

MATERIALS and METHODS

Materials :

All materials were from BDH ,FLUKA and REDLE –DE HAEN . All other solvents were analar grade .

Instrumentations :

Melting points were measured on a Gallan Kamp MFB-600 Melting point apparatus in Al-Mustansyria university –Iraq and were uncorrected .

FTIR spectra were recorded as potassium bromide (KBr) disk on FTIR -8400S Fourier Transform Infrared Spectrophotometer "SHIMADZU" in Al-Mustansyria university-Iraq.

UV-Visible spectra were recorded on CARY 100 Conc UV-Visible Spectrophotometer "VARIAN" in Al-Mustansyria university-Iraq .

¹H NMR spectra were recorded on Burker DMX- 500 NMR (300-600 MHz)Spectrophotometer with using DMSO as a solvent in Jordan University.

Preparation of (C₁) [12]

(7-hydroxy-4-methyl-2H-chromen-2-one)

A mixture of resorcinol (0.05mol, 5.5g), ethylacetoacetate (0.05mol, 6.05g) and H₂SO₄ (50mL,75%) was heated on water bath 100⁰C for 0.5h. The resulting mixture was cooled, poured onto crushed ice, then filtered off. The crude product was washed with distilled water, dried and recrystallized from ethanol. The physical properties are listed in table 1.

Synthesis of (C₂) [13]

(4-methyl-2-oxo-2H-chromen-7-yl acetate)

Compound (C₁) (0.005mol, 0.88g) was dissolved in a mixture of acetic anhydride (1.5mL) and glacial acetic acid (1mL). The mixture was heated on water bath 100⁰C for 2h., with occasional stirring. The reaction mixture was poured onto crushed ice. The precipitated solid was filtered off, washed with distilled water, dried and recrystallized from ethanol. The physical properties are listed in table 1.

Synthesis of (C₃) [14]

(4-methyl-2-oxo-2H-chromen-7-yl bromoacetate)

Compound(C₂)(0.01mol, 1g) was dissolved in (15mL) of absolute ethanol, to this solution bromine (0.01mol,16mL) in glacial acetic acid (10mL) was added drop wise with constant stirring. The reaction mixture was stirred at 40⁰C for 4h. and then cooled and poured onto crushed ice. The precipitated solid was washed with distilled water, dried and recrystallized from ethanol. The physical properties are listed in table 1.

Synthesis of (C₄) [15]

(4-methyl-2-oxo-2H-chromen-7-yl (1,3-benzothiazol-2-ylamino)acetate)

Compound C₃ (0.001mol,0.29g) and 2-aminobenzothiazole(0.001mol, 0.15g) were dissolved in acetone (20mL). The reaction mixture was refluxed for 2h., then it was cooled, filtered off, dried and recrystallized from ethanol . The physical properties are listed in table 1.

Synthesis of (C₅) [16]

(7-chloro-4-methyl-2H-chromen-2-one)

POCl₃ (0.01mol,1.52g) was added to compound (C₁) (0.01 mol,1.76g) and the reaction mixture was refluxed for 0.5h., set aside, then poured onto crushed ice, filtered off, washed well with distilled water, dried and recrystallized from benzene. The physical properties are listed in table 1.

Synthesis of (C₆) [17]

(7-(1,3-benzothiazol-2-ylamino)-4-methyl-2H-chromen-2-one)

A mixture of compound (C₅) (0.002mol, 0.38g) and 2-aminobenzo- thiazole (0.002mol, 0.3g) was dissolved in ethyl acetate (10mL) and then it was refluxed in presence of (1mL) triethyl amine for 6h. After cooling, the precipitated solid was filtered off and washed with ethyl acetate and distilled water. The purity of the synthesized compound was checked by TLC. The physical properties are listed in table 1.

Synthesis of (C₇) [18]

(1-(7-hydroxy-4-methyl-2-oxoquinolin-1(2H)-yl)thiourea)

Solution of compound (C₆) (0.02mol, 3.5g) and thiosemicarbazide (0.02mol, 1.84g) in DMF was refluxed for 8h. After cooling, the precipitated solid was filtered off and washed with cold ethanol. The physical properties are listed in table 1.

Synthesis of (C₈) [19]

(5-methyl-2-sulfanyl[1,2,4]triazolo[1,5-a]quinolin-8-ol)

Compound (C₇) (0.005mol, 1.23g) was added drop wise to(15mL) of 2M NaOH solution. The reaction mixture was refluxed for 24 h. It was allowed to cool and filtered. The filtrate was acidified with 2M HCl. The precipitated solid was filtered off, washed with distilled water, dried and recrystallized from 70% ethanol. The physical properties are listed in table 1.

Synthesis of (C₉) [20]

(2-(1,3-benzothiazol-2-ylamino)-5-methyl[1,2,4]triazolo[1,5-a]quinolin-8-ol)

A mixture of compound (C₈) (0.005mol,1.2g) and 2-aminobenzo- thiazole (0.005mol, 0.7g) in absolute ethanol was refluxed for 8h. It was concentrated and then cooled, the precipitated solid was filtered off, dried and recrystallized from ethanol. The physical properties are listed in table 1.

Synthesis of (C₁₀) [21]

7,7'-(benzo[d]thiazol-2-ylazanediy)bis(4-methyl-2H-chromen-2-one)

A mixture of compound (C₁) (0.004mol, 0.7g) and 2-aminobenzo- thiazole (0.002mol, 0.3g) in absolute ethanol was refluxed in presence of anhydrous ZnCl₂ (0.5g) for 6h. On cooling a solid mass was separated out which was filtered off, washed with acidified distilled water to remove inorganic materials, then it was dried and recrystallized from ethanol. The physical properties are listed in table 1.

RESULTS AND DISCUSSION

The synthesis of compound C₁ was achieved by Pechmann Duisberge reaction of ethylacetoacetate with equimolar amount of resorcinol in presence of sulfuric acid. This reaction produces β-hydroxyester which converts to corresponding coumarin. The structure of compound(C₁) is confirmed by its physical properties and spectral data. FTIR spectrum (Fig.1) shows the appearance of (O-H) stretching frequency at 3502 cm⁻¹ and (C=O) stretching frequency at 1670 cm⁻¹ [22].

Compound C₂ was prepared through acylation of compound C₁ by acetic anhydride . The structure of this compound is confirmed by its physical properties and spectral data. FTIR spectrum shows the disappearance of (O-H) stretching frequency that belongs to compound C₁ while two (C=O) stretching frequencies appear at 1763 and 1695 cm⁻¹.

Bromination of compound C₂ produces bromoester derivative which is important compound in the synthesis of various heterocyclic compounds. The structure of this compound is confirmed by its physical properties and spectral data. FTIR spectrum shows the appearance of (C-Br) stretching

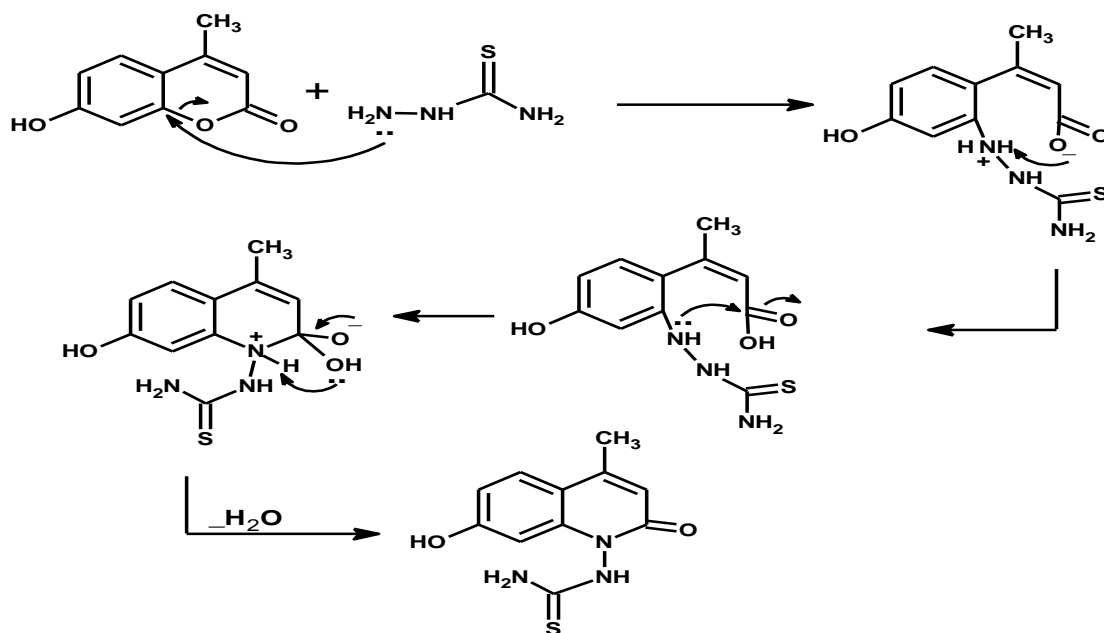
frequency at 752 cm^{-1} . It also show the appearance of two stretching frequencies of two kind of (C=O) groups at 1730 cm^{-1} and at 1716 cm^{-1} beside the appearance of (C-O) stretching frequency at 1140 cm^{-1} and at 1188 cm^{-1} .

Compound C₄ was prepared through the substitution of 2-amino- benzothiazole instead of the brome atom in the compound C₃ through S_N2 mechanism. The structure of this compound is confirmed by its physical properties and spectral data. FTIR spectrum shows the appearance of (N-H) stretching frequency that belongs to 2-aminobenzothiazole at 3265 cm^{-1} and (C=N) stretching frequency at 1635 cm^{-1} . ¹H NMR (Fig.4) spectrum shows the peaks at : 2.2 ppm (3H, CH₃), 4.1 ppm (1H , NH), 4.2 ppm (2H , NH-CH₂COO), 6.34 ppm (1H, olefinic H) , 7.1-7.9 ppm (8H ,Ar-H).

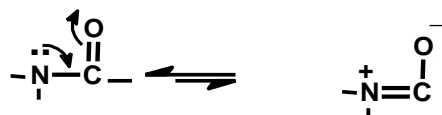
Compound C₅ was prepared through the reaction of compound C₁ with POCl₃ without any other solvent .The structure of this compound is confirmed by its physical properties and spectral data. FTIR spectrum shows the disappearance of (O-H) stretching frequency that belongs to compound C₄ and the appearance of (C-Cl) stretching frequency at 1044 cm^{-1} .

Compound C₆ was prepared through the nucleophilic aromatic substitution of 2-aminobenzothiazole on the aromatic ring of compound C₅ .The structure of this compound is confirmed by its physical properties and spectral data. FTIR spectrum shows the appearance of (N-H) stretching frequency at 3304 cm^{-1} beside the appearance of (C=O) stretching frequency at 1708 cm^{-1} and (C=N) stretching frequency at 1635 cm^{-1} .

Compound C₇ was prepared through the condensation between compound C₁ and thiosemicarbazide as it is illustrated in the mechanism bellow .



The structure of this compound is confirmed by its physical properties and spectral data. FTIR spectrum (Fig. 2) shows the appearance of (O-H) stretching frequency at 3369 cm^{-1} and two bands of (NH₂) stretching frequency at $3267\text{-}3180\text{ cm}^{-1}$. (C=O) stretching frequency decreases from 1708 cm^{-1} in compound C₆ to 1645 cm^{-1} in this compound and this is because of the bonded nitrogen atom which causes resonance in this specific area in the molecule that decreases the force constant of the carbonyl group.

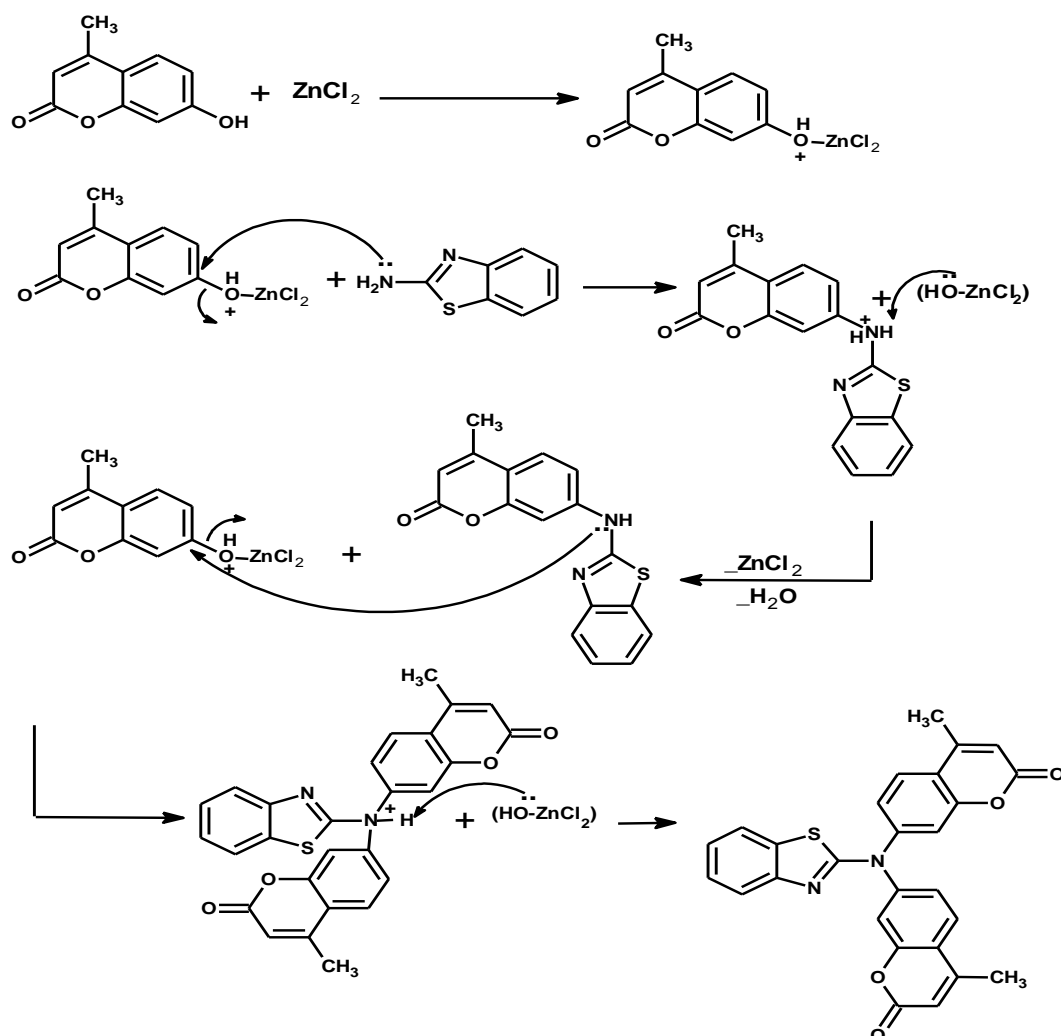


¹ HNMR spectrum (Fig.5) shows the peaks at : 2.2 ppm (3H ,CH₃), 5.1ppm (OH& NH), 6.43 ppm (1H, C-H olefinic) 7.4-7.8 ppm (3H , Ar-H), 8.6 ppm (2H , NH₂) .

Compound C₇ on reaction with aqueous NaOH produces triazole derivative (compound C₈) .The structure of this compound is confirmed by its physical properties and spectral data. FTIR spectrum shows the appearance of (C=N) stretching frequency at 1600 cm⁻¹ and (S-H) stretching frequency at 2364 cm⁻¹. It also shows the disappearance of (C=O) frequency that belongs to compound C₇ .

Compound C₉ was prepared through the reaction between compound C₈ and 2-aminobenzothiazole and this occurs by the nucleophilic attack of amine group of 2-aminobenzothiazole on the carbon atom that hold the sulfur atom in compound C₈ through the Tetrahedral mechanism then H₂S molecule is displaced. The structure of this compound is confirmed by its physical properties and spectral data. FTIR spectrum shows the appearance of (N-H) stretching frequency at 3215 cm⁻¹ and (O-H) stretching frequency at 3338 cm⁻¹ .

Compound C₁₀ was prepared through the condensation of 2-aminobenzothiazole with compound C₁ at ratio of 1:2 in presence of anhydrous ZnCl₂ . The mechanism is expected to be as follows:



The structure of this compound is confirmed by its physical properties and spectral data. FTIR spectrum (Fig.3) shows the appearance of two (C=O) stretching frequencies one at 1772 cm^{-1} and the other at 1737 cm^{-1} , it also shows the disappearance of (NH₂) stretching frequency that belongs to 2-aminobenzothiazole .

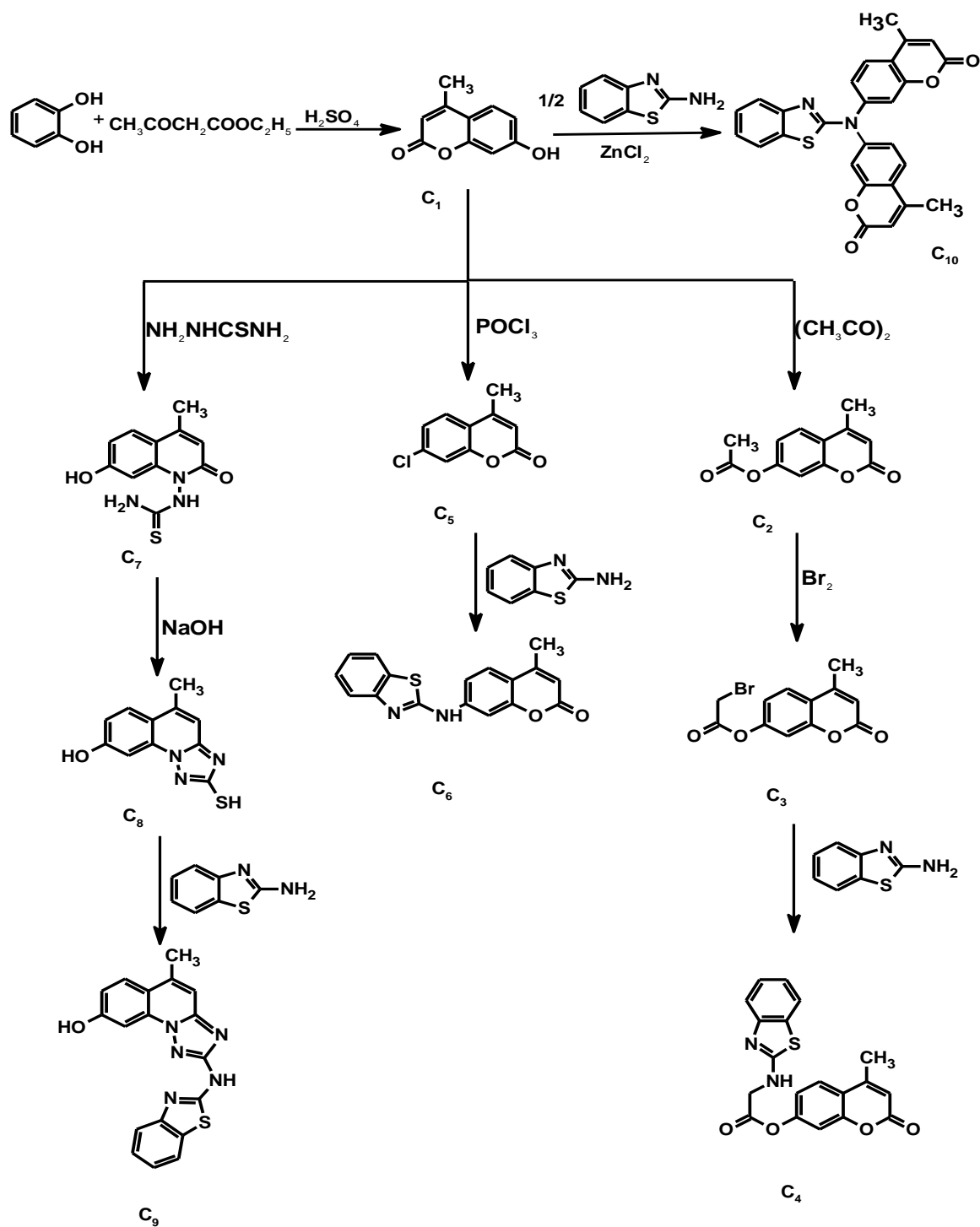
¹ HNMR spectrum (Fig.6) shows the peaks at : 2.3 ppm (6H, 2CH₃) ,6.1 (2H , olefinic H) , 6.4- 8.0 ppm (10H, Ar-H) .

Table 1: physical properties for compounds C₁-C₁₀

Comp .No.	Color	m.p ⁰ C	Yield %	Molecular Formula
C ₁	pale yellow	185-187 Lit: 185	81	C ₁₀ H ₈ O ₃
C ₂	White	141-142	75	C ₁₂ H ₁₀ O ₄
C ₃	Off white	95-97	51	C ₁₂ H ₉ O ₄ Br
C ₄	yellow	190-192	85	C ₁₉ H ₁₄ N ₂ SO ₄
C ₅	brown	217-220	85	C ₁₀ H ₇ O ₂ Cl
C ₆	Light green	200-203	55	C ₁₇ H ₁₂ N ₂ SO ₂
C ₇	White	162-165	60	C ₁₁ H ₁₀ N ₃ SO ₂
C ₈	Pale yellow	198-200	43	C ₁₁ H ₉ N ₃ SO
C ₉	Dark yellow	245-248	60	C ₁₈ H ₁₃ N ₅ SO
C ₁₀	Grey	285-287	40	C ₂₇ H ₁₈ N ₂ SO ₄

Table 2 : Spectral data for compounds C₁-C₁₀

Comp. No.	UV (EtOH)	Characteristic bands of FT-IR(cm ⁻¹ KBr disk)			
	λ max (nm) (10 ⁻⁴ M)	ν (N-H)	ν (C=O)	ν (C-H)	ν (others)
C ₁	323 205	-----	1670	Ar. =3005 Al.=2953	ν (C-O) =1147 ν (O-H)=3502
C ₂	350 313 255 206	-----	1763,1695	Ar. =3057 Al.=2989	ν (C-O) =1147 ,1190
C ₃	336 213		1730,1716	Ar. =3097 Al.=2825	ν (C-Br) =752 ν (C-O) =1140,1188
C ₄	300 219	3265	1722	Ar. =3078 Al.=2729	ν (C=N)=1635 ν (C-N) =1390 ν (C-S) =1166
C ₅	317 204	-----	1707	Ar. =3080 Al.=2983	ν (C-Cl) =1044 ν (C-O) = 1159
C ₆	262 222	3304	1708	Ar. =3072 Al.=2987	ν (C=N)= 1635 ν (C-O)=1124 ν (C-N) =1282
C ₇	351 334 241 205	3267- 3180	1645	Ar. =3043 Al.=2974	ν (O-H) =3369 ν (C=S) =1317
C ₈	321 341 205	3360	-----	Ar. =3068 Al.=2974	ν (C=N) =1600 ν (S-H) = 2364 ν (C-N) =1273 ν (C-S) =1166
C ₉	323 371 219 207	3215	-----	Ar. =3049 Al.=2941	ν (C=N) =1602 ν (O-H) = 3338 ν (C-N) =1292 ν (C-S) =1166
C ₁₀	350 335 260 205	-----	1772,1737	Ar. =3095 Al.=2962	ν (C=N) =1626 ν (C-N) = 1273 ν (C-O)=1058 ν (C-S) =1145



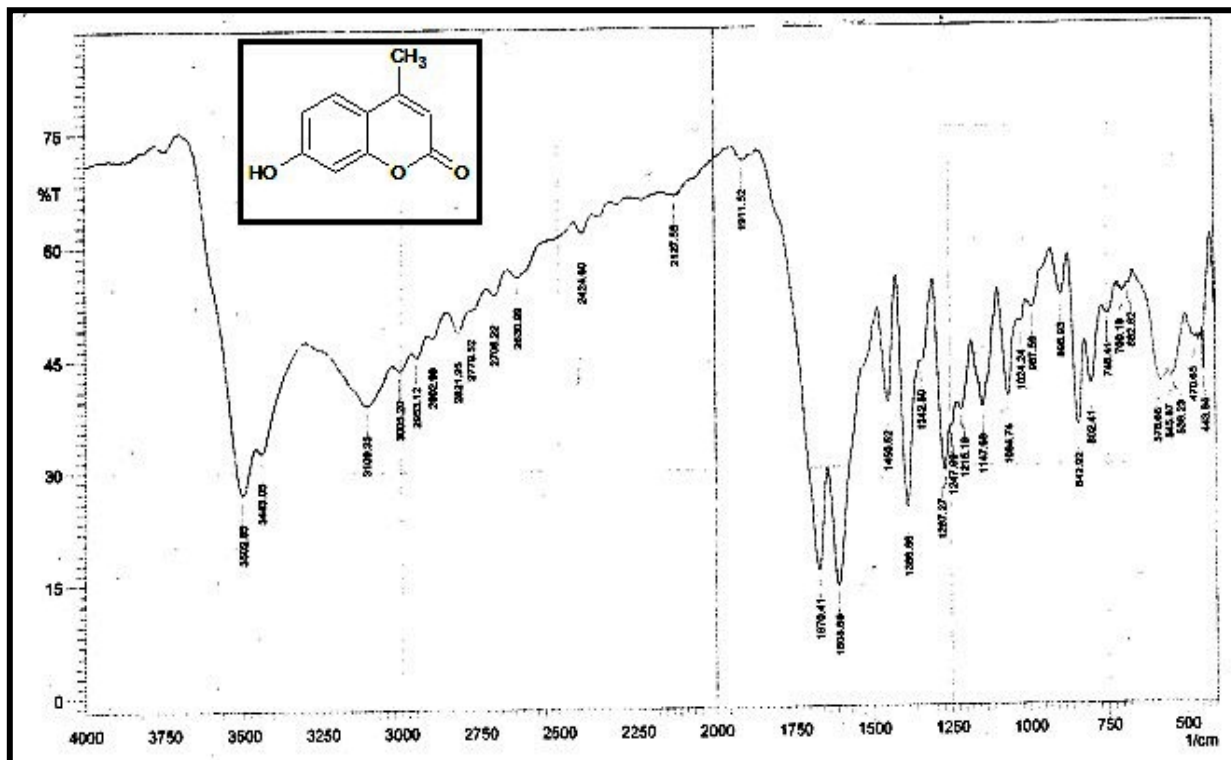


Fig. (1) FTIR Spectrum for compound C₁

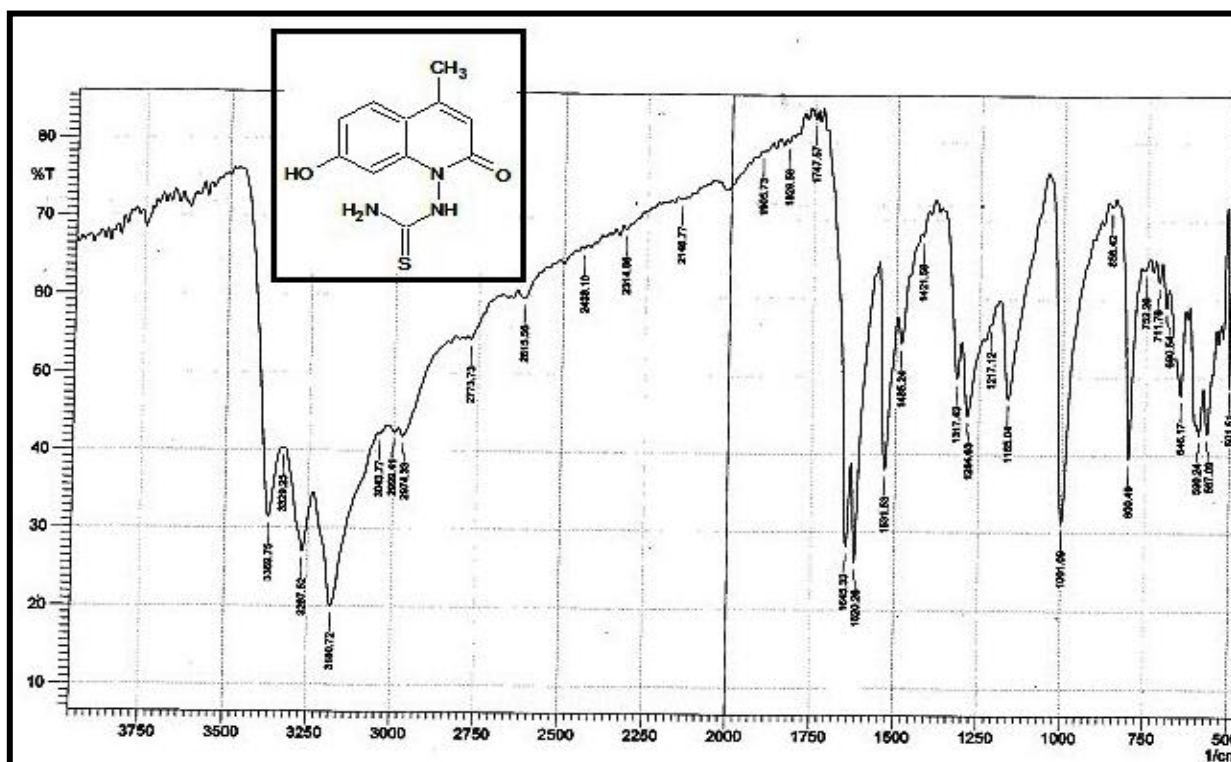


Fig. (2) FTIR Spectrum for compound C₇

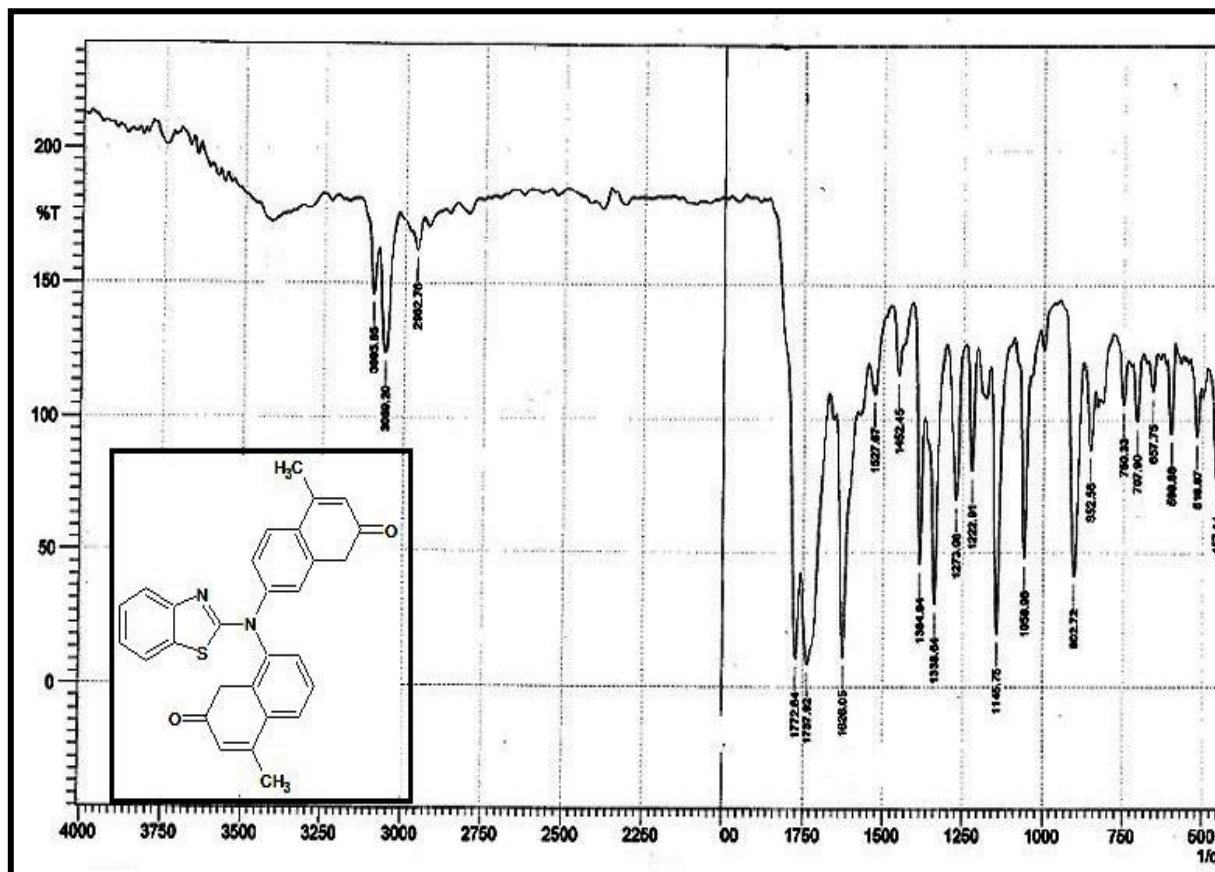


Fig. (3) FTIR Spectrum for compound C₁₀

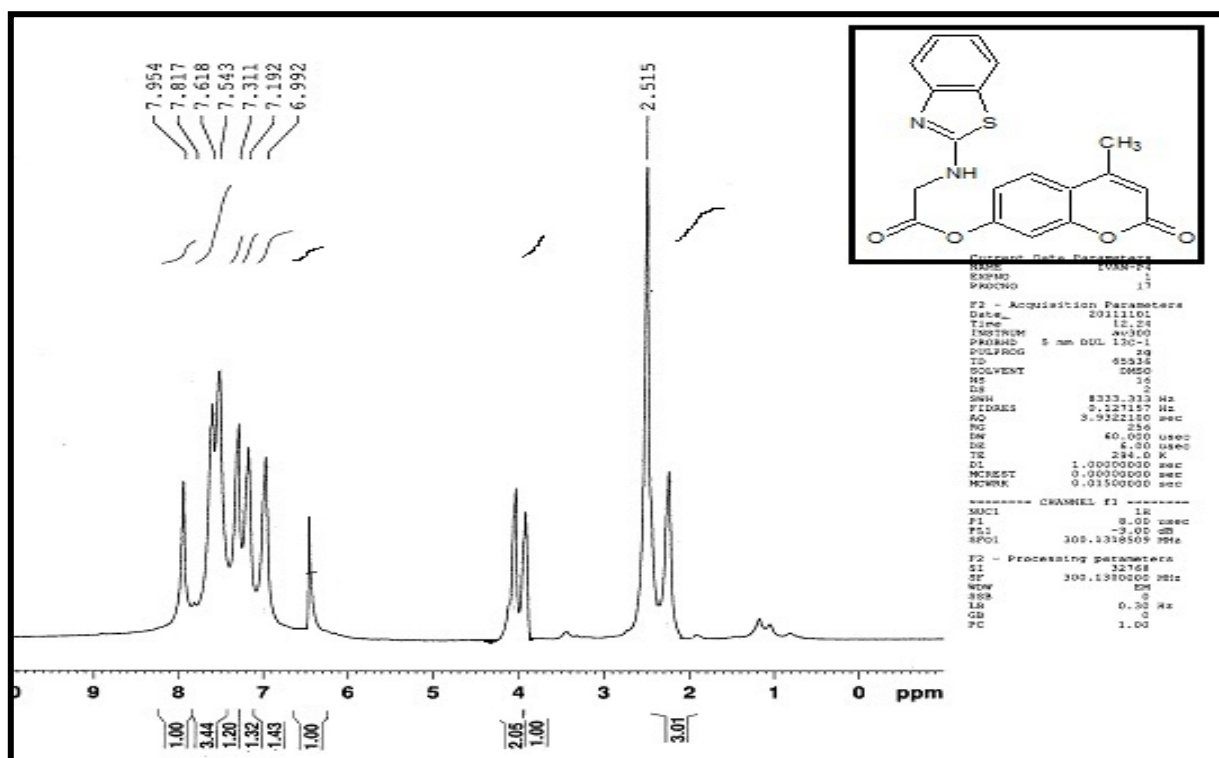


Fig.(4) ¹H NMR Spectrum for compound C₄

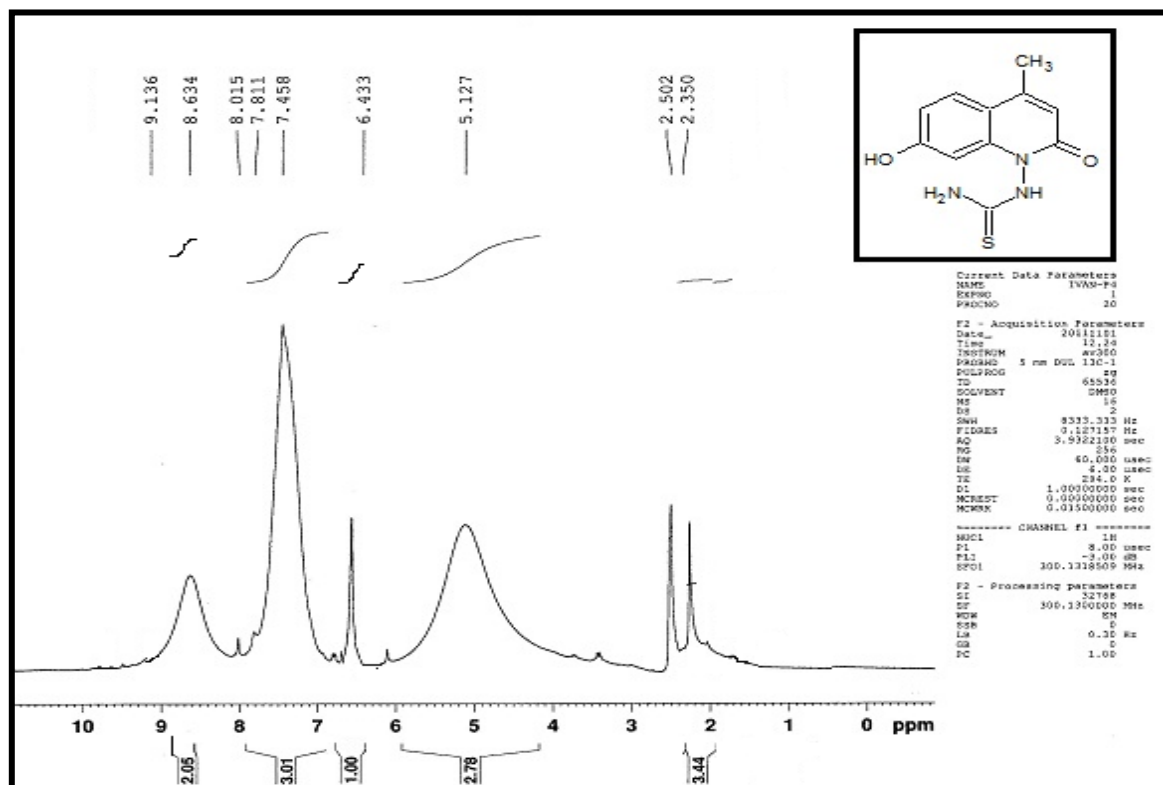


Fig. (5) ^1H NMR Spectrum for compound C₇

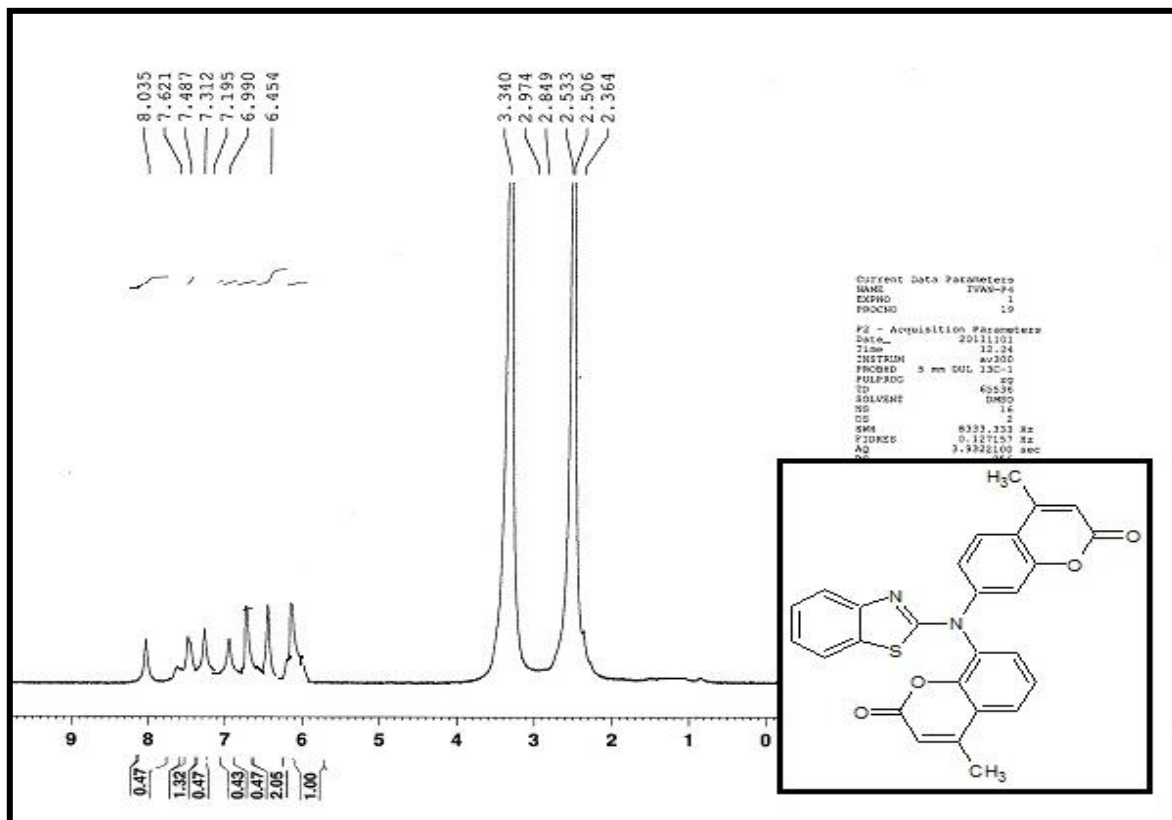


Fig. (6) ^1H NMR Spectrum for compound C₁₀

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