Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2015

# **Supplementary Information**

# Synthesis of benzoyl cyanide through aerobic photooxidation of benzyl cyanide using carbon tetrabromide as a catalyst

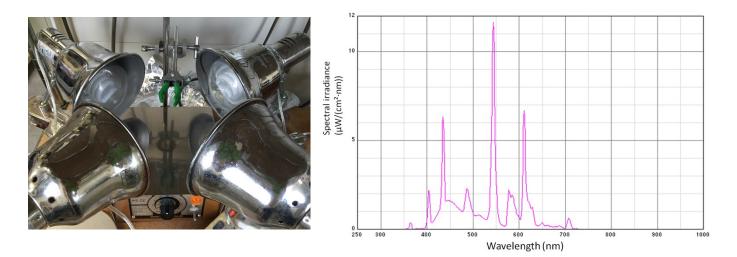
Y. Sugiura,<sup>a</sup> Y. Tachikawa,<sup>a</sup> Y. Nagasawa,<sup>a</sup> N. Tada<sup>a</sup> and A. Itoh<sup>a</sup>

*Gifu Pharmaceutical University 1-25-4, Daigaku-nishi, Gifu 501-1196, Japan Fax: +81-58-230-8108; E-mail: itoha@gifu-pu.ac.jp* 

Append	lix: <sup>1</sup> H and <sup>13</sup> C spectra	SI-6
3.	References	SI-5
2.	General Procedure	SI-2
1.	General Information	SI-2

## 1. General Information

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. The fluorescent lamps were EFR25ED 22W from Panasonic as shown detailed in the bellow.



Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60  $F_{254}$ ) and preparative thin-layer chromatography (PTLC) was carried out using 0.50 mm commercial silica gel plates (Merck silica gel 60  $F_{254}$ ). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a JEOL ECA 500 spectrometer (500 MHz for <sup>1</sup>H NMR and 125 MHz for <sup>13</sup>C NMR) or a JEOL AL 400 spectrometer (400MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR). Chemical shifts ( $\delta$ ) are expressed in parts per million and are internally referenced [0.00 ppm (tetramethylsilane) for <sup>1</sup>H NMR].

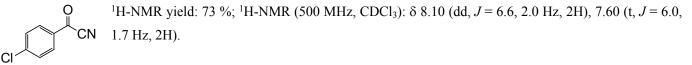
## 2. General Procedure

Synthesis of benzoyl cyanide (2a) and isolation (Table 1): A solution of benzyl cyanide (1a, 0.3 mmol), CBr<sub>4</sub> (0.2 equiv), and H<sub>2</sub>O (1.5 equiv) in EtOAc (5 mL) was stirred and irradiated using fluorescent lamps under an O<sub>2</sub> atmosphere for 20 h. The solvent was removed by rotary evaporation, then we took <sup>1</sup>H NMR. After dryness by rotary evaporation again, it was added H<sub>2</sub>O(140 mL) and conc. H<sub>2</sub>SO<sub>4</sub> (150 mL). The mixture was stirred under reflux for 30 min. After that, the mixture was extracted by 10% NaOH and 2N HCL, and carboxylic acid (**3a**) was obtained. The yields of benzoyl cyanides (**2**) were determined by <sup>1</sup>H NMR with 1,1,2,2-tetrachloroethane as internal standard.

## Benzoyl cyanide (2a)<sup>[S-1]</sup>

<sup>1</sup>H-NMR yield: 74 %; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.16 (dd, J = 7.4, 1.1 Hz, 2H), 7.80 (t, J = 7.4 Hz, CN 1H), 7.62 (t, J = 7.7 Hz, 2H).

## 4-Chlorobenzoyl cyanide (2b) [S-1]



# 4-Bromobenzoyl cyanide (2c)<sup>[S-4]</sup>

Br

<sup>1</sup>H-NMR yield: 88 %; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ 8.00 (dd, *J* = 6.9, 2.3 Hz, 2H), 7.77 (dd, *J* = 7.7, 1.7 Hz, 2H).

# 4-Fluorobenzoyl cyanide (2d)<sup>[S-5]</sup>

<sup>1</sup>H-NMR yield: 45 %; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ 8.23-8.20 (m, 2H), 7.33-7.29 (m, 2H).



# 3-Chlorobenzoyl cyanide (2e)[S-2]

<sup>1</sup>H-NMR yield: 68 %; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.08 (t, *J* = 7.5 Hz, 1H), 7.79-7.22 (m, 3H). CN

# 3-Bromobenzoyl cyanide (2f)<sup>[S-3]</sup>

<sup>1</sup>H-NMR yield: 64 %; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.25 (s, 1H), 8.11 (d, J = 7.2 Hz, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H).

# 2-Chlorobenzoyl cyanide (2g)<sup>[S-2]</sup>

<sup>1</sup>H-NMR yield: 53 %; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.15 (dd, J = 7.7, 1.4 Hz, 1H), 7.64-7.23 (m, 3H). CN

# 4-Methoxybenzoyl cyanide (2k) [S-1]

<sup>1</sup>H-NMR yield: 37 %; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.06 (d, J = 9.1 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 3.80 (s, 3H).

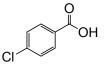
# Benzoic acid (3a)<sup>[S-6]</sup>



MeO

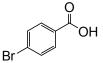
Prepared according to the general procedure. Isolated yield: 73 %; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.13 (d, J = 7.5 Hz, 2H), 7.62 (t, J = 7.5, 1H), 7.49 (t, J = 7.5 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  172.6, 134.0, 130.3, 129.4, 128.6.

# 4-Chlorobenzoic acid (3b)<sup>[S-6]</sup>



Prepared according to the general procedure. Isolated yield: 72 %; <sup>1</sup>H-NMR (500 MHz, DMSO): δ
7.90 (d, J = 7.4 Hz, 2H), 7.52 (d, J = 8.5, 2H). <sup>13</sup>C NMR (125 MHz, DMSO) δ 167.0, 138.3, 131.7, 130.1, 129.3.

## 4-Bromobenzoic acid (3c)<sup>[S-6]</sup>



Prepared according to the general procedure. isolated yield: 71 %; <sup>1</sup>H-NMR (500 MHz, DMSO):  $\delta$  7.82 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6, 2H). <sup>13</sup>C NMR (125 MHz, DMSO)  $\delta$  167.2, 132.2, 131.8, 130.5, 127.4.

## 4-Fluorobenzoic acid (3d)<sup>[S-6]</sup>

Prepared according to the general procedure. Isolated yield: 49 %; <sup>1</sup>H-NMR (400 MHz, DMSO): δ
7.98-7.95 (m, 2H), 7.31-7.26 (m, 2H). <sup>13</sup>C NMR (125 MHz, DMSO) δ 166.4, 166.0, 164.0, 132.2, 13.21, 127.4, 115.8, 115.6.

#### 3-Chlorobenzoic acid (3e)<sup>[S-6]</sup>

Prepared according to the general procedure. Isolated yield: 60 %; <sup>1</sup>H-NMR (400 MHz, DMSO): δ 7.92-7.91 (m, 2H), 7.73-7.70 (m, 1H), 7.58-7.54 (m, 1H). <sup>13</sup>C NMR (100 MHz, DMSO) δ 166.1, 133.4, 132.9, 132.7, 130.7, 128.9, 127.9.

## 3-Bromobenzoic acid (3f)<sup>[8-7]</sup>



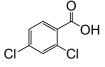
Prepared according to the general procedure. Isolated yield: 67 %; <sup>1</sup>H-NMR (400 MHz, DMSO):  $\delta$  8.06 (t, J = 1.7 Hz, 1H), 7.97-7.94 (m, 1H), 7.86-7.83 (m, 1H), 7.49 (t, J = 7.97 Hz, 1H). <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  166.0, 135.6, 133.1, 131.8, 130.9, 128.3, 121.8.

# 2-Chlorobenzoic acid (3g)<sup>[S-6]</sup>



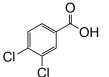
Prepared according to the general procedure. Isolated by preparative thin-layer chromatography (PTLC). Isolated yield: 46 %; <sup>1</sup>H-NMR (400 MHz, DMSO):  $\delta$  7.74 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.52-7.47 (m, 2H), 7.42-7.35 (m, 1H). <sup>13</sup>C NMR (125 MHz, DMSO)  $\delta$  166.8, 132.6, 131.6, 131.5, 130.8, 130.7, 127.3.

#### 2,4-dichlorobenzoic acid (3h)<sup>[S-6]</sup>

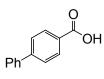


Prepared according to the general procedure. Isolated yield: 40 %; <sup>1</sup>H-NMR (400 MHz, DMSO):  $\delta$  7.83-7.80 (m, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.52-7.50 (m, 1H). <sup>13</sup>C NMR (100Hz, DMSO)  $\delta$  165.9, 136.6, 133.1, 132.4, 130.2, 130.1, 127.5.

#### 3,4-dichlorobenzoic acid (3i)<sup>[S-6]</sup>

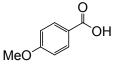


Prepared according to the general procedure. Isolated by preparative thin-layer chromatography (PTLC). Isolated yield: 19 %; <sup>1</sup>H-NMR (400 MHz, DMSO):  $\delta$  8.02 (d, *J* = 2.3 Hz, 1H), 7.84 (dd, *J* = 6.3, 2.0, 1H), 7.75 (d, *J* = 4.2, 1H). <sup>13</sup>C NMR (100Hz, DMSO)  $\delta$  165.5, 135.8, 131.5, 131.4, 131.1, 131.0, 129.3.



Prepared according to the general procedure. Isolated by preparative thin-layer chromatography (PTLC). Isolated yield: 21 %; <sup>1</sup>H-NMR (400 MHz, DMSO):  $\delta$  7.99 (d, *J* = 8.6 Hz, 2H), 7.77-7.66 (m, 2H), 7.50-7.44 (m, 2H), 7.40-7.33 (m, 2H). <sup>13</sup>C NMR (125 MHz, DMSO)  $\delta$  167.7, 144.8, 139.5, 130.5, 130.1, 129.6, 128.8, 127.5, 127.4.

# 4-Methoxybenzoic acid (3k) [S-6]



Prepared according to the general procedure. Isolated by preparative thin-layer chromatography (PTLC). Isolated yield: 34 %; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.65 (dd, *J* = 6.9, 2.3 Hz, 2H), 6.95 (d, *J* = 9.1, 2H), 3.88 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  171.7, 164.0, 132.3, 121.6, 113.7,

55.5.

# 1-Naphthoic acid (3l)<sup>[8-6]</sup>



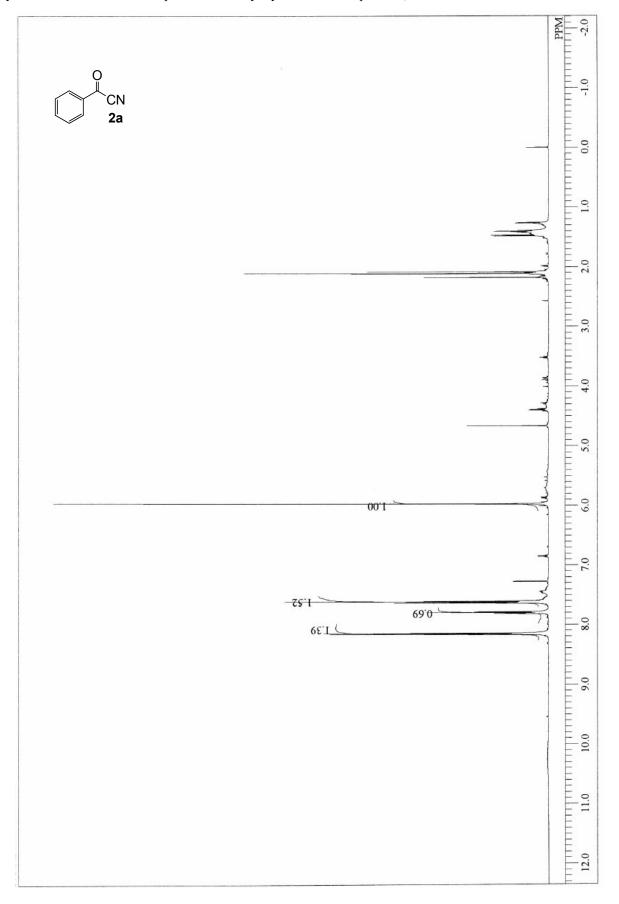
Prepared according to the general procedure. Isolated by preparative thin-layer chromatography (PTLC). Isolated yield: 16 %; <sup>1</sup>H-NMR (400 MHz, DMSO):  $\delta$  8.85 (d, *J* = 8.7 Hz, 1H), 8.14 (t, *J* = 6.8, 2H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.63-7.56(m, 3H). <sup>13</sup>C NMR (125 MHz, DMSO)  $\delta$  173.2, 134.7, 133.9, 131.9, 131.6, 128.7, 128.1, 126.3, 125.9, 125.5, 124.5.

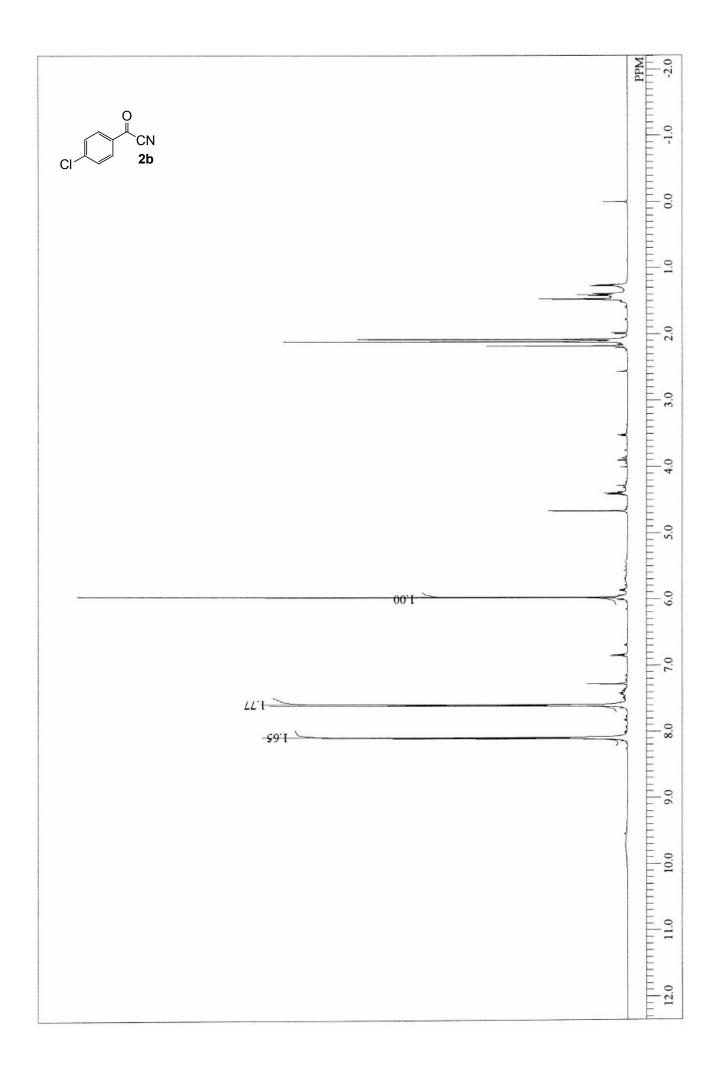
# 4. References

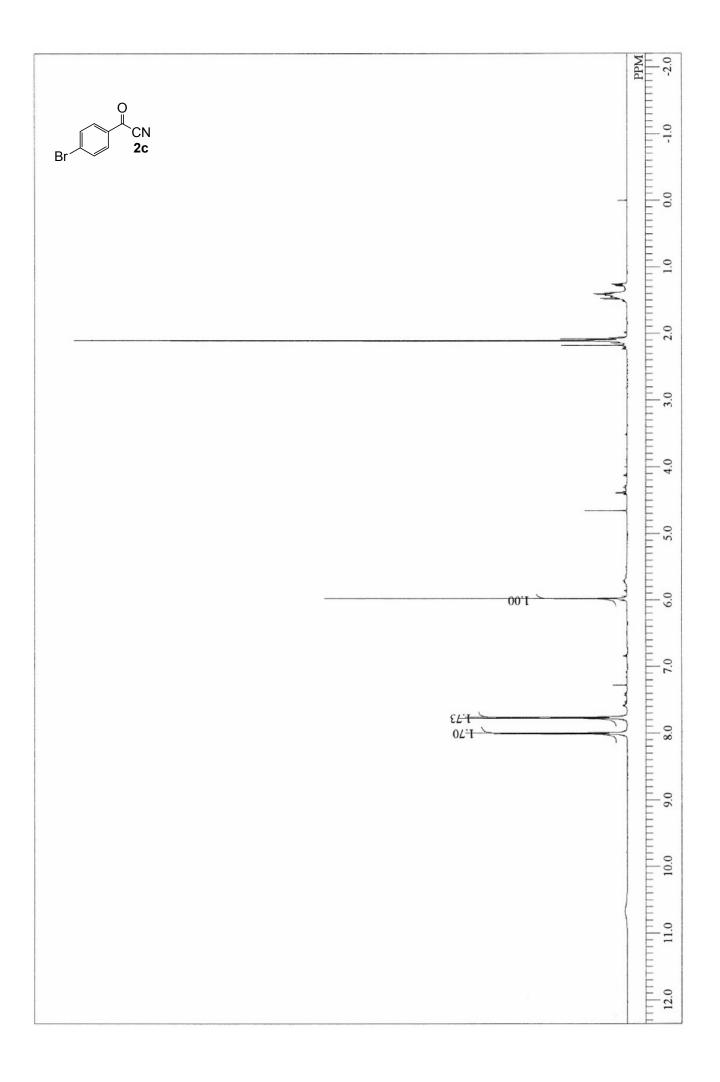
- [S-1] C. Duplais, F. Bures, I. Sapountzis, T. J. Korn, G. Cahiez and P. Knochel, Angew. Chem. Int. Ed., 2004, 43(22), 2968.
- [S-2] Z. Li, S. Shi and J. Yang, *Synlett*, 2006, **15**, 2495.
- [S-3] A. J. Muller, K. Nishiyama, G. W. Griffin, K. Ishikawa and D. M. Gibson, J. Org. Chem., 1982, 47 (12), 2342.
- [S-4] K. Sukata, Bull. Chem. Soc. Jpn., 1987, 60, 1085.
- [S-5] H. Hoffmann, K. Haase, Z. Ismail, S. Preftitsi and A. Weberm, *Chemische Berichte*, 1982, 115, 3880.
- [S-6] AIST: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan))
- [S-7] ACD-A: Sigma-Aldrich (Spectral data were obtained from Advanced Chemistry Development, Inc.)

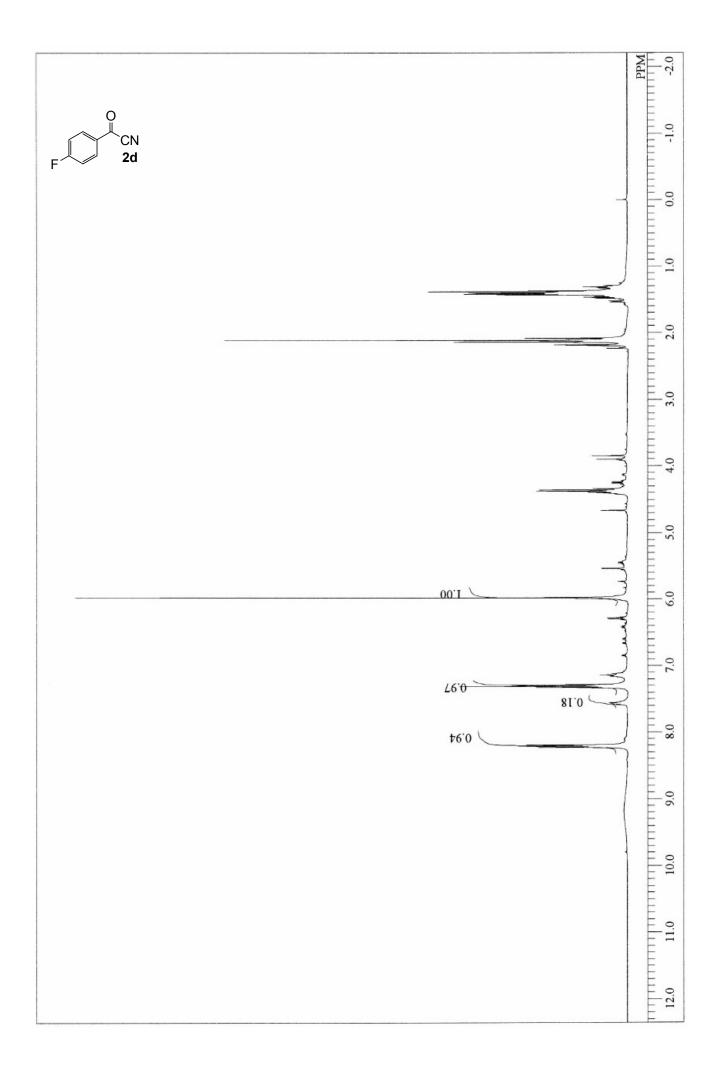
# Appendix: <sup>1</sup>H and <sup>13</sup>C spectra

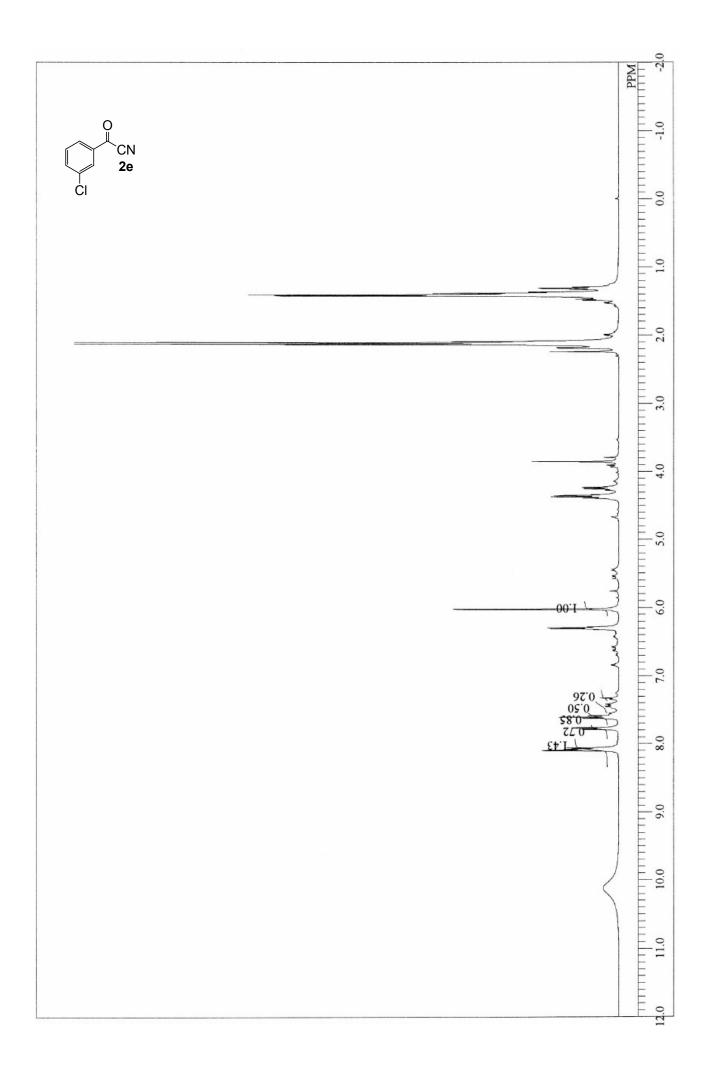
As benzoyl cyanides are generally labile, they were characterized by <sup>1</sup>H NMR and isolated as the corresponding carboxylic acids. So the <sup>1</sup>H NMR spectra of benzoyl cyanides are not purified, it was crude.

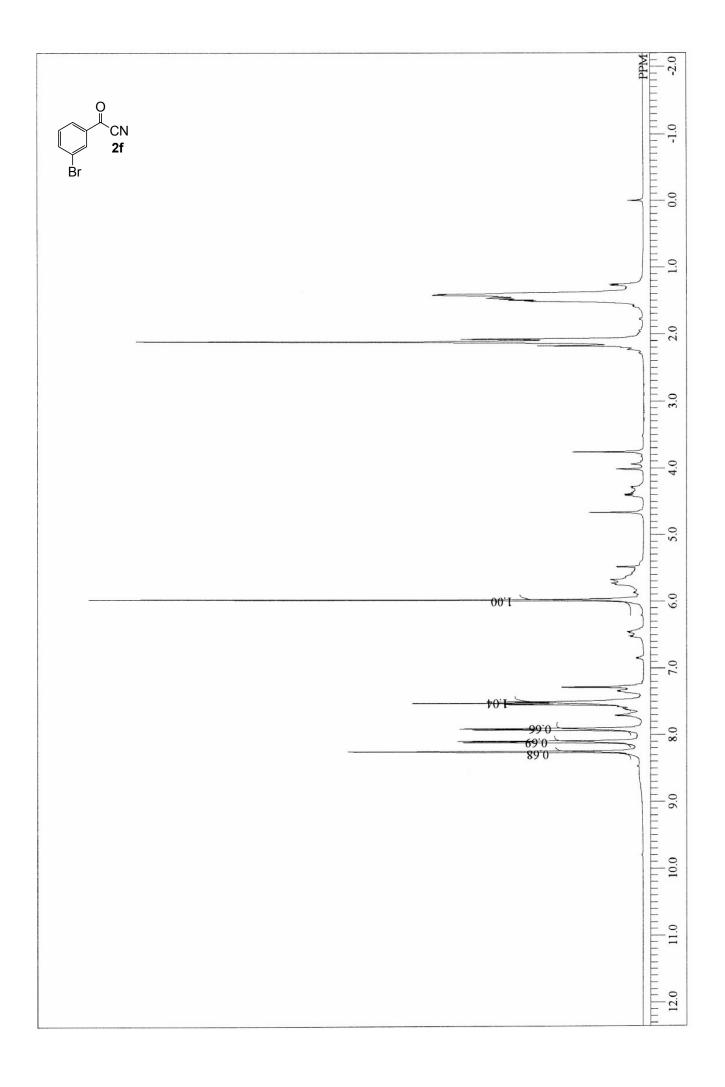


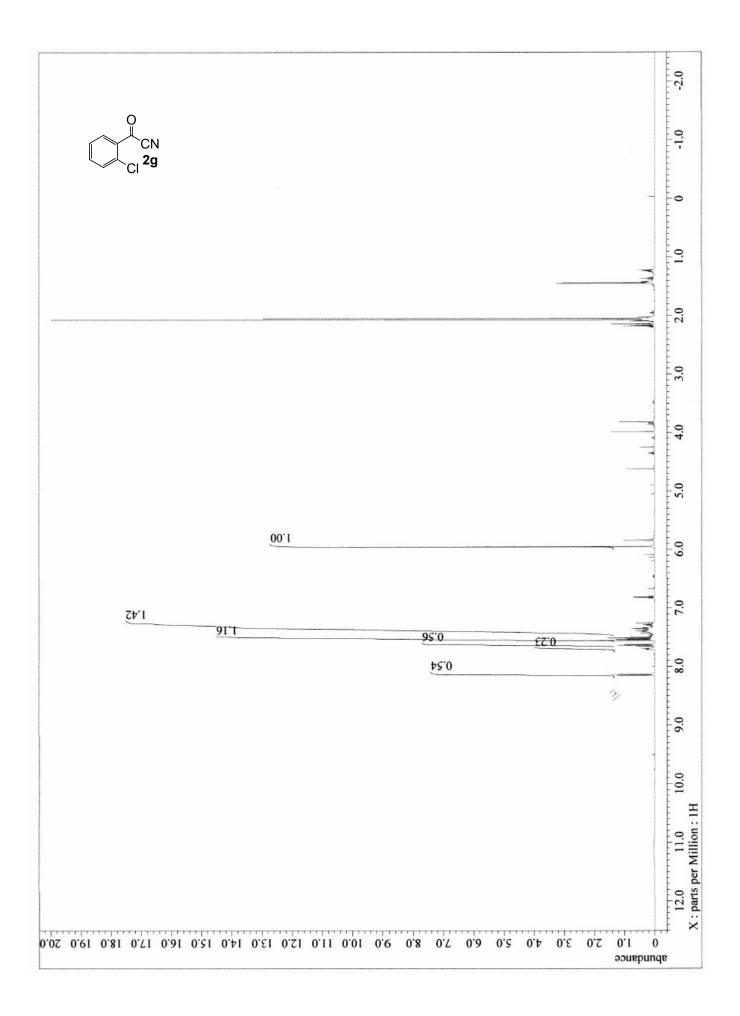


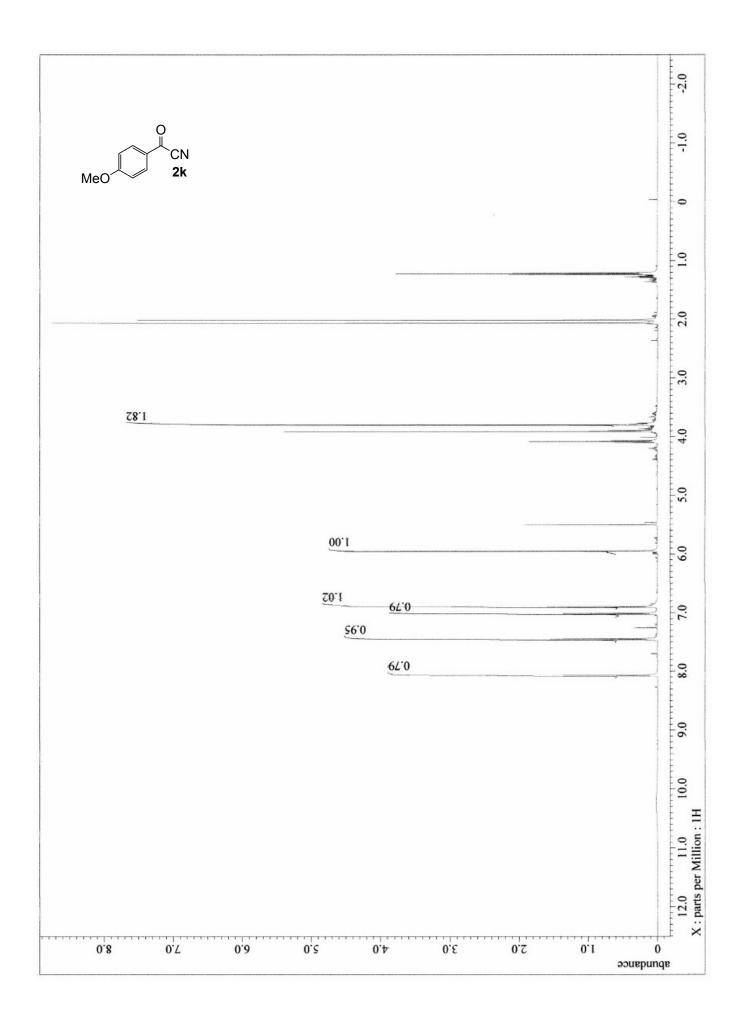


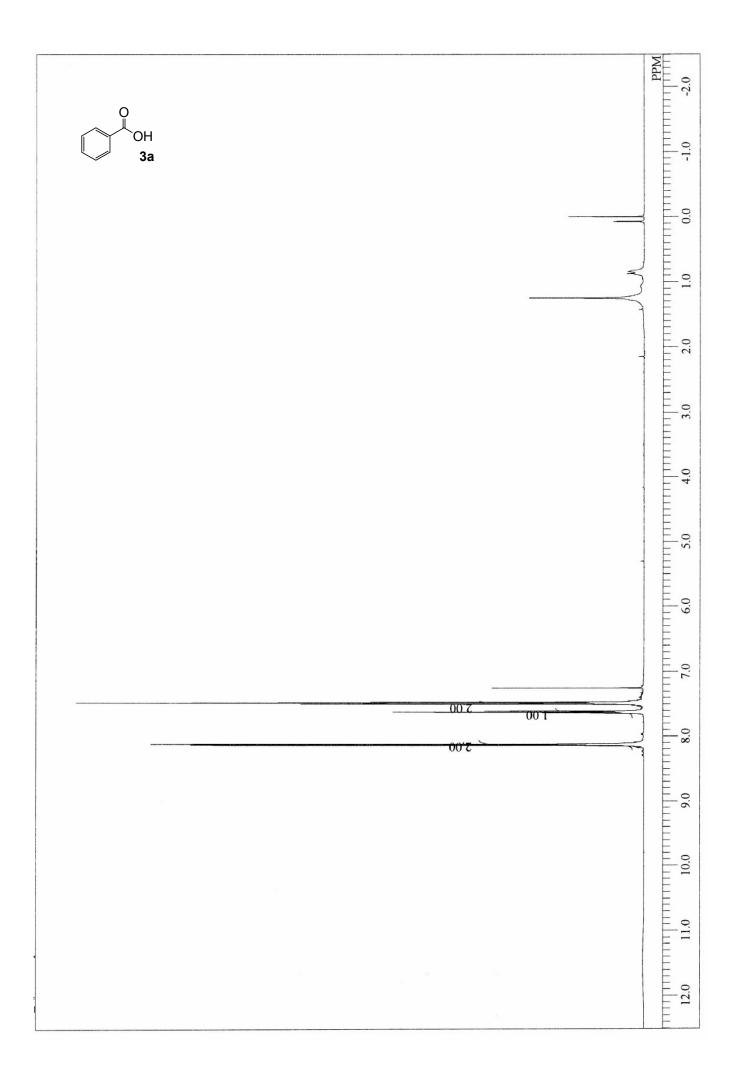




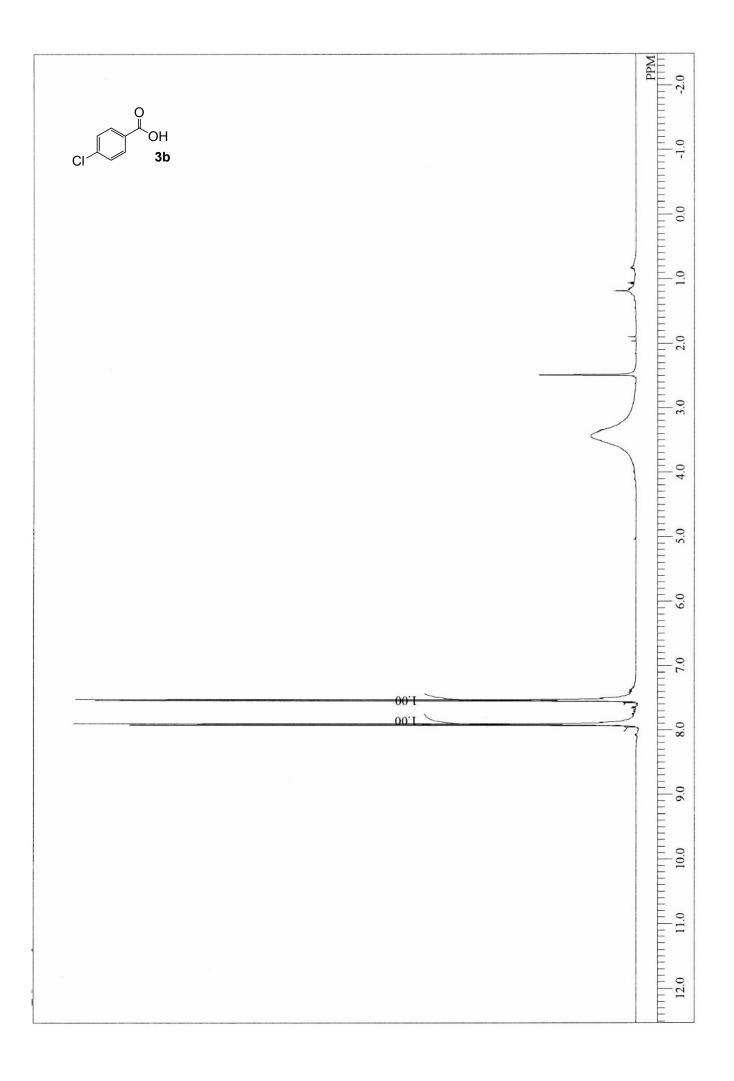




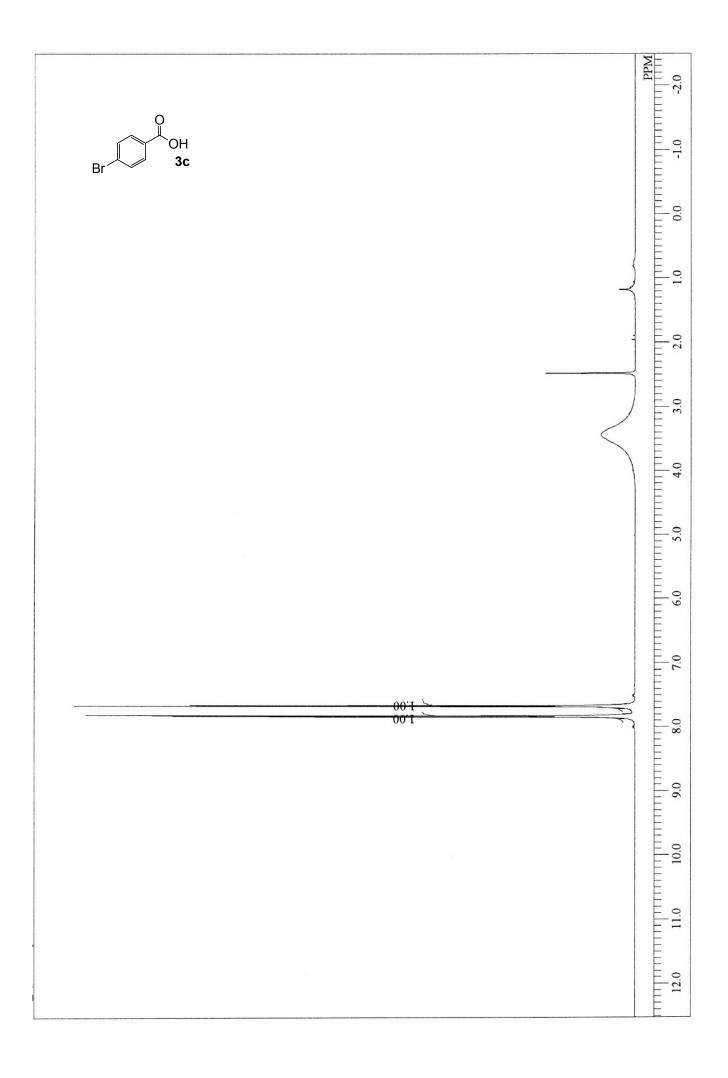




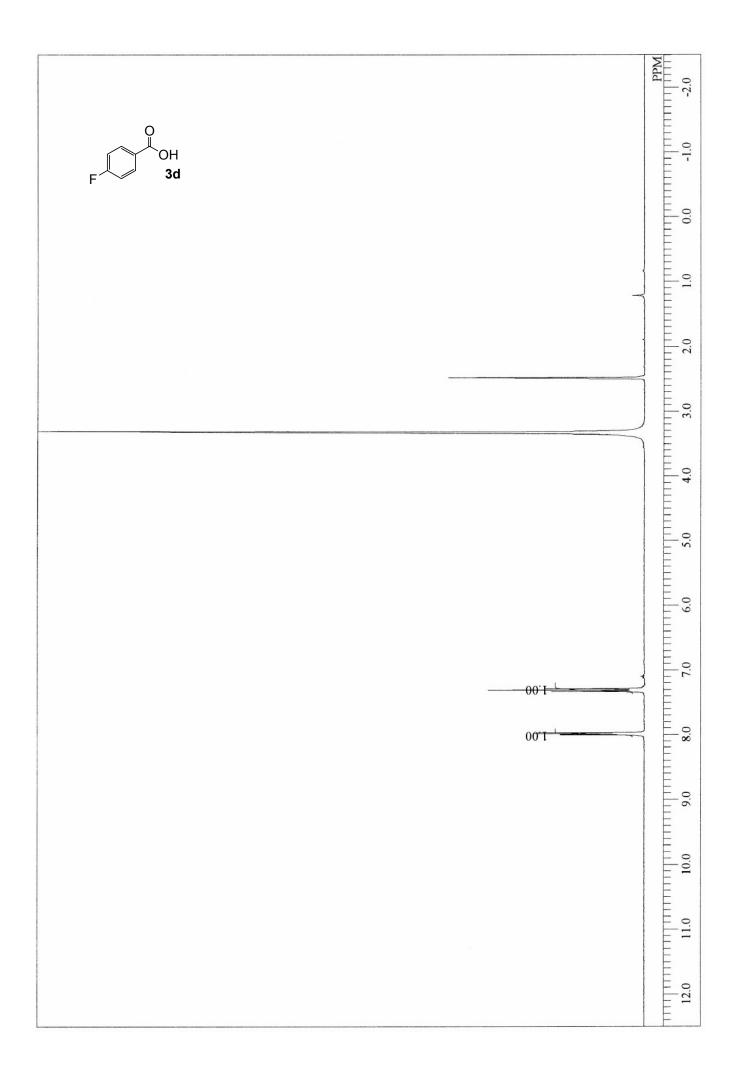
		PPM
		-10.0
		0.0
		10.0
		тприп 20.0
		30.0
		0
		40.0
		тприт 50.0
		2
		60.0
		70.0
-		80.0
		9.06
		100
		0.0
		20.0
		0 1
9		130.
		0.0
		14
		1111 20.0
		0.1
		160.
		0.0
		17
		80.0
		0 1
		190.
		иприниципиции продать в стать ста 200.0 190.0 180.0 170.0 160.0 150.0 150.0 140.0 130.0 120.0 110.0 100.0
		200
		210.0
		) 21
		пиритицитицитицитицитицитицитицитицитицит
	4	E



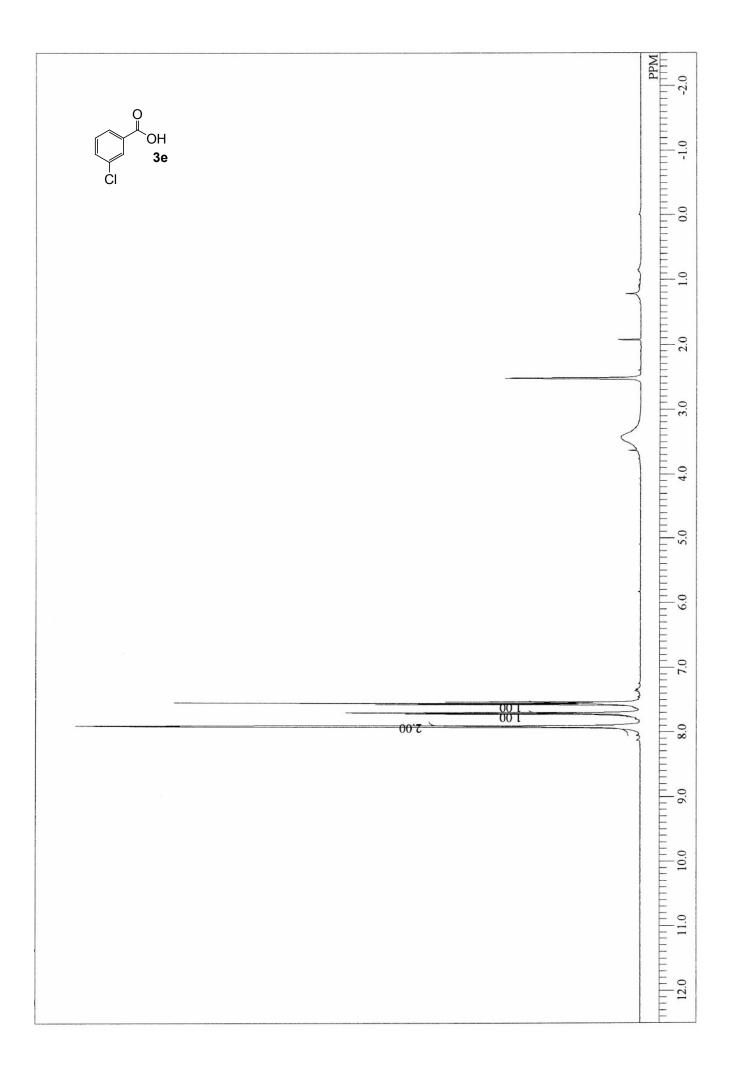
1 SE -
РРМ ППППП -20.0
E
шппп -10.0
-10
инальные маке в соороные сооро Портатириальные соороные соорон 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 130.0 130.0 130.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
шПШ 10.0
1
тприт 20.0
20
E
30.0
40.0
4(
тпрпп 50.0
I E
шПП 60.0
тпртт 70.0
шПП 80.0
шПП 90.06
6
0.0
иприпири 110.0 100.0
Eo
10.
шпппп 120.0
ШШ 12
ш <b>уу</b> 130.0
штрит 140.0
15
ициницинициницини 170.0 160.0 150.0
160
10.01
шпппппп 190.0 180.0
18
0.
шприт 200.0
111 2(
тприп 210.0
21(
шпппп 220.0
<b>7</b> = <b>7</b>



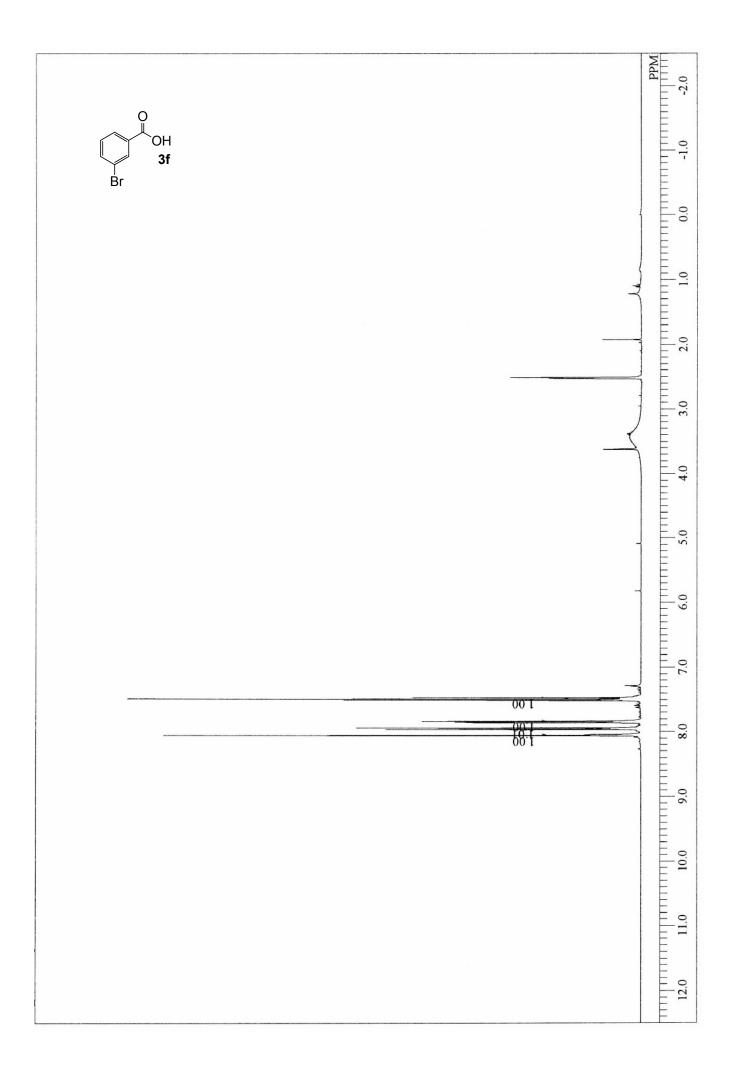
	иприниции полниции прилиции полниции полниции полниции полниции полниции полниции полниции полниции полниции п 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
	ициппициппиципиции 80.0 70.0 60.0 50.0 40.0 3
	ищинитириниципиципици 130.0 120.0 110.0 100.0 90.0 80
	тириниципиции 170.0 160.0 150.0 140.0 130
	220.0 210.0 200.0 190.0 180.0 1



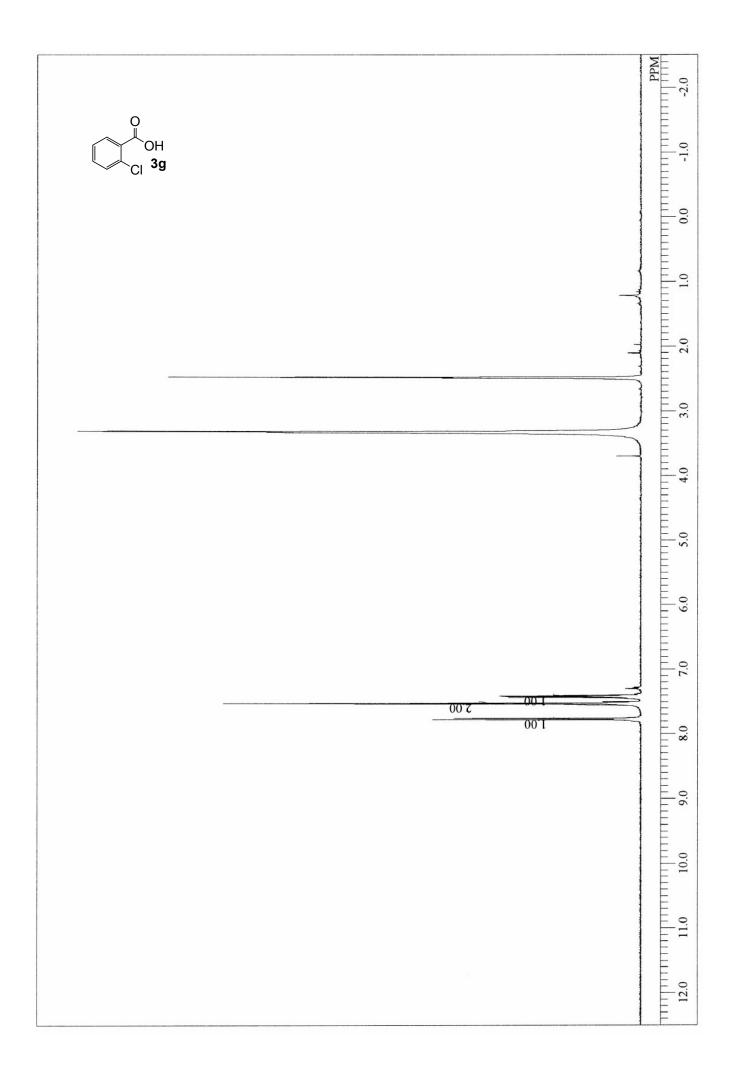
	Mdd
	10.0
	20.0
	0.0
	30.0
	40.0
akini kuto kata	50.0
	60.0
	70.0
	80.0
	90.0
	100.0
	110.0
	0 11
	120.0
	130.0
	140.0
	150.0
	.0
	0.060.0
	170.0
	190.0
	200.0 19
	200



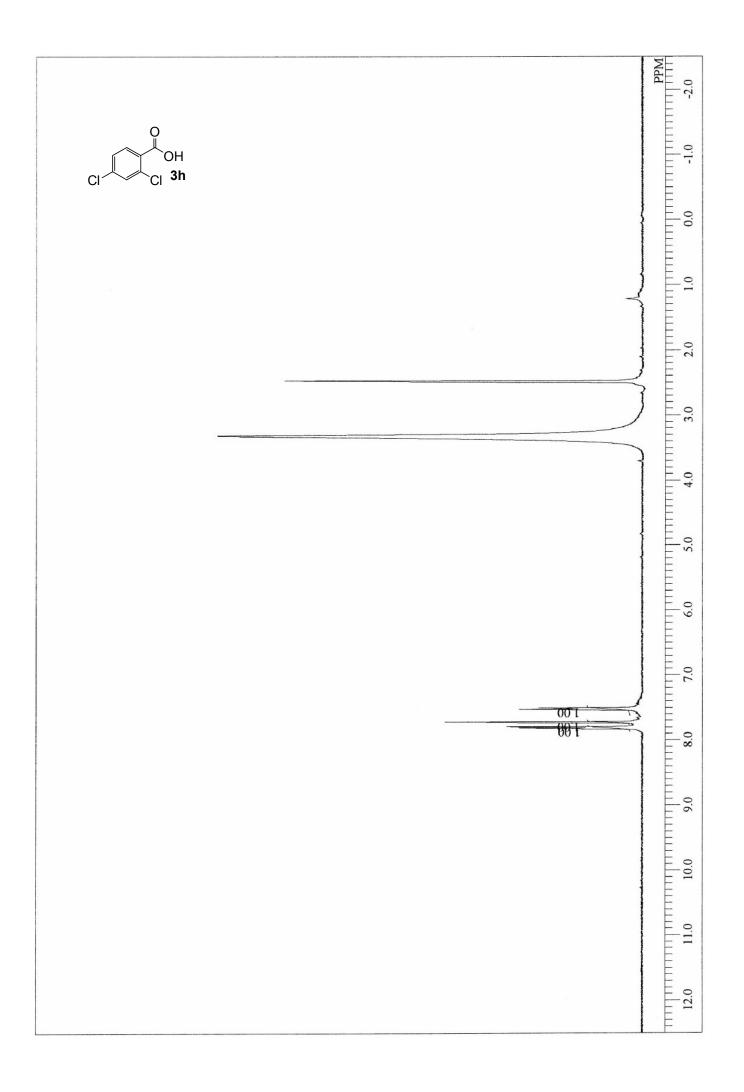
10.0 ومروق والمالية أعراد للمراد والمحمد والالاحدا العرارات وللال 20.0 30.0 40.0 ومقتصفا أطرب بتشاريه فمربع بمراكبته أمرياني ومعاولات والتربيب بتماديا فأربي متقراط والنبل كأنكار والمتريك والترابية للم 50.0 60.0 70.0 80.0 90.06 والمستوادية مترادته بخداء ولتواعد خطرهم لمتاور فوالتمريق والمتراخ المتراخية 120.0 110.0 100.0 ومقوده وتعاليتن أعدانهماه والطريا ويتستعلما والتليد 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0



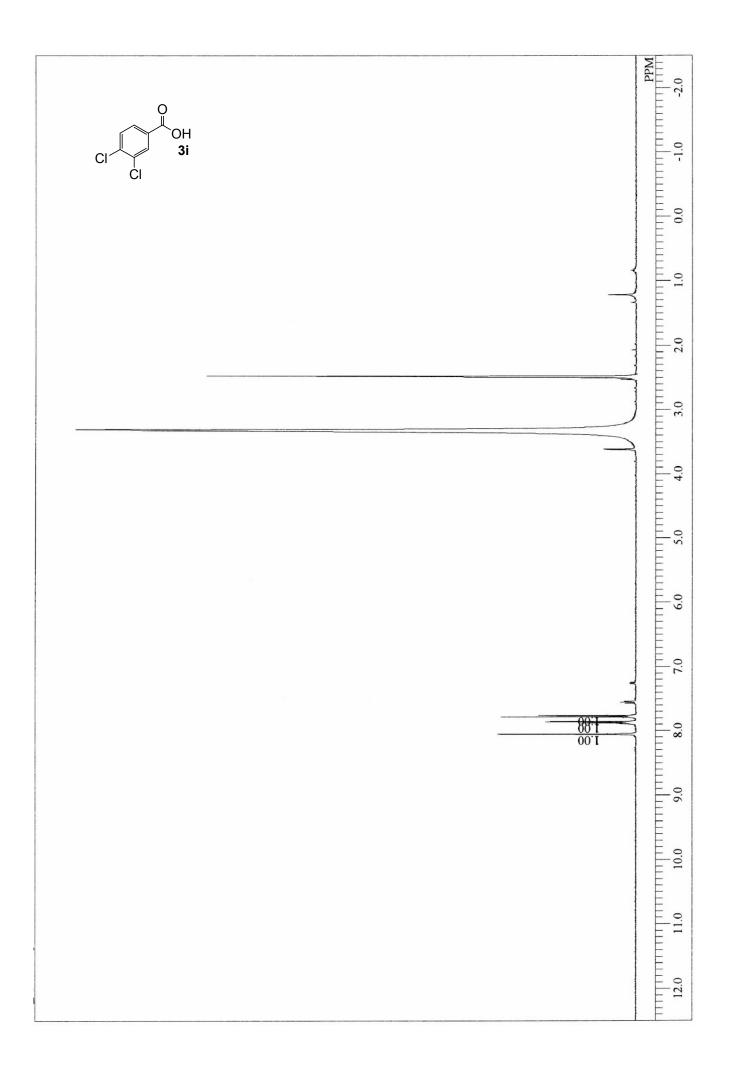
	- V	
	Mdd	0.
-	₹ <sup>-</sup>	=
	-	
		= -
	2	=
	-	. 0
	2	20.0
	ŧ	Ē
	1 1	= _
	1	30.0
	*	_ ~~
		Ē
	畫	40.0
	E	⊟ ) <del>4</del>
		E
		0
	<b>E</b>	50.0
	*	Ξ
	-	Ē
		60.0
	<b></b>	9
		Ξ
	E I	70.0
	2	Ĭ
	畫	=
	*	80.0
		- 8
	1	=
	Ŧ	_ 0
	<b></b>	90.06
		Ξ
	<b>a</b>	= 0
		100.0
	Ī	i i
		Ξ
	2	110.0
	ŝ.	= =
		Ξ
	Ē	.0.
		120.0
	Ē	Ξ
		- 0
		130.0
		-
	£	- 0
		140.0
		- i
	<u> </u>	=
	£	0.0
	E I	150.0
	書	Ξ
		0.0
		160.0
		=
		170.0
	ŧ.	120
		= -
		= 0
		80.
	1	190.0 180.0
	£ :	= _
		0.0
	Ē	19
		0.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10
		200.0
		00

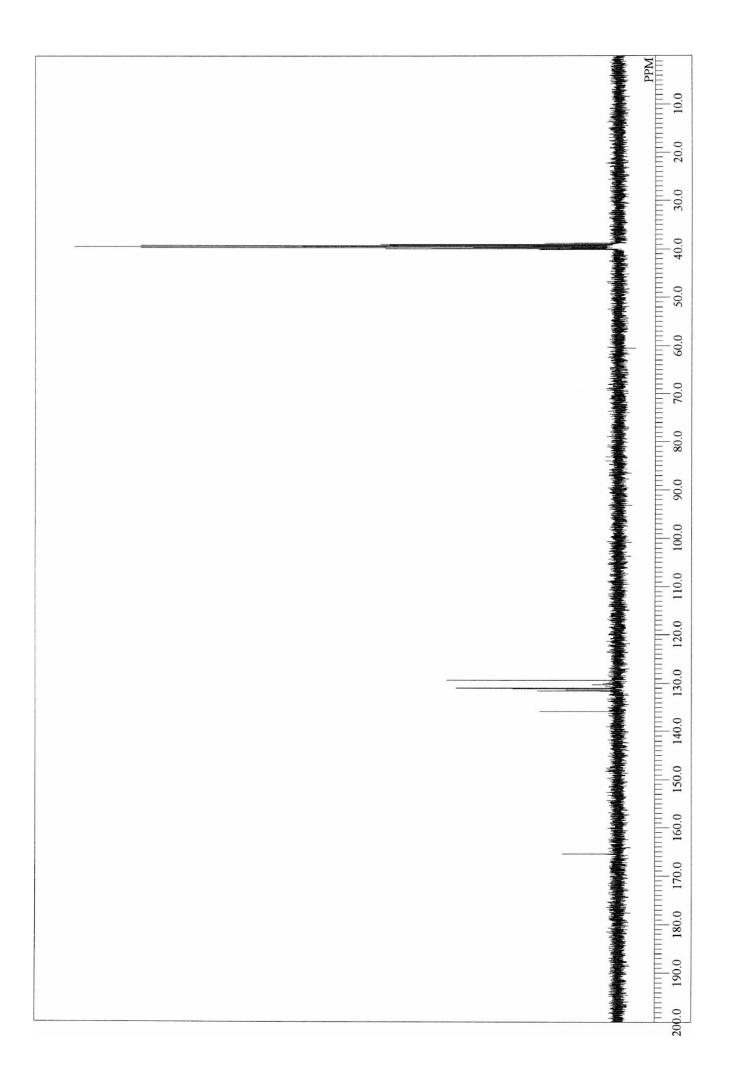


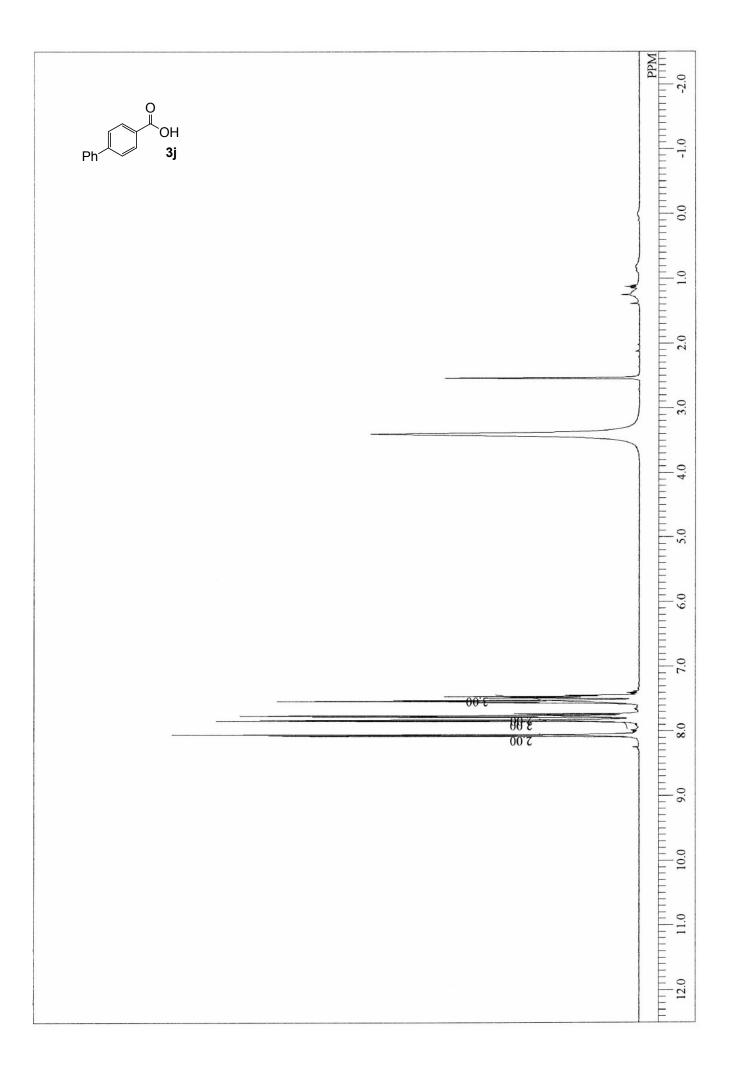
Z	E
A Id	Ë.
ŧ	10.0
	E
¥	20.0
	1111 2
	30.0
	30
主	0
-	40.0
王王	
I	50.0
I	E
	60.09
王子	70.0
The second secon	1111
Ŧ	80.0
The second secon	8
ł	0
*	90.06
重き	0
	100.0
	Ē
	110.0
1 A	120.0
書	
	130.0
	11111 13
ŧ	140.0
ł	14(
	0.
	150.0
Ŧ	0
Ŧ	160.0
THE REAL	Ē
Ŧ	170.0
1	I
ł	180.0
Ŧ	15
	190.0
	0.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
	0.0
	200.0



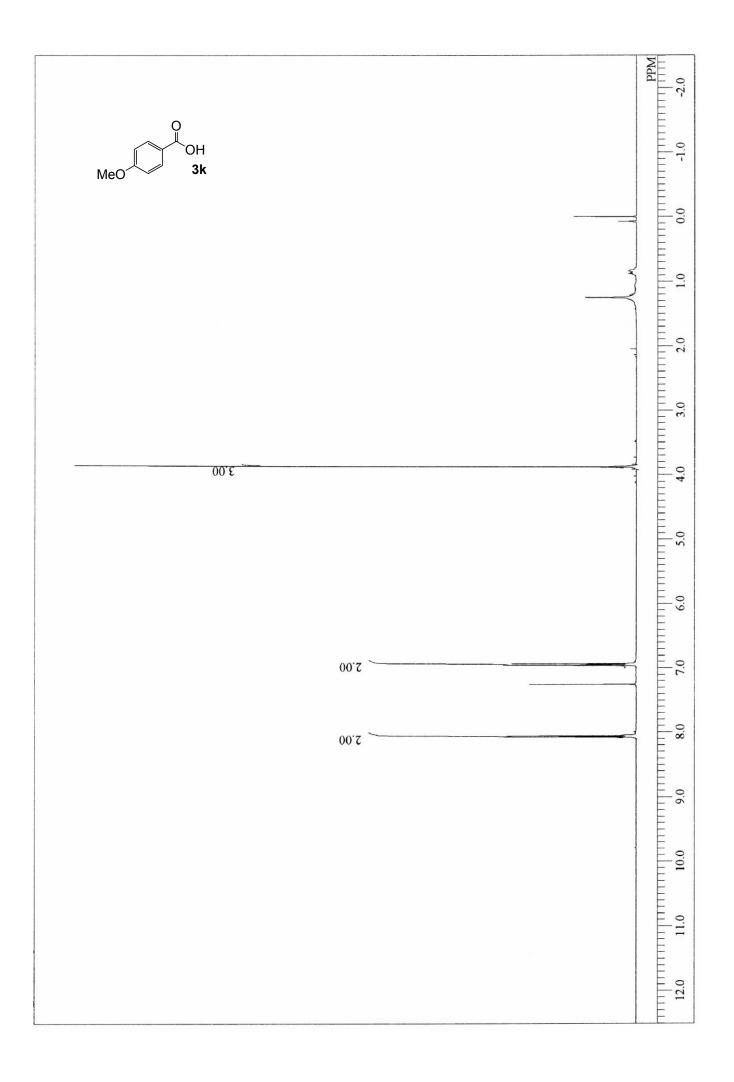
			-
			0.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
			0
	-	1	10.0
			E
		1	20.0
			5
		1	E
		Ŧ	30.0
		-	3
		重	E _
			40.0
		1	Ē
		畫	0
		畫	50.0
		畫	E
			60.09
		Ĩ	60
		ł	E
		-	70.0
		4	Ē
		Ŧ	E c
		1	80.0
		*	Ξ
		Ŧ	0
		羣	90.06
		2	E
		2	100.0
		1	10
			E o
			110.0
		3	FI
			E o
		ž	111/111 120.0
			E
		畫	130.0
		1	13(
		ŧ	E
			140.0
		Ŧ	114
		1	0
		畫	150.0
			E
			160.0
		畫	160
		-	Ē
		1	170.0
			17
		1	Ē.
	-	Ŧ	180.0
			18
		ŧ	C C
			190.0
		in stand production of the stand of the stand of the stand difference of the standard standards and the standards and t	
		Ŧ	0.
		*	200.0

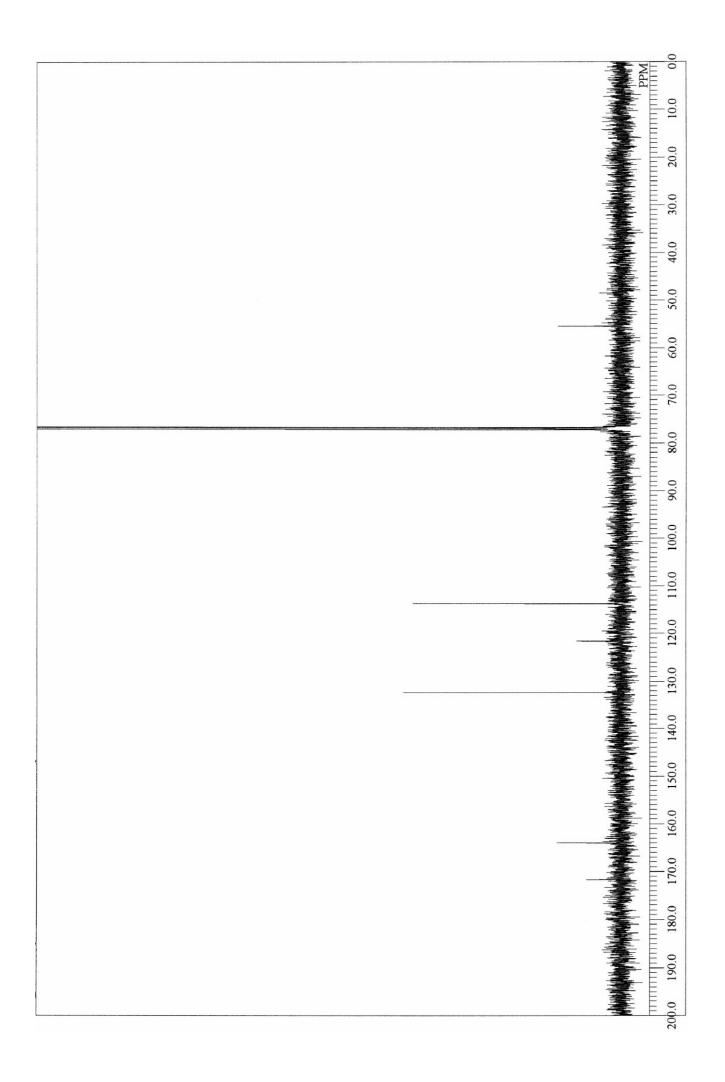


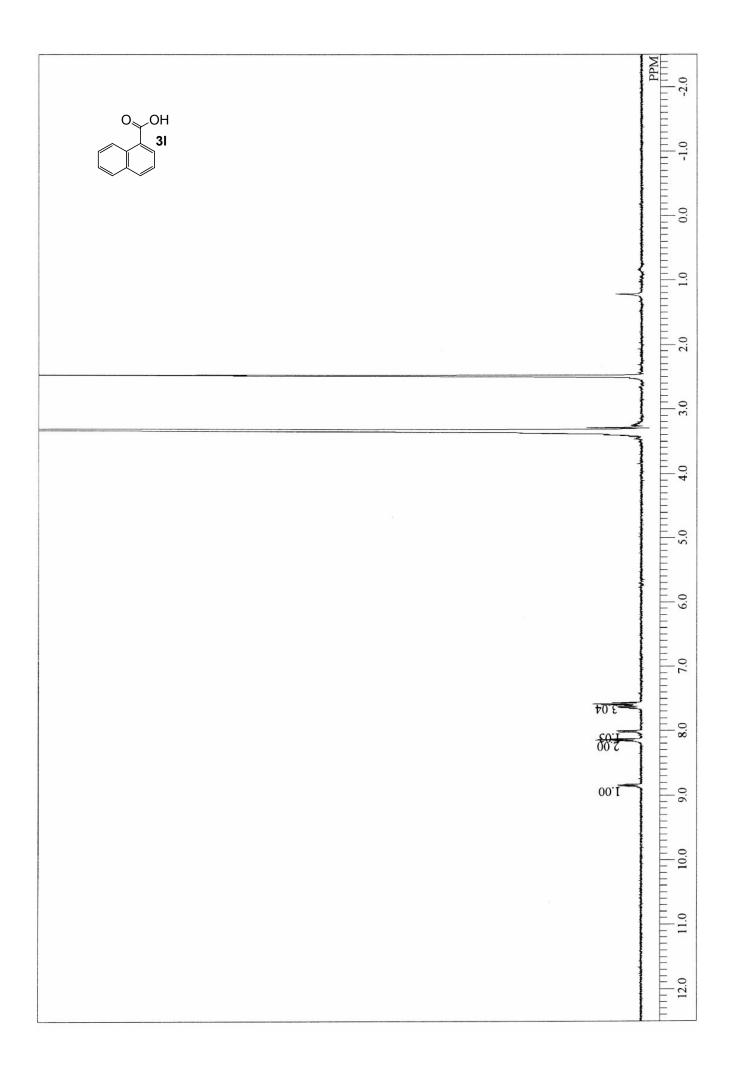




	1 HE
	10.0
	20.0
	5 E 7
	Eo
	30.0
	F E
	40.0
	₹ E
	11/11 50.0
	₹ E %
	<b></b>
	60.0
	E 99
	1
	E 0.
	70.0
	Eo
	80.0
-	
	<b>5</b> E _
	100.0
	F E F
-	110.0
	120.0
	12(
	£ E
	130.0
	130
	\$ E [
	E Fo
	140.0
-	ŧ E o
	150.0
	E -
	160.0
	16
	<b>}</b>
	170.0
	11
	ł
	F E O
	180.0
	EFO
	190.0
	I E _
	200.0
	20







¥ "E
10.0
1
1 = E
<b>1</b> =
11111 20.0
₹ E 8
<b>≨</b> E ``
1 E
1 E a
30.0
E E M
葦戸
£ =
10.0
Eo
<b>1</b> E 4
2 -
1 - E
£ = 0.
50.0
≩ ⊨ "
<b></b>
톨
1 ES
11111 60.0
<b>1</b> =
2 -
70.0
E E F
2 =
80.0
₹ E 8
1 =
5 E
1 E-0
🛓 🗆 6
1 = E
<b>E</b>
2 F O
100.0
₹ E
1 E
110.0
1 - 2
£ = -
<u>₹</u> =
₹ E o
E.J
- A
≸ E "
120.0
130.0 1
130.0 I
130.0 <b>1</b>
1 0.0 130.0 1
1 0.0 130.0 1
140.0 130.0 1
140.0 130.0 1
0 140.0 130.0 1
0.0 140.0 130.0 1
150.0 140.0 130.0 1
150.0 140.0 130.0 1
150.0 140.0 130.0 1
10 150.0 140.0 140.0 130.0 1
иниции и противникали и противники и п 60.0 150.0 140.0 140.0 130.0 1
160.0 150.0 140.0 130.0 1
160.0 150.0 140.0 140.0 130.0 1
160.0 150.0 140.0 130.0 130.0 130.0 1
Operation         Operation <thoperation< th="">         Operation         <thoperation< th="">         Operation         Operation</thoperation<></thoperation<>
10.0 160.0 150.0 150.0 140.0 130.0 1
170.0 160.0 150.0 140.0 130.0 140.0 130.0 1
170.0 160.0 150.0 140.0 140.0 130.0 1
0 170.0 160.0 150.0 150.0 140.0 140.0 130.0 1
римраны - артистик - артистики - артист 7
180.0 170.0 160.0 150.0 150.0 140.0 130.0 1
180.0 170.0 160.0 150.0 150.0 150.0 140.0 130.0 1
ински продати продати и продати и продати продати и продати и продати и продати и продати и продати и продати 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
190.0 180.0 170.0 160.0 150.0 160.0 150.0 140.0 140.0 130.0 1
190.0 180.0 170.0 170.0 160.0 160.0 150.0 150.0 150.0 150.0 150.0 130.0 130.0 130.0 130.0 1
ираталистически продоктически и продоктически продокти продокти продокти продокти продокти продокти продокти п Полновор по продокти по
180.0 170.0 160.0 150.0 150.0 150.0 140.0 130.0