Supporting Information

Asymmetric Allylation of Glycidols Mediated by Allyl Acetate *via* Iridium Catalyzed Hydrogen Transfer

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General Information

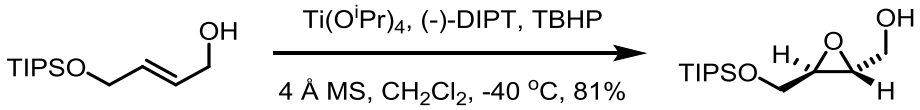
All reactions were run under an atmosphere of argon. Sealed tubes (13x100 mm) were purchased from Fischer Scientific (catalog number 14-959-35C) and were flame dried followed by cooling in a desiccator. Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. Dichloromethane was distilled from calcium hydride under a nitrogen atmosphere prior to use. Anhydrous solvents were transferred by oven-dried syringes. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Dynanmic Absorbents F254). Visualization was accomplished with UV light followed by dipping in potassium permanganate or *p*-anisaldehyde stain solution and then heating. Purification of reactions was carried out by flash chromatography using Silacycle silica gel (40-63 μm, unless indicated specifically). Potassium carbonate was purchased through Fisher Chemical, flame dried prior to use, and stored in a desiccator.

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+Na, or M+K), or a suitable fragment. ^1H nuclear magnetic resonance spectra were recorded on an Agilent MR (400 MHz). 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 an Agilent MR (100 MHz) for $CDCl_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual $CDCl_3$ δ_C (77.0 ppm).

Synthesis of Starting Glycidols 1a-1f

Glycidols **1a**,[1,2] *dehydro*-**1a**,[3] **1b**,[1,4] **1c**,[5] **1d**[4,6] and **1e**[6] were prepared according to the published procedures and were identical in all respects to the reported materials.



To a flame dried round-bottomed flask charged with dry 4 Å molecular sieves (1 g) under an argon atmosphere was added CH_2Cl_2 (33 mL, 0.1 M with respect to allylic alcohol). The reaction vessel was placed in -40 ºC bath and $Ti(O^iPr)_4$ (1.93 mL, 6.54 mmol, 200 mol%) was added followed by D-(–)-diisopropyl tartrate (1.70 mL, 8.1 mmol, 250 mol%). The mixture was stirred vigorously for 30 minutes, at which point *tert*-butyl hydrogen peroxide (1.2 mL, 5.0-6.0 M in decane, 6.54 mmol, 200 mol%). After 30 minutes a solution of allylic alcohol[7] (0.8 g, 3.27 mmol) in dry CH_2Cl_2 (17 mL, 0.2 M) was added slowly and the mixture was stirred for 40 h. The reaction vessel was transferred to an ice batch. Water (30 mL) and NaOH (30 mL, 10% aqueous solution) were added to the reaction mixture. The mixture was allowed to stir for 2 hours. The reaction mixture was filtered (celite) with the aid of CH_2Cl_2 (50 mL) and the filtrate was transferred to a separatory funnel. The organic layer was extracted with CH_2Cl_2 (50 mL × 2) and the combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting oily residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 10:1–7:1) to furnish the title compound as a colorless oil (690 mg, 2.65 mmol) in 81% yield. The spectral data were identical to those reported for the corresponding racemate.[7]

TLC (SiO_2) R_f = 0.29 (hexanes/ethyl acetate = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.94 (m, 2H), 3.77 (dd, *J* = 11.9, 4.1 Hz, 1H), 3.62 (dq, *J* = 12.2, 3.8 Hz, 1H), 3.13 (m, 2H), 1.05 (m, 21H).

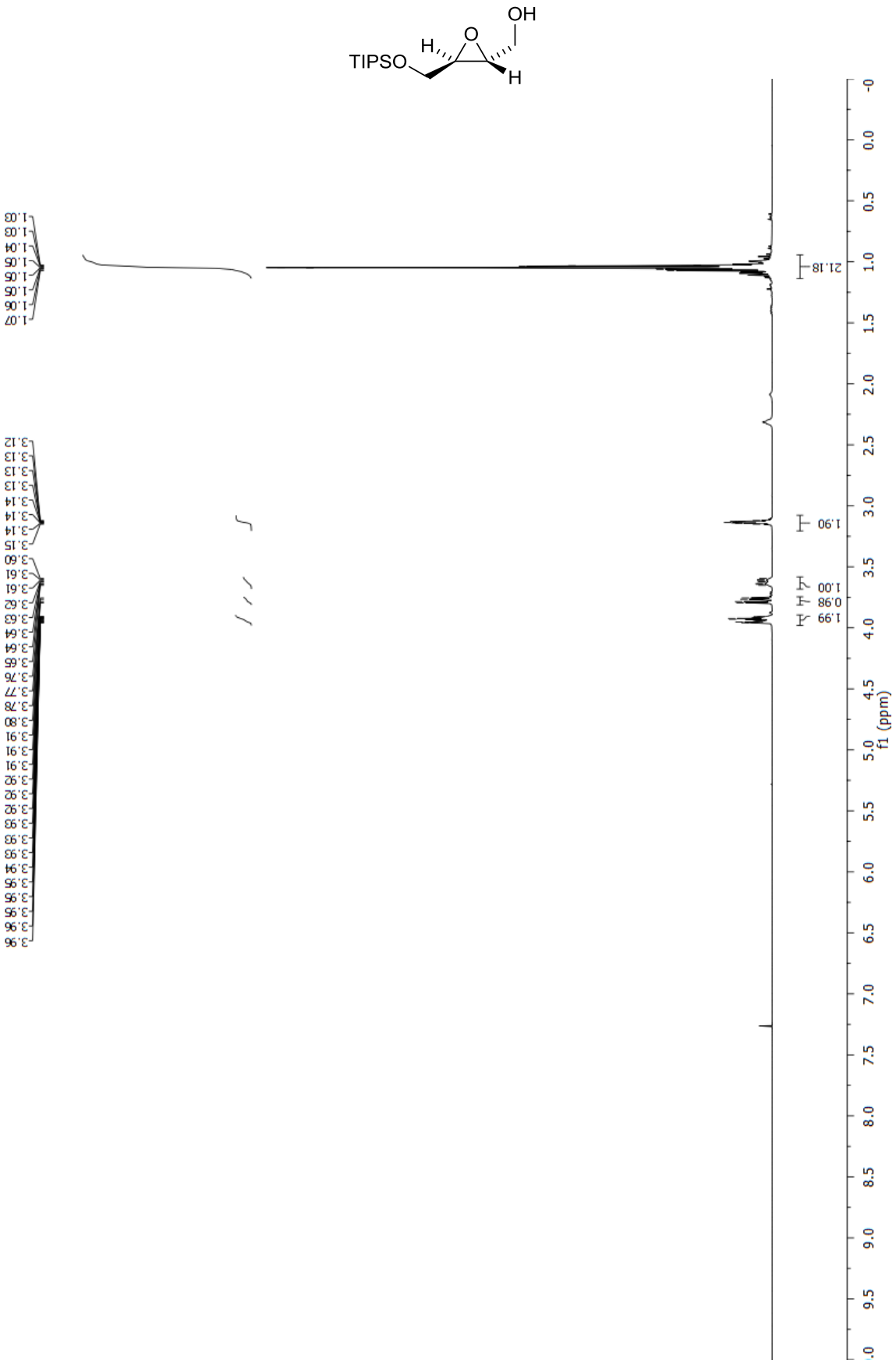
^{13}C NMR (100 MHz, $CDCl_3$): δ = 62.8, 61.3, 56.0, 55.7, 17.8, 11.9.

HRMS (ESI) Calculated for $C_{13}H_{28}O_3Si$ [M+Na^+] = 283.1700, Found 283.1701.

FTIR (neat) 3432, 2942, 2865, 1463, 1112, 1065, 995, 881, 779, 681 cm^{-1}.

$[\alpha]_D^{28}$: +16.33 (*c* 1.0, $CHCl_3$).

HPLC: Enantiomeric excess was determined by HPLC analysis of the benzoate derivative of the product (Chiralcel OD-H column, hexanes:*i*-PrOH = 97:3, 1.00 mL/min, 254 nm), t_{major} = 4.7 min, t_{minor} = 5.5 min; *ee* = 93%.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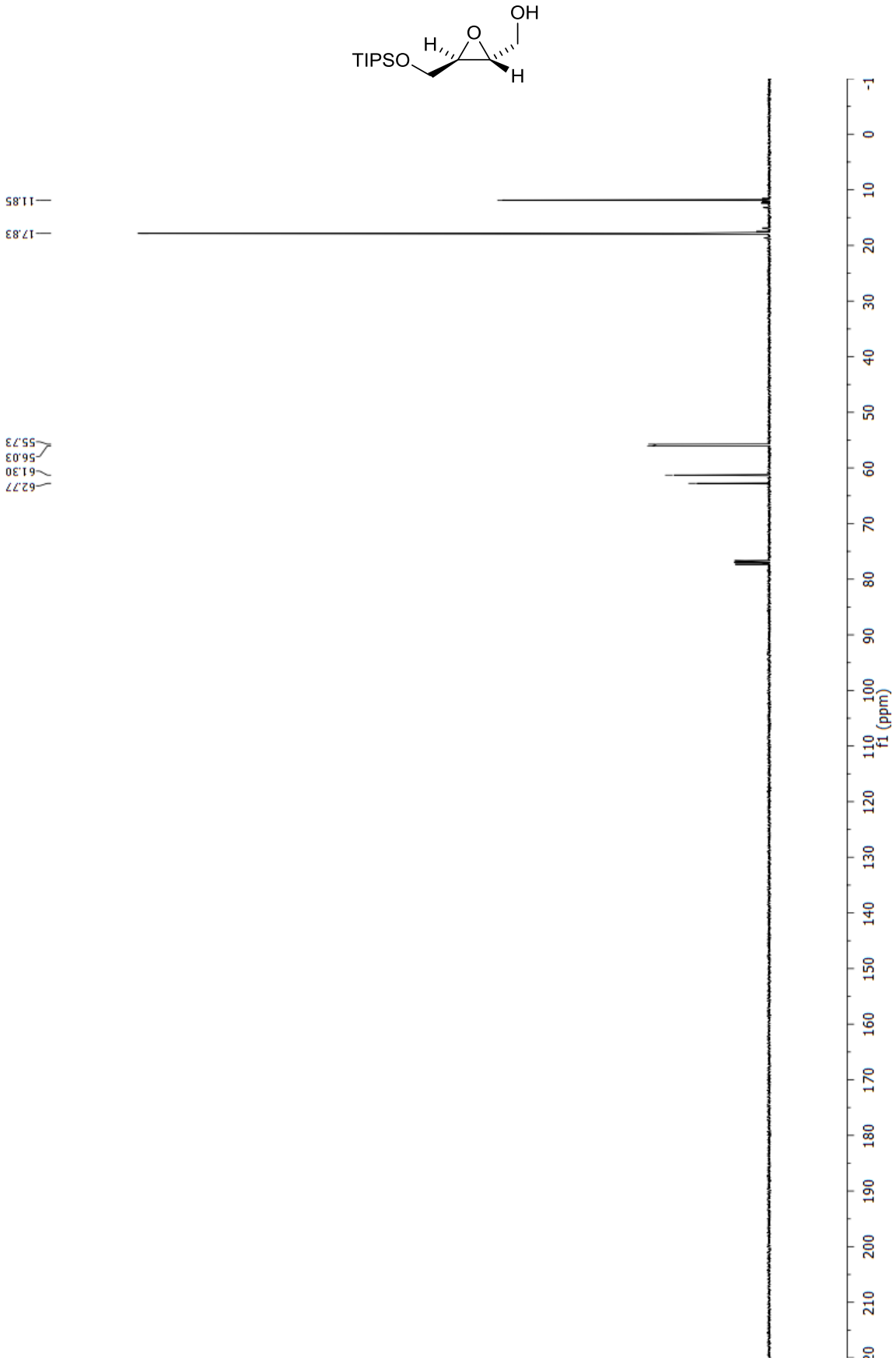
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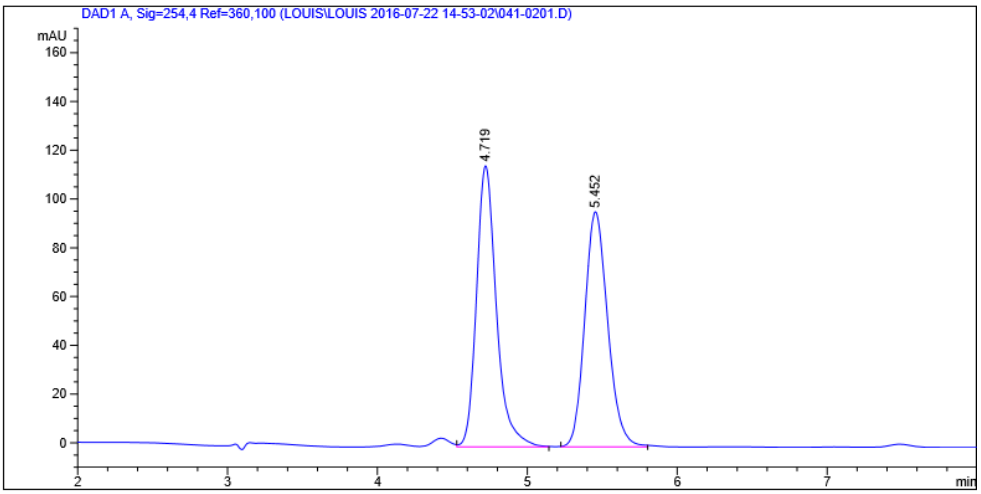

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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1	4.719	VB	0.1416	1063.94421	115.38085	50.9285
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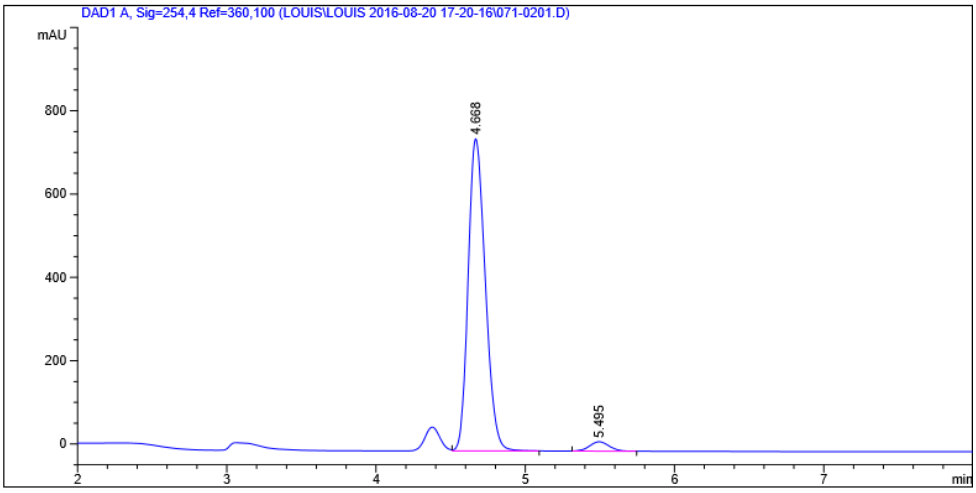
Totals :				2089.09241	211.83346	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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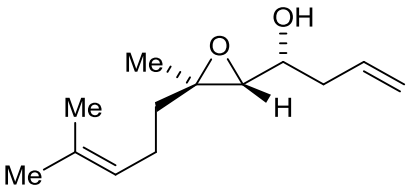
2	5.495	BB	0.1420	205.37094	22.60398	3.3214
Totals :				6183.33383	772.63981	

Procedures and Spectral Data for the Synthesis of Secondary Homoallylic Glycidols 2a-2f, *epi*-2a-2f

(*R*)-1-((2*R*,3*R*)-3-methyl-3-(4-methylpent-3-en-1-yl)oxiran-2-yl)but-3-en-1-ol (2a)



Detailed Procedures

From alcohol oxidation level: An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(R)*-SEGPHOS (6.1 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1a** (34 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (0.5 mL, 0.4 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 15:1–10:1) to furnish the title compound as a colorless oil (35.7 mg, 0.17 mmol, anti:syn = 11:1) in 85% yield.

From alcohol oxidation level: An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (17 mg, 0.025 mmol, 2.5 mol%), *(R)*-SEGPHOS (30.5 mg, 0.05 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (19.0 mg, 0.1 mmol, 10 mol%), alcohol **1a** (170 mg, 1.0 mmol, 100 mol%) and K_2CO_3 (69.0 mg, 0.5 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (2.5 mL, 0.4 M) and allyl acetate (0.22 mL, 2.0 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 15:1–10:1) to furnish the title compound as a colorless oil (171 mg, 0.17 mmol, anti:syn = 10:1) in 81% yield.

From aldehyde oxidation level: An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(R)*-SEGPHOS (6.1 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), aldehyde *dehydro*-**1a** (0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.01 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (0.5 mL, 0.4 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 15:1–10:1) to furnish the title compound as a colorless oil (34.1 mg, 0.16 mmol, anti:syn = 14:1) in 81% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.62 (hexanes/ethyl acetate = 2:1).

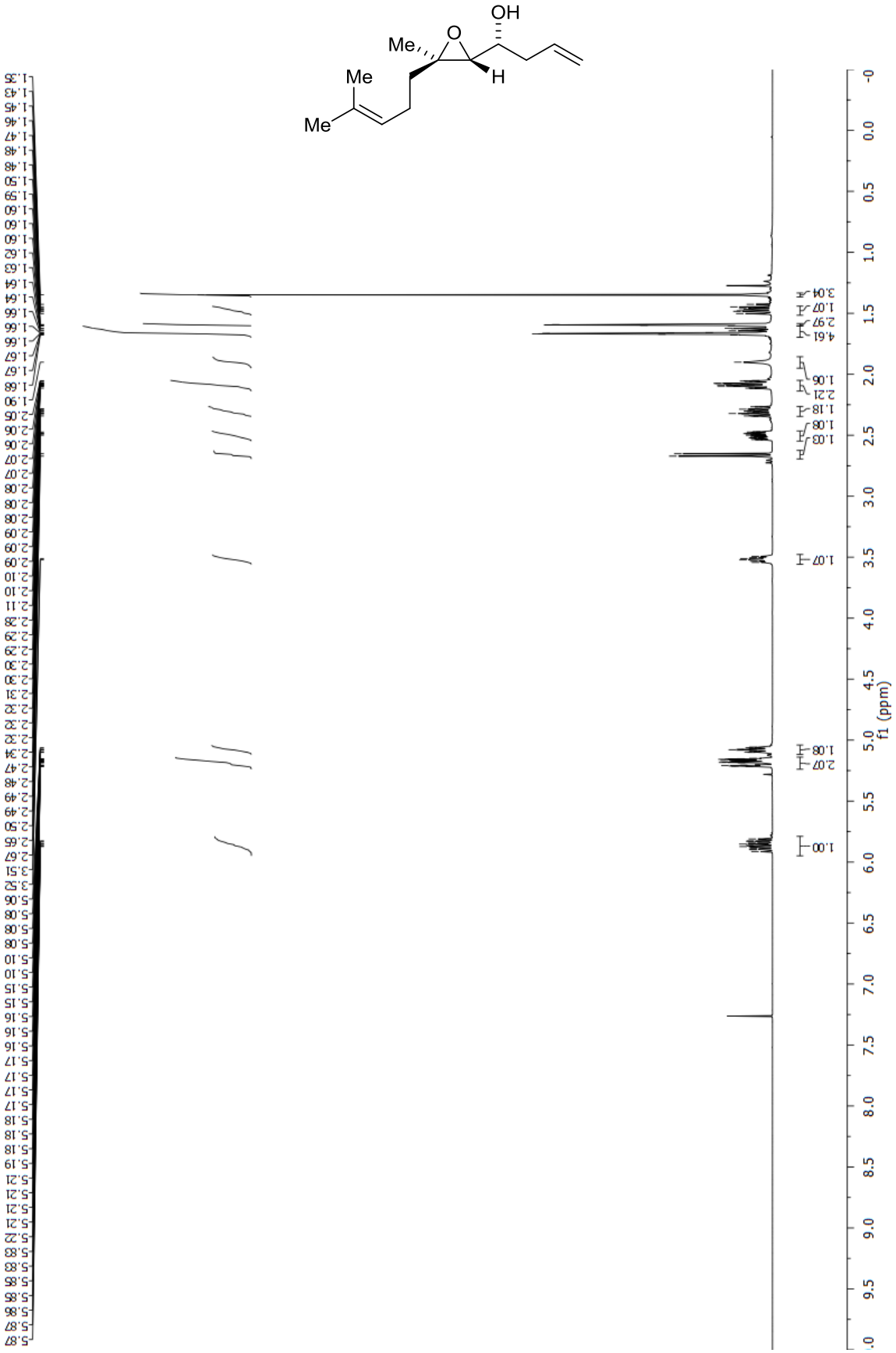
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (m, 1H), 5.19 (m, 2H), 5.08 (m, 1H), 3.52 (td, *J* = 8.1, 3.9 Hz, 1H), 2.66 (d, *J* = 8.1 Hz, 1H), 2.5 (m, 1H), 2.30 (m, 1H), 2.08 (m, 2H), 1.90 (brs, 1H), 1.66 (m, 4H), 1.59 (m, 3H), 1.47 (m, 1H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.6, 132.0, 123.4, 118.7, 68.8, 64.8, 61.4, 39.6, 38.5, 25.6, 23.7, 17.6, 16.5.

HRMS (ESI) Calculated for $C_{13}H_{22}O_2$ [M+Na^+] = 233.1512, Found 233.1506.

FTIR (neat) 3435, 2927, 2358, 1436, 1384, 1072, 986, 914, 819 cm^{-1}.

$[\alpha]_D^{25}$: +21.17 (*c* 1.0, $CHCl_3$)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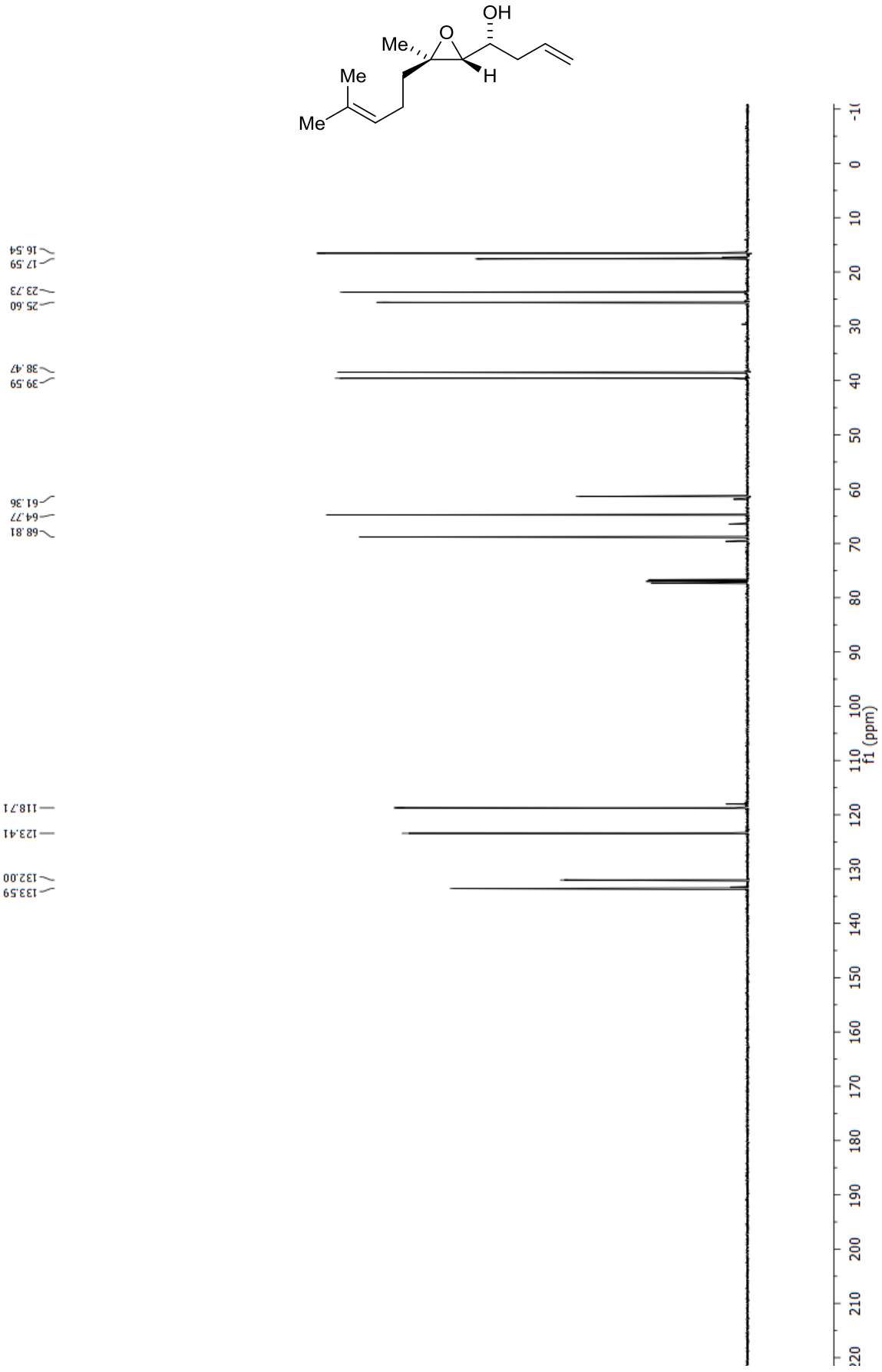
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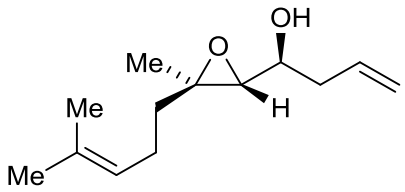
f1 (ppm)

(*S*)-1-((2*R*,3*R*)-3-methyl-3-(4-methylpent-3-en-1-yl)oxiran-2-yl)but-3-en-1-ol (*epi*-2a)



Detailed Procedures

From alcohol oxidation level: An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(S)*-SEGPHOS (6.1 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1a** (34 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (0.5 mL, 0.4 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 15:1–10:1) to furnish the title compound as a colorless oil (36.1 mg, 0.17 mmol, anti:syn = 1:12) in 86% yield.

From aldehyde oxidation level: An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(S)*-SEGPHOS (6.1 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), aldehyde *dehydro*-**1a** (0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.01 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (0.5 mL, 0.4 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 15:1–10:1) to furnish the title compound as a colorless oil (34.9 mg, 0.17 mmol, anti:syn = 1:11) in 83% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.50 (hexanes/ethyl acetate = 2:1).

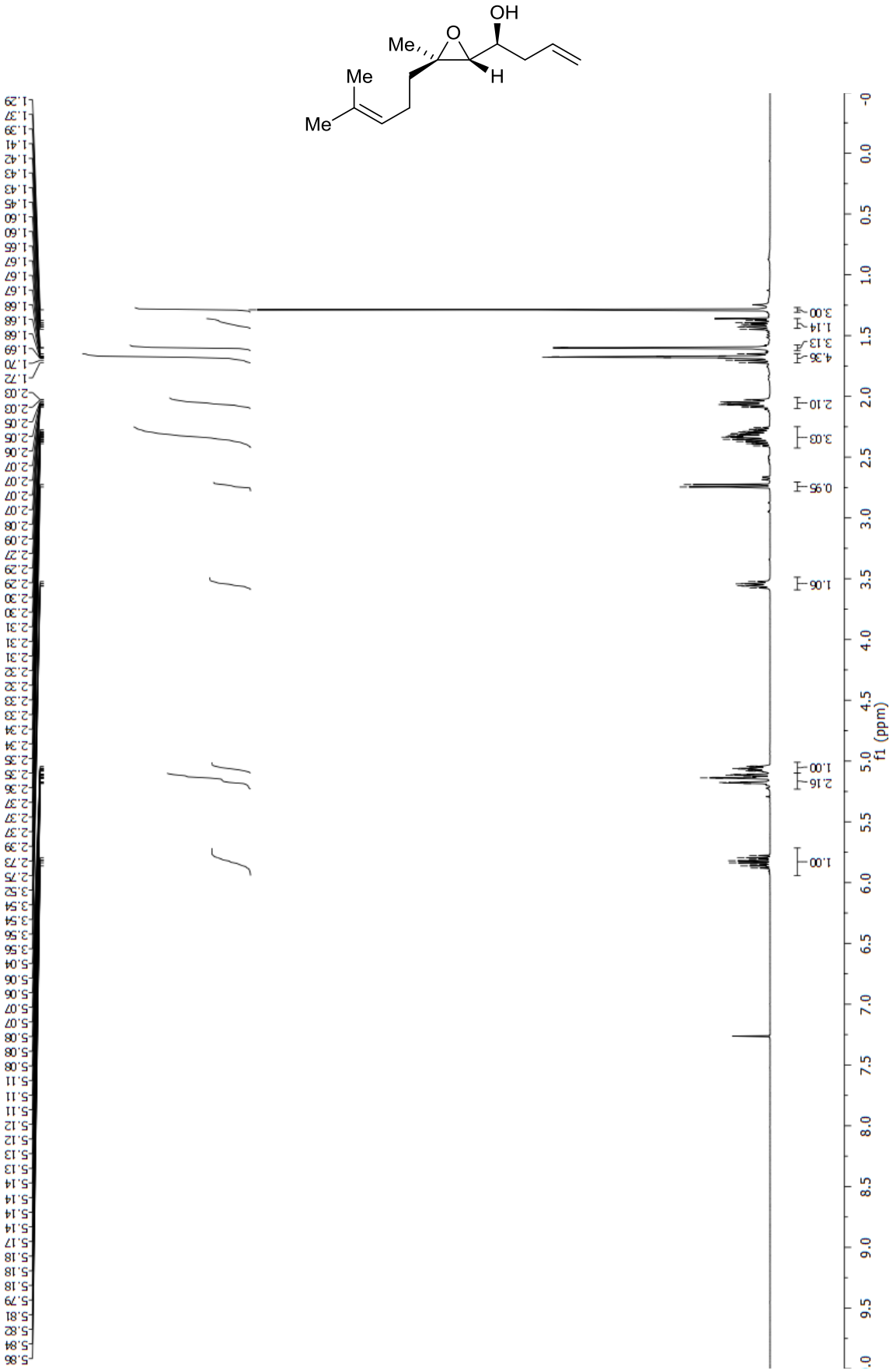
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.82 (m, 1H), 5.23–5.10 (m, 2H), 5.06 (m, 1H), 3.55 (td, *J* = 7.5, 5.9 Hz, 1H), 2.74 (d, *J* = 7.9 Hz, 1H), 2.42–2.25 (m, 3H), 2.08 (m, 2H), 1.69 (m, 4H), 1.60 (m, 3H), 1.41 (m, 1H), 1.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.4, 132.1, 123.4, 118.1, 69.6, 66.4, 61.9, 38.7, 38.6, 25.6, 23.7, 17.6, 17.3.

HRMS (ESI) Calculated for $C_{13}H_{22}O_2$ [M+Na$^+$] = 233.1512, Found 233.1514.

FTIR (neat) 3435, 2924, 2362, 1435, 1383, 1043, 997, 914, 822 cm^{-1}.

$[\alpha]_D^{25}$: −0.33 (*c* 1.0, $CHCl_3$).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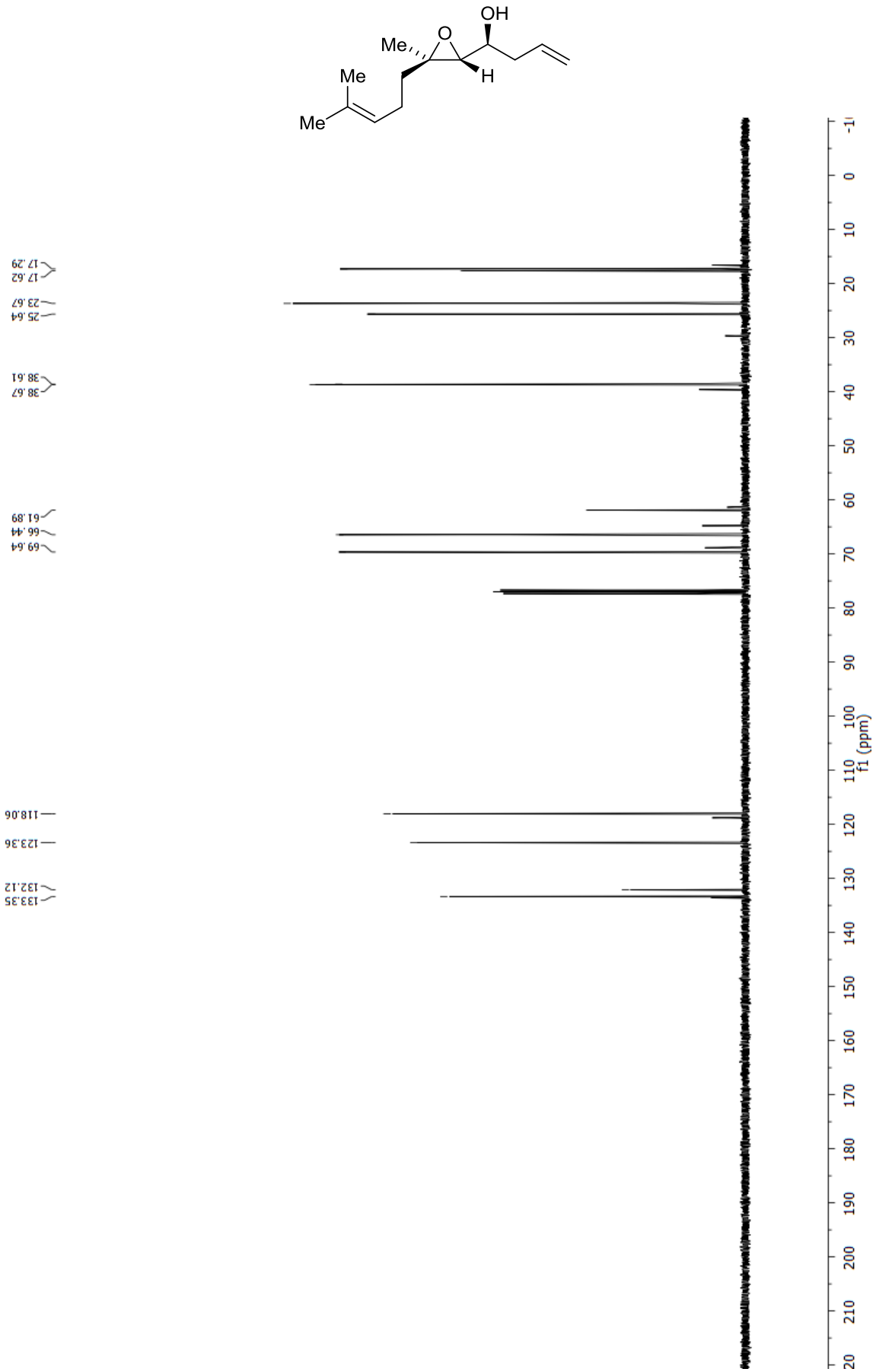
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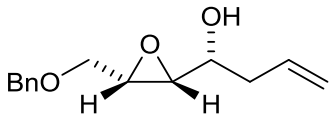
(*R*)-1-((2*R*,3*S*)-3-((benzyloxy)methyl)oxiran-2-yl)but-3-en-1-ol (2b)



Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(R)*-Cl-MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1b** (39 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (1.0 mL, 0.2 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 5:1–3:1) to furnish the title compound as a colorless oil (35.6 mg, 0.15 mmol, anti:syn = 9:1) in 76% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.42 (hexanes/ethyl acetate = 2:1).

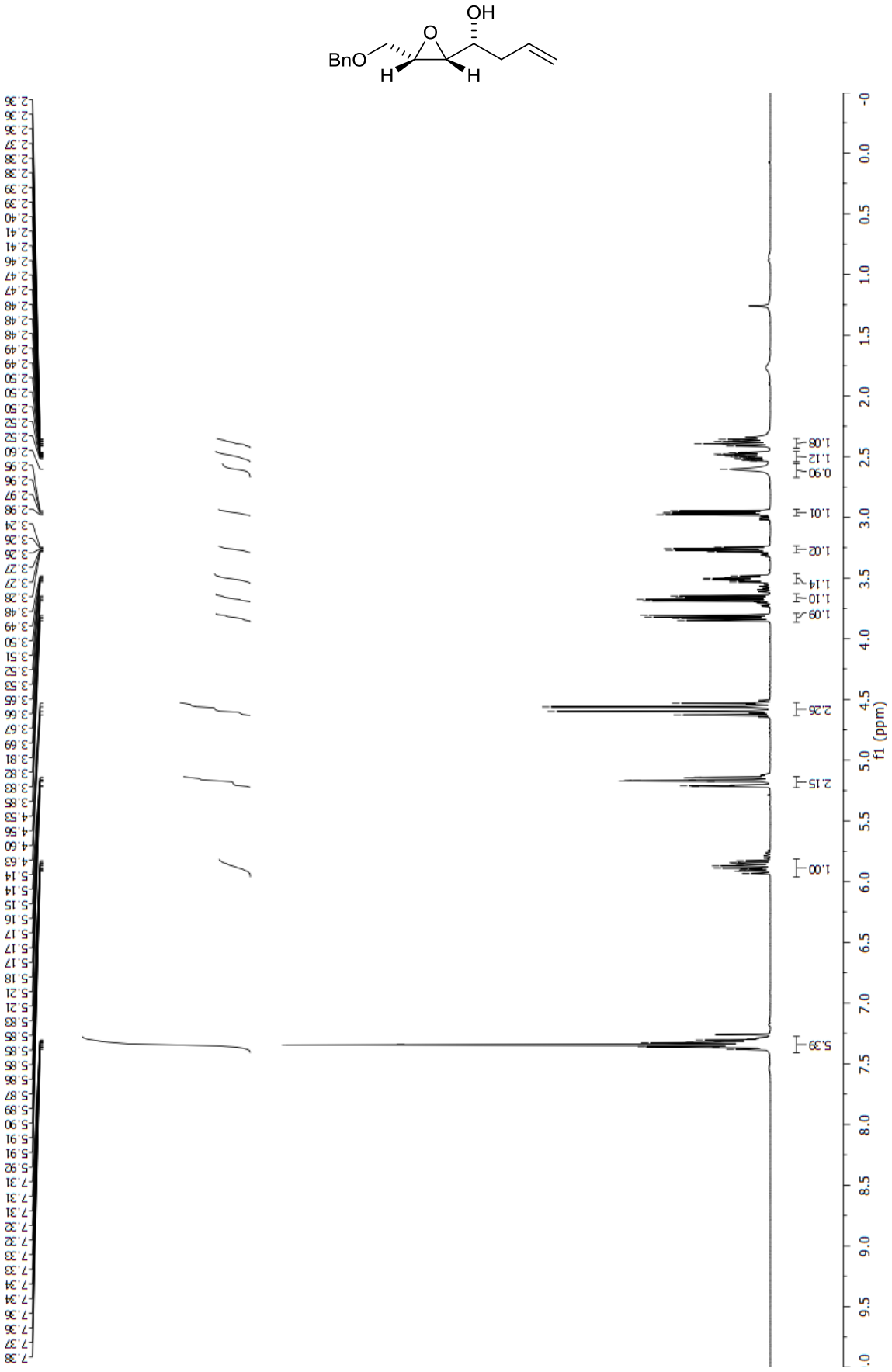
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (m, 5H), 5.88 (m, 1H), 5.17 (m, 2H), 4.58 (m, 2H), 3.83 (dd, *J* = 10.9, 6.0 Hz, 1H), 3.67 (dd, *J* = 10.8, 5.7 Hz, 1H), 3.50 (td, *J* = 7.8, 4.8 Hz, 1H), 3.26 (td, *J* = 5.9, 4.3 Hz, 1H), 2.96 (dd, *J* = 8.0, 4.3 Hz, 1H), 2.60 (brs, 1H), 2.49 (m, 1H), 2.38 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.2, 133.4, 128.5, 128.0, 127.9, 118.2, 73.6, 68.9, 68.4, 57.9, 54.1, 39.3.

HRMS (ESI) Calculated for $C_{14}H_{18}O_3$ $[M+Na^+]$ =257.1148, Found 257.1151.

FTIR (neat) 3454, 2921, 1718, 1453, 1271, 1075, 1028, 918, 698 cm^{-1}.

$[\alpha]_D^{25}$: −55.34 (*c* 1.0, $CHCl_3$).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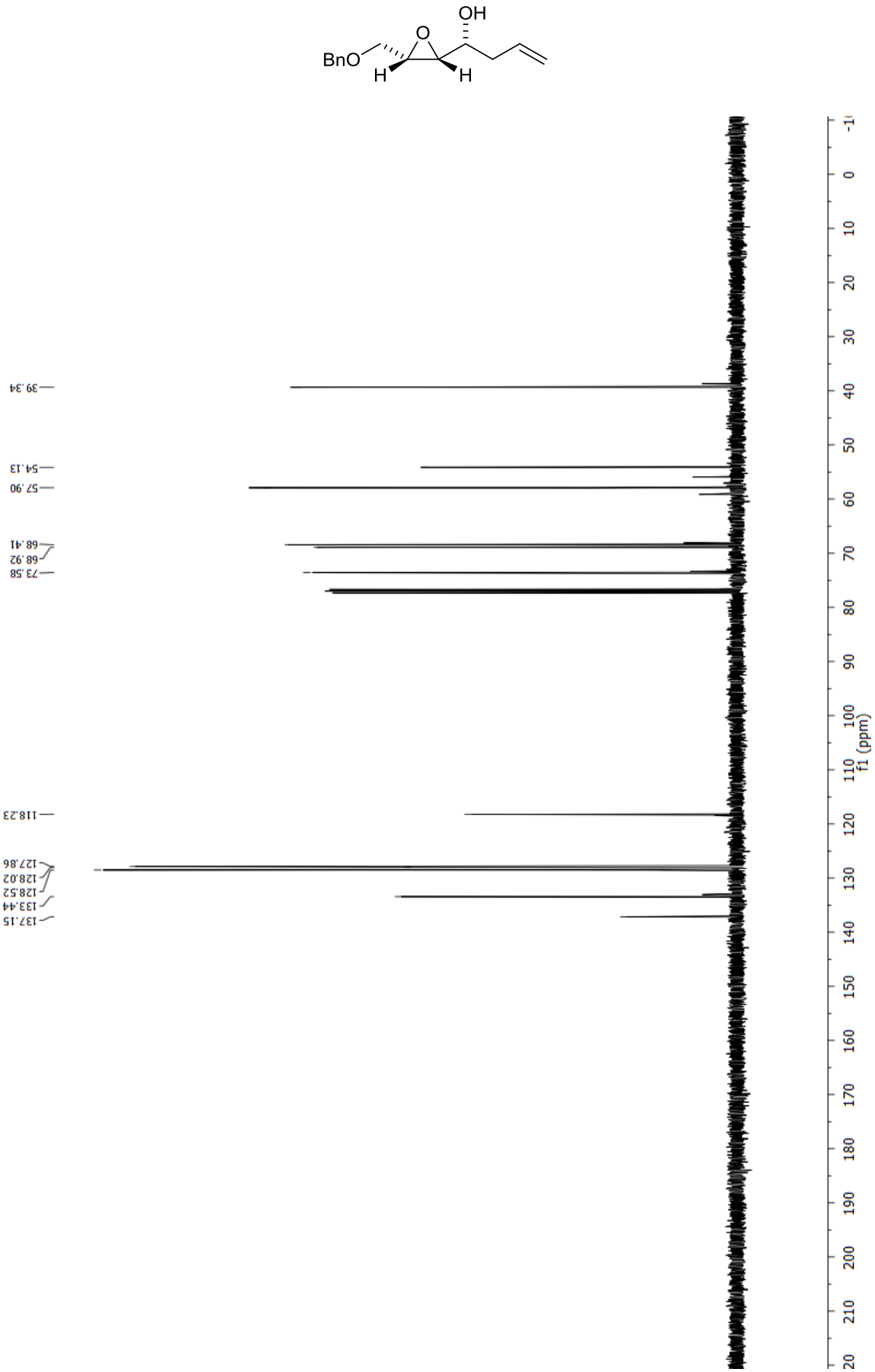
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133.44
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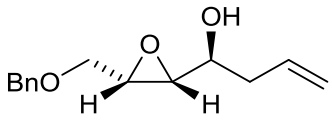
(*S*)-1-((2*R*,3*S*)-3-((benzyloxy)methyl)oxiran-2-yl)but-3-en-1-ol (*epi*-2b)

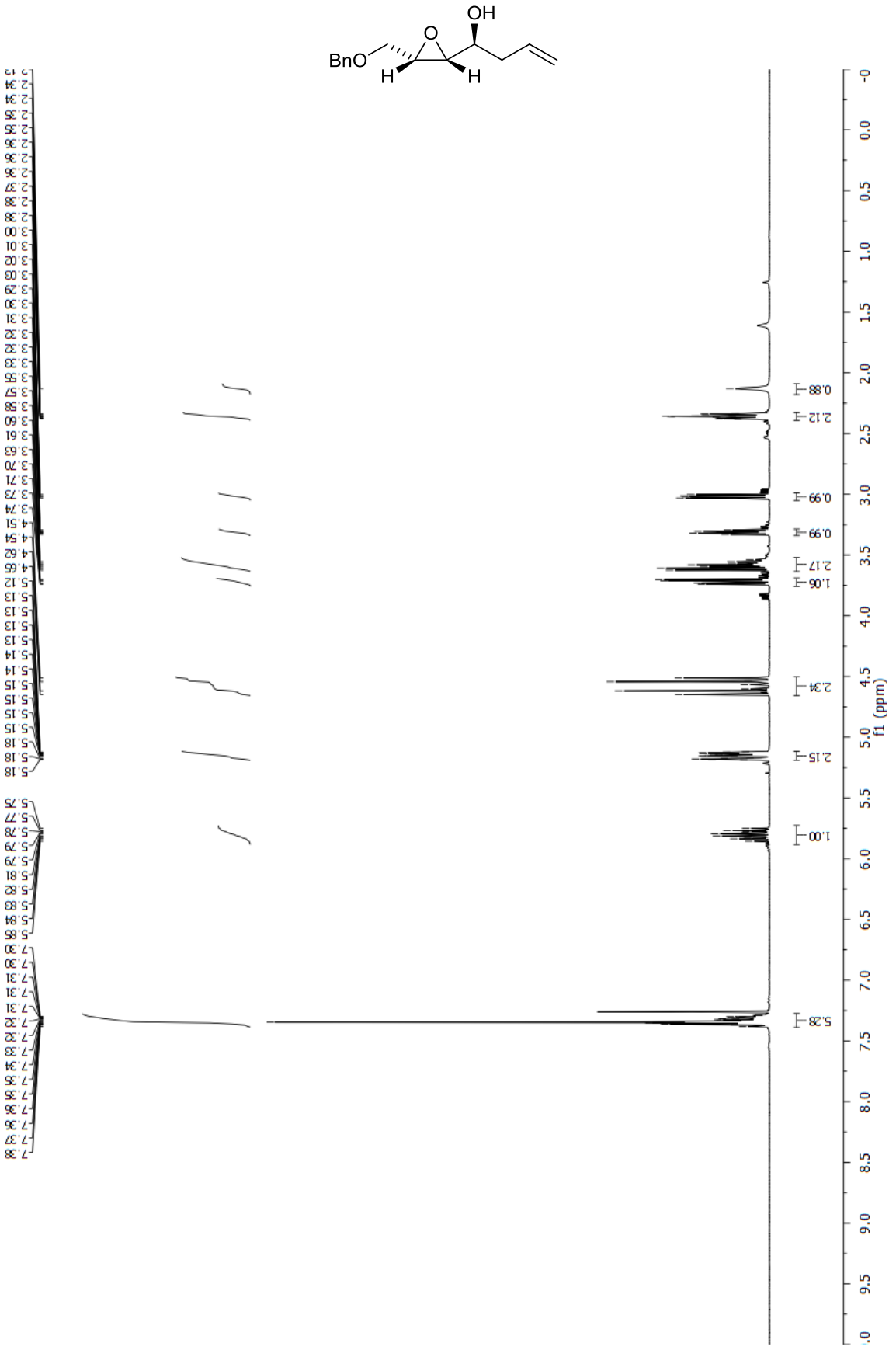


Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(S)*-Cl-MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1b** (39 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (1.0 mL, 0.2 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 5:1–3:1) to furnish the title compound as a colorless oil (37.0 mg, 0.16 mmol, anti:syn = 1:8) in 79% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.35 (hexanes/ethyl acetate = 2:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (m, 5H), 5.80 (m, 1H), 5.15 (m, 2H), 4.58 (m, 2H), 3.72 (dd, *J* = 11.2, 4.1 Hz, 1H), 3.63–3.53 (m, 2H), 3.31 (dt, *J* = 6.5, 4.3 Hz, 1H), 3.02 (dd, *J* = 7.4, 4.5 Hz, 1H), 2.36 (m, 2H), 2.13 (brs, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.6, 133.1, 128.4, 127.8, 127.8, 118.5, 73.3, 69.0, 68.1, 59.2, 56.0, 38.7.
HRMS (ESI) Calculated for $C_{14}H_{18}O_3$ $[M+Na^+]$ =257.1148, Found 257.1155.
FTIR (neat) 3421, 2926, 1737, 1365, 1229, 1094, 1027, 918, 700 cm^{-1}.
$[\alpha]_D^{25}$: −86.67 (*c* 1.0, $CHCl_3$).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BnO
H
H
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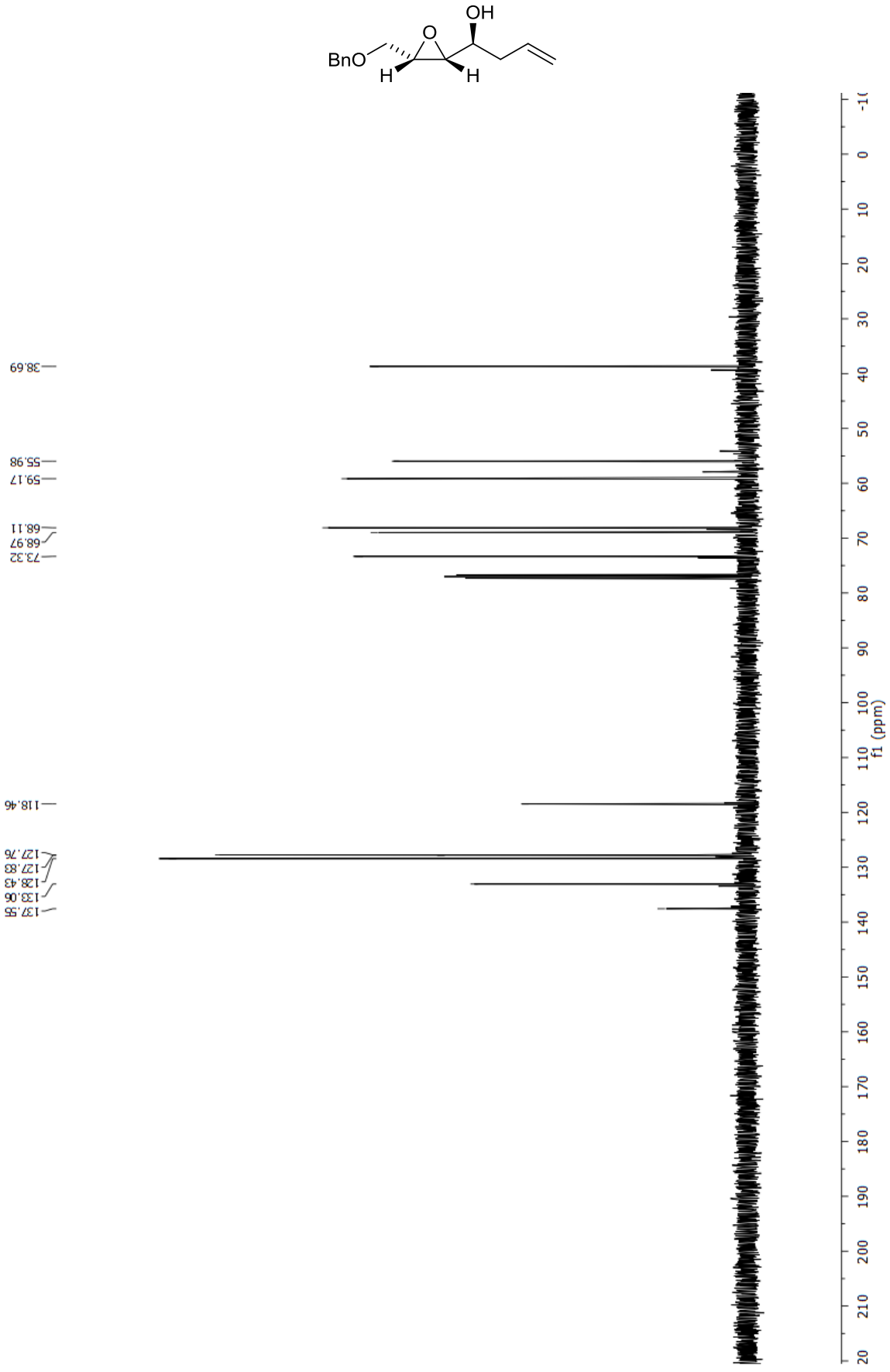
2.12
0.99
0.99
2.17
1.06
2.34
2.15
1.00
5.28
f1 (ppm)


OH
O
BnO
H
H
38.69
55.98
59.17
68.11
68.97
73.32
118.46
127.76
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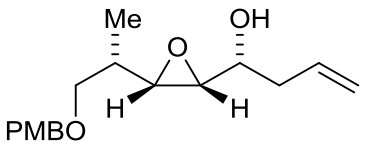
128.43
133.06
137.56
f1 (ppm)

(*R*)-1-((2*R*,3*S*)-3-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)oxiran-2-yl)but-3-en-1-ol (2c)



Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(R)*-Cl-MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1c** (51 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (1.0 mL, 0.2 M) and allyl acetate (43 µL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 6:1–3:1) to furnish the title compound as a colorless oil (49.1 mg, 0.17 mmol, anti:syn = 10:1) in 84% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.36 (hexanes/ethyl acetate = 2:1).

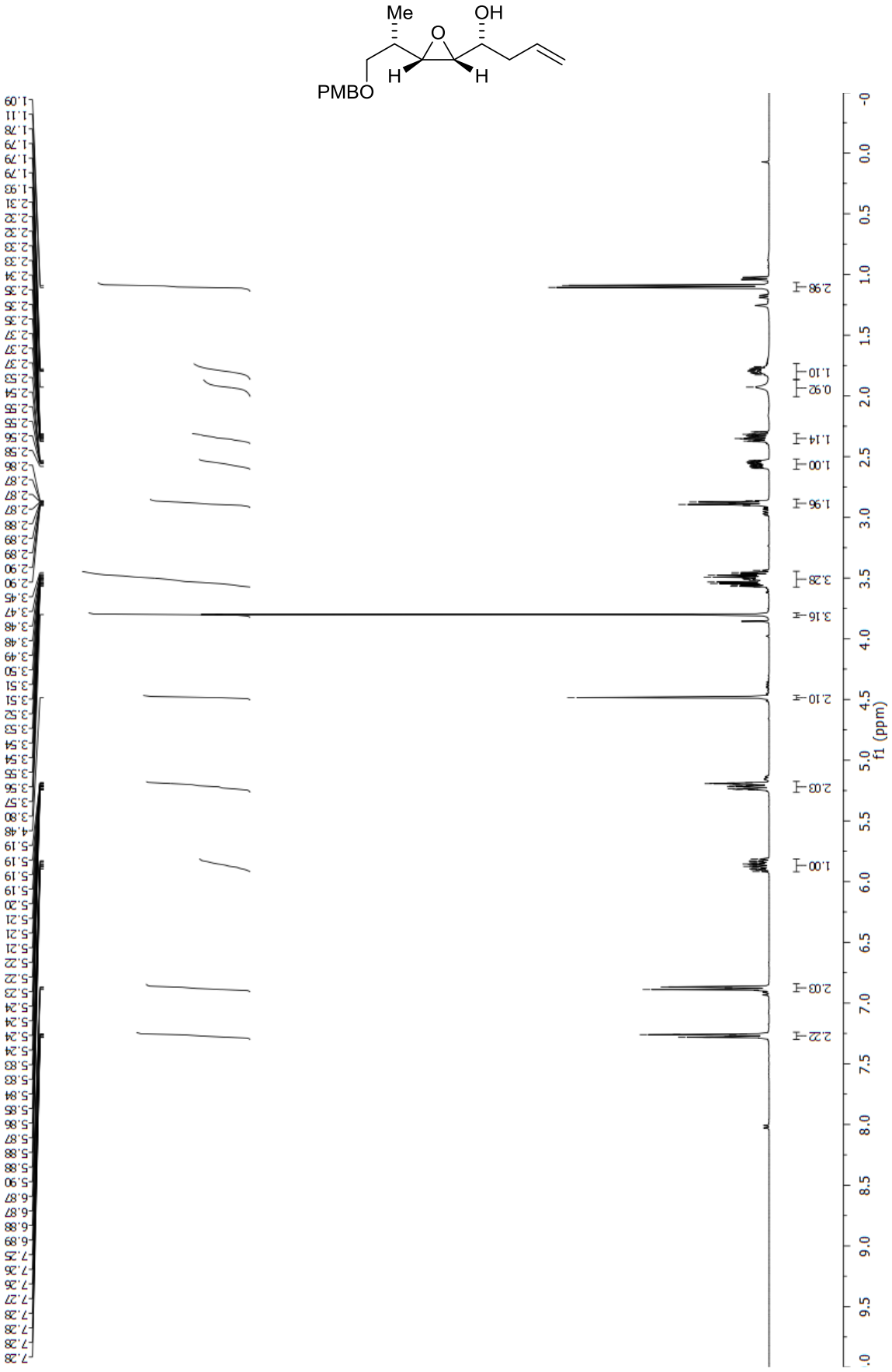
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (m, 2H), 6.88 (m, 2H), 5.86 (m, 1H), 5.21 (m, 2H), 4.48 (s, 2H), 3.80 (s, 3H), 3.52 (m, 3H), 2.88 (m, 2H), 2.56 (m, 1H), 2.34 (m, 1H), 1.93 (brs, 1H), 1.79 (m, 1H), 1.10 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 133.4, 130.5, 129.1, 119.1, 113.7, 73.0, 72.9, 68.0, 59.6, 58.1, 55.2, 40.0, 33.2, 13.8.

HRMS (ESI) Calculated for $C_{17}H_{24}O_4$ [M+Na$^+$] = 315.1567, Found 315.1561.

FTIR (neat) 3438, 2962, 2362, 1612, 1513, 1247, 1088, 1034, 820 cm^{-1}.

$[\alpha]_D^{25}$: +23.00 (*c* 1.0, $CHCl_3$).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O
H
H
PMBO
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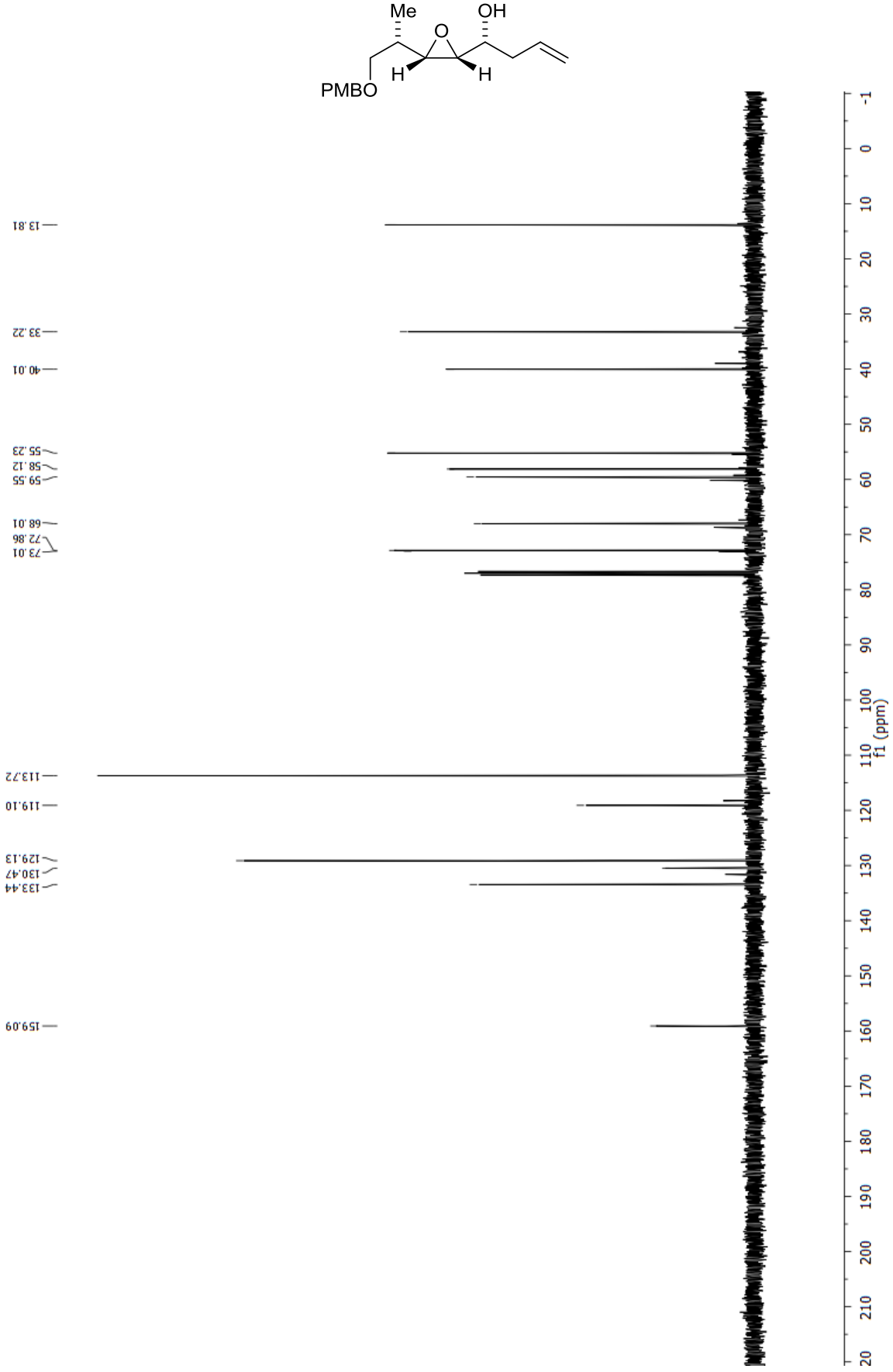
1.10
0.92
1.14
1.00
1.96
3.28
3.16
2.10
2.03
1.00
2.03
2.22
f1 (ppm)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H
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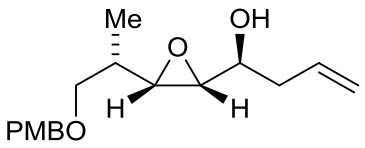
58.12
59.55
68.01
72.86
73.01
113.72
119.10
129.13
130.47
133.44
159.09
f1 (ppm)

(*S*)-1-((2*R*,3*S*)-3-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)oxiran-2-yl)but-3-en-1-ol (*epi*-2c)



Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(S)*-Cl-MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1c** (51 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (1.0 mL, 0.2 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 6:1–3:1) to furnish the title compound as a colorless oil (48.5 mg, 0.17 mmol, anti:syn = 1:6) in 83% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.29 (hexanes/ethyl acetate = 2:1).

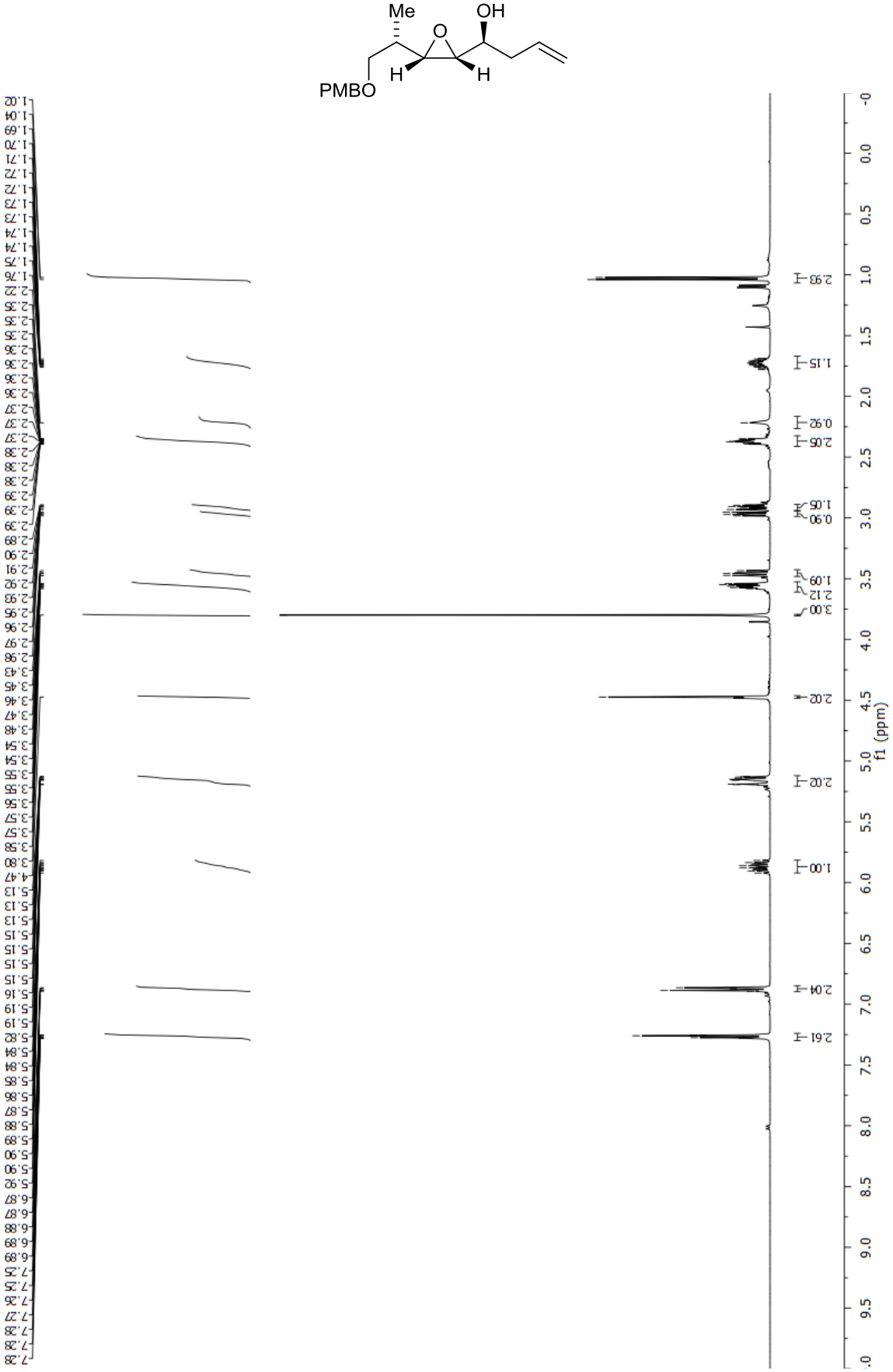
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (m, 2H), 6.87 (m, 2H), 5.86 (m, 1H), 5.16 (m, 2H), 4.47 (s, 2H), 3.80 (s, 3H), 3.56 (m, 2H), 3.45 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.97 (dd, *J* = 7.6, 4.3 Hz, 1H), 2.91 (dd, *J* = 9.5, 4.3 Hz, 1H), 2.37 (m, 2H), 2.21 (brs, 1H), 1.73 (m, 1H), 1.03 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 133.3, 130.5, 129.1, 118.2, 113.7, 72.9, 72.9, 68.7, 60.2, 59.6, 55.2, 39.0, 33.2, 14.0.

HRMS (ESI) Calculated for $C_{17}H_{24}O_4$ [M+Na$^+$] = 315.1567, Found 315.1556.

FTIR (neat) 3423, 2963, 2361, 1612, 1512, 1247, 1088, 1034, 820 cm^{-1}.

$[\alpha]_D^{25}$: +25.00 (*c* 1.0, $CHCl_3$).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H
H
PMBO
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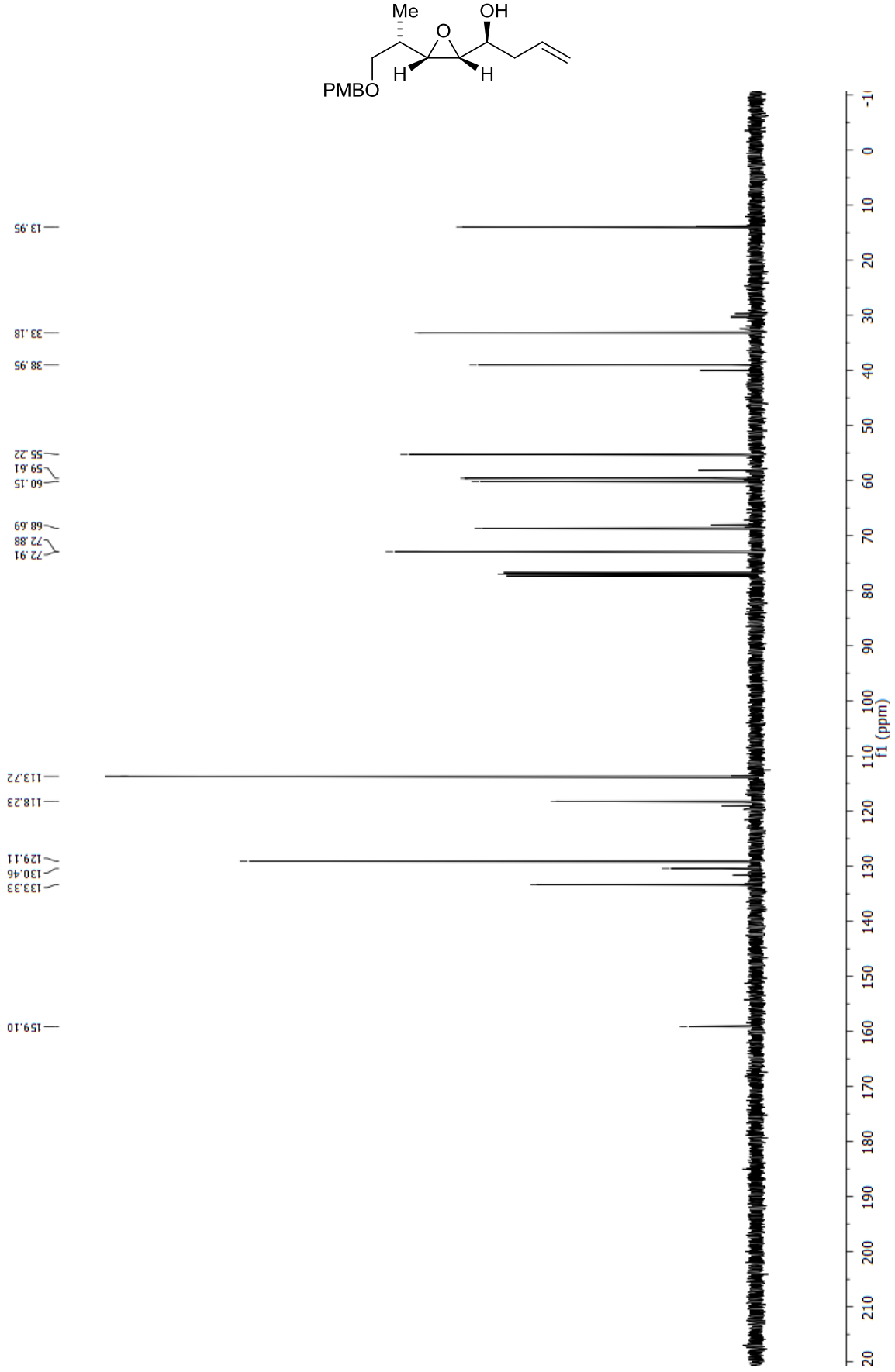
1.15
0.92
2.05
0.90
1.05
1.09
2.12
3.00
2.02
2.02
1.00
2.04
2.61
f1 (ppm)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O
H
H
PMBO
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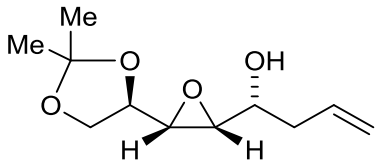
33.18
38.95
55.22
59.61
60.15
68.69
72.88
72.91
113.72
118.23
129.11
130.46
133.33
159.10
f1 (ppm)

(*R*)-1-((2*R*,3*S*)-3-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)oxiran-2-yl)but-3-en-1-ol (2d)



Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(R)*-SEGPHOS (6.1 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1d** (35 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (1.0 mL, 0.2 M) and allyl acetate (43 µL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 6:1–3:1) to furnish the title compound as a colorless oil (32.6 mg, 0.15 mmol, anti:syn = 10:1) in 76% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.42 (hexanes/ethyl acetate = 2:1).

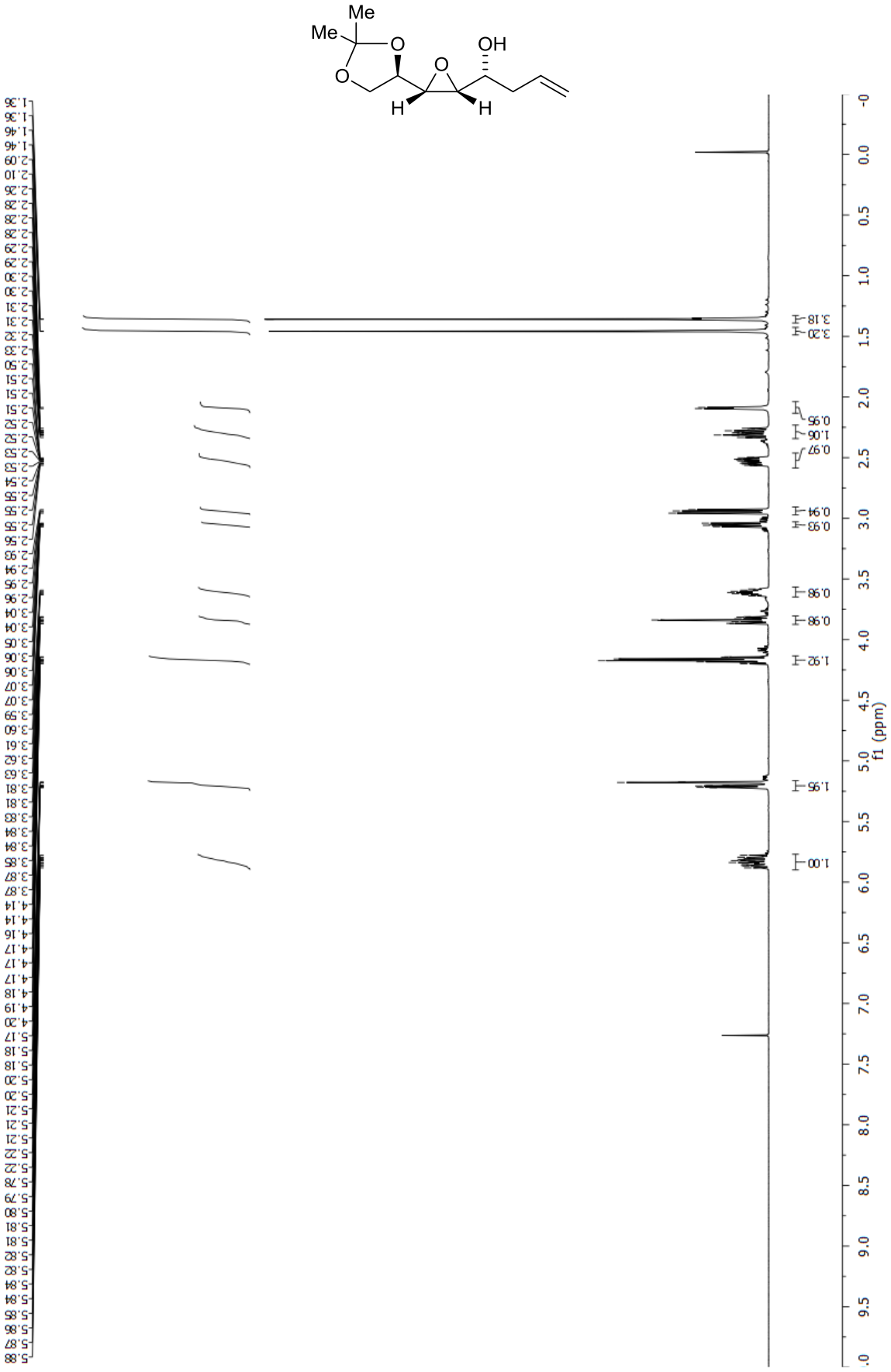
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.84 (m, 1H), 5.22 (m, 2H), 4.18 (m, 2H), 3.85 (m, 1H), 3.63 (dt, *J* = 7.7, 3.9 Hz, 1H), 3.07 (m, 1H), 2.96 (dd, *J* = 7.3, 4.3 Hz, 1H), 2.55 (m, 1H), 2.31(m, 1H), 2.11 (d, *J* = 3.7 Hz, 1H), 1.48 (s, 3H), 1.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.0, 119.3, 110.1, 74.7, 68.6, 66.5, 57.8, 57.6, 40.1, 26.5, 25.4.

HRMS (ESI) Calculated for $C_{11}H_{18}O_4$ $[M+Na^+]$ = 237.1097, Found 237.1095.

FTIR (neat) 3444, 2986, 1372, 1254, 1211,1154, 1058, 916, 840 cm^{-1}.

$[\alpha]_D^{30}$: +89.00 (*c* 1.0, $CHCl_3$).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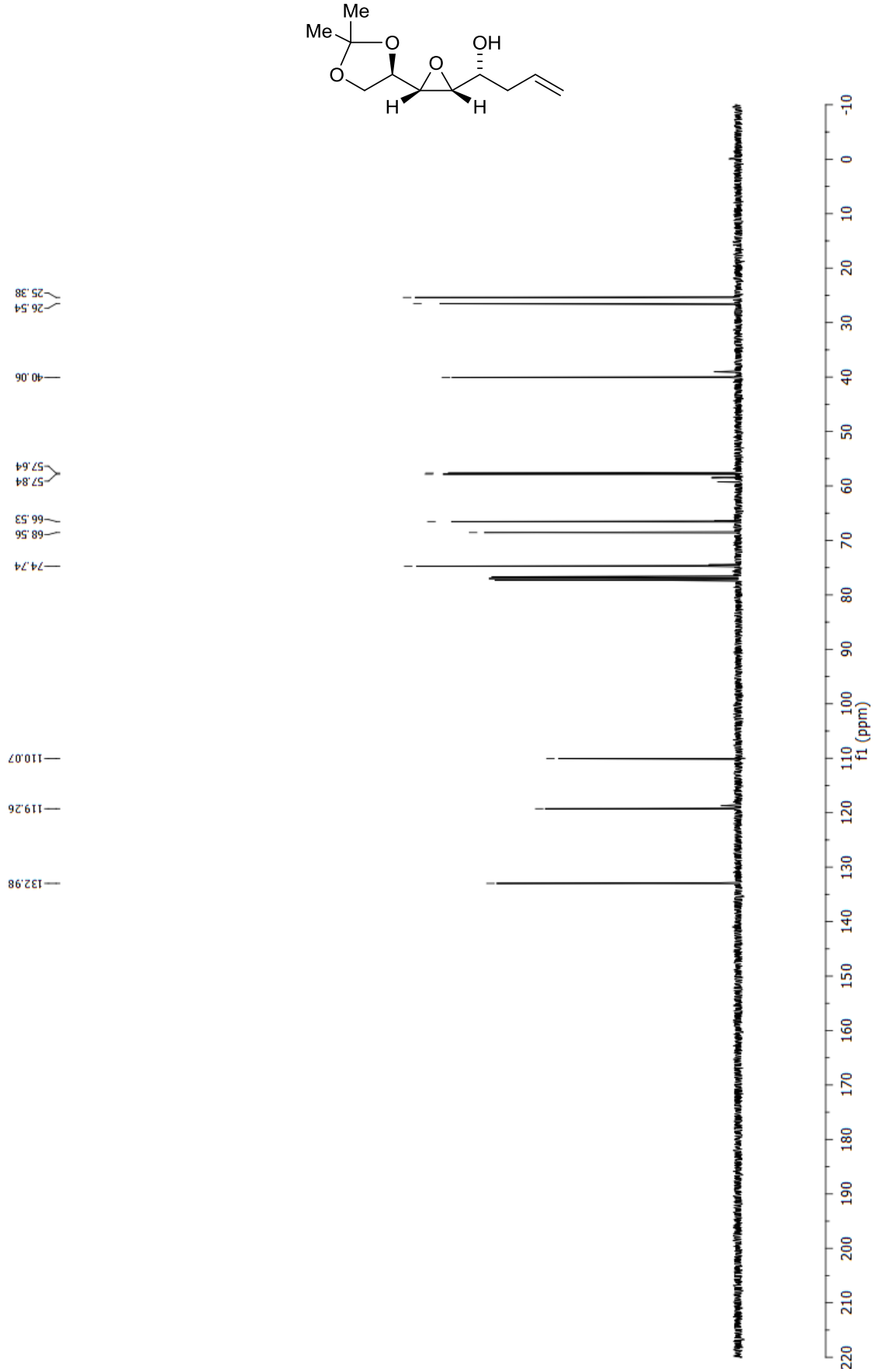
O
OH
H
H
3.18
3.20
0.95
1.06
0.97
0.94
0.93
0.98
0.98
1.92
1.95
1.00
f1 (ppm)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H
H
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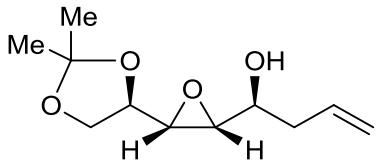
26.54
40.06
57.64
57.84
66.53
68.56
74.74
110.07
119.26
132.98
f1 (ppm)

(*S*)-1-((2*R*,3*S*)-3-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)oxiran-2-yl)but-3-en-1-ol (*epi*-2d)



Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(S)*-SEGPHOS (6.1 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1d** (35 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (1.0 mL, 0.2 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 6:1–3:1) to furnish the title compound as a colorless oil (30.9 mg, 0.14 mmol, anti:syn = 9:1) in 72% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.38 (hexanes/ethyl acetate = 2:1).

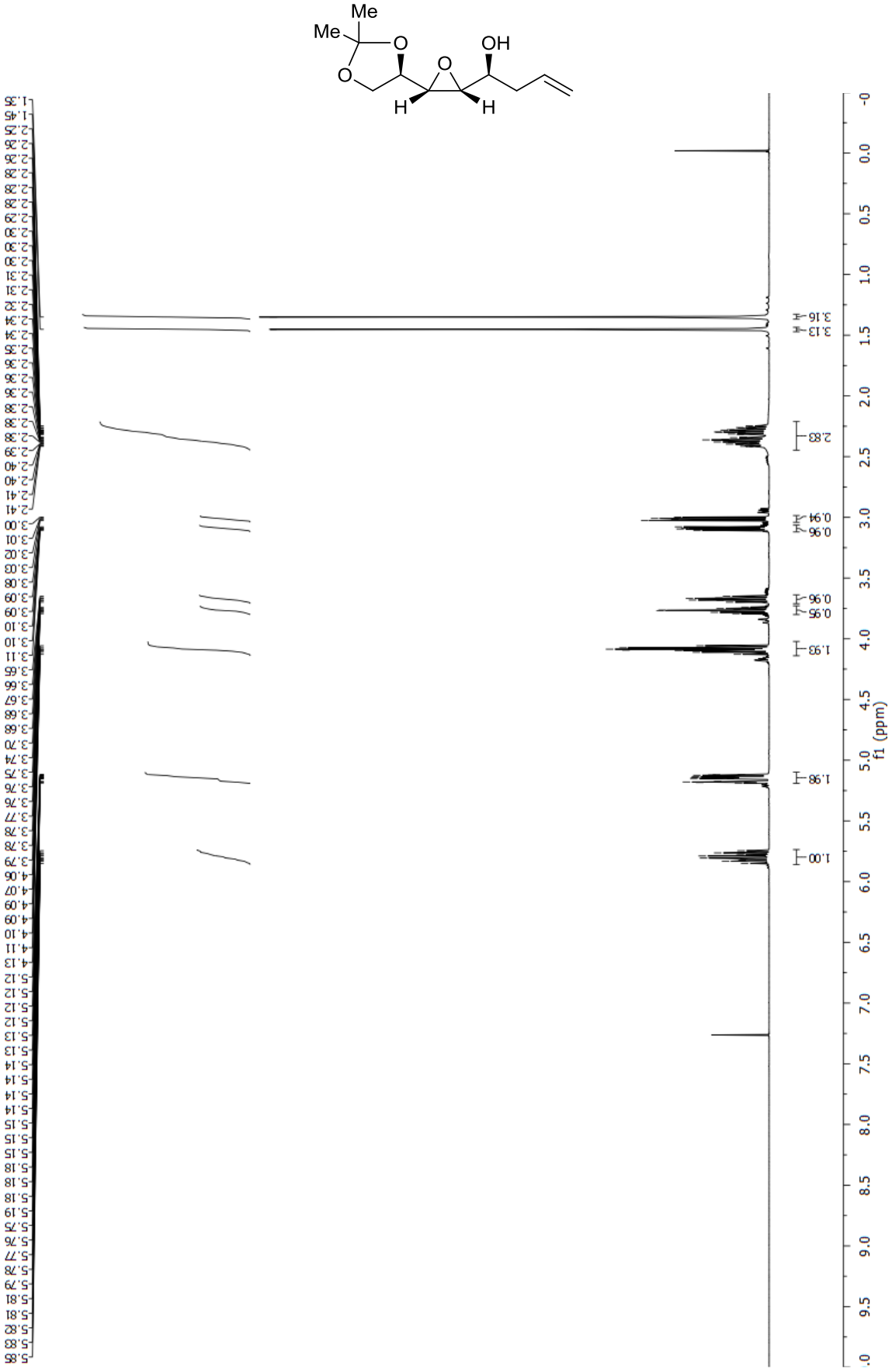
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.82 (m, 1H), 5.17 (m, 2H), 4.11 (dt, *J* = 11.2, 6.3 Hz, 2H), 3.79 (dq, *J* = 7.1, 4.1 Hz, 1H), 3.69 (td, *J* = 7.0, 5.9 Hz, 1H), 3.11 (dd, *J* = 7.1, 4.4 Hz, 1H), 3.03 (dd, *J* = 6.9, 4.4 Hz, 1H), 2.35 (m, 3H), 1.47 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.9, 118.7, 110.1, 74.5, 68.4, 66.4, 59.3, 58.5, 39.0, 26.5, 25.4.

HRMS (ESI) Calculated for $C_{11}H_{18}O_4$ [M+Na^+] = 237.1097, Found 237.1094.

FTIR (neat) 3452, 2985, 1372, 1255, 1211,1154, 1057, 915, 843 cm^{-1}.

$[\alpha]_D^{30}$: +127.33 (*c* 1.0, $CHCl_3$).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O
OH
H
H
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0.96
0.96
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1.93
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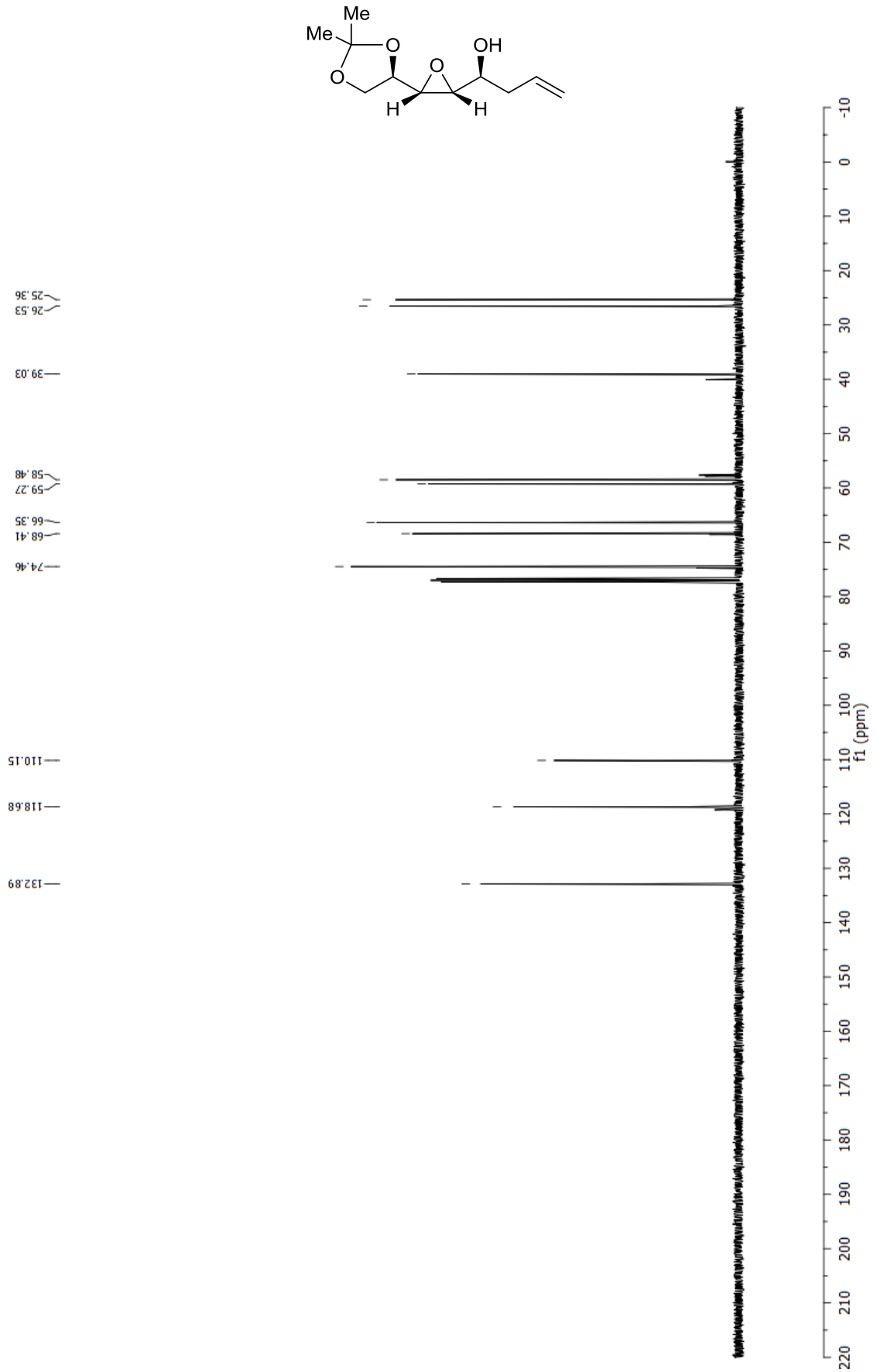
1.00
f1 (ppm)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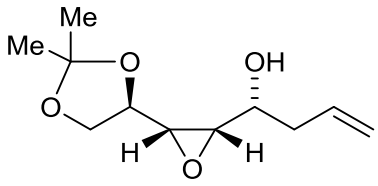
Me
O
O
O
OH
H
H
25.36
26.53
39.03
58.48
59.27
66.35
68.41
74.46
110.15
118.68
132.89
f1 (ppm)

(*R*)-1-((2*S*,3*R*)-3-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)oxiran-2-yl)but-3-en-1-ol (2e)



Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(R)*-SEGPHOS (6.1 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1e** (35 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (1.0 mL, 0.2 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 6:1–3:1) to furnish the title compound as a colorless oil (33.9 mg, 0.16 mmol, anti:syn = 1:10) in 79% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.52 (hexanes/ethyl acetate = 2:1).

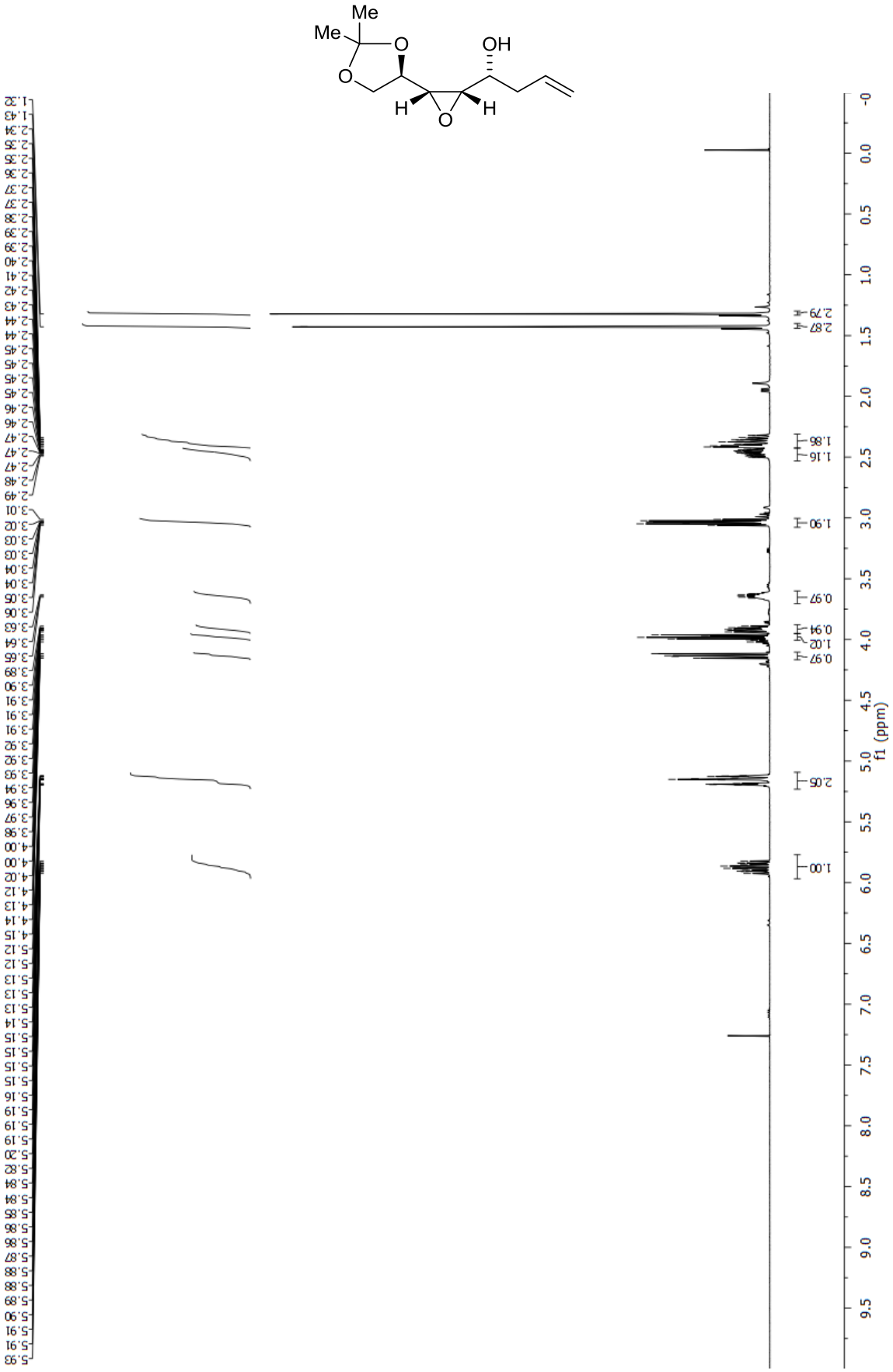
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.88 (m, 1H), 5.16 (m, 2H), 4.14 (dd, *J* = 8.5, 6.1 Hz, 1H), 4.14 (dd, *J* = 8.5, 5.1 Hz, 1H), 3.92 (m, 1H), 3.65 (m, 1H), 3.04 (m, 2H), 2.47 (m, 1H), 2.37 (m, 2H), 1.45 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.4, 118.4, 109.8, 73.4, 69.0, 68.2, 60.0, 57.4, 38.4, 26.8, 25.2.

HRMS (ESI) Calculated for $C_{11}H_{18}O_4$ $[M+Na^+]$ = 237.1097, Found 237.1094.

FTIR (neat) 3447, 2985, 2936, 1642, 1436, 1372, 1253, 1222, 1152, 1065, 918, 845 cm^{-1}.

$[\alpha]_D^{27}$: −108.33 (*c* 1.0, $CHCl_3$).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H
O
H
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1.16
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0.97
0.91
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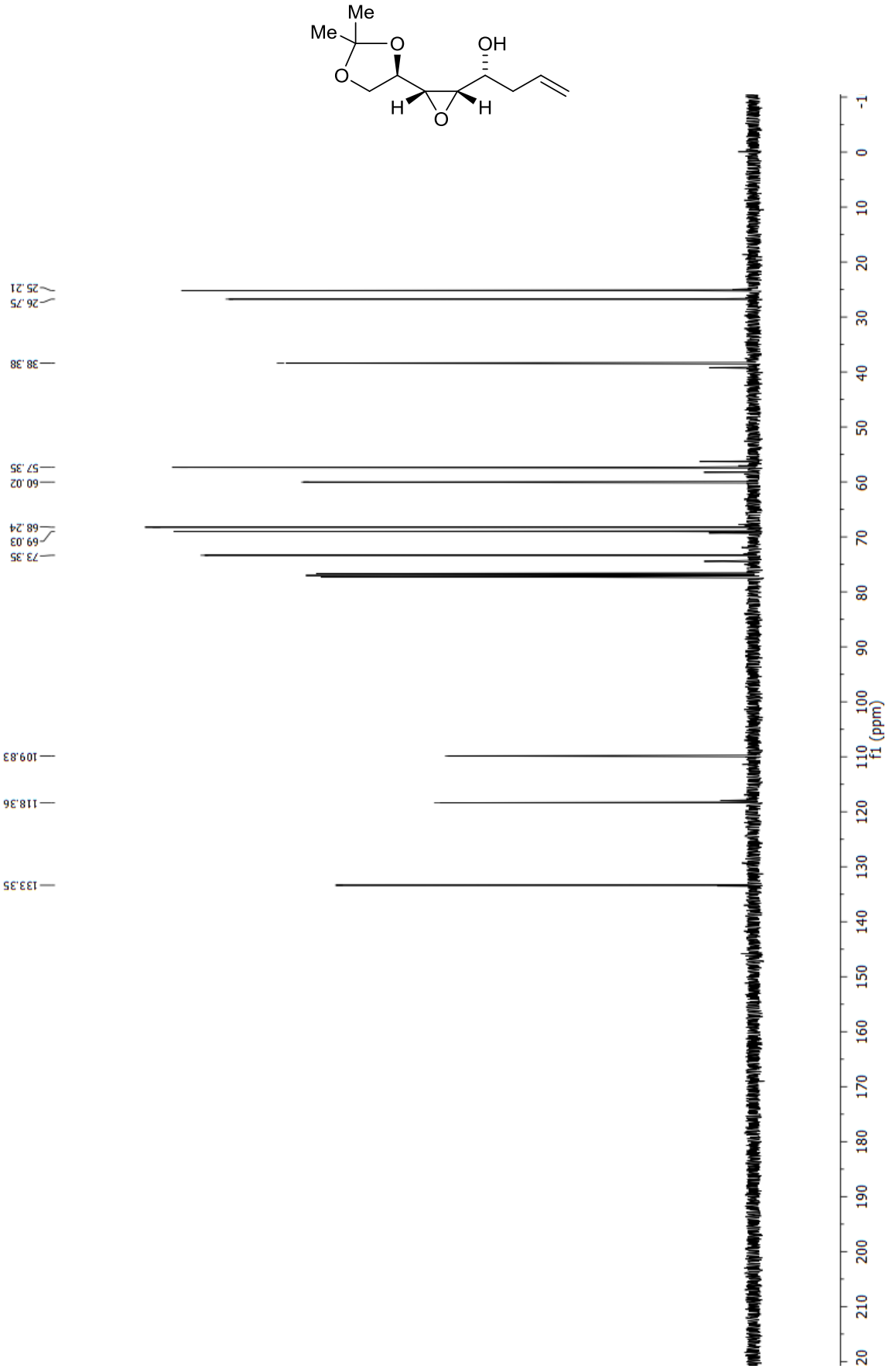
0.97
2.05
1.00
f1 (ppm)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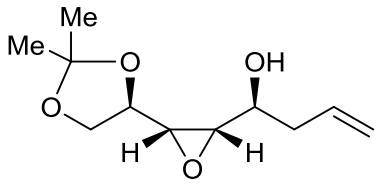
OH
H
O
H
25.21
26.75
38.38
57.35
60.02
68.24
69.03
73.35
109.83
118.36
133.35
f1 (ppm)

(*S*)-1-((2*S*,3*R*)-3-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)oxiran-2-yl)but-3-en-1-ol (*epi*-2e)



Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(S)*-SEGPHOS (6.1 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1e** (35 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (1.0 mL, 0.2 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 6:1–3:1) to furnish the title compound as a colorless oil (31.7 mg, 0.15 mmol, anti:syn = 6:1) in 74% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.48 (hexanes/ethyl acetate = 2:1).

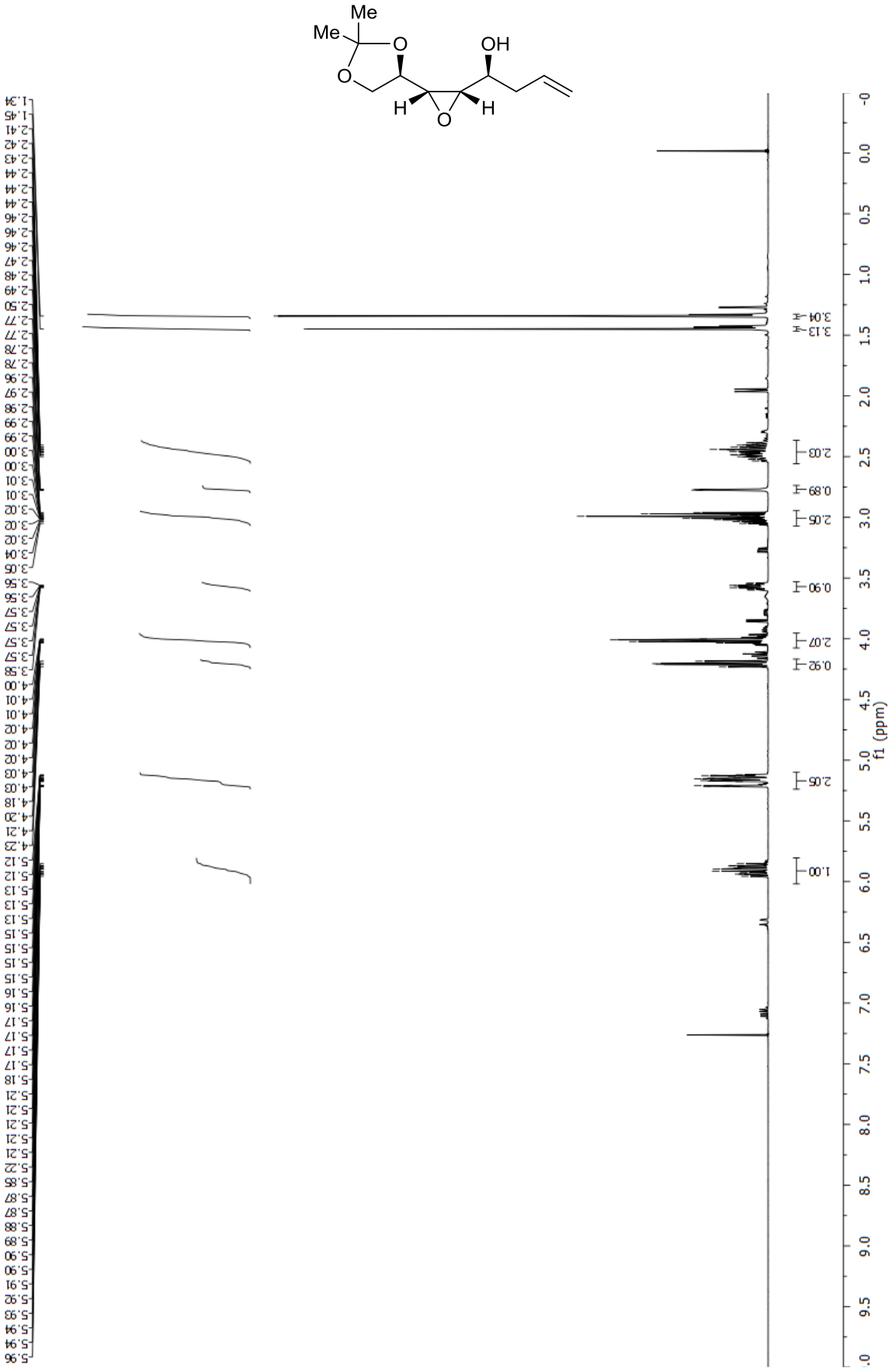
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.90 (m, 1H), 5.17 (m, 2H), 4.20 (m, 1H), 4.02 (m, 1H), 3.57 (m, 1H), 3.00 (m, 2H), 2.77 (dd, *J* = 2.4, 0.8 Hz, 1H), 2.44 (m, 2H), 1.45 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.5, 118.0, 109.8, 74.5, 69.4, 68.4, 58.2, 56.3, 39.2, 26.7, 25.1.

HRMS (ESI) Calculated for $C_{11}H_{18}O_4$ [M+Na^+] = 237.1097, Found 237.1095.

FTIR (neat) 3447, 2985, 2936, 1642, 1436, 1372, 1253, 1222, 1152, 1065, 918, 845 cm^{-1}.

$[\alpha]_D^{26}$: −126.33 (*c* 1.0, $CHCl_3$).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H
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H
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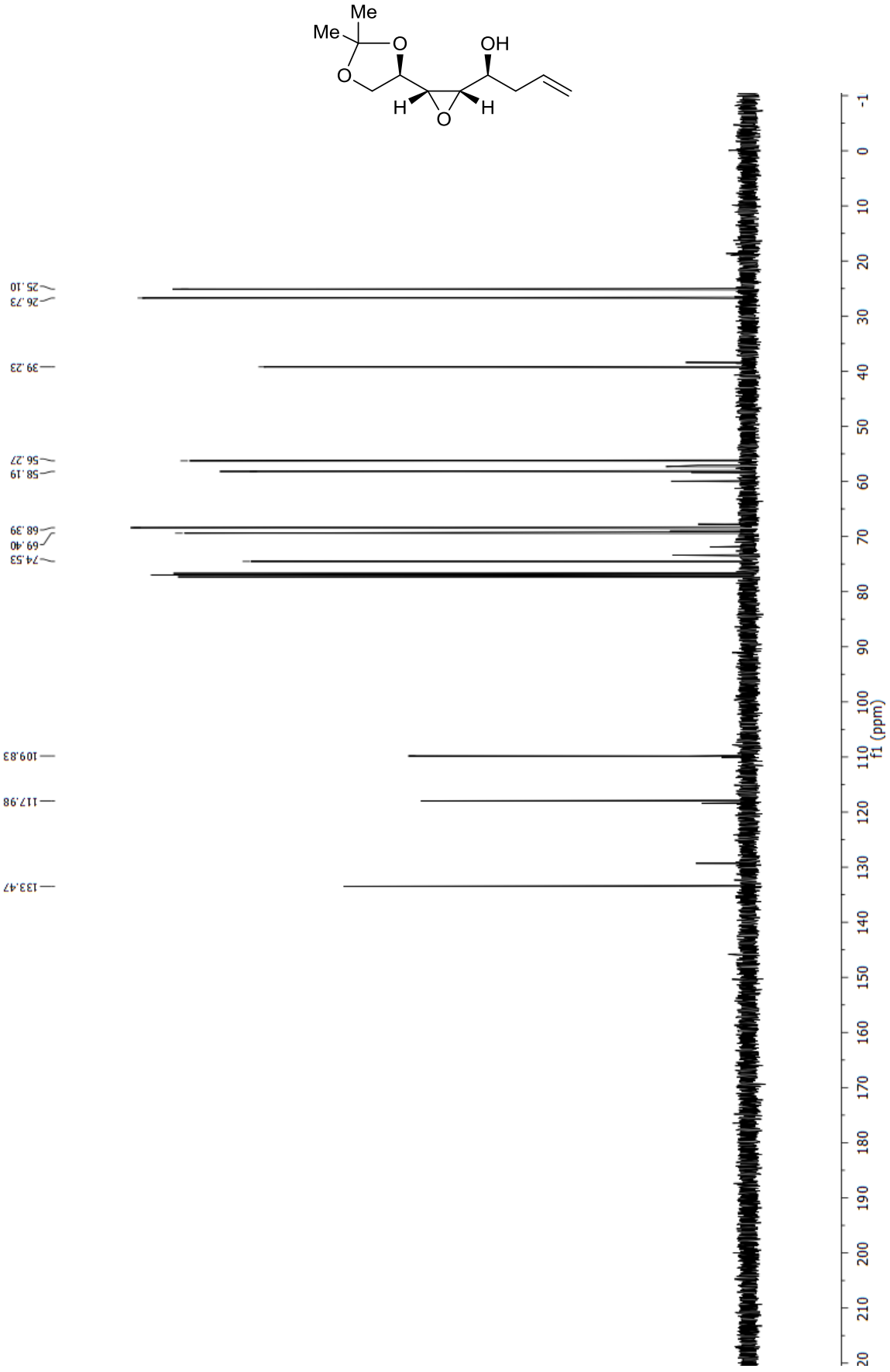
0.92
2.06
1.00
f1 (ppm)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OH
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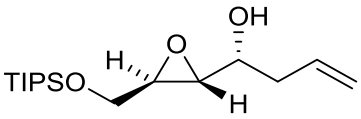
O
H
25.10
26.73
39.23
56.27
58.19
68.39
69.40
74.53
109.83
117.98
133.47
f1 (ppm)

(*R*)-1-((2*R*,3*R*)-3-(((triisopropylsilyl)oxy)methyl)oxiran-2-yl)but-3-en-1-ol (2f)



Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(R)*-Cl-MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1f** (52 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (1.0 mL, 0.2 M) and allyl acetate (43 µL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 15:1–12:1) to furnish the title compound as a colorless oil (39.1 mg, 0.13 mmol, anti:syn = 17:1) in 65% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.58 (hexanes/ethyl acetate = 4:1).

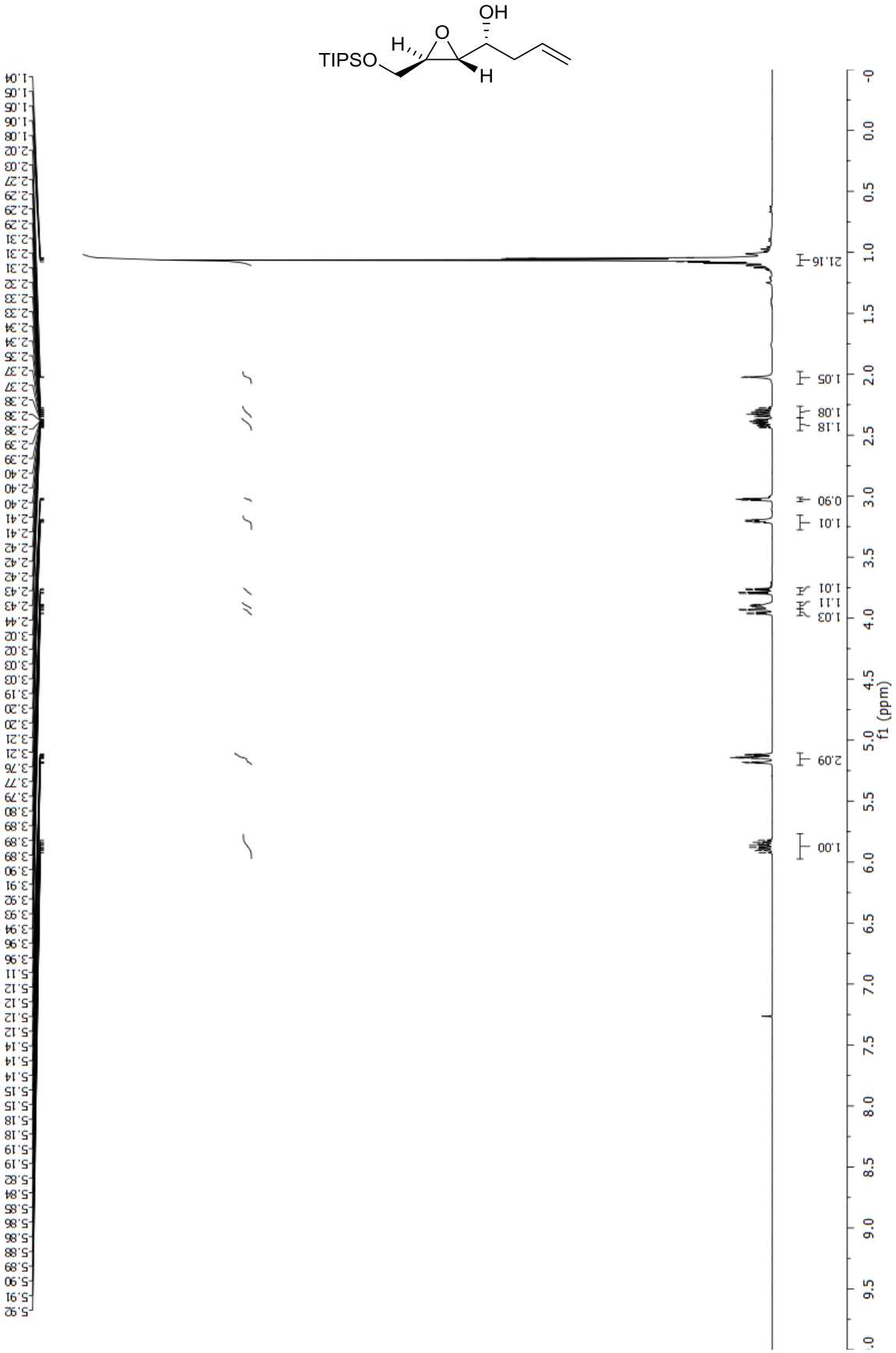
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.87 (m, 1H), 5.14 (m, 2H), 3.94 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.89 (m, 1H), 3.77 (dd, *J* = 11.8, 4.5 Hz, 1H), 3.20 (m, 1H), 3.02 (dd, *J* = 3.3, 2.3 Hz, 1H), 2.40 (m, 1H), 2.31 (m ,1H), 2.02 (brs, 1H), 1.05 (m, 21H).

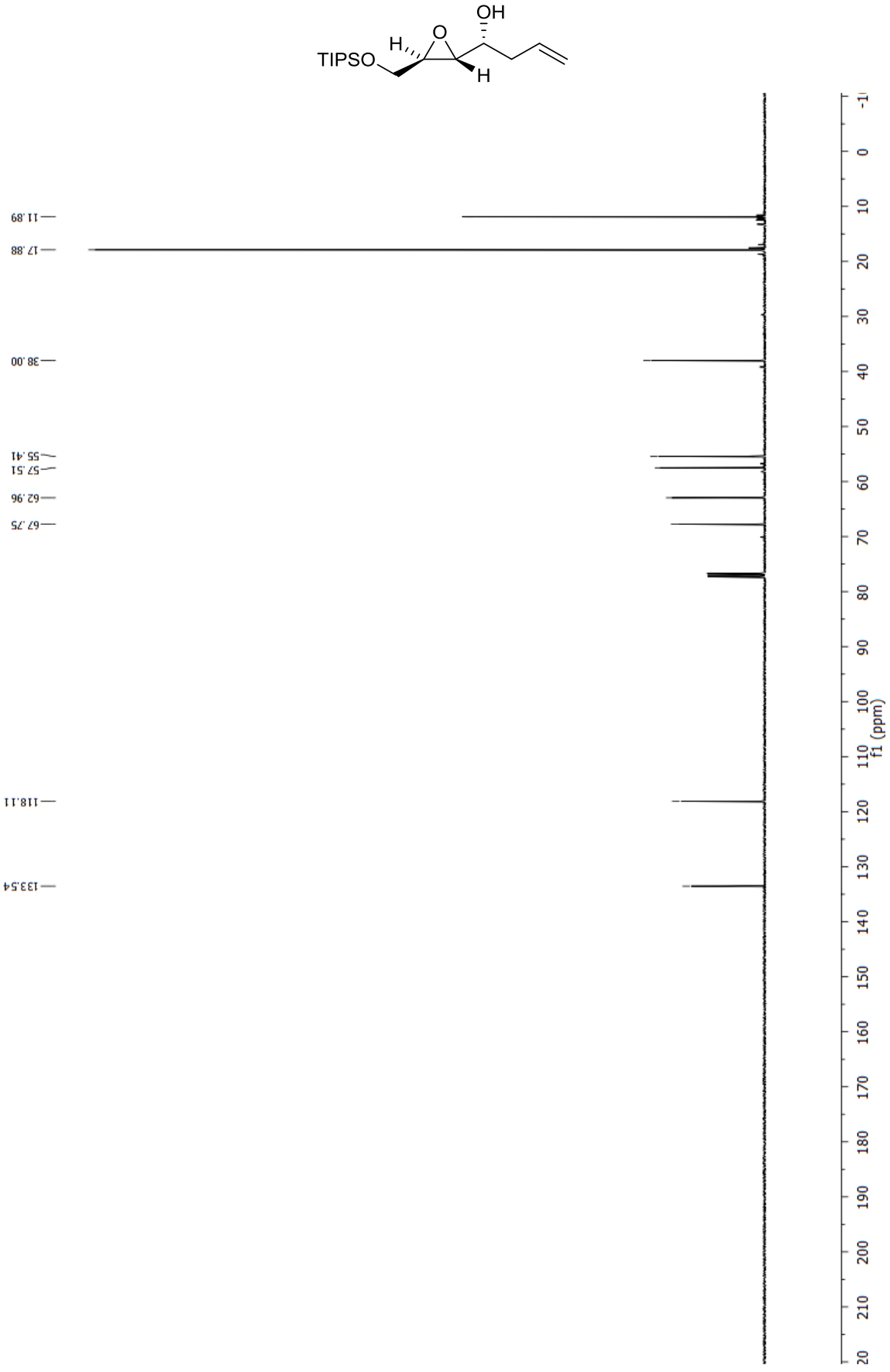
^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.5, 118.1, 67.8, 63.0, 57.5, 55.4, 38.0, 17.9, 11.9.

HRMS (ESI) Calculated for $C_{16}H_{32}O_3Si$ $[M+Na^+]$ =323.2013, Found 323.2013.

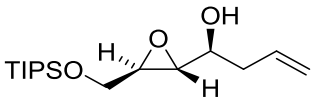
FTIR (neat) 3438, 2942, 1463, 1114, 1067, 996, 882, 777, 682 cm^{-1}.

$[\alpha]_D^{30}$: +106.00 (*c* 1.0, $CHCl_3$).


OH
O
H
TIPSO
H
21.16
1.05
1.18
1.08
0.90
1.01
1.01
1.11
1.03
2.09
1.00
f1 (ppm)


OH
O
H
TIPSO
H
11.89
17.88
38.00
55.41
57.51
62.96
67.75
118.11
133.54
f1 (ppm)

(*S*)-1-((2*R*,3*R*)-3-(((triisopropylsilyl)oxy)methyl)oxiran-2-yl)but-3-en-1-ol (*epi*-2f)



Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mol%), *(S)*-Cl-MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), 4-CN,3-NO-benzoic acid (3.8 mg, 0.02 mmol, 10 mol%), alcohol **1f** (52 mg, 0.2 mmol, 100 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 50 mol%). The vessel was purged with argon for 5 minutes. Anhydrous THF (1.0 mL, 0.2 M) and allyl acetate (43 μL, 0.4 mmol, 200 mol%) were sequentially added via syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 100 ˚C for 48 h. After reaching ambient temperature, the reaction mixture was concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 15:1–12:1) to furnish the title compound as a colorless oil (19.2 mg, 0.06 mmol, anti:syn = 1:7) in 32% yield.

Spectral data is reported for the major isomer.

TLC (SiO_2) R_f = 0.54 (hexanes/ethyl acetate = 4:1).

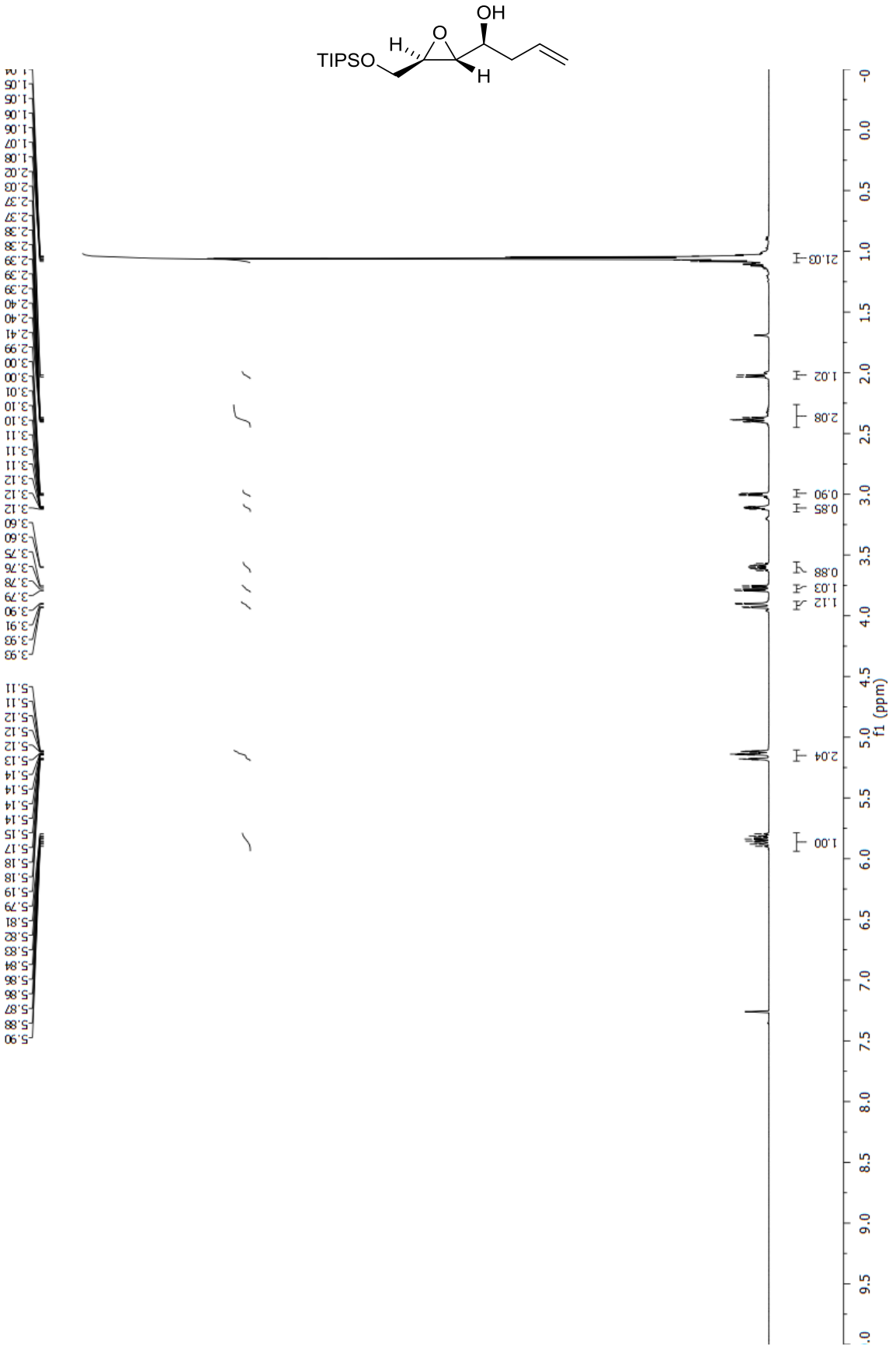
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85 (m, 1H), 5.14 (m, 2H), 3.92 (dd, *J* = 11.7, 2.9 Hz, 1H), 3.77 (dd, *J* = 11.8, 4.5 Hz, 1H), 3.60 (m, 1H), 3.11 (ddd, *J* = 4.6, 3.1, 2.3 Hz, 1H), 3.00 (dd, *J* = 4.7, 2.3 Hz, 1H), 2.39 (m, 2H), 2.03 (m, 1H), 1.06 (m, 21H).

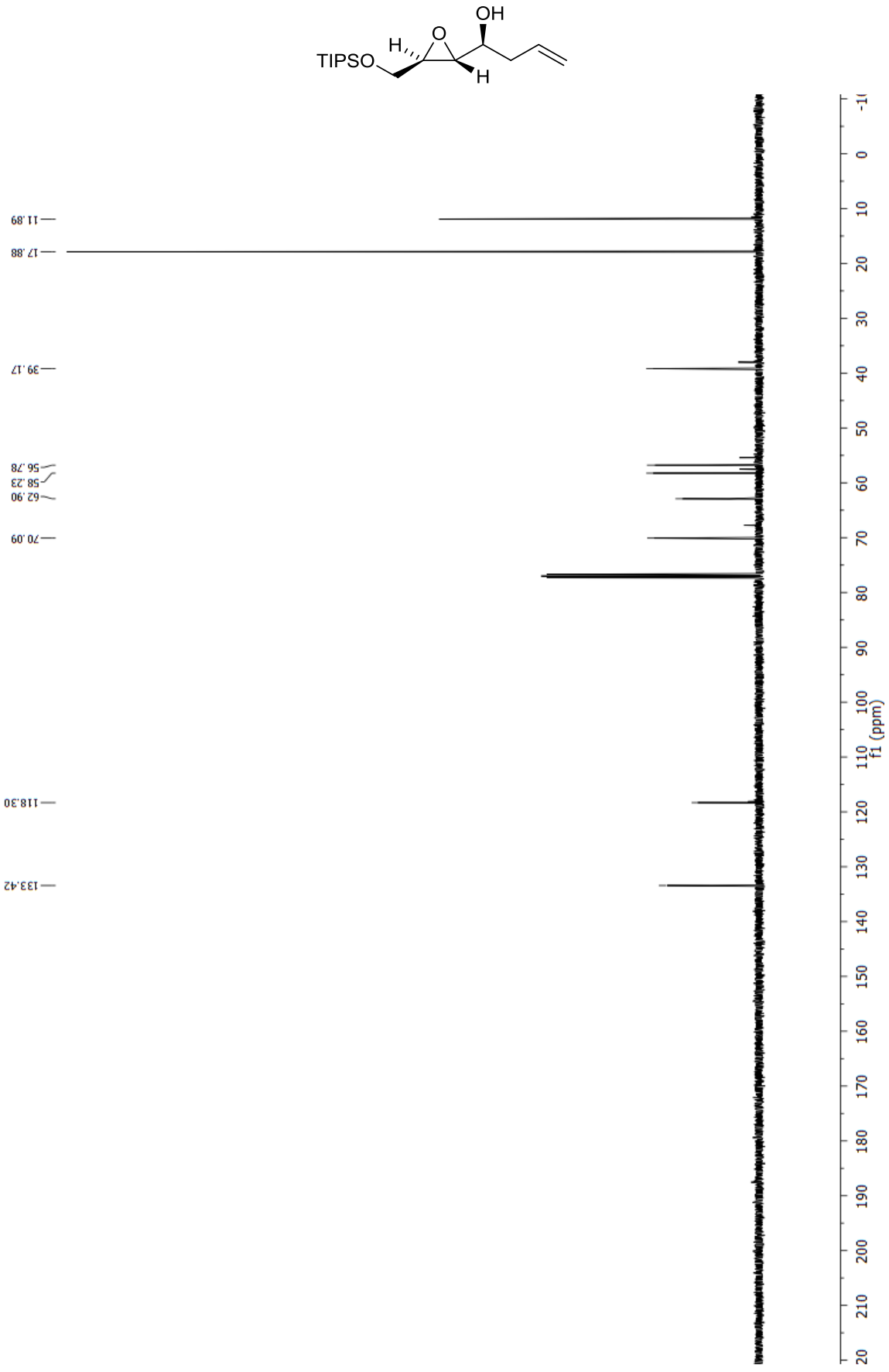
^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.4, 118.3, 70.1, 62.9, 58.2, 56.8, 39.2, 17.9, 11.9.

HRMS (ESI) Calculated for $C_{16}H_{32}O_3Si$ $[M+Na^+]$ =323.2013, Found 323.2014.

FTIR (neat) 3426, 2942, 1463, 1112, 1067, 996, 882, 781, 682 cm^{-1}.

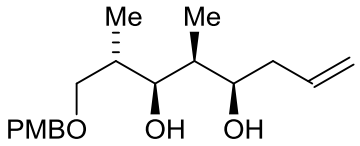
$[\alpha]_D^{30}$: +107.33 (*c* 1.0, $CHCl_3$).


OH
O
H
TIPSO
H
21.03
1.02
2.08
0.90
0.85
0.88
1.03
1.12
2.04
1.00
f1 (ppm)


OH
O
H
TIPSO
H
11.89
17.88
39.17
56.78
58.23
62.90
70.09
118.30
133.42
f1 (ppm)

Procedures and Spectral Data for the Synthesis of 3c

(2*S*,3*S*,4*S*,5*R*)-1-((4-methoxybenzyl)oxy)-2,4-dimethyloct-7-ene-3,5-diol (3c)



Detailed Procedures

To a round-bottomed flask charged with **2c** (30.0 mg, 0.10 mmol) under an argon atmosphere was added 1,2-dichloroethane (3.0 mL, 0.03 M). The reaction vessel was placed in -40 ºC bath and *n*-BuLi (80 µL, 2.5 M in hexanes, 0.25 mmol, 200 mol%) was added. The mixture was stirred for 30 minutes, at which point trimethyl aluminum (0.16 mL, 2.0 M in toluene, 0.31 mmol, 300 mol%) was added dropwise. The mixture was allowed to warm to -15 ºC over 4 h. Water (3 mL) was added to the reaction mixture and reaction the mixture was transferred to a separatory funnel. The aqueous layer was extracted with CH_2Cl_2 (10 mL × 3) and the combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting oily residue was subjected to flash column chromatography (SiO_2, hexanes: ethyl acetate = 7:1–4:1) to furnish the title compound as a colorless oil (23.7 mg, 0.08 mmol) in 77% yield.

TLC (SiO_2) R_f = 0.40 (hexanes/ethyl acetate = 2:1).

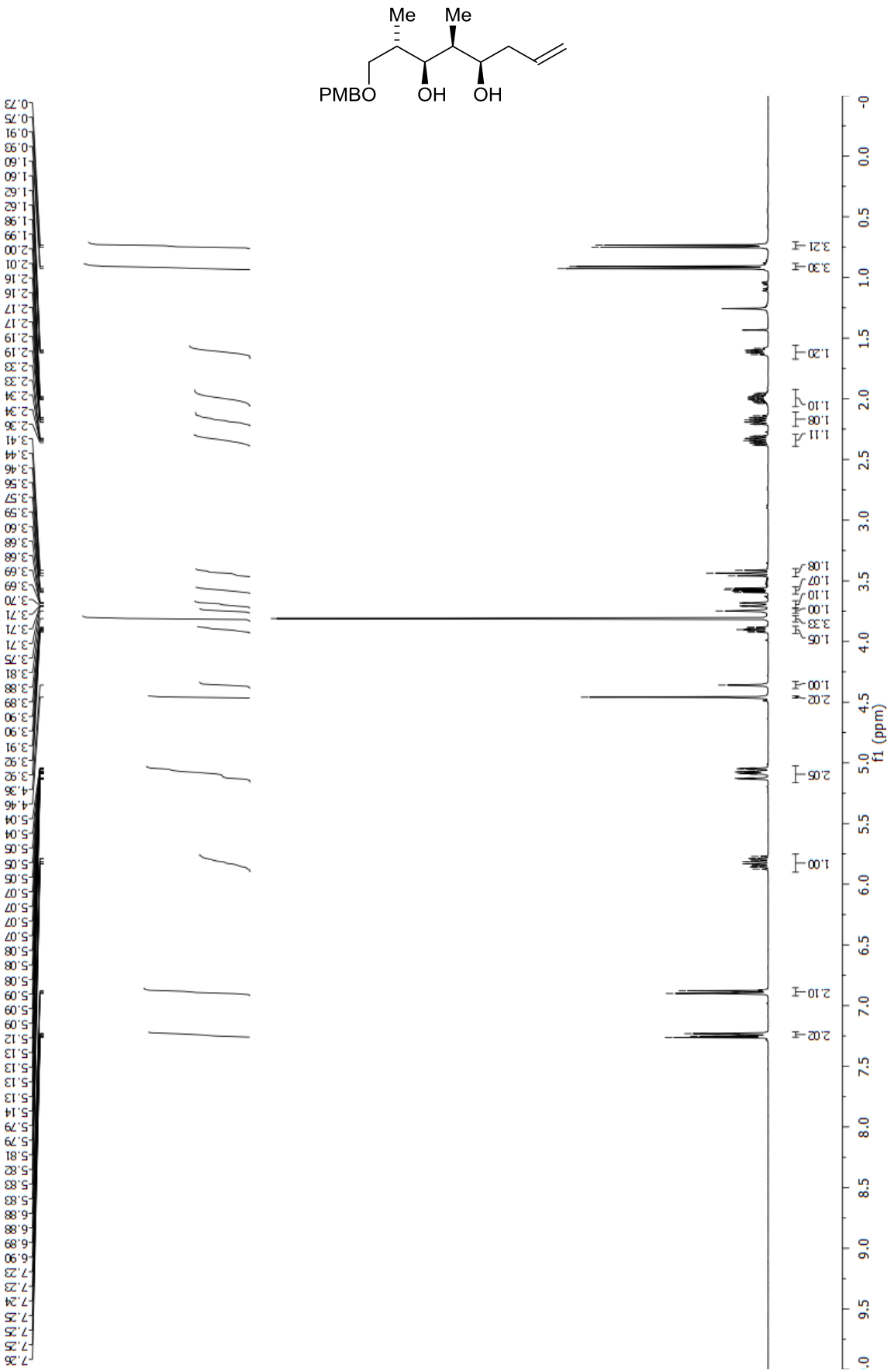
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (m, 2H), 6.89 (m, 2H), 5.82 (m, 1H), 5.09 (m, 2H), 4.46 (s, 2H), 4.36 (brs, 1H), 3.90 (ddd, *J* = 7.8, 6.3, 1.8 Hz, 1H), 3.81 (s, 3H), 3.75 (brs, 1H), 3.70 (m, 1H), 3.58 (dd, *J* = 9.1, 4.0 Hz, 1H), 3.44 (t, *J* = 9.2 Hz, 1H), 2.34 (m, 1H), 2.17 (m, 1H), 2.00 (m, 1H), 1.61 (m, 1H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.74 (d, *J* = 6.9 Hz, 3H).

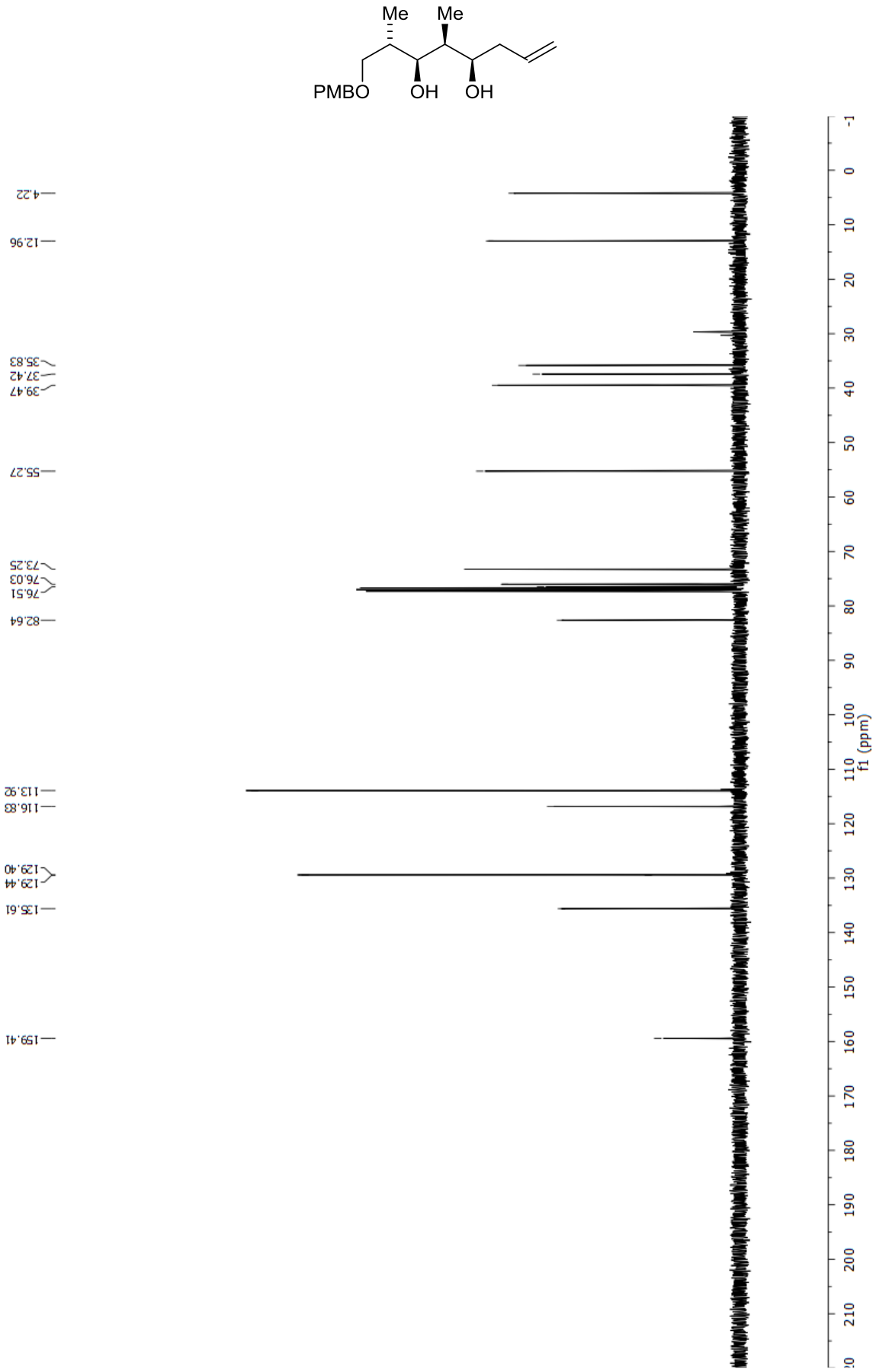
^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 135.6, 129.4, 129.4, 116.8, 113.9, 82.6, 76.5, 76.0, 73.3, 55.3, 39.5, 37.4, 35.8, 13.0, 4.2.

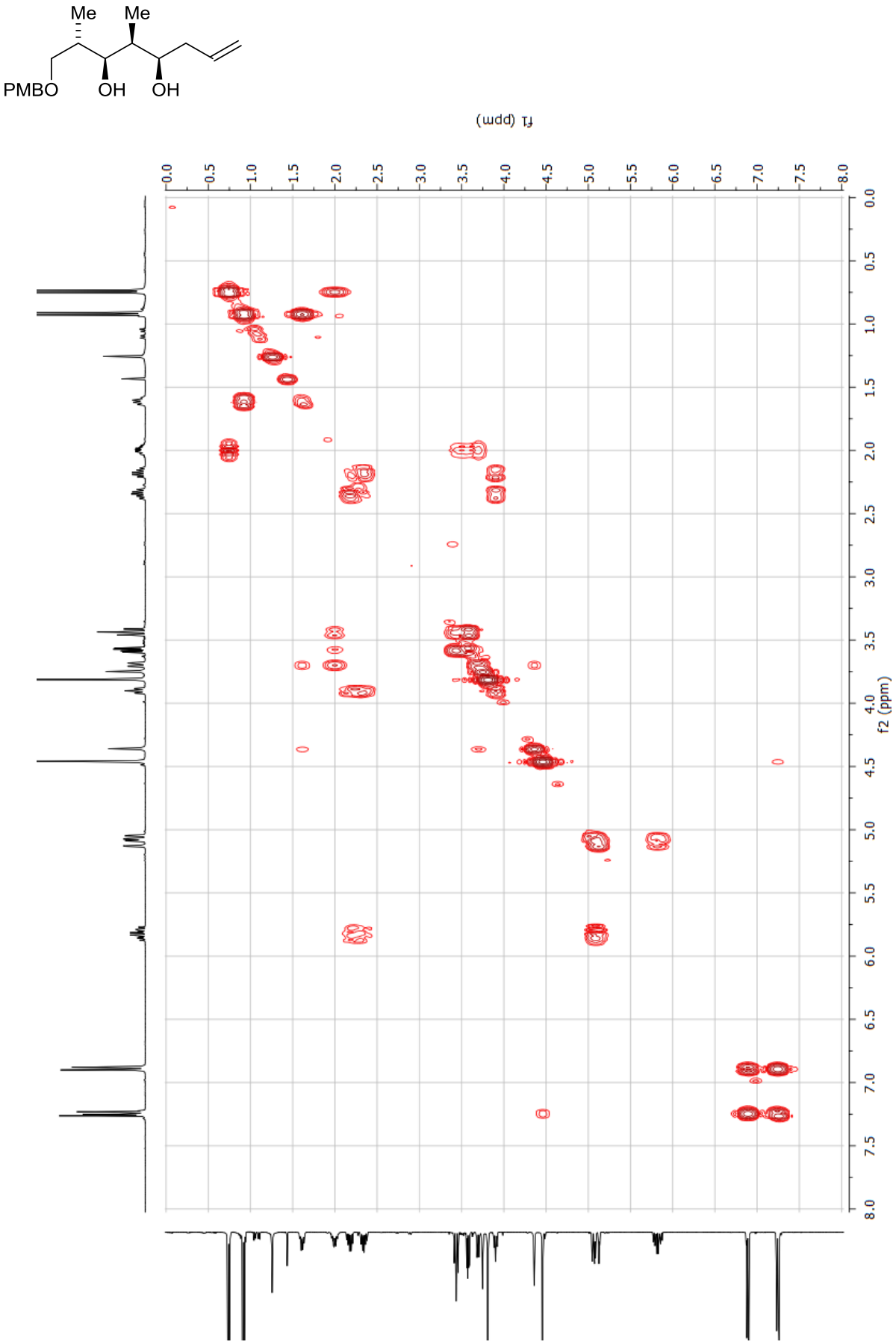
HRMS (ESI) Calculated for $C_{18}H_{28}O_4$ [M+K$^+$] = 347.1619, Found 347.1611.

FTIR (neat) 3431, 2915, 1612, 1513, 1247, 1079, 1035, 970, 753 cm^{-1}.

$[\alpha]_D^{30}$: +42.83 (*c* 1.0, $CHCl_3$).

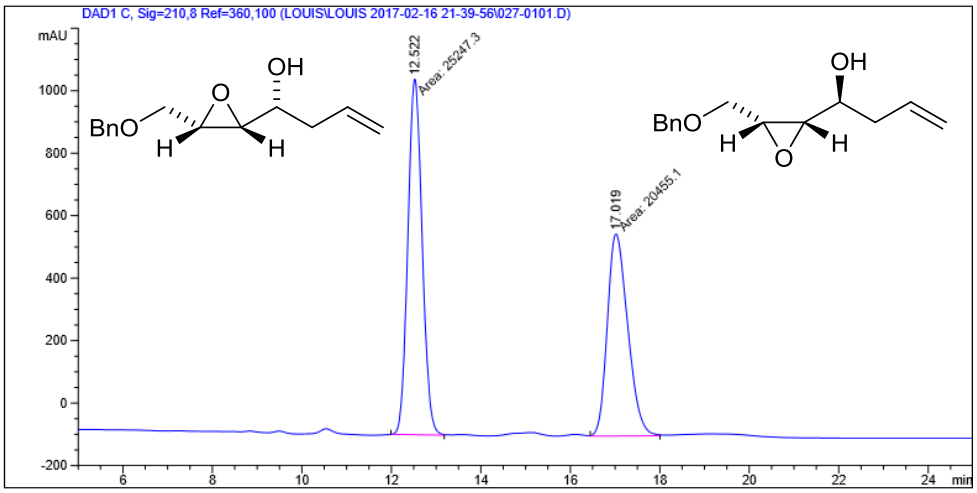

Me
Me
PMBO
OH
OH
f1 (ppm)


Me
Me
PMBO
OH
OH
4.22
12.96
35.83
37.42
39.47
55.27
73.25
76.03
76.51
82.64
113.92
116.83
129.40
129.44
135.61
159.41
f1 (ppm)


Me
Me
PMBO
OH
OH
f1 (ppm)
f2 (ppm)

HPLC Data Establishing the Horeau Effect in the Allylation of Glycidols 2a

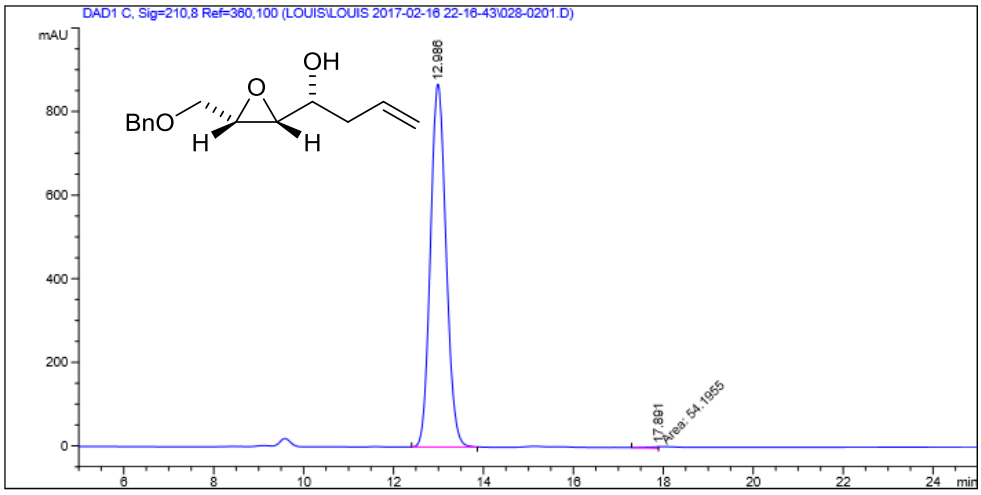
*Authentic sample of racemic epoxides **2b** prepared by mCPBA epoxidation of O-benzyl-cis-butene diol followed by glycidol allylation using the iridium catalyst modified by racemic Cl,MeO-BIPHEP. The resulting racemic diastereomeric mixture was separated by flash silica gel chromatography.*



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.522	MM	0.3696	2.52473e4	1138.46338	55.2428
2	17.019	MM	0.5271	2.04551e4	646.80481	44.7572
Totals :				4.57024e4	1785.26819	

*Enantiomerically enriched glycidol **2b** (99.5% ee) prepared via asymmetric allylation of **1b** (87% ee) using the iridium catalyst modified by (R)-Cl,MeO-BIPHEP. Increased enantiomeric purity of glycidol **2b** is due to the Horeau effect.*



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.986	BB	0.3752	2.09295e4	868.34589	99.7417
2	17.891	MM	0.2433	54.19551	3.71199	0.2583
Totals :				2.09837e4	872.05788	

Both chromatograms were obtained on a Chiralcel OD-H column (hexanes:*i*-PrOH = 90:10, 1.00 mL/min, 210 nm)

References:

1. Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.
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3. Nacro, K.; Baltas, M.; Escudier, J. M.; Gorrichon, L. *Tetrahedron* **1996**, *52*, 9047.
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