

Appendix I: Energy calculations

Energy delivered during 9 hours for Cinnamic acid formation reaction by conventional method

- Voltage input in magnetic stirrer (Model MR 3001K, Heidolph Instruments, Schwabach, Germany) = 230 V
- Current measured using digital multimeter (KUSAM-MECO Model 2718, Kusam Electrical Industries Ltd., Mumbai, India) = 43 mA
- Power input in magnetic stirrer = Voltage input x Current measured
= 230 (V) x 43 (mA) x 10⁻³(A/mA)

= 9.8 W (J/s)
- Efficiency of magnetic stirrer taken for the calculation = 40% (estimated independently using calorimetric studies)
- Actual power input in stirrer = Power input in magnetic stirrer (W) x 40/100
= 9.8 (W) x 40/100
= 3.96 W (J/s)
- Time required for completion of reaction = 9 hours (32400 Seconds)
- Net energy delivered during 9 hours = Power input in magnetic stirrer x Time required for completion of reaction
= 3.96 J/s x 9 hr x 3600 s/hr

= 128304 J = 128.31 kJ
- Quantity of material processed = Quantity of benzaldehyde + Quantity of acetic anhydride + Quantity of sodium acetate trihydrate
- = 0.5g + 0.96g + 1.93g
- = 3.39g
- **Net energy supplied for processing of material during 9 hours** = Net energy delivered during 9 hours / Quantity of material processed
= 128.31 (kJ) / 3.39 (g)

= 37.85 (kJ/g)..... (A)

2 *Energy delivered during 4 hours for Cinnamic acid formation reaction By using DES*

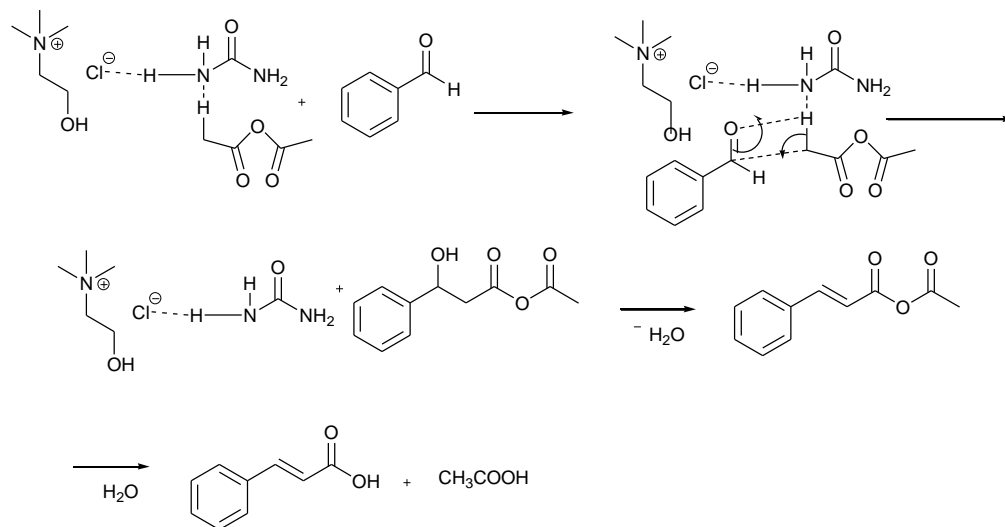
- Voltage input in magnetic stirrer (Model MR 3001K, Heidolph Instruments, Schwabach, Germany) = 230 V
- Current measured using digital multimeter (KUSAM-MECO Model 2718, Kusam Electrical Industries Ltd., Mumbai, India) = 43 mA

- Power input in magnetic stirrer = Voltage input x Current measured
 $= 230 \text{ (V)} \times 43 \text{ (mA)} \times 10^{-3} \text{ (A/mA)}$
 $= 9.8 \text{ W (J/s)}$
 - Efficiency of magnetic stirrer taken for the calculation = 40% (estimated independently using calorimetric studies)
 - Actual power input in stirrer = Power input in magnetic stirrer (W) x 40/100
 $= 9.8 \text{ (W)} \times 40/100$
 $= 3.96 \text{ W (J/s)}$
 - Time required for completion of reaction = 4hours (14400 Seconds)
 - Net energy delivered during 9 hours = Power input in magnetic stirrer x Time required for completion of reaction
 $= 3.96 \text{ J/s} \times 4 \text{ hr} \times 3600 \text{ s/hr}$
 $= 57024 \text{ J} = 57.02 \text{ kJ}$
 - Quantity of material processed = Quantity of benzaldehyde + Quantity of acetic anhydride + Quantity of Deep Eutectic Solvent
 - $= 0.5\text{g} + 0.48\text{g} + 3.05\text{g}$
 - $= 4.03\text{g}$
 - **Net energy supplied for processing of material during 4 hours** = Net energy delivered during 4 hours / Quantity of material processed
 $= 57.02 \text{ (kJ)} / 4.03 \text{ (g)}$
 $= 14.15 \text{ (kJ/g)} \dots\dots\dots \text{ (B)}$
- 3 Net Energy saved for the Oxidation process = Net energy supplied for processing of material during 16 hours (A) – Net energy supplied for processing of material during 4 hours (B)
 $= 37.85 - 14.15 \text{ (kJ/g)}$
 $= 23.70 \text{ (kJ/g)}$

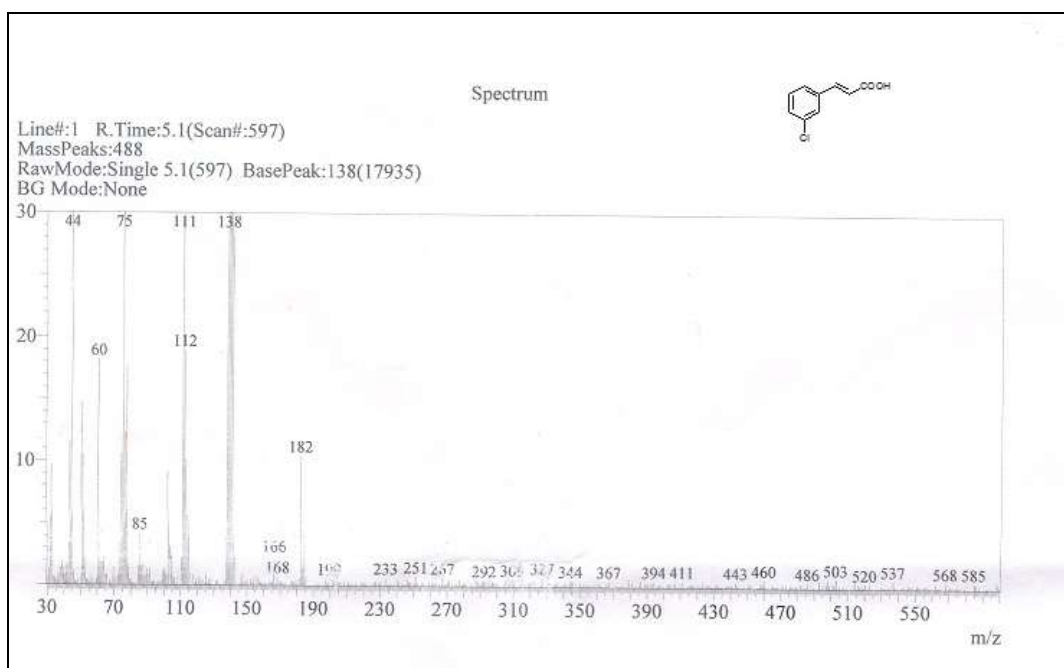
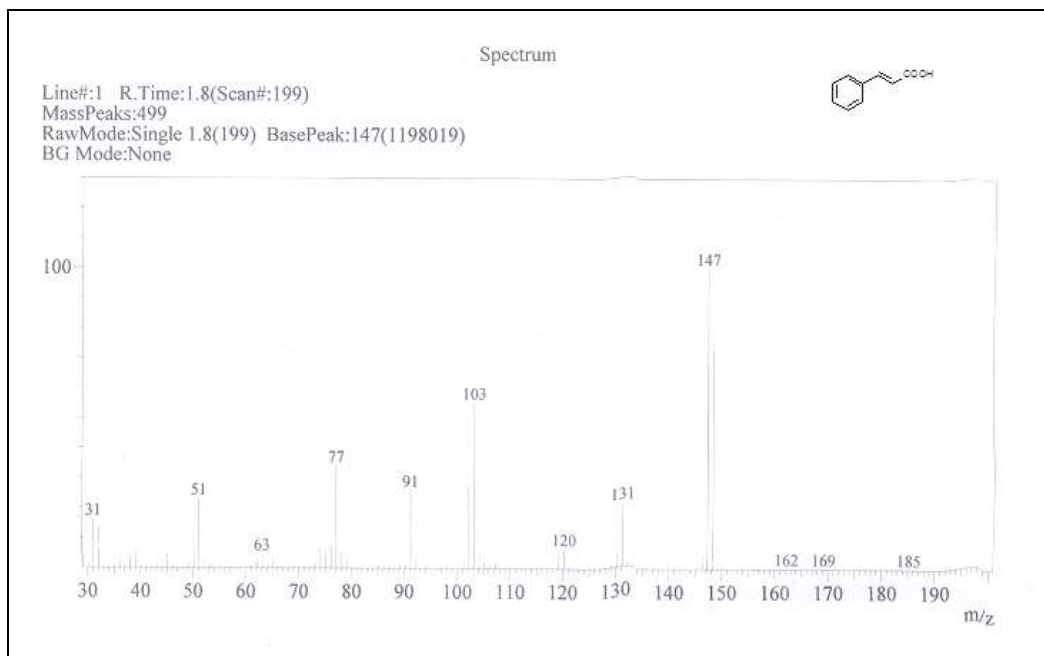
Appendix 2. Reaction mechanism

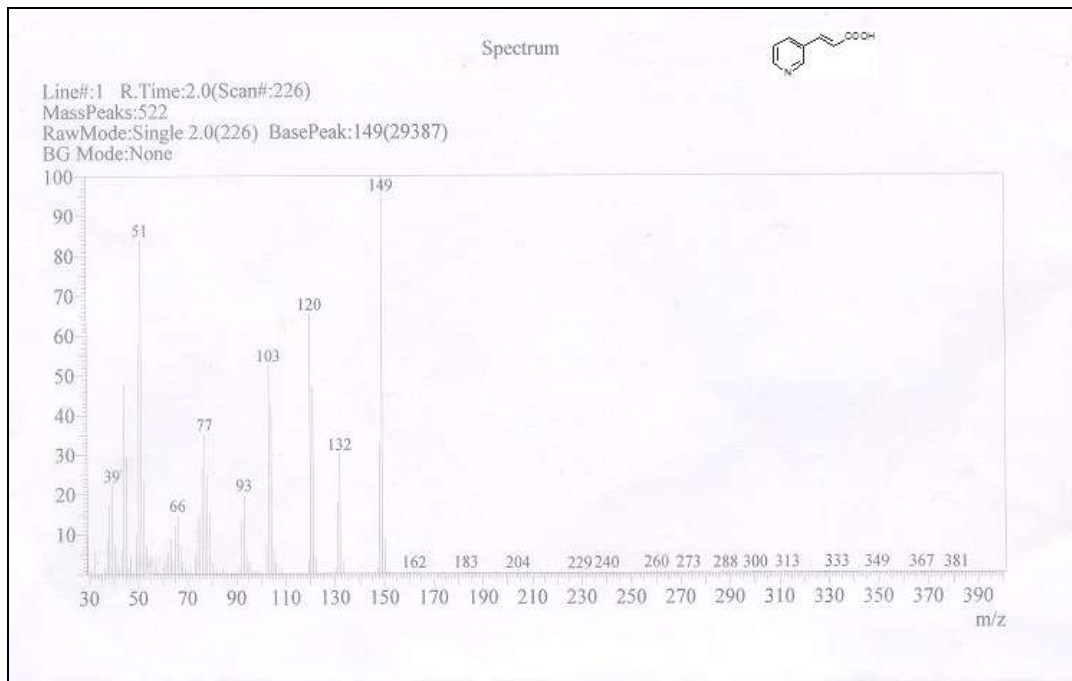
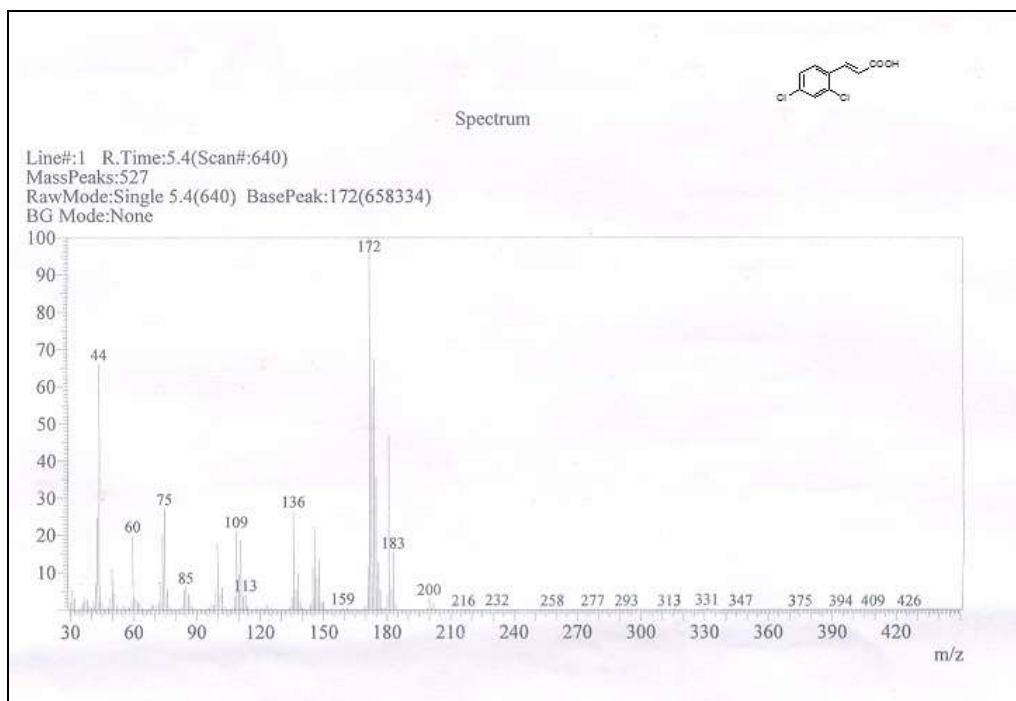
Probable mechanism is given below:

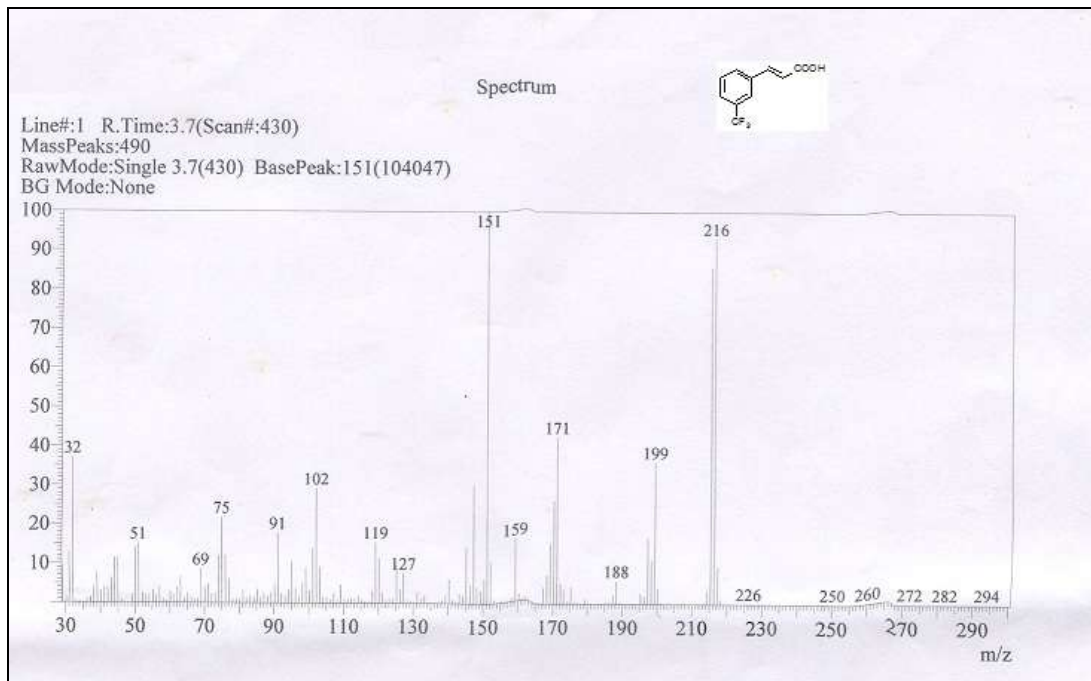
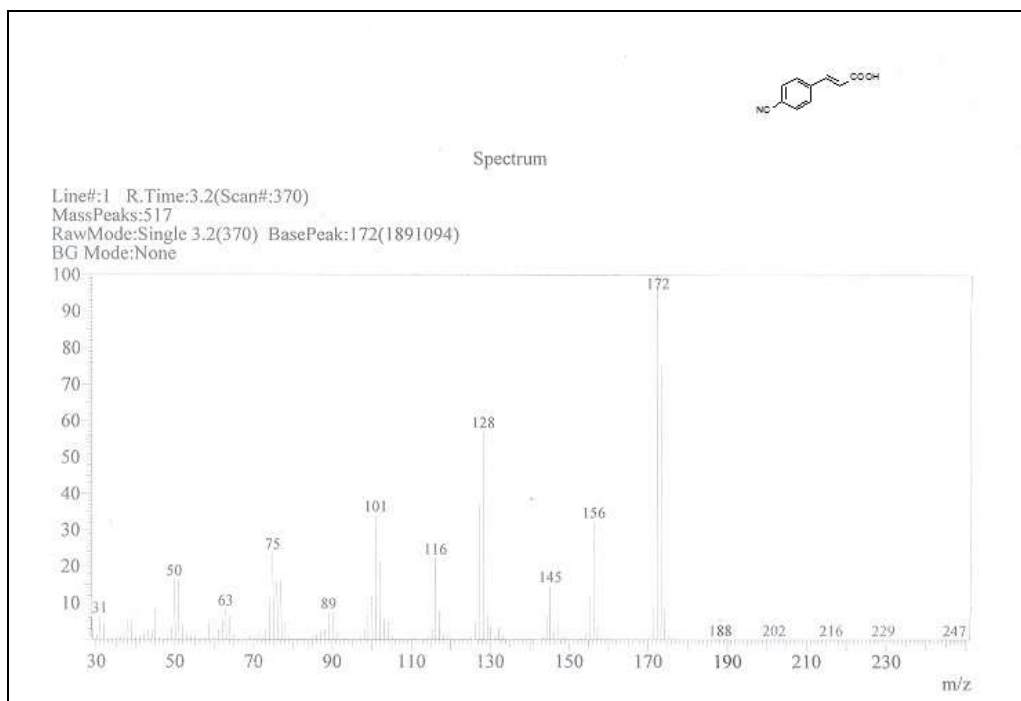
DES is basic in nature. There is hydrogen bonding between Cl^- and hydrogen of urea. Therefore the basicity of that nitrogen increases and it can hold the proton of acetic anhydride. There may be formation of 4-membered cyclic transition state as shown in mechanism.

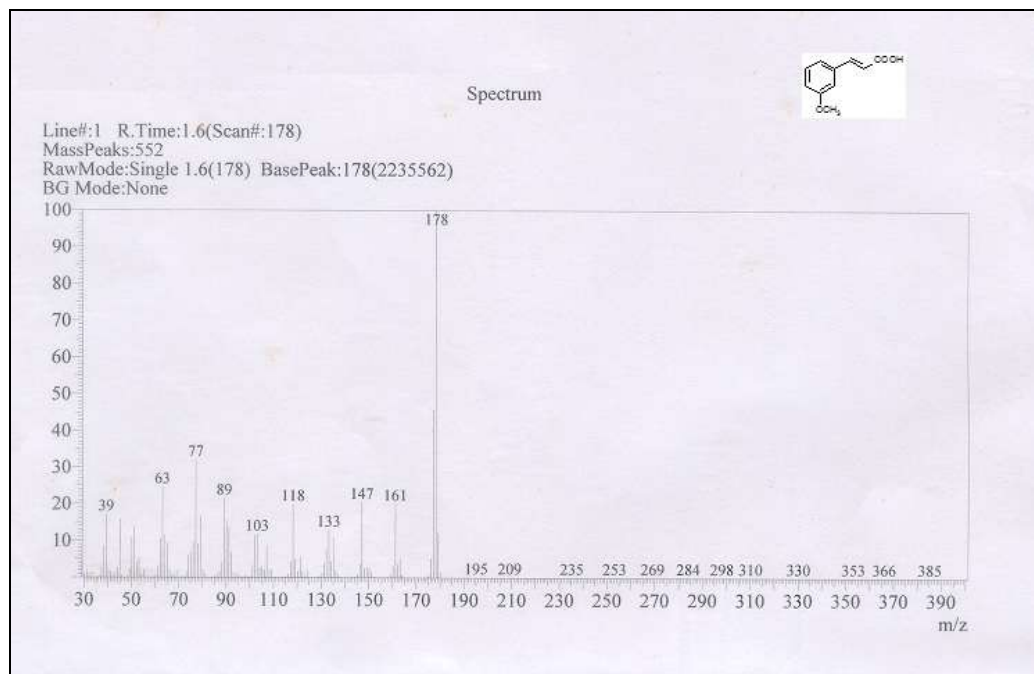
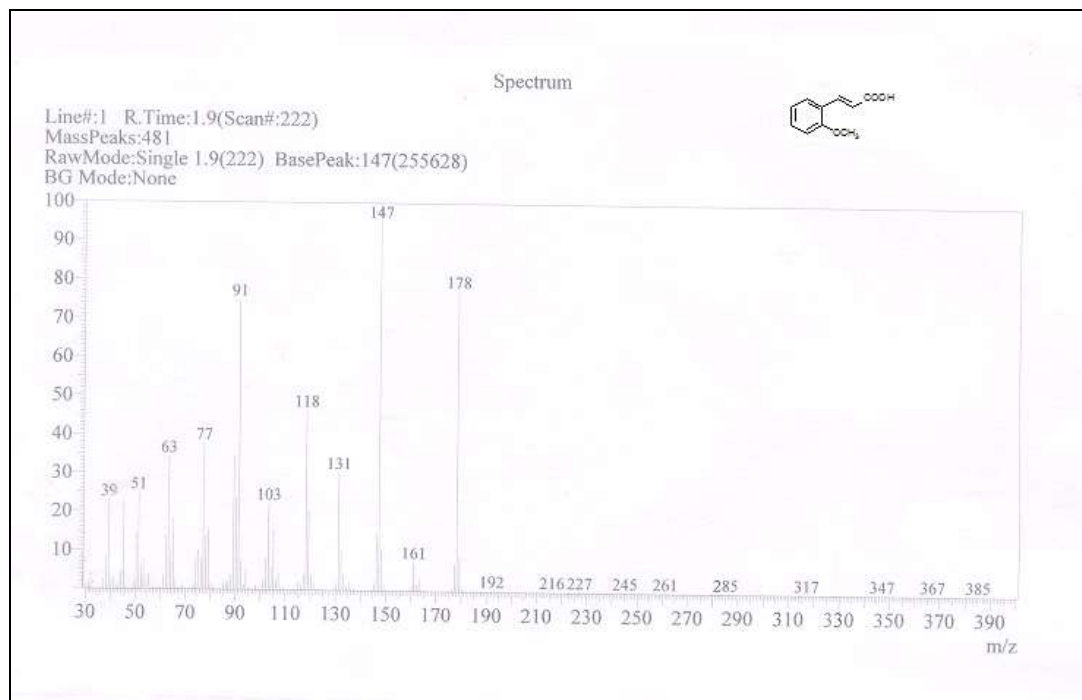


Mass Spectrum

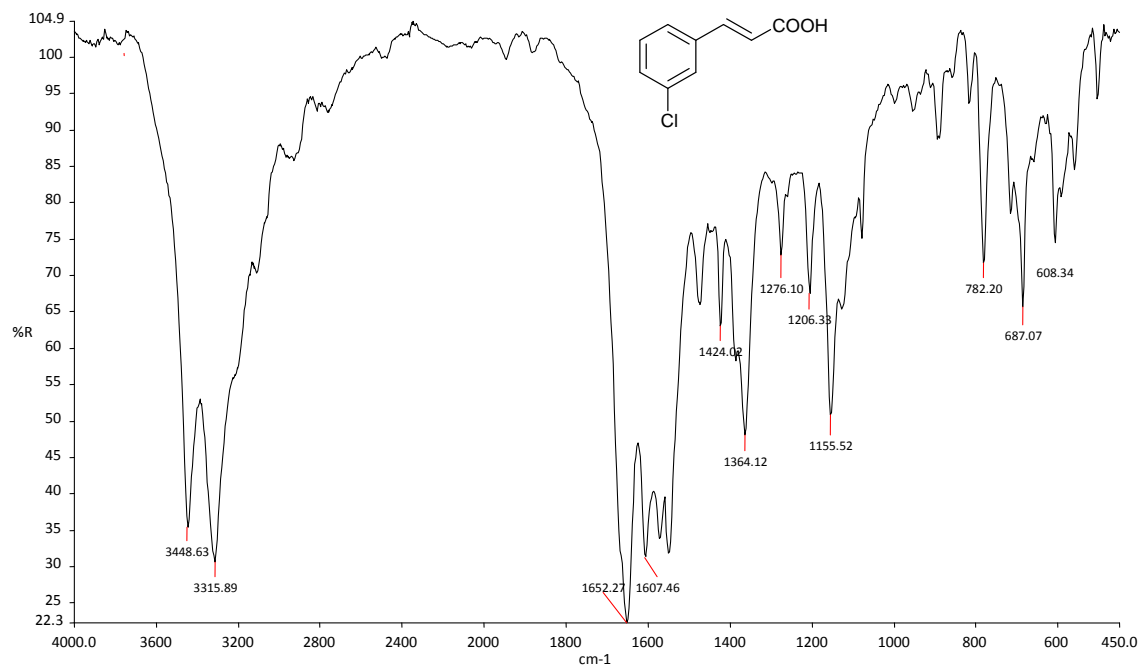
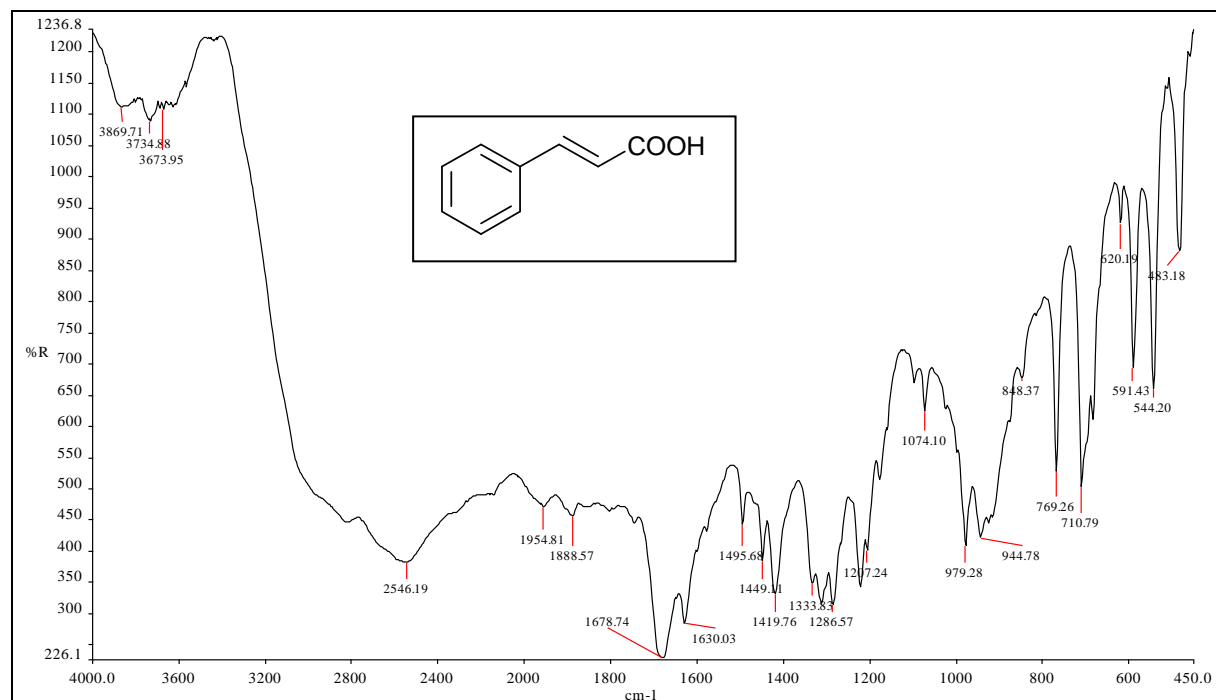


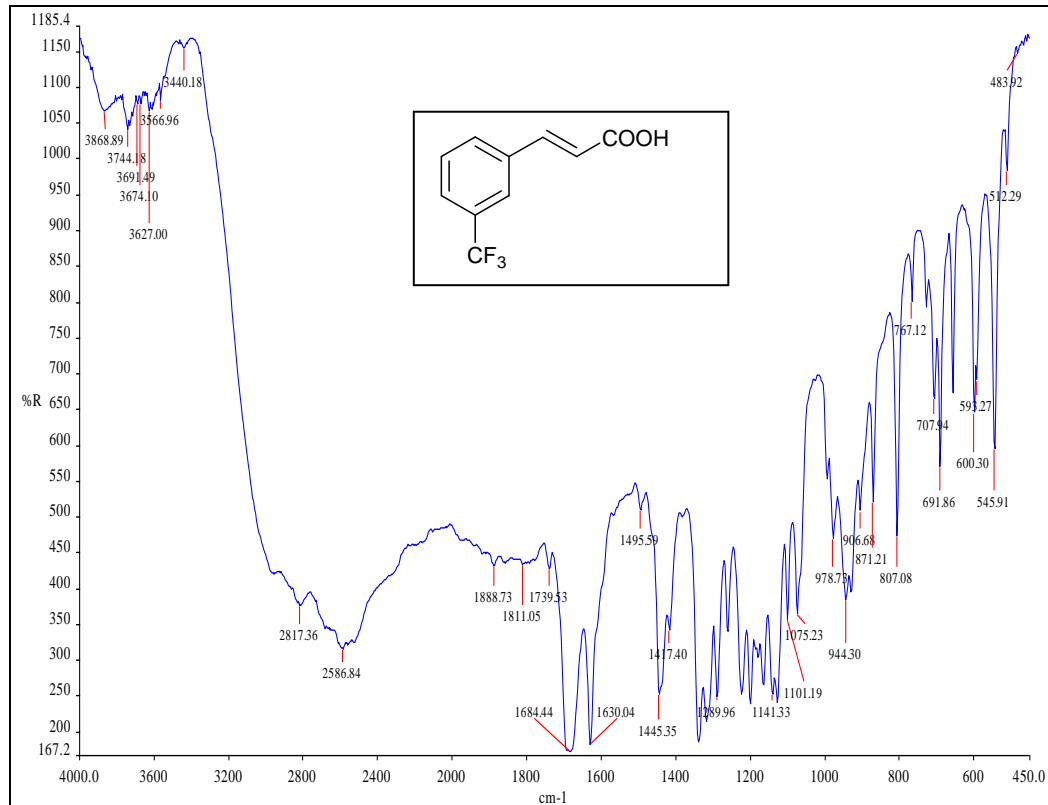
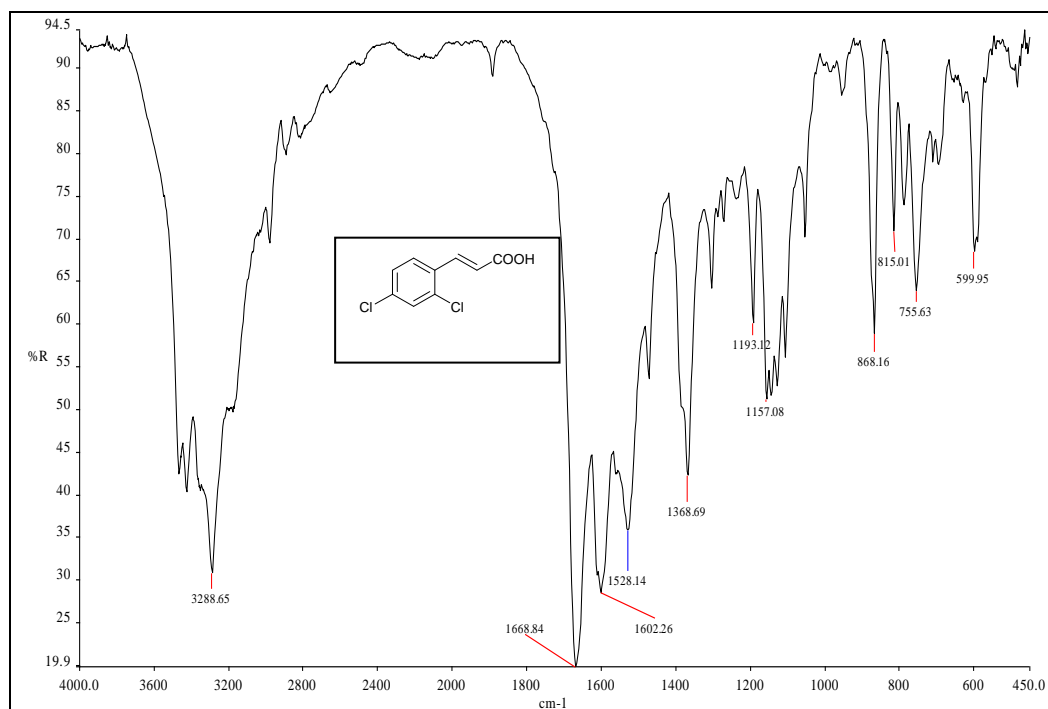


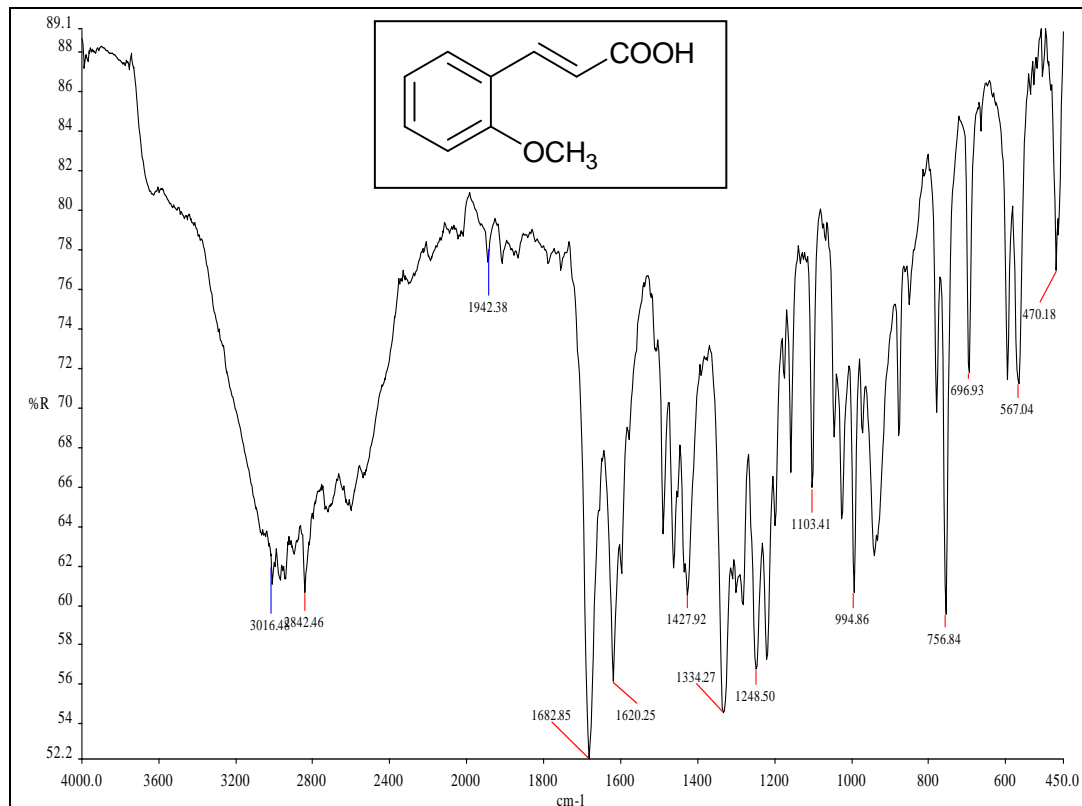
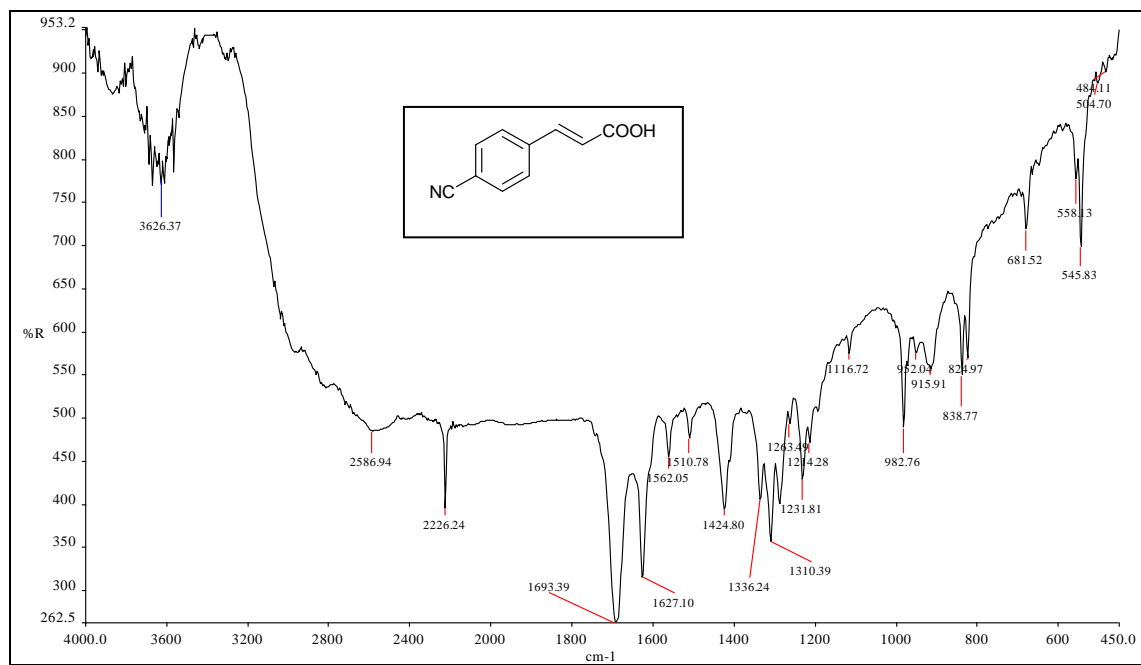


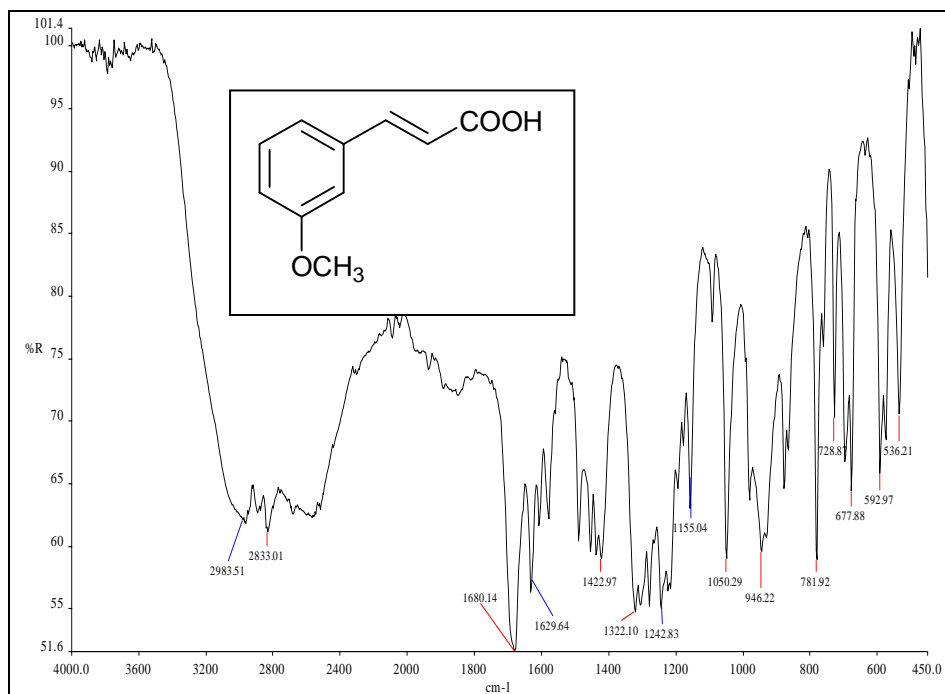
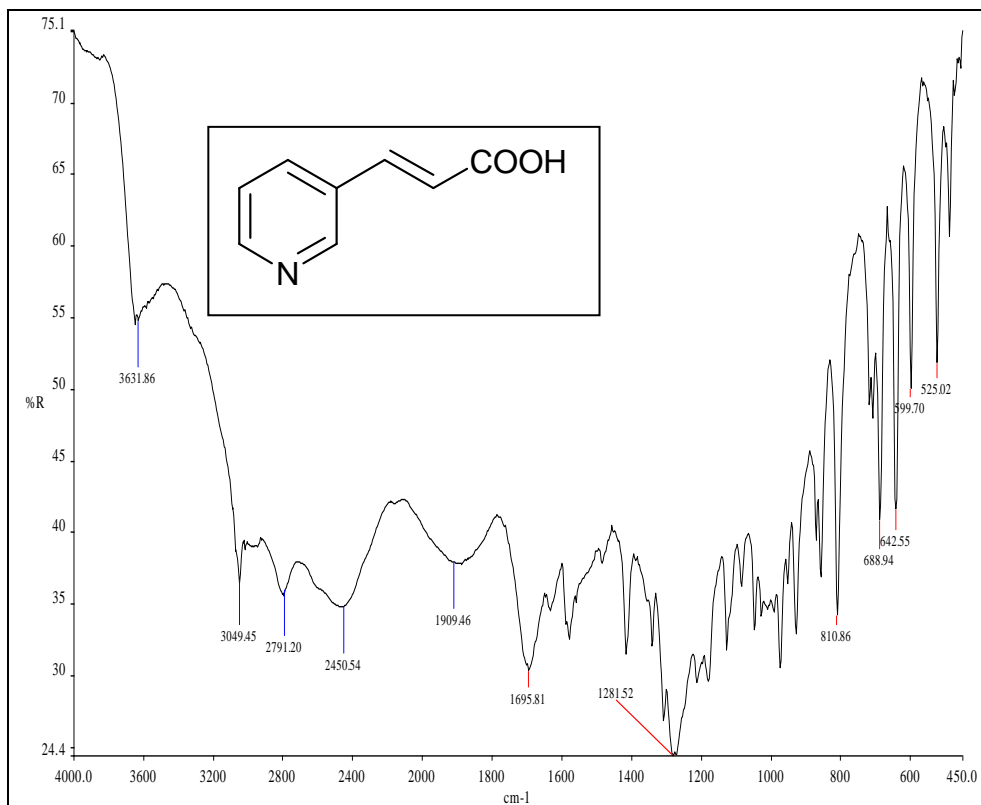


FT-IR Spectrum

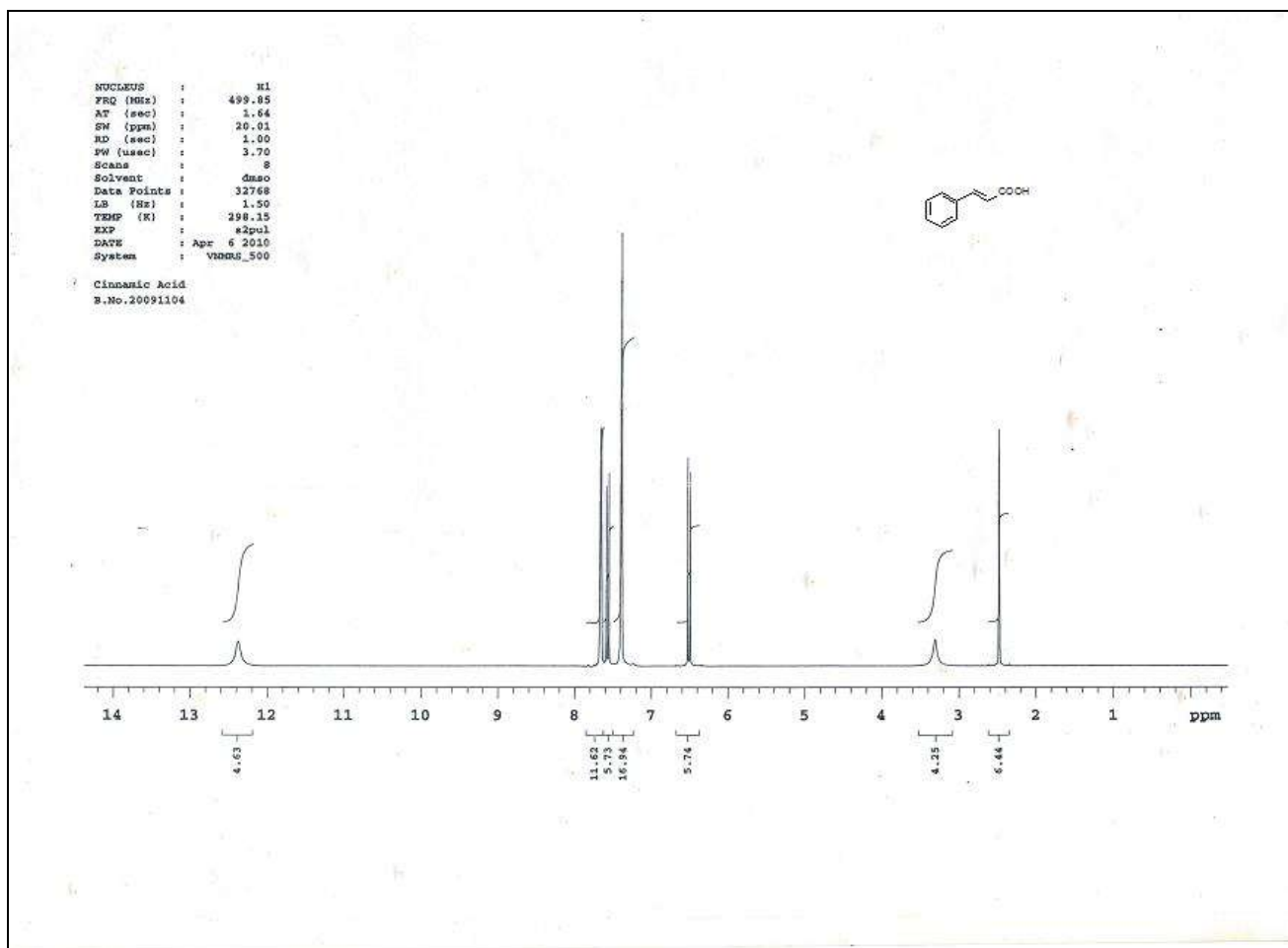




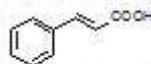




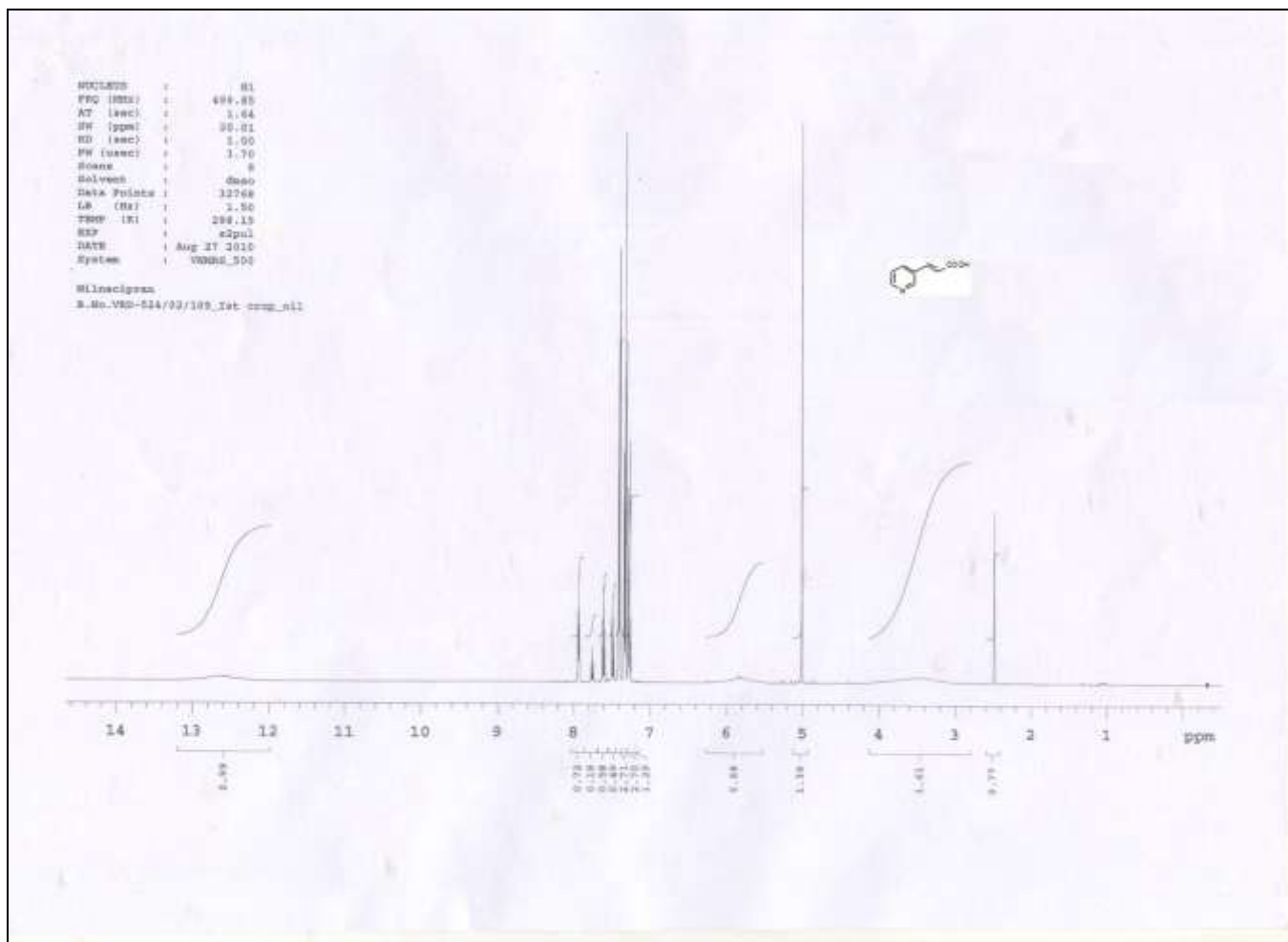
H-1 NMR Spectrum



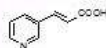
Cinnamic Acid
B.No.20091104



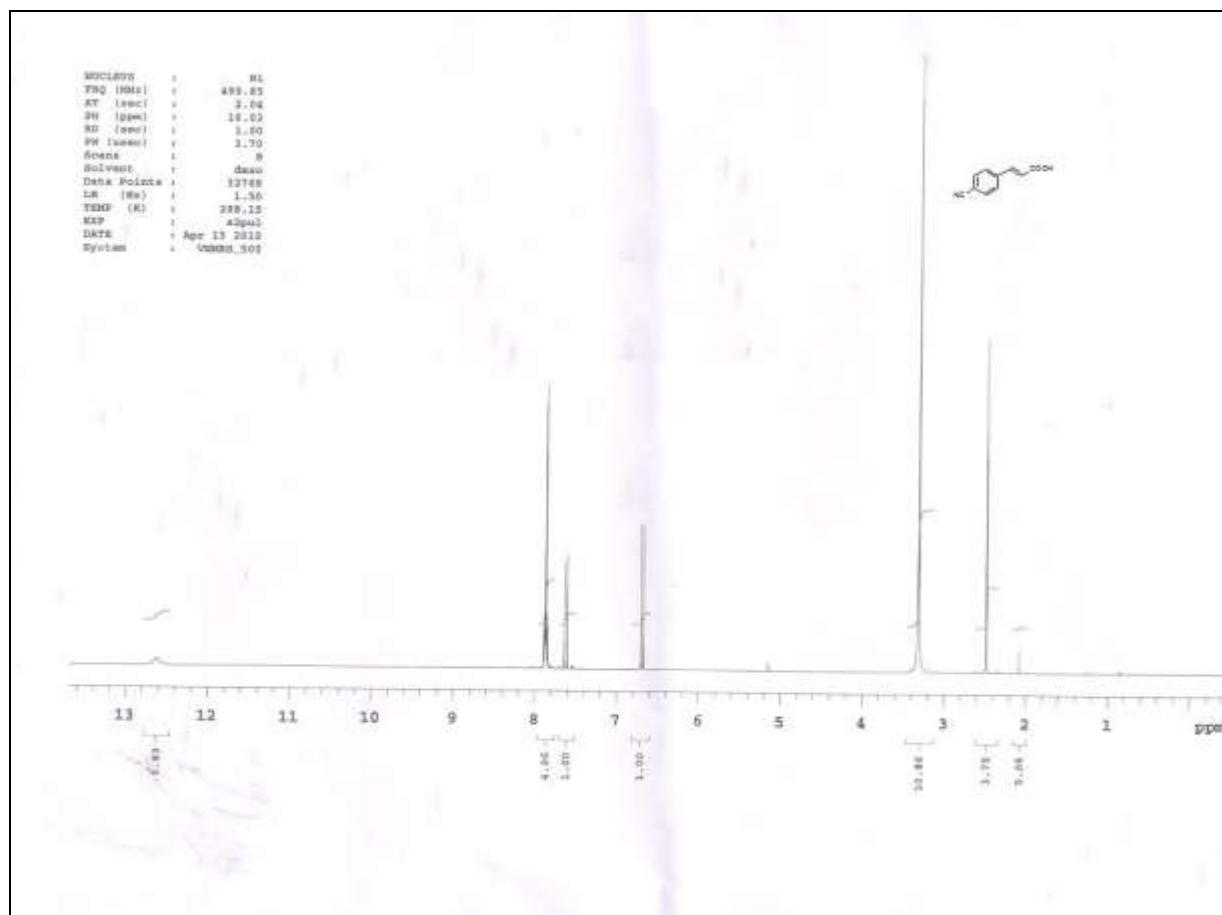
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2	3832.2	7.667	54.2
3	3829.7	7.662	53.3
4	3827.3	7.657	54.8
5	3793.1	7.589	41.1
6	3777.2	7.557	44.1
7	3708.9	7.420	3.3
8	3697.3	7.397	88.7
9	3694.8	7.392	99.0
10	3262.7	6.527	47.8
11	3246.8	6.496	44.3
12	1653.8	3.309	6.1
13	1241.2	2.483	54.1

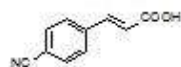


Milnacipran
B.No.VRD-524/02/109_Ist crop_oil

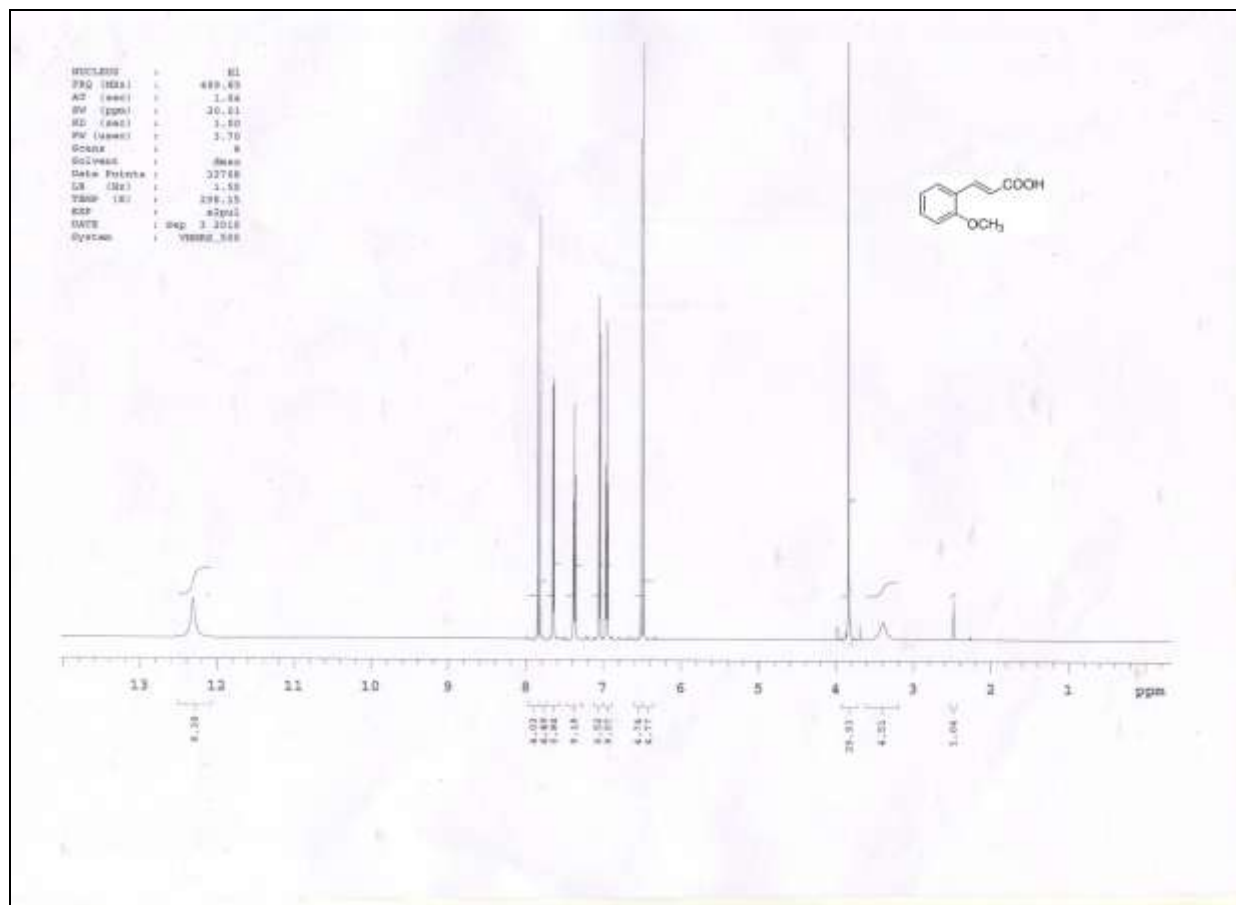


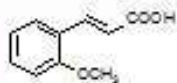
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1	6318.1	12.640	26.7	43	1676.4	3.354	29.5
2	3970.7	7.944	432.4	44	1244.9	2.491	364.1
3	3965.8	7.934	395.8	45	1243.1	2.487	784.9
4	3964.0	7.930	453.7	46	1241.2	2.483	1084.7
5	3959.1	7.921	352.7	47	1239.4	2.480	773.3
6	3882.8	7.768	96.6	48	1237.6	2.476	344.0
7	3881.6	7.766	56.5				
8	3875.5	7.753	222.3				
9	3869.4	7.741	76.7				
10	3868.2	7.739	128.8				
11	3809.0	7.620	334.5				
12	3801.0	7.604	589.3				
13	3793.1	7.589	327.1				
14	3748.5	7.499	348.0				
15	3740.6	7.484	526.8				
16	3732.7	7.468	252.3				
17	3712.5	7.427	41.5				
18	3702.8	7.408	2140.9				
19	3695.4	7.393	2730.6				
20	3687.5	7.377	30.4				
21	3668.6	7.339	1443.1				
22	3661.9	7.326	3461.0				
23	3660.0	7.322	1364.5				
24	3653.9	7.310	1785.0				
25	3639.3	7.281	1221.8				
26	3638.1	7.278	699.7				
27	3634.4	7.271	471.9				
28	3632.0	7.266	1518.8				
29	3629.5	7.261	293.6				
30	3626.5	7.255	250.6				
31	3624.6	7.252	397.4				
32	3623.4	7.249	232.7				
33	2920.3	5.842	41.4				
34	2909.9	5.822	44.5				
35	2504.0	5.010	3521.5				
36	1791.8	3.985	32.0				
37	1745.4	3.492	33.0				
38	1717.3	3.436	34.0				
39	1710.6	3.422	33.8				
40	1694.7	3.390	30.9				
41	1688.0	3.377	29.7				
42	1683.1	3.367	29.7				



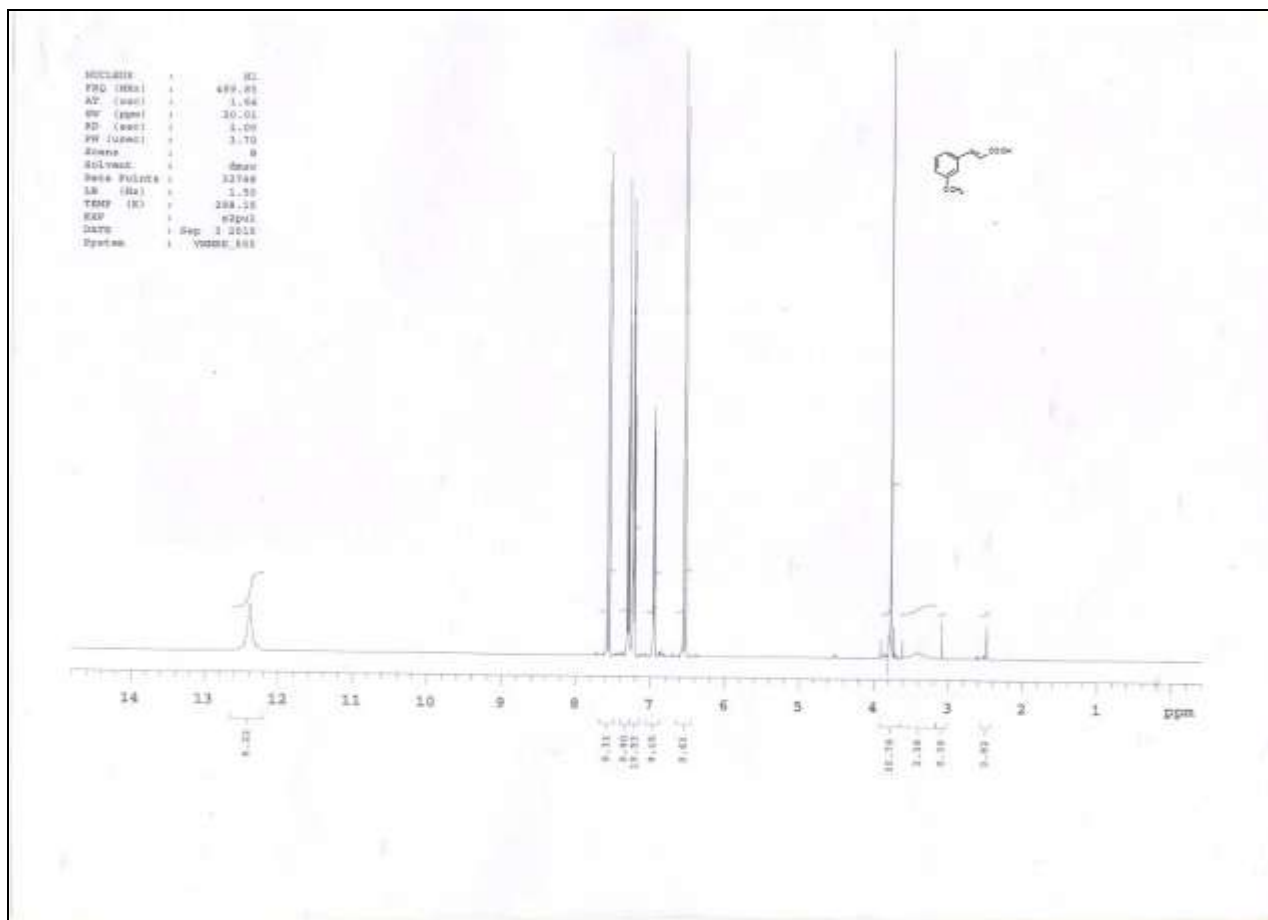


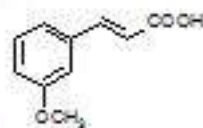
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1	6309.6	12.623	2.6
2	3944.4	7.891	21.5
3	3942.5	7.887	10.4
4	3938.1	7.879	15.2
5	3935.6	7.874	101.4
6	3930.8	7.864	108.7
7	3924.4	7.851	9.2
8	3922.0	7.846	21.3
9	3917.6	7.838	1.7
10	3818.3	7.639	40.6
11	3802.1	7.607	43.4
12	3352.7	6.707	55.2
13	3336.5	6.675	56.1
14	2572.1	5.146	3.2
15	1656.1	3.313	246.0
16	1244.8	2.490	40.4
17	1242.9	2.486	93.4
18	1240.9	2.483	128.0
19	1238.9	2.479	82.5
20	1237.5	2.476	37.5
21	1040.9	2.082	8.6



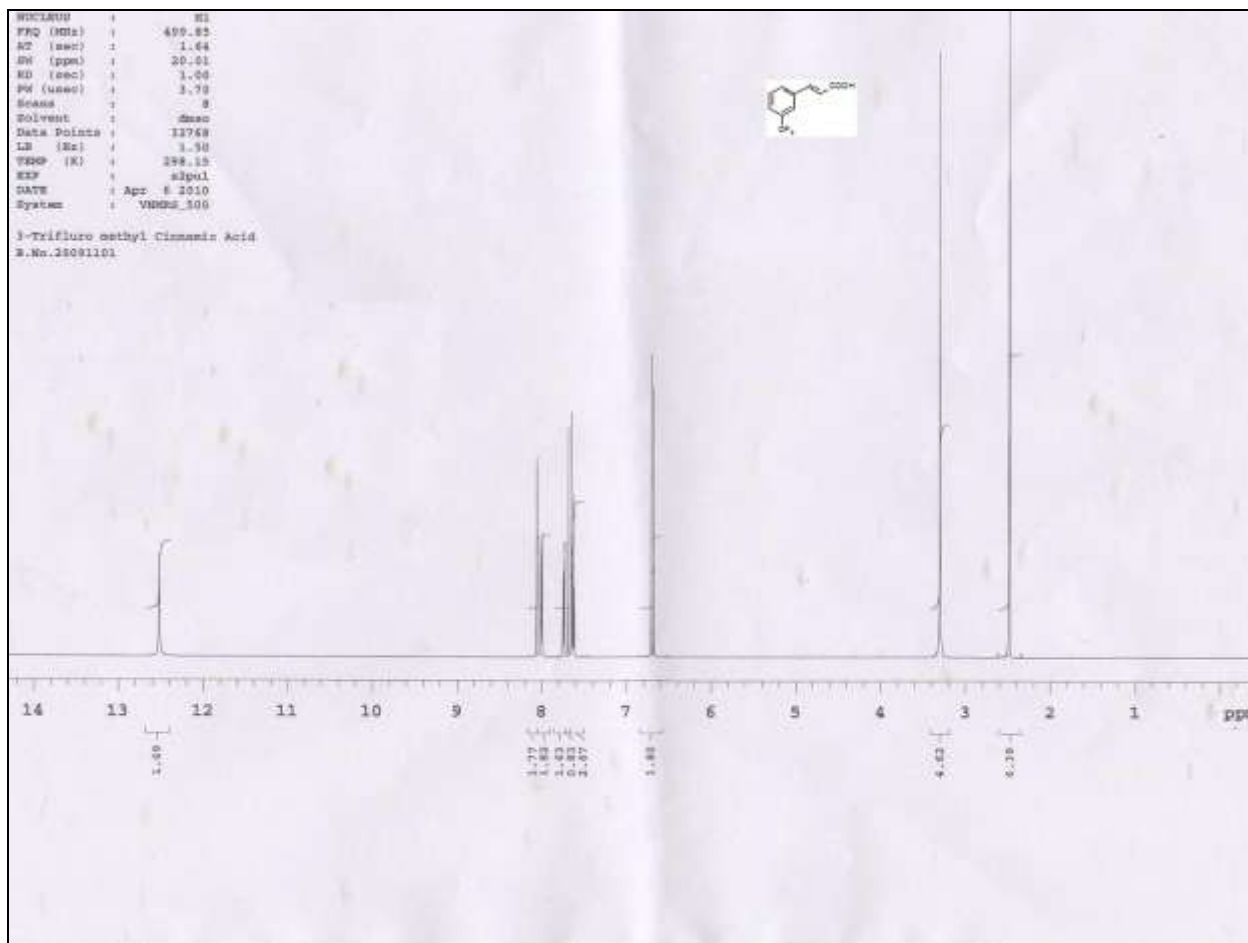


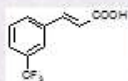
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3	3906.6	7.816	81.2
4	3827.3	7.657	47.9
5	3825.4	7.653	48.7
6	3819.3	7.641	49.4
7	3818.1	7.639	50.2
8	3694.2	7.391	22.0
9	3692.4	7.387	26.0
10	3685.1	7.372	45.2
11	3678.4	7.359	31.3
12	3676.5	7.355	30.5
13	3527.0	7.056	65.8
14	3519.1	7.040	58.6
15	3484.3	6.971	33.4
16	3476.9	6.956	60.8
17	3469.0	6.940	29.7
18	3255.4	6.513	95.7
19	3239.5	6.481	117.5
20	1988.3	3.978	2.5
21	1917.5	3.836	552.3
22	1843.6	3.688	2.9
23	1695.9	3.393	3.2
24	1244.3	2.489	5.3
25	1242.4	2.486	7.4
26	1240.6	2.482	5.5
27	1238.8	2.478	2.6



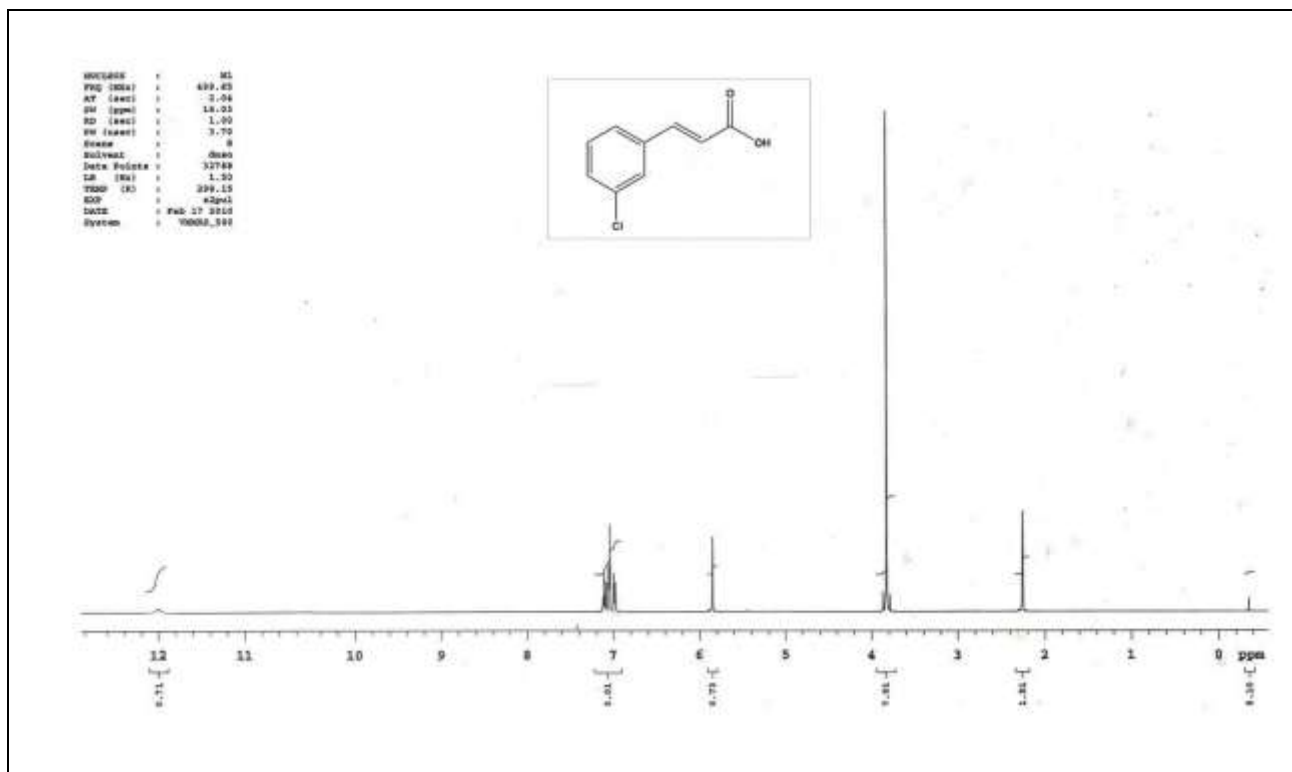


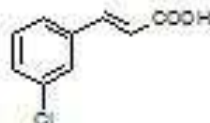
INDEX	FREQUENCY	PPM	HEIGHT
1	6194.2	12.392	7.4
2	3785.2	7.573	75.0
3	3768.7	7.540	79.8
4	3652.7	7.308	36.3
5	3644.8	7.292	75.4
6	3636.8	7.276	52.9
7	3615.5	7.233	72.2
8	3613.7	7.230	64.3
9	3609.4	7.221	64.1
10	3602.1	7.206	41.6
11	3478.8	6.960	39.4
12	3476.3	6.955	37.6
13	3470.8	6.944	35.6
14	3468.4	6.939	33.0
15	3276.7	6.556	98.9
16	3260.9	6.524	87.1
17	1900.4	3.802	3.9
18	1881.5	3.764	511.9
19	1863.2	3.727	4.9
20	1543.3	3.088	5.9
21	1244.3	2.489	4.2
22	1242.4	2.486	5.3
23	1240.6	2.482	4.0



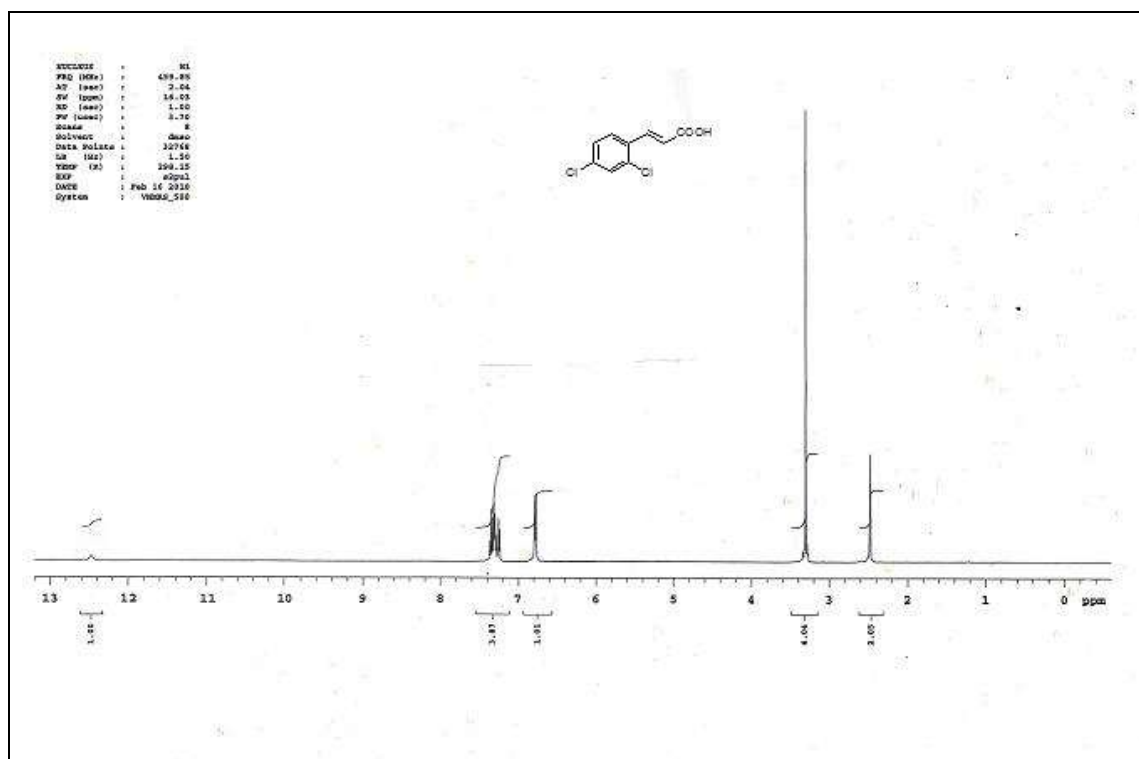


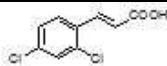
INDEX	FREQUENCY	PPM	HEIGHT
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2	4028.1	8.059	41.6
3	4004.9	8.012	23.9
4	3997.0	7.996	25.6
5	3871.8	7.746	18.0
6	3864.5	7.731	23.9
7	3839.5	7.681	47.8
8	3823.6	7.650	50.8
9	3821.2	7.645	22.6
10	3813.2	7.629	33.5
11	3805.3	7.613	14.0
12	3354.3	6.711	63.2
13	3337.8	6.678	56.5
14	1650.8	3.303	126.0
15	1244.9	2.491	46.2
16	1243.1	2.487	100.4
17	1241.2	2.483	139.0
18	1239.4	2.480	99.2
19	1237.6	2.476	45.6





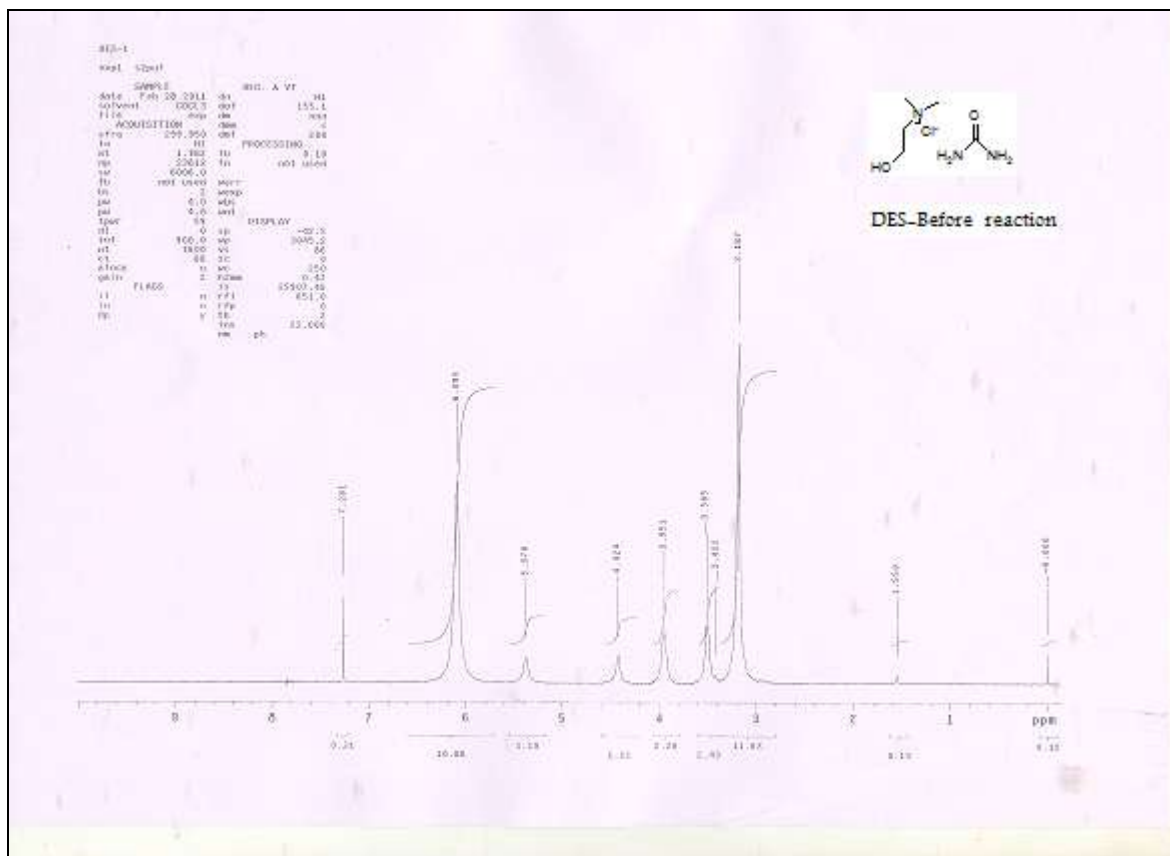
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3	3546.4	7.095	7.9
4	3545.4	7.093	8.2
5	3529.2	7.061	12.1
6	3522.4	7.047	23.3
7	3497.9	6.998	10.4
8	3490.6	6.983	8.1
9	2924.3	5.850	20.0
10	1912.4	3.826	241.0
11	1127.9	2.257	25.3
12	1126.5	2.254	26.9

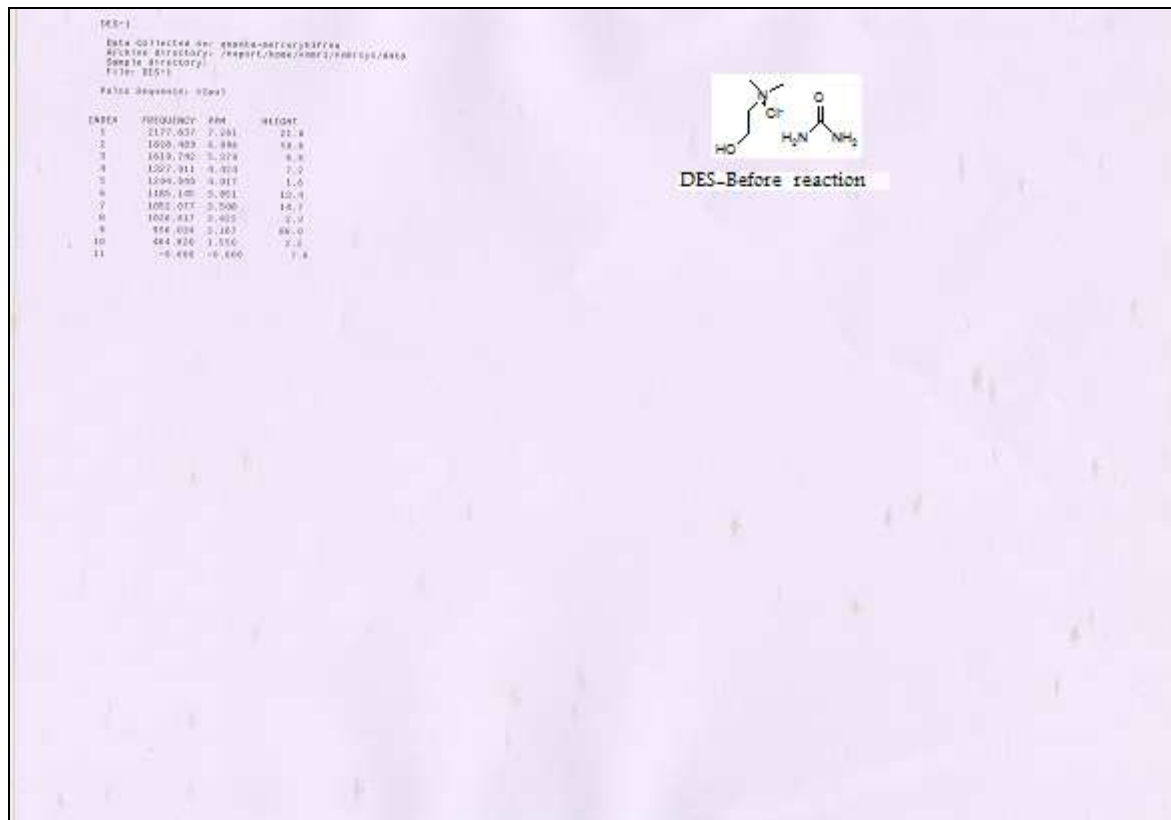




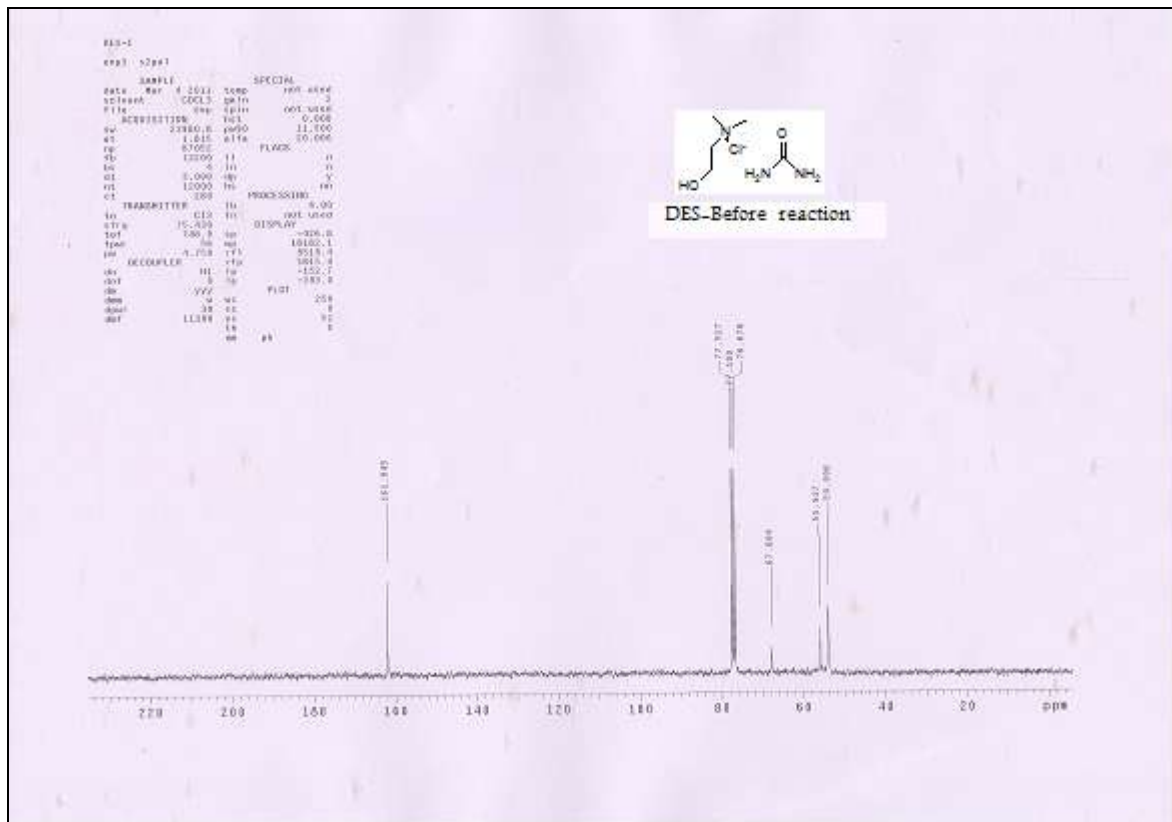
INDEX	FREQUENCY	PPM	HEIGHT
1	6196.2	12.482	3.1
2	3683.8	7.370	16.7
3	3676.0	7.354	42.2
4	3668.6	7.340	35.8
5	3658.8	7.320	50.5
6	3652.5	7.307	38.6
7	3644.7	7.292	21.3
8	3629.0	7.260	34.9
9	3621.7	7.246	26.0
10	3396.7	6.796	53.4
11	3388.4	6.779	55.3
12	1671.3	3.344	8.2
13	1670.3	3.342	8.9
14	1661.0	3.323	11.8
15	1653.7	3.308	363.7
16	1645.8	3.293	8.9
17	1641.9	3.285	15.1
18	1241.4	2.484	84.8
19	1239.9	2.481	86.0

¹H-NMR of DES Before reaction:

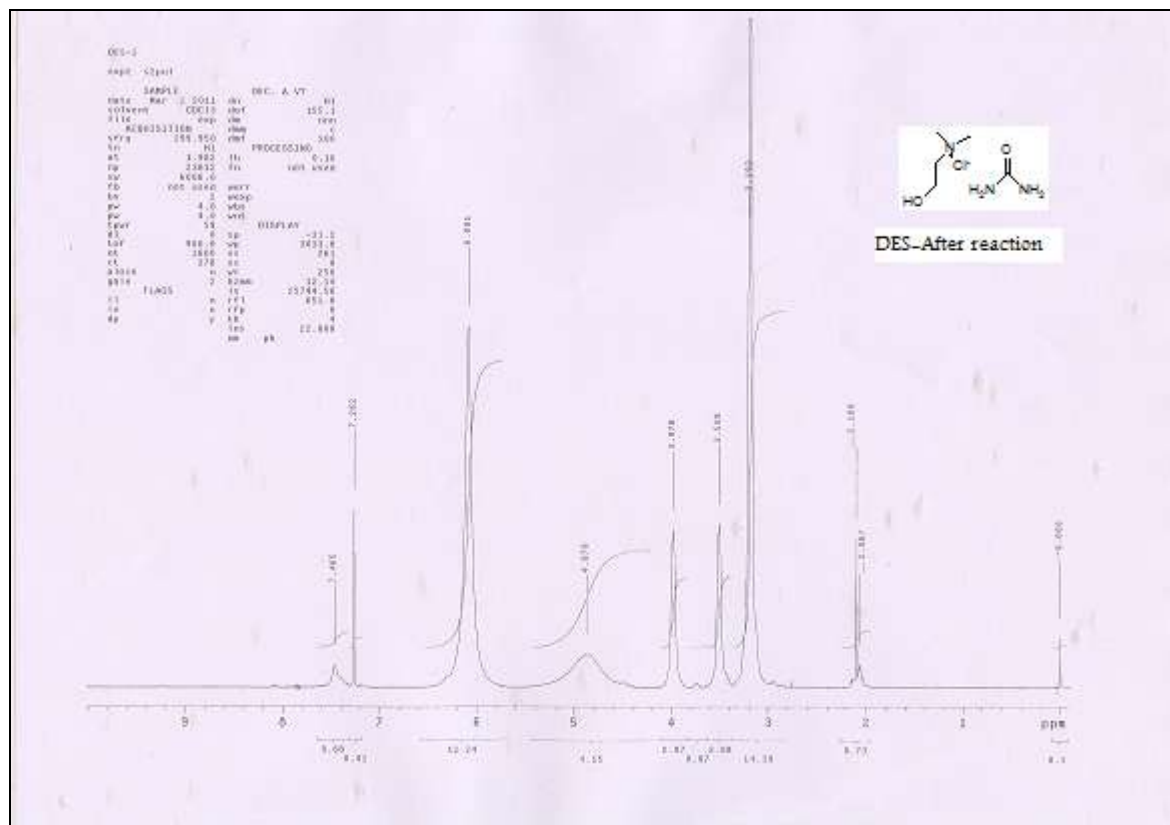


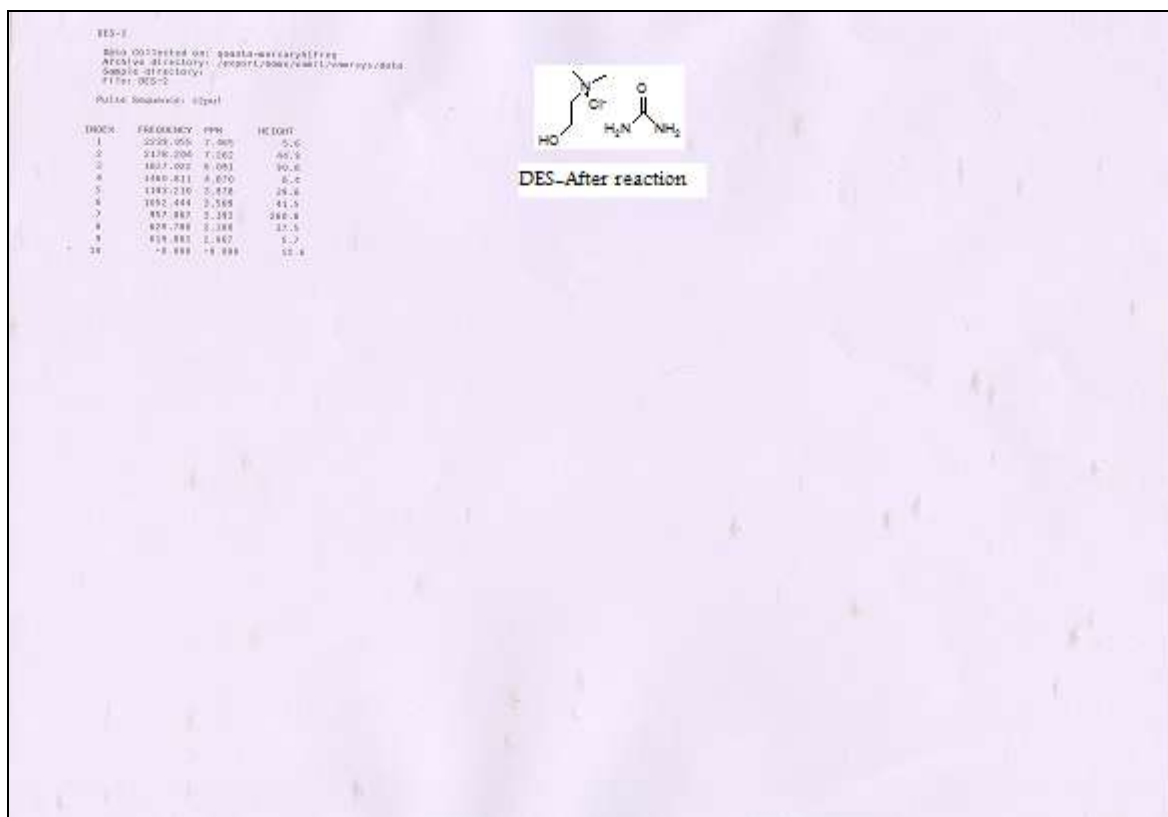


¹³C-NMR of DES Before reaction:



¹H-NMR of DES after reaction:





^{13}C -NMR of DES after reaction:

