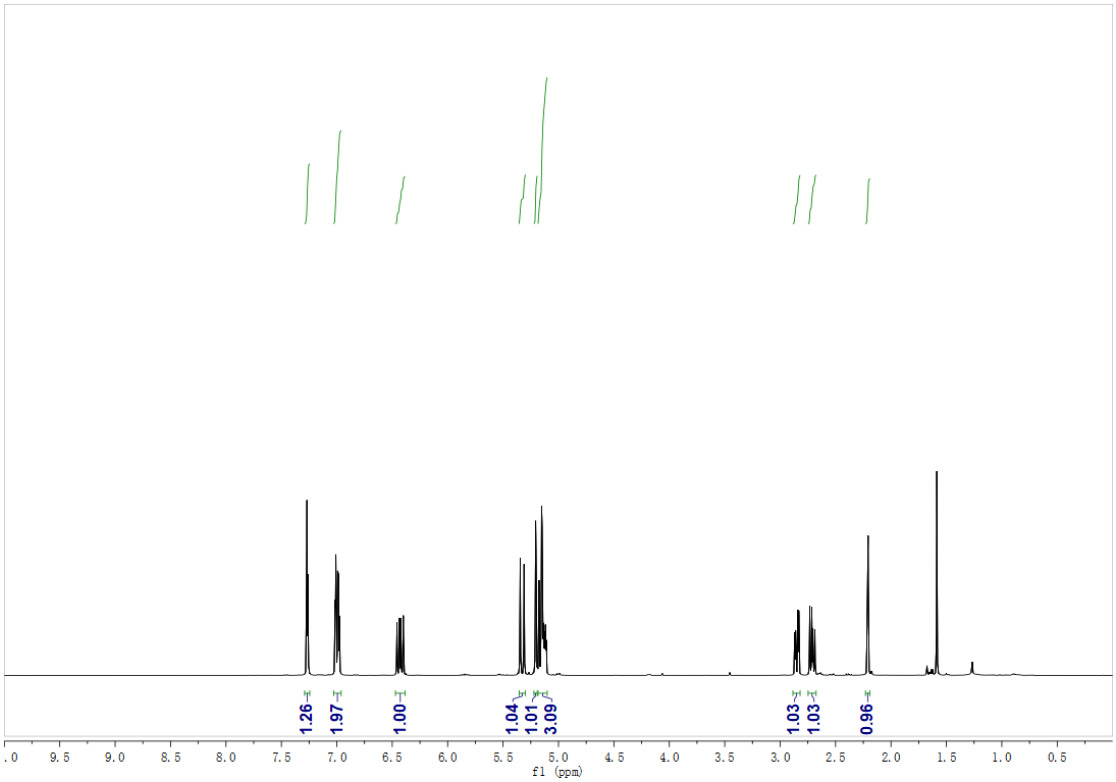
^{13}C NMR (125 MHz, $CDCl_3$): δ 147.9, 142.3, 138.3, 126.7, 124.7, 123.8, 119.4, 114.5, 68.5, 42.3 ppm.

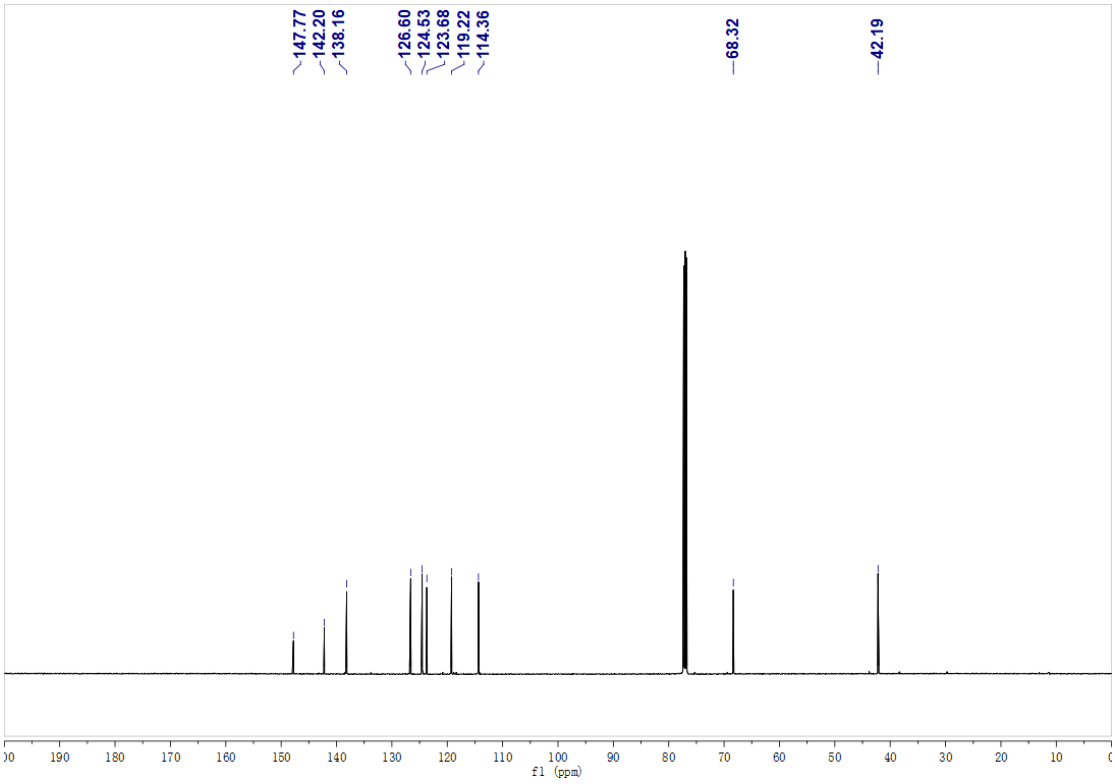
HRMS (ESI) Calculated for $C_{10}H_{12}OS$ $[M]^+$ = 180.0609, Found 180.0607.

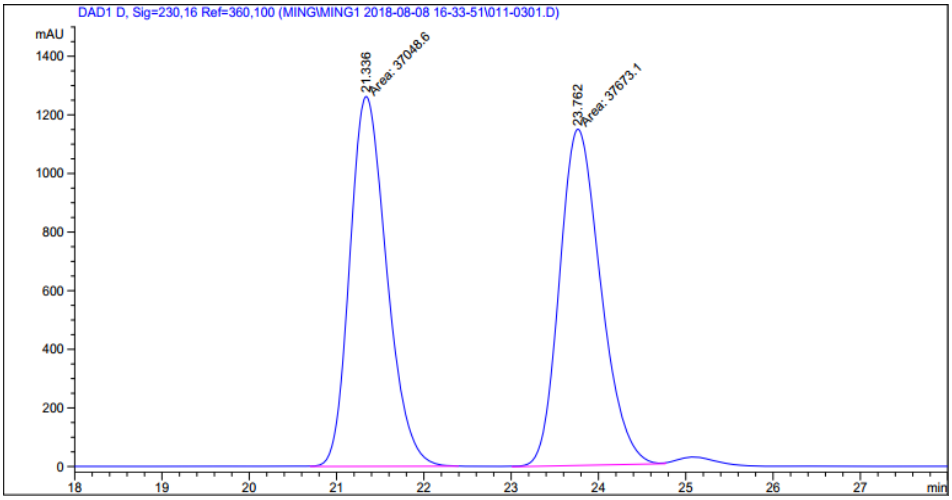
FTIR (neat) 3384, 3086, 1594, 1276, 1031, 991,764, 696 cm^{-1}.

$[\alpha]_D^{34}$: 40 (*c* = 0.4, $CHCl_3$)

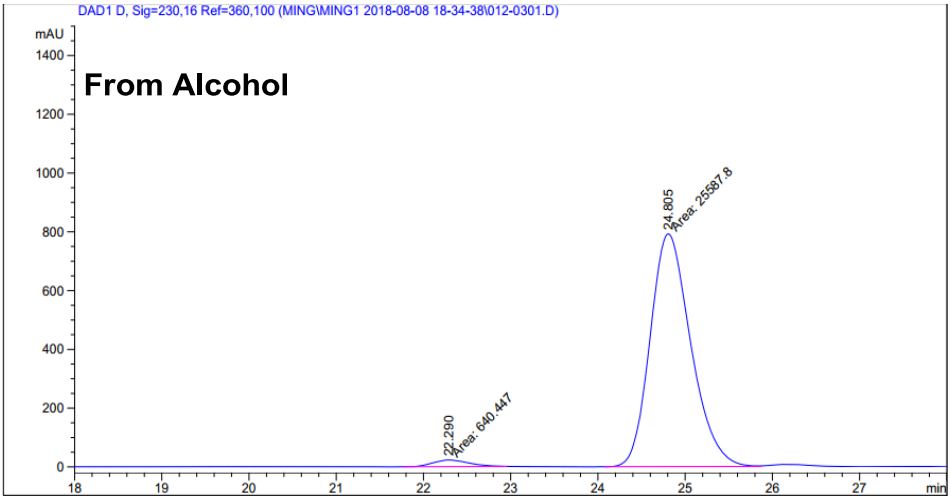
HPLC: (Chiralcel AS-H column, hexanes:*i*-PrOH = 97:3, 1.0 mL/min, 230 nm).


1.26
1.97
1.00
1.04
1.01
3.09
1.03
1.03
0.96
f1 (ppm)

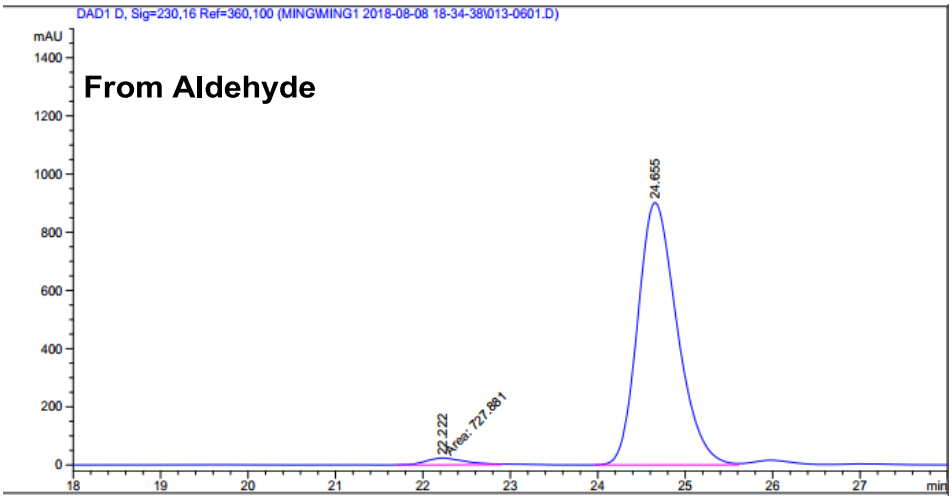

147.77
142.20
138.16
126.60
124.53
123.68
119.22
114.36
68.32
42.19
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.336	MM	0.4893	3.70486e4	1262.01416	49.5822
2	23.762	MM	0.5472	3.76731e4	1147.38342	50.4178

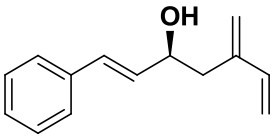


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.290	MM	0.4720	640.44659	22.61472	2.4418
2	24.805	MM	0.5385	2.55878e4	791.97955	97.5582



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.222	MM	0.5150	727.88141	23.55580	2.5232
2	24.655	BV	0.4818	2.81199e4	901.68951	97.4768

(*S*, *E*)-5-methylene-1-phenylhepta-1,6-dien-3-ol (4i)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with (*E*)-cinnamyl alcohol (**1i**, 26.8 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 10:1) to furnish the title compound **4i** as a yellow oil in 67% yield with 94% ee (26.8 mg, 0.134 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with (*E*)-cinnamaldehyde (**2i**, 26.4 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.4 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 10:1) to furnish the title compound **4i** as a yellow oil in 70% yield with 96% ee (28.2 mg, 0.14 mmol).

TLC (SiO_2) R_f = 0.3 (hexanes/ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.5 Hz, 2H), 7.28–7.20 (m, 2H), 7.19–7.15 (m, 1H), 6.54 (d, J = 15.9 Hz, 1H), 6.35 (dd, *J* = 17.6, 11.0 Hz, 1H), 6.18 (dd, *J* = 15.9, 6.4 Hz, 1H), 5.22 (t, *J* = 18.1 Hz, 1H), 5.16–5.03 (m, 3H), 4.40 (dd, *J* = 12.7, 6.3 Hz, 1H), 2.59–2.36 (m, 2H), 1.79 (s, 1H) ppm.

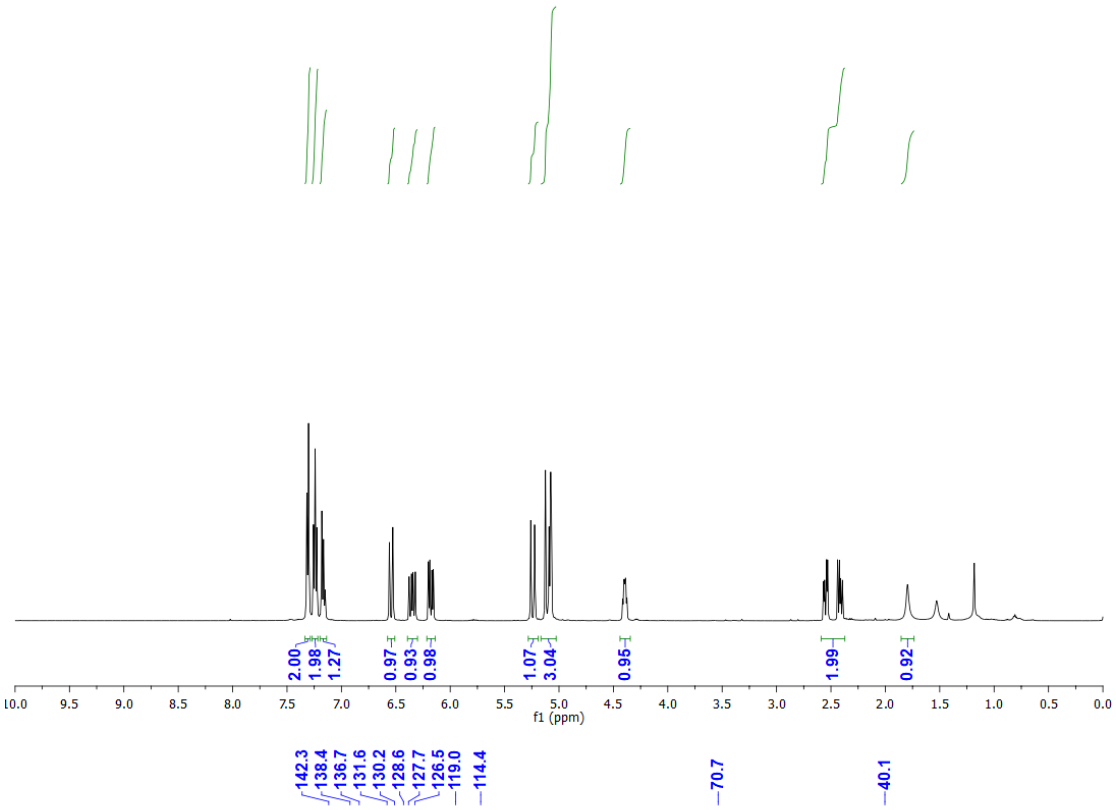
^{13}C NMR (125 MHz, $CDCl_3$): δ 142.3, 138.4, 136.7, 131.6, 130.2, 128.6, 127.7, 126.5, 119.0, 114.4, 77.3, 77.0, 76.8, 70.7, 40.1ppm.

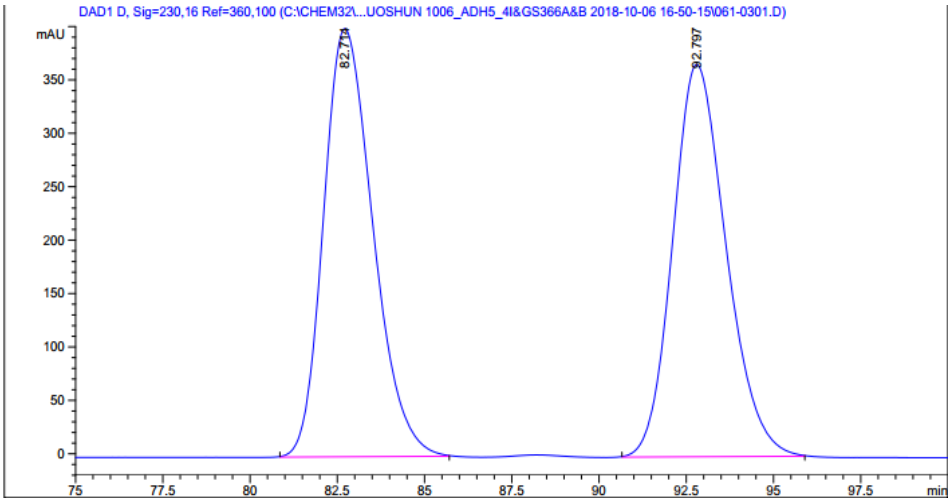
HRMS (ESI) Calculated for $C_{14}H_{16}O$ $[M]^+$ = 200.1201, Found 200.1202.

FTIR (neat) 3386, 3025, 2927, 1594, 1493, 1448, 1097, 1027, 964, 899, 746, 692 cm^{-1}.

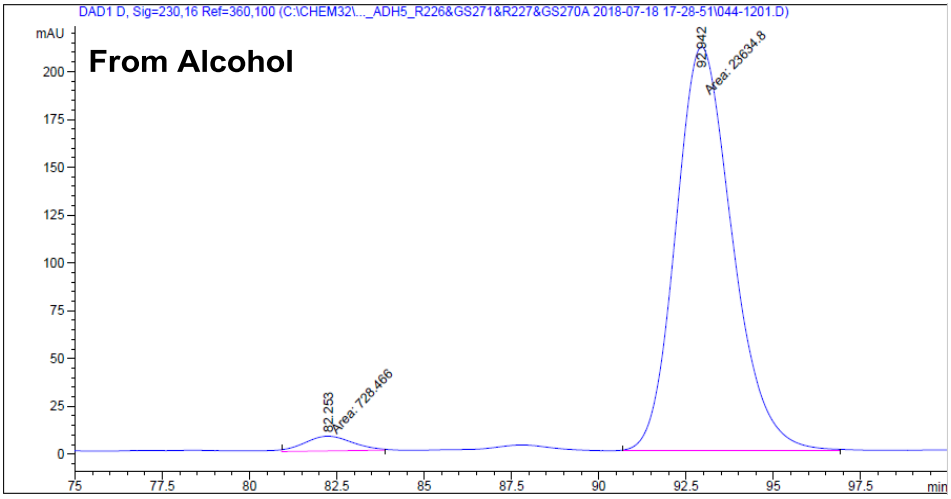
$[\alpha]_D^{31}$: –12.5 (*c* = 0.5, $CHCl_3$)

HPLC: (Chiralcel AD-H column, hexanes:*i*-PrOH = 99:1, 0.50 mL/min, 230 nm).

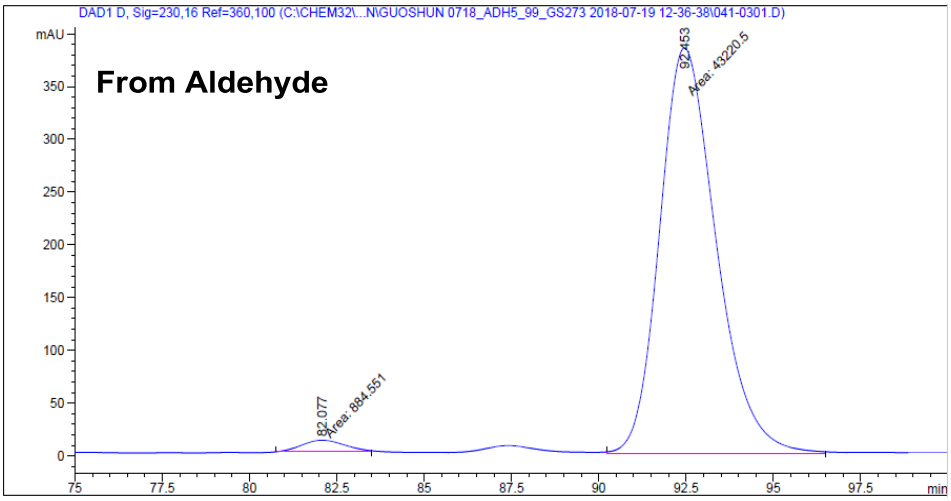

2.00
1.98
1.27
0.97
0.93
0.98
1.07
3.04
0.95
1.99
0.92
f1 (ppm)
142.3
138.4
136.7
131.6
130.2
128.6
127.7
126.5
119.0
114.4
70.7
40.1
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	82.714	BB	1.5268	3.93897e4	400.73526	50.1899
2	92.797	BB	1.6100	3.90917e4	367.20358	49.8101

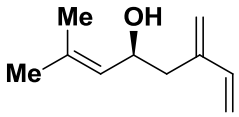


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	82.253	MM	1.1291	728.46631	7.67351	2.9900
2	92.942	MM	1.8686	2.36348e4	210.81120	97.0100



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	82.077	MM	1.3921	884.55060	10.58977	2.0056
2	92.453	MM	1.8753	4.32205e4	384.11826	97.9944

(S)-2-methyl-6-methyleneocta-2,7-dien-4-ol (4j)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 3-methyl-2-buten-1-ol (**1j**, 17.2 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4j** as a colorless oil in 64% yield with 96% ee (19.5 mg, 0.28 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 3-methyl-2-butenal (**2j**, 16.8 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4j** as a colorless oil in 71% yield with 96% ee (21.6 mg, 0.142 mmol).

TLC (SiO_2) R_f = 0.6 (hexanes/ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.40 (dd, *J*=17.6, 10.8 Hz, 1H), 5.28 (d, *J*=17.6 Hz, 1H), 5.22 – 5.18 (m, 1H), 5.16 – 5.08 (m, 3H), 4.55 – 4.49 (m, 1H), 2.41 (qd, *J*=14.0, 6.5 Hz, 2H), 1.73 (s, 3H), 1.68 (s, 3H) ppm.

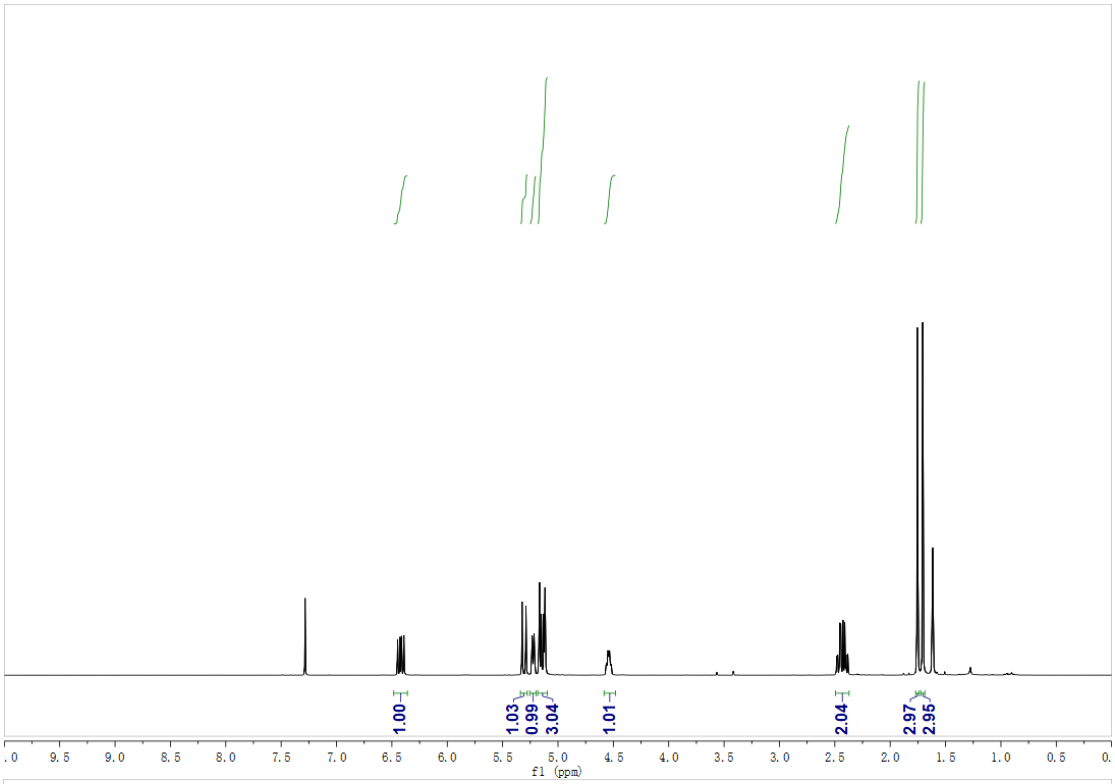
^{13}C NMR (125 MHz, $CDCl_3$): δ 142.8, 138.7, 135.5, 127.5, 118.8, 114.2, 66.8, 40.2, 25.9, 18.4 ppm.

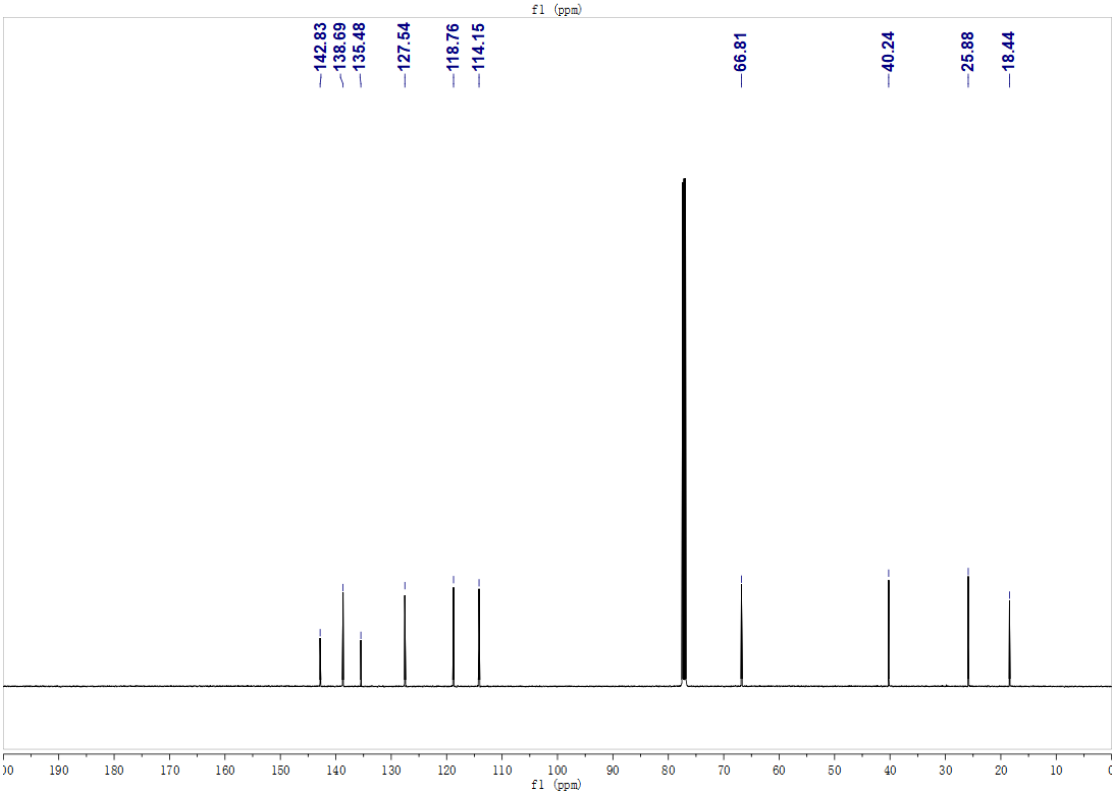
HRMS (ESI) Calculated for $C_{10}H_{16}O$ $[M]^+$ = 152.1201, Found 152.1196.

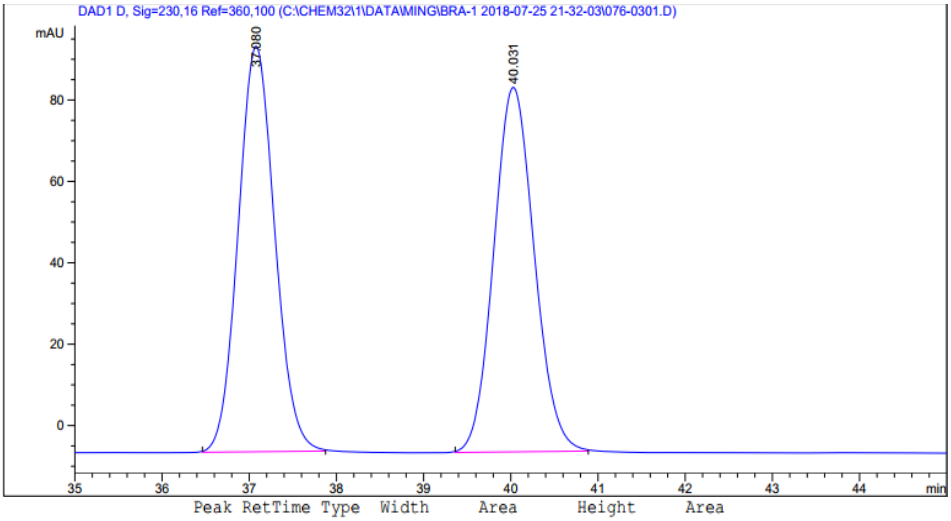
FTIR (neat) 3335, 2988, 1594, 1275, 1019, 990, 897, 764 cm^{-1}.

$[\alpha]_D^{34}$: 14.9 (*c* = 0.5, EtOH)

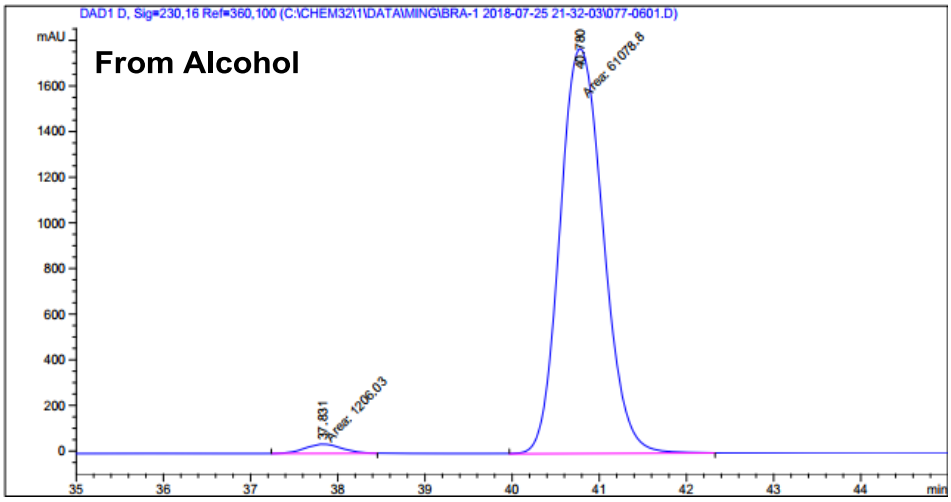
HPLC: (Two connected chiralcel OD-H columns, hexanes:*i*-PrOH = 99:1, 0.50 mL/min, 230 nm).


1.00
1.03
0.99
3.04
1.01
2.04
2.97
2.95
f1 (ppm)

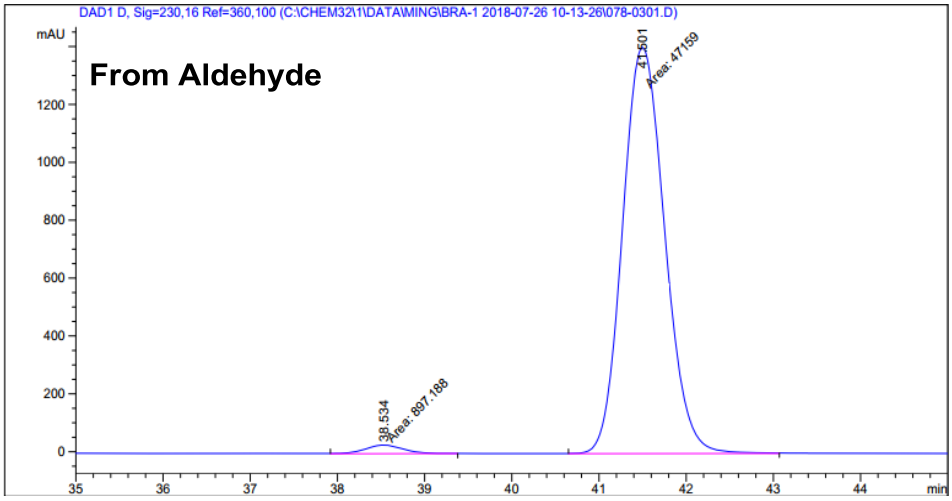

142.83
138.69
135.48
127.54
118.76
114.15
66.81
40.24
25.88
18.44
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.080	BB	0.4538	2902.17090	99.64278	50.0907
2	40.031	BB	0.5006	2891.66626	89.58588	49.9093

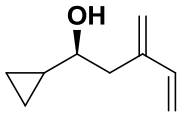


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.831	MM	0.4933	1206.02734	40.74626	1.9363
2	40.780	MM	0.5736	6.10788e4	1774.59863	98.0637



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.534	MM	0.5044	897.18781	29.64531	1.8670
2	41.501	MM	0.5602	4.71590e4	1403.15625	98.1330

(S)-1-cyclopropyl-3-methylenepent-4-en-1-ol (4k)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with cyclopropylmethanol (**1k**, 14.4 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4k** as a colorless oil in 72% yield with 96% ee (19.9 mg, 0.144 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with cyclopropanecarboxaldehyde (**2k**, 14.0 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4k** as a colorless oil in 80% yield with 96% ee (22.1 mg, 0.16 mmol).

TLC (SiO_2) R_f = 0.4 (hexanes/ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.39 (dd, *J*=17.6, 10.8 Hz, 1H), 5.24 (d, *J*=17.6 Hz, 1H), 5.11 (m, 3H), 3.06 (td, *J*=8.5, 2.9 Hz, 1H), 2.66 (dd, *J*=14.0, 3.3 Hz, 1H), 2.43 (dd, *J*=14.0, 8.9 Hz, 1H), 1.69 (s, 1H), 0.98 – 0.90 (m, 1H), 0.57 – 0.48 (m, 2H), 0.39 – 0.29 (m, 1H) ppm.

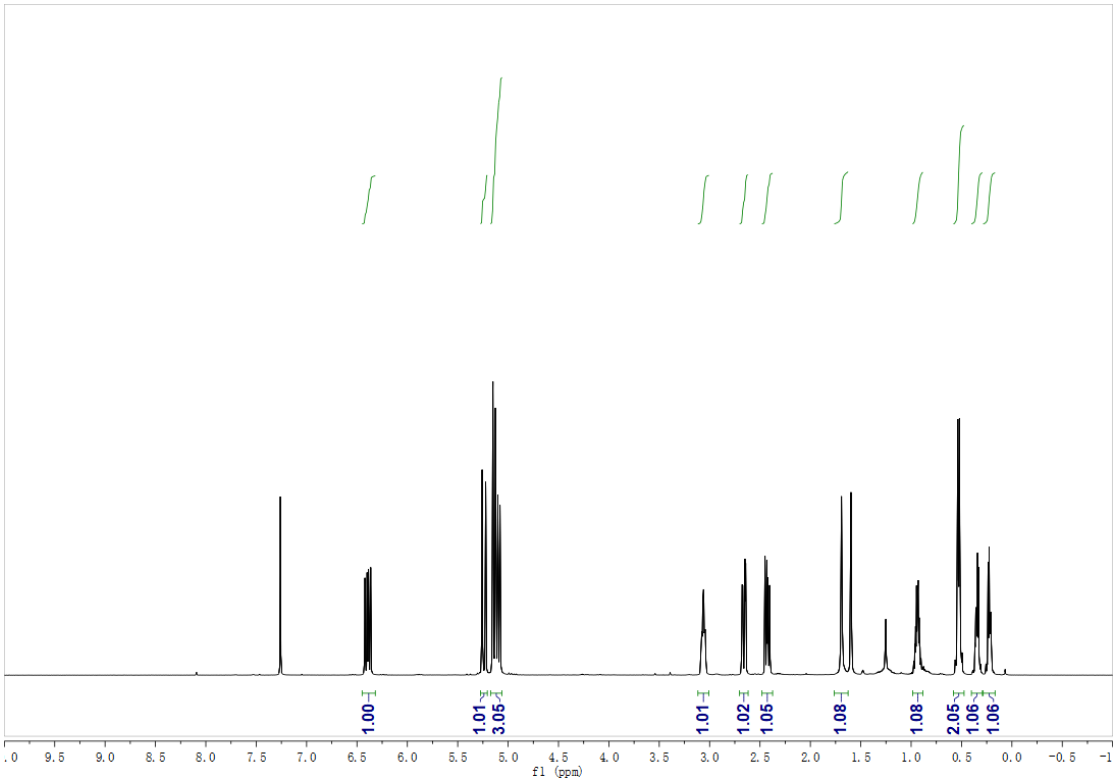
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 138.7, 118.5, 114.2, 74.6, 39.8, 17.8, 3.0, 2.7 ppm.

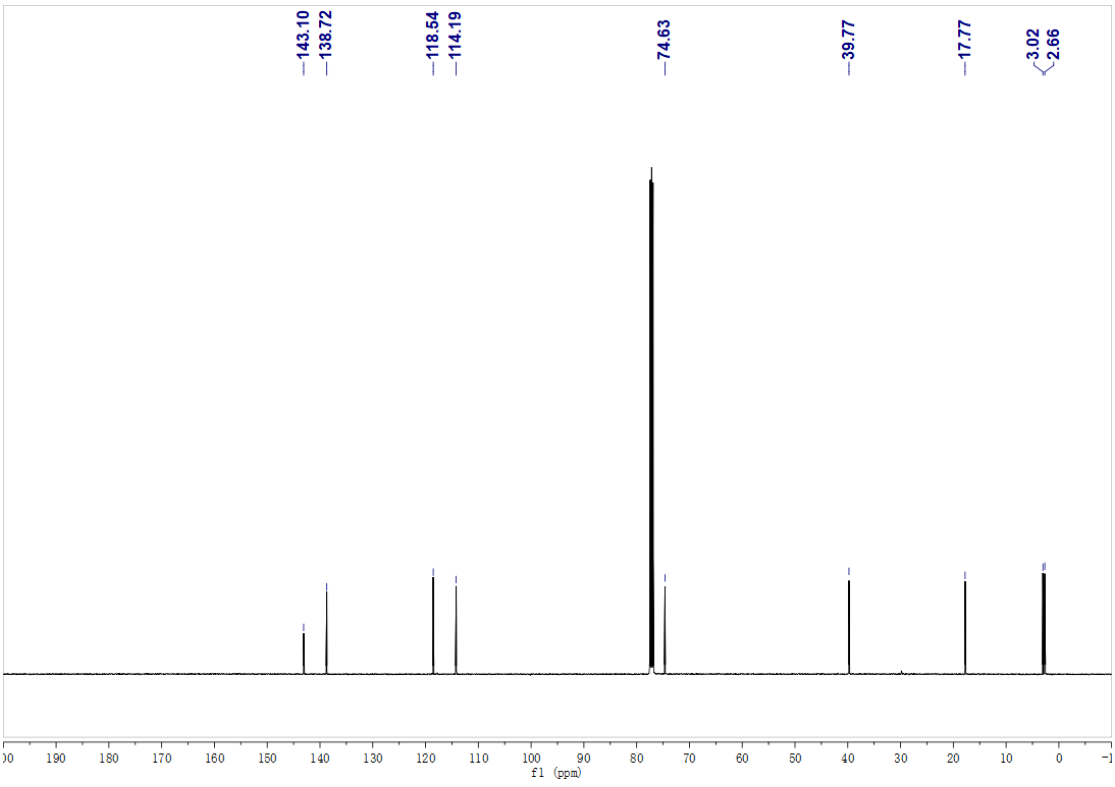
HRMS (ESI) Calculated for $C_9H_{14}O$ $[M]^+$ = 138.1045, Found 138.1050.

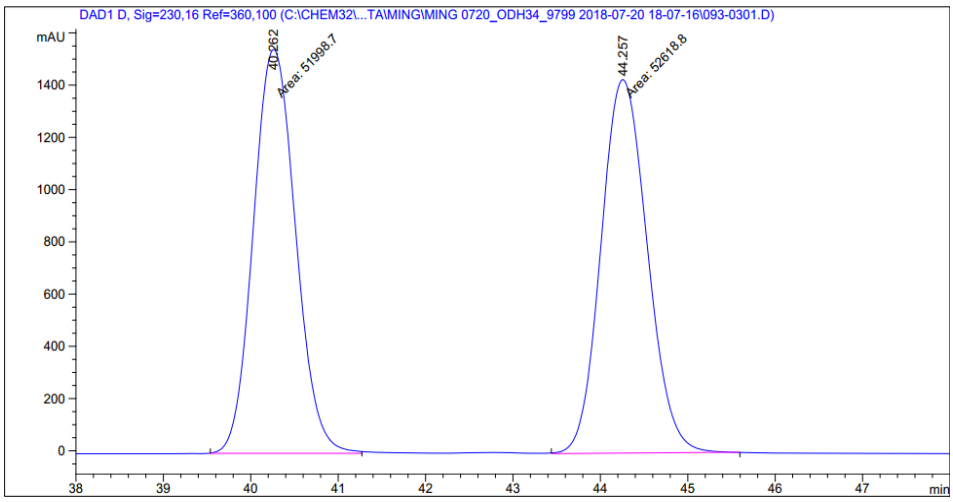
FTIR (neat) 3384, 3081, 1594, 1428, 1260, 1025, 896, 764 cm^{-1}.

$[\alpha]_D^{34}$: –262.5 (*c* = 0.5, $CHCl_3$)

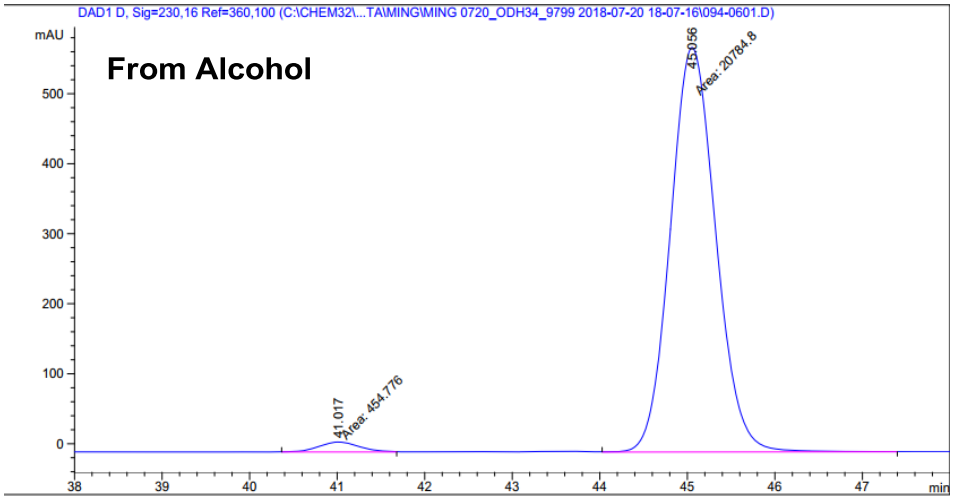
HPLC: (Two connected chiralcel OD-H columns, hexanes:*i*-PrOH = 99:1, 0.50 mL/min, 230 nm).


1.00
1.01
3.05
1.01
1.02
1.05
1.08
1.08
2.05
1.06
1.06
f1 (ppm)

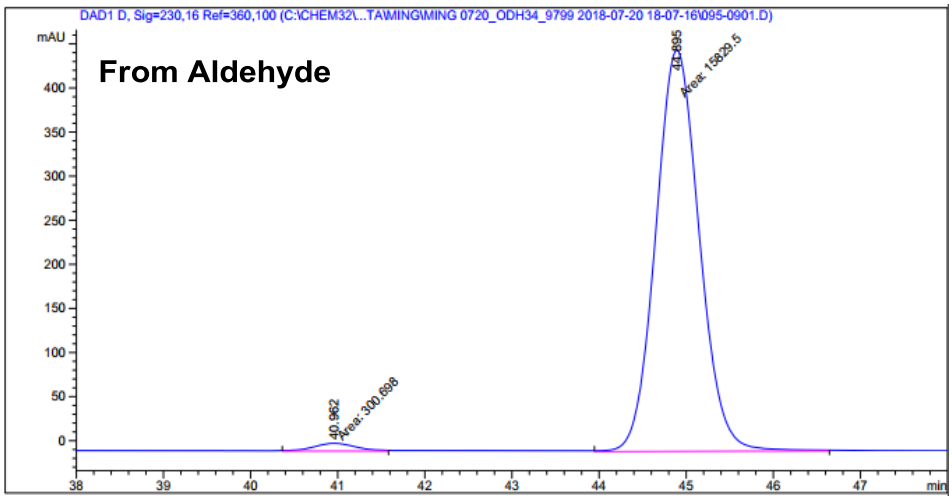

143.10
138.72
118.54
114.19
74.63
39.77
17.77
3.02
2.66
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.262	MM	0.5604	5.19987e4	1546.45911	49.7037
2	44.257	MM	0.6134	5.26188e4	1429.70654	50.2963

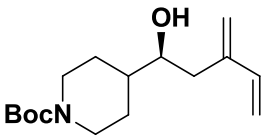


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.017	MM	0.5361	454.77625	14.13857	2.1412
2	45.056	MM	0.5996	2.07848e4	577.77985	97.8588



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.962	MM	0.5628	300.69763	8.90547	1.8642
2	44.895	MM	0.5797	1.58295e4	455.08932	98.1358

(S)-tert-butyl 4-(1-hydroxy-3-methylenepent-4-en-1-yl)piperidine-1-carboxylate (4l)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with tert-butyl 4-(hydroxymethyl)piperidine-1-carboxylate (**1l**, 43.3 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 10:1) to furnish the title compound **4l** as a colorless oil in 75% yield with 94% ee (42.2 mg, 0.15 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 1-Boc-piperidine-4-carboxaldehyde (**2l**, 42.6 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.4 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 10:1) to furnish the title compound **4l** as a colorless oil in 78% yield with 95% ee (43.9 mg, 0.156 mmol).

TLC (SiO_2) R_f = 0.4 (hexanes/ethyl acetate = 2:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.32 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.17–5.10 (m, 2H), 5.05 (d, *J* = 10.5 Hz, 2H), 4.23–3.88 (m, 2H), 3.44 (dd, *J* = 25.8, 18.5 Hz, 1H), 2.62 (s, 2H), 2.54 (dd, *J* = 13.8, 1.3 Hz, 1H), 2.07 (dd, *J* = 13.8, 10.1 Hz, 1H), 1.75 (t, *J* = 26.7 Hz, 1H), 1.62 (d, *J* = 11.6 Hz, 2H), 1.53–1.44 (m, 1H), 1.39 (s, 9H), 1.30–1.18 (m, 2H) ppm.

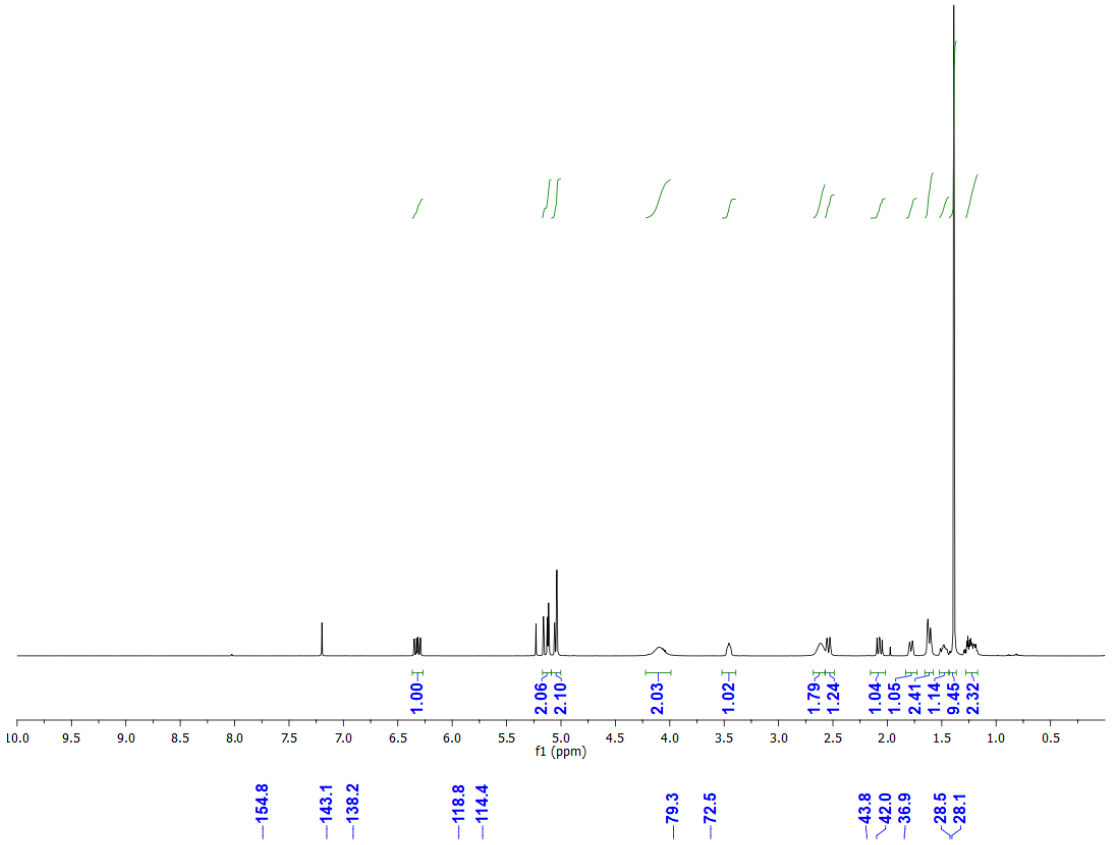
^{13}C NMR (125 MHz, $CDCl_3$): δ 154.8, 143.1, 138.2, 118.8, 114.4, 79.3, 72.5, 43.8, 41.9, 36.9, 28.5, 28.1, 27.6 ppm.

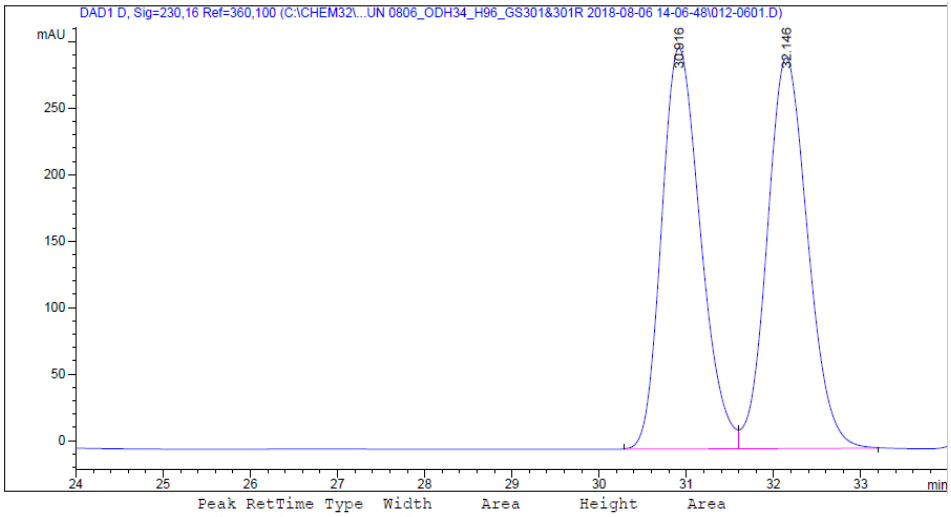
HRMS (ESI) Calculated for $C_{16}H_{27}NO_3$ $[M+Na]^+$ =304.1883, Found 304.1886.

FTIR (neat) 3427, 2929, 1424, 1365, 1294, 1269, 1164, 898, 865 cm^{-1}.

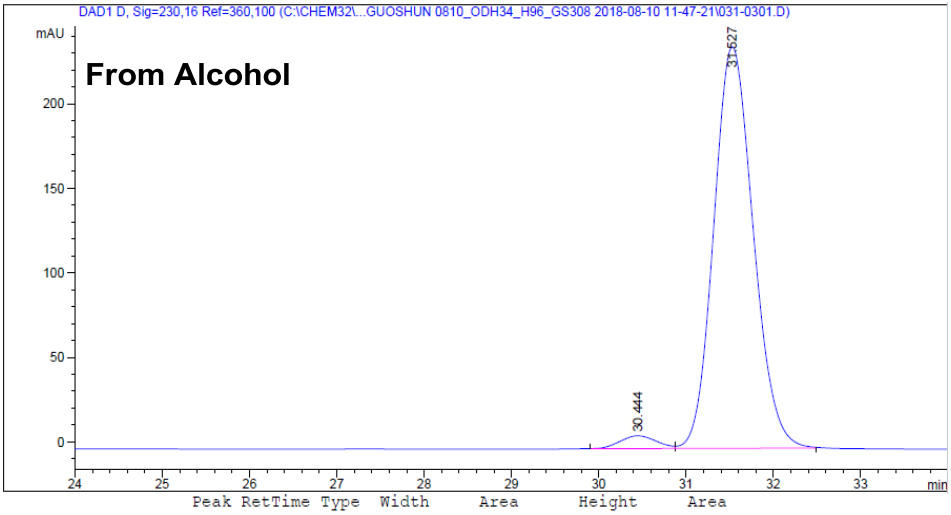
$[\alpha]_D^{34}$: –8.5 (*c* = 1.0, $CHCl_3$)

HPLC: (Two connected chiralcel OD-H columns, hexanes:*i*-PrOH = 96:4, 0.50 mL/min, 230 nm).

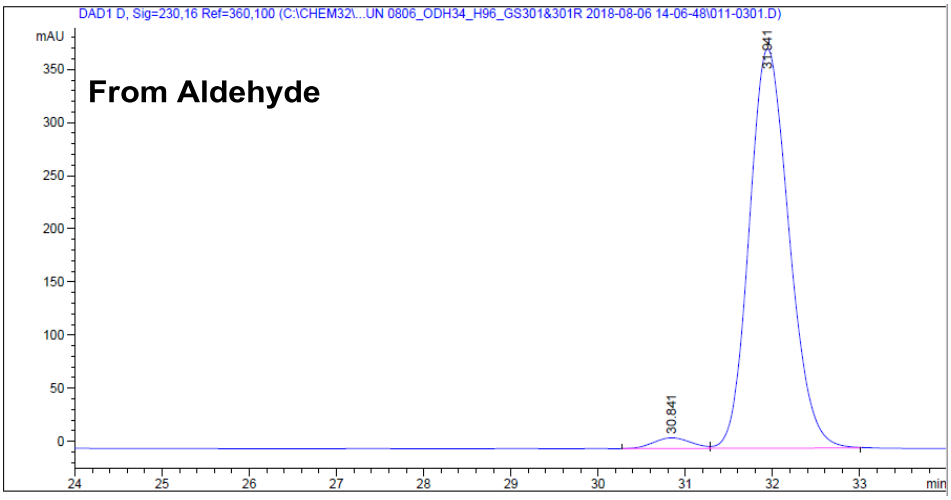

1.00
2.06
2.10
2.03
1.02
1.79
1.24
1.04
1.05
2.41
1.14
9.45
2.32
f1 (ppm)
154.8
143.1
138.2
118.8
114.4
79.3
72.5
43.8
42.0
36.9
28.5
28.1
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.916	BV	0.4809	9337.05371	301.86511	49.5989
2	32.146	VB	0.5006	9488.05957	293.89648	50.4011

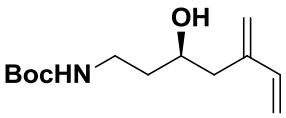


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.444	BV	0.4410	216.85736	7.55229	2.8243
2	31.527	VB	0.4864	7461.40723	237.56573	97.1757



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.841	BV	0.4529	296.17517	10.01879	2.4261
2	31.941	VB	0.4916	1.19115e4	376.00836	97.5739

(S)-tert-butyl (3-hydroxy-5-methylenehept-6-en-1-yl)carbamate (4m)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with N-tert-butoxycarbonyl-3-aminopropanol[2] (**1m**, 35.0 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 48 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 7:3) to furnish the title compound **4m** as a colorless oil in 70% yield with 93% ee (33.8 mg, 0.14 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with N-tert-butoxycarbonyl-3-aminopropanal[2] (**2m**, 34.6 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 48 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 7:3) to furnish the title compound **4m** as a colorless oil in 84% yield with 95% ee (28.0 mg, 0.116 mmol).

TLC (SiO_2) R_f = 0.3 (hexanes/ethyl acetate = 7:3).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.36 (dd, *J*=17.6, 10.7 Hz, 1H), 5.23 (d, *J*=17.6 Hz, 1H), 5.16 – 5.06 (m, 3H), 4.94 (s, 1H), 3.81 (d, *J*=2.9 Hz, 1H), 3.43 (d, *J*=6.7 Hz, 1H), 2.79 (s, 1H), 2.42 (dd, *J*=14.0, 4.6 Hz, 1H), 2.35 (dd, *J*=13.8, 8.3 Hz, 1H), 1.74 – 1.65 (m, 1H), 1.52 (ddd, *J*=13.2, 9.6, 4.7 Hz, 1H), 1.42 (s, 9H) ppm.

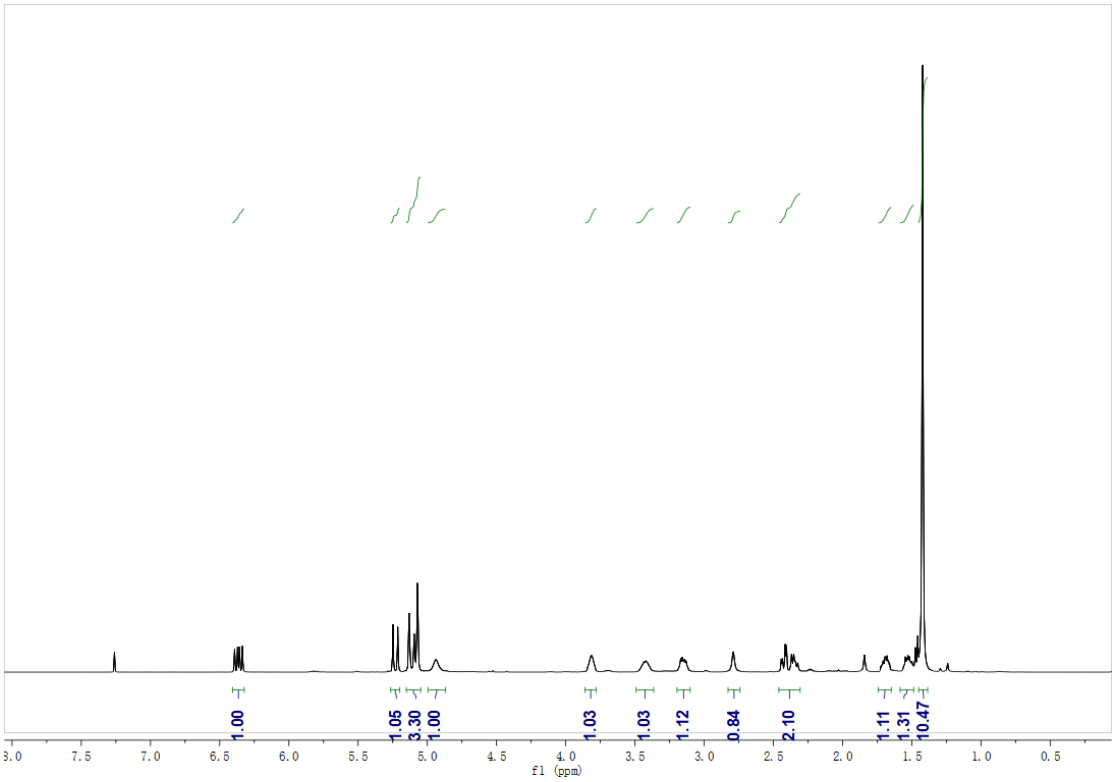
^{13}C NMR (125 MHz, $CDCl_3$): δ 156.9, 143.0, 138.6, 118.5, 114.3, 79.5, 67.6, 39. 9, 37.7, 37.3, 28.5 ppm.

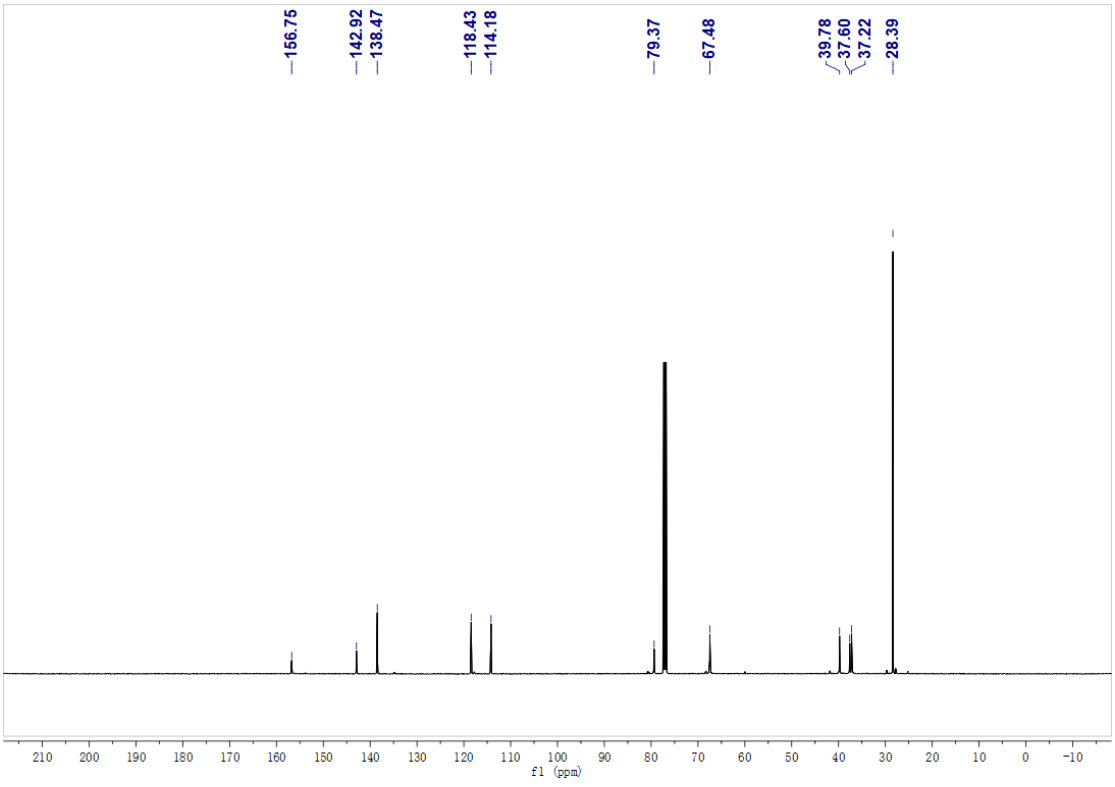
HRMS (ESI) Calculated for $C_{13}H_{23}NO_3$ $[M+Na]^+$ = 264.1576, Found 264.1575.

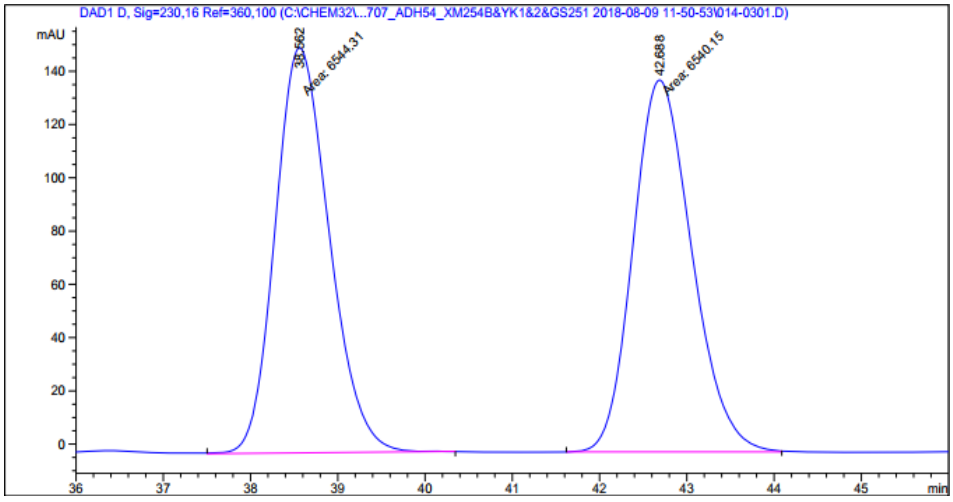
FTIR (neat) 3351, 2980, 1686, 1510, 1275, 1168, 764, 750 cm^{-1}.

$[\alpha]_D^{34}$: 141.1 (*c* = 0.4, $CHCl_3$)

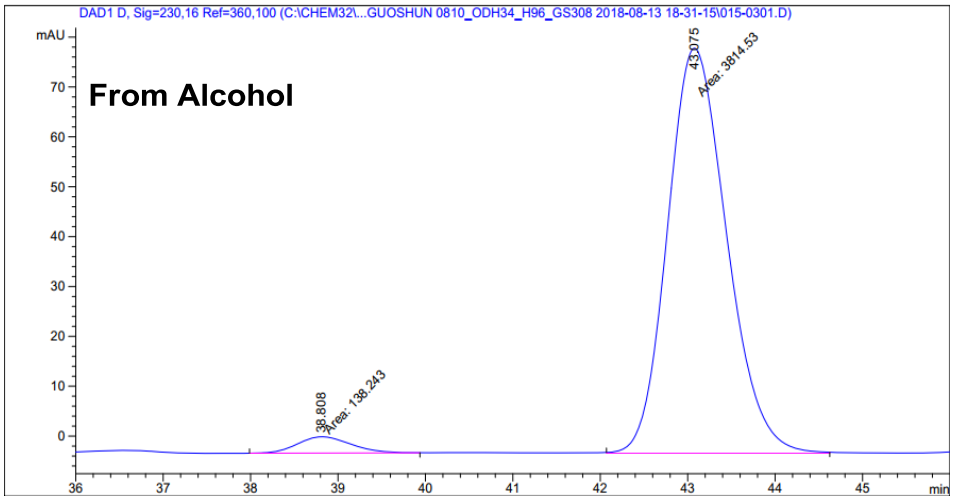
HPLC: (Two connected chiralcel AD-H columns, hexanes:*i*-PrOH = 95:5, 0.50 mL/min, 230 nm).


1.00
1.05
3.30
1.00
1.03
1.03
1.12
0.84
2.10
1.11
1.31
10.47
f1 (ppm)

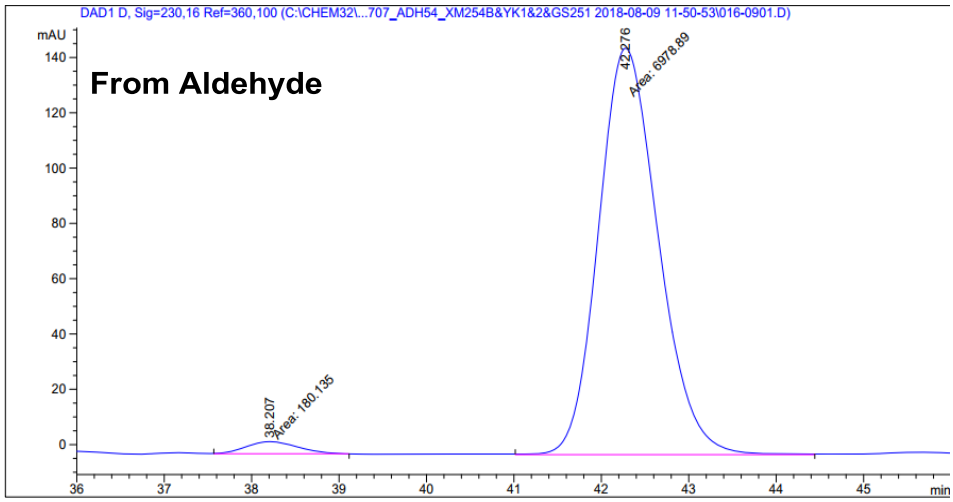

156.75
142.92
138.47
118.43
114.18
79.37
67.48
39.78
37.60
37.22
28.39
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.562	MM	0.7169	6544.30859	152.15077	50.0159
2	42.688	MM	0.7809	6540.14648	139.58435	49.9841

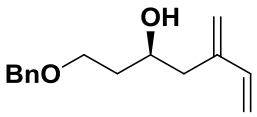


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.808	MM	0.7052	138.24260	3.26702	3.4974
2	43.075	MM	0.7827	3814.52856	81.22769	96.5026



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.207	MM	0.6838	180.13510	4.39036	2.5162
2	42.276	MM	0.7913	6978.88721	146.99161	97.4838

(*S*)-1-(benzyloxy)-5-methylenehept-6-en-3-ol (4n)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with tert-butyl 3-Benzyloxy-1-propanol (**1n**, 33.2 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 10:1) to furnish the title compound **4n** as a colorless oil in 67% yield with 94% ee (31.1 mg, 0.134 mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with 3-Benzyloxypropionaldehyde (**2n**, 32.8 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (1.0 mL, 0.2 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 60 °C for 24 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 10:1) to furnish the title compound **4n** as a colorless oil in 62% yield with 94% ee (28.8 mg, 0.124 mmol).

TLC (SiO_2) R_f = 0.5 (hexanes/ethyl acetate = 2:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29–7.20 (m, 5H), 6.31 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.25–5.14 (m, 1H), 5.03 (dd, *J* = 19.3, 7.8 Hz, 3H), 4.45 (s, 2H), 3.91 (dd, *J* = 17.0, 5.0 Hz, 1H), 3.61 (dtd, *J* = 12.8, 9.4, 5.2 Hz, 2H), 2.70 (s, 1H), 2.38–2.28 (m, 2H), 1.79–1.66 (m, 2H) ppm.

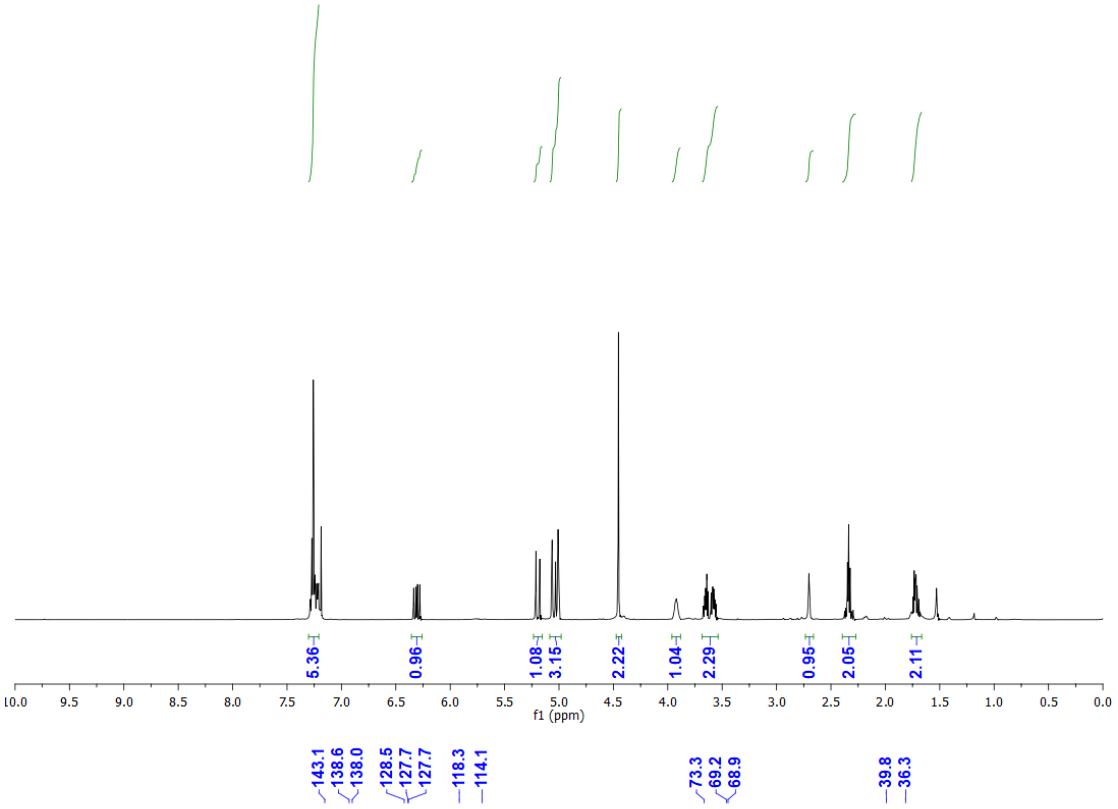
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 138.6, 138.0, 128.5, 127.7, 127.7, 118.3, 114.1, 73.3, 69.2, 68.9, 39.8, 36.3 ppm.

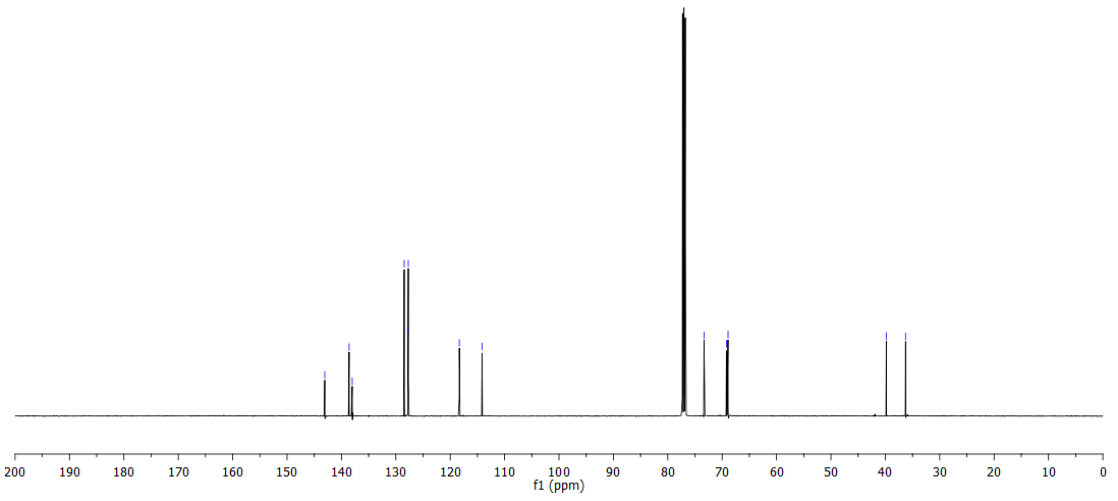
HRMS (ESI) Calculated for $C_{15}H_{20}O_2$ $[M+H]^+$ =233.1542, Found 233.1539.

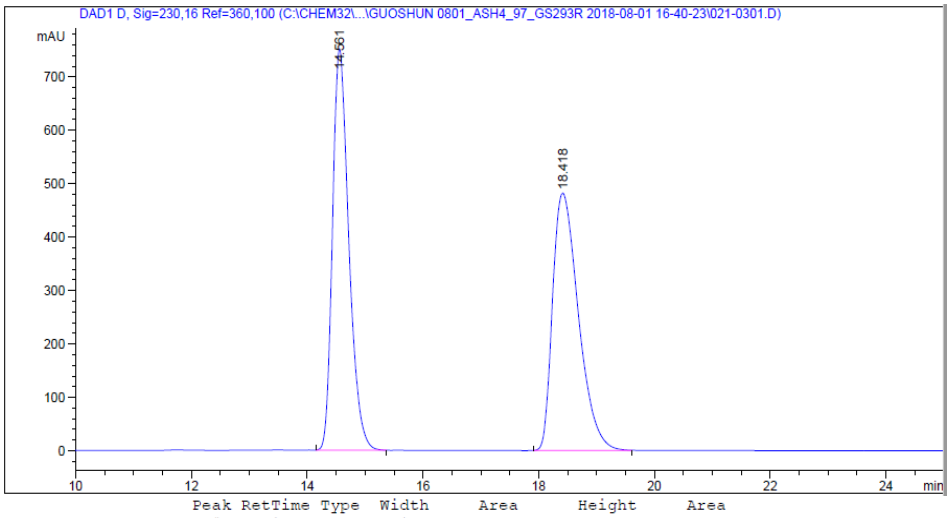
FTIR (neat) 3422, 2919, 1715, 1453, 1363, 1266, 1073, 1026, 753, 741, 698 cm^{-1}.

$[\alpha]_D^{34}$: –7.0 (*c* = 1.0, $CHCl_3$)

HPLC: (Chiralcel AS-H column, hexanes:*i*-PrOH = 97:3, 0.50 mL/min, 230 nm).


5.36
0.96
1.08
3.15
2.22
1.04
2.29
0.95
2.05
2.11
f1 (ppm)


143.1
138.6
138.0
128.5
127.7
127.7
118.3
114.1
73.3
69.2
68.9
39.8
36.3
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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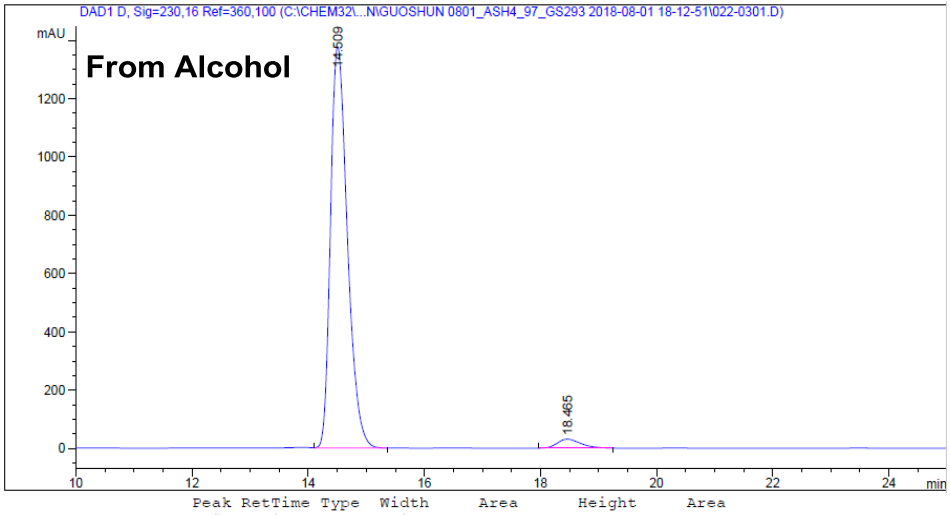
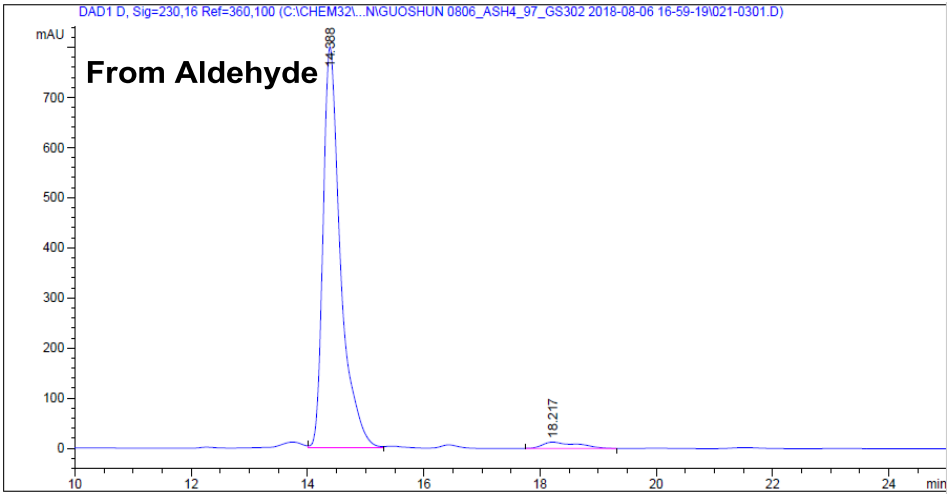
2	18.418	BB	0.4872	1.49228e4	481.97983	50.3072

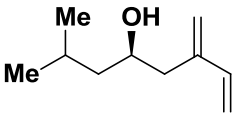


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.509	VB	0.3117	2.78025e4	1376.39832	96.9330
2	18.465	BB	0.4319	879.68134	31.10905	3.0670



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.388	VB	0.3120	1.67202e4	799.49445	96.9360
2	18.217	BB	0.5803	528.50848	12.47469	3.0640

(R)-2-methyl-6-methyleneoct-7-en-4-ol (4o)



From alcohol oxidation level: A pressure tube equipped with a magnetic stir bar was charged with isoamyl alcohol (**1o**, 17.6 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 48 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4o** as a colorless oil in 70% yield with 96% ee (25.6 mg, 0.14mmol).

From aldehyde oxidation level: A pressure tube equipped with a magnetic stir bar was charged with isovaleraldehyde (**2o**, 17.2 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 48 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound **4o** as a colorless oil in 68% yield with 96% ee (21.0 mg, 0.136 mmol).

TLC (SiO_2) R_f = 0.35 (hexanes/ethyl acetate = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.39 (dd, *J*=17.6, 10.8 Hz, 1H), 5.25 (d, *J*=17.6 Hz, 1H), 5.12 (m, 3H), 3.86 – 3.78 (m, 1H), 2.48 (dd, *J*=13.9, 3.0 Hz, 1H), 2.20 (dt, *J*=18.5, 9.2 Hz, 1H), 1.86 – 1.77 (m, 1H), 1.60 (s, 1H), 1.45 (ddd, *J*=14.1, 8.7, 5.6 Hz, 1H), 1.31 – 1.24 (m, 1H), 0.93 (dd, *J*=10.7, 6.6 Hz, 6H) ppm.

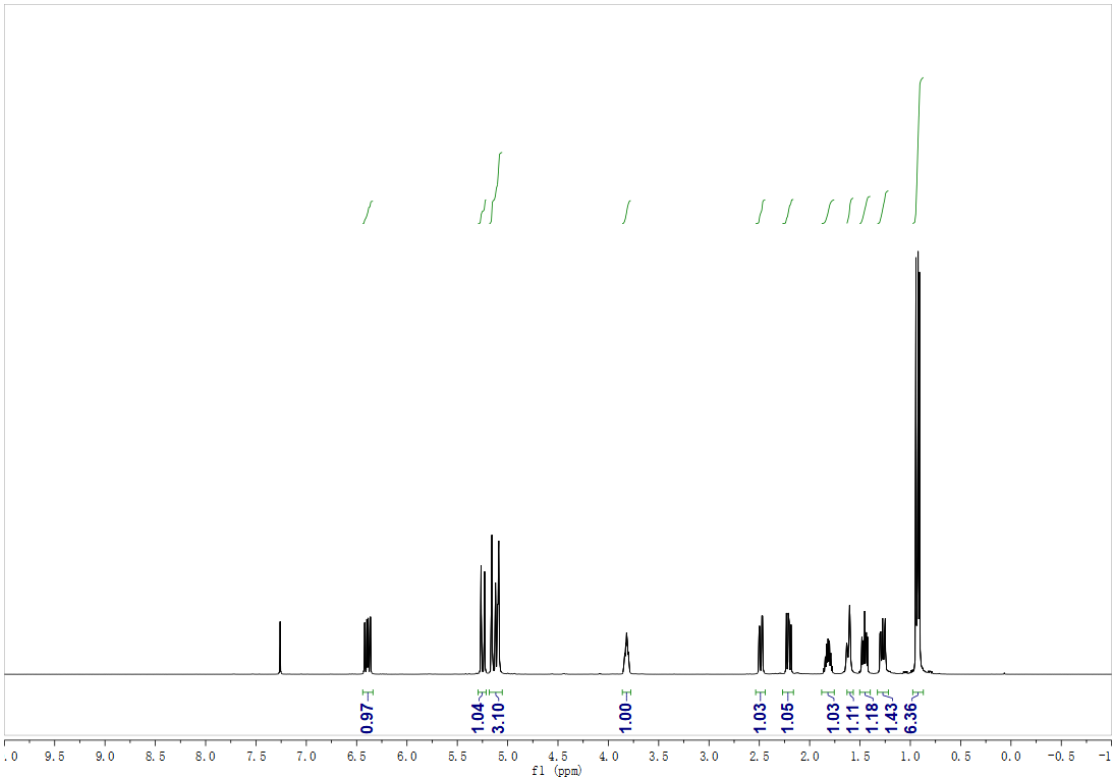
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 138.6, 118.6, 114.4, 67.7, 46.6, 40.7, 24.9, 23.6, 22.6 ppm.

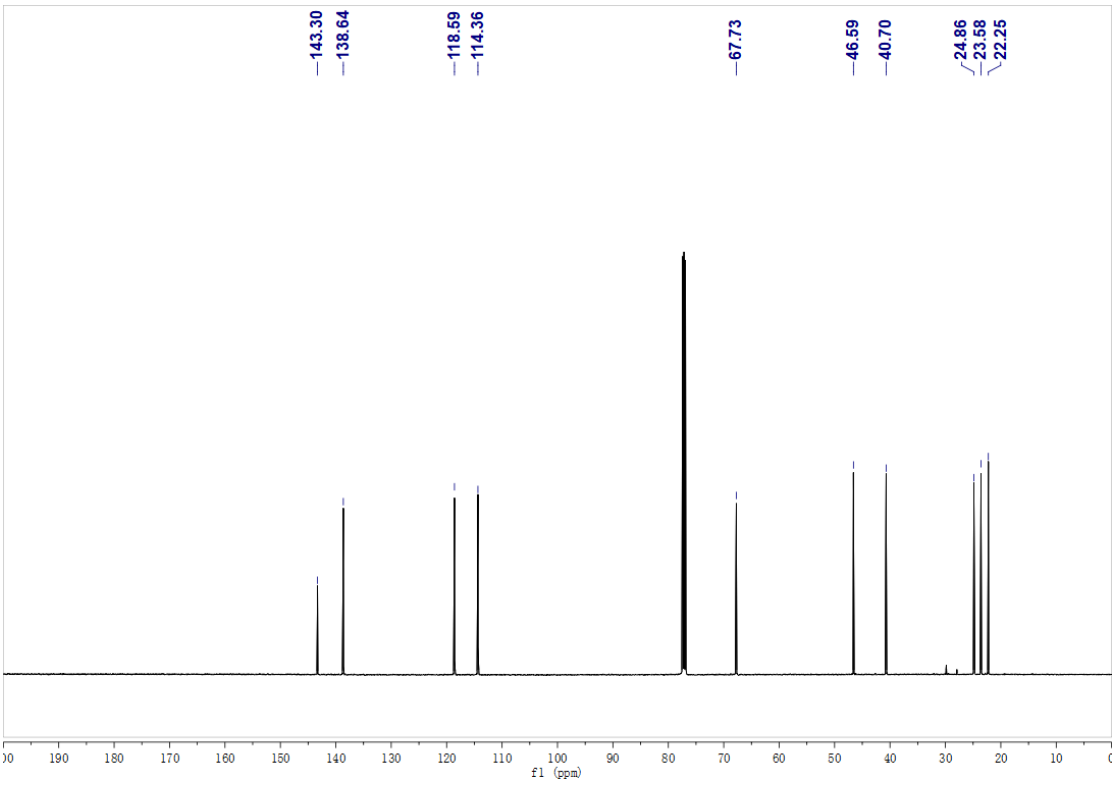
HRMS (ESI) Calculated for $C_{10}H_{18}O$ $[M-H]^+$ = 153.1279, Found 153.1270.

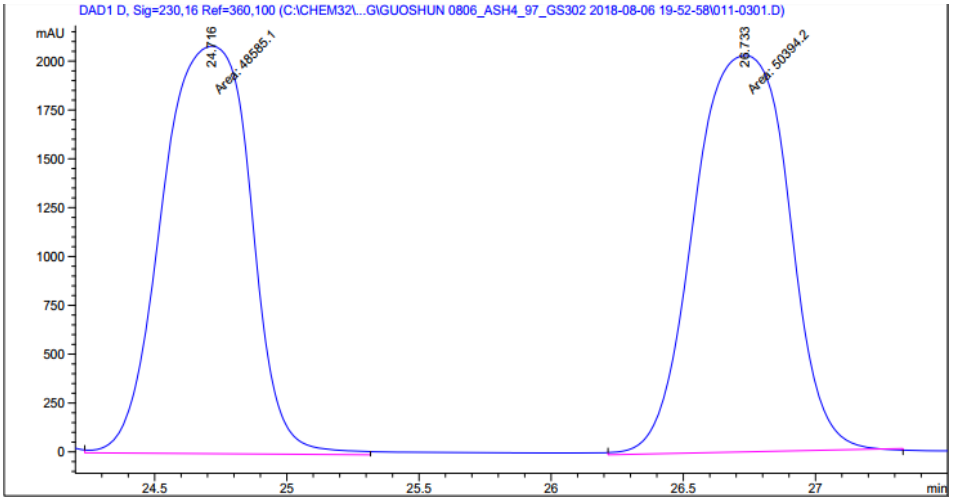
FTIR (neat) 3386, 2955, 2927, 2869, 1594, 1276, 1068, 898 cm^{-1}.

$[\alpha]_D^{34}$: 11.2 (*c* = 0.3, EtOH)

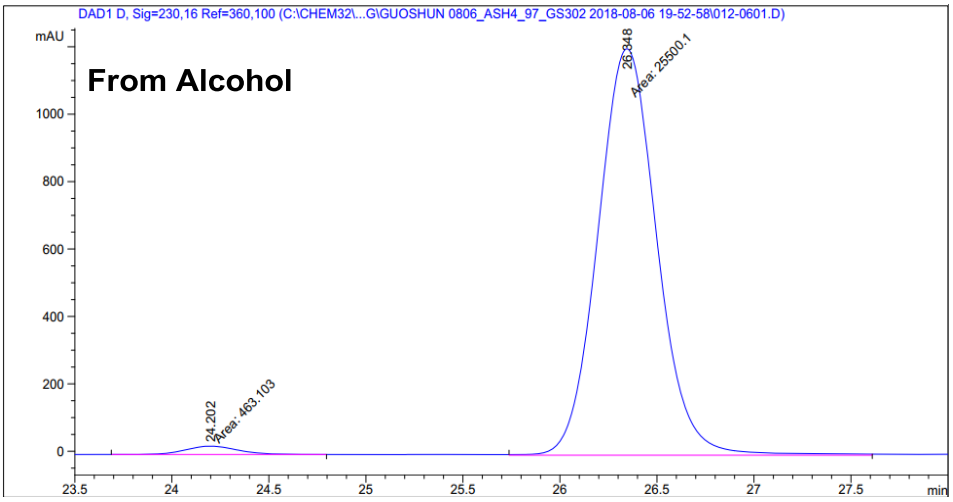
HPLC: (Two connected chiralcel OD-H columns, hexanes:*i*-PrOH = 99:1, 0.50 mL/min, 230 nm)


0.97
1.04
3.10
1.00
1.03
1.05
1.03
1.11
1.18
1.43
6.36
f1 (ppm)

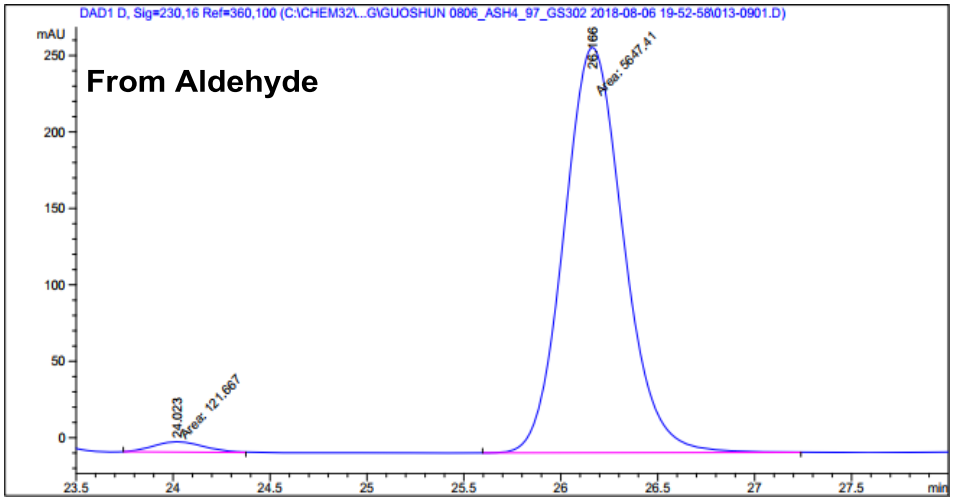

143.30
138.64
118.59
114.36
67.73
46.59
40.70
24.86
23.58
22.25
f1 (ppm)



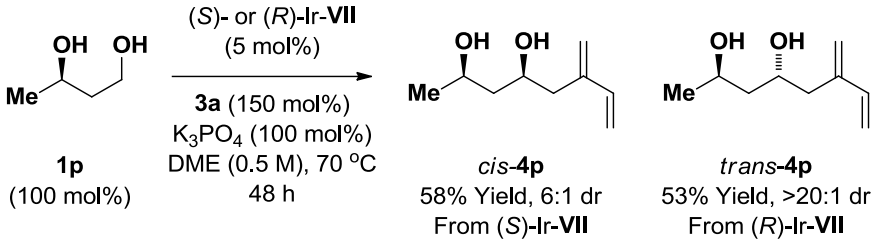
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.080	BB	0.4538	2902.17090	99.64278	50.0907
2	40.031	BB	0.5006	2891.66626	89.58588	49.9093



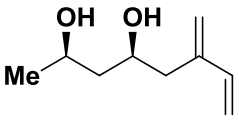
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.202	MM	0.3108	463.10339	24.83518	1.7837
2	26.348	MM	0.3523	2.55001e4	1206.50659	98.2163



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.023	MM	0.3013	121.66704	6.72936	2.1090
2	26.166	MM	0.3550	5647.41064	265.10361	97.8910



(2*R*, 4*S*)-6-methyleneoct-7-ene-2,4-diol (*cis*-4p)



A pressure tube equipped with a magnetic stir bar was charged with (R)-(−)-1, 3-Butanediol (**1p**, 18.1 mg, 0.200 mmol, 100 mol%), K_3PO_4 (18.1 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (55.1 mg, 0.3 mmol, 150 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 48 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 5:1) to furnish the title compound ***cis*-4p** as a colorless oil in 64% yield as a single diastereomer (19.98 mg, 0.128 mmol, d.r. = 6:1 from crude NMR after washing out **3a**).

TLC (SiO_2) R_f = 0.4 (hexanes/ethyl acetate = 1:1).

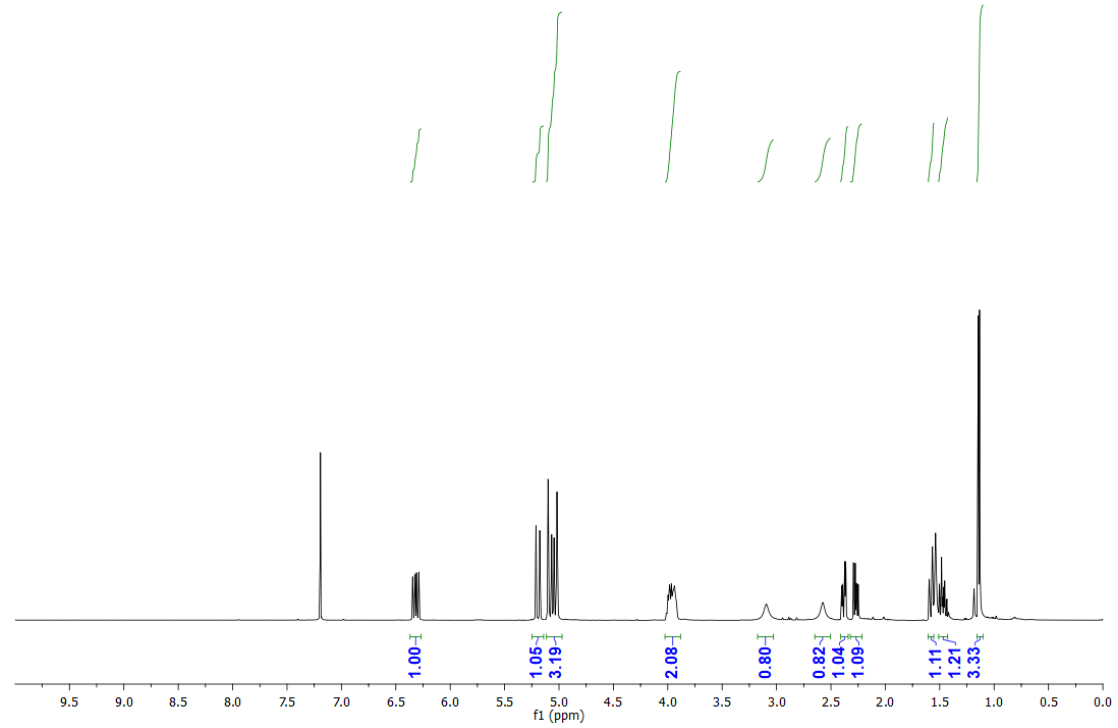
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.32 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.19 (d, *J* = 17.6 Hz, 1H), 5.06 (dd, *J* = 25.8, 14.9 Hz, 3H), 4.05–3.84 (m, 2H), 3.09 (s, 1H), 2.54 (d, *J* = 39.2 Hz, 1H), 2.43–2.31 (m, 1H), 2.27 (dd, *J* = 13.9, 8.3 Hz, 1H), 1.58 (dt, *J* = 14.4, 2.3 Hz, 1H), 1.51–1.41 (m, 1H), 1.14 (d, *J* = 6.2 Hz, 3H) ppm.

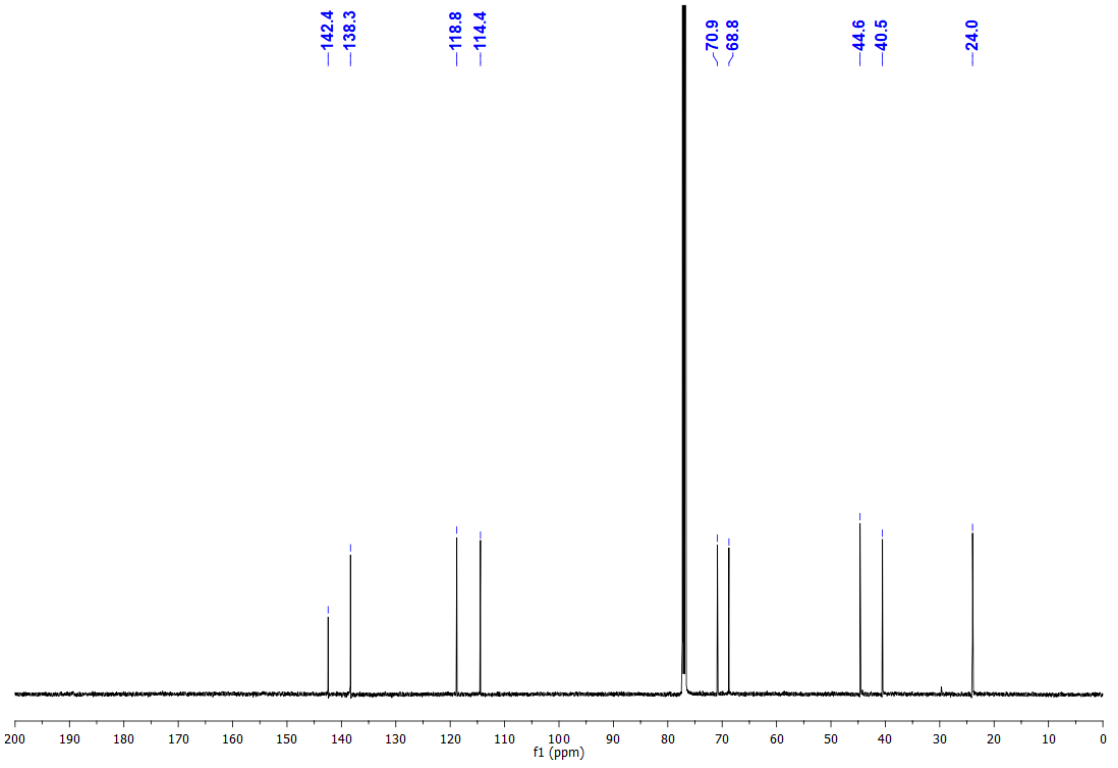
^{13}C NMR (125 MHz, $CDCl_3$): δ 142.5, 138.3, 118.8, 114.4, 70.9, 68.8, 44.6, 40.5, 23.9 ppm.

HRMS (ESI) Calculated for. $C_9H_{16}O_2$ $[M+Na]^+$ =179.1043, Found 179.1040.

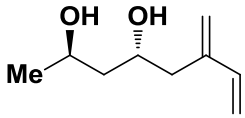
FTIR (neat) 3347, 2967, 2932, 1740, 1594, 1422, 1372, 1278, 1160, 1077, 897, 826 cm^{-1}.

$[\alpha]_D^{34}$: –12 (*c* = 0.5, $CHCl_3$)


1.00
1.05
3.19
2.08
0.80
0.82
1.04
1.09
1.11
1.21
3.33
f1 (ppm)


142.4
138.3
118.8
114.4
70.9
68.8
44.6
40.5
24.0
f1 (ppm)

(2*R*, 4*R*)-6-methyleneoct-7-ene-2,4-diol (*trans*-4p)



A pressure tube equipped with a magnetic stir bar was charged with (R)-(−)-1, 3-Butanediol (**1p**, 18.1 mg, 0.200 mmol, 100 mol%), K_3PO_4 (18.1 mg, 0.200 mmol, 100 mol%) and **(*R*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (55.1 mg, 0.3 mmol, 150 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 48 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 5:1) to furnish the title compound ***trans*-4p** as a colorless oil in 58% yield as a single diastereomer (18.1 mg, 0.116 mmol, d.r. = 20:1 from crude NMR after washing out **3a**).

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

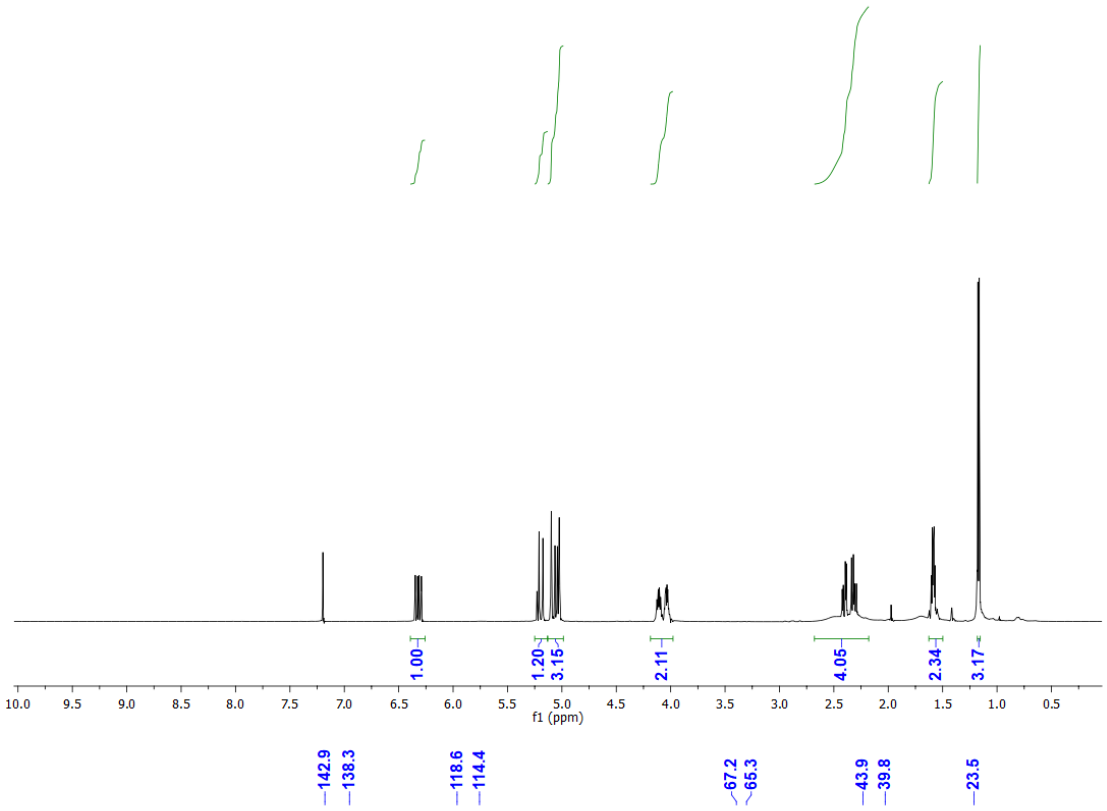
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.32 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.21 (t, *J* = 13.7 Hz, 1H), 5.06 (dd, *J* = 23.5, 12.6 Hz, 3H), 4.17–3.94 (m, 2H), 2.60–2.19 (m, 4H), 1.63–1.51 (m, 2H), 1.17 (t, *J* = 4.8 Hz, 3H) ppm.

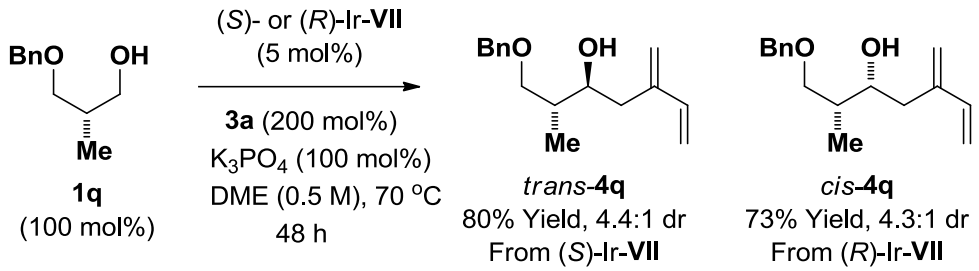
^{13}C NMR (125 MHz, $CDCl_3$): δ 142.9, 138.3, 118.6, 114.4, 67.2, 65.3, 43.9, 39.8, 23.5 ppm.

HRMS (ESI) Calculated for. $C_9H_{16}O_2$ $[M+Na]^+$ =179.1043, Found 179.1042.

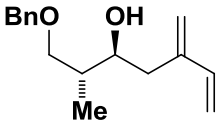
FTIR (neat) 3339, 2966, 2929, 1739, 1594, 1421, 1373, 1254, 1128, 1083, 897, 836 cm^{-1}.

$[\alpha]_D^{34}$: –208 (*c* = 0.5, $CHCl_3$)


1.00
1.20
3.15
2.11
4.05
2.34
3.17
f1 (ppm)
142.9
138.3
118.6
114.4
67.2
65.3
43.9
39.8
23.5
f1 (ppm)



(2R,3S)-1-(benzyloxy)-2-methyl-5-methylenehept-6-en-3-ol (trans-4q)



A pressure tube equipped with a magnetic stir bar was charged with (S)-3-(benzyloxy)-2-methylpropan-1-ol [3] (**1q**, 36.0 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*S*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 48 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound *trans*-**4q** as a colorless oil in 80% yield (39.4 mg, 0.16 mmol) with 4.4:1 dr as inseparable diastereomers.

TLC (SiO_2) R_f = 0.5 (hexanes/ethyl acetate = 4:1).

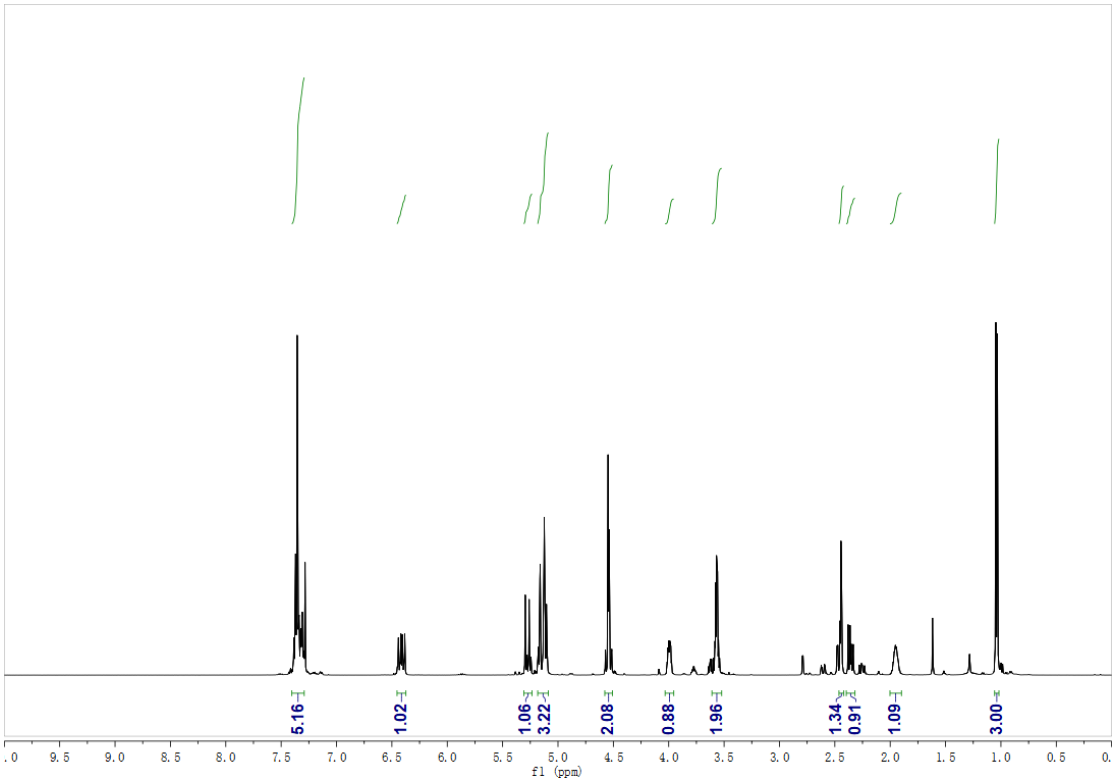
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.28 (m, 5H), 6.42 – 6.36 (m, 1H), 5.25 (d, *J*=17.6 Hz, 1H), 5.16 – 5.07 (m, 3H), 4.56 – 4.49 (m, 2H), 3.97 (tt, *J*=7.6, 3.6 Hz, 1H), 3.57 – 3.51 (m, 2H), 2.43 (dd, *J*=10.4, 6.5 Hz, 1H), 2.33 (dd, *J*=14.0, 8.8 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.01 (d, *J*=7.0 Hz, 3H) ppm.

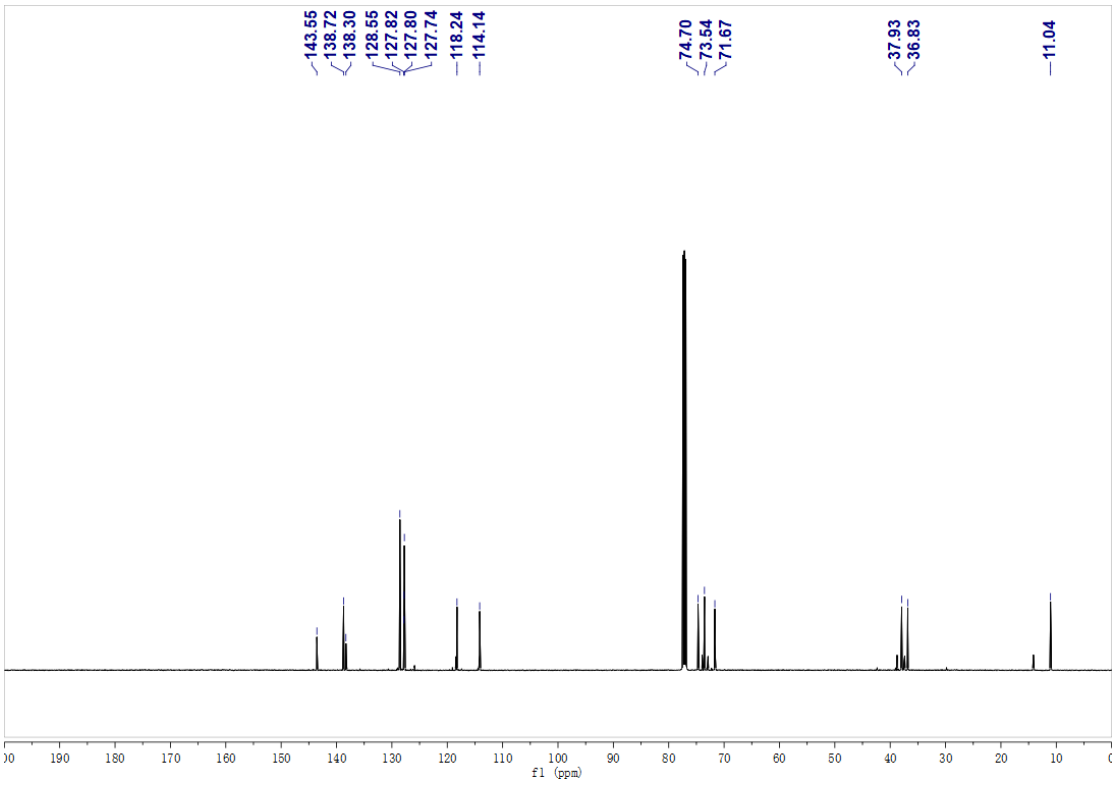
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.6, 138.7, 138.3, 128.6, 127.8, 127.8, 127.7, 118.2, 114.14, 74.7, 73.5, 71.7, 37.9, 36.8, 11.0 ppm.

HRMS (ESI) Calculated for $C_{16}H_{22}O_2$ $[M]^+$ = 246.1620, Found 246.1616.

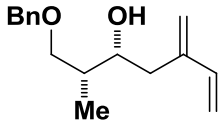
FTIR (neat) 3467, 2857, 1594, 1275, 1260, 1092, 903, 763 cm^{-1}.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 96:4, 0.50 mL/min, 230 nm).


5.16
1.02
1.06
3.22
2.08
0.88
1.96
1.34
0.91
1.09
3.00
f1 (ppm)


143.55
138.72
138.30
128.55
127.82
127.80
127.74
118.24
114.14
74.70
73.54
71.67
37.93
36.83
11.04
f1 (ppm)

(2R,3R)-1-(benzyloxy)-2-methyl-5-methylenehept-6-en-3-ol (cis-4q)



A pressure tube equipped with a magnetic stir bar was charged with (S)-3-(benzyloxy)-2-methylpropan-1-ol (**1q**, 36.0 mg, 0.200 mmol, 100 mol%), K_3PO_4 (42.5 mg, 0.200 mmol, 100 mol%) and **(*R*)-Ir-VII** (11.5 mg, 0.01 mmol, 5 mol%). The reaction vessel was placed under an atmosphere of argon, and DME (0.40 mL, 0.5 M), isopropanol (36 mg, 0.60 mmol, 300 mol%), isoprenyl *tert*-butoxy carbonate **3a** (73.5 mg, 0.40 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was stirred at 70 °C for 48 h. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 20:1) to furnish the title compound cis-**4q** as a colorless oil in 73% yield with 4.3:1 dr as inseparable diastereomers (36.0 mg, 0.146 mmol).

TLC (SiO_2) R_f = 0.5 (hexanes/ethyl acetate = 4:1).

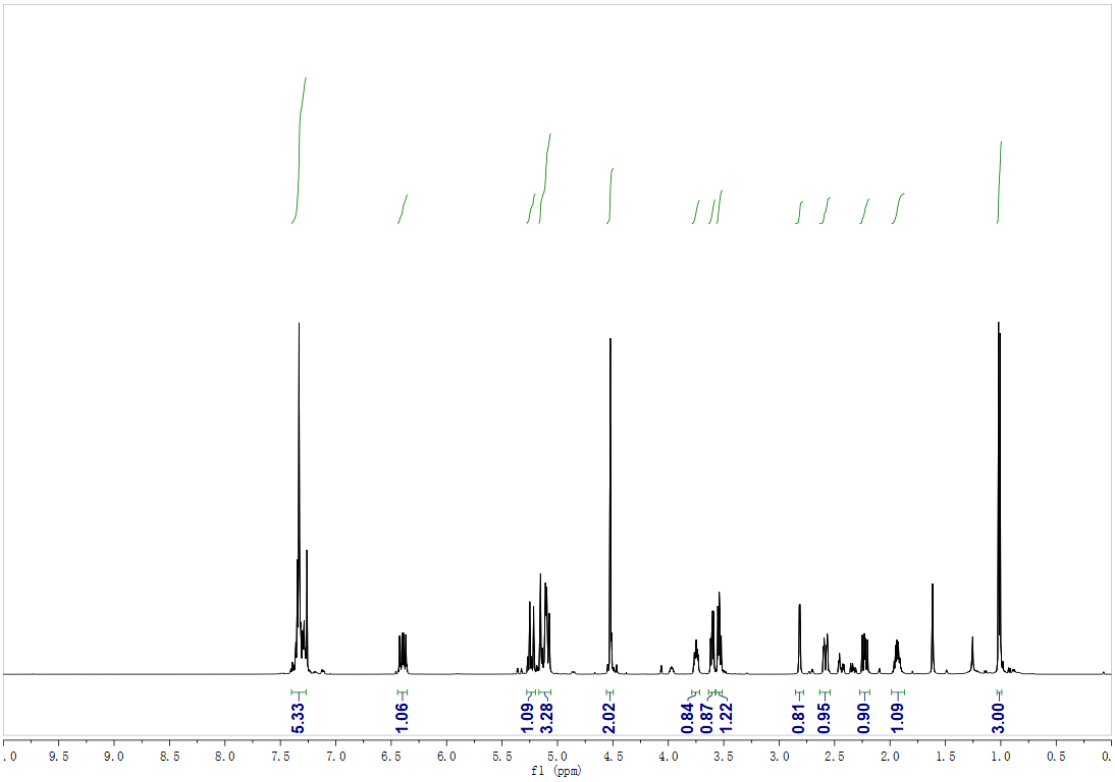
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.28 (m, 5H), 6.43 – 6.36 (m, 1H), 5.23 (d, *J*=17.6 Hz, 1H), 5.16 – 5.07 (m, 3H), 4.52 (s, 2H), 3.75 (ddt, *J*=9.6, 6.4, 3.2 Hz, 1H), 3.60 (dd, *J*=9.3, 5.0 Hz, 1H), 3.57 – 3.51 (m, 1H), 2.81 (d, *J*=3.3 Hz, 1H), 2.58 (dd, *J*=14.0, 2.4 Hz, 1H), 2.22 (dt, *J*=18.9, 9.4 Hz, 1H), 1.94 (dt, *J*=11.7, 6.6 Hz, 1H), 1.01 (t, *J*=6.2 Hz, 3H) ppm.

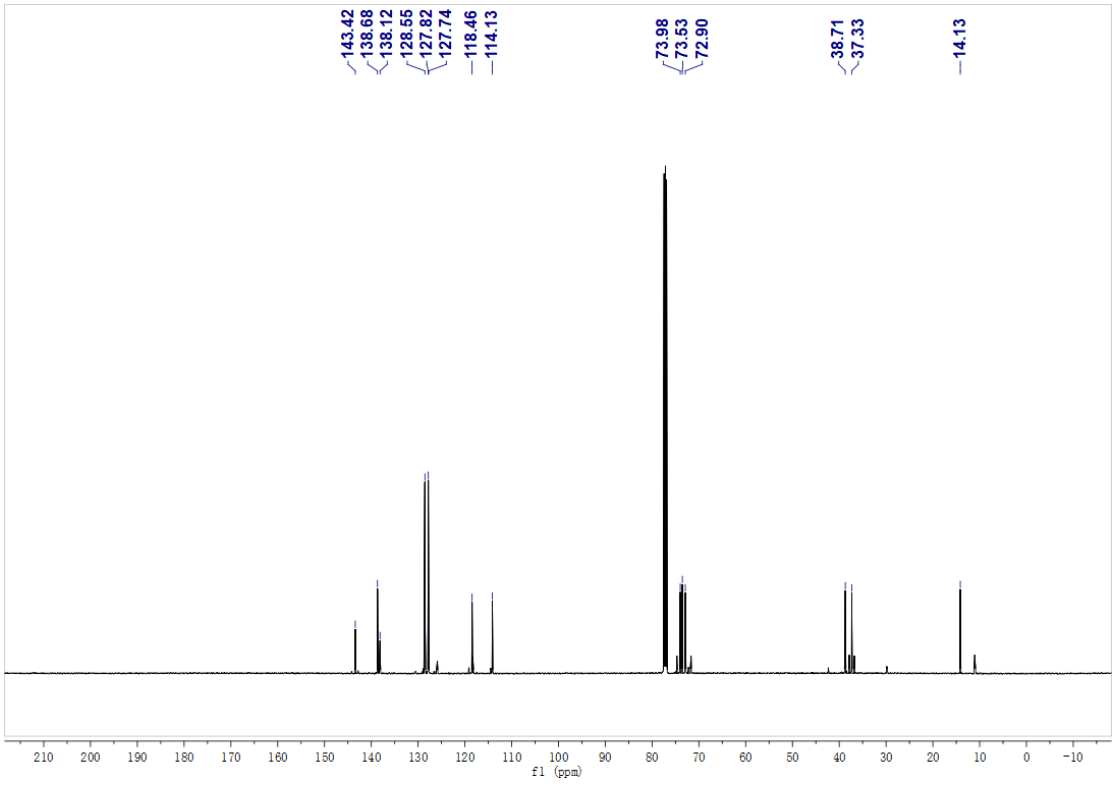
^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 138.7, 138.1, 128.6, 127.8, 127.7, 118.5, 114.1, 74.0, 73.5, 72.9, 38.7, 37.3, 14.1 ppm.

HRMS (ESI) Calculated for $C_{16}H_{22}O_2$ $[M]^+$ = 246.1620, Found 246.1616.

FTIR (neat) 3467, 2857, 1594, 1275, 1260, 1092, 903, 763 cm^{-1}.

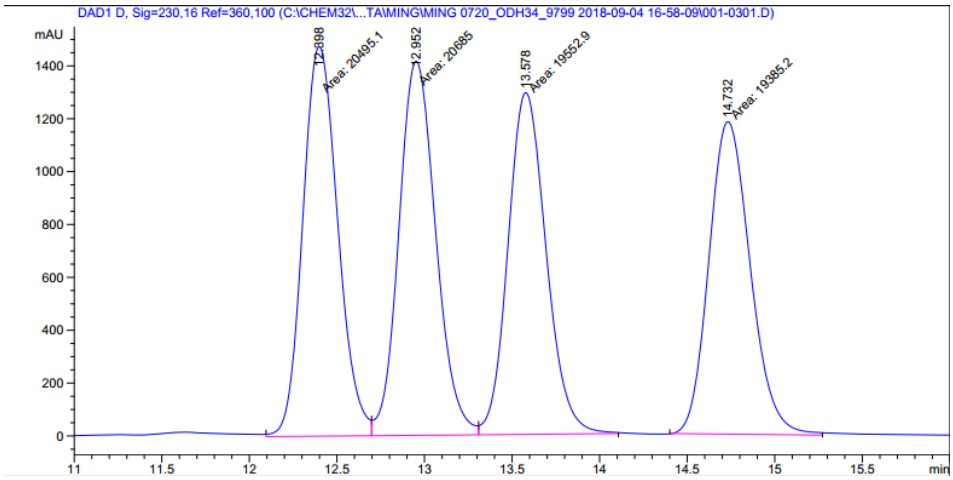
HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 96:4, 0.50 mL/min, 230 nm).


5.33
1.06
1.09
3.28
2.02
0.84
0.87
1.22
0.81
0.95
0.90
1.09
3.00
f1 (ppm)


143.42
138.68
138.12
128.55
127.82
127.74
118.46
114.13
73.98
73.53
72.90
38.71
37.33
14.13
f1 (ppm)

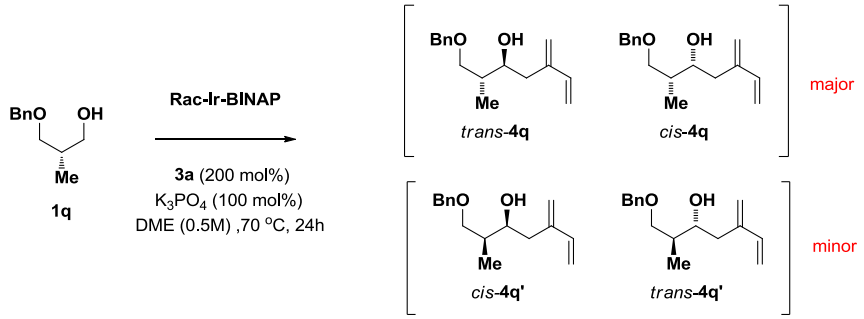
Determination of Diastereomeric Ratio and Stereochemistry Confirmation

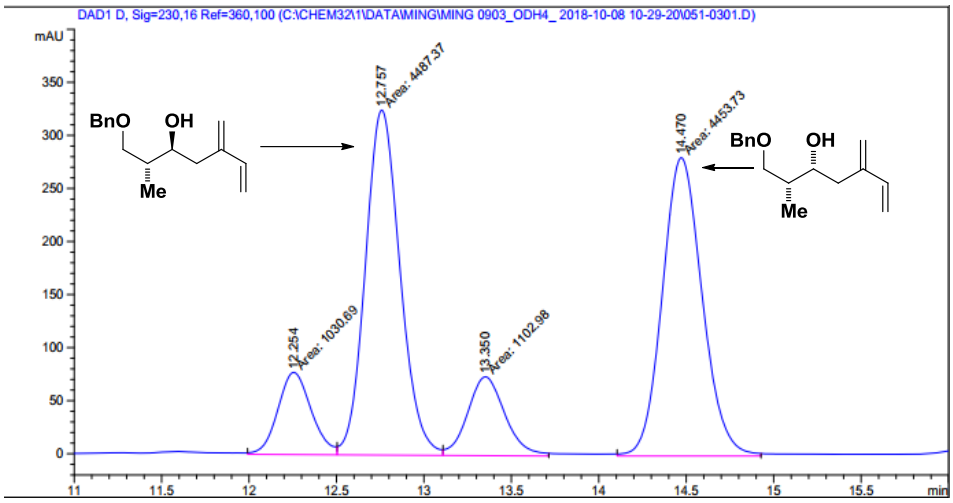
Racemic Sample (stereoisomeric mixture (1:1:1:1 dr))



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.398	MF	0.2316	2.04951e4	1474.73865	25.5811
2	12.952	MF	0.2435	2.06850e4	1415.84546	25.8182
3	13.578	FM	0.2520	1.95529e4	1293.20166	24.4051
4	14.732	MM	0.2733	1.93852e4	1182.21704	24.1957

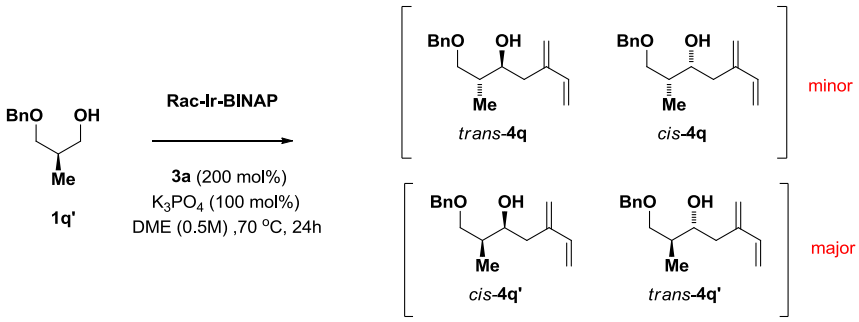
Authentic Sample Derived from an Isoprenylation of the Enantioenriched (*S*)-Alcohol (1q) with Rac-Ir-BINAP.

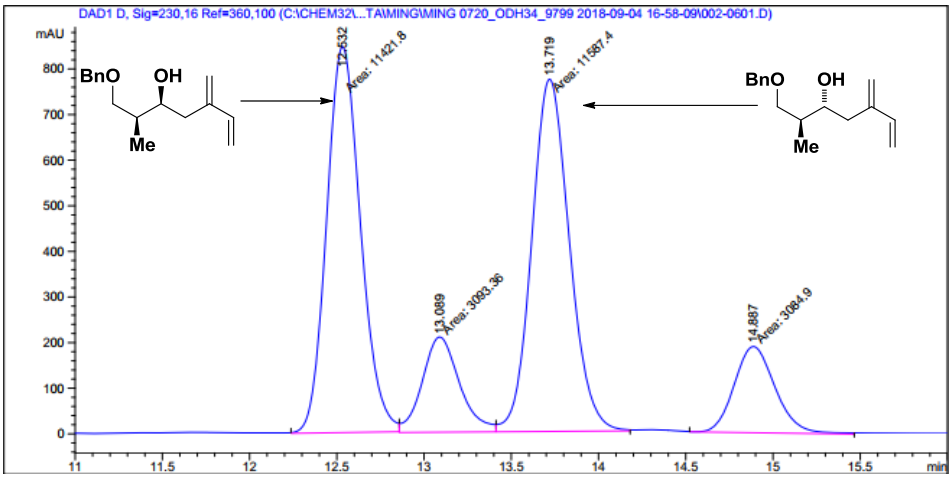




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.254	MF	0.2218	1030.68750	77.43644	9.3066
2	12.757	MF	0.2299	4487.36768	325.29260	40.5188
3	13.350	FM	0.2473	1102.98291	74.32732	9.9594
4	14.470	MM	0.2639	4453.72998	281.25705	40.2151

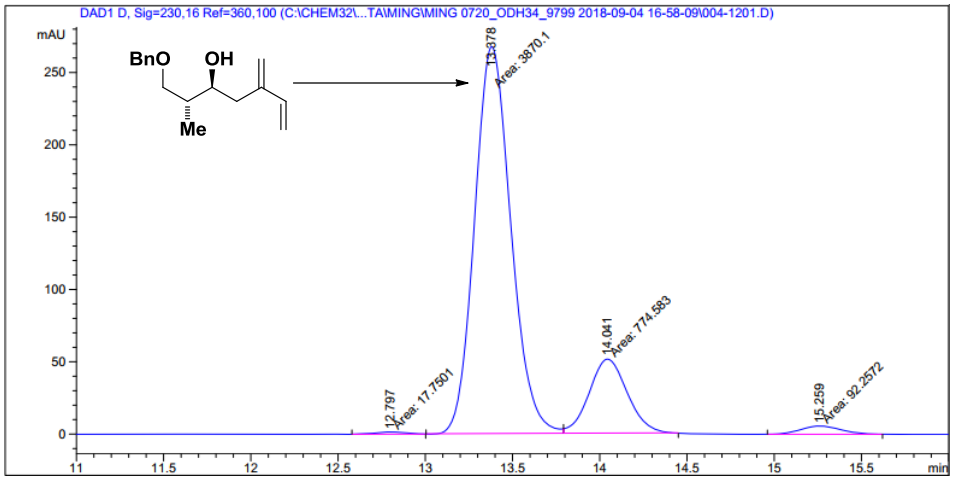
Authentic Sample Derived from an Isoprenylation of the Enantioenriched (*R*)-Alcohol (1q') with Rac-Ir-BINAP.





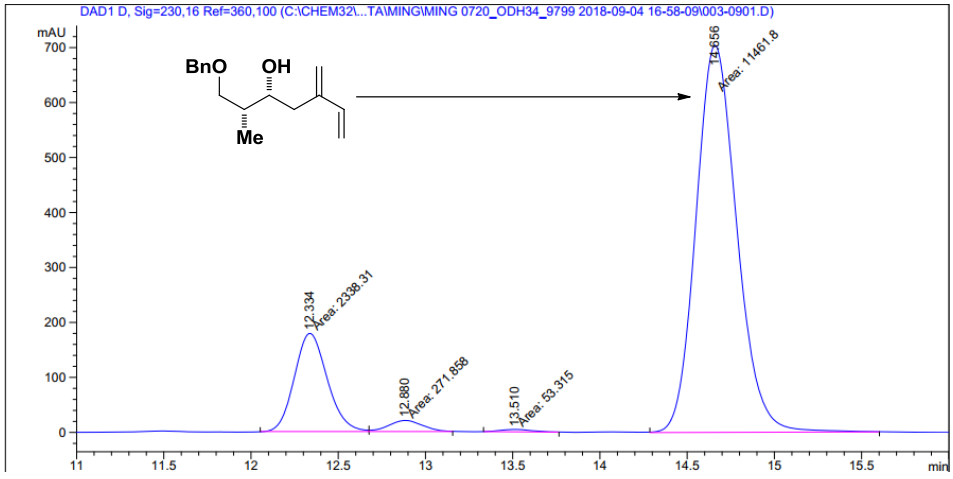
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.532	MM	0.2248	1.14218e4	846.63275	39.1326
2	13.089	MF	0.2468	3093.36011	208.93520	10.5983
3	13.719	FM	0.2499	1.15874e4	772.70355	39.6999
4	14.887	MM	0.2718	3084.90210	189.13344	10.5693

Trans-4q (4.4:1 dr) : isoprenylation of the Enantioenriched (*S*)-Alcohol (1q) with S-Ir-VII.

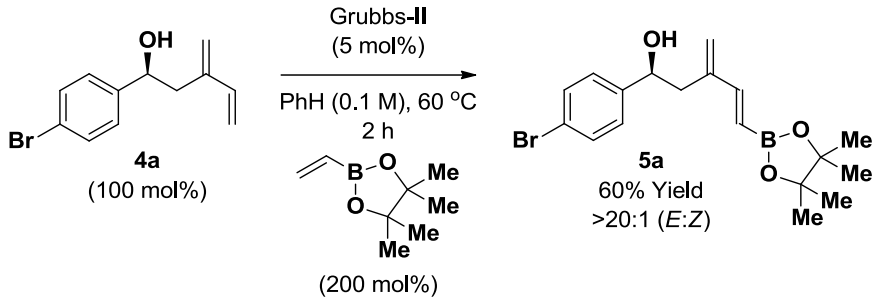


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.797	MM	0.2008	17.75014	1.47354	0.3733
2	13.378	MF	0.2410	3870.09546	267.61871	81.3954
3	14.041	FM	0.2524	774.58289	51.14556	16.2909
4	15.259	MM	0.2689	92.25718	5.71847	1.9403

Cis-4q (4.3:1 dr) : isoprenylation of the Enantioenriched (*S*)-Alcohol (1q) with R-Ir-VII.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.334	MF	0.2181	2338.30786	178.70442	16.5541
2	12.880	FM	0.2239	271.85754	20.23895	1.9246
3	13.510	MM	0.2071	53.31503	4.28962	0.3774
4	14.656	MM	0.2712	1.14618e4	704.49060	81.1439



(S,E)-1-(4-bromophenyl)-3-methylene-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-ol (5a)

An oven-dried tube equipped with a magnetic stir bar was charged with Grubbs-II catalyst (6.4 mg, 0.0075 mmol, 5 mol%) and Benzene (1 mL). Bubbled Argon through the solution for 10min and then 2-Vinyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (46.2 mg, 0.300 mmol, 200 mol%) was added. Let the reaction stir at rt for 5 mins and then a solution of **4a** (38mg, 0.15 mmol, 100 mol%) was added by syringe. Then the reaction was allowed to heated up to 60 °C for 2 hours. The reaction was allowed to cool to ambient temperature and the volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 9:1) to furnish the title compound **5a** as a brown oil in 60% yield (34 mg, 0.09 mmol, E:Z>20:1).

TLC (SiO_2) R_f = 0.3 (hexanes/ethyl acetate = 4:1).

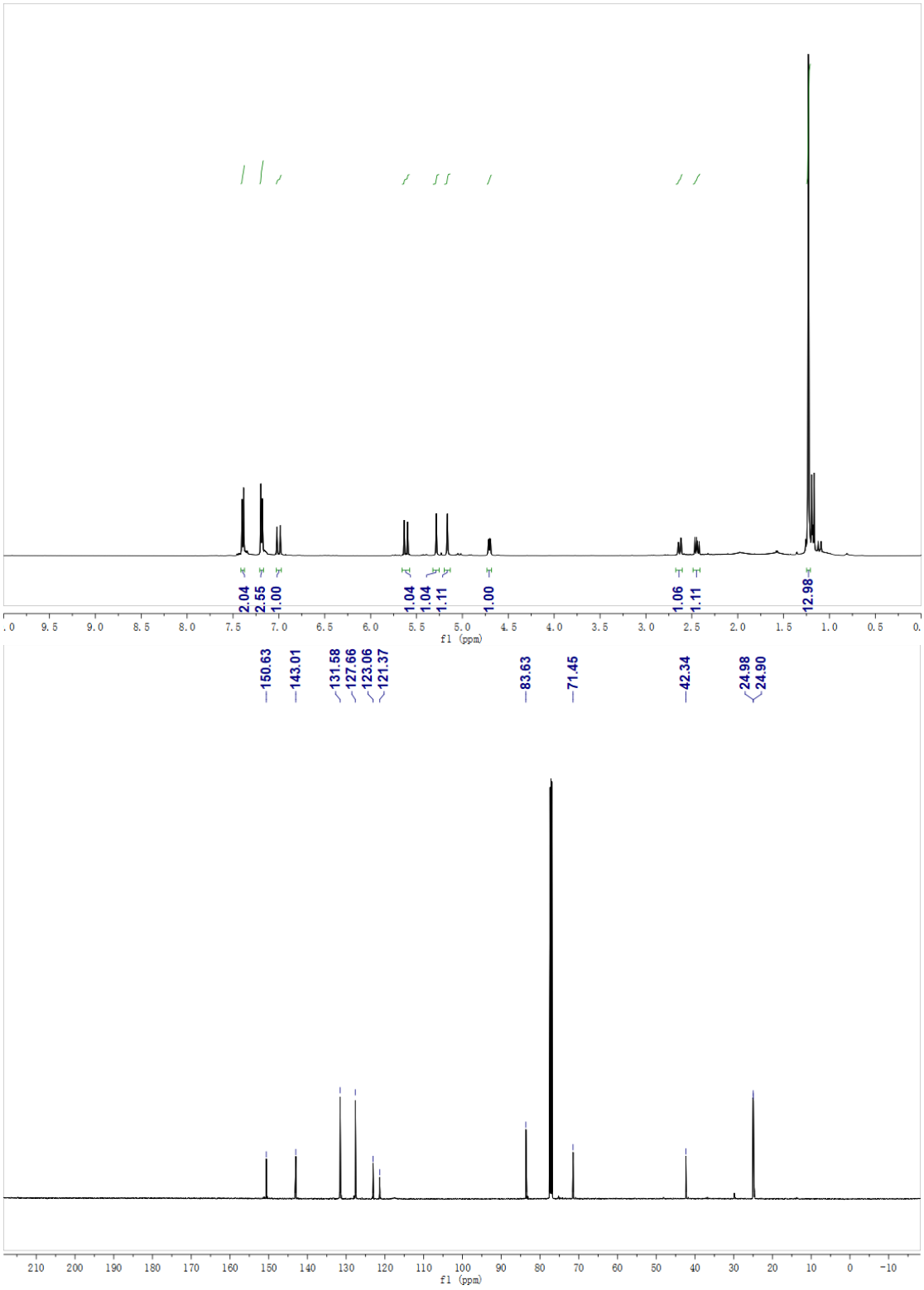
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J*=8.4 Hz, 2H), 7.19 (d, *J*=8.2 Hz, 2H), 7.00 (d, *J*=18.5 Hz, 1H), 5.62 (d, *J*=18.5 Hz, 1H), 5.28 (s, 1H), 5.16 (s, 1H), 4.71 (dd, *J*=9.2, 4.1 Hz, 1H), 2.63 (dt, *J*=10.1, 5.1 Hz, 1H), 2.44 (dd, *J*=13.9, 9.3 Hz, 1H), 1.23 (s, 12H) ppm.

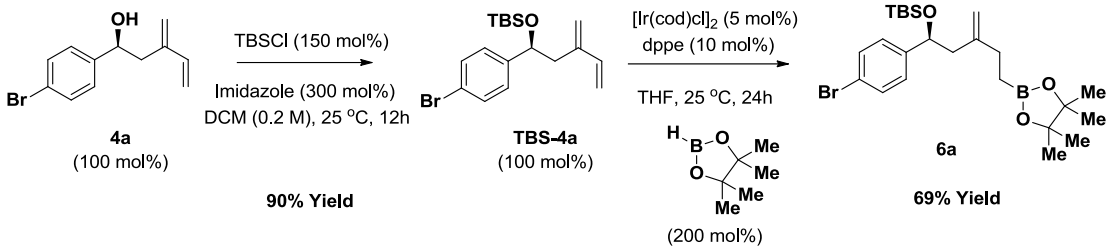
^{13}C NMR (125 MHz, $CDCl_3$): δ 150.6, 143.0, 131.6, 127.7, 123.1, 121.4, 83.6, 71.5, 42.3, 25.0, 24.9 ppm.

HRMS (ESI) Calculated for $C_{18}H_{24}BBrO_3$ $[M-H_2O]^+$ = 362.0876, Found 362.0877.

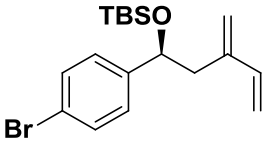
FTIR (neat) 3450, 3008, 1487, 1275, 1260, 904, 749, 667 cm^{-1}.

$[\alpha]_D^{34}$: -33.0 (*c* = 0.9, $CHCl_3$)


2.04
2.55
1.00
1.04
1.04
1.11
1.00
1.06
1.11
12.98
f1 (ppm)
150.63
143.01
131.58
127.66
123.06
121.37
83.63
71.45
42.34
24.98
24.90
f1 (ppm)



(S)-((1-(4-bromophenyl)-3-methylenepent-4-en-1-yl)oxy)(tert-butyl)dimethylsilane (TBS-4a)



An oven-dried tube equipped with a magnetic stir bar was charged with **4a** (202.5mg, 0.800 mmol, 100 mol%) and Imidazole (163.4mg, 2.40 mmol, 300 mol%). DCM (4 mL) was added followed by TBSCl (181mg, 1.20 mmol, 150 mol%). The reaction mixture was allowed to stir at room temperature for 12h. The volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 99:1) to furnish the title compound **TBS-4a** as a colorless oil in 90% yield (264.5 mg, 0.72 mmol).

TLC (SiO_2) R_f = 0.5 (hexanes/ethyl acetate = 98:2).

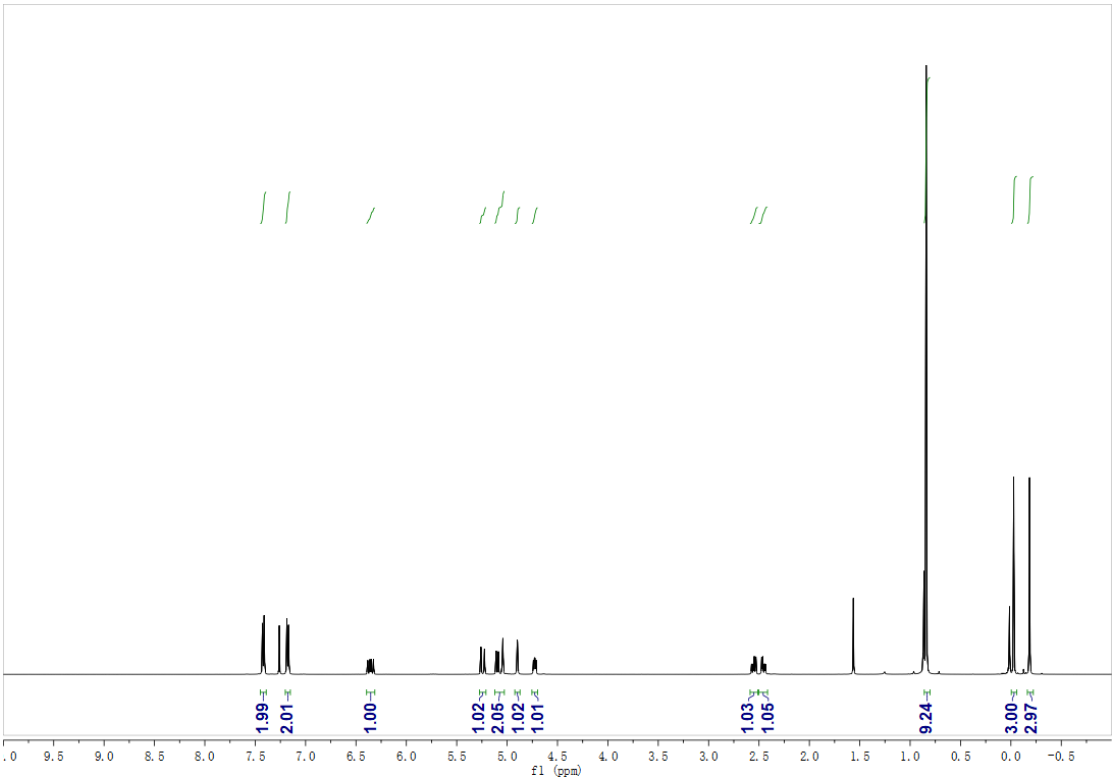
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J*=8.4 Hz, 2H), 7.18 (d, *J*=8.3 Hz, 2H), 6.35 (dd, *J*=17.6, 10.8 Hz, 1H), 5.24 (d, *J*=17.6 Hz, 1H), 5.16 – 5.02 (m, 2H), 4.90 (s, 1H), 4.71 (dt, *J*=36.3, 18.1 Hz, 1H), 2.55 (dd, *J*=13.6, 7.9 Hz, 1H), 2.45 (dd, *J*=13.6, 4.9 Hz, 1H), 0.84 (s, 9H), -0.03 (s, 3H), -0.19 (s, 3H) ppm.

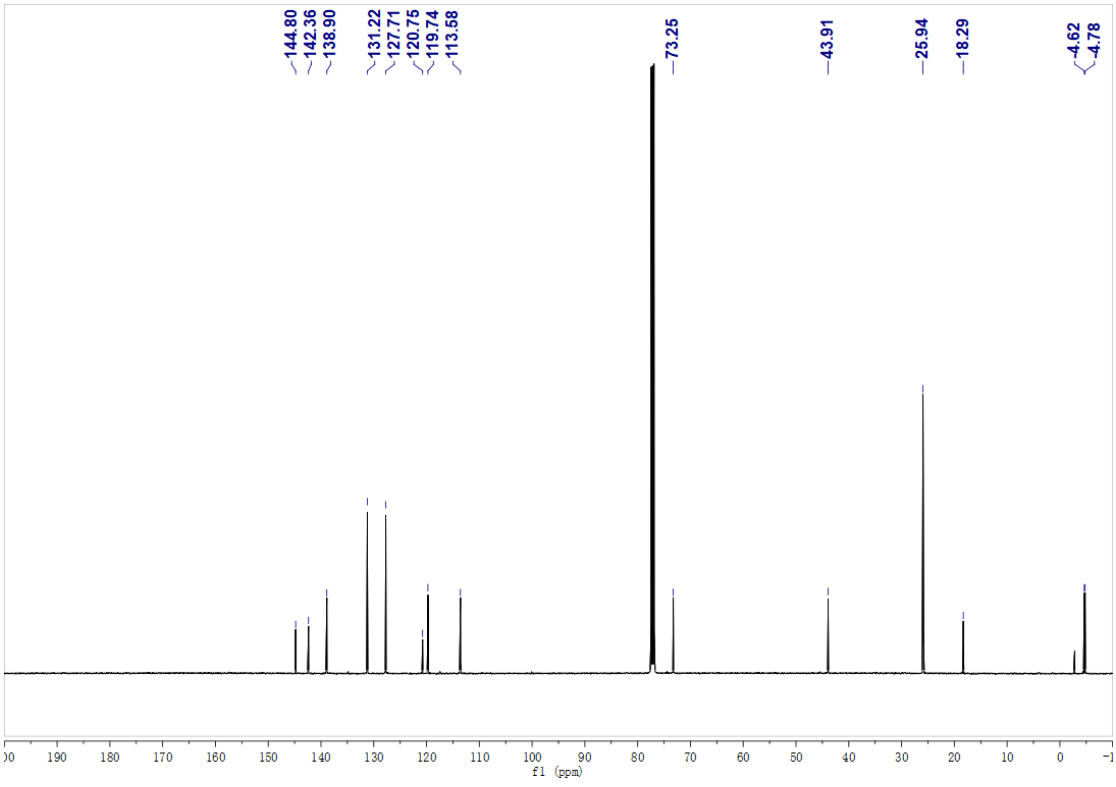
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.8, 142.4, 138.9, 131.2, 127.7, 120.8, 119.7, 113.6, 73.3, 43.9, 25.9, 18.3, -4.6, -4.8 ppm.

HRMS (ESI) Calculated for $C_{18}H_{27}BrOSi$ $[M]^+$ = 366.1015, Found 366.1005.

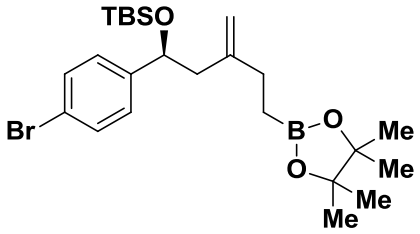
FTIR (neat) 3006, 2360, 1471, 1275, 1260, 1081, 764, 750 cm^{-1}.

$[\alpha]_D^{34}$: -48.0 (*c* = 1.0, $CHCl_3$)


1.99
2.01
1.00
1.02
2.05
1.02
1.01
1.03
1.05
9.24
3.00
2.97
f1 (ppm)


144.80
142.36
138.90
131.22
127.71
120.75
119.74
113.58
73.25
43.91
25.94
18.29
4.62
4.78
f1 (ppm)

(S)-((1-(4-bromophenyl)-3-methylene-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)(tert-butyl)dimethylsilane (6a)

/ 

An oven-dried tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (6.7mg, 0.01 mmol, 5 mmol%), dppe (8.0mg, 0.02 mmol, 10 mmol%), Pinacol Borane (51.2mg, 0.400 mmol, 200 mol%) and THF (0.4 mL). Let the mixture stir at room temperature for 10 mins and then **4a** (50.6mg, 0.200 mmol, 100 mol%) in THF (0.2 mL) was added dropwise. The reaction mixture was allowed to stir at room temperature for 12h. The volatiles were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2: hexanes:ethyl acetate = 98:2) to furnish the title compound **6a** as a colorless oil in 69% yield (68.5 mg, 0.138 mmol).

TLC (SiO_2) R_f = 0.5 (hexanes/ethyl acetate = 9:1).

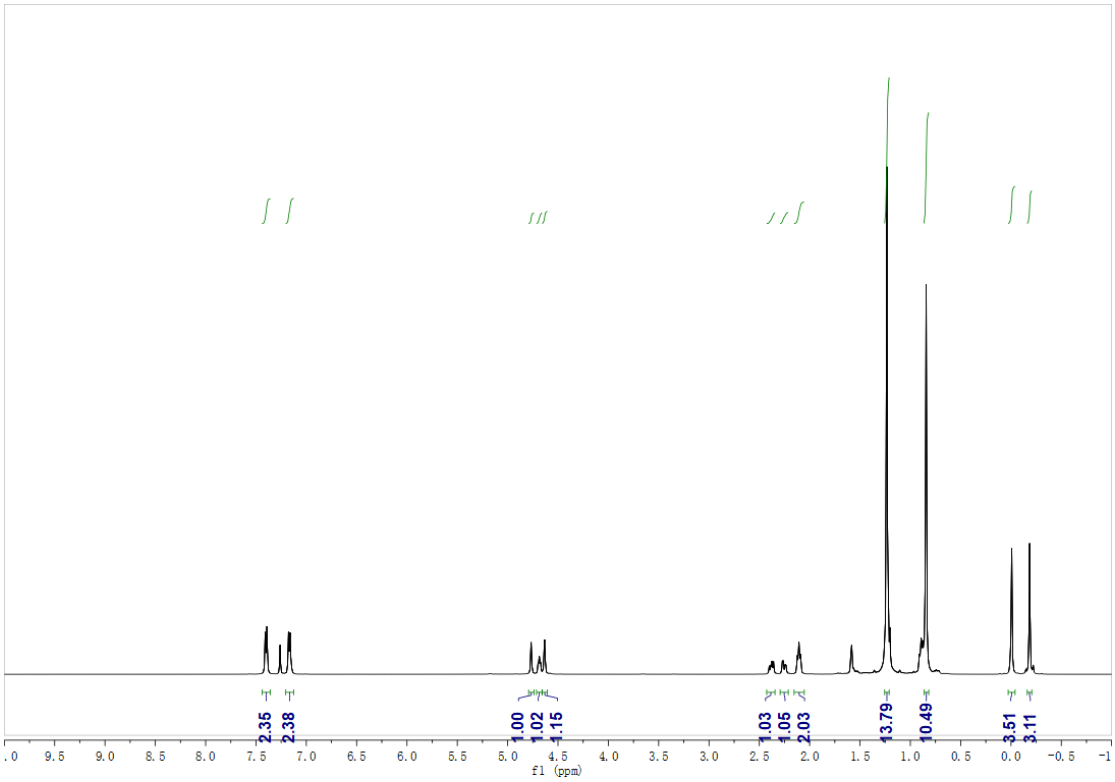
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J*=7.9 Hz, 2H), 7.17 (d, *J*=7.8 Hz, 2H), 4.77 (s, 1H), 4.70 – 4.67 (m, 1H), 4.63 (s, 1H), 2.38 (dd, *J*=13.4, 7.7 Hz, 1H), 2.25 (dd, *J*=13.5, 4.7 Hz, 1H), 2.11 (t, *J*=7.7 Hz, 2H), 1.23 (s, 12H), 0.84 (s, 9H), -0.01 (s, 3H), -0.19 (s, 3H) ppm.

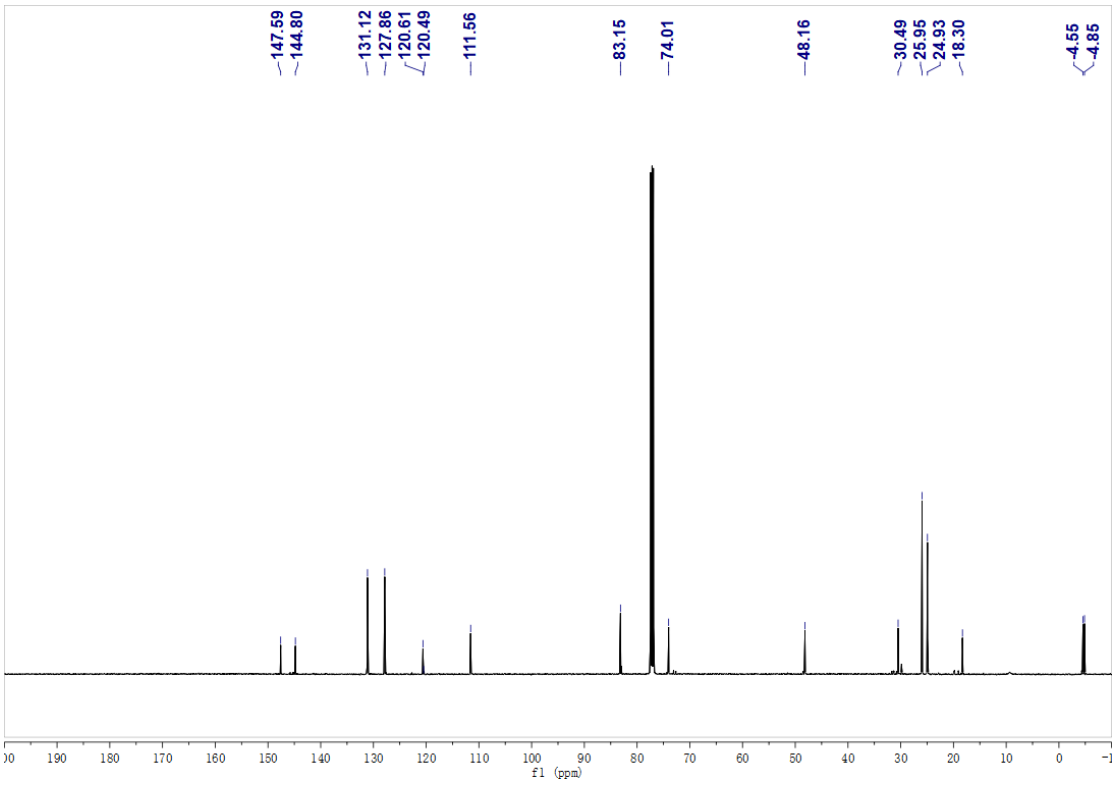
^{13}C NMR (125 MHz, $CDCl_3$): δ 147.6, 144.8, 131.1, 127.9, 120.6, 120.5, 111.6, 83.2, 74.0, 48.2, 30.5, 26.0, 24.9, 18.3, -4.6, -4.9 ppm.

HRMS (ESI) Calculated for $C_{18}H_{27}BrOSi$ $[M]^+$ = 366.1015, Found 366.1005.

FTIR (neat) 2928, 2857, 1371, 1319, 1143, 1070, 835,753 cm^{-1}.

$[\alpha]_D^{34}$: -48.0 (*c* = 1.0, $CHCl_3$)


2.35
2.38
1.00
1.02
1.15
1.03
1.05
2.03
13.79
10.49
3.51
3.11
f1 (ppm)


147.59
144.80
131.12
127.86
120.61
120.49
111.56
83.15
74.01
48.16
30.49
25.95
24.93
18.30
4.55
4.85
f1 (ppm)

Single Crystal Diffraction Data for 4c

X-ray Experimental for **4c** $C_{12}H_{12}Cl_2O$: Crystals grew as clusters of colorless laths by slow evaporation from Hexane. The data crystal was cut from a larger crystal and had approximate dimensions; 0.49 x 0.17 x 0.12 mm. The data were collected at -173 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71073Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 700 low-temperature device. A total of 1858 frames of data were collected using ω-scans with a scan range of 0.6° and a counting time of 24 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using SAINT V8.27B.[4] The structure was solved by direct methods using SHELXT[5] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[6] Structure analysis was aided by use of the programs PLATON[7] and WinGX.[8] The hydrogen atoms bound to carbon atoms were calculated in idealized positions. The hydrogen atoms on O1 was observed in a ΔF map and refined with an isotropic displacement parameter. The absolute configuration was determined using the method of Flack[9] and confirmed using the Hooft y-parameter method, which resulted in a Hooft y-parameter of 0.00(2).[10]

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0347*P)^2 + (0.077*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.0660, with R(F) equal to 0.0278 and a goodness of fit, S, = 1.08. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[11] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[12] All figures were generated using SHELXTL/PC.[13] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 1. Crystal data and structure refinement for **4c**.

Empirical formula	C12 H12 Cl2 O	
Formula weight	243.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.442(2) Å	α= 90°.
	b = 4.8336(11) Å	β= 112.794(5)°.
	c = 12.394(3) Å	γ = 90°.
Volume	576.7(2) $Å^3$	
Z	2	
Density (calculated)	1.400 Mg/m^3	
Absorption coefficient	0.532 mm^{-1}	
F(000)	252	
Crystal size	0.490 x 0.170 x 0.120 mm^3	
Theta range for data collection	3.253 to 30.603°.	
Index ranges	-14<=h<=14, -6<=k<=6, -17<=l<=17	
Reflections collected	14723	
Independent reflections	3482 [R(int) = 0.0365]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.887	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3482 / 1 / 141	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0278, wR2 = 0.0648	
R indices (all data)	R1 = 0.0305, wR2 = 0.0660	
Absolute structure parameter	0.00(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.352 and -0.182 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	5396(2)	1802(4)	8131(2)	12(1)
C2	4390(2)	2944(4)	7132(2)	13(1)
C3	4812(2)	4965(4)	6549(2)	13(1)
C4	6180(2)	5831(4)	6926(2)	12(1)
C5	7179(2)	4638(4)	7929(1)	10(1)
C6	6781(2)	2620(4)	8543(2)	11(1)
C7	8685(2)	5504(4)	8287(1)	10(1)
C8	9418(2)	3632(4)	7699(2)	12(1)
C9	10809(2)	4740(4)	7793(2)	13(1)
C10	10843(2)	6939(4)	6986(2)	19(1)
C11	9770(3)	7925(5)	6093(2)	26(1)
C12	11989(2)	3782(4)	8598(2)	19(1)
O1	9414(1)	5534(3)	9529(1)	12(1)
Cl1	4893(1)	-705(1)	8894(1)	16(1)
Cl2	3577(1)	6501(1)	5312(1)	20(1)

Table 3. Bond lengths [Å] and angles [°] for **4c**.

		C7-C8	1.539(2)
C1-C2	1.391(3)	C7-H7	1.00
C1-C6	1.391(3)	C8-C9	1.510(2)
C1-Cl1	1.7392(18)	C8-H8A	0.99
C2-C3	1.385(3)	C8-H8B	0.99
C2-H2	0.95	C9-C12	1.333(3)
C3-C4	1.384(3)	C9-C10	1.468(3)
C3-Cl2	1.7412(18)	C10-C11	1.322(3)
C4-C5	1.401(2)	C10-H10	0.95
C4-H4	0.95	C11-H11A	0.95
C5-C6	1.395(2)	C11-H11B	0.95
C5-C7	1.518(2)	C12-H12A	0.95
C6-H6	0.95	C12-H12B	0.95
C7-O1	1.430(2)	O1-H1O	0.73(4)

C2-C1-C6	122.22(17)	O1-C7-C8	111.15(14)
C2-C1-Cl1	118.54(14)	C5-C7-C8	110.42(14)
C6-C1-Cl1	119.23(14)	O1-C7-H7	107.6
C3-C2-C1	117.47(17)	C5-C7-H7	107.6
C3-C2-H2	121.3	C8-C7-H7	107.6
C1-C2-H2	121.3	C9-C8-C7	113.28(14)
C4-C3-C2	122.16(16)	C9-C8-H8A	108.9
C4-C3-Cl2	118.94(13)	C7-C8-H8A	108.9
C2-C3-Cl2	118.89(14)	C9-C8-H8B	108.9
C3-C4-C5	119.44(16)	C7-C8-H8B	108.9
C3-C4-H4	120.3	H8A-C8-H8B	107.7
C5-C4-H4	120.3	C12-C9-C10	120.14(18)
C6-C5-C4	119.68(17)	C12-C9-C8	121.12(17)
C6-C5-C7	121.81(15)	C10-C9-C8	118.73(16)
C4-C5-C7	118.45(15)	C11-C10-C9	126.5(2)
C1-C6-C5	119.02(16)	C11-C10-H10	116.7
C1-C6-H6	120.5	C9-C10-H10	116.7
C5-C6-H6	120.5	C10-C11-H11A	120.0
O1-C7-C5	112.12(14)	C10-C11-H11B	120.0

H11A-C11-H11B	120.0
C9-C12-H12A	120.0
C9-C12-H12B	120.0
H12A-C12-H12B	120.0
C7-O1-H1O	108(2)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	14(1)	10(1)	14(1)	-2(1)	8(1)	-2(1)
C2	10(1)	16(1)	14(1)	-3(1)	4(1)	-3(1)
C3	11(1)	14(1)	10(1)	-1(1)	2(1)	1(1)
C4	14(1)	12(1)	11(1)	0(1)	5(1)	0(1)
C5	10(1)	9(1)	10(1)	-3(1)	4(1)	-2(1)
C6	10(1)	10(1)	14(1)	-1(1)	5(1)	0(1)
C7	10(1)	9(1)	10(1)	-1(1)	2(1)	-2(1)
C8	12(1)	12(1)	14(1)	-4(1)	5(1)	-2(1)
C9	14(1)	14(1)	14(1)	-2(1)	8(1)	-2(1)
C10	22(1)	17(1)	23(1)	-2(1)	16(1)	-3(1)
C11	35(1)	24(1)	26(1)	7(1)	20(1)	7(1)
C12	14(1)	26(1)	20(1)	-1(1)	8(1)	-1(1)
O1	13(1)	12(1)	10(1)	-2(1)	2(1)	-1(1)
Cl1	16(1)	13(1)	19(1)	1(1)	9(1)	-4(1)
Cl2	14(1)	26(1)	15(1)	4(1)	-1(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4c**.

	x	y	z	U(eq)
H2	3449	2359	6859	16
H4	6439	7222	6508	14
H6	7446	1816	9231	14
H7	8692	7432	7996	12
H8A	9553	1777	8065	15
H8B	8811	3417	6861	15
H10	11724	7731	7121	23
H11A	8867	7201	5922	31
H11B	9903	9357	5621	31
H12A	12855	4521	8652	23
H12B	11964	2359	9119	23
H1O	9720(30)	4160(80)	9710(20)	34(9)

Table 6. Torsion angles [°] for **4c**.

C6-C1-C2-C3	-0.2(3)
Cl1-C1-C2-C3	179.06(14)
C1-C2-C3-C4	0.5(3)
C1-C2-C3-Cl2	-178.62(14)
C2-C3-C4-C5	0.0(3)
Cl2-C3-C4-C5	179.09(14)
C3-C4-C5-C6	-0.7(3)
C3-C4-C5-C7	176.61(16)
C2-C1-C6-C5	-0.5(3)
Cl1-C1-C6-C5	-179.79(13)
C4-C5-C6-C1	1.0(3)
C7-C5-C6-C1	-176.25(16)
C6-C5-C7-O1	-36.7(2)
C4-C5-C7-O1	146.07(16)
C6-C5-C7-C8	87.9(2)
C4-C5-C7-C8	-89.40(19)
O1-C7-C8-C9	-67.75(19)
C5-C7-C8-C9	167.16(14)
C7-C8-C9-C12	99.6(2)
C7-C8-C9-C10	-79.6(2)
C12-C9-C10-C11	174.3(2)
C8-C9-C10-C11	-6.6(3)

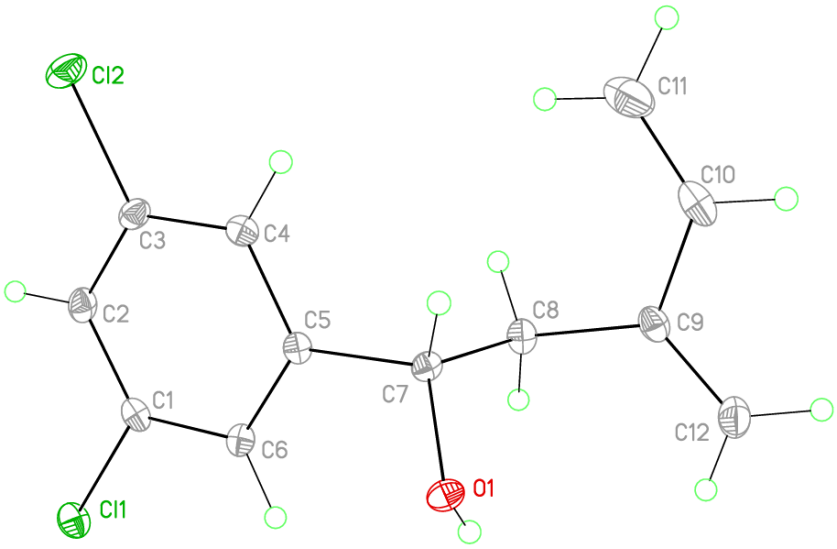
Table 7. Hydrogen bonds for **4c** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1O...O1#1	0.73(4)	2.03(4)	2.7555(14)	170(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y-1/2,-z+2

Figure 1. View of **4c** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



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[11] $R_w(F^2) = \{w(|F_o|^2 - |F_c|^2)^2/w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.

$R(F) = (|F_o| - |F_c|)/|F_o|\}$ for reflections with $F_o > 4(\ (F_o))$.

$S = [w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

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