Organic functionalizsation of ultradispersed nanodiamond: Synthesis and applications

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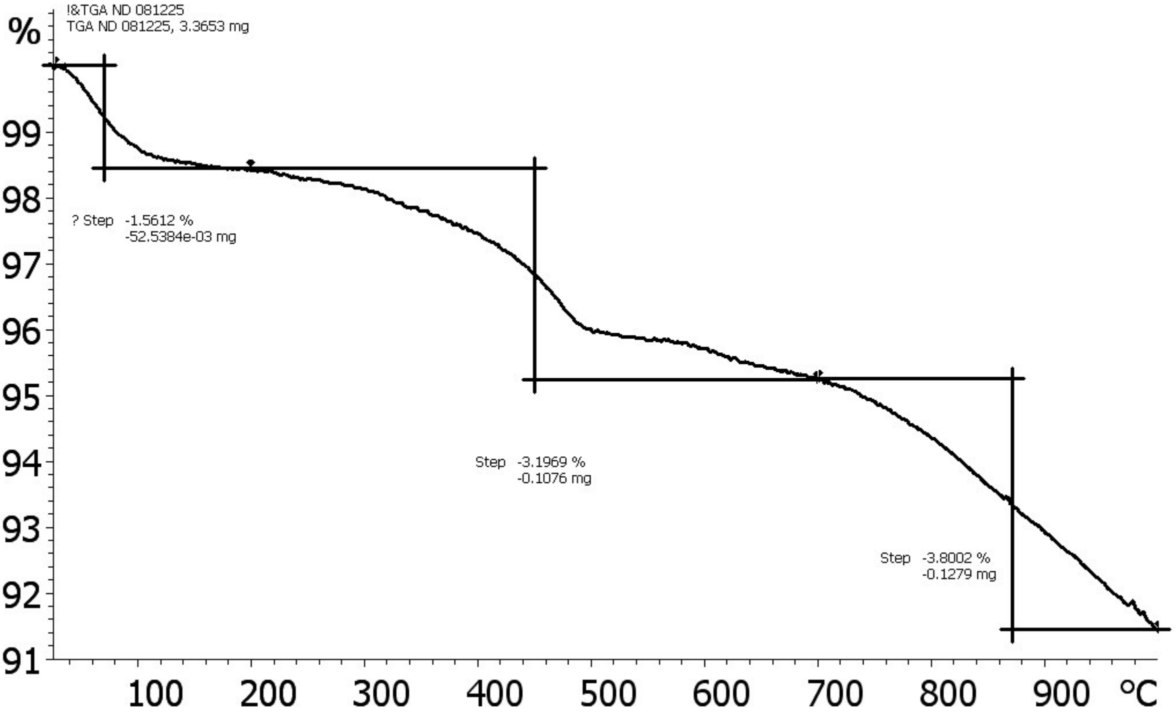
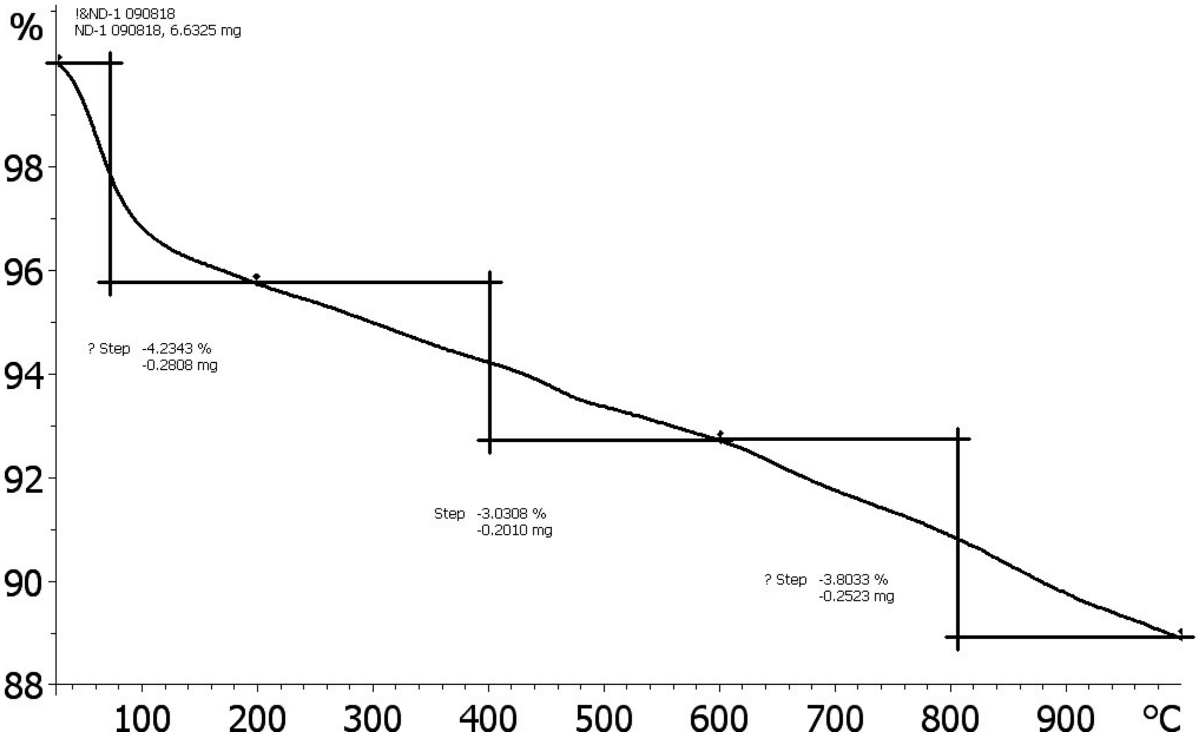
Supplementary material

Thermogravimetric analysis (TGA)

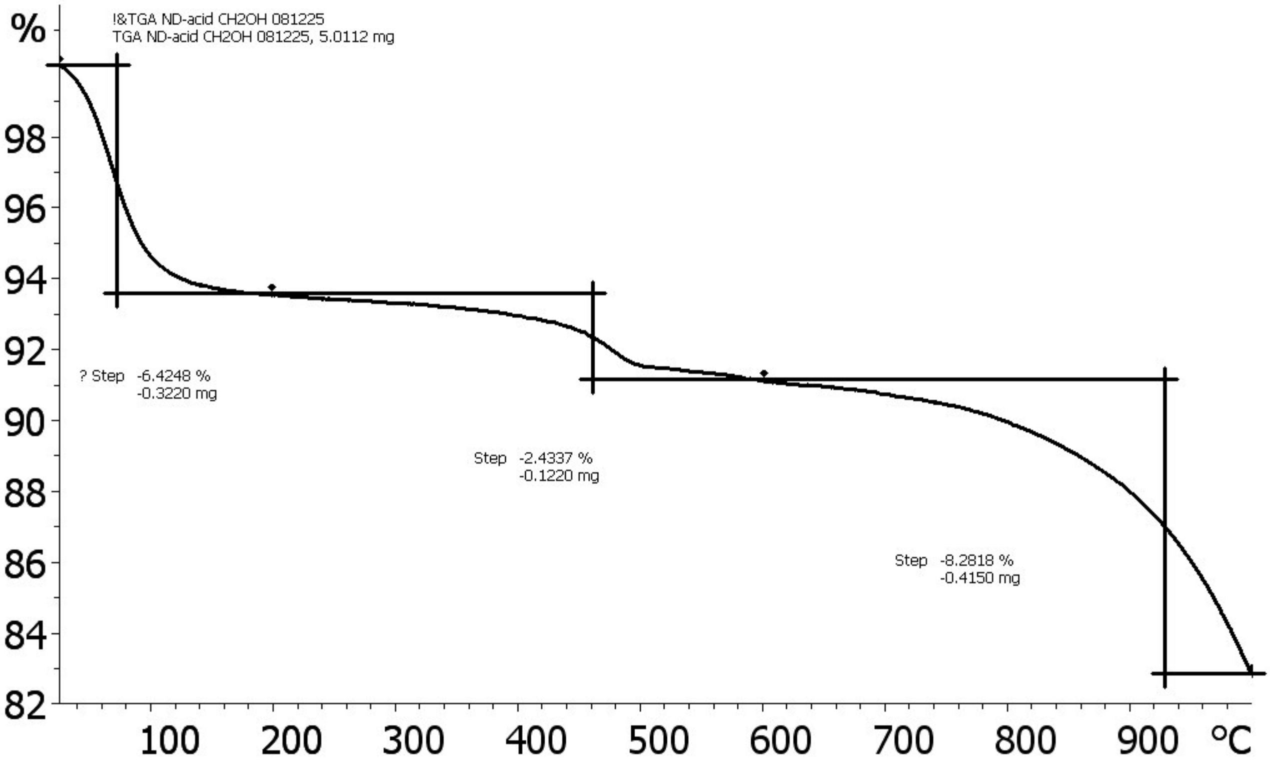
TGA measurements were made in Al_2O_3 crucibles in an atmosphere of nitrogen at a heating rate of 10 K min^{-1} using a TGA/SDTA851e thermobalance.



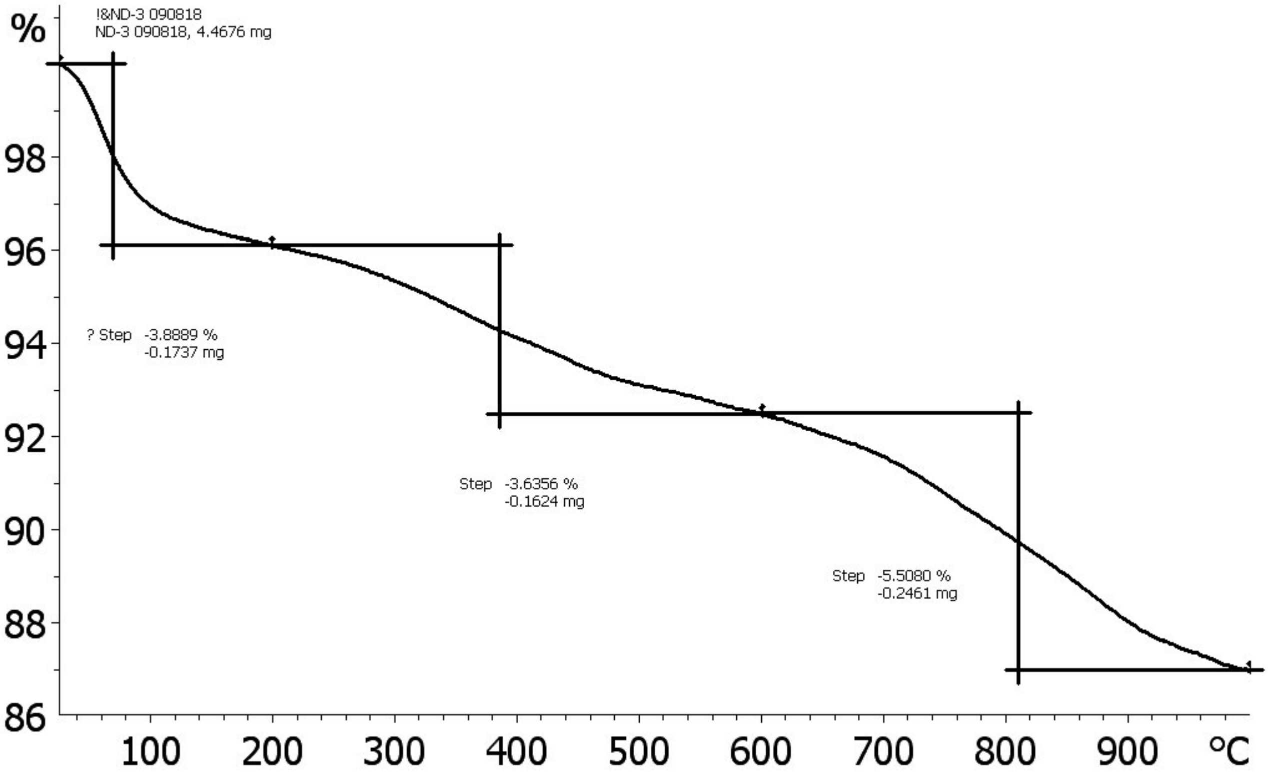
Thermogravimetric analysis of **ND**



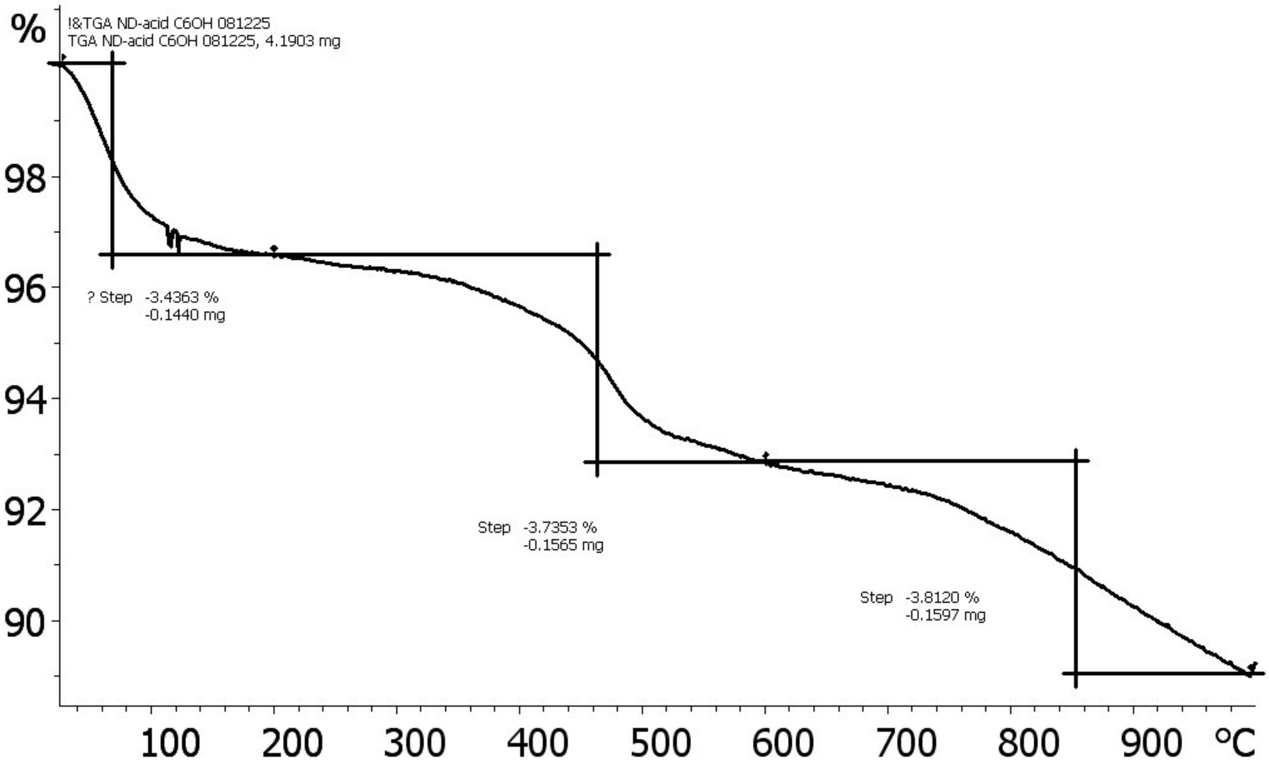
Thermogravimetric analysis of **ND-1**



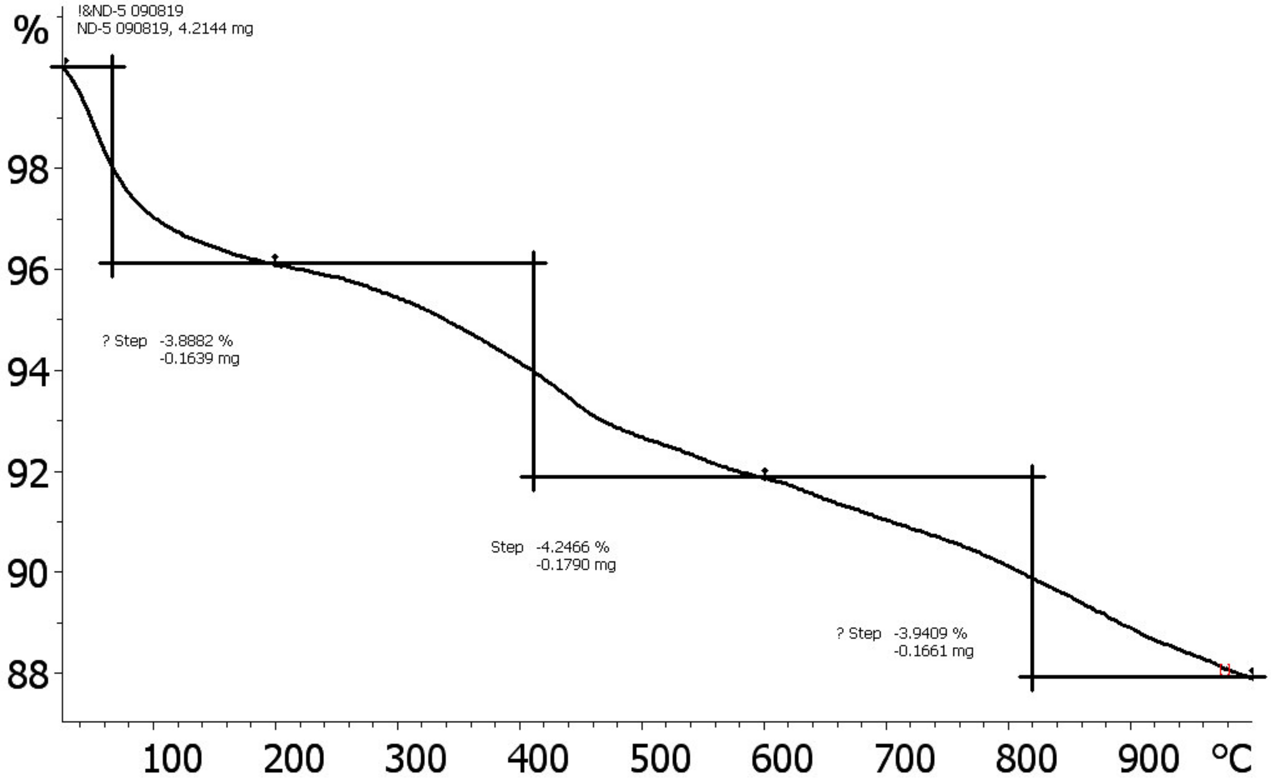
Thermogravimetric analysis of **ND-2**



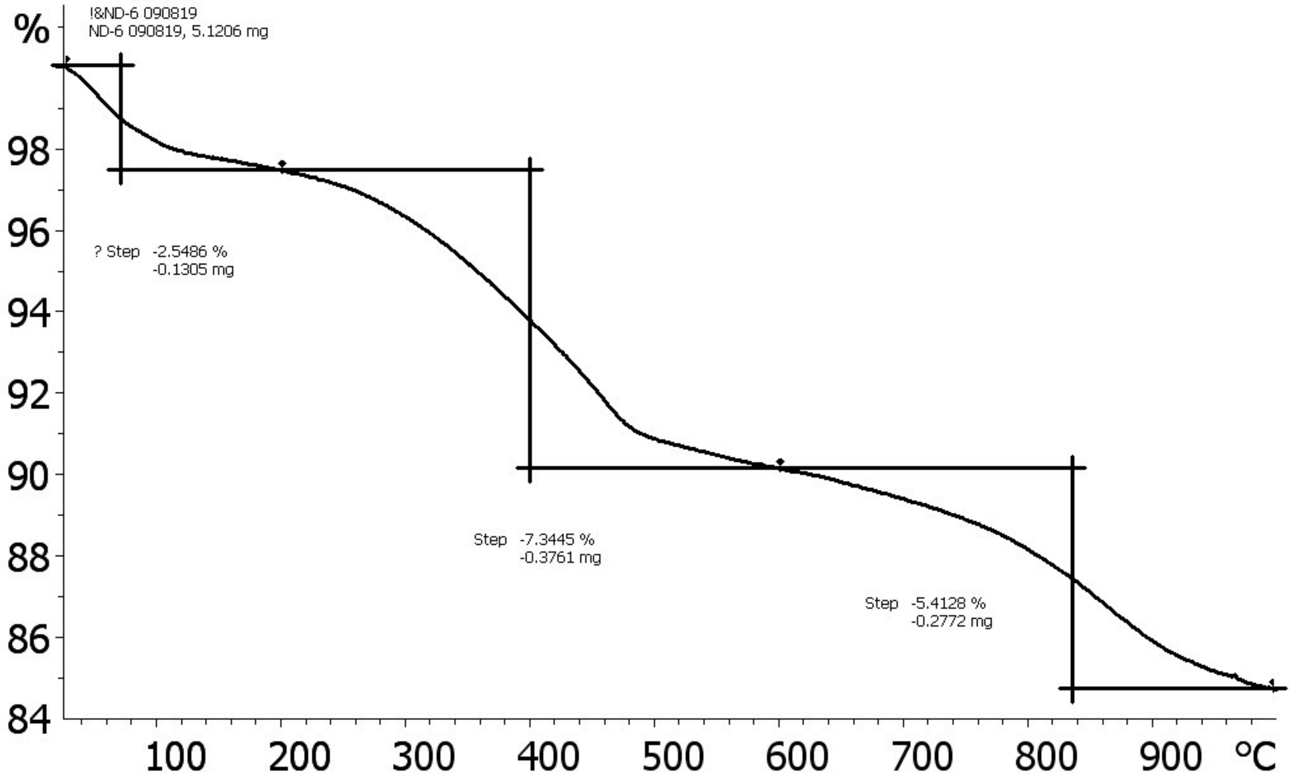
Thermogravimetric analysis of **ND-3**



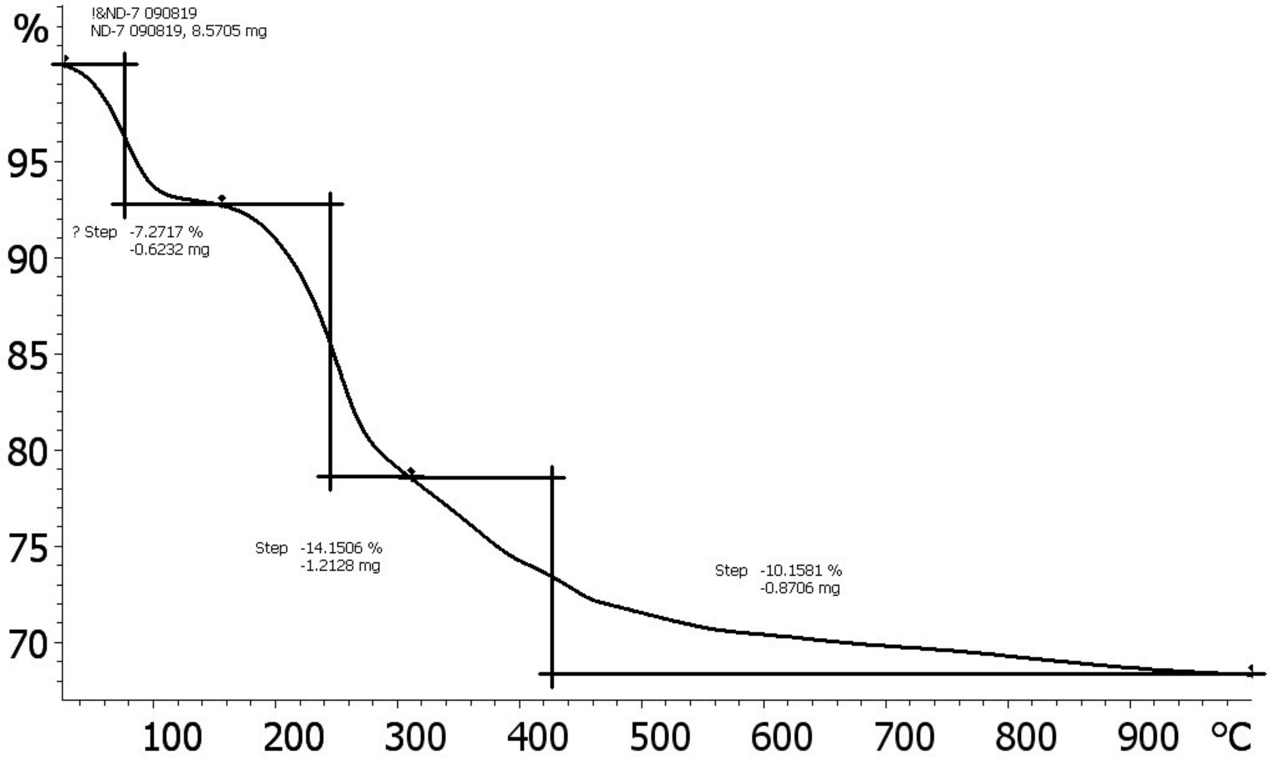
Thermogravimetric analysis of **ND-4**



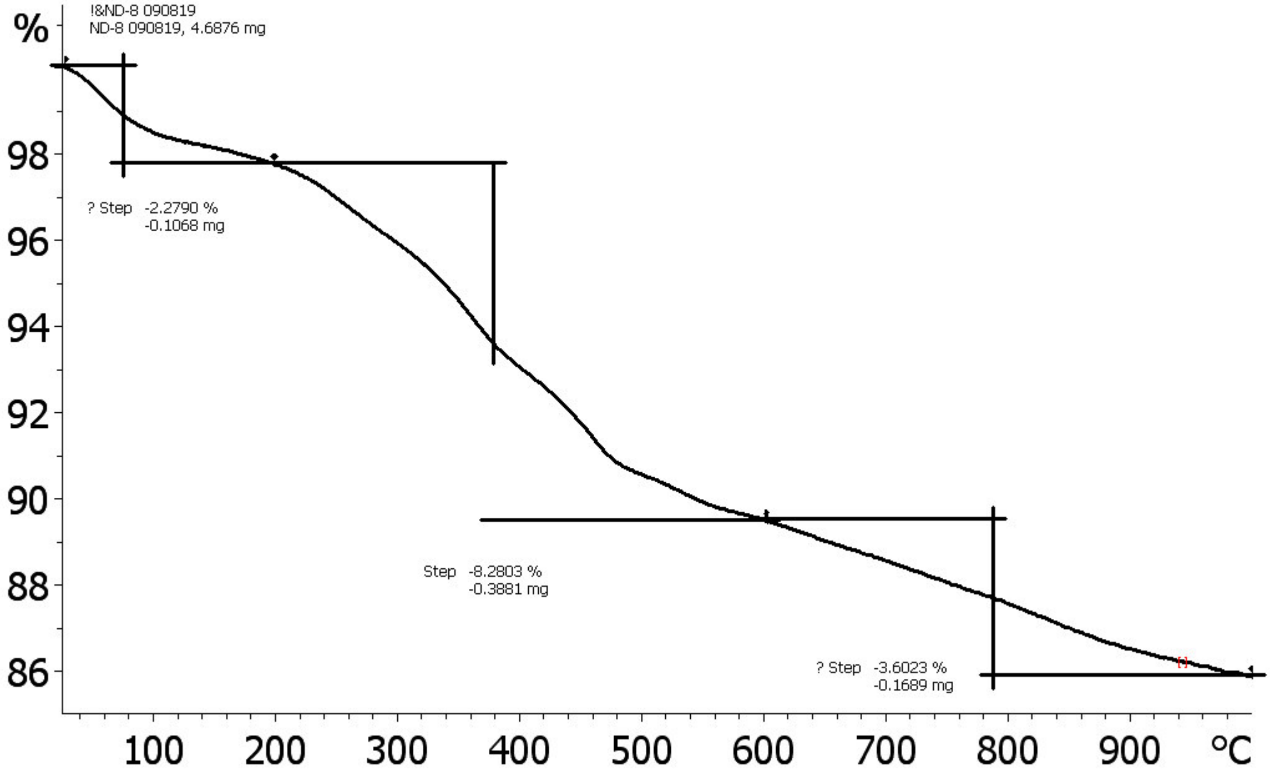
Thermogravimetric analysis of **ND-5**



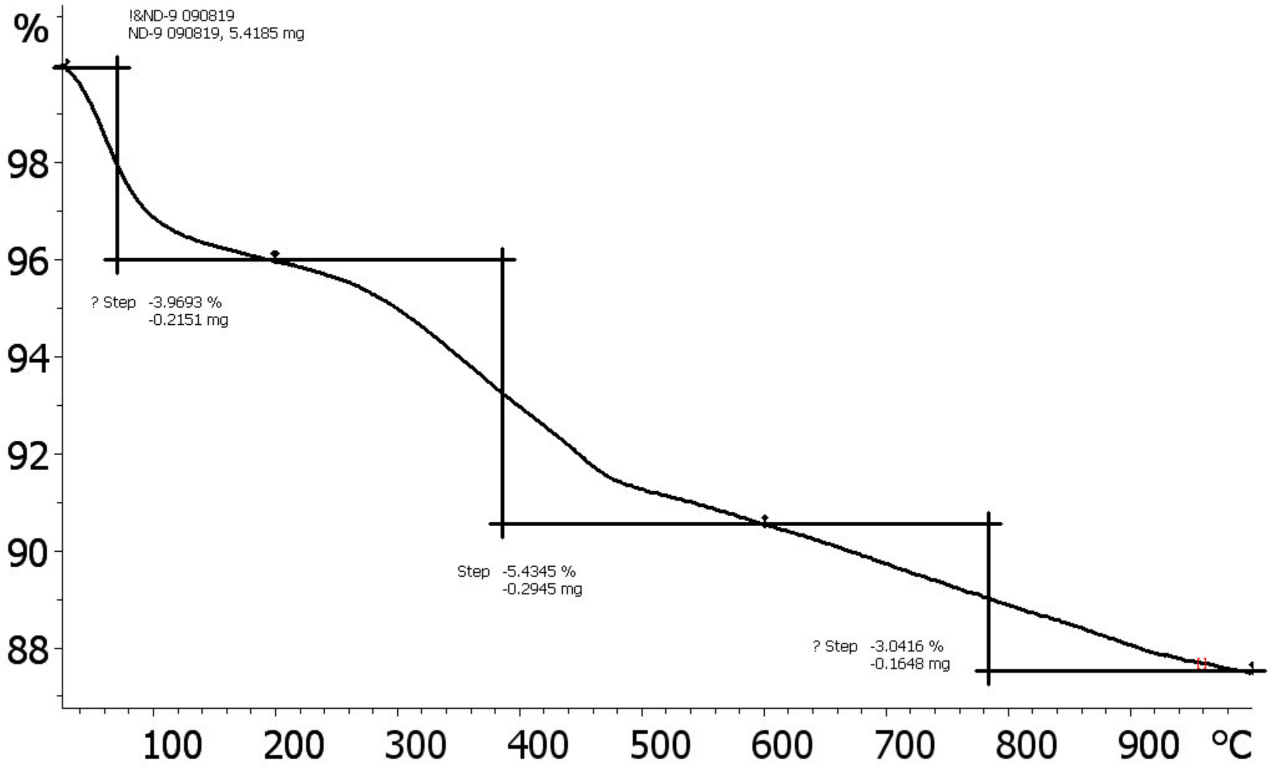
Thermogravimetric analysis of **ND-6**



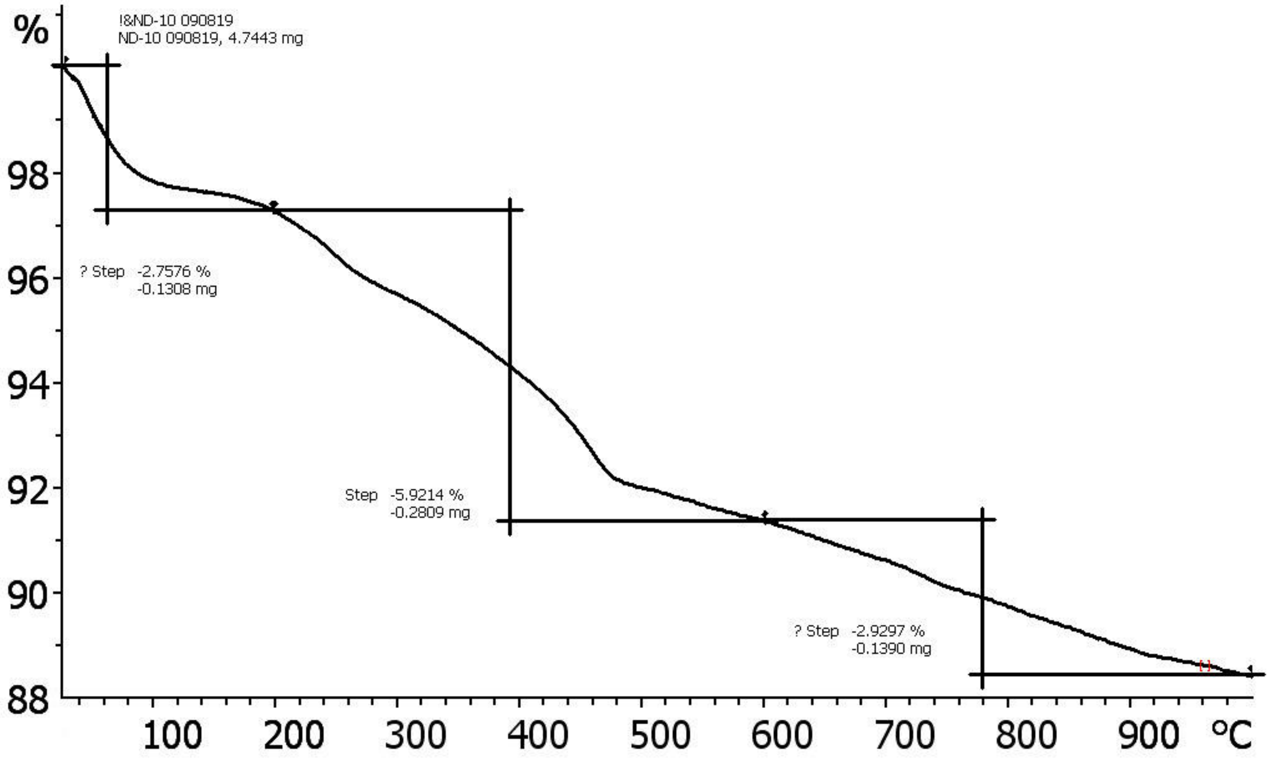
Thermogravimetric analysis of **ND-7**



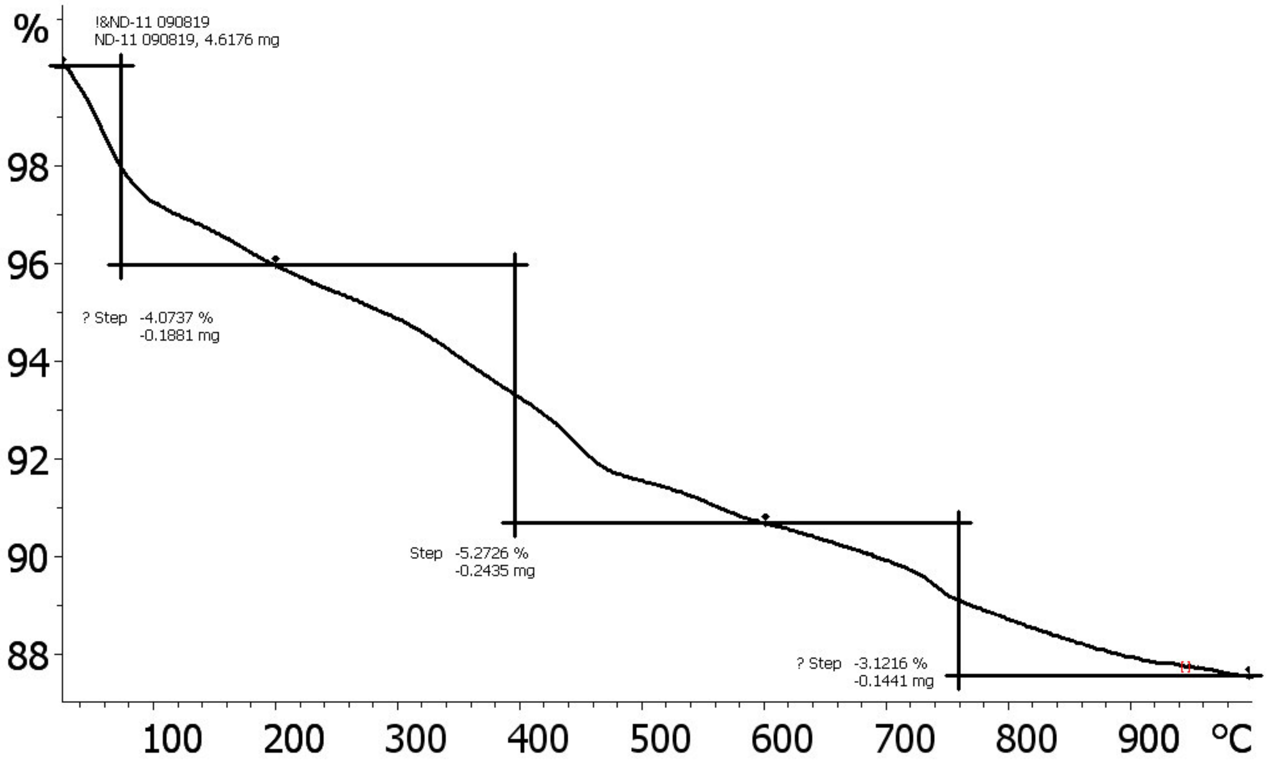
Thermogravimetric analysis of **ND-8**



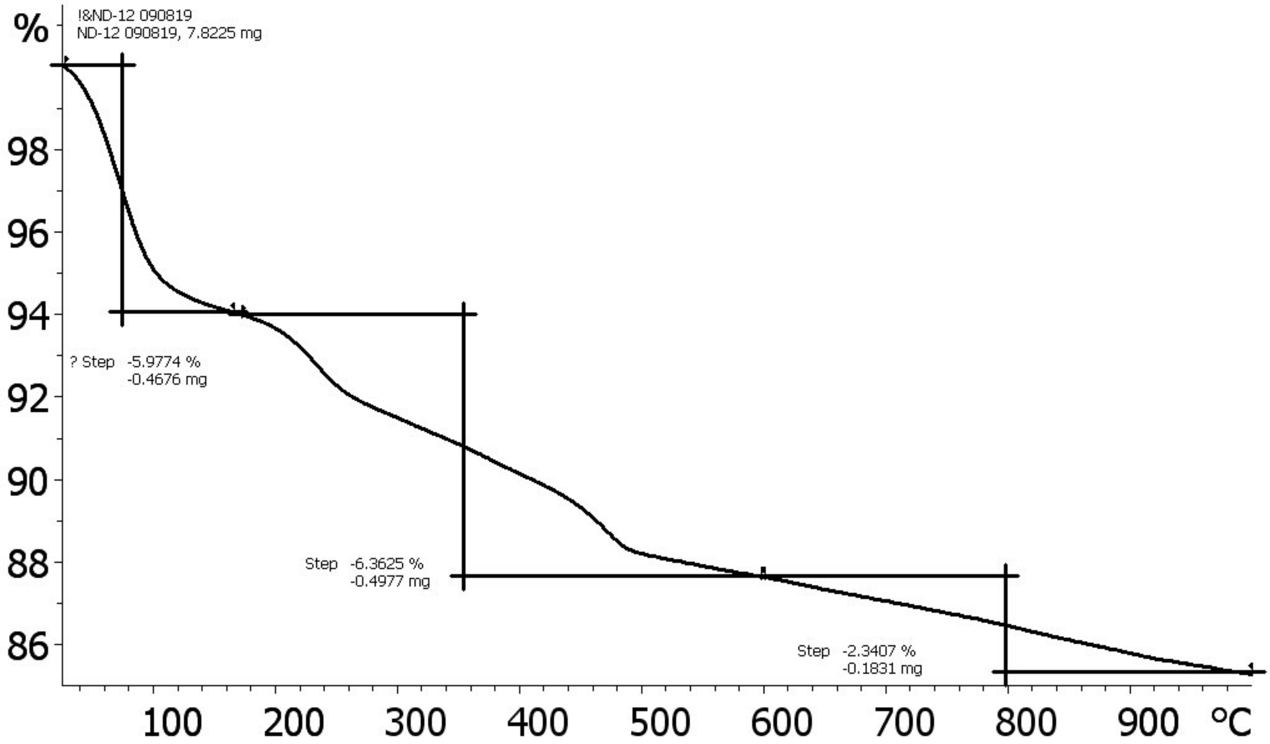
Thermogravimetric analysis of **ND-9**



Thermogravimetric analysis of **ND-10**



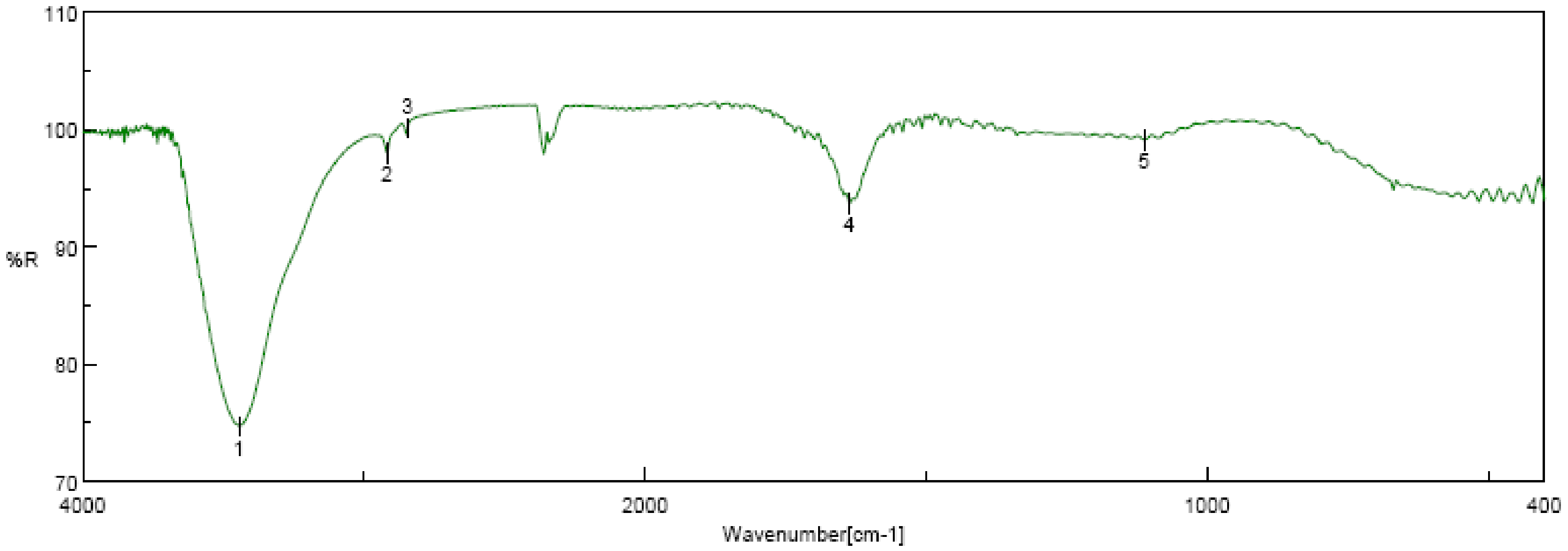
Thermogravimetric analysis of **ND-11**



Thermogravimetric analysis of **ND-12**

General Experimental

All commercial reagents were used without further purification. Solvents were dried according to standard procedures. Raw ND with >95% purity was purchased from Nanostructured and Amorphous Materials, Inc., USA. Transmission FTIR spectra were obtained from KBr pellets using a Perkin Elmer Paragon 1000 FTIR spectrometer, a JASCO FT/IR 410 spectrometer and an ABB FTLA2000 FTIR spectrometer with a MCT detector (samples in vacuum, ~10^{-6} torr). TGA measurements were made in Al_2O_3 crucibles in an atmosphere of nitrogen at a heating rate of 10 K min^{-1} using a TGA/SDTA851e thermobalance. RGA measurements were made using a DYCOR LC series Residual Gas Analyzer (LC 200 series with UHV system, experiment background pressure: 2 x 10^{-7} torr). Energy-dispersive X-ray spectroscopy (EDS) was performed at SEM/EDS, JEOL JSM-7000F. X-ray diffraction analysis of the samples was carried out using an X-ray diffractometer (XRD D8 Advanced, Bruker) with Cu-Ka radiation. X-Ray Photoelectron Spectroscopy (XPS, Thermo K-Alpha) was carried out using an Al-Kα radiation source and electron energy analyzer (Energy resolution, Ag 3d5/2 peak 0.5 eV, PET 0=C-0 peak 0.85eV). The powder was pressed into an indium foil as a carrier for the measurements. ^{1}H NMR spectra were obtained on 400 MHz, and ^{13}C NMR spectra were obtained at 100.6 MHz using a Bruker NMR spectrometer. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 and 77.0 ppm respectively). Electrochemical measurements were made using a model CHI420 electrochemical workstation that was controlled by a personal computer. A three-electrode system was used to make the measurements, with a bare glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. The measurements were made using 5.00 mL of buffer solutions. Enantiomeric excesses were determined using Lab Alliance Series III high performance liquid chromatograph (HPLC) with a chiracel OD-H chiral column (Daicel Chemical Industries, LTD). Optical rotations were measured using a JASCO P-1010 polarimeter at the indicated temperature using a sodium lamp (D line, 589 nm). Flash column chromatography was performed using MN silica gel 60 (70–230 mesh) that was purchased from Macherey-Nagel.



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Zero Filling	ON	Apodization	Cosine		
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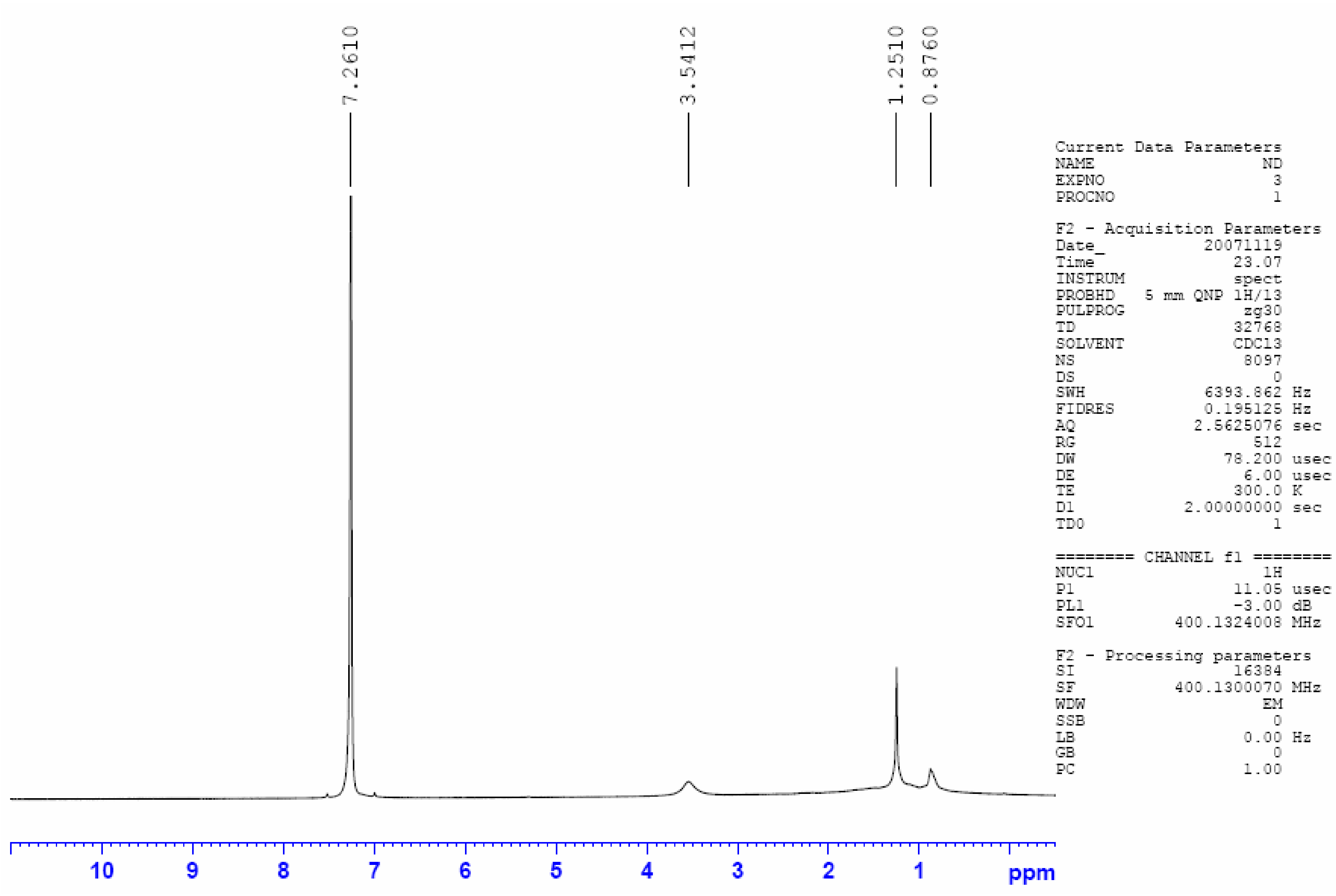
Update	2008/6/5 8:22下午				
Operator	wenwei Cheng				
File Name	3.2nm ND-standard.jws				
Sample Name	3.2nm ND standard				
Comment					

1: 3445.21, 74.72   2: 2918.73, 98.03   3: 2844.49, 100.18   4: 1636.30, 93.73
5: 1111.76, 99.15

Fig. 1 FT-IR spectrum of **ND**

ND

3~5 ND



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PROCNO                1

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PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                 8097
DS                    0
SWH            6393.862 Hz
FIDRES         0.195125 Hz
AQ            2.5625076 sec
RG                  512
DW               78.200 usec
DE                 6.00 usec
TE                300.0 K
D1          2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                11.05 usec
PL1               -3.00 dB
SFO1        400.1324008 MHz

F2 - Processing parameters
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SF          400.1300070 MHz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
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Fig. 2 ^{1}H-NMR spectrum of **ND**

ND
3~5 ND

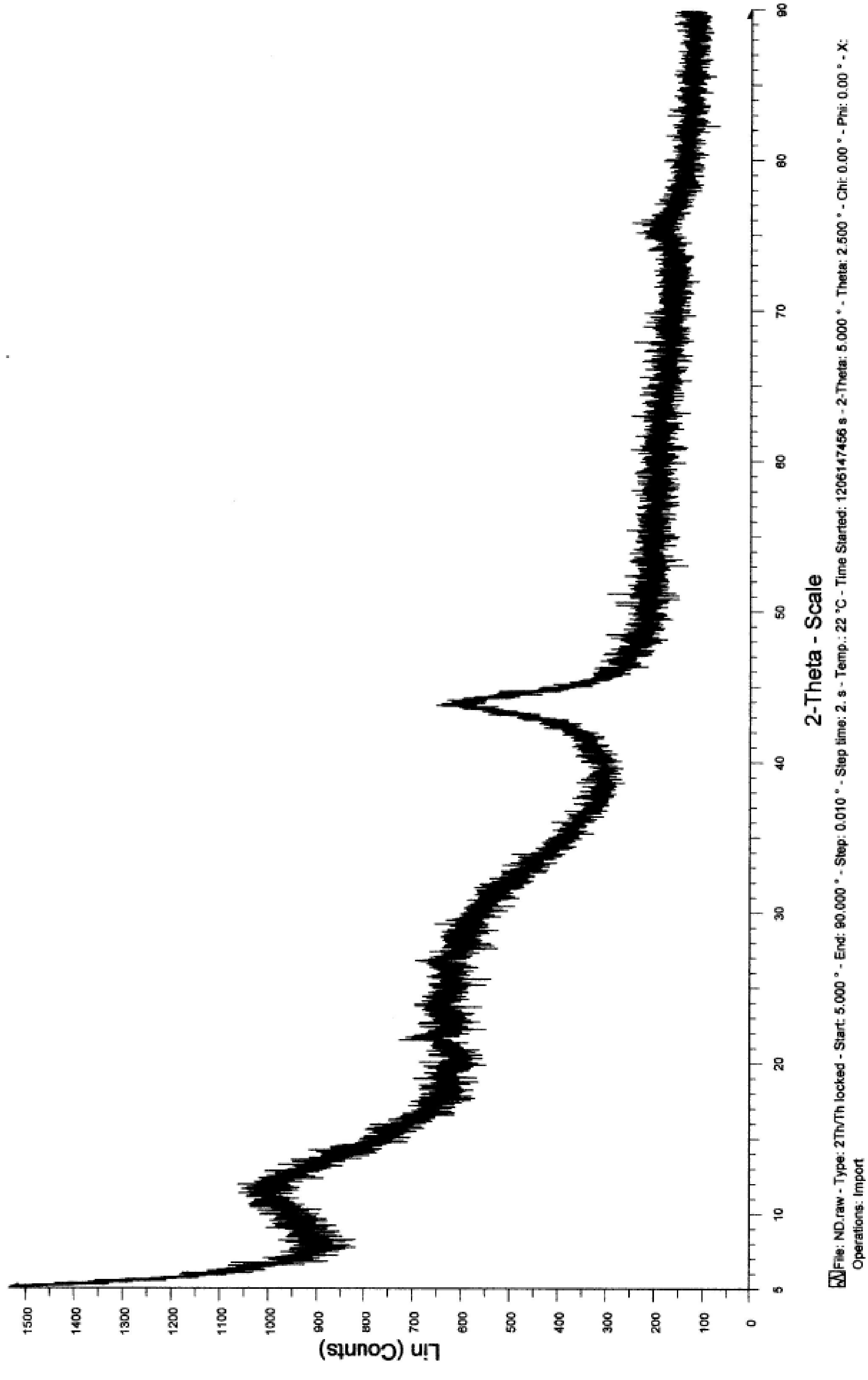
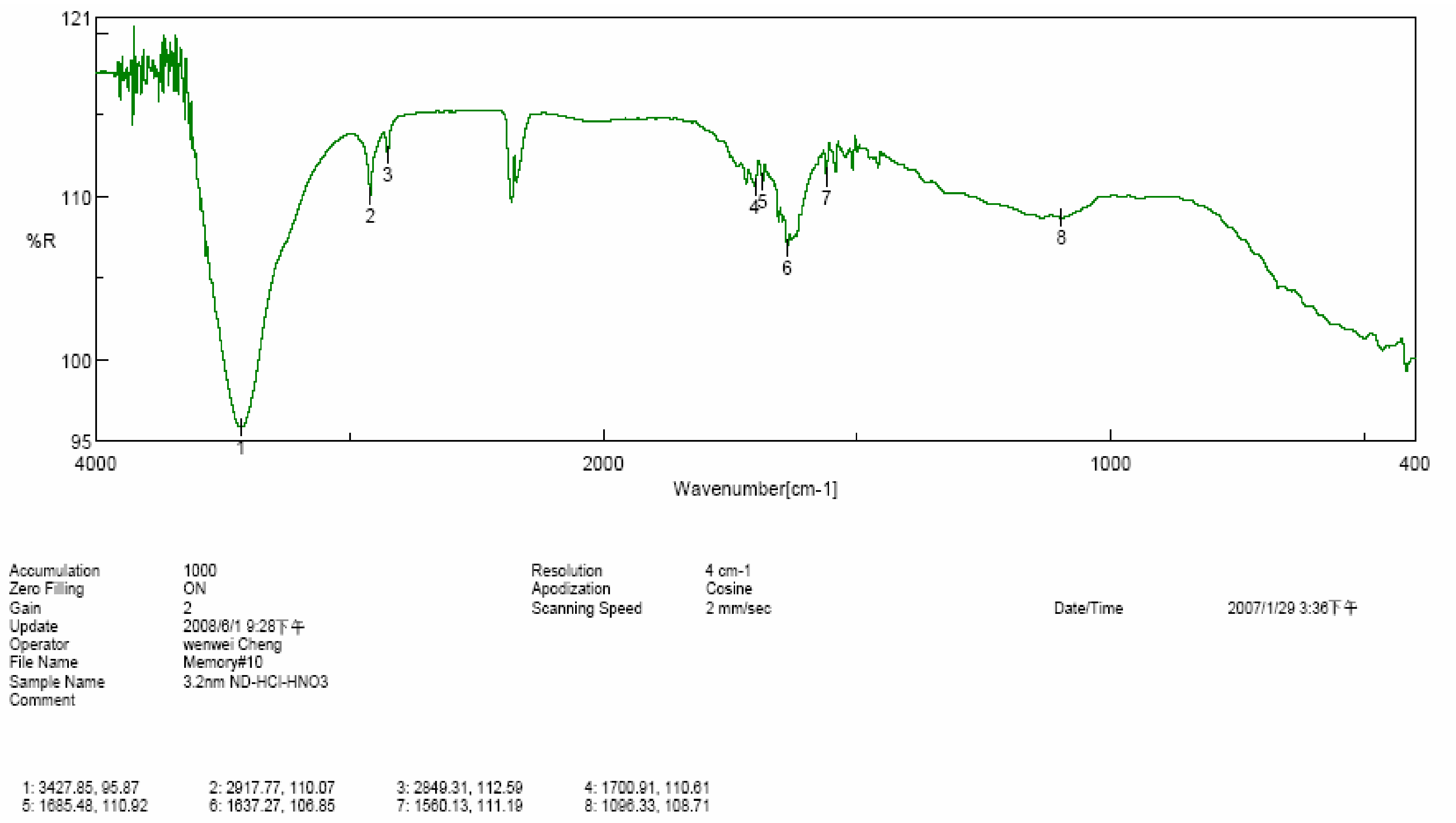


Fig. 3 Powder XRD pattern of **ND**



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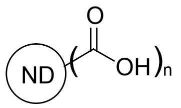
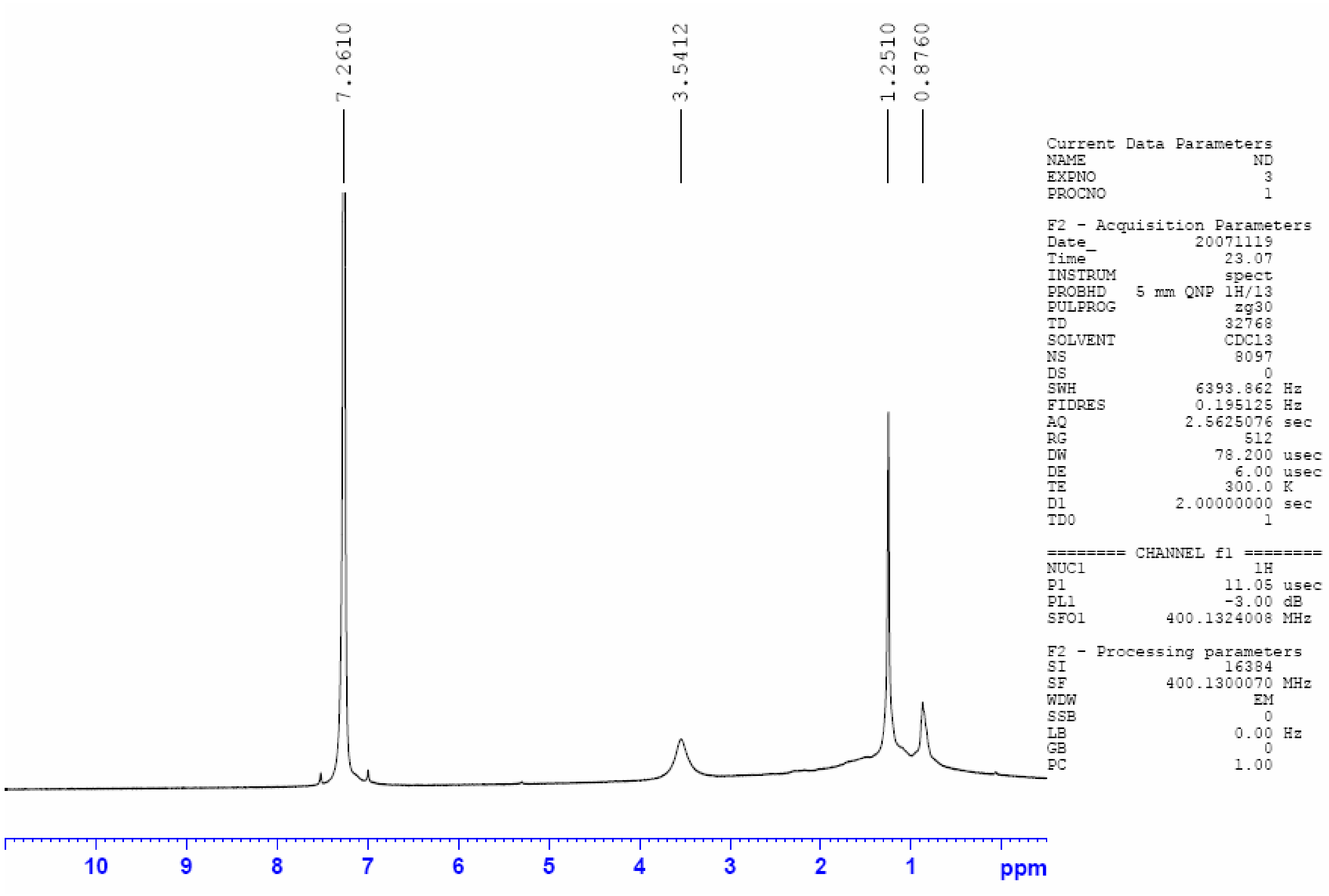
Zero Filling	ON	Apodization	Cosine		
Gain	2	Scanning Speed	2 mm/sec	Date/Time	2007/1/29 3:36下午
Update	2008/6/1 9:28下午				
Operator	wenwei Cheng				
File Name	Memory#10				
Sample Name	3.2nm ND-HCl-HNO3				
Comment					

1: 3427.85, 95.87
2: 2917.77, 110.07
3: 2849.31, 112.59
4: 1700.91, 110.61
5: 1685.48, 110.92
6: 1637.27, 106.85
7: 1560.13, 111.19
8: 1096.33, 108.71



ND-1

Fig. 4 FT-IR spectrum of **ND-1**



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EXPNO                    3
PROCNO                   1

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Time                 23.07
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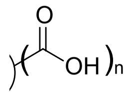
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                    8097
DS                       0
SWH               6393.862 Hz
FIDRES            0.195125 Hz
AQ               2.5625076 sec
RG                     512
DW                  78.200 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
TD0                      1

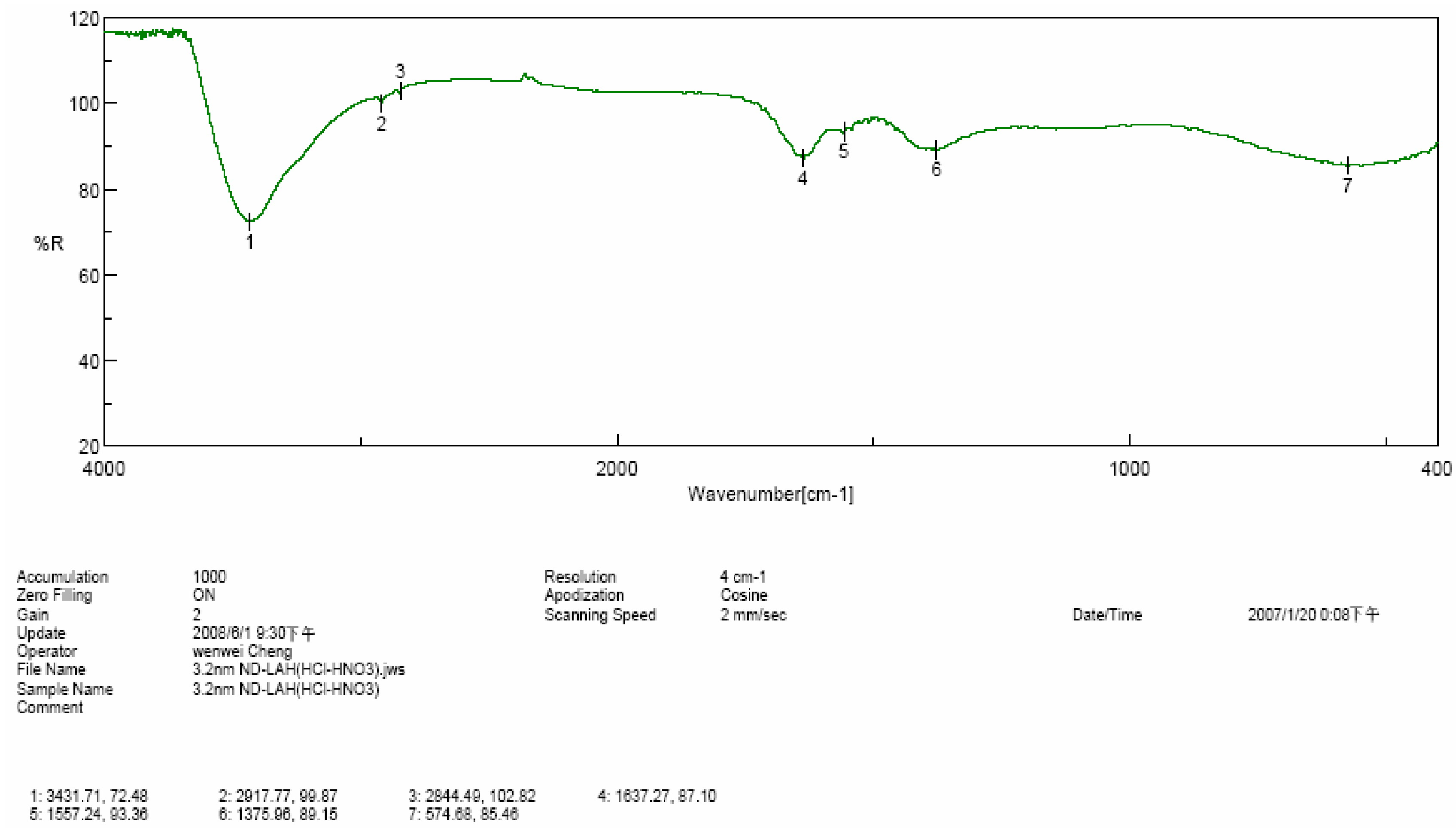
======== CHANNEL f1 ========
NUC1                    1H
P1                   11.05 usec
PL1                  -3.00 dB
SFO1           400.1324008 MHz

F2 - Processing parameters
SI                   16384
SF             400.1300070 MHz
WDW                     EM
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```



ND-1

Fig. 5 ^{1}H-NMR spectrum of **ND-1**



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Gain                2                                 Scanning Speed    2 mm/sec                 Date/Time        2007/1/20 0:08下午
Update              2008/6/1 9:30下午
Operator            wenwei Cheng
File Name           3.2nm ND-LAH(HCl-HNO3).jws
Sample Name         3.2nm ND-LAH(HCl-HNO3)
Comment

  1: 3431.71, 72.48       2: 2917.77, 99.87       3: 2844.49, 102.82       4: 1637.27, 87.10
  5: 1557.24, 93.36       6: 1375.96, 89.15       7: 574.68, 85.46
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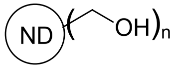
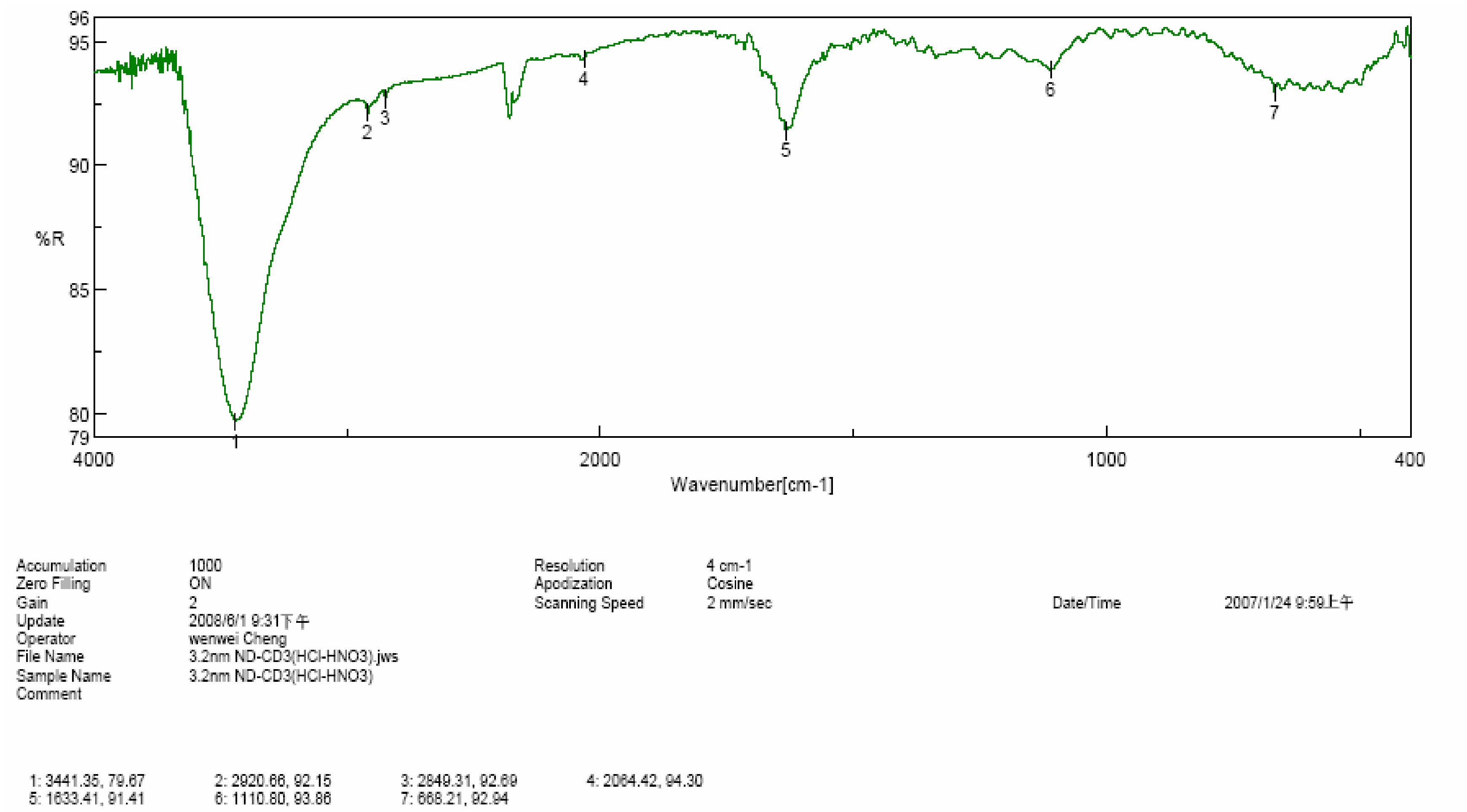


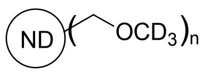
ND-2

Fig. 6 FT-IR spectrum of **ND-2**



Accumulation	1000	Resolution	4 cm-1
Zero Filling	ON	Apodization	Cosine
Gain	2	Scanning Speed	2 mm/sec
Update	2008/6/1 9:31下午	Date/Time	2007/1/24 9:59上午
Operator	wenwei Cheng		
File Name	3.2nm ND-CD3(HCl-HNO3).jws		
Sample Name	3.2nm ND-CD3(HCl-HNO3)		
Comment			

1: 3441.35, 79.67
2: 2920.66, 92.15
3: 2849.31, 92.69
4: 2064.42, 94.30
5: 1633.41, 91.41
6: 1110.80, 93.86
7: 668.21, 92.94



ND-7

Fig. 7 FT-IR spectrum of **ND-7**

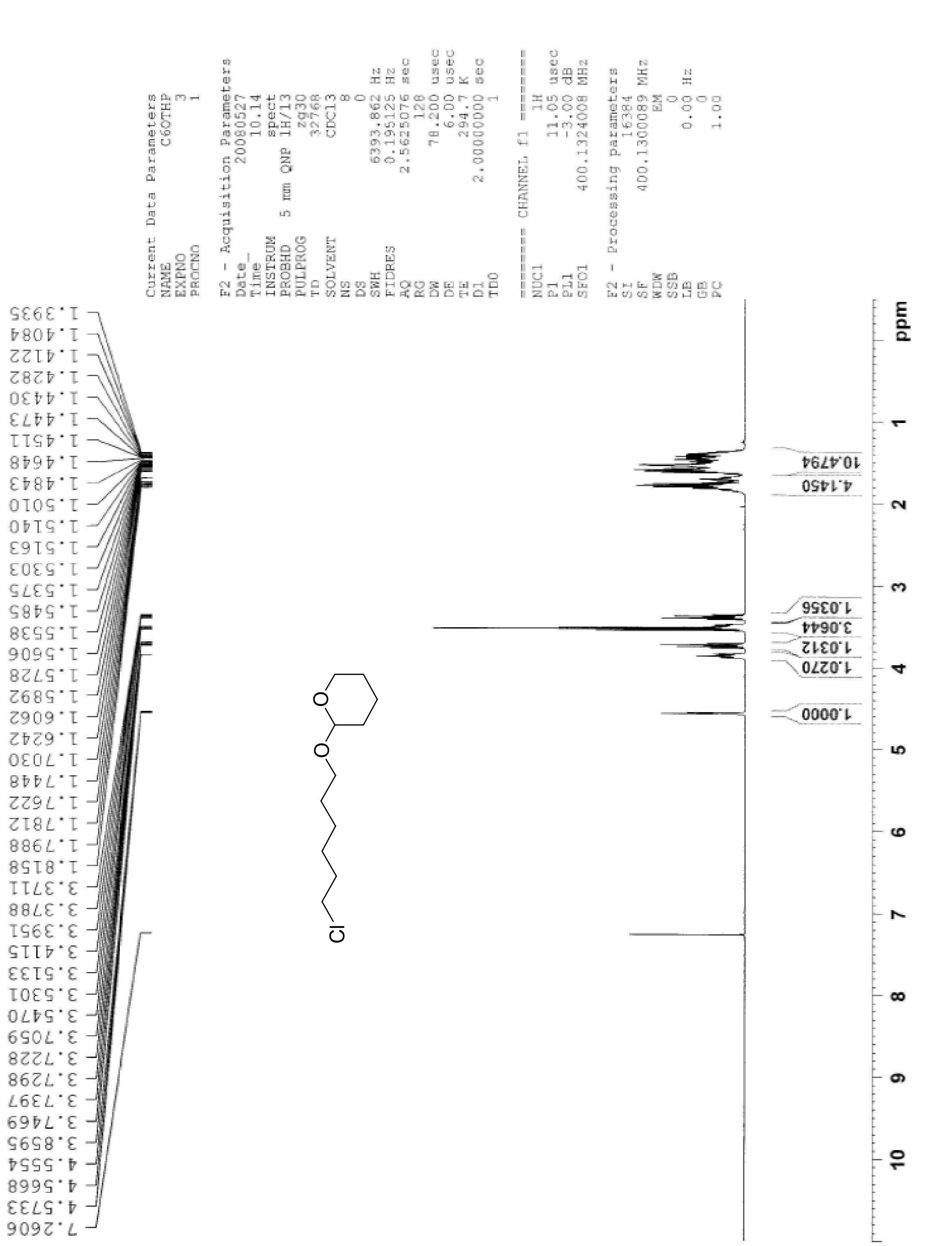
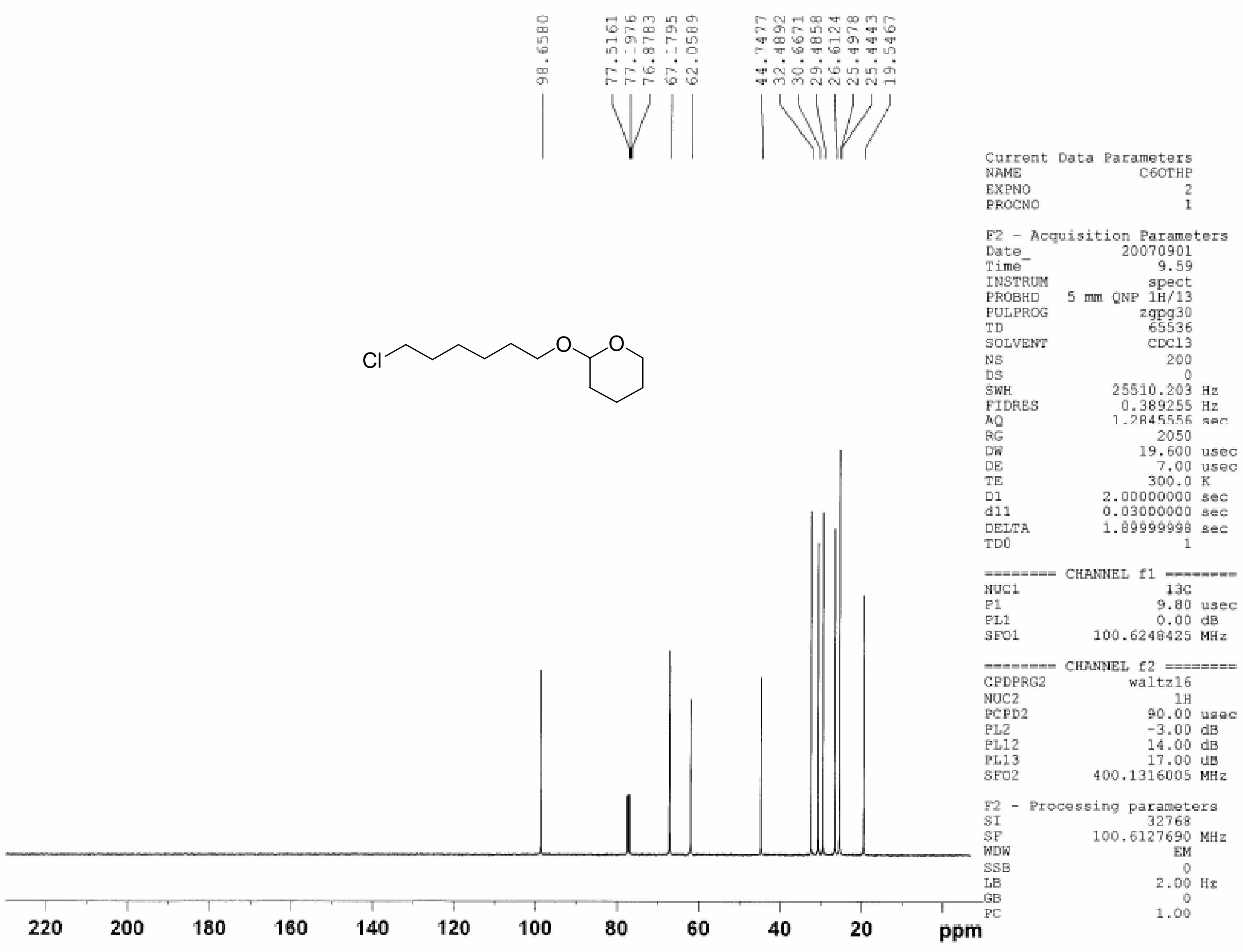


Fig. 8 ^{1}H-NMR spectrum of 6-(chloro-hexyloxy)-tetrahydropyran



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EXPNO                  2
PROCNO                 1

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INSTRUM            spect
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TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     0
SWH            25510.203 Hz
FIDRES          0.389255 Hz
AQ             1.2845556 sec
RG                  2050
DW                19.600 usec
DE                  7.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                 0.00 dB
SFO1         100.6248425 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               14.00 dB
PL13               17.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00
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Fig. 9 ^{13}C-NMR spectrum of 6-(chloro-hexyloxy)-tetrahydropyran

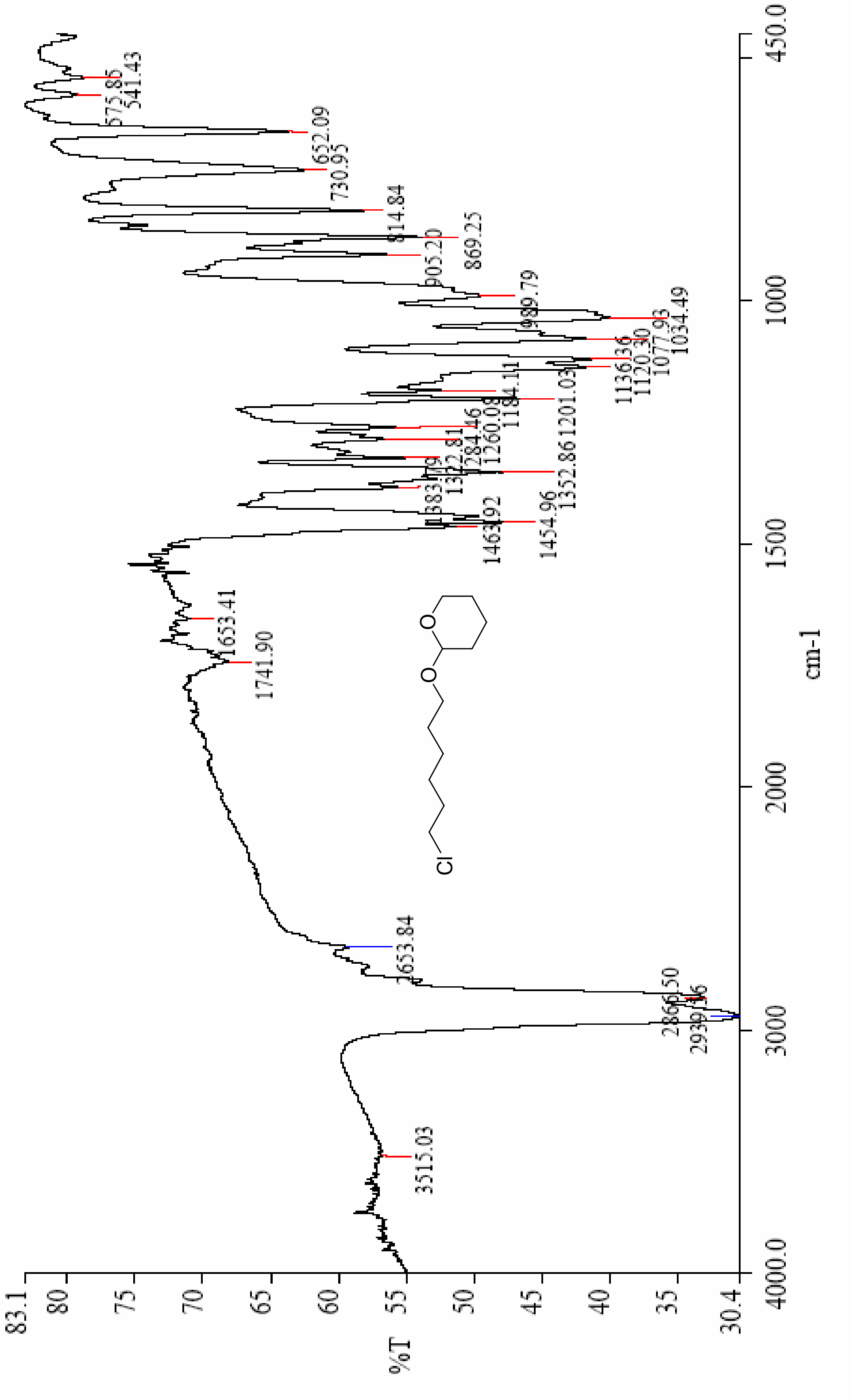
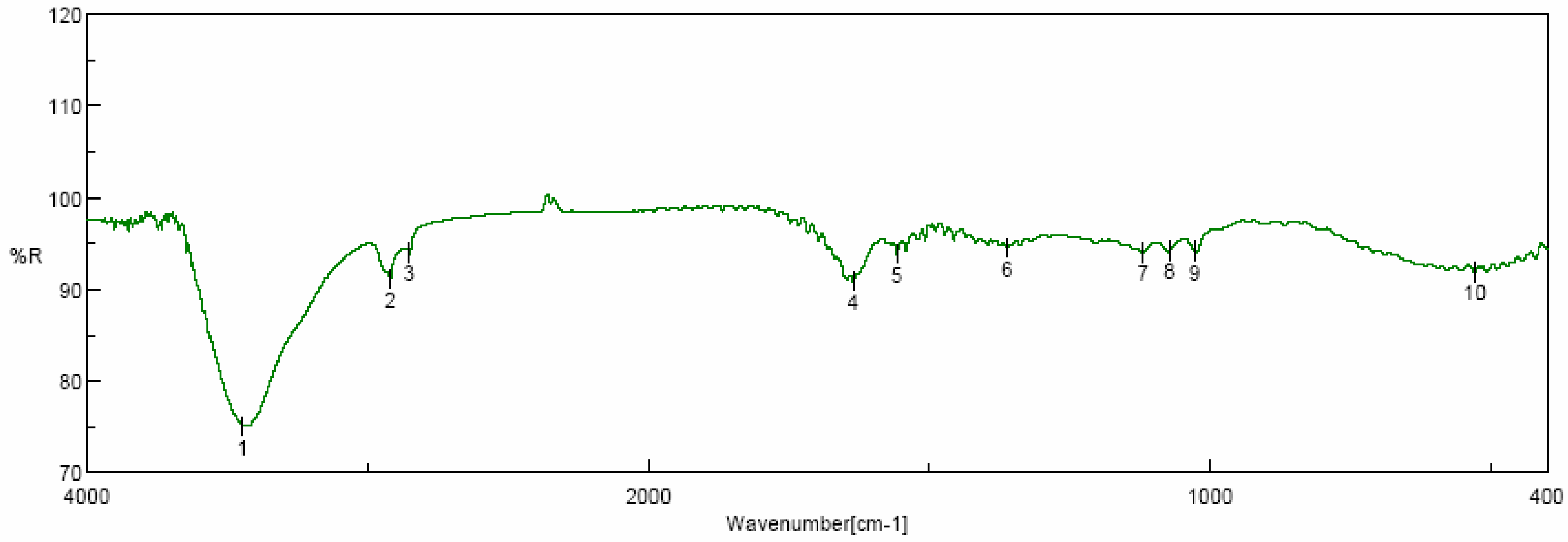


Fig. 10 FT-IR spectrum of 6-(chloro-hexyloxy)-tetrahydropyran tetrahydropyran



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Zero Filling	ON	Apodization	Cosine		
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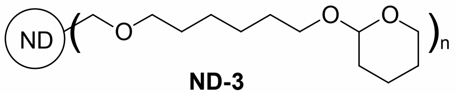
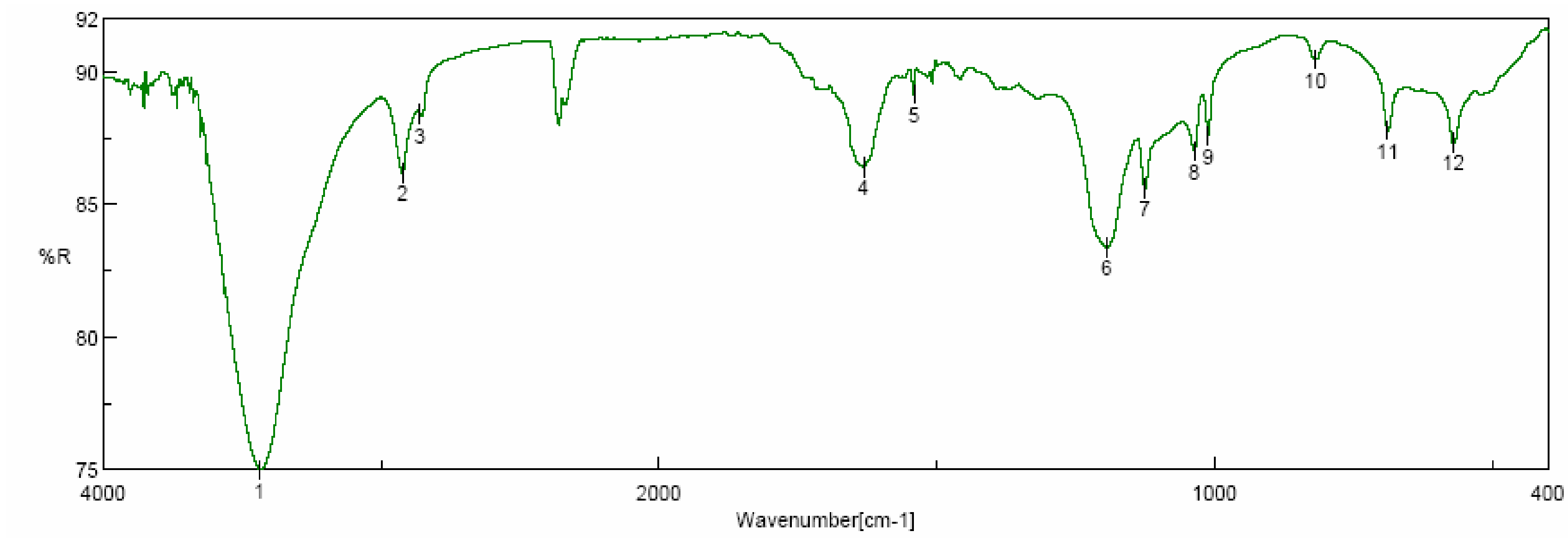
Update	2008/6/1 9:33下午				
Operator	wenwei Cheng				
File Name	3.2nm ND-THP(HCl-HNO3)-2.jws				
Sample Name	3.2nm ND-THP(HCL-HNO3)				
Comment					

1: 3445.21, 75.09 2: 2919.70, 91.08 3: 2853.17, 93.98 4: 1635.34, 90.87
5: 1557.24, 93.87 6: 1361.50, 94.53 7: 1119.48, 93.98 8: 1072.23, 94.20
9: 1027.87, 94.17 10: 528.40, 91.88



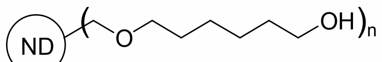
ND-3

Fig. 11 FT-IR spectrum of **ND-3**



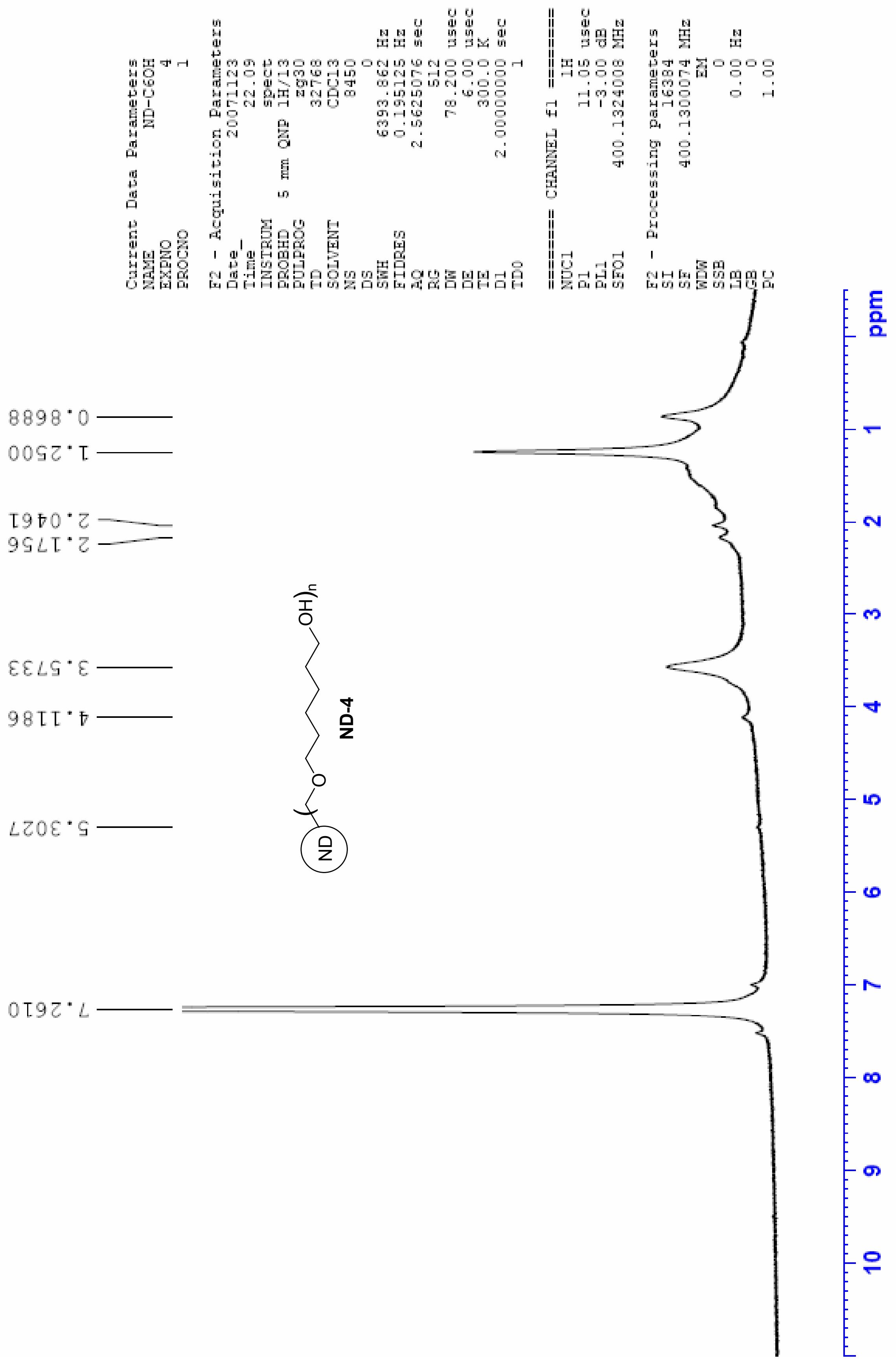
Accumulation	1000	Resolution	4 cm-1
Zero Filling	ON	Apodization	Cosine
Gain	2	Scanning Speed	2 mm/sec
Update	2008/6/1 9:36下午	Date/Time	2007/1/31 3:16下午
Operator	wenwei Cheng		
File Name	Memory#16		
Sample Name	3.2nm ND-OH(HCl-HNO3)		
Comment			

1: 3437.49, 75.02	2: 2923.56, 86.17	3: 2859.92, 88.39	4: 1631.48, 86.38
5: 1540.85, 89.17	6: 1193.72, 83.37	7: 1125.26, 85.60	8: 1036.55, 86.99
9: 1011.48, 87.58	10: 818.63, 90.44	11: 688.46, 87.77	12: 569.86, 87.32



ND-4

Fig. 12 FT-IR spectrum of **ND-4**



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PROCNO               1

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TD               32768
SOLVENT          CDCl3
NS                8450
DS                   0
SWH           6393.862 Hz
FIDRES        0.195125 Hz
AQ           2.5625076 sec
RG                 512
DW              78.200 usec
DE                6.00 usec
TE               300.0 K
D1          2.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               11.05 usec
PL1              -3.00 dB
SFO1       400.1324008 MHz

F2 - Processing parameters
SI               16384
SF         400.1300074 MHz
WDW                 EM
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00
```
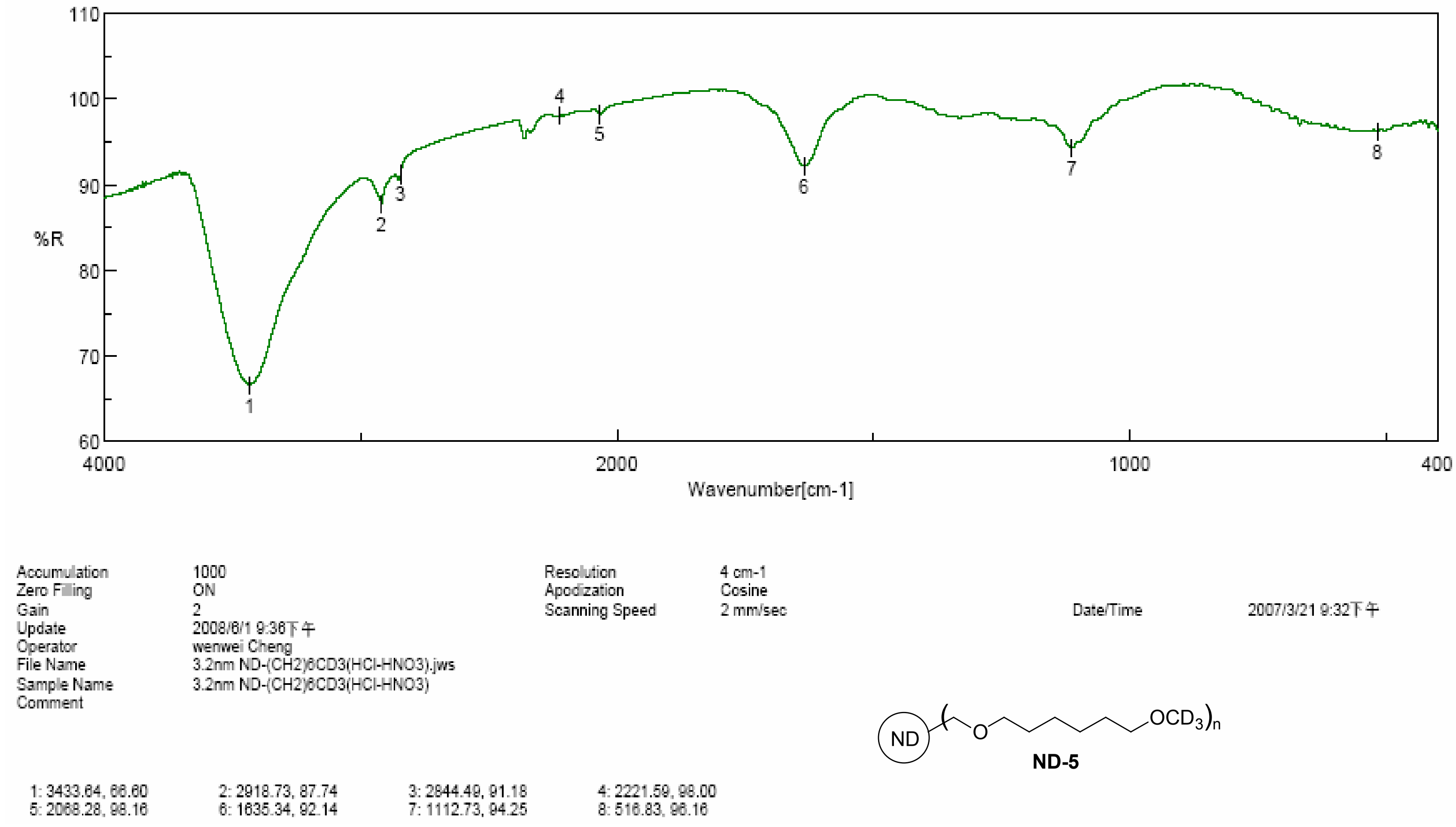

Fig. 13 ^{1}H-NMR spectrum of **ND-4**



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Gain 2
Update 2008/6/1 9:36下午
Operator wenwei Cheng
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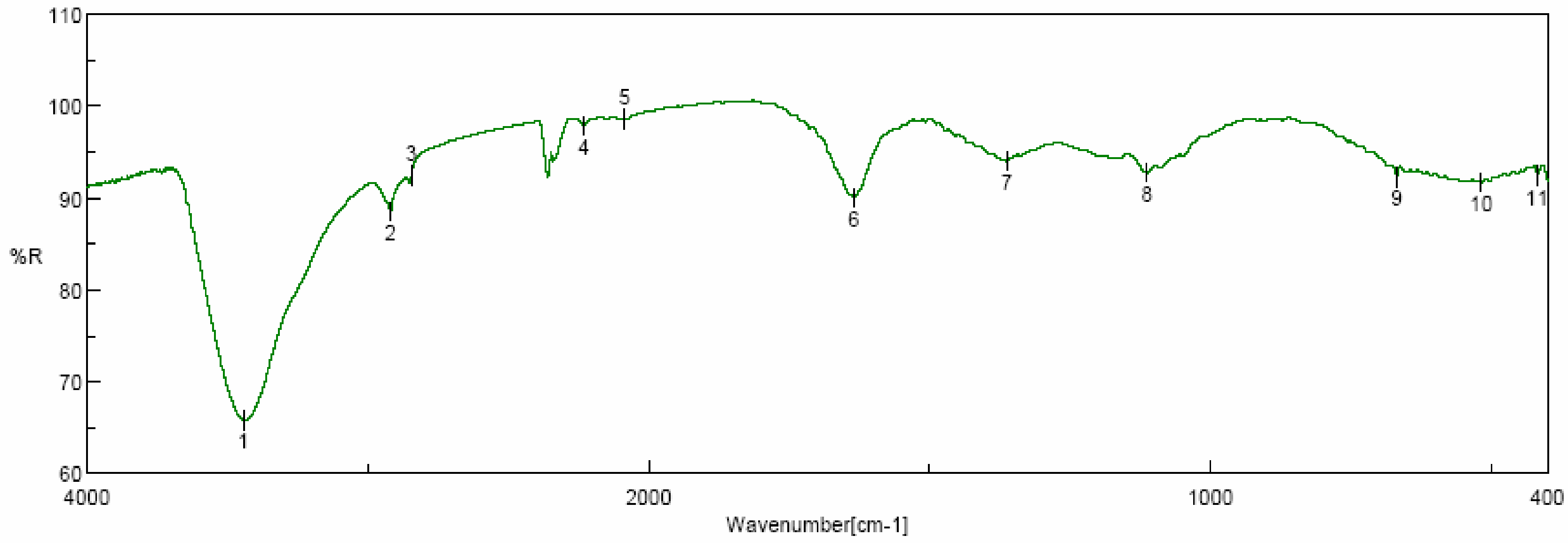
Sample Name 3.2nm ND-(CH2)6CD3(HCl-HNO3)
Comment

Resolution 4 cm-1
Apodization Cosine
Scanning Speed 2 mm/sec

Date/Time 2007/3/21 9:32下午

1: 3433.64, 66.60
2: 2918.73, 87.74
3: 2844.49, 91.18
4: 2221.59, 98.00
5: 2068.28, 98.16
6: 1635.34, 92.14
7: 1112.73, 94.25
8: 516.83, 96.16

Fig. 14 FT-IR spectrum of **ND-5**



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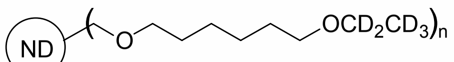
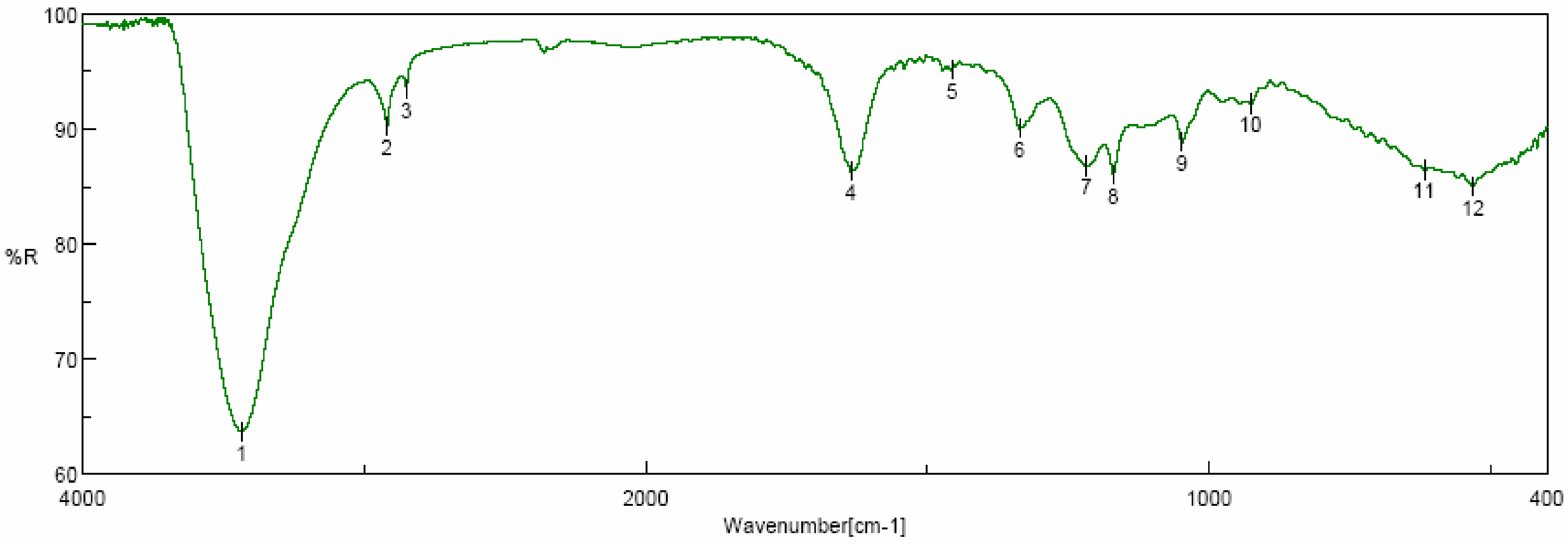
Zero Filling	ON
Gain	2
Update	2008/6/1 9:37下午
Operator	wenwei Cheng
File Name	3.2nm ND-(CH2)6CD2CD3(HCl-HNO3).jws
Sample Name	3.2nm ND-(CH2)6CD2CD3(HCl-HNO3)
Comment	
Resolution	4 cm-1
Apodization	Cosine
Scanning Speed	2 mm/sec
Date/Time	2007/3/21 9:52下午

1: 3443.28, 65.84
2: 2918.73, 88.50
3: 2844.49, 92.43
4: 2230.27, 97.87
5: 2085.64, 98.56
6: 1634.38, 90.05
7: 1362.46, 93.98
8: 1112.73, 92.70
9: 668.21, 92.22
10: 517.79, 91.63
11: 418.48, 92.42



ND-6

Fig. 15 FT-IR spectrum of **ND-6**



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Accumulation        1000                              Resolution        4 cm-1
Zero Filling        ON                                Apodization       Cosine
Gain                2                                 Scanning Speed    2 mm/sec                  Date/Time      2007/2/9 10:02上午
Update              2008/6/1 9:39下午
Operator            wenwei Cheng
File Name           3.2nm ND-Ms(HCl-HNO3)-3.jws
Sample Name         3.2nm ND-Ms(HCl-HNO3)
Comment

 1: 3434.60, 63.74     2: 2918.73, 90.31     3: 2850.27, 93.45     4: 1635.34, 86.33
 5: 1455.99, 95.13     6: 1336.43, 90.06     7: 1217.83, 86.78     8: 1169.62, 86.04
 9: 1048.12, 88.86    10: 926.63, 92.21     11: 618.07, 86.46     12: 531.29, 85.02
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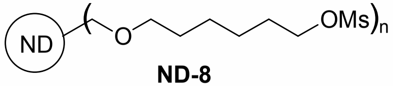
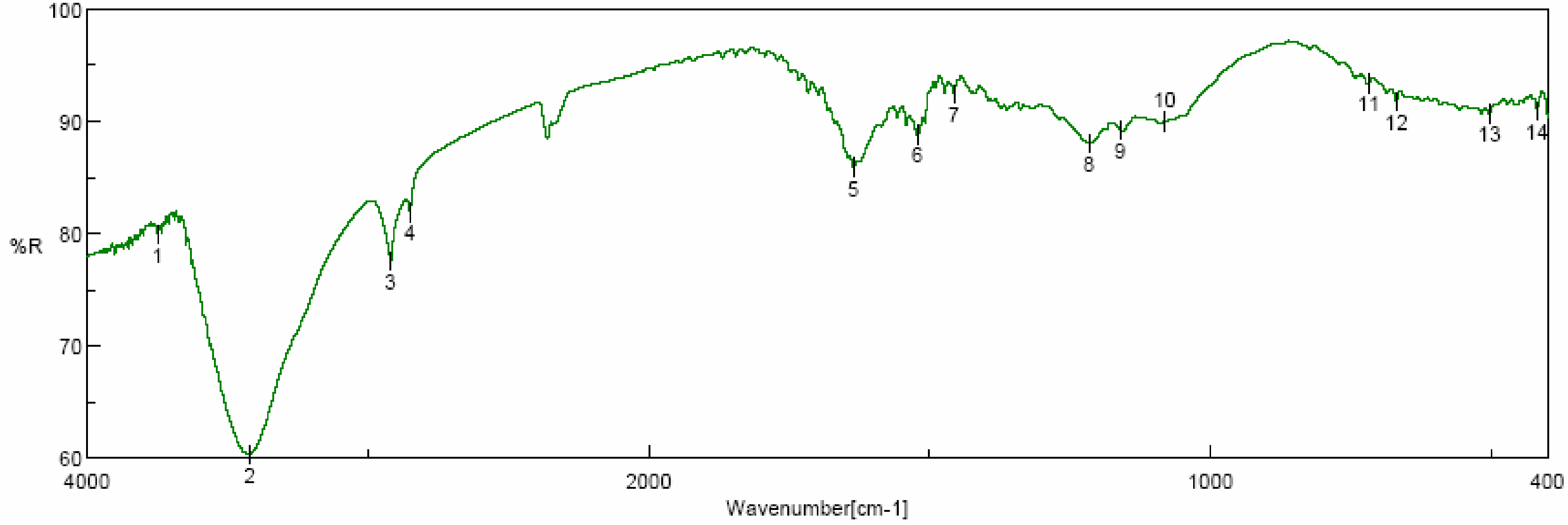


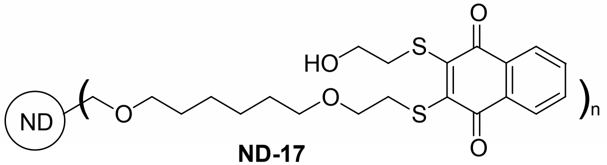
ND-8

Fig. 16 FT-IR spectrum of **ND-8**



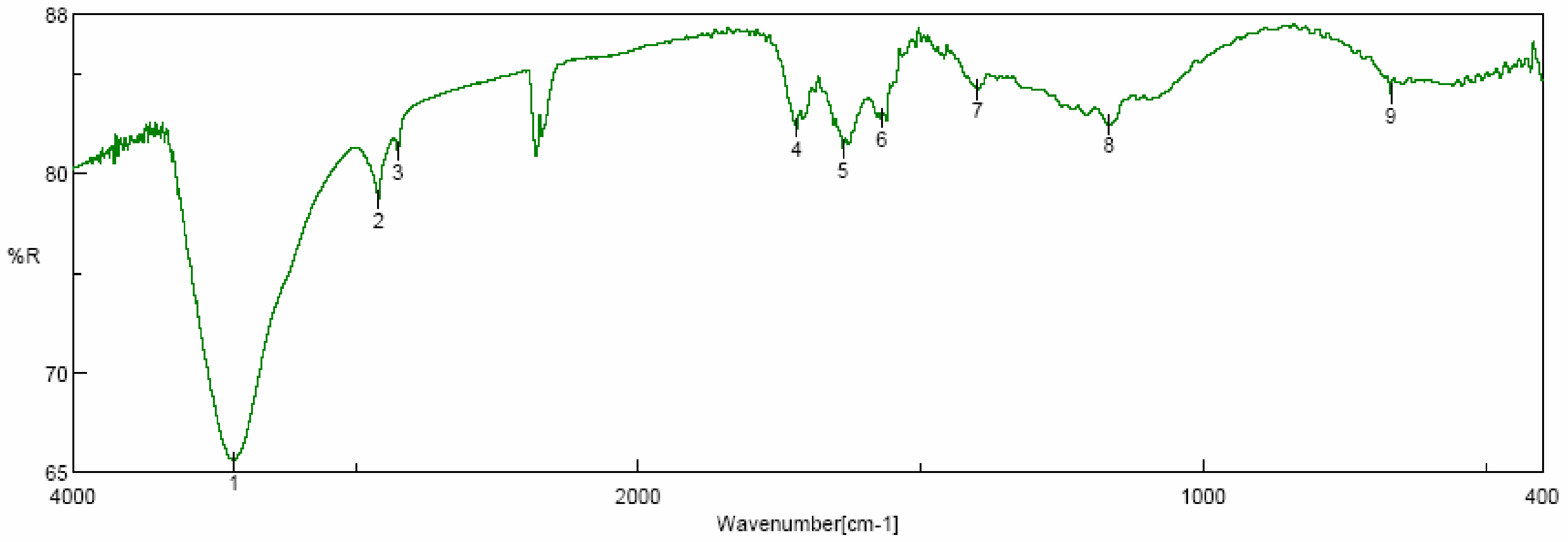
Accumulation	1000	Resolution	4 cm-1
Zero Filling	ON	Apodization	Cosine
Gain	2	Scanning Speed	2 mm/sec
Update	2008/6/1 9:40下午	Date/Time	2007/3/21 10:13下午
Operator	wenwei Cheng		
File Name	3.2nm ND-(CH2)6VK3(HCl-HNO3).jws		
Sample Name	3.2nm ND-(CH2)6VK3(HCl-HNO3)		
Comment			

1: 3748.94, 79.95
2: 3420.14, 60.37
3: 2918.73, 77.59
4: 2850.27, 81.92
5: 1635.34, 85.93
6: 1521.56, 88.85
7: 1456.96, 92.48
8: 1215.90, 88.09
9: 1160.94, 89.22
10: 1081.87, 89.98
11: 718.35, 93.41
12: 669.18, 91.76
13: 503.33, 90.68
14: 418.48, 90.94



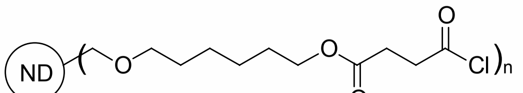
ND-17

Fig. 17 FT-IR spectrum of **ND-17**



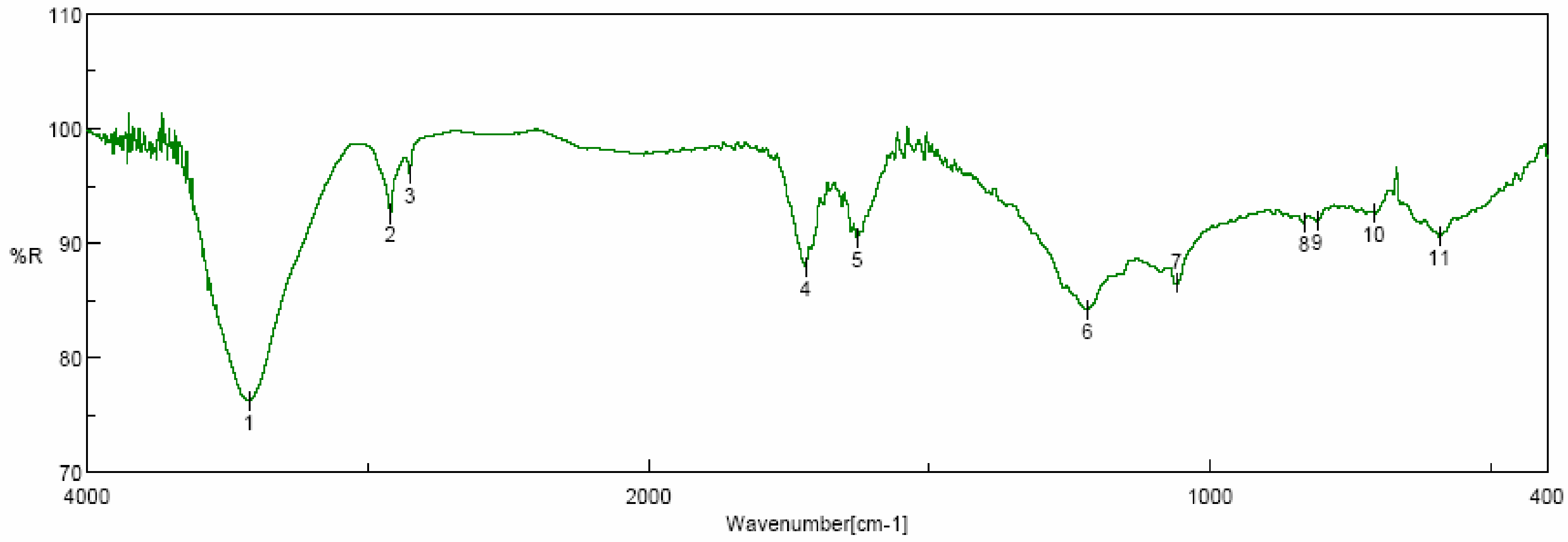
Accumulation	1000	Resolution	4 cm-1
Zero Filling	ON	Apodization	Cosine
Gain	2	Scanning Speed	2 mm/sec
Update	2008/6/1 9:42下午	Date/Time	2007/4/3 3:54下午
Operator	wenwei Cheng		
File Name	3.2nm ND-succinic anhydride(HCl-HNO3).jws		
Sample Name	3.2nm ND-succinic anhydride(HCl-HNO3)		
Comment			

1: 3430.74, 65.61	2: 2918.73, 78.69	3: 2849.31, 81.10	4: 1719.23, 82.27
5: 1637.27, 81.26	6: 1568.81, 82.78	7: 1399.10, 84.19	8: 1166.72, 82.45
9: 668.21, 83.99			



ND-18

Fig. 18 FT-IR spectrum of **ND-18**



Accumulation	1000	Resolution	4 cm-1		
Zero Filling	ON	Apodization	Cosine		
Gain	2	Scanning Speed	2 mm/sec	Date/Time	2007/4/11 11:30上午
Update	2008/6/1 9:45下午				
Operator	wenwei Cheng				
File Name	Memory#22				
Sample Name	3.2nm ND-COCl(HCl-HNO3)				
Comment					

1: 3423.03, 76.25　2: 2919.70, 92.58　3: 2849.31, 96.07　4: 1720.19, 87.96
5: 1628.59, 90.50　6: 1218.79, 84.21　7: 1059.69, 86.54　8: 832.13, 91.84
9: 809.96, 91.96　10: 708.71, 92.63　11: 592.04, 90.59

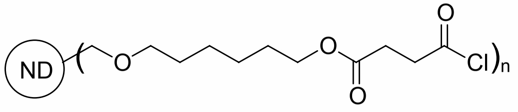
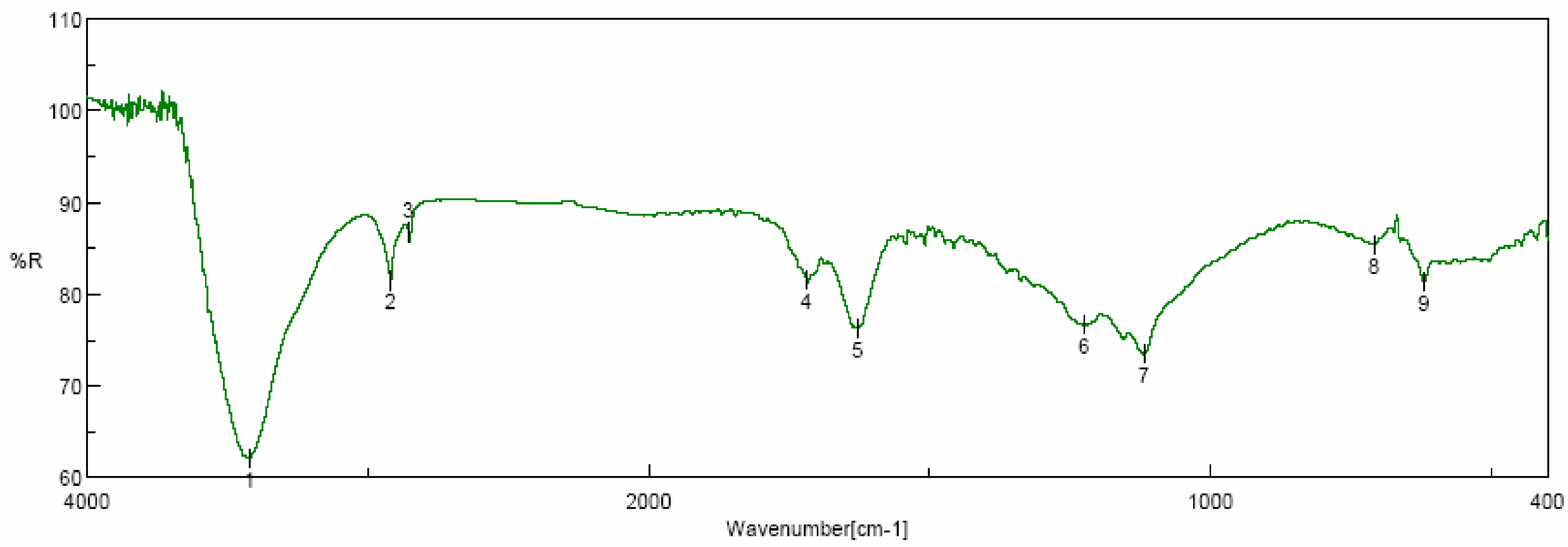


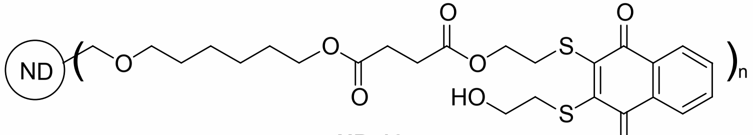
Fig. 19 FT-IR spectrum of acid chloride of **ND-18**



Accumulation	1000	Resolution	4 cm-1
Zero Filling	ON	Apodization	Cosine
Gain	2	Scanning Speed	2 mm/sec
Update	2008/6/1 9:46下午		
Operator	wenwei Cheng		
File Name	Memory#23		
Sample Name	3.2nm ND-COK3-231(HCl-HNO3)		
Comment			

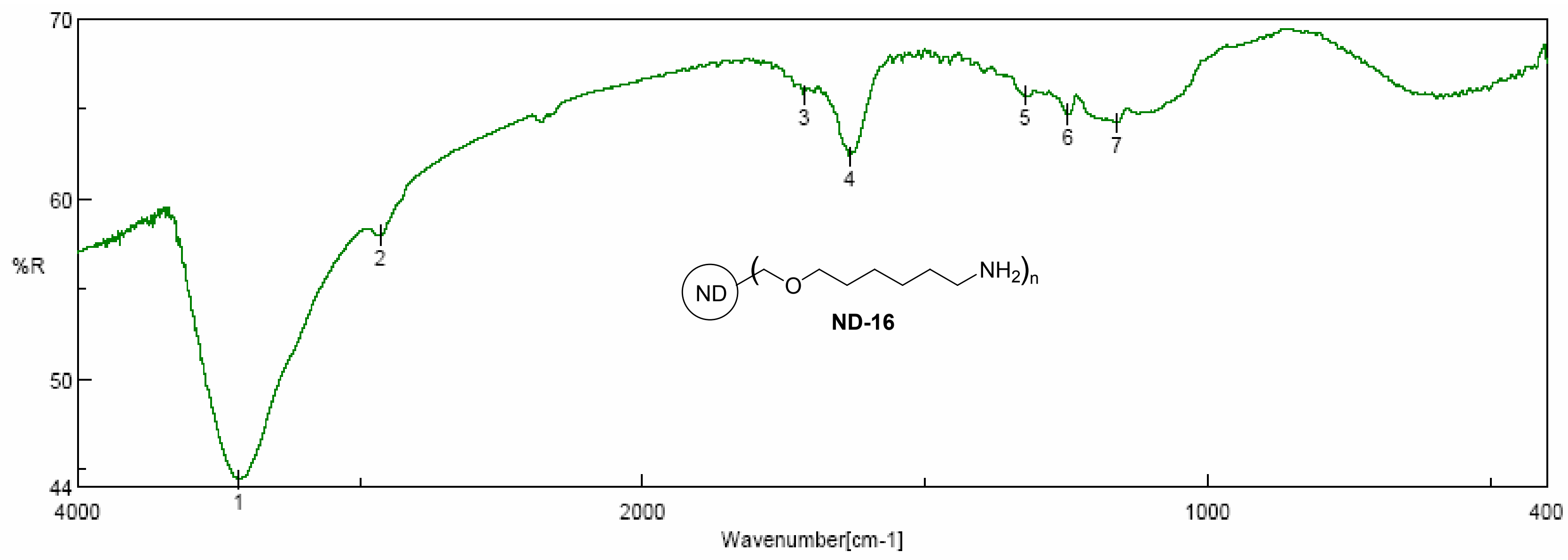
Date/Time 2007/4/11 11:52上午

1: 3422.06, 62.17
2: 2918.73, 81.48
3: 2856.06, 86.73
4: 1719.23, 81.54
5: 1628.59, 76.31
6: 1225.54, 76.69
7: 1118.51, 73.48
8: 708.71, 85.42
9: 620.00, 81.29



ND-19

Fig. 20 FT-IR spectrum of **ND-19**



Accumulation	1000	Resolution	4 cm-1				
Zero Filling	OFF	Apodization	Cosine				
Gain	2	Scanning Speed	2 mm/sec	Date/Time	2007/8/2 5:07下午		
Update	2008/6/2 10:28上午						
Operator	wenwei Cheng						
File Name	3.2nm ND-C6-NH2(HCl-HNO3)-2.jws						
Sample Name	3.2nm ND-C6-NH2(HCl-HNO3)						
Comment							

1: 3430.74, 44.44　2: 2929.34, 58.00　3: 1714.41, 65.78　4: 1633.41, 62.37
5: 1322.93, 65.74　6: 1247.72, 64.69　7: 1160.94, 64.24

Fig. 21 FT-IR spectrum of **ND-16**

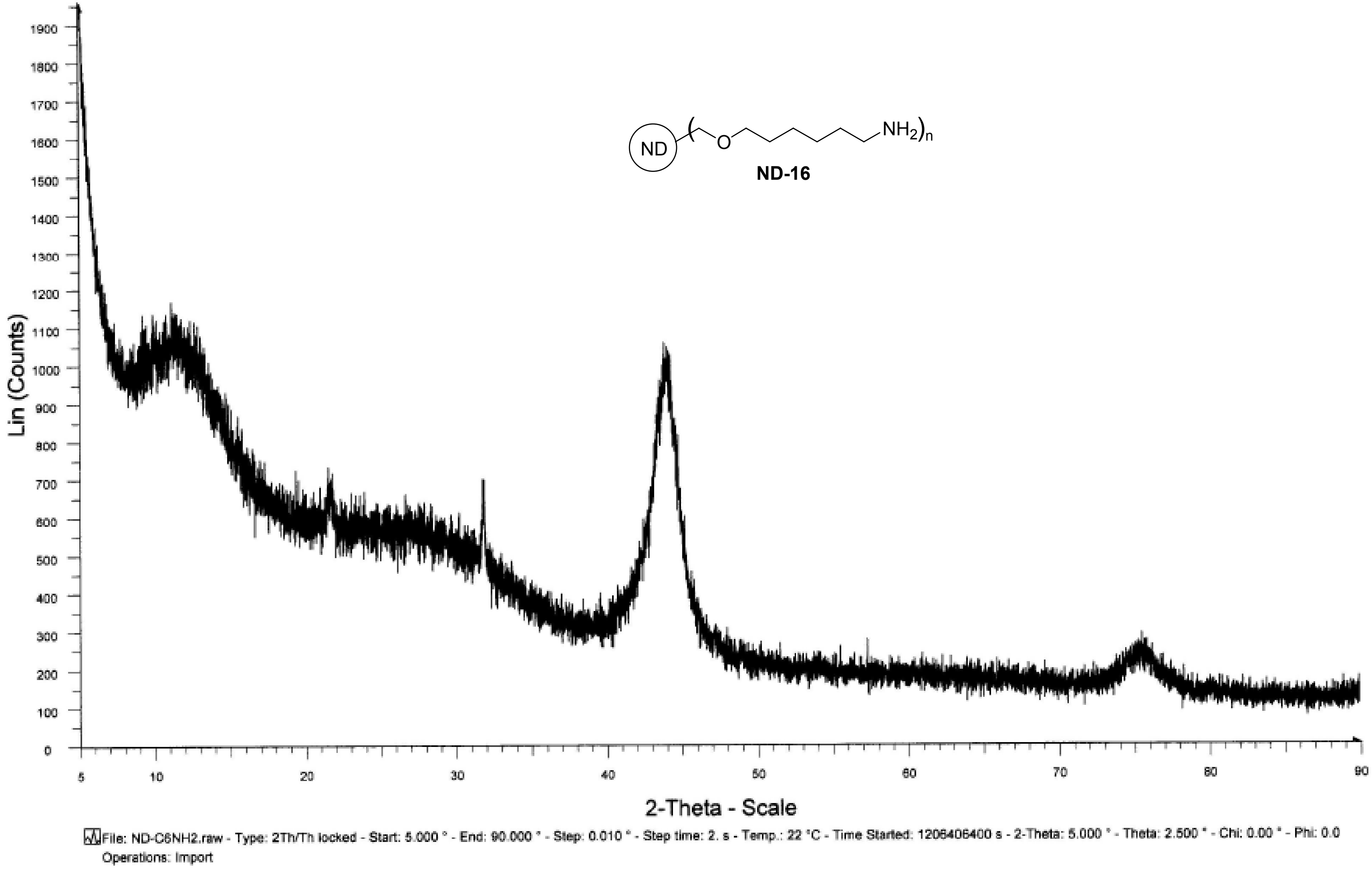


Fig. 22 Powder XRD pattern of **ND-16**

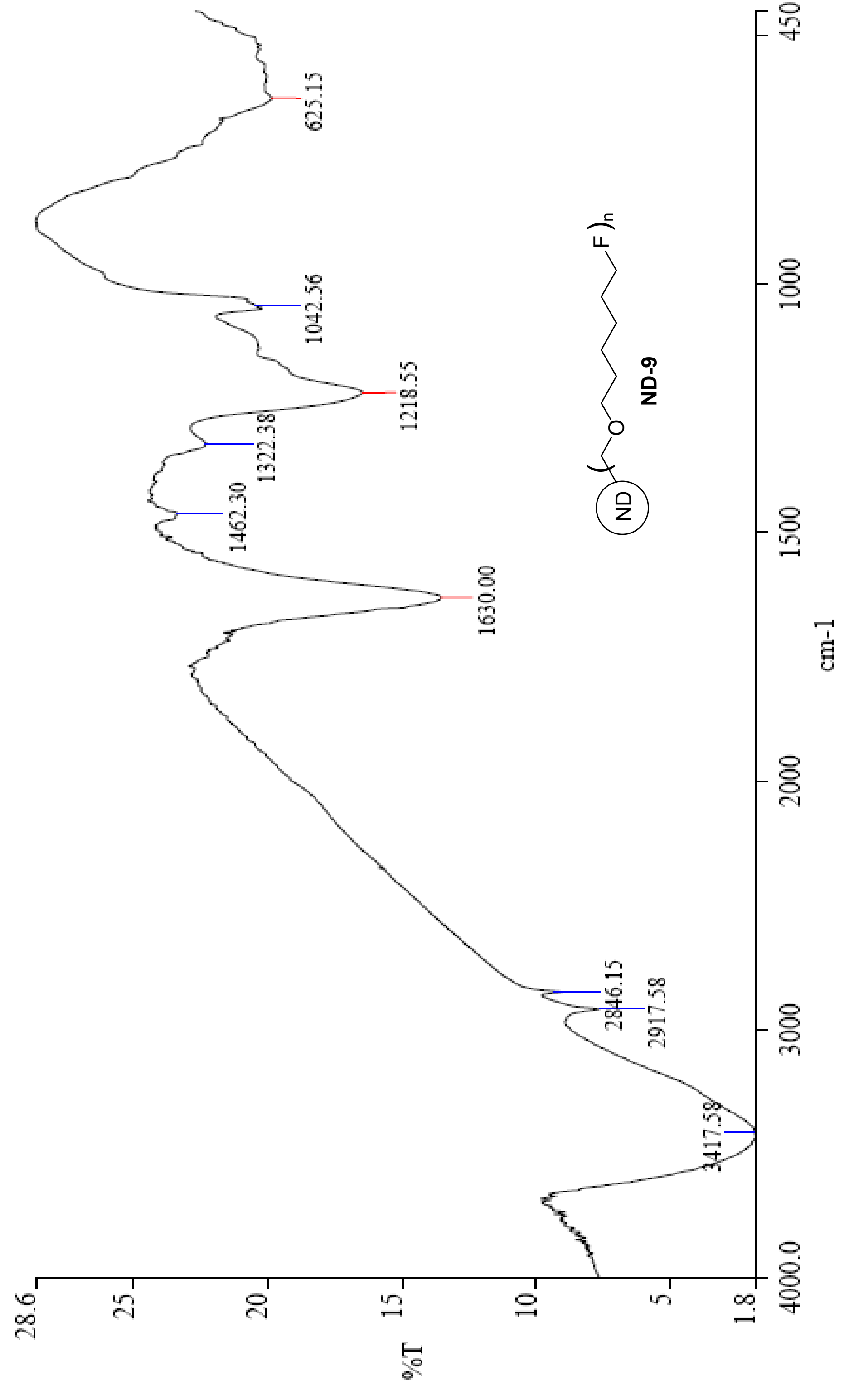


Fig. 23 FT-IR spectrum of **ND-9**

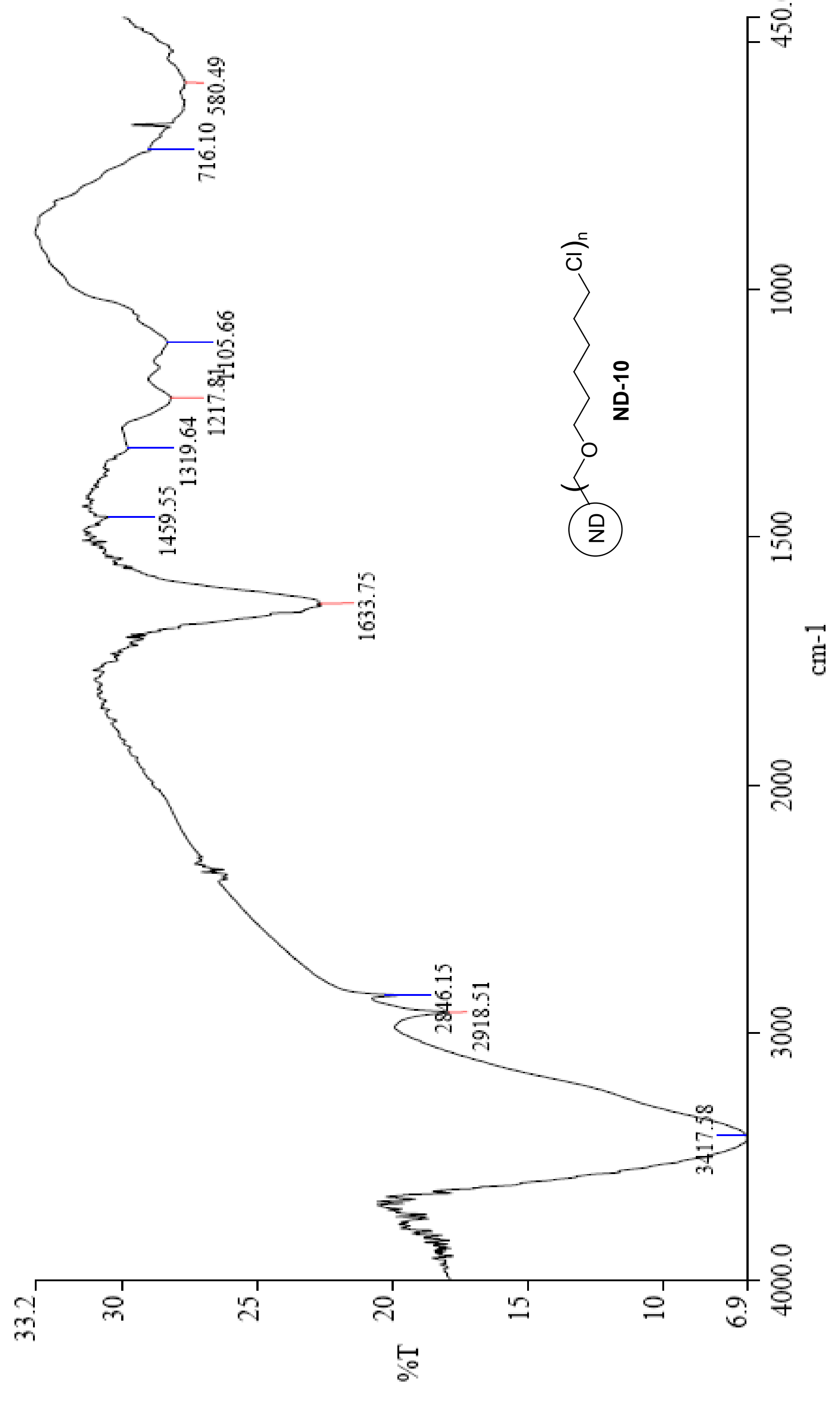


Fig. 24 FT-IR spectrum of **ND-10**

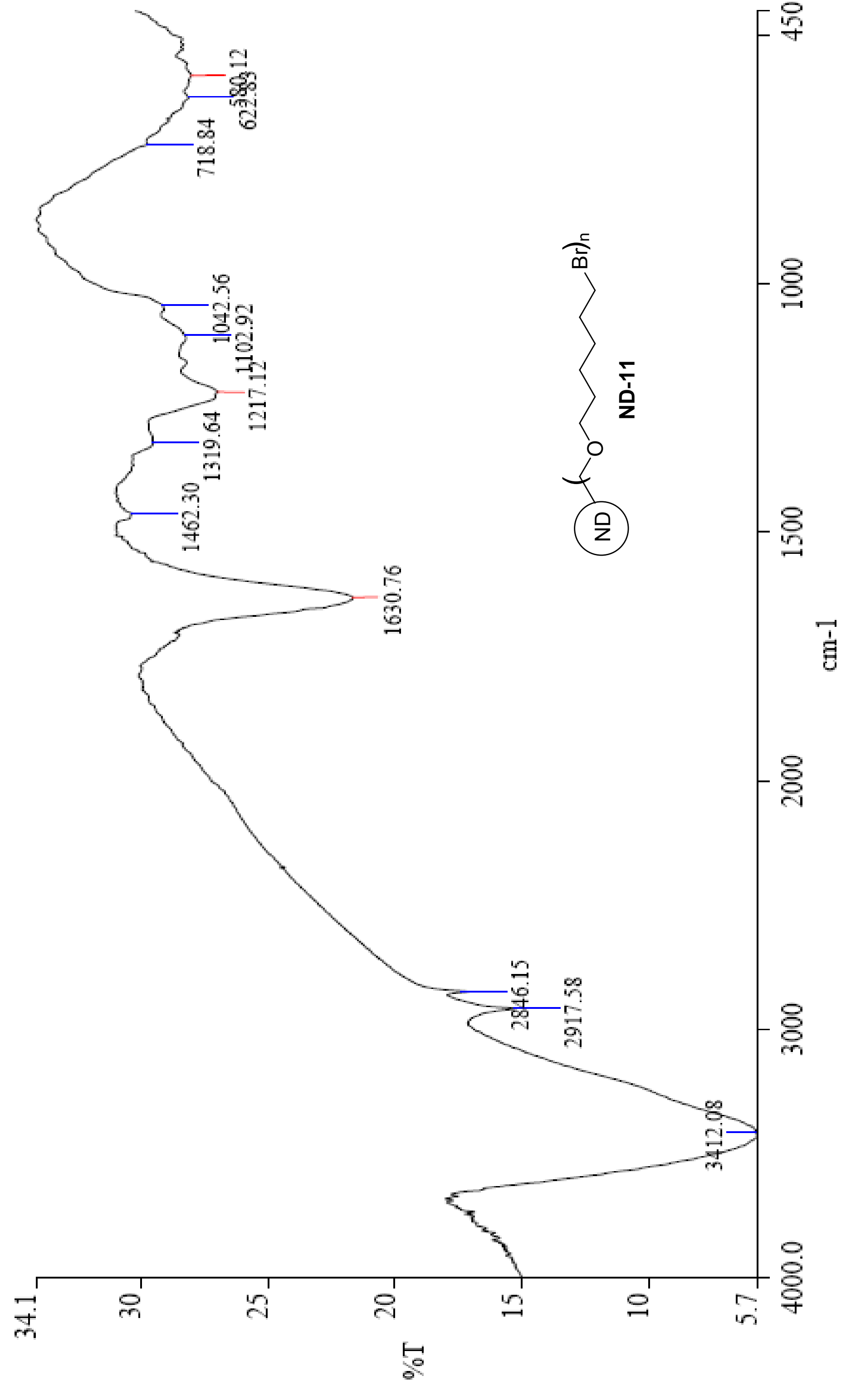


Fig. 25 FT-IR spectrum of **ND-11**

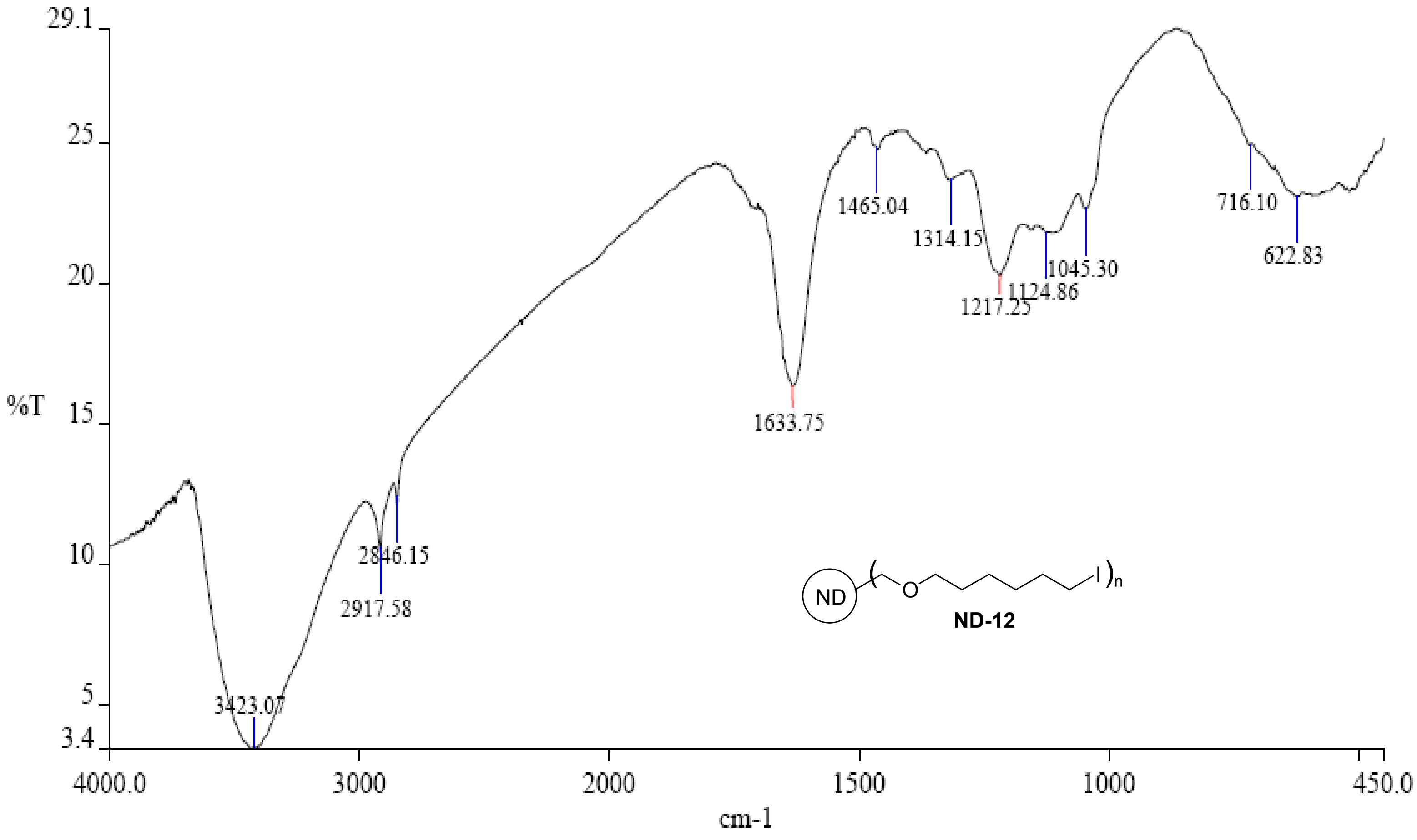


Fig. 26 FT-IR spectrum of **ND-12**

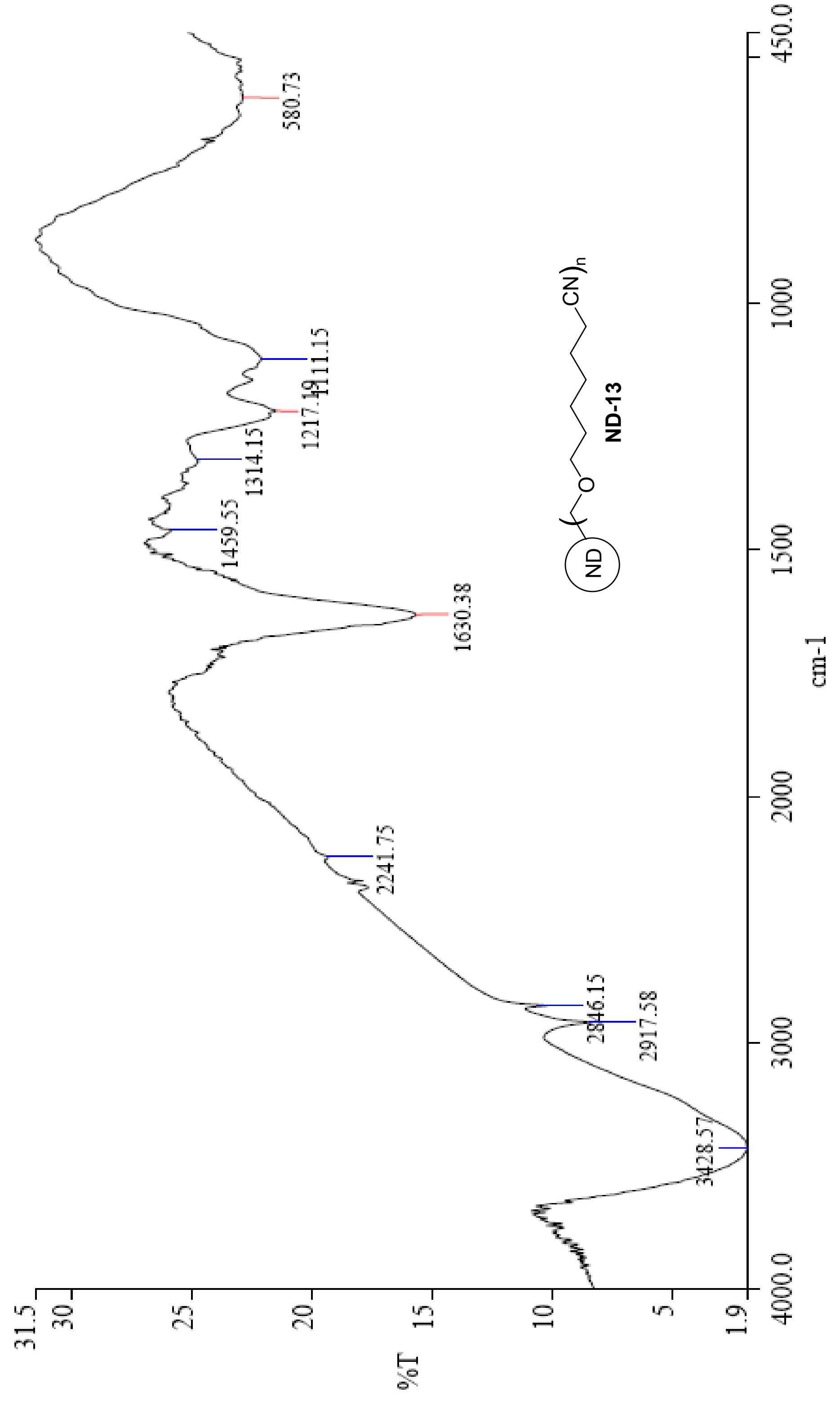


Fig. 27 FT-IR spectrum of **ND-13**

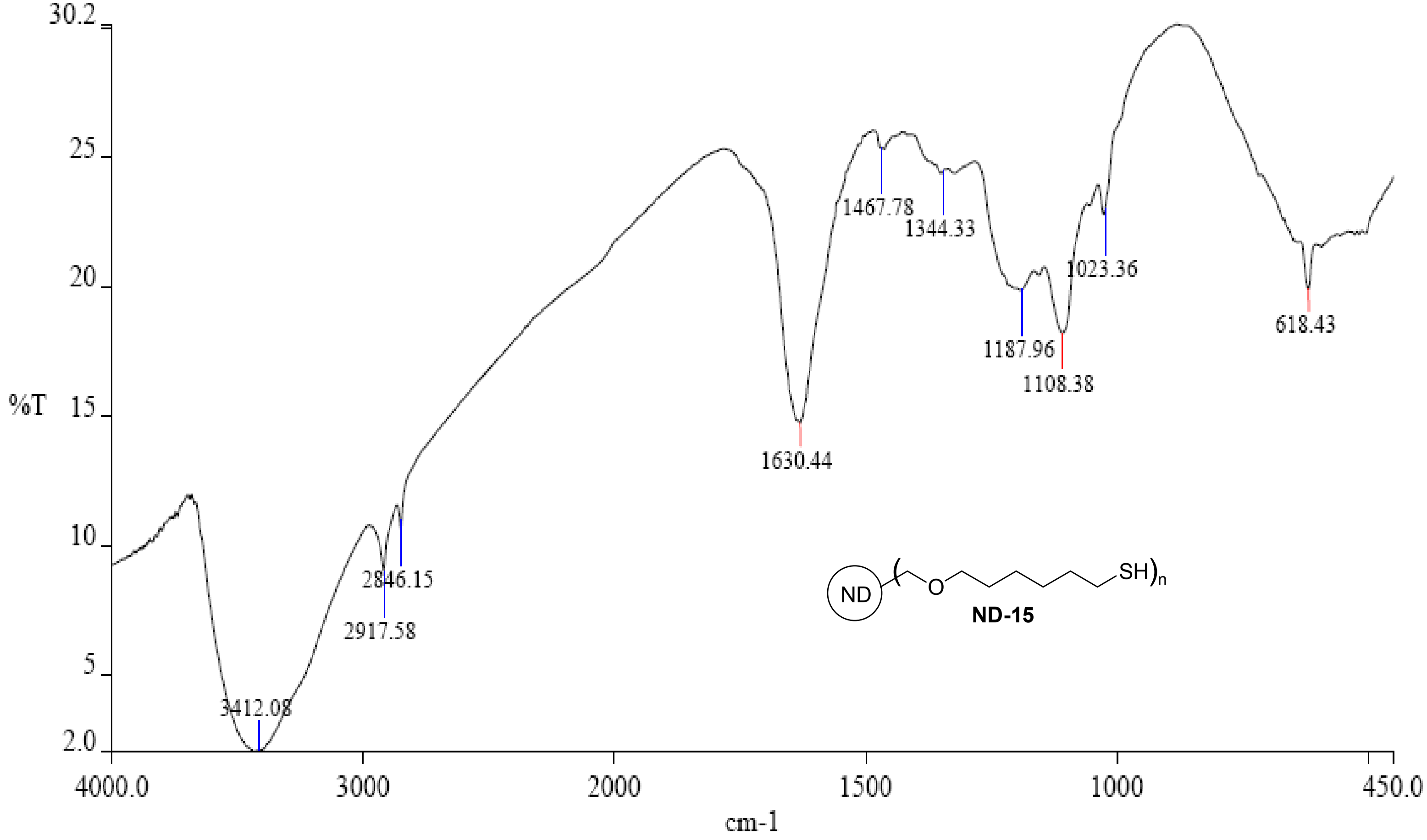


Fig. 28 FT-IR spectrum of **ND-15**

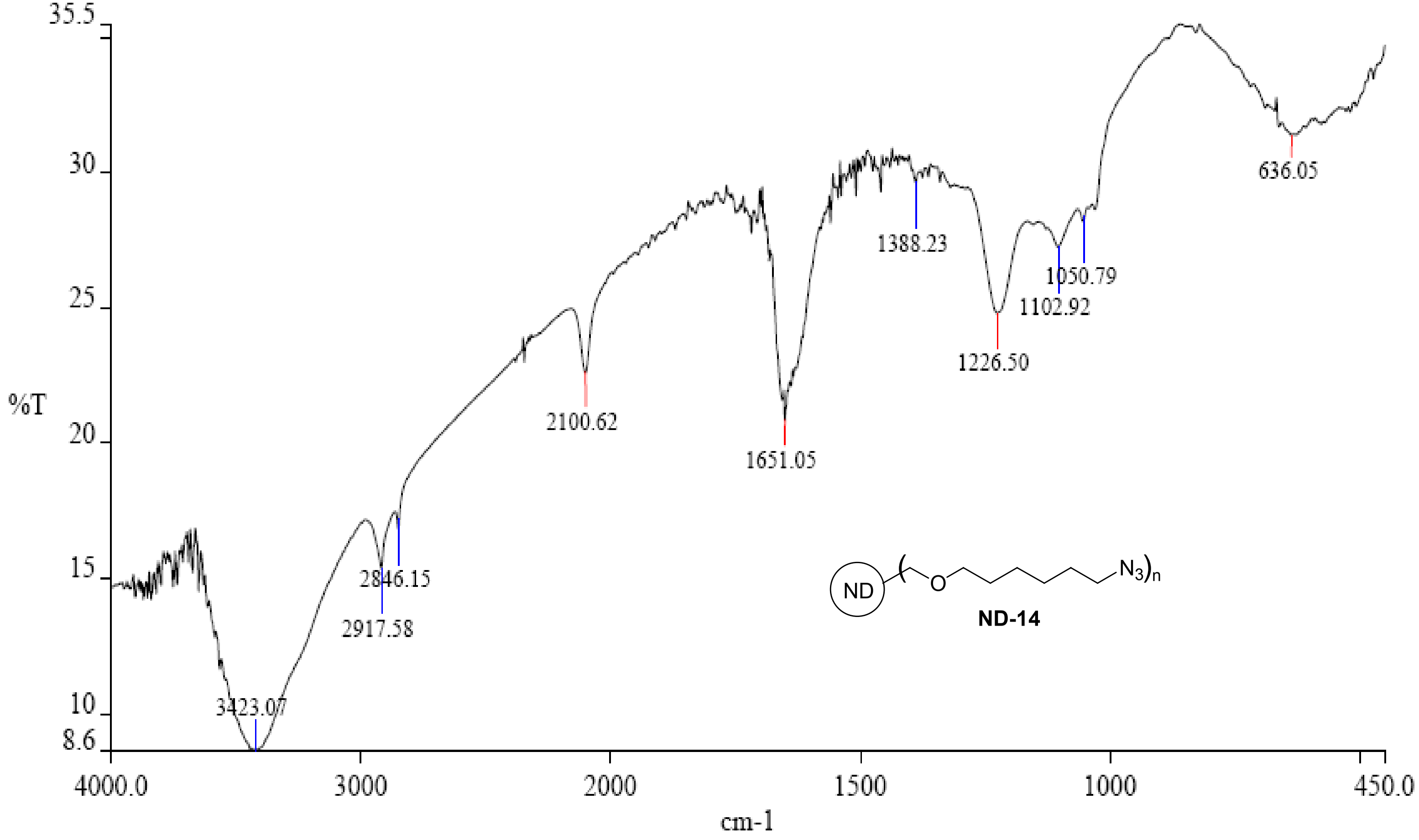


Fig. 29 FT-IR spectrum of **ND-14**

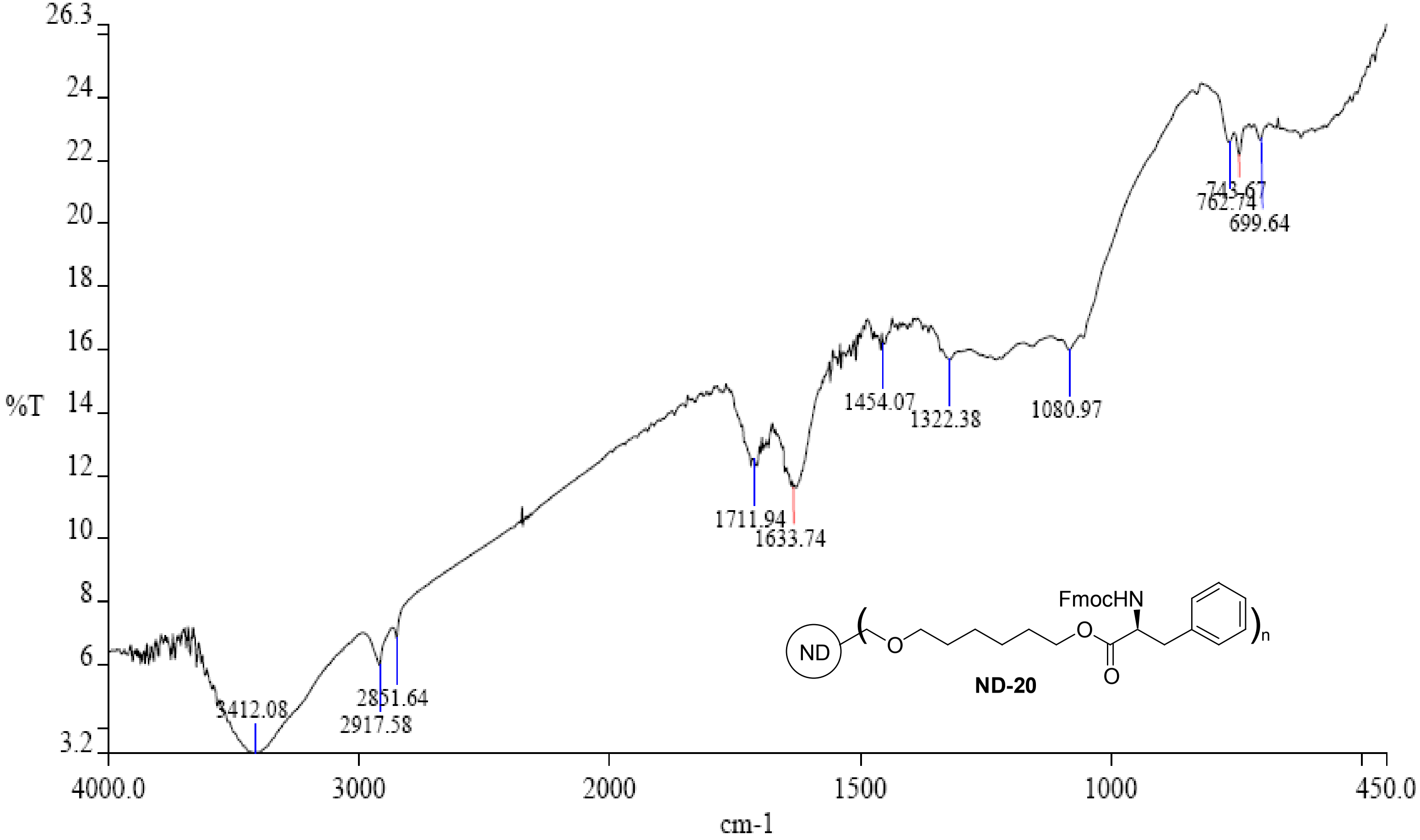


Fig. 30 FT-IR spectrum of **ND-20**

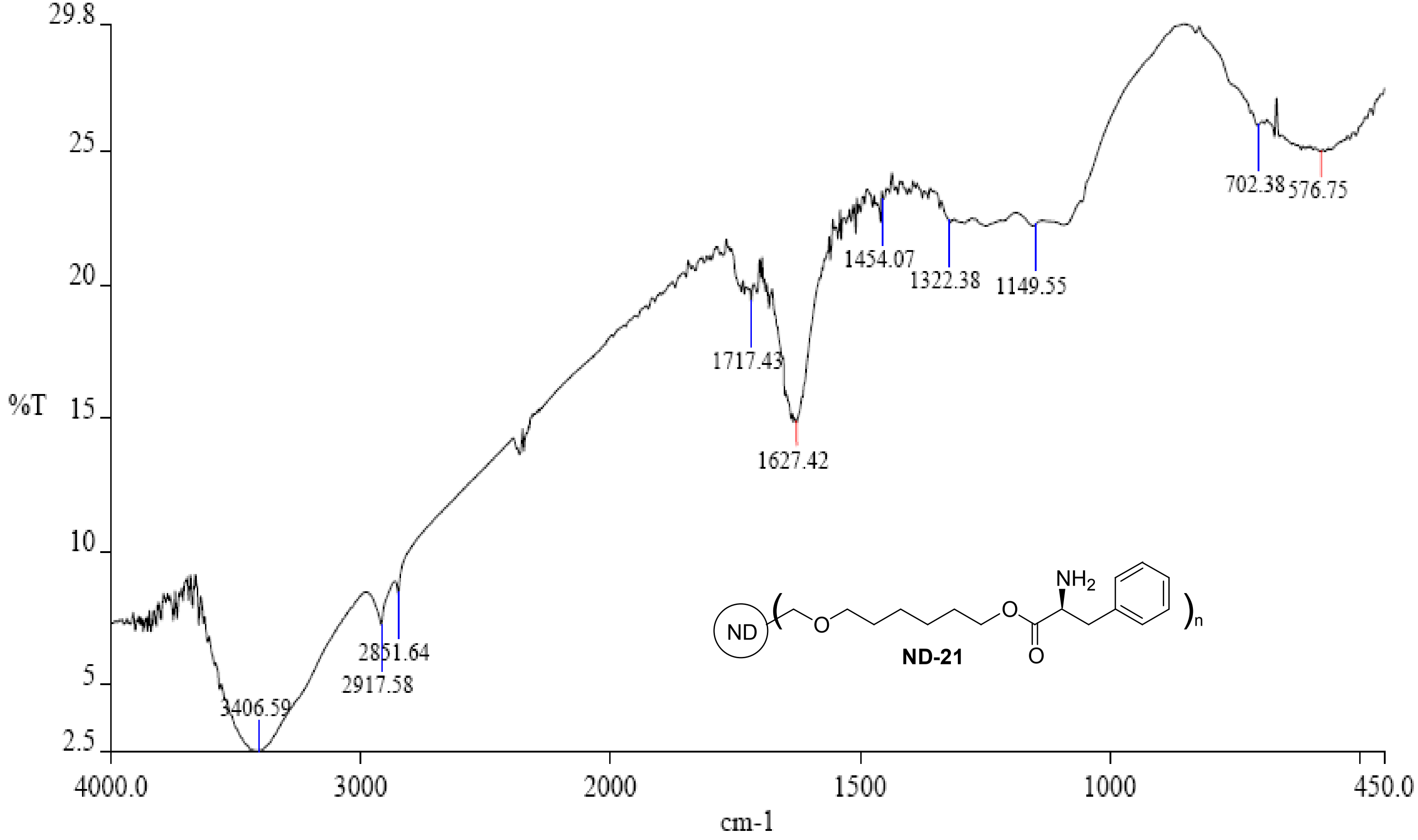


Fig. 31 FT-IR spectrum of **ND-21**

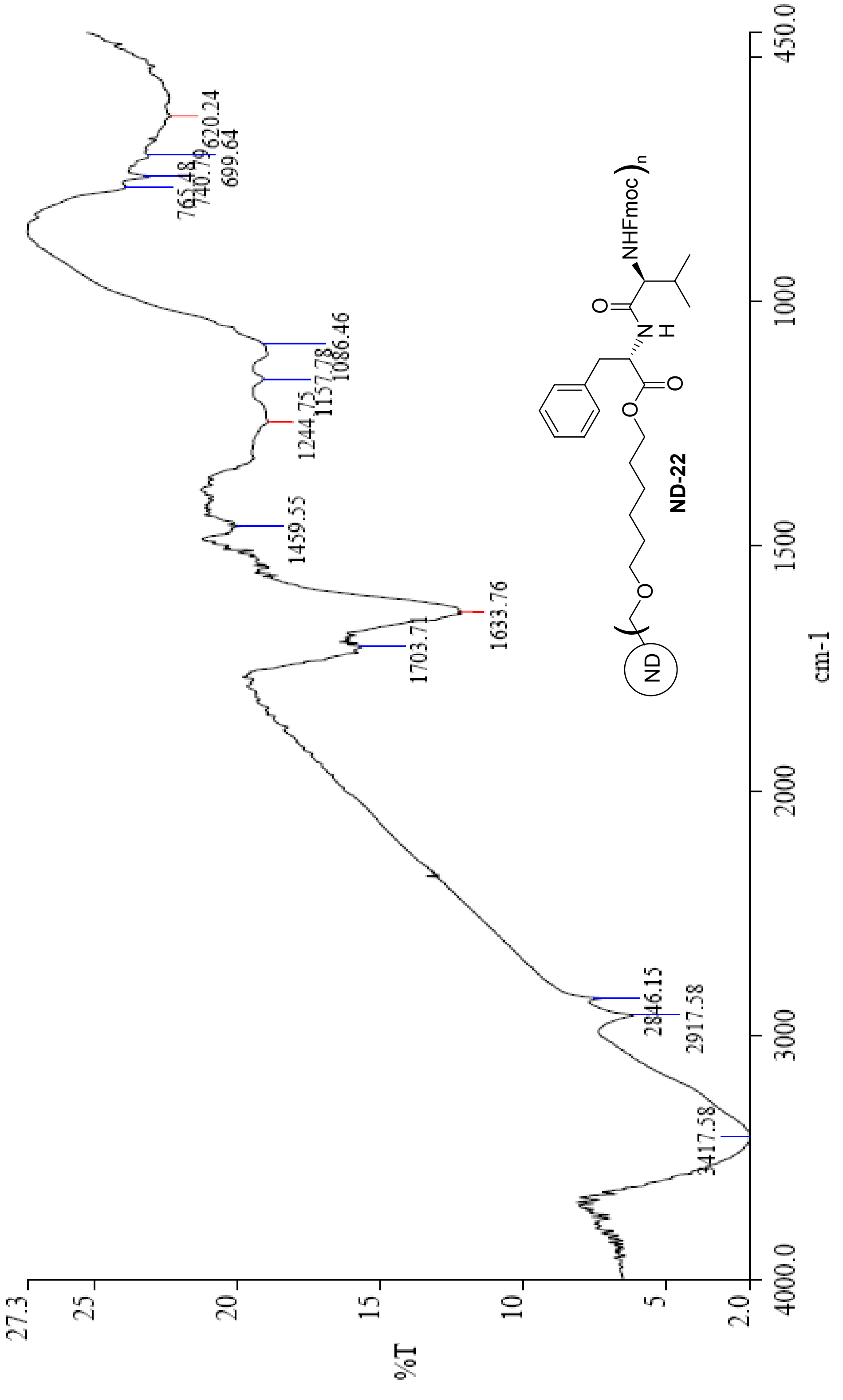


Fig. 32 FT-IR spectrum of ND-22

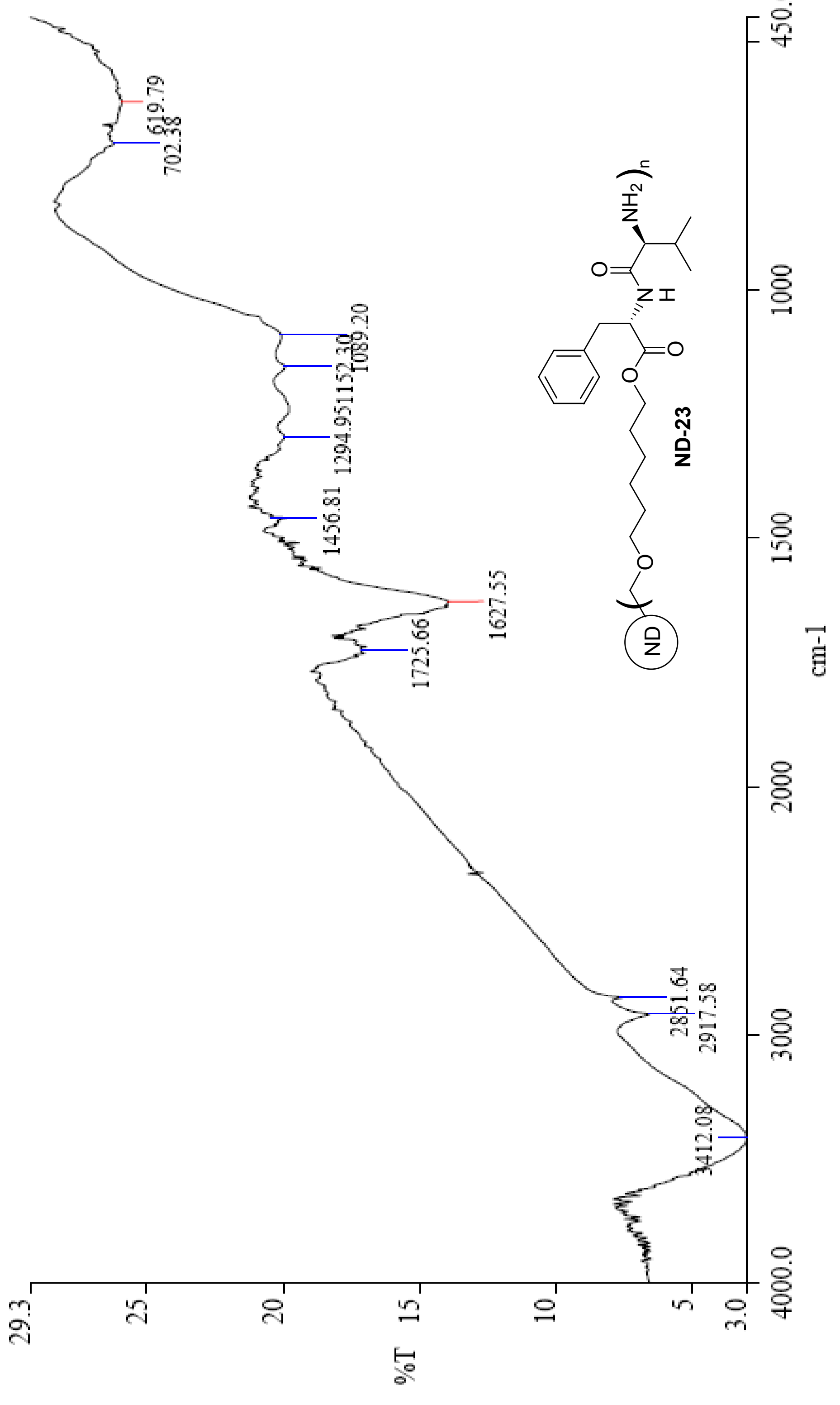


Fig. 33 FT-IR spectrum of **ND-23**

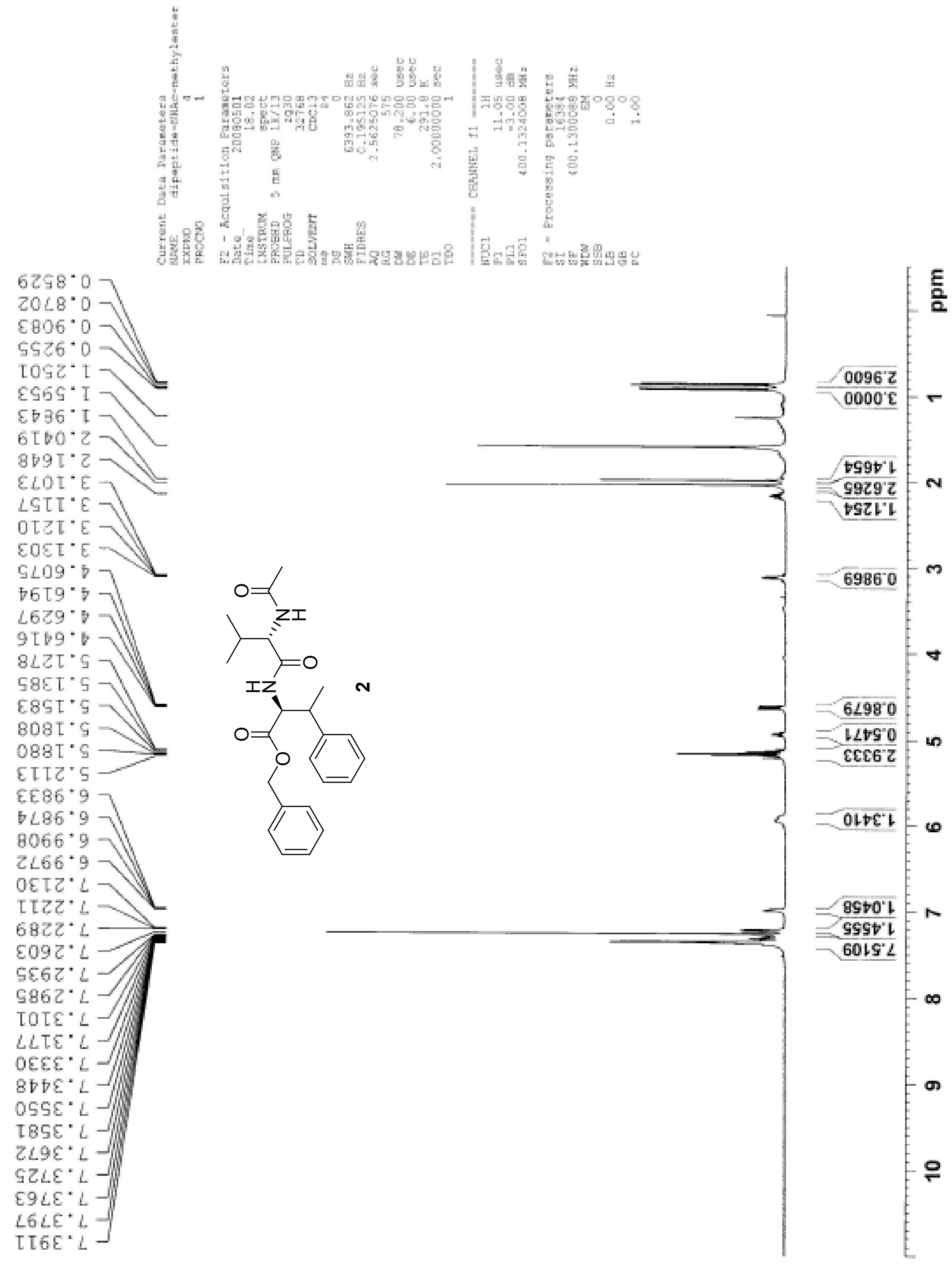


Fig. 34 ^{1}H-NMR spectrum of benzyl ester of **2**

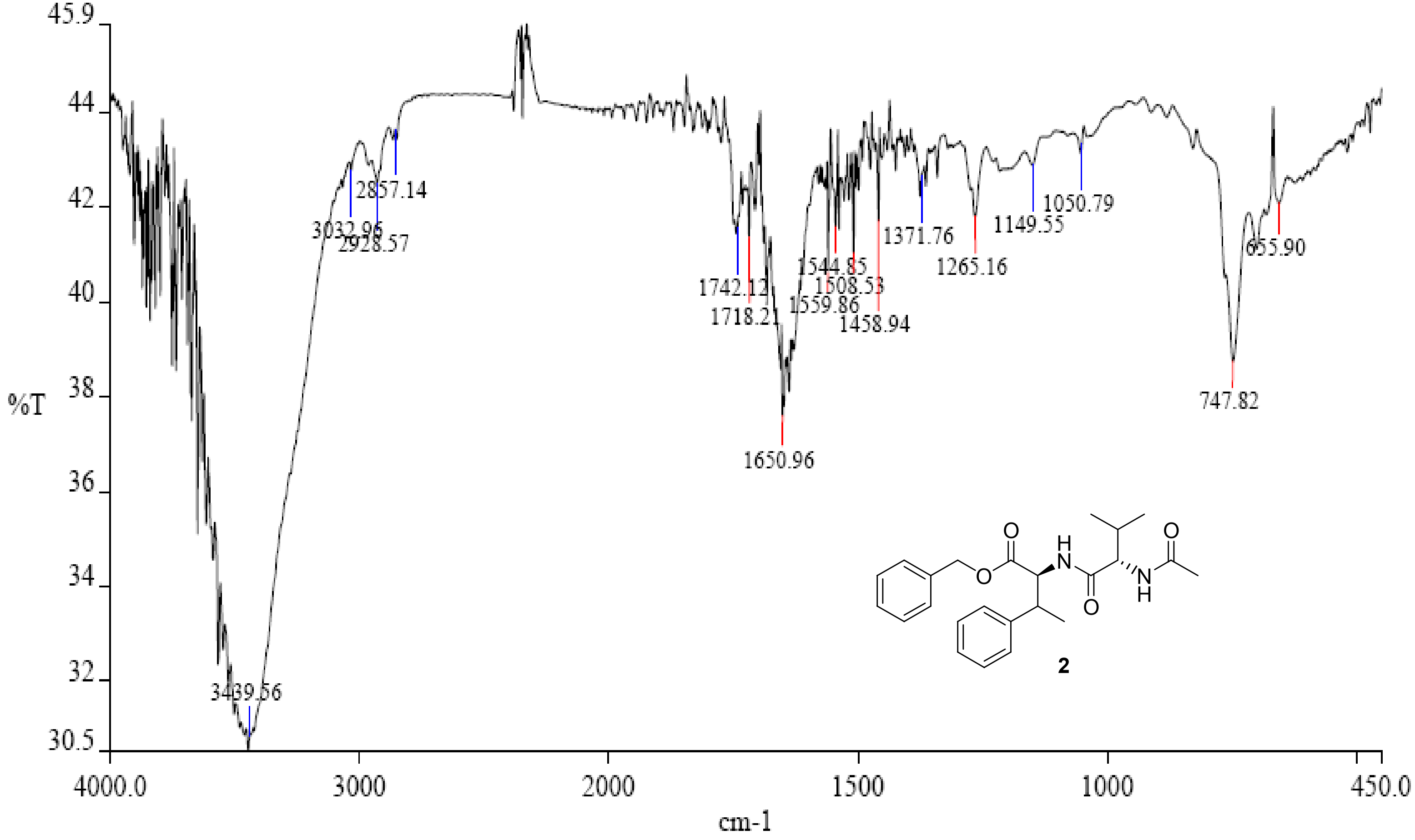
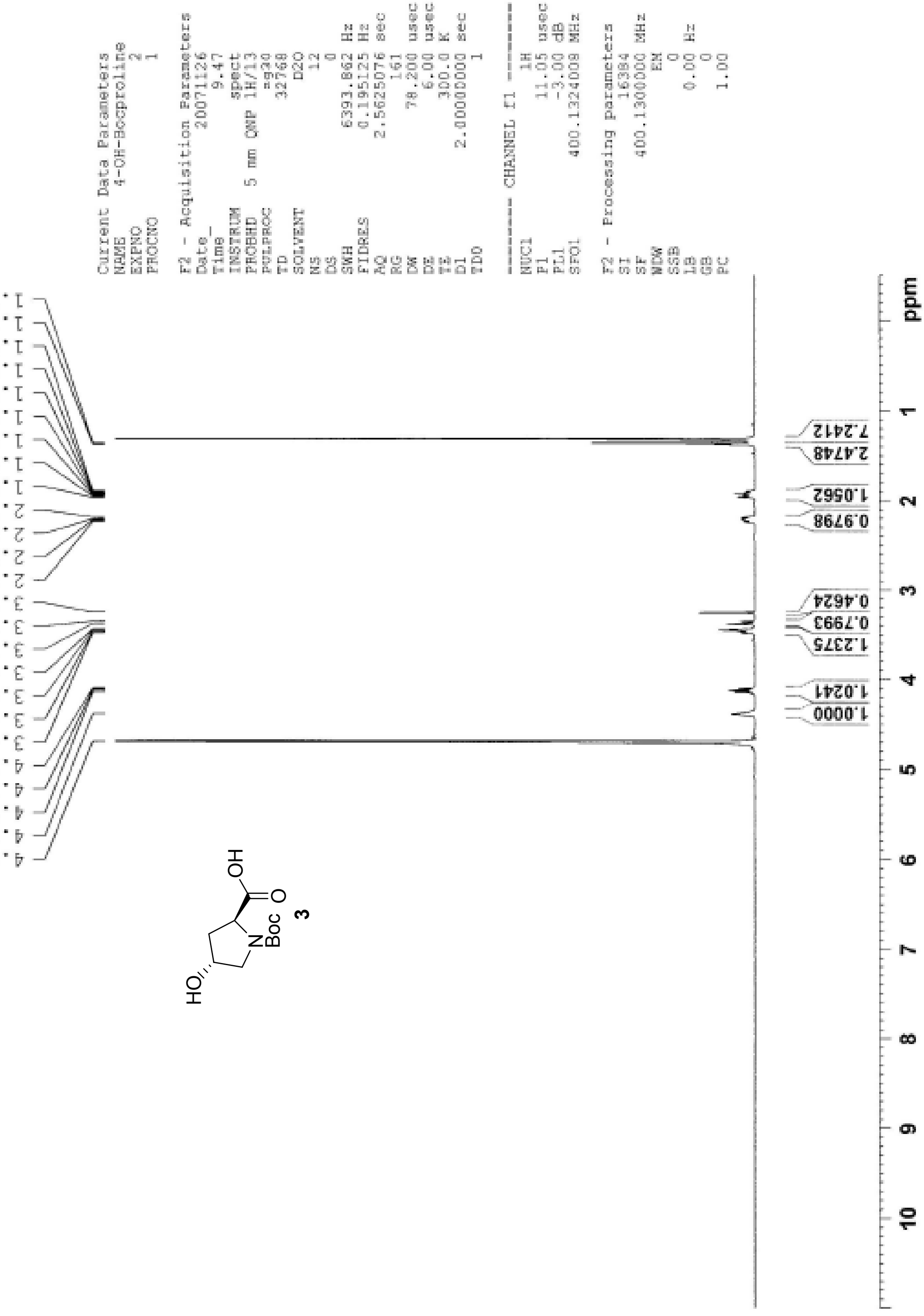


Fig. 35 FT-IR spectrum of benzyl ester of **2**



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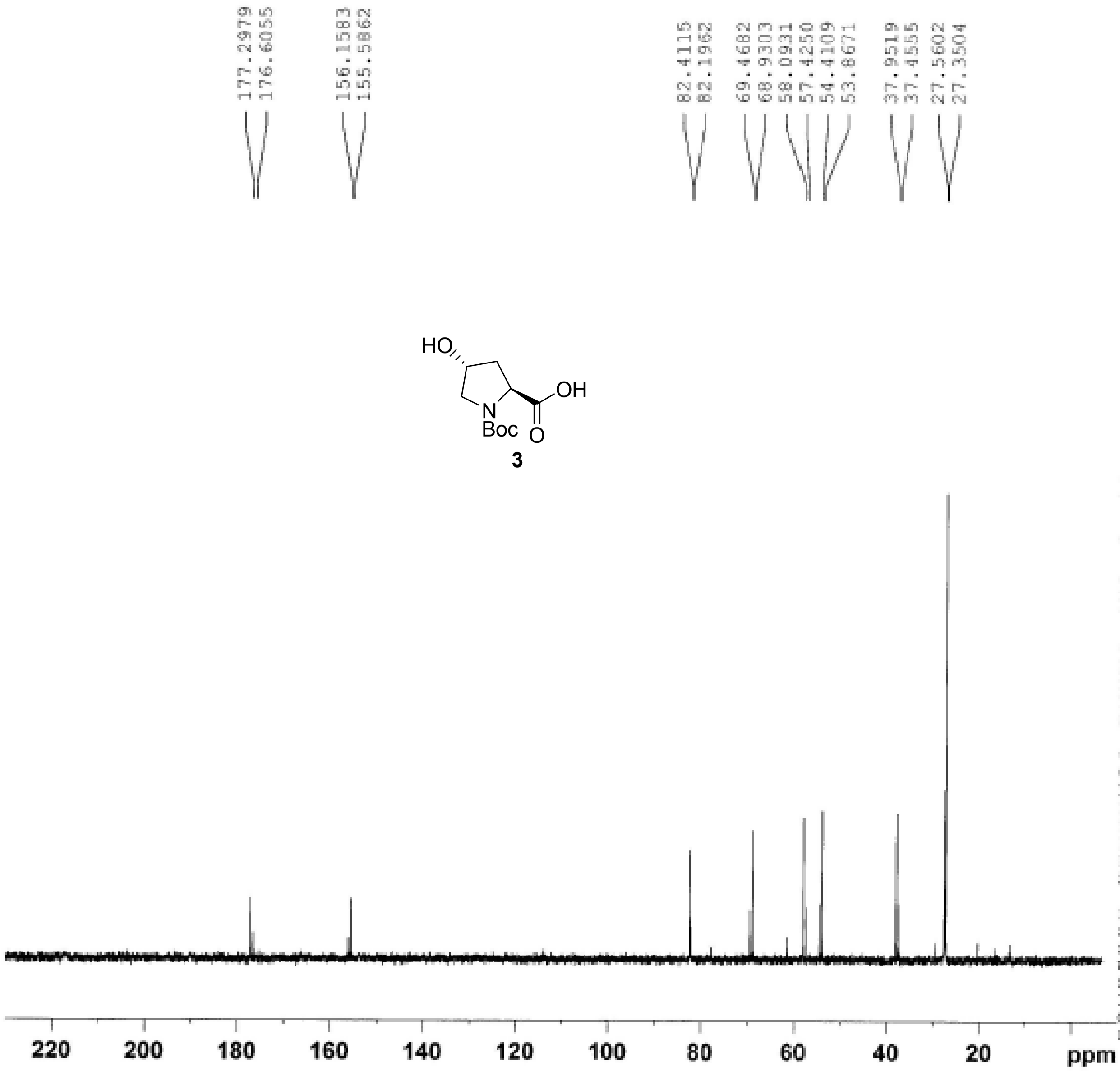
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071126
Time                   9.47
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    32768
SOLVENT                 D2O
NS                       12
DS                        0
SWH               6393.862 Hz
FIDRES            0.195125 Hz
AQ               2.5625076 sec
RG                      161
DW                   78.200 usec
DE                     6.00 usec
TE                    300.0 K
D1              2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.05 usec
PL1                   -3.00 dB
SFO1          400.1324008 MHz

F2 - Processing parameters
SI                    16384
SF            400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

Fig. 36 ^{1}H-NMR spectrum of **3**



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Current Data Parameters
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EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
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Time                10.42
INSTRUM             spect
PROBHD    5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   150
DS                     0
SWH            25510.203 Hz
FIDRES          0.389255 Hz
AQ             1.2845556 sec
RG                  2050
DW                19.600 usec
DE                  7.00 usec
TE                 292.5 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                 0.00 dB
SFO1         100.6248425 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               14.00 dB
PL13               17.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00
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Fig. 37 ^{13}C-NMR spectrum of **3**

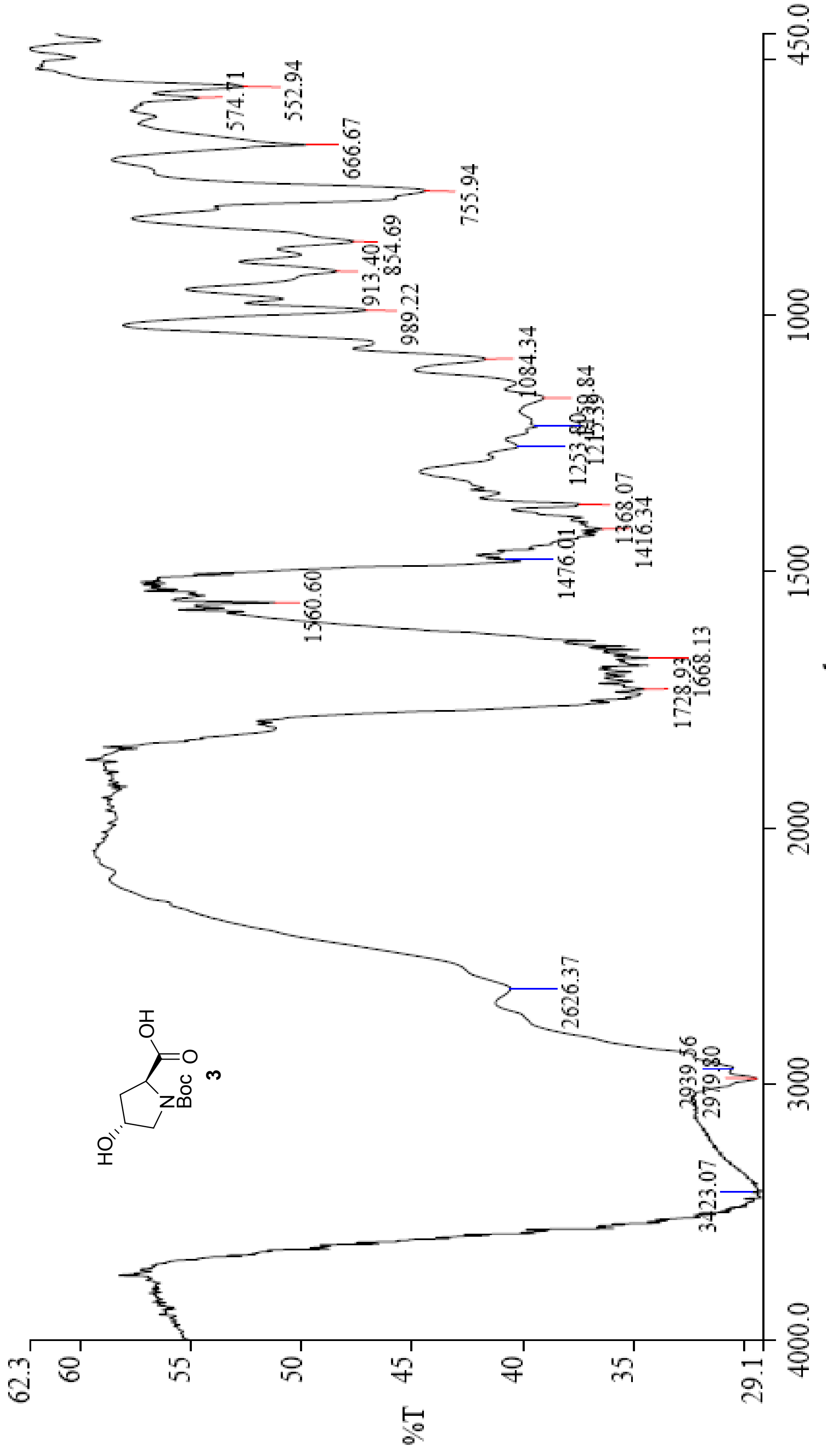


Fig. 38 FT-IR spectrum of **3**

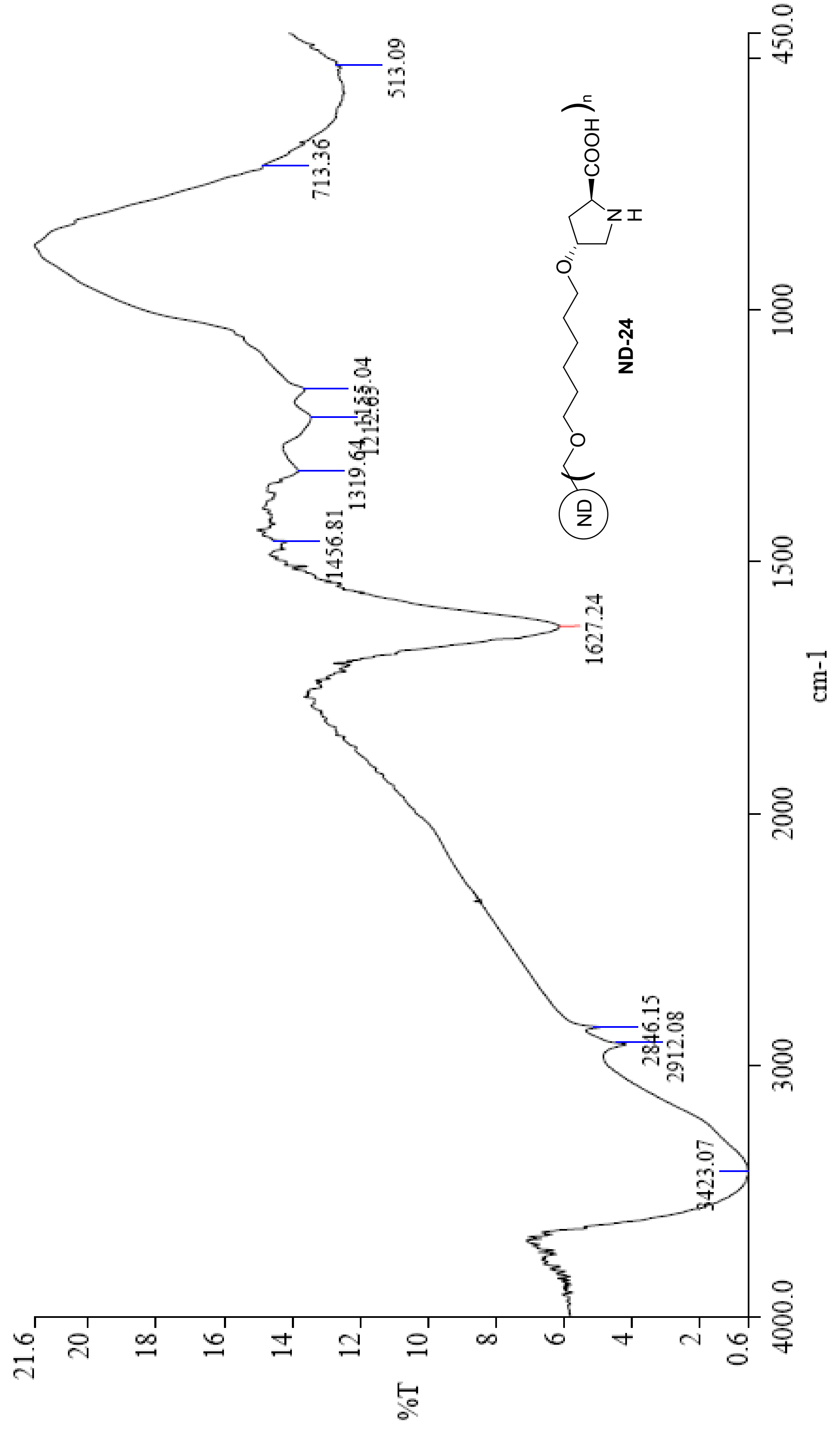


Fig. 39 FT-IR spectrum of **ND-24**

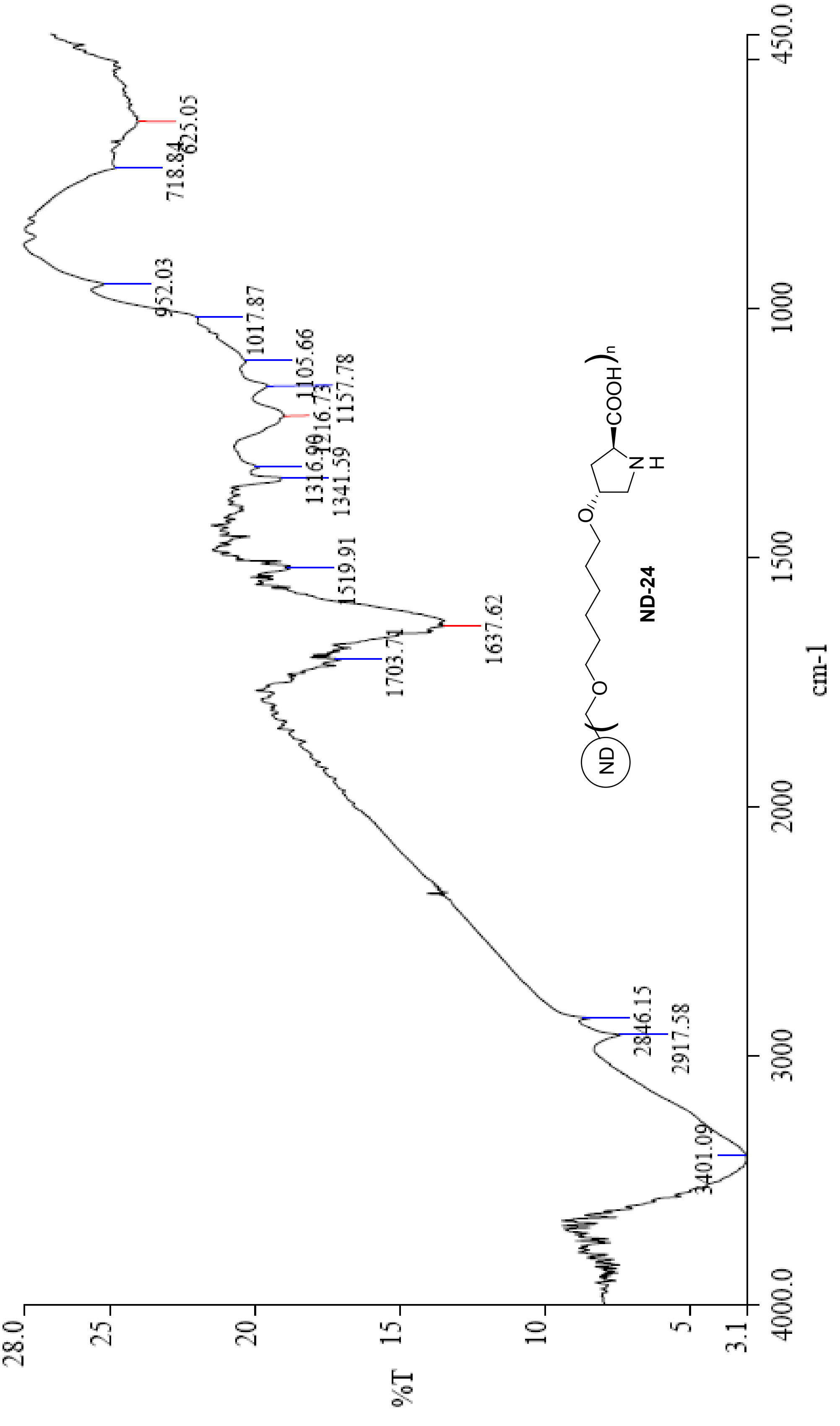
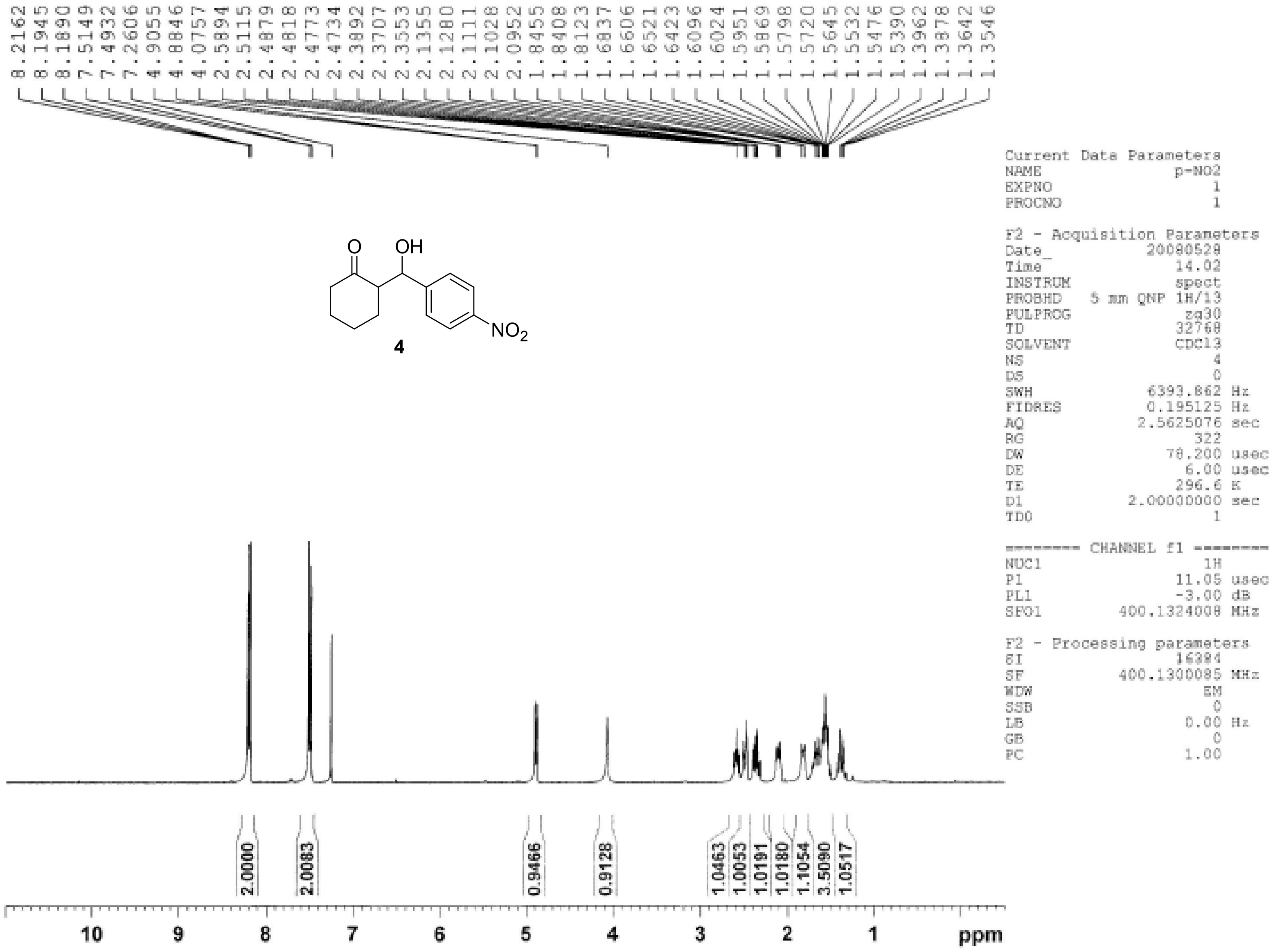


Fig. 40 FT-IR spectrum of **ND-24**



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Current Data Parameters
NAME              p-NO2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20080528
Time              14.02
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    4
DS                    0
SWH            6393.862 Hz
FIDRES         0.195125 Hz
AQ            2.5625076 sec
RG                  322
DW               78.200 usec
DE                 6.00 usec
TE                296.6 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                11.05 usec
PL1               -3.00 dB
SFO1        400.1324008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300085 MHz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

Fig. 41 ^{1}H-NMR spectrum of **4**

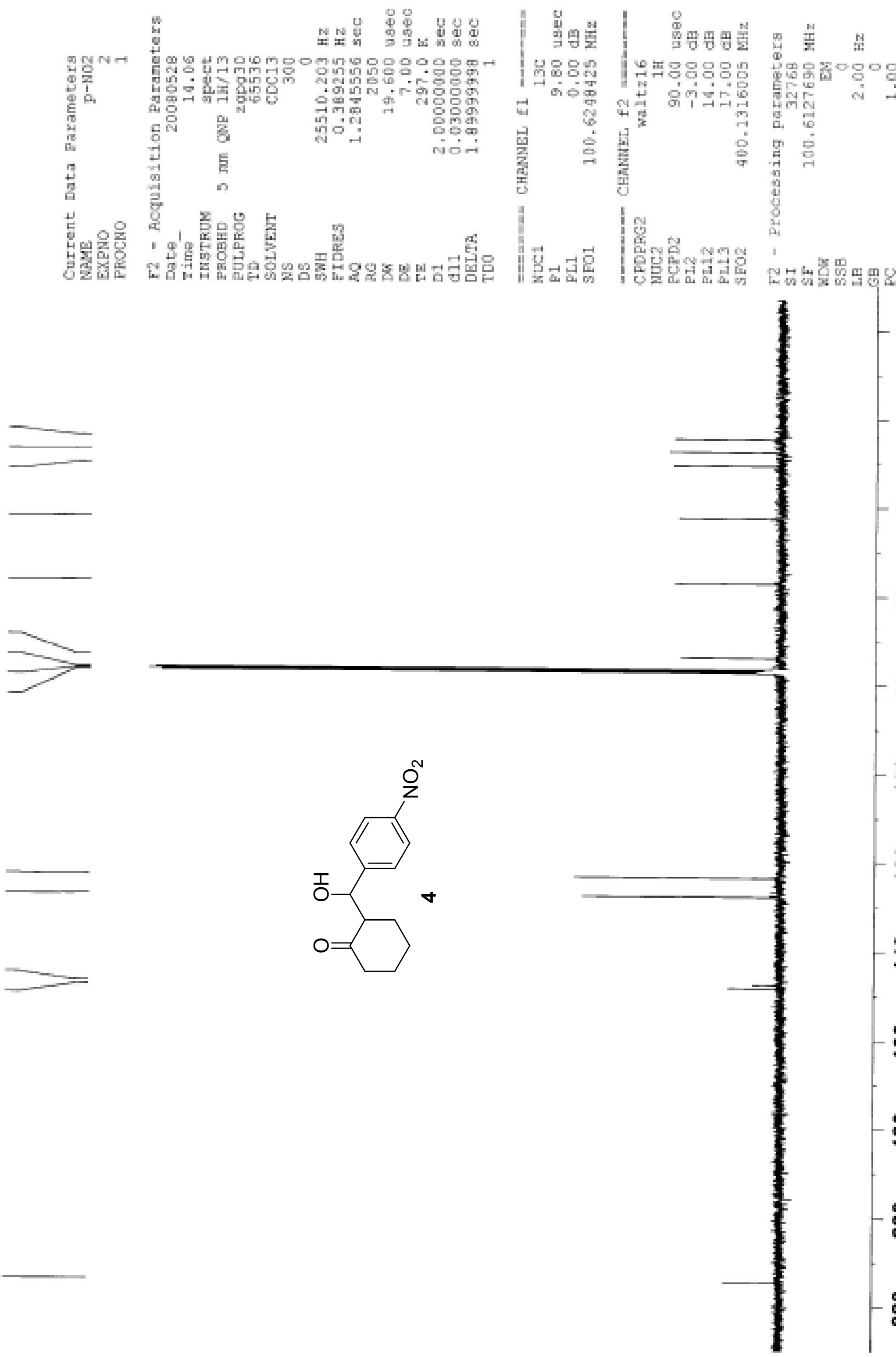


Fig. 42 ^{13}C-NMR spectrum of **4**

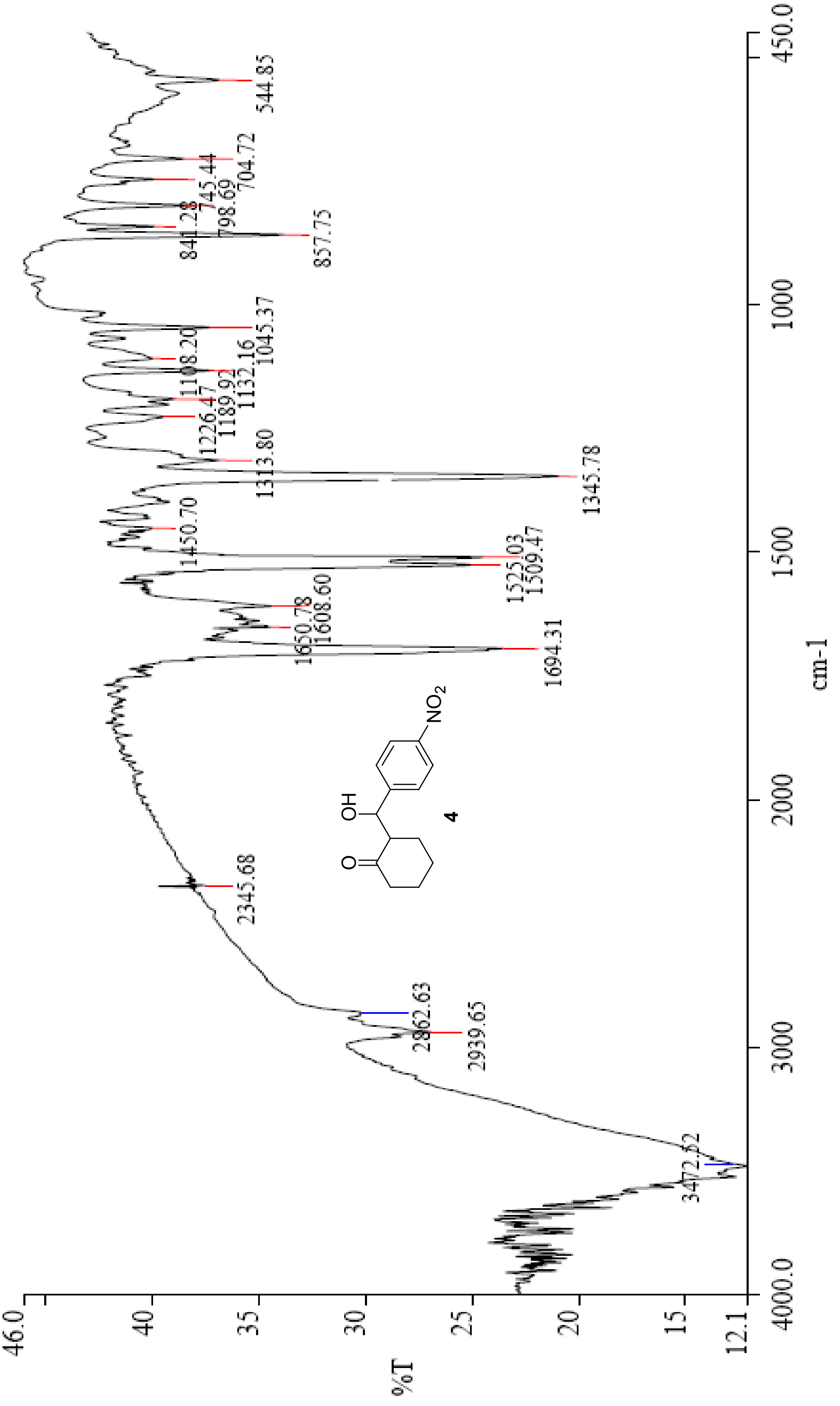


Fig. 43 FT-IR spectrum of **4**

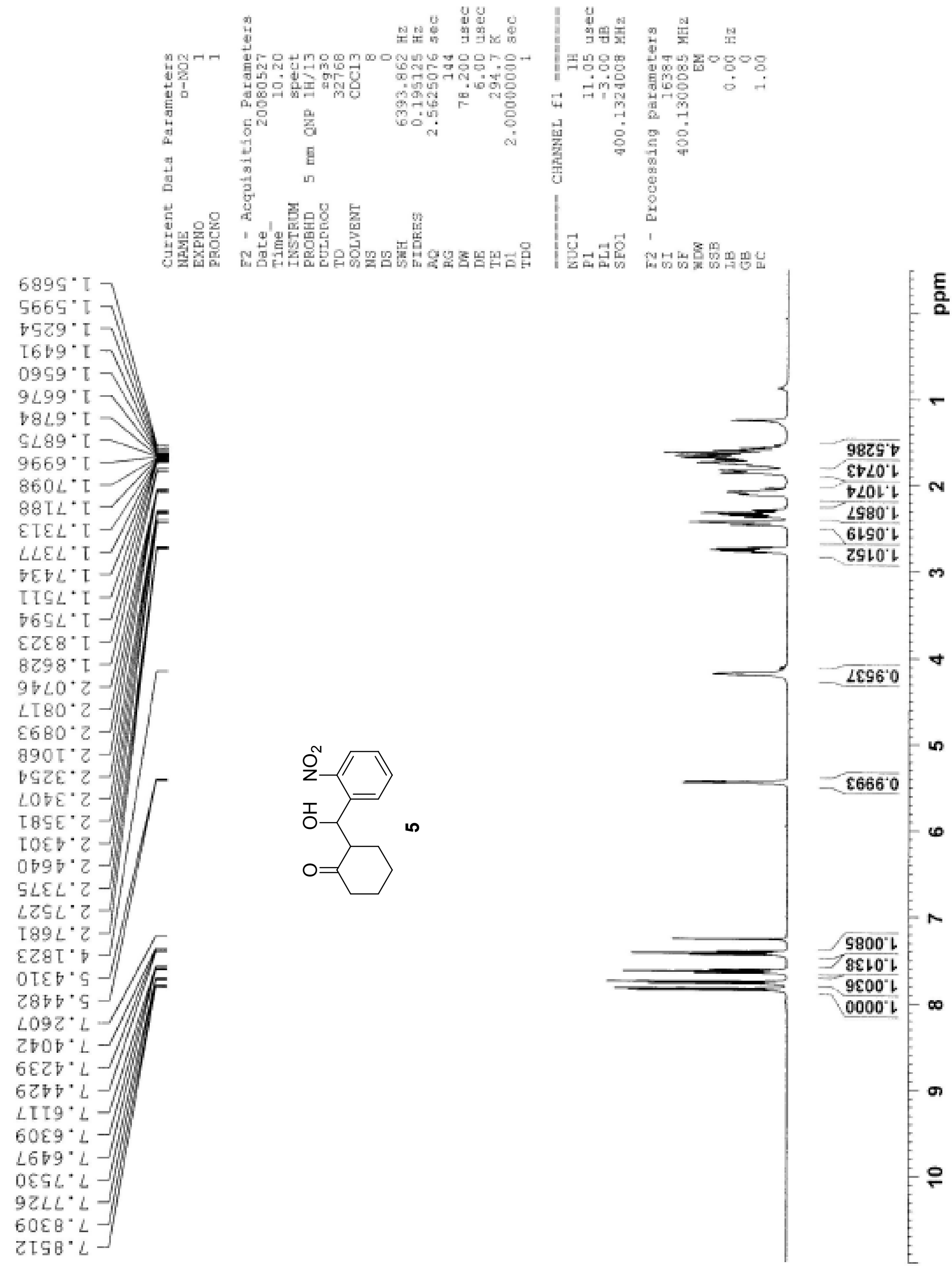
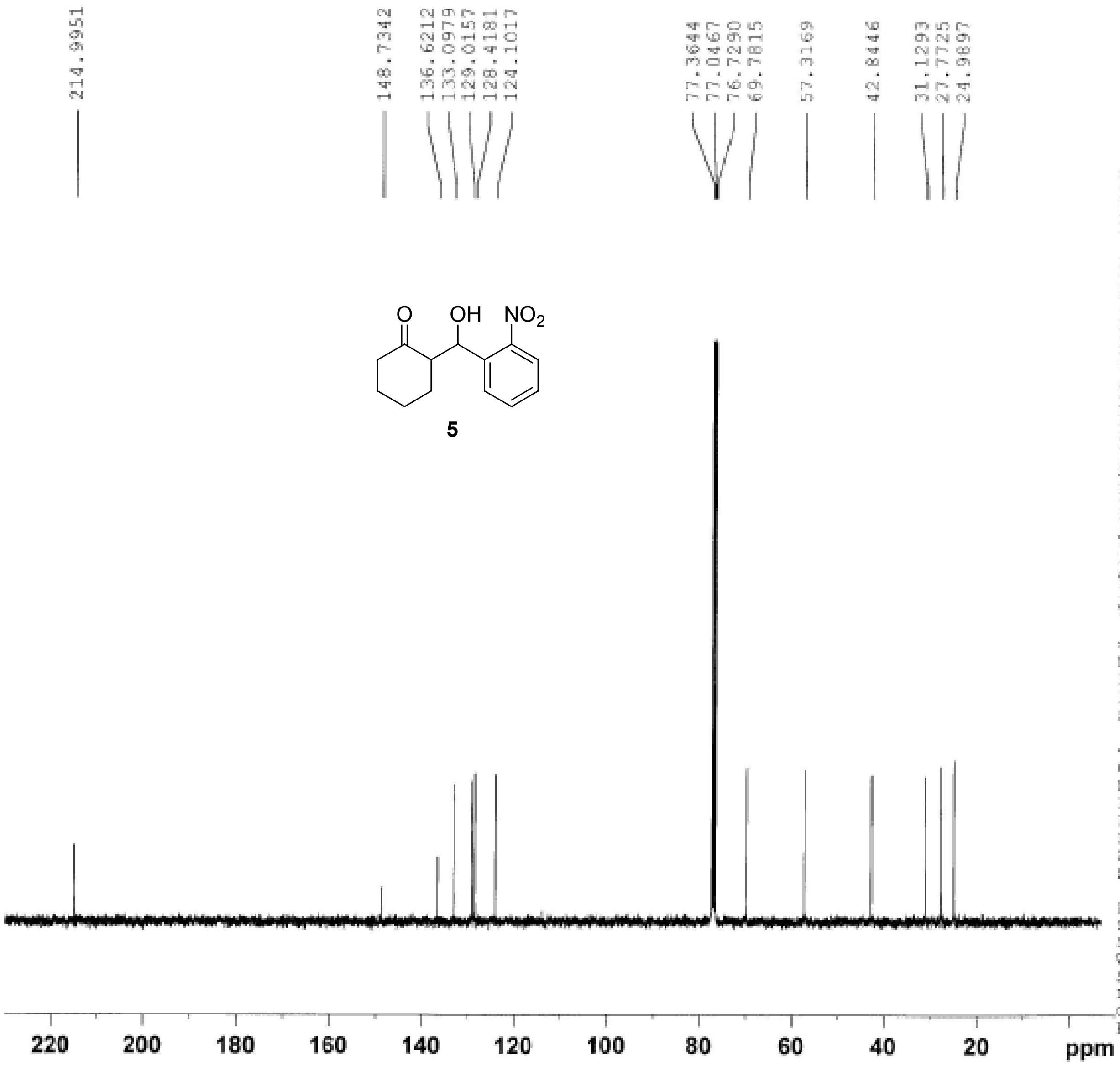


Fig. 44 ^{1}H-NMR spectrum of **5**



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Current Data Parameters
NAME               o-NO2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080527
Time               10.27
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     0
SWH            25510.203 Hz
FIDRES          0.389255 Hz
AQ             1.2845556 sec
RG                  2050
DW                19.600 usec
DE                  7.00 usec
TE                 295.3 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                 0.00 dB
SFO1         100.6248425 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               14.00 dB
PL13               17.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00
```

Fig. 45 ^{13}C-NMR spectrum of **5**

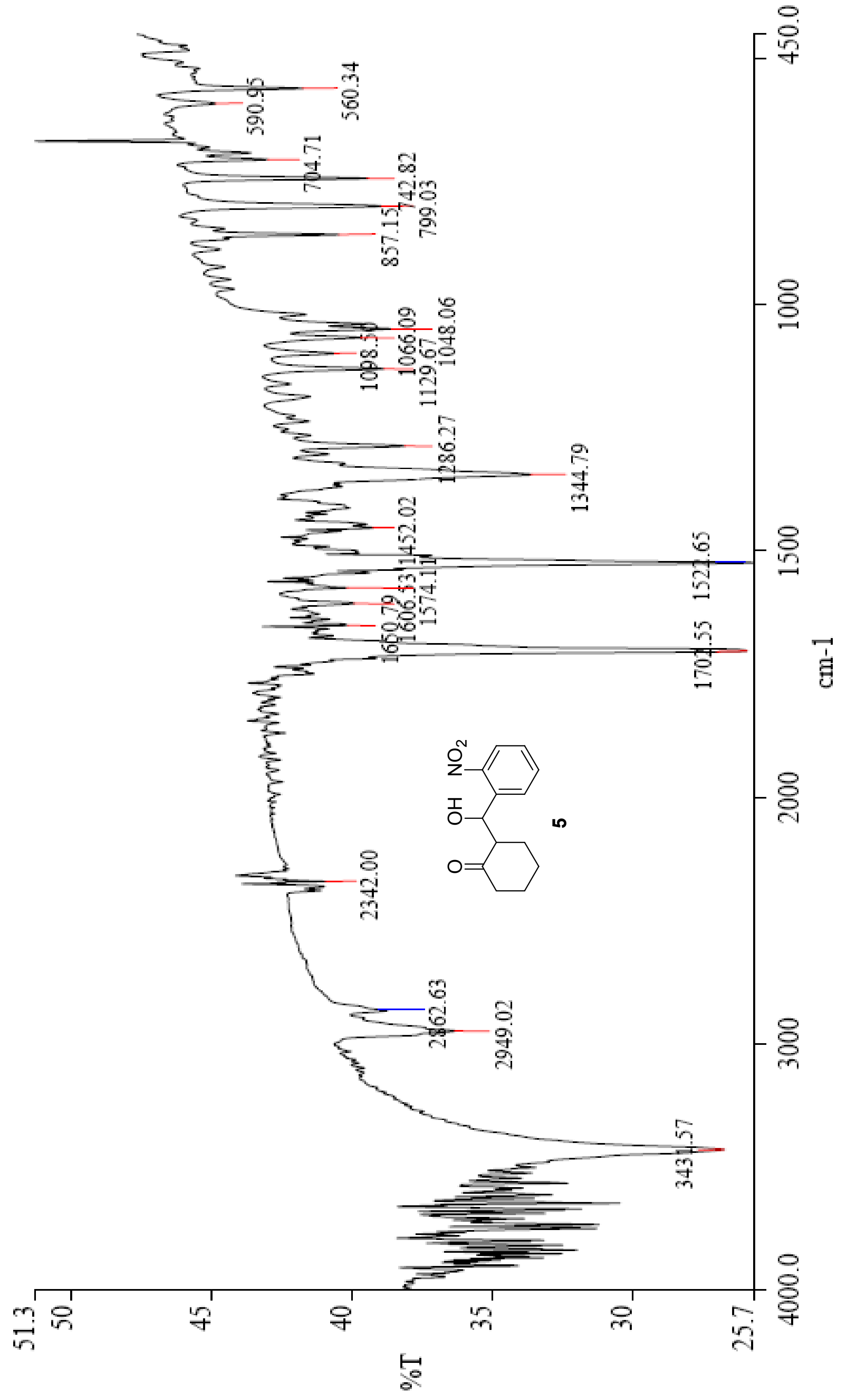
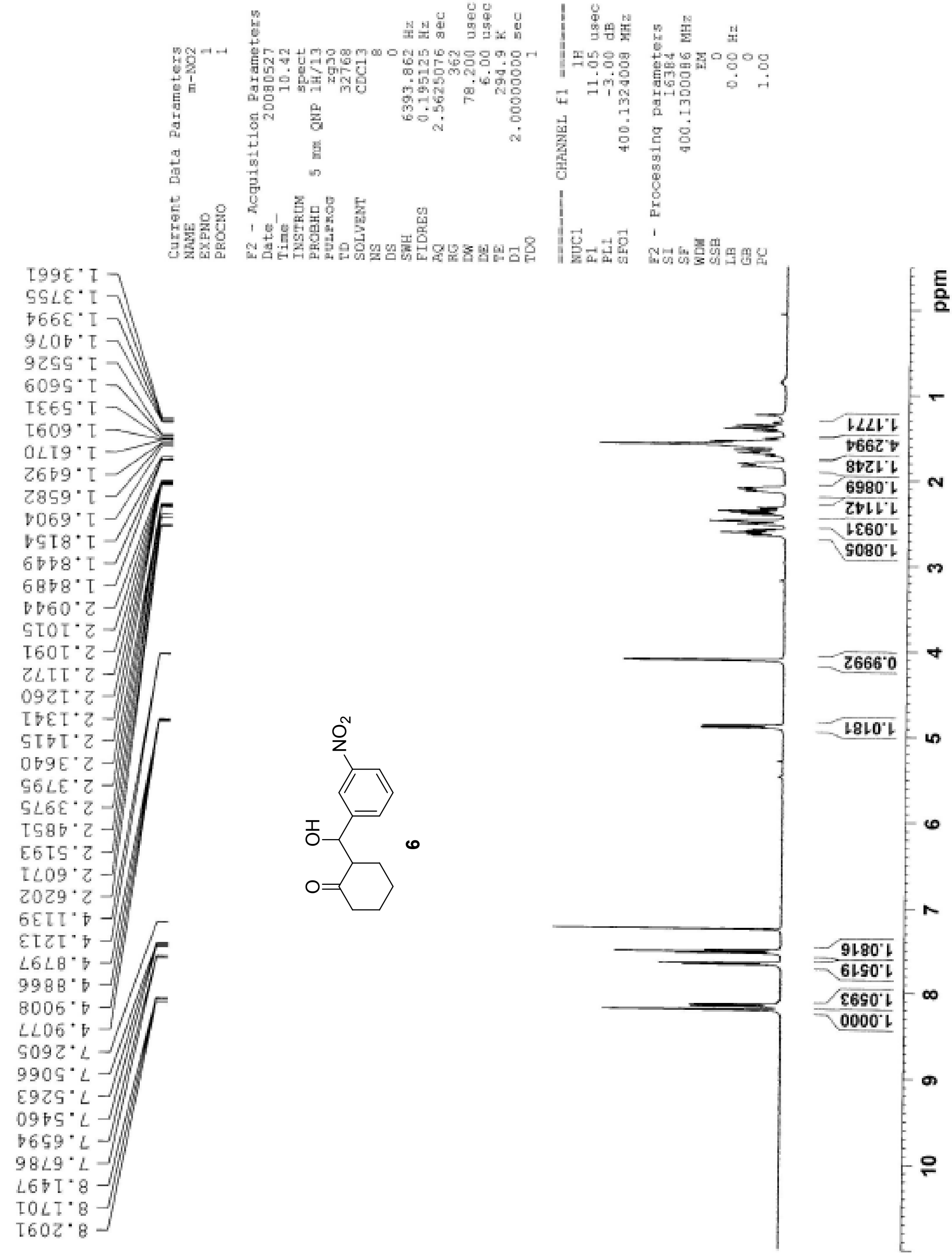


Fig. 46 FT-IR spectrum of **5**



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Current Data Parameters
NAME              m-NO2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20080527
Time_             10.42
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            6393.862 Hz
FIDRES         0.195125 Hz
AQ            2.5625076 sec
RG                  362
DW               78.200 usec
DE                 6.00 usec
TE                294.9 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                11.05 usec
PL1               -3.00 dB
SFO1        400.1324008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300086 MHz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

Fig. 47 ^{1}H-NMR spectrum of **6**

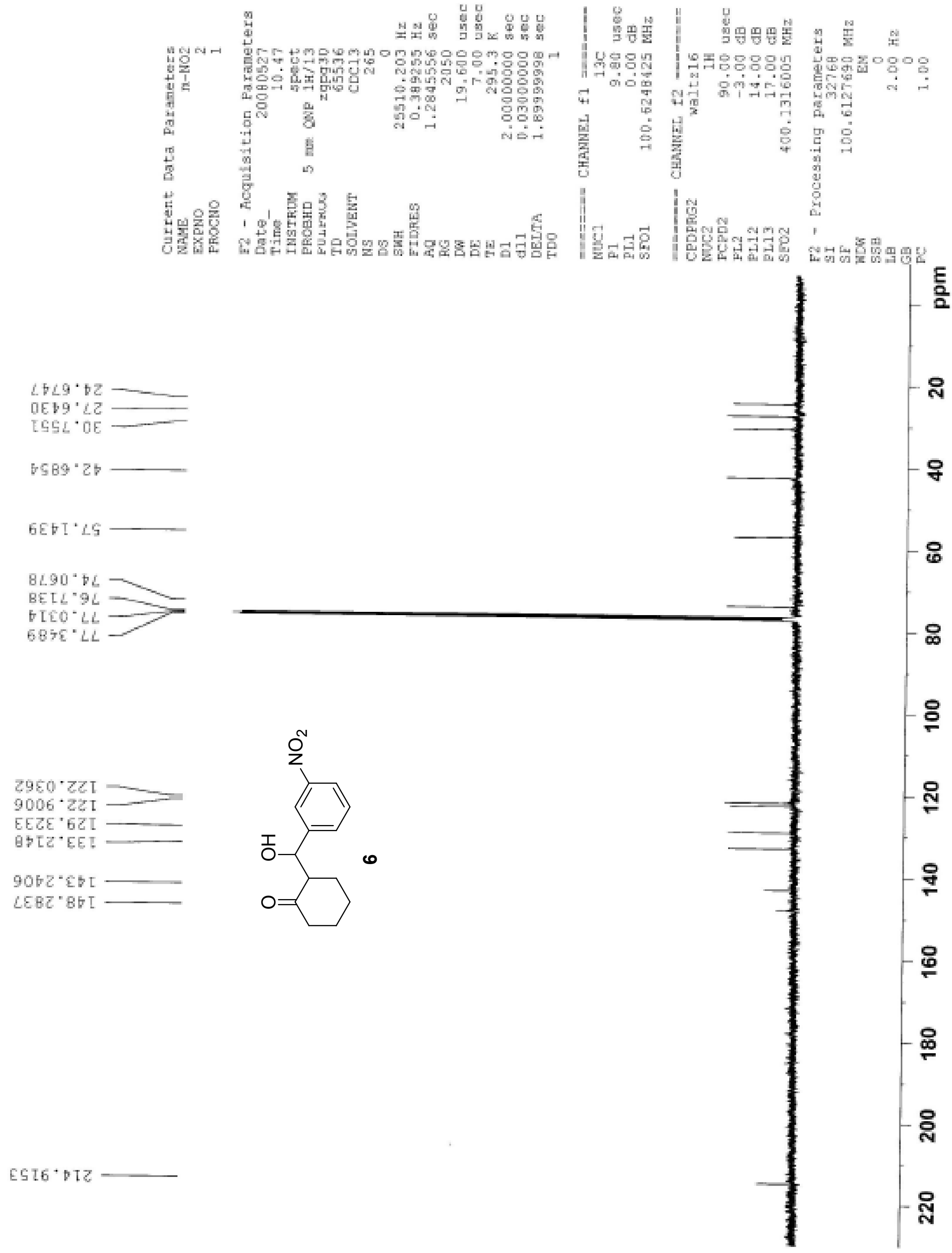


Fig. 48 ^{13}C-NMR spectrum of **6**

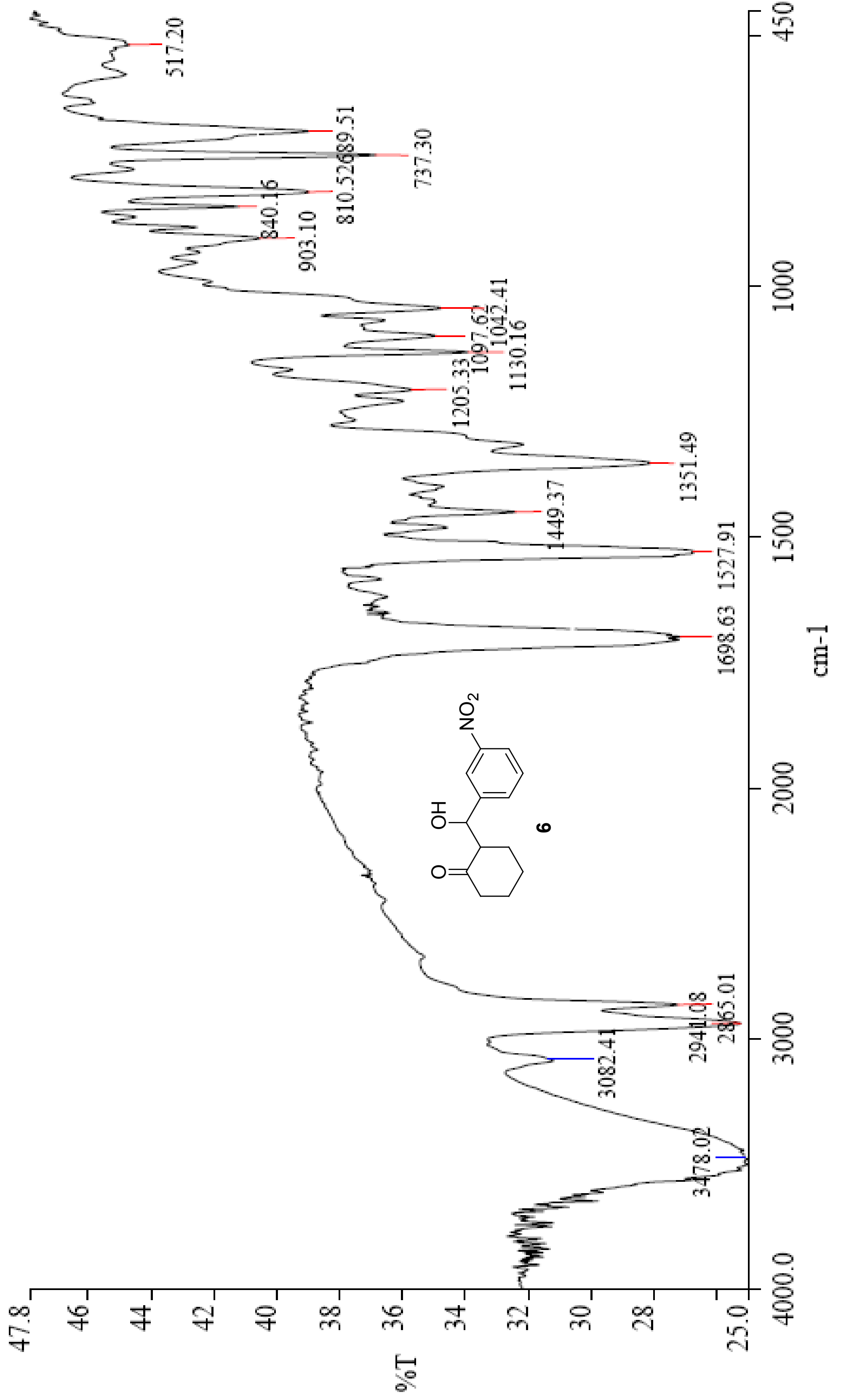


Fig. 49 FT-IR spectrum of **6**

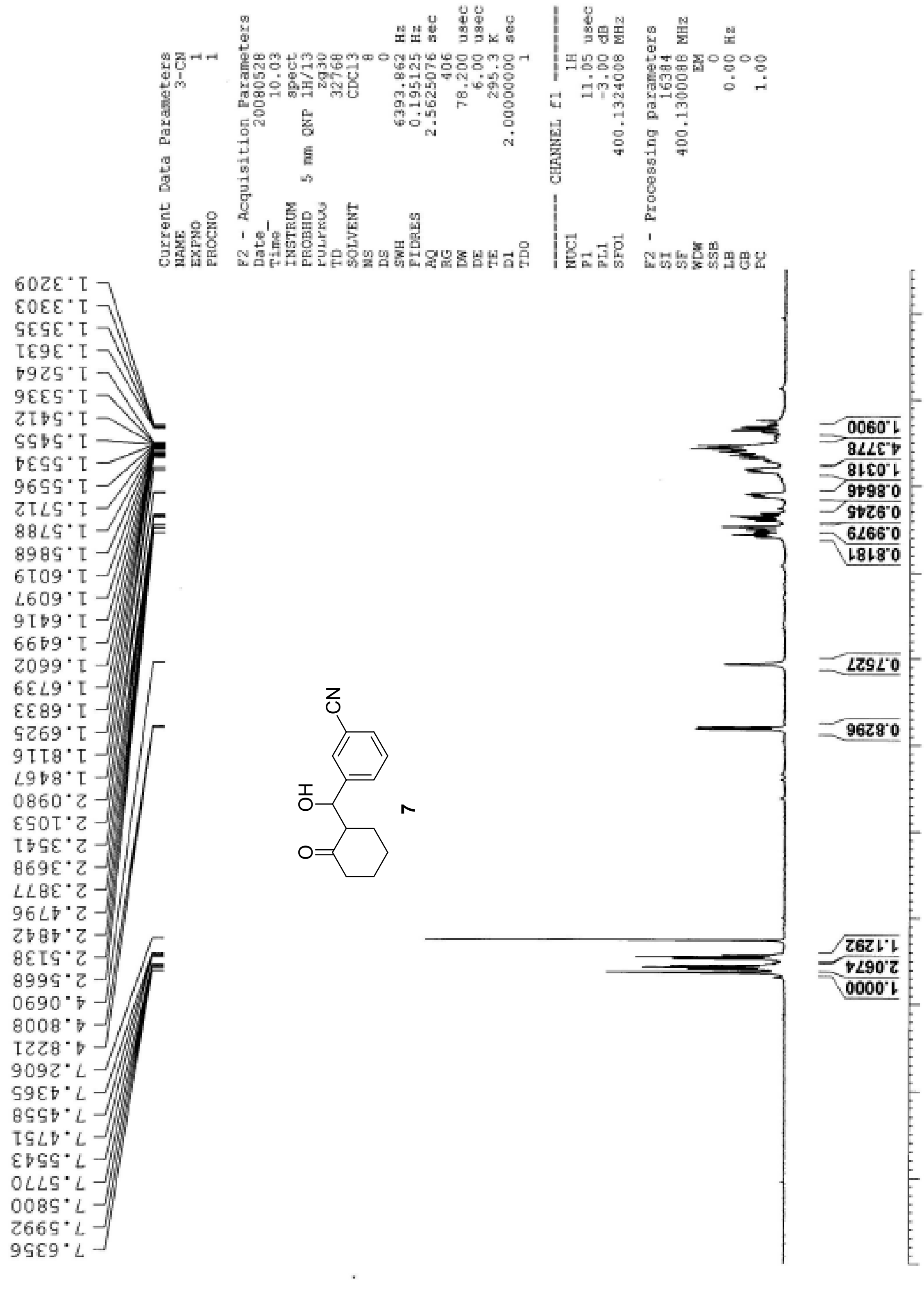
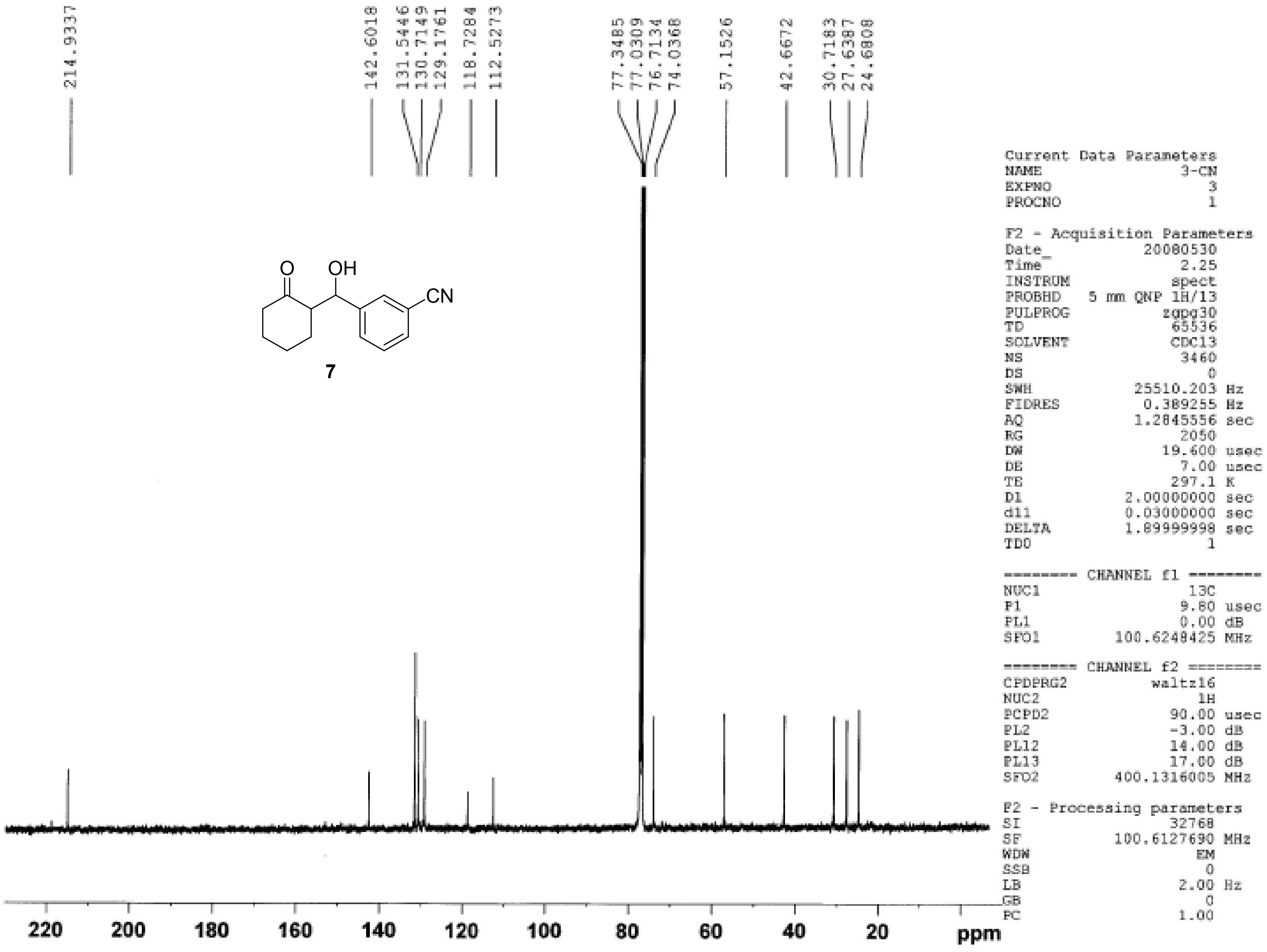


Fig. 50 ^{1}H-NMR spectrum of **7**



```
Current Data Parameters
NAME                3-CN
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080530
Time                2.25
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  3460
DS                     0
SWH            25510.203 Hz
FIDRES          0.389255 Hz
AQ             1.2845556 sec
RG                  2050
DW                19.600 usec
DE                  7.00 usec
TE                 297.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                 0.00 dB
SFO1         100.6248425 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               14.00 dB
PL13               17.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00
```

Fig. 51 ^{13}C-NMR spectrum of **7**

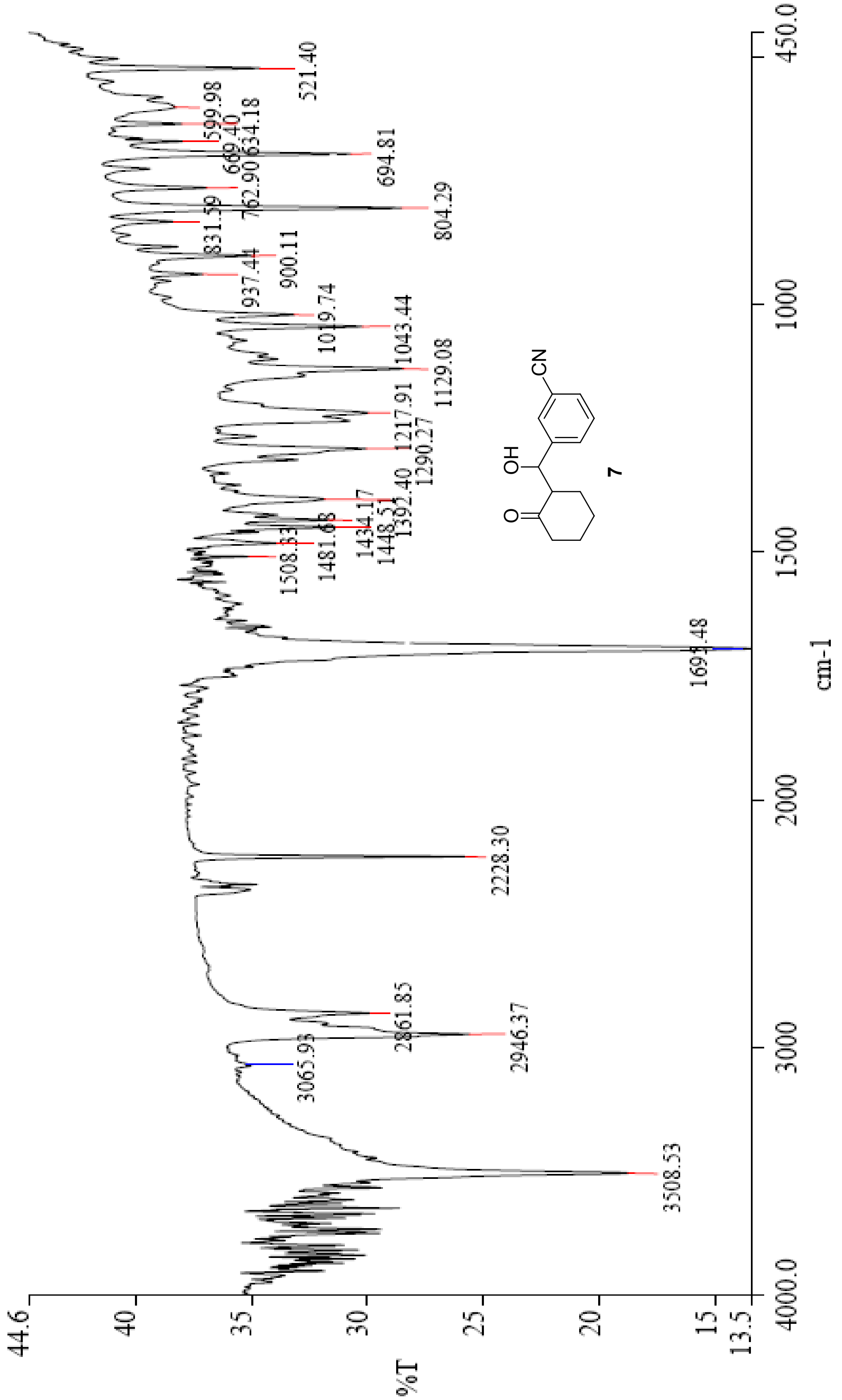


Fig. 52 FT-IR spectrum of **7**

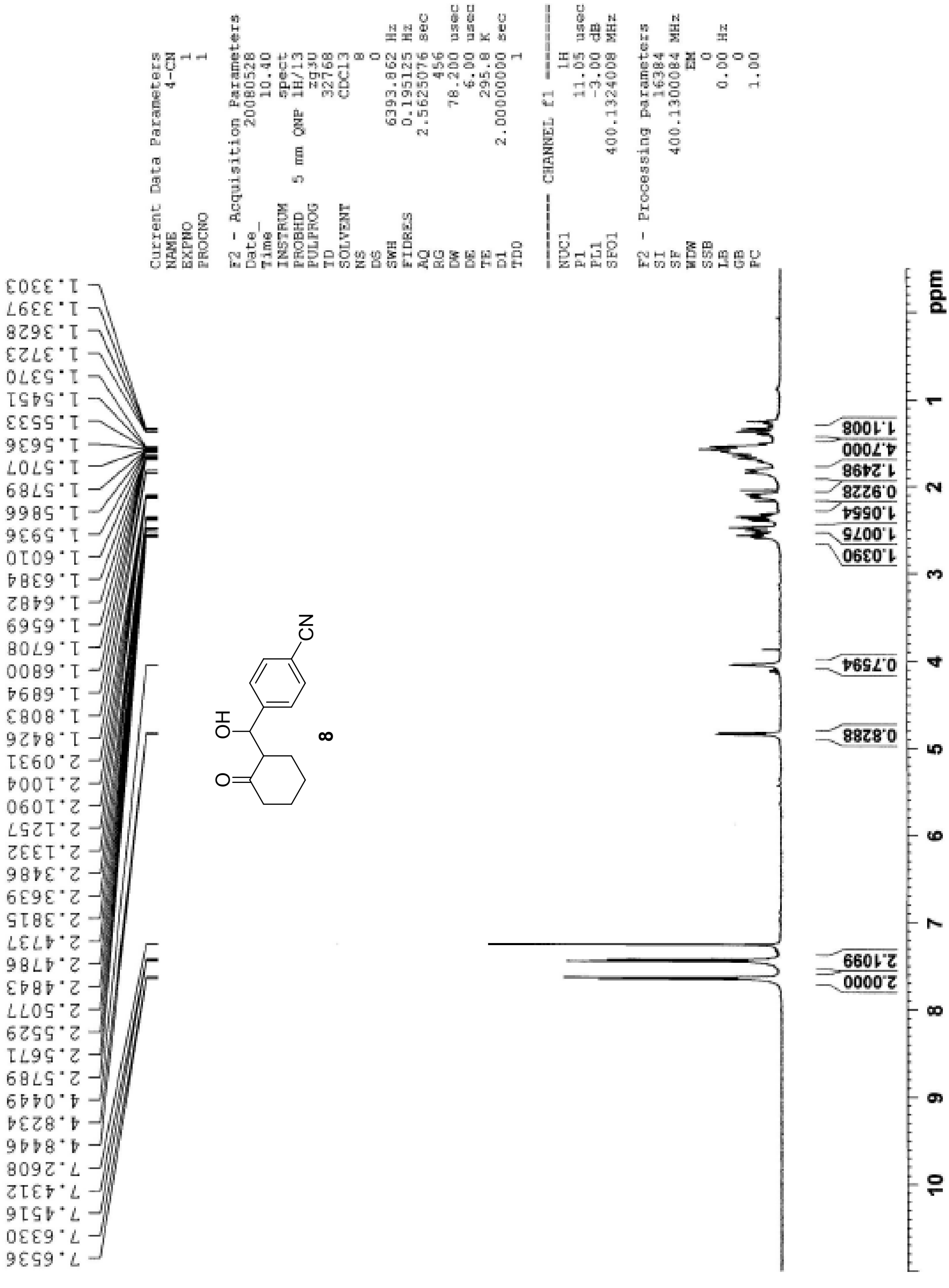
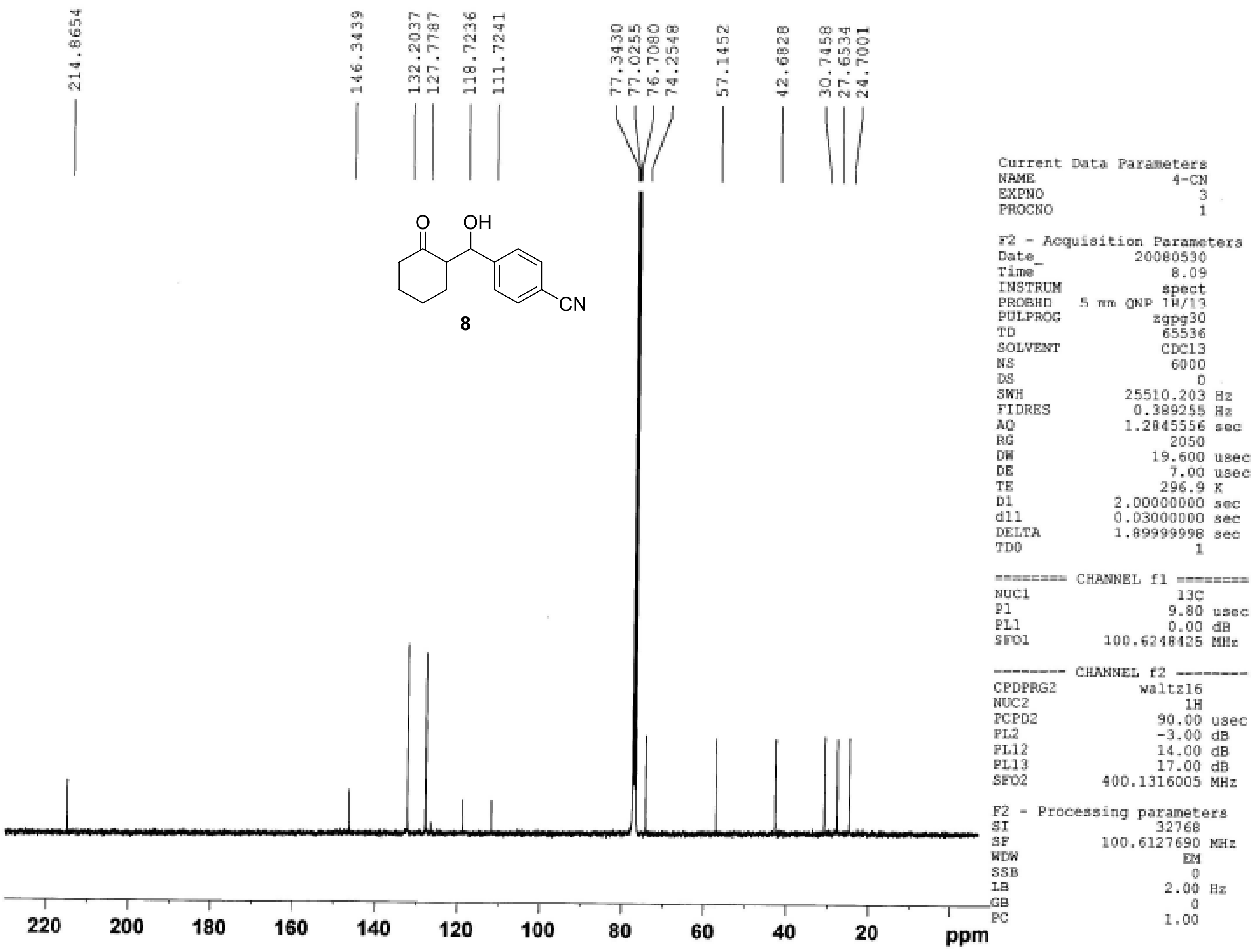


Fig. 53 ^{1}H-NMR spectrum of **8**



```
Current Data Parameters
NAME              4-CN
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_         20080530
Time              8.09
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG        zgpg30
TD               65536
SOLVENT          CDCl3
NS                6000
DS                   0
SWH          25510.203 Hz
FIDRES        0.389255 Hz
AQ           1.2845556 sec
RG                2050
DW              19.600 usec
DE                7.00 usec
TE               296.9 K
D1          2.00000000 sec
d11         0.03000000 sec
DELTA       1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.80 usec
PL1               0.00 dB
SFO1      100.6248425 MHz

-------- CHANNEL f2 --------
CPDPRG2        waltz16
NUC2                1H
PCPD2            90.00 usec
PL2              -3.00 dB
PL12             14.00 dB
PL13             17.00 dB
SFO2      400.1316005 MHz

F2 - Processing parameters
SI               32768
SF        100.6127690 MHz
WDW                 EM
SSB                  0
LB                2.00 Hz
GB                   0
PC                1.00
```

Fig. 54 ^{13}C-NMR spectrum of **8**

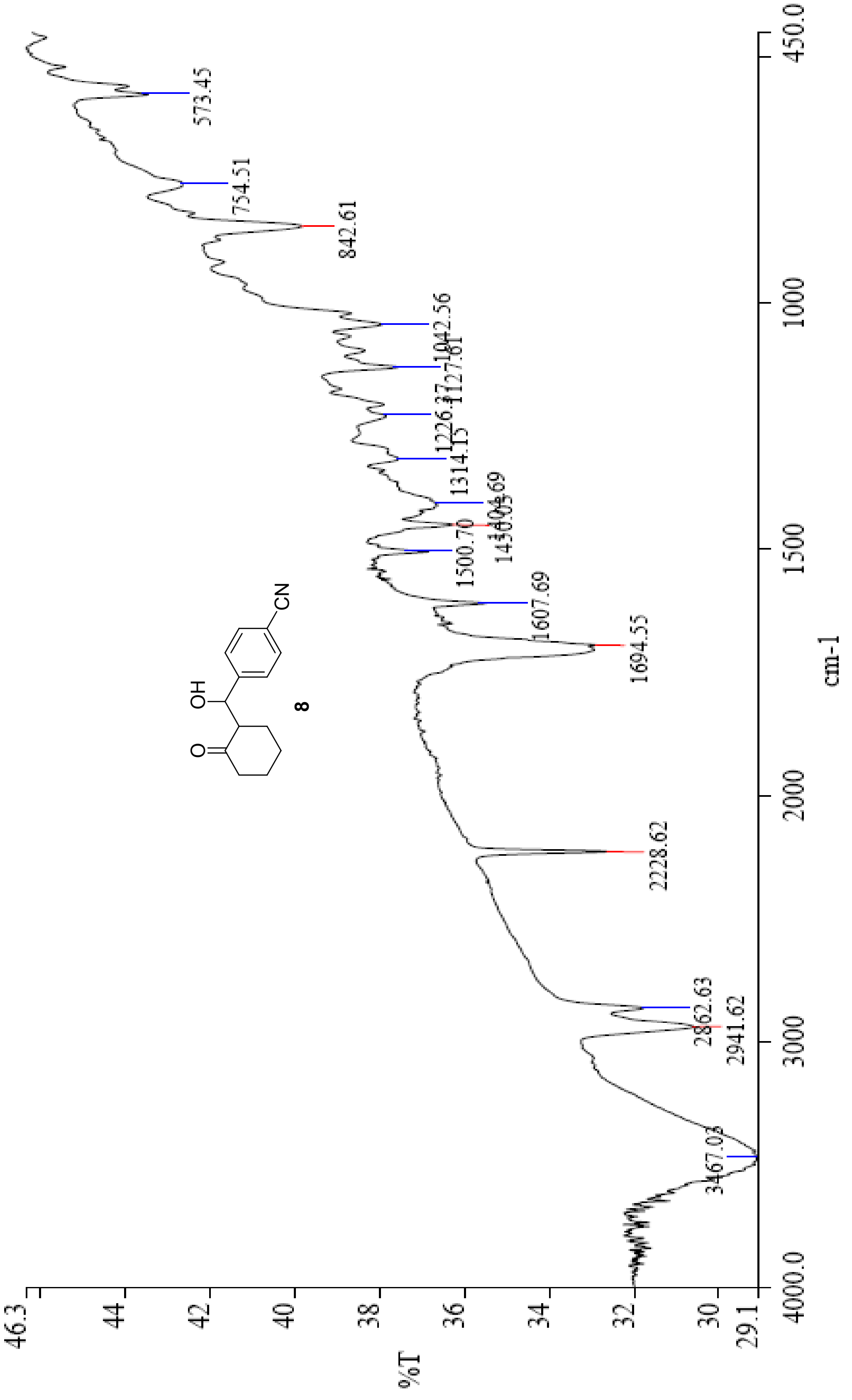


Fig. 55 FT-IR spectrum of **8**

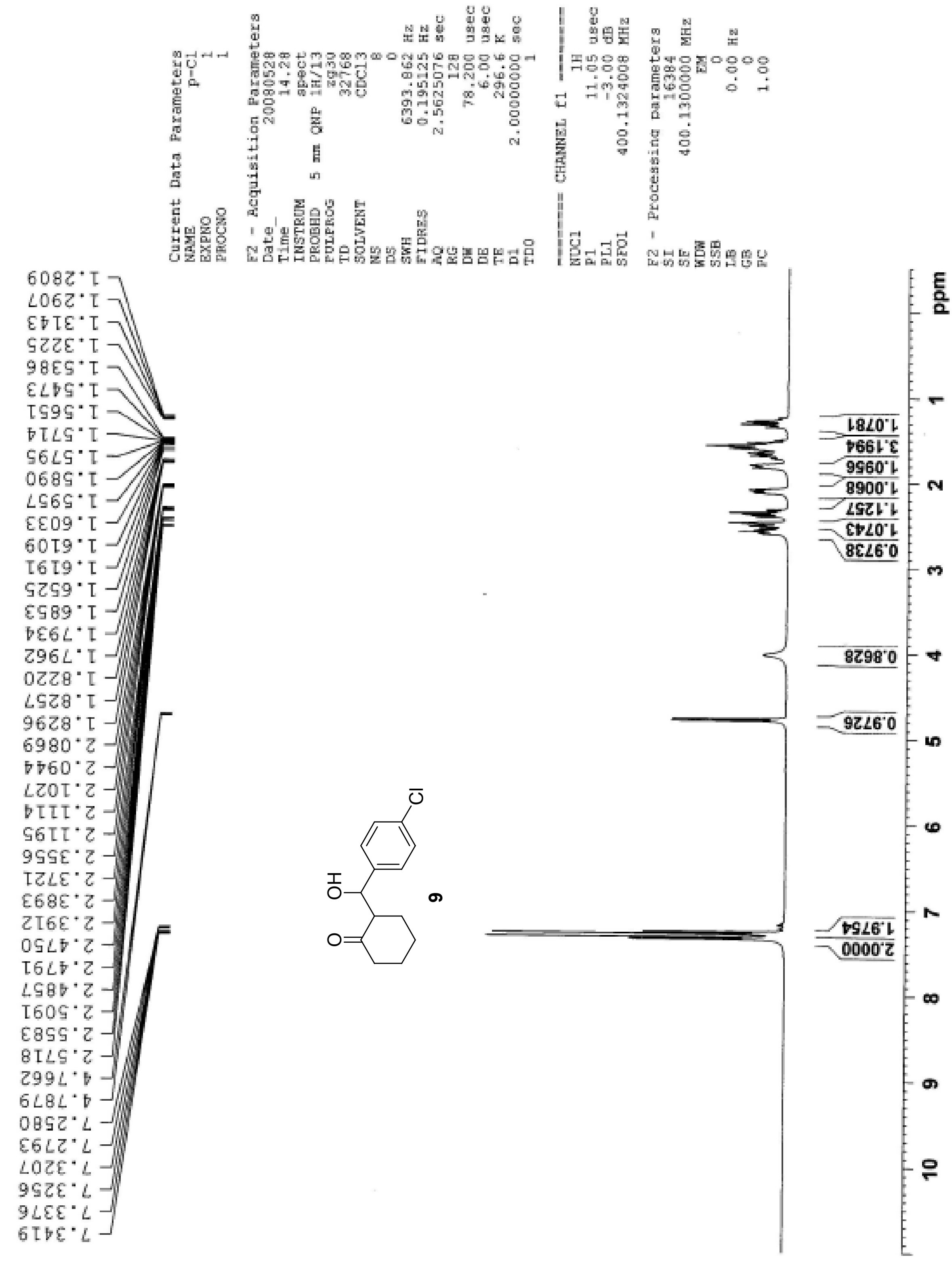
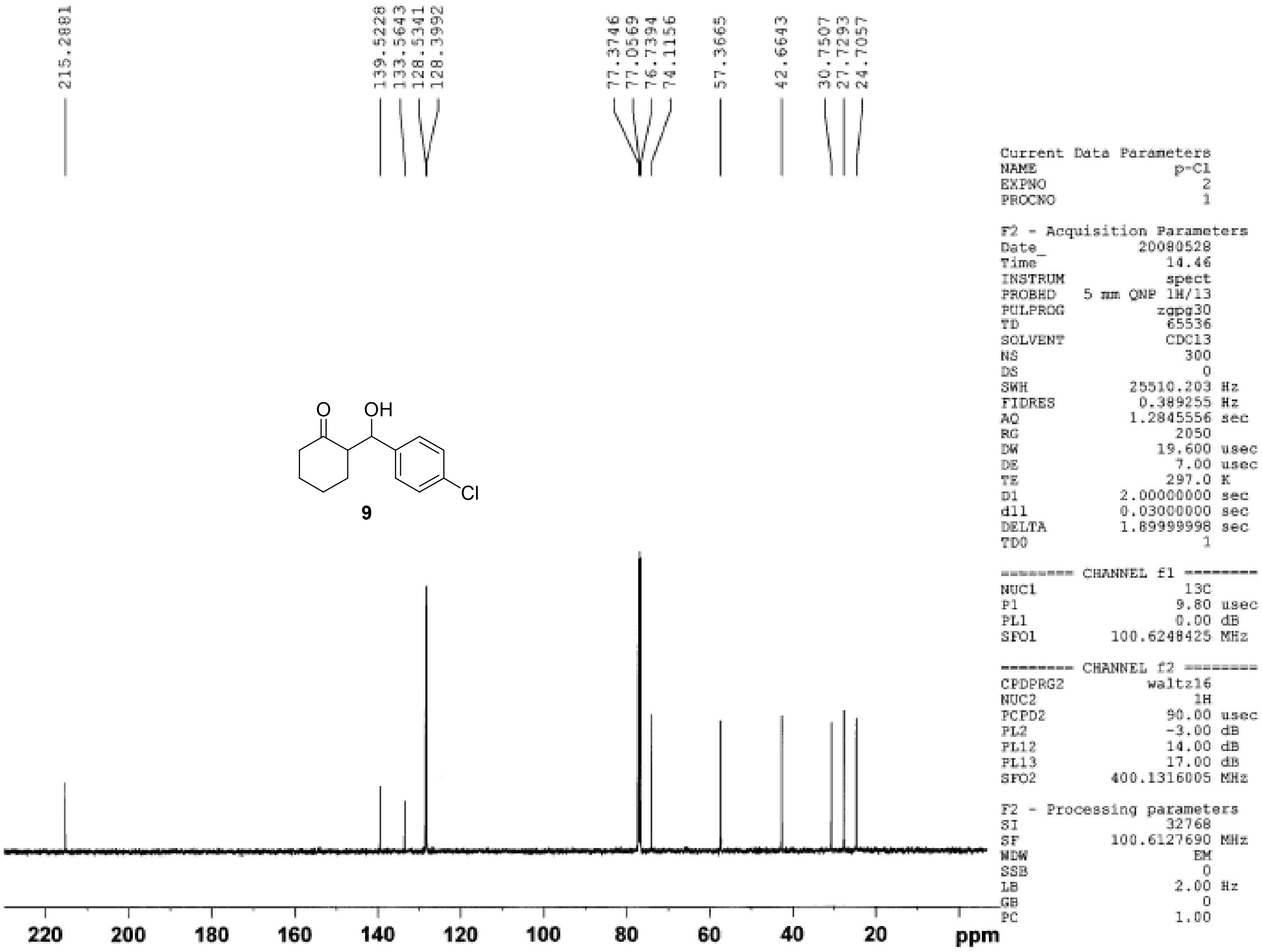


Fig. 56 ^{1}H-NMR spectrum of **9**



```
Current Data Parameters
NAME                 p-Cl
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080528
Time                14.46
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   300
DS                     0
SWH            25510.203 Hz
FIDRES          0.389255 Hz
AQ             1.2845556 sec
RG                  2050
DW                19.600 usec
DE                  7.00 usec
TE                 297.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                 0.00 dB
SFO1         100.6248425 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               14.00 dB
PL13               17.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00
```

Fig. 57 ^{13}C-NMR spectrum of **9**

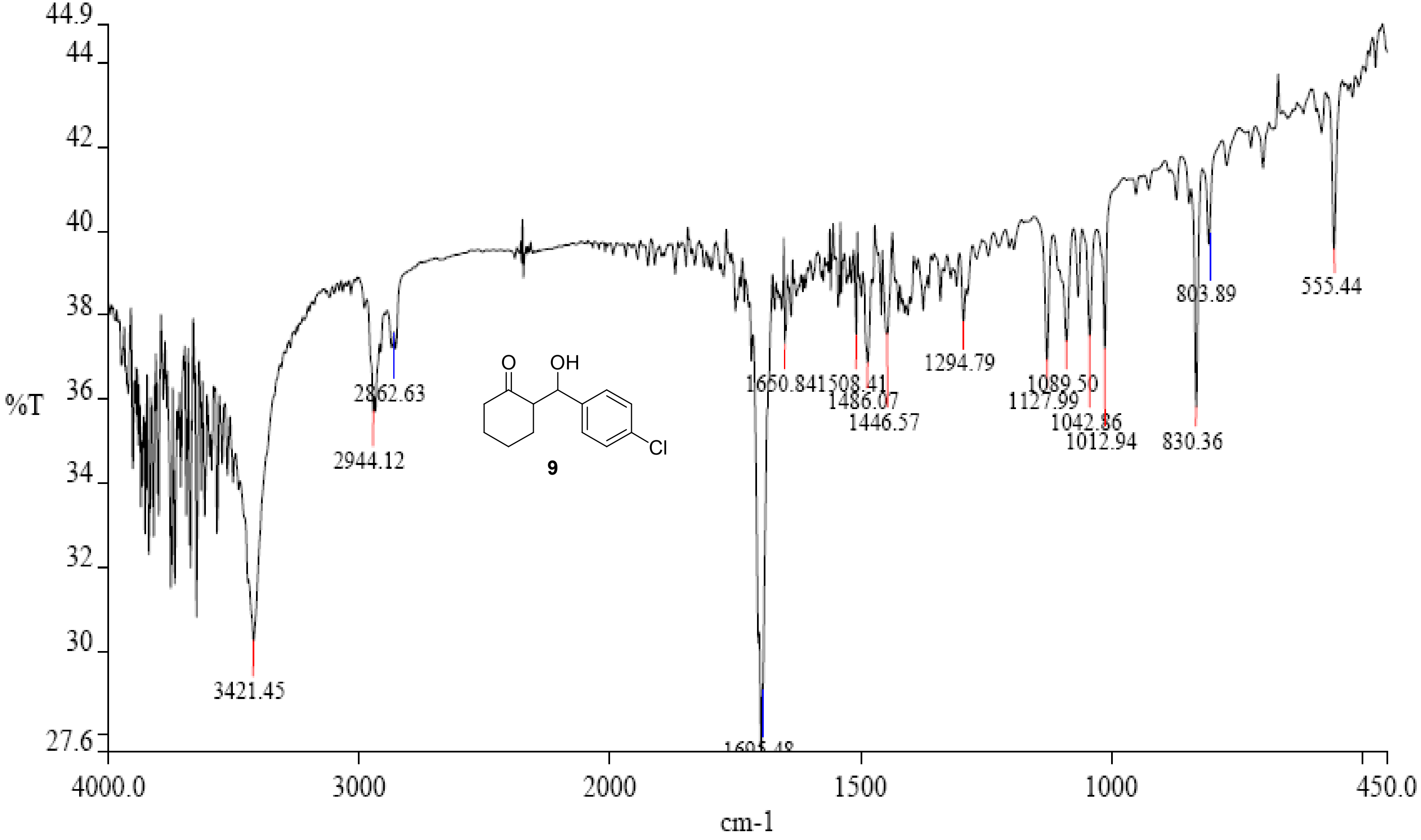
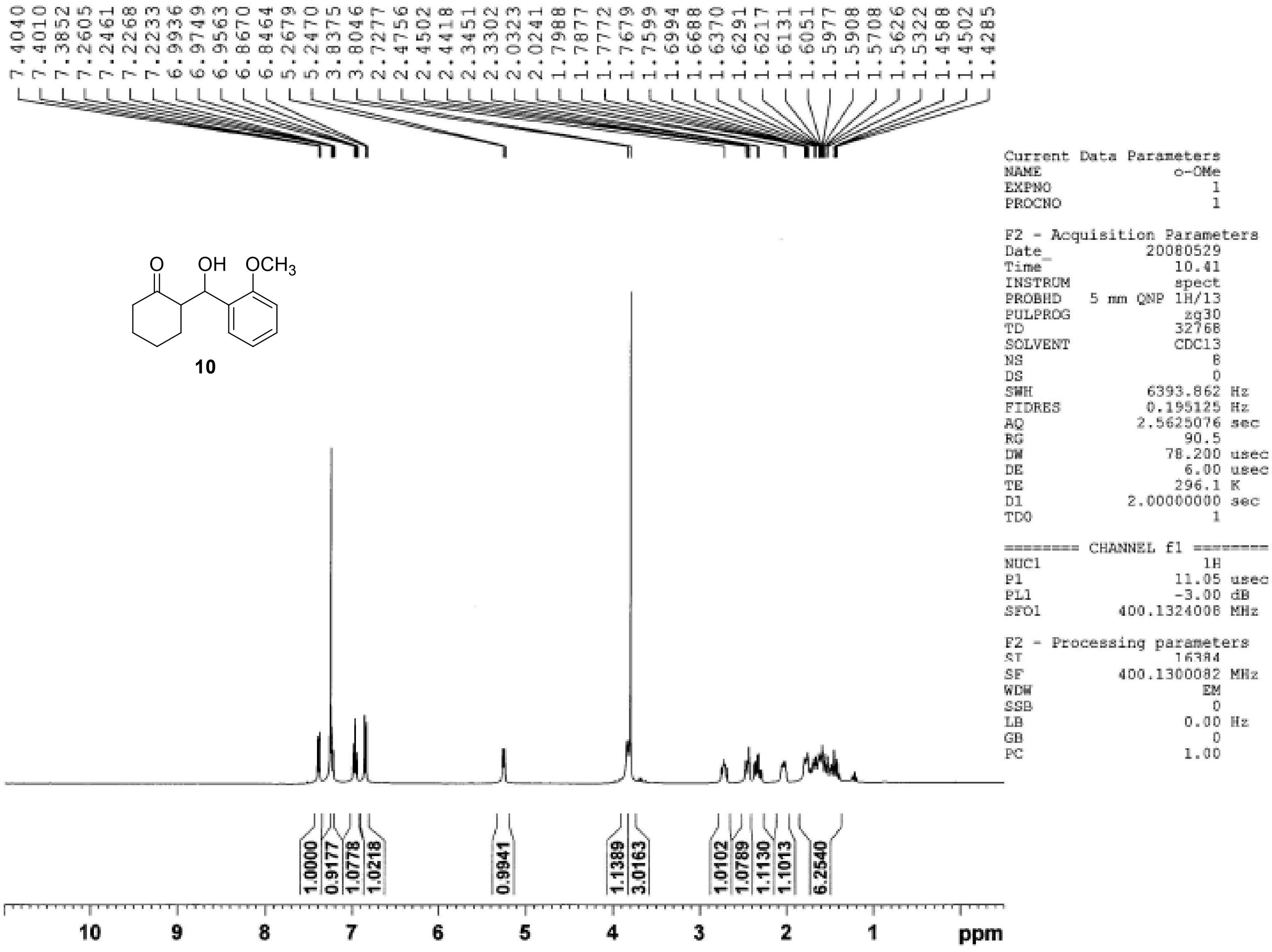


Fig. 58 FT-IR spectrum of **9**



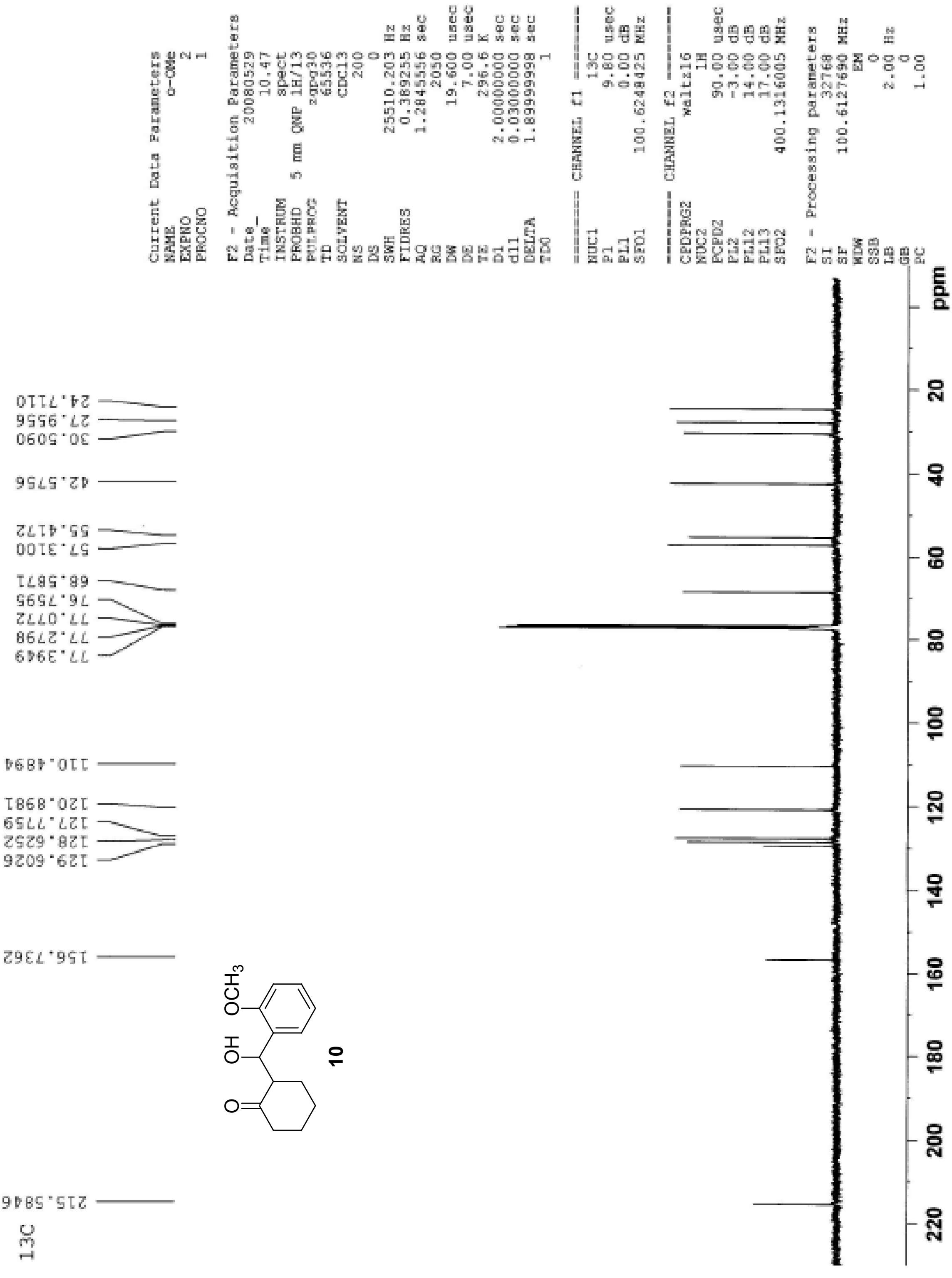
```
Current Data Parameters
NAME                 o-OMe
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080529
Time                 10.41
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               6393.862 Hz
FIDRES            0.195125 Hz
AQ               2.5625076 sec
RG                    90.5
DW                  78.200 usec
DE                    6.00 usec
TE                   296.1 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.05 usec
PL1                  -3.00 dB
SFO1           400.1324008 MHz

F2 - Processing parameters
SI                   16384
SF             400.1300082 MHz
WDW                     EM
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

Fig. 59 ^{1}H-NMR spectrum of **10**



```
Current Data Parameters
NAME          o-OMe
EXPNO             2
PROCNO            1

F2 - Acquisition Parameters
Date_          20080529
Time              10.47
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    0
SWH           25510.203 Hz
FIDRES         0.389255 Hz
AQ            1.2845556 sec
RG                 2050
DW               19.600 usec
DE                 7.00 usec
TE                296.6 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.80 usec
PL1                0.00 dB
SFO1        100.6248425 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -3.00 dB
PL12              14.00 dB
PL13              17.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 2.00 Hz
GB                    0
PC                 1.00
```

Fig. 60 ^{13}C-NMR spectrum of **10**

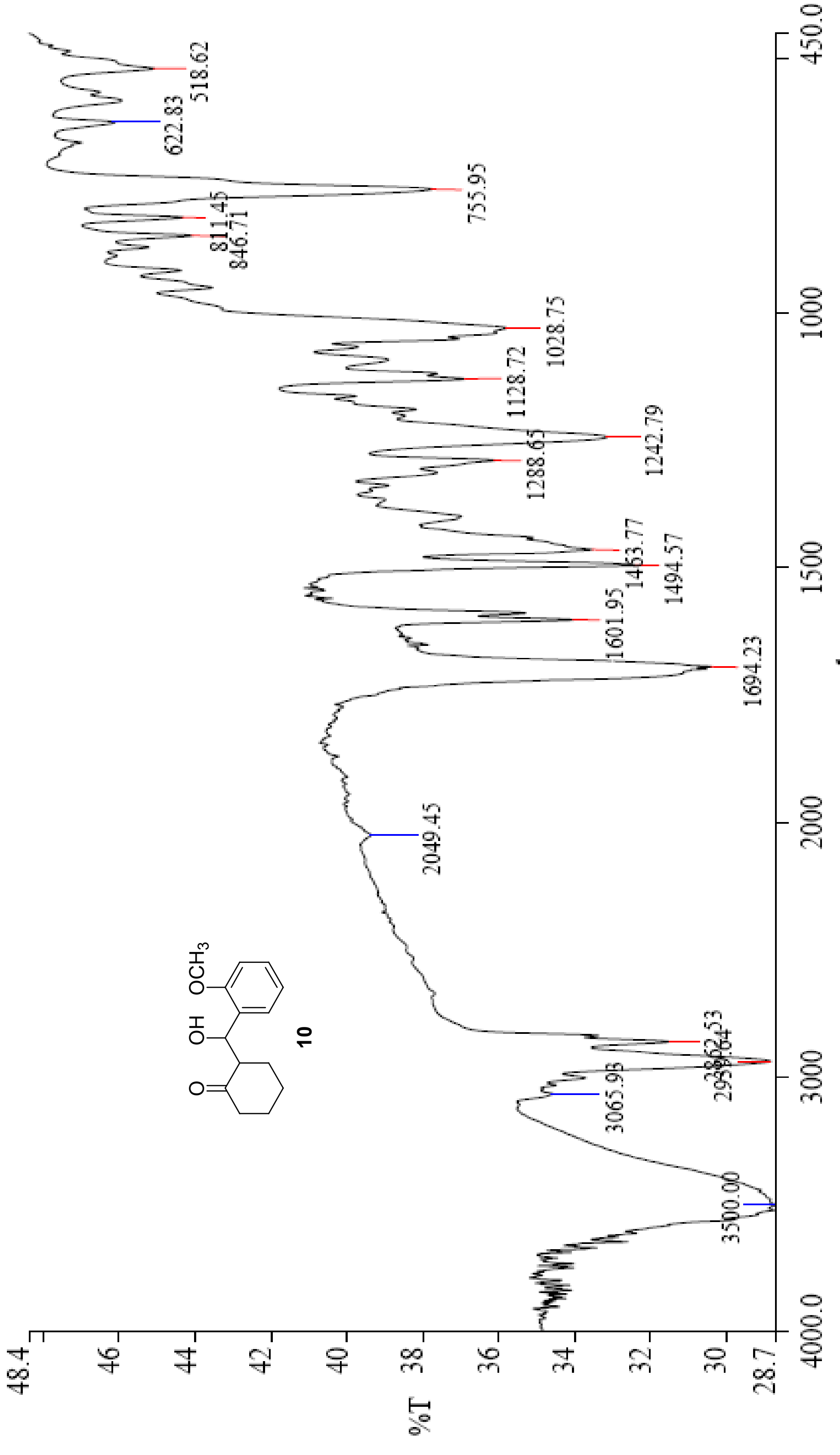
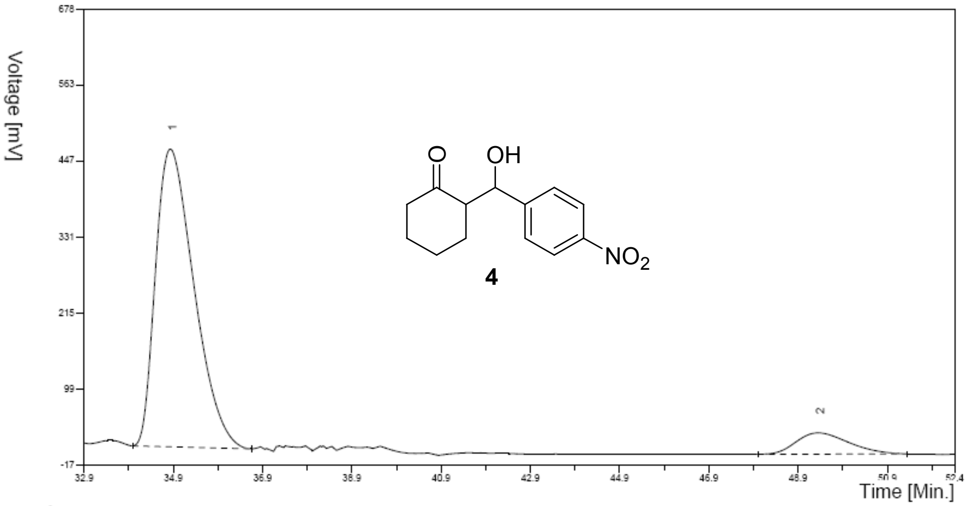


Fig. 62 FT-IR spectrum of **10**

Fig. 63 HPLC analysis of 2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (4).

(Chiralcel OD-H column, hexane:2-propanol = 9:1, 0.5 mL/min, 254 nm UV detector)

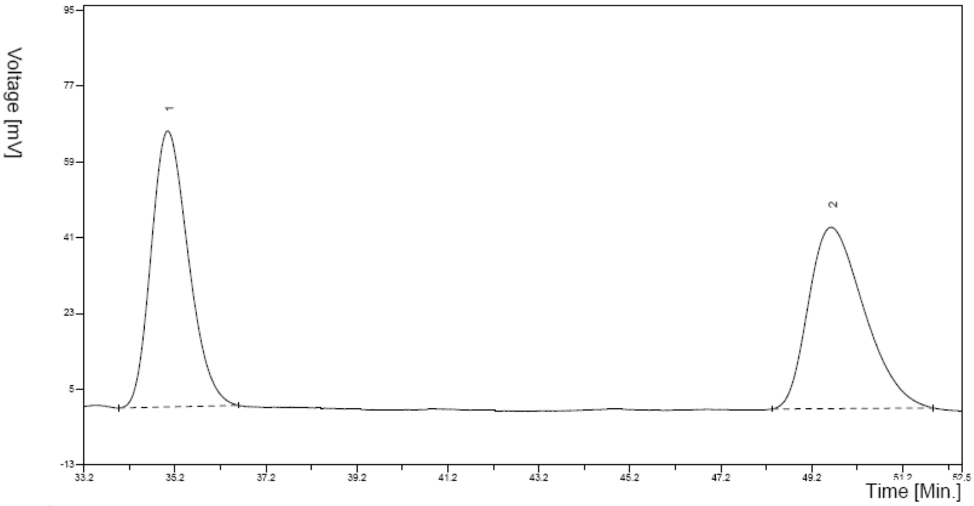
a) 82.3% ee (Table 1; entry 14)



積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
34.79	27143.60	91.1083
49.31	2649.09	8.8917
	29792.70	100

b) racemic (4)



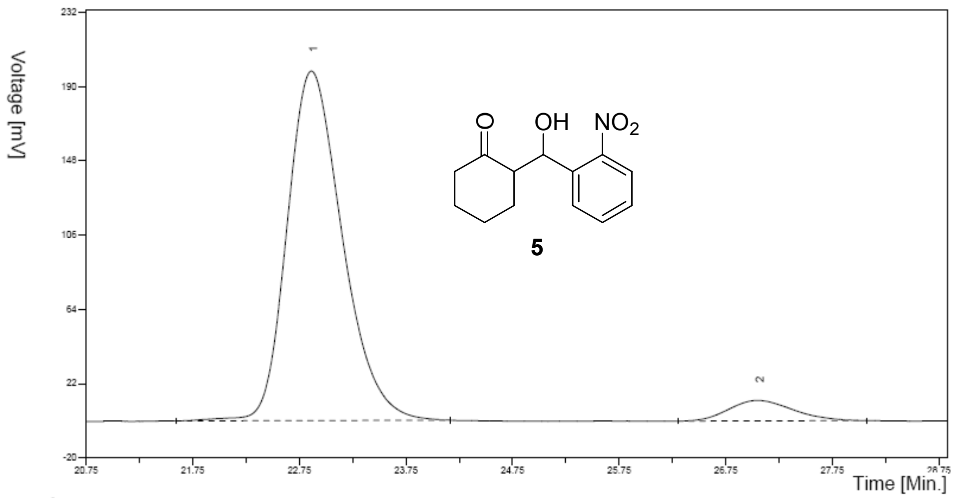
積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
35.04	3720.68	50.3163
49.63	3673.90	49.6837
	7394.58	100

Fig. 64 HPLC analysis of 2-[Hydroxy-(2-nitro-phenyl)-methyl]-cyclohexanone (5).

(Chiralcel OD-H column, hexane:2-propanol = 9:1, 0.5 mL/min, 254 nm UV detector)

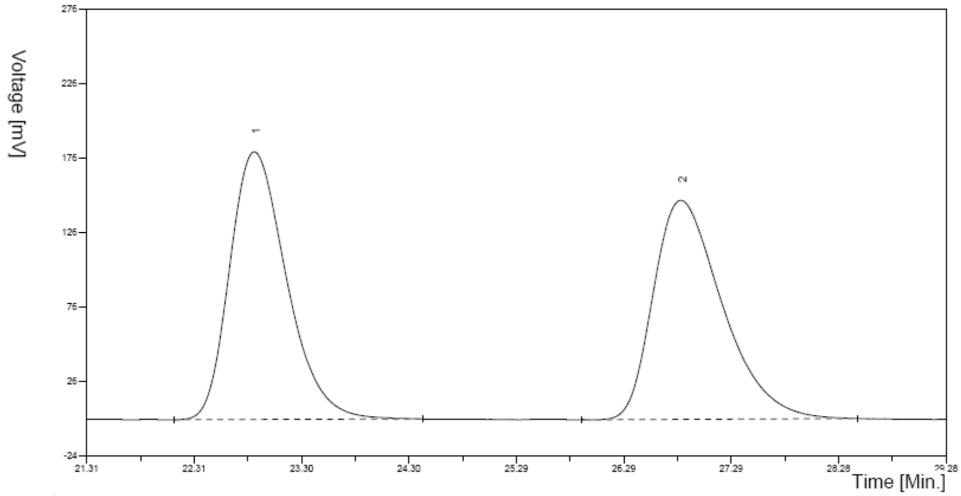
a) 87.3% ee (Table 2; entry 1)



積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
22.86	7115.51	93.6549
27.05	482.07	6.3451
	7597.59	100

b) racemic (5)



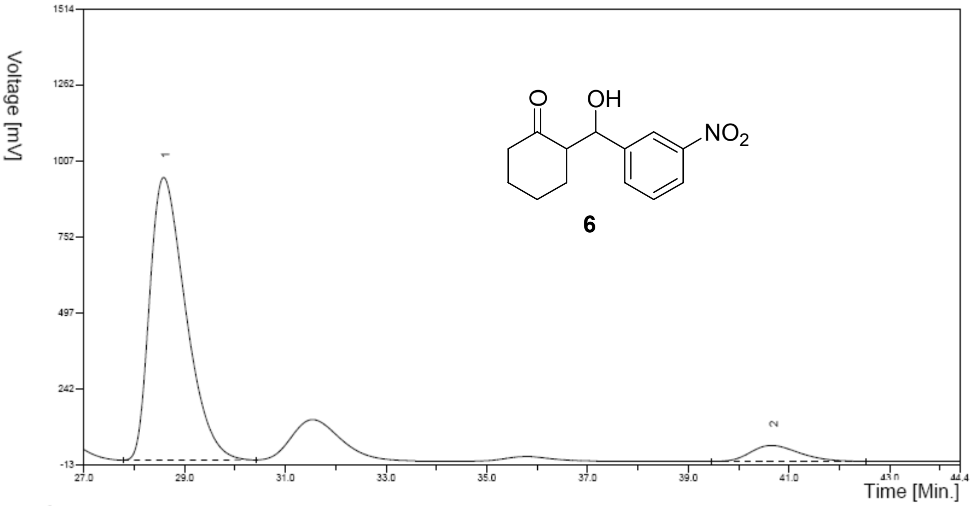
積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
22.86	6578.32	50.1406
26.82	6541.43	49.8594
	13119.75	100

Fig. 65 HPLC analysis of 2-[Hydroxy-(3-nitro-phenyl)-methyl]-cyclohexanone (6).

(Chiralcel OD-H column, hexane:2-propanol = 9:1, 0.5 mL/min, 254 nm UV detector)

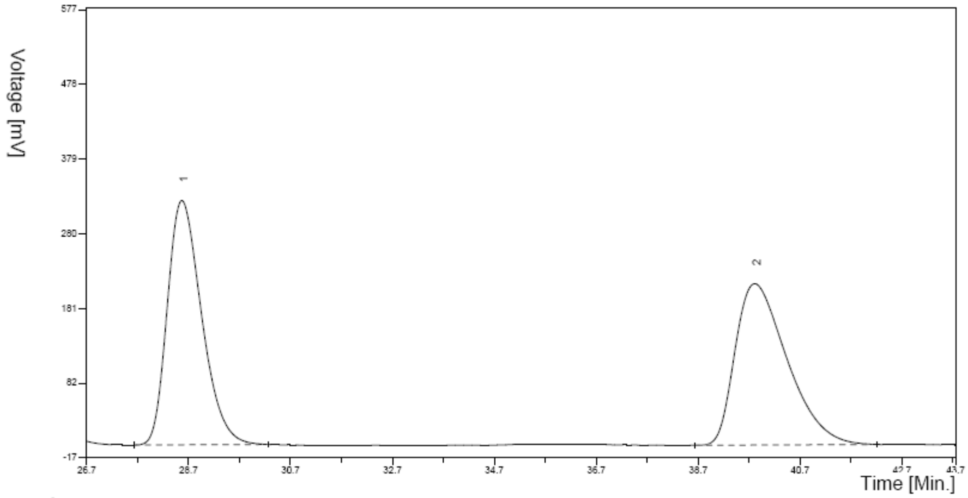
a) 85.7% ee (Table 2; entry 2)



積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
28.62	46928.97	92.8921
40.69	3590.89	7.1079
	50519.86	100

b) racemic (6)



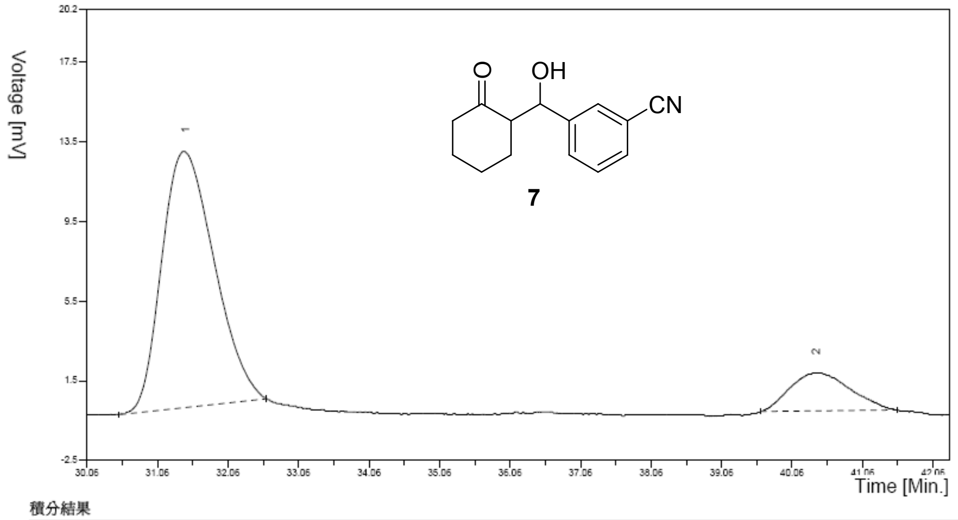
積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
28.57	15115.06	49.9908
39.81	15120.61	50.0092
	30235.67	100

Fig. 66 HPLC analysis of 3-[Hydroxy-(2-oxo-cyclohexyl)-methyl]-benzonitrile (7).

(Chiralcel OD-H column, hexane:2-propanol = 9:1, 0.5 mL/min, 254 nm UV detector)

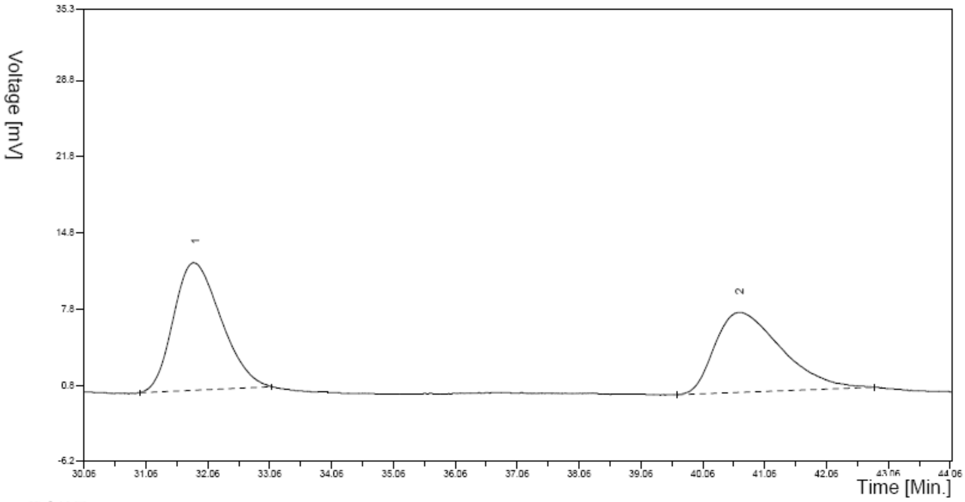
a) 71.1% ee (Table 2; entry 3)



積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
31.43	665.43	85.5330
40.38	112.55	14.4670
	777.98	100

b) racemic (7)



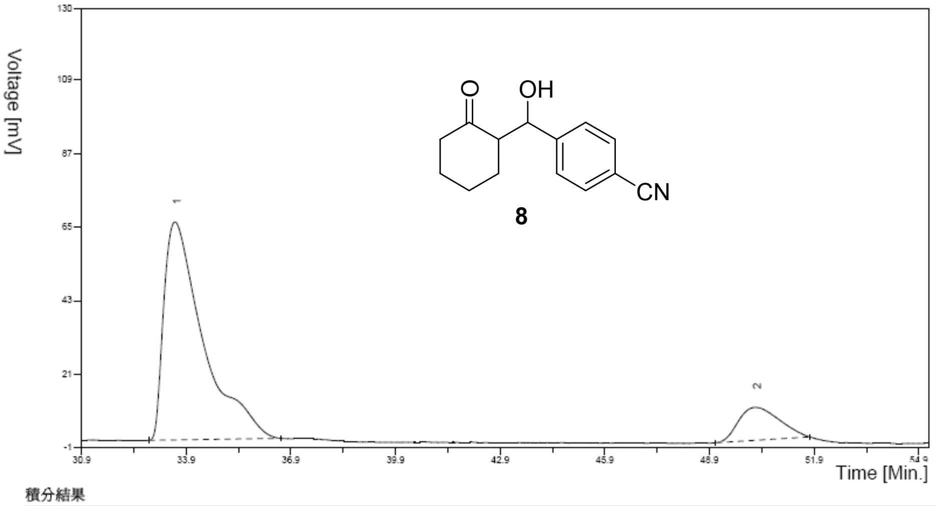
積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
31.83	626.82	53.3460
40.63	548.19	46.6540
	1175.01	100

Fig. 67 HPLC analysis of 4-[Hydroxy-(2-oxo-cyclohexyl)-methyl]-benzonitrile (8).

(Chiralcel OD-H column, hexane:2-propanol = 9:1, 0.5 mL/min, 254 nm UV detector)

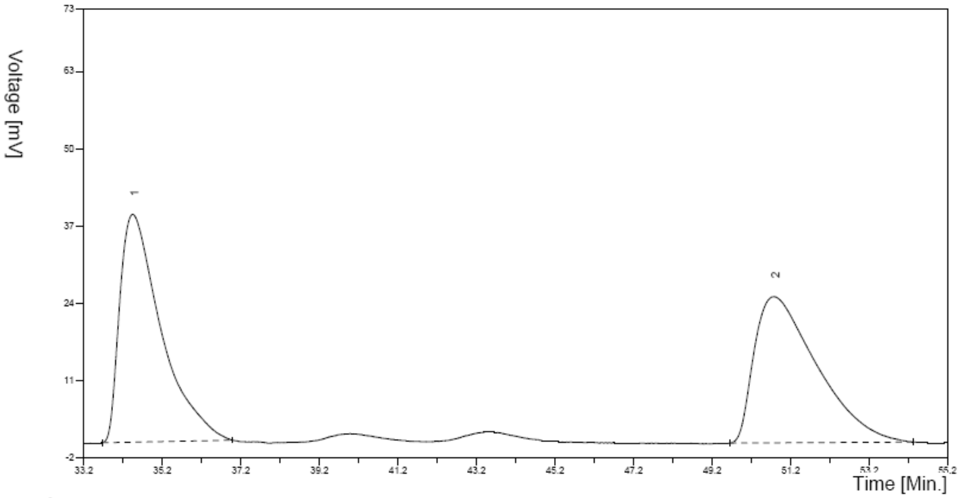
a) 72.9% ee (Table 2; entry 4)



積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
33.55	5094.78	86.4964
50.19	795.39	13.5036
	5890.16	100

b) racemic (8)



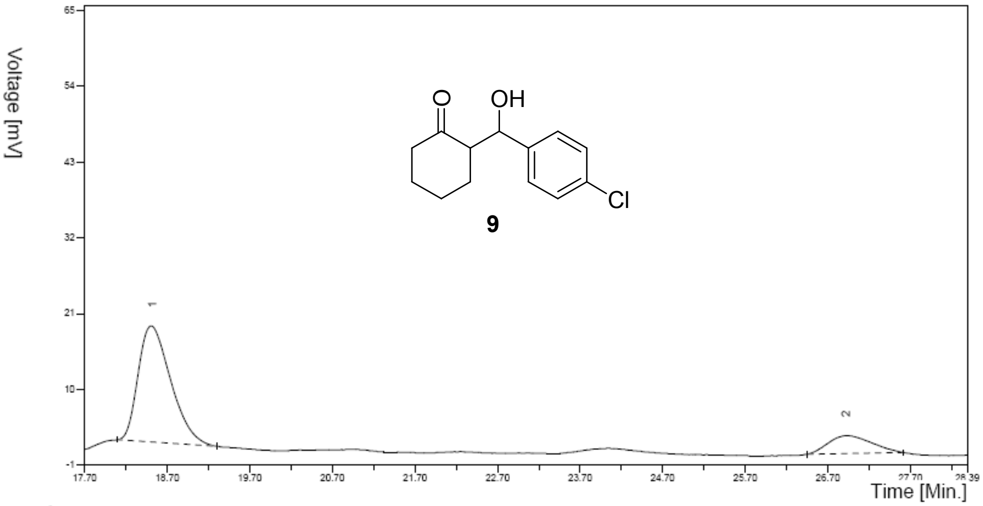
積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
34.45	2802.71	50.7109
50.77	2724.13	49.2891
	5526.83	100

Fig. 68 HPLC analysis of 2-[(4-Chloro-phenyl)-hydroxy-methyl]-cyclohexanone (9).

(Chiralcel OD-H column, hexane:2-propanol = 9:1, 0.5 mL/min, 254 nm UV detector)

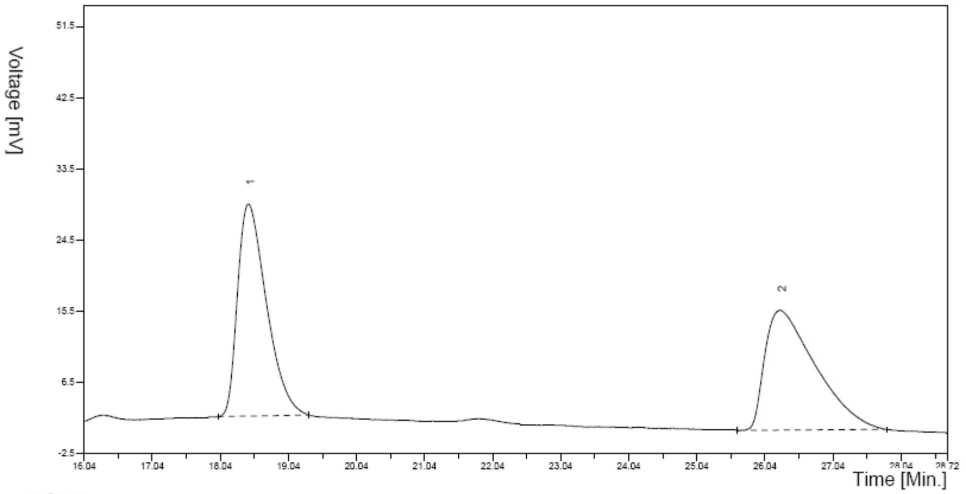
a) 66.3% ee (Table 2; entry 5)



積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
18.49	461.26	83.1191
26.89	93.68	16.8809
	554.93	100

b) racemic (9)



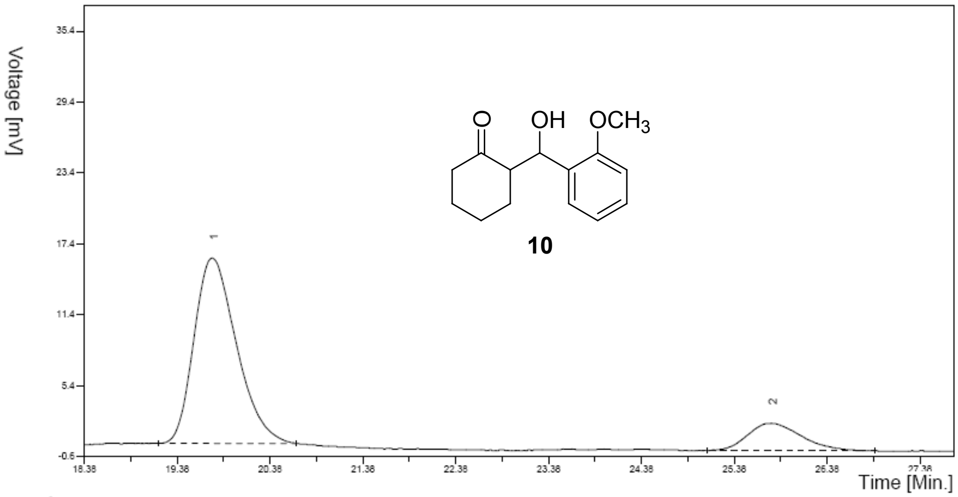
積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
18.45	790.23	50.1975
26.26	784.02	49.8025
	1574.25	100

Fig. 69 HPLC analysis of 2-[Hydroxy-(2-methoxy-phenyl)-methyl]-cyclohexanone (10).

(Chiralcel OD-H column, hexane:2-propanol = 9:1, 0.5 mL/min, 254 nm UV detector)

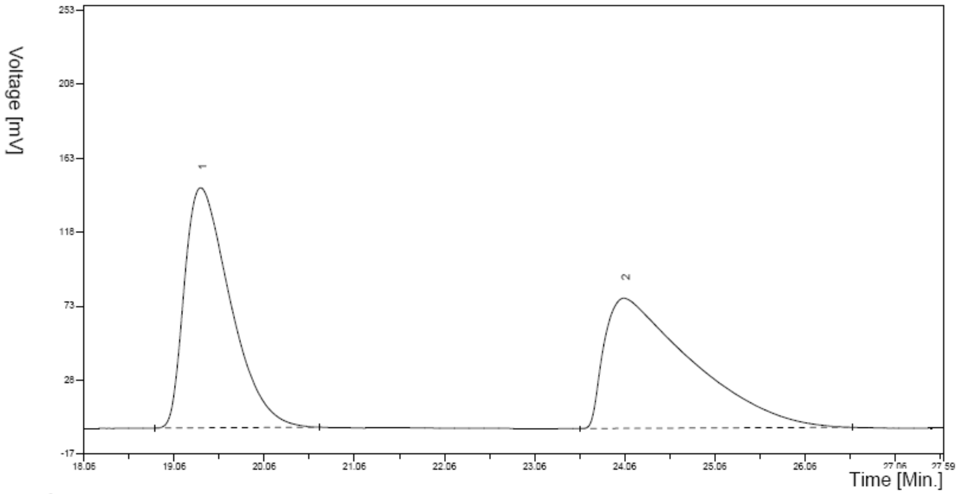
a) 68.9% ee (Table 2; entry 6)



積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
19.75	497.39	84.4280
25.77	91.74	15.5720
	589.13	100

b) racemic (10)



積分結果

擷取時間(min)	Area(mv.sec)	面積百分比(%)
19.35	5165.95	49.2852
24.05	5315.79	50.7148
	10481.74	100