Electronic Supplementary Information

The steric hindrance effect of bulky groups on the formation of columnar superlattices and optoelectronic properties of triphenylene-based discotic liquid crystals

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Table of Contents

S1. Materials

All chemicals were purchased from Aladdin, and all solvents from Aldrich. All chemicals and solvents were used without further purification. Silica gel 60 (200-300 mesh ASTM) and silica gel 60 glass thin-layer chromatography were used for the purification and identification of the reaction, respectively.

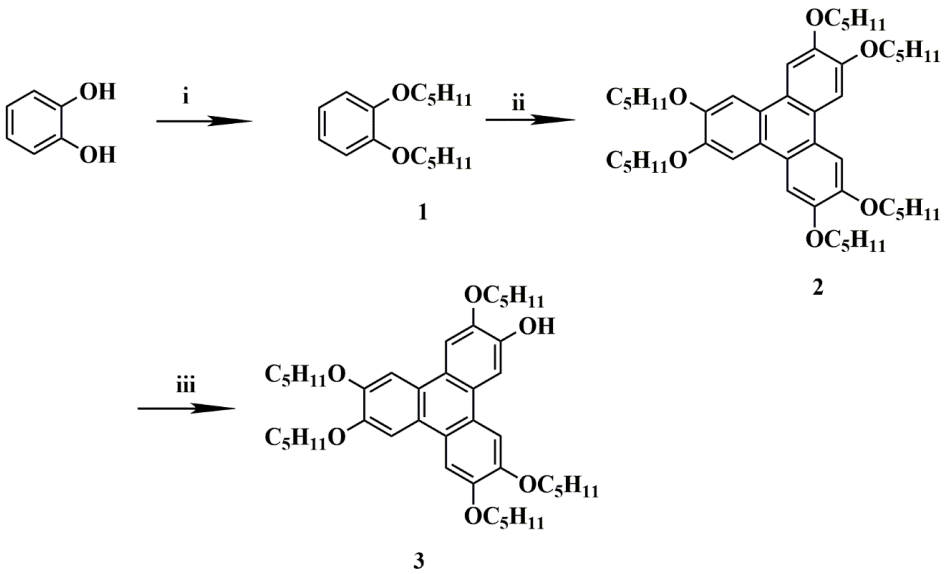
S2. Instrumentations

S2.1. Chemical structure characterizations : The ^{1}H-NMR spectra were recorded by a Bruker NMR spectrometer (DMX 400 MHz) in $CDCl_3$, Chemical shifts are given as units of measurement and expressed in parts per million (δ) with tetra-methylsilane (TMS) as a reference. Multiplicities of peaks are expressed as s = singlet, d = doublet, t = triplet, m = multiplet; The ^{13}C-NMR spectra were recorded by a Bruker 700M NMR spectrometer in $CDCl_3$; The high resolution mass spectrum was recorded on a Bruker Apex IV FTMS mass spectrometer; The KBr pellets were used to make the test samples and the infrared spectrum (FT-IR) was recorded on a Shimadzu FTIR-8400 spectrometer by Fourier transform.

S2.2. Mesophase characterizations of samples: The thermal properties of discotic liquid crystals were characterized by using differential scanning calorimeter (DSC) on a Netzsch DSC 200. Its optical properties were characterized by a Polarizing Microscope (POM) on a Leica DM4500P with a Linkam TMS94 hot stage.

S2.3. Self-assembly properties of samples: The structural characterizations of samples were characterized by 1D wide-angle X-ray diffraction (1DWAXD) through a Bruker D8 Advance diffractometer equipped with a variable temperature controller; two-dimensional wide-angle X-ray diffraction (2DWAXD) using a 40KV FL tube as the X-ray source (Cu Ka).

S3. Syntheses

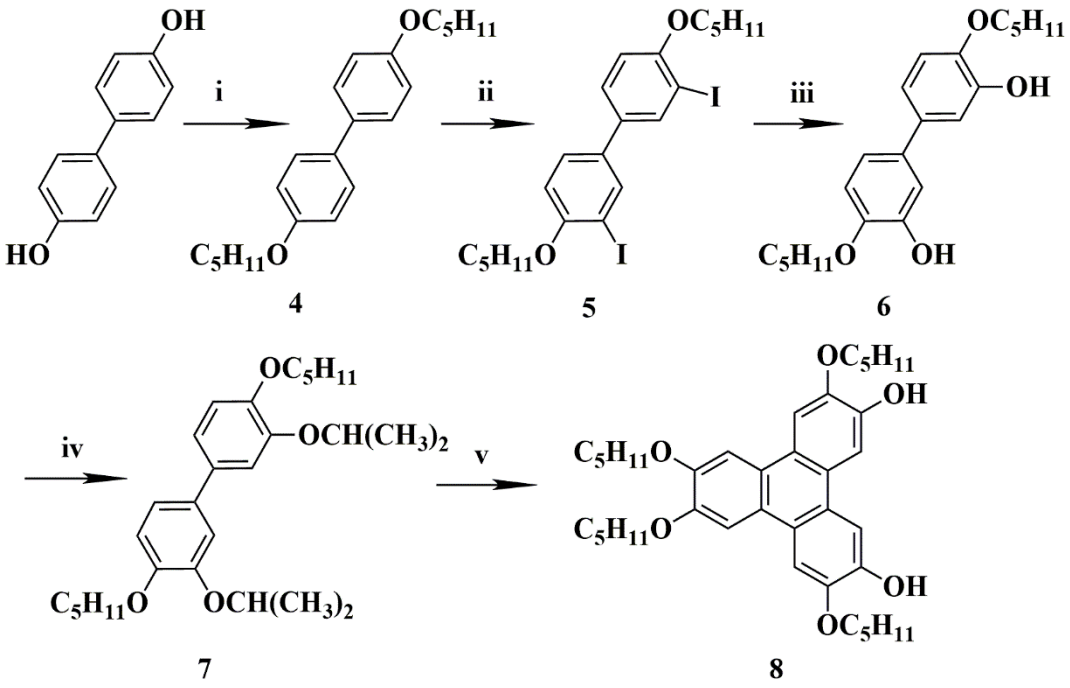


1 2 3

Preparation of 1,2-dipentoxybenzene (1). 1-Bromopentane (181g, 1.2mol) was added to a vigorously stirred solution of catechol (44g, 0.4mol) and potassium carbonate (331g) in ethanol (100ml) and acetone (200ml) under nitrogen. The reaction mixture was stirred under reflux for 24 hours. Then the mixture was filtered and the solvent was removed in vacuo. Distillation of the residue at 120-122℃ afforded as a colorless oil (96g, 96%). TLC R_f: 0.65 (dichloromethane-hexane 1:1). ^{1}HNMR (400 MHz, $CDCl_3$) δ_H: 6.90（m, 4H, Ar-H), 4.02（s, 4H, OCH_2), 1.80-1.87 (m, 4H, OCH_2CH_2), 1.38-1.50 (m, 8H, $OCH_2CH_2CH_2CH_2$), 0.97 (t, 6H,CH_3).

Preparation of 2,3,6,7,10,11-hexapentyloxytriphenylene (2). Compound 1 (15g, 0.06mol) was added to a vigorously stirred suspension of Iron(III) chloride (31.1g, 0.19mol) in dichloromethane (100ml). The reaction occurred with vigorous evolution of gas and was quenched with methanol (700ml) after 2 hours. which was added to bromopentane (18.12g) and potassium carbonate (316.56g) in acetone (150 ml) under nitrogen, then heated to 60℃ and refluxed. The reaction mixture was filtered and the filtrate was concentrated in vacuo to give a pale yellow powder, which was recrystallized from ethanol to give 2 as pale yellow powder (11.8g, 79.3%). ^{1}H NMR (400 MHz, $CDCl_3$), δ_H: 7.85 (s, 6H, Ar-H), 4.25 (t, 12H, OCH_2), 1.92-1.99 (m, 12H, CH_2), 1.42-1.67 (m, 24H, CH_2), 0.99 (t, 18H, CH_3).

Preparation of 2-hydroxy-3,6,7,10,11-pentapentyloxytriphenylene (3). To a cooled suspension of catechol (11g) in CH_2Cl_2 (70 mL), a solution (0 ℃) of BBr_3 (10.6ml) was added slowly with stirring 3h under nitrogen. The mixture was brought to room temperature, the solvent removed and the product distilled under vacuum to give B-Bromocatecholboronane as white solid (9.63g). The solid was then used to make a 0.5 mol/L and this was used for the next ether cleavage reactions. A solution of 2 (14.88g, 0.02 mol) was dissolved in anhydrous CH_2Cl_2 (200ml) and cooled to 0 ℃. To this was added (48ml, 1.2equiv) of B-Bromocatecholboronane solution in CH_2Cl_2under argon and the mixture was stirred at room temperature for 24h. After that it was poured over ice-water and extracted with CH_2Cl_2, the combined extract was dried with anhydrous Na_2SO_4 overnight, solvent was removed under vacuum and the crude product was purified by a silica gel column chromatography, eluting with 1: 32 ethyl acetate: light petroleum to give 3 as white powder which was recrystallized from ethanol (6.2g, 46%). ^{1}H NMR(400 MHz, $CDCl_3$), δ_H: 7.96-7.77 (m, 6H, Ar-H), 5.91 (s, 1H, OH), 4.31-4.19 (t, 10H, CH_2), 1.97-1.90 (m, 10H, OCH_2CH_2), 0.97 (t, 15H, CH_3).



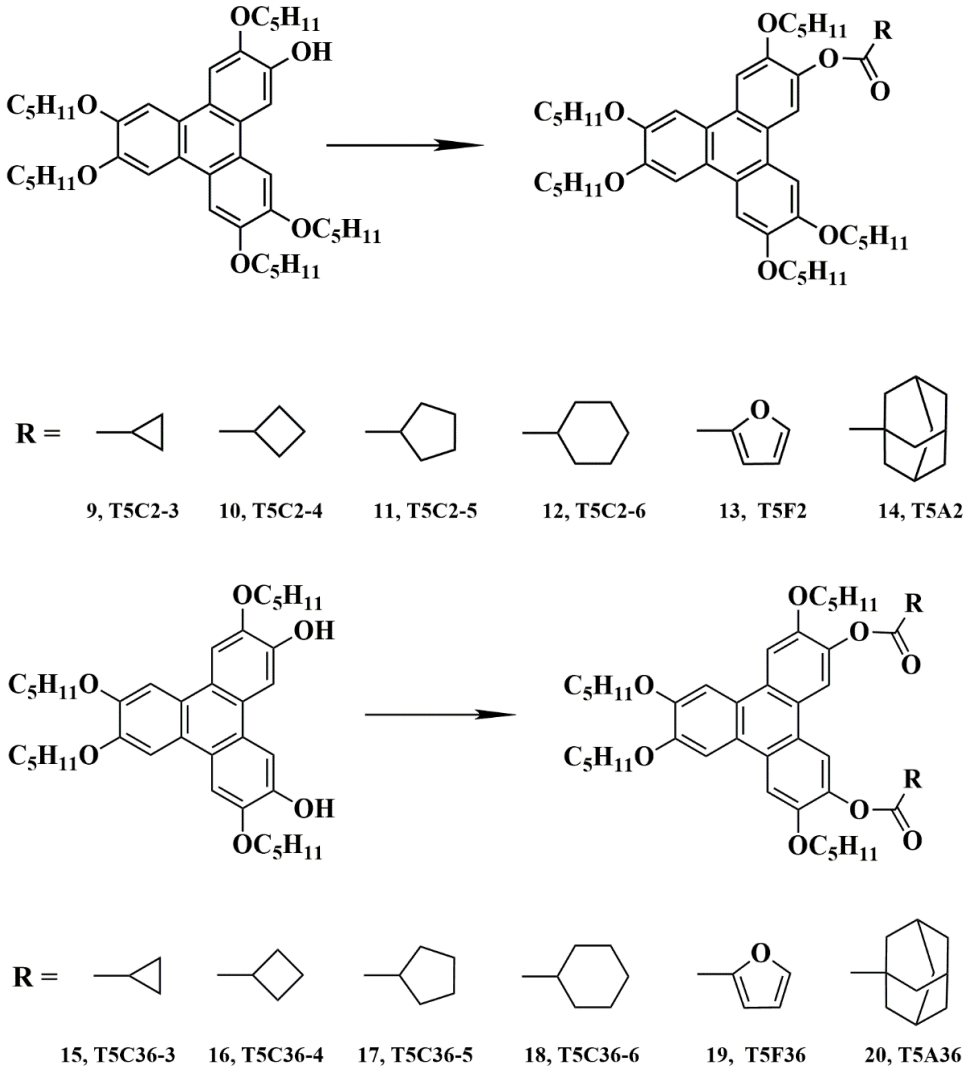
Preparation of 4,4'-dipentyloxyphenyl (4). A mixture of 4,4'-dihydroxybiphenylene (65.2 g, 0.35 mol), K2CO3 (160 g, 1.12 mol), hexadecyl trimethyl ammonium bromide (catalyticamount) and KI catalytic amount in ethanol/acetone (300/100 ml) was refluxed under argon for 1h, then 1-bromopentane (145 g, 0.96 mol) was added, and the mixture was refluxed for another 24 h. Once the reaction was complete, the reaction mixture was poured into 1:1 ice-water to precipitate the product. The white precipitate was filtered and washed several times by water resulting in the crude product. After recrystallization from ethanol, white scaly solid was obtained (109.6 g, 97%). TLC R_f: 0.61 (dichloromethane-hexane 1:1). ^{1}H NMR (400 MHz, $CDCl_3$), δ_H: 7.57-7.38 (m,4H, Ar-H), 6.95 (d, J=6.3Hz, 4H, Ar-H), 4.08-3.97 (m, 4H, OCH_2), 1.86-1.77 (m, 4H, OCH_2CH_2), 1.49-1.28 (m, 8H, CH_2), 0.97-0.85 (m, 6H, CH_3).

Preparation of 3,3'-diiodo-4,4'-dipentyloxyphenyl (5). A mixture of glacial acetic acid 200 g, iodine (42 g, 168 mmol), iodic acid (17.74 g, 100 mmol), deionized water 60 ml, chloroform 140 ml and 4,4'-dipentyloxybiphenyl (65.2 g, 200 mmol) was stirred for a while, and then concentrated sulphuric acid (7.6 g) was added and the mixture was heated with stirring at 85°C for 20 h. After the reaction was complete, 280 ml of chloroform and 120 ml deionized water were added and the mixture was stirred for 10 min. the organic layer was separated and washed by saturated Na2SO3 solution three times and deionized water once. The organic layer was dried over anhydrous sodium sulfate and passed through a short silica column (chloroform) to get the crude product,3,3'-diiodo-4,4'-dipentyloxybiphenyl. The crude product was recrystallized by ethanol to obtain the white solid (109.4 g, 94.6%). TLC R_f: 0.71 (dichloromethane-hexane 1:1). ^{1}H NMR (400 MHz,CDCl3), δ_H: 7.93 (s, 2H, Ar-H), 7.42 (dd, J=1.5Hz, J=8.4Hz, 2H, Ar-H), 6.82 (d, J=8.4Hz, 2H, Ar-H), 4.04 (t, J=6.6Hz, 4H, OCH_2), 1.91-1.82 (m, 4H, OCH_2CH_2), 1.57-1.36 (m, 8H, CH_2), 0.99-0.89 (m, 6H, CH_3).

Preparation of 3,3'-dihydroxy-4,4'-dipentyloxyphenyl (6). A mixture of PEG-400 480 ml, deionized water 120 ml, KOH (67.2 g, 1.2 mol) and 5 (57.8 g, 100 mmol) was stirred under nitrogen protection for 30 min and then CuI (7.8 g, 20 mmol) was added carefully. The mixture was heated to 140°C under nitrogen protection for 36 h. After the reaction was complete, the reaction mixture was cooled to room temperature. Hydrochloric acid (1 M) was added to acidify the solution (pH = 2) and the solution was extracted with ethyl acetate (3×400ml). The organic layer was concentrated and recrystallized by ethanol (very small amount) to give white needle crystal (10.8g, 30%). TLC Rf: 0.28 (dichloromethane-hexane 1:1). ^{1}H NMR (400 MHz, $CDCl_3$), δ_H: 7.15 (s, 2H, Ar-H), 7.02 (dd, J=2.1Hz, J=6.3Hz, 2H, Ar-H), 6.88 (d, J=8.4Hz, 2H, Ar-H), 5.68 (s, 2H, OH), 4.07 (t, 4H, OCH_2), 1.89-1.80 (m, 4H, OCH_2CH_2), 1.51-1.32 (m, 8H, CH_2), 0.98-0.89 (m, 6H, CH_3).

Preparation of 3,3'-diisopropyl-4,4'-dipentyloxyphenyl (7). A mixture of 6 (8g, 22 mmol), K2CO3 (18 g,132 mmol), hexadecyl trimethyl ammonium bromide (catalytic amount) and KI catalytic amount, ethanol/acetone (100/50 ml) was refluxed under argon for 1 h, then 2-bromopropane (5.3 g, 88 mmol) was added and the mixture was refluxed for another 24 h. Once the reaction was complete, the reaction mixture was filtered and the filtrate was concentrated to give the crude product. After recrystallization from ethanol (small amount), white scaly solid was obtained (8.8g, 90%). TLC Rf: 0.52 (dichloromethane-hexane 1:1). ^{1}H NMR(400 MHz, $CDCl_3$), δ_H: 7.12-7.08 (m, 4H, Ar-H), 6.94-6.85 (m, 2H, Ar-H), 4.56-4.46 (m,2H, OCH), 4.01 (d, J=6.6Hz, 4H, OCH_2), 1.88-1.79 (m, 4H, OCH_2CH_2), 1.56-1.50 (m, 20H,$OCH(CH_3)_2$/CH_3), 0.94 (t, J=6.9Hz, 6H, CH_3).

Preparation of 3,6-dihydroxy-2,7,10,11-tetrakis(pentyloxy)triphenylene (8). A mixture of 7 (6.65g, 15 mmol), 1,2-dipentyloxybenzene (5.65 g, 22.5 mmol) and anhydrous dichloromethane (80 ml) was stirred under nitrogen protection for 30 min and then anhydrous ferric chloride (9.25g, 57 mmol) was added slowly. The mixture was stirred vigorously for another 12 h at room temperature. After the reaction was complete, the reaction mixture was poured into 150 ml cool methanol carefully. The mixture was concentrated and filtered. The filter cake was purified by columnar chromatography (silica, CH_2Cl_2: EtOAc = 80:1) to give the final white product (5.4g, 60%) mp 142°C. TLC R_f: 0.27 (ethyl acetate-hexane 1:4). ^{1}H NMR (400 MHz, $CDCl_3$), δ_H: 7.94 (s, 2H, Ar-H), 7.81 (s, 2H, Ar-H), 7.75 (s, 2H, Ar-H), 5.88 (s, 2H, OH), 4.30-4.21 (m, 8H,OCH_2), 2.00-1.91 (m, 8H, OCH_2CH_2), 1.62-1.40 (m, 16H, CH_2), 0.99 (dd, J=6.0Hz, J=7.2Hz,12H, CH_3).



Preparation of 2-ylcyclopropanecarboxylate-3,6,7,10,11-pentakis(pentyloxy)triphenylene (9). A mixture of 2-hydroxy-3,6,7,10,11-pentapentyloxytriphenylene (0.5g, 0.74 mmol), cyclopropanecarboxylic acid (0.19g, 2.2 mmol), 4-Dimethylaminopyridine (catalytic amount) and anhydrous dichloromethane (30 ml) was stirred under nitrogen protection for 30 min then dicyclohexylcarbodiimide (catalytic amount) was added slowly. The mixture was refluxed for another 24 h. After the reaction was complete, the reaction solution was filtered under reduced pressure to remove most of the N, N'-dicyclohexylurea. The filtrate was evaporated to dryness under reduced pressure. The residue crude product was purified by column chromatography on silica eluting with ethyl acetate/petroleum ether (1:10) to give a white solid. The solid was recrystallized by absolute alcohol several times (0.51g, 92.3%). FT-IR (cm^{-1}): 2958, 2937, 2861, 1746, 2922, 1521, 1267, 1158. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.08 (s, 1H), 7.91 – 7.73 (m, 5H), 4.22 (p, J = 6.2 Hz, 10H), 2.01 – 1.86 (m, 11H), 1.61 – 1.37 (m, 22H), 1.31 – 1.23 (m, 2H), 0.97 (td, J = 7.3, 1.5 Hz, 15H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 173.21, 149.24, 139.85, 127.88, 123.15, 116.72, 107.94, 106.89, 106.08, 69.81, 69.59 – 68.65, 29.12, 28.38, 28.26, 22.58, 14.13, 12.87, 9.10. HRMS: calc. m/z 742.48085 ($C_{47}H_{66}O_7$), found m/z 742.47667 $(M)^+$. According to the same method, other triphenylene derivatives were successfully synthesized.

2-ylcyclobutanecarboxylate-3,6,7,10,11-pentakis(pentyloxy)triphenylene (10). FT-IR (cm^{-1}): 2962, 2937, 2864, 1748, 1521, 1267, 1146. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.06 (s, 1H), 7.89 – 7.74 (m, 5H), 4.31 – 4.15 (m, 10H), 3.58 – 3.45 (m, 1H), 2.66 – 2.49 (m, 2H), 2.40 (dddd, J = 10.6, 8.6, 6.5, 3.4 Hz, 2H), 2.14 – 1.82 (m, 12H), 1.58 – 1.37 (m, 20H), 0.97 (tdd, J = 7.2, 3.1, 2.0 Hz, 15H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 173.70, 149.61, 148.83, 139.78, 127.88, 124.61, 123.31, 116.68, 107.97, 107.05, 106.54, 105.83, 69.81, 69.46, 69.23, 68.73, 38.06, 29.27 – 28.99, 28.34, 25.44, 22.58, 18.61, 14.11. HRMS: calc. m/z 756.49650 ($C_{48}H_{68}O_7$), found m/z 756.49831 $(M)^+$.

2-ylcyclopentanecarboxylate-3,6,7,10,11-pentakis(pentyloxy)triphenylene (11). FT-IR (cm^{-1}): 2962, 2935, 2864, 1750, 1521, 1268, 1149. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.05 (s, 1H), 7.89 – 7.71 (m, 5H), 4.32 – 4.15 (m, 10H), 3.12 (p, J = 7.9 Hz, 1H), 2.18 – 2.05 (m, 4H), 2.00 – 1.78 (m, 12H), 1.70 (dp, J = 9.8, 3.2 Hz, 2H), 1.56 – 1.38 (m, 20H), 0.97 (tt, J = 7.2, 2.4 Hz, 15H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 175.05, 149.64, 148.83, 127.84, 123.53, 123.08, 116.69, 108.01, 107.23, 106.89, 106.60, 105.72, 69.89, 69.76, 69.47, 69.26, 68.70, 43.71, 30.17, 29.26 – 29.00, 28.35, 26.06, 22.59, 14.11. HRMS: calc. m/z 770.51215 ($C_{49}H_{70}O_7$), found m/z 770.51042 $(M)^+$.

2-ylcyclohexanecarboxylate-3,6,7,10,11-pentakis(pentyloxy)triphenylene (12). FT-IR (cm^{-1}): 2962, 2938, 2865, 1750, 1521, 1268, 1169. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.04 (s, 1H), 7.90 – 7.75 (m, 5H), 4.21 (dt, J = 11.6, 6.0 Hz, 10H), 2.75 – 2.63 (m, 1H), 2.18 (d, J = 12.9 Hz, 2H), 2.00 – 1.85 (m, 12H), 1.72 (t, J = 11.1 Hz, 4H), 1.55 – 1.28 (m, 22H), 0.97 (tt, J = 7.2, 2.0 Hz, 15H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 174.21, 150.63 – 147.65, 139.81, 127.73, 124.85 – 122.33, 116.83, 107.22, 106.76, 105.71, 69.94 – 69.54, 69.37, 68.71, 43.20, 29.31 – 28.53, 28.35, 25.86, 25.49, 22.58, 14.11. HRMS: calc. m/z 784.52780 ($C_{50}H_{72}O_7$), found m/z 784.52872 $(M)^+$.

2-ylfuran-2-carboxylate-3,6,7,10,11-pentakis(pentyloxy)triphenylene (13). FT-IR (cm^{-1}): 2958, 2939, 2860, 1740, 1514, 1266, 1176. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 (s, 1H), 7.85 (dd, J = 33.7, 13.9 Hz, 6H), 7.47 (dd, J = 3.6, 0.8 Hz, 1H), 6.64 (dd, J = 3.5, 1.8 Hz, 1H), 4.24 (d, J = 8.1 Hz, 10H), 2.05 – 1.79 (m, 10H), 1.54 – 1.22 (m, 20H), 1.03 – 0.84 (m, 15H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 156.79, 151.49 – 148.08, 147.08, 144.15, 139.26, 128.18, 124.66, 123.18, 119.37, 116.87, 112.19, 107.88, 107.24, 106.84, 106.39, 70.02 – 69.27, 69.12, 29.21 – 28.63, 28.49 – 27.71, 22.70 – 22.24, 14.23 – 13.71. HRMS: calc. m/z 768.46012 ($C_{48}H_{64}O_8$), found m/z 768.45976 $(M)^+$.

2-yladamantane-1-carboxylate-3,6,7,10,11-pentakis(pentyloxy)triphenylene(14). FT-IR (cm^{-1}): 2958, 2926, 2850, 1737, 1516, 1265, 1060. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.01 (s, 1H), 7.91 – 7.75 (m, 5H), 4.30 – 4.14 (m, 10H), 2.16 (dd, J = 20.5, 3.0 Hz, 9H), 1.99 – 1.77 (m, 16H), 1.59 – 1.42 (m, 20H), 0.97 (td, J = 7.2, 2.2 Hz, 15H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 175.92, 149.59, 148.81, 139.96, 127.74, 124.56, 123.08, 116.67, 108.00, 107.29 – 106.31, 105.57, 69.88, 69.74, 69.39, 68.61, 41.12, 39.06, 36.6, 29.29 – 29.01, 28.39, 28.07, 22.72 – 22.48, 14.12. HRMS: calc. m/z 836.55910 ($C_{54}H_{76}O_7$), found m/z 836.55659 $(M)^+$.

3,6-diyldicyclopropanecarboxylate-2,7,10,11-tetrakis(pentyloxy)triphenylene (15). FT-IR (cm^{-1}): 2962, 2936, 2868, 1745, 1521, 1267, 1170. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.06 (s, 2H), 7.84 (d, J = 6.1 Hz, 4H), 4.22 (dt, J = 13.4, 6.4 Hz, 8H), 1.99 – 1.84 (m, 10H), 1.44 (dq, J = 14.7, 7.5 Hz,

14H), 1.25 (s, 10H), 1.02-0.93 (m, J = 7.7, 6.6 Hz, 12H). ^{13}C NMR (176 MHz, Chloroform-d) δ 173.01, 149.53, 140.00, 124.05, 122.96, 117.01, 107.56, 106.0, 69.64, 68.87, 29.08, 22.56, 14.11, 9.03. HRMS: calc. m/z 740.42882 ($C_{46}H_{60}O_8$), found m/z 740.42632 $(M)^+$.

3,6-diyldicyclobutanecarboxylate-2,7,10,11-tetrakis(pentyloxy)triphenylene (16). FT-IR (cm^{-1}): 2961, 2932, 2866, 1742, 1521, 1268, 1143. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 (s, 2H), 7.84 (d, J = 9.3 Hz, 4H), 4.22 (dt, J = 16.4, 6.4 Hz, 8H), 3.56 – 3.40 (m, 2H), 2.67 – 2.30 (m, 8H), 2.19 – 1.82 (m, 12H), 1.56 – 1.37 (m, 16H), 0.97 (q, J = 7.2 Hz, 12H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 173.50, 149.65, 139.94, 127.67, 124.07, 122.92, 116.92, 107.60, 105.79, 69.65, 68.75, 38.03, 29.10, 28.34, 25.41, 22.58, 18.60, 14.11. HRMS: calc. m/z 768.46012 ($C_{48}H_{64}O_8$), found m/z 768.46196 $(M)^+$.

3,6-diyldicyclopentanecarboxylate-2,7,10,11-tetrakis(pentyloxy)triphenylene (17). FT-IR (cm^{-1}): 2960, 2937, 2874, 1743, 1520, 1269, 1141. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 (s, 2H), 7.83 (d, J = 12.1 Hz, 4H), 4.22 (dt, J = 18.4, 6.5 Hz, 8H), 3.10 (p, J = 8.0 Hz, 2H), 2.09 (ddd, J = 7.5, 4.9, 2.5 Hz, 8H), 1.95 (dd, J = 8.3, 6.5 Hz, 4H), 1.91 – 1.76 (m, 8H), 1.73 – 1.61 (m, 4H), 1.53 – 1.35 (m, 16H), 0.97 (td, J = 7.2, 6.1 Hz, 12H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 174.84, 149.49, 139.99, 124.08, 122.88, 116.93, 107.62, 105.67, 69.66, 68.70, 43.69, 30.15, 29.12, 28.35, 26.04, 22.59, 14.11. HRMS: calc. m/z 796.49142 ($C_{50}H_{68}O_8$), found m/z 796.49188 $(M)^+$.

3,6-diyldicyclohexanecarboxylate-2,7,10,11-tetrakis(pentyloxy)triphenylene (18). FT-IR (cm^{-1}): 2962, 2936, 2858, 1743, 1521, 1268, 1035. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (s, 2H), 7.76 (d, J = 12.6 Hz, 4H), 4.16 (dd, J = 16.3, 9.6 Hz, 8H), 2.60 (tt, J = 11.1, 3.7 Hz, 2H), 2.12 – 2.05 (m, 4H), 1.89 (q, J = 7.1 Hz, 4H), 1.84 – 1.75 (m, 10H), 1.69 – 1.58 (m, 6H), 1.55 – 1.22 (m, 20H), 0.95 – 0.88 (m, 12H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 174.12, 149.50, 139.96, 127.61, 124.07, 116.95, 107.62, 105.68, 69.66, 68.72, 43.18, 29.15, 28.36, 25.86, 25.48, 22.59, 14.11. HRMS: calc. m/z 824.52272 ($C_{52}H_{72}O_8$), found m/z 824.52078 $(M)^+$.

3,6-diylbis(furan-2-carboxylate)-2,7,10,11-tetrakis(pentyloxy)triphenylene (19). FT-IR (cm^{-1}): 2960, 2938, 2866, 1745, 1519, 1268, 1174. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.17 (s, 2H), 7.88 (d, J = 8.3 Hz, 4H), 7.44 (dd, J = 3.5, 0.9 Hz, 2H), 6.62 (dd, J = 3.5, 1.8 Hz, 2H), 4.24 (dt, J = 11.9, 6.4 Hz, 8H), 1.89 (dt, J = 59.4, 7.3 Hz, 8H), 1.52 – 1.32 (m, 16H), 0.92 (dt, J = 49.7, 7.2 Hz, 12H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 156.60, 149.49, 147.01, 144.17, 139.31, 127.94, 123.96, 122.79, 119.25, 116.77, 112.11, 107.49, 106.32, 69.51, 68.97, 29.14, 28.94, 28.29, 22.62, 22.45, 14.14, 14.00. HRMS: calc. m/z 792.38735 ($C_{48}H_{56}O_{10}$), found m/z 792.38423 $(M)^+$.

3,6-diylbis(adamantane-1-carboxylate)-2,7,10,11-tetrakis(pentyloxy)triphenylene (20). FT-IR (cm^{-1}): 2955, 2910, 2860, 1740, 1520, 1270, 1060. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 (s, 2H), 7.82 (d, J = 18.6 Hz, 4H), 4.21 (dt, J = 23.5, 6.4 Hz, 8H), 2.22 – 2.07 (m, 18H), 2.00 – 1.78 (m, 20H), 1.57 – 1.37 (m, 16H), 0.97 (td, J = 7.2, 4.3 Hz, 12H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 175.68, 149.67, 140.14, 127.53, 124.12, 117.01, 107.68, 105.54, 69.70, 68.64, 41.10, 39.02, 36.61, 29.15, 28.38, 28.06, 22.62, 14.12. HRMS: calc. m/z 928.58532 ($C_{60}H_{80}O_8$), found m/z 928.58408 $(M)^+$.

S4. Supplementary FT-IR results

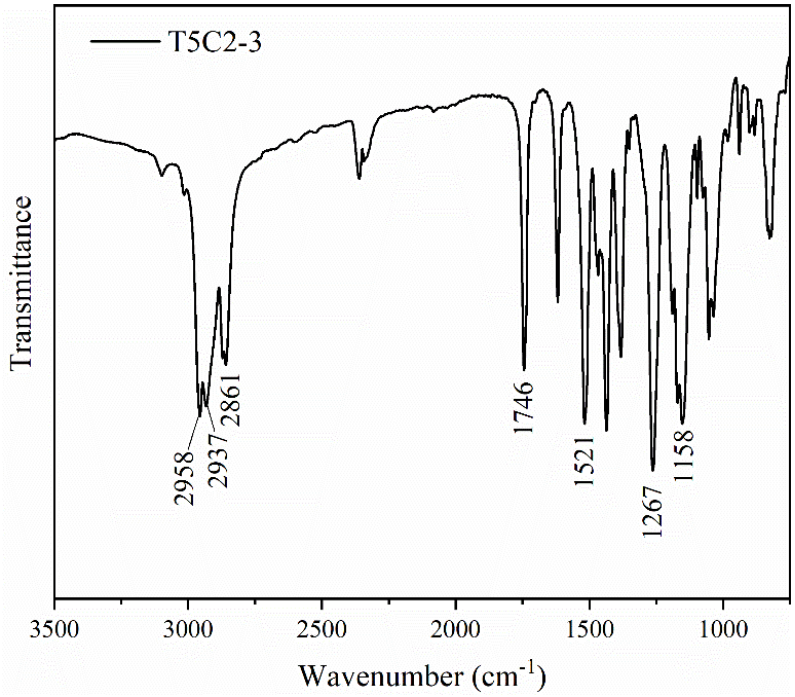


Fig. S1. FT-IR spectrum of Compounds T5C2-3

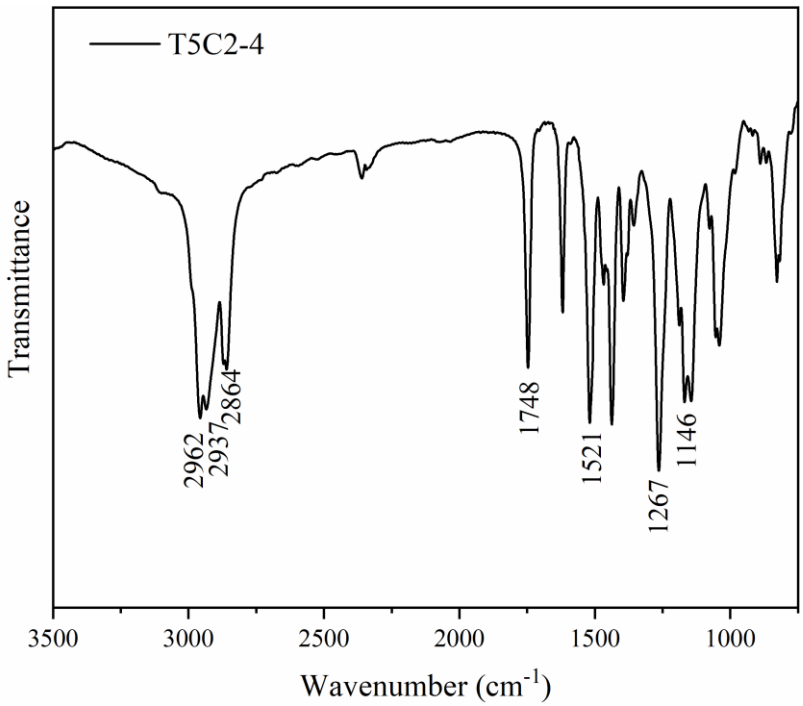


Fig. S2. FT-IR spectrum of Compounds T5C2-4

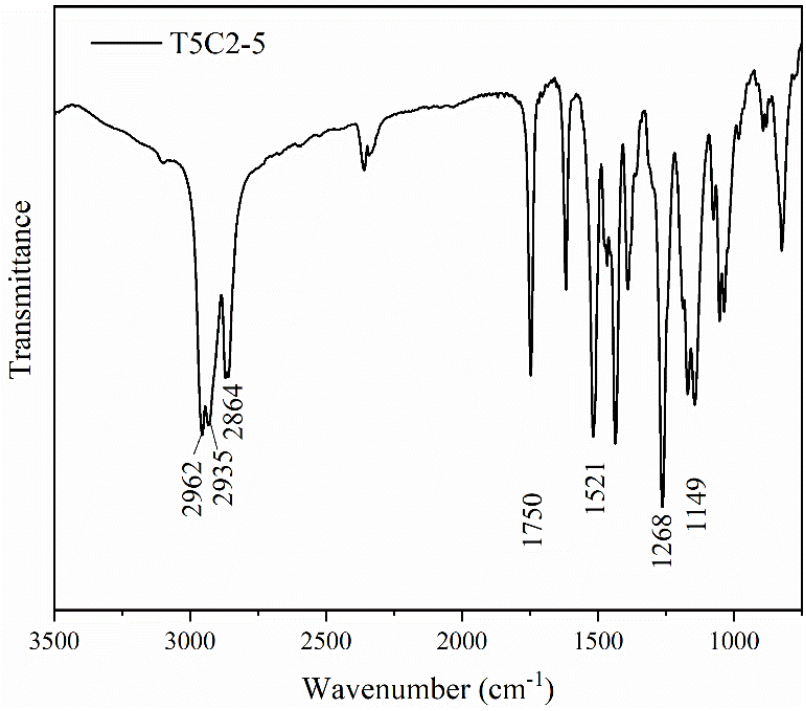


Fig. S3. FT-IR spectrum of Compounds T5C2-5

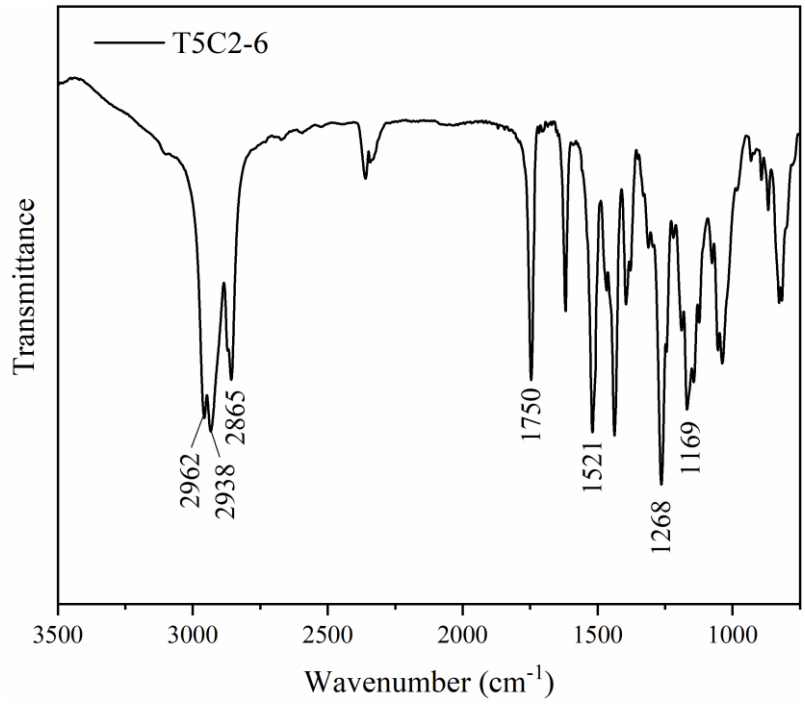


Fig. S4. FT-IR spectrum of Compounds T5C2-6

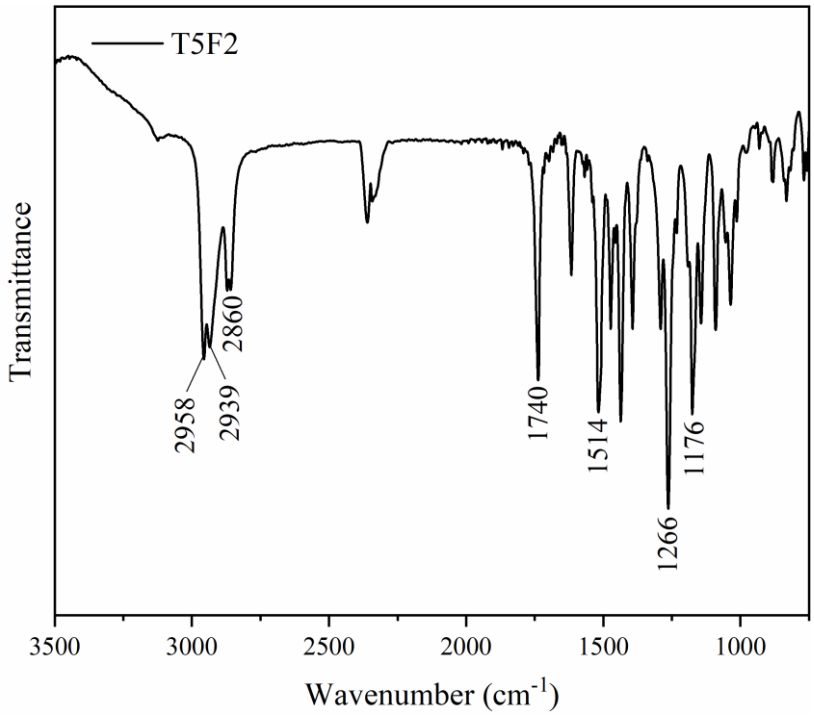


Fig. S5. FT-IR spectrum of Compounds T5F2

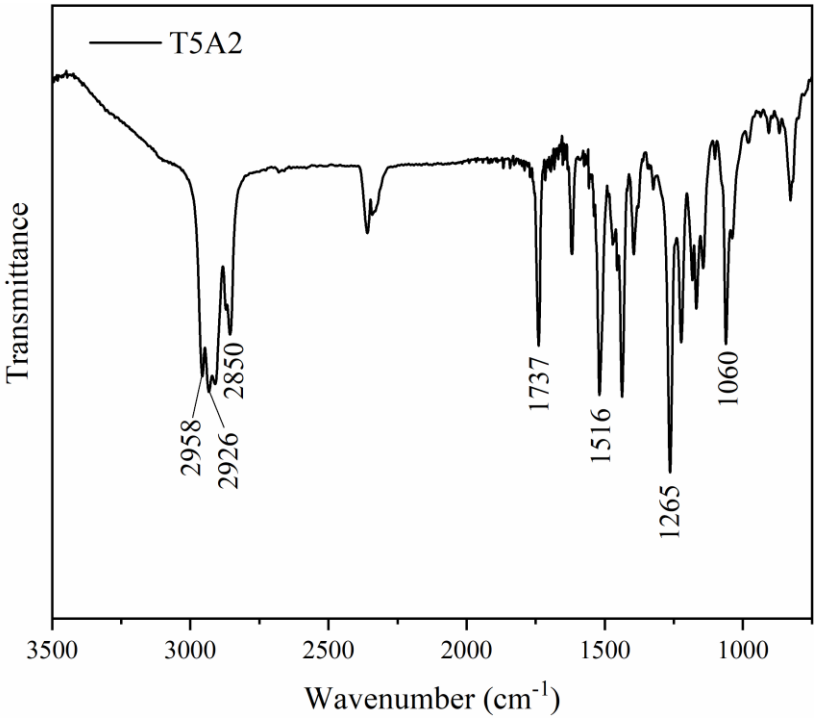


Fig. S6. FT-IR spectrum of Compounds T5A2

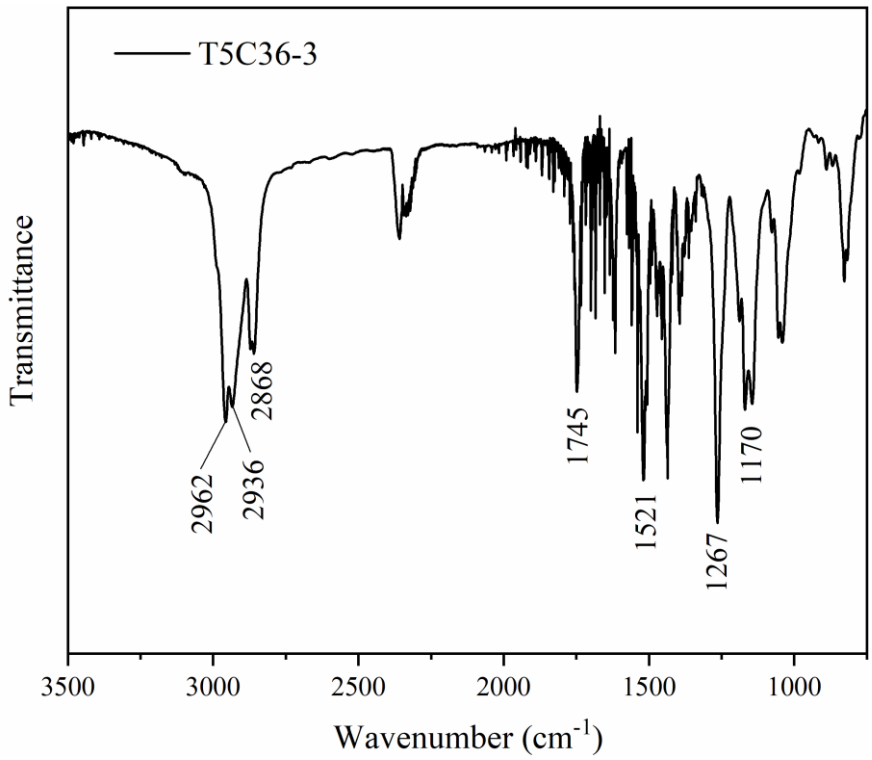


Fig. S7. FT-IR spectrum of Compounds T5C36-3

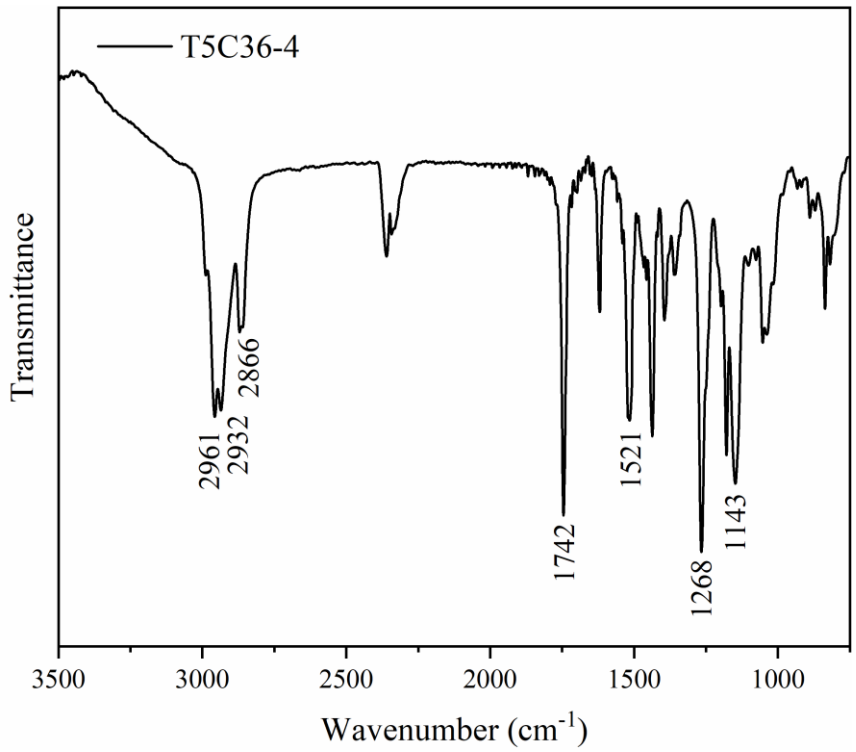


Fig. S8. FT-IR spectrum of Compounds T5C36-4

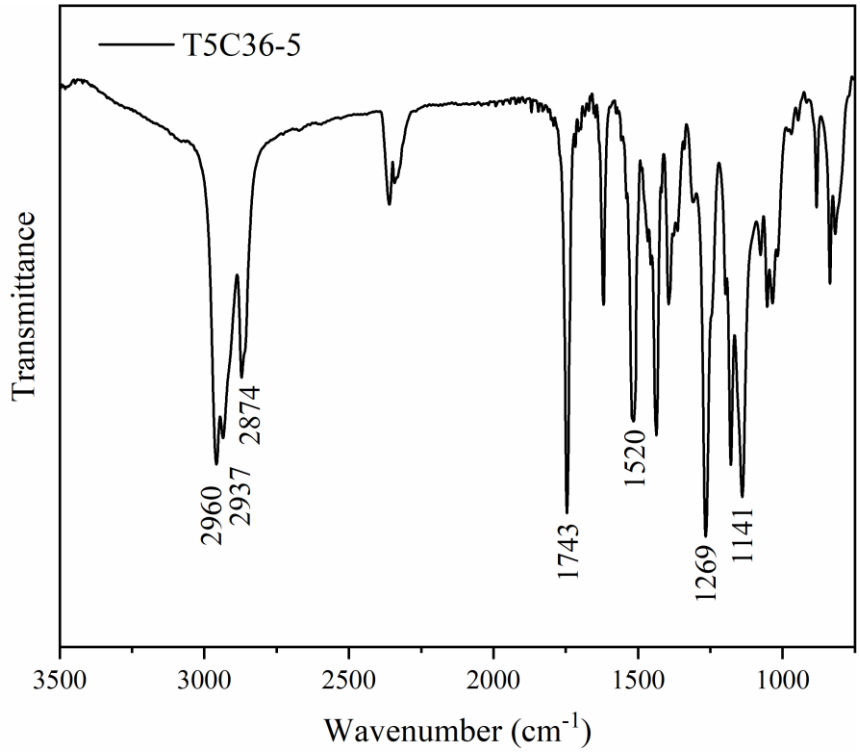


Fig. S9. FT-IR spectrum of Compounds T5C36-5

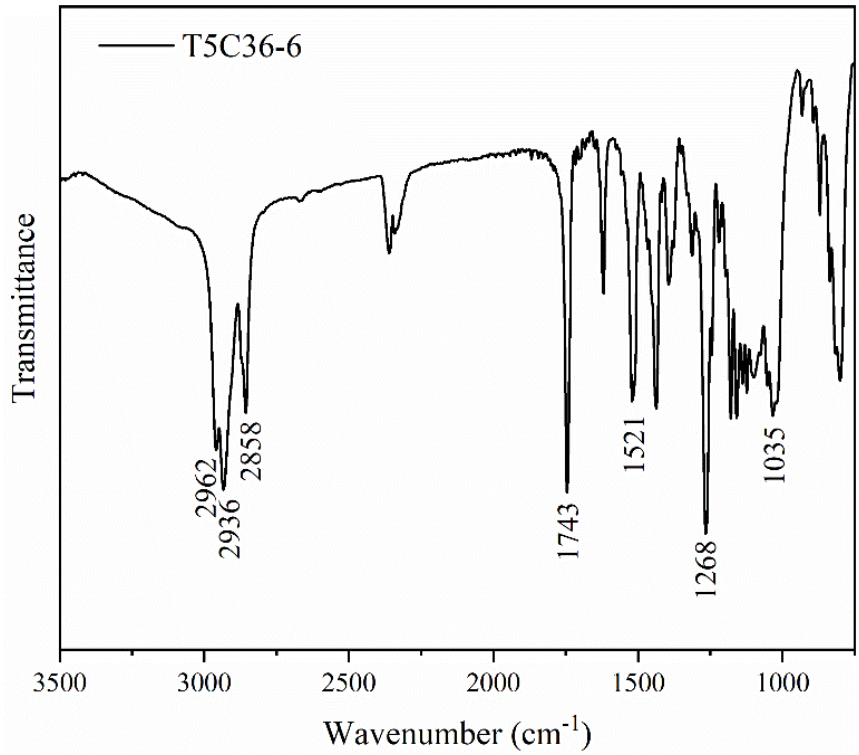


Fig. S10. FT-IR spectrum of Compounds T5C36-6

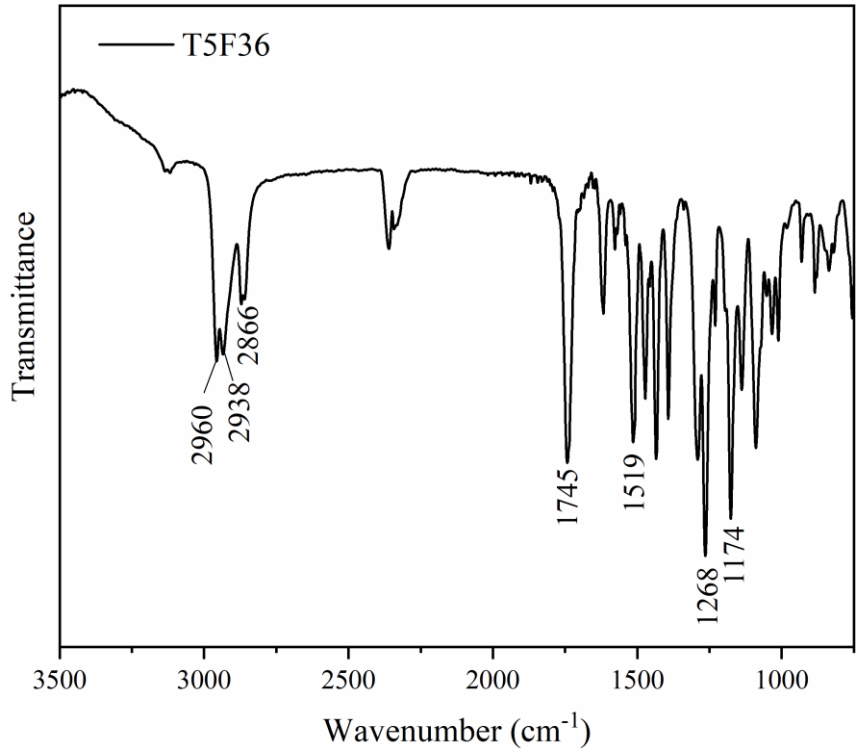


Fig. S11. FT-IR spectrum of Compounds T5F36

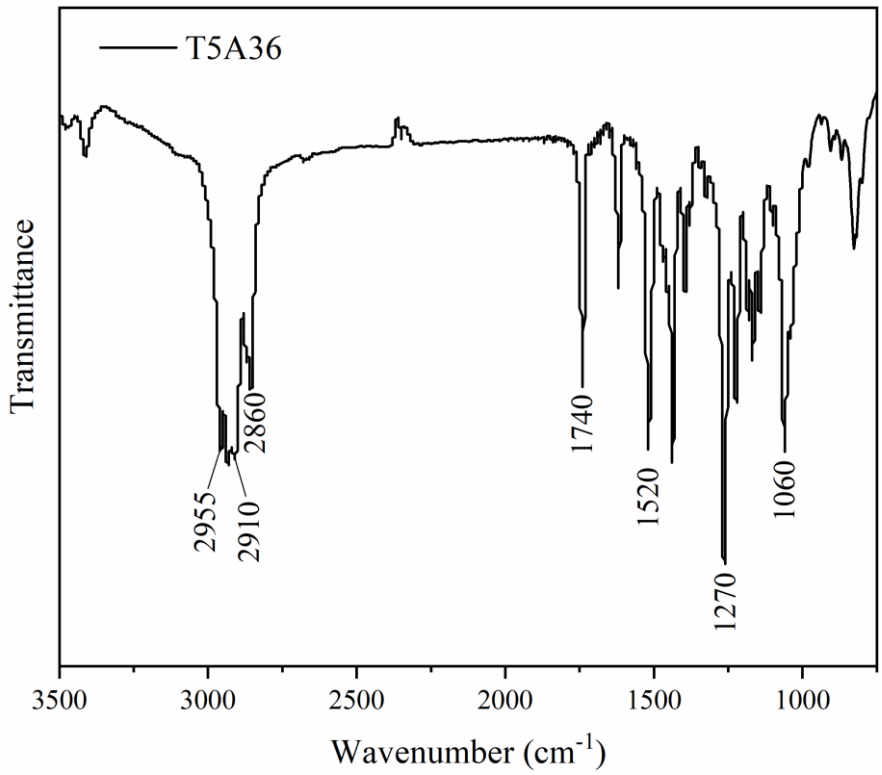


Fig. S12. FT-IR spectrum of Compound T5A36

S5. Supplementary ^{1}H NMR results

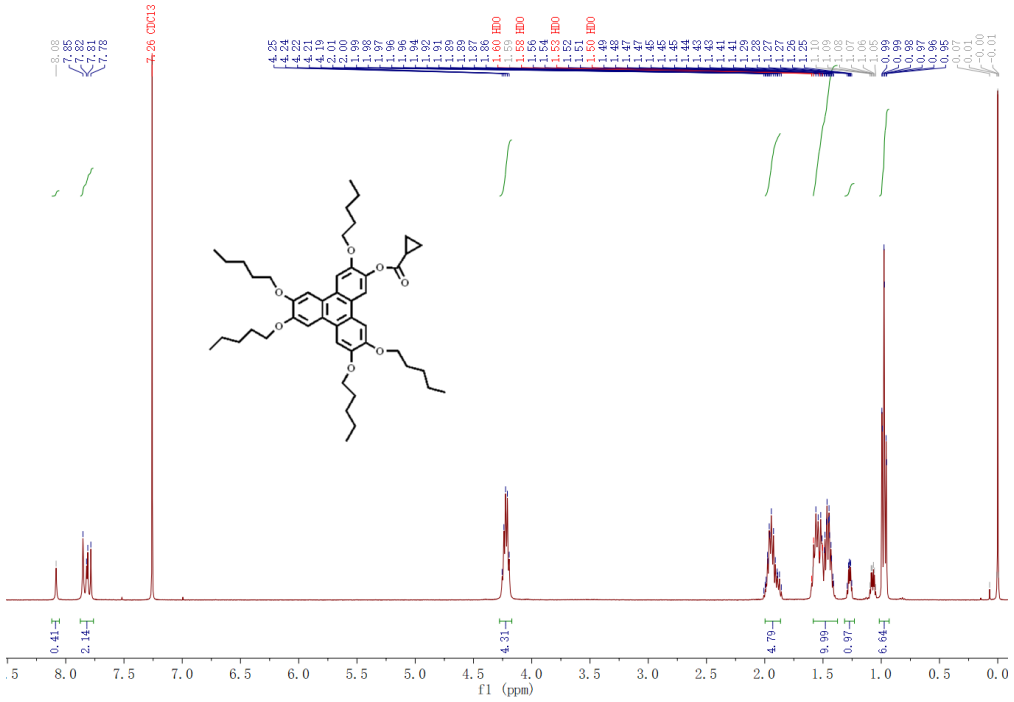


Fig. S13. ^{1}H NMR spectrum of Compound T5C2-3

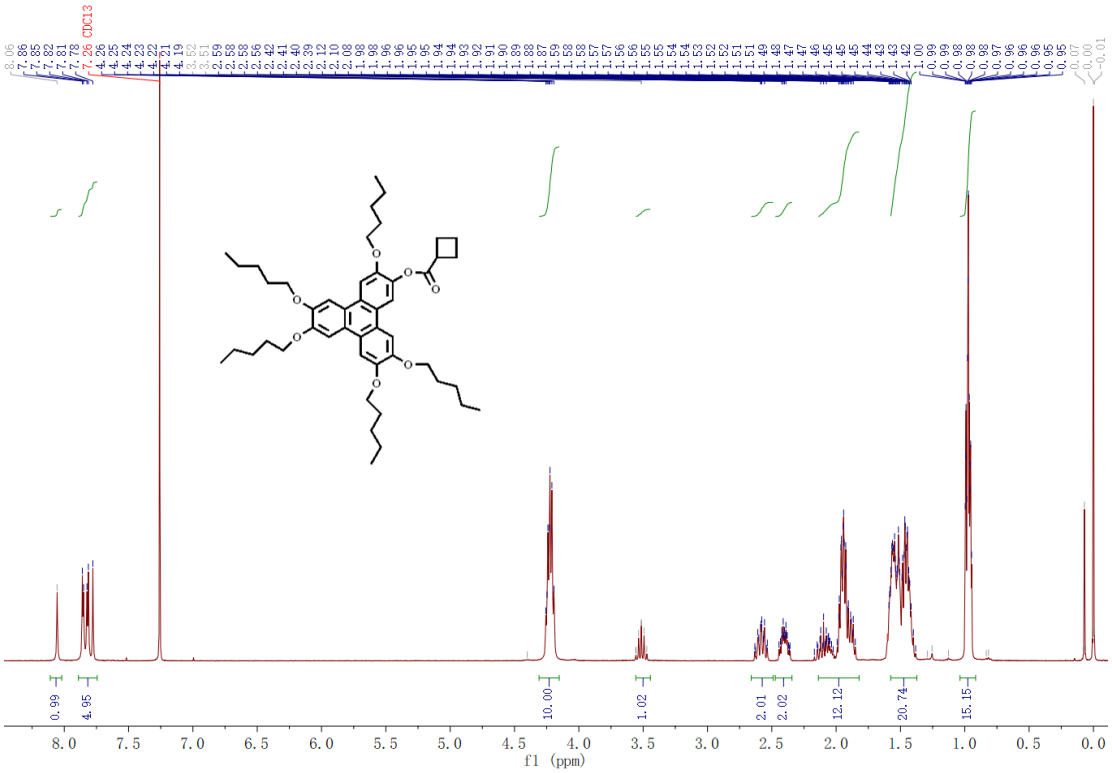


Fig. S14. ^{1}H NMR spectrum of Compound T5C2-4

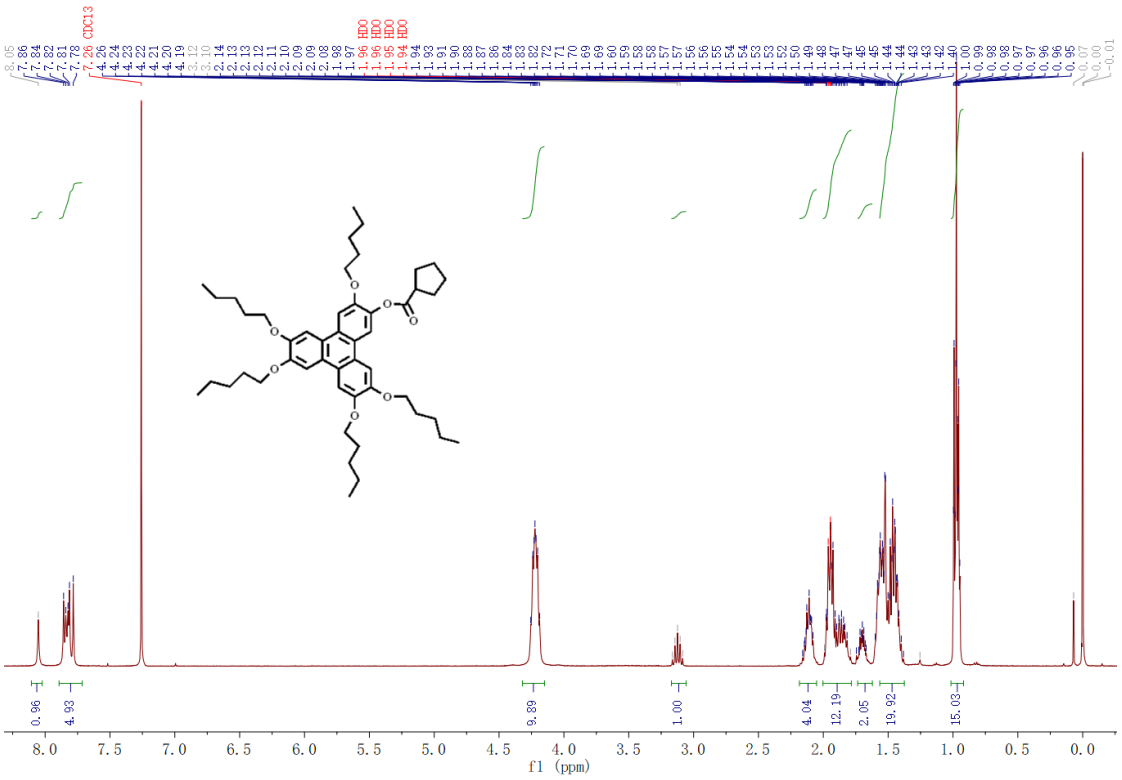


Fig. S15. ^{1}H NMR spectrum of Compound T5C2-5

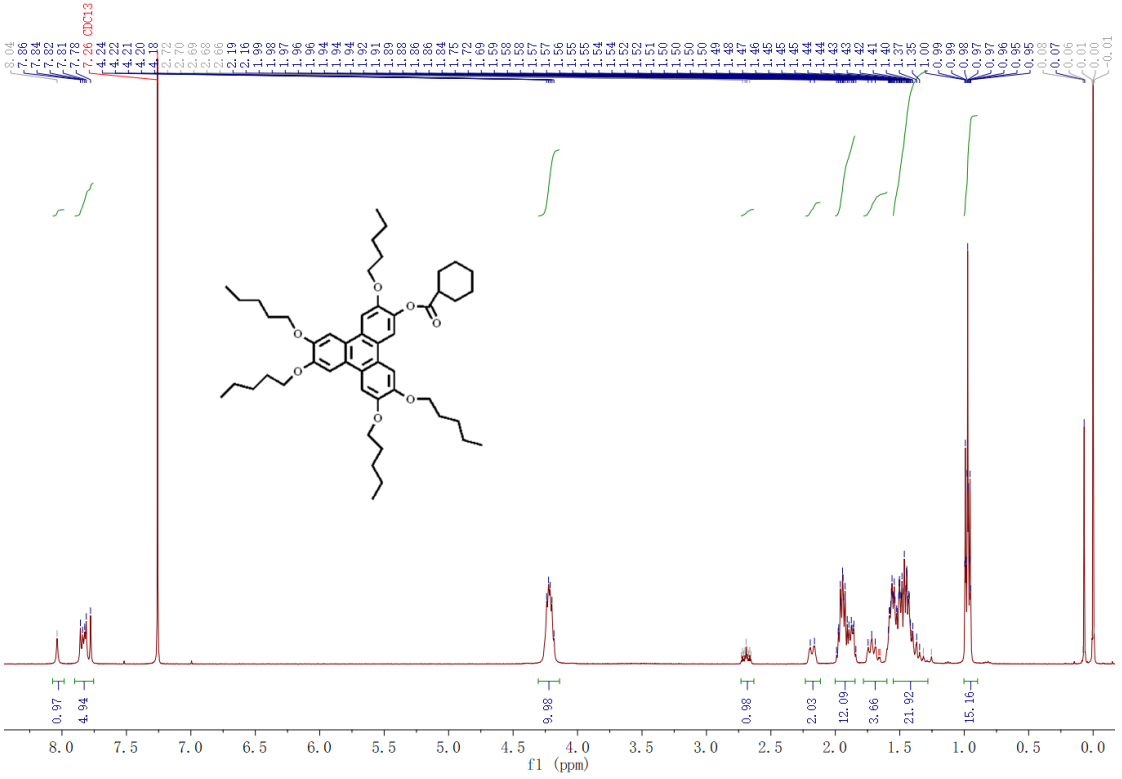


Fig. S16. ^{1}H NMR spectrum of Compound T5C2-6

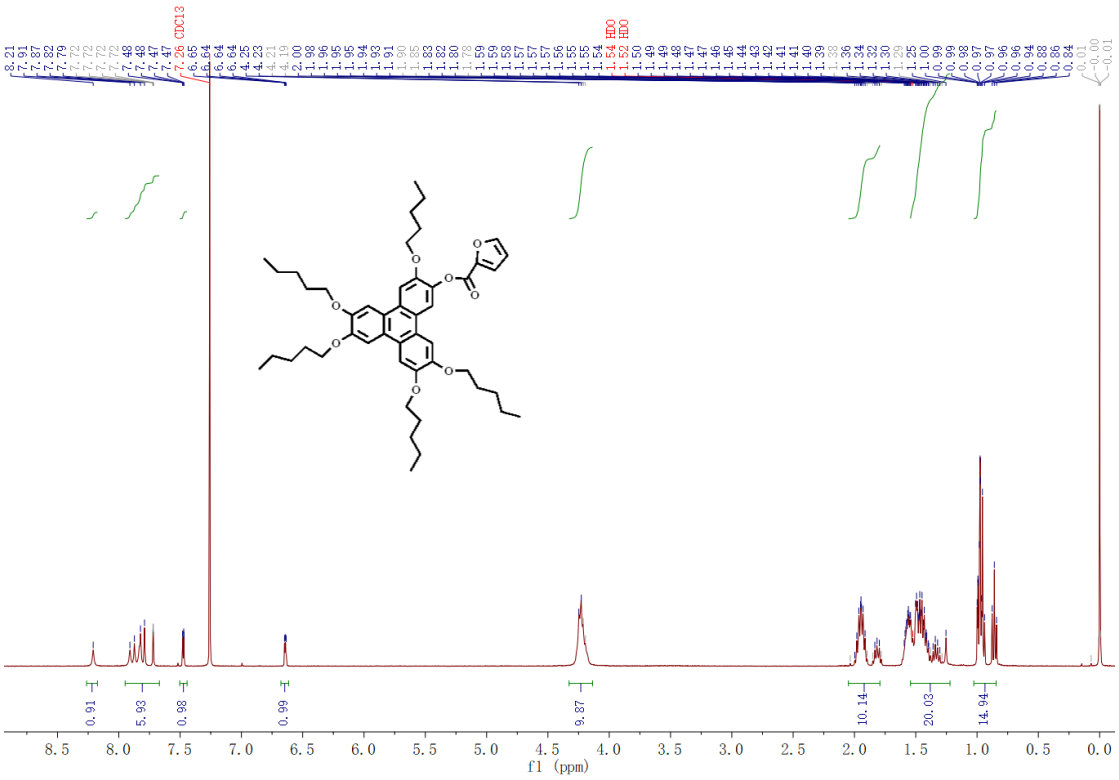


Fig. S17. ^{1}H NMR spectrum of Compound T5F2

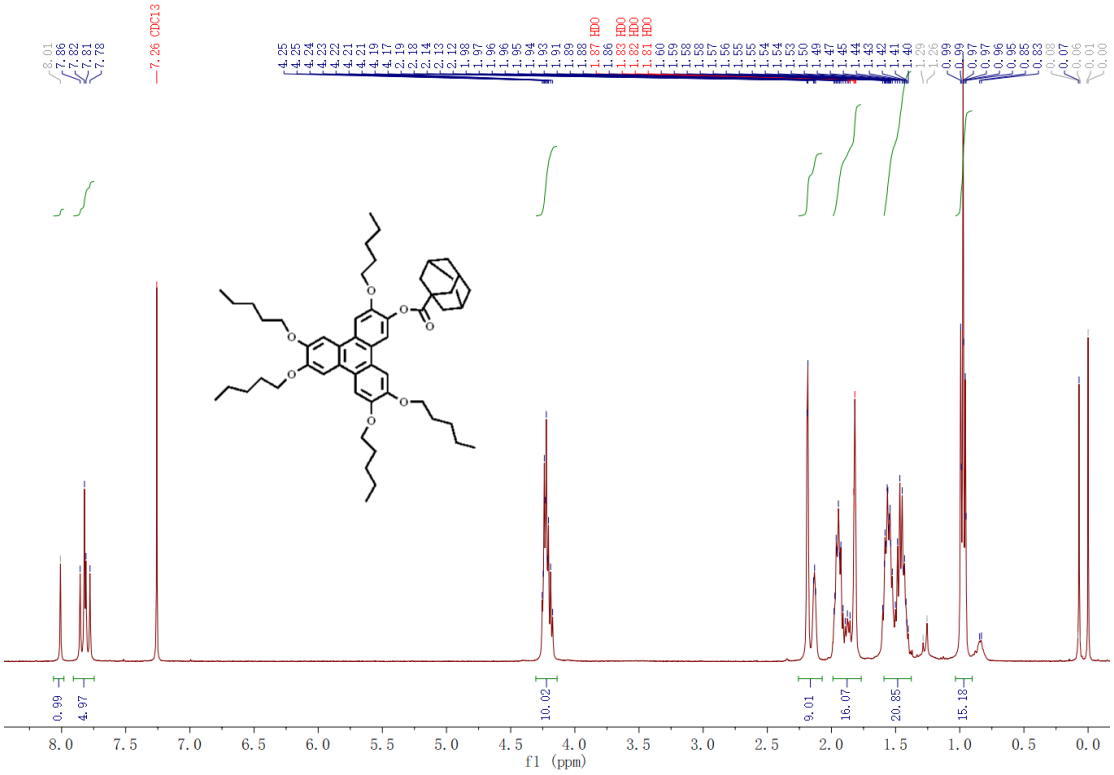


Fig. S18. ^{1}H NMR spectrum of Compound T5A2

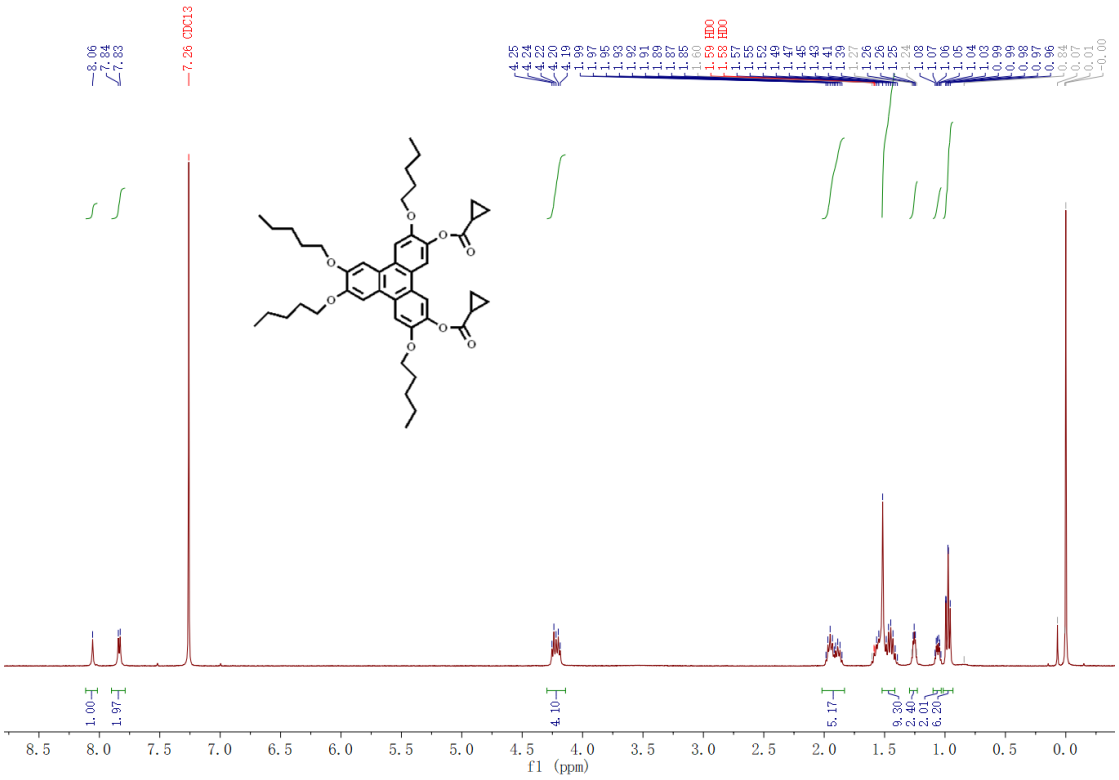


Fig. S19. ^{1}H NMR spectrum of Compound T5C36-3

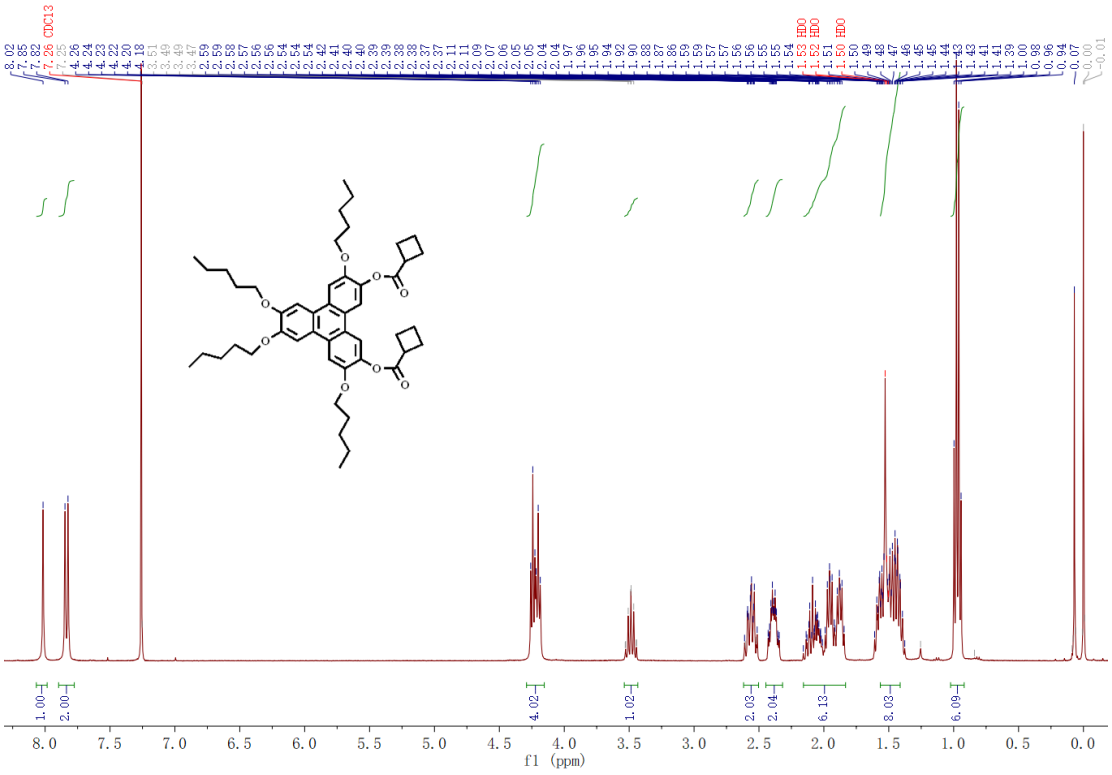


Fig. S20. ^{1}H NMR spectrum of Compound T5C36-4

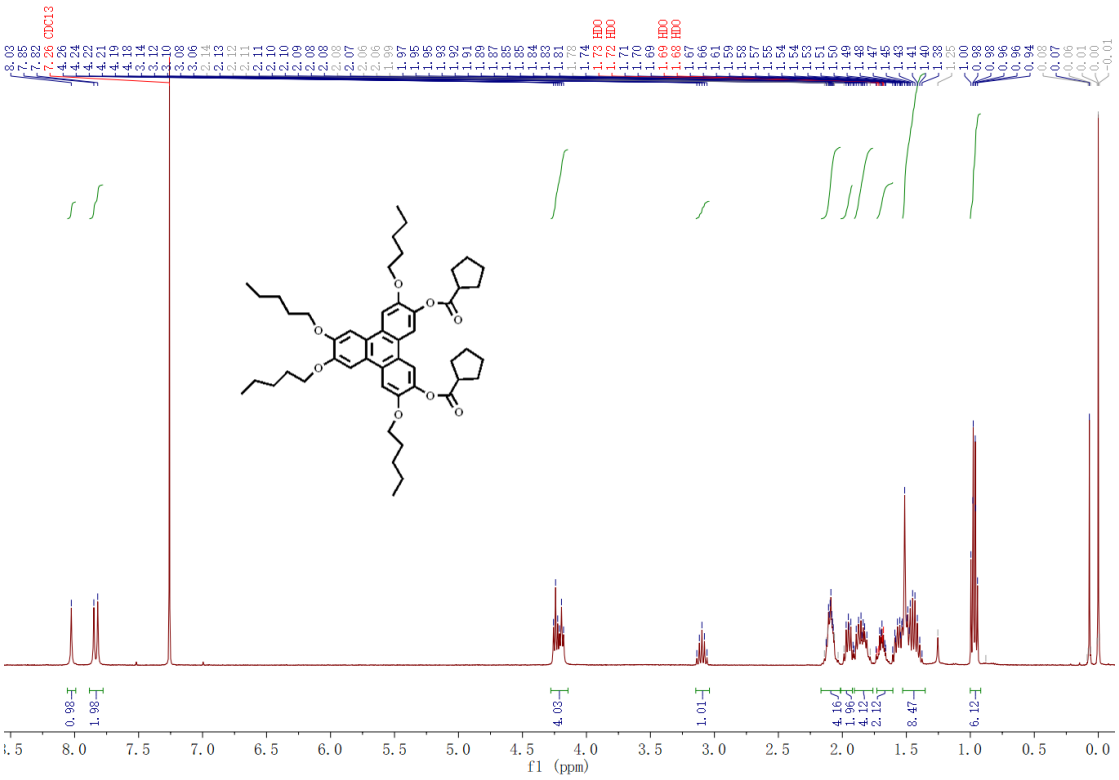


Fig. S21. ^{1}H NMR spectrum of Compound T5C36-5

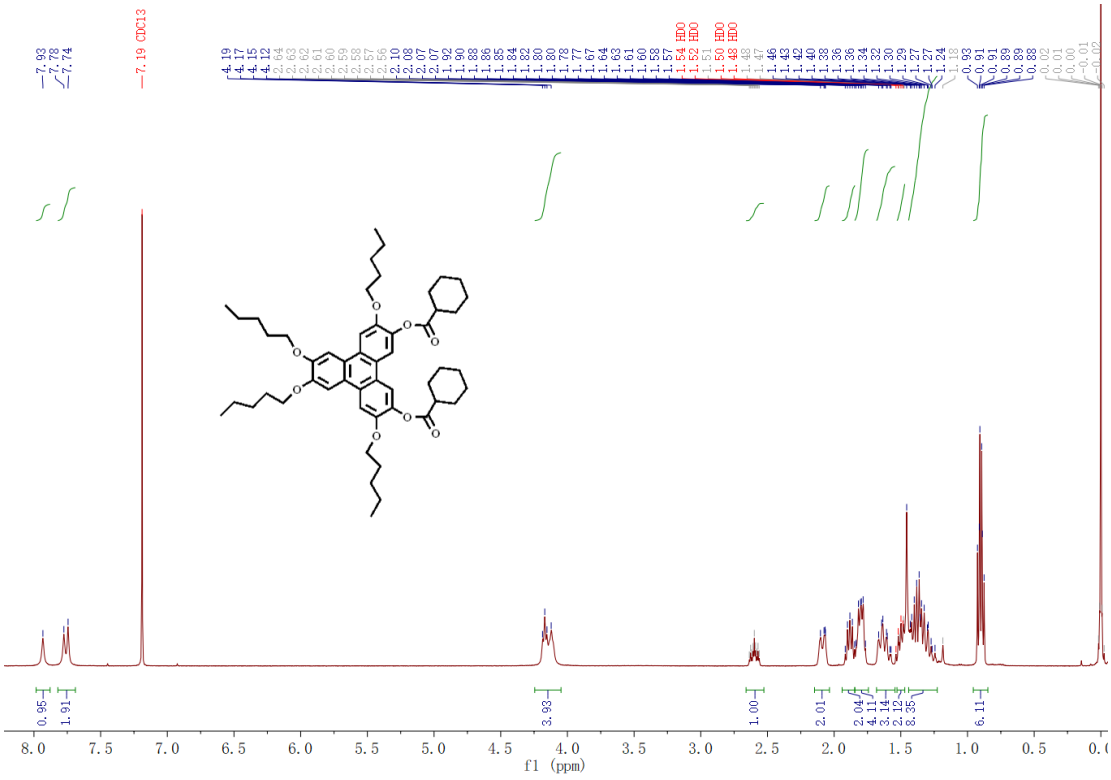


Fig. S22. ^{1}H NMR spectrum of Compound T5C36-6

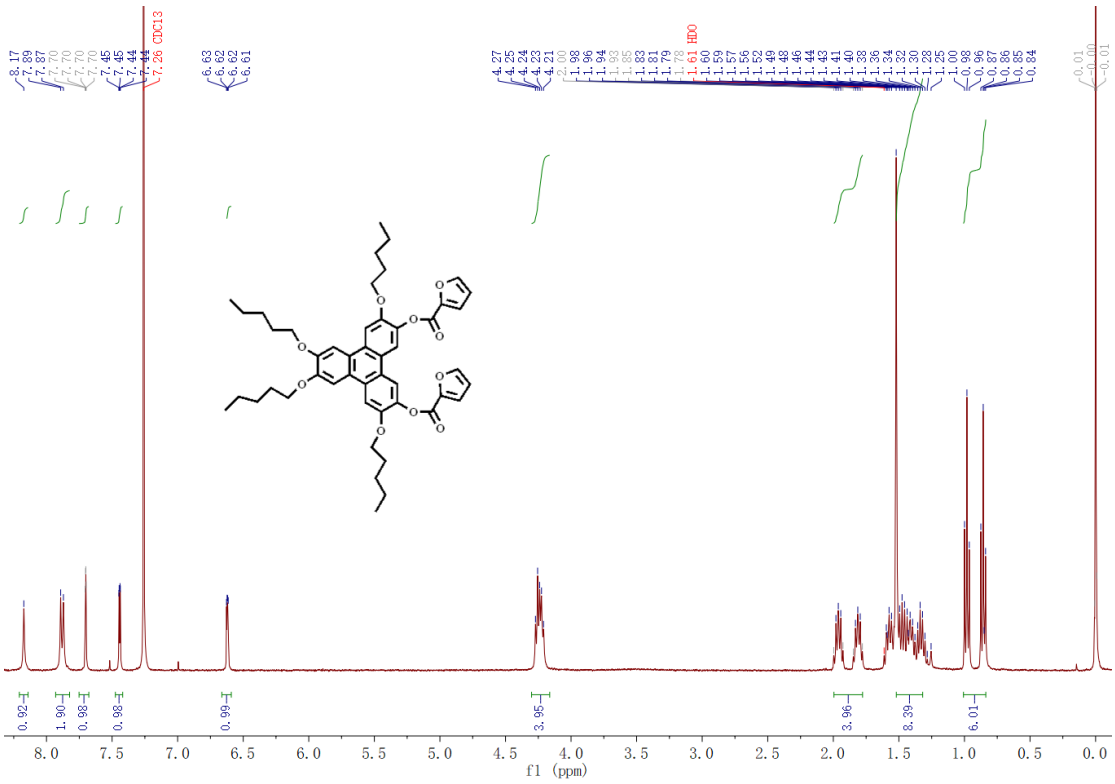


Fig. S23. ^{1}H NMR spectrum of Compound T5F36

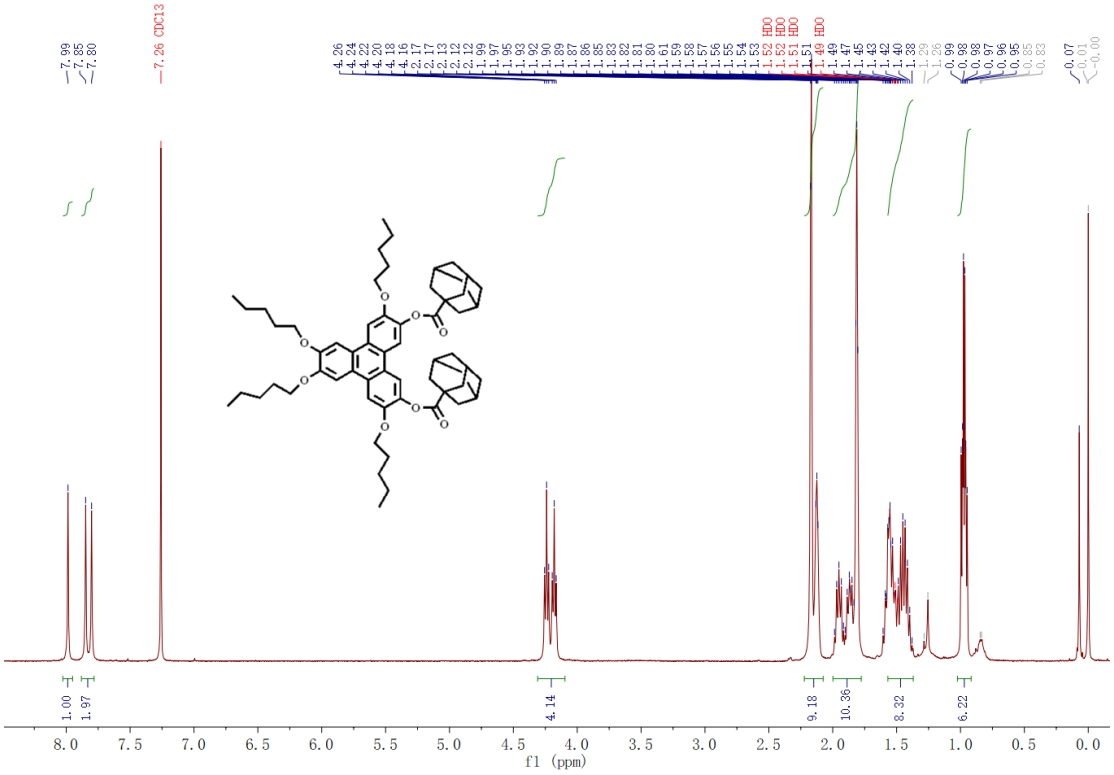


Fig. S24. ^{1}H NMR spectrum of Compound T5A36

S6. Supplementary ^{13}C NMR results

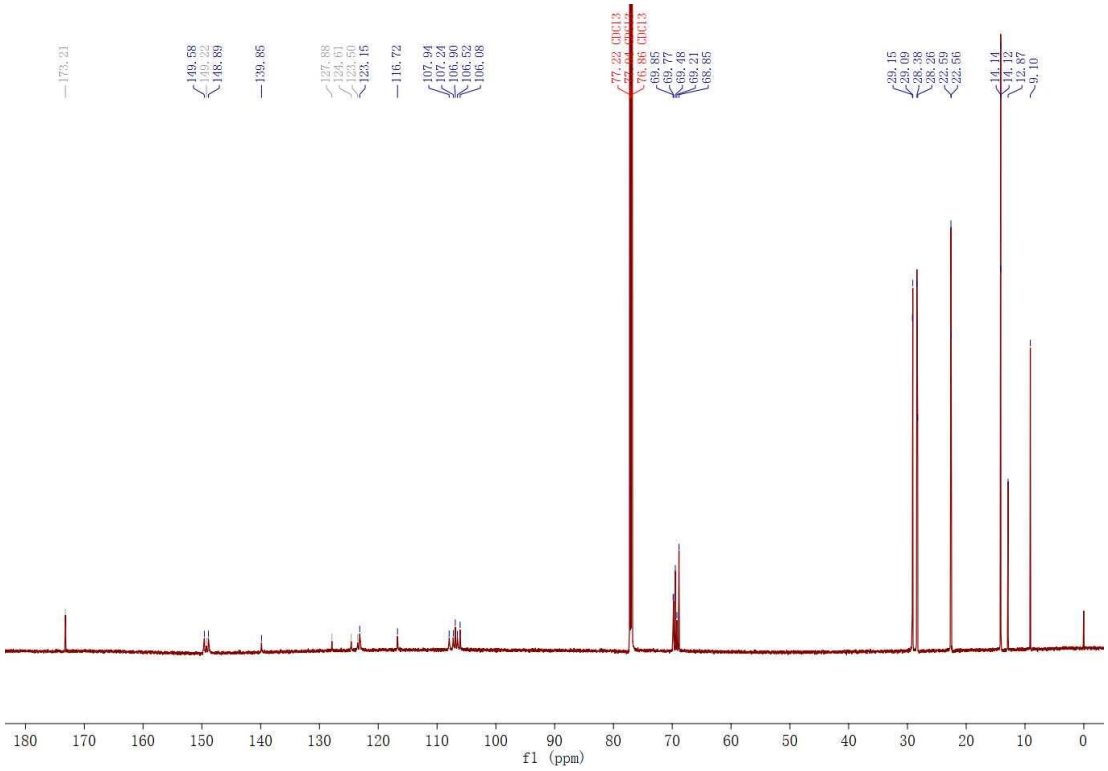


Fig. S25. ^{13}C NMR spectrum of Compound T5C2-3

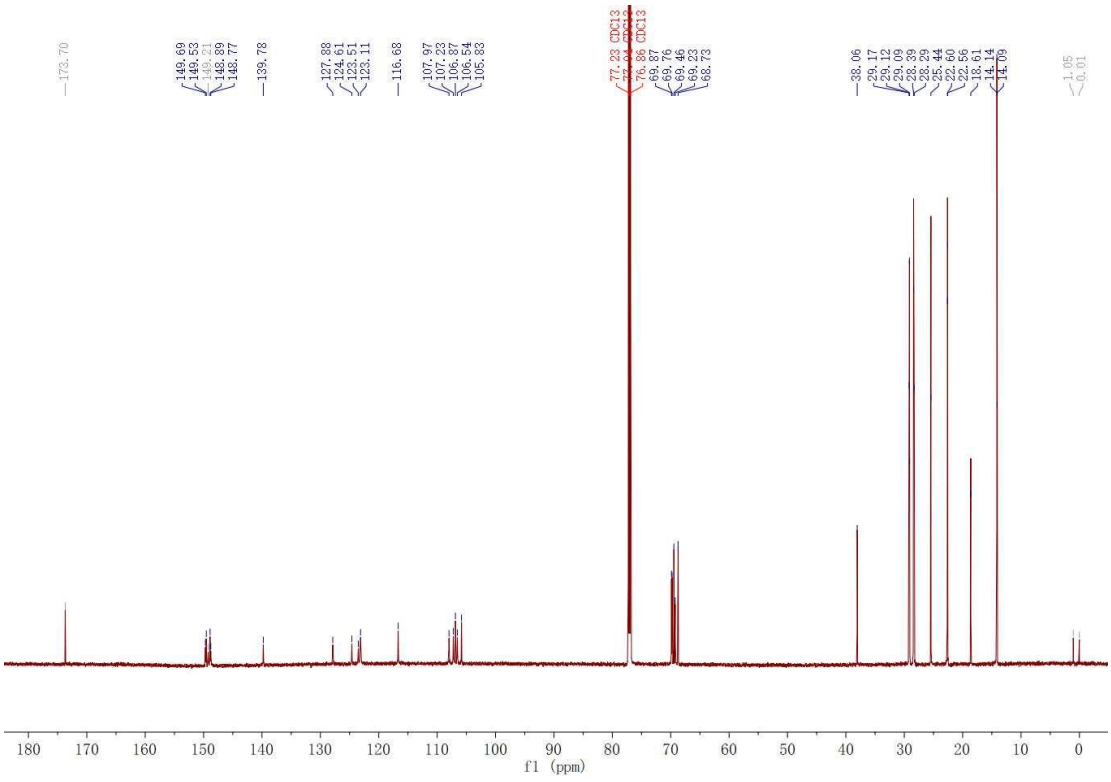


Fig. S26. ^{13}C NMR spectrum of Compound T5C2-4

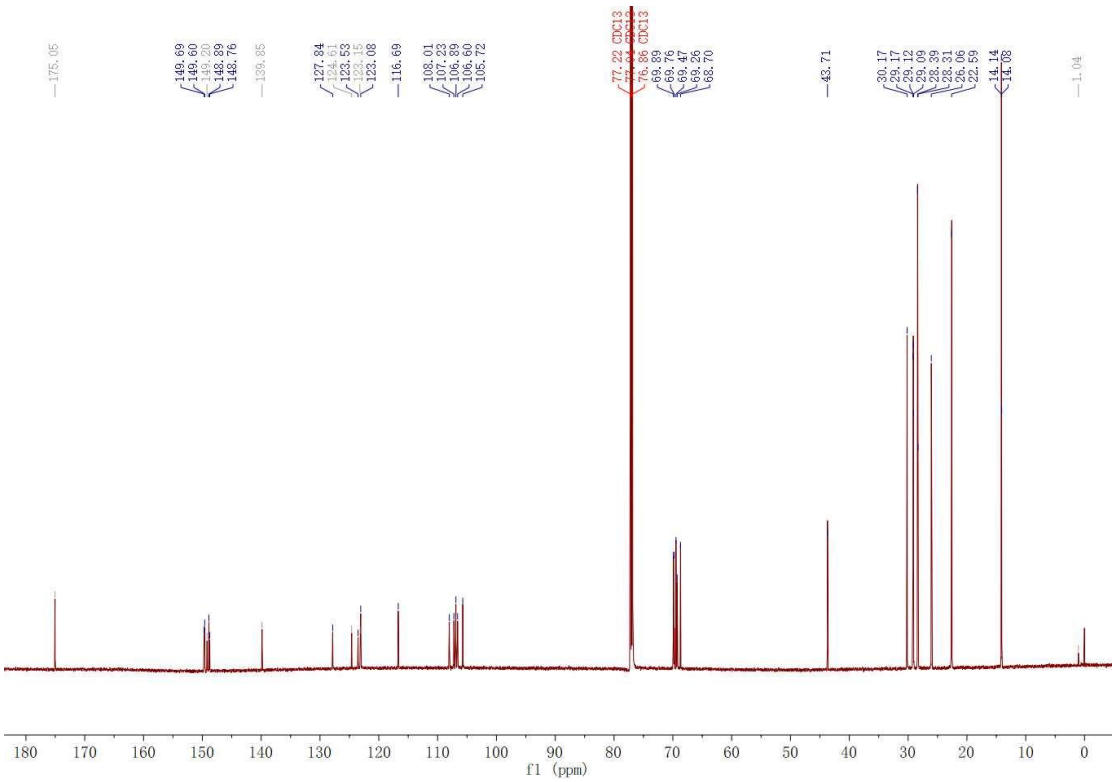


Fig. S27. ^{13}C NMR spectrum of Compound T5C2-5

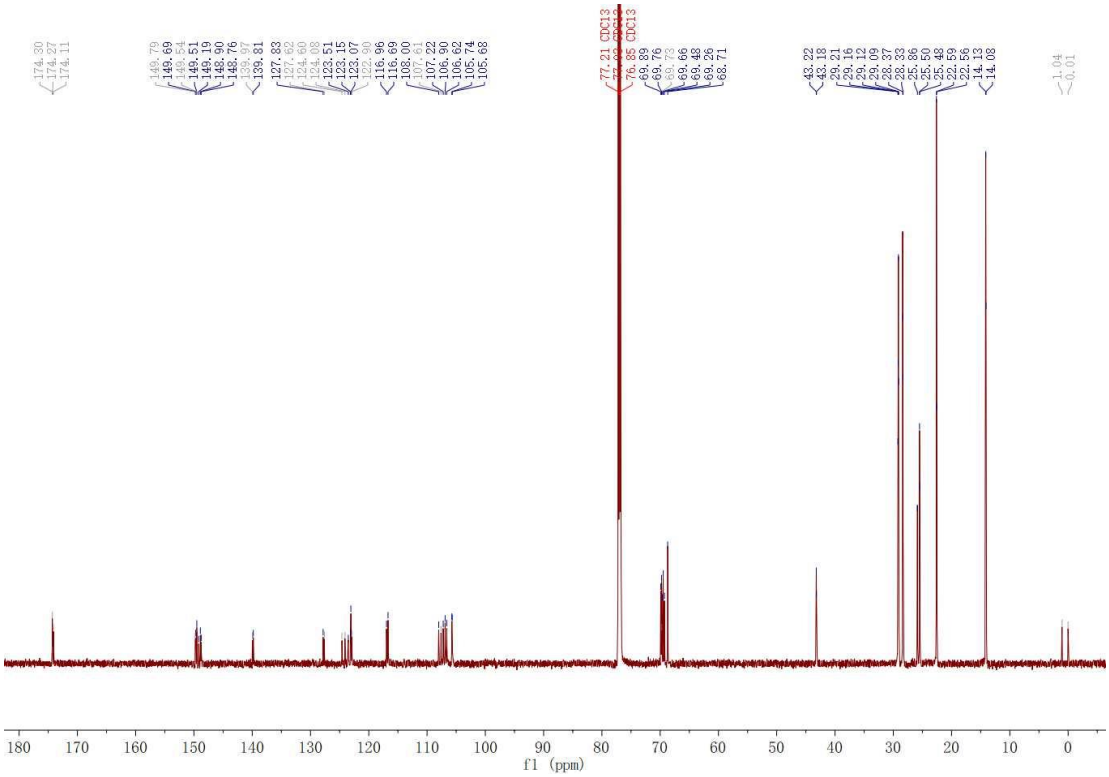


Fig. S28. ^{13}C NMR spectrum of Compound T5C2-6

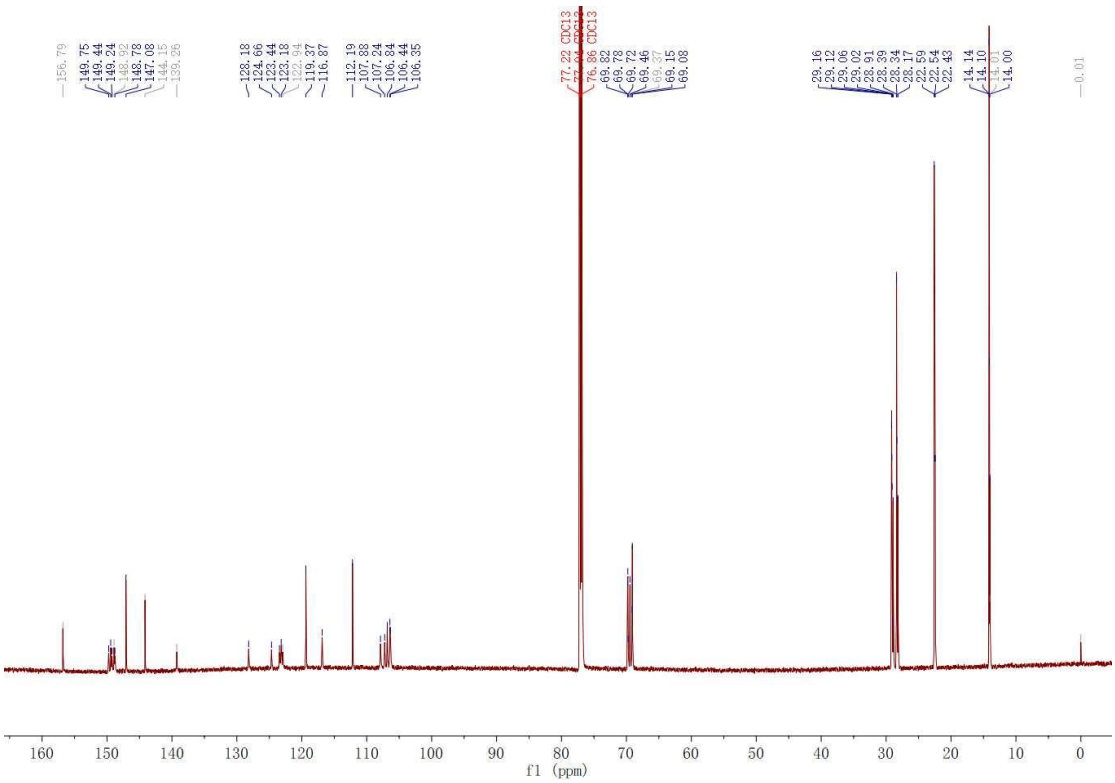


Fig. S29. ^{13}C NMR spectrum of Compound T5F2

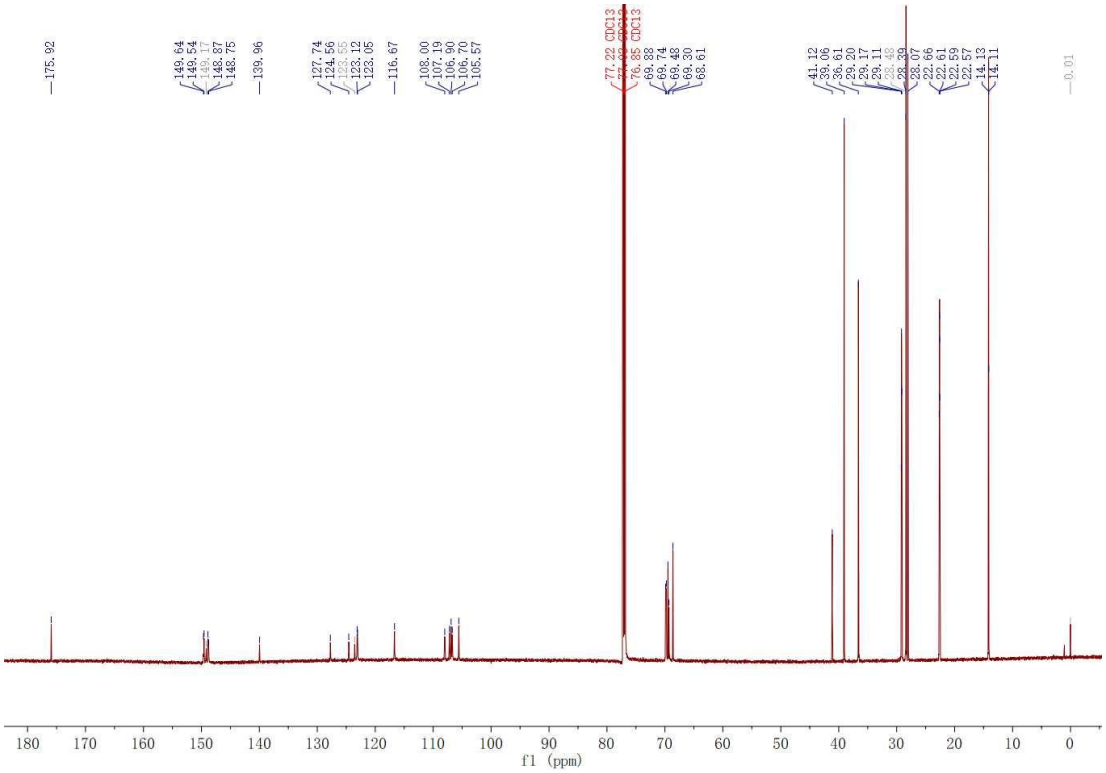


Fig. S30. ^{13}C NMR spectrum of Compound T5A2

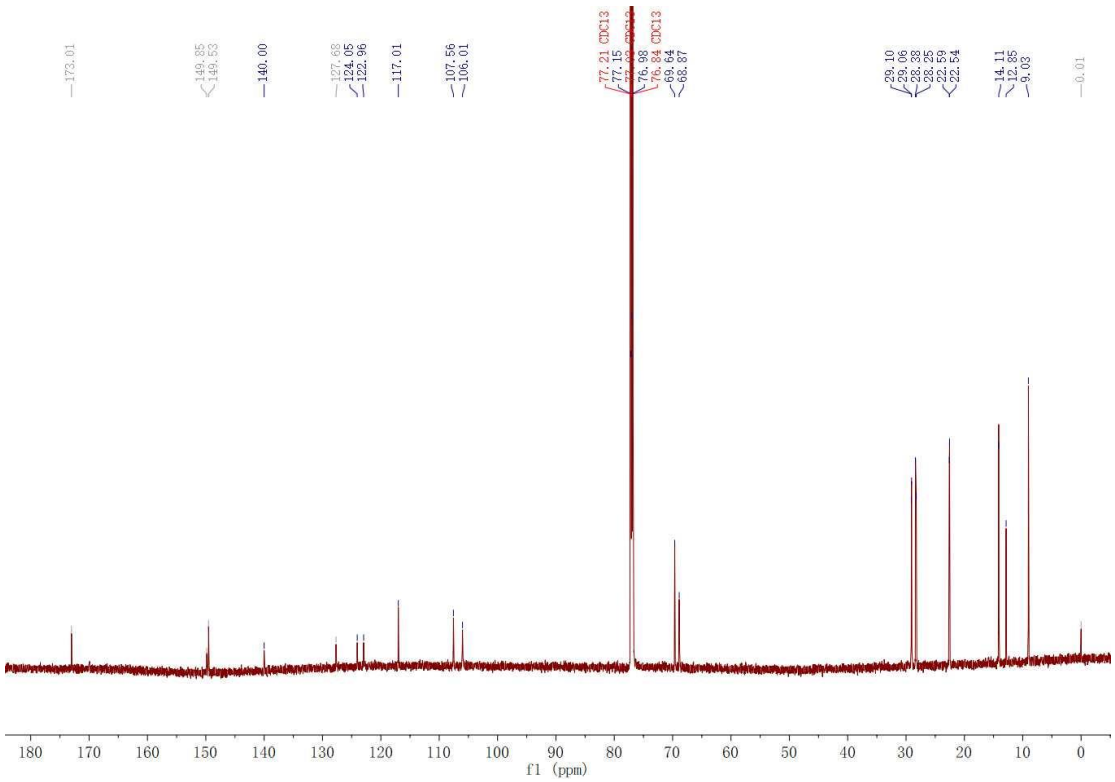


Fig. S31. ^{13}C NMR spectrum of Compound T5C36-3

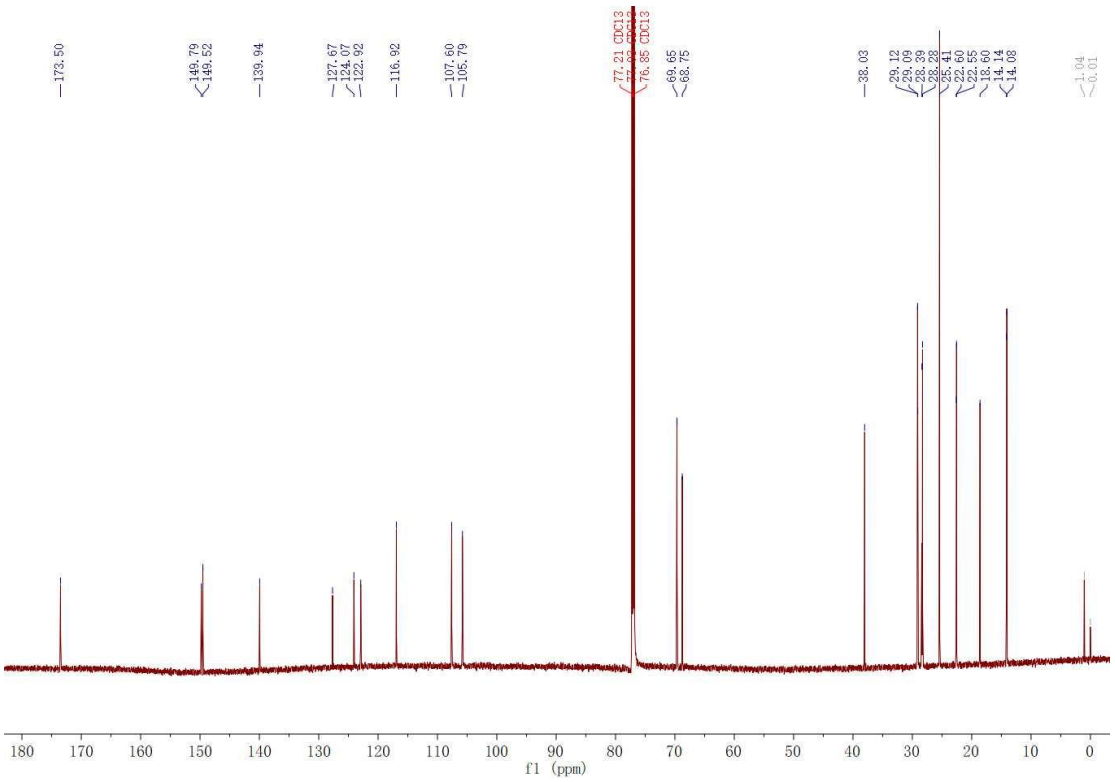


Fig. S32. ^{13}C NMR spectrum of Compound T5C36-4

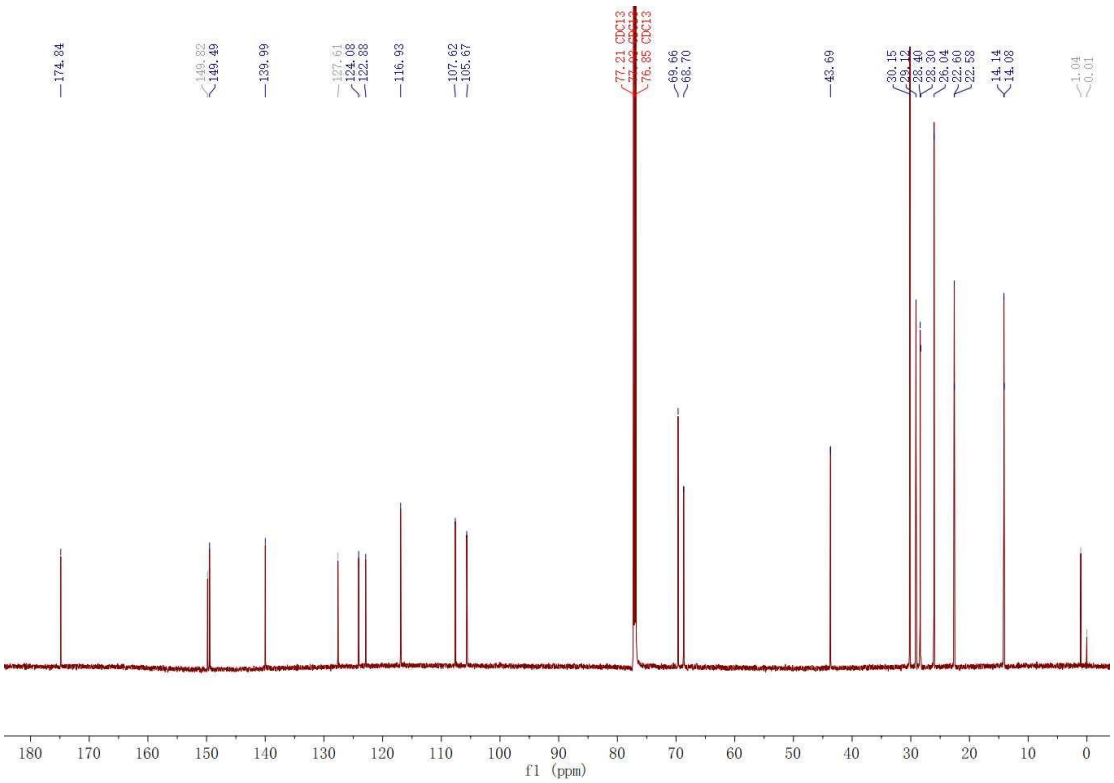


Fig. S33. ^{13}C NMR spectrum of Compound T5C36-5

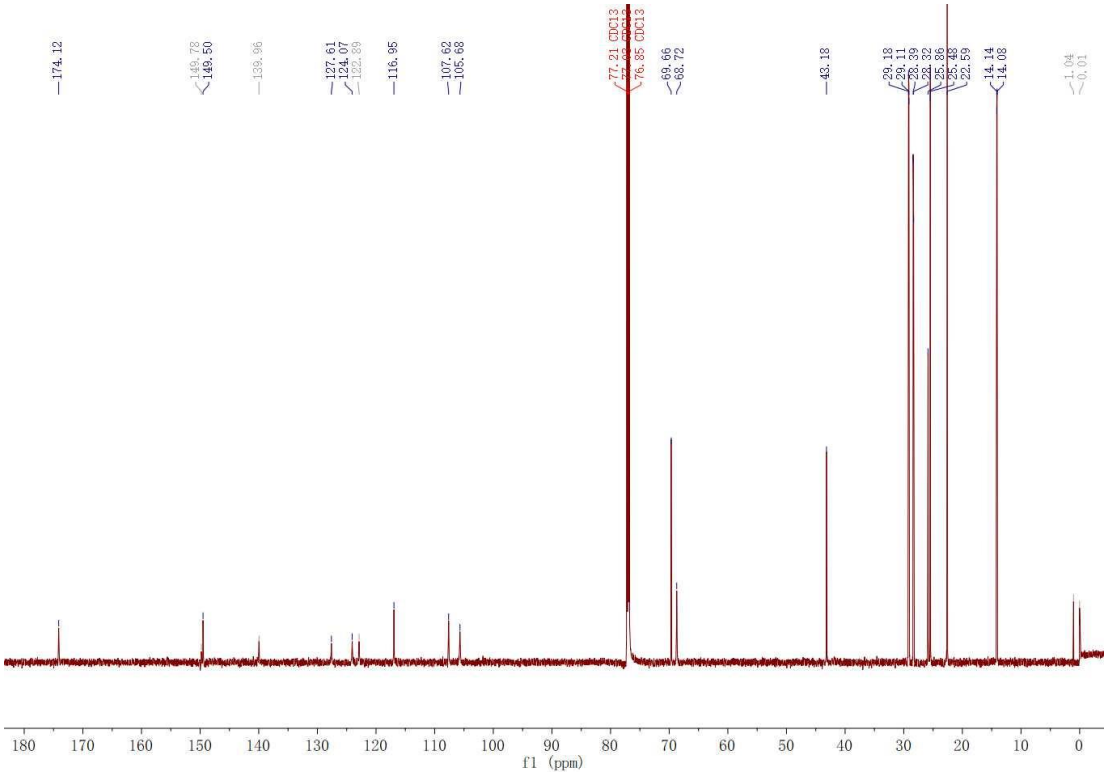


Fig. S34. ^{13}C NMR spectrum of Compound T5C36-6

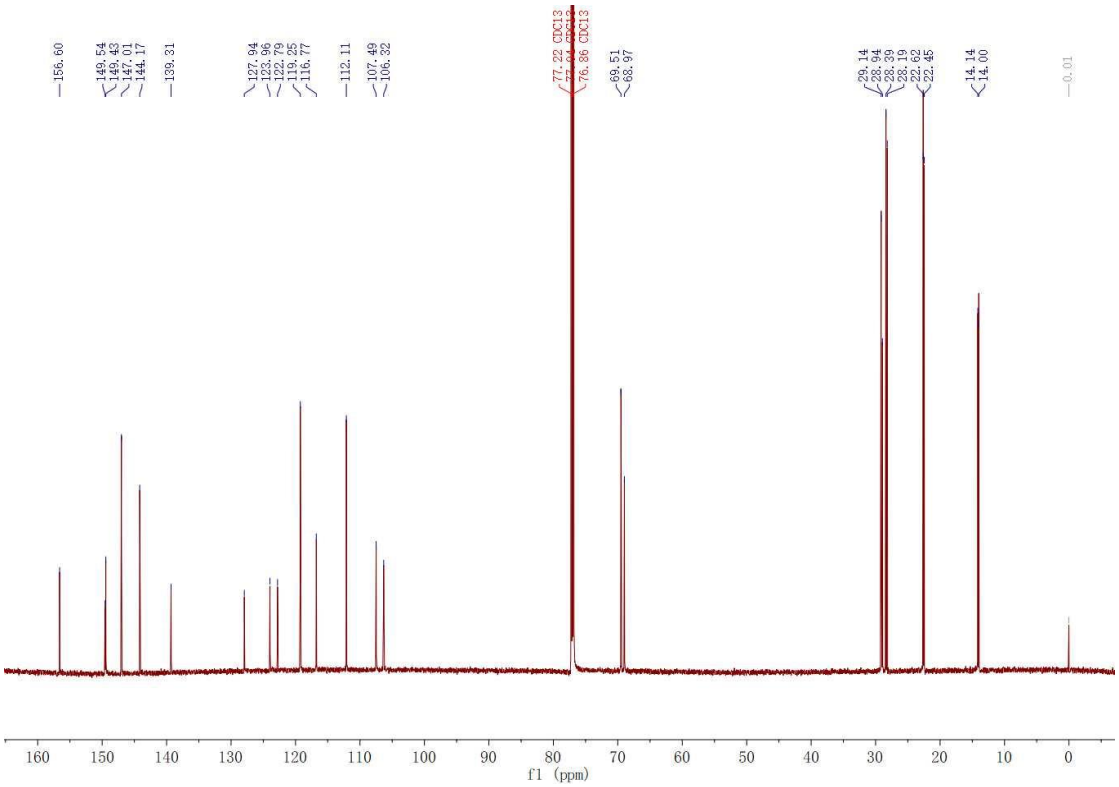


Fig. S35. ^{13}C NMR spectrum of Compound T5F36

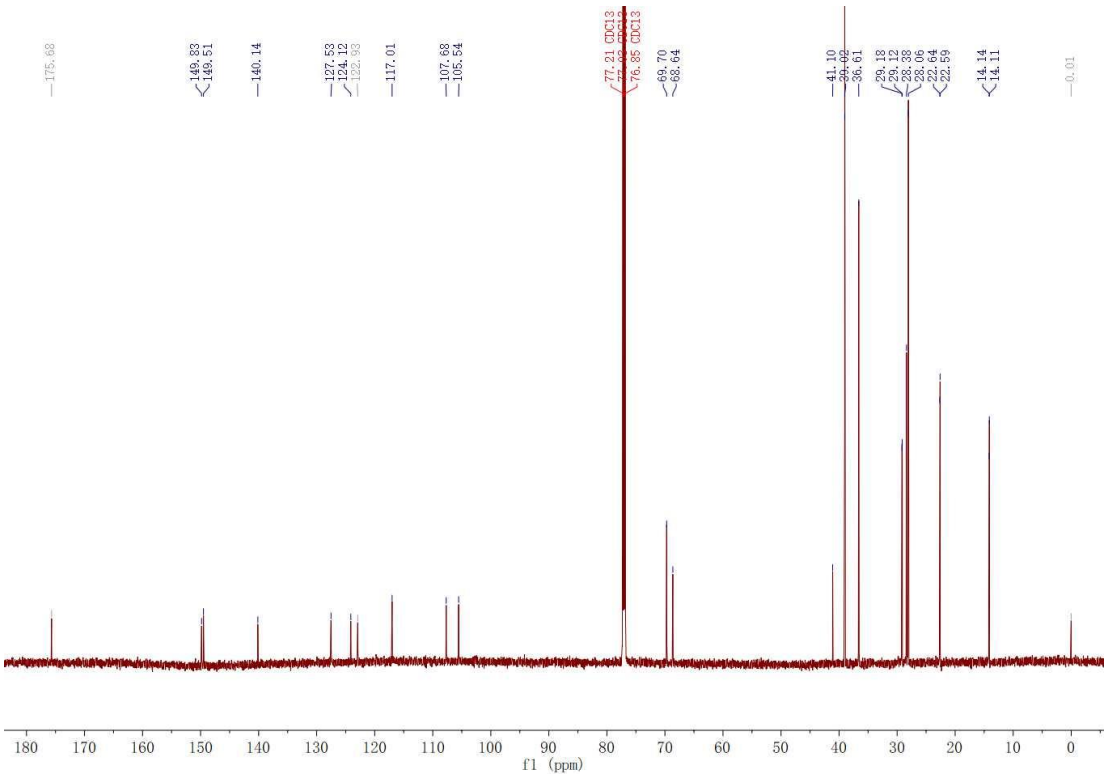
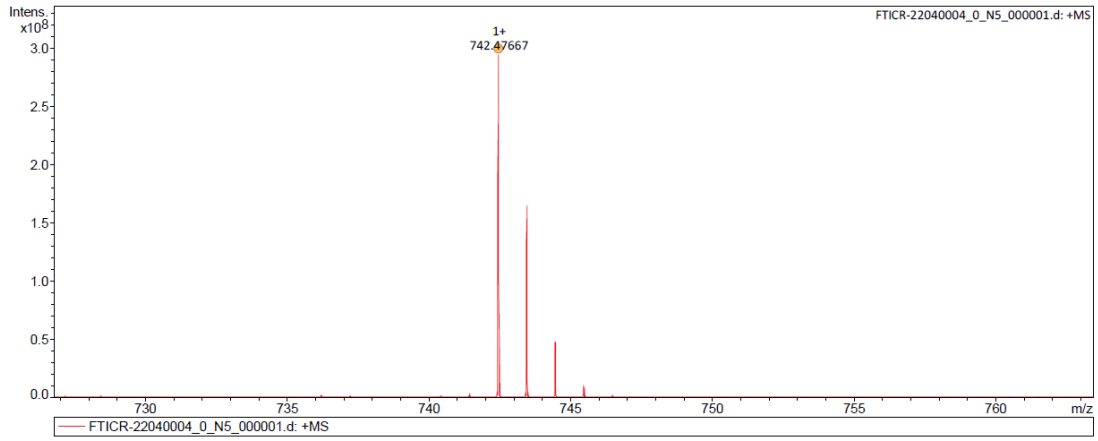


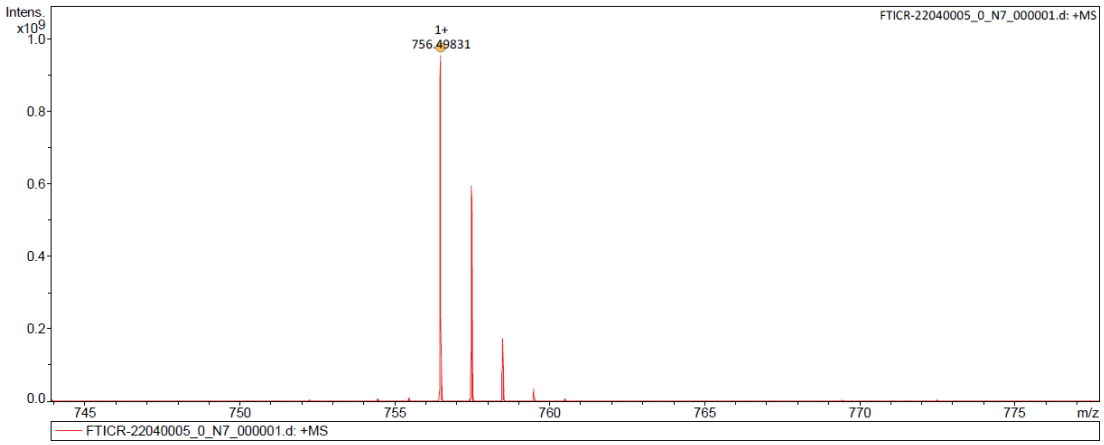
Fig. S36. ^{13}C NMR spectrum of Compound T5A36

S7. Supplementary MS results



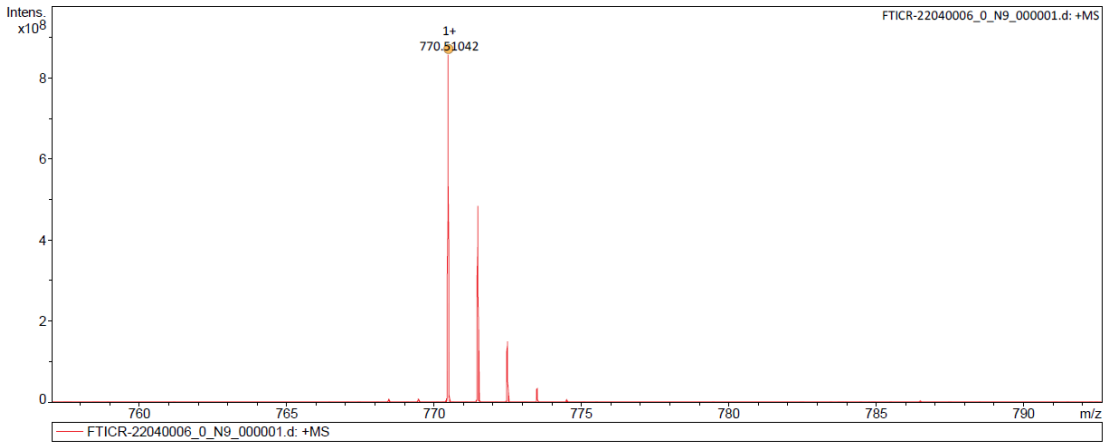
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
742.476667	1	C47H66O7	100.00	742.480306	4.9	4.4	21.7	15.5	odd	ok

Fig. S37. MS spectrum of Compound T5C2-3



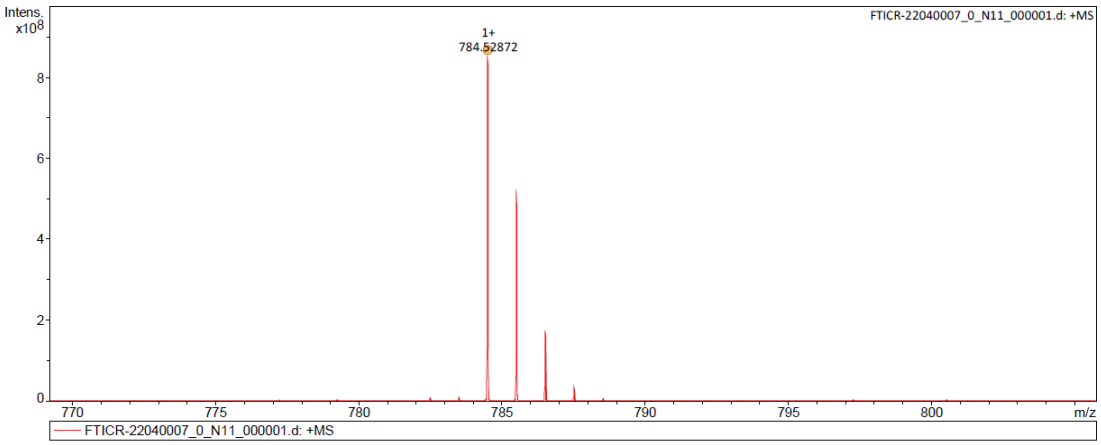
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
756.498308	1	C48H68O7	100.00	756.495956	-3.1	-3.1	48.8	15.5	odd	ok

Fig. S38. MS spectrum of Compound T5C2-4



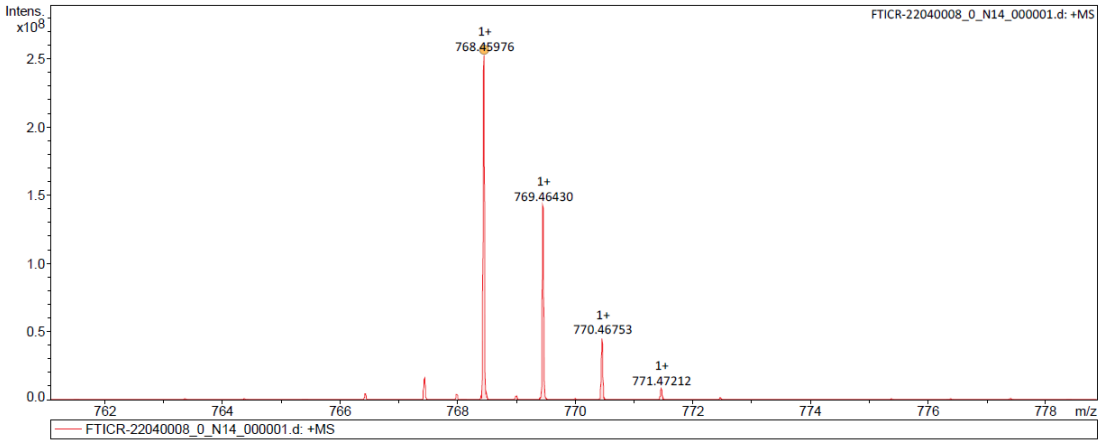
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
770.510422	1	C49H70O7	100.00	770.511606	1.5	0.7	16.6	15.5	odd	ok

Fig. S39. MS spectrum of Compound T5C2-5



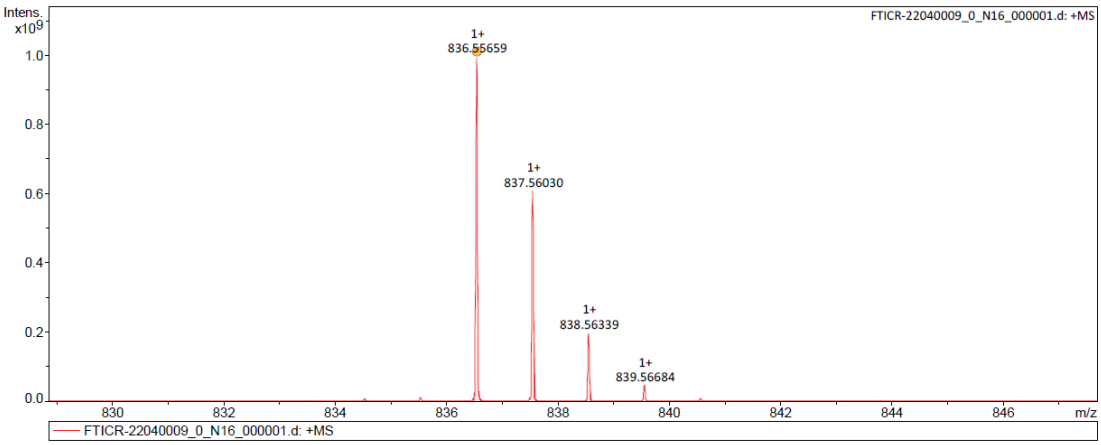
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
784.528722	1	C50H72O7	100.00	784.527256	-1.9	-2.9	38.5	15.5	odd	ok

Fig. S40. MS spectrum of Compound T5C2-6



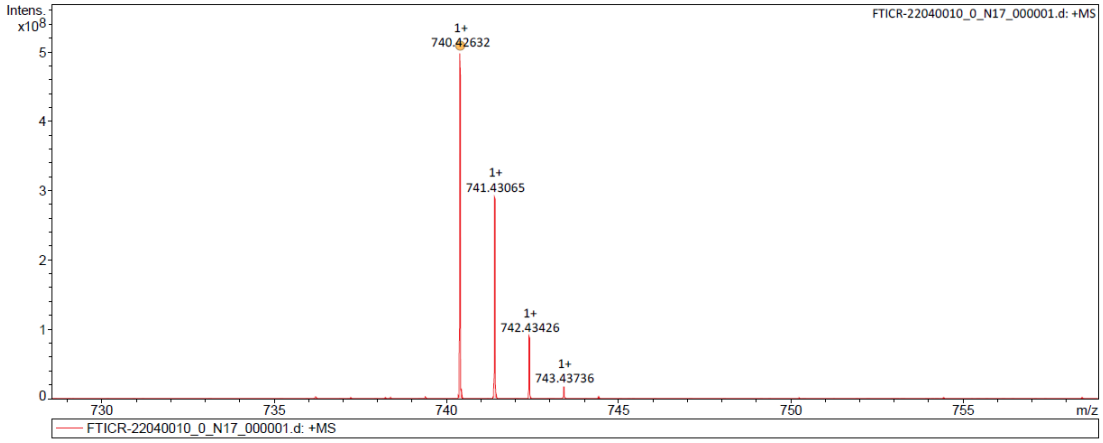
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
768.459759	1	C48H64O8	100.00	768.459570	-0.2	-1.5	22.0	17.5	odd	ok

Fig. S41. MS spectrum of Compound T5F2



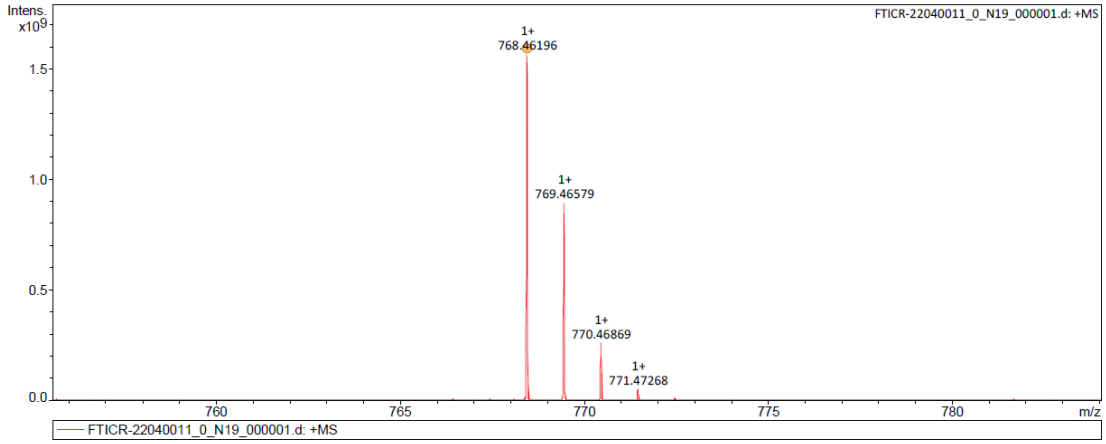
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
836.556591	1	C54H76O7	100.00	836.558556	2.3	2.1	9.8	17.5	odd	ok

Fig. S42. MS spectrum of Compound T5A2



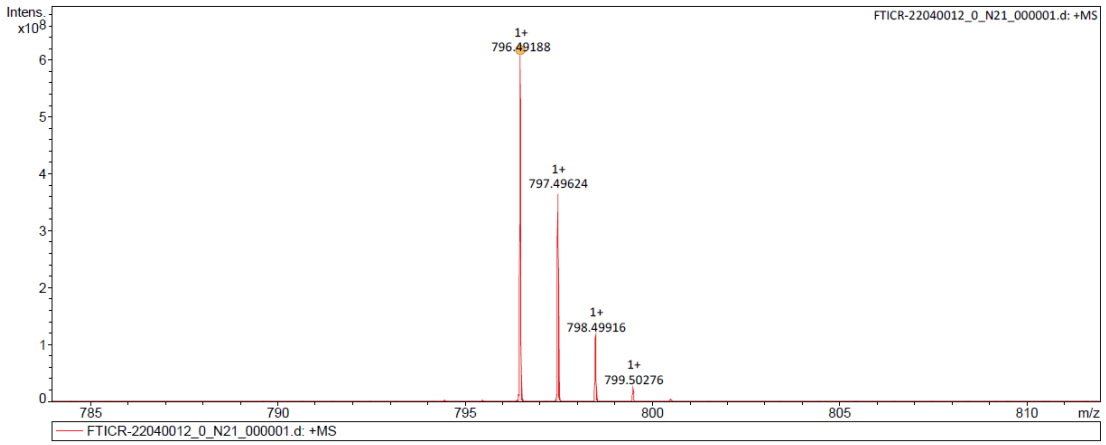
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
740.426322	1	C46H60O8	100.00	740.428270	2.6	1.6	42.8	17.5	odd	ok

Fig. S43. MS spectrum of Compound T5C36-3



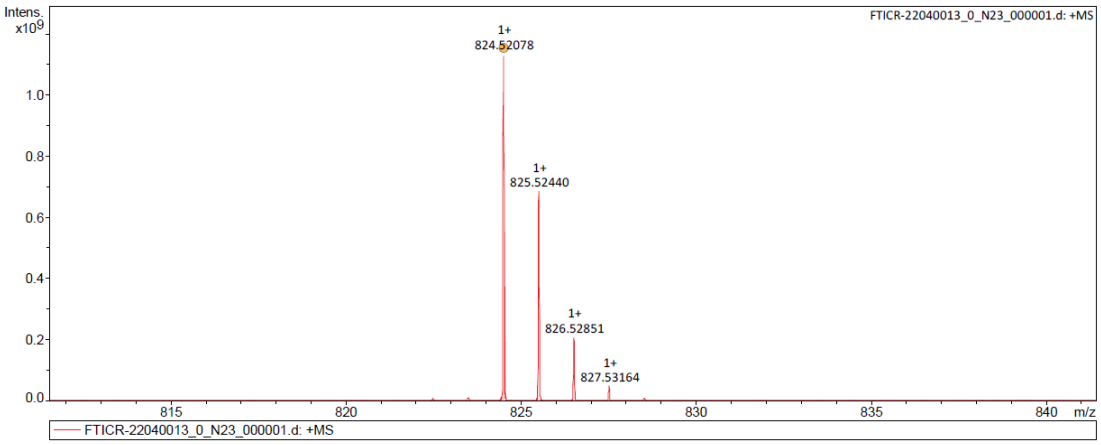
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
768.461956	1	C48H64O8	100.00	768.459570	-3.1	-3.5	21.9	17.5	odd	ok

Fig. S44. MS spectrum of Compound T5C36-4



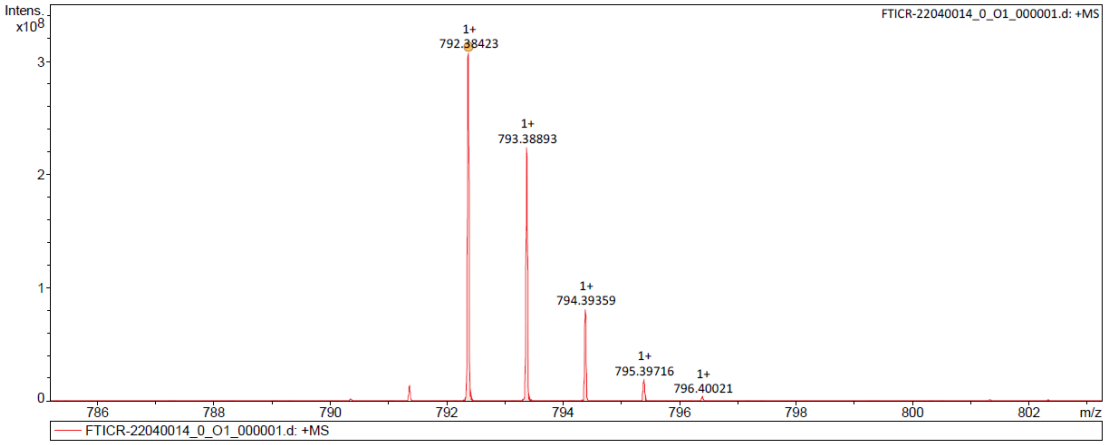
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
796.491878	1	C50H68O8	100.00	796.490871	-1.3	-2.0	29.2	17.5	odd	ok

Fig. S45. MS spectrum of Compound T5C36-5



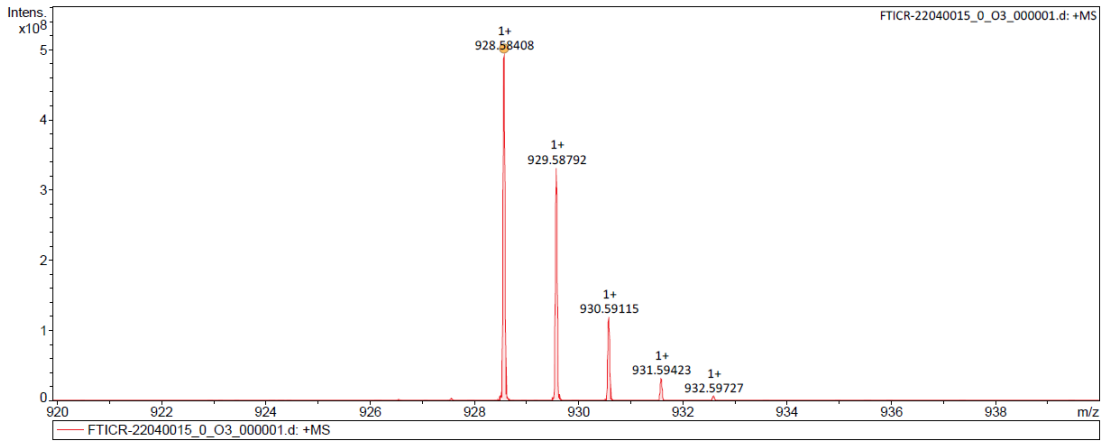
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
824.520780	1	C52H72O8	100.00	824.522171	1.7	1.1	15.5	17.5	odd	ok

Fig. S46. MS spectrum of Compound T5C36-6



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
792.384231	1	C48H56O10	100.00	792.386799	3.2	1.5	112.9	21.5	odd	ok

Fig. S47. MS spectrum of Compound T5F36



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
928.584084	1	C60H80O8	100.00	928.584771	0.7	0.4	6.4	21.5	odd	ok

Fig. S48. MS spectrum of Compound T5A36

S8. Full citations for Gaussian 09 program

Ref Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

S9. Supplementary Gauss stimulation results

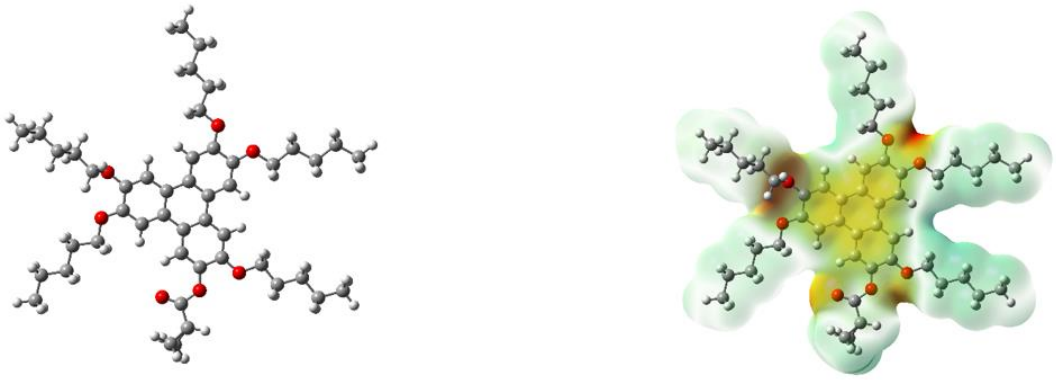


Fig. S49. Molecular optimized conformation and electrostatic potential isosurface calculations of compound T5C2-3

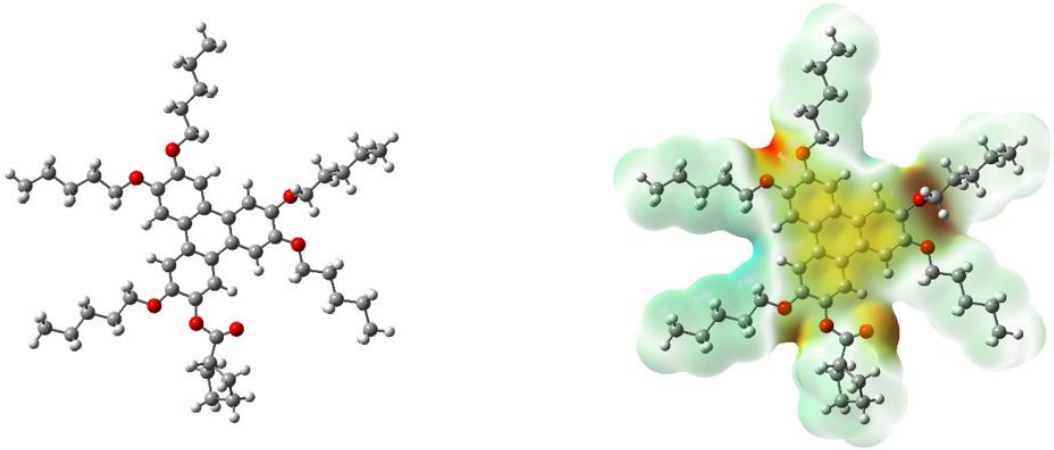


Fig. S50. Molecular optimized conformation and electrostatic potential isosurface calculations of compound T5C2-5

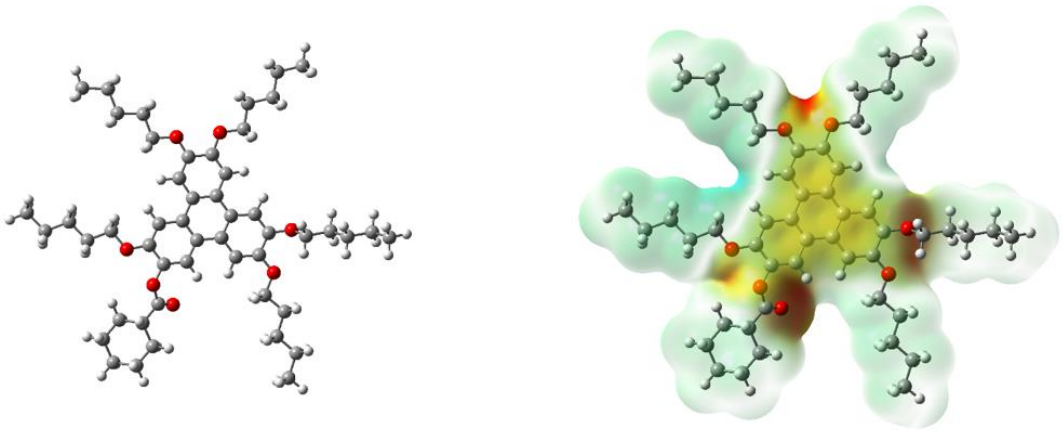


Fig. S51. Molecular optimized conformation and electrostatic potential isosurface calculations of compound T5C2-6

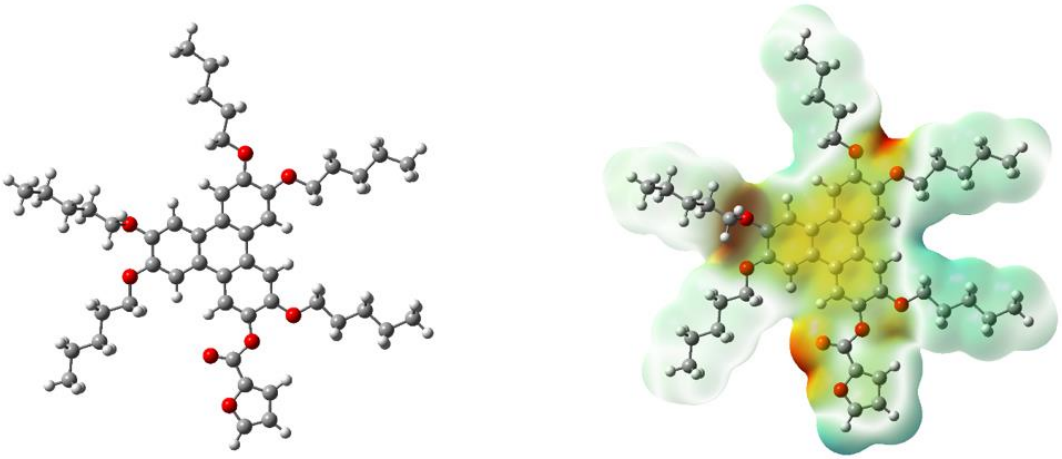


Fig. S52. Molecular optimized conformation and electrostatic potential isosurface calculations of compound T5F2

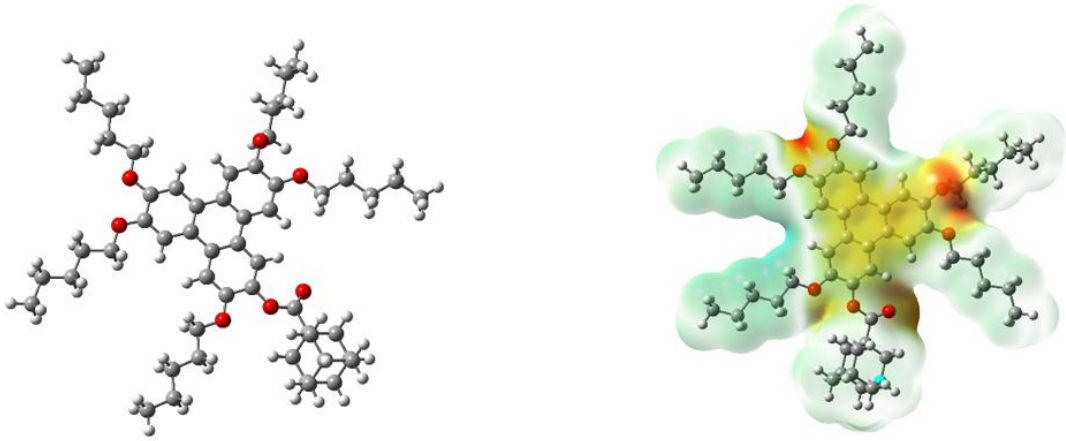


Fig. S53. Molecular optimized conformation and electrostatic potential isosurface calculations of compound T5A2

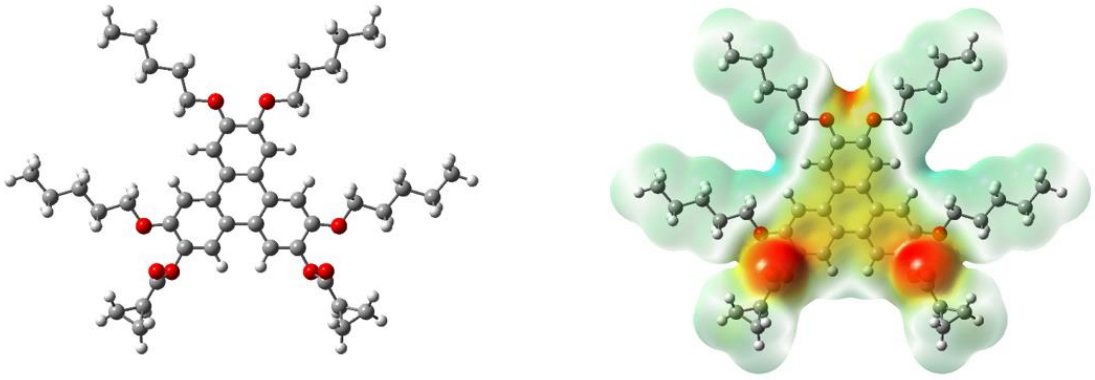


Fig. S54. Molecular optimized conformation and electrostatic potential isosurface calculations of compound T5C36-3

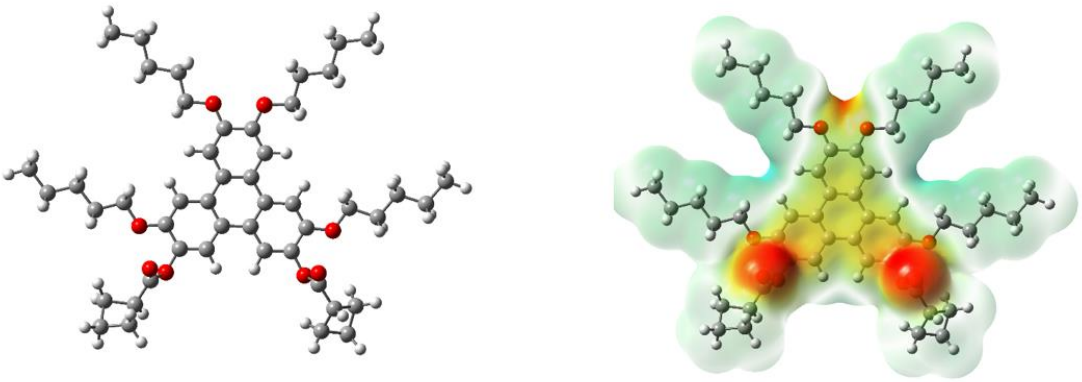


Fig. S55. Molecular optimized conformation and electrostatic potential isosurface calculations of compound T5C36-4

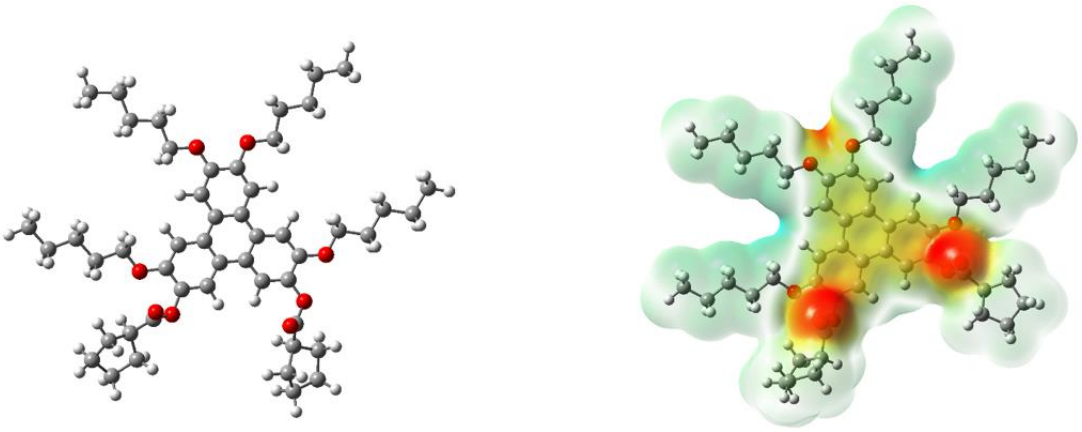


Fig. S56. Molecular optimized conformation and electrostatic potential isosurface calculations of compound T5C36-5

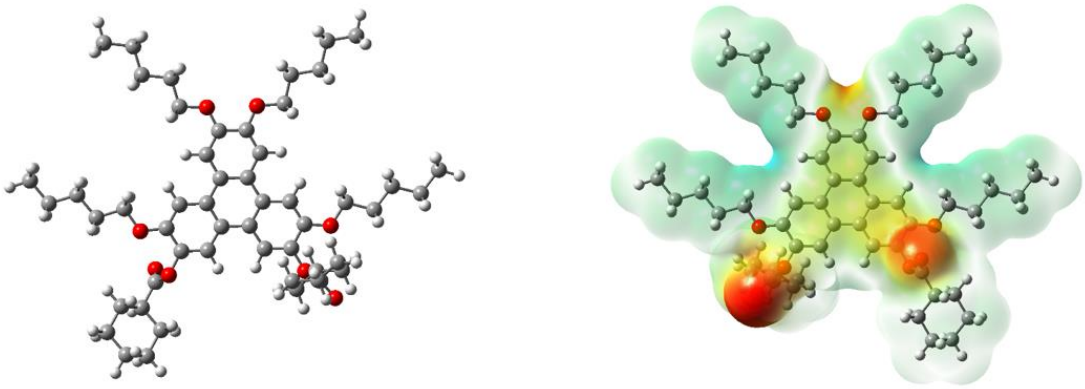


Fig. S57. Molecular optimized conformation and electrostatic potential isosurface calculations of compound T5C36-6

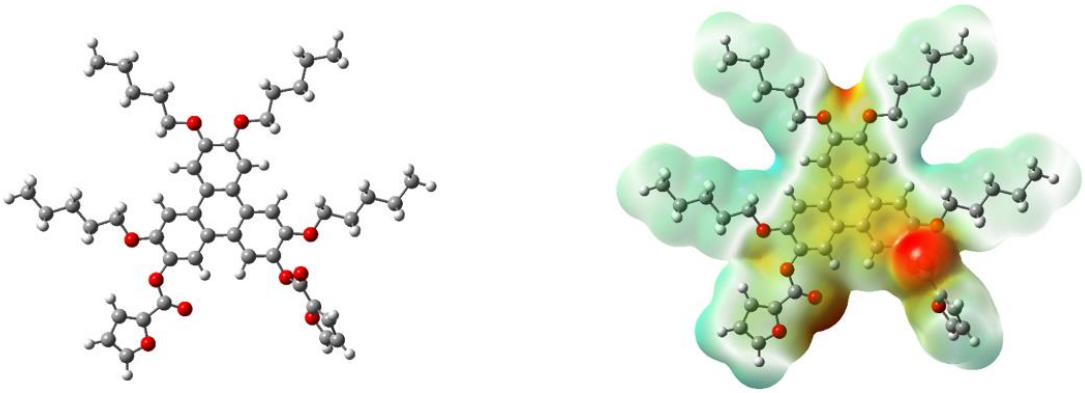


Fig. S58. Molecular optimized conformation and electrostatic potential isosurface calculations of compound T5F36

S10. Table S1 of dipople moments

Compound	Dipomoment(Total)	Dipomoment(x)	Dipomoment(y)	Dipomoment(z)
T5C2-3	3.04 D	2.41 D	-1.46 D	-1.15 D
T5C2-4	2.91 D	2.41 D	-1.26 D	1.04 D
T5C2-5	2.88 D	-2.49 D	-1.35 D	0.58 D
T5C2-6	2.90 D	-2.34 D	0.22 D	1.69 D
T5F2	4.05 D	3.70 D	-1.16 D	1.16 D
T5A2	2.96 D	1.74 D	-2.31 D	-0.64 D
T5C36-3	2.85 D	0 D	2.08 D	-1.95 D
T5C36-4	3.66 D	0.01 D	2.59 D	-2.58 D
T5C36-5	3.31 D	-0.13 D	2.58 D	-2.07 D
T5C36-6	6.97 D	-0.50 D	5.82 D	3.81 D
T5F36	3.28 D	-2.17 D	2.42 D	-0.43 D

S11. Mesophase of T5C2-3 ~ T5C2-6, T5F2 and T5A2

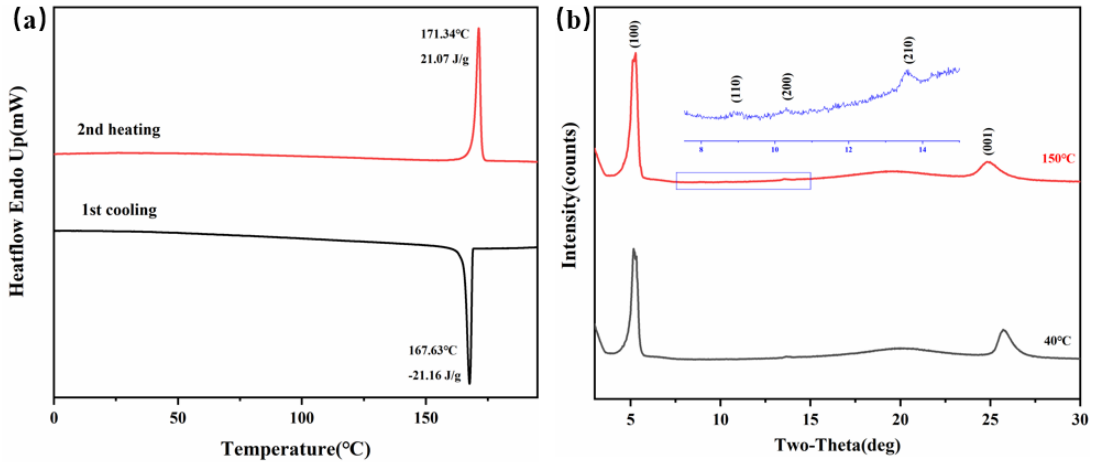


Fig. S59. DSC and 1D WAXD curves of compound T5C2-3

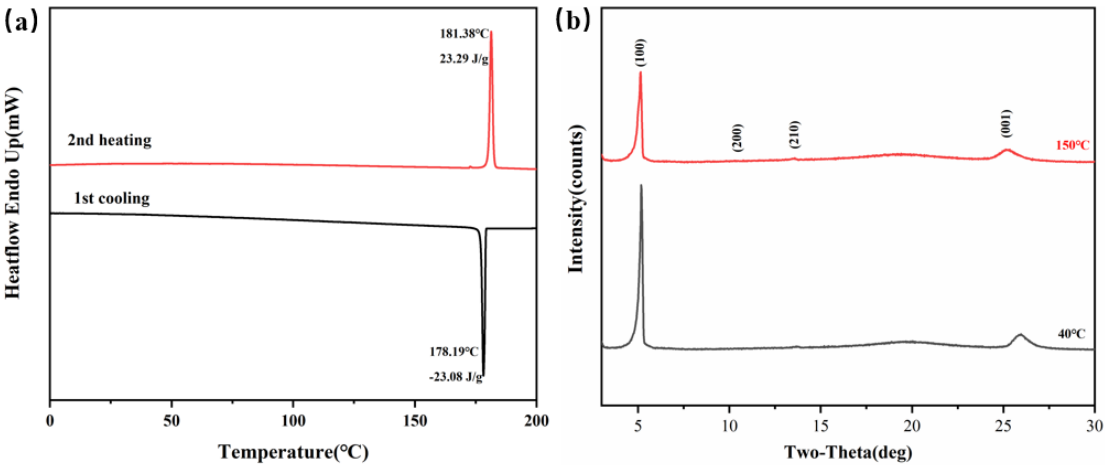


Fig. S60. DSC and 1D WAXD curves of compound T5C2-4

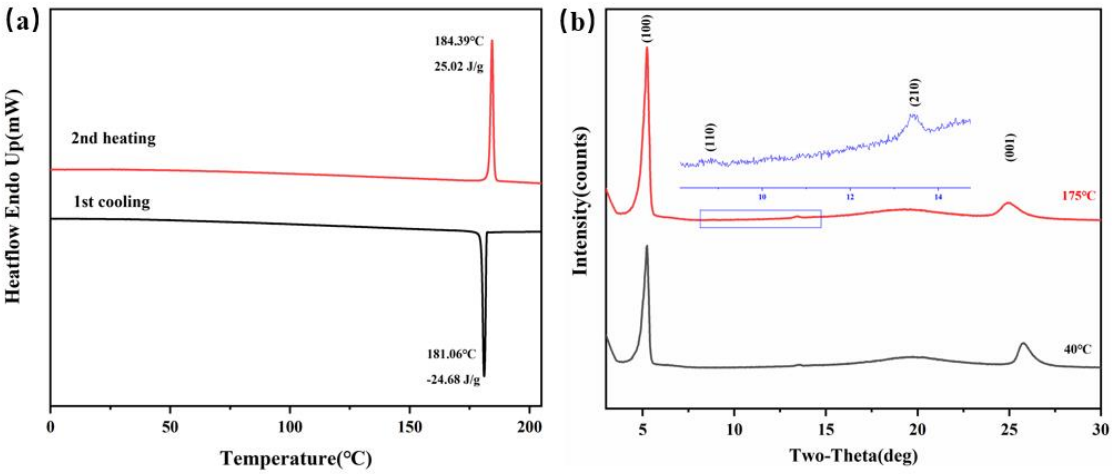


Fig. S61. DSC and 1D WAXD curves of compound T5C2-5

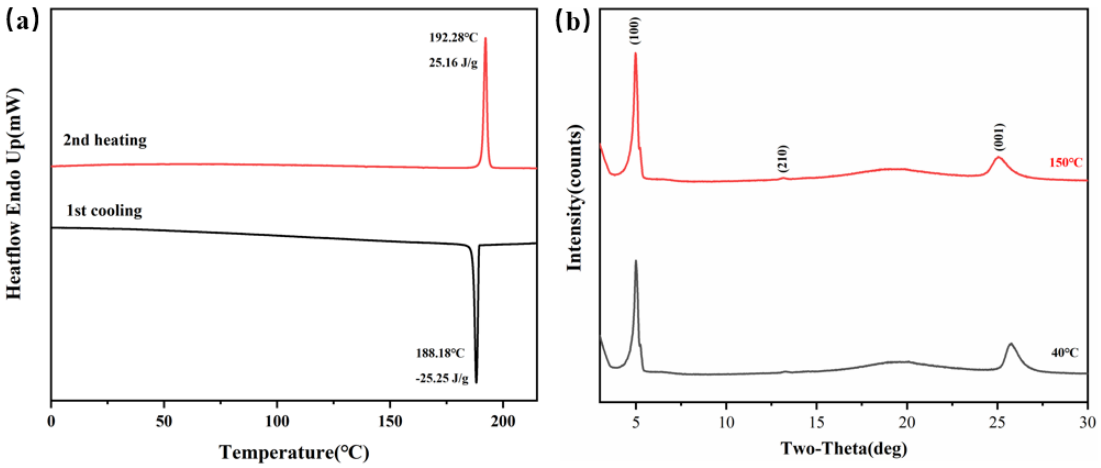


Fig. S62. DSC and 1D WAXD curves of compound T5C2-6

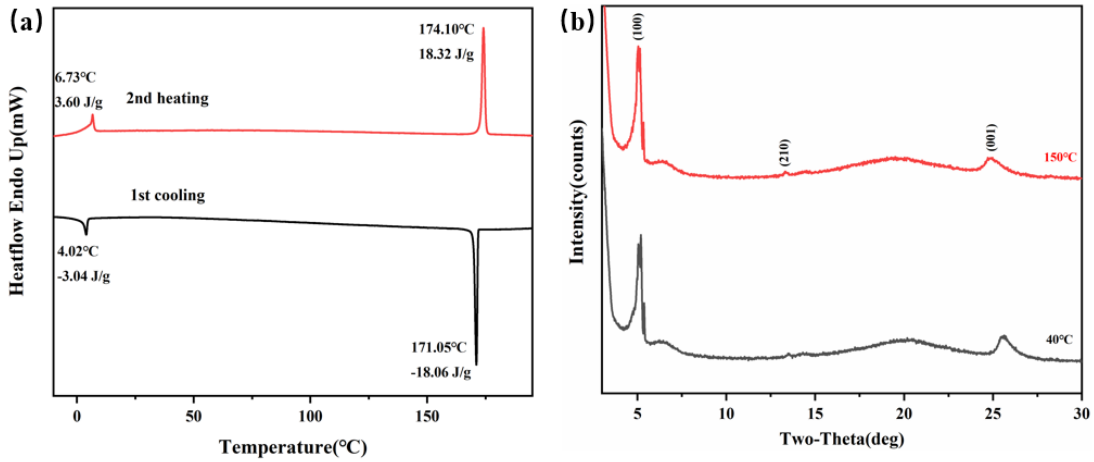


Fig. S63. DSC and 1D WAXD curves of compound T5F2

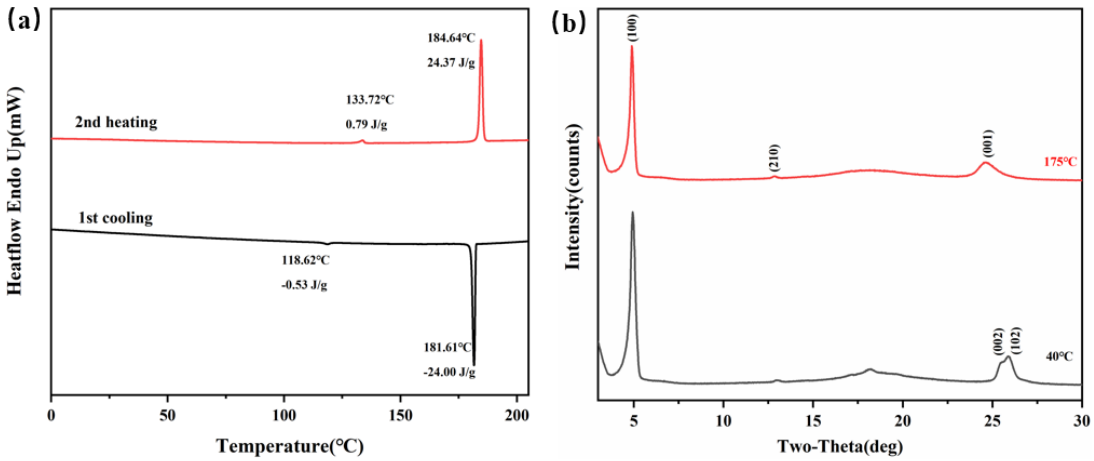


Fig. S64. DSC and 1D WAXD curves of compound T5A2

S12. Mesophase of T5C36-3 ~ T5C36-6, T5F36 and T5A36

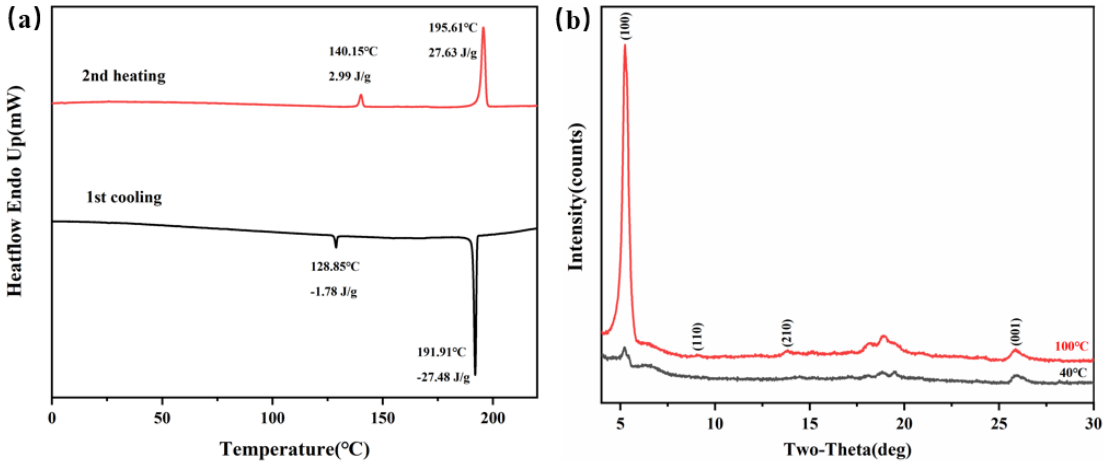


Fig. S65. DSC and 1D WAXD curves of compound T5C36-3

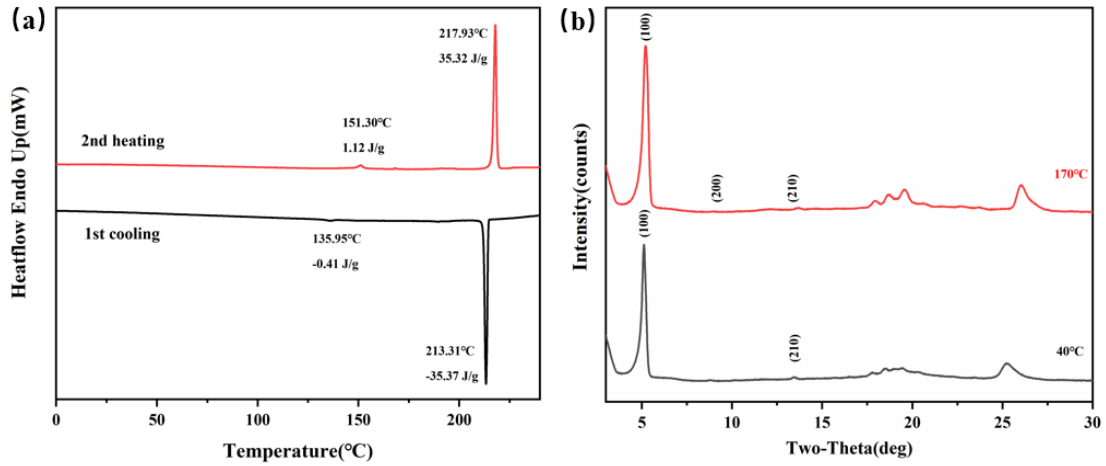


Fig. S66. DSC and 1D WAXD curves of compound T5C36-4

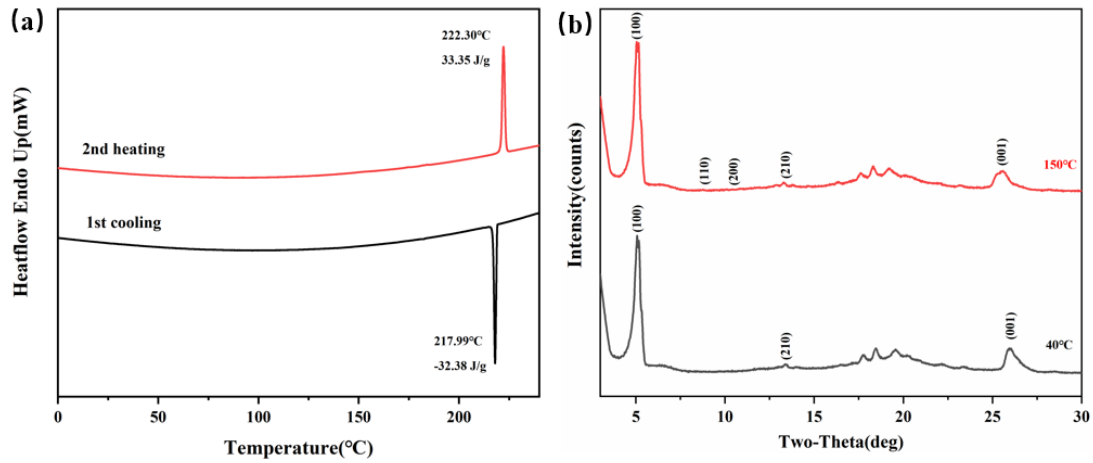


Fig. S67. DSC and 1D WAXD curves of compound T5C36-5

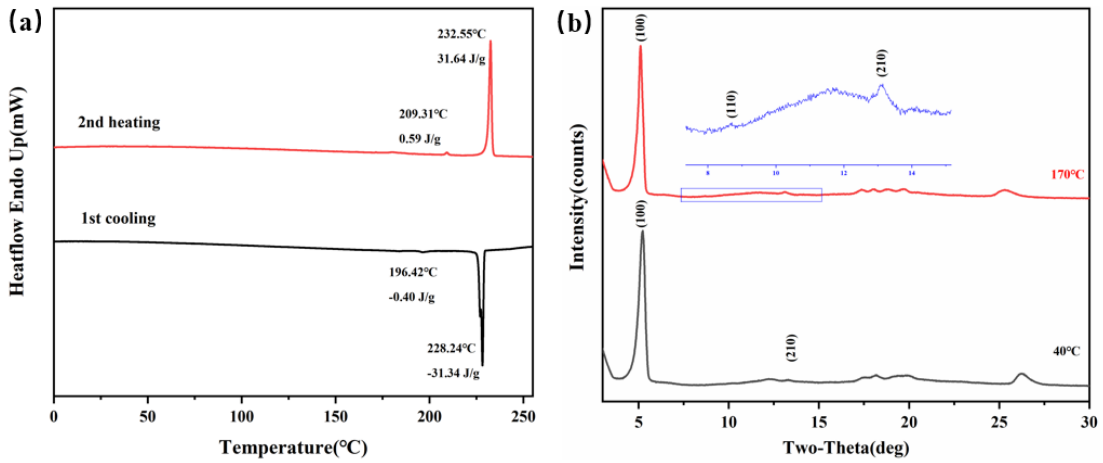


Fig. S68. DSC and 1D WAXD curves of compound T5C36-6

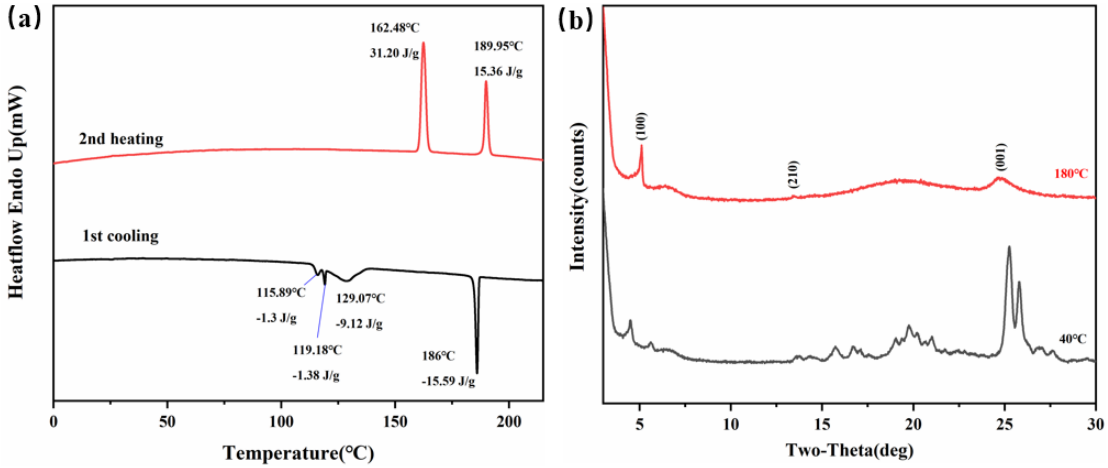


Fig. S69. DSC and 1D WAXD curves of compound T5F36

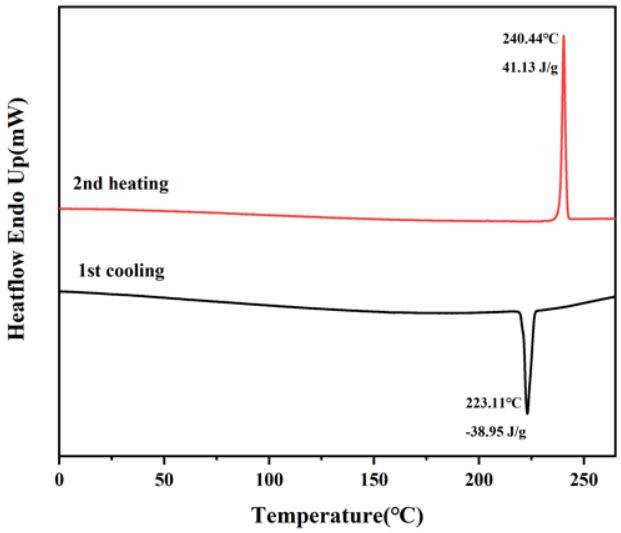


Fig. S70. DSC curve of compound T5A36

S13. Molecular structures and DSC curves of T5E2 and T5E36

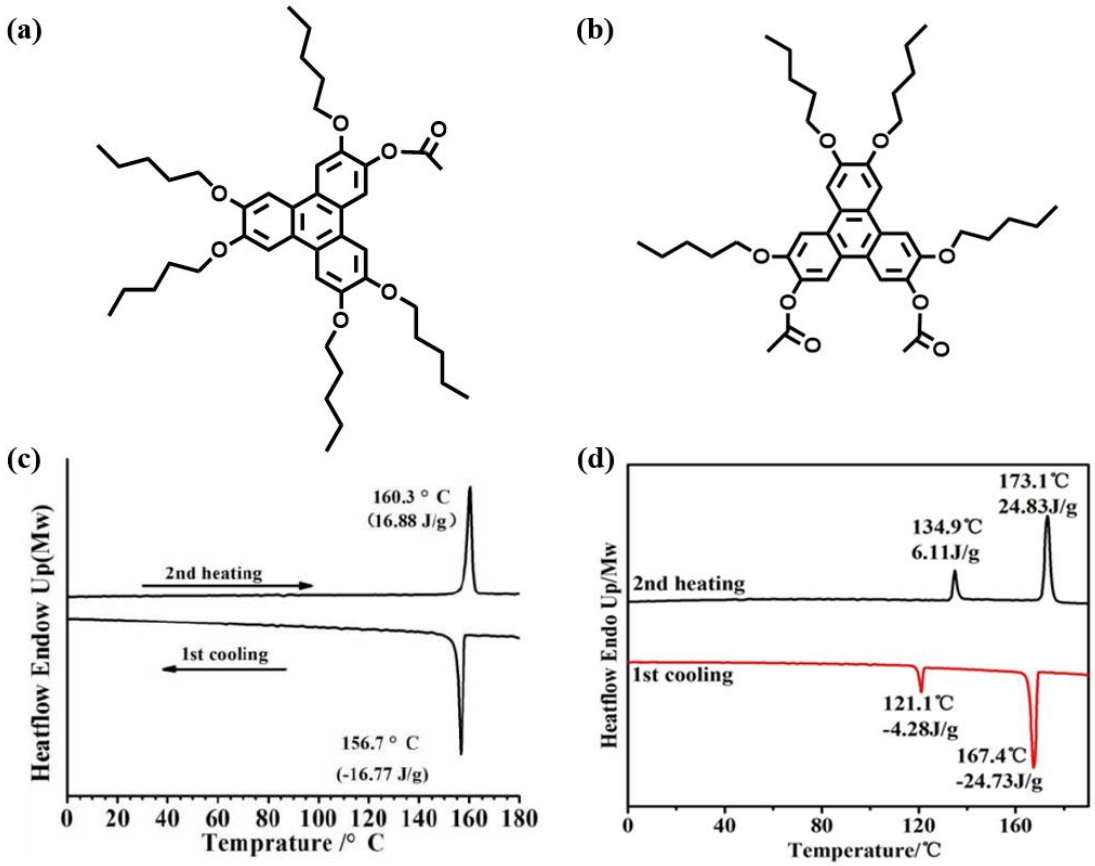


Fig. S71. Molecular structures and DSC curves of compounds (a,c) T5E2 and (b,d) T5E36

S14. POM images of samples T5C2-4, T5C36-4, T5C36-5 and T5C36-6 annealed in the liquid crystal cell

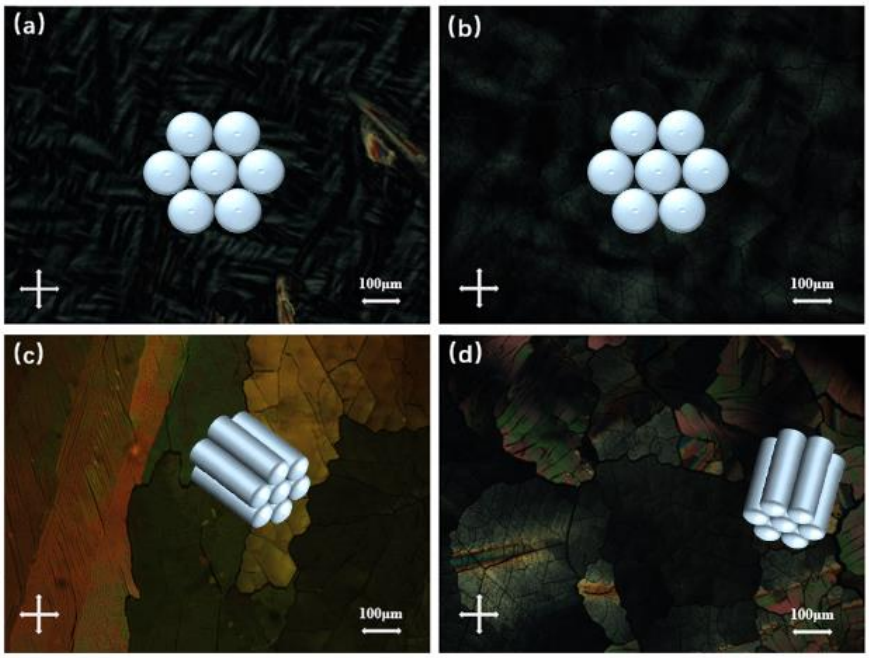


Fig. S72. POM images of samples (a) T5C2-4, (b) T5C36-4, (c) T5C36-5 and (d) T5C36-6 annealed in the liquid crystal cell at 40 °C

S15. Table S2 of charge carrier mobilities

Compound	Hole mobility ($\times 10^{-2}$ cm^2 V^{-1} s^{-1})	Electron mobility ($\times 10^{-2}$ cm^2 V^{-1} s^{-1})
T5C2-3	2.55	0.62
T5C2-4	3.84	1.13
T5C2-5	2.53	2.20
T5C2-6	1.43	1.30
T5F2	1.21	0.76
T5A2	2.34	1.11
T5C36-3	1.44	1.25
T5C36-4	1.75	1.07
T5C36-5	—	—
T5C36-6	—	—
T5F36	0.61	0.71