Supporting Information for: "**A C—H oxidation approach for streamlining synthesis of chiral polyoxygenated motifs "**

Dustin J. Covell and M. Christina White

General Information: The following commercially obtained reagents were used as received; $Pd(OAc)_2$, (Alfa Aesar), (1R,2R)-(-)-[1,2-Cyclohexanediamino-N,N'-bis(3,5-di-t-butylsalicylidene)]Chromium(III)Cl, (1S,2S)-(+)-[1,2-Cyclohexanediamino-N,N'-bis(3,5-di-t-butylsalicylidene)]Chromium(III)Cl (Aldrich), 5-hexene-1-ol (Aldrich), methyl 10-undeceneoate (Aldrich), benzyl bromide (Aldrich), phenyl boronic acid (Aldrich), Novozyme 435, polymer supported (Aldrich), tetrabutylammonium iodide (Aldrich), sodium hydride (95%) (Aldrich), iron ferricyanide (Strem chemicals), potassium carbonate (Fisher), sodium bicarbonate (Fisher), methanesulfonamide (Aldrich), $(DHQD)_2PHAL$ (Aldrich), hexenoic acid methyl ester (TCI), 2-(2-bromoethyl)-1,3-dioxane (TCI), benzoquinone (Aldrich), acetic acid (Fisher). Lewis acid **2** was prepared from commercially available (1R,2R)-(-)-[1,2-Cyclohexanediamino-N,N'-bis(3,5-di-t-butylsalicylidene)]Chromium(III) Chloride as previously described.[i] [i]$Pd(OAc)_2$ was stored in a glove box under an argon atmosphere and weighed out in the air prior to use. Commercially available "White Catalyst" (1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate)(**1**) from Aldrich was found to be equivalent to that prepared freshly by the published procedure.[ii] Solvents 1,4-dioxane, diethyl ether (Et_2O), tetrahydrofuran (THF), and methylene chloride (CH_2Cl_2) were purified prior to use by passage through a bed of activated alumina (Glass Contour, Laguna Beach, California). Ethyl acetate (EtOAc) (Sure/Seal) was obtained from Sigma-Aldrich and used as received. All allylic oxidation reactions were run under air. Achiral gas chromatographic (GC) analyses were performed on Agilent Technologies 6890N Series instrument equipped with FID detectors using a HP-5 (5%-Phenyl)-methylpolysiloxane column (30m, 0.32mm, 0.25μm). Chiral gas chromatographic (GC) analyses were performed on an Agilent Technologies 5890A Series instrument equipped with an FID detector using a J&W Scientific β-cyclodextrin column (30m, 0.25mm, 0.25μm). HPLC analysis was performed on an Agilent Technologies 1100 HPLC system with a model 1100 Quaternary Pump, Diode Array Detector, Thermostat, and Autosampler. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized with UV, potassium permanganate, and ceric ammonium molybdate staining. Flash column chromatography was performed as described by Still et al.[iii] using EM reagent silica gel 60 (230-400 mesh). ^1H NMR spectra were recorded on a Varian Unity 400 (400 MHz) or a Varian Unity 500 (500 MHz), or a Varian Unity Inova 500NB spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C- NMR spectra were recorded on a Varian Unity-500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.0 ppm). IR spectra were recorded as thin films on NaCl plates on a Perkin-Elmer Spectrum BX and are reported in frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained at the University of Illinois Mass Spectrometry Laboratory.

General Procedure for Asymmetric Branched Allylic Acetoxylation: A vial (8 mL borosilicate) was charged with the following: 1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate(**1**) (10 mol%, 0.10 mmol, 50 mg); (1R,2R)-(-)-[1,2-Cyclohexanediamino-N,N'-bis(3,5-di-t-butylsalicylidene)]Chromium(III)F(*R,R*-**2**) (10 mol%, 0.10 mmol, 61.6 mg), 1,4-

benzoquinone (2 equiv., 2.0 mmol, 216 mg), an activated 4Å MS bead (~30 mg), and a Teflon© stir bar. A separate vial (2 mL, borosilicate) was charged with the following: substrate (1.0 mmol), AcOH (1.1 equiv., 63 μL), and EtOAc (200 μL). The liquids were transferred to the solids via pipette and the vial rinsed with EtOAc (3 x 100 μL). After carefully stirring for 48 hrs at room temperature, the reaction mixture was transferred to a separatory funnel with ~3 mL EtOAc and diluted with hexanes (200 mL). The organic layer was rinsed with sat. aq. $NaHSO_3$ (1 x 50 mL) and 5% aq. K_2CO_3 (2 x 50 mL). *Caution should be taken when combining aqueous layers as carbon dioxide is evolved.* The combined aqueous layers were back extracted with hexanes (100 mL). The combined organic layers were dried ($MgSO_4$), filtered, and reduced *in vacuo.* The resulting oil was re-dissolved in hexanes (50 mL) and extracted again with 5% aq. K_2CO_3 (3 x 10 mL) to remove residual hydroquinone. The organic layer was again dried ($MgSO_4$), filtered and reduced *in vacuo* to afford a clean mixture of allylic oxidation products and any unreacted starting material from which the B:L, yield, and conversions were determined (^{1}H NMR). Unless otherwise noted, this material was taken forward without further purification, though each substrate was isolated at least once for characterization purposes. Reported yields and selectivities are an average of at least two runs. Enantiomeric excess was determined by chiral GC (β-cyclodextrin column), as compared to racemic standards generated through our standard branched oxidation chemistry. Slight variations in B:L ratios and ee's were noted based on batch of Cr catalyst.

General Procedure for Cleavage of Allylic Acetates: To a 25 mL flask containing crude allylic acetate (1 mmol, assumed) was added MeOH (5 mL, 0.2 M) and potassium carbonate (0.276 g, 2 mmol). The reaction was vigorously stirred and monitored via thin layer chromatography (TLC). Upon completion, the reaction was transferred to a sepratory funnel with methylene chloride (50 mL). Water (15 mL) was added, and the aqueous layer was extracted with methylene chloride (3 x 50 mL). The combined organics were washed with brine (1 x 10 mL), then dried ($MgSO_4$), filtered, and reduced *in vacuo*. Products were then purified by standard SiO_2 chromatography. While the branched and linear allylic alcohols were commonly separable, it was found that carrying them forward as a mixture had no detrimental effect as the subsequent resolution acylated the linear alcohol rapidly making its separation from branched alcohol trivial. Individual product yields and characterization are reported below.

General Procedure for Resolution with Novozyme 435: To a flame dried round bottom flask containing allylic alcohol to be resolved (1 equiv.) was added vinyl acetate (0.6M) and Novozyme 435 immobilized on polystyrene beads (33.3 mg/1 mmol). The reaction was stirred vigorously at room temperature for 36 hrs. Upon completion, the solid supported enzyme was removed via filtration. The solid support was rinsed thoroughly with diethyl ether and then the filtrate reduced *in vacuo* and purified via standard SiO_2 chromatography. Enantioselectivities were determined by chiral gas chromatographic analysis on the acetylated derivative of each isolated alcohol. It was found that the recovered solid supported enzyme could be used up to 5 times with little diminishment in activity. Individual yields and selectivities are reported below.

General Procedure for Resolution with S. Carlsberg: The active enzyme for resolution was prepared as previously described by Boren and co-workers.[iv] To a flame dried round bottom flask containing allylic alcohol to be resolved (1 equiv.) was added isoproenyl valerate[v] (1.5 equiv), active S. Carlsberg (36 mg/1 mmol), sodium carbonate (1 equiv.) and THF (0.5M). The

reaction was stirred vigorously at room temperature for 60 hrs. Upon completion, the enzyme was removed via filtration. The enzyme was rinsed thoroughly with diethyl ether and then the filtrate reduced *in vacuo* and purified via standard SiO_2 chromatography. Enantioselectivities were determined by chiral gas chromatographic analysis on the acetylated derivative of each isolated alcohol. Individual yields and selectivities are reported below.

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[i] S. E. Schaus, J. Brånalt, E. N. Jacobsen. *J. Org. Chem.* **1998,** *63,* 403.

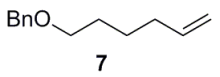
[ii] J. H. Delcamp, M. C. White, *J. Am. Chem. Soc.* **2006,** *128*, 15076.

[iii] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

[iv] L. Boren, B. Martin-Matute, Y. Xu, A. Cordova, and J.-E. Backvall; *Chemistry: A European Journal*, **2006**, *12*, 225-232.

[v] Y. F. Wang, J. J. Lalonde, M. Momongan, D. E. Bergbreiter, C. H. Wong *J. Am. Chem. Soc.* **1998,** *110*, 7200.

l-O-Benzyl-5-hexen-1-ol (7)



7

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DATA PROCESSING
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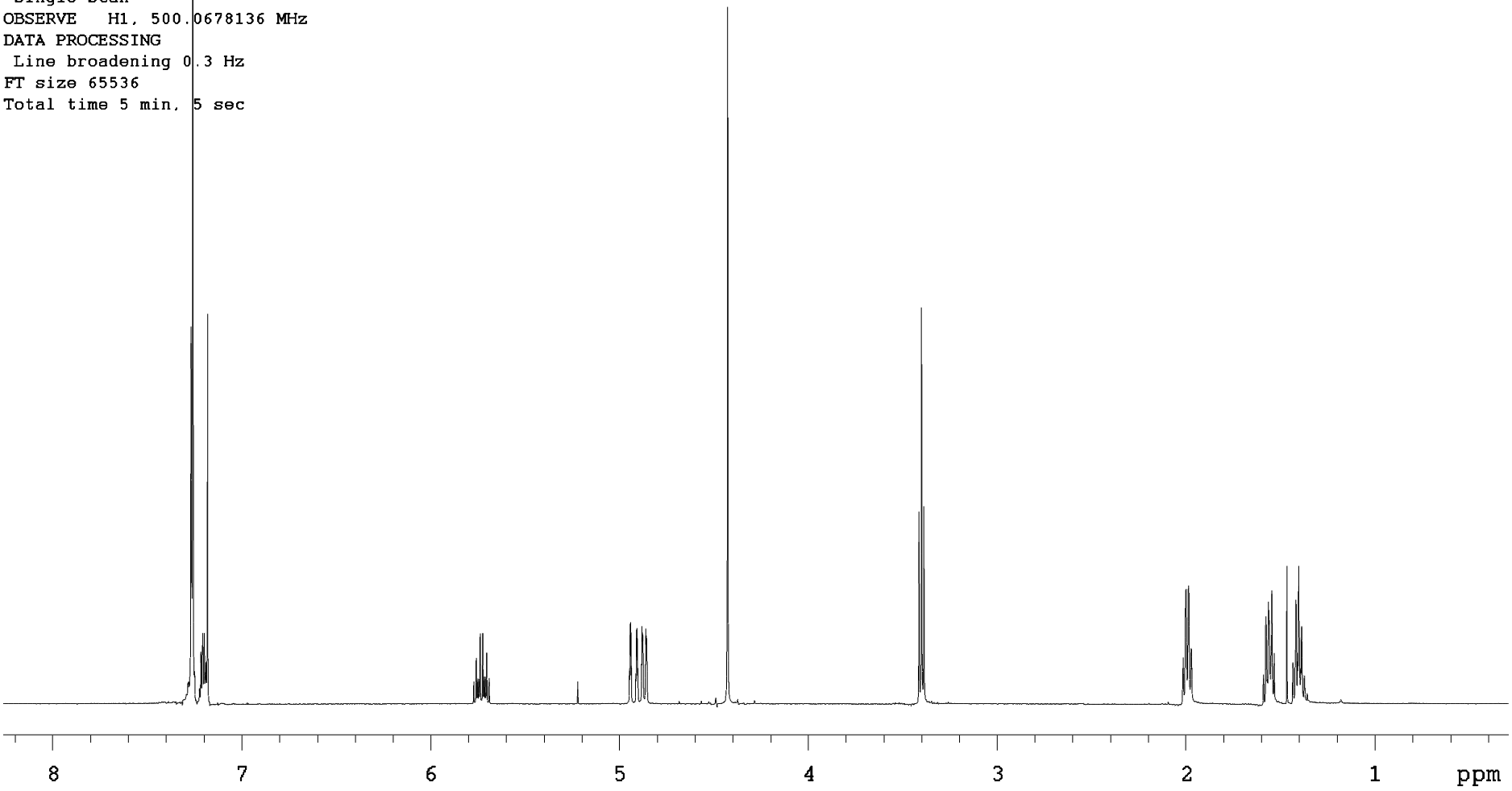
Total time 5 min, 5 sec



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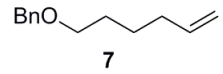
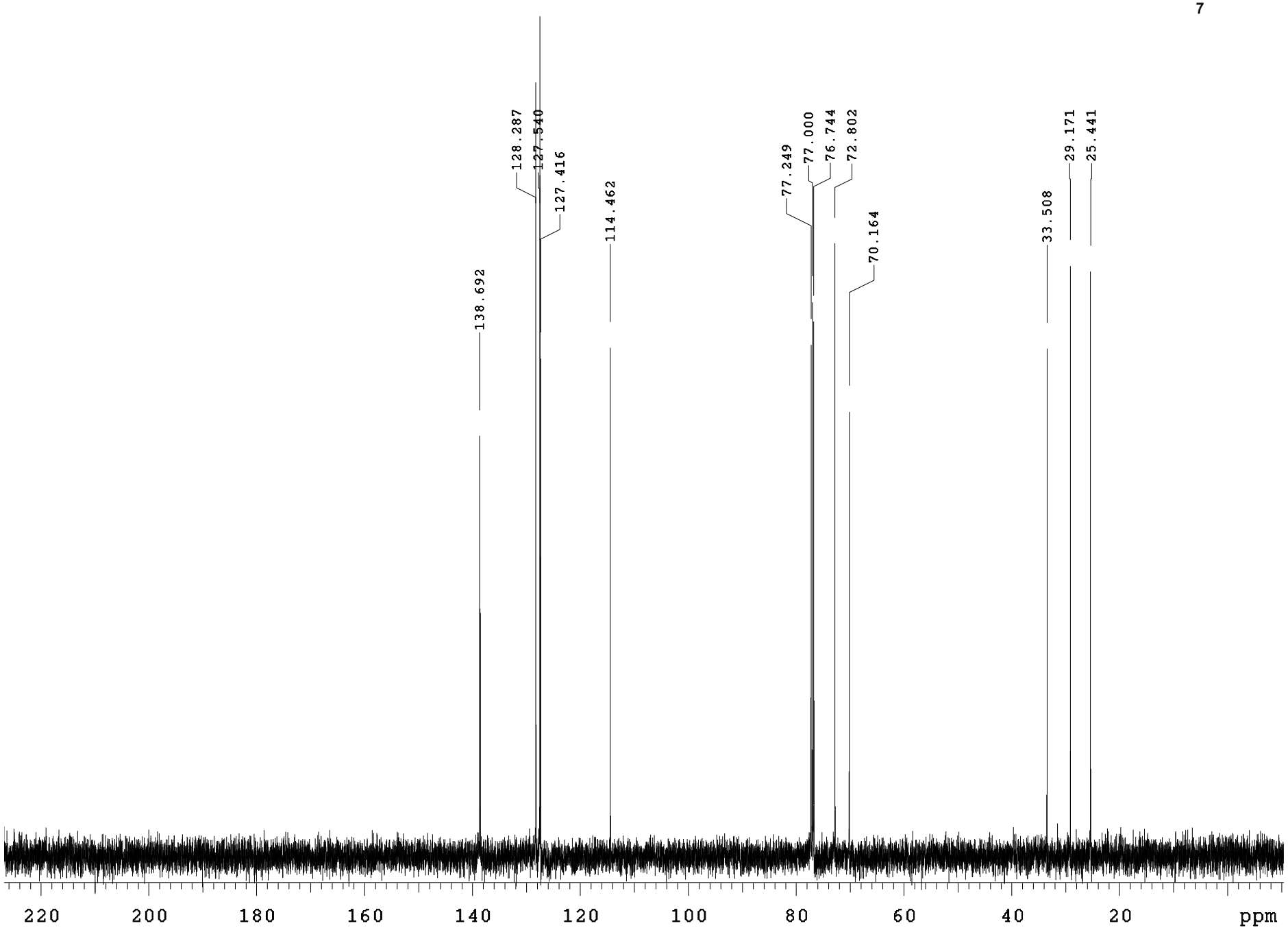
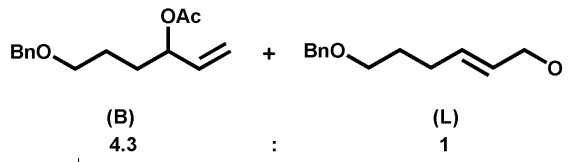


7



(*4R*)-1-O-Benzyl-4-acetoxy-5-hexen-1,4-diol (3-OAc)



(B) : (L)
4.3 : 1

Pulse Sequence: s2pul

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Ambient temperature
File: DJC-4-301-1
INOVA-500 "sunds1"

Relax. delay 20.000 sec
Pulse 45.0 degrees
Acq. time 4.096 sec
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4 repetitions
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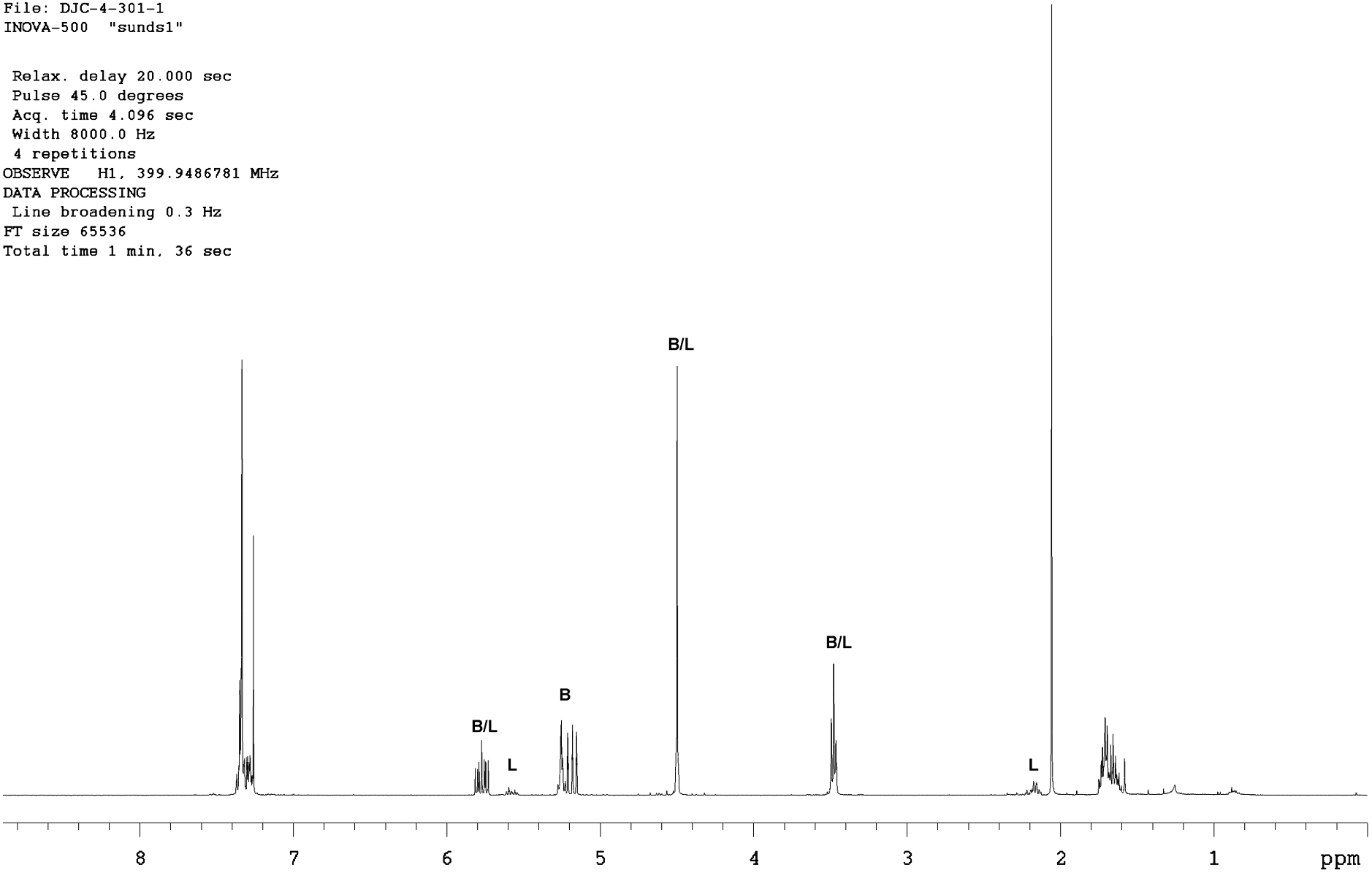
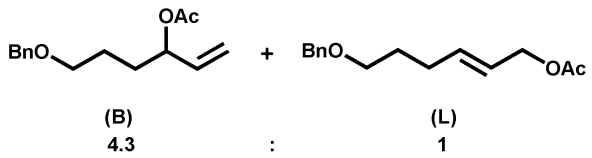
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 36 sec



4R)-1-O-Benzyl-4-acetoxy-5-hexen-1,4-diol (3-OAc)



(B) : (L)
4.3 : 1

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 Ambient temperature
User:  1-14-87
File: DJC-4-301-13C
INOVA-500  "sunds1"

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 Pulse 53.3 degrees
 Acq. time 1.024 sec
 Width 32000.0 Hz
 28 repetitions
OBSERVE  C13, 125.5817522 MHz
DECOUPLE  H1, 499.4315638 MHz
 Power 44 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 40 min, 32 sec
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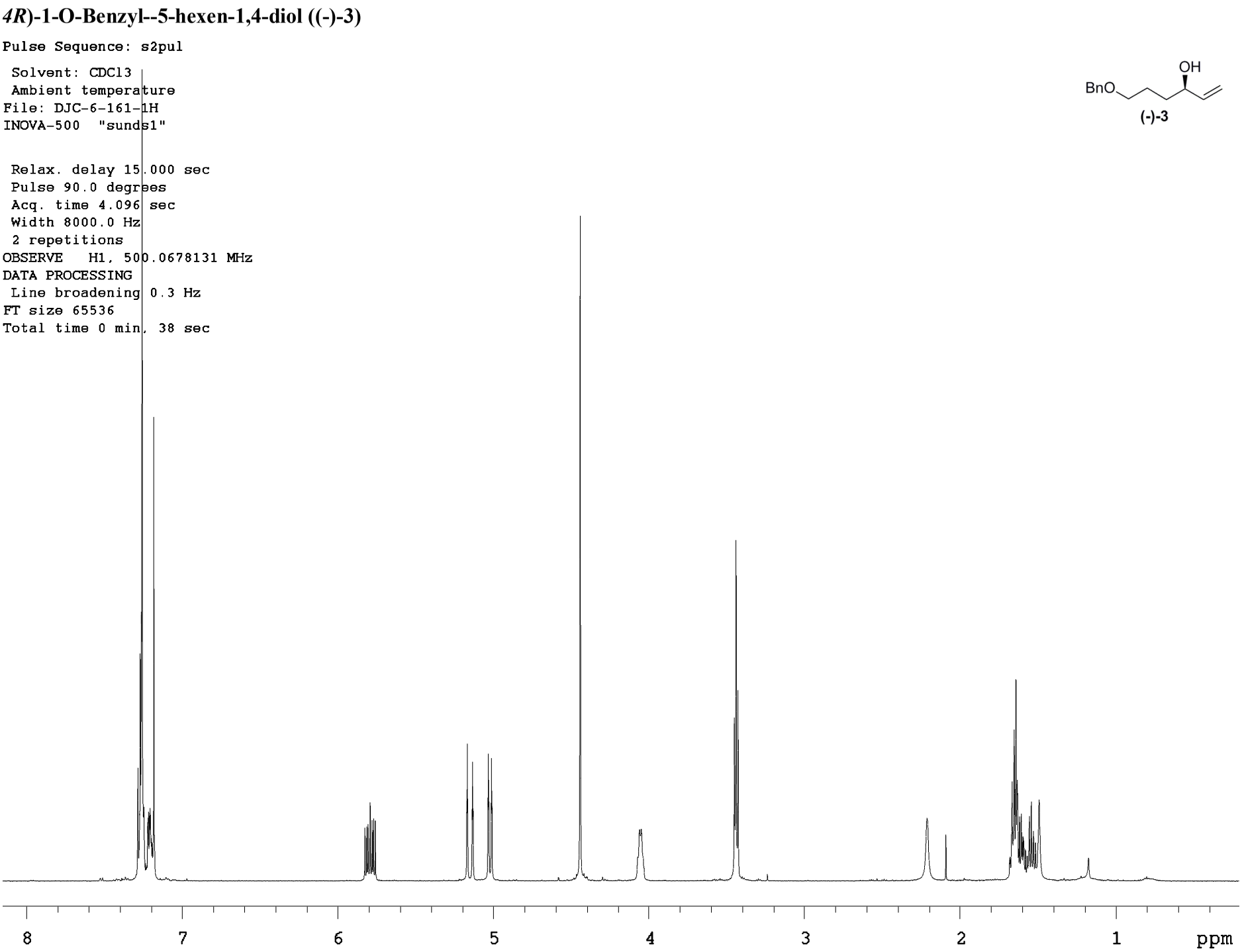
4*R*)-1-O-Benzyl--5-hexen-1,4-diol ((-)-3)



4*R*)-1-O-Benzyl--5-hexen-1,4-diol ((-)-3)

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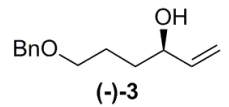
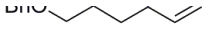


(-)-3



3

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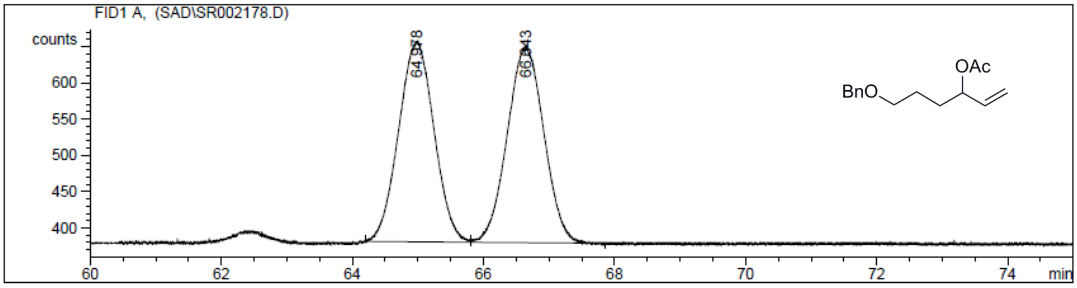
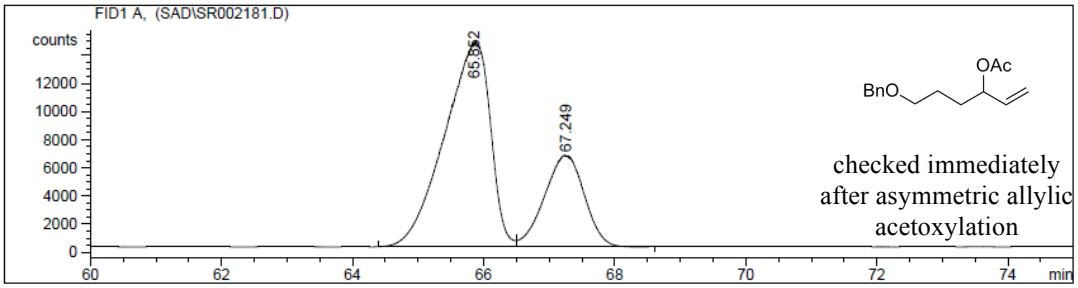
Test



Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	64.978	BV	0.6006	1.03758e4	274.75067	49.70793
2	66.643	VP	0.6327	1.04977e4	268.16049	50.29207

Test

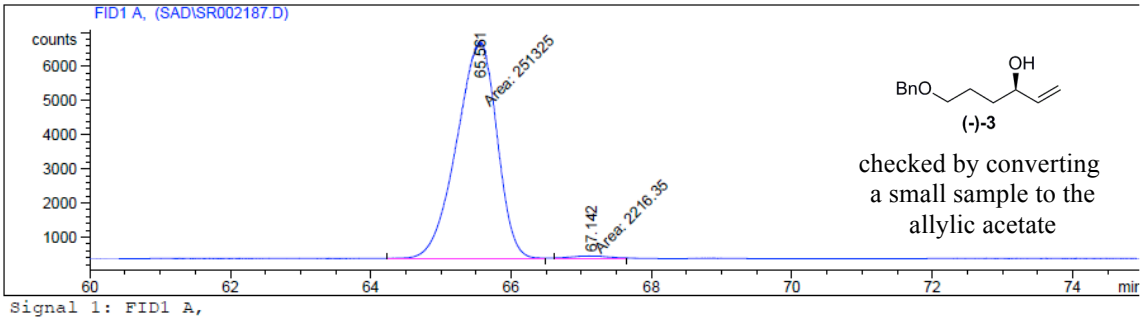


checked immediately after asymmetric allylic acetoxylation

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	65.852	BV	0.7832	7.09046e5	1.43813e4	72.04422
2	67.249	VB	0.6715	2.75136e5	6478.43213	27.95578

Test

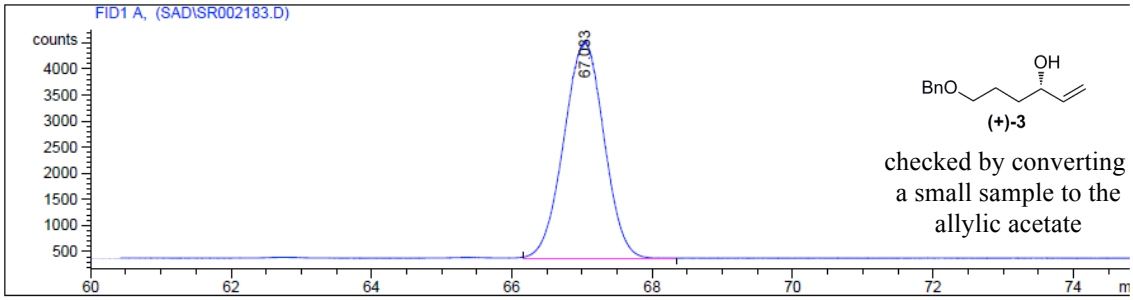


checked by converting a small sample to the allylic acetate

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	65.561	MM	0.6618	2.51325e5	6329.74902	99.12584
2	67.142	MM	0.5854	2216.35474	63.09792	0.87416

Test

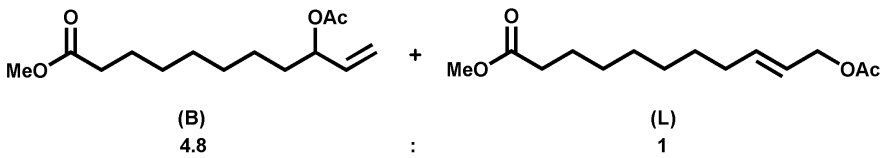


checked by converting a small sample to the allylic acetate

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %

ethyl (*9R*)-9-acetoxyundec-10-eneoate (9-OAc)



(B) : (L)
4.8 : 1

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e: DJC-4-145-2
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dth 8000.0 Hz
repetitions
ERVE   H1, 499.4298992 MHz
A PROCESSING
ne broadening 0.3 Hz
size 65536
al time 1 min, 16 sec
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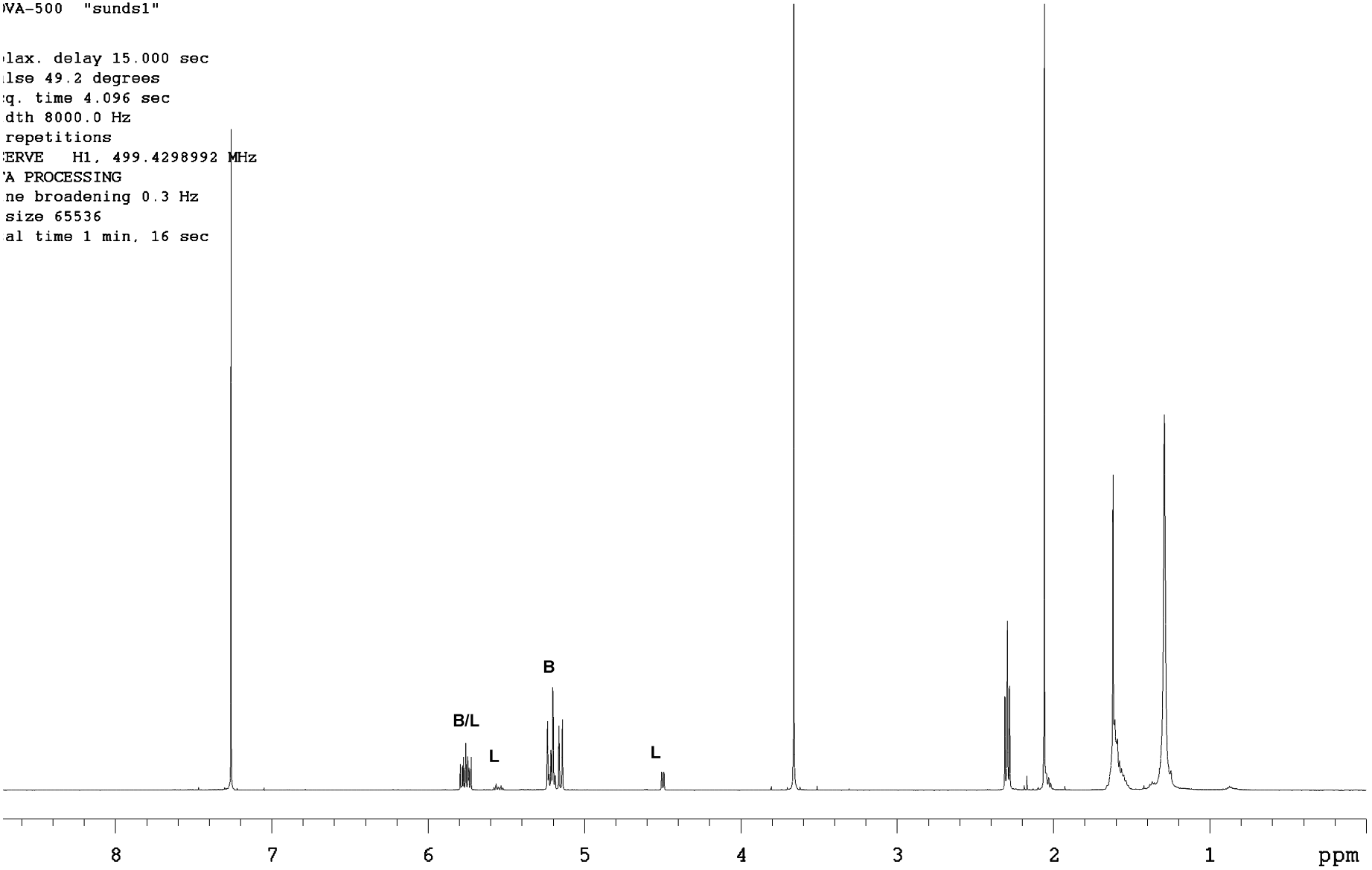
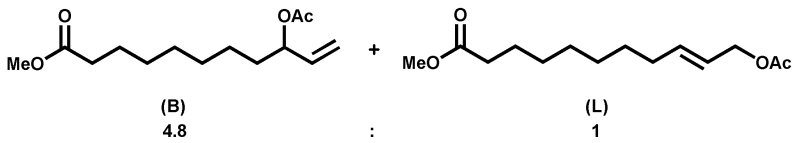


ethyl (*9R*)-9-acetoxyundec-10-eneoate (9-OAc)



(B) : (L)
4.8 : 1

lse Sequence: s2pul

olvent: CDCl3
mbient temperature
er: 1-14-87
le: DJC-4-145-13C
OVA-500 "sunds1"

elax. delay 5.000 sec
ilse 53.3 degrees
cq. time 1.024 sec
idth 32000.0 Hz
5 repetitions
SERVE C13, 125.5817522 MHz
COUPLE H1, 499.4315638 MHz
ower 44 dB
ontinuously on
ALTZ-16 modulated
TA PROCESSING
ine broadening 1.0 Hz
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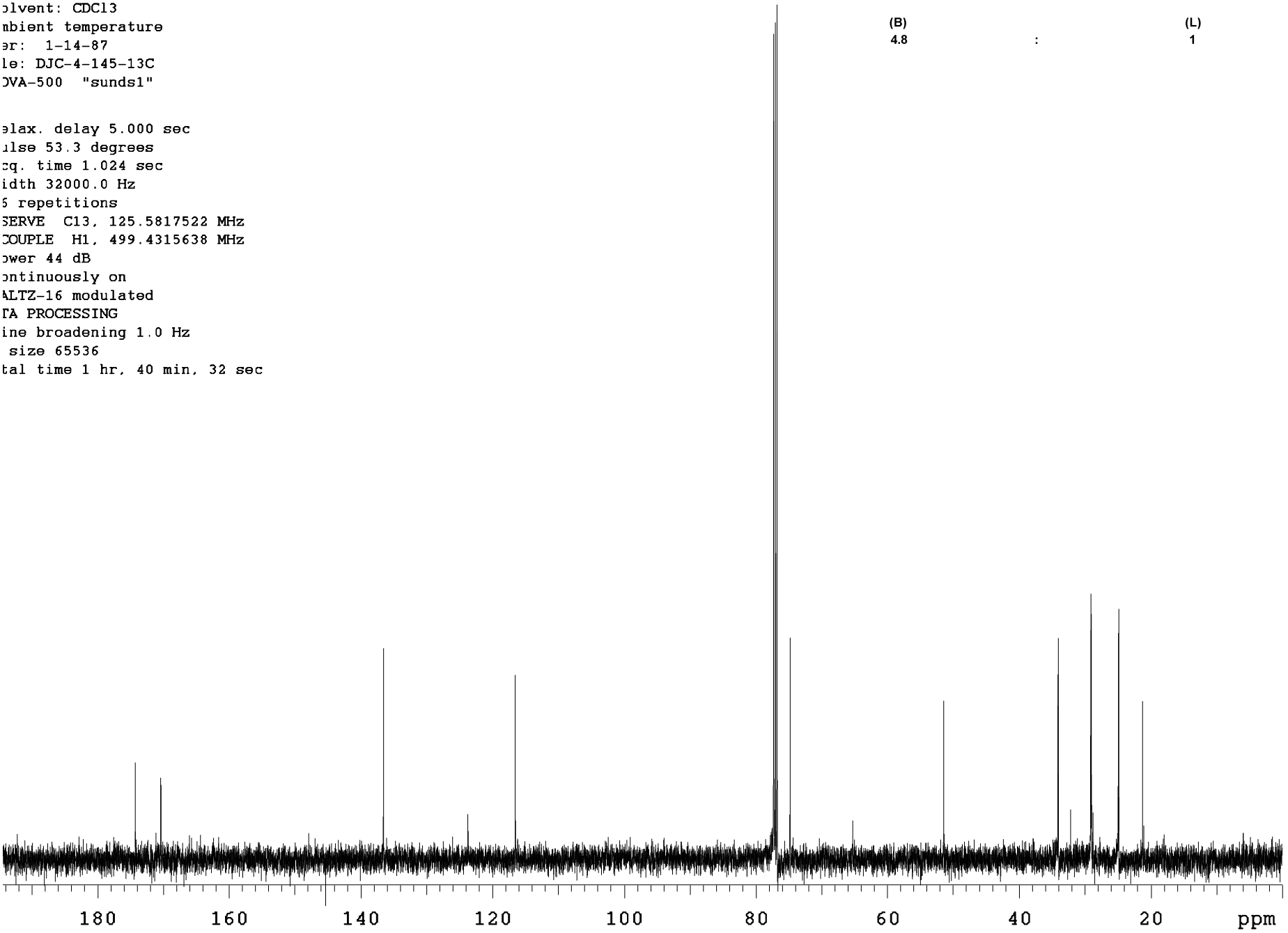

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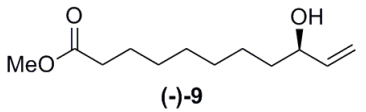

(-)-9

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olvent: CDCl3
mbient temperature
le: DJC-6-233-1H
OVA-500  "sunds1"


elax. delay 20.000 sec
ilse 90.0 degrees
cq. time 4.096 sec
idth 8000.0 Hz
 repetitions
SERVE   H1, 500.0677753 MHz
TA PROCESSING
ine broadening 0.3 Hz
 size 65536
tal time 6 min, 25 sec
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Methyl (*9R*)-9-hydroxyundec-10-eneoate ((-)-9)

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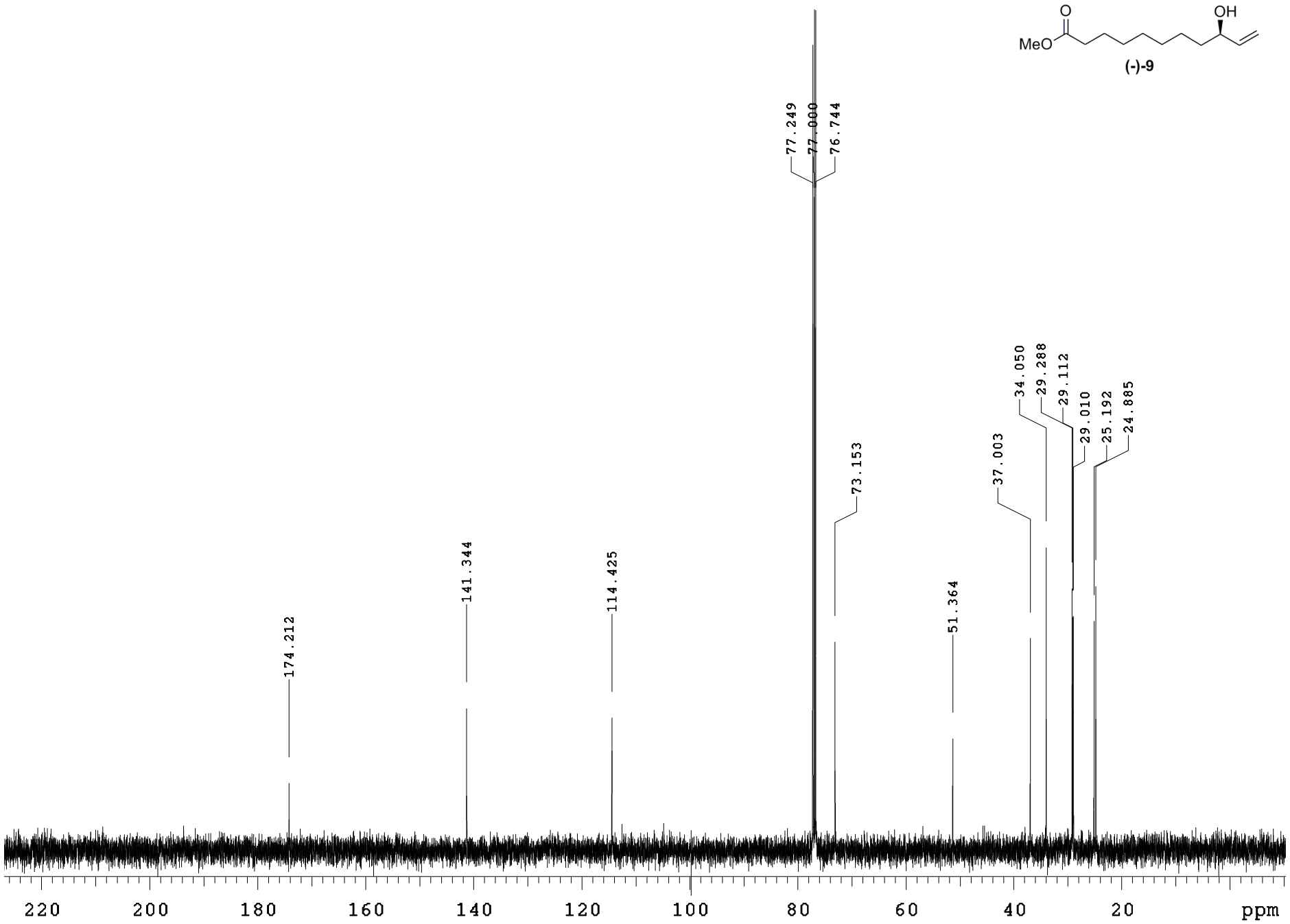

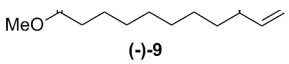


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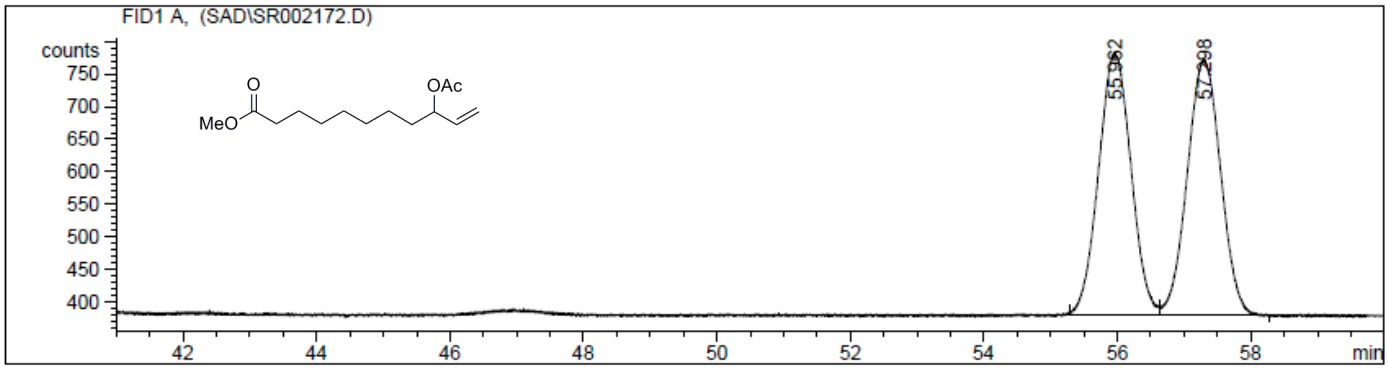

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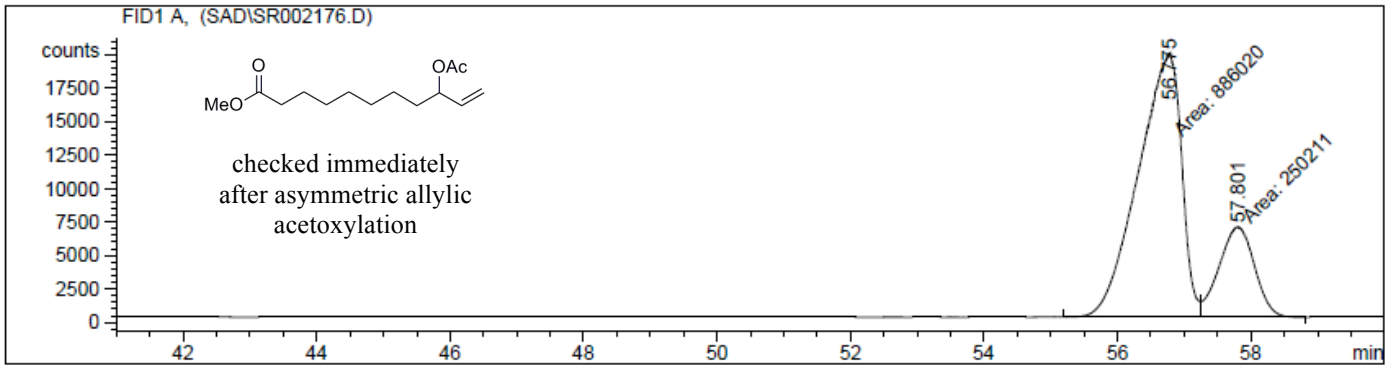
Test



Signal 1: FID1 A,

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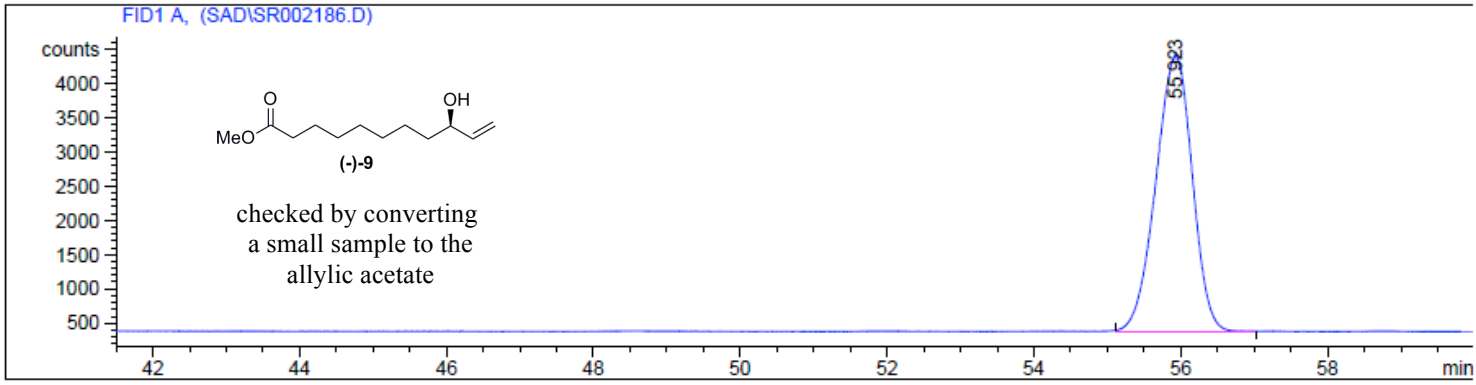
2	57.801	FM	0.6203	2.50211e5	6723.03027	22.02116

Test



Signal 1: FID1 A,

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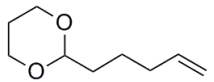


15

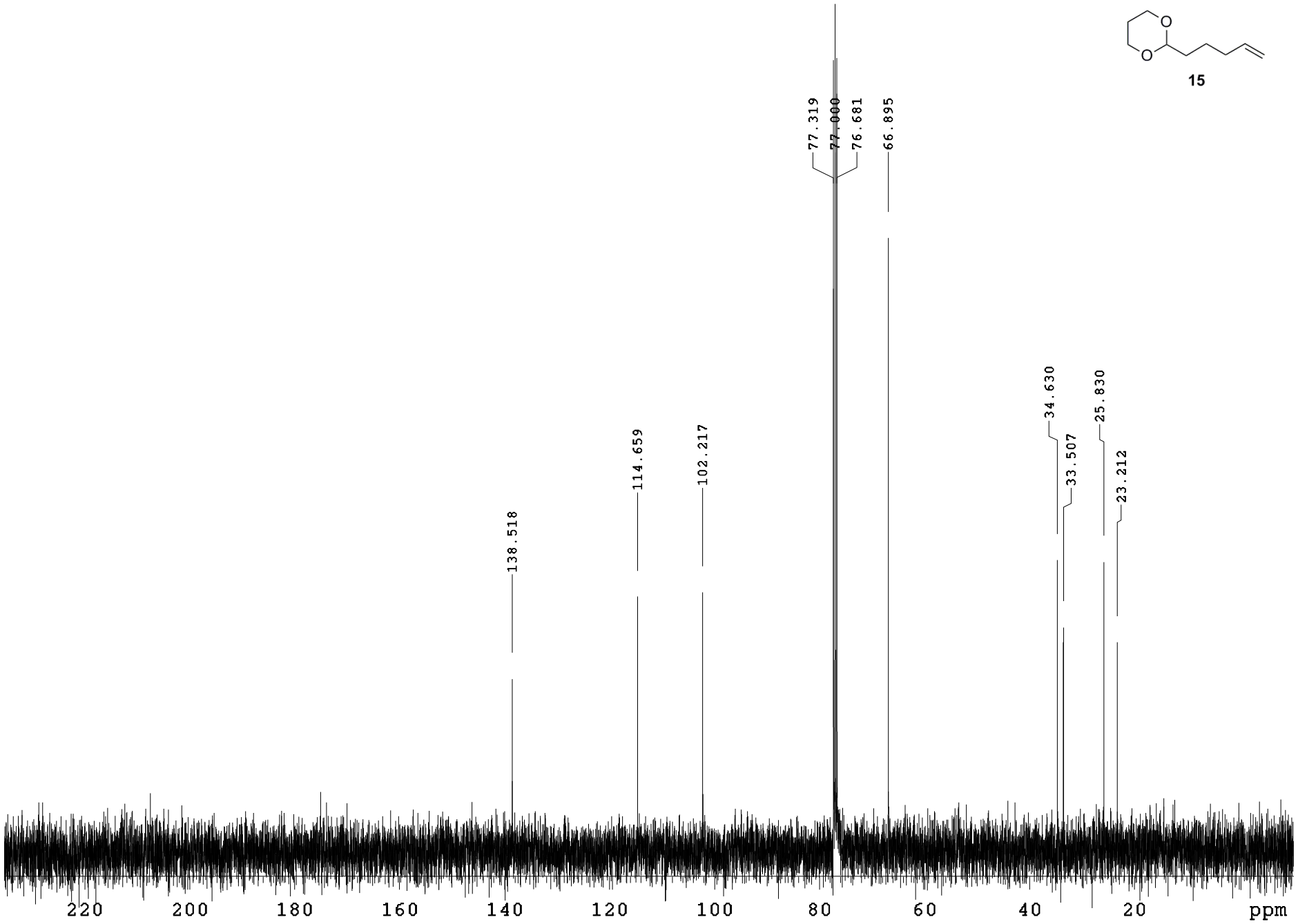
se Sequence: s2pul

lvent: CDCl3
bient temperature
e: DJC-6-193-1H
VA-500 "sunds1"

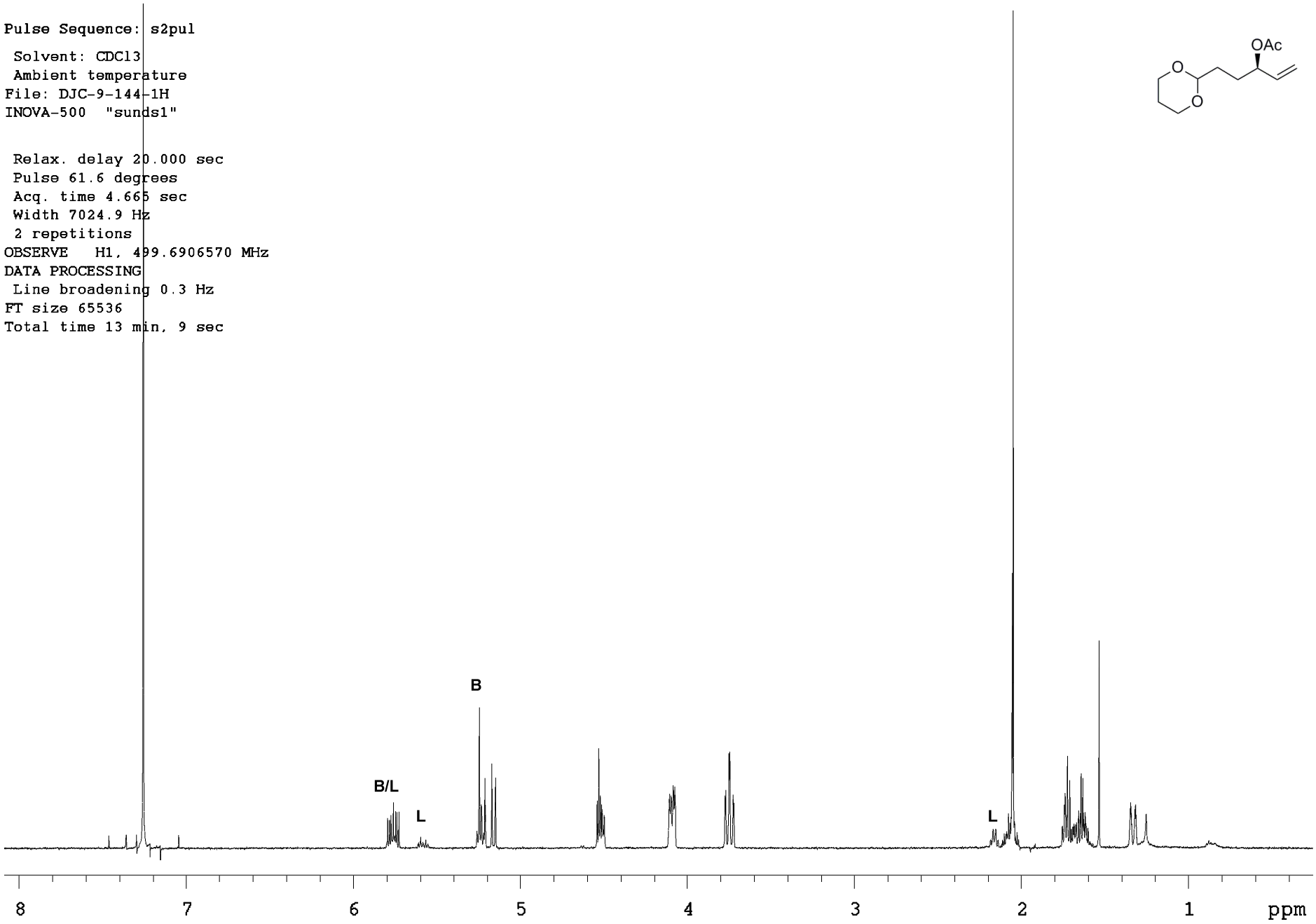
lax. delay 30.000 sec
lse 90.0 degrees
q. time 4.096 sec
dth 8000.0 Hz
ngle scan
ERVE H1, 500.0677753 MHz
A PROCESSING
ne broadening 0.3 Hz
size 65536
al time 4 min, 32 sec

2-(Pent-4-en-1-yl)-1,3-dioxane (15)

Pulse Sequence: s2pul

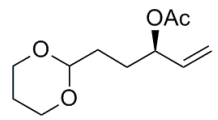


2-((*3R*)-Pent-3-acetoxy-4-en-1-yl-3-ol)-1,3-dioxane (13-OAc)

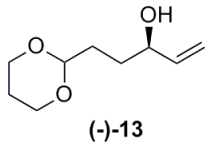


2-((*3R*)-Pent-3-acetoxy-4-en-1-yl-3-ol)-1,3-dioxane (13-OAc)

Pulse Sequence: s2pul



2-((*3R*)-Pent-4-en-1-yl-3-ol)-1,3-dioxane ((-)-13)



(-)-13

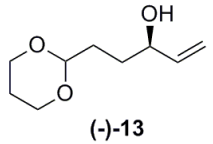
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: DJC-6-171
INOVA-500 "sunds1"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 4.096 sec
Width 8000.0 Hz
4 repetitions
OBSERVE H1, 399.9486778 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 3 min, 45 sec

2-((*3R*)-Pent-4-en-1-yl-3-ol)-1,3-dioxane ((-)-13)

Pulse Sequence: s2pul



(-)-13

```
Acq. Operator    : sad
Acq. Instrument  : Chiral GC                        Inj Volume : Manually
Acq. Method      : C:\HPCHEM\2\METHODS\SUB110DC.M
Last changed     : 10/14/2010 9:46:00 PM by sad
Analysis Method  : C:\HPCHEM\2\METHODS\SUB110DC.M
Last changed     : 10/15/2010 12:55:17 PM by sad
                   (modified after loading)
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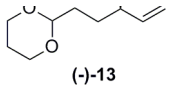
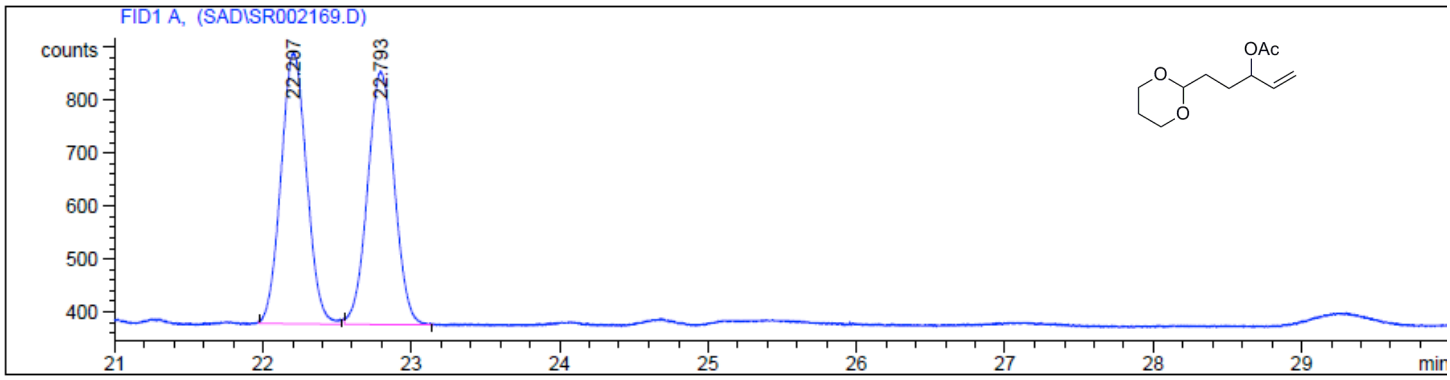


(-)-13

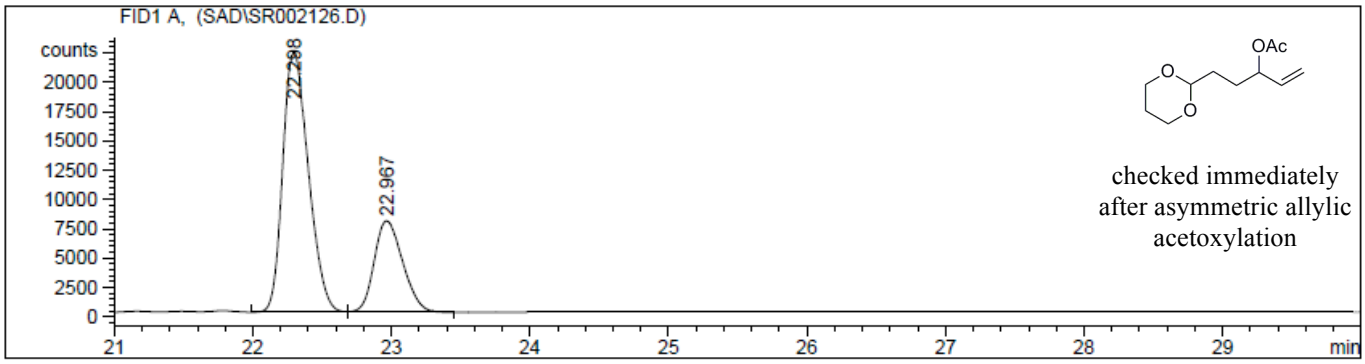
Test



Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	22.207	BB	0.1731	6155.46387	512.69556	50.65797
2	22.793	BP	0.1840	5995.56445	479.18893	49.34203

Test

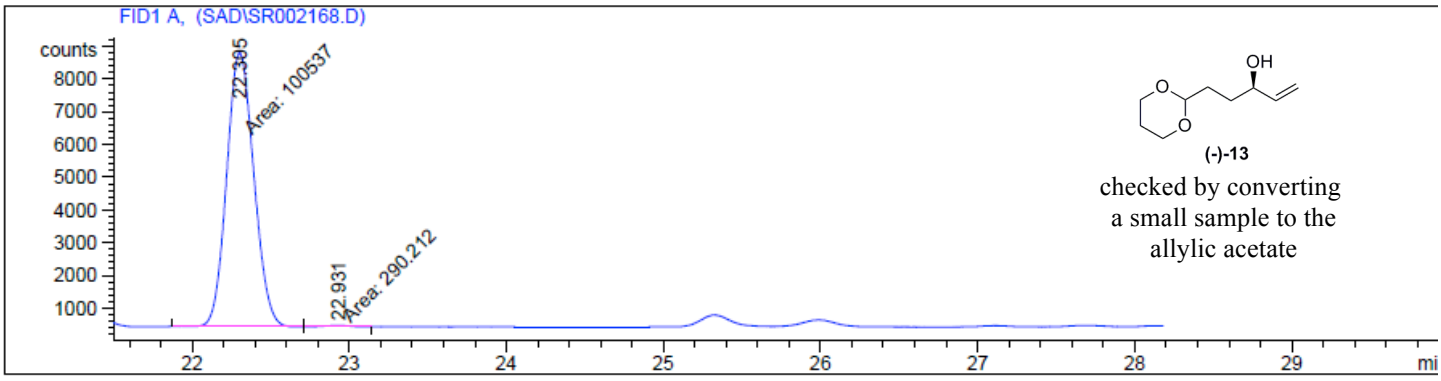


checked immediately after asymmetric allylic acetoxylation

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	22.298	VV	0.1882	2.85705e5	2.21882e4	71.93395
2	22.967	VB	0.2060	1.11472e5	7787.25928	28.06605

Test

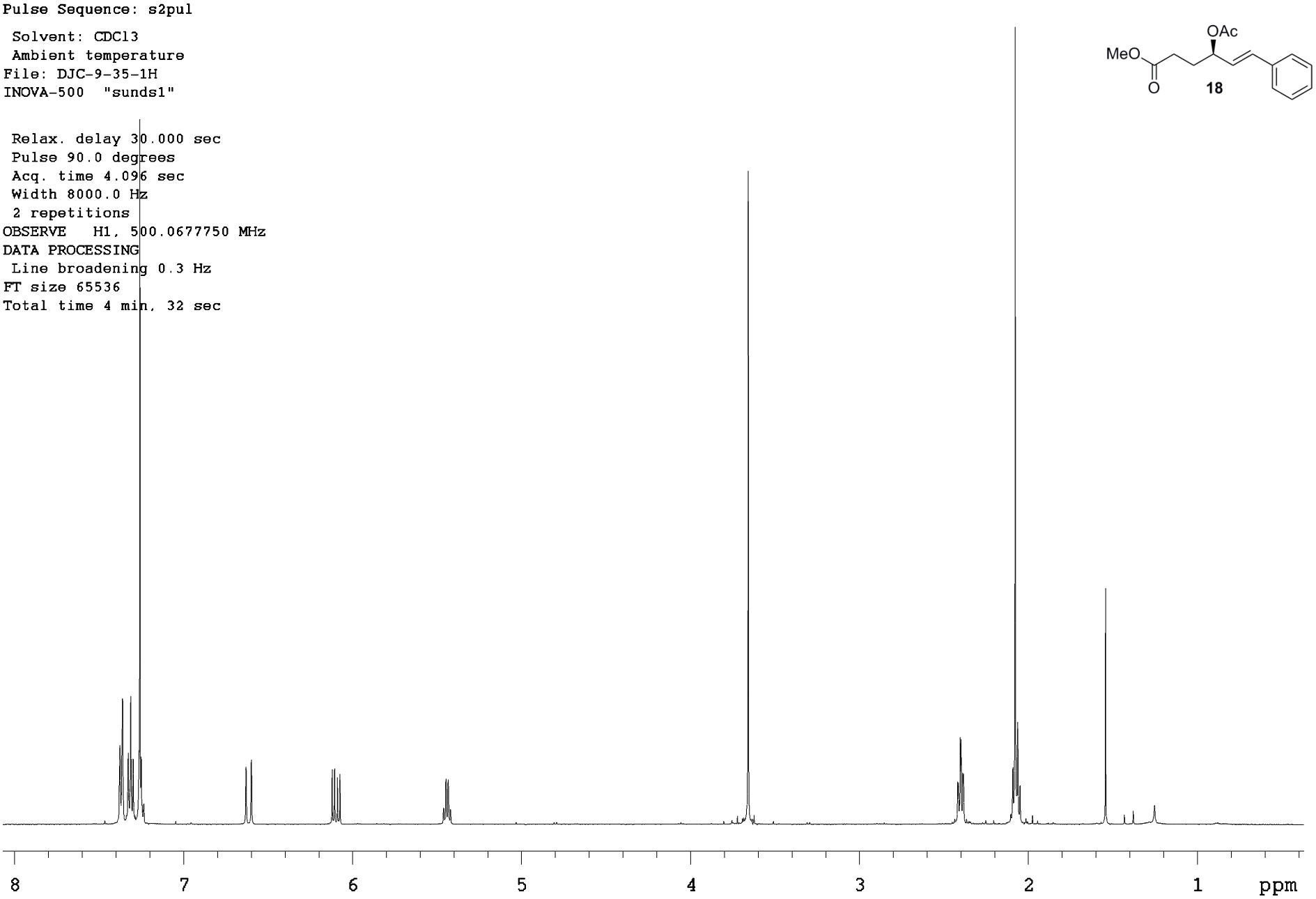


checked by converting a small sample to the allylic acetate

Signal 1: FID1 A,

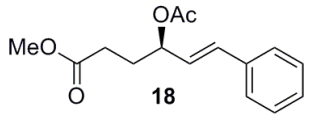
Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %

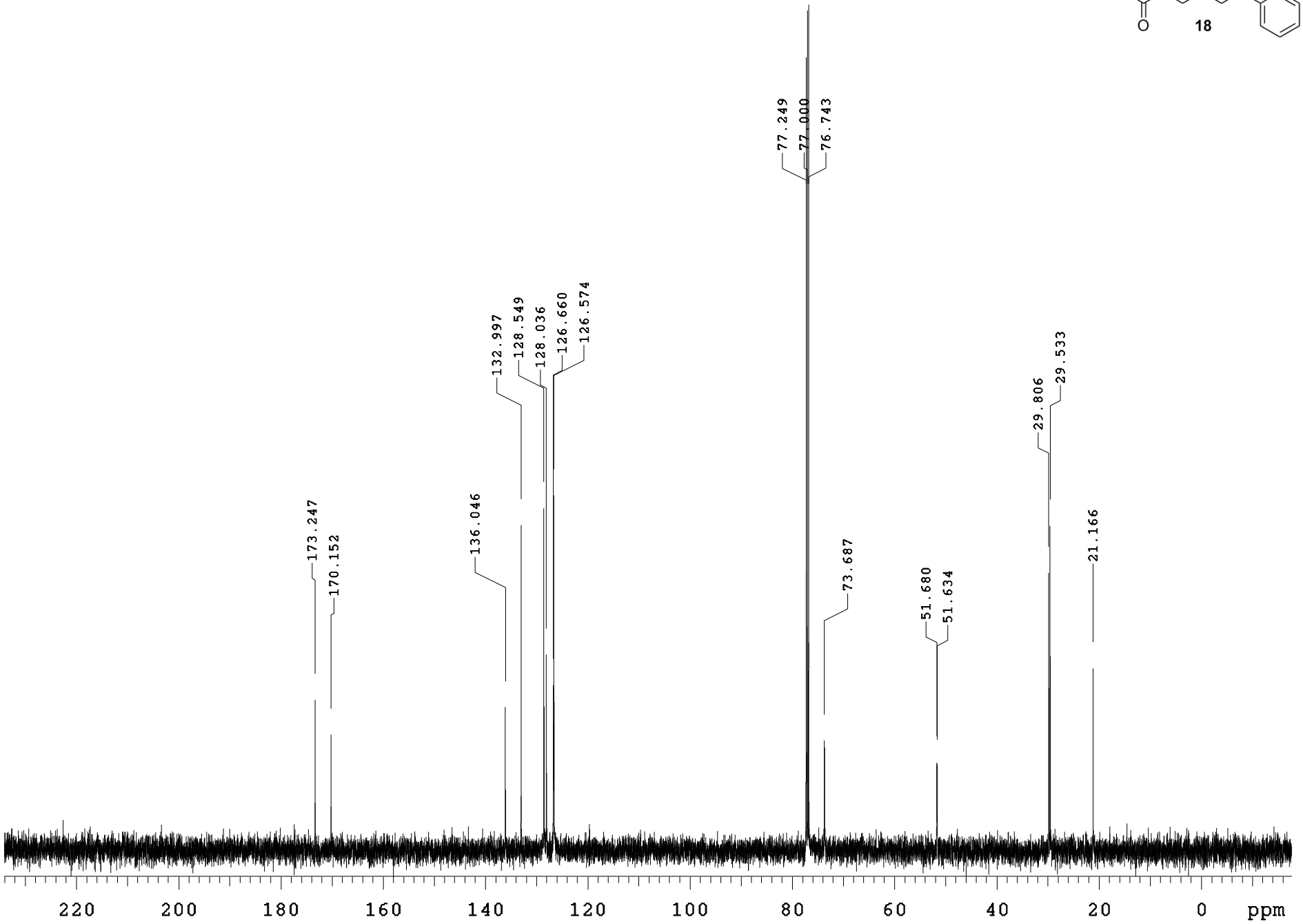
4*R*, *E*)-Methyl 4-acetoxy-6-phenylhex-5-enoate (18)

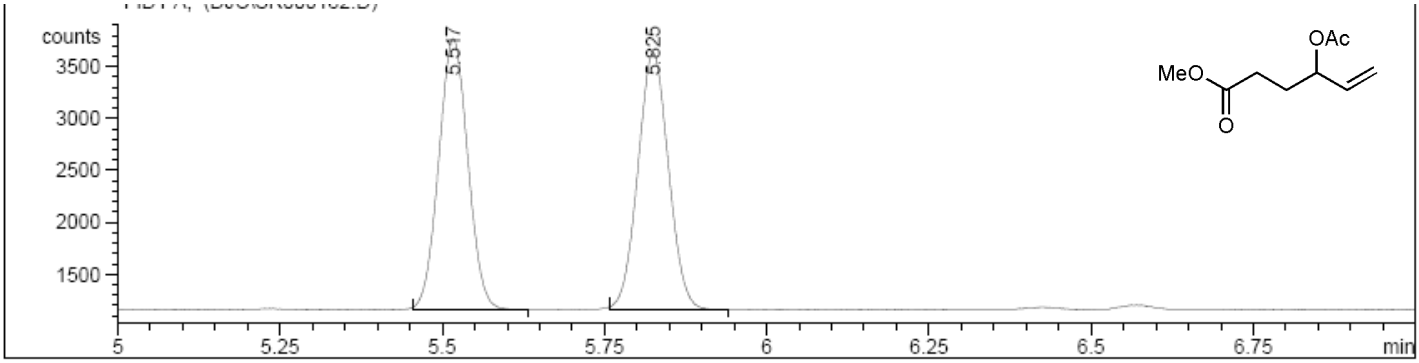


4*R*, *E*)-Methyl 4-acetoxy-6-phenylhex-5-enoate (18)

Pulse Sequence: s2pul



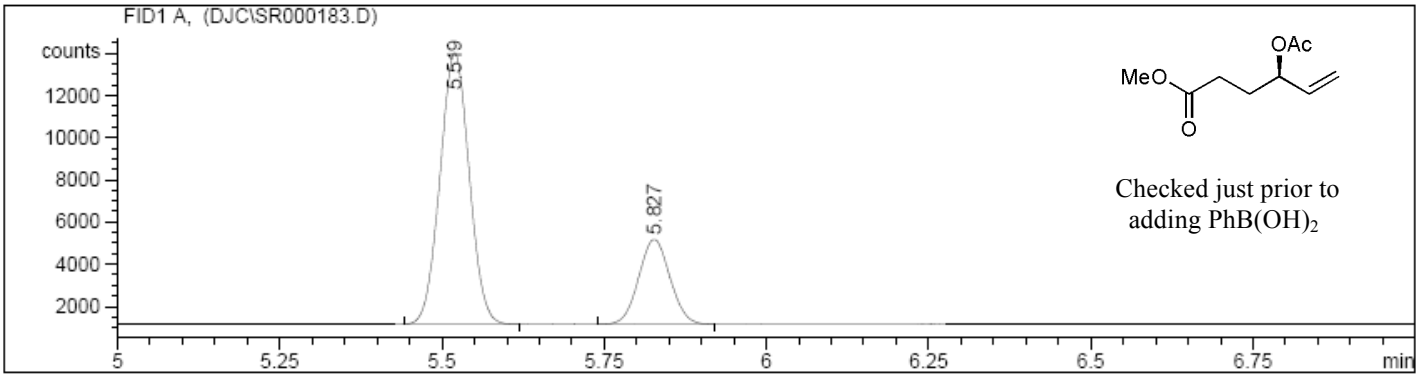




Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	5.517	BB	0.0532	8113.60303	2543.25464	49.97155
2	5.825	BB	0.0554	8122.84131	2403.16333	50.02845
Totals :				1.62364e4	4946.41797	

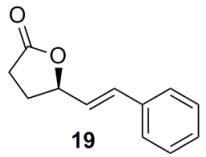
Data File C:\HPCHEM\2\DATA\DJC\SR000183.D Sample Name: 04-MeEst-R



Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	5.519	BB	0.0435	4.02791e4	1.28630e4	75.04569
2	5.827	BB	0.0448	1.33937e4	4003.59375	24.95431
Totals :				5.36728e4	1.68666e4	

(*R*, *E*)-5-styryldihydrofuran-2(3H)-one (19)

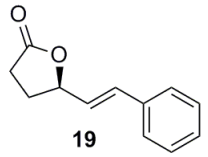



```
Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
File: DJC-9-70-1H
INOVA-500  "sunds1"

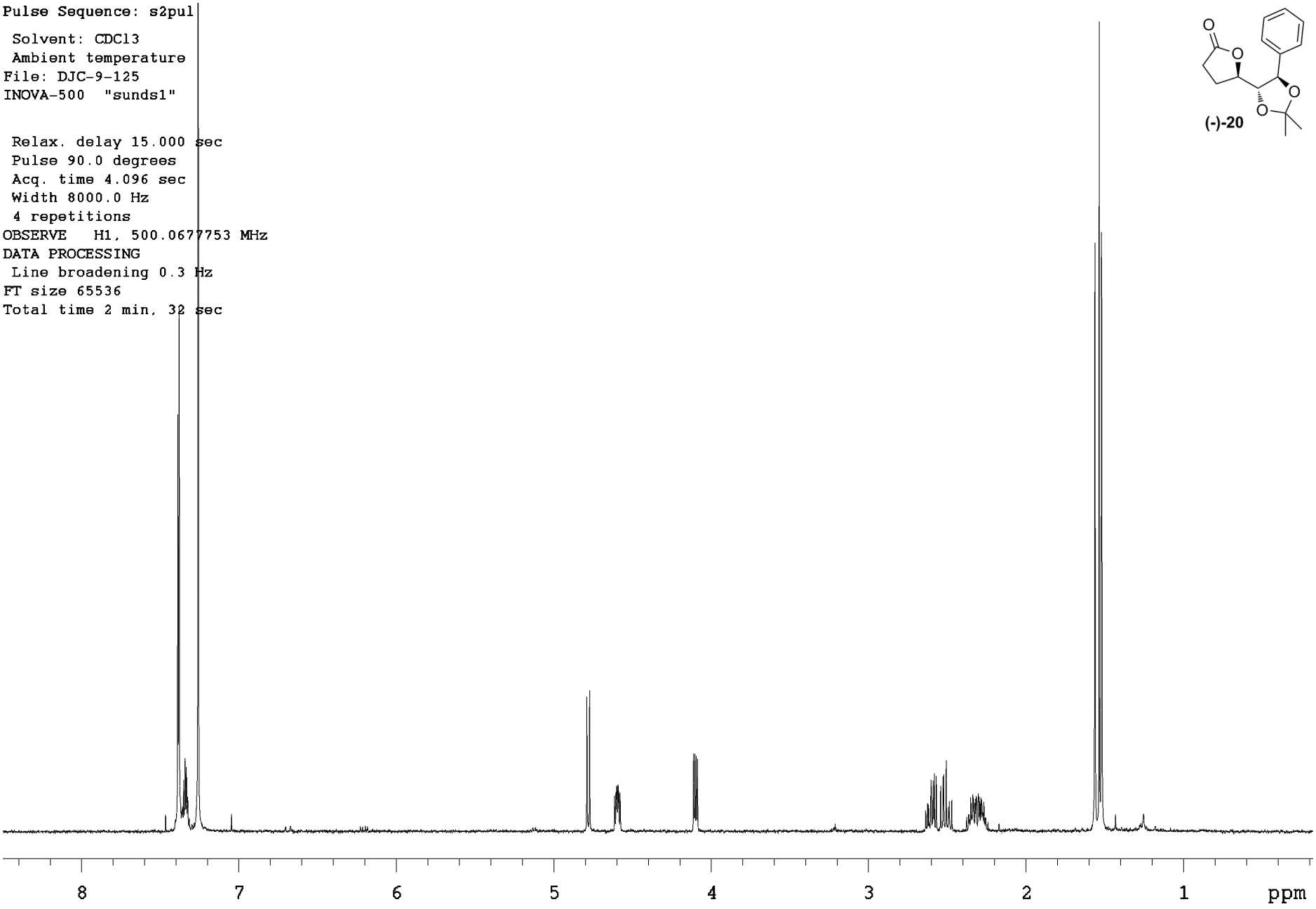
 Relax. delay 30.000 sec
 Pulse 90.0 degrees
 Acq. time 4.096 sec
 Width 8000.0 Hz
 2 repetitions
OBSERVE   H1, 500.0677750 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 4 min, 32 sec
```

***R*, *E*)-5-styryldihydrofuran-2(3H)-one (19)**

Pulse Sequence: s2pul



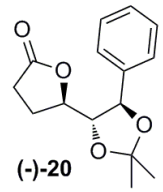
R)-5-((4R,5R)-2,2-dimethyl-5-phenyl-1,3-dioxolan-4-yl)dihydrofuran-2(3H)-one ((-)-20)



(-)-20

R)-5-((4R,5R)-2,2-dimethyl-5-phenyl-1,3-dioxolan-4-yl)dihydrofuran-2(3H)-one ((-)-20)

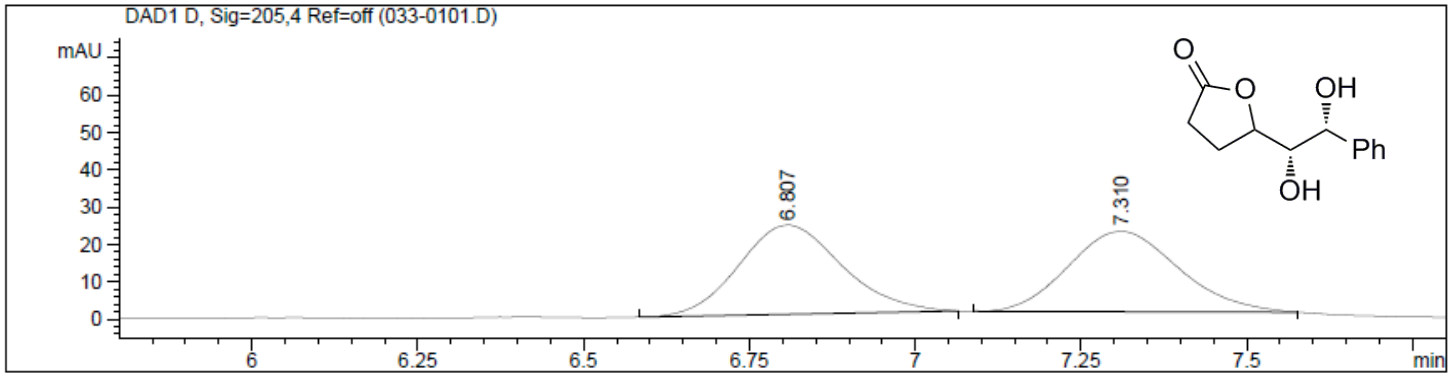
Pulse Sequence: s2pul



(-)-20

```
=====================================================
Injection Date  : 11/23/2010 8:21:02 PM          Seq. Line :   1
Sample Name     : DC-diol-rac                    Location : Vial 33
Acq. Operator   : HPLC Host                          Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 0.5 µl
Sequence File   : C:\HPCHEM\1\SEQUENCE\STANDARD.S
Acq. Method     : C:\HPCHEM\1\METHODS\COLUMNS\REVERSE\CHIRAL\AD-RH\35ACCN.M
Last changed    : 11/23/2010 8:20:08 PM by HPLC Host
Analysis Method : C:\HPCHEM\1\METHODS\COLUMNS\REVERSE\CHIRAL\AD-RH\35ACCN.M
Last changed    : 11/23/2010 8:33:48 PM by HPLC Host
                  (modified after loading)
AD-RH
Reverse Phase Chiral
ACCN35%
```

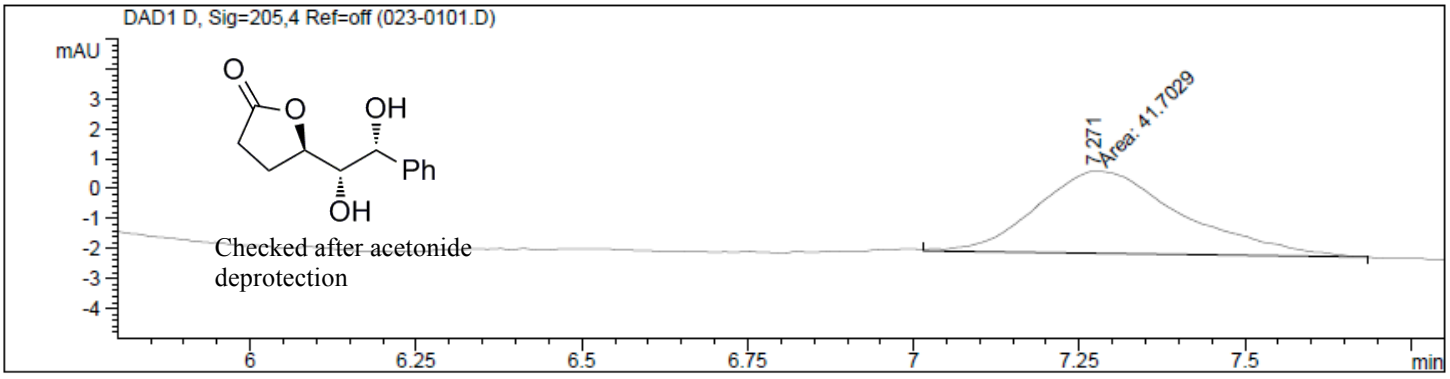
Standard Run



Signal 1: DAD1 D, Sig=205,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.807	BB	0.1665	258.61758	23.89842	50.9221
2	7.310	BB	0.1793	249.25174	21.55332	49.0779

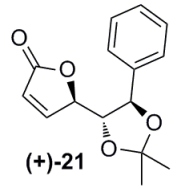
Standard Run



Signal 1: DAD1 D, Sig=205,4 Ref=off

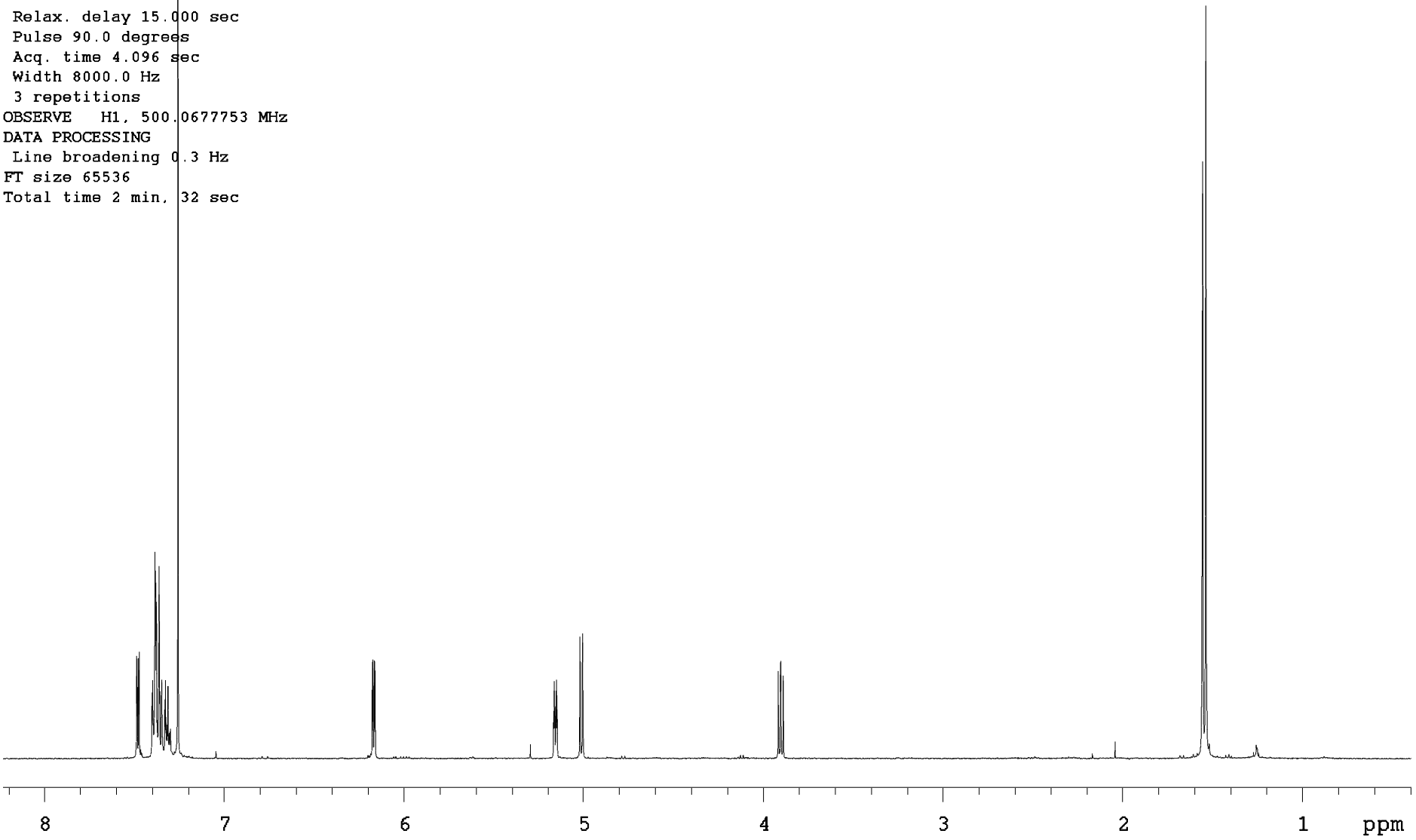
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.271	MM	0.2538	41.70292	2.73845	100.0000

R)-5-((4R,5R)-2,2-dimethyl-5-phenyl-1,3-dioxolan-4-yl)furan-2(5H)-one ((+)-21)



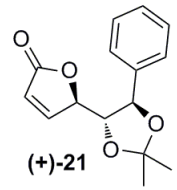

```
Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
File: DJC-9-122-1H
INOVA-500  "sunds1"

 Relax. delay 15.000 sec
 Pulse 90.0 degrees
 Acq. time 4.096 sec
 Width 8000.0 Hz
 3 repetitions
OBSERVE   H1, 500.0677753 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 2 min, 32 sec
```

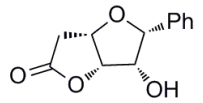


R)-5-((4R,5R)-2,2-dimethyl-5-phenyl-1,3-dioxolan-4-yl)furan-2(5H)-one ((+)-21)

Pulse Sequence: s2pul



3aS,5R,6S,6aS)-6-hydroxy-5-phenyltetrahydrofuro[3,2-b]furan-2(5H)-one((-)-22)



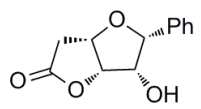
(-)-22

```
Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
File: DJC-9-78-2
INOVA-500  "sunds1"

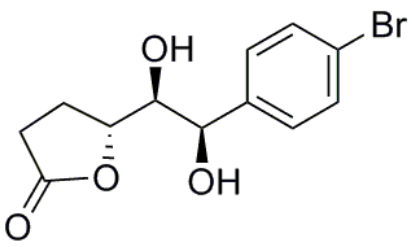
 Relax. delay 15.000 sec
 Pulse 90.0 degrees
 Acq. time 4.096 sec
 Width 8000.0 Hz
 7 repetitions
OBSERVE   H1, 500.0677748 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 2 min, 32 sec
```

3aS,5R,6S,6aS)-6-hydroxy-5-phenyltetrahydrofuro[3,2-b]furan-2(5H)-one((-)-22)

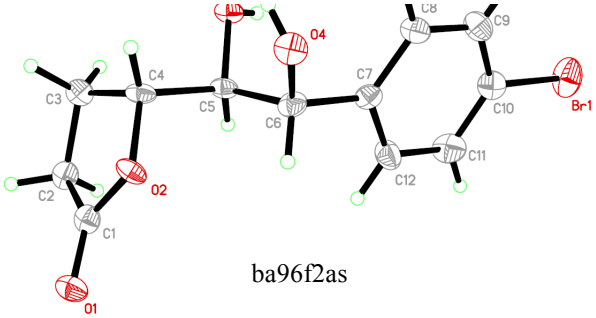
Pulse Sequence: s2pul



(-)-22



p-Bromophenyl· **20**-diol



ba96f2as

```
The Model has Chirality at C4      (Verify) ....          R
The Model has Chirality at C5      (Verify) ....          S
The Model has Chirality at C6      (Verify) ....          R
```

able 1. Crystal data and structure refinement for ba96f2as.		
dentification code	ba96f2as	
mpirical formula	C12 H13 Br O4	
ormula weight	301.13	
emperature	193(2) K	
Vavelength	0.71073 Å	
rystal system	Monoclinic	
pace group	P 21	
nit cell dimensions	a = 10.791(2) Å	α= 90°.
	b = 4.9772(8) Å	β= 101.532(12)°.
	c = 11.585(2) Å	γ = 90°.
olume	609.63(19) $Å^3$	
	2	
ensity (calculated)	1.640 Mg/m^3	
bsorption coefficient	3.371 mm^{-1}	
(000)	304	
rystal size	0.862 x 0.396 x 0.05 mm^3	
heta range for data collection	1.79 to 25.31°.	
ndex ranges	-12<=h<=12, -5<=k<=5, -13<=l<=13	
eflections collected	8519	
ndependent reflections	2168 [R(int) = 0.0829]	
ompleteness to theta = 25.31°	99.6 %	
bsorption correction	Integration	
lax. and min. transmission	0.8408 and 0.2253	
efinement method	Full-matrix least-squares on F^2	
ata / restraints / parameters	2168 / 1 / 156	
oodness-of-fit on F^2	0.970	
inal R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1055	
indices (all data)	R1 = 0.0767, wR2 = 0.1196	
bsolute structure parameter	0.054(19)	
argest diff. peak and hole	0.614 and -0.592 e.$Å^{-3}$	

r ba96f2as. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
r(1)	2483(1)	5824(2)	-957(1)	58(1)
)(1)	110(4)	-3643(8)	6064(3)	36(1)
)(2)	1949(3)	-3189(7)	5495(3)	28(1)
)(3)	4040(3)	1842(7)	4654(3)	27(1)
)(4)	3861(4)	-3368(6)	3542(3)	32(1)
'(1)	1056(6)	-2341(11)	6078(5)	30(1)
'(2)	1441(5)	291(12)	6693(5)	33(2)
'(3)	2834(5)	462(14)	6671(4)	31(1)
'(4)	2986(5)	-1274(11)	5641(5)	28(1)
'(5)	2902(5)	281(10)	4484(5)	26(1)
'(6)	2812(6)	-1543(12)	3396(5)	30(1)
'(7)	2749(5)	139(10)	2300(5)	28(1)
'(8)	3799(5)	570(18)	1793(5)	36(1)
'(9)	3712(6)	2244(13)	815(5)	38(2)
'(10)	2587(6)	3494(12)	353(5)	37(2)
'(11)	1521(6)	3065(14)	829(6)	44(2)
'(12)	1621(6)	1401(12)	1809(5)	39(2)

Table 3. Bond lengths [Å] and angles [°] for ba96f2as.

r(1)-C(10)	1.896(6)
)(1)-C(1)	1.206(7)
)(2)-C(1)	1.350(7)
)(2)-C(4)	1.454(7)
)(3)-C(5)	1.434(6)
)(3)-H(3C)	0.8400
)(4)-C(6)	1.434(7)
)(4)-H(4B)	0.8400
'(1)-C(2)	1.510(8)
'(2)-C(3)	1.511(8)
'(2)-H(2A)	0.9900
'(2)-H(2B)	0.9900
'(3)-C(4)	1.508(8)
'(3)-H(3A)	0.9900
'(3)-H(3B)	0.9900
'(4)-C(5)	1.535(8)
'(4)-H(4A)	1.0000
'(5)-C(6)	1.541(8)
'(5)-H(5A)	1.0000
'(6)-C(7)	1.511(7)
'(6)-H(6A)	1.0000
'(7)-C(12)	1.386(8)
'(7)-C(8)	1.393(7)
'(8)-C(9)	1.394(9)
'(8)-H(8A)	0.9500
'(9)-C(10)	1.374(9)
'(9)-H(9A)	0.9500
'(10)-C(11)	1.387(9)
'(11)-C(12)	1.392(8)
'(11)-H(11A)	0.9500
'(12)-H(12A)	0.9500
'(1)-O(2)-C(4)	110.3(4)
'(5)-O(3)-H(3C)	109.5
'(6)-O(4)-H(4B)	109.5
)(1)-C(1)-O(2)	120.8(5)
)(1)-C(1)-C(2)	128.7(5)
)(2)-C(1)-C(2)	110.6(5)
'(1)-C(2)-C(3)	102.8(5)
'(1)-C(2)-H(2A)	111.2
'(3)-C(2)-H(2A)	111.2
'(1)-C(2)-H(2B)	111.2
'(3)-C(2)-H(2B)	111.2
(2A)-C(2)-H(2B)	109.1

'(4)-C(3)-H(3B)	110.9
[(3A)-C(3)-H(3B)	108.9
)(2)-C(4)-C(3)	105.3(4)
)(2)-C(4)-C(5)	108.6(4)
'(3)-C(4)-C(5)	113.9(4)
)(2)-C(4)-H(4A)	109.6
'(3)-C(4)-H(4A)	109.6
'(5)-C(4)-H(4A)	109.6
)(3)-C(5)-C(4)	104.7(4)
)(3)-C(5)-C(6)	110.1(4)
'(4)-C(5)-C(6)	113.6(4)
)(3)-C(5)-H(5A)	109.4
'(4)-C(5)-H(5A)	109.4
'(6)-C(5)-H(5A)	109.4
)(4)-C(6)-C(7)	110.7(5)
)(4)-C(6)-C(5)	110.9(4)
'(7)-C(6)-C(5)	110.2(4)
)(4)-C(6)-H(6A)	108.3
'(7)-C(6)-H(6A)	108.3
'(5)-C(6)-H(6A)	108.3
'(12)-C(7)-C(8)	118.6(5)
'(12)-C(7)-C(6)	119.0(5)
'(8)-C(7)-C(6)	122.3(5)
'(7)-C(8)-C(9)	120.4(6)
'(7)-C(8)-H(8A)	119.8
'(9)-C(8)-H(8A)	119.8
'(10)-C(9)-C(8)	119.9(6)
'(10)-C(9)-H(9A)	120.1
'(8)-C(9)-H(9A)	120.1
'(9)-C(10)-C(11)	120.9(6)
'(9)-C(10)-Br(1)	119.7(5)
'(11)-C(10)-Br(1)	119.4(5)
'(10)-C(11)-C(12)	118.7(6)
'(10)-C(11)-H(11A)	120.6
'(12)-C(11)-H(11A)	120.6
'(7)-C(12)-C(11)	121.5(5)
'(7)-C(12)-H(12A)	119.3
'(11)-C(12)-H(12A)	119.3

ymmetry transformations used to generate equivalent atoms:

[able 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for ba96f2as. The anisotropic isplacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
r(1)	89(1)	42(1)	42(1)	14(1)	8(1)	-5(1)
)(1)	31(2)	33(3)	47(2)	5(2)	12(2)	-5(2)
)(2)	30(2)	15(2)	42(2)	3(2)	16(2)	-5(2)
)(3)	24(2)	15(2)	42(2)	6(2)	7(2)	-4(2)
)(4)	40(2)	12(2)	44(2)	4(1)	9(2)	4(2)
'(1)	37(4)	20(3)	32(3)	6(2)	5(3)	1(3)
'(2)	39(3)	25(4)	34(3)	1(2)	5(2)	-1(3)
'(3)	37(3)	16(3)	38(3)	5(3)	7(2)	-8(3)
'(4)	18(3)	21(3)	46(4)	7(2)	5(3)	-3(2)
'(5)	21(3)	18(4)	37(3)	4(2)	6(2)	-4(2)
'(6)	26(3)	28(3)	35(3)	8(2)	-1(3)	2(3)
'(7)	30(3)	19(4)	33(3)	-2(2)	3(2)	-6(2)
'(8)	30(3)	36(4)	42(3)	3(4)	9(2)	0(4)
'(9)	42(4)	33(3)	42(4)	5(3)	15(3)	2(3)
'(10)	44(4)	25(3)	42(4)	-1(3)	8(3)	-4(3)
'(11)	38(4)	37(4)	55(4)	15(3)	2(3)	12(3)
'(12)	39(4)	45(5)	35(3)	10(3)	13(3)	6(3)

	x	y	z	U(eq)
[(3C)	3905	3273	4265	41
[(4B)	4492	-2666	3981	48
[(2A)	1299	268	7512	39
[(2B)	969	1815	6264	39
[(3A)	3352	-230	7414	37
[(3B)	3086	2340	6554	37
[(4A)	3811	-2255	5833	34
[(5A)	2154	1511	4367	31
[(6A)	2016	-2619	3304	37
[(8A)	4580	-282	2116	43
[(9A)	4429	2520	469	46
[(11A)	739	3890	492	53
[(12A)	900	1124	2149	47

Table 6. Torsion angles [°] for ba96f2as.

'(4)-O(2)-C(1)-O(1)	179.7(5)
'(4)-O(2)-C(1)-C(2)	-0.6(6)
)(1)-C(1)-C(2)-C(3)	164.4(6)
)(2)-C(1)-C(2)-C(3)	-15.3(6)
'(1)-C(2)-C(3)-C(4)	24.1(6)
'(1)-O(2)-C(4)-C(3)	16.4(6)
'(1)-O(2)-C(4)-C(5)	-105.9(5)
'(2)-C(3)-C(4)-O(2)	-25.2(5)
'(2)-C(3)-C(4)-C(5)	93.7(6)
)(2)-C(4)-C(5)-O(3)	-172.5(4)
'(3)-C(4)-C(5)-O(3)	70.4(6)
)(2)-C(4)-C(5)-C(6)	-52.4(6)
'(3)-C(4)-C(5)-C(6)	-169.4(4)
)(3)-C(5)-C(6)-O(4)	60.7(5)
'(4)-C(5)-C(6)-O(4)	-56.4(6)
)(3)-C(5)-C(6)-C(7)	-62.3(6)
'(4)-C(5)-C(6)-C(7)	-179.3(5)
)(4)-C(6)-C(7)-C(12)	160.5(5)
'(5)-C(6)-C(7)-C(12)	-76.4(7)
)(4)-C(6)-C(7)-C(8)	-22.5(7)
'(5)-C(6)-C(7)-C(8)	100.6(6)
'(12)-C(7)-C(8)-C(9)	0.2(10)
'(6)-C(7)-C(8)-C(9)	-176.8(6)
'(7)-C(8)-C(9)-C(10)	0.5(10)
'(8)-C(9)-C(10)-C(11)	-1.6(10)
'(8)-C(9)-C(10)-Br(1)	178.8(5)
'(9)-C(10)-C(11)-C(12)	1.9(10)
r(1)-C(10)-C(11)-C(12)	-178.4(5)
'(8)-C(7)-C(12)-C(11)	0.2(9)
'(6)-C(7)-C(12)-C(11)	177.3(6)
'(10)-C(11)-C(12)-C(7)	-1.2(10)

ymmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for ba96f2as [Å and °].

)-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
)(3)-H(3C)...O(4)#1	0.84	1.87	2.698(5)	170.6
)(4)-H(4B)...O(3)#2	0.84	2.02	2.759(5)	147.0
)(4)-H(4B)...O(3)	0.84	2.46	2.885(5)	112.6

ymmetry transformations used to generate equivalent atoms:
1 x,y+1,z #2 -x+1,y-1/2,-z+1