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Supporting Information

Photoswitchable Circularly Polarized Luminescent Cholesteric Superstructure: Direct Visualization and Dynamic Modulation of Amplified Luminescence Dissymmetry Factor

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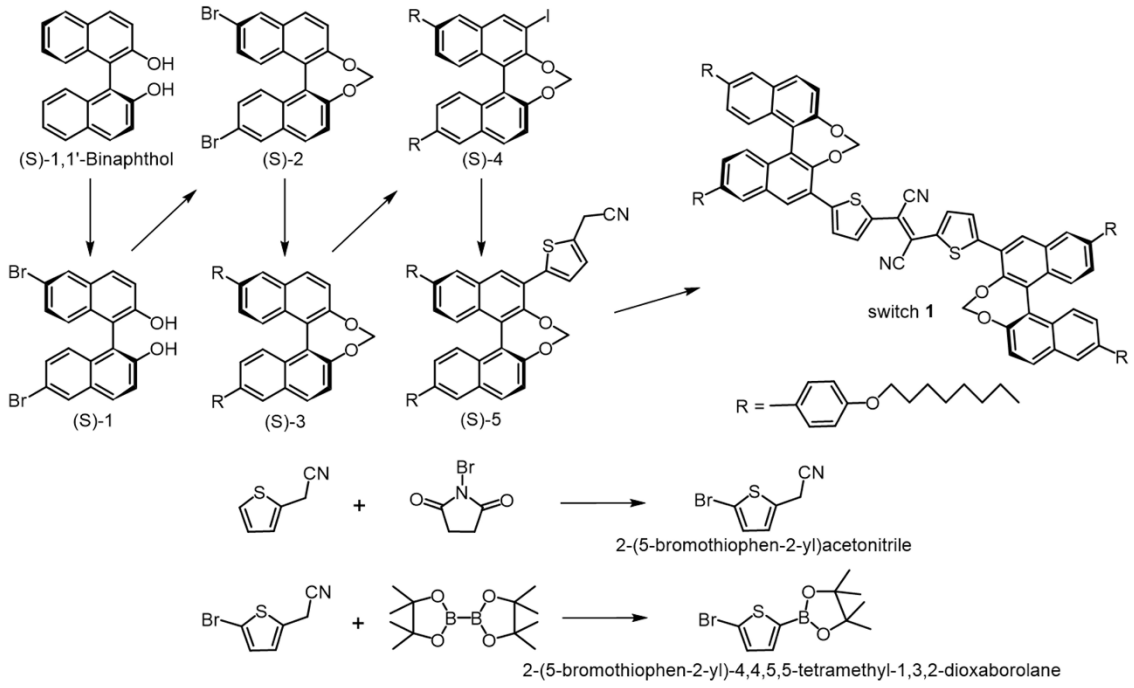
1. General information

Unless otherwise specified, all solvents and reagents were purchased from commercial sources in the study. Column chromatography was carried out on silica gel (200-300 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh GF254 glass plates.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III(400 MHz ^{1}H; 100 MHz ^{13}C) spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported as δ in unit of parts per million (ppm) with the residual solvent peak or tetramethylsilane (TMS) as the internal standard. The coupling constant (J) is reported in Hertz (Hz) and the multiplicities are designated as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. In order to deduct the photoisomerization yield from the ^{1}H NMR spectra, the chiral fluorescent photoswitch in solvent was irradiated for 5 min in both directions.

2. Synthesis of chiral fluorescent photoswitch (switch 1)



Scheme S1. Synthesis of chiral fluorescent molecular switch **1**.

Compound (S)-1:

In a single-necked flask, (S)-1,1'-Binaphthol (8.58 g, 30 mmol) was dissolved in DCM and placed in a 0°C freezer. Then liquid bromine (10.79 g, 67.5 mmol) was added dropwise to the single-necked flask using a constant pressure funnel, and when the addition was completed, it was allowed to react at 0°C for 3 h. After the reaction, DCM and saturated NaCl solution were used for extraction. After the extraction, the lower organic layer was removed for vacuum rotary evaporation of the organic solution, and then dried in a vacuum oven to obtain a pale yellow solid (S)-1.

Compound (S)-2:

Measure about 100 mL of acetonitrile in a 250 mL round bottom flask, and then add intermediate (S)-1, CH_2I_2 (24.11 g, 90 mmol) and anhydrous K_2CO_3 (41.46 g, 300 mmol) into the round bottom flask. Place the device in an oil bath at 80°C to heat and stir. After reacting for 12 h, the flask was taken out and cooled to room temperature, and DCM and saturated NaCl solution were used for extraction and rotary evaporation. The treated product was purified by column chromatography using DCM/petroleum ether (1/2) as eluent to give a white snowflake-like solid (S)-2 (12.13 g, 89 %). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.10 (s, 2H, Ar-H), 7.91-7.88 (d, 2H, Ar-H), 7.51-7.49 (d, 2H, Ar-H), 7.40-7.37 (dd, 2H, Ar-H), 7.32-7.30 (d, 2H, Ar-H), 5.69 (s, 2H, -CH_2-).

Compound (S)-3:

Intermediate (S)-2 (12.13 g, 26.60 mmol) was placed in a 500 mL three-necked flask, 260 mL of anhydrous tetrahydrofuran was added as solvent, and 4-octyloxyphenylboronic acid (14.64 g, 58.52 mmol), tetrakis(triphenylphosphine)palladium (3.07 g, 2.66 mmol) and 20% Na_2CO_3

solution (133 mL) were placed in the flask. The above device was heated and stirred under nitrogen at 70°C for 4 h. After the reaction, DCM and saturated NaCl solution were used for pretreatment. The pretreated product was dissolved in DCM, and separated and purified by column chromatography using DCM/petroleum ether (1/1) as eluent to give a white solid (S)-3 (10.34 g, 55 %). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.11 (s, 2H, Ar-H), 8.04-8.02 (d, 2H, Ar-H), 7.68-7.63 (t, 6H, Ar-H), 7.60-7.59 (d, 2H, Ar-H), 7.57-7.50 (dd, 2H, Ar-H), 7.03-7.01 (d, 4H, Ar-H), 5.73 (s, 2H, -CH_2-), 4.03-4.01 (t, 4H, Ar-H), 1.87-1.80 (m, 4H, -CH_2-), 1.54-1.46 (m, 4H, -CH_2-), 1.38-1.32 (m, 16H, -CH_2-), 0.94-0.90 (t, 6H, -CH_3).

Compound (S)-4:

Intermediate (S)-3 (10.34 g, 14.63 mmol) and anhydrous tetrahydrofuran (100 mL) were placed in a 250 mL three-necked flask. The reaction device under nitrogen was placed in a -78°C freezer, and t-BuLi (13.5 mL, 1.3M in n-pentane, 17.56 mmol) was added dropwise to the three-necked flask and then stirred for 1 h. After the stirring was completed, I_2 (4.83 g, 19.02 mmol) was dissolved in anhydrous THF and added to the three-necked flask and stirred at room temperature for 10 h, then adding an appropriate amount of sodium thiosulfate solution to remove excess I_2. After the reaction, DCM and saturated NaCl solution were used for extraction and rotary evaporation. The obtained solid mixture was dissolved in DCM, and separated and purified by column chromatography using DCM/petroleum ether (1/1) as eluent to give a white solid (S)-4 (5.48 g, 45 %). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.53 (s, 1H, Ar-H), 8.09 (s, 1H, Ar-H), 8.04-8.02 (d, 1H, Ar-H), 7.97 (s, 1H, Ar-H), 7.66-7.61 (m, 4H, Ar-H), 7.58-7.56 (d, 4H, Ar-H), 7.51-7.49 (d, 1H, Ar-H), 7.02-7.00 (dd, 4H, Ar-H), 5.74-5.69 (dd, 2H, -CH_2-), 4.03-4.00 (t, 4H, -CH_2-), 1.86-1.79 (m, 4H, -CH_2-), 1.55-1.45 (m, 4H, -CH_2-), 1.37-1.32 (m, 16H, -CH_2-

), 0.93-0.90 (t, 6H, -CH_3).

2-(5-bromothiophen-2-yl)acetonitrile：

Appropriate amounts of 2-(thiophen-2-yl)acetonitrile (2.46 g, 20 mmol) and 1-bromopyrrolidine-2,5-dione (3.56 g, 20 mmol) were placed in a single-necked flask with 100 ml of acetone, and stirred for 6 h at room temperature. After the reaction, the organic solvent was rotated to evaporate to obtain a crude product. The crude product was separated and purified by column chromatography using DCM/petroleum ether (1/1) as eluent to give a brown-yellow oily liquid (3.54 g, 88 %). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 6,96-6.55 (d, 1H, Ar-H), 6.84-6.83 (d, 1H, Ar-H), 3.85 (s, 2H, -CH_2-).

2-(5-bromothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (5.33 g, 21.01 mmol), anhydrous 1,4-dioxane (40 mL), 2-(5-bromothiophen-2-yl)acetonitrile (3.54 g, 17.51 mmol), potassium acetate (4.30 g, 43.78 mmol), dimethyl sulfoxide (2 mL) and [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (1.28 g, 1.75 mmol) were placed in a 250 mL three-necked flask. The above device under nitrogen was heated and stirred at 90°C for 1 h. After the reaction, DCM and saturated NaCl solution were used for extraction and rotary evaporation. The resulting crude product was dissolved in DCM, and separated and purified by column chromatography using DCM/petroleum ether (3/1) as eluent to give a white crystalline solid (S)-4 (2.18 g, 50 %). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.50-7.49 (d, 1H, Ar-H), 7.13-7.12 (d, 1H, Ar-H), 3.94 (s, 2H, -CH_2-), 1.343.85 (s, 12H, -CH_3).

Compound (S)-5:

(S)-4 (5.48 g, 6.58 mmol), toluene (120 mL), tetrakis(triphenylphosphine)palladium (0.38 g,

0.33 mmol), 2-(5-bromothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.97 g, 7.90 mmol), ethanol (16 mL) and 20% Na_2CO_3 solution (50 mL) were placed in a three-necked flask. Then, the device was heated and stirred at 90°C under nitrogen for 18 h. After the reaction, DCM and saturated NaCl solution were used for extraction. The resulting residue was purified by column chromatography (DCM: petroleum ether =1:1) to give a colorless oily liquid (1.63 g, 30%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.29 (s, 1H, Ar-H), 8.10 (s, 2H, Ar-H), 8.06-8.03 (d, 1H, Ar-H), 7.67-7.65 (dd, 4H, Ar-H), 7.60-7.59 (t, 2H, Ar-H), 7.57-7.55 (t, 3H, Ar-H), 7.53-7.50 (d, 1H, Ar-H), 7.13-7.12 (d, 1H, Ar-H), 7.03-7.00 (dd, 4H, Ar-H), 5.73-5.64 (dd, 2H, -CH_2-), 4.04-4.00 (t, 4H, -CH_2-), 3.97-3.96 (d, 2H, -CH_2-), 1.86-1.79 (m, 4H, -CH_2-), 1.53-1.45 (m, 4H, -CH_2-), 1.37-1.31 (m, 16H, -CH_2-), 0.92-0.89 (t, 6H, -CH_3).

Chiral fluorescent molecular switch 1:

Place anhydrous tetrahydrofuran (60 mL), (S)-5 (1.63 g, 1.98 mmol), and iodine (0.50 g, 1.98 mmol) in a three-necked flask, and place the flask in a freezer at -78°C under nitrogen. An appropriate amount of sodium methoxide solution was dropped into the flask and reacted at -78°C for 1 h, and then transferred to room temperature for 3 h. After the reaction, an appropriate amount of dilute HCl was added for quenching, and finally DCM and saturated NaCl solution were used for extraction and rotary evaporation. The obtained crude product was dissolved in DCM, and separated and purified by column chromatography (DCM: petroleum ether =2:1) to give a red solid (0.82 g, 50%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.41 (s, 2H, Ar-H), 8.14-8.10 (d, 4H, Ar-H), 8.06-8.03 (d, 2H, Ar-H), 7.93-7.92 (d, 2H, Ar-H), 7.79-7.98 (d, 2H, Ar-H), 7.67-7.64 (dd, 8H, Ar-H), 7.59-7.50 (m, 10H, Ar-H), 7.03-7.00 (dd, 8H, Ar-H), 5.81-5.72 (dd, 4H, -CH_2-), 4.04-4.00 (t, 8H, -CH_2-), 1.86-1.78 (m, 8H, -CH_2-), 1.51-1.45 (m, 8H, -CH_2-), 1.39-1.26

(m, 32H, -CH_2-), 0.92-0.88 (t, 12H, -CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 159.07, 158.93, 151.16, 147.08, 144.74, 138.20, 137.43, 136.04, 133.32, 132.84, 132.48, 132.24, 131.83, 130.93, 128.22, 127.55, 127.37, 127.23, 126.82, 126.49, 125.82, 125.67, 125.43, 125.34, 121.07, 116.57, 114.98, 111.69, 102.77, 68.16, 31.85, 29.72, 29.41, 29.33, 29.28, 26.10, 22.69, 14.13.

Table S1. The elemental analysis data of switch **1**

Elemental	N[%]	C[%]	H[%]	S[%]
Test value	1.49	79.46	7.09	3.43

3. Computational study of the trans and cis isomers of switch 1

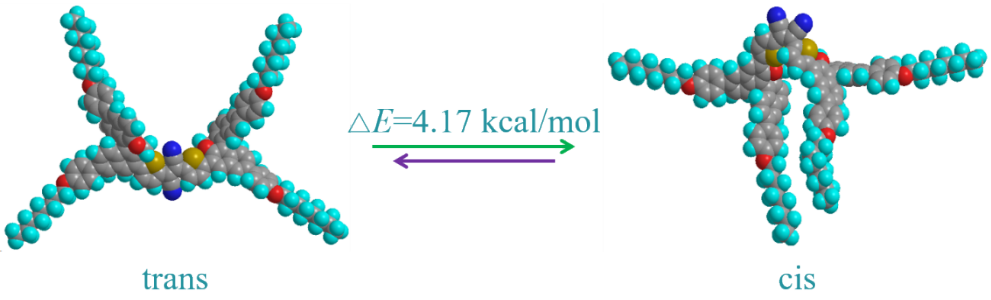


Figure S1. Optimized structure of switch **1** in *trans* and *cis* forms (space filling mode) obtained by Gaussian 09 calculations.

Quantum chemical calculations on both isomers of the chiral fluorescence photoswitch were performed using density functional theory (DFT) at B3LYP/6-31G(d) level incorporated in the Gaussian 09 set of programs. According to the suggestions of theoretical calculations, the simulation results of the two isomers of the *trans* and *cis* of switch **1** are shown in Table S2. For the *trans* isomer, there are three significant electronic transitions, namely, HOMO→LUMO (S1), HOMO-2→LUMO (S3), and HOMO-6→LUMO (S7) transitions. In the green light region, the oscillator strength of the *trans* isomer is 1.3104, and the *cis* isomer is 0.5345, indicating that green light can induce the isomerization process of *trans* to *cis* in switch **1**.

However, in the purple light region, the oscillator strength of the cis isomer is significantly greater than the *trans* isomer, indicating that the purple light can induce the conversion from *cis* isomer to *trans* isomer. This shows that the isomerization process of switch **1** can be effectively induced by green light and purple light.

Table S2. Singlet transitions and corresponding energy gaps, absorption wavelengths, and oscillator strengths of the two isomers of switch **1**, obtained by TD-DFT calculations.

Isomer	Excitation	E_{cal}(eV)	$\lambda_{max,abs}$(nm)	Oscillator Strength(f)
trans	S1 HOMO→LUMO (95%)	2.2284	556.39	1.3104
	S3 HOMO-2→LUMO (90%)	2.3838	520.12	0.5215
	S7 HOMO-6→LUMO (98%)	2.9119	425.78	0.0458
cis	S1 HOMO→LUMO (89%)	2.2828	543.12	0.5345
	S4 HOMO-3→LUMO (78%)	2.4676	502.44	0.1215
	S6 HOMO-5→LUMO (94%)	2.8648	432.79	0.1776

4. Measurement of helical twisting power (HTP) of the chiral dopant

The Grandjean-Cano wedge method is used to measure the pitch length of CLC. We can see disclination lines of the CLC in the wedge cell through a polarizing optical microscope (POM). The pitch length is calculated based on equation p=2Rtanθ, wherein R represents the distance between the two adjacent lines and θ is the angle of the wedge cell (EHC, KCRK-07, tanθ = 0.0183). The ability to induce a helical superstructure in nematic host can be defined by the helical twisting power (HTP). Not only that, the HTP value is related to the pitch of CLC as $\beta=(pc)^{-1}$, where p is the helical pitch length and c is the concentration of chiral dopants.

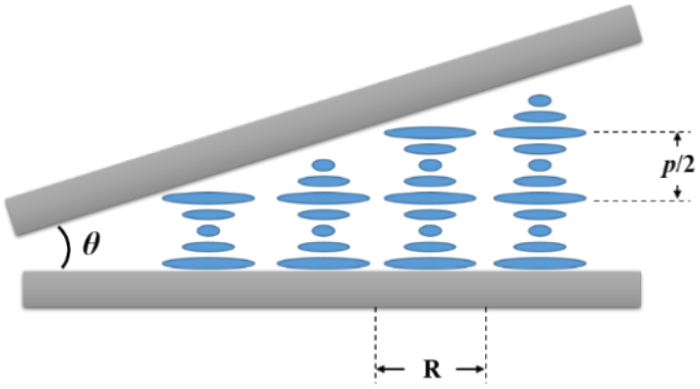


Figure S2. Schematic diagram of Grandjean-Cano wedge method.

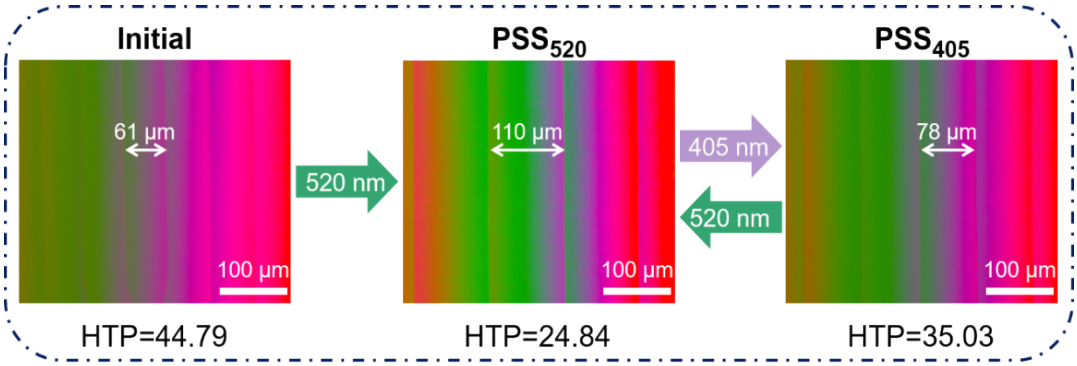


Figure S3. Observe the variations of Carnot line in the LC cell doped with 1.0 wt% switch **1** in SLC1717 through POM.

5. Photoluminescence properties of the CLC doped with 1.0 wt% switch 1

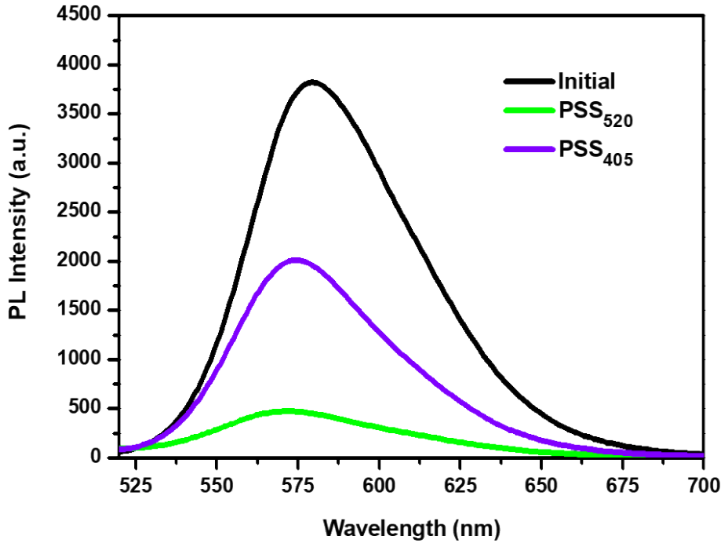


Figure S4. Fluorescence spectrum of photo-responsive CLC doping 1.0 wt% of switch **1** into SLC1717 tuned by 520 nm and 405 nm light.

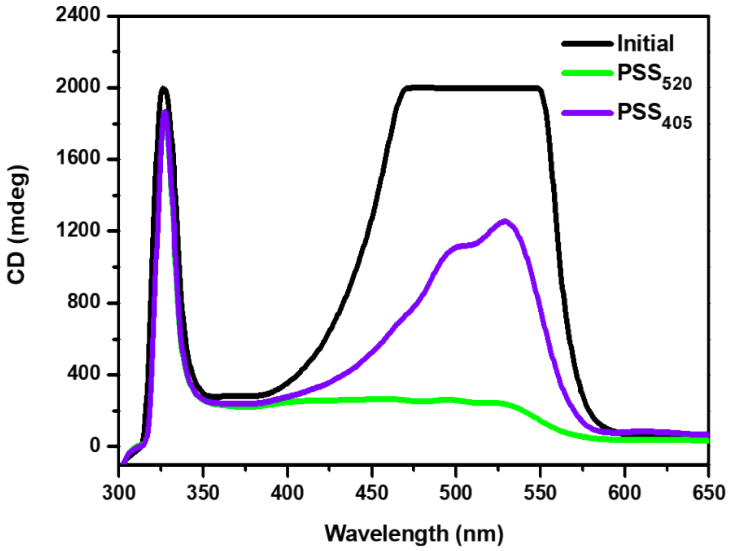


Figure S5. CD spectrum of photo-responsive CLC doping 0.2 wt% of switch **1** into SLC1717 tuned by 520 nm and 405 nm light.

6. Photoluminescence and reflectance properties of the CLC doped with 6.2 wt% switch 1 and 0.8 wt% of R3011

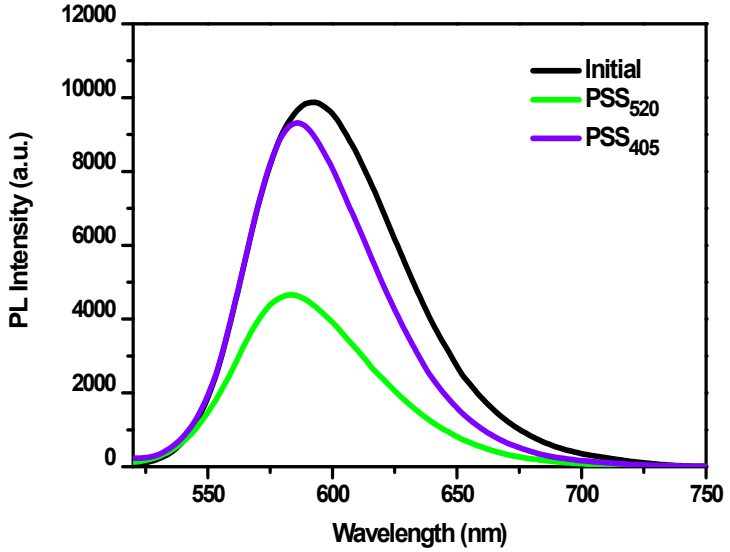


Figure S6. Fluorescence spectrum of photo-responsive CLCs doping 6.2 wt% switch **1** and 0.8 wt% of R3011 into SLC1717 tuned by 520 nm and 405 nm light.

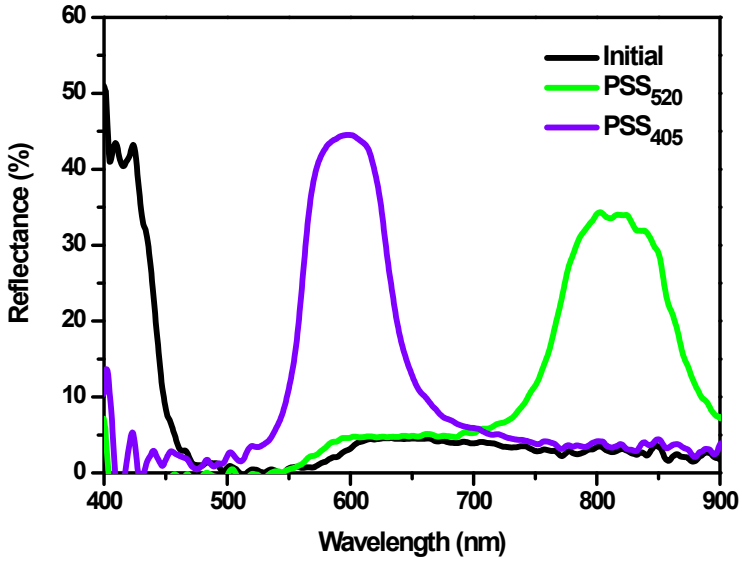


Figure S7. Reflectance spectrum of photo-responsive CLCs doping 6.2 wt% switch **1** and 0.8 wt% of R3011 into SLC1717 tuned by 520 nm and 405 nm light.

7. The fluorescent quantum yields of the CPL-active CLCs

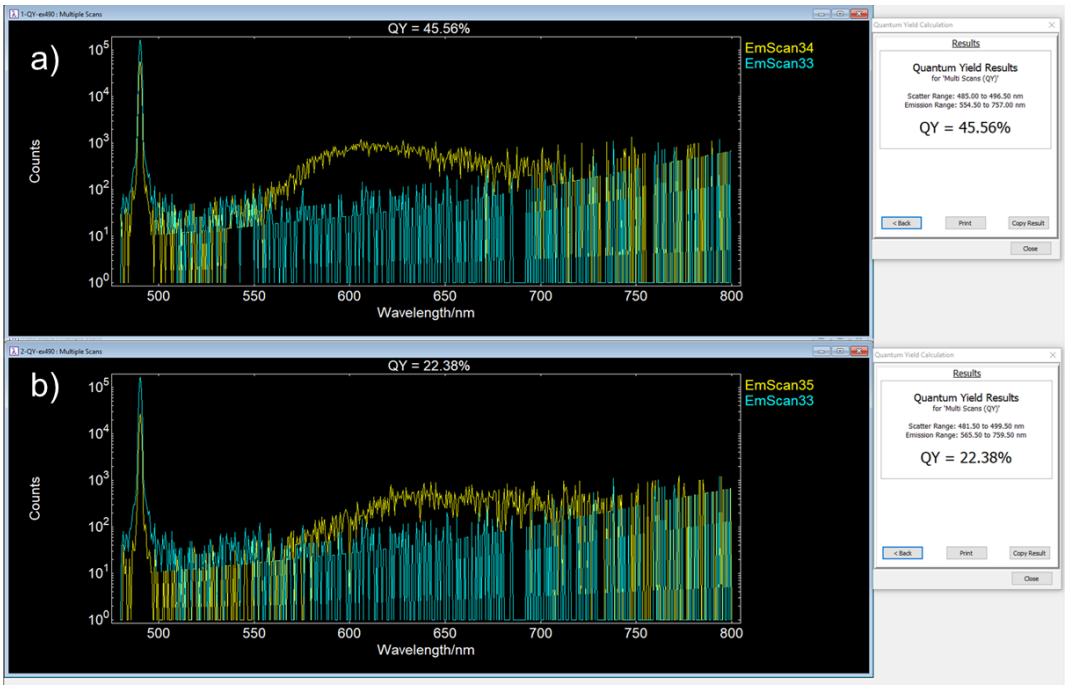
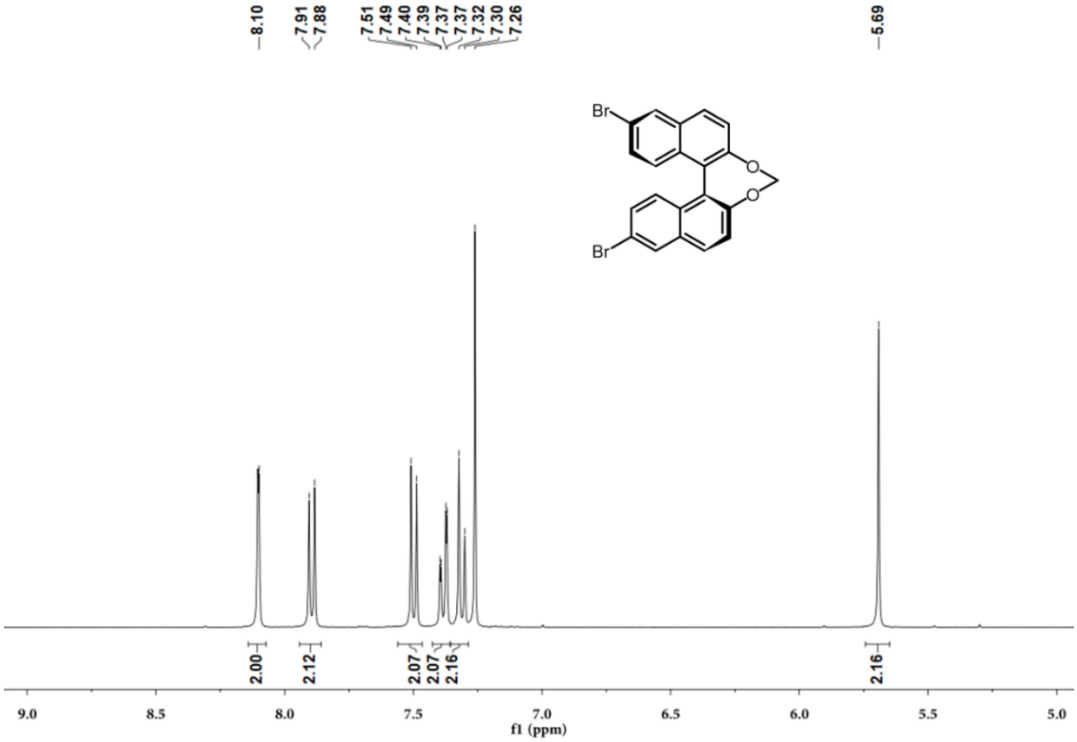


Figure S8. The fluorescent quantum yields of photo-responsive CLCs doping (a) 1.0 wt% switch **1**, (b) 6.2 wt% switch **1** and 0.8 wt% of R3011 into SLC1717.

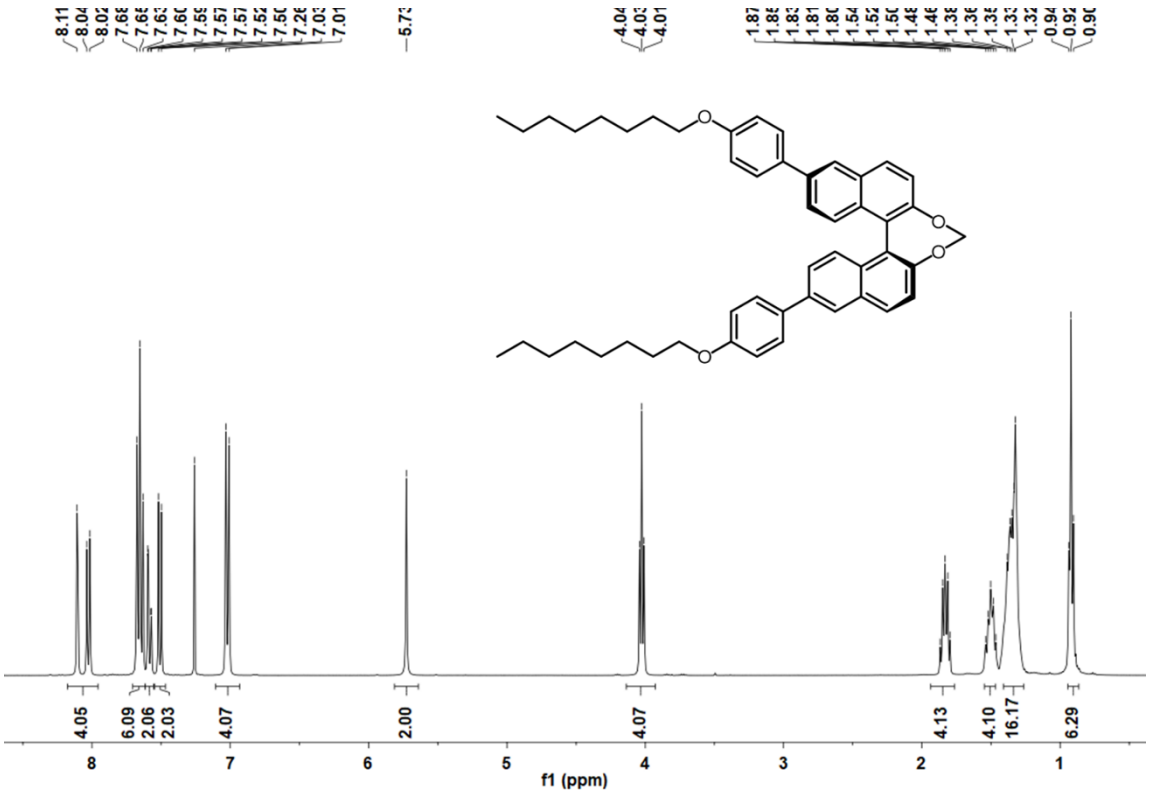
As shown in Figure S8, the fluorescent quantum yields(Φ_F) of two CPL-active CLCs containing 1.0 wt% and 6.2 wt% switch **1** were recorded at Edinburgh Instruments FLS980 fluorescence spectrophotometer. At lower doping concentration, the Φ_F is as high as 45.56%, while the Φ_F decreases with the doped concentration increases in the CPL-active CLC. It is well known that the aggregation state of the fluorescent molecules affects its Φ_F. The increase of mass fraction of switch **1** in the LC matrix makes the π-π stacking stronger, which leads to a decline of Φ_F. A similar variation trend on fluorescence emission intensity of switch **1** in different proportions of water/THF solution was also found. All these observations demonstrate that the doping concentration of switch **1** plays a relevant rule in determining the fluorescent quantum yields(Φ_F) of the CPL-active CLCs

8. ^{1}H-NMR and ^{13}C-NMR spectra

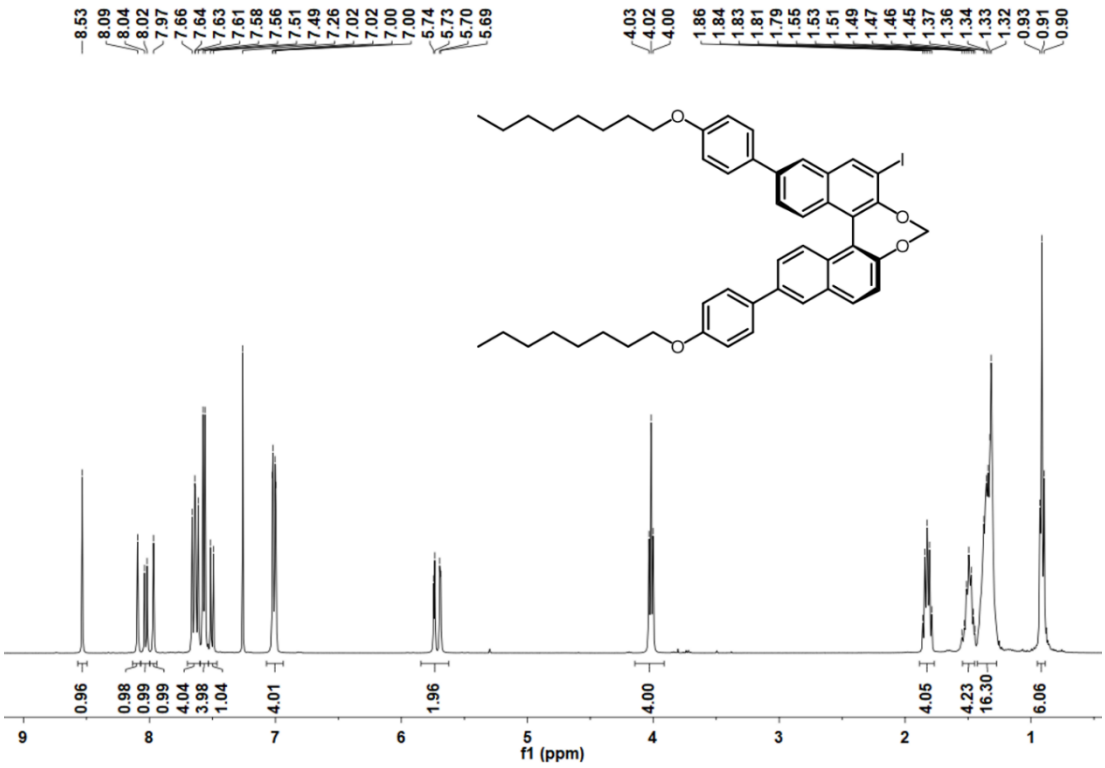
^{1}H-NMR of (S)-2:



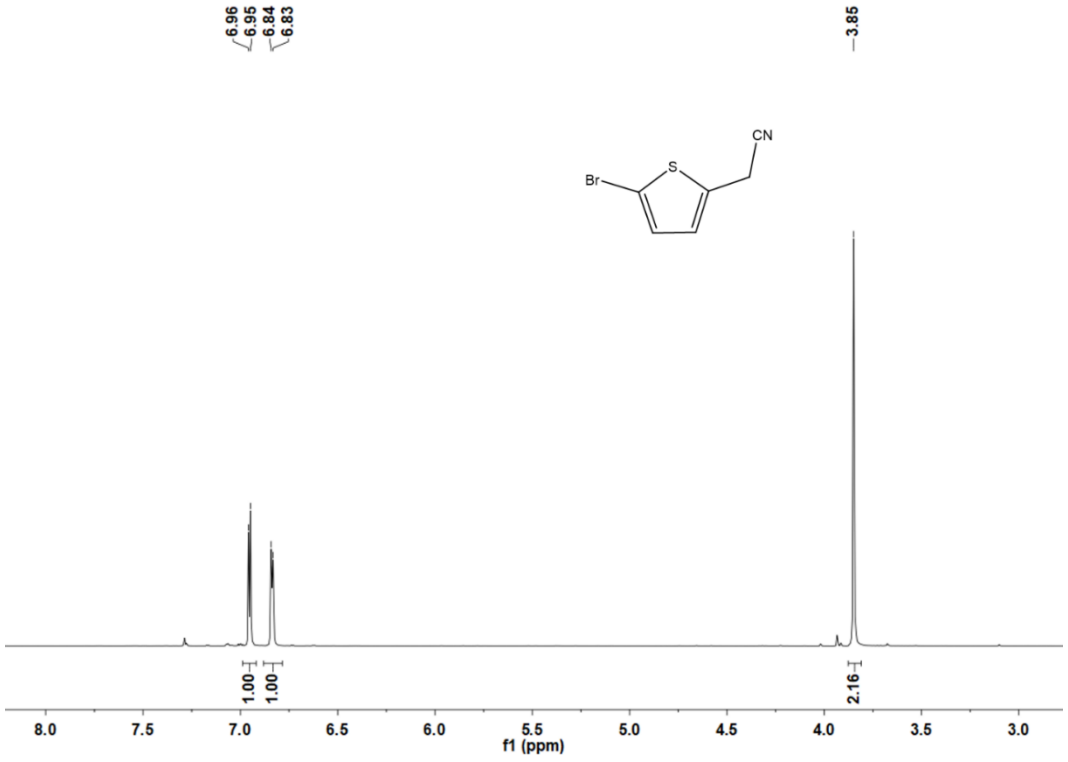
^{1}H-NMR of (S)-3:



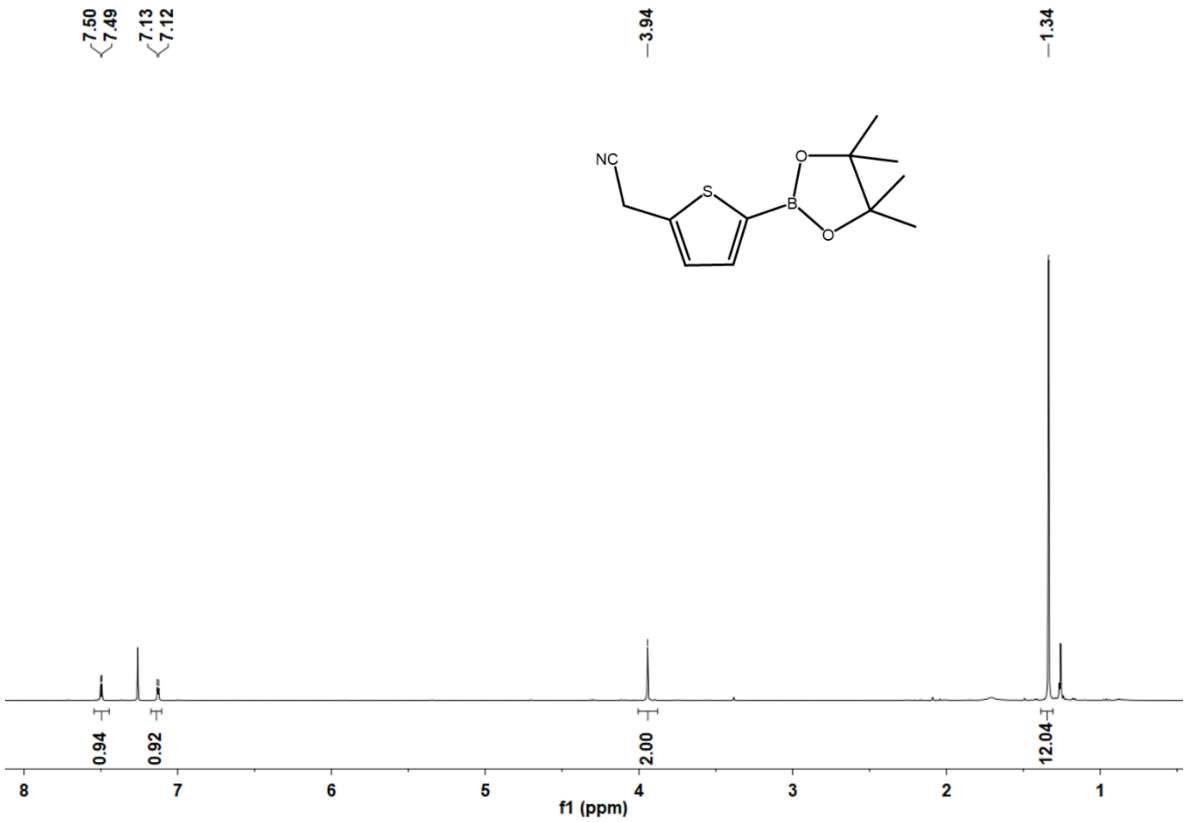
^{1}H-NMR of (S)-4:



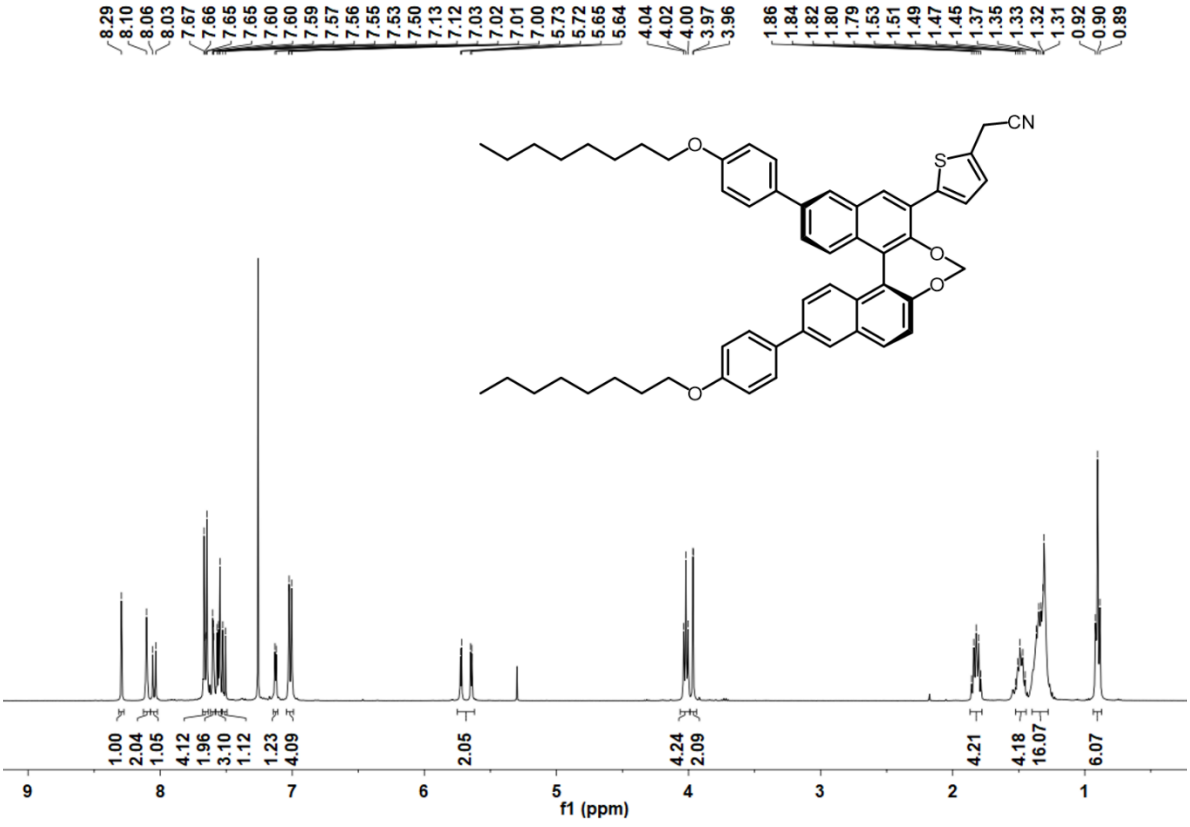
^{1}H-NMR of 2-(5-bromothiophen-2-yl)acetonitrile:



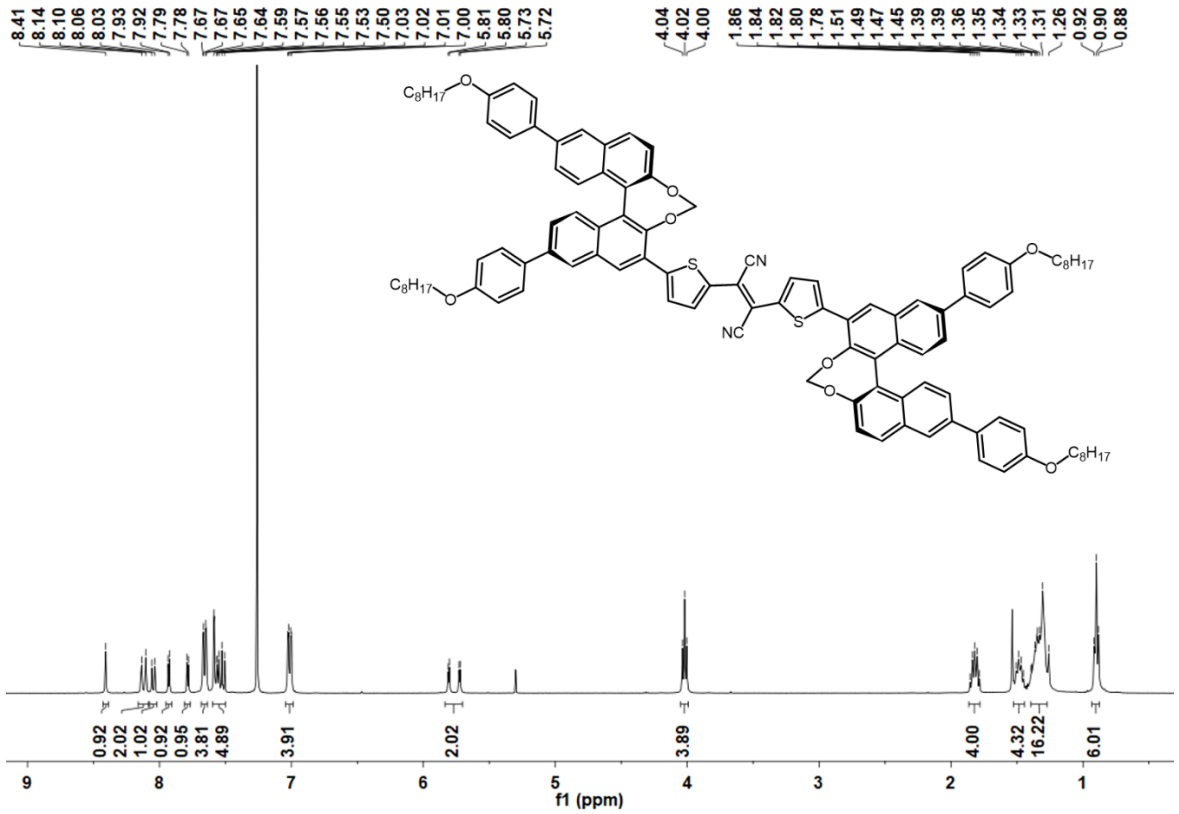
^{1}H-NMR of 2-(5-bromothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:


7.50
7.49
7.13
7.12
3.94
1.34
NC
S
B
O
O
O
0.94
0.92
2.00
12.04
8
7
6
5
4
3
2
1
f1 (ppm)

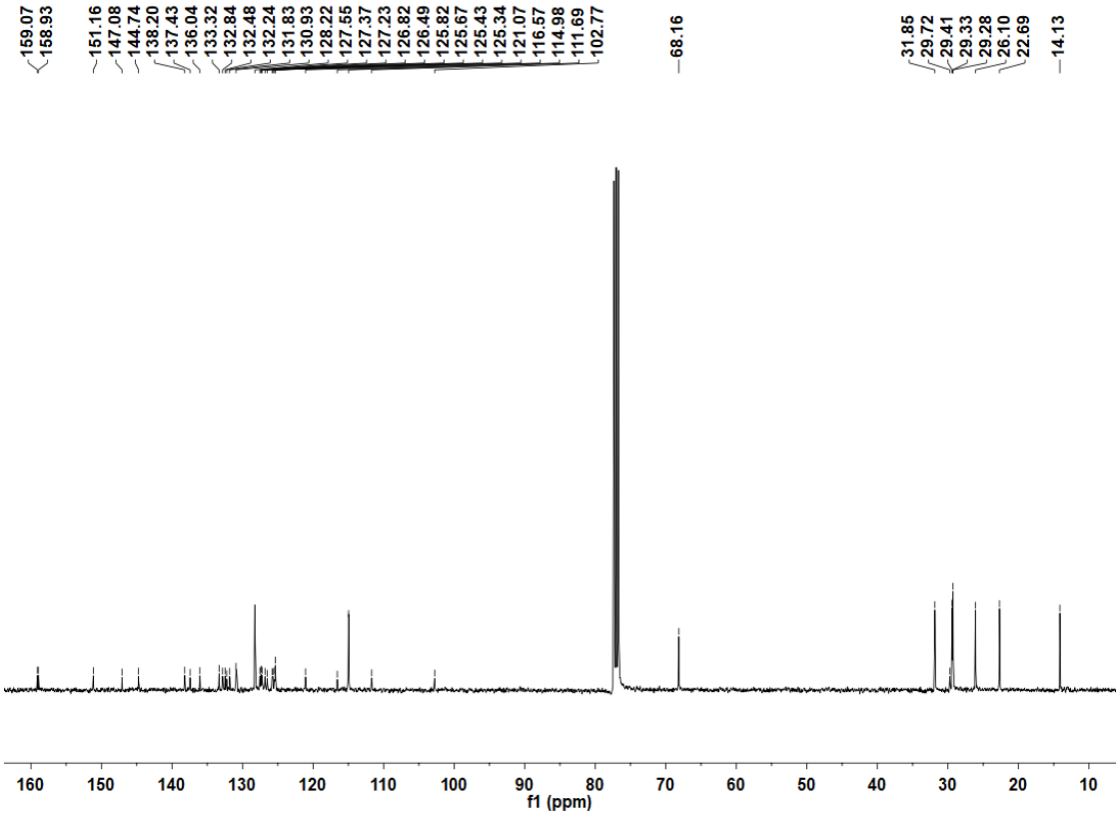
^{1}H-NMR of (S)-5:


8.29
8.10
8.06
8.03
7.67
7.66
7.65
7.65
7.60
7.60
7.59
7.57
7.56
7.55
7.53
7.50
7.13
7.12
7.03
7.02
7.01
7.00
5.73
5.72
5.65
5.64
4.04
4.02
4.00
3.97
3.96
1.86
1.84
1.82
1.80
1.79
1.53
1.51
1.49
1.47
1.45
1.37
1.35
1.33
1.32
1.31
0.92
0.90
0.89
CN
S
O
O
O
O
1.00
2.04
1.05
4.12
1.96
3.10
1.12
1.23
4.09
2.05
4.24
2.09
4.21
4.18
16.07
6.07
9
8
7
6
5
4
3
2
1
f1 (ppm)

^{1}H-NMR of switch 1:



^{13}C-NMR of switch 1:



[1]H-NMR of R3011: