Supporting Information

A Simple Methodology for the Aerobic N-methylation of Substituted Anilines and Aminophenols Catalyzed by Zirconium Oxychloride Octahydrate, $ZrOCl_2.8H_2O$

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List of Tables

Table S1. Reaction of aniline with DMC in presence of different amounts of $ZrOCl_2.8H_2O$.[a]

Entry	Catalyst (mol%)	Catalyst (mg)	Conv. (%)	Selectivity (%)		
				Methylation		Carbamoylation
				Mono	Di	
1	-	-	5	100	-	-
2	1	14	8	100	-	-
3	5	72	20	90	10	-
4	10	144	35	66	32	2
5	20	288	61	63	24	13
6	22	316	65	62	23	15
7	25	360	74	55	25	20

[a]Reaction conditions: aniline(4.5 mmol), DMC (24 mmol), and catalyst were stirred in a sample tube at 90°C for 22 h.

Table S2. Effect of aniline:DMC molar ratio on the conversion of aniline[a].

Entry	Aniline:DMC molar ratio	Conv. (%)	Selectivity (%)		
			Methylation		Carbamoylation
			Mono	Di	
1	1:0.5	45	63	27	10
2	1:1	58	61	25	14
3	1:2	68	59	23	18
4	1:5	74	55	25	20
5	1:10	72	56	25	19
6	1:20	70	57	25	18

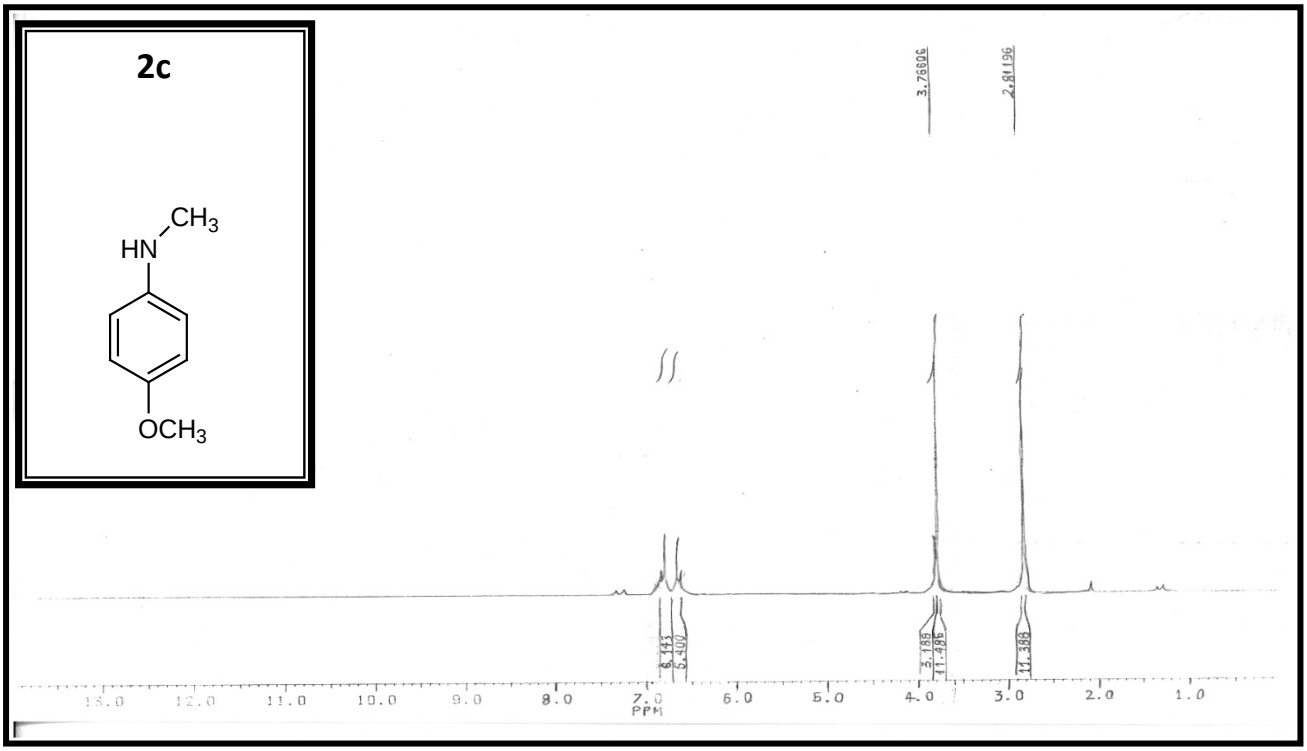
[a]Reaction conditions: aniline, DMC, and catalyst(360mg) were stirred in a sample tube at 90°C for 22 h.

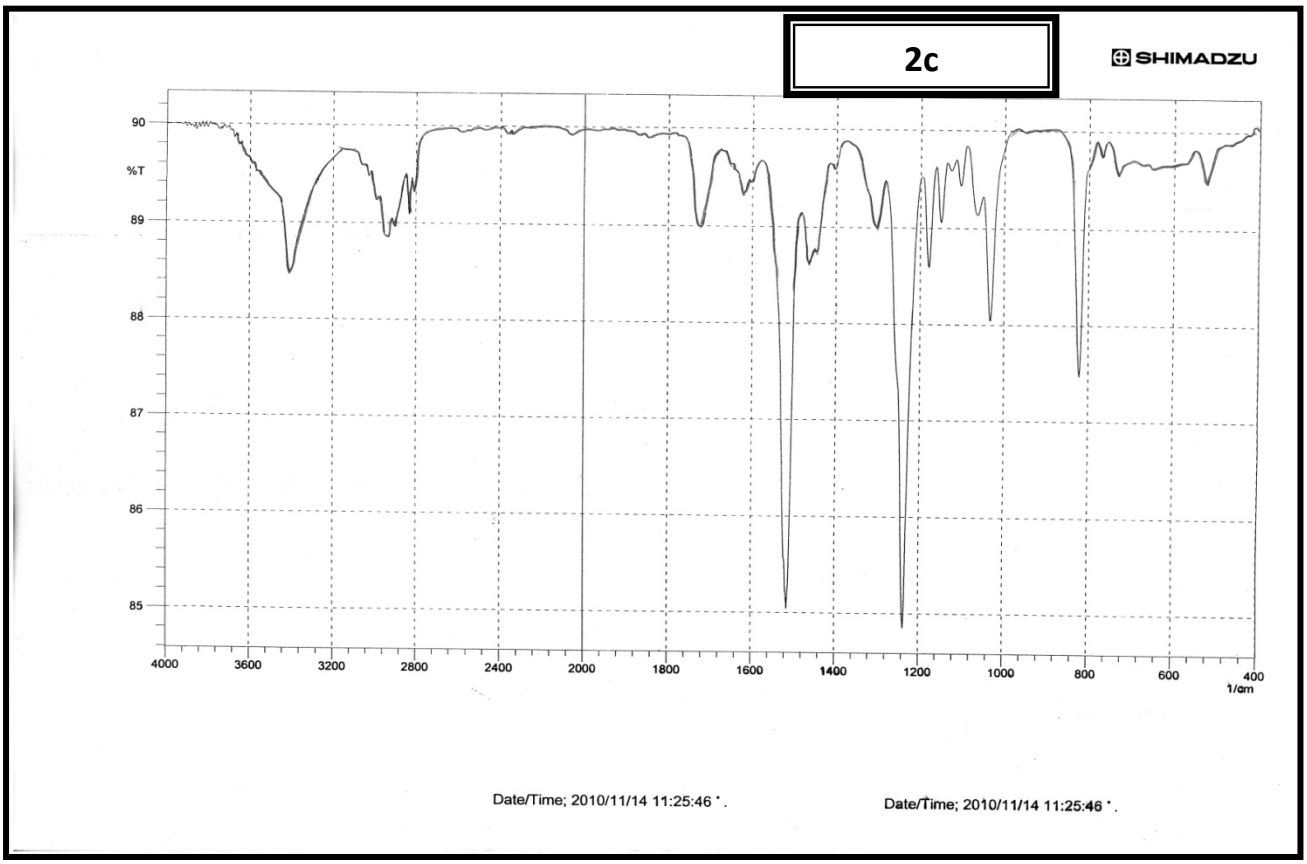
Table S3. Effect of temperature on the conversion of aniline[a].

Entry	Temperature (°C)	Conv. (%)	Selectivity (%)		
			Methylation		Carbamoylation
			Mono	Di	
1	40	0	-	-	-
2	50	7	100	-	-
3	70	20	90	10	-
4	80	53	64	23	13
5	90	74	55	25	20

[a]Reaction conditions: aniline (4.5 mmol), DMC (24 mmol), and catalyst (360mg) were stirred in a sample tube for 22 h.

List of FT-IR and ^{1}H-NMR spectra





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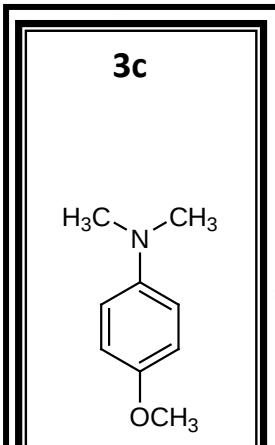

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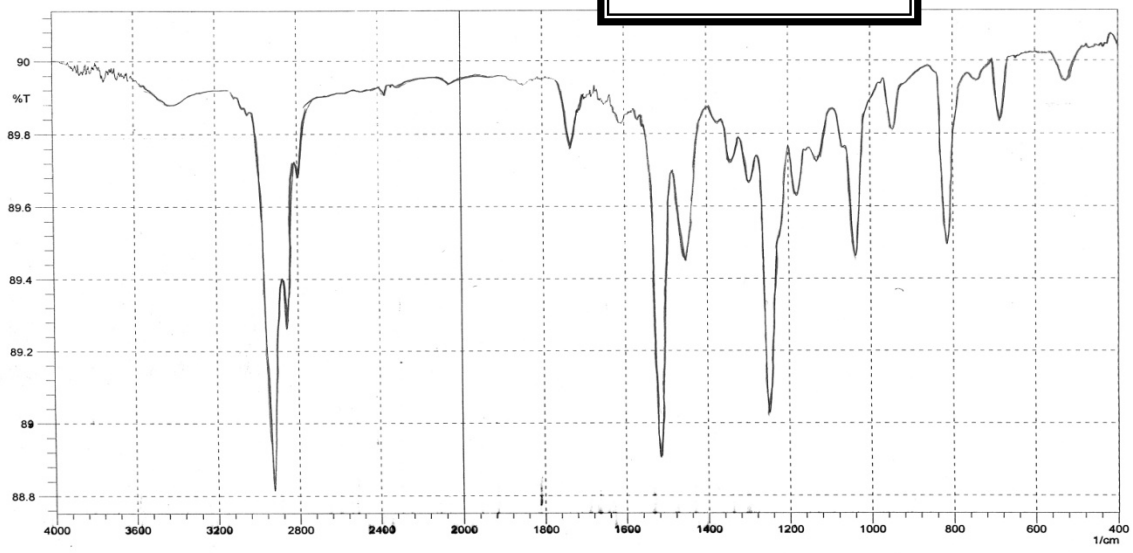

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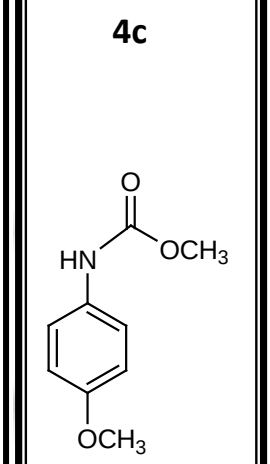

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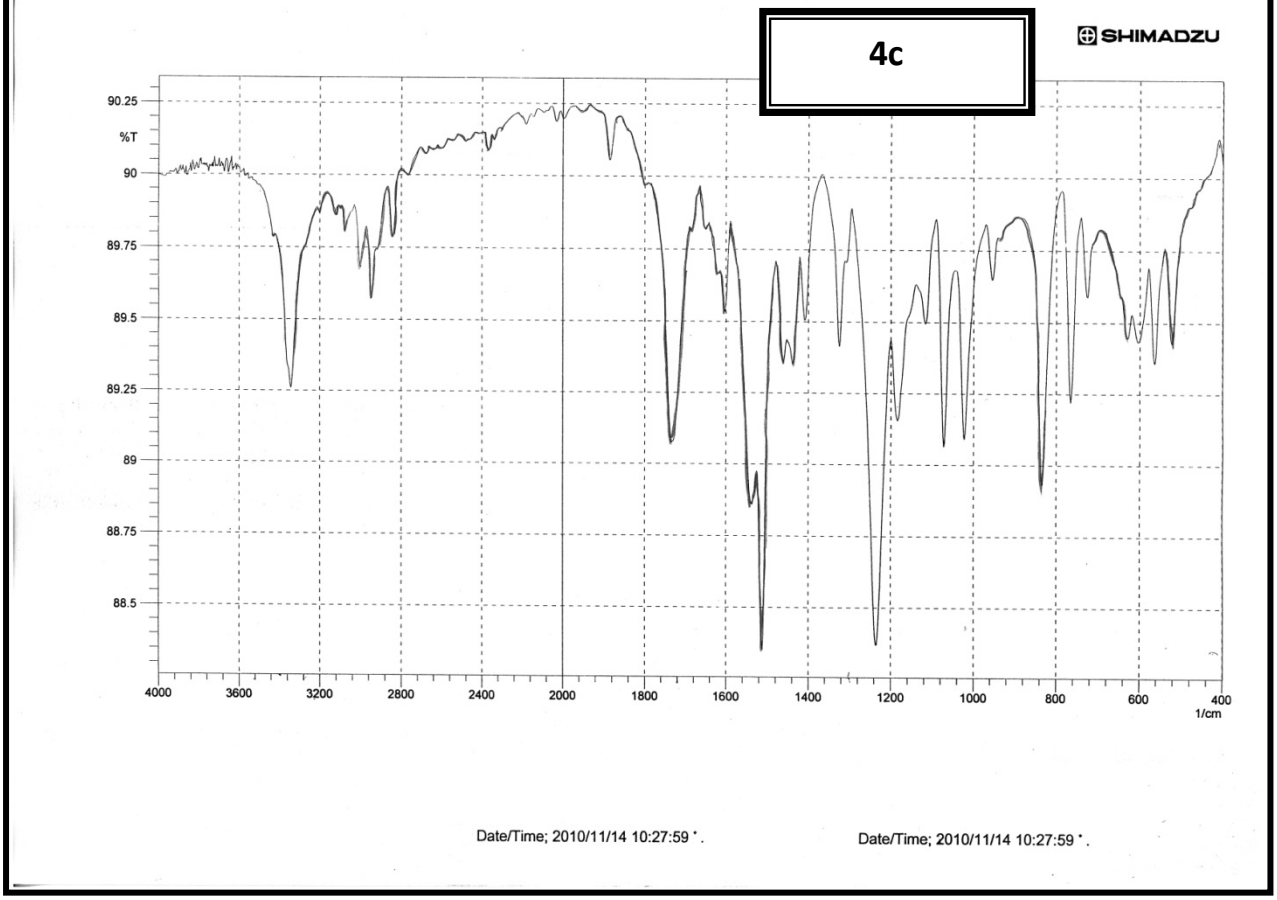

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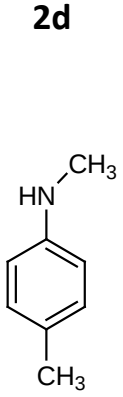

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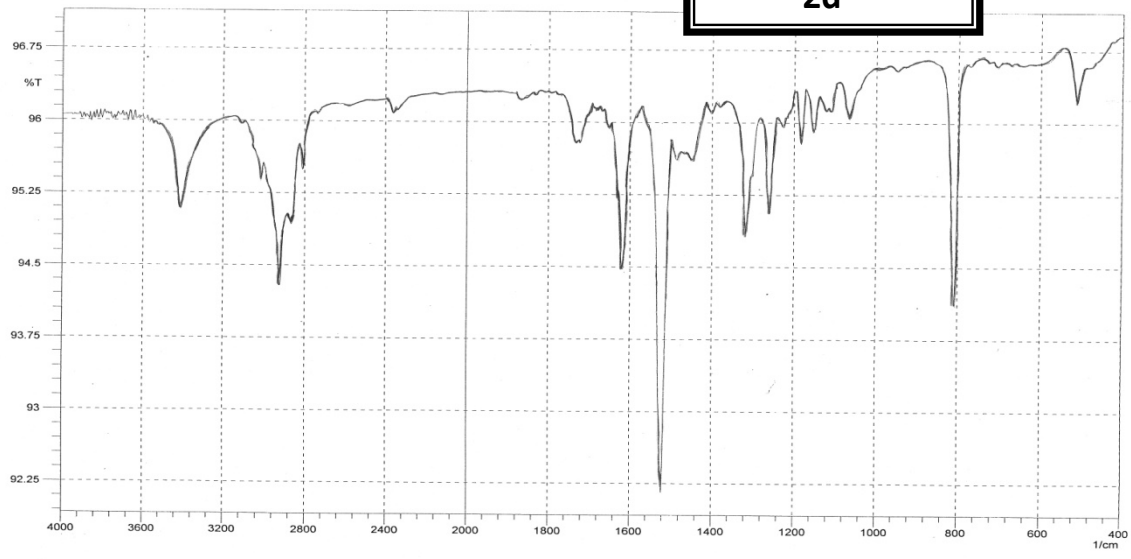

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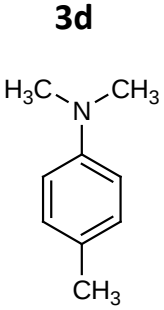

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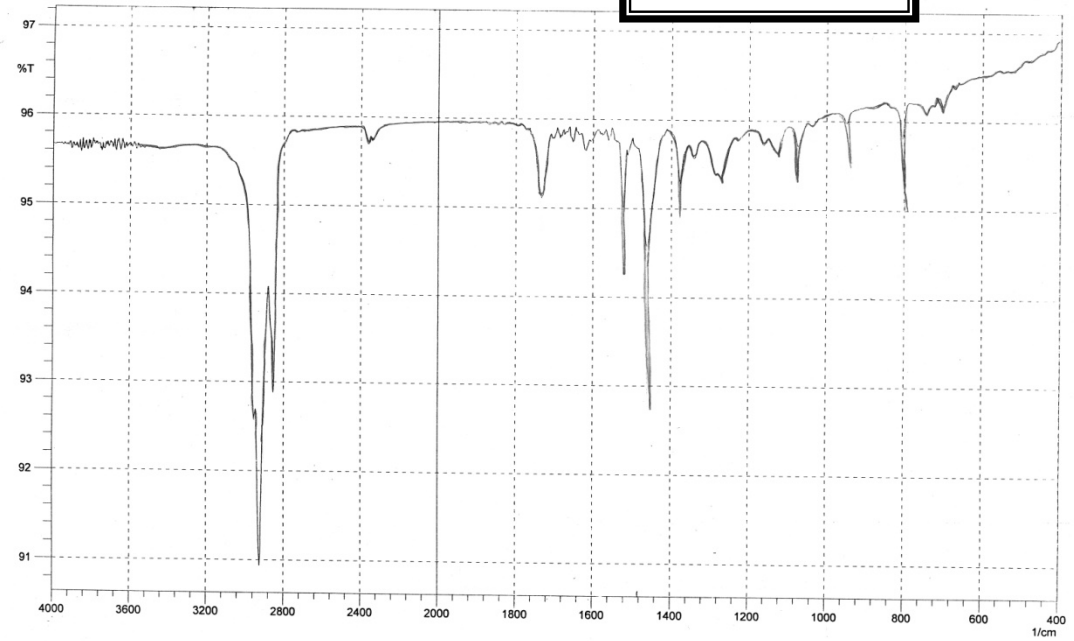

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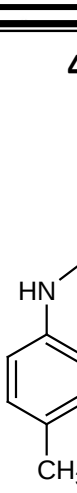
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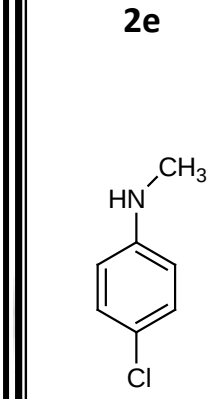

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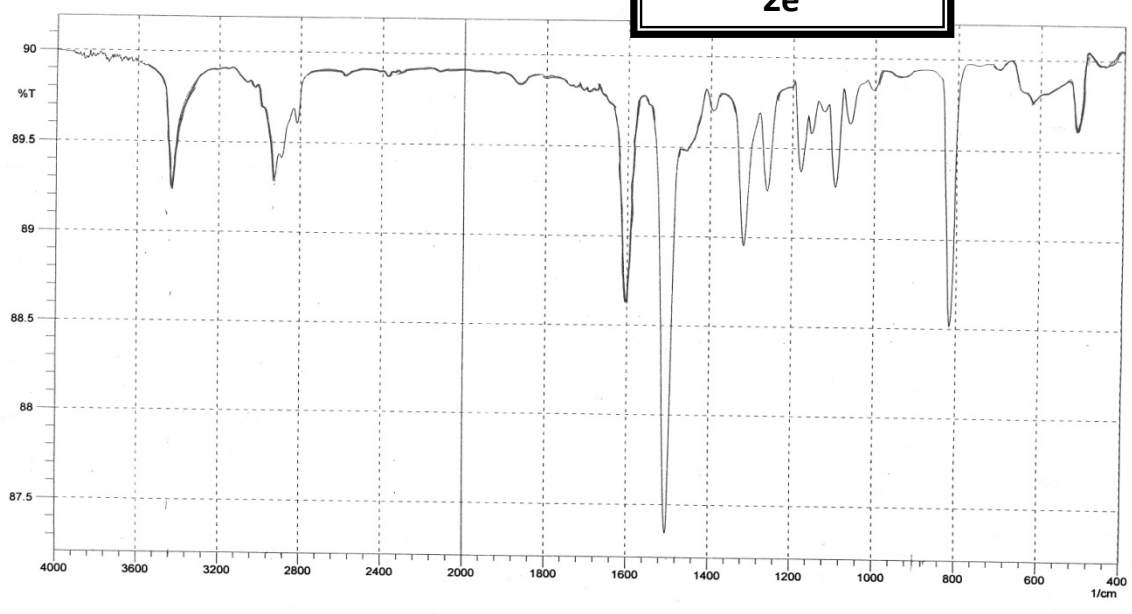

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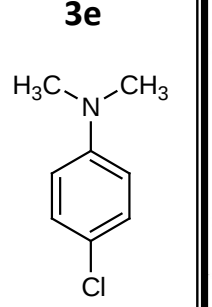

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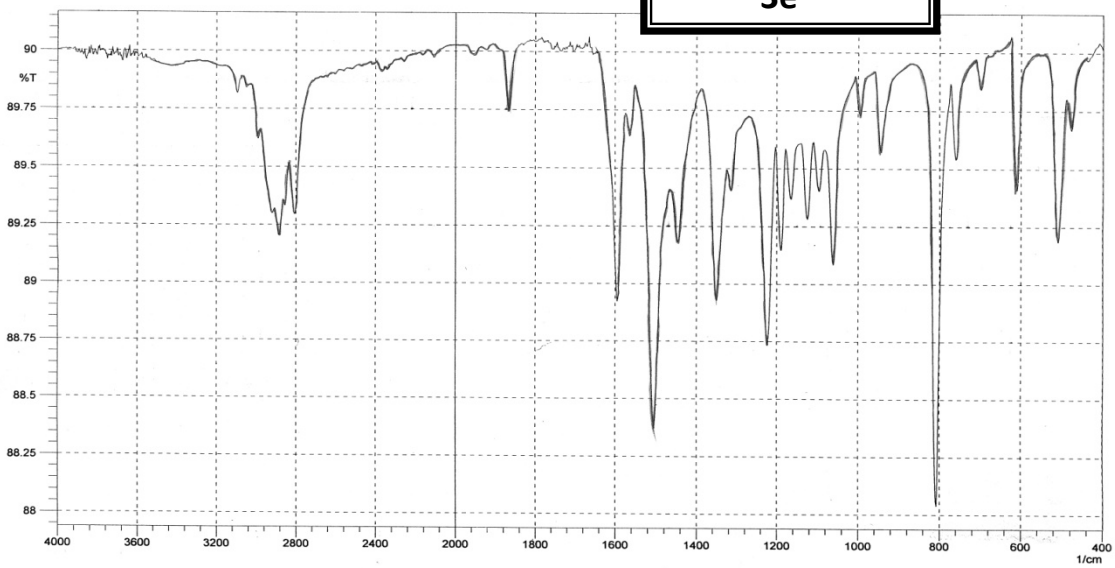

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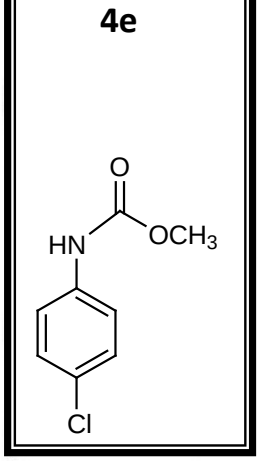

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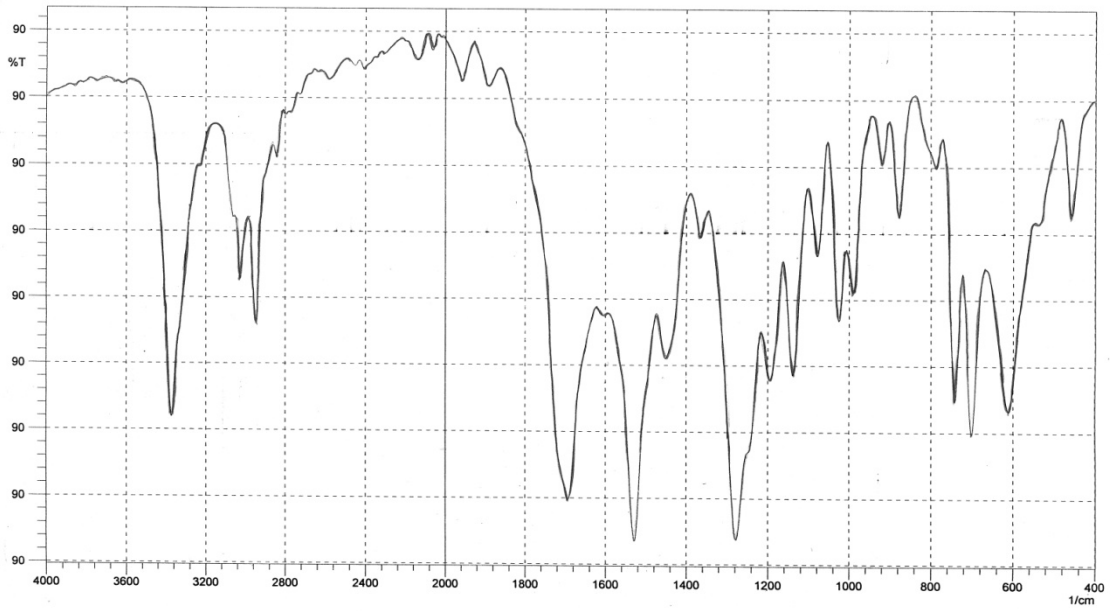

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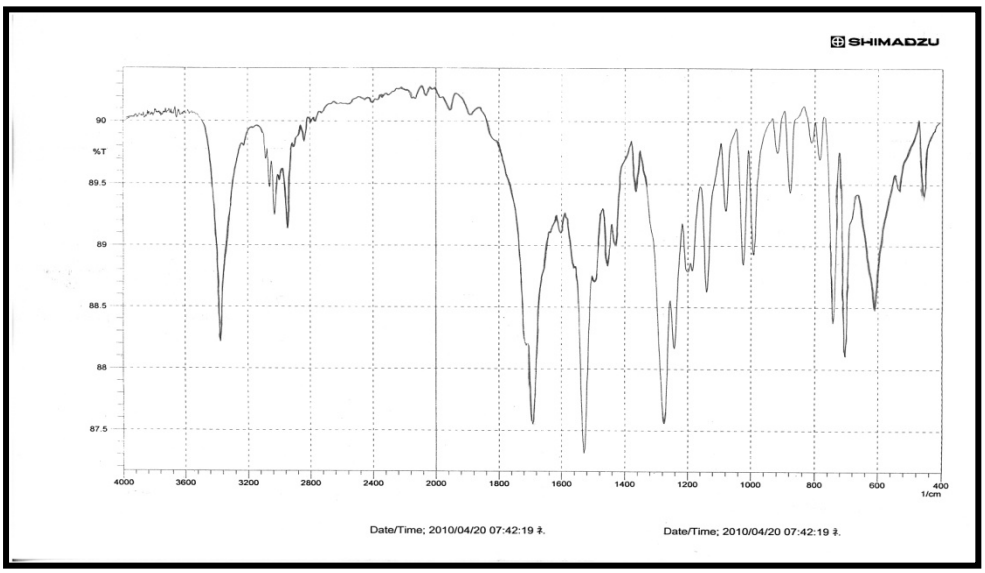
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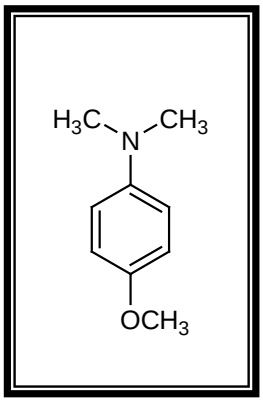
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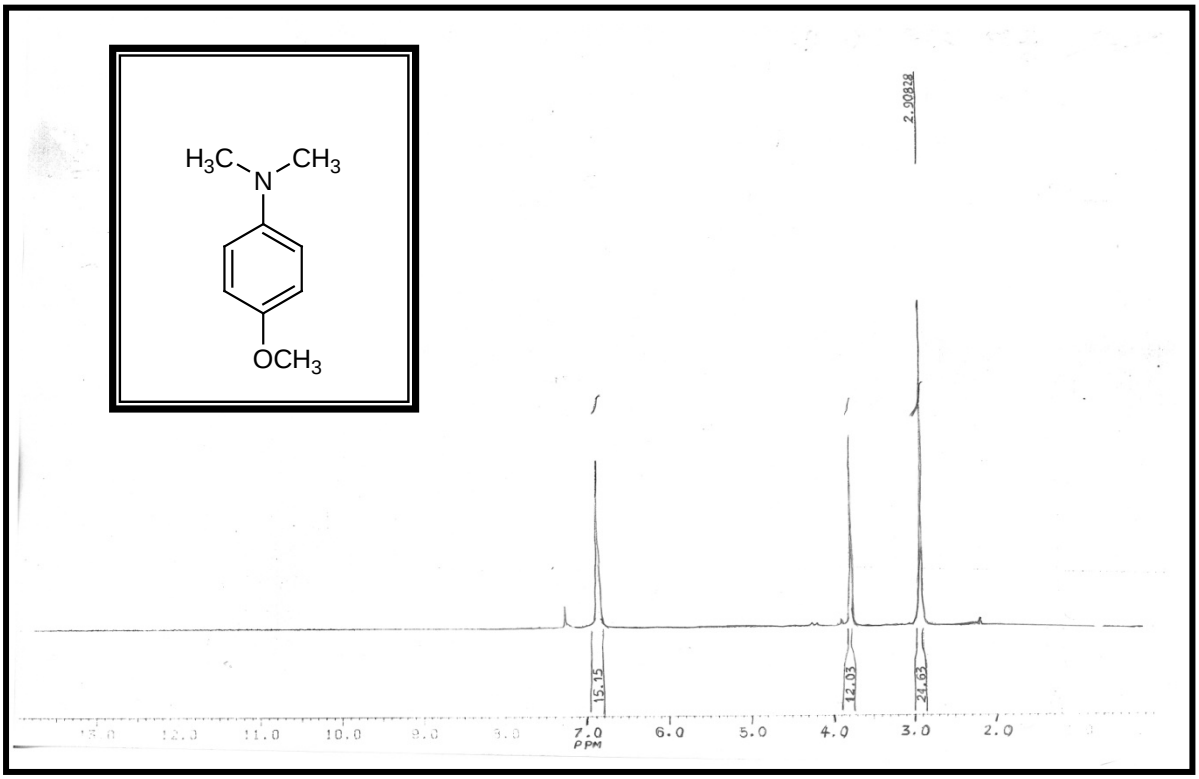
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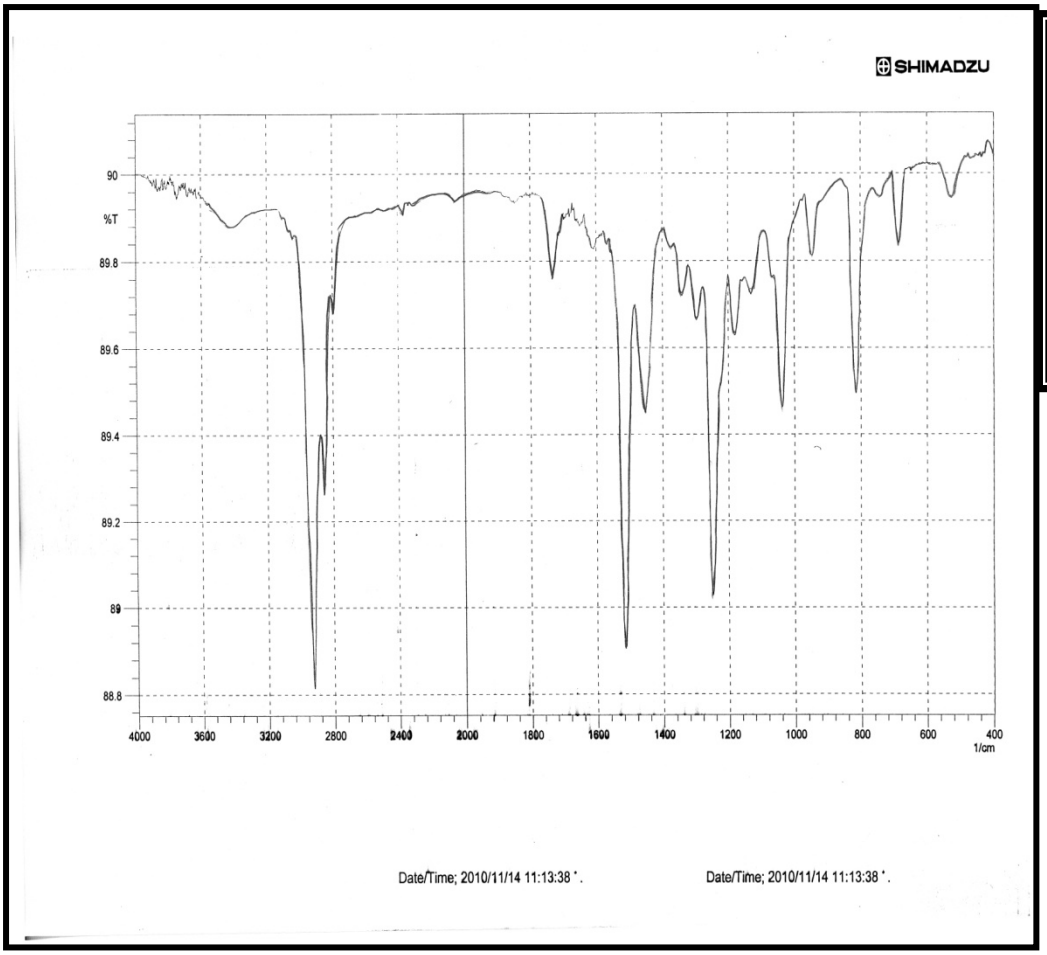
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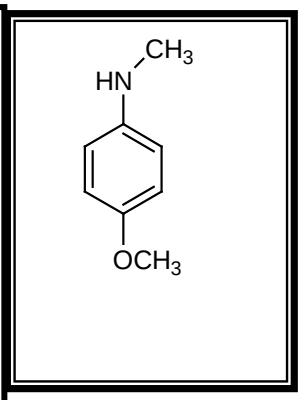
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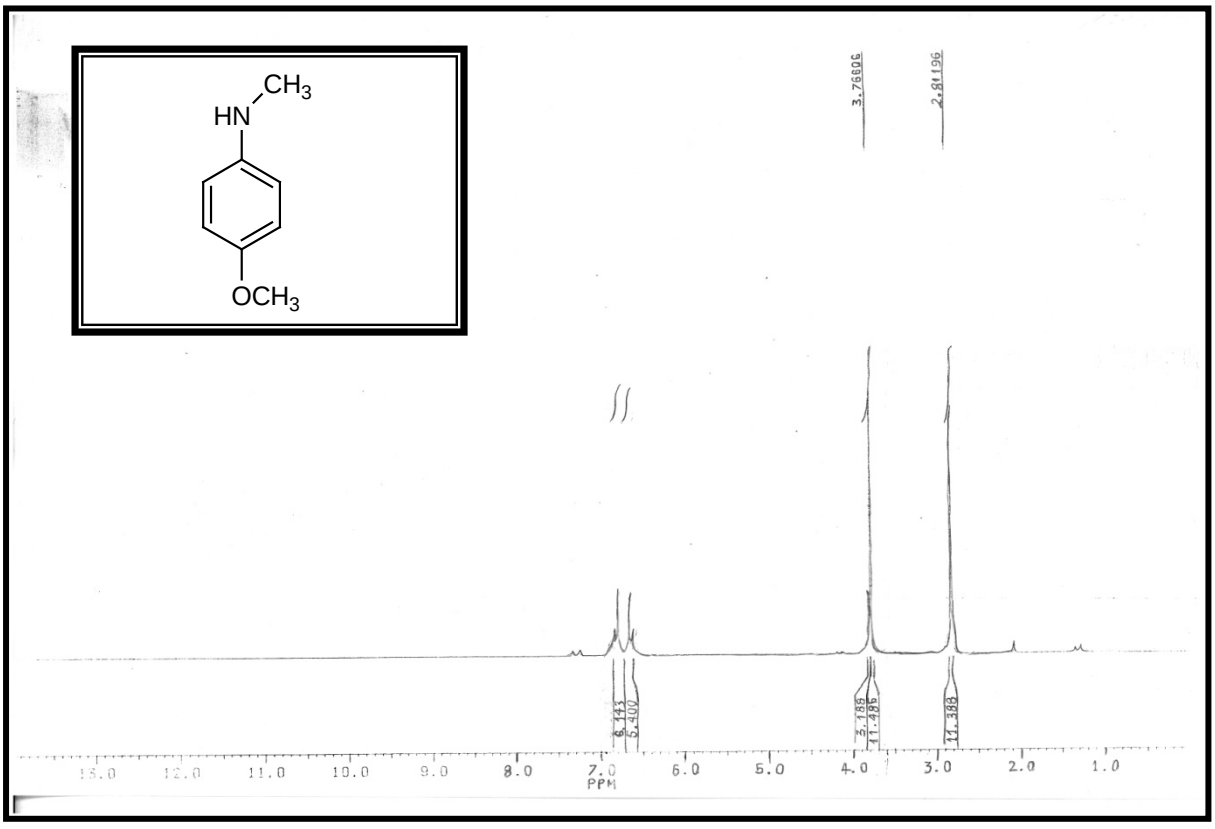
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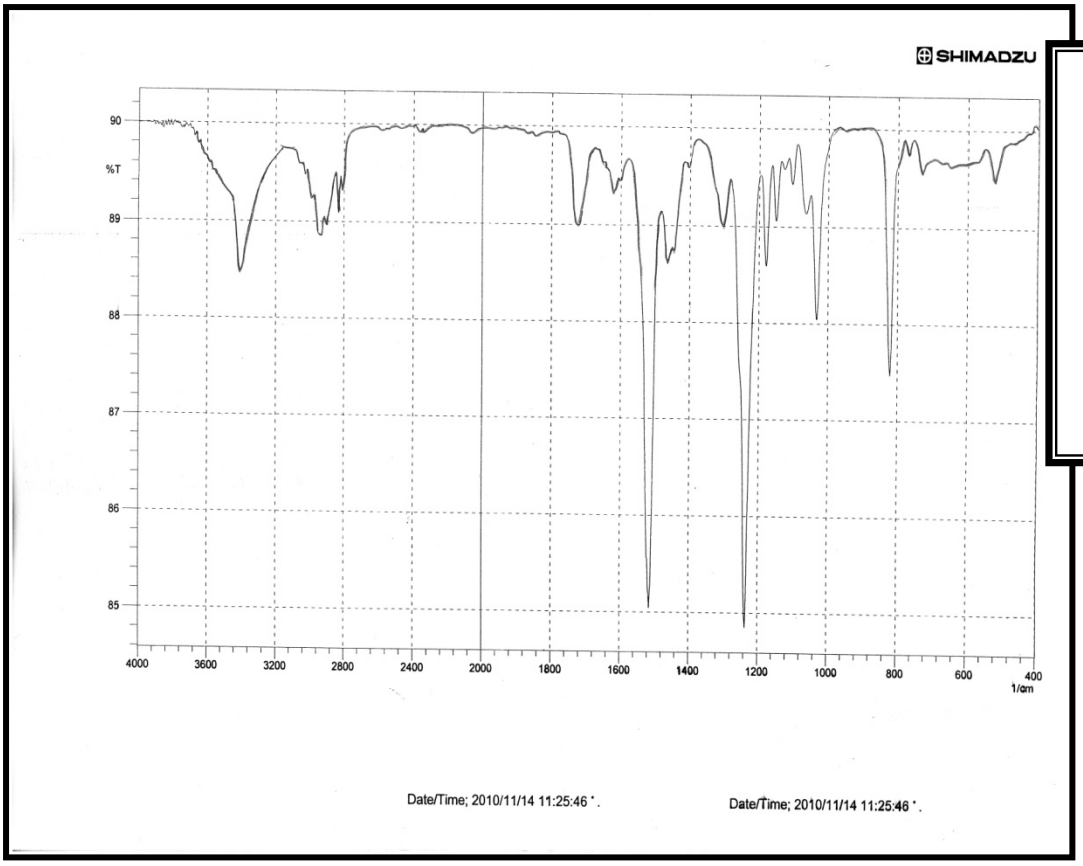
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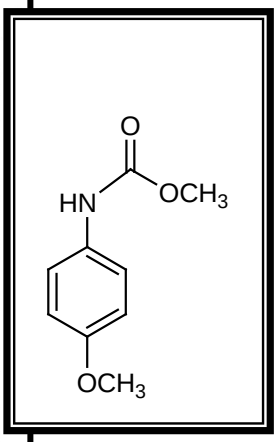
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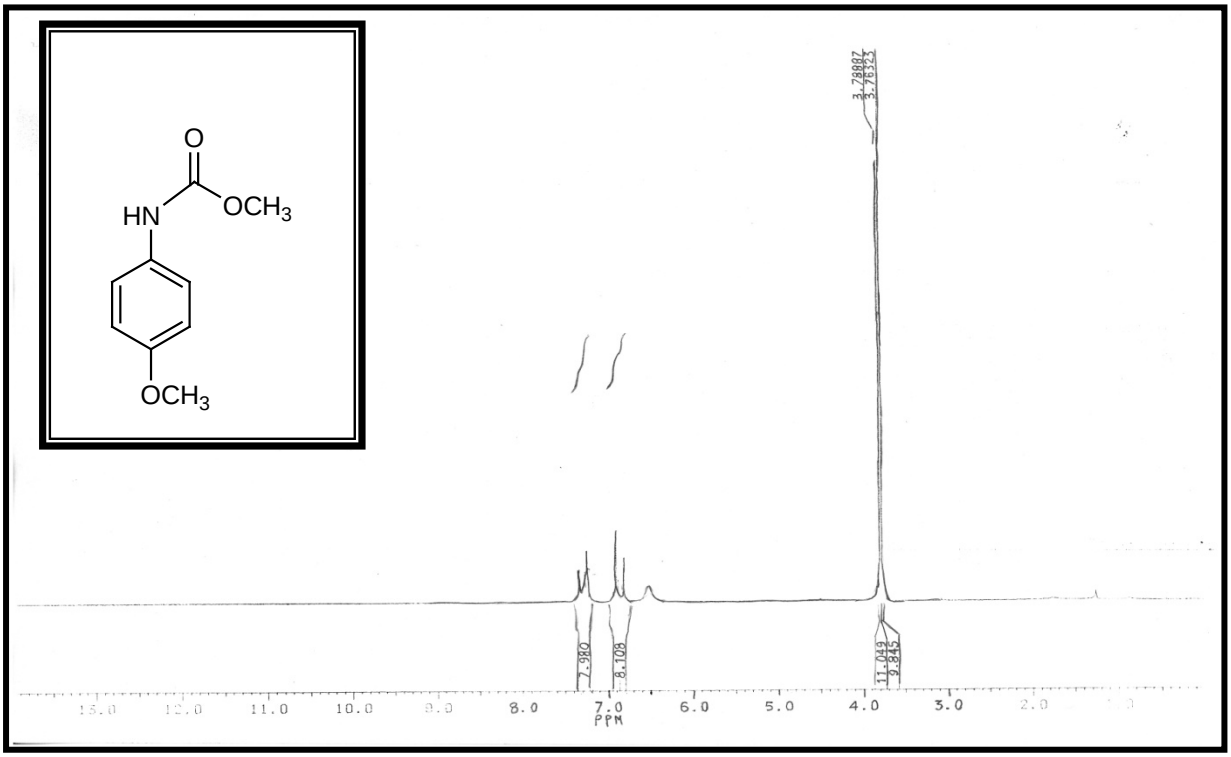
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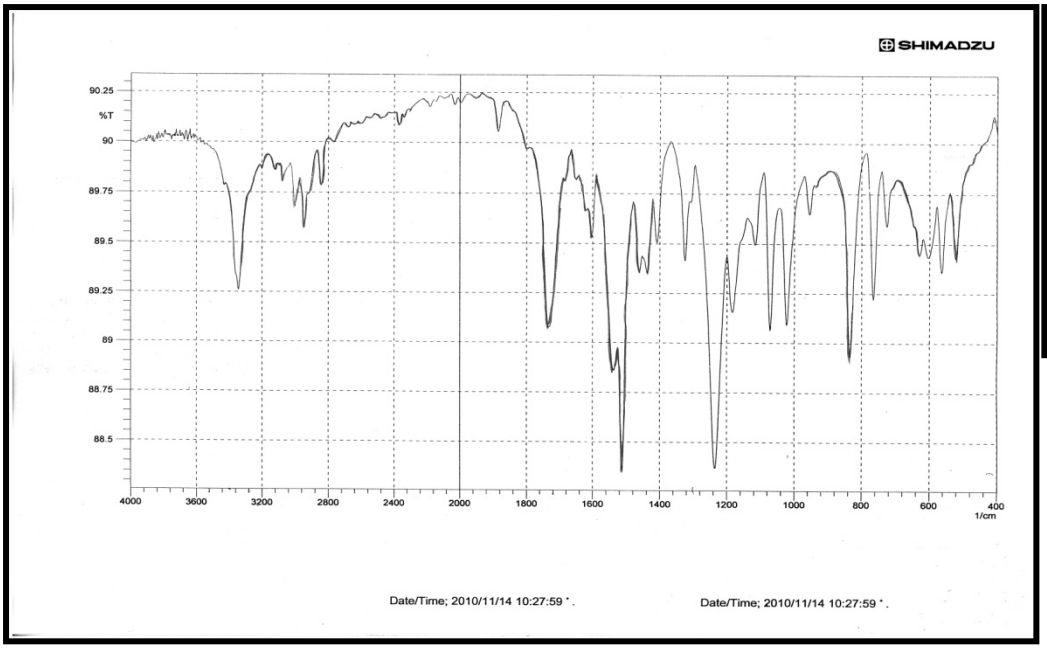
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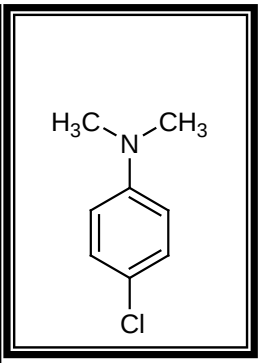
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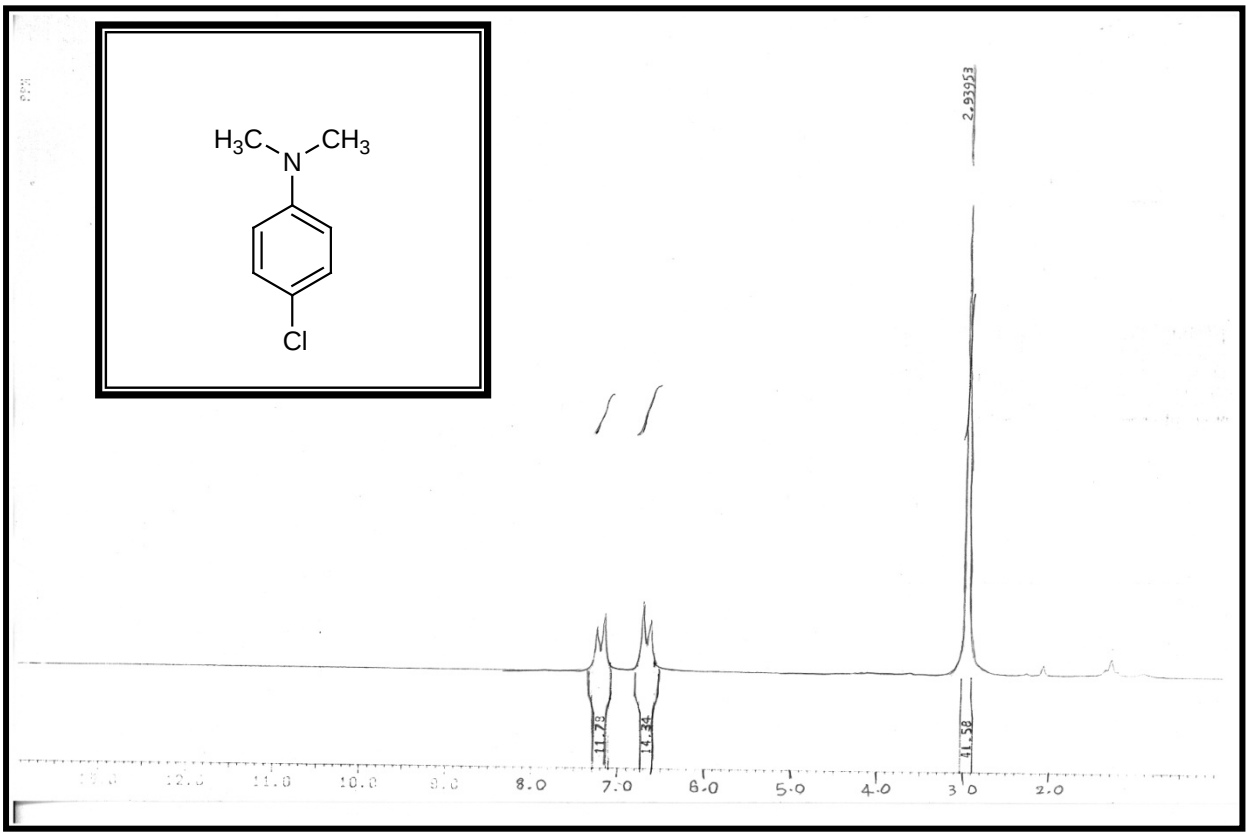
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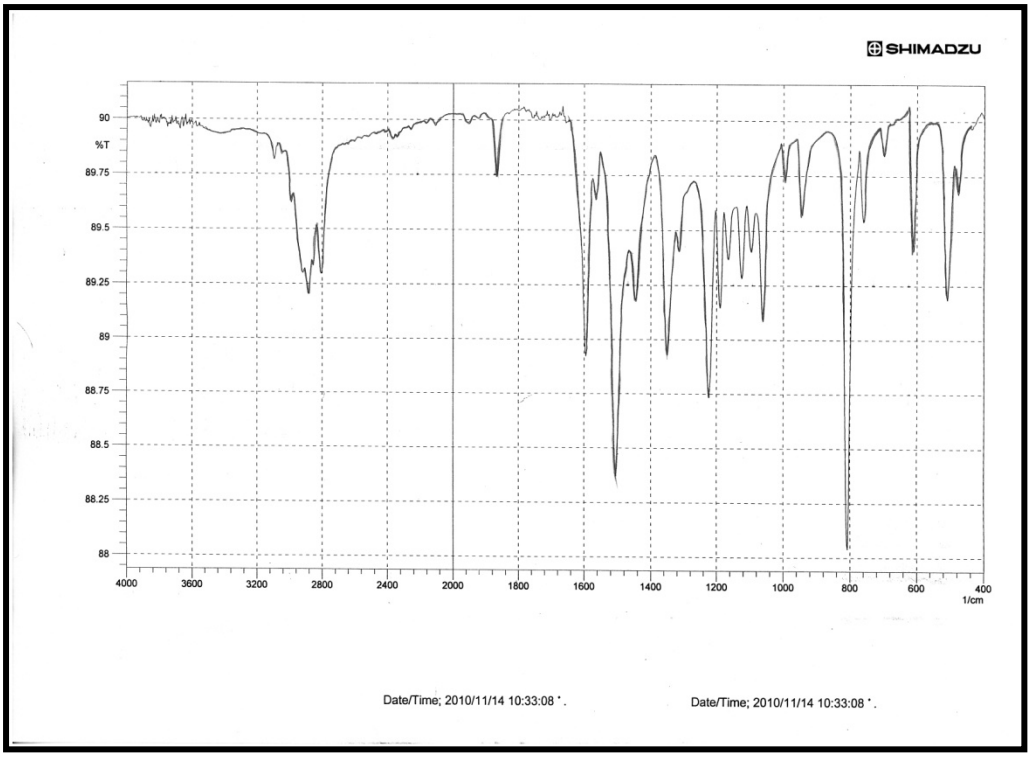
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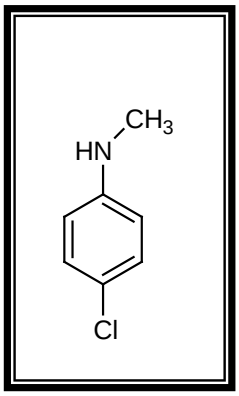
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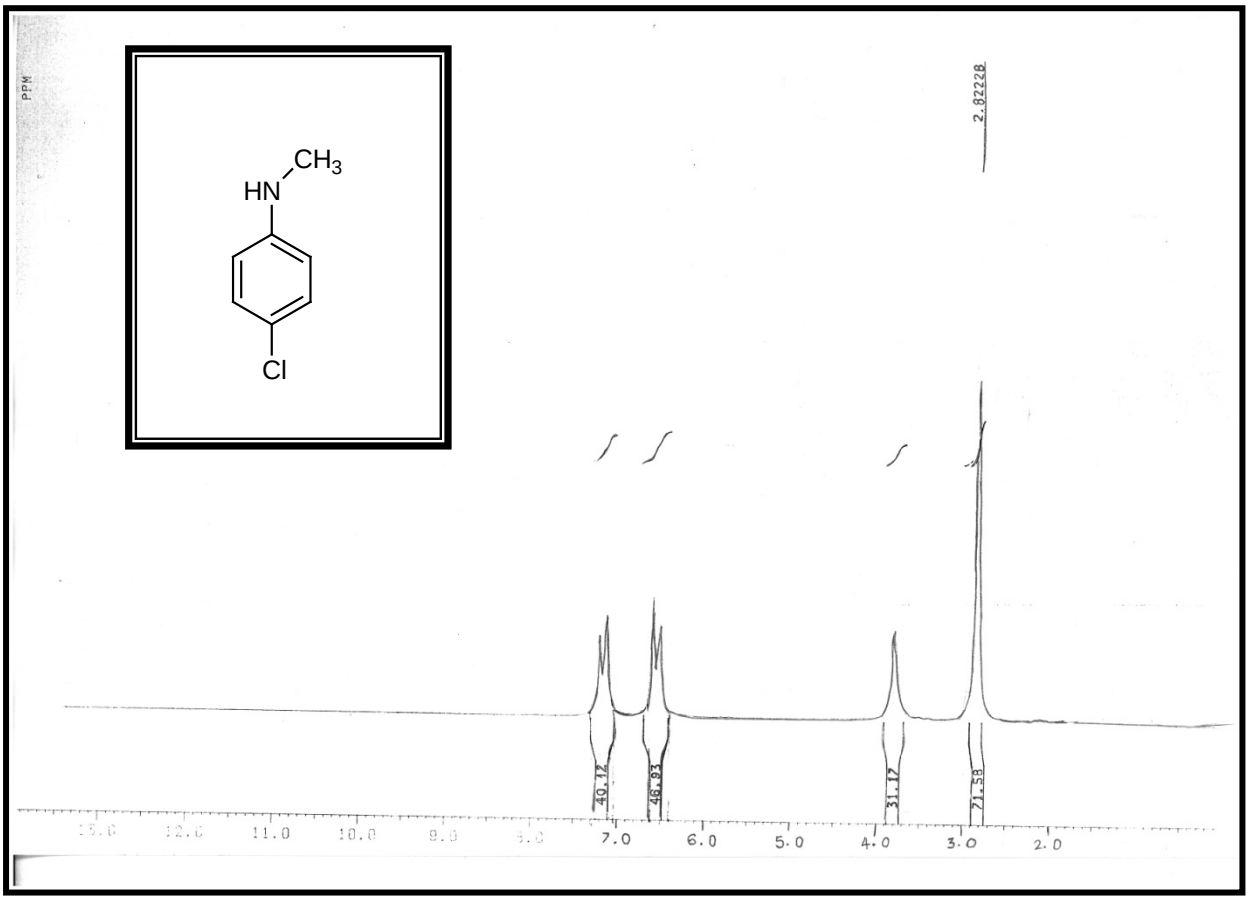
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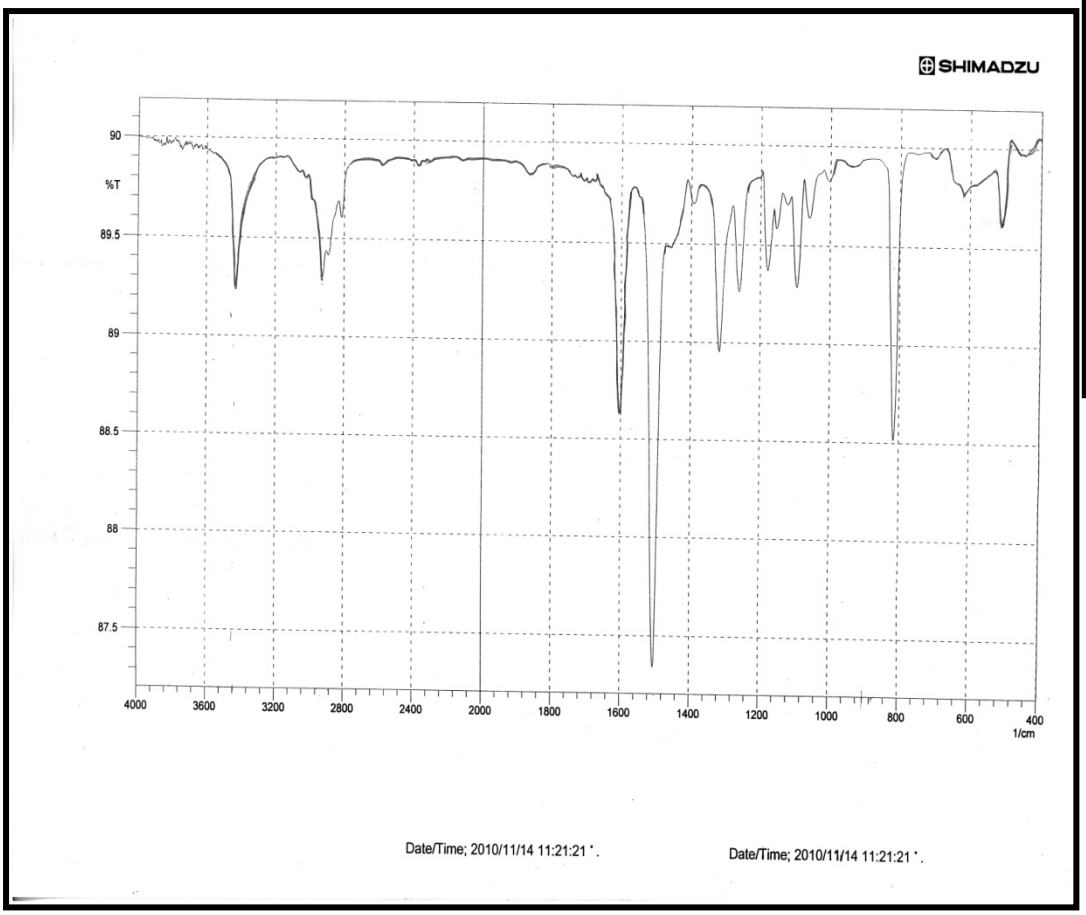
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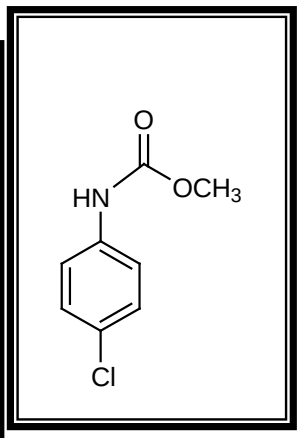
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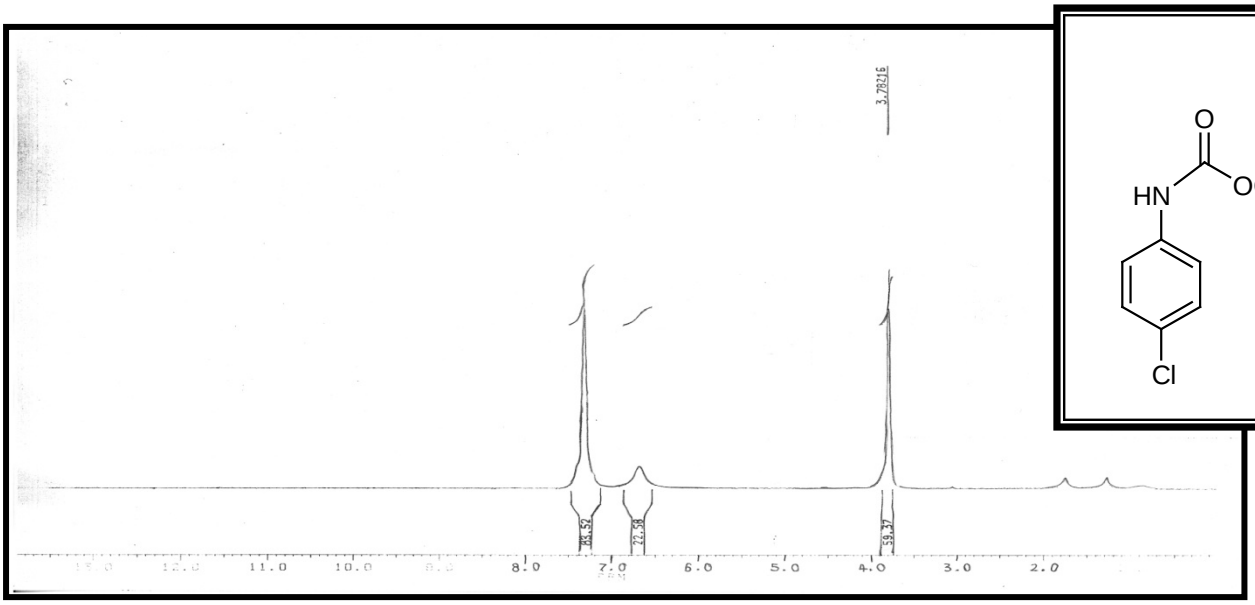
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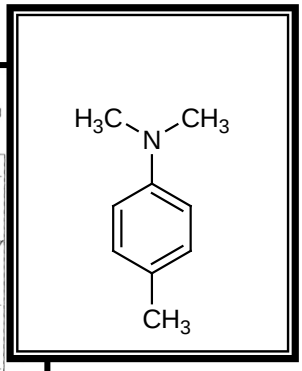
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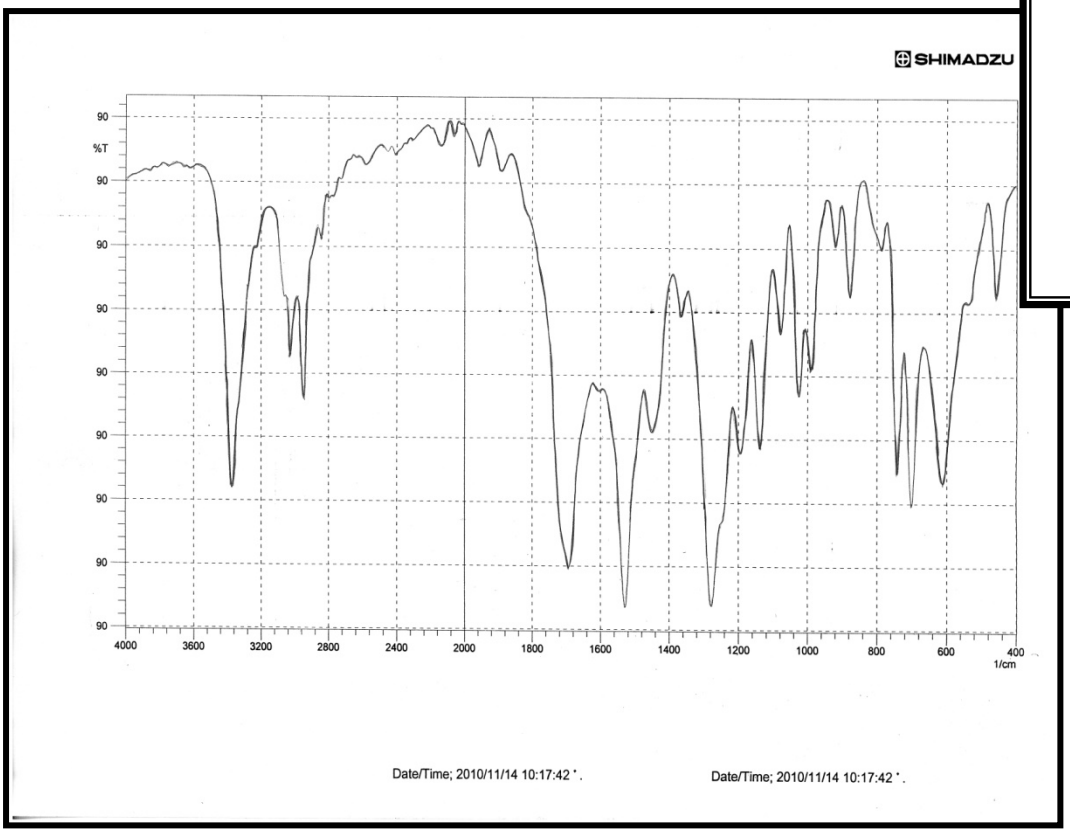
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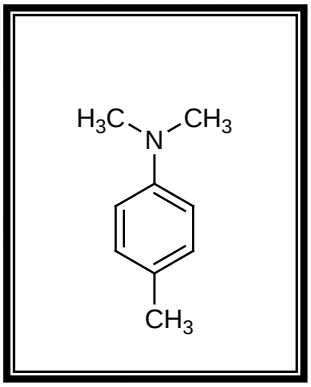
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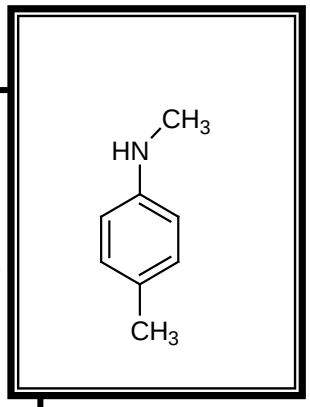
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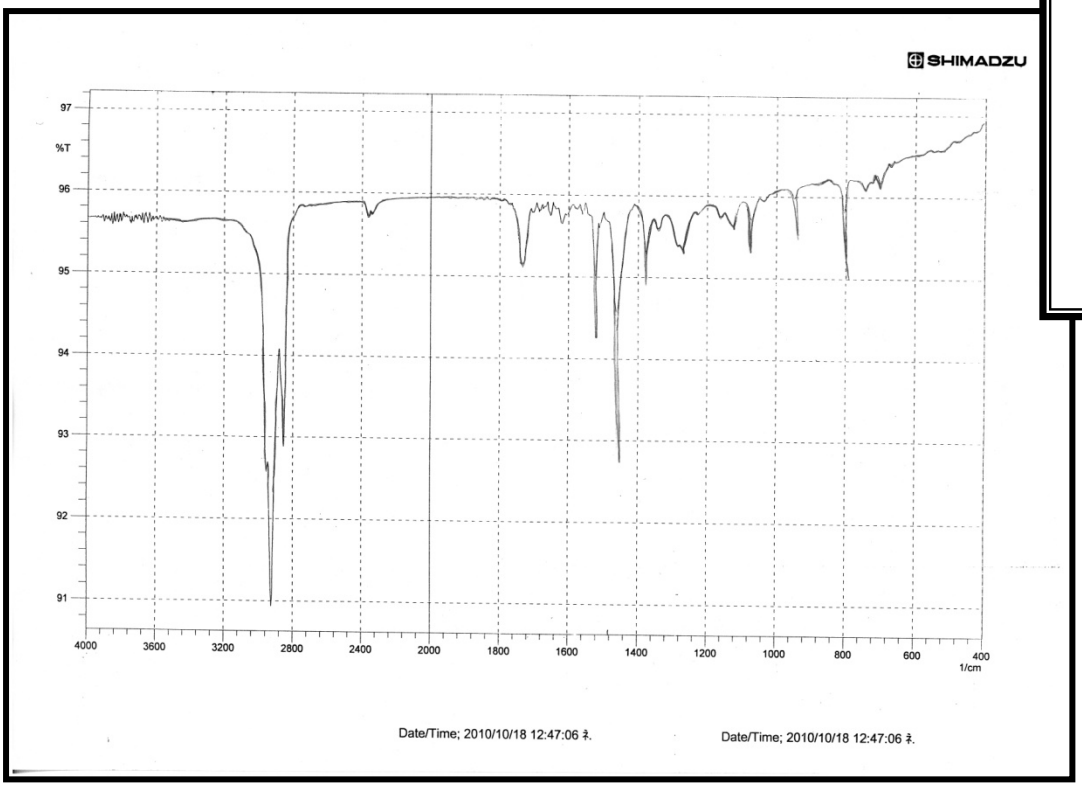
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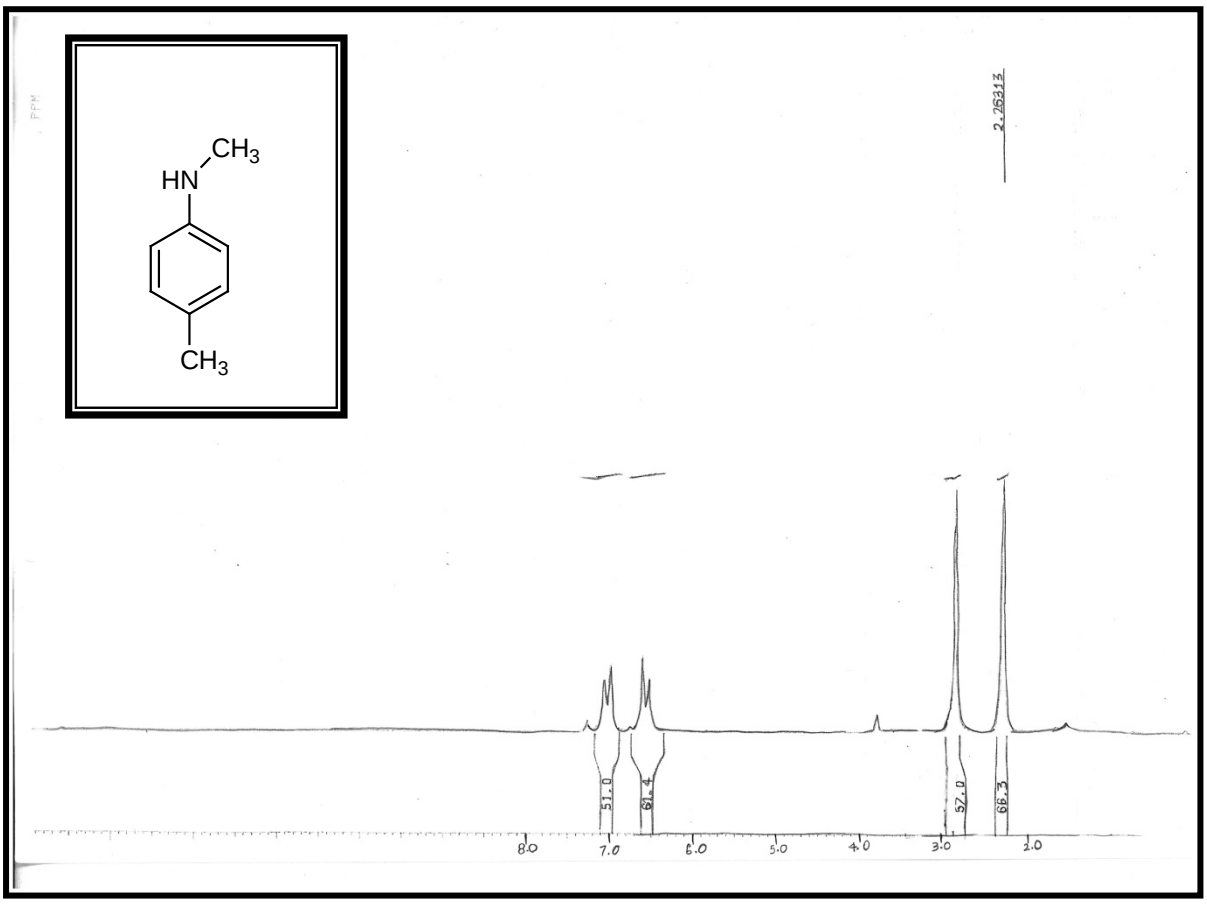
Date/Time; 2010/10/18 12:47:06 ₹.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CH3
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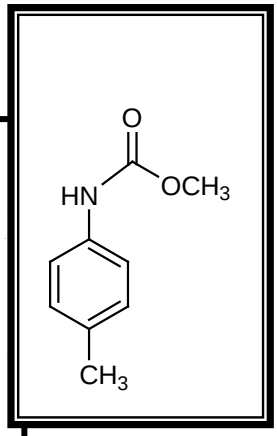
3.0
2.0


O
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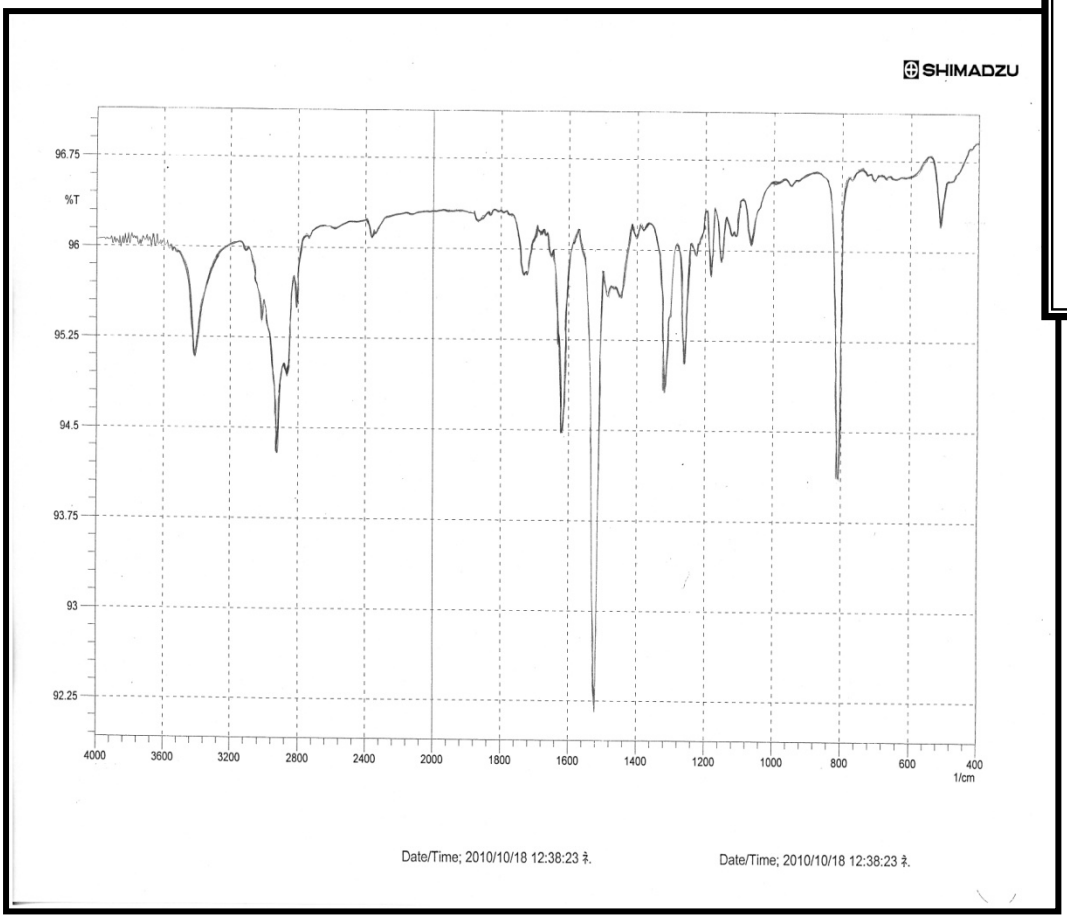
OCH3
CH3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%T
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95.25
94.5
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3200
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2000
1800
1600
1400
1200
1000
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400
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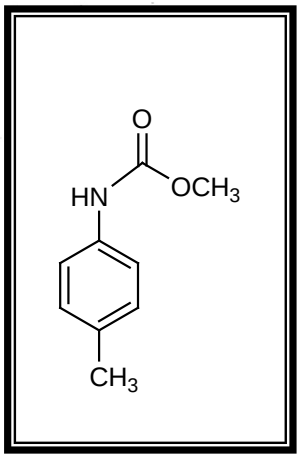
Date/Time; 2010/10/18 12:38:23 ﾈ.


O
HN
OCH3
CH3

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6.0
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4.0
3.0
2.0