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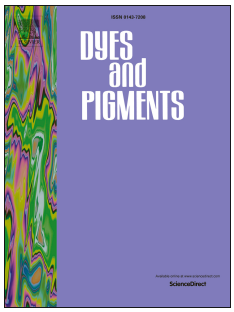

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PII: S0143-7208(15)00140-0

DOI: 10.1016/j.dyepig.2015.04.018

Reference: DYPI 4740

To appear in: *Dyes and Pigments*

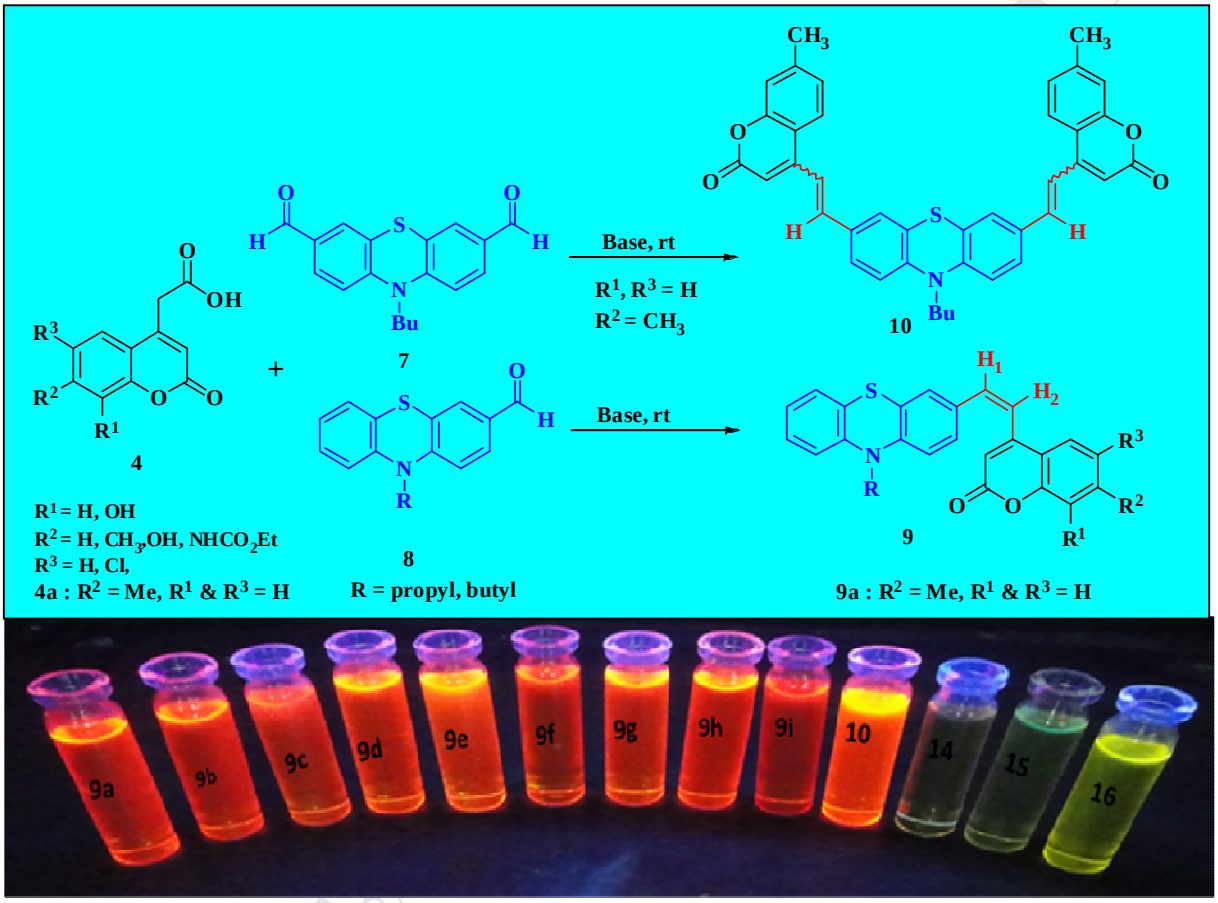
Received Date: 13 January 2015

Revised Date: 5 April 2015

Accepted Date: 10 April 2015

Please cite this article as: Sanap AK, Sanap KK, Shankarling GS, Synthesis and photophysical study of novel coumarin based styryl dyes, *Dyes and Pigments* (2015), doi: 10.1016/j.dyepig.2015.04.018.

Graphical Abstract



Synthesis and photophysical study of novel coumarin based styryl dyes

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Abstract

New organic dyes comprising phenothiazine, carbazole, indole, diphenylamine moieties, as the electron donors, and coumarin ring as the electron acceptor through ethylenic π bridge were synthesized and characterized. The reaction of different coumarin-4-acetic acids with phenothiazine-3-carbaldehyde in the presence of piperidine in methanol gives highly fluorescent styryl derivatives having *cis* configuration of ethylenic double bond. Under similar conditions 7-methylcoumarin-4-acetic acid was condensed with indole-3-carbaldehyde, carbazole-3-carbaldehyde, and diphenyl amine aldehyde to give different styryl derivatives with *trans* configuration of ethylenic double bond. Synthesized compounds were also studied for photophysical properties and show solvatochromism.

***Keywords*:**

Phenothiazine

Coumarin

Fluorescence

Solvatochromism

1. Introduction

Organic dyes with donor-π-acceptor (D–π–A) structures have attracted increasing attention since they can provide photoluminescent materials in molecular electronics, such as efficient nonlinear optical (NLO) materials [1], organic light-emitting diodes (OLEDs) [2], and solar cells [3]. So far, many organic D-π-A compounds have been studied experimentally and theoretically. Various classes, including triarylamines [4], carbazoles [5], fluorenes [6], and thiophenes [7], have mostly been used as electron-donating moieties, whereas quinolines [8], quinoxalines [9], oxadiazoles [10], diarylborons [4], and benzothiadiazoles [11], are commonly used as electron-accepting moieties. In these compounds, donor moiety facilitates hole injection and transport, whereas the acceptor moiety facilitates electron injection and transport. Carbazole, diphenyl amine, and phenothiazine are often adopted as donors, as a result of their good thermal, electrochemical stability, and electron donating abilities [12]. The UV–Vis absorption and photoluminescence (PL) of these compounds suggest significant intramolecular charge transfer (ICT) behavior and solvatochromism. Although remarkable progress has been made in the organic dyes, further optimization of their chemical structures is still of great necessity. Their various properties could be finely tuned by using different donor and acceptor groups.

In 1883, Bernthsen, the father of phenothiazine (PTZ) chemistry, first synthesized phenothiazine compound. The phenothiazines have wide range of applications. Some phenothiazine derivatives, notably lauth's violet and methylene blue were commercially available as dyes even before the discovery of the parent phenothiazine. Various phenothiazine derivatives are used in dye sensitized solar cells (DSSCs) [13], Phenothiazine contains electron-rich sulfur and nitrogen as hetero atoms in the middle

ring exhibits good electrochemical stability and electron-donating ability, and has been considered as a promising donor moiety in organic dyes. Furthermore, the PTZ ring is non-planar with a butterfly conformation in the ground state, which can impede the molecular aggregation and the formation of intermolecular excimers. Therefore, PTZ based organic dyes have attracted broad interest for synthesis of fluorescent compounds.

On the other hand coumarins have also been widely investigated with regard to their outstanding optical properties. They constitute the largest class of fluorescent dyes [14], and are widely used as emission layers in organic light-emitting diodes (OLED) [15], optical brighteners [16], non-linear optical chromophores [17], fluorescent whiteners [18], fluorescent labels as well as probes for physiological measurement [19]. Typical coumarin based fluorescent compounds normally contain an electron donor group at the 7-position and an electron acceptor such as benzoxazole, benzimidazole or benzothiazole ring at the 3-position [20]. There is only one report in which coumarin ring act as acceptor in organic dyes [21]. If we placed electron donating substituent at proper position in coumarin ring, coumarin ring act as an acceptor as it involves delocalization of electron over polar carbonyl group through conjugated 3-4 double bond. Based on these considerations, we have designed and synthesized a series of styryl dyes containing phenothiazine as donor and coumarin as an acceptor.

Recently, Samant et al synthesized coumarin based fluorescent compounds in which one coumarin moiety act as electron donor while other coumarin moiety act as an electron acceptor through ethylenic bridge [21], [22]. These *trans*-biscoumarinylethenes are further studied for photophysical properties. Taking inspiration from this, we have synthesized phenothiazine based coumarin dyes (PTZ-coumarin ethene) which shows some comparable and interesting results as compared to *trans*-biscoumarinylethenes. It

includes 1) in biscoumarinylethenes stereochemistry of ethylenic double bond is *trans* while PTZ-coumarin ethene show *cis* stereochemistry of ethylenic double bond. 2) *trans*-Biscoumarinylethenes have good emission value in polar solvent like dimethyl sulfoxide while PTZ-coumarin ethenes have good emission value in non polar solvent like chloroform. 3) In addition to this, PTZ-coumarin ethenes show higher Em, λ_{Max}, higher Stokes shift and higher quantum yield as compared to *trans*-biscoumarinylethenes.

2. Experimental

2.1. Materials and equipments

Phenothiazine was purchased from commercial suppliers and was used without further purification. Citric acid, phenols and piperidine were purchased from S. D. Fine Chemical Ltd. India. Methanol used in this work was of analytical grade. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Advance NMR spectrometer in $CDCl_3$/DMSO-d_6 with TMS as an internal standard, and the chemical shifts were expressed in δ unit (ppm). Mass spectral data were obtained with micromass-Q-Tof (YA105) spectrometer. Elemental analysis was carried out with a Thermo finnigan, Flash EA 1112. All Infrared spectra were recorded on Jasco-FT/IR 4100 LE ATR PRO450-S spectrometer. All the melting points reported are in degree centigrade and are uncorrected. Absorption spectra were recorded on Perkin-Elmer Lamada 25 UV-vis spectrophotometer. Emission spectra were recorded on a Cary Eclipse fluorescence spectrophotometer. The reactions were monitored by TLC using 0.25 mm E-Merck silica gel 60 F254 precoated plates, which were visualized with UV light.

2.2 Synthesis

2.2.1 Synthesis of 6,7,8-substituted coumarin-4-acetic acid (4)

All coumarin-4-acetic acids (**4**) were synthesized using reported methods [23]. A mixture of anhydrous citric acid (**1**) (192 g, 1 mol) and conc. H_2SO_4 (280 mL) was stirred at room temperature for 1 h and then slowly heated (rate of heating governed by foaming) to 70 ^oC. After 30-35 min at this temperature, with stirring throughout, the evolution of carbon monoxide slackened. The clear solution was rapidly cooled to 0 ^oC. To the cooled solution, *m*-cresol (**3a**) (86.4 g, 0.8 mol) and conc. H_2SO_4 (112 mL) were added with stirring, each in three equal portions, at such a rate that the internal temperature did not exceed 10 ^oC. The resulting mixture was stirred at room temperature for 16 h, poured into ice and the resulting precipitate was filtered and washed thoroughly with water. The precipitate was stirred with saturated $NaHCO_3$ solution (1000 mL) for 15 min at 65 ^oC. The solution was filtered and the insoluble material was washed with water. Acidification with conc. HCl of the combined filtrate gave 110 g, 63% of solid **4a** which was used further without purification.

Using the above procedure different substituted phenols (**3**) were condensed with acetone dicarboxylic acid to obtain a series of 6,7,8-substituted coumarin-4-acetic acids (**4**).

2.2.2 Synthesis of N-butylphenothiazine (6a)

To a phenothiazine (**5**) (30 g, 0.15 mol) solution in dry DMF (100 mL), sodium hydride (10.8 g, 0.45 mol) was slowly added at 0 ^oC for 1 h. Then this reaction mixture was stirred at room temperature for 1 h. After that 1-bromobutane (0.18 mol) was added drop wise to the reaction mass for 1 h which was then slowly heated to 70 ^oC for 3 h. The progress of the reaction was monitored by TLC. After complete consumption of phenothiazine, the reaction mixture was poured into ice cold water and extracted with

ethyl acetate. The organic phase was separated and dried over anhydrous Na_2SO_4. After removing the solvent, the residue was purified by column chromatography using hexane as the eluent to give 35.1 g, 91% of **6a** as colourless viscous liquid.

Using above procedure *N*-propylphenothiazine **6b** was synthesied in 87% yiled

2.2.3 Synthesis of phenothiazine-3-carbaldehyde (8a) and phenothiazine dialdehyde (7a)

7a and **8a** were synthesied using reported method [12].

In a three necked 100 mL round bottom flask fitted with a mercury sealed stirrer, addition dropping funnel topped by calcium chloride guard tube and reflux condenser also topped by calcium chloride guard tube. *N*, *N*-dimethyl formamide (4.58 g, 4.85 mL, 62.7 mmol) was taken and cooled to 0-5 °C with stirring. To the above solution phosphorous oxychloride (7.2 g, 4.3 mL, 47 mmol) was added drop wise maintaining the temperature of the reaction mass at 0-5 °C. The Vilsmeier complex so formed was stirred for further 15 min and compound **6a** (3.97 g, 15.6 mmol) was added in portion wise (15-25 minutes) to the complex. The reaction mixture was stirred at 0-5 °C for 3 h and then allowed to attain room temperature then heated to 75 °C for 8 h. This solution was then cooled to room temperature, poured into ice water, and neutralized to pH 6-7 by drop wise addition of saturated aqueous $NaHCO_3$ solution. The mixture was extracted with dichloromethane. The organic layer was dried with anhydrous Na_2SO_4 and then concentrated on rotary evaporator to obtain crude reaction mixture, which was further purified by FCC using toluene to afforded **7a** (0.37 g, 7%) as light brown oil and **8a** (2.8 g, 64%) as yellow oil.

*Similar way indole-3-carbaldehyde (**11**), carbazole-3-carbaldehyde (**12**) were prepared*

using reported procedure in the literature [24, 25].

2.2.4 General procedure for synthesis of styryl dyes

4a–g (1 mmol) and piperidine (1 mmol) were stirred in methanol (6 mL) for 15 min and corresponding aldehyde (1 mmol) was added slowly at room temperature. The resulting reaction mixture was stirred at room temperature for appropriate time as shown in **Table 3**. After complete consumption of aldehyde, the precipitated solid was collected by filtration and washed with small quantity of cold methanol followed by water to remove traces of piperidine. The products **9** were purified by washing with diethyl ether and the products **14-16** were purified by FCC using toluene.

2.3 Spectral data

_Z_-1(7-Methylcoumarin-4-yl)-2-(10-butyl-10*H*-phenothiazin-3-yl)ethene (9a)

Yield of **9a**: 75%; Red solid; mp: 108-110 °C (ethyl acetate); UV (λ_{max}): 424 nm (chloroform); *Em* (λ_{max}): 632 nm (chloroform); Stokes shift: 208 nm; Quantum yield (Φ_F): 0.21; FTIR (neat, υ/cm^{-1}): 2963 (C-H), 2859 (C-H), 1685 (C=O), 1619 (aromatic C=C), 1469, 1218, 970, and 791; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.95 (3H, t, *J* =7.3Hz, CH_3), 1.45 (2H, sextet, *J* = 7.3 Hz, CH_2), 1.76 (2H, quintet, *J* = 7.1Hz, CH_2), 3.81(2H, t, *J* = 7.4 Hz), 2.44 (3H, s, CH_3), 6.46 (1H, s, C_3'H), 6.74 (1H, d, *J* = 8.6 Hz, ArH), 6.83 (1H, d, *J* = 8.1 Hz, C_6'H), 7.06 –7.17 (7H, m, ArH), 7.28– 7.33 (2H, m, 2H, ArH), 7.64 (1H, d, *J* = 8.1 Hz, C_5'H); ^{13}C NMR (125 MHz, DMSO) δ: 10.9 (CH_3), 19.4 (CH_2), 20.3 (CH_3), 28.4 (CH_2), 48.3 (*N*-CH_2), 107.9 (C_3′), 115.6, 116.0, 116.5, 117.7, 118.0 (C_{4a}'), 122.7 (C_{5a}), 122.8, 123.7 (C_{4a}), 124.9, 125.0, 125.7, 127.1, 127.7, 128.5, 130.2, 132.8, 133.6, 136.8 (C_1), 143.8 (C_{9a}), 145.6 (C_{10a}), 149.8 (C_4'), 151.4 (C_{8a}'), 160.1(C_2'); MS = 440.5 (M+H). *Anal. Calcd. for* $C_{28}H_{25}NO_2S$ (439.57): C, 76.51; H, 5.73; N, 3.19 %.

Found: C, 76.38; H, 5.46; N, 3.25 %.

***Z*-1(6-Methylcoumarin-4-yl)-2-(10-butyl-10*H*-phenothiazin-3-yl)ethene (9b)**

Yield of **9b**: 72%; Yellow solid; mp 148-150 °C (ethyl acetate); UV (λ_{max}): 423 nm (chloroform); *Em* (λ_{max}): 635 nm (chloroform); Stokes shift: 212 nm; Quantum yield (Φ_F): 0.70; FTIR (neat, υ/cm^{-1}): 2941 (C-H), 1687 (C=O), 1625 (aromatic C=C), 1365 (C-N), 1243, 1194, 979, 812 and 745; ^{1}H NMR (300 MHz, DMSO) δ: 0.88 (3H, t, *J* =7.5 Hz, CH_3), 1.40 (2H, sextet, *J* = 7.5 Hz, CH_2), 1.68 (2H, quintet, *J* = 7.5 Hz, CH_2), 2.43 (3H, s, CH_3), 3.91 (2H, t, *J* = 7.5 Hz, *N*-CH_2), 6.72 (1H, s, C_3'H), 6.96 (1H, t, *J* = 7.8 Hz, C_7H), 7.05 (2H, d, *J* = 8.1 Hz, C_6H & C_9H), 7.15-7.23 (2H, m, C_8H & ArH), 7.30 (1H, d, *J* = 8.1 Hz, C_8'H), 7.45 (1H, dd, *J* = 1.2 & 7.3 Hz, C_7'H), 7.57- 7.60 (3H, m, C_9′H, C_{10}′H & ArH) 7.69 (1H, d, *J* = 1.5 Hz, C_4H), 8.05 (1H, s, C_5'H); ^{13}C NMR (125 MHz, DMSO) δ: 13.6 (CH_3), 19.3 (CH_2), 20.3 (CH_3), 28.2 (CH_2), 46.3 (*N*-CH_2), 108.0 (C_3′), 115.6, 115.9, 116.4, 117.6, 118.0 (C_{4a}'), 122.73 (C_{5a}), 122.77, 123.7 (C_{4a}), 124.9, 125.8, 127.1, 127.7, 128.3, 130.2, 132.8, 133.6 (C_6'), 136.7 (C_1), 143.9 (C_{9a}), 145.6 (C_{10a}), 149.8 (C_4'), 151.4 (C_{8a}'), 160.3(C_2'); MS = 440.3 (M+H). *Anal. Calcd. for* $C_{28}H_{25}NO_2S$ (439.57): C, 76.51; H, 5.73; N, 3.19 %. Found: C, 76.34; H, 5.54; N, 3.28 %.

***Z*-1(Coumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene (9c)**

Yield of **9c**: 62%; Yellow solid; mp 126-128 °C (ethyl acetate); UV (λ_{max}): 424 nm (chloroform); *Em* (λ_{max}): 618 nm (chloroform); Stokes shift: 194 nm; Quantum yield (Φ_F): 0.50; FTIR (neat, υ/cm^{-1}): 2963, 2855, 1695 (C=O), 1680, 1629 (aromatic C=C) 1592, 1457, 962, 939 and 744; ^{1}H NMR (300 MHz, DMSO) δ: 0.94 (3H, t, *J* =7.3 Hz, CH_3), 1.70 (2H, sextet, *J* = 7.3 Hz, CH_2), 3.86 (2H, t, *J* = 6.9 Hz, *N*-CH_2), 6.76 (1H, s, C_3'H), 6.96 (1H, t, *J* = 7.3 Hz, C_7H), 7.03 (2H, d, *J* = 8.4 Hz, C_6H & C_9H), 7.15-7.20 (2H,

m, ArH), 7.37-7.42 (2H, m, ArH), 7.55-7.59 (3H, m, ArH & C_9'H), 7.62 (1H, dt, *J* = 1.2 & 7.3 Hz, C_7'H), 7.72 (1H, d, *J* = 1.8 Hz, C_4H), 8.26 (1H, d, *J* = 7.3 Hz, C_5'H); ^{13}C NMR (125 MHz, DMSO) δ: 10.9 (CH_3), 19.4 (CH_2), 48.3 (*N*-CH_2), 108.0 (C_3′), 115.6, 116.0, 116.7, 117.6, 118.3 (C_{4a}'), 122.7 (C_{5a}), 122.8, 123.7 (C_{4a}), 124.2, 125.4, 125.8, 127.1, 127.7, 128.4, 130.2(C_3), 132.0, 137.0, 143.8 (C_{9a}), 145.6 (C_{10a}), 149.9 (C4'), 153.3 (C_{8a}'), 160.2(C_2'); MS = 412.5 (M+H). *Anal. Calcd. for* $C_{26}H_{21}NO_2S$ (411.52): C, 75.88; H, 5.14; N, 3.40 %. Found: C, 75.63; H, 4.96; N, 3.35 %.

***Z*-1(7-Methylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene (9d)**

Yield of **9d**: 75%; Orange solid; mp 160-162 °C (ethyl acetate); UV (λ_{max}): 424 nm (chloroform); *Em* (λ_{max}): 631 nm (chloroform); Stokes shift: 207 nm; Quantum yield (Φ_F): 0.27; FTIR (neat, υ/cm^{-1}): 2954, 1695(C=O), 1617 (aromatic C=C) 1465, 1358, 963 and 734; ^{1}H NMR (300 MHz, DMSO) δ: 0.94 (3H, t, *J* =7.3 Hz, CH_3), 1.70 (2H, sextet, *J* = 7.3 Hz, CH_2), 2.42 (3H, s, CH_3), 3.86 (2H, t, *J* = 7.3 Hz, *N*-CH_2), 6.68 (1H, s, C_3'H), 6.96 (1H, t, *J* = 7.3 Hz, C_7H), 7.03 (2H, d, *J* = 8.4 Hz, C_6H & C_9H), 7.14-7.23 (4H, m, ArH), 7.55-7.58 (3H, m, ArH & C_9'H), 7.71 (1H, d, *J* = 1.8 Hz, C_4H), 8.13 (1H, d, *J* = 8.1 Hz, C_5'H); MS = 426.7 (M+H). *Anal. Calcd. for* $C_{27}H_{23}NO_2S$ (425.54): C, 76.21; H, 5.45; N, 3.29 %. Found: C, 76.28; H, 5.28; N, 3.17 %.

***Z*-1(7-Hydroxylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene (9e)**

Yield of **9e**: 72%; Red solid; mp 222-223 °C (ethyl acetate); UV (λ_{max}): 422 nm (chloroform); *Em* (λ_{max}): 631 nm (chloroform); Stokes shift: 209 nm; Quantum yield (Φ_F): 0.74; FTIR (neat, υ/cm^{-1}): 3237 (O-H), 2959 (C-H), 1680 (C=O), 1615 (aromatic C=C), 1540, 1439, 1363, 955 and 854; ^{1}H NMR (300 MHz, DMSO) δ: 0.94 (3H, t, *J* =7.2 Hz, CH_3), 1.71 (2H, sextet, *J* = 7.3 Hz, CH_2), 2.42 (3H, s, CH_3), 3.87 (2H, t, *J* = 7.5 Hz,

N-CH_2), 6.4 (1H, s, C_3'H), 6.73 (1H, d, *J* = 2.1 Hz, C_8'H), 6.81 (1H, dd, *J* = 2.4 & 8.2 Hz, C_6'H), 6.96 (1H, t, *J* = 7.2 Hz, C_7H), 7.03 (2H, d, *J* = 8.4 Hz, C_6H & C_9H), 7.15-7.24 (3H, m, ArH), 7.53-7.57 (3H, m, ArH), 7.70 (1H, s, C_4H), 8.08 (1H, d, *J* = 8.7 Hz, C_5'H); ^{13}C NMR (125 MHz, DMSO) δ: 10.9 (CH_3), 19.4 (CH_2), 48.3 (*N*-CH_2), 102.4 (C_8'), 103.8 (C_3′), 110.6 (C_{4a}'), 112.7, 115.6, 116.0, 118.1, 119.9, 122.7, 122.8, 125.7, 127.1, 127.7, 128.3, 130.3, 133.8, 136.5, 138.4, 141.5 (C_{9a}), 143.9 (C_7'), 145.5 (C4'), 150.2 (C_{8a}'), 161.2 (C_2'); MS = 428.4 (M+H). *Anal. Calcd. for* $C_{26}H_{21}NO_3S$ (427.51): C, 73.04; H, 4.95; N, 3.28 %. Found: C, 72.91; H, 5.01; N, 3.16 %.

***Z*-1(7,8-Dihydroxylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene (9f)**

Yield of **9f**: 78%; Orange solid; mp 185-186 °C (ethyl acetate); UV (λ_{max}): 427 nm (chloroform); *Em* (λ_{max}): 643 nm (chloroform); Stokes shift: 216 nm; Quantum yield (Φ_F): 0.37; FTIR (neat, υ/cm^{-1}): 3438 (O-H), 3172 (O-H), 1667 (C=O), 1613 (aromatic C=C), 1592, 1461, 960 and 798; ^{1}H NMR (300 MHz, DMSO) δ: 0.94 (3H, t, *J* =7.2 Hz, CH_3), 1.70 (2H, sextet, *J* = 7.2 Hz, CH_2), 3.86 (2H, t, *J* = 7.2 Hz, *N*-CH_2), 6.48 (1H, s, C_3'H), 6.80 (1H, d, *J* = 6.3 Hz, C_8'H), 6.83 (1H, d, *J* = 6.3 Hz, C_6'H), 6.96 (1H, t, *J* = 7.5 Hz, C_7H), 7.03 (2H, d, *J* = 8.1 Hz, C_6H & C_9H), 7.08 (1H, d, *J* = 8.7 Hz), 7.15-7.23 (2H, m, ArH), 7.50 (1H, d, *J* = 2.7 Hz), 7.55 (1H, dd, *J* = 2.0 & 8.0 Hz, C_2H), 7.68 (1H, d, *J* = 1.8 Hz, C_4H); ^{13}C NMR (125 MHz, DMSO) δ: 11.2 (CH_3), 19.4 (CH_2), 48.3 (*N*-CH_2), 103.7 (C_3′), 110.1, 111.4, 111.9, 112.0, 115.4, 115.7, 116.0, 118.4, 123.7, 125.7, 127.1, 127.7, 130.3 (C_{5a}), 132.4 (C_{4a}), 136.2 (C_1), 143.9 (C_{9a}), 145.5 (C_{10a}), 149.4 (C_8'), 149.5 (C_7'), 150.6 (C_4'), 153.8 (C_{8a}'), 160.6 (C_2'); MS = 444.7 (M+H). *Anal. Calcd. for* $C_{26}H_{21}NO_4S$ (443.51): C, 70.41; H, 4.77; N, 3.16%. Found: C, 70.27; H, 4.58; N, 3.14 %.

***Z*-1(7-Carbamatecoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene (9g)**

Yield of **9g**: 60%; Red solid; mp 208-210 °C (ethyl acetate); UV (λ_{max}): 422 nm (chloroform); *Em* (λ_{max}): 635 nm (chloroform); Stokes shift: 213 nm; Quantum yield (Φ_F): 0.62; FTIR (neat, υ/cm^{-1}): 2961, 2869, (C-H), 1686 (C=O), 1593 (aromatic C=C), 1463, 1215 and 741; ^{1}H NMR (300 MHz, DMSO,Me_4Si) δ: 0.94 (3H, t, *J* =7.2 Hz, CH_3), 1.26 (3H, t, *J* = 6.9 Hz, CH_3), 1.70 (2H, sextet, *J* = 7.3 Hz, CH_2), 3.86 (2H, t, *J* = 7.2 Hz, *N*-CH_2), 4.17 (2H, q, *J* = 6.9 Hz, *O*-CH_2), 6.58 (1H, s, C_3'H), 6.95 (1H, t, *J* = 7.8 Hz, C_7H), 7.02 (2H, d, *J* = 8 Hz, C_6H & C_9H), 7.05-7.23 (3H, m, ArH) 7.43 (1H, dd, *J* = 2.4 & 7.6 Hz, C_2H), 7.52-7.56 (3H, m, ArH), 7.69 (1H, d, *J* = 1.5 Hz, C_4H), 8.14 (1H, d, *J* = 9 Hz, C_5'H); ^{13}C NMR (125 MHz, DMSO) δ: 11.1 (CH_3), 14.8 (CH_3), 19.4 (CH_2), 48.3 (*N*-CH_2), 60.0 (*O*-CH_2), 104.6 (C_3′), 105.3 (C_8′), 112.9 (C_{4a}′), 114.0, 115.6, 116.0, 117.7, 122.74 (C_{5a}), 122.79, 123.7 (C_{4a}), 126.2, 127.1, 127.7, 128.4, 129.3, 130.2 (C_3), 136.7, 142.9 (C_7'), 143.8 (C_{9a}), 145.6 (C_{10a}), 149.7 (C_4'), 153.3 (C_{8a}'), 154.3 (CO of $NHCO_2Et$), 160.5 (C_2'); MS = 499.2 (M+H). *Anal. Calcd. for* $C_{29}H_{26}N_2O_4S$ (498.59): C, 69.86; H, 5.26; N, 5.62 %. Found: C, 69.70; H, 5.18; N, 5.87 %.

***Z*-1(6-Methylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene (9h)**

Yield of **9h**: 62%; Orange solid; mp 152-154 °C (ethyl acetate); UV (λ_{max}): 423 nm (chloroform); *Em* (λ_{max}): 637 nm (chloroform); Stokes shift: 214 nm; Quantum yield (Φ_F): 0.76; FTIR (neat, υ/cm^{-1}): 2956 (C-H), 1693 (C=O), 1629 (aromatic C=C), 1588, 1466, 1360, 964, 801, and 743; ^{1}H NMR (300 MHz, DMSO) δ: 0.94 (3H, t, *J* =7.2 Hz, CH_3), 1.71 (2H, sextet, *J* = 6.9 Hz, CH_2), 2.43 (3H, s, CH_3), 3.87 (2H, t, *J* = 7.2 Hz, *N*-CH_2), 6.72 (1H, s, C_3'H), 6.96 (1H, t, *J* = 7.5 Hz, C_7H), 7.04 (2H, d, *J* = 8.4 Hz, C_6H & C_9H), 7.15-7.24 (2H, m, ArH), 7.30 (1H, d, *J* = 8.4 Hz), 7.45 (1H, dd, *J* = 1.5 & 8.2 Hz), 7.57- 7.60 (3H, m, C_9′H, C_{10}′H & ArH) 7.7 (1H, d, *J* = 1.5 Hz, C_4H), 8.05 (1H, s, C_5'H); MS = 426.3 (M+H). *Anal. Calcd. for* $C_{27}H_{23}NO_2S$ (425.54): C, 76.21; H, 5.45; N, 3.29

%. Found: C, 75.99; H, 5.35; N, 3.32 %.

_Z_-1-(6-Chloro-7-methylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene (9i)

Yield of **9i**: 74%; Yellow solid; mp 154-155 °C (ethyl acetate); UV (λ_{max}): 432 nm (chloroform); *Em* (λ_{max}): 648 nm (chloroform); Stokes shift: 216 nm; Quantum yield (Φ_F): 0.77; FTIR (neat, υ/cm^{-1}): 2959(C-H), 2868, 1729 (C=O), 1687 (C=O), 1615 (aromatic C=C),1573, 1223, 955, and 745; ^{1}H NMR (300 MHz, DMSO) δ: 0.96 (3H, t, *J* =7.3 Hz, CH_3), 1.72 (2H, sextet, *J* = 7.3 Hz, CH_2), 2.43 (3H, s, CH_3), 3.88 (2H, t, *J* = 6.9 Hz, *N*-CH_2), 6.77 (1H, s, C_3'H), 6.97 (1H, t, *J* = 7.4 Hz, C_7H), 7.05 (2H, d, *J* = 8.5 Hz, C_6H & C_9H), 7.17 (1H, d, *J* = 7.5 Hz, C_1H), 7.22 (1H, t, *J* = 7.8 Hz), 7.46 (1H, s, C_8'H), 7.59- 7.61 (3H, m, C_9′H, C_{10}′H & ArH), 7.76 (1H, s, C_4H), 8.37 (1H, s, C_5'H); ^{13}C NMR (125 MHz, DMSO) δ: 10.9 (CH_3), 19.4 (CH_2), 19.8 (CH_3), 48.3 (*N*-CH_2), 107.7 (C_3′), 115.6, 116.0, 117.2, 117.7 119.0 (C_{4a}'), 122.7, 122.8, 124.8 125.9, 127.0, 127.7, 128.7, 129.1 (C_{5a}), 130.2 (C_{4a}), 137.4, (C_1), 140.0, 143.8 (C_{9a}), 145.7 (C_{10a}), 149.0 (C_6'), 150.8 (C_4'), 151.9 (C_{8a}'), 159.9 (C_2'); MS = 460.9 (M+H). *Anal. Calcd. for* $C_{27}H_{22}ClNO_2S$ (459.11): C, 70.50; H, 4.82; N, 3.05%. Found: C, 70.34; H, 4.68; N, 2.97 %.

4-(2-(10-Butyl-7-(2-(7-methyl-coumarin-4-yl)vinyl)-10*H*-phenothiazin-3-yl)vinyl)-7-methylcoumarin (10)

Yield of **10**: 64%; Brown solid; mp 287-288 °C (ethyl acetate); UV (λ_{max}): 441 nm (chloroform); *Em* (λ_{max}): 620 nm (chloroform); Stokes shift: 179 nm; Quantum yield (Φ_F): 0.83; FTIR (neat, υ/cm^{-1}): 2961 (C-H), 2866, 1698 (C=O), 1620 (aromatic C=C), 1572, 1141, 964 and 798; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.98 (3H, t, *J* = 7.4 Hz, CH_3), 1.50 (2H, d, *J* = 7.6 Hz, CH_2), 1.83 (2H, quintet, CH_2), 2.47 (s, 6H, 2xCH3), 3.91 (2H, t, *J* = 7.6 Hz, *N*-CH_2), 6.51(s, 2H), 6 89 (2H, d, *J* = 8.4 Hz), 7.14 (2H, dd, *J* = 8.1 & 1.1

Hz), 7.18-7.21 (6H, m, ArH), 7.32–7.38 (m, 4H), 7.68 (2H, d, *J* = 8.1 Hz). *Anal. Calcd. for* $C_{40}H_{33}NO_4S$ (401.45): C, 77.02; H, 5.33; N, 2.25 %. Found: C, 76.88 H, 5.16; N, 2.18 %.

(*E*)-1-(7-Methylcoumarin-4-yl)-2-(1-butyl-1*H*-indol-3-yl)ethene (14)

Yield of **14**: 60%; Orange solid; mp 136-138 °C (ethyl acetate); UV (λ_{max}): 398 nm (chloroform); *Em* (λ_{max}): 474 nm (chloroform); Stokes shift: 118 nm; Quantum yield (Φ_F): 0.05; FTIR (neat, υ/cm^{-1}): 2954 (C-H), 2870, 1682 (C=O), 1618 (aromatic C=C), 1520, 1391 (C-N), 1190 and 734; ^{1}H NMR (300 MHz, DMSO) δ: 0.90 (3H, t, *J* =7.4 Hz, CH_3), 1.28 (2H, q, *J* = 7.4 Hz, CH_2), 1.79 (2H, sextet, *J* = 7.4 Hz, CH_2), 2.43 (3H, s, CH_3), 4.23 (2H, t, *J* = 7.0 Hz, *N*-CH_2), 6.72 (1H, s, C_3'H), 7.21-7.27 (4H, m, ArH), 7.41 (1H, d, J = 16 Hz, C_9′H), 7.57 (1H, d, *J* = 8 Hz, C_5'H), 7.95 (1H, d, *J* = 16 Hz, C_{10}'H), 8.07-8.09 (2H, m, ArH), 8.11 (1H, d, *J* = 7 Hz, ArH); ^{13}C NMR (125 MHz, DMSO) δ: 13.5 (CH_3), 19.4 (CH_3), 20.9 (CH_2), 31.6 (CH_2), 45.5 (*N*-CH_2), 104.4 (C_3′), 110.6, 112.7, 113.1 (C_{4a}'), 117.8, 120.1, 120.7, 122.3, 124.1, 125.2, 131.8, 131.9, 135.9, 138.3, 142.6 (C_7'), 143.2 (C_{9a}), 150.5 (C_{10a}), 151.1 (C_4'), (C_{8a}'), 160.6 (C_2'); MS = 358.3 (M+H). *Anal. Calcd. for* $C_{24}H_{23}NO_2$ (357.44): C, 80.64; H, 6.49; N, 3.92 %. Found: C, 80.58; H, 6.23; N, 3.99 %.

(*E*)-1-(7-Methylcoumarin-4-yl)-2-(9-hexyl-9*H*-carbazol-3-yl)ethene (15)

Yield of **15**: 61%; Yellow solid; mp 121-122 °C (ethyl acetate); UV (λ_{max}): 393 nm (chloroform); *Em* (λ_{max}): 504 nm (chloroform); Stokes shift: 137 nm; Quantum yield (Φ_F): 0.38; FTIR (neat, υ/cm^{-1}): 2923 (C-H), 2853, 1701 (C=O), 1620 (aromatic C=C), 1583, 1379 (C-N), 1325, 1144, 961 and 725; ^{1}H NMR (300 MHz, DMSO) δ: 0.79 (3H, t, *J* =6.8 Hz, CH_3), 1.19-1.27 (6H, multiplet, 3 xCH_2), 1.77 (2H, quintet, *J* = 8Hz, CH_2),

2.40 (3H, s, CH_3), 4.41 (2H, t, *J* = 6.8 Hz, *N*-CH_2), 6.75 (1H, s, C_3'H), 7.21 (1H, t, *J* = 7.3 Hz, C_6H), 7.26 (2H, m, C_6'H & C_8'H), 7.48 (1H, t, *J* = 7.3 Hz, C_7H), 7.62-7.67 (2H, m, ArH), 7.71 (1H, d, *J* = 16 Hz, C_9'H), 7.87 (1H, d, *J* = 16 Hz, C_{10}'H), 7.93 (1H, d, *J* = 8 Hz, C_1H), 8.18-8.21 (2H, m, ArH), 8.67 (1H, s, C_4H); ^{13}C NMR (125 MHz, DMSO) δ: 13.7 (CH_3), 21.0 (CH_3), 21.9 (CH_2), 26.0 (CH_2), 28.4 (CH_2), 30.9 (CH_2), 42.2 (*N*-CH_2), 106.2 (C_3′), 109.5, 109.7, 113.2 (C_{4a}'), 116.0, 116.3, 116.8, 119.2, 120.4, 122.1, 125.0, 125.3, 126.1, 126.8, 129.6, 138.4, 139.3, 140.9 (C_7'), 142.8 (C_{9a}), 149.3 (C_{10a}), 150.2 (C_4'), 153.5 (C_{8a}'), 161.7 (C_2'); MS = 436.3 (M+H). *Anal. Calcd. for* $C_{30}H_{29}NO_2$ (435.56): C, 82.73; H, 6.71; N, 3.22 %. Found: C, 82.55; H, 6.65; N, 3.14 %.

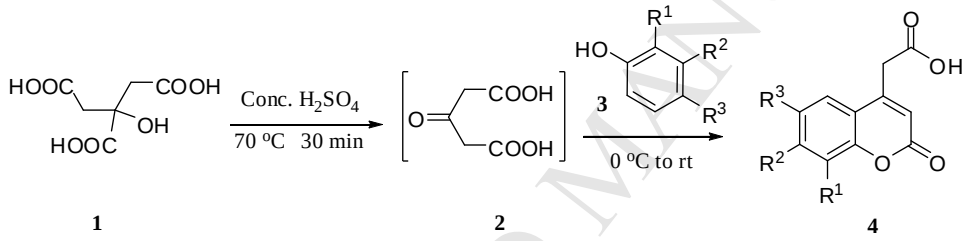
(*E*)-4-(4-(Hexyl(phenyl)amino)styryl)-7-methylcoumarin (16)

Yield of **16**: 66%; Orange solid; mp 80 °C (ethyl acetate); UV (λ_{max}): 424 nm (chloroform); *Em* (λ_{max}): 544 nm (chloroform); Stokes shift: 151 nm; Quantum yield (Φ_F): 0.05; FTIR (neat, υ/cm^{-1}): 2923 (C-H), 2852, 1698 (C=O), 1619 (aromatic C=C), 1512, 1379 (C-N), 1183, 978, 803 and 697; ^{1}H NMR (300 MHz, DMSO) δ: 0.84 (3H, t, *J* =6.4 Hz, CH_3), 1.24-1.31 (6H, multiplet, 3 xCH_2), 1.58 (2H, quintet, *J* = 6.4 Hz, CH_2), 2.42 (3H, s, CH_3), 3.73 (2H, t, *J* = 6.4 Hz, *N*-CH_2), 6.65 (1H, s, C_3'H), 6.82 (2H, d, *J* = 8.6 Hz, ArH), 7.15-7.23 (5H, m, ArH) 7.38- 7.44 (3H, m, ArH & C_9'H), 7.59 (1H, d, *J* = 16 Hz, C_{10}'H), 7.64 (2H, d, *J* = 8.6 Hz, ArH), 8.07 (1H, d, *J* = 8 Hz, C_5'H); ^{13}C NMR (125 MHz, DMSO) δ: 13.8 (CH_3), 20.9 (CH_3), 22.0 (CH_2), 25.9 (CH_2), 26.8 (CH_2), 31.0 (CH_2), 51.4 (*N*-CH_2), 105.9 (C_3′), 115.3, 116.0 (C_{4a}'), 116.1 (2xC), 116.8, 124.0, 124.6 (2xC), 124.8, 125.2, 126.1, 129.4 (2xC), 129.6(2xC), 138.0, 142.6 (C_7'), 146.3, 148.9, 150.0 (C_4'), 153.4 (C_{8a}'), 160.4 (C_2'); MS = 438.4 (M+H). *Anal. Calcd. for* $C_{30}H_{31}NO_2$ (437.57): C, 82.35; H, 7.14; N, 3.20 %. Found: C, 82.20; H, 6.99; N, 3.23 %.

3. Results and discussion

3.1 Synthesis of starting materials

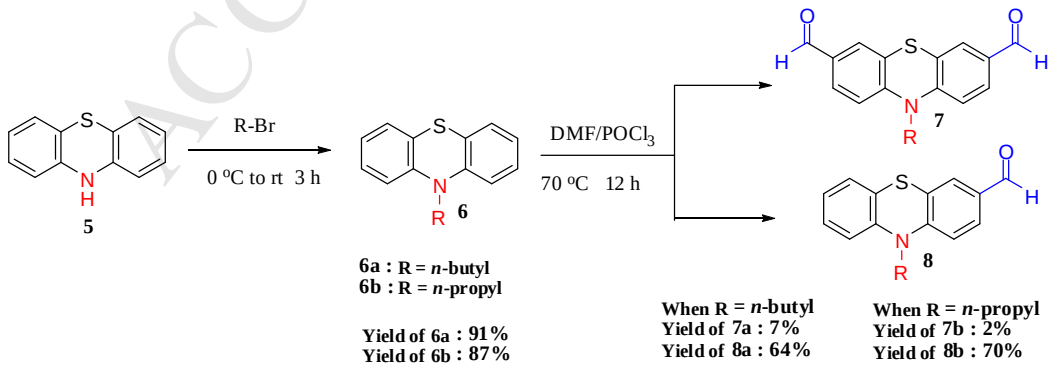
In the initial part coumarin-4-acetic acids (**4**) and PTZ-3-carbaldehyde (**8**) were synthesized using literature methods. In the synthesis of **4**, acetone dicarboxylic acid (**2**), was prepared *in situ* by reacting citric acid (**1**) with conc. H_2SO_4 and in next step substituted phenols (**3**) were condensed with **2** to obtain substituted coumarin-4-acetic acids (**4**) (**Scheme 1**) [23]. Compounds **3** containing electron-withdrawing groups does not react adequately with **2** to form the corresponding **4**. Thus we were unable to prepare **9** with electron withdrawing group on the acceptor coumarin ring.



1 **2** **3** **4**

Scheme 1 Synthesis of coumarin-4-acetic acids

In the synthesis of **8**, firstly phenothiazine (**5**) was alkylated to give **6,** which on Vilsmeier condition gave **8** with good yield and small amount of dialdehyde (**Scheme 2**) [12].



6a : R = *n*-butyl
6b : R = *n*-propyl

Yield of 6a : 91%
Yield of 6b : 87%

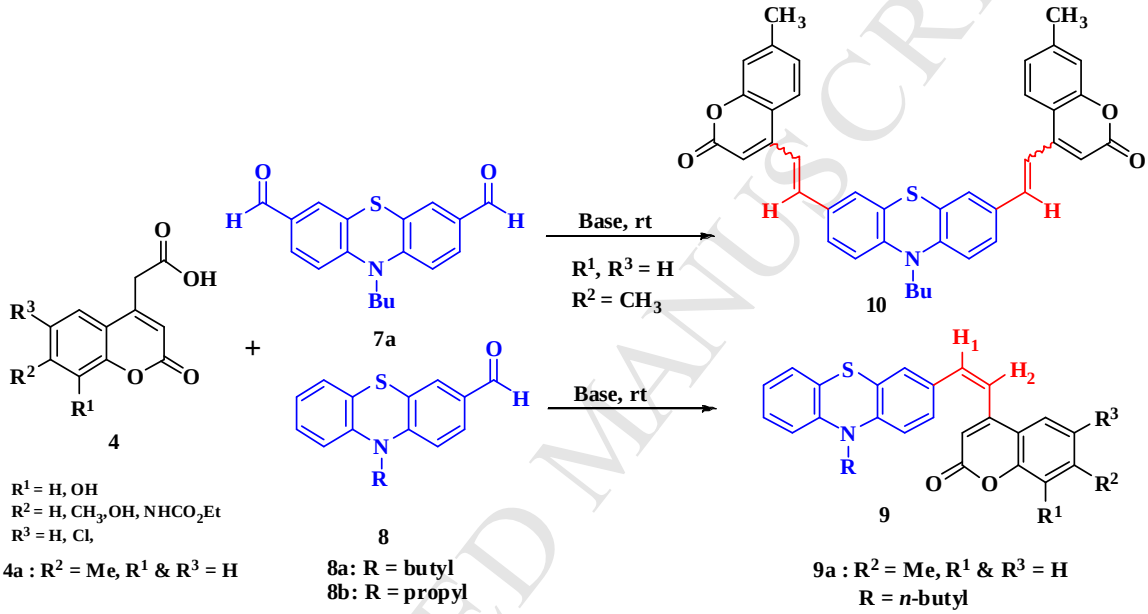
When R = *n*-butyl
Yield of 7a : 7%
Yield of 8a : 64%

When R = *n*-propyl
Yield of 7b : 2%
Yield of 8b : 70%

Scheme 2 Synthesis of phenothiazine-3-carbaldehyde (**8**) and phenothiazine dialdehyde (**7**)

3.2 Optimization study for condensation of 7-methylcoumarin-4-acetic acid (4a) and n-butylphenothiazine-3-carbaldehyde (8a)

Condensation of **4** with 7-diethylaminocoumarin-3-carbaldehyde is known and using this pathway [21] reaction of **4a** with **8a** was carried out at room temperature (35 ± 2 °C) (**Scheme 3**).



Scheme 3 Condensation of coumarin-4-acetic acids (**4**) with phenothiazine-3-carbaldehyde (**8**)/ phenothiazine dialdehyde (**7**)

The reaction of **4a** with **8a** was carried out in the presence of different inorganic bases such as NaOH, NaH, NaOAc, NaOEt, KOtBu, and K_2CO_3 at room temperature (**Table 1).** In NaOH, instead of condensation, decarboxylation of **4a** results into the 4,7-dimethylcoumarin as by-product **(Table 1, entry 1).** All other bases such as NaH, NaOAc, NaOEt, KOtBu, and K_2CO_3 found to be ineffective and no reaction was observed (**Table 1, entries 2-6**).

Table 1 Influence of inorganic bases on styryl formation[a]

Entry	Base	Solvent	Time (h)	Result
1	NaOH	Ethanol	48	Coumarin decarboxylation
2	NaH	Tetrahydrofuran	48	NR
3	NaOAc	Ethanol	48	NR
4	NaOEt	Ethanol	48	NR
5	KOtBu	THF	48	NR
6	K_2CO_3	Ethanol	48	NR

[a]**Reaction conditions: 8a** (1 mmol), **4a** (1 mmol), base (1 mmol), solvent: (6 mL), room temperature (35 ± 2 °C), NR : No reaction

Organic bases such as pyridine, pyrrolidine, piperidine, morpholine, Et_3N, and DIEPA were also tried for the condensation of **4a** with **8a** (**Table 2**). At room temperature pyridine in methanol gives 60 % yield of **9a** while pyrrolidine in ethanol gives 66% yield of **9a** (**Table 2, entry 1 & 2**). This conversion was also effected with piperidine in methanol to give 75% yield of **9a** at room temperature (**Table 2, entry 3**), while at reflux condition in 12 h gave 49% yield (**Table 2, entry 4**). Here, we have noticed that at reflux condition in piperidine/methanol, **4a** undergoes decarboxylation and hence the less yield of **9a** was observed. Other bases were found to be inefficient (**Table 2, entries 5-7**).

Table 2 Influence of organic bases on styryl formation[a]

Entry	Base	Solvent	Time (h)	Yield[c] (%)
1	Pyridine	Methanol	48	60
2	Pyrrolidine	Ethanol	48	66
3	Piperidine	Methanol	48	75
4[b]	Piperidine	Methanol	12	49
5	Morpholine	Ethanol	48	NR

6	Triethylamine	Methanol	48	NR
7	DIEPA	Acetonitrile	48	NR
8	Choline hydroxide	-	48	NR
9	ChCl: Urea DES	-	48	NR
10	ChCl: glycerol	-	48	NR

[a]**Reaction conditions: 8a** (1 mmol), **4a** (1 mmol), base (1 mmol) / DES (5 mL), solvent: (6 mL), room temperature (35 ± 2 °C), [b]reflux temp, [c]isolated yield, NR : No reaction.

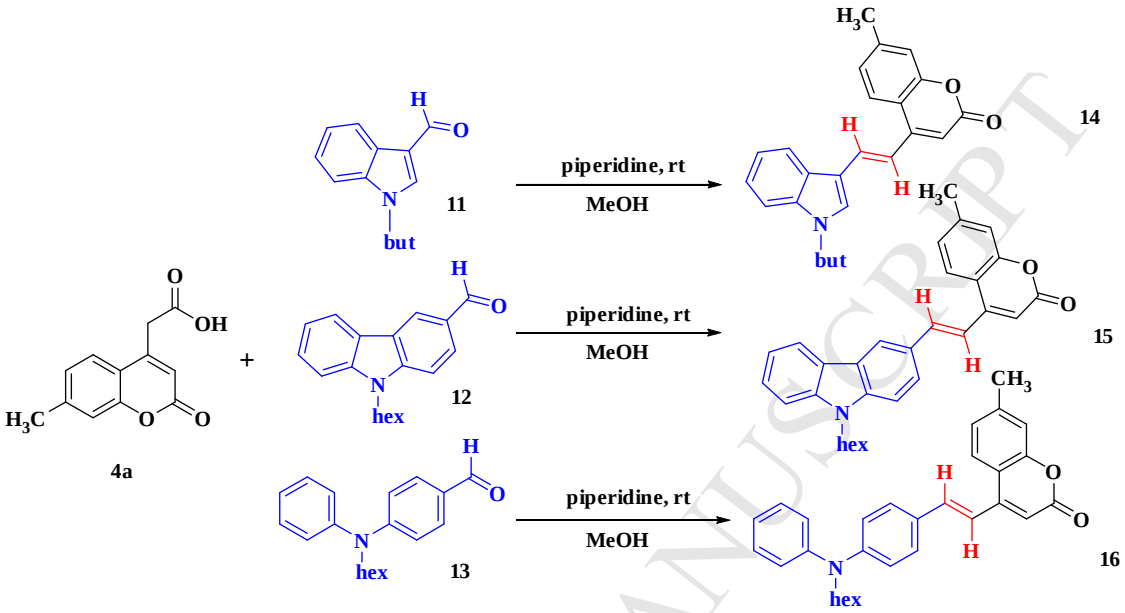
As our group is more familiar with organic synthesis in deep eutectic solvents (DES) [26-28], consequently we have tried condensation of **4a** with **8a** in different DES such as ChCl: urea DES, ChCl: glycerol DES, and choline hydroxide (**Table 2, entries 8-10**). There was no formation of desired product at room temperature. At higher temperature (80 ^{o}C or more) decarboxylation of **4a** is more pronounced than condensation, resulting in 4,7-dimethyl coumarin as by-product.

3.3 Synthesis of different styryl dyes

To get series of different fluorescent compounds having coumarin as acceptor moiety, different 6,7,8-substituted coumarin-4-acetic acids (**4**) were reacted with phenothiazine-3-carbaldehyde **(8)** at room temperature (35 ± 2 °C) (**Scheme 3)**. Similarly phenothiazine dialdehyde (**7**) was reacted with **4a** to give corresponding distyryl compound (**10**) (**Scheme 3)**. Thus compounds **9** were prepared showing *cis* stereochemistry of ethylenic double bond confirmed by ^{1}H NMR (J = 8-10 Hz).

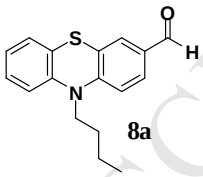
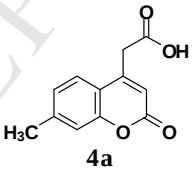
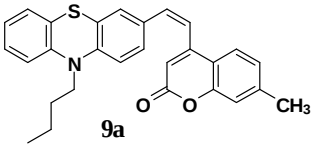
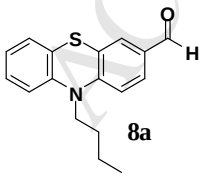
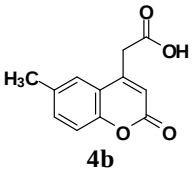
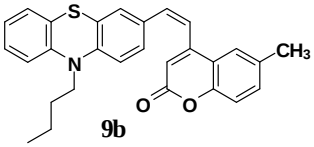
Other different aldehydes such as indole-3-carbaldehyde (**11**), carbazole-3-carbaldehyde (**12**), and 4,4'-(hexylimino)bis(benzaldehyde) (**13**) were condensed with **4a** to get different styryl dyes (**14-16**) (**Scheme 4)**. Compounds **14**, **15** and **16** thus prepared have *trans* streochemistry of the double bond which was confirmed by ^{1}H NMR (J = 16 Hz).

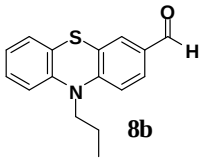
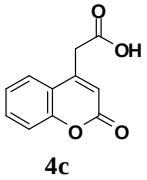
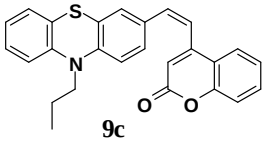
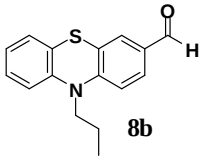
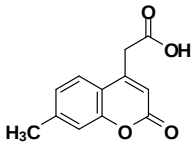
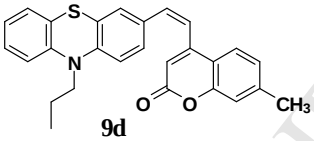
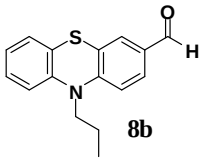
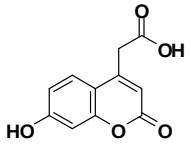
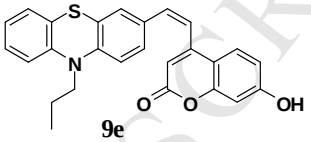
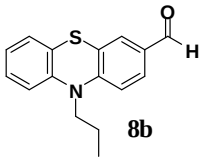
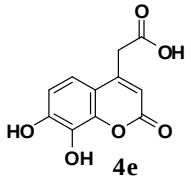
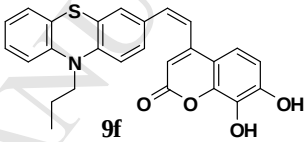
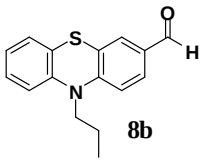
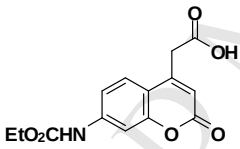
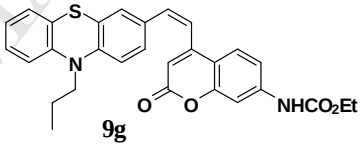
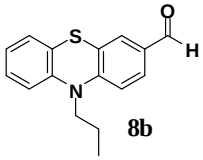
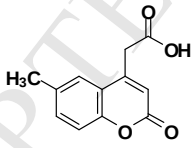
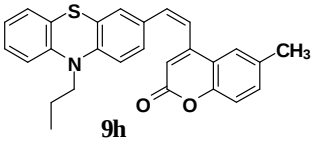
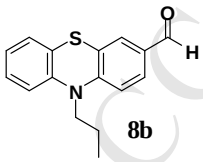
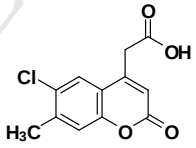
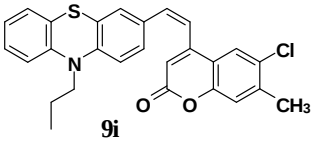
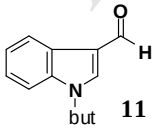
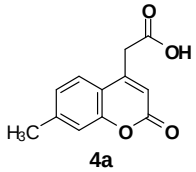
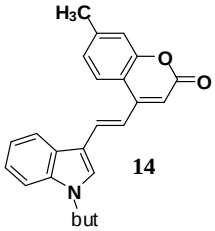
These compounds are in resemblance with 1,2-biscoumarinylethenes in *trans* stereochemistry of the ethylenic double bond.

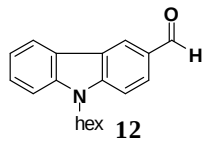
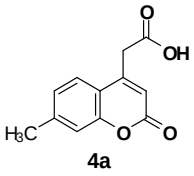
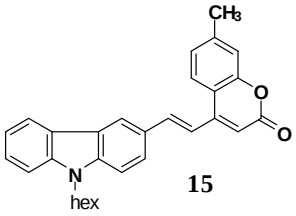
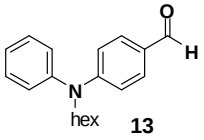
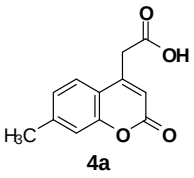
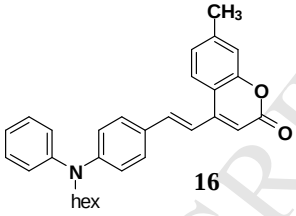
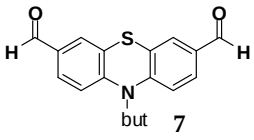
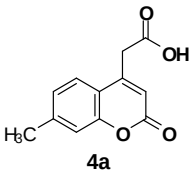
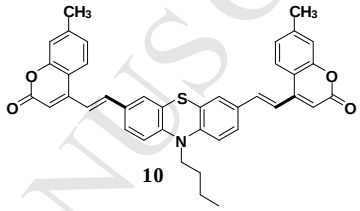


Scheme 4 Condensation of 7-methylcoumarin-4-acetic acid (**4a**) with **11**, **12**, and **13**

Table 3 Synthesis of tyryl derivatives **9**, **10**, and **14-16**[a]

Entry	Aldehyde	Coumarin (4)	Product	[b]Time (h) [c](Yield) (%)
1	 **8a**	 **4a**	 **9a**	45 (75)
2	 **8a**	 **4b**	 **9b**	45 (72)

3	 **8b**	 **4c**	 **9c**	48 (62)
4	 **8b**	 **4a**	 **9d**	46 (75)
5	 **8b**	 **4d**	 **9e**	50 (72)
6	 **8b**	 **4e**	 **9f**	49 (78)
7	 **8b**	 **4f**	 **9g**	52 (60)
8	 **8b**	 **4b**	 **9h**	48 (62)
9	 **8b**	 **4g**	 **9i**	46 (74)
10	 **11**	 **4a**	 **14**	51 (60)

11	 **12**	 **4a**	 **15**	48 (61)
12	 **13**	 **4a**	 **16**	45 (66)
13	 **7**	 **4a**	 **10**	58 (64)

[a]**Reaction conditions:** Aldehyde (1 mmol), **4** (1 mmol), Piperidine (1 mmol), Methanol (6 mL), [b]Time in hour for total consumption of aldehyde, Temp.: RT (35 ± 2 °C), [c]Isolated yield.

3.4 Photophysical properties

The geometry of the optimized structure of **9c** is depicted in **Fig.1**. In **9,** the donor auxochrome *N*-atom of phenothiazine ring plays an important role in increasing the electron density in conjugated part and lowering the HOMO-LUMO gap. Due to the wide-range of π conjugation, compound **9a** showed red emission under UV-lamp (365 nm) (**Fig. 4**). Hence, we thought that the related compounds would be good candidates for studying their photophysical properties. Using the optimized conditions, series of compounds were prepared having phenothiazine ring and coumarin ring tethered by ethylenic link extending the conjugation. Surprisingly all these PTZ styryl derivatives (**9a-9i**) show *cis* stereochemistry of ethylenic double bond.

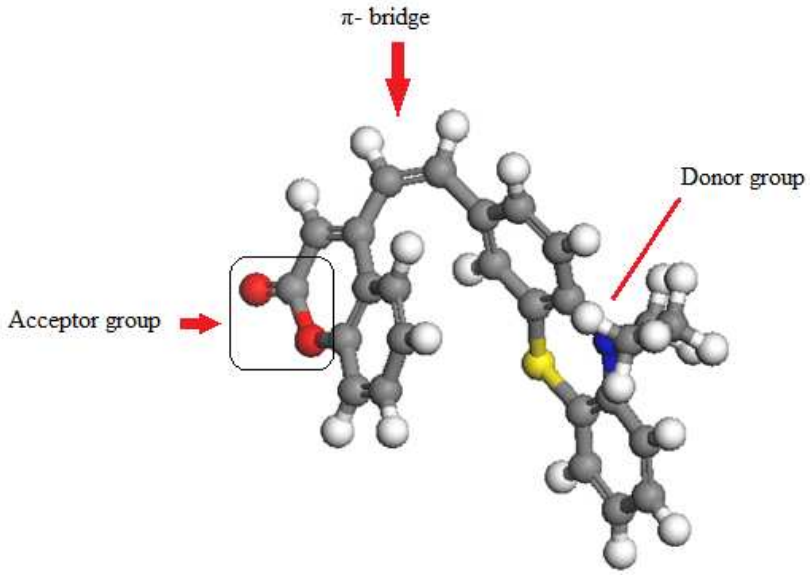


Fig. 1 Energy optimized structure of **9c**

All the compounds are yellow to red in colour and emit in green to red region hence, they were further studied for photophysical properties. The UV-Visible absorption (**Fig. 2**) and emission spectra (**Fig. 3**) of **9**, **10**, and **14-16** were recorded in chloroform at room temperature using 10 μM solutions (emission photograph **Fig. 4**). 1-(coumarin-4-yl)-2-(phenothiazine-3-yl)ethene (**9**) in chloroform absorbs (Visible λ_{Max}) in the range of 422 to 432 nm while they emit (E_m λ_{Max}) in the range of 618-648 nm. The compounds **9** did not showed good absorption and emission behaviour in polar solvents like acetonitrile, dimethyl sulfoxide, *N*,*N*-dimethyl formamide, methanol. Unlikely, compounds, **14** and **15** show lower range of absorption (393-398 nm) and emission (474-504 nm) in chloroform. Compound **16** show absorption at 424 nm and emission at 544 nm in chloroform. As these compounds (**14-16**) have different orbital characteristic and structural properties they behave differently in polar solvents (dimethyl sulfoxide, *N*,*N*-dimethyl formamide, methanol) and show good absorption and emission as compared with chloroform. Compounds **9** show better Stokes shift in the range of 194 to 216 nm. Quantum yields of

all compounds **9, 10** and **14-16** were recorded by using rhodamine 6G (Rhodamine 6G in ethanol, Φf = 0.95) as a standard in chloroform at room temperature. Among compounds **9**, compound **9i** has the lowest HOMO-LUMO gap, as it contains an electron withdrawing chlorine atom on acceptor coumarin moiety which makes facile charge transfer and hence absorbs at longer wavelength (432 nm).

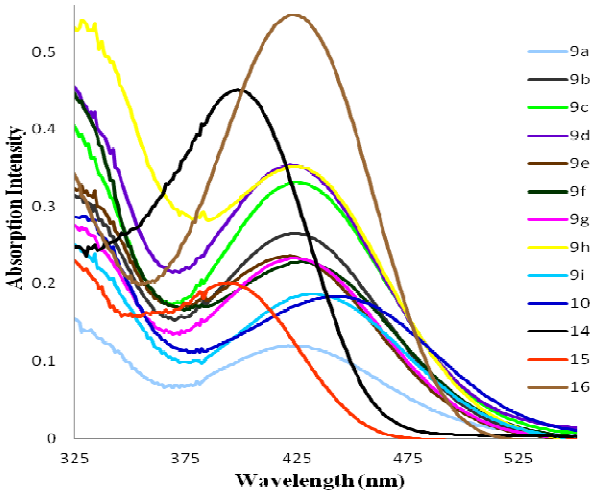


Fig. 2 Absorption spectra of **9**, **10**, and **14-16** in chloroform

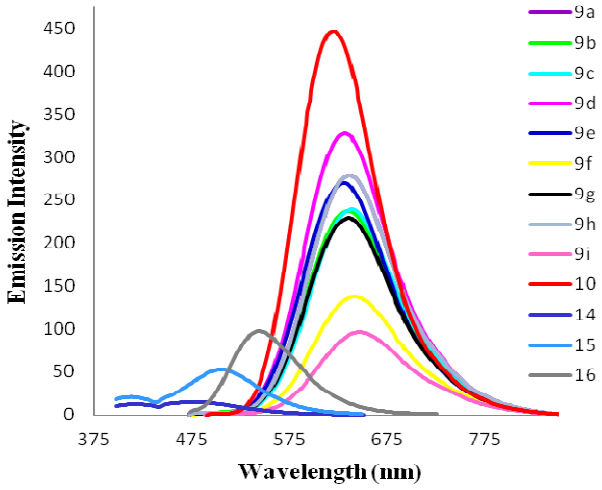


Fig. 3 Emission spectra of **9**, **10**, and **14-16** in chloroform

Table 4 Electronic absorption (UV-Visible λ_{Max}), emission (E_m λ_{Max}), Stokes shifts, and quantum yield of **9**, **10**, **14-16** in chloroform

Entry	Compound	UV (λ_{Max}) (nm)	Em (λ_{Max}) (nm)	Stokes shift (nm)	Quantum yield
1	**9a**	424	632	208	0.21
2	**9b**	423	635	212	0.70
3	**9c**	424	618	194	0.50
4	**9d**	424	631	207	0.27
5	**9e**	422	631	209	0.74
6	**9f**	427	643	216	0.37
7	**9g**	422	635	213	0.62
8	**9h**	423	637	214	0.76
9	**9i**	432	648	216	0.77
10	**10**	441	620	179	0.83
11	**14**	398 (414)[b]	474 (532)[b]	76 (118)	0.05
12	**15**	393 (405)[b]	504 (542)[b]	111 (137)	0.38
13	**16**	424 (432)[b]	544 (583)[b]	120 (151)	0.05

[b]Absorption and emission value in DMSO

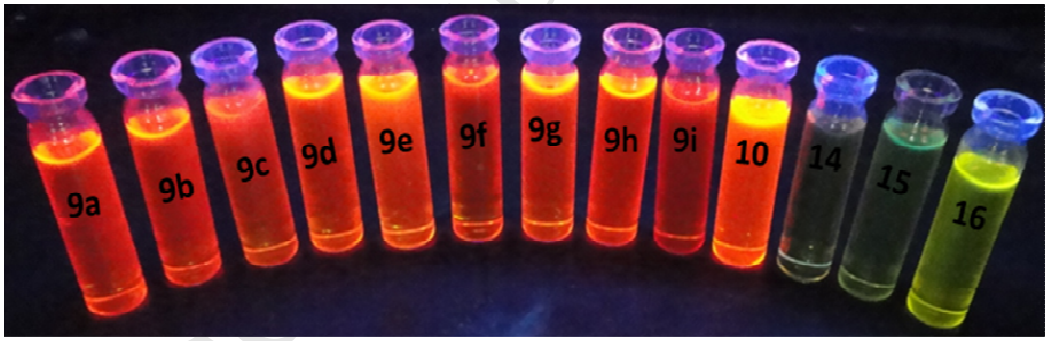


Fig.4 Emission of **9, 10,** and **14-16** under UV lamp (365 nm)

3.5 Solvatochromism

Solvatochromism can be defined as the phenomenon whereby a compound changes color, either by change in the absorption or emission spectra of the molecule, when dissolved in different solvents. Solvatochromic effects are best monitored by means of UV/VIS

spectroscopy. A hypsochromic shift of the UV/VIS absorption band, with increasing solvent polarity is usually called negative solvatochromism. The corresponding bathochromic shift, with increasing solvent polarity is termed as positive solvatochromism. Compounds **9** and **10** showed negative solvatochromism (**Fig. 5**) whereas compounds **14, 15** and **16** showed positive solvatochromism (**Fig. 6**).

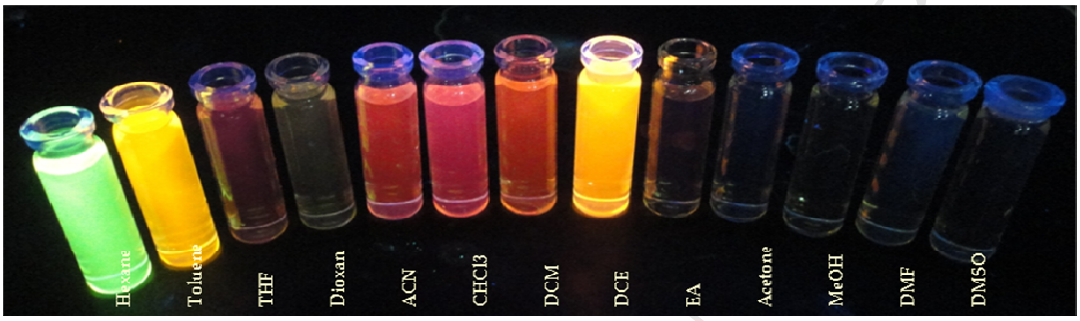


Fig. 5 Negative Solvatochromism shown by compound **9a** (Hypsochromic shift)

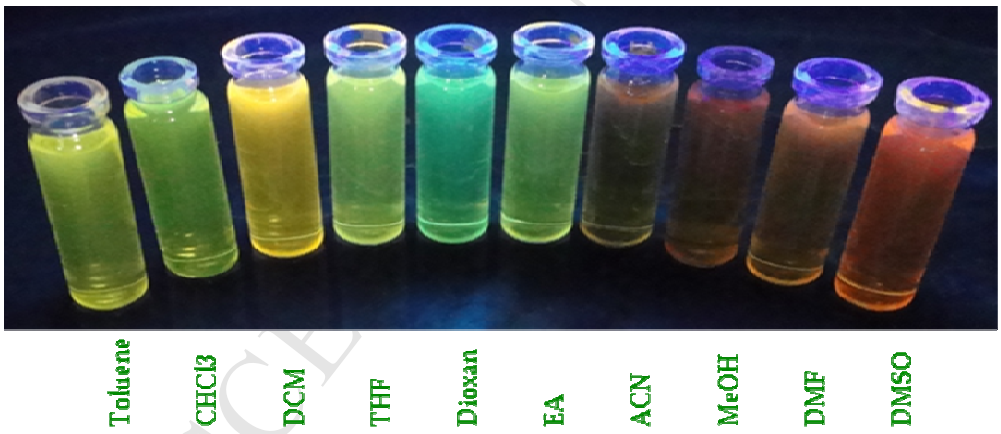


Fig. 6 Positive Solvatochromism shown by compound **16** (Bathochromic shift)

Conclusions

In conclusion, we have successfully designed and synthesized a series of novel styryl dyes with the different electron-donor and electron-acceptor groups. The coumarin based

styryl dyes **9**, **10**, **14-16** are valuable as new fluorescent chromophores having long absorption maxima and emission maxima. The relative strength of fluorescence in **9** was affected by the substituents on coumarin ring, while in **14-16** it was affected by type of donor ring. The presence of an electron acceptor group like -Cl on acceptor coumarin moiety at 6-position caused a pronounced bathochromic shift. Compound **9** and **10** shows negative solvatochromism while compounds **14-16** shows positive solvatochromism.

Acknowledgements

A.K.S. is thankful to UGC-CAS for providing financial assistance and IIRBS, Mahatma Gandhi University, Kottayam for ^{1}H and ^{13}C-NMR.

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Highlights

- Novel coumarin based highly fluorescent styryl compounds were prepared
- Stereochemistry of double bond depends upon the type of substitution
- These dyes show brilliant color in daylight
- Synthesized compounds studied for UV-Vis absorption and show solvatochromism

Supporting Information

Synthesis and photophysical study of novel coumarin based styryl dyes

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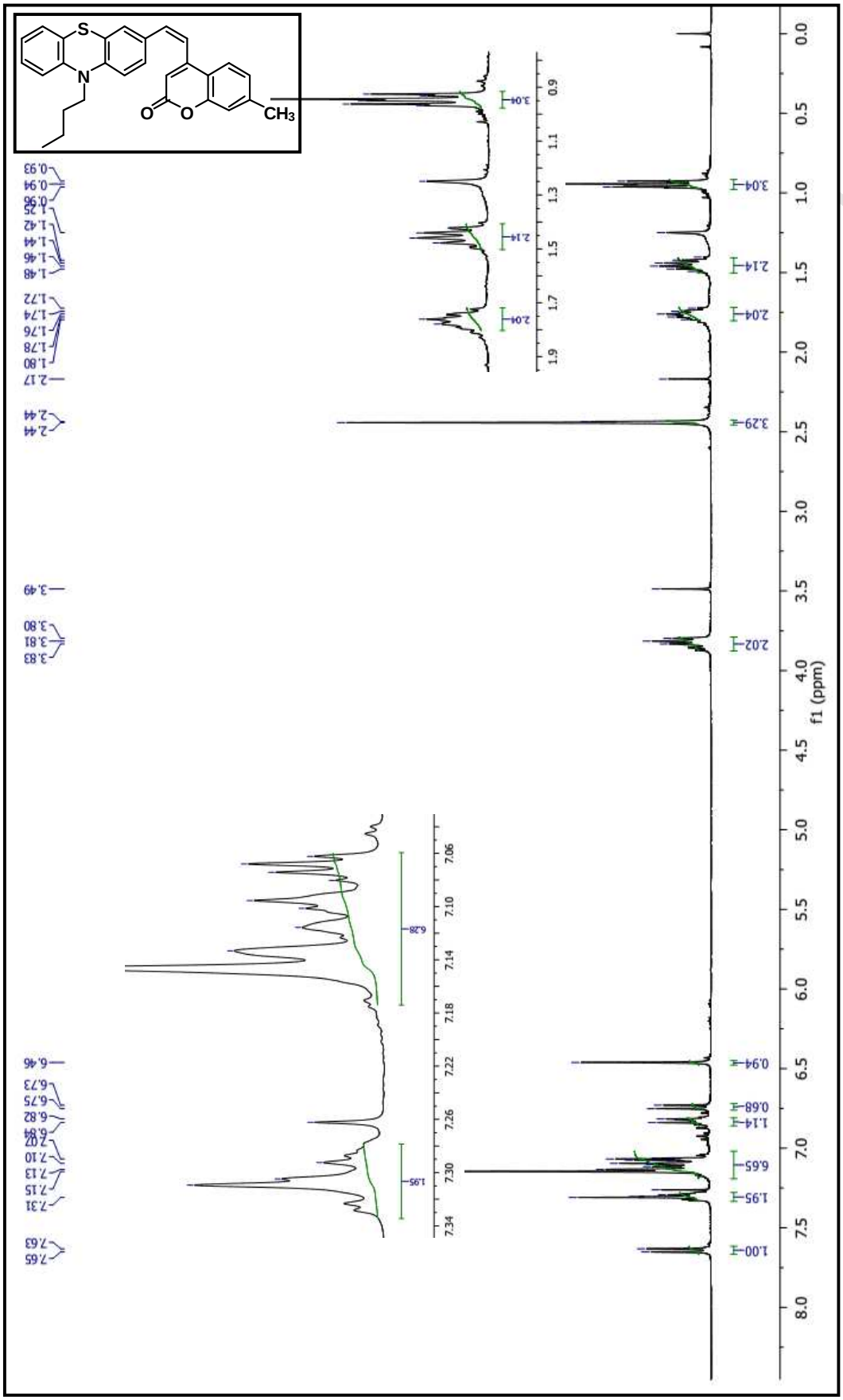
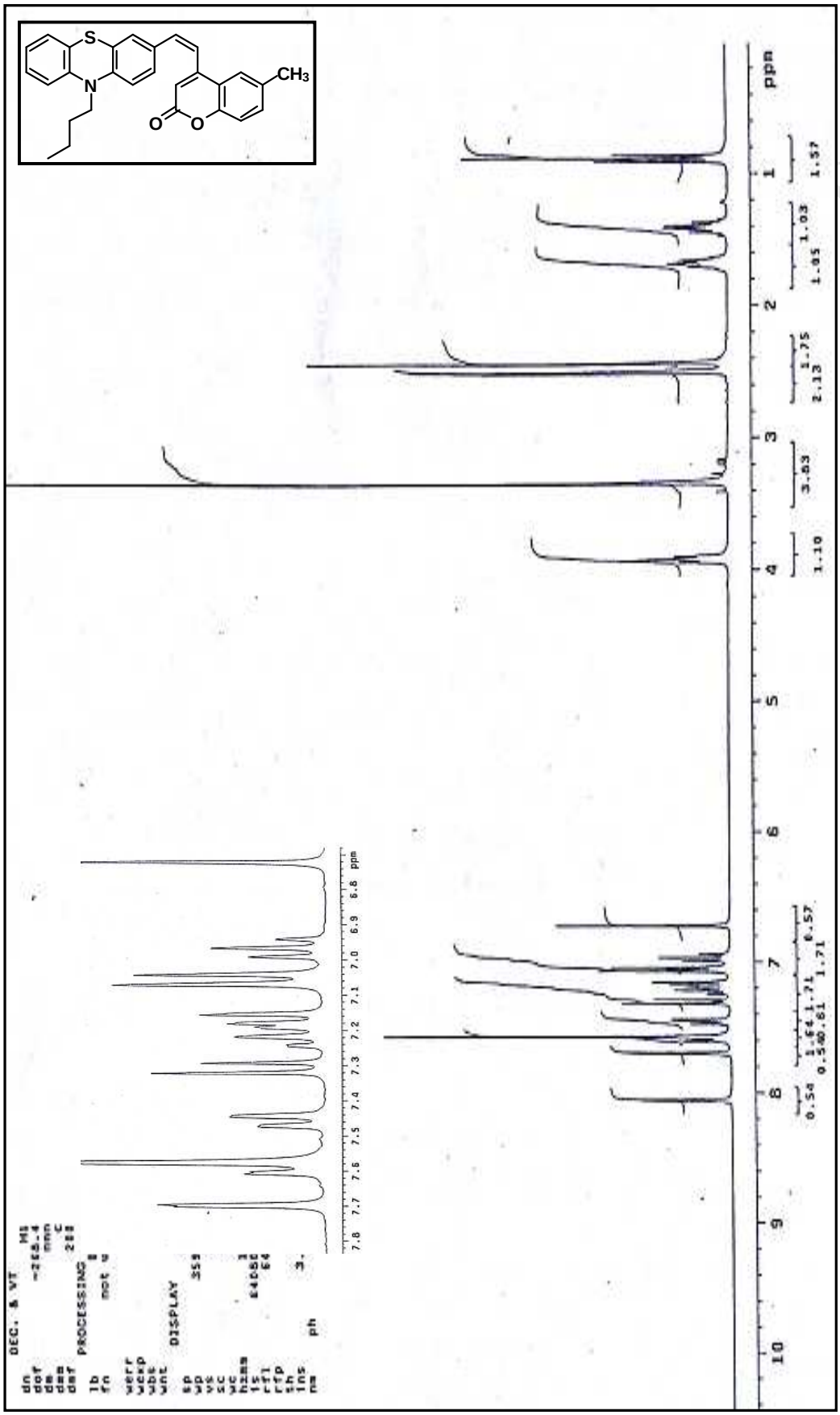
Sr. No.	Content	Page no.
1.	^{1}H NMR Spectra	2-14
2.	^{13}C NMR Spectra	15-23



Z-1-(7-Methylcoumarin-4-yl)-2-(10-butyl-10*H*-phenothiazin-3-yl)ethene **(9a)**



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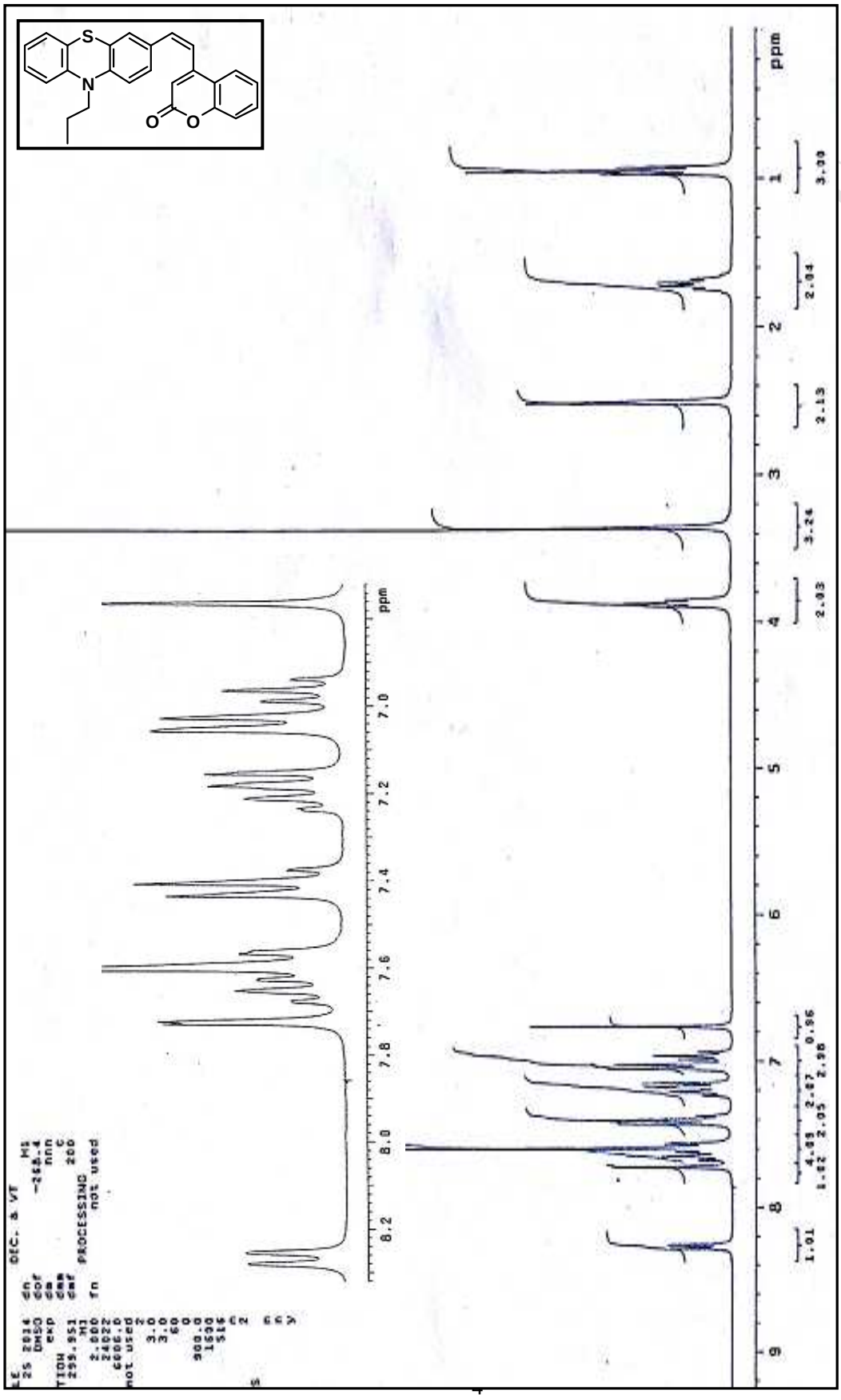
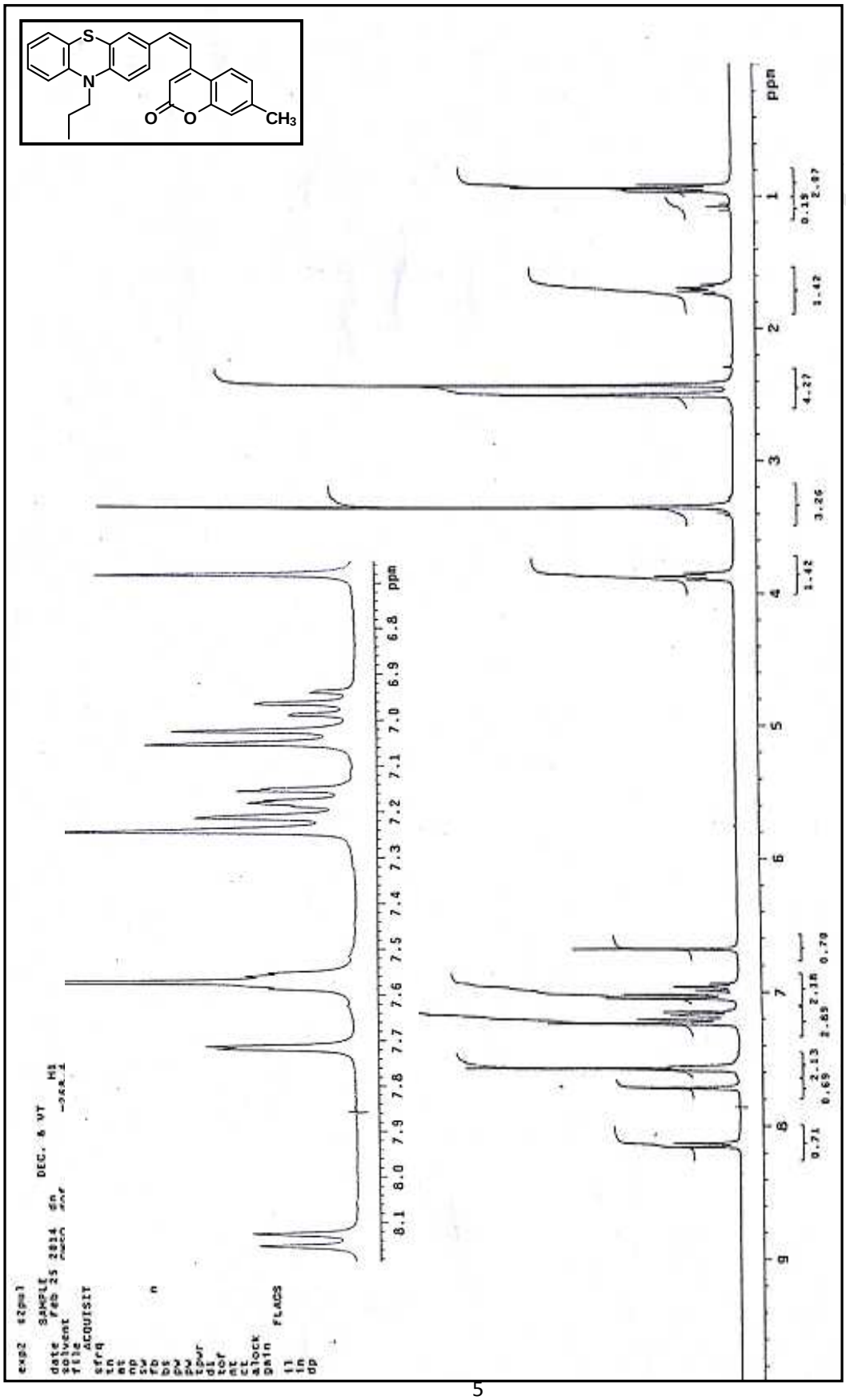


Z-1-(Coumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene **(9c)**



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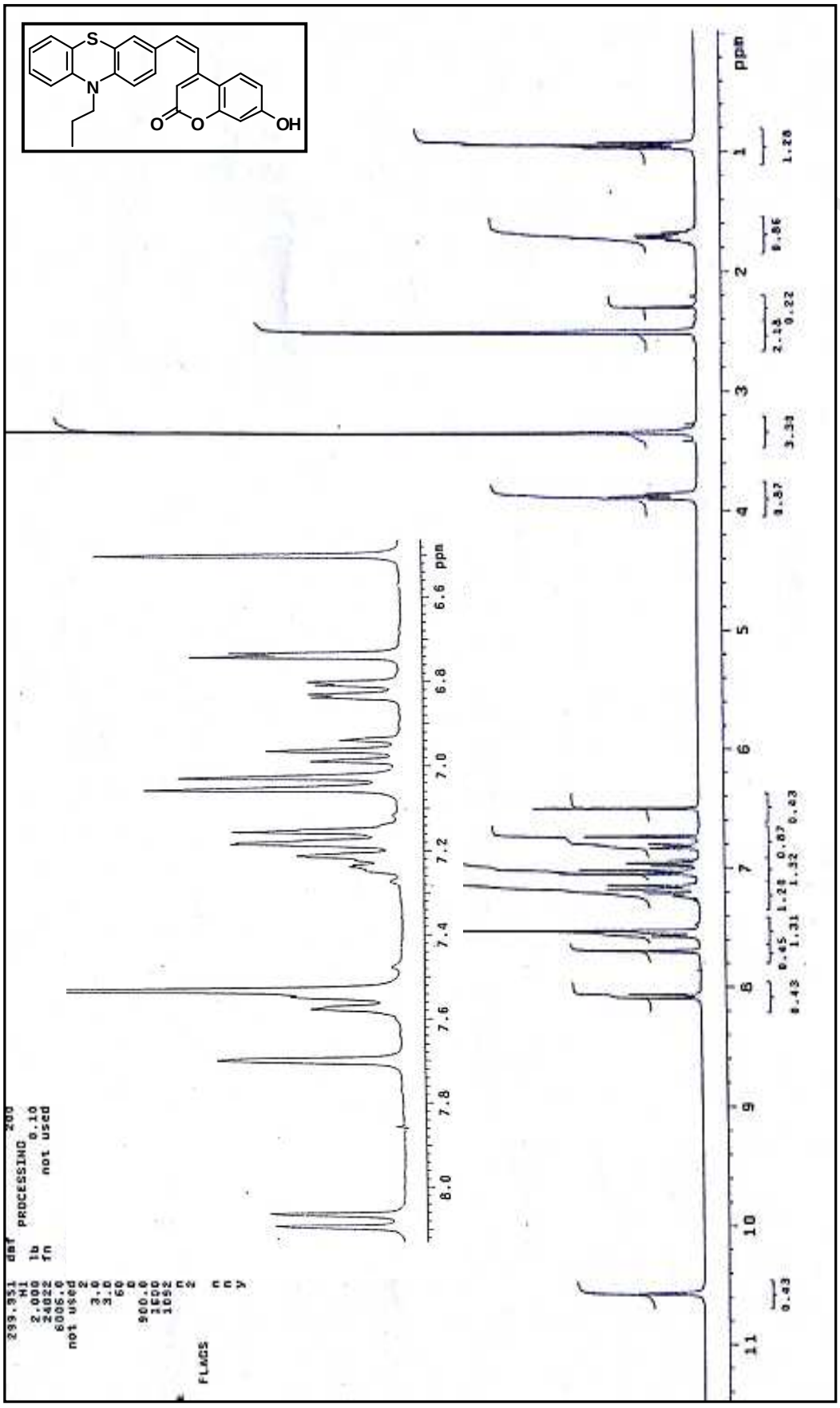

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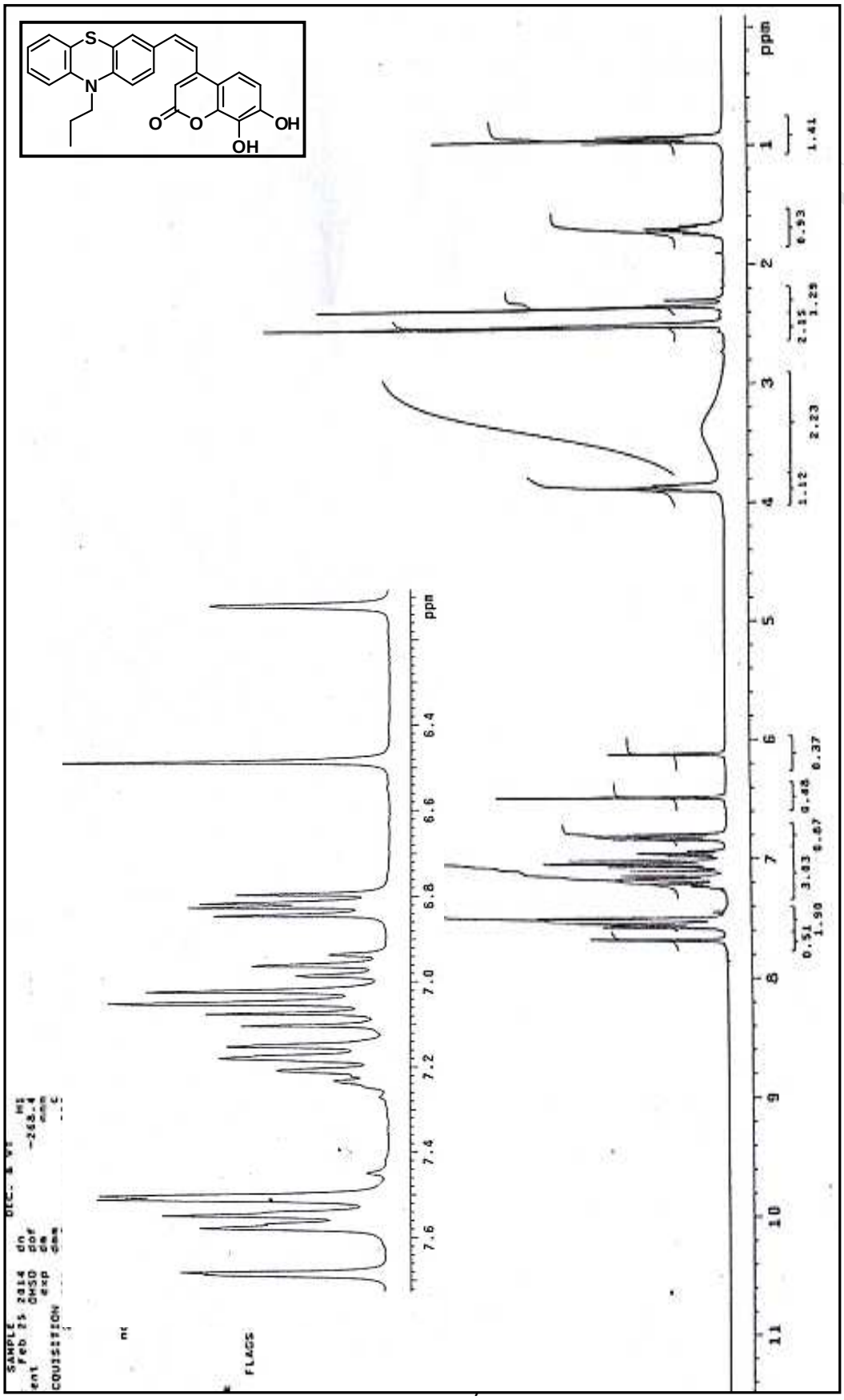
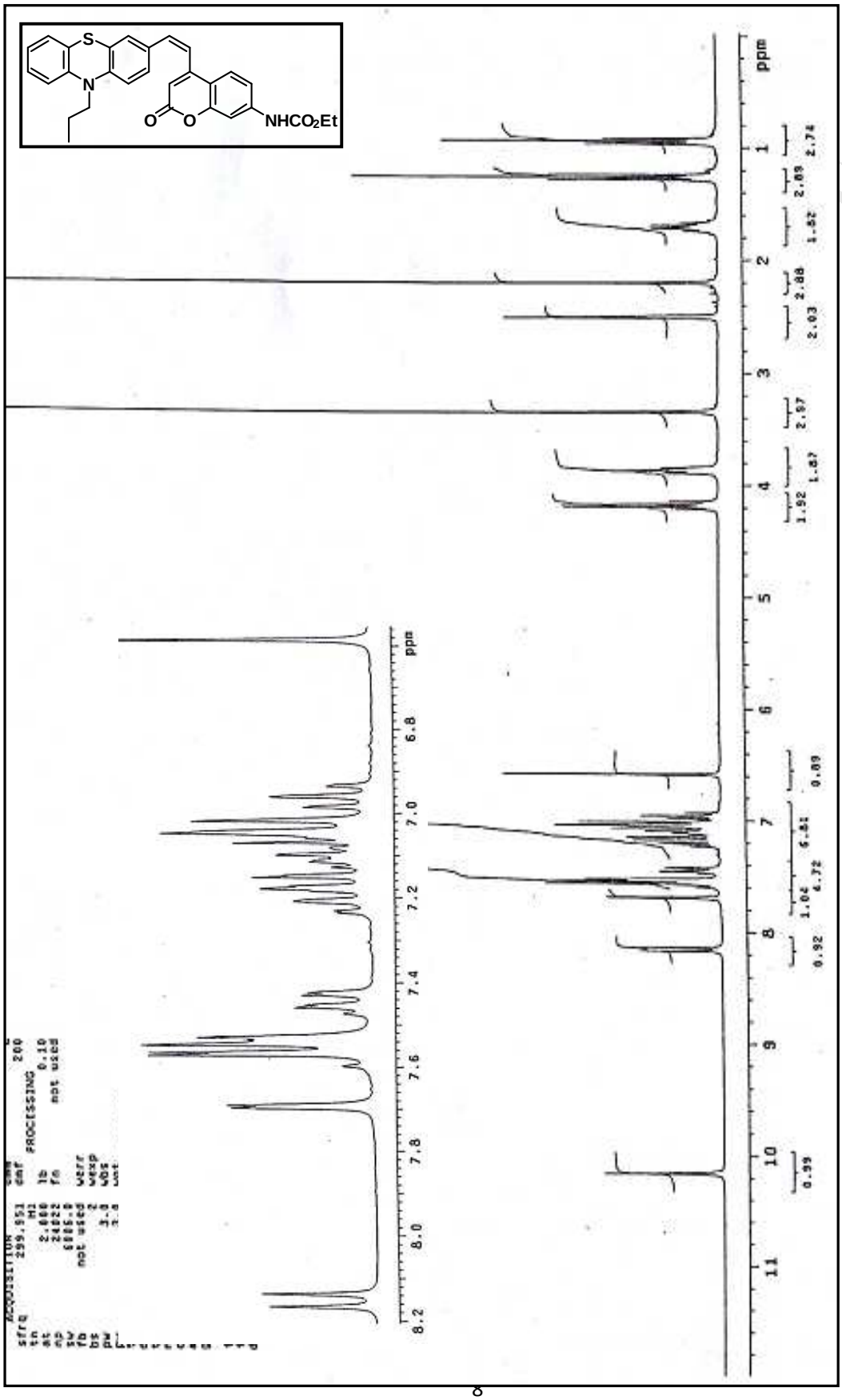
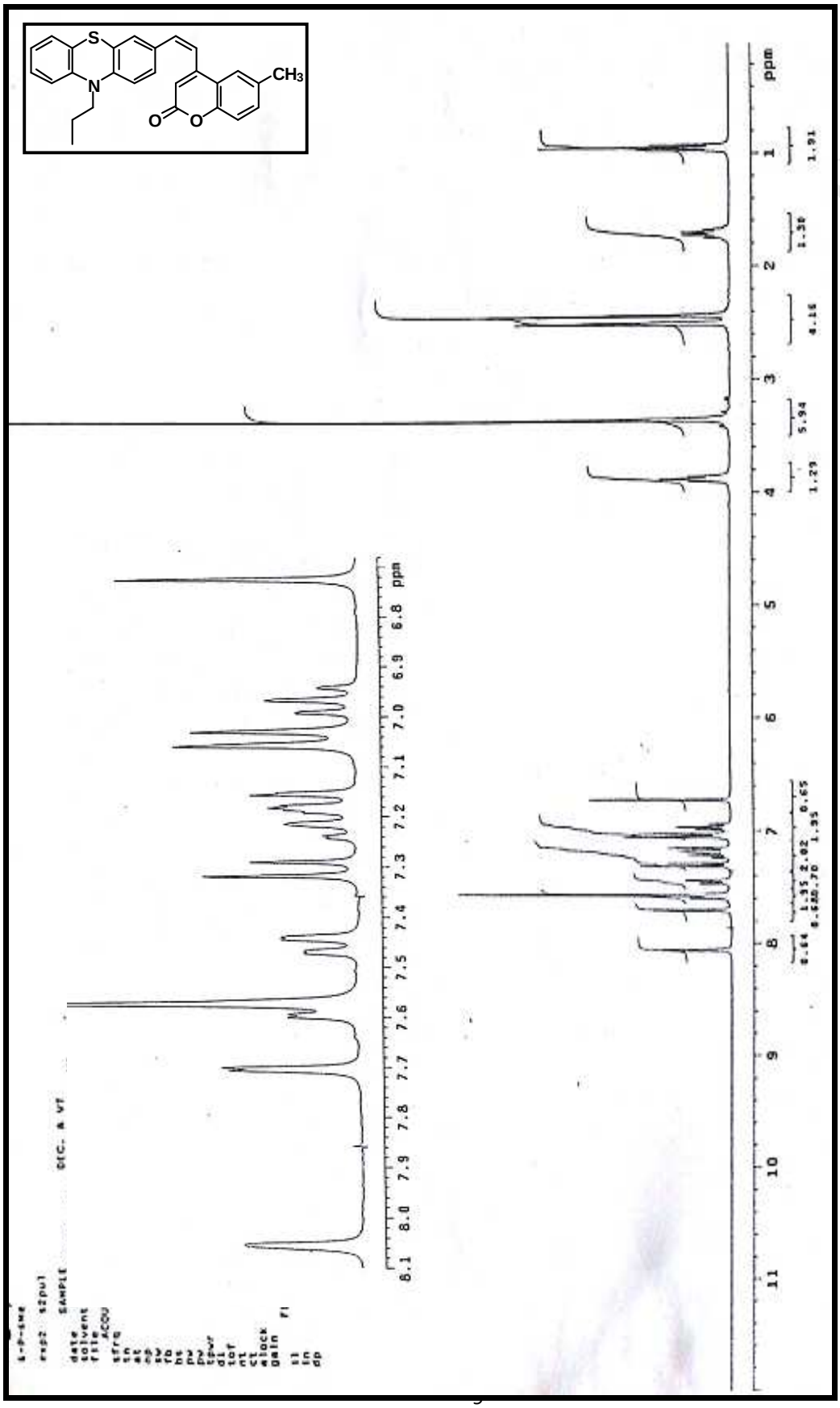


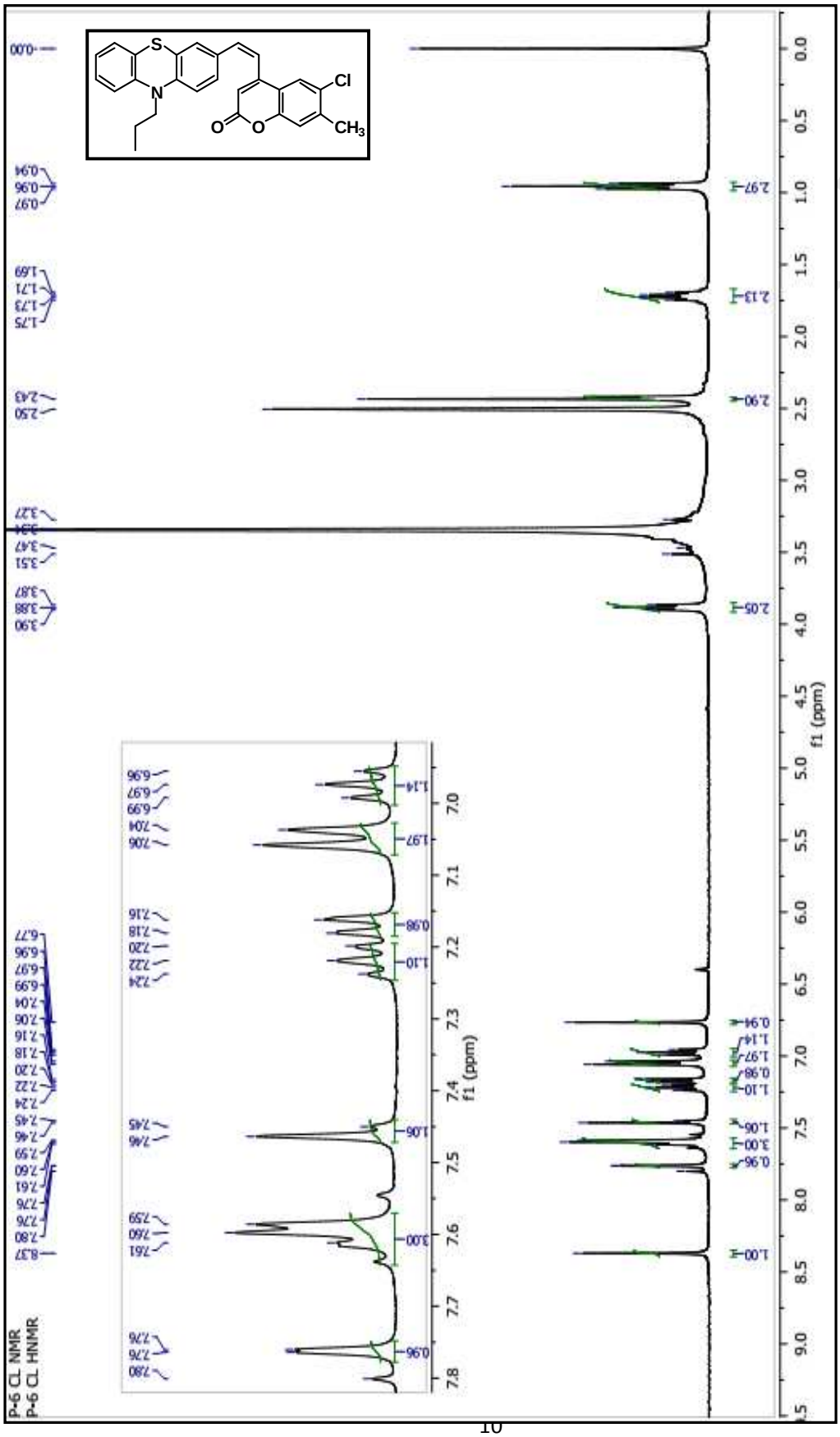
Z-1-(7,8-Dihydroxylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene (**9f**)



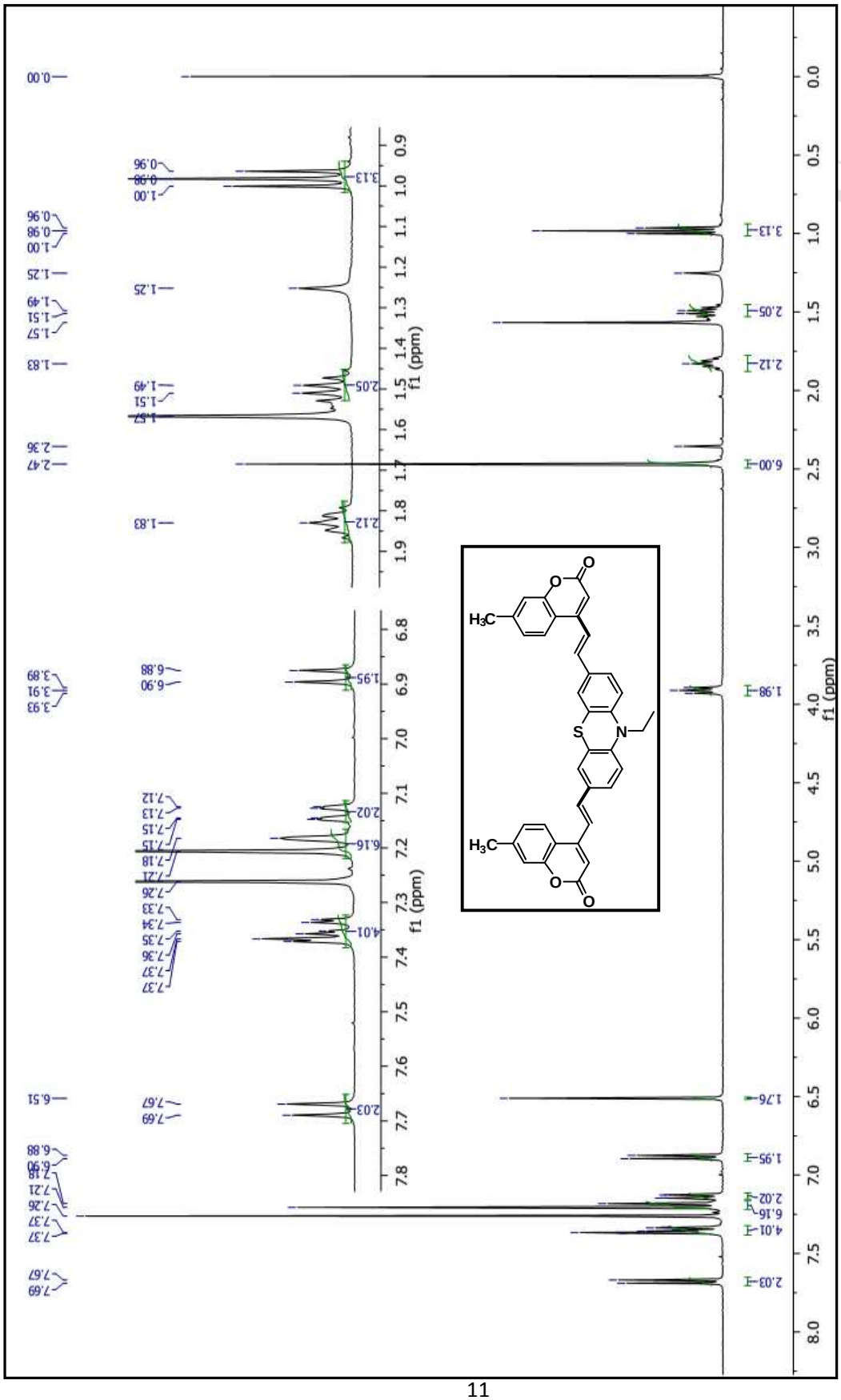
Z-1-(7-Carbamatecoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene **(9g)**



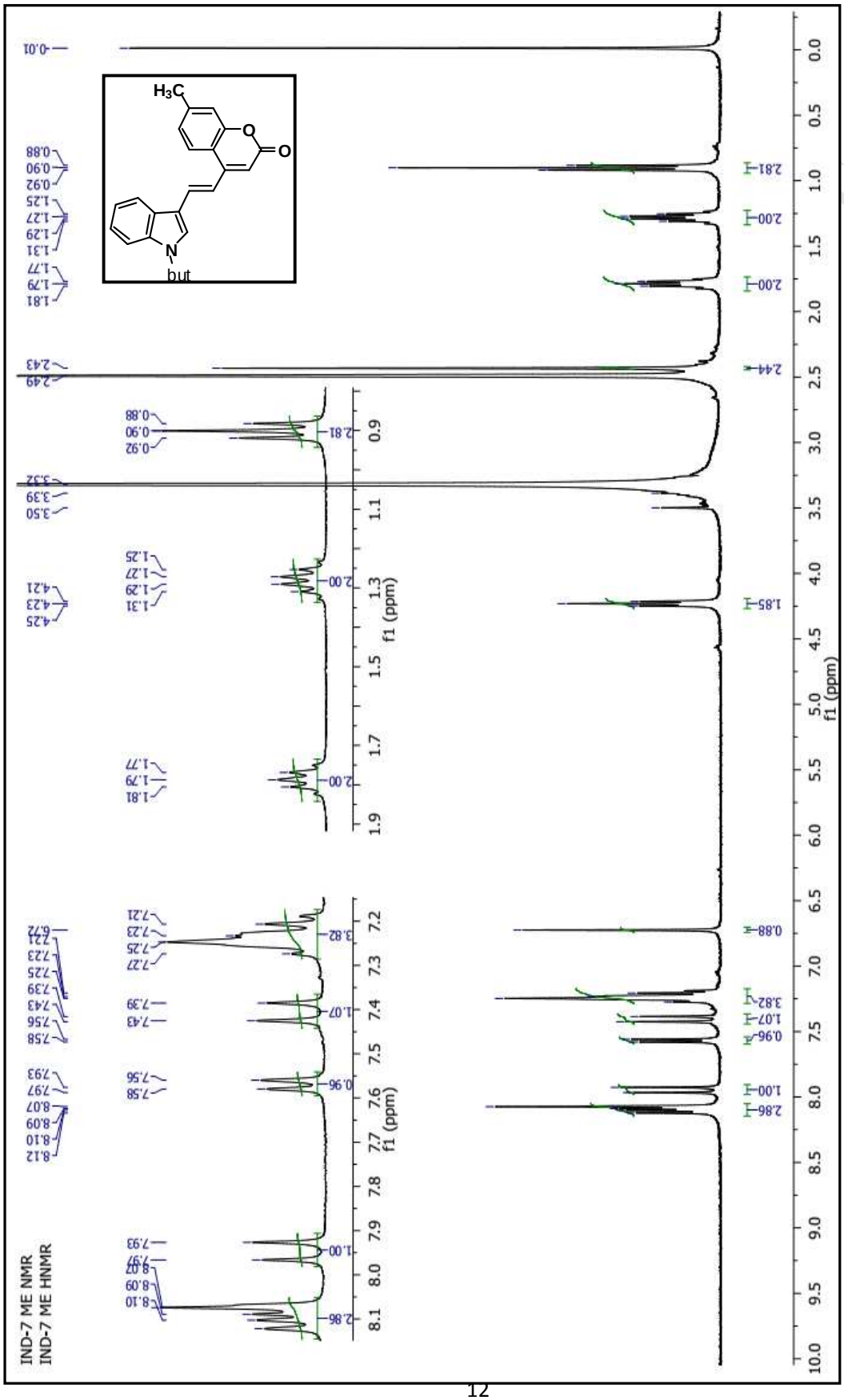
Z-1-(6-Methylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene **(9h)**



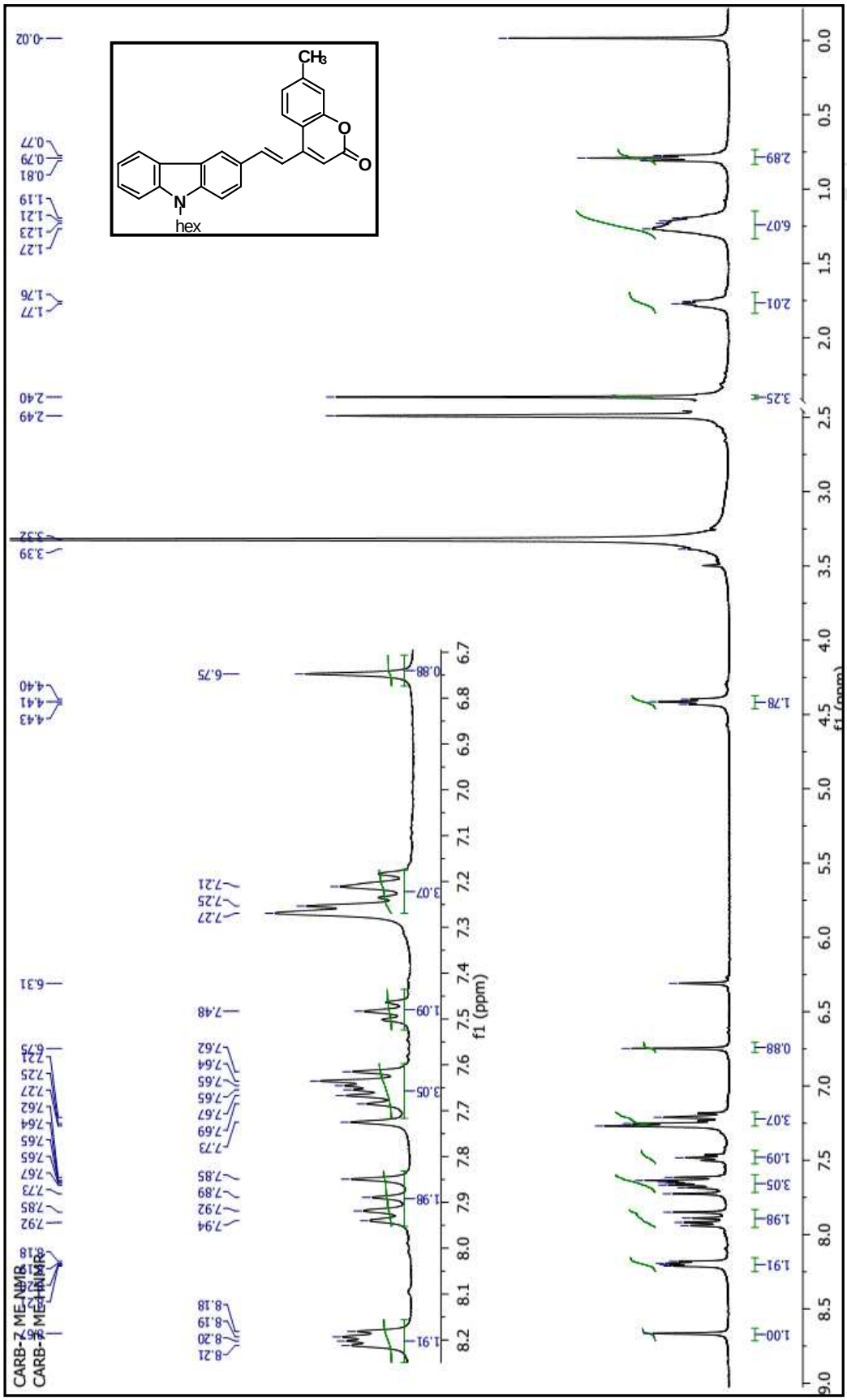
Z-1-(6-Chloro-7-methylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene **(9i)**



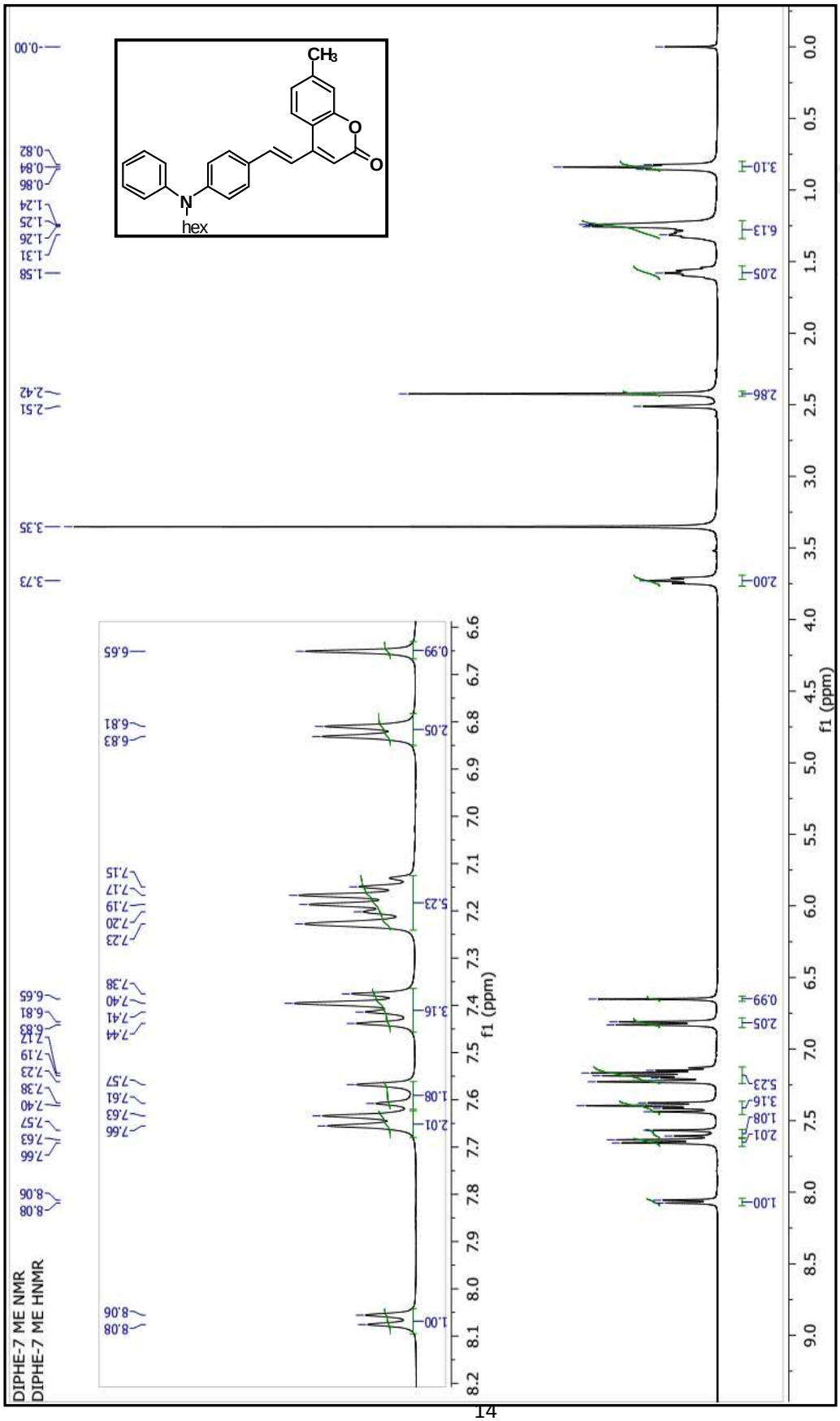
4,4'-(1*E*,1'*E*)-2,2'-(10-Butyl-10*H*-phenothiazine-3,7-diyl)bis(ethene-2,1-diyl)bis(7-methyl-2*H*-chromen-2-one) **(10)**



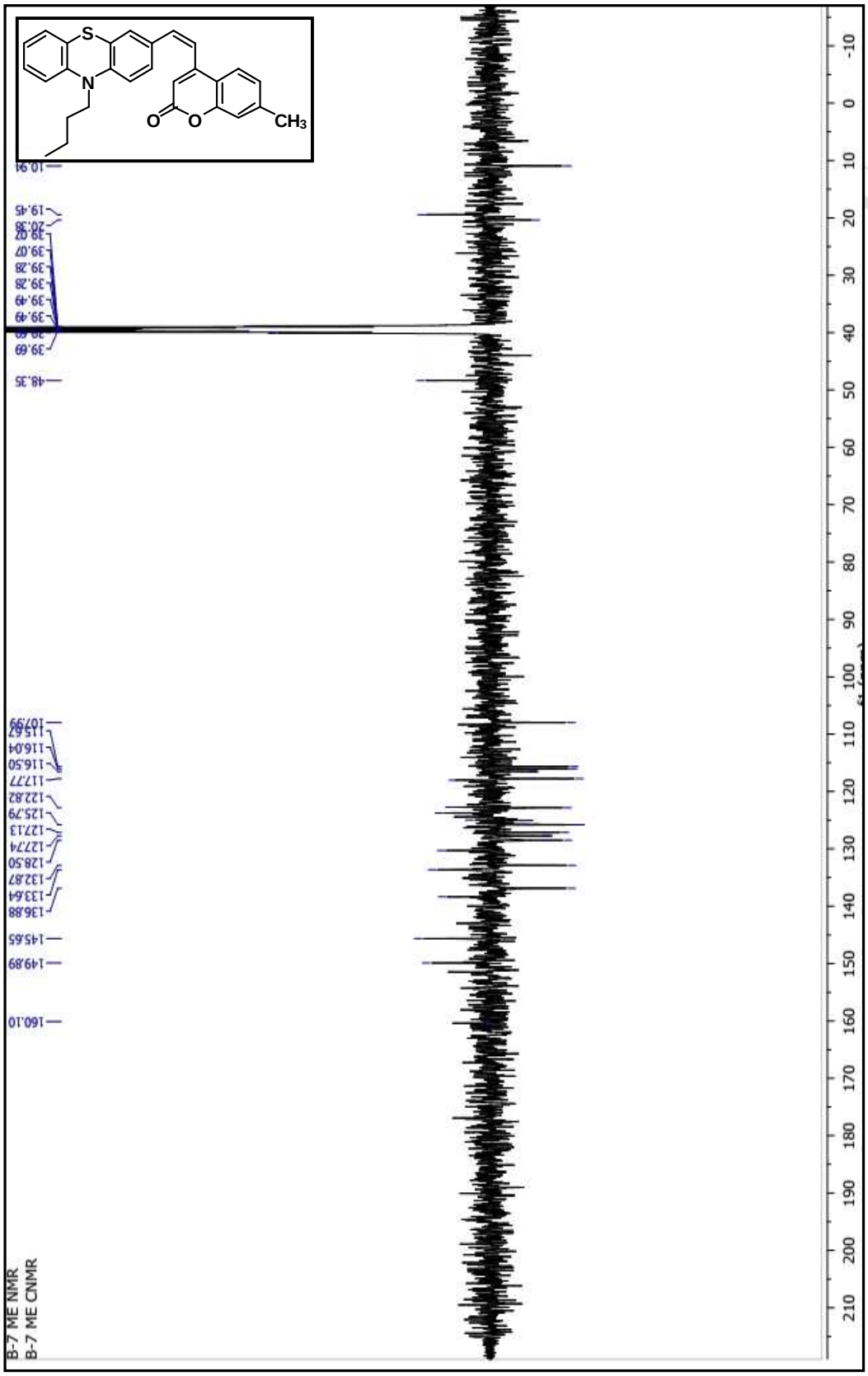
(*E*)-1-(7-Methylcoumarin-4-yl)-2-(1-butyl-1*H*-indol-3-yl)ethene **(14)**



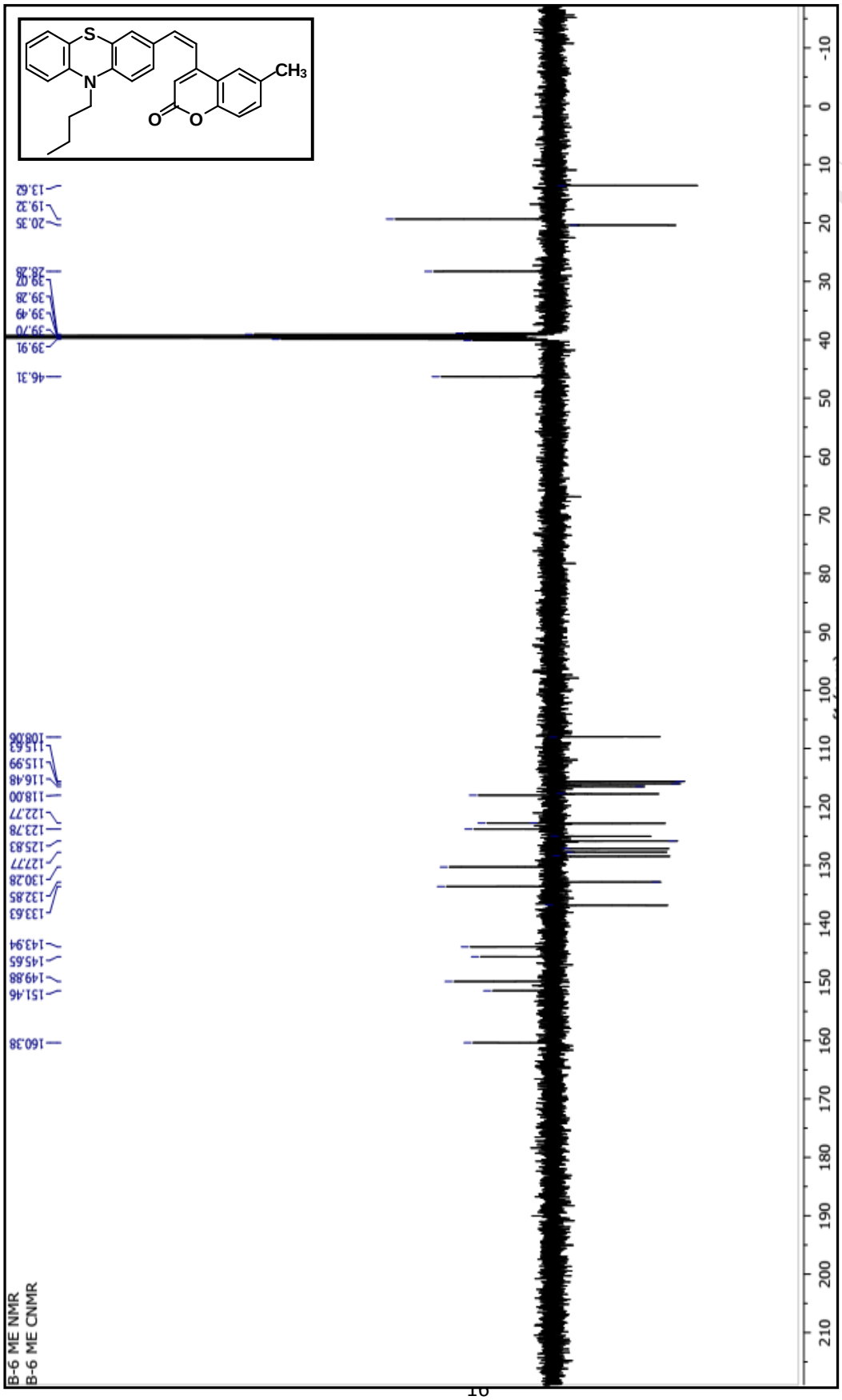
(*E*)-1-(7-Methylcoumarin-4-yl)-2-(9-hexyl-9*H*-carbazol-3-yl)ethene **(15)**



(*E*)-1-(7-Methylcoumarin-4-yl)-2-(9-hexyl-9*H*-4,4' -(hexylimino)bis(benzaldehyde) 3-yl)ethene **(16)**



Z-1-(7-Methylcoumarin-4-yl)-2-(10-butyl-10*H*-phenothiazin-3-yl)ethene **(9a)**



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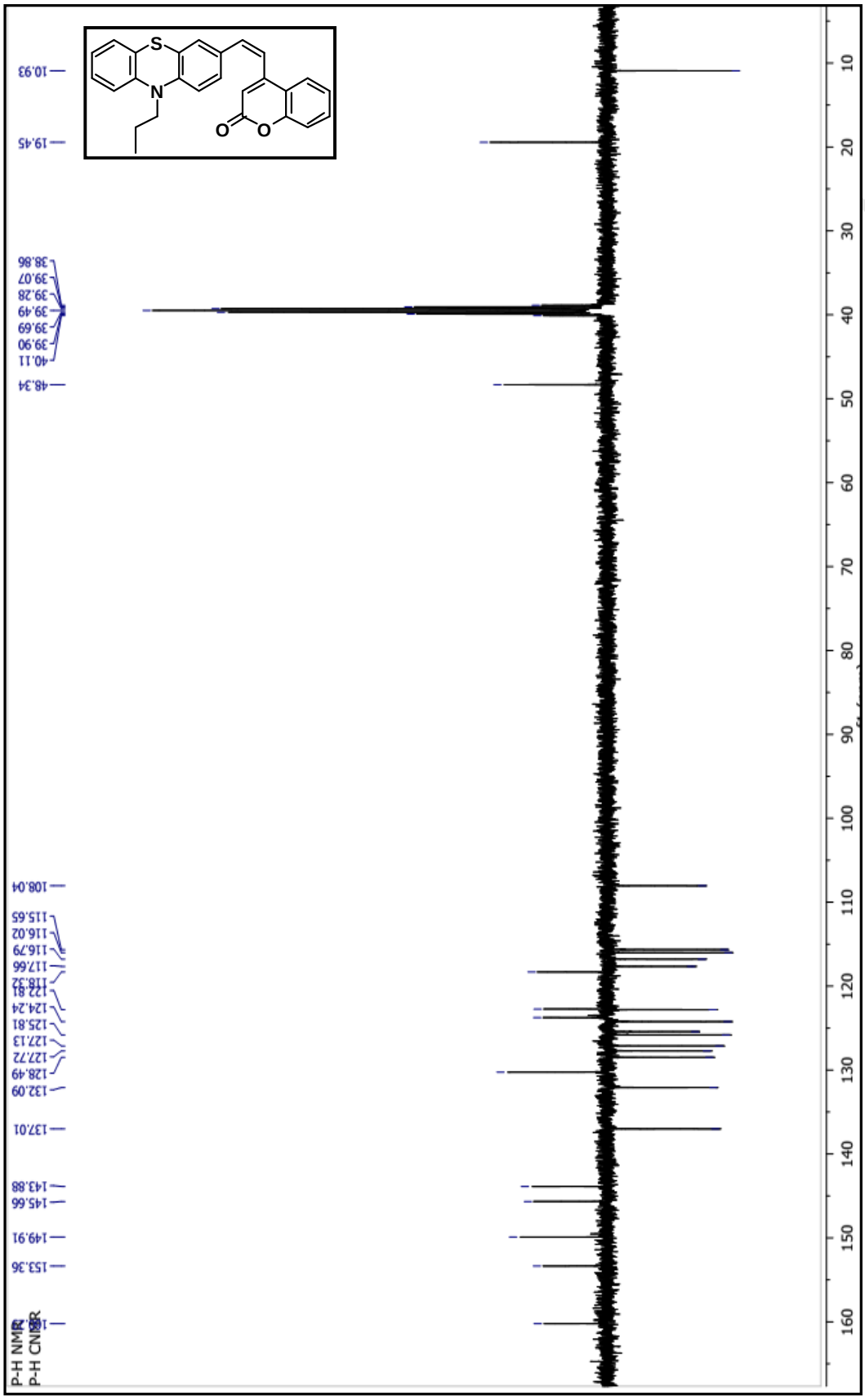
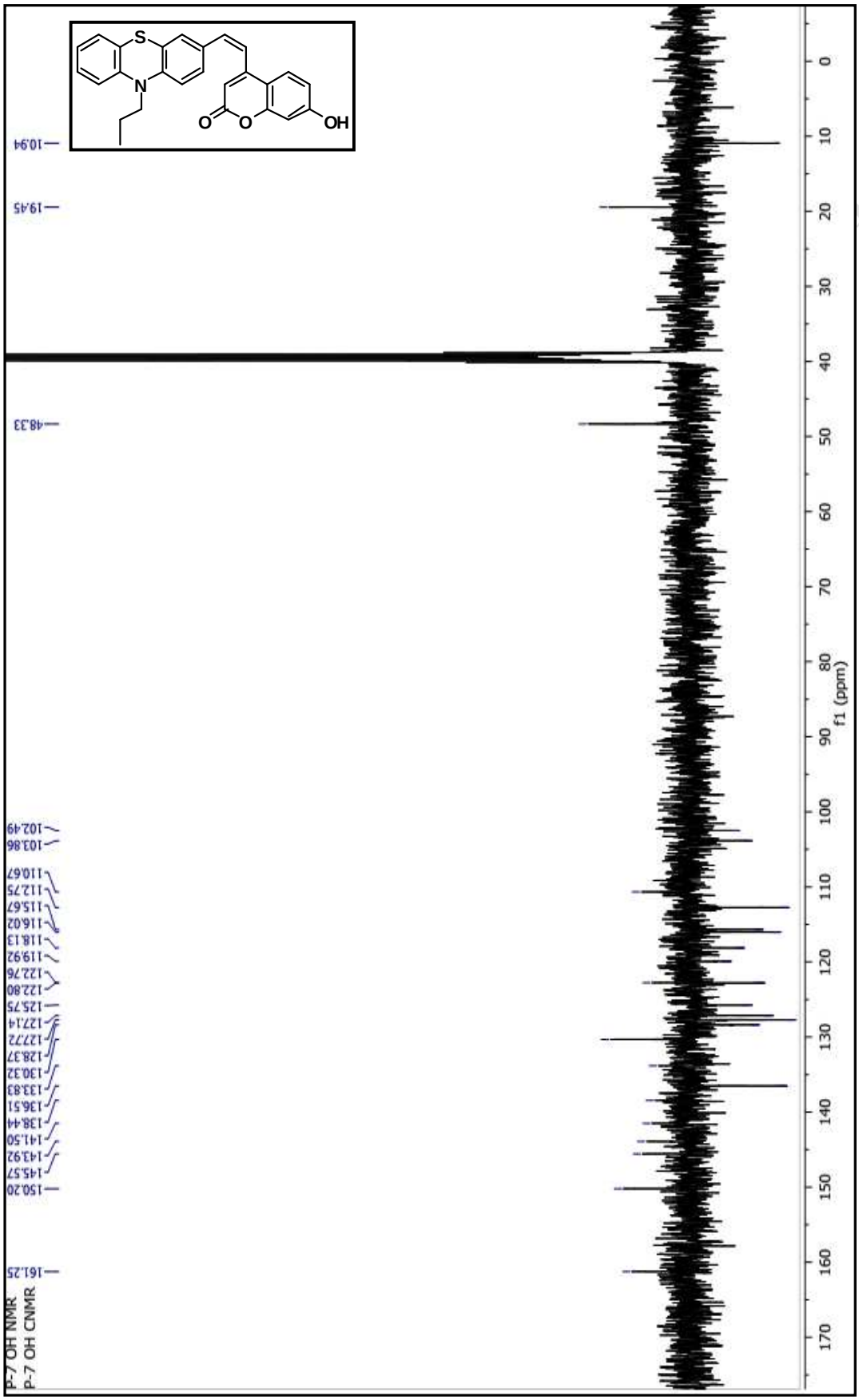
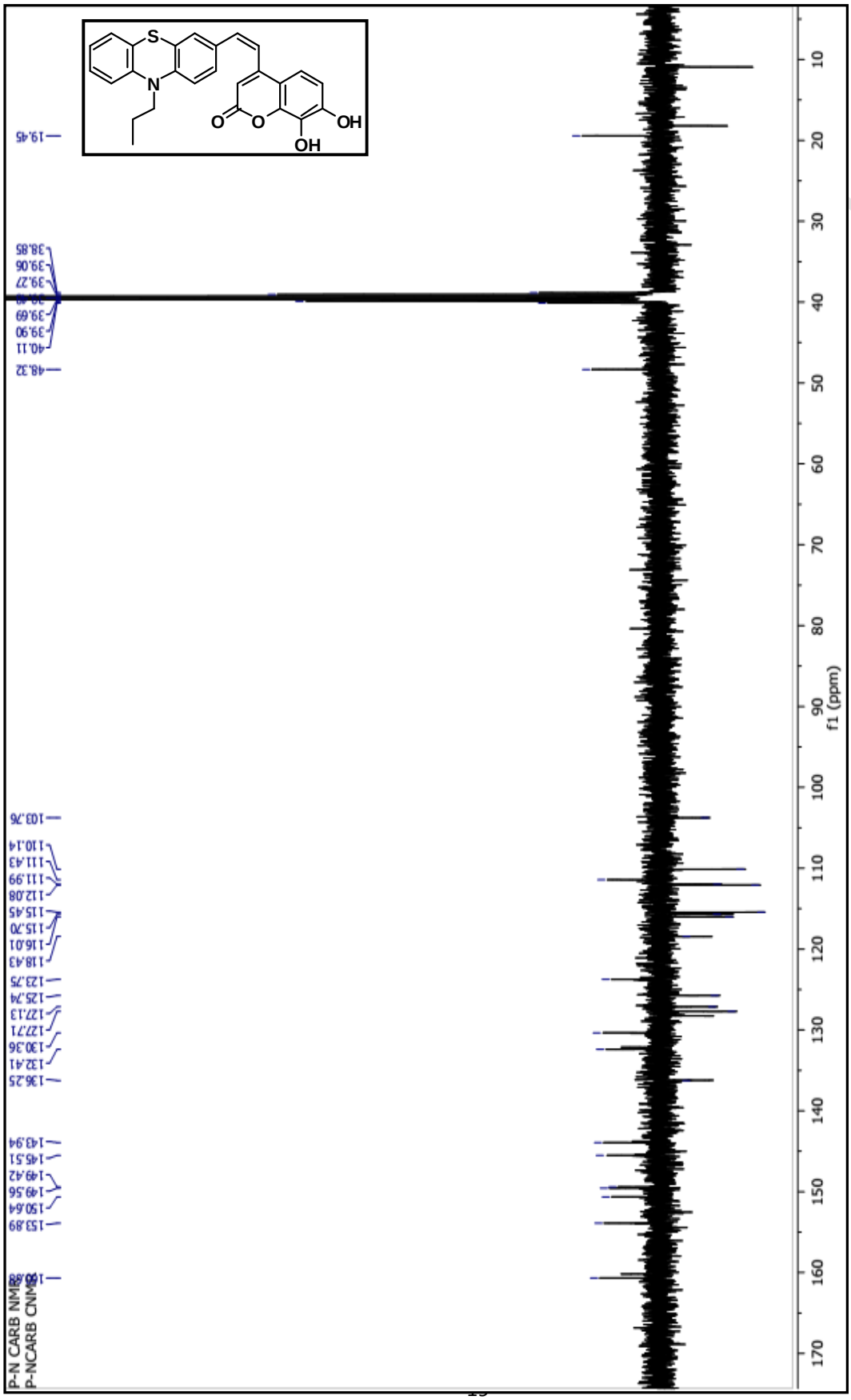


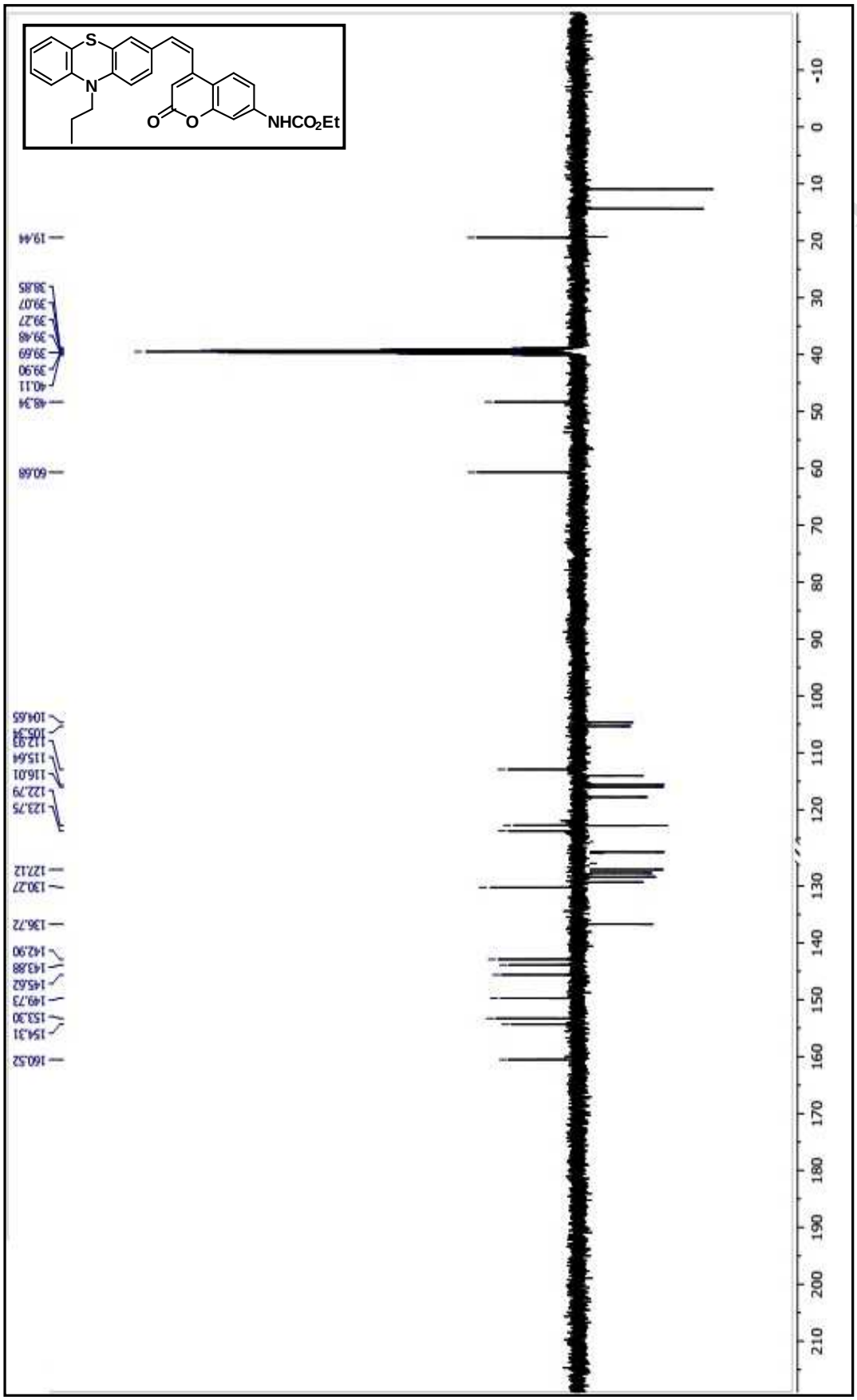
Z-1-(Coumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene **(9c)**



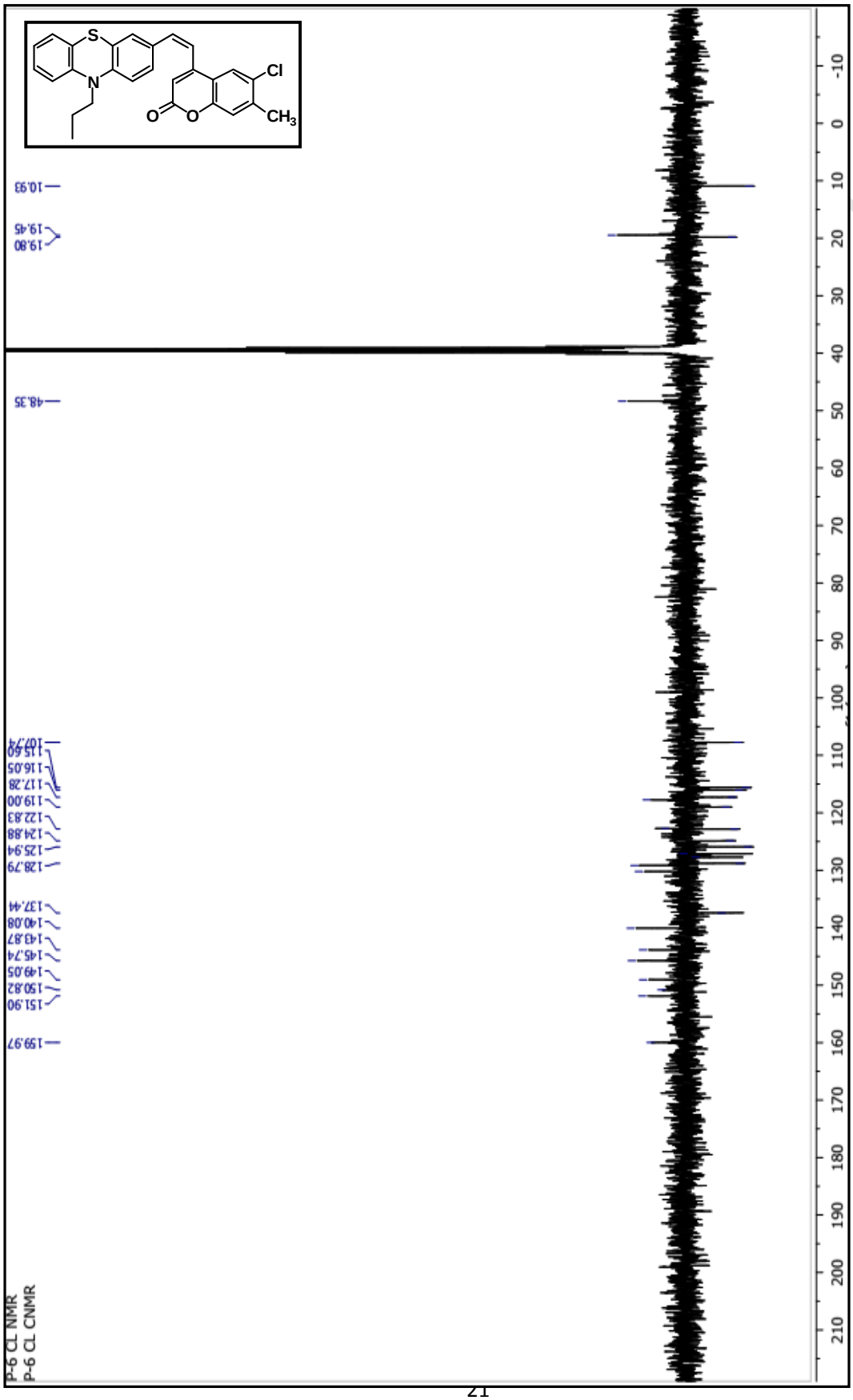
Z-1-(7-Hydroxylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene **(9e)**



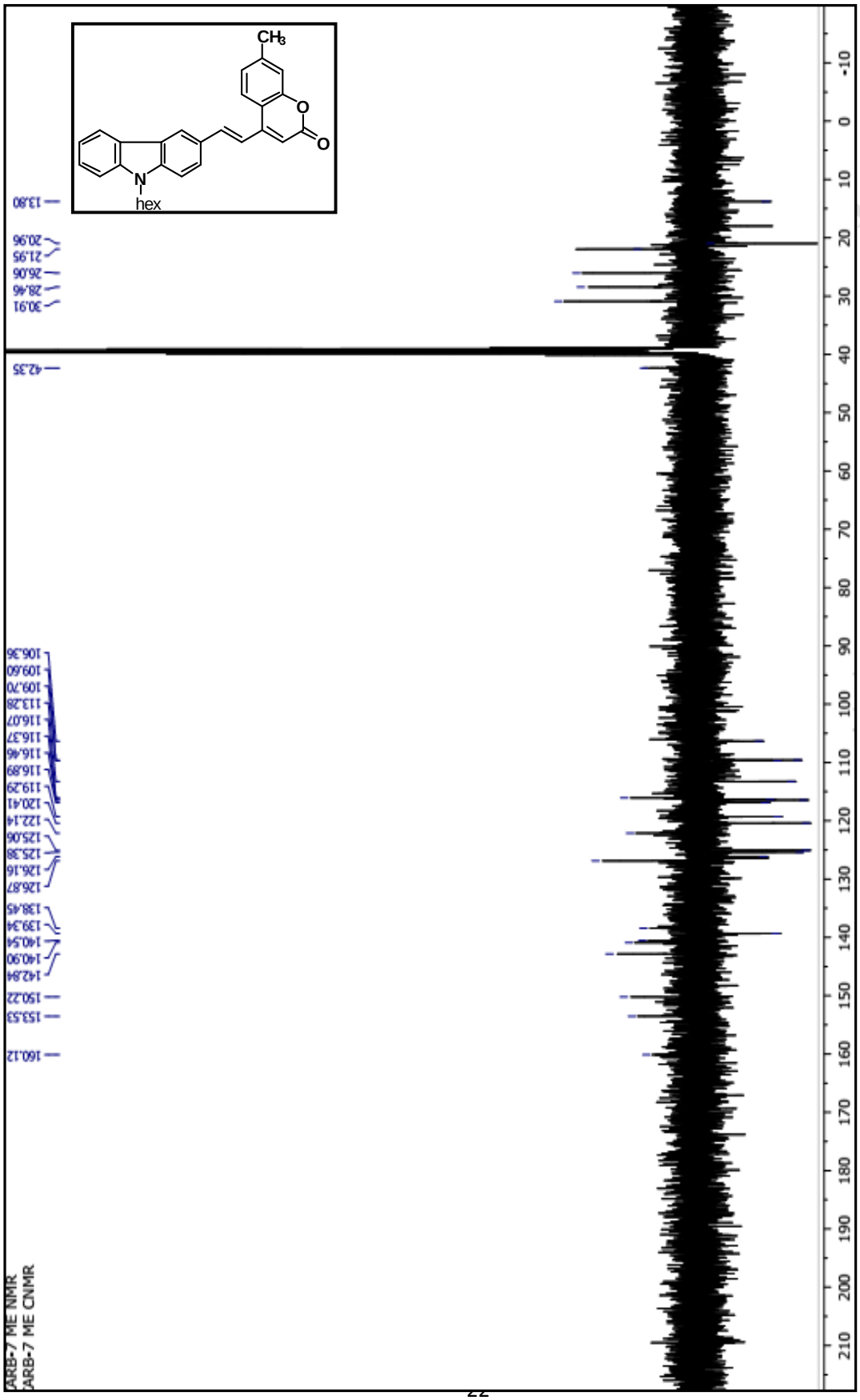
Z-1-(7,8-Dihydroxylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene (**9f**)



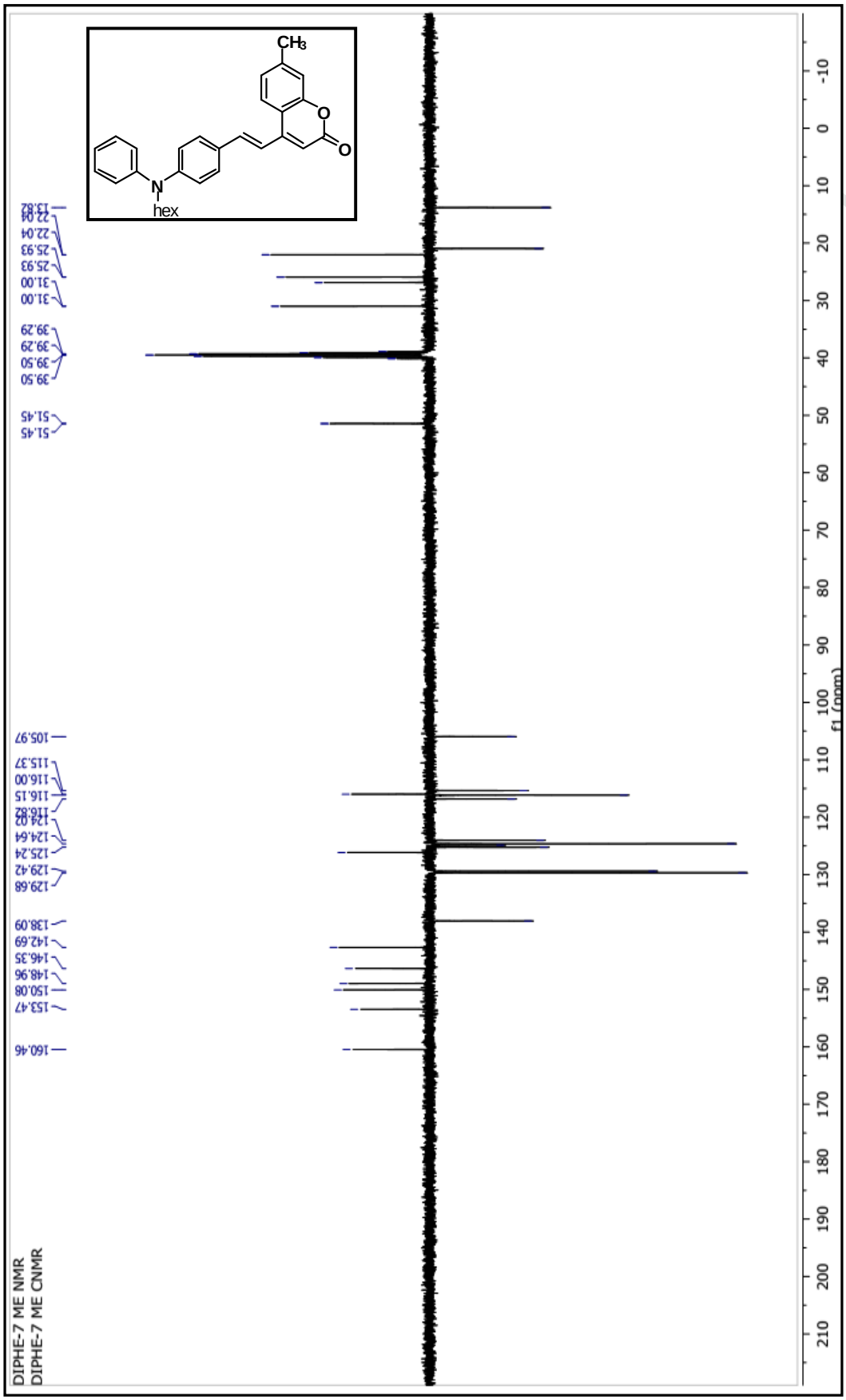
Z-1-(7-Carbamatecoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene **(9g)**



Z-1-(6-Chloro-7-methylcoumarin-4-yl)-2-(10-propyl-10*H*-phenothiazin-3-yl)ethene (**9i**)



(*E*)-1-(7-Methylcoumarin-4-yl)-2-(9-hexyl-9*H*-carbazol-3-yl)ethene **(15)**



(*E*)-1-(7-Methylcoumarin-4-yl)-2-(9-hexyl-9*H*-4,4' -(hexylimino)bis(benzaldehyde) 3-yl)ethene **(16)**