Sulfated tungstate: A Highly Efficient Catalyst for Transamidation of Carboxamides with Amines

Sagar P. Pathare, Ashishkumar H. Jain and Krishnacharya G. Akamanchi*

**Department of Pharmaceutical Sciences and Technology,*

Institute of Chemical Technology, Matunga, Mumbai 400 019.

kgap@rediffmail.com

SUPPORTING INFORMATION

Contents

A) Experimental……(01)

B) Copy of HPLC Chromatogram.....(03)

C) Copy of ^{1}H NMR of some selected compounds……(43)

D) Optical Purity Data……..(57)

A) Experimental

a) Reagents:

All chemicals were purchased from Spectrochem Pvt. Ltd. India and were used without further purification.

b) Preparation of sulfated tungstate

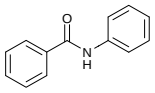
Anhydrous sodium tungstate (32.9g, 0.1mol) was added portionwise, maintaining the temperature between 0 to 5 °C, to a stirred solution of chlorosulfonic acid (23.2g, 0.2mol) in chloroform (150 ml) contained in a 250ml round bottom flask fitted with $CaCl_2$ drying tube, placed in an ice bath. After completion of addition, the mixture was stirred further for 1 h. A yellowish-white solid obtained was filtered, washed repeatedly with deionized water until filtrate was neutral and free from chloride ions (detected by $AgNO_3$ test) and dried in an oven for 2 h at 100 °C to get 34g of sulfated tungstate.

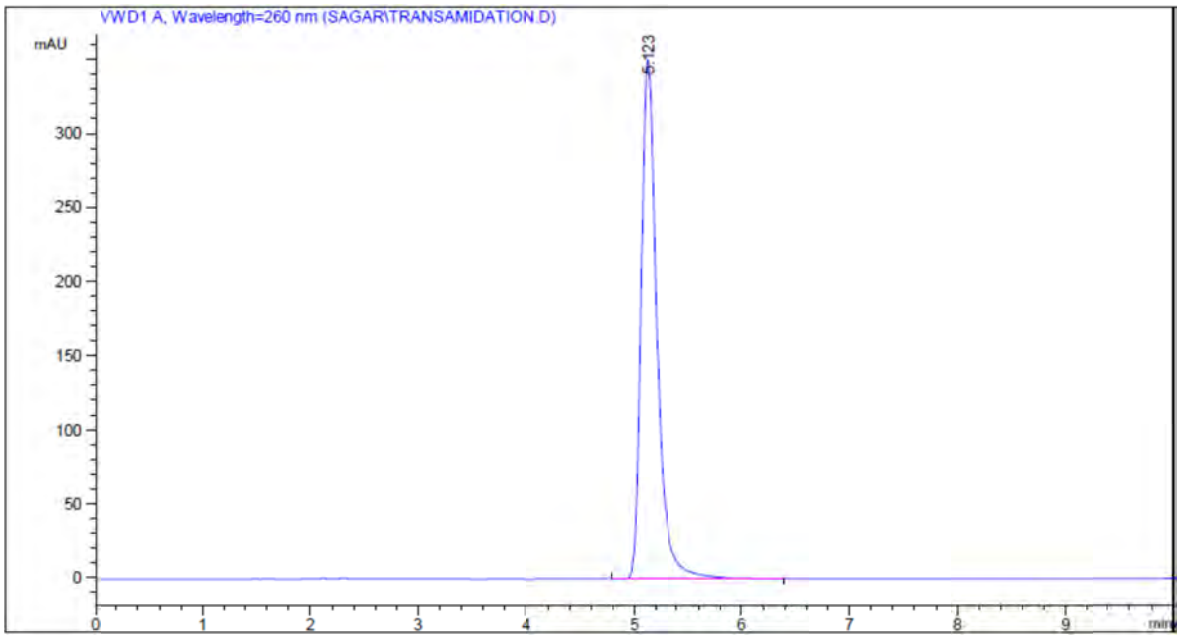
c) General procedure for Transamidation:

Sulfated tungstate (0.40 g, 20 wt%) was added to a solution of benzamide (1g, 9.25 mmol) and benzylamine (1.02g, 9.25 mmol) in toluene (15 ml), and the suspension was stirred at reflux temperature. The progress of the reaction was monitored by TLC. After the completion of the reaction, reaction mixture was cooled and filtered to recover the catalyst. The filtrate was distilled under reduced pressure to remove toluene. The residue obtained was dissolved in ethyl acetate (30 ml), washed with water (10 ml), dried over Na_2SO_4 and concentrated under reduced pressure to give crude product which was purified by chromatography on silica gel (#60-120) with hexane-ethyl acetate (8 : 2) as eluent to get pure *N*-benzylbenzamide as a white solid (Table 1, entry 2).

B) Transamidation HPLC purity Data :

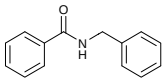
***N*-phenyl benzamide:**

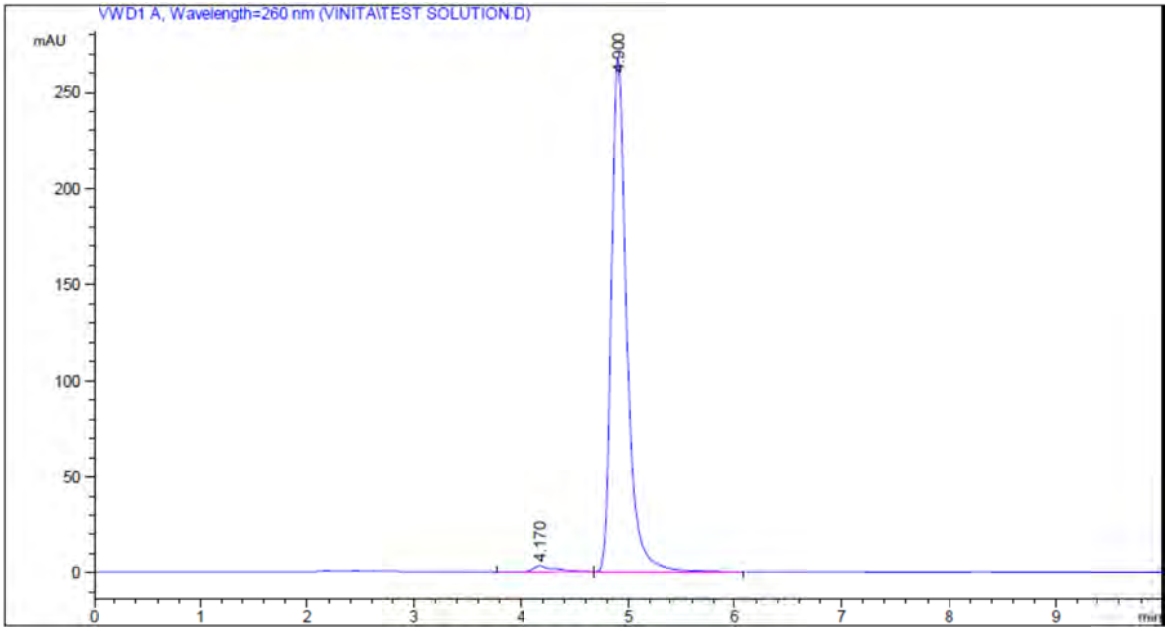




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	5.123	BB	0.1546	3594.54346	350.41006	100
Totals				3594.54346	350.41006	

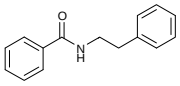
***N*-benzyl benzamide:**

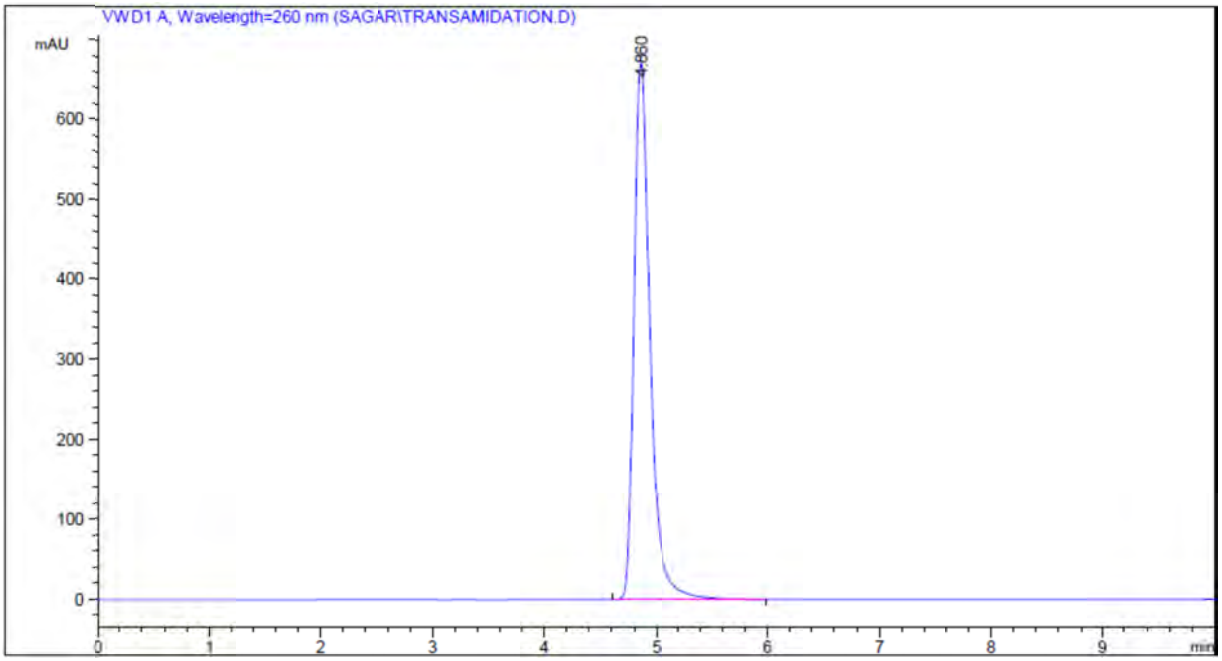




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	4.170	BV	0.2027	46.30233	3.11133	1.7100
2	4.900	VB	0.1510	2661.46021	267.53738	98.2900
Totals				2707.76253	270.64872	

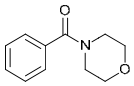
***N*-phenylethylbenzamide**

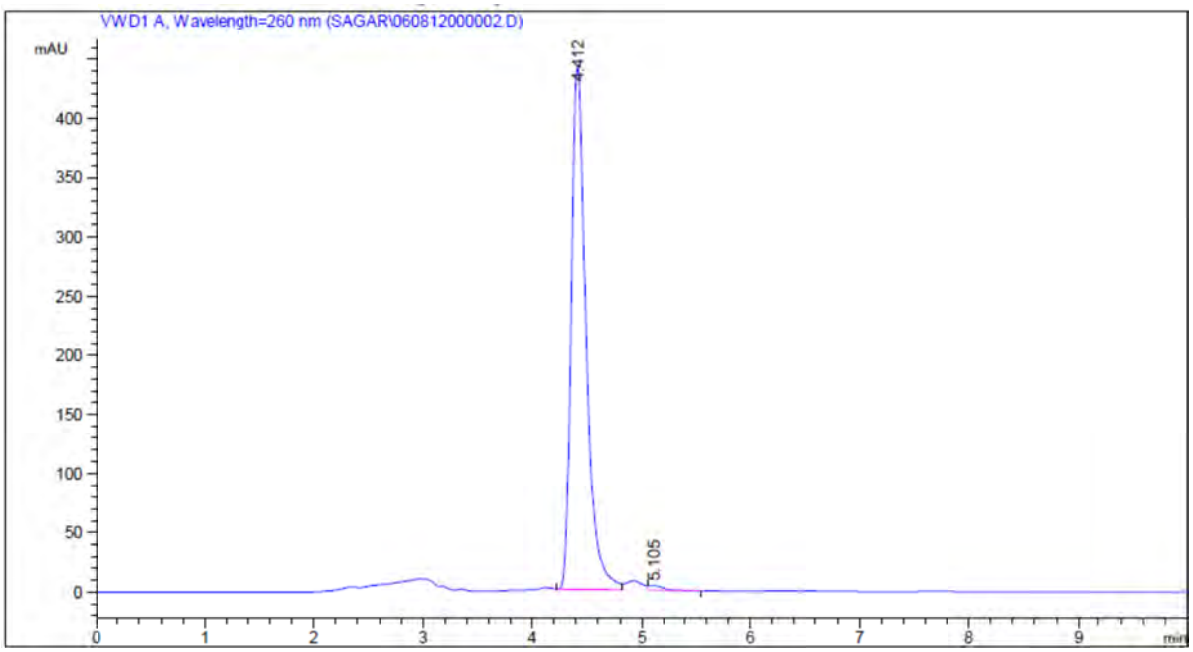




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.860	BB	0.1521	6755.10205	672.60925	100
Totals				6755.10205	672.60925	

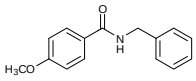
***N*-benzoylmorpholine:**

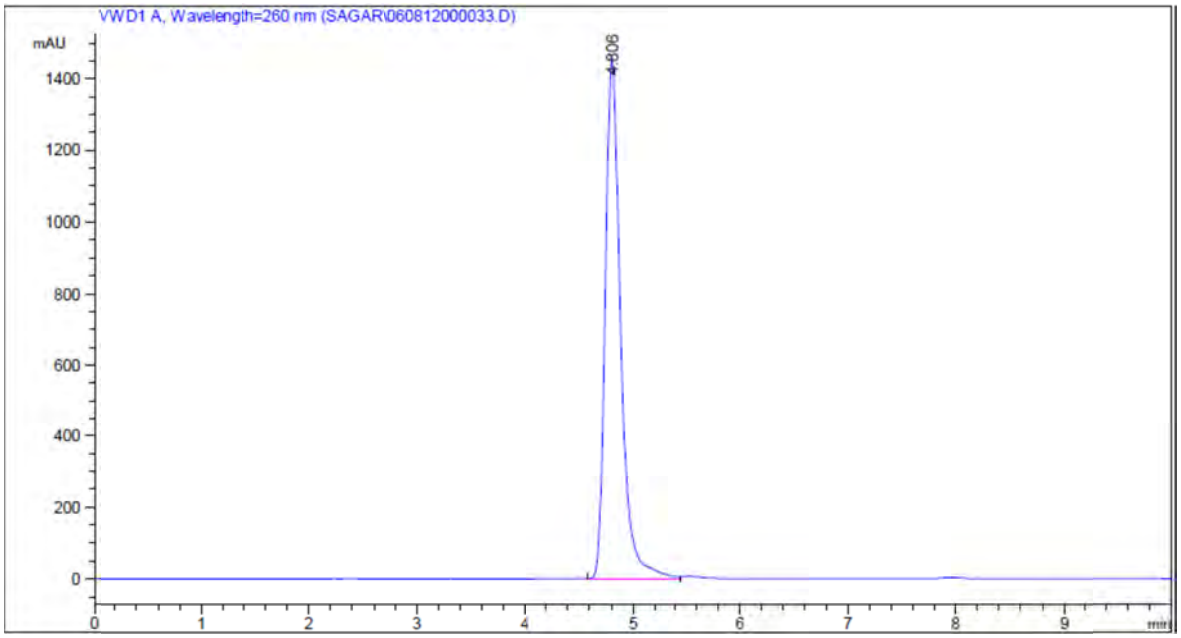




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.412	BV	0.1428	4138.49365	441.67966	99.0757
2	5.105	VB	0.1414	38.61065	4.01119	0.9243
Totals				4177.10430	445.69085	

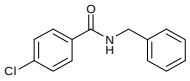
***N*-benzyl-4-methoxybenzamide**

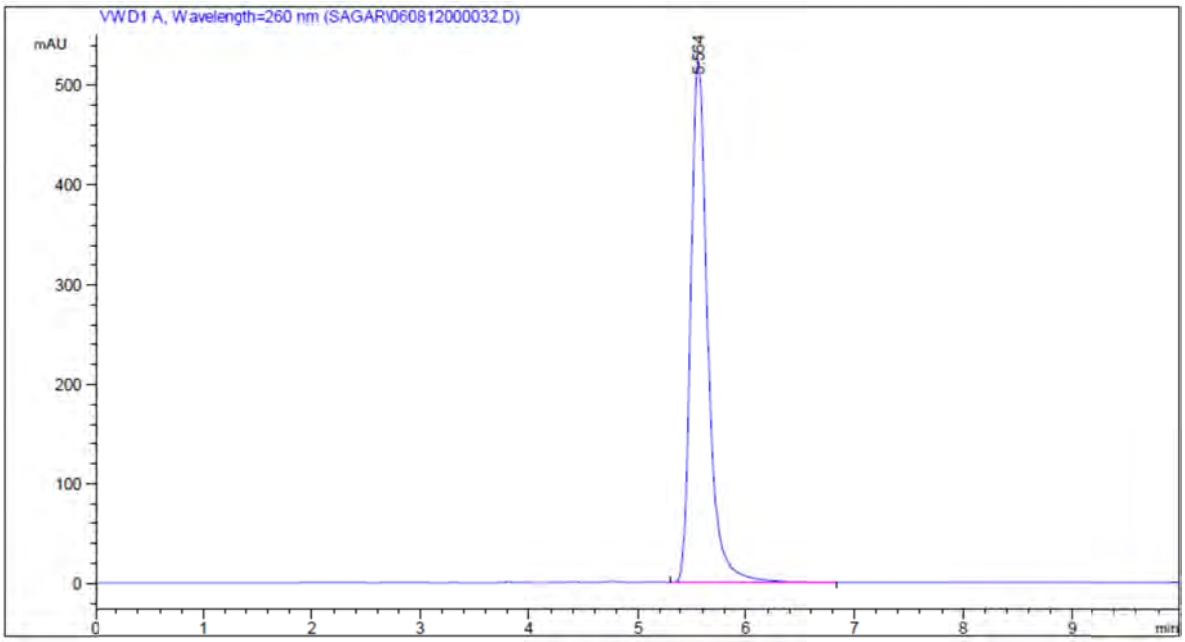




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	4.806	BV	0.1491	1.43681e4	1450.04688	100
Totals				1.43681e4	1450.04688	

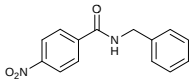
***N*-benzyl-4-chlorobenzamide**

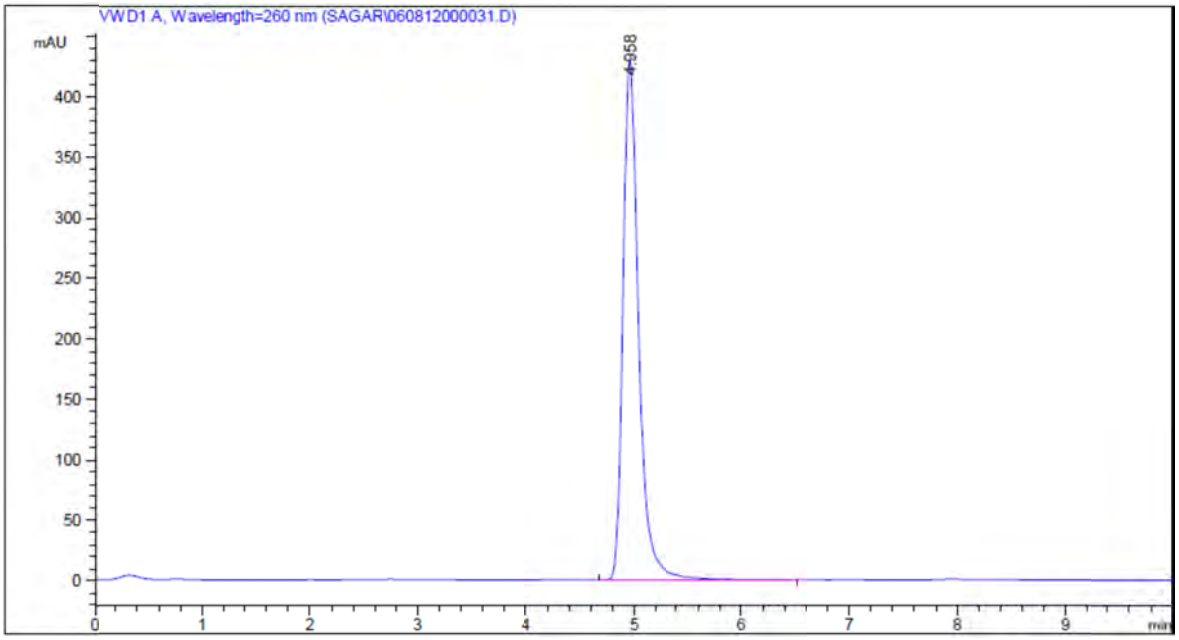




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	5.564	VB	0.1640	5666.91162	524.22565	100
Totals				5666.91162	524.22565	

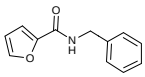
***N*-benzyl-4-nitrobenzamide**

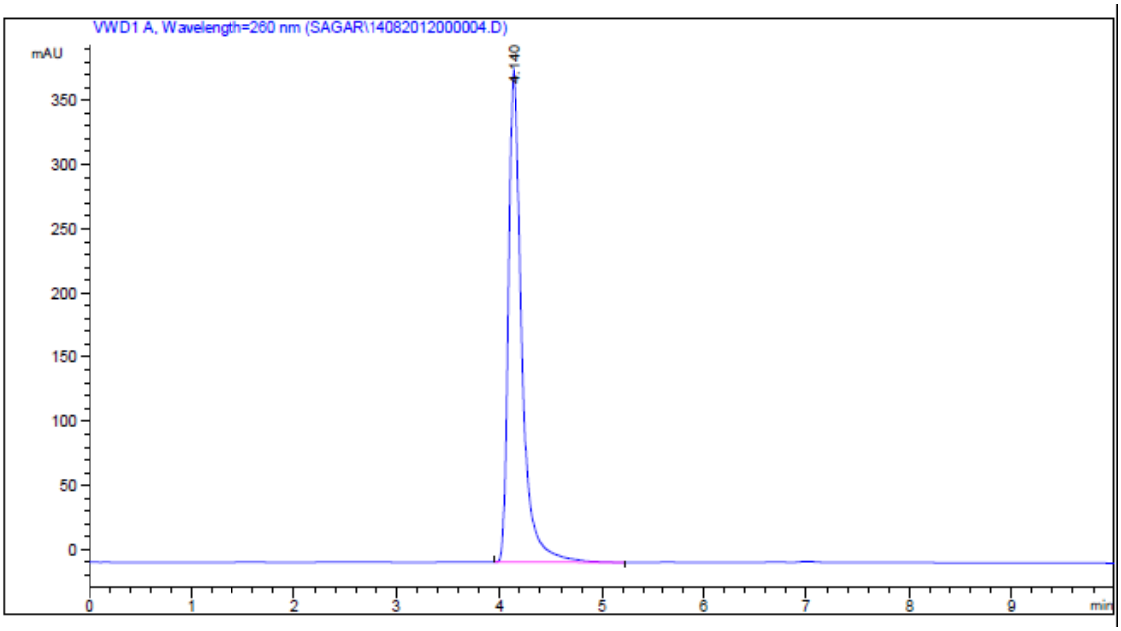




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	4.958	BB	0.1517	4303.97510	430.22739	100
Totals				4303.97510	430.22739	

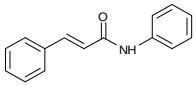
***N*-benzyl furamide**

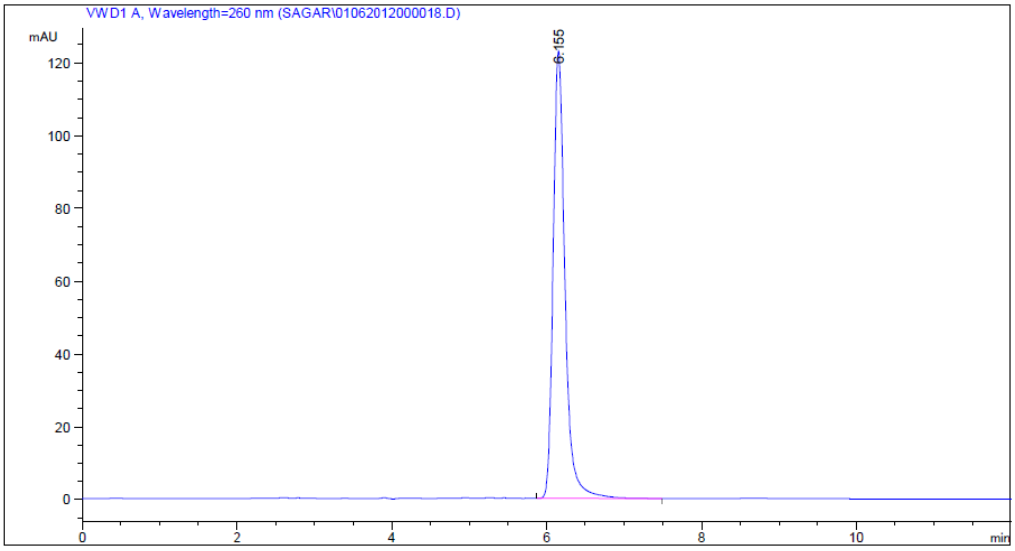




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.140	BB	0.1417	3604.86011	383.63824	100.0000
Totals :				3604.86011	383.63824	

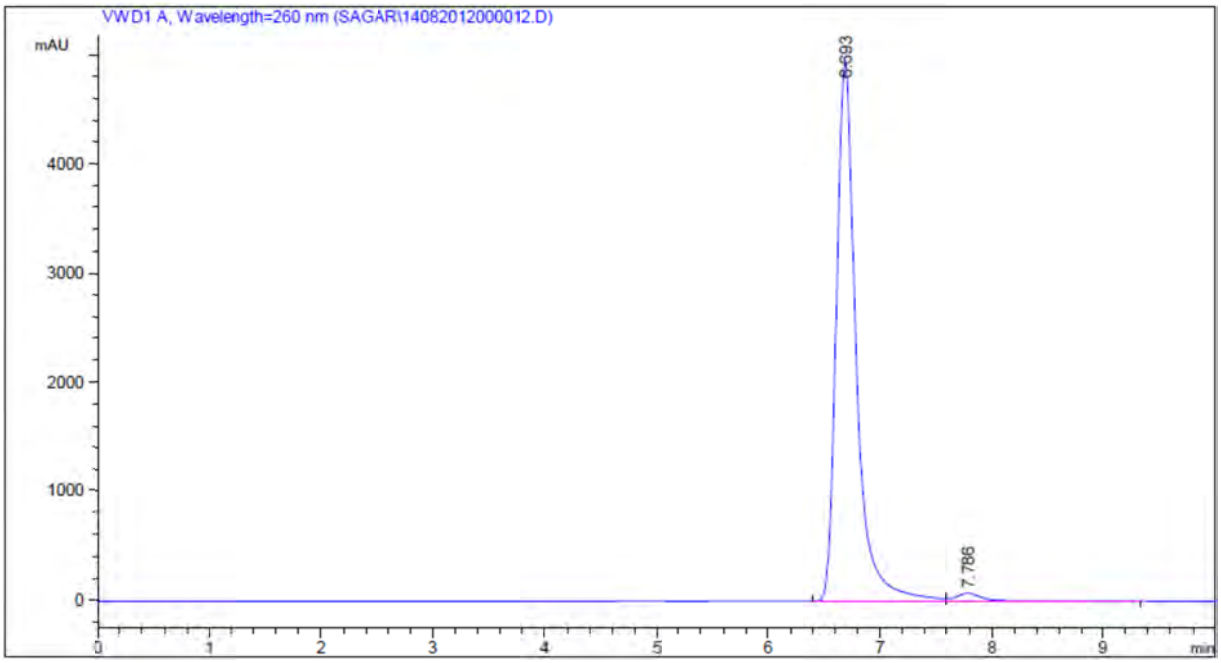
_N_-phenylcinnamamide





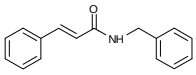
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.155	BB	0.1591	1292.47974	122.87954	100.0000
Totals :				1292.47974	122.87954	

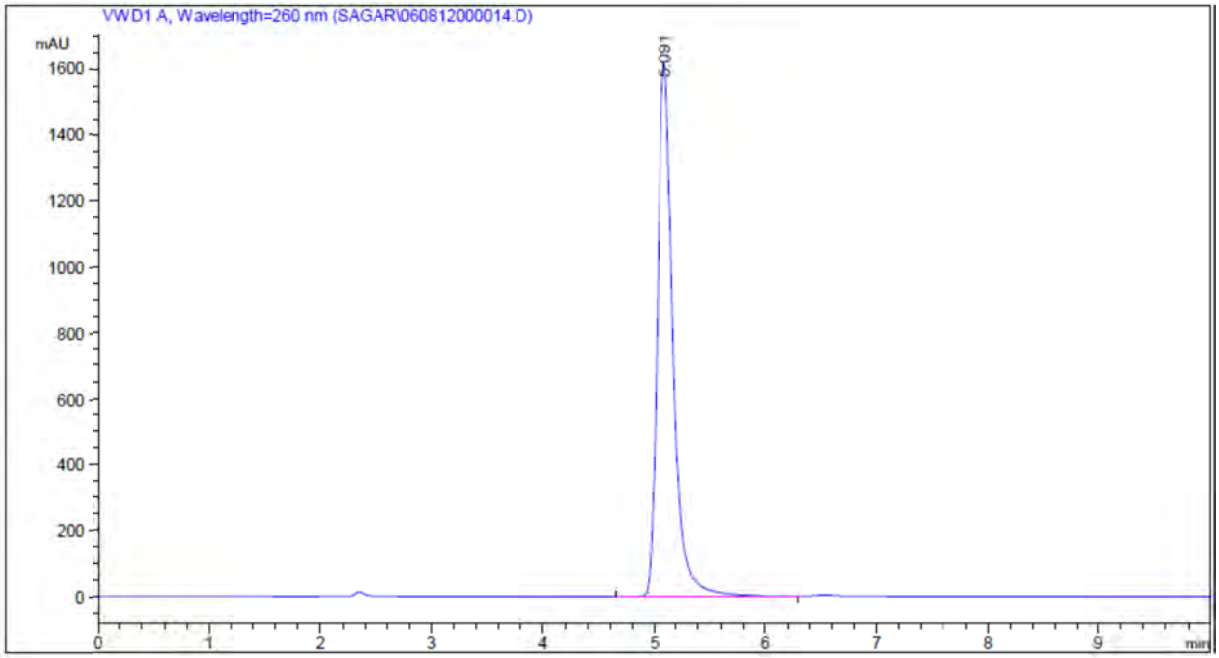
***N*-(4-chlorophenyl)cinnamamide**



Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	6.693	BV	0.1870	6.05722e4	4931.37012	98.1196
2	7.786	VB	0.2360	1160.79785	72.62513	1.8804
Totals				6.17330e4	5003.99525	

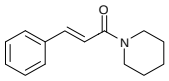
***N*-benzylcinnamamide**

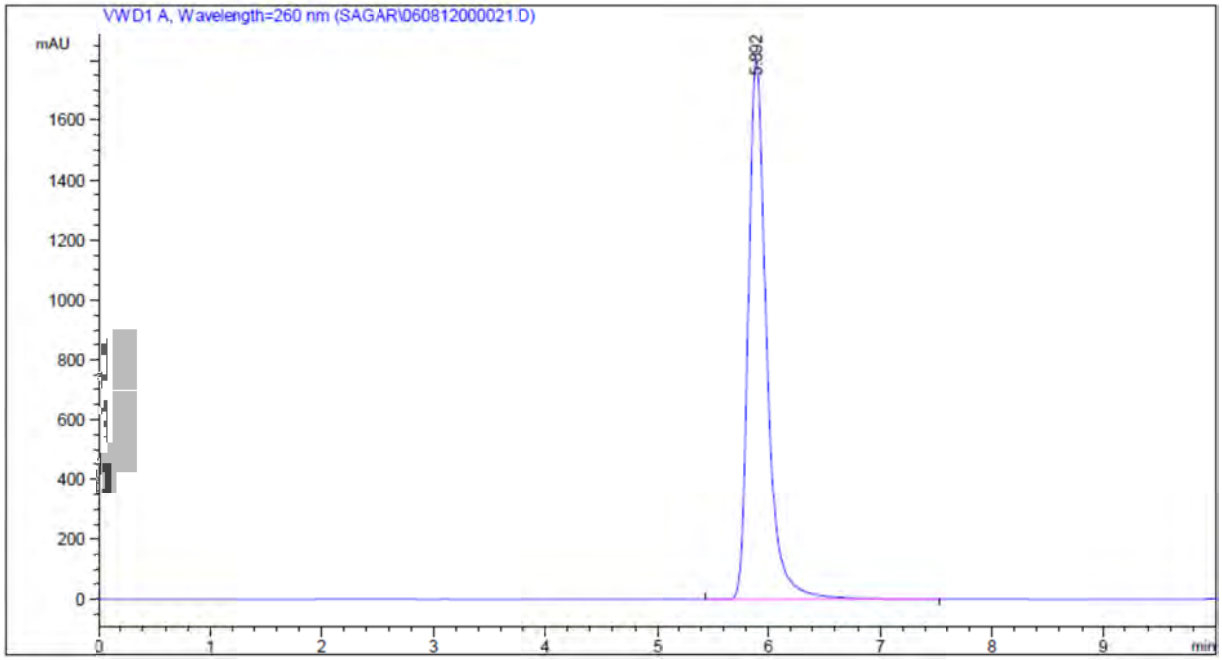




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	5.091	BV	0.1536	1.64958e4	1621.63037	100
Totals				1.64958e4	1621.63037	

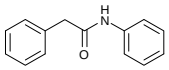
***N*-cinnamamide piperidine :**

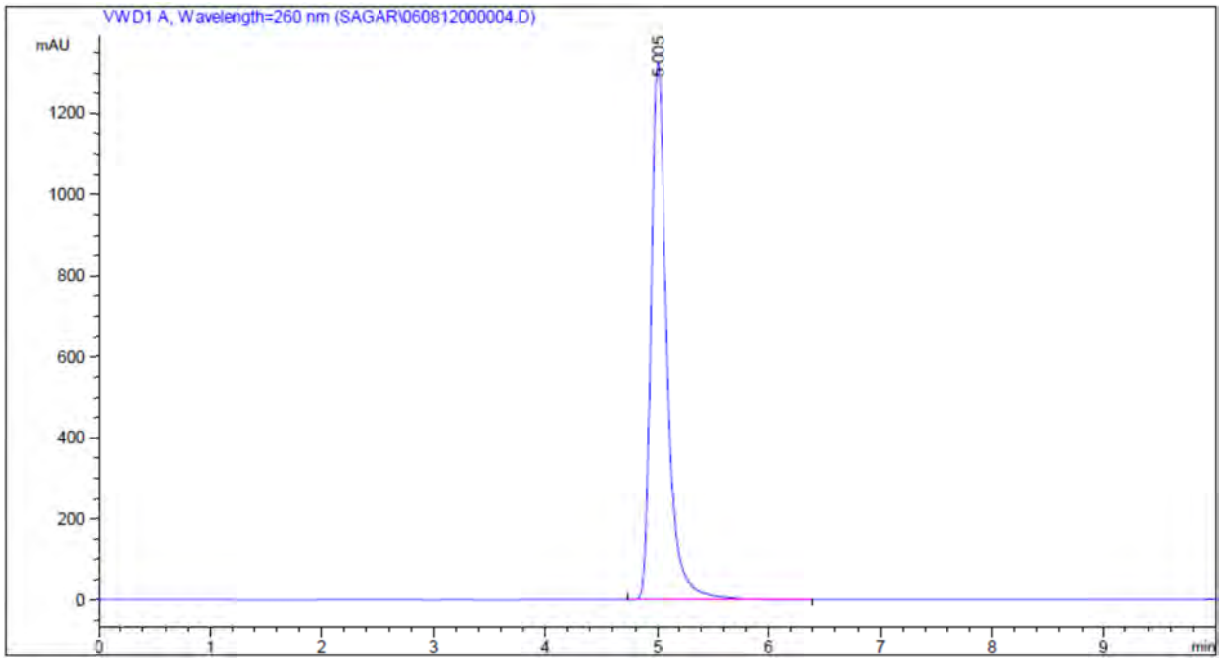




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	5.892	BB	0.1714	2.03518e4	1797.35193	100
Totals				2.03518e4	1797.35193	

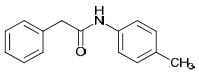
***N*-phenyl-2-phenylacetamide**

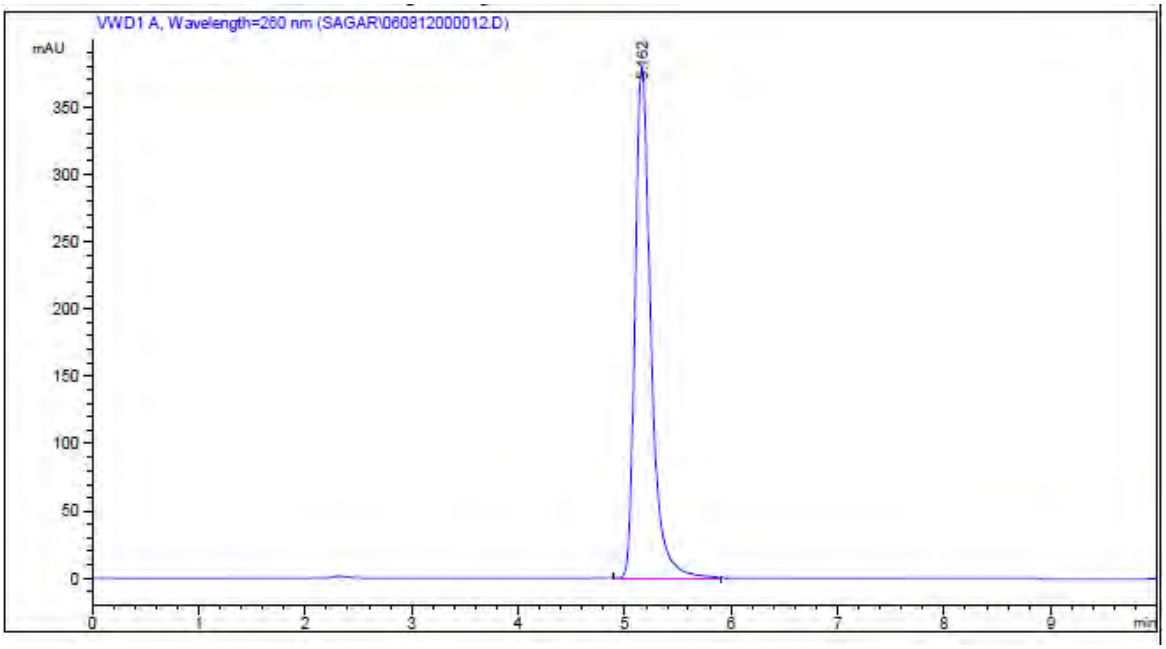




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	5.005	BB	0.1569	1.36917e4	1325.22571	100
Totals				1.36917e4	1325.22571	

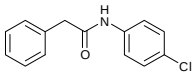
***N*-(4-methyl phenyl)-2-phenylacetamide**

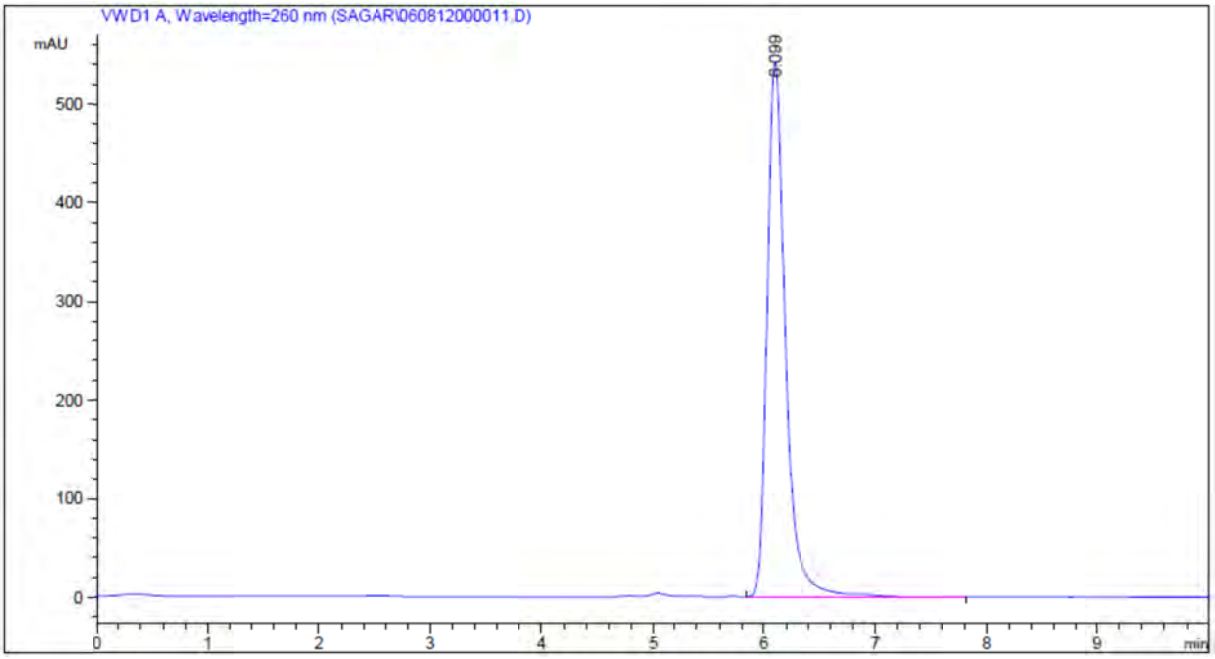




Peak #	*Ret Time [min]*	*Type*	*Width [min]*	*Area mAU*S*	*Hight [mAU]*	*Area %*
1	*5.162*	*VV*	*0.1556*	*3936.91406*	*380.60452*	*100*
Totals				*3936.91406*	*380.60452*	

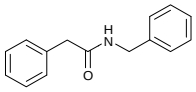
***N*-(4-chloro phenyl)-2-phenylacetamide**

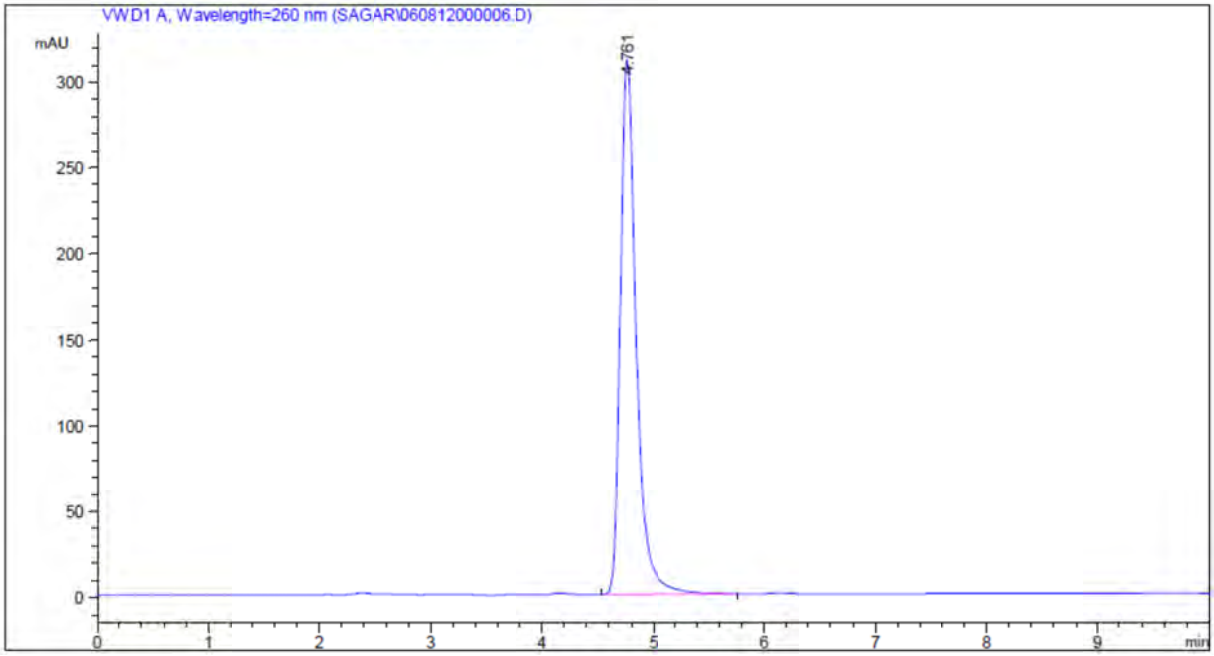




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	6.099	VB	0.1748	6225.19043	541.93048	100
Totals				6225.19043	541.93048	

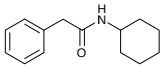
***N*-benzyl-2-phenylacetamide**

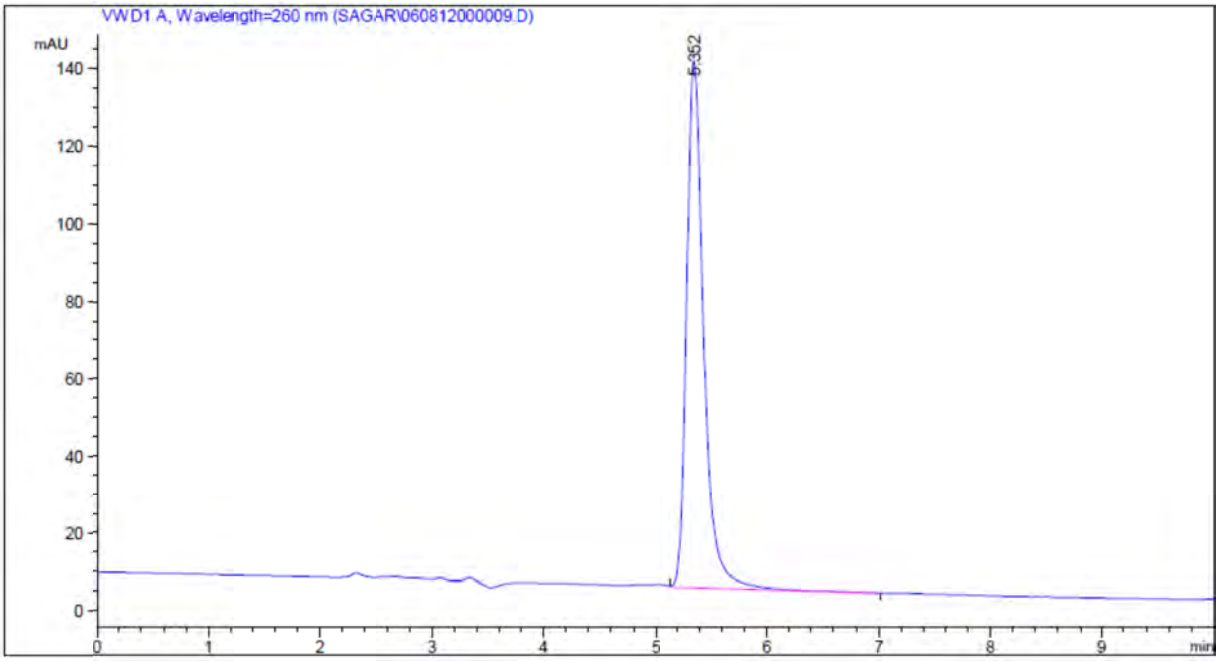




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	4.761	BB	0.1489	3073,09204	310.51840	100
Totals				3073,09204	310.51840	

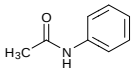
***N*-cyclohexyl-2-phenylacetamide**

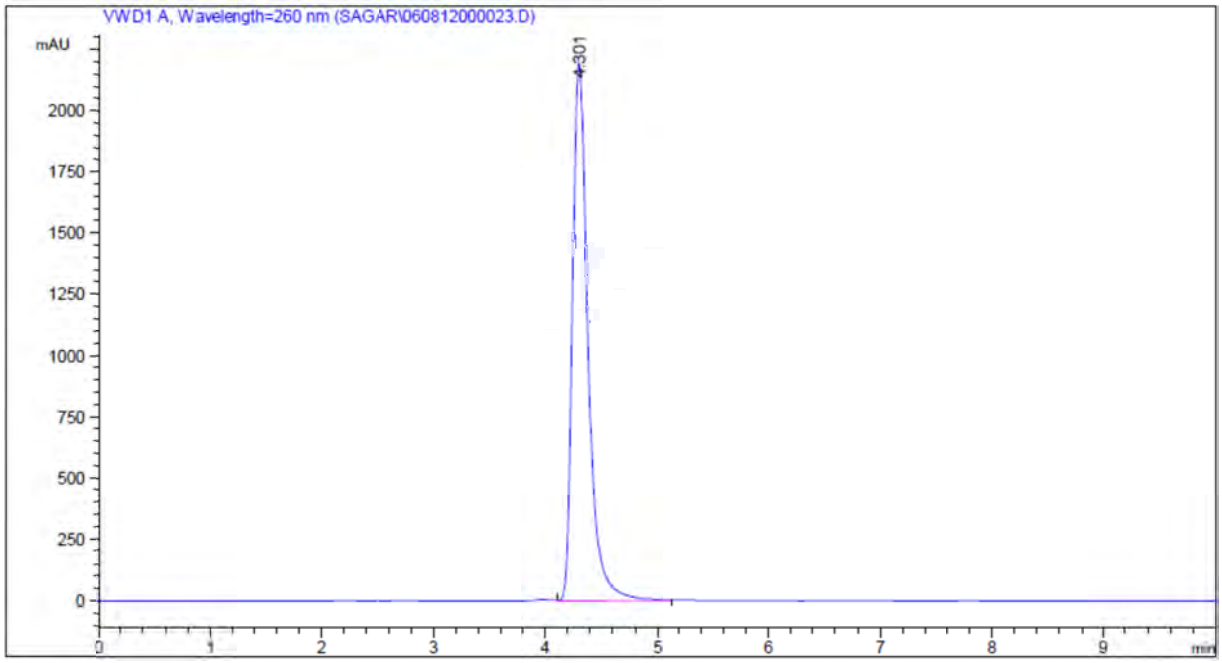




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	5.352	VB	0.1611	1436.71448	135.97876	100
Totals				1436.71448	135.97876	

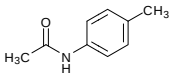
***N*-phenylacetamide**

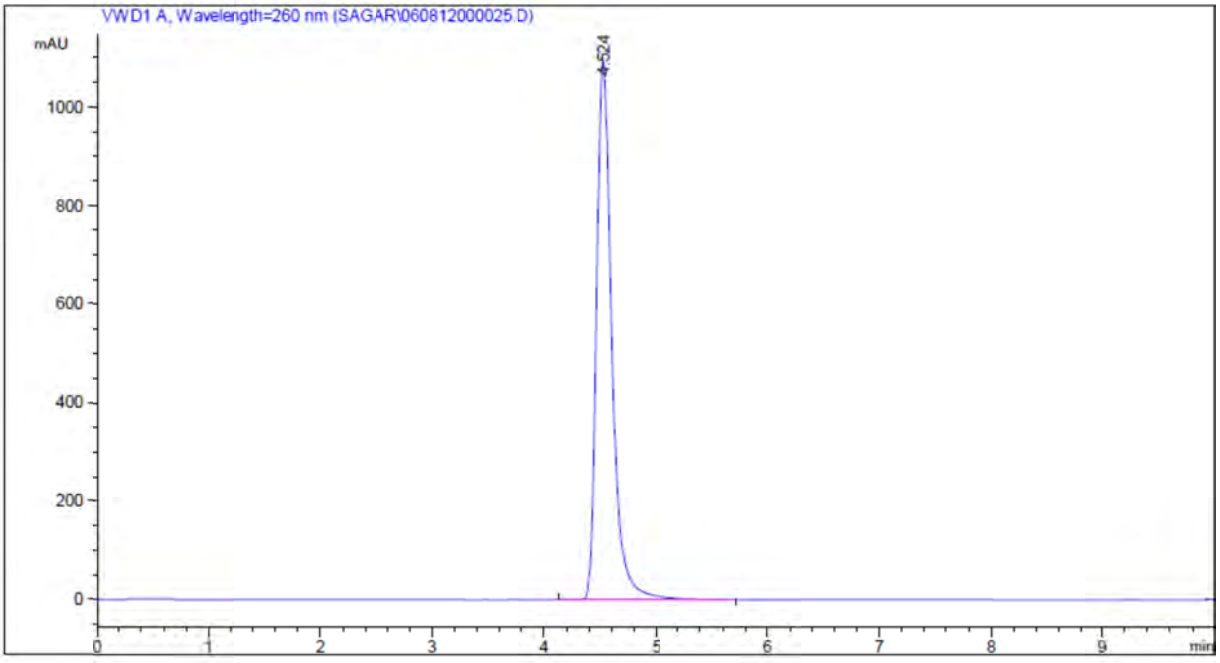




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.301	VV	0. 1456	2.10988e4	2196.25146	100
Totals				2.10988e4	2196.25146	

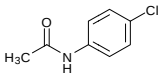
***N*-(4-methylphenyl)acetamide**

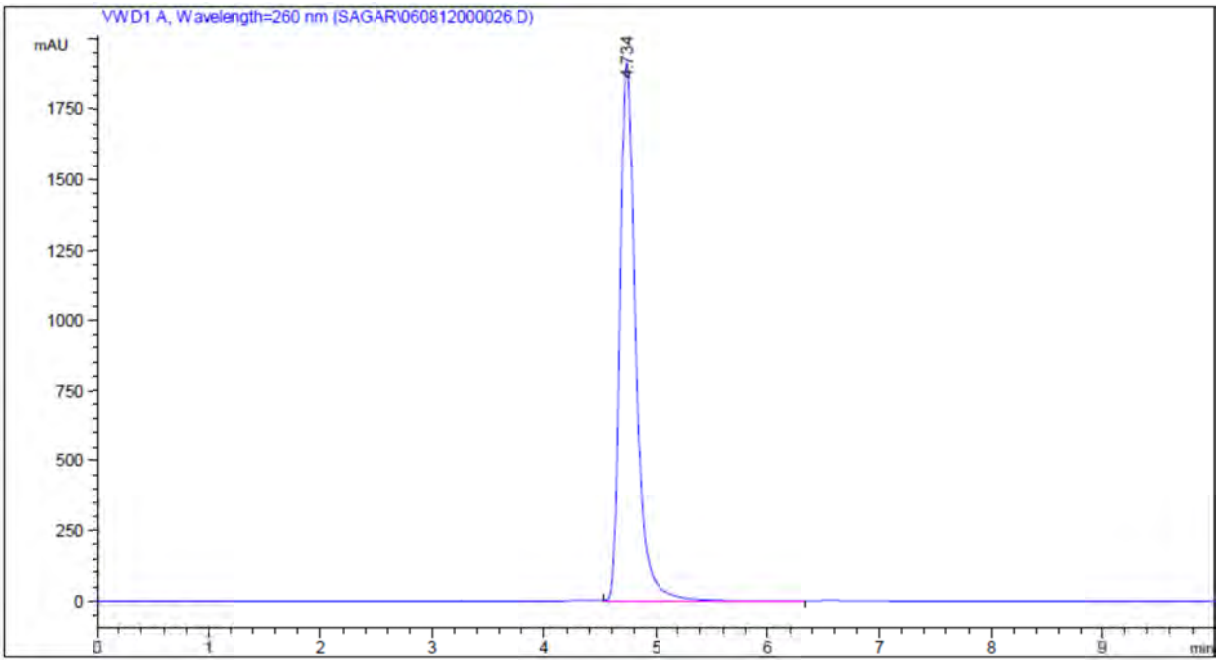




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	4.524	BV	0. 1440	1.03496e4	1092.24756	100
Totals				1.03496e4	1092.24756	

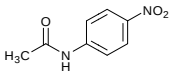
***N*-(4-chlorophenyl)acetamide**

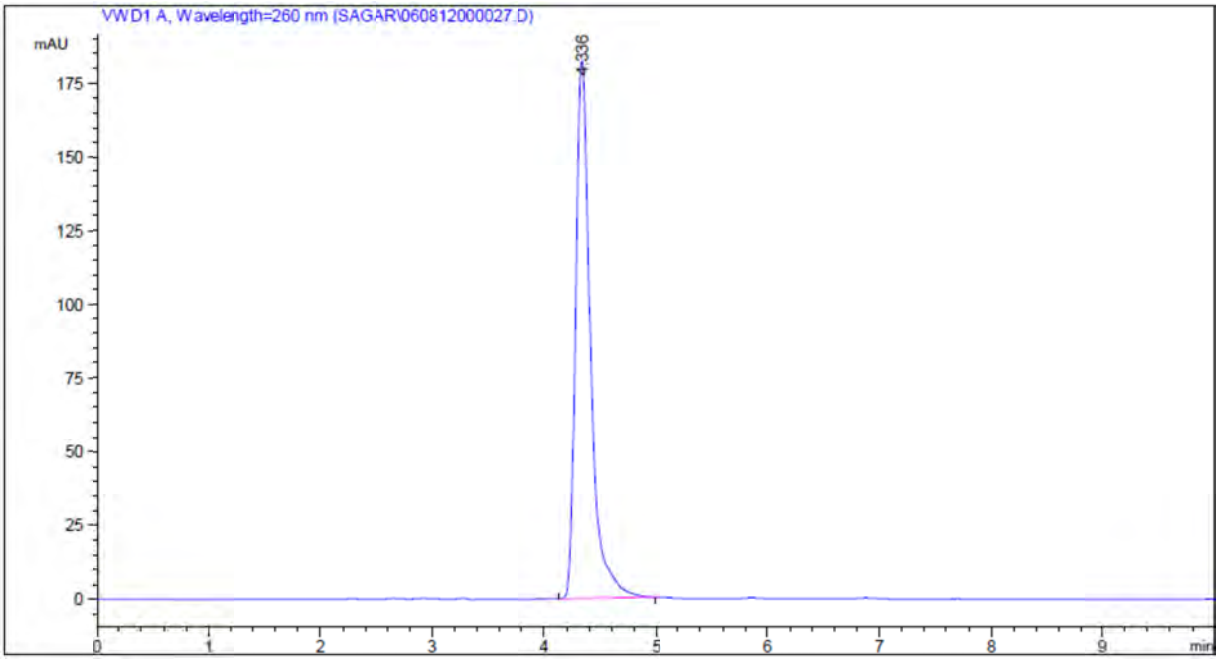




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	4.734	VB	0. 1505	1.89470e4	1913.21802	100
Totals				1.89470e4	1913.21802	

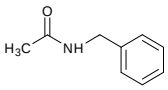
***N*-(4-nitrophenyl)acetamide**

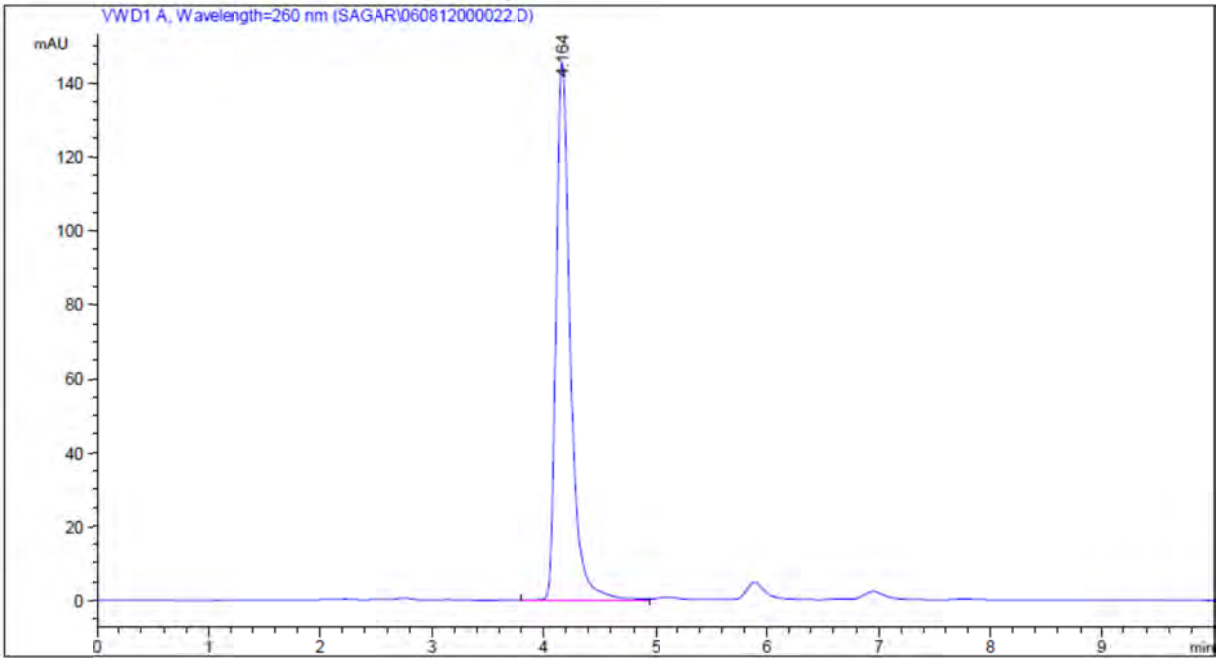




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.336	BB	0. 1375	1667.35596	181.91312	100
Totals				1667.35596	181.91312	

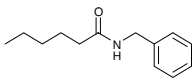
***N*-benzyl acetamide**

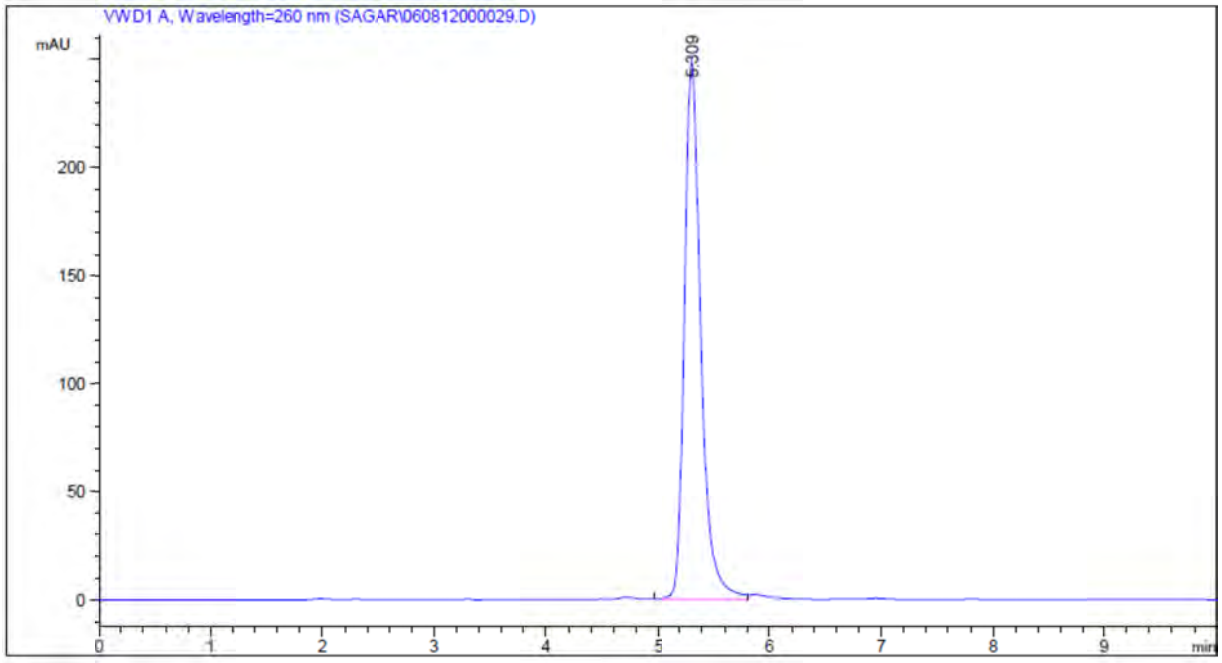




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.164	BV	0. 1330	1278.44934	145.59338	100
Totals				1278.44934	145.59338	

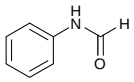
***N*-benzyl hexanamide**

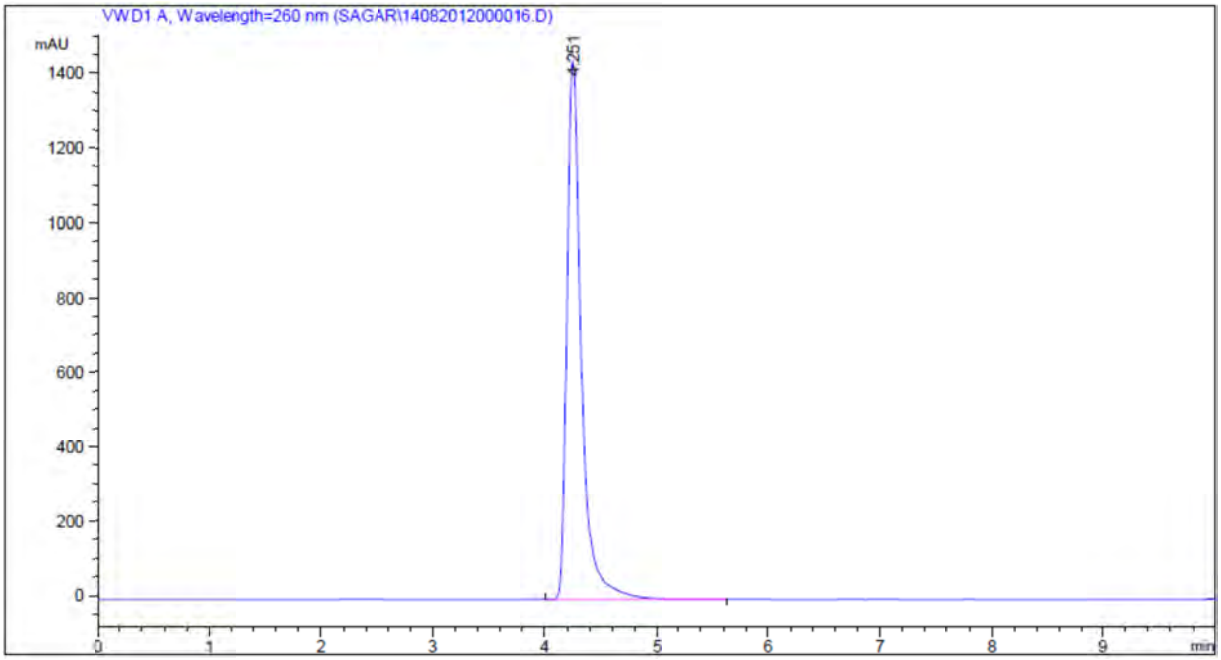




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	5.309	BV	0. 1553	2528.16309	248.07887	100
Totals				2528.16309	248.07887	

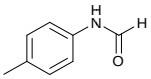
***N*-phenylformamide**

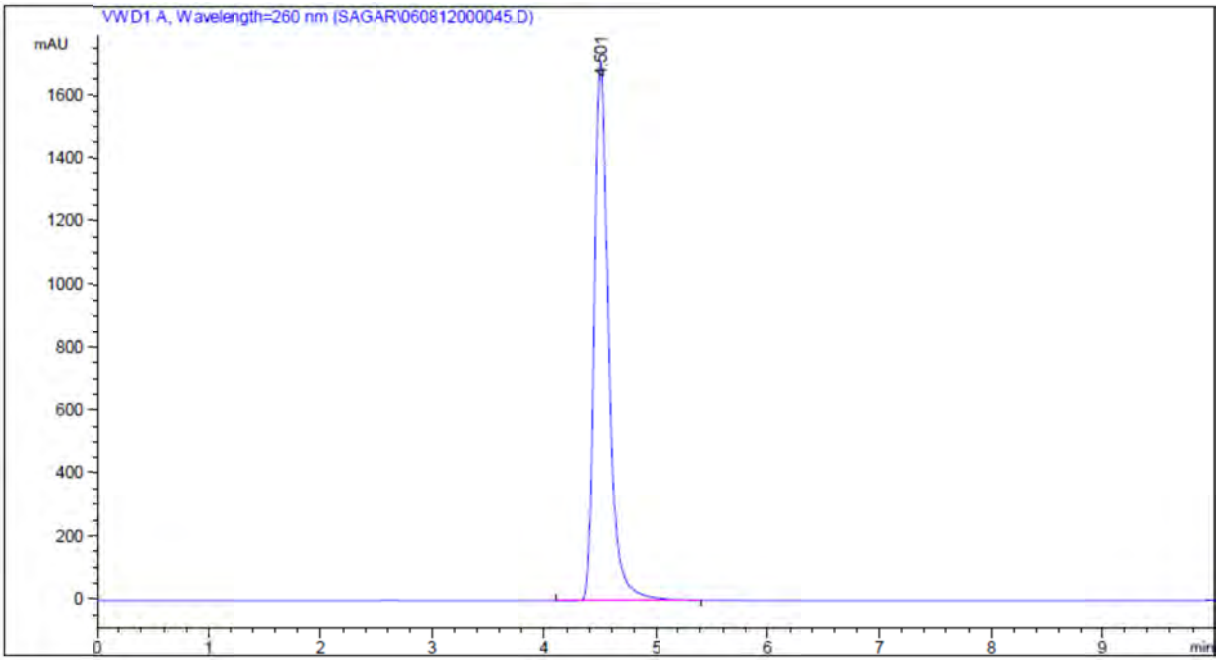




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	4.251	VB	0. 1333	1.28796e4	1441.82849	100
Totals				1.28796e4	1441.82849	

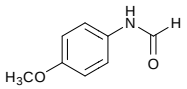
***N*-(4-methylphenyl)formamide**

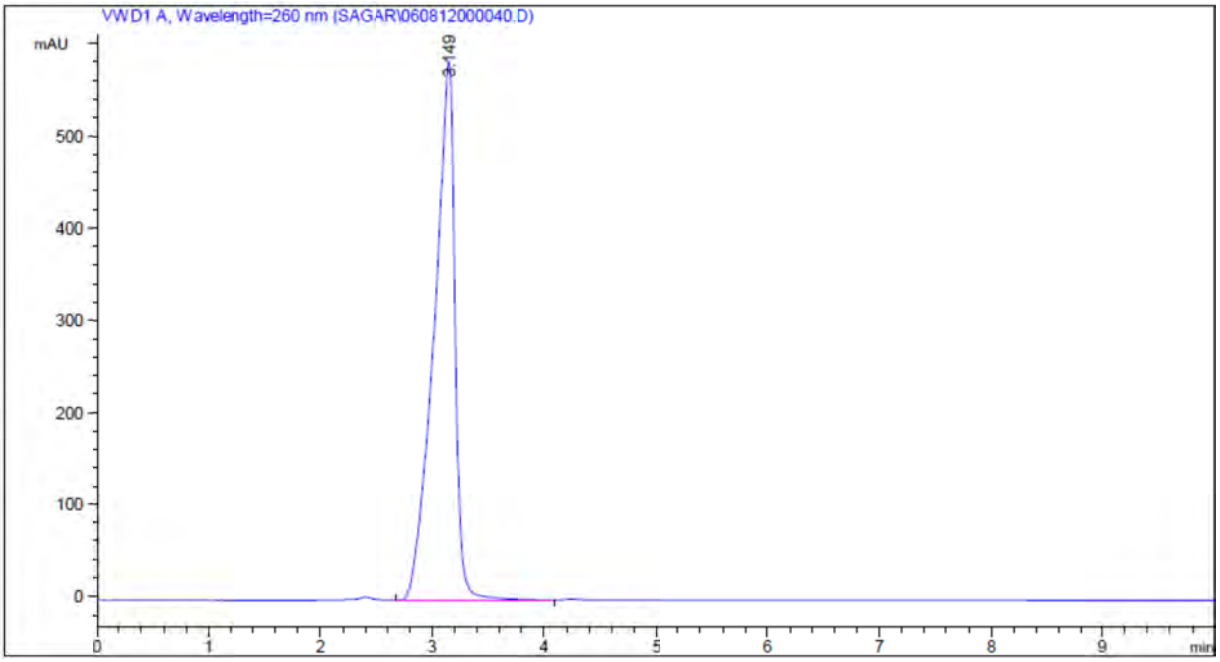




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.501	BV	0. 1346	1.52463e4	1709.85718	100
Totals				1.52463e4	1709.85718	

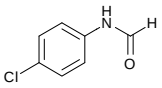
***N*-(4-methoxyphenyl)formamide**

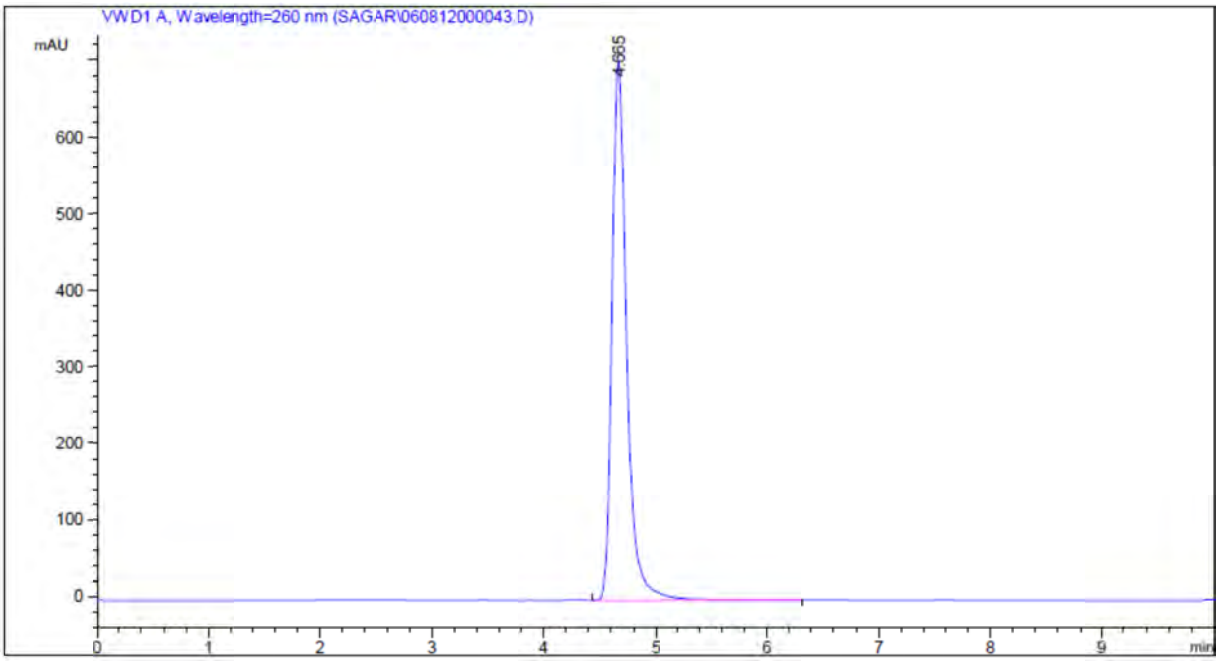




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	3.149	VV	0. 1810	7527.37988	583.72052	100
Totals				7527.37988	583.72052	

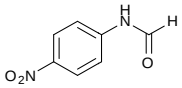
***N*-(4-chlorophenyl)formamide**

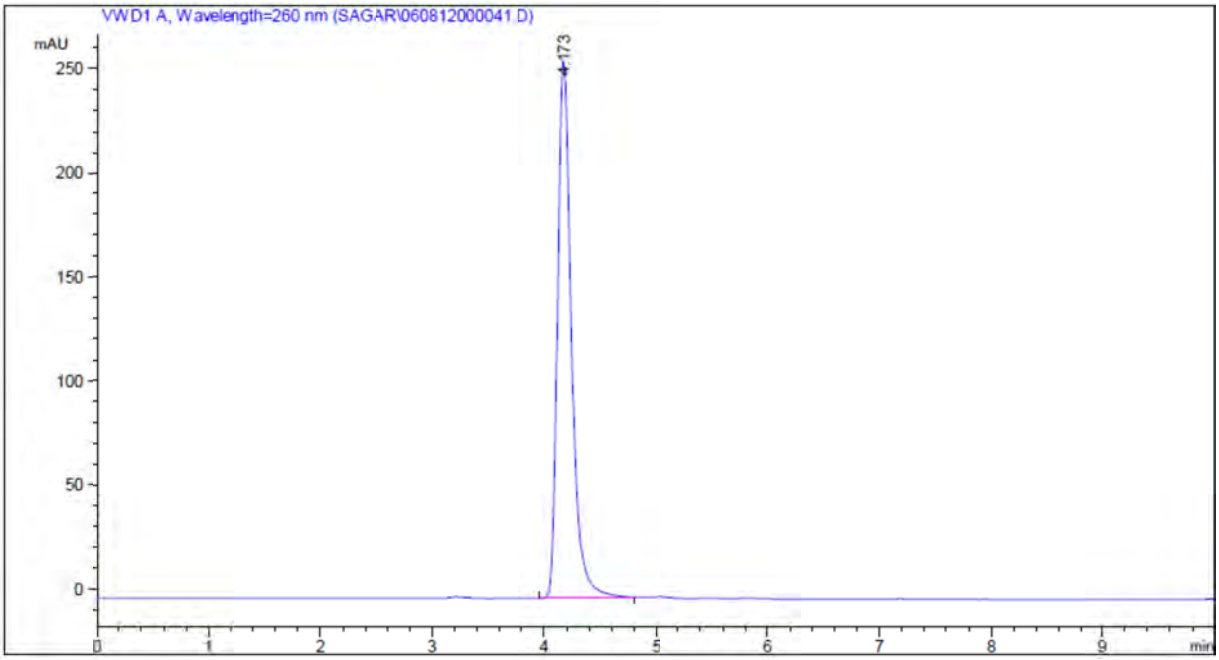




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.665	VB	0. 1360	6349.87598	702.43195	100
Totals				6349.87598	702.43195	

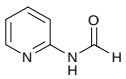
***N*-(4-nitrophenyl)formamide**

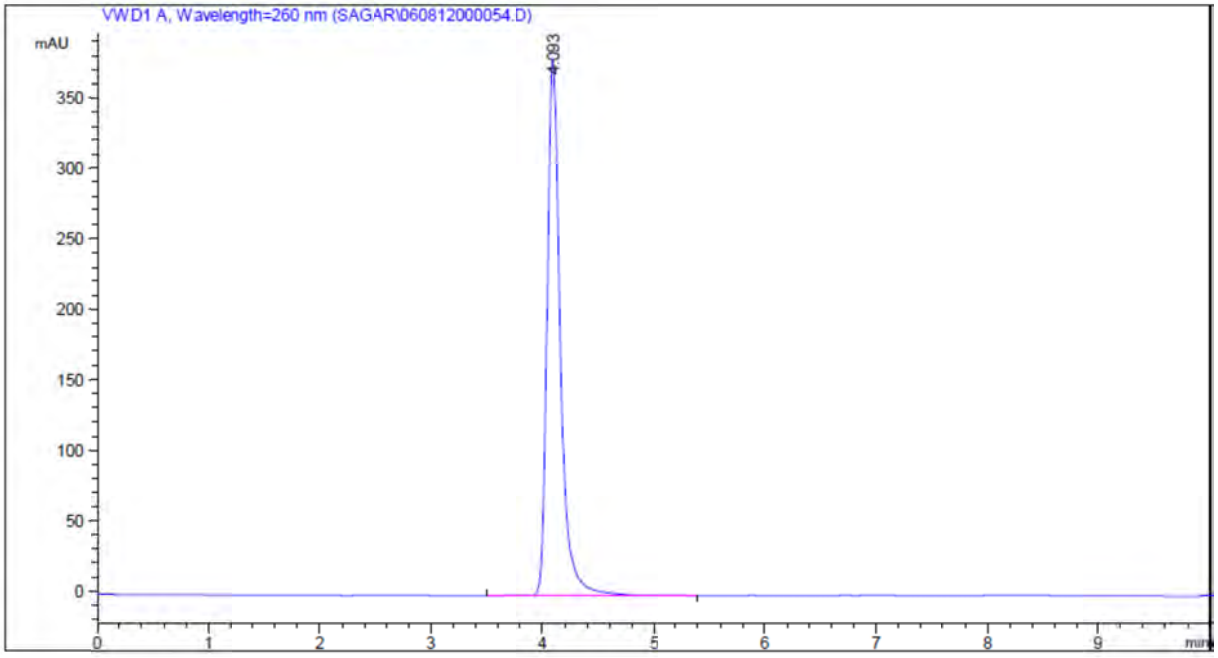




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.173	BV	0. 1310	2218.66553	257.80832	100
Totals				2218.66553	257.80832	

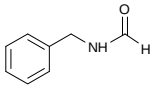
***N*-(pyridin-2-yl)formamide**

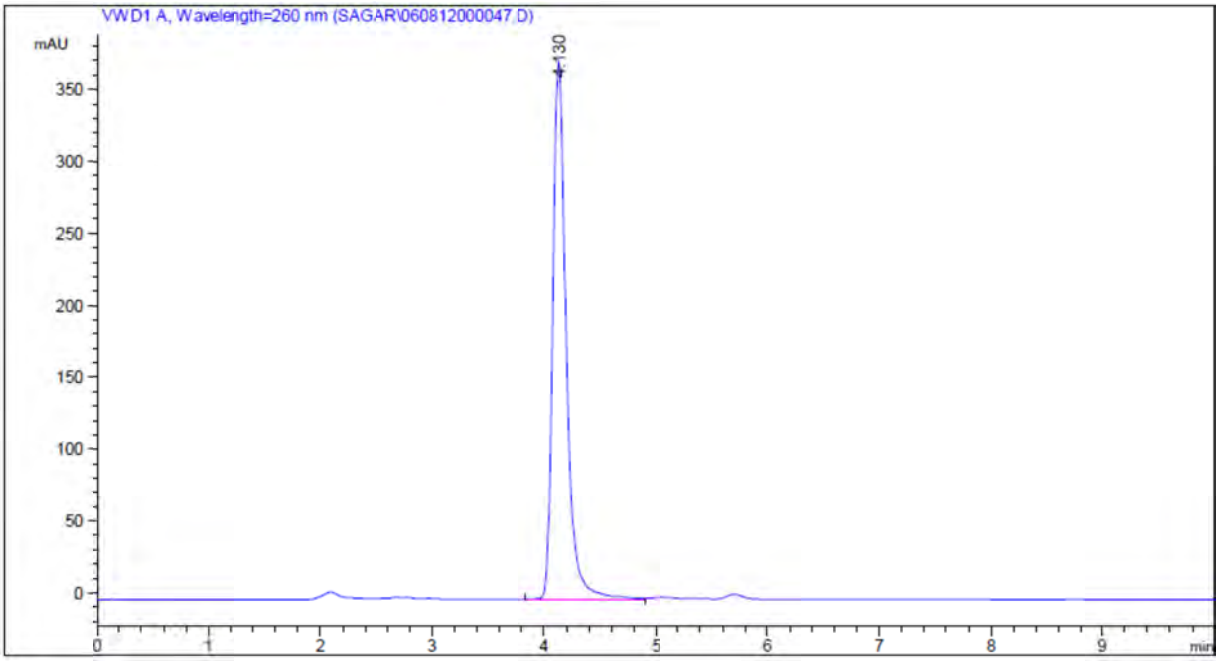




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.093	BB	0. 1234	3121.31860	380.19952	100
Totals				3121.31860	380.19952	

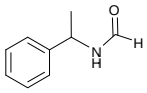
***N*-benzylformamide**

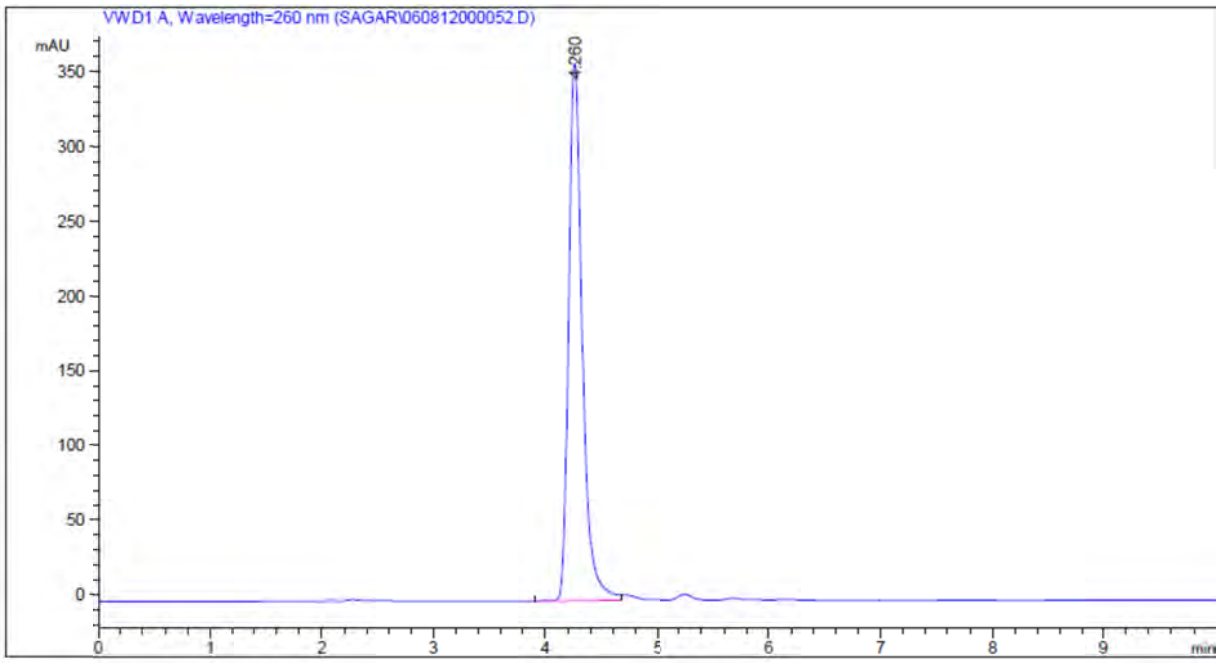




Peak	Ret Time	Type	Width	Area	Hight	Area
#	[min]		[min]	mAU*S	[mAU]	%
1	4.130	BV	0. 1260	3100.99048	373.30362	100
Totals				3100.99048	373.30362	

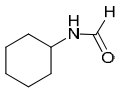
***N*-(1-phenylethyl)formamide**

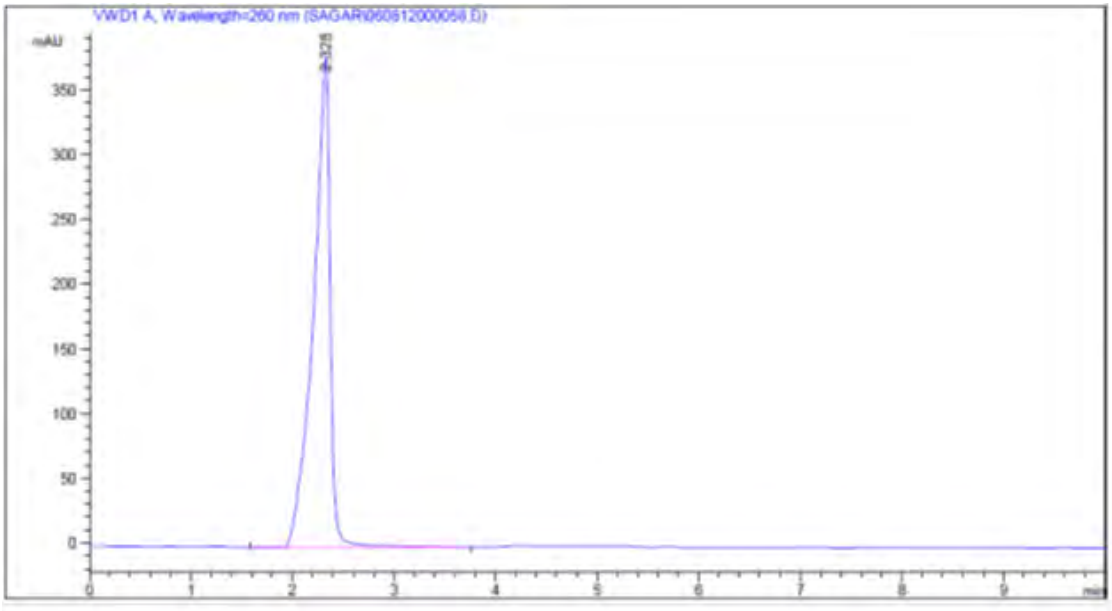




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.260	BV	0. 1273	3019.14771	358.88025	100
Totals				3019.14771	358.88025	

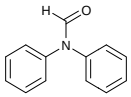
***N*-(cyclohexyl)formamide**

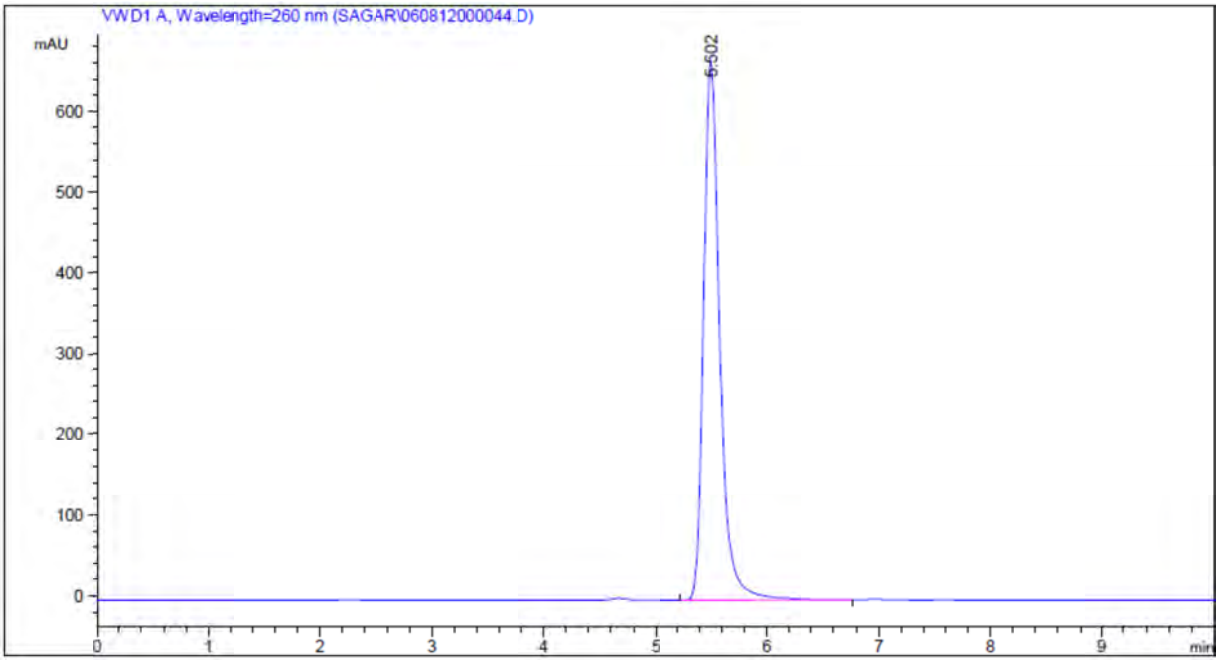




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	2.328	BB	0. 1637	4364.91455	378.43146	100
Totals				4364.91455	378.43146	

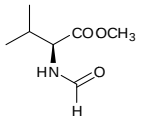
***N,N*-diphenylformamide**

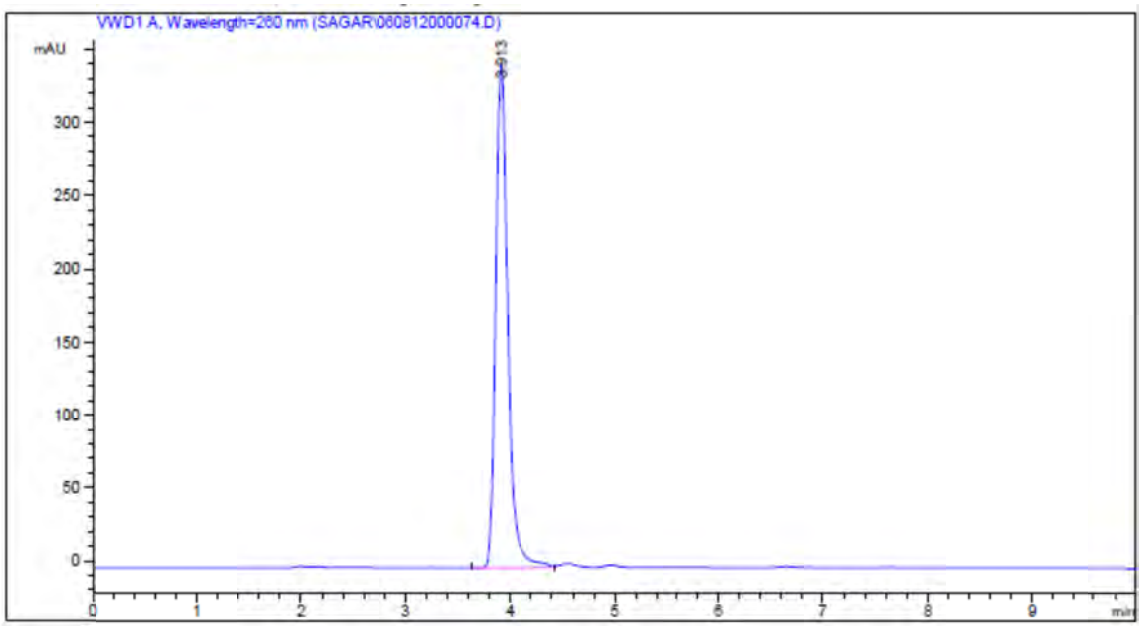




Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	5.502	BB	0. 1518	6670.62451	665.88672	100
Totals				6670.62451	665.88672	

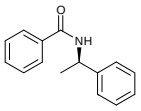
***N*-formyl-L-valine methyl ester:**

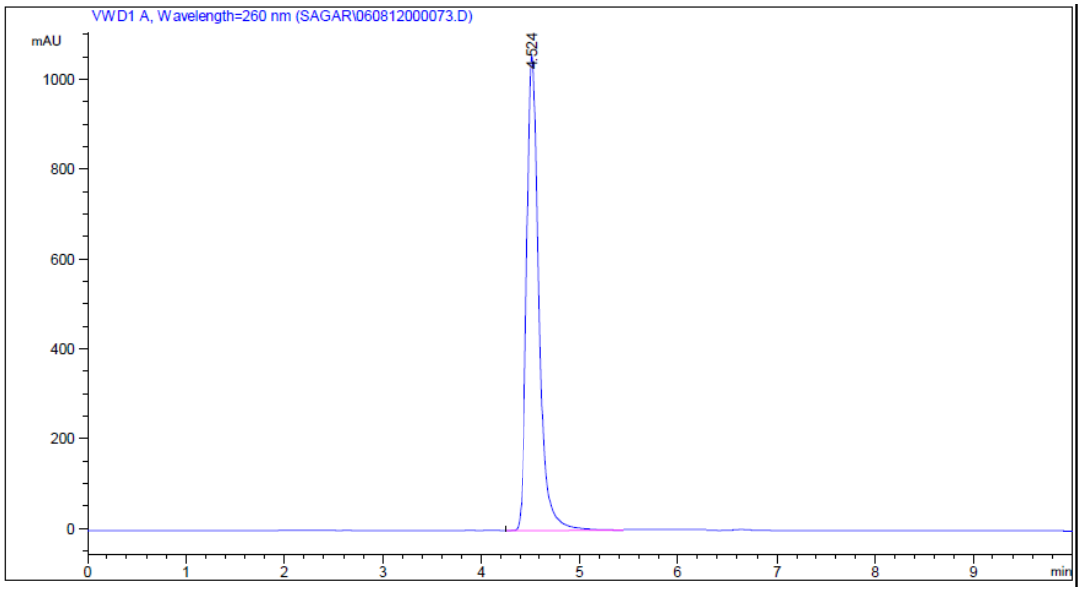




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	3.913	BV	0.1241	2800.51880	343.86136	100.0000
Totals :				2800.51880	343.86136	

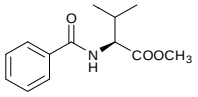
***(R)*-*N*-(1-phenylethyl)benzamide**

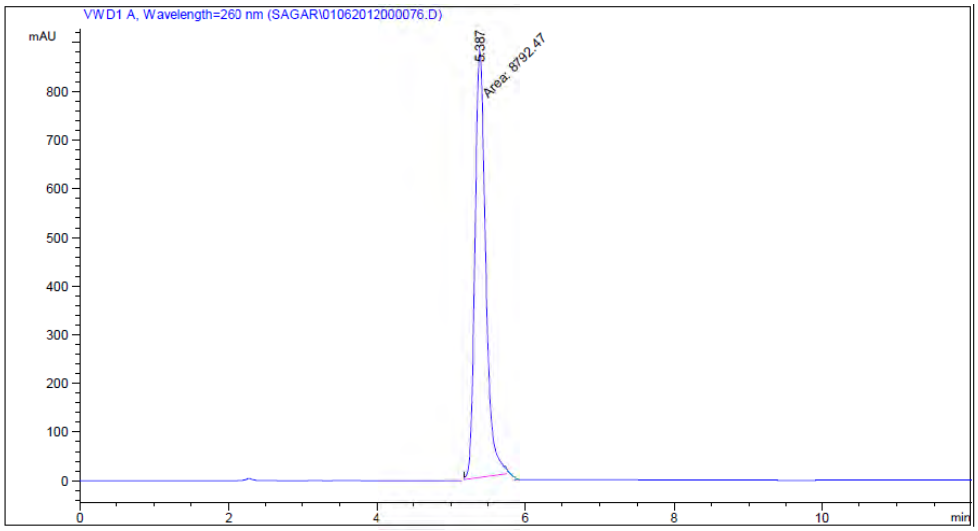




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.524	BV	0.1334	9309.78125	1056.52515	100.0000
Totals :				9309.78125	1056.52515	

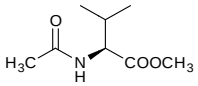
***N*-benzoyl-L-valine methyl ester**

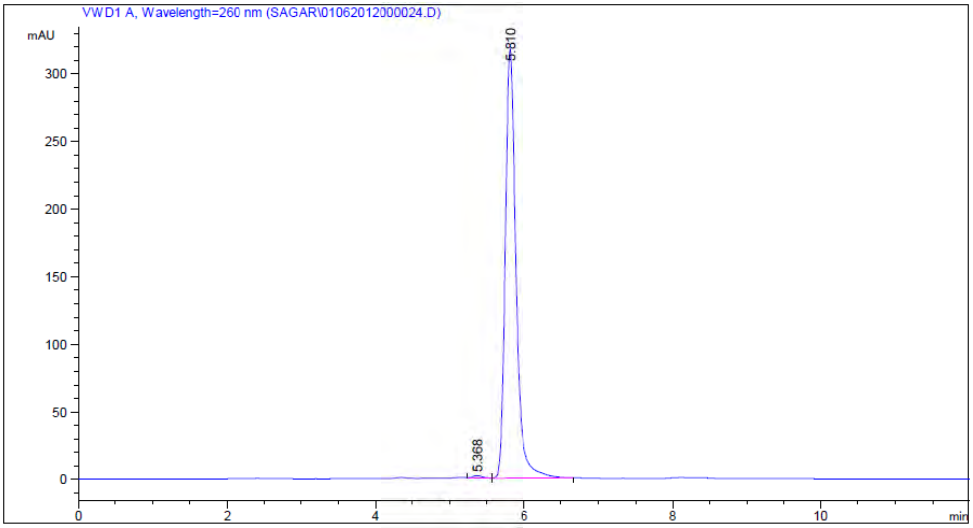




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.387	MM	0.1672	8792.47363	876.42371	100.0000

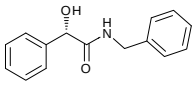
***N*-acetyl-L-valine methyl ester**

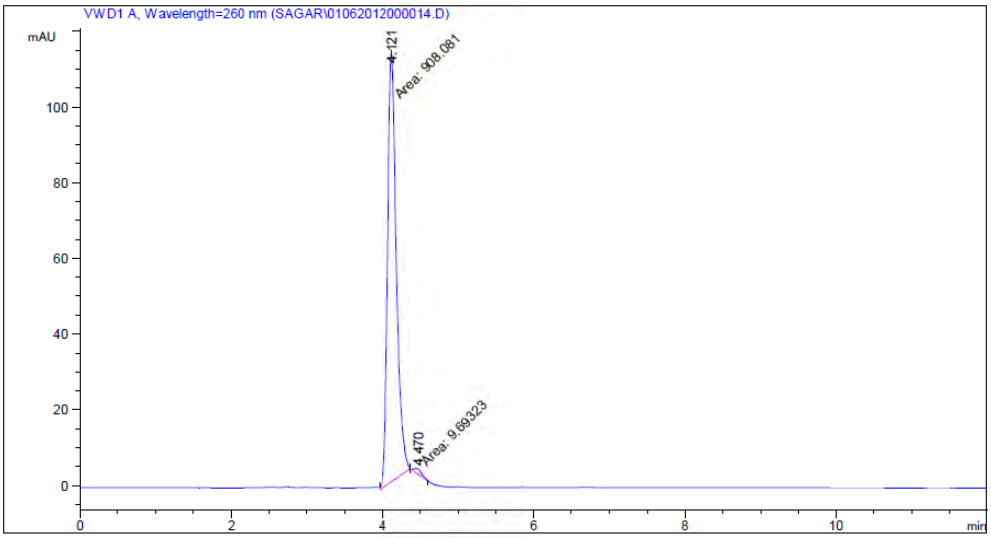




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.368	VV	0.1395	17.28621	1.90225	0.5430
2	5.810	VB	0.1514	3166.06885	317.29254	99.4570
Totals :				3183.35505	319.19479	

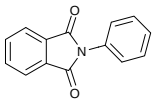
***(R)-N*-benzyl mandeloamide**

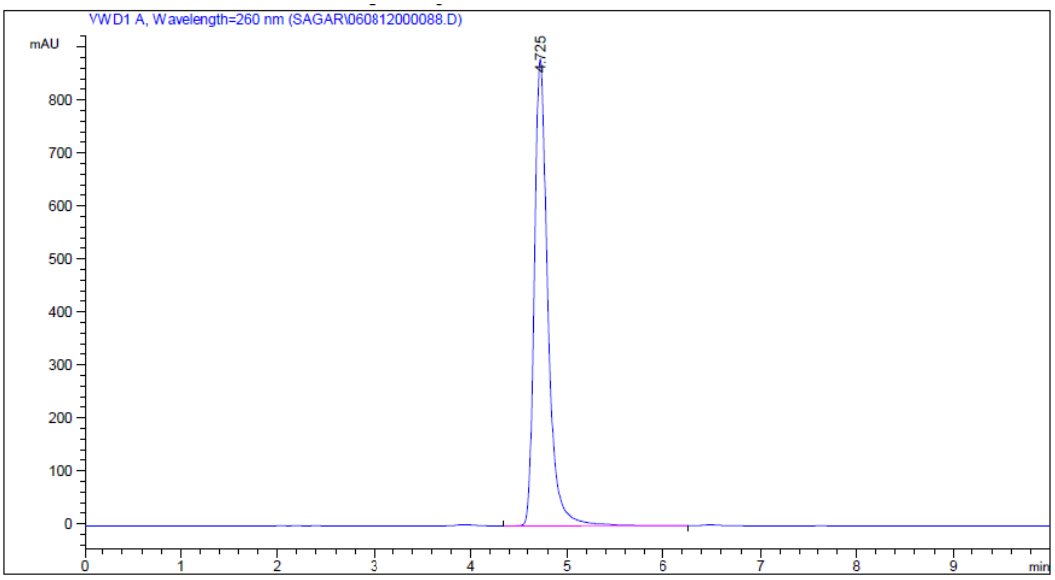




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.121	MM	0.1329	908.08148	113.90934	98.9438
2	4.470	MM	0.1171	9.69323	1.37976	1.0562
Totals :				917.77471	115.28910	

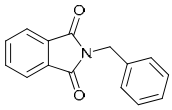
***N*-phenylphthalimide**

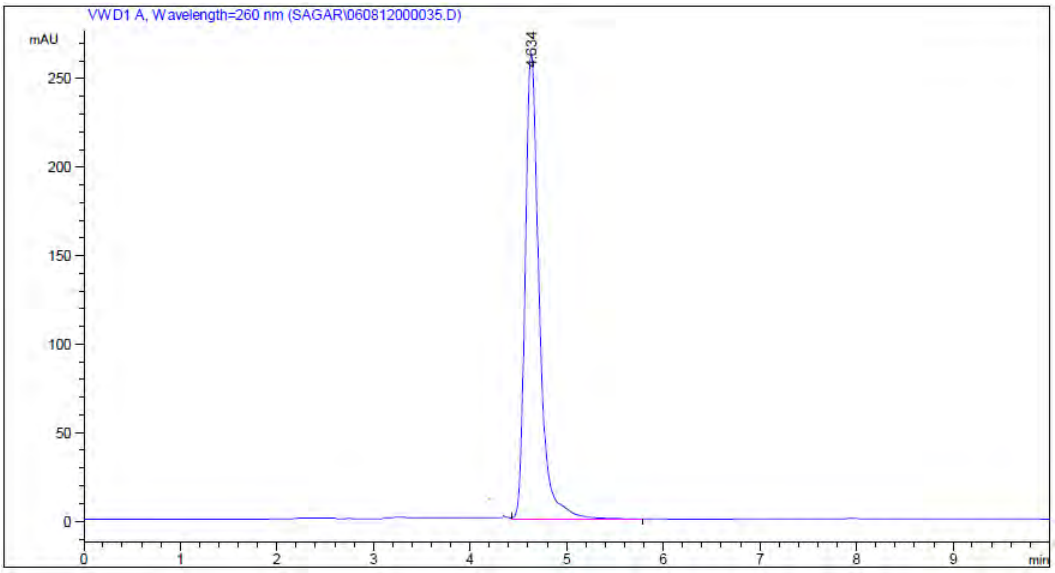




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.725	BB	0.1462	8506.14941	880.43115	100.0000
Totals :				8506.14941	880.43115	

***N*-benzylphthalimide**

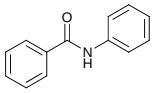


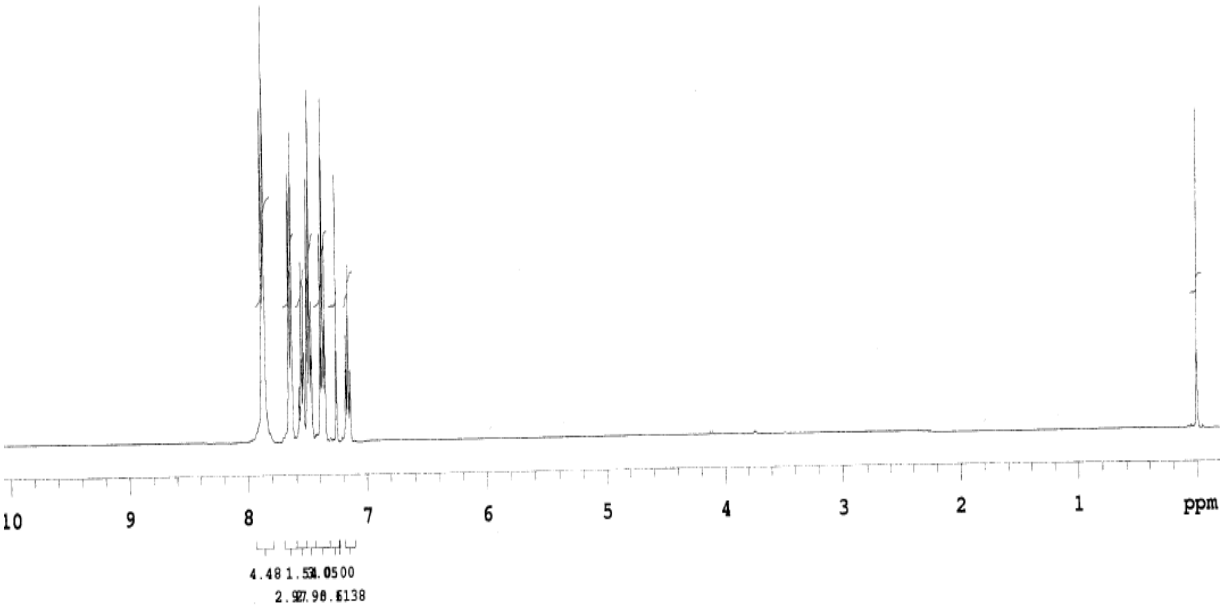


Peak #	Ret Time [min]	Type	Width [min]	Area mAU*S	Hight [mAU]	Area %
1	4.634	VB	0. 1531	2654.29419	262.16690	100
Totals				2654.29419	262.16690	

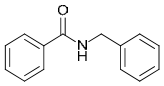
Copy of ^{1}H NMR of some selected compounds:

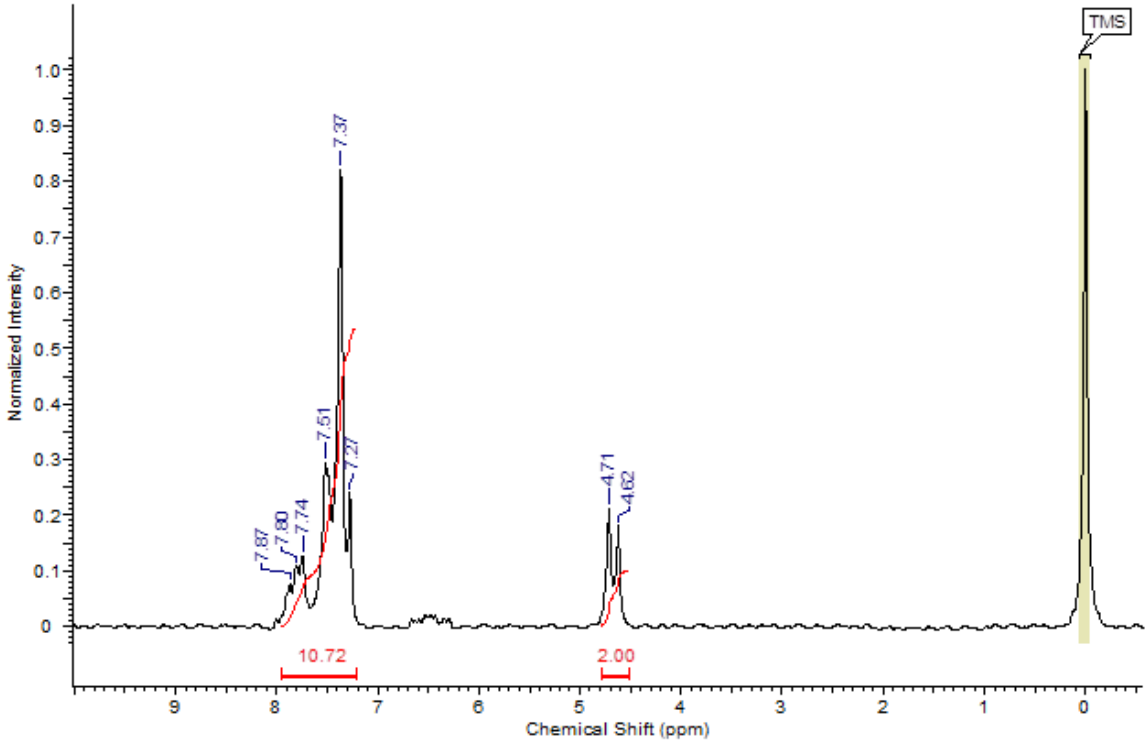
***N*-phenyl benzamide:**



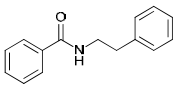


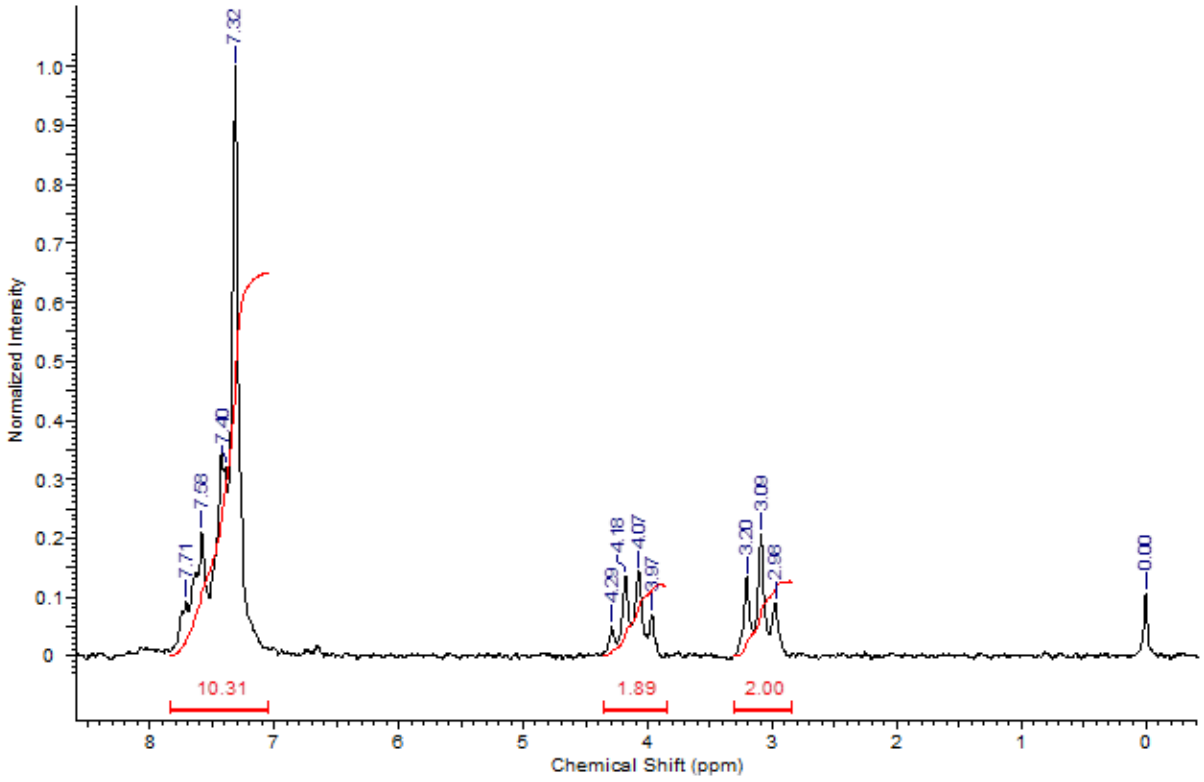
***N*-benzylbenzamide:**



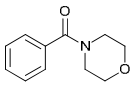


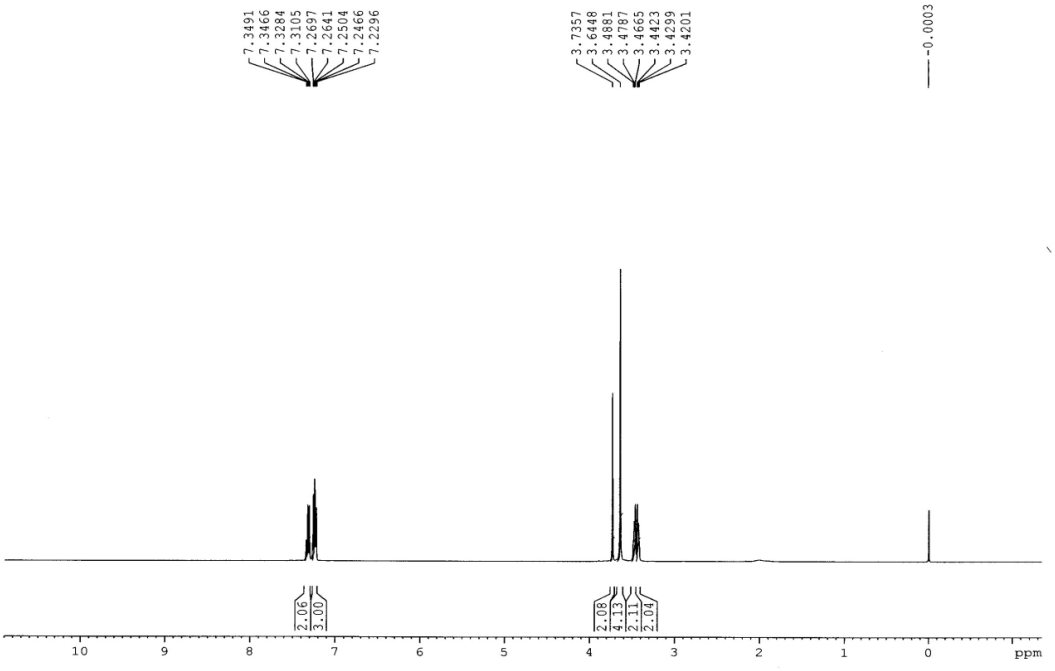
***N*-phenethylbenzamide:**



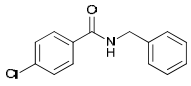


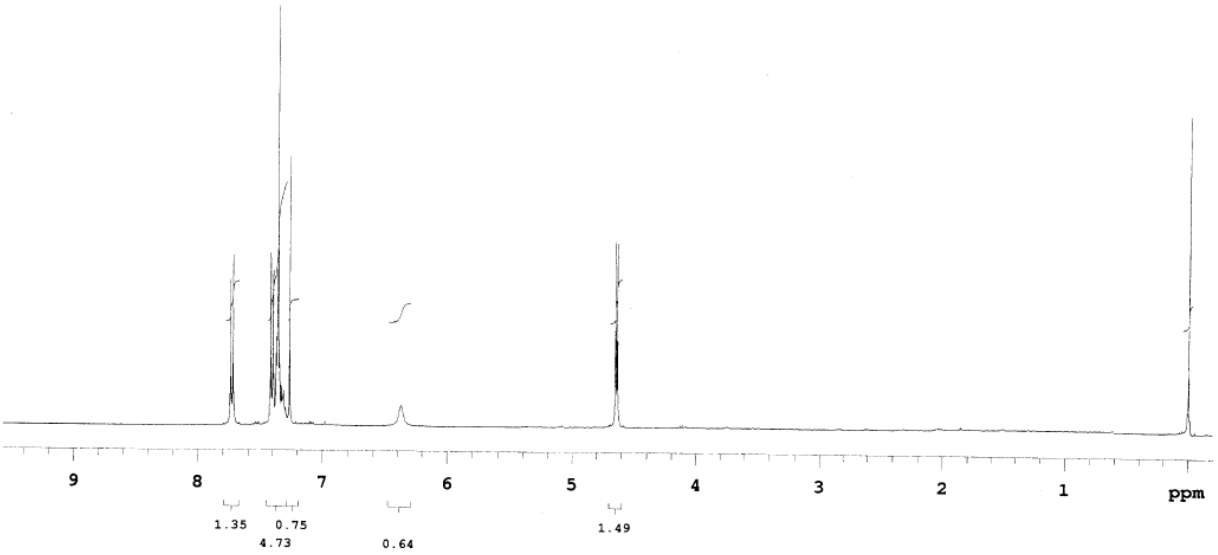
***N*-benzoylmorpholine**



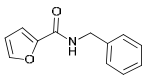


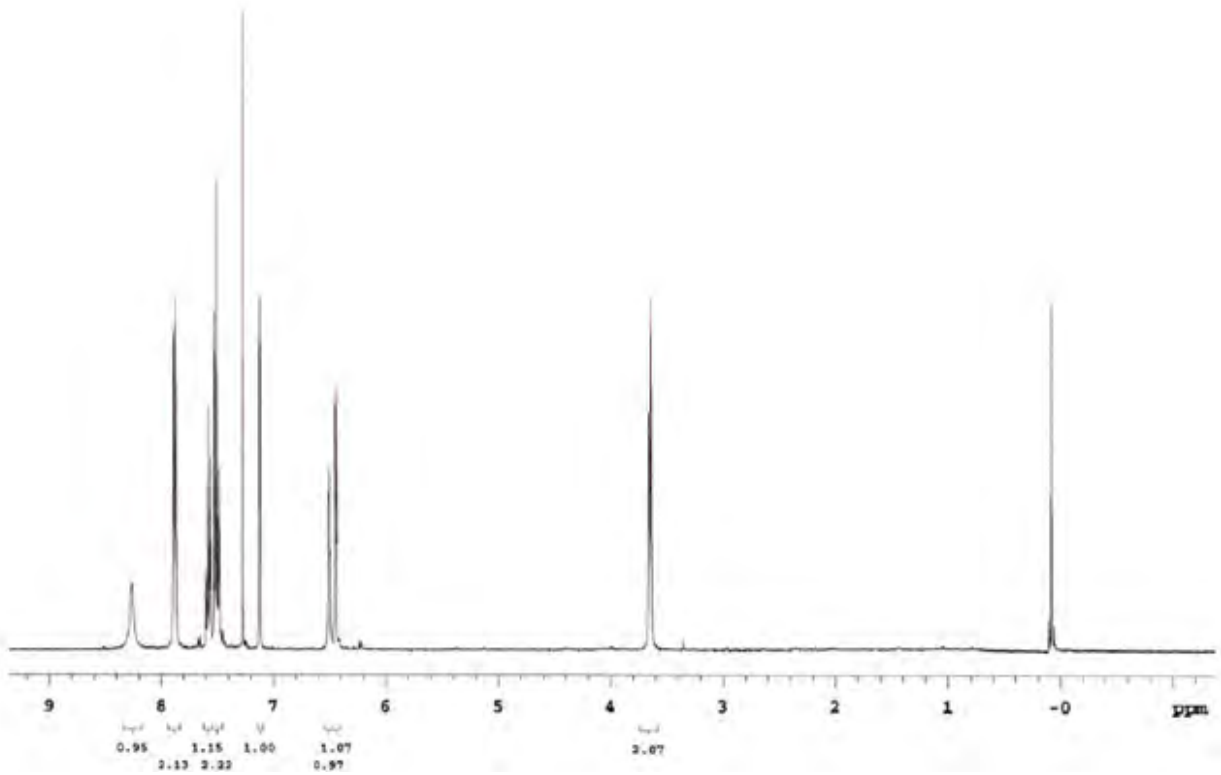
***N*-benzyl-4-chlorobenzamide:**



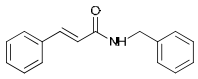


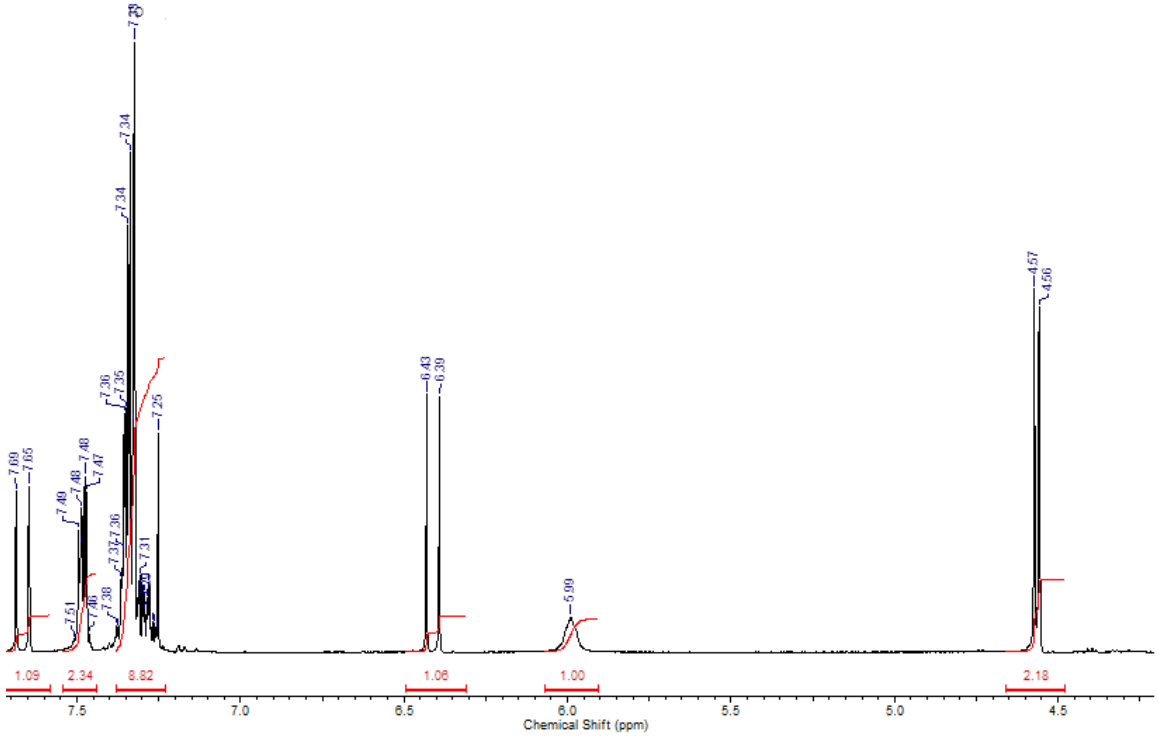
***N*-benzyl furamide:**



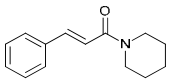


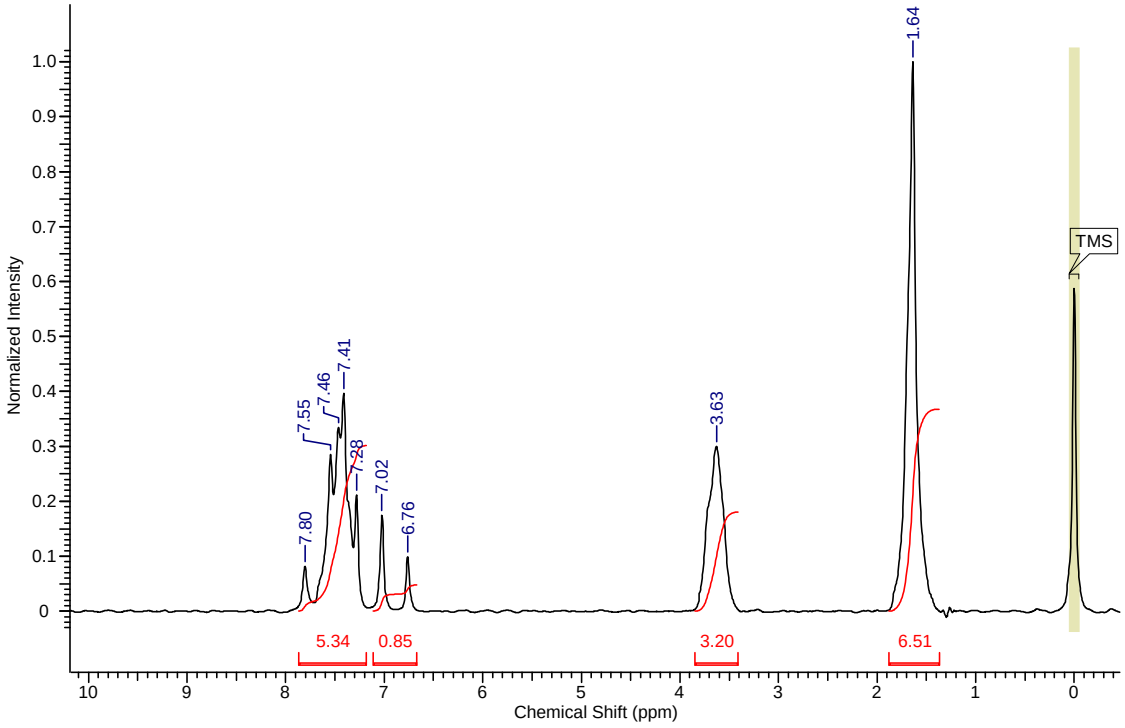
***N*-benzylcinnamamide:**



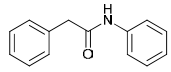


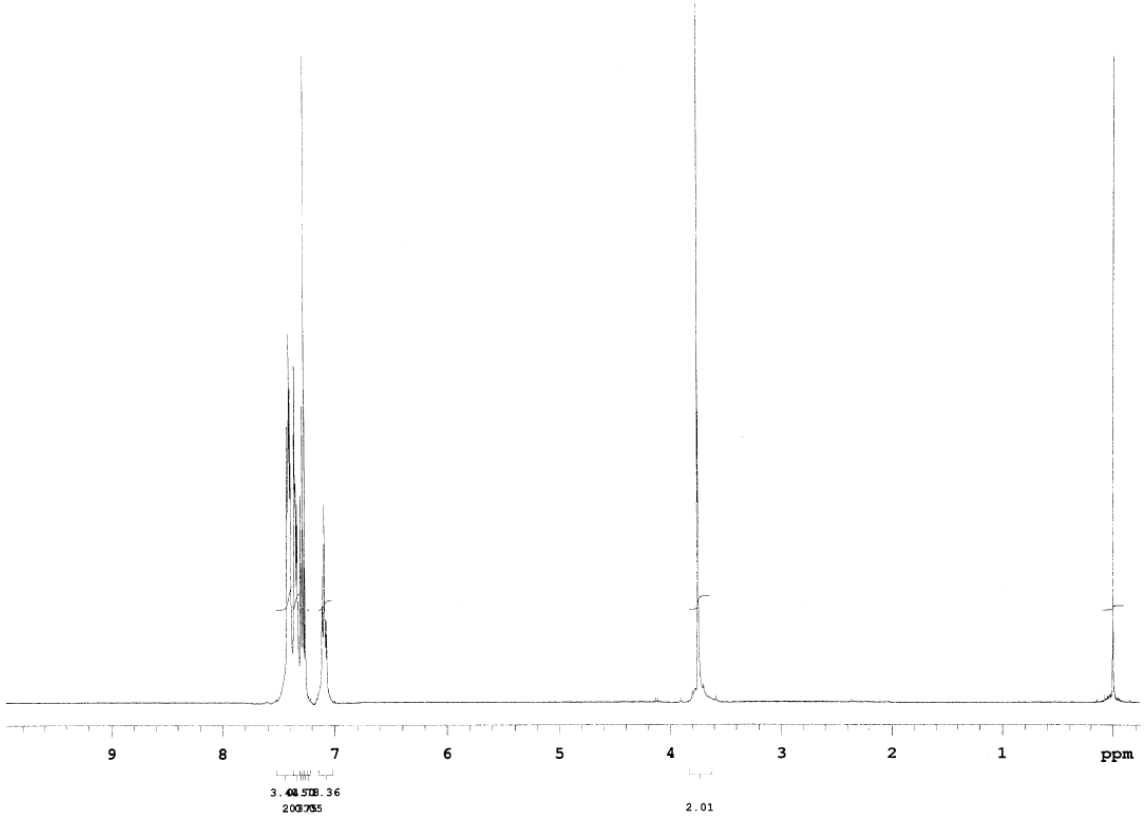
***3*-phenyl-1-(piperidine-1-yl)prop-2-en-1-one**



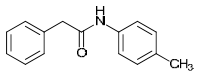


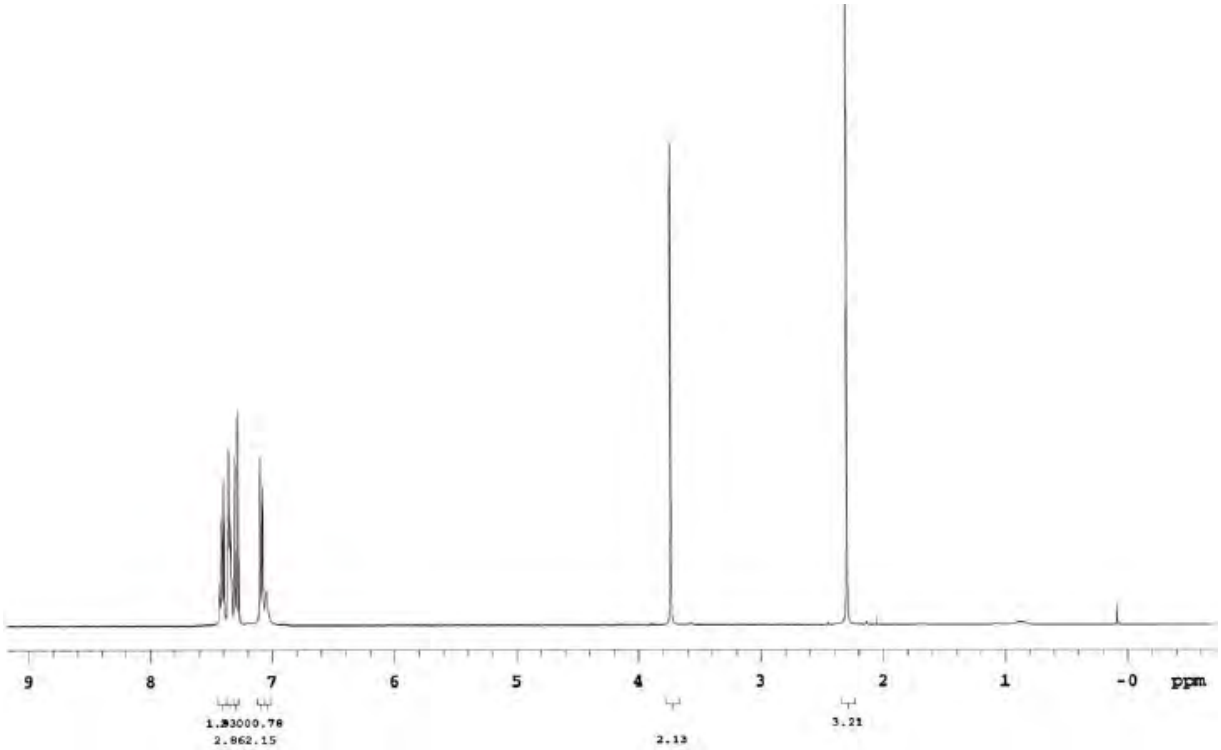
***N*-phenyl-2-phenylacetamide:**



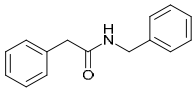


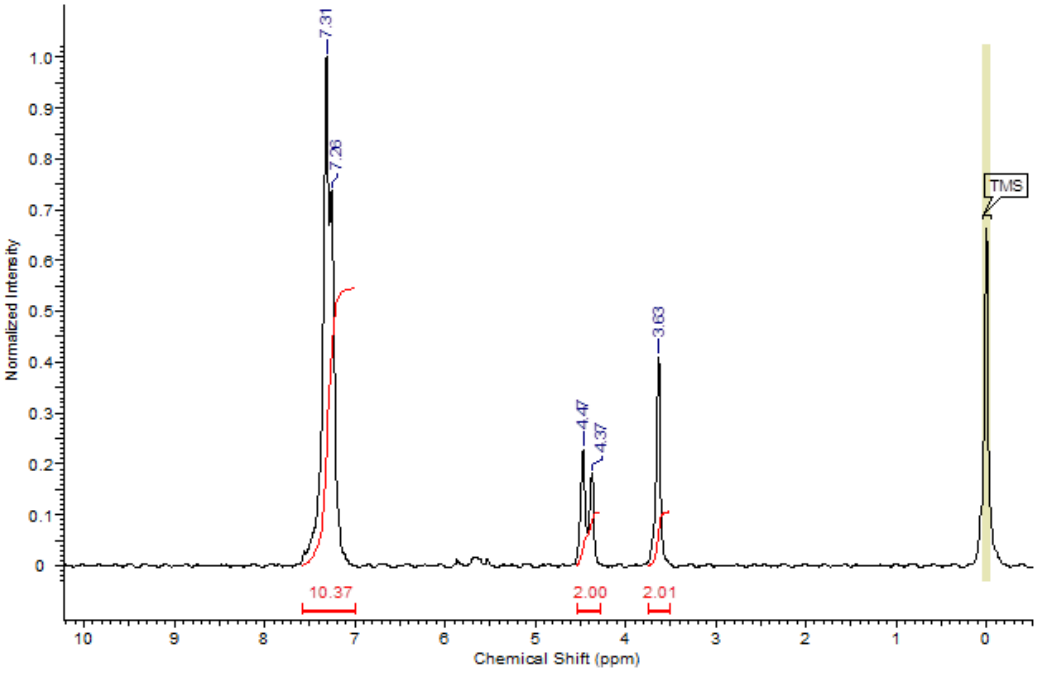
***N*-(4-methyl phenyl)-2-phenylacetamide:**



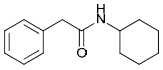


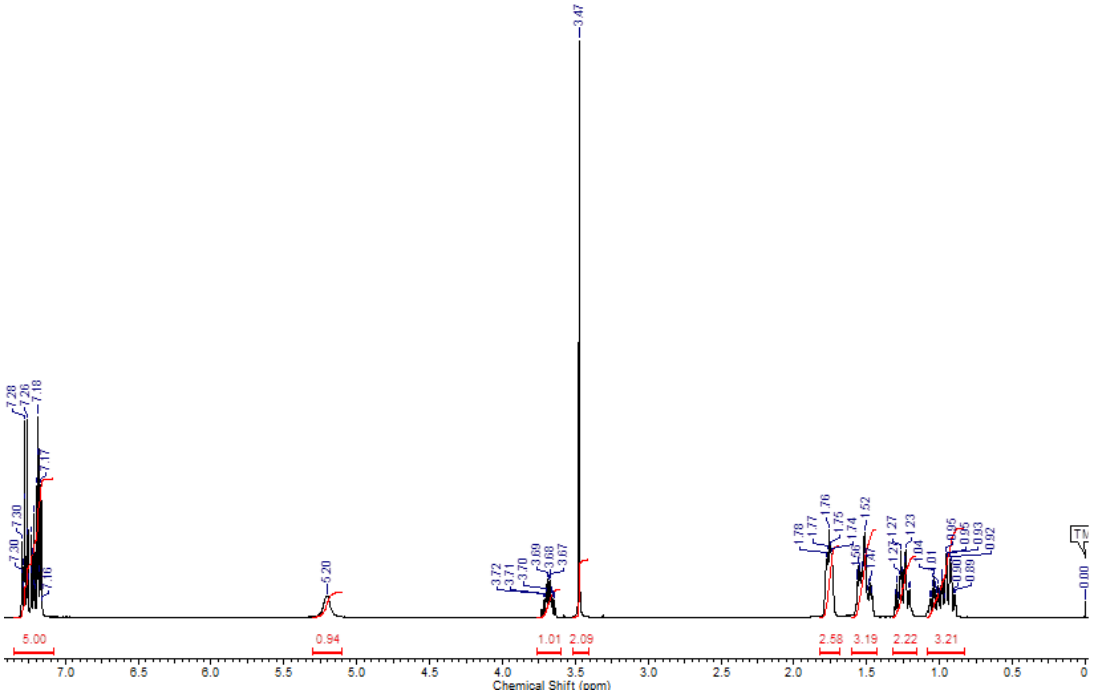
***N*-(4-methyl phenyl)-2-phenylacetamide:**



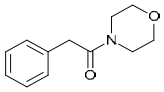


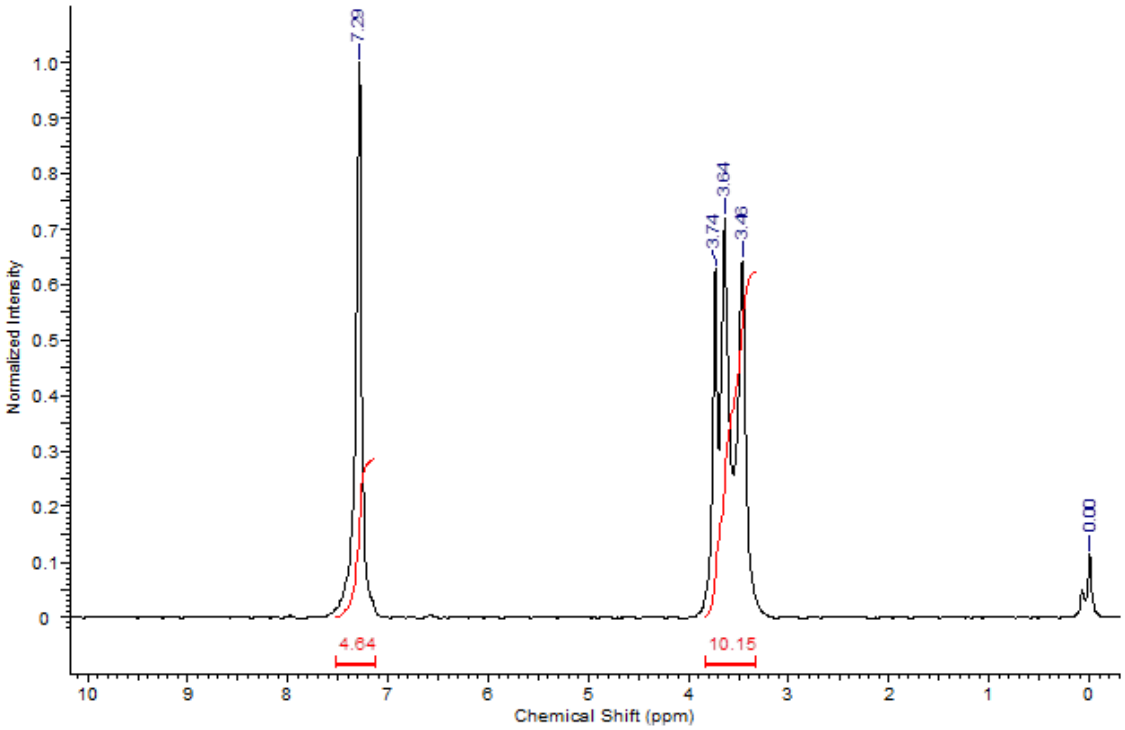
***N*-cyclohexyl-2-phenylacetamide:**



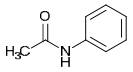


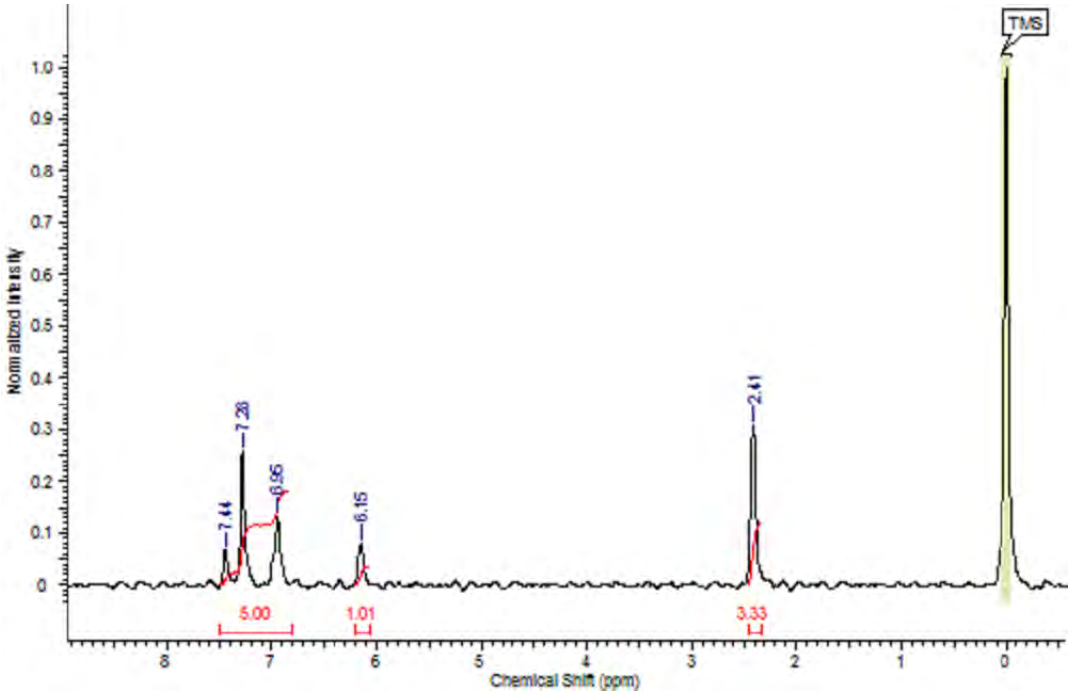
4-(phenylacetyl)morpholine:



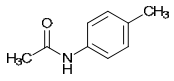


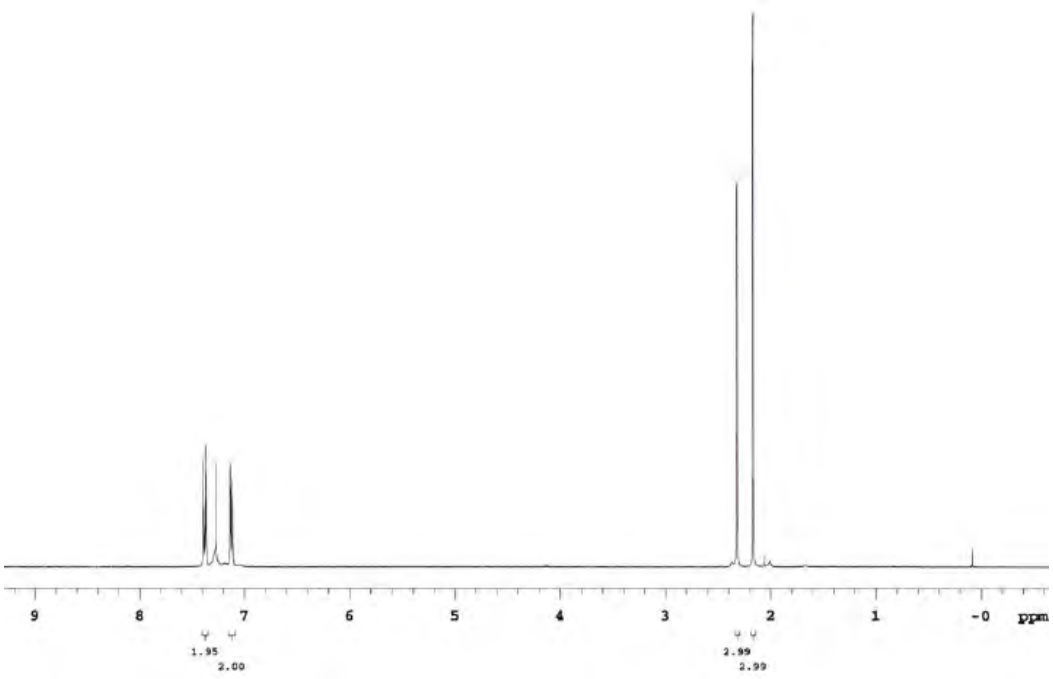
***N*-(phenyl)acetamide:**



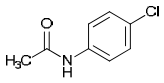


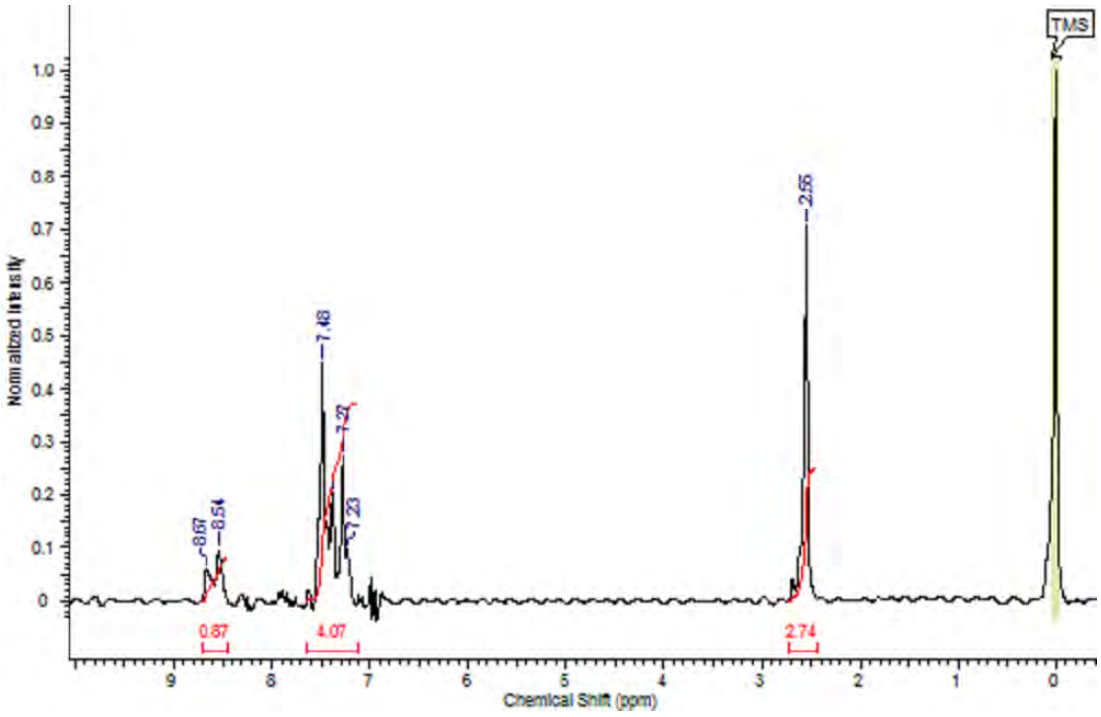
***N*-(4-methylphenyl)acetamide:**



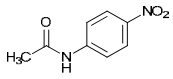


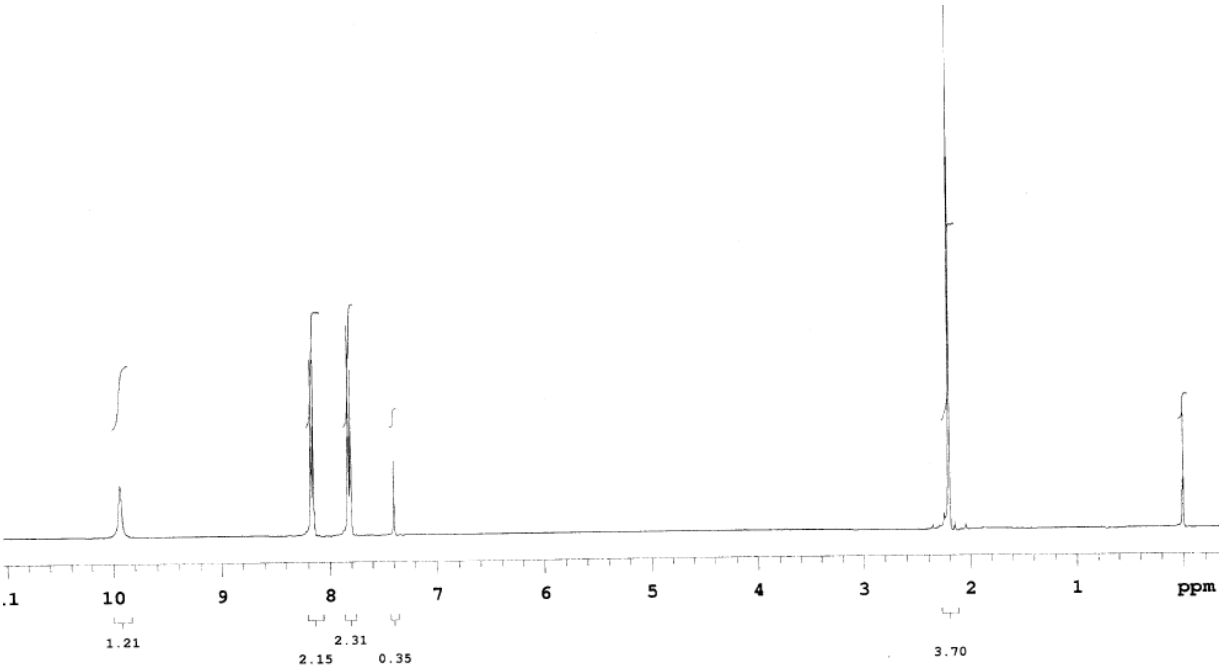
***N*-(4-chlorophenyl)acetamide:**



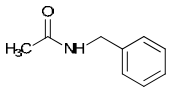


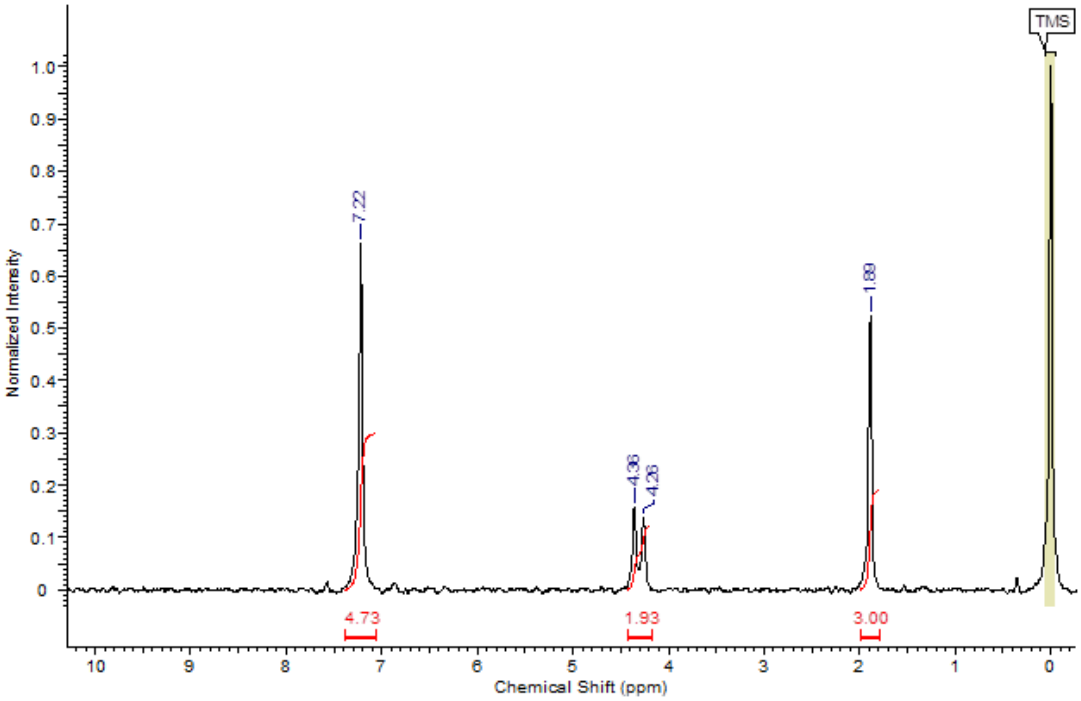
***N*-(4-nitrophenyl)acetamide:**



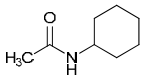


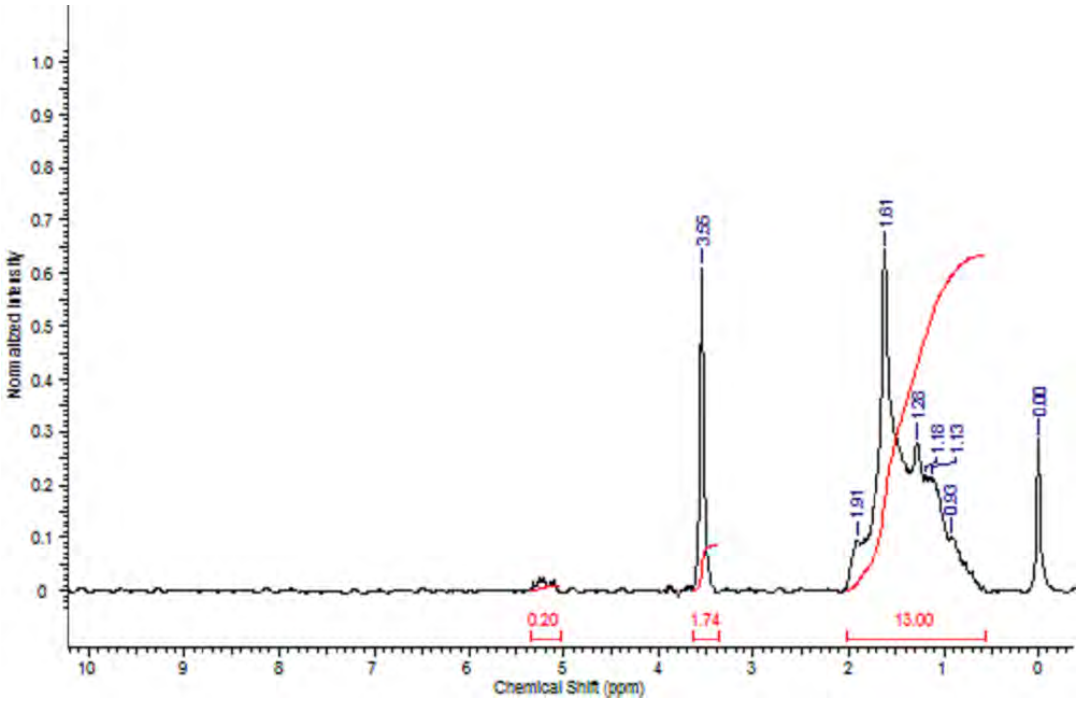
***N*-(benzyl)acetamide:**



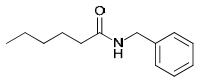


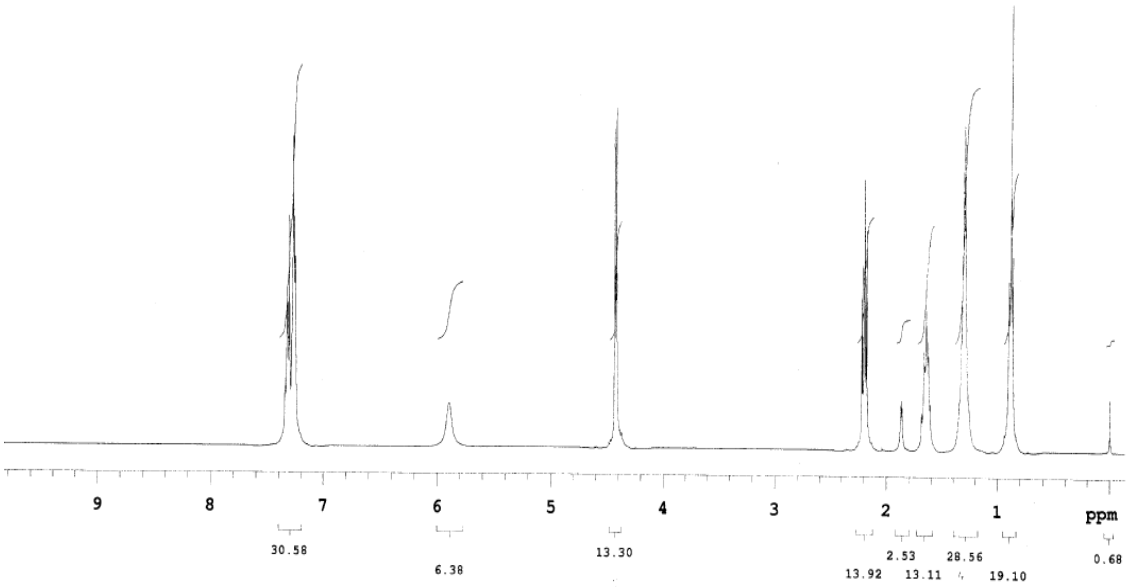
***N*-(cyclohexyl)acetamide:**



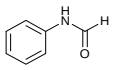


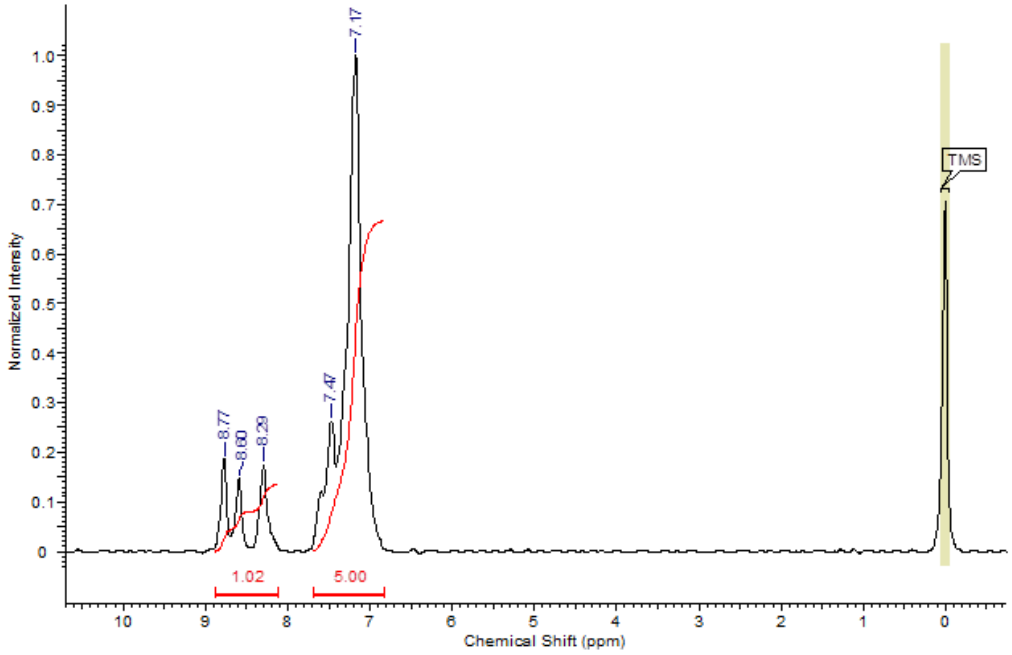
***N*-benzyl hexanamide:**



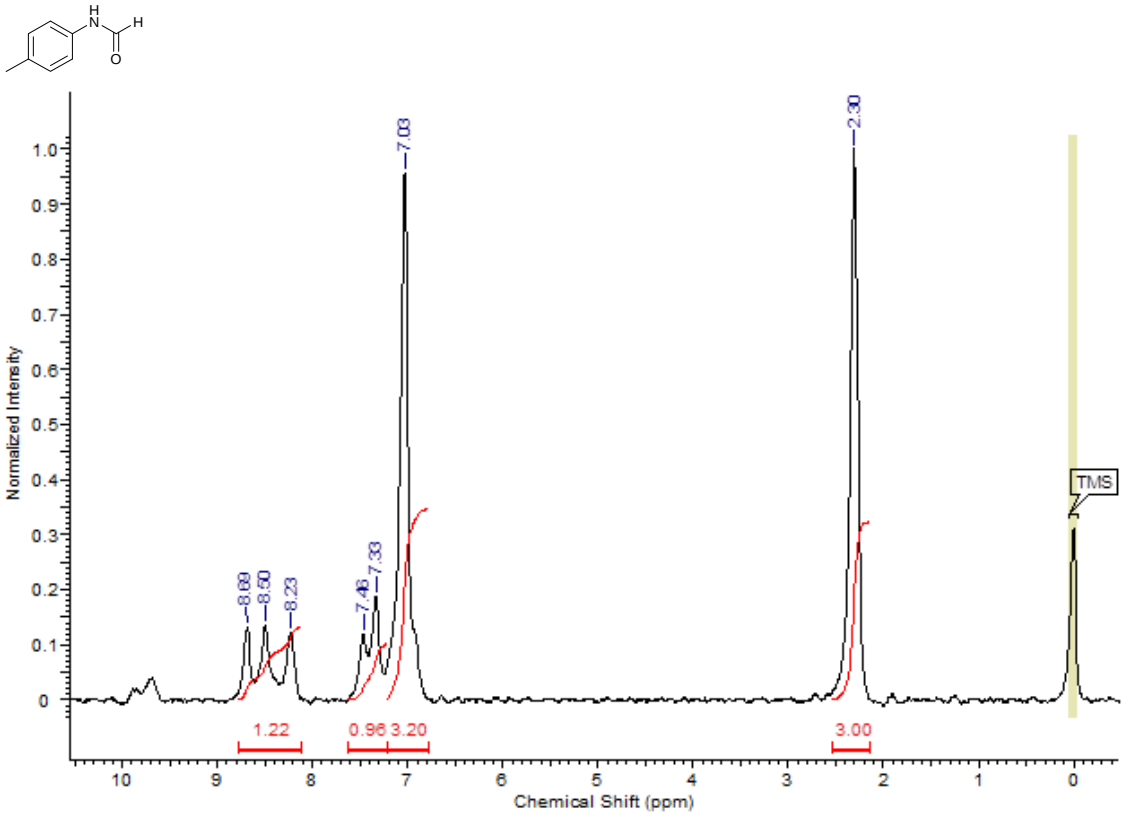


***N*-Phenyl formamide:**

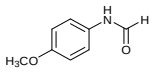


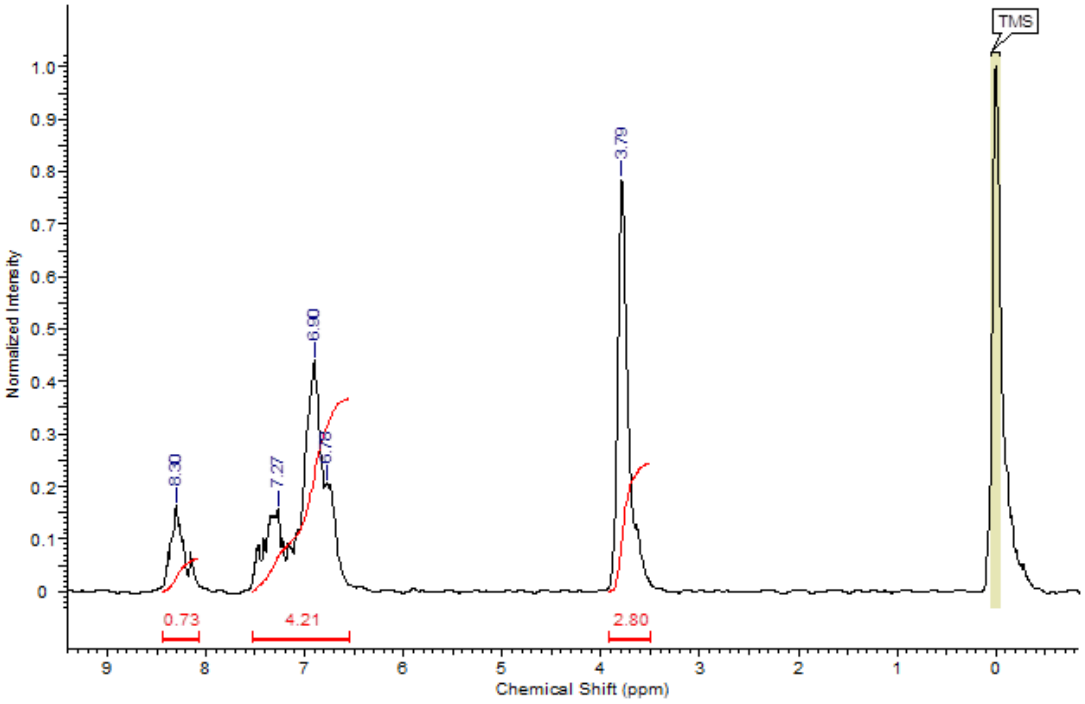


***N*-(4-Methylphenyl) formamide:**

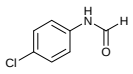


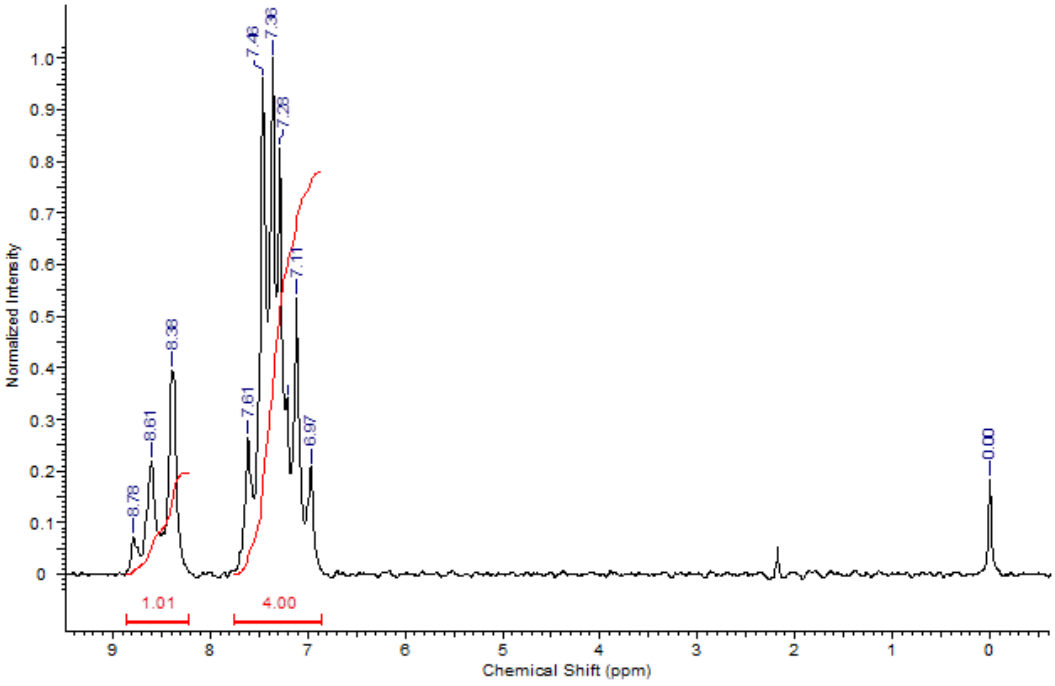
***N*-(4-Methoxyphenyl) formamide:**



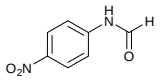


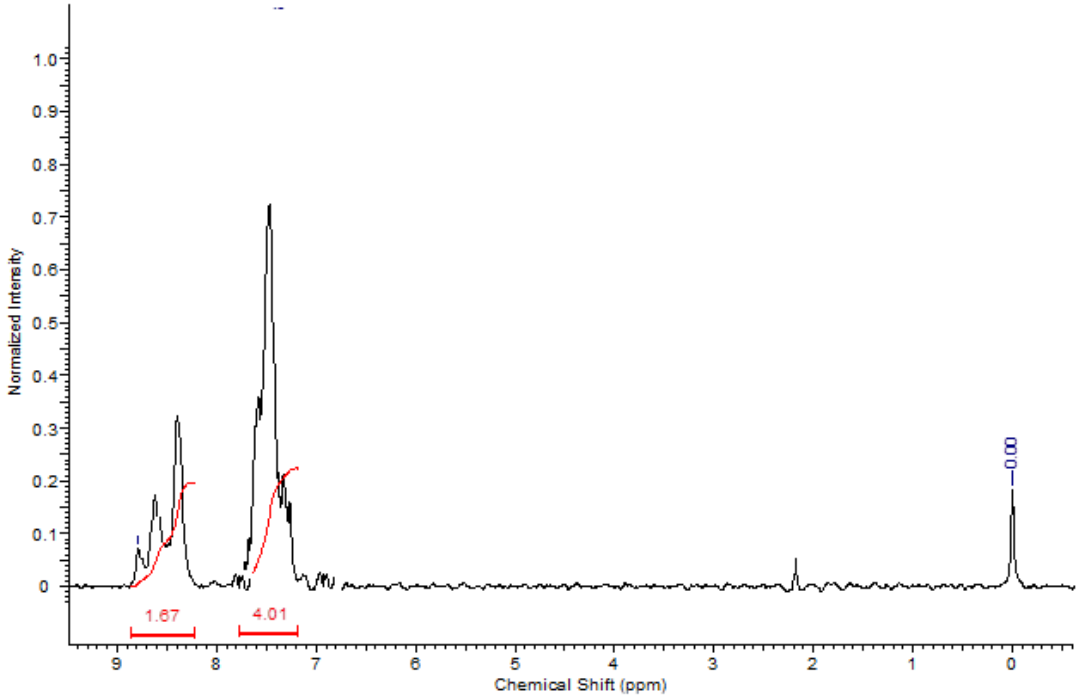
***N*-(4-Chlorophenyl) formamide:**



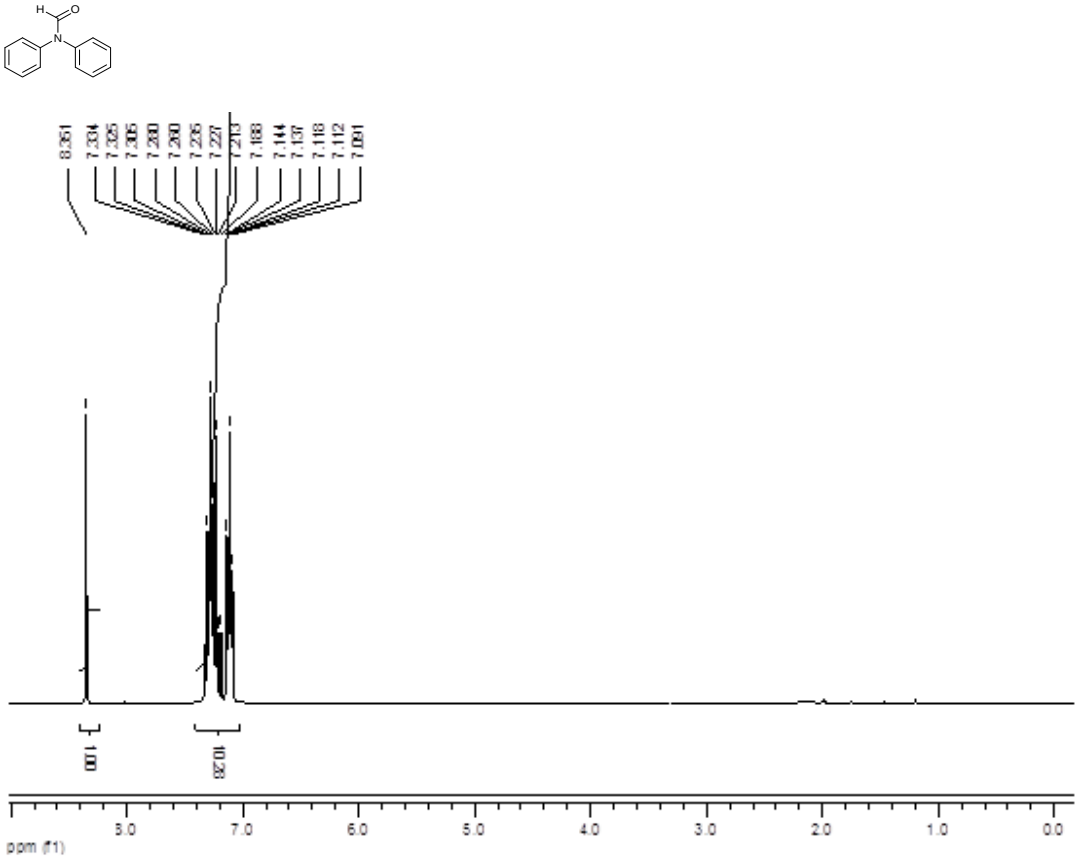


***N*-(4-Nitrophenyl) formamide:**

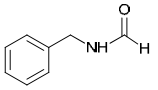


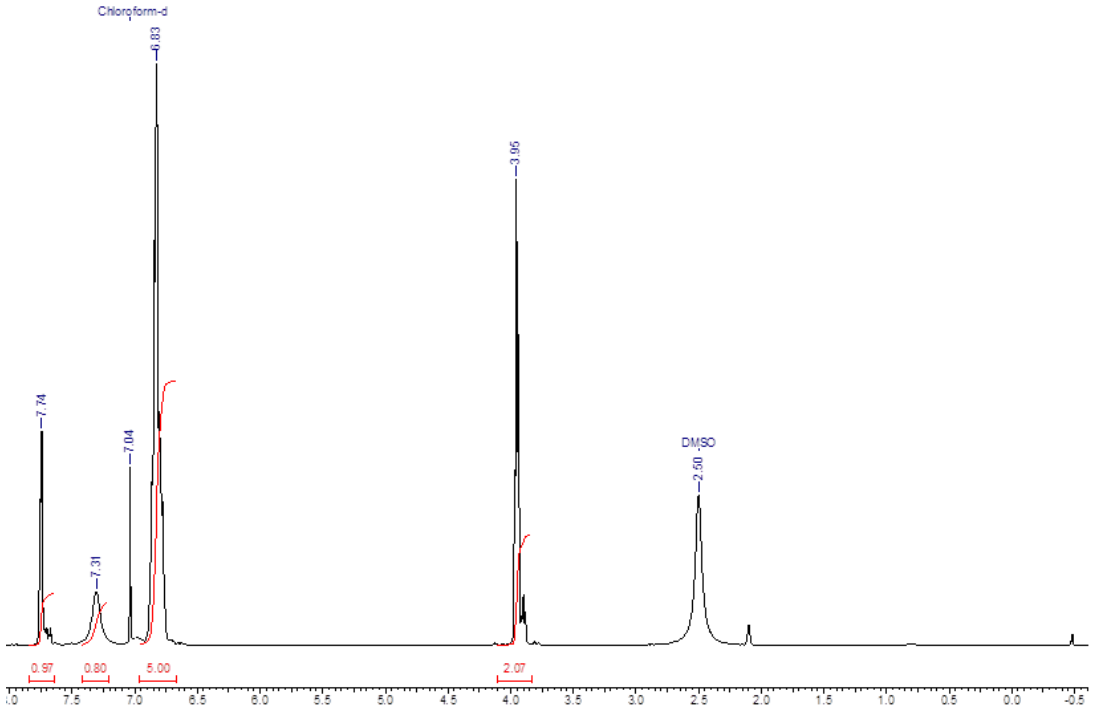


***N,N*-diphenylformamide:**

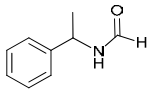


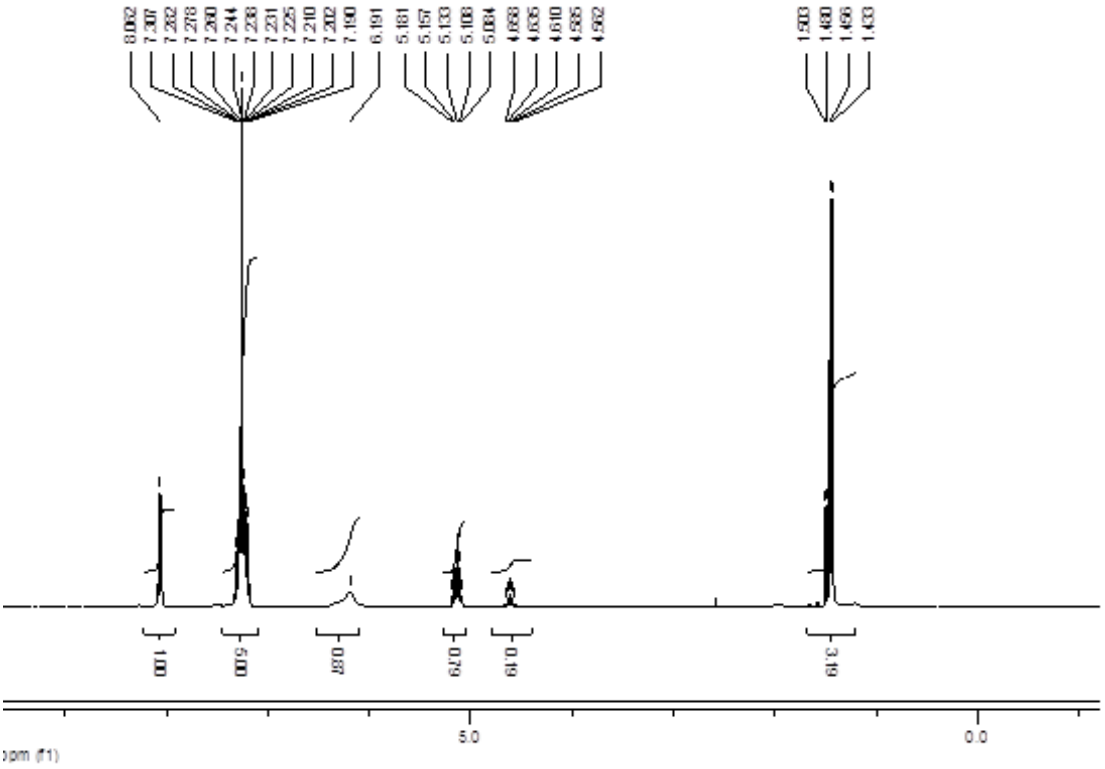
***N*-benzylformamide:**



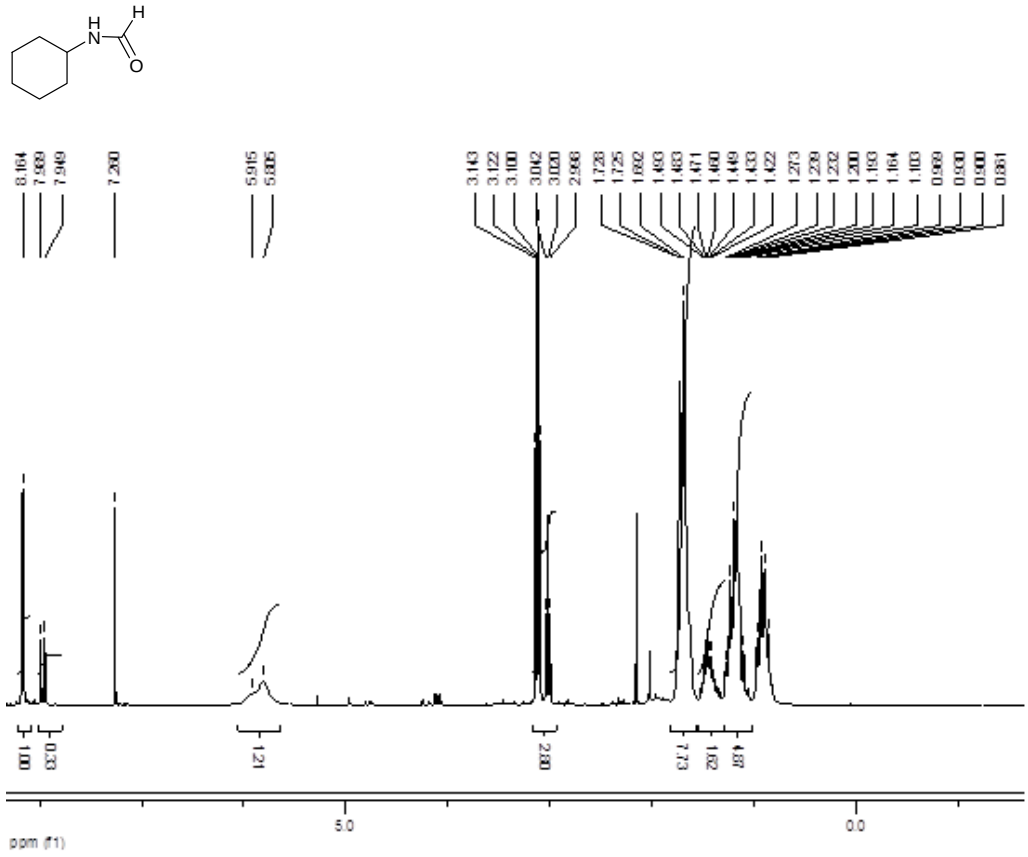


***N*-(1-phenylethyl)formamide:**

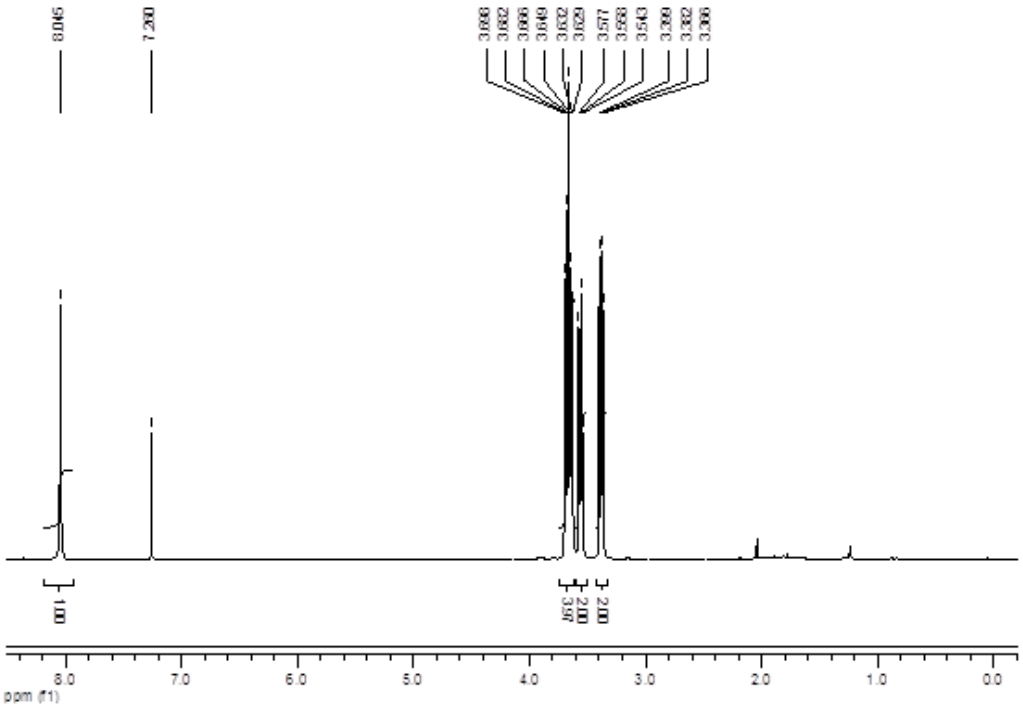




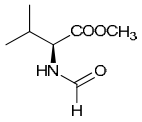
***N*-cyclohexylformamide:**

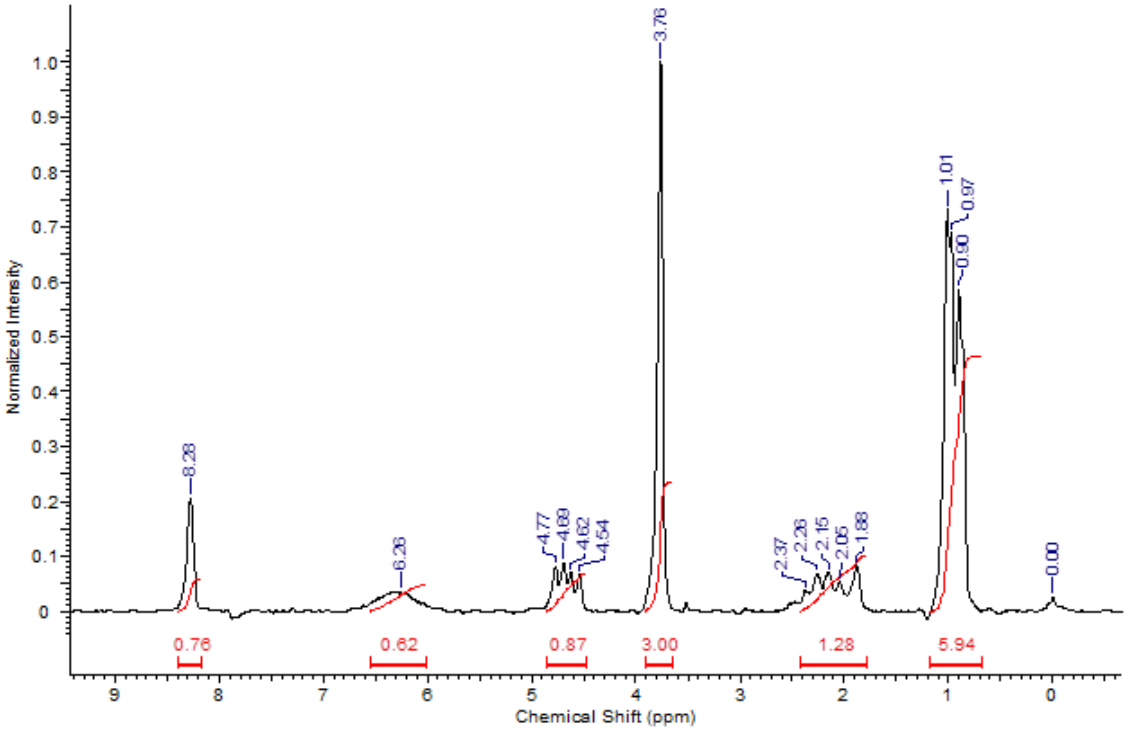


***N*-formyl-morpholine:**

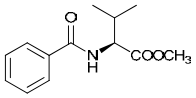


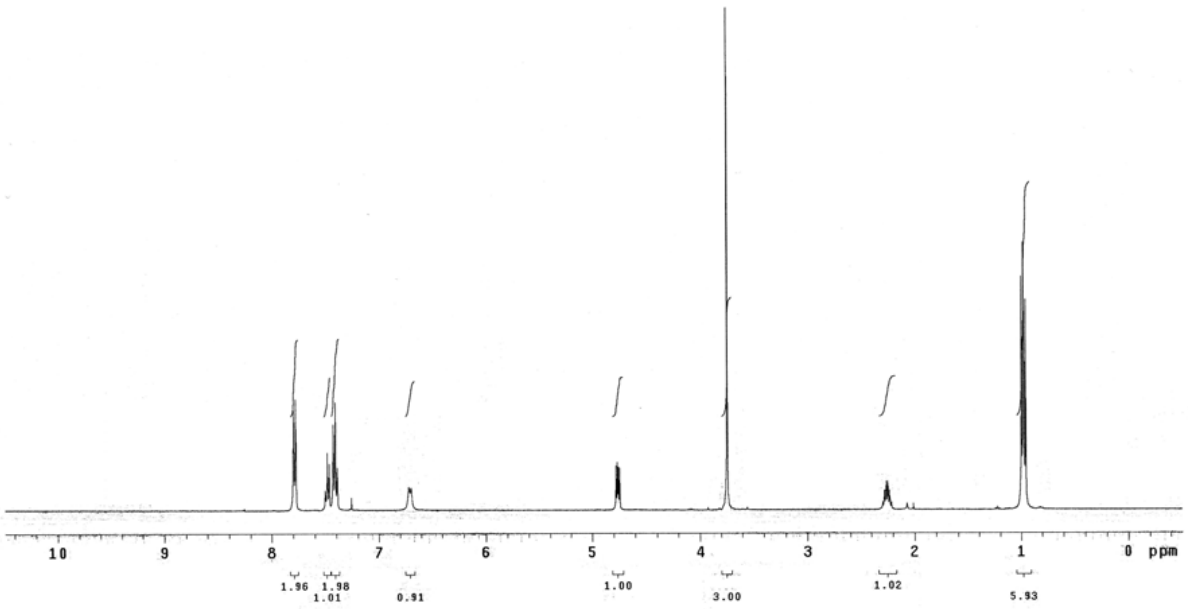
***N*-formyl-L-valine methyl ester:**



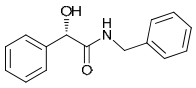


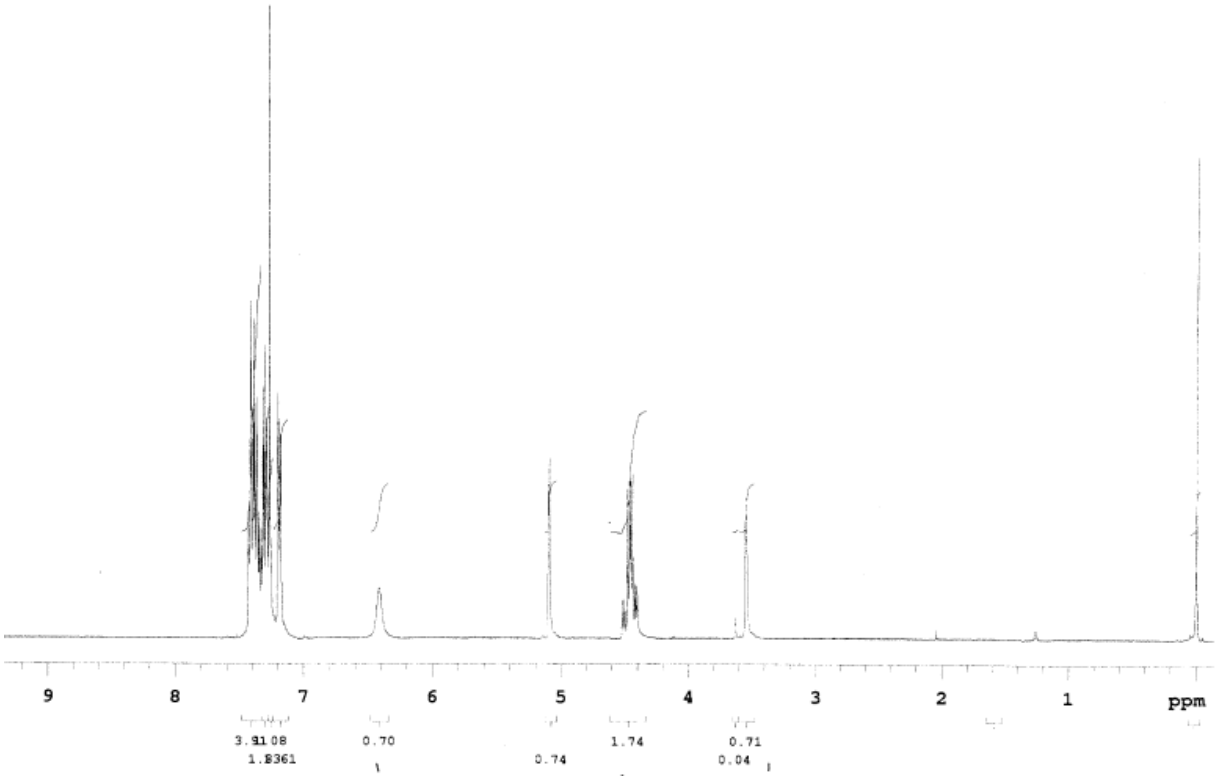
***N*-benzoyl-L-valine methyl ester:**



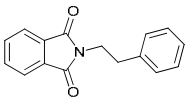


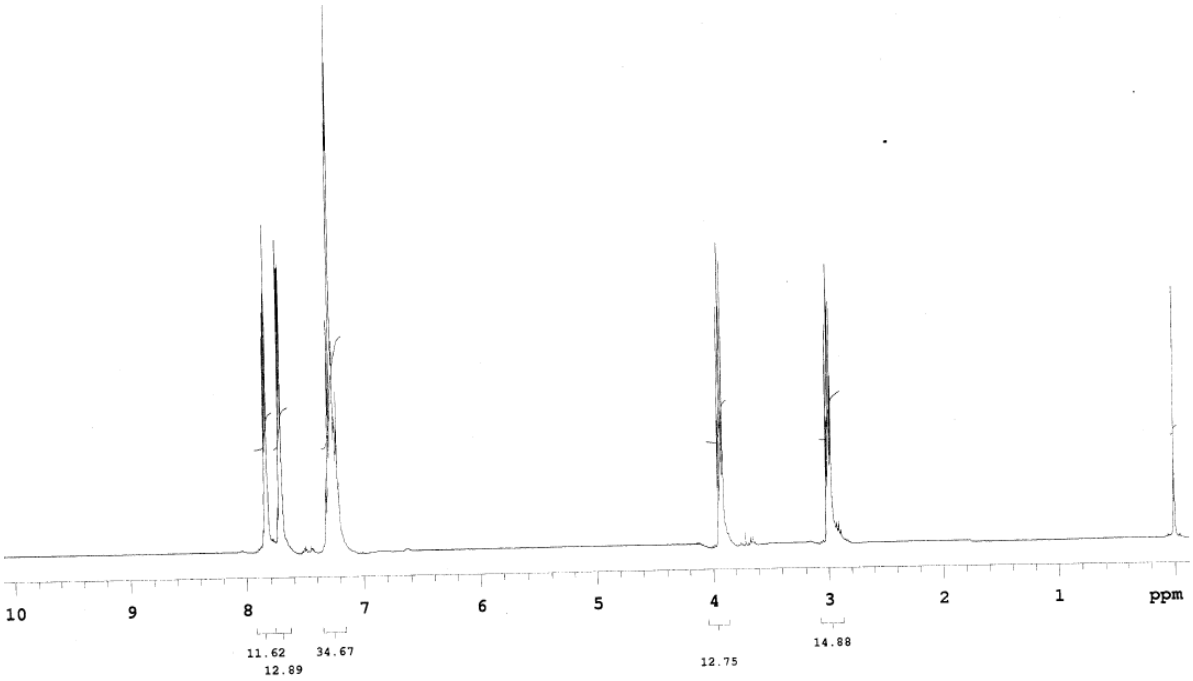
***(R)-N*-benzyl mandeloamide**





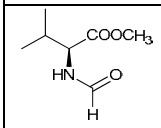
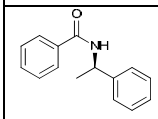
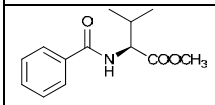
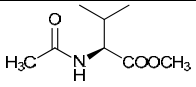
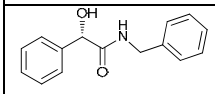
***N*-phenylethylphthalimide:**





Optical Purity Data:

Optical rotations were recorded. It was found that, specific rotation of chiral amides were very close to literature values, indicating no racemization.

Chiral amides	Observed Value [α] (c=1)	Literature Value [α] (c=1)
	-26.40	-27.20
	18.5	19.9
	43	46.4
	25.6	27
	-81.1	-82.4