

ESI for

**Poly(*N*-isopropylacrylamide-*co*-*L*-proline)-catalyzed
Claisen-Schmidt and Knoevenagel condensations:
unexpected enhanced catalytic activity of the polymer
catalyst**

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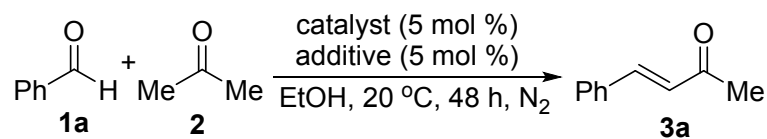
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S1 Condition optimizations

Table S1. Screenings of the catalyst and additive.^a



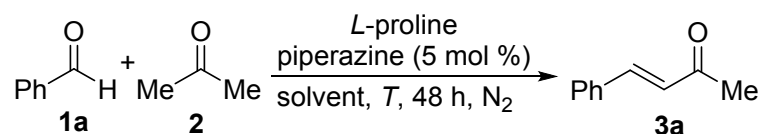
Entry	Catalyst	Additive	Yield (%) ^b
1	<i>L</i> -Proline	-	44
2	<i>L</i> -Proline	1-Methylpiperazine	55
3	<i>L</i> -Proline	Morpholine	61
4	<i>L</i> -Proline	Pyrrolidine	49
5	<i>L</i>-Proline	Piperazine	70
6	<i>L</i> -Proline	Et ₂ NH	36
7	<i>L</i> -Proline	(<i>i</i> -Pr) ₂ NH	34
8	<i>L</i> -Proline	Pyridine	32
9	<i>L</i> -Proline	Et ₃ N	28
10	<i>L</i> -Proline	1-Methylpiperidine	43
11	<i>L</i> -Proline	PhNH ₂	48
12	-	Piperazine	15
13	<i>L</i> -Cysteine	Piperazine	29
14	<i>L</i> -Histidine	Piperazine	22
15	<i>L</i> - Arginine	Piperazine	12
16	<i>L</i> -Norvaline	Piperazine	52

17	5-Aminopentanoic acid	Piperazine	17
18	Piperidine-2-carboxylic acid	Piperazine	25
19	Pyrrolidine-3-carboxylic acid	Piperazine	32

^a1 mmol of **1a**, 3 mmol of acetone and 1 mL of EtOH were employed.

^bIsolated yields of **3a** based on **1a**.

Table S2. Condition optimizations.^a



Entry	Solvent	2/1a ^b	Cat% ^c	<i>T</i>	Yield
				(°C) ^d	(%) ^e
1	EtOH	3	5	20	70
2	EtOH/H ₂ O (4:1)	3	5	20	64
3	EtOH/H ₂ O (1:1)	3	5	20	60
4	MeOH	3	5	20	50
5	<i>i</i> -PrOH	3	5	20	66
6	<i>t</i> -BuOH	3	5	20	57
7	Acetone	-	5	20	37
8	Acetone/EtOH (90:10)	-	5	20	46
9	EtOH	2	5	20	68
10	EtOH	5	5	20	64
11	EtOH	3	3	20	58
12	EtOH	3	0	20	15

13	EtOH	3	10	20	64
14	EtOH	3	20	20	45
15	EtOH	3	5	40	67

^a1 mmol of **1a**, and 1 mL of solvent were employed.

^bMolar ratio of acetone vs. **1a**.

^cCatalyst amount (mol %) based on **1a**.

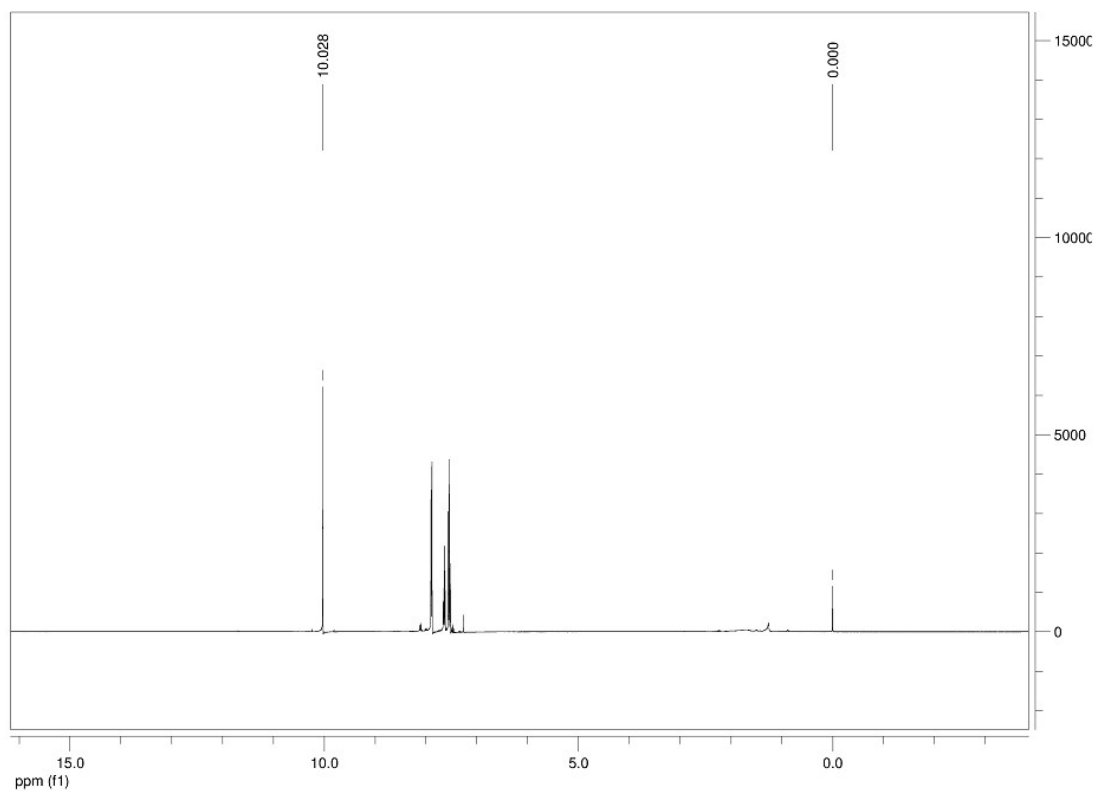
^dReaction temperature.

^eIsolated yields of **3a** based on **1a**.

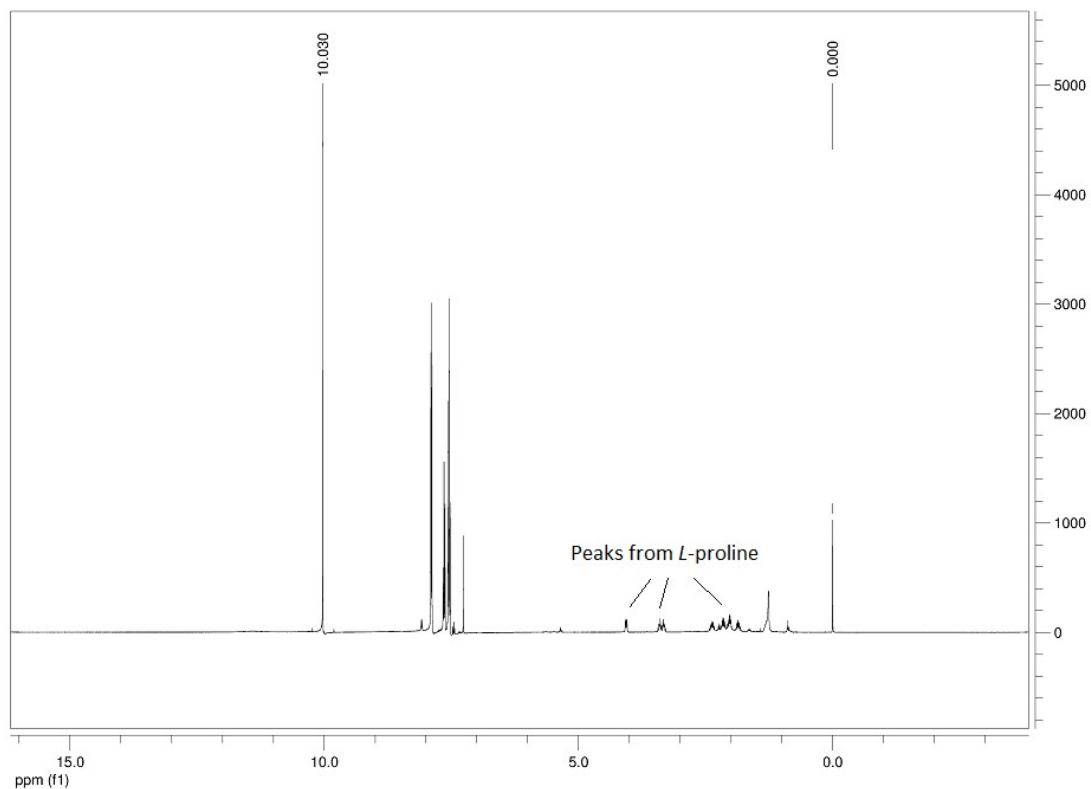
S2 Original ^1H NMR spectra of benzaldehyde in mechanism study experiments

Instruction: The original spectra were given here to confirm that the chemical shifts of aldehyde-H were referred to the internal standard Me_4Si at 0 ppm. Although the solubility of *L*-proline was low in CDCl_3 , it obviously affected the chemical shift of the aldehyde-H, which moved to the low field region (from 10.028 ppm to 10.030 ppm).

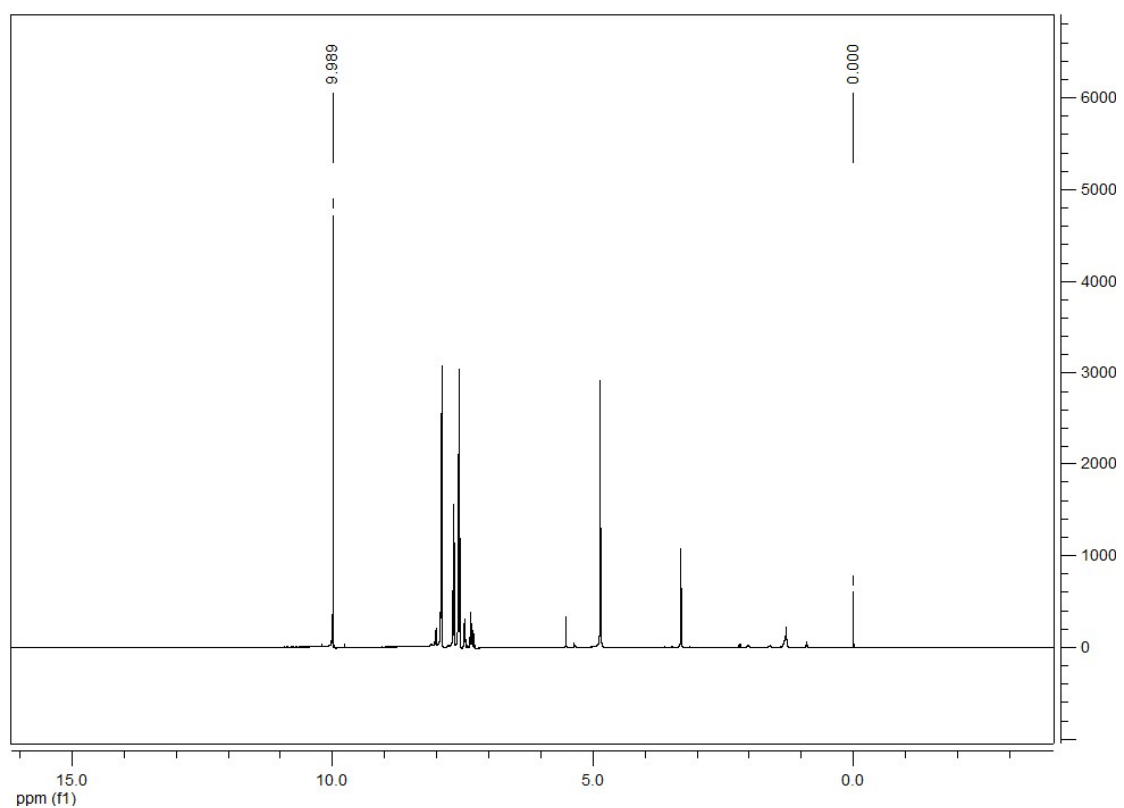
S3.1 Without *L*-proline (CDCl_3 , 400 MHz; aldehyde-H at 10.028 ppm; Me_4Si at 0 ppm)



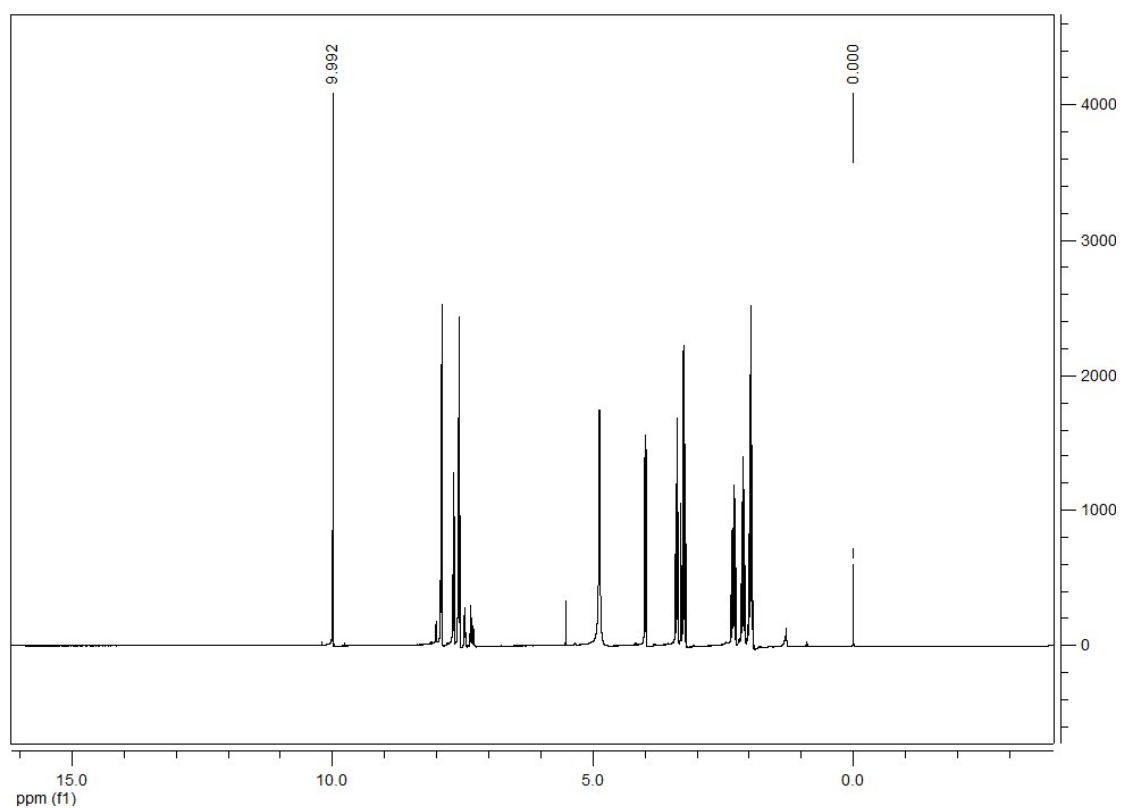
S3.2 After adding *L*-proline (CDCl₃, 400 MHz; aldehyde-H at 10.030 ppm; Me₄Si at 0 ppm)



S3.3 Without *L*-proline (Methanol-D₄, 400 MHz; aldehyde-H at 9.989 ppm; Me₄Si at 0 ppm)



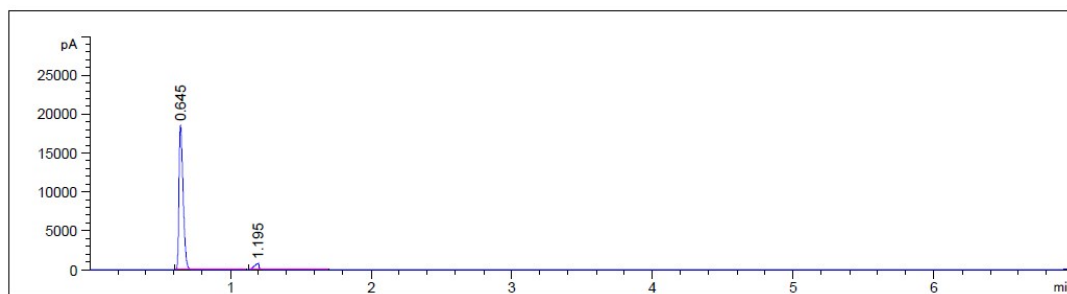
S3.4 After adding *L*-proline (Methanol-D₄, 400 MHz; aldehyde-H at 9.992 ppm; Me₄Si at 0 ppm)



S3 GC data and spectra of the polymer absorption test

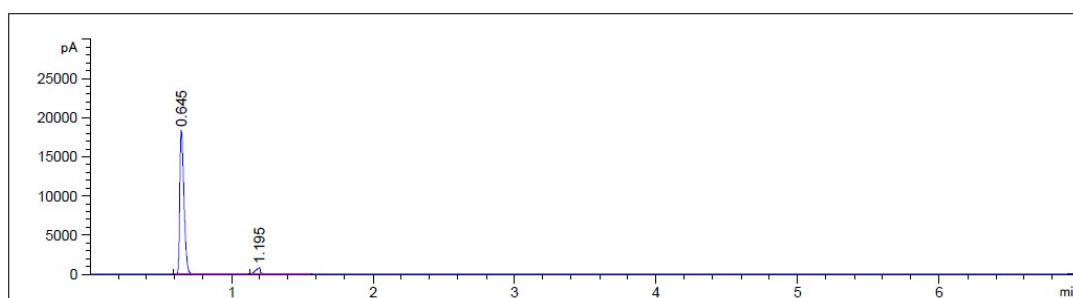
S3.1 GC analysis data of the sample PhCHO/EtOH without polymer 8

1st time



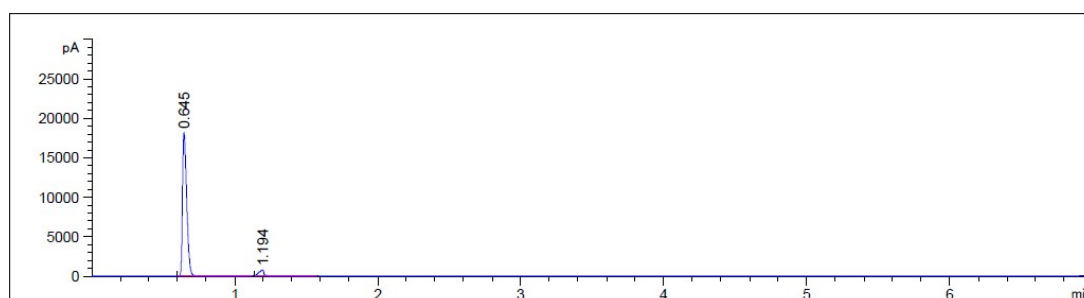
Compound	Retention time/min	Peak wide/min	Peak area	Peak area %	PhCHO / EtOH
PhCHO	1.195	0.0399	792.13324	4.77030	0.05009
EtOH	0.645	0.0318	18516.6	95.22970	

2nd time



Compound	Retention time/min	Peak wide/min	Peak area	Peak area %	PhCHO / EtOH
PhCHO	1.195	0.0373	793.18103	4.77037	0.05009
EtOH	0.645	0.0319	18318.2	95.22963	

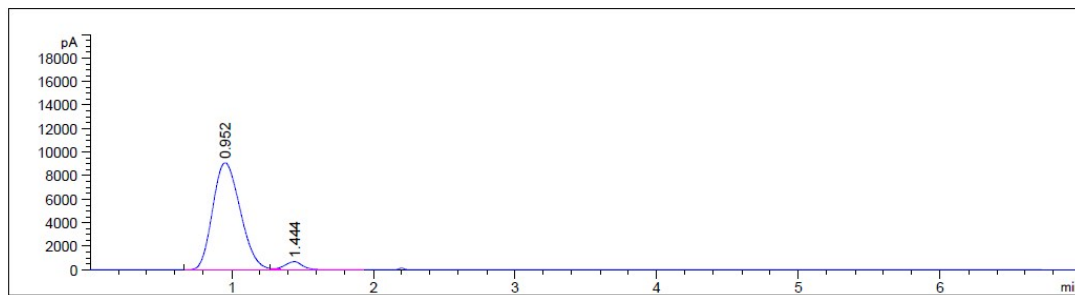
3rd time



Compound	Retention time/min	Peak wide/min	Peak area	Peak area %	PhCHO / EtOH
PhCHO	1.194	0.0361	769.51642	4.76944	0.05008
EtOH	0.645	0.0318	18123.6	95.23056	
Average:					0.05009

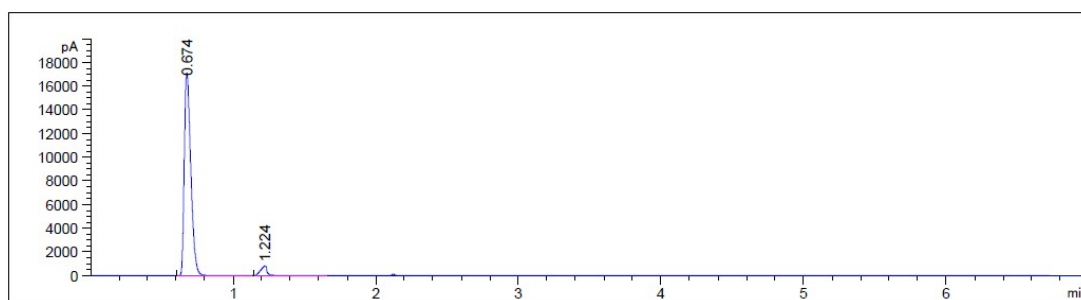
S3.2 GC analysis data of the sample PhCHO/EtOH after adding polymer 8

1st time



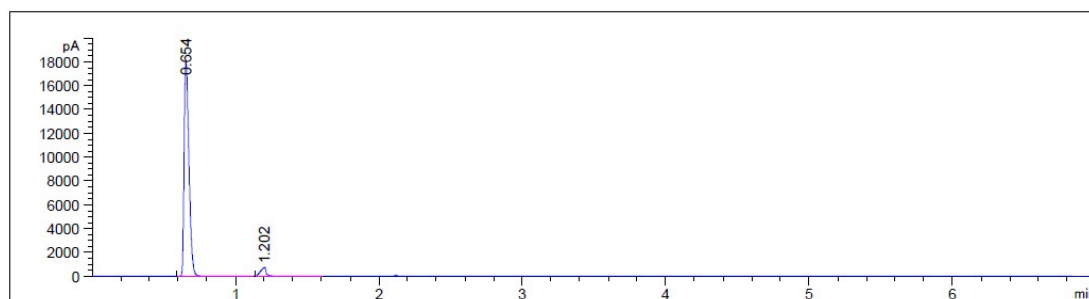
Compound	Retention time/min	Peak wide/min	Peak area	Peak area %	PhCHO / EtOH
PhCHO	1.444	0.1059	667.29846	4.34212	0.04539
EtOH	0.952	0.2125	9075.36621	95.65788	

2nd time



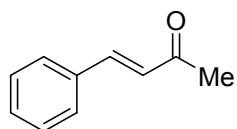
Compound	Retention time/min	Peak wide/min	Peak area	Peak area %	PhCHO / EtOH
PhCHO	1.224	0.0476	808.49634	4.27906	0.04470
EtOH	0.674	0.0488	17106.3	95.72094	

3rd time

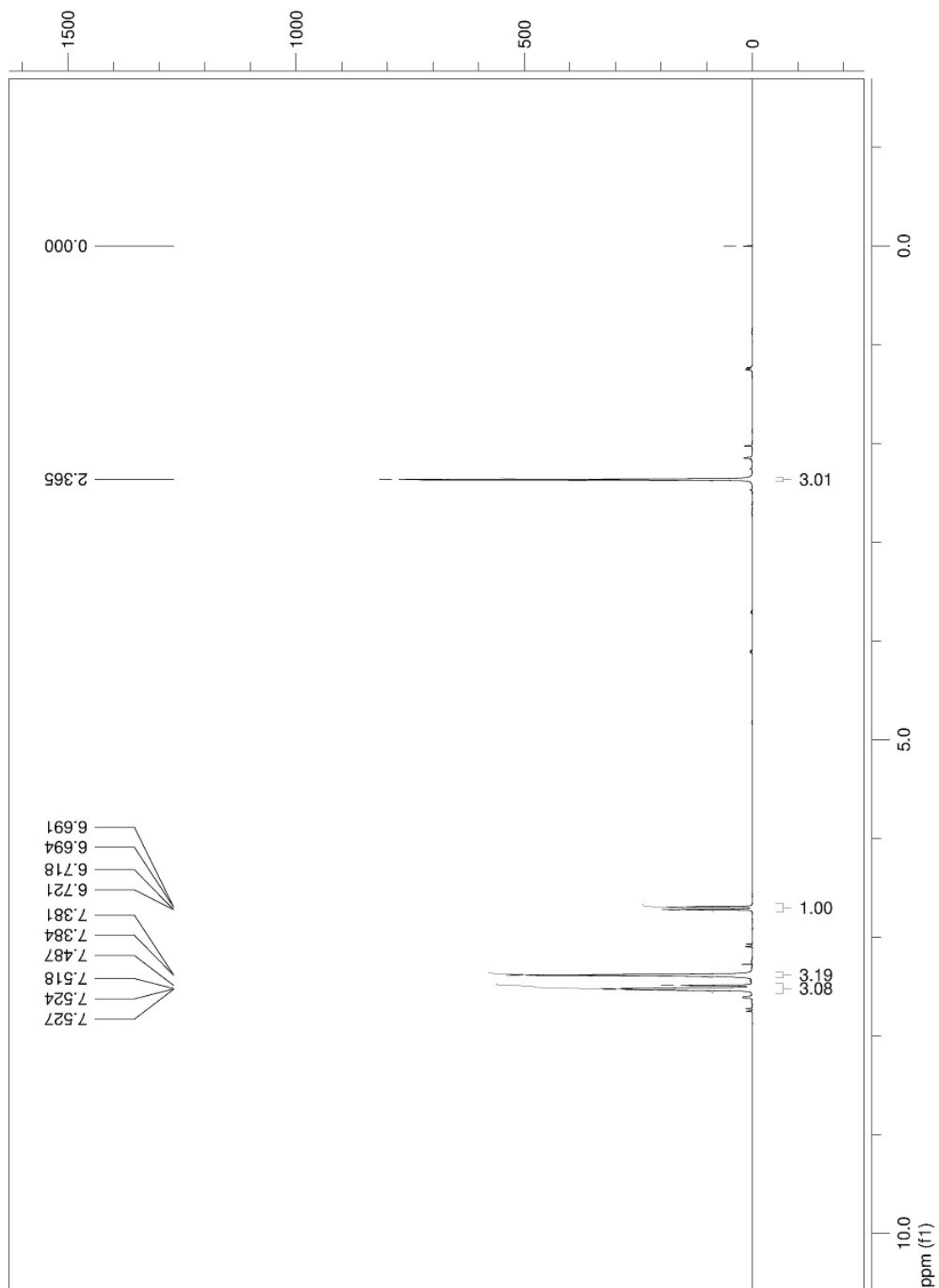


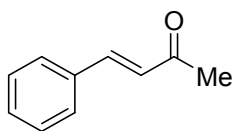
Compound	Retention time/min	Peak wide/min	Peak area	Peak area %	PhCHO / EtOH
PhCHO	1.202	0.0407	706.14410	4.28743	0.04479
EtOH	0.654	0.0361	17985.0	95.71257	
Average:					0.04496

S4 NMR Spectra of the products

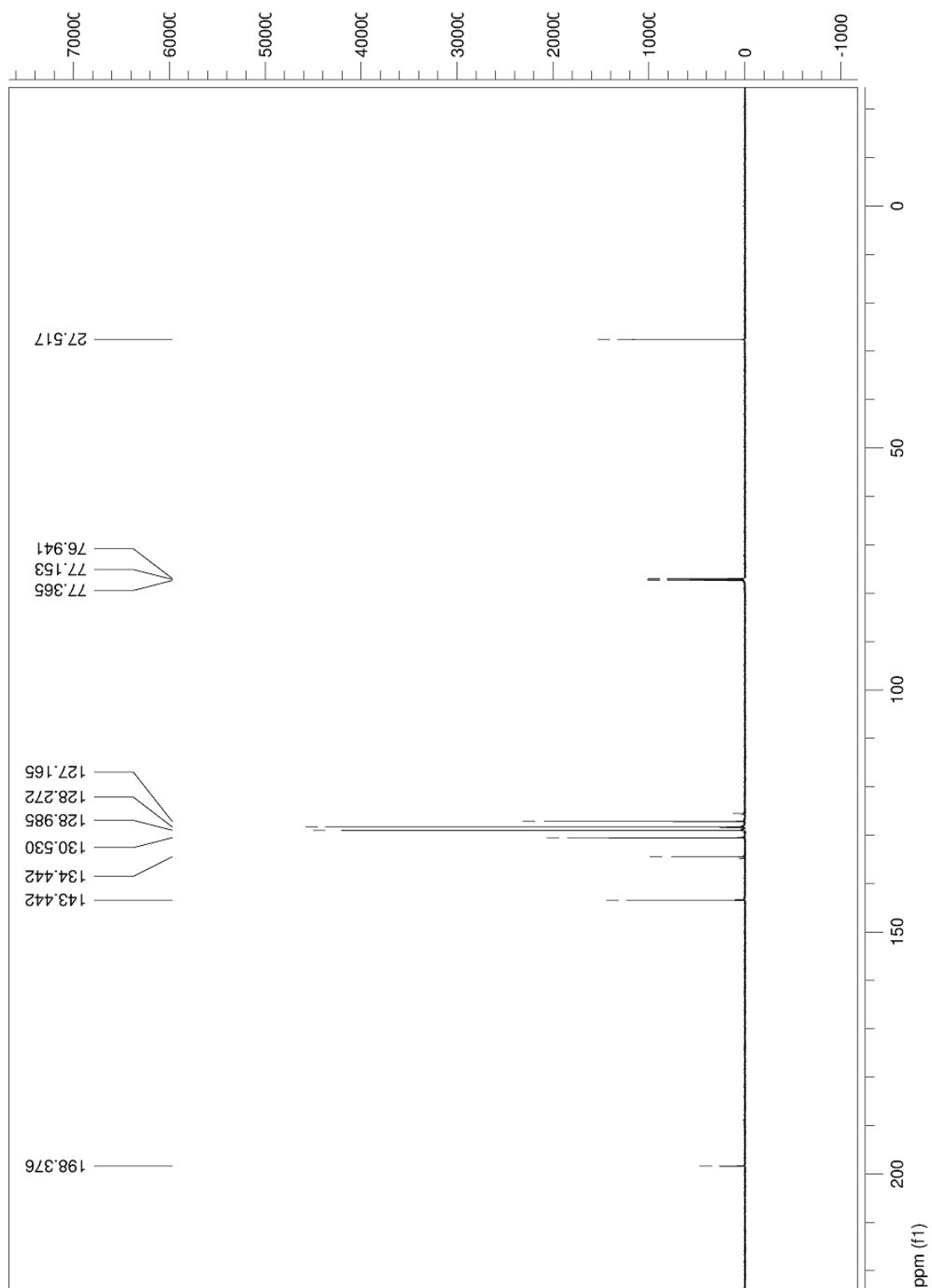


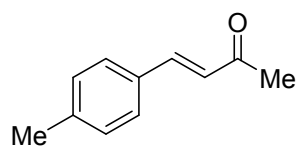
3a, CDCl₃, 600 MHz



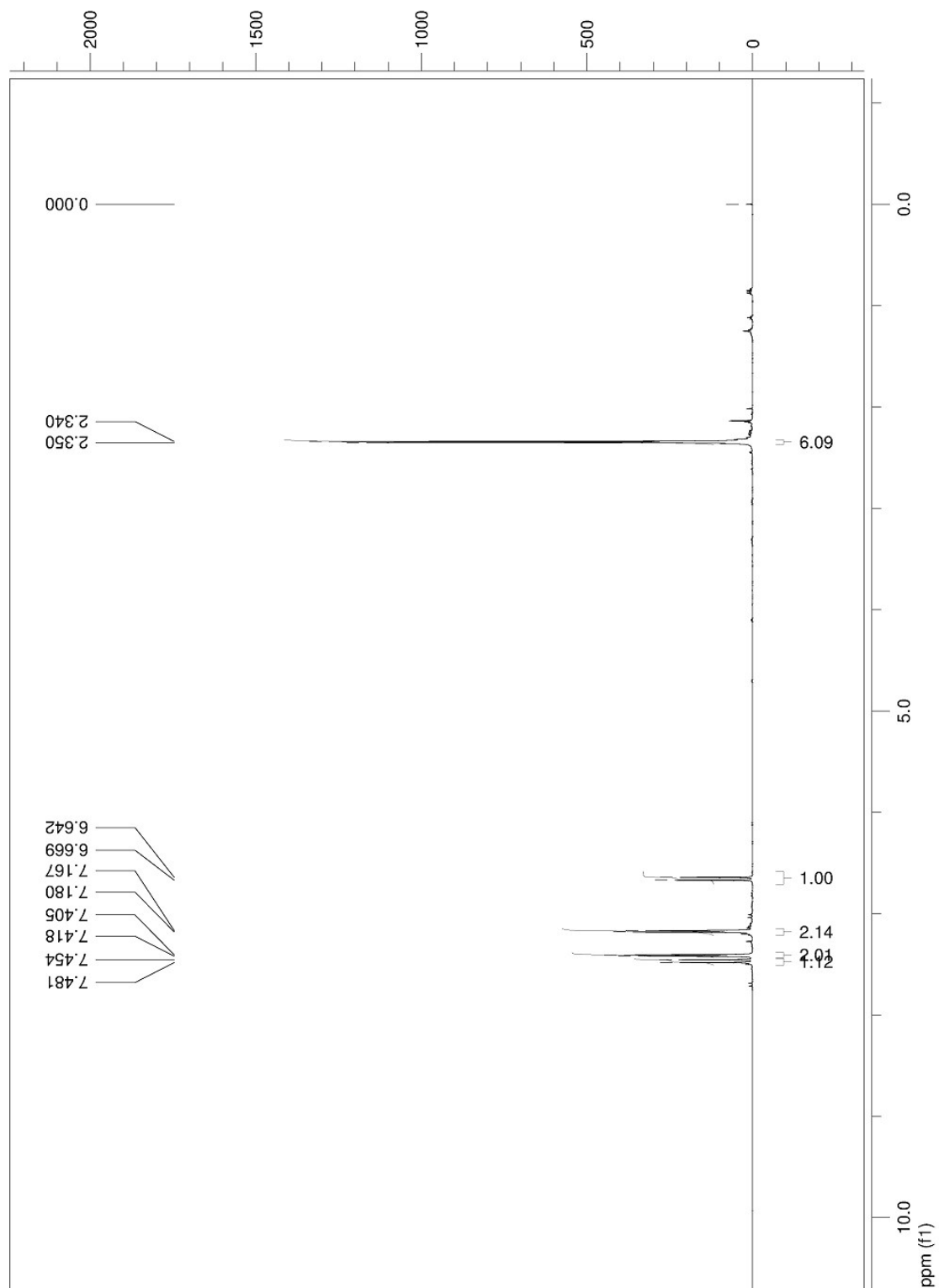


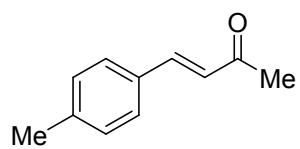
3a, CDCl₃, 150 MHz



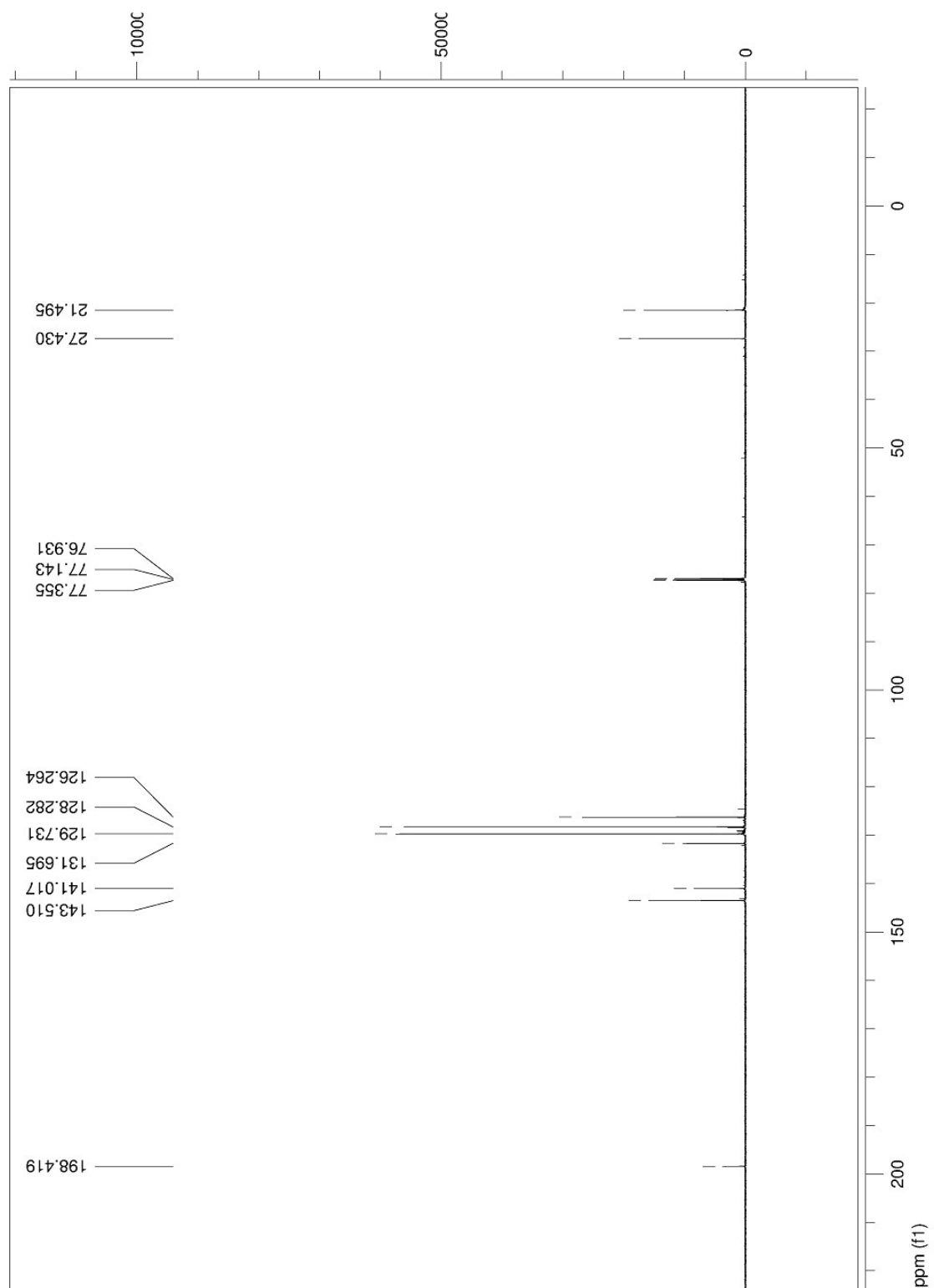


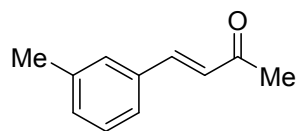
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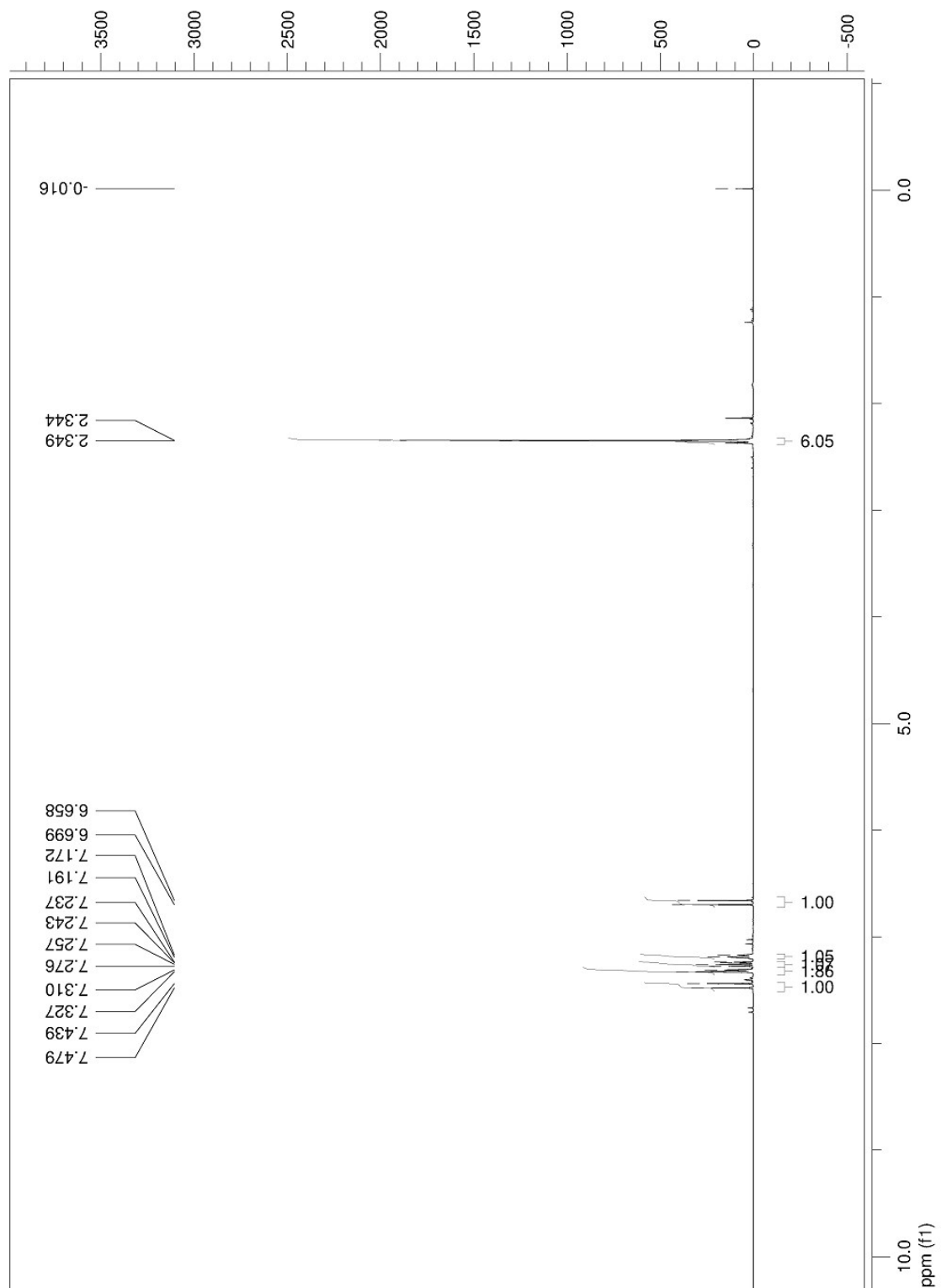


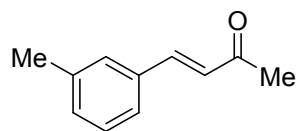
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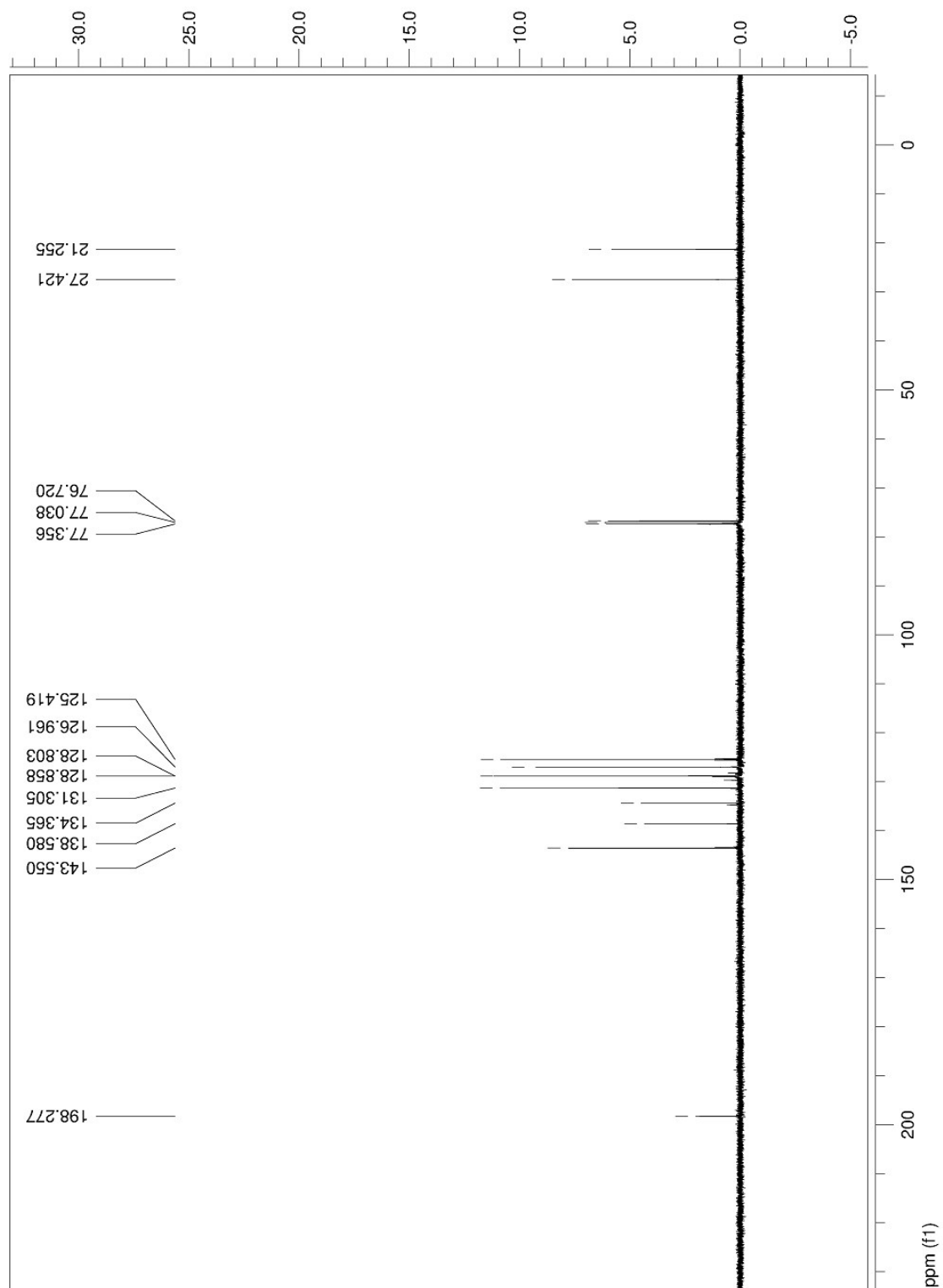


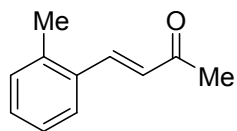
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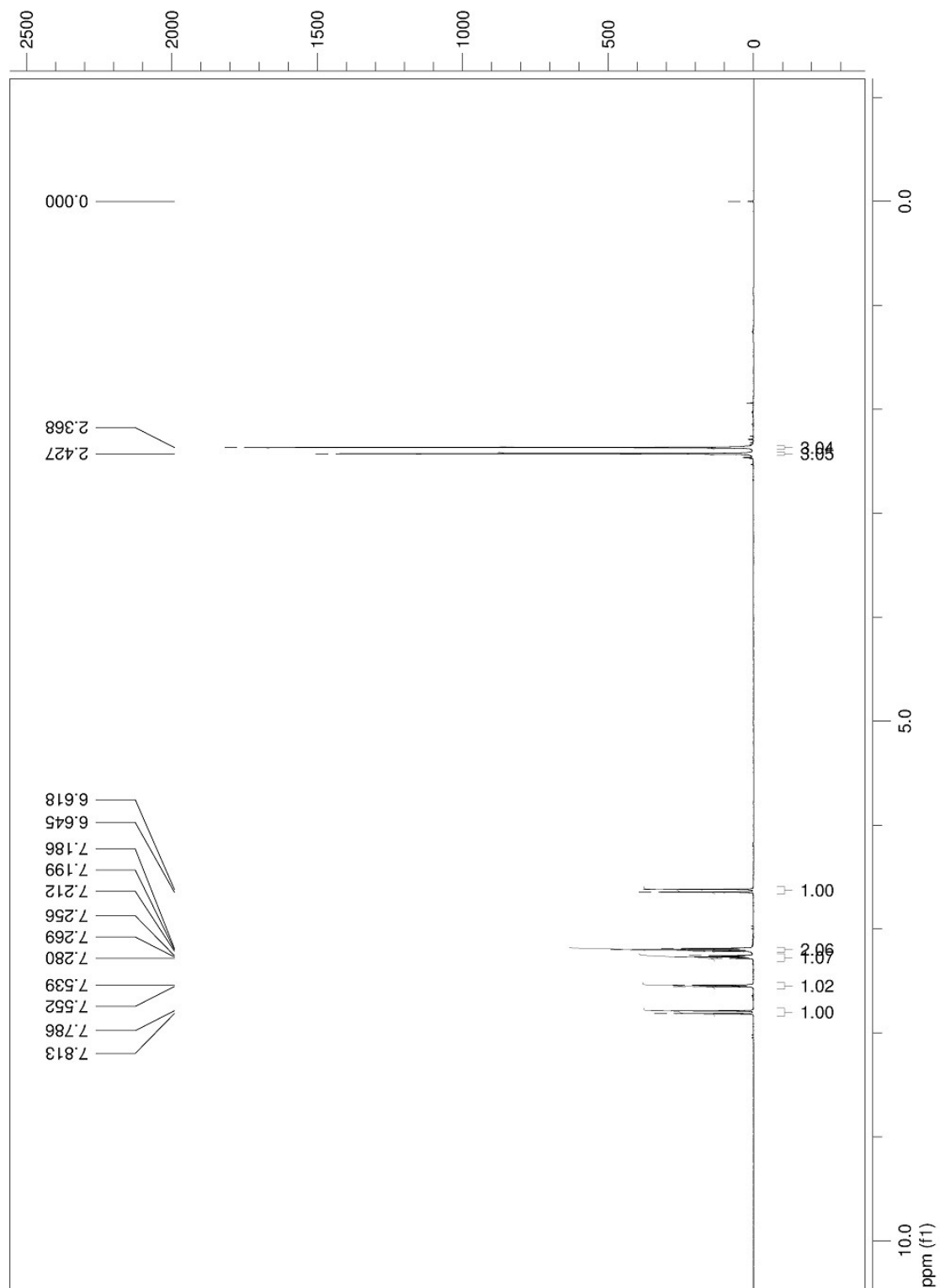


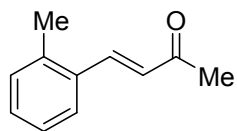
3c, CDCl₃, 100 MHz



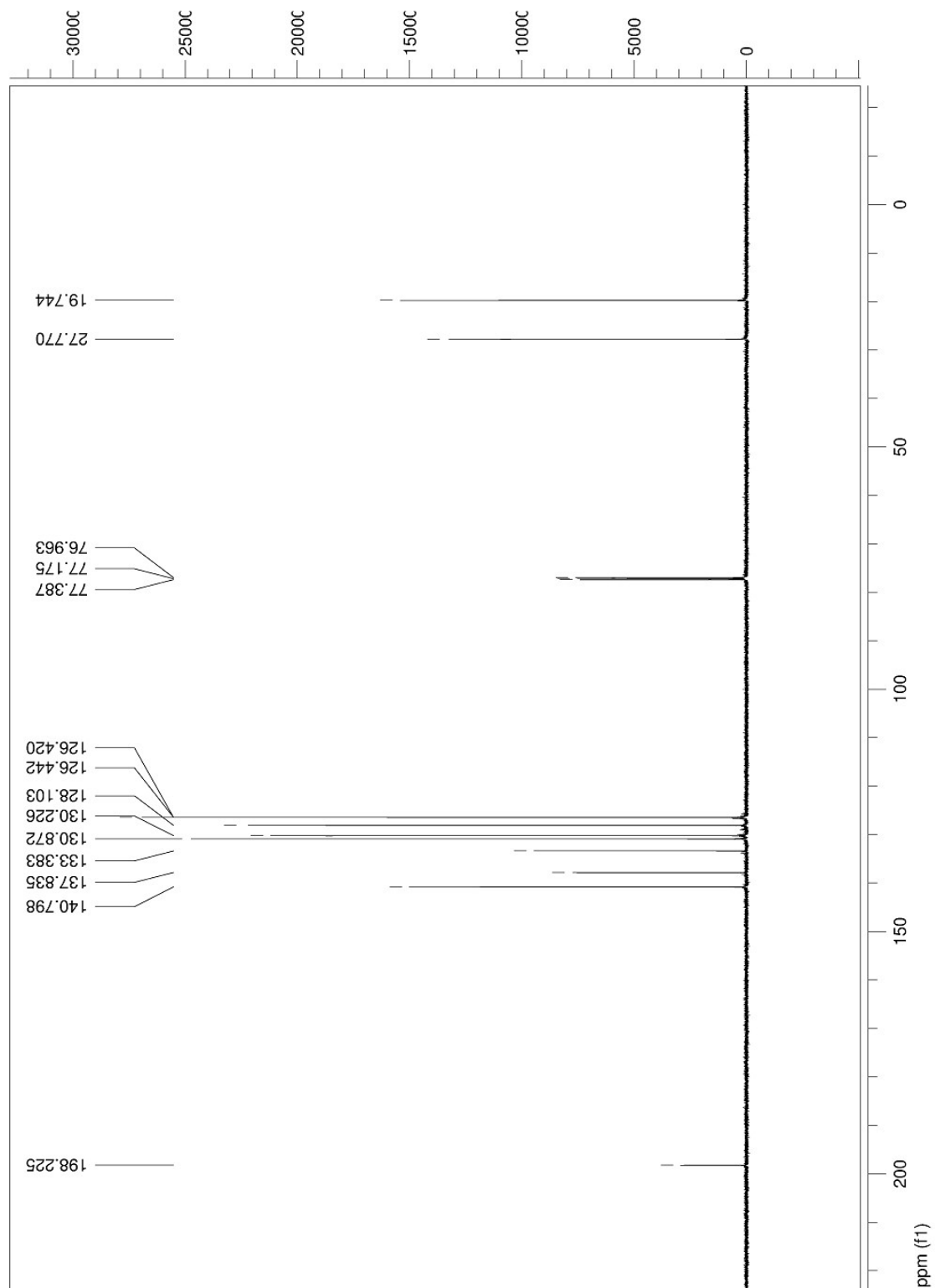


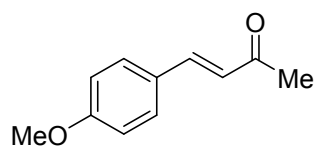
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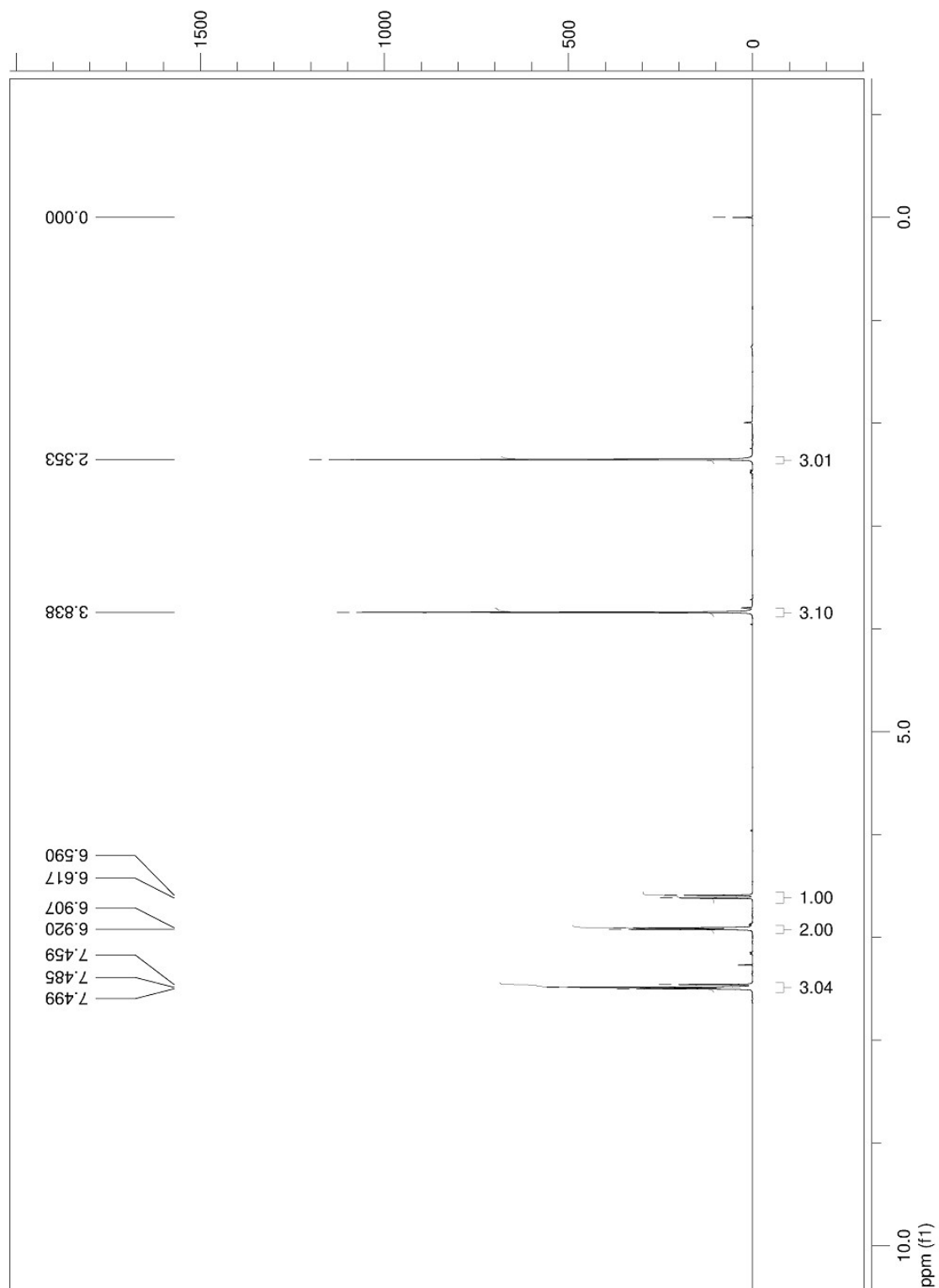


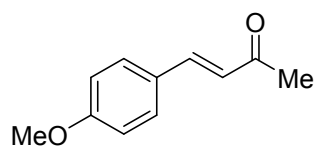
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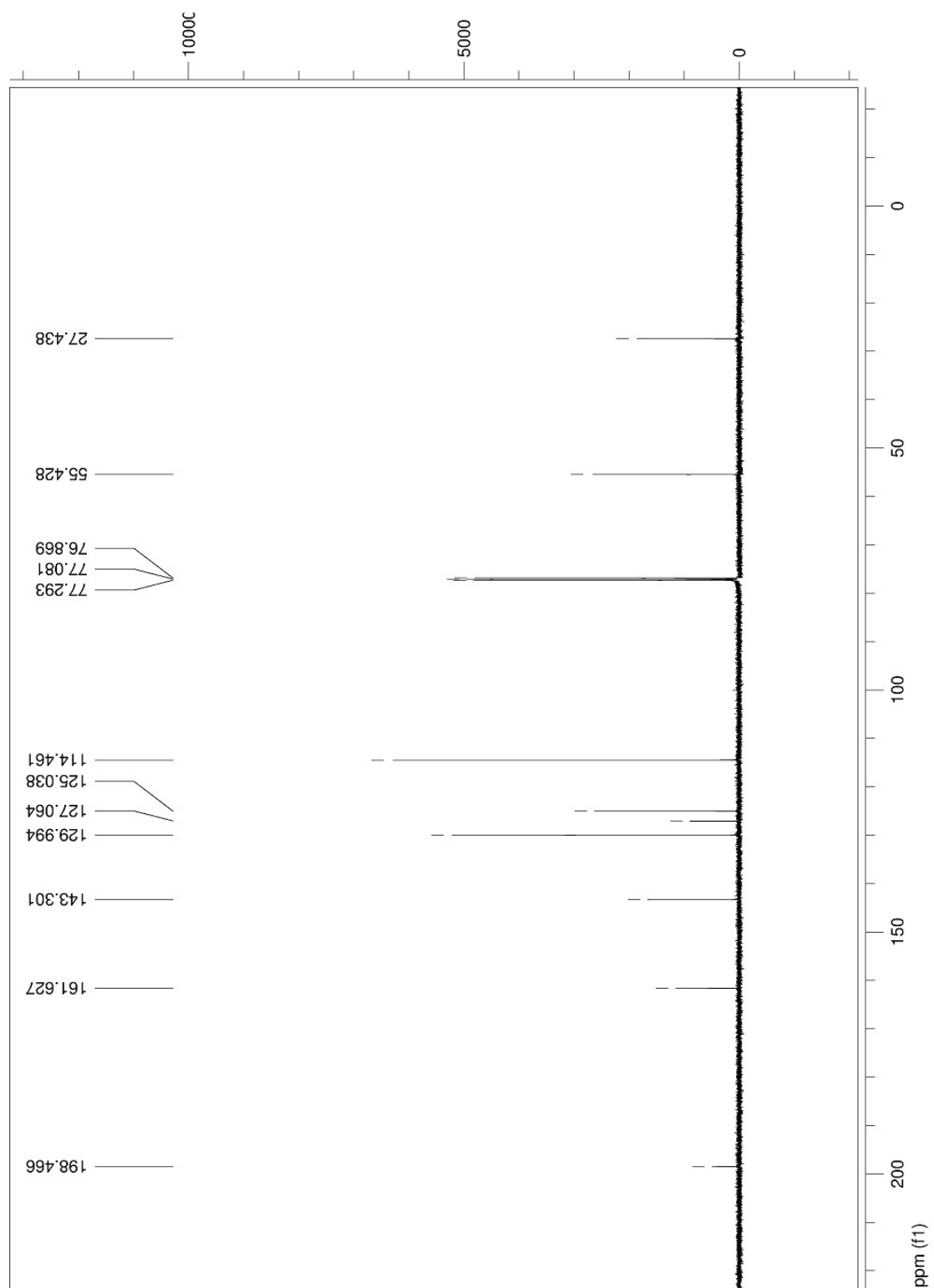


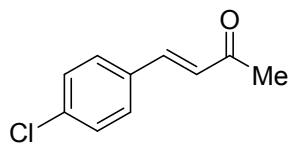
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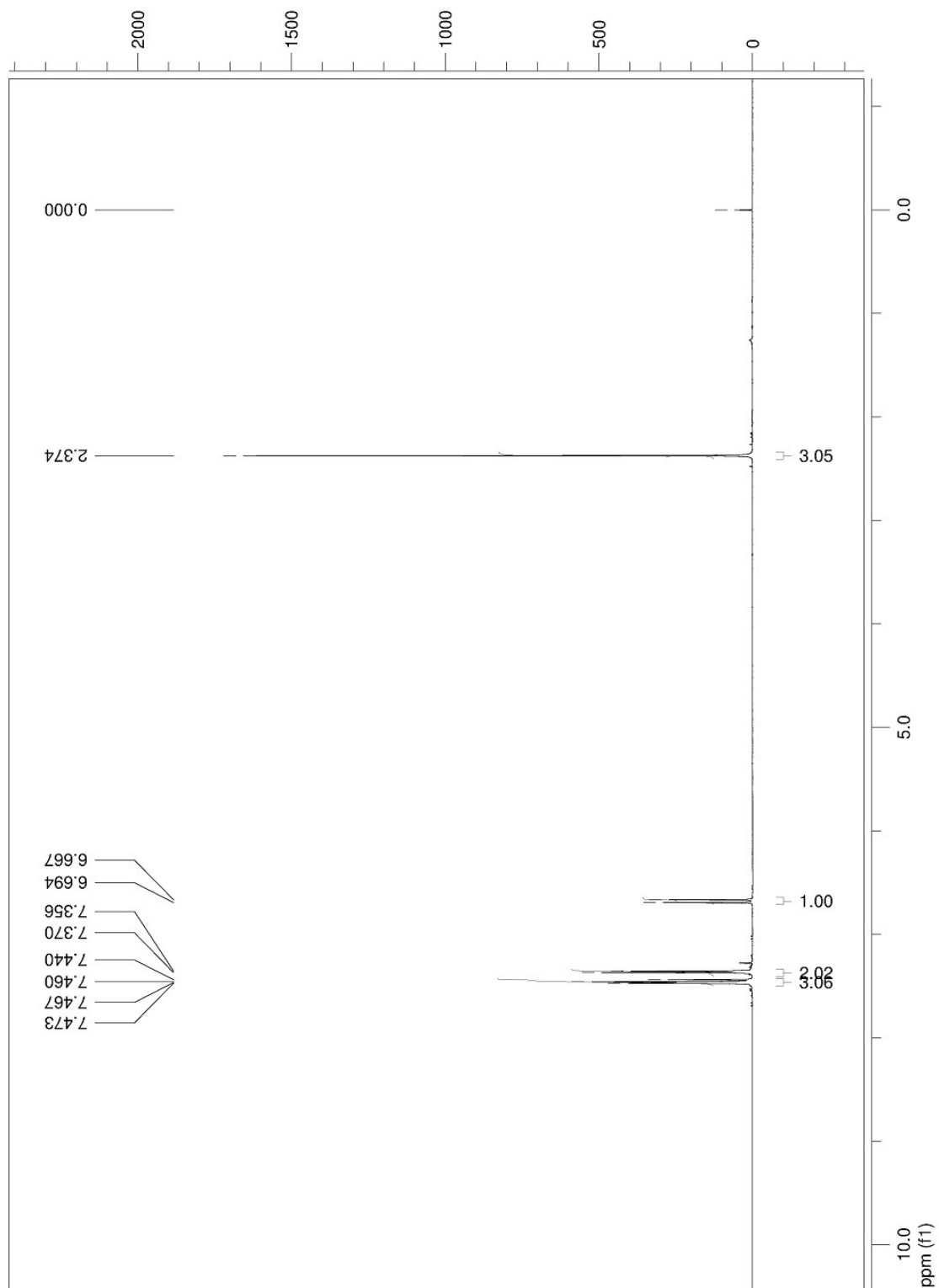


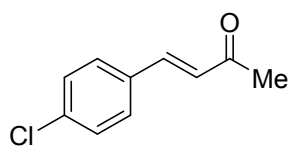
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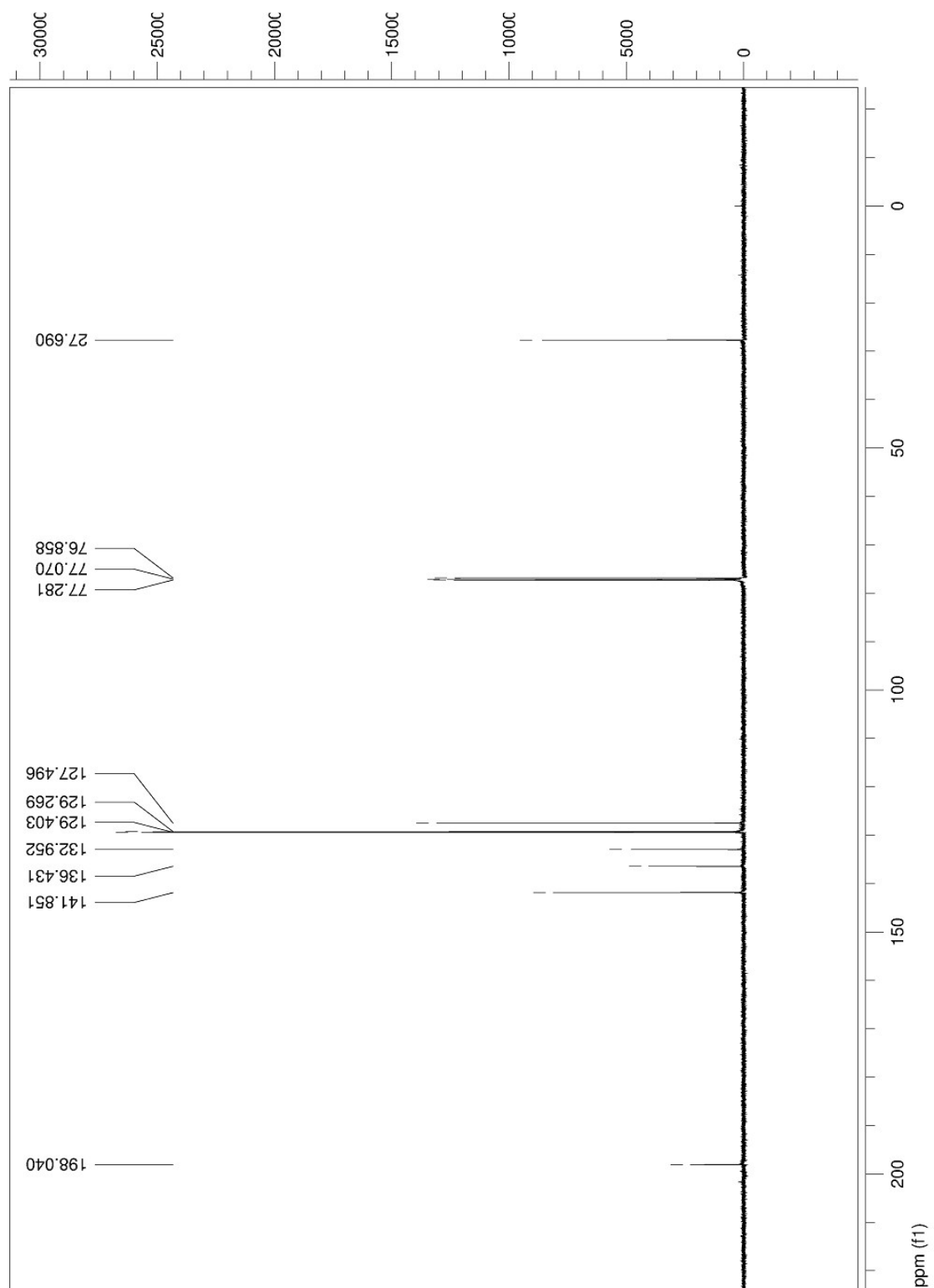


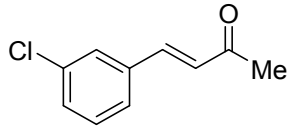
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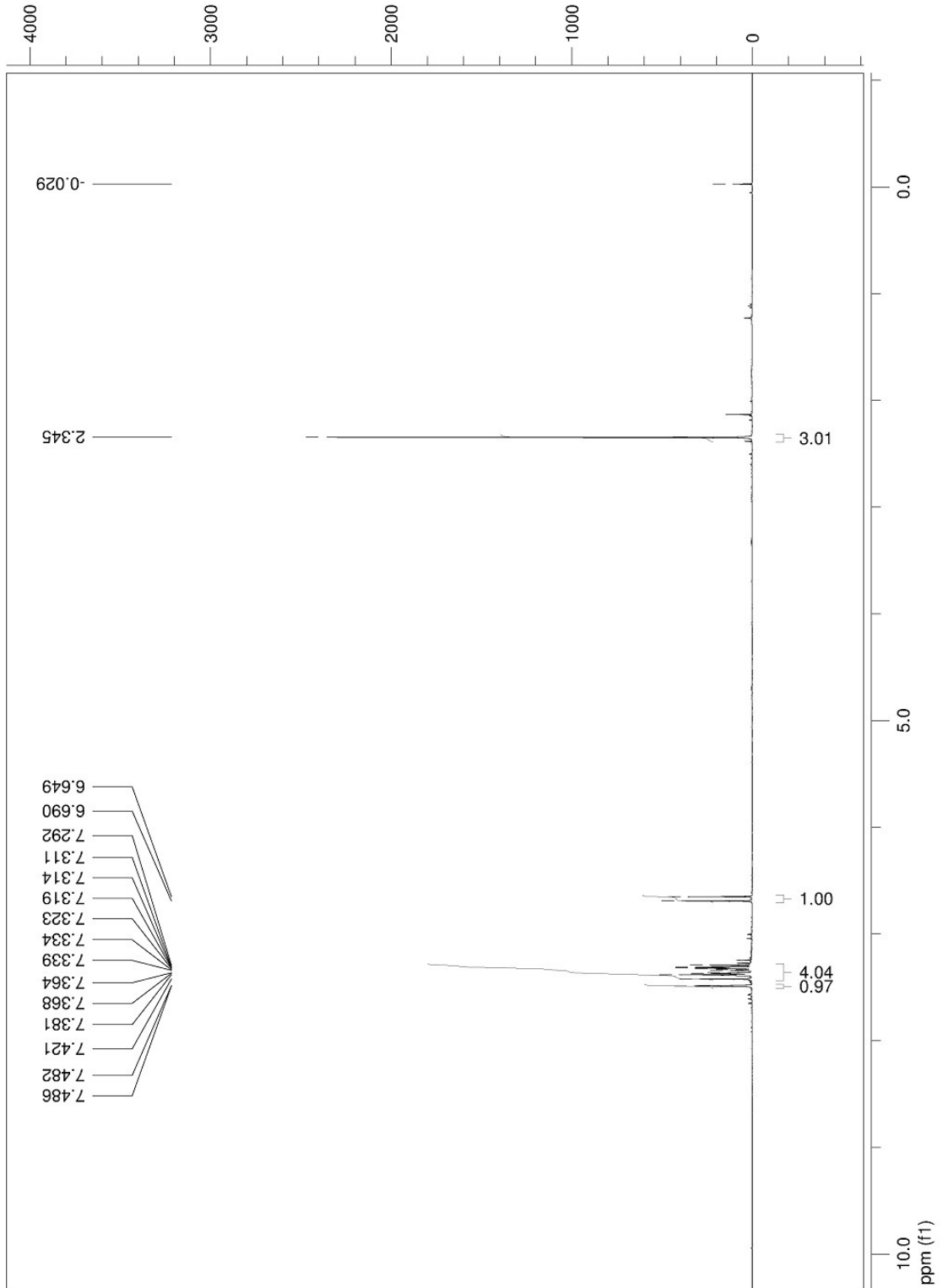


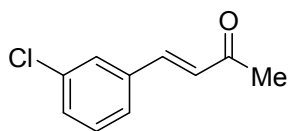
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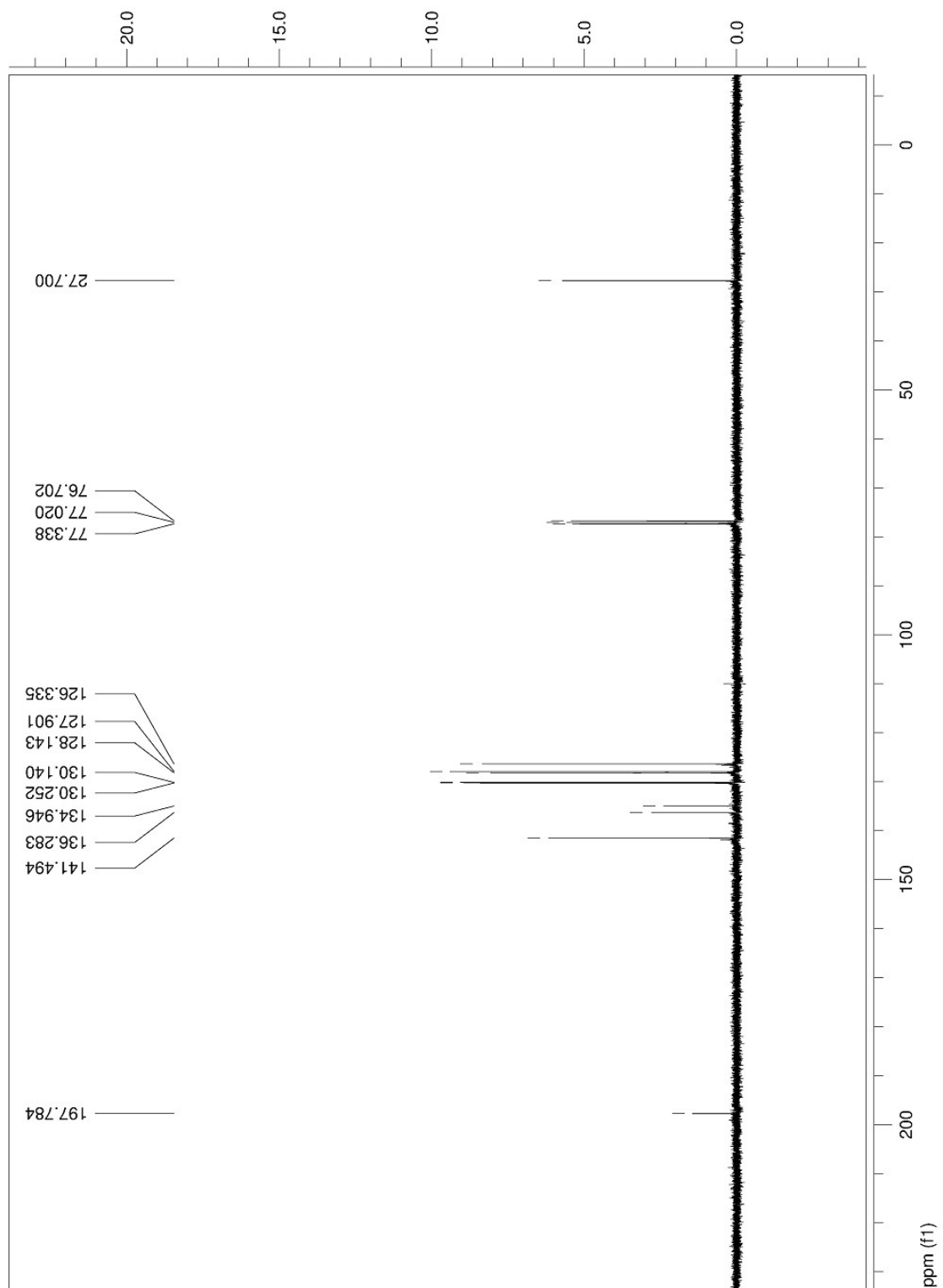


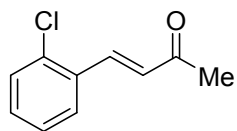
3g, CDCl₃, 400 MHz



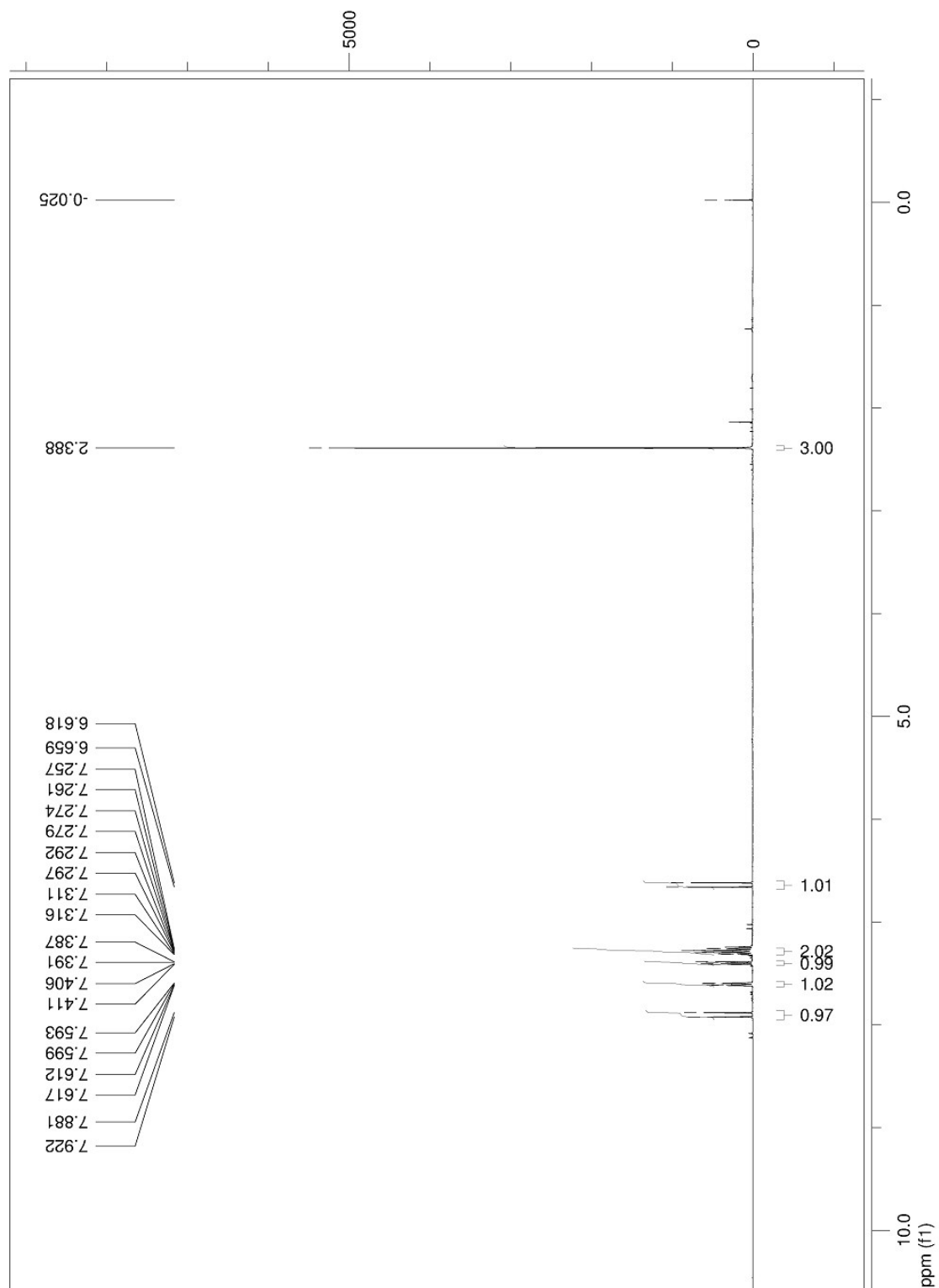


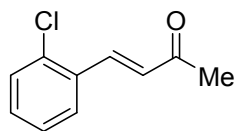
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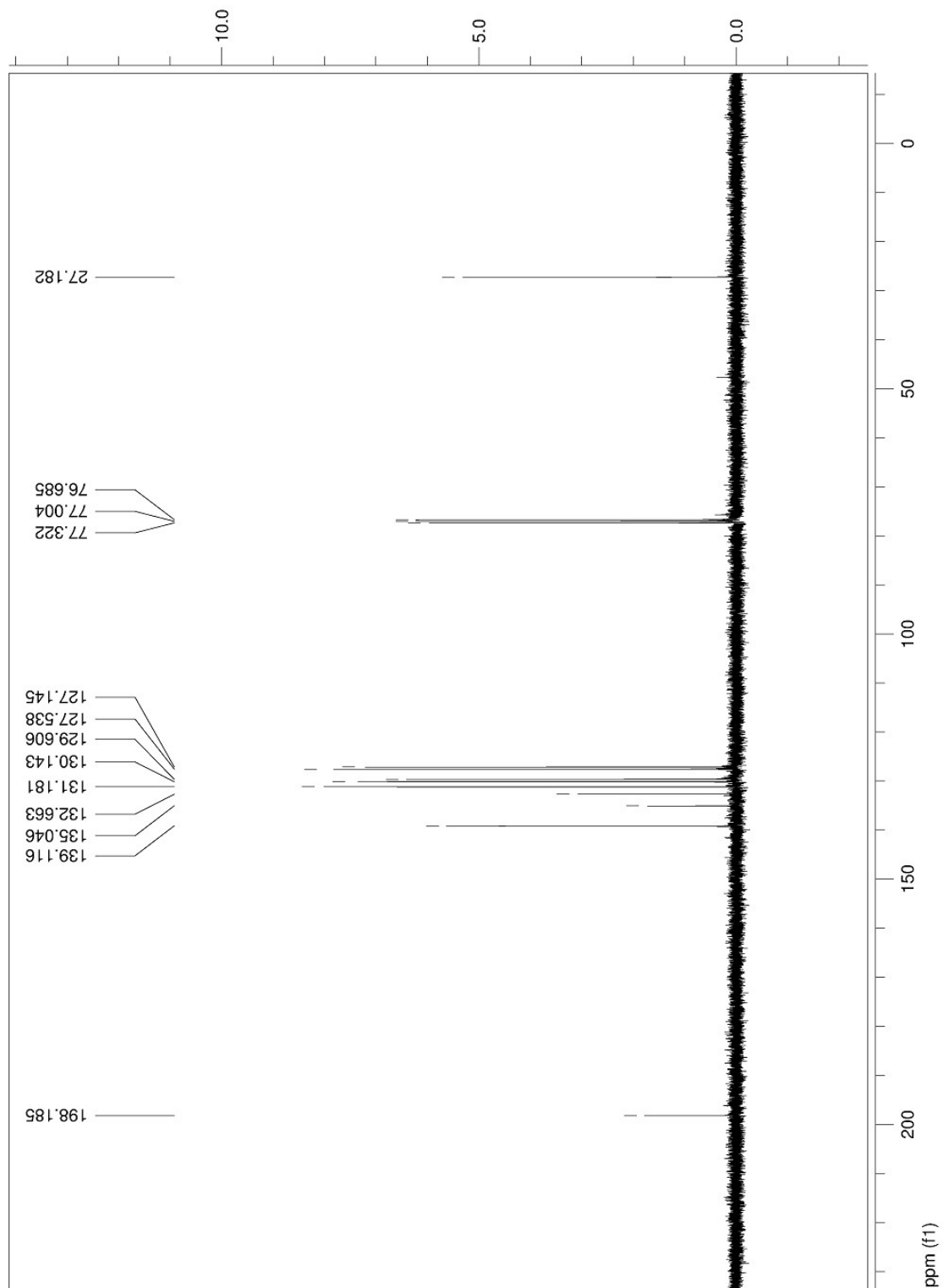


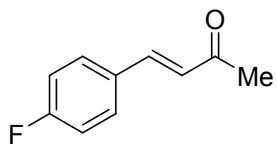
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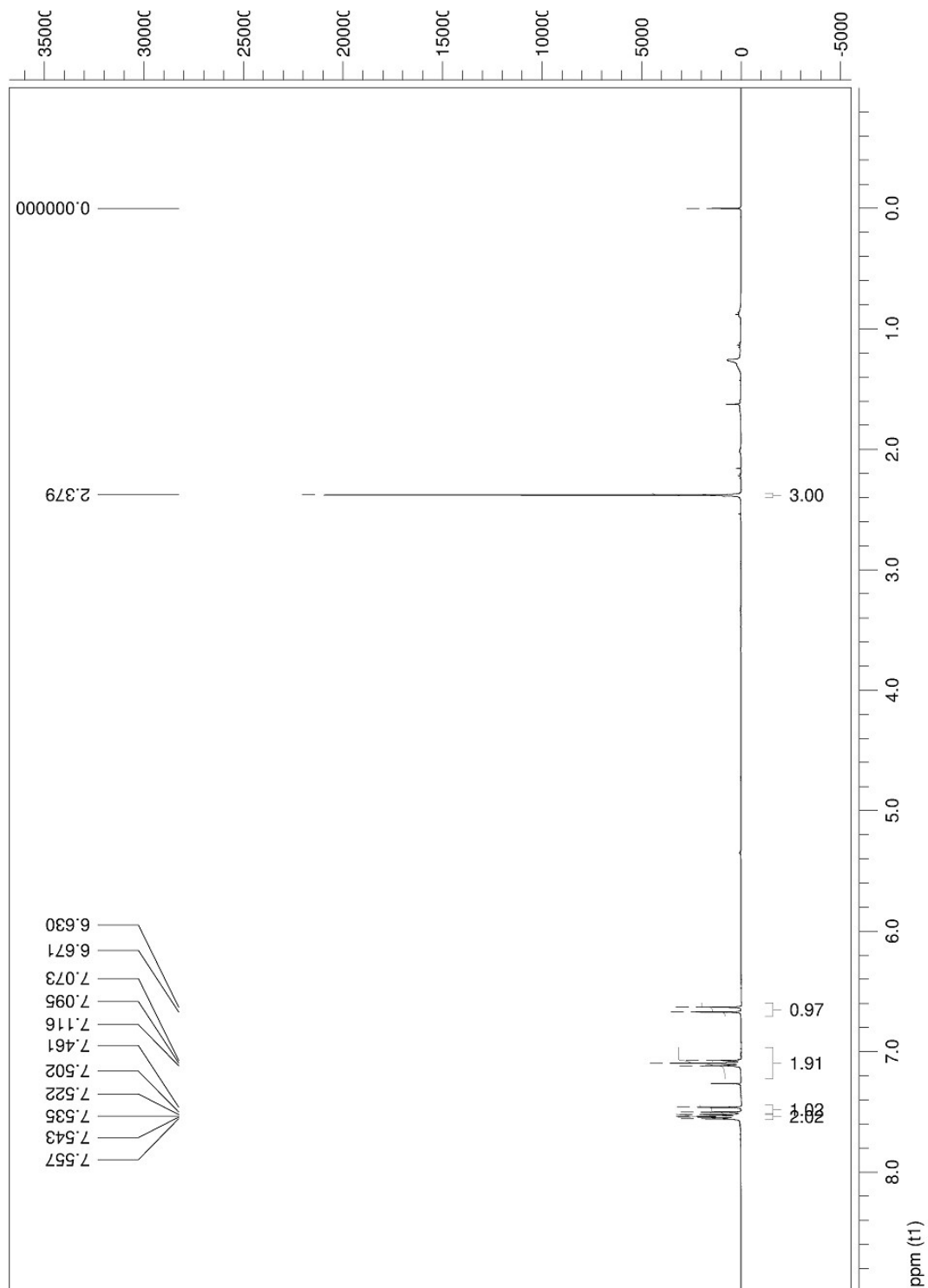


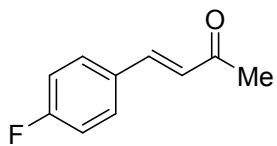
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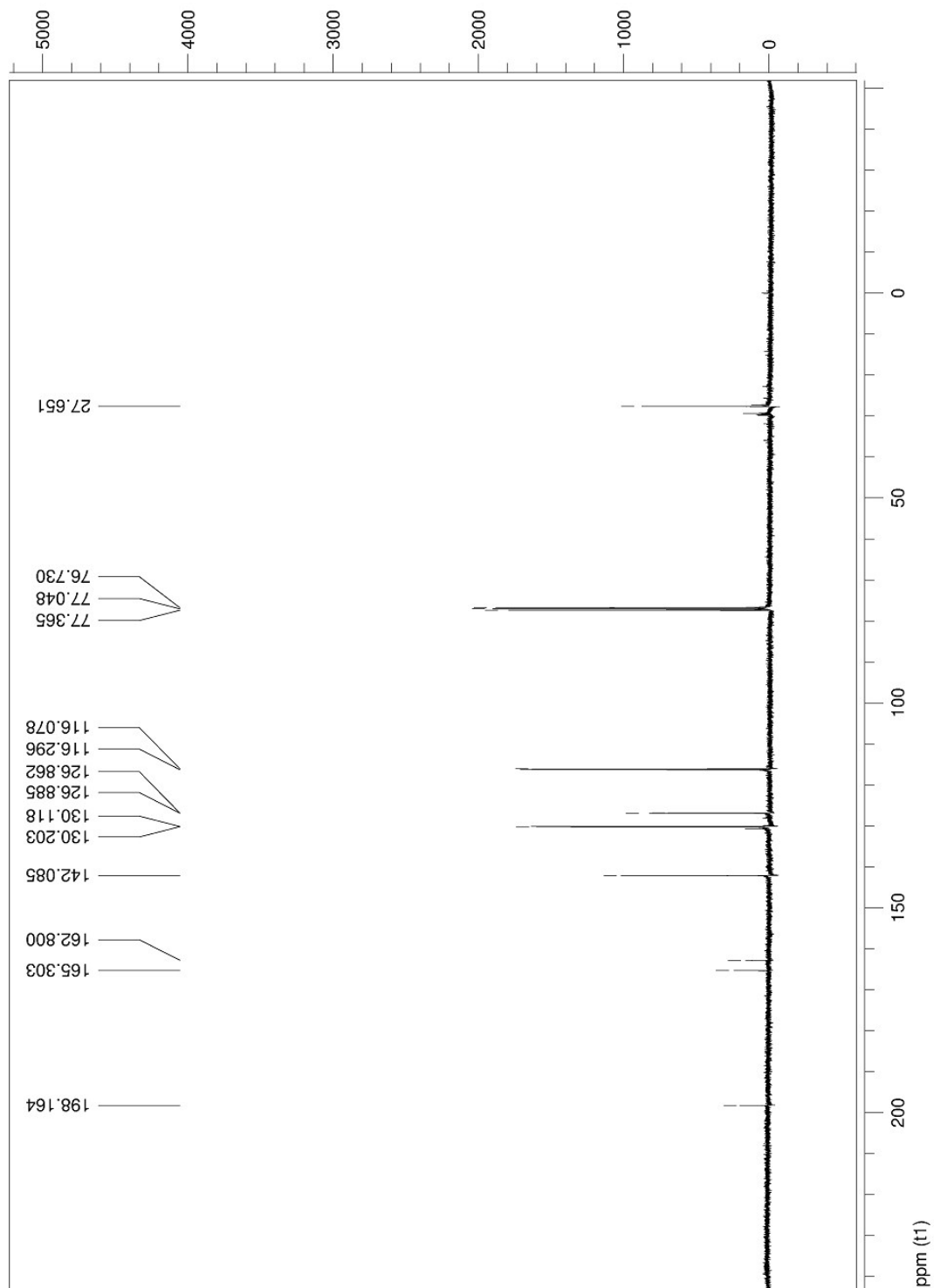


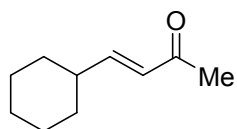
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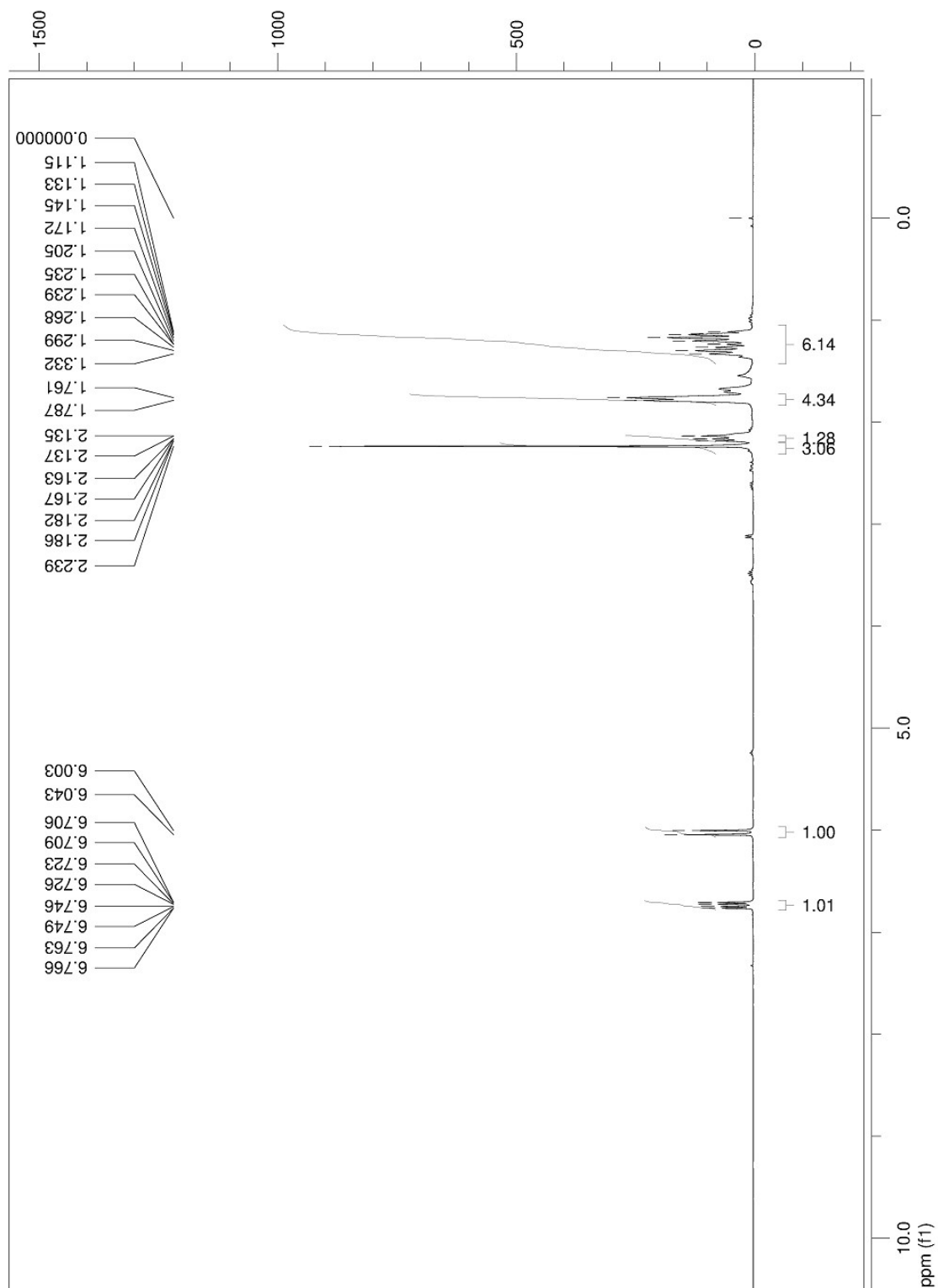


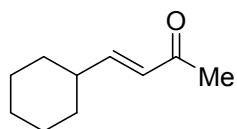
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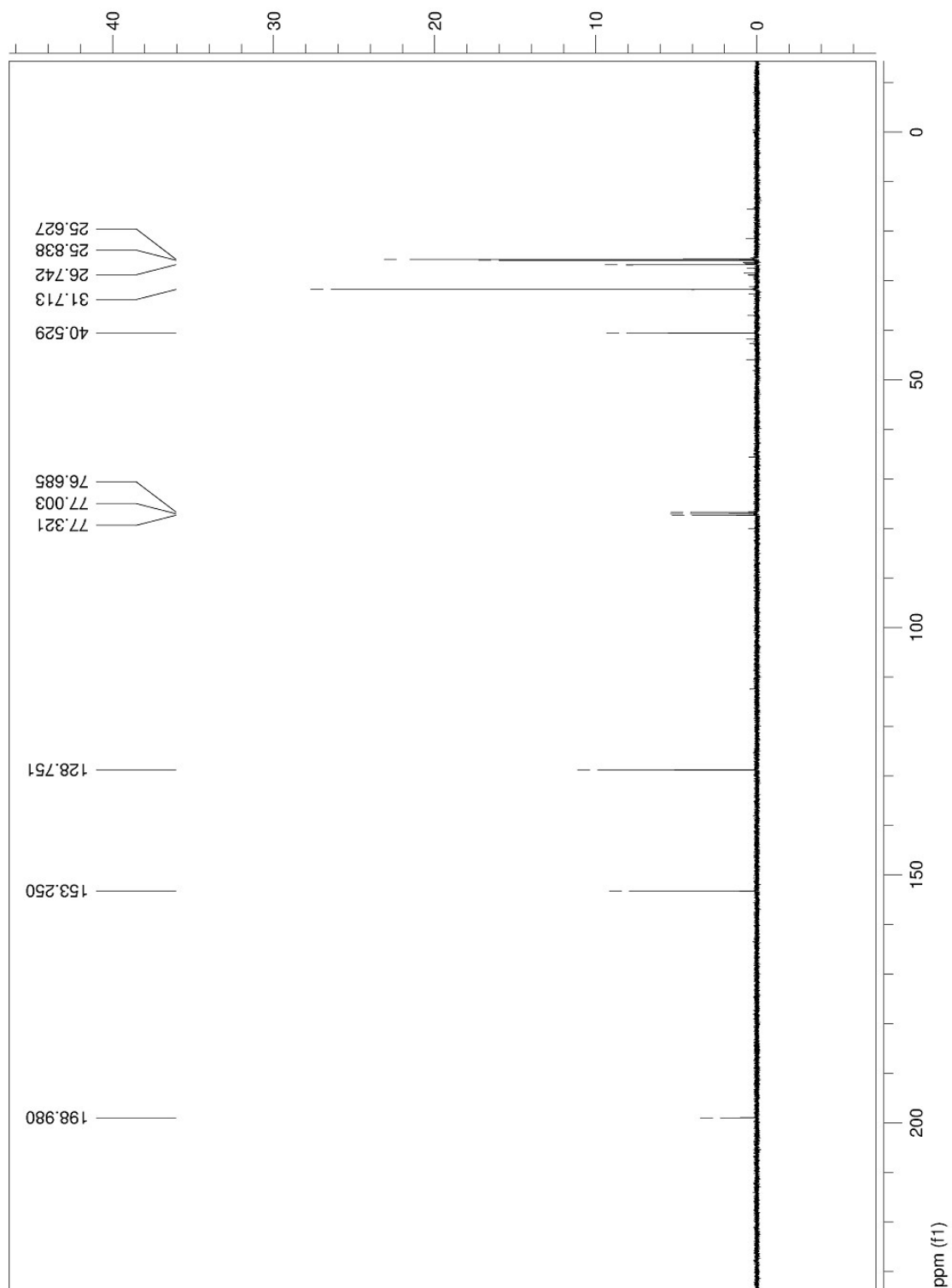


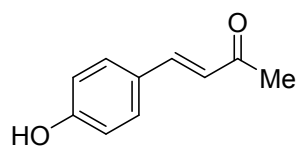
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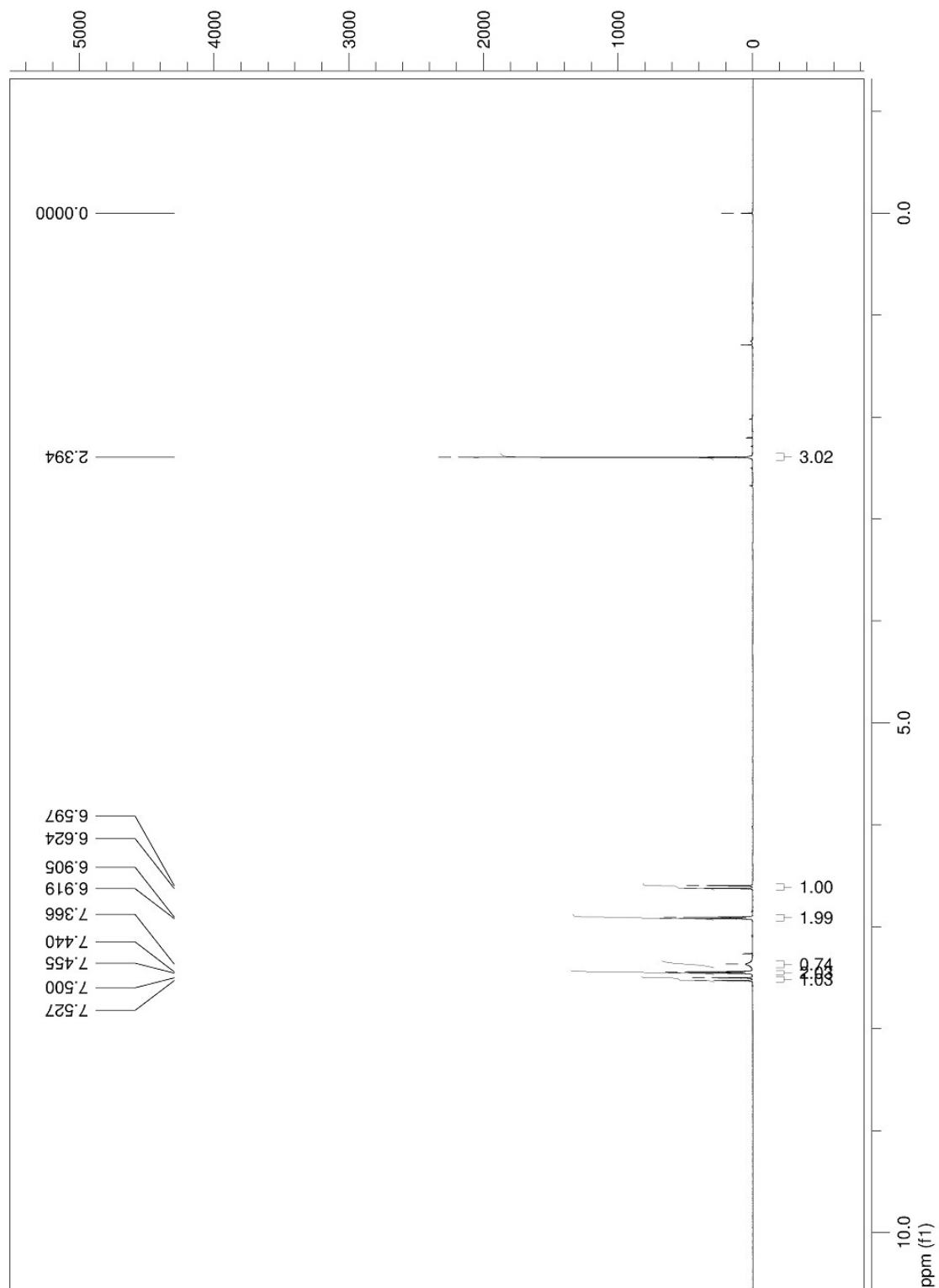


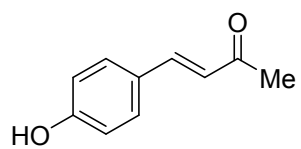
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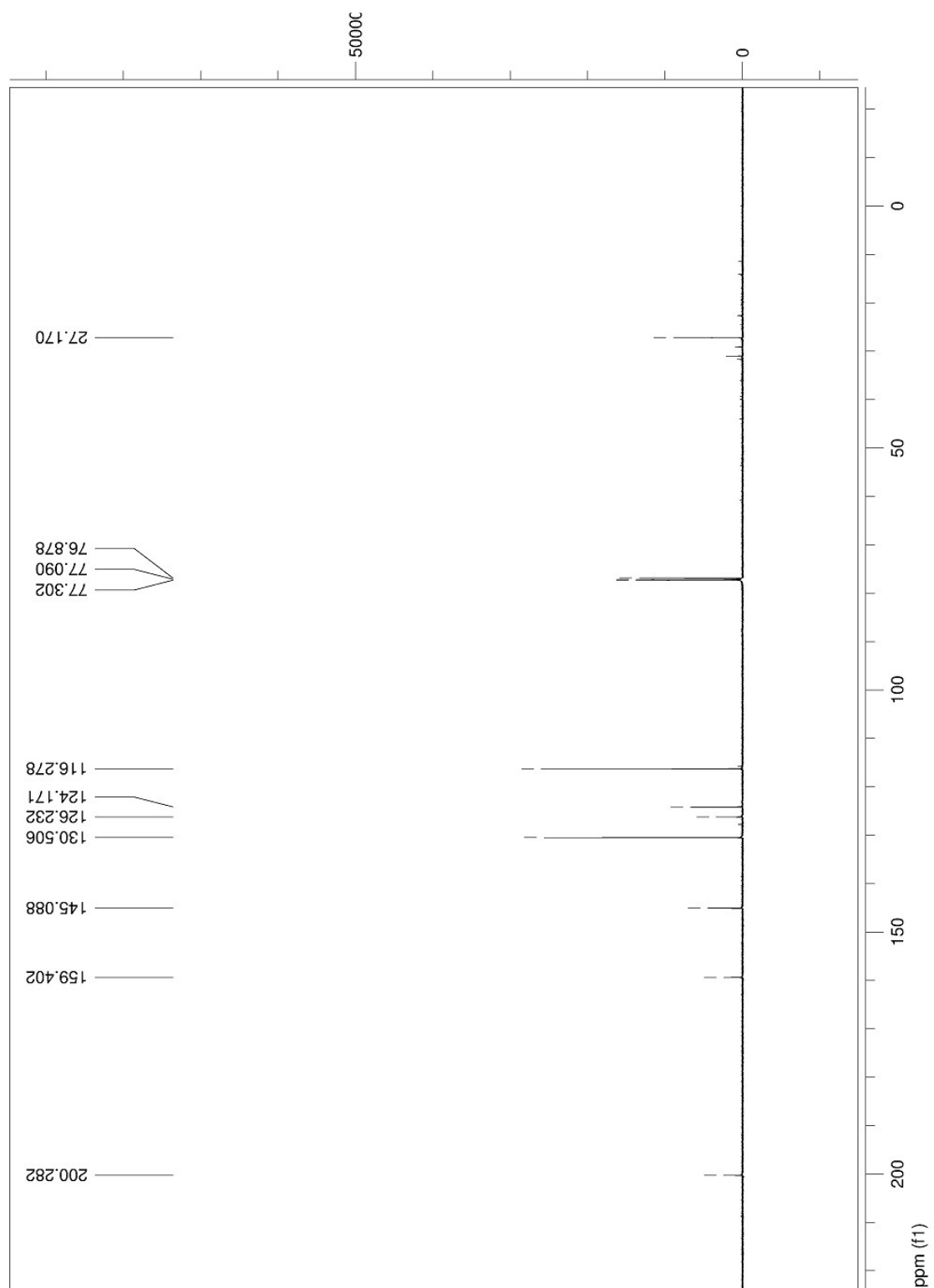


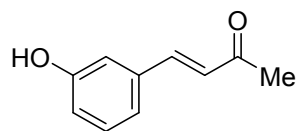
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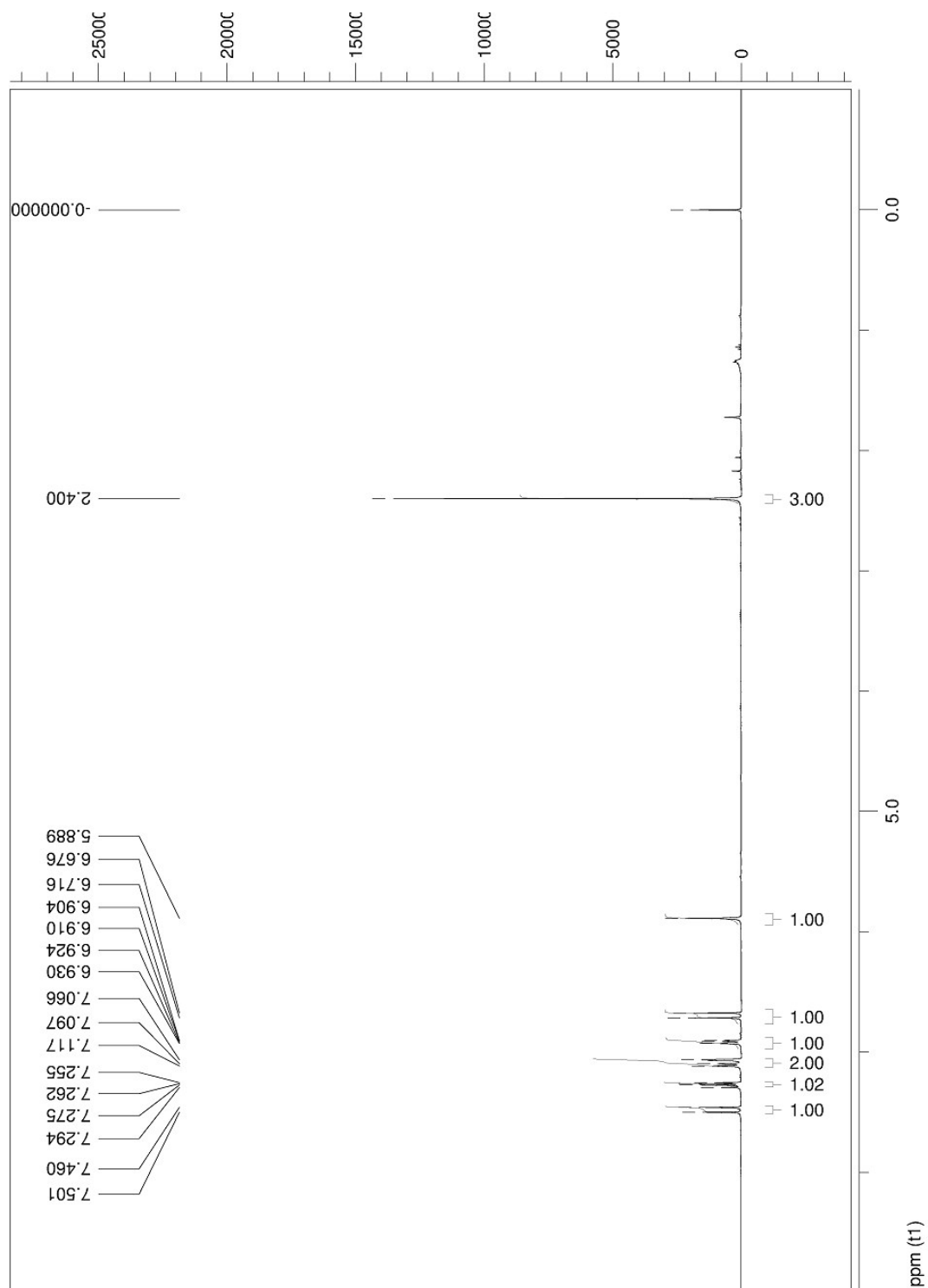


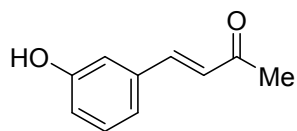
3k, CDCl₃, 150 MHz



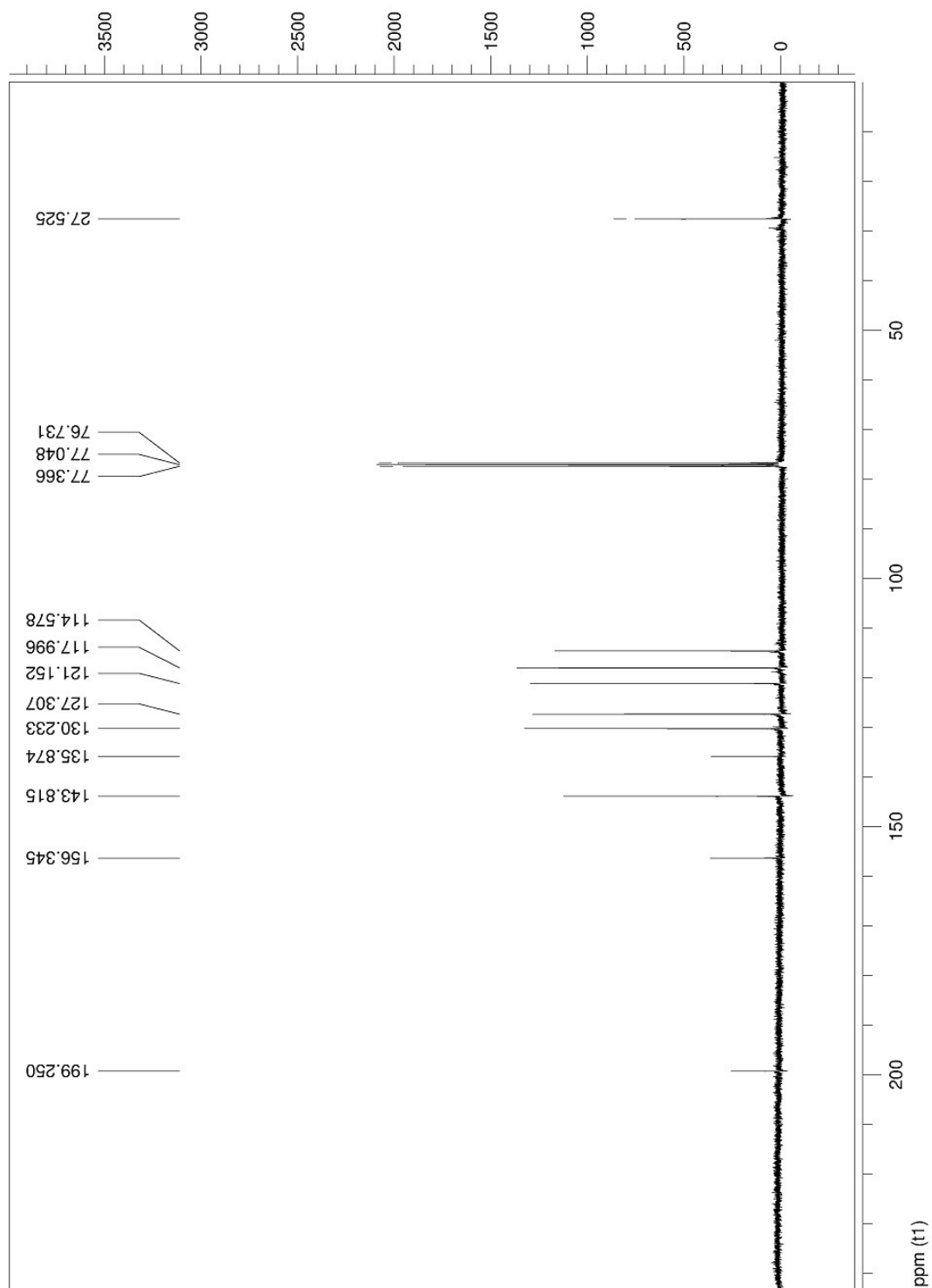


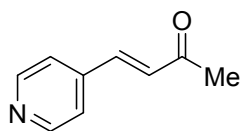
31, CDCl₃, 400 MHz



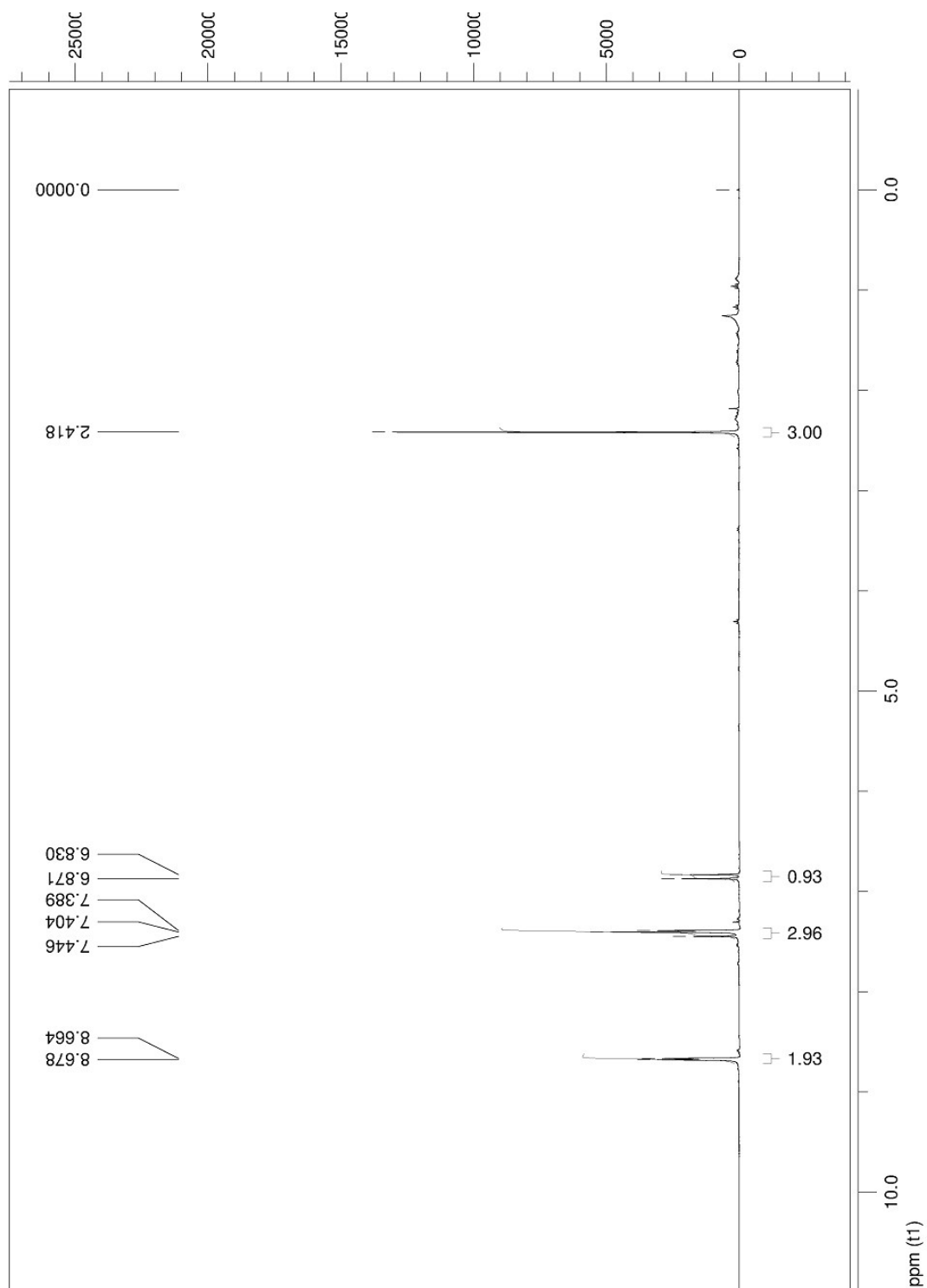


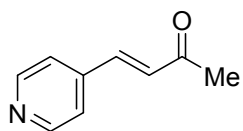
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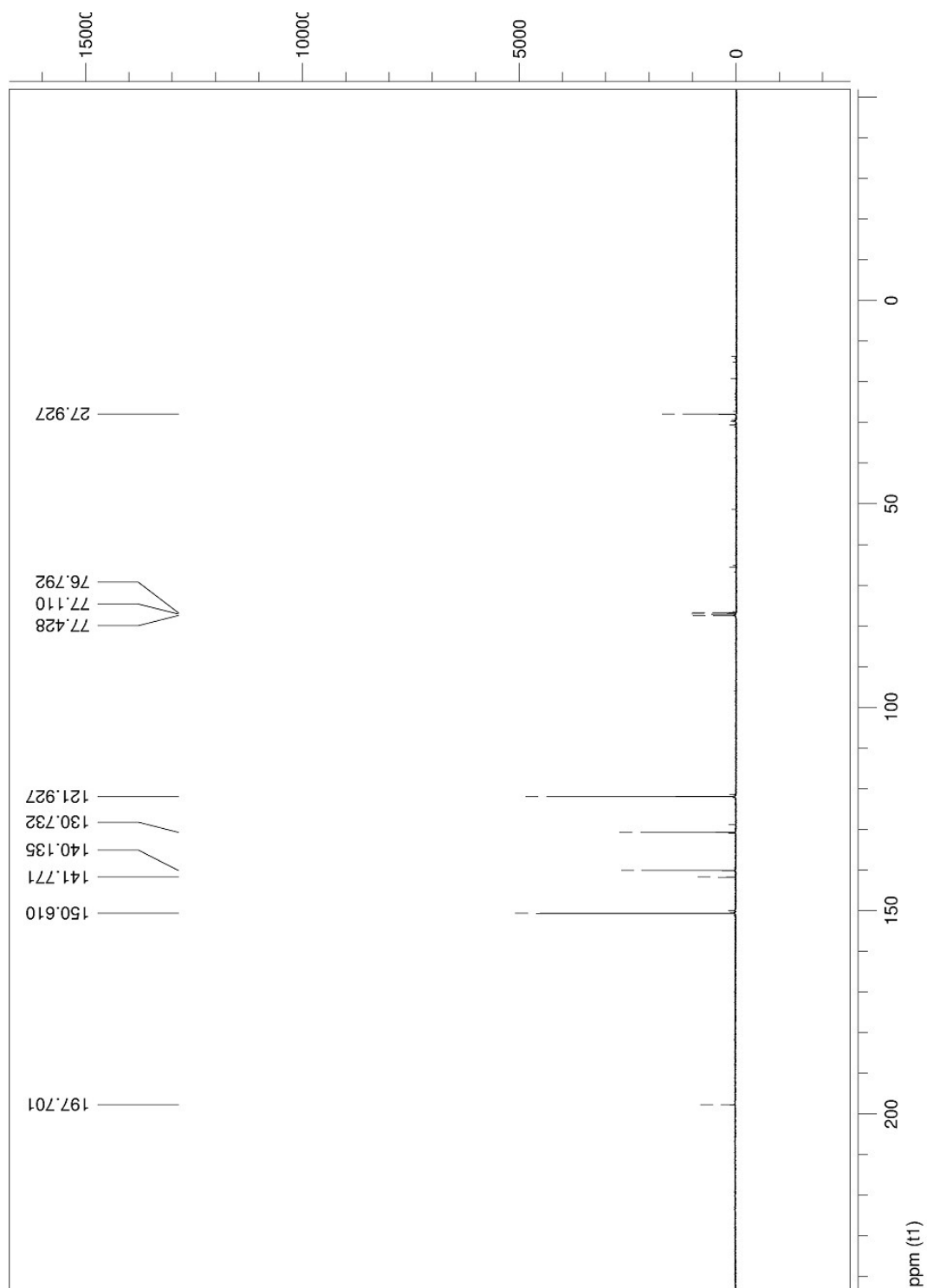


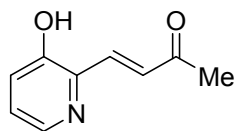
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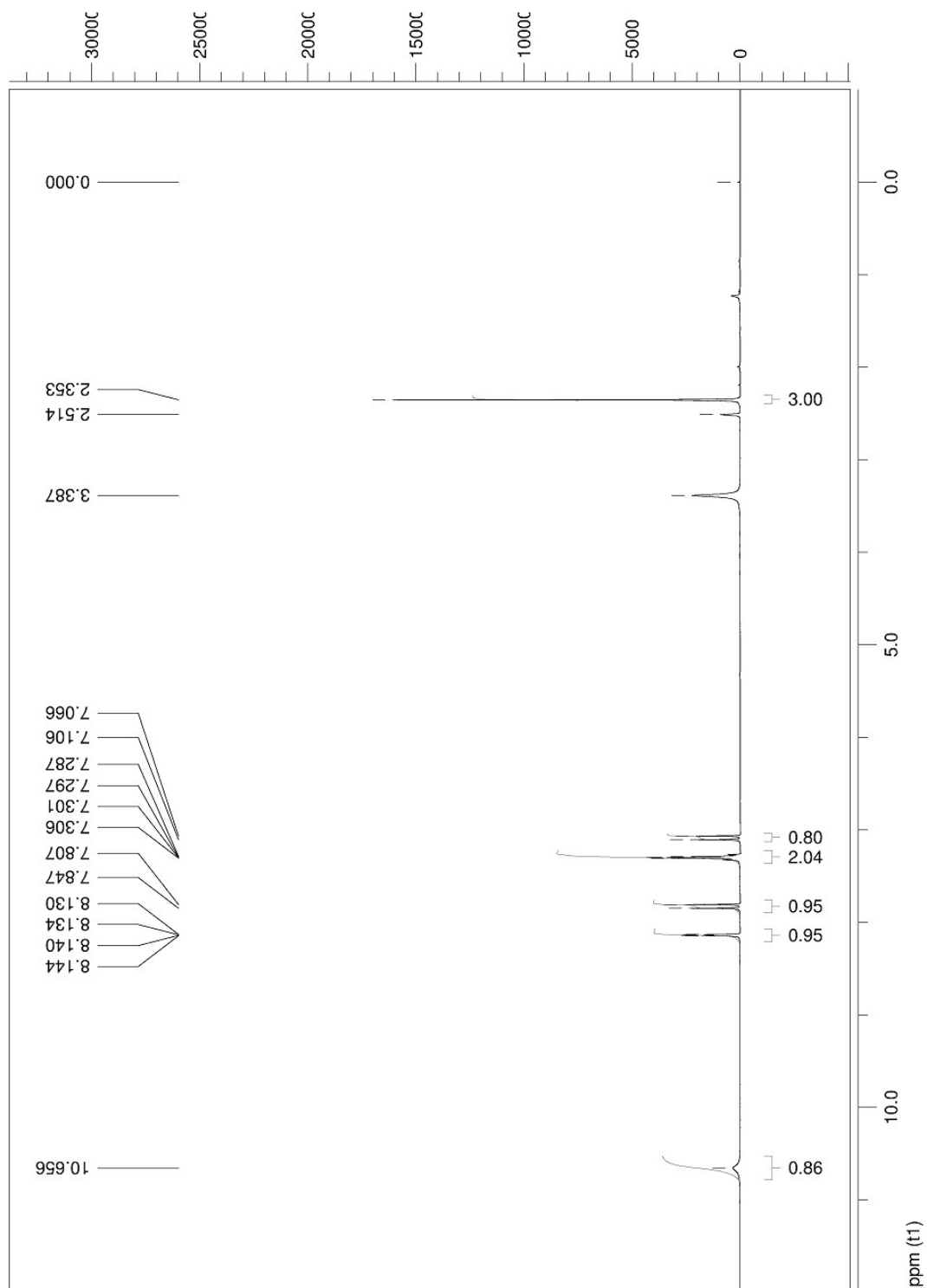


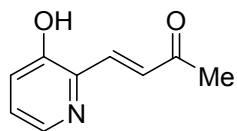
3m, CDCl₃, 100 MHz



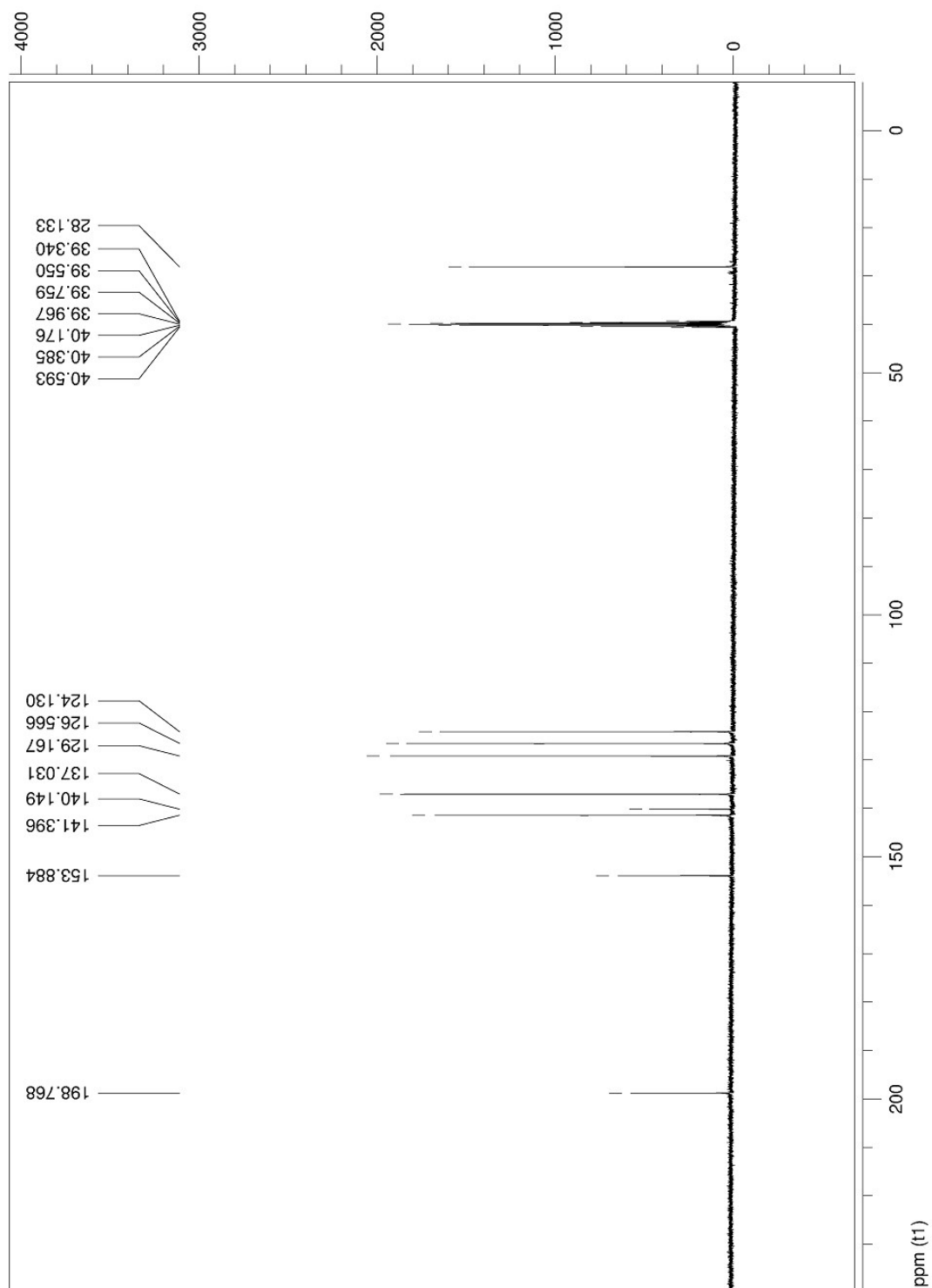


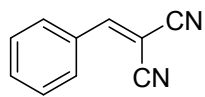
3n, DMSO-*d*₆, 400 MHz



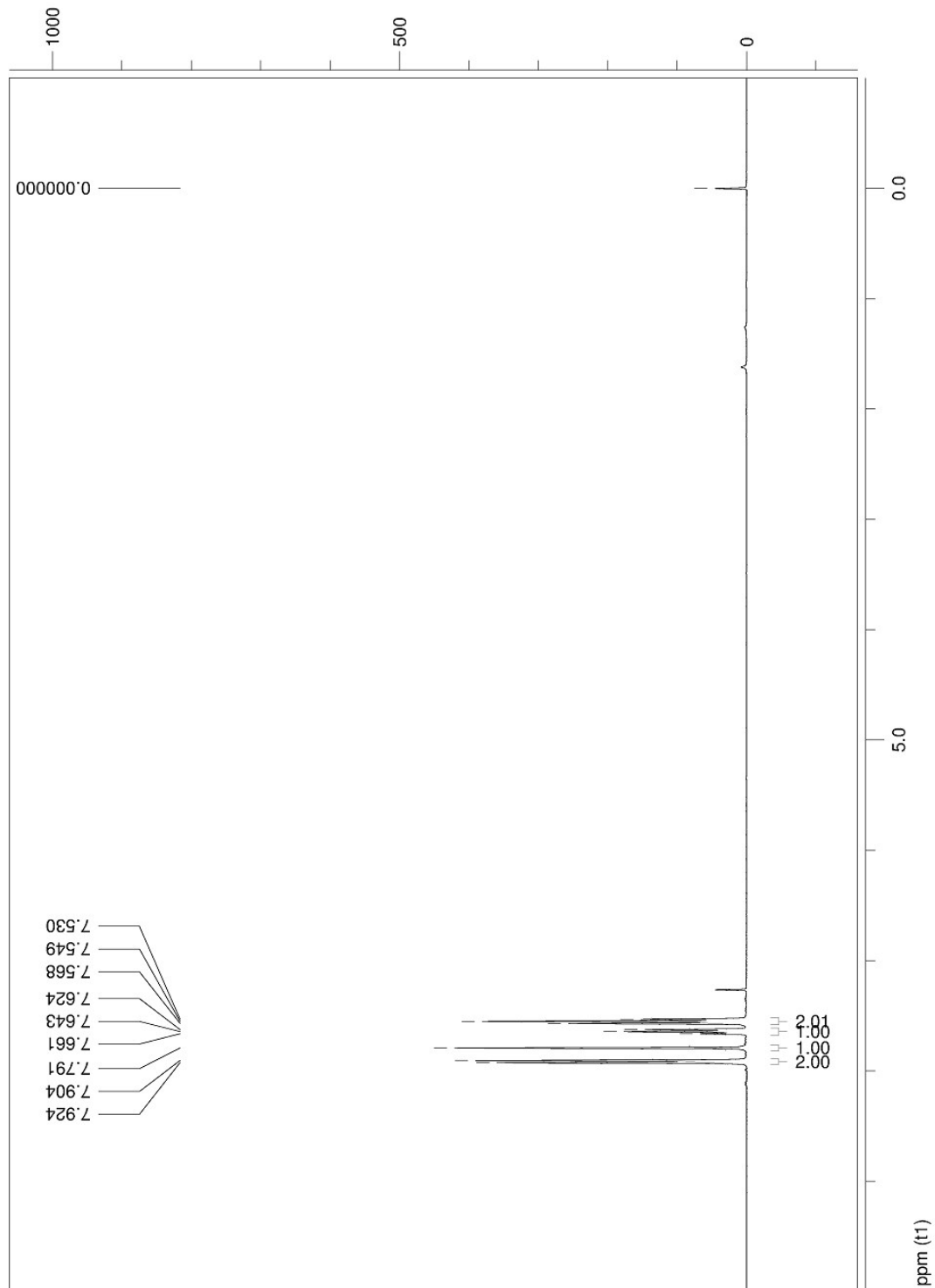


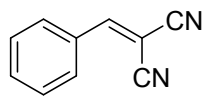
3n, DMSO-*d*₆, 100 MHz



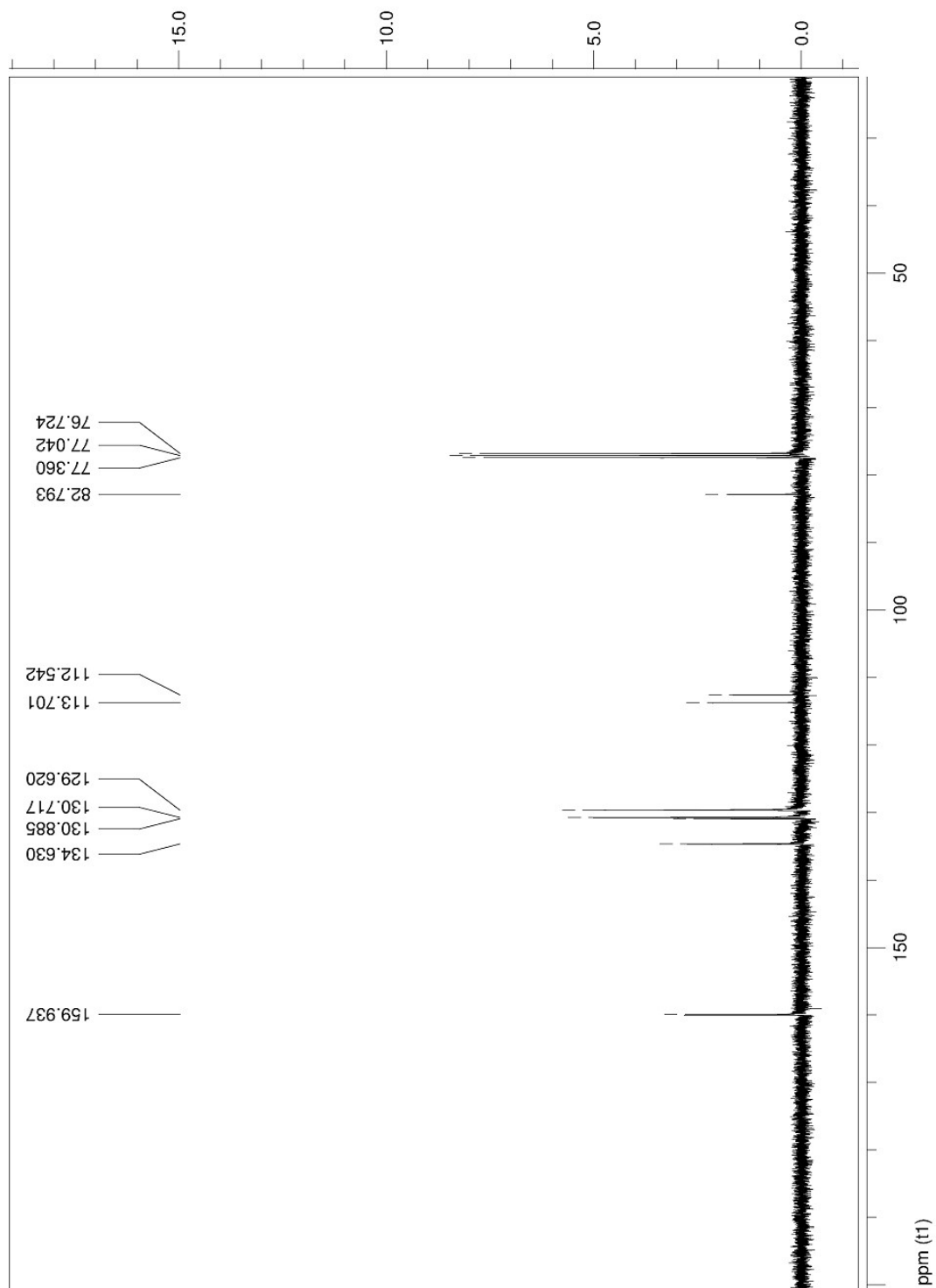


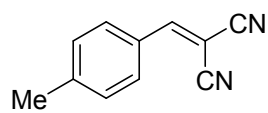
10a, CDCl₃, 400 MHz



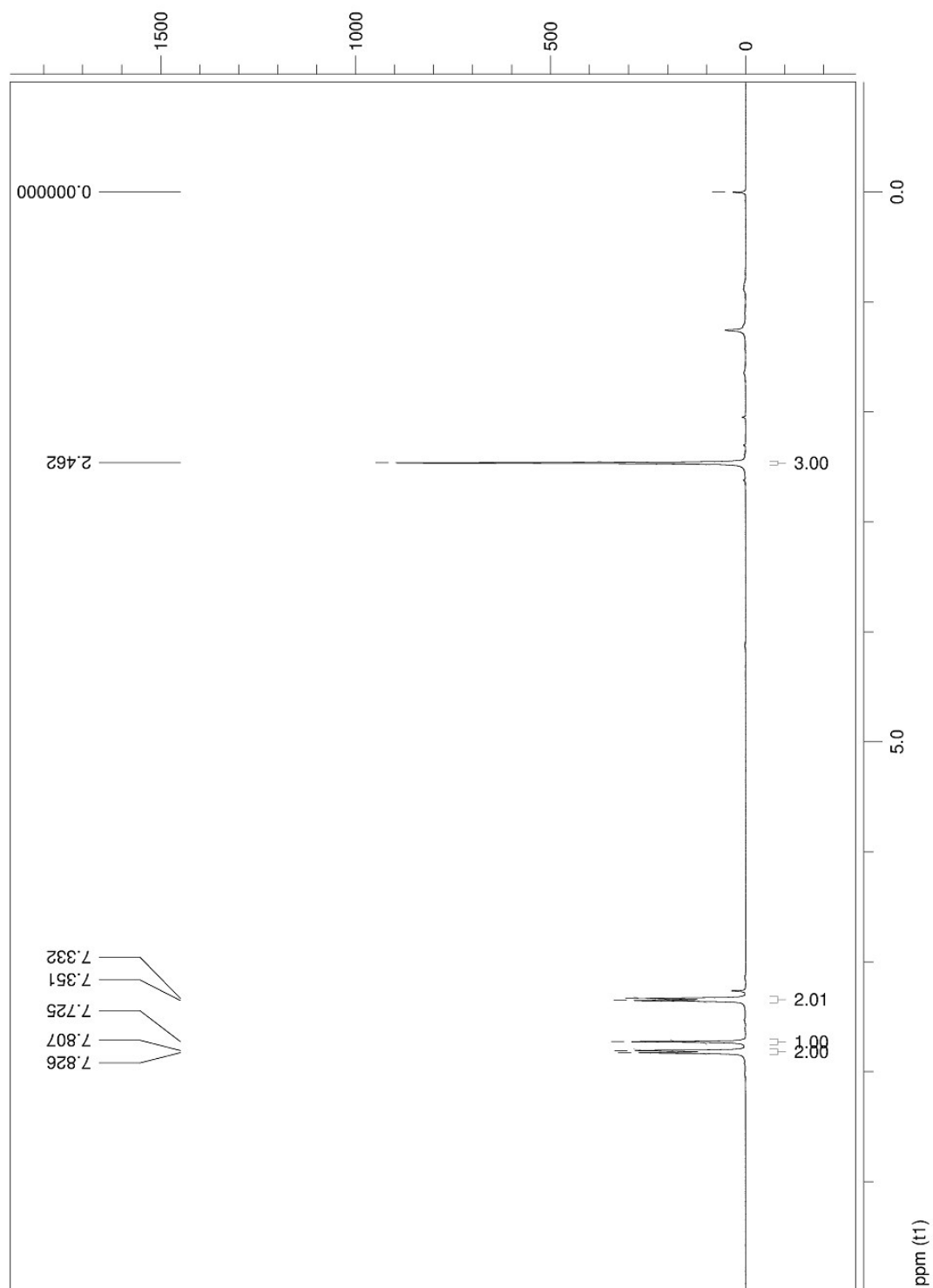


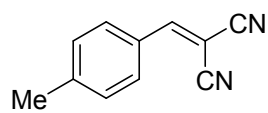
10a, CDCl₃, 100 MHz



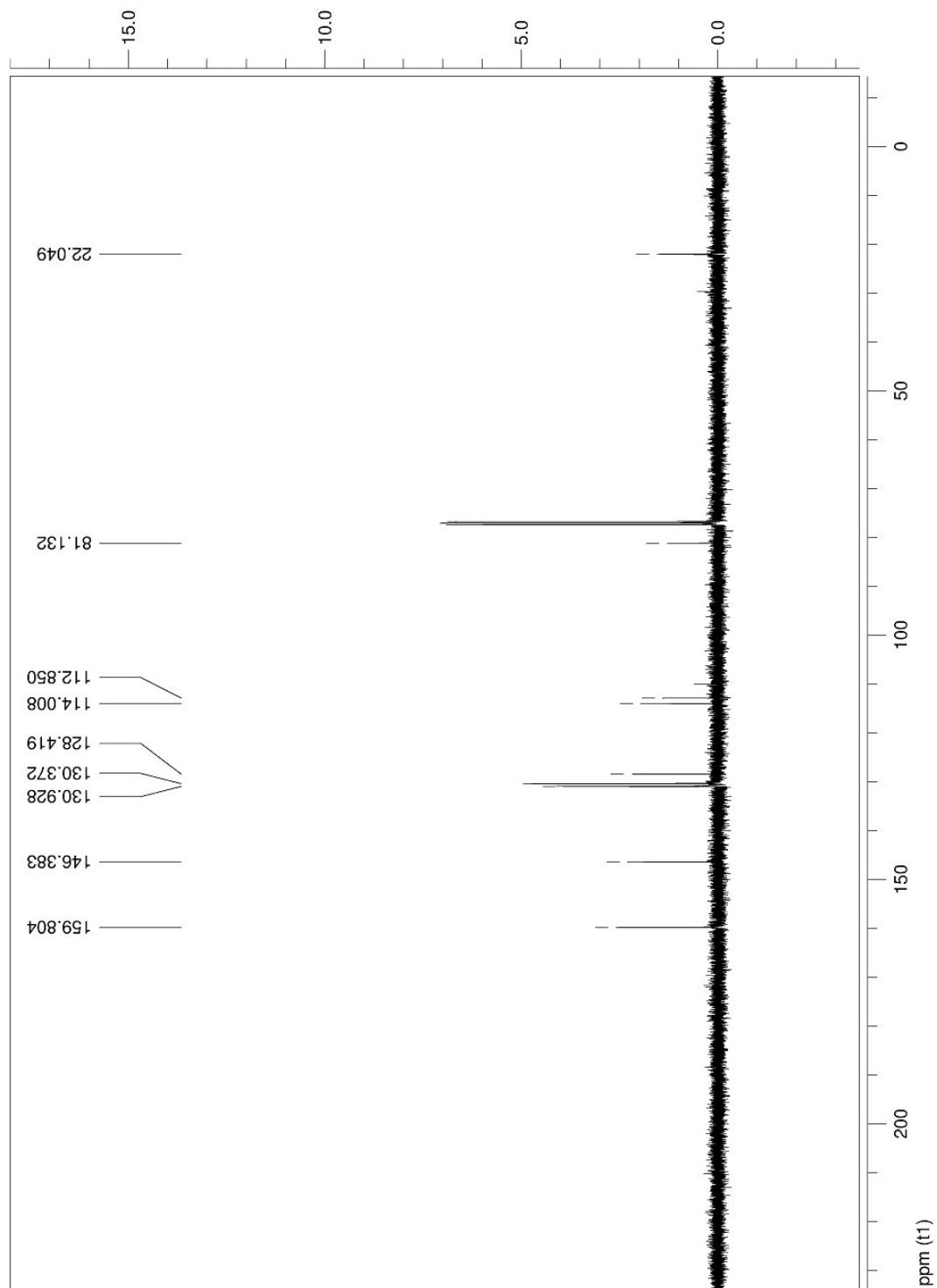


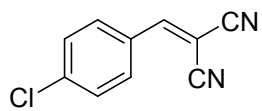
10b, CDCl₃, 400 MHz



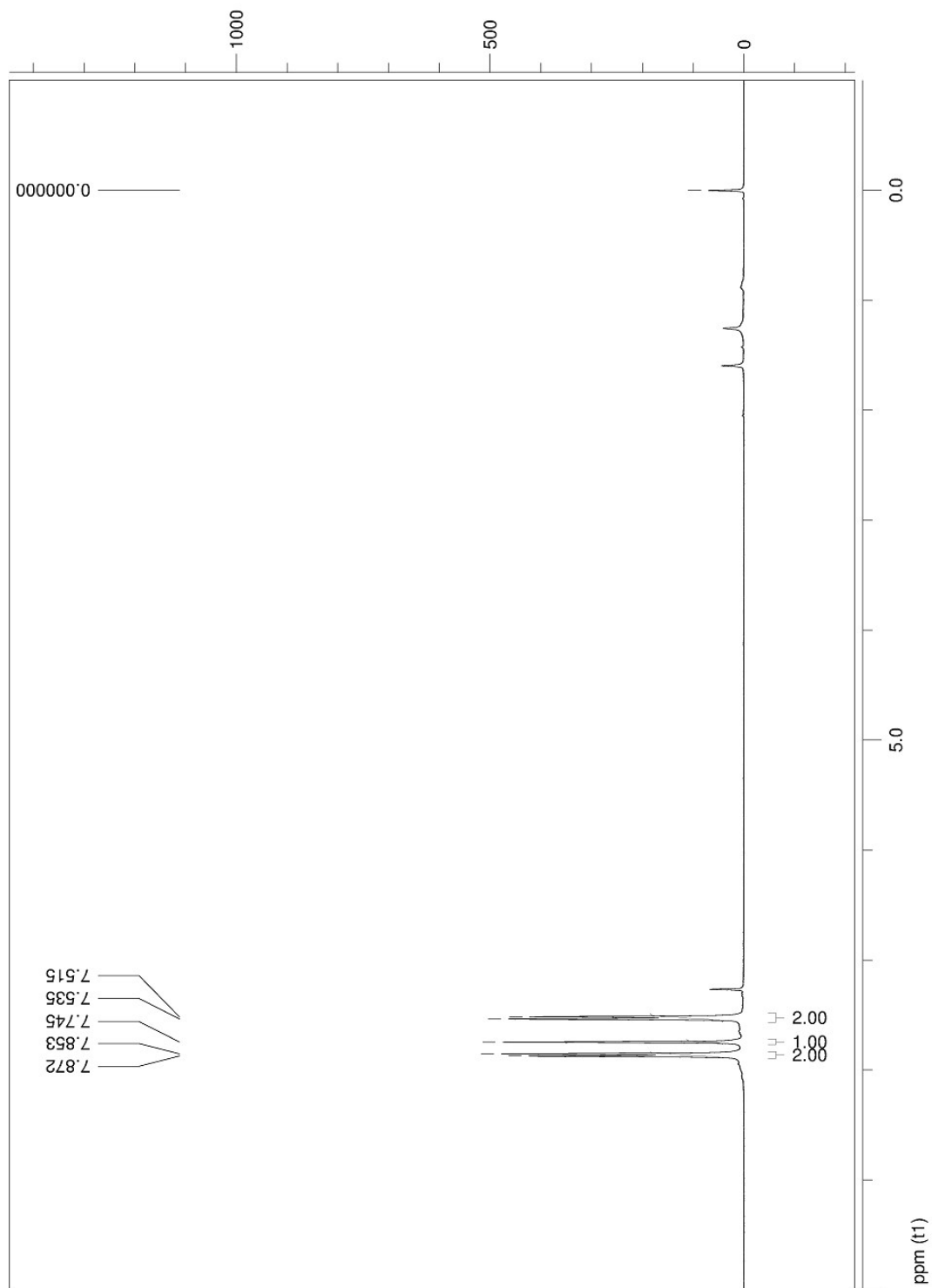


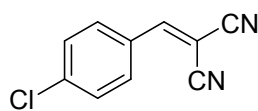
10b, CDCl₃, 100 MHz



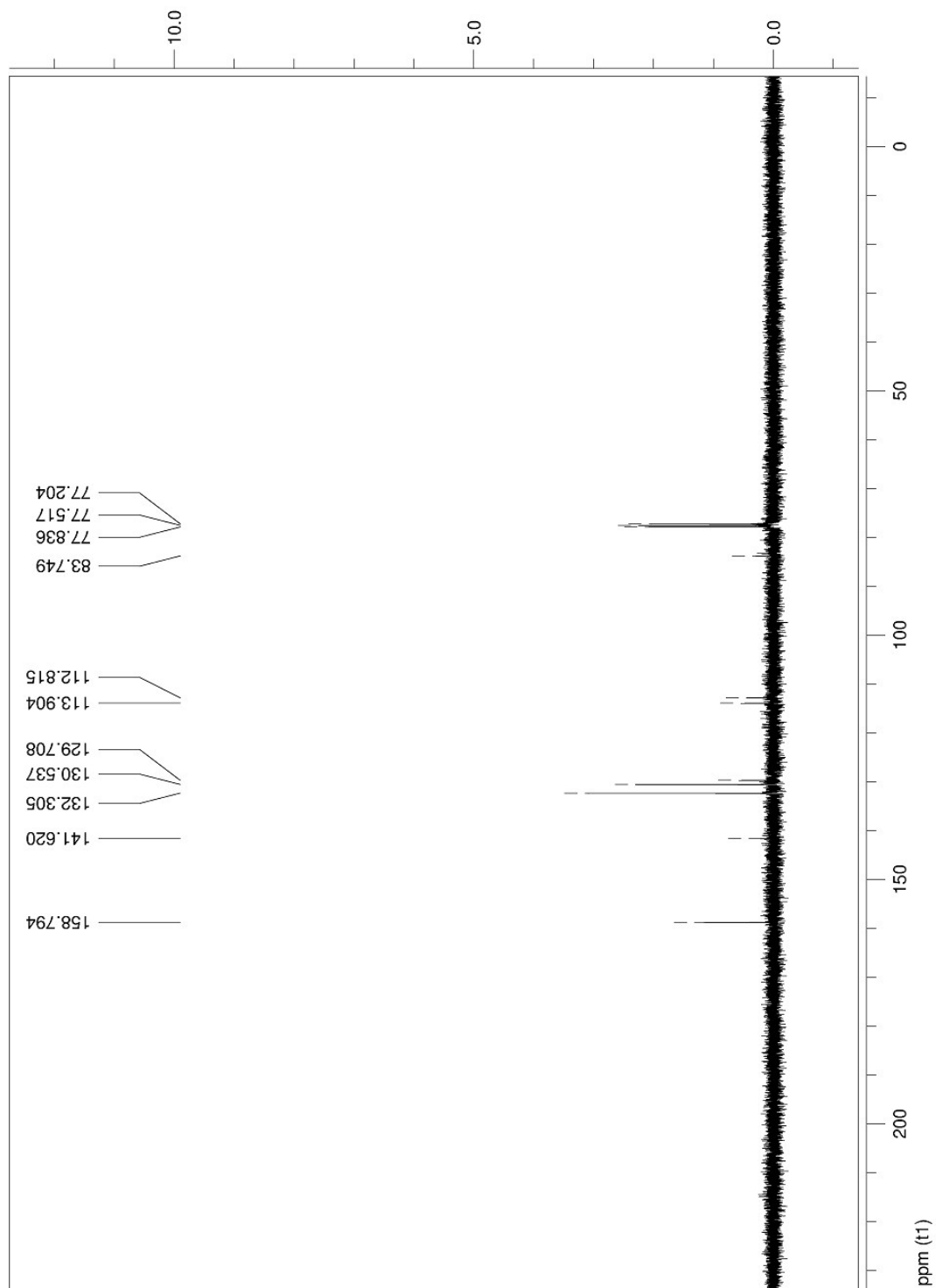


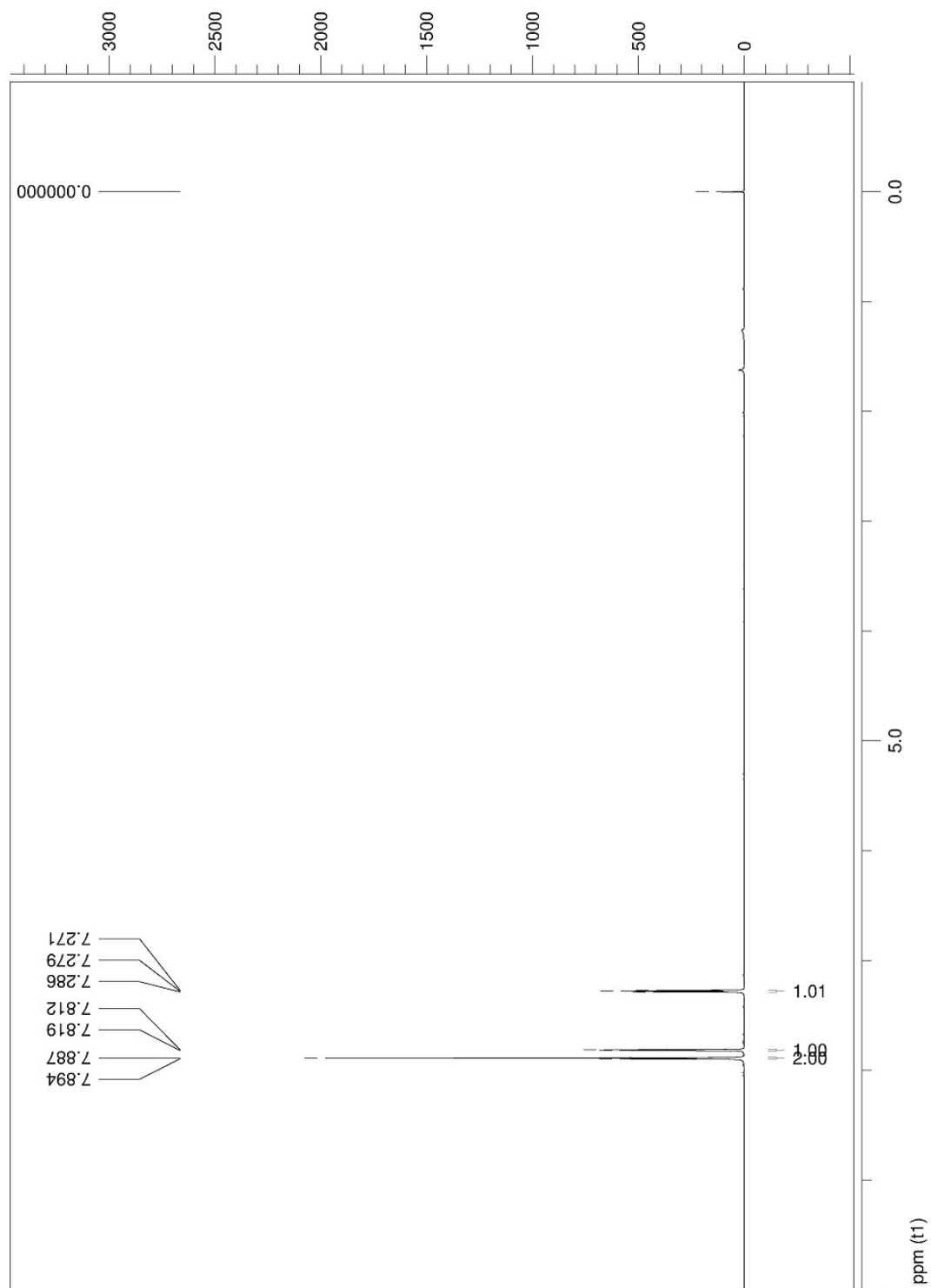
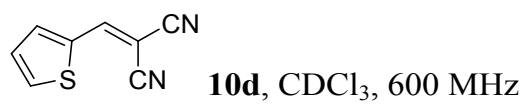
10c, CDCl₃, 400 MHz

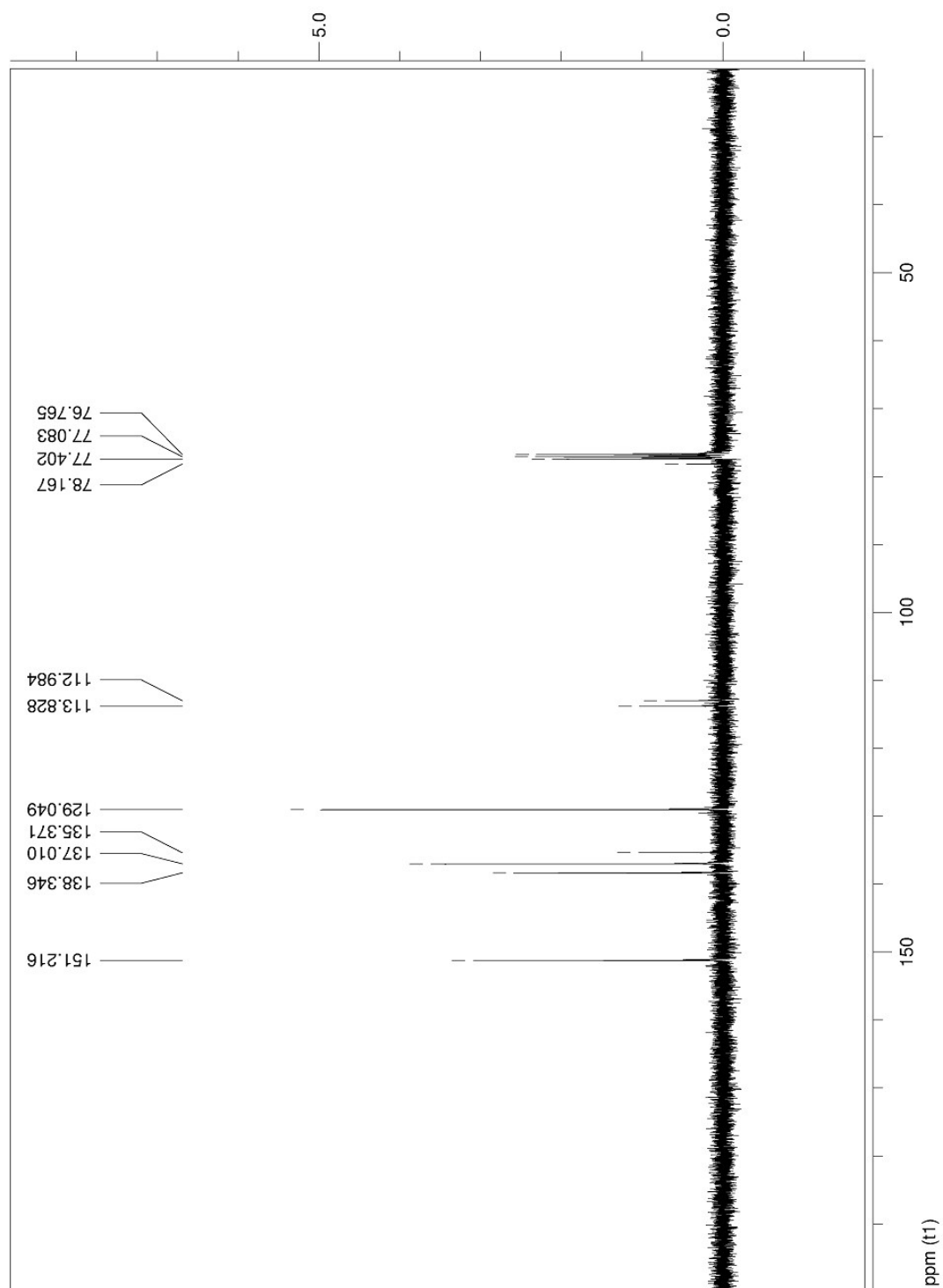
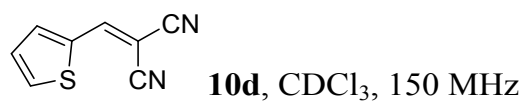


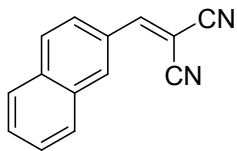


10c, CDCl₃, 100 MHz

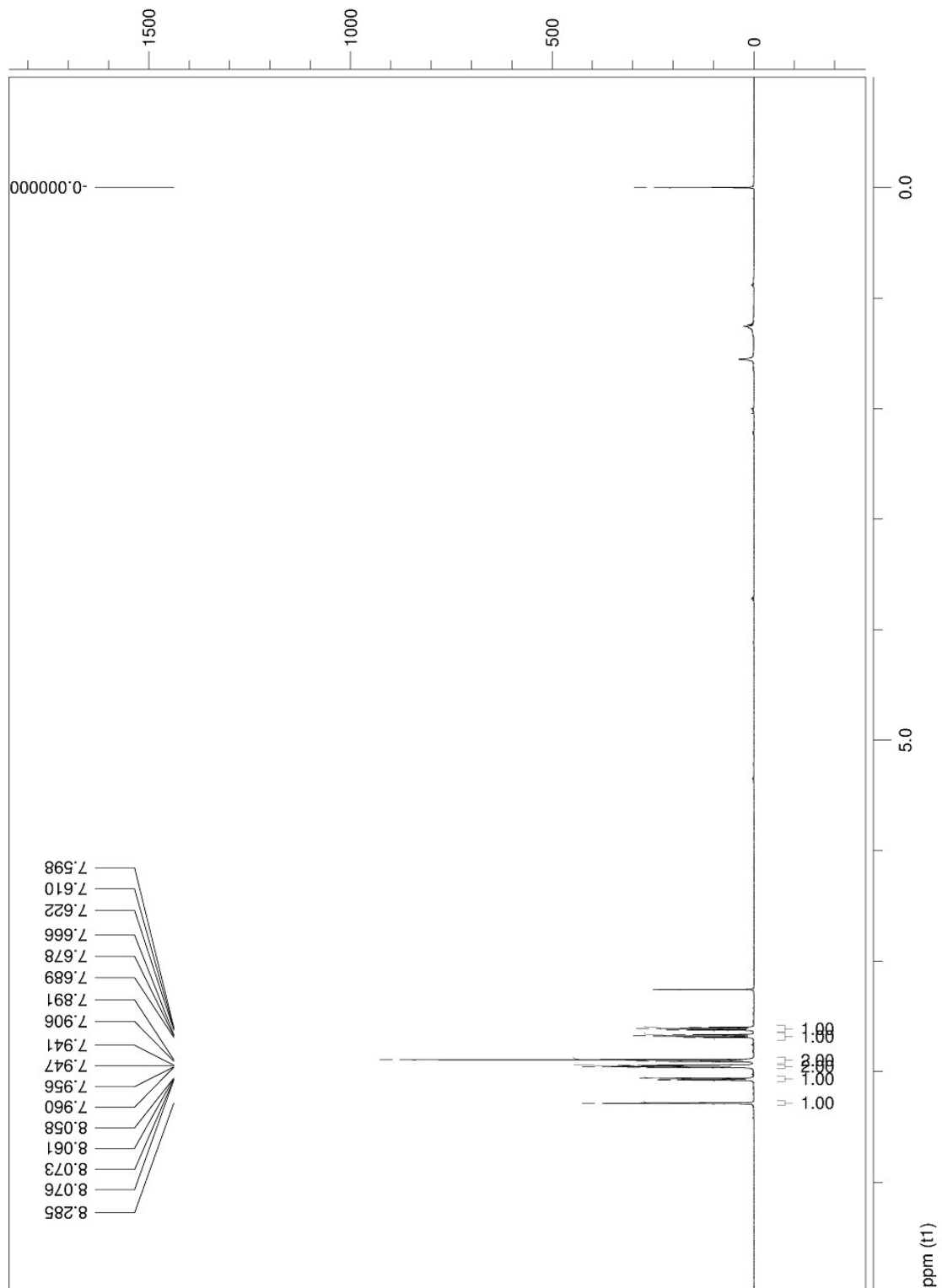


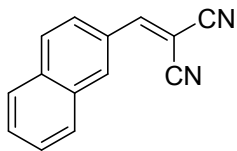




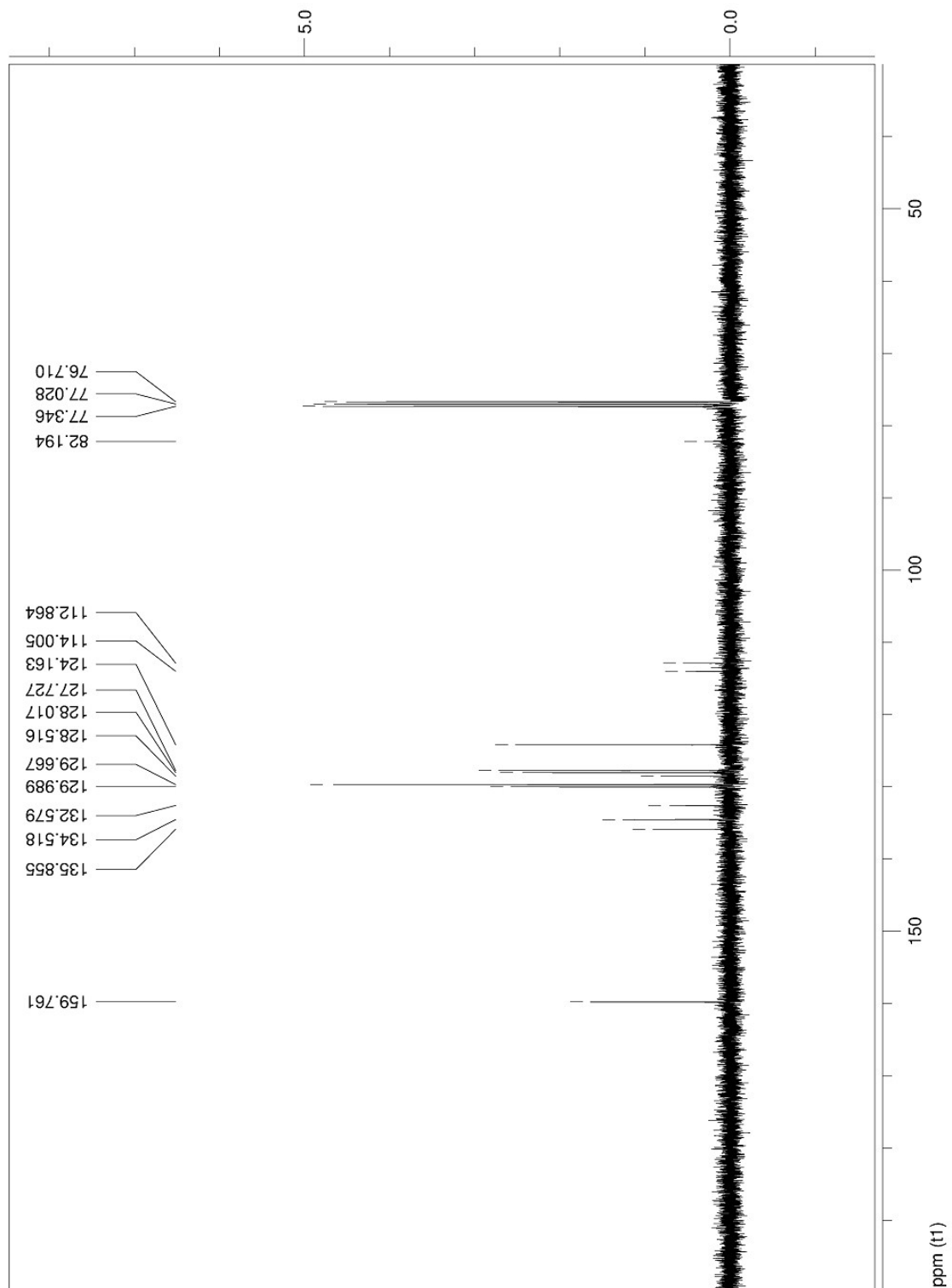


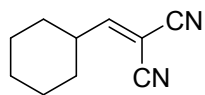
10e, CDCl₃, 600 MHz



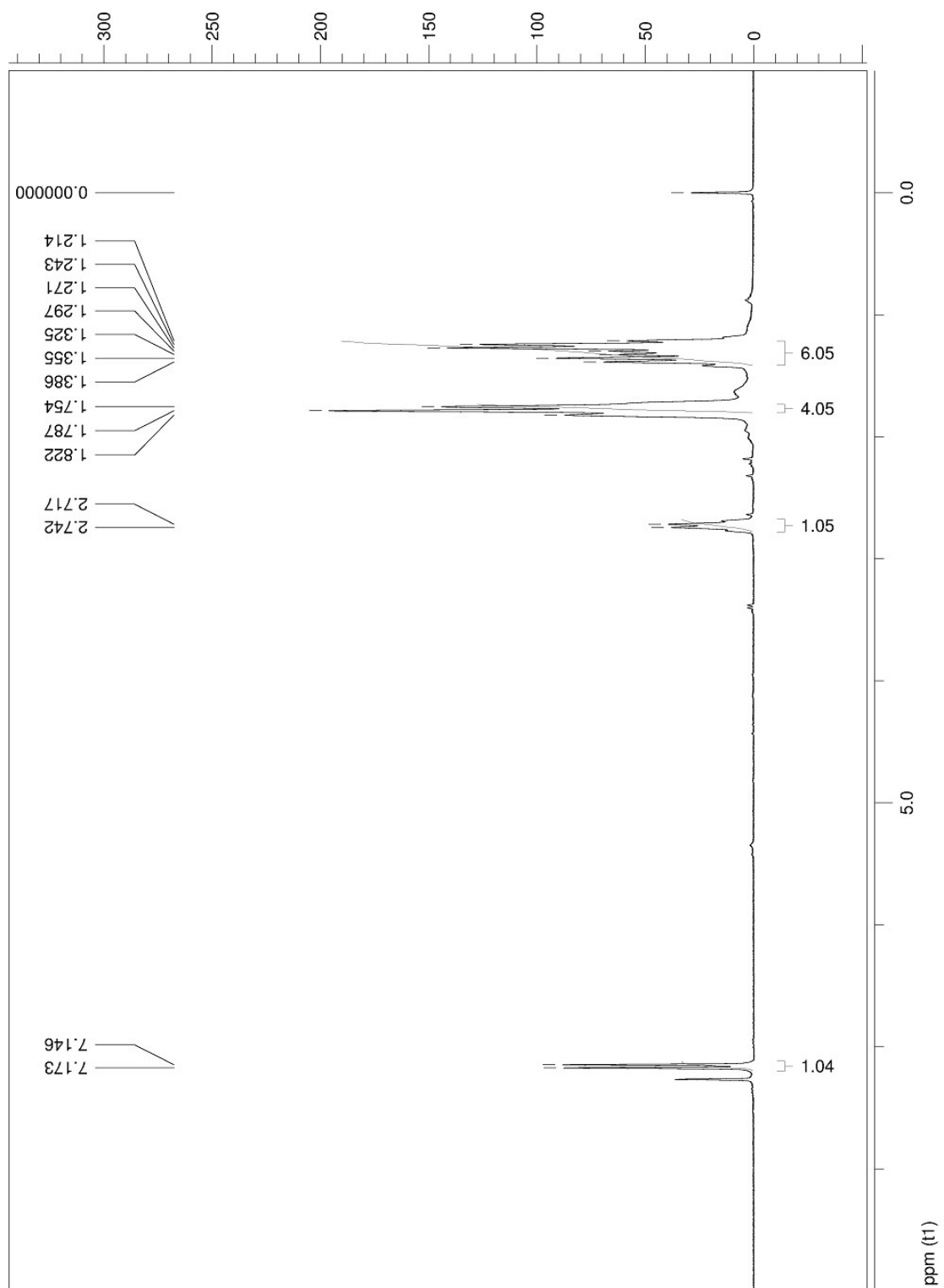


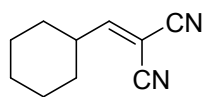
10e, CDCl₃, 100 MHz





10f, CDCl₃, 400 MHz





10f, CDCl₃, 100 MHz

