

The catalytic activity of titania nanostructures in the synthesis of amides under solvent-free conditions

Sangaraiah Nagarajan^a, Park Ran^b, Poovan Shanmugavelan^a, Murugan Sathishkumar^a, Alagusundaram Ponnuswamy^{*a}, Kee Suk Nahm^{*b}, and G. Gnana kumar^{*c}

^a Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Tamilnadu 625 021, India.
Email: ramradkrish@yahoo.co.in; Tel: +91 9600868323

^b Specialized Graduate School of Hydrogen and Fuel Cell Engineering, Chonbuk National University, Jeonju 561-756, Republic of Korea. Email: nahmks@chonbuk.ac.kr; Fax: +82 63 270 2306

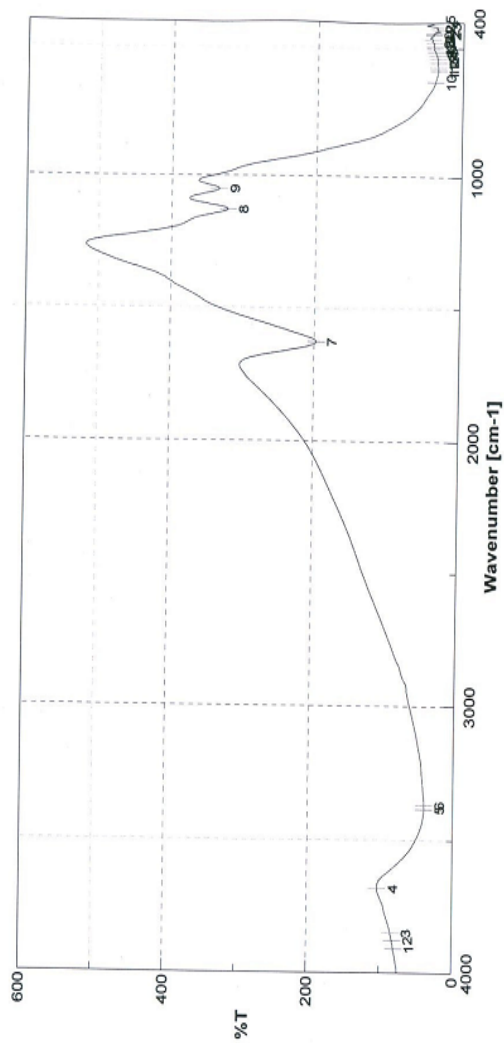
^c Department of Physical Chemistry, School of Chemistry, Madurai Kamaraj University, Tamilnadu 625021, India.
Email: kumarg2006@gmail.com; Tel: +91 9585752997

Supporting Information

General Experimental section

All chemicals and solvents were of commercially high purity grade purchased from Acros organics Synthesis Pvt. Ltd. and Sigma-Aldrich Ltd, India. Melting points were obtained on electro-thermal apparatus and are uncorrected. Conventional transmission electron micrographs were recorded on JEOL JEM-2010 transmission electron microscope equipped with an energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction patterns of the prepared materials were characterized by using a (D-Max-3A, Rigaku XRD) diffractometer. FT-IR spectrum of the sulfated titania nanotubes was recorded between 400-4000 cm^{-1} transmittance mode using Jasco FT-IR spectrophotometer. Textural properties of the prepared materials were characterized by using BET surface area analyzer BELSORP. Thermal behavior of the prepared nanostructured materials was examined on a Perkin-Elmer (Wellesley, MA) instrument under a nitrogen atmosphere at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ from 30 to 800 $^{\circ}\text{C}$. ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker Avance 300 MHz spectrometer and the chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane, with J values in Hertz. The splitting patterns in ^1H NMR spectra are reported as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. ^{13}C NMR data are reported with the solvent peak ($\text{CDCl}_3 = 77.0$) as the internal standard. The spectral data of all known compounds are consistent with those reported previously.

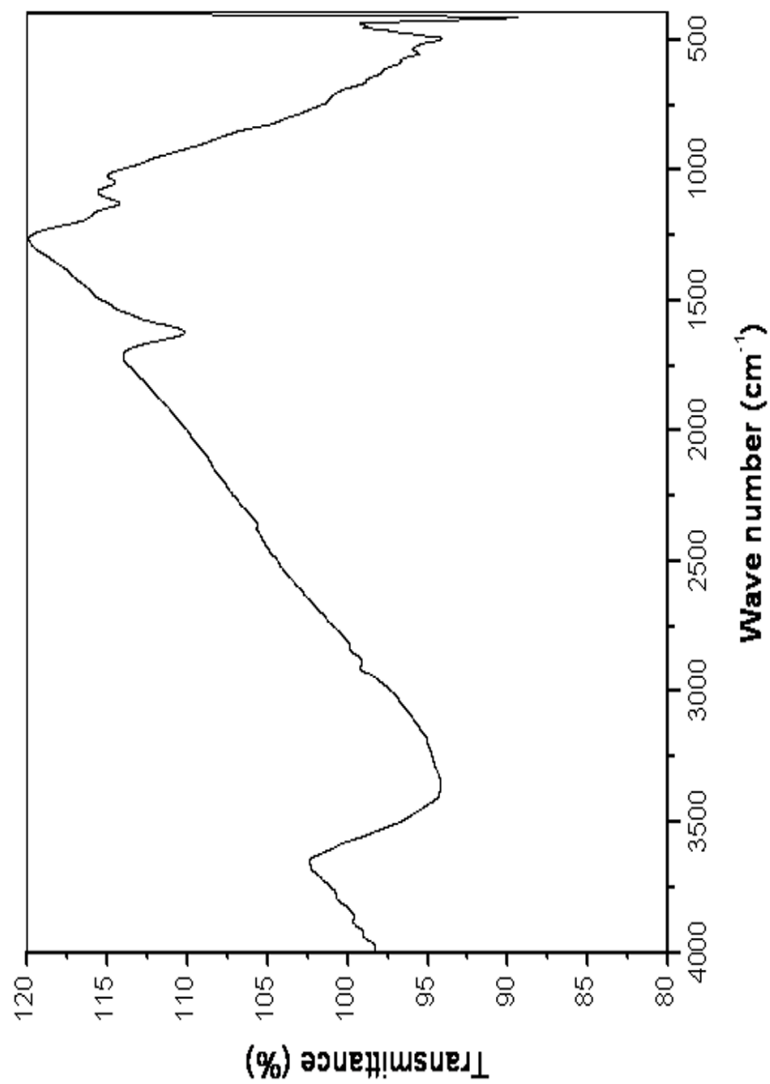
COPIES OF FT-IR, ¹H AND ¹³C NMR SPECTRA OF REPRESENTATIVE AMIDES



Accumulation 16
 Resolution 2 cm-1
 Zero Filling OFF
 Apodization Cosine
 Gain Auto (4)
 Scanning Speed Auto (2 mm/sec)
 Date/Time 1/12/2012 0:04AM
 Path C:\Users\Operator\Documents\11/21/2011 10:10PM
 Operator
 File Name Memory#3
 Sample Name
 Comment

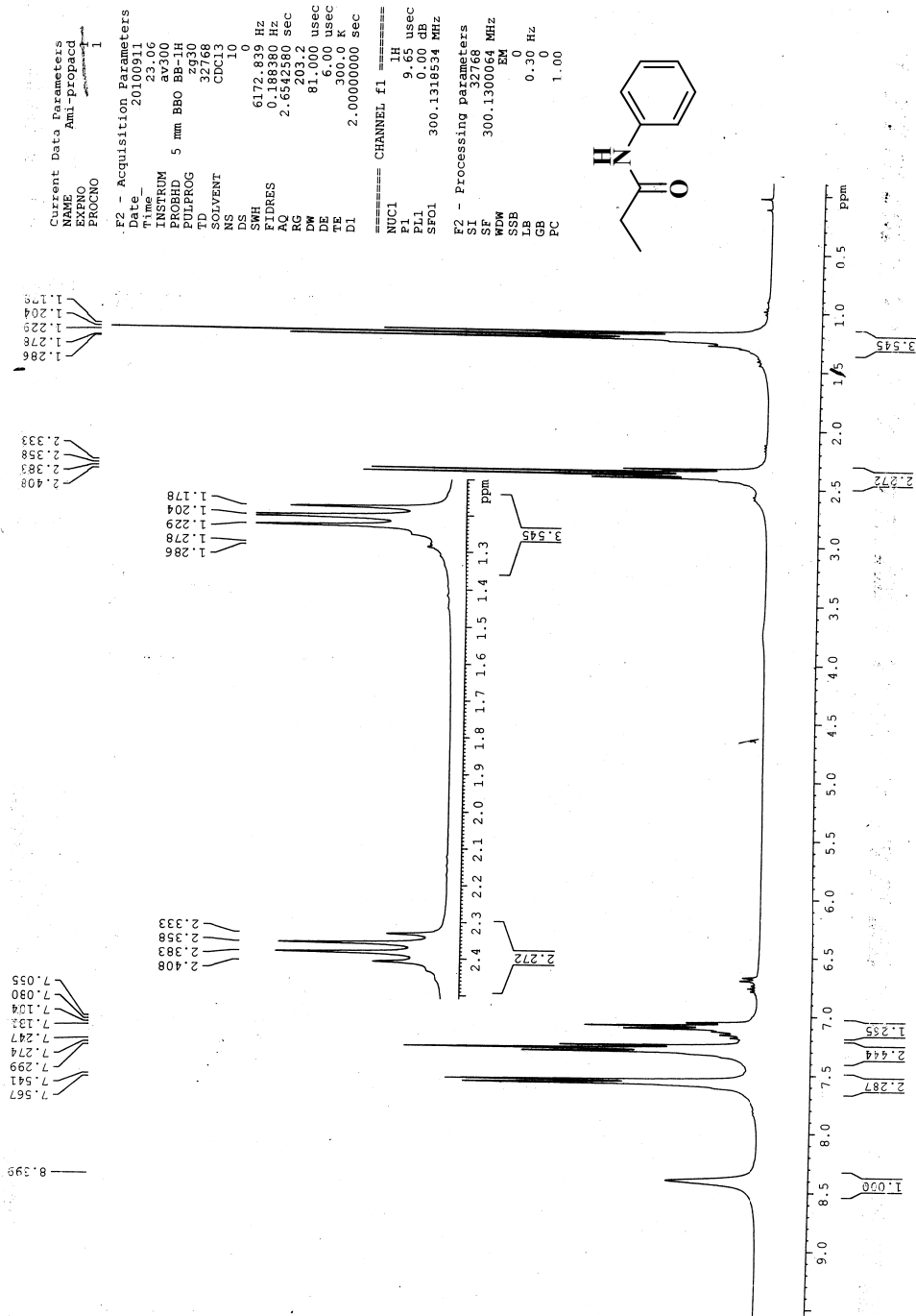
No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3969.48	80.3876	2	3876.22	82.116	3	3848.26	84.5244
4	3660.48	103.391	5	3384.46	40.102	6	3369.03	40.245
7	1625.7	196.932	8	1130.08	321.905	9	1051.98	334.341
10	631.573	38.346	11	587.218	34.5358	12	574.683	34.8162
13	556.363	35.0993	14	540.935	35.2086	15	527.436	36.4078
16	513.936	38.6634	17	500.437	40.6838	18	483.688	40.4152
19	479.224	40.699	20	463.796	42.9057	21	448.369	41.6672
22	441.619	40.8351	23	431.977	32.2657	24	420.406	34.7765
25	402.085	40.8352						

FT-IR spectrum of the sulfated titania nanoparticles

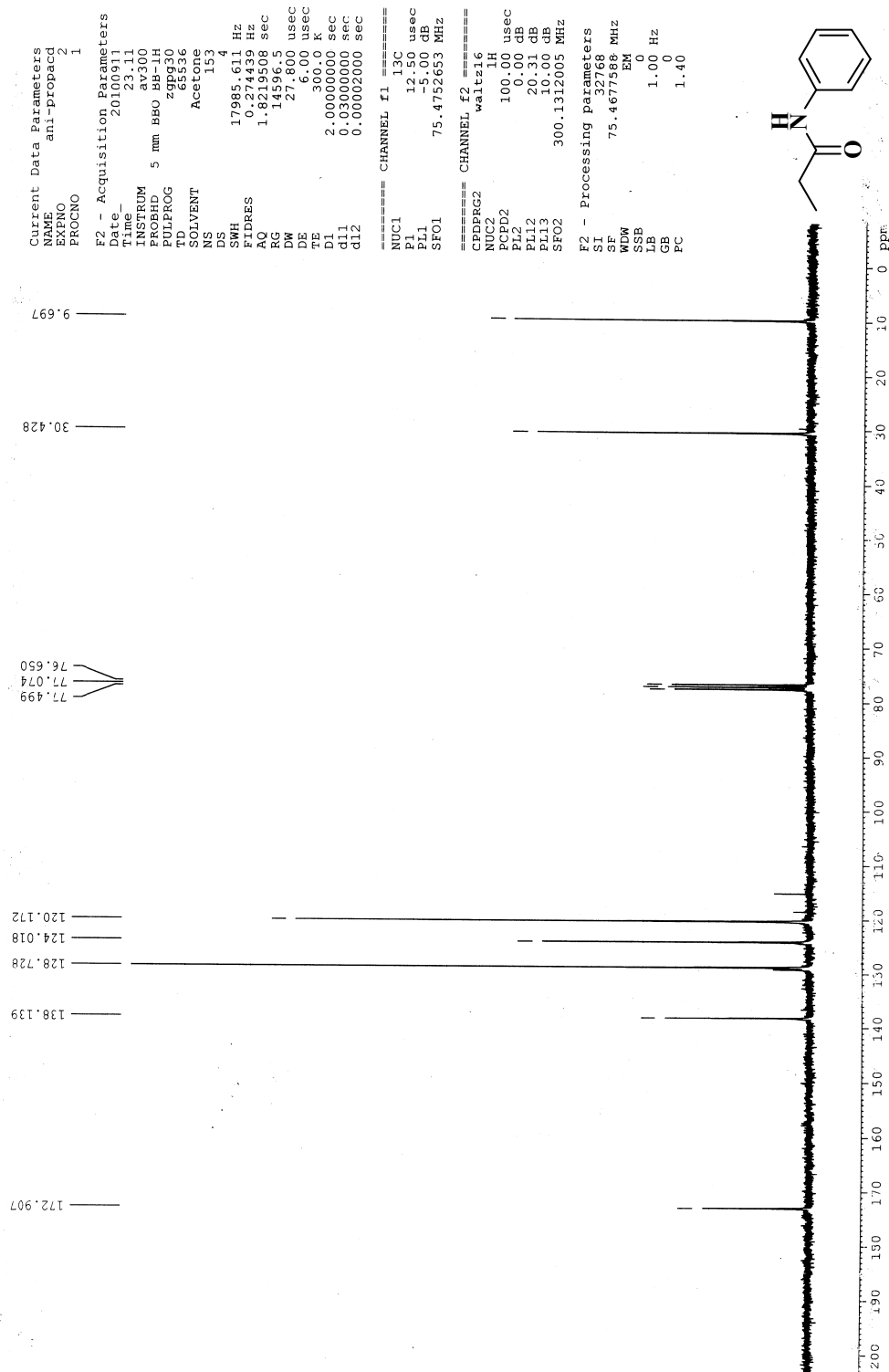


FT-IR spectrum of the sulfated titania nanotubes

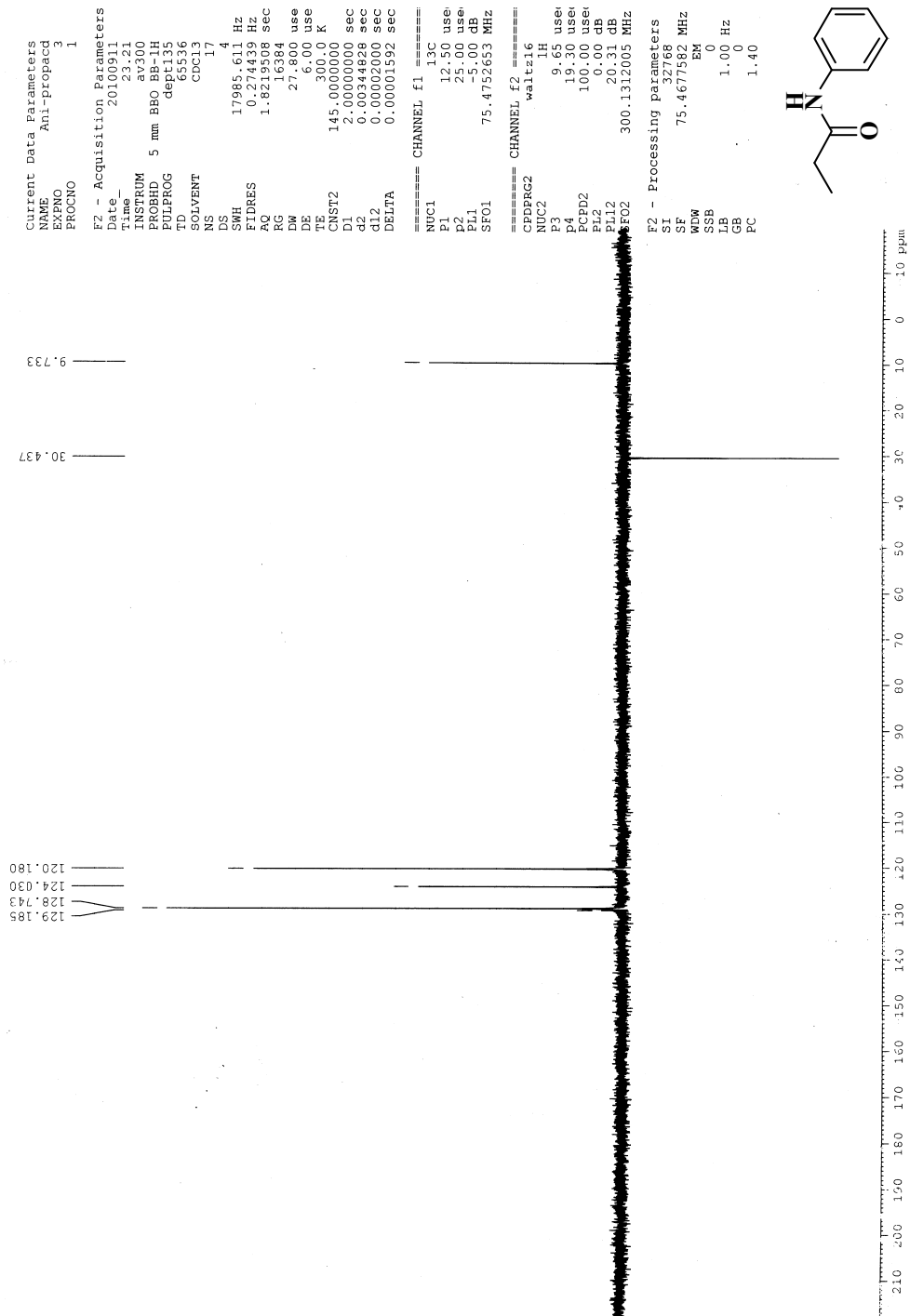
Figure exhibits infrared spectrum of the sulfated titanium oxide nanotubes and the obtained peaks are assigned as follows. Intensive bands observed at 3437 and 1636 cm^{-1} are attributed to the stretching vibration of hydroxyl groups and adsorbed water molecules, respectively. The S=O stretching of the sulfated titania nanotubes were found at 1052 and 1132 cm^{-1} which represent the successful implantation of sulfonic acid moieties over the titania nanotubes. Significant bands observed in the region 400-1000 cm^{-1} , represents Ti-O framework stretching frequencies.



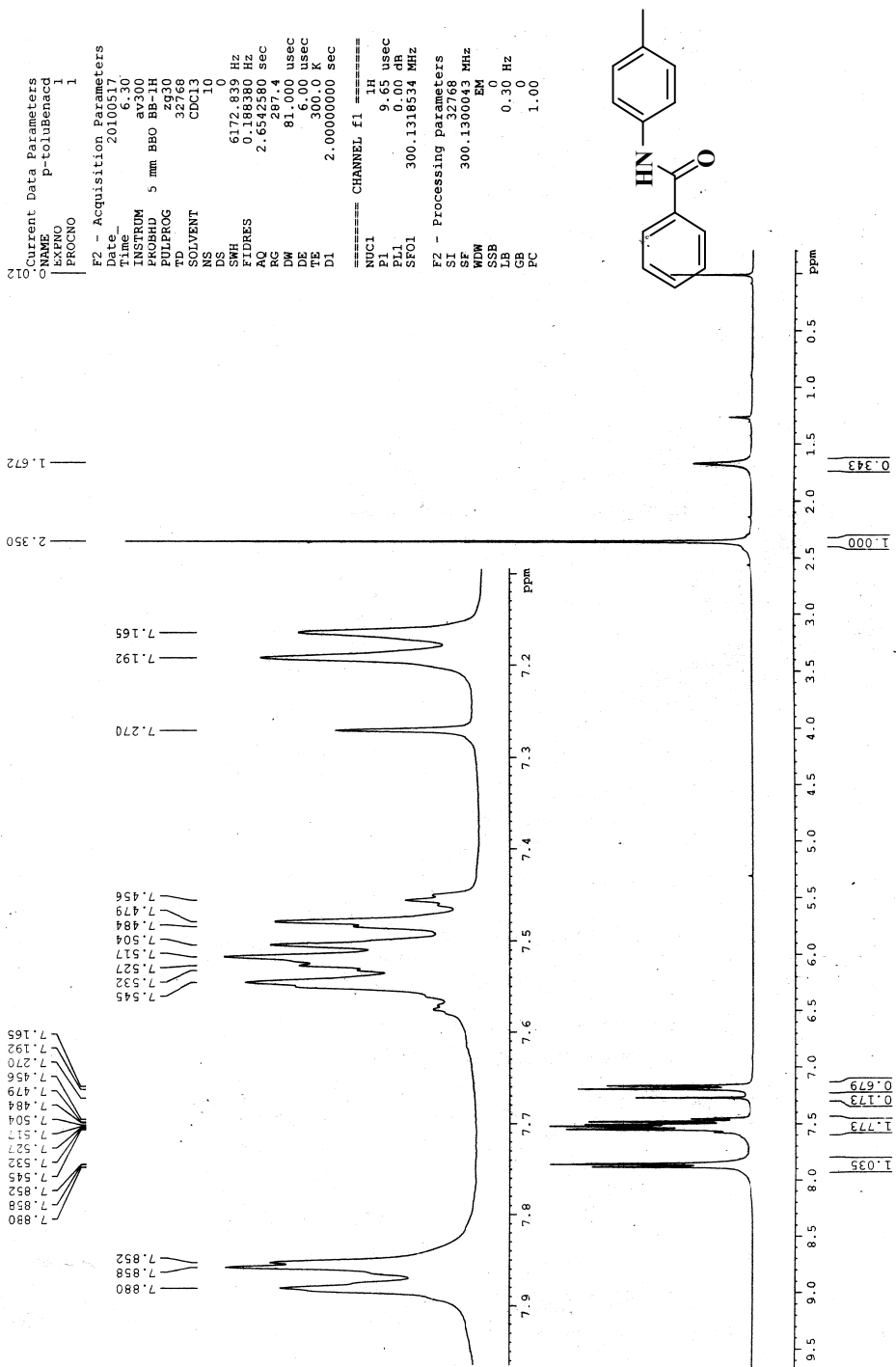
¹H NMR spectrum of N-phenylpropionamide(1i)

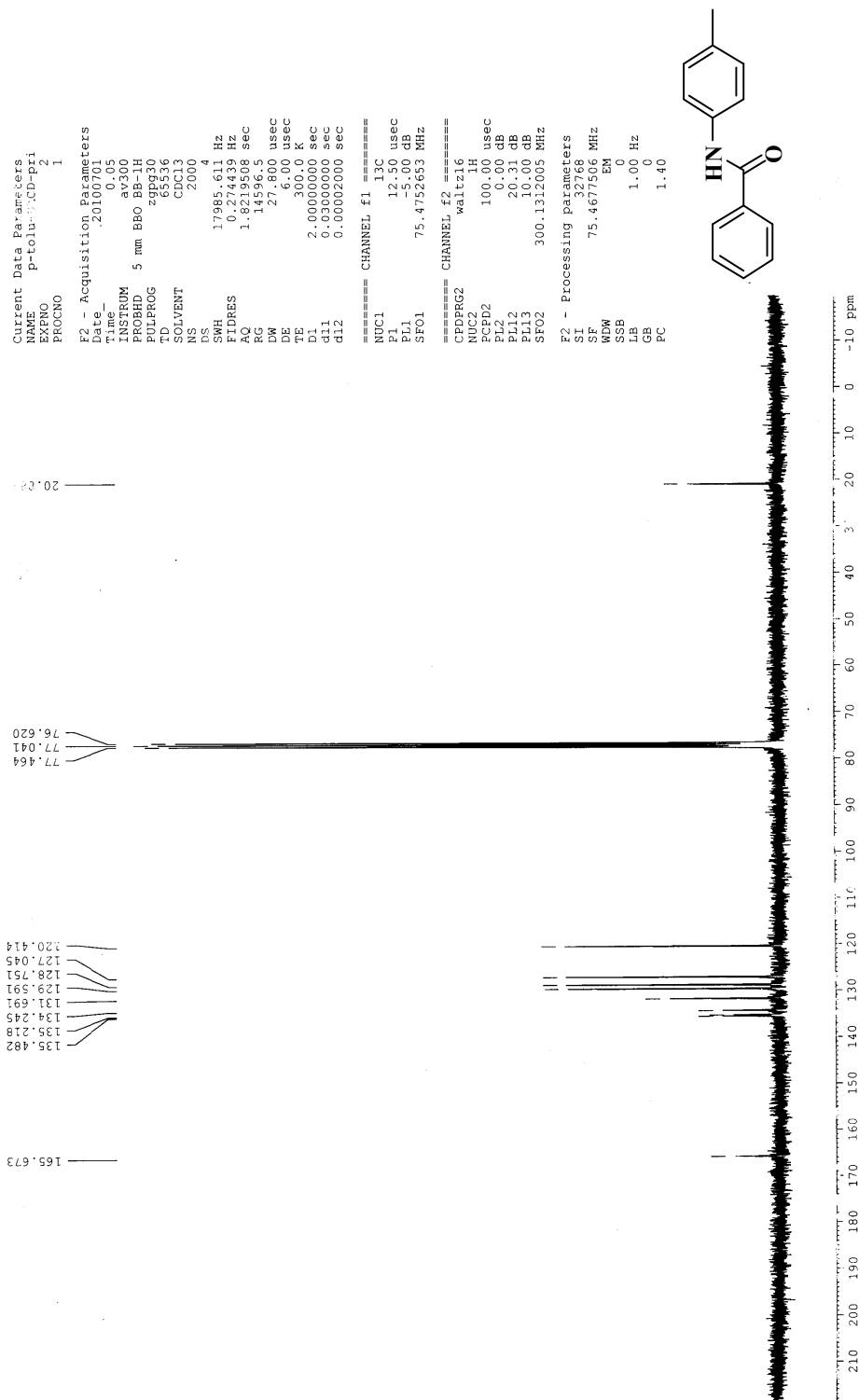


¹³C NMR spectrum of N-phenylpropionamide(1i)

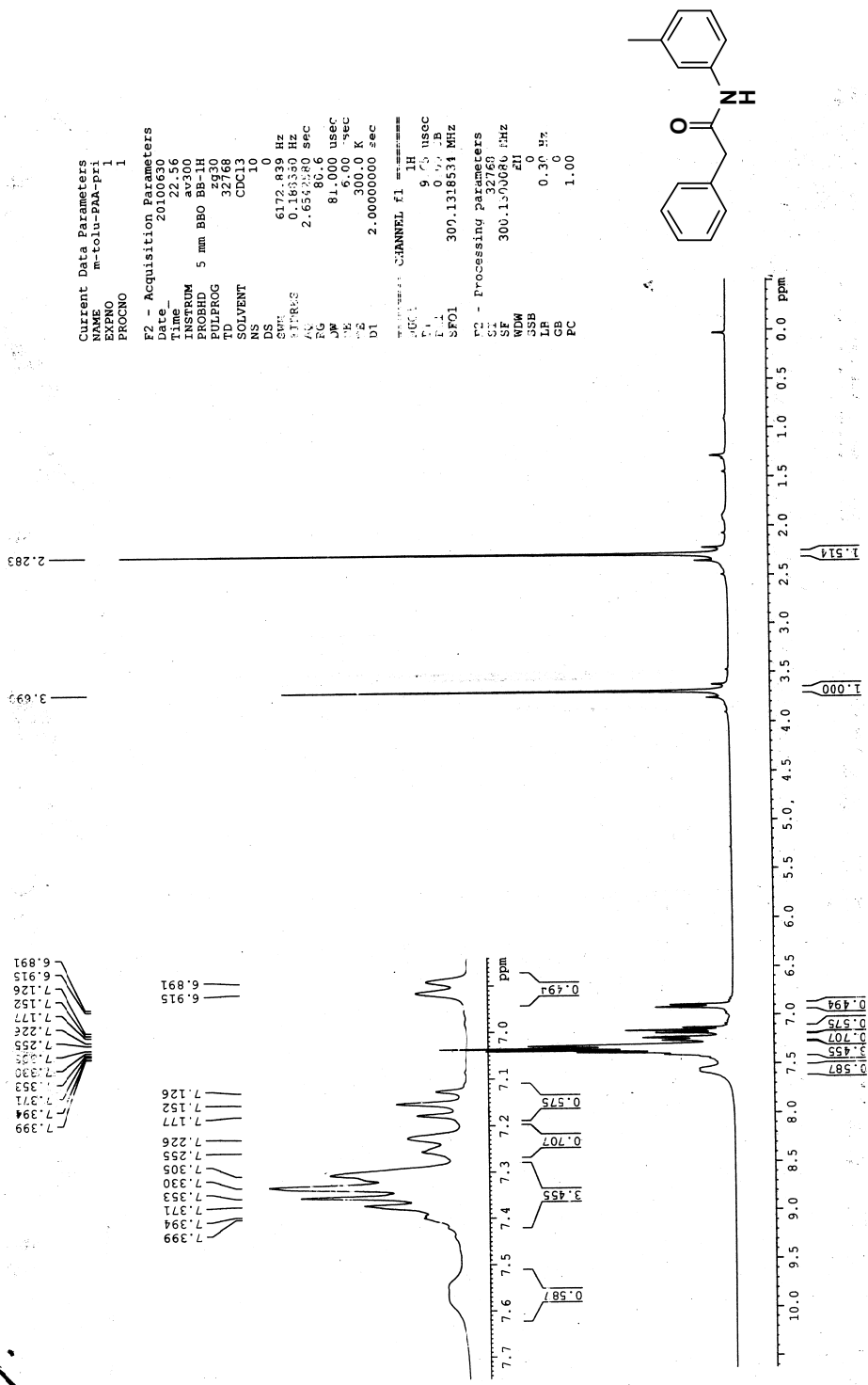


DEPT135 spectrum of N-phenylpropionamide(1i)





¹³C NMR spectrum of N-p-tolylbenzamide



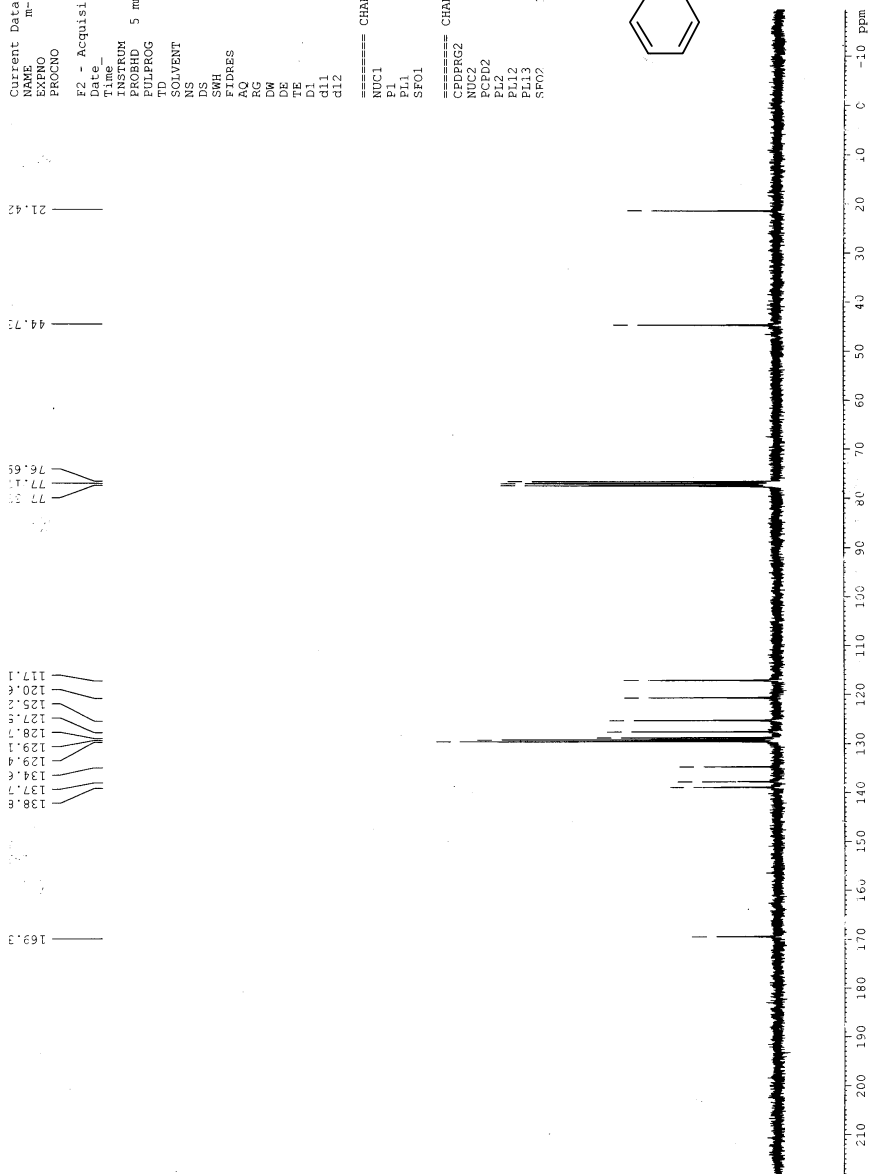
¹H NMR spectrum of N-m-tolylbenzamide (3a)

```
Current Data Parameters
NAME          m-coupram-p12
EXNO         21
PROCNO       1

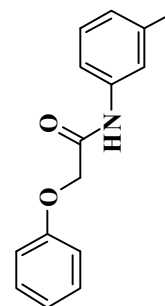
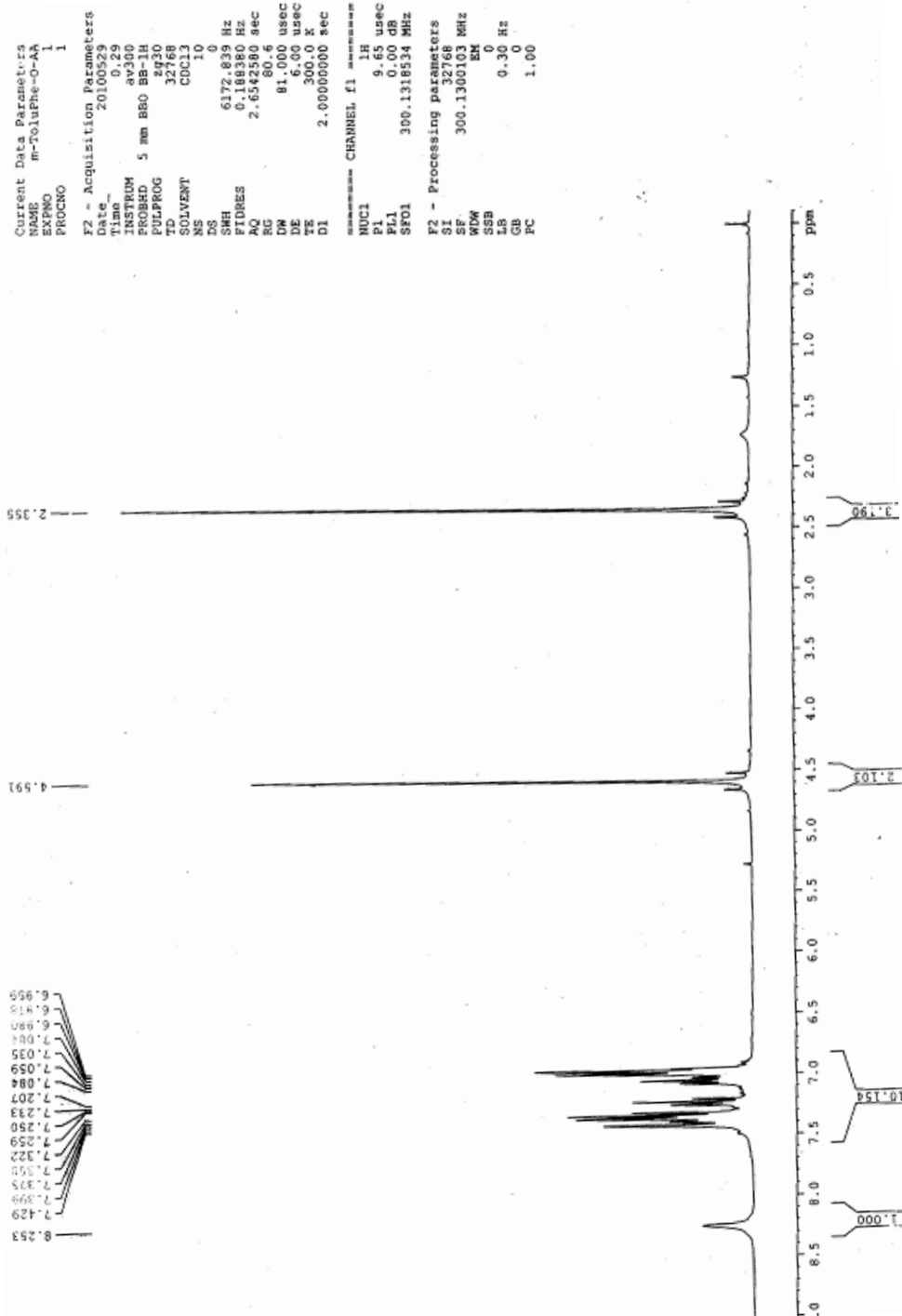
F2 - Acquisition Parameters
Date_         20100630
Time_         4:30
INSTRUM      spect
PROBHD       5 mm BBO BB-1H
PULPROG      zgpg30
TD            65536
SOLVENT      CDCl3
NS            251
DS            4
SWH           17985.611 Hz
FIDRES        0.2774439 Hz
AQ            1.8219508 sec
RG            14596.5
DM            27.800 use
DE            6.00 use
TE            300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

===== CHANNEL f1 =====
NUC1          13C
P1            12.50 use
PL1           -5.00 dB
SFO1          75.4752653 MHz

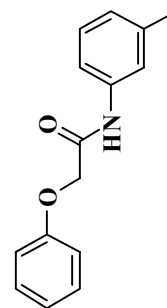
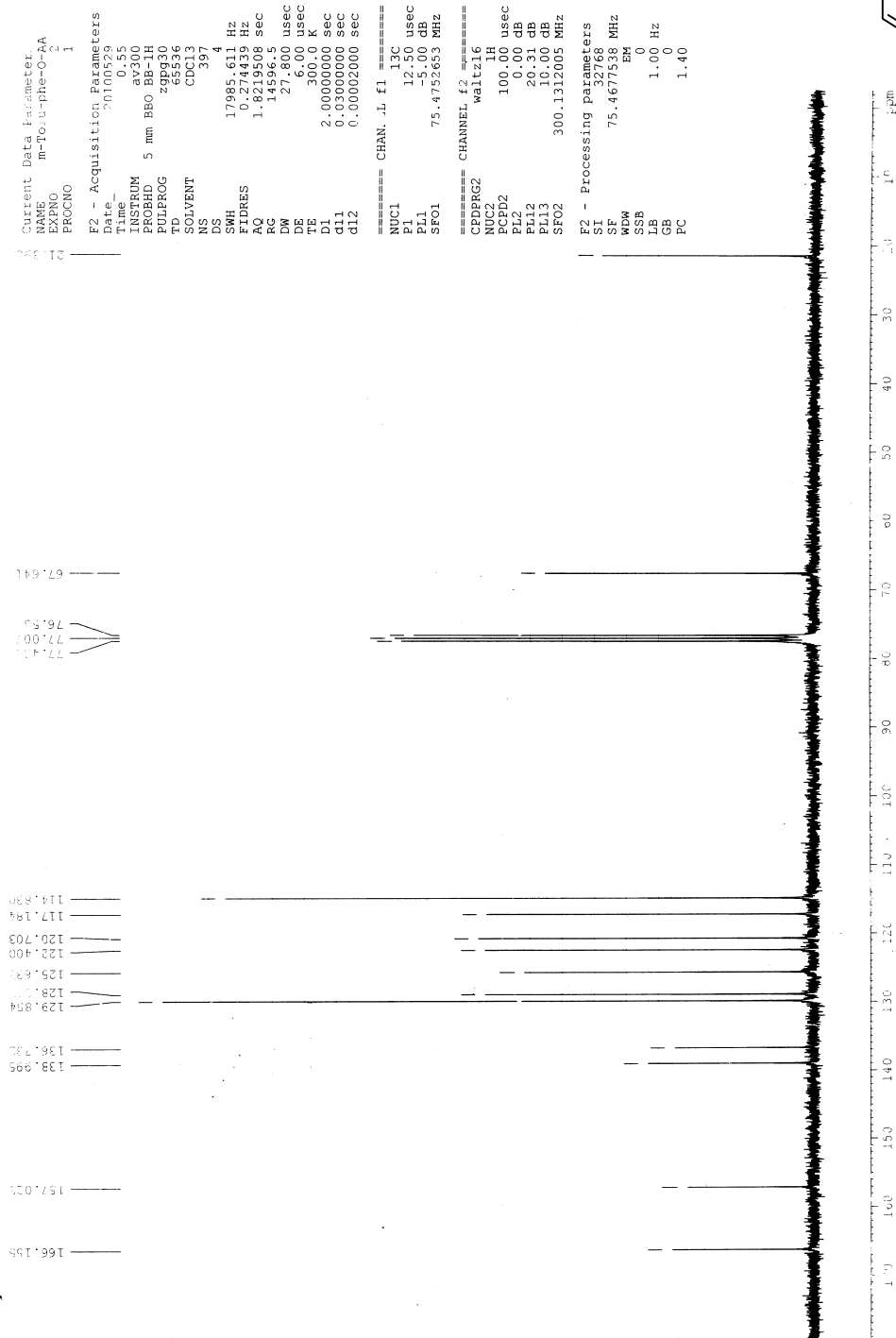
===== CHANNEL f2 =====
CPDPRG2      waltz16
NUC2          13C
PCPD2        100.00 use
PL2           0.00 dB
PL12         20.31 dB
PL13         10.00 dB
SFO2         300.1317005 MHz
```



¹³C NMR spectrum of N-m-tolylbenzamide (3a)



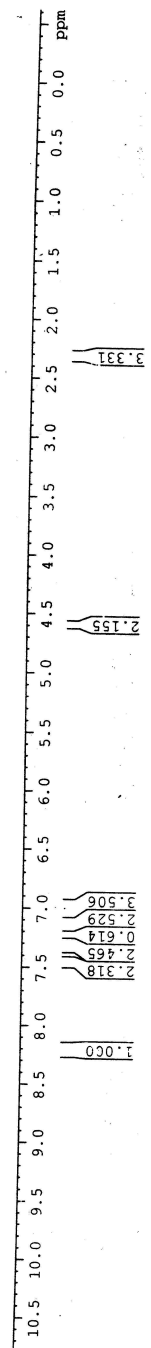
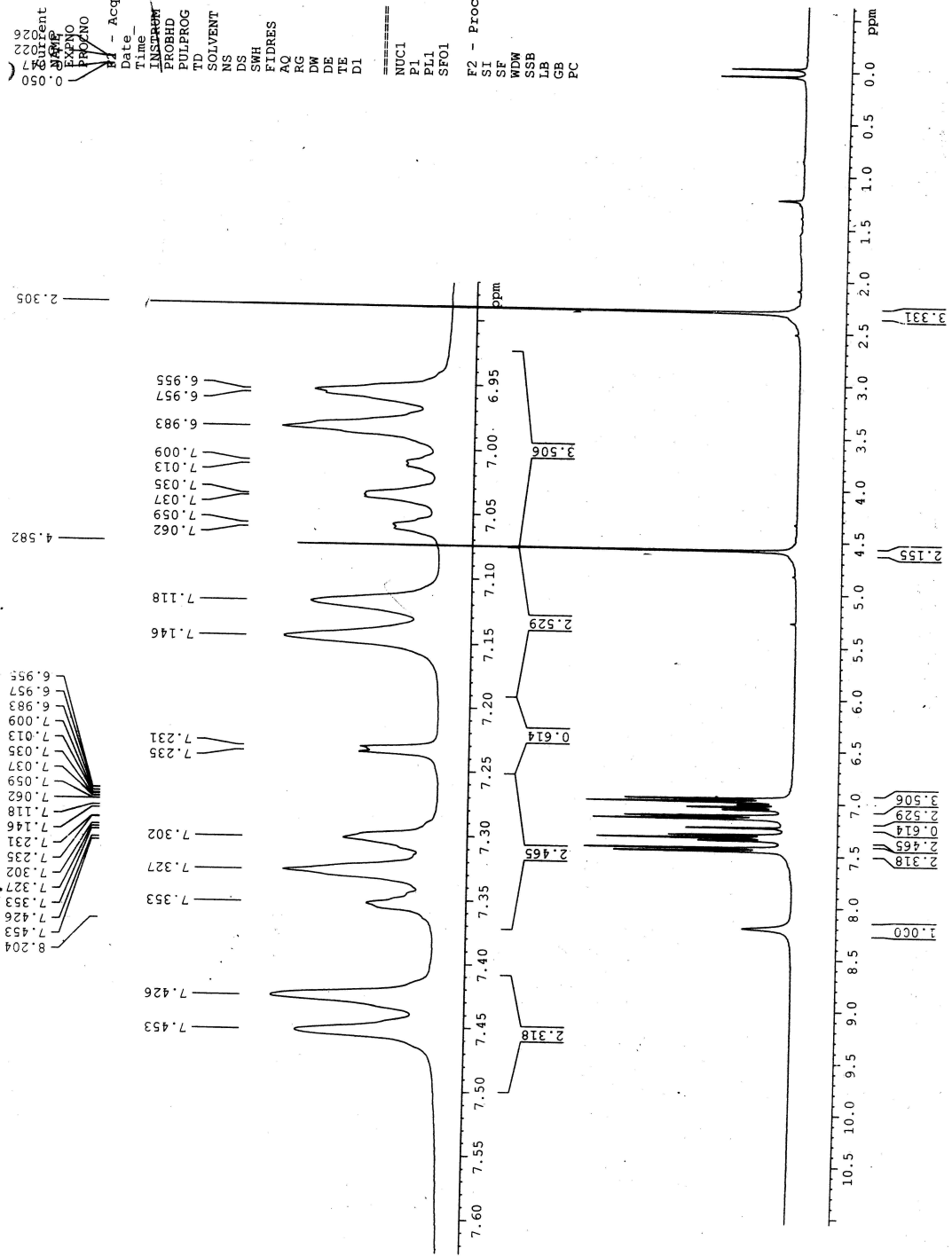
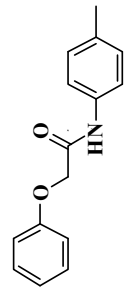
¹H NMR spectrum of 2-phenoxy-N-m-tolylacetamide (3c)



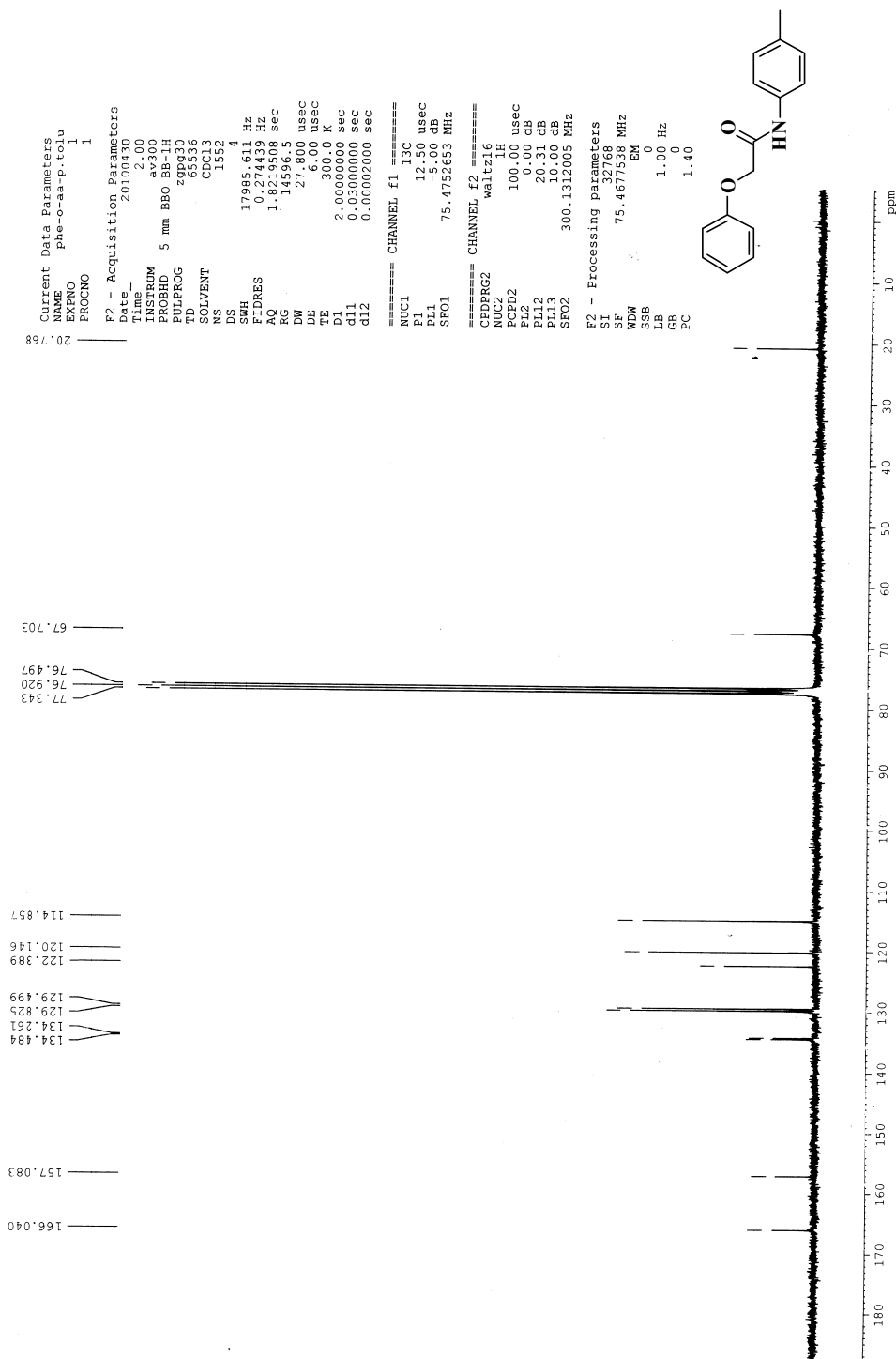
¹³C NMR spectrum of 2-phenoxy-N-m-tolylacetamide (3c)

```

=====
Current Data Parameters
Date_ 20100429
Time_ 22:29
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 10
DS 0
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 1613
DE 81.000 usec
TE 300.0 K
D1 2.00000000 sec
=====
CHANNEL f1
=====
NUC1 1H
P1 9.65 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
=====
F2 - Processing parameters
SI 32768
SF 300.1300154 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
    
```



¹H NMR spectrum of 2-phenoxy-N-p-tolylacetamide (2c)



¹³C NMR spectrum of 2-phenoxy-N-p-tolylacetamide (2c)