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Synthesis of New Amide and Thioueas compounds

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Abstract: In the present work, a series of new N-(chloro [Ar] methyl)-N- (1,3-dihydroxy-2-hydroxymethyl) Propan-2-yl) [Ar] amides (8-21) have been synthesized from reaction of N-(2-hydroxymethyl) 1,3-(dihydroxy) propan-2-yl) [Ar] imine (1-7) with benzoyl chloride once, and 2-chlorobenzoyl chloride time another. Subsequent the compounds (8-21) were reactions with thiourea to give thioureas corresponding compounds (22-35). The compounds were identified by their mps, elemental analysis, IR and UV-Vis. spectra. Their structural formulas therefore were confirmed.

Introduction:

Schiff bases are used as substrates in the preparation of number of industrial and biologically active compounds via ring closure, cycloaddition, replacement, and addition reactions[1-6].

Thioureas are commercially used in photographic films, plastics and textiles. Thioureas have shown anti-bacterial, anti-fungi, hypnotic, and antipyretic activities. Some of thioureas are screened for anticancer activity[7].

Schiff bases reaction with acid chloride give amides compounds. Amides compounds reaction with thiourea probably give thioureas compounds[8].

Literature survey reveals that there is no work on reactions N-(chloro [Ar] methyl)-N-(1,3-dihydroxy – 2 - (hydroxymethyl) propan-2-yl) [Ar] amide with thiourea to give corresponding thioureas compounds.

Experimental:

Chemical materials and solvents were obtained from MERCK, BCH and GCC. Melting points were determined in open capillary using Galleukamp melting point apparatus and are uncorrected .Their elemental analysis were given in table (1).IR spectra were recorded in (KBr) on FT-IR Nicolet IR 100 Spectrophotometer tables (2&3). The UV-Vis. spectra were recorded in ethanol on spectroscan 60 DV double beam spectrophotometer, Bio Tech management Co.LTD. UK table (4).

Preparation of Schiff bases (1-7):

Schiff bases (1-7) were prepared by condensation of Tris (hydroxyl methyl) methyl amine with benzaldehyde and substituted benzaldehyde. Benzaldehyde or substituted benzaldehyde (0.05mol) was added to solution of tris (hydroxymethyl) methyl amine (0.05mol) in absolute ethanol (30ml) and the mixture was refluxed for 2hr. The product solid was filtered, washed with small quantity of cold alcohol. The product was dried and purified by recrystallization from ethanol (Table1).

Preparation of N- (Chloro[Aryl] methyl)-N-(1,3-dihydroxy-2-(hydroxy- methyl) propan-2-yl) benzamide or (2- Chloro benzamide) (8-21):

Schiff bases (1-7) (0.001mol) were added to solution of benzoly chloride (or 2-chloro benzoyl chloide) (0.015mol) in dry benzene (25ml) and the mixture was refluxed for 6hr. The product was cooled, filtered and recrystallized from absolute ethanol [9] (Table1).

Preparation of thioureas compounds (22-35):

The compounds (8-21) (0.001mol) were added to solution of thiourea (0.002mol) and Na2CO3 (0.002mol) in absolute ethanol (25ml) and the mixture was refluxed for 3hr. The product was cooled, filtered and recrystalized from ethanol (Table1).

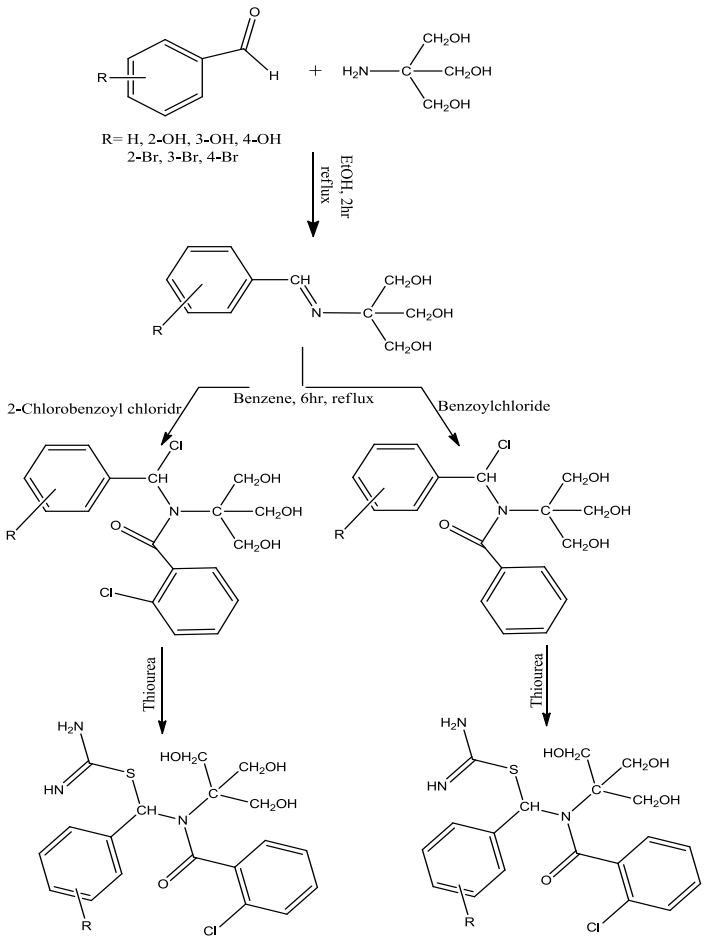
Results and Discussion:

Schiff bases (1-7) were synthesized by condensation of tris (hydroxymethyl) methylamine with benzaldehyde or substituted benzaldehyde (o-,m-,p- hydroxybe nzaldehyde and o-,m-,p- bromo benzaldehyde). The physical properties of Schiff bases were prepared summarized in (Table1).

Both IR and UV absorptions are in agreement with those reported in the literatures for similar absorbing groups and chromophores[10].

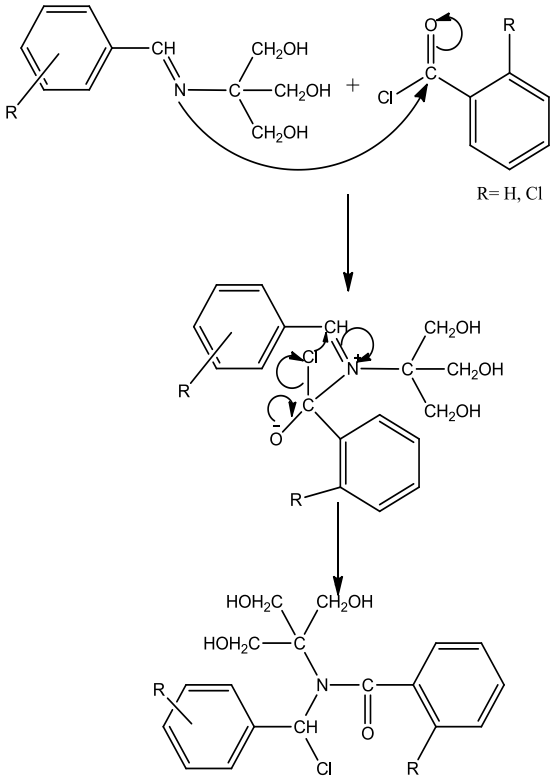
The reaction was followed by appearance of absorption bands (1596-1640cm^{-1}) for (C=N) at in their IR spectra. In this work, the reactions of Schiff bases (1-7) with benzoyl chloride (or 2-chlorobenzoyl chloride) to give corresponding derivatives amides compounds. Subsequent amides compounds (8-21) were reacted with thiourea to give corresponding derivatives thioureas (22-35). The summery of reactions is shown in scheme (1).

However, upon treatment of Schiff bases with acid chloride result formation amides compounds that content on new two groups is (C-Cl, Ar-C=O).



Scheme 1

This reaction was followed by appearance of absorption bands at (1035-748 cm^{-1}) and (1732-1720 cm^{-1}) which were to (C=Cl) and (C=O) respectively, but this reaction due to disappearance of absorption bands for (C=N). The reaction was involved the attack of azomethic nitrogen by the carbonyl group of the aroyl chlorides, displacing the chloride as chloride anion and forming the iminium cation, iminium cation was unstable ,so the -Cl attacked $-N^{+}=C$ moiety and afforded more stable covalently bonded compound (8-21) scheme 2.

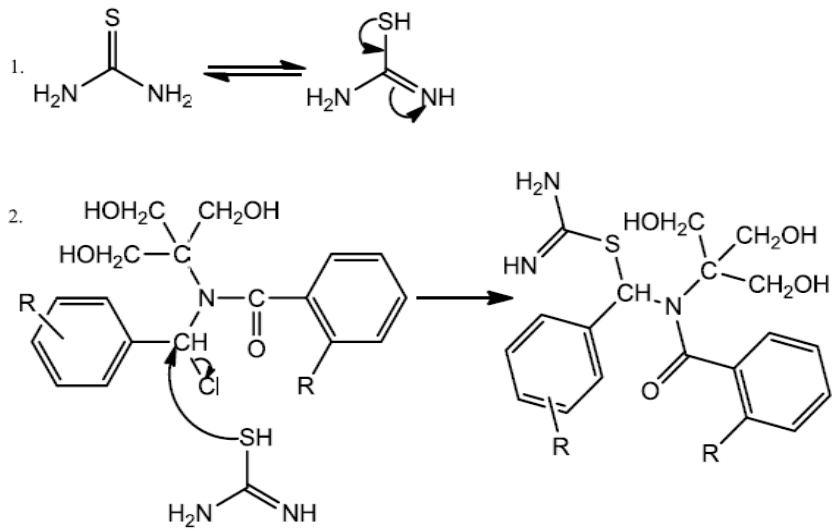


Scheme 2

The amides compounds (8-21) were treatment with thiourea and the presence of Na_2CO_3 for 3hr reflux. This is reaction led to the uncleophilic substitution of Cl by (—SC=NH / NH_2), and compounds (22-35) were afforded formed through the following mechanism scheme 3.

The IR spectra of compounds (22-35) are show doublet absorption bands in the zone (3285-3270 cm^{-1}) were attributed to (NH_2) and (NH) function moieties, and appearance the bands in the zone (1241-1246 cm^{-1}) were attributed to (υ C-S).

They show strong absorption ranging from (224-226)nm. These absorption were due(π-π*) transition or n-electrons of nitrogen atom which was in conjugation with bring groups. The UV-visible spectra showed the following maxima (230-245) nm and (300-380)nm, due to the presence of aromatic ring and a variety of substituent groups.



Scheme 3

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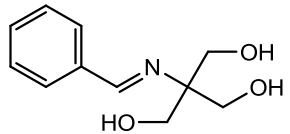
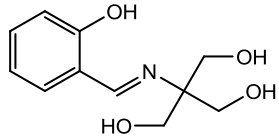
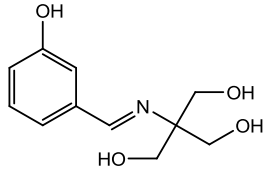
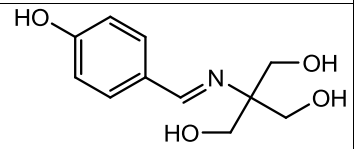
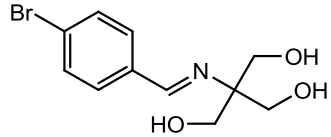
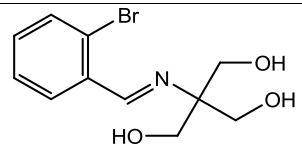
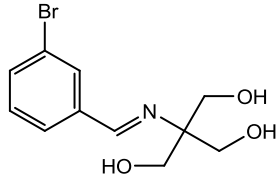
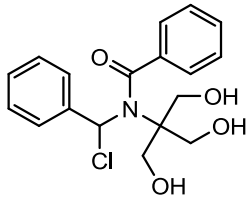
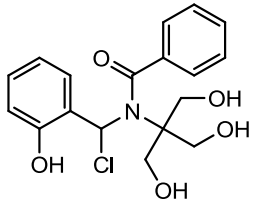
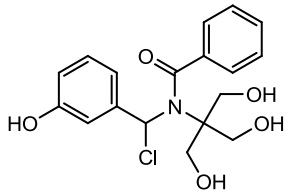
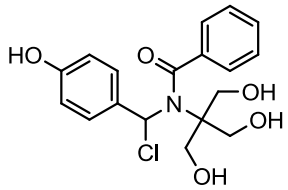
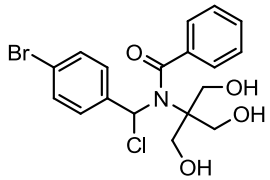
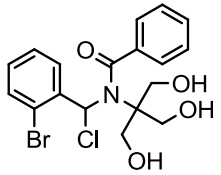
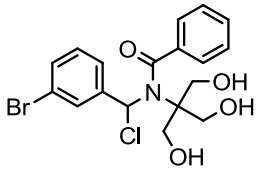
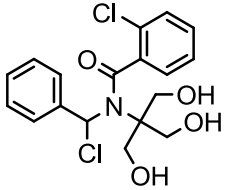
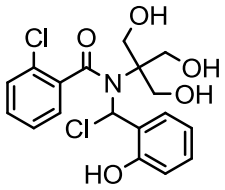
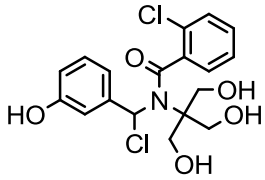
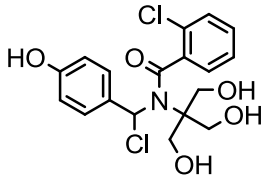
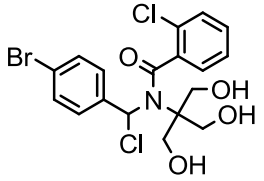
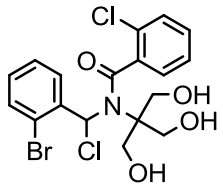
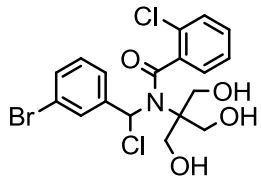
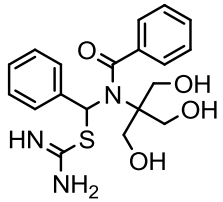
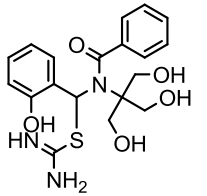
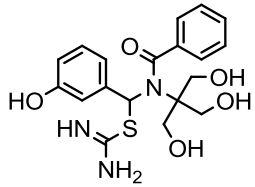
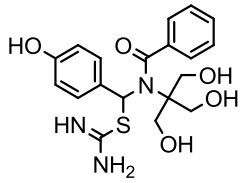
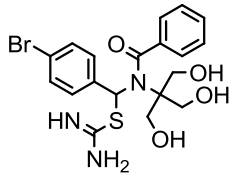
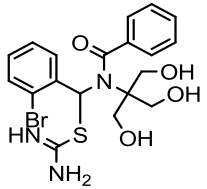
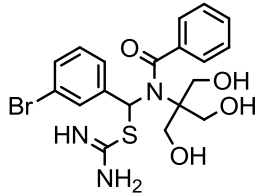
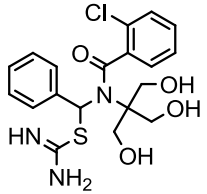
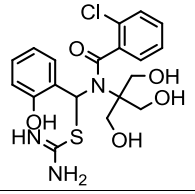
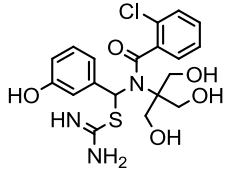
Table 1 :Some physical properties of compounds 1-35

Comp. No.	m.P.\c°	Yield %	Color	M.F	Name of compounds	% Analysis / Calc.(Found)			Structure
						C%	H%	N%	
1	146	96.5	White	$C_{11}H_{15}NO_3$	2-(Benzylideneamino-(2-)hydroxylmethyl)propane-1,3 -diol	63.14 (63.04)	7.23 (7.18)	6.69 (6.65)	
2	138	82.3	Yellow	$C_{11}H_{15}NO_4$	2-(2-hydroxybenzylideneamino-(2-)hydroxymethyl) propane-1,3-diol	58.66 (58.56)	6.71 (6.54)	6.22 (6.12)	
3	Gums	88.3	Black	$C_{11}H_{15}NO_4$	2-(3-hydroxybenzylideneamino-(2-)hydroxymethyl) propane-1,3-diol	58.66 (58.61)	6.71 (6.68)	6.22 (6.26)	
4	80	99	Brown	$C_{11}H_{15}NO_4$	2-(4-hydroxybenzylideneamino-(2-)hydroxymethyl) propane-1,3-diol	58.66 (58.63)	6.71 (6.69)	6.22 (6.75)	
5	84	91	White	$C_{11}H_{14}BrNO_3$	2-(4-bromobenzylideneamino-(2-)hydroxymethyl) propane-1,3-diol	45.85 (45.80)	4.90 (4.85)	4.86 (4.90)	
6	Gums	81.8	Yellow	$C_{11}H_{14}BrNO_3$	2-(2-bromobenzylideneamino-(2-)hydroxymethyl) propane-1,3-diol	45.85 (45.79)	4.90 (4.95)	4.86 (4.80)	
7	Gums	89	Yellow	$C_{11}H_{14}BrNO_3$	2-(3-bromobenzylideneamino-(2-)hydroxymethyl) propane-1,3-diol	45.85 (45.82)	4.90 (4.88)	4.86 (4.84)	

8	98	60	Brown	$C_{18}H_{20}ClNO_4$	N-(chloro(phenyl)methyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	61.80 (61.70)	5.76 (5.70)	4.00 (4.08)	
9	142	69	Black	$C_{18}H_{20}ClNO_5$	N-(chloro(2-hydroxyphenyl)methyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	59.10 (59.06)	5.51 (5.41)	3.83 (3.79)	
10	135	58	Brown	$C_{18}H_{20}ClNO_5$	N-(chloro(3-hydroxyphenyl)methyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	59.10 (59.06)	5.51 (5.45)	3.83 (3.85)	
11	Gums	40	Black	$C_{18}H_{20}ClNO_5$	N-(chloro(4-hydroxyphenyl)methyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	59.10 (59.01)	5.51 (5.41)	3.83 (3.78)	
12	148	70	Light brown	$C_{18}H_{19}BrNO_4$	N-((4-bromophenyl)chloromethyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	50.43 (50.48)	4.47 (4.44)	3.27 (3.23)	
13	142	62	White	$C_{18}H_{19}BrNO_4$	N-((2-bromophenyl)chloromethyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	50.43 (50.33)	4.47 (4.49)	3.27 (3.17)	

14	140	58	White	$C_{18}H_{19}BrNO_4$	N-((3-bromophenyl)chloromethyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	50.43 (50.48)	4.47 (4.37)	3.27 (3.15)	
15	213	56	White	$C_{18}H_{19}Cl_2NO_4$	2-chloro-N-(chloro(phenyl)methyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	56.26 (56.30)	4.98 (5.01)	3.65 (3.70)	
16	144	40	White	$C_{18}H_{19}Cl_2NO_5$	2-chloro-N-(chloro(2-hydroxyphenyl)methyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	54.01 (54.05)	4.78 (4.73)	3.50 (3.45)	
17	Gums	44	Black	$C_{18}H_{19}Cl_2NO_5$	2-chloro-N-(chloro(3-hydroxyphenyl)methyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	54.01 (53.98)	4.78 (4.67)	3.50 (3.40)	
18	Gums	48	Brown	$C_{18}H_{19}Cl_2NO_5$	2-chloro-N-(chloro(4-hydroxyphenyl)methyl)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	54.01 (54.03)	4.78 (4.73)	3.50 (3.43)	
19	Gums	41	Black	$C_{18}H_{18}BrCl_2NO_4$	N-((4-bromophenyl)chloromethyl)-2-chloro-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	46.68 (46.63)	3.92 (3.88)	3.02 (2.97)	

20	150	36	White	$C_{18}H_{18}BrCl_2NO_4$	N-((2-bromophenyl)chloromethyl)-2-chloro-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	46.68 (46.58)	3.92 (3.82)	3.02 (3.15)	
21	140	39	White	$C_{18}H_{18}BrCl_2NO_4$	N-((3-bromophenyl)chloromethyl)-2-chloro-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamide	46.68 (46.64)	3.92 (3.95)	3.02 (3.05)	
22	350 Comp.	45	Light brown	$C_{19}H_{23}N_3O_4S$	(N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)(phenyl)methyl carbamimidothioate	58.59 (58.52)	5.95 (5.90)	10.79 (10.70)	
23	230 Comp.	54.7	Light brown	$C_{19}H_{23}N_3O_5S$	(N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)(2-hydroxyphenyl)methyl carbamimidothioate	56.28 (56.20)	5.72 (5.62)	10.36 (10.30)	
24	248 Comp.	37	White	$C_{19}H_{23}N_3O_5S$	(N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)(3-hydroxyphenyl)methyl carbamimidothioate	56.28 (56.18)	5.72 (5.68)	10.36 (10.26)	
25	350 Comp.	40.8	Light brown	$C_{19}H_{23}N_3O_5S$	(N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)(4-hydroxyphenyl)methyl carbamimidothioate	56.28 (56.21)	5.72 (5.63)	10.36 (10.30)	

26	380 Comp.	41.2	Light brown	$C_{19}H_{22}BrN_3O_4S$	(4-bromophenyl)(N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)methyl carbamimidothioate	48.72 (48.68)	4.73 (4.65)	8.97 (8.87)	
27	345 Comp.	34	White	$C_{19}H_{22}BrN_3O_4S$	(2-bromophenyl)(N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)methyl carbamimidothioate	48.72 (48.75)	4.73 (4.62)	8.97 (8.89)	
28	280 Comp.	15	White	$C_{19}H_{22}BrN_3O_4S$	(3-bromophenyl)(N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)methyl carbamimidothioate	48.72 (48.70)	4.73 (4.60)	8.97 (8.95)	
29	246 Comp.	40	White	$C_{19}H_{22}ClN_3O_4S$	(2-chloro-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)(phenyl)methyl carbamimidothioate	53.83 (53.80)	5.23 (5.12)	9.91 (9.88)	
30	368 Comp.	35	White	$C_{19}H_{22}ClN_3O_5S$	(2-chloro-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)(2-hydroxyphenyl)methyl carbamimidothioate	51.87 (51.76)	5.04 (5.01)	9.55 (9.46)	
31	290 Comp.	15	Brown	$C_{19}H_{22}ClN_3O_5S$	(2-chloro-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)(3-hydroxyphenyl)methyl carbamimidothioate	51.87 (51.77)	5.04 (5.06)	9.55 (9.61)	

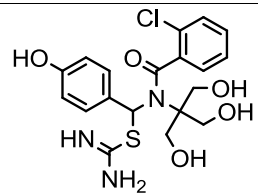
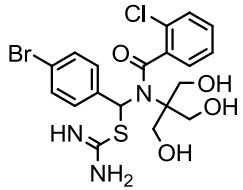
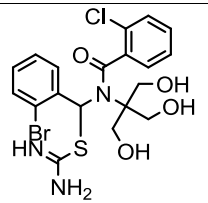
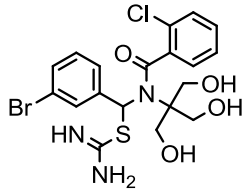
32	190 Comp.	54	Brown	$C_{19}H_{22}ClN_3O_5S$	(2-chloro-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)(4-hydroxyphenyl)methyl carbamimidothioate	51.87 (51.90)	5.04 (5.01)	9.55 (9.50)	
33	300 Comp.	48	White	$C_{19}H_{21}BrClN_3O_4S$	(4-bromophenyl)(2-chloro-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)methyl carbamimidothioate	45.39 (45.28)	4.21 (4.15)	8.36 (8.30)	
34	218 Comp.	55.5	White	$C_{19}H_{21}BrClN_3O_4S$	(2-bromophenyl)(2-chloro-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)methyl carbamimidothioate	45.39 (45.35)	4.21 (4.25)	8.36 (8.29)	
35	350 Comp.	50	Light brown	$C_{19}H_{21}BrClN_3O_4S$	(3-bromophenyl)(2-chloro-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)benzamido)methyl carbamimidothioate	45.39 (45.27)	4.21 (4.11)	8.36 (8.39)	

Table 2 : IR Spectra data of Compounds (1-21)

Comp. No.	υ O-H cm^{-1}	υ C-H ar. cm^{-1}	υ C-H al. cm^{-1}	υ C=O cm^{-1}	υ C-N cm^{-1}	υ C=N cm^{-1}	υ C-O cm^{-1}	υ C=C cm^{-1}	υ C-Br cm^{-1}	υ C-Cl cm^{-1}
1	3420	3090	2937	-	1401	1635	1070	1546	-	-
2	3425	3064	2937	-	1393	1636	1057	1533	-	-
3	3415	3070	2939	-	1392	1596	1048	1540	-	-
4	3430	3085	2968	-	1403	1637	1054	1539	-	-
5	3433	3070	2870	-	1400	1637	1052	1544	701	-
6	3417	3040	2933	-	1398	1634	1043	1540	700	-
7	3424	3085	2934	-	1402	1640	1048	1550	696	-
8	3427	3068	2934	1722	1404	-	1070	1545	-	1026
9	3433	3073	2937	1721	1404	-	1067	1547	-	748
10	3410	3064	2935	1720	1402	-	1071	1542	-	1024
11	3427	3068	2933	1721	1401	-	1070	1584	-	1026
12	3435	3060	2946	1720	1402	-	1064	1553	712	1035
13	3420	3065	2940	1723	1404	-	1067	1550	710	1020
14	3427	3063	2943	1720	1401	-	1071	1547	701	1024
15	3430	3083	2936	1722	1404	-	1069	1543	-	1026
16	3420	3065	2935	1729	1403	-	1050	1544	-	1024
17	3425	3068	2933	1730	1401	-	1050	1540	-	1015
18	3421	3071	2934	1732	1406	-	1051	1545	-	1025
19	3423	3068	2934	1730	1403	-	1050	1548	694	1015
20	3430	3065	2940	1721	1402	-	1052	1547	705	1020
21	3427	3063	2933	1723	1404	-	1051	1545	710	1026

Table 3 : IR Spectra data of Compounds (22-35)

Comp. No.	υ N-H cm^{-1}	υ O-H cm^{-1}	υ C-H ar. cm^{-1}	υ C-H al. cm^{-1}	υ C=O cm^{-1}	υ C-N cm^{-1}	υ C=N cm^{-1}	υ C-O cm^{-1}	υ C=C cm^{-1}	υ C-Br cm^{-1}	υ C-S cm^{-1}	υ C-Cl cm^{-1}
22	3276	3420	3090	2937	-	1401	1635	1070	1546	-	1243	-
23	3278	3425	3064	2937	-	1393	1636	1057	1533	-	1242	-
24	3275	3415	3070	2939	-	1392	1596	1048	1540	-	1245	-
25	3285	3430	3085	2968	-	1403	1637	1054	1539	-	1241	-
26	3270	3433	3070	2870	-	1400	1637	1052	1544	701	1244	-
27	3274	3417	3040	2933	-	1398	1634	1043	1540	700	1241	-
28	3276	3424	3085	2934	-	1402	1640	1048	1550	696	1246	-
29	3280	3427	3068	2934	1722	1404	-	1070	1545	-	1246	1026
30	3277	3433	3073	2937	1721	1404	-	1067	1547	-	1241	748
31	3281	3410	3064	2935	1720	1402	-	1071	1542	-	1244	1024
32	3276	3427	3068	2933	1721	1401	-	1070	1584	-	1245	1026
33	3281	3435	3060	2946	1720	1402	-	1064	1553	712	1242	1035
34	3276	3420	3065	2940	1723	1404	-	1067	1550	710	1243	1020
35	3275	3427	3063	2943	1720	1401	-	1071	1547	701	1241	1024

Table 4: UV-Vis. Spectra data of Compounds (1-35)

Compound	UV-Visible absorption maxima λ/nm	Compound	UV-Visible absorption maxima λ/nm
1	224,230, 268, 300	19	224, 238, 244, 308
2	224,230,254, 262,380	20	226, 240, 276, 308
3	226,231,262,305	21	224, 240, 278, 310
4	224,230,252,278,332	22	226, 242, 282,330
5	226,230, 258, 330	23	224, 240, 275, 325
6	224,240,260, 376	24	226, 240, 282, 334
7	226,300,259, 374	25	226, 242, 280, 335
8	225, 245, 278,310	26	226, 240, 276, 340
9	226, 236, 275, 305	27	225, 245, 278, 310
10	224, 238, 278, 316	28	226, 238, 281, 330
11	226, 240, 264, 315	29	224, 240, 276, 360
12	226, 242, 262, 372	30	226, 245, 278, 342
13	226, 238, 272, 365	31	226, 243, 275, 315
14	226, 240, 272, 325	32	224, 237, 245, 310
15	226, 240, 276, 362	33	226, 264, 273, 325
16	226, 240, 276, 362	34	224, 244, 264, 308
17	226, 242, 278, 315	35	226, 245, 278, 317
18	226, 242, 282, 314		