

## Supporting information

(NMR Spectral Data)

### **Total Synthesis of (+)-petromyroxol via tandem $\alpha$ -aminoxylation-allylation and asymmetric dihydroxylation- $S_N2$ cyclization approach†‡**

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Telephone number: +91-20-25902627

Fax number: +91-20-25902629

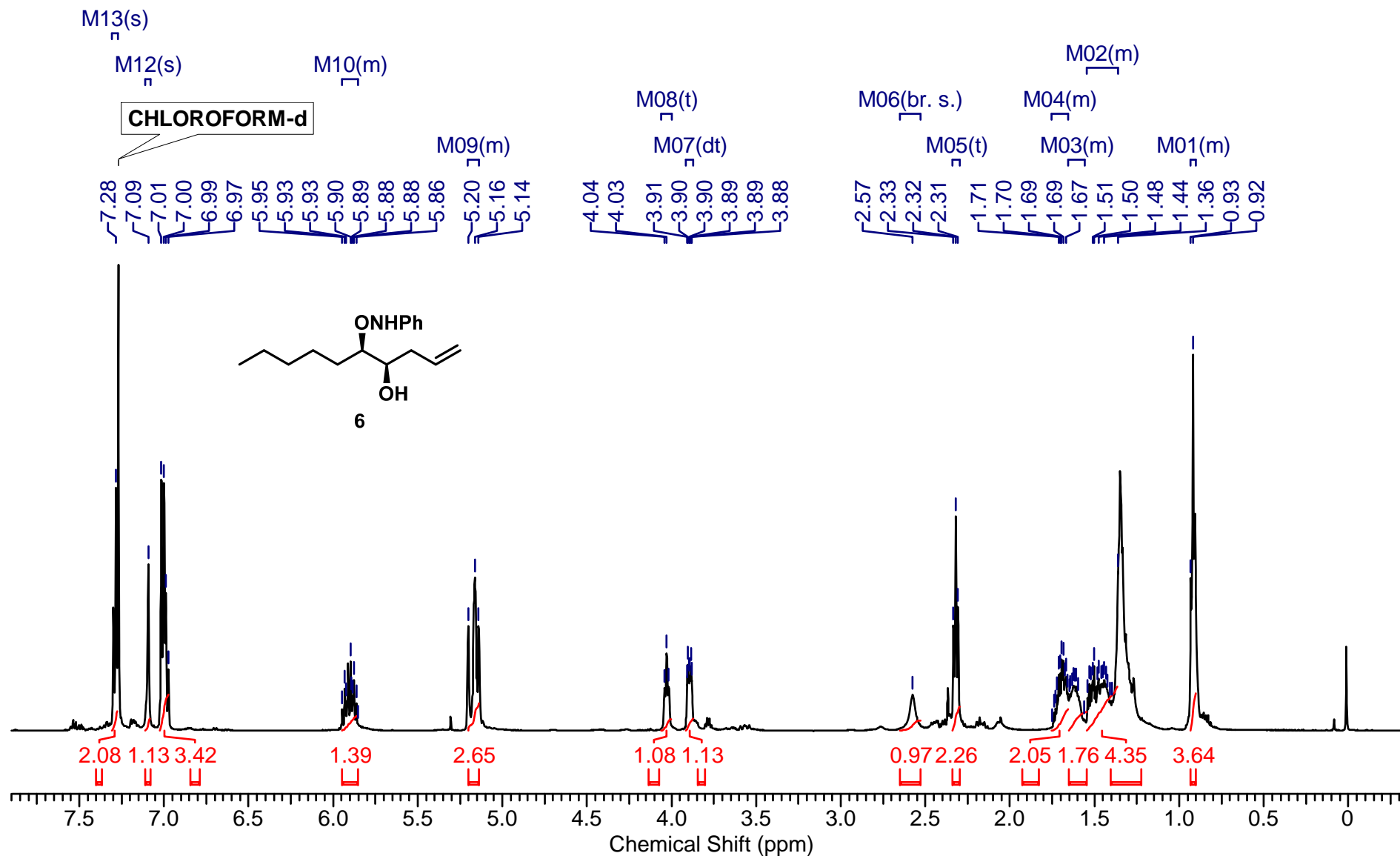
*E-mail:* pk.tripathi@ncl.res.in

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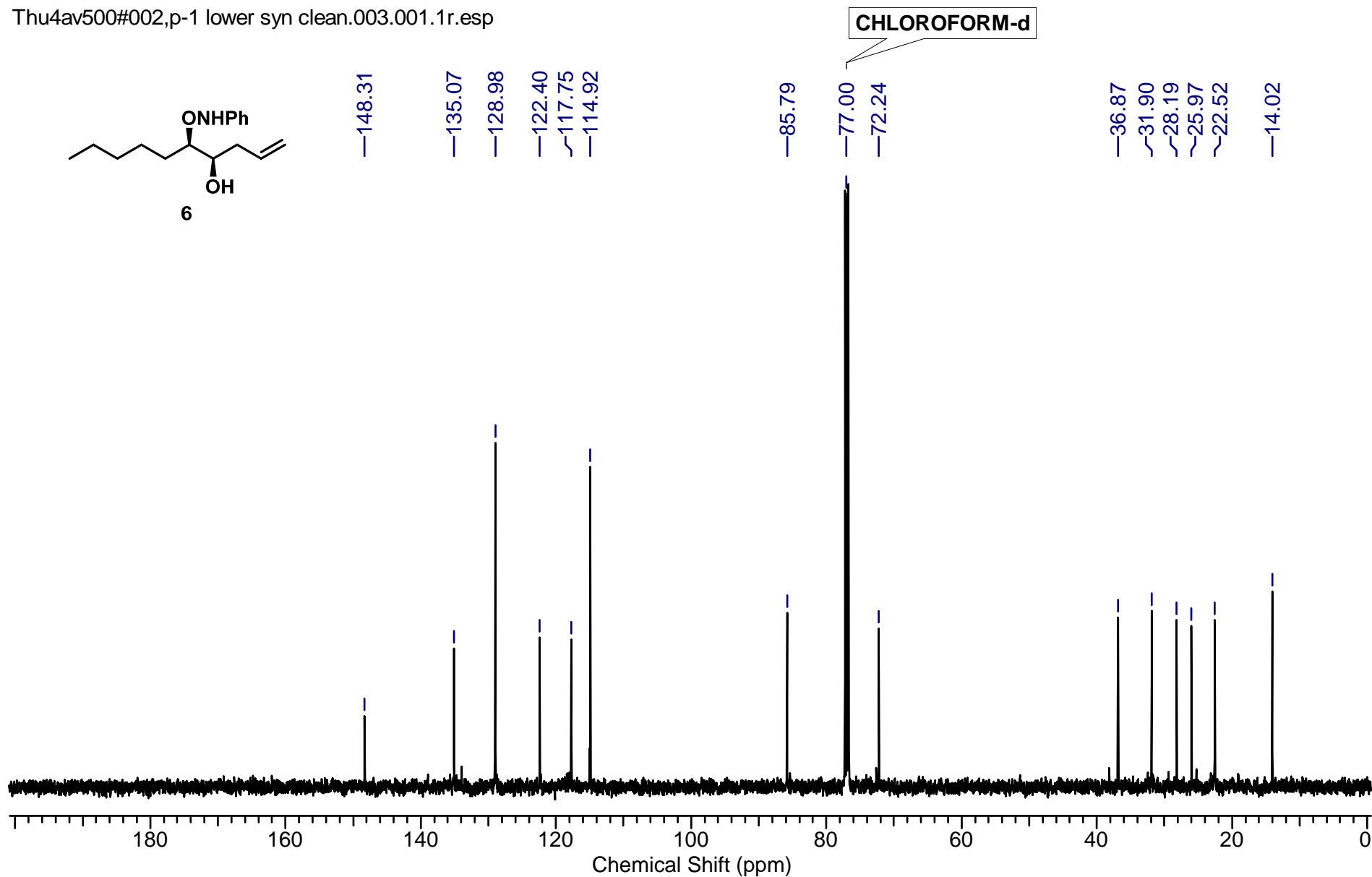
# $^1\text{H}$ NMR (500MHz, $\text{CDCl}_3$ ) of the compound (4*R*,5*R*)-5-((phenylamino)oxy)dec-1-en-4-ol 6:

Thu4av500#002(m) lower syn clean.001.001.1r.esp

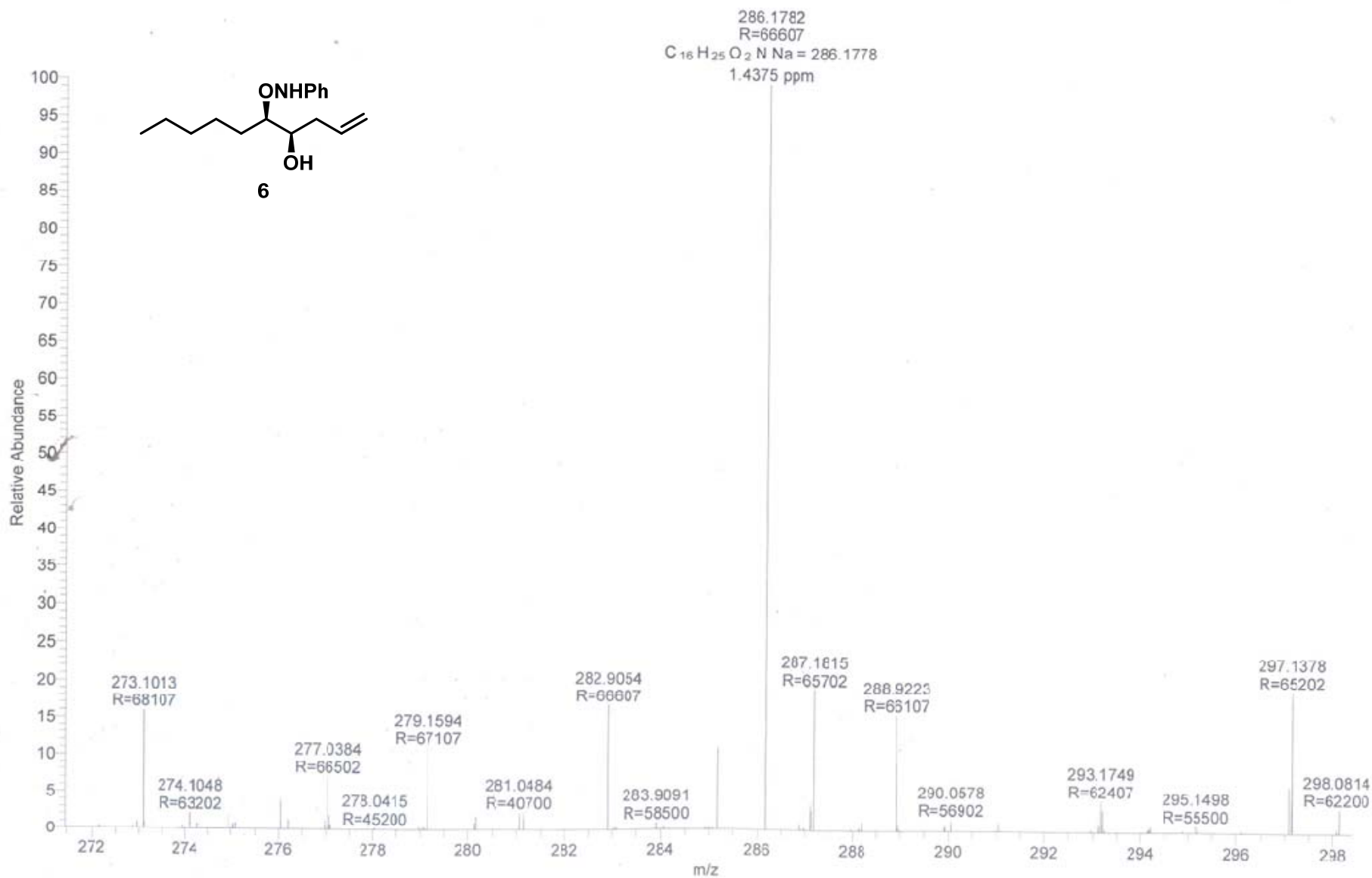


# $^{13}\text{C}$ NMR (125MHz, $\text{CDCl}_3$ ) of the compound (4*R*,5*R*)-5-((phenylamino)oxy)dec-1-en-4-ol 6:

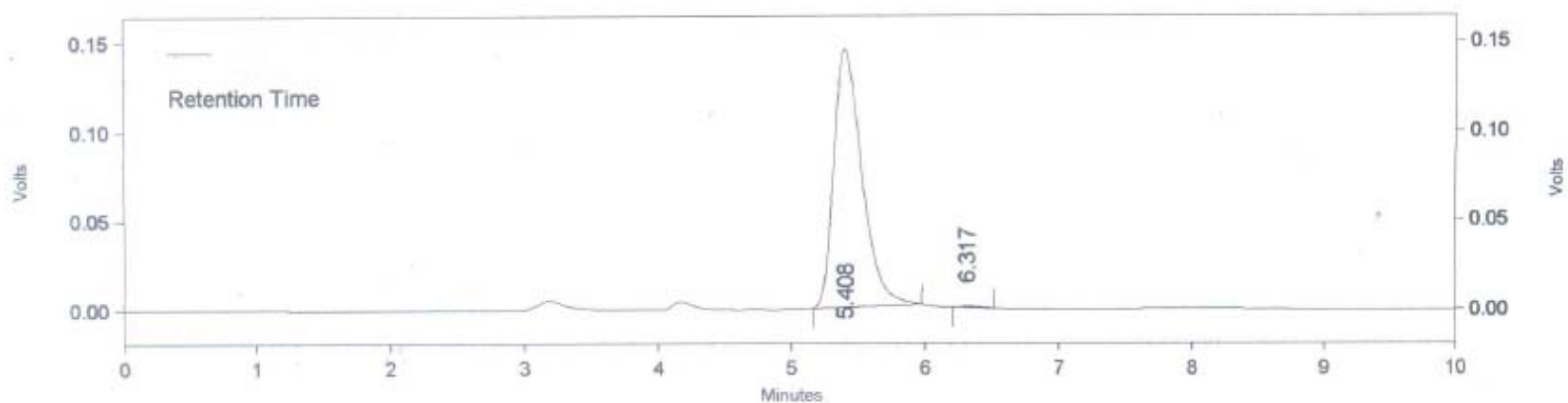
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UNR-A-1 #132 RT: 0.59 AV: 1 NL: 2.54E7  
T: FTMS + p ESI Full ms [36.00-1290.00]



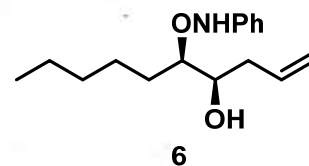
## HPLC (*ee*) of the compound (4*R*,5*R*)-5-((phenylamino)oxy)dec-1-en-4-ol 6:



Detector A - 1 (230nm)

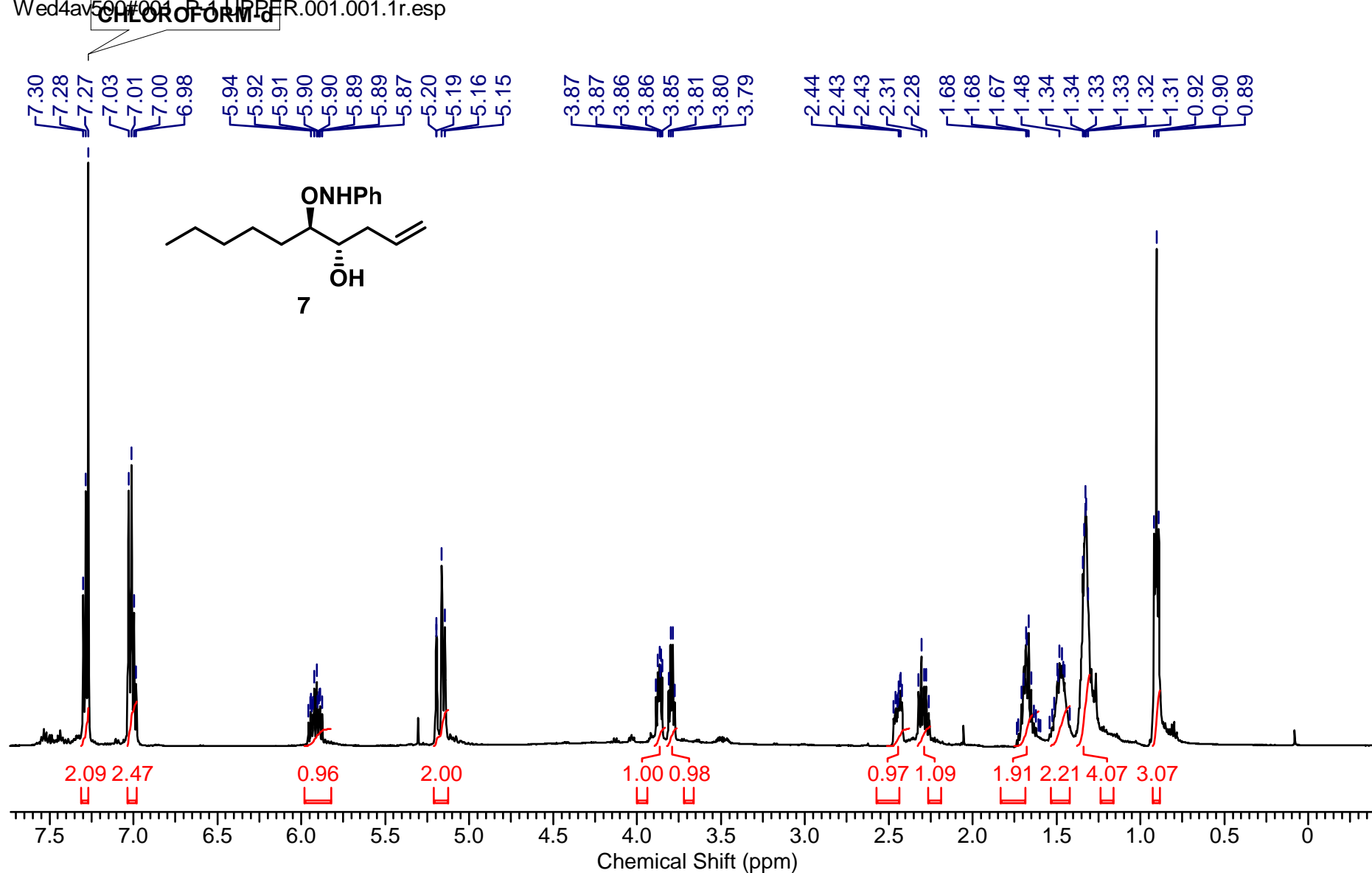
Pk #	Retention Time	Area	Area %
1	5.408	2119412	99.713
2	6.317	6108	0.287
<b>Totals</b>		<b>2125520</b>	<b>100.000</b>

Project Leader :Dr. Tripathi P.K.  
 Column :Chiralcel OD-H (250mm x 4.6mm)  
 Mobile Phase :IPA:n-Hexane (10 : 90)  
 Wavelength : 230nm  
 Flow Rate :1mL/min (620psi)  
 Conc. : 1mg/1ml  
 Inj vol- : 2uL



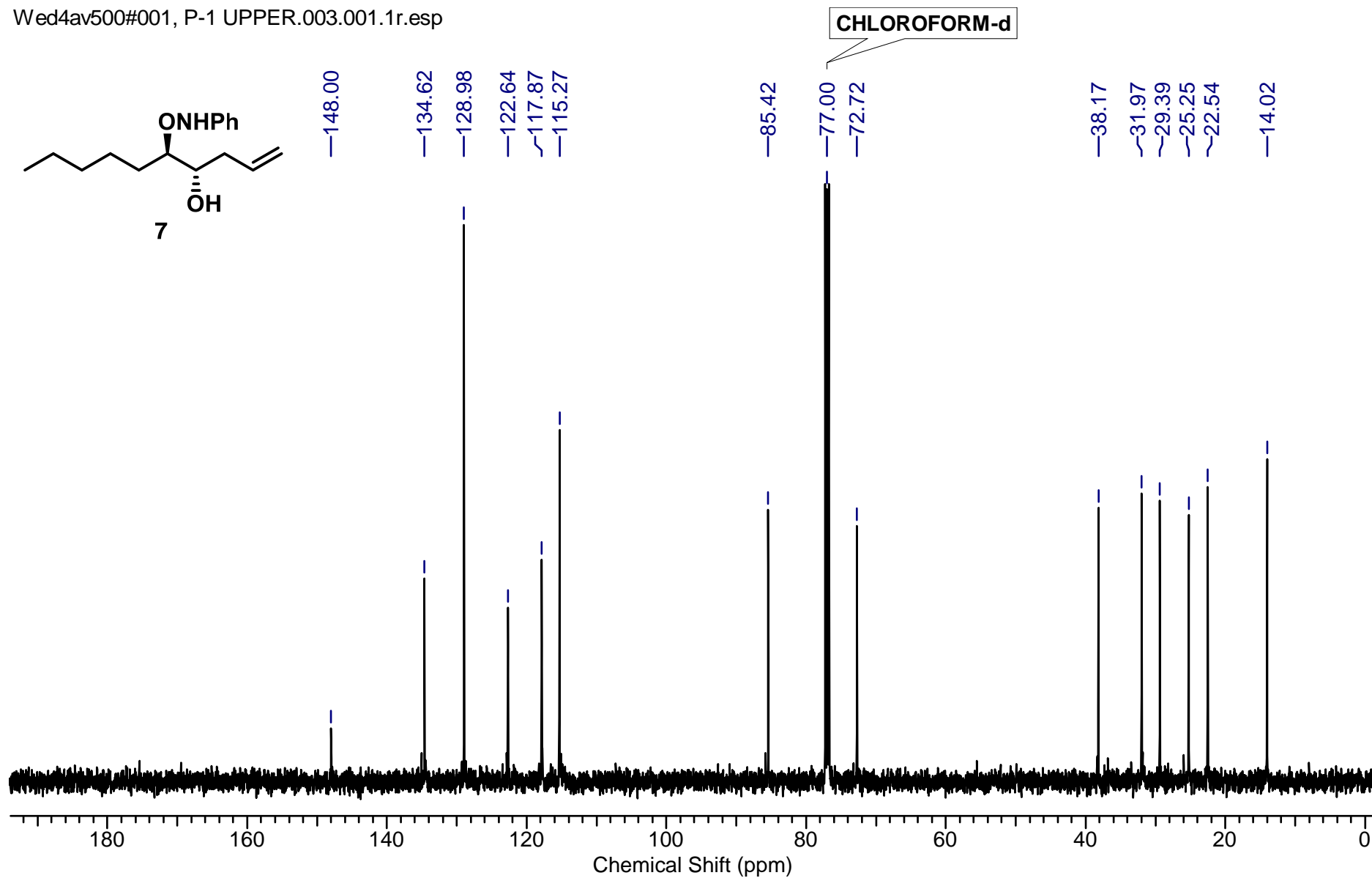
# $^1\text{H}$ NMR (500MHz, $\text{CDCl}_3$ ) of the compound (4*S*,5*R*)-5-((phenylamino)oxy)dec-1-en-4-ol 7:

Wed4av500#001\_P-1\_LIPFER.001.001.1r.esp

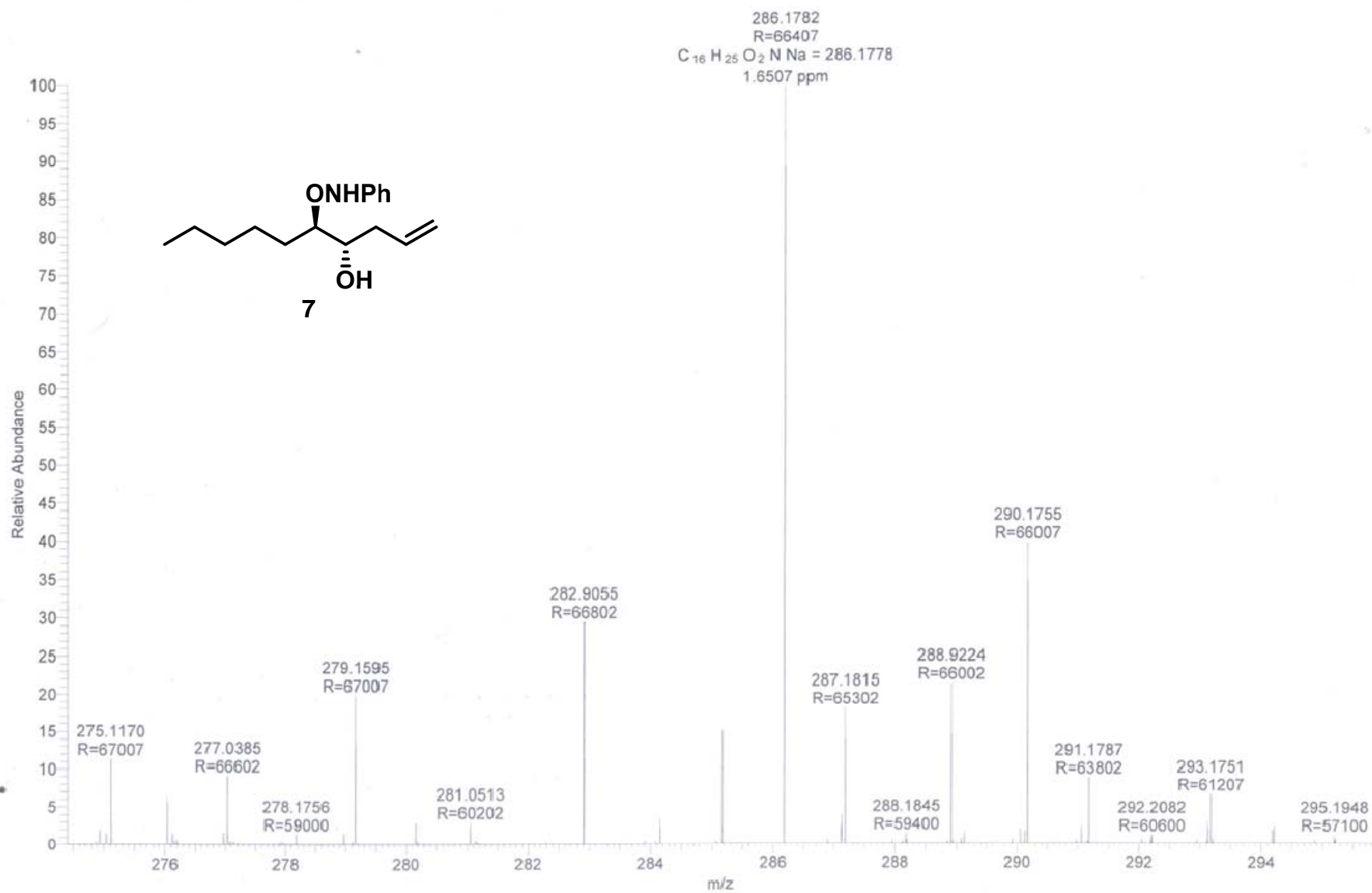


# $^{13}\text{C}$ NMR (125MHz, $\text{CDCl}_3$ ) of the compound (4*S*,5*R*)-5-((phenylamino)oxy)dec-1-en-4-ol 3:

Wed4av500#001, P-1 UPPER.003.001.1r.esp

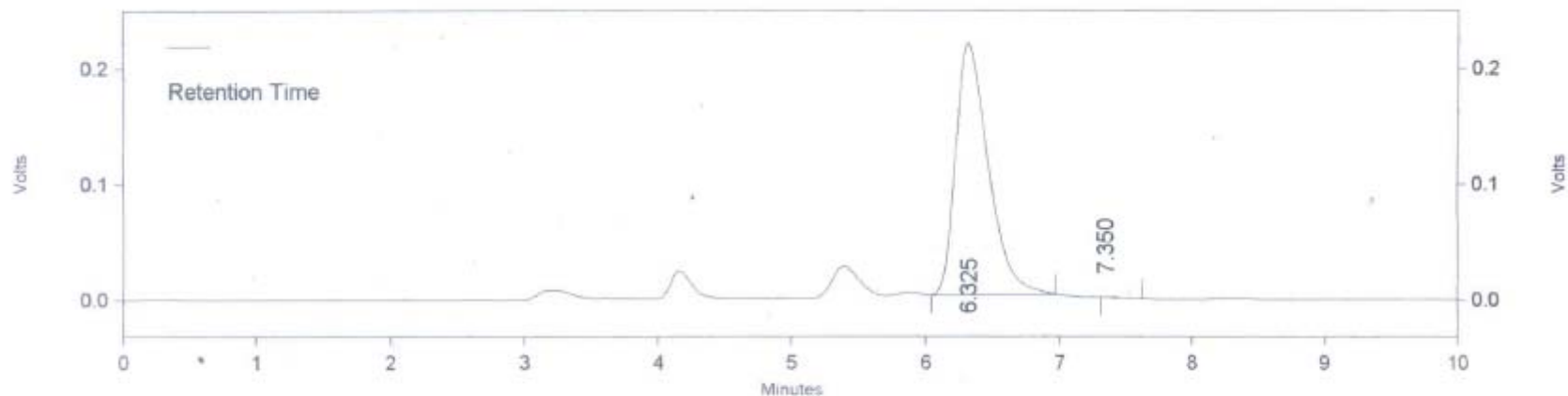


UNR-A-11 #137 RT: 0.61 AV: 1 NL: 1.80E7  
T: FTMS + p ESI Full ms [86.00-1290.00]





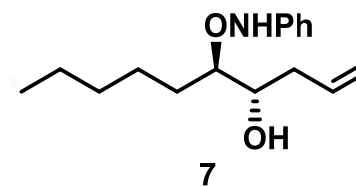
# HPLC (*ee*) of the compound (4*S*,5*R*)-5-((phenylamino)oxy)dec-1-en-4-ol 7:



Detector A - 1 (230nm)

Pk #	Retention Time	Area	Area %
1	6.325	3693207	99.915
2	7.350	3129	0.085
Totals		3696336	100.000

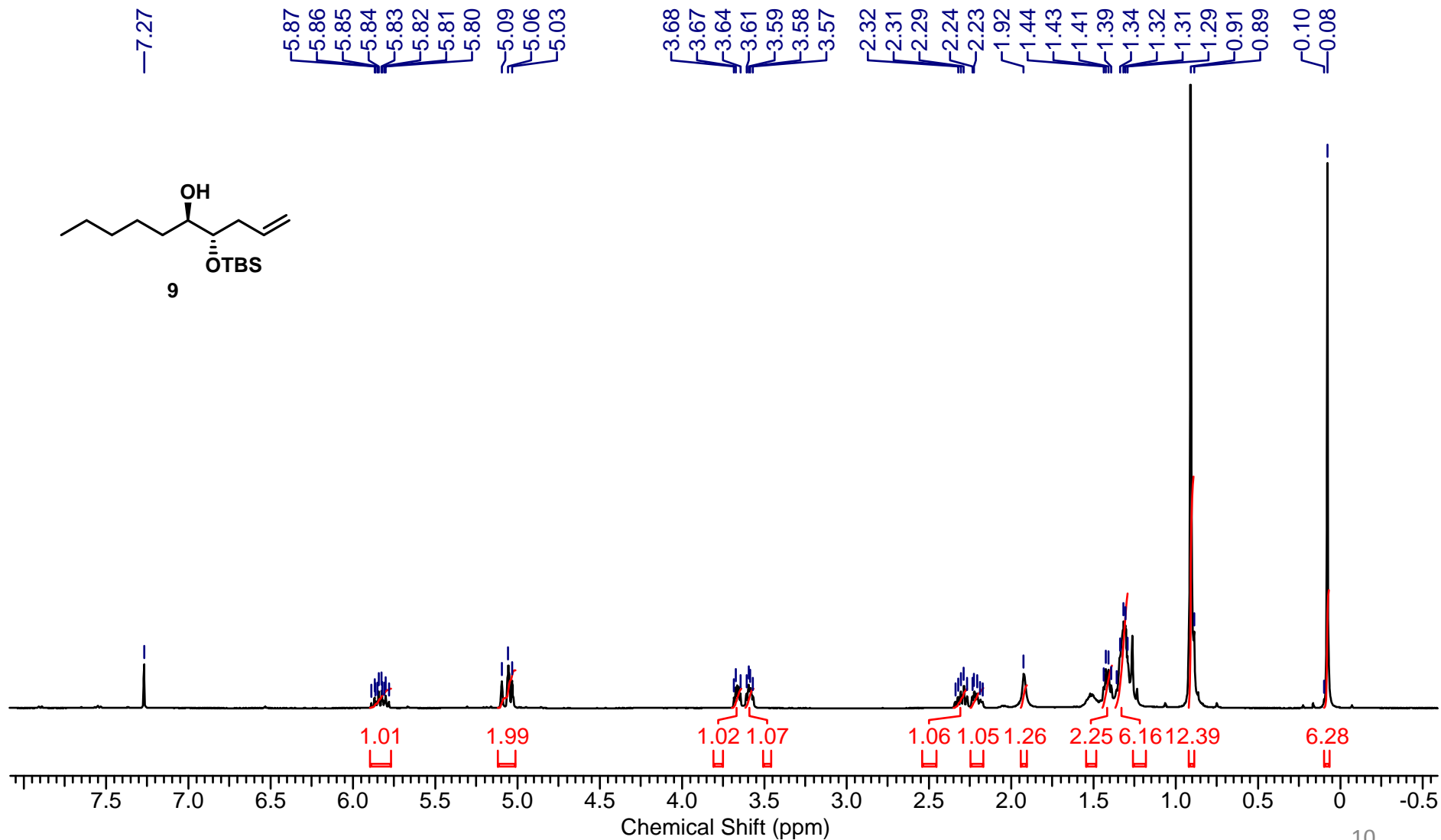
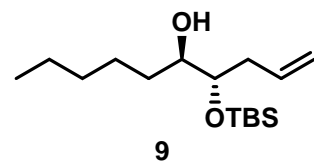
Project Leader : Dr. Tripathi P.K.  
 Column : Chiralcel OD-H (250mm x 4.6mm)  
 Mobile Phase : IPA:n-Hexane (10 : 90)  
 Wavelength : 230nm  
 Flow Rate : 1mL/min (620psi)  
 Conc. : 1mg/1ml  
 Inj vol- : 2uL



**$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) of the compound (4*S*,5*R*)-4-((tert-butyldimethylsilyl)oxy)dec-1-en-5-ol 9:**

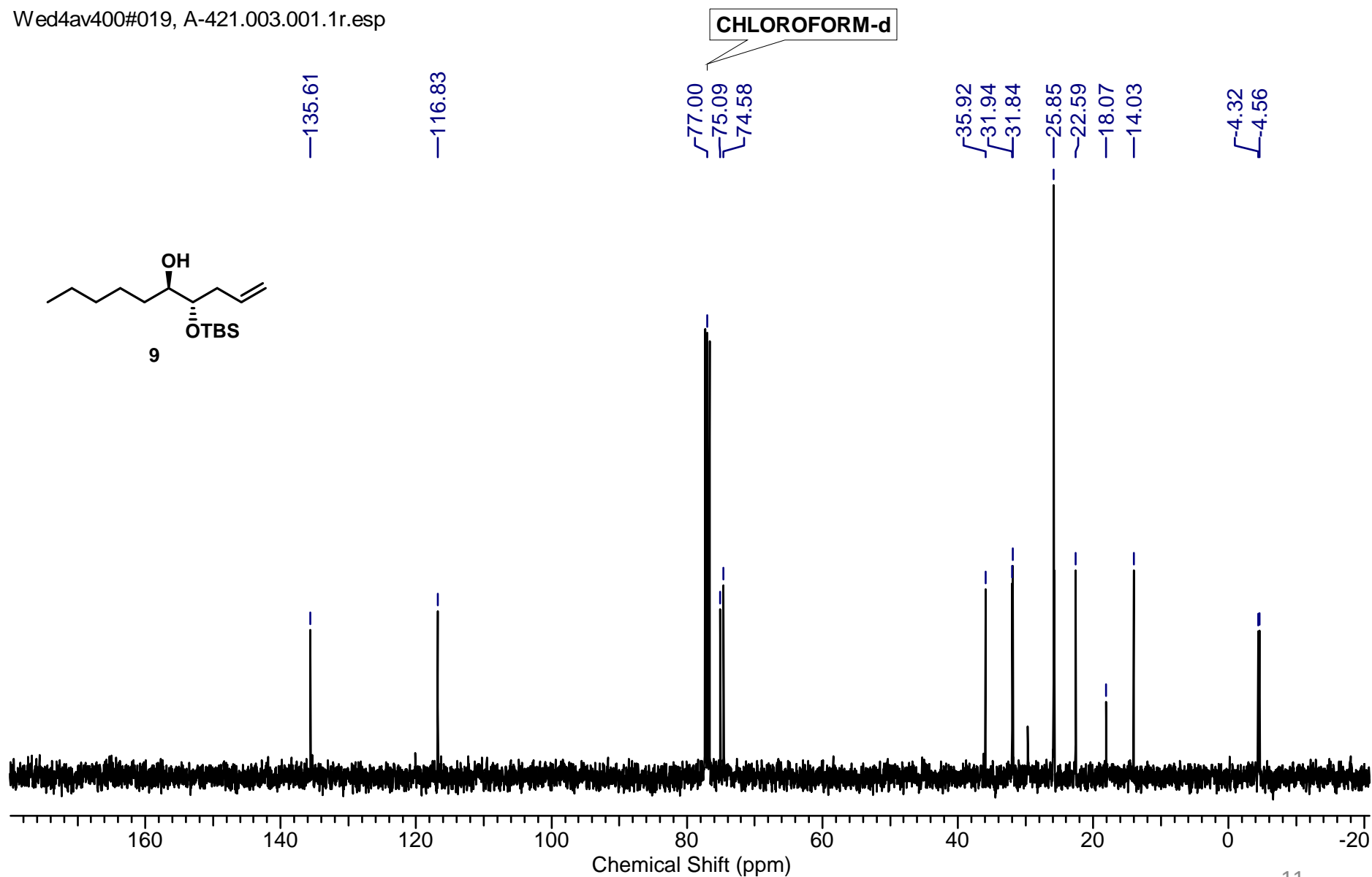
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CHLOROFORM-d



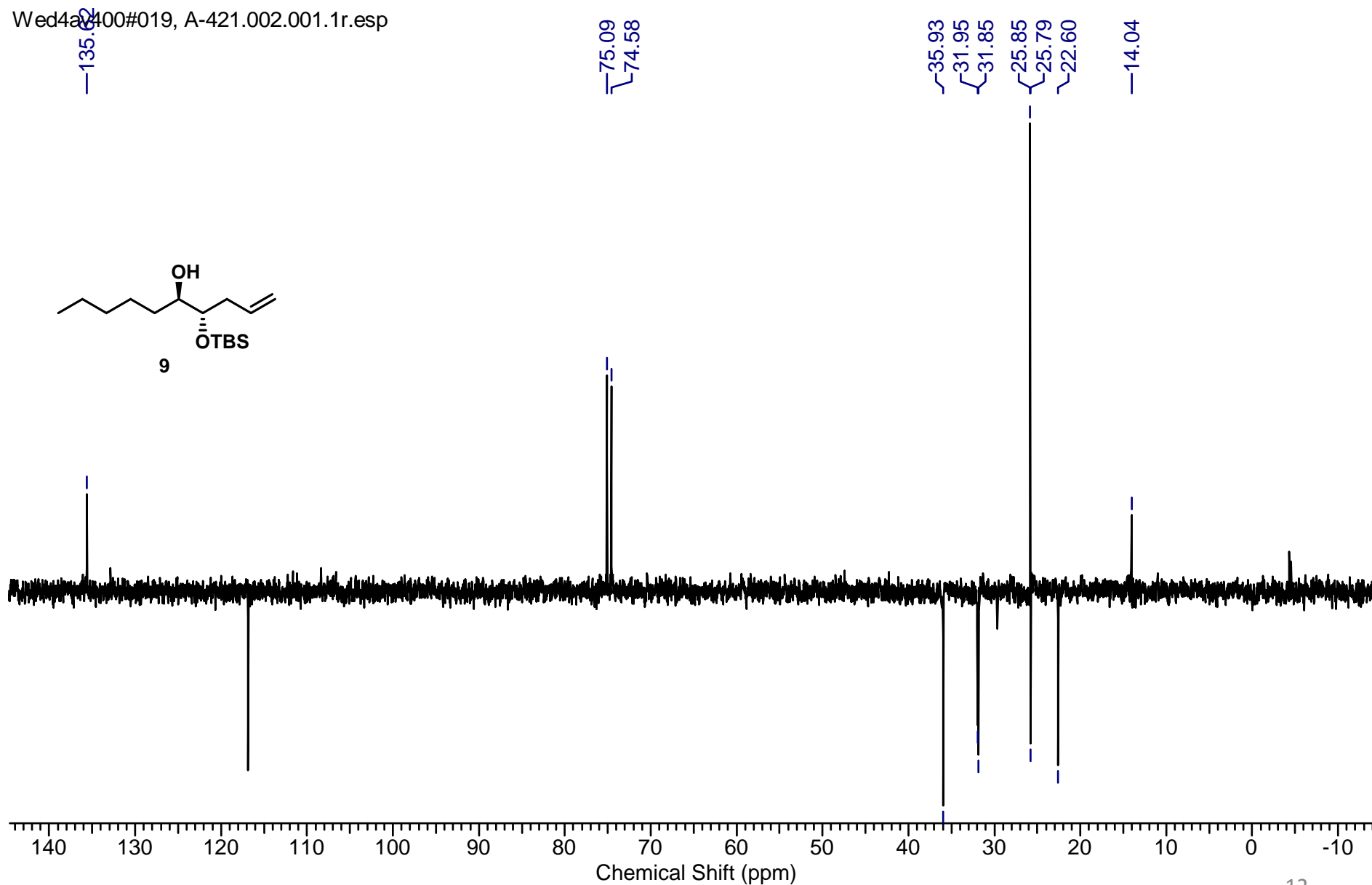
**$^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ) of the compound (4*S*,5*R*)-4-((tert-butyldimethylsilyl)oxy)dec-1-en-5-ol 9:**

Wed4av400#019, A-421.003.001.1r.esp

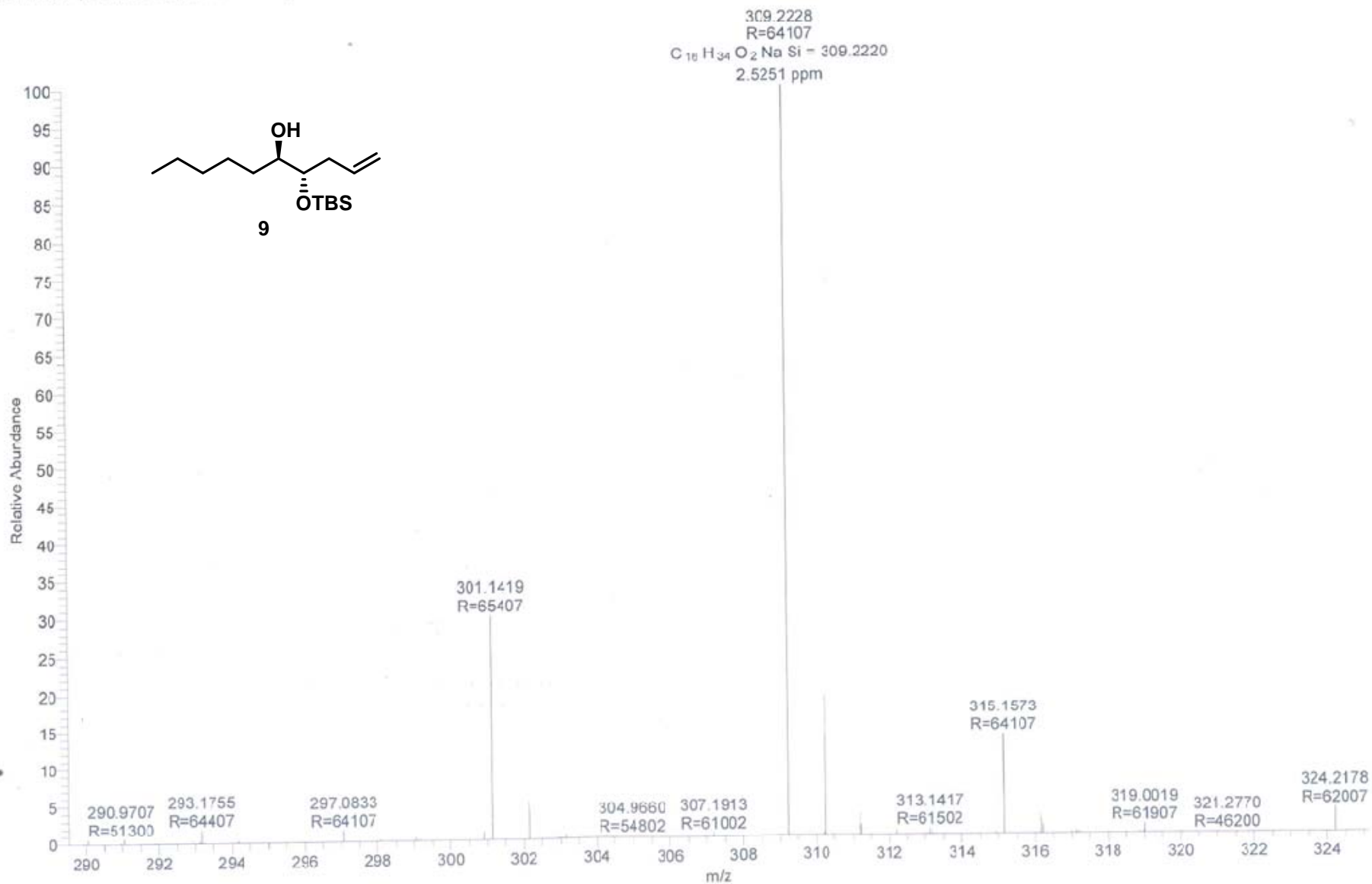
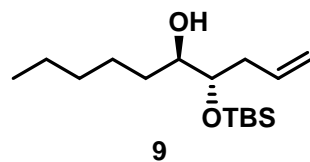


# DEPT NMR (100MHz, CDCl<sub>3</sub>) of the compound (4*S*,5*R*)-4-((*tert*-butyldimethylsilyl)oxy)dec-1-en-5-ol 9:

Wed4a04100#019, A-421.002.001.1r.esp

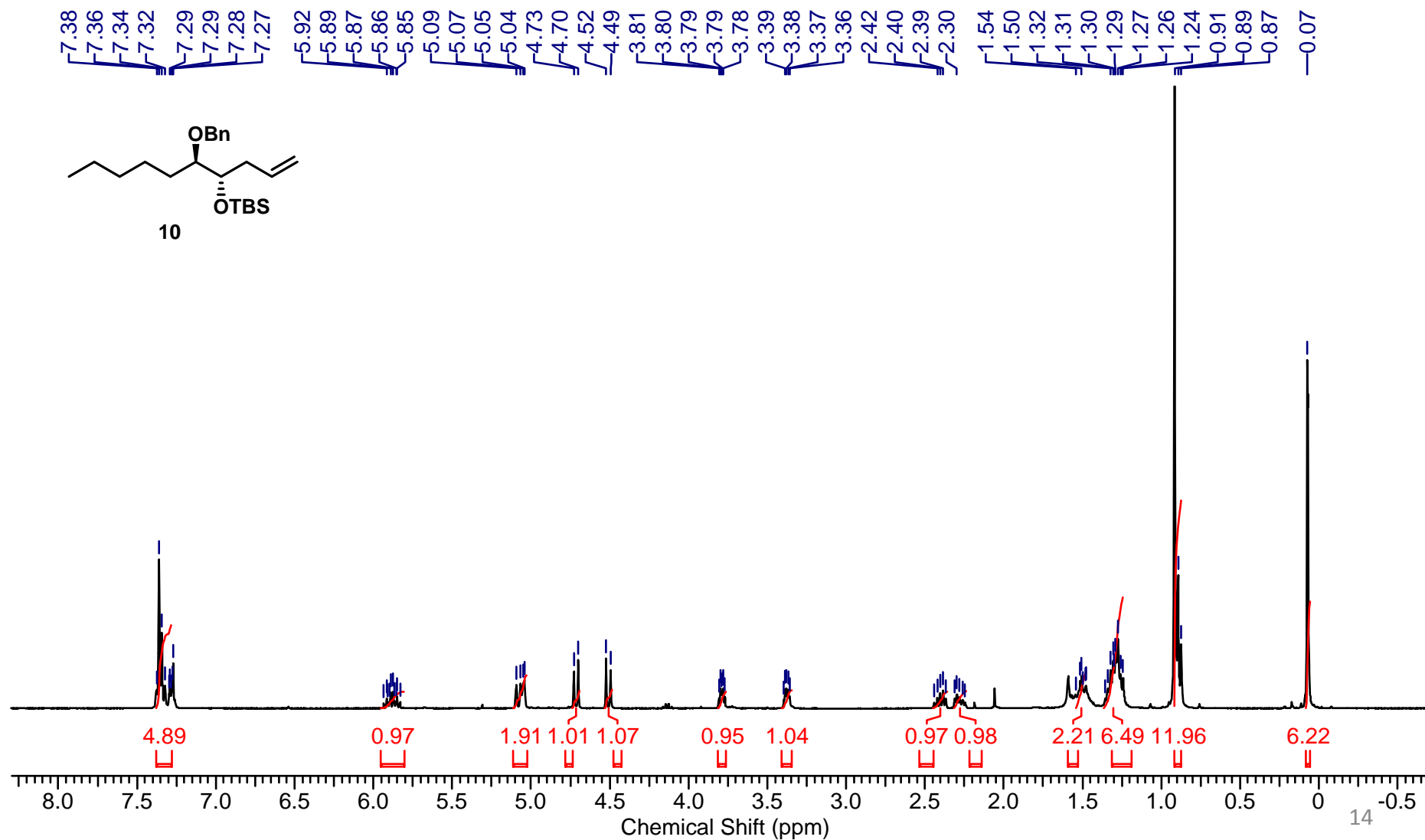


UNR-A-12 #253 RT: 1.12 AV: 1 NL 9.51E7  
T: FTMS + p ESI Full ms [80.00-1290.00]



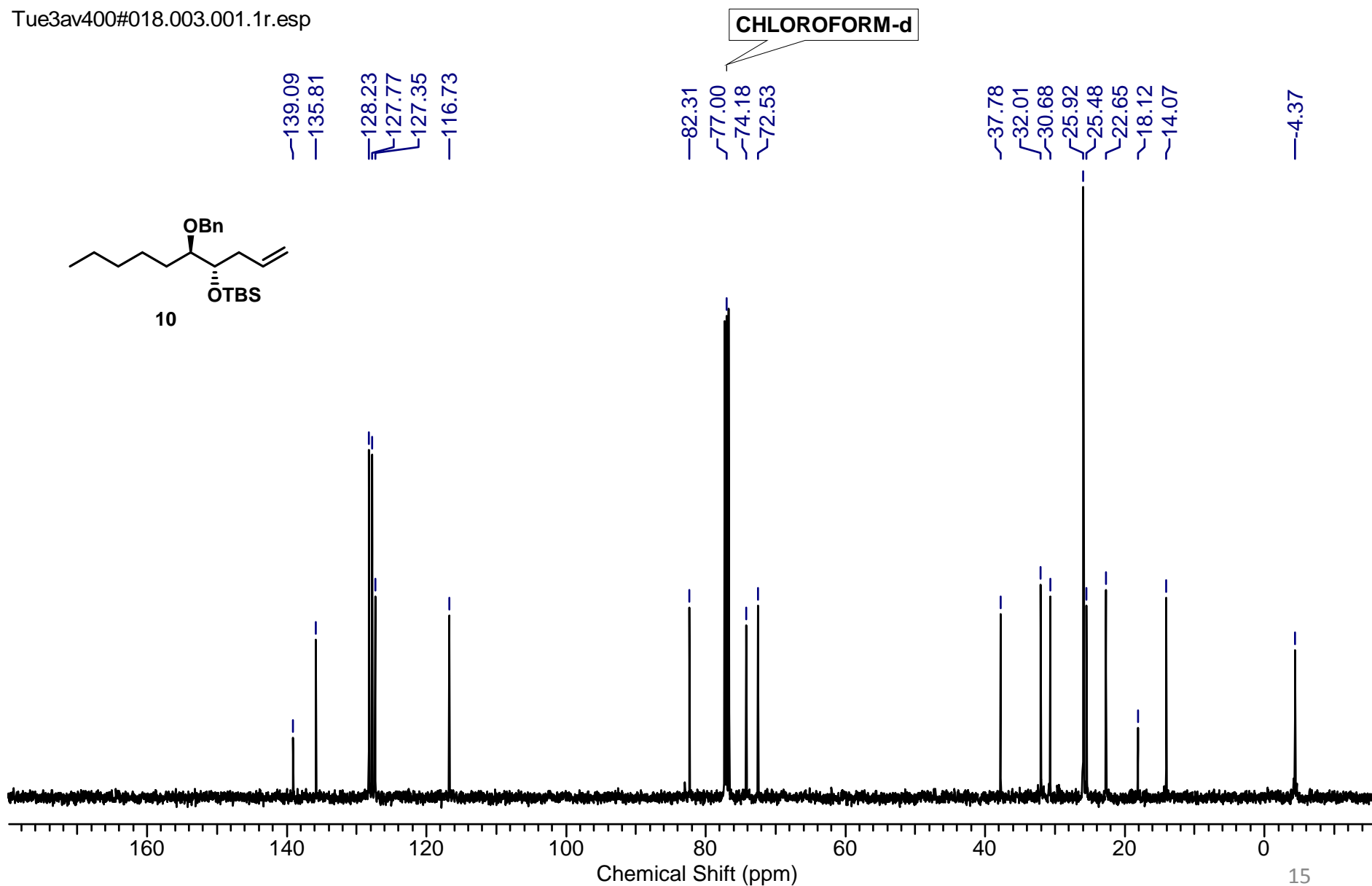
**$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) of the compound (((4*S*,5*R*)-5-(benzyloxy)dec-1-en-4-yl)oxy)(*tert*-butyl) dimethylsilane 10:**

Tue3av400#018.0010011-000  
CHLOROFORM-d

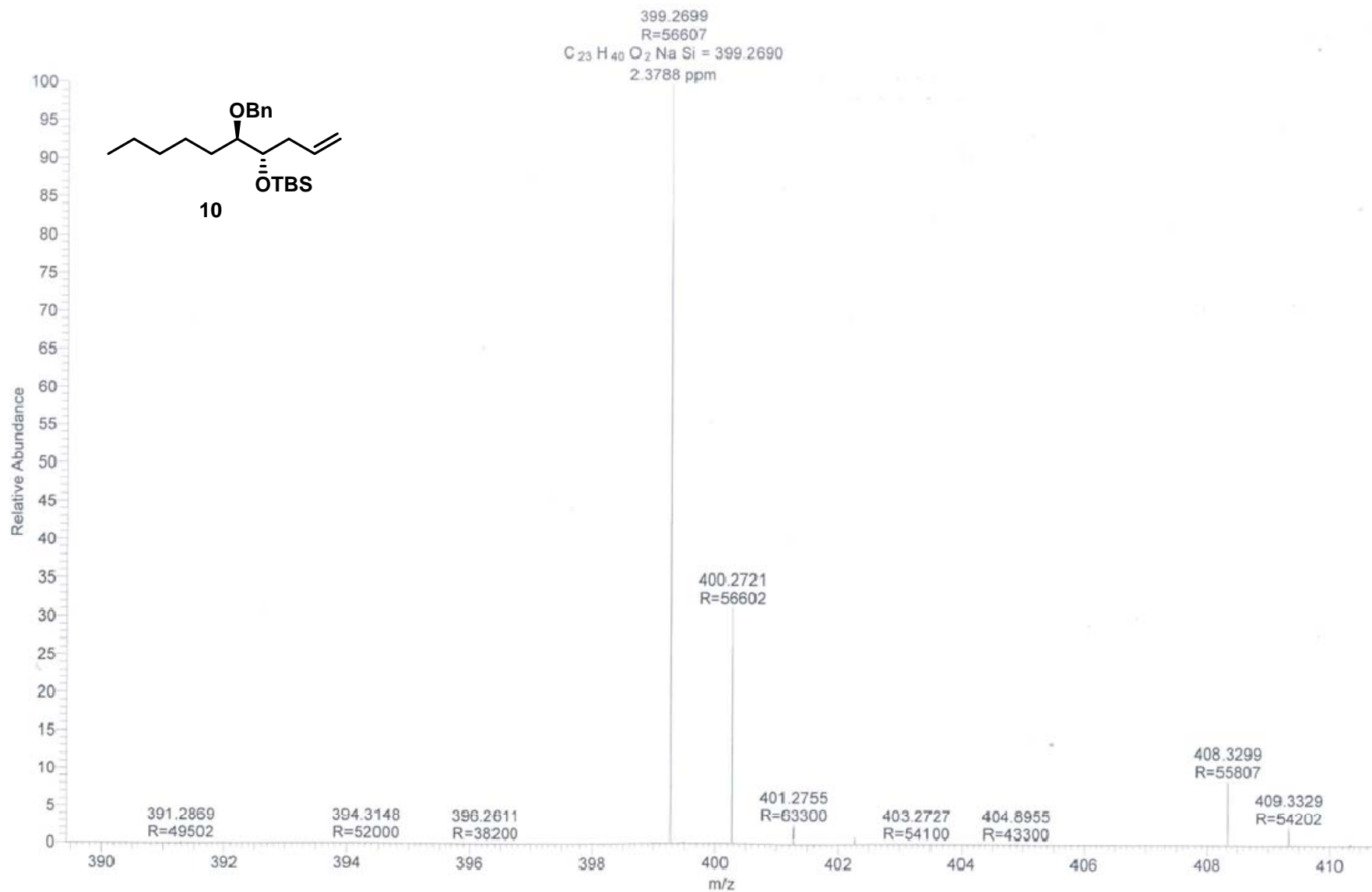


**$^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ) of the compound (((4*S*,5*R*)-5-(benzyloxy)dec-1-en-4-yl)oxy)(tert-butyl)dimethylsilane 10:**

Tue3av400#018.003.001.1r.esp



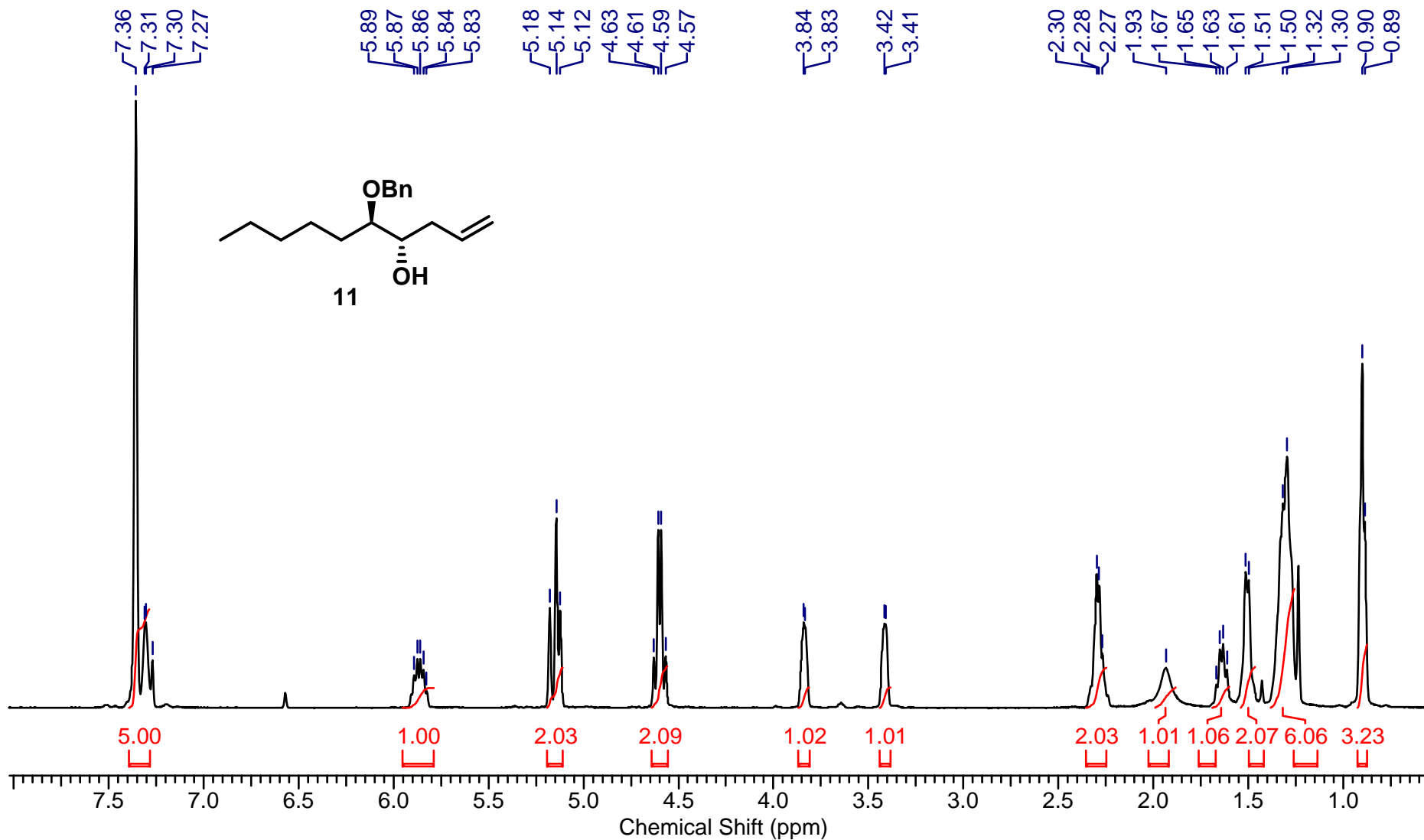
UNR-A-13 #709 RT: 3.16 AV: 1 NL: 3.97E8  
T: FTMS + p ESI Full ms [86.00-1290.00]





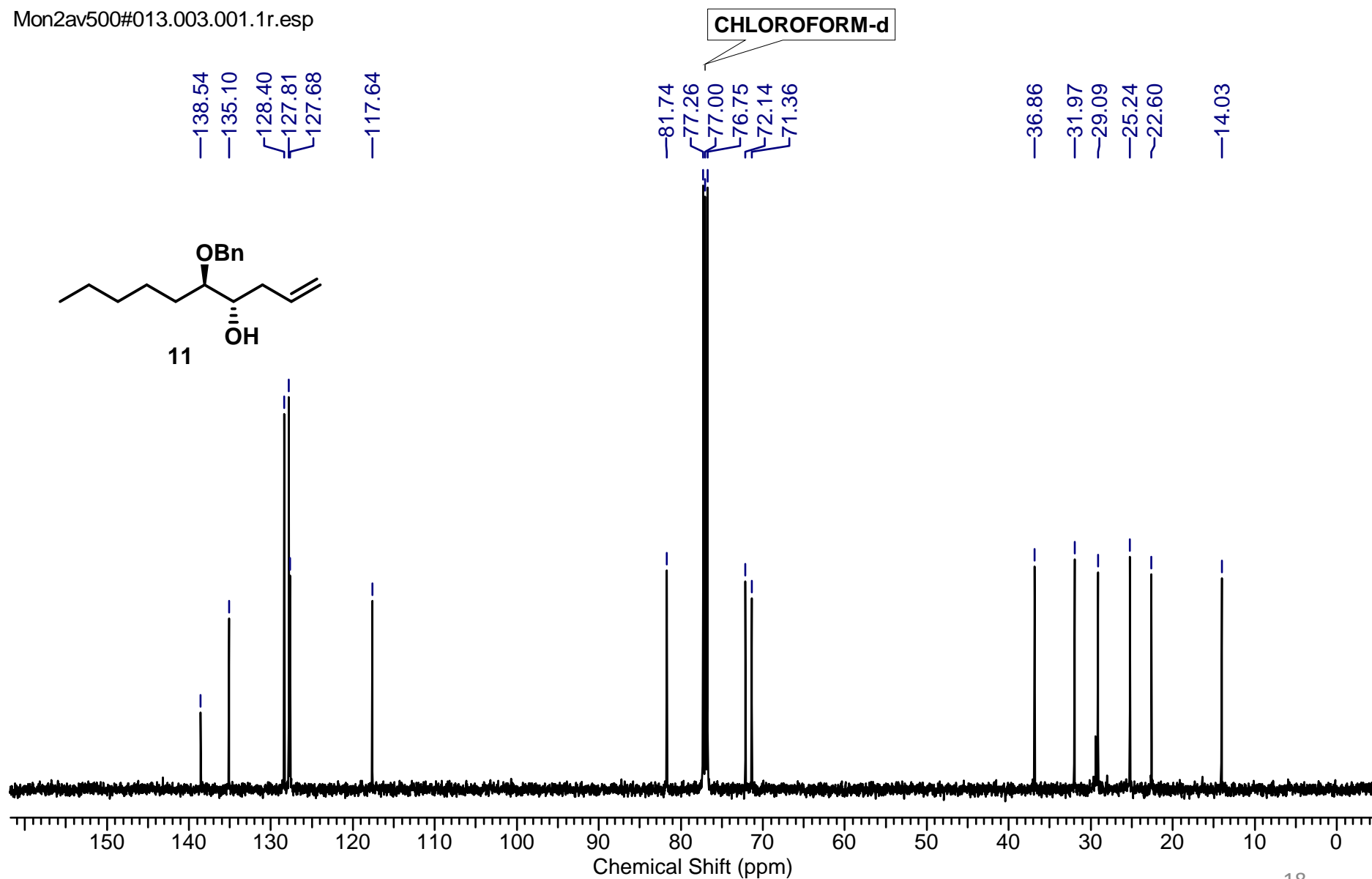
# $^1\text{H}$ NMR (500MHz, $\text{CDCl}_3$ ) of the compound (4*S*,5*R*)-5-(benzyloxy)dec-1-en-4-ol 11:

Mon2av500#013-001-001-1-esp  
CHLOROFORM-d

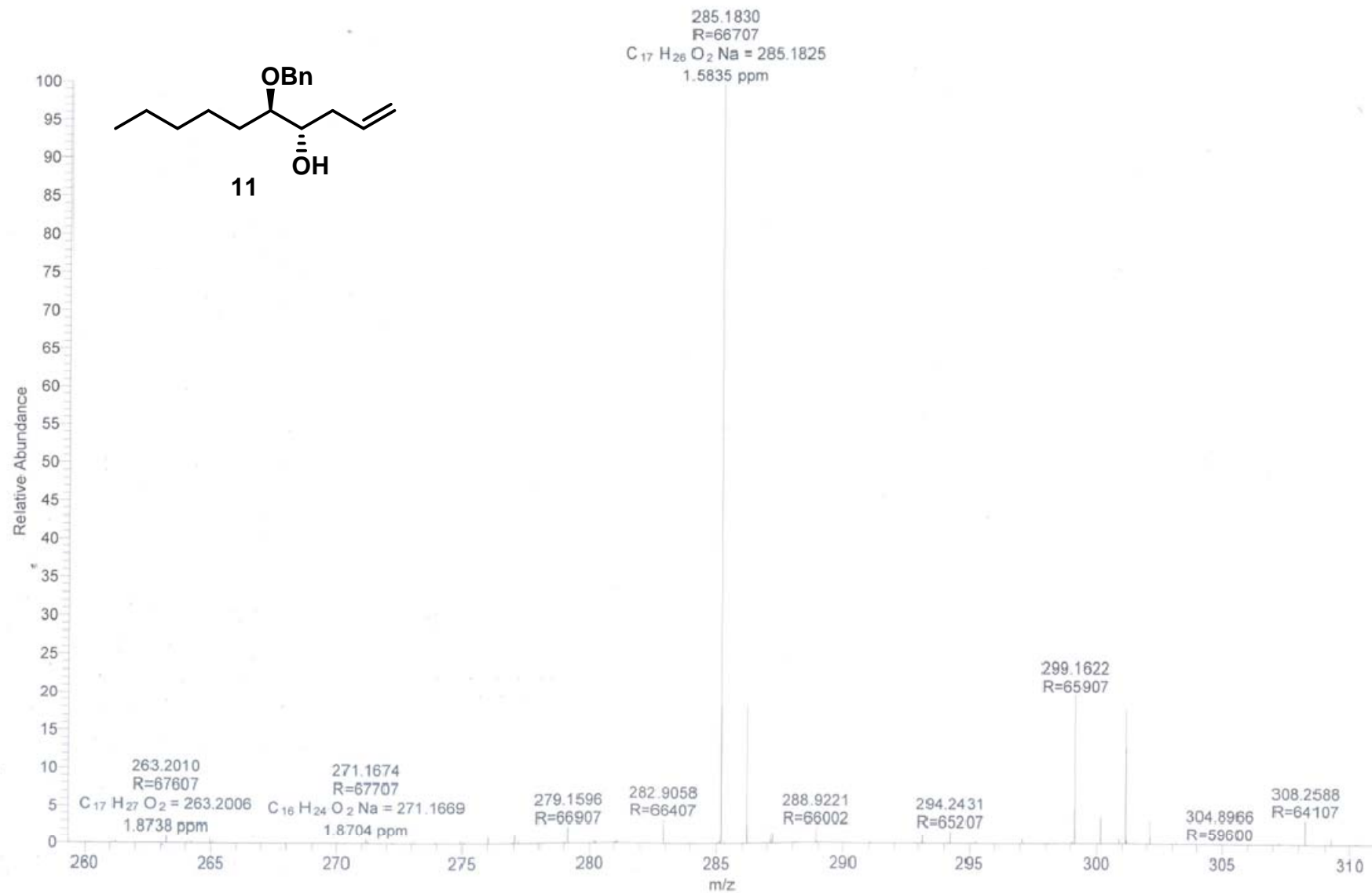


# $^{13}\text{C}$ NMR (125MHz, $\text{CDCl}_3$ ) of the compound (4*S*,5*R*)-5-(benzyloxy)dec-1-en-4-ol 11:

Mon2av500#013.003.001.1r.esp

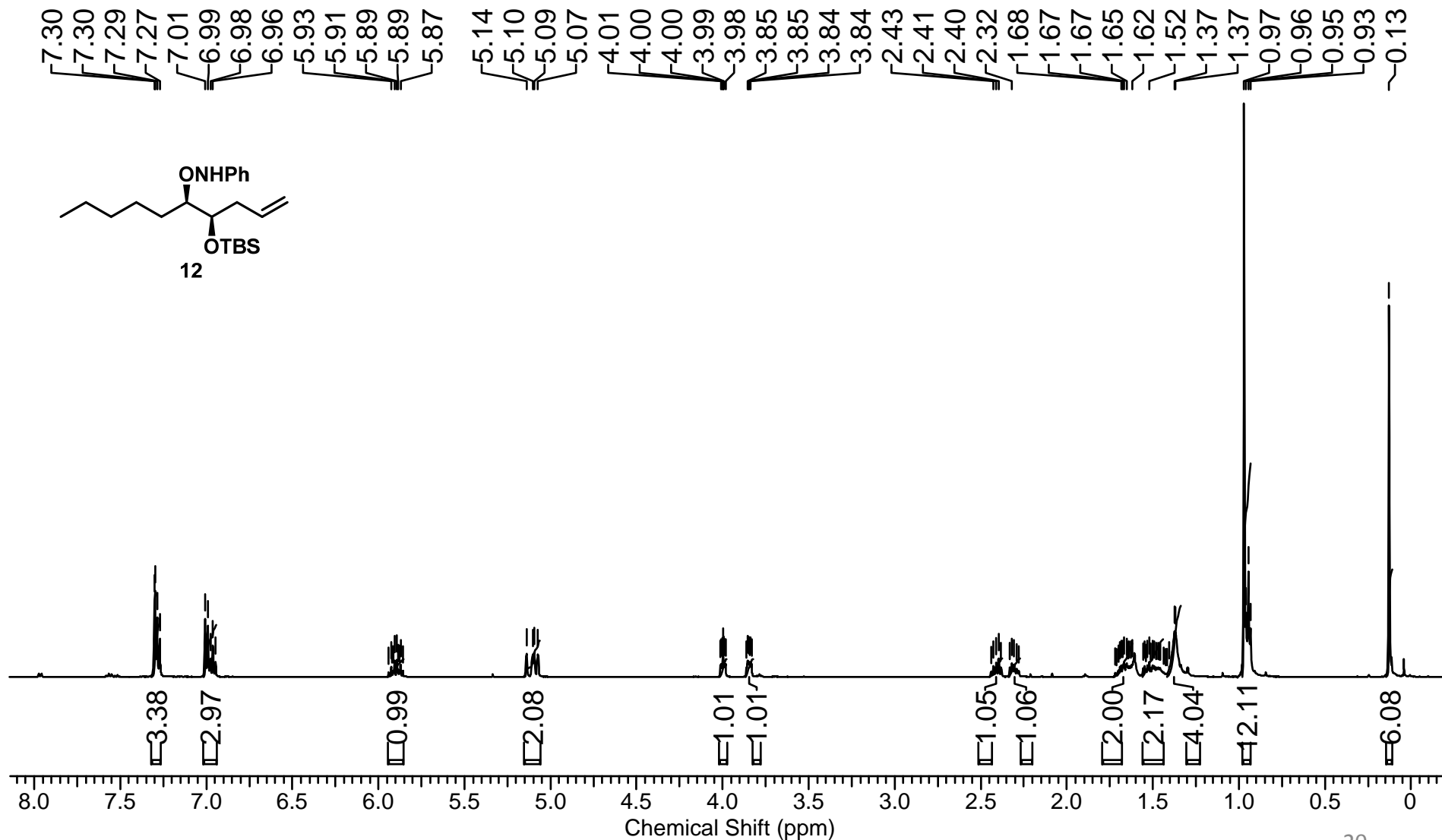


UNR-A-6 #140 RT: 0.62 AV: 1 NL: 1.64E8  
T: FTMS + p ESI Full ms [86.00-1290.00]



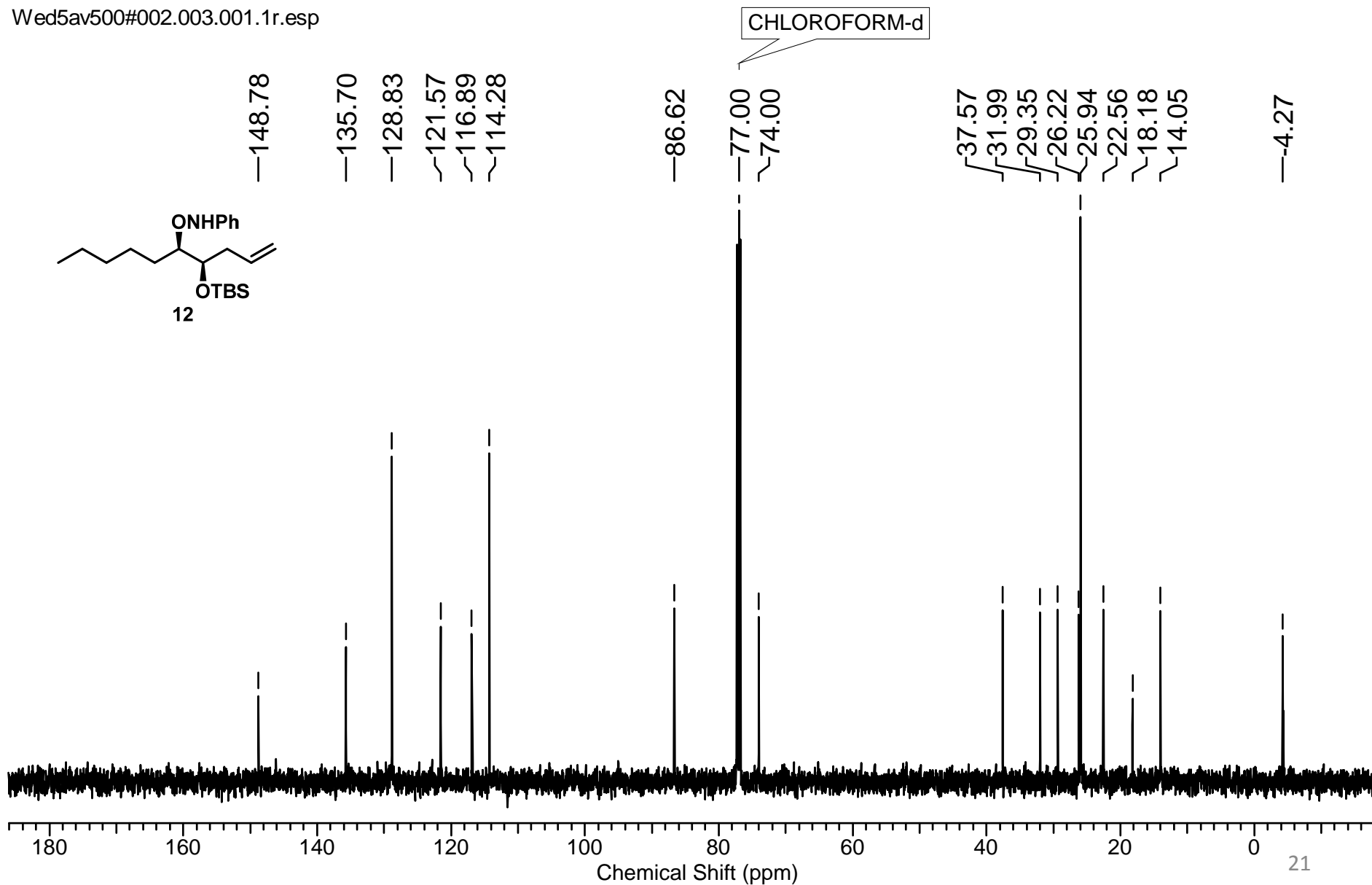
**<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of the compound O-((4R,5R)-4-((tert-butyldimethylsilyl)oxy)dec-1-en-5-yl)-N-phenylhydroxylamine 12:**

Wed5av500#002001500140899  
CHLOROFORM-d

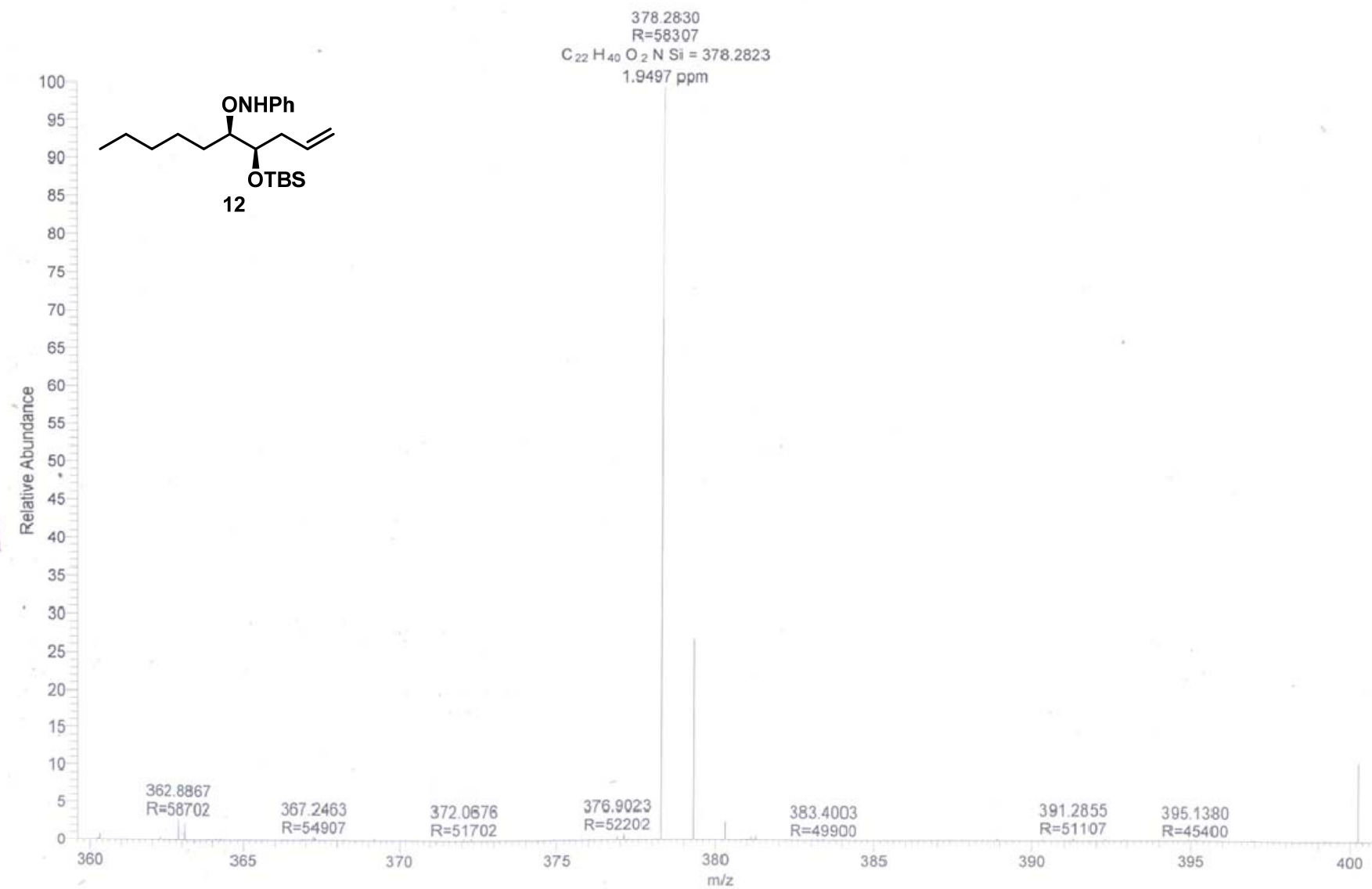


**$^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ) of the compound O-((4R,5R)-4-((tert-butyldimethylsilyl)oxy)dec-1-en-5-yl)-N-phenylhydroxylamine 12:**

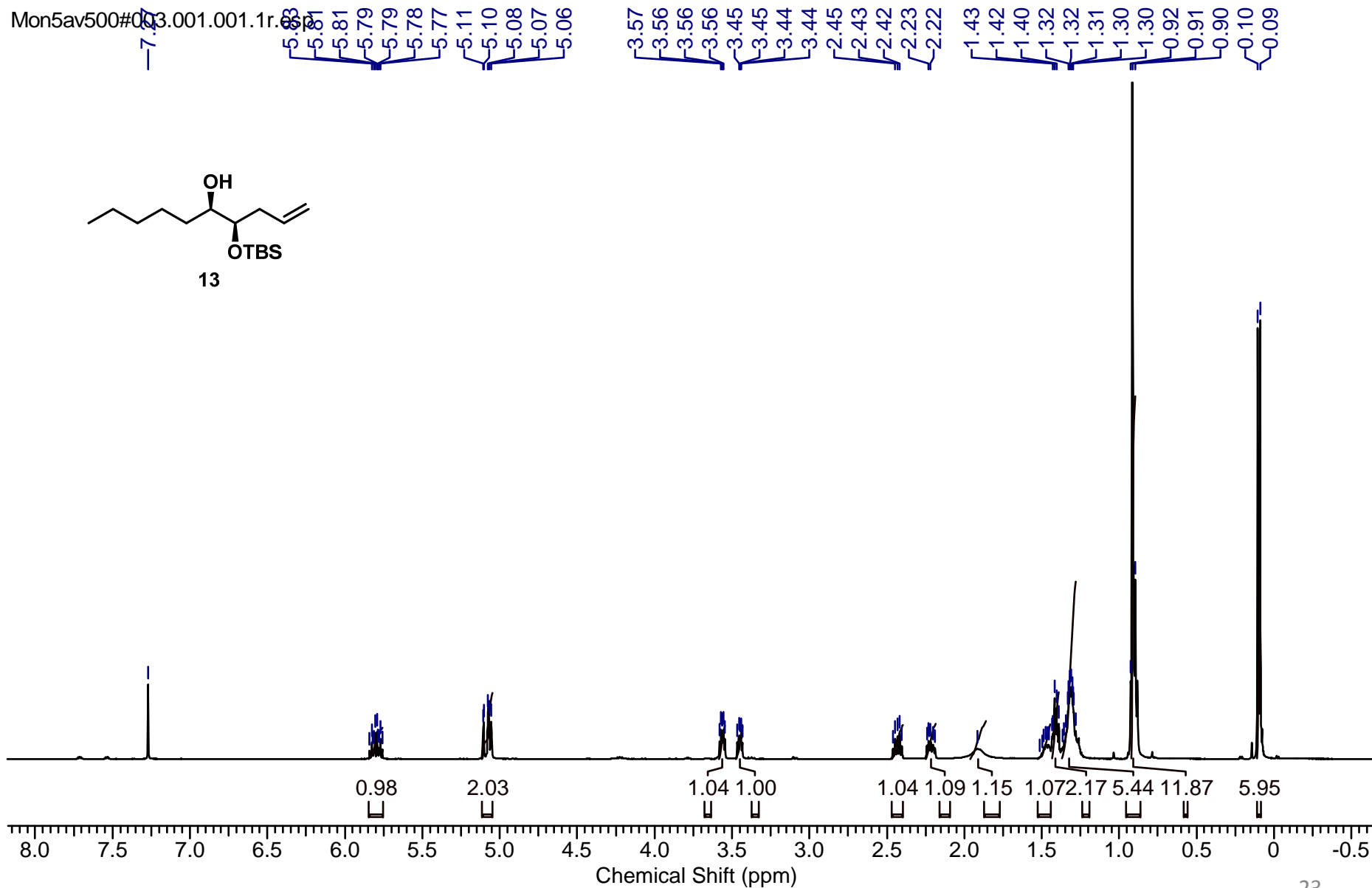
Wed5av500#002.003.001.1r.esp



UNR-A-2 #466 RT: 2.08 AV: 1 NL: 6.39E7  
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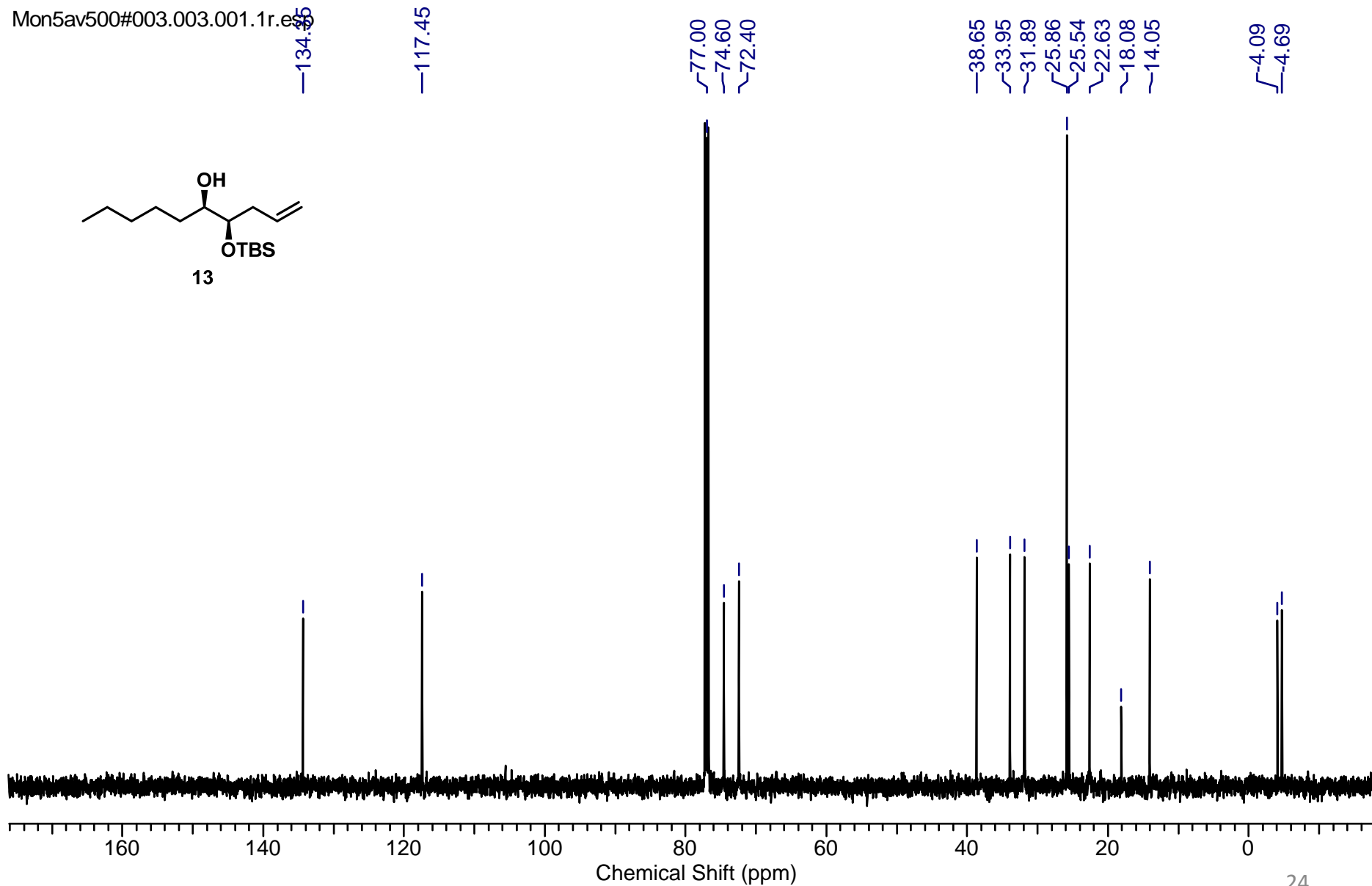
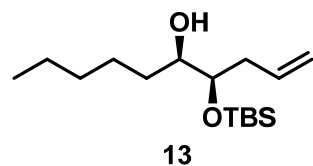


**$^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of the compound (4*R*,5*R*)-4-((tert-butyldimethylsilyl)oxy)dec-1-en-5-ol 13:**



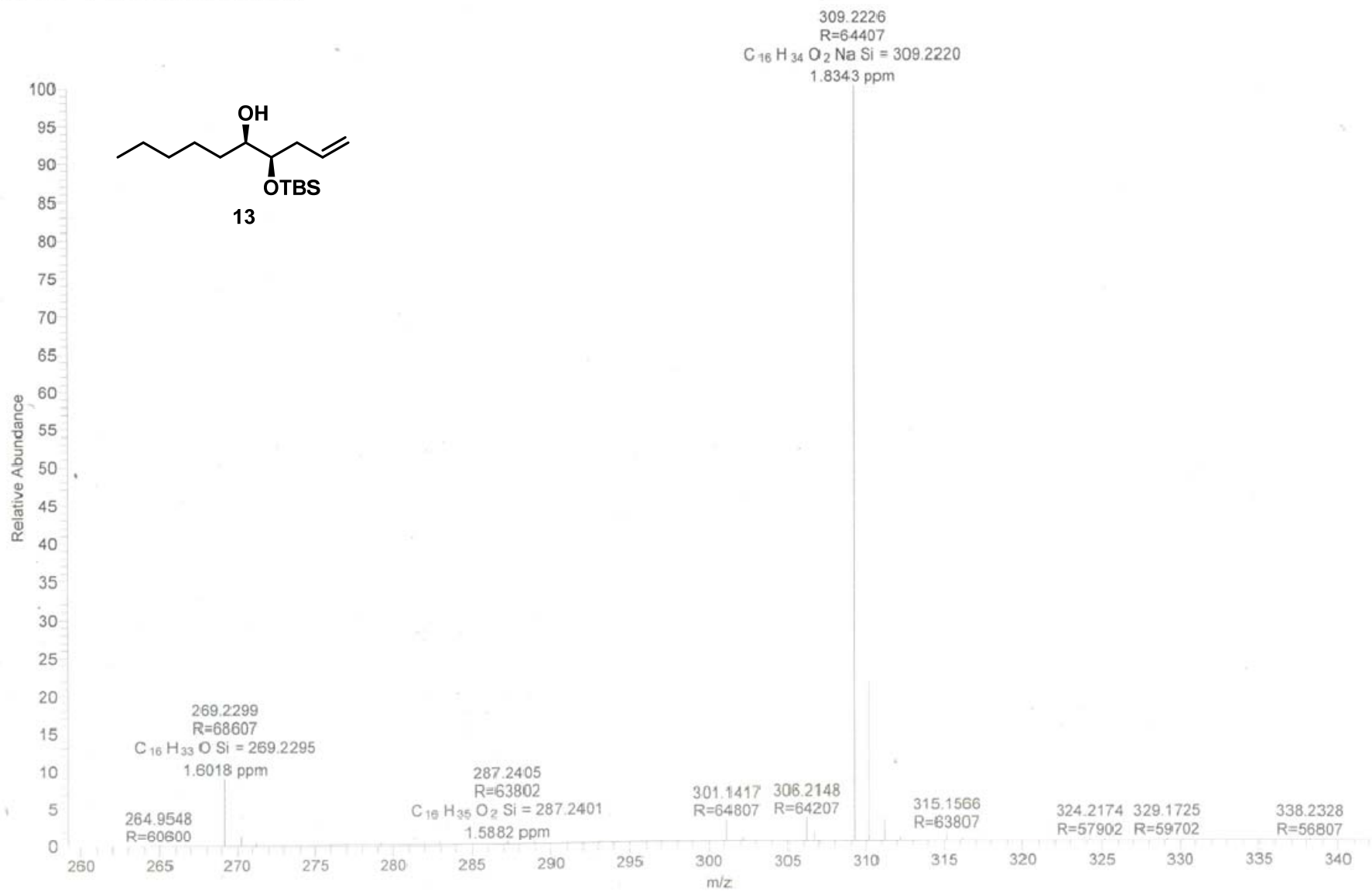
**$^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ) of the compound (4*R*,5*R*)-4-((tert-butyldimethylsilyl)oxy)dec-1-en-5-ol 13:**

Mon5av500#003.003.001.1r.e



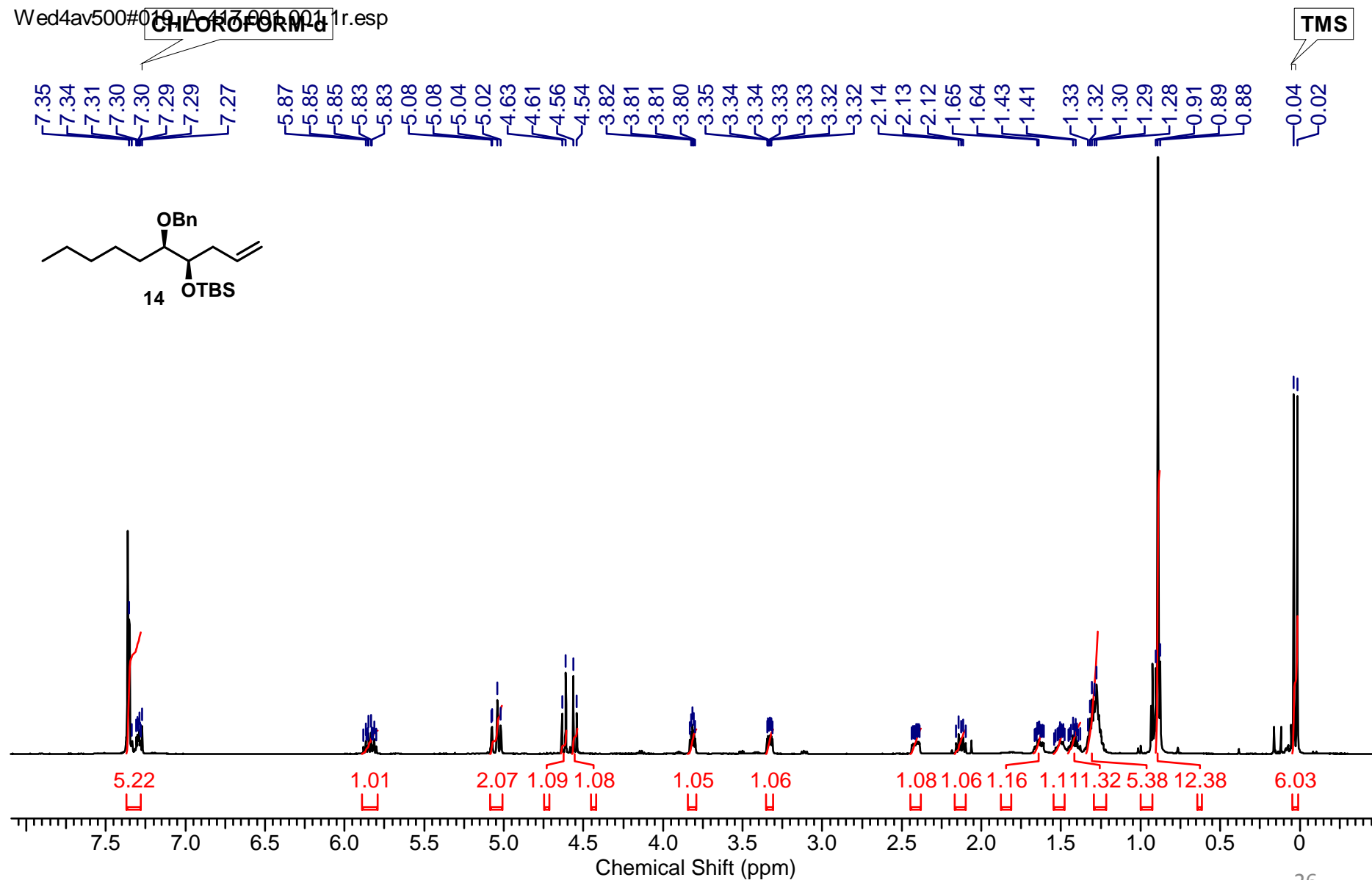


UNR-A-3 #254 RT: 1.13 AV: 1 NL: 1.12E9  
T: FTMS + p ESI Full ms [86.00-1290.00]



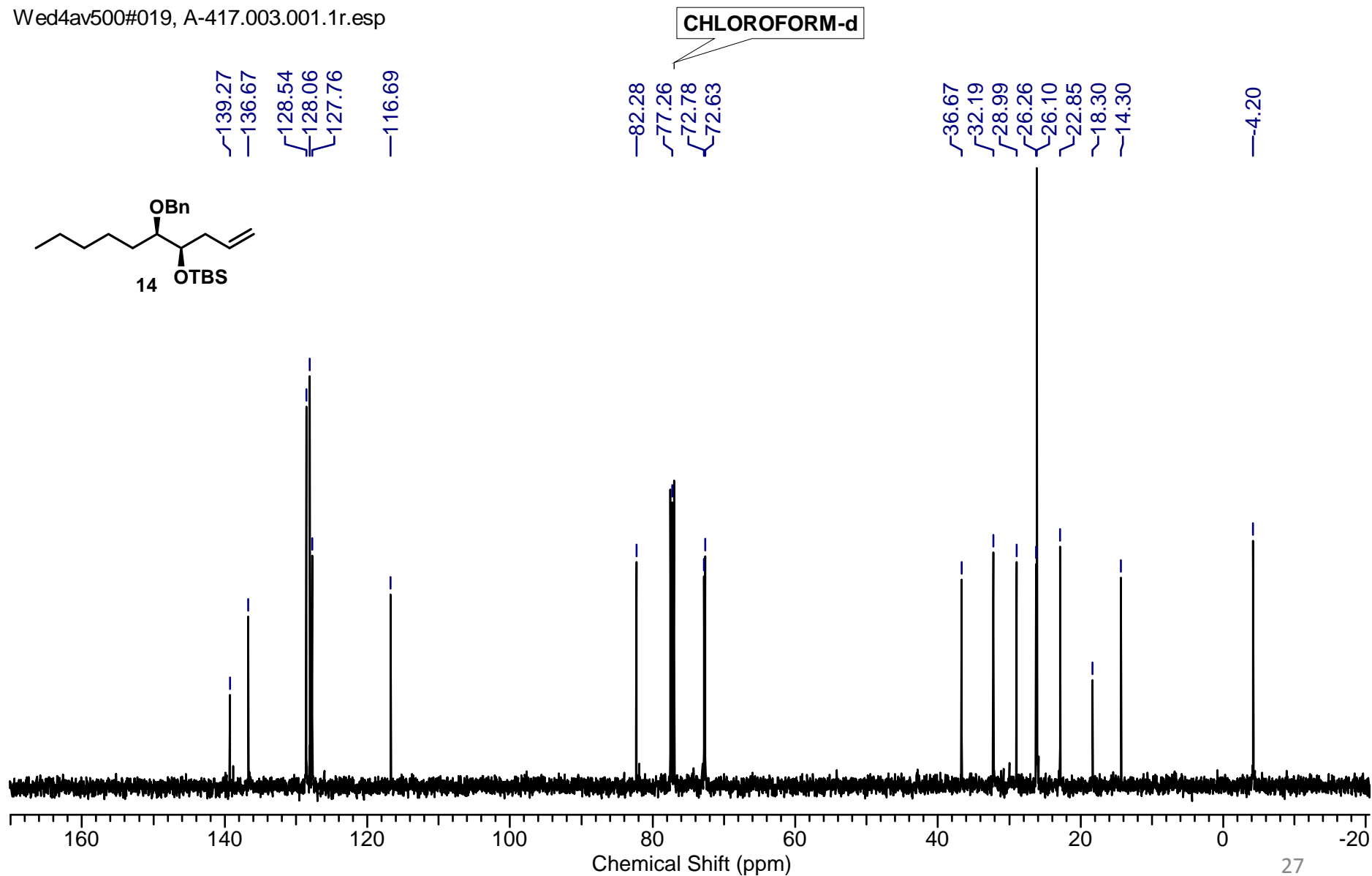
**$^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of the compound (((4*R*,5*R*)-5-(benzyloxy)dec-1-en-4-yl)oxy)(tert-butyl)dimethylsilane 14:**

Wed4av500#019\_A\_417\_001\_001\_1r.esp

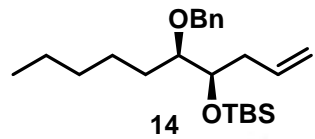
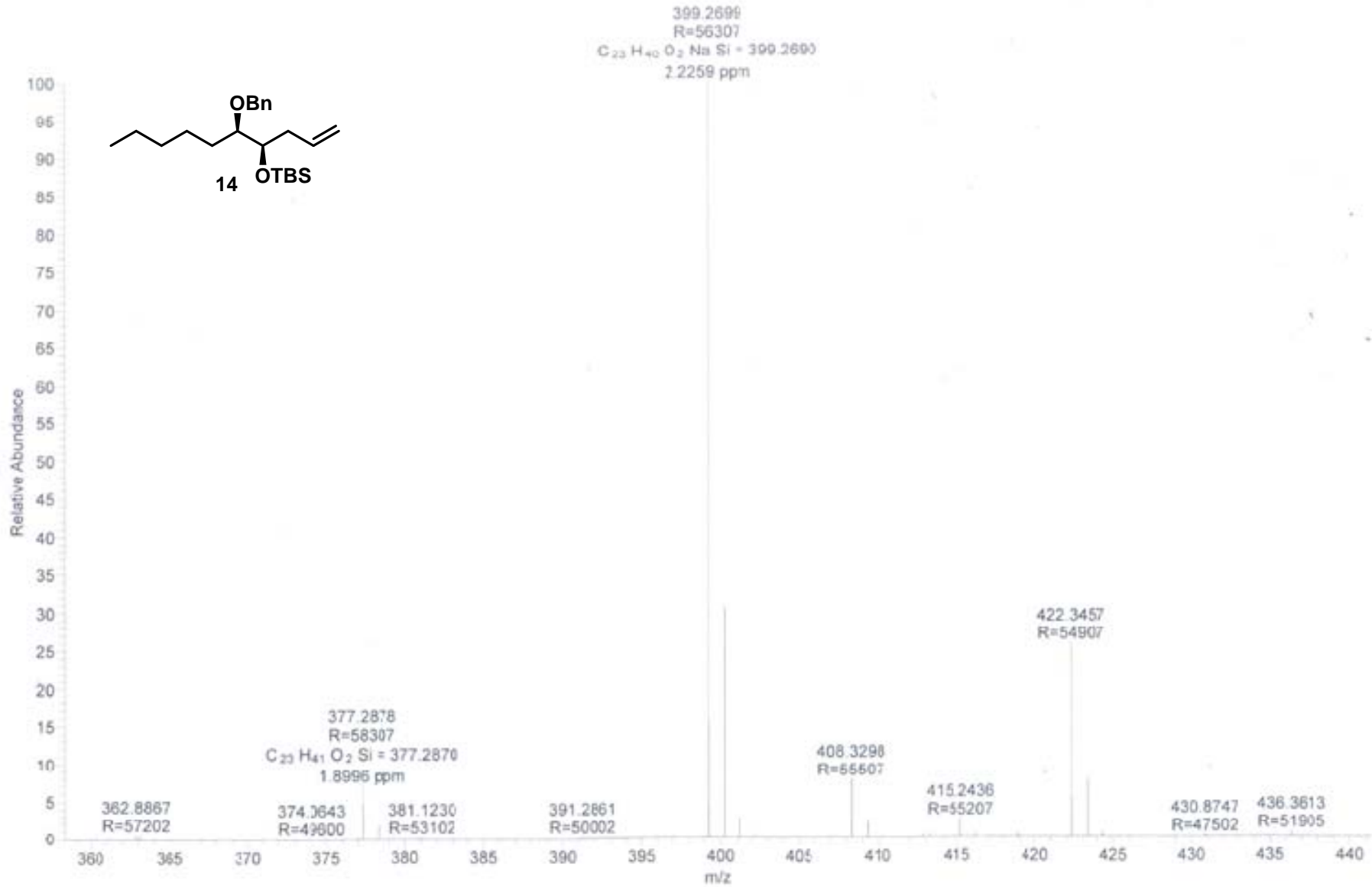


**$^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ) of the compound (((4*R*,5*R*)-5-(benzyloxy)dec-1-en-4-yl)oxy)(tert-butyl)dimethylsilane 14:**

Wed4av500#019, A-417.003.001.1r.esp

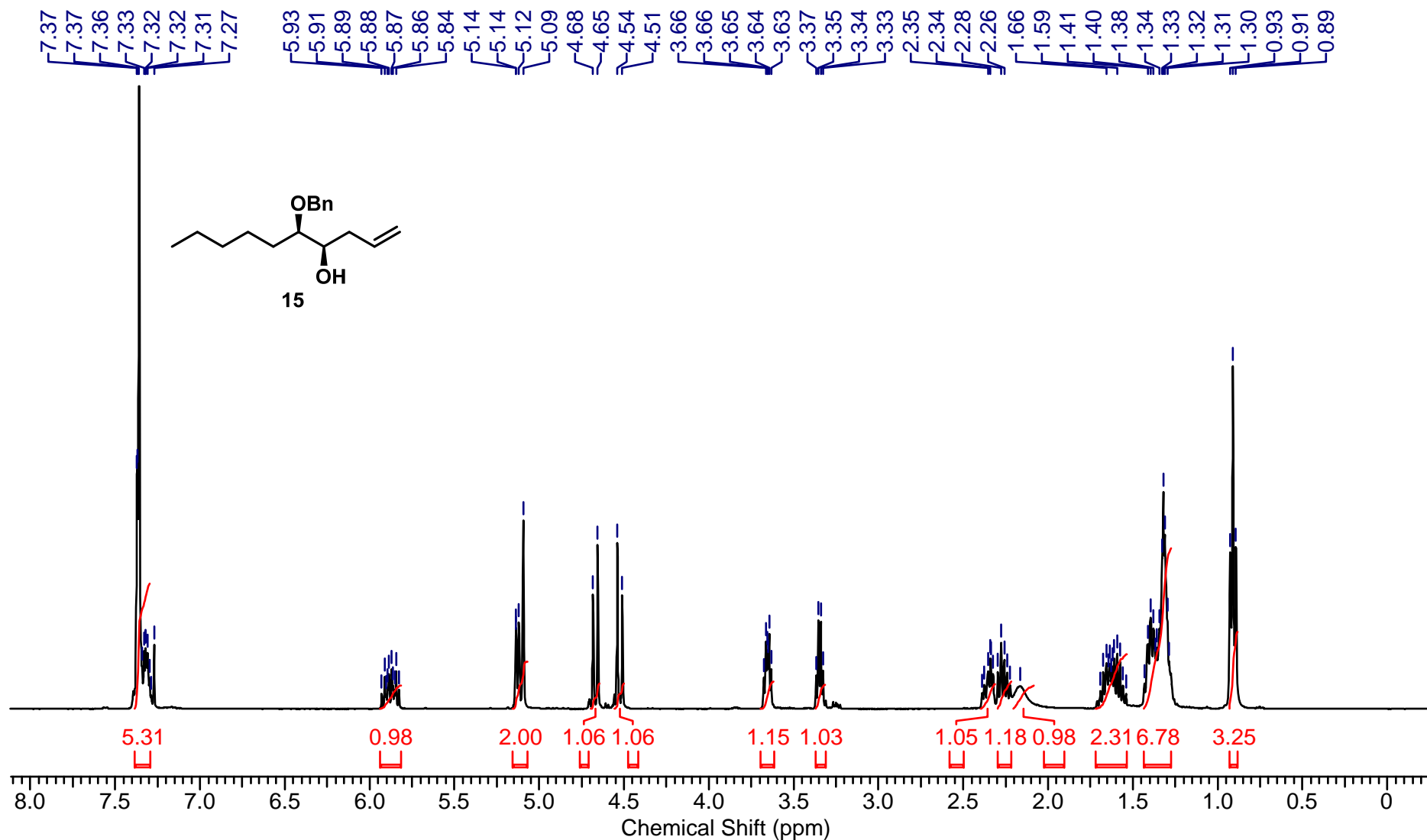


UNR-A-4 #653 RT: 2.91 AV: 1 NL: 3.02E8  
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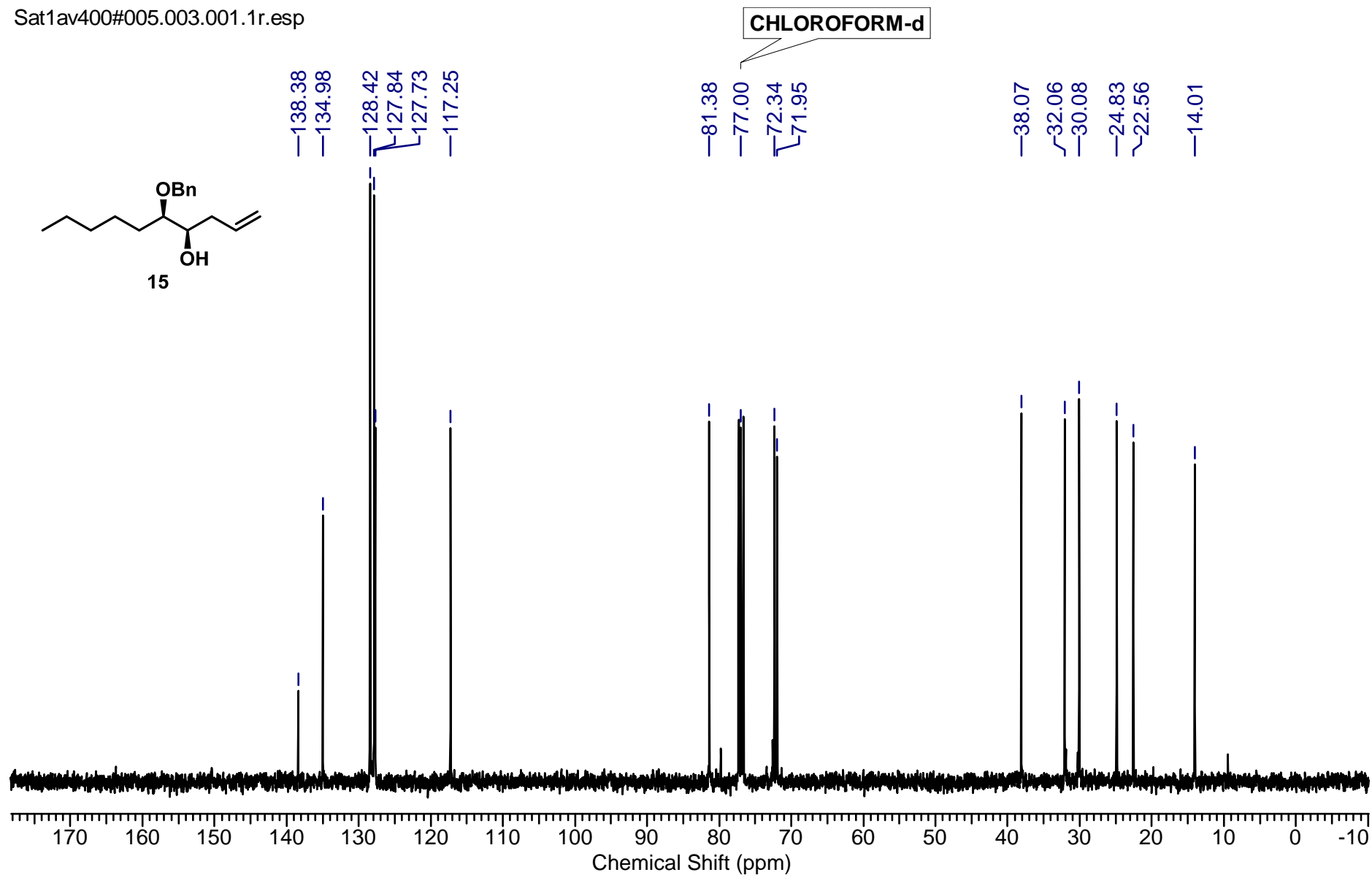
**$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) of the compound (4*R*,5*R*)-5-(benzyloxy)dec-1-en-4-ol 15:**

Sat1av400#00500100111931  
CHLOROFORM-d

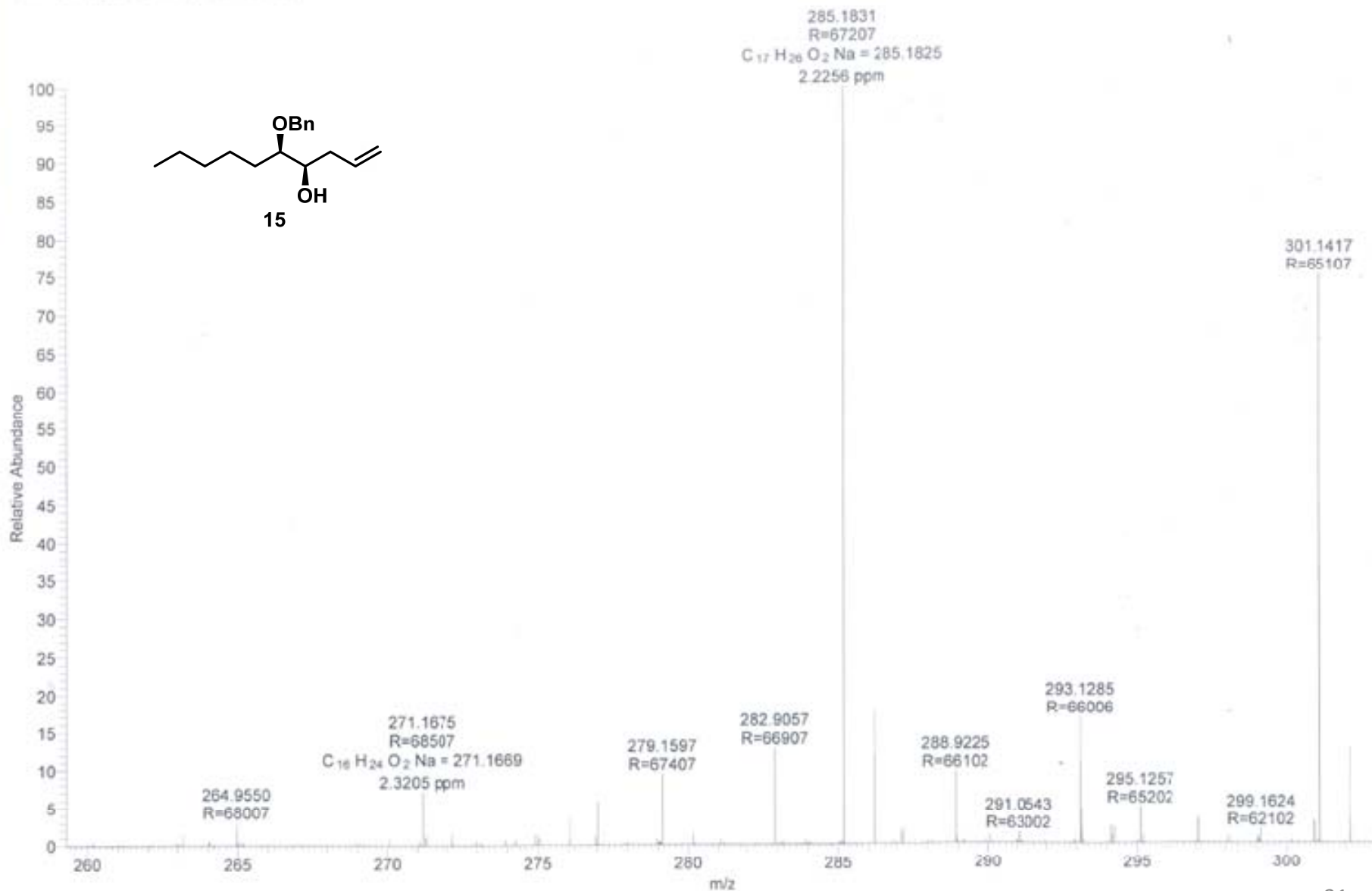


# $^{13}\text{C}$ NMR (100MHz, $\text{CDCl}_3$ ) of the compound (4*R*,5*R*)-5-(benzyloxy)dec-1-en-4-ol 15:

Sat1av400#005.003.001.1r.esp



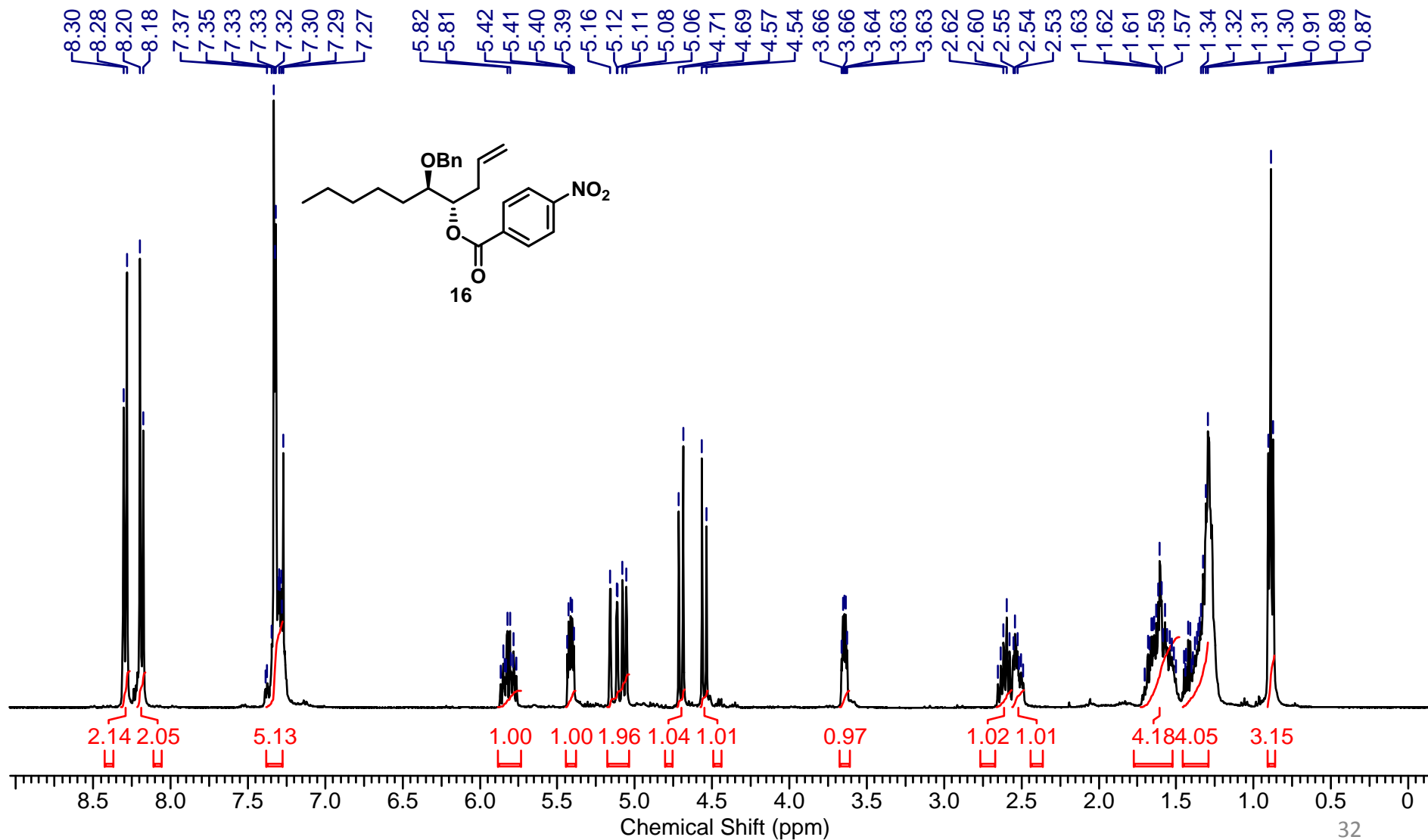
UNR-A-5 #142 RT: 0.63 AV: 1 NL: 3.71E7  
T: FTMS + p ESI Full ms [86.00-1290.00]



**<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) of the compound (4*S*,5*R*)-5-(benzyloxy)dec-1-en-4-yl 4-nitrobenzoate 16:**

Sat1av400#002.001.001.1r.epp

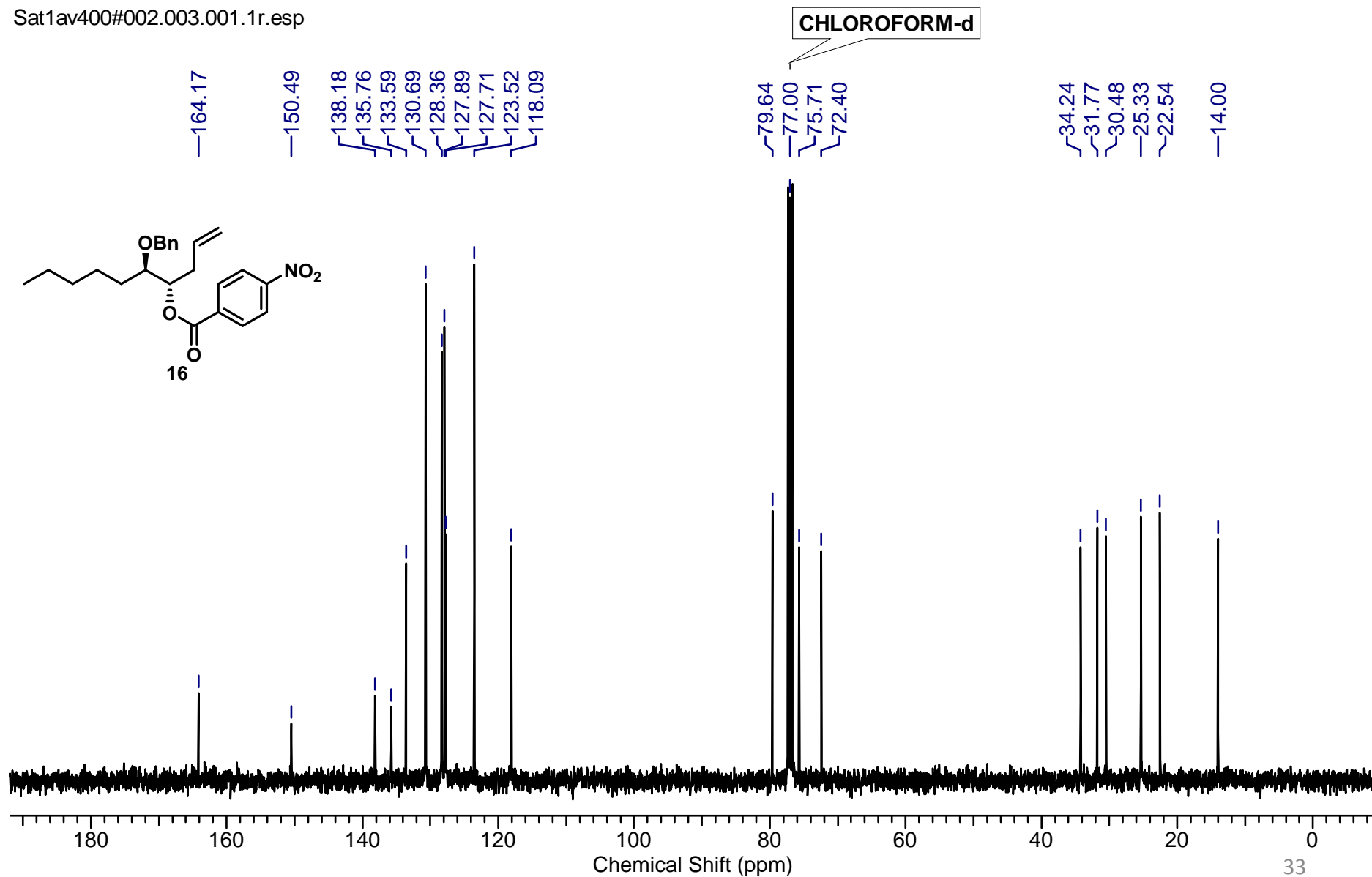
CHLOROFORM-d



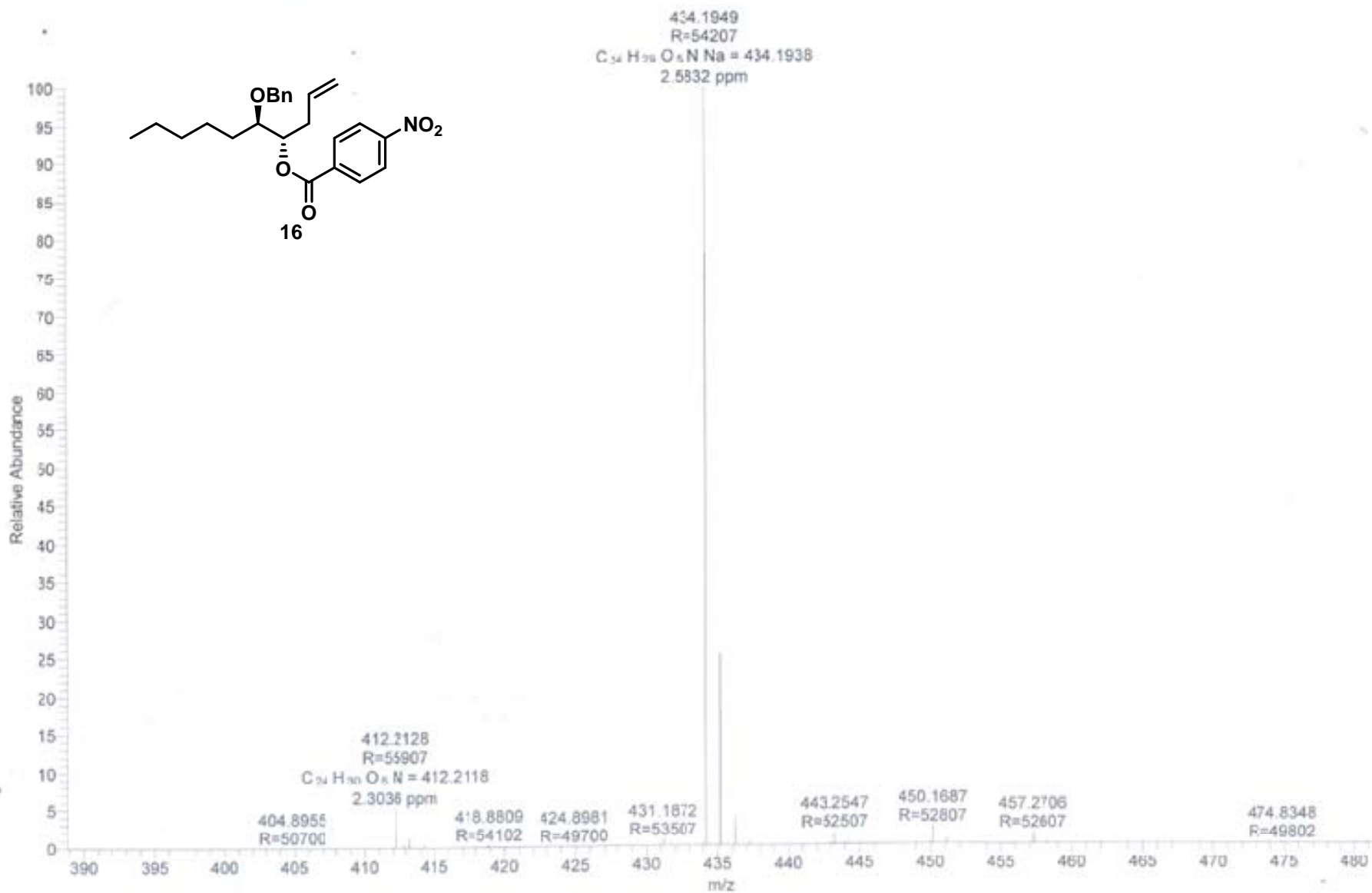


**$^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ) of the compound (4*S*,5*R*)-5-(benzyloxy)dec-1-en-4-yl 4-nitrobenzoate 16:**

Sat1av400#002.003.001.1r.esp

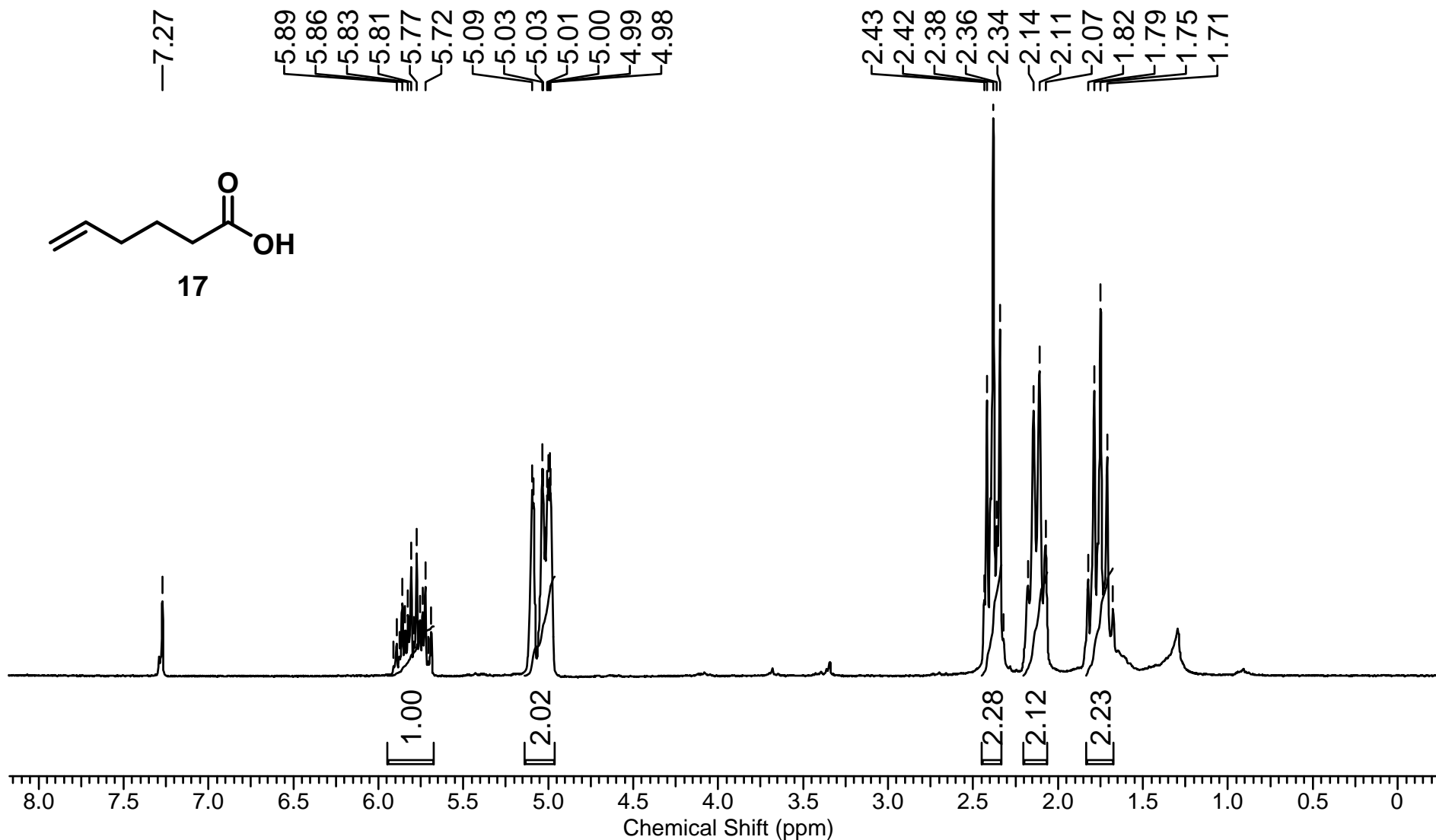


UNR-A-9 #231 RT: 1.03 AV: 1 NL: 4.46EB  
T: FTMS + p ESI Full ms [86 00-1200 00]



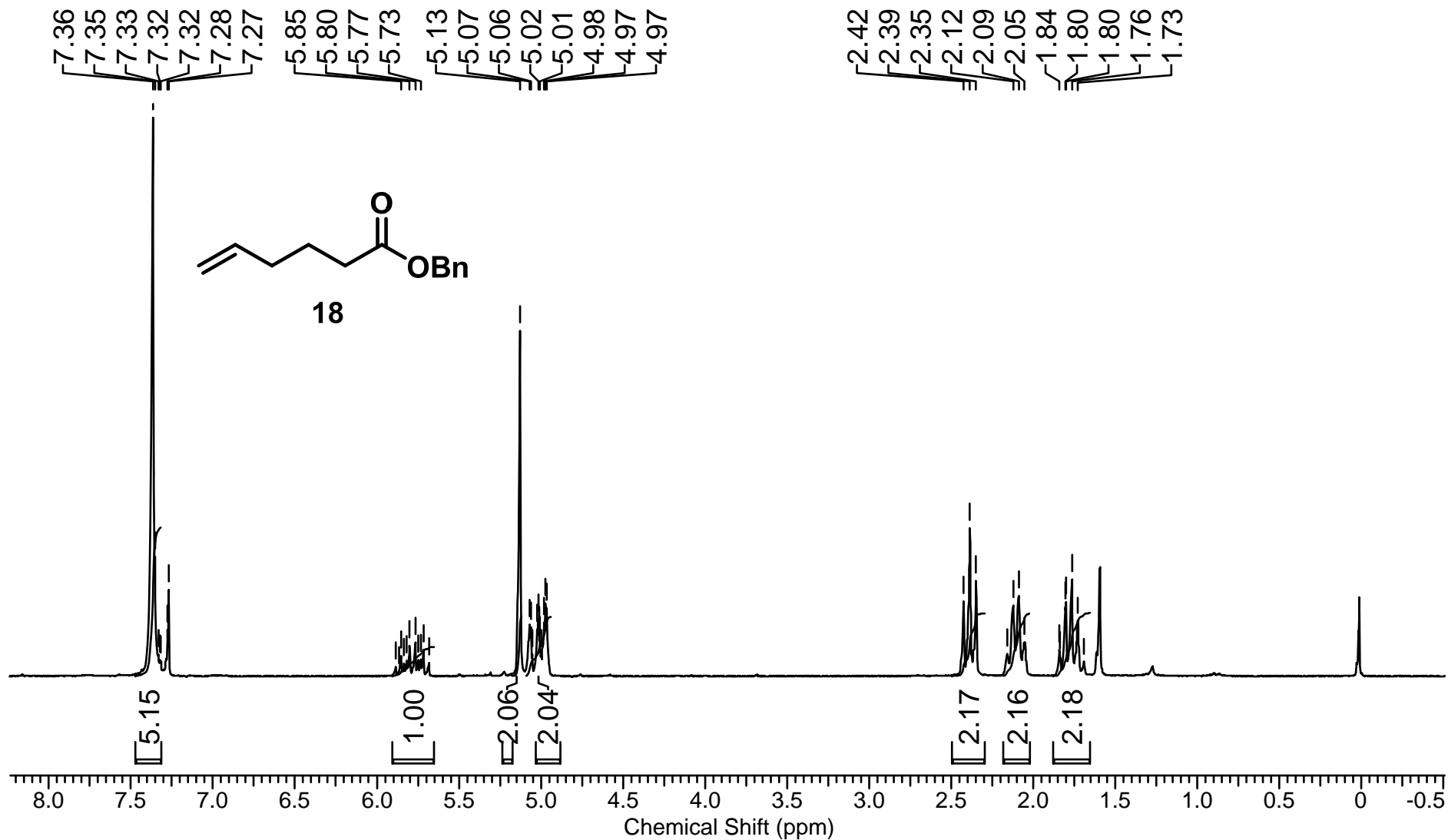
# $^1\text{H}$ NMR (200MHz, $\text{CDCl}_3$ ) of the compound hex-5-enoic acid 17:

Wed1av2#140.0010011 F01  
CHLOROFORM-d



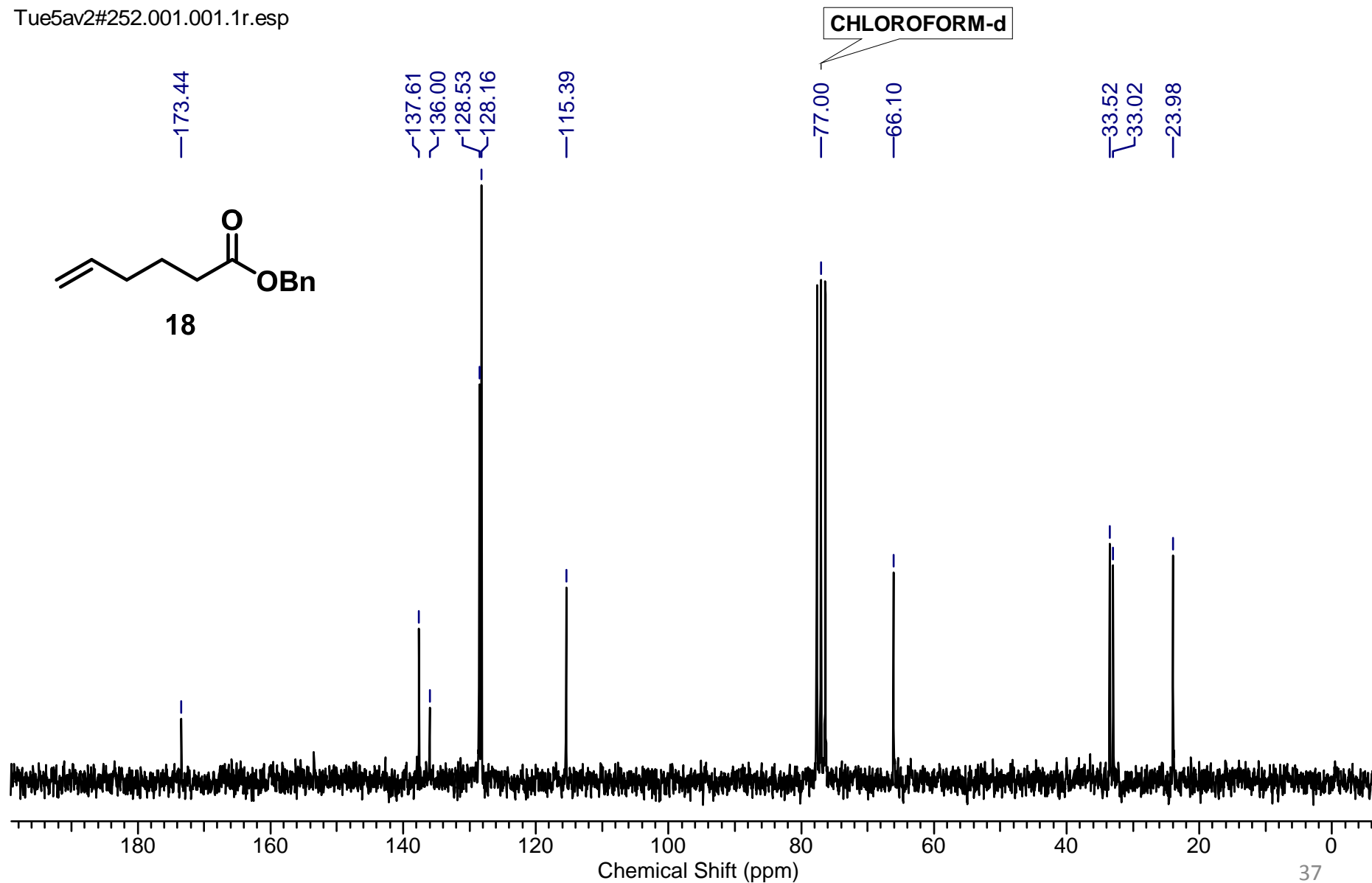
**$^1\text{H}$  NMR (200MHz,  $\text{CDCl}_3$ ) of the compound benzyl hex-5-enoate 18:**

Wed2av2#020.001.001.1089  
CHLOROFORM-d

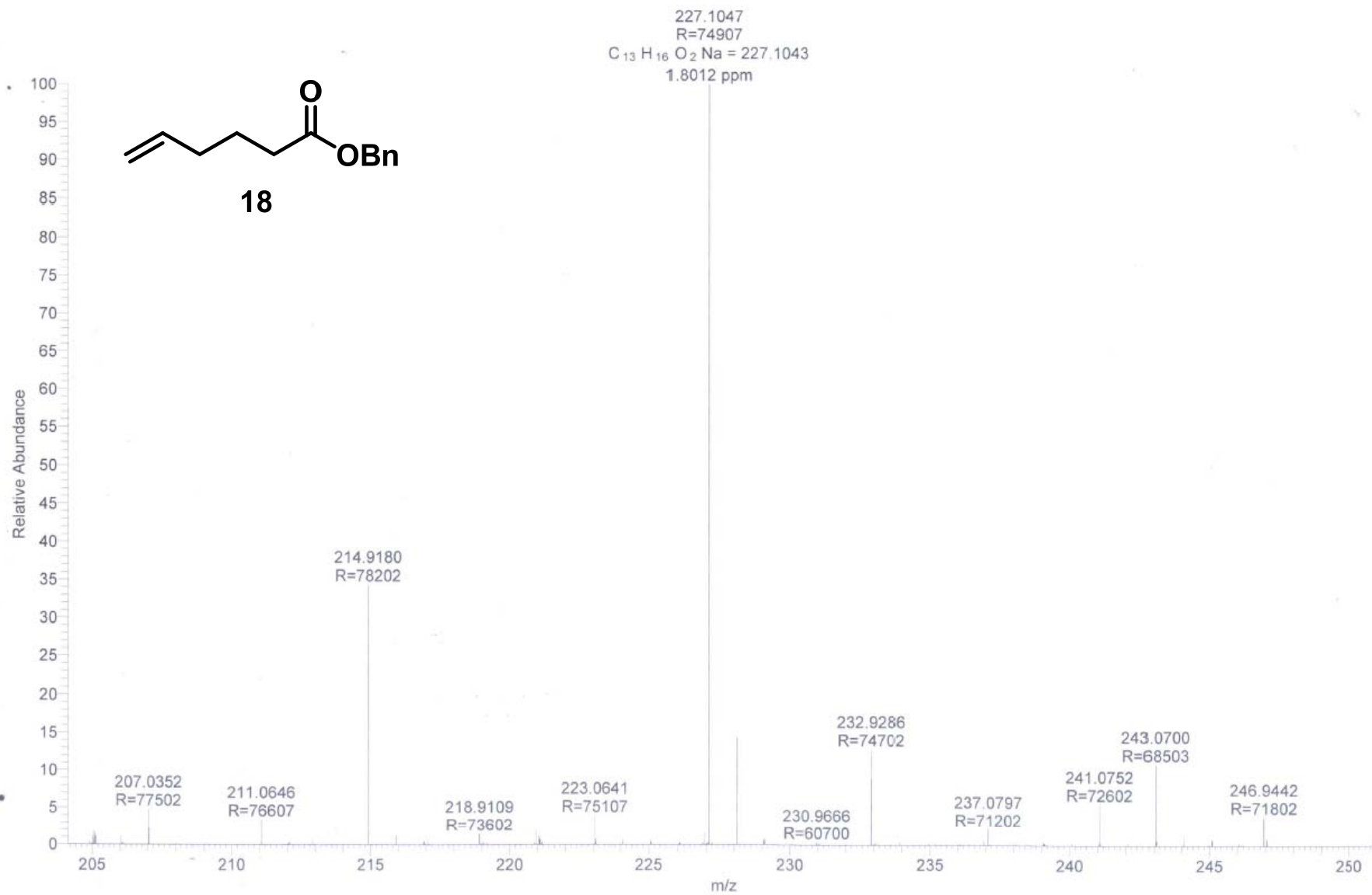


# $^1\text{H}$ NMR (50MHz, $\text{CDCl}_3$ ) of the compound benzyl hex-5-enoate 18:

Tue5av2#252.001.001.1r.esp

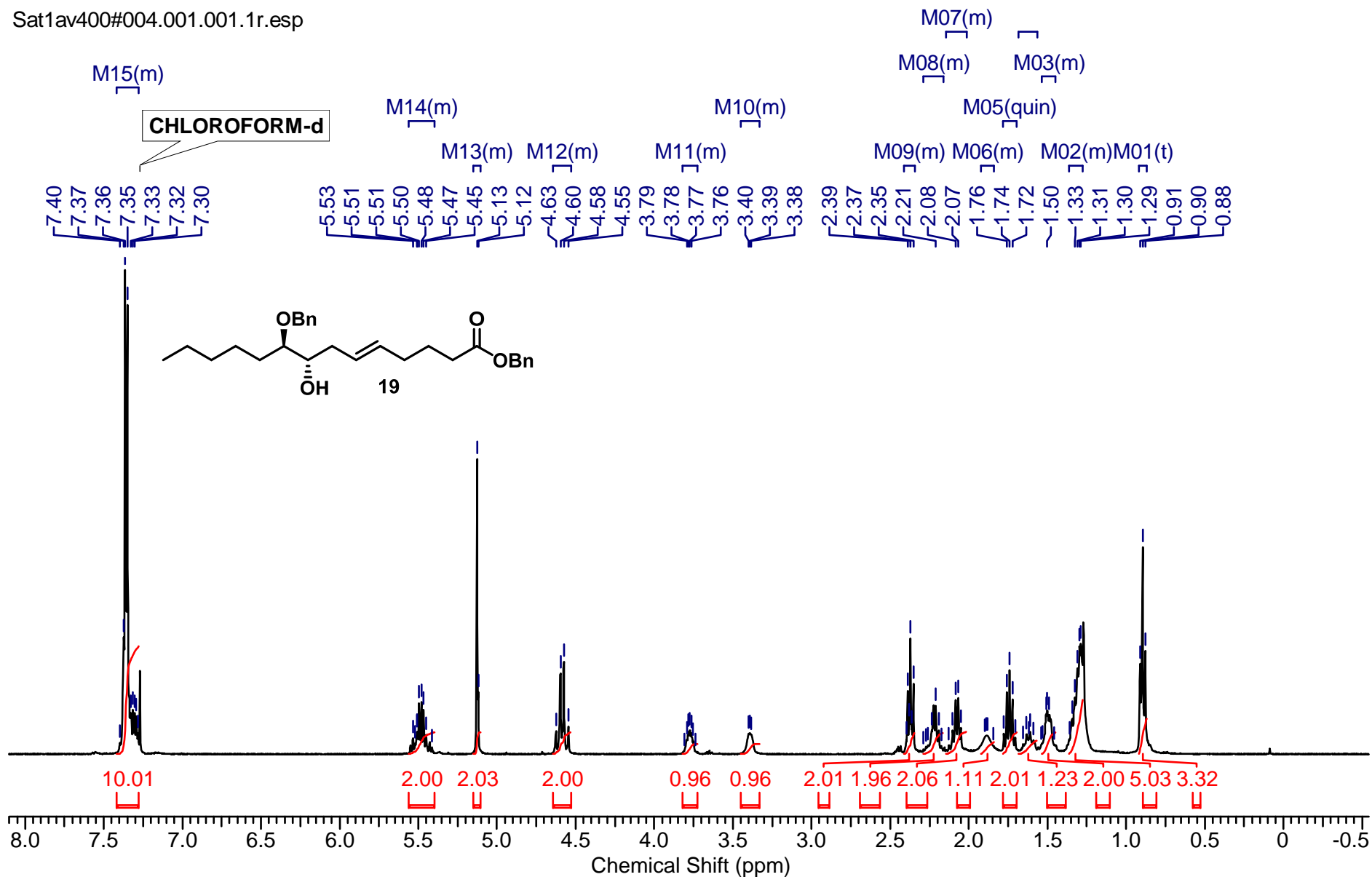


UNR-A-22 #130 RT: 0.58 AV: 1 NL: 9.23E7  
T: FTMS + p ESI Full ms [86.00-1290.00]



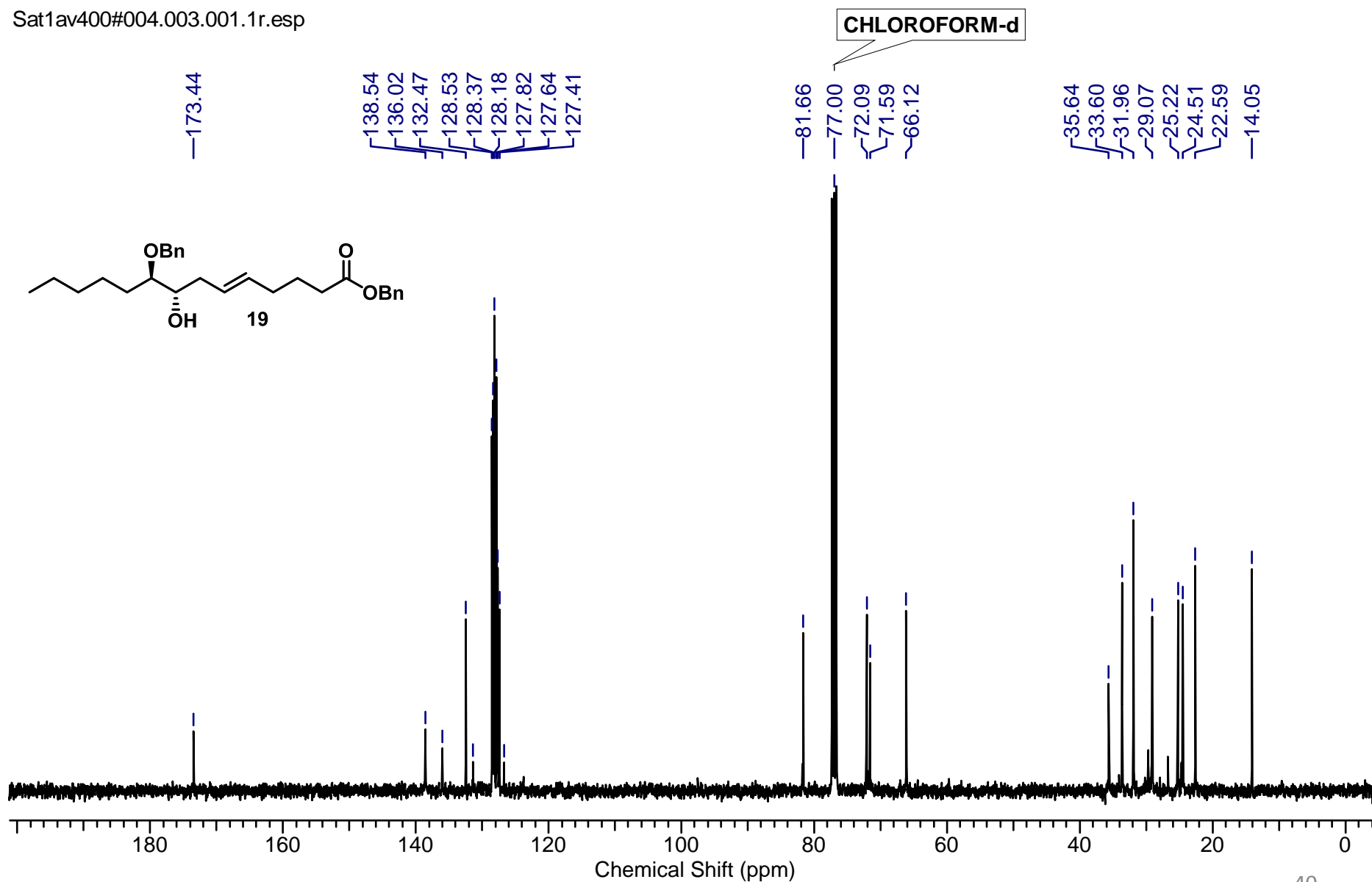
**$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) of the compound benzyl (8*S*,9*R*,*E*)-9-(benzyloxy)-8-hydroxytetradec-5-enoate 19:**

Sat1av400#004.001.001.1r.esp



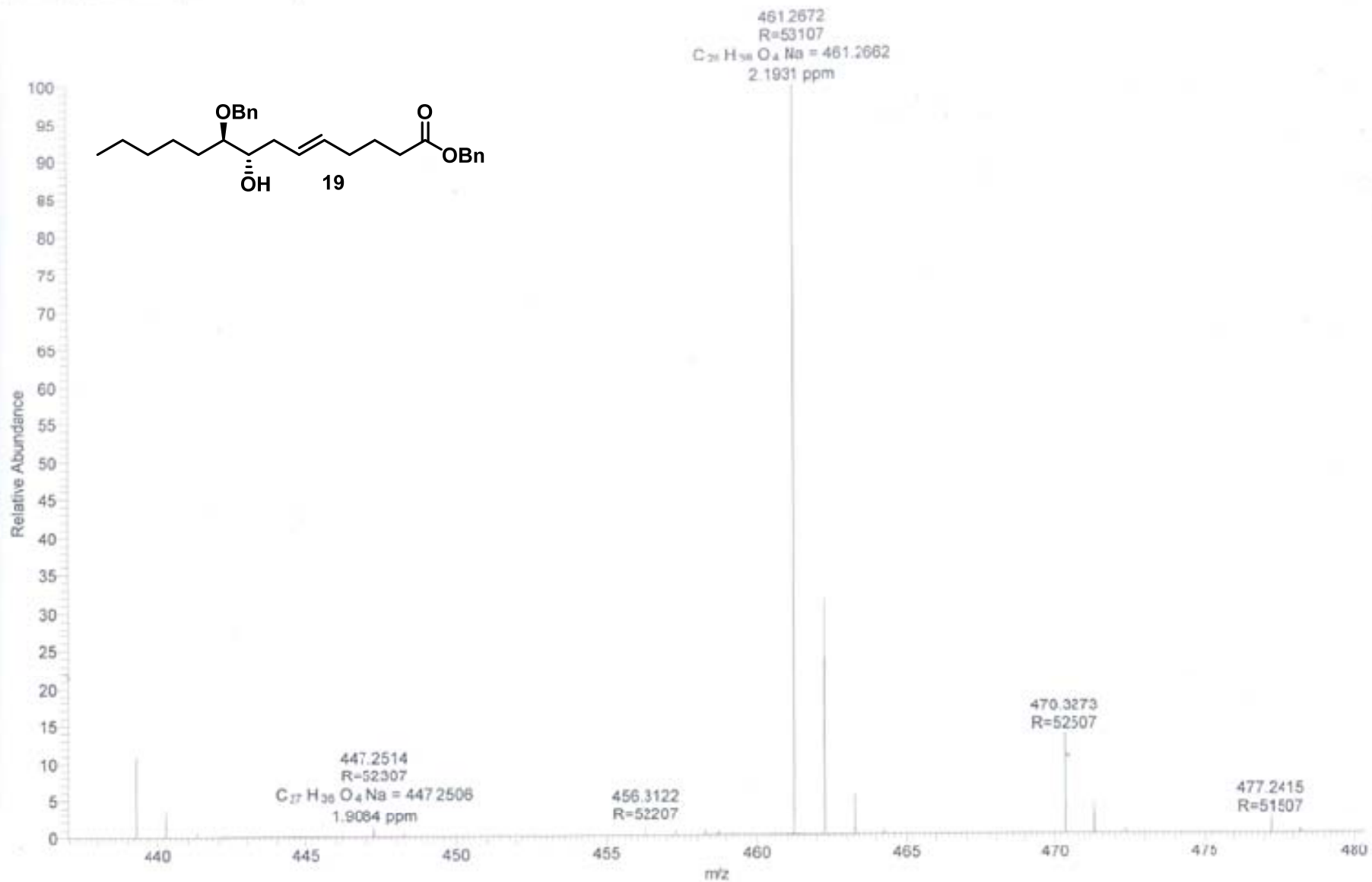
**$^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ) of the compound benzyl (8*S*,9*R*,*E*)-9-(benzyloxy)-8-hydroxytetradec-5-enoate 19:**

Sat1av400#004.003.001.1r.esp



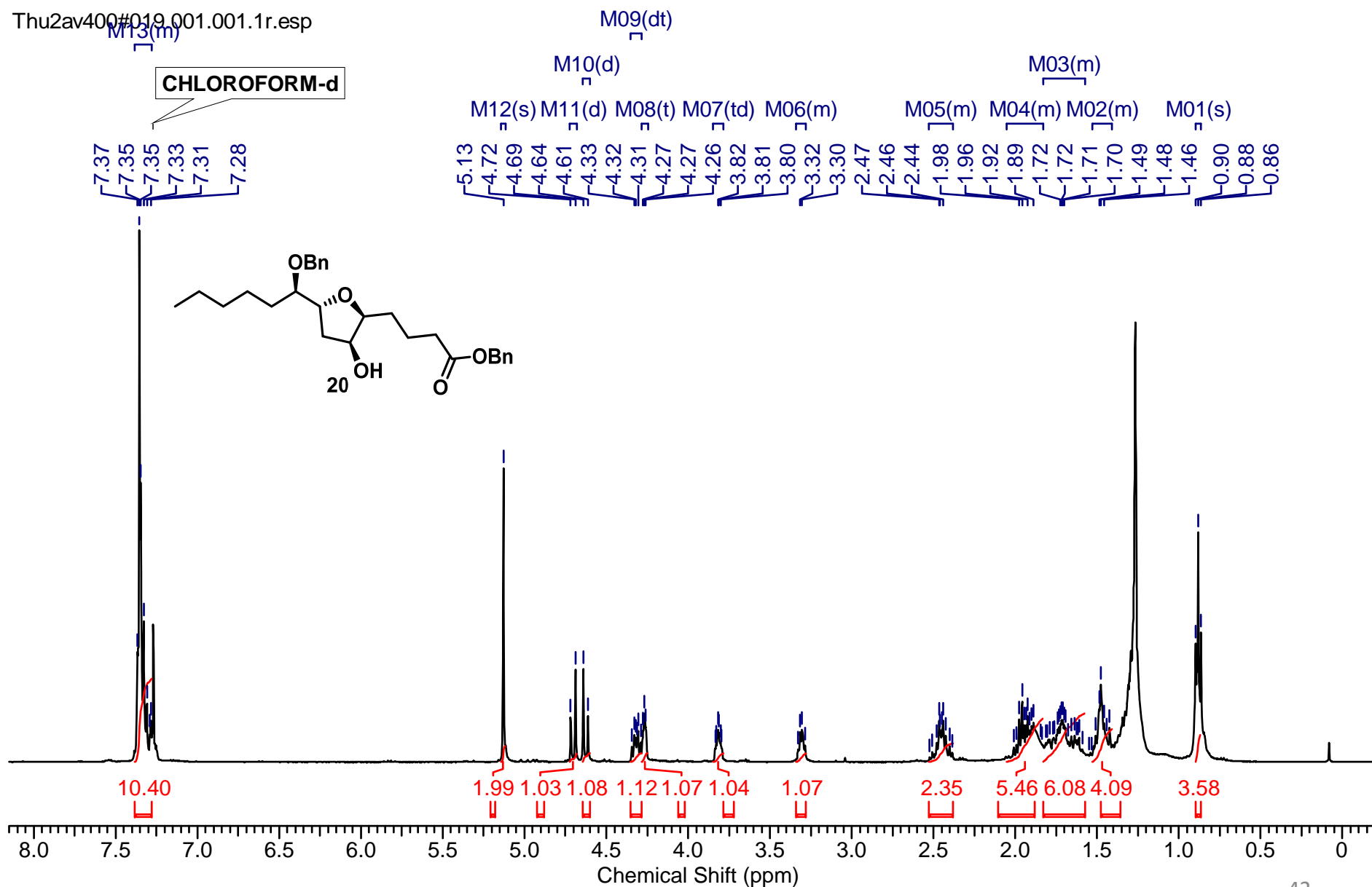


UNR-A-7 #197 RT: 0.88 AV: 1 NL: 8.77E8  
T: FTMS + p ESI Full ms [86.00-1290.00]



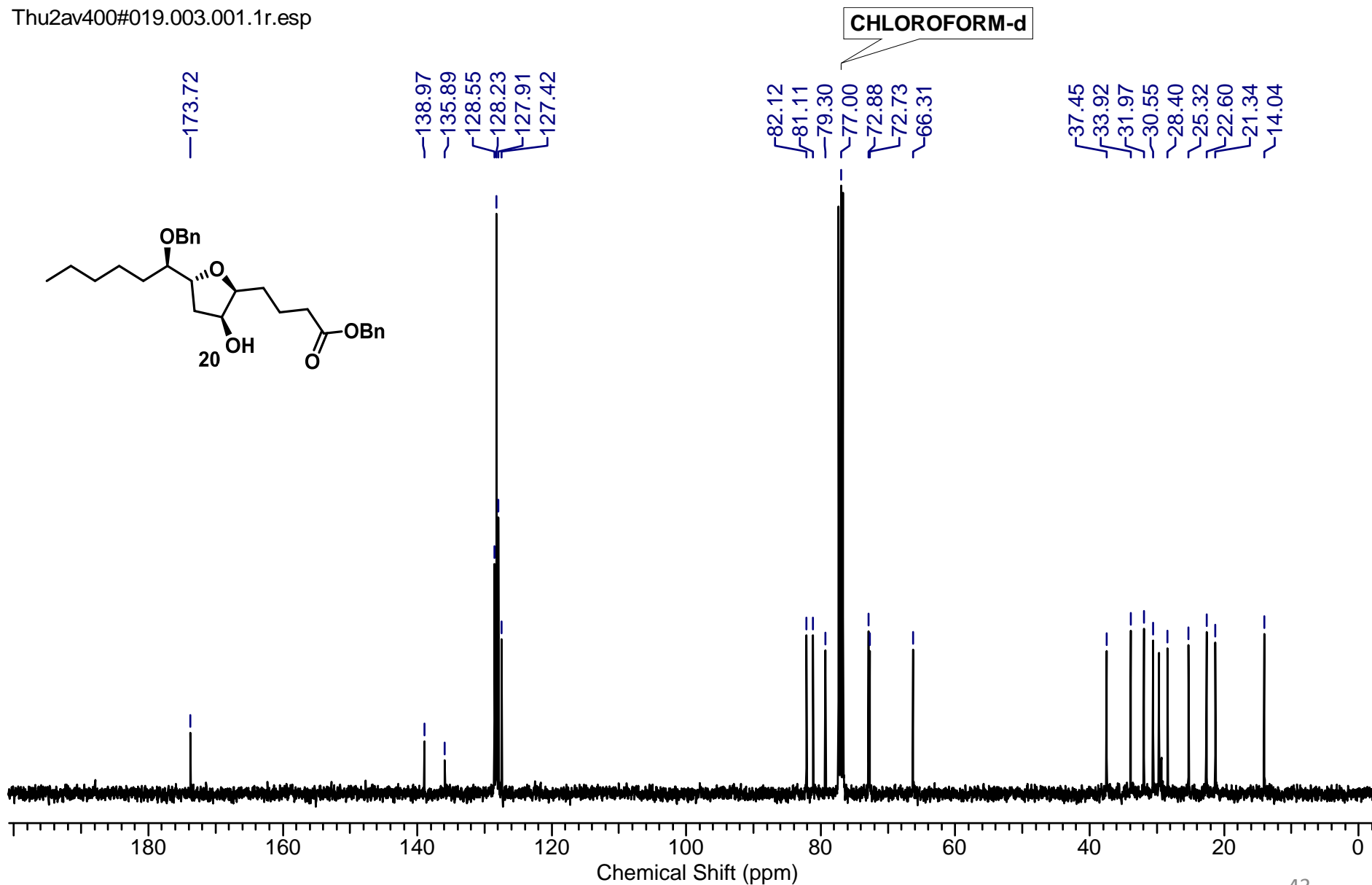
# $^1\text{H}$ NMR (400MHz, $\text{CDCl}_3$ ) of the compound benzyl 4-((2S,3S,5R)-5-((R)-1-(benzyloxy)hexyl)-3-hydroxytetrahydrofuran-2-yl)butanoate 20:

Thu2av400#019.001.001.1r.esp

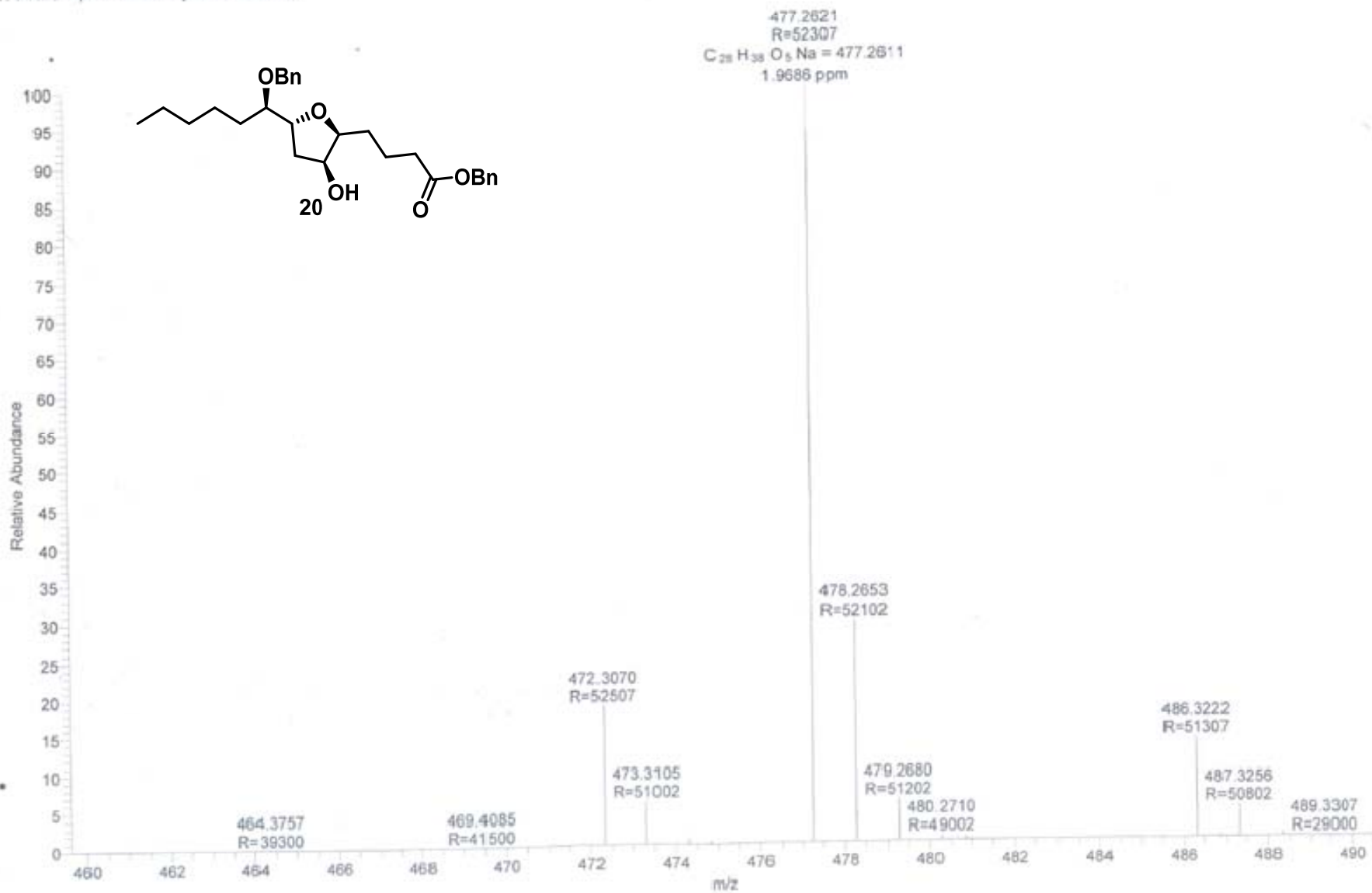


**$^{13}\text{C}$ NMR (100MHz,  $\text{CDCl}_3$ ) of the compound benzyl 4-((2*S*,3*S*,5*R*)-5-((*R*)-1-(benzyloxy)hexyl)-3-hydroxytetrahydrofuran-2-yl) butanoate 20:**

Thu2av400#019.003.001.1r.esp



UNR-A-8 #162 RT: 0.72 AV: 1 NL: 3.21E8  
T: FTMS + p ESI Full ms [86.00-1290.00]

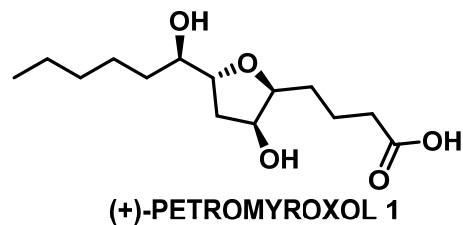


# $^1\text{H}$ NMR (500MHz, $\text{CDCl}_3$ ) of the compound (+)-Petromyroxol 1:

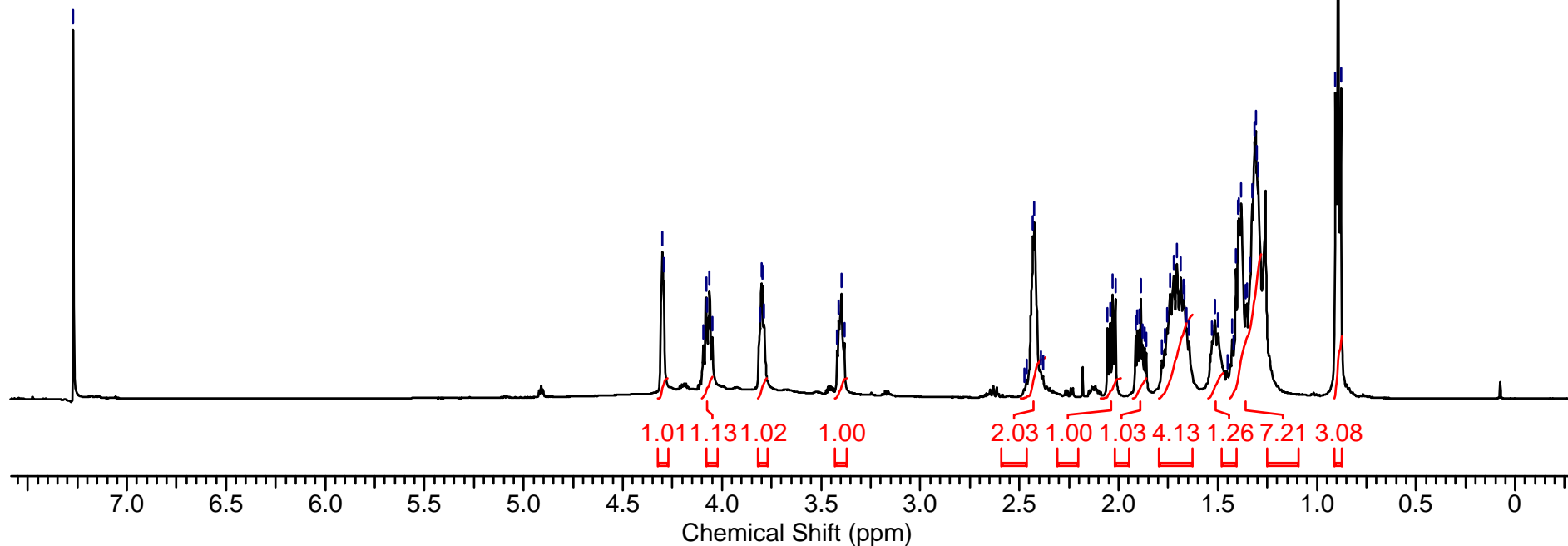
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CHLOROFORM-d

-7.27

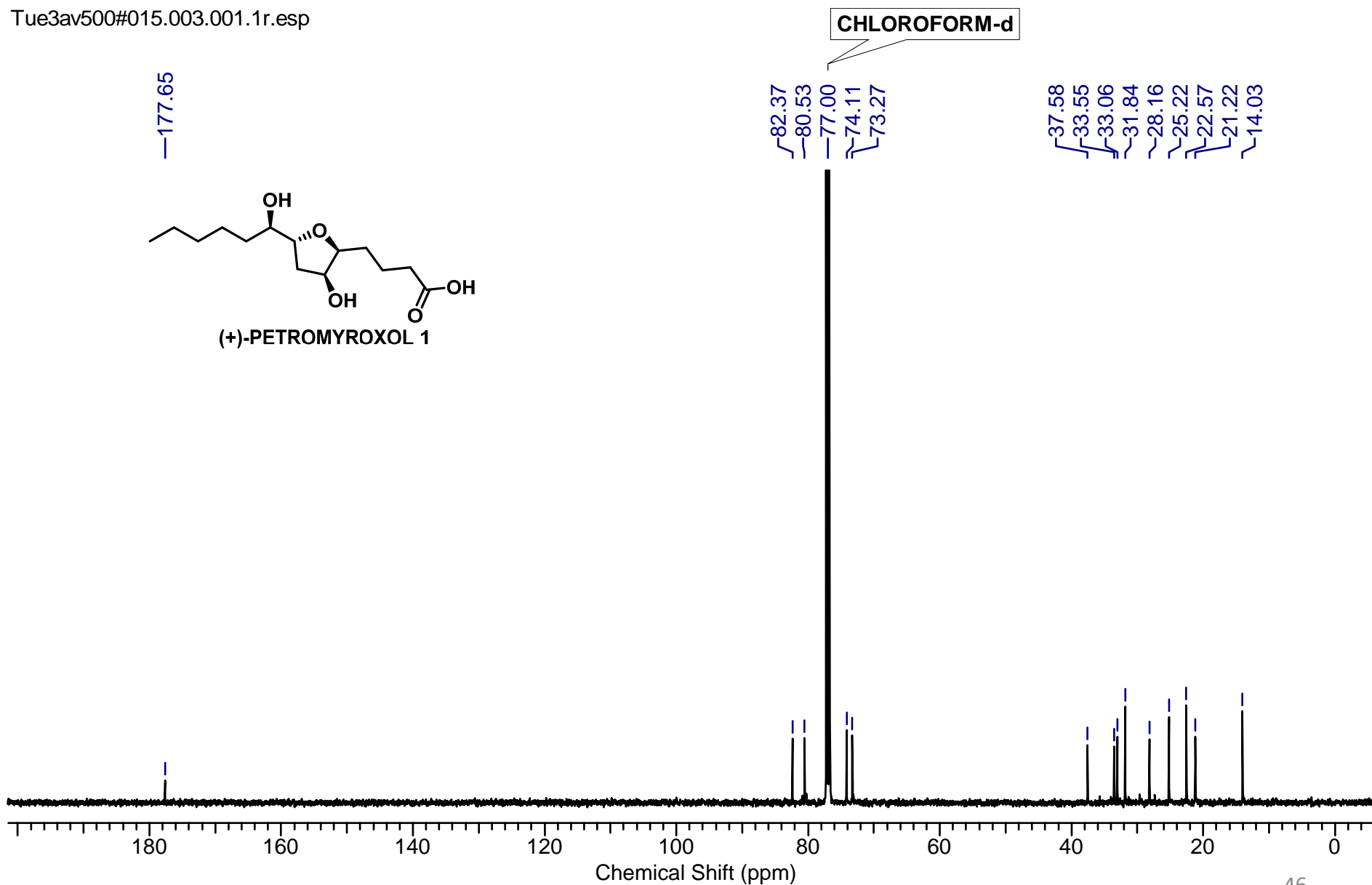


4.30  
4.29  
4.09  
4.08  
4.08  
4.06  
4.05  
3.81  
3.80  
3.80  
3.79  
3.41  
3.40  
3.38  
2.43  
2.42  
2.04  
1.74  
1.72  
1.71  
1.40  
1.39  
1.38  
1.33  
1.31  
1.31  
1.30  
1.29  
0.91  
0.89  
0.88

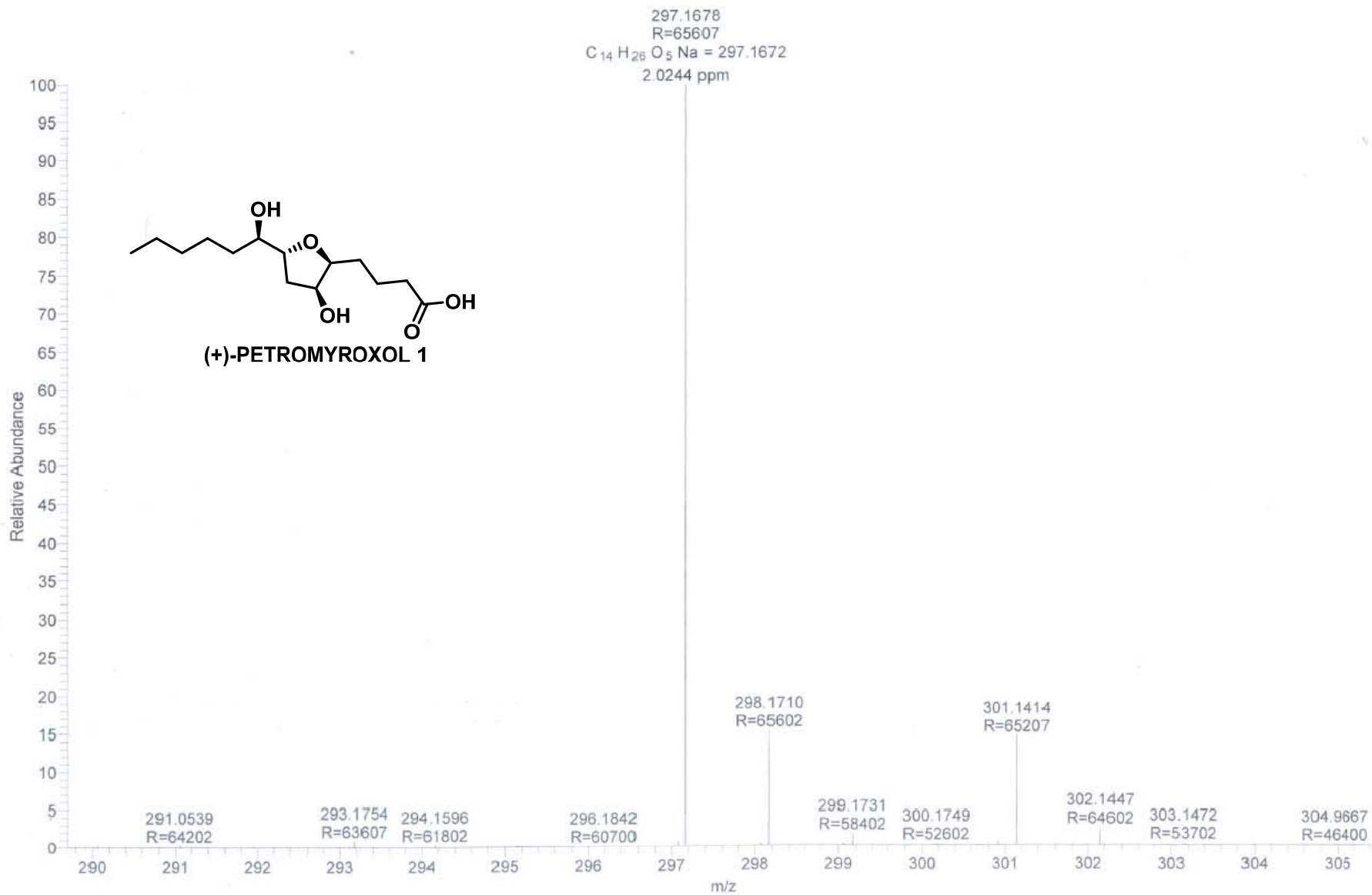


# $^{13}\text{C}$ NMR (125MHz, $\text{CDCl}_3$ ) of the compound (+)-Petromyroxol 1:

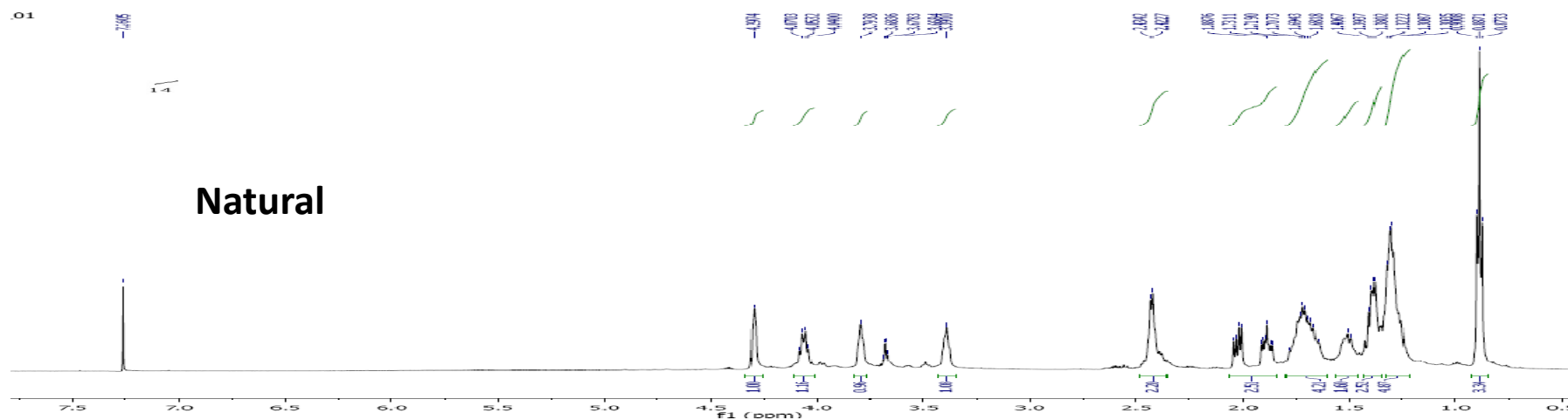
Tue3av500#015.003.001.1r.esp



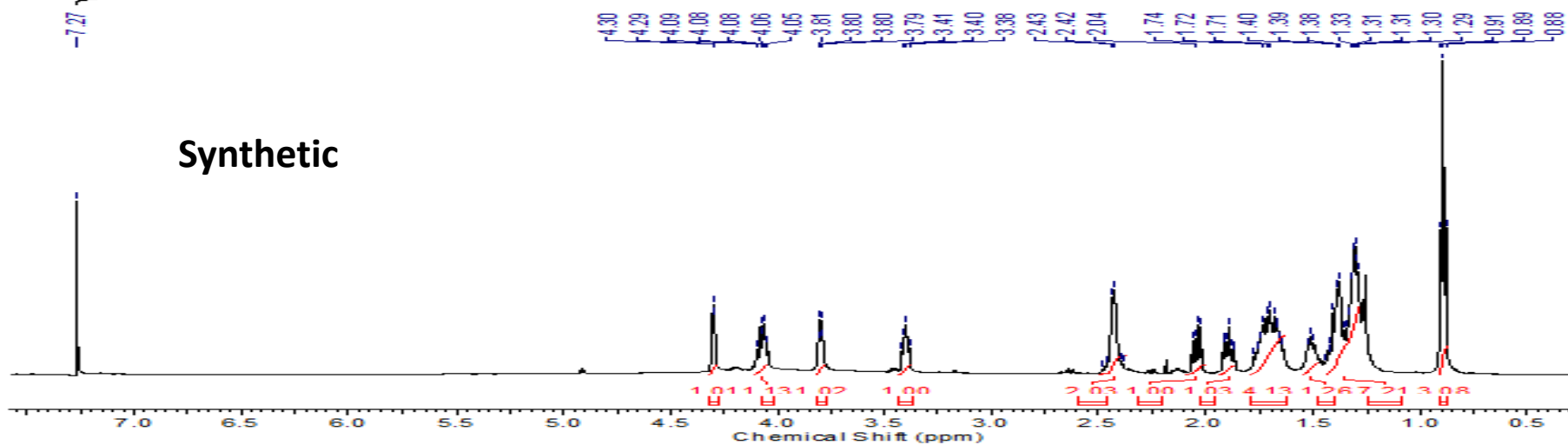
UNR-A-10 #104 RT: 0.46 AV: 1 NL: 1.74E8  
T: FTMS + p ESI Full ms [86.00-1290.00]



# Comparison of <sup>1</sup>H NMR

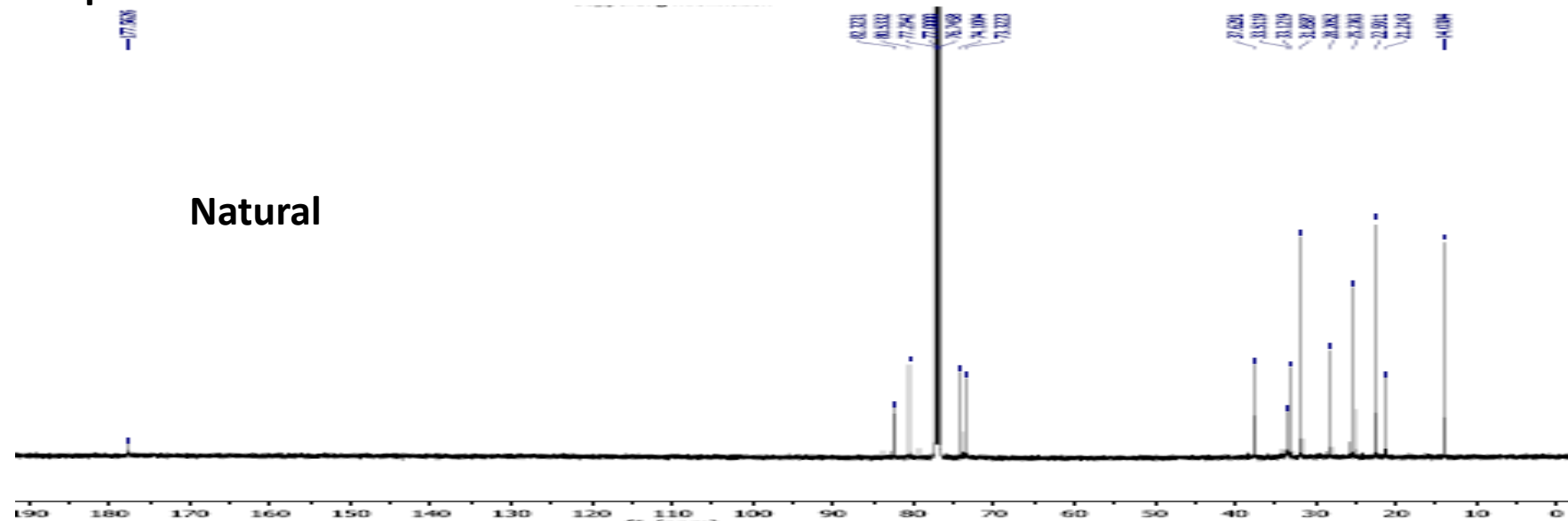


Tue34 CHLOROFORM-d Ir.esp

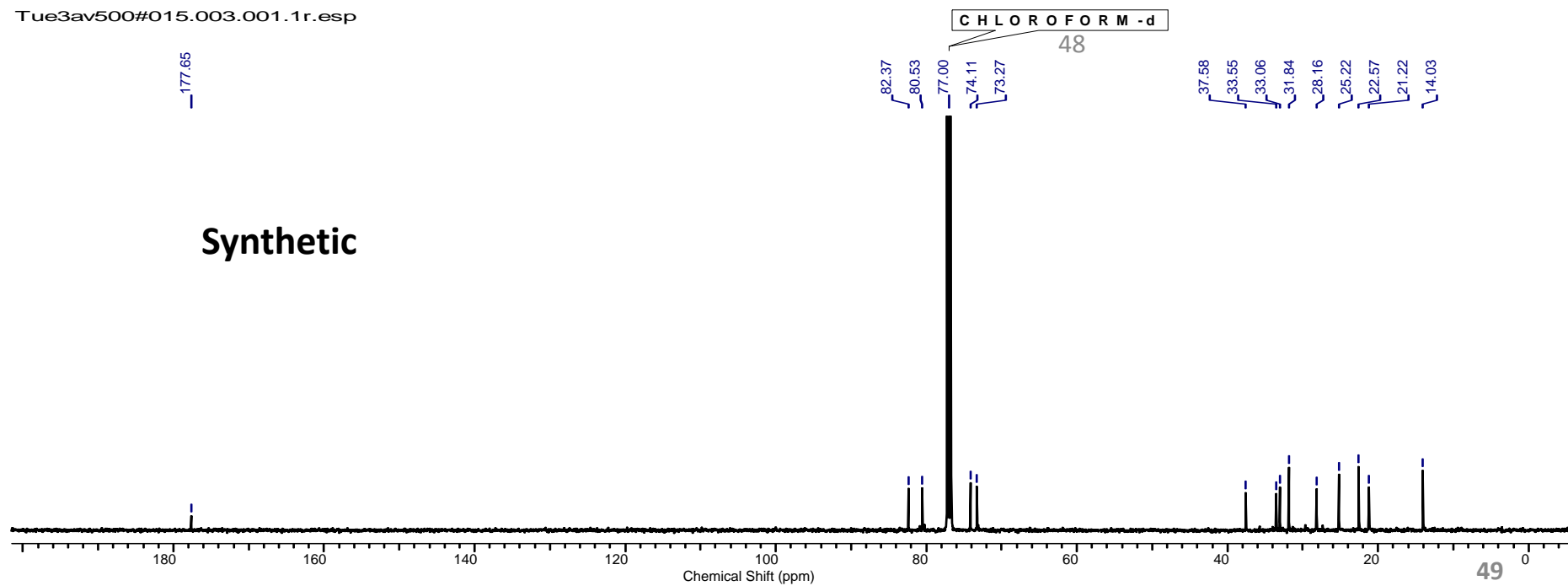




# Comparison of $^{13}\text{C}$ NMR



Tue3av500#015.003.001.1r.esp



**Comparison of  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of both natural and synthetic (+)-Petromyroxol**

Synthetic (+)-Petromyroxol spectroscopic data (500MHz, $\text{CDCl}_3$ )			Natural (+)-Petromyroxol spectroscopic data (500MHz, $\text{CDCl}_3$ )	
S.No.	$(\delta_{\text{H}}, J \text{ in Hz})$	$\delta_{\text{C}}$	$(\delta_{\text{H}}, J \text{ in Hz})$	$\delta_{\text{C}}$
1.		177.7		177.6, C
2.	2.49 - 2.37 m	33.5	2.43, m	33.7, $\text{CH}_2$
3.	1.80 - 1.63 m	21.2	1.77 m, 1.70 m	21.4, $\text{CH}_2$
4.		28.2	1.72 m, 1.67 m	28.4, $\text{CH}_2$
5.	3.82 - 3.77 ddd ( $J = 2.4, 6.5, 6.5$ )	82.4	3.79 ddd ( $J = 2.5, 6.5, 6.5$ )	82.5, CH
6.	4.32 - 4.27 dd ( $J = 3.5, 3.5$ )	73.3	4.30 dd ( $J = 3.5, 3.5$ )	73.5, CH
7.	1.89 ddd ( $J = 4.6, 9.1, 13.5$ )	37.6	1.89 ddd ( $J = 4.6, 9.2, 13.7$ )	37.8, $\text{CH}_2$
	2.04 dd ( $J = 6.6, 13.3$ )		2.02 dd ( $J = 6.6, 13.4$ )	
8.	4.10 - 4.04 ddd ( $J = 6.4, 6.7, 8.9$ )	80.5	4.06 ddd ( $J = 6.5, 6.5, 8.9$ )	80.7, CH
9.	3.43 - 3.37 ddd ( $J = 4.0, 6.4, 7.3$ )	74.1	3.39 m	74.3, CH
10.	1.55 - 1.47 m	33.1	1.40 m	33.3, $\text{CH}_2$
11.		25.2	1.51 m, 1.38 m	25.4, $\text{CH}_2$
12.	1.44 - 1.28 m	31.8	1.29 m	32.0, $\text{CH}_2$
13.		22.6	1.31 m	22.8, $\text{CH}_2$
14.	0.89 t ( $J = 6.9$ )	14.0	0.89 t ( $J = 6.9$ )	14.2, $\text{CH}_2$