Angewandte Chemie
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Supporting Information

69451 Weinheim, Germany

Highly Enantioselective Palladium-Catalyzed Asymmetric Alkylation of Acyclic Amides

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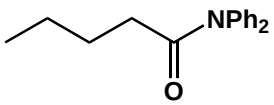
1. General Information

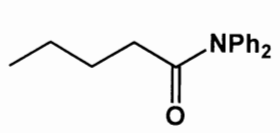
Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a NMR instruments (300 MHz and 75 MHz, respectively). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s =singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Ligand (***S, S$_{phos}$, S*-L6**) was synthesized using our previously reported procedures.[1] Amides **2g**[2], **2h**[3], **2j**[4], **2k**[5] and **2o**[6] were prepared according to the literature procedures.

2. Synthesis of amides 2

N, N-diphenylpentamide (2i)



Pentanoic acid (0.67 g, 6.6 mmol) was dissolved in 10 mL of dry CH_2Cl_2 containing 2 drops of DMF. Oxalyl chloride (1.05 g, 8.2 mmol) and 10.0 mL of dry methylene chloride was added dropwise under N_2. After stirring the solution at ambient temperature for 2 h, the



2i

7.351 7.331 7.264 7.238

2.281 2.256 2.231

1.692 1.667 1.641 1.617 1.592 1.323 1.297 1.271 1.249 0.864 0.840 0.815

9.97

1.98 1.97 2.11 3.00

10 8 6 4 2 PPM

spect, CDCl3,

USER: sioc -- DATE: Fri Dec 08 05:13:50 2006

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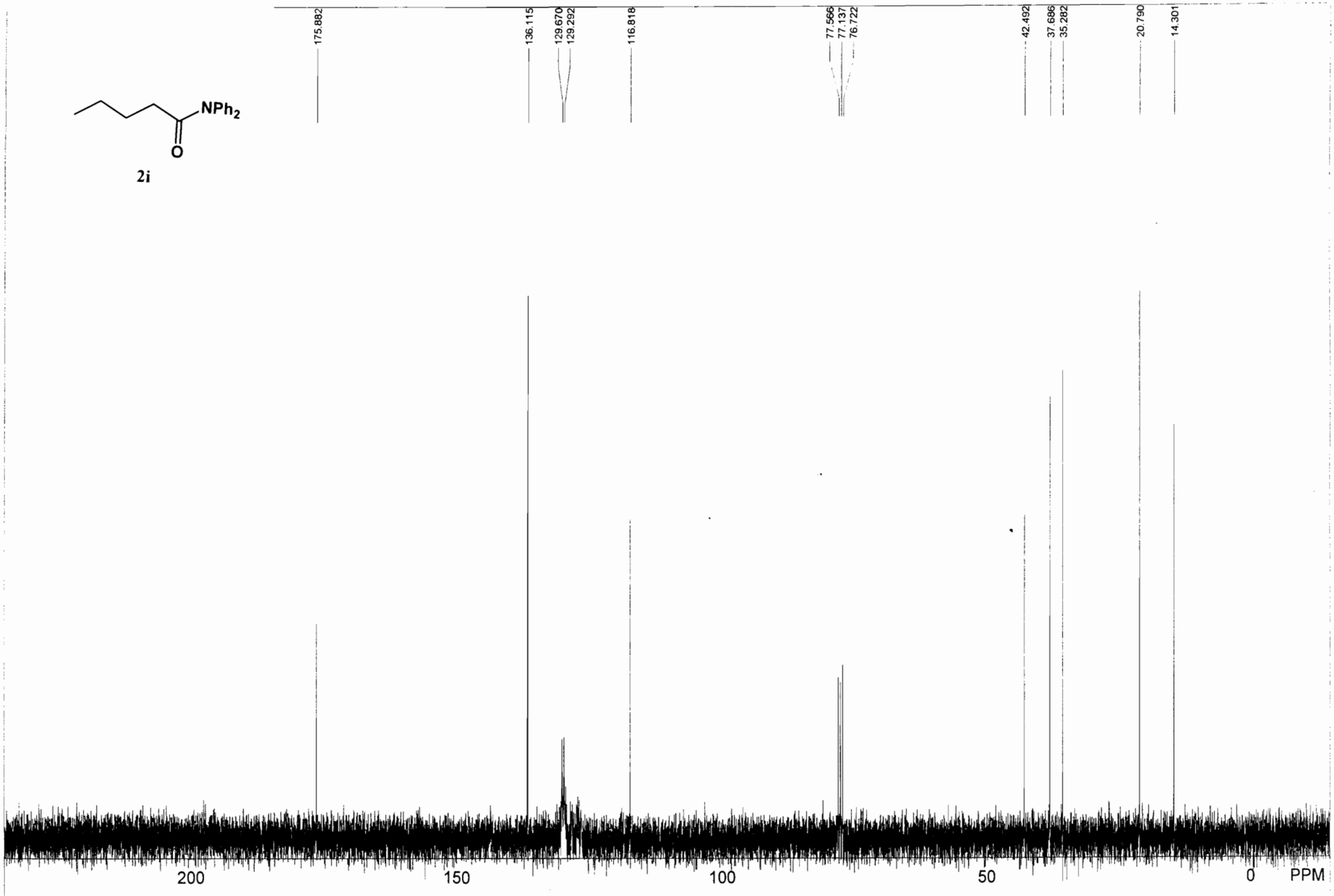
2i



zk-9-88-C

USER: -- DATE: Jan 15 2007

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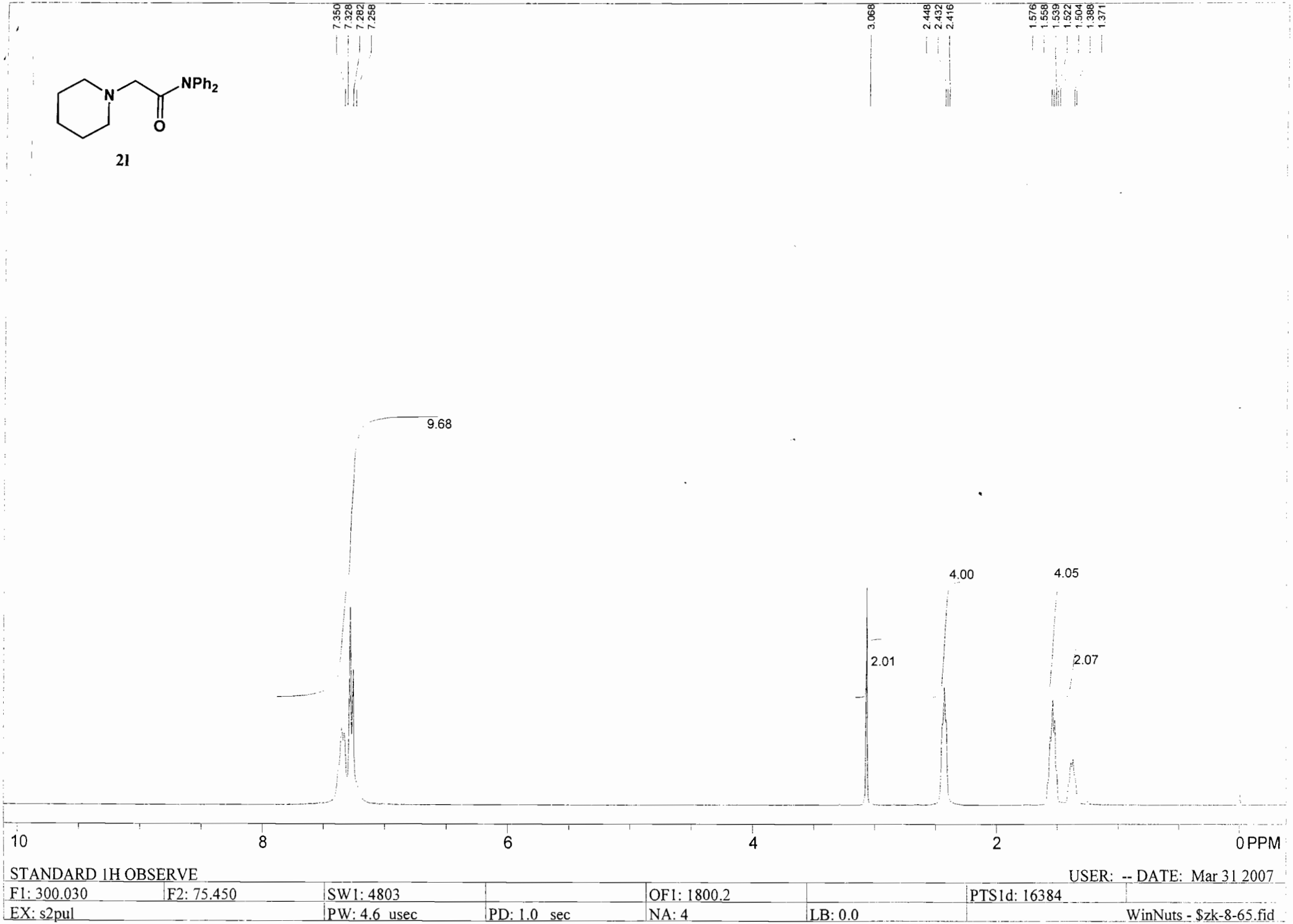
2l



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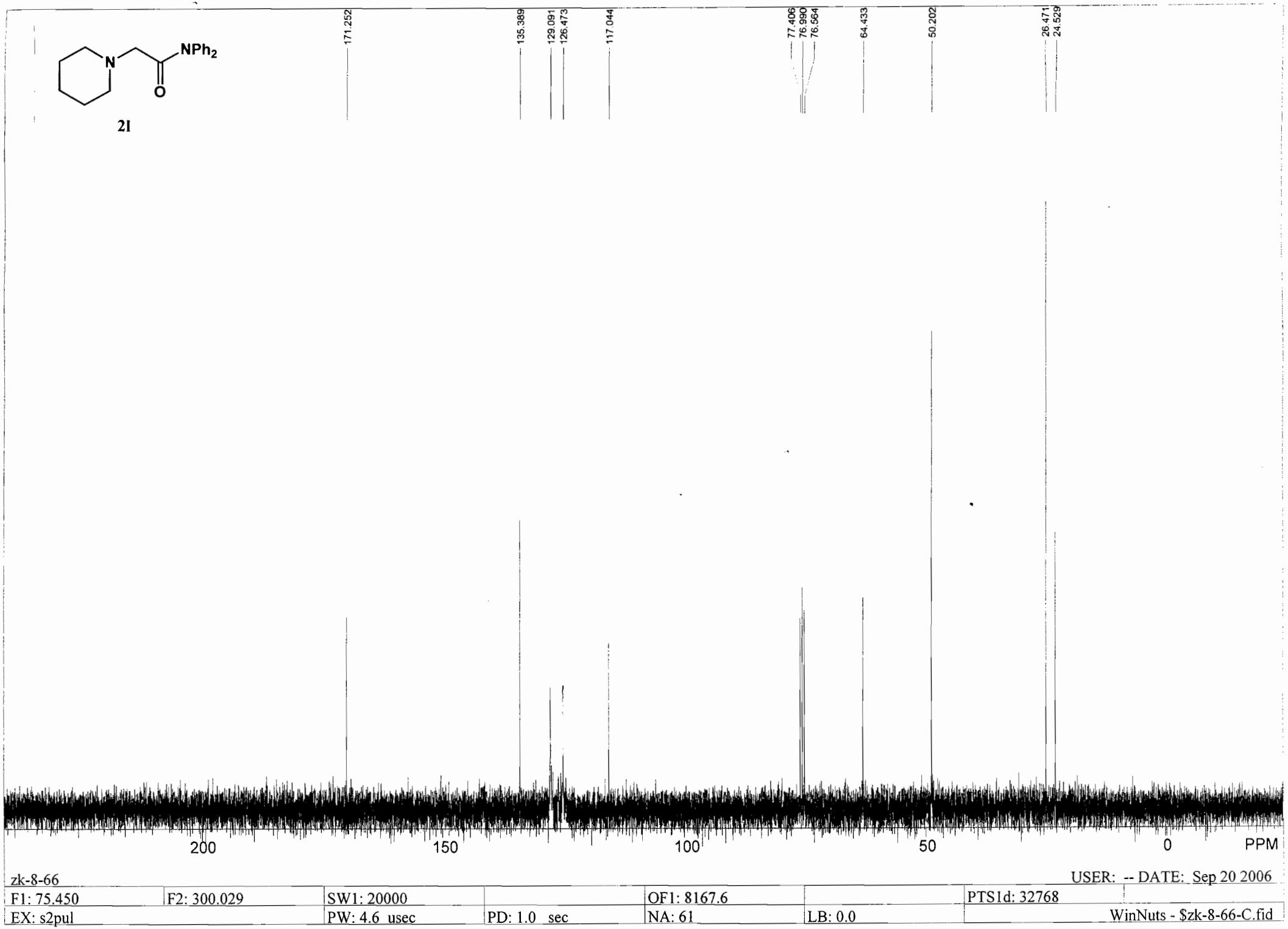

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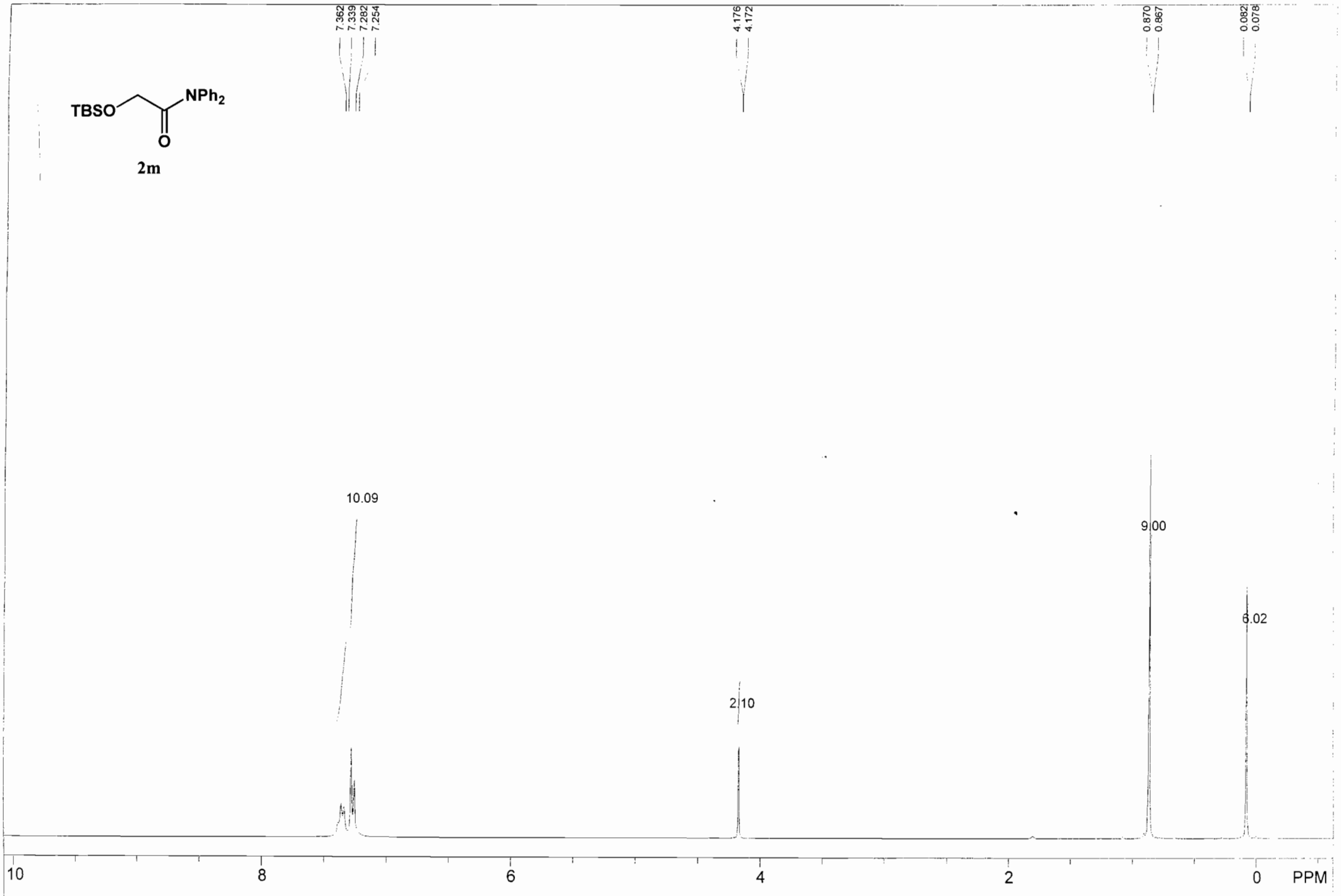

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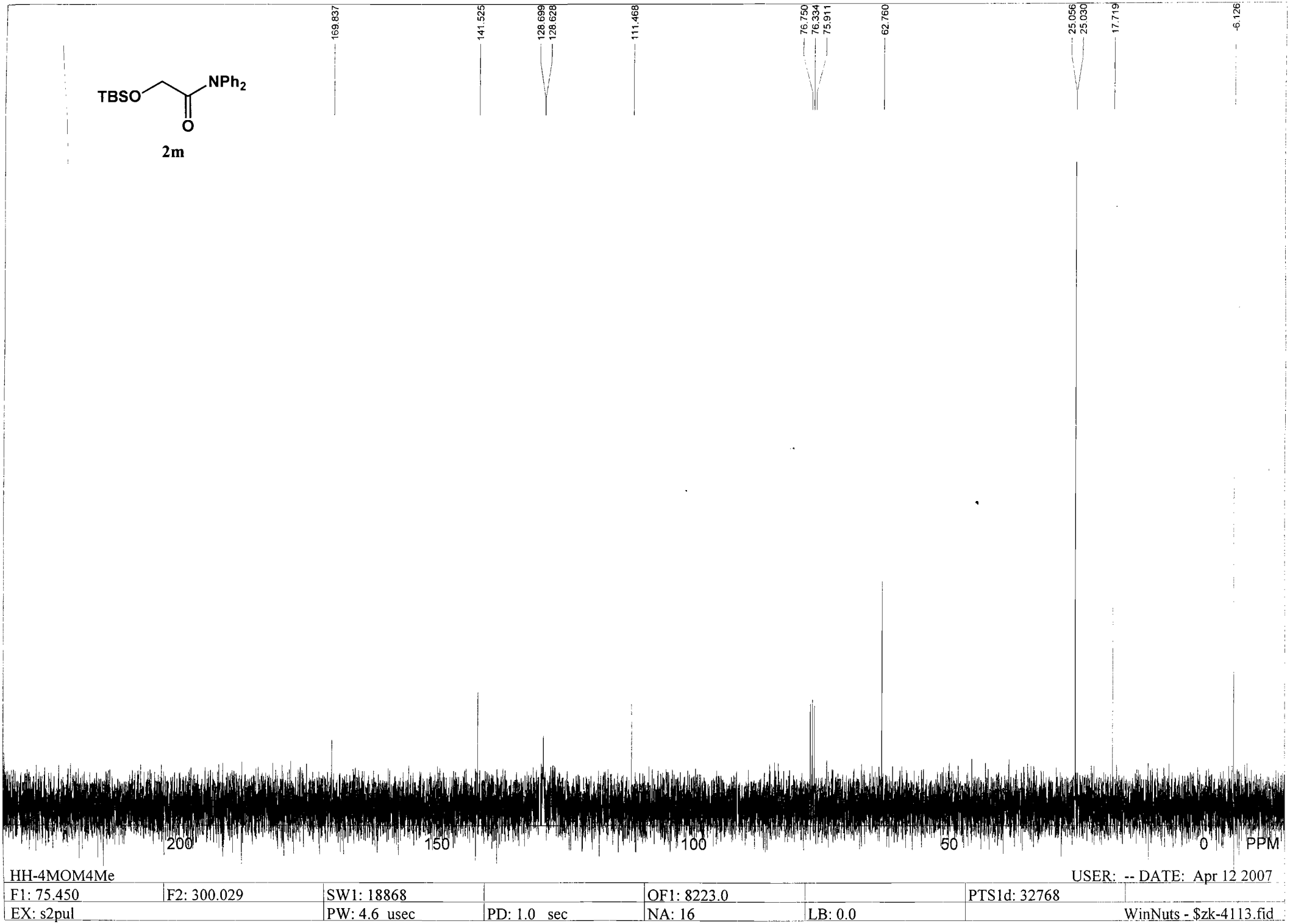

HH-4MOM4Me

USER: -- DATE: Apr 12 2007

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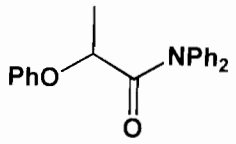

2n

7.344 7.287 7.280 7.272 7.255 7.250 7.233 7.226 6.994 6.991 6.970 6.948 6.945 6.830 6.826 6.820 6.800 6.797 4.917 4.896 4.874 4.852 1.599 1.578

12.89 2.11 1.11 1.00 3.00

10 8 6 4 2 PPM

STANDARD 1H OBSERVE USER: -- DATE: Apr 3 2007

F1: 300.030	F2: 75.450	SW1: 4803		OF1: 1800.2		PTS1d: 16384
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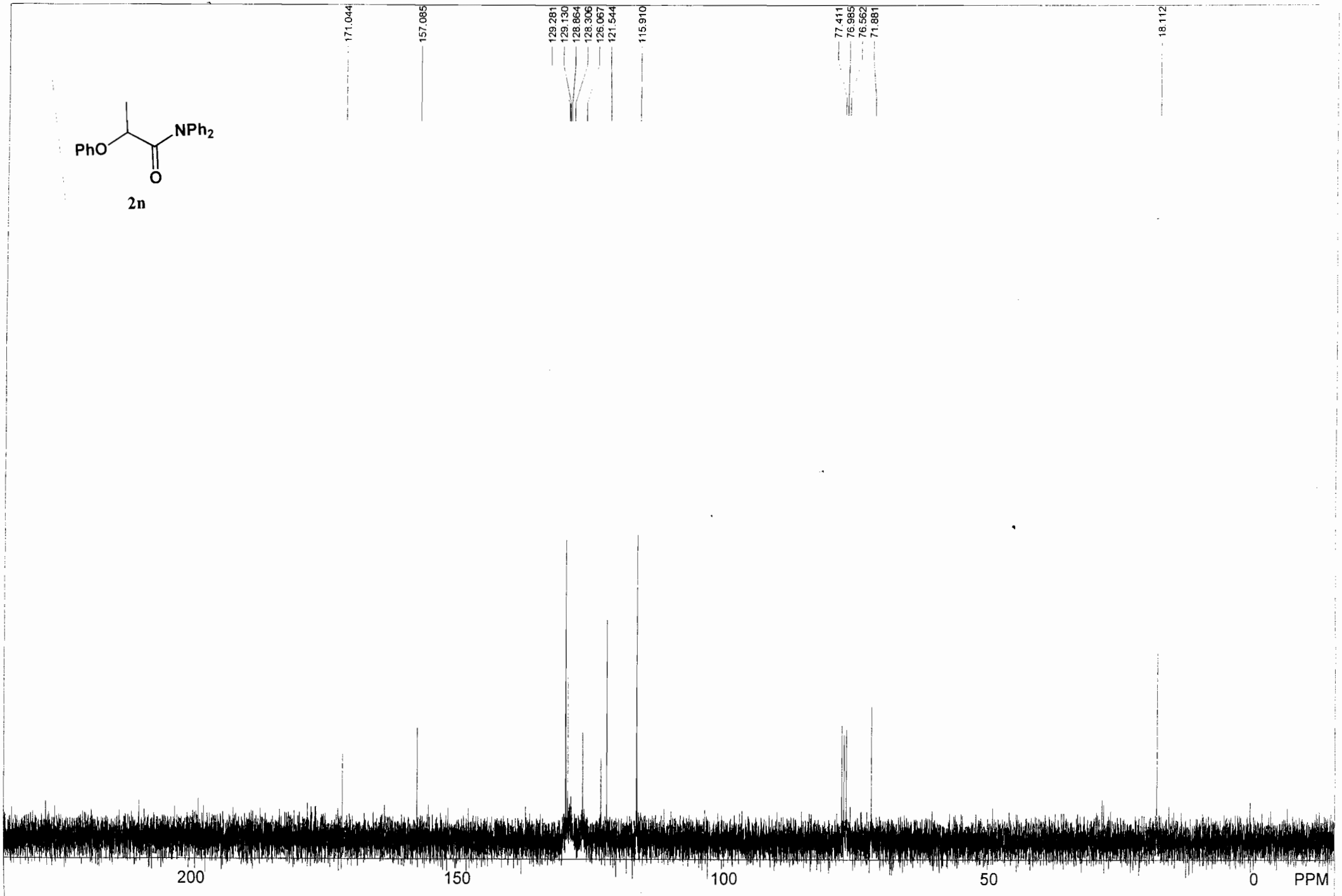

zk-9-55C

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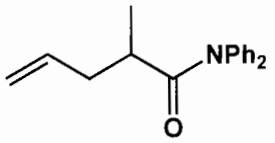

4g

7.347
7.257
7.229
5.797
5.772
5.762
5.749
5.739
5.716
5.706
5.692
5.682
5.658
5.110
5.060
5.028
2.707
2.685
2.679
2.664
2.659
2.637
2.556
2.531
2.509
2.486
2.459
2.149
2.128
2.126
2.104
2.081
2.060
1.163
1.140
0.006

10.05
1.01
2.07
1.00
1.09
1.17
3.13

10
8
6
4
2
PPM

STANDARD 1H OBSERVE
USER: -- DATE: Jun 24 2007

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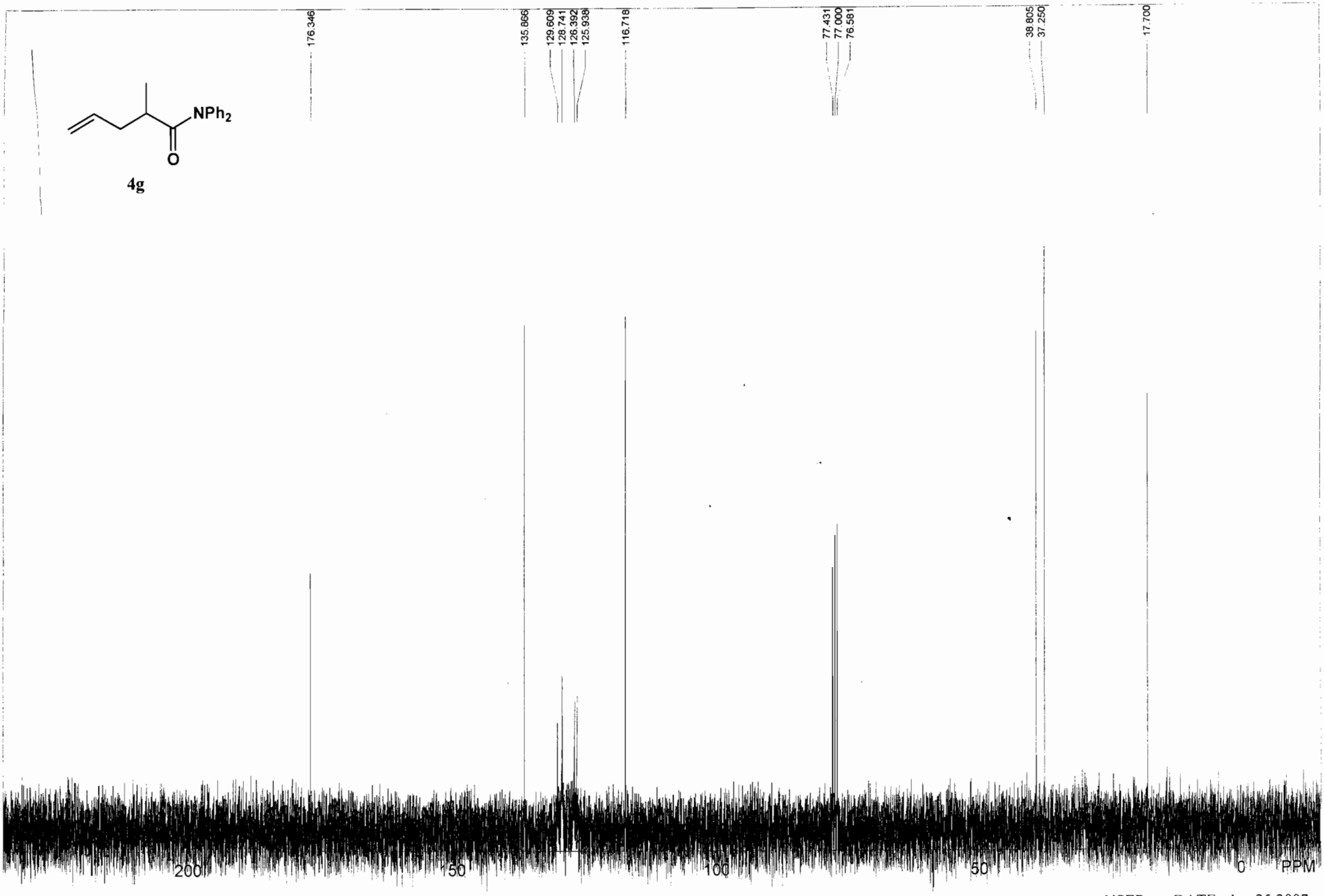

zk-proallyl

USER: -- DATE: Jun 25 2007

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色谱分析报告

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样品文件名:zk-7-7rac.che
样品批号:
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分析时间:13:39
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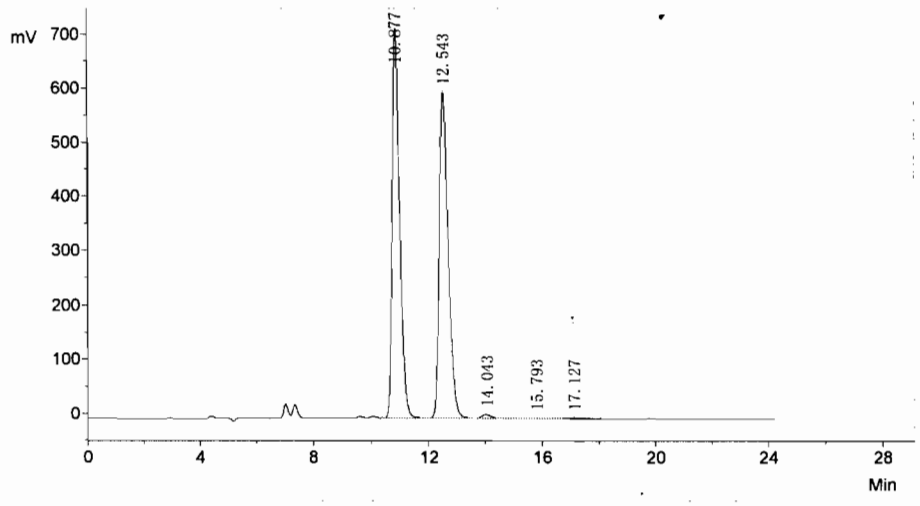
流速:
检测波长:



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2	2	Unknown	12.543	601149.4	13146420.5	49.7894
3	3	Unknown	14.043	6853.5	165787.3	0.6279
4	4	Unknown	15.793	676.9	18434.7	0.0698
5	5	Unknown	17.127	688.1	18503.6	0.0701
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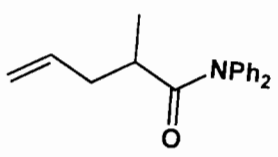

4g

色谱分析报告

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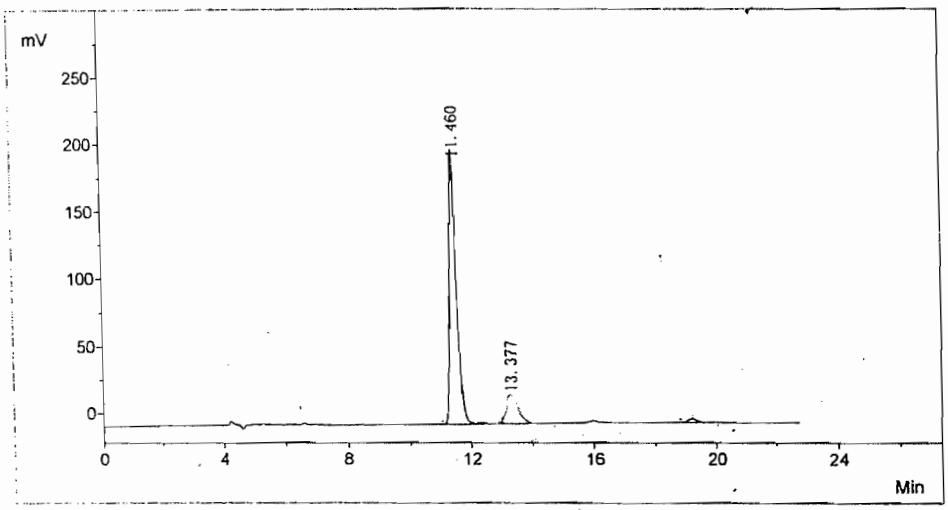

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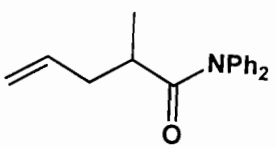

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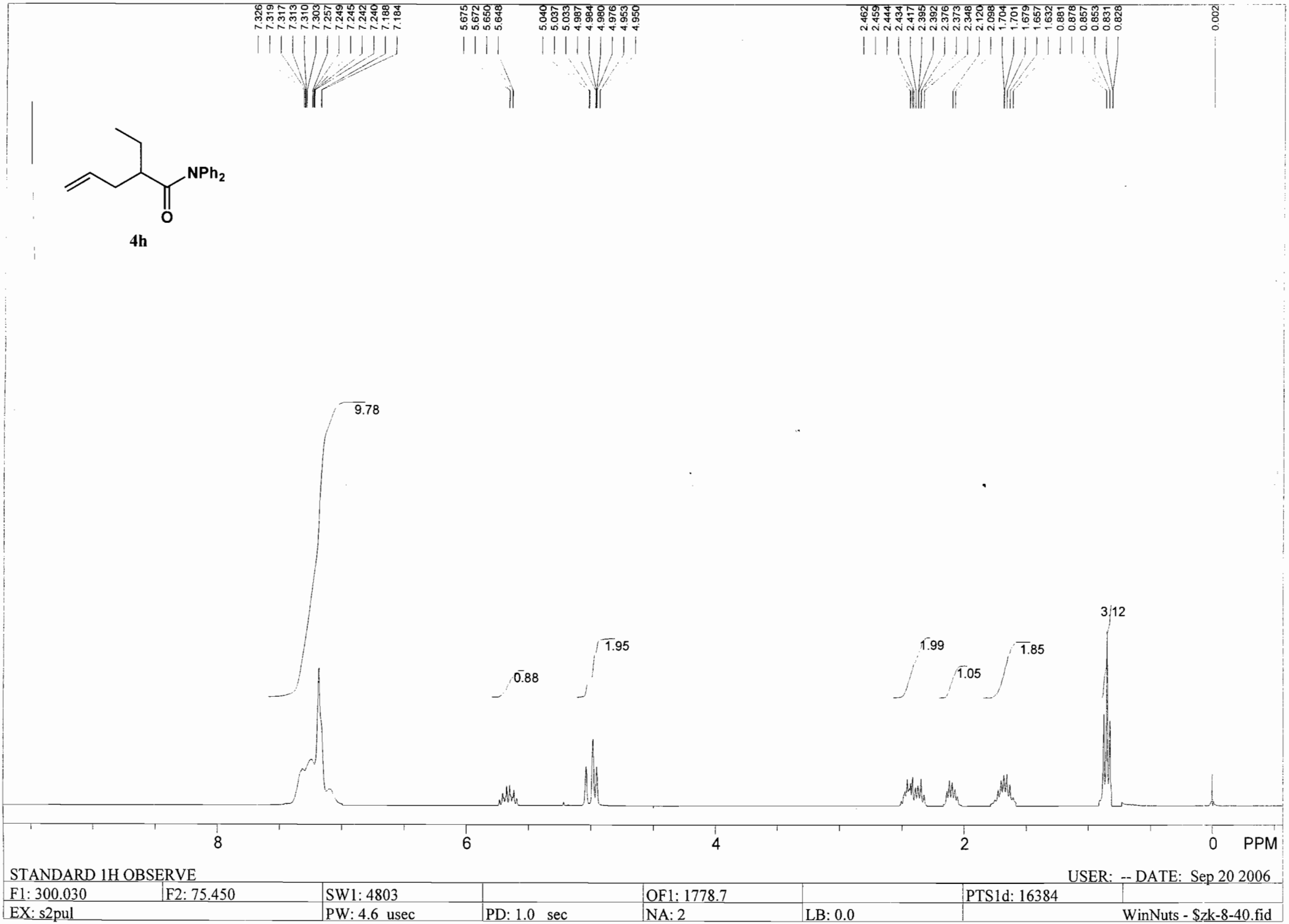

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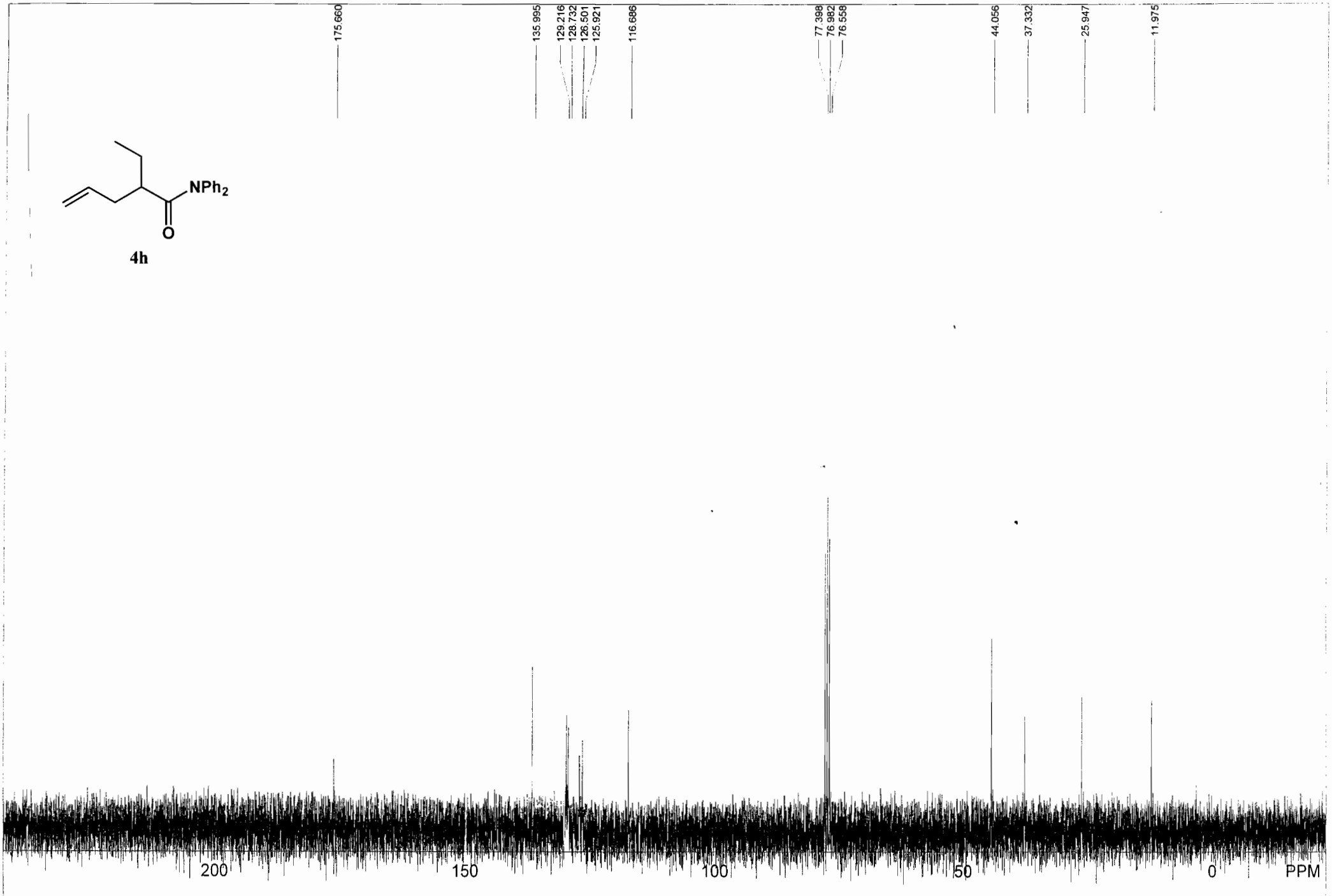

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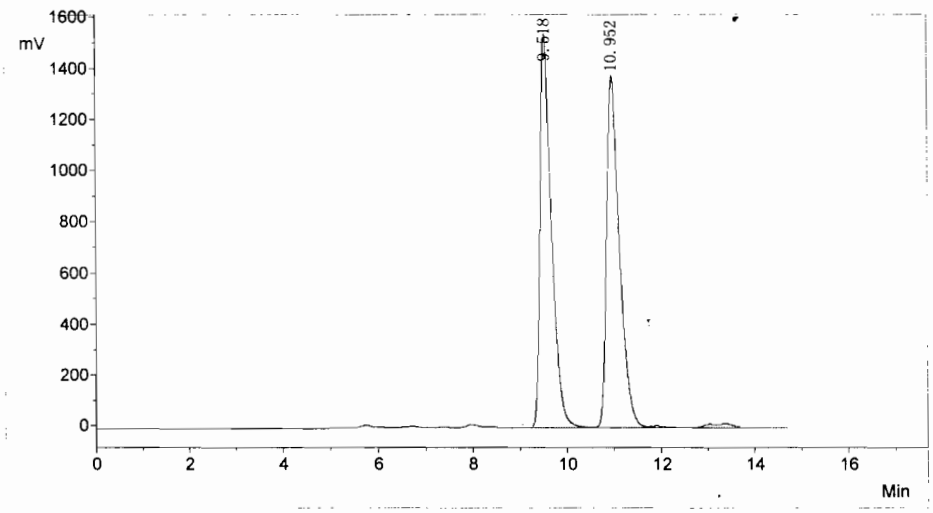

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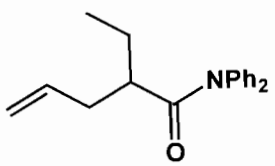

4h

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样品批号:　　分析者:

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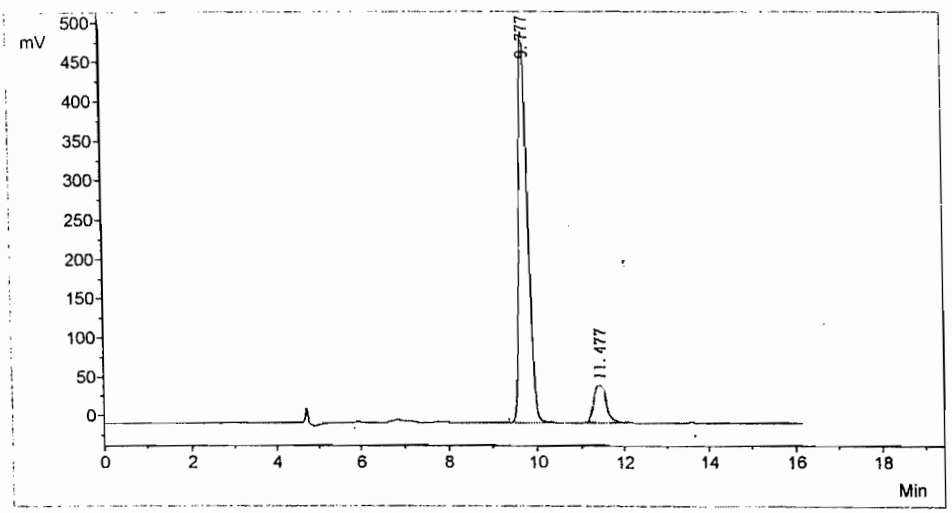
色谱柱:　　流动相:

流速:　　检测波长:



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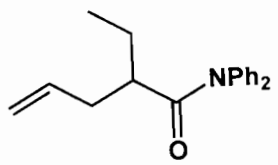

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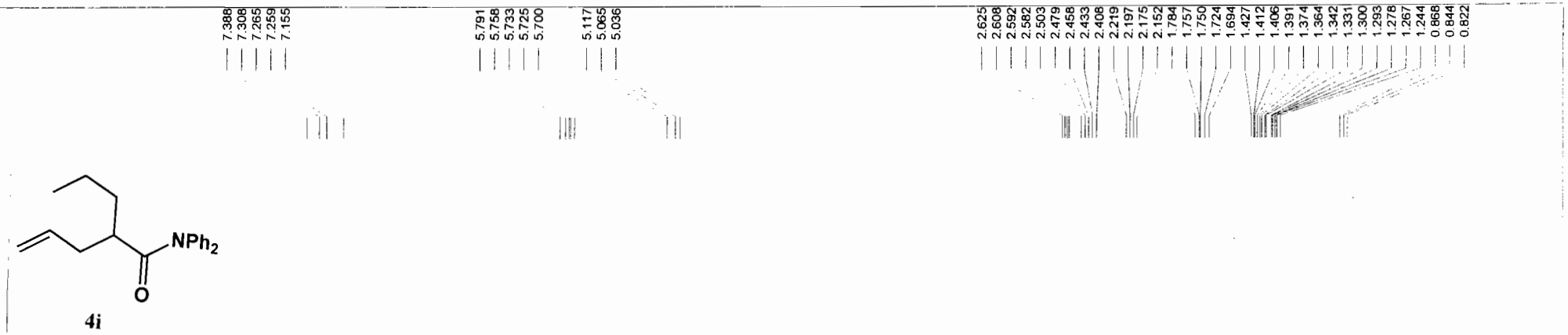
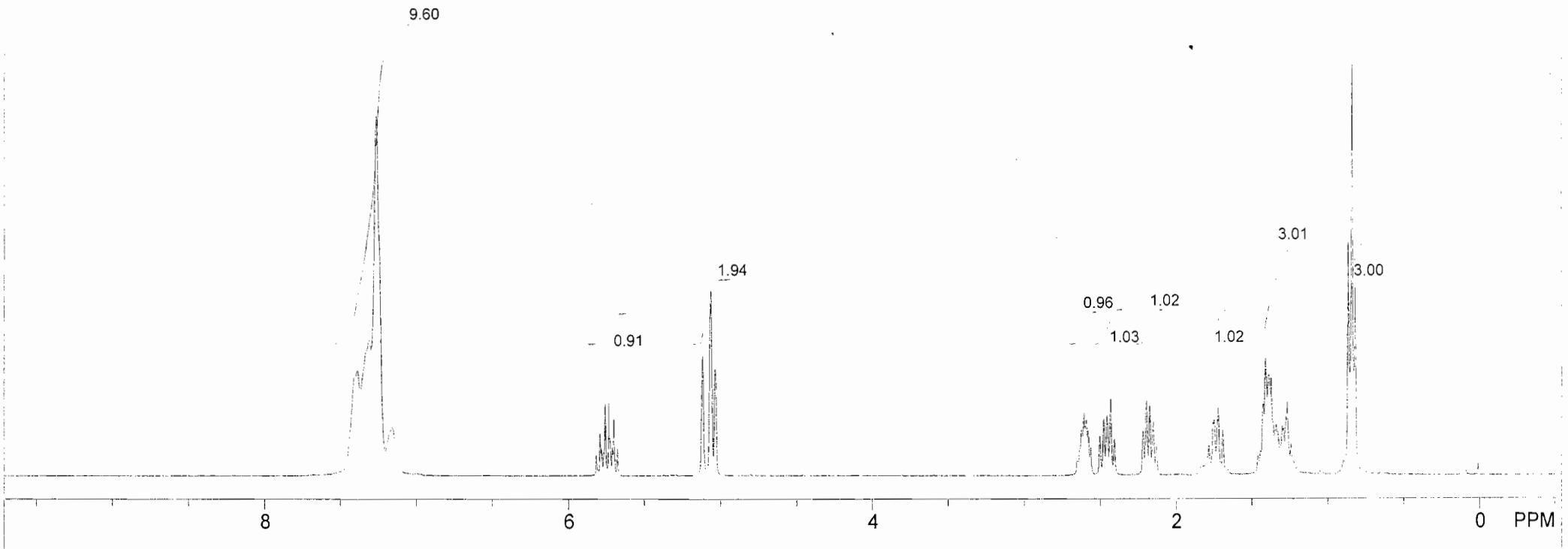


4i



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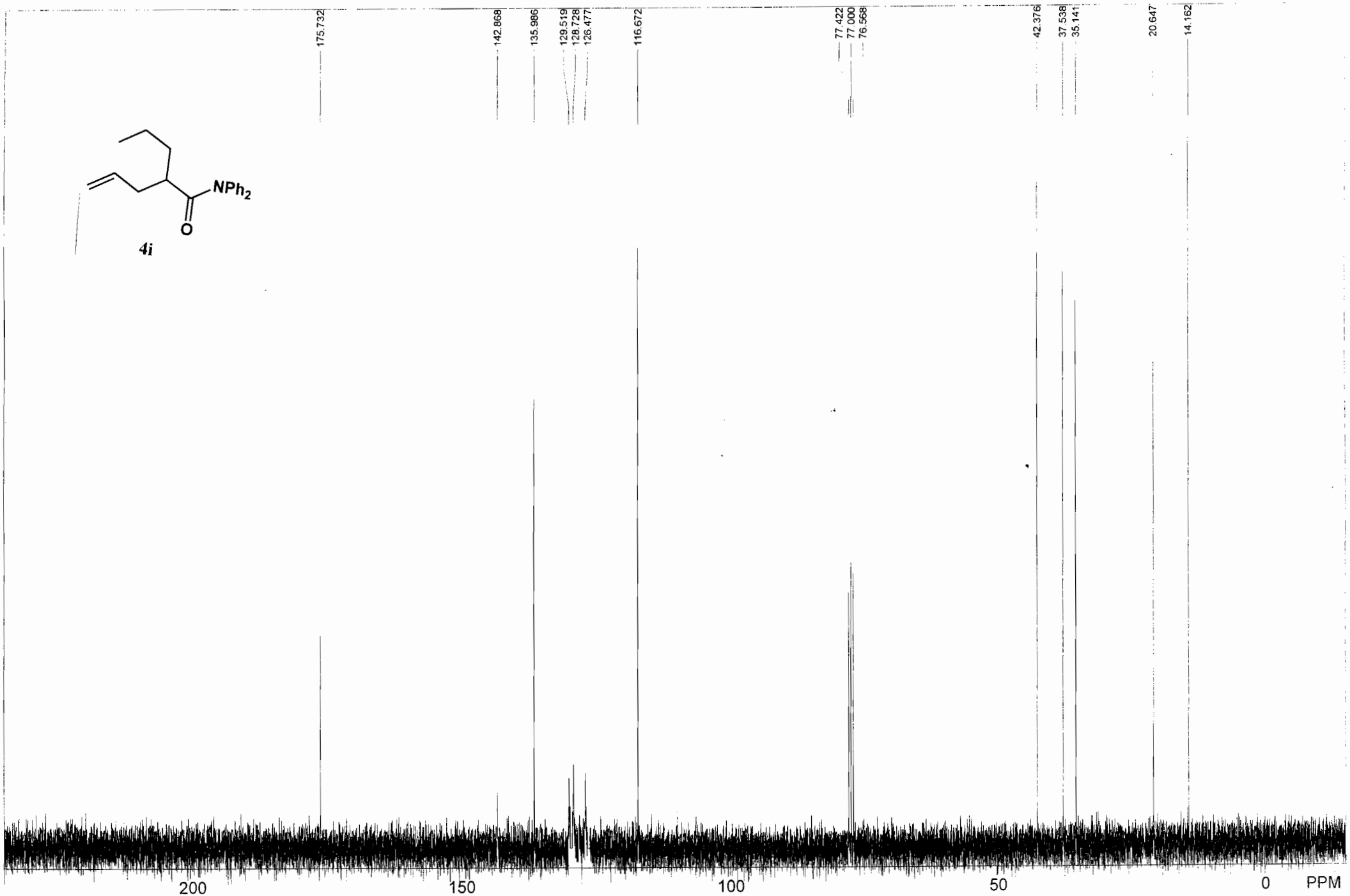

zk-9-88-C

USER: -- DATE: Dec 21 2006

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WinNuts - $zk-9-88-C fid

色谱分析报告

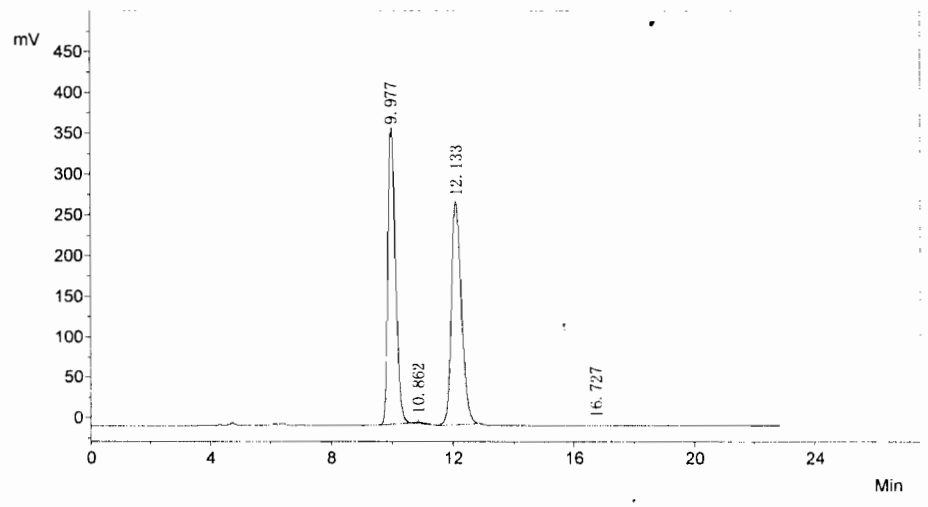
样品名称:分析谱图　　样品文件名:zk9-88rac.che

样品批号:　　分析者:

分析日期:2006-12-21　　分析时间:13:48

色谱柱:　　流动相:

流速:　　检测波长:



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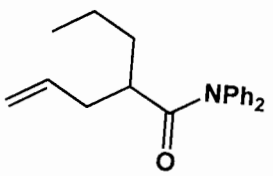
2	2	Unknown	10.862	1165.4	22801.3	0.1807
3	3	Unknown	12.133	271501.3	6298665.7	49.9299
4	4	Unknown	16.727	532.2	12413.8	0.0984
Total				632439.5	12615011.6	100.0000



4i

色谱分析报告

样品名称:分析谱图　　样品文件名:zk-9-88.che

样品批号:　　分析者:

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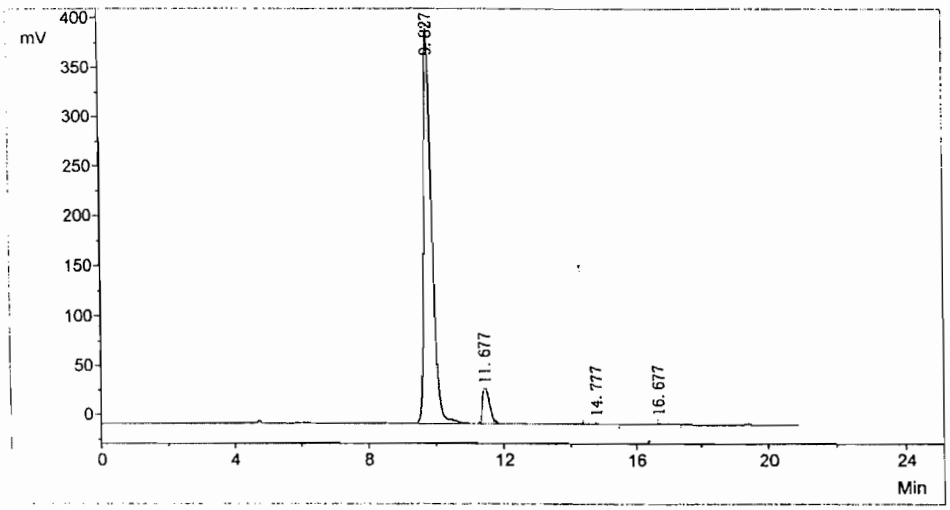
色谱柱:　　流动相:

流速:　　检测波长:



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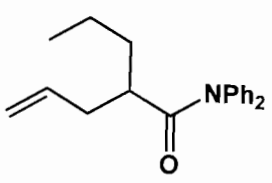
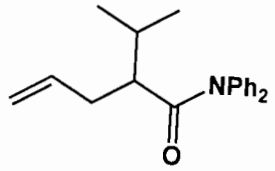
3	3	Unknown	14.777	463.0	11873.2	0.1591
4	4	Unknown	16.677	677.8	16712.6	0.2173
Total				443802.0	7453245.5	100.0000



4i



4j

7.398 7.376 7.304 7.274 7.259 7.258 7.171 7.151
5.877 5.843 5.819 5.786 5.761
5.162 5.106 5.072
2.465 2.439 2.408 2.393 2.384 2.377 2.351 2.276 2.245 2.219 2.018 1.996 1.973 1.949
1.010 0.988 0.919 0.896
0.004 0.002

9.73
0.88
1.87
1.89
0.97
0.95
3.01
3.00

10 8 6 4 2 PPM

STANDARD 1H OBSERVE USER: -- DATE: Apr 29 2007

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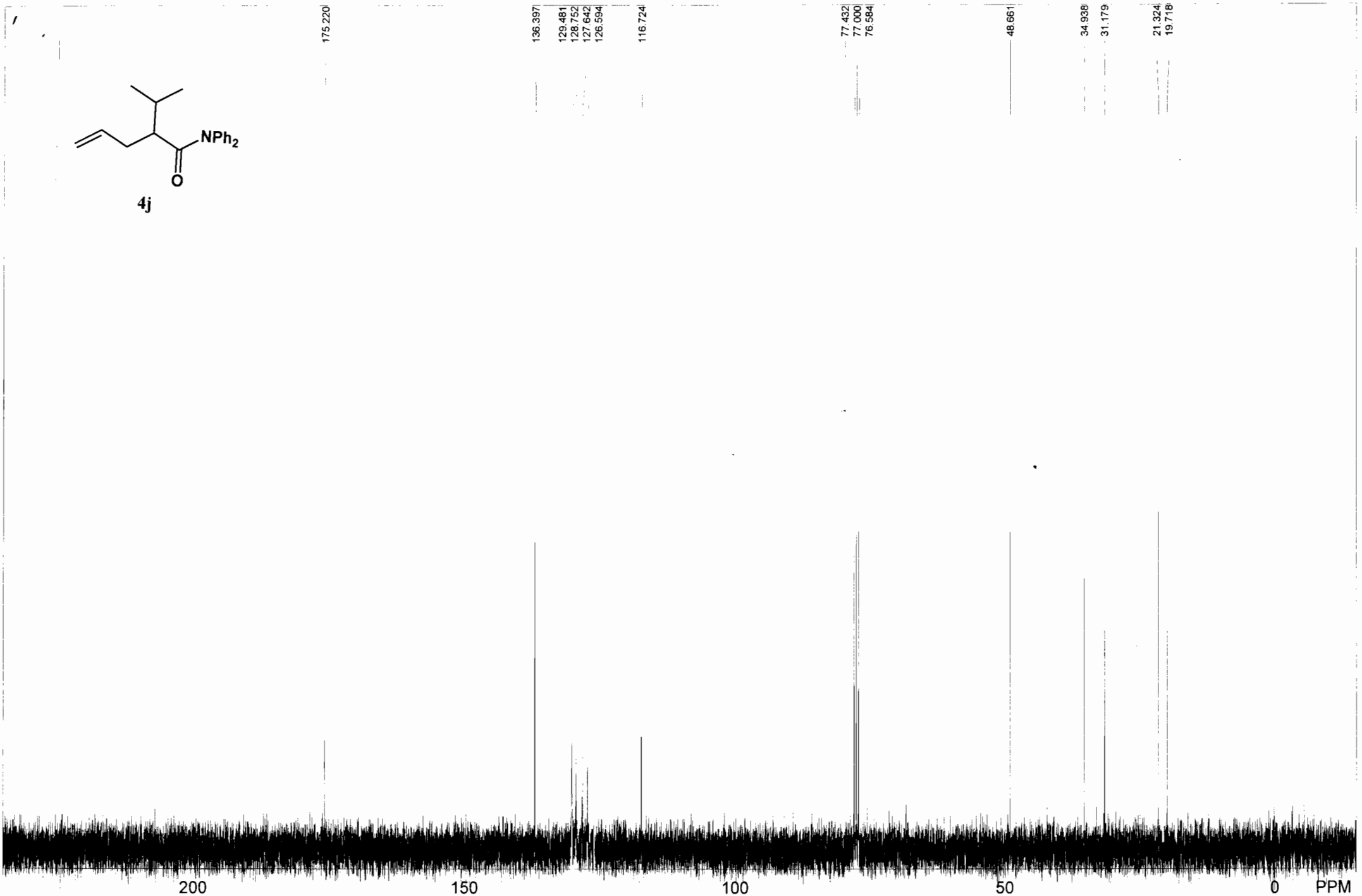

zk-10-82C
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USER: -- DATE: Apr 29 2007

色谱分析报告

样品名称:分析谱图　　样品文件名:zk-8-731.che

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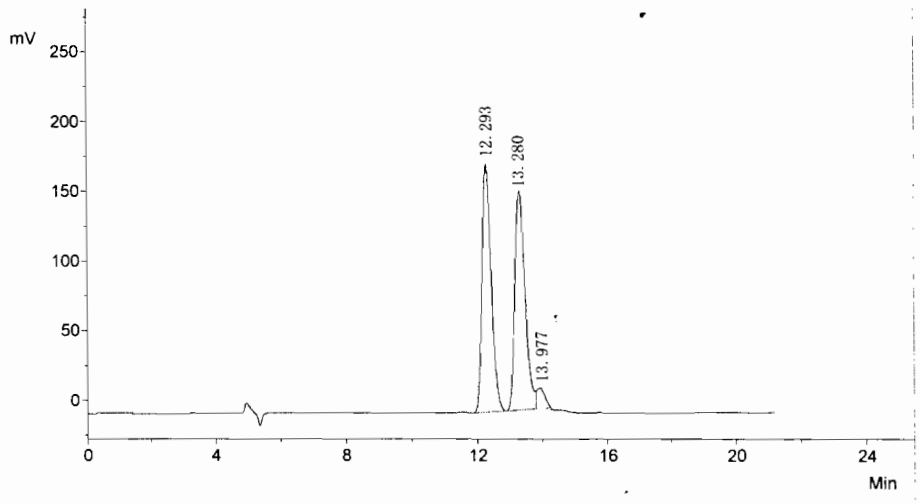
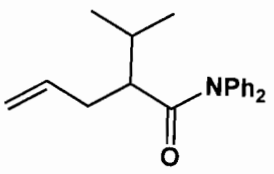
色谱柱:　　流动相:

流速:　　检测波长:



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	12.293	176936.2	3492929.6	48.5690
2	2	Unknown	13.280	153803.0	3435721.5	47.7735
3	3	Unknown	13.977	13533.8	263035.0	3.6575
Total				344273.0	7191686.1	100.0000



4j

色谱分析报告

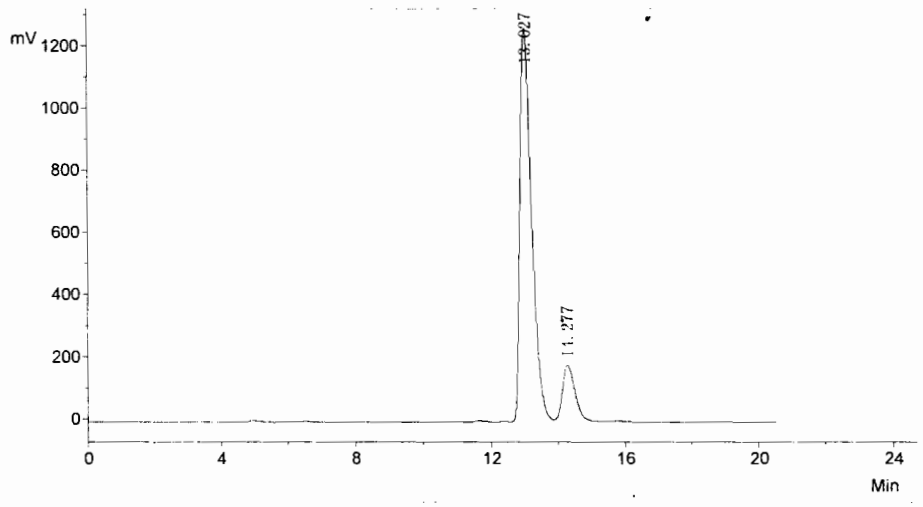
样品名称:分析谱图　　样品文件名:ZK-Li1.che

样品批号:　　分析者:

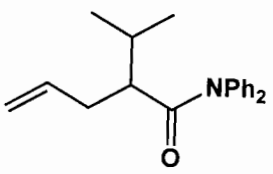
分析日期:2007-04-10　　分析时间:15:16

色谱柱:　　流动相:

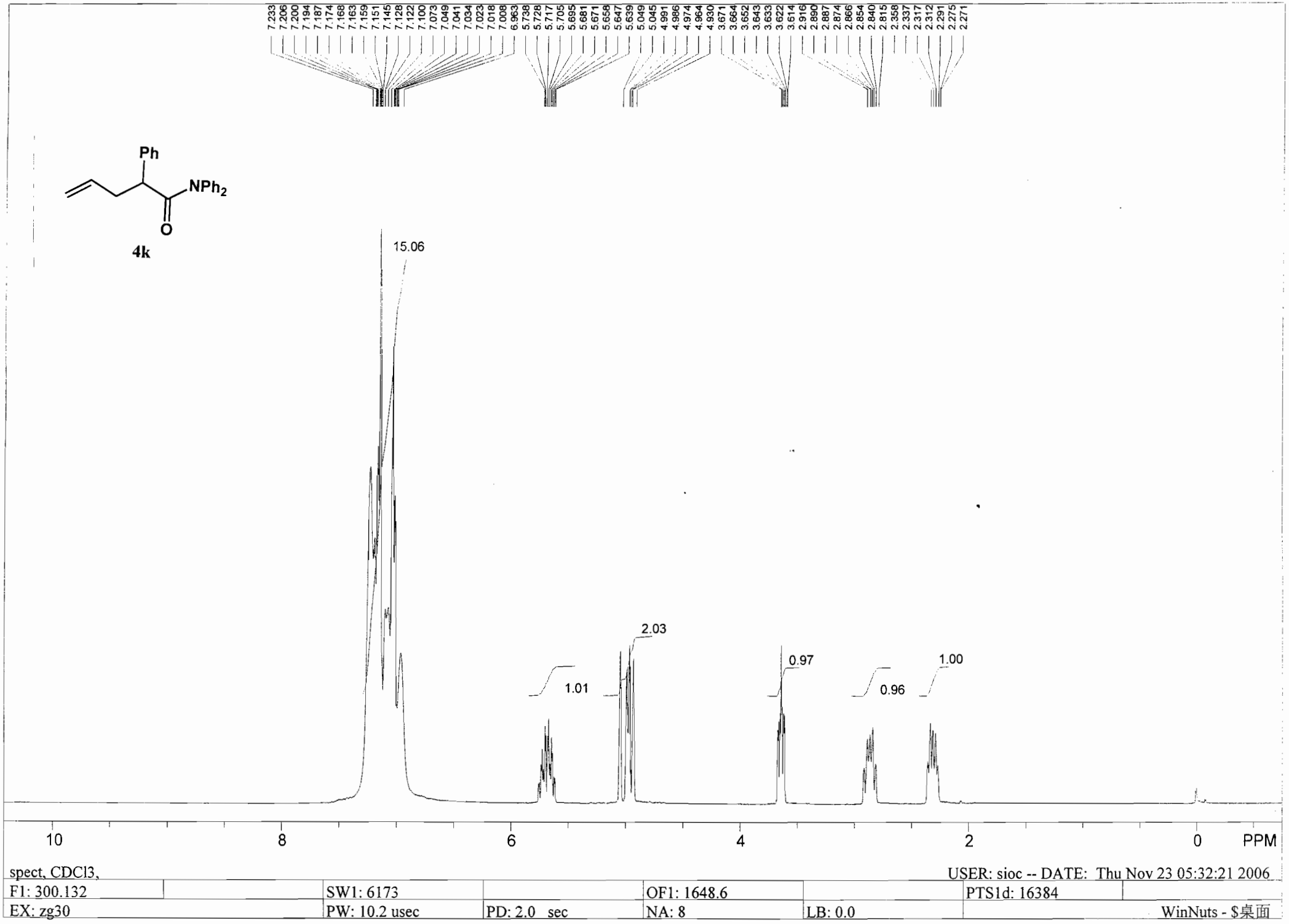
流速:　　检测波长:



序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	13.027	1260472.2	30428633.7	86.4541
2	2	Unknown	14.277	181539.3	4767667.0	13.5459
合计:				1442011.4	35196300.7	100.0000



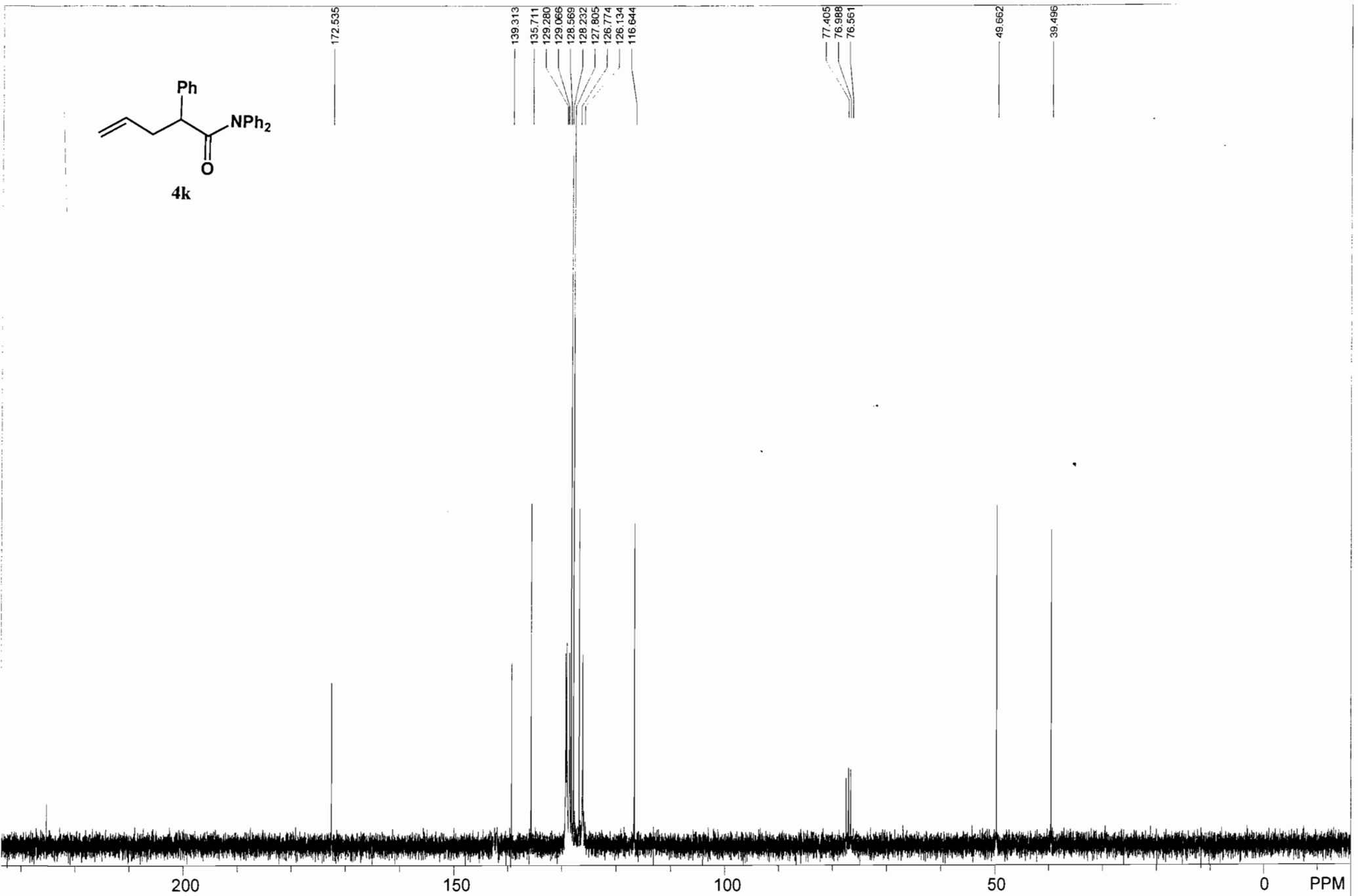
4j



spect, CDCl3,

USER: sioc -- DATE: Thu Nov 23 05:32:21 2006

F1: 300.132		SW1: 6173		OF1: 1648.6		PTS1d: 16384	
EX: zg30		PW: 10.2 usec	PD: 2.0 sec	NA: 8	LB: 0.0		WinNuts - $桌面



zk-9-59-C USER: -- DATE: Dec 7 2006

F1: 75.450	F2: 300.029	SW1: 18868		OF1: 8203.0		PTS1d: 32768	
EX: s2pul		PW: 4.6 usec	PD: 1.0 sec	NA: 96	LB: 0.0		WinNuts - $zk-9-59-C.fid

色谱分析报告

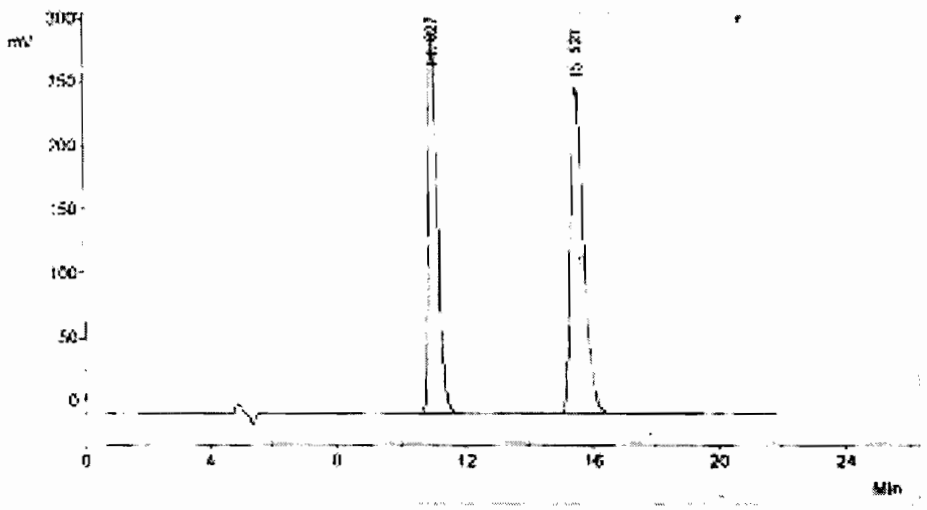
样品名称:分析谱图　　样品文件名:zk9-59rac.che

样品批号:　　分析者:

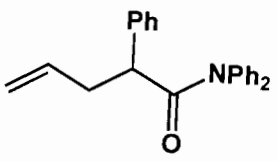
分析日期:2006-11-30　　分析时间:13:58

色谱柱:　　流动相:

流速:　　检测波长:



No.	PeakNo	ID Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	11.027	297034.9	5723338.1	49.7575
2	2	Unknown	15.527	254867.1	5779125.0	50.2425
Total				551902.0	11502463.1	100.0000



4k

色谱分析报告

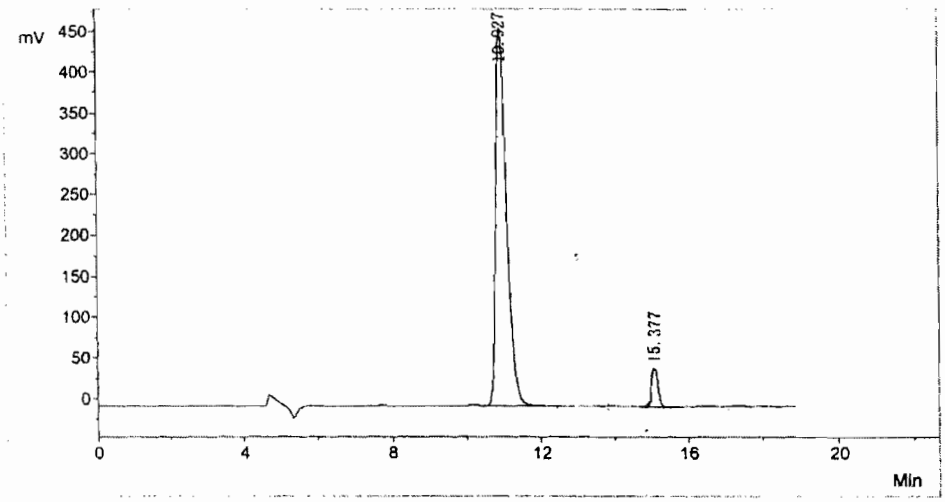
样品名称:分析谱图　　样品文件名:zk-9-59.che

样品批号:　　分析者:

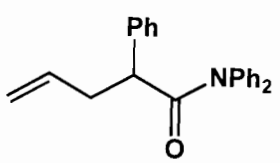
分析日期:2006-11-30　　分析时间:13:10

色谱柱:　　流动相:

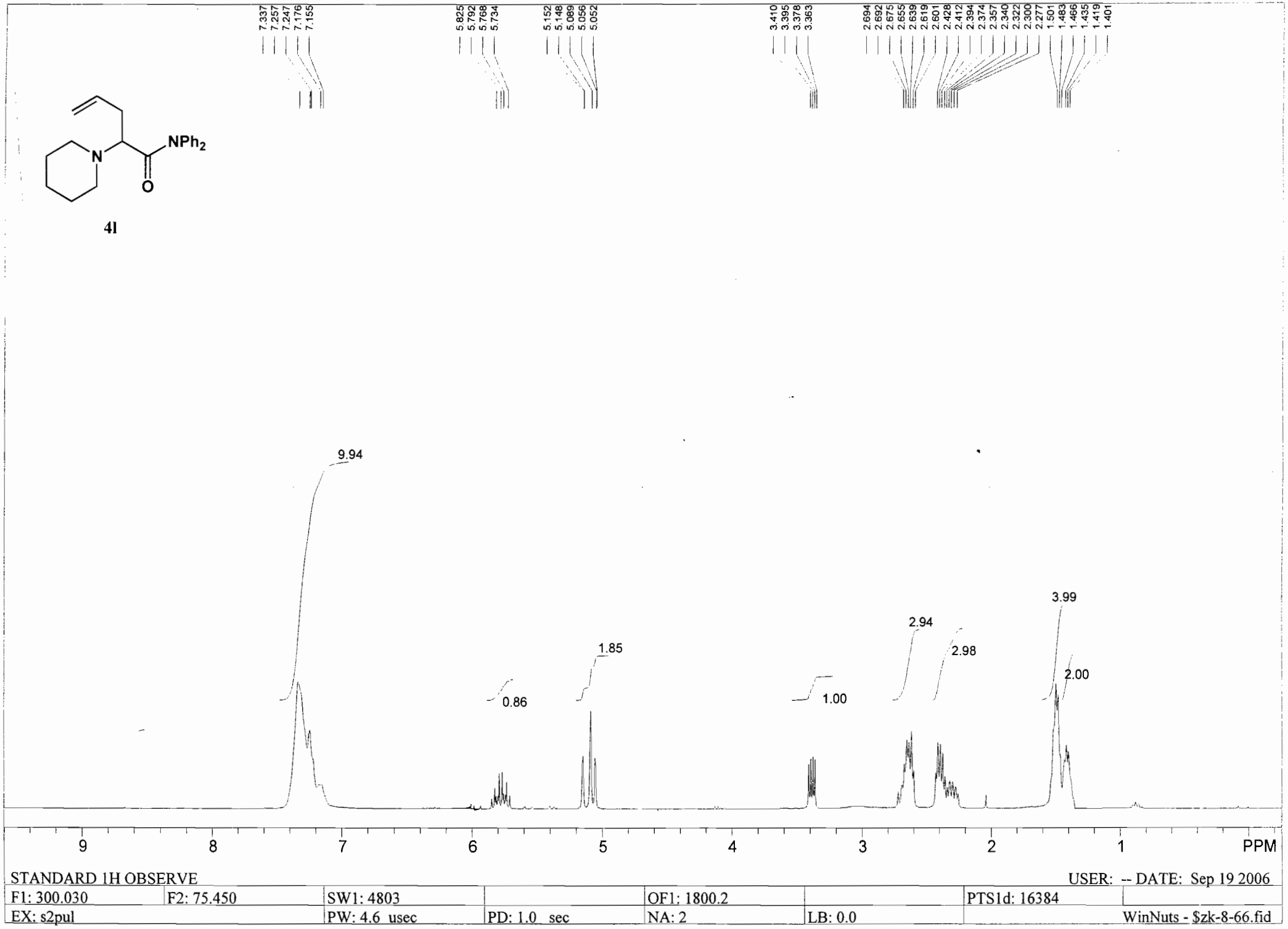
流速:　　检测波长:

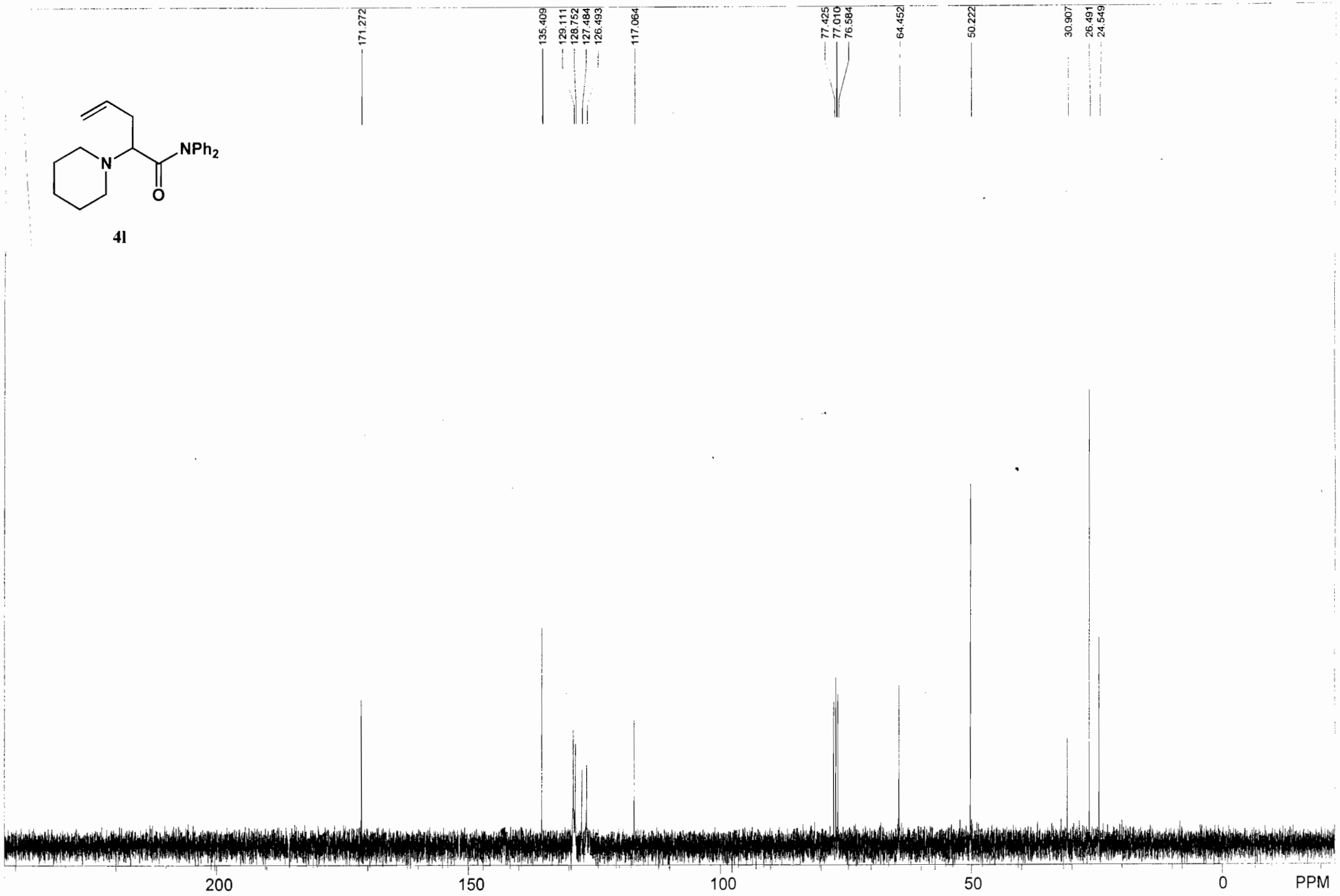


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	10.927	457841.7	102692424.1	94.0881
2	2	Unknown	15.377	46696.5	6452541.2	5.9119
Total				504538.2	109144965.3	100.0000



4k


7.337
7.257
7.247
7.176
7.155
5.825
5.792
5.768
5.734
5.152
5.148
5.089
5.056
5.052
3.410
3.395
3.378
3.363
2.694
2.692
2.675
2.655
2.639
2.619
2.601
2.428
2.412
2.394
2.374
2.357
2.340
2.322
2.300
2.277
1.501
1.483
1.466
1.435
1.419
1.401
NPh2
N
O
4l
9.94
0.86
1.85
1.00
2.94
2.98
3.99
2.00
9
8
7
6
5
4
3
2
1
PPM
STANDARD 1H OBSERVE
USER: -- DATE: Sep 19 2006
F1: 300.030
F2: 75.450
SW1: 4803
OF1: 1800.2
PTS1d: 16384
EX: s2pul
PW: 4.6 usec
PD: 1.0 sec
NA: 2
LB: 0.0
WinNuts - $zk-8-66.fid



4l

zk-8-66 USER: -- DATE: Sep 20 2006

F1: 75.450 F2: 300.029 SW1: 20000 OF1: 8274.9 PTS1d: 32768

EX: s2pul PW: 4.6 usec PD: 1.0 sec NA: 61 LB: 0.0 WinNuts - $zk-8-66-C.fid

色谱分析报告

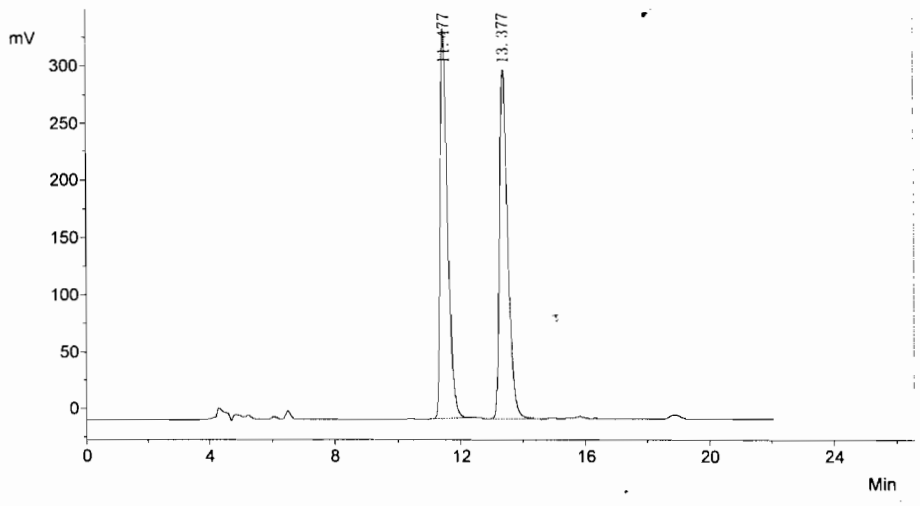
样品名称:分析谱图　　样品文件名:zk-8-662rac.che

样品批号:　　分析者:

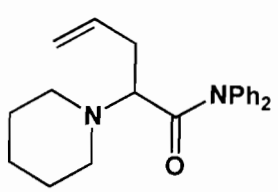
分析日期:2006-09-18　　分析时间:16:06

色谱柱:　　流动相:

流速:　　检测波长:



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	11.477	340029.6	5531414.5	49.7387
2	2	Unknown	13.377	303512.8	5589539.8	50.2613
Total				643542.3	11120954.3	100.0000



4l

色谱分析报告

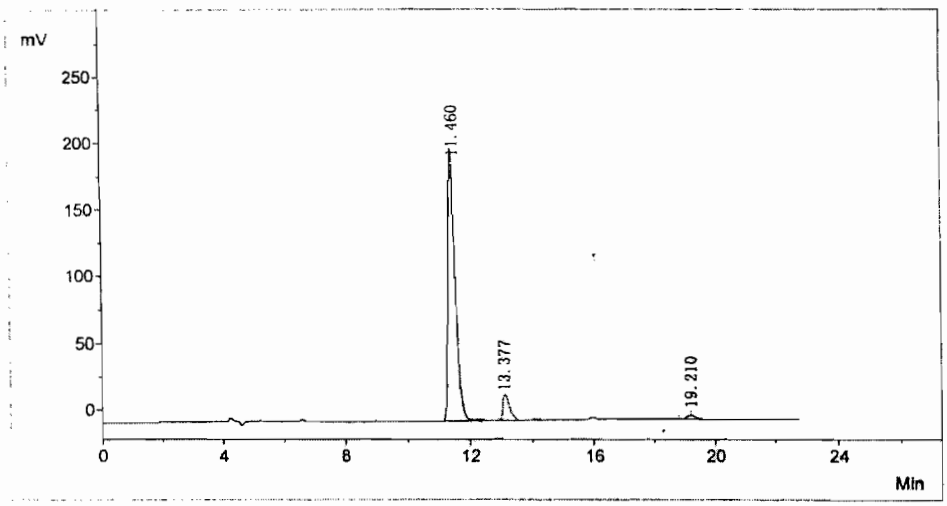
样品名称:分析谱图　　样品文件名:zk-8.che

样品批号:　　分析者:

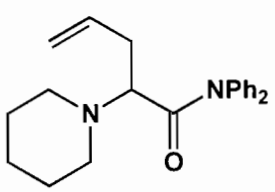
分析日期:2006-09-19　　分析时间:08:51

色谱柱:　　流动相:

流速:　　检测波长:

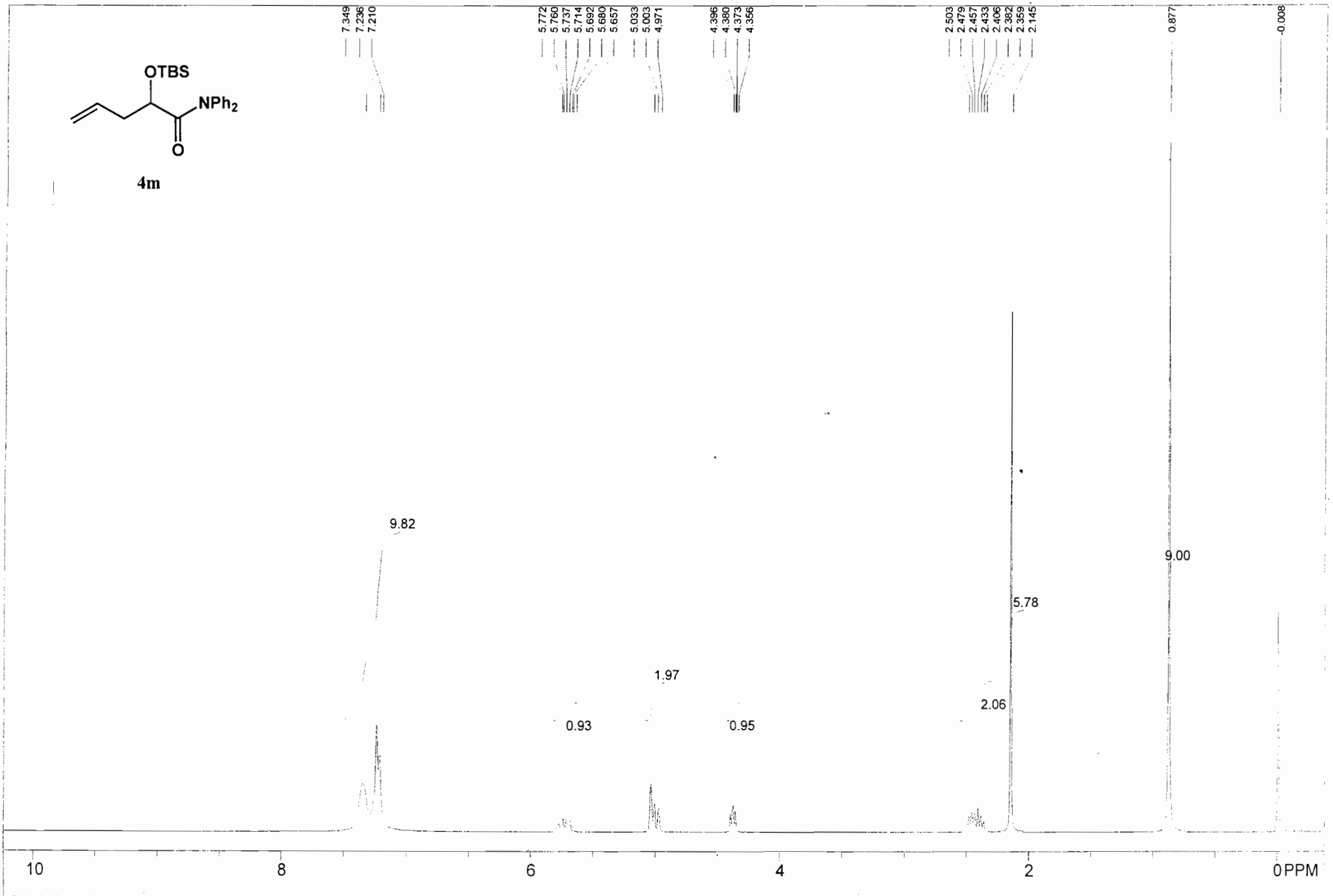


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	11.460	191877.5	4266655.8	91.7338
2	2	Unknown	13.377	19945.5	324839.4	6.9841
3	3	Unknown	19.210	2722.7	59632.1	1.2821
Total				214545.7	4651127.3	100.0000



4l

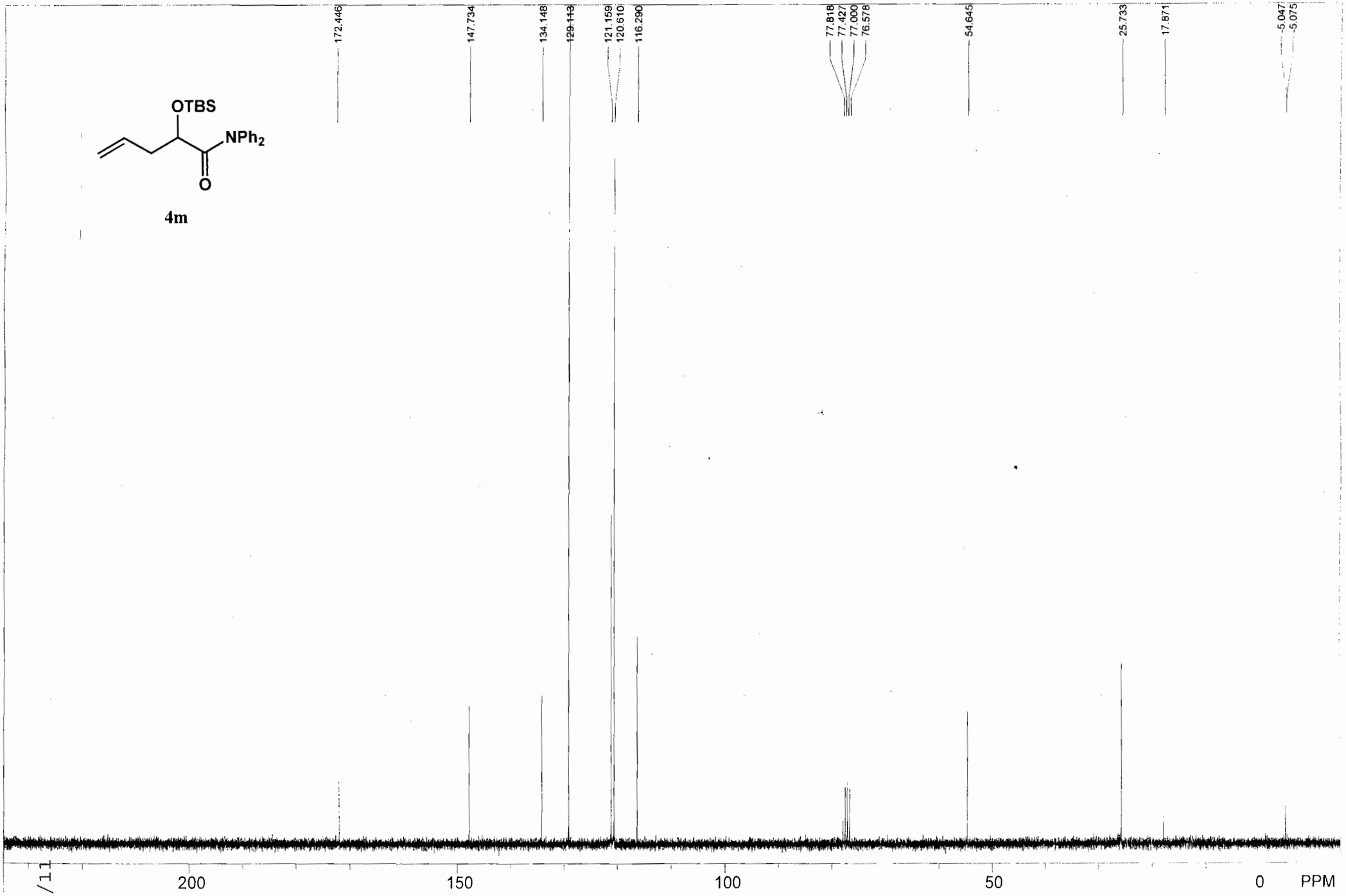
4m



STANDARD 1H OBSERVE

USER: -- DATE: Feb 5 2007

F1: 300.030	F2: 75.450	SW1: 4803		OF1: 1800.2		PTS1d: 16384
EX: s2pul		PW: 4.6 usec	PD: 1.0 sec	NA: 6	LB: 0.0	WinNuts - $zk-10-48H.fid



zk10-48PCnew USER: -- DATE: Mar 12 2007

F1: 75.450	F2: 300.029	SW1: 18868		OF1: 8272.4		PTS1d: 32768
EX: 32pul		PW: 4.6 usec	PD: 1.0 sec	NA: 70	LB: 0.0	WinNuts - $zk-10-48PCnewC.fid

2007/11

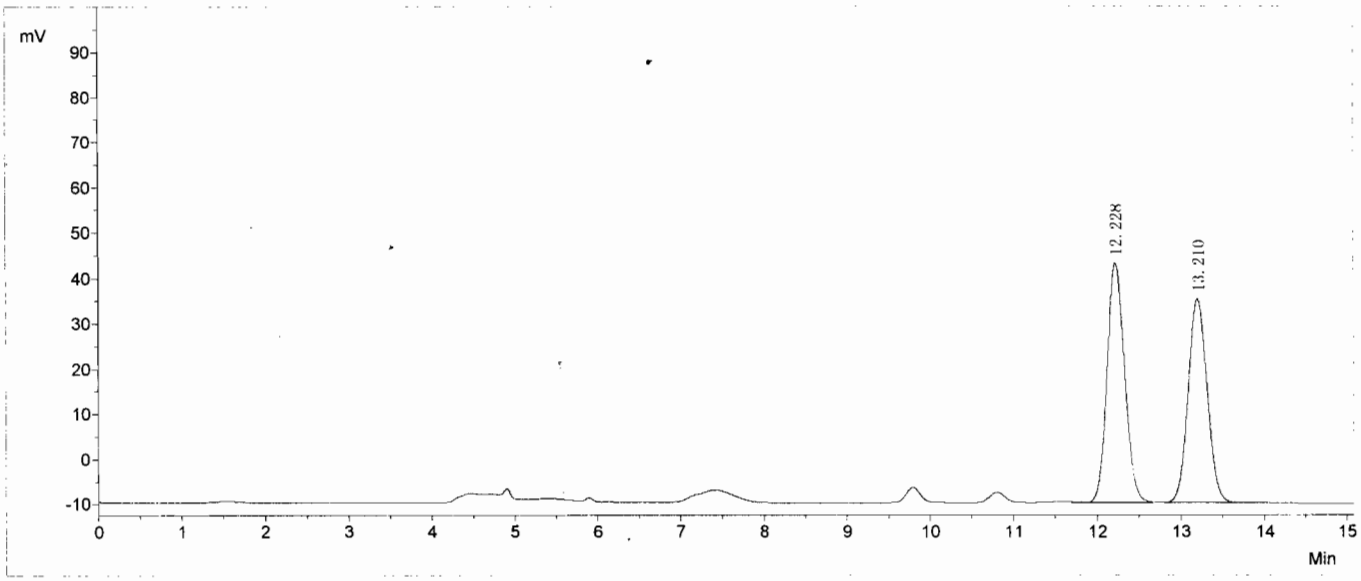
金属有机HPLC分析报告

样品文件名:zk-7-2-4.che　　分析者:

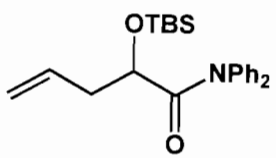
分析日期:2006-04-27　　色谱柱:

流动相:　　流速:

检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	12.228	52350.5	774551.6	51.9828
2	13.210	44923.3	715462.8	48.0172
Total		97273.8	1490014.4	100.0000



4m

色谱分析报告

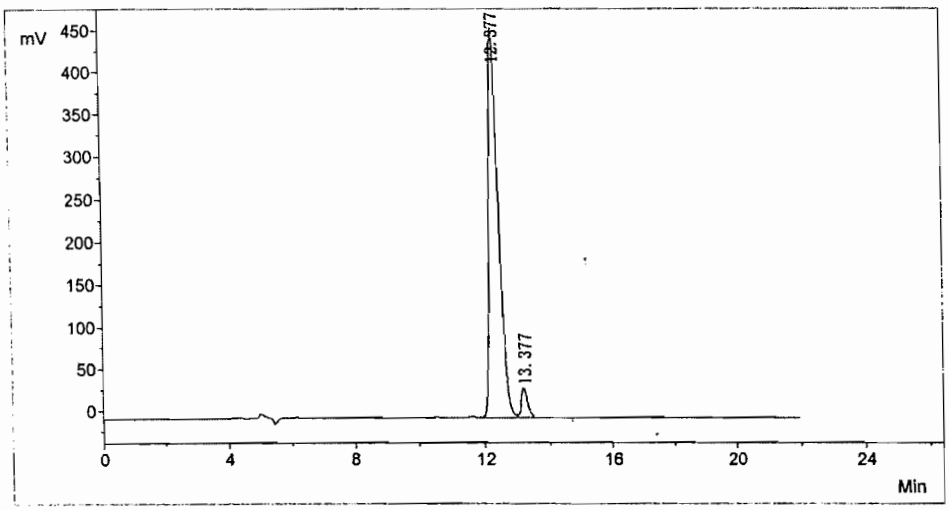
样品名称:分析谱图　　样品文件名:zk-7-42.che

样品批号:　　分析者:

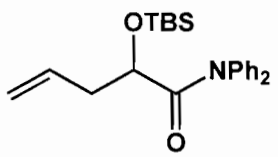
分析日期:2006-06-13　　分析时间:09:14

色谱柱:　　流动相:

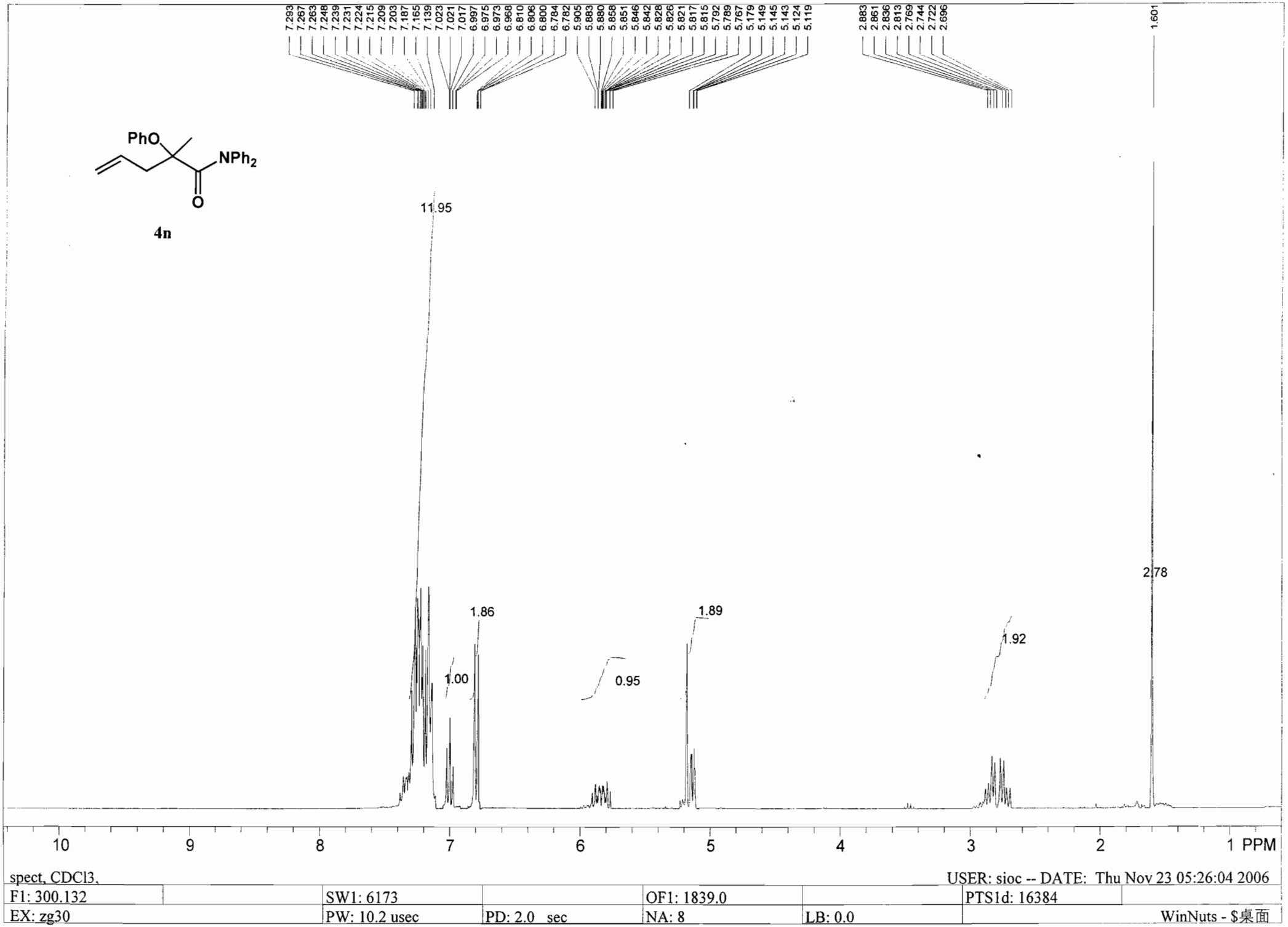
流速:　　检测波长:

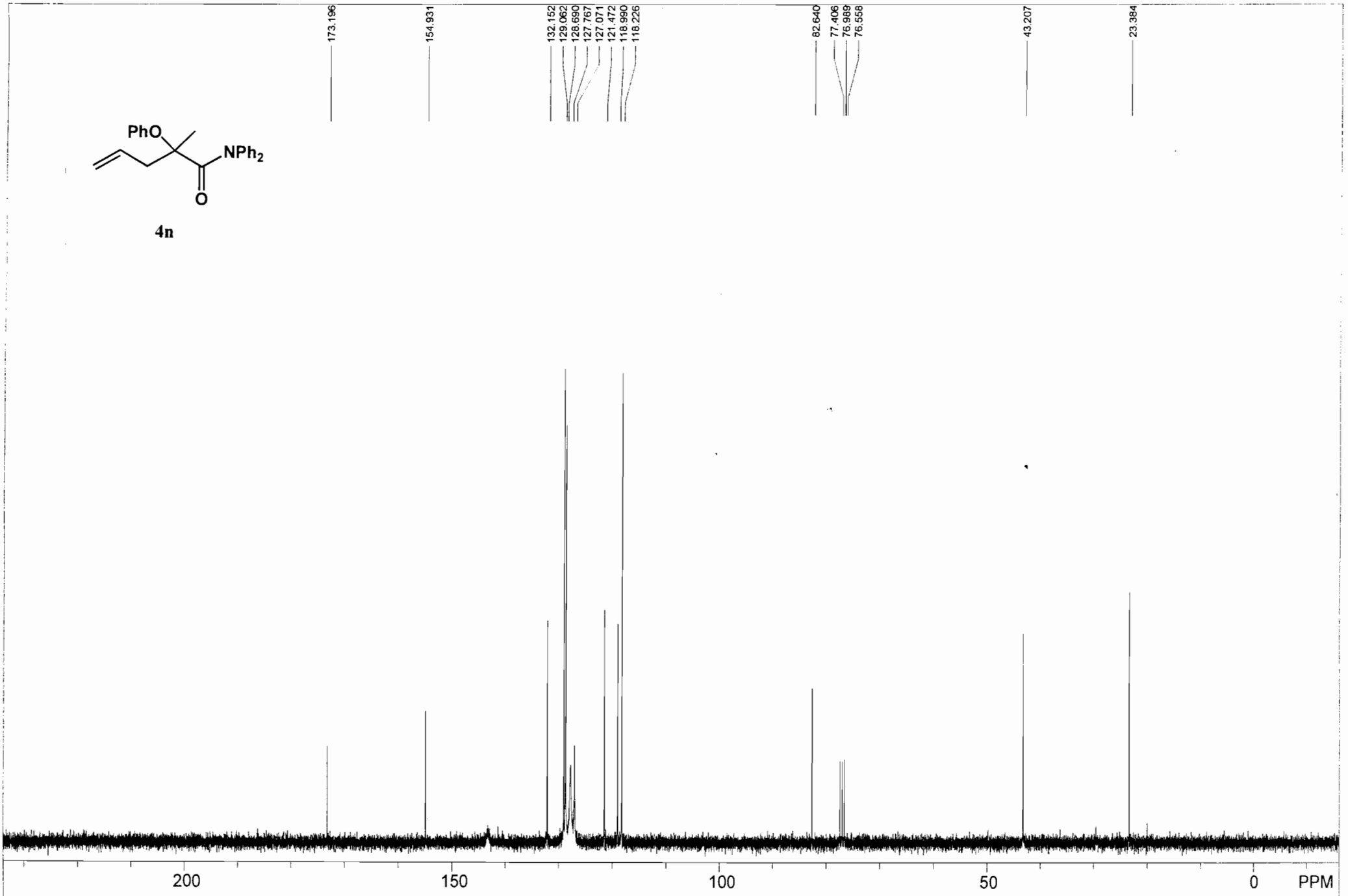


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	12.377	449351.1	9453950.1	95.5237
2	2	Unknown	13.377	37657.2	443018.0	4.4763
Total				487008.3	9896968.1	100.0000



4m


7.293
7.267
7.263
7.248
7.239
7.231
7.224
7.215
7.209
7.203
7.187
7.165
7.139
7.023
7.021
7.017
6.997
6.975
6.973
6.968
6.810
6.806
6.800
6.784
6.782
5.905
5.883
5.880
5.858
5.851
5.846
5.842
5.828
5.826
5.821
5.817
5.815
5.792
5.789
5.767
5.179
5.149
5.145
5.143
5.124
5.119
2.883
2.861
2.836
2.813
2.769
2.744
2.722
2.696
1.601
PhO
NPh2
O
4n
11.95
1.86
1.00
0.95
1.89
1.92
2.78
10
9
8
7
6
5
4
3
2
1 PPM
spect, CDCl3,
USER: sioc -- DATE: Thu Nov 23 05:26:04 2006
F1: 300.132
SW1: 6173
OF1: 1839.0
PTS1d: 16384
EX: zg30
PW: 10.2 usec
PD: 2.0 sec
NA: 8
LB: 0.0
WinNuts - $桌面



zk-9-58-C

USER: -- DATE: Dec 7 2006

F1: 75.450	F2: 300.029	SW1: 18868		OF1: 8214.0		PTS1d: 32768
EX: s2pul		PW: 4.6 usec	PD: 1.0 sec	NA: 180	LB: 0.0	WinNuts - $zk-9-58-C.fid

色谱分析报告

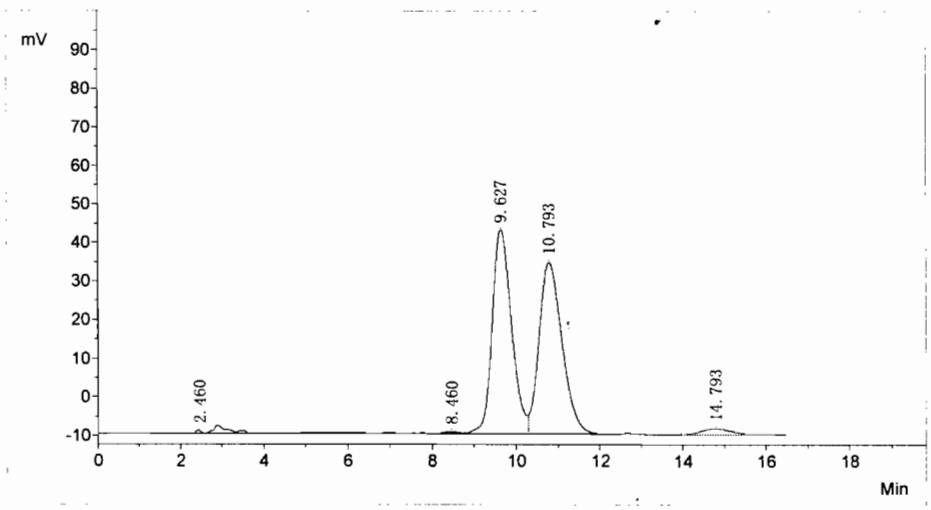
样品名称:分析谱图　　样品文件名:zk-rac as 95.che

样品批号:　　分析者:

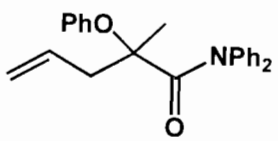
分析日期:2005-12-29　　分析时间:11:13

色谱柱:　　流动相:

流速:　　检测波长:



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	2.460	670.3	9352.9	0.2618
2	2	Unknown	8.460	539.8	111580.9	3.1227
3	3	Unknown	9.627	52694.3	1691918.0	47.3505
4	4	Unknown	10.793	44306.8	1689855.7	47.2928
5	5	Unknown	14.793	1486.1	70467.8	1.9721
Total				99697.3	3573175.3	100.0000



4n

色谱分析报告

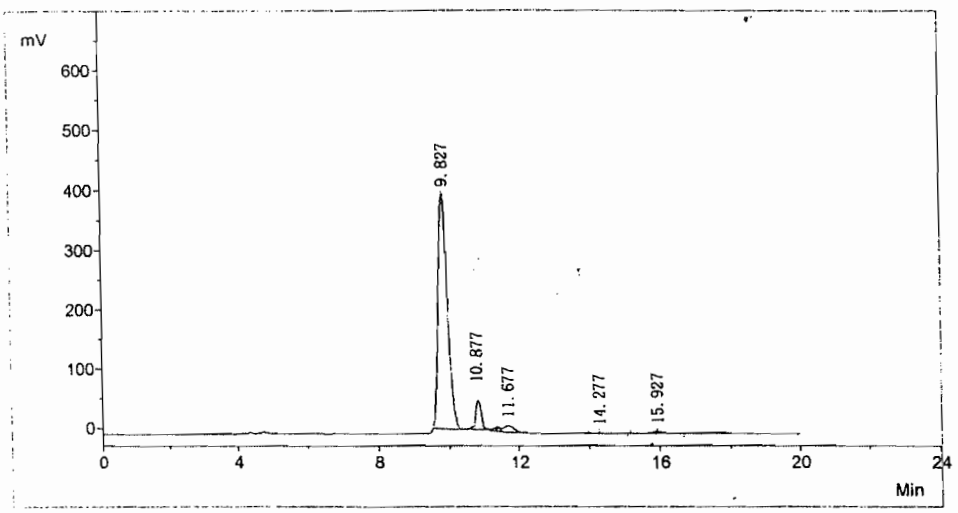
样品名称:分析谱图　　样品文件名:zk9-58.che

样品批号:　　分析者:

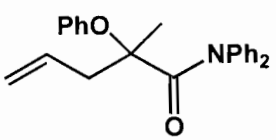
分析日期:2006-12-21　　分析时间:14:44

色谱柱:　　流动相:

流速:　　检测波长:

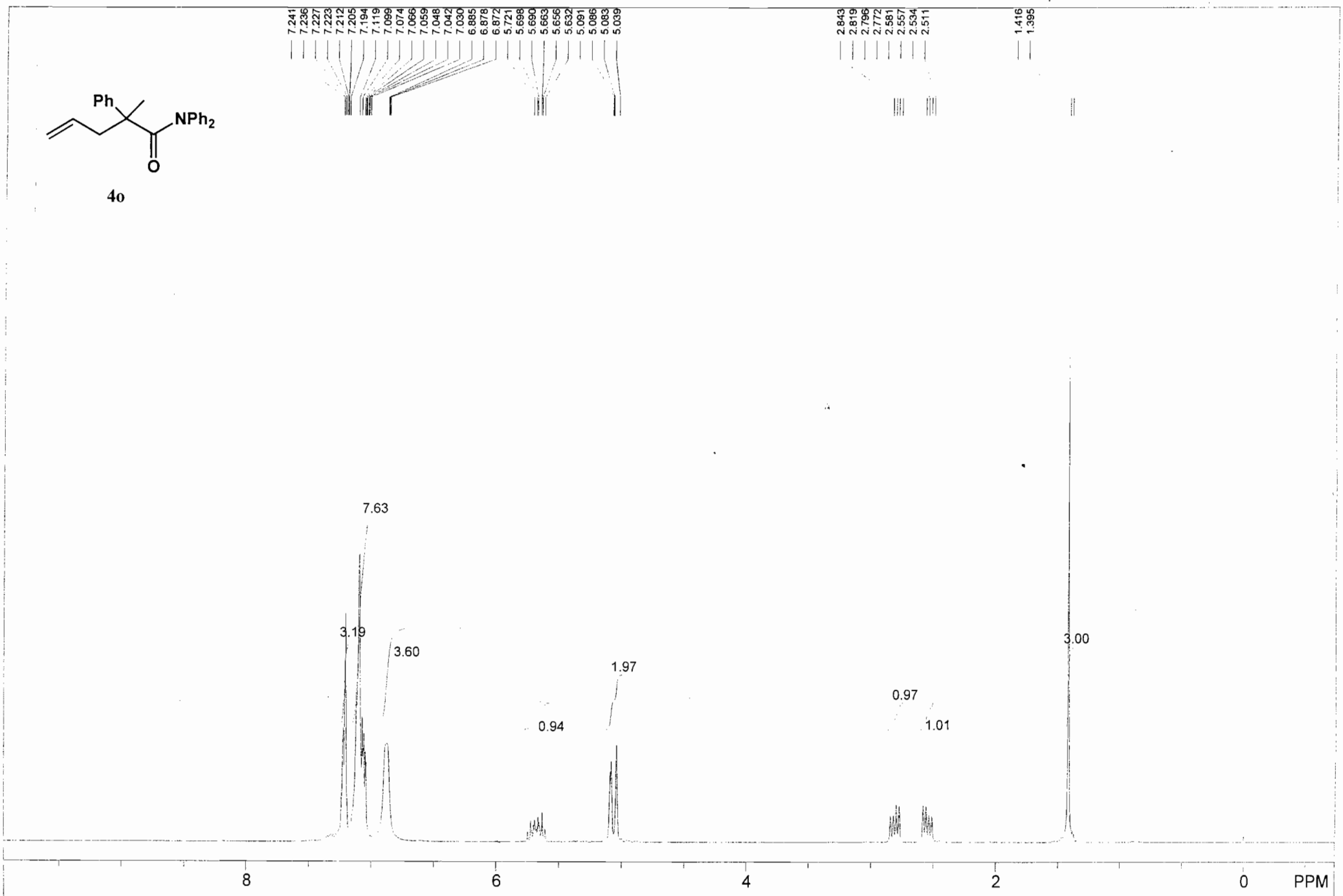


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	9.827	394194.1	7441320.3	94.5783
2	2	Unknown	10.877	42516.3	277445.1	3.5263
3	3	Unknown	11.677	9728.2	95571.2	1.2147
4	4	Unknown	14.277	400.0	6428.1	0.0817
5	5	Unknown	15.927	3001.0	47128.6	0.5990
Total				459839.6	7867893 3	100.0000



4n

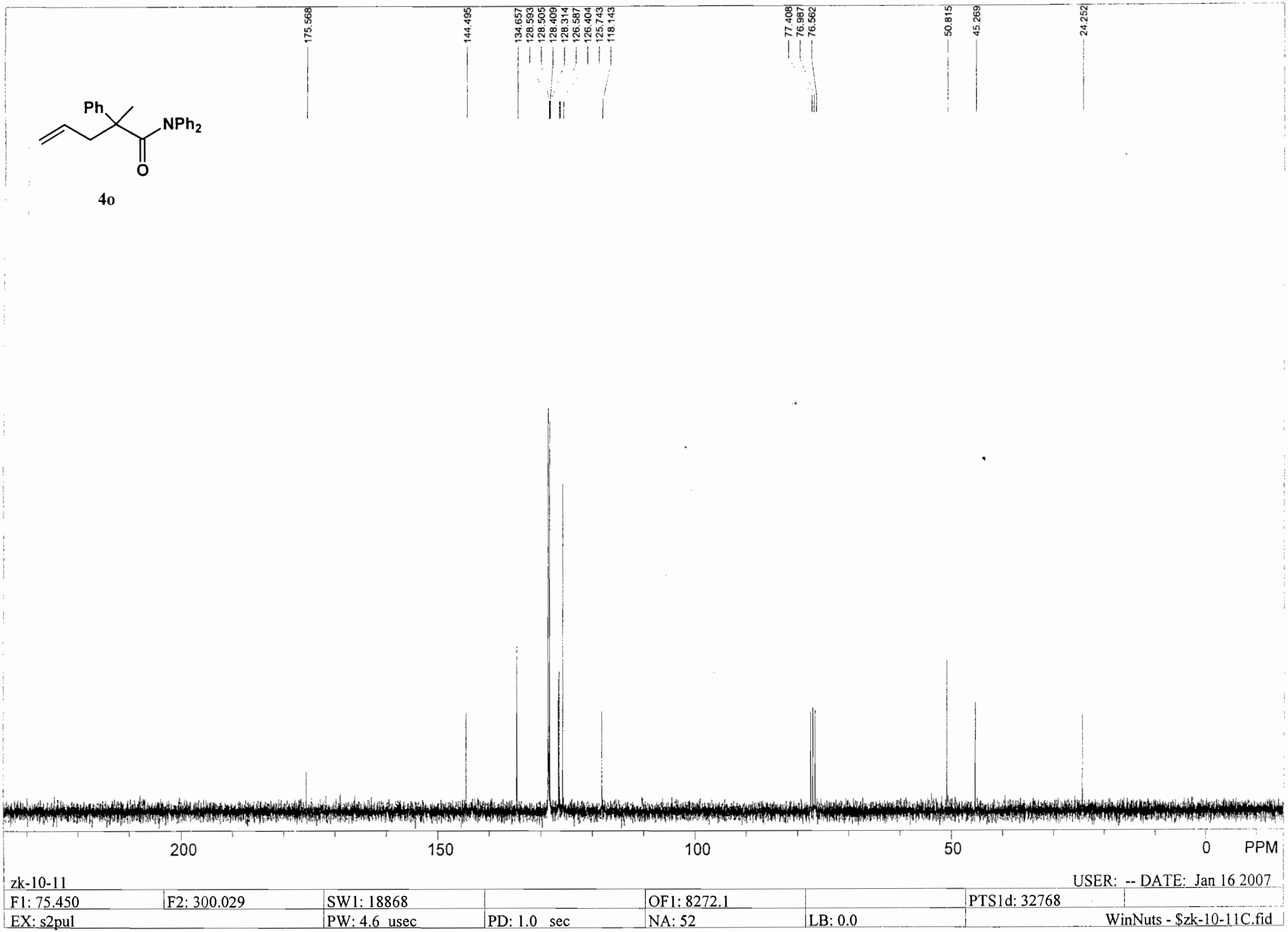
4o



STANDARD 1H OBSERVE

USER: -- DATE: Jan 16 2007

F1: 300.030	F2: 75.450	SW1: 4803		OF1: 1793.5		PTS1d: 16384	
EX: s2pul		PW: 4.6 usec	PD: 1.0 sec	NA: 6	LB: 0.0		WinNuts - $zk-10-11.fid



4o

zk-10-11						USER: -- DATE: Jan 16 2007
F1: 75.450	F2: 300.029	SW1: 18868		OF1: 8272.1		PTS1d: 32768
EX: s2pul		PW: 4.6 usec	PD: 1.0 sec	NA: 52	LB: 0.0	WinNuts - $zk-10-11C.fid

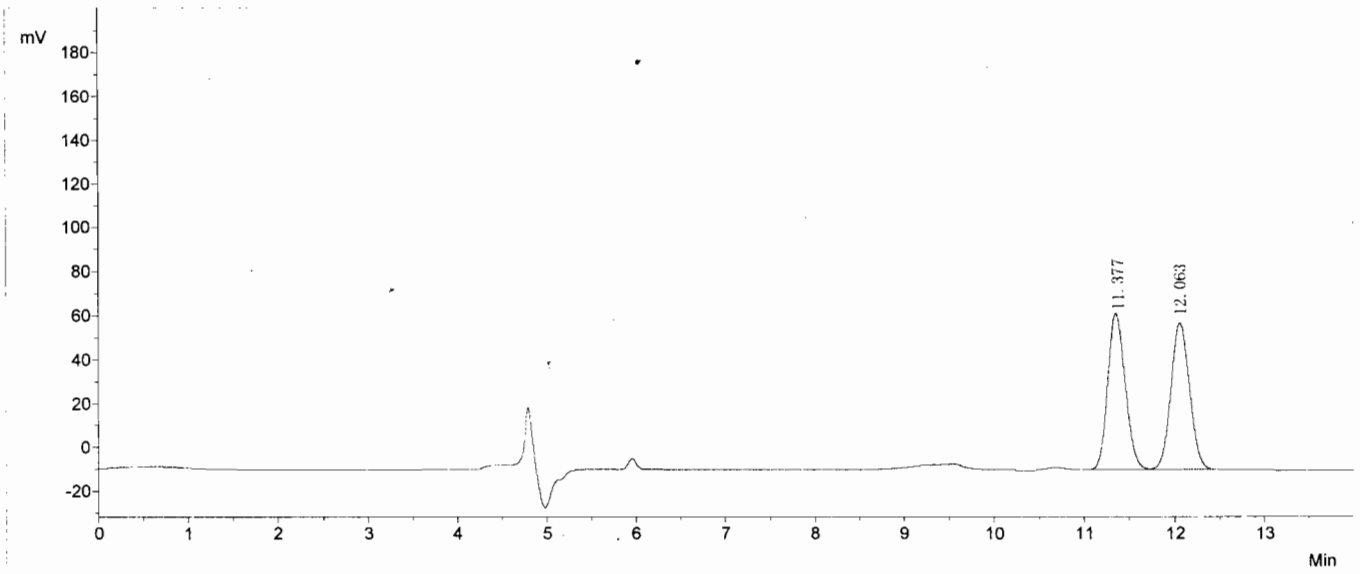
金属有机HPLC分析报告

样品文件名:zk-7-8-2.che　　分析者:

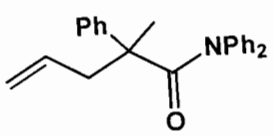
分析日期:2006-05-11　　色谱柱:

流动相:　　流速:

检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	11.377	68913.8	960855.5	50.1742
2	12.063	66402.4	954181.7	49.8258
Total		135316.1	1915037.2	100.0000



4o

色谱分析报告

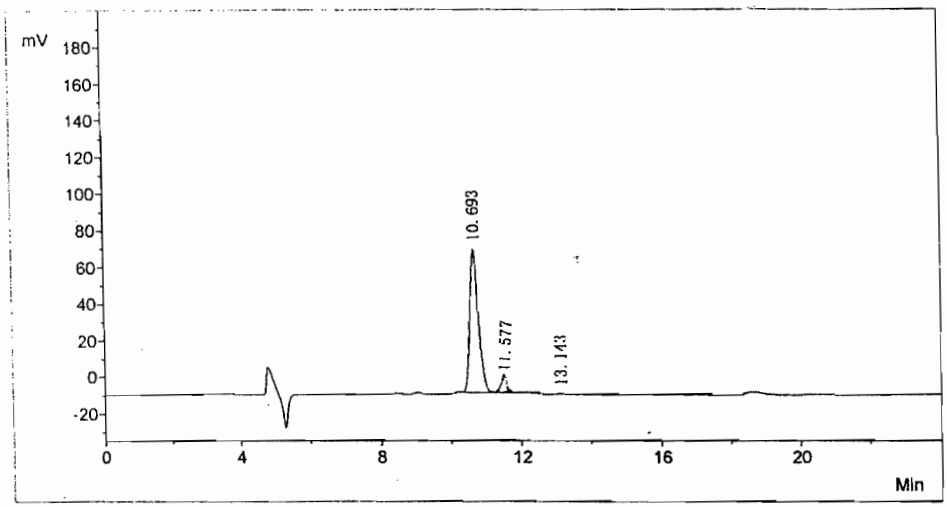
样品名称:分析谱图　　样品文件名:zk-8-471.che

样品批号:　　分析者:

分析日期:2006-09-18　　分析时间:14:02

色谱柱:　　流动相:

流速:　　检测波长:



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	10.693	77965.6	1811374.7	95.7281
2	2	Unknown	11.577	9921.9	69357.0	3.6654
3	3	Unknown	13.143	494.4	11476.2	0.6065
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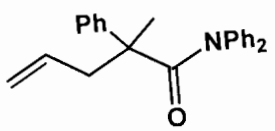
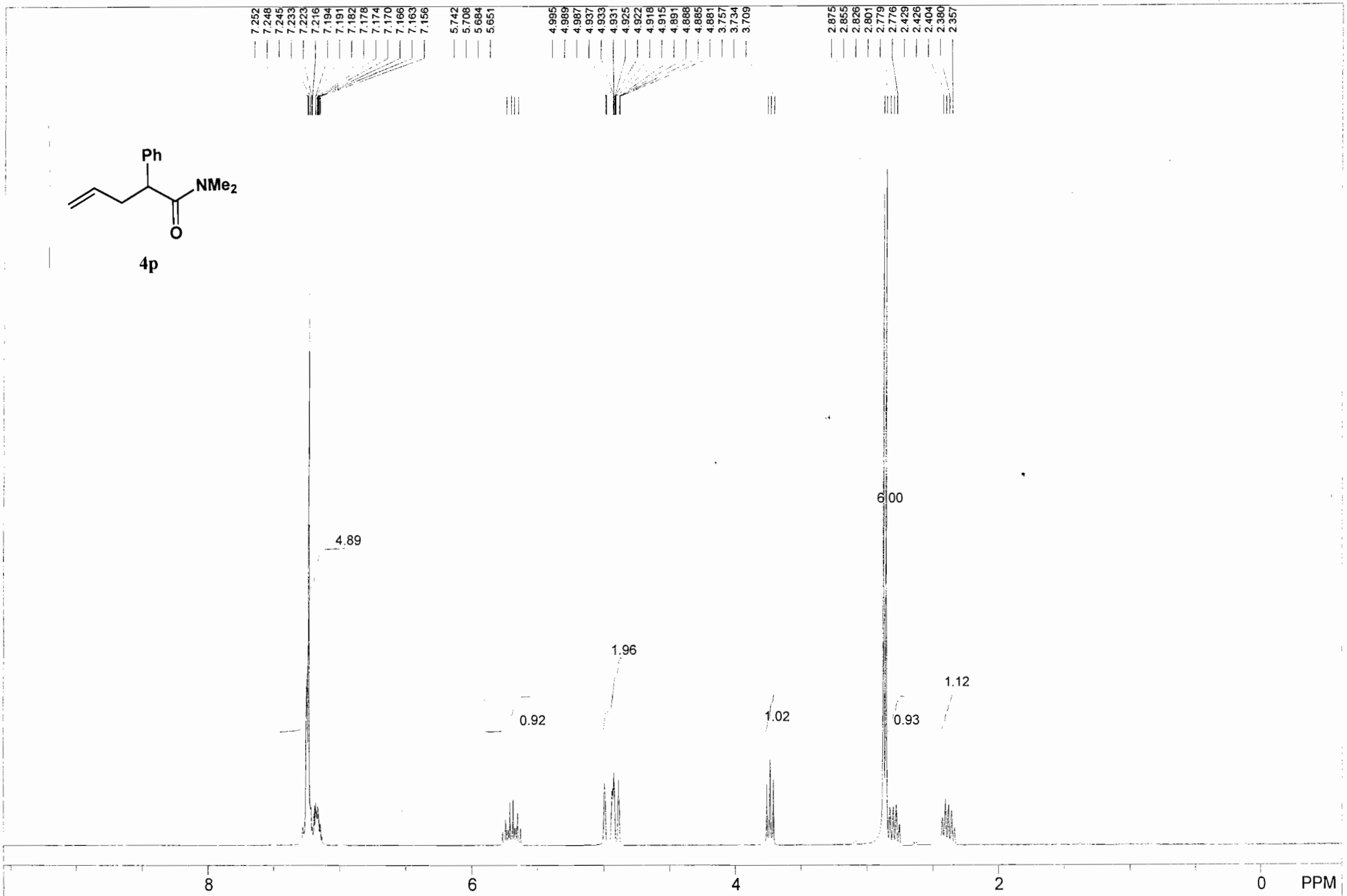
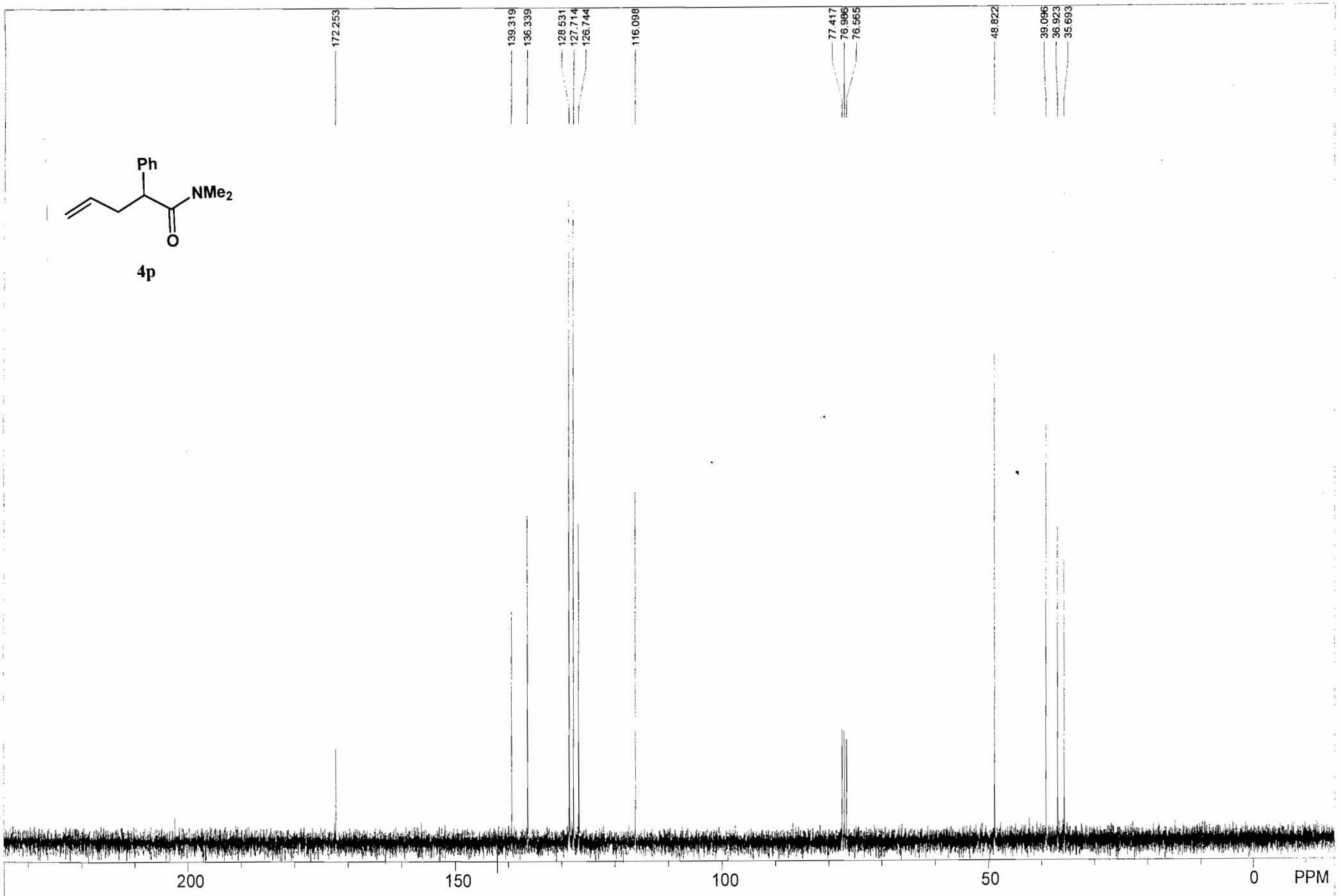


4o



STANDARD 1H OBSERVE USER: -- DATE: Mar 30 2006

F1: 300.030	F2: 75.450	SW1: 4803		OF1: 1800.2		PTS1d: 16384	
EX: s2pul		PW: 4.6 usec	PD: 1.0 sec	NA: 16	LB: 0.0		WinNuts - $zk-6-821.fid



zk-6-821 USER: -- DATE: Jan 16 2007

F1: 75.450	F2: 300.029	SW1: 18868		OF1: 8268.1		PTS1d: 32768
EX: s2pul		PW: 4.6 usec	PD: 1.0 sec	NA: 58	LB: 0.0	WinNuts - $zk-6-821C.fid

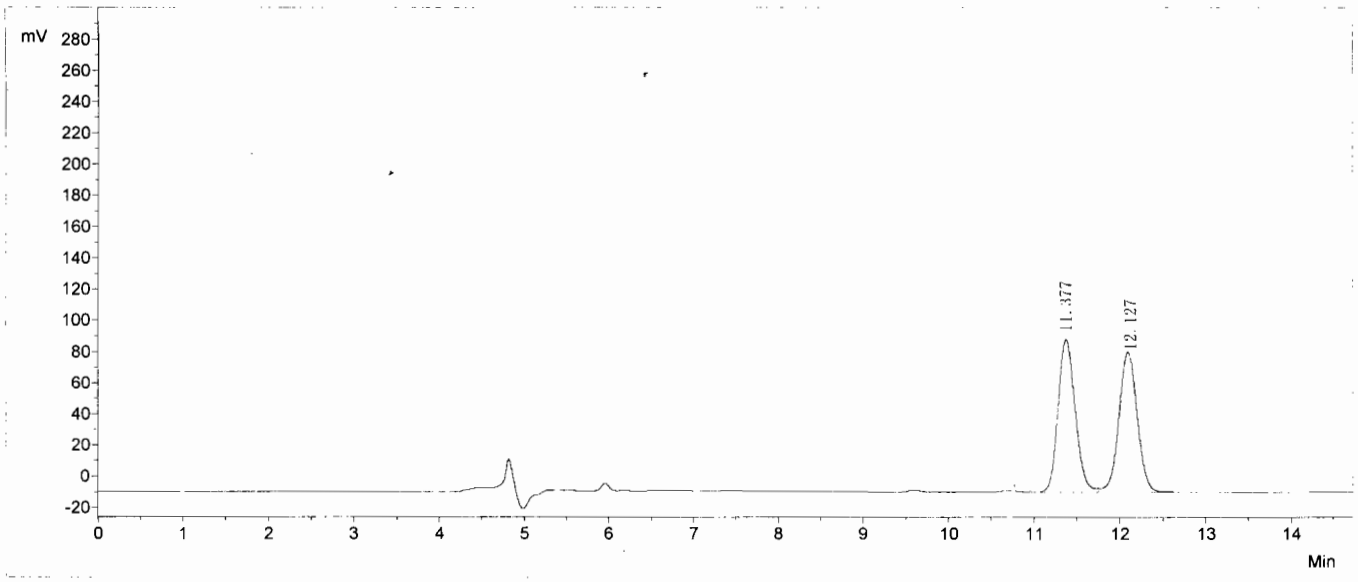
金属有机HPLC分析报告

样品文件名:zk-7-8-1.che　　分析者:

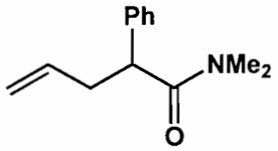
分析日期:2006-05-11　　色谱柱:

流动相:　　流速:

检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	11.377	97843.1	1354299.0	50.4227
2	12.127	86025.0	1331592.7	49.5773
Total		183868.1	2685891.7	100.0000



4p

色谱分析报告

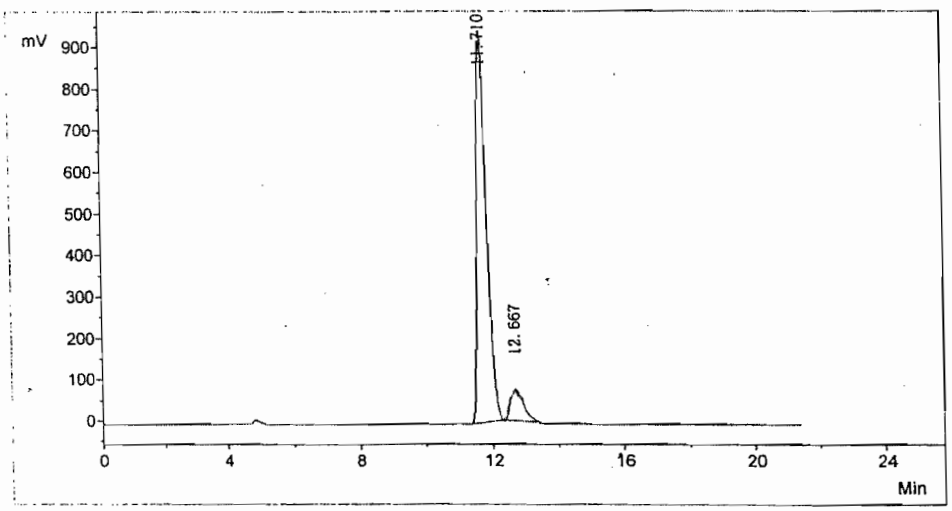
样品名称:分析谱图　　样品文件名:zk-9-2

样品批号:　　分析者:

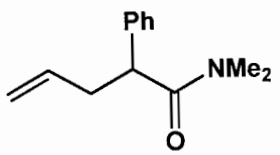
分析日期:2006-11-02　　分析时间:11:35

色谱柱:　　流动相:

流速:　　检测波长:

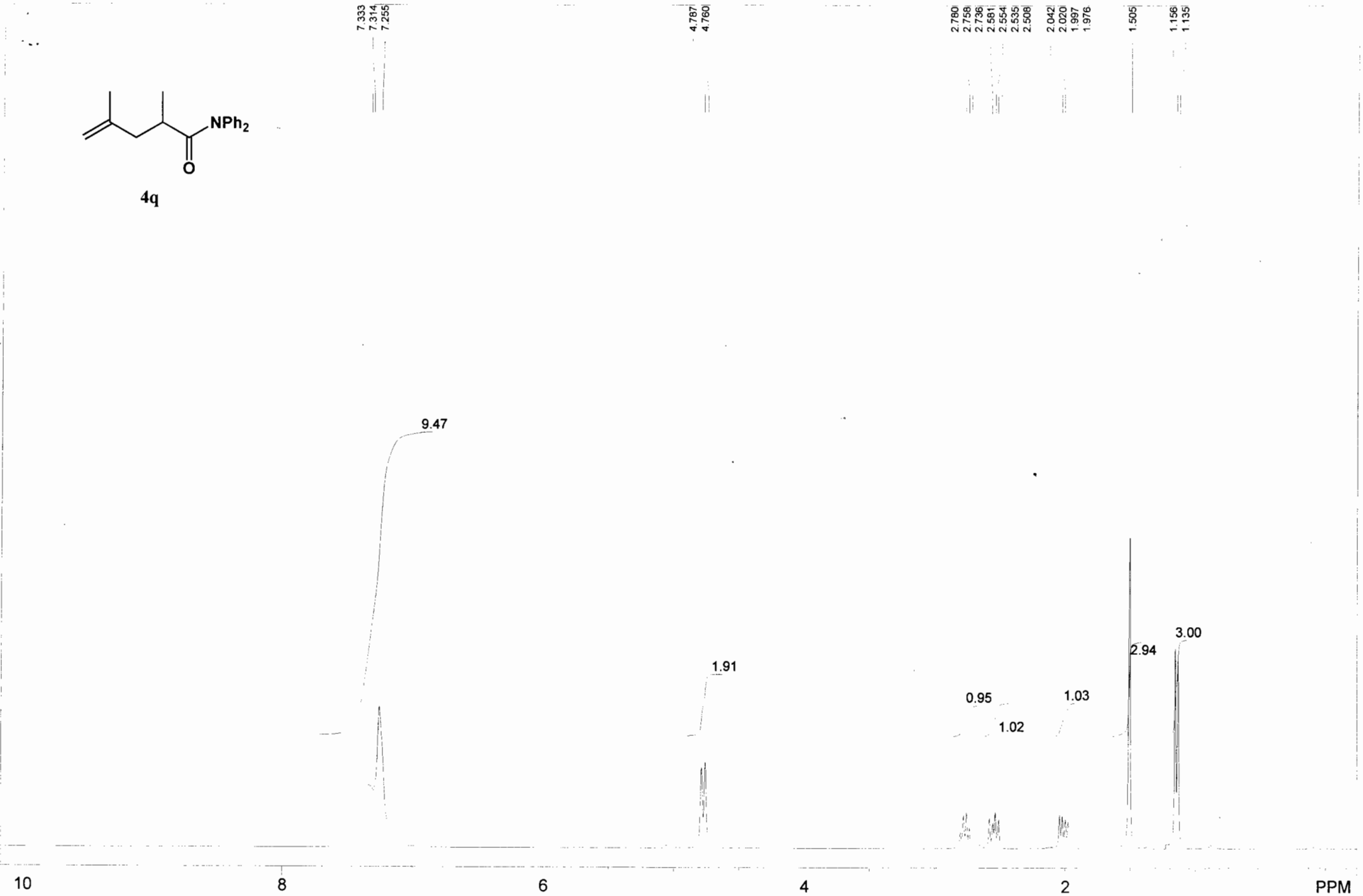


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	11.710	920452.7	47750917.1	94.0032
2	2	Unknown	12.667	87859.2	3046201.6	5.9968
Total				1008311.9	50797118.7	100.0000



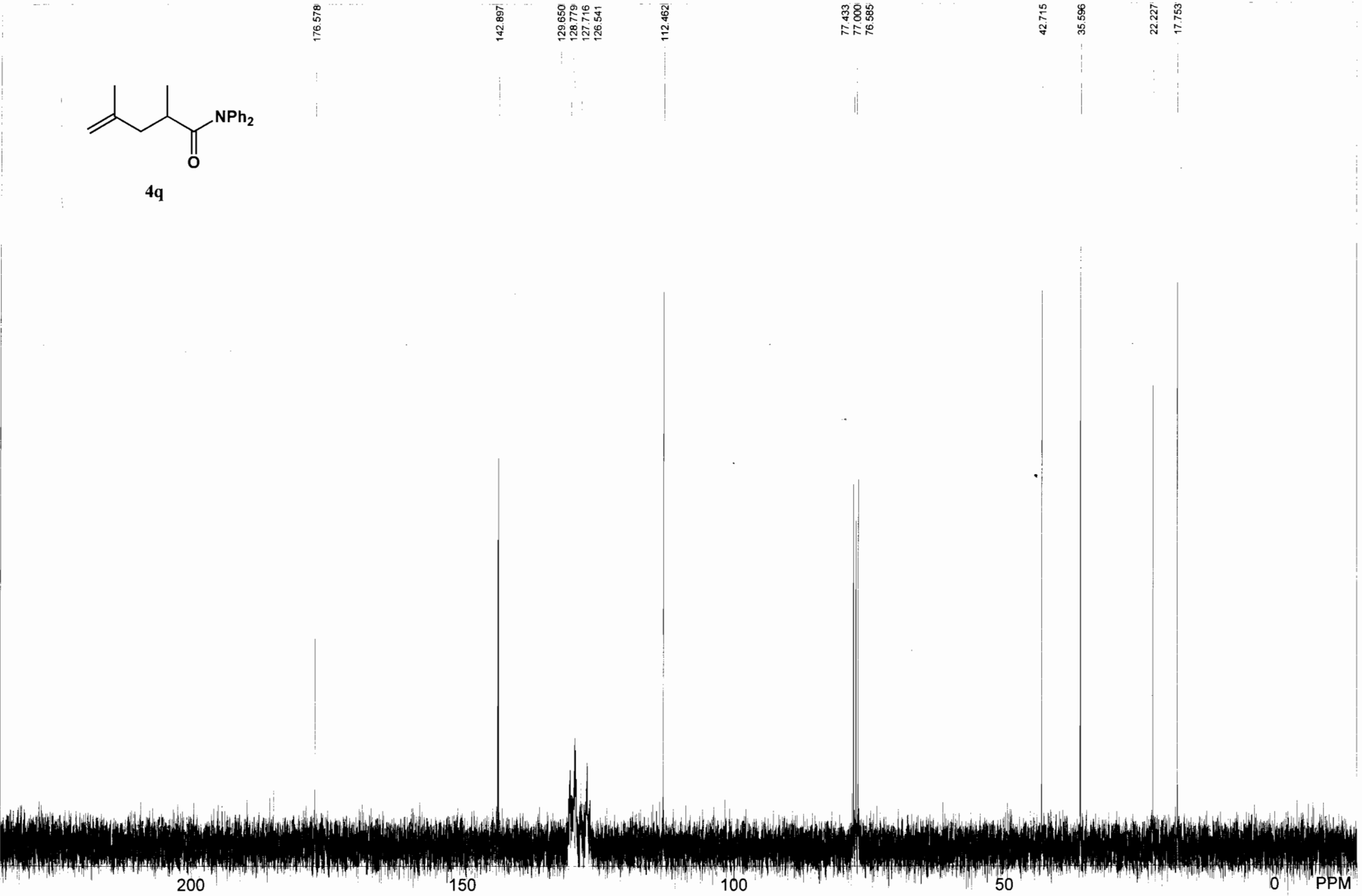
4p

4q



STANDARD 1H OBSERVE
F1: 300.030 F2: 75.450
EX: s2pul
SW1: 4803
PW: 4.6 usec PD: 1.0 sec
OF1: 1799.9
NA: 12 LB: 0.0
PTS1d: 16384
USER: -- DATE: Aug 6 2007
WinNuts - $zk-IBUXI-H.fid

4q



zk-lBUXI-C
F1: 75.450 F2: 300.029 SW1: 18868 OF1: 8276.2 PTS1d: 32768
EX: s2pul PW: 4.6 usec PD: 1.0 sec NA: 142 LB: 0.0
USER: -- DATE: Aug 6 2007
WinNuts - $zk-IBUXI-C.fid

色谱分析报告

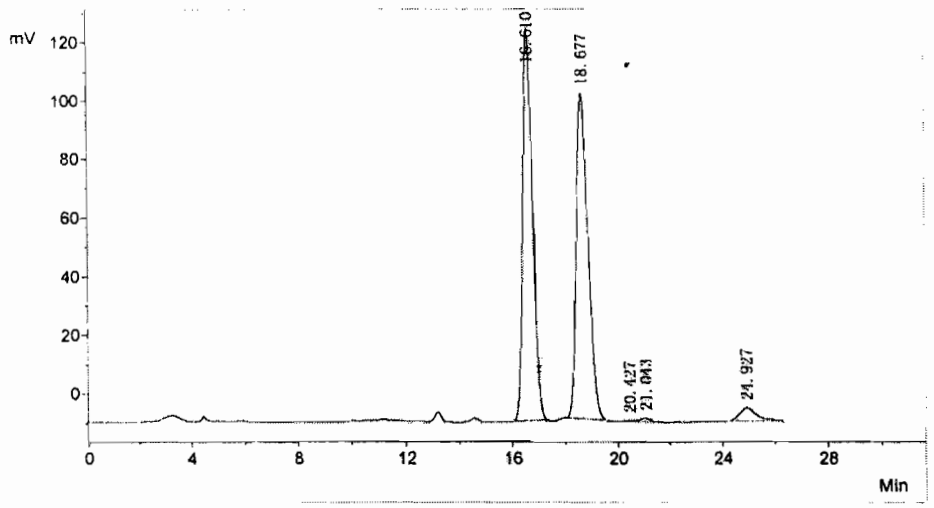
样品名称:分析谱图　　样品文件名:zk-rac-4.che

样品批号:　　分析者:

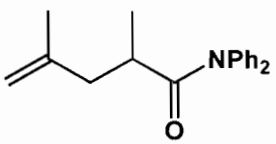
分析日期:2006-01-04　　分析时间:14:29

色谱柱:　　流动相:

流速:　　检测波长:



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	16.610	133322.5	3404100.6	48.4462
2	2	Unknown	18.677	110913.2	3397354.0	48.3502
3	3	Unknown	20.427	203.6	3984.2	0.0567
4	4	Unknown	21.043	877.7	23117.5	0.3290
5	5	Unknown	24.927	4341.2	198001.3	2.8179
Total				249658.1	7026557.6	100.0000



4q

色谱分析报告

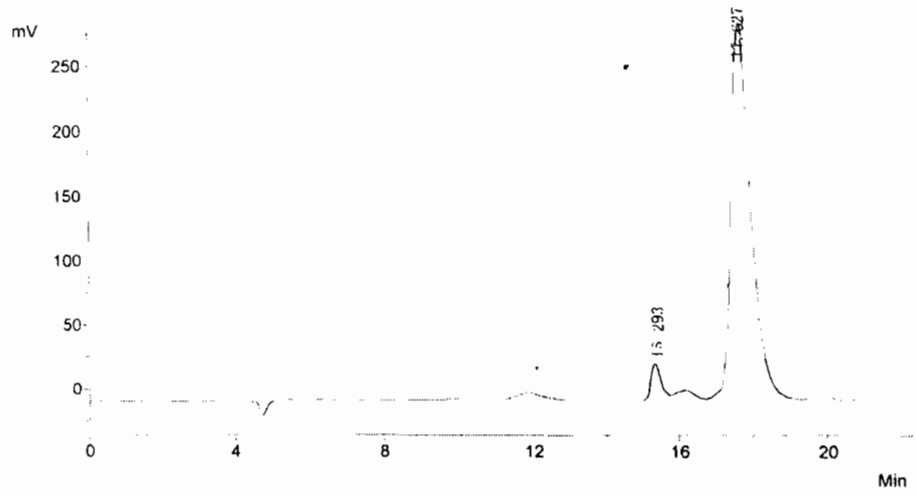
样品名称:分析谱图　　样品文件名:zk-buxi ad 98.che

样品批号:　　分析者:

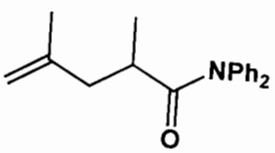
分析日期:2007-08-23　　分析时间:16:07

色谱柱:　　流动相:

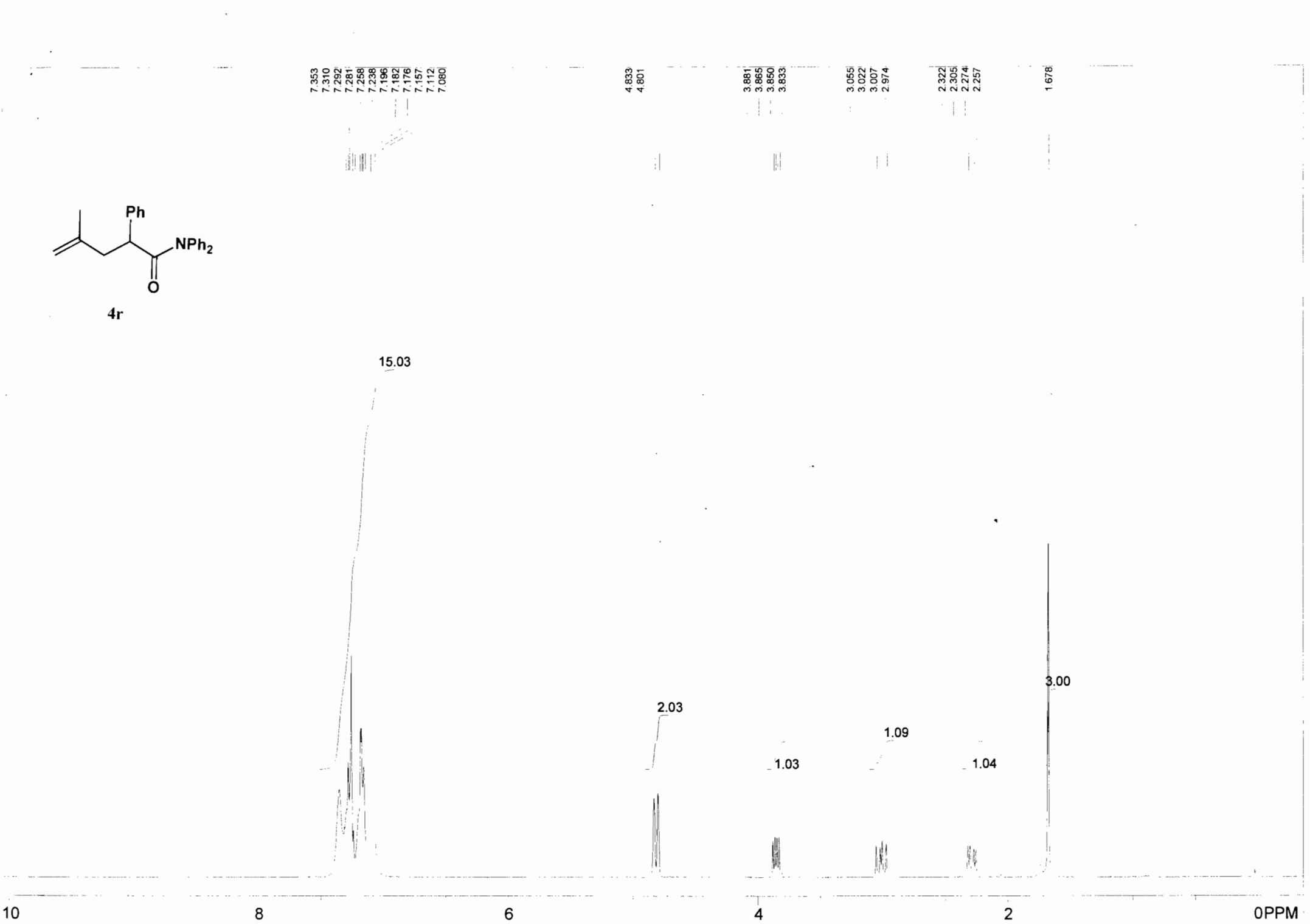
流速:　　检测波长:



序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	15.293	21626.6	544781.8	4.7258
2	2	Unknown	17.627	291888.7	10983039.0	95.2742
合计:				313515.3	11527820.8	100.0000



4q

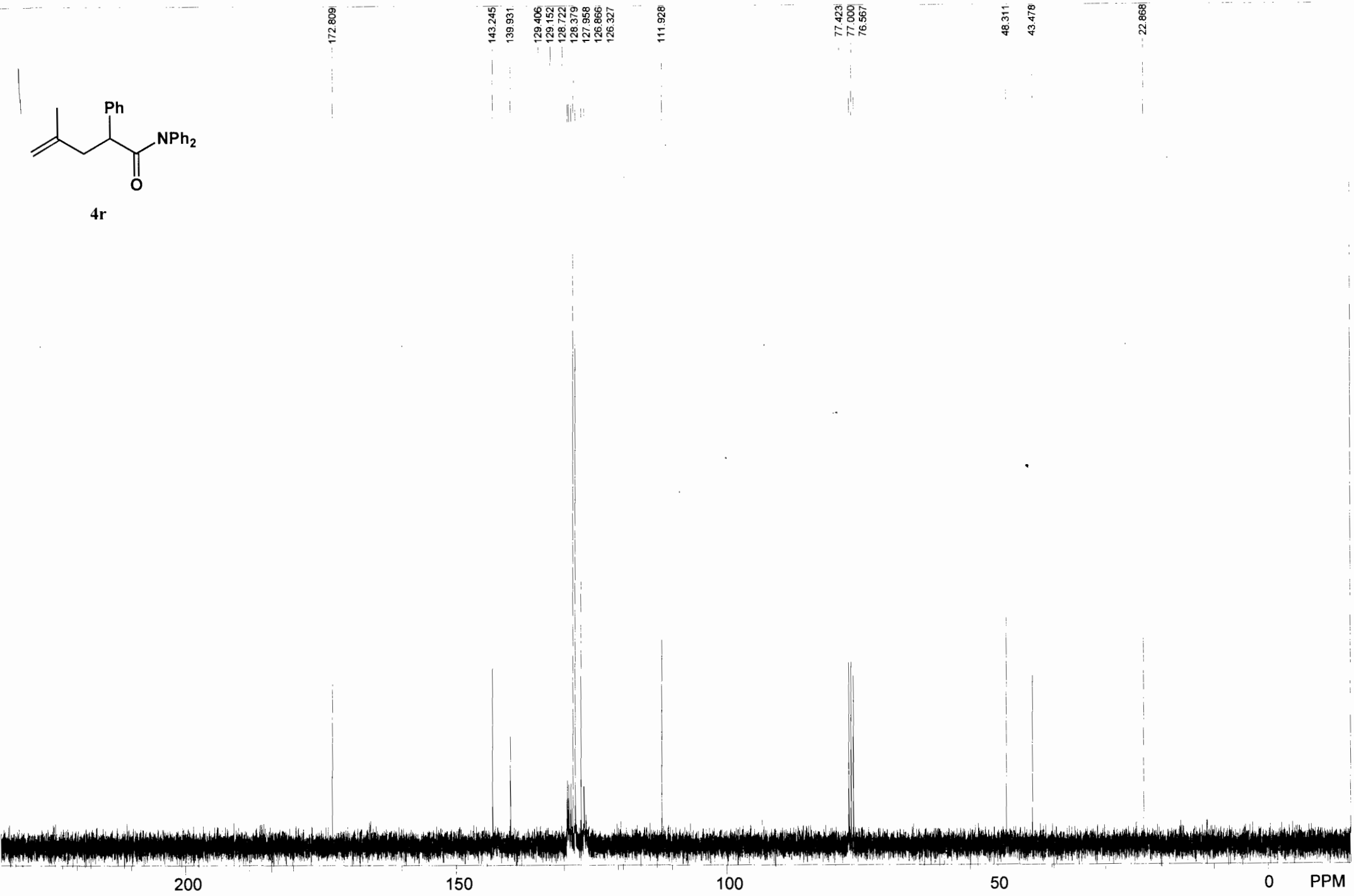


STANDARD 1H OBSERVE
USER: -- DATE: Aug 17 2007

F1: 300.030 F2: 75.450 SW1: 4803 OF1: 1800.2 PTS1d: 16384

EX: s2pul PW: 4.6 usec PD: 1.0 sec NA: 4 LB: 0.0 WinNuts - $zk-PHBUXI.fid

4r



zk-PHBUXI
USER: -- DATE: Aug 17 2007
F1: 75.450 F2: 300.029 SW1: 18868 OF1: 8274.6 PTS1d: 32768
EX: s2pul PW: 4.6 usec PD: 1.0 sec NA: 58 LB: 0.0

色谱分析报告

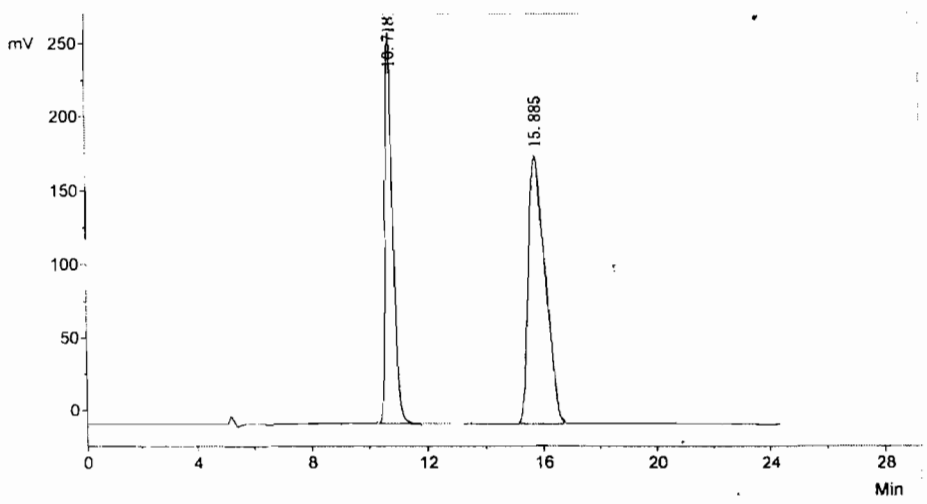
样品名称:分析谱图　　样品文件名:zk-9-38.che

样品批号:　　分析者:

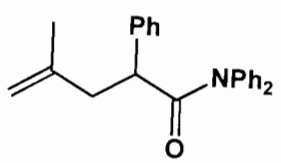
分析日期:2006-11-13　　分析时间:13:42

色谱柱:　　流动相:

流速:　　检测波长:



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	10.718	264192.7	4843717.2	50.3627
2	2	Unknown	15.885	169939.6	4773950.6	49.6373
Total				434132.3	9617667.8	100.0000

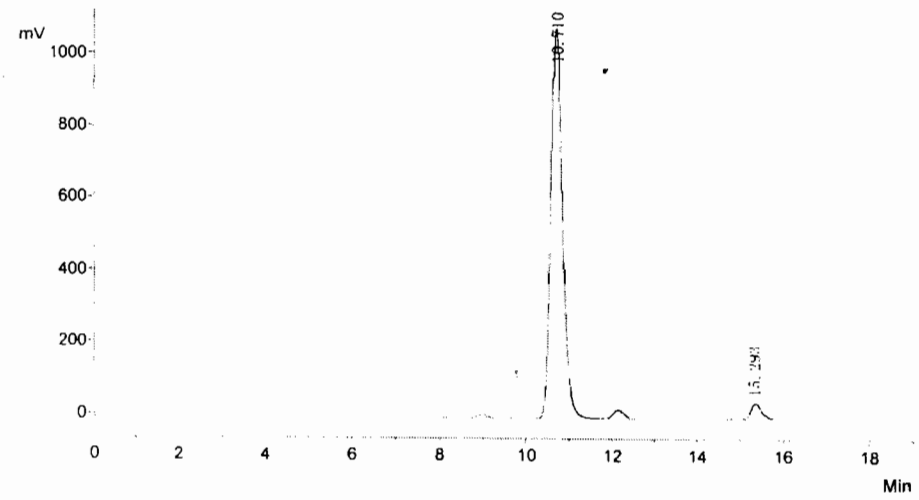


4r

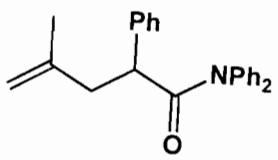
色谱分析报告

样品名称:分析谱图
样品批号:
分析日期:2007-08-23
色谱柱:
流速:

样品文件名:zk-phxj as 95.chc
分析者:
分析时间:11:03
流动相:
检测波长:



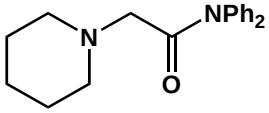
序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	10.710	1075809.3	20389162.1	95.3945
2	2	Unknown	15.293	44477.9	984357.4	4.6055
合计:				1120287.2	21373519.5	100.0000



4r

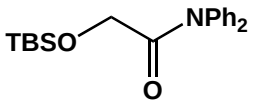
volatiles (unreacted oxalyl chloride) were removed in vacuo to yield a yellow oily residue. The residue was mixed with 20 mL of dry methylene chloride and *N, N*-diphenylamine (1.01 g, 6.0 mmol). The mixture was stirred overnight and quenched with 20 mL of water. The organic layer was washed twice with saturated $NaHCO_3$ and concentrated in vacuo. The residue was purified by preparative TLC (Petroleum ether/ethyl acetate 20/1) to give white solid (0.50 g, 33% yield). ^{1}H NMR (300MHz, $CDCl_3$): δ 0.84 (t, *J* = 7.5 Hz, 3H), 1.25-1.32 (m, 2H), 1.59-1.69 (m, 2H), 2.26 (t, *J* = 7.2 Hz), 7.24-7.35 (m, 10H); ^{13}C HMR (75Hz, $CDCl_3$): δ 14.3, 20.8, 35.3, 37.7, 42.5, 116.8, 129.3, 129.7, 136.1, 175.9; IR(KBr, cm^{-1}): 2964, 1667, 1592, 1490, 1379, 1250, 759, 746, 696. HRMS for $C_{17}H_{19}NO^+$: 253.1463, Found: 253.1467;

_N, N_-diphenyl-2-(piperidin-1-yl)acetamide (2l)



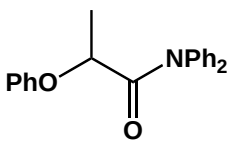
Chloroacetyl chloride (2.26 g, 20.0 mmol) and *N, N*-di-phenylamine (3.38 g, 20.0 mmol) were dissolved in 40 mL of dry CH_2Cl_2 under N_2. After stirring overnight, the mixture was quenched with 40 mL of water. The organic layer was washed twice with saturated $NaHCO_3$ and concentrated in vacuo. The residue was purified by preparative TLC (Petroleum ether/ethyl acetate 5/1) to give 2-chloro-*N, N*-diphenylactamide (4.20 g, 86 %) as white solid. 1.90 g (7.7 mmol) of this solid was dissolved in 150 mL of anhydrous acetonitrile, and 3.0 g of KI, 4.20 g of K_2CO_3, and 3.2 mL (30.8 mmol) of *N, N*-diethylamine were added. The mixture was refluxed overnight until a substantial amount of product was formed. The reaction mixture was diluted with water and extracted with ether. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude oil was purified by column chromatography on silica gel for purification (ethyl acetate/petroleum = 1/1) to give pale yellow solid (2.0g, 88% yield)[7]. ^{1}H NMR (300MHz, $CDCl_3$): δ 1.38 (d, *J* = 4.5 Hz, 2H), 1.50-1.58 (m, 4H), 2.43 (t, *J* = 4.8 Hz, 4H), 3.07 (s, 2H), 7.26-7.35 (m, 10H); ^{13}C HMR (75Hz, $CDCl_3$): δ 24.5, 26.5, 50.2, 64.4, 117.0, 126.5, 129.1, 135.4, 171.3; HRMS for $C_{17}H_{19}NO^+$: 253.1463, Found: 253.1467.

2-(*tert*-butyldimethylsilyoxy)-*N,N*-diphenyacetamide (2m)



Glycolic acid (4.19 g, 55 mmol) and *tert*-butyldimethylchlorosilane (17.72 g, 117 mmol) were stirred in 10 mL of dry DMF. Imidazole (15.62 g, 229.5 mmol) was added to the mixture and stirred under N_2 for 18 h. The mixture was poured into deionized water (approximately 250 mL) and extracted with petroleum ether (3×100 mL). The organic fractions were combined, washed with saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo to give 15.28 g (91 %) of *tert*-butyldimethylchlorosilyl 2-(*tert*-butyldimethylchlorosilyloxy) acetate as a pale yellow liquid. This product (2.01 g, 6.6 mmol) was dissolved in 10 mL of dry CH_2Cl_2 containing 2 drops of DMF. Oxalyl chloride (1.05 g, 8.2 mmol) and 10.0 mL of dry methylene chloride was added dropwise under N_2. After stirring the solution at ambient temperature for 2 h, the volatiles (unreacted oxalyl chloride) were removed in vacuo to yield a yellow oily residue. The residue was mixed with 20 mL of dry methylene chloride and *N, N*-diphenylamine (1.01 g, 6.0 mmol). The mixture was stirred overnight and quenched with 20 mL of water. The organic layer was washed twice with saturated aqueous sodium chloride and concentrated in vacuo. The residue was purified by preparative TLC (Petroleum ether/ethyl acetate 10/1) to give pale solid (1.5 g, 67% yield)[8]. ^{1}H NMR (300MHz, $CDCl_3$): δ 0.08 (s, 6H), 0.87 (s, 9H), 4.17(s, 2H); 7.25-7.36 (m, 10H); ^{13}C HMR (75Hz, $CDCl_3$): δ -6.1, 17.7, 25.0, 62.8, 111.5, 128.6, 128.7, 141.5, 169.8; IR(KBr, cm^{-1}): 2947, 2931, 2856, 1683, 1494, 1300, 1133, 839, 778, 757, 703, 691. HRMS for $C_{20}H_{28}NO_2Si^+$: 342.1874, Found: 342.1884.

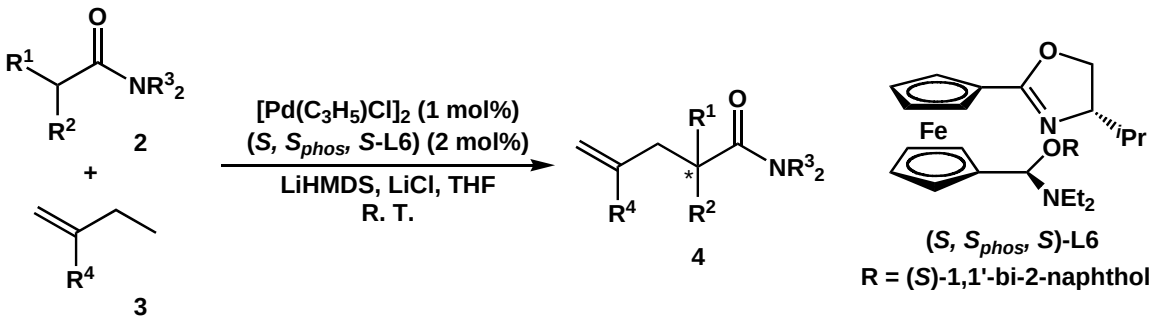
2-phenoxy-*N, N,* 2-diphenylpropanamide (2n)



2-Phenoxypropanoic acid (1.10 g, 6.6 mmol) was dissolved in 10 mL of dry CH_2Cl_2 containing 2 drops of DMF. Oxalyl chloride (1.05 g, 8.2 mmol) and 10.0 mL of dry methylene

chloride was added dropwise under N_2. After stirring the solution at ambient temperature for 2 h, the volatiles (unreacted oxalyl chloride) were removed in vacuo to yield a yellow oily residue, which was mixed with 20 mL of dry methylene chloride and *N, N*-diphenylamine (1.01 g, 6.0 mmol). The mixture was stirred overnight and quenched with 20 mL of water. The organic layer was washed twice with saturated $NaHCO_3$ and concentrated in vacuo. The residue was purified by preparative TLC (Petroleum ether/ethyl acetate 20/1) to give white solid (1.30 g, 68% yield).^{1}H NMR (300MHz, $CDCl_3$): δ 1.58 (d, J = 6.3 Hz, 3H), 4.88 (q, J = 6.6 Hz, 1H), 6.78-6.83 (m, 2H), 6.95-6.99 (m, 1H), 7.23-7.34 (m, 13H); ^{13}C HMR (75Hz, $CDCl_3$): δ 18.1, 71.9, 115.9, 121.5, 126.1, 128.3, 128.9, 129.3, 157.1, 171.0; IR (KBr, cm^{-1}): 1680, 1601, 1588, 1491, 1452, 1385, 1275, 1245, 1129, 1091, 761, 755, 708, 698, 688, 666. HRMS for $C_{21}H_{19}NO_2^+$: 317.1419, Found: 317.1416;

3. General Procedure for the palladium-catalyzed asymmetric allylic alkylation of amides:

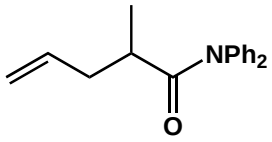


4g. R^1 = Me, R^2 = H, R^3 = Ph, R^4 = H
4h. R^1 = Et, R^2 = H, R^3 = Ph, R^4 = H
4i. R^1 = Pr, R^2 = H, R^3 = Ph, R^4 = H
4j. R^1 = ^{i}Pr, R^2 = H, R^3 = Ph, R^4 = H
4k. R^1 = Ph, R^2 = H, R^3 = Ph, R^4 = H
4l. R^1 = *N*-piperidinyl, R^2 = H, R^3 = Ph, R^4 = H
4m. R^1 = TMSO, R^2 = H, R^3 = Ph, R^4 = H
4n. R^1 = PhO, R^2 = Me, R^3 = Ph, R^4 = H
4o. R^1 = Ph, R^2 = Me, R^3 = Ph, R^4 = H
4p. R^1 = Ph, R^2 = H, R^3 = Me, R^4 = H
4q. R^1 = Me, R^2 = H, R^3 = Ph, R^4 = Me
4r. R^1 = Ph, R^2 = H, R^3 = Ph, R^4 = Me

$[Pd(C_3H_5)Cl]_2$ (0.9 mg, 0.005mmol), ligand (***S, S$_{phos}$, S*)-L6** (6.8 mg, 0.01 mmol), allyl acetate (50 mg, 0.50 mmol) and LiCl (0.4 mg, 0.01 mmol) were dissolved in dry tetrahydrofuran (1 ml) in dried Schlenk tube under argon, and stirred at room temperature. In the other Schlenk tube, a solution of amide (0.30 mmol) in THF was added to a solution of LiHMDS (1.0 M in tetrahydrofuran, 0.25 ml, 0.25 mmol) at 0^{o}C. The resulting solution in two

tubes were stirred for 20 min respectively and mixed together. The mixture was stirred at room temperature and monitored by TLC. After completion, the reaction mixture was diluted with DCM (20ml) and washed twice with saturated aqueous sodium chloride. Concentration and purification by preparative TLC (Petroleum ether/ethyl acetate 5/1) gave the product. The enantiomeric excess was determined by chiral HPLC.

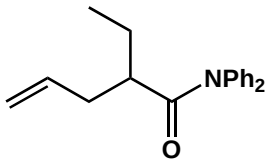
2-Methyl-*N, N*-diphenylpent-4-enaminde (4g)



Yield : 82%; ee : 85%

$[\alpha]_{25}^{D}$ = +91.6° (*c* = 0.3, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.15 (d, *J* = 6.9Hz, 3H), 2.06-2.15 (m, 1H), 2.46-2.56 (m, 1H), 2.64-2.71 (m, 1H), 5.03-5.11 (m, 2H), 5.66-5.80 (m, 1H), 7.23-7.35 (m, 10H); ^{13}C HMR(75Hz, $CDCl_3$): δ 17.7, 37.3, 38.8, 116.7, 125.9, 126.4, 128.7, 129.6. 135.9, 176.3; IR(KBr, cm^{-1}): 1673, 1593, 1492, 1382, 1288, 1272, 916, 757, 702, 693; HRMS for $C_{18}H_{19}NO^+$: 265.1467, Found: 265.1647. HPLC (Chiralcel OD-H, hexane/*i*-propanol = 98/2, 0.5 mL/min, 254 nm) t_R = 11.71 min, 13.38 min.

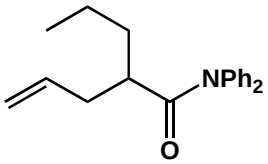
2-Ethyl-*N, N*-diphenylpent-4-enaminde (4h)



Yield : 78%; ee : 82%

$[\alpha]_{25}^{D}$ = -18.4° (*c* = 0.8, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.5 Hz, 3H), 1.63-1.70 (m, 2H), 2.10-2.12 (m, 1H), 2.35-2.46 (m, 2H), 4.95-5.04 (m, 2H), 5.65-5.68 (m, 1H), 7.18-7.33 (m, 10H); ^{13}C HMR(75Hz, $CDCl_3$): δ 12.0, 25.95, 37.3, 44.1, 116.7, 125.9, 126.5, 128.7, 129.2, 136.0. 175.7; IR(KBr, cm^{-1}): 1666, 1491, 1386, 1272, 1243, 912, 756, 702, 693; HRMS for $C_{19}H_{21}NO^+$: 279.1623, Found: 279.1627. HPLC (Chiralcel AS, hexane/*i*-propanol = 98/2, 0.5 mL/min, 254 nm) t_R = 9.78 min, 11.48 min.

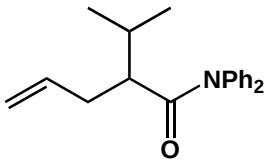
2-propyl-*N, N*-diphenylpent-4-enaminde (4i)



Yield : 75%; ee : 83%

$[\alpha]_{25}^{D}$ = -15.8° (*c* = 0.8, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 0.84 (t, *J* = 6.6Hz, 3H), 1.24-1.43 (m, 3H), 1.69-1.78 (m, 1H), 2.15-2.22 (m, 1H), 2.41-2.50 (m,1H), 2.58-2.63 (m, 1H), 5.04-5.12 (m, 2H), 5.70-5.79 (m, 1H), 7.16-7.39 (m, 10H); ^{13}C HMR (75Hz, $CDCl_3$): δ 14.2, 20.6, 35.1, 37.5, 42.4, 116.7, 126.5, 128.7, 129.5, 136.0, 142.9, 175.7 IR(KBr, cm^{-1}): 1669, 1593, 1492, 1386, 1291, 1272, 913, 756, 732, 701, 693; HRMS for $C_{20}H_{23}NO^+$: 293.1780, Found: 293.1780. HPLC (Chiralcel AS, hexane/*i*-propanol = 98/2, 0.5 mL/min, 254 nm) t_R =9.83 min, 11.68 min.

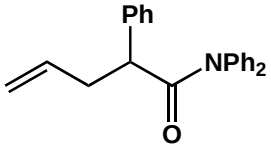
2-Isopropyl-*N, N*-diphenyl-4-enamide (4j)



Yield : 80%; ee : 73%

$[\alpha]_{25}^{D}$ = -17.3° (*c* = 0.65, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 0.91 (d, *J* = 6.9 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H), 1.95-2.02 (m, 1H), 2.22-2.28 (m, 1H), 2.35-2.47 (m, 2H), 5.07-5.16 (m, 2H), 5.76-5.88 (m, 1H), 7.15-7.40 (m, 10H); ^{13}C HMR (75Hz, $CDCl_3$): δ 19.72, 21.32, 31.18, 34.94, 48.66, 116.7, 126.6, 127.6, 128.8, 129.5, 136.4, 175.2; IR(KBr, cm^{-1}): 2961, 1670, 1492, 1379, 1267, 703, 693; HRMS for $C_{20}H_{23}NO^+$: 293.1781, Found: 293.1780. HPLC (Chiralcel OD-H, hexane/*i*-propanol = 98/2, 0.5 mL/min, 254 nm) t_R =12.38 min, 13.38 min.

***N, N*, 2-triphenyl-4-enamide (4k)**

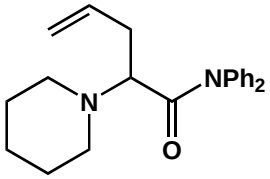


Yield : 98%; ee : 88%

$[\alpha]_{25}^{D}$ = -11.4° (*c* = 0.4, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.27-2.36 (m, 1H), 2.82-2.92 (m,1H), 3.61-3.67 (m. 1H), 4.93-5.05 (m, 2H), 5.64-5.74 (m, 1H), 6.96-7.23 (m, 15H); ^{13}C

HMR(75Hz, $CDCl_3$): δ 39.5, 49.7, 116.6, 126.1, 126.8, 127.8, 128.6, 129.1, 129.3, 135.7, 139.3, 172.5; IR (KBr, cm^{-1}): 1661, 1592, 1491, 1363, 1278, 918, 754, 744, 693; HRMS for $C_{23}H_{21}NO^+$: 327.1623, Found: 327.1617. HPLC (Chiralcel OD-H, hexane/*i*-propanol = 98/2, 0.5 mL/min, 254 nm) t_R = 12.16 min, 13.13 min.

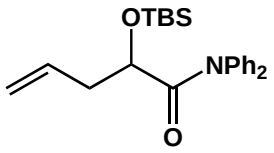
_N, N_-diphenyl-2-(piperidin-1-yl)pent-4-enamide (4l)



Yield : 95%; ee : 85%

$[\alpha]_{25}^{D}$ = -39.9° (*c* = 1.2, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.42 (t, *J* = 5.4Hz, 2H), 1.47-1.50 (m, 4H), 2.28-2.43 (m, 3H), 2.60-2.70 (m, 3H), 3.39 (dd, *J* = 9.6Hz), 5.05-5.15 (m, 2H), 5.73-5.83 (m, 1H), 7.16-7.34 (m, 10H); ^{13}C HMR(75Hz, $CDCl_3$): δ 24.5, 26.5, 30.9, 50.2, 64.4, 117.0, 126.5, 127.5, 128.8, 129.1, 135.4, 171.2; IR(KBr, cm^{-1}): 2934, 1672, 1594, 1492, 1289, 1266, 756, 736, 700; HRMS for $C_{22}H_{27}N_2O^+$: 335.2114, Found: 335.2118. HPLC (Chiralcel OD-H, hexane/*i*-propanol = 95/5, 0.5 mL/min, 254 nm) t_R = 11.46 min, 13.38 min.

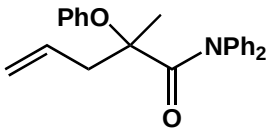
2-(*tert*-Butyldimethylsilyoxy)-*N,N*-diphenylpent-4-enamide (4m)



Yield : 78%; ee : 90%

$[\alpha]_{25}^{D}$ = +86.6° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 0.88 (s, 9H), 2.15 (s, 6H), 2.36-2.50 (m, 2H), 4.38 (dd, J = 6.9 Hz, 1H), 4.97-5.03 (m, 2H), 5.66-5.77 (m, 1H), 7.21-7.35 (m, 10H); ^{13}C HMR (75Hz, $CDCl_3$): δ -5.07, -5.05, 17.9, 25.7, 54.6, 77.8, 116.3, 120.6, 121.2, 129.1, 134.1, 147.7, 172.4; HRMS for $C_{23}H_{31}NO_2SiNa^+$: 404.2014, Found: 404.2016. HPLC (Chiralcel OD-H, hexane/*i*-propanol = 98/2, 0.5 mL/min, 254 nm) t_R = 12.38 min, 13.38 min.

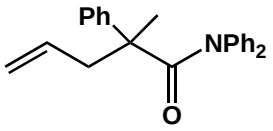
2-Methyt-2-phenoxy-*N, N*-diphenylpent-4-enamide (4n)



Yield : 99%; ee : 93%

$[\alpha]_{25}^{D}$ = -47.3° (*c* = 0.8, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.60 (s, 3H), 2.70-2.88 (m, 2H), 5.12-5.18 (m 2H), 5.77-5.91 (m, 1H), 6.78-6.81 (m, 2H), 6.97-7.02 (m, 1H), 7.14-7.29 (m, 12H); ^{13}C HMR(75Hz, $CDCl_3$): δ 23.4. 43.2, 82.6, 118.2, 119.0, 121.5, 127.0. 127.8, 128.7, 129.0, 132.2, 154.9, 173.2; IR(KBr, cm^{-1}): 1659, 1596, 1492, 1342, 1228, 753, 705, 694; HRMS for $C_{24}H_{23}NO_2^+$: 357.1729, Found: 357.1730. HPLC (Chiralcel AS, hexane/*i*-propanol = 100/1, 0.5 mL / min, 254 nm) t_R = 9.83 min, 10.88 min.

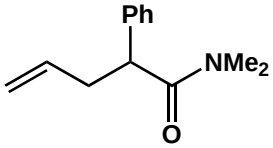
2-Methyl-*N, N,* 2-triphenyl-4-enamide (4o)



Yield : 75%; ee : 92%

$[\alpha]_{25}^{D}$ = -12.6° (*c* = 0.15, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.42 (s, 3H), 2.51-2.58 (m, 1H), 2.77-2.84 (m, 1H), 5.04-5.09 (m, 2H), 5.63-5.72 (m, 1H), 6.88-6.89 (m, 4H), 7.03-7.12 (m, 8H), 7.19-7.24 (m, 3H); ^{13}C HMR (75Hz, $CDCl_3$): δ 24.3, 45.3, 50.8, 118.1, 125.7, 126.4, 126.6, 128.3, 128.4, 128.5, 128.6, 134.7, 144.5, 175.6; IR(KBr, cm^{-1}): 1656, 1596, 1492, 1450, 1322, 1278, 916, 702; HRMS for $C_{24}H_{23}NO^+$: 341.1780, Found: 341.1771. HPLC (Chiralcel AS, hexane/*i*-propanol = 98/2, 0.5 mL/min, 254 nm) t_R = 10.69 min, 11.58 min.

***N, N*-dimethyl-2-phenylpent-4-enamide (4p)**

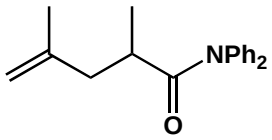


Yield : 75%; ee : 88%

$[\alpha]_{25}^{D}$ = +43.0° (*c* = 0.7, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.36-2.43 (m, 1H), 2.77-2.83 (m, 1H), 2.86 (s, 3H), 2.88 (s, 3H), 3.73 (t, *J* = 7.5 Hz, 1H), 4.88-5.00 (m, 2H),

5.65-5.74 (m, 1H), 7.16-7.25 (m, 5H); ^{13}C HMR (75Hz, $CDCl_3$): δ 35.7, 36.9, 39.1, 48.8, 116.1, 126.7, 127.7, 128.5, 136.3, 139.3, 172.3; IR(KBr, cm^{-1}): 1647, 1492, 1396, 1145, 915, 702; HRMS for $C_{13}H_{17}NO^+$: 203.1310, Found: 203.1310. HPLC (Chiralcel AS, hexane/*i*-propanol = 98/2, 0.5 mL/min, 254 nm) t_R =11.71 min, 12.67 min.

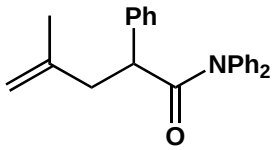
2,4-Dimethyl-N, N-diphenylpent-4-enamide (4q)



Yield : 85%; ee : 91%

$[\alpha]_{25}^{D}$ = +187.8° (*c* = 1.3, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): 1.15 (d, *J* = 6.3Hz, 3H), 1.51 (s, 3H), 2.01 (dd *J* = 13.5 Hz, 1H), 2.54 (dd, *J* = 13.8Hz, 1H), 2.76 (q, *J* = 6.6 Hz, 1H), 4.77 (d, *J* = 8.1 Hz, 2H), 7.26-7.33 (m, 10H); ^{13}C HMR (75Hz, $CDCl_3$): δ 17.75, 22.23, 35.60, 42.72, 112.5, 127.7, 128.8, 129.7, 142.9, 176.7; HRMS for $C_{19}H_{22}NO^+$: 279.1623, Found: 279.1617. HPLC (Chiralcel AD-H, hexane/*i*-propanol = 98/2, 0.7 mL/min, 230 nm) t_R =15.29 min, 17.63 min.

4-Methyl-*N*, *N*, 2-triphenyl-4-enamide (4r)



Yield : 90%; ee% : 90%

$[\alpha]_{25}^{D}$ = +52.6° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): 1.68 (s, 3H), 2.29 (dd, *J* = 14.4 Hz, 1H), 3.01 (dd, *J* = 14.4 Hz, 1H), 3.86 (dd, *J* = 9.6 Hz, 1H), 4.82 (d, *J* = 9.6 Hz, 2H), 7.08-7.35 (m, 15H); ^{13}C HMR (75Hz, $CDCl_3$): δ 22.87, 43.48, 48.31, 111.9, 126.3, 126.9, 128.0, 128.4, 128.7, 129.2, 129.4, 139.9, 143.2, 172.8; HRMS(ESI) for $C_{24}H_{24}NO^+$: 341.1780, Found: 342.1786; HPLC (Chiralcel AS-H, hexane/*i*-propanol = 95/5, 0.7 mL/min, 230 nm) t_R =10.71 min, 15.29 min.

4. Determination of absolute configuration of 2-methyl-*N,N*-diphenylpent-4-enaminde (4g)

a) Resolution of 2-methylpent-4-enoic acid.[9]

Quinine (5.2 g, 16 mmol) was added gradually to a solution of the racemic 2-methylpent-4-enoic acid (1.83 g, 16 mmol) in boiling acetone (38 mL), the resulting solution was filtered and left overnight. The quinine salt was precipitated. Partially resolved laevorotarory acid (1.35 g) obtained from the mother liquor of the first crystallization of the quinine salt of the dextrorotarory enantiomer, was resolved in ether (30 mL) and a solution of (+)-phenylethylamine (1.40 g) in ether (40 mL) was added cautiously (heat is evolved during the formation of the salt). Crystallization was allowed to take place overnight at a temperature of -15^{o}C. The salt crystallized in the form of long thin needles. The salt was recrystallized from successively volumes of ether and the course of the resolution followed by measuring the rotation of acid isolated from the mother liquors. Seven crystallizations were needed. The crystallization of quinine salt of the laevorotatory enantiomer was decomposed with 30 mL of 1 M hydrochloric acid. The aqueous solutions were extracted four times with ethyl ether, and the extracts were dried with 4Å sieves. Evaporation of the solvent gave (*R*)-(-)-2-methylpent-4-enoic acid[9] (330mg, 18%), $[\alpha]_D^{25}$: -8.0^{o} (lit[10]: $[\alpha]_D^{19}$: -8.25^{o}).

b) The synthesis of optical *N, N*-diphenyl amide from *N, N*-diphenylamine and (*R*)-(-)-2-methylpent-4-enoic acid.

(*R*)-(-)-2-methylpent-4-enoic acid (320 mg, 2.8 mmol) was dissolved in 4 mL of dry CH_2Cl_2. Oxalyl chloride (711 mg, 5.6 mmol) under N_2. After stirring the solution at ambient temperature for 2 h, the volatiles (unreacted oxalyl chloride) were removed in vacuo to yield a yellow oily residue. The residue was mixed with 20 mL of dry methylene chloride and *N, N*-diphenylamine (473 mg, 2.8 mmol). The mixture was stirred overnight and quenched with 20 mL of water. The organic layer was washed twice with saturated $NaHCO_3$. The residue was purified by preparative TLC (Petroleum ether / ethyl acetate 10 / 1) to give (*R*)-2-methyl-*N,N*-diphenylpent-4-enaminde **4g** (300 mg, 40%). $[\alpha]_D^{25}$: +85.6^{o} ($CHCl_3$, *c* = 1.4). The enantiomeric excess was 83%.

The absolute configuration of 2-methyl-*N,N*-diphenylpent-4-enaminde **4g** obtained by Pd-catalyzed AAA reaction is (***R***) by comparison its HPLC and optical rotation sign with that of synthetic sample.

Determination of absolute configuration of 2-ethyl-*N,N*-diphenylpent-4-enaminde (4h)

a) Resolution of 2-ethylpent-4-enoic acid

Quinine (5.85 g, 18 mmol) was added gradually to a solution of the racemic 2-ethylpent-4-enoic acid (2.30g, 18 mmol) in boiling acetone (70 mL), the resulting solution was filtered and left overnight. The quinine salt was precipitated. Partially resolved laevorotarory acid (1.82 g) obtained from the mother liquor of the first crystallization of the quinine salt of the dextrorotarory enantiomer, was resolved in ether (50 mL) and a solution of (+)-phenylethylamine (1.80 g) in ether (50 mL) was added cautiously (heat is evolved during the formation of the salt). Crystallization was allowed to take place overnight at a temperature of -15^{o}C. The salt crystallized in the form of long thin needles. The salt was recrystallized from successively volumes of ether and the course of the resolution followed by measuring the rotation of acid isolated from the mother liquors. Five crystallizations were needed. The crystallization of quinine salt of the laevorotatory enantiomer was decomposed with 30 mL of 1 M hydrochloric acid. The aqueous solutions were extracted four times with ethyl ether, and the extracts were dried with 4Å sieves. Evaporation of the solvent gave (*R*)-(+)-2-ethylpent-4-enoic acid[9,11] (530mg, 23%), $[\alpha]_D^{25}$: +2.2^{o} (lit: $[\alpha]_D^{19}$: +2.9^{o}).

b) The synthesis of optical *N, N*-diphenyl amide from *N, N*-diphenylamine and (*R*)-(+)-2-ethylpent-4-enoic acid

(*R*)-(+)-2-ethylpent-4-enoic acid (256 mg, 2.0 mmol) was dissolved in 4 mL of dry CH_2Cl_2. Oxalyl chloride (508 mg, 4.0 mmol) under N_2. After stirring the solution at ambient temperature for 2 h, the volatiles (unreacted oxalyl chloride) were removed in vacuo to yield a yellow oily residue. The residue was mixed with 20 mL of dry methylene chloride and *N, N*-diphenylamine (338 mg, 2.0 mmol). The mixture was stirred overnight and quenched with 20 mL of water. The organic layer was washed twice with saturated $NaHCO_3$. The residue was purified by preparative TLC (Petroleum ether / ethyl acetate 10 / 1) to give (*R*)-2-ethyl-*N,N*- diphenylpent-4-enaminde **4h** (251 mg, 45%). $[\alpha]_D^{25}$: -15.4^{o}. The enantiomeric excess was 67%.

The absolute configuration of 2-ethyl-*N*,*N*-diphenylpent-4-enaminde **4h** obtained by Pd-catalyzed AAA reaction is (***R***) by comparison its HPLC and optical rotation sign with that of synthetic sample.

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