π-Aryl/Heteroaryl Conjugated Coumarin-Thiazoles: Synthesis, Optical Spectral and Nonlinear Optic Properties

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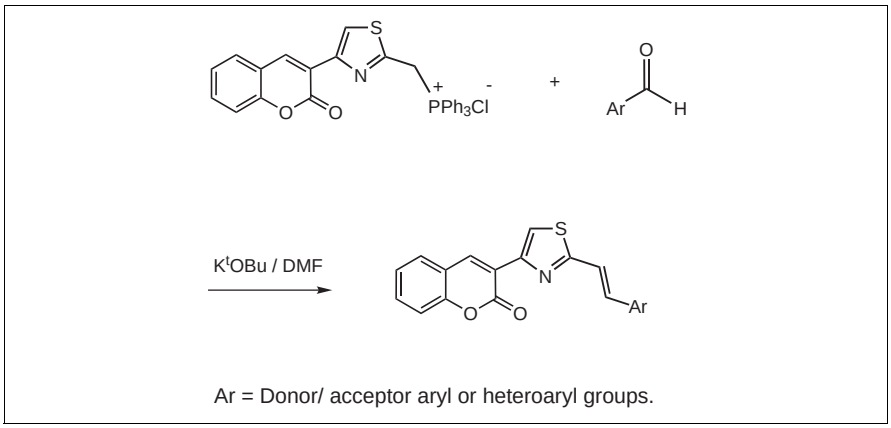

A series of π-aryl/heteroaryl conjugated coumarin-thiazole systems **8a-f** has been synthesized by using Hantzsch thiazole protocol and Wittig olefination as the keys. In the UV-Visible spectra of **8a-f**, a main absorption band associated with a dominant π-π* transition is observed in the region of 338 to 390 nm. Qualitatively, the values of λ_{max} have been found to correlate satisfactory with the donor/acceptor characteristics of the π-attached chromophores. Marked changes observed in the absorption maxima of **8a** under acidic conditions are rationalized on the basis of mono-or bis-protonation and modification of the donor/acceptor properties of chromophores undergoing protonation. The emission spectra of **8a-f**, obtained by exciting the molecules at their main absorption bands showed emission maxima in the region of 429 nm to 537 nm, with relatively high Stokes shifts of 145 and 171 nm being observed for **8a** and **8e**, carrying a π-donor, dimethylaminophenyl and a π-acceptor, *p*-nitrophenyl chromophore, respectively. Although, the first hyperpolarisability β, measured by the hyper-Reileigh scattering (HRS) technique are modest (12 to 23 × 10^{-30} esu), all the compounds exhibited complete transparency in the frequency doubling region at 532 nm and showed high thermal stability (T_d from 330 to 365 °C).

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Introduction.

Natural and synthetic coumarins continue to engage interest for their wide ranging applications *e.g.*, in the areas of biological activities [1-4], laser dyes [5-10], fluorescence brighteners [11-14] and fluorochromophores [15-18]. Among a class of 3-(heteroaryl) coumarins, a variety of 3-(thiazolyl) coumarins containing a biologically significant heterocycle, thiazole has been synthesized and evaluated as pharmaceutically active agents, fluorescence probes and laser dyes [19-22]. In addition, π-conjugated polymers consisting of recurring thiazole rings are known to display interesting electronic, optical and electric properties [23,24]. Despite the popularity of coumarin-thiazole systems (type A structures, Chart 1), there appears to be no report on the design of π-aryl/heteroaryl conjugated coumarin-thiazole systems, represented by type B structures shown in Chart 1.

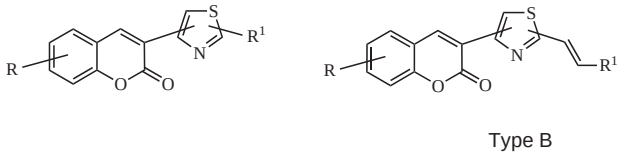
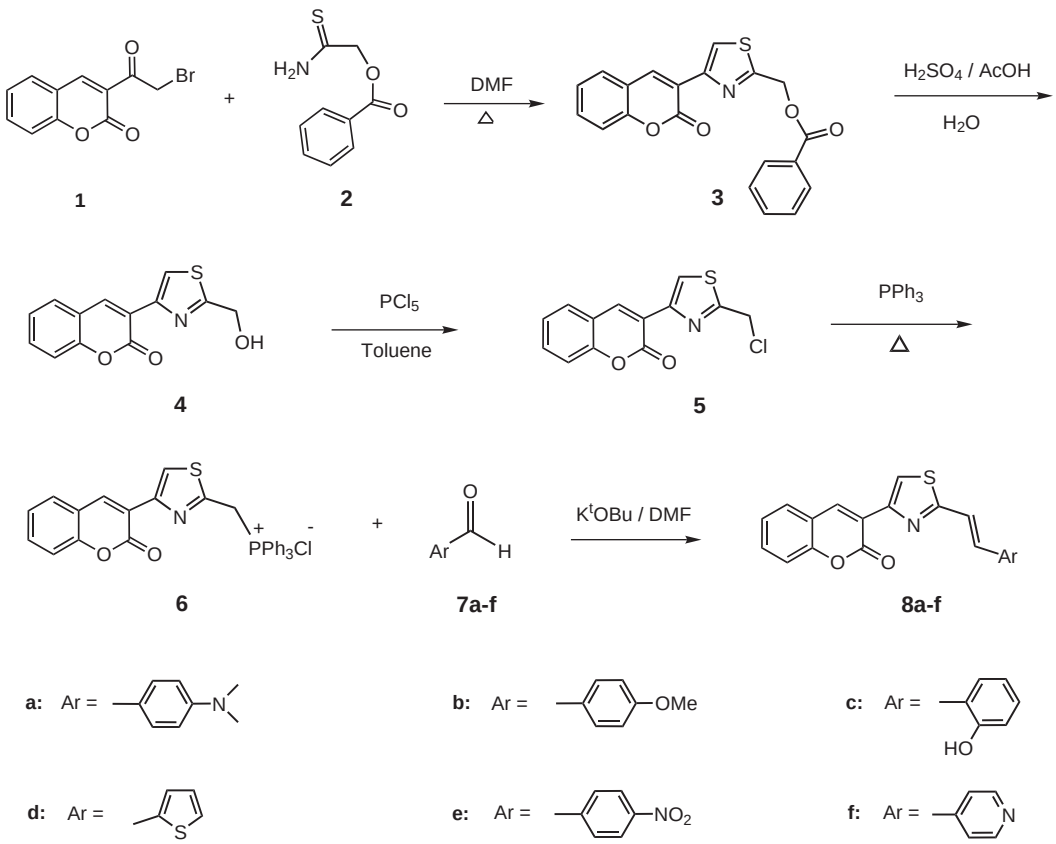


Chart 1

We became interested in the study of these molecules on consideration that the presence of a π-polarised framework might impart these systems with potentially useful electronic, photo-physical and nonlinear optic properties. In pursuit of our interest in the electronic properties of novel heterocyclic systems [25-27], we herein describe synthesis, optical spectral studies and nonlinear optic properties of one of the type B systems, exemplified by structures **8a-f** depicted in Scheme 1. These compounds are characterized by the linkages of π-aryl/heteroaryl chromophore and the coumarin motif at the C4 and C2 positions of the thiazole nucleus, respectively.

Scheme 1



Synthetic route for the preparation of compounds **8a-f**

Table 1

^{1}H-nmr data (500MHz, $CDCl_3$) of **8a-f**

Compounds	^{1}H-nmr (δ)
8a	3.01 (6H, s), 6.71 (1H, d, *J*= 8 Hz), 7.13 (1H, d, *J*=14 Hz, olefinic H), 7.32 (1H, t, *J*=8Hz), 7.37 (1H, d, *J*=8 Hz), 7.38 (1H, d, *J*=14 Hz, olefinic H), 7.45 (1H, d, *J*=8 Hz), 7.54 (1H, t, *J*=8Hz), 7.64 (1H, d, *J*=8 Hz), 8.30 (1H, s, thiazole H), 8.78 (1H, s, coumarin H).
8b	3.8 (6H, s), 6.93 (1H, d, *J*=8 Hz),7.20 (d, *J*=16 Hz, olefinic H), 7.32 (1H, t, *J*=8Hz), 7.38 (1H, d, *J*=8 Hz), 7.42 (1H, d, *J*=16 Hz, olefinic H), 7.52 (1H, d, *J*=8 Hz), 7.55 (1H, t, *J*=8Hz), 7.65 (1H, d, *J*=8 Hz), 8.38 (1H, s, thiazole H), 8.79 (1H, s, coumarin H).
8c	6.85, (1H, t, *J*=8Hz), 6.92 (1H, d, *J*=8 Hz), 7.18 (1H, t, *J*=8Hz), 7.4 (1H, t, *J*=8Hz), 7.45 (1H, d, *J*=8 Hz), 7.54 (d, *J*=18 Hz, olefinic H), 7.64 (1H, d, *J*=8 Hz), 7.65 (1H, t, *J*=8Hz), s7.71 (1H, d, *J*=18 Hz, olefinic H), 7.95 (1H, d, *J*=8 Hz), 8.38 (1H, s, thiazole H), 8.89 (1H, s, coumarin H), 10.15 (1H, s, OH).
8d	7.11-7.42 (4H, m, ArH & thiophene H), 7.18 (1H d, *J*=16 Hz, olefinic H), 7.4 (1H, d, *J*=8 Hz), 7.6 (1H, t, *J*=8Hz), 7.61-7.71 (m, 2H, Ar H & olefinic H), 8.45 (1H, s, thiazole H), 8.84 (1H, s, coumarin H).
8e	7.34 (1H, t, *J*=8Hz), 7.39 (1H, d, *J*=8 Hz),7.48 (1H, d, *J*=18 Hz, olefinic H), 7.53 (1H, d, *J*=18 Hz, olefinic H), 7.55 (1H, t, *J*=8Hz), 7.66 (1H, d, *J*=8 Hz), 7.71 (1H, d, *J*=8 Hz), 8.26 (1H, d, *J*=8 Hz), 8.51 (1H, s, thiazole H), 8.81 (1H, s, coumarin H).
8f	7.34 (1H, t, *J*=8Hz), 7.39 (1H, d, *J*=8 Hz), 7.41(1H, d, *J*=15 Hz, olefinic H), 7.49(1H, d, *J*=16.5 Hz, olefinic H), 7.55 (1H, t, *J*=8Hz), 7.66 (1H, d, *J*=8 Hz), 7.71 (2H, d, *J*=6 Hz, pyridine H), 8.49 (1H, s, thiazole H), 8.65 (2H, d, *J*=6 Hz, pyridine H), 8.81 (1H, s, coumarin H).

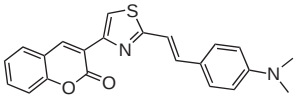
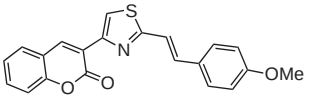
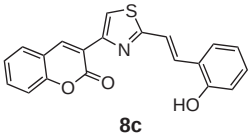
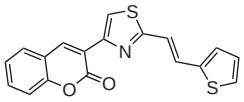
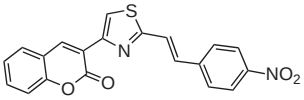
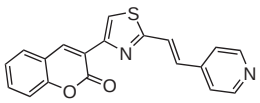
Results and Discussion.

The coumarin-thiazole π-conjugated systems **8a-f** were readily synthesized (Scheme 1) by employing the well-known Hantzsch thiazole protocol and the Wittig olefination as the key steps. To start with, 3-α-bromo-acetyl coumarin **1** was subjected to the Hantzsch condensation with benzoyloxy thioacetamide **2** in dry DMF to obtain the desired coumarin-thiazole benzoyl ester **3** in good yield. The structure **3** is fully supported by analysis and spectral data as given in the experimental. Hydrolysis of **3** was accomplished by heating (100 °C, 6 h) in a mixture of acetic acid, water and sulphuric acid (v/v/v 5:5:1). Hydrolyzed product **4**, thus obtained was converted into the chloro derivative **5** by heating with PCl_5 in refluxing toluene for 2hr under N_2 atmosphere. Fusion of an intimate mixture of **5** with an equivalent quantity of PPh_3 (100 °C, 6hr) provided the phosphonium salt **6**. The Wittig condensation of **6** with 4-*N*,*N*-dimethylaminobenzaldehyde **7a** was performed in dry DMF at room temperature using freshly prepared potassium *t*-butoxide. Extractive work-up of the reaction gave a dark-red crude showing a single major spot on TLC. Purification of the crude by flash column chromatography on silica gel led to the isolation of pure **8a** in 60 % yield as a deep yellow solid, mp 187-189 °C.

The compound analyzed correctly for its molecular formula $C_{22}H_{18}N_2O_2S$ and showed in the IR spectrum strong bands at 1720 and 1622 cm^{-1} due to the presence of a lactone carbonyl and olefinic group, respectively. In the ^1H NMR spectrum, a sharp singlet at δ 3.0 (6H) is seen for the -NMe_2 group, whereas singlets located at δ 8.3 and 8.78 could be assigned to C4 coumarin and C5 thiazole protons, respectively. The olefinic protons are discernible as doublets each at δ 7.13 and 7.38 with high *J* of 14 Hz, thereby indicating "E" olefinic geometry. These data fully endorse the structural assignment to **8a**. After having established the viability of the synthetic protocol, we submitted several π-rich (**7b-d**) and π-

Table 2

UV- Vis., Emission, NLO and TG-DTA data of compounds **8a-f**

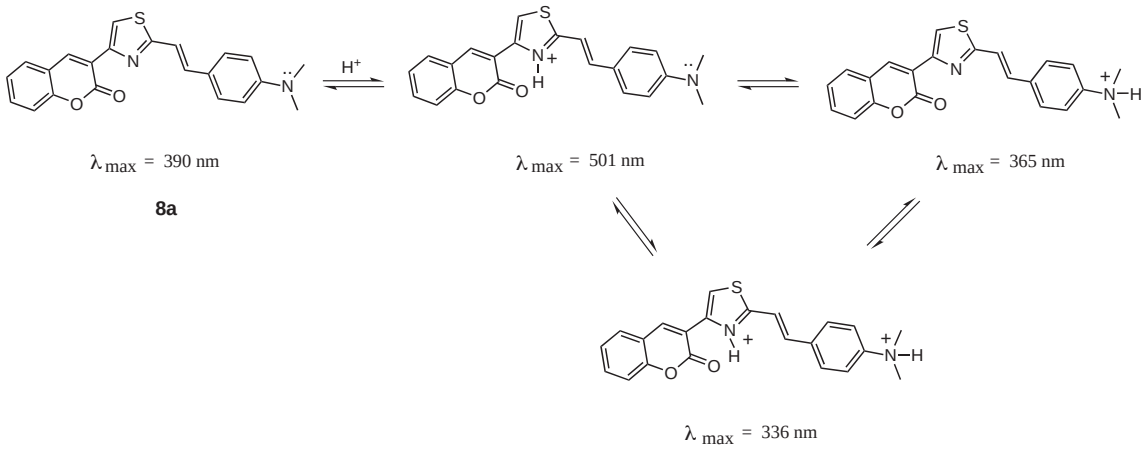
Compounds	$CHCl_3$ λ_{ab} nm	$\varepsilon_{max}x10^4$	$CHCl_3$ λ_{em} nm	Stokes shift Δλ nm	β-value 10^{-30}esu[a]	TG-DTA (T_d)
 **8a**	390	2.82	537	147	23.2	350 °C
 **8b**	354	1.85	463	109	12.2	330 °C
 **8c**	356	2.60	453	97	17.2	348 °C
 **8d**	363	1.52	452	89	14.3	362 °C
 **8e**	346	1.90	517	171	21.05	349 °C
 **8f**	338	1.95	429	91	17.03	365 °C

[a] First hyperpolarisability β was measured with respect to the reference *p*-nitroaniline in $CHCl_3$ (17.8×10^{-30} esu).

deficient aldehydes (**7e-f**) to the Wittig reaction with **6** to access the corresponding thiazole-coumarin π-conjugated products **8b-f** as the pure *trans* isomers (*J* = 15 to 18 Hz) either by crystallization or silica gel purification in 40-60 % yield. The products showed expected elemental analysis and spectral features and their ^{1}H NMR data are collected in Table 1.

minor changes in the λ_{max} ($\Delta\ \lambda_{max} \pm$ 2-7 nm). Judging from the absence of significant solvatochromism, we propose that no appreciable charge redistribution occurs upon excitation in more polar solvents [28]. Accordingly, the coumarin local π-π^* excitation appears to be the dominant mode of electronic transition with rather weak charge transfer character in the excited state.

Scheme 2



Optical Spectral Studies

The UV-Visible spectral analysis **8a-f** was carried out in $CHCl_3$ solvent and the data are collected in Table 2. The absorption spectra of **8a-f** are characterized by a single broad absorption band in the region of 338 to 390 nm, the λ_{max} being dependent upon the donor/acceptor nature of the π-attached aryl/ heteroaryl chromophores. Consistent with very powerful donor ability of the dimethylaminophenyl donor, the compound **8a** showed λ_{max} at 390 nm, which is the most bathochromically shifted absorption in the series. For the cases of **8b-d**, the λ_{max} appeared in the order **8d**>**8c**>**8b**, an observation which is in keeping with the increasing π-donor properties of the π-attached *p*-anisyl, 2-hydroxyphenyl and thiophene chromophores, respectively [27]. For the cases of **8e** and **8f** carrying π-acceptor, *p*-nitrophenyl group and pyridyl rings, the λ_{max} appeared much blue shifted (346 and 338 nm, respectively) relative to those recorded for π-attached donor chromophoric systems **8a-d** (λ_{max} 354 to 390 nm). The blue shifts are in agreement with the reduced π-electronic delocalization in π-acceptor substituted **8e** and **8f**. Furthermore, the appearance of λ_{max} at slightly lower energy at 346 nm for the case of *p*-nitrophenyl analog **8e** compared to 338 nm observed for pyridyl analog **8f** probably indicates relatively greater polarisation in the former system. Upon changing the solvent from $CHCl_3$ to the more polar CH_3CN and CH_3OH, the UV-Visible spectra for **8a-f** suffered only

Although, not studied in detail, we have also investigated the affect of addition of acid on the λ_{max} of **8a**. Since, this compound carries two potential protonation sites, one on the acceptor *i.e.* thiazole and another on the donor *i.e.* dimethylamino- chromophore, it was of interest to see how the protonation on either one or both sites would affect the UV-Visible spectral behaviour. As expected, the UV-Visible spectra of **8a** recorded in $CHCl_3$ containing *ca.* 1% trifluoroacetic acid (TFA) produced marked changes in the positions of λ_{max} (Figure 1), depending upon the site and degree of protonation. As shown in Figure 1, in the presence of TFA, three new absorption bands, one at a longer λ_{max} at 501 nm and two

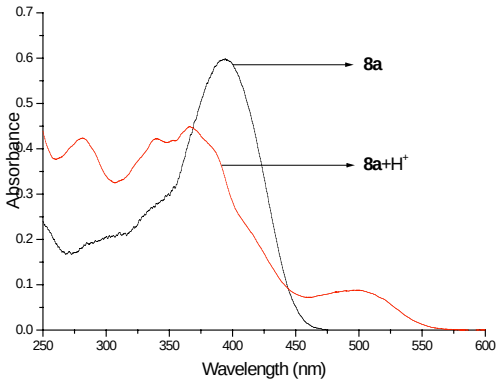


Figure 1. UV-Vis of **8a** in $CHCl_3$ and in $CHCl_3$ + 1% TFA.

at shorter λ_{max} at 365 and 336 nm are seen at the expense of the original 390 nm absorption band recorded in plain $CHCl_3$. The appearance of one red and two blue shifted bands suggests the formation of three distinct protonated species, depending upon whether the dimethylamino group or the basic thiazole nitrogen or both are undergoing protonation. Various protonation equilibria involved in the protonation of **8a** are illustrated in Scheme 2. The appearance of the red shifted 501 nm absorption is most likely the consequence of protonation occurring at the thiazole nitrogen since, the resulting thiazolium ring in **8a**+H^+, being a stronger π-acceptor compared to the thiazole ring in **8a**, would induce greater charge transfer from the donor, dimethylamino group and hence the t red shift. On the other hand, the origin of the band at 365 nm is likely a consequence of the protonation of donor, dimethylamino group. The protonated dimethylamino group, being a weak electron donor would diminish the charge transfer interaction compared to that prevalent in neutral **8a**, thereby causing the blue shift. Finally, the most blue shifted 336 nm band probably has its origin in the bis-protonated species, wherein the charge transfer is expected to be virtually inhibited. Similar observations have been reported by Mitewa *et al* for the case of 2-(4-*N*,*N*-dimethylaminophenyl)benzothiazole and analogs under acidic conditions [29,30].

The emission spectra for **8a-f** in $CHCl_3$ were obtained by exciting these molecules at their main absorption bands (Table 2). The emission maxima, λ_{em} are observed from a low of 429 nm to a high of 537 nm. However, no clear trend based on π-donor or acceptor ability of the π-conjugated aryl/heteroaryl groups is discernible in the series. In particular, high Stokes shifts of 145 and 171 nm are observed for systems **8a** and **8e** carrying a π-attached donor, dimethylaminophenyl and an acceptor, *p*-nitrophenyl chromophore, respectively. The relatively higher values of Stokes shifts for these molecules indicate that the dominant local excitations reach the vibrationally relaxed states (*i.e.* the Franck-Condon states) prior to the emission. In comparison to **8a** and **8f**, the lower values of Stokes shifts for **8b-d** and **8f** (89 to 108 nm) are indicative of relatively destabilized emitting states.

Nonlinear Optical Properties and Thermal Stability.

Since, π-conjugated chromophoric systems are widely known to display high molecular first hyperpolarisability β [31,32], coumarin-thiazoles mofits **8a-f**, being π-conjugated chromophoric systems are also expected to exhibit NLO properties. Accordingly, **8a-f** were evaluated for their first hyperpolarisability β by using the HRS technique with the laser of frequency of 1064 nm. External reference method was applied using *p*-nitroaniline (β = 17.8×10^{-30} esu) as the reference standard [33]. The results are summarized in Table 2. The first hyperpolarisabilities were found to range from 12 to 23×10^{-30} esu. For reasons not yet known, curiously both **8a** (β= 23×10^{-30} esu) and **8e** (β of 21×10^{-30} esu), carrying respectively a strong donor, dimethylaminophenyl group and a strong acceptor *p*-nitrophenyl group exhibited comparable β values. For the remaining systems, the first hyper-polarisability varied from a low of 12×10^{-30} esu for **8b** to a high of 17×10^{-30} esu for **8c** and **8f**. Unfortunately, no clear correlation of β with the nature of π-attached aryl/heteroaryl chromophores is available from these data. Although, the β values for **8a-f** compare favorably with *p*-nitroaniline (17.8×10^{-30} esu), however, they are sizeably lower than the value of 73×10^{-30} esu reported for the well-known NLO benchmark, 4-dimethylamino-4'-nitrostilbene (DANS) [34]. Nevertheless, it is noteworthy that systems **8a-f** showed complete optical transparency beyond 465 nm. Hence, despite the moderate β, these systems fully conform to the transparency-nonlinearity trade-off condition required for the design of the NLO materials. Further, we have also evaluated the thermal stability of **8a-f** using TG-DTA method. The compounds exhibited the decomposition temperatures (T_d) in the range 330 to 366 °C (Table 2). Thus, the thermal stability of this class of compounds is superior to that reported for DANS (T_d = 290 °C) [35], a feature which is significant for NLO applications.

Conclusion.

Hantzsch thiazole protocol and the Wittig olefination have been used to append thiazole and π-aryl/heteroaryl chromophores onto the coumarin motif to construct a series of π-conjugated aryl/heteroaryl coumarin-thiazole systems **8a-f**. The UV-Visible data could be correlated satisfactorily with respect to the characteristic of π-attached donor or acceptor chromophores. The UV-Visible spectral data of molecules **8a** under acidic conditions have been interpreted in terms of modification of donor/acceptor properties of the chromophores undergoing protonation. Although, the first hyper-polarisability for this class of compounds were found to be rather modest, nevertheless the molecules showed complete transparency in the frequency doubling region at 564 nm. In addition, compounds were found to be thermally robust at least up to 330°C These latter properties are critical for ultimate device fabrications. In light of these encouraging results, it would be worthwhile to study other aryl/heteroaryl coumarin-thiazole frameworks represented by the type B structures (Chart 1), as well as to introduce appropriate substituent(s) on one or more rings to fine-tune the electronic and other properties.

EXPERIMENTAL.

The chemicals, solvents for synthesis and spectral grade solvents were purchased from SD Fine Chemicals (India) and used as received. Melting points (uncorrected) were determined on a Gallenkamp apparatus. Ir spectra were recorded on a Shimadzu FTIR-420 spectrophotometer. ^{1}H nmr spectra were recorded on a Bruker-AMX-500 spectrometer with TMS as an internal standard. UV-Visible spectra were taken on Shimadzu UV-visible spectrophotometer UV-2100 and Fluorescence spectra were recorded on a Shimadzu spectrofluoremeter RF-5301 PC.

Coumarin-3-(2-benzoyloxy methyl thiazol-4yl) (**3**).

A mixture of bromoacetyl coumarin **1** (24.03 g, 90 mmole) and benzoyloxy thioamide **2** (17.55 g, 90 mmole) in dry DMF (150 ml) was stirred and heated to 90 °C for 24 hr. The reaction mixture was cooled to room temperature, poured in cooled water and neutralized with sodium hydrogen carbonate. The solid that precipitated out was collected by filtration, washed with water and dried. The crude product was purified using SiO_2 column chromatography (elution $CHCl_3$) to give pure **3**, mp 172-175 °C in 68 % yield. ir (KBr, ν cm^{-1}): 3010, 1720, 1730, 1600, 1460, 1360, 1120, 720; ^{1}H-nmr ($CDCl_3$, 500 MHz): δ 5.7 (s, CH_2 proton), 7.31 (t, Ar H), 7.38 (d, *J*=8 Hz, Ar H), 7.49 (d, *J*=8 Hz, Ar 2H), 7.55 (t, Ar H), 7.61 (d, *J*=8 Hz, Ar H), 8.13 (d, *J*= 8Hz, Ar 2H) 8.51 (s, thiazole H), 8.8 (s, coumarin H).

Anal. Calcd. for $C_{20}H_{13}NO_4S$: C, 66.11; H, 3.58; N, 3.85; S, 8.81. Found: C, 66.21; H, 3.34; N, 3.69; S, 8.52%.

Coumarin-3-(2-hydroxylmethylthiazolyl) (**4**).

Coumarin derivative **3** (21.78 g, 60 mmole) was added to a solution made up of acetic acid (50 ml), water (50 ml) and conc. sulphuric acid (10 ml). The reaction mixture was heated to reflux until a clear solution was obtained (*ca*. 6 hr). The reaction mixture was cooled and poured over crushed ice. The precipitated solid was collected by filtration, washed thoroughly with water and air dried. The crude product was purified by SiO_2 column chromatography (elution; $CHCl_3$ + 2% CH_3OH) to give 13.2 g (85 %) of pure **4**, mp 185-190 °C. ir (KBr ν cm^{-1}): 3400, 1720, 1620, 1020, 1060, 1080, 760; ^{1}H-nmr ($CDCl_3$, 500MHz): δ 5.01 (s, CH_2 proton), 5.03 (s, OH proton), 7.32 (t, Ar H), 7.38 (d, *J*=8 Hz, Ar H), 7.58 (t, Ar H), 7.61 (d, *J*=8 Hz, Ar H) , 8.45 (s, thiazole H), 8.71 (s, coumarin H),

Anal. Calcd. for $C_{13}H_9NO_3S$: C, 65.25; H, 3.47; N, 5.40; S, 12.35. Found: C, 65.02; H, 3.29; N, 5.13; S, 12.09%.

Coumarin-3-(2-chloromethyl thiazol-4-yl) (**5**).

Coumarin derivative **4** (12.95 g, 50 mmole) and PCl_5 (10.4 g, 50 mmole) were taken in dry toluene (200 ml) and the reaction was refluxed and stirred for 2 hr. Most of the toluene was removed by distillation under vacuum and residue neutralized with saturated aqueous sodium carbonate. The crude solid product (13 g) thus obtained was purified by SiO_2 column chromatography (elution; $CHCl_3$) to afford the desired product **5**, mp 155 °C in 75 % yield (10.4 g). ir (KBr ν cm^{-1}): 3010, 1720, 1620, 1480, 1180, 1000, 760; ^{1}H-nmr ($CDCl_3$, 500MHz): δ 5.01 (s, CH_2 proton), 5.03 (s, OH proton), 7.33 (t, Ar H), 7.38 (d, *J*=8 Hz, Ar H), 7.56 (t, Ar H), 7.63 (d, *J*=8 Hz, Ar H) , 8.5 (s, thiazole 1H), 8.74 (s, coumarin 1H).

Anal. Calcd. for $C_{13}H_8NO_2SCl$: C, 56.31; H, 2.88; Cl, 12.8; N, 5.05; S, 11.55. Found: C, 56.15; H, 2.74; Cl, 12.71; N, 5.13; S, 11.33%.

Preparation of Phosphonium Salt **6**.

A powdered mixture of **5** (9.69 g, 35 mmole) and triphenylphosphine (10.48 g, 40 mmole) was heated in an oil bath for 1 hr at 100-110 °C. The reaction mixture was cooled and repeatedly triturated with benzene to remove unreacted starting materials. Finally, the solid was washed with isopropanol and dried in vacuum dessicator to give phosphonium salt **6** in 77 % yield (14.52 g), mp 240-245 °C.

Anal. Calcd. for $C_{31}H_{23}Cl\ PNO_2S$: C, 69.01; H, 4.26, Cl, 6.58; N, 2.59; S, 5.93. Found: C, 68.89; H, 4.02; Cl, 6.42; N, 2.31; S, 5.78%.

Typical Procedure for the Wittig Reaction.

3-{2-[2-(4-Dimethylamino-phenyl)-vinyl]-thiazol-4-yl}-chromen-2-one (**8a**).

Phosphonium salt **6** (1.08 g, 2 mmole) and *p-N,N*-dimethylamino benzaldehyde **7a** (0.298 g, 2 mmole) were dissolved in dry DMF (15 ml) to which an excess of freshly prepared potassium *t*-butoxide (1 g) was added. The reaction mixture was stirred at room temperature for 2 hr and then decomposed in cold 5 % HCl. A red colored solid precipitated which was collected by filtration, washed with water and air dried. The crude solid was purified by SiO_2 column chromatography (elution; $CHCl_3$ + 2% methanol) to afford **8a** as a yellow solid, mp 187-189 °C in 60 % yield (0.45 g). ir (KBr ν cm^{-1}): 3010, 1720, 1620, 1540, 1360, 1240, 1090, 760, 780; ^{1}H-nmr, see Table 1.

Anal. Calcd. for $C_{22}H_{18}N_2O_2S$: C, 70.58; H, 4.8; N, 7.48; S, 8.55. Found: C, 70.35; H, 4.55; N, 7.32; S, 8.35%.

3-{2-[2-(4-Methoxy-phenyl)-vinyl]-thiazol-4-yl}-chromen-2-one (**8b**).

This compound was prepared from phosphonium salt **6** (1.08 g, 2 mmole) and *p*-methoxy benzaldehyde **7b** (2 mmol) in dry DMF following the typical procedure described for **8a**; mp 184-187 °C, yield 58 %; ir (KBr ν cm^{-1}): 3010, 1720, 1620, 1520, 1260, 1180, 1100, 760, 780; ^{1}H-nmr, see Table 1.

Anal. Calcd. for $C_{21}H_{15}NO_3S$: C, 69.80; H, 4.15; N, 3.87; S, 8.86. Found: C, 69.67; H, 4.05; N, 3.73; S, 8.93%.

3-{2-[2-(2-Hydroxy-phenyl)-vinyl]-thiazol-4-yl}-chromen-2-one (**8c**).

This compound was prepared from phosphonium salt **6** (1.08 g, 2 mmole) and salicaldehyde **7c** (2 mmol) in dry DMF following the typical procedure; mp 225 °C, yield 50 %; ir (KBr, ν cm^{-1}): 3400, 1720, 1600, 1460, 1100, 960, 760; ^{1}H-nmr, see Table 1.

Anal. Calcd. for $C_{20}H_{13}NO_3S$: C, 69.16; H, 3.74; N, 4.03; S, 9.22. Found: C, 69.05; H, 3.59; N, 3.89; S, 9.13%.

3-[2-(2-Thiophen-2-yl-vinyl)-thiazol-4-yl]-chromen-2-one (**8d**).

This compound was prepared from phosphonium salt **6** (1.08 g, 2 mmole) and thiophene-2-carboxaldehyde **7d** (2 mmol) in dry DMF following the typical procedure; mp 162-165 °C, yield 60 %; ir (KBr, ν cm^{-1}): 3010, 1720, 1620, 1480, 1245, 1180, 940, 760, 780, 700. ^{1}H-nmr, see Table 1.

Anal. Calcd. for $C_{18}H_{11}NO_2S_2$: C, 64.09; H, 3.26; N, 4.15; S, 18.99. Found: C, 63.79; H, 3.18; N, 3.87; S, 18.74%.

3-{2-[2-(4-Nitro-phenyl)-vinyl]-thiazol-4-yl}-chromen-2-one (**8e**).

This compound was prepared from phosphonium salt **6** (1.08 g, 2 mmole) and *p*-nitro benzaldehyde **7e** (2 mmol) in dry DMF following the typical procedure; mp 252- 255 °C, yield 40 %; ir (KBr, ν cm^{-1}): 3010, 1720, 1600, 1520, 1340, 940, 760, 780; ^{1}H-nmr, see Table 1.

Anal. Calcd. for $C_{20}H_{12}N_2O_4S$: C, 63.82; H, 3.19; N, 7.44; S, 8.51. Found: C, 63.64; H, 3.04; N, 7.14; S, 8.24%.

3-{2-[2-(4-Pyridyl)-vinyl]-thiazol-4-yl}-chromen-2-one (**8f**).

This compound was prepared from phosphonium salt **6** (1.08 g, 2 mmole) and pyridine-4-carboxaldehyde **7f** (2 mmol) in dry DMF following the typical procedure; mp 224-226 °C, yield 40 %; ir (KBr, ν cm^{-1}): 3010, 1720, 1620, 1480, 1410, 1180, 1100, 760, 780. ^{1}H-nmr, see Table 1.

Anal. Calcd. for $C_{19}H_{12}N_2O_2S$: C, 68.67; H, 3.61; N, 8.43; S, 9.63. Found: C, 68.46; H, 3.75; N, 8.34; S, 9.49%.

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