Supporting Information for

Tin(II) chloride Assisted Synthesis of *N*-protected *γ*- amino *β*-keto esters through Semipinacol Rearrangement.

Anupam Bandyopadhyay, Neha Agarwal, Sachidanand M. Mali, Sandip V. Jadhav and Hosahudya N. Gopi*

Department of Chemistry, Indian Institute of Science Education and Research, Garware Circle, Pashan, Pune-411021, India.

hn.gopi@iiserpune.ac.in

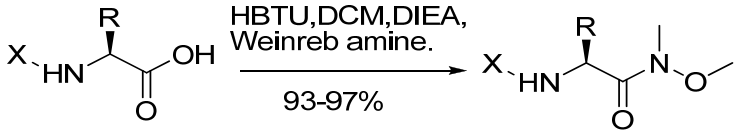
General Experimental Details

All amino acids, ethyl diazoacetate, LAH, DiPEA, Tin(II) chloride, TFA , DMP, Cs_2CO_3, Cbz-Cl were purchased from Aldrich. THF, DCM, DMF, were purchased from Merck. Isobutyl chloroformate, $NaBH_4$, HBTU, HOBT, Methanesulfonic acid, di-tert-butyl dicarbonate, Fmoc-OSu, 3-Methoxy phenol, Benzyl bromide were obtained from spectrochem and used without further purification. THF and DiPEA were dried over sodium and distilled immediately prior to use. Column chromatography were performed on Merck silica gel (120-200 mesh) and flash chromatography (Combi Flash R_f). The ^{1}H spectra were recorded Brucker 500 MHz (or 125 MHz for ^{13}C) and Jeol 400 MHz (or 100 MHz for ^{13}C) spectrometers using residual solvents signals as an internal reference ($CDCl_3$ δ_H, 7.24 ppm, δ_c 77.0 ppm). The chemical shifts (δ) are reported in *ppm* and coupling constants in (J) in Hz. Specific rotations were recorded using MeOH as a solvent (Rudolph Analytical Research). UV and Fluorescence data were performed on Thermo Scientific and Fluorolog (Horiba Jobin Yvin) spectrophotometers, respectively. High-resolution mass spectra obtained from HRMS-ESI (waters), LCMS/MS (waters) and MALDI TOF/TOF (Applied Biosciences).

General procedure to make Cbz-/Boc-Weinreb amides

We used the reported procedure for the synthesis of Weinreb amides.[1, 2] In a typical experiment, the protected amino acid (15 mmol) was dissolved in dry DCM (30 mL) and then treated

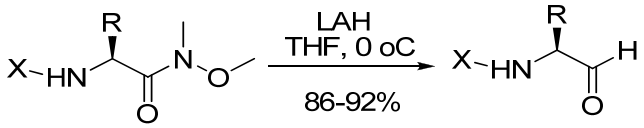
with HBTU (15 mmol, 5.68 g) and DiEPA (45 mmol , 4.54 g), the reaction mixture was cooled to 0 ^{o}C. After stirring for 5 min hydrochloride salt (18 mmol, 1.74g) of *N, O*-dimethylhydroxylamine was added. The progress of the reaction was monitored by TLC. After completion of the reaction (roughly 2hrs), DCM was evaporated and the residue was diluted with 150 mL of ethyl acetate and washed with 5% HCl (5 % by vol. in water, 2 x 30 mL), 10 % sodium carbonate solution in water (2 × 40 mL) and followed by brine (30 mL). The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The pure Boc-Weinreb amides were isolated after column chromatography using EtOAc/ pet.ether (60-80 ^{o}C) solvent system.



R = -Me, -^{i}Pr, -^{i}Bu, -Bnz, X= -Boc, -Cbz

General procedure to make Cbz-/Boc-amino aldehydes[1, 2]

The *N*-Protected Weinreb amide (15 mmol) was dissolved in 120 mL of dry THF under N_2 atmosphere, cooled to 0 ^{o}C, and then $LiAlH_4$ (18.75 mmol, 0.712 g) was added slowly during 10 min. Reaction was stirred for another 20 min to complete the reaction. Reaction was quenched with 5% HCl (5 % by volume in water) very slowly in ice cool condition (*p*H 3). THF was evaporated from the reaction mixture and the *N*-protected amino aldehyde was extracted with ether (3 × 80 mL). Combined ether layer was washed with brine (40 mL) and dried over anhydrous Na_2SO_4. Organic layer was concentrated under reduced pressure to get oily product and immediately used for next step without purification.



R = -Me, -^{i}Pr, -^{i}Bu, -Bnz,

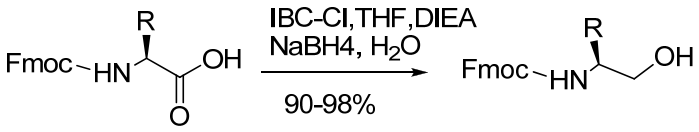
X= -Boc, -Cbz

Compounds	**Yield**

Boc-ala-H **(3a)**	89%, (2.02 g)
D-Boc-ala-H **(3b)**	90%, (2.05g)
Boc-val-H **(3c)**	90%, (2.47 g)
Boc-leu-H **(3d)**	90%, (2.58 g)
Boc-Pheala-H **(3e)**	92%, (3.06 g)
Boc-Ileu-H **(3f)**	86%, (2.77g)
Cbz-ala-H **(3g)**	88%, (2.73g)
Cbz-val-H **(3h)**	91%, (3.20g)
Cbz-leu-H **(3i)**	87%, (3.25g)

General procedure for the synthesis of Fmoc-amino alcohol[3-5]

The Fmoc-protected amino acid (10 mmol) was dissolved in dry THF (20 mL) under nitrogen atmosphere, and cooled -15 ^{o}C , and then treated with DiPEA (10.2 mmol, 1.32g) followed by isobutyl chloroformate (10 mmol, 1.366g). White hydrochloride salt of DiPEA was precipitated out immediately after addition of isobutyl chloroformate. The reaction was continued to stir for another 10 min. The hydrochloride salt of DiPEA was filtered and washed with THF (2 × 10 mL). The filtrate was again cooled to -15 ^{o}C under nitrogen atmosphere, and then a solution of $NaBH_4$ (20 mmol, 720 mg) in 3mL of water was added with vigorous stirring. Immediate evolution of gas was observed after the addition. THF was evaporated from the reaction mixture and diluted with EtOAc (150 mL). The organic layer was washed with 5% HCl (5 % by volume in water, 2 × 50 mL), 5 % sodium carbonate solution in water (2 x50 mL), followed by brine (50 mL). Organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The Fmoc-alcohol was purified using column chromatography and used for the next step.

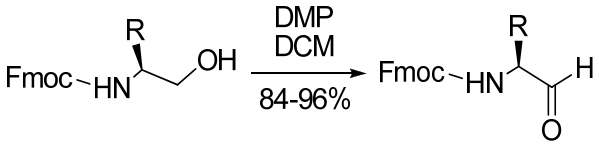


R= -iBu, -(CH_2)-NH-Boc, -$CH_2CO_2{}^{t}$Bu, -CH_2-Ph-O^{t}Bu

Product	**Yield**
(*S*)-(9H-fluoren-9-yl)methyl (1-hydroxy-4-methylpentan-2-yl)carbamate	92% (3.123g)
(*S*)-*tert*-butyl 3-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-4-hydroxybutanoate	90% (3.572g)
(*S*)-(9H-fluoren-9-yl)methyl *tert*-butyl (6-hydroxyhexane-1,5-diyl)dicarbamate	98% (4.443g)
(*S*)-(9H-fluoren-9-yl)methyl (1-(4-(*tert*-butoxy)phenyl)-3-hydroxypropan-2-yl) Carbamate	91% (4.045g)

General procedure for the synthesis of Fmoc-amino aldehydes[3-6]

The Fmoc-amino alcohol (5mmol) was dissolved in 50 mL of DCM at rt and then 2.1 g (7.5mmol) Dess-Martin periodinane (DMP) was added . Resulting reaction mixture was stirred for 1hr, the progress of the reaction was monitored by TLC. Reaction mixture was diluted with diethylether (50mL) followed by 10% Na_2CO_3 solution (50mL) with vigorous stirring. After 10 min organic layer was separated and washed with 10% Na2CO3 solution (50 mL × 2) and brine. Organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get Fmoc-amino aldehyde and it was immediately used in the next step without purification.



R= -iBu, -(CH_2)-NH-Boc, -$CH_2CO_2{}^tBu$, -CH_2-Ph-O^tBu

Compound	**Yield**
(*S*)-(9H-fluoren-9-yl)methyl (4-methyl-1-oxopentan-2-yl)carbamate **(6a)**	92% (1.55gm)
(*S*)-*tert*-butyl 3-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-4-oxobutanoate **(6b)**	88% (1.735gm)
(*S*)-(9H-fluoren-9-yl)methyl *tert*-butyl (6-oxohexane-1,5-diyl)dicarbamate **(6c)**	96% (2.164gm)
(*S*)-(9H-fluoren-9-yl)methyl(1-(4-(*tert*-butoxy)phenyl)-3-oxopropan-2-yl)carbamate**(6d)**	84% (1.858gm)

References

(1) J. –A, Fehrentz, B. Castro, *Synthesis,* 1983**,** 676.

(2) S. Benetti, C. D. Risi, P. Marchetti, G. P. Pollini, V. Zanirato, *Synthesis,* 2002, 331-338.

(3) J. J. Wen, C. M. Crews, *Tetrahedron: Asymm*. 1998, **9**, 1855

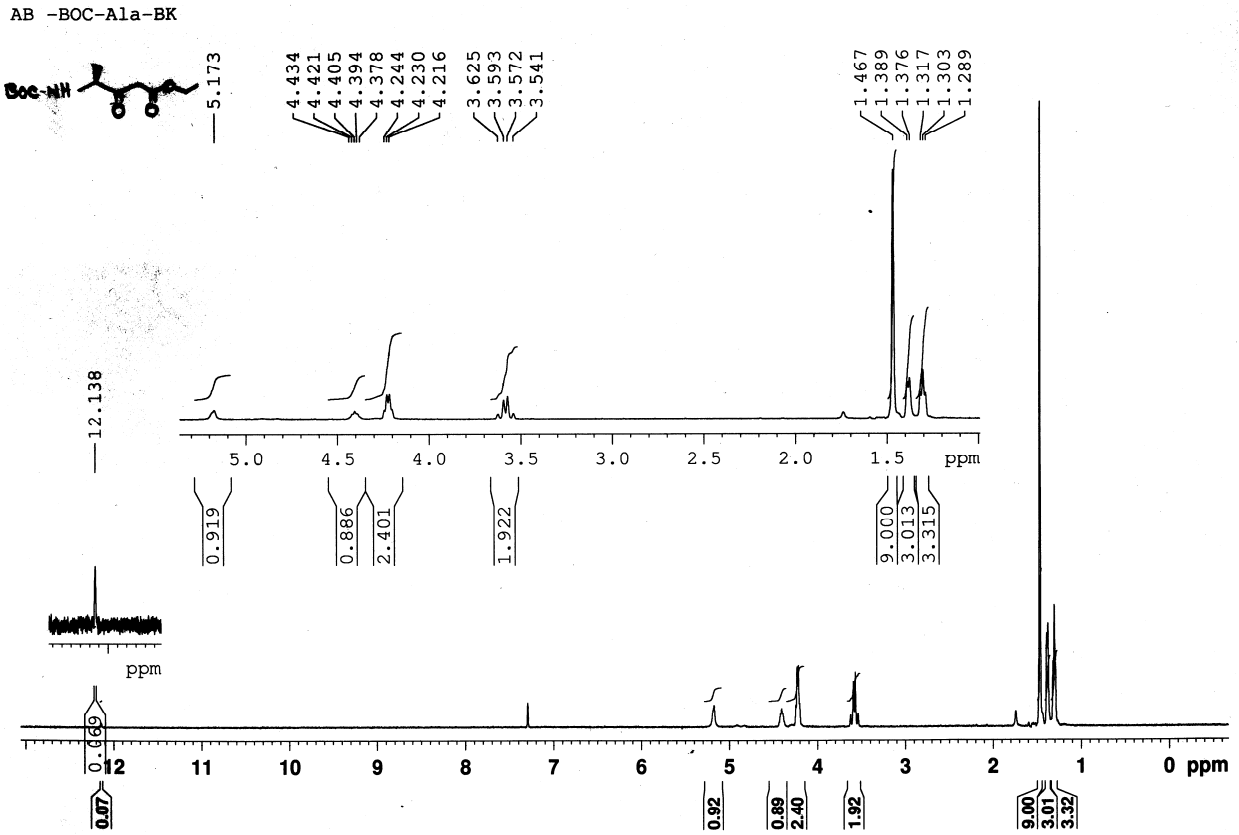
(4) M. Rodriguez, M. Llinares, S. Doulut, A. Hintz, J. Martinez, *Tetrahedron Lett.* 1991, **32**, 923.

(5) Q. Wang, R. J. Linhardt, *J. Org. Chem.* 2003, **68**, 2668.

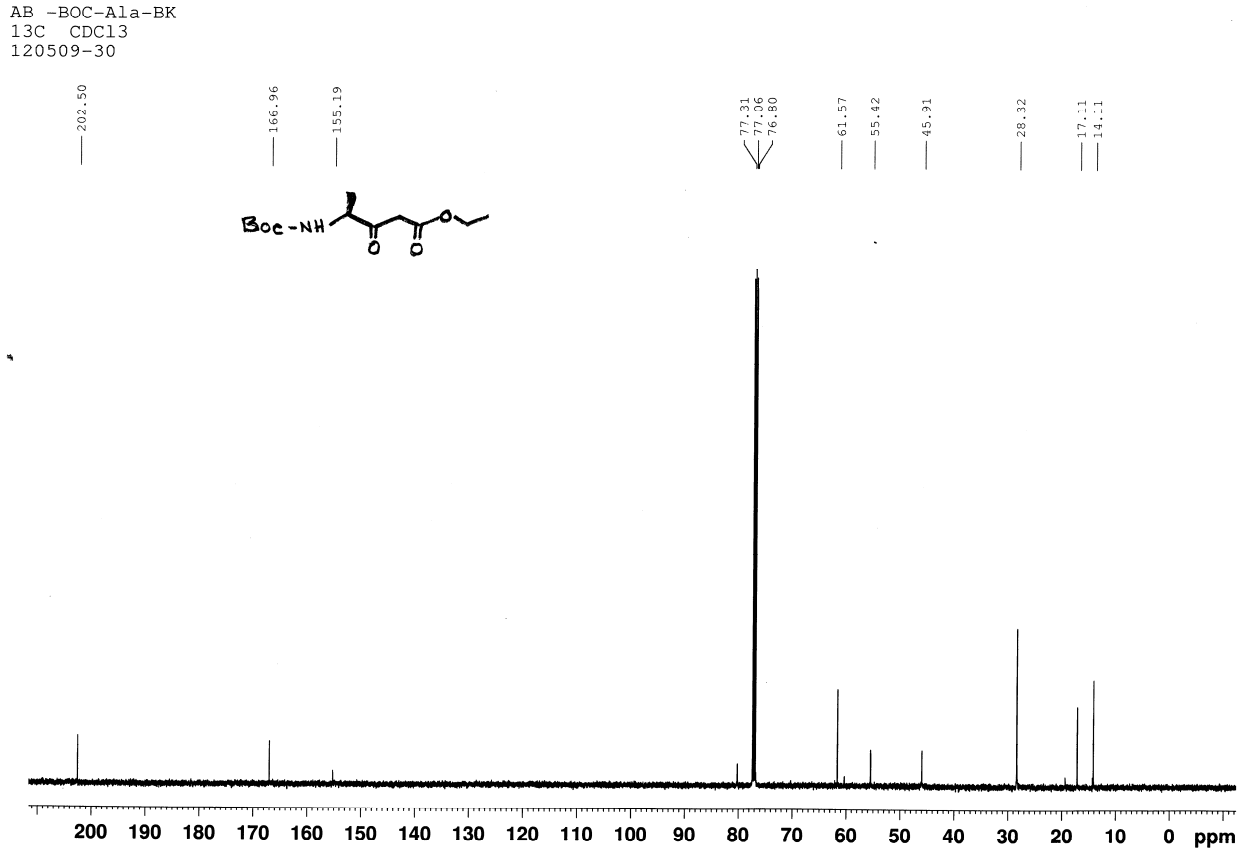
(6) D. B. Dess, J. C. Martin, *J. Org. Chem.* 1983**, 43**, 4155.

Copies of ^{1}H , ^{13}CNMR and Mass Spectra for Products

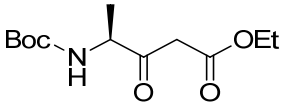
4a

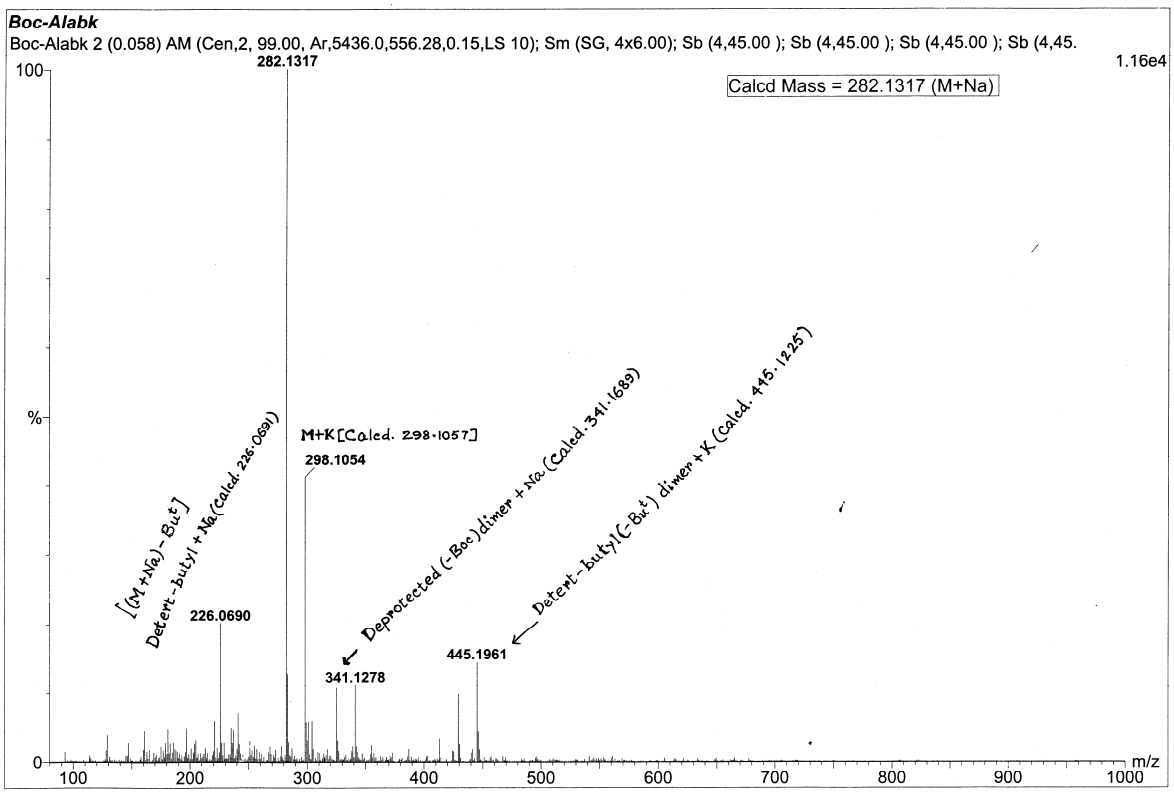


4a

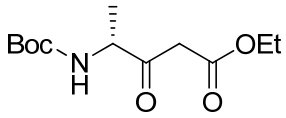

AB -BOC-Ala-BK
13C CDCl3
120509-30
202.50
166.96
155.19
77.31
77.06
76.80
61.57
55.42
45.91
28.32
17.11
14.11
Boc-NH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

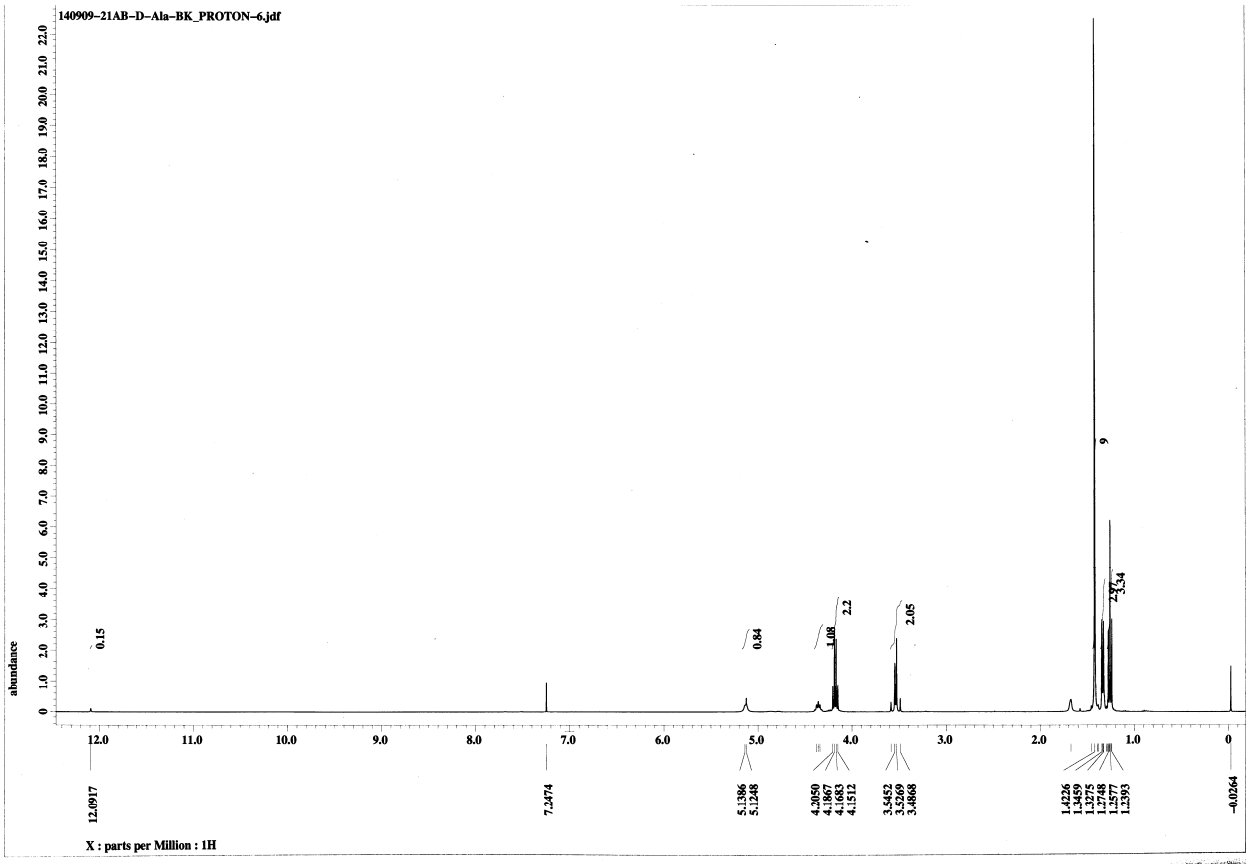
4a


Boc
N
H
O
O
OEt

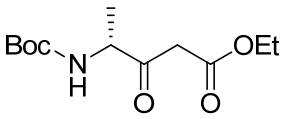

Boc-Alabk
Boc-Alabk 2 (0.058) AM (Cen,2, 99.00, Ar,5436.0,556.28,0.15,LS 10); Sm (SG, 4x6.00); Sb (4,45.00); Sb (4,45.00); Sb (4,45.00); Sb (4,45.
1.16e4
282.1317
Calcd Mass = 282.1317 (M+Na)
100
%
0
M+K[Calcd. 298.1057]
298.1054
[(M+Na)- But]
Detert-butyl+Na(Calcd. 226.0691)
226.0690
Deprotected (-Boc)dimer+Na (Calcd 341.1689)
341.1278
Detert-butyl(-But) dimer+K (Calcd. 445.1225)
445.1961
100
200
300
400
500
600
700
800
900
1000
m/z

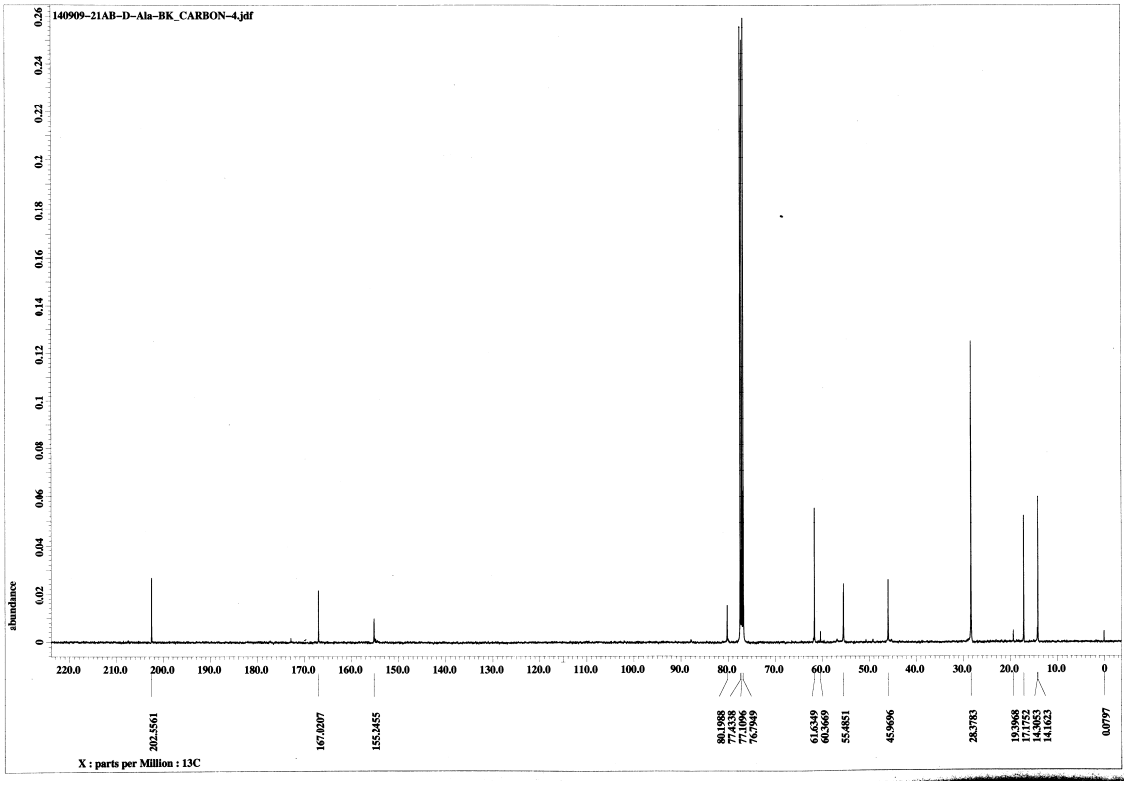
4b


Boc
N
H
O
O
OEt

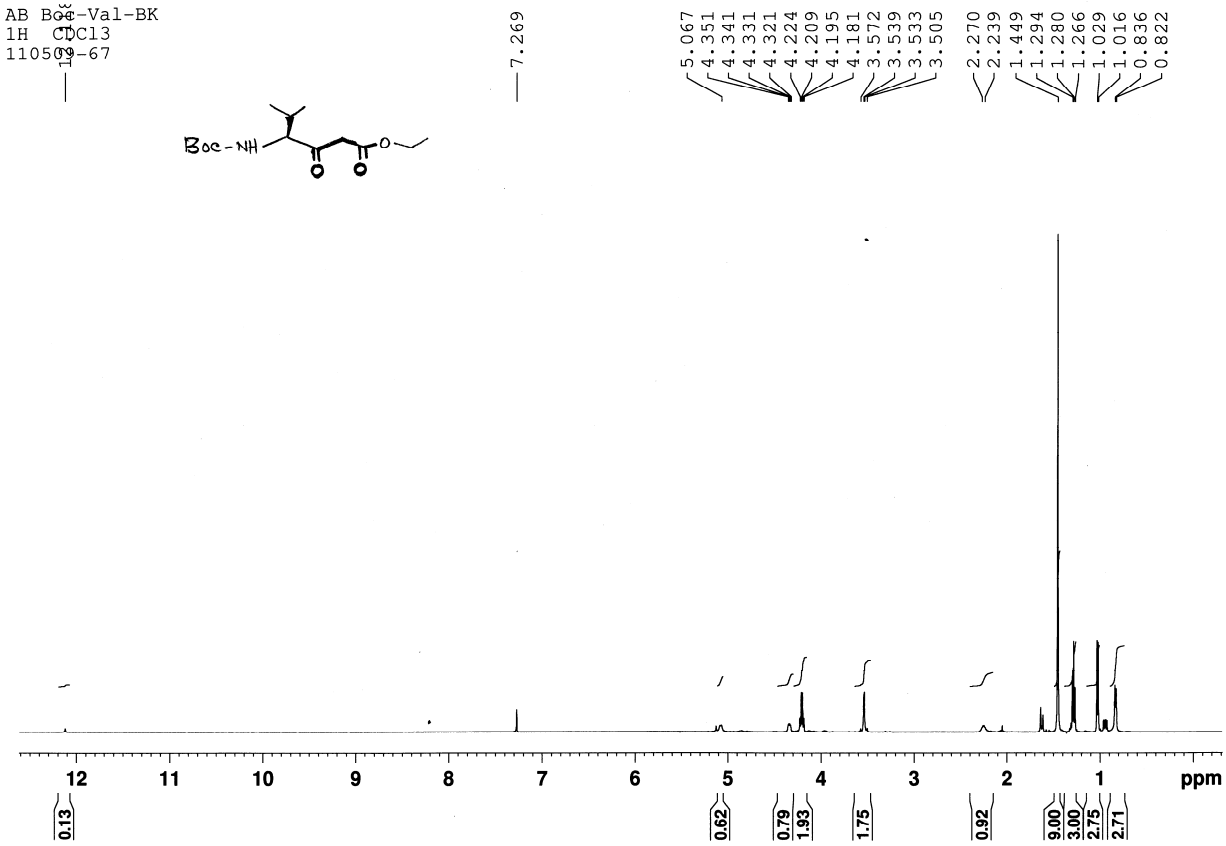

140909-21AB-D-Ala-BK_PROTON-6.jdf
abundance
0.15
0.84
1.08
2.2
2.05
9
2.34
3.34
12.0917
7.2474
5.1386
5.1248
4.3050
4.1967
4.1683
4.1512
3.5452
3.5269
3.4868
1.4236
1.3459
1.3275
1.2748
1.2577
1.2393
-0.0264
X : parts per Million : 1H

4b

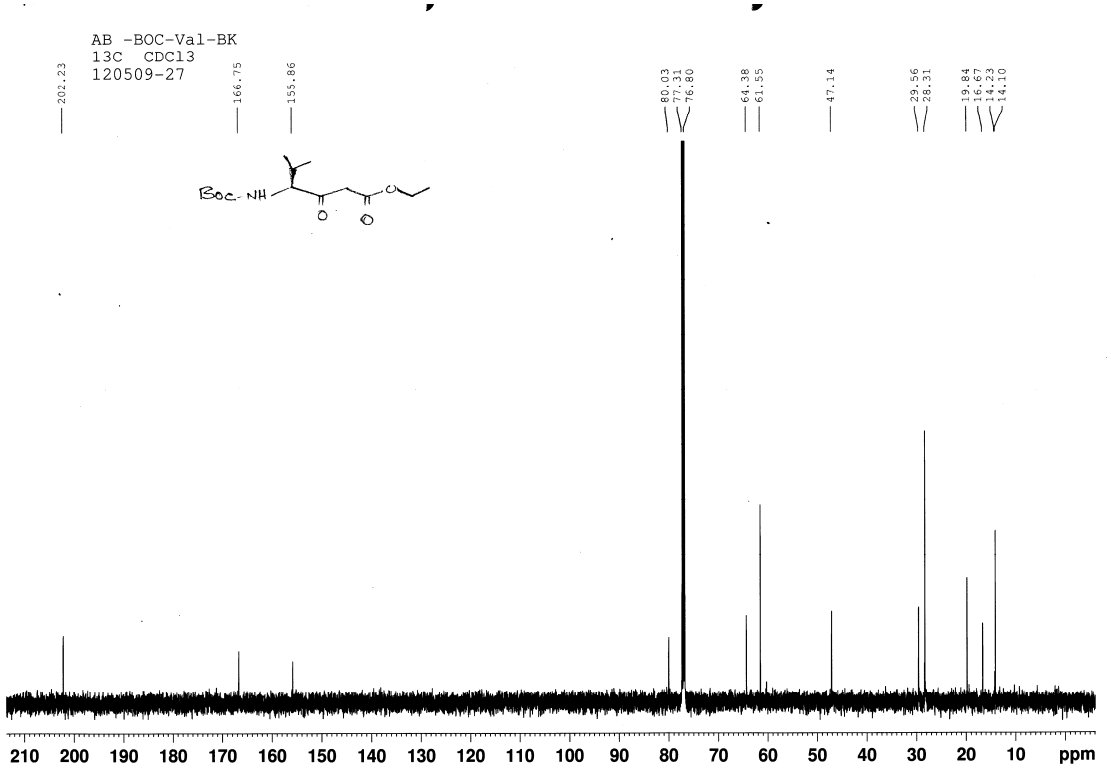

Boc
N
H
O
O
OEt


140909-21AB-D-Ala-BK_CARBON-4.jdf
abundance
X : parts per Million : 13C
202.5561
167.0207
155.2455
80.1988
77.4438
77.1096
76.7949
61.6349
60.3669
55.4851
45.9696
28.3783
19.3968
17.1753
14.3053
14.1623
0.0797

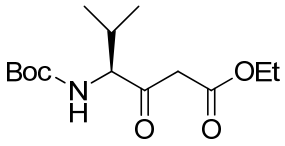
4c

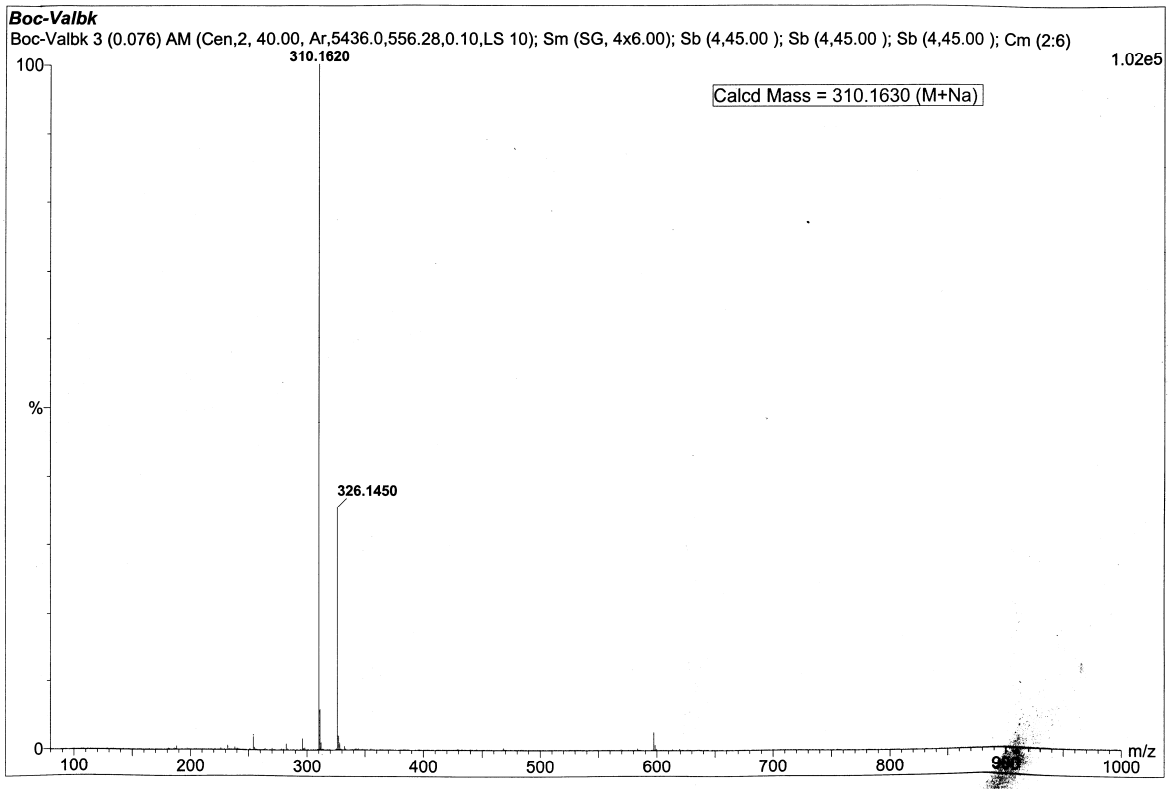

AB Boc-Val-BK
1H CDCl3
1105
7.269
5.067
4.351
4.341
4.331
4.321
4.224
4.209
4.195
4.181
3.572
3.539
3.533
3.505
2.270
2.239
1.449
1.294
1.280
1.266
1.029
1.016
0.836
0.822
Boc-NH
O
O
O
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.13
0.62
0.79
1.93
1.75
0.92
9.00
3.00
2.75
2.71

4c

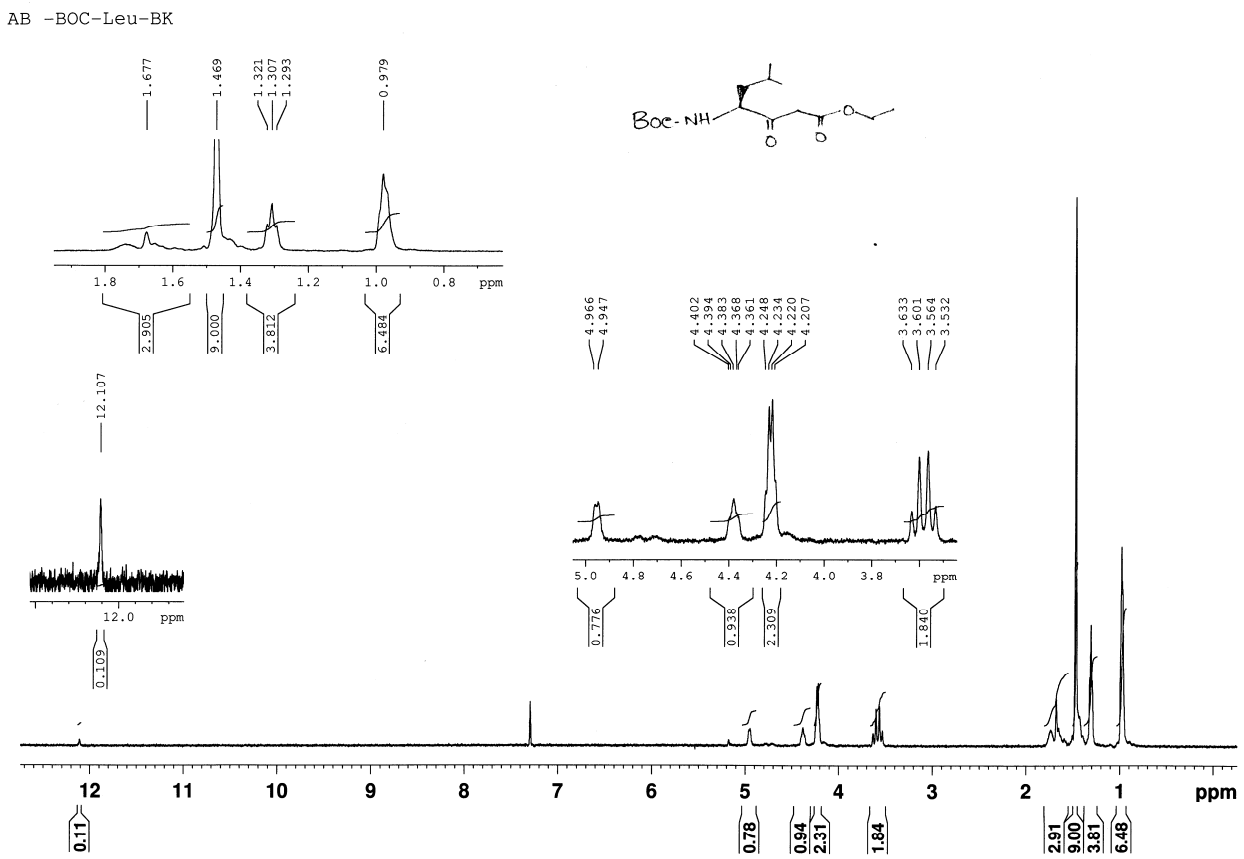


4c

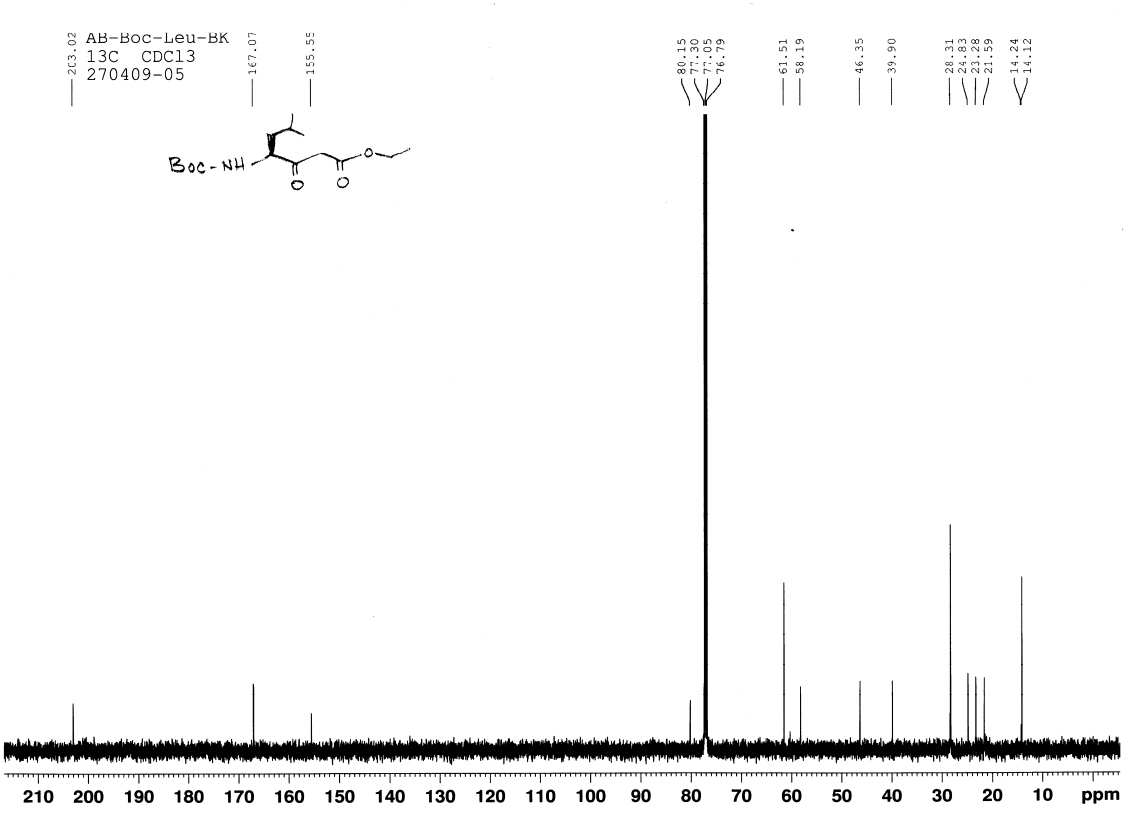

Boc
N
H
O
O
OEt


Boc-Valbk
Boc-Valbk 3 (0.076) AM (Cen,2, 40.00, Ar,5436.0,556.28,0.10,LS 10); Sm (SG, 4x6.00); Sb (4,45.00); Sb (4,45.00); Sb (4,45.00); Cm (2:6)
1.02e5
100
%
0
310.1620
326.1450
Calcd Mass = 310.1630 (M+Na)
100
200
300
400
500
600
700
800
1000
m/z

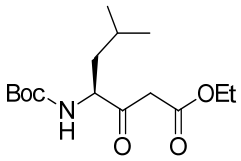
4d

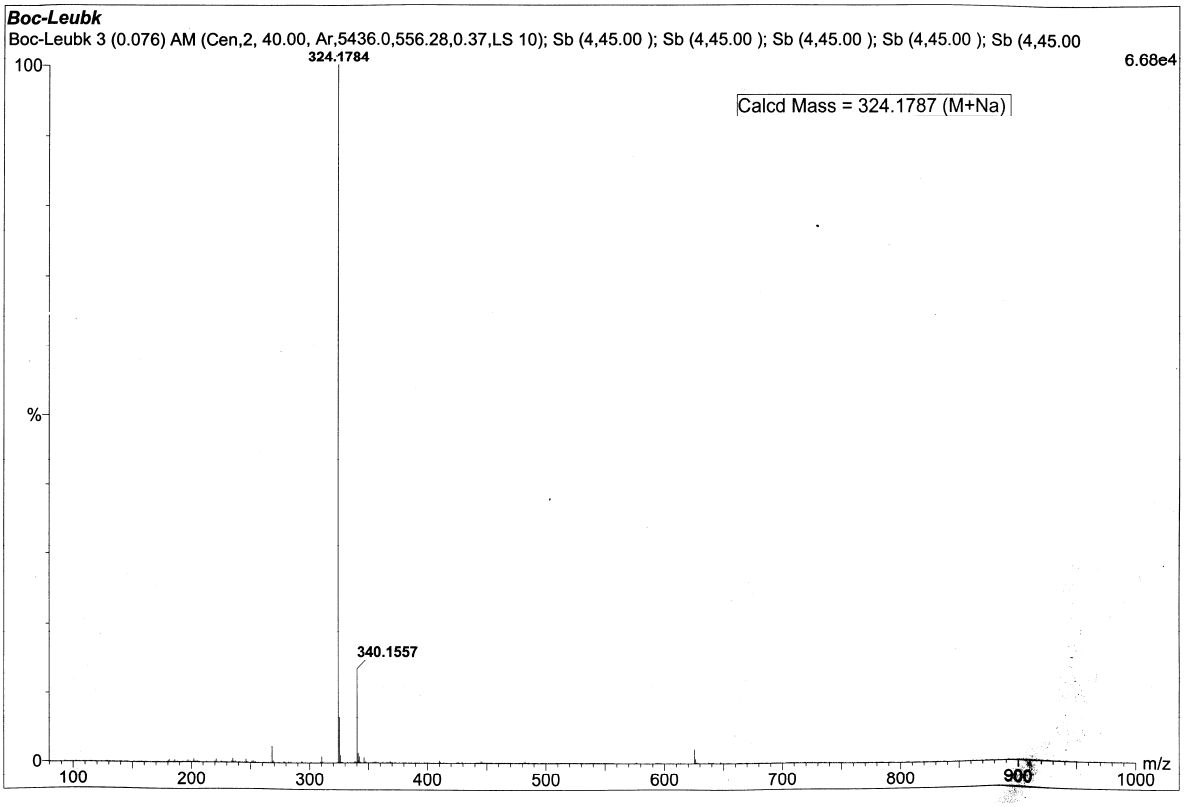

AB -BOC-Leu-BK
Boc-NH
1.677
1.469
1.321
1.307
1.293
0.979
2.905
9.000
3.812
6.484
12.107
0.109
4.966
4.947
4.402
4.394
4.383
4.368
4.361
4.248
4.234
4.220
4.207
3.633
3.601
3.564
3.532
0.776
0.938
2.309
1.840
0.11
0.78
0.94
2.31
1.84
2.91
9.00
3.81
6.48
ppm

4d

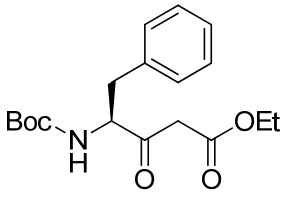

AB-Boc-Leu-BK
13C CDCl3
270409-05
203.02
167.07
155.55
80.15
77.30
77.05
76.79
61.51
58.19
46.35
39.90
28.31
24.83
23.28
21.59
14.24
14.12
Boc-NH
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

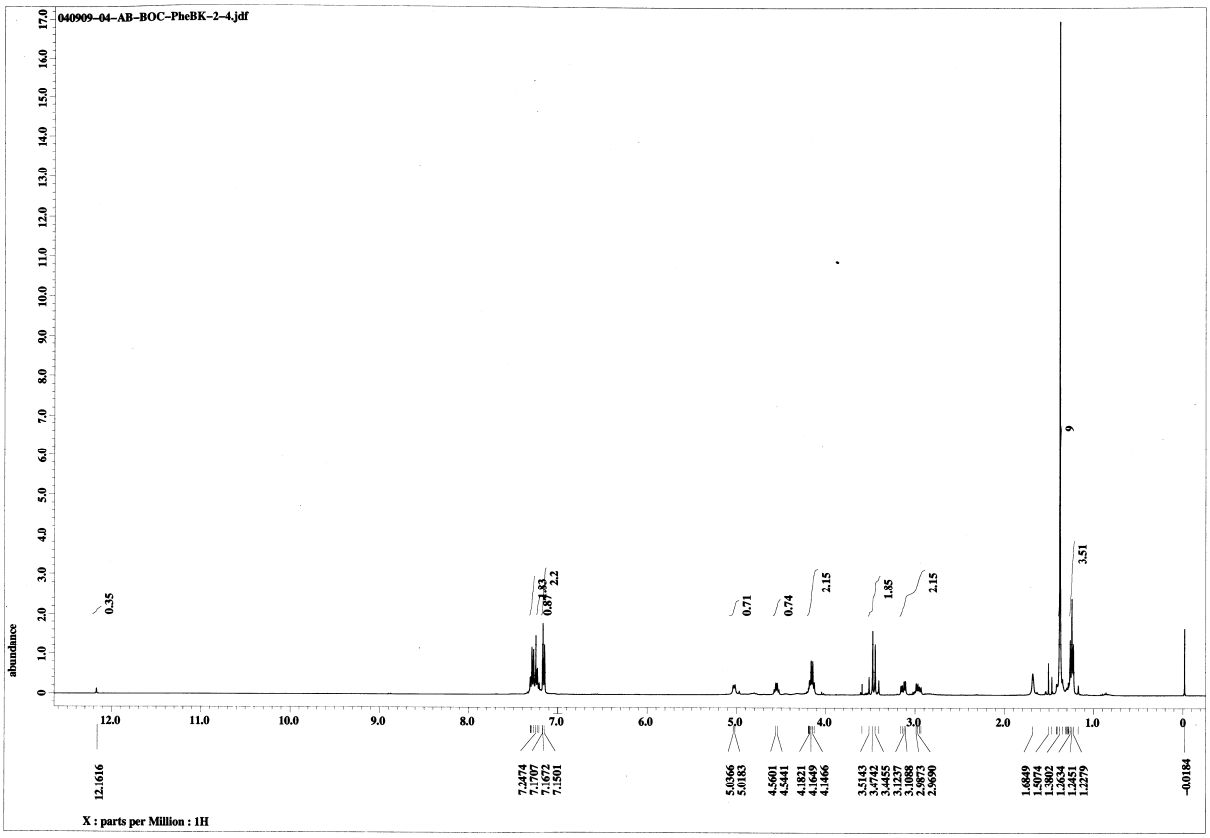
4d


Boc
N
H
O
O
OEt

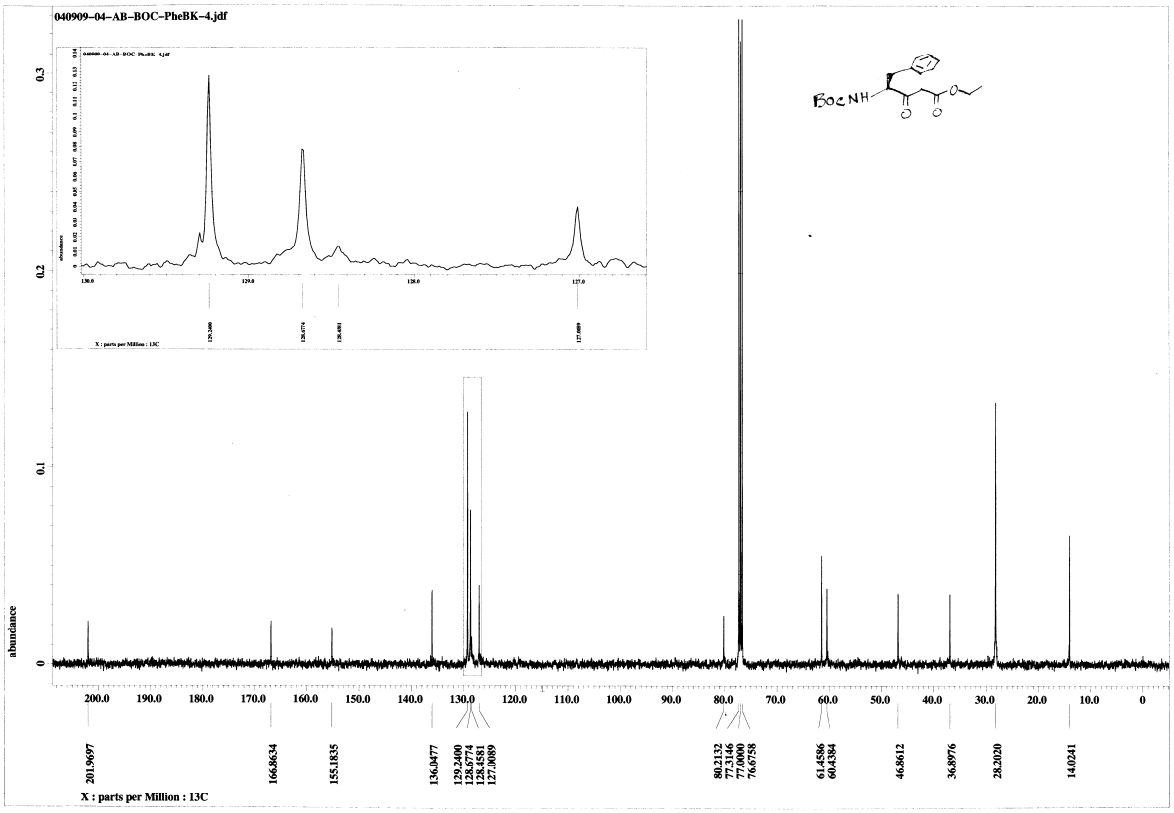

Boc-Leubk
Boc-Leubk 3 (0.076) AM (Cen,2, 40.00, Ar,5436.0,556.28,0.37,LS 10); Sb (4,45.00); Sb (4,45.00); Sb (4,45.00); Sb (4,45.00); Sb (4,45.00
324.1784
6.68e4
Calcd Mass = 324.1787 (M+Na)
100
%
0
340.1557
100
200
300
400
500
600
700
800
900
1000
m/z

4e

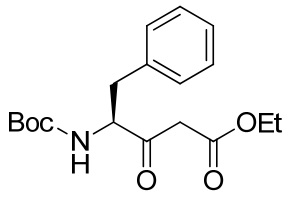

Boc
N
H
O
O
OEt

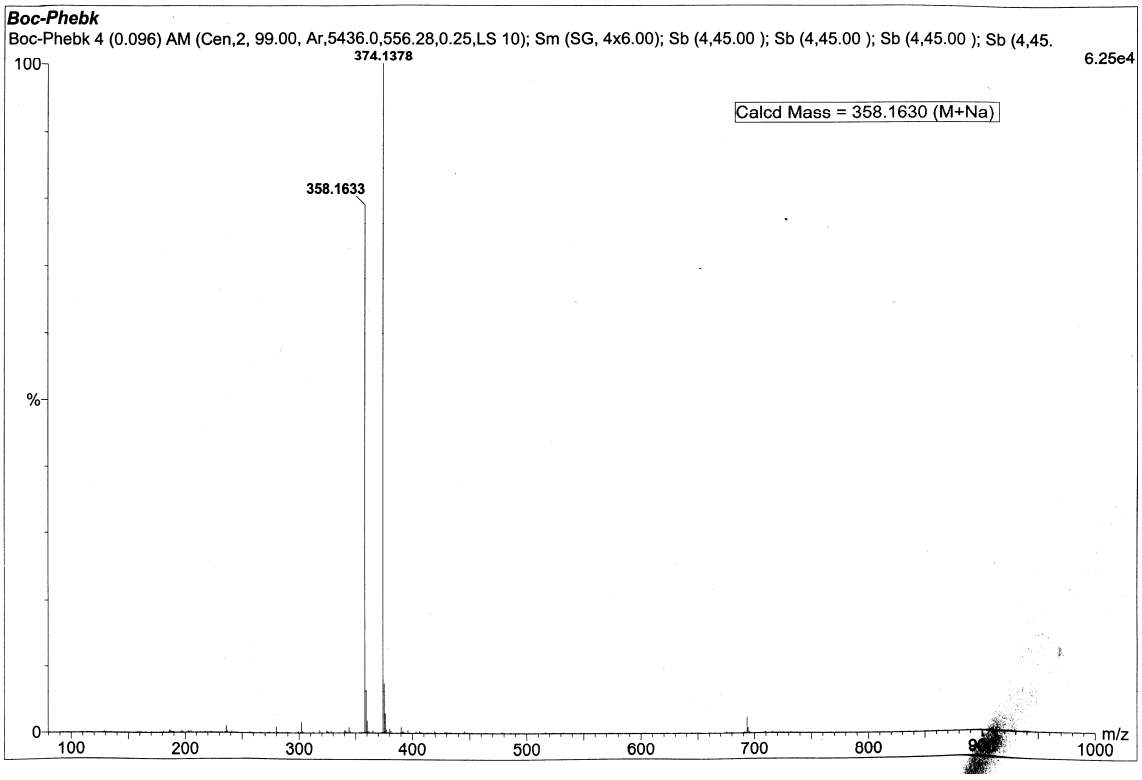

040909-04-AB-BOC-PheBK-2-4.jdf
abundance
0.35
0.87
1.83
2.2
0.71
0.74
2.15
1.85
2.15
9
3.51
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
12.1616
7.2474
7.1672
7.1501
5.0366
5.0183
4.5601
4.5441
4.1821
4.1660
4.1466
3.5143
3.4742
3.4455
3.1237
3.1098
2.9873
2.9690
1.6849
1.5974
1.3802
1.2634
1.2451
1.2279
-0.0184
X : parts per Million : 1H

4e

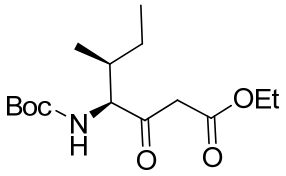

040909-04-AB-BOC-PheBK-4.jdf
BocNH
abundance
X : parts per Million : 13C
201.9697
166.8634
155.1835
136.0477
129.3400
128.6774
128.4581
127.5089
80.2132
77.3146
77.0000
76.6758
61.4586
60.4384
46.8612
36.8976
28.2020
14.0241

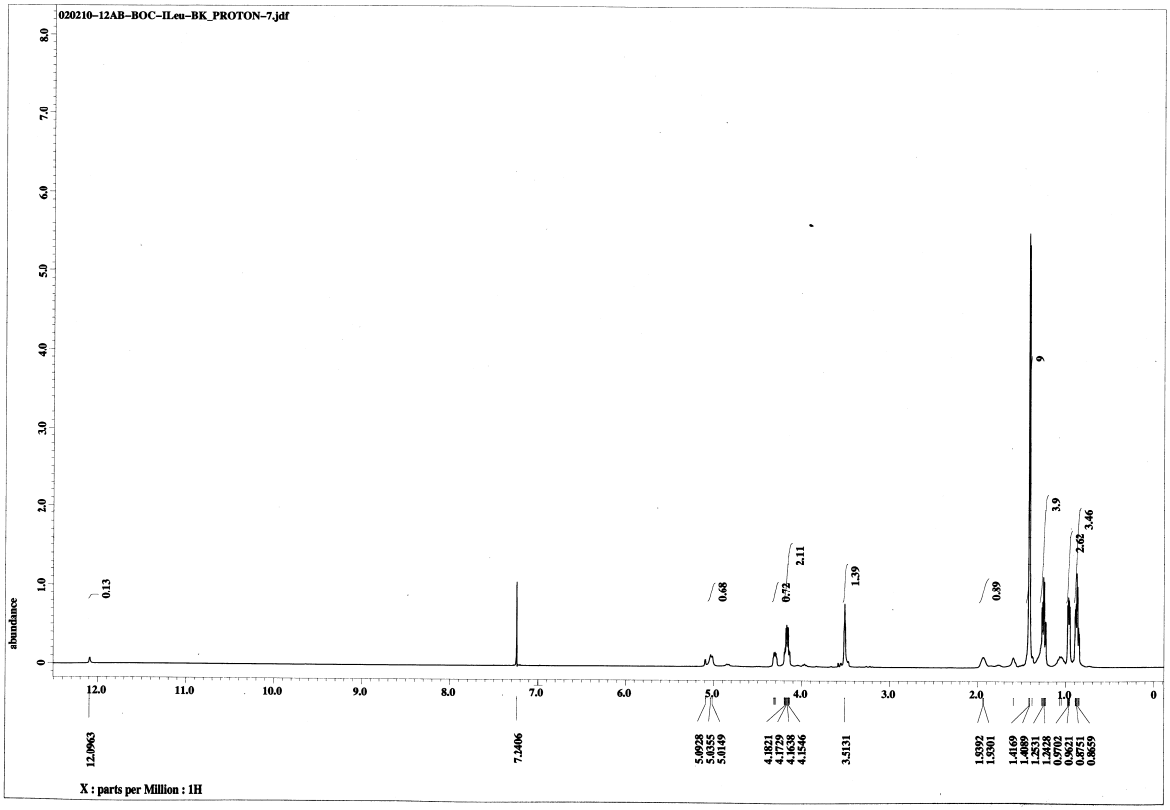
4e


Boc
N
H
O
O
OEt

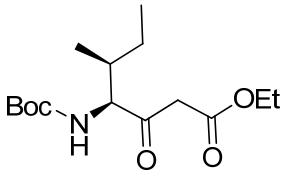

Boc-Phebk
Boc-Phebk 4 (0.096) AM (Cen,2, 99.00, Ar,5436.0,556.28,0.25,LS 10); Sm (SG, 4x6.00); Sb (4,45.00); Sb (4,45.00); Sb (4,45.00); Sb (4,45.
374.1378
6.25e4
100
Calcd Mass = 358.1630 (M+Na)
358.1633
%
0
100
200
300
400
500
600
700
800
1000
m/z

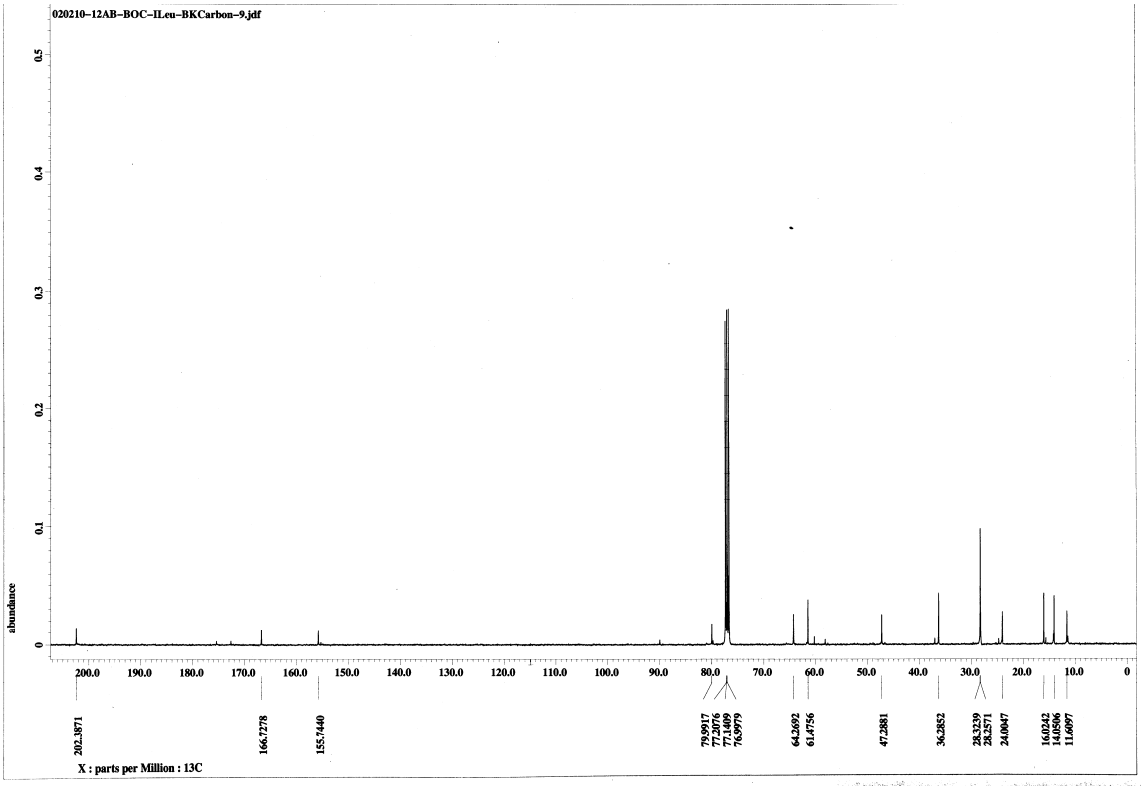
4f


Boc
N
H
O
O
OEt

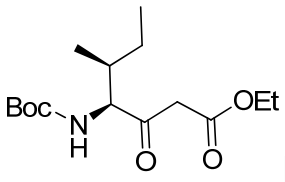

020210-12AB-BOC-ILeu-BK_PROTON-7.jdf
abundance
0.13
0.68
0.72
2.11
1.39
0.89
9
3.9
2.62
3.46
12.0963
7.2406
5.0928
5.0355
5.0149
4.1821
4.1729
4.1638
4.1546
3.5131
1.5392
1.5201
1.4169
1.4089
1.2831
1.2428
0.9702
0.9621
0.9571
0.8659
X : parts per Million : 1H

4f

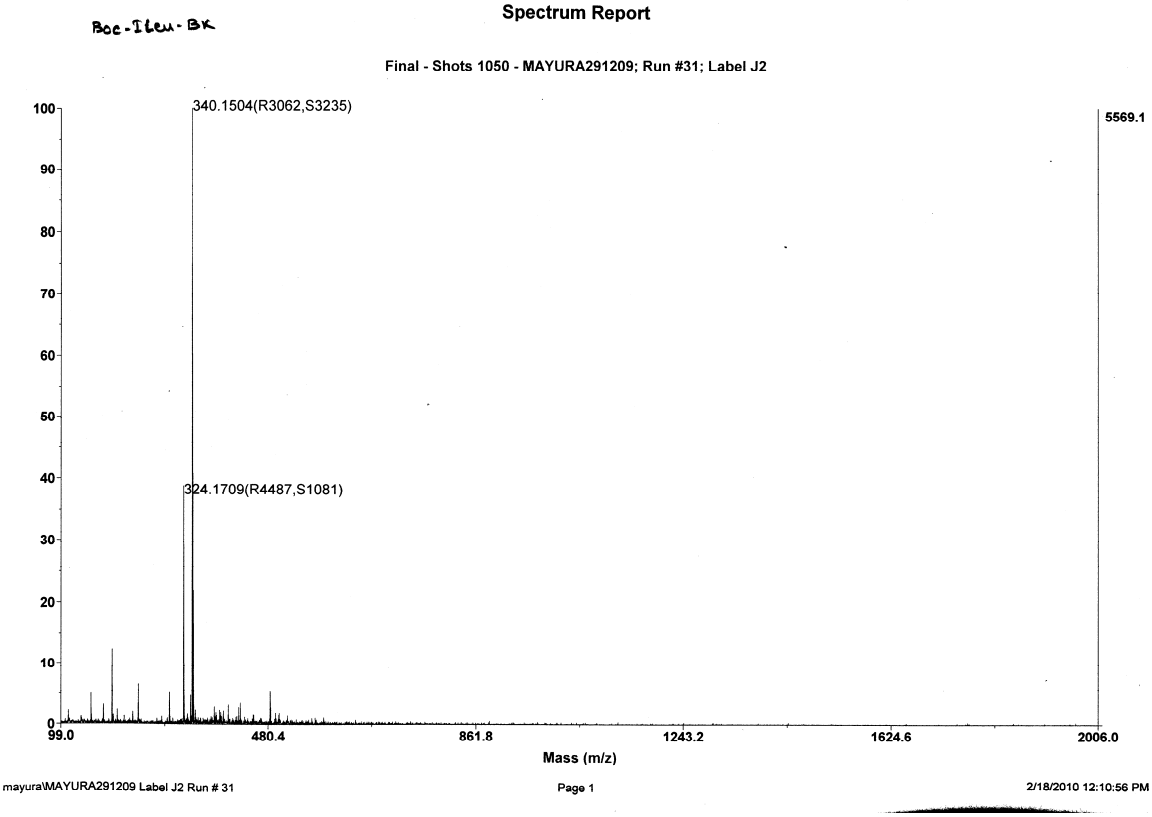

Boc
N
H
O
O
OEt


020210-12AB-BOC-ILeu-BKCarbon-9.jdf
abundance
0
0.1
0.2
0.3
0.4
0.5
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
202.3871
166.7278
155.7440
79.5917
77.3795
77.1409
76.9979
64.3692
61.4756
47.2381
36.2852
28.3239
28.2571
24.0047
16.0242
14.0506
11.6097
X : parts per Million : 13C

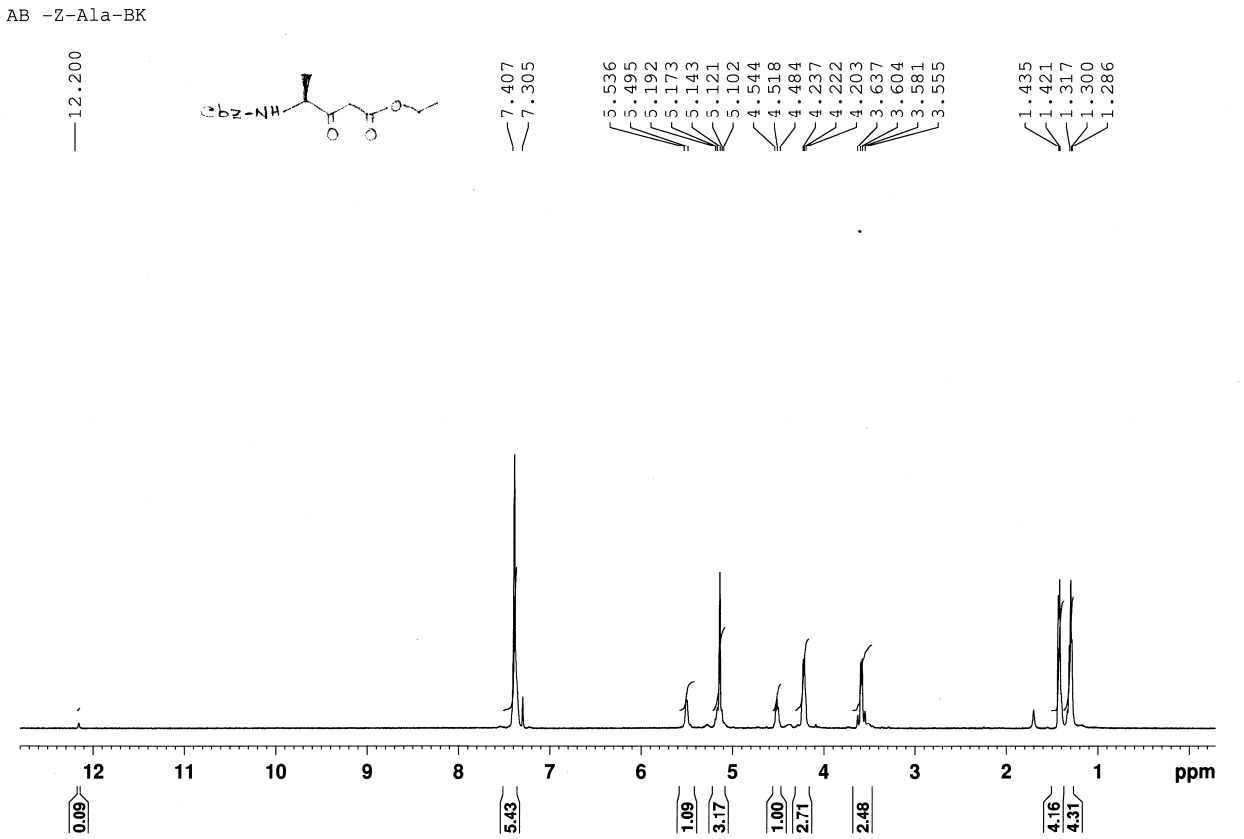
4f



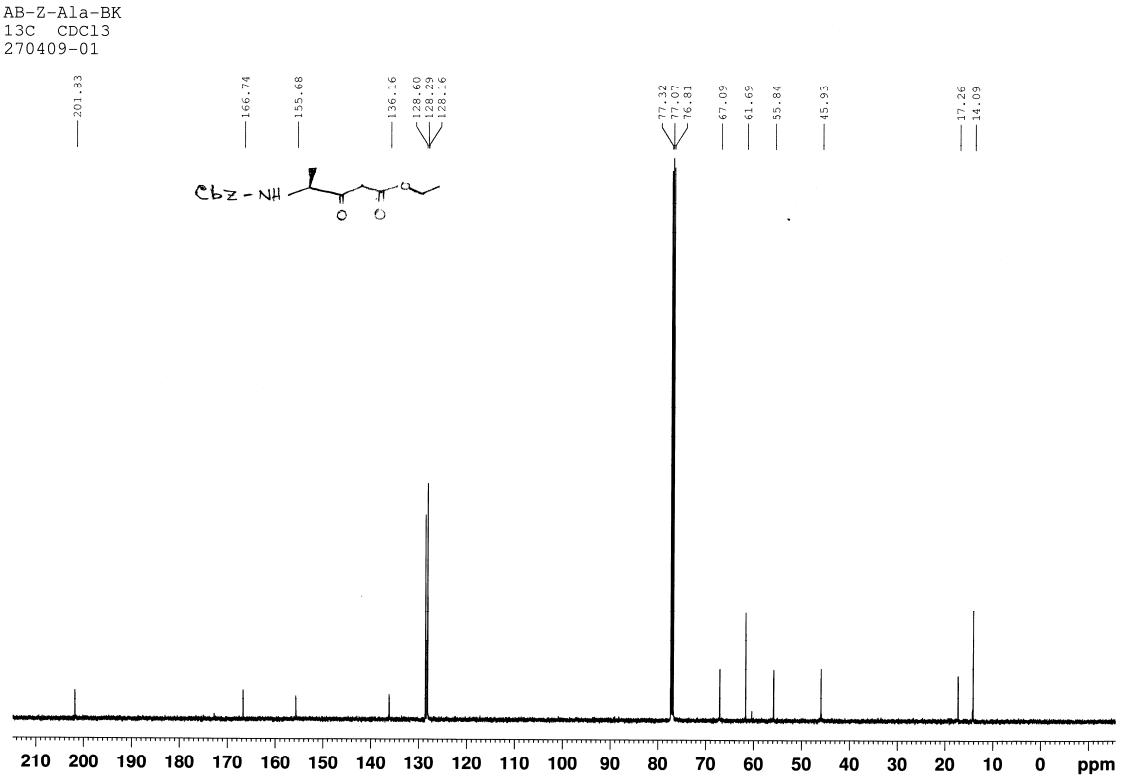
[Calcd mass=324.1787(M+Na)]



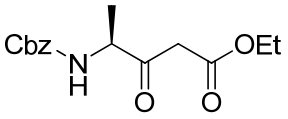
4g


AB -Z-Ala-BK
12.200
7.407
7.305
5.536
5.495
5.192
5.173
5.143
5.121
5.102
4.544
4.518
4.484
4.237
4.222
4.203
3.637
3.604
3.581
3.555
1.435
1.421
1.317
1.300
1.286
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.09
5.43
1.09
3.17
1.00
2.71
2.48
4.16
4.31

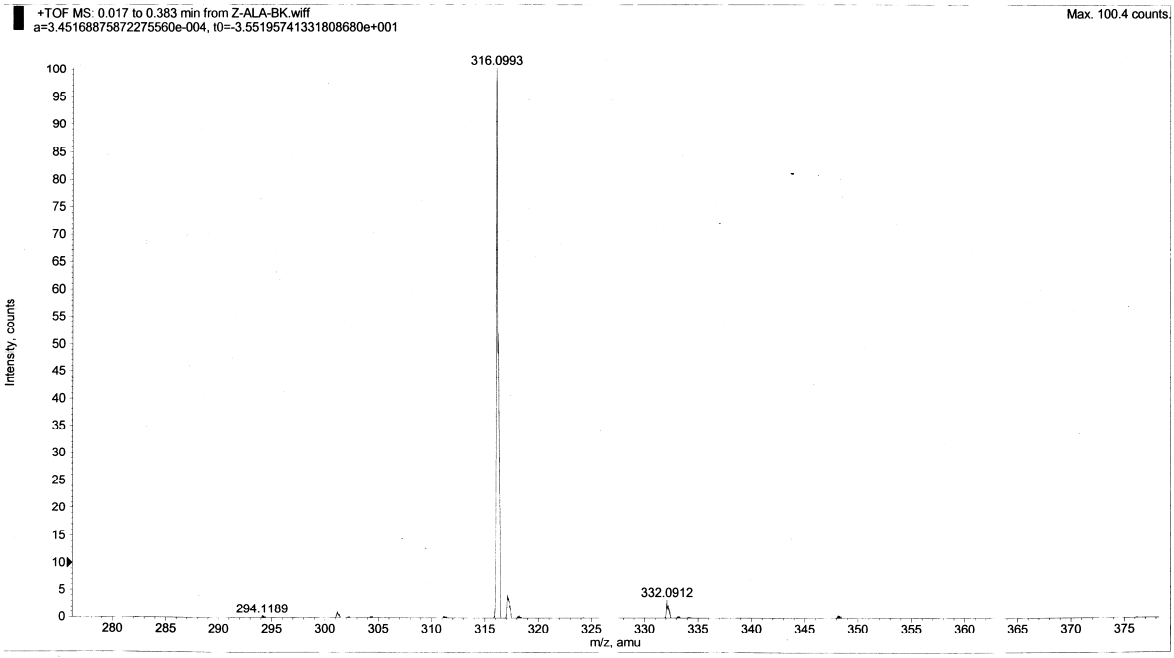
4g


AB-Z-Ala-BK
13C CDCl3
270409-01
201.33
166.74
155.68
136.16
128.60
128.29
128.16
77.32
77.07
76.81
67.09
61.69
55.84
45.93
17.26
14.09
Cbz - NH
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

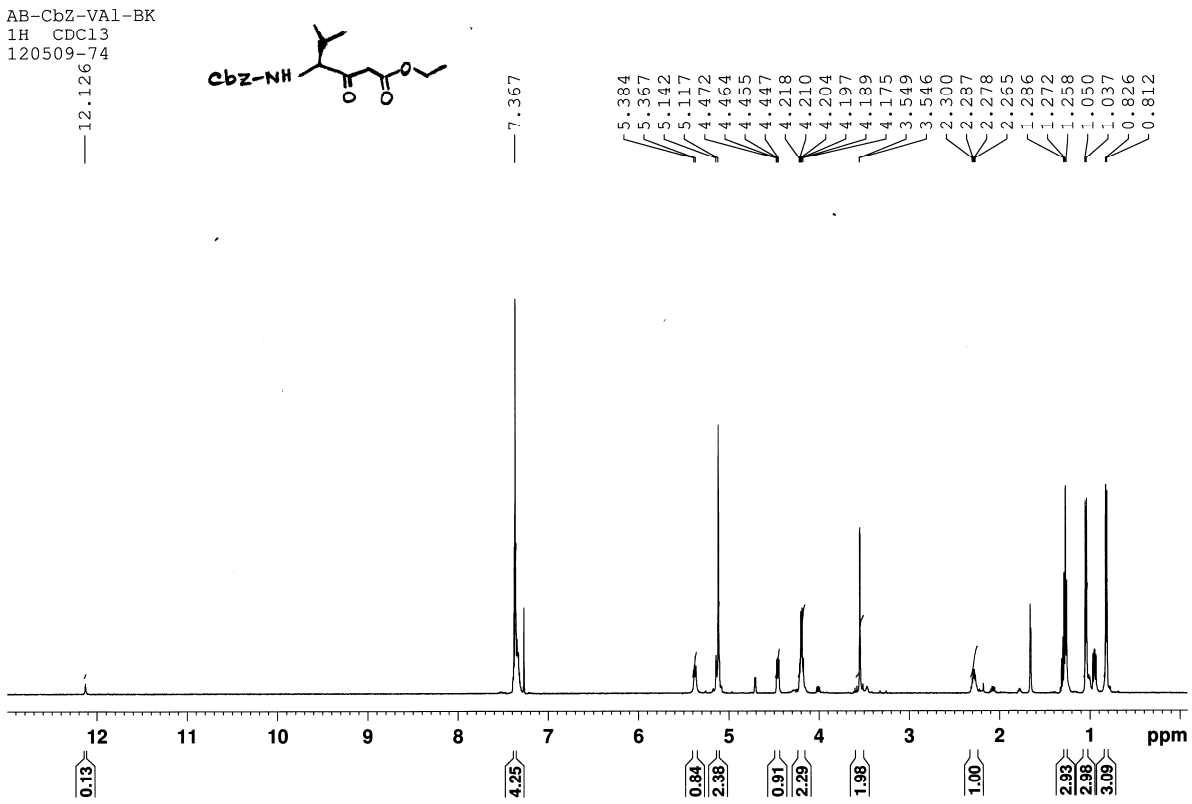
4g



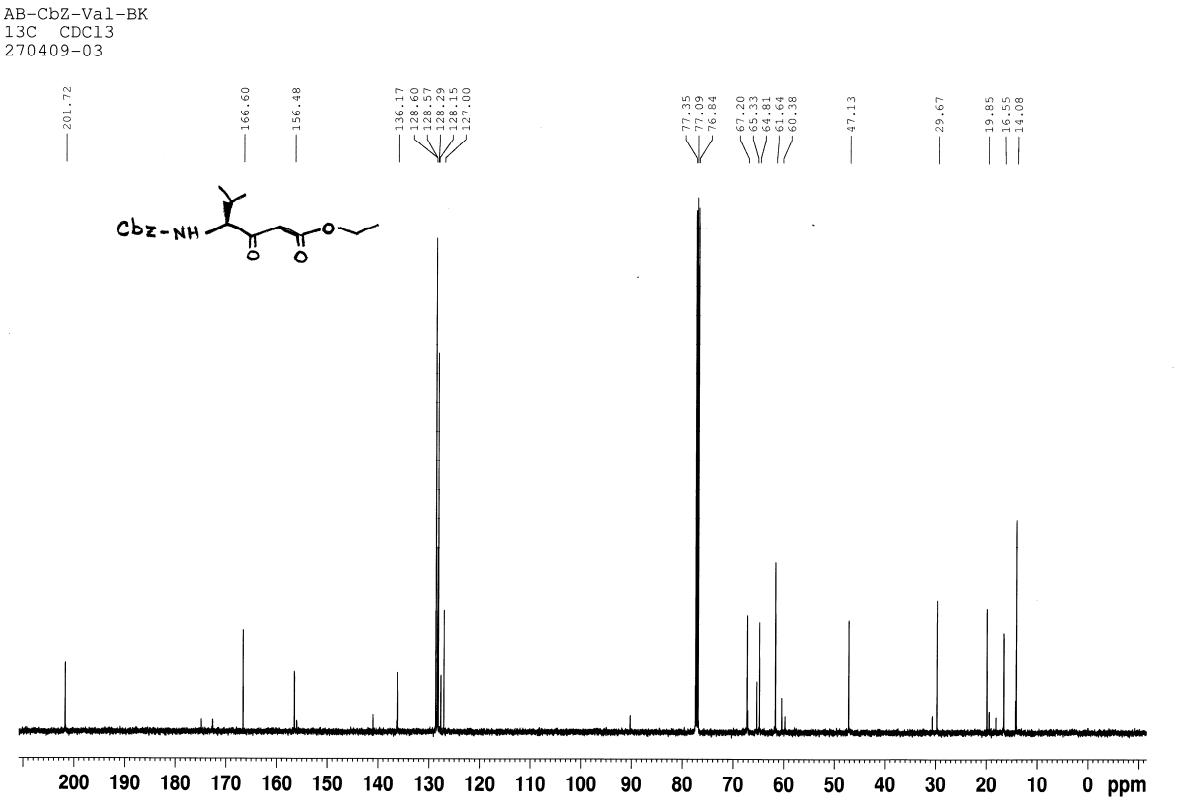
[Calcd. Mass=332.0900(M+K)]



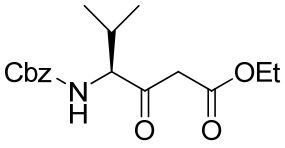
4h


AB-CbZ-VAl-BK
1H CDCl3
120509-74
12.126
7.357
5.384
5.357
5.142
5.117
4.472
4.464
4.455
4.447
4.218
4.210
4.204
4.197
4.189
4.175
3.549
3.546
2.300
2.287
2.278
2.265
1.286
1.272
1.258
1.050
1.037
0.826
0.812
CbZ-NH
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.13
4.25
0.84
2.38
0.91
2.29
1.98
1.00
2.93
2.98
3.09

4h


AB-CbZ-Val-BK
13C CDCl3
270409-03
201.72
166.60
156.48
136.17
128.60
128.57
128.29
128.15
127.00
77.35
77.09
76.84
67.20
65.33
64.81
61.64
60.38
47.13
29.67
19.85
16.55
14.08
Cbz-NH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

4h

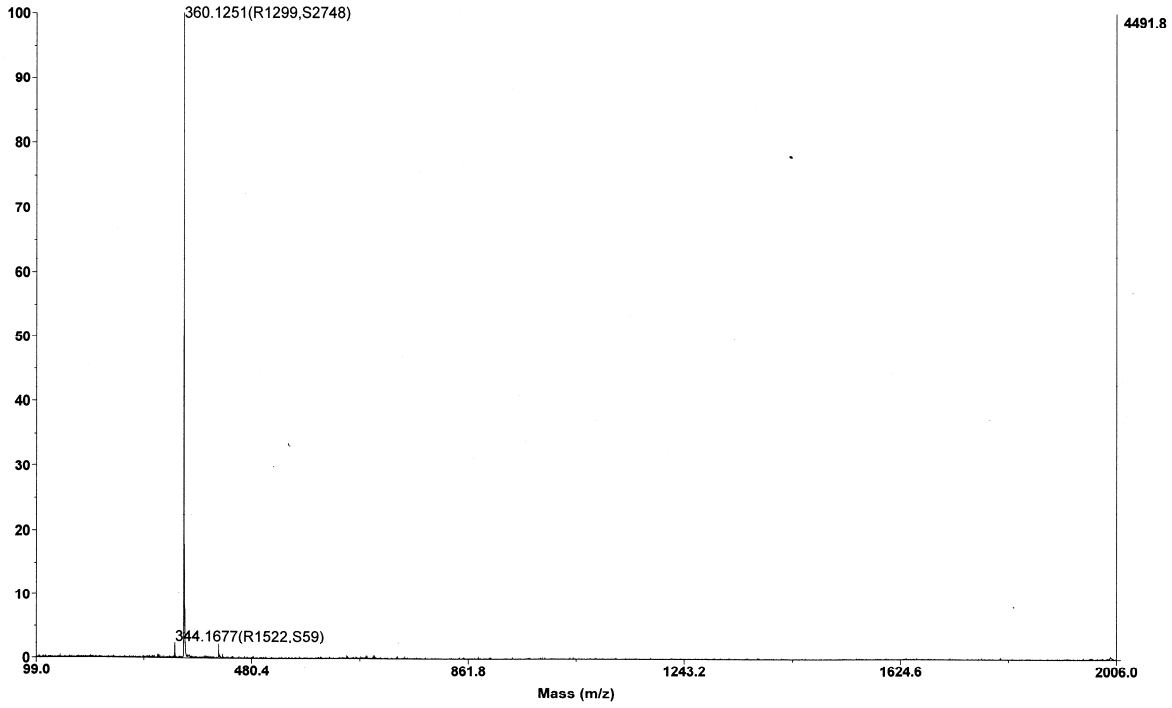


[Calcd Mass=360.1213 (M+K)]

Spectrum Report

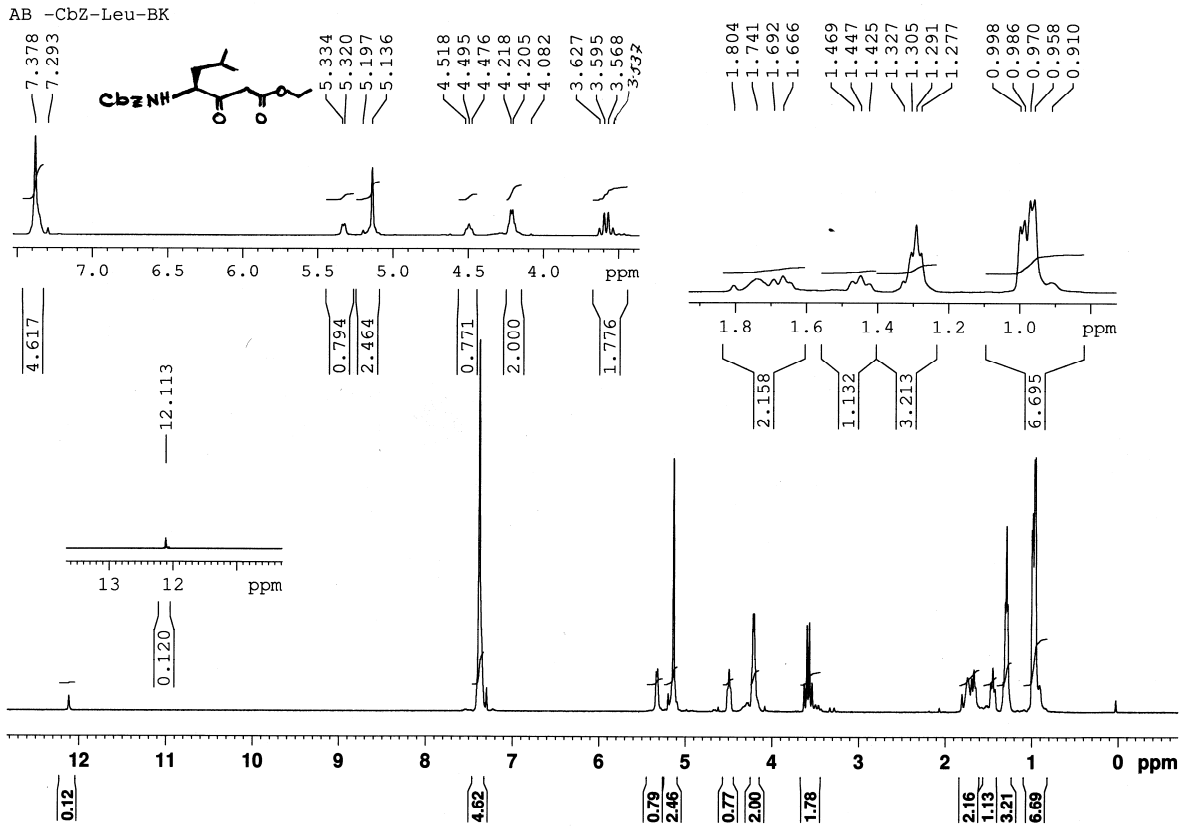
Z-Val BK

Final - Shots 500 - MAYURA291209; Run #30; Label K1

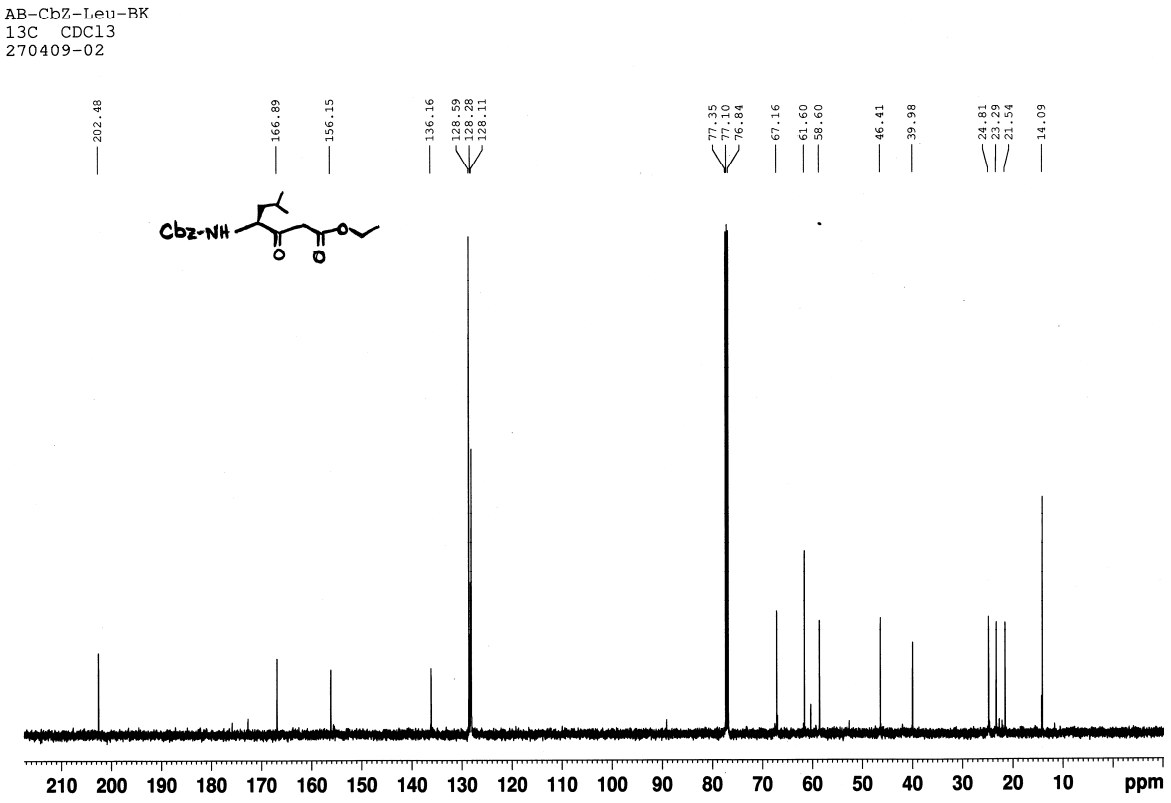


mayura\MAYURA291209 Label K1 Run # 30 Page 1 2/17/2010 2:35:43 PM

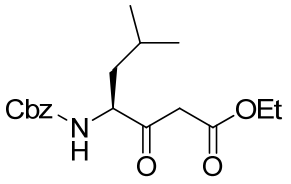
4i


AB -CbZ-Leu-BK
CbzNH
7.378
7.293
5.334
5.320
5.197
5.136
4.518
4.495
4.476
4.218
4.205
4.082
3.627
3.595
3.568
1.804
1.741
1.692
1.666
1.469
1.447
1.425
1.327
1.305
1.291
1.277
0.998
0.986
0.970
0.958
0.910
12.113
ppm

4i


AB-CbZ-Leu-BK
13C CDCl3
270409-02
202.48
166.89
156.15
136.16
128.59
128.28
128.11
77.35
77.10
76.84
67.16
61.60
58.60
46.41
39.98
24.81
23.29
21.54
14.09
Cbz-NH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

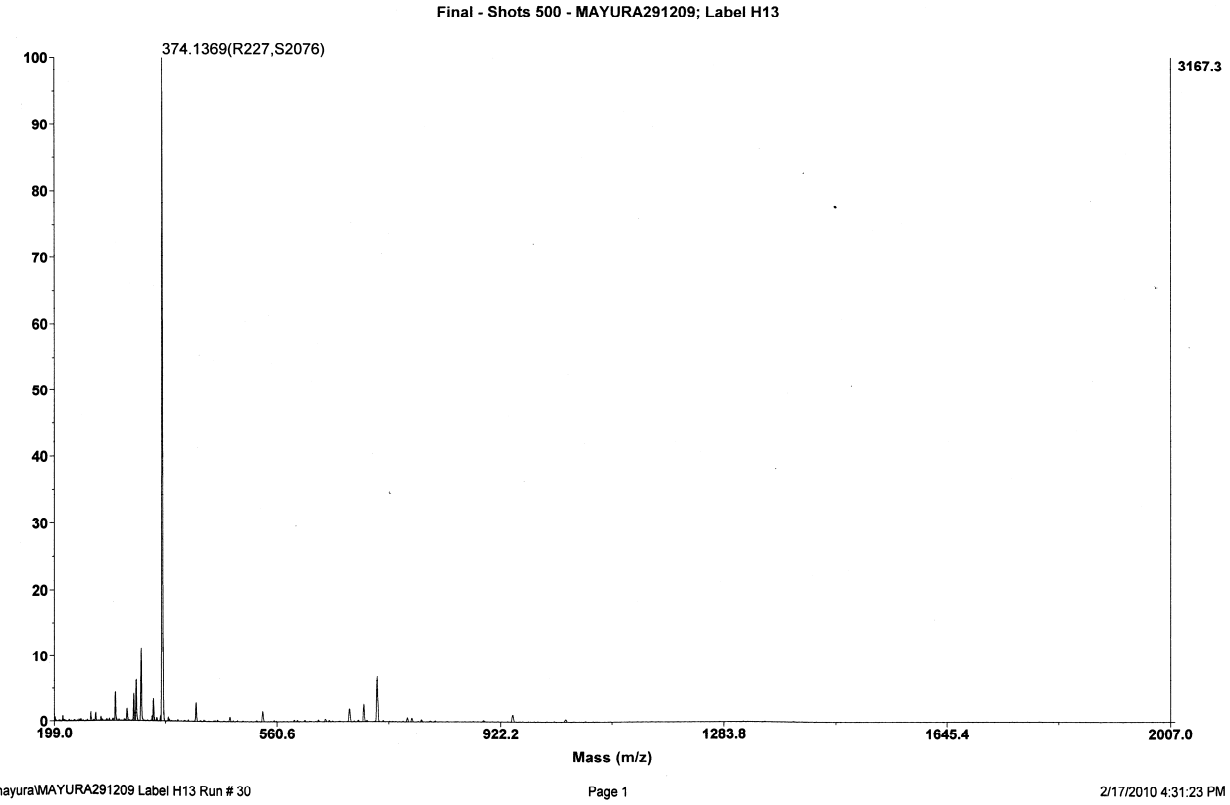
4i



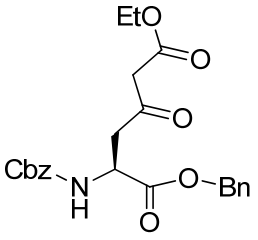
[Calcd mass= 374.1370(M+K)]

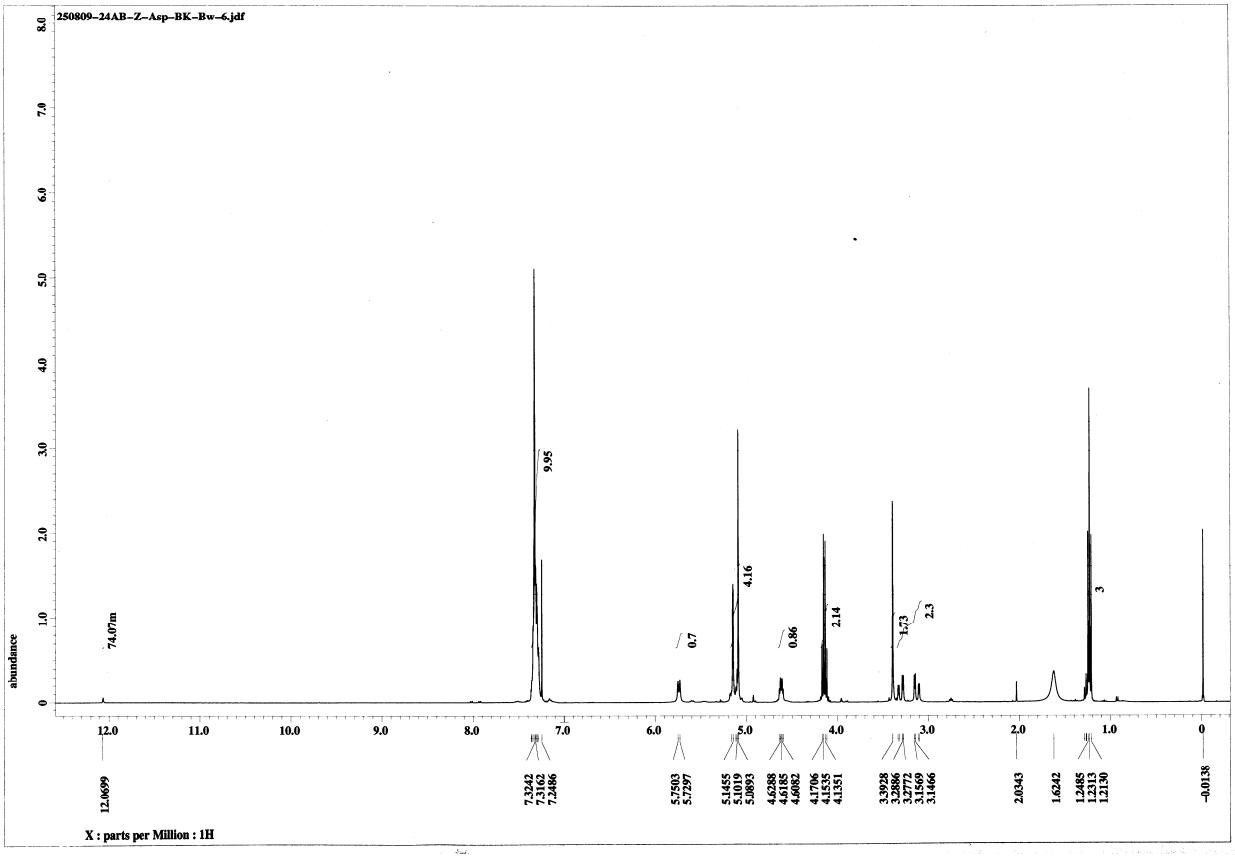
Z - Leu - βK

Spectrum Report

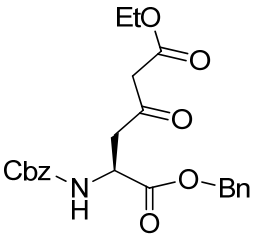


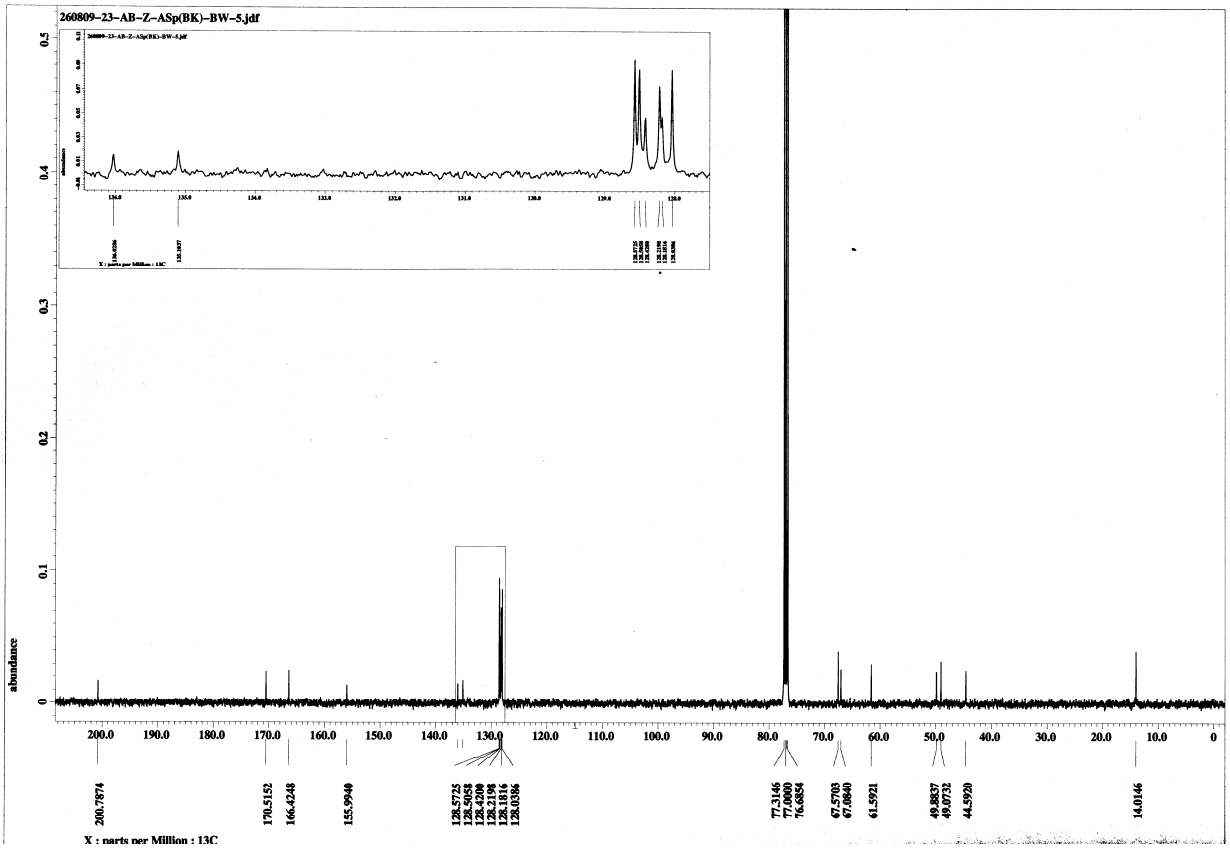
4j


EtO
O
O
Cbz
N
H
O
O
Bn

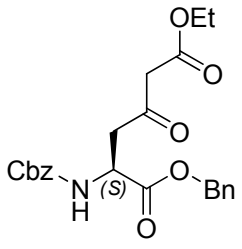

250809-24AB-Z-Asp-BK-Bw-6.jdf
abundance
74.07m
9.95
0.7
4.16
0.86
2.14
1.73
2.3
3
X : parts per Million : 1H

4j

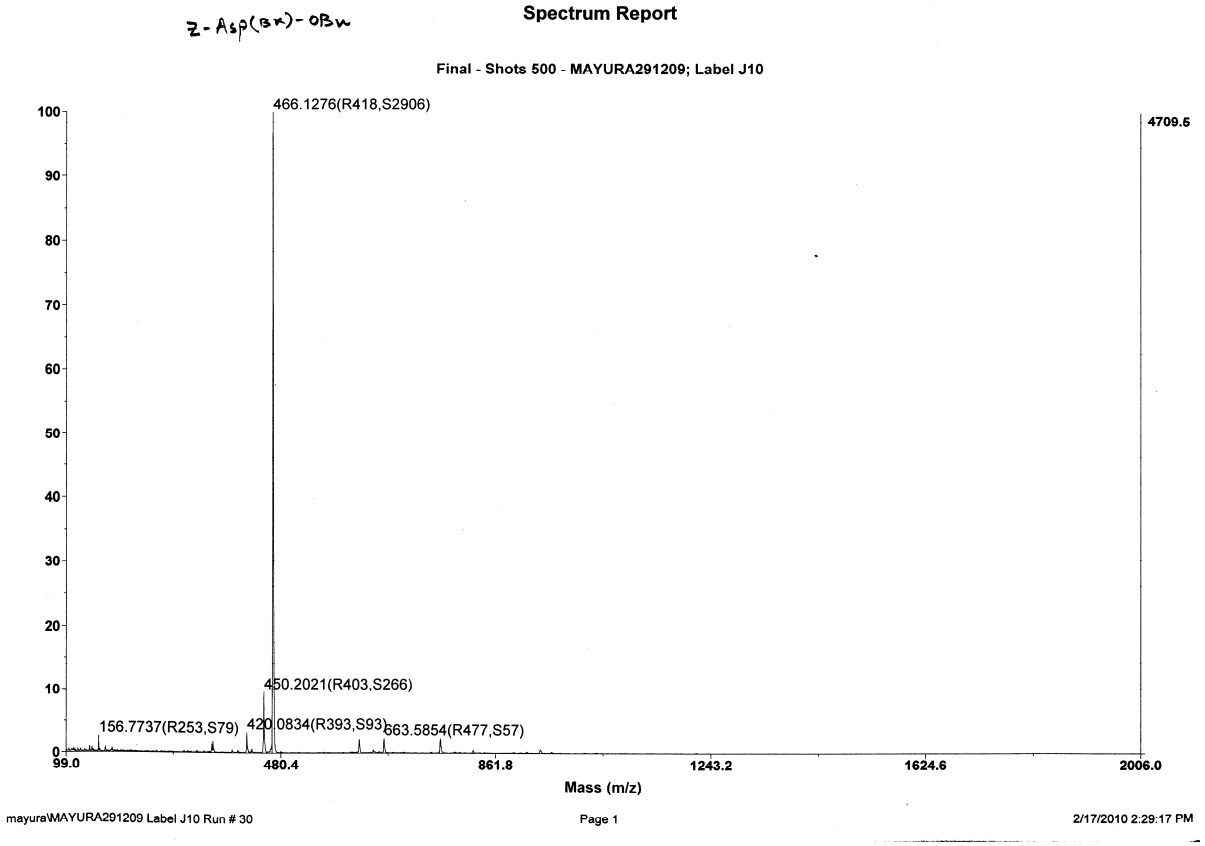

EtO
O
O
Cbz
N
H
O
O
Bn


260809-23-AB-Z-ASp(BK)-BW-5.jdf
abundance
X : parts per Million : 13C
200.7874
170.5152
166.4248
155.9940
128.5725
128.5058
128.4200
128.2134
128.1814
128.0386
77.3146
77.0000
76.6854
67.5703
67.0840
61.5921
49.8837
49.0732
44.5920
14.0146

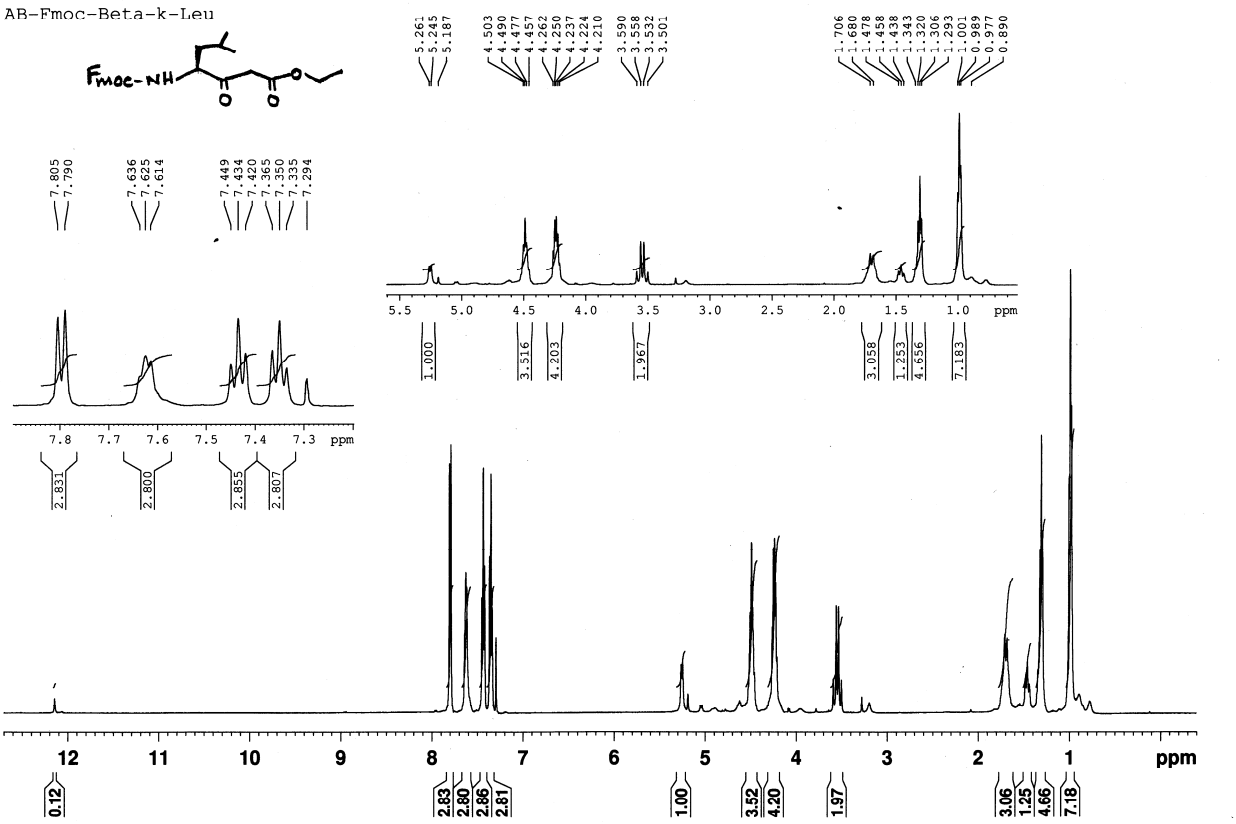
4j



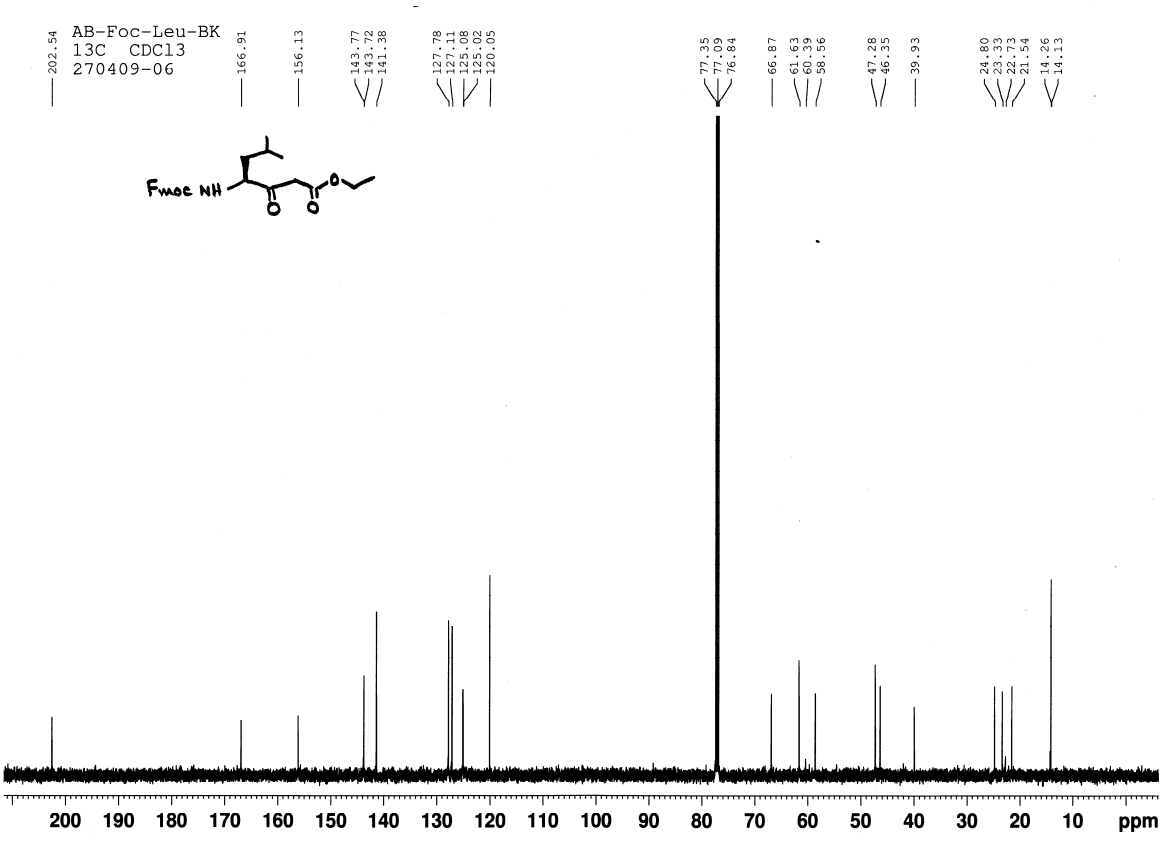
[Calcd mass=466.1268(M+K)]



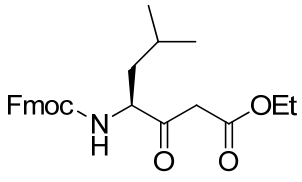
4k


AB-Fmoc-Beta-k-Leu
Fmoc-NH
O
O
5.261
5.245
5.187
4.503
4.490
4.477
4.457
4.262
4.250
4.237
4.224
4.210
3.590
3.558
3.532
3.501
1.706
1.680
1.478
1.458
1.438
1.343
1.320
1.306
1.293
1.001
0.989
0.977
0.890
7.805
7.790
7.636
7.625
7.614
7.449
7.434
7.420
7.365
7.350
7.335
7.294
ppm
1.000
3.516
4.203
1.967
3.058
1.253
4.556
7.183
2.831
2.800
2.855
2.807
0.12
2.83
2.80
2.86
2.81
1.00
3.52
4.20
1.97
3.06
1.25
4.66
7.18

4k



4k

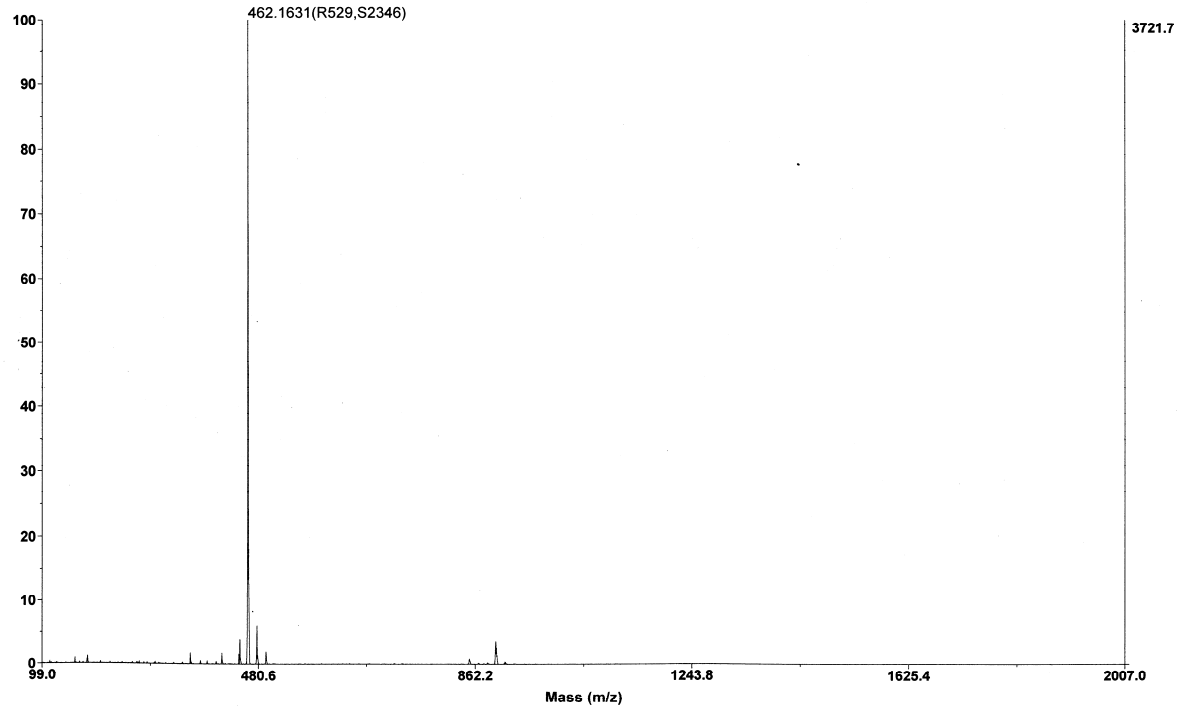


[Calcd mass=462.1683(M+K)]

Fmoc-Leu-BK

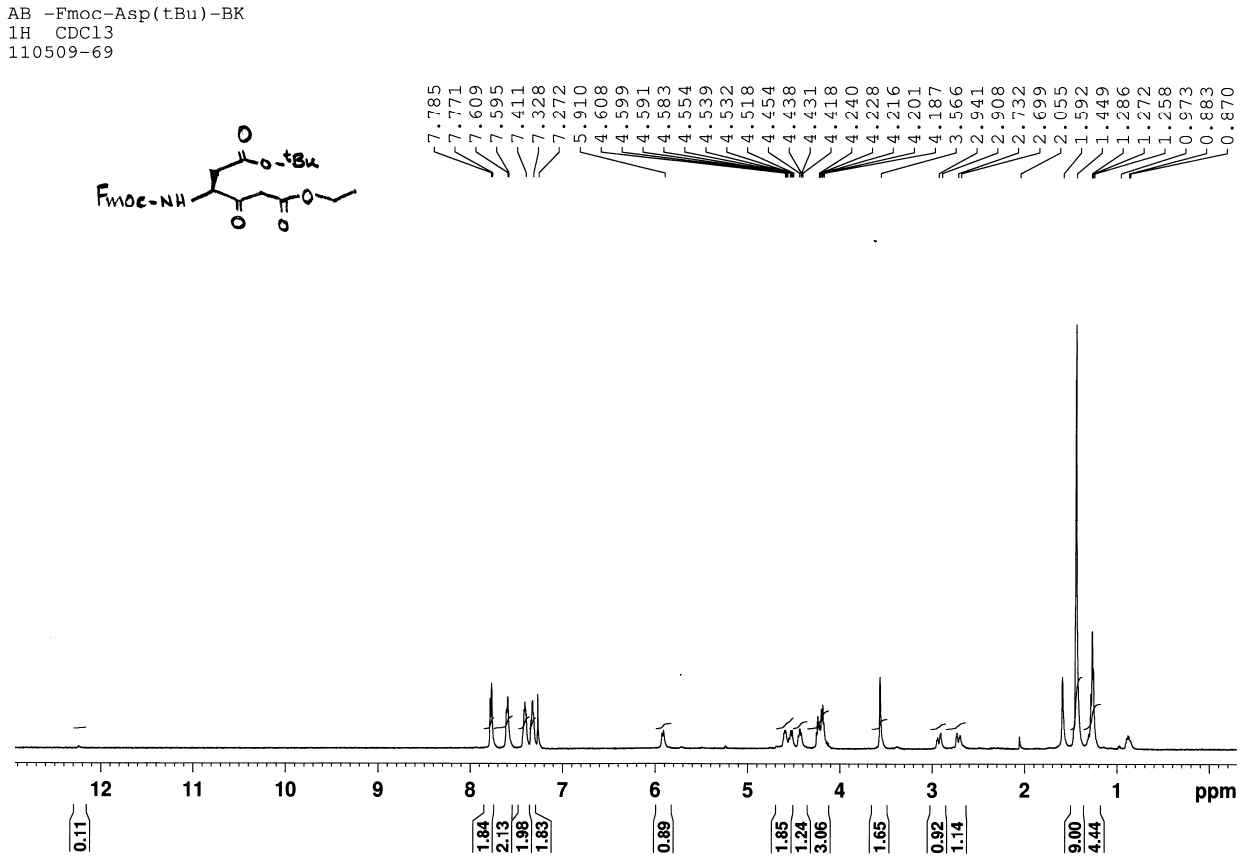
Spectrum Report

Final - Shots 500 - MAYURA291209; Run #30; Label K5

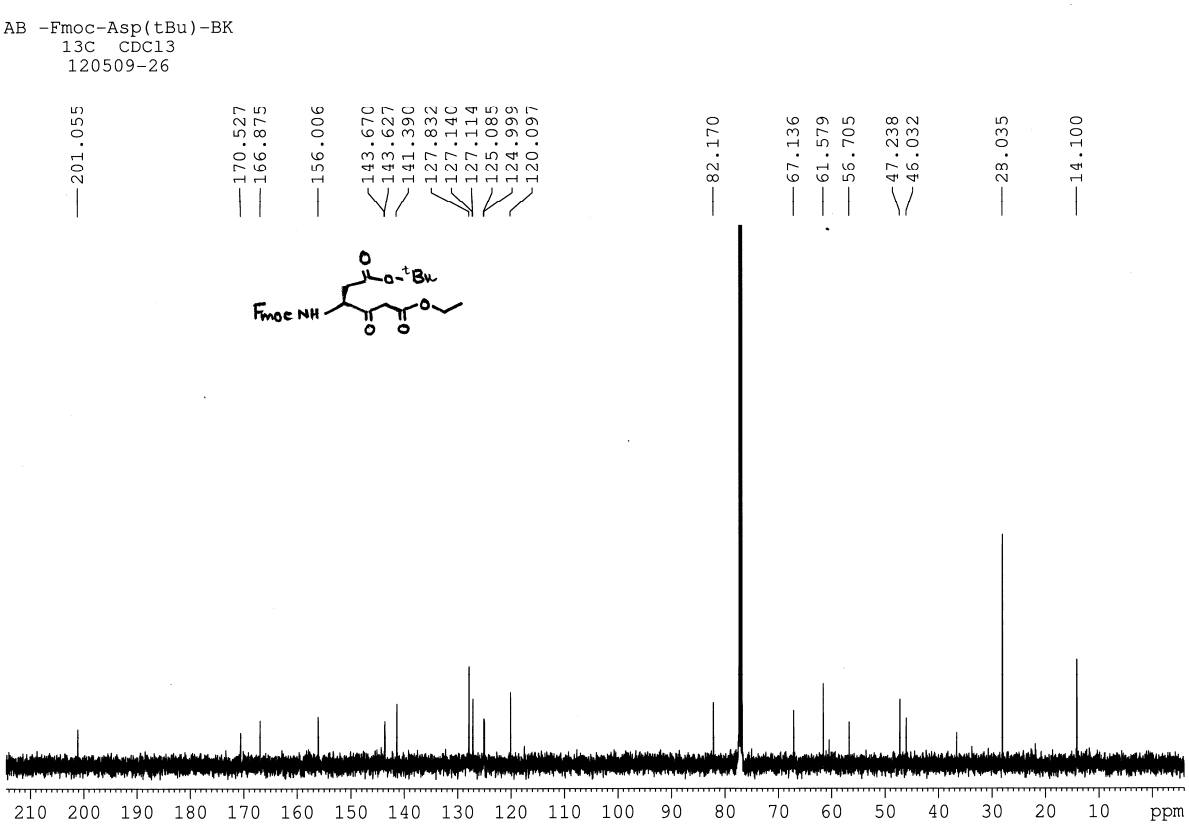


mayura\MAYURA291209 Label K5 Run # 30 Page 1 2/17/2010 4:43:24 PM

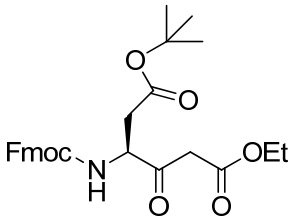
4l

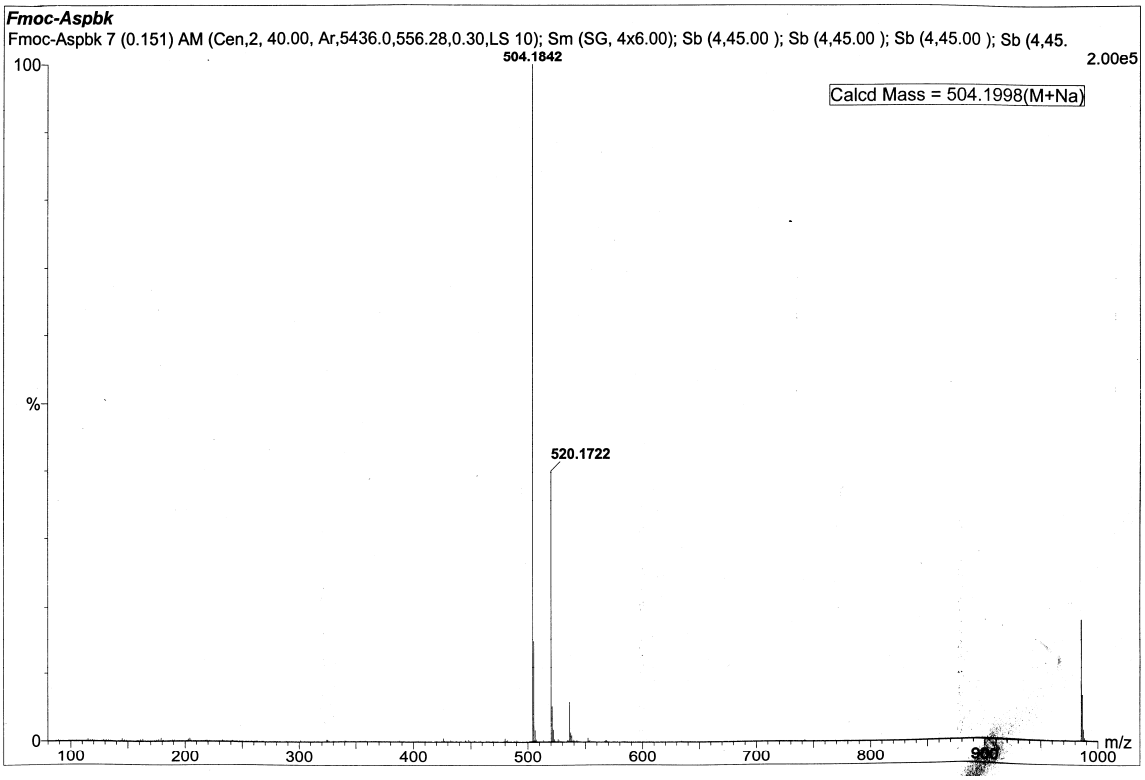

AB -Fmoc-Asp(tBu)-BK
1H CDCl3
110509-69
7.785
7.771
7.609
7.595
7.411
7.328
7.272
5.910
4.608
4.599
4.591
4.583
4.554
4.539
4.532
4.518
4.454
4.438
4.431
4.418
4.240
4.228
4.216
4.201
4.187
3.566
2.941
2.908
2.732
2.699
2.055
1.592
1.449
1.286
1.272
1.258
0.973
0.883
0.870
Fmoc-NH
O
O-tBu
O
O
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.11
1.84
2.13
1.98
1.83
0.89
1.85
1.24
3.06
1.65
0.92
1.14
9.00
4.44

4l

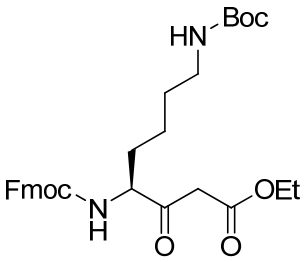

AB -Fmoc-Asp(tBu)-BK
13C CDCl3
120509-26
201.055
170.527
166.875
156.006
143.670
143.627
141.390
127.832
127.140
127.114
125.085
124.999
120.097
82.170
67.136
61.579
56.705
47.238
46.032
28.035
14.100
Fmoc NH
O-tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

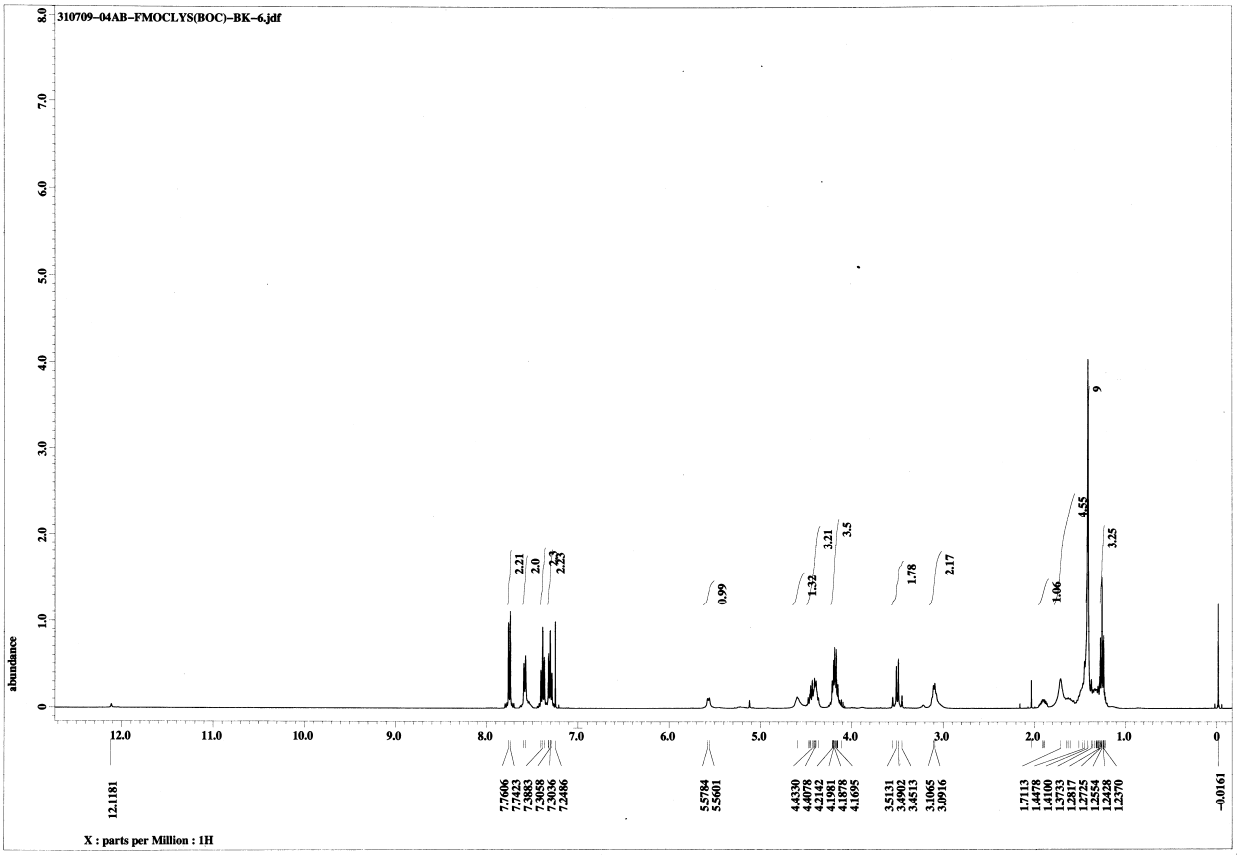
4l


O
O
Fmoc
N
H
OEt
O
O

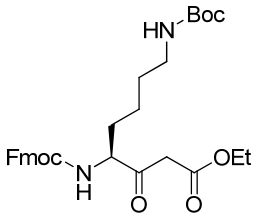

Fmoc-Aspbk
Fmoc-Aspbk 7 (0.151) AM (Cen,2, 40.00, Ar,5436.0,556.28,0.30,LS 10); Sm (SG, 4x6.00); Sb (4,45.00); Sb (4,45.00); Sb (4,45.00); Sb (4,45.
504.1842
2.00e5
Calcd Mass = 504.1998(M+Na)
100
%
520.1722
0
100
200
300
400
500
600
700
800
900
1000
m/z

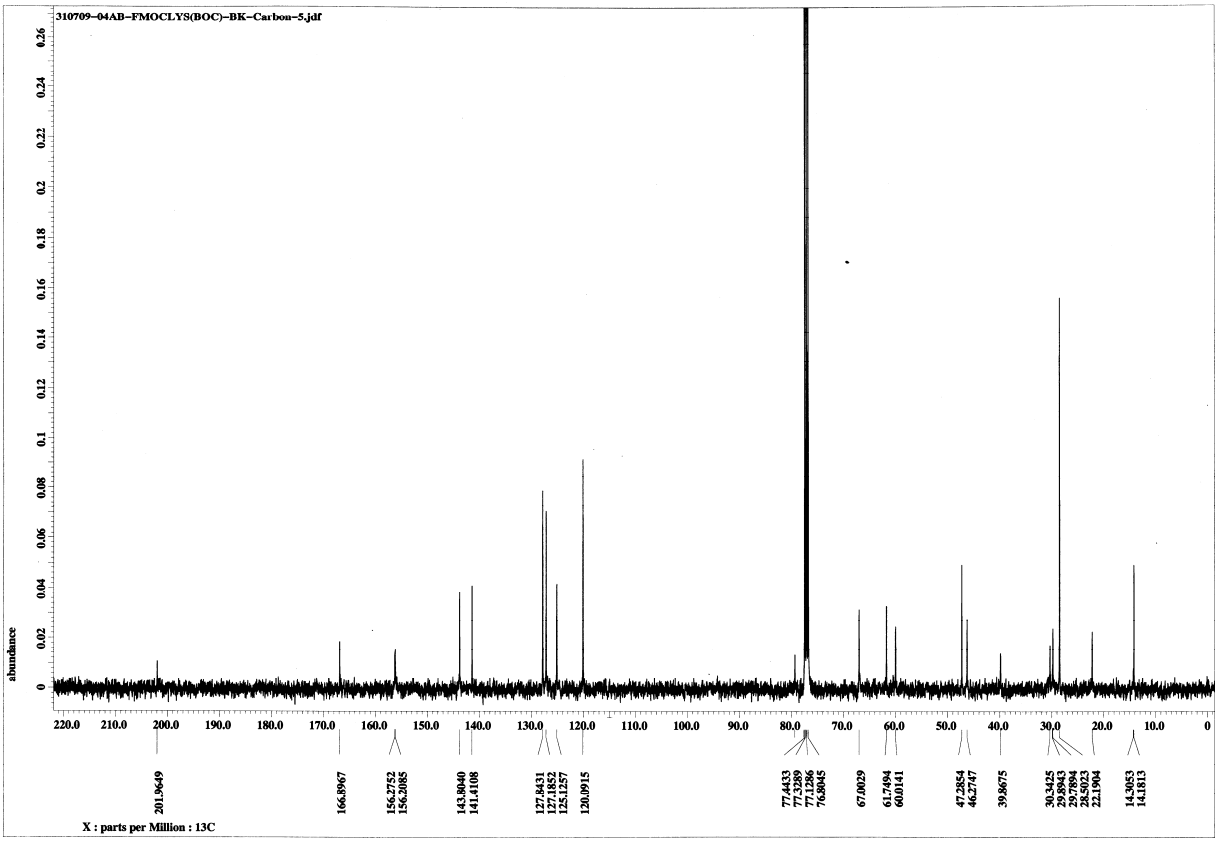
4m


HN
Boc
Fmoc
N
H
O
O
OEt

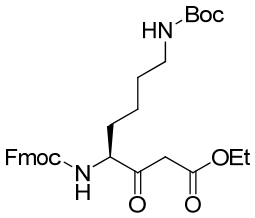

310709-04AB-FMOCLYS(BOC)-BK-6.jdf
abundance
X : parts per Million : 1H
12.1181
7.7606
7.7423
7.3488
7.3058
7.3036
7.2486
5.5784
5.5601
4.4330
4.4078
4.2142
4.1981
4.1878
4.1695
3.5131
3.4902
3.4513
3.1065
3.0916
1.7113
1.4478
1.4100
1.3737
1.2817
1.2725
1.2554
1.2428
1.2370
-0.0161

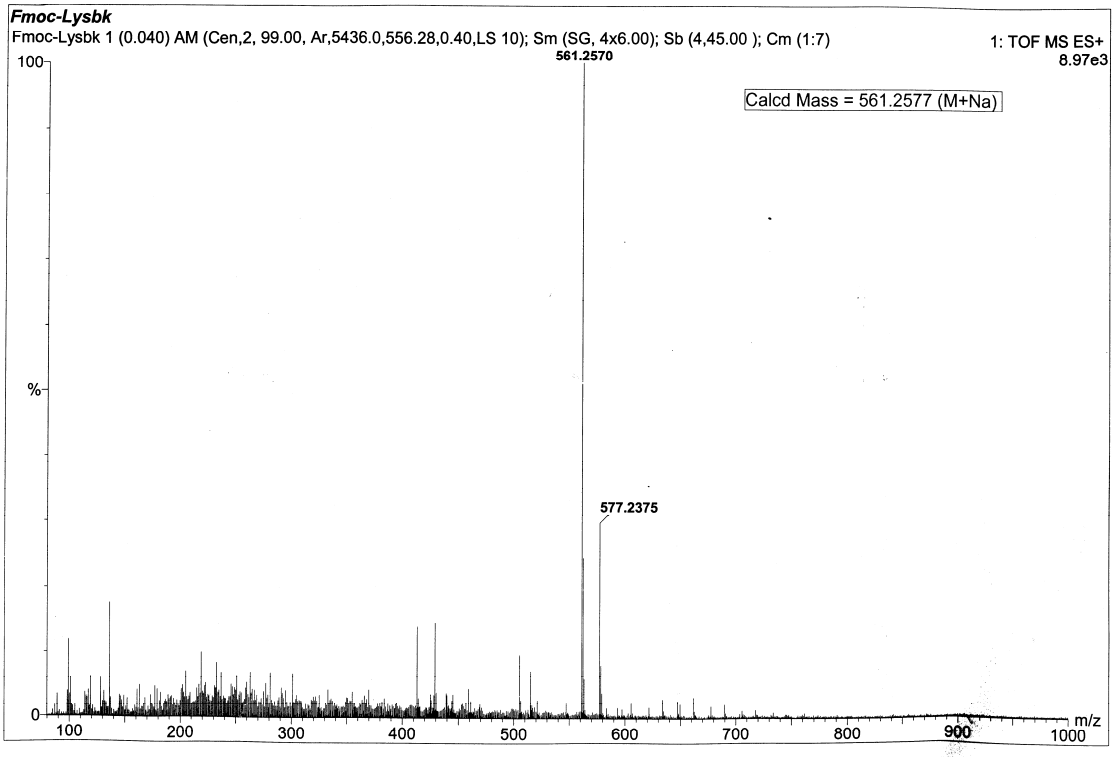
4m


HN
Boc
Fmoc
N
H
O
O
OEt

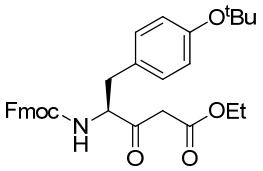

310709-04AB-FMOCLYS(BOC)-BK-Carbon-5.jdf
abundance
X : parts per Million : 13C
201.9649
166.8967
156.3752
156.2085
143.8040
141.4108
127.8431
127.1852
125.1257
120.0915
77.4433
77.1299
77.1286
76.8045
67.0029
61.7494
60.0141
47.2854
46.2747
39.8675
30.3425
29.8943
29.7894
28.5023
22.1904
14.3053
14.1813

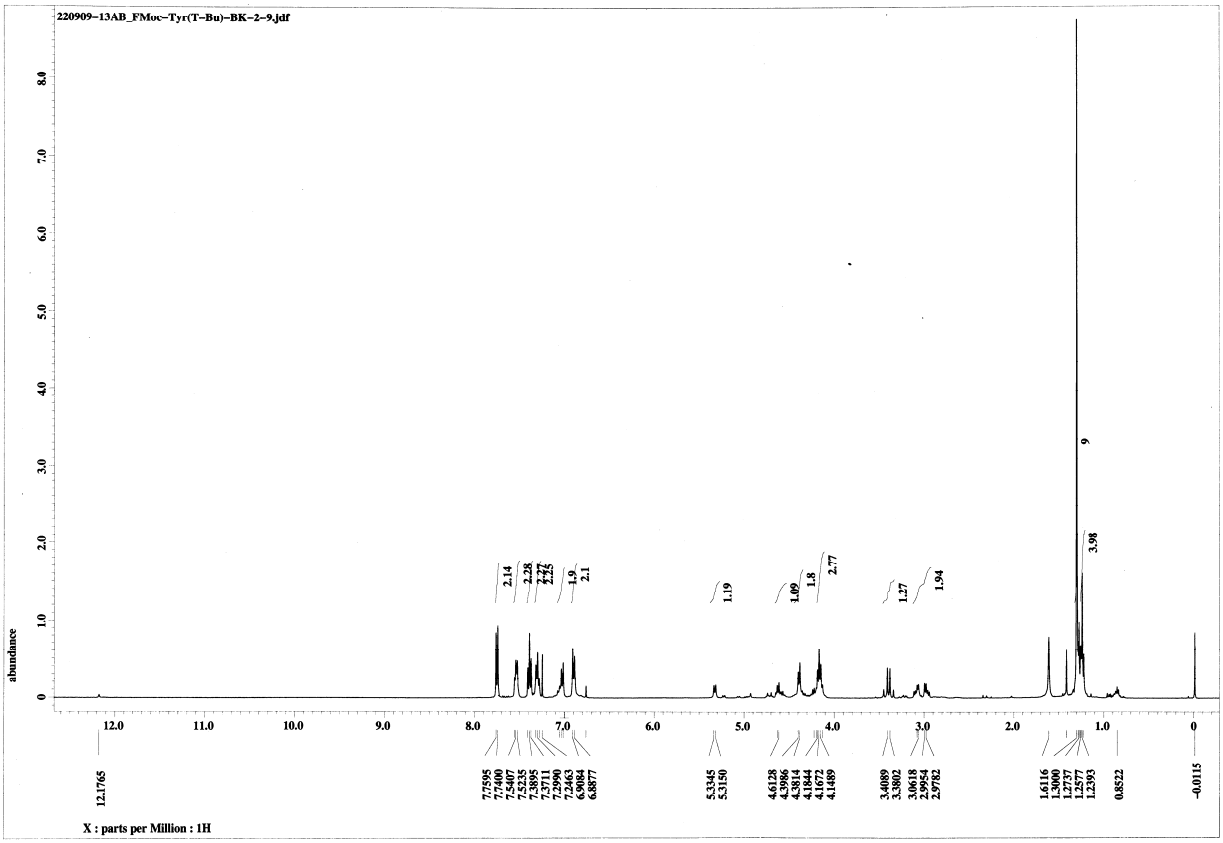
4m


HN
Boc
Fmoc
N
H
OEt
O
O

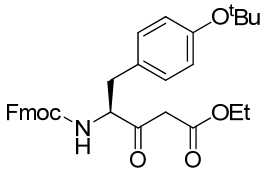

Fmoc-Lysbk
Fmoc-Lysbk 1 (0.040) AM (Cen,2, 99.00, Ar,5436.0,556.28,0.40,LS 10); Sm (SG, 4x6.00); Sb (4,45.00); Cm (1:7)
1: TOF MS ES+
8.97e3
561.2570
Calcd Mass = 561.2577 (M+Na)
577.2375
100
%
0
100
200
300
400
500
600
700
800
900
1000
m/z

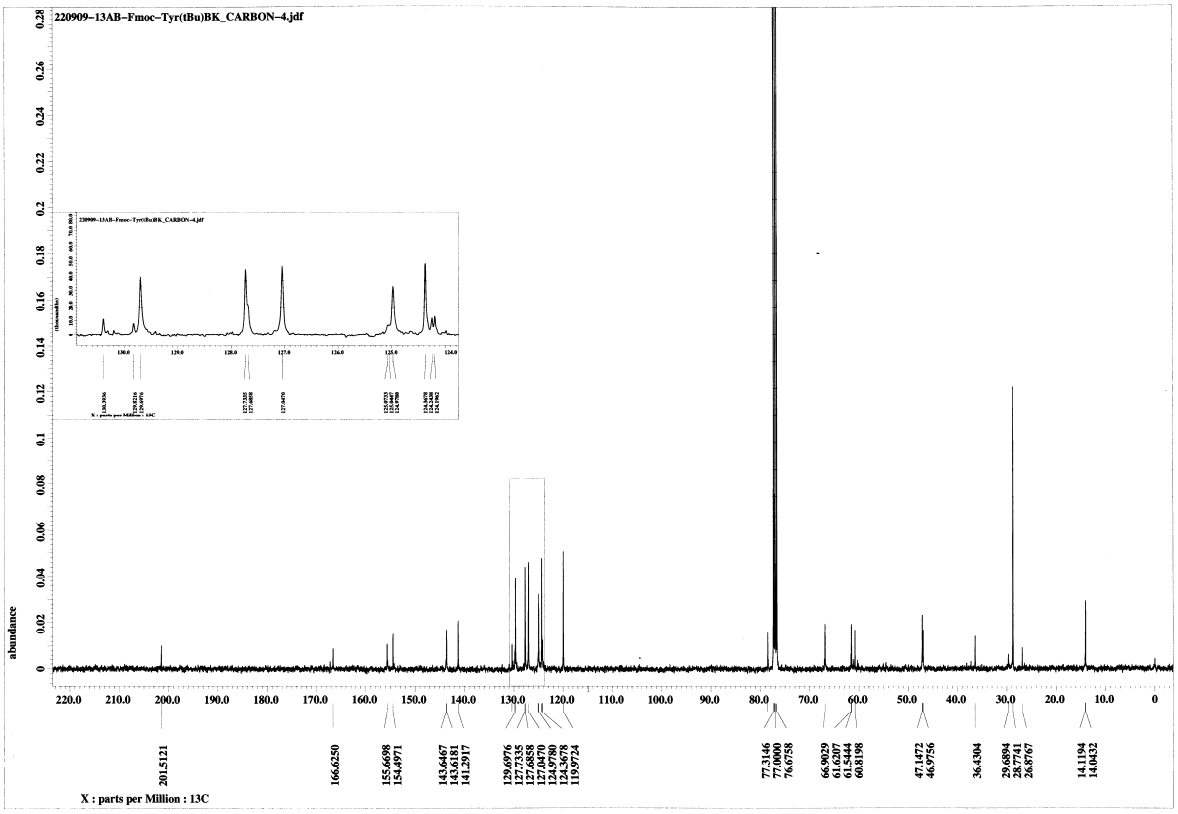
4n


O^{t}Bu
Fmoc
N
H
OEt
O
O

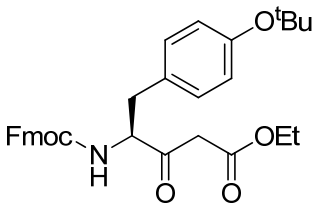

220909-13AB_FMoc-Tyr(T-Bu)-BK-2-9.jdf
abundance
X : parts per Million : 1H

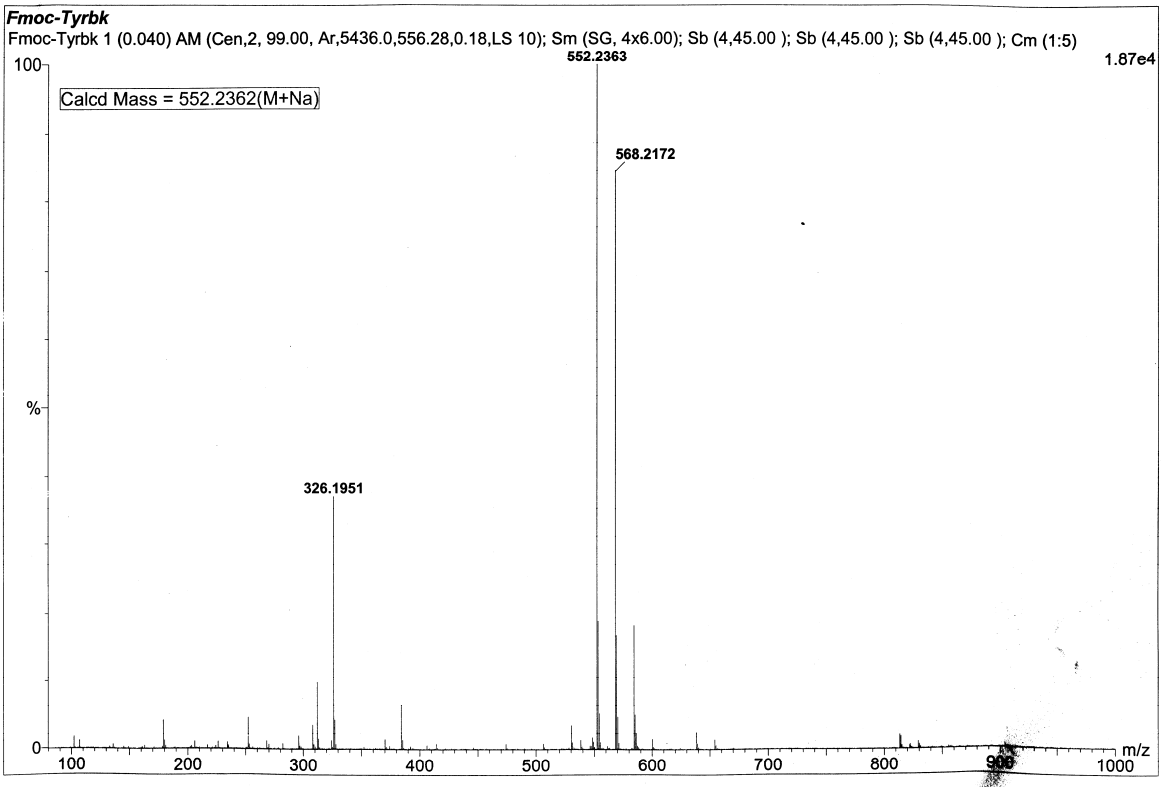
4n


O^{t}Bu
Fmoc
N
H
OEt
O
O


220909-13AB-Fmoc-Tyr(tBu)BK_CARBON-4.jdf
abundance
X : parts per Million : 13C

4n


O^{t}Bu
Fmoc
N
H
OEt
O
O


Fmoc-Tyrbk
Fmoc-Tyrbk 1 (0.040) AM (Cen,2, 99.00, Ar,5436.0,556.28,0.18,LS 10); Sm (SG, 4x6.00); Sb (4,45.00); Sb (4,45.00); Sb (4,45.00); Cm (1:5)
100
%
0
Calcd Mass = 552.2362(M+Na)
552.2363
1.87e4
568.2172
326.1951
100
200
300
400
500
600
700
800
900
1000
m/z

Temperature Experiment of **4a** in $CDCl_3$: The peak at δ 12.1 ppm indicating the existence of enol from of β-keto ester at various temperatures.