

Synthesis of New Schiff Bases and 2, 3-Disubstituted -1, 3-Thiazolidin-4-One Derivatives Containing Fluorene Moiety

Thawra Ahmad Chemistry Department, Faculty of Sciences, Damascus University, Damascus, Syria

Farouk Kandil Chemistry Department, Faculty of Sciences, Damascus University, Damascus, Syria

Chahid Moustapha Chemistry Department, Faculty of Sciences, Tishreen University, Lattakia, Syria

Keywords

Schiff Bases, 2-Acetyl Fluorene, 5-Nitro-2-Amino Thiazole, 5-Amino-1,3,4-Thiadiazole-2-Thiitol, Thiazolidine-4-One

Three series of Schiff Bases and 2,3-disubstituted-1,3-thiazolidin-4-one derivatives. The first series of new Schiff Bases was synthesized by reaction of primary amine (5-nitro,2-amino thiazole) was condensed with aromatic ketone (2-acetyl fluorine) in DMF (dimethyl form amide) in the presence of conc. HCl acid as catalyst to yield the Schiff bases (I,II,III). Two series of Schiff Bases and 2,3-disubstituted-1,3-thiazolidin-4-one derivatives were synthesized by reaction of (5-amino-1,3,4-thiadiazole,2-thiole) with (2-acetyl fluorine) in DMF in the presence of conc. HCl acid as catalyst to yield the Schiff base (IV). The Schiff base (IV) with α -chloro acetic acid gave compound (V). Esterification of carboxylic moiety of compound (V), using absolute methanol in the presence of conc. H_2SO_4 yielded a corresponding ester (VI), which was condensed with hydrazine hydrate to give acid hydrazide (VII). The new Schiff bases (VIII) were synthesized by reaction of acid hydrazide with terephthalaldehyde in the presence of glacial acetic acid. The thiazolidinone derivatives (IX) have been obtained from the azomethines through the addition of α -mercaptoacetic acid. The structures of synthesized compounds has been established on the basis of their spectral (FT-IR, Mass, 1H , ^{13}C -NMR, elemental analysis) data. The purity of the compounds was confirmed by TLC.

Introduction

Thiazolidin-4-one derivatives have attracted a great deal of interest due to their antibacterial¹⁻³, anti-inflammatory⁴, fungicidal activity⁵, antifeedant activity, acaricidal activity, contact toxicity, and stomach toxicity⁶. Over views of their synthesis, properties reactions and applications have been published^{7,8}. Fluorene derivatives have been reported to have broad range of biological activities^{9,10}. These findings focused particular interest on incorporating thiazolidinone and 2-acetyl fluorine in one framework, which could be useful for biological and pharmacological screening.

The development of simple synthesis route to widely used heterocyclic organic compounds, using readily available reagents is one of the main objective of organic synthesis, Nitrogen, Oxygen and sulfur heterocycles are of a special interests because they constitute an important class of natural and non-natural products, many of which exhibit useful biological activities, one-pot efficient synthesis of heterocyclic derivatives, may permit the development of novel drugs for the treatment of inflammation, pain, infection and other diseases¹¹.

In this paper we have synthesized new Schiff bases, and heterocyclic derivatives from 2-acetyl fluorine with primary amine because these compounds have many applications in medicine and industry.

Material and Methods

General Procedures

Melting points were determined in open glass capillaries on Agallenkamp apparatus and are uncorrected. TLC was performed to assess the reactions and the purity of the products. IR spectra were recorded in KBr (pellet forms) on a Nicolet-Avatar-330FT-IR spectrophotometer and noteworthy absorption values (cm^{-1}) are listed. ^1H and ^{13}C -NMR Spectra were recorded at 400 MHz Bruker AMX using CDCl_3 as solvent. The MS spectra were recorded on a Bruker Daltonics LC-MS Spectrometer. Satisfactory microanalysis was obtained on Carlo Erba 1106 CHN analyzer.

Chemical and Starting Materials

2-acetyl fluorine, 5-nitro-2-amino thiazole, 5-amino-1,3,4-thiadiazole-2-thiol, α -chloro acetic acid, α -mercaptoacetic acid, glacial acetic acid, hydrazine hydrate, dioxan, terephthalaldehyde, conc. HCl acid, conc. H_2SO_4 acid, thiourea and acetyl chloride (all from Aldrich) were used as supplied, without further purification.

General Procedure for Synthesis of Schiff Base and Its Derivatives

Preparation of Schiff Bases (I,IV)

Schiff bases (I,IV) were prepared by the reaction of two primary amines (5-nitro-2-amino thiazole, 5-amino-1,3,4-thiadiazole, 2-thiol) (0.02 mol), with 2-acetylfluorene (0.02 mol), in 50 ml DMF and few drops of conc. HCl acid. This mixture was refluxed for (12-14) hrs. The mixture was cooled. The formed precipitate was recrystallized from absolute ethanol¹²⁻¹³.

Preparation of compounds (II,III)

Preparation of N-Acetyl-N-[1-Chloroethyl-1-(2-Fluorenyl) Amino-5-Nitro] Thiazole Compound (II)

Schiff base (I) (0.015 mole) was added to acetyl chloride (0.015 mole) in (absolute) ethanol (50 ml). The mixture was refluxed for (16 hrs.), cooled, filtered and recrystallized from absolute ethanol¹⁴.

Preparation of N-Acetyl-N-[1-Thioamidinoethyl-1-(2-Fluorenyl)-2-Amino-5-Nitro] Thiazole Compound (III)

The mixture of compound (II) (0.001 mol), thiourea (0.001 mol) and Na_2CO_3 (0.002 mol) in absolute ethanol (50 ml) was refluxed for (16 hrs.), cooled and filtered. The filtrate was poured into crushed ice, the separated solid was collected and recrystallized from 1, 4-dioxane solvent¹⁵.

Preparation of Schiff Base Compound (V)

To a stirred mixture of α -chloro acetic acid (0.01 mol) and 10% aqueous sodium hydroxide (10 ml), a solution of Schiff base (IV) (0.01 mol) in 10% aqueous solution of sodium hydroxide (10 ml) was added. The mixture was refluxed for 12 hrs. After cooling, the solution was acidified with concentrated hydrochloric acid. The precipitate was filtered and recrystallized from ethanol¹⁶.

Preparation of Schiff Base Compound (VI)

Schiff base (VI) was prepared by the reaction of compound (V) (0.02 mol), with methanol (0.02 mol), in 50 ml DMF and few drops of conc. H_2SO_4 acid. This mixture was refluxed for 16 hrs. The mixture was cooled. The formed precipitate was recrystallized from absolute ethanol¹⁷.

Preparation of Schiff Base Compound (VII)

Schiff base (VII) was prepared from the reaction of compound (VI) (0.006mol) with hydrazinehydrate (0.006mol) solution(24%) in 50ml DMF and few drops of conc. HCl acid, this mixture was refluxed for 20 hrs. The mixture was cooled. The obtained precipitate was recrystallized from methanol¹⁸.

Preparation of Schiff Base Compound (VIII)

A mixture of compound(VII)2(0.005mol) terephthalaldehyde (0.005mol), three drops of glacial acetic acid and absolute ethanol (50ml) was refluxed for 18 hours. The reaction mixture was concentrated, cooled and the formed precipitate was filtered off, dried and then recrystallized using chloroform to give yellowish whitecrystals¹⁹.

Preparation of Bis [N-(2-Thioacetylhydrazide-5-(1(2-Fluorinel)-1-Ethylidin))Thiadiazole]-1,3-Thiazolidin-2-4-Oxo-p-Benzene Compound (IX)

A mixture of Schiff base (VIII) (0.01 mol), α -mercaptoacetic acid (0.022mol) was refluxed in dry benzene 50ml for 18hours. The solvent was evaporated and the reaction mixture was neutralized with cold dilute sodium bicarbonate solution, the formed product was filtered off and recrystallized from acetone²⁰.

Results and Discussion

The present work involved four steps

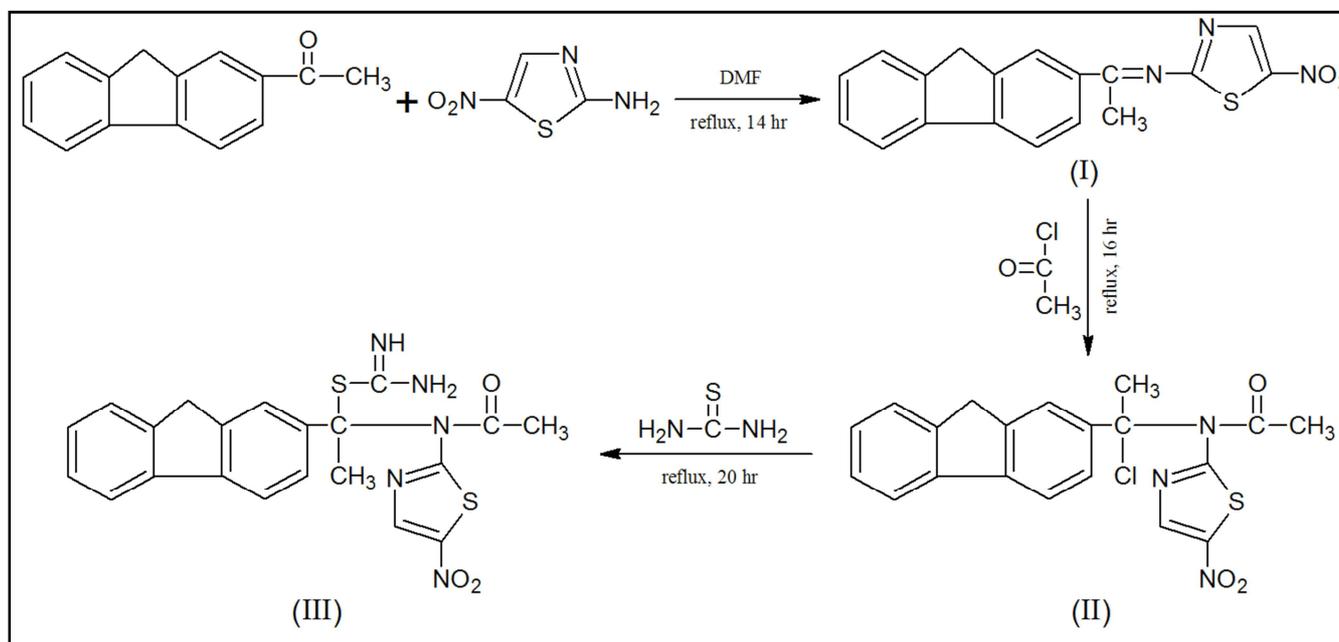
First step: Includes preparation of new two Schiff bases (I, IV). The two compounds were prepared by reaction of two primary amine with 2-acetylfluorine. The synthesis of two compounds were carried out as shown in Scheme (1,2) and the tables (1,2) includes the physical properties, elemental analysis for Schiff bases(I,IV)and these compounds were identified by FT-IR Spectroscopy, LC-MS, ¹H, ¹³C-NMR. FT-IR spectra of compounds(I,IV) showed the appearance of absorption band at(2610) due to (SH) stretching with the appearance of a band at (1636.3, 1638.38) cm⁻¹ assignable to imine group(C=N). The spectra also showed the bands at (3036.34-3039.98) cm⁻¹due to aromatic C-H stretching, and the bands at (2992-2993.39) cm⁻¹ due to aliphatic C-H stretching. Table (3) exhibited the characteristic FT IR absorption bands of these compounds. ¹H-NMR spectrum showed the following characteristics chemical shifts (CDCl₃ as a solvent) singlet signal at (10.87) ppm could be attributed to the proton of (SH) group of compound(IV),The spectra also showed a singlet signal at (1.77, 1.80) ppm for six protons of the methyl groups of compounds(I, IV) and a multiplet signal at(7.49-7.79) ppm for aromatic protons of two fluorene rings of compounds (I, IV).Table(3) exhibited the characteristic 1H-NMR peaks of these compounds. ¹³C-NMR spectra of compounds(I, IV) showed signals at (125 - 142) ppm due to aromatic carbons of two fluorene rings and signals at (160.93, 162.2) ppm due to (C=N)imine group carbon, and signals at (13.58, 13.69) ppm due to two carbons of (CH₃)of the methyl groups. Table (3) exhibited the characteristic ¹³C-NMR peaks of these compounds²⁰.

Second step: The second step include preparation of new two compounds (II, III) were prepared by reaction of Schiff base (I) with acetyl chloride to give (II) then (II)was treated with thiourea to give(III).The synthesis of these compounds was carried out lined in Scheme (1) and the tables (1,2) includes the physical properties, elemental analysis for Schiff bases (II, III) and these compounds were identified by FT-IR Spectroscopy, LC-MS, ¹H, ¹³C-NMR. FT-IR spectra of compounds (II, III) showed new doublet absorption bands in the region (3440-3280)cm⁻¹ were attributed to (NH₂) and (NH) functional moieties of compound (III) with the appearance of a bands at (1677.77,1678.73) cm⁻¹assignable to(C=O). The spectra also showed the appearance of a bands at (1637.38, 1639.2) cm⁻¹ assignable to (azomethine) imine group (C=N). Table(3) exhibited the characteristic FT IR absorption bands of these compounds. ¹H-NMR spectrum showed the following characteristics chemical shifts (CDCl₃as a solvent) singlet signal at (4.72) ppm could be attributed to the two protons of (NH₂) group and singlet signal at (8.99) ppm due to the proton of (C=NH) of compound (III). The spectra also showed a singlet signal at (0.89, 0.91) ppm for six protons of (CH₃) (a) the methyl groups and a singlet signal at (2.09, 2.10) ppm for six protons of (CH₃)(b)the methyl groups of compounds (II, III), and a multiplet signal at (7.47 -7.79) ppm for aromatic protons of two fluorene rings of compounds (II, III). Table (3) exhibited the characteristic ¹H-NMR peaks of these compounds. ¹³C-NMR spectra of compounds (II, III) showed signals at (122 - 141) ppm due to aromatic carbons of two fluorene rings, and signals at (15.11,15.13) ppm due to two carbons of (CH₃)(a) of the methyl groups and signals at (31.83,33.43) ppm due to two carbons of (CH₃)(b) of the methyl groups . Table (3) exhibited the characteristic ¹³C-NMR peaks of these compounds²¹.

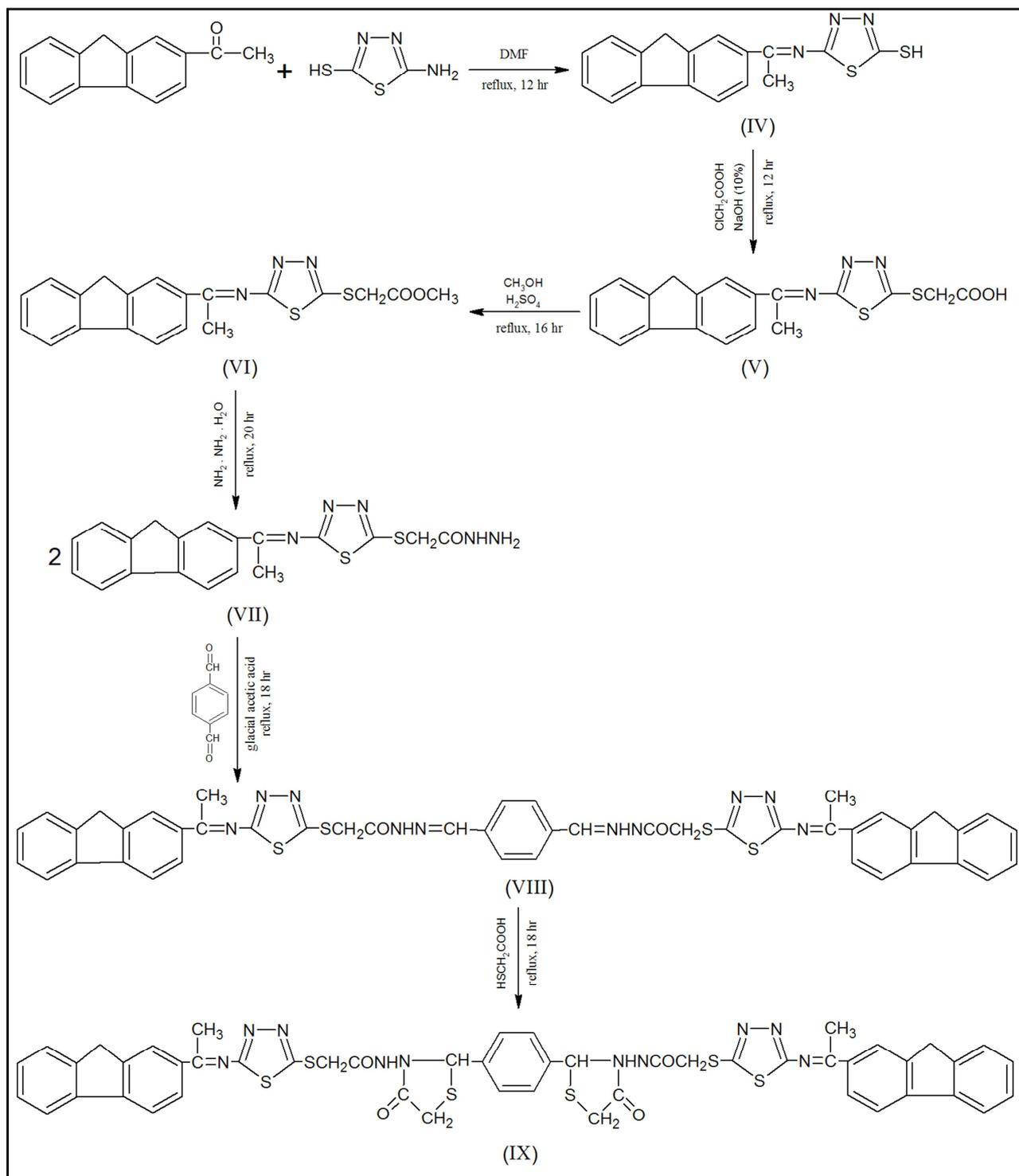
Third step: The third step include preparation of new four Schiff bases (V,VI,VII,VIII) were prepared by reaction of Schiff

base (IV) in (First step) with α -chloro acetic acid to give (V), then (V) was treated with methanol to give (VI), the (VI) was treated with hydrazine hydrate to give (VII), the (VII) was treated with terephthalaldehyde to give (VIII). The synthesis of these compounds which carried out are lined in scheme(2). and the tables (1,2) includes the physical properties, elemental analysis for Schiff bases (V,VI,VII,VIII) and these compounds were identified by FT-IR, LC-MS and ^1H , ^{13}C -NMR. FT-IR spectra of compound (V) showed clear absorption bands at $(1758.33)\text{cm}^{-1}$ due to the $(\text{C}=\text{O})$ acidic, $(3333.36)\text{cm}^{-1}$ due to the (OH) , $(1654.13)\text{cm}^{-1}$ due to the $(\text{C}=\text{N})$ azomethine. The spectra of compound (VI) also showed absorption bands at $(1736.8)\text{cm}^{-1}$ due to the $(\text{C}=\text{O})$ esteric, $(1644.33)\text{cm}^{-1}$ due to the $(\text{C}=\text{N})$ azomethine, in addition to absorption bands for compound (VII) at $(3413.39, 3243.68)$ were attributed to (NH_2) and band at $(3197)\text{cm}^{-1}$ due to the (CONH) , $(1679.86)\text{cm}^{-1}$ due to the $(\text{C}=\text{O})$ amide. Finally, the spectrum of compound (VIII) showed absorption bands at $(1680.66)\text{cm}^{-1}$ due to the $(\text{C}=\text{O})$ amide, $(1642.52)\text{cm}^{-1}$ due to the $(\text{HC}=\text{N})$ azomethine, $(1616.22)\text{cm}^{-1}$ due to the $(\text{C}=\text{N})$ azomethine. The ^1H -NMR spectrum of compound (V), showed multiplet signals at $(6.48-7.77)$ ppm due to aromatic protons and a singlet signal at (4.89) ppm due to two protons of (SCH_2) group, a singlet signal at (1.86) ppm due to three protons of (CH_3) group, singlet signal at (10.98) ppm due to proton of (OH) group. Table (3) exhibited the characteristic ^1H -NMR peaks of these compounds. ^{13}C -NMR spectrum of compound (V) showed signals at $(124-141)$ ppm due to aromatic carbons and signals at (177.02) ppm due to $(\text{C}=\text{O})$ acidic carbon, and signals at (60.21) ppm due to (SCH_2) carbon, signals at (159.93) ppm due to $(\text{C}=\text{N})$ azomethine carbon, and signals at (13.31) ppm due to (CH_3) carbon²². Table (3) exhibited the characteristic ^{13}C -NMR peaks of these compounds.

Fourth step: The fourth step includes preparation of new 2, 3-disubstituted -1, 3-thiazolidin-4-one derivative containing fluorene moiety (IX) was prepared by reaction of Schiff base (VIII) in (third step) with α -mercapto acetic acid indioxane. The synthesis of this compound was carried out lined in scheme(2). And the physical properties of thiazolidinone-4 derivative (IX) including melting point $(286)^\circ\text{C}$ and %Yield was (82) and this compound was identified by FT-IR, LC-MS and ^1H , ^{13}C -NMR. FT-IR spectrum of compound (IX) showed clear absorption bands at $(1737)\text{cm}^{-1}$ due to the $(\text{C}=\text{O})$ of thiazolidinone-4 ring, $(1663.17)\text{cm}^{-1}$ due to the $(\text{C}=\text{O})$ amide, $(3248.57)\text{cm}^{-1}$ due to the (NH) amide, $(1643.32)\text{cm}^{-1}$ due to the $(\text{C}=\text{N})$ azomethine. The ^1H -NMR spectrum of compound (IX), showed multiplet signals at $(7.71-8.03)$ ppm due to aromatic protons and a singlet signal at (6.98) ppm due to (NH) amide, a singlet signal at (4.47) ppm due to (SCH_2) group protons, and a singlet signal at (5.07) ppm due to (CH) group proton of thiazolidinone-4 ring, and a singlet signal at (5.42) ppm due to (CH_2) group protons of thiazolidinone-4 ring. ^{13}C -NMR spectrum of compound (IX) showed signals at $(122-142)$ ppm due to aromatic carbons and signals at (170.28) ppm due to $(\text{C}=\text{O})$ carbon of Thiazolidinone-4, (175.02) ppm due to $(\text{C}=\text{O})$ amide and signals at (68.63) ppm due to (CH) carbon of thiazolidinone-4 ring, signals at (32.02) ppm due to (CH_2) carbon of thiazolidinone-4 ring²³. Table (3) exhibited the characteristic ^{13}C -NMR peaks of this compound.



Scheme 1. Synthesis of Schiff bases (I, II, III) R: primary amine



Scheme 2. Synthesis of Schiff base (IV-IX) R: primary amine.

Table 1. Melting points, yield, molecular formula (M. F.), molecular weight (M. Wt.), colour and Rf of compounds [I-IX]

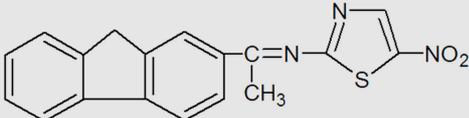
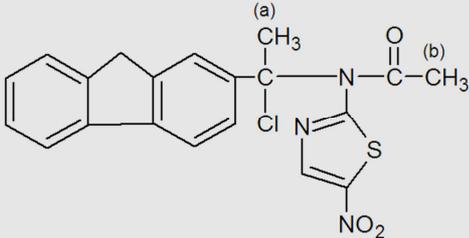
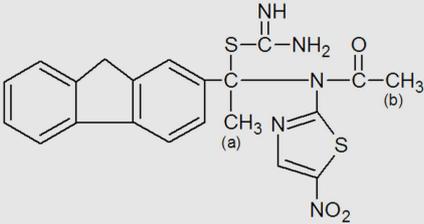
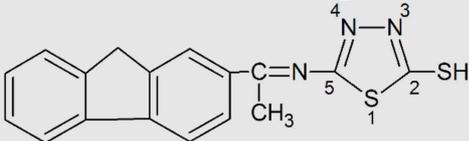
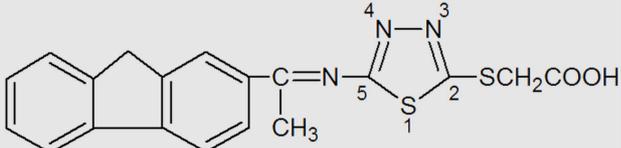
Comp.	R	M. Wt.	M.F.	Yield (%)	M.P. (°C)	Colour	Rf (eter: hexan) (1:3)
I		335	C ₁₈ N ₅ SO ₂ H ₁₃	85	92-94	brown	0.36
II		413.5	C ₂₁ N ₅ SO ₃ Cl H ₁₈	74	103-104	black	0.55

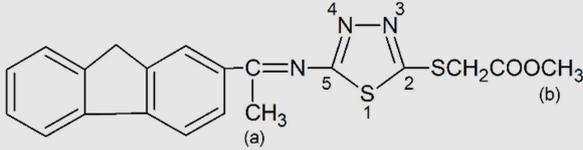
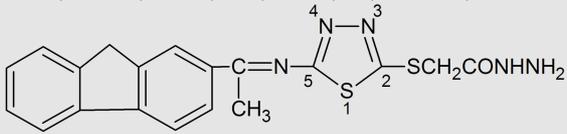
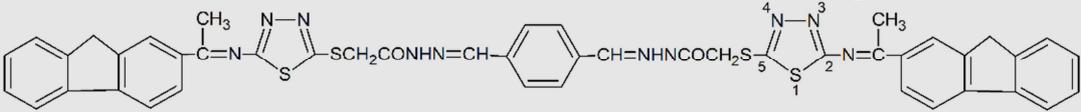
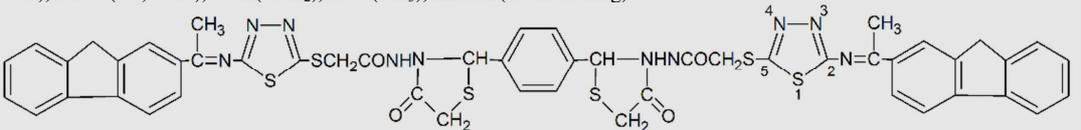
Comp.	R	M. Wt.	M.F.	Yield (%)	M.P (^o C)	Colour	Rf (eter: hexan) (1:3)
III		453	C ₂₁ N ₅ S ₂ O ₃ H ₁₉	86	108	brown	0.25
IV		323	C ₁₇ N ₃ S ₂ H ₁₃	92	97-99	dirty white	0.33
V		381	C ₁₉ N ₃ S ₂ O ₂ H ₁₅	80	126-127	baige	0.47
VI		395	C ₂₀ N ₃ S ₂ O ₂ H ₁₇	95	110-113	dirty white	0.58
VII		395	C ₁₉ N ₅ S ₂ OH ₁₇	96	304-305	yellow	0.31
VIII		888	C ₄₆ N ₁₀ S ₄ O ₂ H ₃₆	87	280	yellowish white	0.66
IX		1036	C ₅₀ N ₁₀ S ₆ O ₄ H ₄₀	82	286	yellowish green	0.62

Table 2. Depicted elemental analysis (C.H.N) of synthesized compounds [I-IX]

Compound	R	Found				Calculated			
		C%	H%	N%	S%	C%	H%	N%	S%
I		64.50	3.74	12.65	9.61	64.48	3.88	12.54	9.55
II		60.99	4.42	10.34	7.69	60.94	4.35	10.16	7.74
III		55.77	4.35	15.38	14.26	55.63	4.19	15.45	14.13
IV		63.21	4.13	13.21	19.97	63.16	4.02	13.00	19.81
V		59.89	3.88	11.12	16.82	59.84	3.94	11.02	16.79
VI		60.81	4.26	10.58	16.18	60.76	4.31	10.63	16.20
VII		57.91	4.25	17.69	16.12	57.72	4.30	17.72	16.20
VIII		62.27	4.09	15.79	14.37	62.16	4.05	15.77	14.41
IX		57.90	3.79	13.60	18.51	57.92	3.86	13.51	18.53

Table 3. Spectroscopical data of synthesized compounds [I-IX]

Comp. NO	Spectroscopy data
I	<p>IR (KBr, cm^{-1}): 3036.34 [$\nu(\text{C-H})_{\text{Ar}}$], 2992 [$\nu(\text{C-H})_{\text{Aliphatic}}$], 1636.3 [$\nu(\text{C=N})_{\text{azomethine}}$], 1558.98 [$\nu(\text{C=C})_{\text{Ar}}$]. LC-MS: $m/z = 335.07$ $^1\text{H-NMR}$ (400 MHz, CDCl_3, ppm)δH: 3.52 (S, 2H, CH_2fluorene ring), 8.39 (S, 1H, C-H thiazole), 1.77 (S, 3H, CH_3), 7.49-7.77 (m, 7H, aromatic ring). $^{13}\text{C-NMR}$ (400MHz, CDCl_3, ppm)δC: 41.82(CH_2fluorene ring), 134.75(C=N thiazole), 139.68(C-NO_2), 141.68(CH thiazole), 162.2(C=N azomethine), 13.58 (CH_3), 127-142(aromatic ring).</p> 
II	<p>IR (KBr, cm^{-1}): 3029.68 [$\nu(\text{C-H})_{\text{Ar}}$], 2997, 2985 [$\nu(\text{C-H})_{\text{Aliphatic}}$], 1677.77 [$\nu(\text{C=O})$], 1637.38 [$\nu(\text{C=N})_{\text{azomethine}}$], 1565.92 [$\nu(\text{C=C})_{\text{Ar}}$], 737.64 [$\nu(\text{C-Cl})$]. LC-MS: 413.19 $^1\text{H NMR}$ (400 MHz, CDCl_3, ppm) δH: 3.49(S, 2H, CH_2fluorene ring), 0.89 (S, 3H, CH_3(a)), 2.10 (S, 3H, CH_3(b)), 8.39 (S, 1H, C-Hthiazole), 7.48-7.78(m, 7H, aromatic ring). $^{13}\text{C-NMR}$ (400MHz, CDCl_3, ppm)δC: 41.87(CH_2fluorene ring), 139.66(C-NO_2), 15.11(CH_3(a)), 31.83(CH_3(b)), 141.56(CH thiazole), 70.84(C-Cl), 134.76(C=N thiazole), 174.76(C=O), 122-141(aromatic ring).</p> 
III	<p>IR (KBr, cm^{-1}): (3440, 3340)[$\nu(\text{NH}_2)$], (3280)[$\nu(\text{C=NH})$], 3067.23 [$\nu(\text{C-H})_{\text{Ar}}$], (2997.8, 2922.59) [$\nu(\text{C-H})_{\text{Aliphatic}}$], 1678.73 [$\nu(\text{C=O})$], 1639.2 [$\nu(\text{C=N})_{\text{azomethine}}$], 1564.95 [$\nu(\text{C=C})_{\text{Ar}}$], 1265.07 [$\nu(\text{C-S})$]. LC-MS: 453.09 $^1\text{HNMR}$ (400 MHz, CDCl_3, ppm)δH: 3.52 (S, 2H, CH_2fluorene ring), 0.91 (S, 3H, CH_3(a)), 2.09 (S, 3H, CH_3 (b)), 8.42 (S, 1H, C-H thiazole), 4.72(S, 2H, NH_2), 8.99(S, 1H, C=NH), 7.47-7.79(m, 7H, aromatic ring). $^{13}\text{C-NMR}$ (400MHz, CDCl_3, ppm)δC: 41.89(CH_2fluorene ring), 139.65(C-NO_2), 15.13(CH_3(a)), 33.43(CH_3(b)), 142.61(CH thiazole), 72.84(C-S), 134.74(C=N thiazole), 174.79(C=O), 122-141(aromatic ring).</p> 
IV	<p>IR (KBr, cm^{-1}): (2610)[$\nu(\text{SH})$], 3039.98 [$\nu(\text{C-H})_{\text{Ar}}$], (2993.39) [$\nu(\text{CH})_{\text{Aliphatic}}$], 1638.38 [$\nu(\text{C=N})_{\text{azomethine}}$], 1588.06 [$\nu(\text{C=C})_{\text{Ar}}$]. LC-MS: 323.06 $^1\text{H-NMR}$ (400MHz, CDCl_3, ppm)δH: 3.47(S, 2H, CH_2fluorene ring), 10.87(S, 1H, SH), 1.80(S, 3H, CH_3), 7.50-7.79(m, 7H, aromatic ring). $^{13}\text{C-NMR}$ (400MHz, CDCl_3, ppm)δC: 41.93(CH_2fluorene ring), 13.96(CH_3), 160.93(C=N azomethine), 131.23(C_2, C=N), 132.33(C_5, C=N), 125-141(aromatic ring).</p> 
V	<p>IR (KBr, cm^{-1}): (3333.36)[$\nu(\text{OH})$], 3048.29 [$\nu(\text{C-H})_{\text{Ar}}$], (2999.73, 2922.59) [$\nu(\text{CH})_{\text{Aliphatic}}$], 1758.33 [$\nu(\text{C=O})_{\text{acidic}}$], 1654.13 [$\nu(\text{C=N})_{\text{azomethine}}$], 1584.92 [$\nu(\text{C=C})_{\text{Ar}}$]. LC-MS: 381.08 $^1\text{H-NMR}$ (400MHz, CDCl_3, ppm)δH: 3.48(S, 2H, CH_2fluorene ring), 10.98 (S, H, COOH), 1.86(S, 3H, CH_3), 4.89(S, 2H, SCH_2), 6.48-7.77(m, 7H, aromatic ring). $^{13}\text{C-NMR}$ (400MHz, CDCl_3, ppm)δC: 41.92(CH_2fluorene ring), 177.02(COOH), 13.31(CH_3), 159.93(C=N azomethine), 130.80(C_2, C=N), 131.95(C_5, C=N), 60.21(SCH_2), 124-141(aromatic ring).</p> 

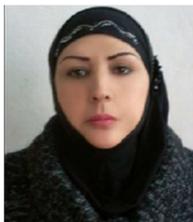
Comp. NO	Spectroscopy data
VI	<p>IR (KBr, cm^{-1}): 3049.87[$\nu(\text{C-H})_{\text{Ar}}$], (2991,2909.09)[$\nu(\text{CH})_{\text{Aliphatic}}$], 1736.8 [$\nu(\text{C=O})_{\text{ester}}$],1644.33 [$\nu(\text{C=N})_{\text{azomethine}}$],1565.92 [$\nu(\text{C=C})_{\text{Ar}}$]. LC-MS:395.08 $^1\text{H-NMR}$(400MHz, CDCl_3, ppm)δH:3.50(S, 2H, CH_2fluorene ring), 3.7(S, 3H, COOCH_3),1.95(S, 3H, CH_3(a)), 4.39(S, 2H,SCH_2), 7.49-7.78(m, 7H, aromatic). $^{13}\text{C-NMR}$(400MHz, CDCl_3, ppm)δC:41.97(CH_2fluorenering), 180.02(C=O), 160.38(C=N azomethine), 130.99(C2,C=N), 131(C5, C=N),37.73(SCH_2),13.33(CH_3 (a)), 51.71(CH_3 (b)), 125-141(aromatic ring).</p> 
VII	<p>IR (KBr, cm^{-1}):(3413.39,4243.68)[$\nu(\text{NH}_2)$], (3197)[$\nu(\text{CONH})$],3045.05[$\nu(\text{C-H})_{\text{Ar}}$], (2993,2912.49) [$\nu(\text{CH})_{\text{Aliphatic}}$], 1679.86 [$\nu(\text{C=O})_{\text{amide}}$], 1643.67[$\nu(\text{C=N})_{\text{azomethine}}$], 1564.95[$\nu(\text{C=C})_{\text{Ar}}$]. LC-MS:395.09 $^1\text{H-NMR}$ (400MHz, CDCl_3, ppm)δH:2.94(S, 2H, CH_2fluorene ring),4.87(S, 2H, NH_2), 8.93 (S, 1H, CONH), 1.91(S, 3H, CH_3), 4.41(S, 2H, SCH_2), 7.46-7.77(m, 7H, aromatic ring). $^{13}\text{C-NMR}$(400MHz, CDCl_3, ppm)δC: 42.05(CH_2fluorene ring), 172.72(C=O), 159.35(C=N azomethine), 130.98(C2, C=N), 131.44(C5, C=N), 34.52(SCH_2), 14.03(CH_3), 124-142(aromatic ring)..</p> 
VIII	<p>IR(KBr,cm^{-1}):(3243.97)[$\nu(\text{CONH})$],3047.94[$\nu(\text{C-H})_{\text{Ar}}$],(2996,2922.59)[$\nu(\text{CH})_{\text{Aliphatic}}$],1680.66 [$\nu(\text{C=O})_{\text{amide}}$], 1642.52[$\nu(\text{HC=N})_{\text{azomethine}}$],1616.22[$\nu(\text{C=N})_{\text{azomethine}}$],1577.49[$\nu(\text{C=C})_{\text{Ar}}$]. LC-MS:888.19 $^1\text{H-NMR}$ (400MHz, CDCl_3, ppm)δH:3.47(S, 4H, CH_2fluorene ring),6.60(S, 2H, CONH), 1.93(S, 6H, CH_3), 4.36(S, 4H, SCH_2), 8.86(S, 2H, HC=N azomethine), 7.72-8.02(m, 18H, aromatic ring). $^{13}\text{C-NMR}$ (400MHz, CDCl_3, ppm) δC:42.39(CH_2 fluorene ring), 174.72(C=O), 158.35(C=N azomethine), 164.37(HC=N azomethine), 130.18(C-2,C=N), 130.64 (C-5,C=N), 39.62(SCH_2), 15.12(CH_3),123-143(aromaticring).</p> 
IX	<p>IR(KBr,cm^{-1}):(3248.57)[$\nu(\text{CONH})$],3043.12[$\nu(\text{C-H})_{\text{Ar}}$],(2998,2921.63)[$\nu(\text{CH})_{\text{Aliphatic}}$],1737[$\nu(\text{C=O})_{\text{thiazolidinone}}$],1663.17 [$\nu(\text{C=O})_{\text{amide}}$], 1643.32[$\nu(\text{C=N})_{\text{azomethine}}$],1588.46 [$\nu(\text{C=C})_{\text{Ar}}$]. LC-MS:1036.18 $^1\text{H-NMR}$(400MHz, CDCl_3, ppm)δH: 3.02(S, 4H, CH_2fluorene ring), 6.98(S, 2H, CONH), 1.89(S, 6H, CH_3), 4.47(S, 4H,SCH_2), 5.42(S, 2H, CH thiazolidinone), 2.69(S, 4H, CH_2thiazolidinone), 7.71-8.03(m, 18H, aromatic ring). $^{13}\text{C-NMR}$ (400MHz, CDCl_3, ppm) δC:41.78(CH_2fluorene ring), 175.02(CONH),170.28(C=Othiazolidinone), 68.63 (CHthiazolidinone), 32.02 (CH_2thiazolidinone), 158.24(C=N azomethine), 164.37(HC=N azomethine), 130.97(C2, C=N),131.66(C5, C=N),36.82(SCH_2),14.77(CH_3),122-142(aromatic ring).</p> 

Conclusions

The main aim of the present study is to synthesize Schiff bases and new heterocyclic derivatives containing, fluorene moiety. Nine new heterocyclic with fluorine substituted compounds were synthesized, and characterized by IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and LC-MS spectral methods and elemental analysis. We depended on refluxing to synthesize all prepared new compounds. The yields were excellent and the reactions times were acceptable. We hope from our research to discover new structures serving as potential broad spectrum antimicrobial and anti-corrosion agents.

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Thawra Ahmad

1-Born 1975
 2-Bachelor of Science – Major in Chemistry, University of Damascus, Damascus, Syria
 3-Master in Chemistry, University of Damascus, Damascus, Syria, 2011
 4-Ph.D. Candidate, Organic Chemistry, Damascus University, Syria
 5-Lecturer at the Chemistry Department in Damascus University since 2006
 thawra.ahmad.a@gmail.com



Farouk Kandil

Bachelor degree in chemical and physical sciences, University of Damascus – 1963.
 Ph.D degree in Chemistry from Moscow State University -1972.
 Professor of Organic Chemistry, Department of Chemistry since 1982
 Number of teaching years: Forty three years, during which I taught the Organic chemistry for students of 2nd, 3rd and 4th classes in Faculties of Sciences, pharmacy and Medicine in Syrians Universities.
 farouk-k@windowslive.com

Chahid Moustapha

Member Of Doctorate And Master Thesis's evaluation and scientific Works Appreciation Committee in Syrian univ.



Mammberr Of Analytical industrial Chemistry Group of Chemistry Dep.University Courses Taught And Books:

Quantum Chemistry Tishreen Univ. Publishers, 1992.
 Organic Chemistry For Agriculture Students, Tishreen Univ. Publishers, 1993.
 Experimental Of Organic Chemistry, Tishreen Univ. Publishers, 1992.
 Organic Chemistry For Apply chemistry Students, Tishreen Univ. Publishers, 2008.
 Experimental Of Organic Chemistry for Apply Chemistry Students, Tishreen Univ. Publishers, 2008.
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