

## Supporting Information

# Cholesterol appended cyanostyryl thiophene positional isomers with multistimuli responsive emission switching and liquid crystalline properties

Nellyulla Kappumchalil Ramya,<sup>a</sup> Parappurath Athira,<sup>a</sup> Manoj Mathews<sup>b</sup>, Doddamane S. Shankar Rao,<sup>c</sup> and Reji Thomas<sup>\*a</sup>

<sup>a</sup>Department of Chemistry, Farook College (Autonomous), Kozhikode, Kerala- 67363, India

<sup>b</sup>Department of Chemistry, St. Joseph's College (Autonomous), Devagiri, Kozhikode - 673008, Kerala, India

<sup>c</sup> Centre for Nano and Soft Matter Sciences (CeNS), Bangalore, Karnataka, India

### Section 1: Synthesis and Characterization

Scheme S1 showing the synthesis of compounds cholesterol substituted amino benzyl cyanide, **1**, **CS-1** and **CS-2** .....S4

### Section 2: Figures and Tables

Figure S1: <sup>1</sup>H NMR Spectra of cholesterol appended 2-(4-aminophenyl) acetonitrile, **1**.....S8

Figure S2: <sup>13</sup>C NMR spectra of cholesterol appended 2-(4-aminophenyl) acetonitrile, **1**. ....S9

Figure S3: <sup>1</sup>H NMR spectra of **CS-1** ..... S10

Figure S4: <sup>13</sup>C NMR spectra of **CS-1**.....S11

Figure S5: <sup>1</sup>H NMR spectra of **CS-2**.....S12

Figure S6: <sup>13</sup>C NMR spectra of **CS-2** .....S13

Figure S7: UV-Visible spectra of <b>CS-1</b> and <b>CS-2</b> .....	S14
Figure S8: Emission spectra of <b>CS-2</b> recorded in THF/water mixtures.....	S15
Figure S9: Fluorescent intensity in response to the changes of water fractions in THF–H <sub>2</sub> O mixtures for <b>CS-1</b> and <b>CS-2</b> .....	S16
Figure S10: ORTEP plot of asymmetric unit present in the single crystals structure of <b>CS-1</b> .....	S17
Table S1: Crystallographic and structure refinement details of <b>CS-1</b> .....	S18
Figure S11: Differential Scanning Calorimetric (DSC) thermograms of compounds <b>CS-1</b> and <b>CS-2</b> .....	S19
Figure S12: Polarizing optical photomicrograph of <b>CS-1</b> .....	S20
Figure. S13: X-ray diffraction pattern of CS-1 (a) and CS-2 (b) at different temperatures in the N*phase.....	S 21

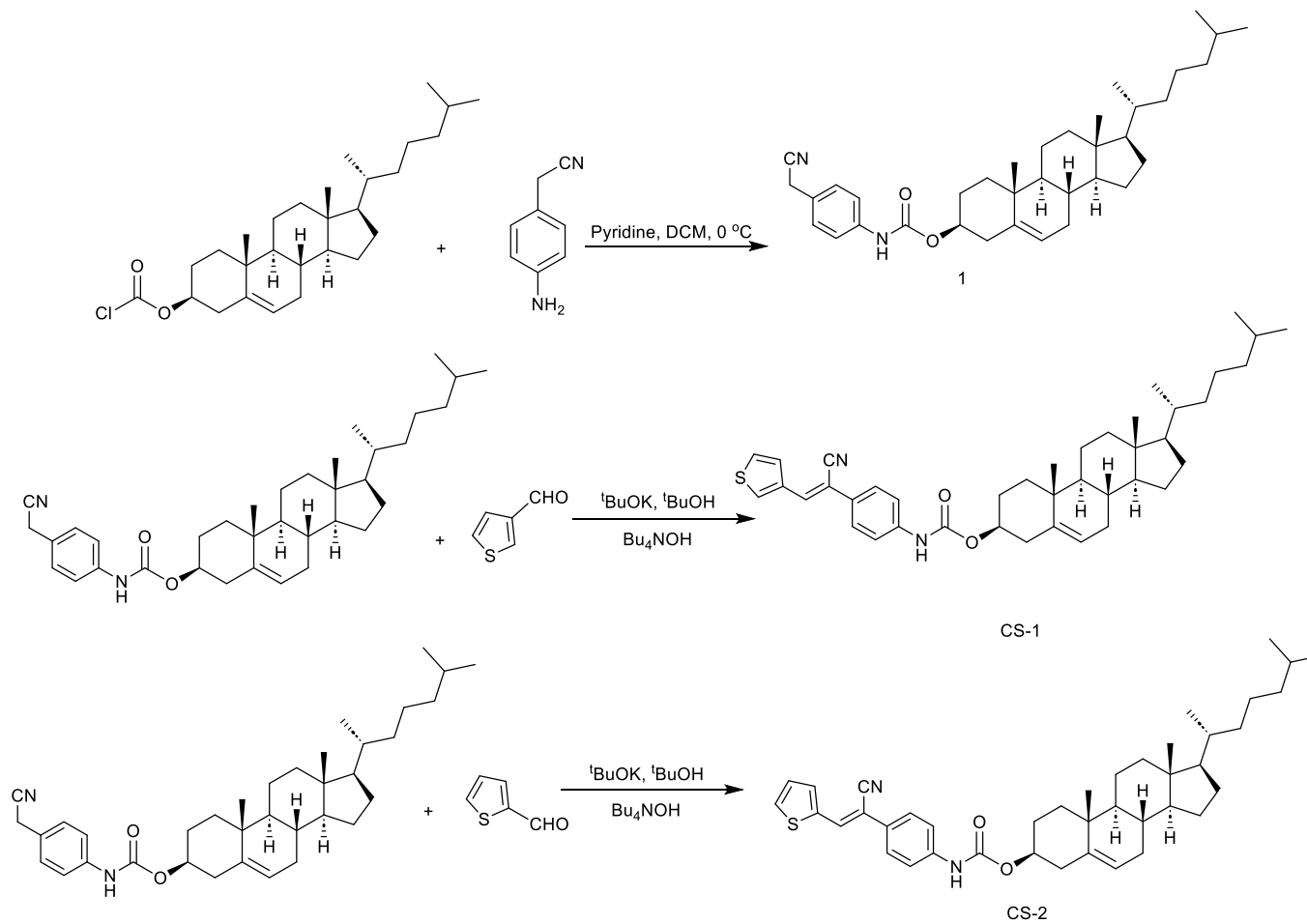
### Section 3: References

References .....	S21
------------------	-----

## Synthesis and characterization

**Materials.** Solvents and chemicals for the synthesis and photophysical studies were purchased from Sigma Aldrich, Alfa Aeser and TCI and used without further purification.

**Characterization.** The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained from a Bruker Avance 400 MHz spectrometer operating at room temperature. Photoluminescence spectra and lifetime experiments were performed using Fluorolog-3 with TCSPC spectrofluorometer (model FL 3C-221). The mass spectra of the compounds were recorded on a Waters Xevo G2 XS QToF mass spectrometer. The single crystal X-ray diffraction data of **CS-1** was collected on Bruker D8 Venture diffractometer attached with PHOTON II detector with CMOS-sensor. The data collection was conducted at room temperature using Mo K $\alpha$  radiation operated at 50 kV and 40 mA. The powder X-ray diffraction data was collected using PANalytical X'Pert3 Powder X-Ray Diffractometer. X-ray diffraction (XRD) measurements were carried out on powder samples in Lindemann capillaries with CuK  $\alpha$  ( $\lambda = 0.15418$  nm) radiation using either an Image plate (IP) detector (GeniX3D, Xenocs) from a source operating at 50 kV and 0.6 mA in conjunction with a multilayer mirror was used to illuminate the sample or PANalytical X'Pert PRO MP machine consisting of a focusing elliptical mirror and a fast high-resolution detector (PIXCEL).



**Scheme S1: Synthetic route to CS-1 and CS-2**

*Synthesis of 2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-10,13-dimethyl-17-(6-methylheptan-2-yl)-1H-cyclopenta[a]phenanthren-3-yl 4-(cyanomethyl)phenylcarbamate, 1*

The compound **1** was synthesized following the reported procedure.<sup>1</sup> 2-(4-aminophenyl) acetonitrile (5 mmol) is dissolved in minimum quantity of dichloromethane and cooled to 0 °C in an ice bath. The cholesterol chloroformate (4.8 mmol) was added to the reaction mixture followed 0.5 ml pyridine and stirring was continued for 6 hours. The reaction mixture was quenched with water and extracted with dichloromethane. Combined organic layers were washed with brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. Solvent was evaporated and the residue was purified by column chromatography on silica gel using hexane ethyl acetate (4/1) as eluent to afford compound **1** as a colourless crystalline solid on re-crystallization from ethyl acetate. The product was characterized using <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy.

Yield: 87 %, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 0.67 (s, 3H), 0.87 (m, 6H), 0.91 (t, *J* = 6 Hz, 3H), 0.98 (m, 6H), 1.13 (m, 7H), 1.29 (m, 4H), 1.47 (m, 5H), 1.62 (m, 1H), 1.91 (m, 5H), 2.38 (m, 2H), 3.69 (s, 2H), 4.59 (m, 1H), 5.40 (m, 1H), 6.57 (s, 1H), 7.24 (d, *J* = 8 Hz, 3H), 7.38 (d, *J* = 12 Hz, 2H).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 11.87, 18.71, 19.34, 21.04, 22.57, 22.83, 23.02, 23.83, 24.29, 28.02, 28.07, 28.24, 31.86, 35.80, 36.18, 36.57, 39.51, 39.72, 42.31, 49.99, 56.12, 56.68, 75.18, 117.94, 119.00, 122.87, 124.38, 128.64, 137.99, 139.49, 152.90.

*General method for the synthesis of compounds CS-1 and CS-2*

The compounds **CS-1** and **CS-2** were synthesized by adopting reported procedures with suitable modifications.<sup>2</sup> Compound **1** (545 mg, 1 mmol) and thiophene-2-carbaldehyde or thiophene-3-carbaldehyde (1 mmol) were dissolved in a mixture of <sup>t</sup>BuOH (11 ml) and THF (5

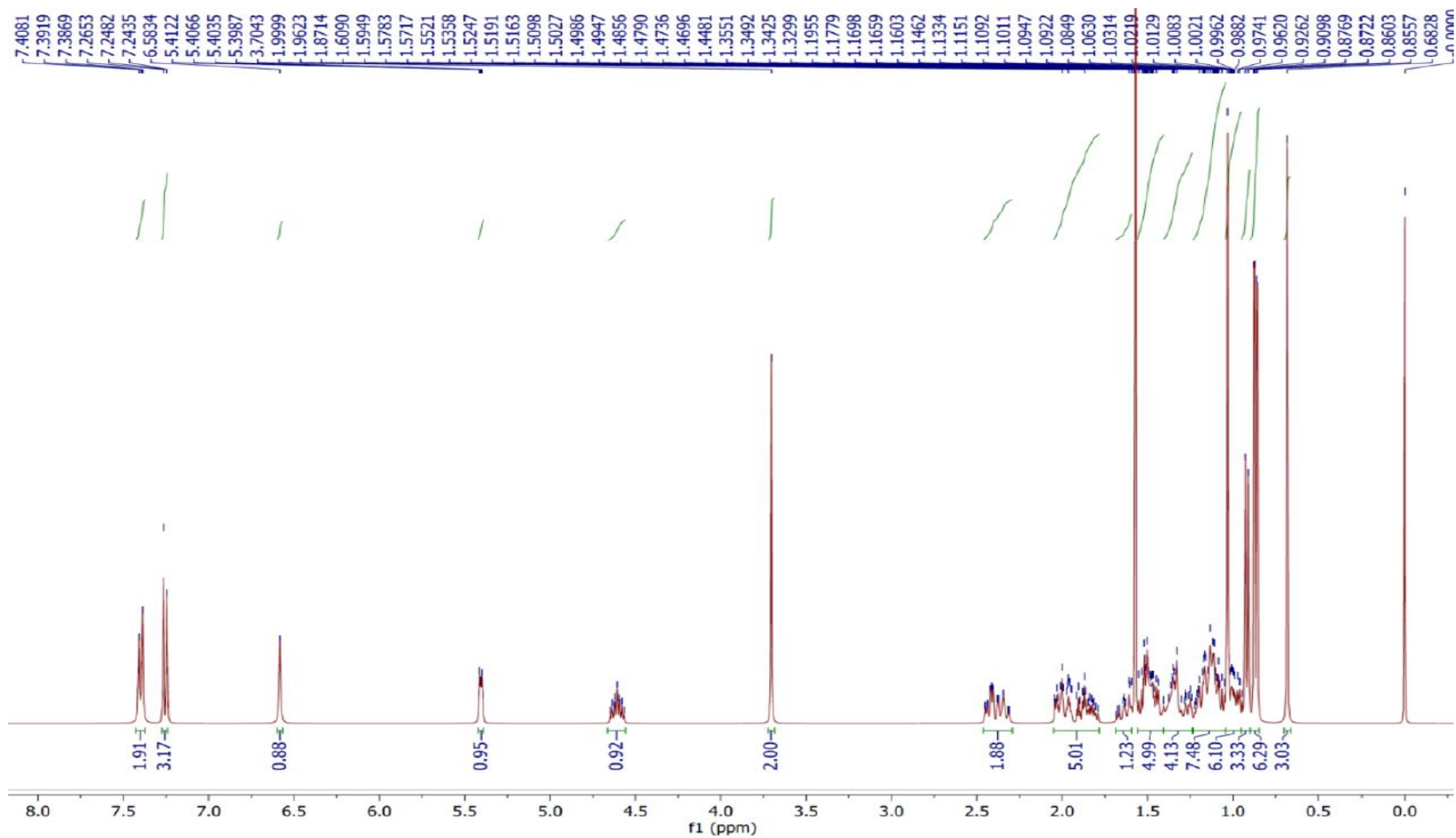
ml) at 50° C. <sup>t</sup>BuOK (0.11 ml of a 1 M solution in THF, 0.11 mmol) and n-Bu<sub>4</sub>NOH (1 ml of a 1 M solution in MeOH, 1 mmol) were added. An orange precipitate started to form immediately and was stirred for 15 minutes at 70° C. The reaction mixture was cooled to room temperature and poured into acidified methanol (50 ml containing 1 drop of conc.CH<sub>3</sub>COOH). The resulting precipitate was filtered and washed with methanol. The compounds were further re-precipitated 5 times from dichloromethane solutions by adding excess methanol

**Compound CS-1:** Yield: 87 %, M.P. 188 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 0.69 (s, 3H), 0.86 (d, 3H, J=1.84 Hz), 0.88 (d, 3H, J=1.84 Hz), 0.92 (d, 3H, J=6.52 Hz), 0.99 (m, 3H), 1.04 (s, 4H), 1.13 (m, 7H), 1.24 (m, 2H), 1.35 (m, 3 H), 1.49 (m, 5H), 1.66 (m, 1H), 1.86 (m, 2H), 1.99 (m, 3H), 2.42 (m, 2H), 4.62 (m, 1H), 5.42 (m, 1H), 6.66 (s, 1H), 7.41 (m, 1H), 7.47 (d, 2H, J=1.96Hz), 7.59 (m, 2H), 7.76 (dd, 1H, J=5.16Hz and 1.32 Hz), 7.92 (m, 1H).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 11.87, 18.72, 19.34, 21.05, 22.57, 22.83, 23.84, 24.29, 28.02, 28.23, 31.87, 31.91, 35.80, 36.18, 36.58, 36.95, 38.42, 39.52, 39.72, 42.32, 50.00, 56.13, 56.68, 75.31, 109.36, 118.45, 118.67, 122.92, 126.54, 126.63, 127.33, 128.95, 129.02, 134.05, 136.11, 138.87, 139.47, 152.69. HRMS (ESI) m/z calculated 638.3906; Found: 639.4040 [M+H]<sup>+</sup>.

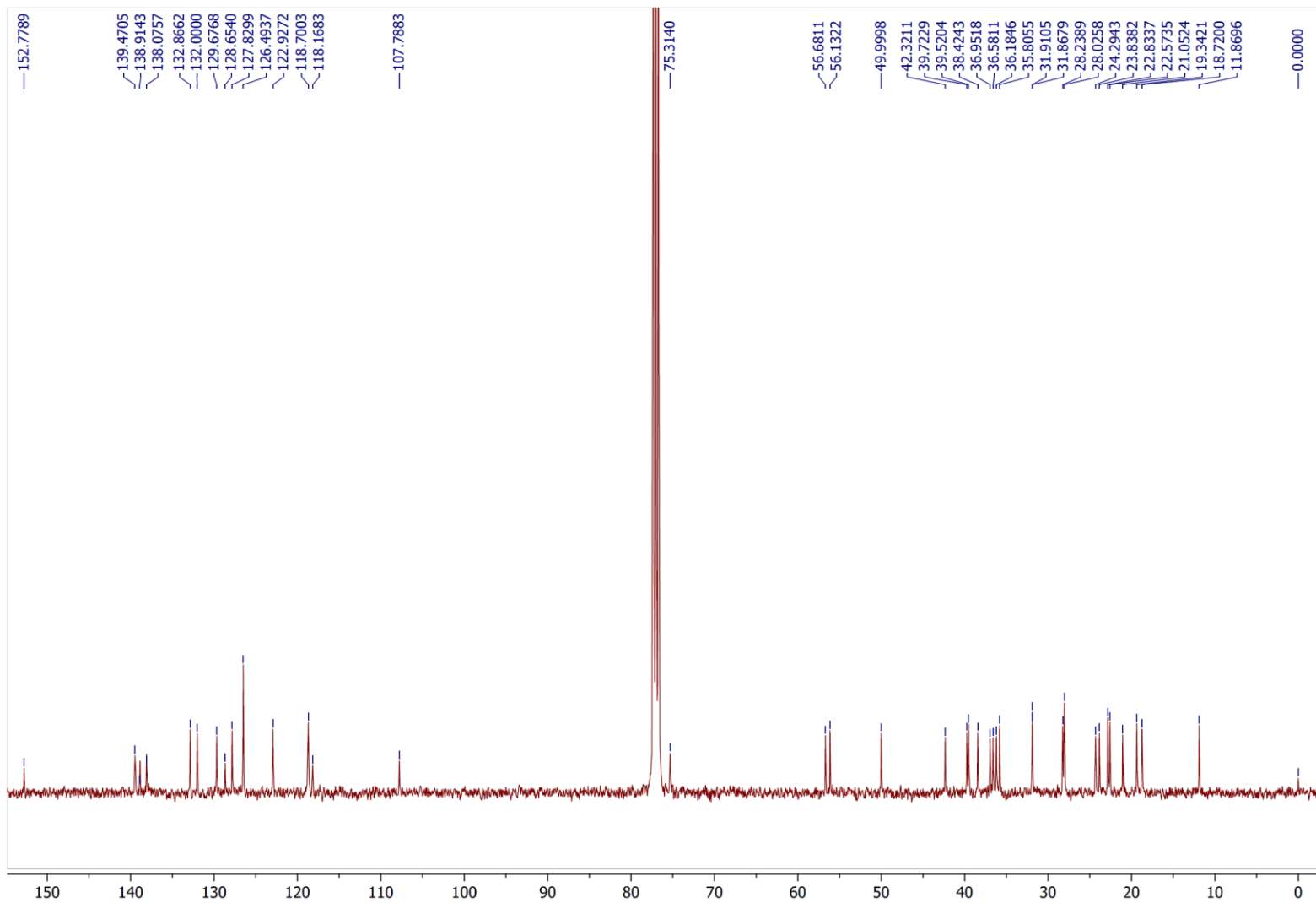
**Compound CS-2:** Yield: 83 %, M.P. 179 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) : 0.69 (s, 3H), 0.88 (m, 6H), 0.93 (t, 3H, J=6Hz), 1.01 (m, 6H), 1.12 (m, 7H), 1.30 (m, 5H), 1.48 (m, 5H), 1.63 (m, 2H), 1.92 (m, 5H), 2.41 (m, 2H), 4.62 (m, 1H), 5.41 (d, 1H, J= 4Hz), 6.68 (d, 1H, J= 4Hz), 7.15 ( m, 1H) 7.45 (m, 1H), 7.47 (m, 1H), 7.53 (t, 1H, J = 4Hz), 7.58 (t, 2H, J= 8Hz), 7.65 (t, 1H, J= 4Hz).

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 11.87, 18.72, 19.34, 21.05, 22.57, 22.83, 23.84, 24.29, 28.02, 28.24, 31.87, 31.91, 35.80, 36.18, 36.58, 36.95, 38.42, 39.52, 39.72, 42.32, 50.00, 56.13, 56.68, 75.31, 107.79, 118.17, 118.70, 122.93, 126.49, 127.83, 128.65, 129.68, 132.00, 132.87, 138.08, 138.91, 139.47, 152.78. HRMS (ESI)  $m/z$  calculated 638.3906; Found: 639.3990  $[\text{M}+\text{H}]^+$ .

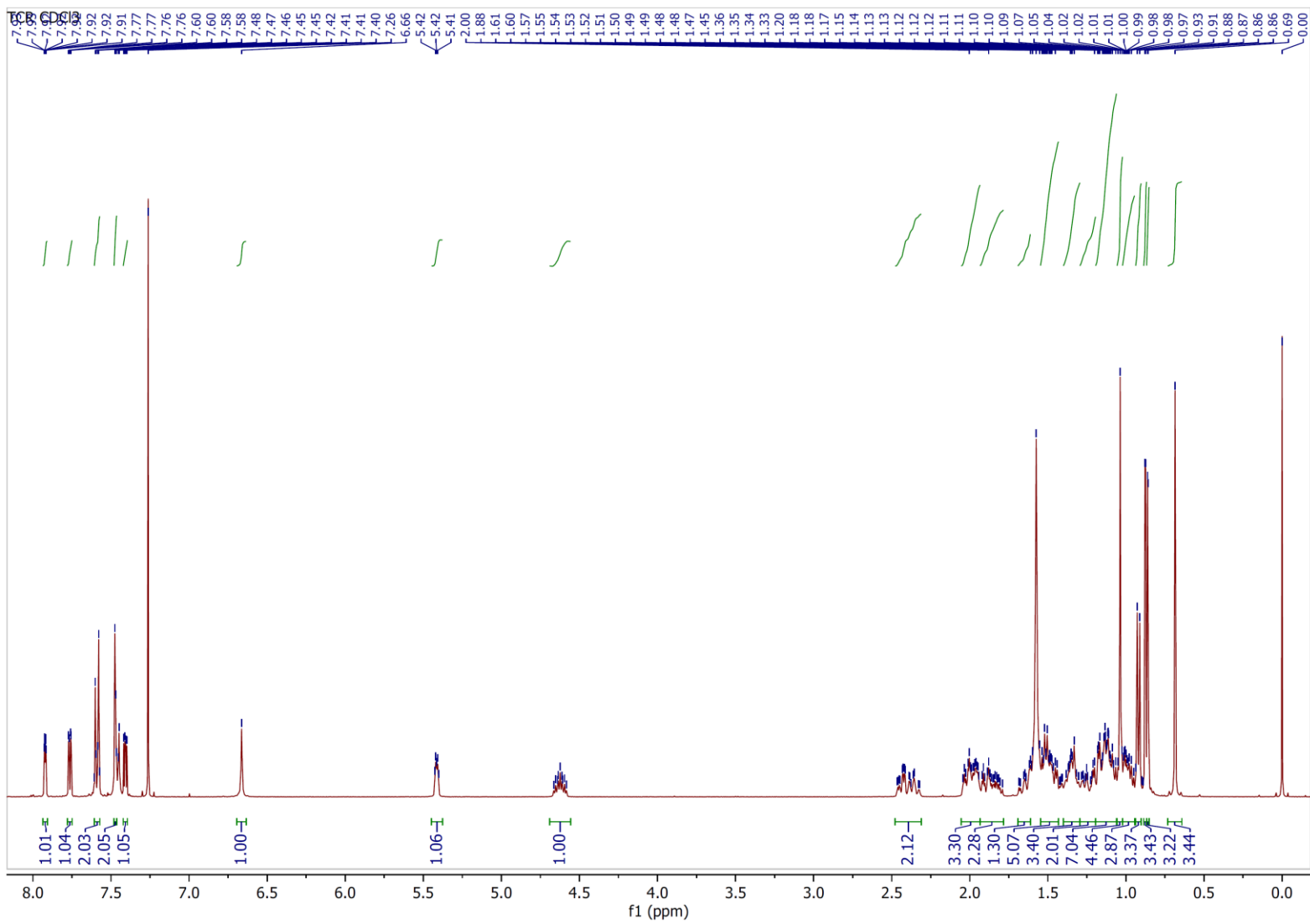


**Fig. S1**  $^1\text{H}$  NMR spectra of **1** in  $\text{CDCl}_3$

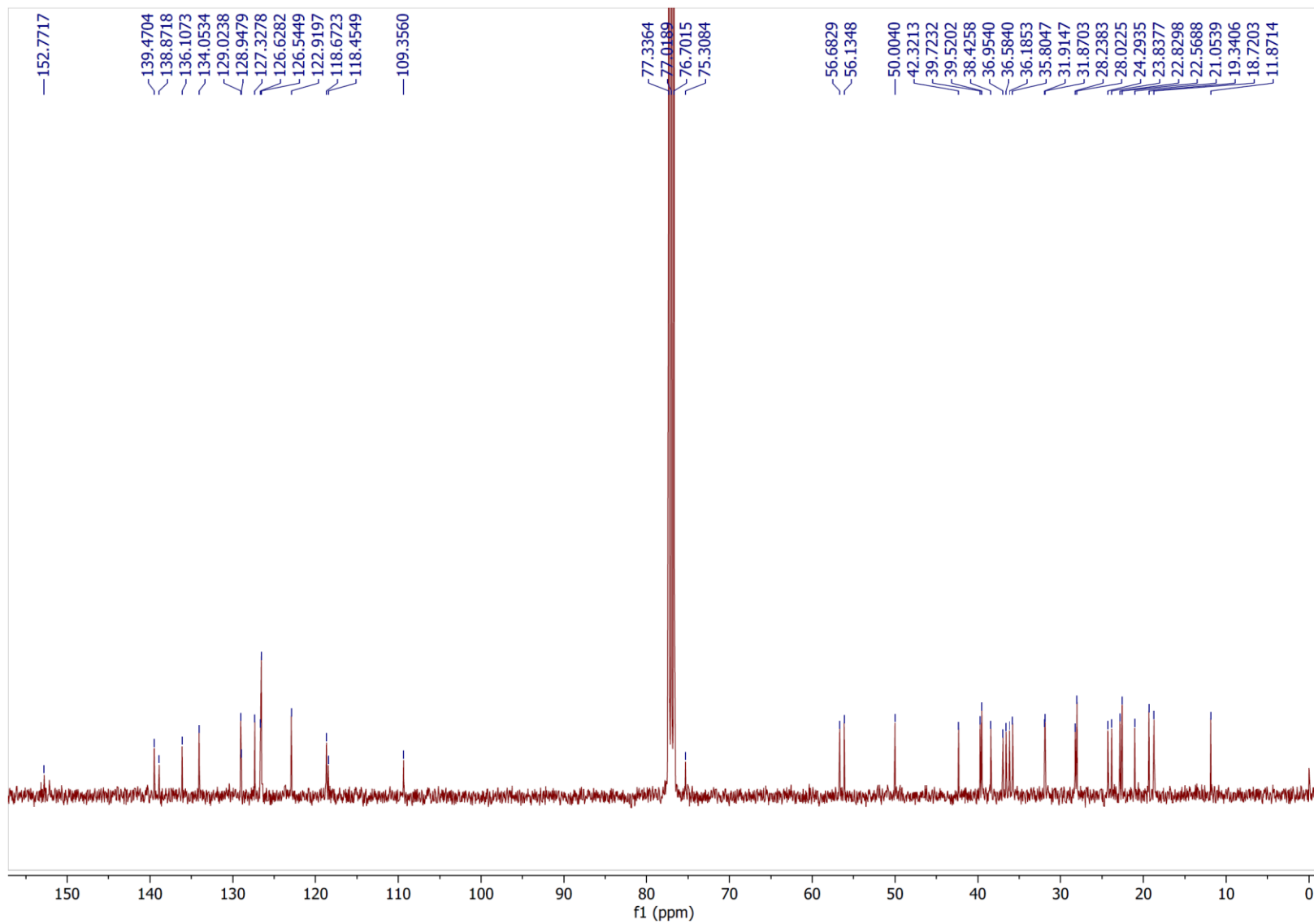




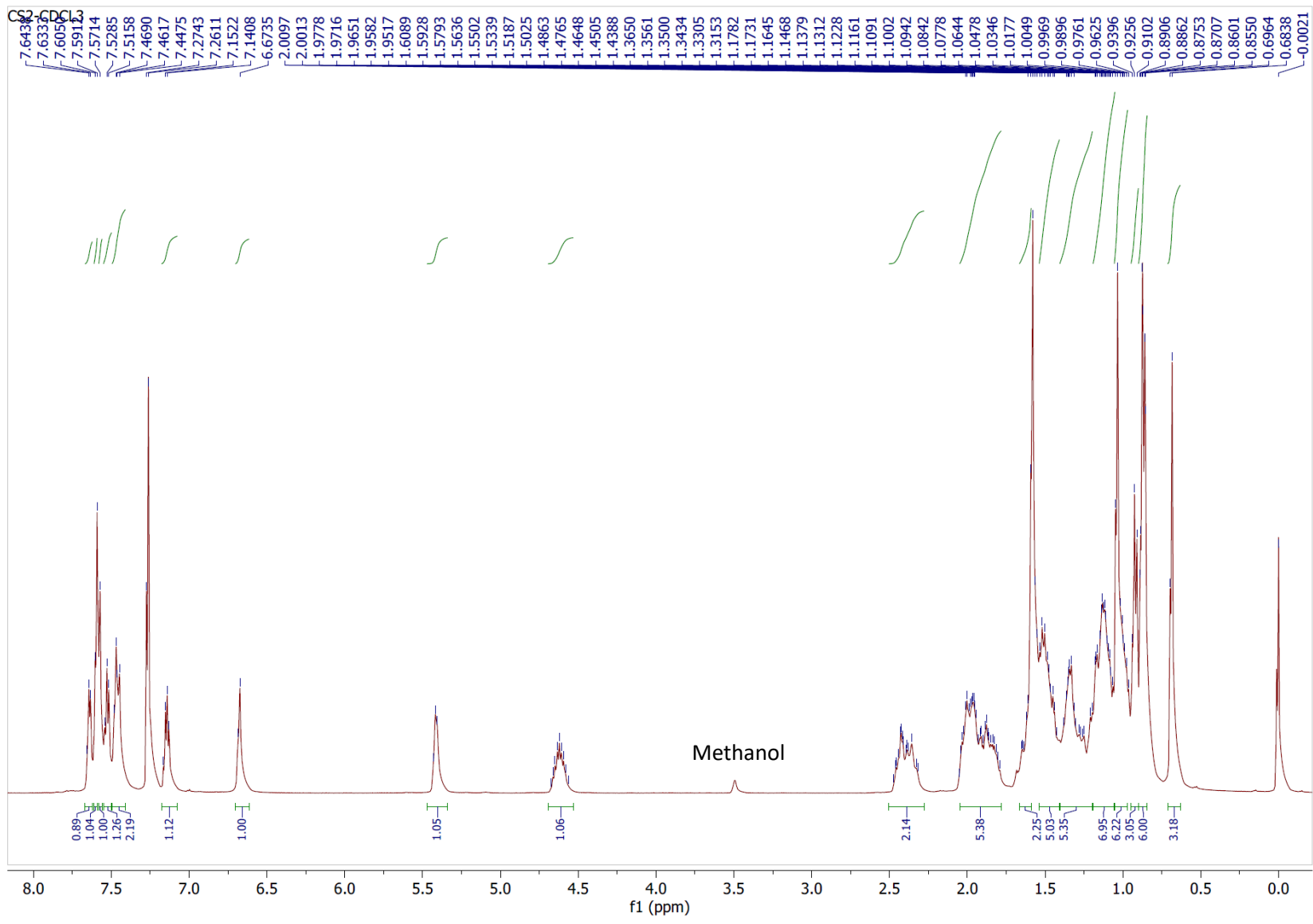
**Fig. S2**  $^{13}\text{C}$  NMR spectra of **1** in  $\text{CDCl}_3$



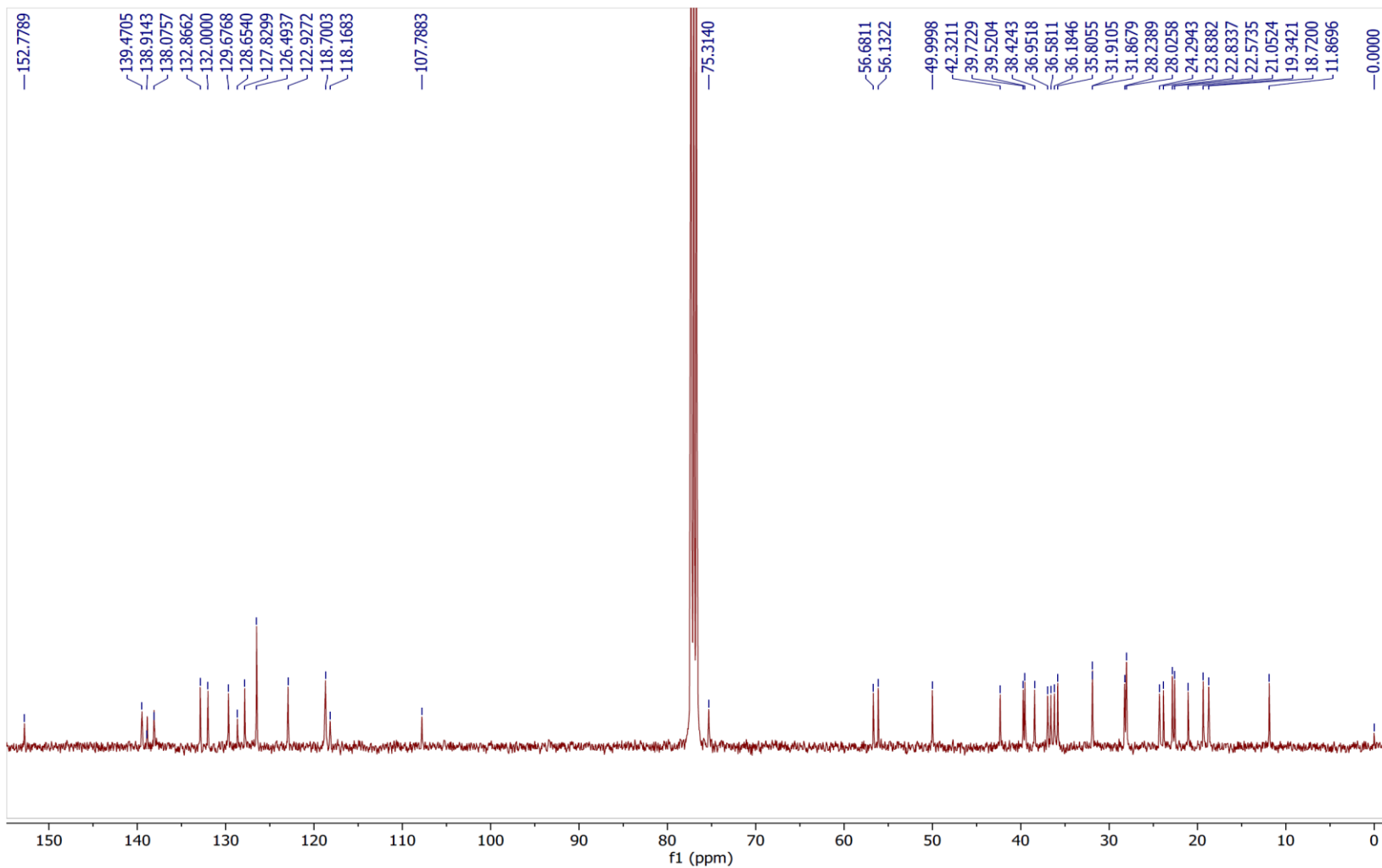
**Fig. S3**  $^1\text{H}$  NMR spectra of CS-1 in  $\text{CDCl}_3$



**Fig S4**  $^{13}\text{C}$  NMR spectra of **CS-1** in  $\text{CDCl}_3$



**Fig. S5**  $^1\text{H}$  NMR spectra of CS-2 in  $\text{CDCl}_3$



**Fig. S6**  $^{13}\text{C}$  NMR spectra of CS-2 in  $\text{CDCl}_3$

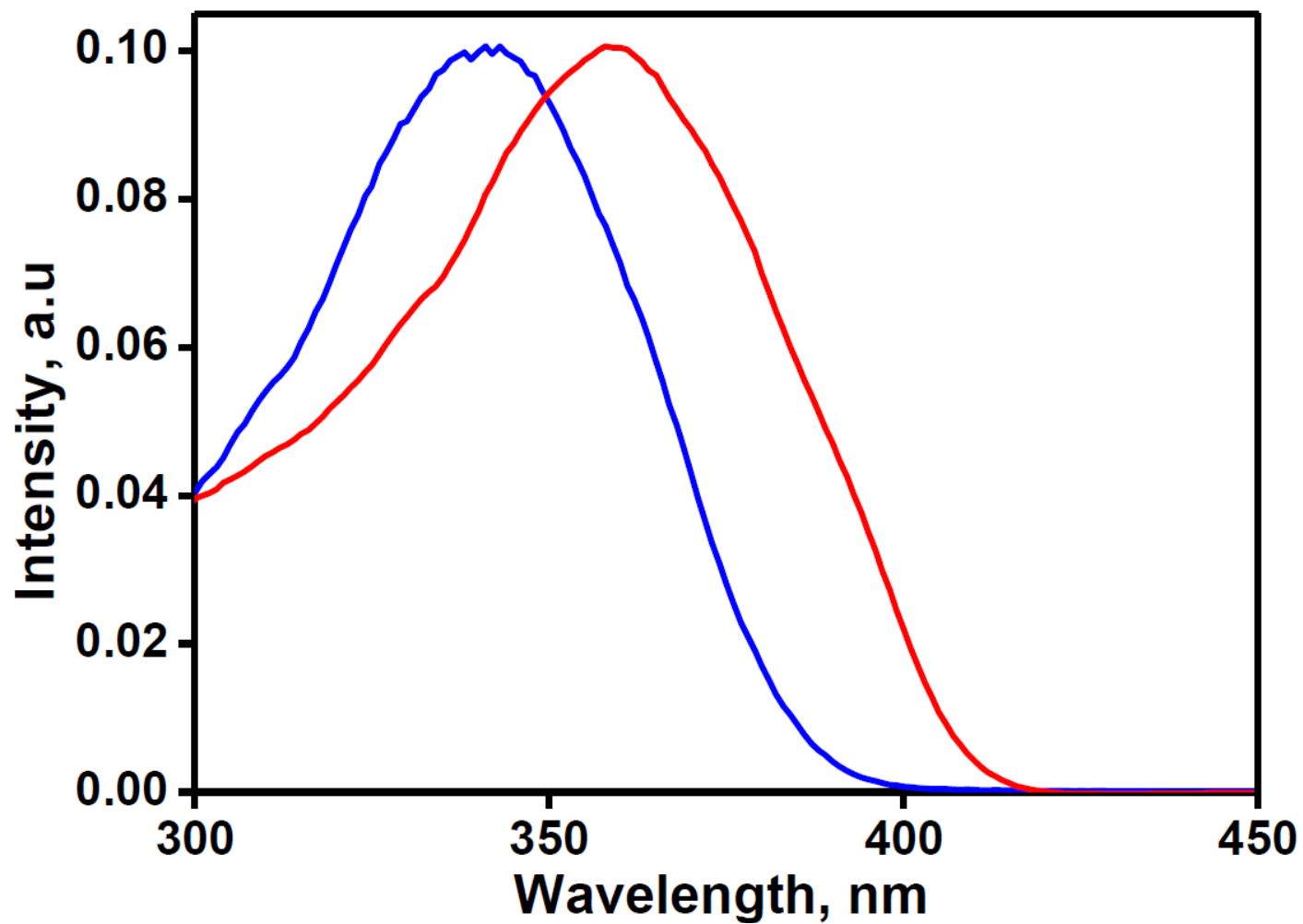
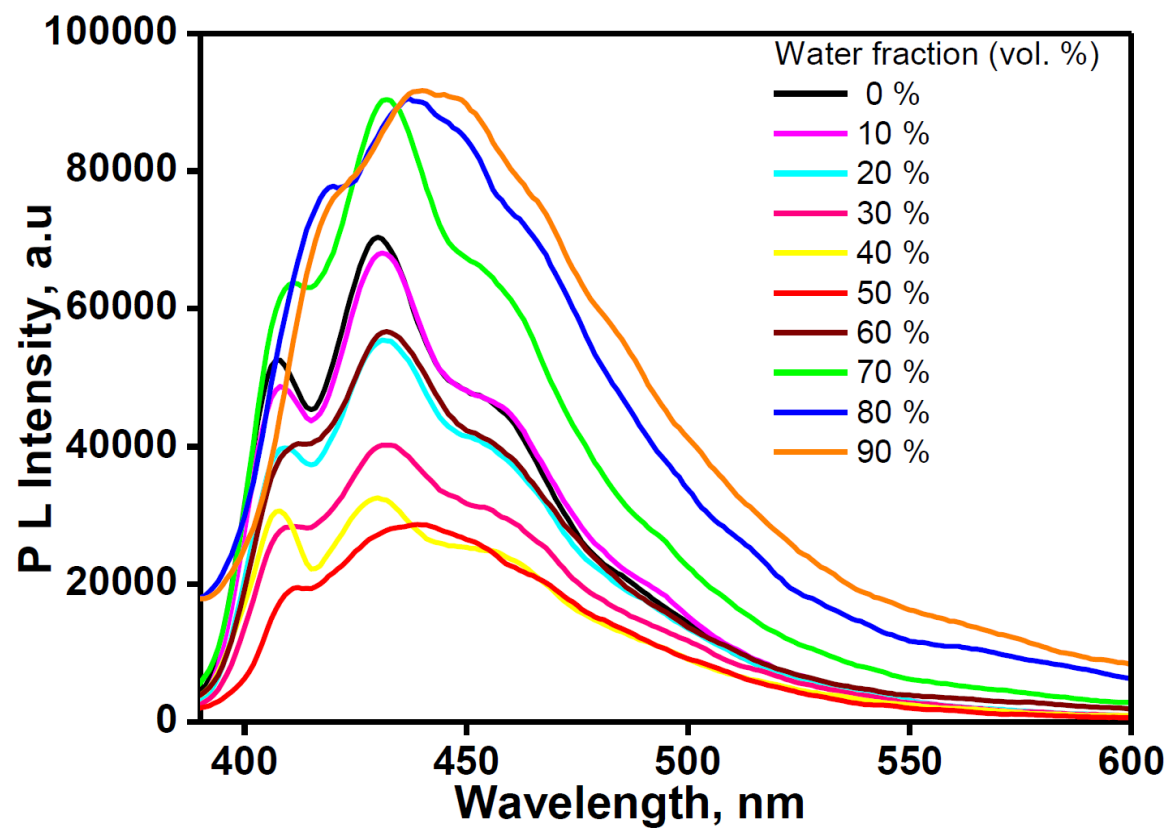
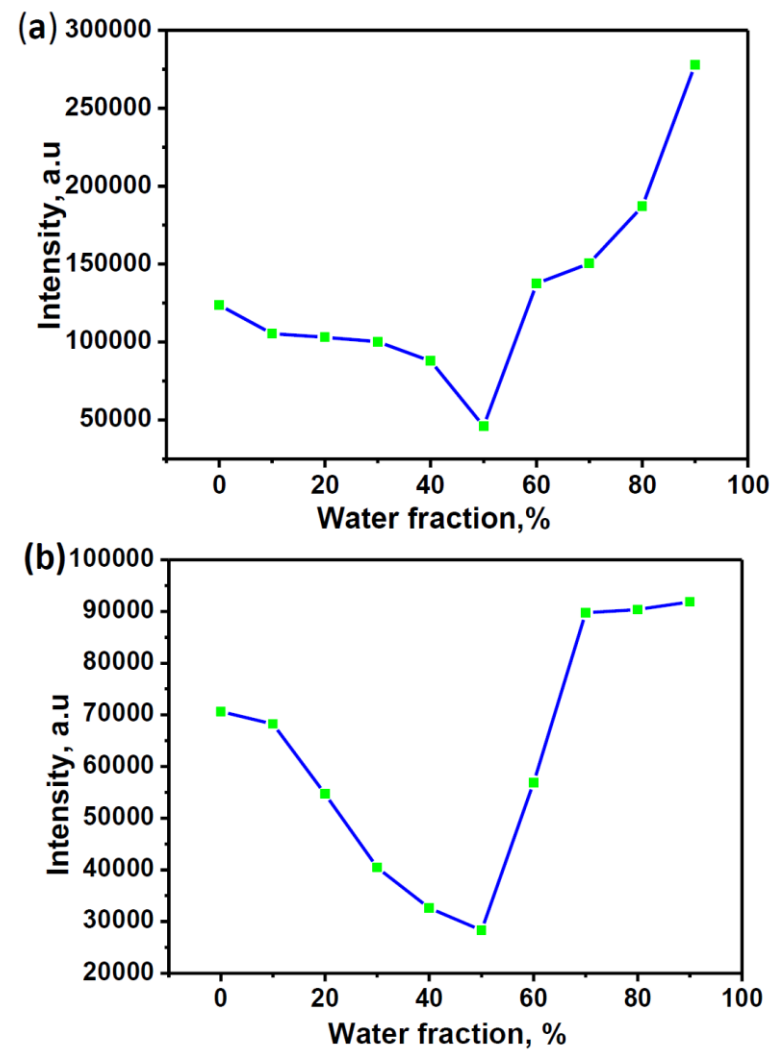


Fig. S7 UV-visible absorption spectra of CS-1 (blue curve) and CS-2 (red curve) in THF (1 μM)



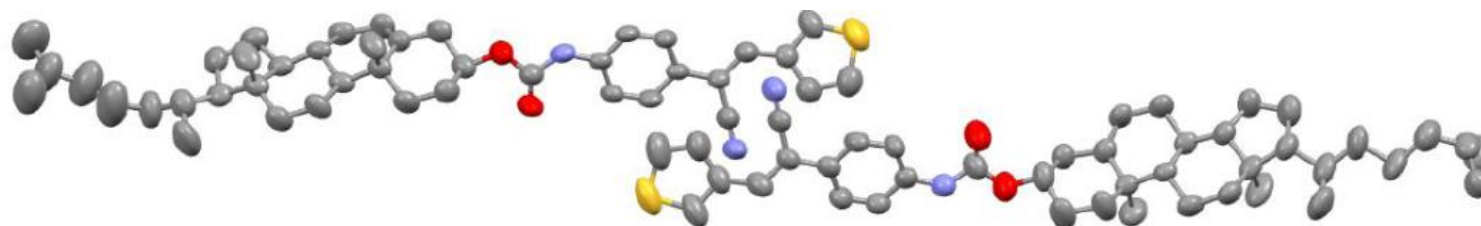
**Fig. S8** Emission spectra of CS-2 recorded in THF/water mixtures (50  $\mu$ M) by varying the water fraction. ( $\lambda_{\text{ex}} = 370$  nm)



**Fig. S9** Fluorescent intensity in response to the changes of water fractions in THF-H<sub>2</sub>O mixtures (a) **CS-1** and (b)**CS-2** Concentration:

$50 \times 10^{-6}$  M;  $\lambda_{ex}$ : 370nm.

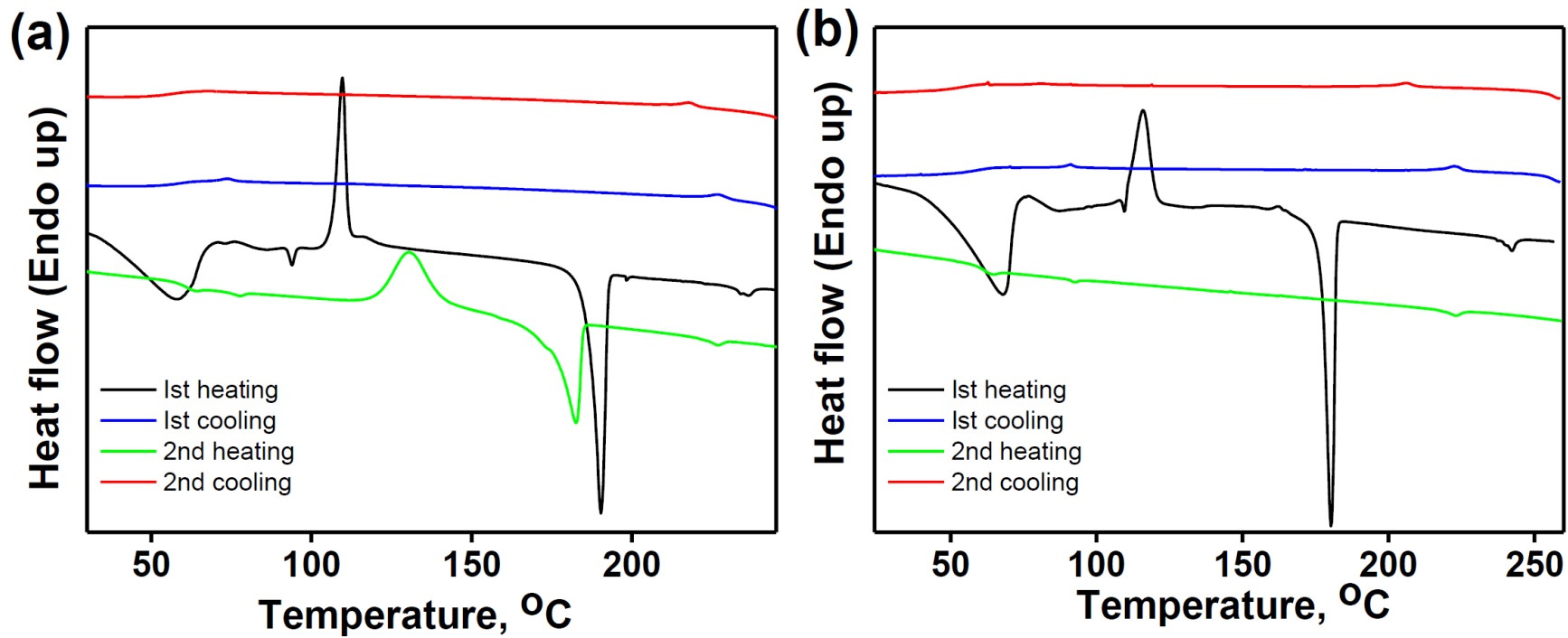




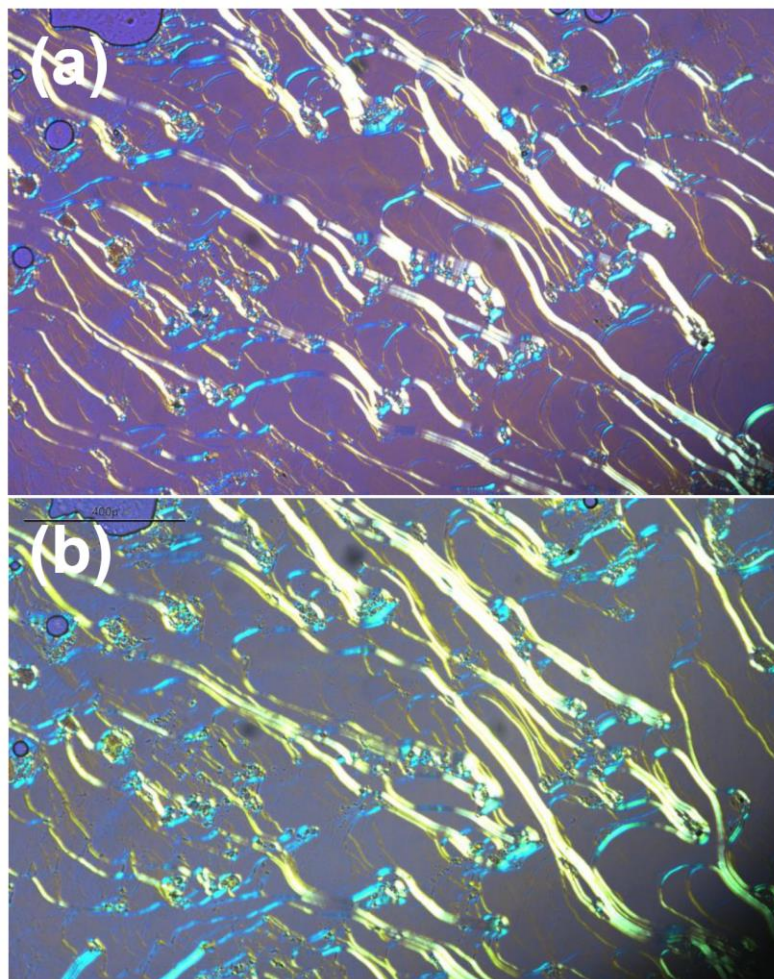
**Fig. S10** ORTEP plot of the asymmetric unit present in the single crystals structure of **CS-1** (ellipsoids are drawn at 50 % probability, and hydrogen atoms are removed for clarity)

**Table S1.** Crystallographic and structure refinement details of **CS-1**.

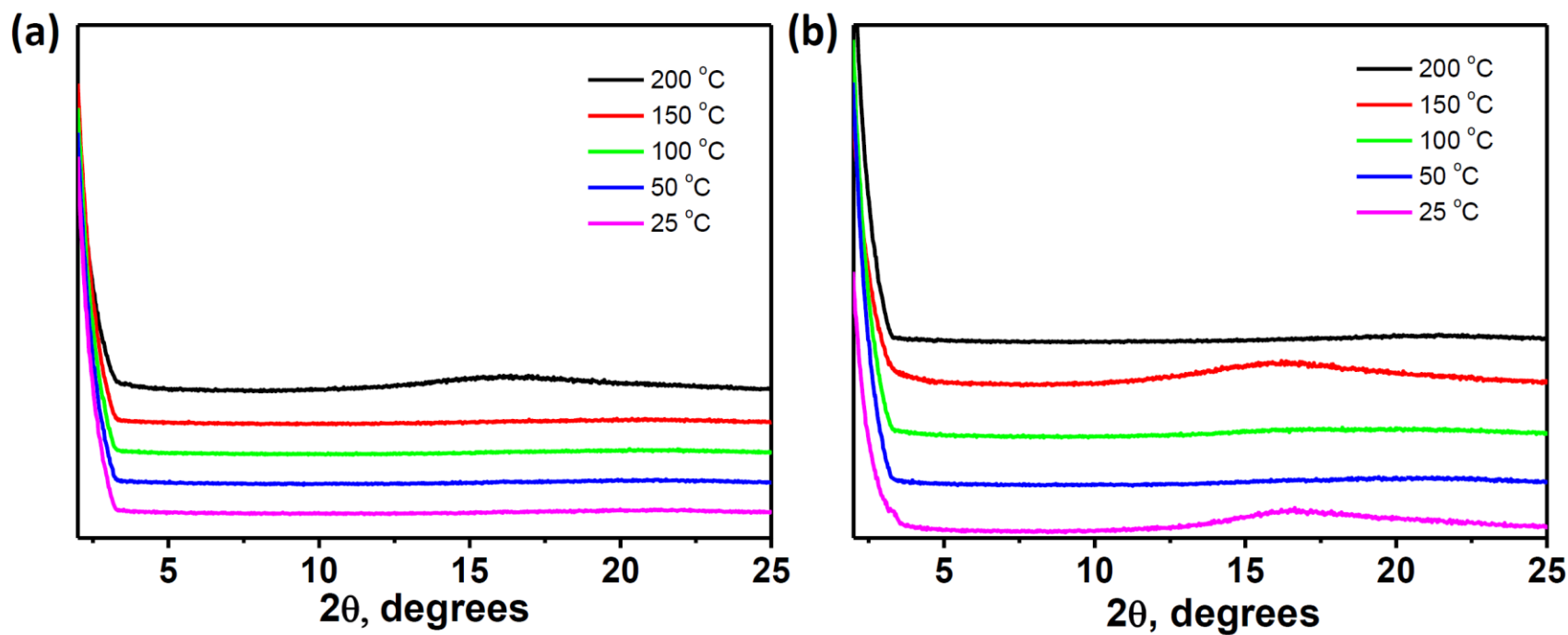
Identification code	<b>CS-1</b>
Empirical formula	C <sub>41</sub> H <sub>54</sub> N <sub>2</sub> O <sub>2</sub> S
Formula weight	638.92
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21
Unit cell dimensions	a = 18.357(11) Å      α = 90°. b = 12.475(7) Å      β = 115.78(2) °. c = 18.564(13) Å      γ = 90°.
Volume	3828(4) Å <sup>3</sup>
Z	4
Density (calculated)	1.109 mg/m <sup>3</sup>
Absorption coefficient	0.119 mm <sup>-1</sup>
F(000)	1384
Crystal size	0.396 x 0.189 x 0.114 mm <sup>3</sup>
Theta range for data collection	2.464 to 25.496°.
Index ranges	-22<=h<=22, -15<=k<=15, -22<=l<=22
Reflections collected	108710
Independent reflections	14206 [R(int) = 0.0836]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7455 and 0.6707
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	14206 / 511 / 934
Goodness-of-fit on F <sup>2</sup>	1.107
Final R indices [I>2sigma(I)]	R1 = 0.0703, wR2 = 0.1309
R indices (all data)	R1 = 0.1327, wR2 = 0.1616
Absolute structure parameter	0.03(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.354 and -0.201 e Å <sup>-3</sup>
CCDC No	2293176



**Fig. S11** DSC traces of first heating and cooling and second heating and cooling cycles of (a) **CS-1** and (b) **CS-2** recorded at a scan rate of 5 °C/minutes.



**Fig. S12** Polarizing optical photomicrograph of **CS-1** showing (a) characteristic oily streak texture of the N\* phase at 188 °C and (b) glassy N\* phase obtained at room temperature.



**Fig. S13** Small angle X-ray diffraction pattern of (a) CS-1 and (b) CS-2 at different temperatures.

## References

- 1 L. Wen, J. Sun, C. Li, C. Zhu, X. Zhang, Z. Wang, Q. Song, C. Lv and Y. Zhang, *New J. Chem.*, 2021, **45**, 11530-11535.
- 2 M. Kinami, B.R. Crenshaw, and C. Weder, *Chem. Mater.*, 2006, **18**, 4, 946–955.