Supporting information

Stereoselective Approach to Indolizidine and Pyrrolizidine Alkaloids: Total Synthesis of (-)-Lentiginosine, (-)-epi-Lentiginosine and Dihydroxypyrrolizidine

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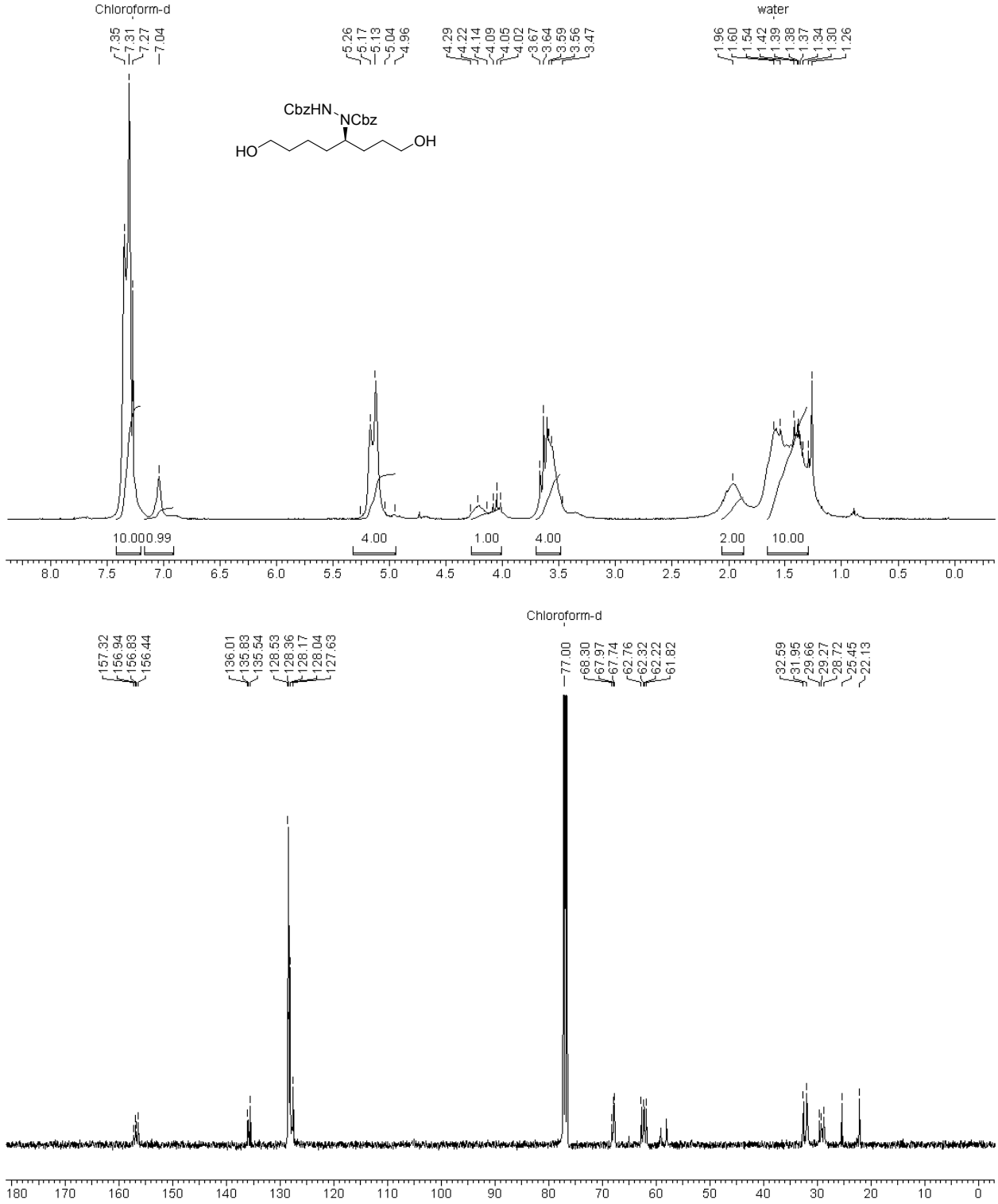
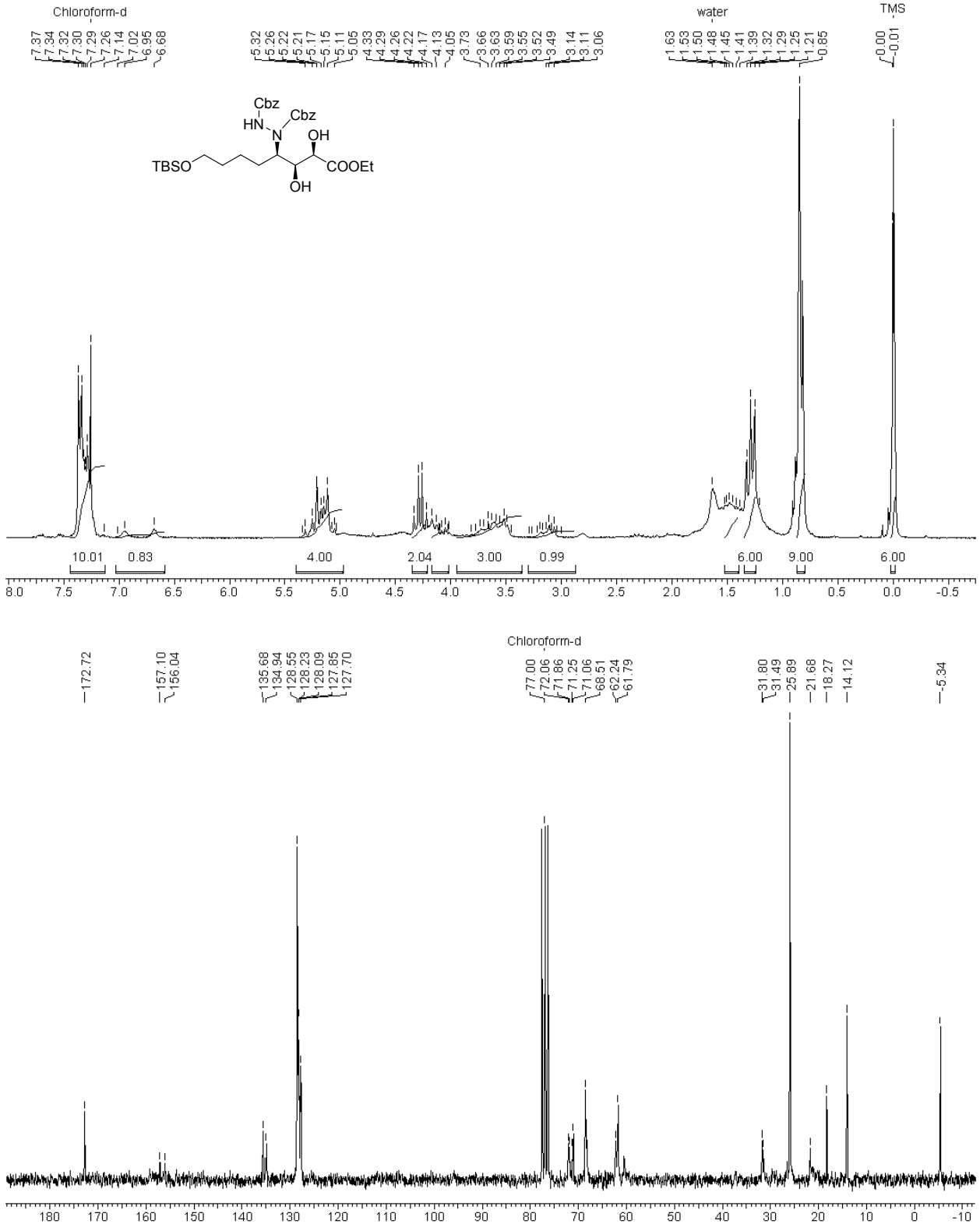
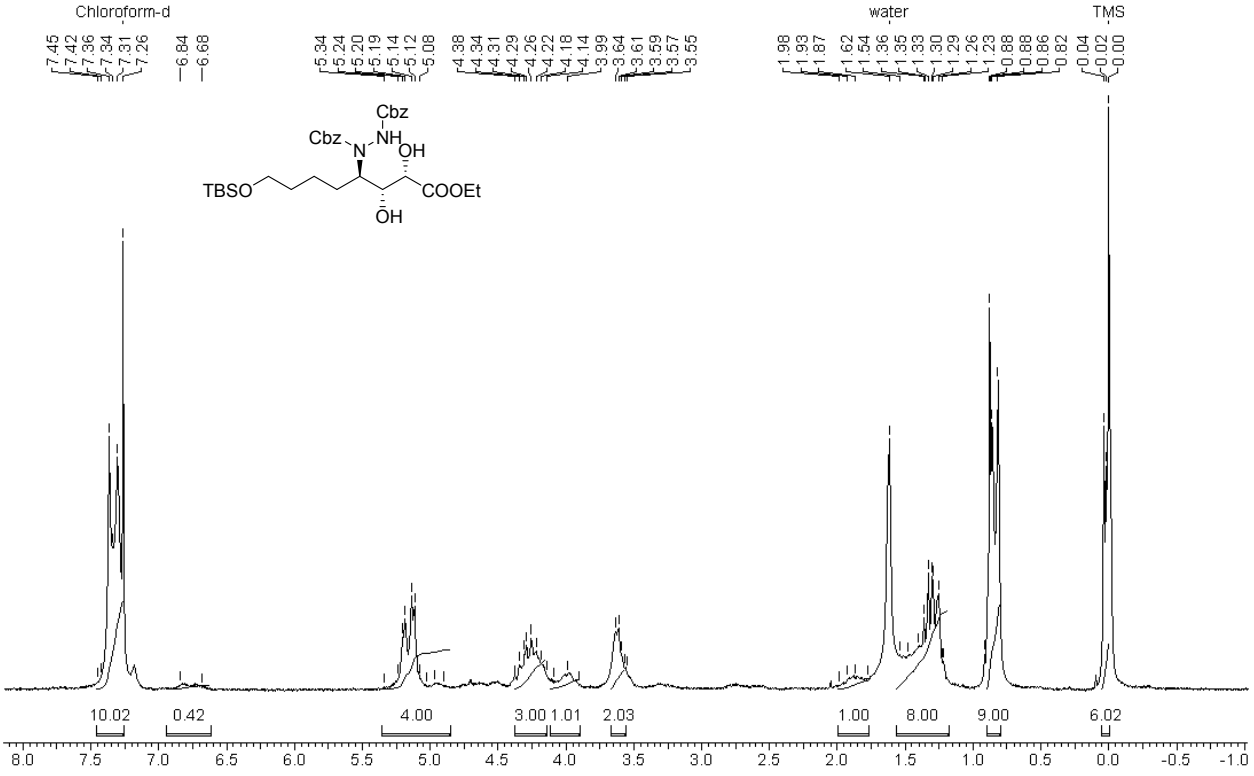
Dibenzyl (*R*)-1-(1,8-dihydroxyoctan-4-yl)hydrazine-1,2-dicarboxylate (9):

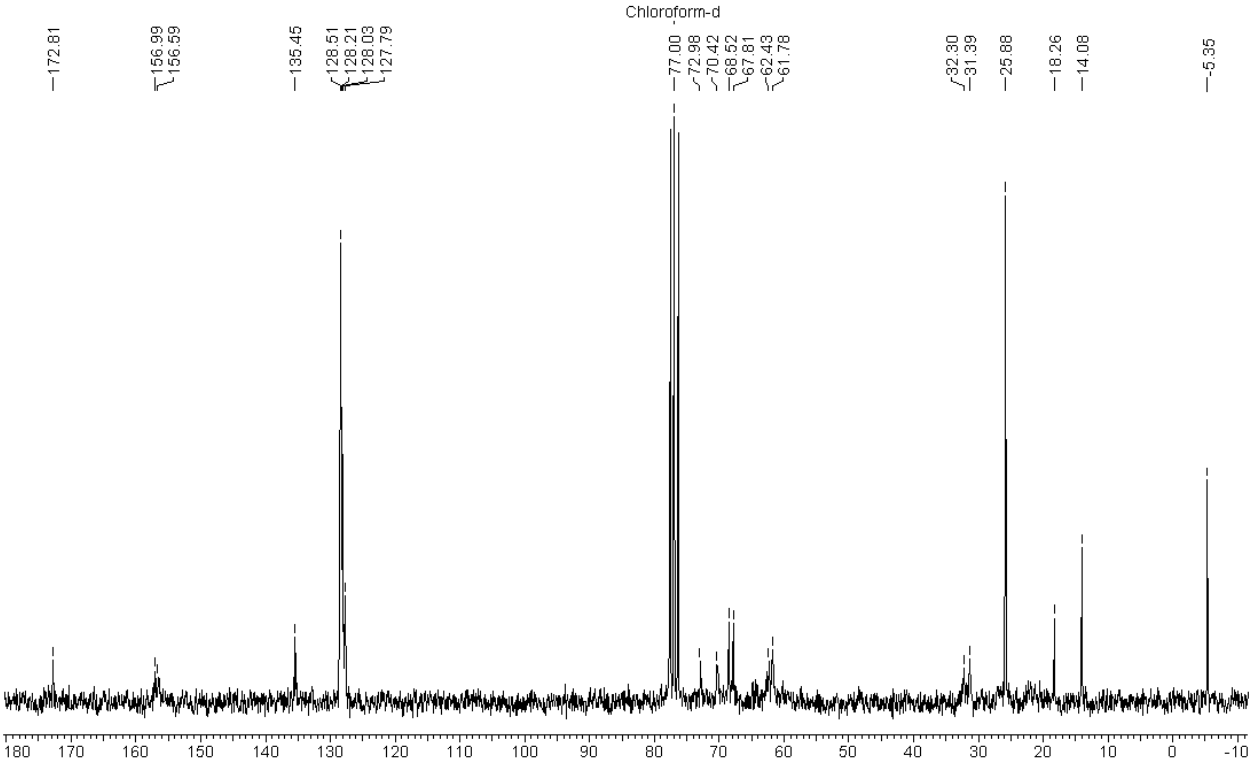


Dibenzyl 1-((2*R*,3*S*,4*R*)-8-((*tert*-butyldimethylsilyl)oxy)-1-ethoxy-2,3-dihydroxy-1-oxooctan-4-yl)hydrazine-1,2-dicarboxylate (10):

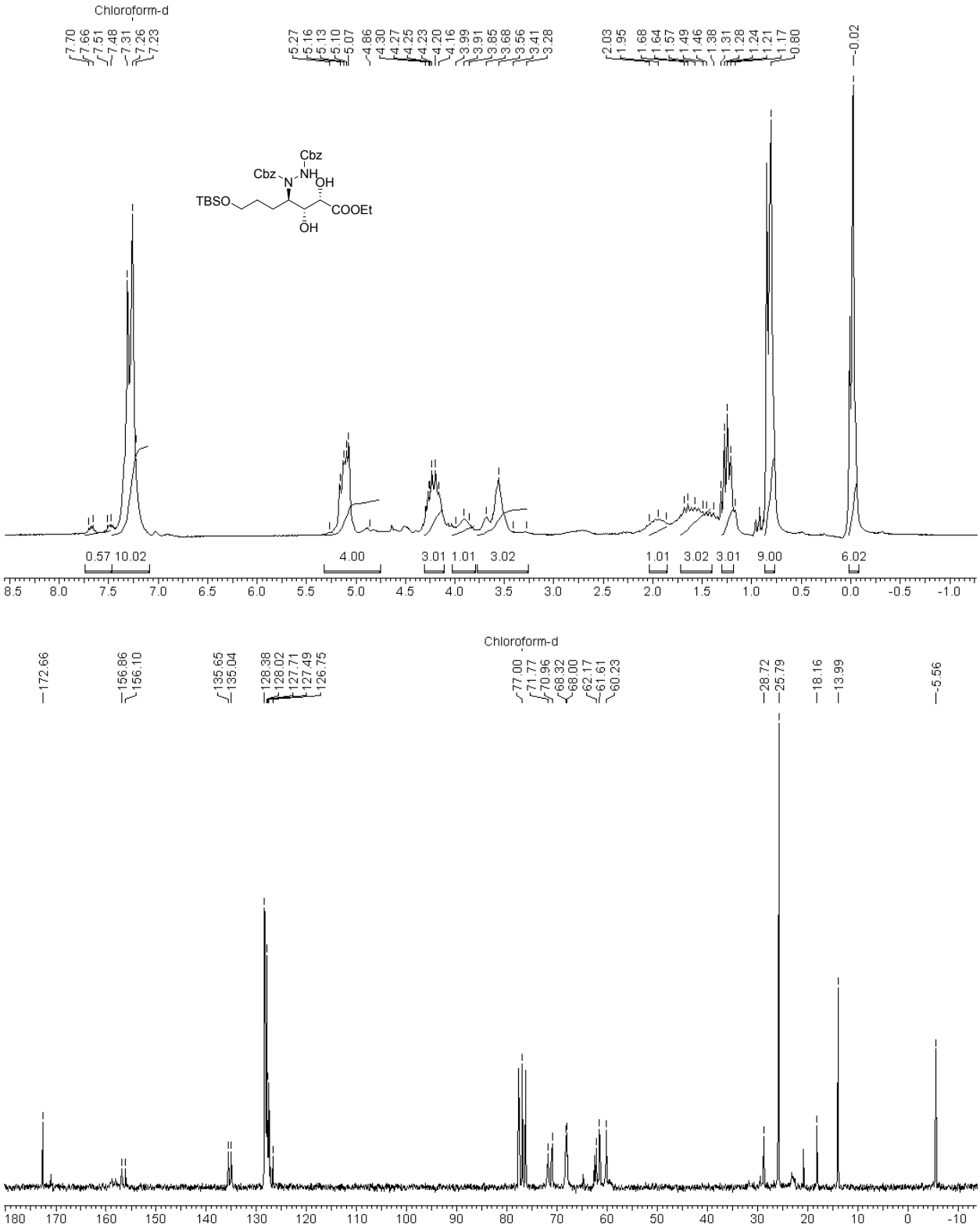


Dibenzyl 1-((2*S*,3*R*,4*R*)-8-((*tert*-butyldimethylsilyl)oxy)-1-ethoxy-2,3-dihydroxy-1-oxooctan-4-yl)hydrazine-1,2-dicarboxylate (11) :

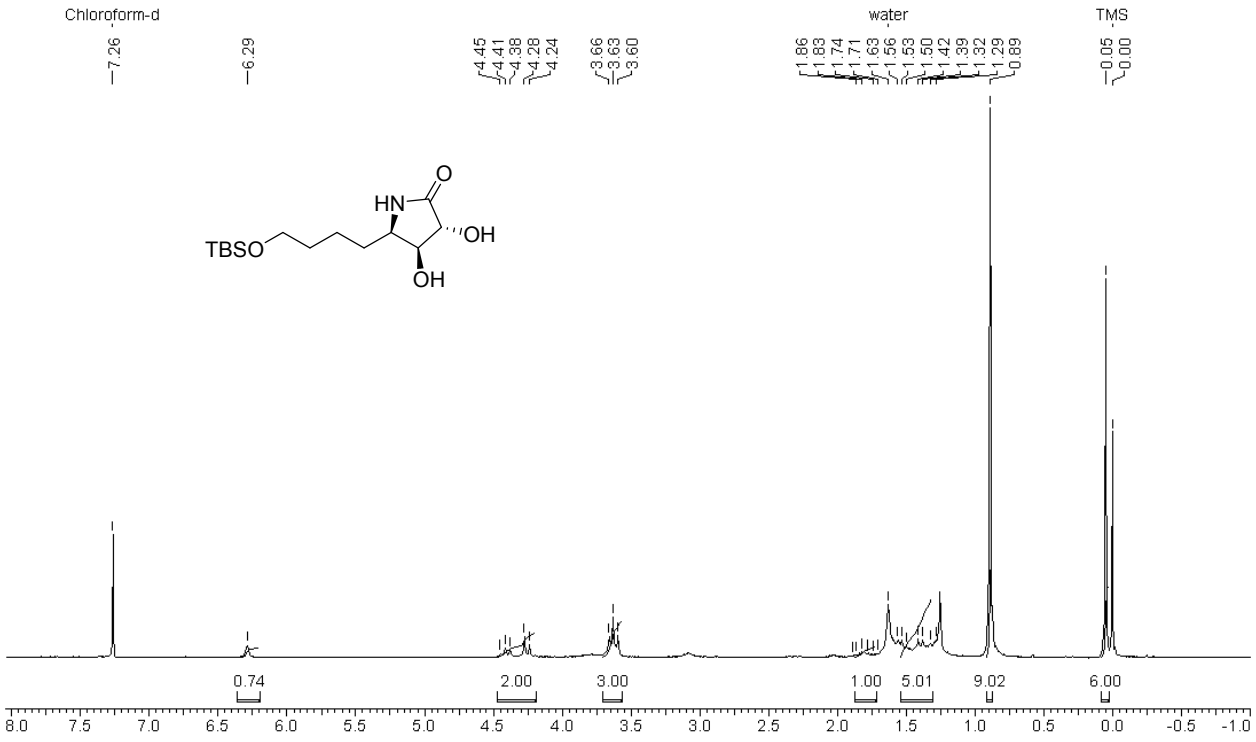


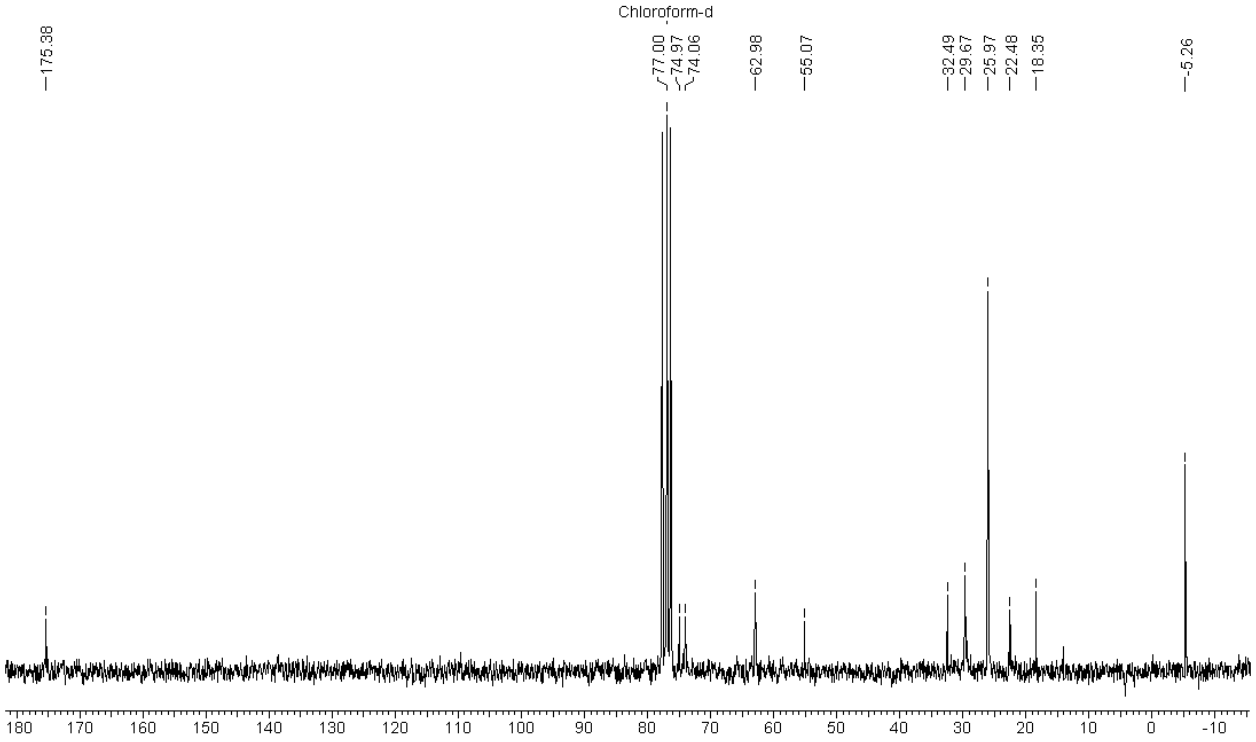


Dibenzyl 1-((2*S*,3*R*,4*R*)-7-((*tert*-butyldimethylsilyl)oxy)-1-ethoxy-2,3-dihydroxy-1-oxoheptan-4-yl)hydrazine-1,2-dicarboxylate (16):



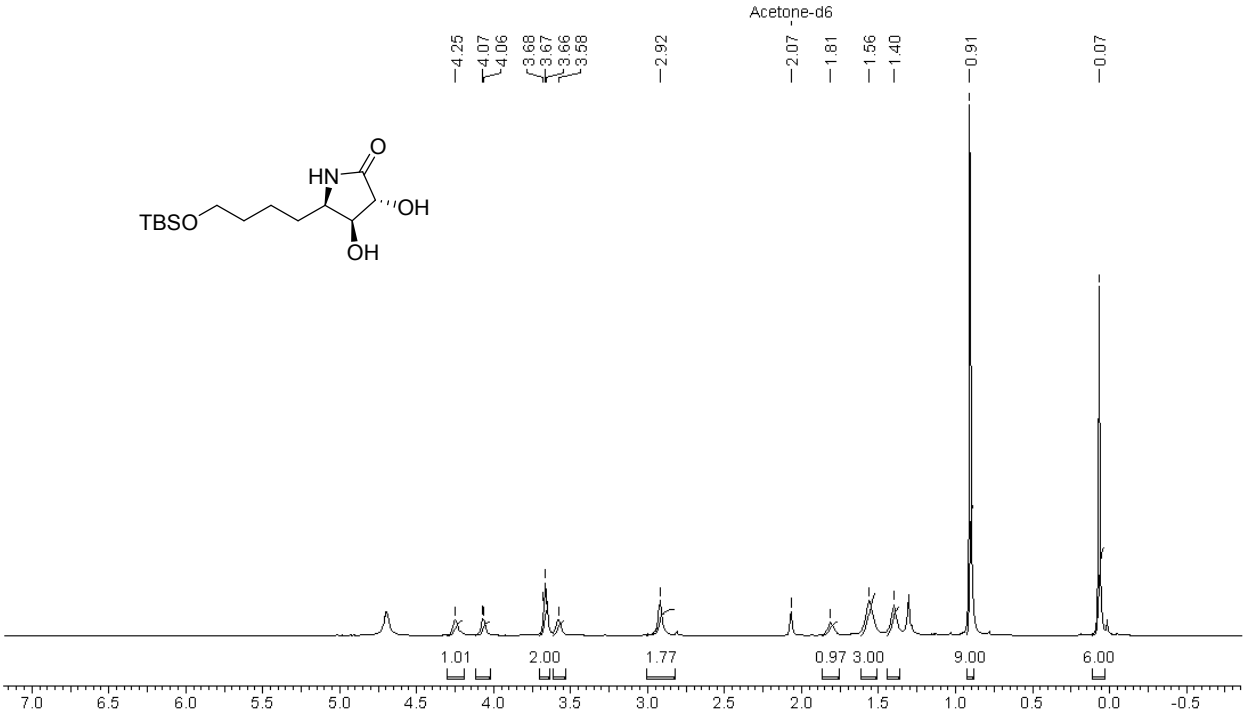
(3*R*,4*S*,5*R*)-5-(4-((*tert*-butyldimethylsilyl)oxy)butyl)-3,4-dihydroxypyrrolidin-2-one (12):



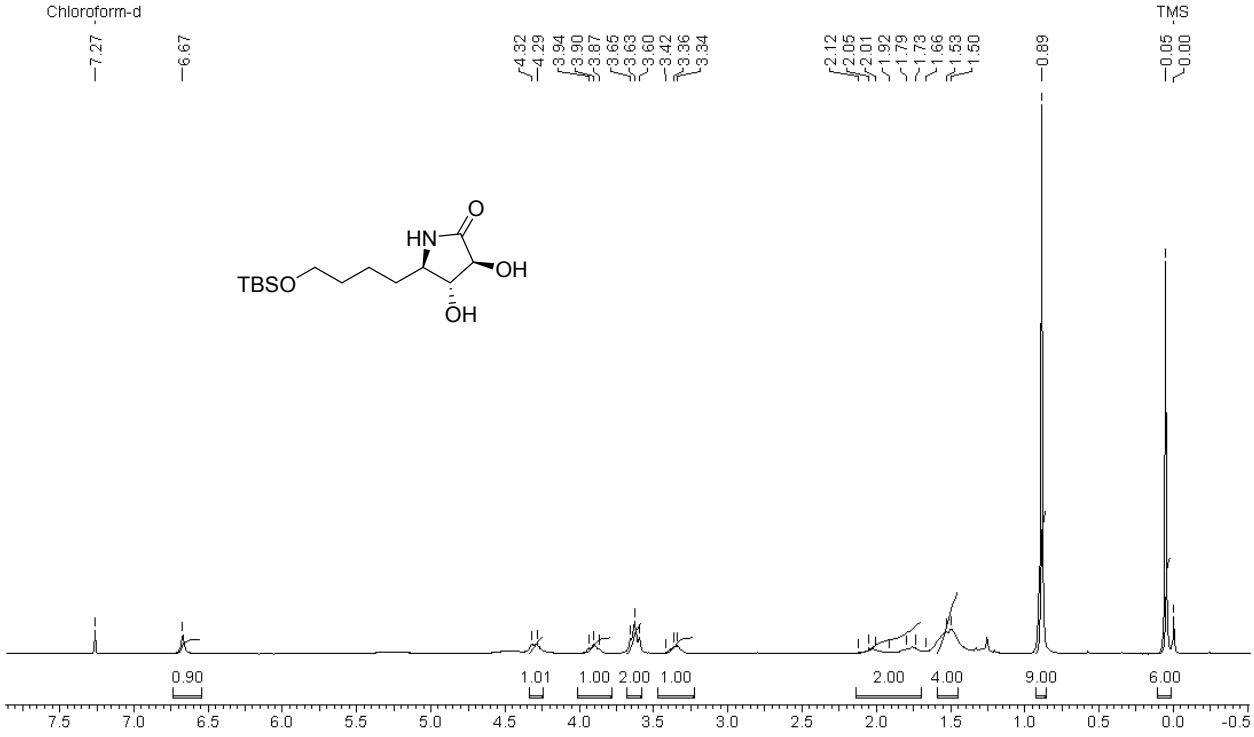


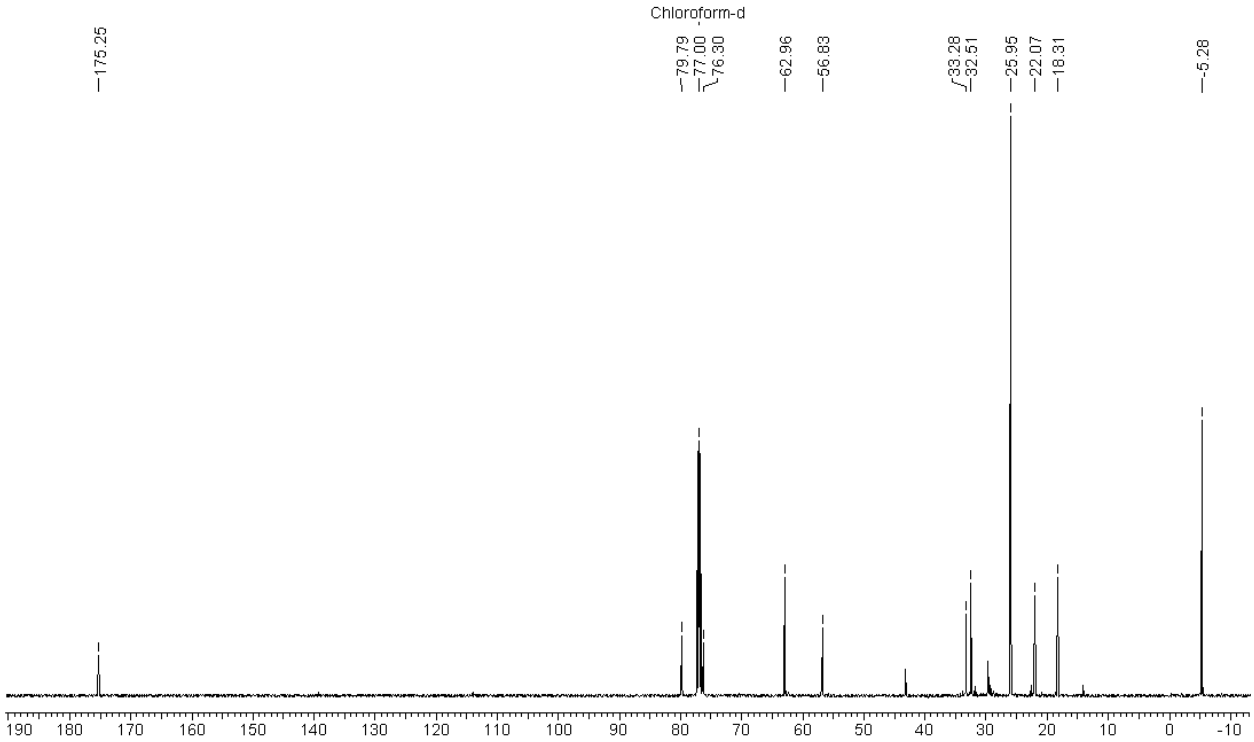
(3*R*,4*S*,5*R*)-5-(4-((*tert*-butyldimethylsilyl)oxy)butyl)-3,4-dihydroxypyrrolidin-2-one (12):

[1]HNMR in Acetone-d6:



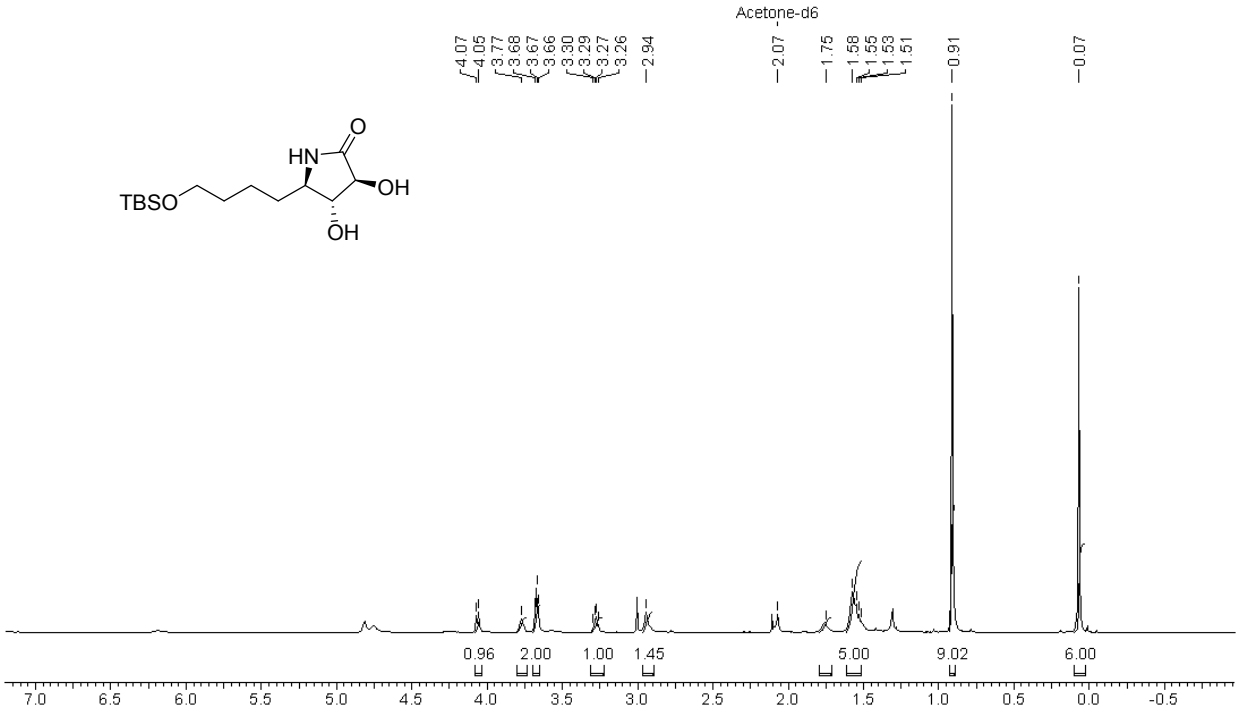
(3*S*,4*R*,5*R*)-5-(4-((*tert*-butyldimethylsilyl)oxy)butyl)-3,4-dihydroxypyrrolidin-2-one (13):



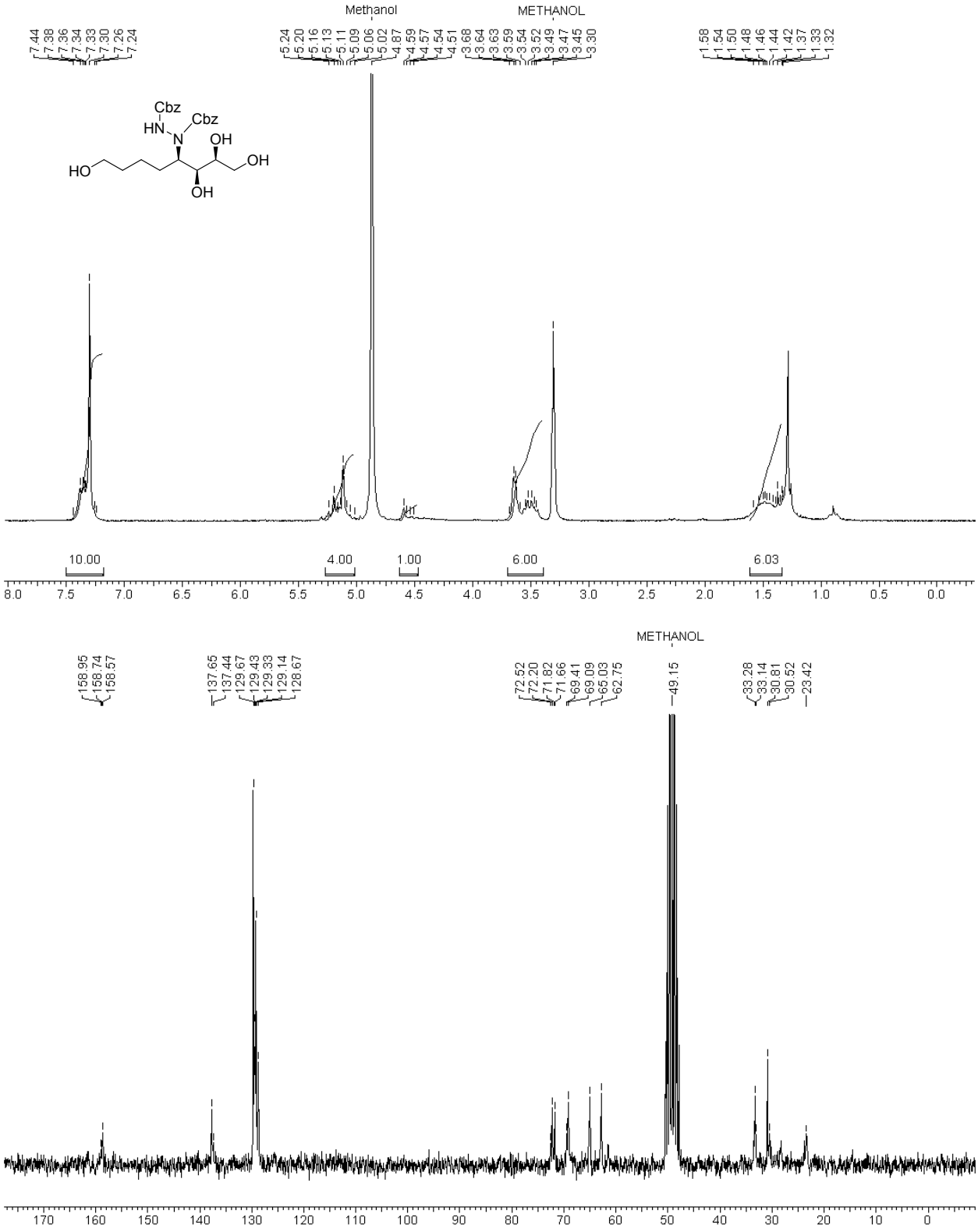


(3*S*,4*R*,5*R*)-5-(4-((*tert*-butyldimethylsilyl)oxy)butyl)-3,4-dihydroxypyrrolidin-2-one (13):

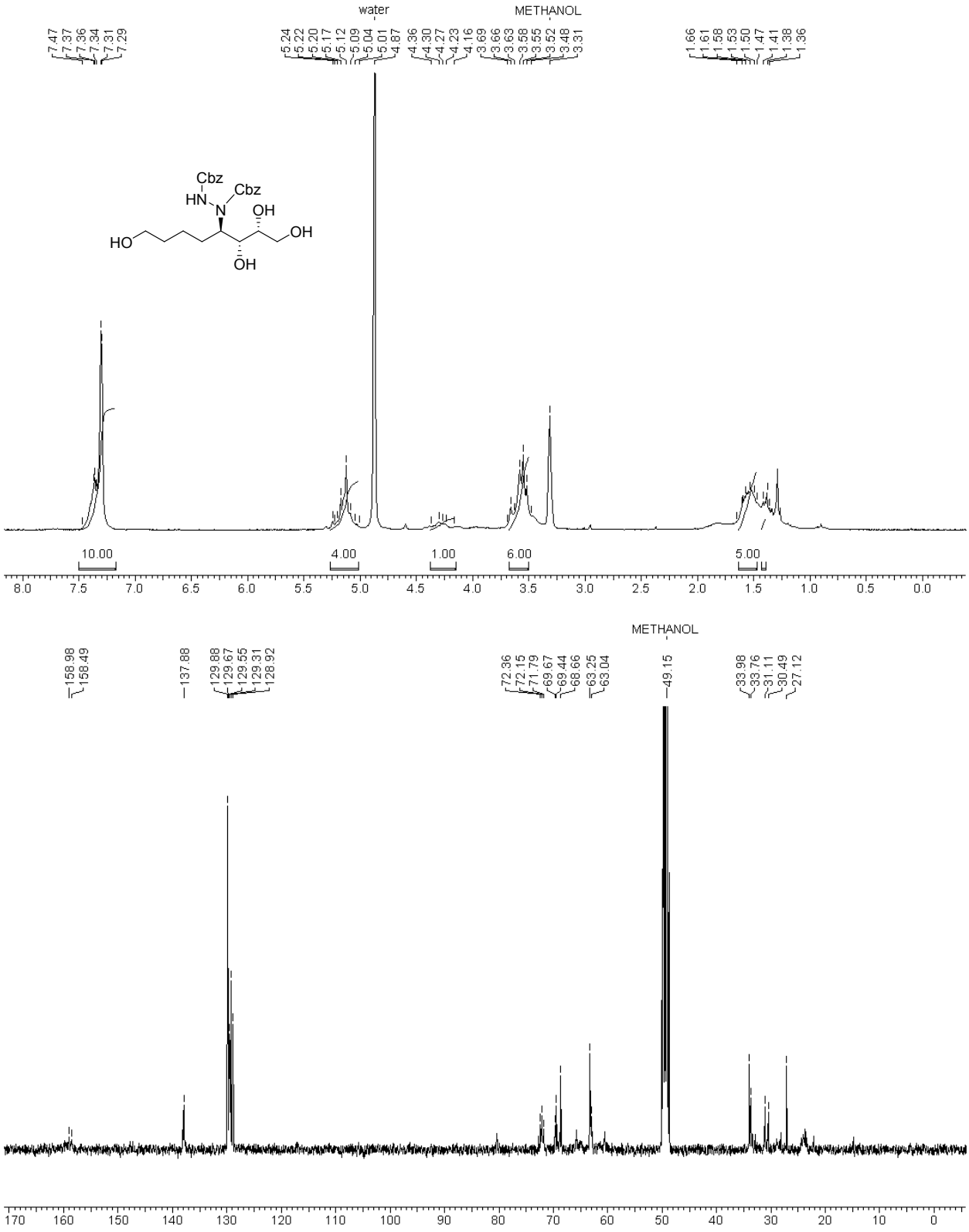
^{1}HNMR in Acetone-d6:



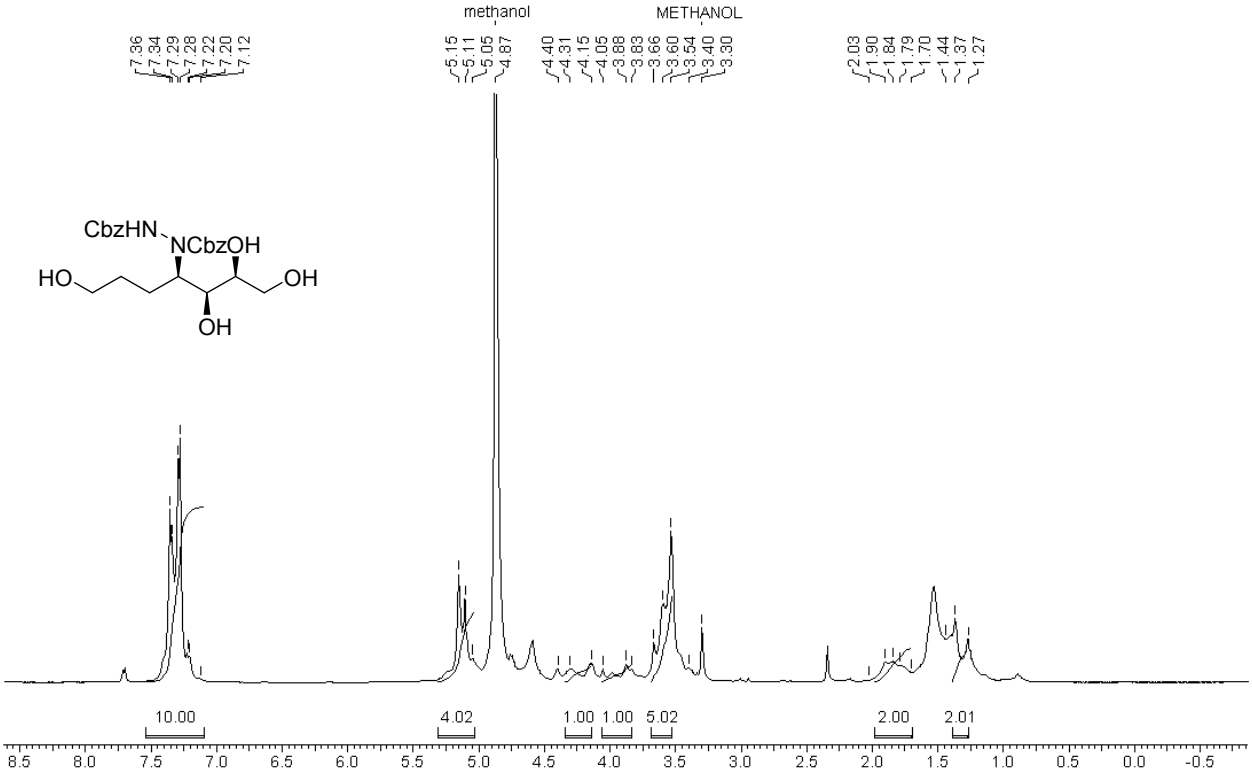
Dibenzyl 1-((2*S*,3*S*,4*R*)-1,2,3,8-tetrahydroxyoctan-4-yl)hydrazine-1,2-dicarboxylate (14):

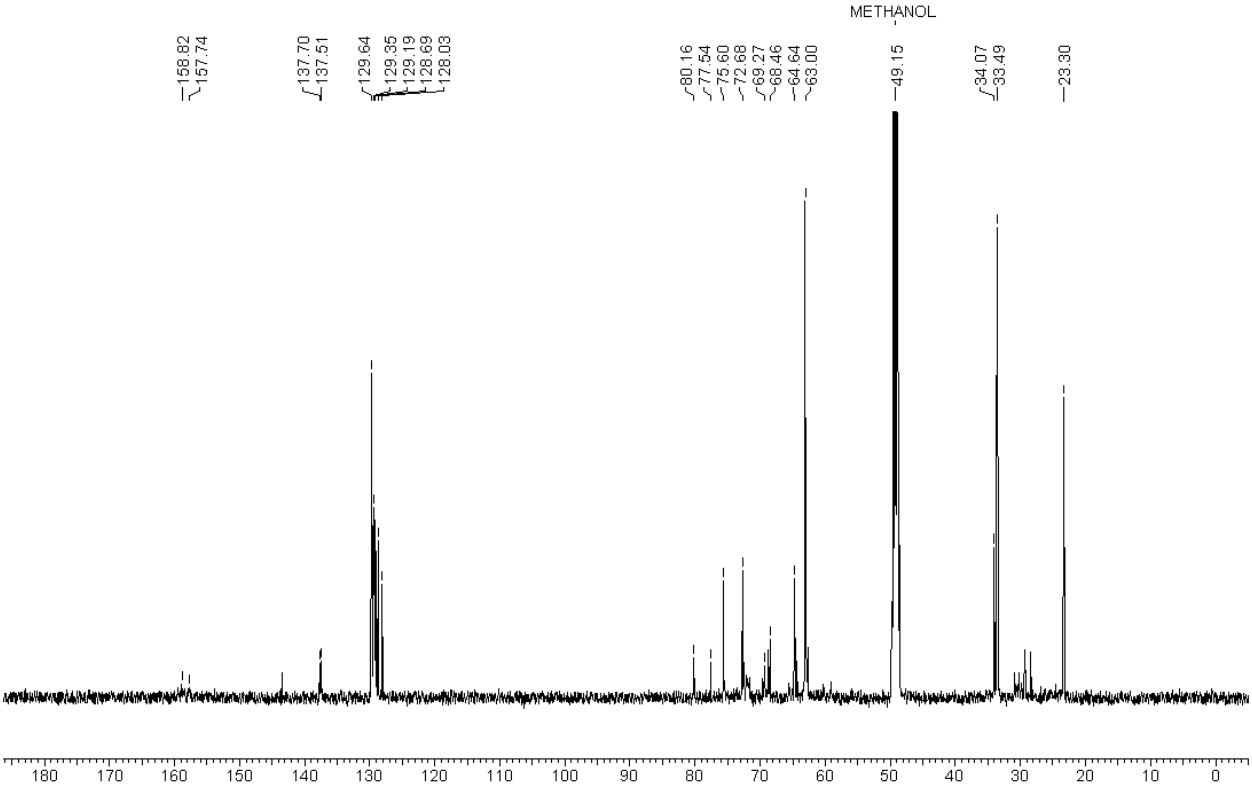


Dibenzyl 1-((2*R*,3*R*,4*R*)-1,2,3,8-tetrahydroxyoctan-4-yl)hydrazine-1,2-dicarboxylate (15):

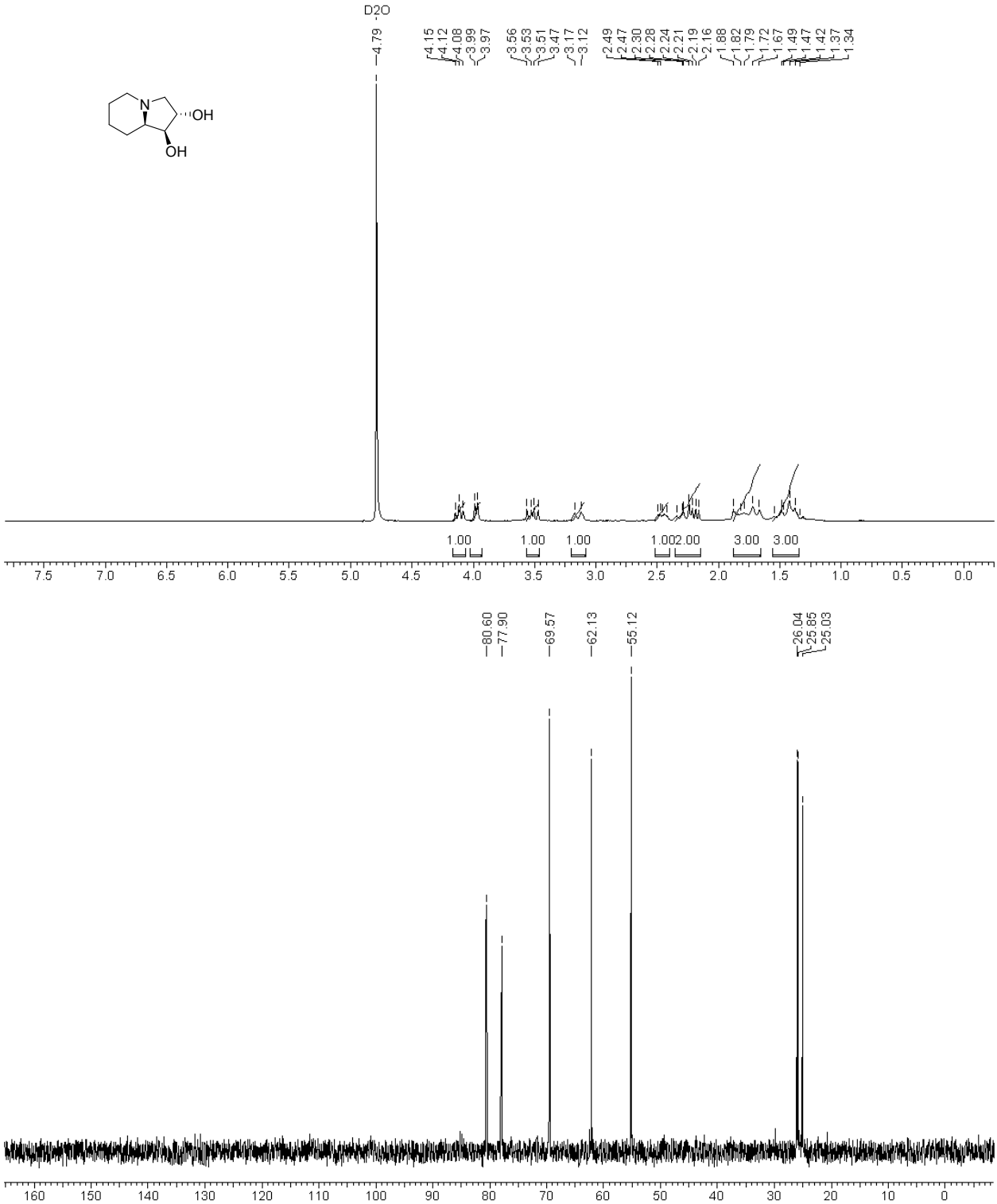


Dibenzyl 1-((2*R*,3*R*,4*R*)-1,2,3,7-tetrahydroxyheptan-4-yl)hydrazine-1,2-dicarboxylate (17):

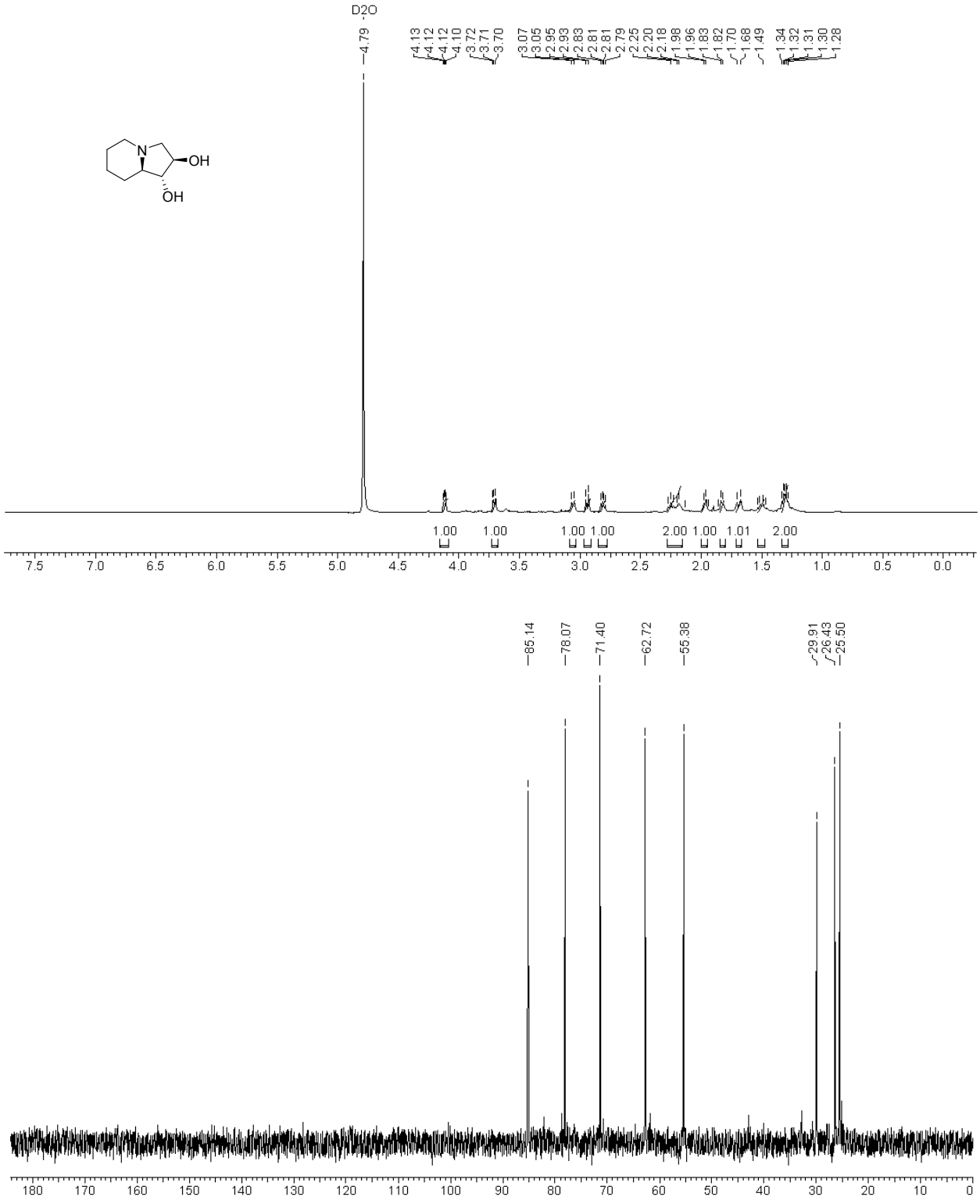




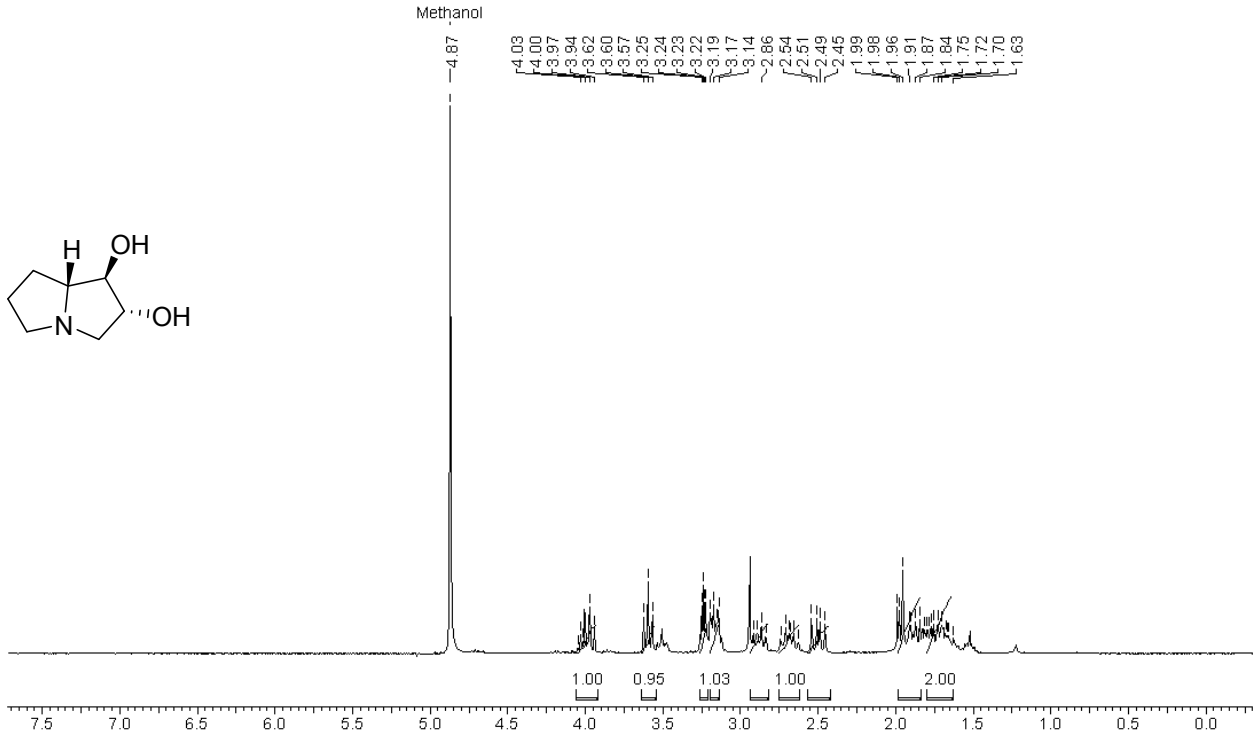
(1*S*,2*S*,8a*R*)- octahydroindolizine-1,2-diol (3):

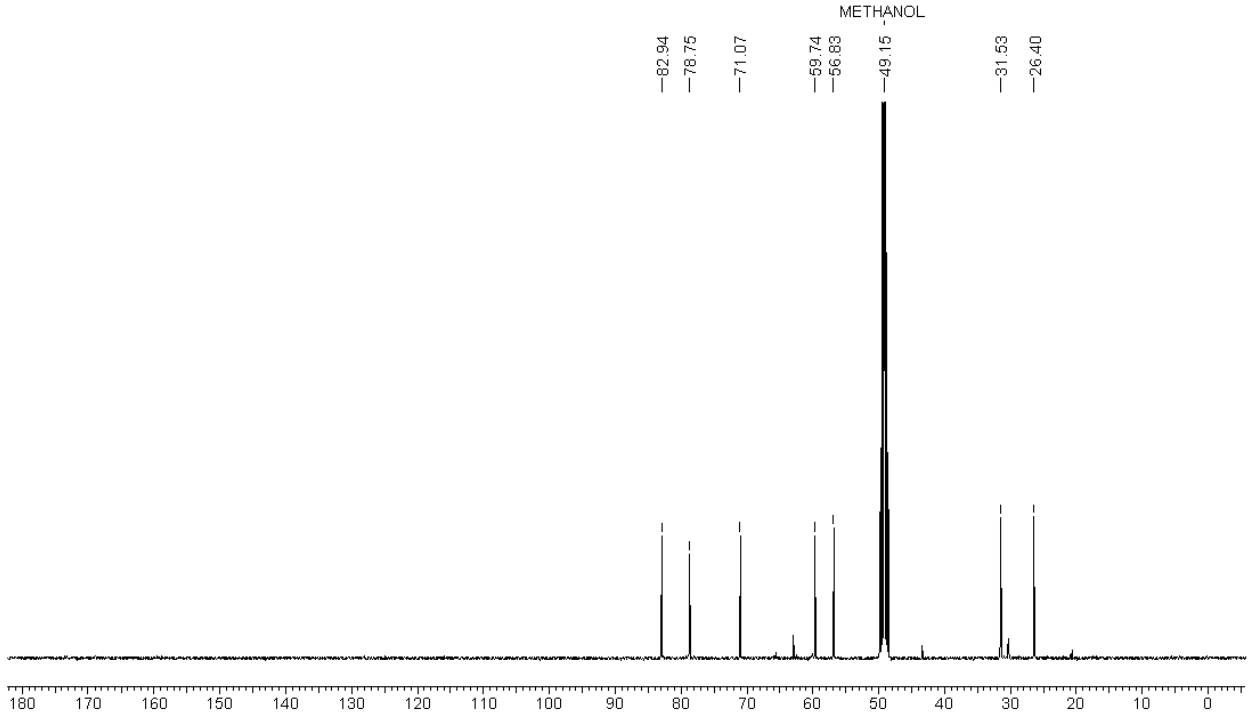


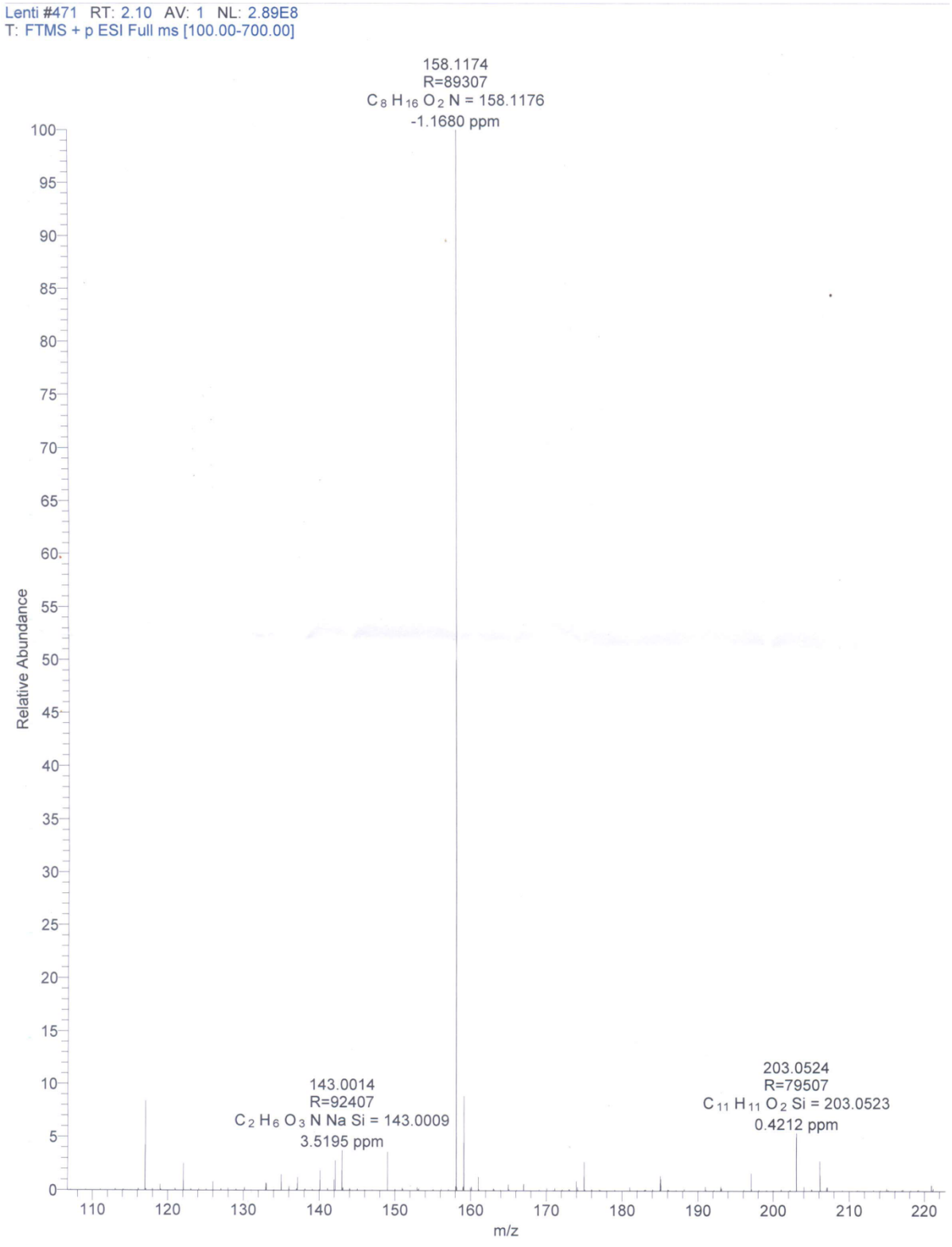
(1*R*,2*R*,8a*R*)-octahydroindolizine-1,2-diol (2):

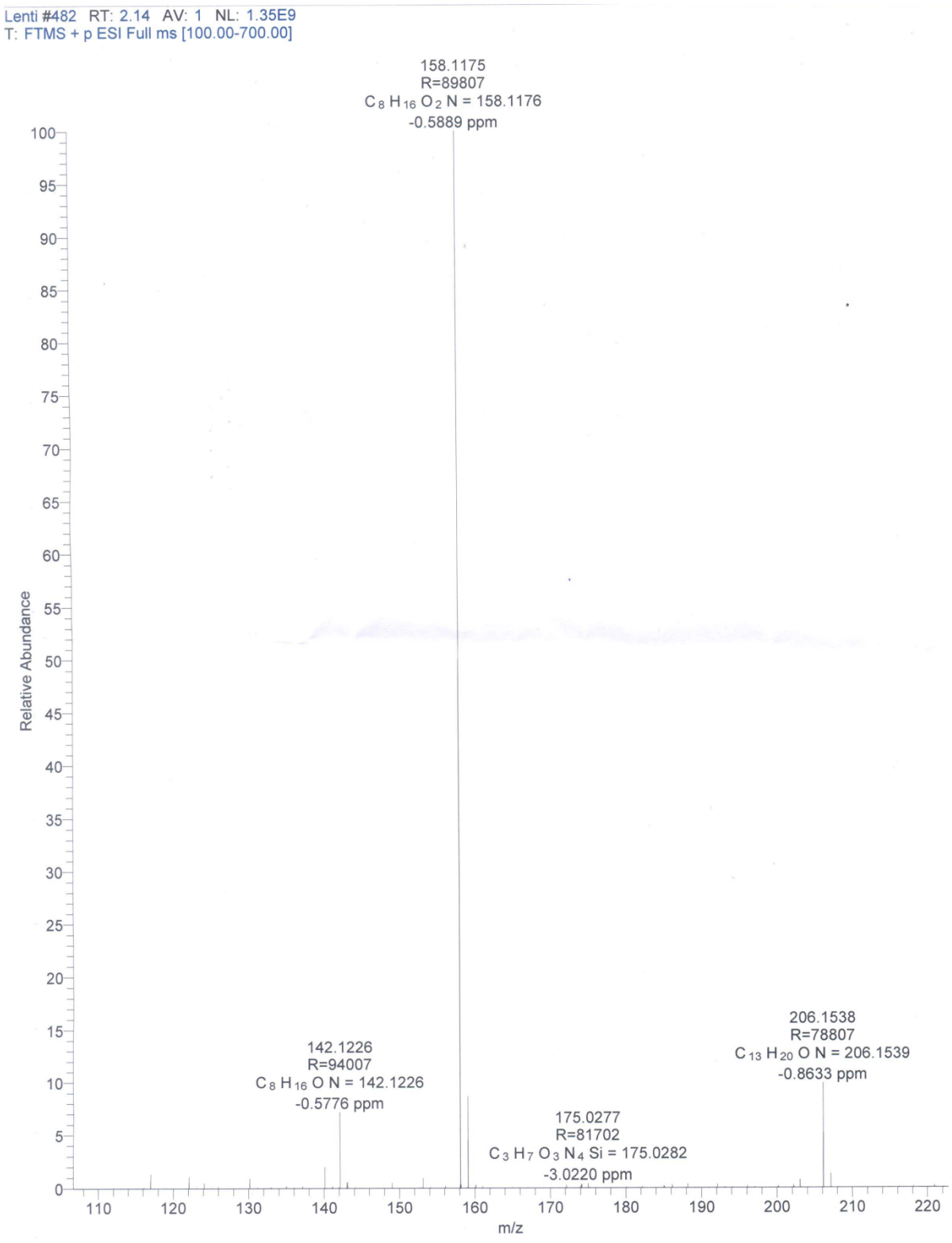


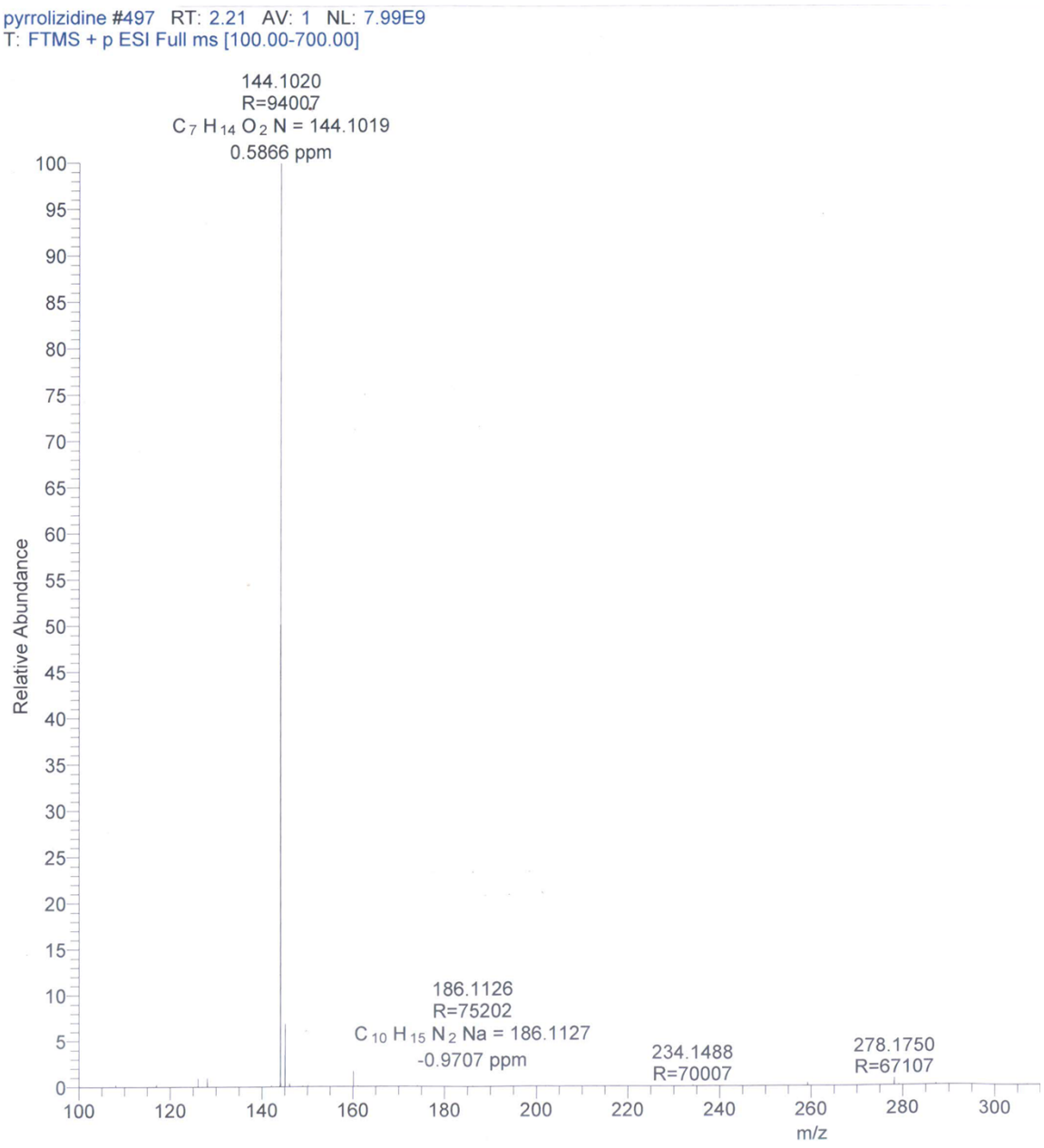
(1*R*,2*R*,7a*R*)-hexahydro-1H-pyrrolizine-1,2-diol (4):



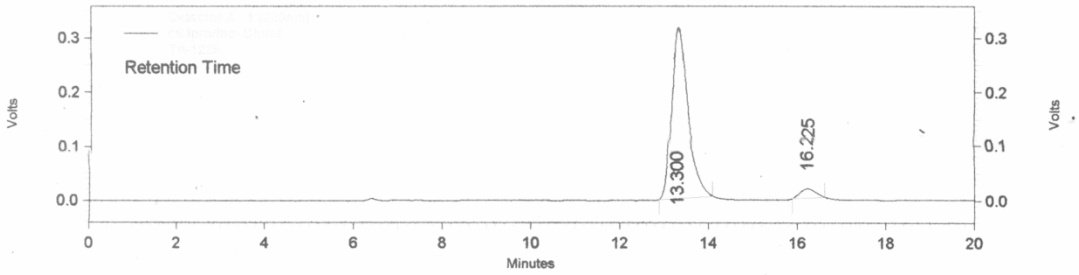



Lenti #471 RT: 2.10 AV: 1 NL: 2.89E8
T: FTMS + p ESI Full ms [100.00-700.00]
158.1174
R=89307
C 8 H 16 O 2 N = 158.1176
-1.1680 ppm
143.0014
R=92407
C 2 H 6 O 3 N Na Si = 143.0009
3.5195 ppm
203.0524
R=79507
C 11 H 11 O 2 Si = 203.0523
0.4212 ppm
Relative Abundance
m/z


Lenti #482 RT: 2.14 AV: 1 NL: 1.35E9
T: FTMS + p ESI Full ms [100.00-700.00]
158.1175
R=89807
C 8 H 16 O 2 N = 158.1176
-0.5889 ppm
142.1226
R=94007
C 8 H 16 O N = 142.1226
-0.5776 ppm
175.0277
R=81702
C 3 H 7 O 3 N 4 Si = 175.0282
-3.0220 ppm
206.1538
R=78807
C 13 H 20 O N = 206.1539
-0.8633 ppm
Relative Abundance
m/z


pyrrolizidine #497 RT: 2.21 AV: 1 NL: 7.99E9
T: FTMS + p ESI Full ms [100.00-700.00]
144.1020
R=94007
C 7 H 14 O 2 N = 144.1019
0.5866 ppm
186.1126
R=75202
C 10 H 15 N 2 Na = 186.1127
-0.9707 ppm
234.1488
R=70007
278.1750
R=67107
Relative Abundance
m/z

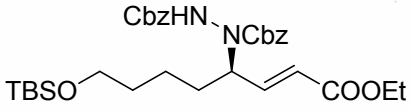
Enantiomeric excess of compound 8a and 8b:

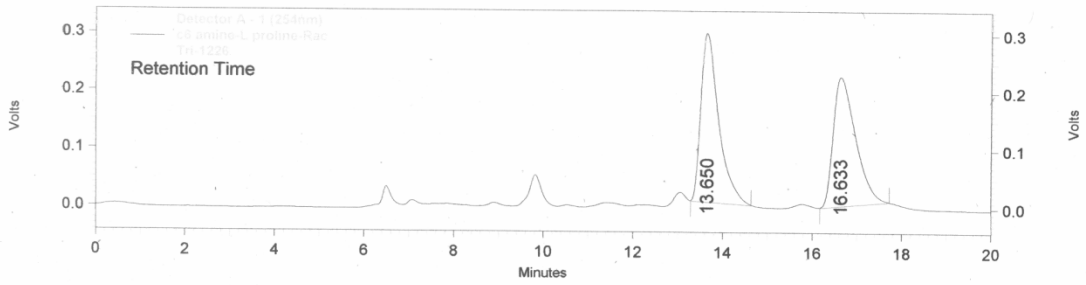


Detector A - 1 (230nm)

Retention Time	C Area	Area %
13.300	8015760	95.313
16.225	394165	4.687
Totals	8409925	100.000

Project Leader : Dr. Pradeep kumar
Column : Kromasil 5-AmyCoat(250x4.6 mm)
Mobile Phase :IPA: Pet ether (10:90)
Wavelength :230nm
Flow Rate :0.5ml/min(396psi)
conc. : 1mg/1.0 mL
Inj vol- :5ul

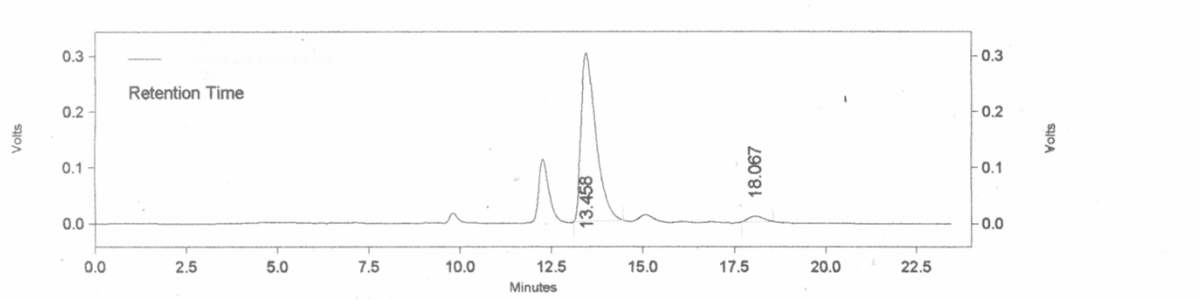




Detector A - 1 (254nm)

Retention Time	C Area	Area %
13.650	8063940	51.217
16.633	7680650	48.783
Totals	15744590	100.000

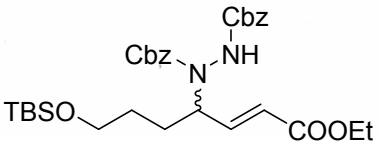
Project Leader : Dr.P.K.TRIPATHI
Column :Kromasil 5-AmyCoat (250x4.6 mm)
Mobile Phase :IPA: Pet Ether (10:90)
Wavelength :254nm
Flow Rate :0.5ml/min(29Kgf)
conc. : 1mg/1.0 mL
Inj vol- :5 ul

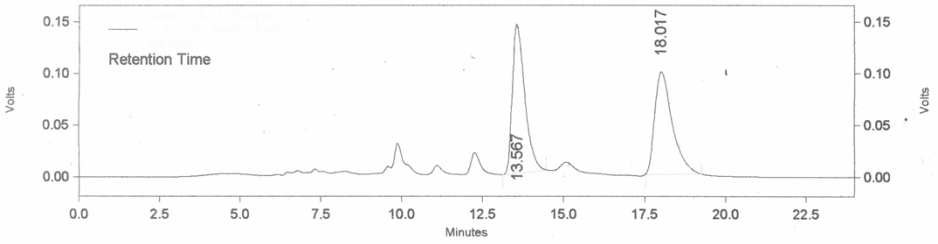


Detector A - 1 (254nm)

Retention Time	C Area	Area %
13.458	8409897	96.917
18.067	267556	3.083
Totals	8677453	100.000

Project Leader : Dr.P.K.TRIPATHI
Column :Kromasil 5-AmyCoat (250x4.6 mm)
Mobile Phase :IPA: Pet Ether (10:90)
Wavelength :254nm
Flow Rate :0.5ml/min(29Kgf)
conc. : 1mg/1.0 mL
Inj vol- :5 ul





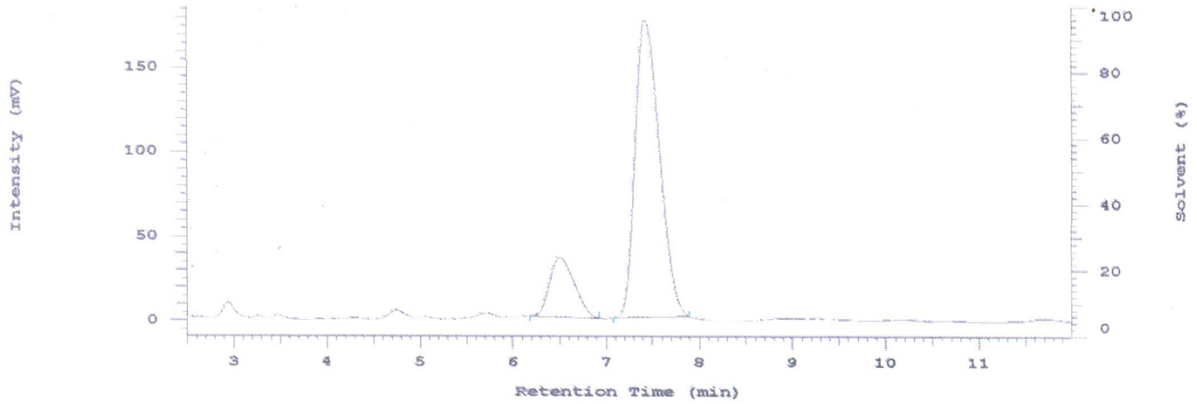
Detector A - 1 (254nm)

Retention Time	C Area	Area %
13.567	3832587	50.664
18.017	3732153	49.336
Totals	7564740	100.000

Project Leader : Dr.P.K.TRIPATHI
Column :Kromasil 5-AmyCoat (250x4.6 mm)
Mobile Phase :IPA: Pet Ether (10:90)
Wavelength :254nm
Flow Rate :0.5ml/min(29Kgf)
conc. : 1mg/1.0 mL
Inj vol- :5 ul

Diastereomeric ratio of compounds 10,11 and 16

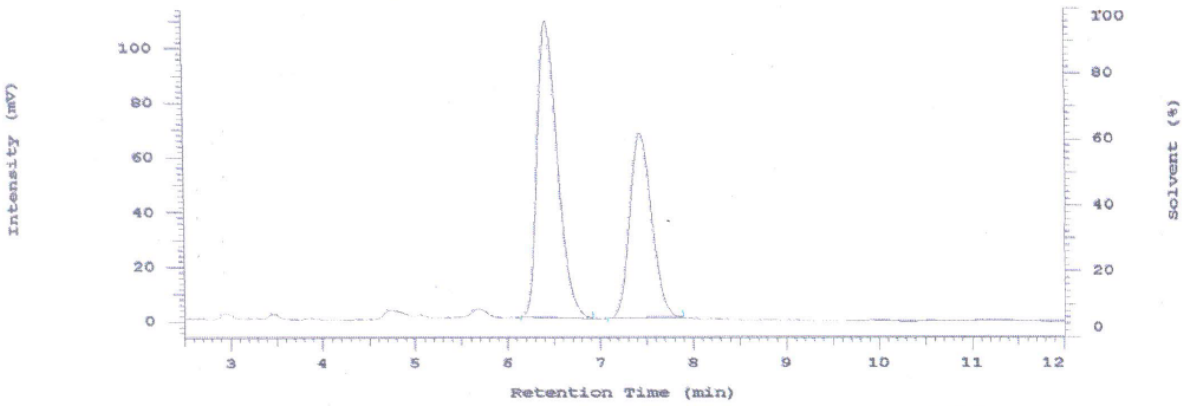
Chrom Type: HPLC Channel : 1



Peak Quantitation: AREA Calculation Method: AREA%

No.	RT	Height	Area	Area %
1	6.50	35587	659151	17.058
2	7.42	176691	3205137	82.942
		212278	3864288	100.000

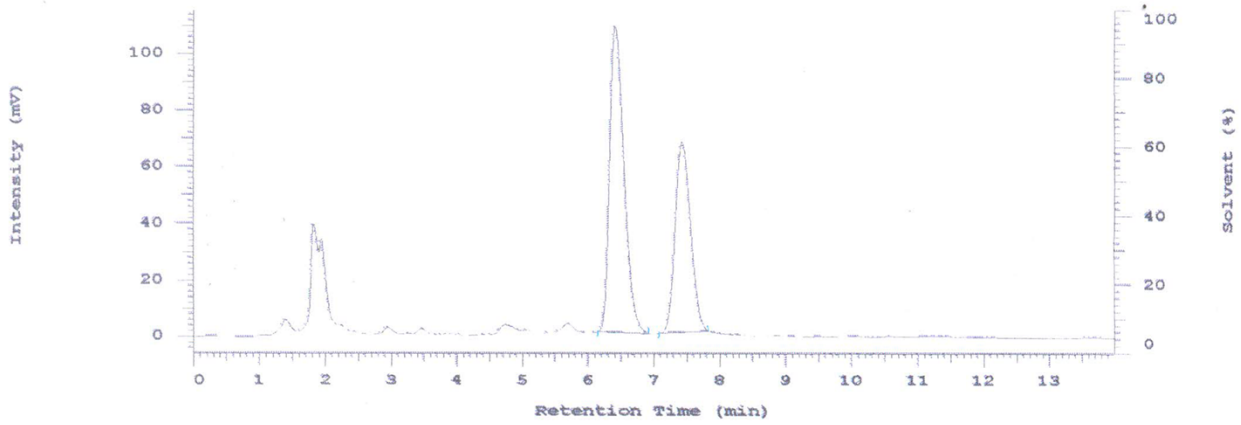
Chrom Type: HPLC Channel : 1



Peak Quantitation: AREA Calculation Method: AREA%

No.	RT	Height	Area	Area %
1	6.42	108336	1637966	59.800
2	7.43	67280	1101099	40.200
		175616	2739065	100.000

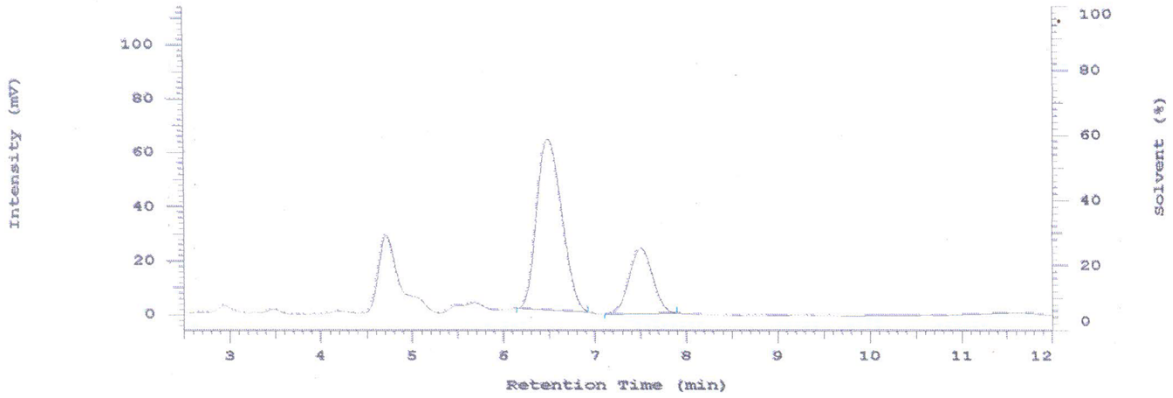
Chrom Type: HPLC Channel : 1



Peak Quantitation: AREA Calculation Method: AREA%

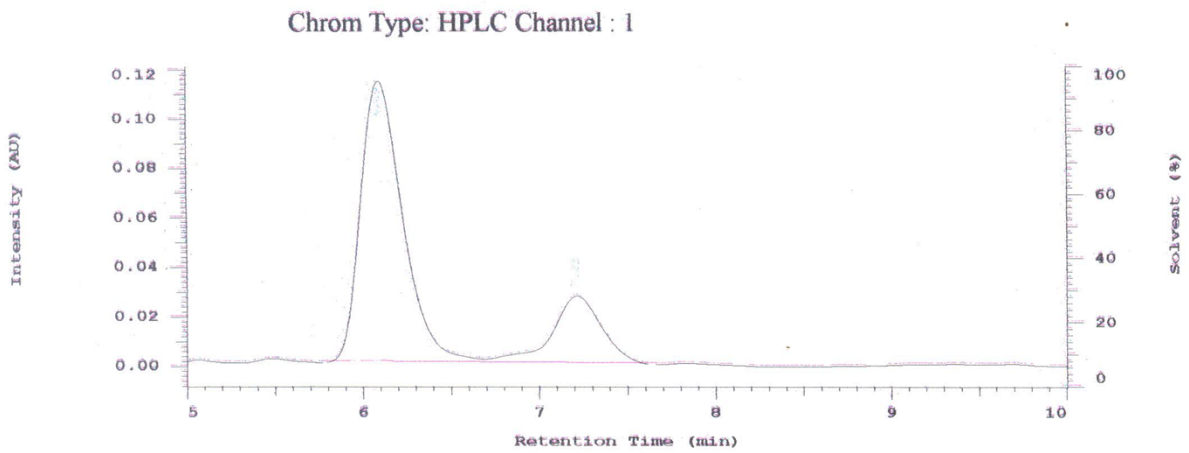
No.	RT	Height	Area	Area %
1	6.42	108336	1637966	60.016
2	7.43	67091	1091240	39.984
		175427	2729206	100.000

Chrom Type: HPLC Channel : 1



Peak Quantitation: AREA Calculation Method: AREA%

No.	RT	Height	Area	Area %
1	6.49	63111	1204084	73.668
2	7.50	24267	430392	26.332
		87378	1634476	100.000



No.	RT	Height	Area	Area %
1	6.09	56928	950097	77.155
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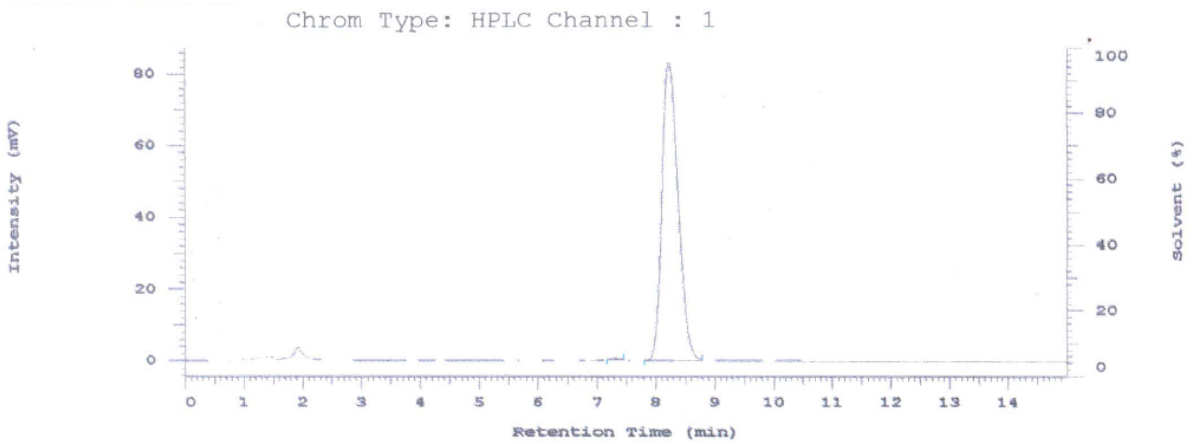
		70715	1231415	100.000



Peak Quantitation: AREA Calculation Method: AREA%

No.	RT	Height	Area	Area %
1	7.33	362	3613	0.228
2	8.23	83063	1579306	99.772
		83425	1582919	100.000