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The indium(III) chloride catalyzed synthesis of sulfur incorporated 3-acylcoumarins; their photochromic and acetate sensing properties.

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Abstract: Synthesis and evaluation of photochromic properties of 3-acylcoumarins is very important as they exhibit selective sensing properties. We found that InCl_3 efficiently catalyzes condensation of 2-hydroxybenzaldehydes and β -keto esters to provide near quantitative yield of 3-acylcoumarins. The 3-(phenylsulfanyl/phenylsulfinyl/phenylsulfonyl)propanoyl coumarins with electron-donating NMe_2 group at C7 position were prepared to evaluate the influence of sulfur on emission and acetate ion sensing properties. Our studies revealed that 7-(diethylamino)-3-(3-(phenylsulfanyl/phenylsulfinyl/phenylsulfonyl)propanoyl)-2*H*-chromen-2-one exhibits excellent fluorescence emission in hexane and ethyl acetate ($\Phi \approx 80\%$). The 3-acylcoumarin with sulfone in the C3-acyl side-chain detects acetate anions selectively and this property can be conveniently followed by fluorescence emission spectroscopy.

Keywords: Coumarin, indium(III) chloride, fluorescence, acetate sensor.

Introduction

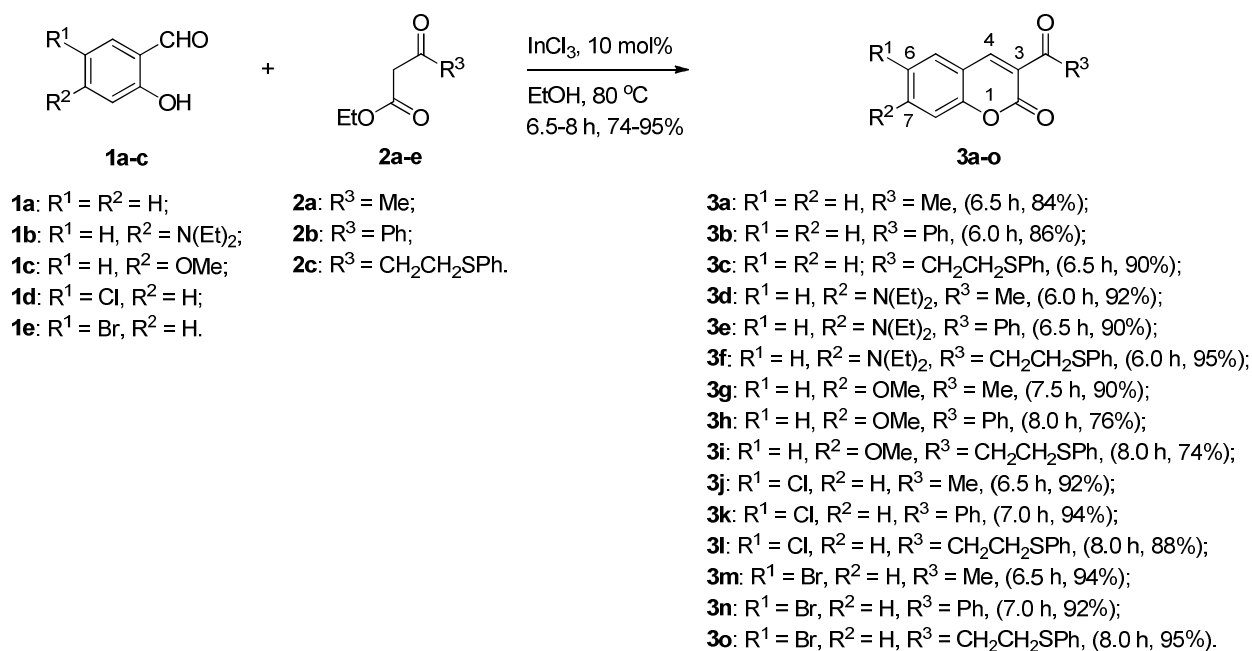
Coumarins (2*H*-1-benzopyran-2-ones; benzo-annulated oxygen heterocycles) are a distinct class¹ of heterocyclic compounds because of their natural occurrence, beneficial medicinal² and lasing³ properties. Among them, the 3-acylcoumarins having electron

withdrawing acyl group at C3 position and electron donating dialkylamino group at C7 position exhibit high intensity fluorescence emission, a property useful for lasing applications.⁴ Furthermore, suitably substituted 3-acylcoumarins act as acetate anions sensors.⁵ Thus, there is continuing interest in synthesis, characterization and evaluation of photochromic properties of 3-acylcoumarins. Knoevenagel condensation of a 2-hydroxybenzaldehyde (salicylaldehyde) derivative and an acetoacetic acid ester under basic conditions is a general method for synthesis of 3-acylcoumarins.⁶ Since fluorescence emission is highly susceptible to microenvironment,⁷ we became interested in synthesis and evaluation of fluorescence properties of hitherto unknown 3-acylcoumarins with a sulfur atom in C3-acyl side-chain, e.g. **3c** (Scheme 1). We attempted synthesis of 3-acylcoumarin **3c** from 2-hydroxybenzaldehyde **1a** and the β -keto ester **2c** in presence of catalytic or stoichiometric amounts of bases like piperidine,⁸ piperidinium acetate,⁹ 1,8-diazabicycloundec-7-ene (DBU)⁹ which have been previously used for coumarin synthesis. Instead of formation of the coumarin **3c**, above reactions lead to disintegration of the β -keto ester **2c** into thiophenol and a mixture of unidentified products. Alternately, we employed Lewis acid catalysts like ZnCl_2 ,¹⁰ SnCl_4 ,¹¹ and TiCl_4 ,¹² but the reactions were unsuccessful. Finally, when we employed catalytic amounts of InCl_3 the condensation took place smoothly to deliver 3-acylcoumarin in excellent yield (Scheme 1). We now present details of InCl_3 catalyzed condensation of 2-hydroxybenzaldehydes **1** and β -keto esters **2** for synthesis of a combinatorial library of 3-acylcoumarins **3** (Scheme 1) and fluorescence emission properties of the 3-acylcoumarins having sulfanyl, sulfone or sulfoxide functional groups. Furthermore, we delineate an application of the 3-acylcoumarin with sulfone functional group for efficiently sensing acetate anions. In recent years, InCl_3 has become a catalyst of choice in promoting plethora of reactions where soft Lewis acid is required.¹³ Noteworthy features of InCl_3 catalysis

include high chemo- and regio-selectivity, tolerance to sensitive functional groups, compatibility with wide variety of solvents including water, true catalytic nature and stability of the catalyst.

Results and Discussion

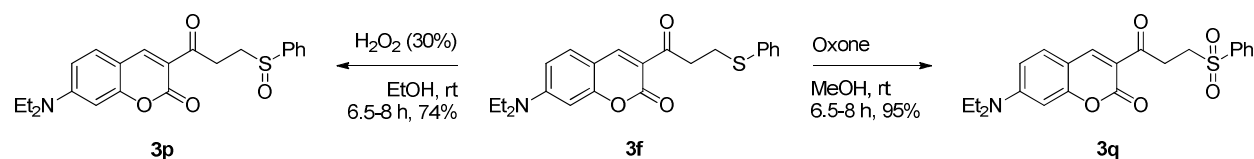
We selected condensation of 2-hydroxybenzaldehyde **1a** and ethyl 3-oxo-5-(phenylthio)pentanoate **2c** to form 3-acylcoumarin **3c** to determine suitable solvent and minimum quantity of InCl₃. When we used solvents such as toluene (non-polar), ethyl acetate (moderately polar, aprotic), dimethyl formamide (polar aprotic) or acetonitrile (polar aprotic) at their respective reflux temperatures, **2c** was decomposing and the reaction mixture was turning black. In ethanol (polar protic) reflux, however, the reaction was clean and **3c** was obtained in excellent yield (Scheme 1). Next, we varied mol% of InCl₃ and found that with 1 mol% the reaction was taking more than 24 h for completion and isolated yield of **3c** was low (< 30%). With 10 mol% of the catalyst the reaction was clean and took 6.5 h for completion to provide **3c** in 90% yield. There was no significant improvement in yield or rate of the reaction when mol% of InCl₃ was increased to 20%. From these experiments we concluded that 10 mol% of InCl₃ in EtOH reflux is optimal for preparation of 3-acylcoumarins. Apart from the anticipated signals, the ¹H NMR spectrum of **3c** displayed diagnostic singlet at δ 8.5 ppm for C4H of the coumarin portion of the molecule. With the optimal conditions in hand, we examined the scope of the condensation for synthesis of a combinatorial library of coumarins. The InCl₃ mediated condensation of five 2-hydroxybenzaldehydes **1a-e** and three β-keto esters **2a-c** furnished fifteen coumarins **3a-o** without any complication (Scheme 1). The spectral and analytical data of each one of them matched well with the parent **3a**.



Scheme 1. InCl₃ catalyzed synthesis of 3-acylcoumarins **3a-o** (time taken for the reaction and the yield are given in parenthesis).

Among the coumarins prepared in this study **3d-e** are highly fluorescent owing to rigid framework of the coumarin scaffold and extended conjugation emanating from electron donating C7 diethylamino group to electron withdrawing C3 acyl group. Fluorimetric detection of fluorescent compounds is the most sensitive analytical technique and widely used in many scientific fields.^[7] Fluorescent emission maximum and intensity are highly susceptible to structural changes in the molecule and environment. Indeed, such changes are the basis for design of molecular sensors. Hitherto unknown **3f** was prepared with an intention to study influence of the sulfur atom on the fluorescence emission characteristics of the coumarin fluorophore. Similarly, coumarins **3p** with sulfoxide and **3q** with sulfone functional groups in the side chain were prepared to study the influence of sulfur as well as oxygen atoms on the fluorescence emission (Scheme 2). Furthermore, the 3-acylcoumarins like **3q** are suitable for ion

sensing properties, and such property can be followed through changes in fluorescence emission. Oxidation of the coumarin **3f** with 30% aqueous H₂O₂ provided sulfoxide **3p**. On the other hand, oxidation of **3f** with potassium monoperoxosulfate (Oxone) provided sulfone **3q** (Scheme 2).



Scheme 2. Oxidation of sulphide **3f** to sulfone **3q** and to sulfoxide **3p**.

Absorption and emission characteristics of 3-acylcoumarins **3d**, **3f**, **3p** and **3q**

The UV absorption spectra of the parent **3d**, sulfide **3f**, sulfoxide **3p** and sulfone **3q** were recorded in five different types of solvents, namely, hexane (non-polar), ethyl acetate (EtOAc, moderately polar aprotic), methanol (MeOH, polar protic), acetonitrile (MeCN, polar aprotic) and dimethylformamide (DMF, highly polar and aprotic; Figure 1, Table 1 and supplementary information). The solvatochromic studies showed that absorption behavior of the chromophore in the parent **3d**, sulfide **3f**, sulfoxide **3p** and sulfone **3q** are similar in each one the solvents. The maximum bathochromic shift from non-nonpolar solvent hexane to polar solvent acetonitrile is about 16 nm. Similarity of absorption spectra of sulfone **3q** and its parent **3d** in each solvent indicates that sulfur present in the side chain of **3q** has little influence on the absorption characteristics of the chromophore.

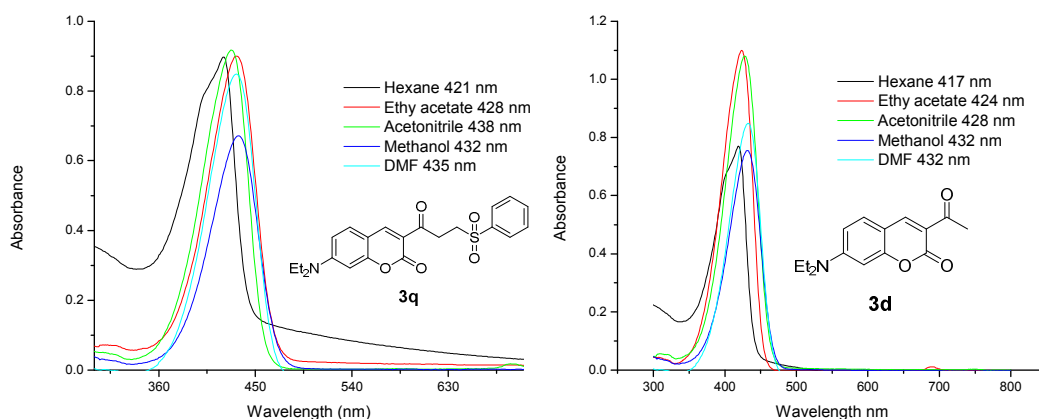


Figure 1. Absorption spectra of sulfone **3q** (9.8 μM) and parent **3d** (10.8 μM) in hexane (black), EtOAc (red), MeCN (green), MeOH (blue), DMF (cyan)

Table 1. Absorption characteristics of parent **3d**, sulfide **3f**, sulfoxide **3p** and sulfone **3q** in hexane, EtOAc, acetonitrile, methanol and DMF

Compound	λ_{max} (ϵ in $\text{cm}^{-1}\text{mol}^{-1}$)					$\Delta\lambda_{\text{max}}$
	Hexane	EtOAc	DMF	MeOH	MeCN	
3q	421	428	435	432	438	17
	69424	79346	76871	767202	74352	
3f	418	424	432	430	434	16
	68924	79545	77347	76802	74678	
3p	417	425	433	432	433	16
	69345	81246	75487	78402	76734	
3d	417	424	432	432	428	15
	70126	88426	79234	89240	77456	

Fluorescence spectra of parent **3d**, sulfide **3f**, sulfoxide **3p** and sulfone **3q** are gathered in Figure 2 and the data in Table 2. Solvatochromic effects on fluorescence emission of the parent **3d**, sulfide **3f**, sulfoxide **3p** and sulfone **3q** was evaluated in five solvents namely hexane, EtOAc, MeOH, DMF and MeCN. Similar to that of the parent **3d**, solutions of sulfide **3f**, sulfoxide **3p** and sulfone **3q** were strongly fluorescent in EtOAc and noticeable to naked eye. We calculated quantum yield with reference to parent **3d**.¹⁴ Compared to the parent **3d** ($\Phi = 66\%$)

the sulfide **3f** exhibited higher quantum yield ($\Phi = 80\%$) in EtOAc, which indicated that the sulfur in the side chain had positive influence on emission, possibly by stabilizing S_0 excited state. Solvent polarity profoundly influenced emission intensities of sulfide **3f**, sulfoxide **3p** and sulfone **3q**. In MeOH (polar protic) and DMF (polar aprotic), the emission was much lower than EtOAc (moderately polar aprotic). Similar to the parent **3d**, the sulfide **3f**, sulfoxide **3p** and sulfone **3q** exhibited maximum Stokes shift of about 50 nm in DMF which indicates that in all of them the dipolar excited state is stabilized in polar solvents. Interestingly, the sulfone **3q** displayed hundred-fold increase in emission intensity in hexane compared to others. Its quantum yield ($\Phi = 30\%$) was nearly five times higher than that of the sulfoxide **3p** ($\Phi = 6\%$).

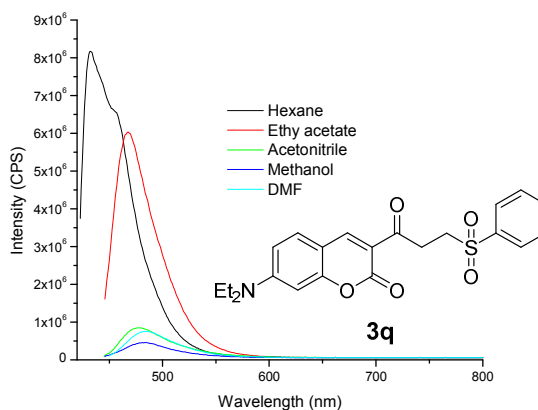
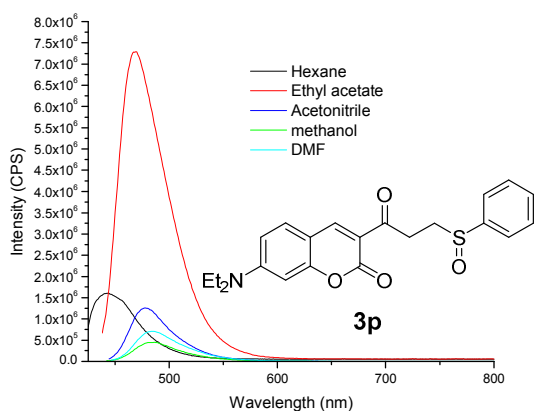
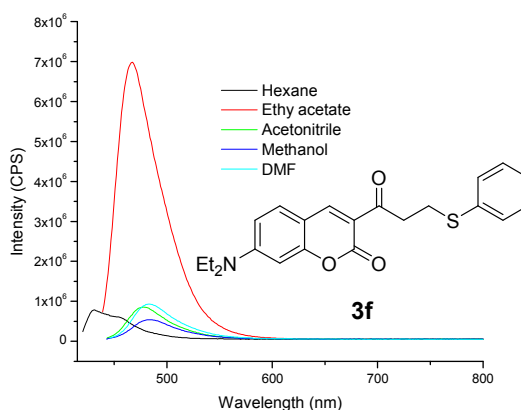
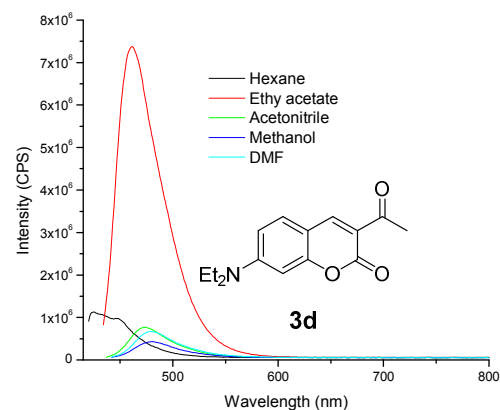


Figure 2. Fluorescence emission of parent **3d** (2.3 μM), sulfide **3f** (2.2 μM), sulfoxide **3p** (2.2 μM) and sulfone **3q** (2.3 μM) in hexane (black), EtOAc (red), MeCN (green), MeOH (blue) and DMF (cyan)

Table 2. Emission characteristics of parent **3d**, sulfide **3f**, sulfoxide **3p** and sulfone **3q** in hexane, EtOAc, MeOH, DMF and MeCN.

Coumarin	λ_{max} (emission)					$\Delta\lambda_{\text{max}}$	Φ				
	Hexane	EtOAc	MeCN	MeOH	DMF		Hexane	EtOAc	MeCN	MeOH	DMF
Parent 3d ¹⁴	428	461	475	480	480	52	0.05 (5%)	0.66 (66%)	0.025 (1%)	0.021 (2.1%)	0.031 (3.1%)
Sulfide 3f	433	467	481	483	483	50	0.03 (3%)	0.80 (80%)	0.018 (1.8%)	0.016 (1.6%)	0.024 (2.4%)
Sulfoxide 3p	432	466	480	482	480	51	0.06 6%	0.68 68%	0.028 2.8%	0.013 1.3%	0.023 2.5%
Sulfone 3q	432	468	478	484	483	51	0.298 29.8%	0.51 51%	0.030 3%	0.023 2.3%	0.035 3.5%

Acetate anion sensing properties of sulfone **3q**

Coumarin based fluorescent chemosensors are highly valuable tools for detection of various cations, anions and biologically relevant molecules.¹⁵ Functional groups present on 3-acyl coumarin scaffold namely lactone conjugated to cinnamoyl moiety and the side-chain on the acyl groups can be fine-tuned to recognize target ions. For example, recently Lin and coworkers have demonstrated that coumarin **4** selectively recognizes acetate anion present in water or in DMSO through binding mode (**4A**) as shown in Figure 3.¹⁶ They used colorimetric titration method for this purpose. As the coumarins made in this study namely, sulfide **3f**, sulfoxide **3p** and sulfone **3q** possess structural similarities to **4** we considered to study their acetate anion sensing properties by following fluorescence emission.

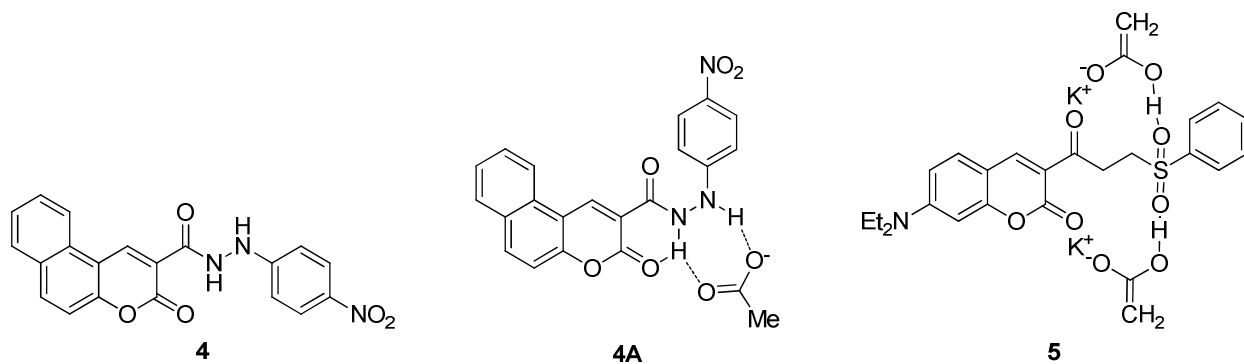


Figure 3. Structure of fluorescent coumarin **4**, its acetate complex **4A** and sulfone acetate complex **5**.

Initially, absorption and emission spectra of sulfide **3f**, sulfoxide **3p** and sulfone **3q** were recorded in MeOH in the absence (blank) and in presence of excess (4 equivalents) of potassium acetate (KOAc) and the results are shown in Figure 4. It is evident from the spectra that only the emission of sulfone **3q** responds to potassium acetate, while absorption and emission maxima (λ_{max}) and the respective intensities of other coumarins **3f** and **3p** are more or less remained as such. Even in the case of sulfone **3q** the maximum for both absorption and emission remained unchanged, although emission intensity doubled by a factor of 2 indicating that the fluorescence emission is sensitive to the presence of potassium acetate.

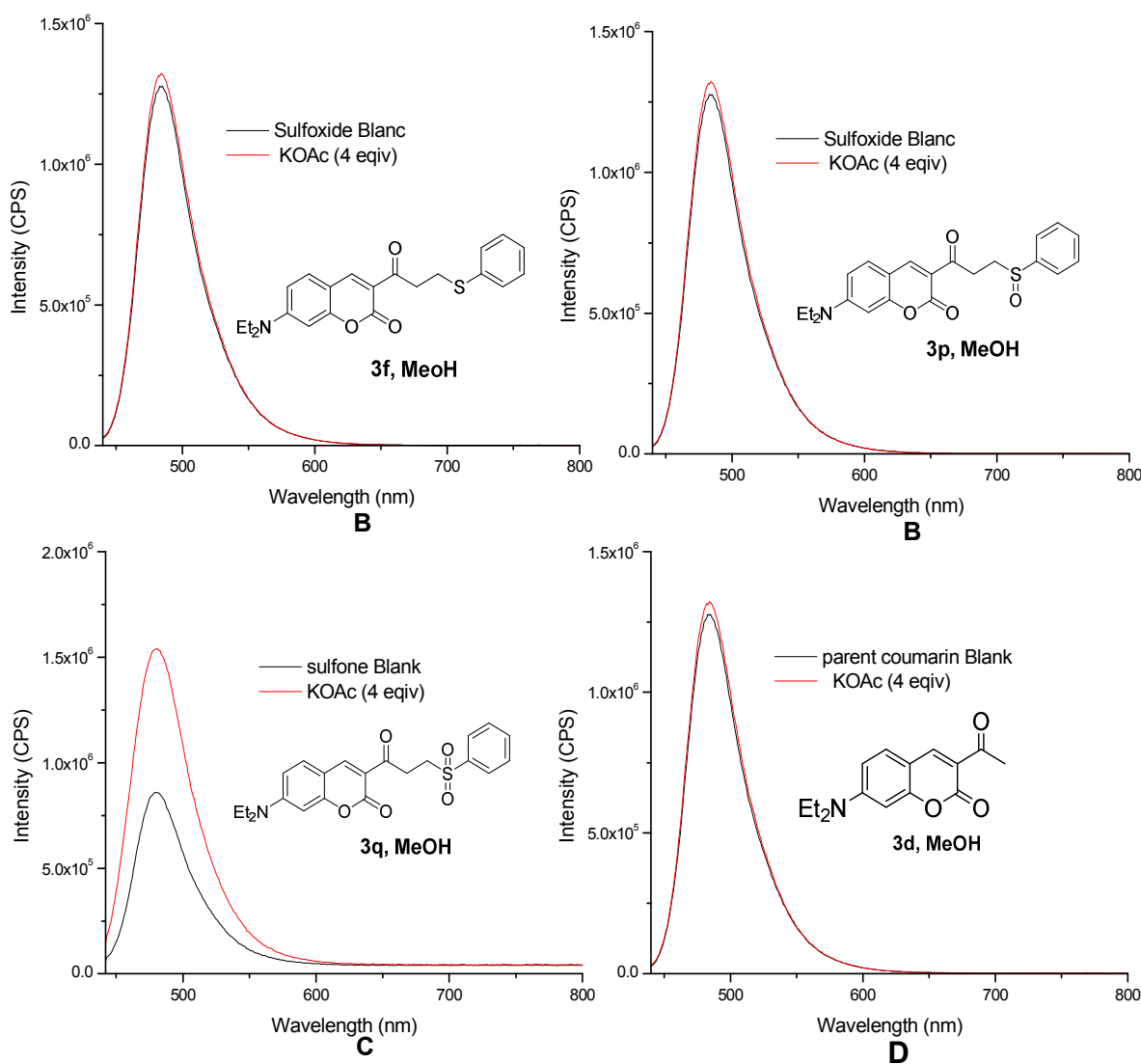


Figure 4. A: Emission spectra of the sulfide **3f** (blank) (1.42×10^{-7} molar) and with excess (4 equiv) potassium acetate (KOAc) in MeOH. B: Emission spectra of the sulfoxide **3p** (blank) (1.52×10^{-7} molar) and with excess KOAc in MeOH. C: Emission spectra of the sulfone **3q** (blank) (1.32×10^{-7} molar) and with excess KOAc in MeOH. D: Emission spectra of the 3-acyl coumarin **3d** (blank) (1.47×10^{-7} molar) and with excess KOAc in MeOH

To ascertain the enhancement of emission intensity is due to the presence of acetate anion rather than potassium cation, we changed counter cations. We recorded emission spectra of **3q** in

presence of excess (4 equiv) metal acetate salts such as sodium acetate, copper(II) acetate, magnesium acetate, manganese(II) acetate, cobalt(II) acetate, zinc acetate and lead(II) acetate (Figure 5A). The spectra indicate that cations do not have much effect on the acetate sensing characteristics of the sulfone **3q** except possibly Zn(II) and Pb(II) where the intensity enhancement is not much. After these set of experiments, we recorded emission spectra of **3q** in presence of different potassium salts to establish acetate anion's role in emission intensity enhancement. The spectra of sulfone **3q** were recorded with different monodentate salts like potassium bisulfate, potassium chloride, potassium azide, potassium nitrate, and bidentate salt like potassium tartarate (Figure 5B). The spectra clearly show that only acetate anion has influence in fluorescence emission enhancement.

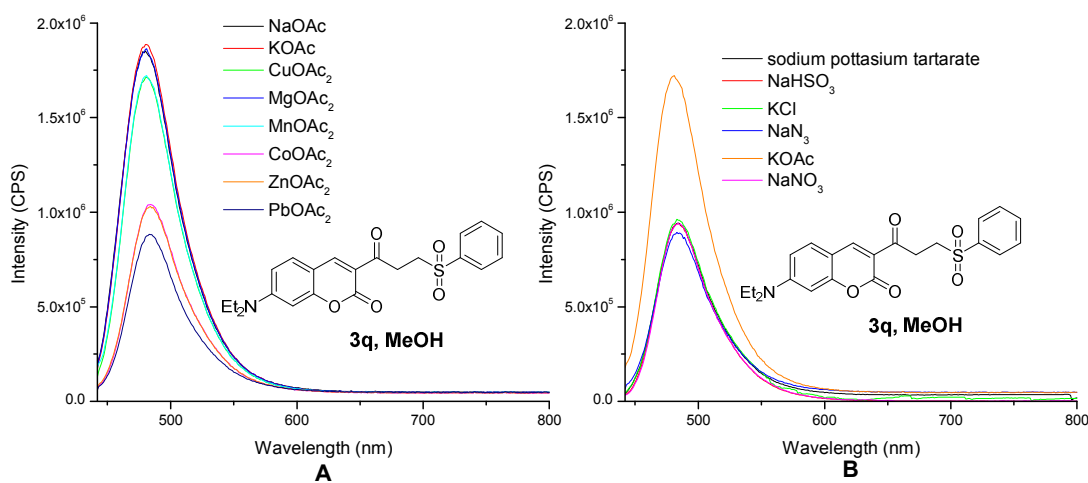


Figure 5. A) Emission of sulfone **3q** (1.32×10^{-7} molar) in MeOH in presence of different cations associated with acetate. B) Emission of sulfone **3q** (1.32×10^{-7} molar) in MeOH in presence of different anions associated with potassium.

After establishing fluorescence emission enhancement by acetate anion we set out to determine the stoichiometric ratio of sulfone **3q** to that of acetate anion. We titrated sulfone **3q** with increasing amount of potassium acetate and recorded fluorescence spectra after each titration

(Figure 6A). The emission enhancement showed Sigmoidal relationship (Figure 6B) until potassium acetate concentration reached two molar equivalents. Further addition of KOAc did not change emission intensity indicating that two units of acetate anion complexes with the coumarin **3q**.

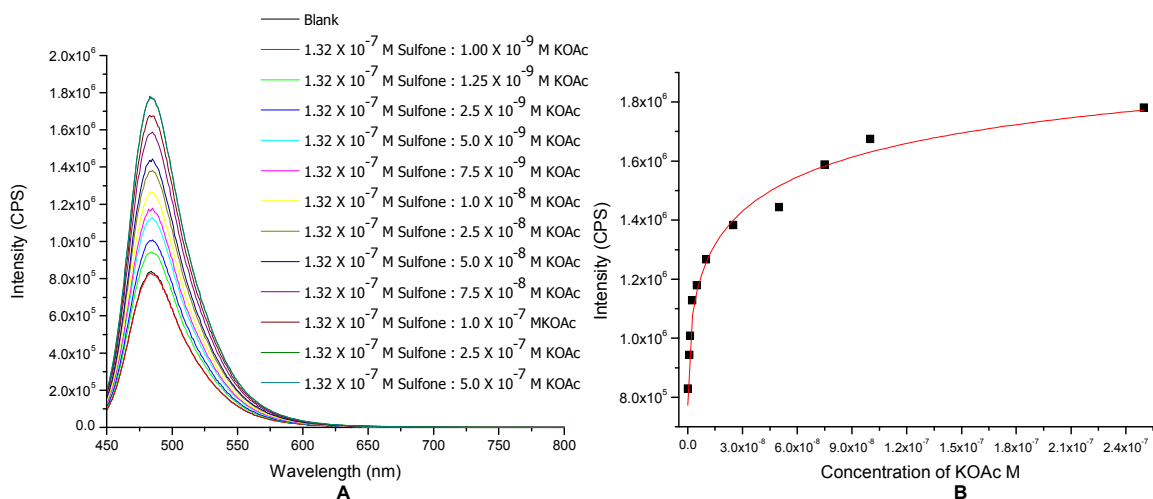


Figure 6. A) Emission of sulfone **3q** (1.32×10^{-7}) in MeOH in presence of different concentrations of KOAc (1×10^{-9} to 5.0×10^{-7} molar). B) Sigmoidal plot of fluorescence intensity and concentration of KOAc (1×10^{-9} to 5.0×10^{-7} molar).

We determined the detection limit of acetate ions by the sensor coumarin **3q** by keeping concentration of sensor constant and varying acetate ion concentration gradually (Figure 6A). Minimum concentration of KOAc required for its detection was 1.25×10^{-9} mol per the sensor **3q** concentration of 1.32×10^{-7} mol. This study indicates that **3q** can detect up to about one hundredth concentration of acetate ions compared to its own concentration.

Generally, the mechanism of recognition of target ions by coumarin based chemosensors could be through (i) intramolecular charge transfer (ICT), (ii) photoinduced electron transfer (PET) and (iii) fluorescence resonance energy transfer (FRET).¹⁷ Among the three, ICT

mechanism is predominant for anion sensing.¹⁸ The coumarin prepared by Lin and coworkers appear to sense acetate anions through ICT mechanism. Hydrogen bonding interactions of the acetate with hydrogen atoms present on two adjacent nitrogen atoms stabilizes coumarin scaffold in a particular conformation (Structure 4A, Figure 3).^[16] In our case the acetate anion sensing could be through hydrogen bonding and electrostatic interactions of the enolate tautomer of the acetate anion as shown in structure **5** (Figure 3). Such an intermediate could restrict conformational mobility of **3q** leading to enhancement of fluorescence emission (Figure 5).

Conclusion

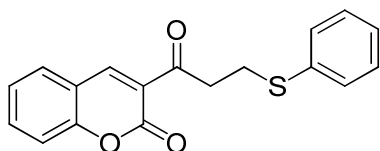
In summary, we have developed an efficient InCl_3 catalyzed condensation reaction of 2-hydroxybenzaldehydes and β -keto esters to furnish coumarins **3a-o**. It is noteworthy that the condensation worked under InCl_3 catalysis in cases where other catalysts failed. The coumarins with C3-acyl group and C7-diethylamino group were highly fluorescent in ethyl acetate and hexane. One of the coumarins with sulfone group in the C3-acyl side-chain, **3q** detects acetate anion efficiently.

Experimental procedure:

General: Analytical thin-layer chromatography (TLC) was performed on in-house coated silica gel glass plates (0.25 mm, silica gel G, LOBA Chemicals, UV silica gel GF 254). TLC spots were visualized under UV light and iodine. Column chromatography was carried out using silica gel 100-200 mesh (LOBA Chemicals) and eluent mixture of increasing amounts of ethyl acetate in hexanes. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer as dilute solutions in $\text{CDCl}_3 + \text{CCl}_4$ (1:1) mixture. The chemical shifts values (δ) are expressed in parts per million relative to the residual solvent peak ($\delta = 7.26$ ppm for ^1H , $\delta = 77.0$ ppm for ^{13}C) where possible or alternatively to SiMe_4 ($\delta = 0.00$ ppm) as internal standard. Coupling constants

(*J*) are given in Hz and multiplicities are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or broad (br). DEPT-135 NMR spectra were recorded for all the samples to determine number of hydrogen atoms present on each carbon. IR spectra were recorded as KBr pellets on a Thermo Nicolet-6700 spectrometer. Samples for melting point determination were recrystallized from hexane and ethyl acetate (9:1). Melting points were determined by using open-ended capillary tubes on VEEGO VMP-DS instrument and are uncorrected. The 2-hydroxybenzaldehydes **1a-e** and β -keto esters **2a-b** were procured from commercial sources and were used as obtained. The β -keto ester **2c** was prepared via Blaise reaction according our reported procedure.¹⁹ Coumarins **3c**, **3f**, **3i**, **3l** and **3o** are unknown compounds whose preparation and spectral data are given in the following section. Rest of the coumarins prepared in this study are known compounds.²⁰

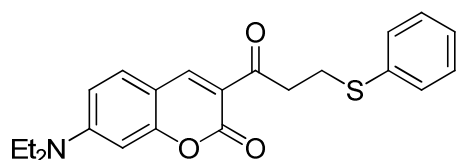
Representative procedure for synthesis of coumarins: 3-(3-(Phenylthio)propanoyl)-2H-chromen-2-one 3c:



To 2-hydroxy benzaldehyde **1a** (58.2 mg, 0.47 mmol) and ethyl 3-(phenylthio)propanoate **2c** (100.6 mg, 0.39 mmol) taken in a 10 mL test tube indium(III) chloride (8.9 mg, 0.03 mmol) in ethanol (2 mL) was added at rt. The reaction vessel was then placed in a pre-heated oil bath (80 °C) for 6.5 h by which time TLC indicated completion of the reaction. Contents of the test-tube were transferred into a round-bottomed flask and ethanol was removed under reduced pressure. Remaining reaction mixture was diluted with 20 mL dichloromethane (DCM). The DCM solution was washed with water and brine solution followed by removal of DCM under reduced pressure. Trituration of the remaining viscous liquid with hexane lead to formation of 3-(3-

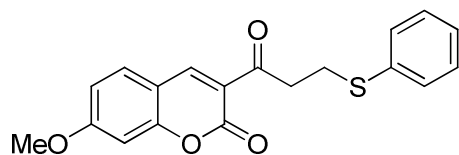
(phenylthio)propanoyl)-2*H*-chromen-2-one **3c** (99.6 mg) as a colorless solid. Analytical sample was obtained by recrystallization with ethyl acetate and hexane (95:5). Yield 90%; mp 134 °C; IR Data (ν) 3055, 2930, 1726, 1675, 1573, 1171, 752 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CCl}_4$) δ 8.48 (s, 1H), 7.66-7.63 (m, 2H), 7.37-7.31 (m, 4H), 7.28-7.26 (m, 2H), 7.24-7.16 (m, 1H), 3.49-3.46 (t, $J = 6.8$ Hz, 2H), 3.29-3.25 (t, $J = 7.2$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CCl}_4$) δ 195.9, 155.4, 147.8, 136.1, 134.6, 130.4, 129.8, 129.1, 126.4, 125.1, 124.3, 118.4, 116.9, 96.3, 42.6, 28.2 ppm; HRMS (ESI^+) calcd for $\text{C}_{18}\text{H}_{14}\text{O}_3\text{SNa}$ ($\text{M} + \text{Na}$) 333.0561; found 333.0558.

7-(Diethylamino)-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 3f:



Yield 95%; Mp 148 °C; IR Data (ν) 3045, 2965, 1715, 1665, 1572, 1171, 815 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CCl}_4$) δ 8.42 (s, 1H), 7.39-7.35 (m, 3H), 7.28-7.24 (m, 2H), 7.16-7.14 (m, 1H), 6.66-6.58 (m, 1H), 6.45-6.44 (m, 1H), 3.48-3.43 (m, 6H), 3.29-3.25 (t, $J = 7.2$ Hz, 2H), 1.26-1.22 (t, $J = 8.0$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CCl}_4$) δ 195.9, 160.6, 158.9, 153.2, 148.3, 136.8, 132.1, 129.5, 129.1, 126.1, 115.9, 109.9, 108.5, 96.8, 45.99, 42.4, 28.4, 12.7 ppm; HRMS (ESI^+) calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_3\text{SNa}$ ($\text{M} + \text{Na}$) 404.1296; found 404.1295.

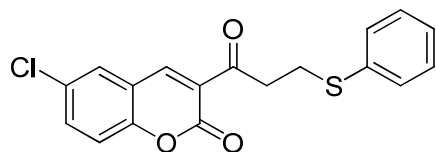
7-Methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 3h:



Yield 75%; Mp 142 °C; IR Data (ν) 3064, 2985, 1713, 1656, 1566, 1171, 792 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CCl}_4$) δ 8.47 (s, 1H), 7.54-7.52 (d, $J = 8.8$ Hz, 1H), 7.37-7.34 (m, 2H), 7.28-7.24 (m, 2H), 7.17-7.15 (m, 1H), 6.90-6.80 (m, 2H), 3.91 (s, 3H), 3.48-3.44 (t, $J = 6.8$ Hz, 2H),

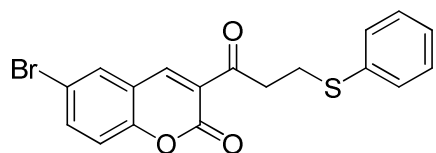
3.28-3.25 (t, $J = 6.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CCl}_4$) δ 195.8, 165.5, 159.5, 157.9, 148.2, 136.3, 131.7, 129.7, 129.1, 126.3, 120.4, 114.1, 112.2, 100.4, 56.1, 42.5, 28.2 ppm; HRMS (ESI^+) calcd for $\text{C}_{19}\text{H}_{16}\text{O}_4\text{SNa}$ ($\text{M} + \text{Na}$) 363.0667; found 363.0663.

6-Chloro-3-(3-(phenylthio)propanoyl)-2H-chromen-2-one 3l:



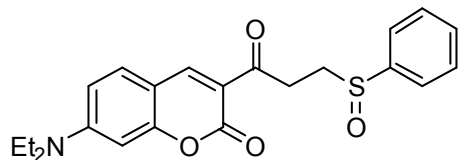
Yield 88%; Mp 139 °C; IR Data (ν) 3064, 2985, 1713, 1656, 1566, 1171, 792 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CCl}_4$) δ 8.31 (s, 1H), 7.55-7.50 (m, 2H), 7.29-7.18 (m, 5H), 7.11-7.10 (m, 1H), 3.41-3.38 (t, $J = 6.8$ Hz, 2H), 3.28-3.25 (t, $J = 6.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CCl}_4$) δ 195.6, 158.4, 153.7, 146.4, 136.1, 134.4, 130.5, 129.9, 129.2, 129.1, 126.5, 125.2, 119.3, 118.3, 42.6, 28.1 ppm; HRMS (ESI^+) calcd for $\text{C}_{18}\text{H}_{13}\text{ClO}_3\text{SNa}$ ($\text{M} + \text{Na}$) 367.0172; found 367.0175.

6-Bromo-3-(3-(phenylthio)propanoyl)-2H-chromen-2-one 3o:



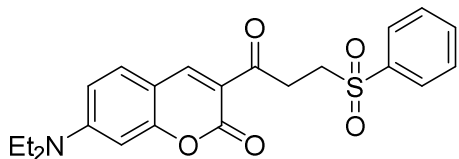
Yield 95%; Mp 135 °C; IR Data (ν) 3030, 2930, 1740, 1678, 1558, 1295, 758 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CCl}_4$) δ 8.37 (s, 1H), 7.77-7.70 (m, 2H), 7.36-7.34 (m, 2H), 7.26-7.16 (m, 4H), 3.48-3.44 (t, $J = 6.8$ Hz, 2H), 3.28-3.24 (t, $J = 6.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CCl}_4$) δ 195.5, 158.3, 154.2, 146.4, 137.2, 136.0, 132.4, 129.8, 129.1, 126.4, 125.1, 119.8, 118.5, 117.7, 42.6, 28.1 ppm; HRMS (ESI^+) calcd for $\text{C}_{18}\text{H}_{13}\text{BrO}_3\text{SNa}$ ($\text{M} + \text{Na}$) 410.9666; found 410.9669.

7-(Diethylamino)-3-(3-(phenylsulfinyl)propanoyl)-2H-chromen-2-one 3p:



To the coumarin **3f** (1.15 g, 3.01 mol) solution in acetonitrile (20 mL) aqueous H₂O₂ solution (30%, 0.5 mL) was added and the reaction mixture was stirred at rt for 22 h. TLC showed the absence of **3f**. Acetonitrile was evaporated and the resulting solid was washed with water and dried under vacuum to get **3p** as a faint yellow solid. Yield = 1.10 g (90%); Mp 165 °C; IR Data (v) 3045, 2964, 1713, 1665, 1572, 1171, 815 cm⁻¹; ¹H NMR (400 MHz, CDCl₃ + CCl₄) δ 8.36 (s, 1H), 7.33-7.29 (m, 3H), 7.21-7.17 (m, 2H), 7.10-7.08 (m, 1H), 6.55-6.52 (m, 1H), 6.39-6.38 (m, 1H), 3.41-3.35 (m, 6H), 3.23-3.19 (t, *J* = 7.2 Hz, 2H), 1.18-1.15 (t, *J* = 8.0 Hz, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃ + CCl₄) δ 195.9, 160.7, 158.9, 153.2, 148.3, 136.6, 132.1, 129.4, 129.1, 126.1, 115.7, 109.9, 108.4, 96.8, 45.3, 42.3, 28.3, 12.5 ppm; HRMS (ESI⁺) calcd for C₂₂H₂₃NO₄SNa (M + Na) 420.4788; found 436.4785

7-(Diethylamino)-3-(3-(phenylsulfonyl)propanoyl)-2H-chromen-2-one 3q:



To the coumarin **3f** (1.20 g, 3.21 mol) taken in MeOH (10 mL) oxone (5.52 g, 9.0 mmol) dissolved in 10 mL of water was added slowly during 10 min. Resulting reaction mixture was stirred for 8 h at rt by which time **3f** was absent in TLC. Methanol and water were removed in reduced pressure and the resulting solid was washed with water and dried under vacuum to get yellow solid **3q**. Yield = 1.27 g (97%); Mp 175 °C; IR Data (v) 3045, 2965, 1712, 1618, 1572, 1171, 815 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H), 7.97-7.95 (m, 2H), 7.64-7.62 (m,

1H), 7.58-7.54 (m, 2H), 7.38-7.36 (d, $J = 9$ Hz, 1H) 6.62-6.60 (m, 1H), 6.45-6.44 (m, 1H), 3.55-3.53 (m, 4H), 3.46-3.43 (m, 4H), 1.25-1.24 (t, $J = 8.0$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 193.3, 160.6, 159.1, 153.5, 148.5, 139.1, 133.8, 132.2, 129.4, 128.4, 114.7, 110.2, 108.3, 96.7, 51.3, 45.3, 35.9, 12.5 ppm; HRMS (ESI⁺) calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_5\text{SNa}$ (M + Na) 436.1195; found 436.1192.

Quantum yield calculation:

3-Acetyl coumarin **3d** was taken as reference to calculate quantum yields of the coumarins **3f**, **3p**, **3q**, since all of them share the chromophore. Indeed, the absorption characteristics of **3f**, **3p**, **3q** overlapped with that of the parent **3d**. Quantum yields were calculated using the formula given below by keeping the absorbance maximum between 0.02 – 0.08 to avoid inner filter effects and to ensure linear response on the intensity.

$$Q = Q_R \frac{I}{I_R} \frac{A_R}{A} \frac{n^2}{n_R^2}$$

I = Integrated fluorescence intensity

A = Absorbance at the excitation wavelength

η = refractive index of the solvent

Q_R = quantum yield of the reference compound

It is to be noted that refractive index does not have a role in the above formula as absorption and emission spectra of 3-acetyl-7-diethylaminocoumarin **3d** (standard) and the coumarins **3f**, **3p**, **3q** were freshly recorded in respective solvents. Therefore, the refractive index values for each solvent nullify as they appear both in the numerator and the denominator. Excitation wavelengths and calculated quantum yields of reference **3d** and the coumarins **3f**, **3p**, **3q** are given in Table 1 and Table 2 respectively.

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The indium(III) chloride catalyzed synthesis of sulfur incorporated 3-acylcoumarins; their photochromic and acetate sensing properties.

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