

Electronic Supplementary Information for:

## Synthesis of liquid crystals bearing 1,3-dioxane structures and characterization of their ferroelectricity in the nematic phase

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### Reagents

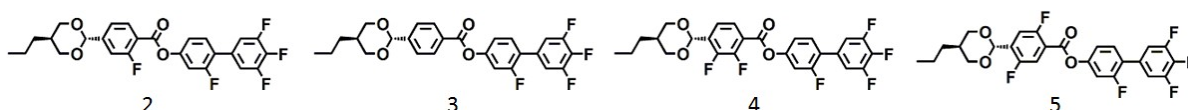
Anhydrous magnesium sulfate ( $\text{MgSO}_4$ ), anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), *p*-toluenesulfonate monohydrate ( $\text{TsOH}\cdot\text{H}_2\text{O}$ ), 2-*n*-propyl-1,3-propanediol, [1,1'-bis(diphenylphosphino)ferrocene] palladium(II) dichloride ( $\text{Pd}(\text{dppf})\text{Cl}_2$ ), and tetrakis(triphenylphosphine) palladium (0) ( $\text{Pd}(\text{PPh}_3)_4$ ) were obtained from Wako Pure Chemical Co., Ltd. *N,N*-Diisopropylethylamine (DIPEA), *n*-butyl lithium hexane solution ( $1.6 \text{ mol L}^{-1}$ ), 1-ethyl-3-(3-diaminopropyl)carbodiimide hydrochloride (WSC), 4-dimethylaminopyridine (DMAP), allyl bromide, 4-bromo-3-chlorobenzaldehyde, methyl terephthalaldehyde and other fluorinated benzene derivatives were purchased from Tokyo Chemical Industry Co., Ltd. 4-(3,4,5-Trifluorophenyl)-3-fluorophenol was synthesized according to literature procedure or obtained from JNC Co., Ltd. These reagents and solvents were used without any purification.

### Measurements

NMR spectra were recorded on a JNM-ECZ400 spectrometer (JEOL Co., Ltd.) at 400 MHz for  $^1\text{H}$  NMR, 100 MHz for  $^{13}\text{C}$  NMR and 376 MHz for  $^{19}\text{F}$  NMR. Chemical shifts in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are given in parts per million (ppm) downfield using tetramethylsilane as an internal standard. For  $^{19}\text{F}$  NMR, trifluoroacetic acid was used. The high resolution mass spectroscopy (HRMS) were conducted on a JMS-700 instrument (JEOL Co., Ltd.) with an electron ionization mode.

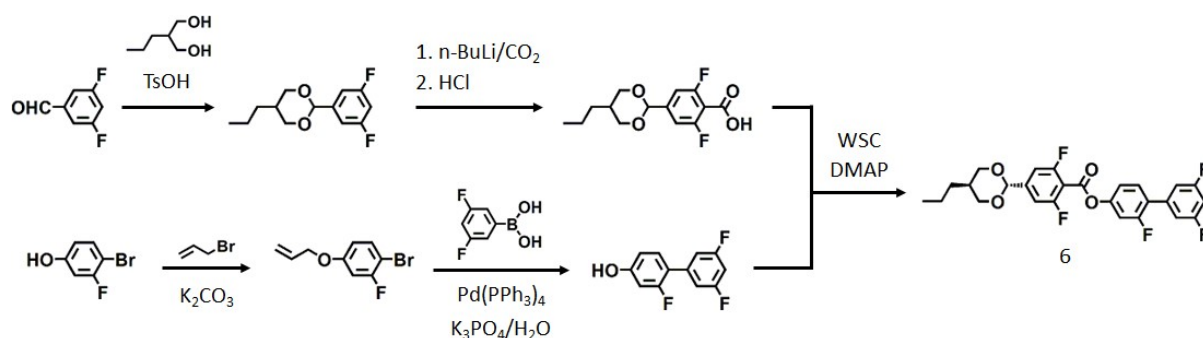
## 1. Synthesis

### 1-1. Synthesis of C3-DIO analogs 2-5

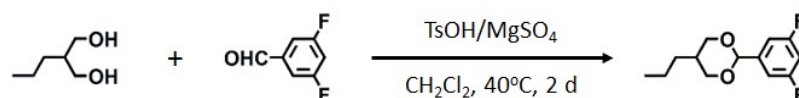


C3-DIO analogs **2-5** were synthesized according to the literature procedures.

### 1-2. Synthesis of 4-(3,5-difluorophenyl)-3-fluorophenyl 2,6-difluoro-4-(*trans*-5-*n*-propyl-1,3-dioxane-2-yl)benzoate (**6**)

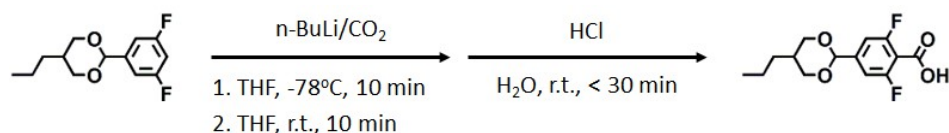


#### 1-2-1. 3,5-Difluoro-1-(5-*n*-propyl-1,3-dioxan-2-yl)benzene



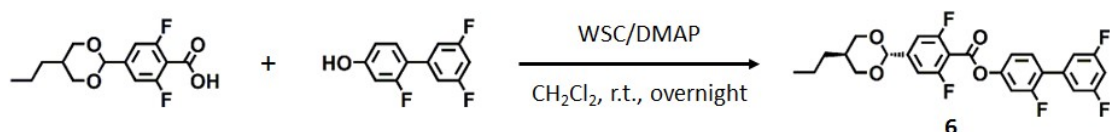
To  $\text{CH}_2\text{Cl}_2$  (50 mL) were added 3,5-difluorobenzaldehyde 7.11 g (50 mmol), 2-*n*-propyl-1,3-propanediol 7.09 g (60 mmol),  $\text{TsOH}\cdot\text{H}_2\text{O}$  950 mg (5 mmol, 10 mol%) and anhydrous  $\text{MgSO}_4$  27 g (240 mmol). The mixture was stirred at  $40^\circ\text{C}$  for 2 days and then added in cold water (200 mL). After extraction with  $\text{CH}_2\text{Cl}_2$  (200 mL), the organic layer was washed with distilled water (200 mL x 3) and the dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporation, colorless liquids were obtained. Yield: 12.4 g (>99%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  7.25 (t,  $J = 9.8$  Hz, 1H; phenyl), 7.08 (d,  $J = 8.0$  Hz, 1H; phenyl), 5.54 (s, 0.4H; *cis*-form acetal), 5.45 (s, 0.6H; *trans*-form acetal), 4.14 (dd,  $J = 12, 4.8$  Hz, 1.2H;  $-\text{CH}_2\text{-O-}$  in *trans*-form), 4.07-3.93 (m, 1.6H; *cis*-form  $-\text{CH}_2\text{-O-}$ ), 3.52 (t,  $J = 11$  Hz, 1.2H;  $-\text{CH}_2\text{-O-}$  in *trans*-form), 2.01-1.92 (m, 0.6H;  $-\text{CH}-\text{CH}_2\text{O-}$  in *trans*-form), 1.64 (q,  $J = 7.9$  Hz, 0.8H;  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$  in *cis*-form), 1.47-1.43 (m, 0.4H;  $-\text{CH}-\text{CH}_2\text{O-}$  in *cis*-form), 1.41-1.34 (m, 0.8H;  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$  in *cis*-form), 1.34-1.24 (m, 1.2H;  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$  in *trans*-form), 1.04 (q,  $J = 7.7$  Hz, 1.2H;  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$  in *trans*-form), 0.93-0.85 (m, 3H;  $\text{CH}_3\text{-}$ ).

1-2-2. 2,6-Difluoro-4-(5-*n*-propyl-1,3-dioxan-2-yl)benzoic acid



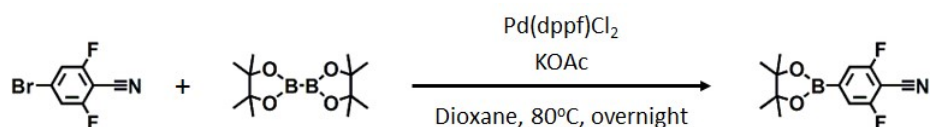
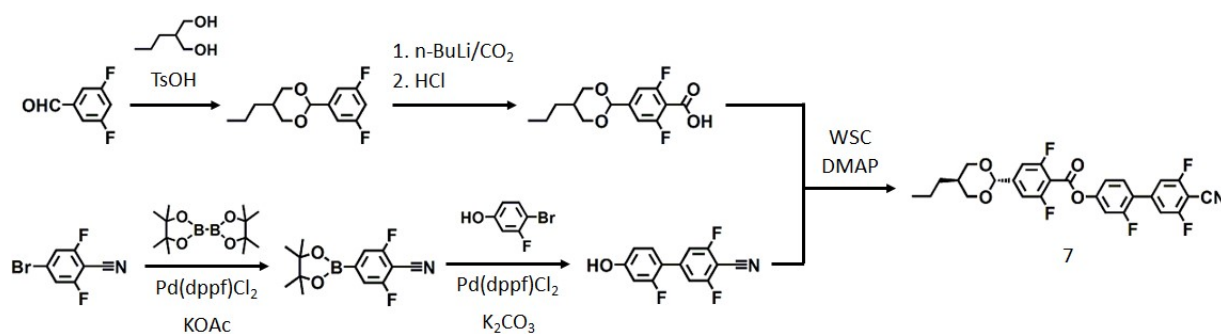
To a THF solution (15 mL) of 3,5-difluoro-1-(5-*n*-propyl-1,3-dioxan-2-yl)benzene 2.42 g (10.0 mmol) was added dropwise 1.6 M *n*-butyl lithium *n*-hexane solution (7.5 mL, 12 mmol, 1.2 equiv.) at  $-78^\circ\text{C}$  under  $\text{N}_2$  atmosphere. After stirring for 10 min, dry ice 10 g (230 mmol) was added and then stirred at  $-78^\circ\text{C}$  for 10 min. The mixture was stirred at ambient temperature for 10 min,  $\text{H}_2\text{O}$  (3 mL) was added and the solvents were removed by rotary evaporator. The residues were dissolved in distilled water (50 mL) and washed with  $\text{CH}_2\text{Cl}_2$  (50 mL). The aqueous layer was collected and its pH was adjusted to 2-3 by an addition of 1M HCl aq. The resulting precipitates were collected by suction filtration and washed with distilled water. After drying under reduced pressure, white solids were obtained. Yield: 2.24 g (78.3%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , ppm):  $\delta$  8.21 (br, 1H; COOH), 7.13 (d,  $J = 8.8$  Hz, 2H; phenyl), 5.48 (s, 0.3H; *cis*-form acetal), 5.38 (s, 0.7H; *trans*-form acetal), 4.24 (dd,  $J = 12, 4.0$  Hz, 1.4H;  $-\text{CH}_2\text{-O-}$  in *trans*-form), 4.10-4.04 (m, 1.2H; *cis*-form  $-\text{CH}_2\text{-O-}$ ), 3.53 (t,  $J = 11$  Hz, 1.4H;  $-\text{CH}_2\text{-O-}$  in *trans*-form), 2.19-2.09 (m, 0.7H;  $-\text{CH-CH}_2\text{O-}$  in *trans*-form), 1.72 (q,  $J = 7.7$  Hz, 0.6H;  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$  in *cis*-form), 1.64-1.29 (m, 2.3H;  $-\text{CH-CH}_2\text{O-}$  in *cis*-form,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$ ), 1.09 (q,  $J = 7.5$  Hz, 1.4H;  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$  in *trans*-form), 0.97-0.91 (m, 3H;  $\text{CH}_3\text{-}$ ).

1-2-3. 4-(3,5-Difluorophenyl)-3-fluorophenyl 2,6-difluoro-4-(*trans*-5-*n*-propyl-1,3-dioxane-2-yl)benzoate (6)



2,6-Difluoro-4-(5-*n*-propyl-1,3-dioxan-2-yl)benzoic acid 1.72 g (6.01 mmol), WSC 1.41 g (7.20 mmol) and DMAP 156 mg (1.28 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL) and stirred at rt. for 30 min. After that, 4-(3,5-difluorophenyl)-2-fluorophenol 1.61 g (7.20 mmol) was added and then the mixture was stirred at ambient temperature for 5 d. After  $\text{CH}_2\text{Cl}_2$  (100 mL) was added, the solution was washed three times with ultrapure water (100 mL). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then the solvent was evaporated to obtain orange liquid (3.46 g). The liquid was purified by silica-gel column chromatography (*n*-hexane/ $\text{CH}_2\text{Cl}_2 = 1:3$  by Vol.) followed by recrystallization with *n*-hexane to give a white solid in *trans*-form. Yield: 343 mg (11.6%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.47 (t, 1H,  $J = 8.8$  Hz, phenyl), 7.20-7.15 (m, 4H, phenyl), 7.08 (d, 2H,  $J = 7.2$  Hz, phenyl), 6.84 (tt, 1H,  $J = 9.0, 2.4$  Hz, phenyl), 5.40 (s, 1H, *trans*-acetal), 4.25 (dd, 2H,  $J = 12, 4.8$  Hz,  $-\text{CH}_2\text{-O}$  in *trans*-form), 3.54 (t, 2H,  $J = 11$  Hz,  $-\text{CH}_2\text{-O}$  in *trans*-form), 2.20-2.09 (m, 1H,  $\text{C}_3\text{H}_7\text{-CH-}$ ), 1.40-1.30 (m, 2H,  $\text{C}_2\text{H}_5\text{-CH}_2\text{-}$ ), 1.10 (q, 2H,  $J = 7.7$  Hz,  $\text{CH}_3\text{-CH}_2\text{-}$ ), 0.94 (t, 3H,  $J = 7.2$  Hz,  $\text{CH}_3\text{-}$ ). HRMS (EI)  $m/z$ :  $[\text{M}^+]$  calcd for  $\text{C}_{26}\text{H}_{21}\text{F}_5\text{O}_4$ : 492.1360; found: 492.1360.

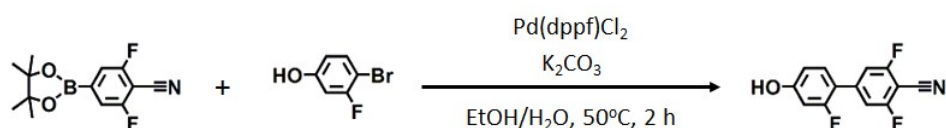
### 1-3. Synthesis of 4-(4-cyano-3,5-difluorophenyl)-3-fluorophenyl 2,6-difluoro-4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoate (7)



#### 1-3-1. 2,6-Difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile

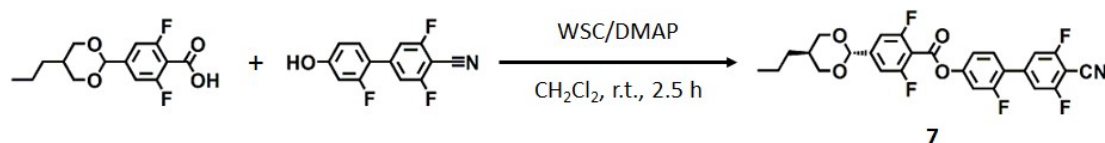
To dehydrated 1,4-dioxane (50 mL) were added 4-bromo-2,6-difluorobenzonitrile 5.00 g (22.9 mmol), bis(pinacolato)diboron 6.41 g (25.2 mmol), Pd(dppf)Cl<sub>2</sub> 560 mg (0.687 mmol) and KOAc 6.74 g (68.7 mmol). The mixture was stirred under N<sub>2</sub> atmosphere at 0°C for 30 min and then stirred at 80°C overnight. After evaporation, the residue was washed with *n*-hexane (250 mL) and the insoluble was separated by suction filtration. The filtrates were washed with distilled water (250 mL x 3) and the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation, the solids were purified by recrystallization from *n*-hexane to give pale yellow solids. Yield: 4.5 g (74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.43 (d, *J* = 7.6 Hz, 2H; phenyl), 1.35 (s, 12H; CH<sub>3</sub>-).

#### 1-3-2. 4-(4-Cyano-3,5-difluorophenyl)-3-fluorophenol



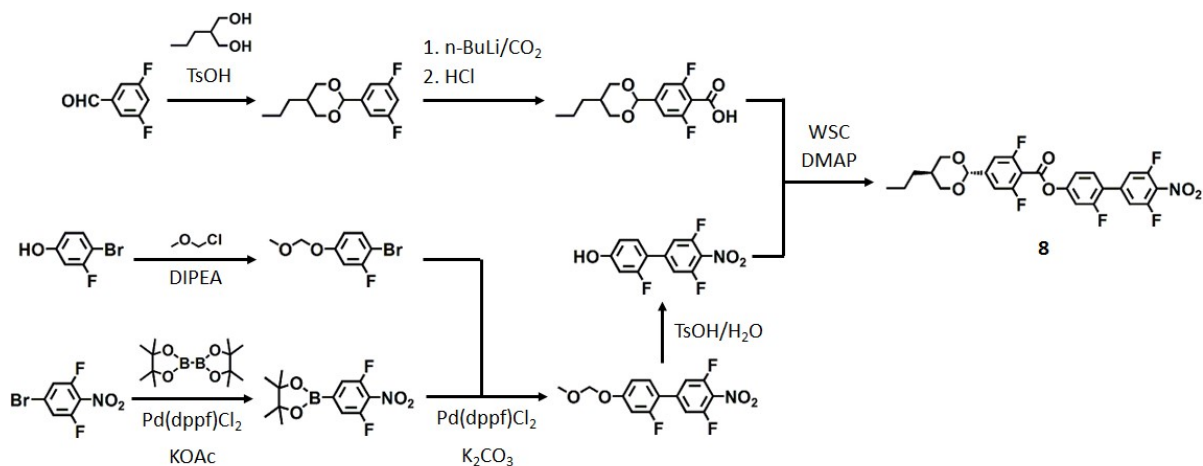
To EtOH (52 mL) were added 2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile 4.24 g (16.0 mmol), 4-bromo-3-fluorophenol 2.54 g (13.3 mmol), Pd(dppf)Cl<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> 327 mg (0.4 mmol). To the solution, an aqueous solution (13 mL) of K<sub>2</sub>CO<sub>3</sub> 3.68 g (26.6 mmol) was added and then the mixture was stirred under N<sub>2</sub> atmosphere at 50°C for 2 h. After concentration, the residue was washed with distilled water and then the brown insoluble was washed with CH<sub>2</sub>Cl<sub>2</sub>. After drying under reduced pressure, pale gray solids were obtained. Yield: 1.10 g (33.2%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 10.5 (br, 1H; OH), 7.59 (d, *J* = 10 Hz, 2H; phenyl), 7.53 (t, *J* = 9.2 Hz, phenyl), 6.77-6.72 (m, 2H; phenyl).

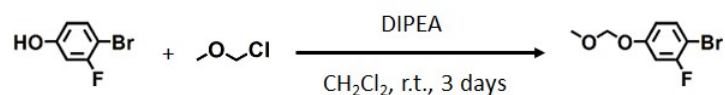
1-3-3. 4-(4-Cyano-3,5-difluorophenyl)-3-fluorophenyl 2,6-difluoro-4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoate (**7**)



To  $\text{CH}_2\text{Cl}_2$  (8 mL) were added 2,6-difluoro-4-(5-*n*-propyl-1,3-dioxan-2-yl)benzoic acid 1.12 g (3.91 mmol) and WSC 825 mg (4.30 mmol) and then the solution was stirred at ambient temperature for 30 min. To the solution, 4-(4-cyano-3,5-difluorophenyl)-3-fluorophenol 975 mg (3.91 mmol) and DMAP 95 mg (0.78 mmol) were added and then the mixture stirred at the temperature for 2.5 h. The solution was added in  $\text{CH}_2\text{Cl}_2$  (100 mL) and washed with distilled water (100 mL) followed by ultrapure water (100 mL x 3). After drying over anhydrous  $\text{Na}_2\text{SO}_4$ , the organic layer was concentrated and then the residues were reprecipitated from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ . The solids were further purified by silica-gel column chromatography using  $\text{CH}_2\text{Cl}_2$  as an eluent followed by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  to give needle-like crystals. Yield: 581 mg (28.7%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.50 (t,  $J = 8.8$  Hz, 1H; phenyl), 7.29-7.19 (m, 6H; phenyl), 5.41 (s, 1H; acetal), 4.26 (dd,  $J = 12, 4.6$  Hz, 2H; -O- $\text{CH}_2$ -), 3.55 (t,  $J = 12$  Hz, 2H; -O- $\text{CH}_2$ -), 2.17-2.12 (m, 1H; - $\text{CH}$ - $\text{CH}_2$ O-), 1.40-1.31 (m, 2H;  $\text{CH}_3$ - $\text{CH}_2$ -), 1.11 (q,  $J = 7.6$  Hz, 2H;  $\text{CH}_3$ - $\text{CH}_2$ - $\text{CH}_2$ -), 0.94 (t,  $J = 7.0$  Hz, 3H;  $\text{CH}_3$ -). HRMS (EI)  $m/z$ :  $[\text{M}^+]$  calcd for  $\text{C}_{27}\text{H}_{20}\text{F}_5\text{NO}_4$ : 517.1312; found: 517.1312. Anal. calcd for  $\text{C}_{27}\text{H}_{20}\text{F}_5\text{NO}_4$ : C 62.67, H 3.90, N 2.71; found: C 62.74, H 3.77, N 2.70.

1-4. Synthesis of 4-(3,5-difluoro-4-nitrophenyl)-3-fluorophenyl 2,6-difluoro-4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoate (**8**)

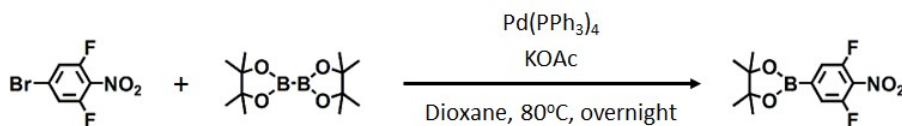




#### 1-4-1. 1-Bromo-2-fluoro-4-methoxymethoxybenzene

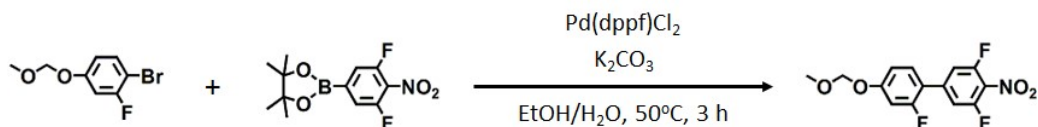
To a  $\text{CH}_2\text{Cl}_2$  solution (100 mL) of 4-bromo-3-fluorophenol 9.60 g (50.3 mmol) and DIPEA 7.11 g (55.0 mmol) were added slowly methoxymethyl chloride 4.03 g (50.1 mmol). The solution was stirred at ambient temperature for 3 days and then washed with an aqueous solution (150 mL) of  $\text{NaHCO}_3$  followed by distilled water (200 mL x 2). After dried over anhydrous  $\text{Na}_2\text{SO}_4$ , the organic layer was concentrated. The resulting orange liquids were purified by silica-gel column chromatography (*n*-hexane/ $\text{CH}_2\text{Cl}_2$  volume ratio of 2:1) to give colorless liquids. Yield: 10.6 g (90.5%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.41 (t,  $J = 8.8$  Hz, 1H; phenyl), 6.87 (dd,  $J = 10, 2.8$  Hz, 1H; phenyl), 6.76-6.73 (m, 1H; phenyl), 5.15 (s, 2H;  $-\text{CH}_2\text{-OPh}$ ), 3.47 (s, 3H;  $\text{CH}_3$ -).

#### 1-4-2. 3,5-Difluoro-4-nitrophenylboronic acid pinacol ester

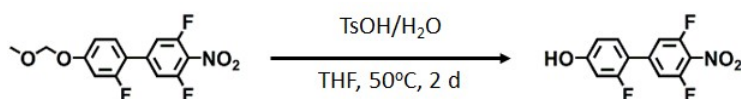


To dehydrated 1,4-dioxane (60 mL) were added 4-bromo-2,6-difluoronitrobenzene 5.00 g (21.0 mmol), bis(pinacolato)diboron 5.91 g (23.3 mmol),  $\text{Pd}(\text{PPh}_3)_4$  730 mg (0.63 mmol) and  $\text{KOAc}$  6.18 g (63.0 mmol) under  $\text{N}_2$  atmosphere. After stirred at  $0^\circ\text{C}$  for 30 min, the mixture was heated at  $80^\circ\text{C}$  for 13 h. After evaporation, the residue was washed with *n*-hexane and the insoluble was removed by suction filtration. The filtrate was washed with distilled water (200 mL x 3) and then dried with anhydrous  $\text{Na}_2\text{SO}_4$ . After concentration and dryness under reduced pressure, pale brown solids were obtained. Yield: 4.79 g (80.0%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.49 (d,  $J = 7.6$  Hz, 2H; phenyl), 1.35 (s, 12H;  $\text{CH}_3$ -).

#### 1-4-3. 4-(3,5-Difluoro-4-nitrophenyl)-3-fluorophenyl methoxymethyl ether



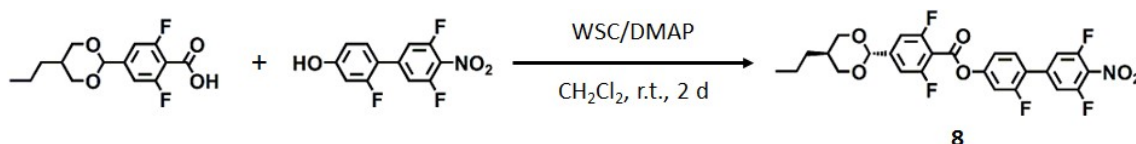
To EtOH (60 mL) were added 1-bromo-2-fluoro-4-methoxymethoxybenzene 3.76 g (16.0 mmol), 3,5-difluoro-4-nitrophenylboronic acid pinacol ester 4.59 g (16.0 mmol) and  $\text{Pd}(\text{dppf})\text{Cl}_2$  351 mg (0.48 mmol). To the solution, an aqueous solution (16 mL) of  $\text{K}_2\text{CO}_3$  4.42 g (32.0 mol) was added and then the mixture was stirred under  $\text{N}_2$  atmosphere at  $50^\circ\text{C}$  for 3 h. After evaporation, the residues were added in  $\text{CH}_2\text{Cl}_2$  (100 mL) and then the solution was washed with distilled water (100 mL x 3). After dried over anhydrous  $\text{Na}_2\text{SO}_4$ , the organic layer was concentrated and the solids were washed with MeOH. The insoluble was purified by silica-gel column chromatography (*n*-hexane/ $\text{CH}_2\text{Cl}_2$  volume ratio of 1:1) to give white solids. Yield: 1.72 g (34.3%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.35 (t,  $J = 8.8$  Hz, 1H; phenyl), 7.27 (d,  $J = 9.2$  Hz, 2H; phenyl), 6.97-6.91 (m, 2H; phenyl), 5.23 (s, 2H;  $-\text{CH}_2\text{-OPh}$ ), 3.51 (s, 3H;  $\text{CH}_3$ -).



#### 1-4-4. 4-(3,5-Difluoro-4-nitrophenyl)-3-fluorophenol

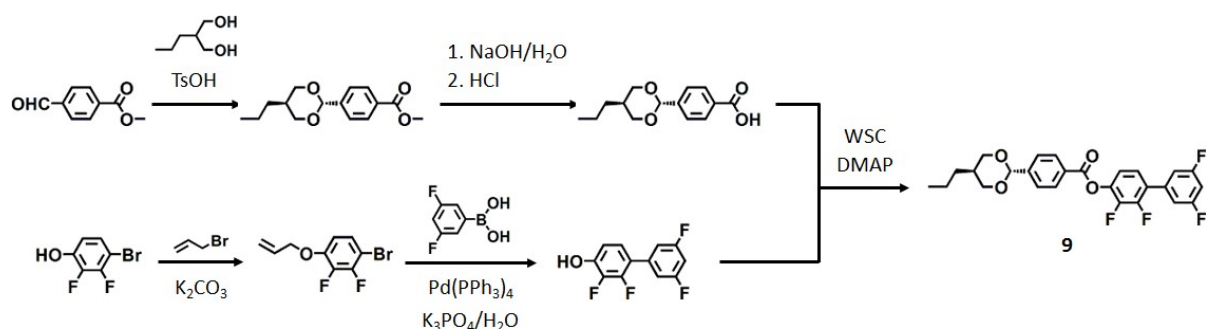
To THF (40 mL) were added 4-(3,5-difluoro-4-nitrophenyl)-3-fluorophenyl methoxymethyl ether, TsOH·H<sub>2</sub>O 1.0 g (5.3 mmol) and H<sub>2</sub>O (5 mL). After the solution was stirred at 50°C for 2 d, the solvents were evaporated. The residues were washed with distilled water and the insoluble was collected by suction filtration. After drying under reduced pressure, yellow solids were obtained. Yield: 1.36 g (91.9%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 10.5 (br, 1H; OH), 7.63 (d, *J* = 12 Hz, 2H; phenyl), 7.54 (d, *J* = 9.0 Hz, 1H; phenyl), 6.78-6.72 (m, 2H; phenyl).

#### 4-5. 4-(3,5-Difluoro-4-nitrophenyl)-3-fluorophenyl 2,6-difluoro-4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoate (8)

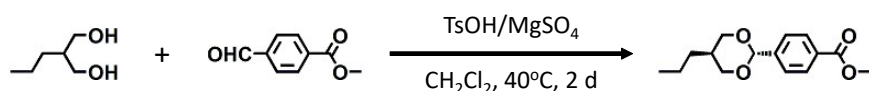


To anhydrous CH<sub>2</sub>Cl<sub>2</sub> (8 mL) were added 2,6-difluoro-4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoic acid 909 mg (3.18 mmol) and WSC 670 mg (3.49 mmol). After the solution was stirred at ambient temperature for 40 min, 4-(3,5-difluoro-4-nitrophenyl)-3-fluorophenol 856 mg (3.18 mmol) and DMAP 95 mg (0.78 mmol) were added and then the mixture stirred at the temperature for 2 days. The solution was added in CH<sub>2</sub>Cl<sub>2</sub> (150 mL) and then washed with distilled water (100 mL) followed by ultrapure water (100 mL x 2). After dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, the organic layer was concentrated and added in MeOH. The resulting precipitates were collected by suction filtration and purified by silica-gel column chromatography (Eluent; CH<sub>2</sub>Cl<sub>2</sub>). The solids consisting in *cis/trans* mixture were further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to give *trans*-form compounds as needle-like crystals. Yield: 294 mg (17.2%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.49 (t, *J* = 8.8 Hz, 1H; phenyl), 7.31 (d, 2H; phenyl), 7.25-7.19 (m, 4H; phenyl), 5.40 (s, 1H; acetal), 4.26 (dd, *J* = 12, 4.4 Hz, 2H; -O-CH<sub>2</sub>-), 3.55 (t, *J* = 11 Hz, 2H; -O-CH<sub>2</sub>-), 2.20-2.09 (m, 1H; -CH-CH<sub>2</sub>O-), 1.40-1.31 (m, 2H; CH<sub>3</sub>-CH<sub>2</sub>-), 1.11 (q, *J* = 7.6 Hz, 2H; CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 0.94 (t, *J* = 7.2 Hz, 3H; CH<sub>3</sub>-). HRMS (EI) *m/z*: [M<sup>+</sup>] calcd for C<sub>26</sub>H<sub>20</sub>F<sub>5</sub>NO<sub>6</sub>: 537.1211; found: 537.1211. Anal. calcd for C<sub>26</sub>H<sub>20</sub>F<sub>5</sub>NO<sub>6</sub>: C 58.11, H 3.75, N 2.61; found: C 58.17, H 3.84, N 2.55.

**1-5. Synthesis of 2,3-difluoro-4-(3,5-difluorophenyl)phenyl 4-(*trans*-5-*n*-propyl-1,3-dioxane-2-yl)benzoate (9)**

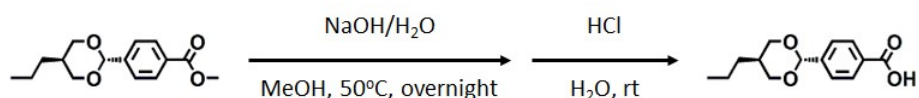


**1-5-1. 4-(*trans*-5-*n*-Propyl-1,3-dioxan-2-yl)benzoic acid methyl ester**



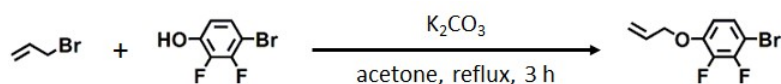
To a  $\text{CH}_2\text{Cl}_2$  solution (20 mL) of 2-*n*-propyl-1,3-propanediol 1.42 g (12.0 mmol) and methyl terephthalaldehyde 1.64 g (10.0 mmol) were added  $\text{TsOH}\cdot\text{H}_2\text{O}$  190 mg (1.00 mmol) and anhydrous  $\text{MgSO}_4$  12.0 g (100 mmol). The mixture was stirred at  $40^\circ\text{C}$  for 2 days and then added into cold distilled water (100 mL). After extraction with  $\text{CH}_2\text{Cl}_2$  (200 mL), the organic layer was washed with distilled water (200 mL x 3) and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After concentration, the resulting solids (crude yield, 2.58 g) was purified by recrystallization from MeOH. White solids were obtained. Yield: 1.17 g (44.3%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  7.96 (d,  $J = 8.8$  Hz, 2H; phenyl), 7.55 (d,  $J = 7.6$  Hz, 2H; phenyl), 5.51 (s, 1H; acetal), 4.15 (dd,  $J = 12, 4$  Hz, 2H; m, 2H:  $-\text{O}-\text{CH}_2-$ ), 3.54 (t,  $J = 12$  Hz, 2H:  $-\text{O}-\text{CH}_2-$ ), 3.86 (s, 3H;  $-\text{COOCH}_3$ ), 1.99-1.95 (m, 1H;  $-\text{CH}-\text{CH}_2\text{O}-$ ), 1.34-1.24 (m, 2H,  $\text{CH}_3-\text{CH}_2-$ ), 1.08-1.02 (m, 2H;  $\text{CH}_3-\text{CH}_2-\text{CH}_2-$ ), 0.88 (t,  $J = 7.4$  Hz, 3H,  $\text{CH}_3-\text{CH}_2-$ ).

**1-5-2. 4-(*trans*-5-*n*-Propyl-1,3-dioxan-2-yl)benzoic acid**



To a methanol solution (30 mL) of *trans*-4-(5-*n*-propyl-1,3-dioxan-2-yl)benzoic acid methyl ester 1.17 g (5.00 mmol) was added an aqueous solution (5.0 mL) of NaOH 2.0 g (50 mmol). The mixture was stirred at  $50^\circ\text{C}$  for 13 h and then concentrated by rotary evaporator. The residue was dissolved in distilled water (50 mL) and the pH of the solution was adjusted to 5 by an addition of 1M HCl aq. The precipitates were collected by suction filtration and then washed with distilled water. After drying under reduced pressure, 4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoic acid was obtained as a white solid. Yield: 1.07 g (85.3%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  13.0 (br, 1H: COOH), 7.94 (d,  $J = 8.0$  Hz, 2H; phenyl), 7.52 (d,  $J = 8.8$  Hz, 2H; phenyl), 5.51 (s, 1H; acetal), 4.15 (dd,  $J = 12, 4.8$  Hz, 2H;  $-\text{O}-\text{CH}_2-$ ) 3.54 (t,  $J = 11$  Hz, 2H;  $-\text{O}-\text{CH}_2-$ ), 2.02-1.93 (m, 1H;  $-\text{CH}-\text{CH}_2\text{O}-$ ), 1.34-1.24 (m, 2H,  $\text{CH}_3-\text{CH}_2-$ ), 1.08-1.02 (m, 2H;  $\text{CH}_3-\text{CH}_2-\text{CH}_2-$ ), 0.88 (t,  $J = 7.4$  Hz, 3H,  $\text{CH}_3-\text{CH}_2-$ ).





### 1-5-3. 1-Allyloxy-4-bromo-2,3-difluorobenzene

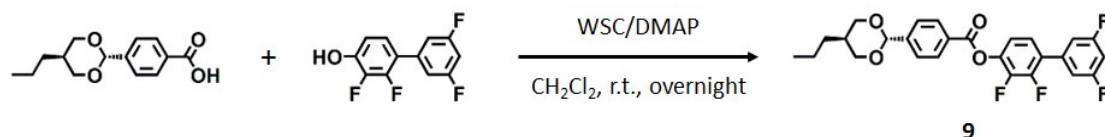
To acetone (20 mL) containing 4-bromo-2,3-difluorophenol 4.81 g (23.0 mmol) and  $K_2CO_3$  4.77 g (34.5 mmol) was added slowly allyl bromide (2.1 mL, ca. 25 mmol, 1.1 equiv.). The mixture was refluxed for 3 h and then solids were separated by suction filtration. The filtrates were concentrated and added in  $CH_2Cl_2$  (50 mL) and then washed with 10wt% NaOH aq. (50 mL x 2) followed by distilled water (50 mL x 3). After drying over anhydrous  $Na_2SO_4$ , the organic layer was concentrated and dried under reduced pressure to give colorless liquids. Yield: 5.62 g (98.1%).  $^1H$  NMR (400 MHz,  $DMSO-d_6$ , ppm):  $\delta$  7.47 (t,  $J$  = 8.2 Hz, 1H; phenyl), 7.05 (t,  $J$  = 8.8 Hz, 1H; phenyl), 6.09-6.00 (m, 1H;  $H_2C=CH-$ ), 5.43 (dd,  $J$  = 17, 2.0 Hz, 1H;  $H_2C=CH-$ ), 5.31 (d,  $J$  = 11 Hz, 1H;  $H_2C=CH-$ ), 4.70 (dd,  $J$  = 4.0, 2.0 Hz, 2H; -O-Ph).

### 1-5-4. 2,3-Difluoro-4-(3,5-difluorophenyl)phenol



To a DMF solution (80 mL) of 1-allyloxy-4-bromo-2,3-difluorobenzene 4.98 g (20.0 mmol), 3,5-difluorophenylboronic acid 4.11 g (26.0 mmol, 1.3 equiv.) and  $Pd(PPh_3)_4$  240 mg (0.21 mmol, 1 mol%) was added an aqueous solution (20 mL) of  $K_3PO_4$  8.4 g (40 mmol). The mixture was heated under  $N_2$  atmosphere at  $100^\circ C$  for 15 h. After the removal of DMF, the residues were added in distilled water (200 mL) and then extracted with  $CH_2Cl_2$  (200 mL). The organic layer was washed with distilled water (200 mL x 3) and then dried with anhydrous  $Na_2SO_4$ . After evaporation, the resulting brown solid was purified with silica-gel column chromatography (*n*-hexane/ $CHCl_3$  volume ratio of 1:1 to 1:4) to give pale yellow solids. Yield: 3.59 g (74.1%).  $^1H$  NMR (400 MHz,  $DMSO-d_6$ , ppm):  $\delta$  10.8 (br, 1H; OH), 7.30-7.22 (m, 4H; phenyl), 6.88 (td,  $J$  = 8.6, 1.6 Hz, 1H, phenyl).

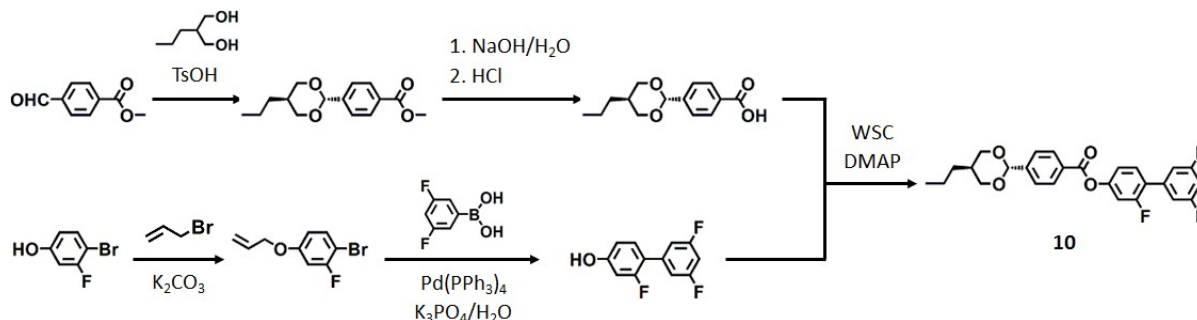
### 1-5-5. 2,3-Difluoro-4-(3,5-difluorophenyl)phenyl 4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoate (9)



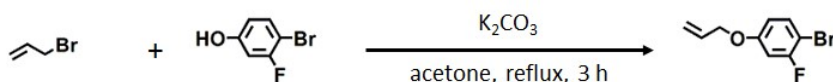
4-(*trans*-5-*n*-Propyl-1,3-dioxan-2-yl)benzoic acid 2.00 g (8.00 mmol) and WSC 2.00 g (10.5 mmol) were dissolved in  $CH_2Cl_2$  (20 mL) and the solution stirred at ambient temperature for 30 min. To the solution, 2,3-difluoro-4-(3,5-difluorophenyl)phenol 2.32 g (9.60 mmol) and DMAP 98 mg (0.80 mmol) were added and the solution was stirred at rt. for 16 h. The solution was added in  $CH_2Cl_2$  (50 mL) and washed with distilled water (50 mL x 3) and then the organic layer was dried over anhydrous  $Na_2SO_4$ . After concentration, the resulting solids were purified by recrystallization from  $CH_2Cl_2$ /MeOH to give white solids. Yield: 1.49 g (39.3%).  $^1H$  NMR (400 MHz,  $DMSO-d_6$ , ppm):  $\delta$  8.17 (d,  $J$  = 7.6 Hz, 2H; phenyl), 7.67 (d,  $J$  = 8.0 Hz, 2H; phenyl), 7.57-7.47 (m, 2H; phenyl), 7.43-7.37 (m, 3H; phenyl), 5.58 (s, 1H; acetal), 4.17 (dd,  $J$  = 12, 4.4 Hz, 2H; -O- $CH_2-$ ), 3.57 (t,  $J$  =

11 Hz, 2H; -O-CH<sub>2</sub>-), 2.04-1.96 (m, 1H, -CH-CH<sub>2</sub>O-), 1.34-1.25 (m, 2H; CH<sub>3</sub>-CH<sub>2</sub>-), 1.06 (q, *J* = 7.6 Hz, 2H; CH<sub>3</sub>-CH<sub>2</sub>-), 0.88 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>-CH<sub>2</sub>-). HRMS (EI) *m/z*: [M<sup>+</sup>] calcd for C<sub>26</sub>H<sub>22</sub>F<sub>4</sub>O<sub>4</sub>: 474.1454; found: 474.1454. Anal. calcd for C<sub>26</sub>H<sub>22</sub>F<sub>4</sub>O<sub>4</sub>: C 65.82, H 4.67; found: C 65.77, H 4.70.

### 1-6. Synthesis of 4-(3,5-difluorophenyl)-3-fluorophenyl trans-4-(5-n-propyl-1,3-dioxan-2-yl)benzoate (10)

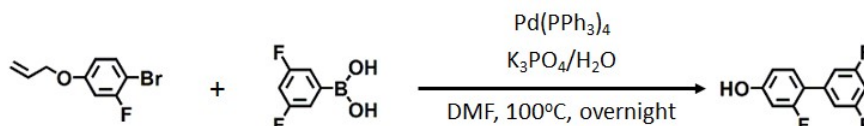


#### 1-6-1. 1-Allyloxy-4-bromo-3-fluorobenzene



To an acetone solution of 4-bromo-3-fluorophenol 1.91 g (10.0 mmol) and K<sub>2</sub>CO<sub>3</sub> 2.07 g (15.0 mmol) was added dropwise allyl bromide 1.45 g (12.0 mmol). After the mixture was refluxed for 3 h, solids were separated by filtration and the filtrates were concentrated. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and then washed with aqueous solution (20 mL) of K<sub>2</sub>CO<sub>3</sub> 1.38 g (10.0 mmol) followed by distilled water (20 mL x 2). After dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the organic layer was concentrated and dried under reduced pressure. Pale yellow liquids were obtained in quantitative yield (2.36 g, >99%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ): 7.58 (t, *J* = 8.8 Hz, 1H; phenyl), 7.06 (dd, *J* = 11, 2.8 Hz, 1H; phenyl), 6.81 (dd, *J* = 9.2, 2.4 Hz, 1H; phenyl), 6.07-5.97 (m, 1H; H<sub>2</sub>C=CH-), 5.40 (d, *J* = 18 Hz, 1H; H<sub>2</sub>C=CH-), 5.28 (d, *J* = 11 Hz, 1H; H<sub>2</sub>C=CH-), 4.60 (d, *J* = 4.8 Hz, 2H; -O-Ph).

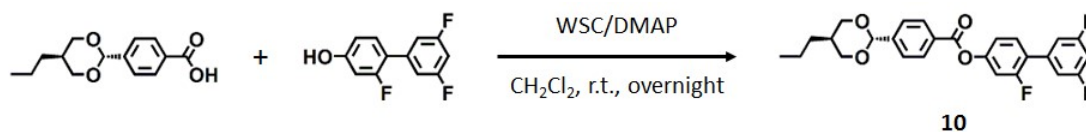
#### 1-6-2. 4-(3,5-Difluorophenyl)-3-fluorophenol



To a DMF solution (4.0 mL) containing 1-allyloxy-4-bromo-3-fluorobenzene 231 mg (1.00 mmol), 3,5-difluorophenylboronic acid 189 mg (1.20 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> 23 mg (0.020 mmol, 2 mol%) was added an aqueous solution (1.0 mL) of K<sub>3</sub>PO<sub>4</sub> 424 mg (2.00 mmol). The mixture was stirred under N<sub>2</sub> atmosphere at 100°C for 16 h. After cooled to ambient temperature, the reaction mixture was added in distilled water (50 mL) and then the resulting precipitates were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 mL). The organic layer was washed three times with distilled water (25 mL) and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation, the brown residue was purified by silica-gel column chromatography (*n*-hexane/EtOAc volume ratio of 5:1) to give pale yellow solids. Yield: 214 mg (68.6%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 10.3 (br, 1H; OH), 7.43 (t, *J* = 8.8

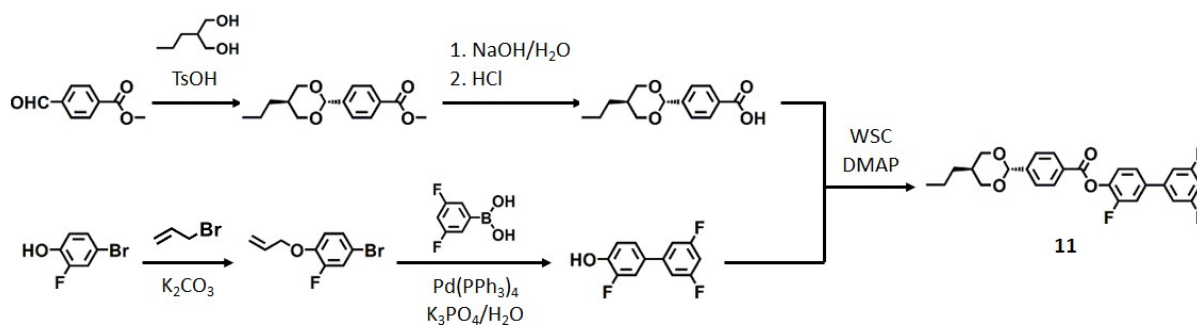
Hz, 1H; phenyl), 7.23-7.18 (m, 3H; phenyl), 6.73-6.68 (m, 2H; phenyl).

### 1-6-3. 4-(3,5-Difluorophenyl)-3-fluorophenyl trans-4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoate (**10**)

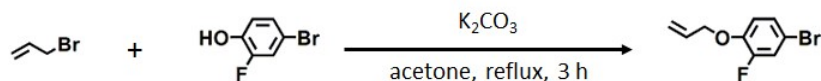


To a CH<sub>2</sub>Cl<sub>2</sub> solution (2.0 mL) of 4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoic acid 250 mg (1.00 mmol) was added WSC 230 mg (1.20 mmol) and the mixture was stirred at ambient temperature for 30 min. To the mixture, 4-(3,5-difluorophenyl)-3-fluorophenol 270 mg (1.20 mmol) and DMAP 24 mg (0.20 mmol) was added and then the mixture was stirred at ambient temperature for 23 h. After that, CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added in the mixture and then washed with distilled water (20 mL x3). After dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the organic layer was concentrated. The resulting yellow solids were purified by recrystallization from MeOH to give white solids. Yield: 234 mg (51.2%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 8.15 (d, *J* = 8.4 Hz, 2H; phenyl), 7.72 (t, *J* = 8.8 Hz, 1H; phenyl), 7.65 (d, *J* = 7.6 Hz, 2H; phenyl), 7.49 (dd, *J* = 11, 2.0 Hz, 1H; phenyl), 7.37-7.31 (m, 4H; phenyl), 5.57 (s, 1H; acetal), 4.18 (dd, *J* = 12, 3.8 Hz, 2H; -O-CH<sub>2</sub>-), 3.57 (t, *J* = 12 Hz, 2H; -O-CH<sub>2</sub>-), 2.05-1.97 (m, 1H, -CH-CH<sub>2</sub>O-), 1.35-1.26 (m, 2H; CH<sub>3</sub>-CH<sub>2</sub>-), 1.09-1.04 (m, 2H; CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 0.89 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>-CH<sub>2</sub>-). HRMS (EI) *m/z*: [M<sup>+</sup>] calcd for C<sub>26</sub>H<sub>23</sub>F<sub>3</sub>O<sub>4</sub>: 456.1548; found: 456.1549. Anal. calcd for C<sub>26</sub>H<sub>23</sub>F<sub>3</sub>O<sub>4</sub>: C 68.41, H 5.08; found: C 68.49, H 4.94.

### 1-7. Synthesis of 4-(3,5-difluorophenyl)-2-fluorophenyl 4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoate (**11**)



#### 1-7-1. 1-Allyloxy-4-bromo-2-fluorobenzene



To acetone (20 mL) containing 4-bromo-2-fluorophenol 4.78 g (25.0 mmol) and K<sub>2</sub>CO<sub>3</sub> 5.18 g (37.5 mmol) was added slowly allyl bromide (2.5 mL, ca. 30 mmol). The mixture was refluxed for 3 h and then solids were separated by suction filtration. After the filtrates were concentrated, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). After washed with 10wt% NaOH aq. (50 mL) followed by distilled water (50 mL x 3), the organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated. After drying under reduced pressure, 1-allyloxy-4-bromo-2-fluorobenzene was obtained as colorless liquids. Yield: 5.89 g (quantitative). <sup>1</sup>H NMR (400 MHz,

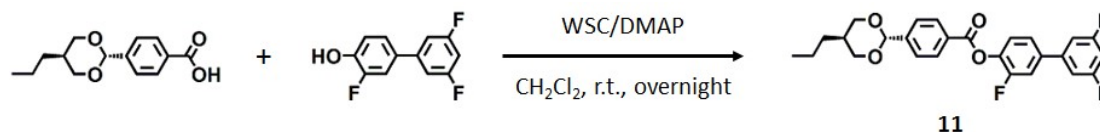
DMSO-*d*<sub>6</sub>, ppm): δ 7.53 (dd, *J* = 12, 2.4 Hz, 1H; phenyl), 7.33 (dt, *J* = 8.8, 1.8 Hz, 1H; phenyl), 7.15 (t, *J* = 8.4 Hz, 1H; phenyl), 6.08-5.99 (m, 1H; H<sub>2</sub>C=CH-), 5.43-5.38 (m, 1H; H<sub>2</sub>C=CH-), 5.31-5.28 (m, 1H; H<sub>2</sub>C=CH-), 4.65 (dd, *J* = 6.8, 2.0 Hz, 2H; -O-Ph).

#### 1-7-2. 4-(3,5-Difluorophenyl)-2-fluorophenol



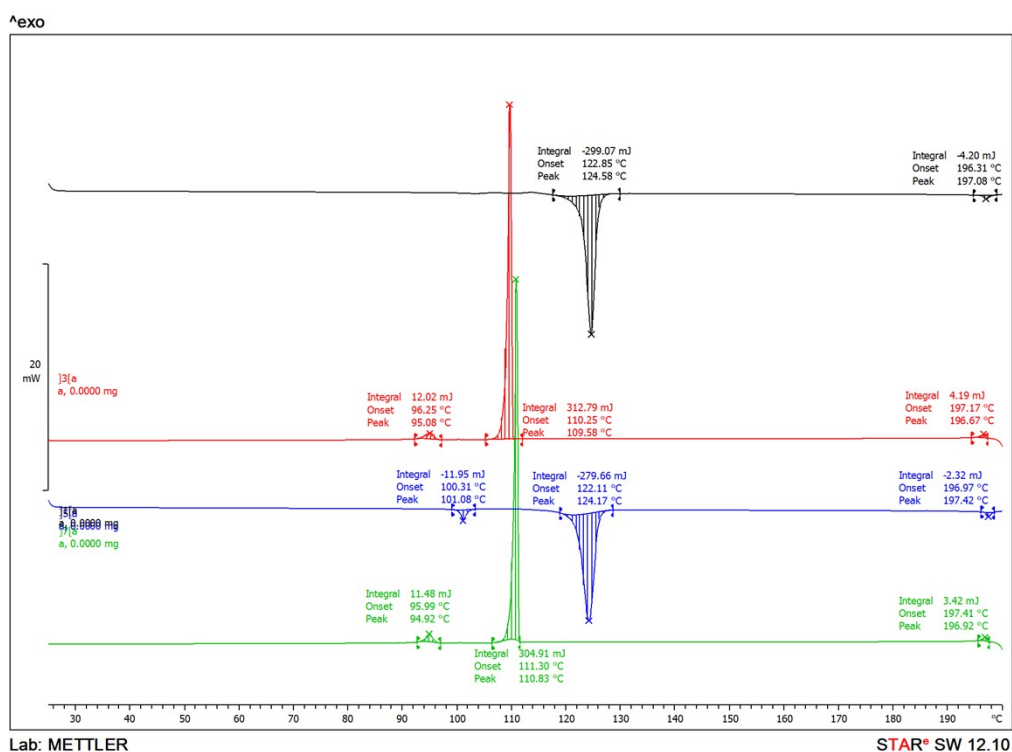
To a DMF solution of 1-allyloxy-4-bromo-2-fluorobenzene 4.62 g (20.0 mmol), 3,5-difluorophenylboronic acid 4.11 g (26.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> 480 mg (0.42 mmol, 2 mol%) were added a aqueous solution of K<sub>3</sub>PO<sub>4</sub> 8.48 g (40.0 mmol). The mixture was stirred under N<sub>2</sub> atmosphere at 100°C for 14 h. After DMF was removed, the residues were dissolved in distilled water (200 mL) and then extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL x 2). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated. The resulting orange solid was purified by silica-gel column chromatography (*n*-hexane/CHCl<sub>3</sub> volume ratio of 1:1 to 1:4) to afford white solids. Yield: 1.95 g (43.6%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 10.2 (br, 1H; OH), 7.63 (dd, *J* = 13, 2.4 Hz, 1H; phenyl), 7.45-7.40 (m, 3H; phenyl), 7.16 (tt, *J* = 9.4, 2.4 Hz, 1H; phenyl), 7.03 (t, *J* = 9.2 Hz, 1H, phenyl).

#### 1-7-3. 4-(3,5-Difluorophenyl)-2-fluorophenyl 4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoate (**11**)

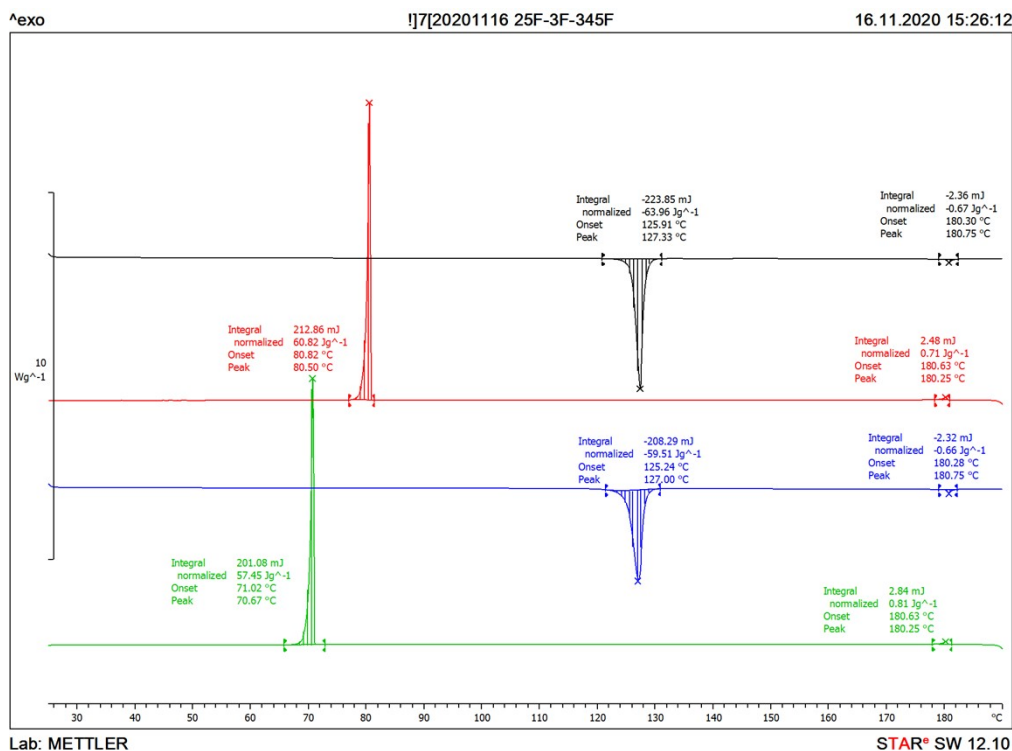


To a CH<sub>2</sub>Cl<sub>2</sub> solution (15 mL) of 4-(*trans*-5-*n*-propyl-1,3-dioxan-2-yl)benzoic acid 1.54 g (6.15 mmol) was added WSC 1.53 g (7.98 mmol). After the mixture was stirred at ambient temperature for 30 min, 4-(3,5-difluorophenyl)-2-fluorophenol 1.79 g (8.00 mmol) and DMAP 75 mg (0.62 mmol) were added and then the mixture was further stirred at rt. for 14 h. CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added the mixture and then washed three times with distilled water (50 mL). The organic layer dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated. The resulting pale yellow solid was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to give white solids. Yield: 1.73 g (61.7%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 8.17 (d, *J* = 7.2 Hz, 2H; phenyl), 7.92 (d, *J* = 12 Hz, 1H; phenyl), 7.73-7.57 (m, 6H; phenyl), 7.30 (t, *J* = 9.2 Hz, 1H; phenyl), 5.58 (s, 1H; acetal), 4.18 (dd, *J* = 11, 4.4 Hz, 2H; -O-CH<sub>2</sub>-), 3.57 (t, *J* = 11 Hz, 2H; -O-CH<sub>2</sub>-), 2.05-1.96 (m, 1H, -CH-CH<sub>2</sub>O-), 1.35-1.26 (m, 2H; CH<sub>3</sub>-CH<sub>2</sub>-), 1.06 (q, *J* = 7.5 Hz, 2H; CH<sub>3</sub>-CH<sub>2</sub>-), 0.89 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>-CH<sub>2</sub>-). HRMS (EI) *m/z*: [M<sup>+</sup>] calcd for C<sub>26</sub>H<sub>23</sub>F<sub>3</sub>O<sub>4</sub>: 456.1548; found: 456.1548. Anal. calcd for C<sub>26</sub>H<sub>23</sub>F<sub>3</sub>O<sub>4</sub>: C 68.41, H 5.08; found: C 68.24, H 4.98.

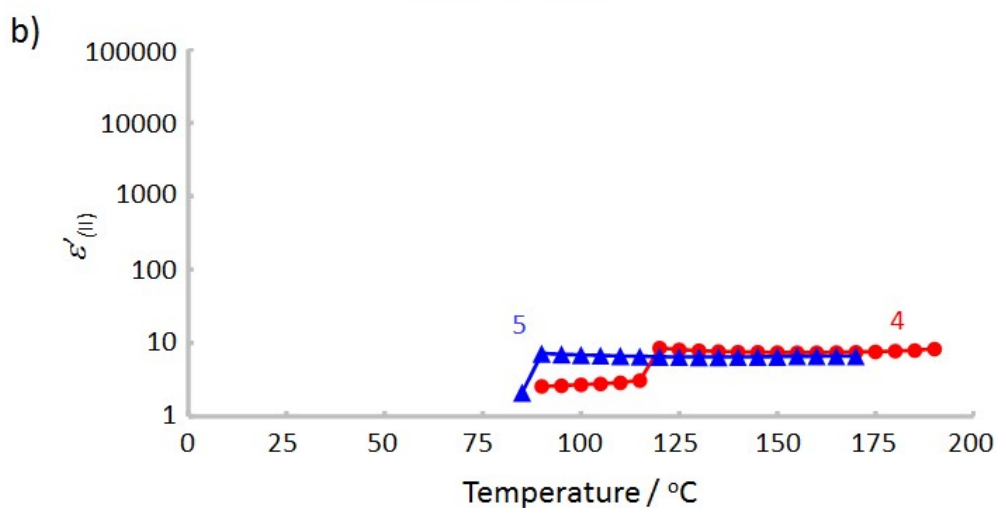
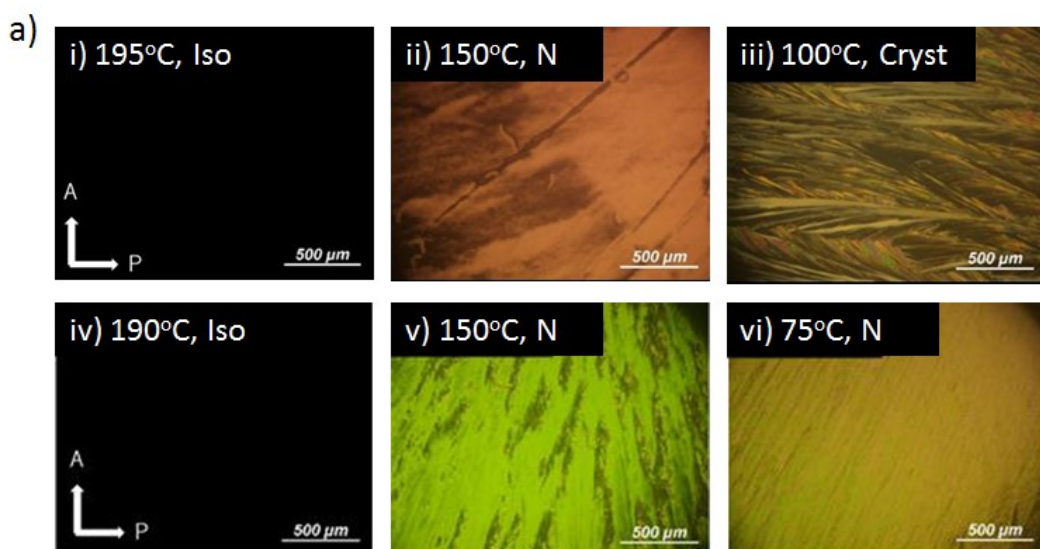
## 2. Characterization of C3-DIO analogues in Group I



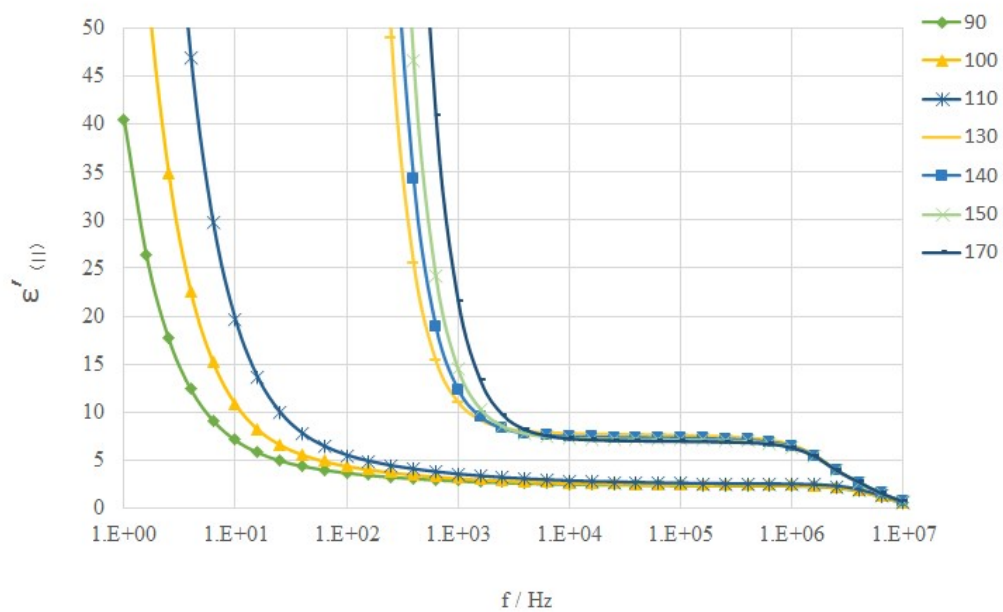
**Figure S1** DSC charts of **4**. Black line: 1st heating. Red line: 1st cooling. Blue line: 2nd heating. Green line: 2nd cooling. Rate: 5°C min<sup>-1</sup>.



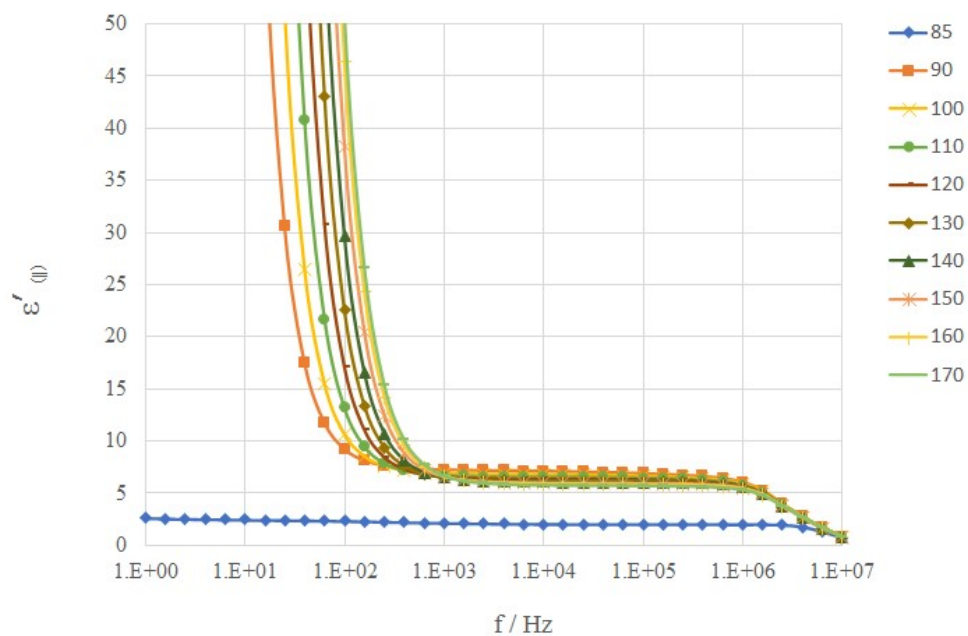
**Figure S2** DSC charts of **5**. Black line: 1st heating. Red line: 1st cooling. Blue line: 2nd heating. Green line: 2nd cooling. Rate: 5°C min<sup>-1</sup>.



**Figure S3** a) POM images of **4** (i-iii) and **5** (iv-vi) in the cooling run. The samples were introduced in the cell composed of non-treated glass substrates and then observed. b) temperature dependence of dielectric constants of **4** (red circles) and **5** (blue triangles) in the cooling run.  $f = 10$  kHz.  $0.1 V_{rms}$ .

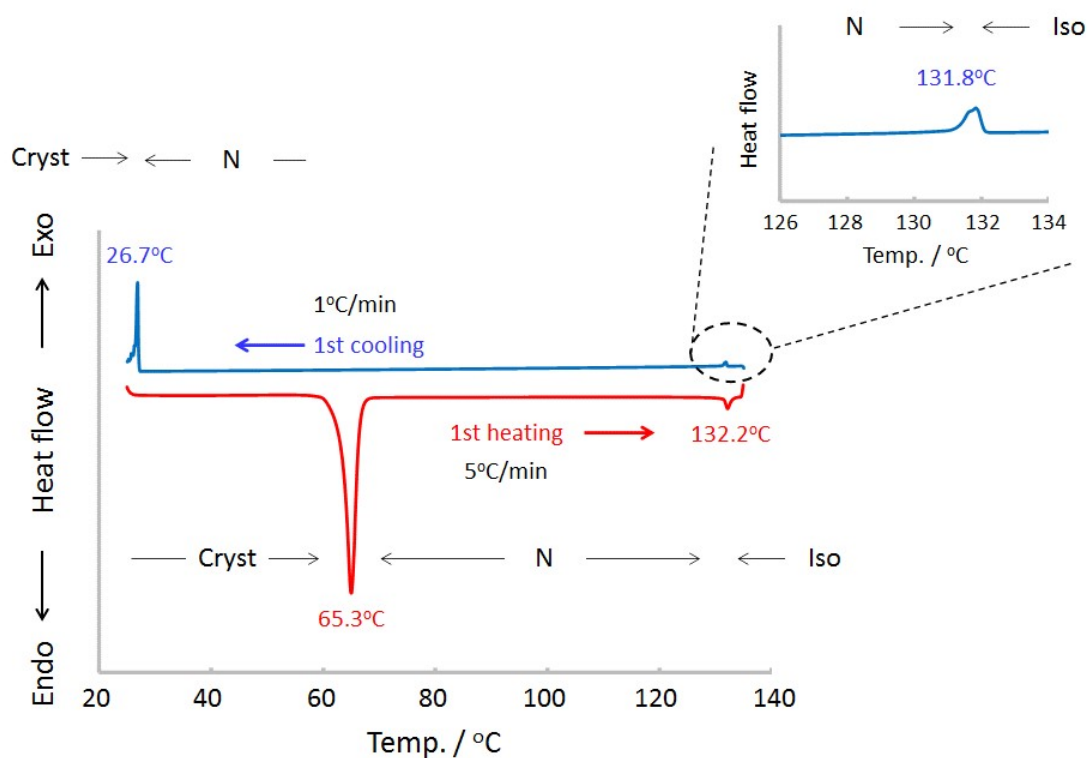


**Figure S4** Frequency dependences of dielectric constant of **4** in the cooling process.

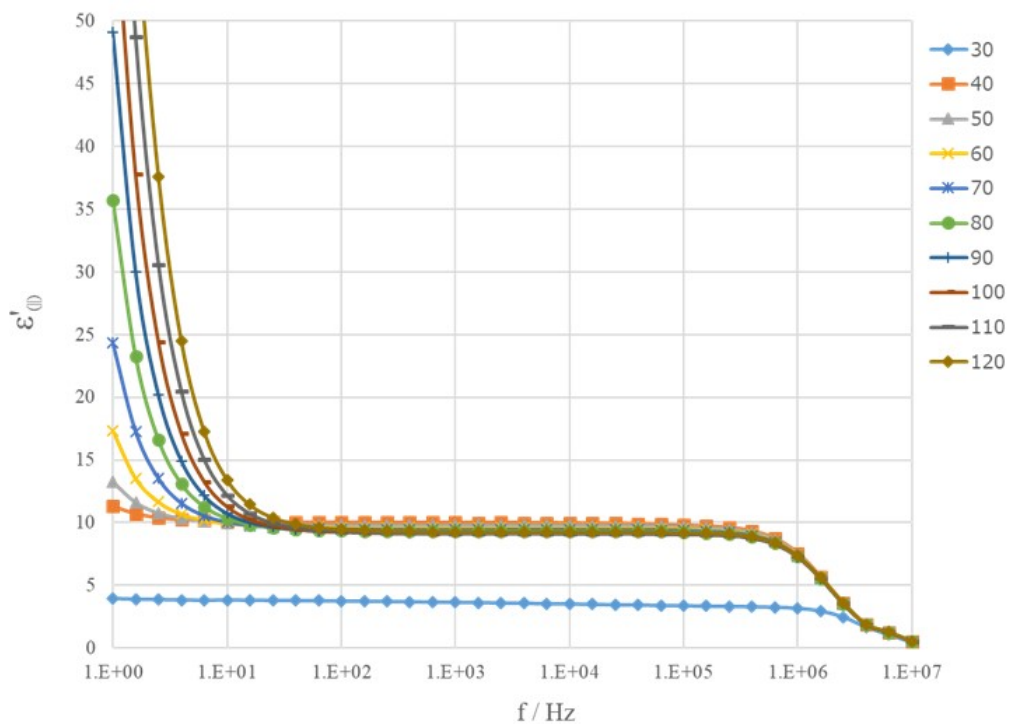


**Figure S5** Frequency dependences of dielectric constant of **5** in the cooling process.

### 3. Characterization of C3-DIO analogues in Group II

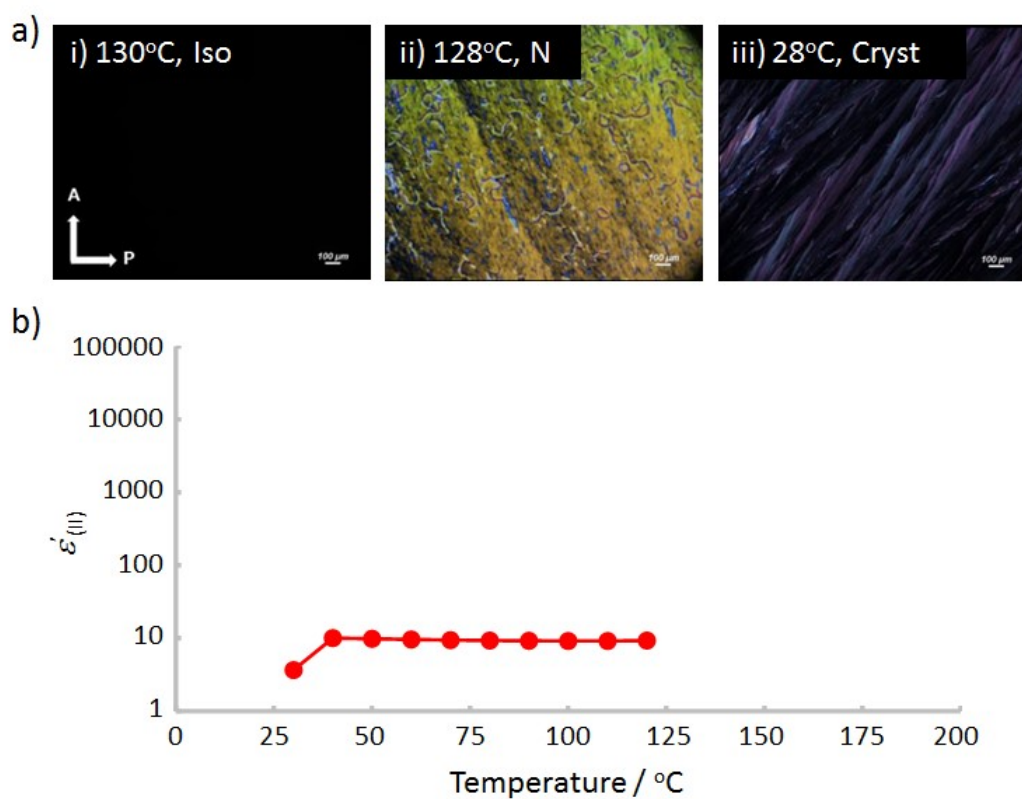


**Figure S6** DSC charts of **6**. Red line: 1st heating run at 5°C min<sup>-1</sup>. Blue line: 1st cooling run at 1°C min<sup>-1</sup>.

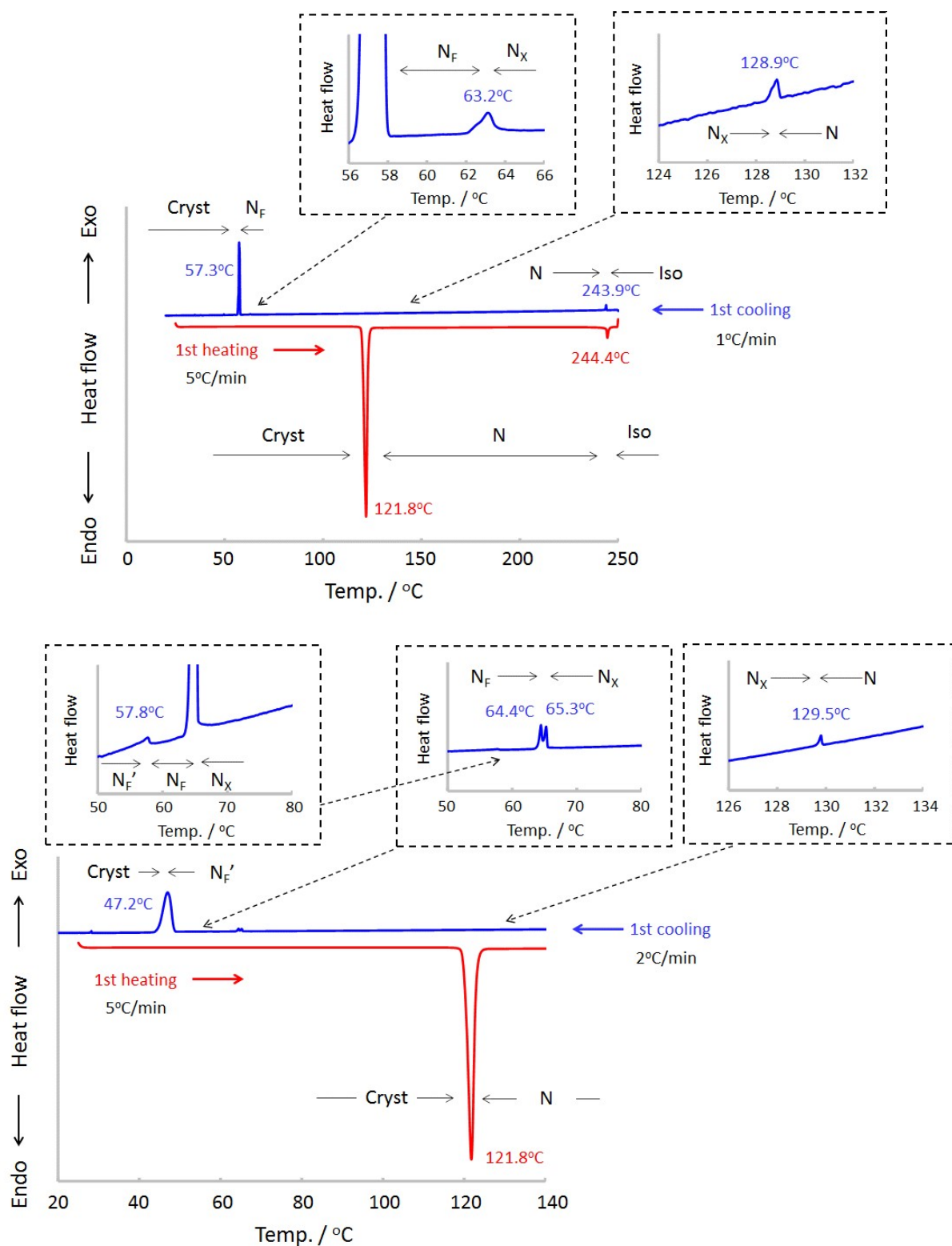


**Figure S7** Frequency dependences of dielectric constant of **6** in the cooling process.

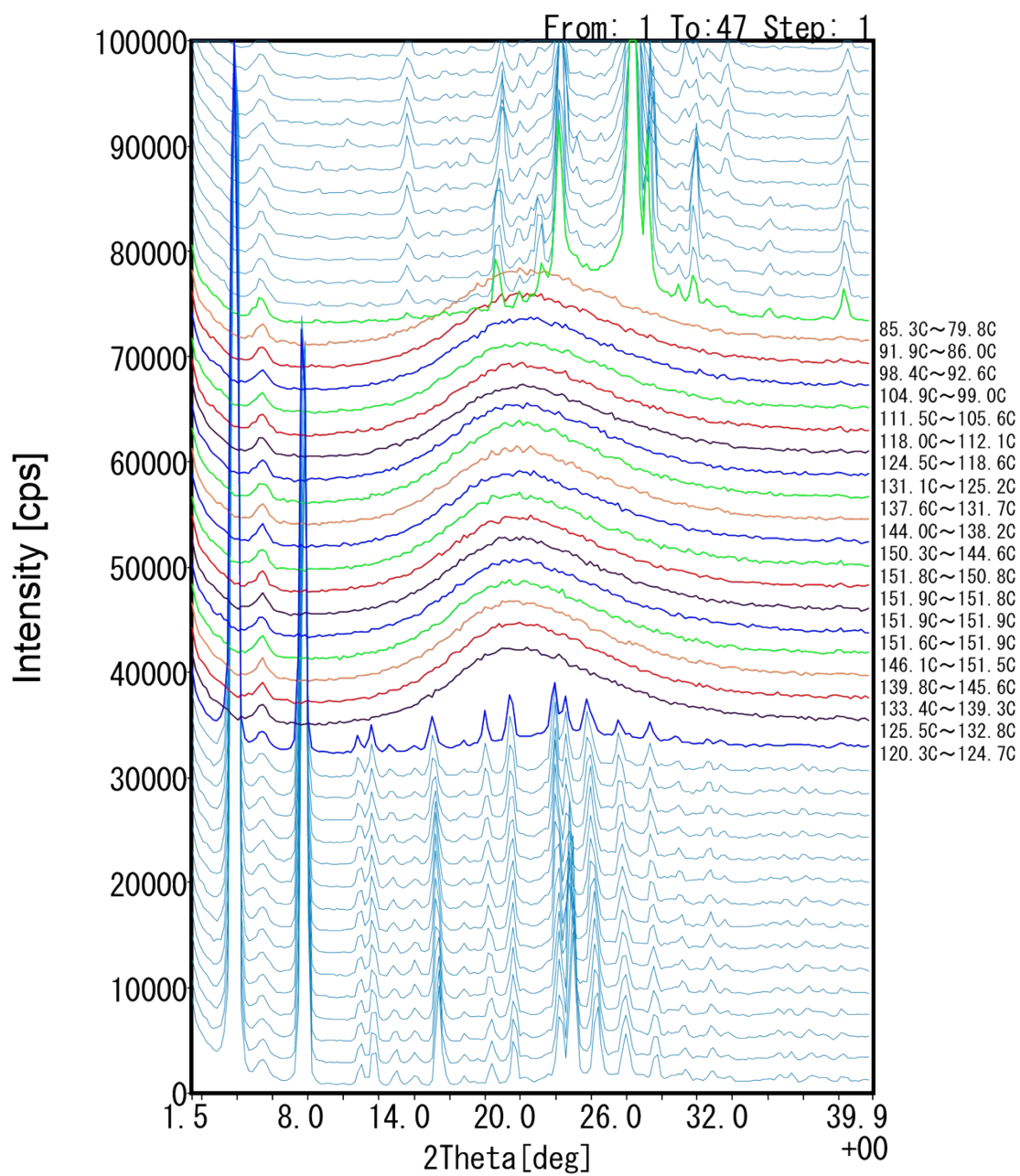




**Figure S8** a) POM images of **6** in the cooling run. POM sample was introduced in cell of non-treated glass substrates and then observed for its phase transition behavior. b) Temperature dependence of dielectric constants of **6** in the cooling run.  $f = 1$  kHz.  $0.1 V_{rms}$ .



**Figure S9** Top: DSC charts of **7** measured at different heating/cooling rates. Red line: 1st heating run at 5°C min<sup>-1</sup>. Blue line: 1st cooling run at 1°C min<sup>-1</sup>. Bottom: DSC charts of **7** measured at different heating/cooling rates. Red line: 1st heating run at 5°C min<sup>-1</sup>. Blue line: 1st cooling run at 2°C min<sup>-1</sup>.



**Figure S10** XRD profiles of **7** at different temperatures on a cooling rate of 5 °C min<sup>-1</sup>.

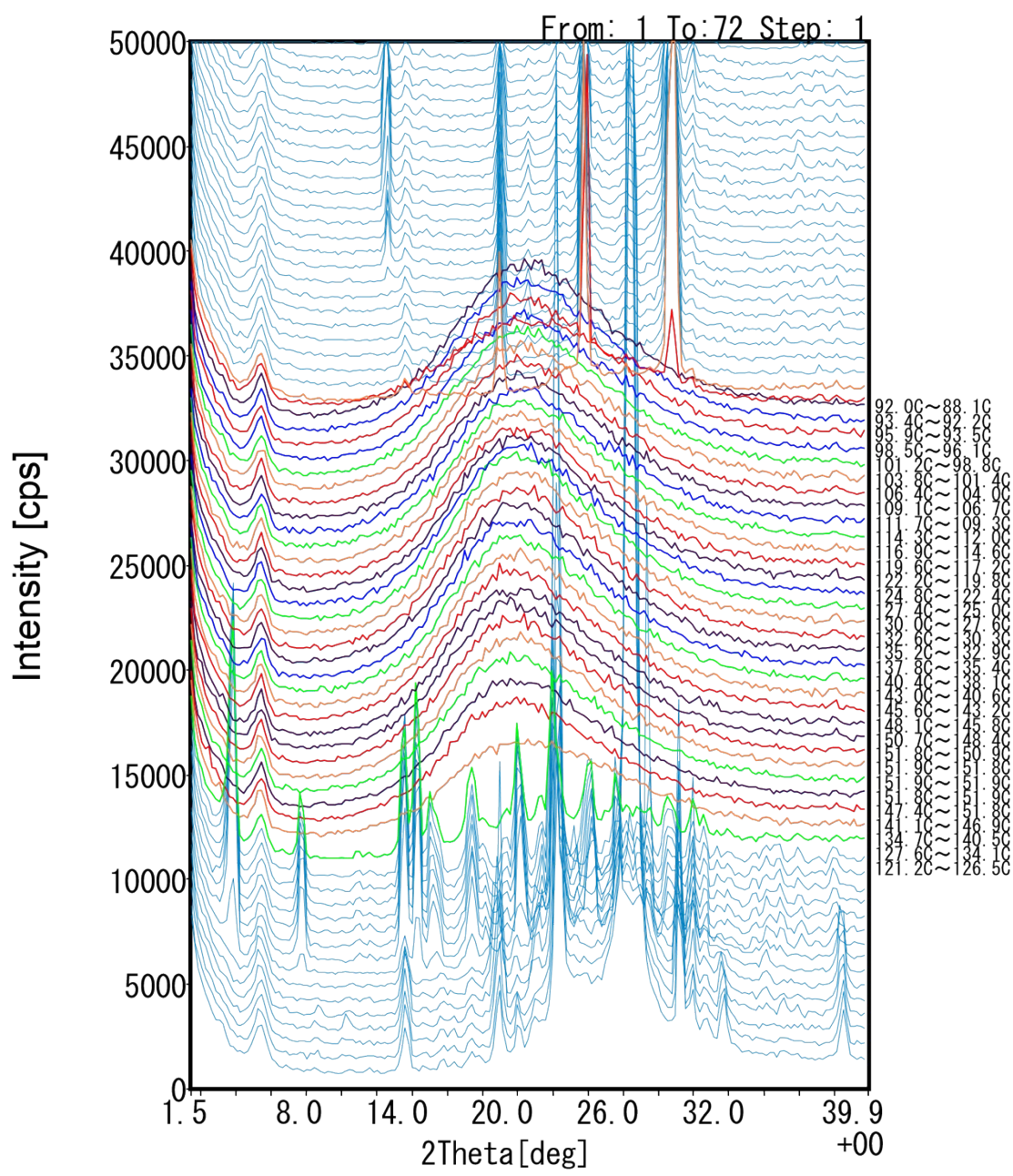
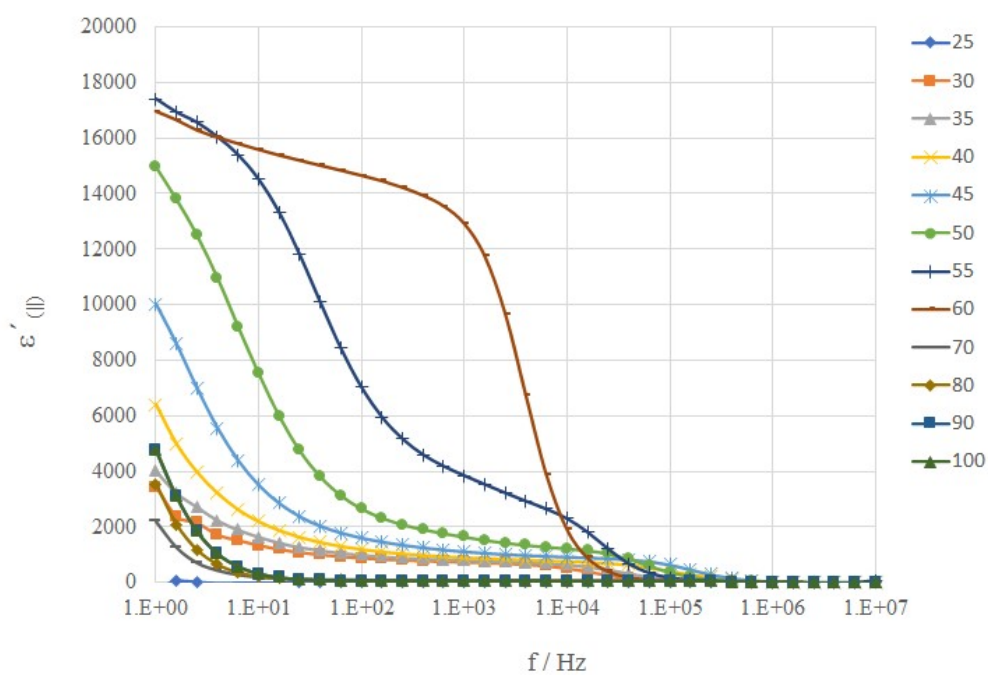
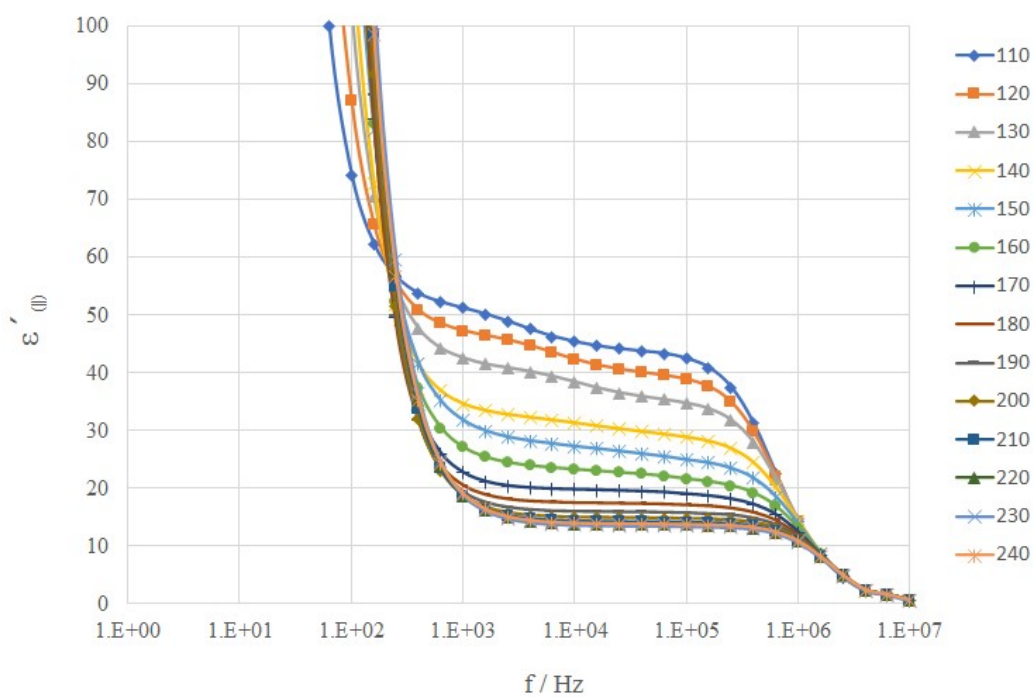
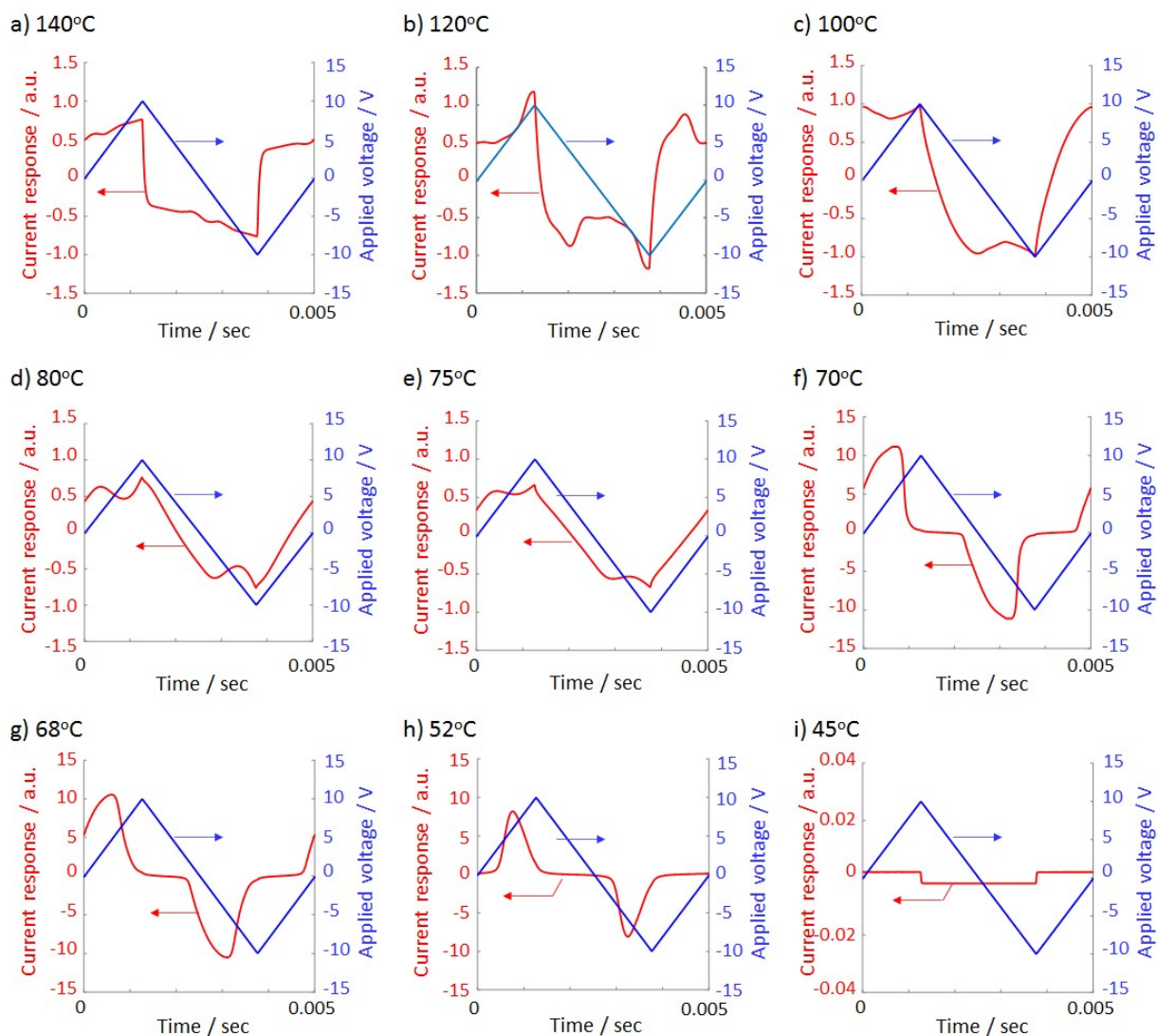


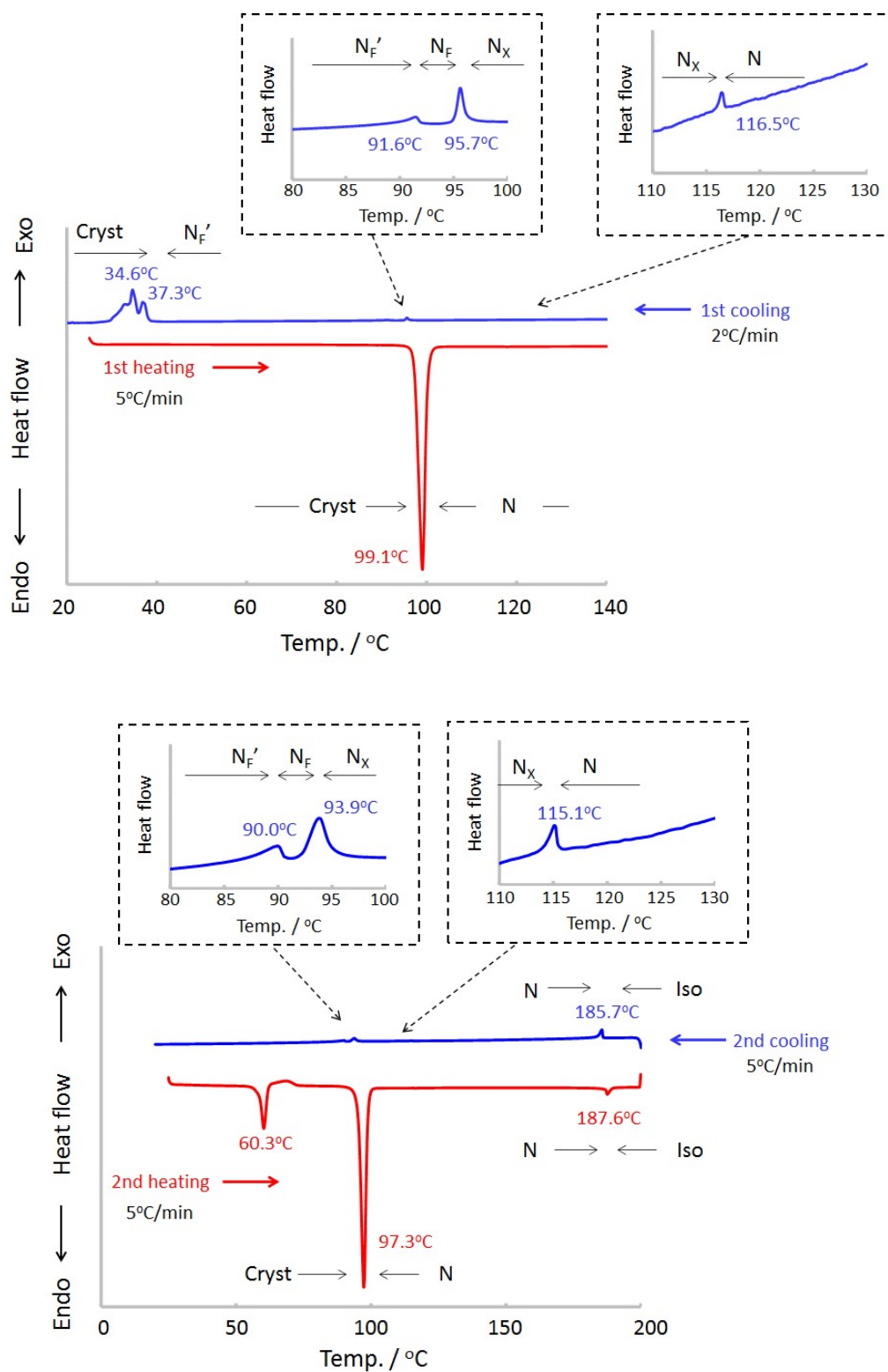
Figure S11 XRD profiles of **7** at different temperatures on a cooling rate of 2 °C min<sup>-1</sup>.



**Figure S12** Frequency dependences of dielectric constant of **7** in the cooling process. Top: 110-240°C. Bottom: 25-100°C.



**Figure S13** Switching current response of **7** under an applied triangular wave voltage in the 1st cooling run.  $V_{pp} = 20$  V.  $f = 200$  Hz. Red and blue lines denote current response and applied triangular wave voltage, respectively.



**Figure S14** Top: DSC charts of **8** measured at different heating/cooling rates. Red line: 1st heating run at 5 °C min<sup>-1</sup>. Blue line: 1st cooling run at 2 °C min<sup>-1</sup>. Bottom: DSC charts of **8** measured at different heating/cooling rates. Red line: 2nd heating run at 5 °C min<sup>-1</sup>. Blue line: 2nd cooling run at 5 °C min<sup>-1</sup>.

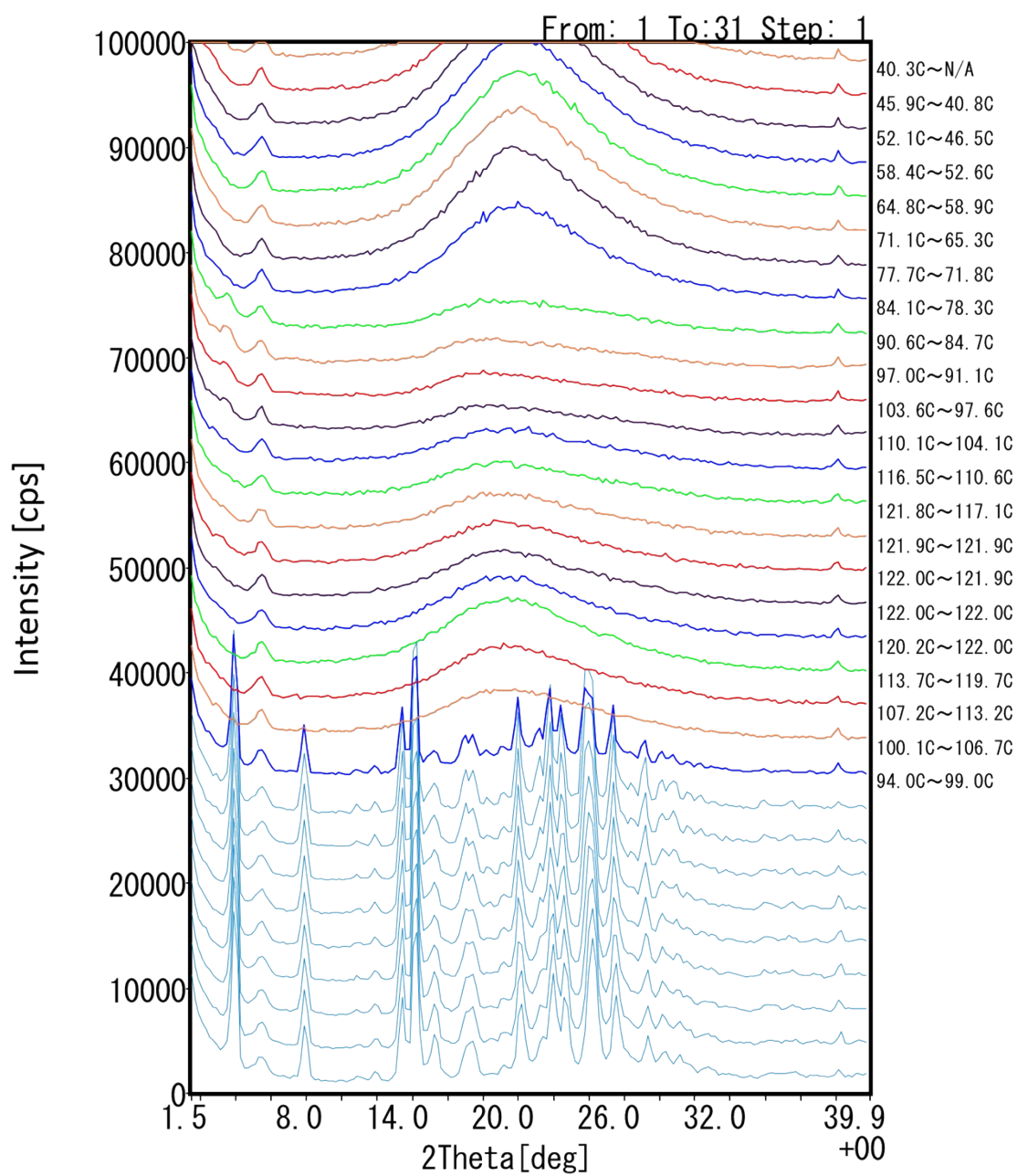


Figure S15 XRD profiles of **8** at different temperatures on a cooling rate of 5 °C min<sup>-1</sup>.



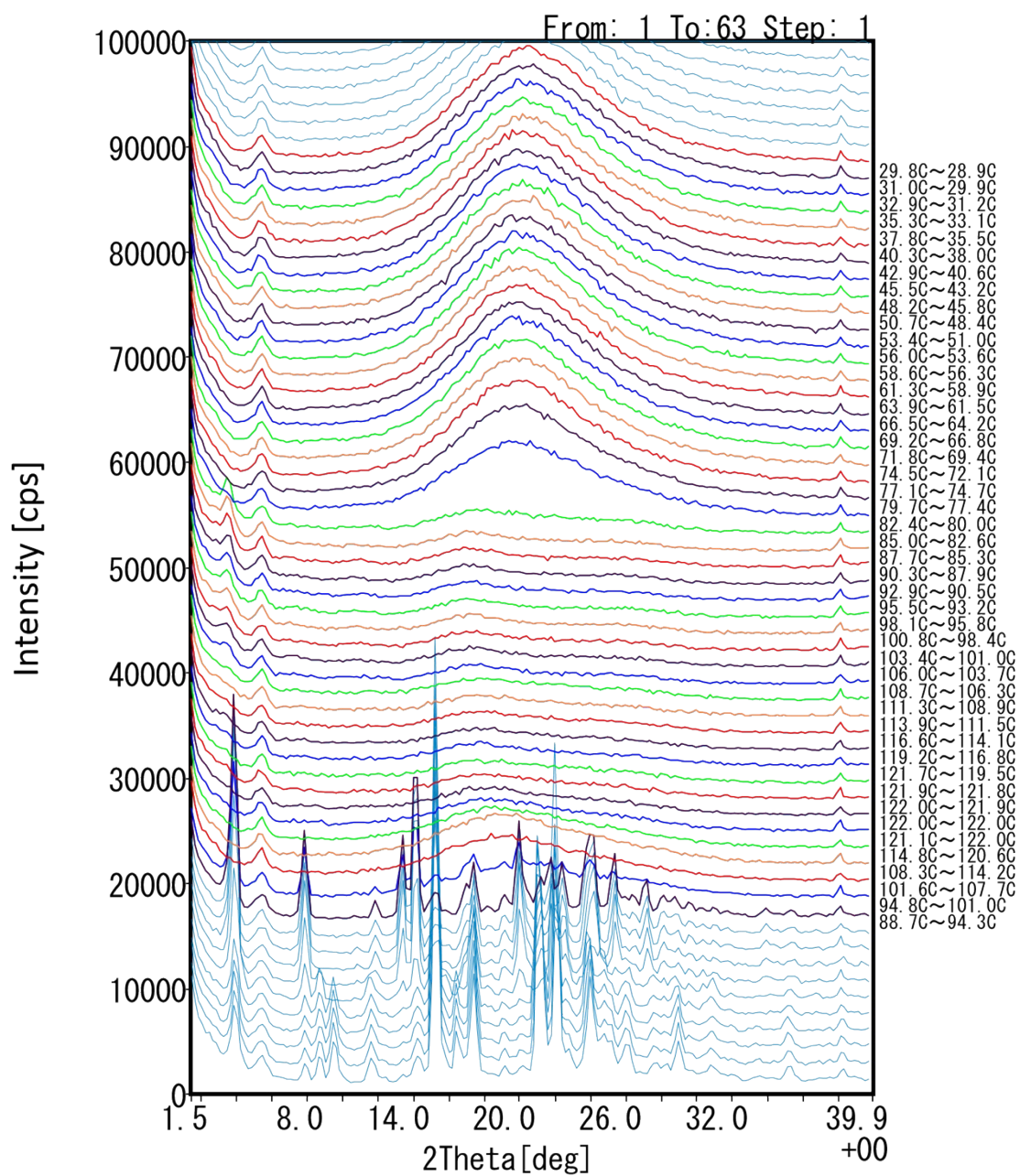
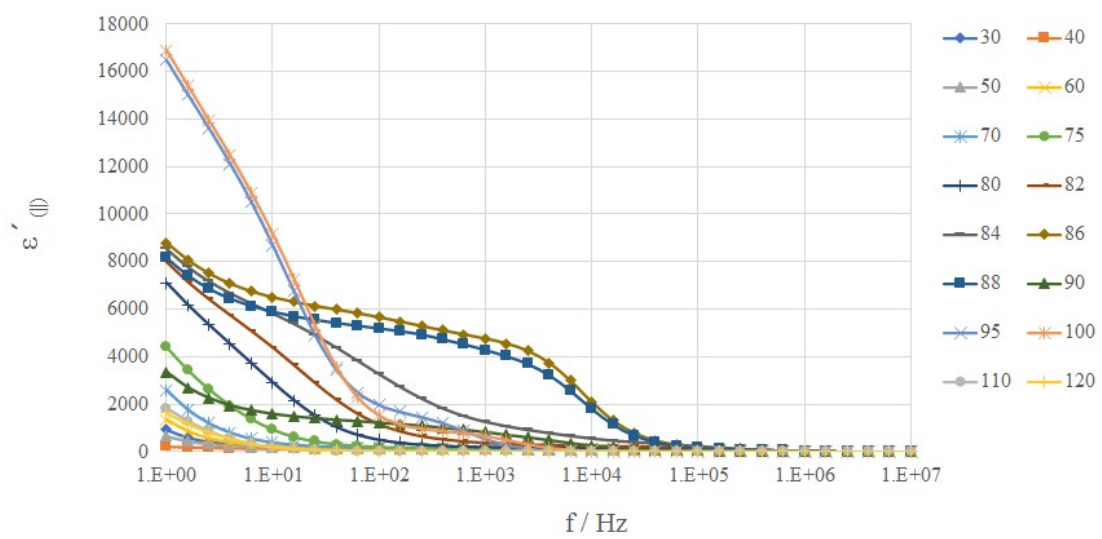
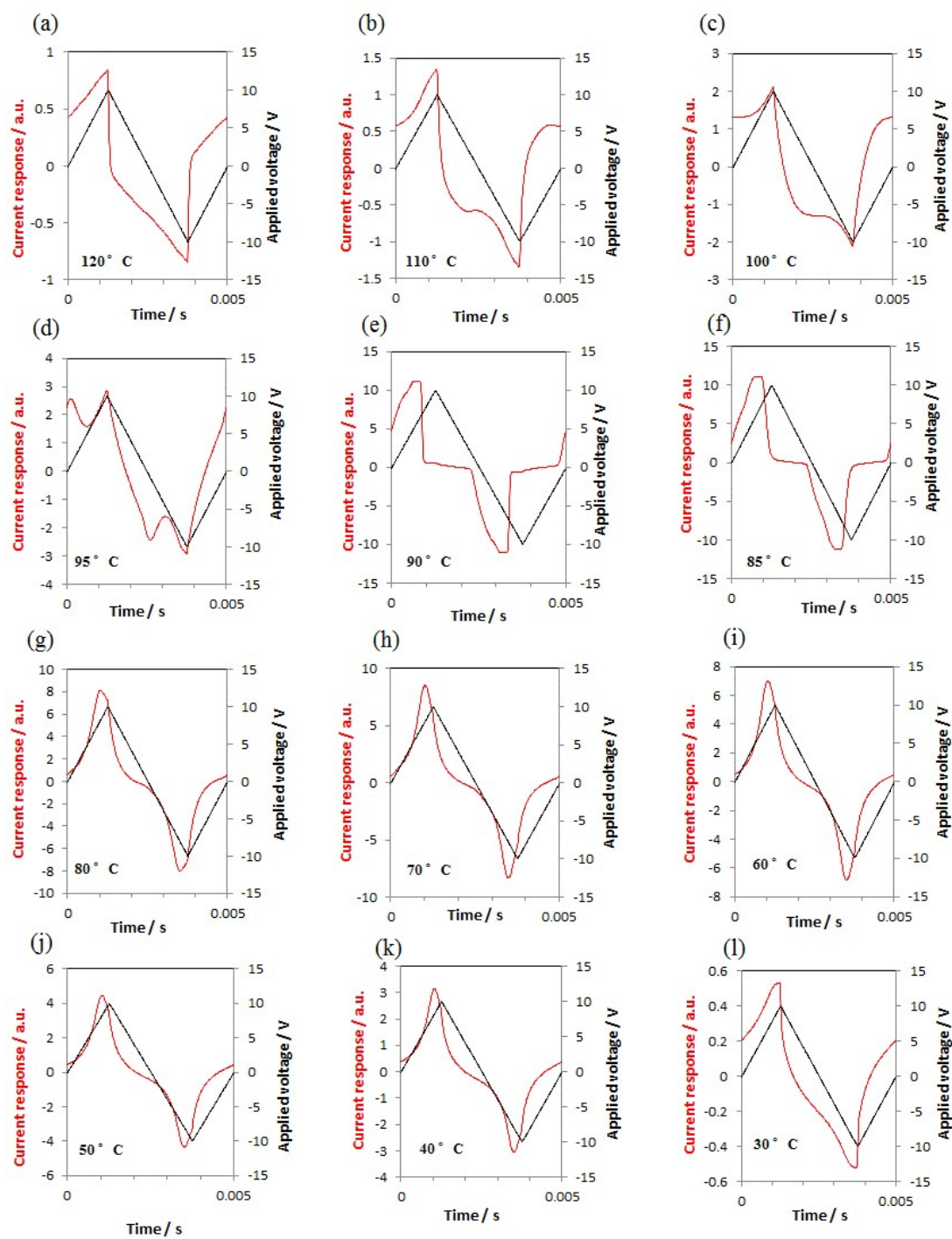


Figure S16 XRD profiles of **8** at different temperatures on a cooling rate of 2 °C min<sup>-1</sup>.



**Figure S17** Frequency dependences of dielectric constant of **8** in the cooling process.



**Figure S18** Switching current response of **8** under an applied triangular wave voltage in the cooling run.  $V_{pp} = 20$  V.  $f = 200$  Hz. Red and black lines denote current response and applied triangular wave voltage, respectively.

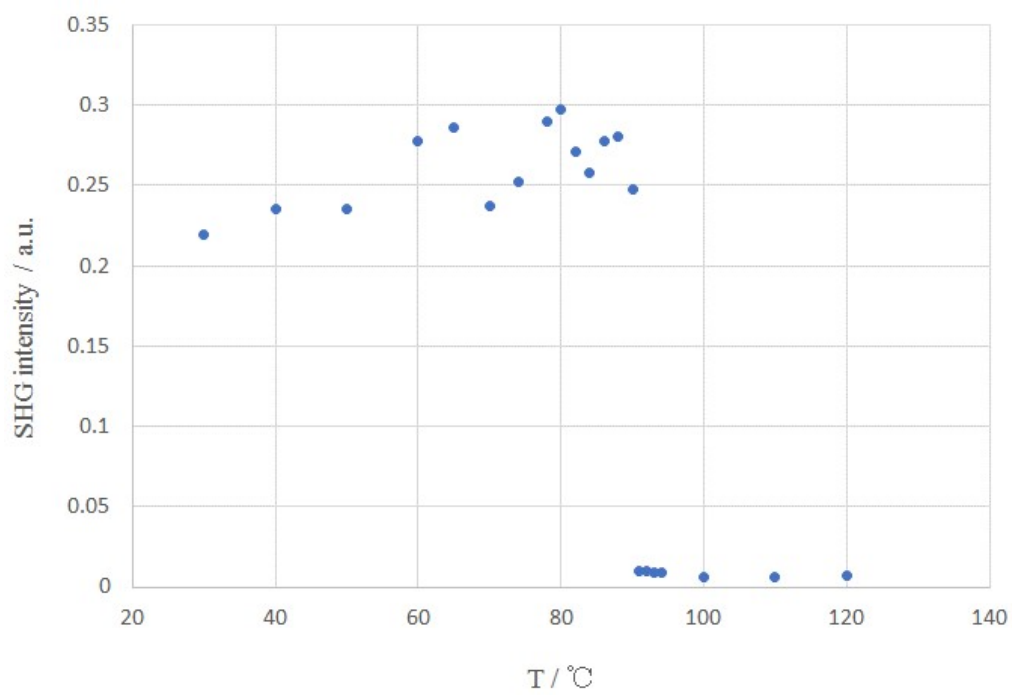
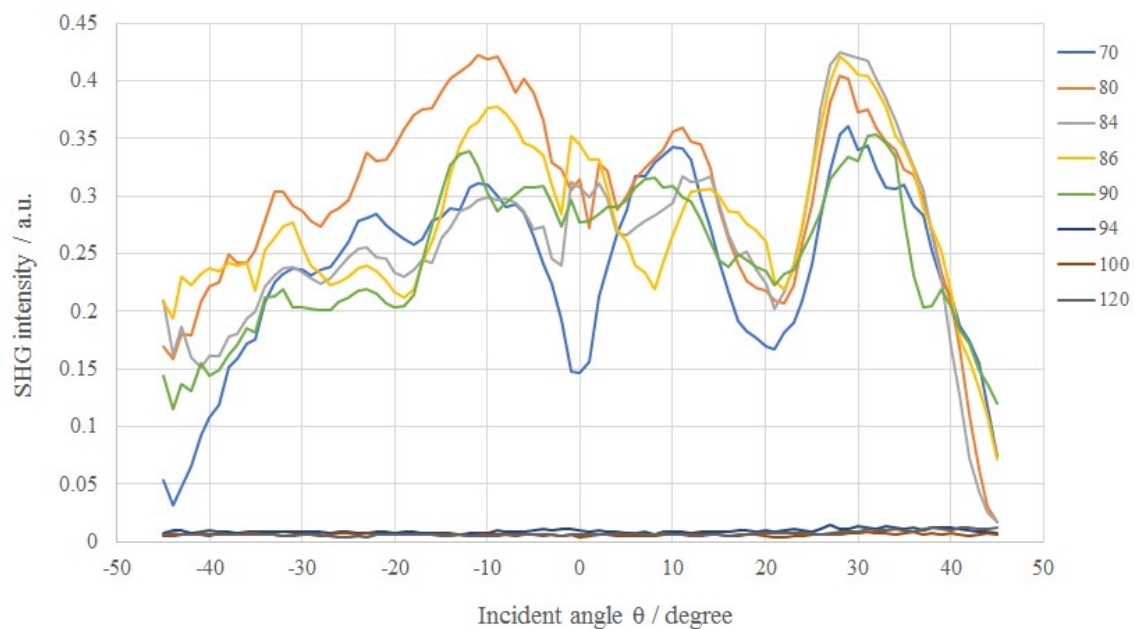


Figure S19 SHG results of 8.

#### 4. Characterization of C3-DIO analogues in Group III

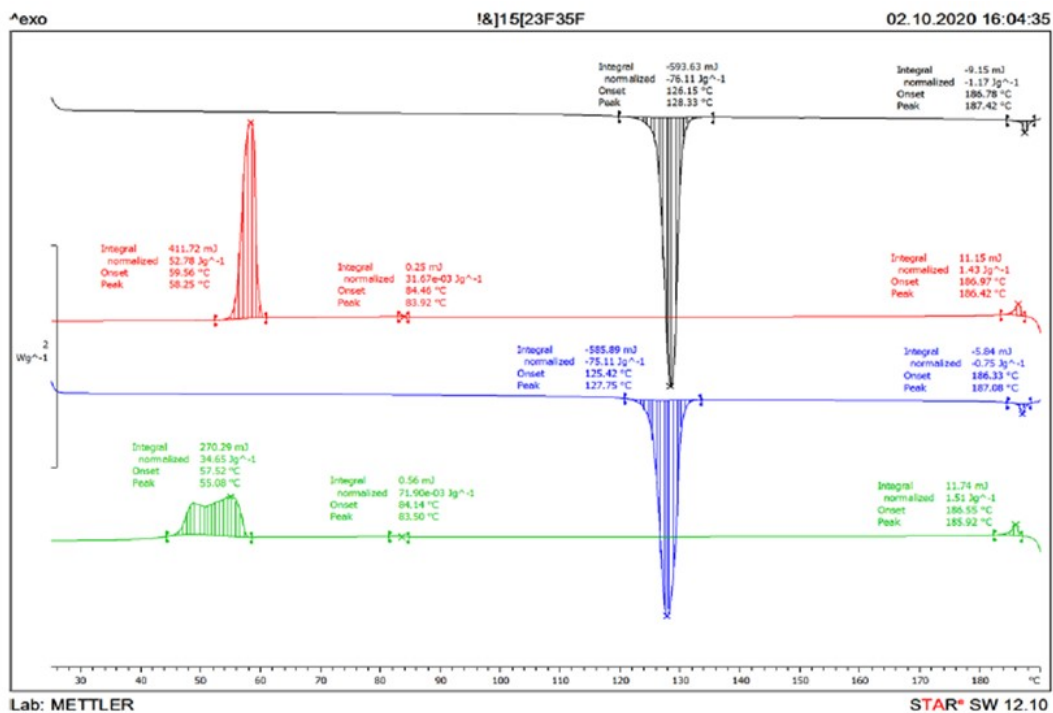


Figure S20 DSC charts of 9. Black line: 1st heating. Red line: 1st cooling. Blue line: 2d heating. Green line: 2nd cooling. Rate: 5°C min<sup>-1</sup>

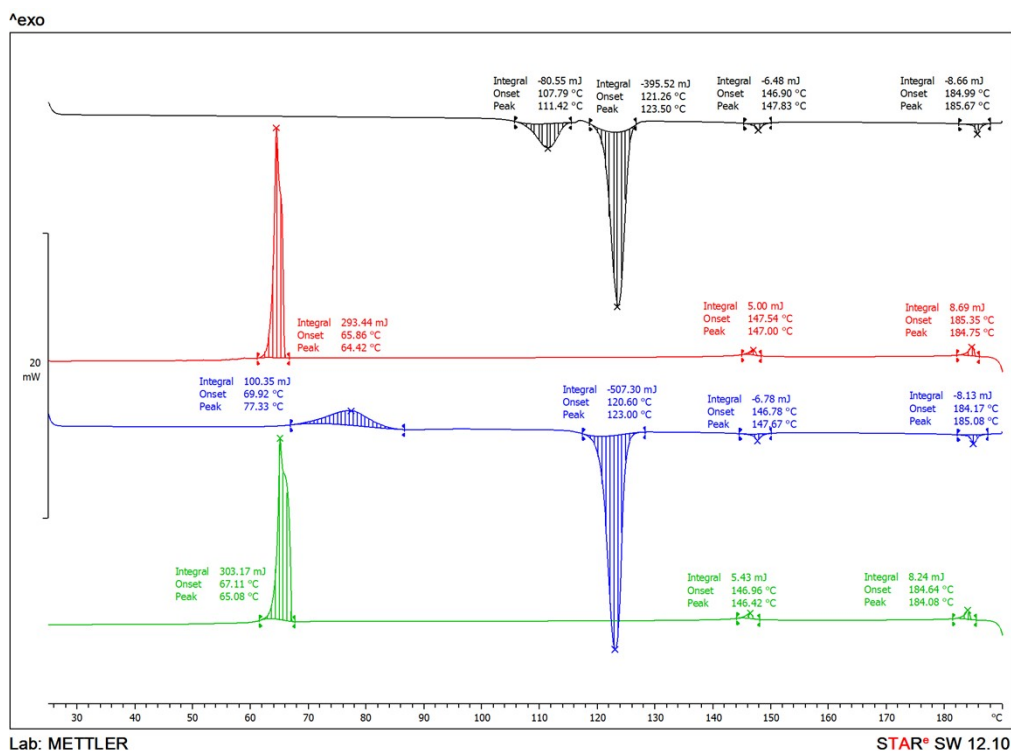
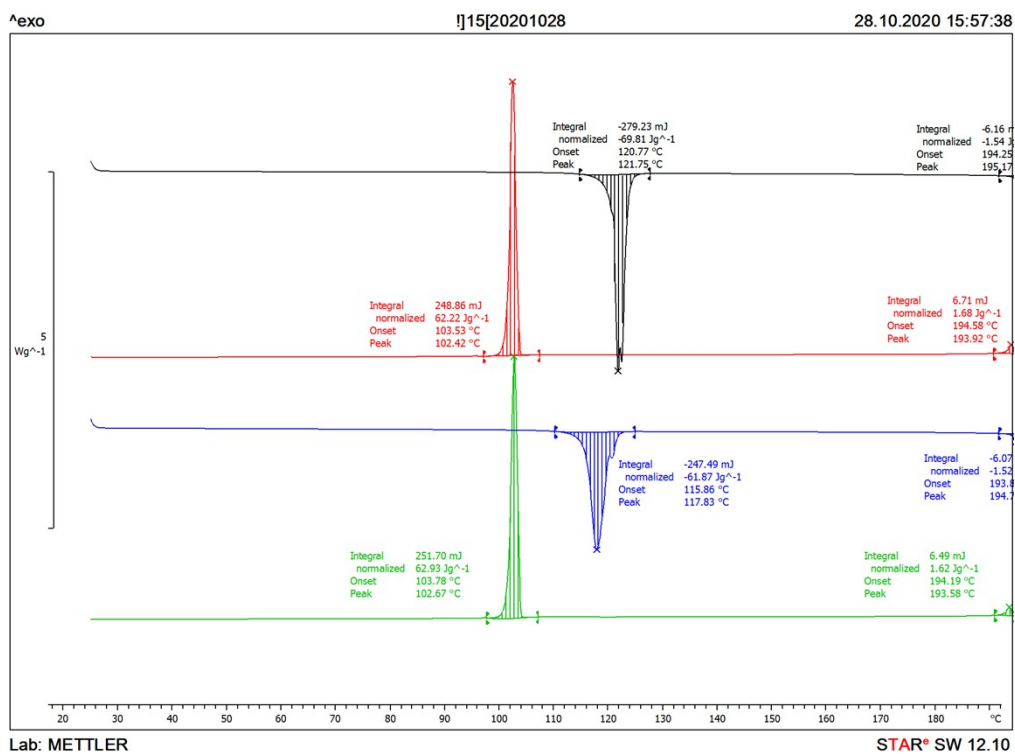
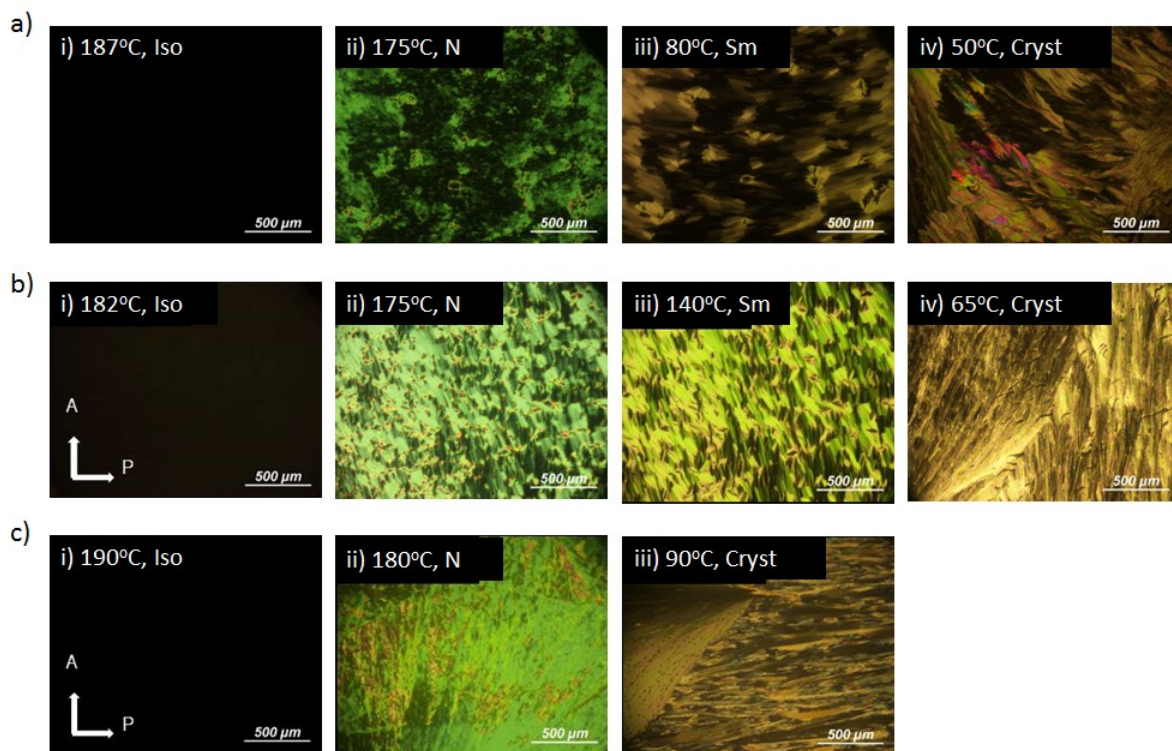


Figure S21 DSC charts of 10. Black line: 1st heating. Red line: 1st cooling. Blue line: 2d heating. Green line:

2nd cooling. Rate: 5°C min<sup>-1</sup>.

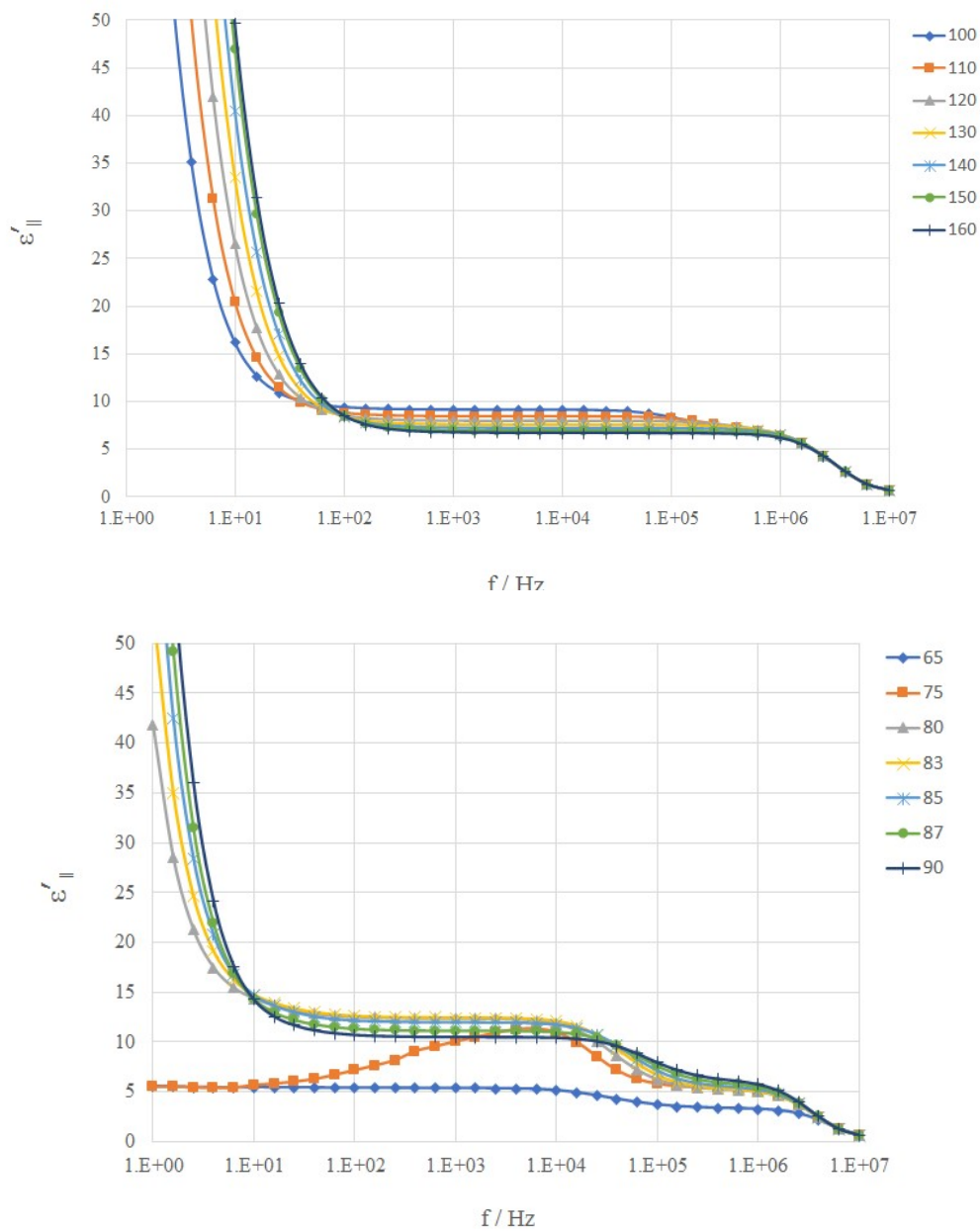


**Figure S22** DSC charts of **11**. Black line: 1st heating. Red line: 1st cooling. Blue line: 2d heating. Green line: 2nd cooling. Rate: 5°C min<sup>-1</sup>

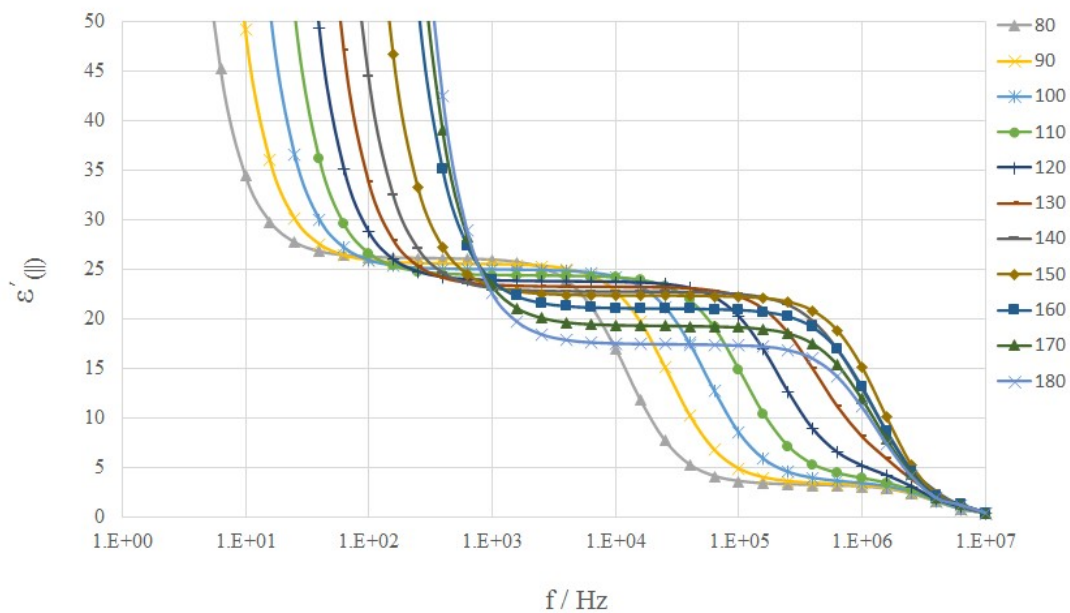


**Figure S23** POM images of a) **9**, b) **10** and c) **11** in the cooling run. The samples were introduced in cells

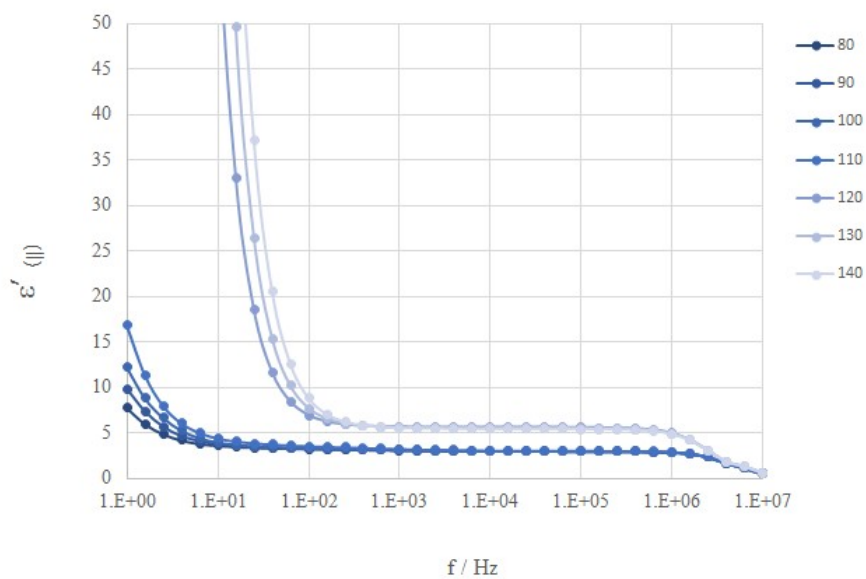
composed of non-treated glass substrates and then observed for their phase transition behavior.



**Figure S24** Frequency dependences of dielectric constant of **9** in the cooling process. Top: 100-160°C. Bottom: 65-90°C.

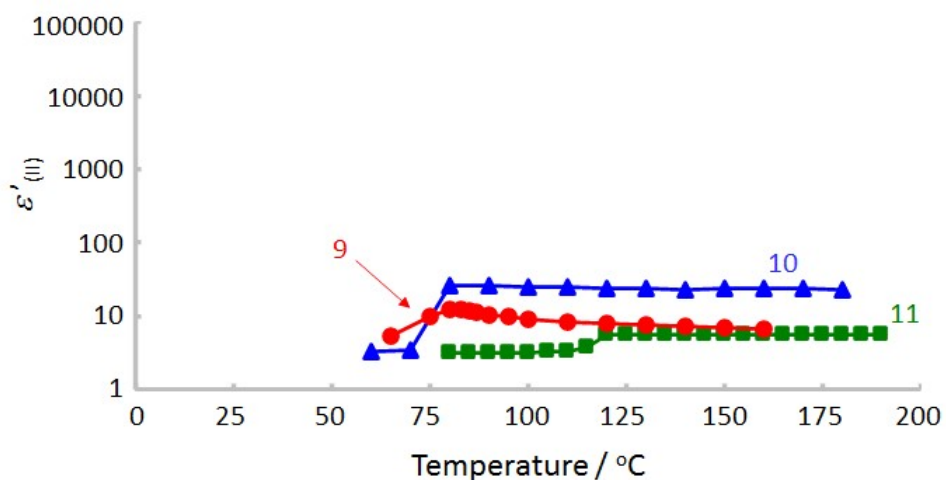


**Figure S25** Frequency dependences of dielectric constant of **10** in the cooling process.

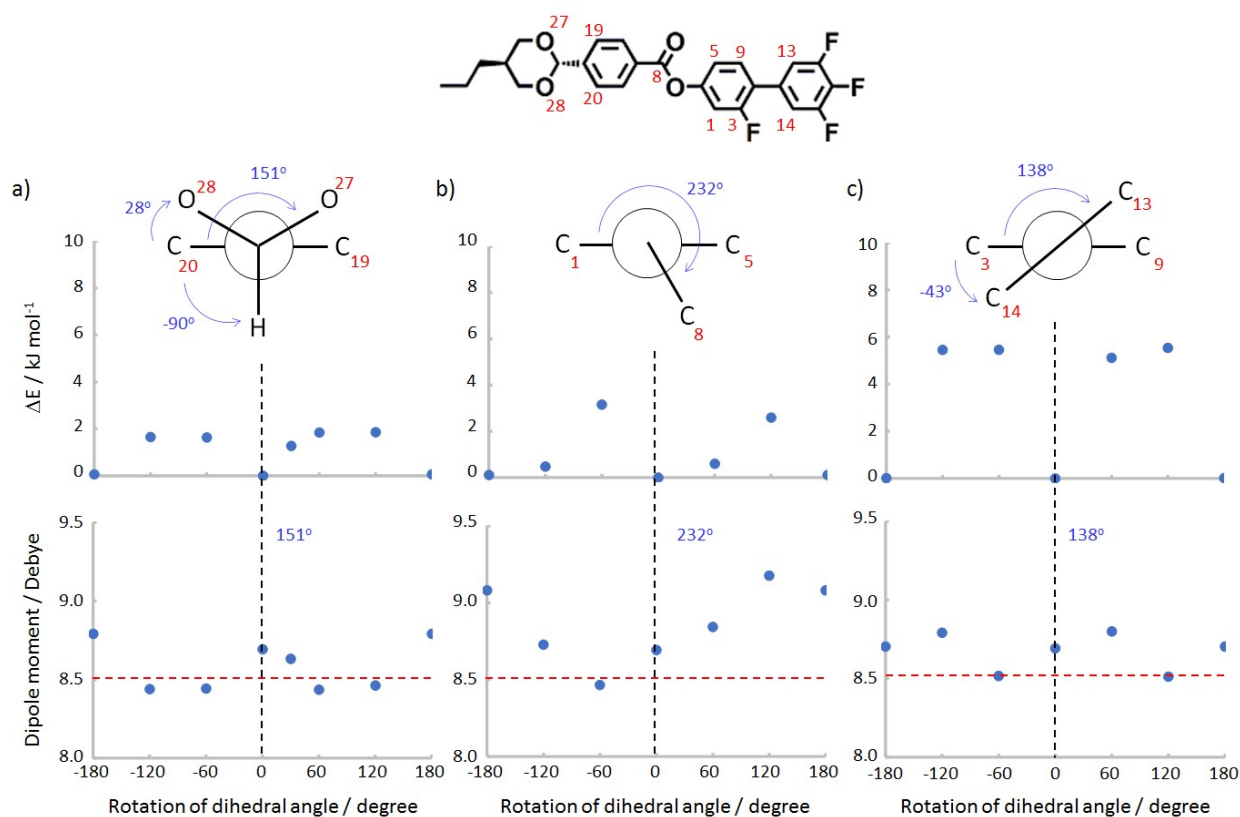


**Figure S26** Frequency dependences of dielectric constant of **11** in the cooling process.



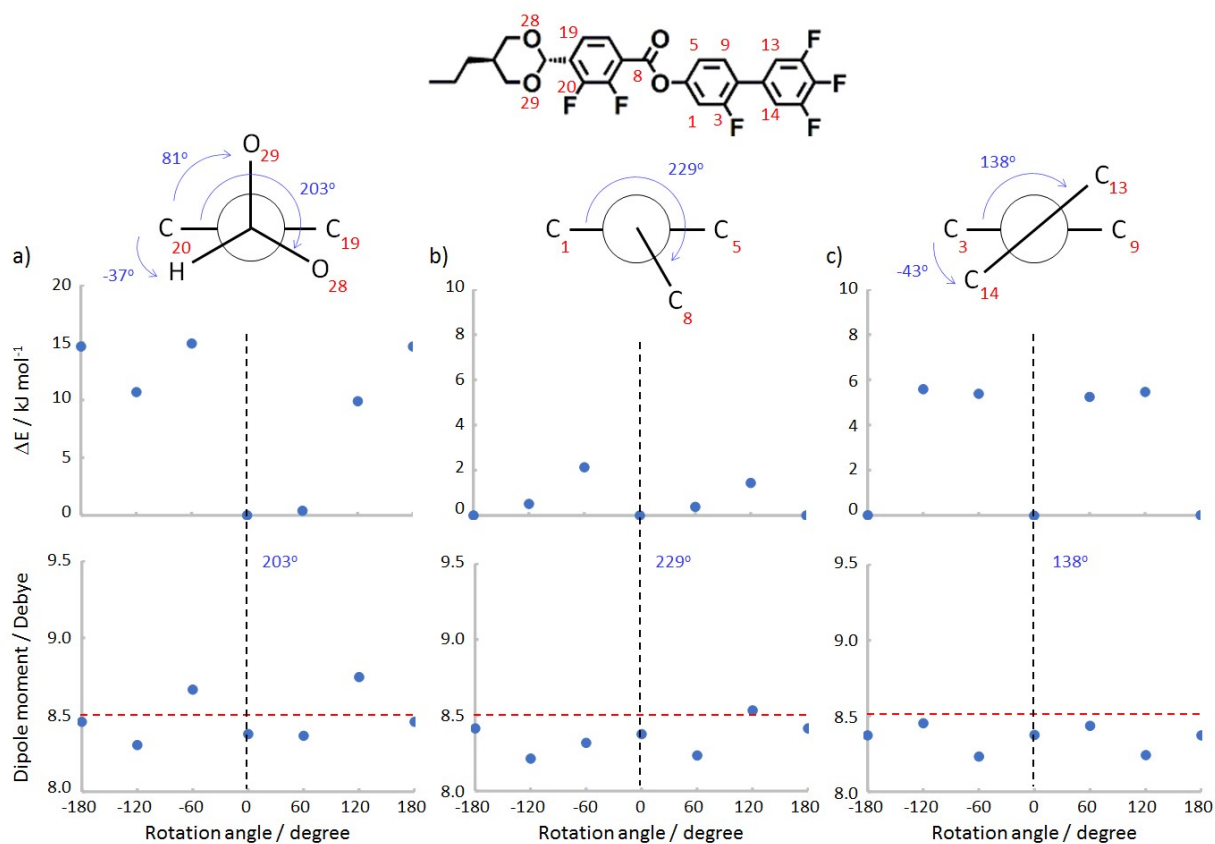


**Figure S27** Temperature dependence of dielectric constants of **9** (red circles), **10** (blue triangles) and **11** (green squares) in the cooling run.  $f = 1$  kHz.  $0.1 V_{rms}$ .



**Figure S28** Energy and dipole changes as a function of the rotation of a) dioxane-phenyl, b) O-phenyl and c) phenyl-phenyl bonds of **3**. Horizontal axes mean the change of dihedral angles of a) O27-C-C-C20, b) C8-O-C-

C1 and c) C13-C-C-C3. Zero positions are 151, 232 and 138° for O27-C-C-C20, C8-O-C-C1 and C13-C-C-C3, respectively.



**Figure S29** Energy and dipole changes as a function of the rotation of a) dioxane-phenyl, b) O-phenyl and c) phenyl-phenyl bonds of **4**. Horizontal axes mean the change of dihedral angles of a) O28-C-C-C20, b) C8-O-C-C1 and c) C13-C-C-C3. Zero positions are 203, 229 and 138° for O28-C-C-C20, C8-O-C-C1 and C13-C-C-C3, respectively.