Supporting Information

Reversible photoresponsive chiral liquid crystal and multistimuli responsive organogels based on a cholesterol-azobenzene dimesogen

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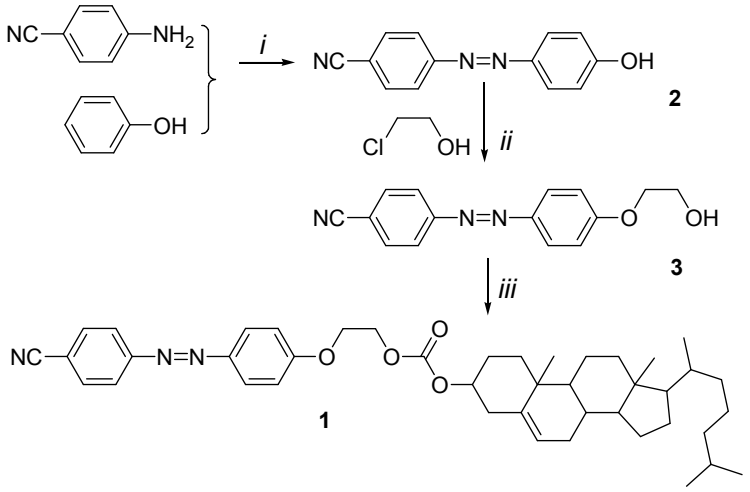
1. Materials synthesis and analytical data

Synthesis of the materials was performed as outlined in Scheme 1. Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 °C). Commercially available chemicals were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-DRX-500 spectrometer. Microanalysis were performed using a Leco CHNS-932 elemental analyzer. Column chromatography was performed with silica gel 60 (230-400 mesh) from Merck.



Scheme 1 Synthesis of compound **1**; *Reagents and conditions*: (*i*) HCl, $NaNO_2$, H_2O, 0~5 °C, 2 h, 80%; (*ii*) 2chlorethanol, K_2CO_3, KI, DMF, 90 °C, 24 h, 87%; (*iii*) toluene, pyridine, cholesteryl chloroformate, 100 °C, 9 h, 78%.

4-(4-Hydroxyphenyldiazenyl)benzonitrile 2[S1]

4-Aminobenzonitrile (1.0 g, 8.5 mmol) was dissolved in aqueous hydrochloric acid (1 M, 4.5 mL), the mixture was cooled to 0 °C. $NaNO_2$ (484 mg, 7.0 mmol) dissolved in water (3 mL) was added dropwise. The mixture was stirred at °C for 20 min and was filtered to obtain the diazonium salt solution. The diazonium salt solution was added dropwise into a mixture of phenol (796 mg, 8.5 mmol) and NaOH (1 g, 25 mmol) and water (9 mL), where the temperature was controlled to be 0 °C. After 2 h, the raw product was obtained by pouring the reaction solution into an excess of water. The precipitate was collected by filtration and washed with water. After drying, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1). Yield: 1.5 g, 80 %; yellow crystal. m.p.179-181°C. ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 7.95-7.91 (m, 4 H, Ar**H**), 7.81-7.78 (d, *J* = 4.8 Hz, 2 H, Ar**H**), 6.98-6.96 (d, *J* = 4.8 Hz, 2 H, Ar**H**), 5.45 (s, 1 H, ArO**H**).

General procedure for the synthesis of 3 [S2]

A mixture of **2** (223 mg, 1 mmol), K_2CO_3 (414 mg, 3 mmol) and KI (15 mg) was dissolved in DMF (10 mL), and chloroethanol (88 mg, 1.1 mmol) dissolved in DMF (4 mL) was added dropwise. The resulting mixture was stirred at 120 ^oC for 72 h. The reaction was stopped by addition of excess water to the mixture. The crude product was precipitated. The precipitate was filtered off and recrystallized twice from ethanol to give the product. Yield: 230 mg, 87 %; yellow crystal. m.p.160-162 °C. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 7.97-7.91 (m, 4 H, Ar**H**), 7.80-7.78 (d, *J* = 8.1 Hz, 2 H, Ar**H**), 7.07-7.04 (t, *J* = 8.7 Hz, 2 H, Ar**H**), 4.21-4.18 (t, *J* = 4.2 Hz, 2 H, OC$\mathbf{H_2}$C$\mathbf{H_2}$), 4.04-4.03 (t, *J* = 3.9 Hz, 2 H, OCH_2C$\mathbf{H_2}$), 2.05 (s, 1 H, CH_2O**H**).

Procedure for the synthesis of 1 [S3]

Under a nitrogen atmosphere, cholesteryl chloroformate (228 mg, 0.51 mmol) in dry toluene (3 mL) was added dropwise to a solution of compound **3** (134 mg, 0.50 mmol) and pyridine (2 mL) in toluene (5 mL), the mixture was refluxed for 9 h at 100 ^oC. After the reaction was complete (TLC), the mixture was cooled to room temperature, toluene was evaporated in *vacuo*. The residues was dissolved in CH_2Cl_2 (30 mL), and washed with 10 % HCl solution (3×30 mL), H_2O (3×30 mL), dried over $MgSO_4$ and the solvent was evaporated in *vacuo*. The crude product was purified by column chromatography (petroleum ether/dichlometane/ethyl acetate ＝15:5:1). Yield: 265 mg, 78 %; yellow crystal. ^{1}HNMR (500 MHz, $CDCl_3$): δ = 7.94-7.92 (m, 4 H, Ar**H**), 7.79-7.77 (d, *J* = 8.4 Hz, 2 H, Ar**H**), 7.04-6.99 (d，*J* = 8.8 Hz, 2 H, Ar**H**), 5.41-5.39 (m, 1 H, CH_2C=C**H**CH_2), 4.53-4.47 (m, 3 H, ArOC$\mathbf{H_2}$$CH_2$, OCOC**H**), 4.30-4.28 (t, *J* = 4.5 Hz, 2 H, $ArOCH_2$C$\mathbf{H_2}$), 2.42-2.36 (m, 2 H, C$\mathbf{H_2}$C=CHC$\mathbf{H_2}$), 2.05-0.82 (m, 38 H, other hydrogen in cholesteryl unit), 0.66 (s, 3 H, CC$\mathbf{H_3}$). ^{13}CNMR ($CHCl_3$, 125 MHz): δ = 162.2 (1C), 155.1 (1C), 154.8 (1C), 147.5 (1C), 139.7 (1C), 133.6

(2C), 125.9 (2C), 123.5 (2C), 129.0 (1C), 115.4 (2C), 113.8 (1C), 66.5, 65.9, 57.1, 50.4, 42.7, 40.1, 39.9, 38.4, 37.3~19.1(multi carbons in cholesteryl chains), 12.3; elemental analysis calcd (%) for $C_{43}H_{57}N_3O_4$ (679.93): C 75.96, H 8.45, N 6.18; found: C 75.81, H 8.47, N 6.17.

2. Methods

A Mettler heating stage (KER3100-08S) was used for polarizing optical microscopy (POM, XPN-203E). The phase transition temperature was tested by Differential Scanning Calorimetry were recorded with a DSC 200 F3 Maia calorimeter (NETZSCH), UV-vis absorption spectra were recorded on a UV-240 UV–visible spectrophotometer (Shimadzu, Japan). The UV irradiation was carried out by a 10 mW/cm^2 UV lamp with a 365 nm peak wavelength (LAMPLIC, UVEC-4IIB, DUANG DONG, CHINA). SEM and AFM experiments were carried out on a QUNT200 scanning electron microscopy (SEM, USA) and a SPA-400 atomic force microscope (AFM, JAPAN) respectively. All pictures were taken digitally. For the sample preparation, the gel was firstly placed on an aluminium foil and dried under vacuum. The aluminium foil was further coated with a thin layer of gold and observed by scanning electron microscopy. The dry gel on an aluminium foil was also investigated by AFM.

3. Additional data

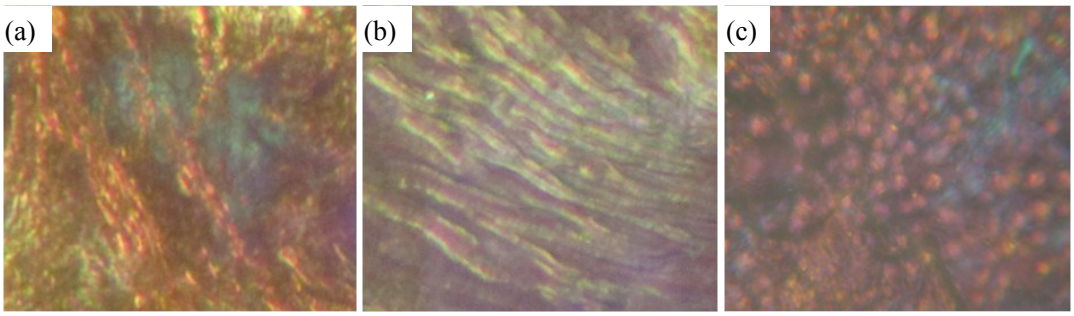


Fig. S1 The structure of **1** was observed by POM in DMF (1 mg/ml): (a) fibrous structures of gel, (b) filamentous structure between two thin ordinary glass plates slides, (c) vesicular structures of solution.

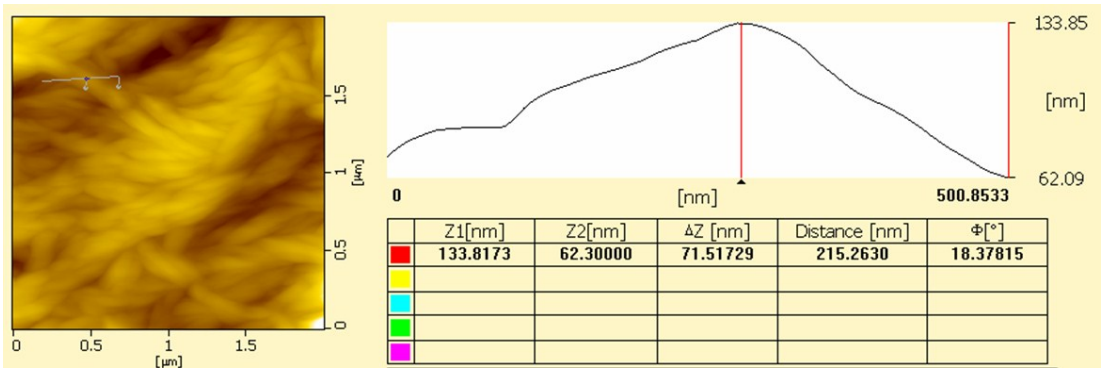


Fig. S2 AFM image of the xerogel of the azobenzene compound **1** (the xerogel formed by **1** in DMF), the approximate diameter of the fibers is 72 nm.

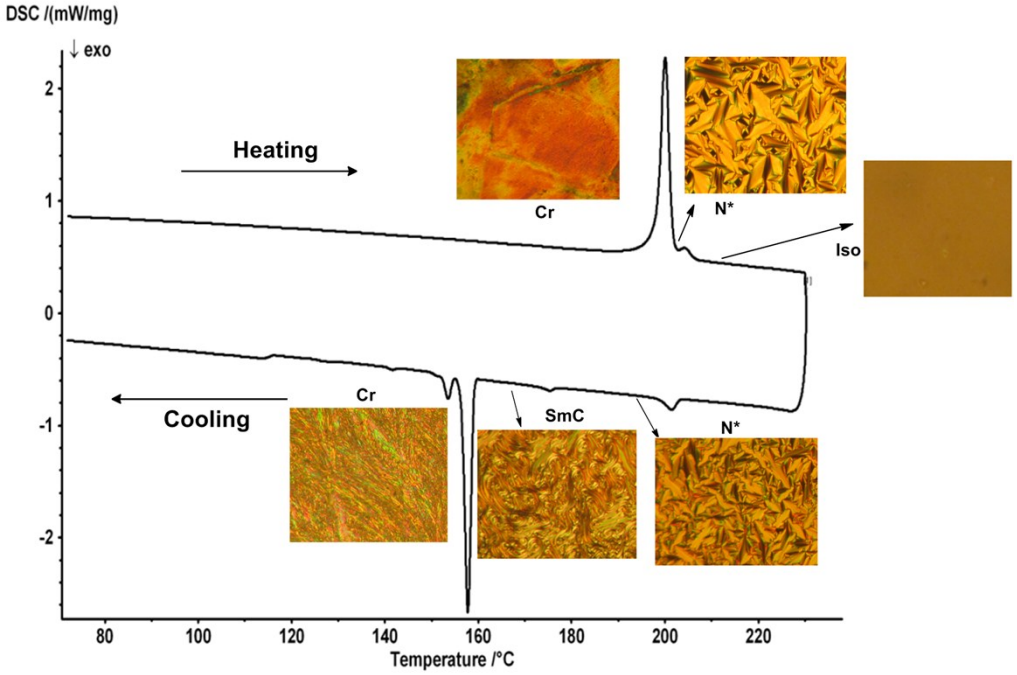


Fig. S3 DSC heating and cooling curves of **1** (5K min^{-1}); the textures show phase types correspounding to the temperature ranges.

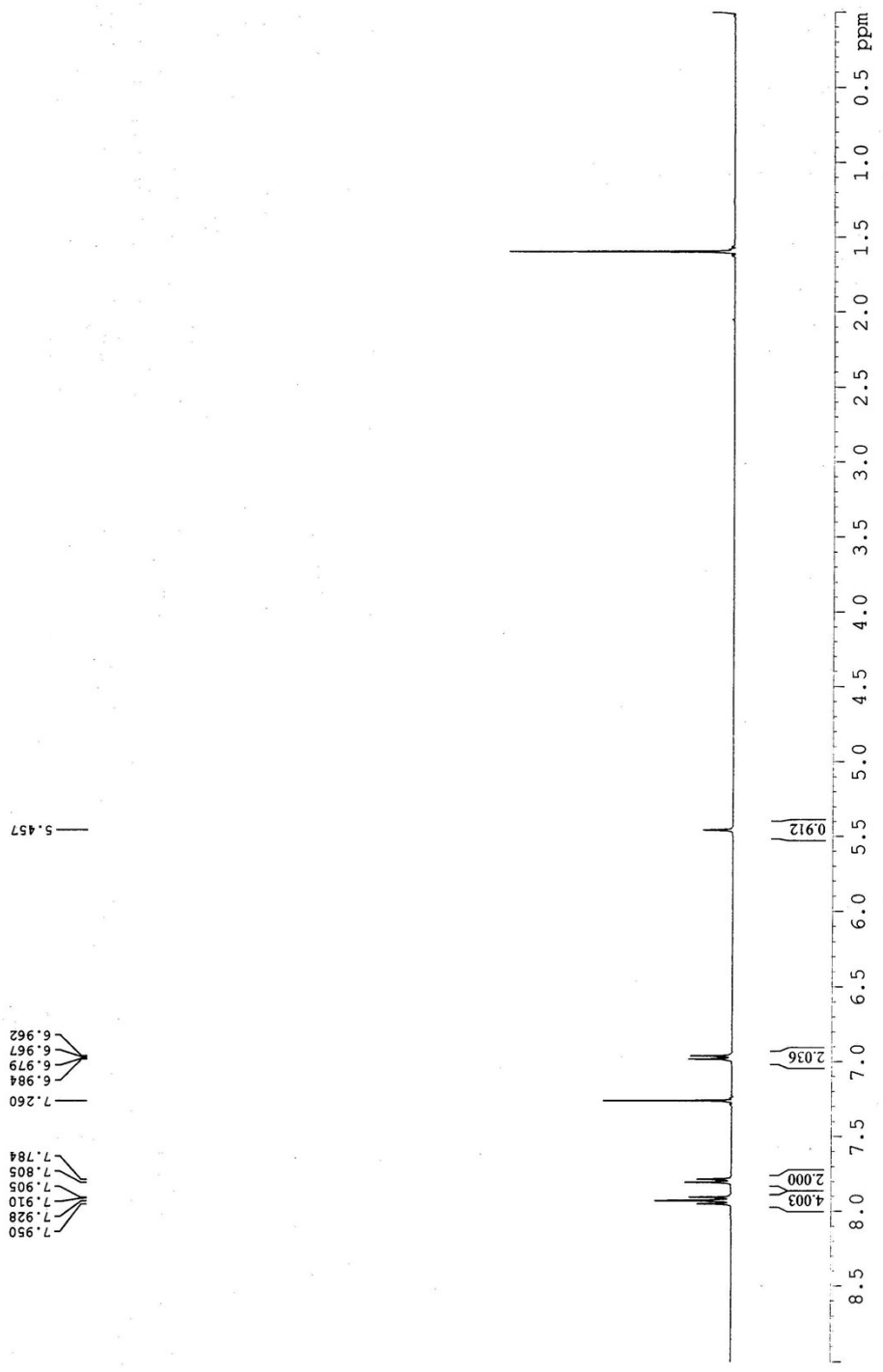


Fig. S4 ^{1}H-NMR spectrum of compound **2** (400 MHz in $CDCl_3$)

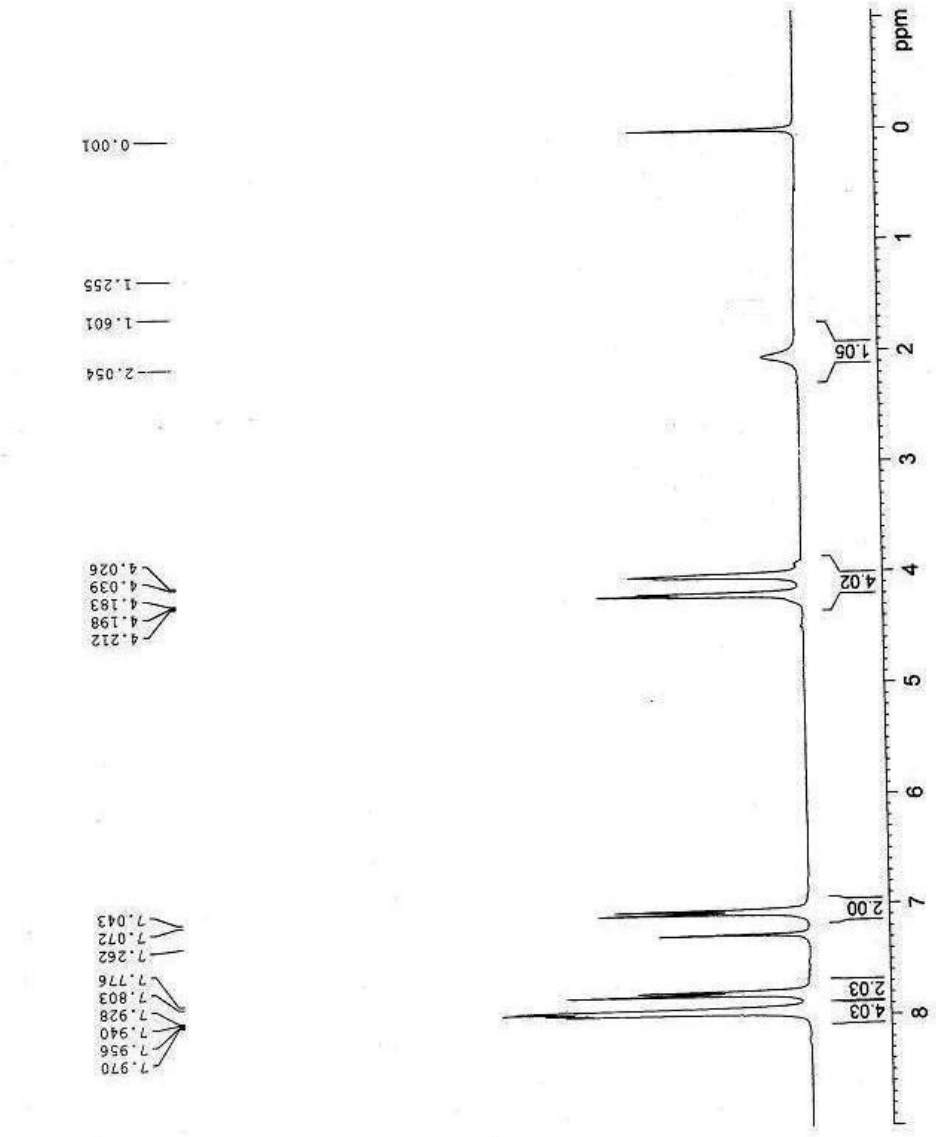
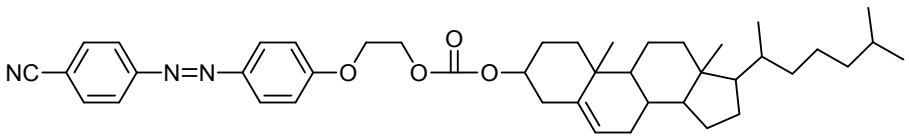


Fig. S5 ^{1}H-NMR spectrum of compound **3** (300 MHz in $CDCl_3$)



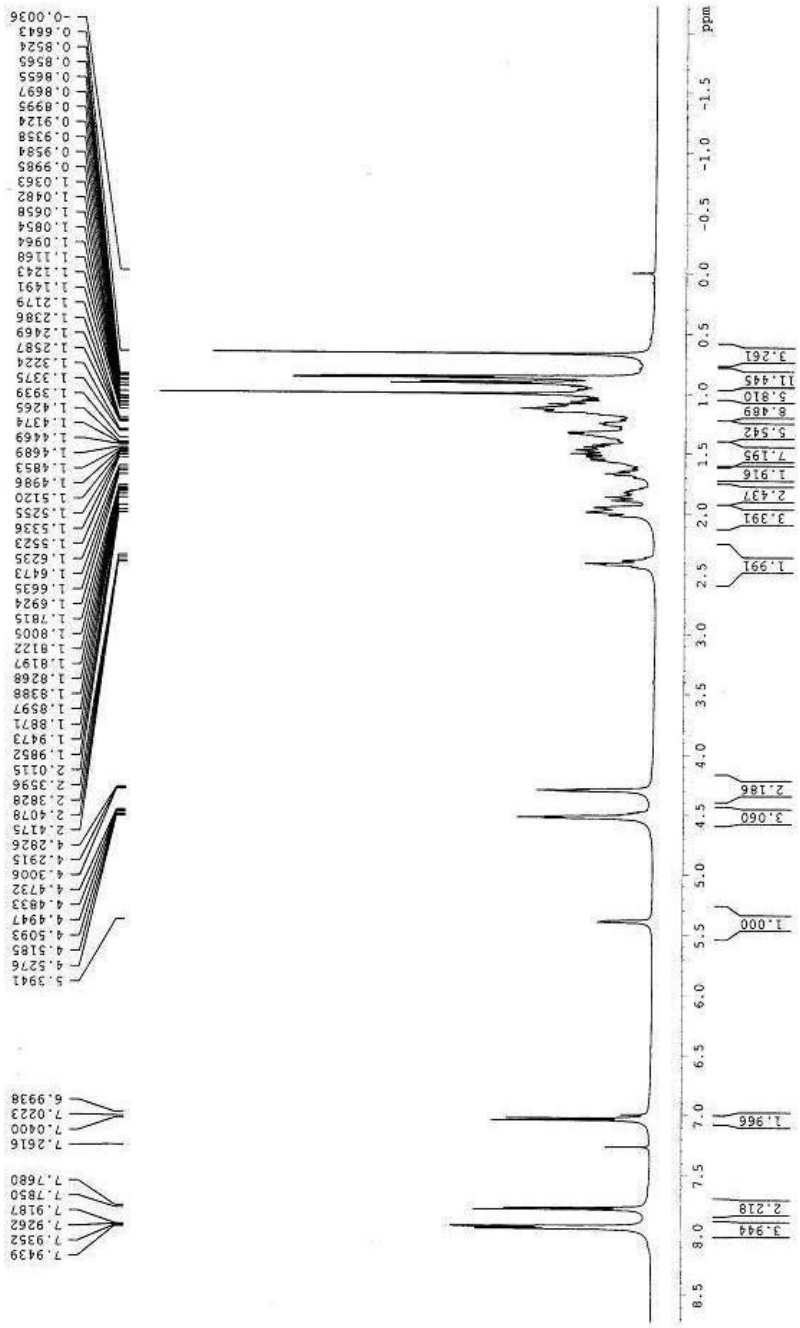


Fig. S6 ^{1}H-NMR spectrum of compound **1** (500 MHz in $CDCl_3$)

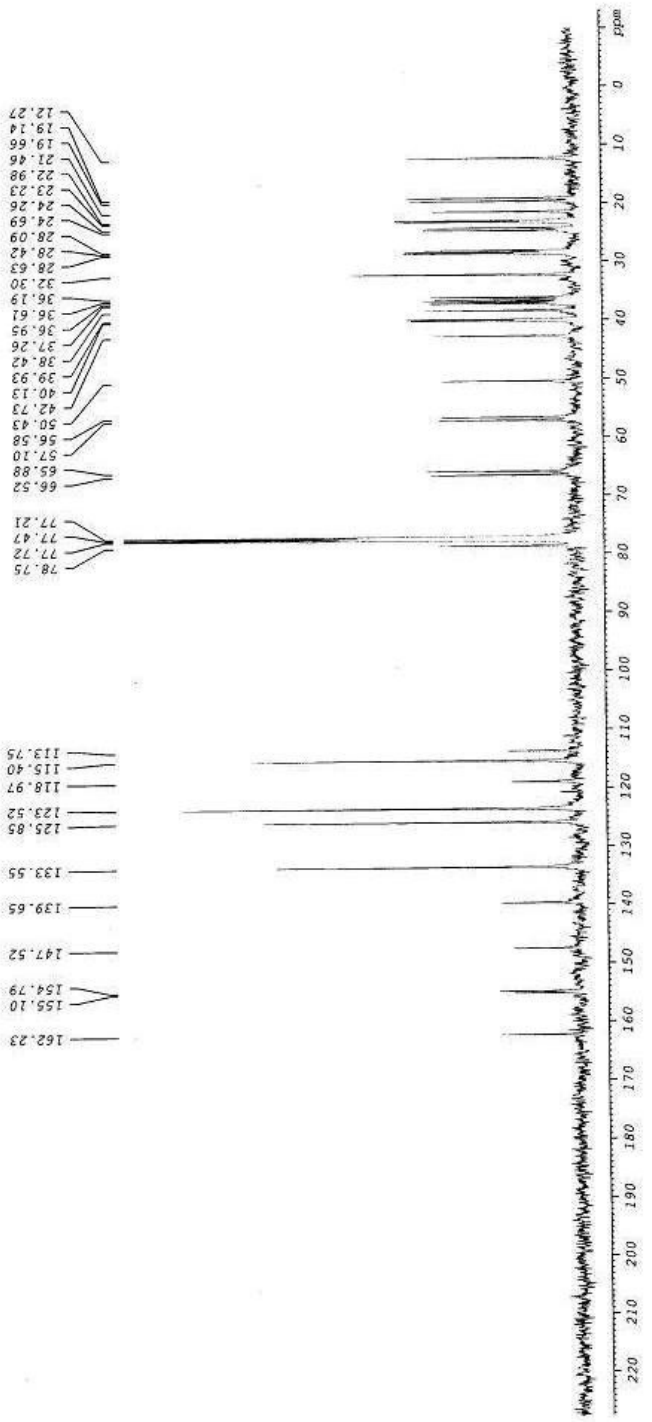


Fig. S7 ^{13}C-NMR spectrum of compound **1** (125 MHz in $CDCl_3$)

4. References

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