

## Supporting Information

# Liquid Crystalline Oligomers Derived from Cholesterol: Synthesis and Columnar Mesomorphism

Jie Xiong<sup>a</sup>, Xiaoru Lin<sup>a</sup>, Hongyu Guo<sup>a\*</sup>, Fafu Yang<sup>a,b,c\*</sup>, and Jianbin Lai<sup>a</sup>

<sup>a</sup>College of Chemistry and Chemical Engineering, Fujian Normal University, Fuzhou 350007, China

<sup>b</sup>Fujian Key Laboratory of Polymer Materials, Fuzhou 350007, P.R. China

<sup>c</sup>Fujian provincial Key Laboratory of Advanced Materials Oriented Chemical Engineering, Fuzhou 350007, P. R. China

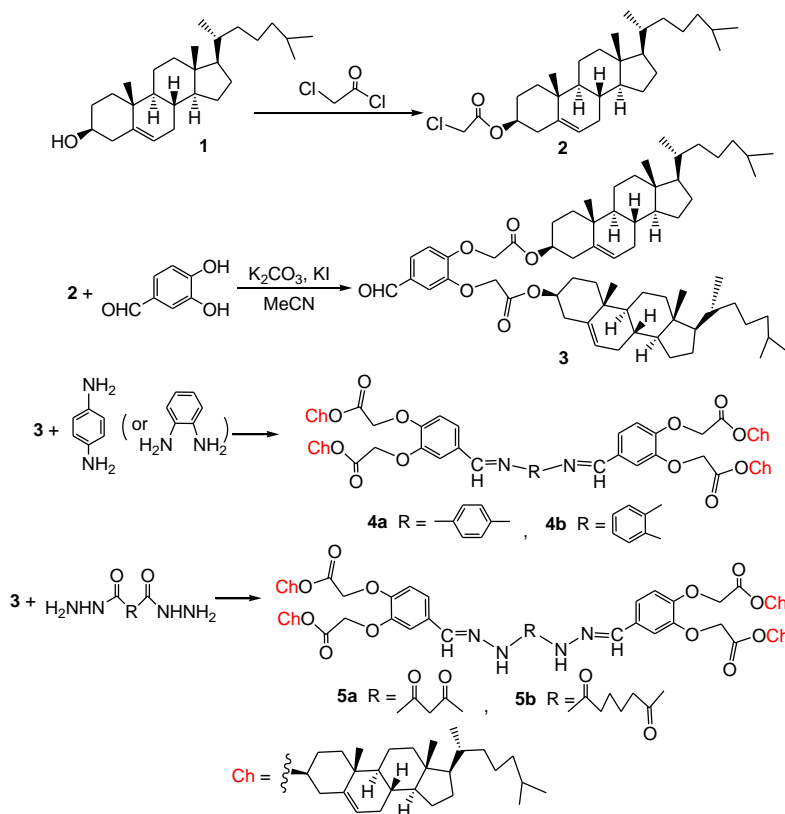
E-mail: yangfafu@fjnu.edu.cn

## 1. General

1. All chemical reagents were obtained from commercial suppliers and used without further purification. The other organic solvents and inorganic reagents were purified according to standard anhydrous methods before use. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker-ARX 400 instrument at 25°C. Chemical shifts are reported in ppm, using tetramethylsilane (TMS) as internal standard. MS spectra were obtained from Bruker MALDI-TOF mass spectrometer. POM (Leica DMRX) was used along with a hot stage (Linkam THMSE 600) to examine phase transitions. Thermal analysis of the materials was carried out using DSC (Thermal Analysis Q100) at a scanning rate of 10°C/min under N<sub>2</sub> atmosphere. XRD experiments were performed on SEIFERT-FPM (XRD7), using Cu K $\alpha$  1.5406Å as the radiation source with 40 kV, 30 mA power. Compound **2** was synthesized by the literature (*Tetrahedron Lett.*, **2015**, 56, 866-870).

---

\* Corresponding author. Tel.: +0086-591-83465225; fax: +0086-591-83465225; e-mail: yangfafu@fjnu.edu.cn



## 2 The synthetic procedure of compound 3

Under N<sub>2</sub> atmosphere, a mixture of compound **2** (0.462g, 1mmol), 3, 4-dihydroxybenzaldehyde (0.065g, 0.47mmol), K<sub>2</sub>CO<sub>3</sub>(0.21g, 1.5mmol) and KI(0.1g, 0.6 mmol) was stirred and refluxed in 50 mL of dry acetonitrile for 24h. TLC detection indicated the disappearance of starting materials. Then the solvent was evaporated under reduced pressure. The residue was treated with 50 mL distilled water and subsequently was extracted with 3×20 mL of CHCl<sub>3</sub>. The CHCl<sub>3</sub> solution was concentrated and was further purified by recrystallization with CH<sub>3</sub>OH:CH<sub>2</sub>Cl<sub>2</sub> (4:1). Compound **3** was obtained as white solid in yield of 65%. Compound **3**: FT-IR(KBr),  $\nu/\text{cm}^{-1}$ : 2933(C-H), 1746(C=O),1688(C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm: 9.84(s, 1H, CHO), 7.48(d, *J*=8.0Hz, 1H, ArH), 7.39(s, 1H, ArH), 6.93(d, *J*=8.0Hz, 1H, ArH), 5.37(bs, 2H, C=CH), 4.74-4.79 (m, 6H, OCH<sub>2</sub> and OCH), 0.62-2.30(m, 86H, CH, CH<sub>2</sub> and CH<sub>3</sub>).

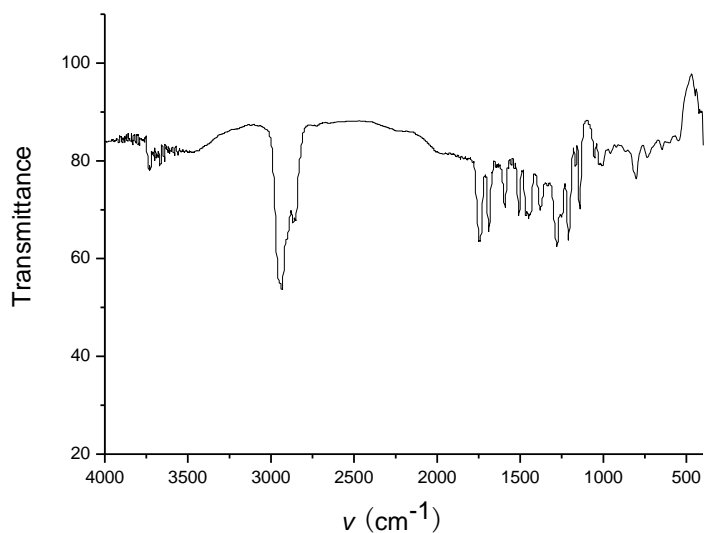


Figure S1 The FT-IR spectrum of compound **3**

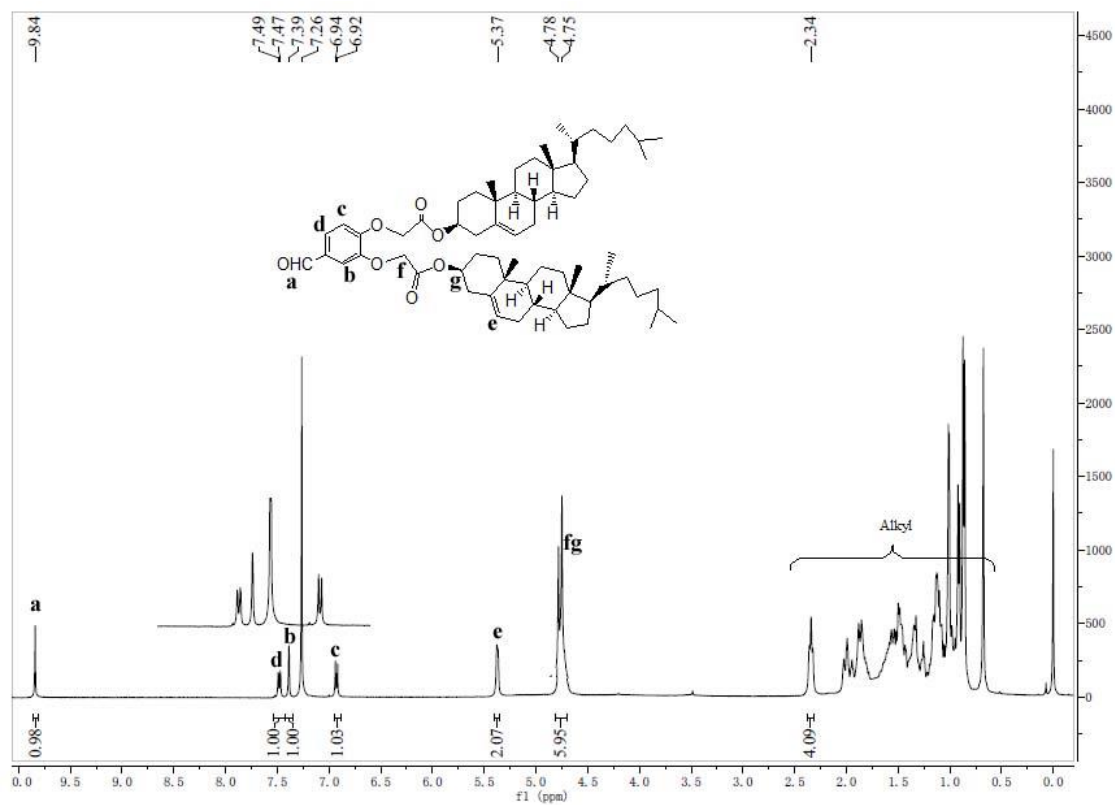


Figure S2 The  $^1\text{H}$  NMR spectrum of compound **3**

### 3 The synthetic procedure of compound **4a**

The mixture of compound **3** (0.30g, 0.3 mmol) and *p*-phenylenediamine (0.016g, 0.15 mmol) were refluxed in 25 mL of  $\text{CHCl}_3/\text{MeOH}$  (1:3, V:V) by using 0.3 mL of glacial acetic acid as catalyst under  $\text{N}_2$

atmosphere for 12h. TLC detection suggested the disappearance of compound **3**. After cooling, the solution was stored in refrigerator overnight and the white precipitates were obtained. Then the white precipitates were filtered and washed with methanol. The crude product was purified by recrystallization with CH<sub>3</sub>OH:CH<sub>2</sub>Cl<sub>2</sub> (5:1). The compound **4a** was obtained as white solid in the yield of 82%.

Compound **4a**: FT-IR(KBr),  $\nu/\text{cm}^{-1}$ : 2939(C-H), 1752(C=O), 1601(C=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm: 8.67(s, 2H, CH=N), 7.46(d,  $J=8.0\text{Hz}$ , 2H, ArH), 7.36(s, 2H, ArH), 7.28(s, 4H, ArH), 6.91(d,  $J=8.0\text{Hz}$ , 2H, ArH), 5.34(bs, 4H, C=CH), 4.70-4.77 (m, 12H, OCH<sub>2</sub> and OCH), 0.61-2.34(m, 172H, CH, CH<sub>2</sub> and CH<sub>3</sub>).

<sup>13</sup>C-NMR(100MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 168.10, 167.37, 153.03, 148.36, 139.30, 130.79, 126.74, 122.83, 122.23, 121.62, 115.57, 113.63, 75.65, 75.33, 66.41, 66.17, 56.51, 56.08, 49.86, 42.24, 39.44, 36.11, 35.70, 27.92, 23.75, 22.46, 20.95, 19.20, 18.63, 11.77.

HR-MS:  $m/z$  calculated for C<sub>136</sub>H<sub>200</sub>N<sub>2</sub>O<sub>12</sub> 2093.4766 [M+K]<sup>+</sup>; found 2093.4744.

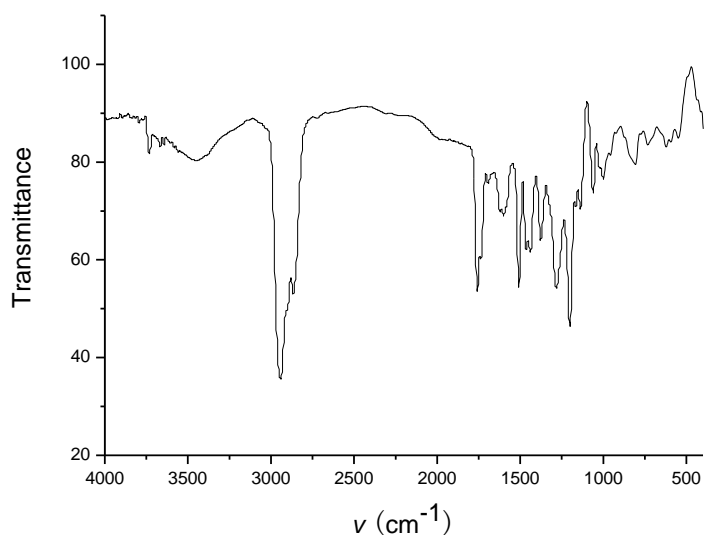


Figure S3 The FT-IR spectrum of compound **4a**

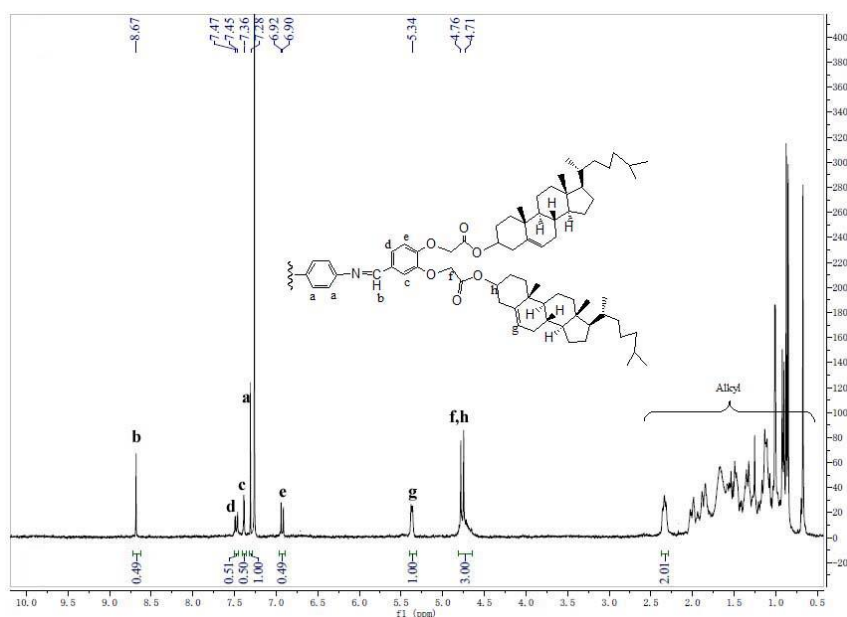


Figure S4 The  $^1\text{H}$  NMR spectrum of compound **4a**

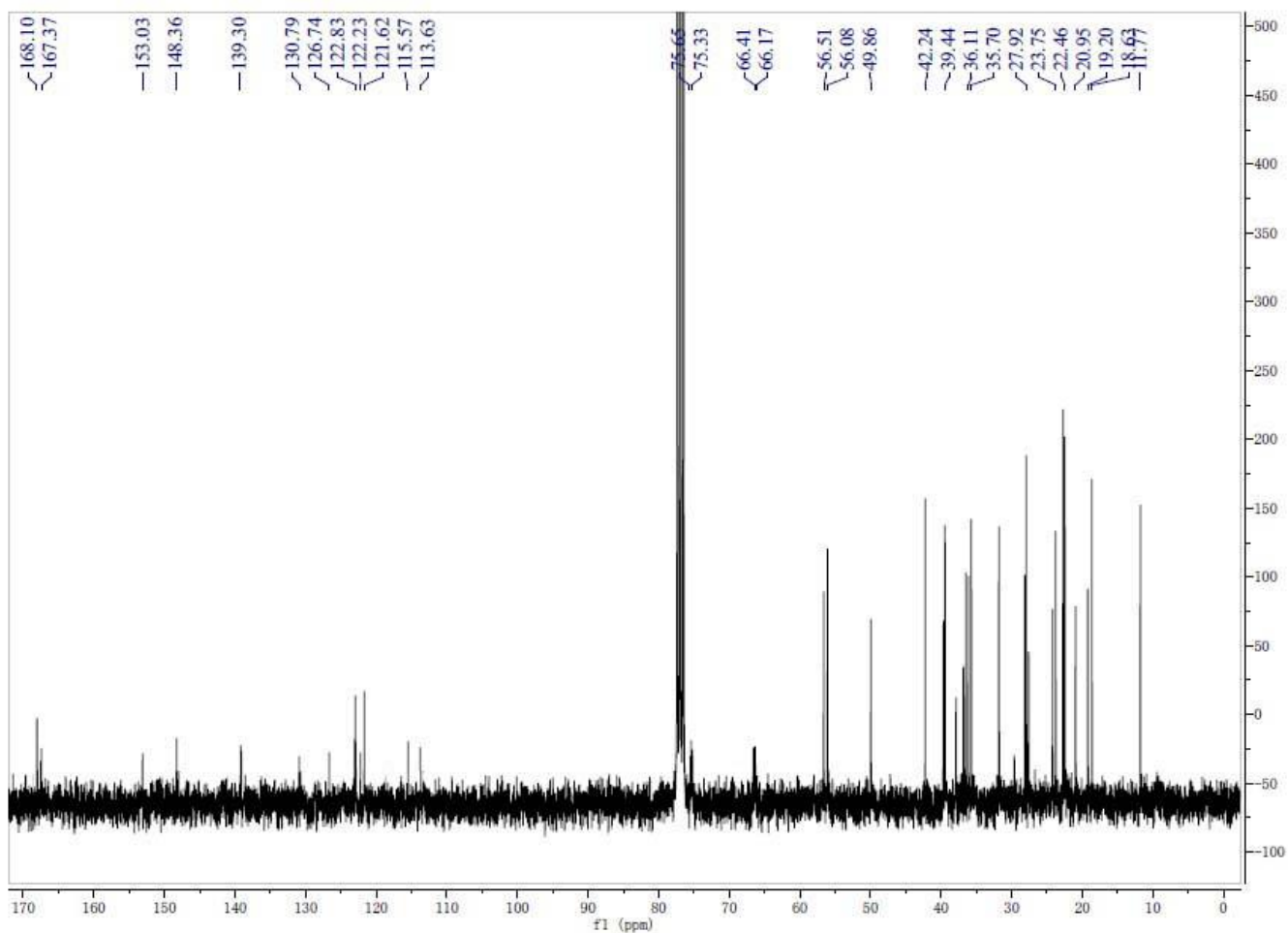


Figure S5 The  $^{13}\text{C}$  NMR spectrum of compound **4a**

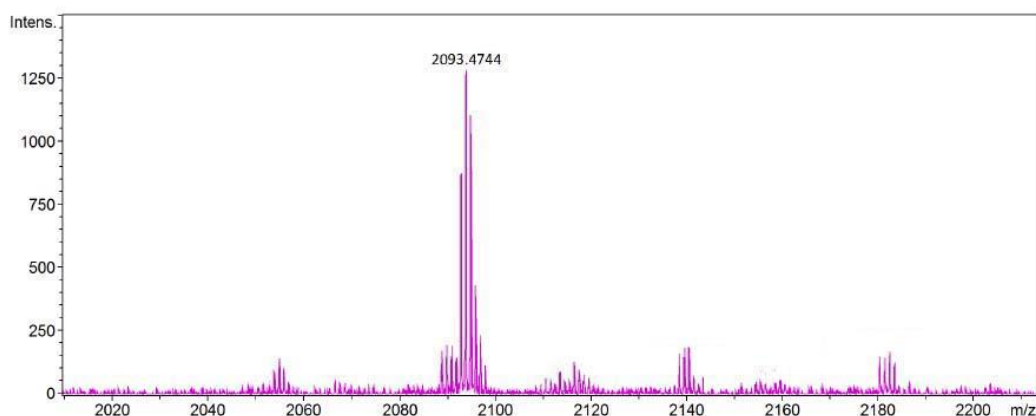


Figure S6 The HR-MS spectrum of compound **4a**

#### 4 The synthetic procedure of compound **4b**

Under N<sub>2</sub> atmosphere, the mixture of compound **3** (0.30g, 0.3 mmol) and *o*-phenylenediamine (0.016g, 0.15 mmol) were refluxed by using 0.3 mL of glacial acetic acid as catalyst in 25 mL of CHCl<sub>3</sub>/EtOH (1:4, V:V) for 12h. TLC detection suggested the disappearance of compound **3**. After cooling, the solution was stored in refrigerator overnight and the white precipitates were obtained. Then the white precipitates were filtered and washed with methanol. The crude product was purified by recrystallization with CH<sub>3</sub>OH:CH<sub>2</sub>Cl<sub>2</sub> (5:1). The compound **4b** was obtained as white solid in the yield of 75%.

Compound **4b**: FT-IR(KBr),  $\nu/\text{cm}^{-1}$ : 2944(C-H), 1757(C=O), 1606(C=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm: 8.02(bs, 2H, CH=N), 7.78 (d, 2H, *J*=8.8Hz, ArH), 7.71 (d, 2H, *J*=8.8Hz, ArH), 7.46(bs, 2H, ArH), 7.20(d, 2H, *J*=8.0Hz, ArH), 6.93(d, 2H, *J*=8.0Hz, ArH), 5.38(bs, 4H, C=CH), 5.04(bs, 4H, OCH), 4.75 (bs, 8H, OCH<sub>2</sub>), 0.62-2.49(m, 172H, CH, CH<sub>2</sub> and CH<sub>3</sub>).

<sup>13</sup>C-NMR(100MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 168.77, 167.90, 150.75, 149.37, 148.22, 147.89, 139.15, 126.66, 123.04, 122.71, 114.24, 113.40, 75.34, 75.24, 66.40, 66.05, 56.62, 56.14, 49.94, 42.24, 39.44, 36.48, 31.81, 28.13, 27.92, 24.19, 22.71, 22.46, 19.20, 18.64, 11.77.

HR-MS: m/z calculated for C<sub>136</sub>H<sub>200</sub>N<sub>2</sub>O<sub>12</sub> 2093.4766 [M+K]<sup>+</sup>; found 2093.4761.

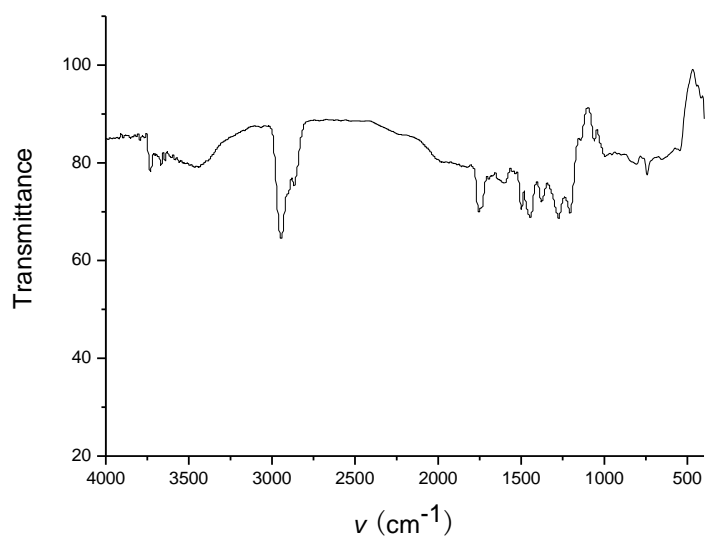


Figure S7 The FT-IR spectrum of compound **4b**

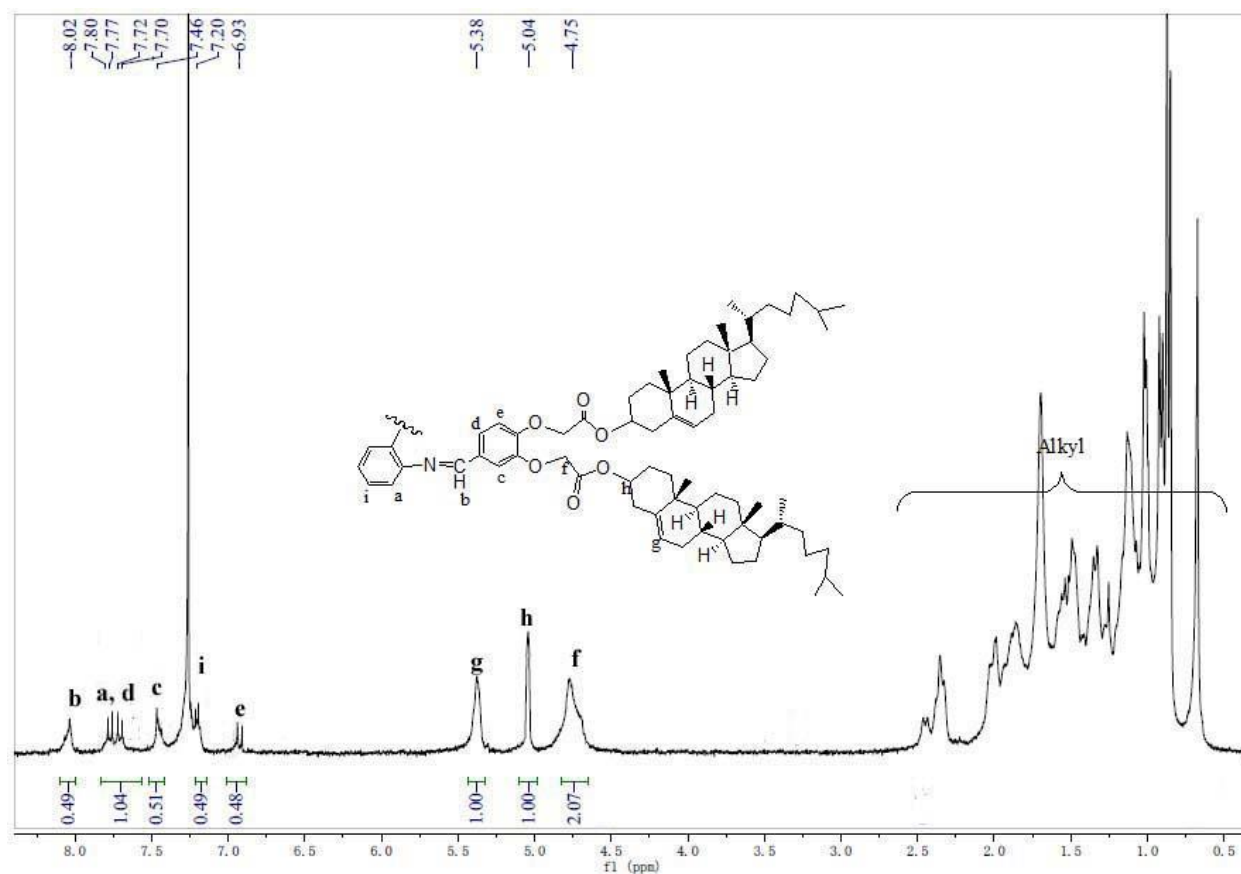


Figure S8 The  $^1\text{H}$  NMR spectrum of compound **4b**

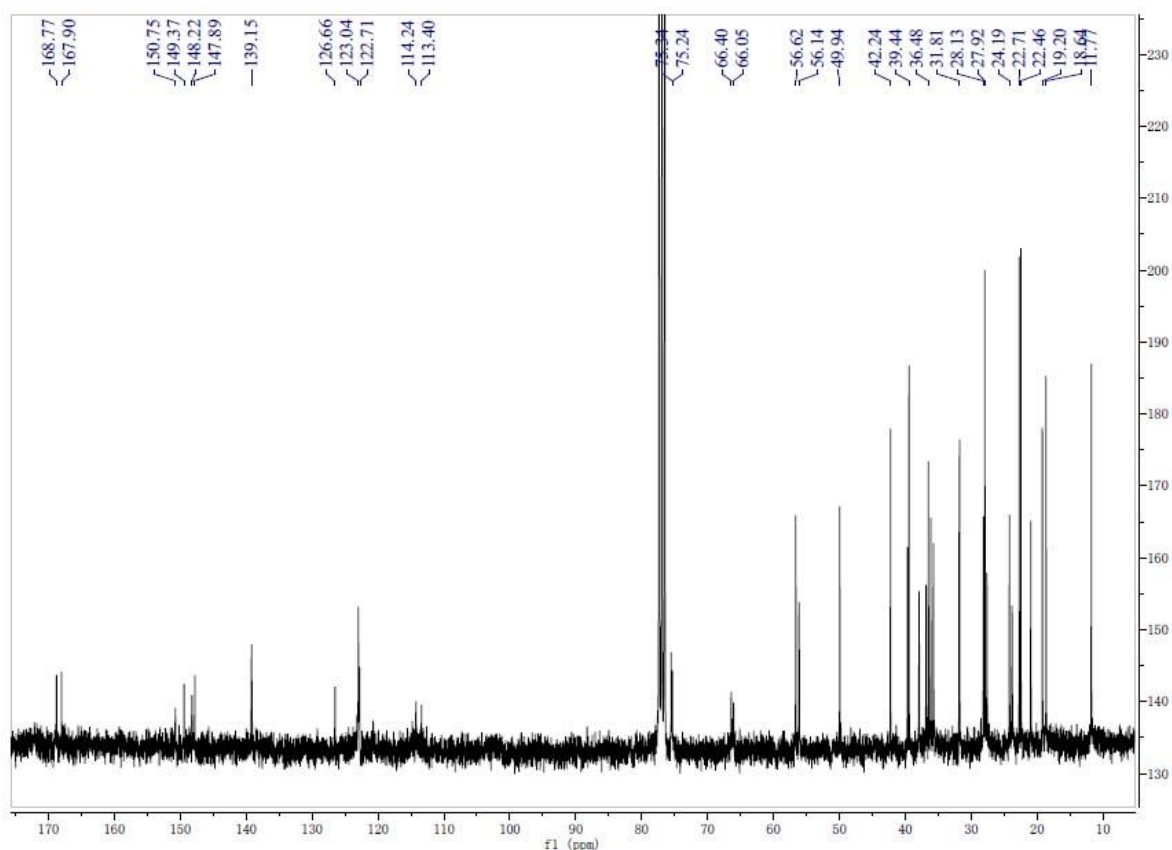


Figure S9 The  $^{13}\text{C}$  NMR spectrum of compound **4b**

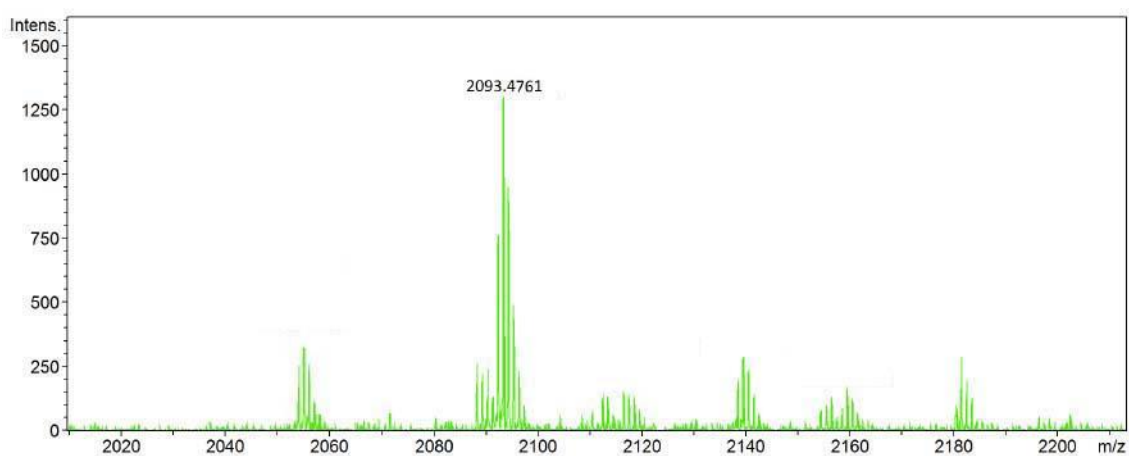


Figure S10 The HR-MS spectrum of compound **4b**

## 5 The synthetic procedure of compound **5a**

Under  $\text{N}_2$  atmosphere, the mixture of compound **3** (0.30g, 0.3 mmol) and malonic dihydrazide (0.02g, 0.15 mmol) were refluxed by using 0.3 mL of glacial acetic acid as catalyst in 25 mL of  $\text{CHCl}_3/\text{EtOH}$  (1:4, V:V) for 12h. TLC detection suggested the disappearance of compound **3**. After cooling, the mixture was stored in refrigerator overnight and the white precipitates were obtained. Then the white



precipitates were filtered and washed with methanol. The crude product was purified by recrystallization with CH<sub>3</sub>OH:CH<sub>2</sub>Cl<sub>2</sub> (5: 1). The compound **5a** was obtained as white solid in the yield of 78%.

Compound **5a**: FT-IR(KBr),  $\nu/\text{cm}^{-1}$ : 2944(C-H), 1760(C=O), 1693(C=O), 1602(C=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm: 8.09(s, 2H, CH=N), 7.61(s, 2H, NH), 7.47(d,  $J=12.0\text{Hz}$ , 2H, ArH), 7.38(s, 2H, ArH), 6.93(d,  $J=12.0\text{Hz}$ , 2H, ArH), 5.36(bs, 4H, C=CH), 4.70-4.78 (m, 12H, OCH<sub>2</sub> and OCH), 3.49(s, 2H, COCH<sub>2</sub>CO), 0.61-2.34(m, 172H, CH, CH<sub>2</sub> and CH<sub>3</sub>).

<sup>13</sup>C-NMR(100MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 169.32, 167.82, 150.50, 149.52, 148.27, 139.11, 128.33, 128.19, 122.78, 114.41, 113.27, 75.30, 75.18, 66.59, 66.48, 56.52, 56.03, 49.93, 42.24, 39.65, 36.12, 35.72, 31.77, 28.14, 27.92, 27.60, 24.20, 20.95, 19.20, 11.77.

HR-MS:  $m/z$  calculated for C<sub>133</sub>H<sub>200</sub>N<sub>4</sub>O<sub>14</sub> 2101.4987 [M+Na]<sup>+</sup>; found 2101.4907.

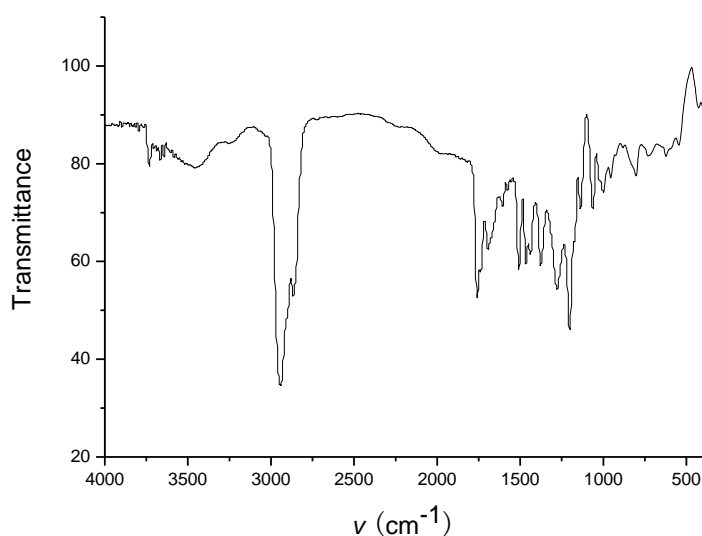
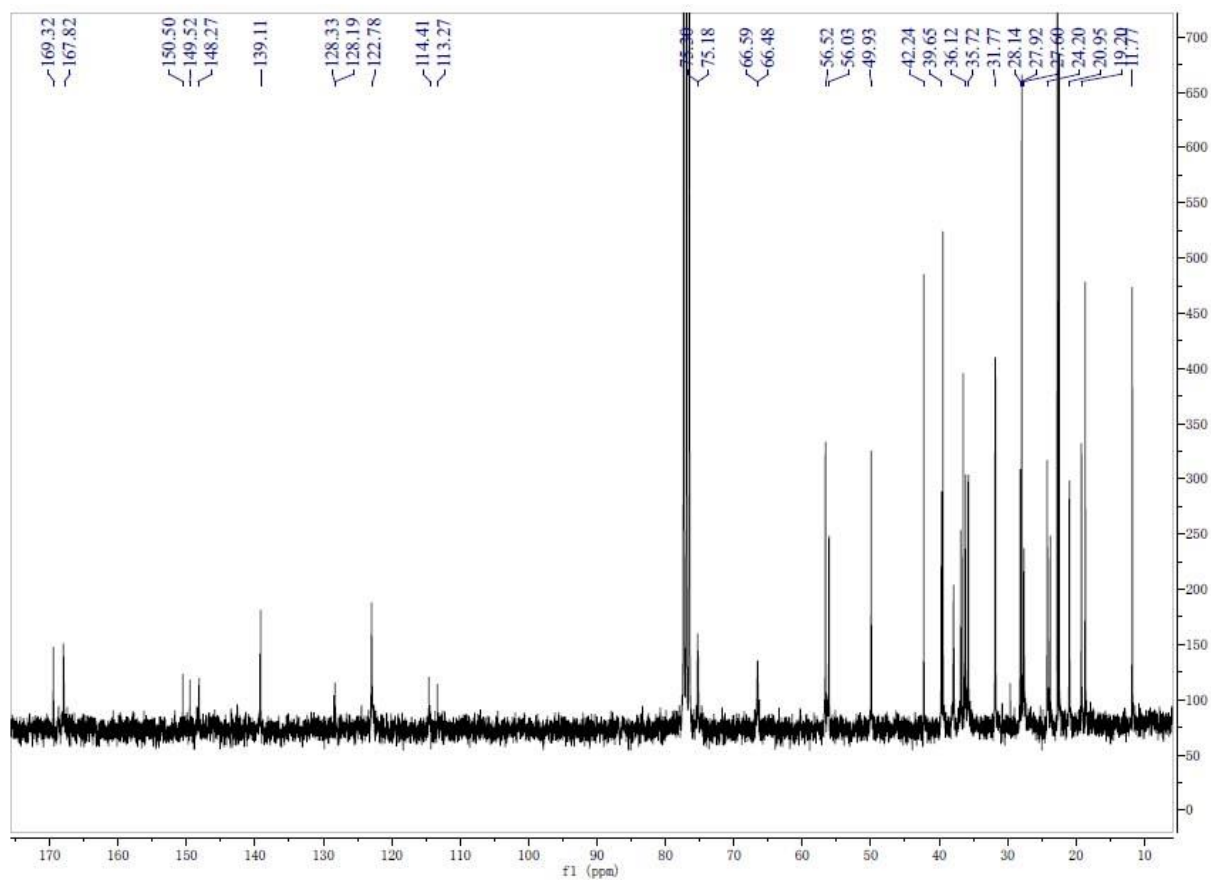
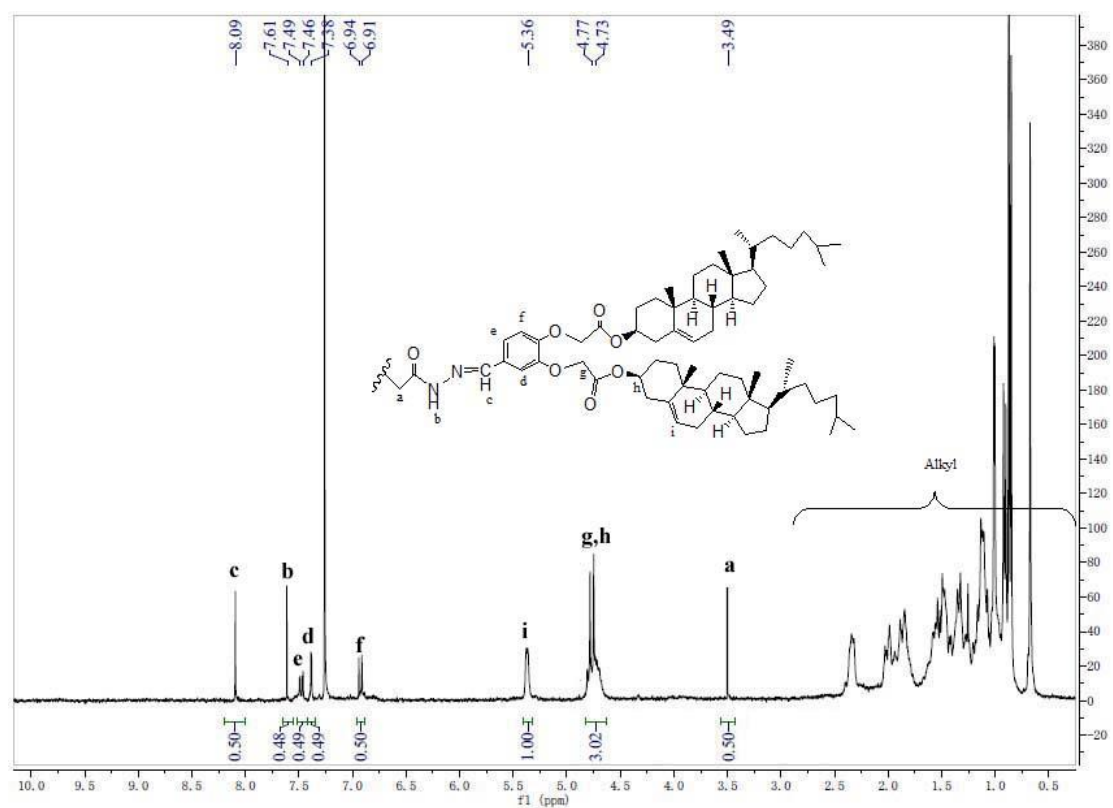


Figure S11 The FT-IR spectrum of compound **5a**



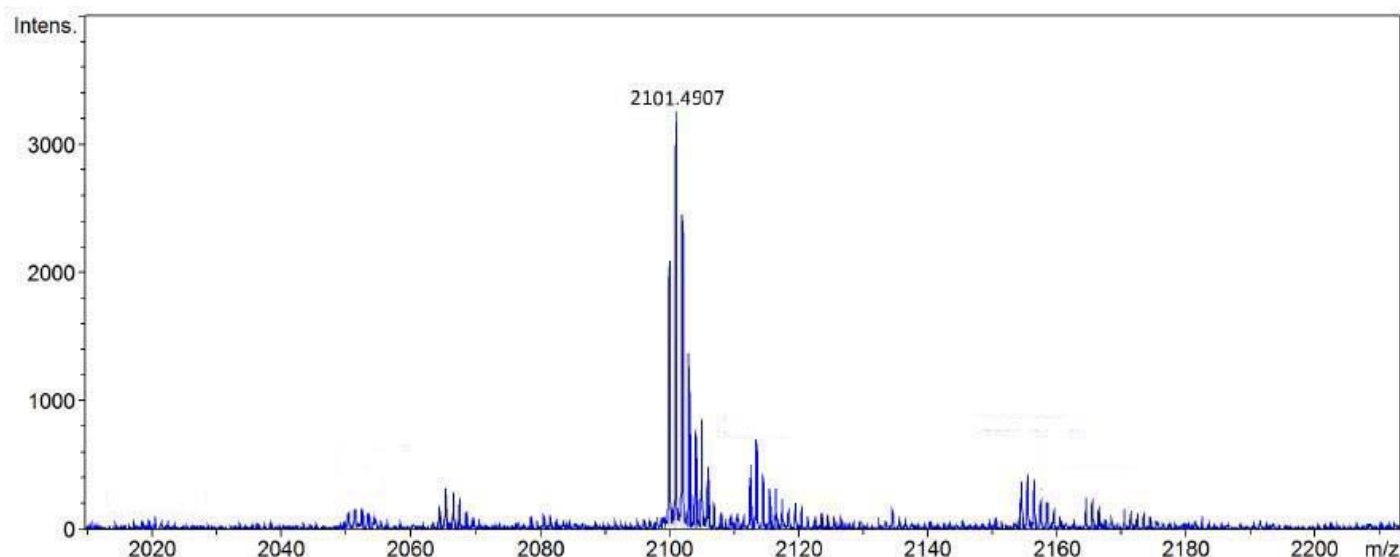


Figure S14 The HR-MS spectrum of compound **5a**

## 6 The synthetic procedure of compound **5b**

Under N<sub>2</sub> atmosphere, the mixture of compound **3** (0.30g, 0.3 mmol) and adipic dihydrazide (0.026g, 0.15 mmol) were refluxed by using 0.3 mL of glacial acetic acid as catalyst in 25 mL of CHCl<sub>3</sub>/EtOH (1:4, V:V) for 12h. TLC detection suggested the disappearance of compound **3**. After cooling, the mixture was stored in refrigerator overnight and the white precipitates formed. Then the white precipitates were filtered and washed with methanol. The crude product was purified by recrystallization with CH<sub>3</sub>OH:CH<sub>2</sub>Cl<sub>2</sub> (5: 1). The compound **5b** was obtained as white solid in the yield of 72%.

Compound **5b**: FT-IR(KBr),  $\nu/\text{cm}^{-1}$ : 2942(C-H), 1760(C=O), 1690(C=O), 1614(C=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm: 8.66(s, 2H, CH=N), 7.59 (s, 2H, NH), 7.47(d,  $J=12.0\text{Hz}$ , 2H, ArH), 7.38(s, 2H, ArH), 6.93(d,  $J=12.0\text{Hz}$ , 2H, ArH), 5.37(bs, 4H, C=CH), 4.70-4.79 (m, 12H, OCH<sub>2</sub> and OCH), 0.61-2.34(m, 180H, CH, CH<sub>2</sub> and CH<sub>3</sub>).

<sup>13</sup>C-NMR(100MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 168.28, 167.91, 149.69, 1448.09, 139.40, 139.19, 128.19, 122.95, 122.41, 114.64, 113.24, 75.26, 75.19, 66.88, 66.52, 56.61, 56.11, 49.94, 39.65, 39.44, 36.48, 36.12, 35.72, 27.92, 27.62, 23.79, 22.71, 22.47, 19.20, 11.77.

HR-MS: m/z calculated for C<sub>136</sub>H<sub>206</sub>N<sub>4</sub>O<sub>14</sub> 2143.5456 [M+Na]<sup>+</sup>; found 2143.5487.

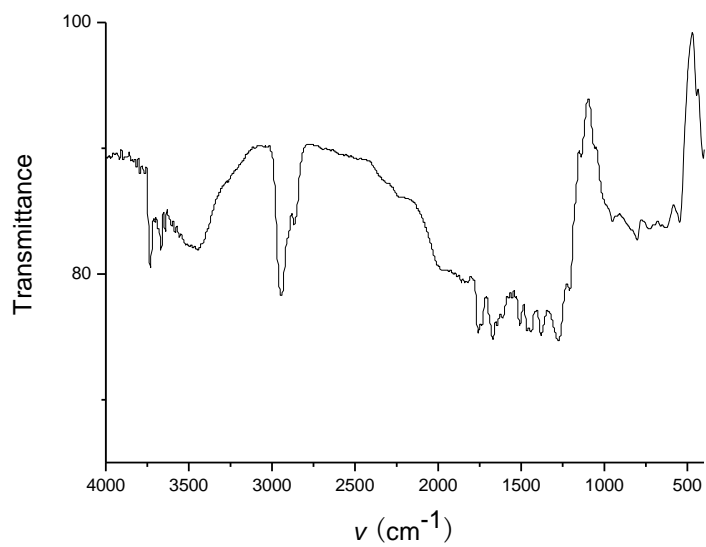


Figure S15 The FT-IR spectrum of compound **5b**

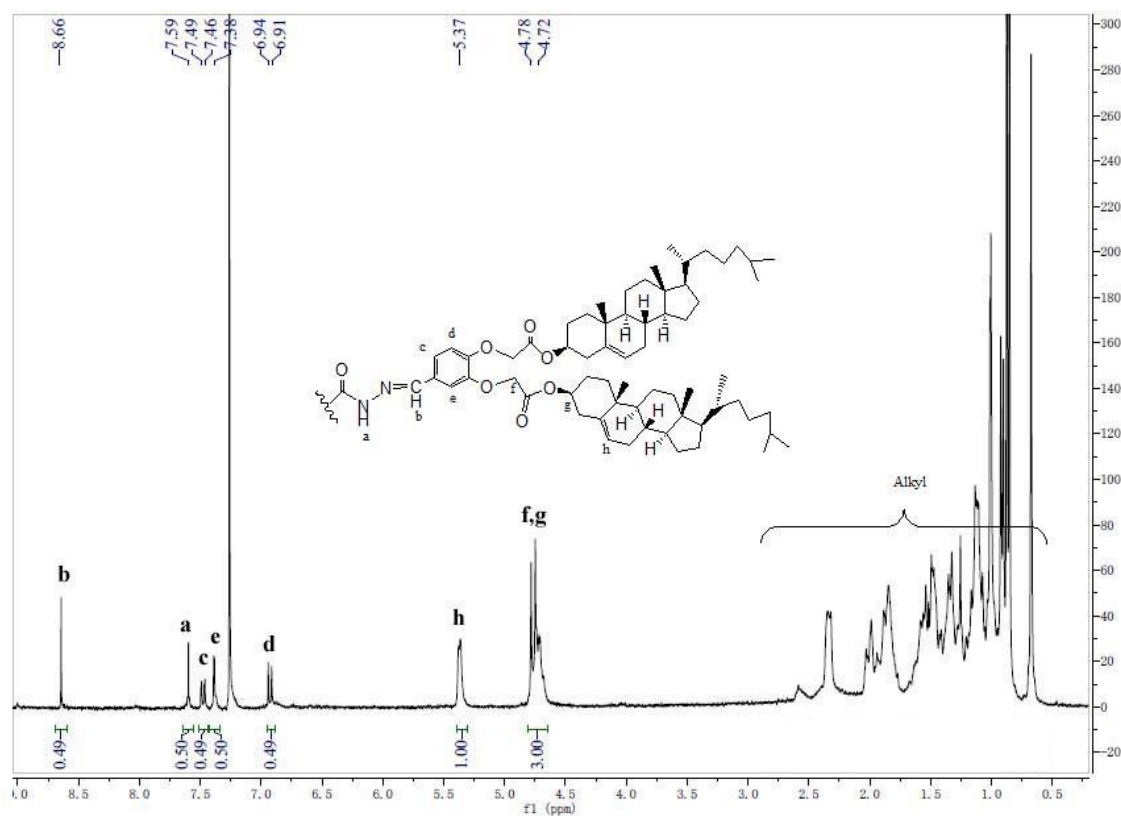


Figure S16 The <sup>1</sup>H NMR spectrum of compound **5b**

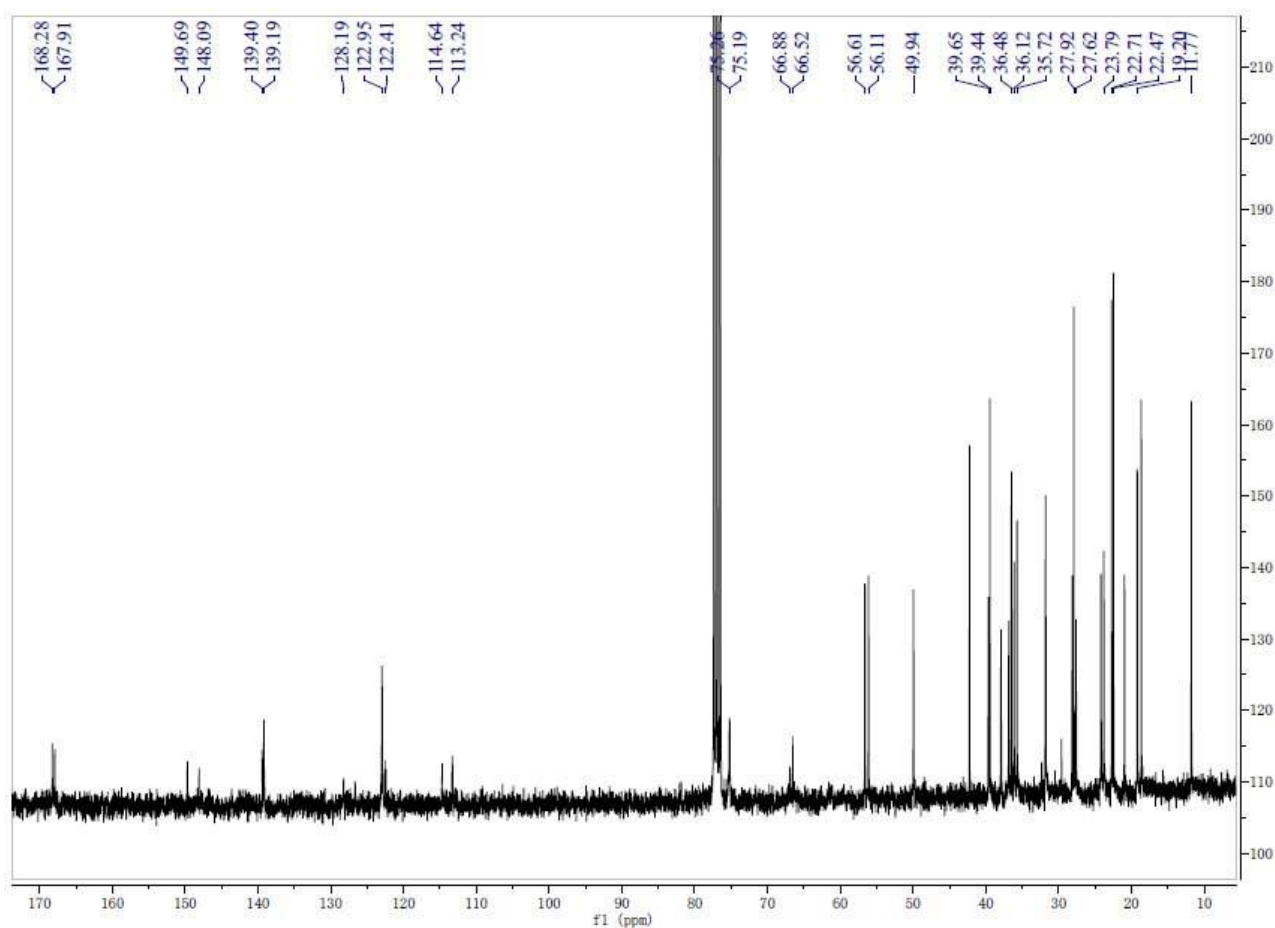


Figure S17 The  $^{13}\text{C}$  NMR spectrum of compound **5b**

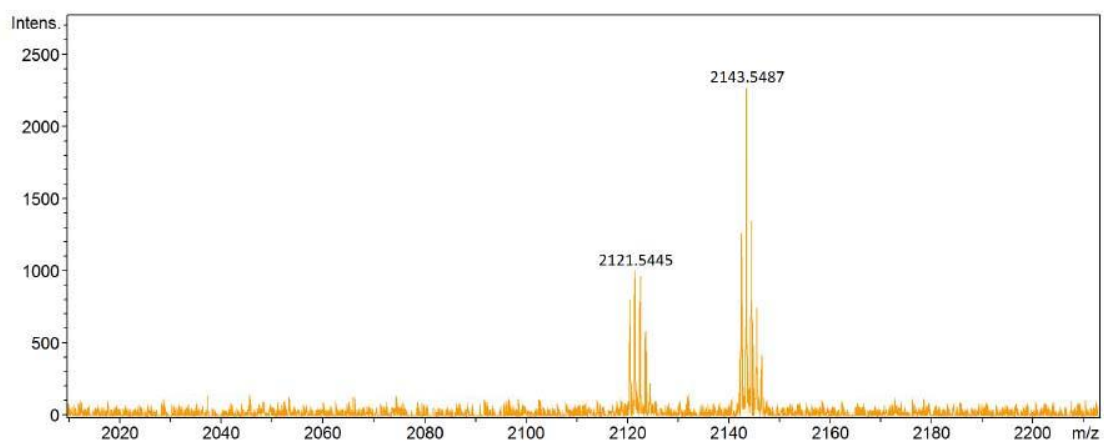


Figure S18 The HR-MS spectrum of compound **5b**

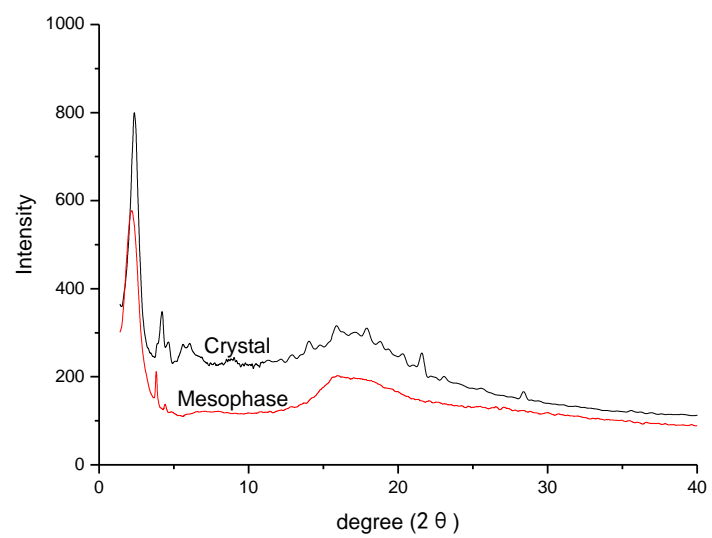


Figure S19 The XRD traces of compound **4b** at mesophase (140°C) and crystal phase (25°C)