Supplementary Information

# Self-Assembly and Chiroptical Property of Tetraphenylethylene Dicycle Tetracholesterol with AIE Effect

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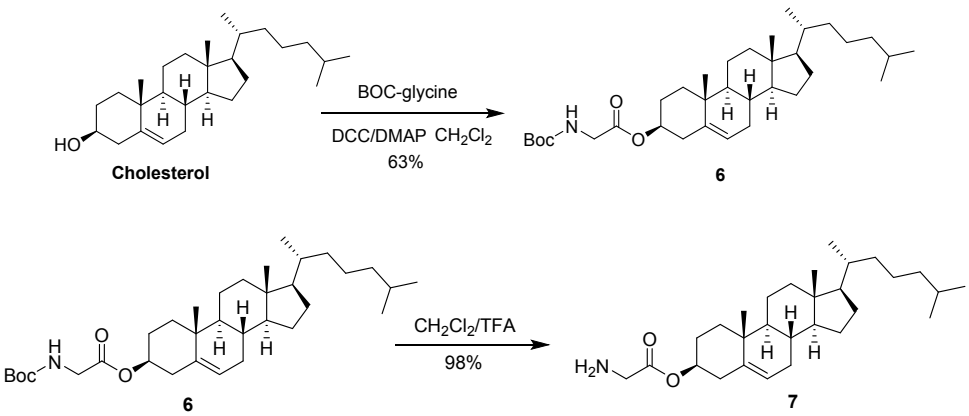
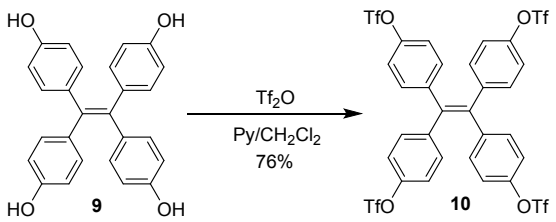
## Synthesis of tetraphenylethylene cholesterol derivative.

### Synthesis route of 7.

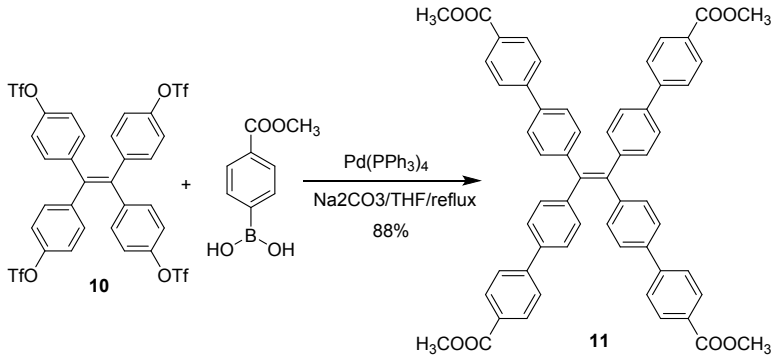



### Synthesis of 10.



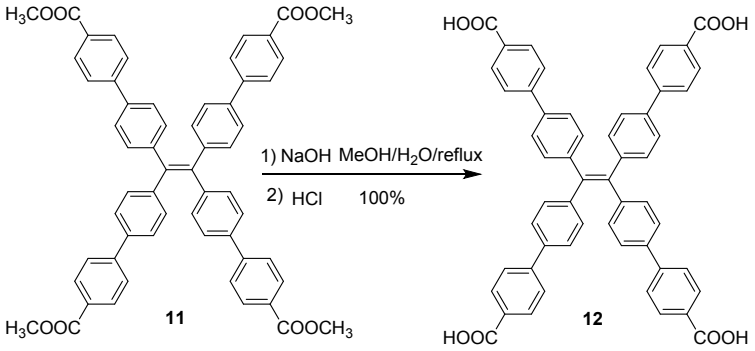
To a 200 mL round bottom flask was added tetrahydroxyTPE **9** (1.0 g, 2.50 mmol), freshly distilled pyridine (2 mL) and dry dichloromethane (50 mL). Trifluoromethanesulfonic anhydride ($Tf_2O$) (4 mL) in dry dichloromethane (50 mL) was dropped into the mixture solution in an iced bath under stirring over 0.5 h. After the dropping was finished, the mixture was stirred at room temperature for 12 h and filtered through a layer of Celite. The filtrate was evaporated to dryness and the obtained solid was dissolved in dichloromethane (60 mL). After the solution was washed with water for three times, dried over anhydrous sodium and filtered, the solvent was removed under reduced pressure. The residue was subjected to column chromatography (silica gel, ethyl acetate : petroleum 1:15) to afford **10** as white solid (1.8 g, 76%). Mp = 153.9 – 154.3 $^oC$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.18-6.97 (m, 16H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 148.64, 141.85, 140.08, 132.78, 121.39, 117.08; IR (KBr) *v* 3451, 3112,1625, 1502, 1426, 1220, 1139,1017,888, 606, 512 $cm^{-1}$; $ESI^+$ HRMS m/z calcd for $C_{30}H_{16}F_{12}S_4$ [M+Na]946.92, found $[M+Na]^+$ 946.92.

**Synthesis of 11.**



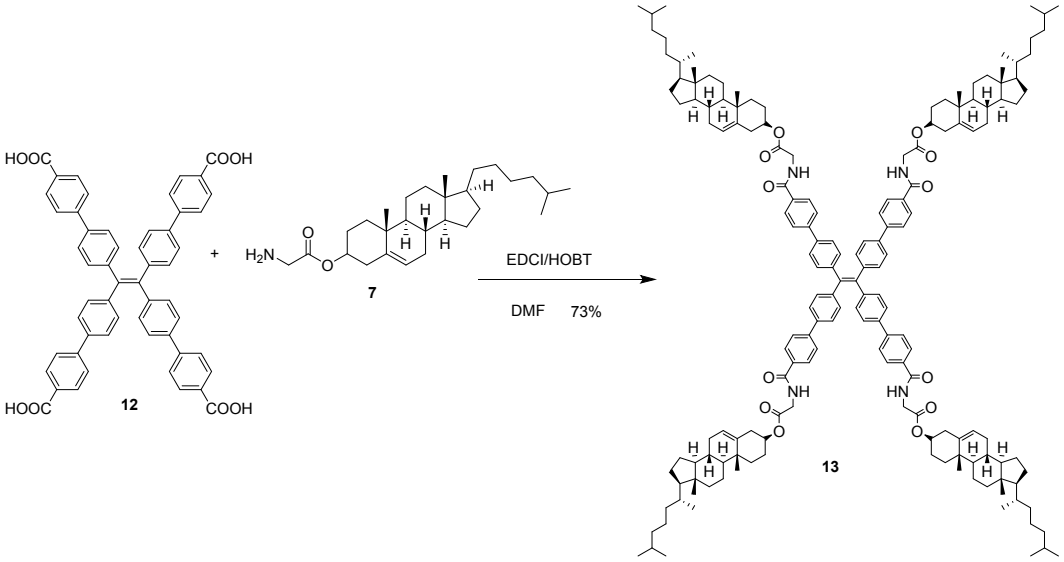

To a 100 mL round bottom flask was added **10** (480 mg, 0.52 mmol), THF (50 mL) and water (10 mL). After air in the mixture was replaced by nitrogen, $Pd(pph_3)_4$ (180 mg, 0.15 mmol) and $Na_2CO_3$(160 mg, 1.52 mmol) were added. Under nitrogen protection, the mixture was refluxed for about 6 h before solvent was removed. Water and dichloromethane were added to give two phases solution. Organic phase was separated and water phase was extracted two times with dichloromethane. The combined organic phase was dried over anhydrous $Na_2SO_4$, filtered and evaporated to dryness. The residue was subjected to column chromatography (silica gel, ethyl acetate : dichloromethane 1:50) to afford **11** as a yellow solid (420 mg, 88%). Mp = 284.3 − 285.1 $^oC$: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 8H), 7.64 (d, *J* = 8.3 Hz, 8H), 7.45 (d, *J* = 8.2 Hz, 8H), 7.21 (d, *J* = 8.2 Hz, 8H), 3.93 (s, 12H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 166.96, 144.87, 143.43, 140.64, 138.10, 132.04, 130.09, 128.88, 126.76, 126.69, 52.13; IR (KBr) *v* 3449, 2940,1718, 1613, 1430, 1390, 1280,1186, 1108, 829, 769, 511 $cm^{-1}$; $ESI^+$ HRMS m/z calcd for $C_{58}H_{44}O_8$ [M+Na]891.29, found $[M+Na]^+$891.29.

**Synthesis of 12.**




To a 250 mL round bottom flask was added **4** (380 mg, 0.44 mmol), methanol (30 mL) and 6 M NaOH (20 mL). After the mixture was refluxed for about 30 h, methanol was removed by rotary evaporator. Hydrochloric acid (6 M) was dropped into the mixture solution in an iced bath under stirring until pH = 2. The resultant precipitates were collected by filtering. The solid was washed with water and dried to afford **12** as a yellow solid (360 mg, 100%). Mp > 300 $^{o}$C: $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 12.98 (s, 4H), 7.97 (d, *J* = 7.9 Hz, 8H), 7.76 (d, *J* = 7.9 Hz, 8H), 7.60 (d, *J* = 7.8 Hz, 8H), 7.17 (d, *J* = 7.7 Hz, 8H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 167.55, 143.84, 143.54, 140.69, 137.52, 132.08, 130.40, 130.04, 126.97, 126.92; IR (KBr) *v* 3454, 3029, 2919,2668, 2540, 1696, 1611, 1422, 1283, 1119,1006, 776,631, 548 cm$^{-1}$; ESI$^{+}$ HRMS m/z calcd for $C_{54}H_{44}O_8$ [M+Na]835.23, found [M+Na]$^{+}$835.22.

**Synthesis of 13.**




To a 25 mL round bottom flask was added **12** (90 mg, 0.11mmol), DMF (15 mL) and HOBT (81 mg, 0.60mmo).The mixture solution at room temperature under stirring for 2 h. Then add EDCI (114 mg, 0.60 mmol) and **7** (443 mg, 1.03 mmol)and continue to stirring for 24 h. The solution was evaporated to dryness and the obtained solid was dissolved in dichloromethane.

The residue was subjected to column chromatography (silica gel, MeOH : dichloromethane 1 : 100) to afford **13** as yellow solid (200 mg, 73%). Mp > 230 °C (decomposed); $[\alpha]_D^{25}$ = +11.2° (5mg/mL in THF); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 8H), 7.61 (d, *J* = 7.9 Hz, 8H), 7.42 (d, *J* = 7.9 Hz, 8H), 7.20 (d, *J* = 7.9 Hz, 8H), 6.79 (t, *J* = 5.1 Hz, 4H), 5.39 (d, *J* = 4.9 Hz, 4H), 4.73 (dtd, *J* = 12.4, 8.6, 4.1 Hz, 4H), 4.23 (d, *J* = 4.8 Hz, 8H), 2.37 (d, *J* = 8.2 Hz, 8H), 2.06 – 1.78 (m, 22H), 1.73 – 1.40 (m, 40H), 1.38 – 0.96 (m, 58H), 0.91 – 0.80 (m, 32H), 0.68 (s, 12H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.57, 167.05, 143.75, 143.31, 140.56, 139.28, 138.01, 132.39, 132.05, 127.62, 126.94, 126.60, 123.05, 75.63, 56.70, 56.15, 50.01, 42.32, 42.12, 39.72, 39.52, 38.04, 36.91, 36.58, 36.19, 35.80, 31.91, 31.84, 28.23, 28.02, 27.73, 24.29, 23.84, 22.82, 22.57, 21.04, 19.31, 18.72, 11.87; IR (KBr) *v* 3442, 2942, 2861,1774, 1648, 1539, 1385, 1315, 1200, 1117,1002, 829,770, 609, 512 cm$^{-1}$; Molecular formula is $C_{170}H_{224}N_4O_{12}$, Mol. wt. 2515.62. MALDI-TOF HRMS m/z calcd for $C_{170}H_{244}N_4O_{12}$ $[M+Na]^+$ 2537.6967, found $[M+Na]^+$ 2537.6976. Elem. Anal. : C 81.17, H 8.98, N 2.23, O 9.20, found C 80.50, H 8.84, N 2.20.

**$^1$H/$^{13}$C-NMR, IR and HRMS spectra of compound 2, 3, 4, 5, 6, 7, 8, 10, 11, 12 and 13.**

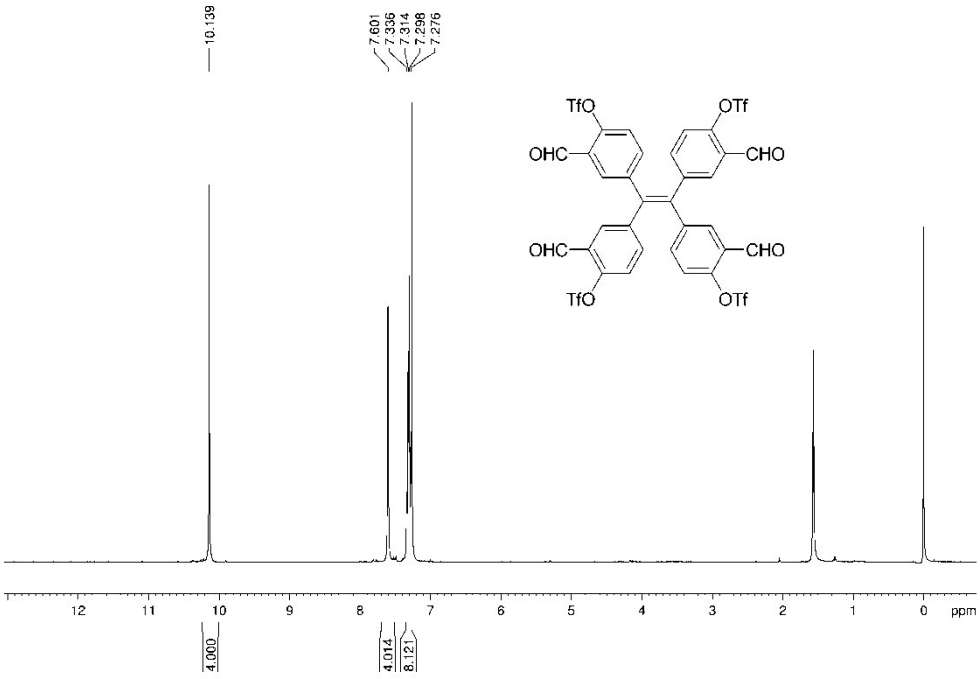



**Fig. S1**. $^1$H NMR spectrum of compound **2** in $CDCl_3$.

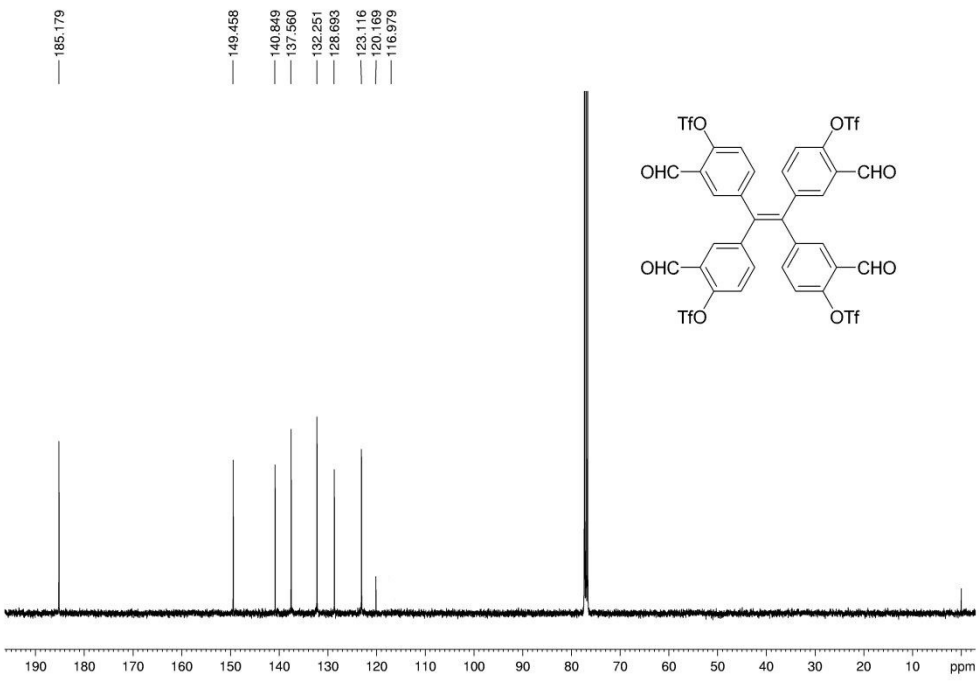



**Fig. S2**. $^{13}C$ NMR spectrum of compound **2** in $CDCl_3$.

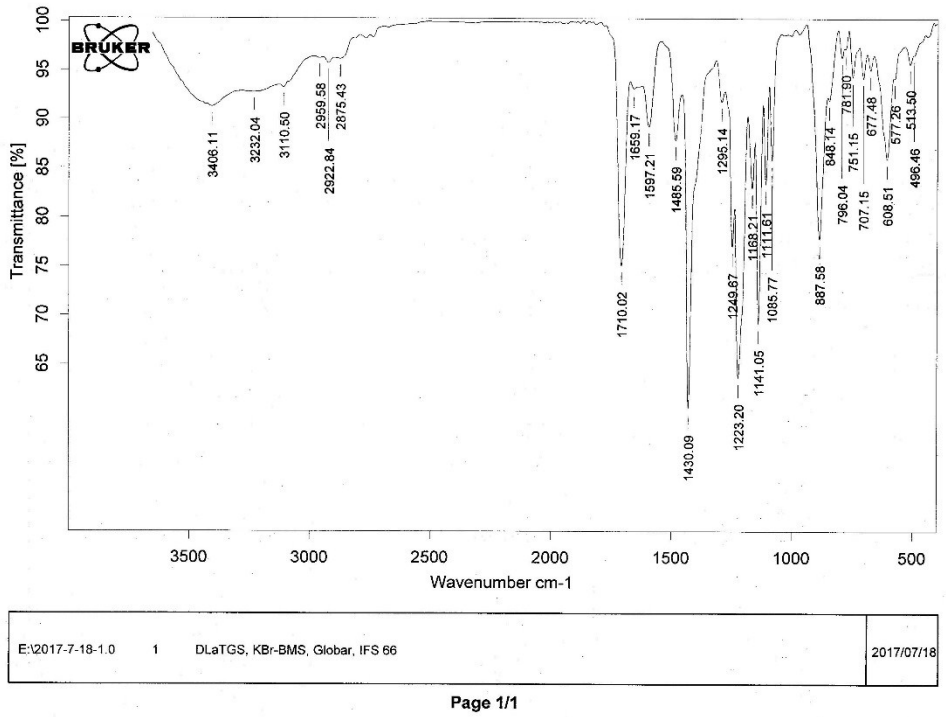



**Fig. S3**. IR spectrum of compound **2**.

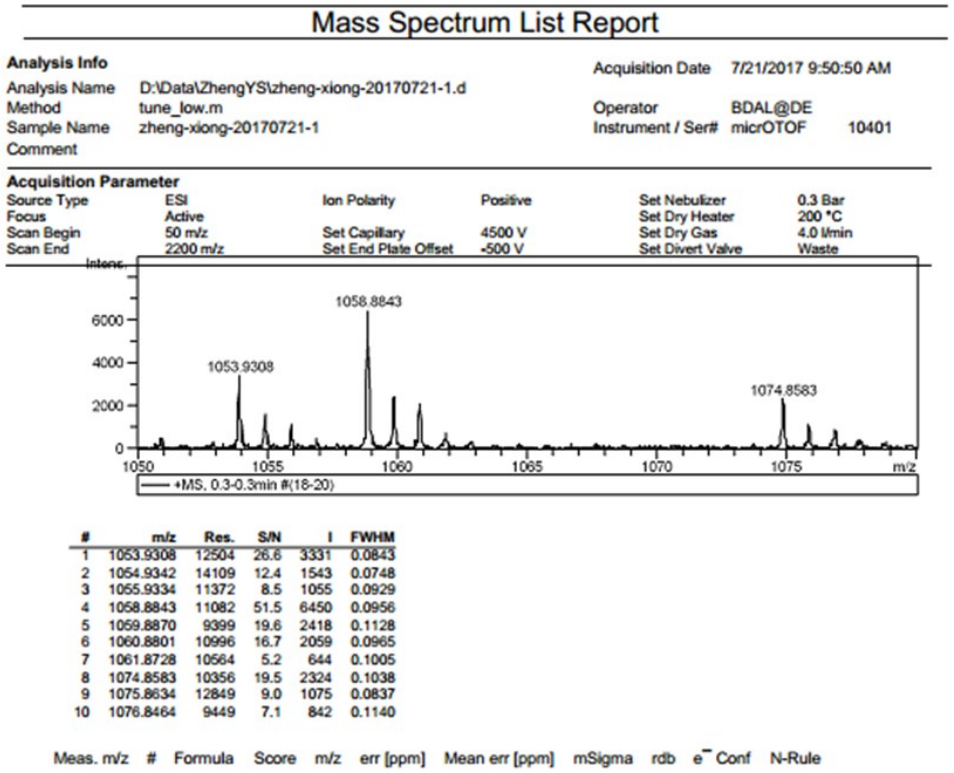



**Fig. S4**. HRMS spectrum of compound **2**.

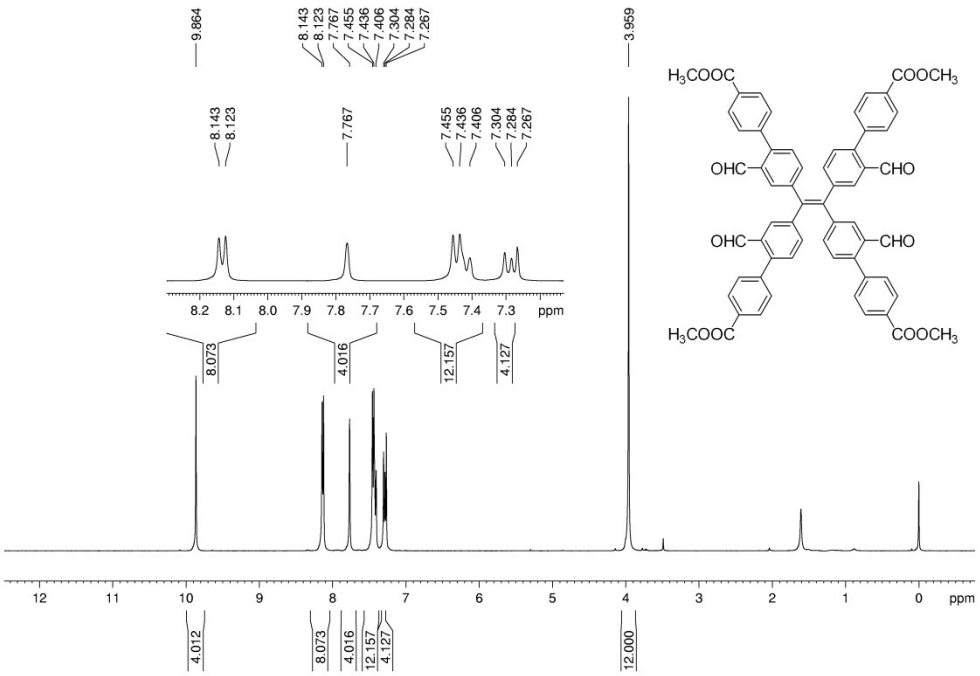



**Fig. S5**. $^{1}H$ NMR spectrum of compound **3** in $CDCl_3$.

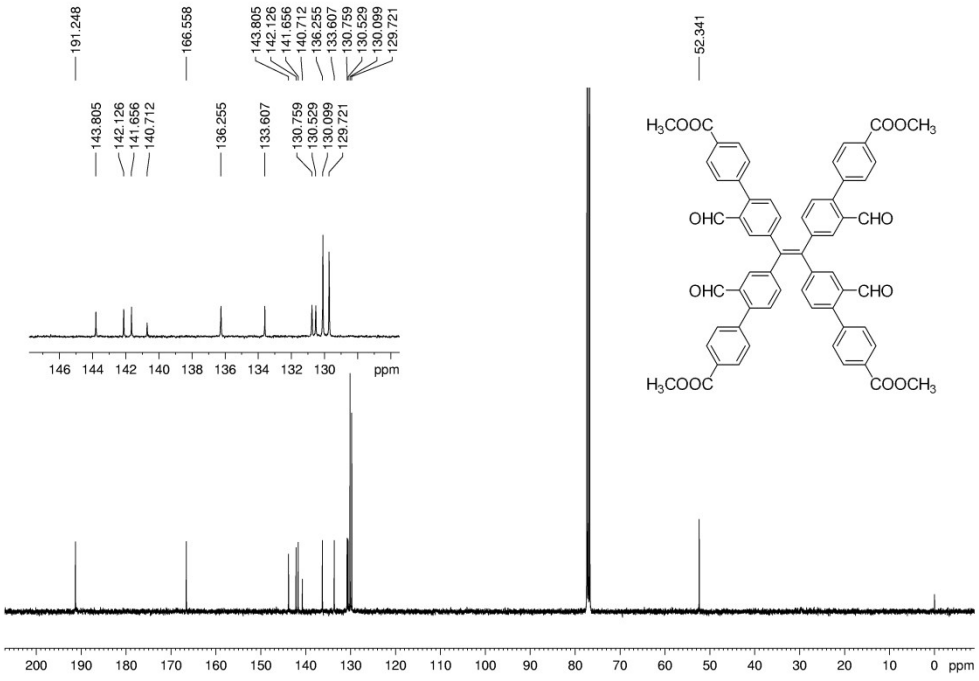



**Fig. S6**. $^{13}C$ NMR spectrum of compound **3** in $CDCl_3$.

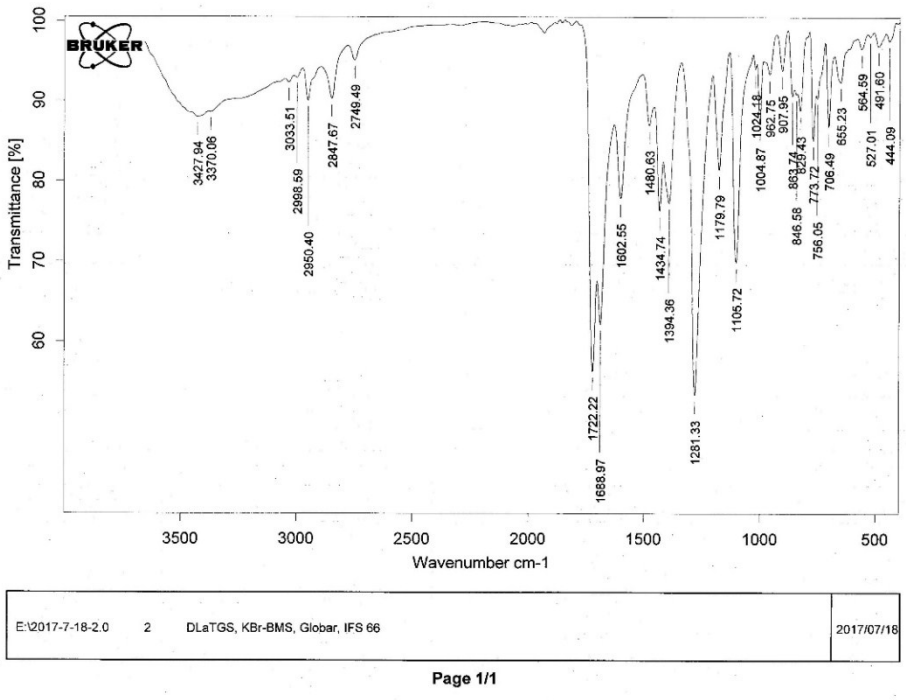



**Fig. S7**. IR spectrum of compound **3**.

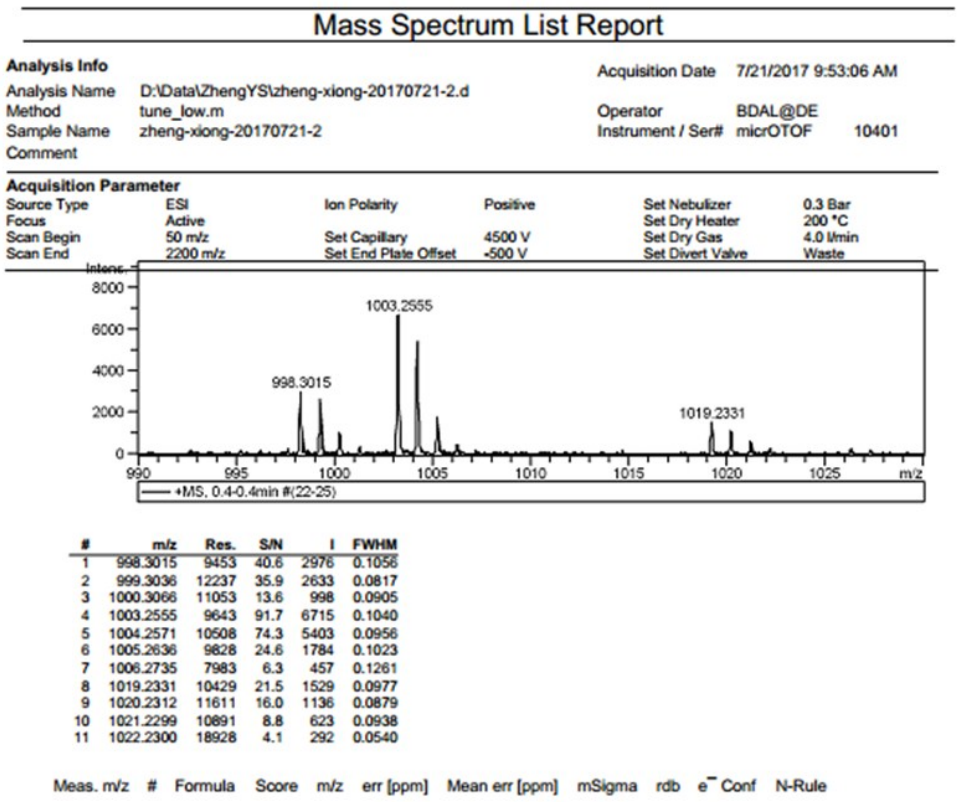



**Fig. S8**. HRMS spectrum of compound **3**.

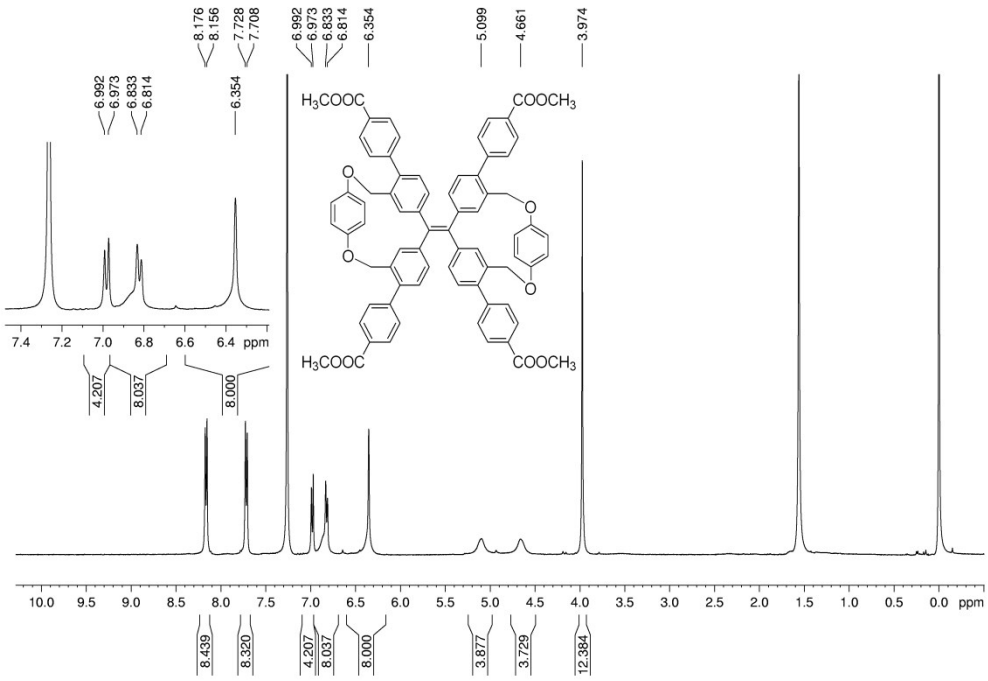



**Fig. S9**. $^{1}H$ NMR spectrum of compound **4** in $CDCl_3$.

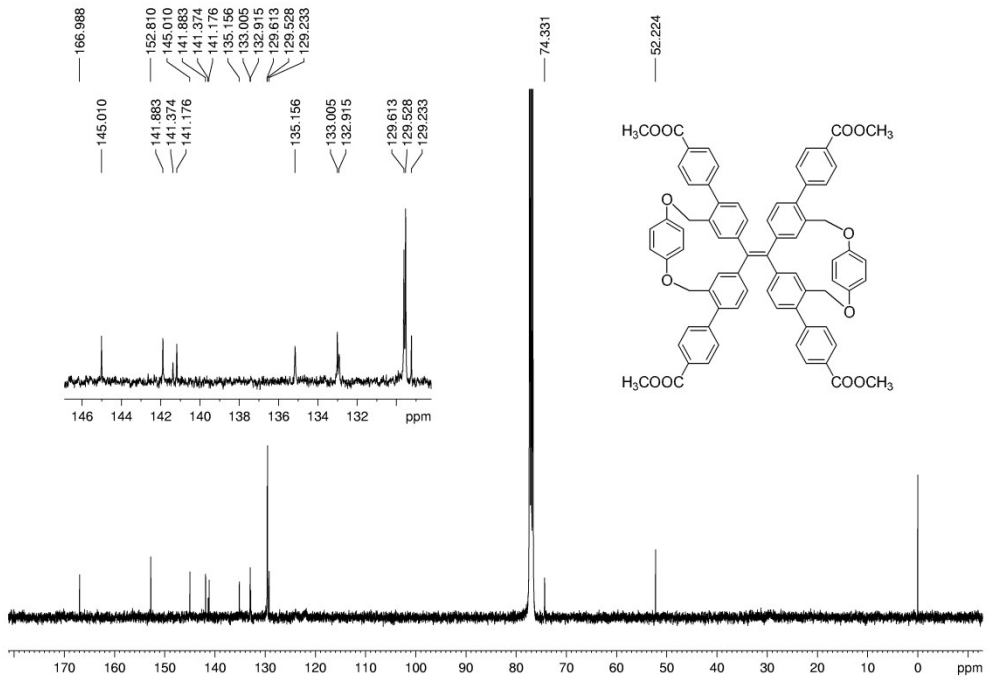



**Fig. S10**. $^{13}C$ NMR spectrum of compound **4** in $CDCl_3$.

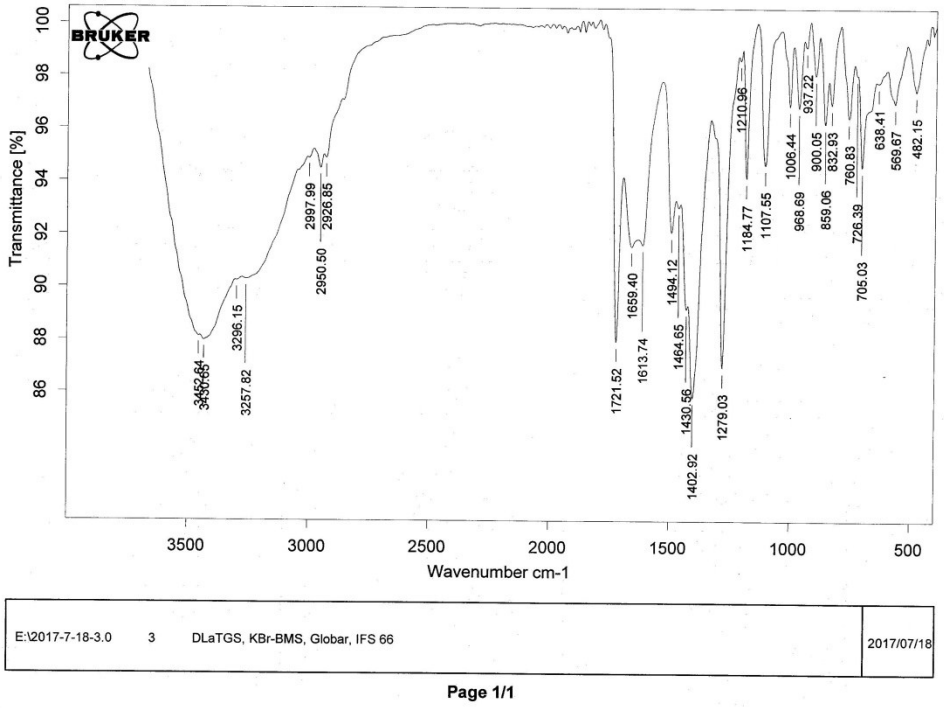



**Fig. S11**. IR spectrum of compound **4**.

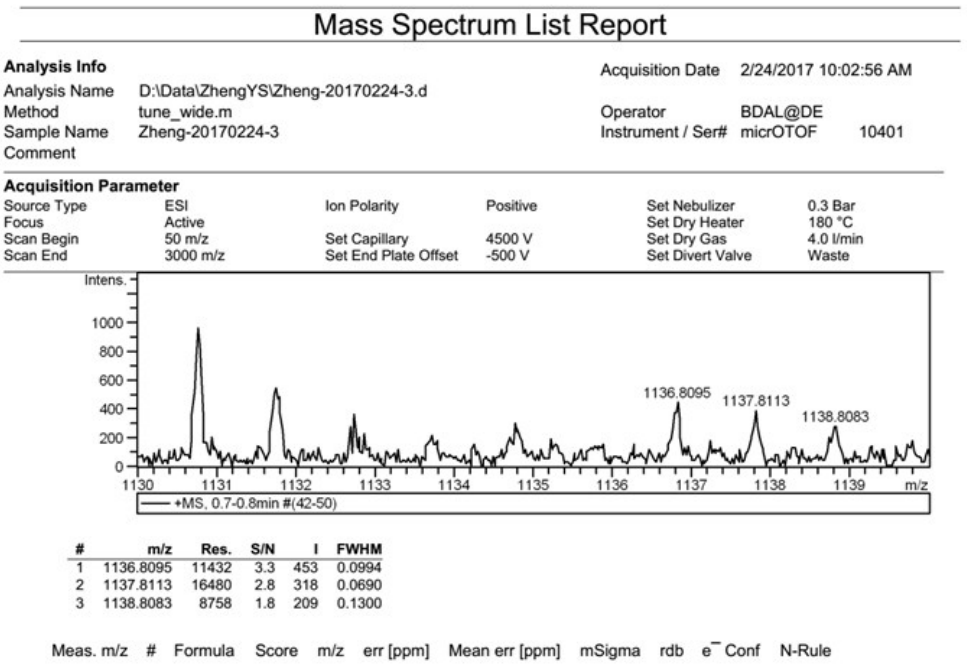



**Fig. S12.** HRMS spectrum of compound 4.

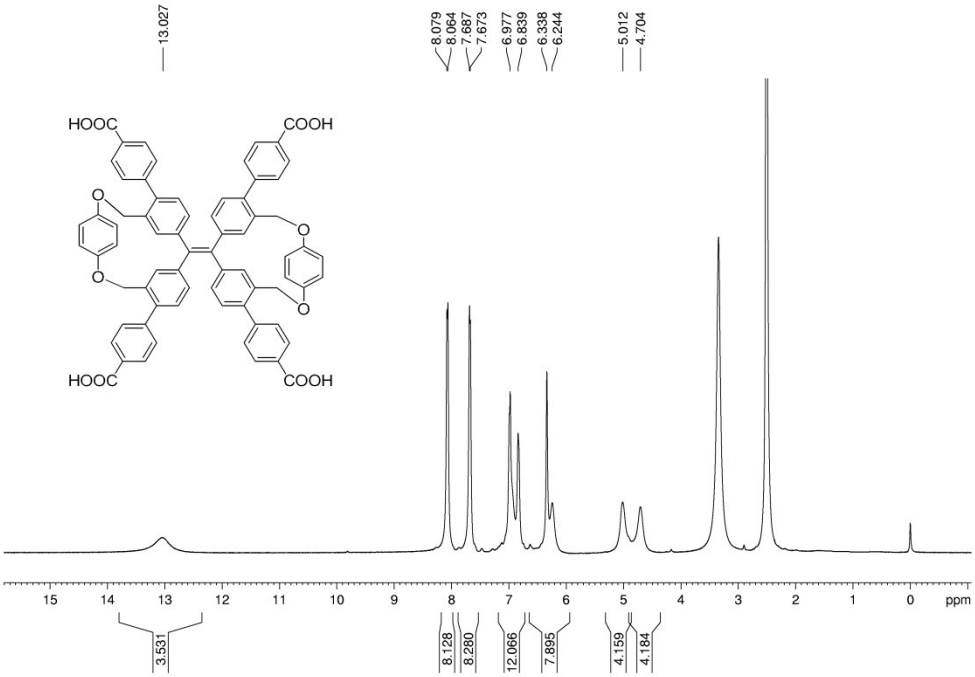



**Fig. S13**. $^{1}$H NMR spectrum of compound **5** in DMSO-$d_6$.

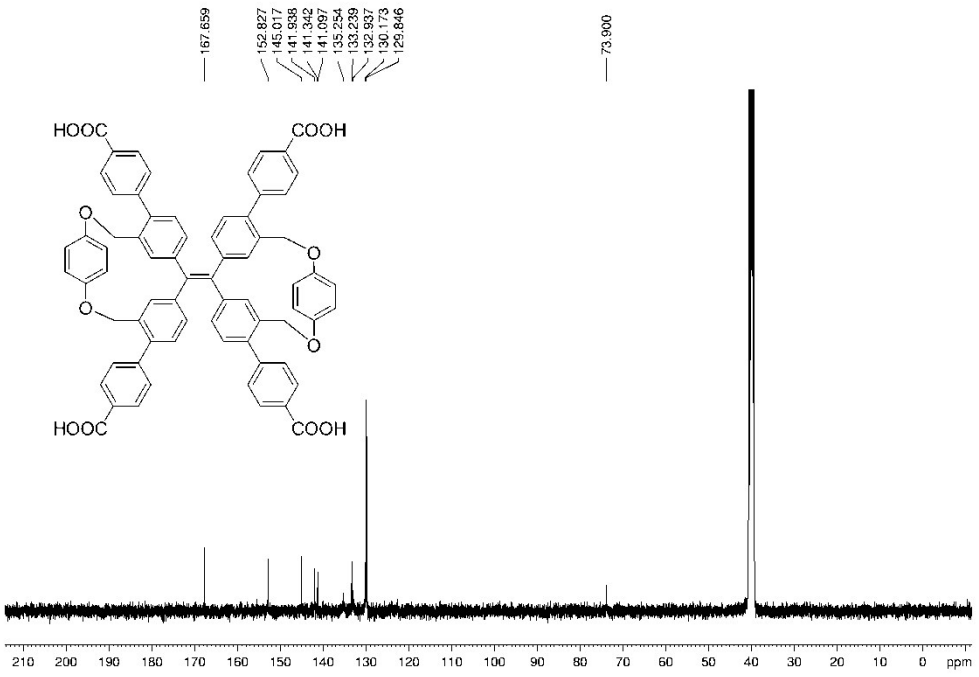



**Fig. S14**. $^{13}C$ NMR spectrum of compound **5** in DMSO-$d_6$.

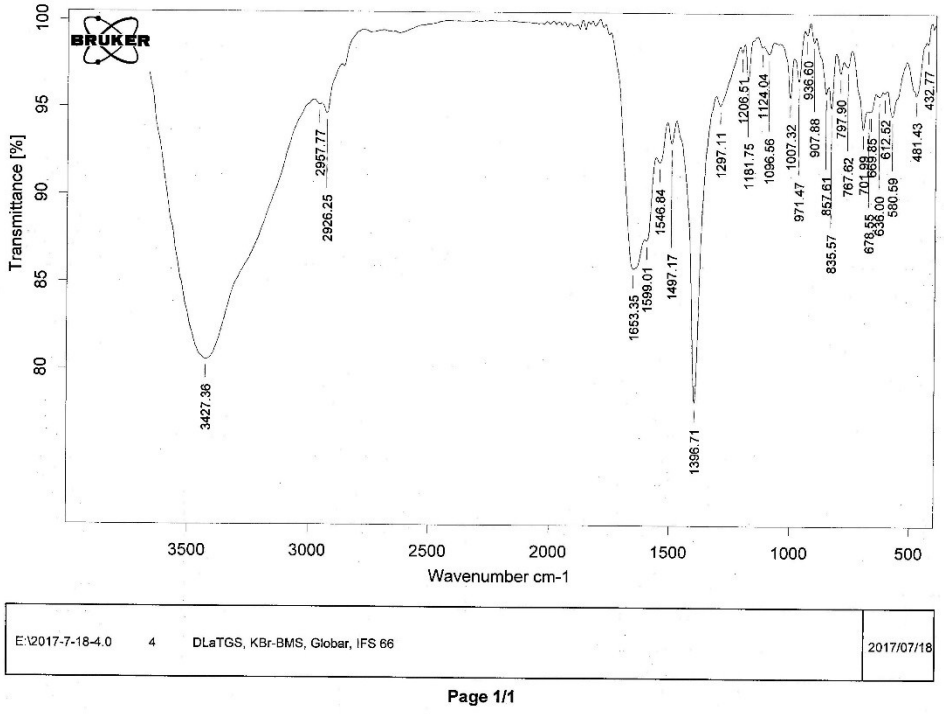



**Fig. S15**. IR spectrum of compound **5**.

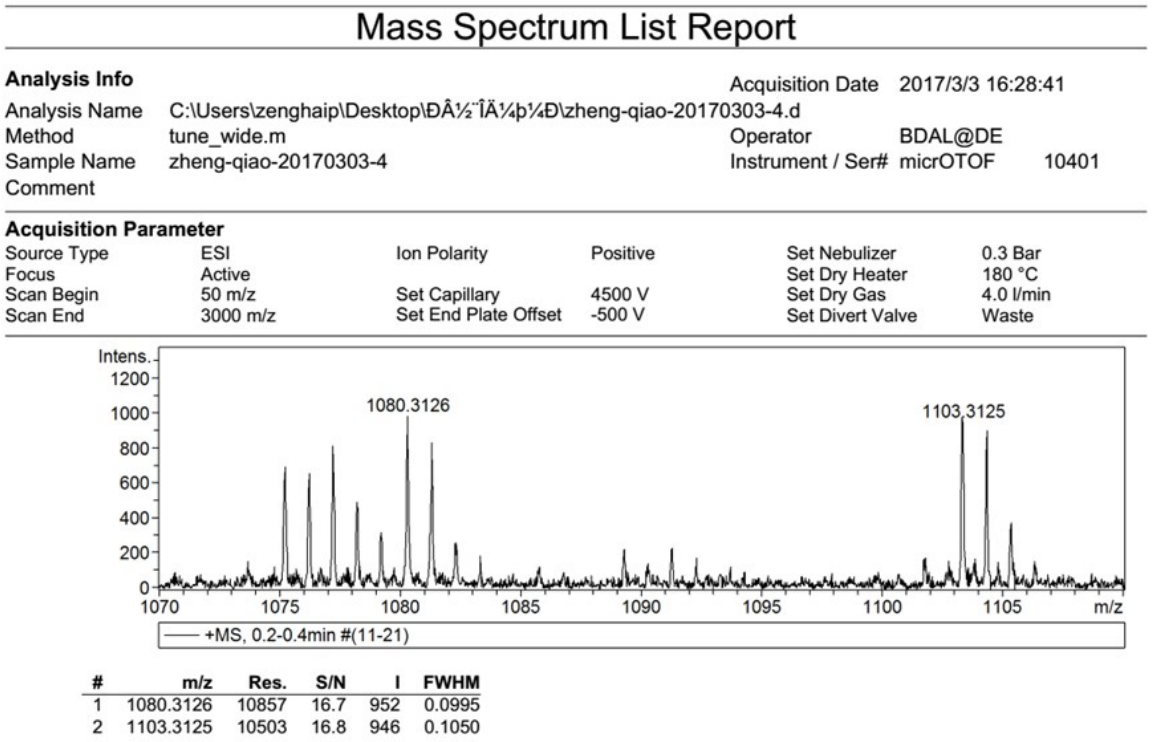



**Fig. S16**. HRMS spectrum of compound **5**.

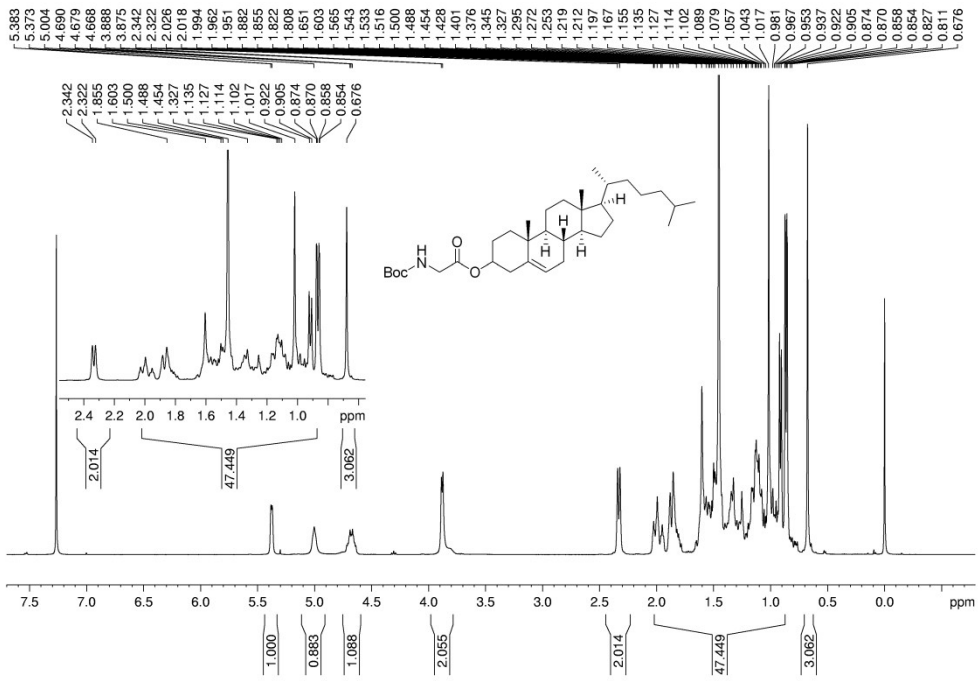



**Fig. S17**. $^{1}$H NMR spectrum of **6** in $CDCl_3$.

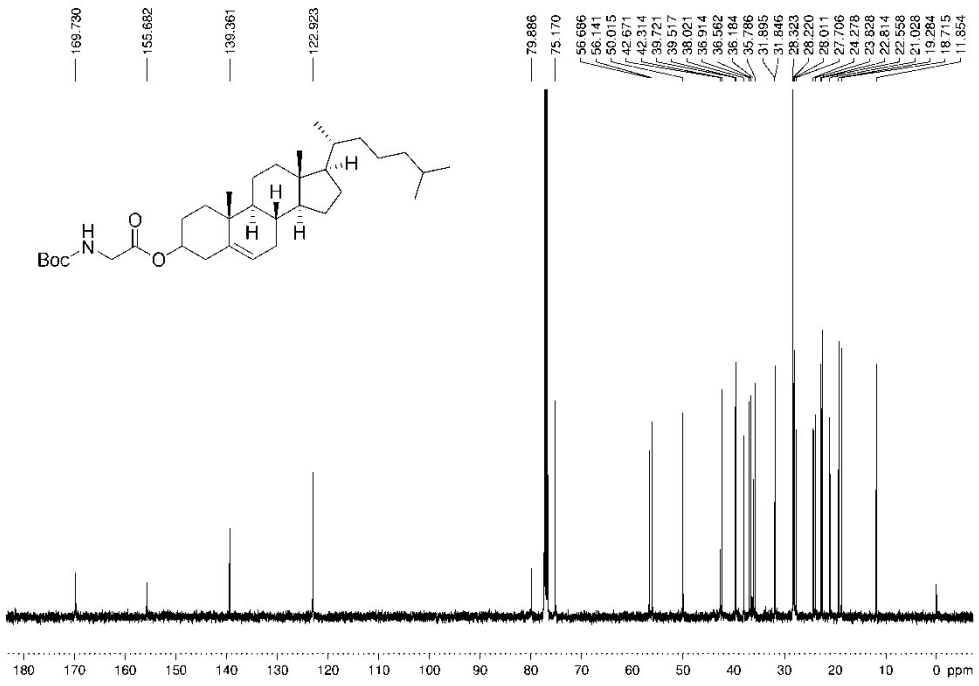



**Fig. S18**. $^{13}C$ NMR spectrum of compound **6** in $CDCl_3$.

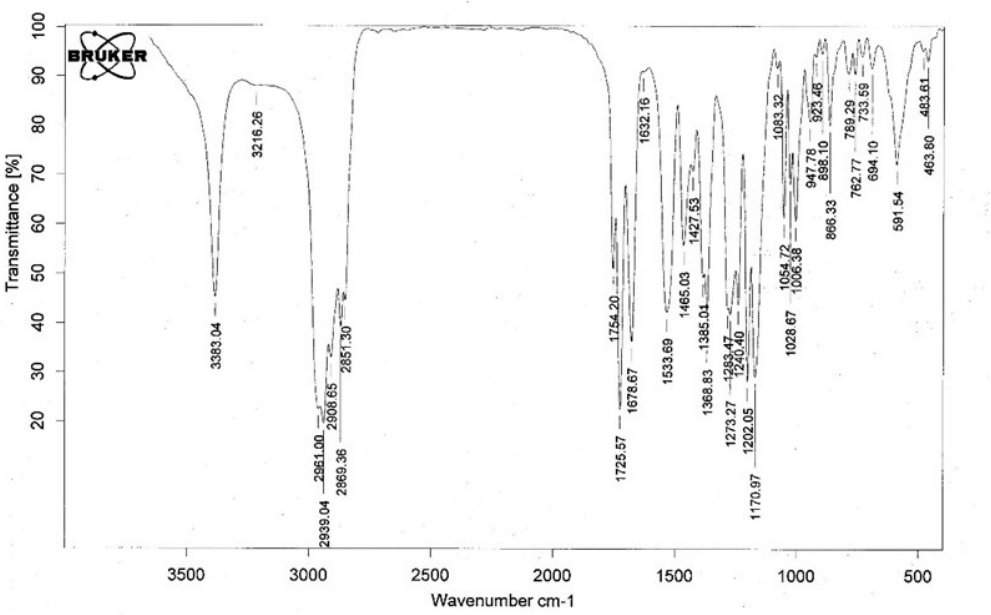



**Fig. S19**. IR spectrum of compound **6**.

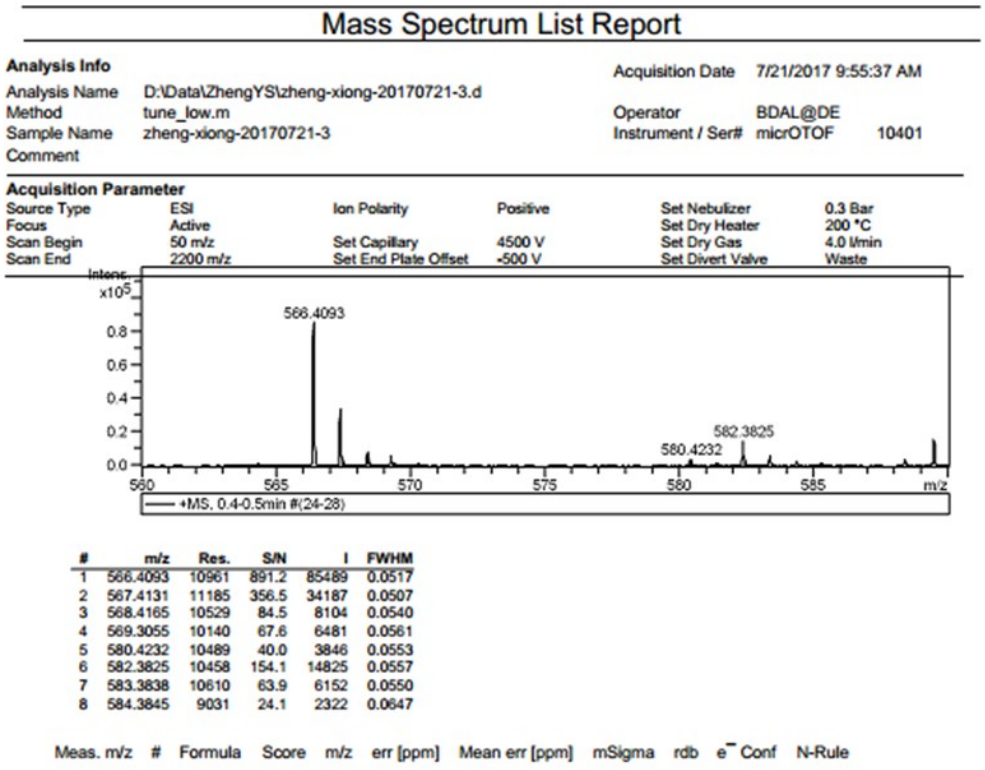



**Fig. S20**. HRMS spectrum of compound **6**.

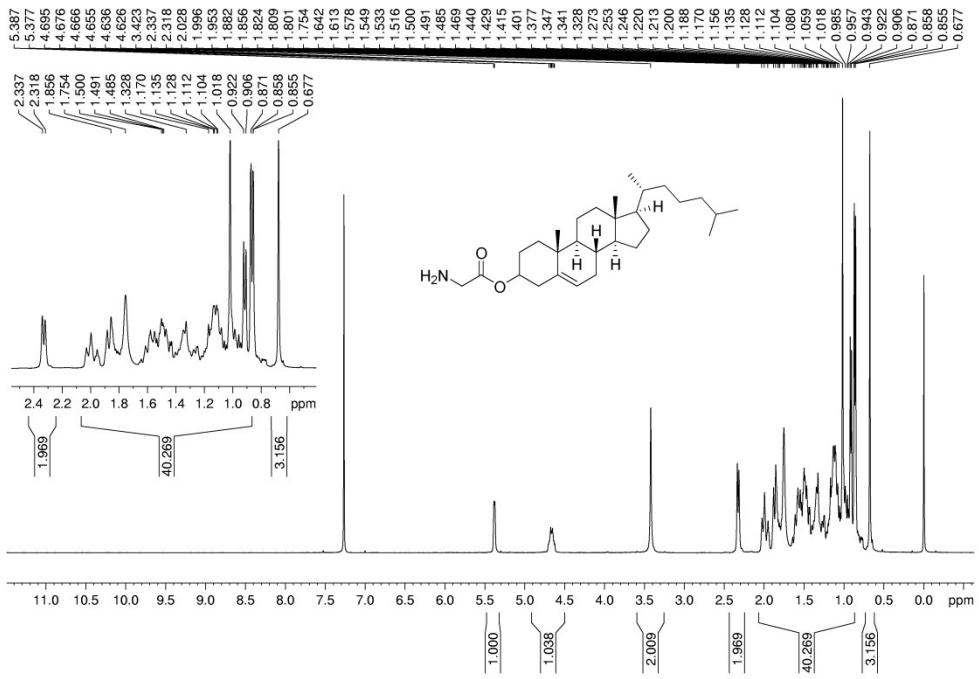



**Fig. S21**. $^{1}H$ NMR spectrum of compound **7** in $CDCl_3$.

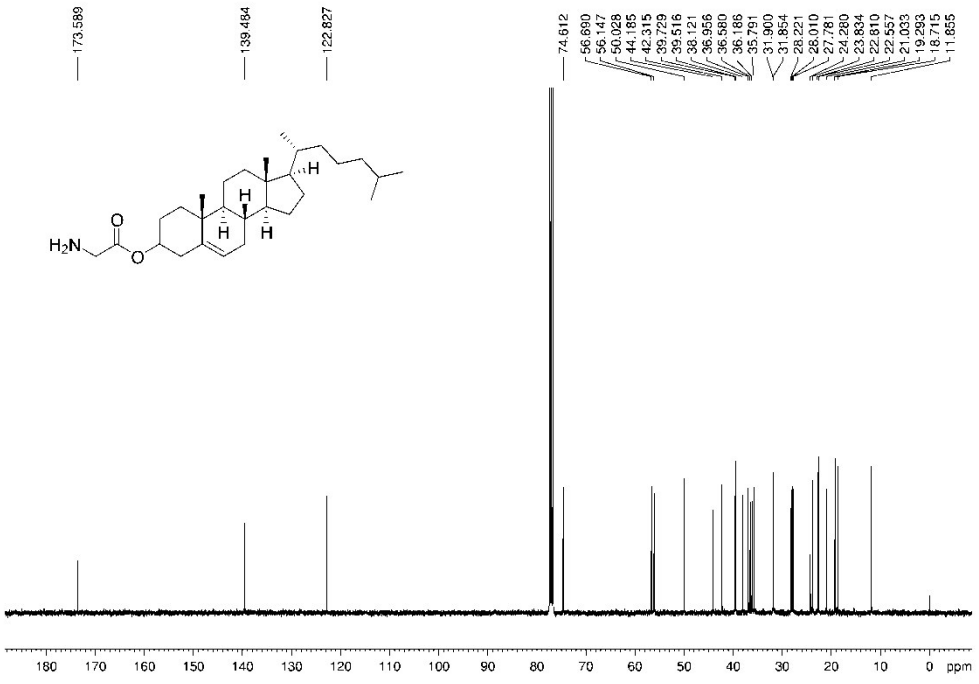



**Fig. S22**. $^{13}C$ NMR spectrum of compound **7** in $CDCl_3$.

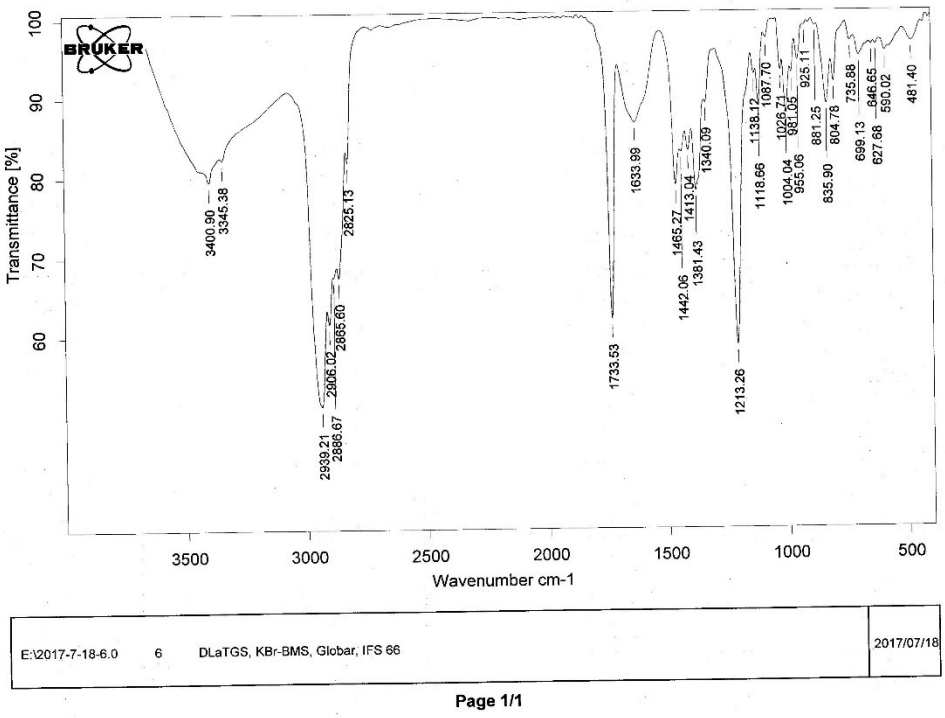



**Fig. S23**. IR spectrum of compound **7**.

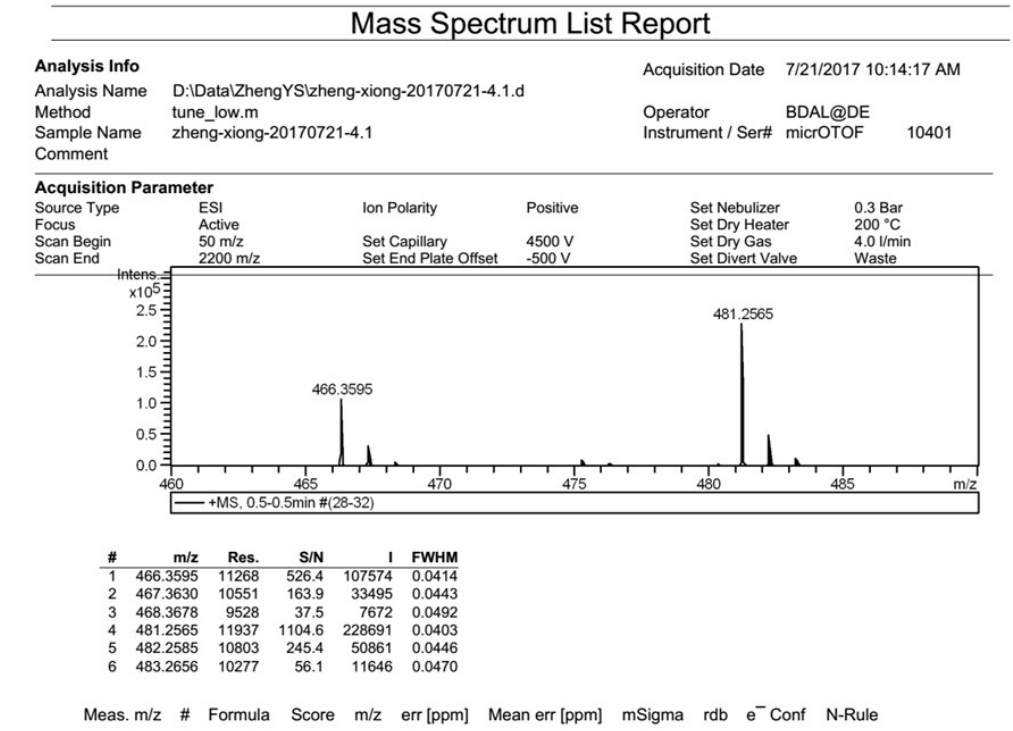



**Fig. S24**. HRMS spectrum of compound **7**.

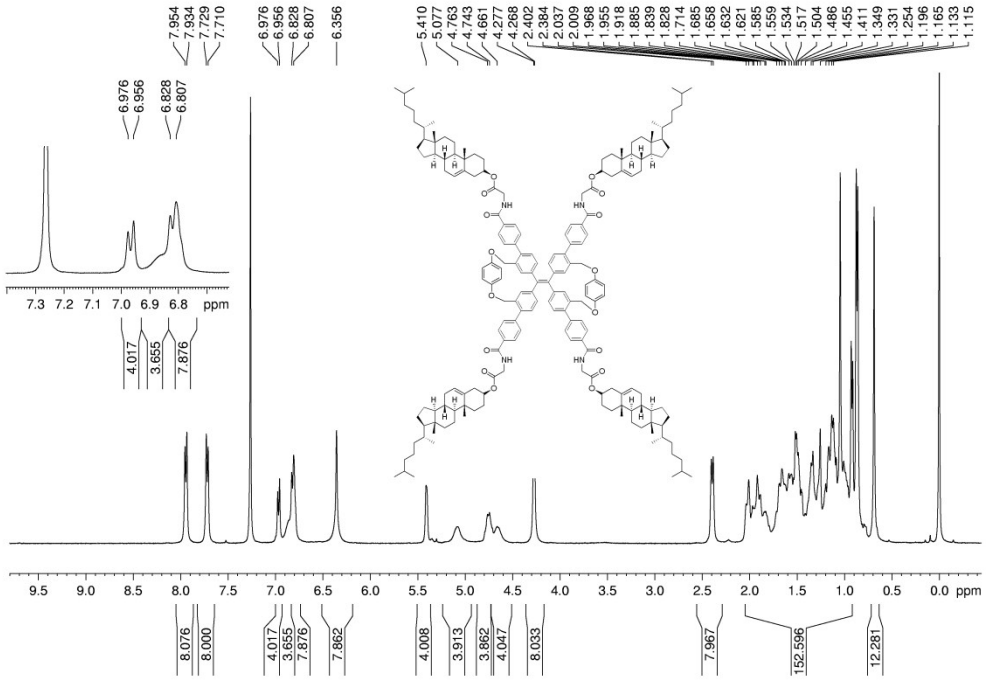



**Fig. S25**. $^{1}H$ NMR spectrum of compound **8** in $CDCl_3$.

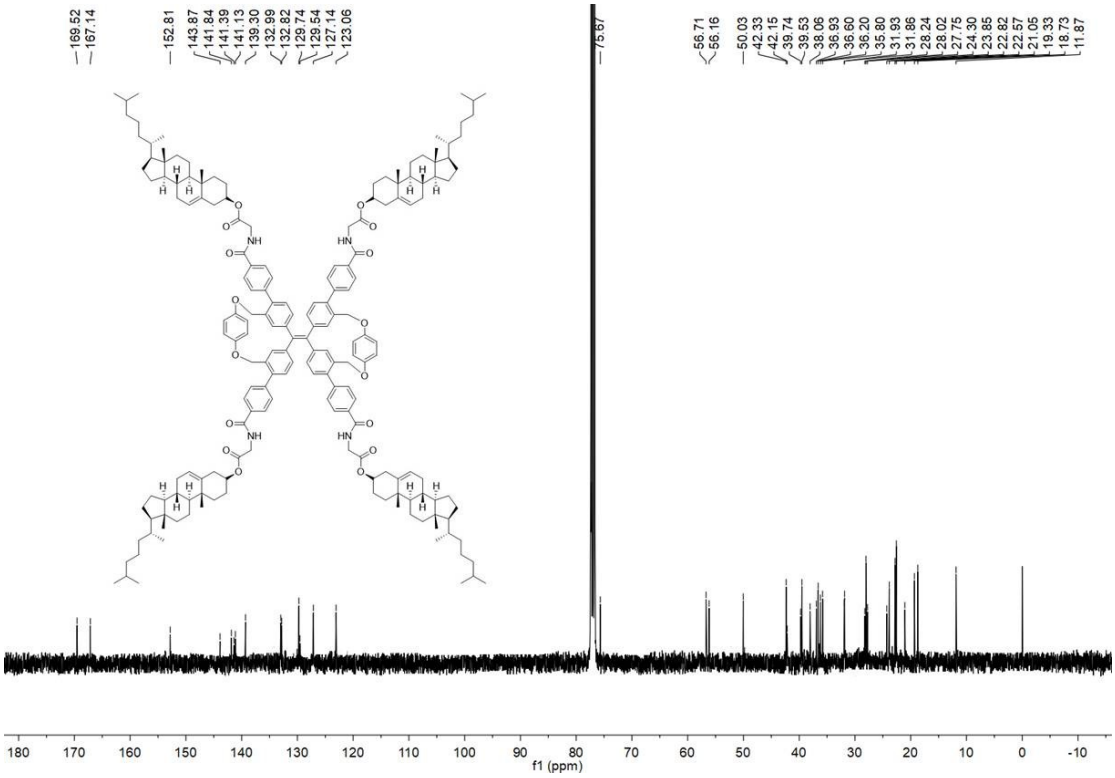



**Fig. S26**. $^{13}C$ NMR spectrum of compound **8** in $CDCl_3$.

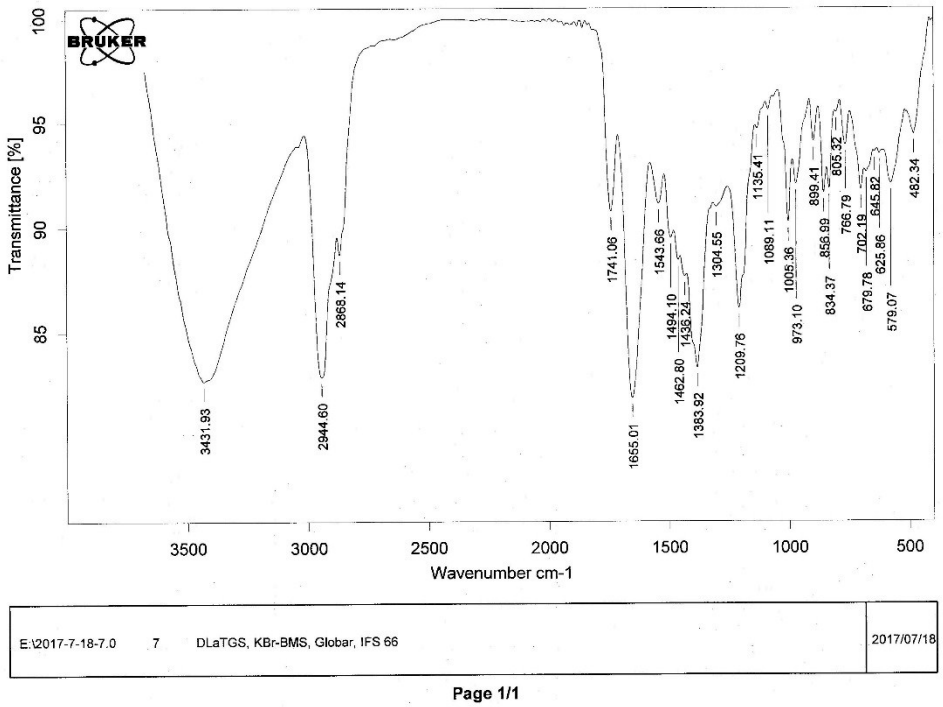



**Fig. S27**. IR spectrum of compound **8**.

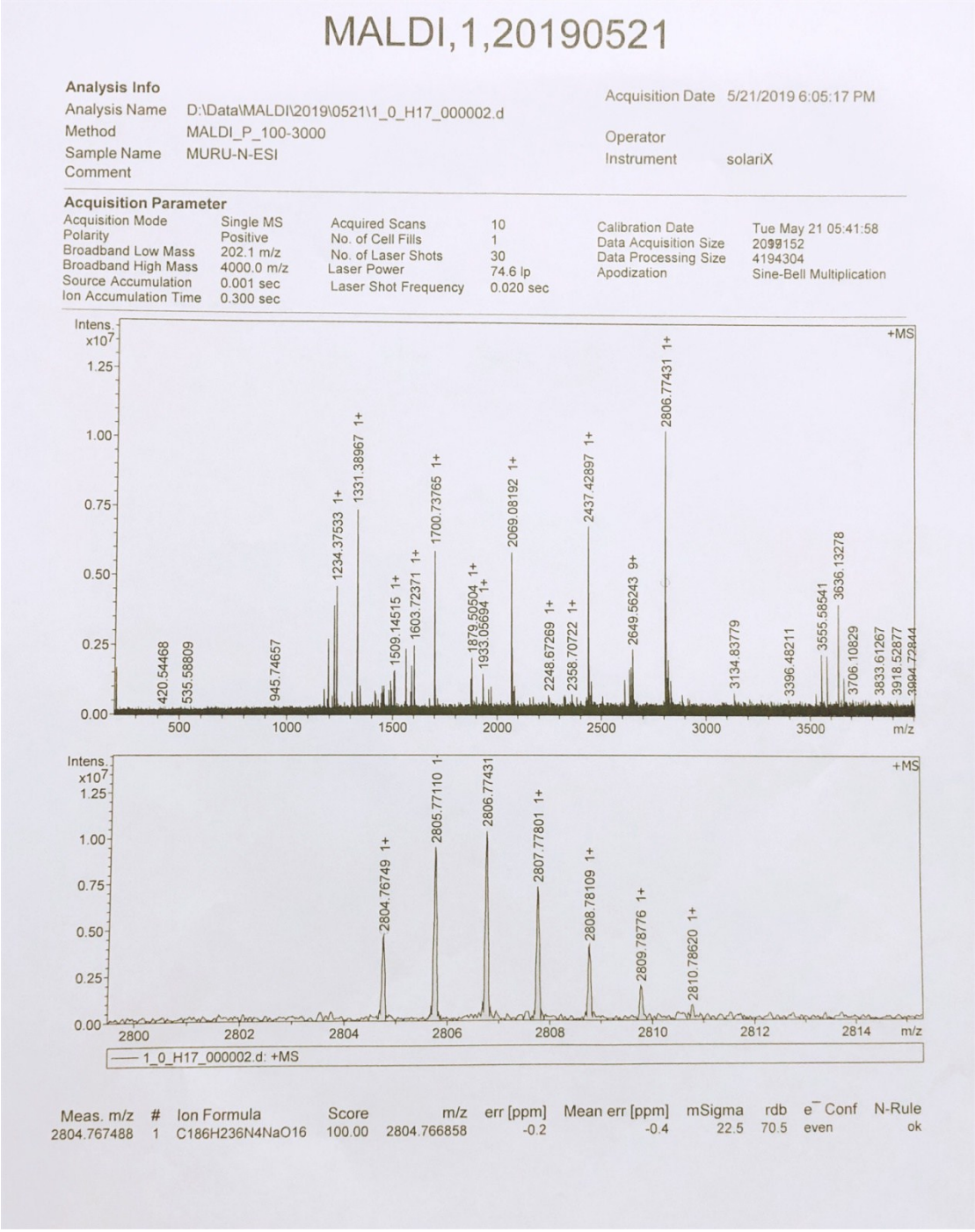



**Fig. S28.** HRMS spectrum of compound **8**.

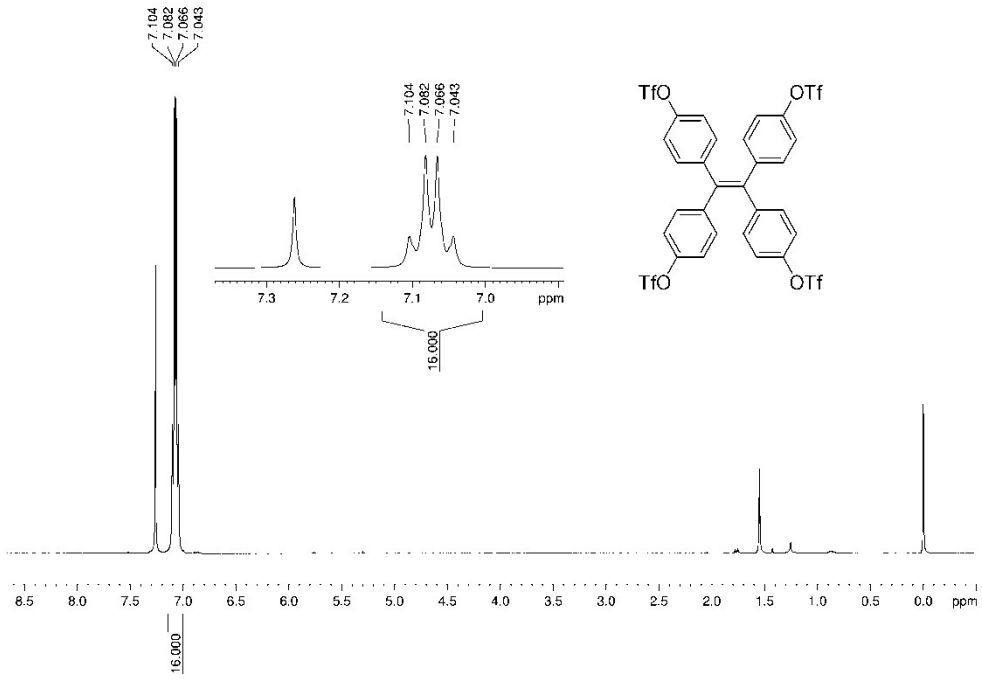



**Fig. S29**. $^{1}$H NMR spectrum of compound **10** in $CDCl_3$.

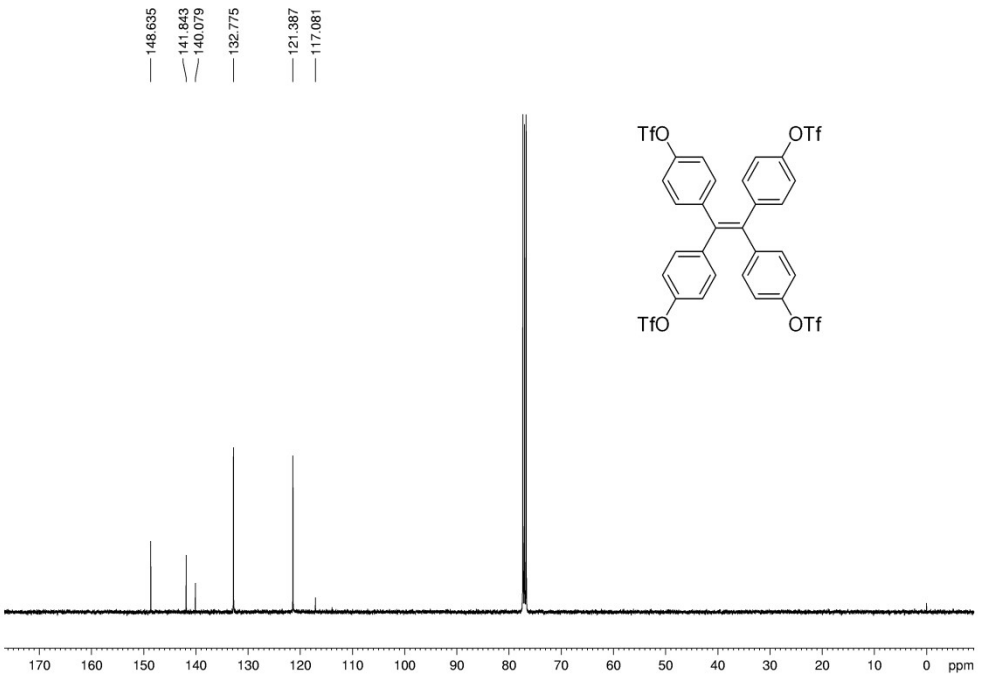



**Fig. S30**. $^{13}$C NMR spectrum of compound **10** in $CDCl_3$.

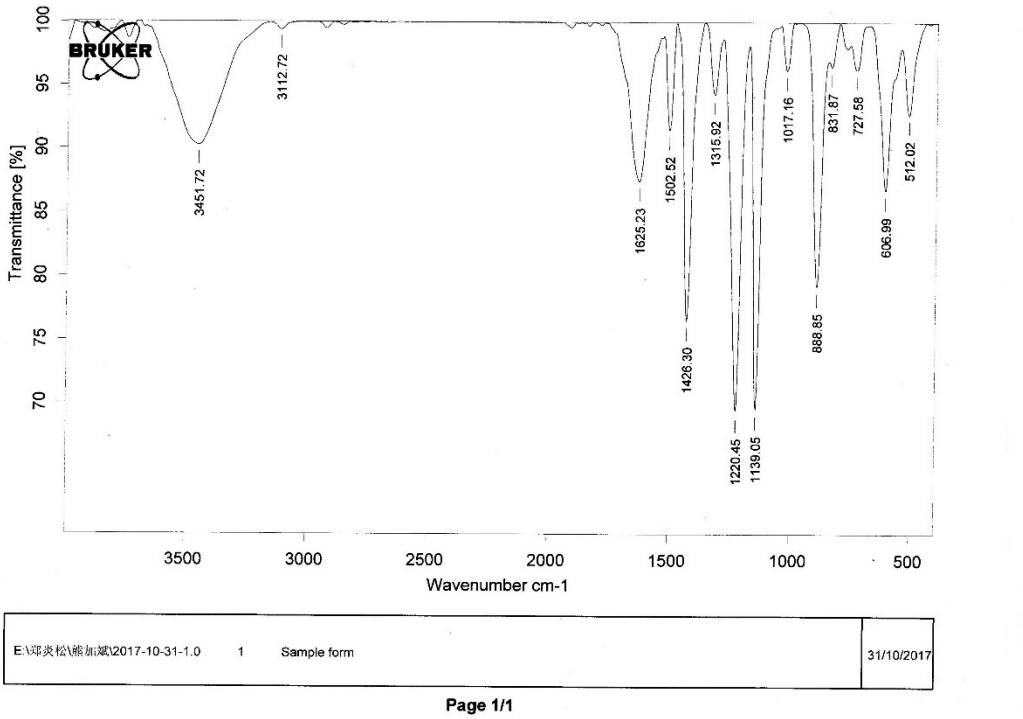
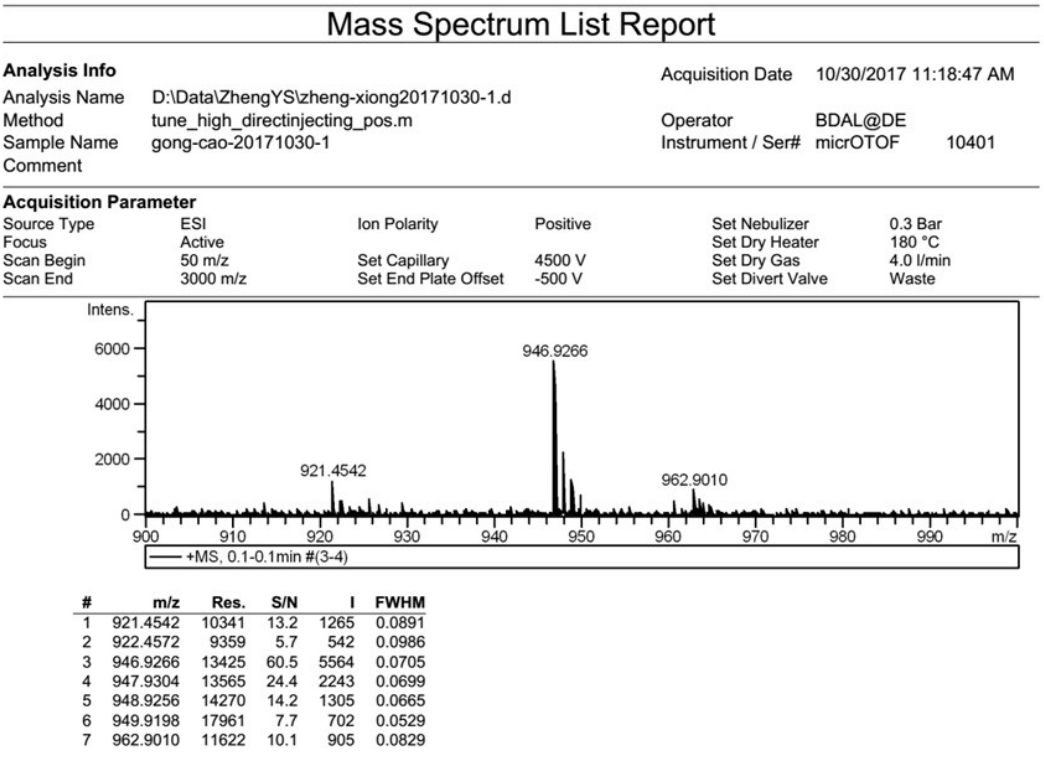



**Fig. S31**. IR spectrum of compound **10**.




| # | m/z | Res. | S/N | I | FWHM |
|---|---|---|---|---|---|
| 1 | 921.4542 | 10341 | 13.2 | 1265 | 0.0891 |
| 2 | 922.4572 | 9359 | 5.7 | 542 | 0.0986 |
| 3 | 946.9266 | 13425 | 60.5 | 5564 | 0.0705 |
| 4 | 947.9304 | 13565 | 24.4 | 2243 | 0.0699 |
| 5 | 948.9256 | 14270 | 14.2 | 1305 | 0.0665 |
| 6 | 949.9198 | 17961 | 7.7 | 702 | 0.0529 |
| 7 | 962.9010 | 11622 | 10.1 | 905 | 0.0829 |

**Fig. S32**. HRMS spectrum of compound **10**.

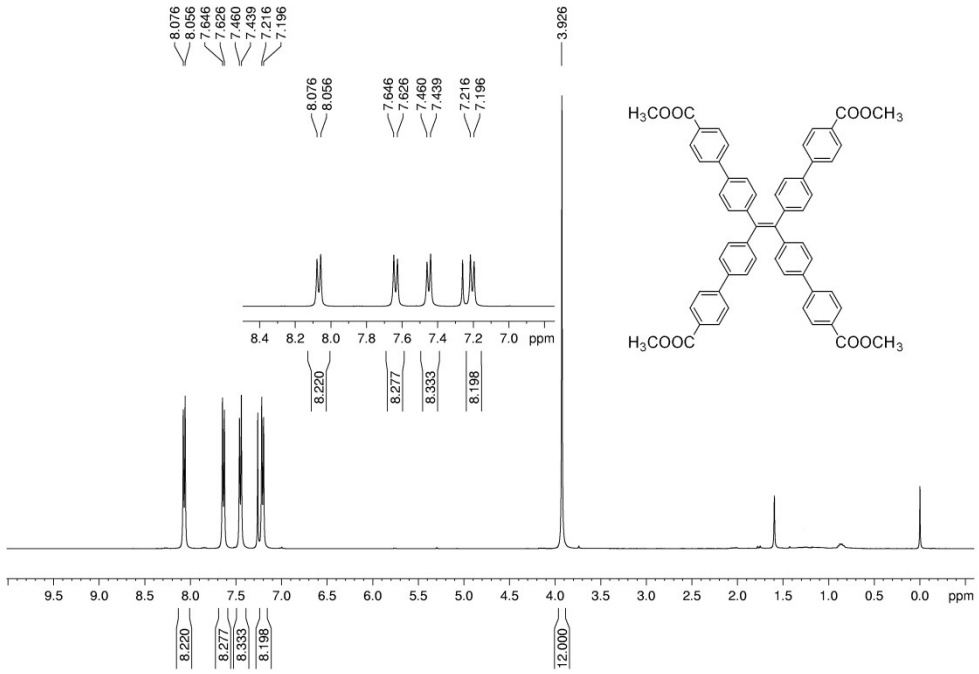



**Fig. S33**. $^{1}H$ NMR spectrum of compound **11** in $CDCl_3$.

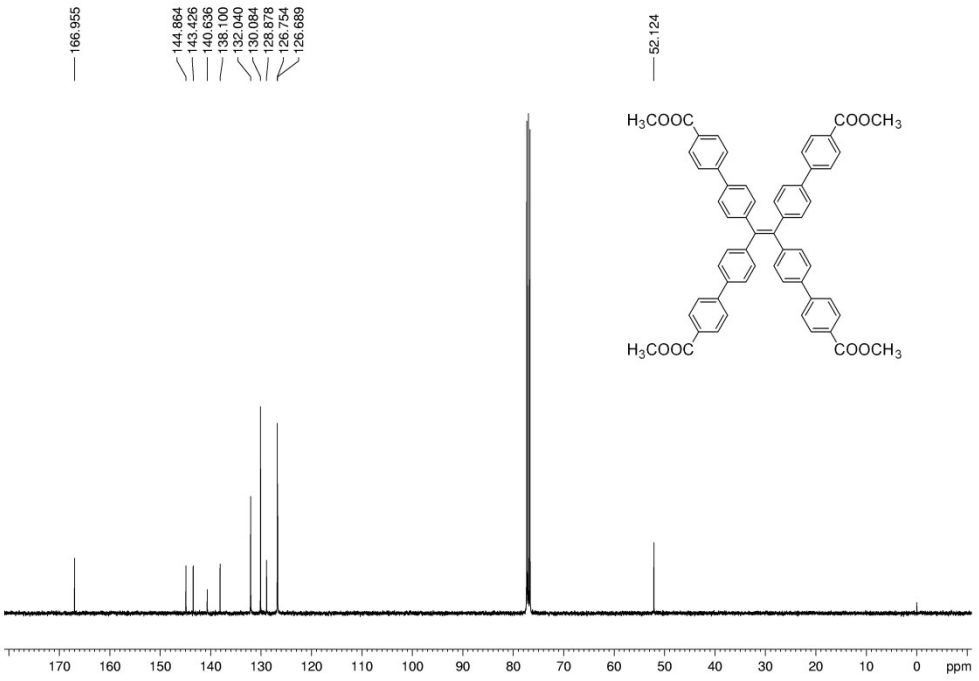



**Fig. S34**. $^{13}C$ NMR spectrum of compound **11** in $CDCl_3$.

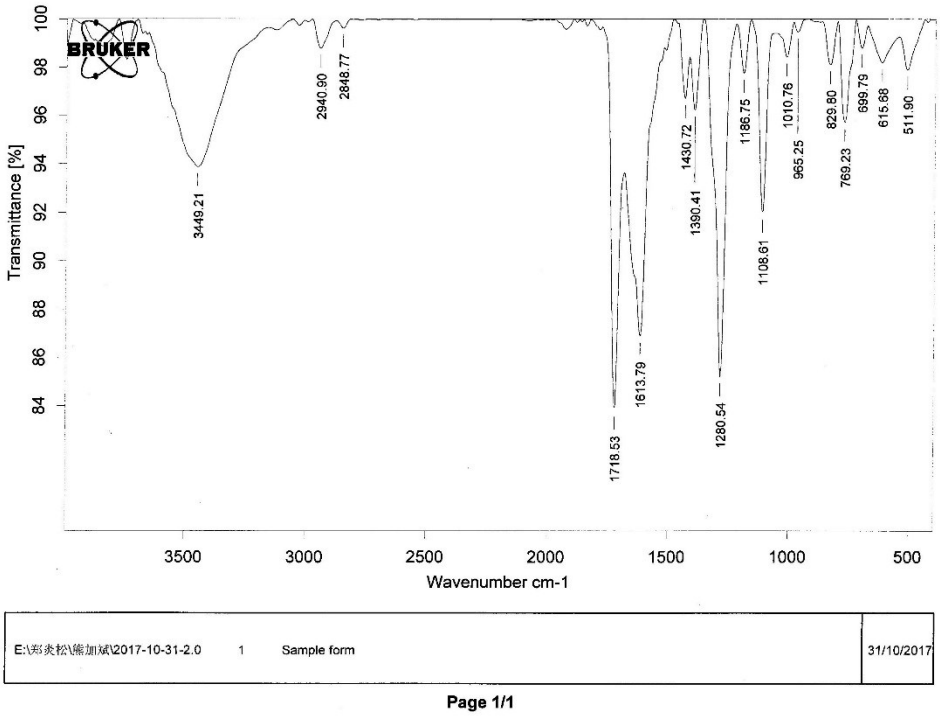
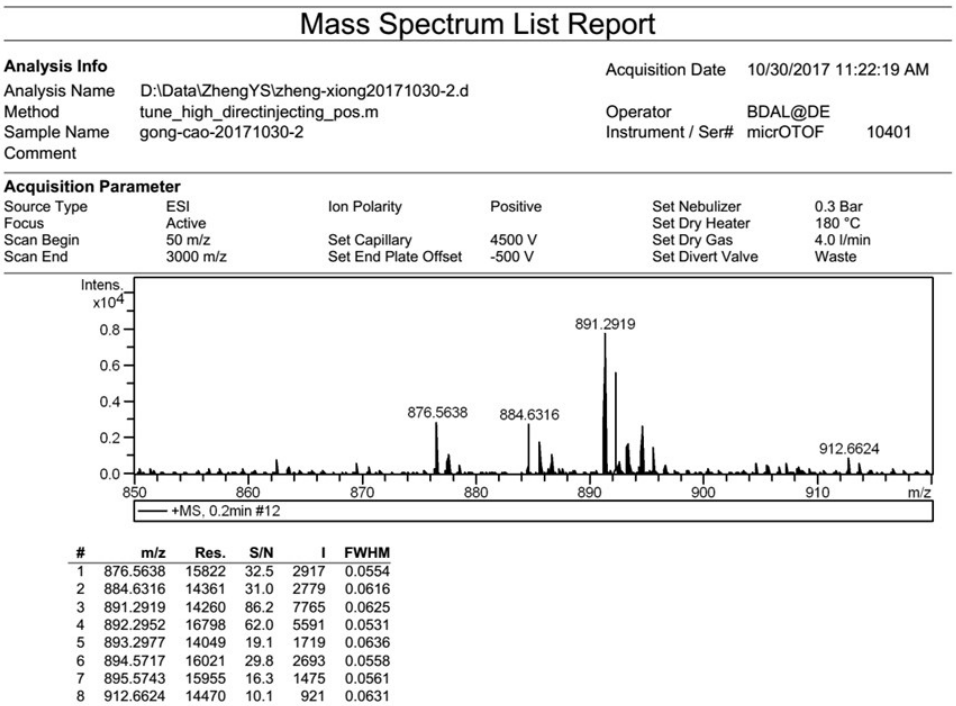



**Fig. S35**. IR spectrum of compound **11**.




| # | m/z | Res. | S/N | I | FWHM |
|---|---|---|---|---|---|
| 1 | 876.5638 | 15822 | 32.5 | 2917 | 0.0554 |
| 2 | 884.6316 | 14361 | 31.0 | 2779 | 0.0616 |
| 3 | 891.2919 | 14260 | 86.2 | 7765 | 0.0625 |
| 4 | 892.2952 | 16798 | 62.0 | 5591 | 0.0531 |
| 5 | 893.2977 | 14049 | 19.1 | 1719 | 0.0636 |
| 6 | 894.5717 | 16021 | 29.8 | 2693 | 0.0558 |
| 7 | 895.5743 | 15955 | 16.3 | 1475 | 0.0561 |
| 8 | 912.6624 | 14470 | 10.1 | 921 | 0.0631 |

**Fig. S36**. HRMS spectrum of compound **11**.

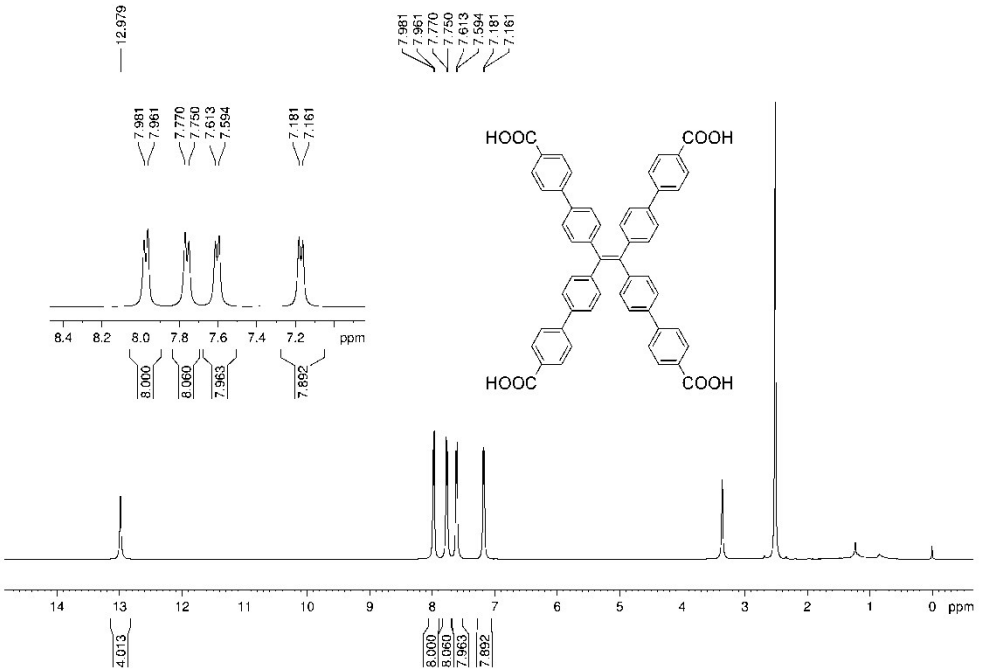



**Fig. S37**. $^{1}H$ NMR spectrum of compound **12** in $CDCl_3$.

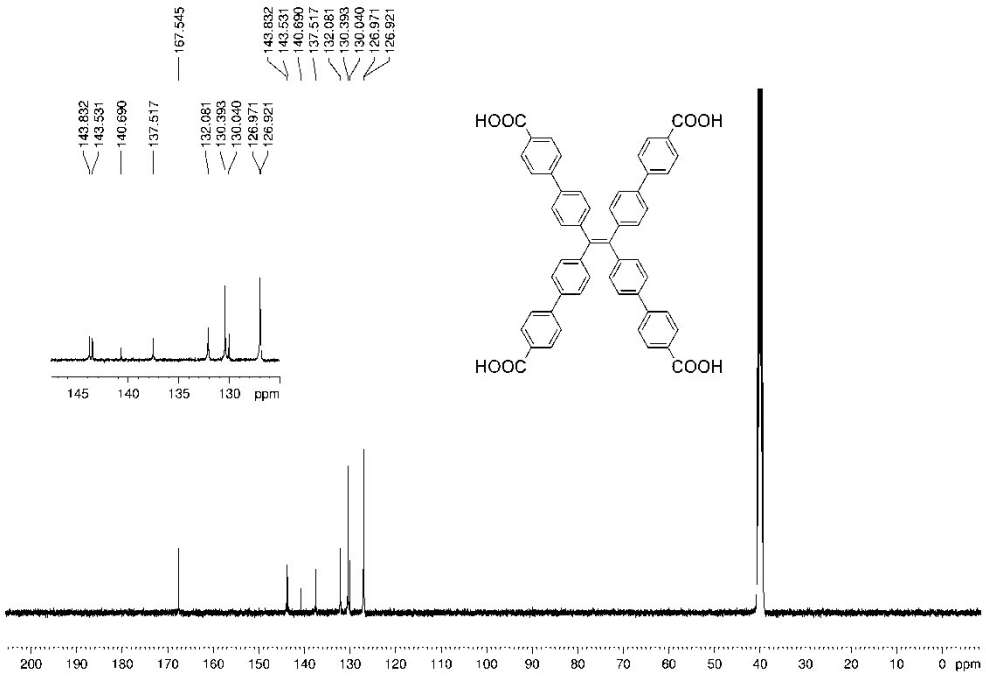



**Fig. S38**. $^{13}C$ NMR spectrum of compound **12** in $CDCl_3$.

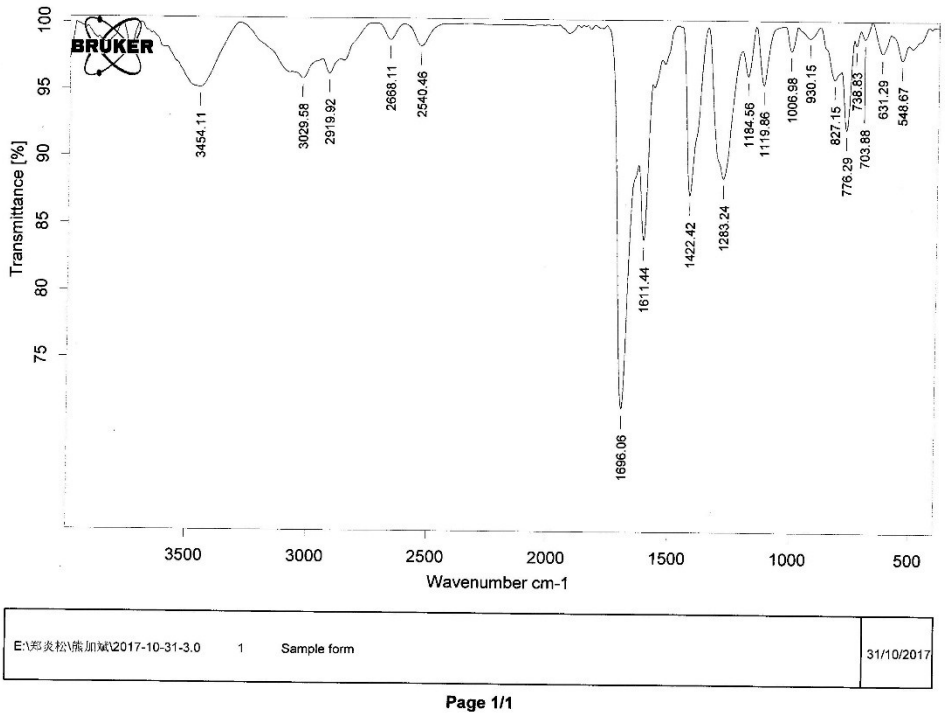
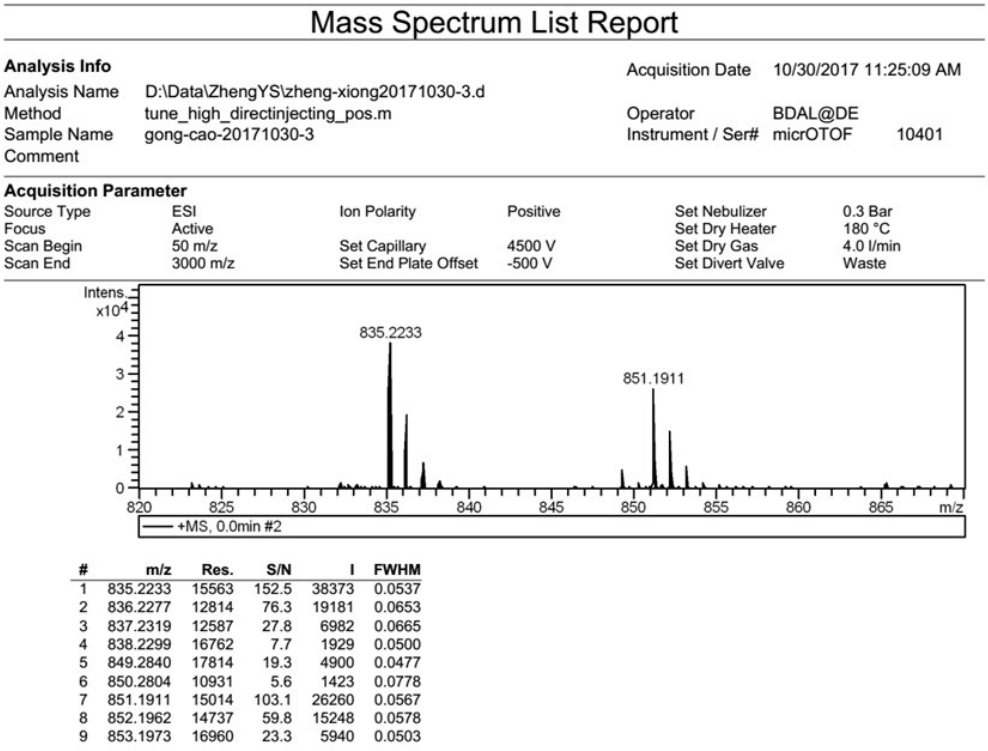



**Fig. S39**. IR spectrum of compound **12**.




| # | m/z | Res. | S/N | I | FWHM |
|---|---|---|---|---|---|
| 1 | 835.2233 | 15563 | 152.5 | 38373 | 0.0537 |
| 2 | 836.2277 | 12814 | 76.3 | 19181 | 0.0653 |
| 3 | 837.2319 | 12587 | 27.8 | 6982 | 0.0665 |
| 4 | 838.2299 | 16762 | 7.7 | 1929 | 0.0500 |
| 5 | 849.2840 | 17814 | 19.3 | 4900 | 0.0477 |
| 6 | 850.2804 | 10931 | 5.6 | 1423 | 0.0778 |
| 7 | 851.1911 | 15014 | 103.1 | 26260 | 0.0567 |
| 8 | 852.1962 | 14737 | 59.8 | 15248 | 0.0578 |
| 9 | 853.1973 | 16960 | 23.3 | 5940 | 0.0503 |

**Fig. S40**. HRMS spectrum of compound **12**.

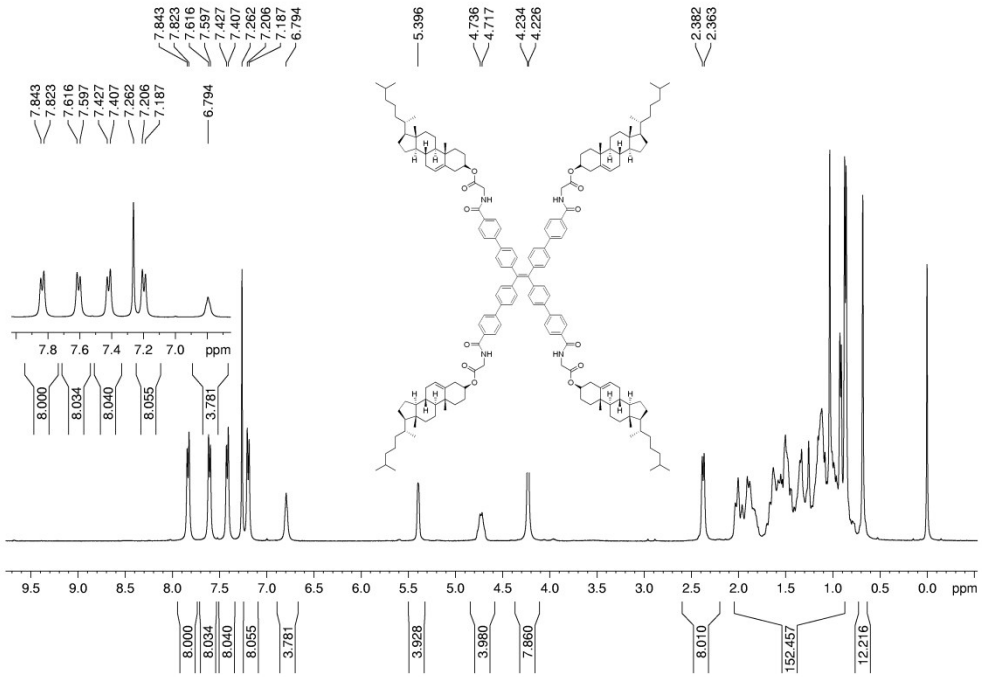


**Fig. S41**. $^{1}$H NMR spectrum of compound **13** in $CDCl_3$.

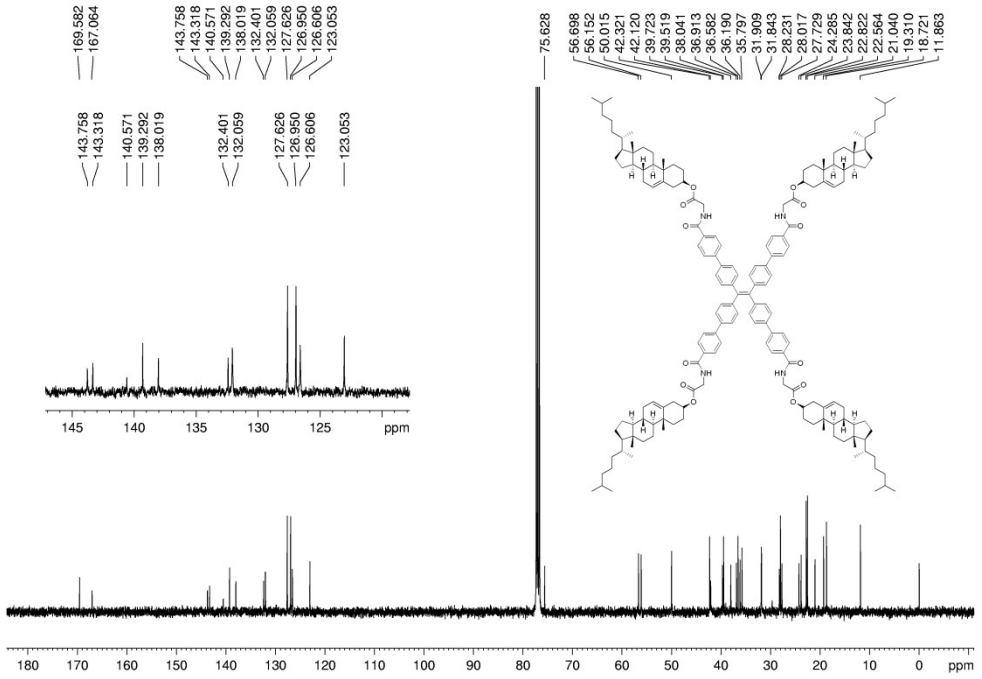


**Fig. S42**. $^{13}$C NMR spectrum of compound **13** in $CDCl_3$.

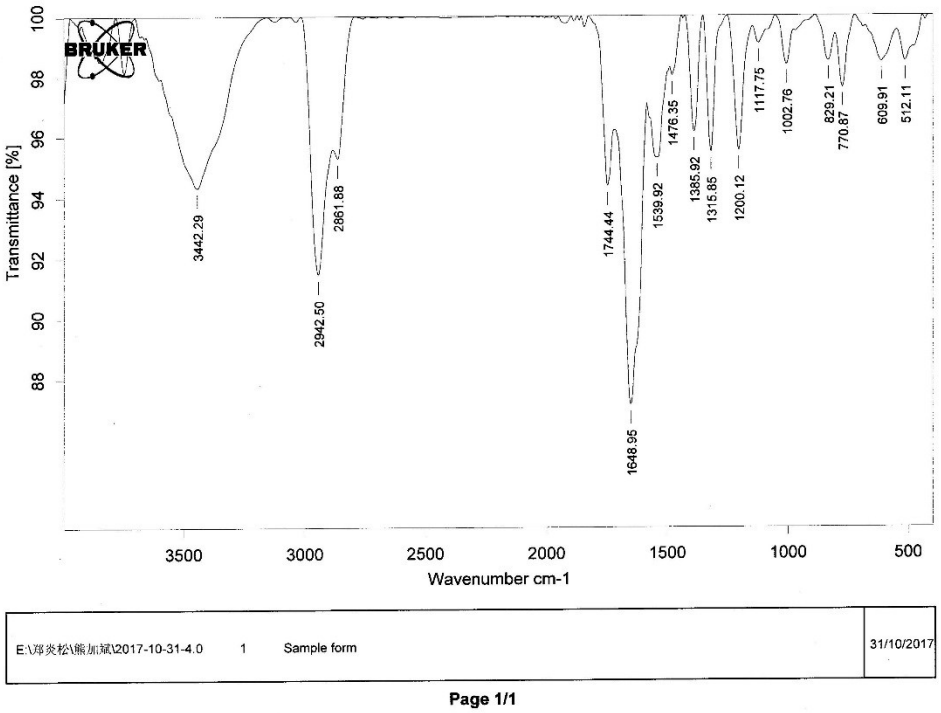



**Fig. S43**. IR spectrum of compound **13**.

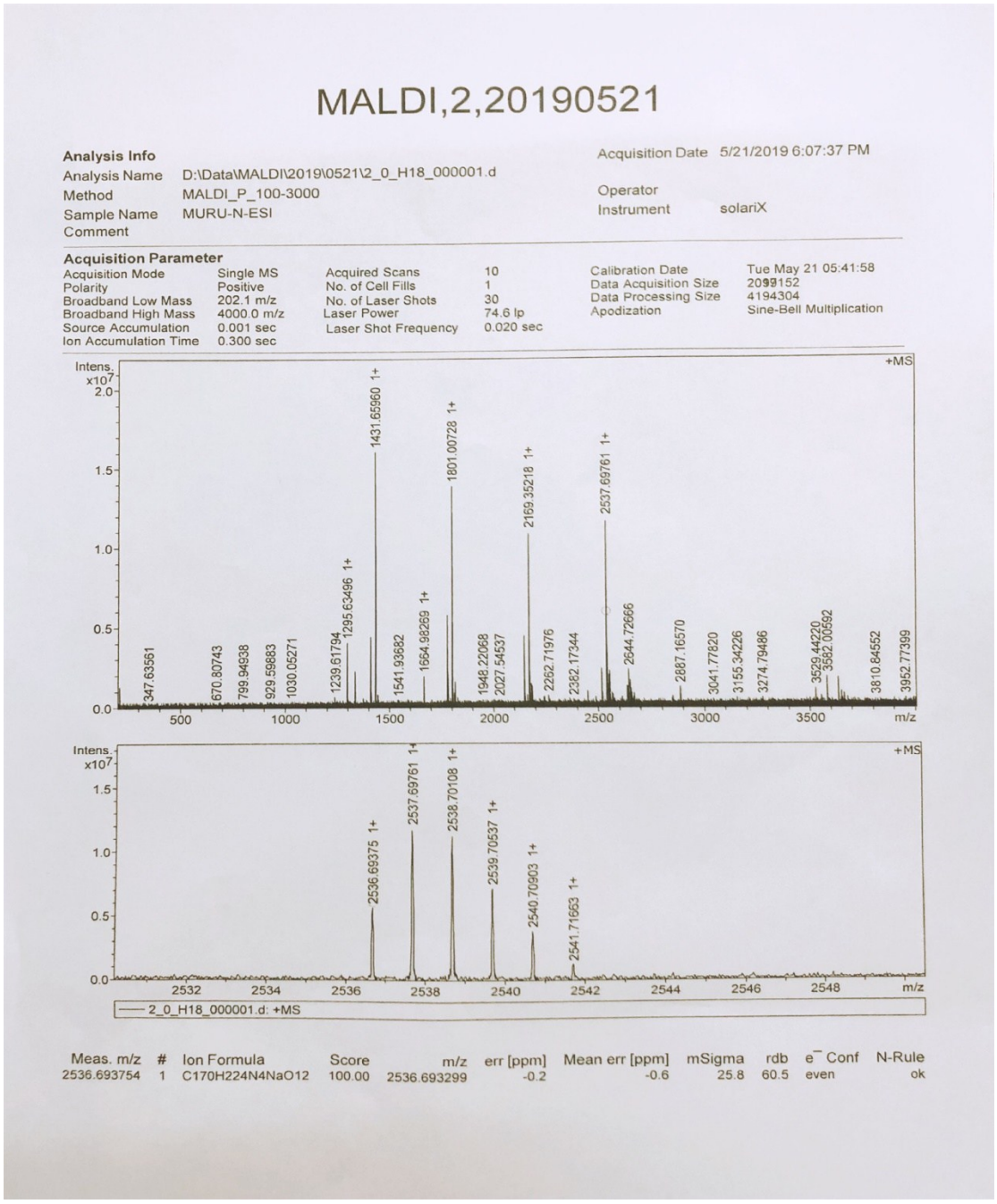



**Fig. S44.** HRMS spectrum of compound **13**.

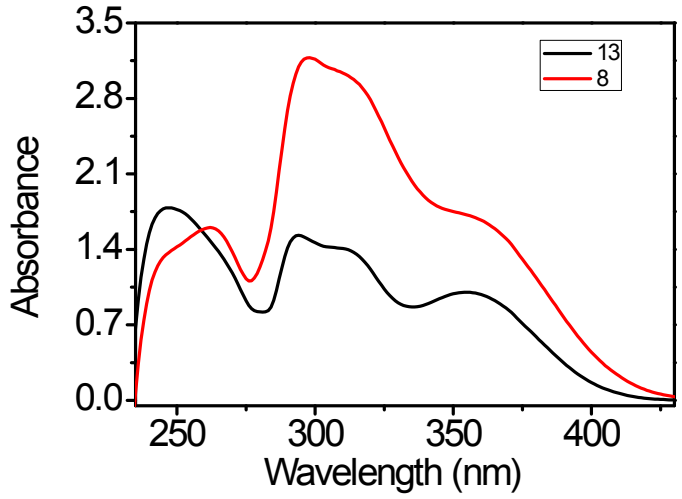



**Fig. S45**. The absorption spectra of **8** and **13** in THF. [**8**] = [**13**] = $5.0 \times 10^{-5}$ M.

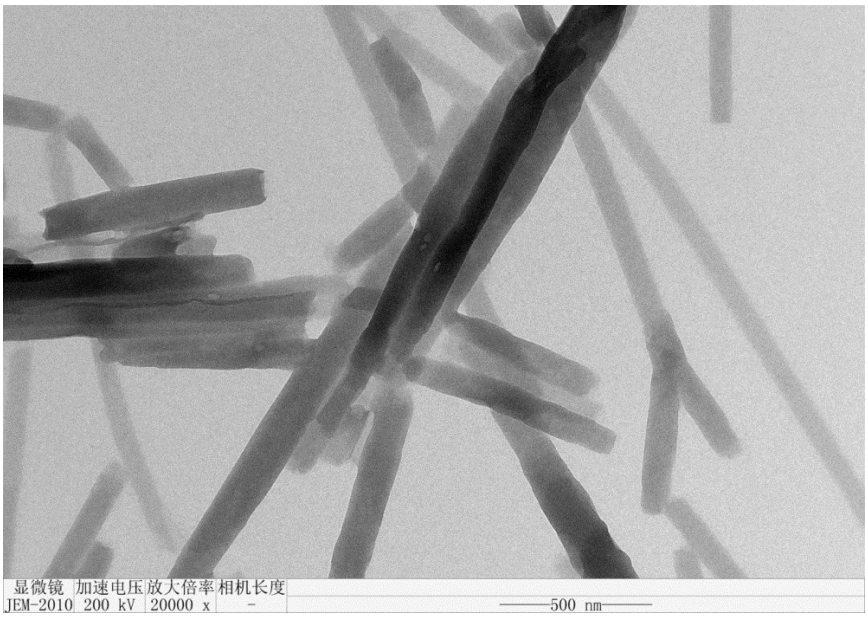



**Fig. S46.** TEM image of suspension of **8** in DCE instantly observed after the suspension was produced by heating and cooling to room temperature.

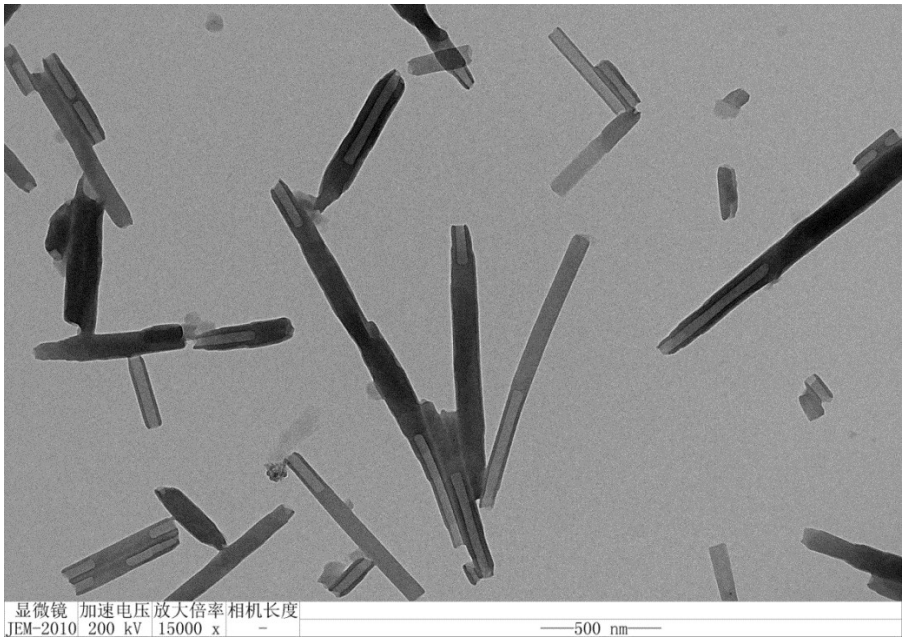



**Fig. S47.** TEM image of suspension of **8** in DCE observed after the suspension was left to stand for one week at room temperature.

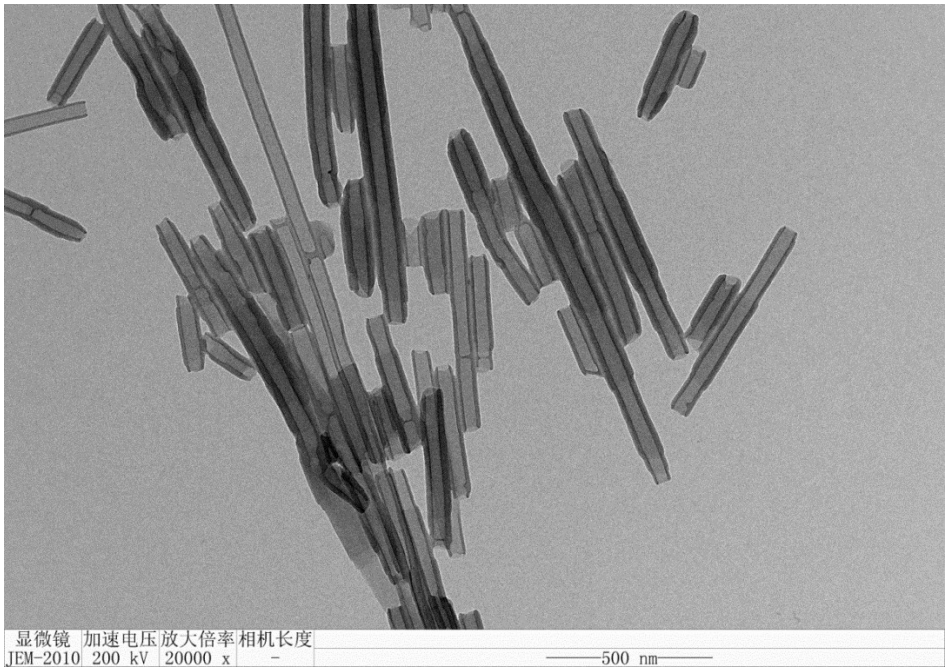



**Fig. S48.** TEM image of suspension of **8** in DCE observed after the suspension was left to stand for two months at room temperature.

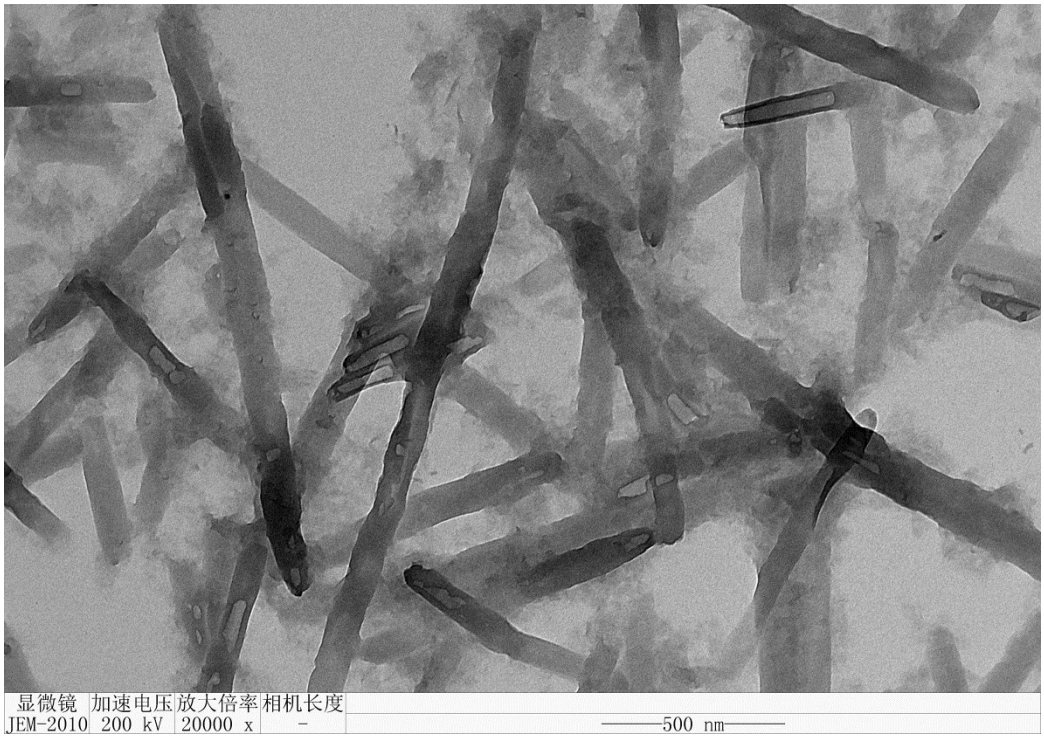



**Fig. S49.** TEM image of suspension of **8** in DCE observed after the suspension was produced by slow cooling to room temperature at 3 °C per hour.

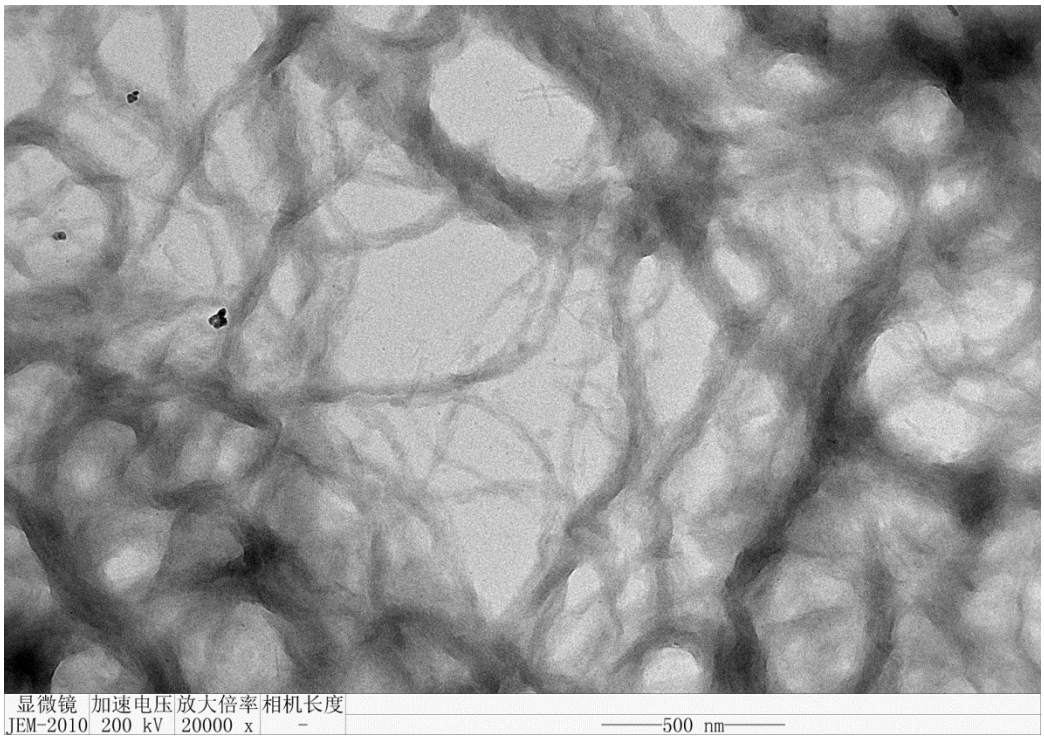



**Fig. S50.** TEM image of suspension of **13** in DCE observed after the suspension was produced by slow cooling to room temperature at 3 °C per hour.

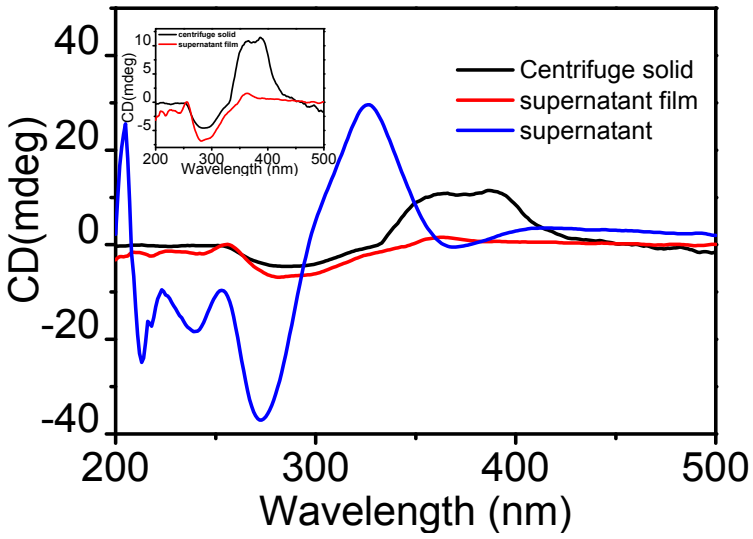
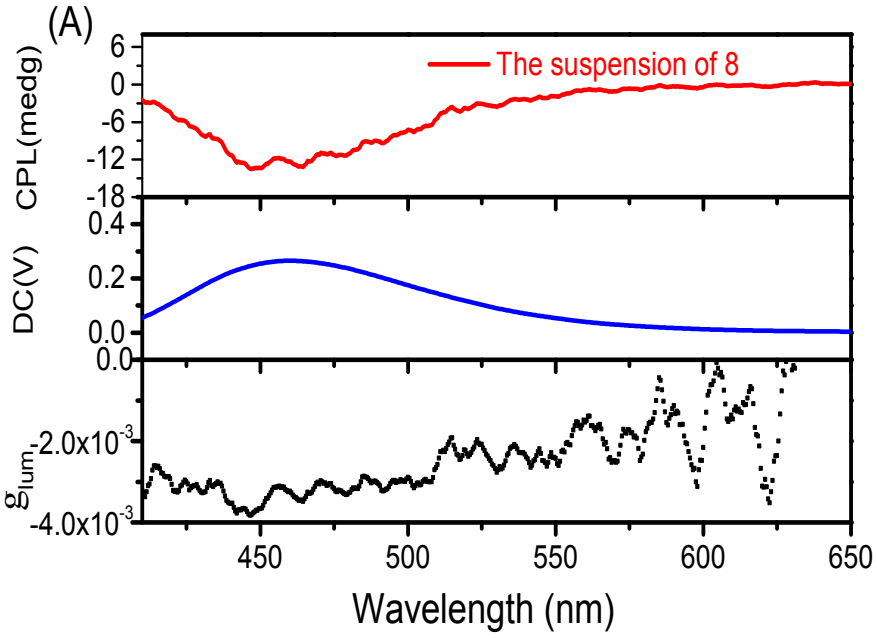
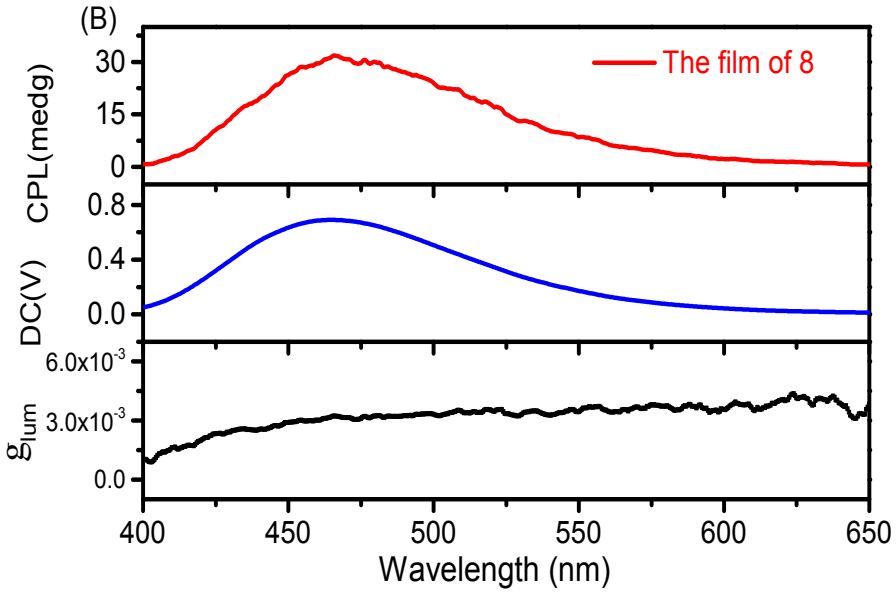
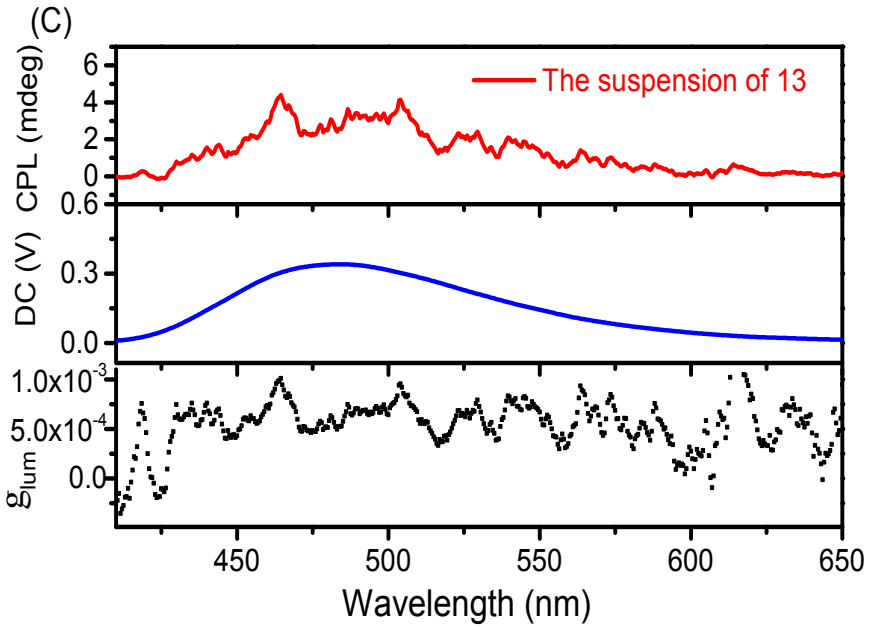



**Fig. S51**. CD spectra of the supernatant of **8**, the corresponding film from the supernatant of **8** and solid of **8** obtained from the suspension of **8** in DCE by centrifuge method.




(B)
The film of 8
CPL(medg)
30
15
0
DC(V)
0.8
0.4
0.0
$g_{lum}$
$6.0x10^{-3}$
$3.0x10^{-3}$
0.0
400
450
500
550
600
650
Wavelength (nm)


(C)
The suspension of 13
CPL (mdeg)
6
4
2
0
DC (V)
0.6
0.3
0.0
$g_{lum}$
$1.0x10^{-3}$
$5.0x10^{-4}$
0.0
450
500
550
600
650
Wavelength (nm)

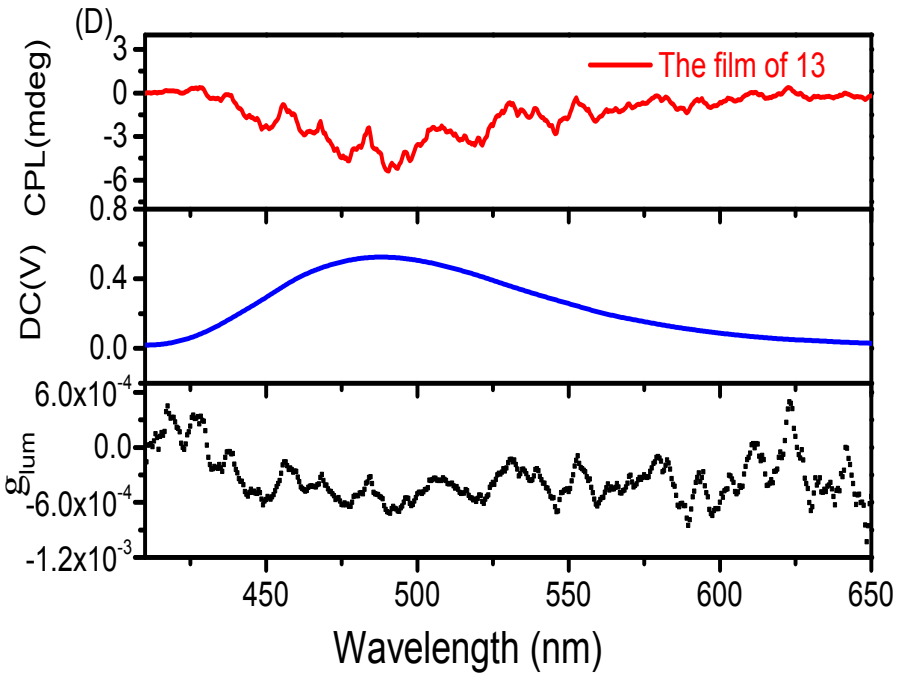
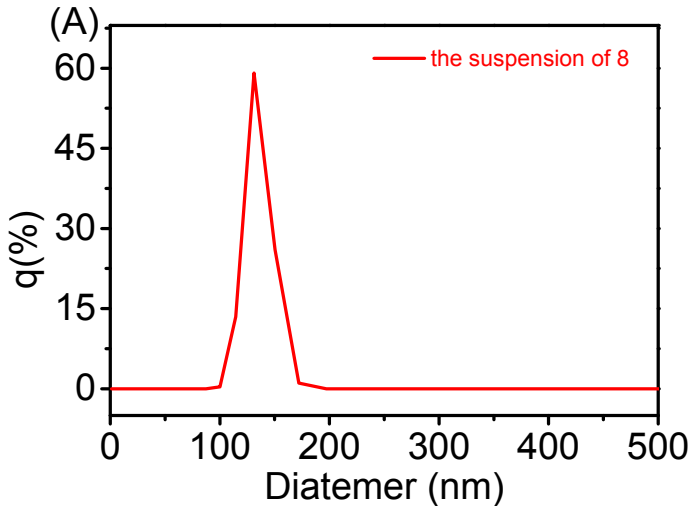



**Fig. S52.** CPL spectrum and $g_{lum}$ spectrum of the suspension of **8** (A) and **13** (C), and that of the films of **8** (B) and **13** (D). [**8**] = [**13**] = $1.0 \times 10^{-3}$ M in DCE.



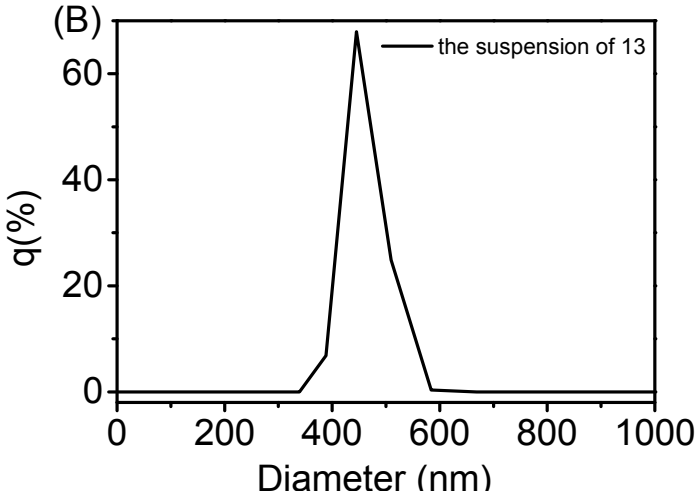
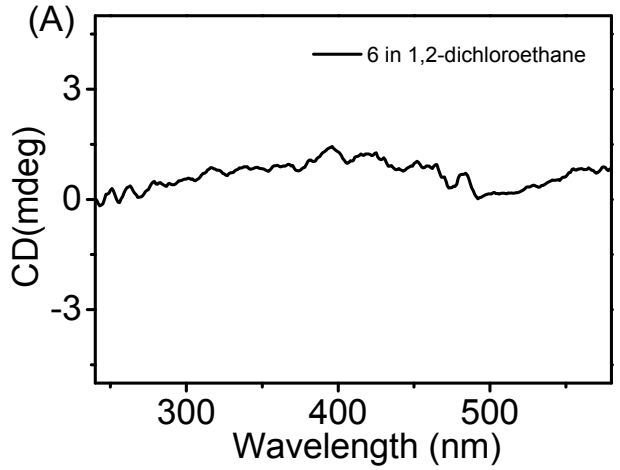
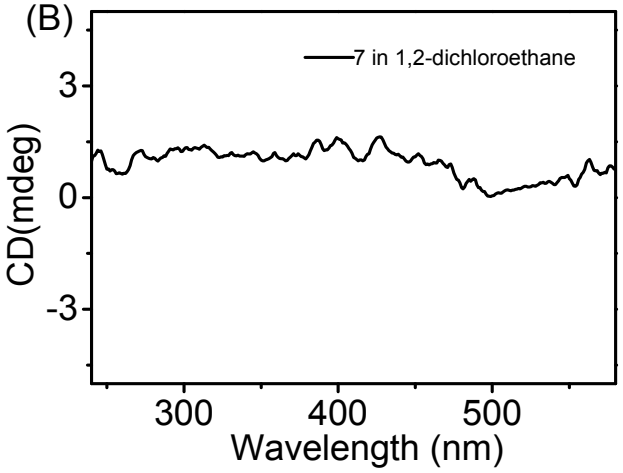



**Fig. S53.** DLS diagram of the suspension of **8** (A) and **13** (B). [**8**] = [**13**] = $5.0 \times 10^{-4}$ M in DCE.



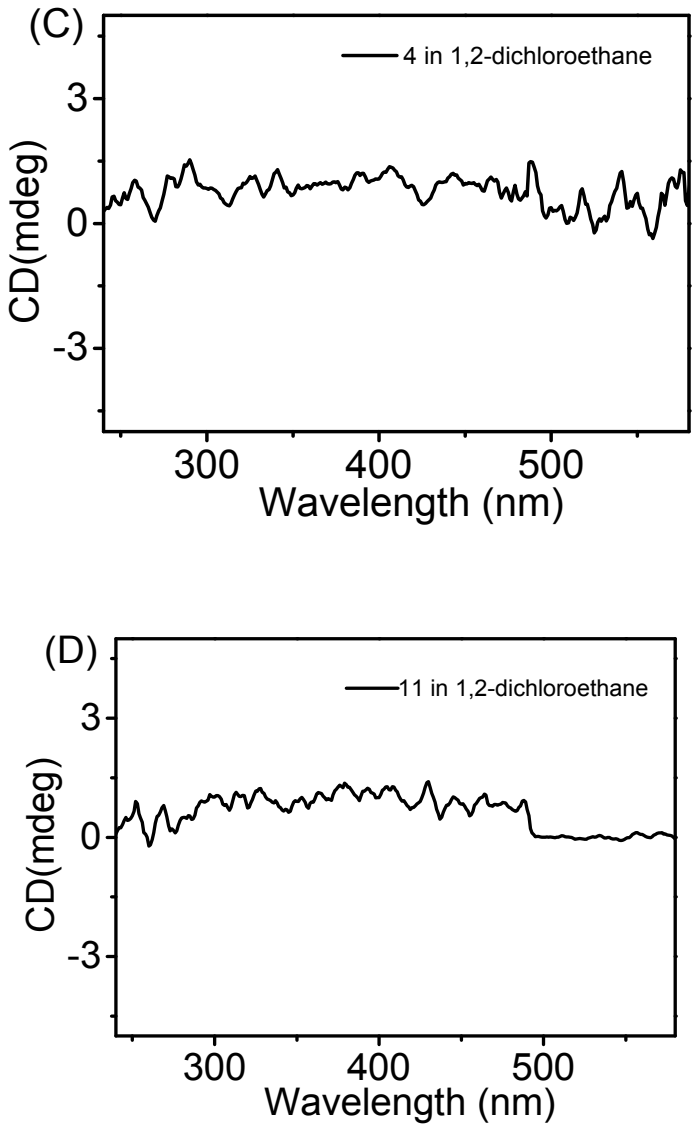



**Fig. S54.** CD spectra of the solution of **6** (A), **7** (B), **4** (C) and **11** (D) in DCE. [**6**] = [**7**] = [**4**] = [**11**]=1.0 × $10^{-3}$ M.

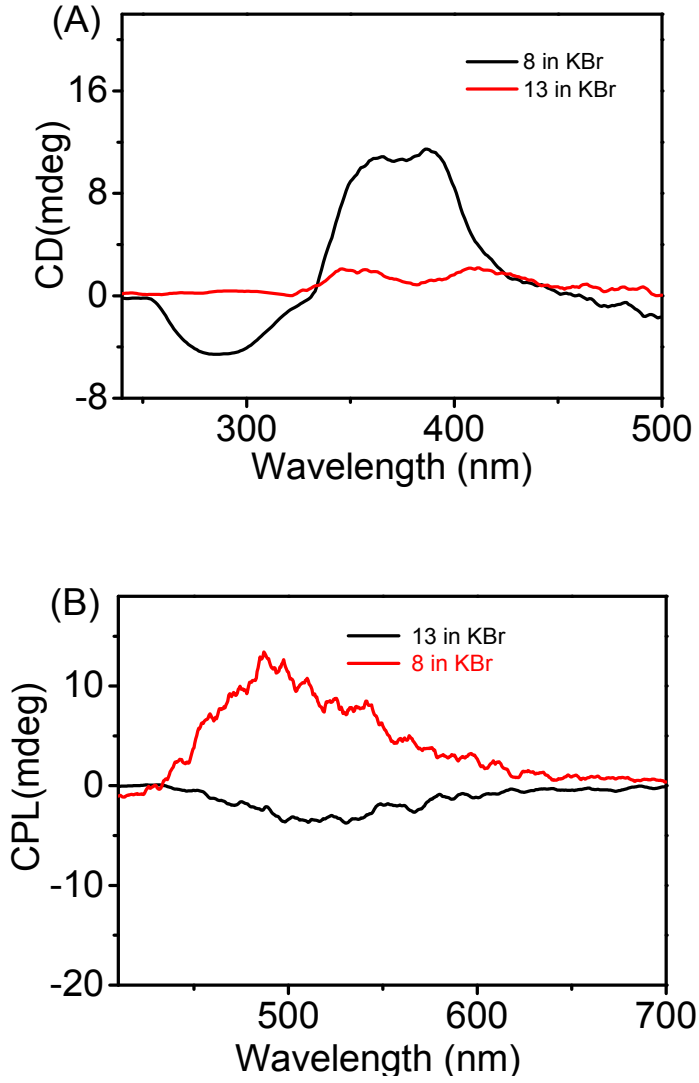



**Fig. S55.** CD (A) and CPL (B) spectra of **8** and **13** in KBr. [**8**] = [**13**] = 0.2 $\mu$mol in 200 mg of KBr.