Supporting Information

Asymmetric Ruthenium-Catalyzed Carbonyl Allylations by Gaseous Allene via Hydrogen Auto-Transfer: 1º vs 2º Alcohol Dehydrogenation Streamlines Polyketide Construction

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General Information

All reactions were run under an atmosphere of argon, unless otherwise indicated. Resealable pressure tubes (13x100 mm) were purchased from Fischer Scientific (catalog number 14–959–35C) and were flame dried followed by cooling in a desiccator or under a stream of argon prior to use. All commercial reagents $Ru_3(CO)_{12}$, allyl Iodide, Sl-J502-1, Sl-J502-2, dippf) and anhydrous solvents were used as received from vendors (Strem Chemicals, Fischer Scientific, Sigma Aldrich and Combi-Blocks) without further purification. Purification of reaction products was carried out by flash column chromatography using 40-63 μm silica gel. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Dynamic Absorbents F254).

Spectroscopy, Spectrometry, and Data Collection

Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were isolated on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+, M+H, M+Na), or a suitable fragment ion. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian INOVA (400, 500 MHz) spectrometer equipped with a Bruker AVANCE III cryoprobe. Data reported as multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Integration and coupling constants were reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian INOVA (101, 126 MHz) spectrometer and were routinely run with broadband decoupling. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were recorded with a Varian INOVA (390, 470 MHz) spectrometer. Deuterium nuclear magnetic resonance (^{2}H NMR) spectra were recorded in $CHCl_3$ solution with a Varian Gemini 500 (92 MHz) spectrometer (relaxation delay 2.00s).

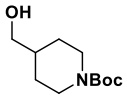
Known Dienes

1a
commercial

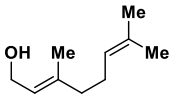
1b
commercial

Known Alcohols

2a
commercial



2b
commercial



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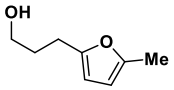
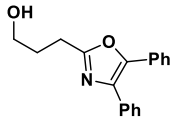
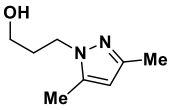


2d
ref. 1



2e
commercial



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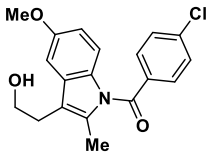

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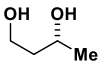
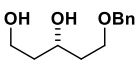
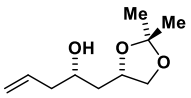


2h
commercial

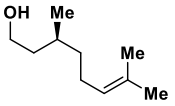


2i
ref. 4

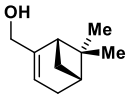


2j
commercial

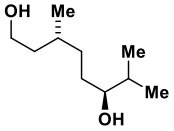
2k
ref. 5



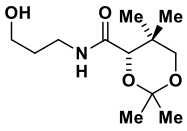
2l
commercial



2m
commercial



2n
commercial



2o
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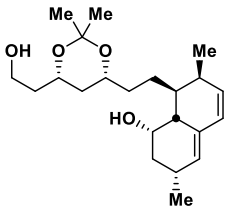

2p
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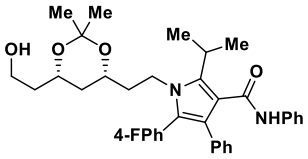

2q
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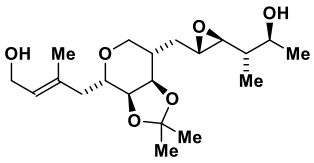
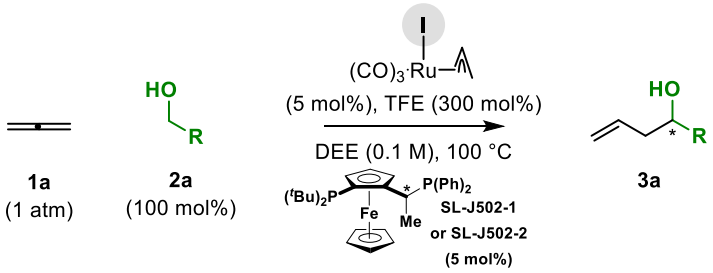


2r
ref. 6

Products 3a-3r

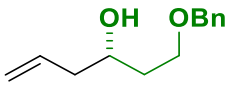
General Procedure



An oven-dried pressure tube equipped with a magnetic stir bar was charged with alcohol **2a-2r** (0.2 mmol, 100 mol%), $RuI(CO)_3(\eta_3\text{-}C_3H_5)$ (0.2 mmol, 5 mol%), **SL-J502-1** (0.2 mmol, 5 mol%) or **SL- J502-2** (0.2 mmol, 5 mol%) under an argon atmosphere. The vessel was evacuated and backfilled with allene gas **1a** (1 atm), followed by the addition of trifluoroethanol (43 μL, 0.6 mmol, 300 mol%) and freshly distilled DEE (2.0 mL, 0.1 M). The reaction mixture was cooled to 0 °C and allowed to stir for 5 minutes. The tube was sealed with a PTFE lined cap and the reaction vessel was placed in a 110 °C bath and stirred for 48 hours. After reaching ambient temperature, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (SiO_2) under the noted conditions to furnish products **3a**-**3r**. Diastereomeric ratios were determined by ^1H NMR of crude reaction mixtures and enantiomeric excesses were determined by chiral stationary phase HPLC.

Racemic reactions were performed using dppf (2.2 mg, 0.01 mmol, 5 mol%) as ligand.

(S)-1-(benzyloxy)hex-5-en-3-ol (3a)



Alcohol **2a** (498.6 mg, 3.0 mmol) was subjected to standard reaction conditions at 1.5 mol% catalyst loading with **SL-J502-01** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 5:95 EtOAc:hexanes) the title compound **3a** was isolated as a yellow oil in 87% yield (538.4 mg, 2.61 mmol, 90% ee).

Aldehyde *dehydro*-**2a** (32.8 mg, 0.2 mmol) was subjected to standard reaction conditions (80°C, 48 h) with HCO_2H (15 µL, 0.4 mmol, 200 mol%) and **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 3:97 EtOAc:hexanes), the title compound **3a** was isolated as a yellow oil in 80% Yield (33.0 mg, 0.16 mmol, 90% ee).

TLC (SiO_2): R_f = 0.5 (1:4 EtOAc:hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.27 (m, 5H), 5.84 (ddt, J = 17.1, 9.5, 7.0 Hz, 1H), 5.16 – 5.06 (m, 2H), 4.53 (s, 2H), 3.88 (p, J = 6.0 Hz, 1H), 3.72 (dt, J = 10.3, 5.4 Hz, 1H), 3.65 (dt, J = 8.8, 6.2 Hz, 1H), 2.89 (s, 1H), 2.25 (t, J = 6.4 Hz, 2H), 1.77 (dt, J = 8.4, 5.0 Hz, 2H).

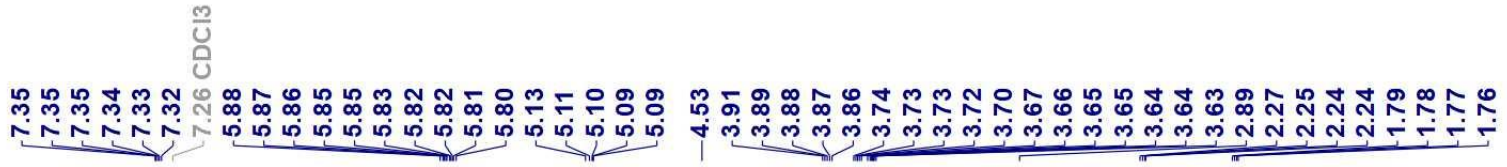
^{13}C NMR (130 MHz, $CDCl_3$): δ 138.1, 135.0, 128.6, 127.9, 127.8, 117.7, 73.4, 70.5, 69.1, 42.1, 36.0.

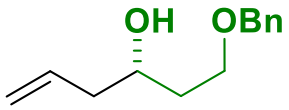
HRMS (Na+, *m/z*) for $C_{13}H_{18}O_2$: calcd. = 229.1199; found = 229.1208.

FTIR (neat): 3433, 3067, 3030, 2917, 2862, 1096, 1027, 996 cm^{-1}.

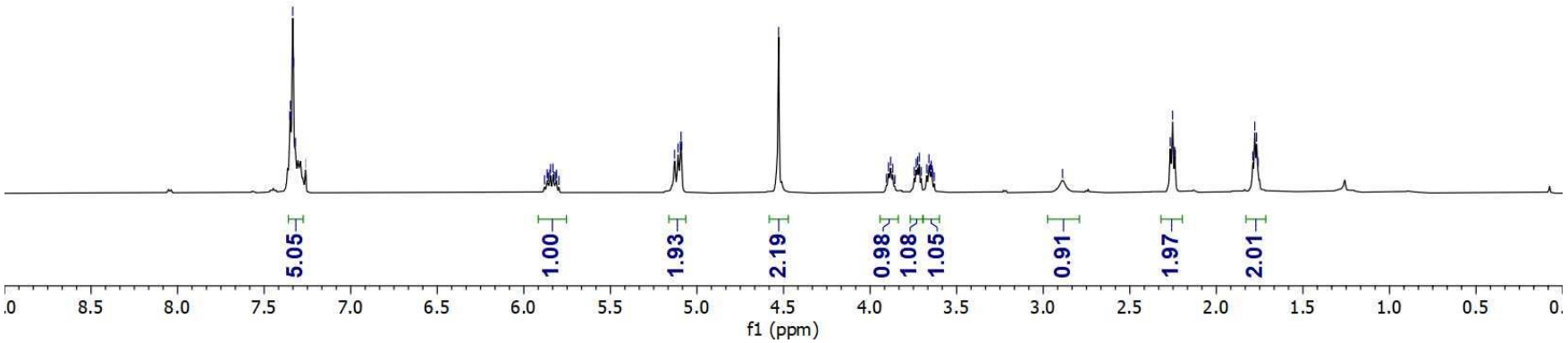
HPLC: (Chiralcel columns OB-H, Hexane:2-PrOH = 99:01, 0.5 mL/min, 210 nm).

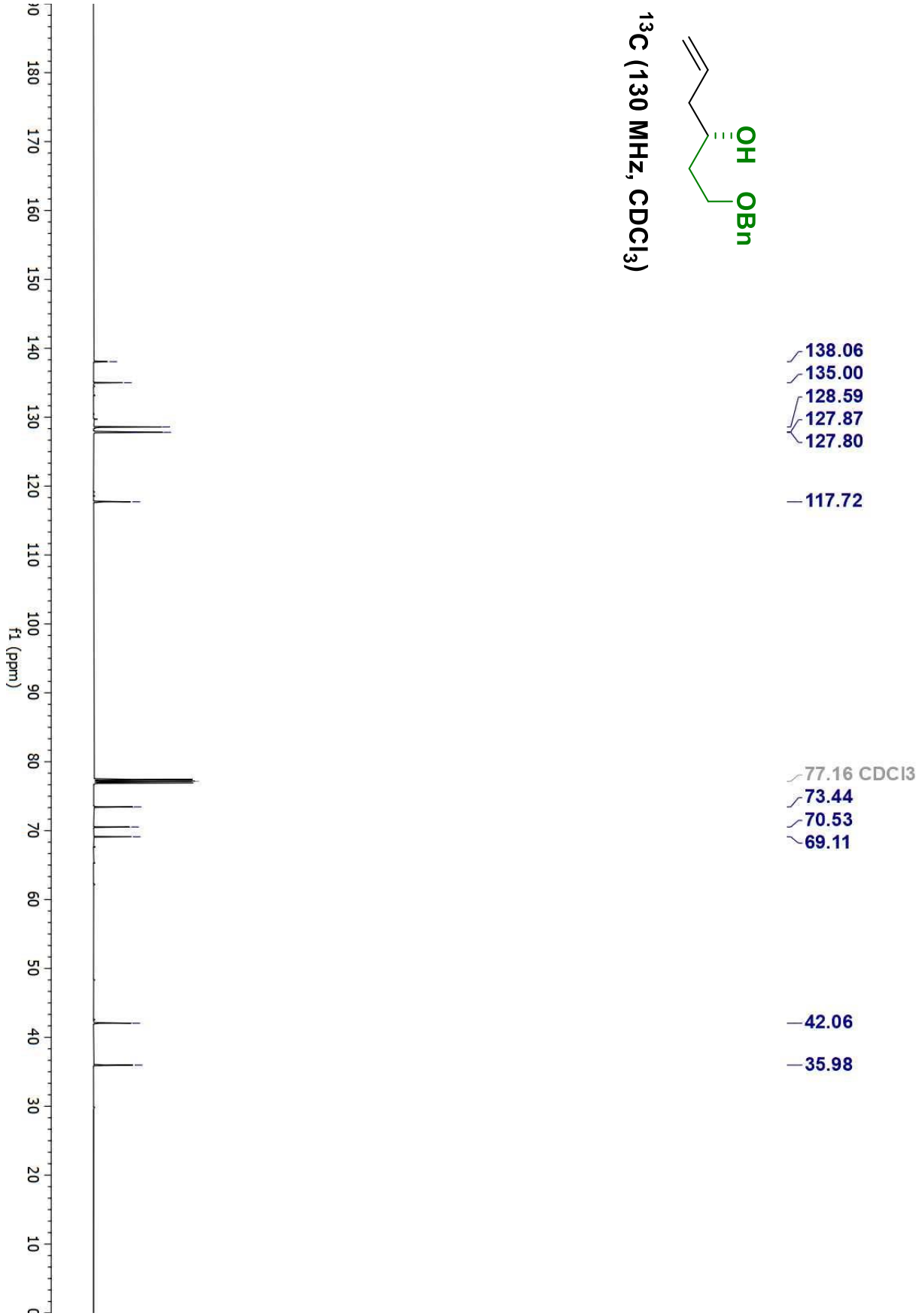
$[\alpha]_D^{24}$ = 4.7 (c = 2.26, $CHCl_3$).



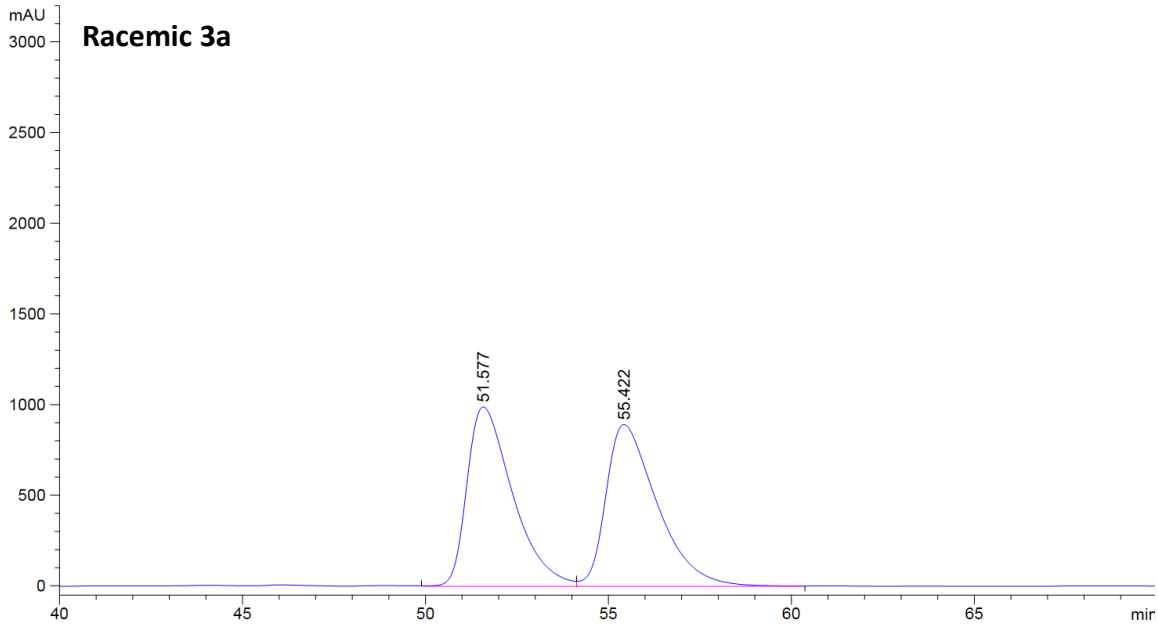


^{1}H (500 MHz,$CDCl_3$)




^{13}C (130 MHz, CDCl$_3$)
OH
OBn
138.06
135.00
128.59
127.87
127.80
117.72
77.16 CDCl3
73.44
70.53
69.11
42.06
35.98
f1 (ppm)

Racemic 3a



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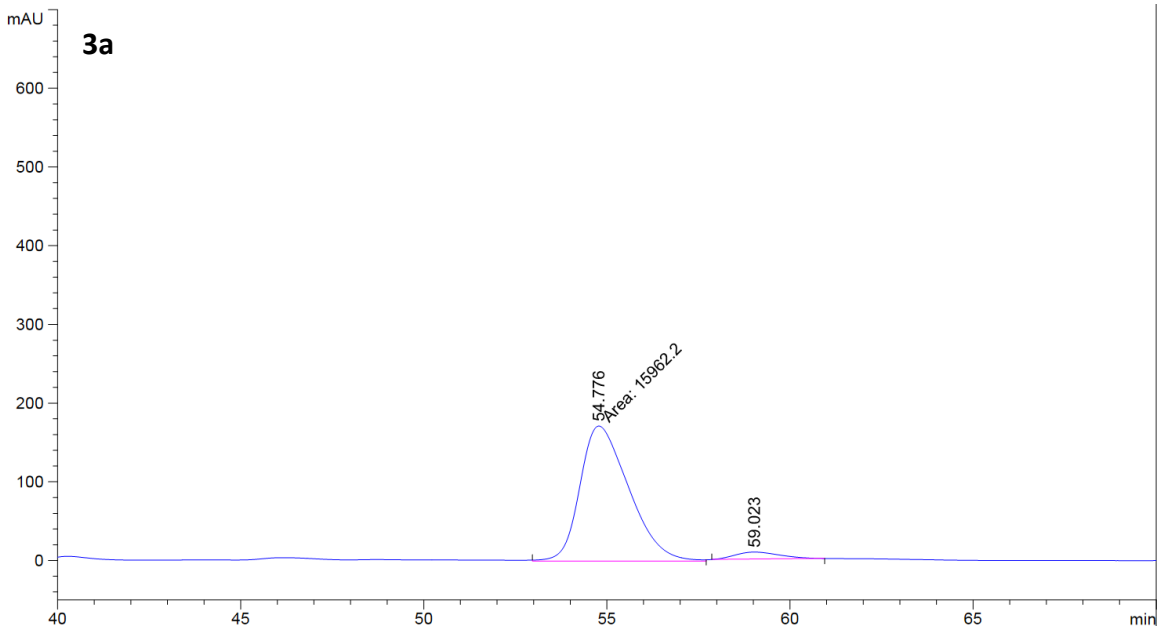
3a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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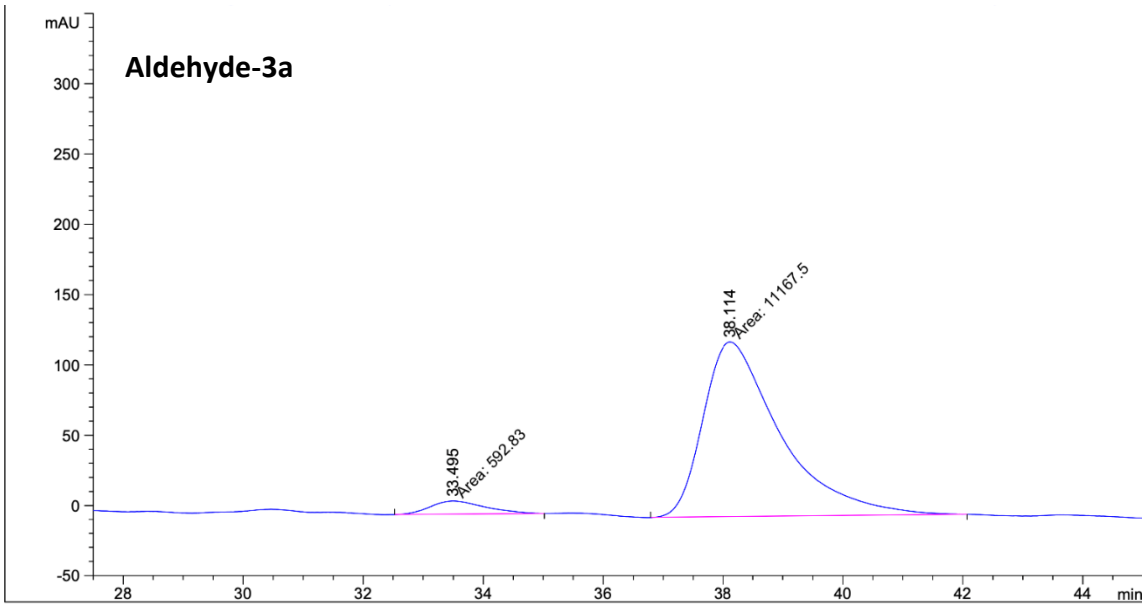
2	59.023	BB	1.0219	779.70752	9.06148	4.6572



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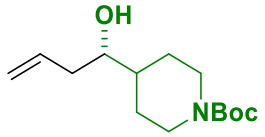
***tert*-butyl (*S*)-4-(1-hydroxybut-3-en-1-yl)piperidine-1-carboxylate (3b)**



Alcohol **2b** (43.1 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 7:93 EtOAc:hexanes) the title compound **3b** was isolated as a brown-yellow oil in 86% yield (44.0 mg, 0.17 mmol, 91% ee).

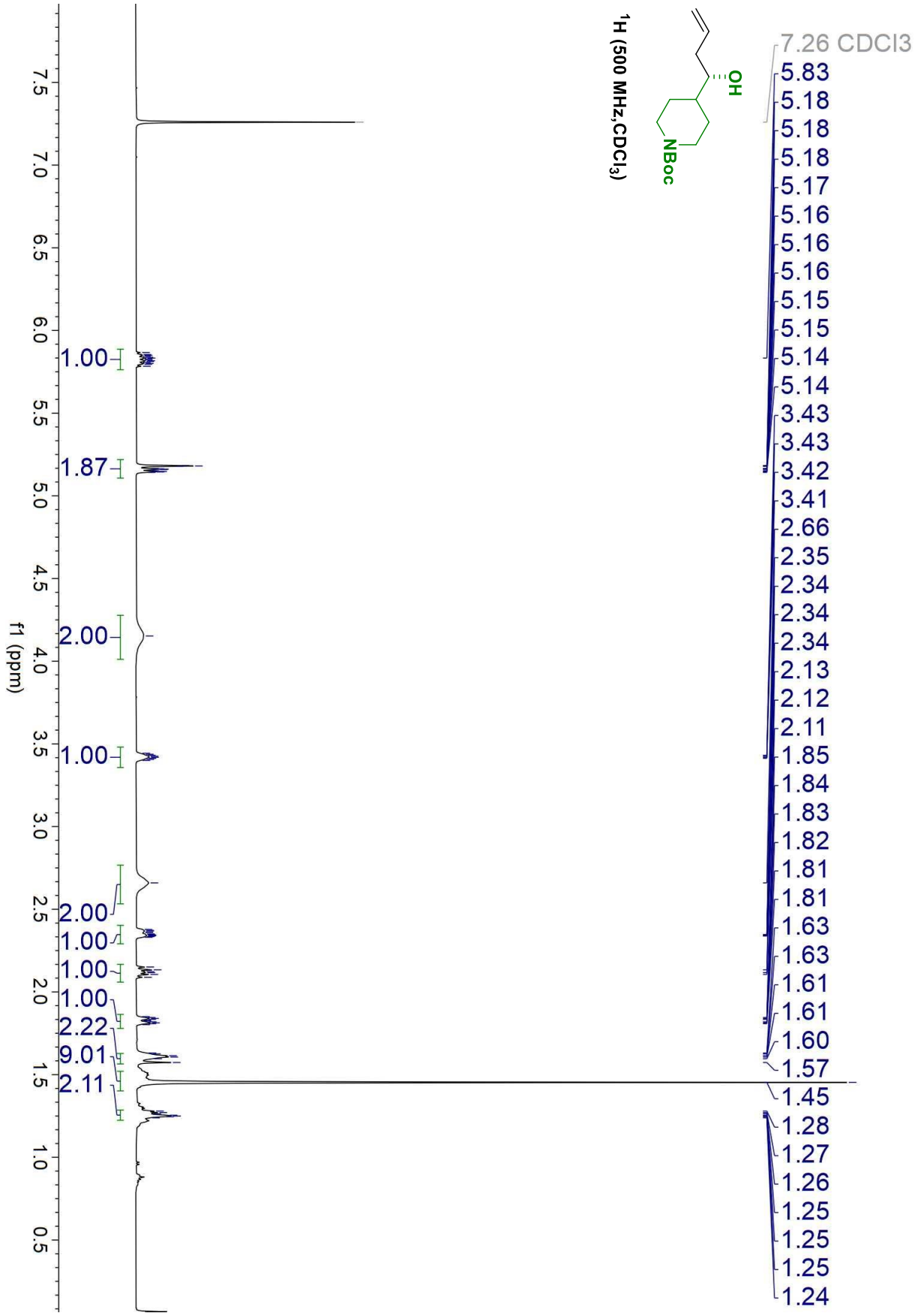
TLC (SiO_2): R_f = 0.5 (1:1 EtOAc:Hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.83 (dddd, *J* = 16.8, 11.1, 8.3, 6.1 Hz, 1H), 5.20 – 5.13 (m, 2H), 4.15 (s, 3H), 3.42 (ddt, *J* = 9.5, 6.5, 3.2 Hz, 1H), 2.66 (s, 2H), 2.40 – 2.31 (m, 1H), 2.12 (dt, *J* = 13.9, 8.5 Hz, 1H), 1.83 (dp, *J* = 12.9, 2.6 Hz, 1H), 1.65 – 1.56 (m, 3H), 1.45 (s, 9H), 1.29 – 1.23 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 155.0, 134.9, 118.8, 79.5, 77.4, 73.8, 41.6, 39.0, 28.6, 28.2.

HPLC: (Chiralcel column OJ-H 2, Hexane: 2-PrOH = 97:03, 1.0 mL/60min, 254 nm).

All spectral data were found in accordance with literature values.[9]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OH
NBoc
7.26 CDCl3
5.83
5.18
5.18
5.18
5.17
5.16
5.16
5.16
5.15
5.15
5.14
5.14
3.43
3.43
3.42
3.41
2.66
2.35
2.34
2.34
2.34
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1.25
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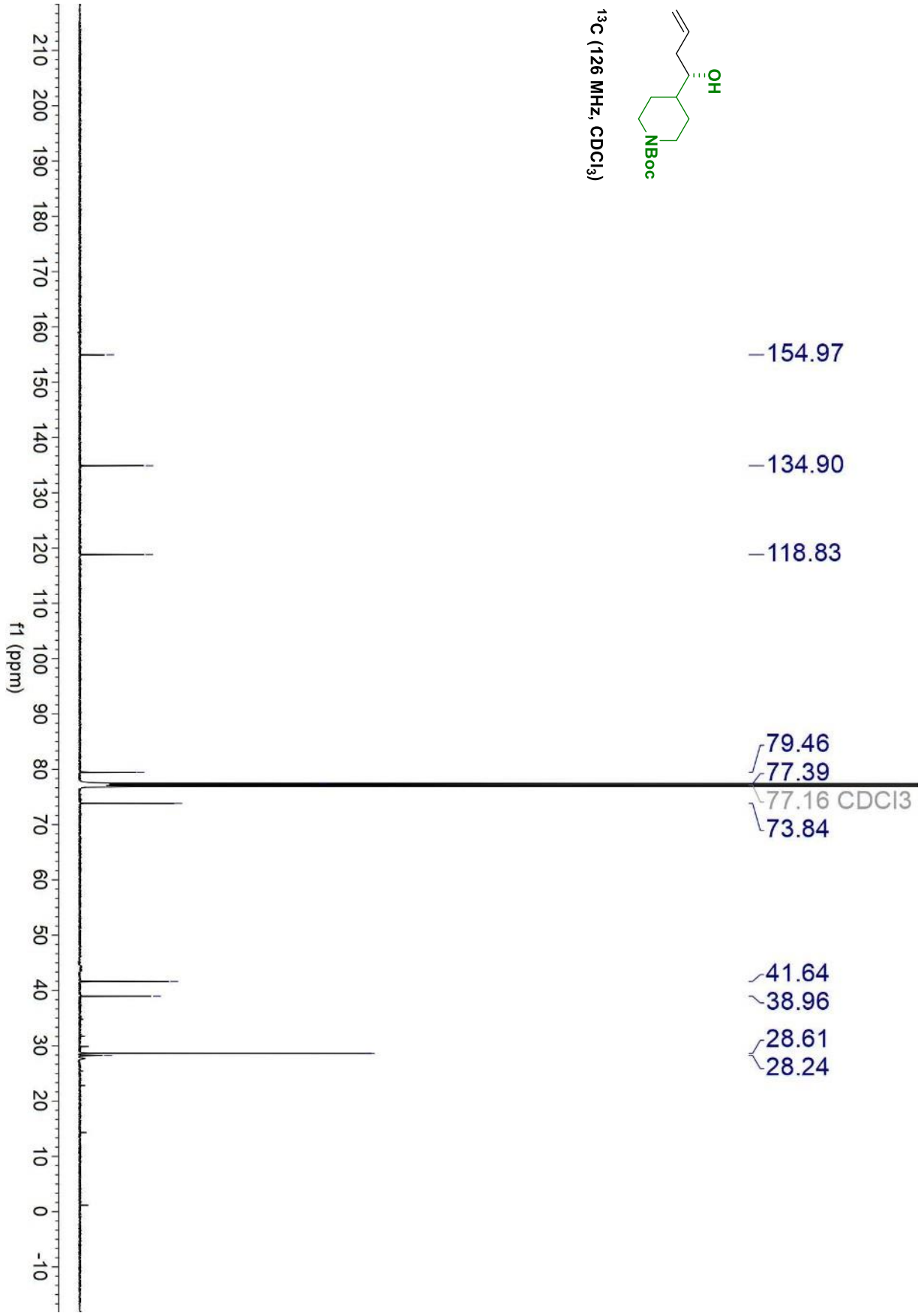
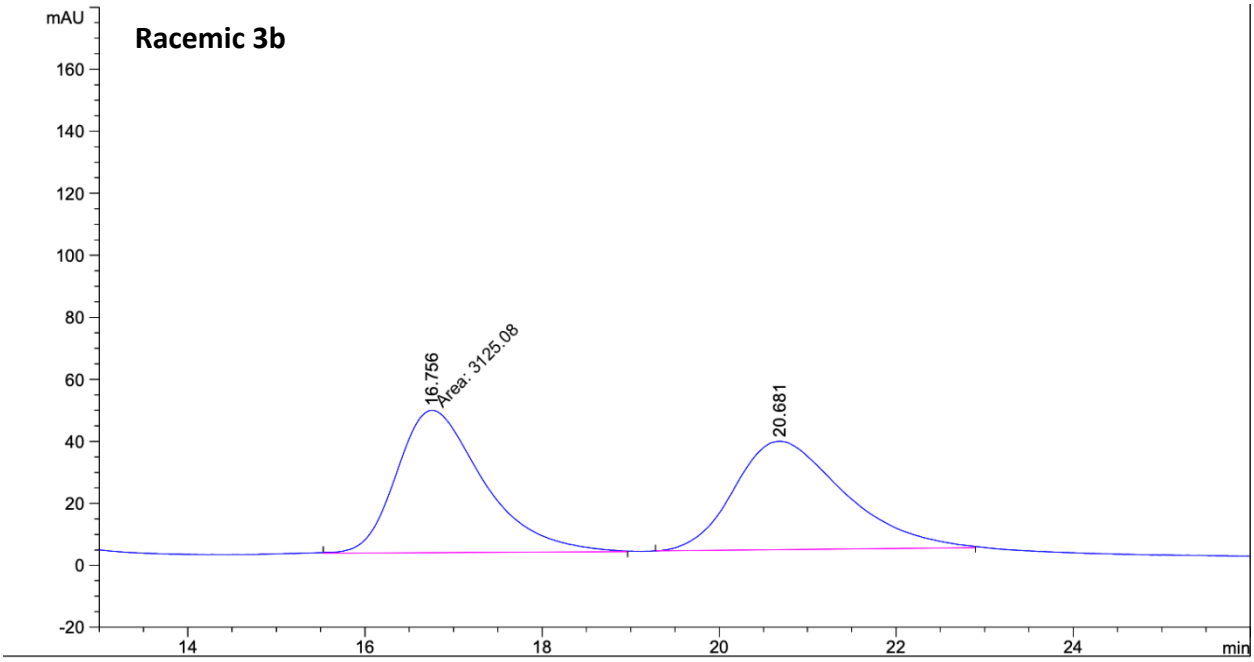
1.00
2.22
9.01
2.11
f1 (ppm)


^{13}C (126 MHz, CDCl$_3$)
OH
NBoc
154.97
134.90
118.83
79.46
77.39
77.16 CDCl3
73.84
41.64
38.96
28.61
28.24
f1 (ppm)



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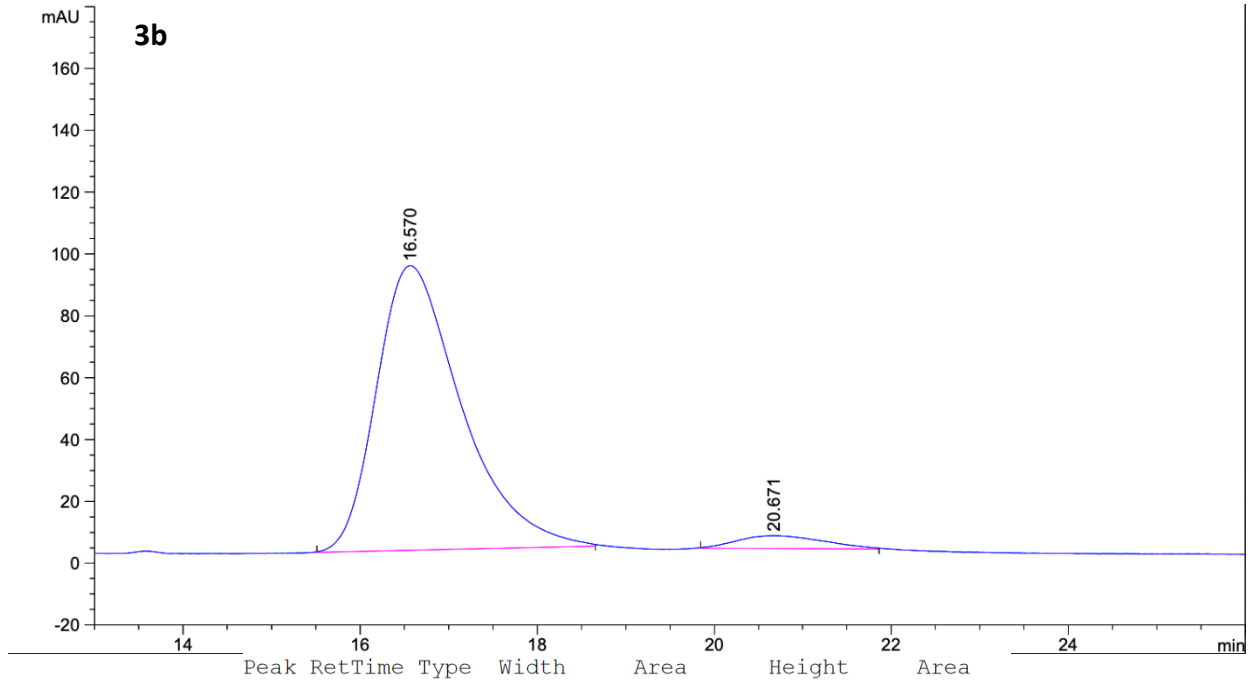
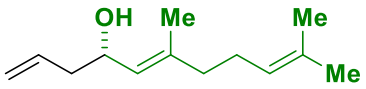


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	54.776	MM	1.5490	1.59622e4	171.75047	95.3428
2	59.023	BB	1.0219	779.70752	9.06148	4.6572

(*S*,*E*)-6,10-dimethylundeca-1,5,9-trien-4-ol (3c)



Alcohol **2c** (30.9 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 1:99 EtOAc:hexanes) the title compound **3c** was isolated as a brown-red oil in 65% yield (24.9 mg, 0.13 mmol, 98% ee).

Aldehyde *dehydro*-**2c** (30.4 mg, 0.2 mmol) was subjected to standard reaction conditions (80°C, 48 h) with HCO_2H (15 µL, 0.4 mmol, 200 mol%) and **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 2:98 EtOAc:hexanes), the title compound **3c** was isolated as a yellow oil in 75% Yield (29.0 mg, 0.15 mmol, 95% ee).

TLC (SiO_2): R_f = 0.5 (1:4 EtOAc:Hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.80 (ddt, *J* = 17.3, 10.1, 7.2 Hz, 1H), 5.22 – 5.04 (m, 4H), 4.42 (q, *J* = 7.1 Hz, 1H), 2.28 (td, *J* = 6.8, 3.7 Hz, 2H), 2.09 (t, *J* = 7.2 Hz, 2H), 2.04 – 1.99 (m, 2H), 1.68 (s, 6H), 1.60 (s, 3H), 1.51 (s, 1H).

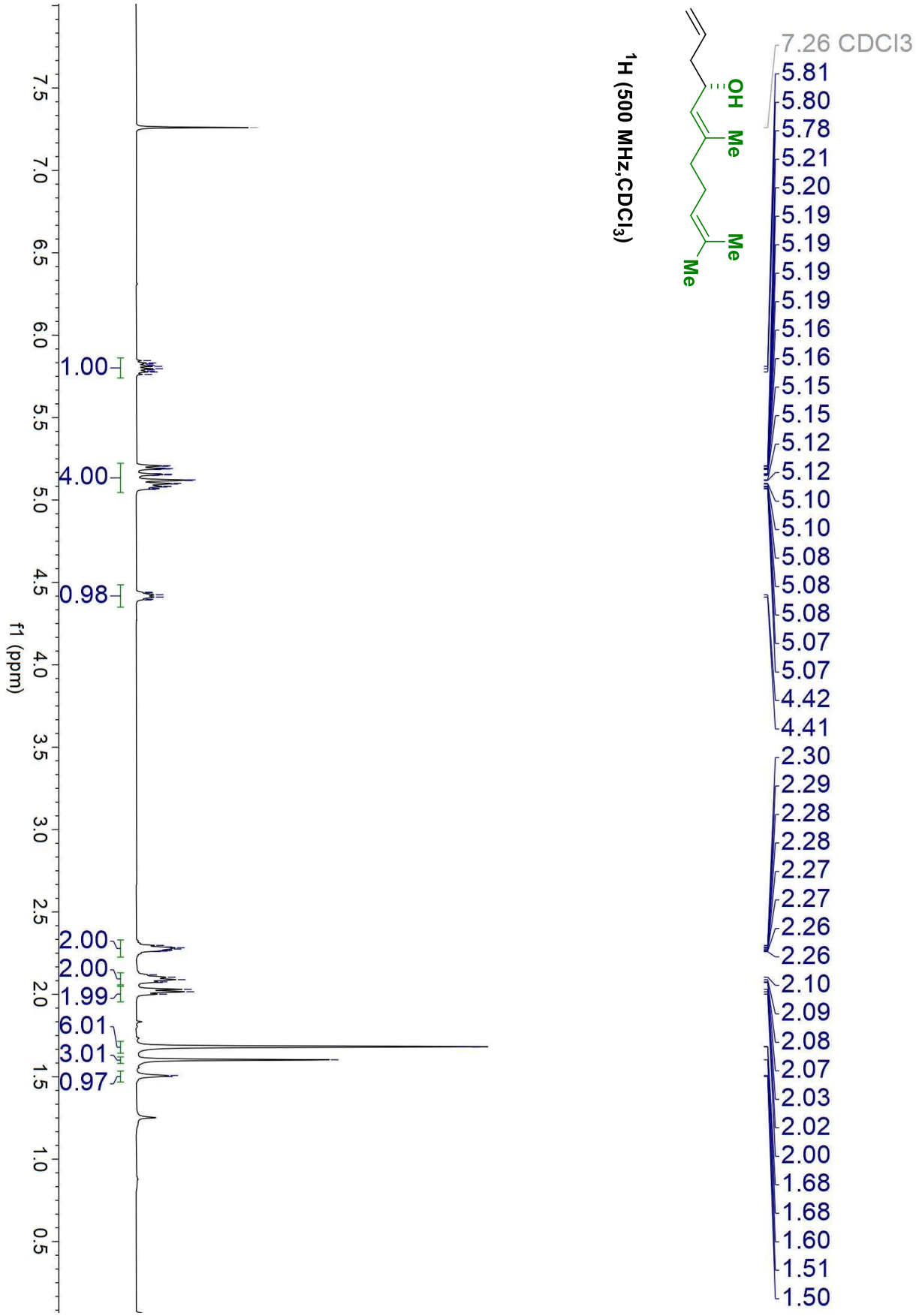
^{13}C NMR (126 MHz, $CDCl_3$): δ 138.9, 134.7, 131.8, 127.1, 124.0, 118.0, 67.9, 42.3, 39.6, 26.5, 25.8, 17.8, 16.8.

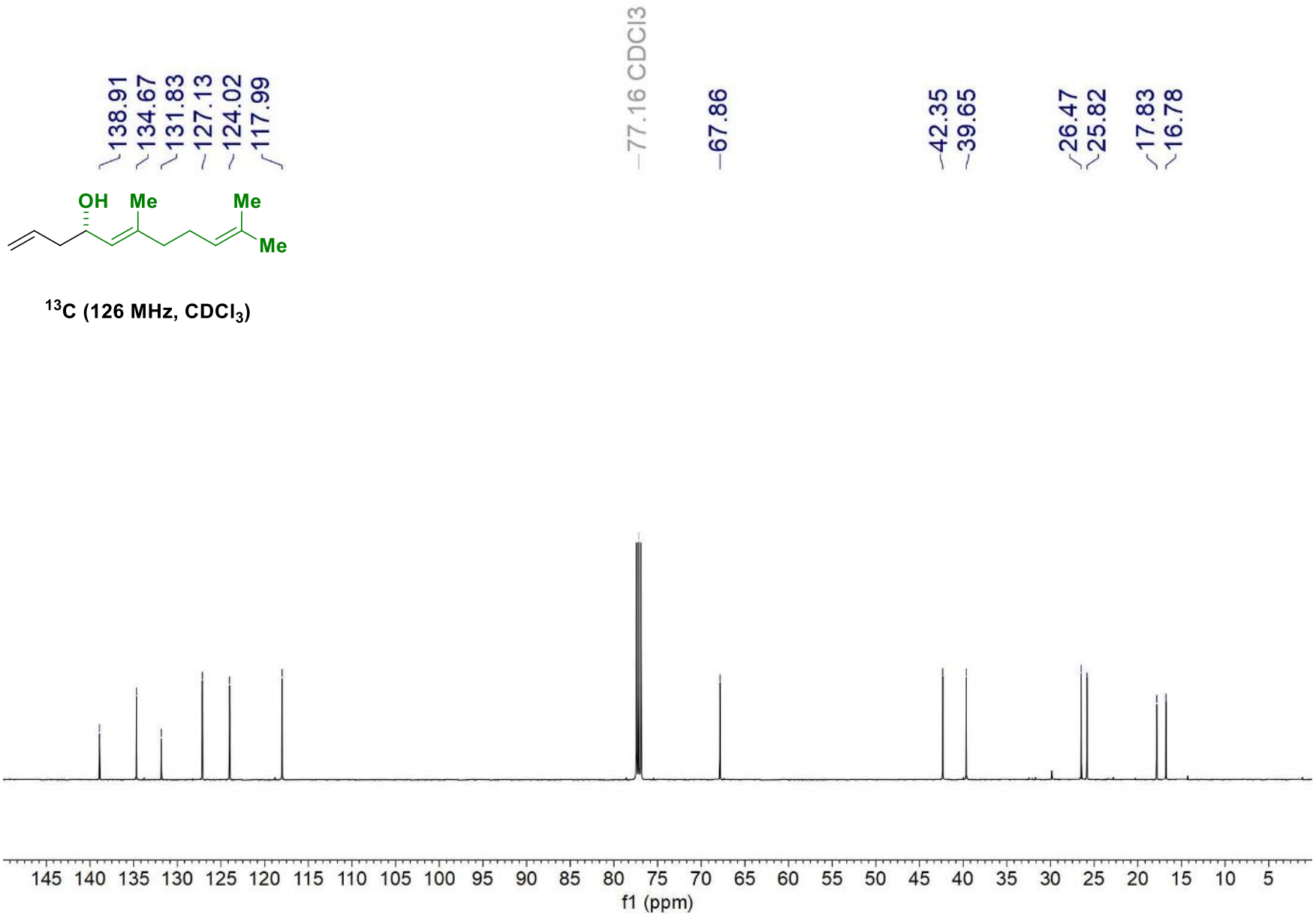
HRMS (Na+, *m/z*): for $C_{13}H_{22}O$ calcd. = 217.1563; found = 217.1562.

FTIR (neat): 3354, 2918, 1641, 995, 912 cm^{-1}.

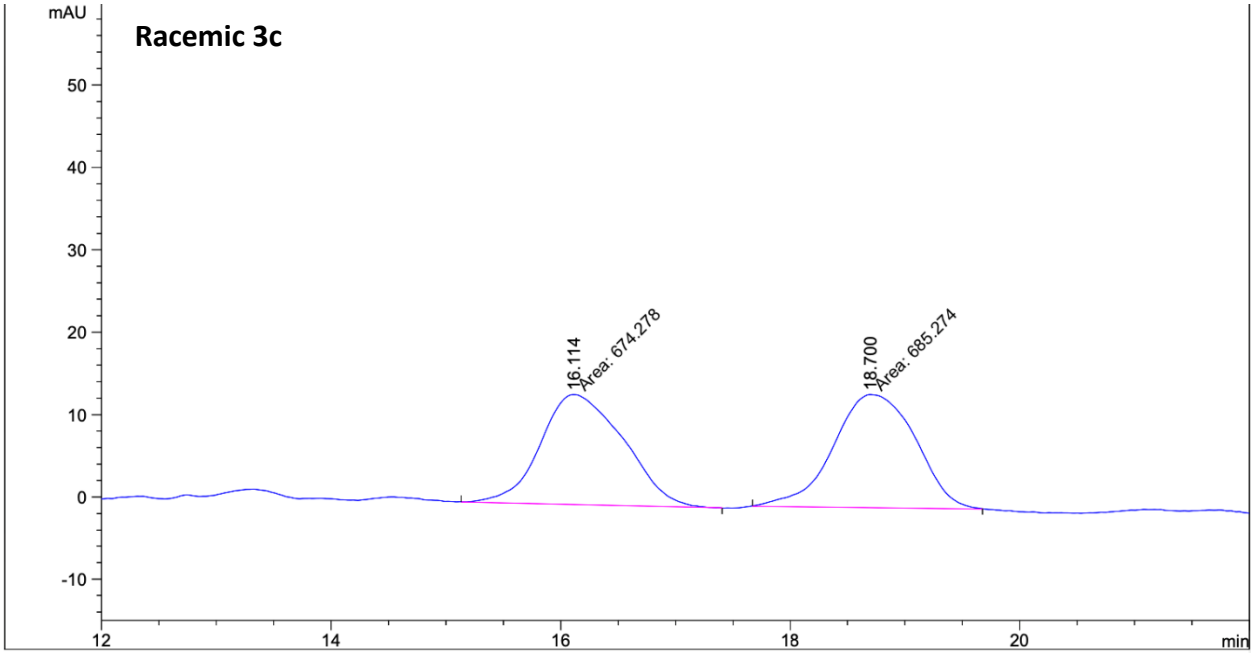
HPLC: (Diacel Chemistry CHIRALPAK ASH-2, Hexane: 2-PrOH = 995:005, 0.5 mL/30min, 254 nm).

$[\alpha]_D^{24}$ = 10.2 (c = 0.4, $CHCl_3$)

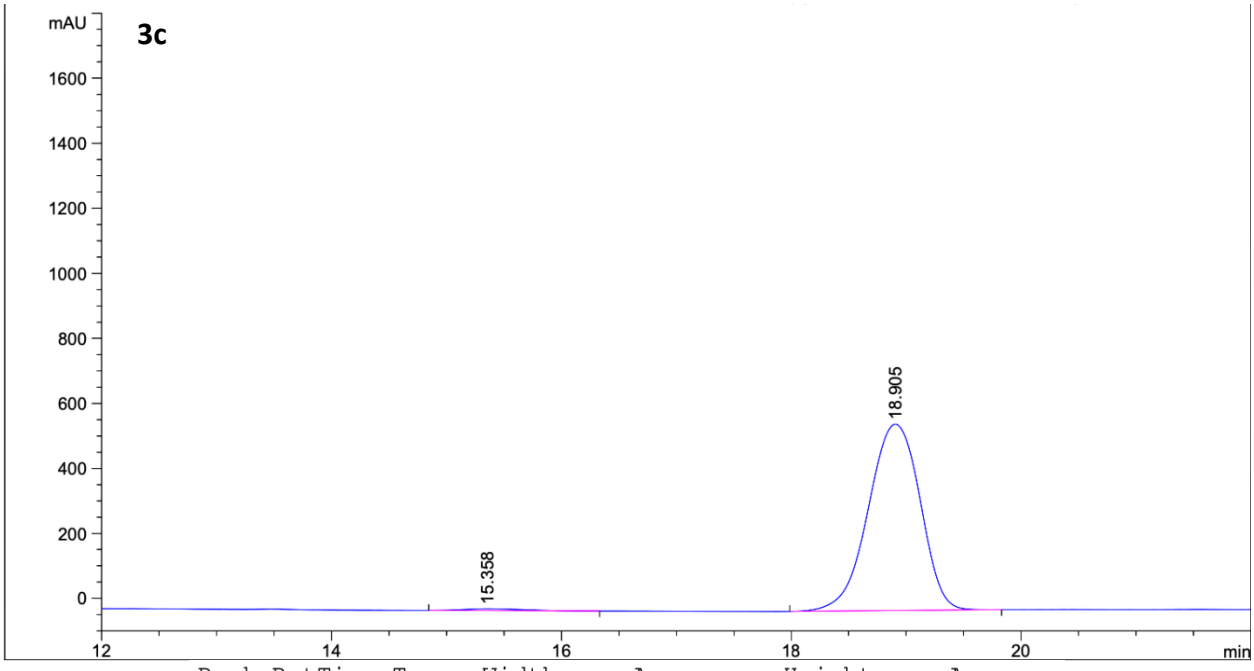

^{1}H (500 MHz,CDCl$_3$)
OH
Me
Me
Me
7.26 CDCl3
5.81
5.80
5.78
5.21
5.20
5.19
5.19
5.19
5.19
5.16
5.16
5.15
5.15
5.12
5.12
5.10
5.10
5.08
5.08
5.08
5.07
5.07
4.42
4.41
2.30
2.29
2.28
2.28
2.27
2.27
2.26
2.26
2.10
2.09
2.08
2.07
2.03
2.02
2.00
1.68
1.68
1.60
1.51
1.50
1.00
4.00
0.98
2.00
2.00
1.99
6.01
3.01
0.97
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



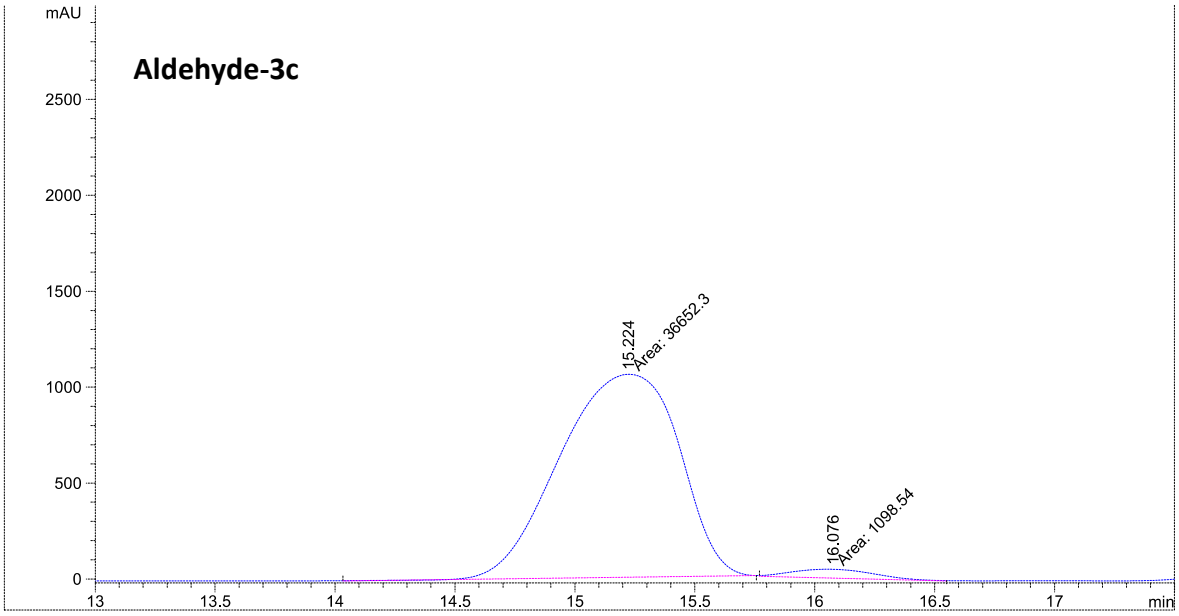
^{13}C (126 MHz, $CDCl_3$)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.114	MM	0.8408	674.27777	13.36558	49.5956
2	18.700	MM	0.8311	685.27362	13.74189	50.4044

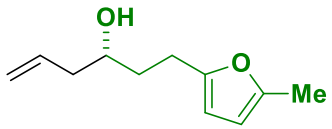


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.358	BB	0.4495	218.13478	5.87026	1.1968
2	18.905	BB	0.5038	1.80082e4	574.31494	98.8032



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.224	MM	0.5772	3.66523e4	1058.38611	97.0900
2	16.076	MM	0.3959	1098.53699	46.24778	2.9100

(*R*)-1-(5-methylfuran-2-yl)hex-5-en-3-ol (3d)



Alcohol **2d** (28.0 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 4:96 EtOAc:hexanes) the title compound **3d** was isolated as a yellow oil in 83% yield (30.0 mg, 0.17 mmol, 88% ee).

TLC (SiO_2): R_f = 0.2 (0.5:4.5 EtOAc:hexanes)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 – 5.83 (m, 2H), 5.83 – 5.76 (m, 1H), 5.19 – 5.13 (m, 1H), 5.14 – 5.11 (m, 1H), 3.69 (tq, *J* = 8.2, 4.3 Hz, 1H), 2.76 (ddd, *J* = 15.0, 8.8, 5.9 Hz, 1H), 2.67 (dt, *J* = 15.4, 7.8 Hz, 1H), 2.38 – 2.26 (m, 1H), 2.25 (s, 3H), 2.25 – 2.12 (m, 1H), 1.88 – 1.79 (m, 1H), 1.79 – 1.69 (m, 1H), 1.64 (d, *J* = 4.1 Hz, 1H).

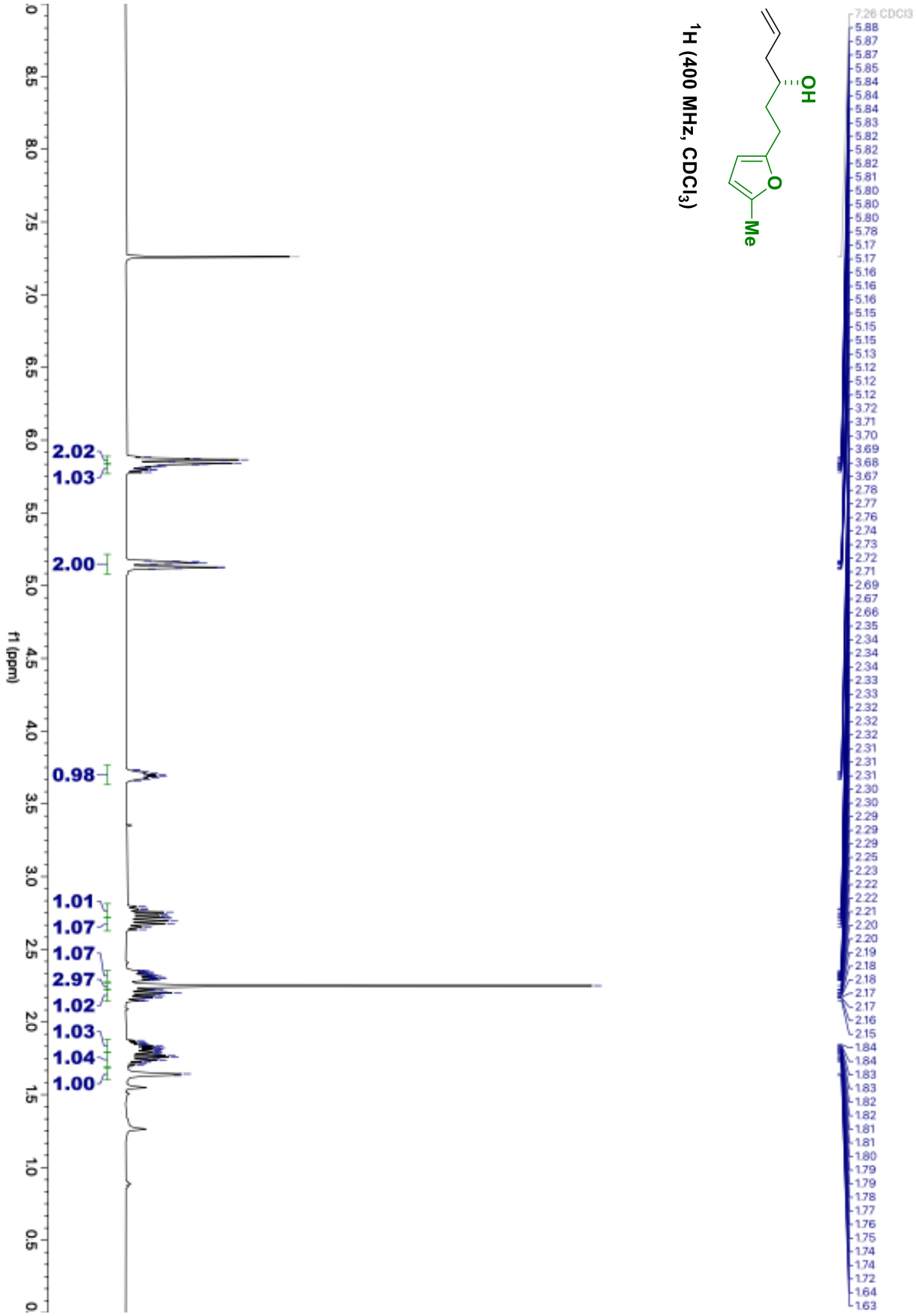
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0, 150.5, 134.8, 118.4, 106.0, 105.7, 70.1, 42.1, 35.4, 24.5, 13.6.

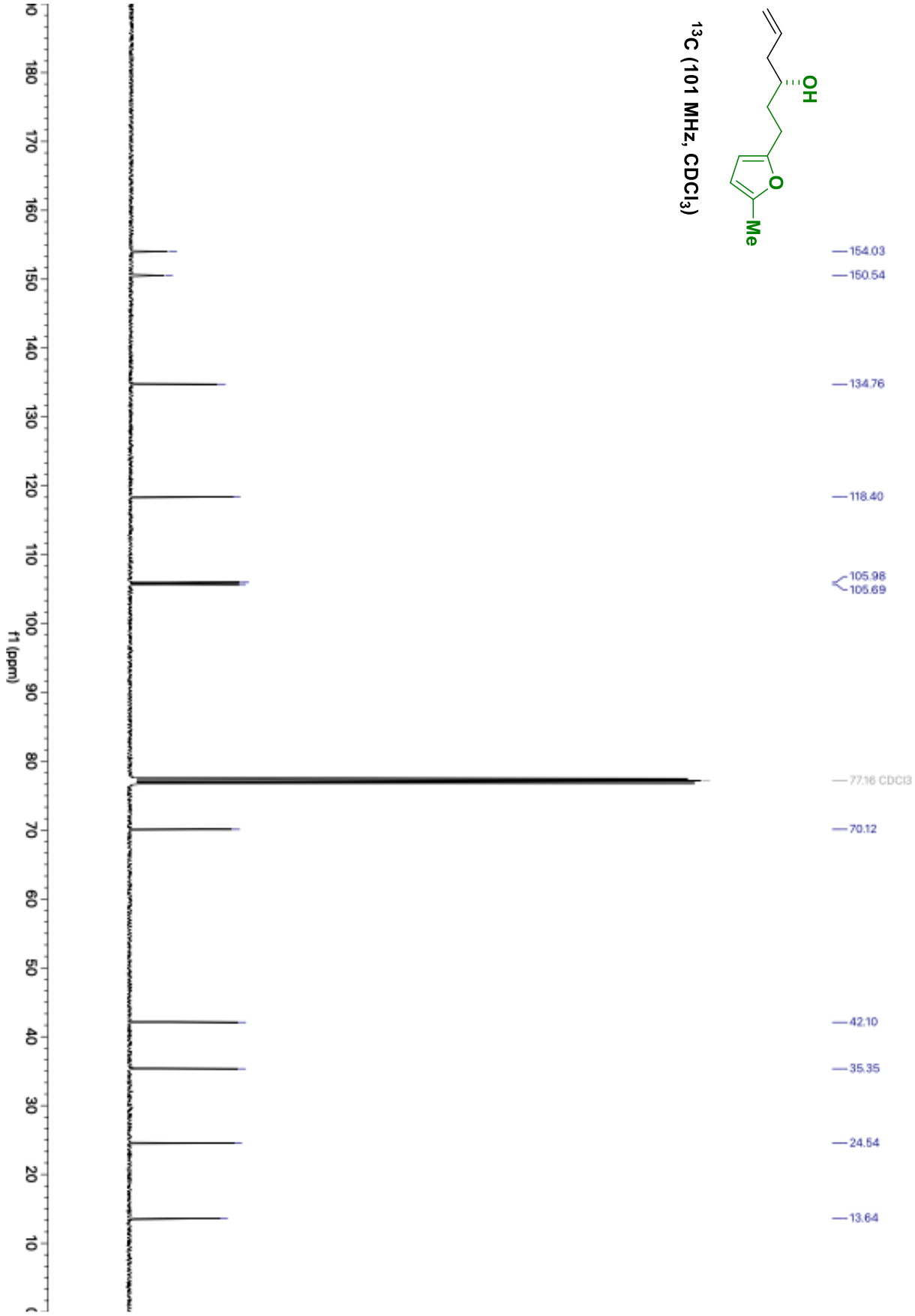
HRMS (CI, *m/z*): for $C_{11}H_{16}O_2$: calcd. = 180.1150; found = 180.1142.

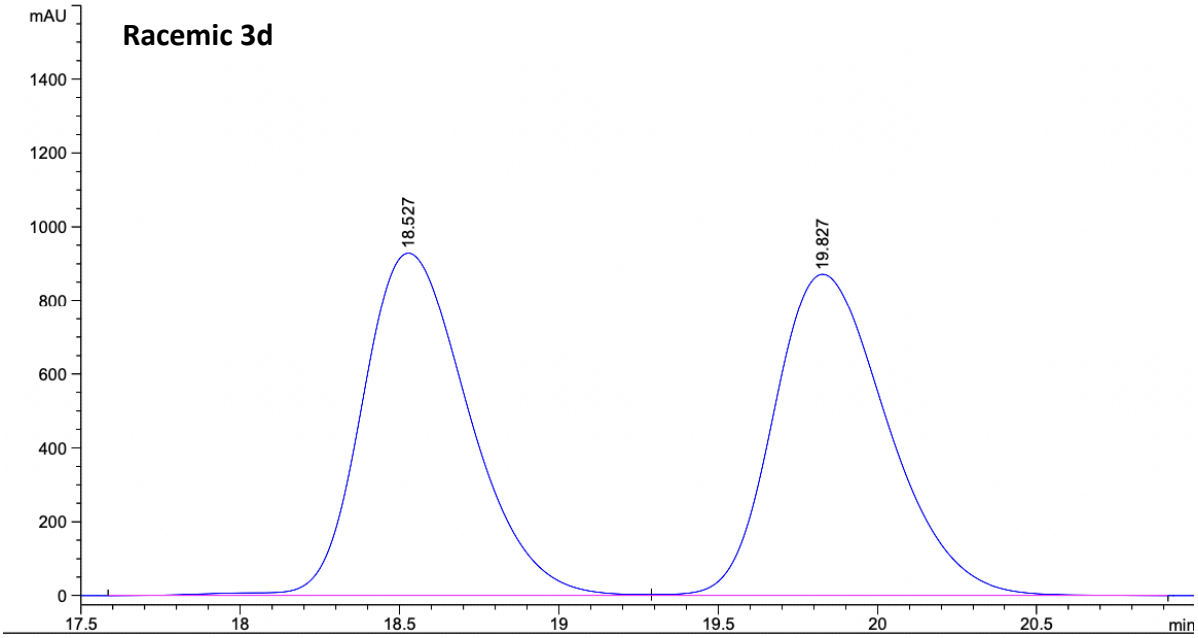
FTIR (neat): 3382, 3080, 2978, 2923, 2856, 1569, 1444, 1224, 1062, 915 cm^{-1}.

HPLC: (Chiralcel column Amylose 2, Hexane: 2-PrOH = 98:02, 0.5 mL/min, 210 nm).

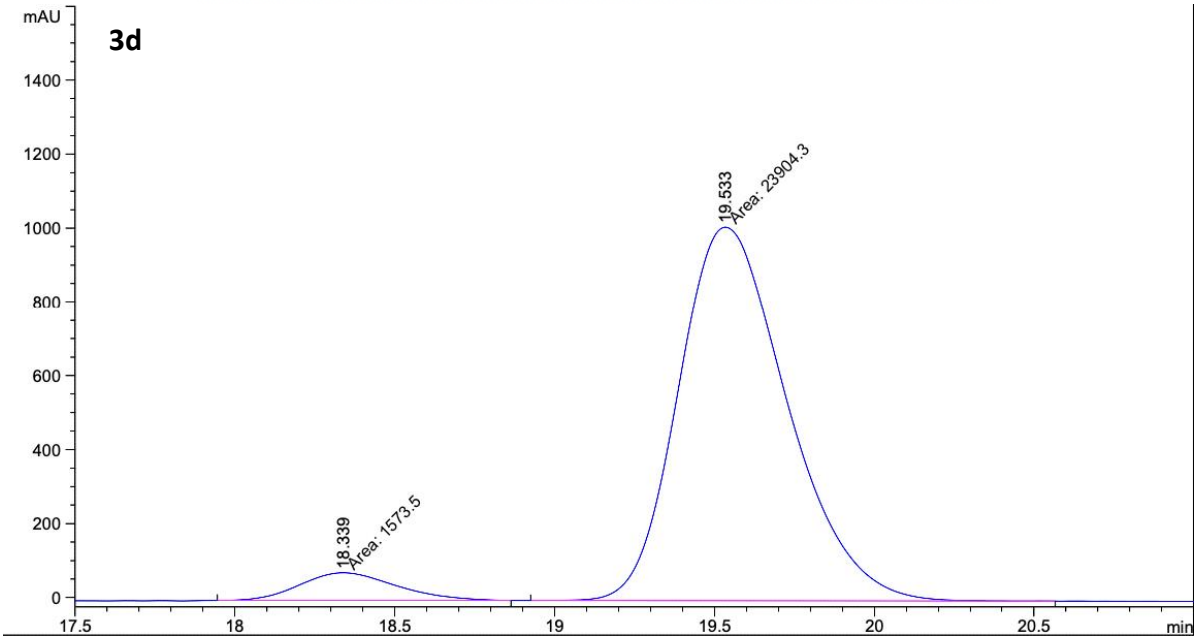
$[\alpha]_D^{24}$ = -6.2 (c = 0.1, $CHCl_3$).


^{1}H (400 MHz, CDCl$_3$)
OH
O
Me
7.26 CDCl3
f1 (ppm)
2.02
1.03
2.00
0.98
1.01
1.07
1.07
2.97
1.02
1.03
1.04
1.00


^{13}C (101 MHz, $CDCl_3$)
OH
O
Me
154.03
150.54
134.76
118.40
105.98
105.69
77.16 CDCl3
70.12
42.10
35.35
24.54
13.64
f1 (ppm)

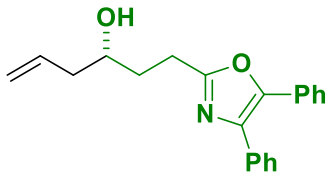


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.527	VV	0.3610	2.15877e4	929.26007	49.9848
2	19.827	VB	0.3850	2.16008e4	872.05762	50.0152



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.339	MM	0.3497	1573.49731	74.99251	6.1759
2	19.533	MM	0.3938	2.39043e4	1011.69702	93.8241

(*R*)-1-(4,5-diphenylfuran-2-yl)hex-5-en-3-ol (3e)



Alcohol **2e** (55.9 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 13:87 EtOAc:hexanes) the title compound **3e** was isolated as a yellow oil in 78% yield (49.6 mg, 0.16 mmol, 90% ee).

TLC (SiO_2): R_f = 0.4 (2:3 EtOAc:hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 6.8, 1.7 Hz, 2H), 7.58 (dd, *J* = 6.8, 1.7 Hz, 2H), 7.39 – 7.30 (m, 6H), 5.87 (ddt, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.19 – 5.13 (m, 2H), 3.83 (tt, *J* = 7.7, 4.1 Hz, 1H), 3.03 (t, *J* = 7.2 Hz, 3H), 2.36 (dt, *J* = 12.2, 6.2 Hz, 1H), 2.28 (dt, *J* = 14.3, 7.5 Hz, 1H), 2.09 (dtd, *J* = 14.5, 7.3, 3.3 Hz, 1H), 2.03 – 1.92 (m, 1H).

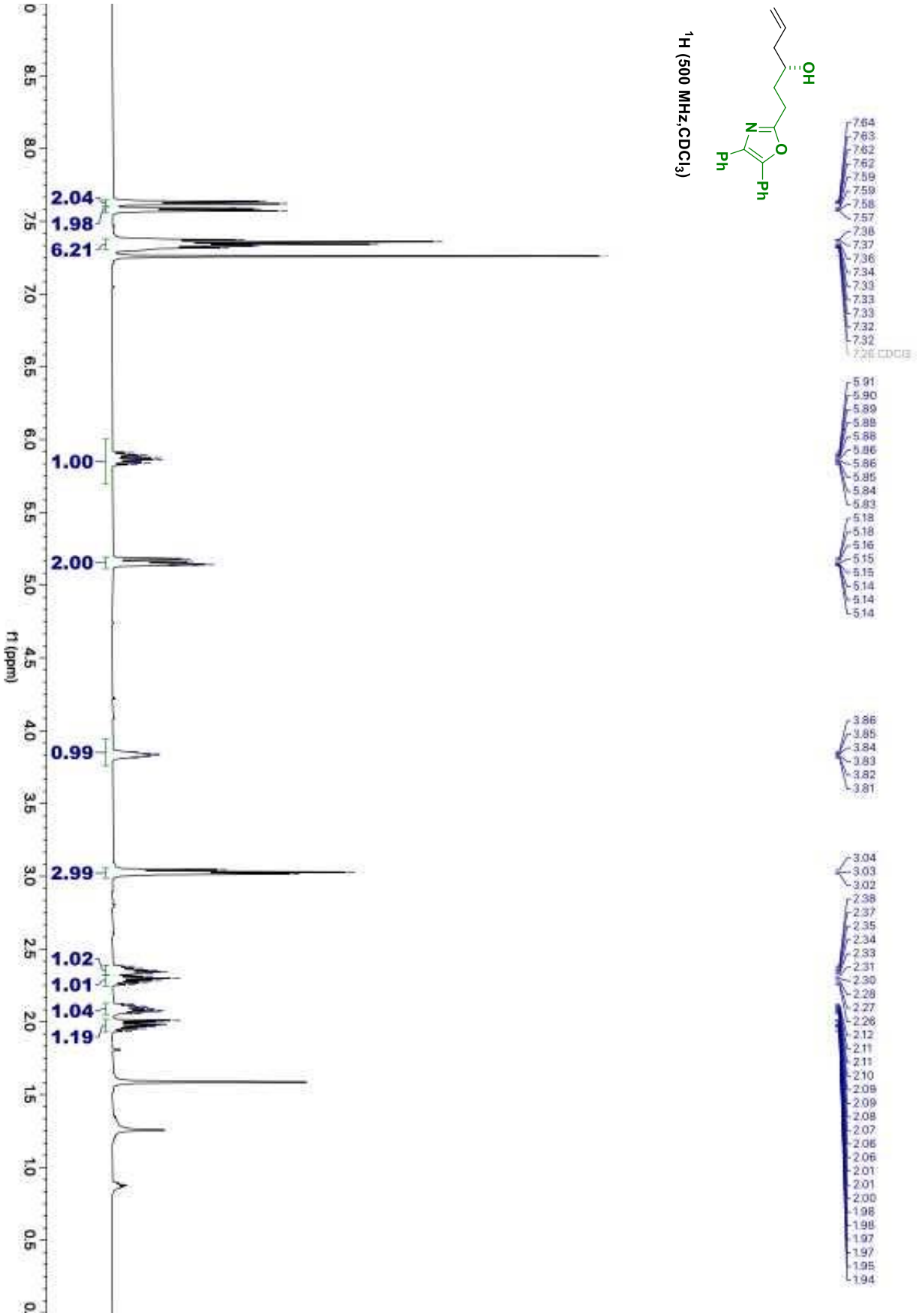
^{13}C NMR (126 MHz, $CDCl_3$): δ 163.8, 145.4, 135.0, 134.8, 132.4, 129.1, 128.8, 128.7, 128.6, 128.2, 128.0, 126.6, 118.3, 70.4, 42.2, 33.5, 25.2.

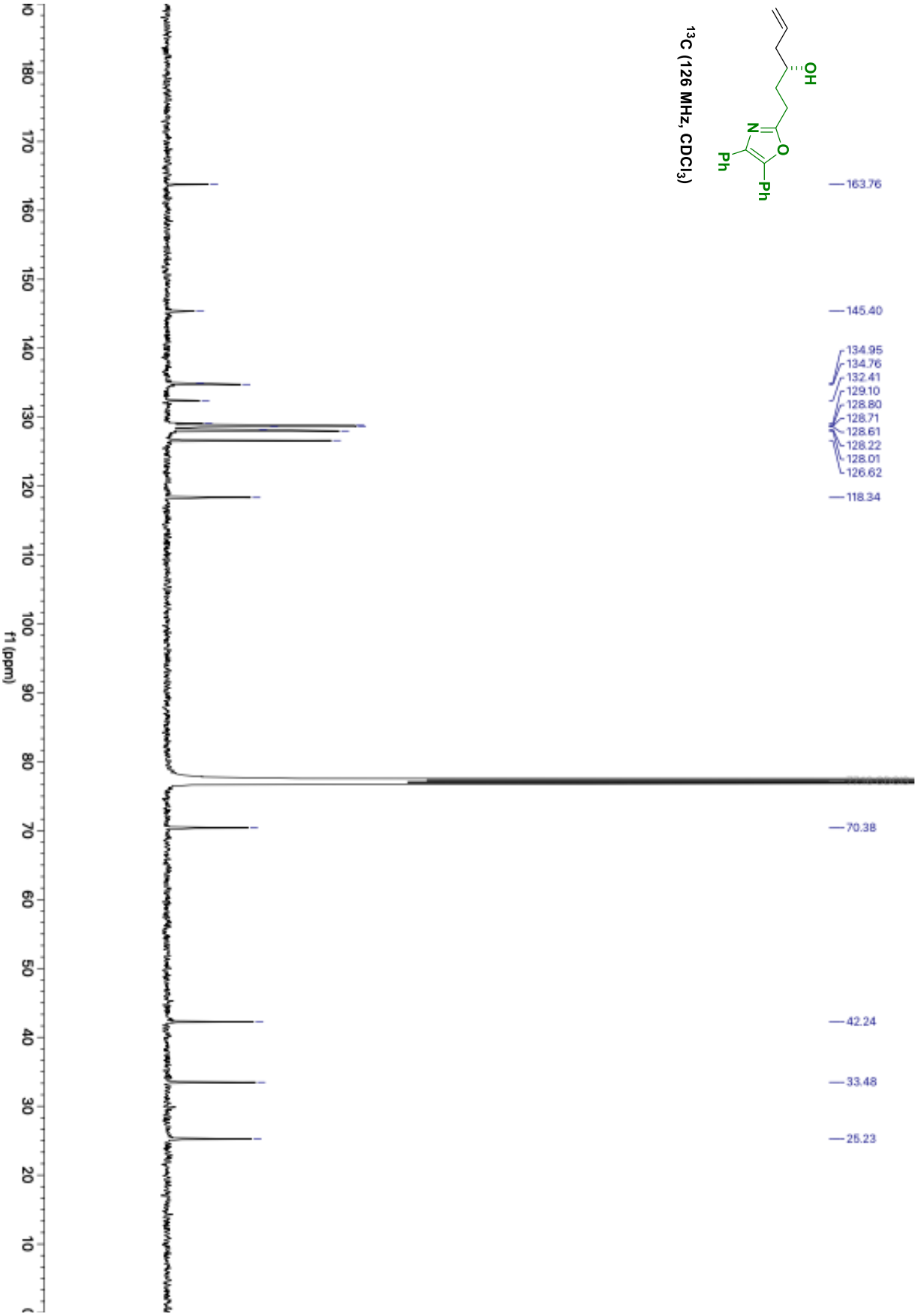
HRMS (Na+, *m/z*): for $C_{21}H_{21}NO_2$: calcd. = 320.1645; found = 320.1641.

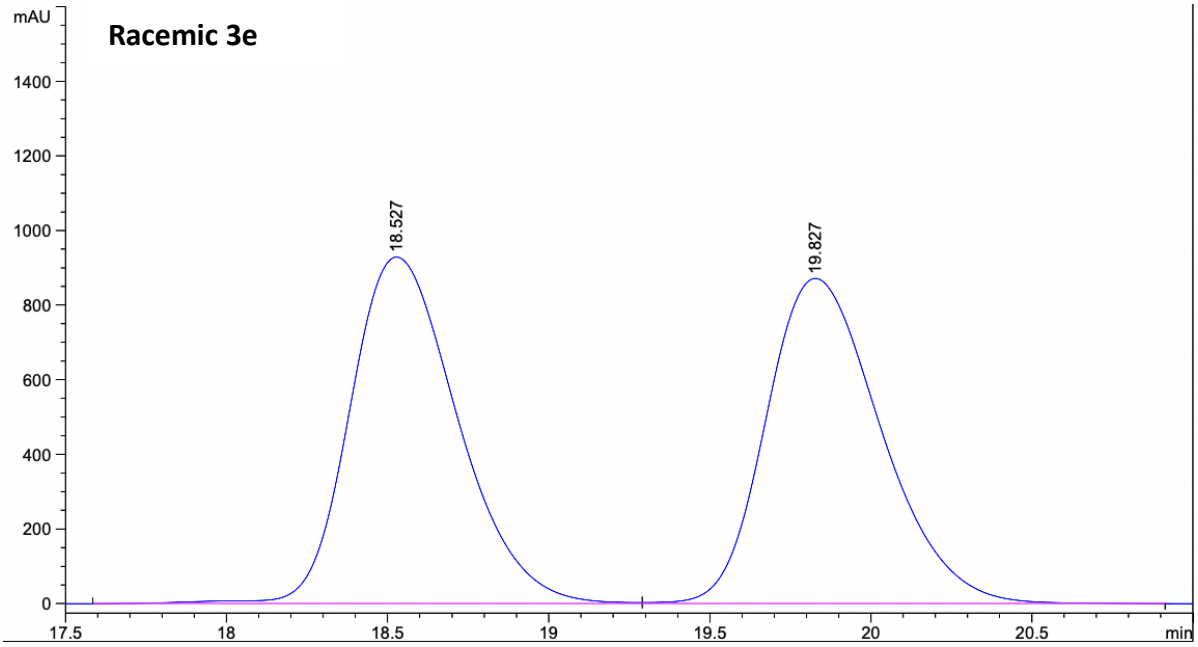
FTIR (neat): 3346, 2957, 2925, 2873, 1460, 1378, 1160, 952, 913, 743 cm^{-1}.

HPLC: (Chiralcel columns Cellulose 2 + Cellulose 5, Hexane: 2-PrOH = 98:02, 0.5 mL/min, 230 nm).

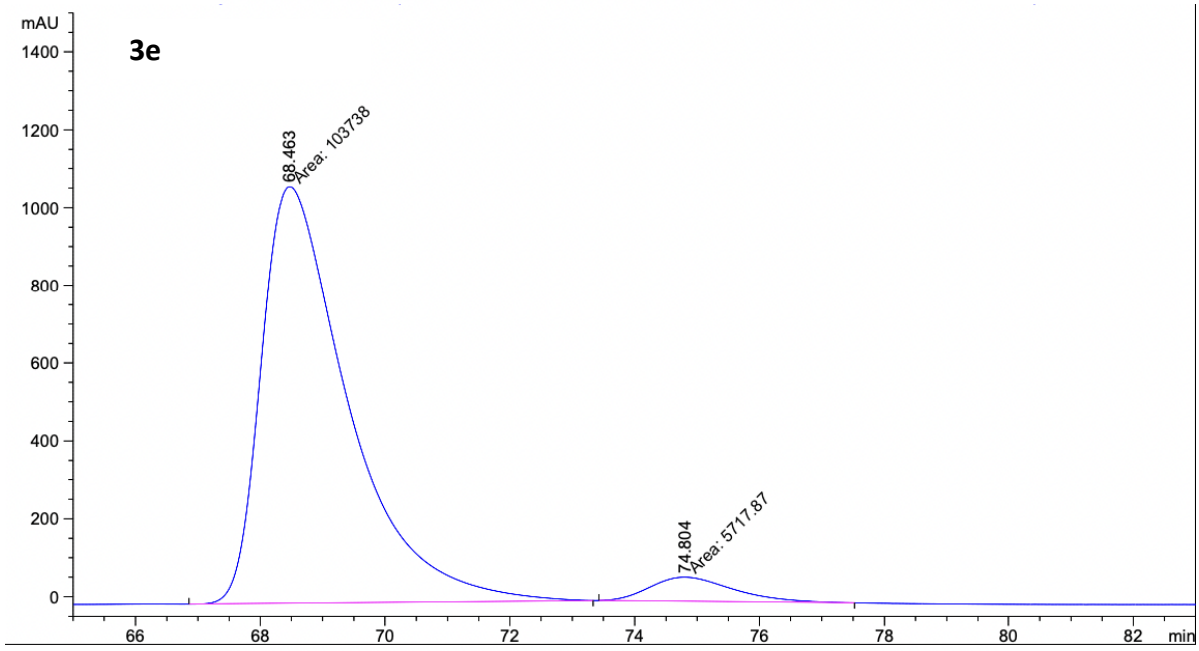
$[\alpha]_D^{24}$ = +9.4 (c = 0.1, $CHCl_3$).


^{1}H (500 MHz,CDCl$_3$)
OH
N
O
Ph
Ph
2.04
1.98
6.21
1.00
2.00
0.99
2.99
1.02
1.01
1.04
1.19
f1 (ppm)


^{13}C (126 MHz, CDCl$_3$)
OH
N
O
Ph
Ph
163.76
145.40
134.95
134.76
132.41
129.10
128.80
128.71
128.61
128.22
128.01
126.62
118.34
70.38
42.24
33.48
25.23
f1 (ppm)

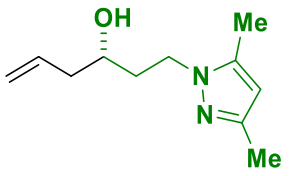


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	69.065	MM	1.7357	1.46579e4	140.75215	49.9993
2	75.079	MM	1.8282	1.46583e4	133.62791	50.0007



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	68.463	MM	1.6152	1.03738e5	1070.44922	94.7761
2	74.804	MM	1.5413	5717.87109	61.83091	5.2239

(*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)hex-5-en-3-ol (3f)



Alcohol **2f** (28.0 mg, 0.18 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 33:66 EtOAc:hexanes) the title compound **3f** was isolated as a yellow oil in 72% yield (26.0 mg, 0.13 mmol, 89% ee).

TLC (SiO_2): R_f = 0.5 (EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.82 (dt, *J* = 17.1, 8.7 Hz, 1H), 5.77 (s, 1H), 5.14 – 5.06 (m, 2H), 4.18 (ddd, *J* = 14.3, 8.8, 5.3 Hz, 1H), 4.06 (dt, *J* = 14.2, 5.7 Hz, 1H), 3.60 (dtd, *J* = 9.3, 6.2, 2.8 Hz, 1H), 2.26 – 2.23 (m, 2H), 2.22 (s, 3H), 2.19 (s, 3H), 1.96 (dddd, *J* = 14.6, 8.9, 5.8, 2.7 Hz, 1H), 1.74 (ddt, *J* = 14.9, 10.4, 5.4 Hz, 1H).

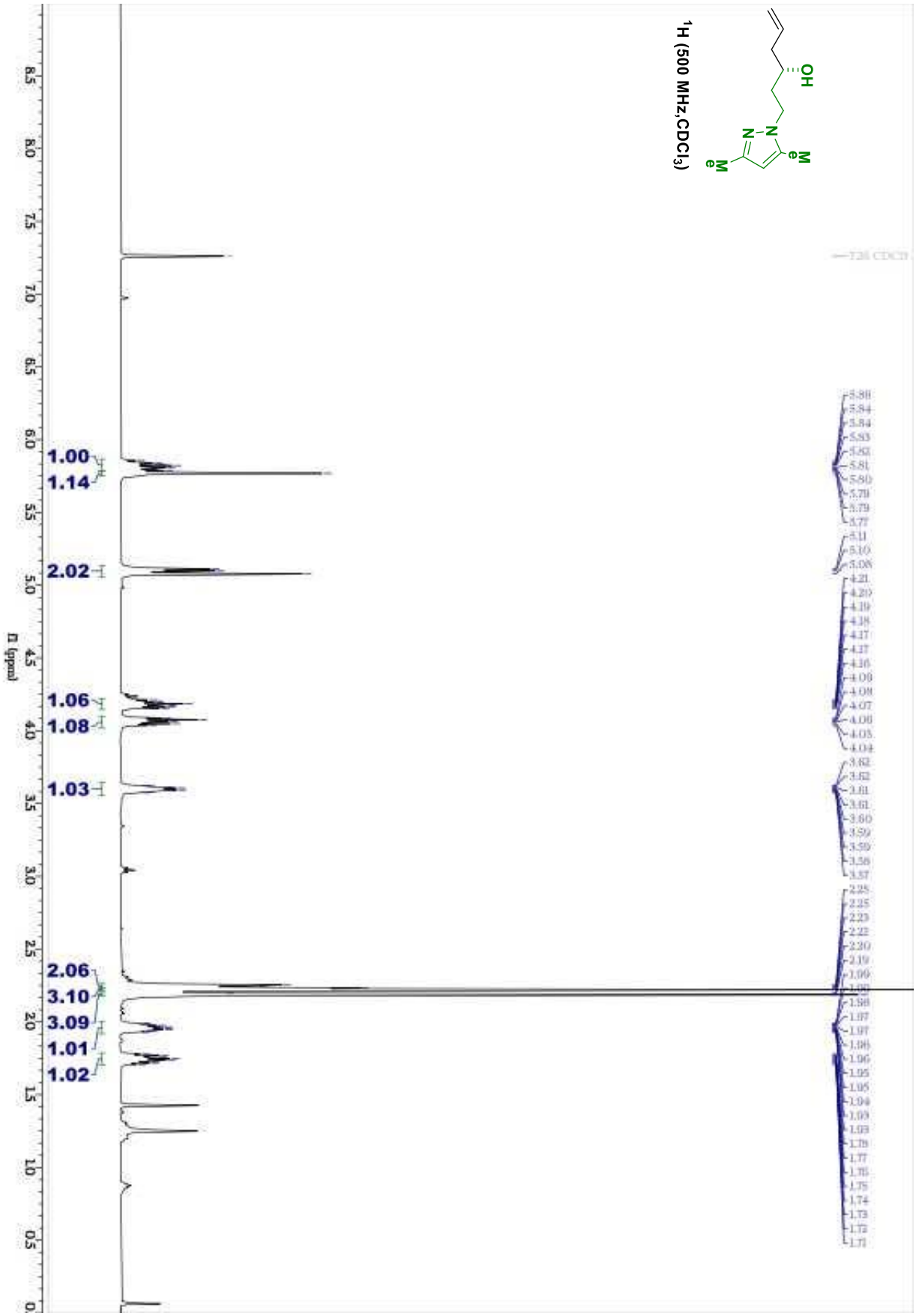
^{13}C NMR (126 MHz, $CDCl_3$): δ 147.6, 139.1, 135.0, 117.8, 105.1, 68.4, 45.7, 42.1, 36.8, 15.3, 11.1.

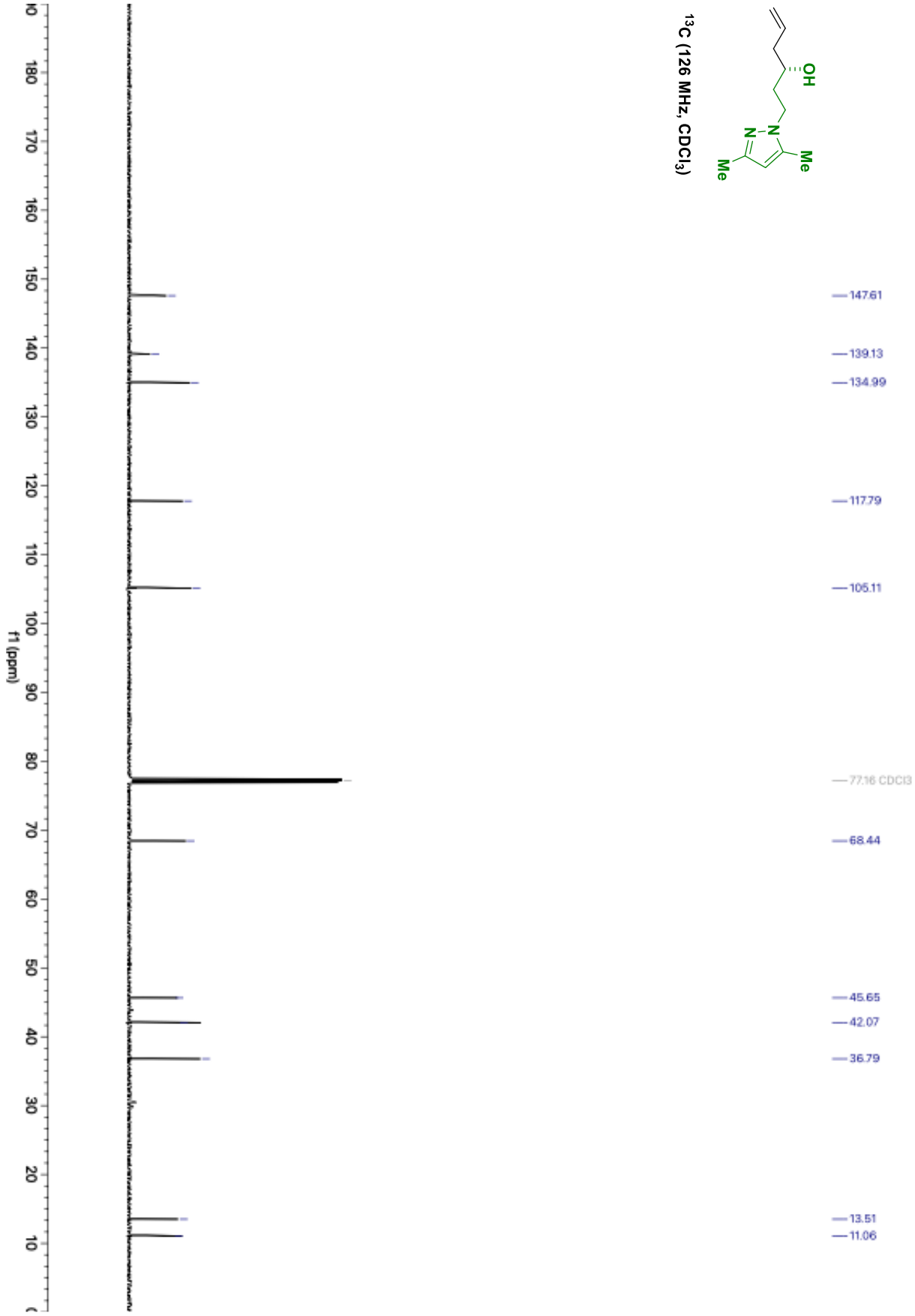
HRMS (Na+, *m/z*): for $C_{11}H_{18}N_2O$: calcd. = 195.1492; found = 195.1491.

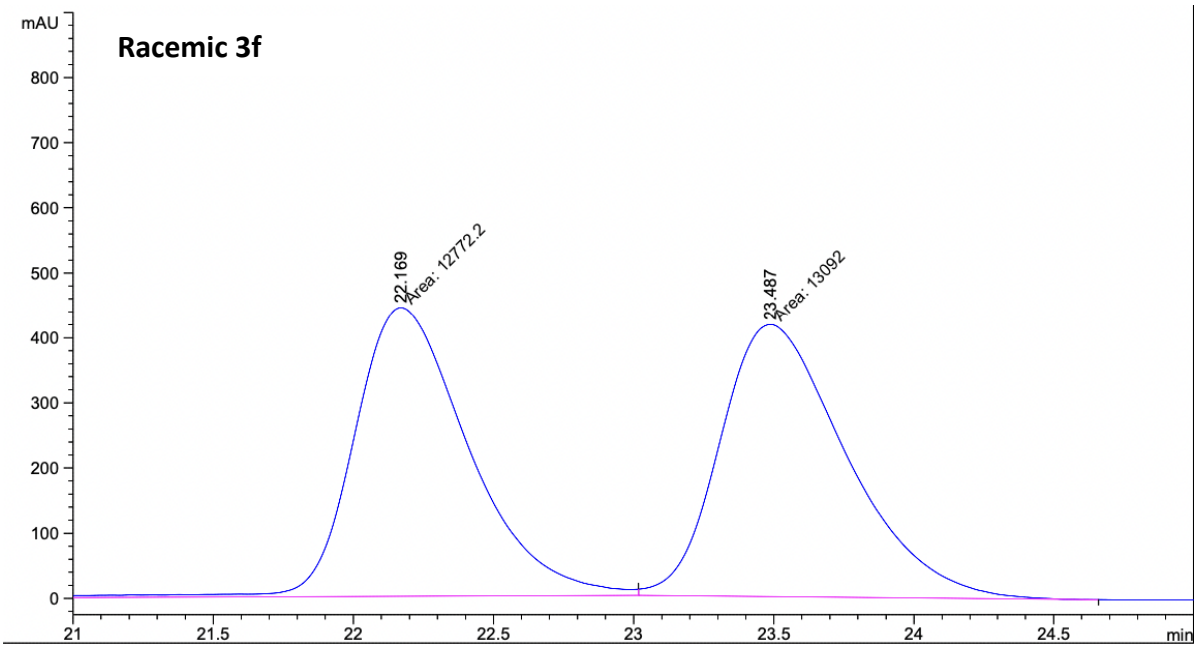
FTIR (neat): 3319, 3076, 2923, 1550, 1460, 1384, 1062, 909, 797 cm^{-1}.

HPLC: (Chiralcel column Amylose 2, Hexane: 2-PrOH = 94:06, 0.5 mL/min, 210 nm).

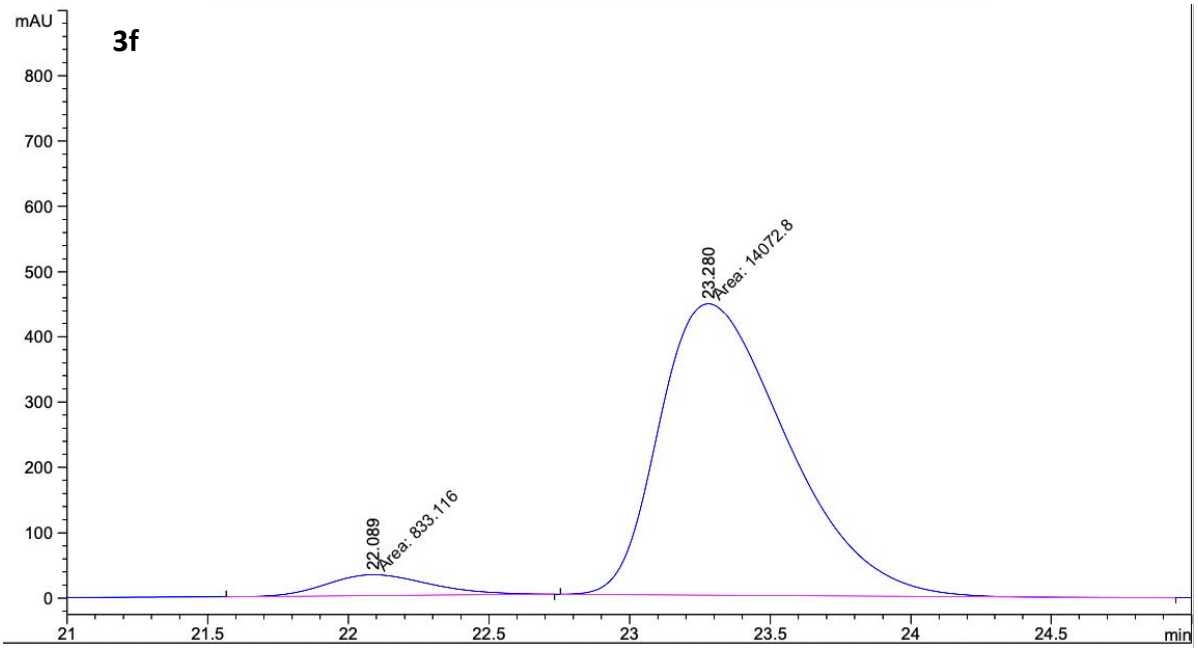
$[\alpha]_D^{24}$ = +4.5 (c = 0.1, $CHCl_3$).


^{1}H (500 MHz,CDCl$_3$)
OH
N
N
Me
Me
1.00
1.14
2.02
1.06
1.08
1.03
2.06
3.10
3.09
1.01
1.02
f1 (ppm)


^{13}C (126 MHz, CDCl$_3$)
OH
N
N
Me
Me
147.61
139.13
134.99
117.79
105.11
77.16 CDCl3
68.44
45.65
42.07
36.79
13.51
11.06
f1 (ppm)

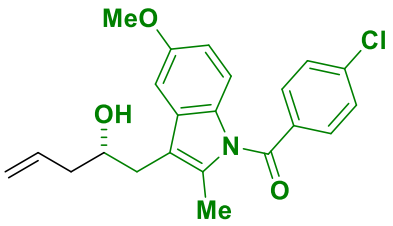


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.169	MM	0.4798	1.27722e4	443.65454	49.3819
2	23.487	MM	0.5222	1.30920e4	417.85358	50.6181



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.089	MM	0.4307	833.11554	32.23835	5.5892
2	23.280	MM	0.5249	1.40728e4	446.83960	94.4108

(*S*)-(4-chlorophenyl)(3-(2-hydroxypent-4-en-1-yl)-5-methoxy-2-methyl-1*H*-indol-1-yl)methanone (3g)



Alcohol **2g** (69.8 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 5:95 EtOAc:hexanes) the title compound **3g** was isolated as a brown-yellow oil in 61% yield (46.7 mg, 0.12 mmol, 89% ee).

TLC (SiO_2): R_f = 0.3 (2:3 EtOAc:Hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 – 7.62 (m, 2H), 7.49 – 7.44 (m, 2H), 6.95 (s, 1H), 6.89 – 6.83 (m, 1H), 6.69-6.64 (dt, *J* = 9.0, 2.2 Hz, 1H), 5.94 – 5.82 (m, 1H), 5.24 – 5.15 (m, 2H), 4.01 – 3.90 (m, 1H), 3.84 (d, *J* = 1.8 Hz, 3H), 2.87 – 2.82 (m, 2H), 2.43 – 2.35 (m, 4H), 2.31-2.23 (dt, *J* = 15.0, 8.4 Hz, 1H), 1.86 – 1.77 (m, 1H).

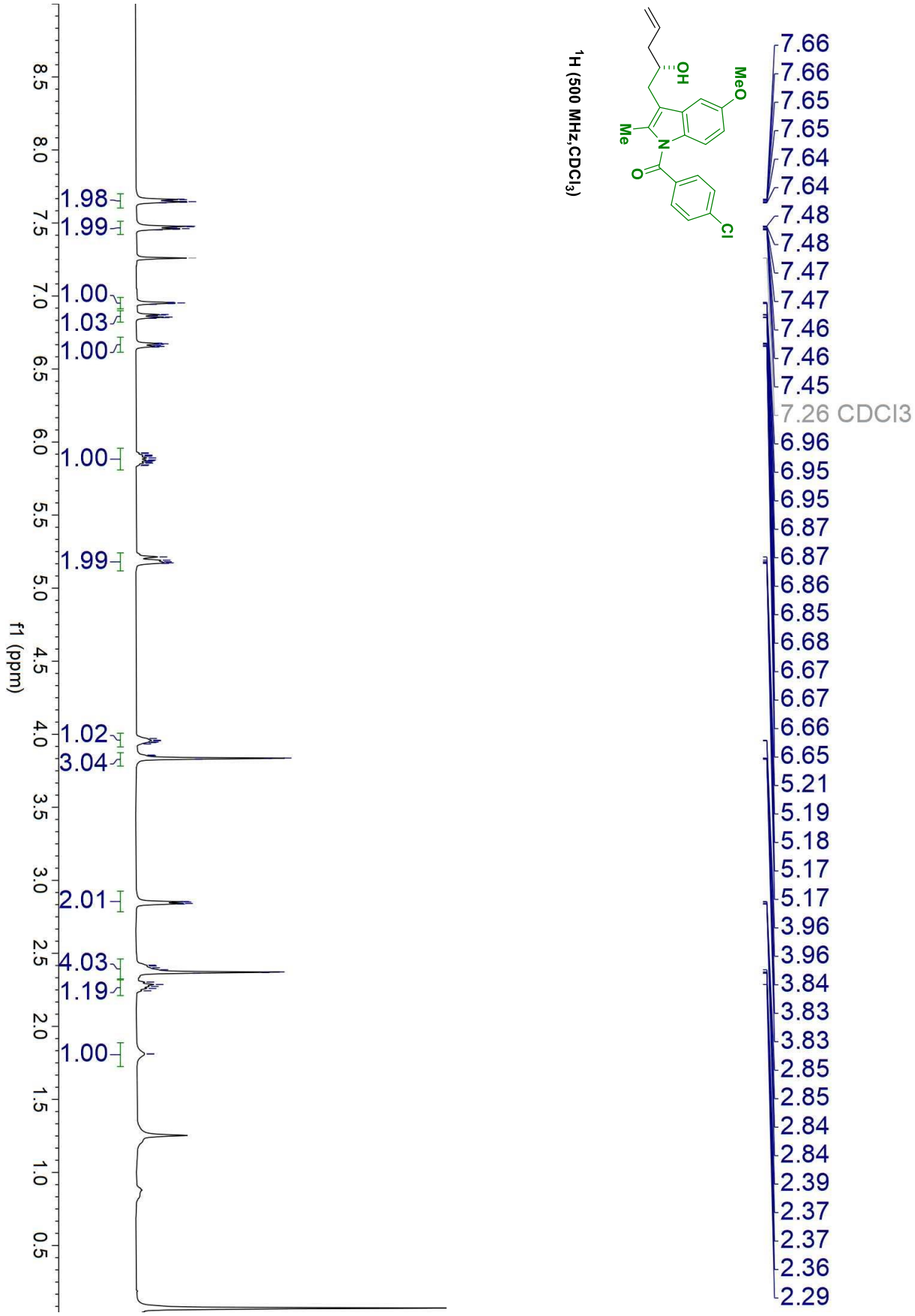
^{13}C NMR (126 MHz, $CDCl_3$): δ 168.5, 156.1, 139.3, 135.8, 134.8, 134.2, 131.4, 131.3, 131.1, 129.3 (d, *J* = 3.0 Hz), 118.6, 116.2, 115.1, 111.4, 101.8, 70.7, 55.9, 41.7, 31.9, 29.9, 13.7, 1.2.

HRMS (Na+, *m/z*): for $C_{22}H_{22}ClNO_3$ calcd. = 406.1180; found = 406.1177.

FTIR (neat): 3301, 3038, 2684, 1949, 1724, 1608, 1188, 736 cm^{-1}.

HPLC: (Phenomenex LC Column Cellulose-5, Hexane: 2-PrOH = 94:06, 0.5 mL/120min, 254 nm).

$[\alpha]_D^{24}$ = +24.2 (c = 0.4, $CHCl_3$)


^{1}H (500 MHz,CDCl$_3$)
OH
MeO
Me
N
O
Cl
7.66
7.66
7.65
7.65
7.64
7.64
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.26 CDCl3
6.96
6.95
6.95
6.87
6.87
6.86
6.85
6.68
6.67
6.67
6.66
6.65
5.21
5.19
5.18
5.17
5.17
3.96
3.96
3.84
3.83
3.83
2.85
2.85
2.84
2.84
2.39
2.37
2.37
2.36
2.29
1.98
1.99
1.00
1.03
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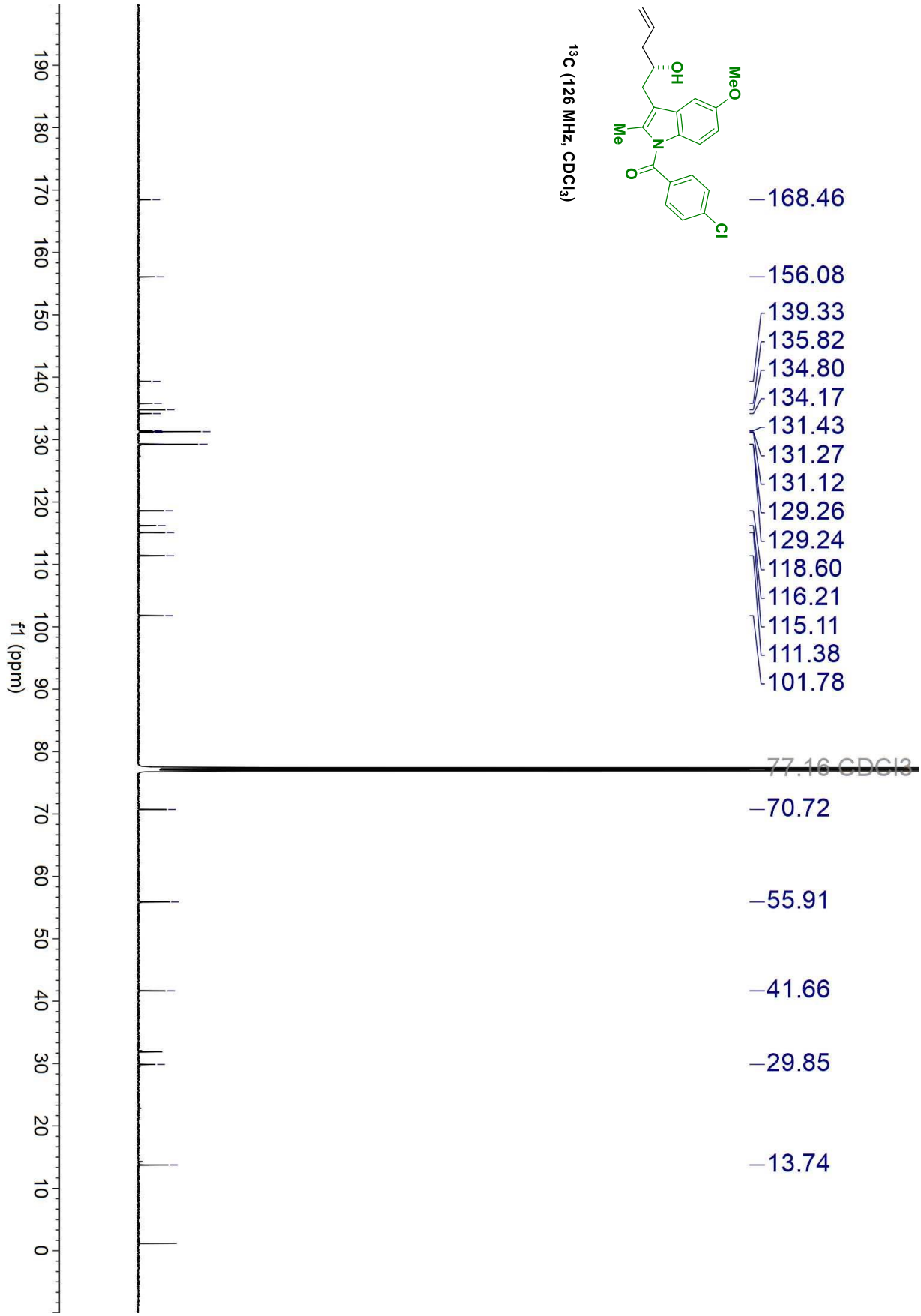
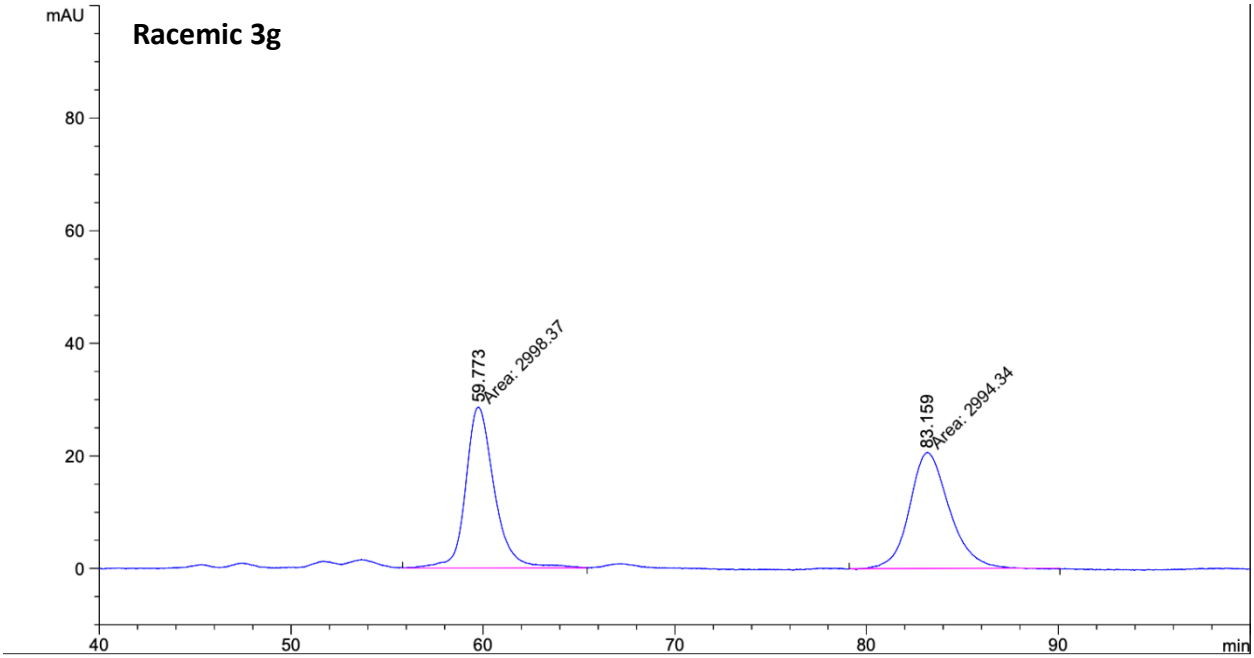
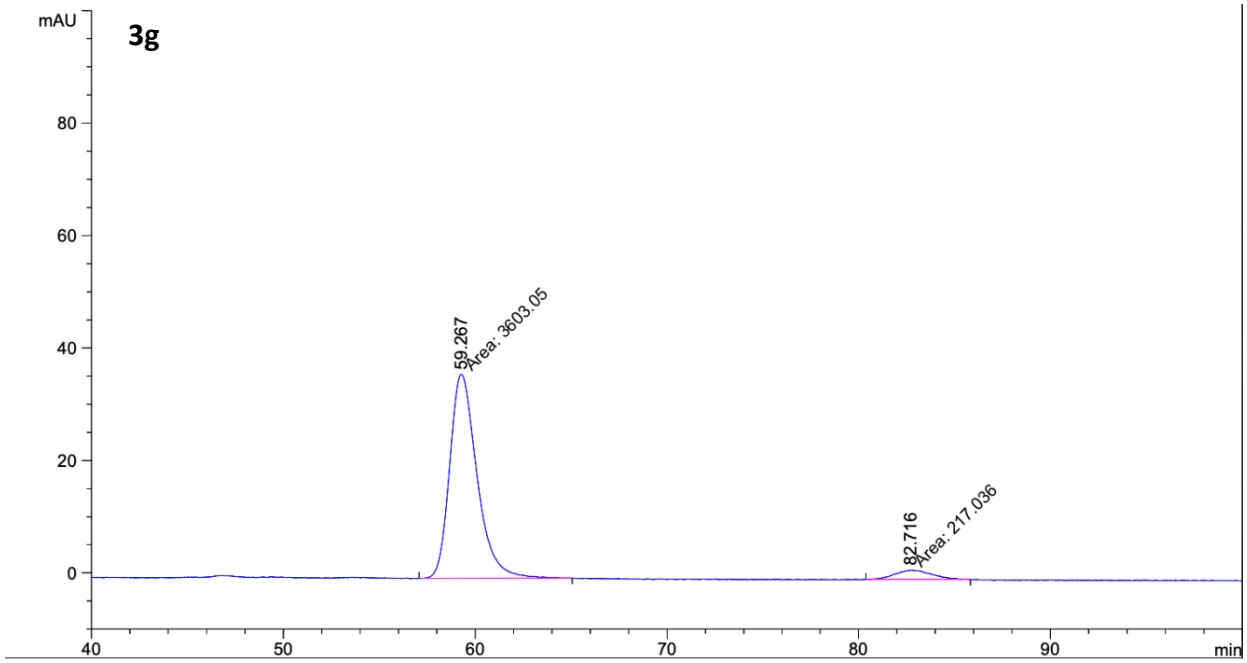
1.00
1.99
1.02
3.04
2.01
4.03
1.19
1.00
f1 (ppm)


^{13}C (126 MHz, CDCl$_3$)
OH
MeO
Me
N
O
Cl
168.46
156.08
139.33
135.82
134.80
134.17
131.43
131.27
131.12
129.26
129.24
118.60
116.21
115.11
111.38
101.78
77.16 CDCl3
70.72
55.91
41.66
29.85
13.74
f1 (ppm)

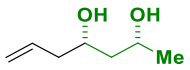


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	59.773	MM	1.7448	2998.36743	28.64117	50.0336
2	83.159	MM	2.4098	2994.34253	20.70942	49.9664



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	59.267	MM	1.6533	3603.04687	36.32074	94.3185
2	82.716	MM	2.1845	217.03621	1.65588	5.6815

(2R,4S)-hept-6-ene-2,4-diol (3h)



Alcohol **2h** (18.0 mg, 0.2 mmol) was subjected to standard reaction conditions with **SL-J502-01** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 20:80 EtOAc:hexanes) the title compound **3h** was isolated as a yellow oil in 98% yield (25.5 mg, 0.19 mmol, >20:1 dr).

TLC (SiO_2): R_f = 0.5 (1:2 EtOAc:hexanes)

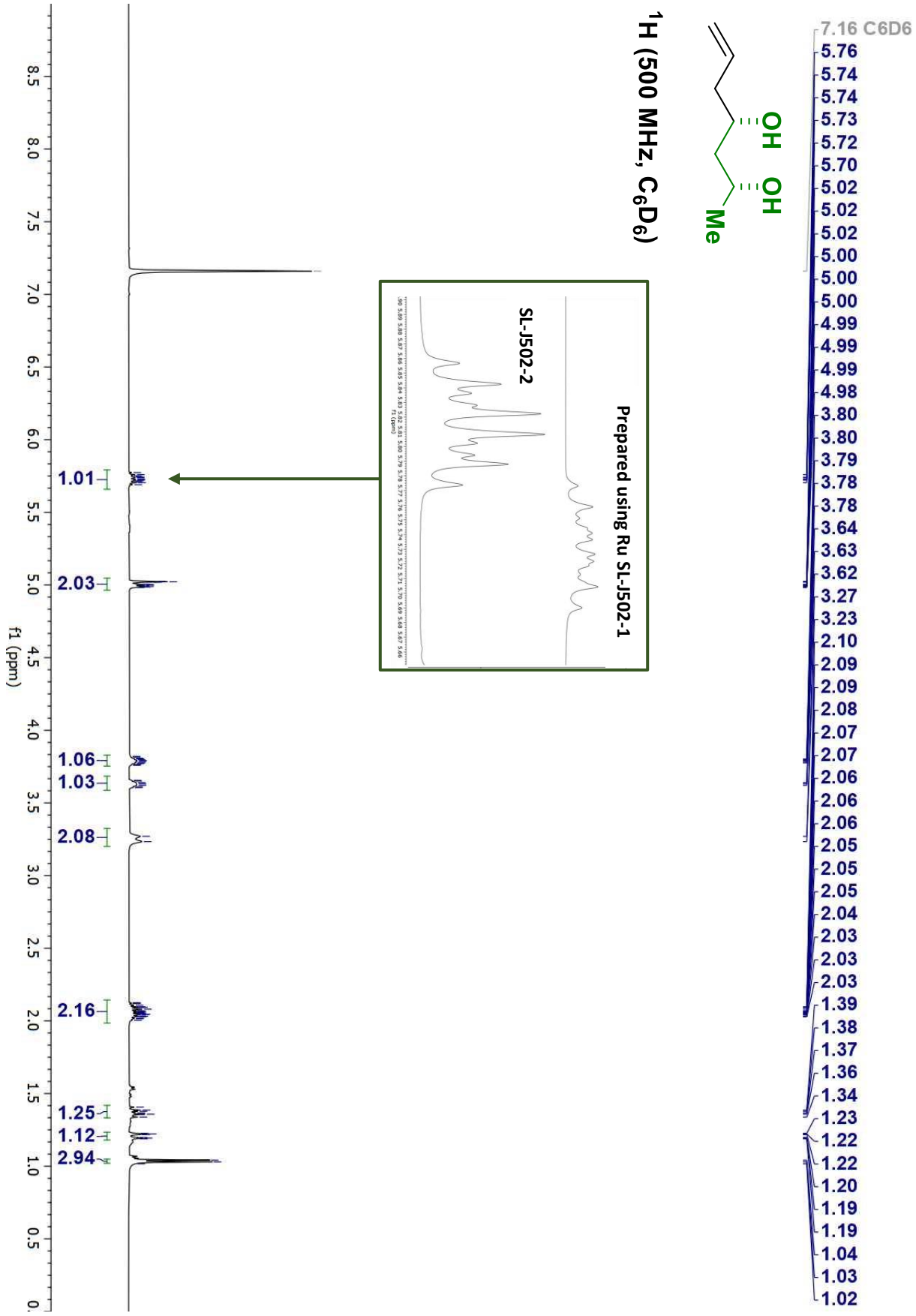
^{1}H NMR (500 MHz, C_6D_6): δ 5.73 (ddt, J = 15.8, 11.4, 7.2 Hz, 1H), 5.02 (d, J = 1.4 Hz, 1H), 5.01 – 4.97 (m, 1H), 3.79 (dqd, J = 8.6, 6.1, 2.2 Hz, 1H), 3.68 – 3.59 (m, 1H), 3.25 (d, J = 18.0 Hz, 2H), 2.14 – 1.99 (m, 2H), 1.37 (dt, J = 14.3, 10.1 Hz, 1H), 1.21 (dt, J = 14.3, 2.3 Hz, 1H), 1.04 (d, J = 6.2 Hz, 3H).

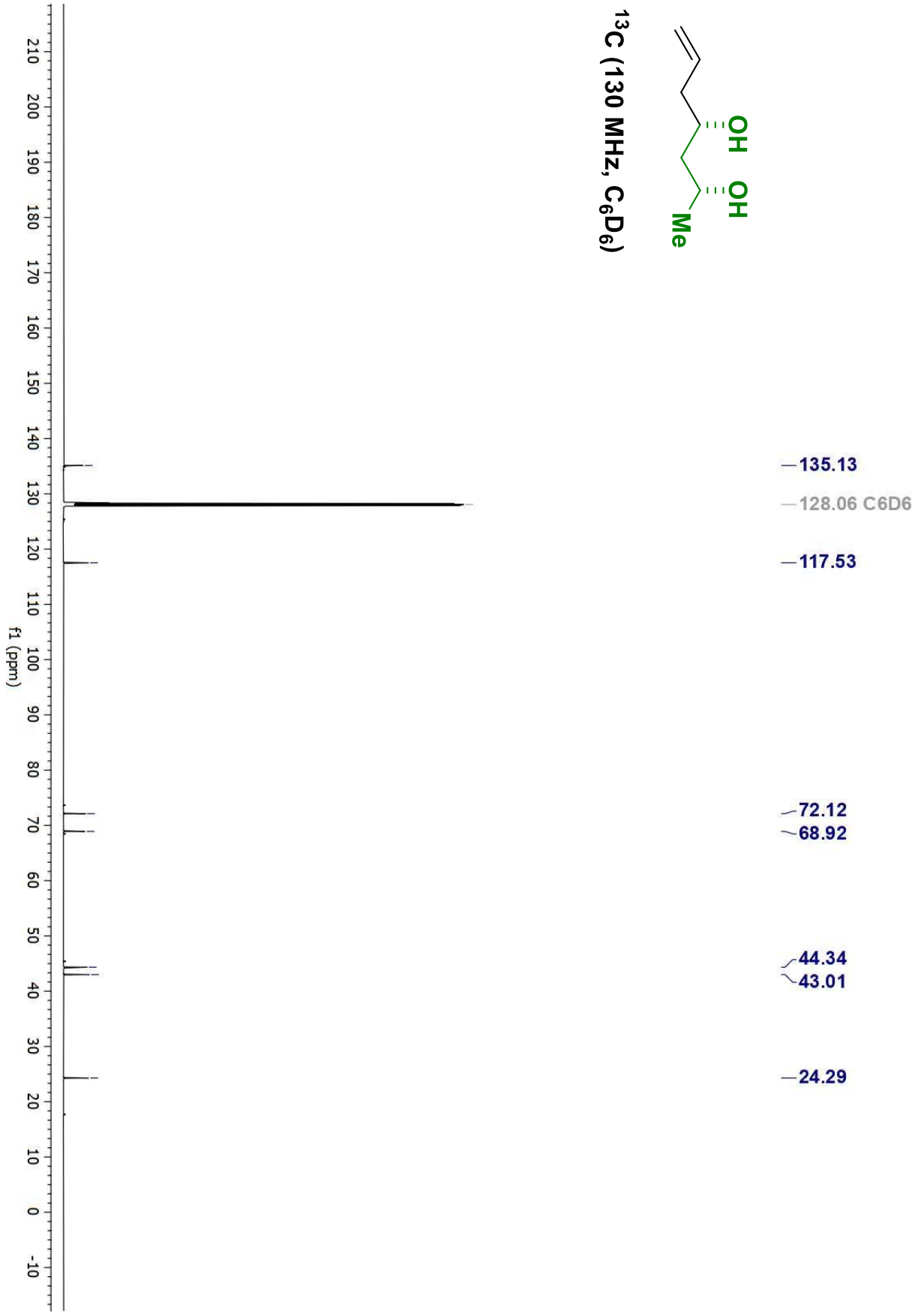
^{13}C NMR (130 MHz, C_6D_6): δ 135.1, 117.5, 72.1, 68.9, 44.3, 43.0, 24.3.

HRMS (H+, *m/z*): for $C_7H_{14}O_2$: calcd. = 130.0994; found = 130.0995.

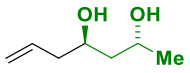
FTIR (neat): 3364, 2970, 2931, 1642, 1432, 1375, 1325, 1081 cm^{-1}.

$[\alpha]_D^{24}$ = -24.0 (c = 1.0, $CHCl_3$).


^{1}H (500 MHz, C_6D_6)
OH
OH
Me
7.16 C6D6
5.76
5.74
5.74
5.73
5.72
5.70
5.02
5.02
5.02
5.00
5.00
5.00
4.99
4.99
4.99
4.98
3.80
3.80
3.79
3.78
3.78
3.64
3.63
3.62
3.27
3.23
2.10
2.09
2.09
2.08
2.07
2.07
2.06
2.06
2.06
2.05
2.05
2.05
2.04
2.03
2.03
2.03
1.39
1.38
1.37
1.36
1.34
1.23
1.22
1.22
1.20
1.19
1.19
1.04
1.03
1.02
Prepared using Ru SL-J502-1
SL-J502-2
1.01
2.03
1.06
1.03
2.08
2.16
1.25
1.12
2.94
f1 (ppm)


^{13}C (130 MHz, C_6D_6)
OH
OH
Me
135.13
128.06 C6D6
117.53
72.12
68.92
44.34
43.01
24.29
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

(2R,4R)-hept-6-ene-2,4-diol (*epi*-3h)



Alcohol **2h** (18.0 mg, 0.2 mmol) was subjected to standard reaction conditions with **SL-J502-02** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 20:80 EtOAc:hexanes) the title compound ***epi*-3h** was isolated as a yellow oil in 96% yield (24.9 mg, 0.19 mmol, >20:1 dr).

TLC (SiO_2): R_f = 0.5 (1:2 EtOAc:hexanes)

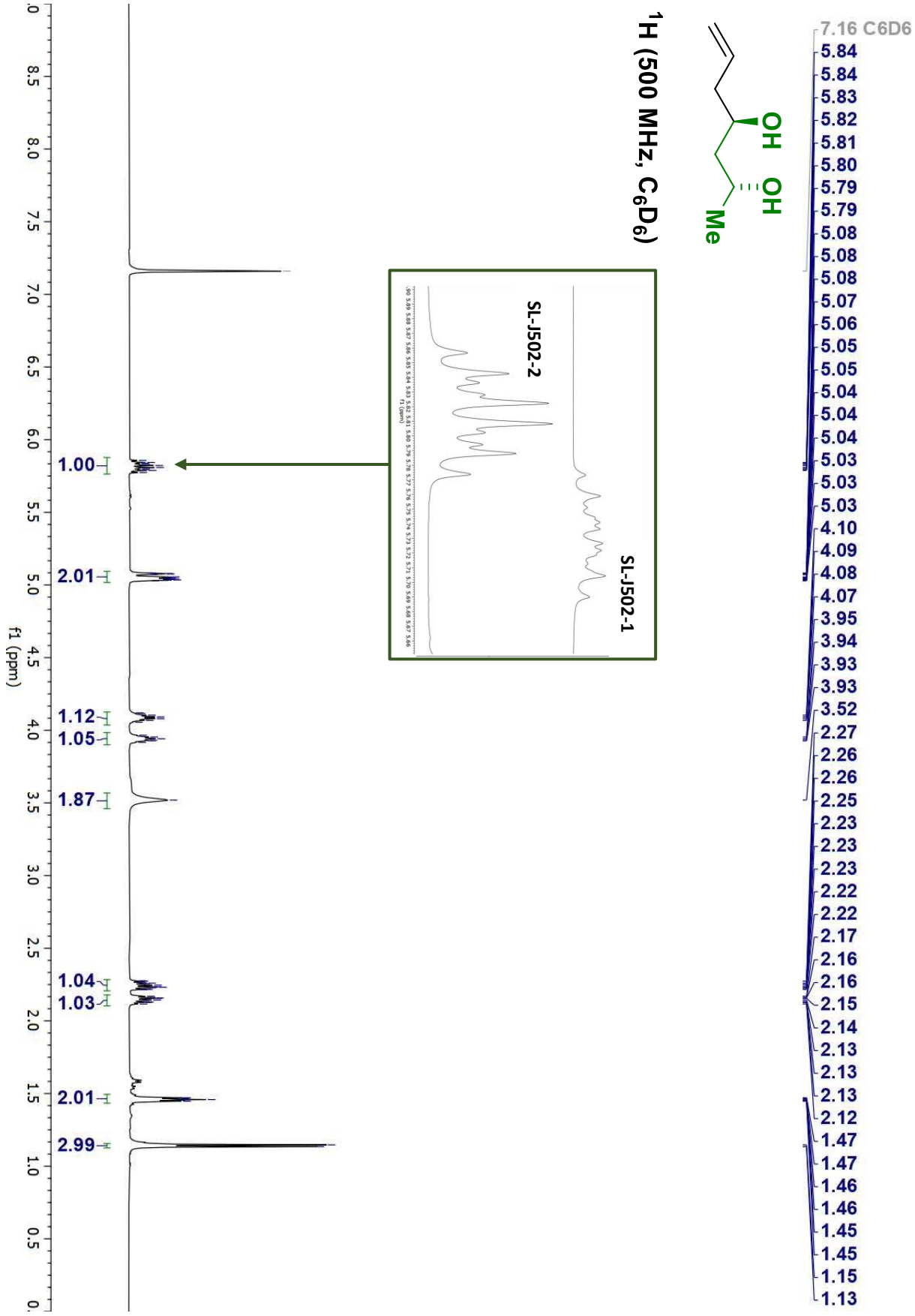
^{1}H NMR (500 MHz, C_6D_6): δ 5.82 (ddt, J = 17.2, 10.1, 7.0 Hz, 1H), 5.09 – 5.02 (m, 2H), 4.09 (dqd, J = 6.3, 6.2, 6.2 Hz, 1H), 3.98 – 3.90 (m, 1H), 3.52 (s, 2H), 2.28 – 2.21 (m, 1H), 2.18 – 2.10 (m, 1H), 1.49 – 1.43 (m, 2H), 1.14 (d, J = 6.2 Hz, 3H).

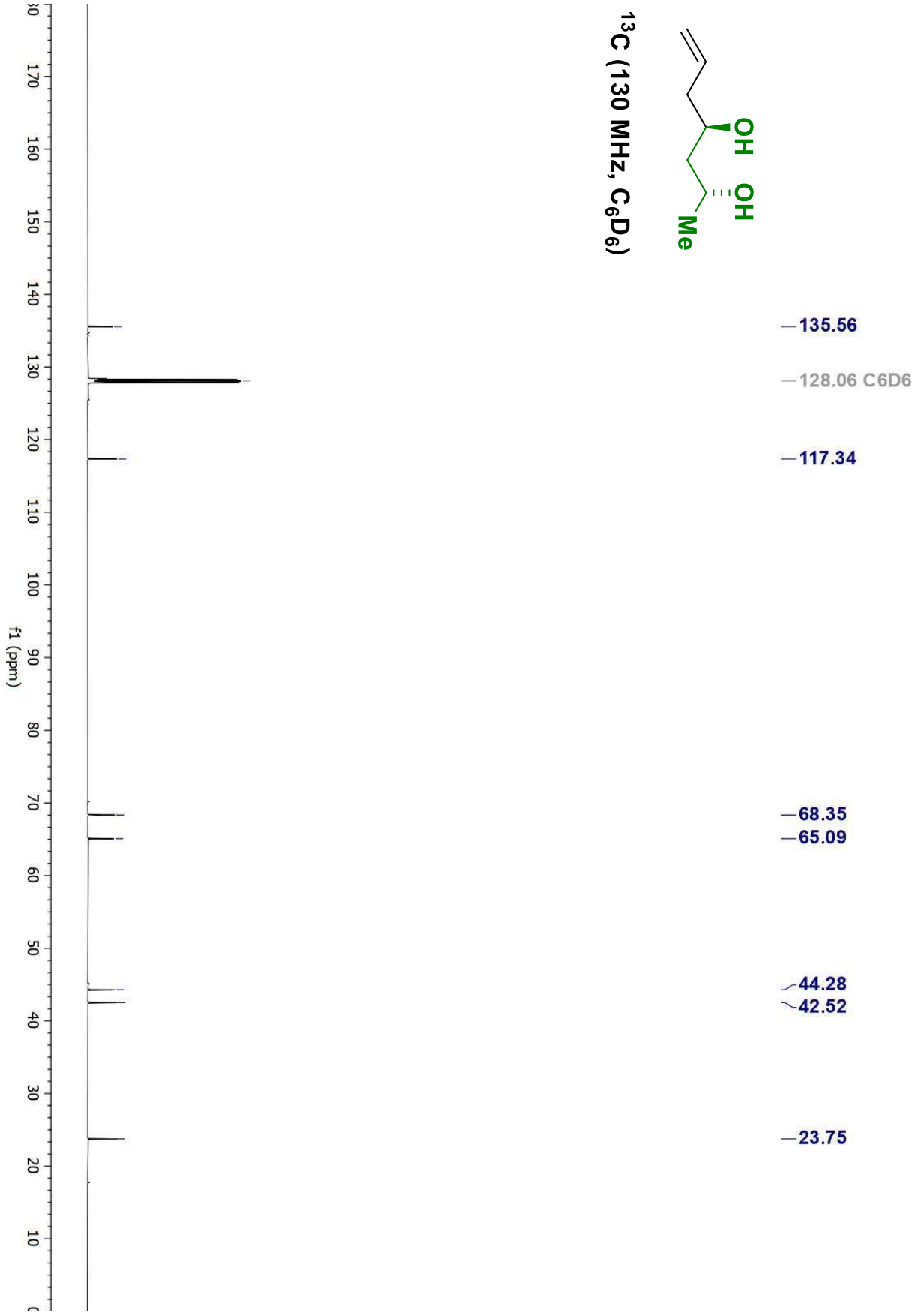
^{13}C NMR (130 MHz, C_6D_6): δ 135.6, 117.3, 68.3, 65.1, 44.3, 42.5, 23.7.

HRMS (H+, *m/z*): for $C_7H_{14}O_2$: calcd. = 130.0994; found = 130.0995.

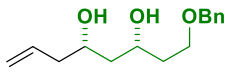
FTIR (neat): 3365, 2973, 2934, 1646, 1435, 1379, 1325, 1081 cm^{-1}.

$[\alpha]_D^{24}$ = 22.5 (c = 0.61, $CHCl_3$).


^{1}H (500 MHz, C_6D_6)
OH
OH
Me
7.16 C6D6
5.84
5.84
5.83
5.82
5.81
5.80
5.79
5.79
5.08
5.08
5.08
5.07
5.06
5.05
5.05
5.04
5.04
5.04
5.03
5.03
5.03
4.10
4.09
4.08
4.07
3.95
3.94
3.93
3.93
3.52
2.27
2.26
2.26
2.25
2.23
2.23
2.23
2.22
2.22
2.17
2.16
2.16
2.15
2.14
2.13
2.13
2.13
2.12
1.47
1.47
1.46
1.46
1.45
1.45
1.15
1.13
SL-J502-2
SL-J502-1
1.00
2.01
1.12
1.05
1.87
1.04
1.03
2.01
2.99
f1 (ppm)


13C (130 MHz, C6D6)
OH
OH
Me
135.56
128.06 C6D6
117.34
68.35
65.09
44.28
42.52
23.75
f1 (ppm)

(3R,5S)-1-(benzyloxy)oct-7-ene-3,5-diol (3i)



Alcohol **2i** (42.0 mg, 0.2 mmol) was subjected to standard reaction conditions with **SL-J502-1** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 10:90 EtOAc:hexanes) the title compound **3i** was isolated as a yellow oil in 94% yield (47.9 mg, 0.19 mmol, >20:1 dr).

TLC (SiO_2): R_f = 0.5 (1:4 EtOAc:hexanes)

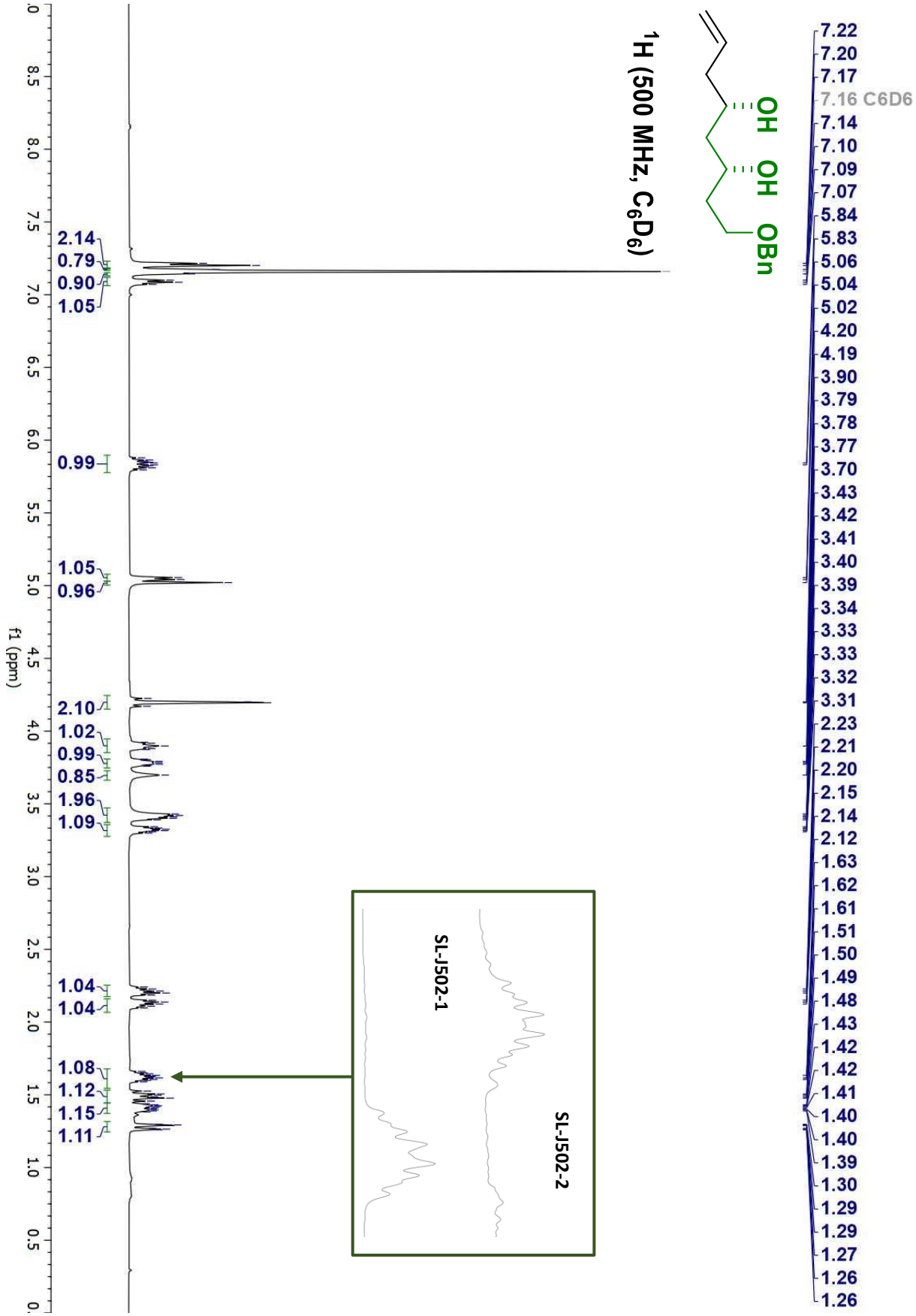
^{1}H NMR (500 MHz, C_6D_6): δ 7.21 (d, J = 7.6 Hz, 2H), 7.17 (s, 1H), 7.14 (s, 1H), 7.09 (t, J = 7.3 Hz, 1H), 5.84 (ddt, J = 17.3, 10.8, 7.1 Hz, 1H), 5.05 (d, J = 6.8 Hz, 1H), 5.02 (s, 1H), 4.20 (d, J = 3.1 Hz, 2H), 3.95 – 3.85 (m, 1H), 3.78 (dt, J = 11.9, 6.4 Hz, 1H), 3.70 (s, 1H), 3.47 – 3.37 (m, 2H), 3.32 (td, J = 8.5, 4.5 Hz, 1H), 2.21 (dt, J = 13.8, 6.9 Hz, 1H), 2.12 (dt, J = 13.4, 6.4 Hz, 1H), 1.62 (dp, J = 16.9, 4.3 Hz, 1H), 1.49 (dt, J = 14.5, 10.1 Hz, 1H), 1.41 (ddt, J = 14.2, 6.7, 3.7 Hz, 1H), 1.28 (dt, J = 14.4, 2.4 Hz, 1H).

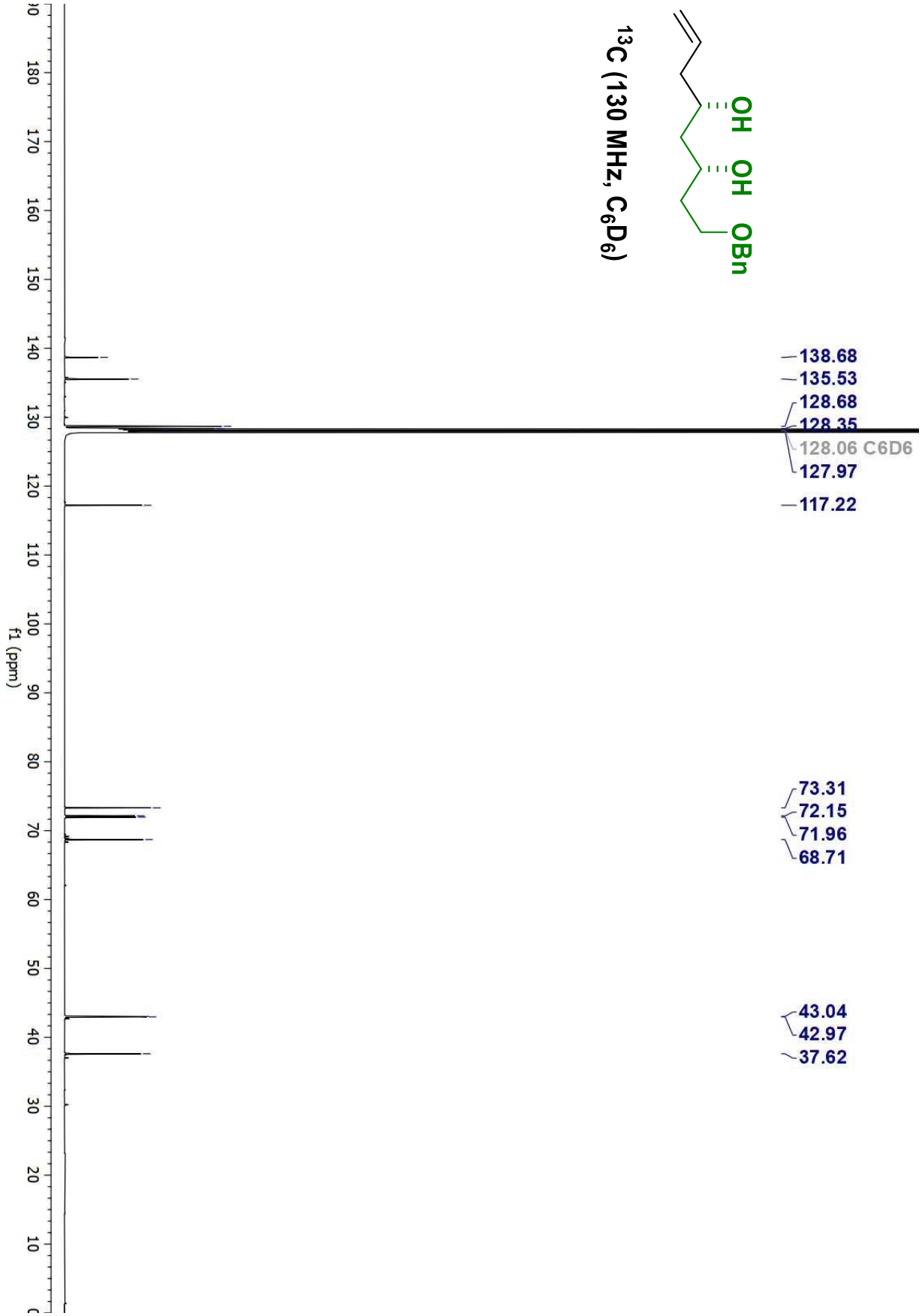
^{13}C NMR (130 MHz, C_6D_6): δ 138.7, 135.5, 128.7, 128.4, 128.0, 117.2, 73.3, 72.1, 72.0, 68.7, 43.0, 43.0, 37.6.

HRMS (H+, *m/z*): for $C_{15}H_{22}O_3$: calcd. = 251.2114; found = 251.2100.

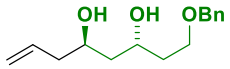
FTIR (neat): 3394, 1650, 1625, 1589, 1574, 1337, 1285, 1188, 1100, 1076 cm^{-1}.

$[\alpha]_D^{24}$ = 21 (c = 0.81, $CHCl_3$).


^{1}H (500 MHz, C_6D_6)
OH OH OBn
7.16 C6D6
SL-J502-1
SL-J502-2
f1 (ppm)


^{13}C (130 MHz, C_6D_6)
OH OH OBn
138.68
135.53
128.68
128.35
128.06 C6D6
127.97
117.22
73.31
72.15
71.96
68.71
43.04
42.97
37.62
f1 (ppm)

(3R,5R)-1-(benzyloxy)oct-7-ene-3,5-diol (*epi*-3i)



Alcohol **2i** (42.0 mg, 0.2 mmol) was subjected to standard reaction conditions with **SL-J502-02** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 10:90 EtOAc:hexanes) the title compound ***epi*-3i** was isolated as a yellow oil in 92% yield (47.0 mg, 0.19 mmol, >20:1 dr).

TLC (SiO_2): R_f = 0.5 (1:4 EtOAc:hexanes)

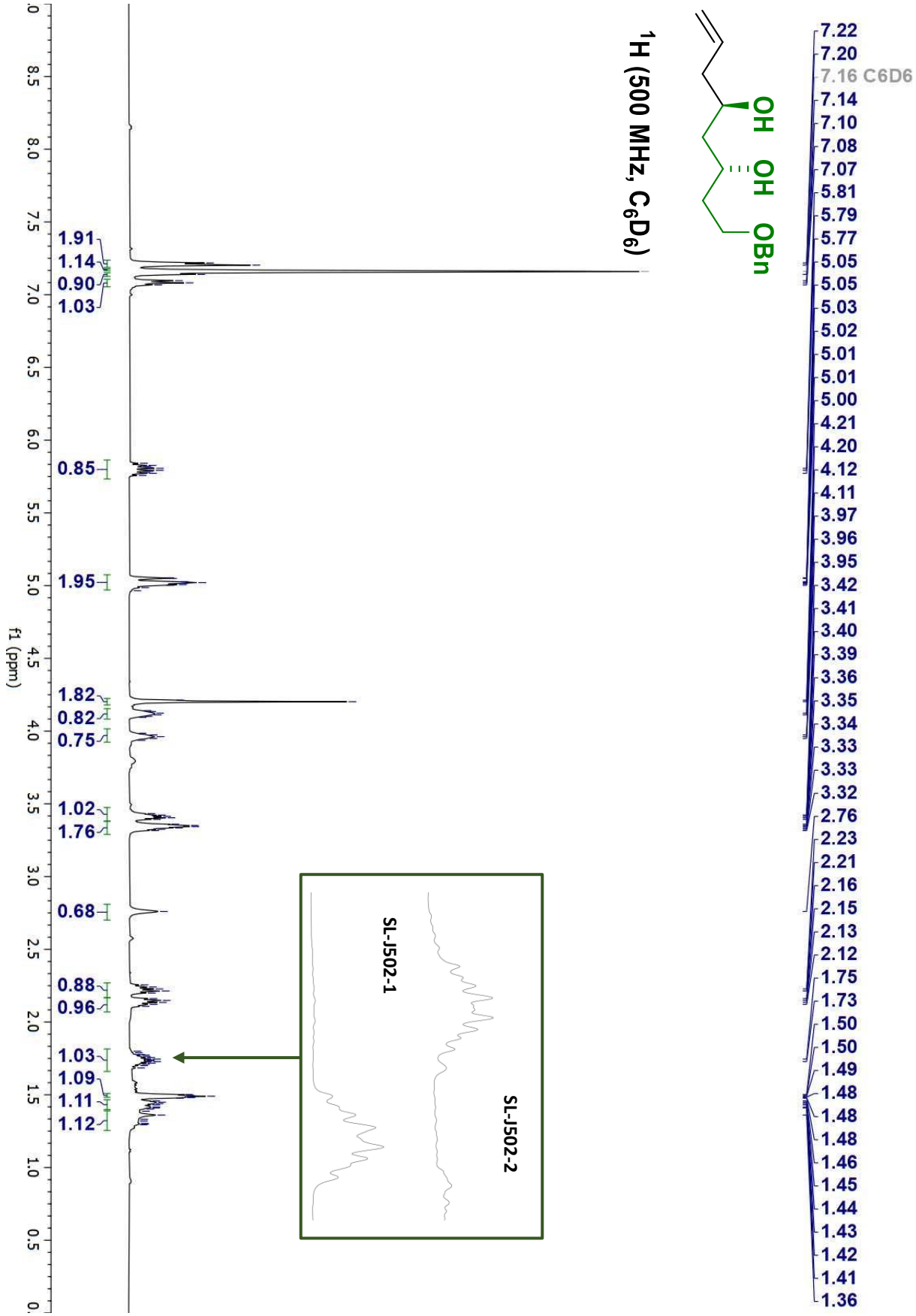
^{1}H NMR (500 MHz, C_6D_6): δ 7.21 (d, J = 7.4 Hz, 2H), 7.14 (s, 1H), 7.08 (t, J = 7.3 Hz, 1H), 5.80 (ddt, J = 17.3, 10.2, 7.2 Hz, 1H), 5.02 (qd, J = 11.7, 5.1 Hz, 2H), 4.21 (d, J = 5.3 Hz, 2H), 4.12 (q, J = 7.0 Hz, 1H), 3.96 (p, J = 6.0 Hz, 1H), 3.41 (dt, J = 10.3, 5.3 Hz, 1H), 3.34 (dp, J = 9.0, 4.8 Hz, 2H), 2.76 (s, 1H), 2.23 (dt, J = 14.2, 7.2 Hz, 1H), 2.13 (dt, J = 13.5, 6.3 Hz, 1H), 1.81 – 1.66 (m, 1H), 1.49 (dd, J = 5.5, 3.0 Hz, 1H), 1.43 (dt, J = 14.3, 5.5 Hz, 1H), 1.35 (q, J = 14.0 Hz, 1H).

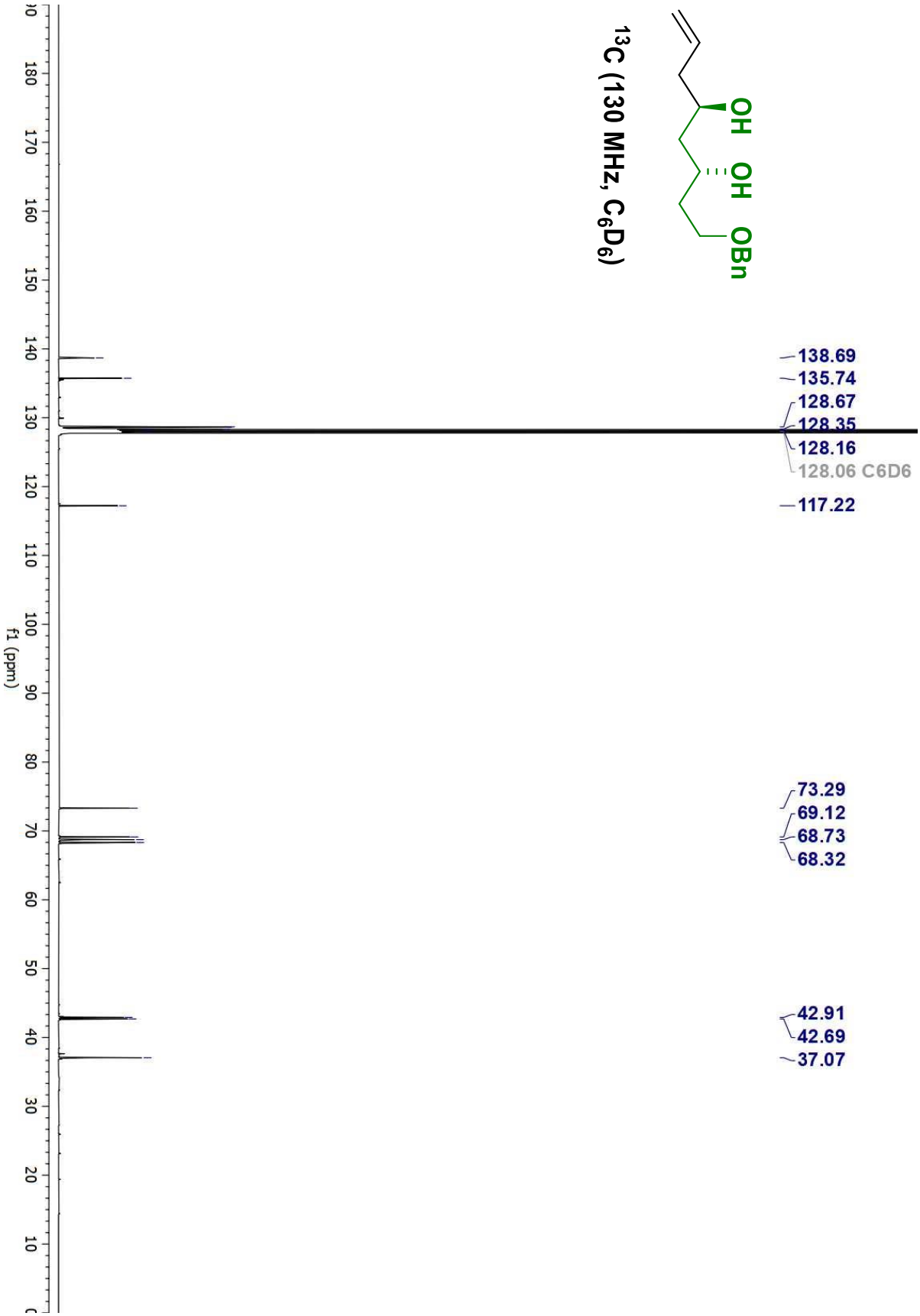
^{13}C NMR (130 MHz, C_6D_6): δ 138.7, 135.7, 128.7, 128.4, 128.2, 117.2, 73.3, 69.1, 68.7, 68.3, 42.9, 42.7, 37.1.

HRMS (H+, *m/z*): for $C_{15}H_{22}O_3$: calcd. = 251.2114; found = 251.2100.

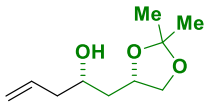
FTIR (neat): 3394, 1650, 1625, 1589, 1574, 1337, 1285, 1188, 1100, 1076 cm^{-1}.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{24}}$ = -13.2 (c = 1.0, $CHCl_3$).


1H (500 MHz, C6D6)
OH OH OBn
7.22
7.20
7.16 C6D6
7.14
7.10
7.08
7.07
5.81
5.79
5.77
5.05
5.05
5.03
5.02
5.01
5.01
5.00
4.21
4.20
4.12
4.11
3.97
3.96
3.95
3.42
3.41
3.40
3.39
3.36
3.35
3.34
3.33
3.33
3.32
2.76
2.23
2.21
2.16
2.15
2.13
2.12
1.75
1.73
1.50
1.50
1.49
1.48
1.48
1.48
1.46
1.45
1.44
1.43
1.42
1.41
1.36
1.91
1.14
0.90
1.03
0.85
1.95
1.82
0.82
0.75
1.02
1.76
0.68
0.88
0.96
1.03
1.09
1.11
1.12
f1 (ppm)
SL-J502-1
SL-J502-2


13C (130 MHz, C6D6)
OH OH OBn
138.69
135.74
128.67
128.35
128.16
128.06 C6D6
117.22
73.29
69.12
68.73
68.32
42.91
42.69
37.07
f1 (ppm)

(S)-1-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-4-en-2-ol (3j)



Alcohol **2j** (29.2 mg, 0.2 mmol) was subjected to standard reaction conditions with **SL-J502-1** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 1:99 EtOAc:hexanes) the title compound **3j** was isolated as a yellow oil in 92% yield (34.7 mg, 0.19 mmol, >20:1 dr).

TLC (SiO_2): R_f = 0.5 (1:8 EtOAc:hexanes)

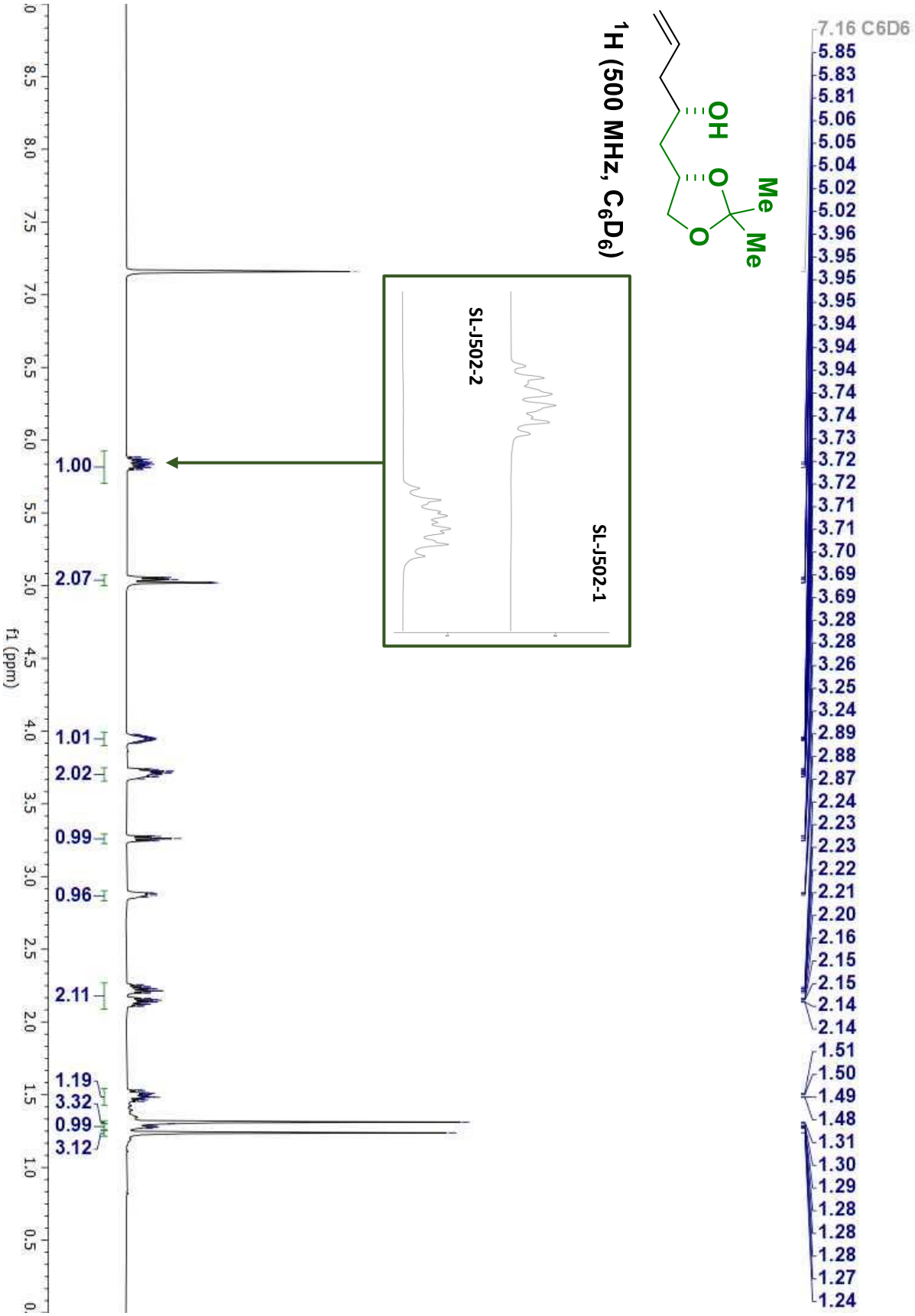
^{1}H NMR (500 MHz, C_6D_6): δ 5.93 – 5.69 (m, 1H), 5.07 – 5.00 (m, 2H), 3.95 (ddddd, J = 9.4, 7.6, 6.1, 4.1, 2.2 Hz, 1H), 3.75 – 3.66 (m, 2H), 3.29 – 3.23 (m, 1H), 2.90 – 2.83 (m, 1H), 2.27 – 2.09 (m, 2H), 1.55 – 1.43 (m, 1H), 1.31 (s, 3H), 1.28 (dt, J = 4.4, 2.5 Hz, 1H), 1.24 (s, 3H).

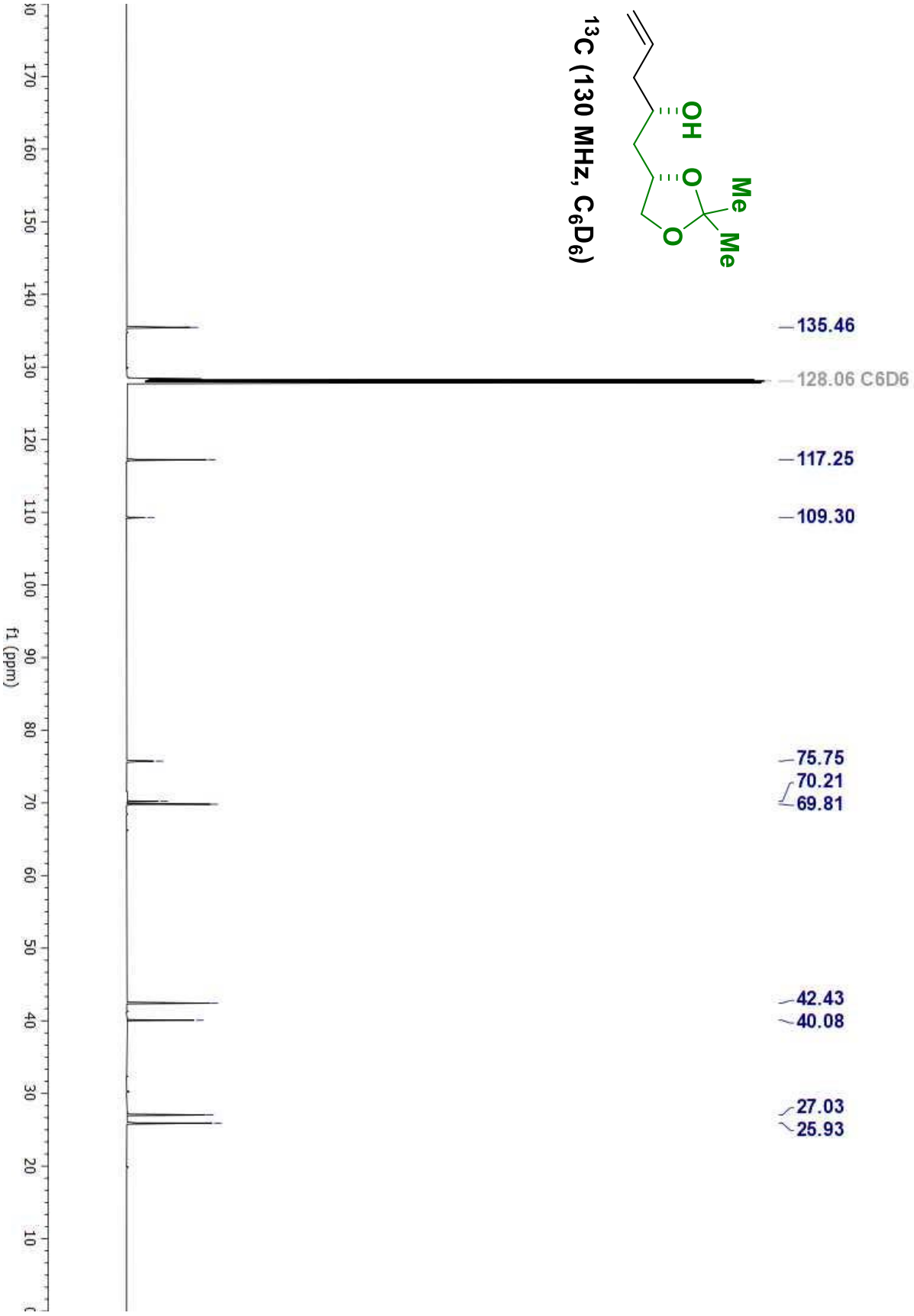
^{13}C NMR (130 MHz, C_6D_6): δ 135.5, 117.3, 109.3, 75.7, 70.2, 69.8, 42.4, 40.1, 27.0, 25.9.

HRMS (Na+, *m/z*): for $C_{10}H_{18}O_3$: calcd. = 209.1148; found = 209.1147.

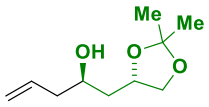
FTIR (neat): 2984, 2935, 1774, 1370, 1215, 1157, 1057, 996, 915, 862 cm^{-1}.

$[\alpha]_D^{24}$ = 12.6 (c = 1.0, $CHCl_3$).


^{1}H (500 MHz, C_6D_6)
OH
O
O
Me
Me
SL-J502-2
SL-J502-1
7.16 C6D6
5.85
5.83
5.81
5.06
5.05
5.04
5.02
5.02
3.96
3.95
3.95
3.95
3.94
3.94
3.94
3.74
3.74
3.73
3.72
3.72
3.71
3.71
3.70
3.69
3.69
3.28
3.28
3.26
3.25
3.24
2.89
2.88
2.87
2.24
2.23
2.23
2.22
2.21
2.20
2.16
2.15
2.15
2.14
2.14
1.51
1.50
1.49
1.48
1.31
1.30
1.29
1.28
1.28
1.28
1.27
1.24
1.00
2.07
1.01
2.02
0.99
0.96
2.11
1.19
3.32
0.99
3.12
f1 (ppm)


^{13}C (130 MHz, C_6D_6)
OH
O
O
Me
Me
135.46
128.06 C6D6
117.25
109.30
75.75
70.21
69.81
42.43
40.08
27.03
25.93
f1 (ppm)

(R)-1-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-4-en-2-ol (*epi*-3j)



Alcohol **2j** (29.2 mg, 0.2 mmol) was subjected to standard reaction conditions with **SL-J502-2** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 1:99 EtOAc:hexanes) the title compound ***epi*-3j** was isolated as a yellow oil in 95% yield (35.4 mg, 0.19 mmol, >20:1 dr).

TLC (SiO_2): R_f = 0.5 (1:8 EtOAc:hexanes)

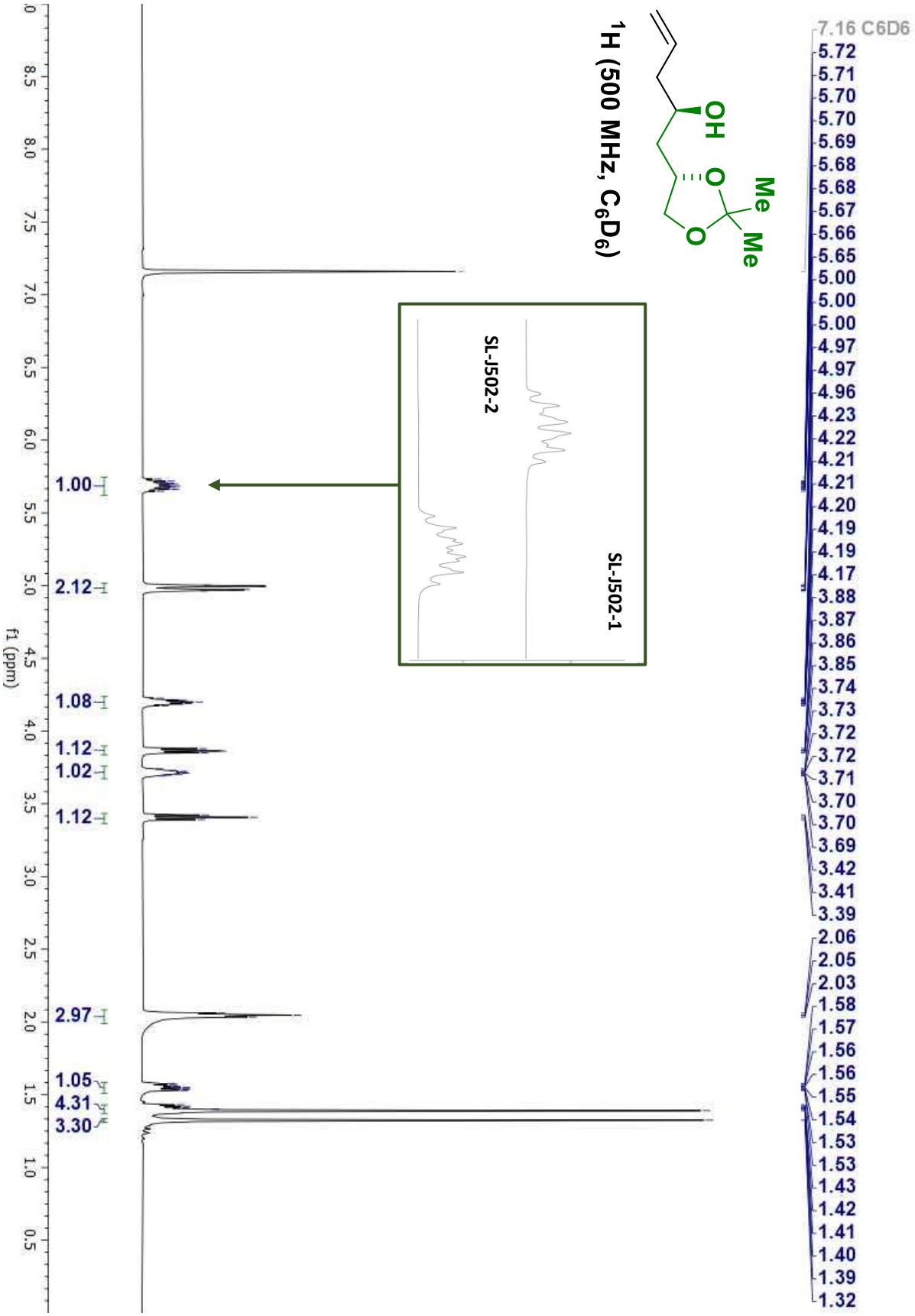
^{1}H NMR (500 MHz, C_6D_6): δ 5.75 – 5.62 (m, 1H), 5.01 – 4.95 (m, 2H), 4.20 (ddd, J = 12.8, 7.5, 5.3 Hz, 1H), 3.87 (dd, J = 8.1, 6.0 Hz, 1H), 3.71 (dp, J = 9.2, 3.9 Hz, 1H), 3.41 (t, J = 7.8 Hz, 1H), 2.08 – 1.99 (m, 3H), 1.55 (ddd, J = 14.0, 7.5, 2.7 Hz, 1H), 1.45 – 1.37 (m, 4H), 1.32 (s, 3H).

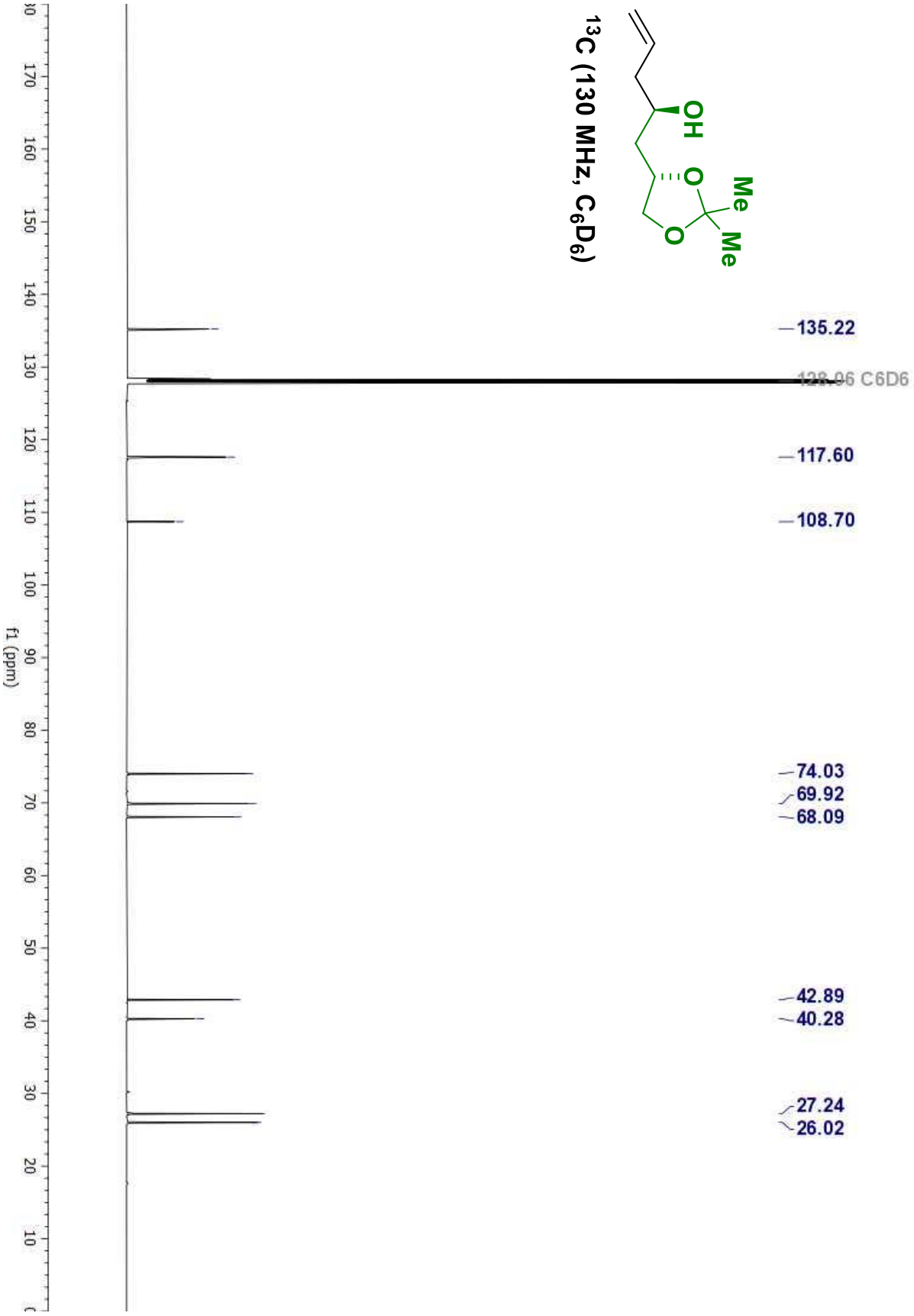
^{13}C NMR (130 MHz, C_6D_6): δ 135.2, 117.6, 108.7, 74.0, 69.9, 68.1, 42.9, 40.3, 27.2, 26.0.

HRMS (Na+, *m/z*): for $C_{10}H_{18}O_3$: calcd. = 209.1148; found = 209.1147.

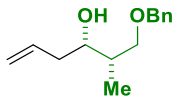
FTIR (neat): 2984, 2935, 1774, 1370, 1215, 1157, 1057, 996, 915, 862 cm^{-1}.

$[\alpha]_D^{24}$ = 8.4 (c = 1.5, $CHCl_3$).


^{1}H (500 MHz, C_6D_6)
OH
O
O
Me
Me
SL-J502-2
SL-J502-1
f1 (ppm)
1.00
2.12
1.08
1.12
1.02
1.12
2.97
1.05
4.31
3.30
7.16 C6D6
5.72
5.71
5.70
5.70
5.69
5.68
5.68
5.67
5.66
5.65
5.00
5.00
5.00
4.97
4.97
4.96
4.23
4.22
4.21
4.21
4.20
4.19
4.19
4.17
3.88
3.87
3.86
3.85
3.74
3.73
3.72
3.72
3.71
3.70
3.70
3.69
3.42
3.41
3.39
2.06
2.05
2.03
1.58
1.57
1.56
1.56
1.55
1.54
1.53
1.53
1.43
1.42
1.41
1.40
1.39
1.32


13C (130 MHz, C6D6)
OH
O
O
Me
Me
135.22
128.06 C6D6
117.60
108.70
74.03
69.92
68.09
42.89
40.28
27.24
26.02
f1 (ppm)

(2S,3S)-1-(benzyloxy)-2-methylhex-5-en-3-ol (3k)



Alcohol **2k** (36.0 mg, 0.2 mmol) was subjected to standard reaction conditions with **SL-J502-1** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 2:98 EtOAc:hexanes) the title compound **3k** was isolated as a yellow oil in 85% yield (37.5 mg, 0.17 mmol, 5:1 dr).

TLC (SiO_2): R_f = 0.5 (1:8 EtOAc:hexanes)

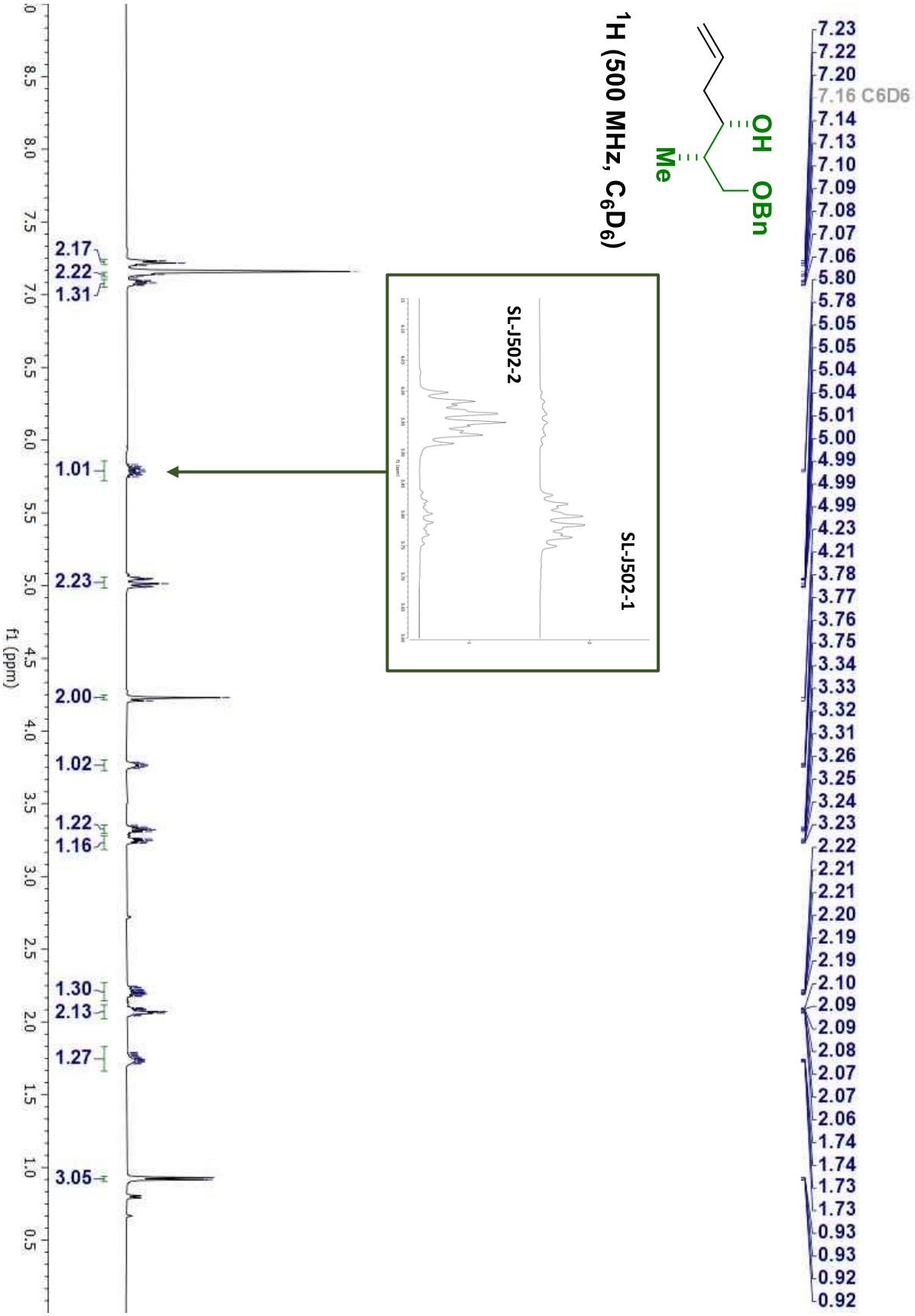
^{1}H NMR (500 MHz, C_6D_6): δ 7.23 (d, J = 7.5 Hz, 2H), 7.14 (s, 2H), 7.10 – 7.05 (m, 1H), 5.79 (ddt, J = 17.1, 10.1, 7.1 Hz, 1H), 5.06 – 4.98 (m, 2H), 4.23 (s, 2H), 3.77 (dq, J = 8.4, 4.0 Hz, 1H), 3.32 (dd, J = 8.9, 6.3 Hz, 1H), 3.24 (dd, J = 8.9, 5.0 Hz, 1H), 2.21 (dddd, J = 14.0, 8.4, 7.0, 1.4 Hz, 1H), 2.12 – 2.02 (m, 2H), 1.83 – 1.66 (m, 1H), 0.95 – 0.90 (m, 3H).

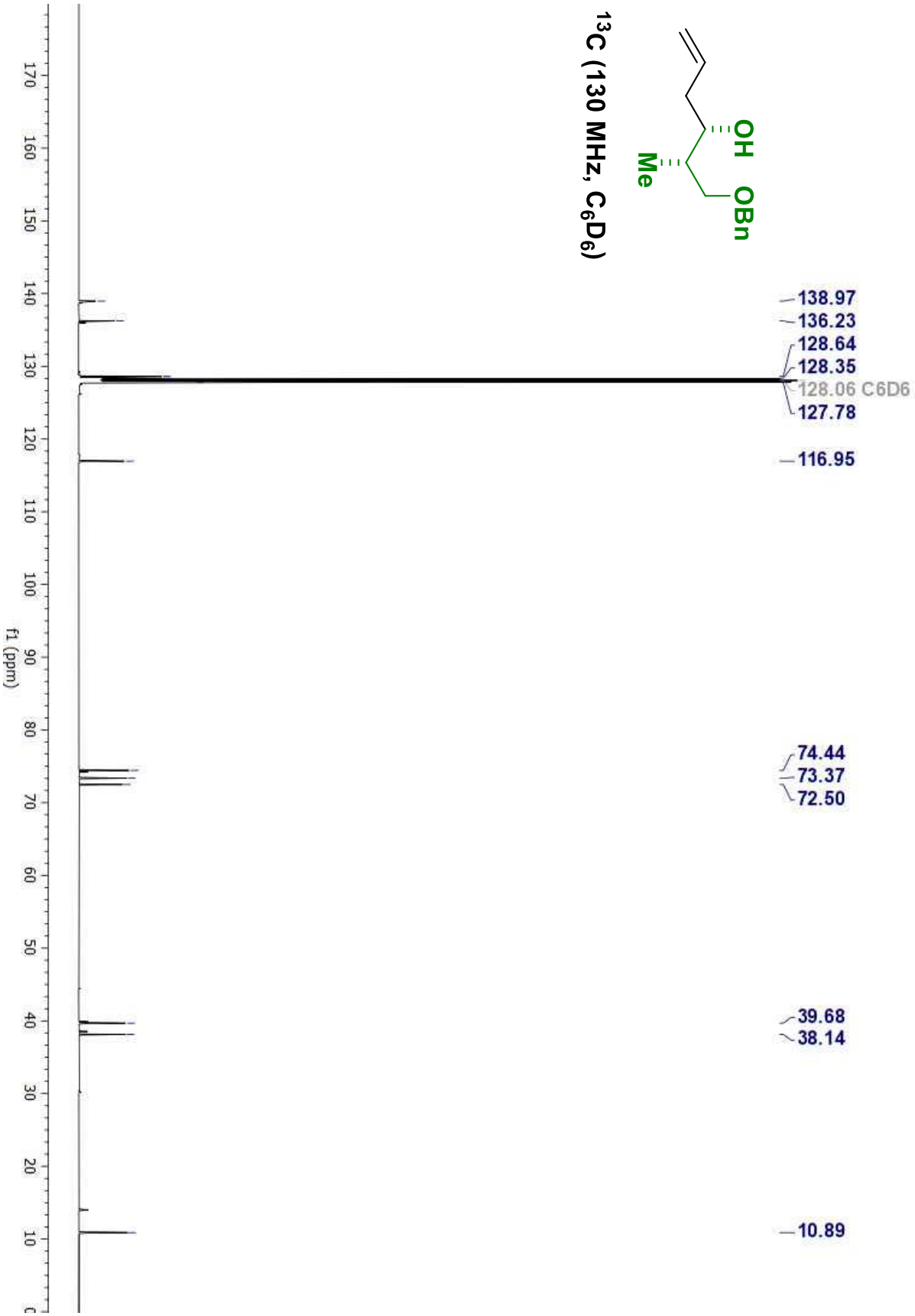
^{13}C NMR (130 MHz, C_6D_6): δ 139.0, 136.2, 128.6, 128.4, 127.8, 116.9, 74.4, 73.4, 72.5, 39.7, 38.1, 10.9.

HRMS (Na+, *m/z*): for $C_{14}H_{20}O_z$: calcd. = 243.1360; found = 243.1366.

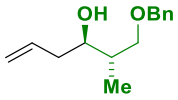
FTIR (neat): 3449, 2921, 2857, 1640, 1454, 1363, 1094, 913, 740, 698 cm^{-1}.

$[\alpha]_D^{24}$ = 8.5 (c = 1.5, $CHCl_3$).


^{1}H (500 MHz, C_6D_6)
OH
OBn
Me
SL-J502-2
SL-J502-1
f1 (ppm)
7.23
7.22
7.20
7.16 C6D6
7.14
7.13
7.10
7.09
7.08
7.07
7.06
5.80
5.78
5.05
5.05
5.04
5.04
5.01
5.00
4.99
4.99
4.99
4.23
4.21
3.78
3.77
3.76
3.75
3.34
3.33
3.32
3.31
3.26
3.25
3.24
3.23
2.22
2.21
2.21
2.20
2.19
2.19
2.10
2.09
2.09
2.08
2.07
2.07
2.06
1.74
1.74
1.73
1.73
0.93
0.93
0.92
0.92
2.17
2.22
1.31
1.01
2.23
2.00
1.02
1.22
1.16
1.30
2.13
1.27
3.05


^{13}C (130 MHz, C_6D_6)
OH
OBn
Me
138.97
136.23
128.64
128.35
128.06 C6D6
127.78
116.95
74.44
73.37
72.50
39.68
38.14
10.89
f1 (ppm)

(2S,3R)-1-(benzyloxy)-2-methylhex-5-en-3-ol (*epi*-3k)



Alcohol **2k** (36.0 mg, 0.2 mmol) was subjected to standard reaction conditions with **SL-J502-2** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 2:98 EtOAc:hexanes) the title compound ***epi*-3k** was isolated as a yellow oil in 95% yield (41.9 mg, 0.19 mmol, 7:1 dr).

TLC (SiO_2): R_f = 0.5 (1:8 EtOAc:hexanes)

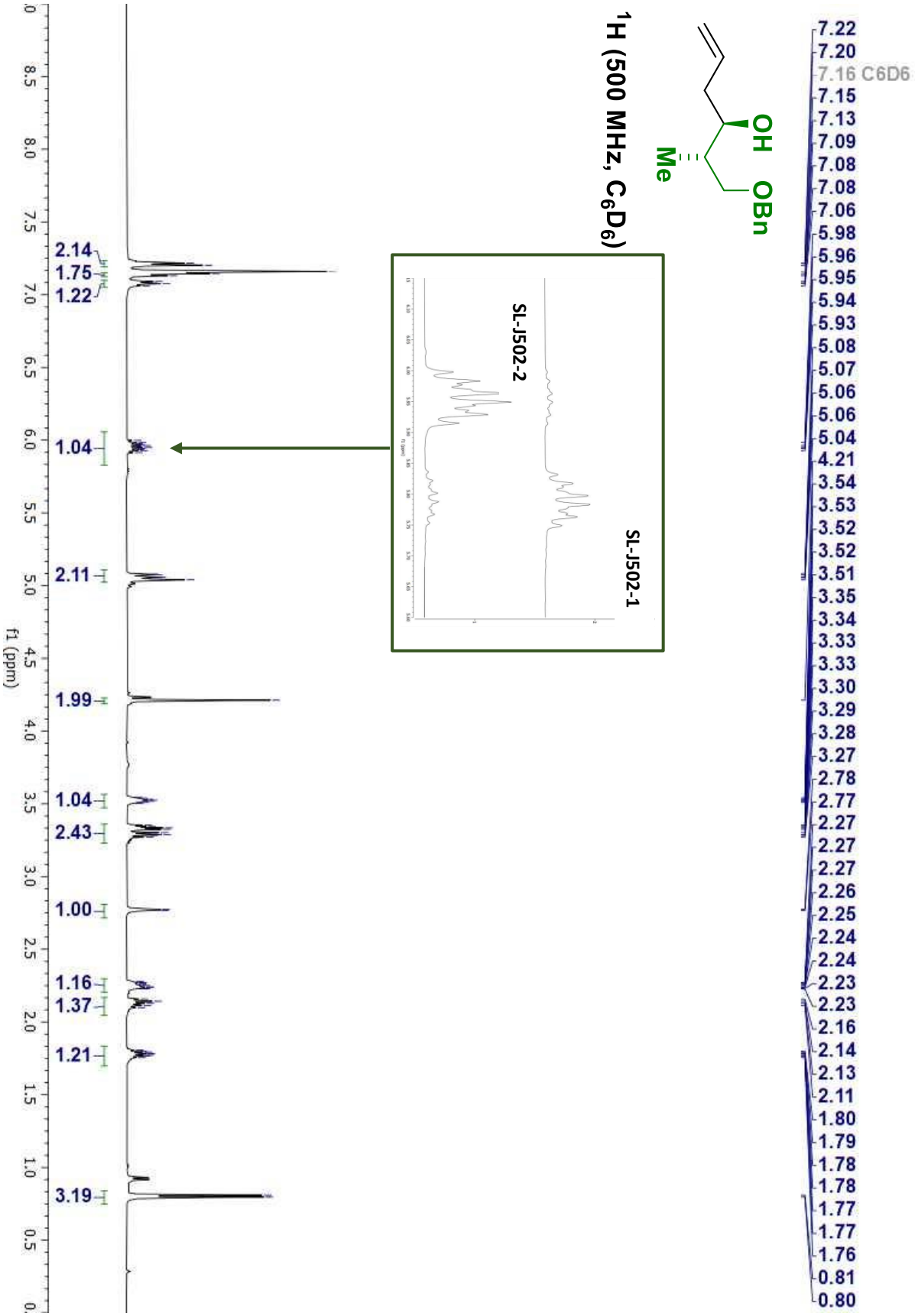
^{1}H NMR (500 MHz, C_6D_6): δ 7.21 (d, J = 7.5 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 7.08 (dd, J = 8.6, 6.2 Hz, 1H), 5.96 (ddt, J = 17.2, 10.4, 7.1 Hz, 1H), 5.07 (dd, J = 9.5, 2.4 Hz, 1H), 5.05 – 5.03 (m, 1H), 4.21 (s, 2H), 3.52 (tt, J = 7.5, 3.5 Hz, 1H), 3.37 – 3.23 (m, 2H), 2.77 (d, J = 3.7 Hz, 1H), 2.25 (ddt, J = 15.2, 5.3, 2.3 Hz, 1H), 2.13 (dt, J = 14.3, 7.5 Hz, 1H), 1.78 (qd, J = 7.0, 5.1 Hz, 1H), 0.80 (d, J = 7.0 Hz, 3H).

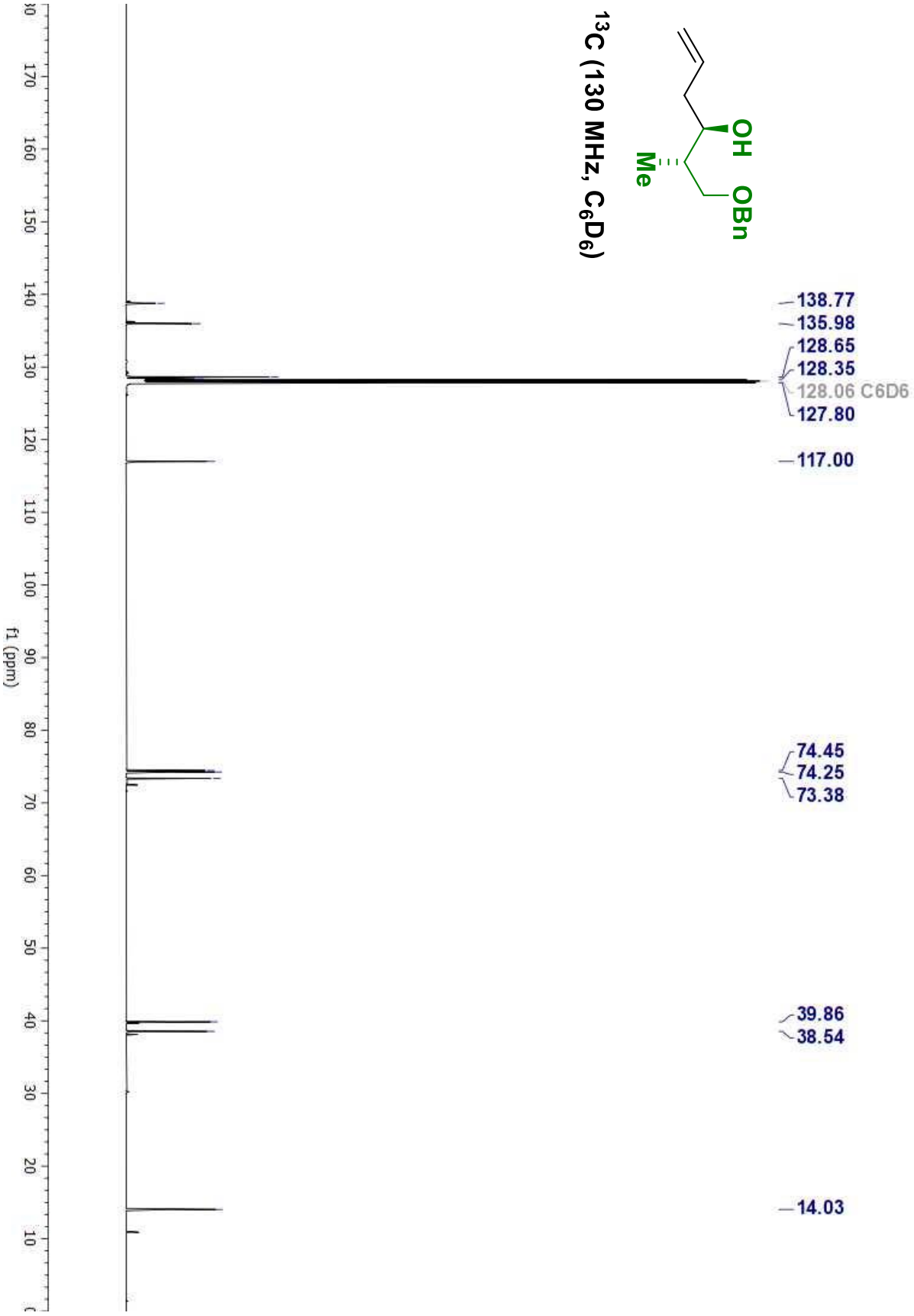
^{13}C NMR (130 MHz, C_6D_6): δ 138.8, 136.0, 128.6, 128.4, 127.8, 117.0, 74.5, 74.3, 73.4, 39.9, 38.5, 14.0.

HRMS (Na+, *m/z*): for $C_{14}H_{20}O_z$: calcd. = 243.1360; found = 243.1366.

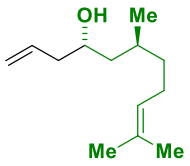
FTIR (neat): 3449, 2921, 2857, 1640, 1454, 1363, 1094, 913, 740, 698 cm^{-1}.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{24}}$ = -13.5 (c = 1.5, $CHCl_3$).


^{1}H (500 MHz, C_6D_6)
OH
OBn
Me
SL-J502-2
SL-J502-1
f1 (ppm)
7.16 C6D6
2.14
1.75
1.22
1.04
2.11
1.99
1.04
2.43
1.00
1.16
1.37
1.21
3.19


^{13}C (130 MHz, C_6D_6)
OH
OBn
Me
138.77
135.98
128.65
128.35
128.06 C6D6
127.80
117.00
74.45
74.25
73.38
39.86
38.54
14.03
f1 (ppm)

(4S,6S)-6,10-dimethylundeca-1,9-dien-4-ol (3i)



Alcohol **2i** (31.3 mg, 0.2 mmol) was subjected to standard reaction conditions with **SL-J502-1** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 2:98 EtOAc:hexanes) the title compound **3i** was isolated as a yellow oil in 88% yield (34.5 mg, 0.18 mmol, 15:1 dr).

TLC (SiO_2): R_f = 0.5 (1:9 EtOAc:hexanes)

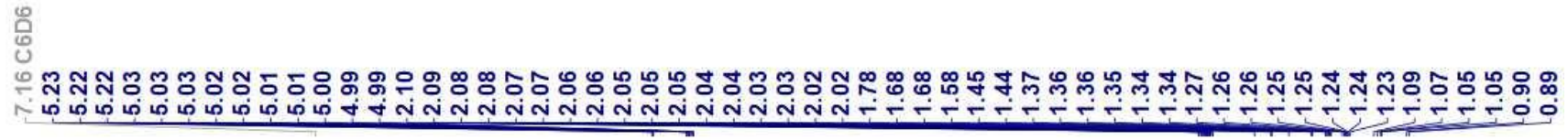
^{1}H NMR (500 MHz, C_6D_6): δ 5.80 – 5.64 (m, 1H), 5.27 – 5.18 (m, 1H), 5.07 – 4.94 (m, 2H), 3.66 – 3.48 (m, 1H), 2.10 – 1.97 (m, 4H), 1.78 (dddd, J = 13.6, 10.5, 6.6, 4.0 Hz, 1H), 1.71 – 1.65 (m, 3H), 1.58 (s, 3H), 1.44 (ddd, J = 13.8, 9.7, 4.1 Hz, 1H), 1.38 – 1.21 (m, 3H), 1.11 – 1.01 (m, 1H), 0.90 (d, J = 6.7 Hz, 3H).

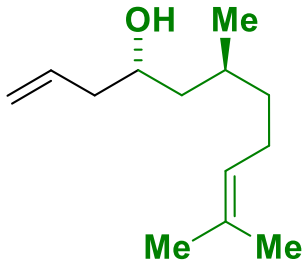
^{13}C NMR (130 MHz, C_6D_6): δ 135.6, 131.0, 125.5, 117.5, 68.4, 44.6, 43.5, 38.4, 29.2, 26.0, 25.9, 19.4, 17.8.

HRMS (H+, *m/z*): for $C_{13}H_{24}O$: calcd. = 197.1237; found = 197.1237.

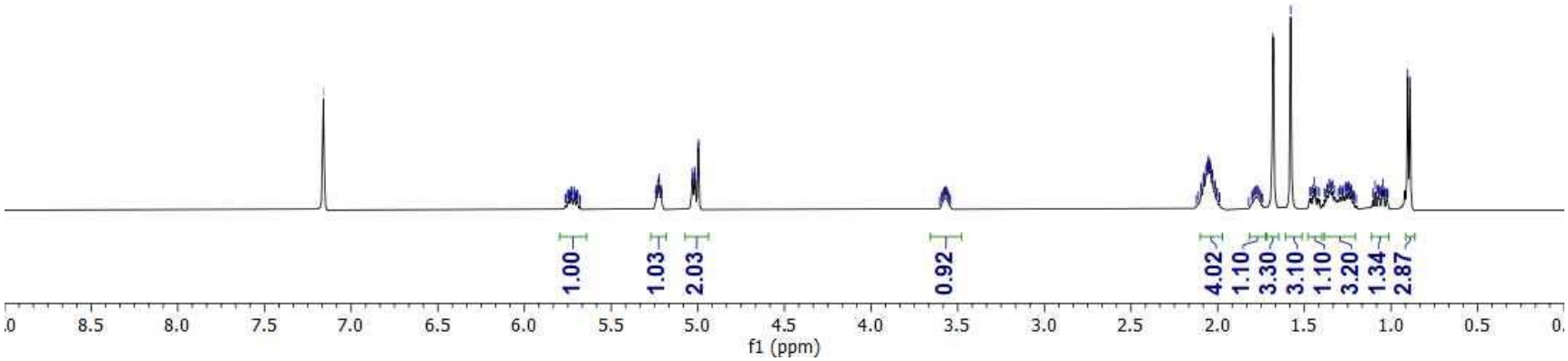
FTIR (neat): 2981, 2960, 1475, 1285, 1086, 1346, 738, 693 cm^{-1}.

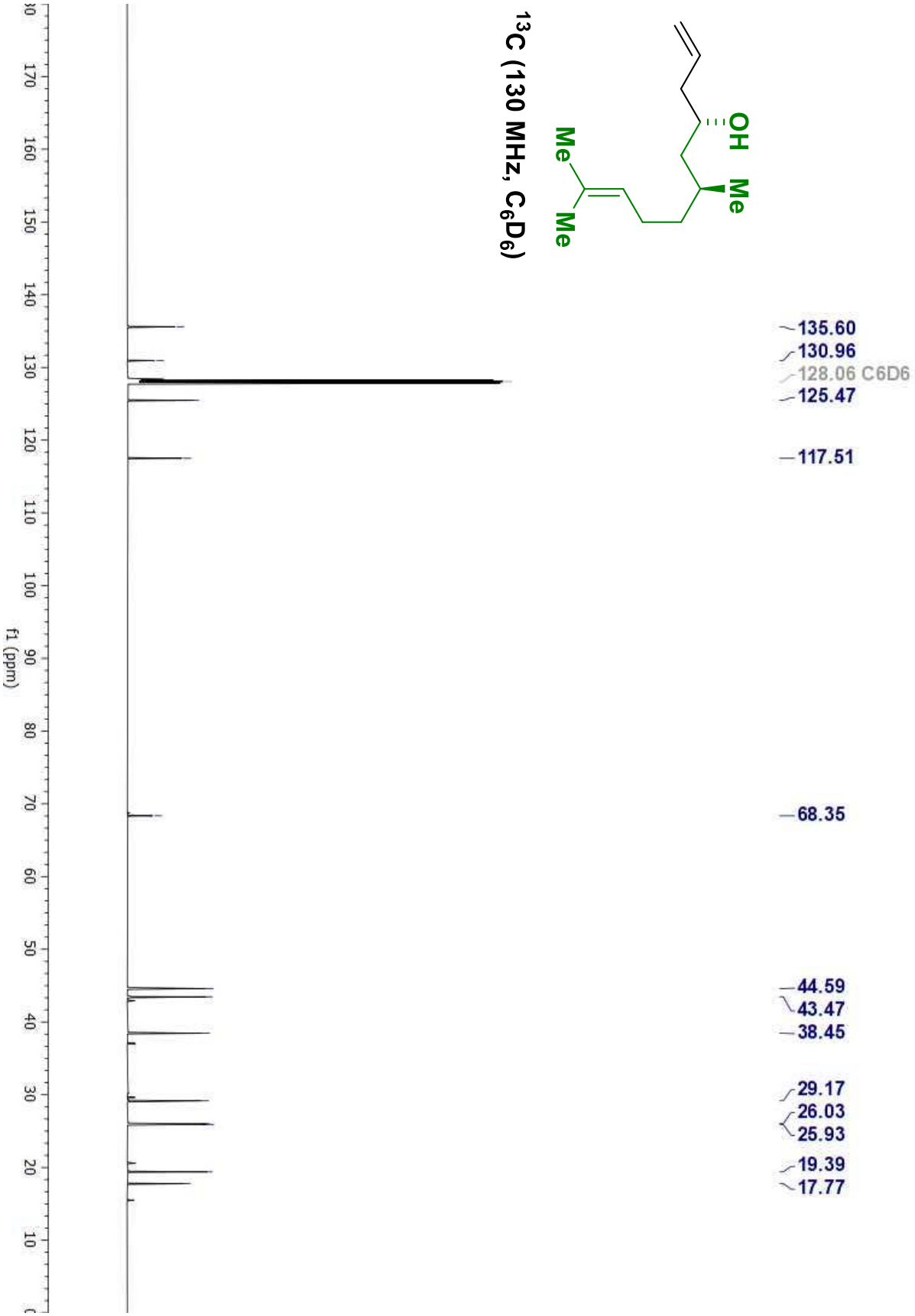
$[\alpha]_D^{24}$ = -1.8 (c = 0.1, $CHCl_3$).



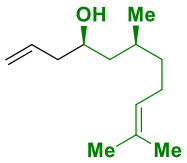


^{1}H (500 MHz, C_6D_6)




^{13}C (130 MHz, C_6D_6)
OH
Me
Me
Me
135.60
130.96
128.06 C6D6
125.47
117.51
68.35
44.59
43.47
38.45
29.17
26.03
25.93
19.39
17.77
f1 (ppm)

(4R,6S)-6,10-dimethylundeca-1,9-dien-4-ol (*epi*-3l)



Alcohol **2l** (31.3 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h. Upon flash column chromatography (SiO_2: 2:98 EtOAc:hexanes) the title compound ***epi*-3l** was isolated as a yellow oil in 94% yield (36.9 mg, 0.19 mmol, >20:1 dr).

TLC (SiO_2): R_f = 0.5 (1:9 EtOAc:hexanes)

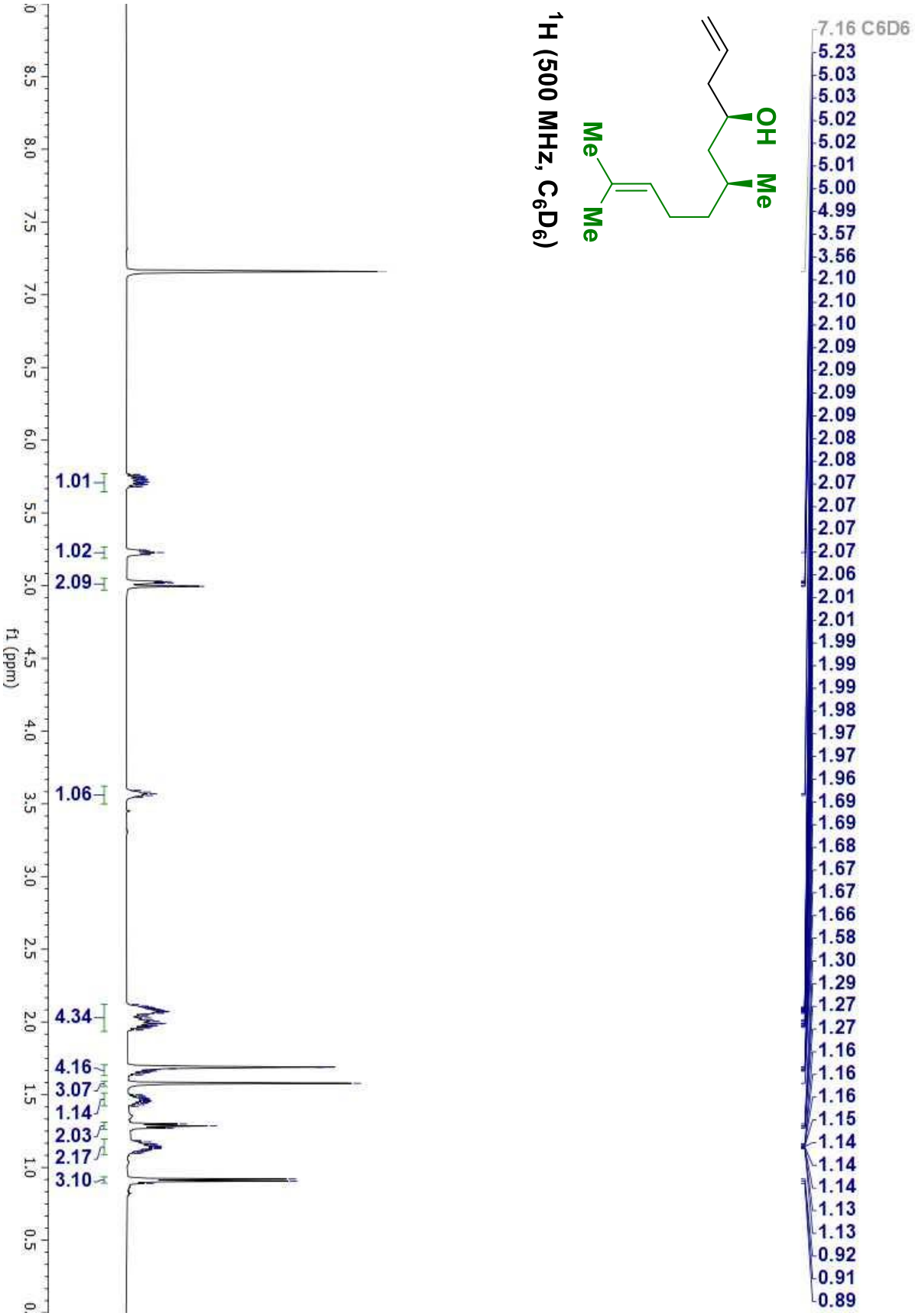
^{1}H NMR (500 MHz, C_6D_6): δ 5.77 – 5.65 (m, 1H), 5.26 – 5.19 (m, 1H), 5.05 – 4.97 (m, 2H), 3.57 (p, J = 6.7 Hz, 1H), 2.12 – 1.94 (m, 4H), 1.71 – 1.63 (m, 4H), 1.58 (s, 3H), 1.51 – 1.42 (m, 1H), 1.29 (t, J = 7.0 Hz, 2H), 1.19 – 1.09 (m, 2H), 0.91 (d, J = 6.7 Hz, 3H).

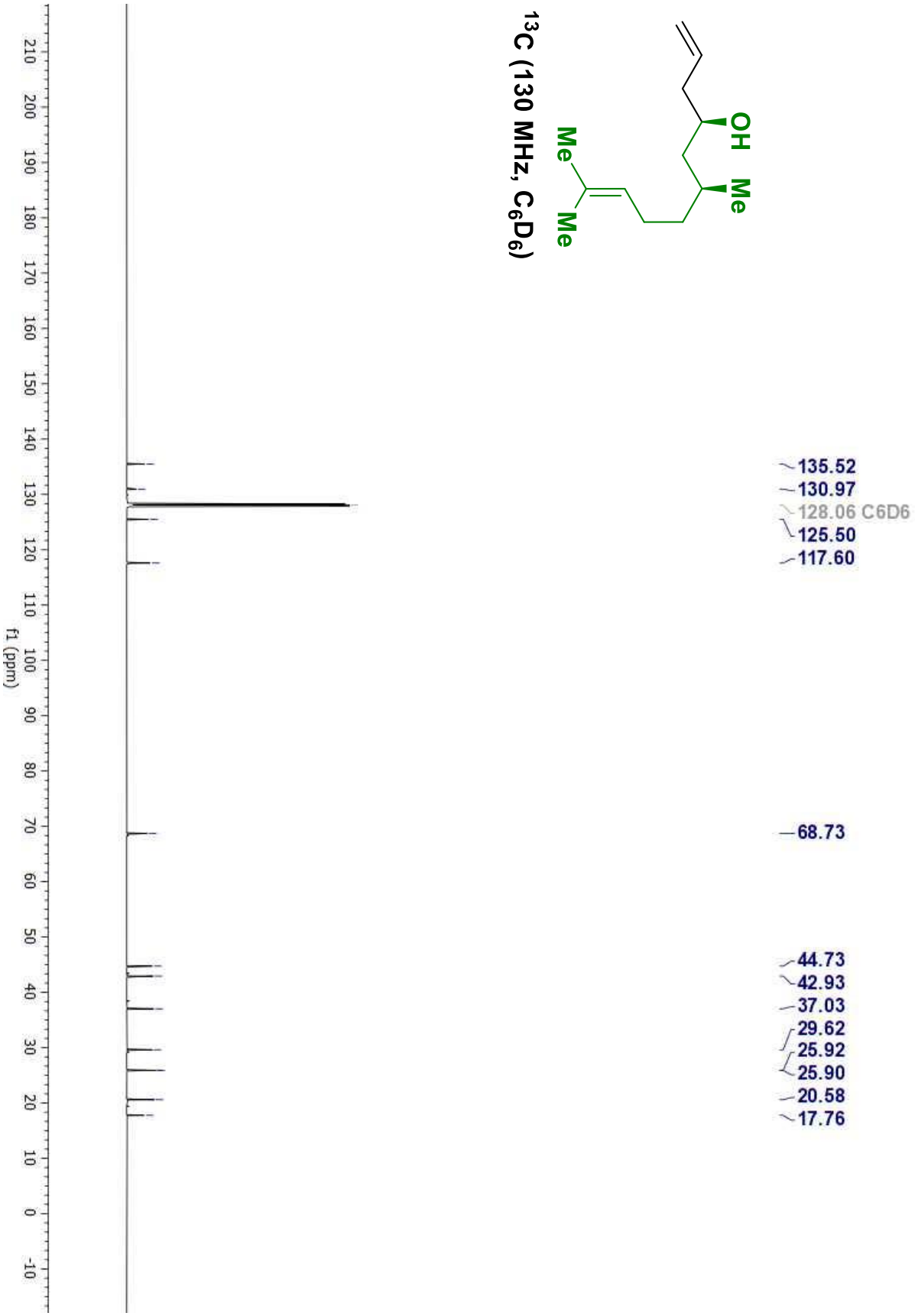
^{13}C NMR (130 MHz, C_6D_6): δ 135.5, 131.0, 125.5, 117.6, 68.7, 44.7, 42.9, 37.0, 29.6, 25.9, 25.9, 20.6, 17.8.

HRMS (H+, *m/z*): for $C_{13}H_{24}O$: calcd. = 197.1237; found = 197.1237.

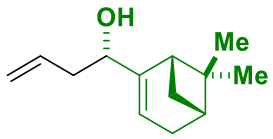
FTIR (neat): 2981, 2960, 1475, 1285, 1086, 1346, 738, 693 cm^{-1}.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{24}}$ = -24.5 (c = 1.1, $CHCl_3$).


^{1}H (500 MHz, C_6D_6)
OH
Me
Me
Me
7.16 C6D6
5.23
5.03
5.03
5.02
5.02
5.01
5.00
4.99
3.57
3.56
2.10
2.10
2.10
2.09
2.09
2.09
2.09
2.08
2.08
2.07
2.07
2.07
2.07
2.06
2.01
2.01
1.99
1.99
1.99
1.98
1.97
1.97
1.96
1.69
1.69
1.68
1.67
1.67
1.66
1.58
1.30
1.29
1.27
1.27
1.16
1.16
1.16
1.15
1.14
1.14
1.14
1.13
1.13
0.92
0.91
0.89
1.01
1.02
2.09
1.06
4.34
4.16
3.07
1.14
2.03
2.17
3.10
f1 (ppm)


^{13}C (130 MHz, C_6D_6)
OH
Me
Me
Me
135.52
130.97
128.06 C6D6
125.50
117.60
68.73
44.73
42.93
37.03
29.62
25.92
25.90
20.58
17.76
f1 (ppm)

(*S*)-1-((1*S*,5*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)but-3-en-1-ol (3m)



Alcohol **2m** (30.5 mg, 0.2 mmol) was subjected to standard reaction conditions with **SL-J502-1** as ligand (110 °C, 48 h). Upon flash column chromatography (SiO_2: 1:99 EtOAc:hexanes) the title compound **3m** was isolated as a brown-yellow oil in 84% yield (32.3 mg, 0.17 mmol, 5:1 dr).

TLC (SiO_2): R_f = 0.5 (1:6 EtOAc:Hexanes)

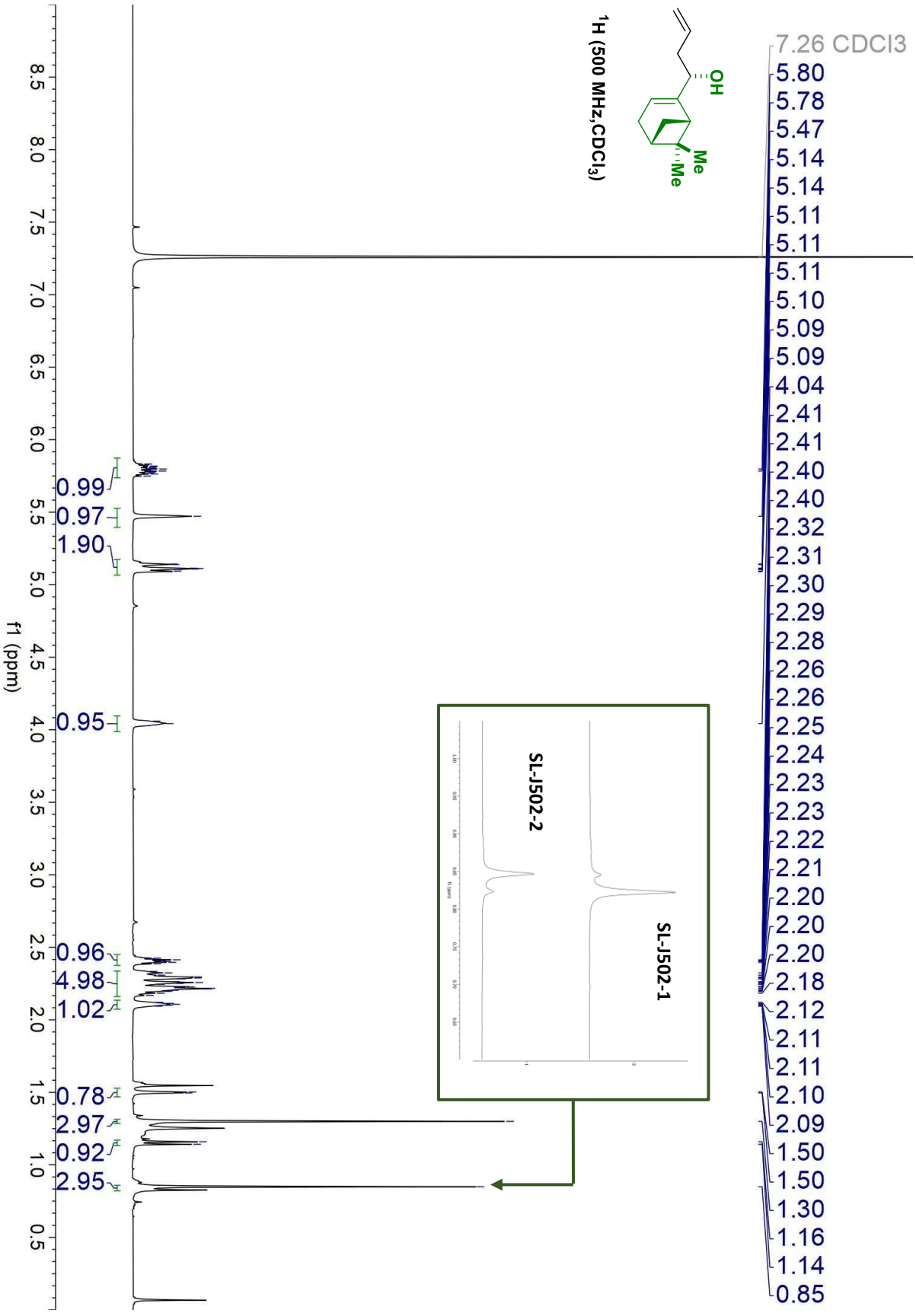
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.47 (s, 1H), 5.17 – 5.08 (m, 2H), 4.04 (s, 1H), 2.41 (dt, *J* = 8.7, 5.6 Hz, 1H), 2.35 – 2.16 (m, 5H), 2.11 (s, 1H), 1.50 (d, *J* = 3.4 Hz, 1H), 1.30 (s, 3H), 1.15 (d, *J* = 8.8 Hz, 1H), 0.85 (s, 3H).

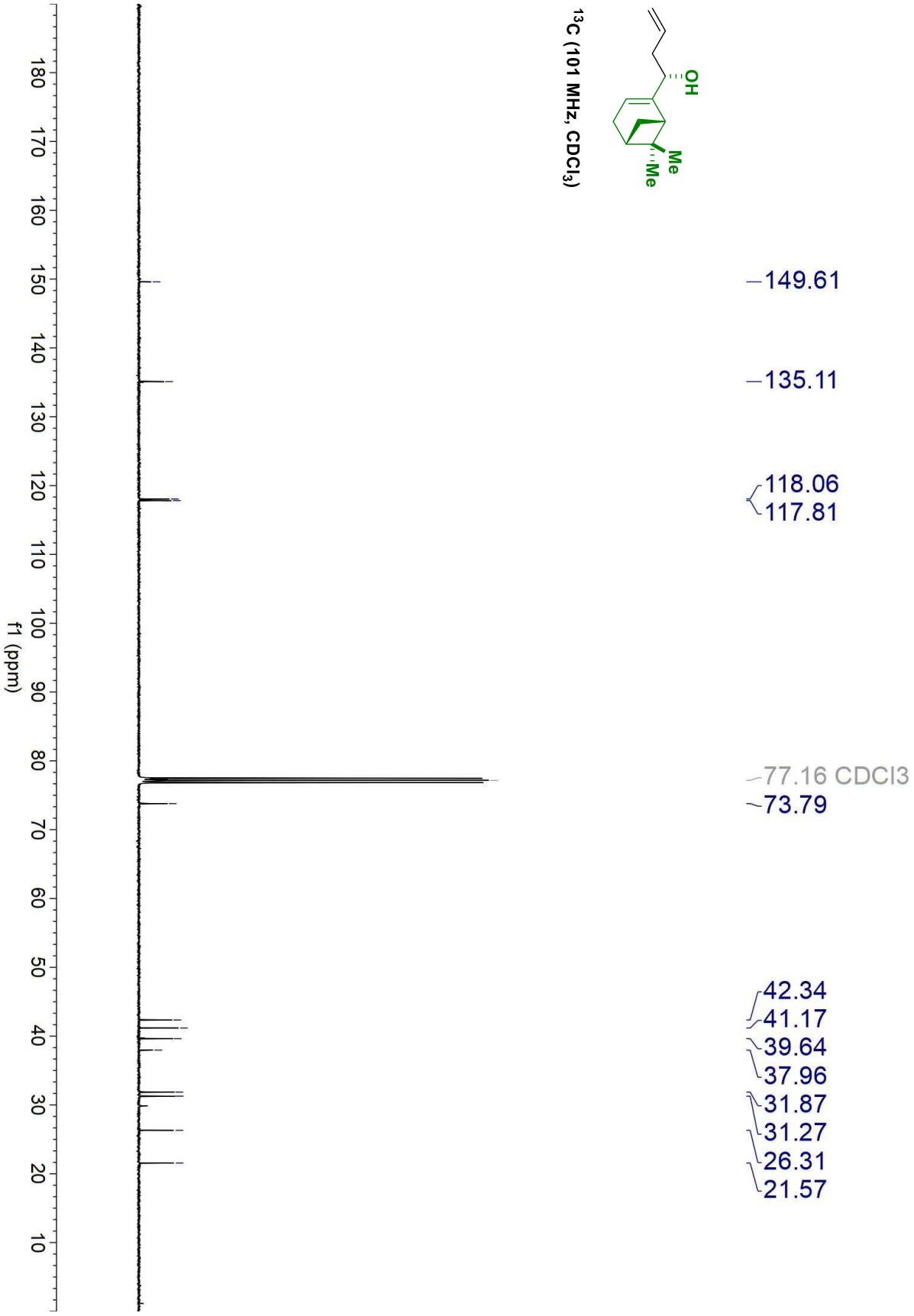
^{13}C NMR (101 MHz, $CDCl_3$): δ 149.6, 135.1, 118.1, 118.0, 117.9, 117.8, 73.8, 73.8, 42.4, 42.3, 41.2, 39.6, 38.0, 31.9, 31.3, 29.9, 26.3, 21.6.

HRMS (-H^+, *m/z*): for $C_{13}H_{20}O$ calcd. = 191.1436; found = 191.1441.

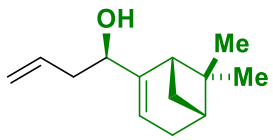
FTIR (neat): 2987, 1675, 1421, 1265, 896, 734, 704 cm^{-1}.

$[\alpha]_D^{24}$ = -2.9 (c = 0.5, $CHCl_3$).


^{1}H (500 MHz,CDCl$_3$)
OH
Me
Me
7.26 CDCl3
5.80
5.78
5.47
5.14
5.14
5.11
5.11
5.11
5.10
5.09
5.09
4.04
2.41
2.41
2.40
2.40
2.32
2.31
2.30
2.29
2.28
2.26
2.26
2.25
2.24
2.23
2.23
2.22
2.21
2.20
2.20
2.20
2.18
2.12
2.11
2.11
2.10
2.09
1.50
1.50
1.30
1.16
1.14
0.85
0.99
0.97
1.90
0.95
0.96
4.98
1.02
0.78
2.97
0.92
2.95
f1 (ppm)
SL-J502-2
SL-J502-1


^{13}C (101 MHz, CDCl$_3$)
OH
Me
Me
149.61
135.11
118.06
117.81
77.16 CDCl3
73.79
42.34
41.17
39.64
37.96
31.87
31.27
26.31
21.57
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

(*R*)-1-((1*S*,5*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)but-3-en-1-ol (epi-3m)



Alcohol **2m** (30.5 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-2** as ligand. Upon flash column chromatography (SiO_2: 1:99 EtOAc:hexanes) the title compound ***epi*-3m** was isolated as a brown-yellow oil in 78% yield (30.1 mg, 0.16 mmol, 9:1 dr).

TLC (SiO_2): R_f = 0.5 (1:6 EtOAc:Hexanes)

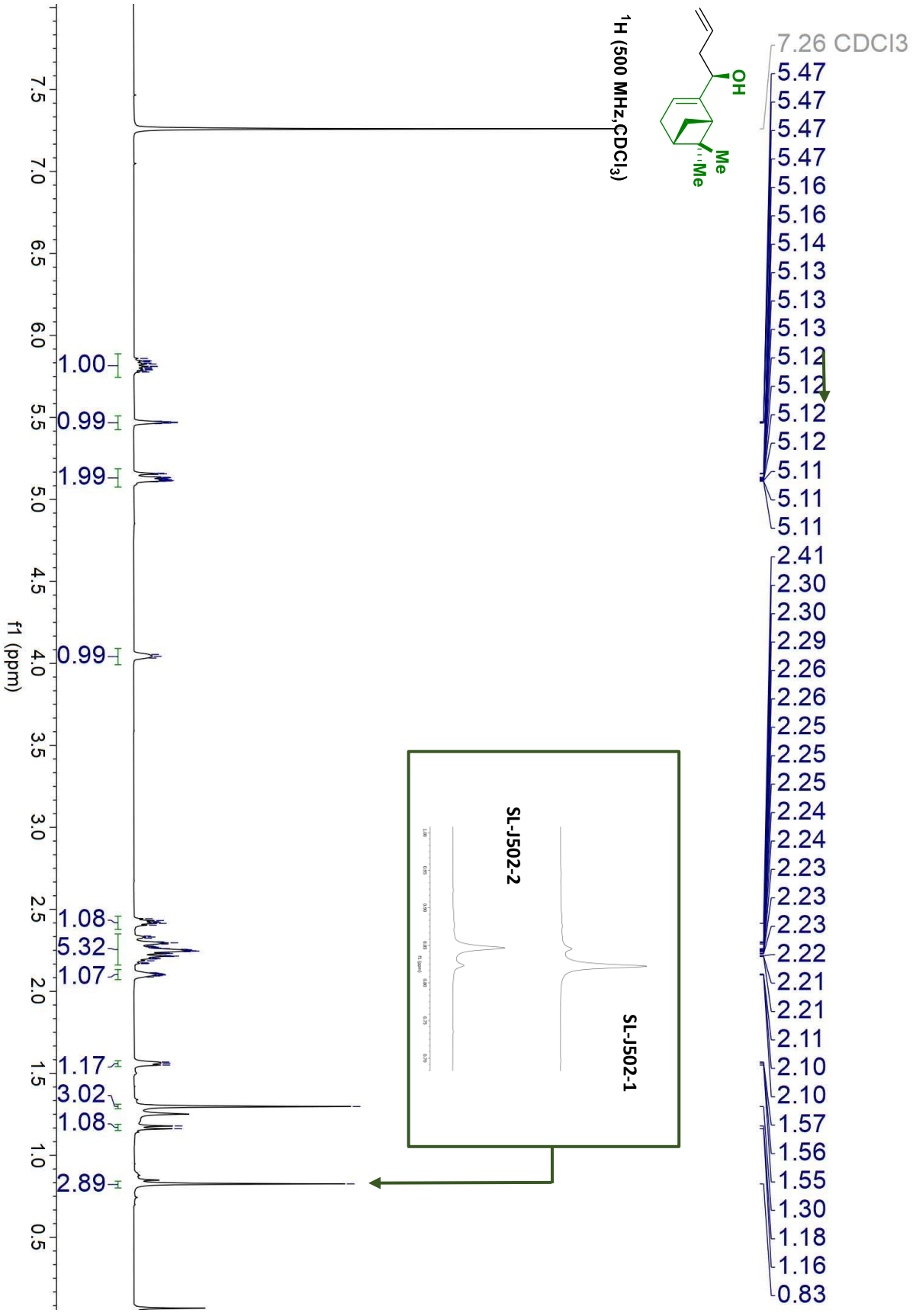
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.88 – 5.77 (m, 1H), 5.47 (s, 1H), 5.17 – 5.09 (m, 2H), 4.04 (s, 1H), 2.42 (dt, *J* = 8.7, 5.6 Hz, 1H), 2.35 – 2.16 (m, 5H), 2.13 – 2.07 (m, 1H), 1.56 (d, 1H), 1.30 (s, 3H), 1.17 (d, *J* = 8.7 Hz, 1H), 0.83 (s, 3H).

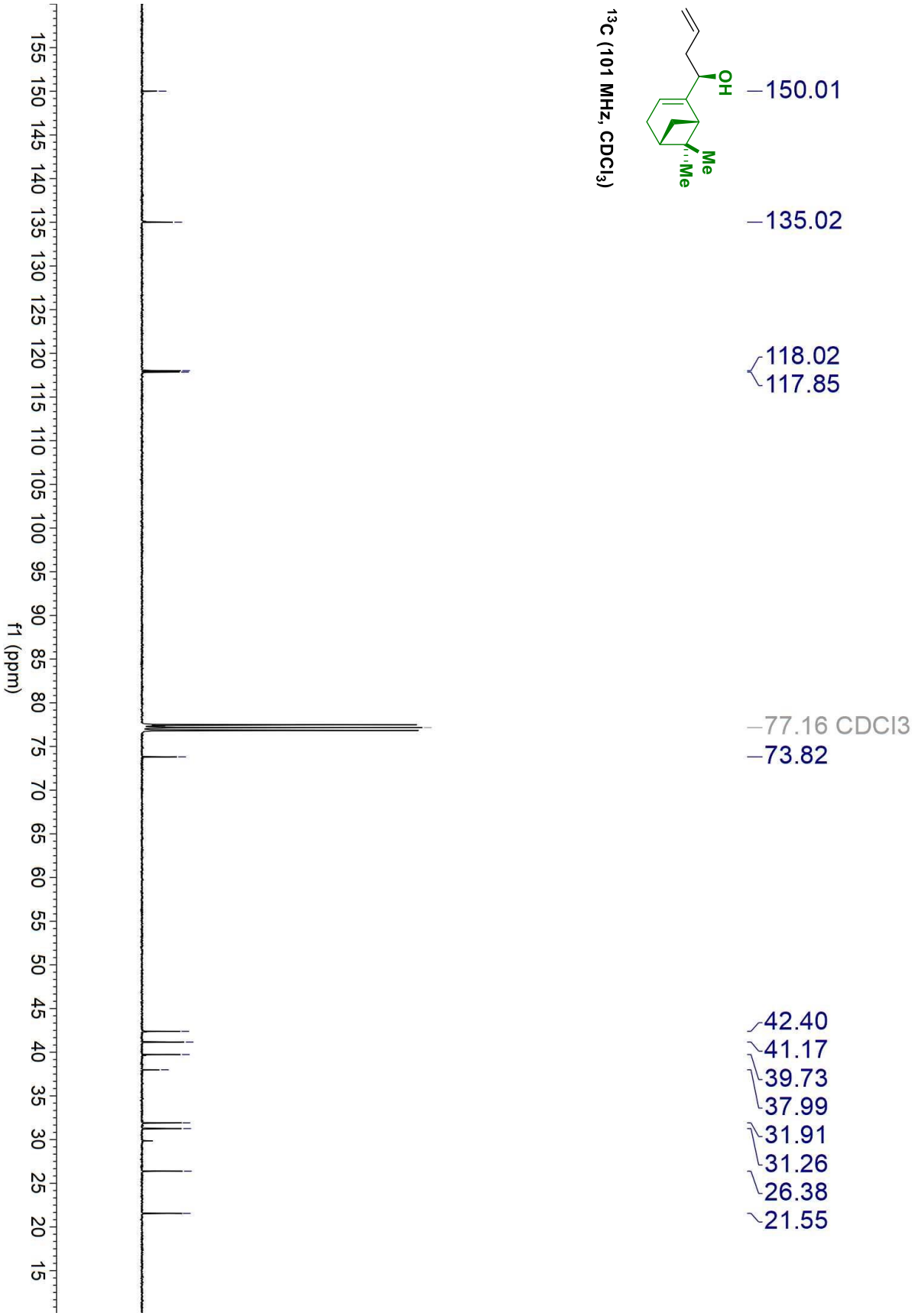
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.0, 135.0, 118.0, 117.9, 73.8, 42.4, 41.2, 39.7, 38.0, 31.9, 31.3, 26.4, 21.6.

HRMS (-H^+, *m/z*): for $C_{13}H_{20}O$ calcd. = 191.1436; found = 191.1427.

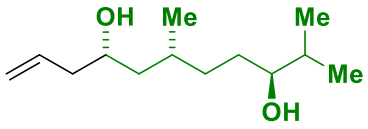
FTIR (neat): 2920, 1676, 1433, 1265, 1000, 735, 704 cm^{-1}.

$[\alpha]_D^{24}$ = -3.0 (c = 0.7, $CHCl_3$).


^{1}H (500 MHz, CDCl$_3$)
OH
Me
Me
7.26 CDCl3
5.47
5.47
5.47
5.47
5.16
5.16
5.14
5.13
5.13
5.13
5.12
5.12
5.12
5.12
5.11
5.11
5.11
2.41
2.30
2.30
2.29
2.26
2.26
2.25
2.25
2.25
2.24
2.24
2.23
2.23
2.23
2.22
2.21
2.21
2.11
2.10
2.10
1.57
1.56
1.55
1.30
1.18
1.16
0.83
SL-J502-2
SL-J502-1
1.00
0.99
1.99
0.99
1.08
5.32
1.07
1.17
3.02
1.08
2.89
f1 (ppm)


^{13}C (101 MHz, CDCl$_3$)
OH
Me
Me
150.01
135.02
118.02
117.85
77.16 CDCl3
73.82
42.40
41.17
39.73
37.99
31.91
31.26
26.38
21.55
f1 (ppm)
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15

(3*S*,6*R*,8*S*)-2,6-dimethylundec-10-ene-3,8-diol (3n)



Alcohol **2n** (35.7 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 15:85 EtOAc:hexanes) the title compound **3n** was isolated as a yellow oil in 86% yield (36.9 mg, 0.17 mmol, 15:1 dr).

TLC (SiO_2): R_f = 0.8 (1:1 EtOAc:hexanes)

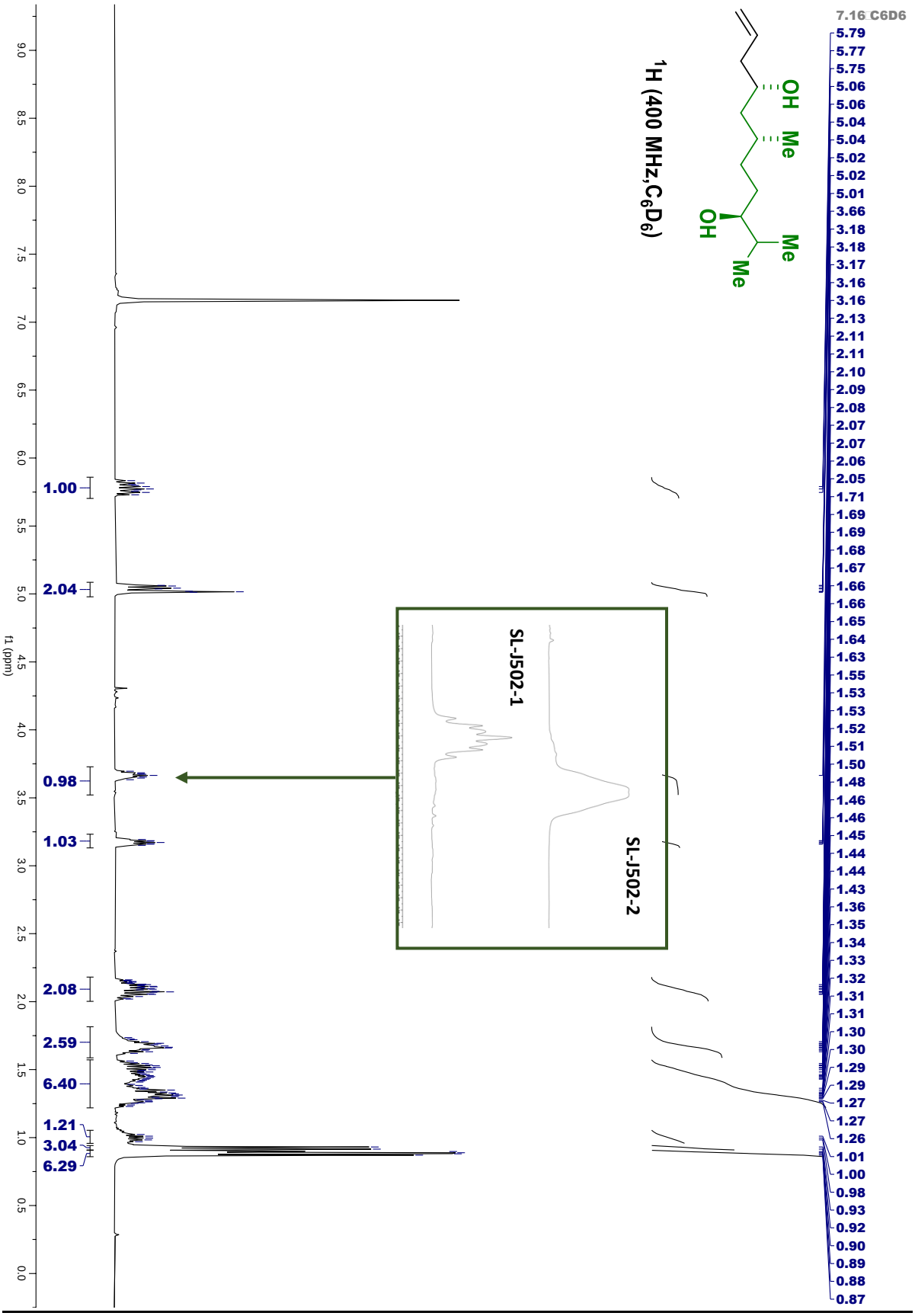
^{1}H NMR (400 MHz, C_6D_6): δ 5.78 (ddt, *J* = 17.4, 10.4, 7.1 Hz, 1H), 5.25 – 4.86 (m, 2H), 3.73 – 3.59 (m, 1H), 3.17 (ddd, *J* = 8.6, 4.9, 3.4 Hz, 1H), 2.24 – 1.92 (m, 2H), 1.67 (m, 3H), 1.60 – 1.19 (m, 6H), 1.00 (dt, *J* = 10.6, 5.2 Hz, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 3.8 Hz, 3H), 0.88 (d, *J* = 3.9 Hz, 3H).

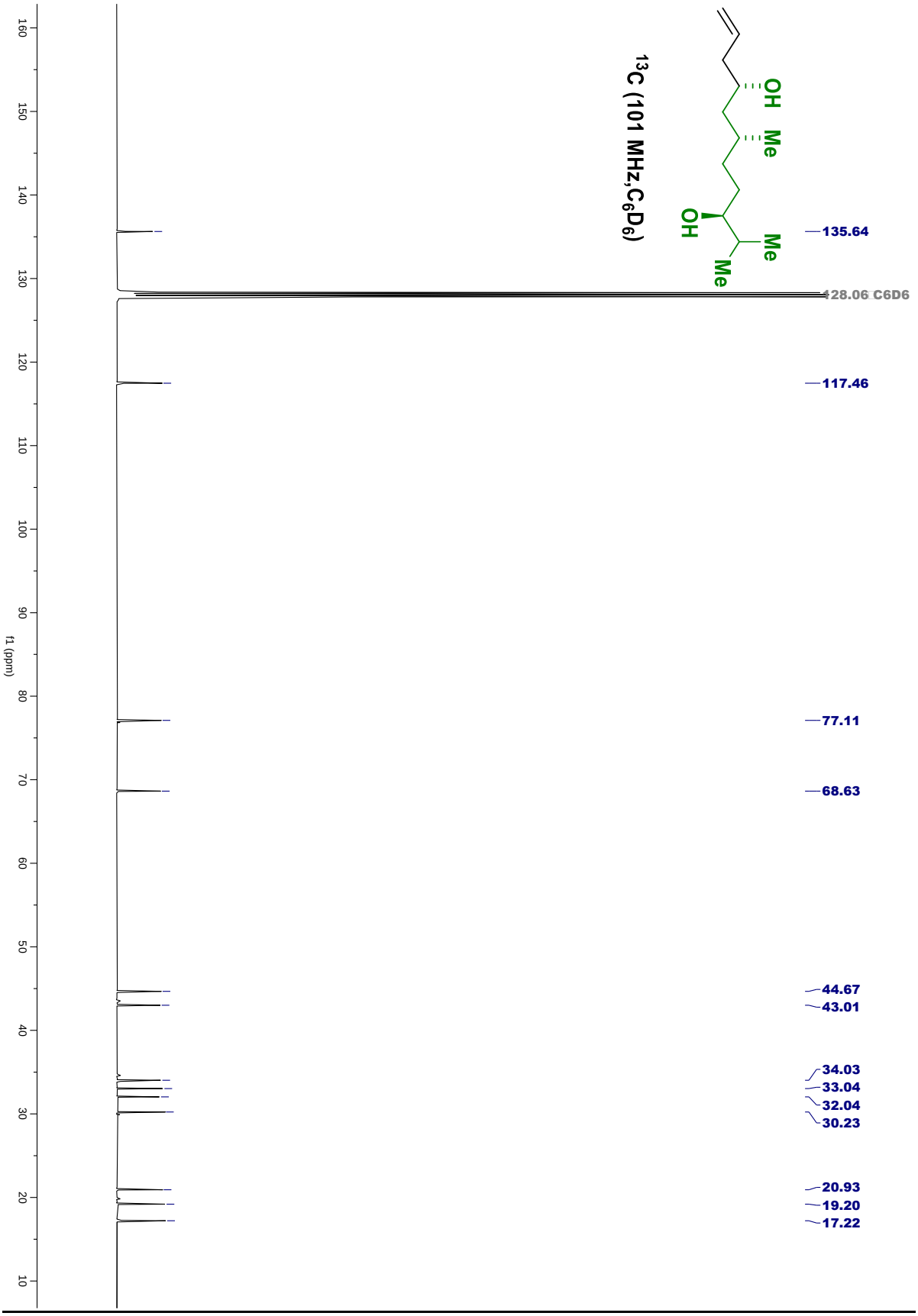
^{13}C NMR (101 MHz, C_6D_6): δ 135.6, 117.5, 77.1, 68.6, 44.7, 43.0, 34.0, 33.0, 32.0, 30.2, 20.9, 19.2, 17.2.

HRMS (Na+, *m/z*): for $C_{13}H_{26}O_2$: calcd. = 237.1825; found = 237.1825.

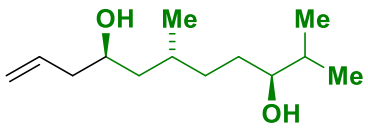
FTIR (neat): 2962, 2890, 1496, 1380, 1200, 1051, 997, 820 cm-1.

$[\alpha]_D^{24}$ = -4.5 (c = 0.1, $CHCl_3$).


^{1}H (400 MHz,C_6D_6)
OH
Me
OH
Me
Me
7.16 C6D6
5.79
5.77
5.75
5.06
5.06
5.04
5.04
5.02
5.02
5.01
3.66
3.18
3.18
3.17
3.16
3.16
2.13
2.11
2.11
2.11
2.10
2.09
2.08
2.07
2.07
2.06
2.05
1.71
1.69
1.69
1.68
1.67
1.66
1.66
1.65
1.64
1.63
1.55
1.53
1.53
1.52
1.51
1.50
1.48
1.46
1.46
1.45
1.44
1.44
1.43
1.36
1.35
1.34
1.33
1.32
1.31
1.31
1.30
1.30
1.29
1.29
1.27
1.27
1.26
1.01
1.00
0.98
0.93
0.92
0.90
0.89
0.88
0.87
SL-J502-1
SL-J502-2
1.00
2.04
0.98
1.03
2.08
2.59
6.40
1.21
3.04
6.29
f1 (ppm)


^{13}C (101 MHz,C_6D_6)
OH
Me
OH
Me
Me
135.64
128.06 C6D6
117.46
77.11
68.63
44.67
43.01
34.03
33.04
32.04
30.23
20.93
19.20
17.22
f1 (ppm)

(3*S*,6*R*,8*R*)-2,6-dimethylundec-10-ene-3,8-diol (*epi*-3n)



Alcohol **2n** (35.7 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 15:85 EtOAc:hexanes) the title compound ***epi*-3n** was isolated as a yellow oil in 75% yield (32.2 mg, 0.15 mmol, 15:1 dr).

TLC (SiO_2): R_f = 0.8 (1:1 EtOAc:hexanes)

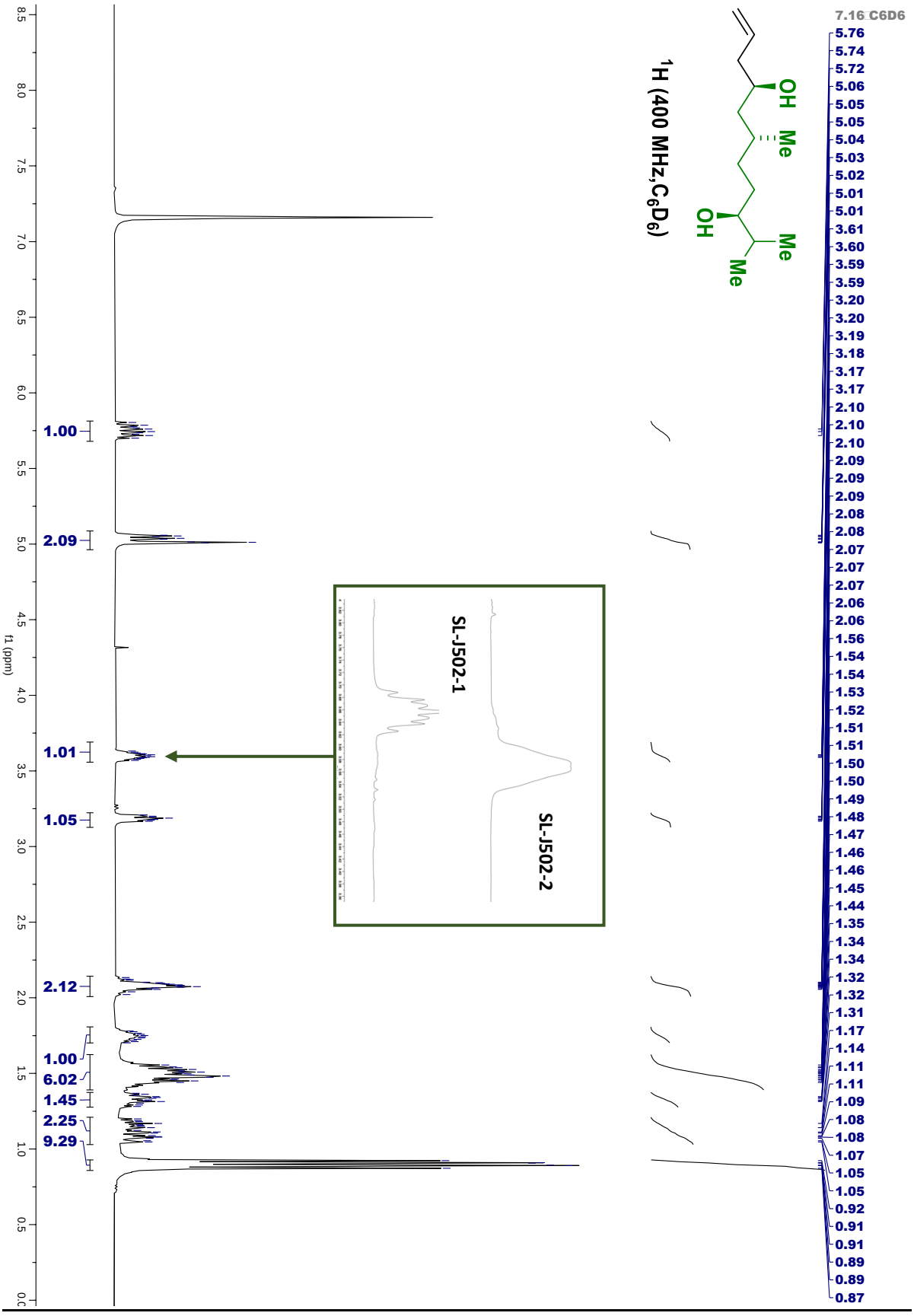
^{1}H NMR (400 MHz, C_6D_6): δ 5.75 (ddt, *J* = 17.4, 10.5, 7.2 Hz, 1H), 5.09 – 4.94 (m, 2H), 3.60 (dddd, *J* = 9.9, 7.0, 5.2, 3.0 Hz, 1H), 3.19 (ddd, *J* = 8.3, 5.0, 3.2 Hz, 1H), 2.23 – 1.90 (m, 2H), 1.75 (dtd, *J* = 13.0, 6.0, 2.9 Hz, 1H), 1.50 (m, 6H), 1.33 (dtd, *J* = 15.1, 8.8, 3.4 Hz, 1H), 1.24 – 1.02 (m, 2H), 0.99 – 0.77 (m, 9H).

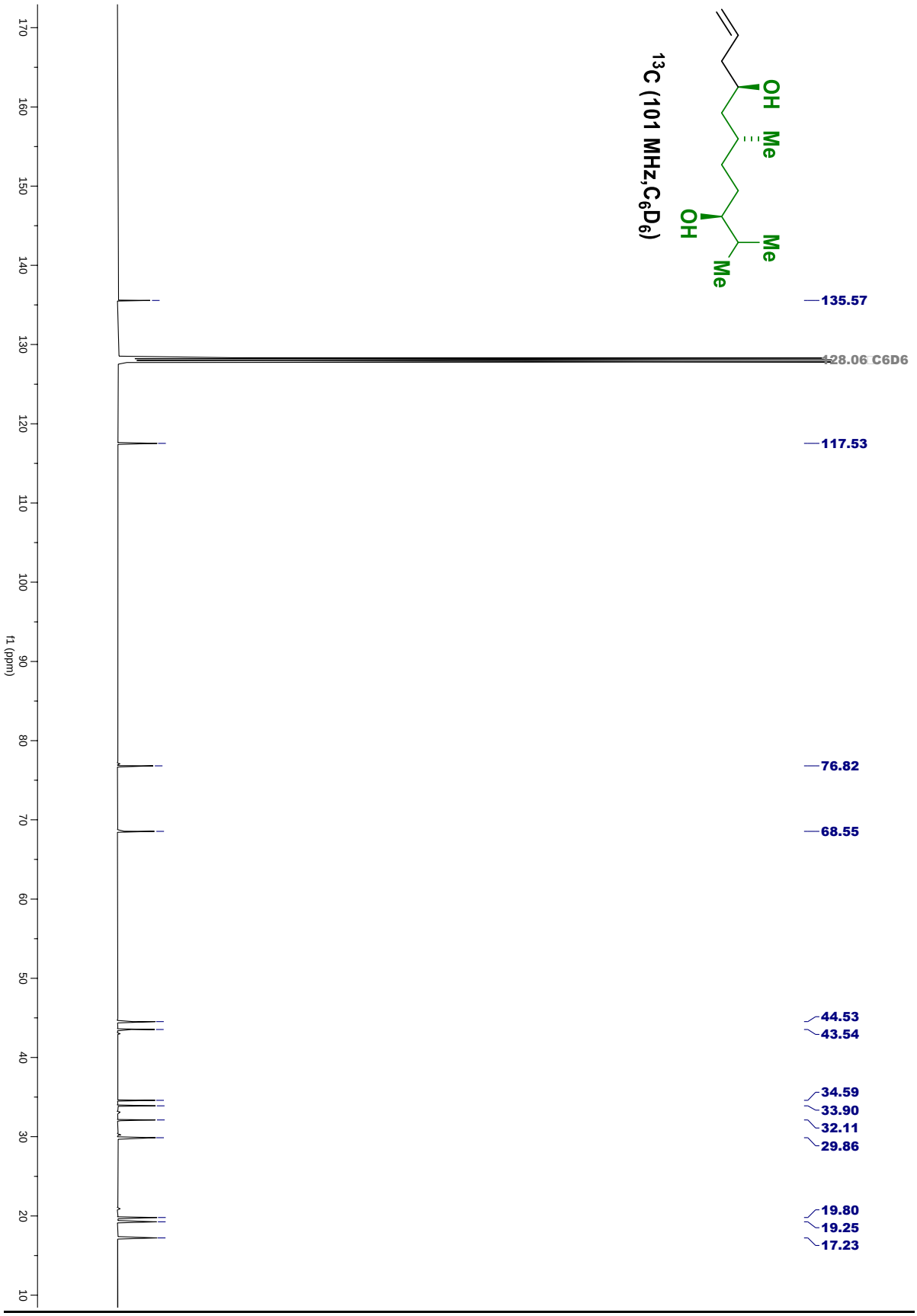
^{13}C NMR (101 MHz, C_6D_6): δ 135.6, 117.5, 76.8, 68.6, 44.5, 43.5, 34.6, 33.9, 32.1, 29.9, 19.8, 19.2, 17.2.

HRMS (Na+, *m/z*): for $C_{13}H_{26}O_2$: calcd. = 237.1825; found = 237.1826.

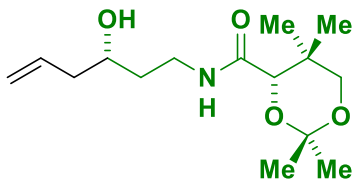
FTIR (neat): 2962, 2890, 1496, 1380, 1200, 1051, 997, 820 cm-1.

$[\alpha]_D^{24}$ = -31.1 (c = 0.1, $CHCl_3$).


^{1}H (400 MHz,C_6D_6)
OH
Me
OH
Me
Me
7.16 C6D6
5.76
5.74
5.72
5.06
5.05
5.05
5.04
5.03
5.02
5.01
5.01
3.61
3.60
3.59
3.59
3.20
3.20
3.19
3.18
3.17
3.17
2.10
2.10
2.10
2.09
2.09
2.09
2.08
2.08
2.07
2.07
2.07
2.06
2.06
1.56
1.54
1.54
1.53
1.52
1.51
1.51
1.50
1.50
1.49
1.48
1.47
1.46
1.46
1.45
1.44
1.35
1.34
1.34
1.32
1.32
1.31
1.17
1.14
1.11
1.11
1.09
1.08
1.08
1.07
1.05
1.05
0.92
0.91
0.91
0.89
0.89
0.87
1.00
2.09
1.01
1.05
2.12
1.00
6.02
1.45
2.25
9.29
f1 (ppm)
SL-J502-1
SL-J502-2


^{13}C (101 MHz,C_6D_6)
OH
Me
OH
Me
Me
135.57
128.06 C6D6
117.53
76.82
68.55
44.53
43.54
34.59
33.90
32.11
29.86
19.80
19.25
17.23
f1 (ppm)

(*S*)-*N*-((*S*)-3-hydroxyhex-5-en-1-yl)-2,2,5,5-tetramethyl-1,3-dioxane-4-carboxamide (3o)



Alcohol **2o** (49.1 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 15:85 EtOAc:hexanes) the title compound **3o** was isolated as a yellow oil in 75% yield (42.8 mg, 0.17 mmol, 12:1 dr).

TLC (SiO_2): R_f = 0.4 (1:9 MeOH:DCM)

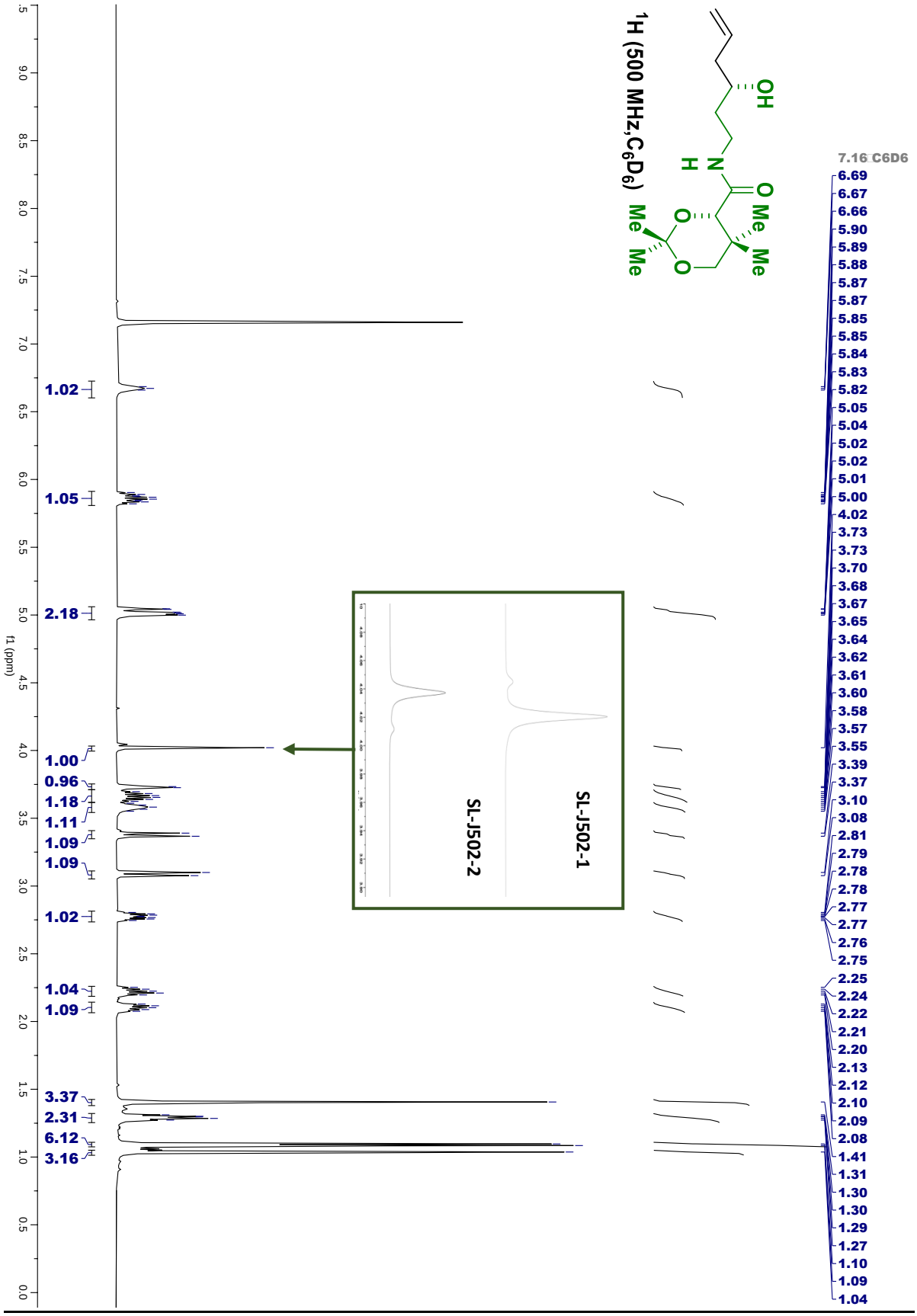
^{1}H NMR (500 MHz, C_6D_6): δ 6.67 (t, *J* = 6.4 Hz, 1H), 5.86 (ddt, *J* = 17.2, 10.1, 7.0 Hz, 1H), 5.13 – 4.92 (m, 2H), 4.02 (s, 1H), 3.73 (d, *J* = 3.9 Hz, 1H), 3.66 (dq, *J* = 14.6, 7.3 Hz, 1H), 3.59 (q, *J* = 8.0, 7.3 Hz, 1H), 3.38 (d, *J* = 11.6 Hz, 1H), 3.09 (d, *J* = 11.6 Hz, 1H), 2.78 (dq, *J* = 13.9, 5.2 Hz, 1H), 2.22 (dt, *J* = 14.1, 7.0 Hz, 1H), 2.10 (dt, *J* = 13.6, 6.2 Hz, 1H), 1.41 (s, 3H), 1.34 – 1.23 (m, 2H), 1.09 (d, *J* = 5.8 Hz, 6H), 1.04 (s, 3H).

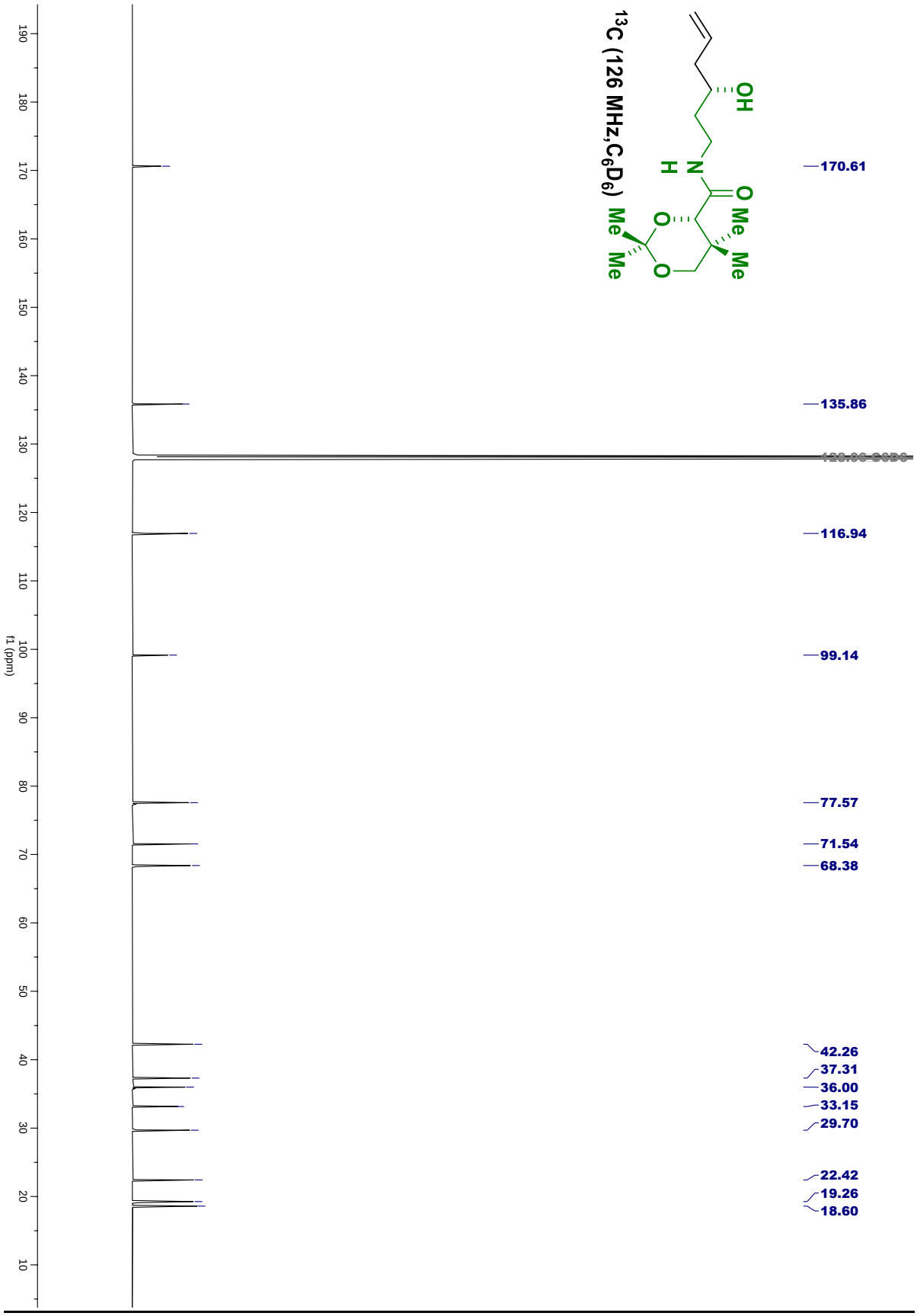
^{13}C NMR (126 MHz, C_6D_6): δ 170.6, 135.9, 116.9, 99.1, 77.6, 71.5, 68.4, 42.3, 37.3, 36.0, 33.2, 29.7, 22.4, 19.3, 18.6.

HRMS (Na+, *m/z*): for $C_{15}H_{27}NO_4$: calcd. = 308.1832; found = 308.1831.

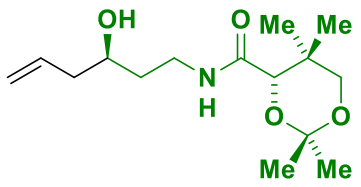
FTIR (neat): 3340, 2954, 1650, 1521, 1442, 1147, 1044, 907 .cm^{-1}.

$[\alpha]_D^{24}$ = -33.5 (c = 0.1, $CHCl_3$).


^{1}H (500 MHz,C_6D_6)
SL-J502-1
SL-J502-2
f1 (ppm)
7.16 C6D6


^{13}C (126 MHz,C$_6$D$_6$)
OH
N
H
O
Me
Me
O
O
Me
Me
170.61
135.86
116.94
99.14
77.57
71.54
68.38
42.26
37.31
36.00
33.15
29.70
22.42
19.26
18.60
f1 (ppm)

(*S*)-*N*-((*R*)-3-hydroxyhex-5-en-1-yl)-2,2,5,5-tetramethyl-1,3-dioxane-4-carboxamide (*epi*-3o)



Alcohol **2o** (49.1 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-2** as ligand. Upon flash column chromatography (SiO_2: 15:85 EtOAc:hexanes) the title compound ***epi*-3o** was isolated as a yellow oil in 75% yield (42.8 mg, 0.17 mmol, 12:1 dr).

TLC (SiO_2): R_f = 0.4 (1:9 MeOH:DCM)

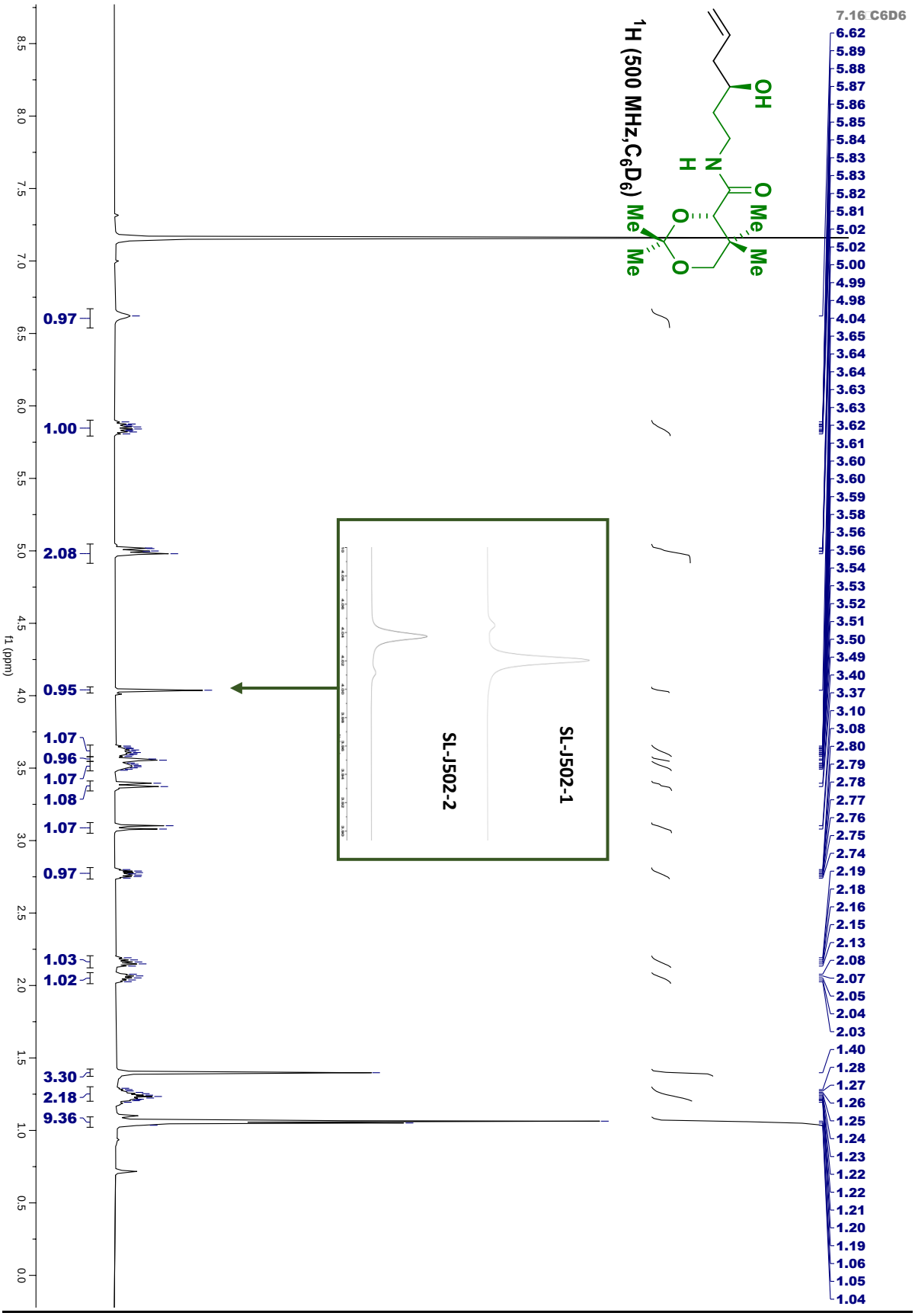
^{1}H NMR (500 MHz, C_6D_6): δ 6.62 (s, 1H), 5.85 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.10 – 4.90 (m, 2H), 4.04 (s, 1H), 3.67 – 3.58 (m, 1H), 3.58 – 3.46 (m, 2H), 3.38 (d, *J* = 11.6 Hz, 1H), 3.09 (d, *J* = 11.7 Hz, 1H), 2.77 (dq, *J* = 14.7, 5.1 Hz, 1H), 2.16 (dt, *J* = 14.1, 7.2 Hz, 1H), 2.05 (dt, *J* = 13.5, 6.1 Hz, 1H), 1.40 (s, 3H), 1.32 – 1.19 (m, 2H), 1.06 (m, 9H).

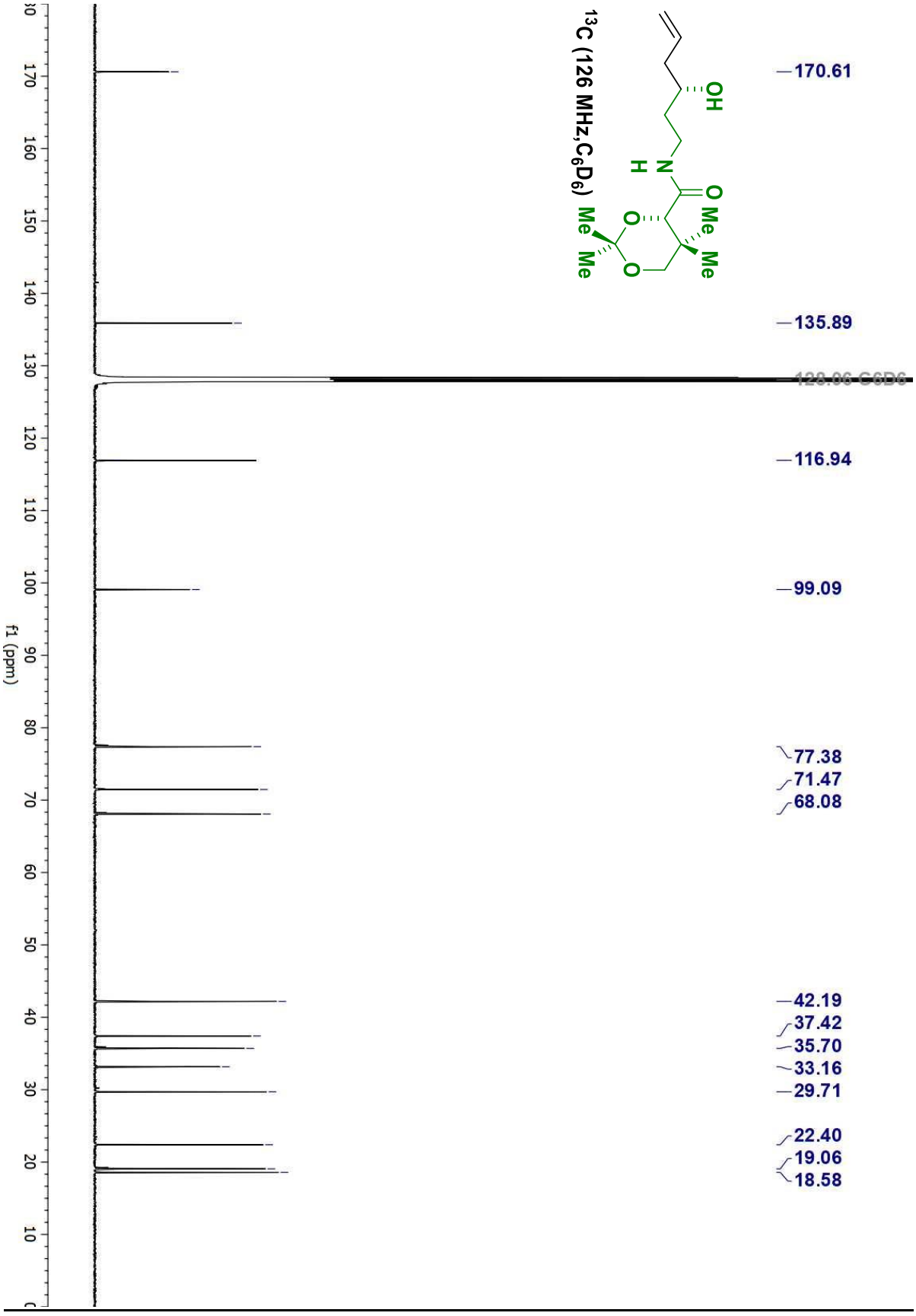
^{13}C NMR (126 MHz, C_6D_6): δ 170.2, 135.5, 116.6, 98.7, 77.0, 71.1, 67.7, 41.8, 37.1, 35.3, 32.8, 29.4, 22.0, 18.7, 18.2.

HRMS (Na+, *m/z*): for $C_{15}H_{27}NO_4$: calcd. = 308.1832; found = 308.1832.

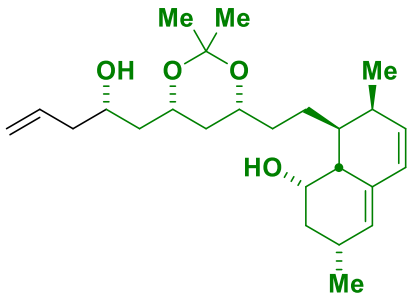
FTIR (neat): 3340, 2954, 1650, 1521, 1442, 1147, 1044, 907 .cm^{-1}.

$[\alpha]_D^{24}$ = -58.4 (c = 0.1, $CHCl_3$).


^{1}H (500 MHz,C_6D_6)
7.16 C6D6
SL-J502-1
SL-J502-2
f1 (ppm)
0.97
1.00
2.08
0.95
1.07
0.96
1.07
1.08
1.07
0.97
1.03
1.02
3.30
2.18
9.36


^{13}C (126 MHz,C_6D_6)
170.61
135.89
128.06 C6D6
116.94
99.09
77.38
71.47
68.08
42.19
37.42
35.70
33.16
29.71
22.40
19.06
18.58
f1 (ppm)

(1*R*,3*S*,7*R*,8*R*)-8-(2-((4*R*,6*S*)-6-((*S*)-2-hydroxypent-4-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)ethyl)-3,7-dimethyl-1,2,3,7,8,8a-hexahydronaphthalen-1-ol (3p)



Alcohol **2p** (73.0 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 15:85 EtOAc:hexanes) the title compound **3p** was isolated as a yellow oil in 80% yield (64.0 mg, 0.16 mmol, 17:1 dr).

TLC (SiO_2): R_f = 0.5 (2:3 EtOAc:hexanes)

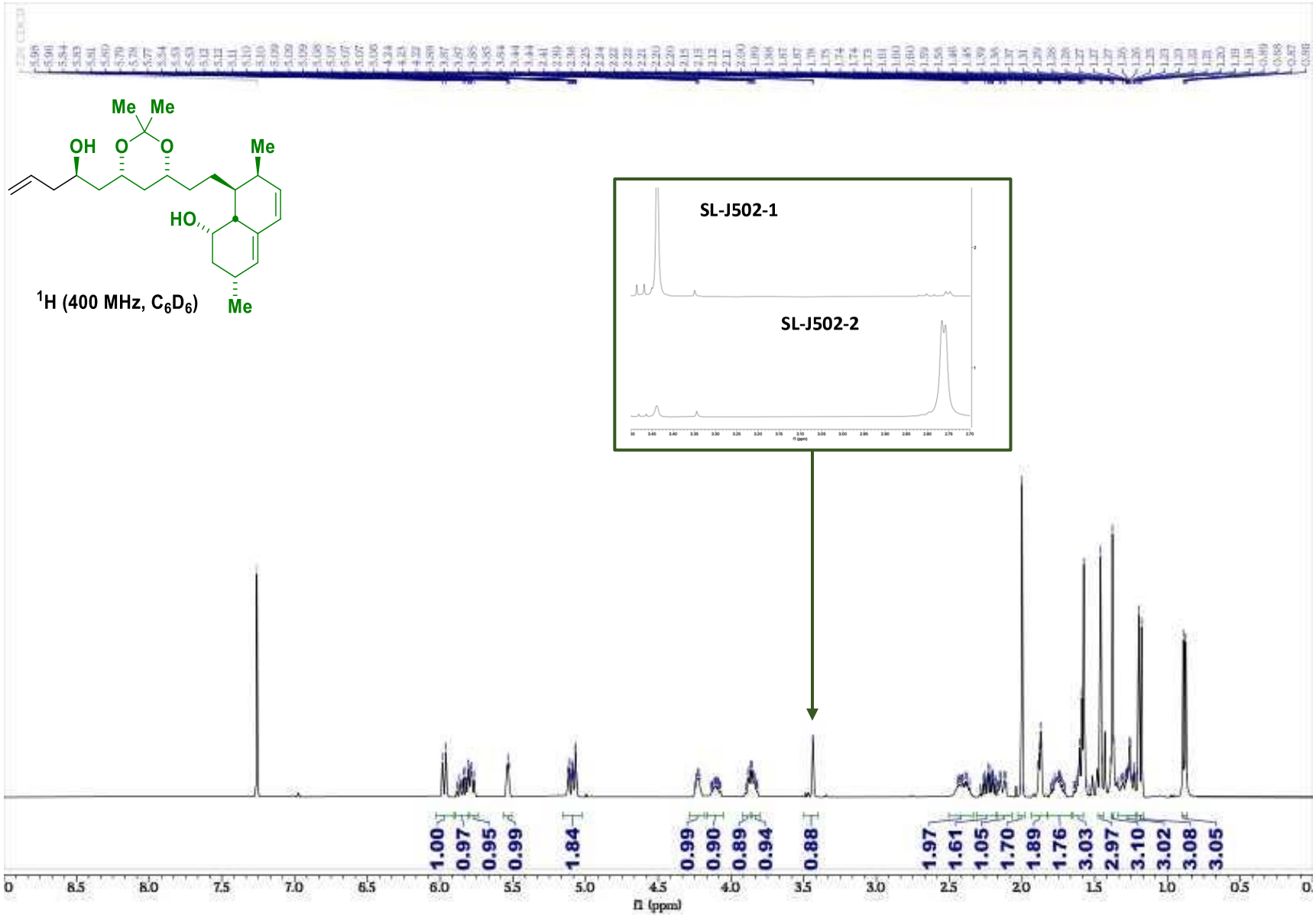
^{1}H NMR (400 MHz, C_6D_6): δ 5.97 (d, *J* = 9.6 Hz, 1H), 5.89 – 5.80 (m, 1H), 5.80 – 5.75 (m, 1H), 5.53 (t, *J* = 3.3 Hz, 1H), 5.14 – 5.05 (m, 2H), 4.23 (dt, *J* = 7.1, 3.4 Hz, 1H), 4.11 (dddd, *J* = 13.3, 8.3, 6.0, 3.1 Hz, 1H), 3.91 – 3.86 (m, 1H), 3.86 – 3.81 (m, 1H), 3.44 (d, *J* = 1.4 Hz, 1H), 2.48 – 2.32 (m, 2H), 2.30 – 2.18 (m, 2H), 2.18 – 2.09 (m, 1H), 2.00 (s, 2H), 1.93 – 1.84 (m, 2H), 1.83 – 1.68 (m, 2H), 1.65 – 1.58 (m, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.34 – 1.22 (m, 3H), 1.19 (d, *J* = 7.5 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H).

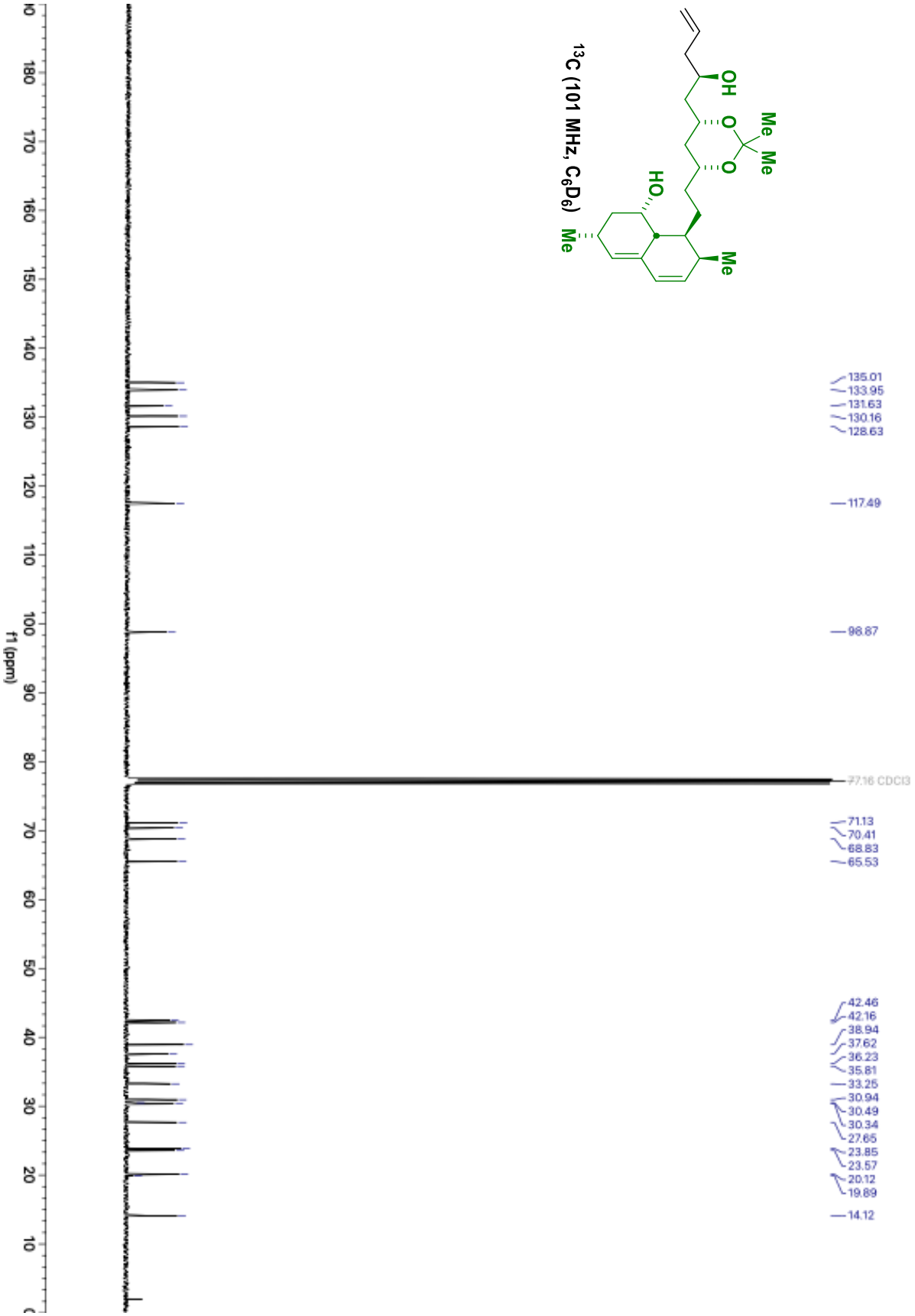
^{13}C NMR (101 MHz, C_6D_6): δ 135.0, 134.0, 131.6, 130.2, 128.6, 117.5, 98.9, 71.1, 70.4, 68.8, 65.6, 42.5, 42.2, 38.9, 37.6, 36.2, 35.8, 33.3, 30.9, 30.5, 30.3, 27.7, 23.9, 23.6, 20.2, 19.9, 14.1.

HRMS (Na+, *m/z*): for $C_{25}H_{40}O_4$: calcd. = 427.2819; found = 427.2815.

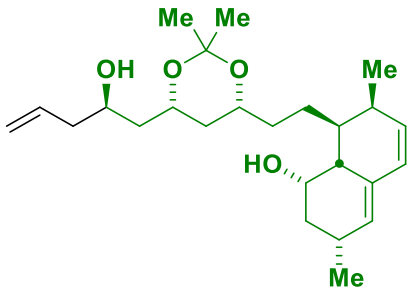
FTIR (neat): 3459, 2995, 2939, 2890, 1454, 1380, 913, 730 cm^{-1}.

$[\alpha]_D^{24}$ = +72.7 (c = 0.1, $CHCl_3$).


Me Me
OH O O
Me
HO
Me
^{1}H (400 MHz, C_6D_6)
SL-J502-1
SL-J502-2
1.00 0.97 0.95 0.99 1.84 0.99 0.90 0.89 0.94 0.88 1.97 1.61 1.05 1.70 1.89 1.76 3.03 2.97 3.10 3.02 3.08 3.05
f1 (ppm)


^{13}C (101 MHz, C_6D_6)
OH
O
O
Me Me
HO
Me
Me
135.01
133.95
131.63
130.16
128.63
117.49
98.87
77.16 CDCl3
71.13
70.41
68.83
65.53
42.46
42.16
38.94
37.62
36.23
35.81
33.25
30.94
30.49
30.34
27.65
23.85
23.57
20.12
19.89
14.12
f1 (ppm)

(1*R*,3*S*,7*R*,8*R*)-8-(2-((4*R*,6*S*)-6-((*R*)-2-hydroxypent-4-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)ethyl)-3,7-dimethyl-1,2,3,7,8,8a-hexahydronaphthalen-1-ol (*epi*-3p)



Alcohol **2p** (73.0 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-2** as ligand. Upon flash column chromatography (SiO_2: 15:85 EtOAc:hexanes) the title compound ***epi*-3p** was isolated as a yellow oil in 84% yield (68.0 mg, 0.17 mmol, 17:1 dr).

TLC (SiO_2): R_f = 0.5 (2:3 EtOAc:hexanes)

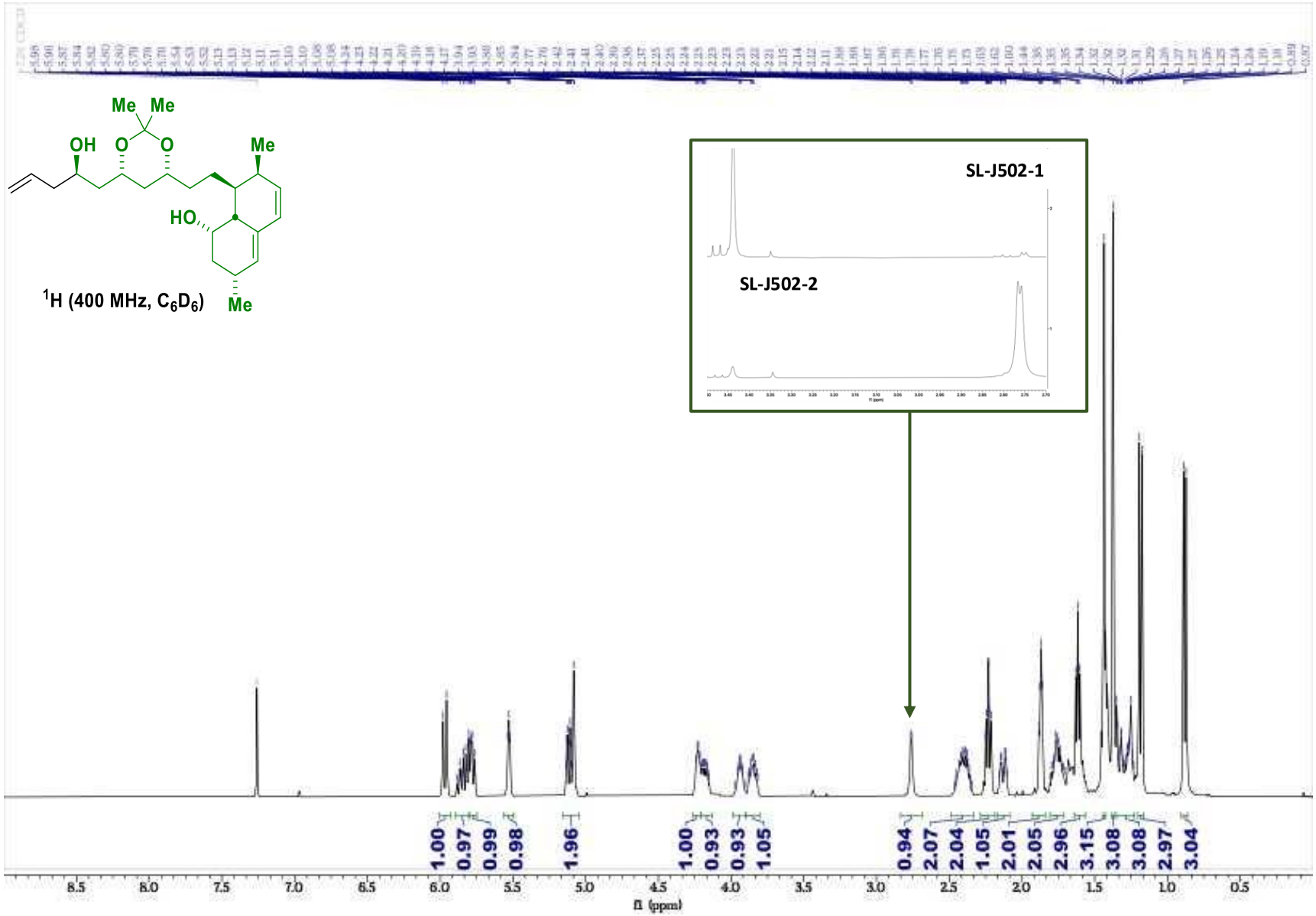
^{1}H NMR (400 MHz, C_6D_6): δ 5.97 (d, *J* = 9.6 Hz, 1H), 5.89 – 5.80 (m, 1H), 5.78 (dd, *J* = 8.4, 5.1 Hz, 1H), 5.53 (t, *J* = 3.2 Hz, 1H), 5.15 – 5.06 (m, 2H), 4.23 (q, *J* = 3.8 Hz, 1H), 4.17 (ddt, *J* = 8.0, 5.2, 2.6 Hz, 1H), 3.93 (tt, *J* = 9.1, 4.6 Hz, 1H), 3.85 (ddt, *J* = 11.1, 7.3, 3.5 Hz, 1H), 2.76 (d, *J* = 3.8 Hz, 1H), 2.40 (dqt, *J* = 17.8, 6.8, 4.1 Hz, 2H), 2.26 – 2.18 (m, 2H), 2.13 (dq, *J* = 12.0, 2.9 Hz, 1H), 1.92 – 1.83 (m, 2H), 1.82 – 1.70 (m, 2H), 1.62 (t, *J* = 5.6 Hz, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.35 – 1.23 (m, 3H), 1.18 (d, *J* = 7.5 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H).

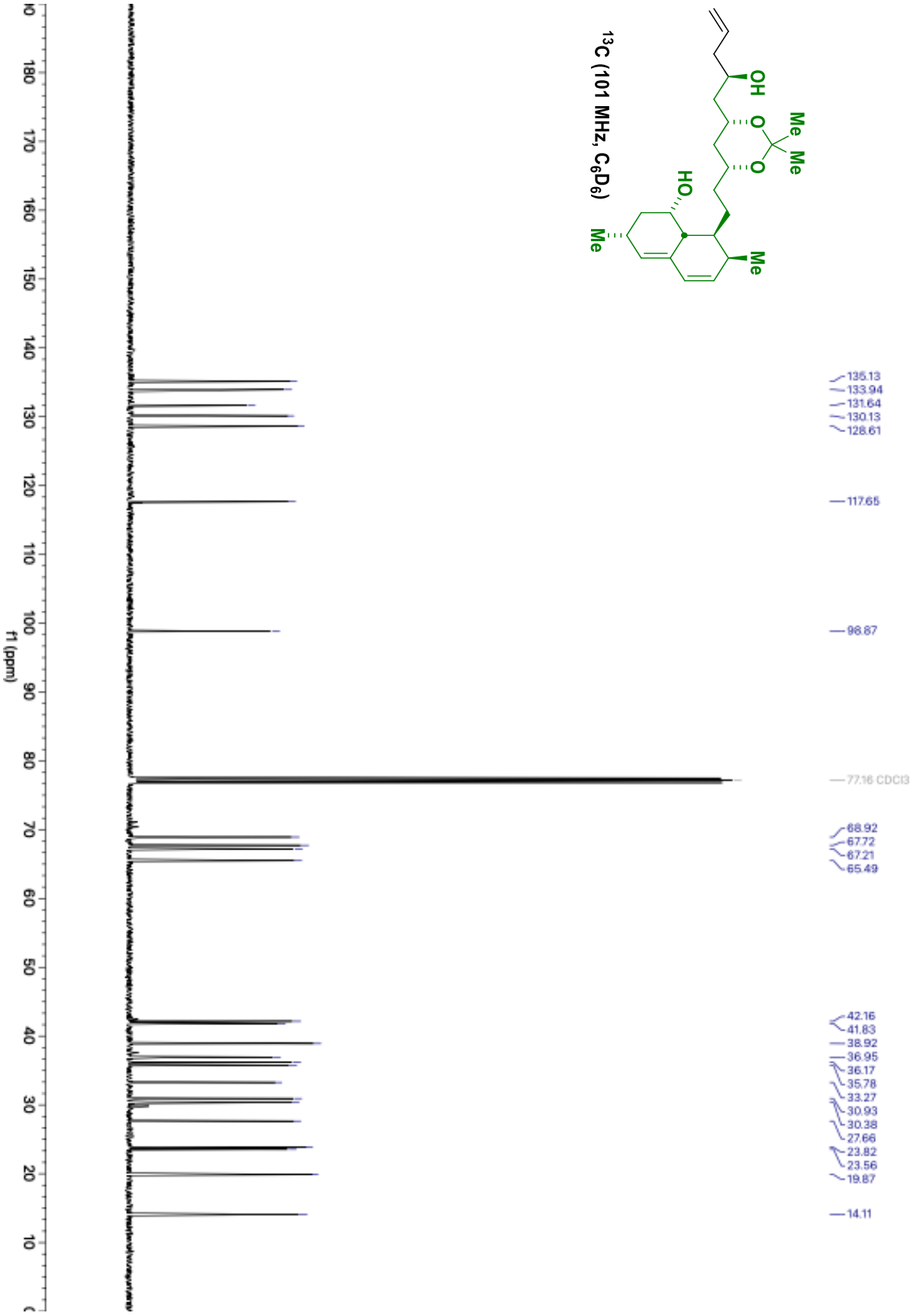
^{13}C NMR (101 MHz, C_6D_6): δ 135.1, 133.9, 131.6, 130.1, 128.6, 117.7, 98.9, 68.9, 67.7, 67.2, 65.5, 42.2, 41.8, 38.9, 37.0, 36.2, 35.8, 33.3, 30.9, 30.4, 27.7, 23.8, 23.6, 19.9, 14.1.

HRMS (Na+, *m/z*): for $C_{25}H_{40}O_4$: calcd. = 427.2819; found = 427.2815.

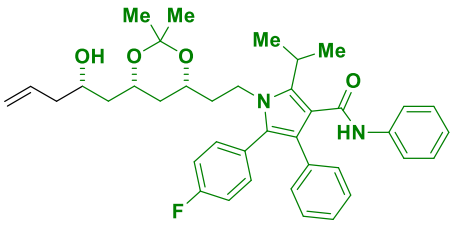
FTIR (neat): 3480, 3013, 2888, 2821, 1451, 1330, 931, 801 cm^{-1}.

$[\alpha]_D^{24}$ = +16.7 (c = 0.1, $CHCl_3$).


Me Me
OH O O
Me
HO
Me
^{1}H (400 MHz, C_6D_6)
SL-J502-1
SL-J502-2
1.00 0.97 0.99 0.98 1.96 1.00 0.93 0.93 1.05 0.94 2.07 2.04 1.05 2.01 2.05 2.96 3.15 3.08 3.08 2.97 3.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


^{13}C (101 MHz, C_6D_6)
OH
O
O
Me
Me
HO
Me
Me
135.13
133.94
131.64
130.13
128.61
117.65
98.87
77.16 CDCl3
68.92
67.72
67.21
65.49
42.16
41.83
38.92
36.95
36.17
35.78
33.27
30.93
30.38
27.66
23.82
23.56
19.87
14.11
f1 (ppm)

5-(4-fluorophenyl)-1-(2-((4R,6S)-6-((S)-2-hydroxypent-4-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)ethyl)-2-isopropyl-N,4-diphenyl-1H-pyrrole-3-carboxamide (3q)



Alcohol **2q** (116.9 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h. Upon flash column chromatography (SiO_2: 10:90 EtOAc:hexanes) the title compound **3q** was isolated as a yellow oil in 80% yield (99.9 mg, 0.16 mmol, 11:1 dr).

TLC (SiO_2): R_f = 0.5 1:2 EtOAc:hexanes)

^{1}H NMR (500 MHz, C_6D_6): δ 7.39 (d, J = 6.9 Hz, 2H), 7.23 (d, J = 7.4 Hz, 2H), 7.04 (dd, J = 8.4, 4.7 Hz, 4H), 6.91 (dt, J = 14.8, 6.9 Hz, 4H), 6.82 (t, J = 7.4 Hz, 1H), 6.70 (t, J = 8.5 Hz, 2H), 5.92 (ddt, J = 17.3, 10.3, 7.1 Hz, 1H), 5.14 – 5.03 (m, 2H), 4.04 (ddd, J = 15.0, 10.7, 4.8 Hz, 1H), 3.76 (tt, J = 10.5, 5.4 Hz, 2H), 3.66 (q, J = 7.3 Hz, 2H), 3.34 – 3.23 (m, 1H), 3.01 – 2.91 (m, 1H), 2.29 (dt, J = 13.6, 6.7 Hz, 1H), 2.19 (dt, J = 13.6, 6.5 Hz, 1H), 1.75 (d, 6H), 1.65 – 1.51 (m, 3H), 1.30 (dt, J = 4.4, 2.0 Hz, 1H), 1.27 (s, 3H), 1.11 (s, 3H), 0.85 (q, J = 11.8 Hz, 1H), 0.66 (dq, J = 13.5, 3.2 Hz, 1H).

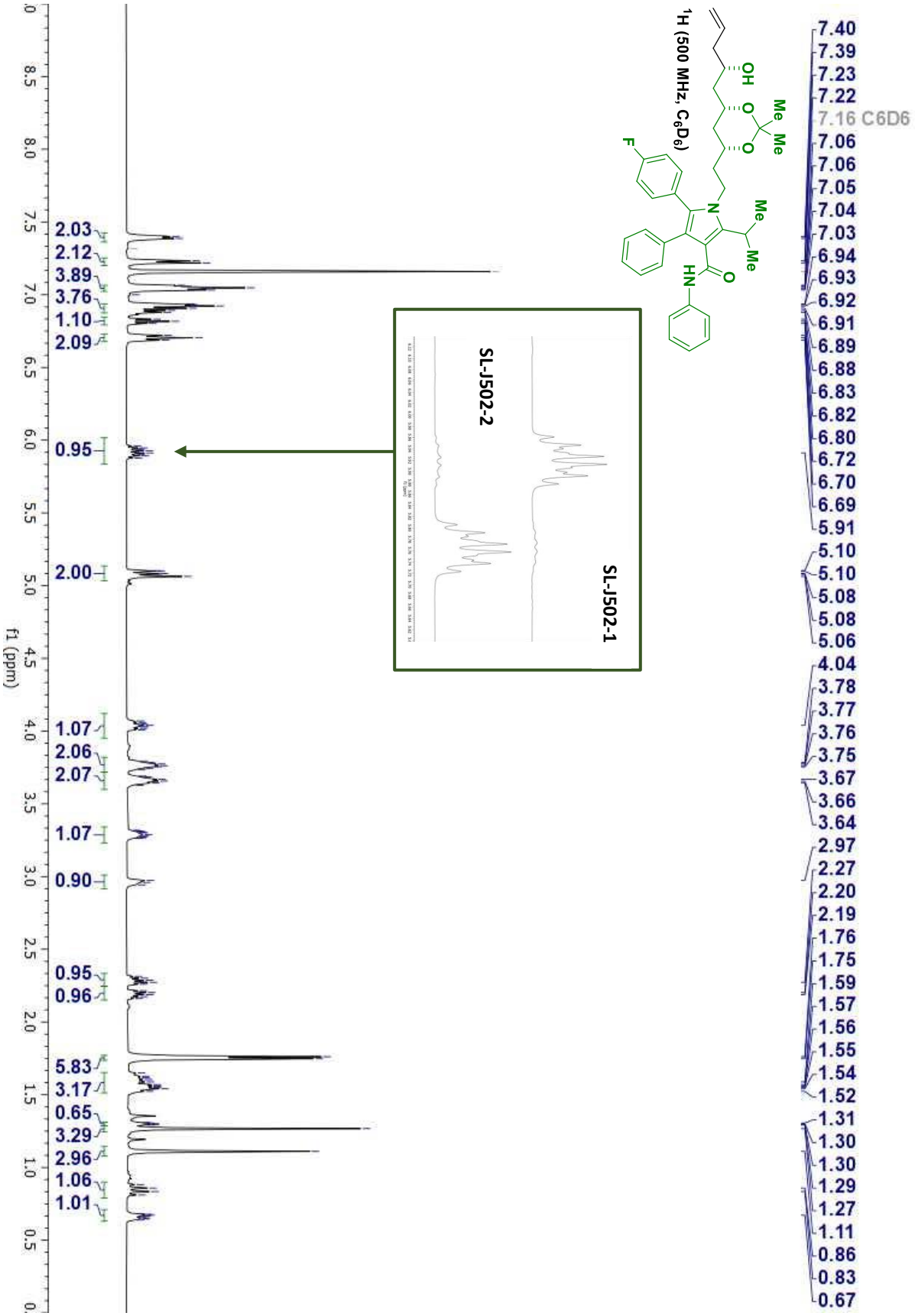
^{13}C NMR (130 MHz, C_6D_6): δ 163.6, 163.23 (d, J = 392.9 Hz), 141.7, 139.6, 135.5, 135.2, 133.60 (d, J = 8.1 Hz), 130.8, 129.0, 129.0, 129.0, 128.98 (d, J = 3.6 Hz), 126.8, 123.6, 122.5, 119.4, 117.3, 117.0, 115.69 (d, J = 21.4 Hz), 98.7, 70.1, 69.3, 66.7, 42.7, 42.6, 41.0, 38.5, 36.5, 30.1, 26.8, 22.2, 21.9, 19.8.

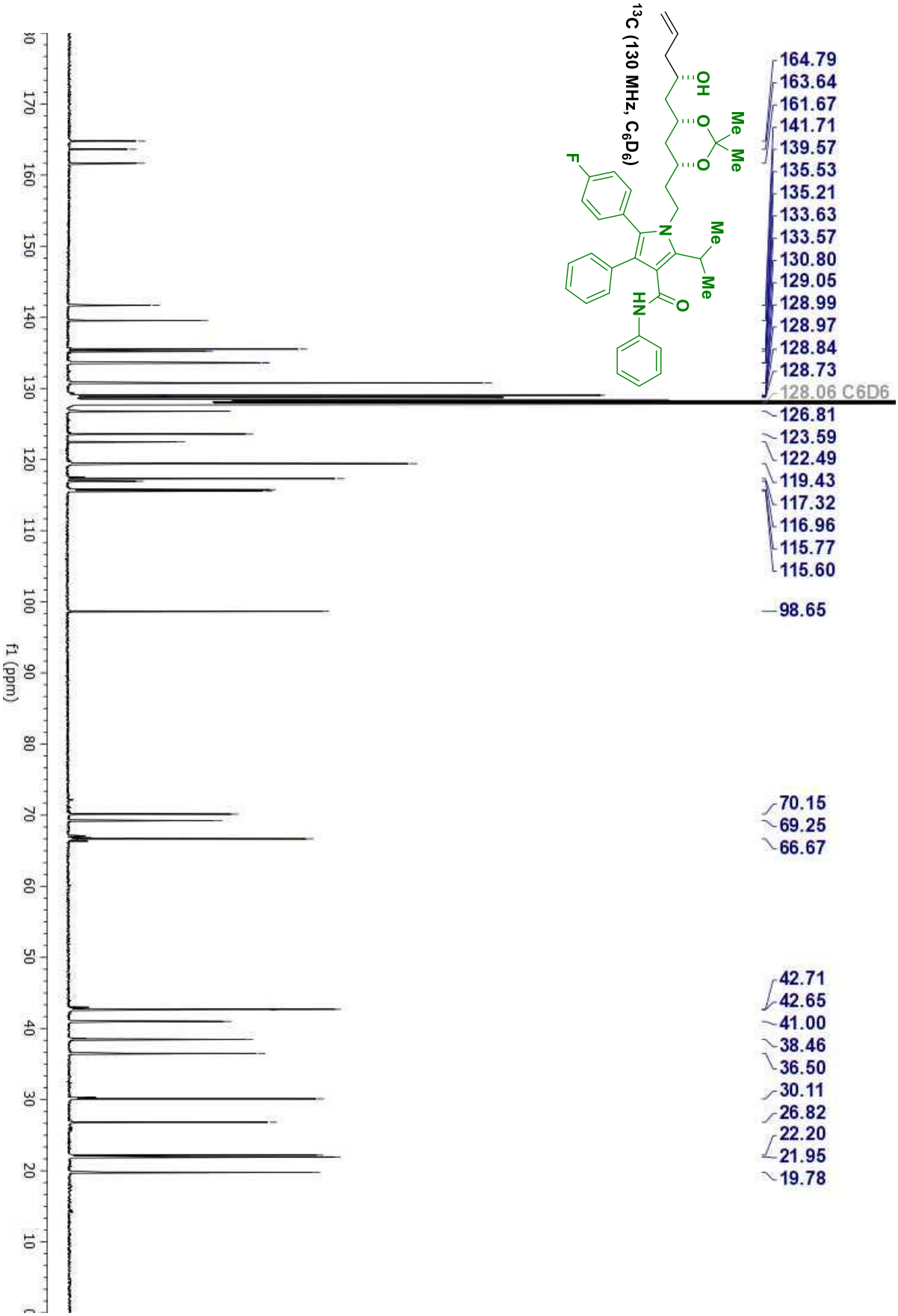
^{19}F NMR (471 MHz, C_6D_6) δ: -113.45 (p, J = 7.0 Hz).

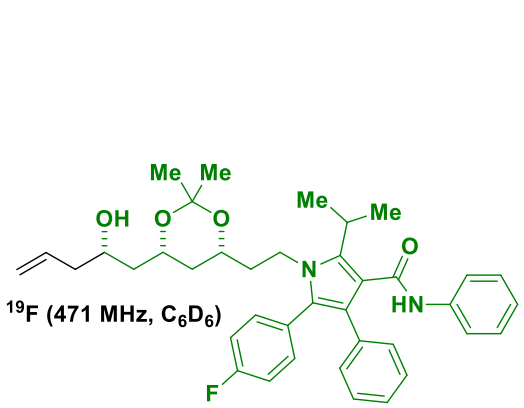
HRMS (Na+, *m/z*): for $C_{39}H_{45}FN_2O_4$: calcd. = 647.3312; found = 647.3300.

FTIR (neat): 2987, 2926, 1762, 1364, 1210, 1143, 1056, 986, 928, 873 cm^{-1}.

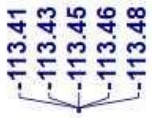
$[\alpha]_D^{24}$ = -31.5 (c = 2.1, $CHCl_3$).

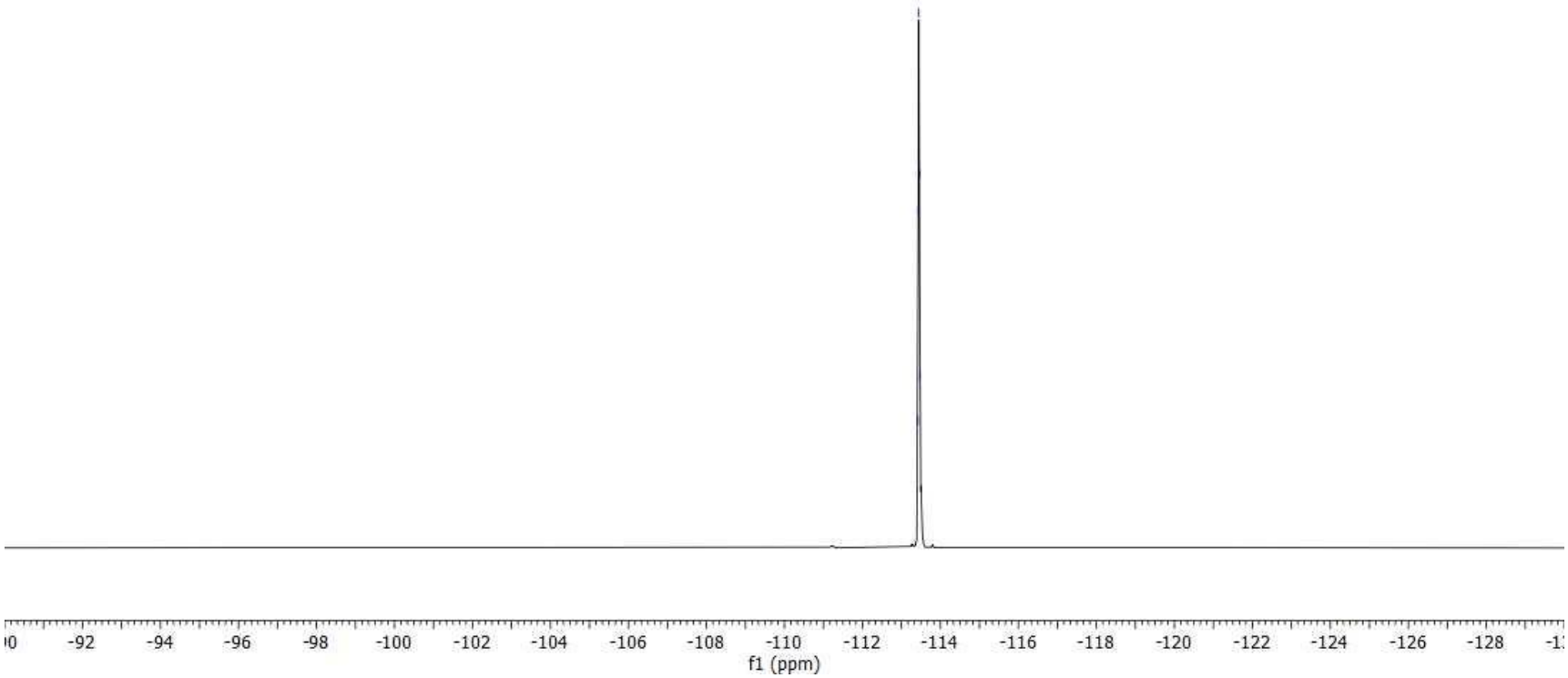

^{1}H (500 MHz, C_6D_6)
SL-J502-1
SL-J502-2
f1 (ppm)
7.16 C6D6


^{13}C (130 MHz, C_6D_6)
f1 (ppm)
164.79
163.64
161.67
141.71
139.57
135.53
135.21
133.63
133.57
130.80
129.05
128.99
128.97
128.84
128.73
128.06 C6D6
126.81
123.59
122.49
119.43
117.32
116.96
115.77
115.60
98.65
70.15
69.25
66.67
42.71
42.65
41.00
38.46
36.50
30.11
26.82
22.20
21.95
19.78

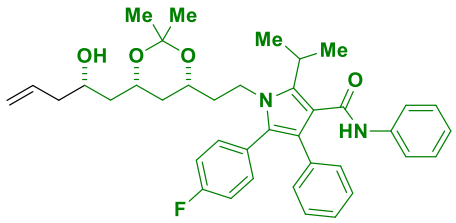


^{19}F (471 MHz, C_6D_6)





5-(4-fluorophenyl)-1-(2-((4R,6S)-6-((S)-2-hydroxypent-4-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)ethyl)-2-isopropyl-N,4-diphenyl-1H-pyrrole-3-carboxamide (*epi*-3q)



Alcohol **2q** (116.9 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h. Upon flash column chromatography (SiO_2: 10:90 EtOAc:hexanes) the title compound ***epi*-3q** was isolated as a yellow oil in 91% yield (113.7 mg, 0.16 mmol, 11:1 dr).

TLC (SiO_2): R_f = 0.5 (1:4 EtOAc:hexanes)

^{1}H NMR (500 MHz, C_6D_6): δ 7.39 (d, J = 6.9 Hz, 2H), 7.23 (d, J = 7.4 Hz, 2H), 7.04 (dd, J = 8.4, 4.7 Hz, 4H), 6.91 (dt, J = 14.8, 6.9 Hz, 4H), 6.82 (t, J = 7.4 Hz, 1H), 6.70 (t, J = 8.5 Hz, 2H), 5.92 (ddt, J = 17.3, 10.3, 7.1 Hz, 1H), 5.14 – 5.03 (m, 2H), 4.04 (ddd, J = 15.0, 10.7, 4.8 Hz, 1H), 3.76 (tt, J = 10.5, 5.4 Hz, 2H), 3.66 (q, J = 7.3 Hz, 2H), 3.34 – 3.23 (m, 1H), 3.01 – 2.91 (m, 1H), 2.29 (dt, J = 13.6, 6.7 Hz, 1H), 2.19 (dt, J = 13.6, 6.5 Hz, 1H), 1.75 (d, 6H), 1.65 – 1.51 (m, 3H), 1.30 (dt, J = 4.4, 2.0 Hz, 1H), 1.27 (s, 3H), 1.11 (s, 3H), 0.85 (q, J = 11.8 Hz, 1H), 0.66 (dq, J = 13.5, 3.2 Hz, 1H).

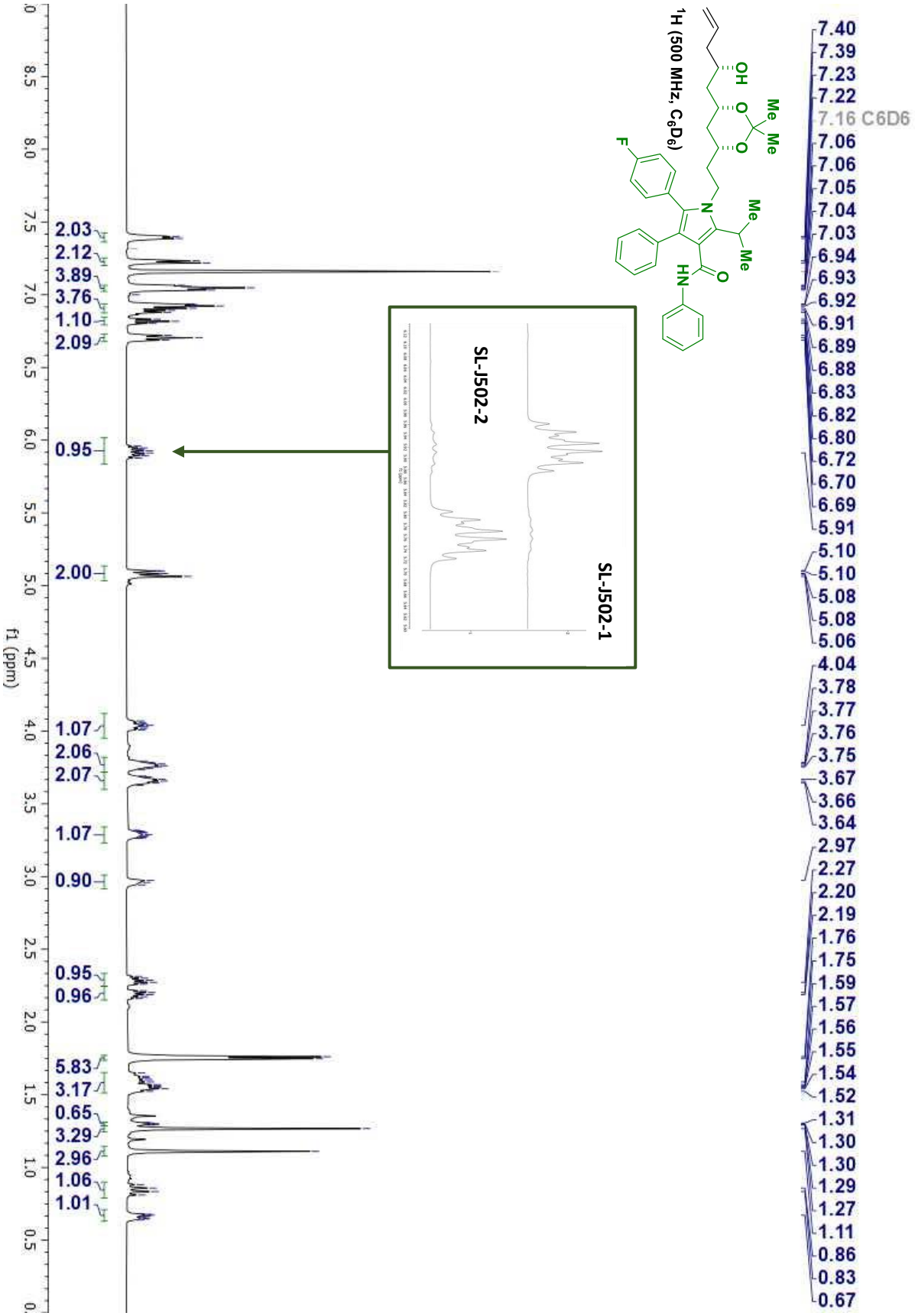
^{13}C NMR (130 MHz, C_6D_6): δ 163.6, 163.23 (d, J = 392.9 Hz), 141.7, 139.6, 135.5, 135.2, 133.60 (d, J = 8.1 Hz), 130.8, 129.0, 129.0, 129.0, 128.98 (d, J = 3.6 Hz), 126.8, 123.6, 122.5, 119.4, 117.3, 117.0, 115.69 (d, J = 21.4 Hz), 98.7, 70.1, 69.3, 66.7, 42.7, 42.6, 41.0, 38.5, 36.5, 30.1, 26.8, 22.2, 21.9, 19.8.

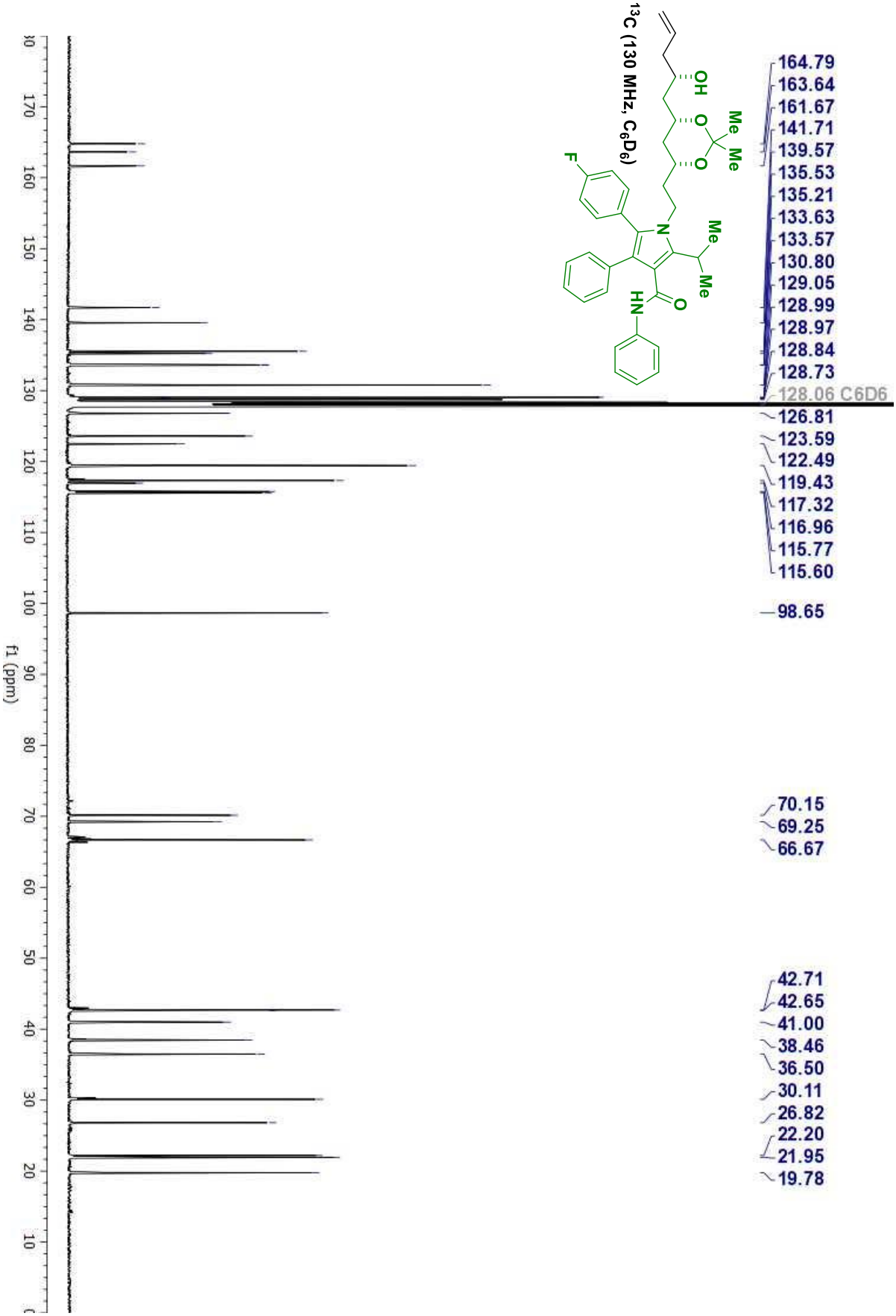
^{19}F NMR (471 MHz, C_6D_6) δ: -113.45 (p, J = 7.0 Hz).

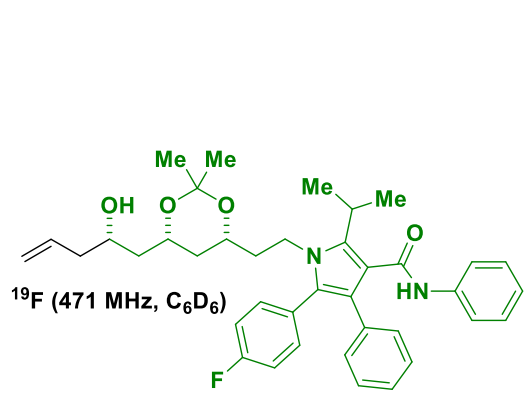
HRMS (Na+, *m/z*): for $C_{39}H_{45}FN_2O_4$: calcd. = 647.3312; found = 647.3300.

FTIR (neat): 2987, 2926, 1762, 1364, 1210, 1143, 1056, 986, 928, 873 cm^{-1}.

$[\alpha]_D^{24}$ = 15.2 (c = 2.1, $CHCl_3$).

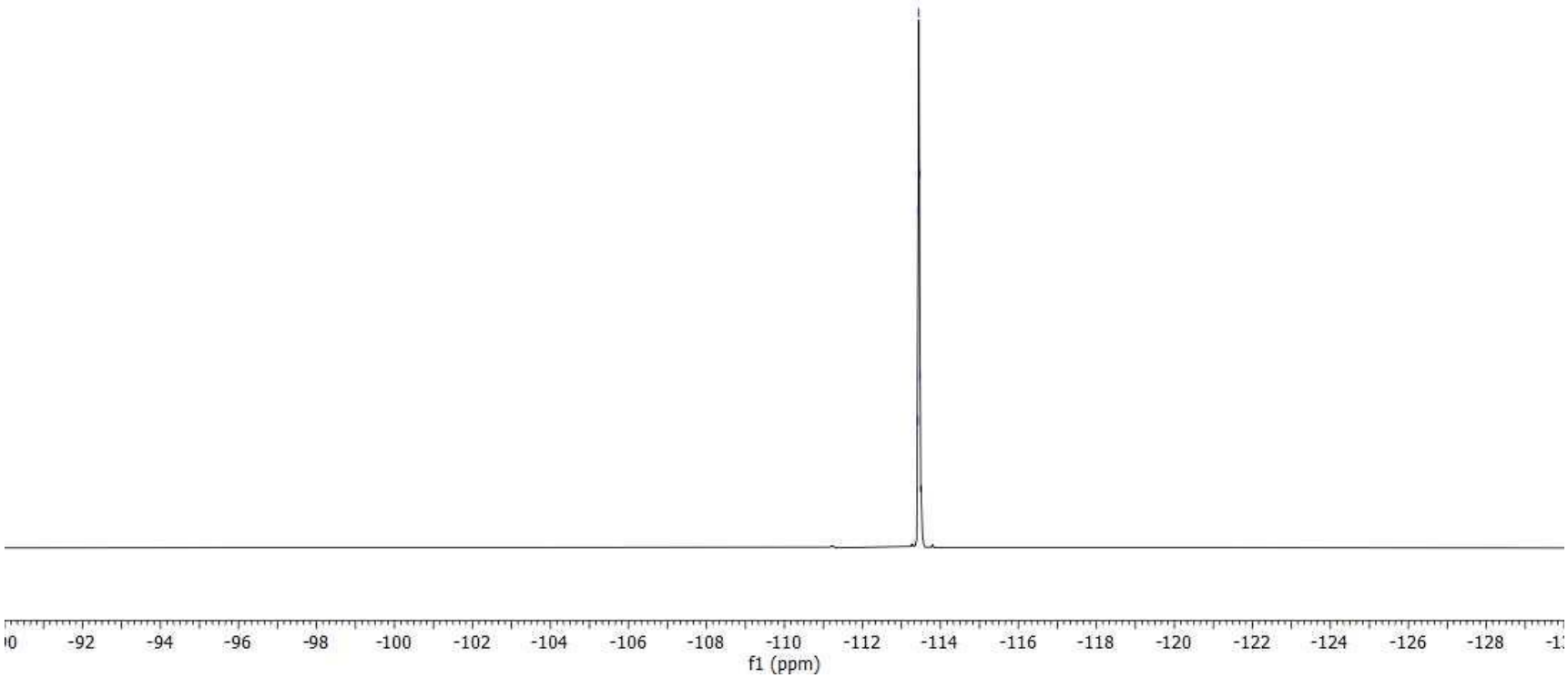

^{1}H (500 MHz, C_6D_6)
SL-J502-2
SL-J502-1
f1 (ppm)
7.16 C6D6


^{13}C (130 MHz, C_6D_6)
f1 (ppm)
164.79
163.64
161.67
141.71
139.57
135.53
135.21
133.63
133.57
130.80
129.05
128.99
128.97
128.84
128.73
128.06 C6D6
126.81
123.59
122.49
119.43
117.32
116.96
115.77
115.60
98.65
70.15
69.25
66.67
42.71
42.65
41.00
38.46
36.50
30.11
26.82
22.20
21.95
19.78

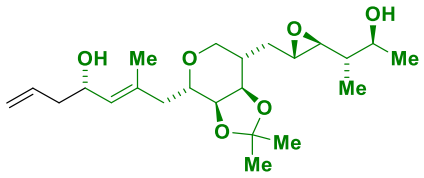


^{19}F (471 MHz, C_6D_6)

-113.41
-113.43
-113.45
-113.46
-113.48



(*S*,*E*)-7-((3a*S*,4*S*,7*S*,7a*R*)-7-(((2*S*,3*S*)-3-((2*S*,3*S*)-3-hydroxybutan-2-yl)oxiran-2-yl)methyl)-2,2-dimethyltetrahydro-4*H*-[1,3]dioxolo[4,5-*c*]pyran-4-yl)-6-methylhepta-1,5-dien-4-ol (3r)



Alcohol **2r** (37.0 mg, 0.1 mmol) was subjected to standard reaction conditions (80 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 15:85 EtOAc:hexanes) the title compound **3r** was isolated as a yellow oil in 76% yield (31.2 mg, 0.08 mmol, >20:1 dr).

TLC (SiO_2): R_f = 0.5 (2:1 Acetone:hexanes)

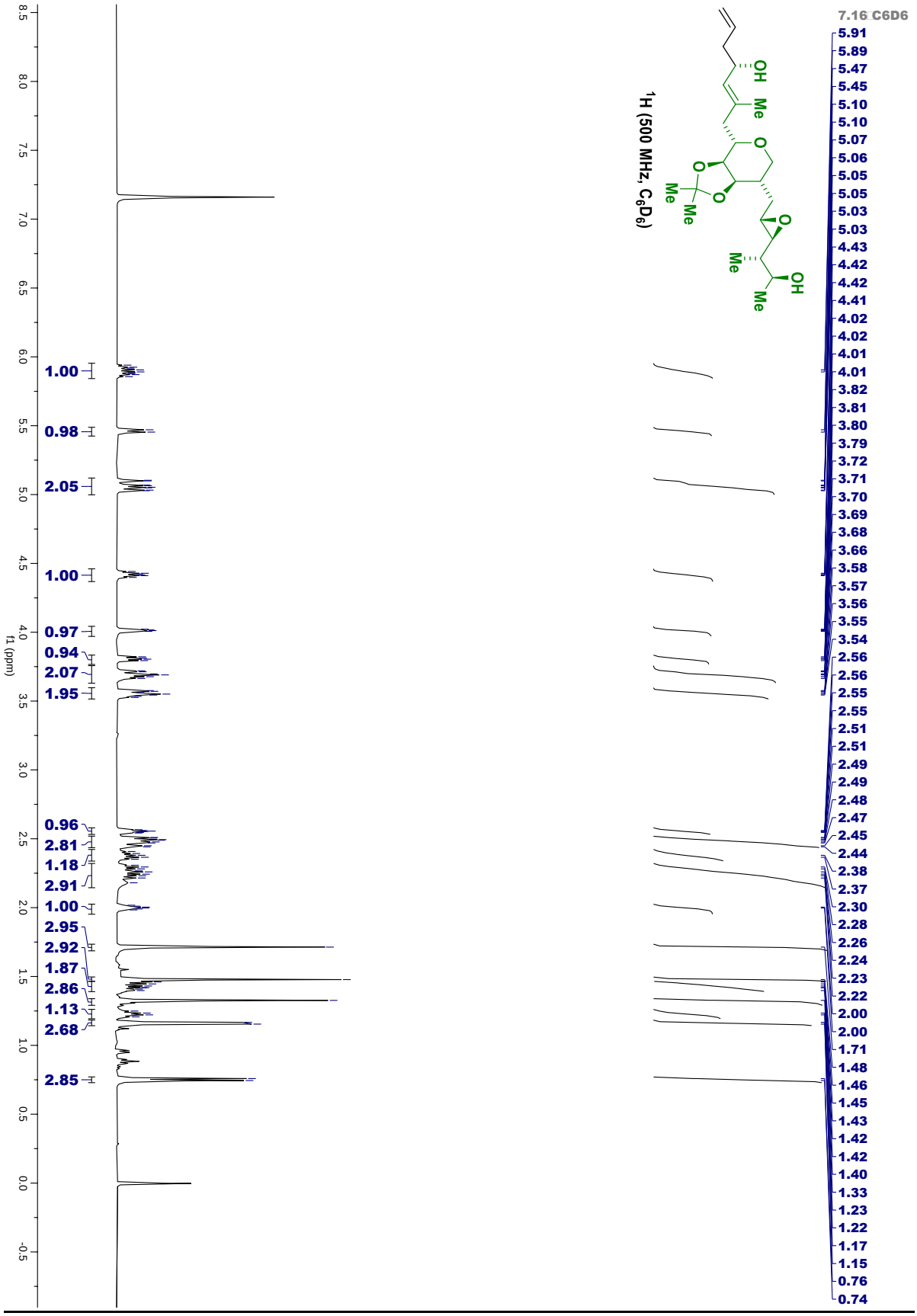
^{1}H NMR (500 MHz, C_6D_6): δ 5.90 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.46 (d, *J* = 8.5 Hz, 1H), 5.17 – 4.97 (m, 2H), 4.42 (dt, *J* = 8.4, 6.5 Hz, 1H), 4.01 (dd, *J* = 5.1, 2.7 Hz, 1H), 3.81 (dd, *J* = 8.8, 5.1 Hz, 1H), 3.69 (td, *J* = 12.7, 12.2, 4.8 Hz, 2H), 3.55 (ddd, *J* = 12.3, 8.1, 3.2 Hz, 2H), 2.55 (td, *J* = 4.9, 2.5 Hz, 1H), 2.53 – 2.42 (m, 3H), 2.38 (dt, *J* = 14.0, 7.0 Hz, 1H), 2.32 – 2.14 (m, 3H), 2.00 (td, *J* = 6.9, 3.4 Hz, 1H), 1.71 (s, 3H), 1.48 (s, 3H), 1.46 – 1.38 (m, 2H), 1.33 (s, 3H), 1.23 (q, *J* = 7.1 Hz, 1H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.75 (d, *J* = 7.0 Hz, 3H).

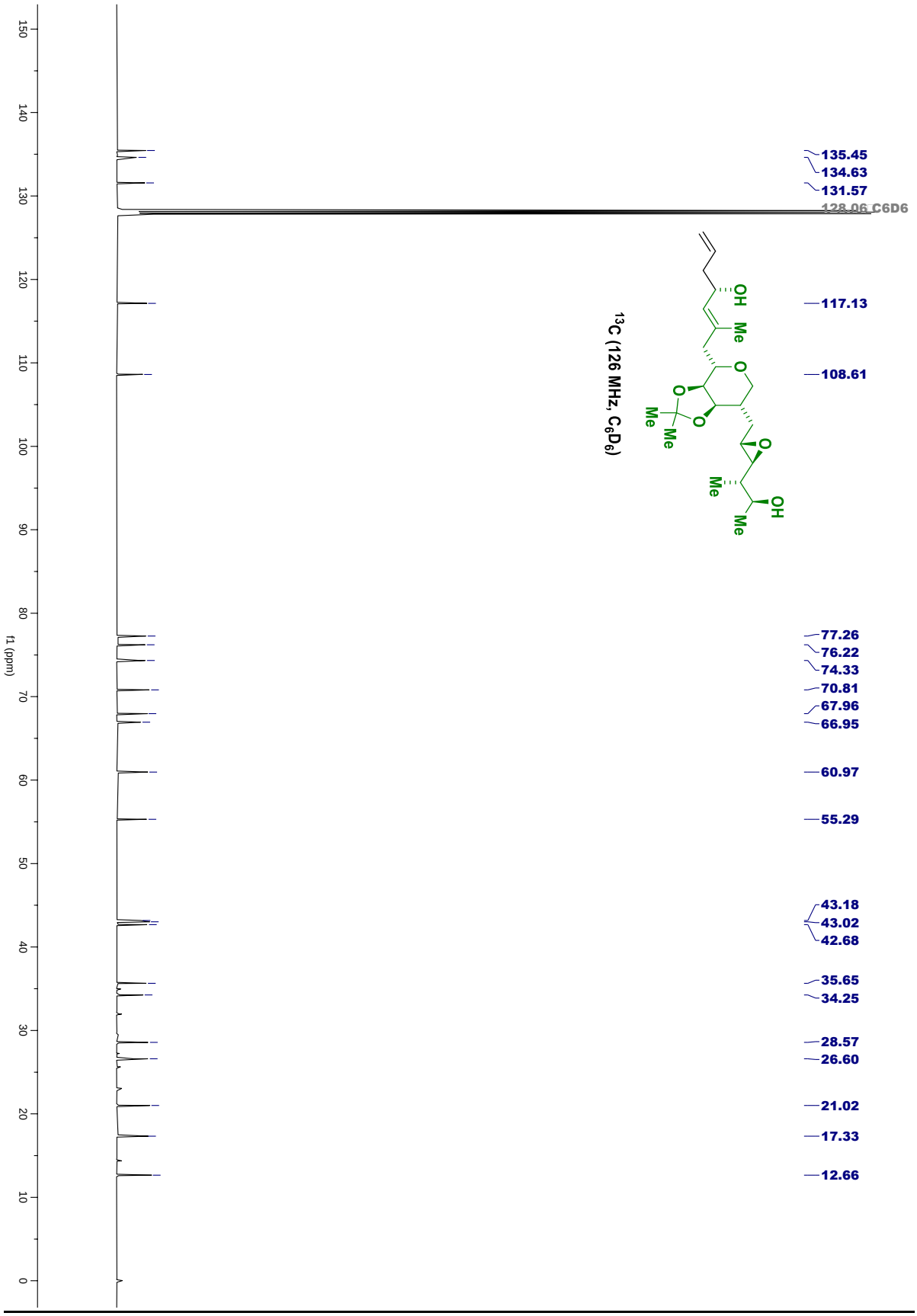
^{13}C NMR (126 MHz, C_6D_6): δ 135.5, 134.6, 131.6, 117.1, 108.6, 77.3, 76.2, 74.3, 70.8, 68.0, 66.9, 61.0, 55.3, 43.2, 43.0, 42.7, 35.7, 34.3, 28.6, 26.6, 21.0, 17.3, 12.7.

HRMS (Na+, *m/z*): for $C_{23}H_{38}O_6$: calcd. = 433.2561; found = 433.2557.

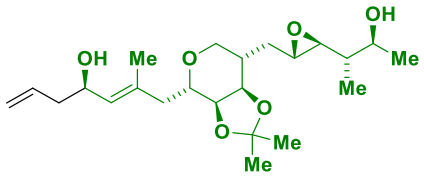
FTIR (neat): 3462, 3430, 1225, 1146, 1103, 1050, 834, 678 cm-1.

$[\alpha]_D^{24}$ = -50.0 (c = 0.1, $CHCl_3$).


^{1}H (500 MHz, C_6D_6)
7.16 C6D6
f1 (ppm)
1.00
0.98
2.05
1.00
0.97
0.94
2.07
1.95
0.96
2.81
1.18
2.91
1.00
2.95
2.92
1.87
2.86
1.13
2.68
2.85
OH
Me
O
Me
Me
O
O
Me
OH
Me


135.45
134.63
131.57
128.06 C6D6
117.13
108.61
77.26
76.22
74.33
70.81
67.96
66.95
60.97
55.29
43.18
43.02
42.68
35.65
34.25
28.57
26.60
21.02
17.33
12.66
^{13}C (126 MHz, C_6D_6)
f1 (ppm)

(*R*,*E*)-7-((3a*S*,4*S*,7*S*,7a*R*)-7-(((2*S*,3*S*)-3-((2*S*,3*S*)-3-hydroxybutan-2-yl)oxiran-2-yl)methyl)-2,2-dimethyltetrahydro-4*H*-[1,3]dioxolo[4,5-*c*]pyran-4-yl)-6-methylhepta-1,5-dien-4-ol (*epi*-3r)



Alcohol **2r** (37.0 mg, 0.1 mmol) was subjected to standard reaction conditions (75 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 3:17 EtOAc:hexanes) the title compound ***epi*-3r** was isolated as a yellow oil in 82% yield (33.8 mg, 0.08 mmol, >20:1 dr).

TLC (SiO_2): R_f = 0.5 (2:1 acetone:hexanes)

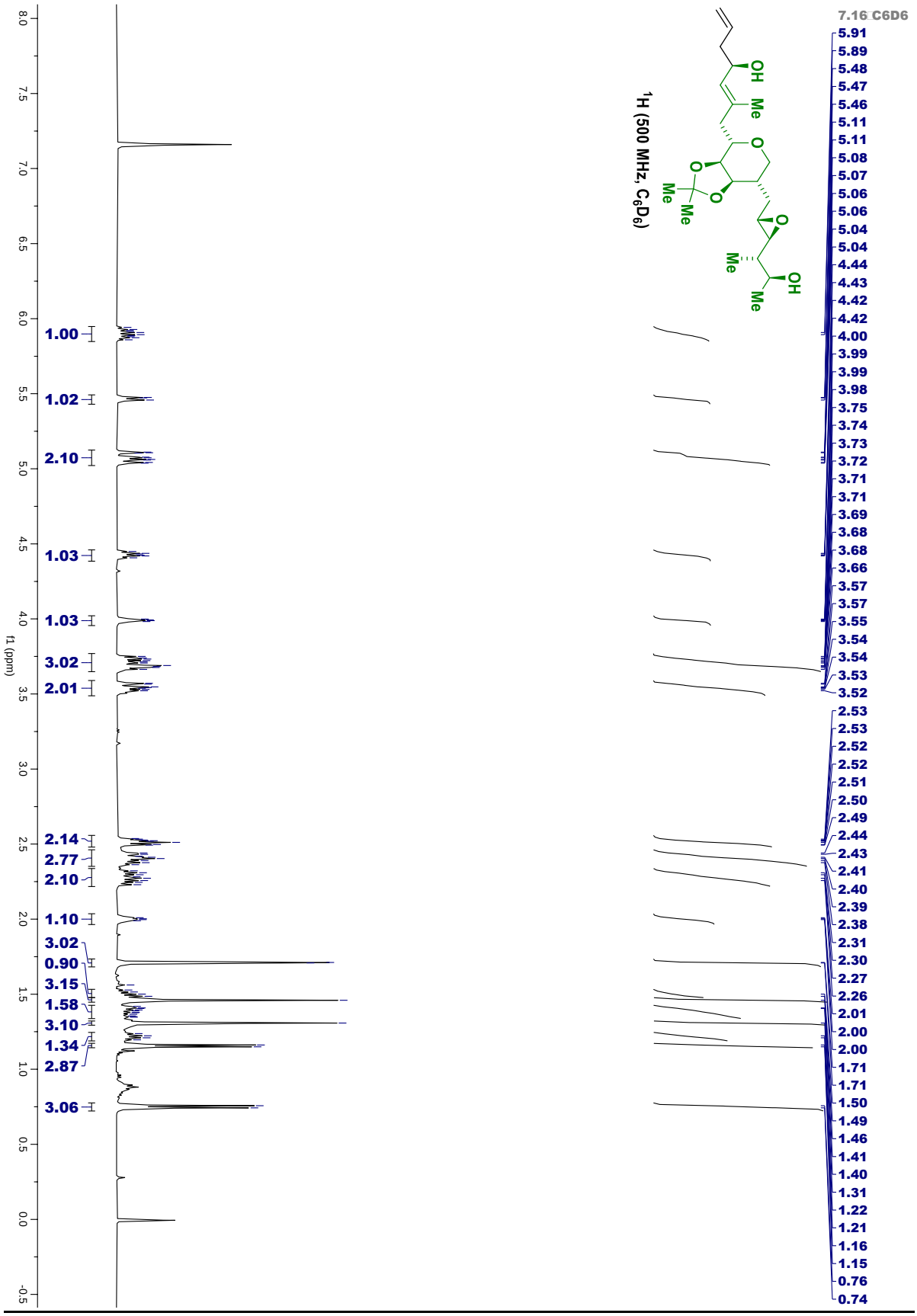
^{1}H NMR (500 MHz, C_6D_6): δ 5.90 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.55 – 5.38 (m, 1H), 5.19 – 4.91 (m, 2H), 4.43 (dt, *J* = 8.5, 6.4 Hz, 1H), 3.99 (dd, *J* = 5.2, 2.8 Hz, 1H), 3.84 – 3.63 (m, 3H), 3.63 – 3.45 (m, 2H), 2.64 – 2.46 (m, 2H), 2.40 (m, 3H), 2.28 (m, 2H), 2.00 (dd, *J* = 6.6, 3.7 Hz, 1H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.58 – 1.48 (m, 1H), 1.46 (s, 3H), 1.43 – 1.33 (m, 2H), 1.31 (s, 3H), 1.22 (q, *J* = 7.0 Hz, 1H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.75 (d, *J* = 7.0 Hz, 3H).

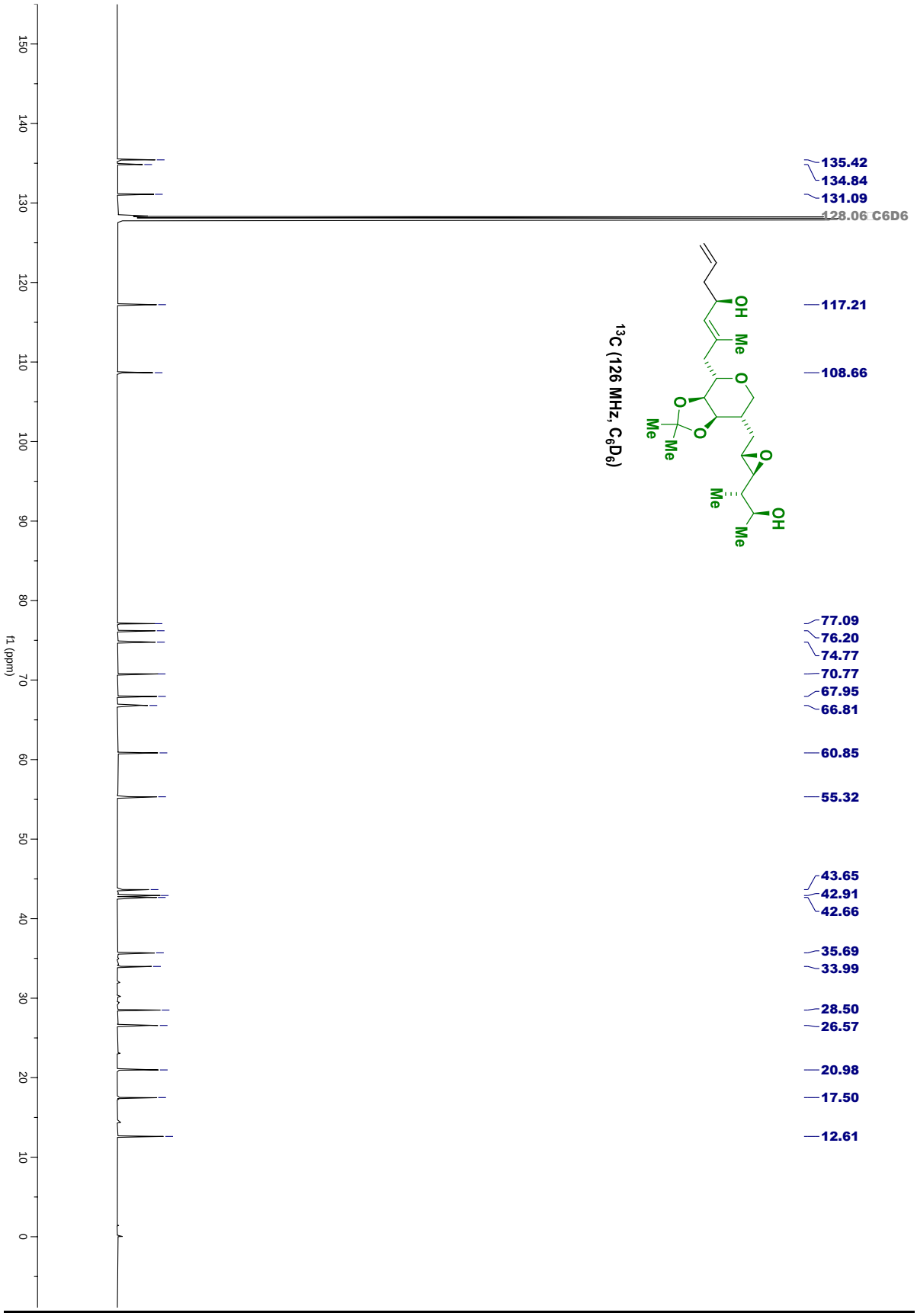
^{13}C NMR (126 MHz, C_6D_6): δ 135.4, 134.8, 131.1, 117.2, 108.7, 77.1, 76.2, 74.8, 70.8, 68.0, 66.8, 60.8, 55.3, 43.6, 42.9, 42.7, 35.7, 34.0, 28.5, 26.6, 21.0, 17.5, 12.6.

HRMS (Na+, *m/z*): for $C_{23}H_{38}O_6$: calcd. = 433.2561; found = 433.2555.

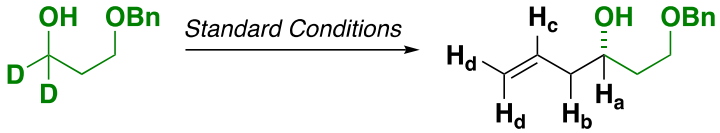
FTIR (neat): 3462, 3430, 1225, 1146, 1103, 1050, 834, 678 cm-1.

$[\alpha]_D^{24}$ = -25.0 (c = 0.1, $CHCl_3$).


^{1}H (500 MHz, C_6D_6)
7.16 C6D6
f1 (ppm)
1.00
1.02
2.10
1.03
1.03
3.02
2.01
2.14
2.77
2.10
1.10
3.02
0.90
3.15
1.58
3.10
1.34
2.87
3.06


135.42
134.84
131.09
128.06 C6D6
117.21
108.66
77.09
76.20
74.77
70.77
67.95
66.81
60.85
55.32
43.65
42.91
42.66
35.69
33.99
28.50
26.57
20.98
17.50
12.61
^{13}C (126 MHz, C_6D_6)
f1 (ppm)
OH
Me
O
Me
Me
O
O
Me
OH
Me

Deuterium Labeling Study



deuterio-**2a**
(100 mol%)

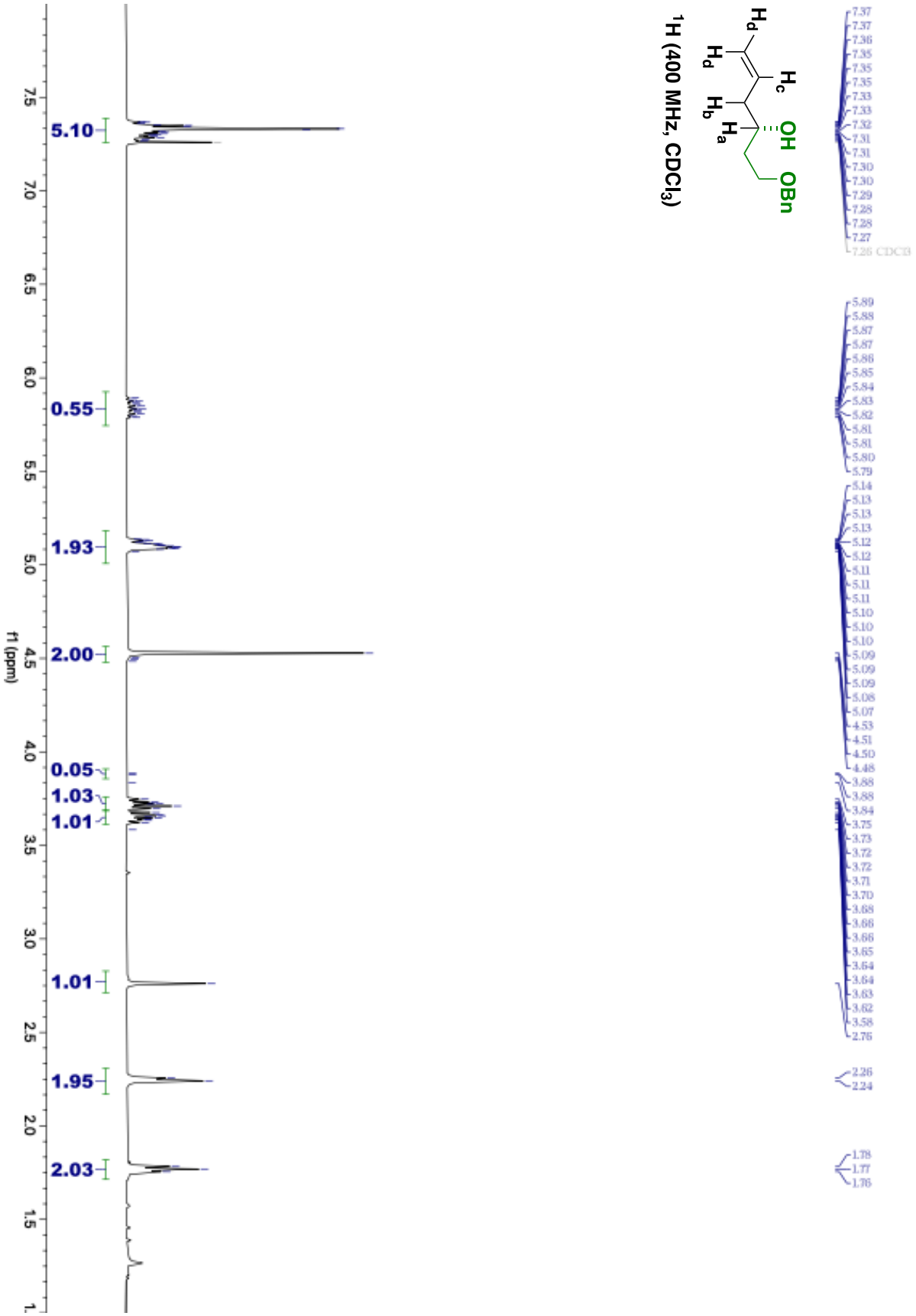
deuterio-**3a**, 53% Yield
H_a (95% ^2H), H_b (5% ^2H)
H_c (44% ^2H), H_d (5% ^2H)

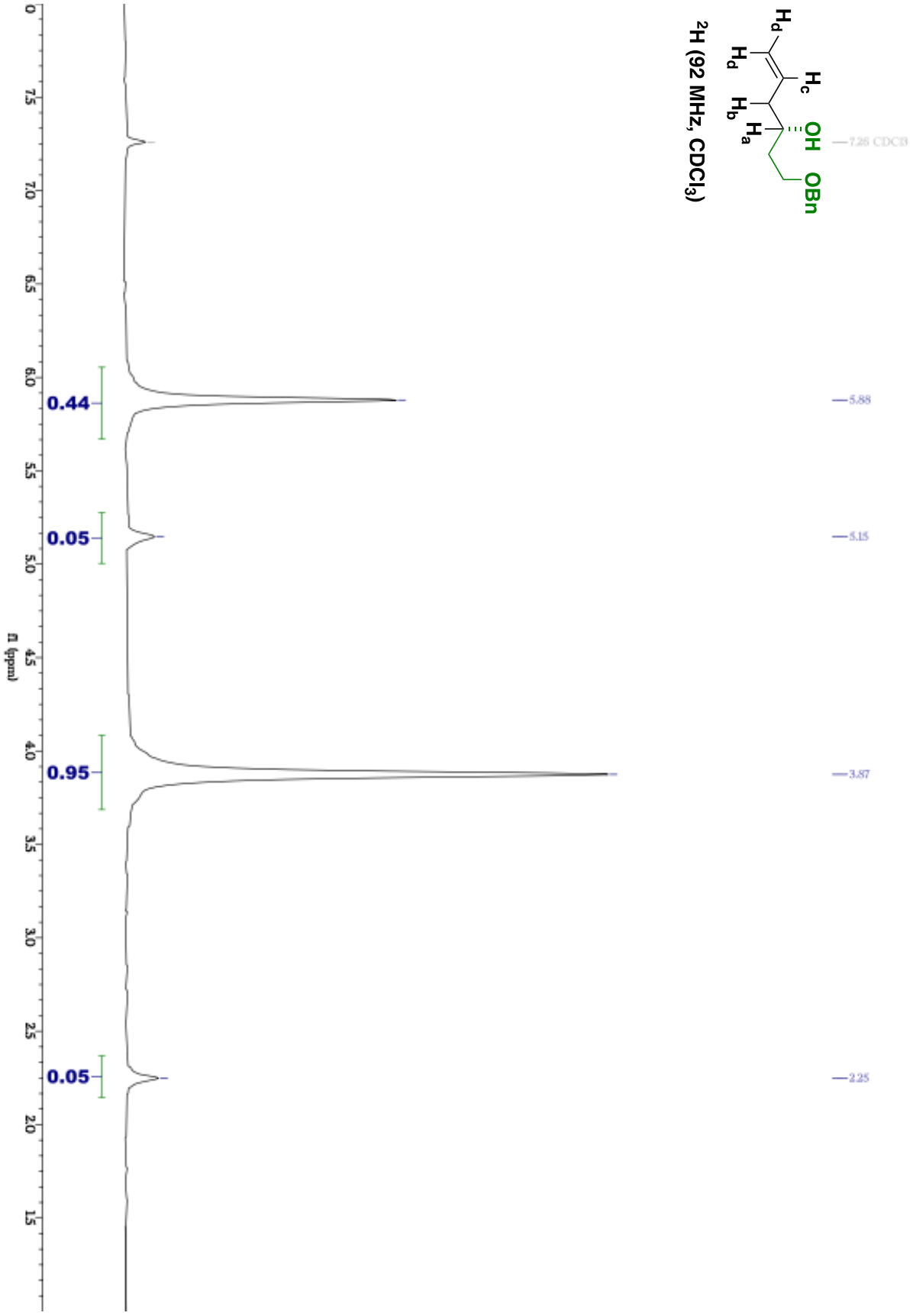
Alcohol *deuterio*-**2a** (33.6 mg, 0.2 mmol) was subjected to standard reaction conditions (110 °C, 48 h) with **SL-J502-1** as ligand. Upon flash column chromatography (SiO_2: 5:95 EtOAc:hexanes) the title compound *deuterio*-**3a** was isolated as a yellow oil in 53% yield (22.9 mg, 0.11 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.26 (m, 5H), 5.84 (ddt, *J* = 17.4, 10.4, 7.1 Hz, 0.55H), 5.16 – 5.05 (m, 1.93H), 4.53 (s, 2H), 3.92 – 3.81 (m, 0.05H), 3.72 (dt, *J* = 9.3, 5.4 Hz, 1H), 3.65 (ddd, *J* = 9.4, 7.1, 5.4 Hz, 1H), 2.76 (s, 1H), 2.25 (d, *J* = 5.9 Hz, 1.95H), 1.77 (t, *J* = 5.4 Hz, 2H).

^{2}H NMR (92 MHz, $CDCl_3$): δ 5.88 (s, 1H), 5.15 (s, 0H), 3.87 (s, 2H), 2.25 (s, 0H).

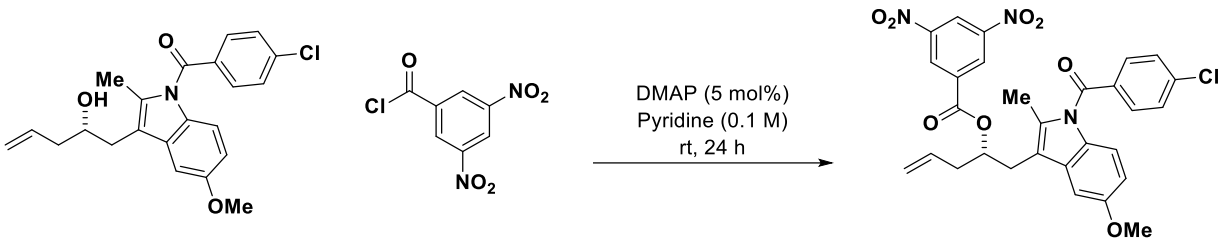
HRMS (Na+, *m/z*): for $C_{13}H_{17}DO_2$: calcd. = 230.1262; found = 230.1262.
(Na+, *m/z*): for $C_{13}H_{16}D_2O_2$: calcd. = 231.1296; found = 231.1321.
(Na+, *m/z*): for $C_{13}H_{15}D_3O_2$: calcd. = 232.1322; found = 232.1356.
(Na+, *m/z*): for $C_{13}H_{14}D_4O_2$: calcd. = 233.1348; found = 233.1379.
(Na+, *m/z*): for $C_{13}H_{13}D_5O_2$: calcd. = 234.1375; found = 234.1396.


^{1}H (400 MHz, CDCl$_3$)
H$_d$
H$_d$
H$_c$
H$_b$
H$_a$
OH
OBn
7.37
7.37
7.36
7.35
7.35
7.35
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26 CDCl3
5.89
5.88
5.87
5.87
5.86
5.85
5.84
5.83
5.82
5.81
5.81
5.80
5.79
5.14
5.13
5.13
5.13
5.12
5.12
5.11
5.11
5.11
5.10
5.10
5.10
5.09
5.09
5.09
5.08
5.07
4.53
4.51
4.50
4.48
3.88
3.88
3.84
3.75
3.73
3.72
3.72
3.71
3.70
3.68
3.66
3.66
3.65
3.64
3.64
3.63
3.62
3.58
2.76
2.26
2.24
1.78
1.77
1.76
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.
5.10
0.55
1.93
2.00
0.05
1.03
1.01
1.01
1.95
2.03


^{2}H (92 MHz, CDCl$_3$)
H_d
H_d
H_c
H_b
H_a
OH
OBn
7.26 CDCl3
5.88
5.15
3.87
2.25
0.44
0.05
0.95
0.05
f1 (ppm)
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

Synthesis of 3g-(3,5-dinitrobenzoate)

(*S*)-1-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)pent-4-en-2-yl 3,5-dinitrobenzoate



3g (100 mol%) **(300 mol %)** **3g-(3,5-dinitrobenzoate)**

To a 25 mL round-bottomed flask equipped with a magnetic stir bar under an argon atmosphere were added **3g** (20 mg, 0.05 mmol, 100 mol%), 3,5-dinitrobenzoyl chloride (42 mg, 0.15 mmol, 300 mol%), and DMAP (1 mg, 0.003 mmol, 5 mol%). Pyridine (5 mL, 0.01 M) was added via syringe. The reaction mixture was allowed to stir at room temperature for 24 hours. The reaction was quenched with aqueous NH_4Cl (saturated, 10 mL) in a 25 mL separatory funnel. The separated organic layer was washed with aqueous NaCl (saturated, 10 mL) before drying with Na_2SO_4. The solvent was concentrated *in vacuo* and the resulting oil was subjected to flash chromatography (SiO_2: 2:98 EtOAc/Hexanes) to furnish the title compound **3g-(3,5-dinitrobenzoate)** as a yellow crystalline solid in 34% yield (10 mg, 0.017 mmol).

TLC (SiO_2): R_f = 0.6 (1:4 EtOAc:Hexanes)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (t, *J* = 2.2 Hz, 1H), 9.03 (d, *J* = 2.1 Hz, 2H), 7.68 – 7.58 (m, 3H), 7.47 (dd, *J* = 8.3, 1.6 Hz, 3H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.60 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.86 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.24 – 5.12 (m, 3H), 3.82 (d, *J* = 14.5 Hz, 3H), 2.61 (t, *J* = 6.6 Hz, 2H), 2.42 (s, 3H).

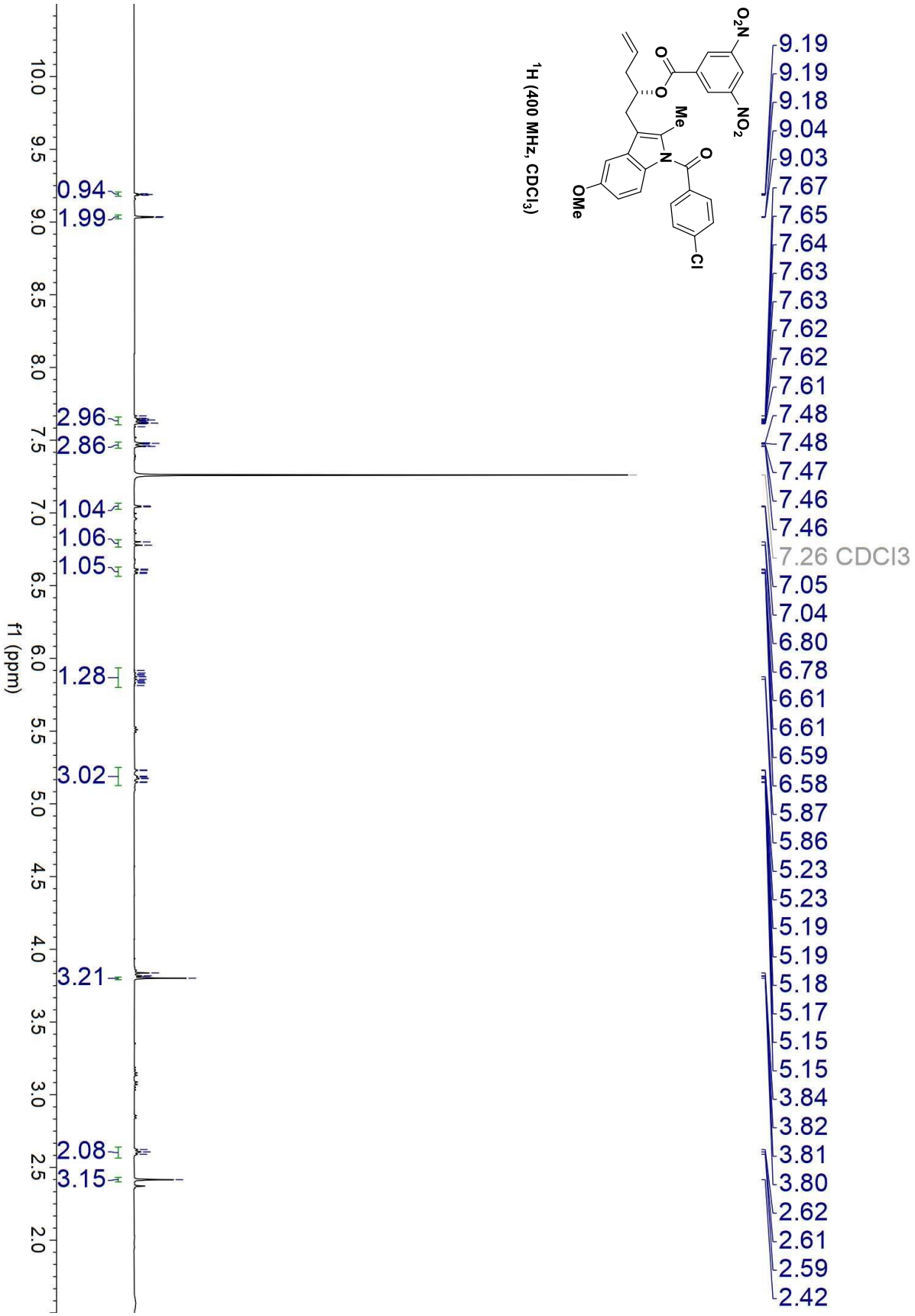
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4, 156.1, 148.8, 132.9, 131.3, 131.0, 129.4, 129.3, 122.4, 119.1, 115.1, 111.2, 101.9, 77.4, 76.1, 55.8, 53.6, 38.3, 32.1, 29.8, 29.5, 29.0, 22.8, 14.2, 13.6, 1.2.

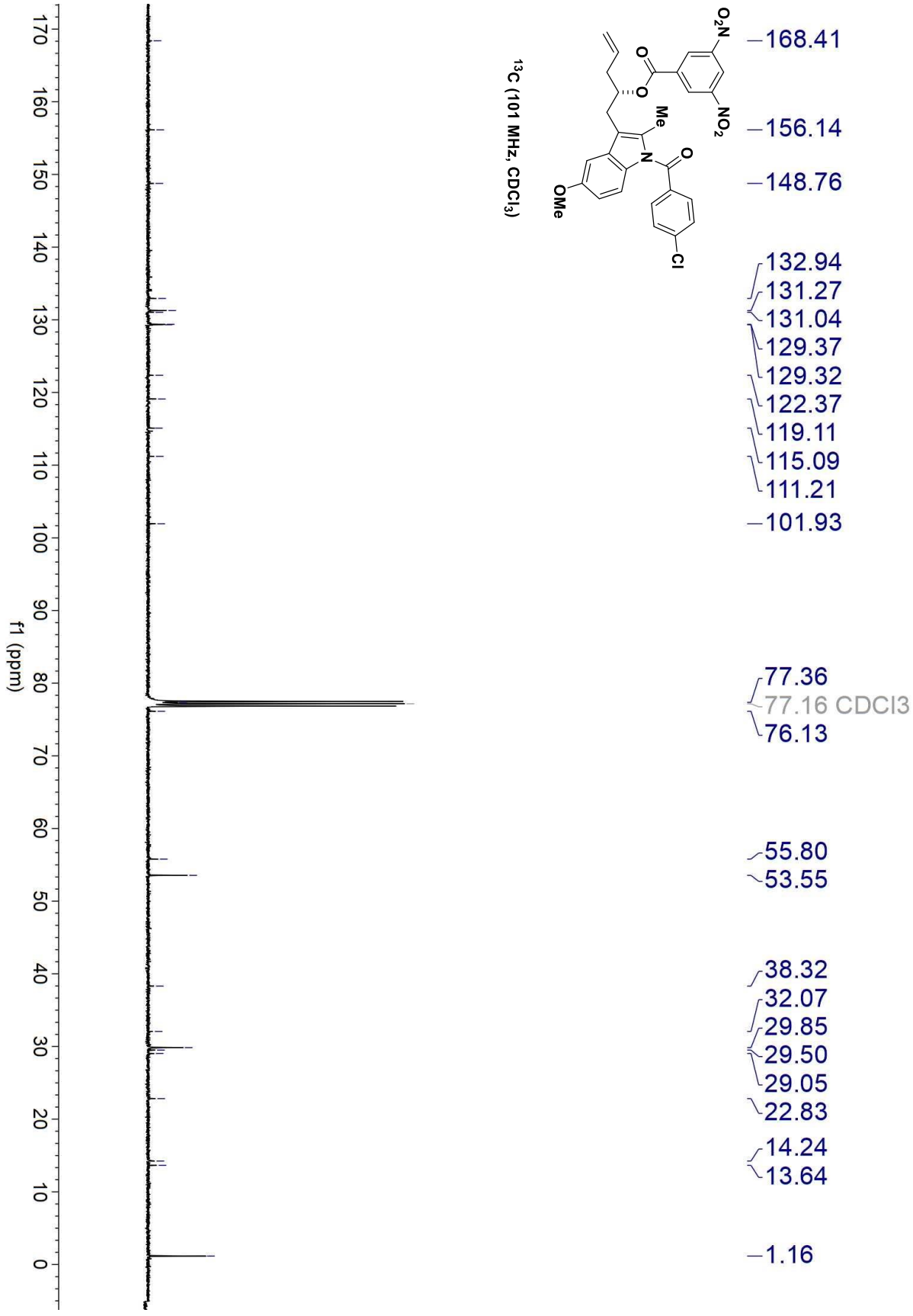
HRMS (Na+, *m/z*): for $C_{29}H_{24}ClN_3O_8$ calcd. = 600.1144; found = 600.1132.

FTIR (neat): 2970, 2931, 2839, 1718, 1540, 1476, 1342, 1094, 797 cm^{-1}.

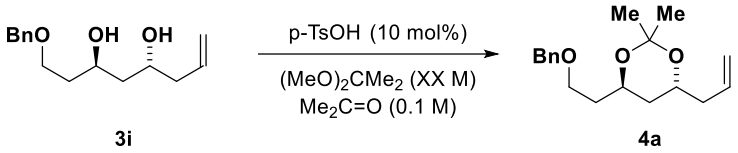
$[\alpha]_D^{24}$ = +80.0 (c = 0.25, $CHCl_3$)

MP: 127-131˚C


^{1}H (400 MHz, CDCl$_3$)
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
0.94
1.99
2.96
2.86
1.04
1.06
1.05
1.28
3.02
3.21
2.08
3.15
O2N
NO2
O
O
Me
N
O
OMe
Cl
9.19
9.19
9.18
9.04
9.03
7.67
7.65
7.64
7.63
7.63
7.62
7.62
7.61
7.48
7.48
7.47
7.46
7.46
7.26 CDCl3
7.05
7.04
6.80
6.78
6.61
6.61
6.59
6.58
5.87
5.86
5.23
5.23
5.19
5.19
5.18
5.17
5.15
5.15
3.84
3.82
3.81
3.80
2.62
2.61
2.59
2.42

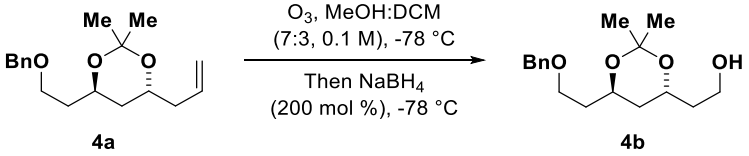

^{13}C (101 MHz, CDCl$_3$)
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O$_2$N
NO$_2$
O
O
Me
N
O
OMe
Cl
168.41
156.14
148.76
132.94
131.27
131.04
129.37
129.32
122.37
119.11
115.09
111.21
101.93
77.36
77.16 CDCl3
76.13
55.80
53.55
38.32
32.07
29.85
29.50
29.05
22.83
14.24
13.64
1.16

Synthesis of C7-C15 of Spirastrellolide A (4a, 4b, 5, 6)



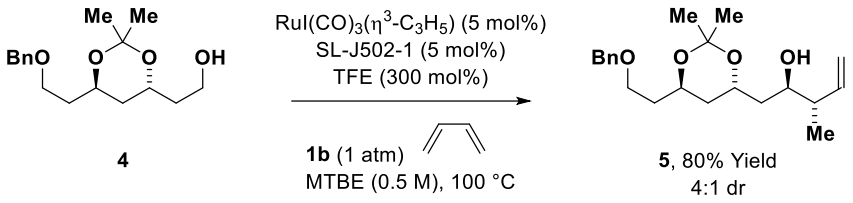
3i 4a

To a 50 mL flame-dried round-bottom flask equipped with a magnetic stir bar were added p-toluenesulfonic Acid (PTSA) (25 mg, 0.14 mmol, 10 mol%), and **3i** (345 mg, 1.4 mmol, 100 mol%) in anhydrous acetone (15 mL, 0.1 M) under an atmosphere of argon. The reaction vessel was stirred at ambient temperature for 16 hours, at which point the reaction was filtered and concentrated in vacuo. The residue was subjected to silica gel column chromatography (3:97 EtOAc/Hexanes) to afford the title compound **4a** as a yellow oil in 85% yield (345.6 mg, 1.19 mmol). All spectral data were found to be in accordance with the literature values.[10]



4a 4b

To a 25 mL round-bottomed flask equipped with a magnetic stir bar under an argon atmosphere were added methanol:dichloromethane (7:3 v/v , 10 mL, 0.1 M) and **4a** (289 mg, 1.0 mmol, 100 mol%). The reaction mixture was cooled to -78˚C and subjected to a stream of O_3/O_2 (~ 1 mmol/min of O_3) through a glass pipet for 20 minutes. Upon which a stream of N_2 was sparged through the reaction mixture via a glass pipet for 10 minutes. The reaction mixture was maintained at -78˚C, $NaBH_4$ (75.6 mg, 2.0 mmol, 200 mol%) was added and the reaction mixture was allowed to reach room temperature and stir for 16 hours. The solvent was concentrated in vacuo and the residue was subjected to flash chromatography (SiO_2: 5:95 EtOAc/Hexanes) to furnish the title compound **4b** as a yellow oil in 82% yield (241.4 mg, 0.82 mmol). All spectral data were found to be in accordance with the literature values.[10]



An oven-dried pressure tube equipped with a magnetic stir bar was charged with alcohol **4** (30.0 mg, 0.1 mmol, 100 mol%), $RuI(CO)_3(\eta_3\text{-}C_3H_5)$ (3.6 mg, 5 mol%), SL-J502-1 (5.4 mg, 5 mol%) under an argon atmosphere. The atmosphere was evacuated and backfilled with butadiene **1b** (1 atm), followed by the addition of trifluoroethanol (43 µL, 0.6 mmol, 300 mol%) and MTBE (0.4 mL, 0.5 M). The reaction mixture was cooled to 0 ˚C and allowed to stir for 5 minutes. The tube was sealed with a PTFE lined cap and the reaction vessel was placed in a 100 ˚C bath and stirred for 48 hours. After reaching ambient temperature, the solvent was removed in vacuo and the residue was subjected to flash chromatography (SiO_2: 2:98 EtOAc/Hexanes) to furnish the title compound **5** as an orange oil in 80% yield (28.0 mg, 0.080 mmol, 4:1 dr). Diastereomeric ratios were determined by ^{1}H NMR of crude reaction mixtures.

TLC (SiO_2): R_f = 0.45 (1:2 EtOAc:Hexanes)

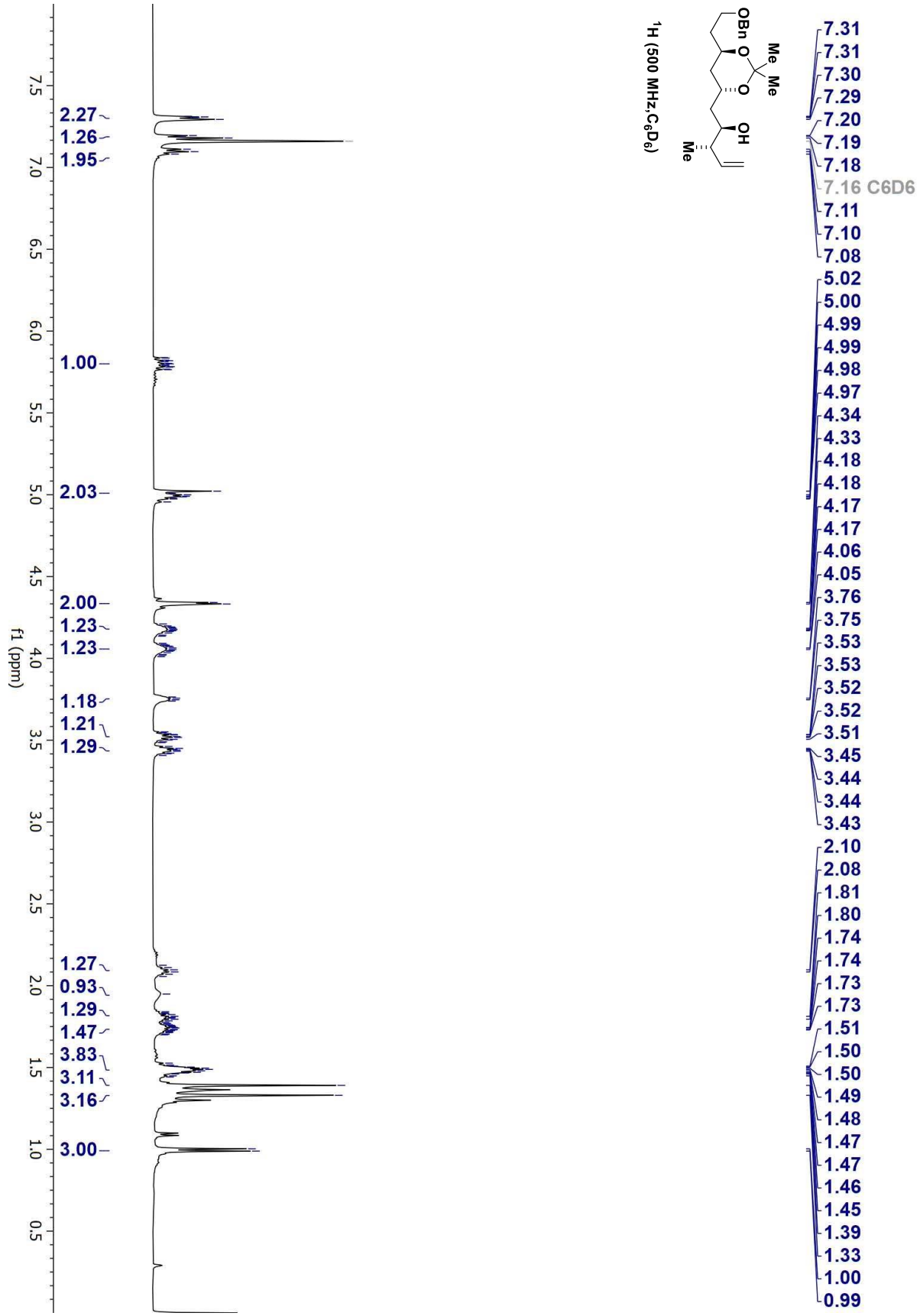
^{1}H NMR (500 MHz, C_6D_6): δ 7.32 – 7.28 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 2H), 5.84 – 5.76 (m, 1H), 5.03 – 4.95 (m, 2H), 4.34 (d, *J* = 4.4 Hz, 2H), 4.22 – 4.13 (m, 1H), 4.10 – 4.00 (m, 1H), 3.75 (dd, *J* = 8.6, 4.1 Hz, 1H), 3.56 – 3.48 (m, 1H), 3.44 (dt, *J* = 9.1, 5.8 Hz, 1H), 2.09 (h, *J* = 7.0 Hz, 1H), 1.95 (br s, 1H), 1.81 (tt, *J* = 10.7, 4.2 Hz, 1H), 1.74 (ttd, *J* = 11.2, 5.5, 2.5 Hz, 1H), 1.54 – 1.43 (m, 4H), 1.39 (s, 3H), 1.33 (s, 3H), 1.00 (d, *J* = 6.9 Hz, 3H).

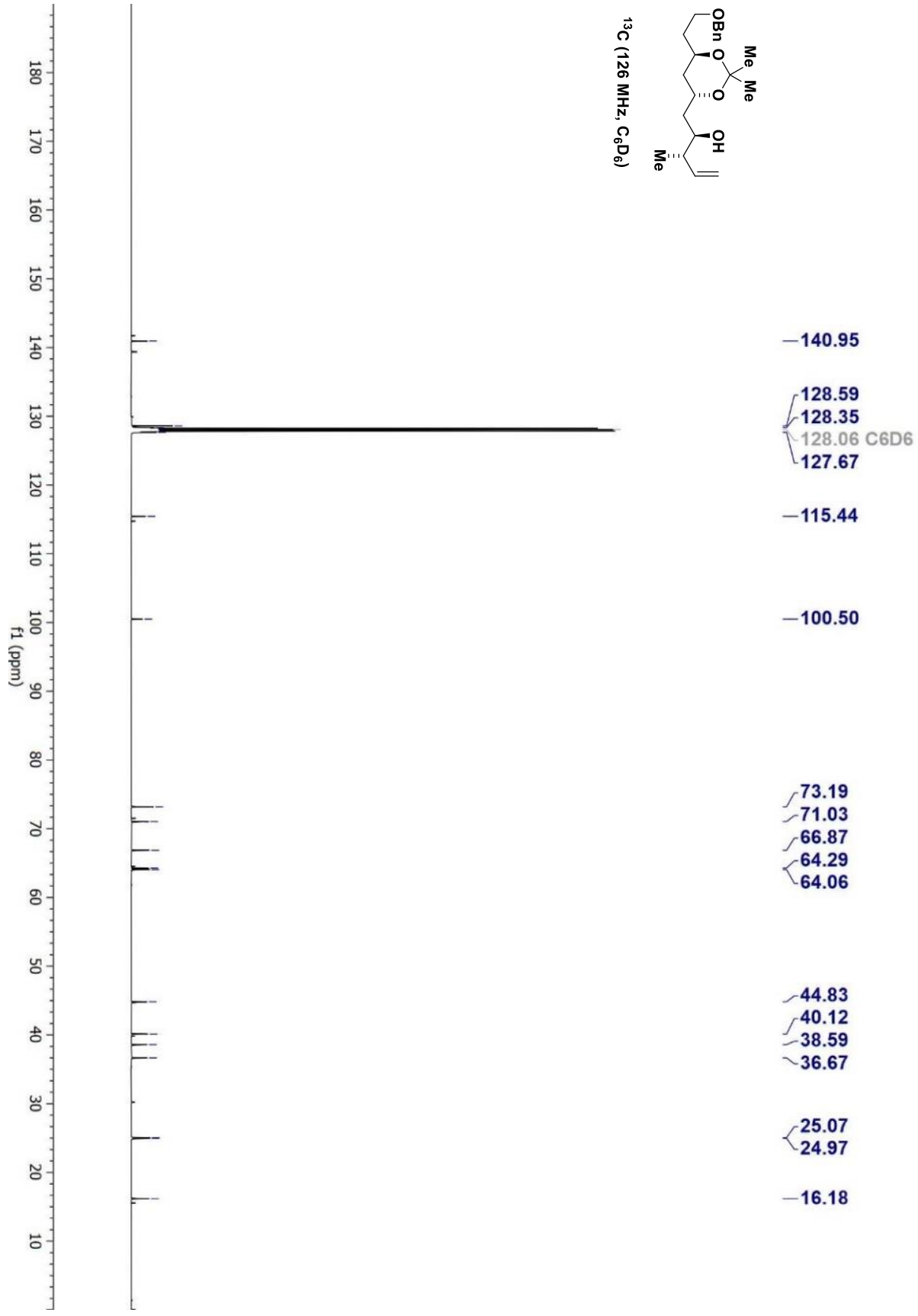
^{13}C NMR (126 MHz, C_6D_6): δ 141.0, 128.6, 128.4, 127.7, 115.4, 100.5, 73.2, 71.0, 66.9, 64.3, 64.1, 44.8, 40.1, 38.6, 36.7, 25.1, 25.0, 16.2.

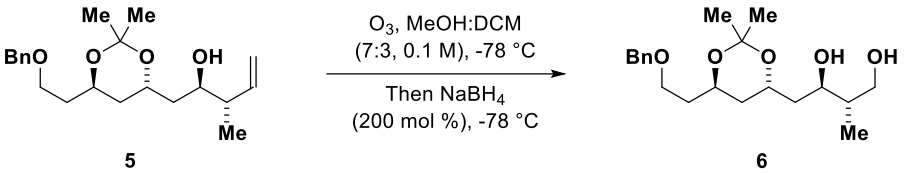
HRMS (Na+, *m/z*): for $C_{21}H_{32}O_4$ calcd. = 371.2193; found = 371.2199.

FTIR (neat): 2937, 1379, 1223, 1167, 1100, 908, 736, 697 cm^{-1}.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{24}}$ = -22.0 (c = 0.25, $CHCl_3$)


^{1}H (500 MHz,C_6D_6)
OBn
Me Me
OH
Me
7.31
7.31
7.30
7.29
7.20
7.19
7.18
7.16 C6D6
7.11
7.10
7.08
5.02
5.00
4.99
4.99
4.98
4.97
4.34
4.33
4.18
4.18
4.17
4.17
4.06
4.05
3.76
3.75
3.53
3.53
3.52
3.52
3.51
3.45
3.44
3.44
3.43
2.10
2.08
1.81
1.80
1.74
1.74
1.73
1.73
1.51
1.50
1.50
1.49
1.48
1.47
1.47
1.46
1.45
1.39
1.33
1.00
0.99
2.27
1.26
1.95
1.00
2.03
2.00
1.23
1.23
1.18
1.21
1.29
1.27
0.93
1.29
1.47
3.83
3.11
3.16
3.00
f1 (ppm)


^{13}C (126 MHz, C_6D_6)
OBn
O
O
Me
Me
OH
Me
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
140.95
128.59
128.35
128.06 C6D6
127.67
115.44
100.50
73.19
71.03
66.87
64.29
64.06
44.83
40.12
38.59
36.67
25.07
24.97
16.18



To a 12 mL scintillation vial equipped with a magnetic stir bar under an argon atmosphere were added methanol:dichloromethane (7:3 v/v , 1.2 mL, 0.1 M) and **5** (20 mg, 0.057 mmol, 100 mol%). The reaction mixture was cooled to -78˚C and subjected to a stream of O_3/O_2 (~ 1 mmol/min of O_3) through a glass pipet for 10 minutes. Upon which a stream of N_2 was sparged through the reaction mixture via a glass pipet for 10 minutes. The reaction mixture was maintained at -78˚C, $NaBH_4$ (4.3 mg, 0.114 mmol, 200 mol%) was added and the reaction mixture was allowed to reach room temperature and stir for 16 hours. The reaction mixture was diluted with EtOAc (10 mL) and NH_4Cl (10 mL) was added. The reaction mixture was transferred to a separatory funnel and the organic layer was washed with deionized water (3 x 10 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The resulting residue was subjected to flash chromatography (SiO_2: 5:95 EtOAc/Hexanes) to furnish the title compound **6** as a yellow oil in 72% yield (14.5 mg, 0.041 mmol).

TLC (SiO_2): R_f = 0.2 (1:1 EtOAc:Hexanes)

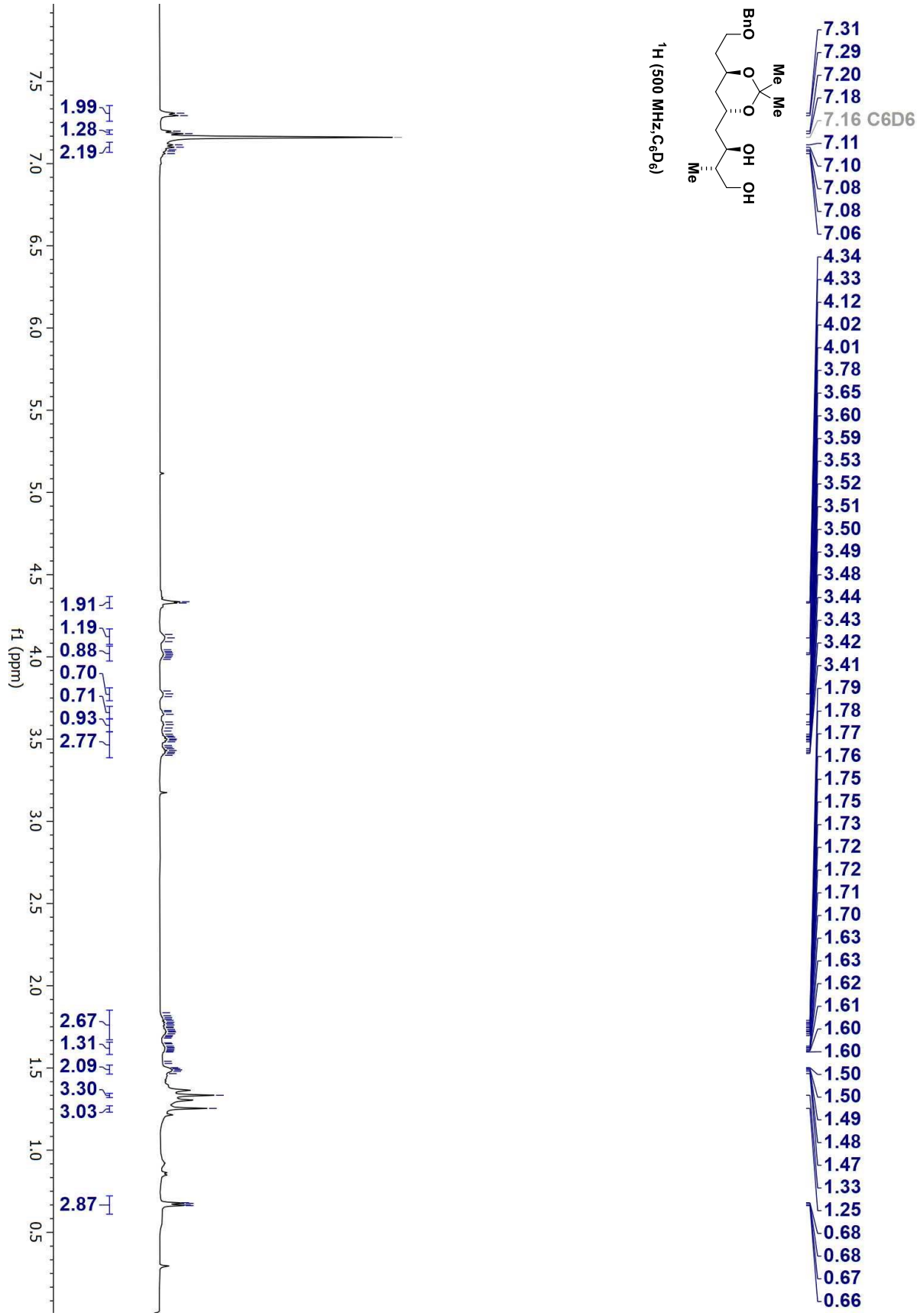
^{1}H NMR (500 MHz, C_6D_6): δ 7.3 (d, *J* = 7.4 Hz, 2H), 7.2 (d, *J* = 7.5 Hz, 1H), 7.1 – 7.1 (m, 2H), 4.3 (d, *J* = 4.0 Hz, 2H), 4.1 (d, *J* = 11.7 Hz, 1H), 4.0 (tt, *J* = 9.6, 5.6 Hz, 1H), 3.8 (d, *J* = 8.4 Hz, 1H), 3.7 (d, *J* = 11.5 Hz, 1H), 3.6 (q, *J* = 8.5 Hz, 1H), 3.5 (dtd, *J* = 41.2, 9.2, 5.6 Hz, 1H), 1.8 (dddd, *J* = 26.6, 12.9, 9.3, 5.5 Hz, 3H), 1.6 (dp, *J* = 10.7, 3.0 Hz, 1H), 1.5 (dd, *J* = 7.5, 3.7 Hz, 2H), 1.3 (s, 3H), 1.3 (s, 3H), 0.7 (dd, *J* = 6.9, 1.7 Hz, 3H).

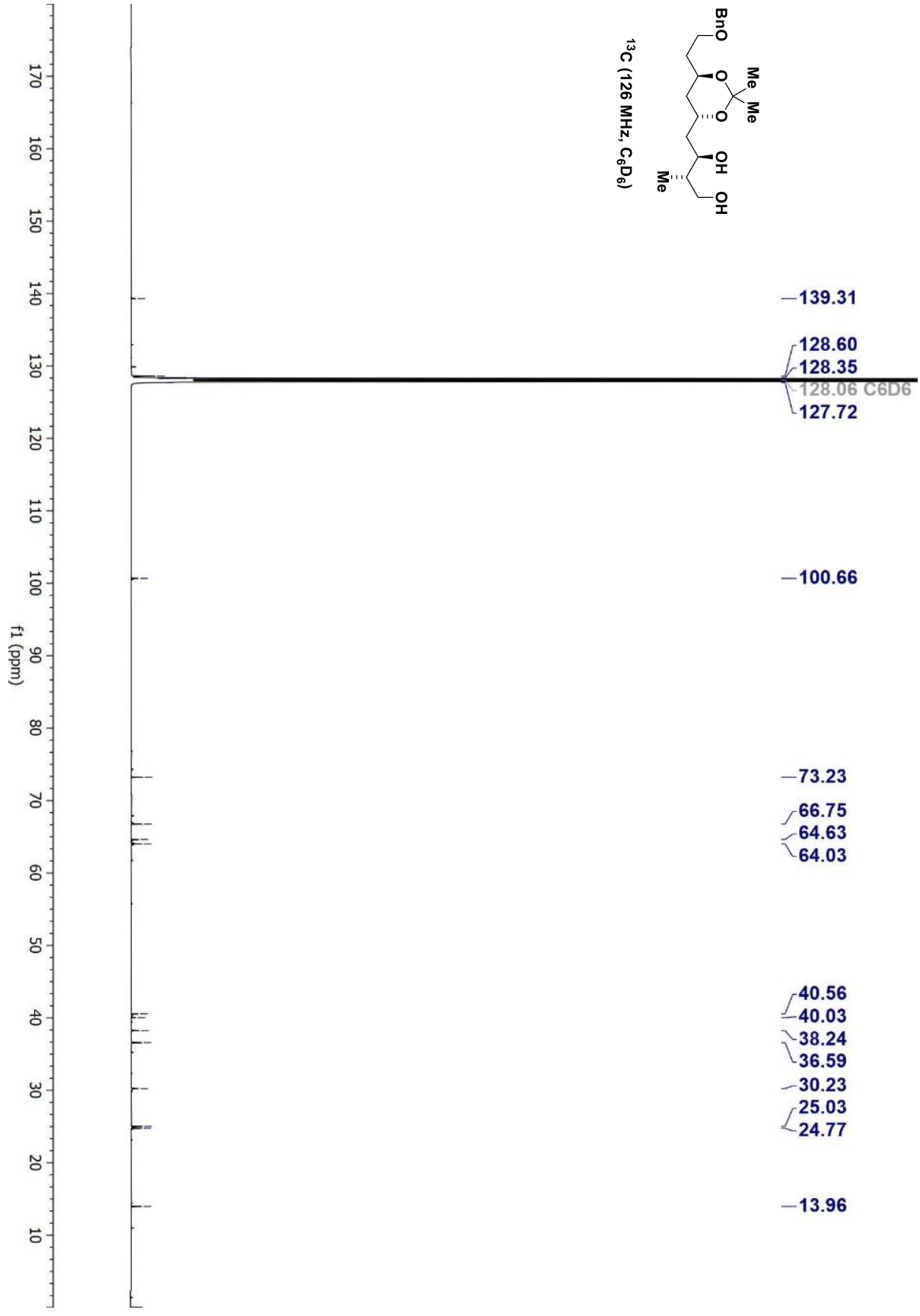
^{13}C NMR (126 MHz, C_6D_6): δ 139.3, 128.6, 128.4, 127.7, 100.7, 73.2 (d, *J* = 2.2 Hz), 66.7, 64.6, 64.0, 40.6, 40.0, 38.2, 36.6, 30.2, 25.0, 24.8, 14.0.

HRMS (Na+, *m/z*): for $C_{20}H_{32}O_5$ calcd. = 375.2142; found = 375.2143.

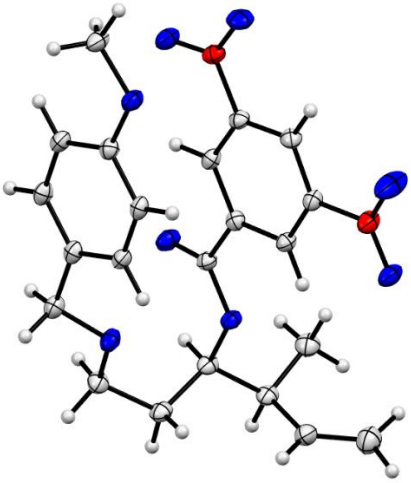
FTIR (neat): 2957, 1660, 1592, 1573, 1511, 1257, 1172, 733 cm^{-1}.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{24}}$ = +4.5 (c = 0.23, $CHCl_3$)


1H (500 MHz,C6D6)
BnO
Me Me
OH OH
Me
7.31
7.29
7.20
7.18
7.16 C6D6
7.11
7.10
7.08
7.08
7.06
4.34
4.33
4.12
4.02
4.01
3.78
3.65
3.60
3.59
3.53
3.52
3.51
3.50
3.49
3.48
3.44
3.43
3.42
3.41
1.79
1.78
1.77
1.76
1.75
1.75
1.73
1.72
1.72
1.71
1.70
1.63
1.63
1.62
1.61
1.60
1.60
1.50
1.50
1.49
1.48
1.47
1.33
1.25
0.68
0.68
0.67
0.66
1.99
1.28
2.19
1.91
1.19
0.88
0.70
0.71
0.93
2.77
2.67
1.31
2.09
3.30
3.03
2.87
f1 (ppm)


^{13}C (126 MHz, C_6D_6)
BnO
Me Me
OH OH
Me
139.31
128.60
128.35
128.06 C6D6
127.72
100.66
73.23
66.75
64.63
64.03
40.56
40.03
38.24
36.59
30.23
25.03
24.77
13.96
f1 (ppm)

Single Crystal Diffraction Data for 3g-(3,5-dinitrobenzoate):



Crystals grew as colorless prisms by slow evaporation from hexanes and ether. The data crystal was cut from a longer crystal and had approximate dimensions; 0.23 x 0.16 x 0.11 mm. The data were collected on a Rigaku Oxford Diffraction HyPix6000E Synergy-S diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 3224 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 7 seconds per frame for frames collected with a detector offset of +/- 48.3° and 28 seconds per frame with frames collected with a detector offset of 111.0°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.41.123a.[1] The structure was solved by direct methods using SHELXT[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3.[3] Structure analysis was aided by use of the programs PLATON[4] and OLEX2.[5] The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl groups). The absolute structure was determined using the method of Flack[6] and confirmed using the Hooft y-parameter method, which resulted in a Hooft y-parameter of 0.03(3).[7]

X-ray Experimental for $C_{29}H_{24}N_3O_8Cl$: Crystals grew as clusters of yellowish needles by slow evaporation from hexanes and ether. The data crystal was cut from a longer crystal and had approximate dimensions; 0.22 x 0.083 x 0.054 mm. The data were collected on a Rigaku Oxford Diffraction HyPix6000E Synergy-S diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 4162 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 13 seconds per frame for frames collected with a detector offset of +/- 47.8° and 42 seconds per frame with frames collected with a detector offset of 104.5°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.41.123a. The structure was solved by direct methods using SHELXT and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3. Structure analysis was aided by use of the programs PLATON and OLEX2. The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom. The crystal was twinned by a 180º rotation about the 100 direct cell axis. The twin law was determined to be (1,0,0; 0,-1,0;-0.251,0,1). The absolute structure was determined using the method of Flack and confirmed using the Hooft y-parameter method, which resulted in a Hooft y-parameter of 0.009(2).

The function, Σw(|Fo|2 - |Fc|2)2, was minimized, where w = 1/[(σ(Fo))2 + (0.853P)2 + (3.486*P)] and P = (|Fo|2 + 2|Fc|2)/3. Rw(F2) refined to 0.173, with R(F) equal to 0.0640 and a goodness of fit, S, = 1.08. Definitions used for calculating R(F), Rw(F2) and the goodness of fit, S, are given below. The data were checked for secondary extinction effects 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). All figures were generated using SHELXTL/PC. Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table S1. Crystal data and structure refinement for 1.

Empirical formula	C29 H24 Cl N3 O8	
Formula weight	577.96	
Temperature	99.9(7) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 6.91979(14) Å	a= 90°.
	b = 20.7100(4) Å	b= 92.6374(17)°.
	c = 18.9205(3) Å	g = 90°.
Volume	2708.60(9) Å3	
Z	4	
Density (calculated)	1.417 Mg/m3	
Absorption coefficient	1.745 mm-1	
F(000)	1200	
Crystal size	0.22 x 0.083 x 0.054 mm3	
Theta range for data collection	2.338 to 76.590°.	
Index ranges	-8<=h<=8, -25<=k<=25, -23<=l<=23	
Reflections collected	17131	
Independent reflections	17131	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.70505	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	17131 / 1 / 744	
Goodness-of-fit on F2	1.080	
Final R indices [I>2sigma(I)]	R1 = 0.0640, wR2 = 0.1719	
R indices (all data)	R1 = 0.0654, wR2 = 0.1730	
Absolute structure parameter	0.06(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.408 and -0.323 e.Å-3	

Figure S1. View of molecule 1 in **3g-dinotrobenzoate** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

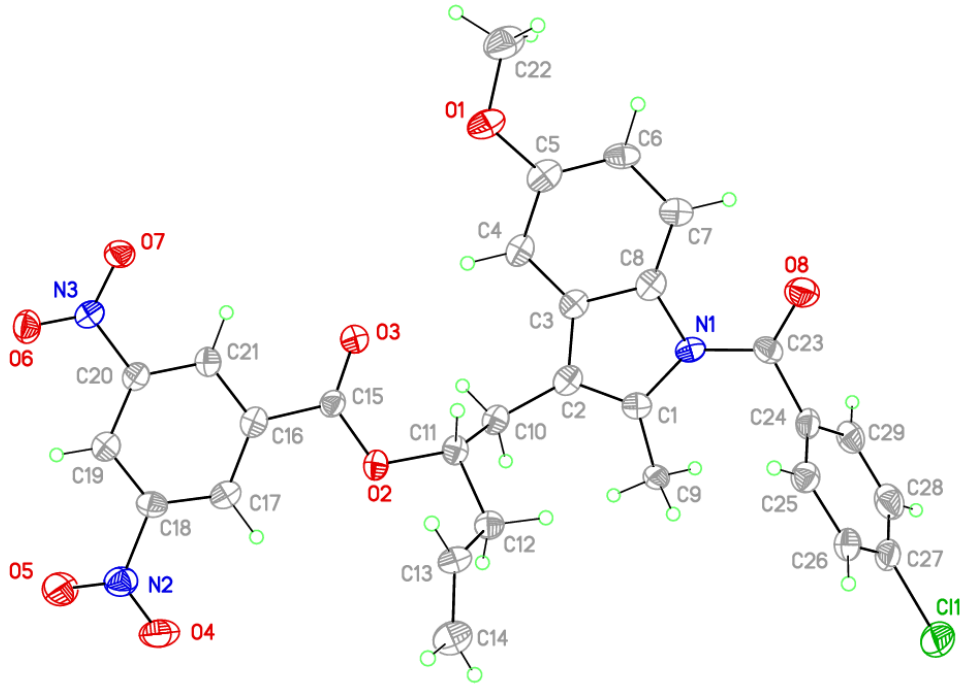
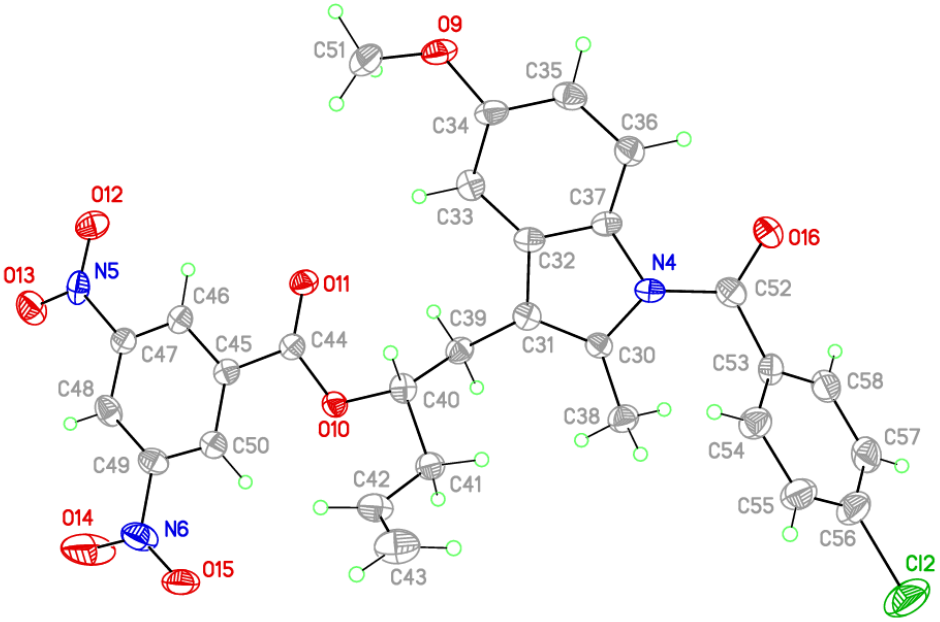


Figure S2. View of molecule 2 in **3g-dinotrobenzoate** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



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