**Supporting information for**

# Sulfur-based ferroelectric nematic liquid crystals

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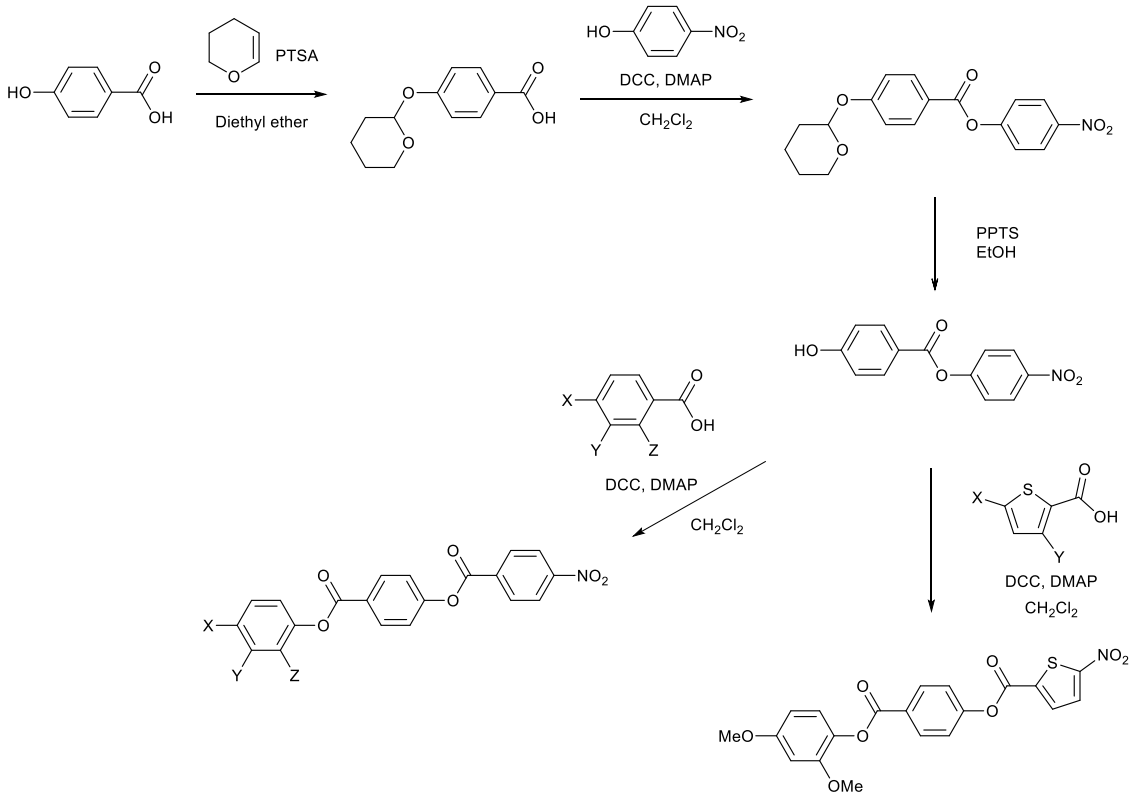
**Table of Contents**

## 1. Synthesis

### 1.1. Synthesis of 1–5 and 8–19

Compounds **1**–**5** and **8**–**19** were synthesized as shown in Scheme S1. The synthesis procedures are described below.




Scheme S1. Synthesis of compounds **1**–**5** and **8**–**19**.

4-[(Tetrahydro-2H-pyran-2-yl)oxy]benzoic acid

4-Hydroxybenzoic acid (12.0 g, 86.9 mmol), *p*-toluenesulfonic acid monohydrate (PTSA) (12.0 g, 86.9 mmol), and diethyl ether (100 mL) were put in a two-neck ground flask, which was purged with an argon gas. The mixture (suspension) was cooled to 0°C on an ice bath and 3,4-Dihydro-2H-pyran (10 mL, 111 mmol) was subsequently added dropwise to the suspension, causing a transparent solution. After stirring for 20h at ambient temperature, a white solid was precipitated in the solution and collected through vacuum filtration and washing with a plenty amount of diethyl ether, obtaining 10.7 g of 4-[(etrahydro-2H-pyran-2-yl)oxy]benzoic acid. Yield: 55%. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 9.0 Hz, 2H), 7.10 (d, *J* = 9.0 Hz, 2H), 5.53 (t, *J* = 3.0 Hz, 1H), 3.91–3.82 (m, 1H), 3.67–3.60 (m, 1H), 2.09–1.95 (m, 1H), 1.94–1.86 (m, 2H), 1.79–1.65 (m, 2H), 1.65–1.57 (m, 1H) ppm.

4-Nitrophenyl 4-[(tetrahydro-2H-pyran-2-yl)oxy]benzoate

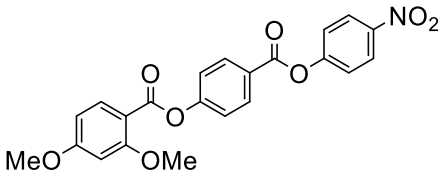
4-[(Tetrahydro-2H-pyran-2-yl)oxy]benzoic acid (2.00 g, 9.00 mmol), 4-nitrophenol (1.25 g, 9.00 mmol), and 4-dimethylaminopyridine (DMAP) (0.55 g, 4.5 mmol) were dissolved in dehydrated dichloromethane (10 mL) in a double-necked flask with an argon atmosphere. In another double-necked round ground flask, *N*,*N*′-dicyclohexylcarbodiimide (DCC) (2.80 g, 13.6 mmol) was dissolved in dehydrated dichloromethane (10 mL) under an argon atmosphere, and then the solution was dropwise to the prior mixture at 0°C on an ice bath. After stirring for 1 h at room temperature, the mixture was filtrated off to remove insoluble solids, and volatiles were evaporated. The residue was purified by column chromatography on silica gel with an eluent of a mixed solvent (dichloromethane/hexane = 1/1, v/v) to afford 2.63 g of 4-nitrophenyl 4-[(tetrahydro-2H-pyran-2-yl)oxy]benzoate. Yield: 85%. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 9.5 Hz, 2H), 8.14 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 9.5 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 5.67 (t, *J* = 3.0 Hz, 1H), 3.90–3.82 (m, 1H), 3.69–3.61 (m, 1H), 2.08–1.98 (m, 1H), 1.96–1.88 (m, 2H), 1.79–1.67 (m, 2H), 1.67–1.59 (m, 1H) ppm.

4-Nitrophenyl 4-hydroxybenzoate

A mixture of 4-nitrophenyl 4-[(tetrahydro-2H-pyran-2-yl)oxy]benzoate (2.61 g, 7.59 mmol), pyridinium *p*-toluenesulphonate (PPTS) (0.388 g, 1.54 mmol), THF (30 mL), and EtOH (30 mL) was stirred at 60°C for 6h. The reaction mixture was extracted with ethyl acetate and washed with water and brine. The volatiles were evaporated to give 2.00 g of nitrophenyl 4-hydroxybenzoate as a colorless solid. The obtained compound was used for next esterification reactions without further purification. Yield: >100%. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 9.0 Hz, 2H), 8.12 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 5.36 (s, 1H) ppm.

The target compounds **1**–**5** and **8**–**19** were synthesized in similar procedures to the typical condensation esterification with DCC as above mentioned.

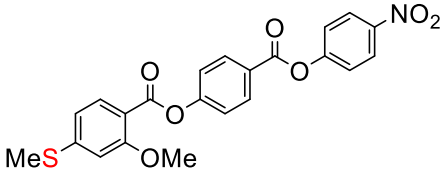
4-((4-nitrophenoxy)carbonyl)phenyl 2,4-dimethoxybenzoate (**1**, **RM734**)




$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 9.0 Hz, 2H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 6.59 (dd, *J* = 2.5 and

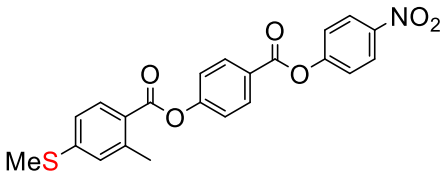
9.0 Hz, 1H), 6.55 (dd, $J$ = 2.5 Hz, 1H), 3.06 (s, 3H), 3.00 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.4, 163.6, 162.8, 162.5, 156.0, 155.7, 145.4, 134.6, 131.9, 125.6, 125.3, 122.6, 122.5, 110.4, 105.0, 99.0, 56.0, 55.6 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{22}H_{17}NNaO_8$, 446.0846; found, 446.0846.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-methoxy-4-(methylthio)benzoate (**2**)



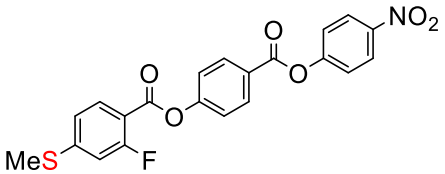

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, $J$ = 8.5 Hz, 2H), 8.26 (d, $J$ = 8.5 Hz, 2H), 8.02 (d, $J$ = 8.0 Hz, 1H), 7.44 (d, $J$ = 9.0 Hz, 2H), 7.40 (d, $J$ = 9.0 Hz, 2H), 6.90–6.86 (m, 2H), 3.96 (s, 3H), 2.56 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.6, 162.9, 160.5, 155.8, 155.7, 148.4, 145.4, 132.9, 131.9, 125.7, 125.3, 122.6, 122.4, 116.6, 114.0, 109.0, 56.1, 14.8 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{22}H_{17}NNaO_7S$, 462.0618; found, 462.0618.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-methyl-4-(methylthio)benzoate (**3**)




$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, $J$ = 9.0 Hz, 2H), 8.29 (d, $J$ = 9.0 Hz, 2H), 8.02 (d, $J$ = 9.0 Hz, 1H), 7.44 (d, $J$ = 9.0 Hz, 2H), 7.39 (d, $J$ = 9.0 Hz, 2H), 7.18–7.14 (m, 2H), 2.67 (s, 3H), 2.55 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.5, 163.4, 155.7, 155.6, 146.1, 145.5, 142.4, 132.0, 131.8, 128.2, 125.9, 125.3, 123.5, 122.6, 122.5, 122.4, 22.2, 14.6 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{22}H_{17}NNaO_6S$, 446.0669; found, 446.0666.

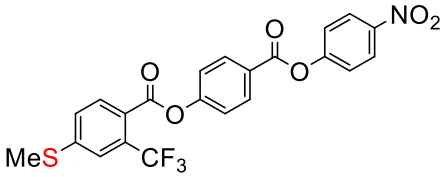
4-((4-Nitrophenoxy)carbonyl)phenyl 2-fluoro-4-(methylthio)benzoate (**4**)




$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, $J$ = 9.0 Hz, 2H), 8.28 (d, $J$ = 9.0 Hz, 2H), 8.01 (dd, $J$ = 8.0 and 10.0 Hz, 1H), 7.44 (d, $J$ = 9.0 Hz, 2H), 7.42 (d, $J$ = 9.0 Hz, 2H), 7.11 (dd,

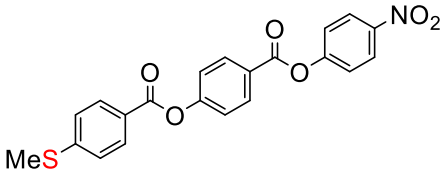
*J* = 2.0 and 10.0 Hz, 1H) 7.03 (dd, *J* = 2.0 and 10.0 Hz, 1H), 2.56 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.7, 163.5, 161.8, 161.7, 161.6, 155.6, 155.3, 150.0, 149.9, 145.5, 132.5, 132.0, 126.1, 125.3, 122.6, 122.3, 120.9, 120.8, 113.2, 113.0, 112.9, 112.8, 14.7 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{21}H_{14}FNNaO_6S$, 450.0418; found, 450.0422.

4-((4-Nitrophenoxy)carbonyl)phenyl 4-(methylthio)-2-(trifluoromethyl)benzoate (**5**)



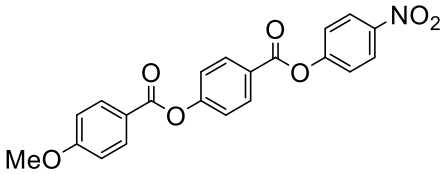

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 9.0 Hz, 2H), 8.29 (d, *J* = 9.0 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.64 (brs, 1H), 7.49 (dd, *J* = 2.0 and 5.0 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 2H) 7.43 (d, *J* = 9.0 Hz, 2H), 2.59 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.7, 163.4, 155.6, 155.2, 146.4, 145.5, 132.1, 131.9, 130.1, 129.9, 127.7, 126.4, 125.3, 124.7, 124.2, 123.81, 123.76, 123.7, 122.6, 121.9, 14.8 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{22}H_{14}F_3NNaO_6S$, 500.0386; found, 500.0393.

4-((4-Nitrophenoxy)carbonyl)phenyl 4-(methylthio)benzoate (**8**)




$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.29 (d, *J* = 9.0 Hz, 2H), 8.11 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 2H), 2.57 (s, 3H) ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{21}H_{15}NNaO_6S$, 432.0512; found, 432.0503.

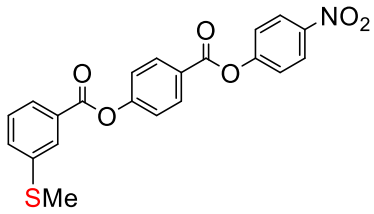
4-((4-Nitrophenoxy)carbonyl)phenyl 4-methoxybenzoate (**9**)




$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 2H), 8.28 (d, *J* = 9.0 Hz, 2H), 8.17 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 3H) ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{21}H_{15}NNaO_7$, 416.0741;

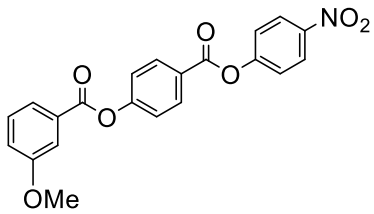
found, 416.0741.

4-((4-Nitrophenoxy)carbonyl)phenyl 3-(methylthio)benzoate (**10**)



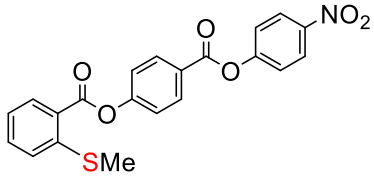

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 9.0 Hz, 2H), 8.30 (d, *J* = 9.0 Hz, 2H), 8.07 (brs, *J* = 8.5 Hz, 1H), 8.00–7.96 (m, 1H), 7.56–7.51 (m, 1H), 7.48–7.39 (m, 5H), 2.57 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.2, 163.4, 155.60, 155.57, 145.5, 140.0, 132.1, 131.8, 129.5, 129.1, 127.6, 126.7, 126.2, 125.3, 122.6, 122.3, 15.6 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{21}H_{15}NNaO_6S$, 432.0512; found, 432.0503.

4-((4-Nitrophenoxy)carbonyl)phenyl 3-methoxybenzoate (**11**)



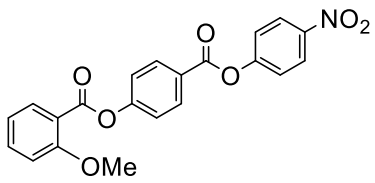

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 9.0 Hz, 2H), 8.30 (d, *J* = 9.0 Hz, 2H), 7.85–7.79 (m, 1H), 7.73–7.70 (m, 1H),7.48–7.39 (m, 5H), 7.24–7.20 (m, 1H), 3.90 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.4, 163.5, 159.8, 155.7, 155.6, 145.5, 132.0, 130.1, 129.8, 126.1, 125.3, 122.7, 122.6, 122.3, 120.5, 114.7, 55.5 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{21}H_{15}NNaO_7$, 416.0741; found, 416.0744.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-(methylthio)benzoate (**12**)



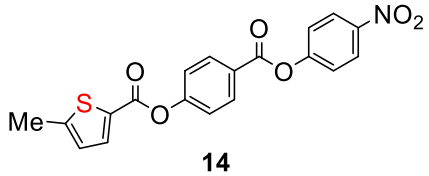

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.31–8.25 (m, 3H), 7.62–7.56 (m, 1H), 7.43 (d, *J* = 2.5 Hz, 2H), 7.41 (d, *J* = 2.5 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 1H), 2.51 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.9, 163.5, 155.6, 155.5, 145.5, 145.0, 133.5, 132.1, 132.0, 126.0, 125.3, 125.1, 124.6, 123.6, 122.6, 122.4, 15.6 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{21}H_{15}NNaO_6S$, 432.0512; found, 432.0503.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-methoxybenzoate (**13**)




$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.5 Hz, 2H), 8.27 (d, *J* = 8.5 Hz, 2H), 8.10–8.03 (m, 1H), 7.63–7.55 (m, 1H), 7.44 (d, *J* = 9.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.63–7.55 (m, 2H), 3.97 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.54, 163.46, 160.2, 155.8, 155.7, 145.4, 134.9, 132.3, 131.9, 125.8, 125.3, 122.6, 122.4, 120.3, 118.2, 112.3, 56.1 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{21}H_{15}NNaO_7$, 416.0741; found, 416.0736.

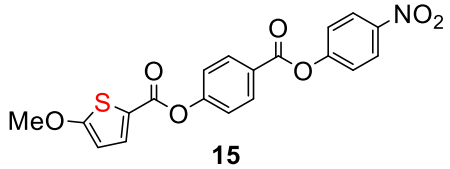
4-((4-Nitrophenoxy)carbonyl)phenyl 5-methylthiophene-2-carboxylate (**14**)




**14**

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.27 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 4.0 Hz, 1H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 4.0 Hz, 1H), 2.60 (s, 3H) ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{19}H_{13}NNaO_6S$, 406.0356; found, 406.0364.

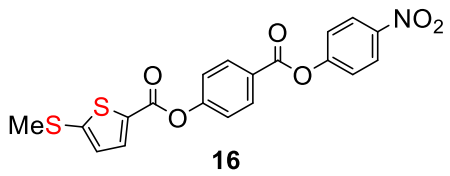
4-((4-Nitrophenoxy)carbonyl)phenyl 5-methoxythiophene-2-carboxylate (**15**)




**15**

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 4.0 Hz, 1H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.34 (d, *J* = 4.0 Hz, 1H), 4.01 (s, 3H) ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{19}H_{13}NNaO_7S$, 422.0305; found, 422.0317.

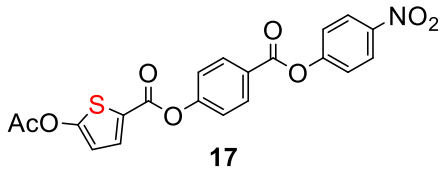
4-((4-Nitrophenoxy)carbonyl)phenyl 5-(methylthio)thiophene-2-carboxylate (**16**)




**16**

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 2H), 8.27 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 4.0 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 4.0 Hz, 1H), 2.64 (s, 3H) ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{19}H_{13}NNaO_6S_2$, 438.0076; found, 438.0069.

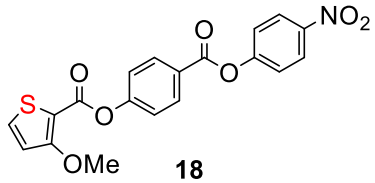
4-((4-Nitrophenoxy)carbonyl)phenyl 5-acetoxythiophene-2-carboxylate (**17**)




**17**

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.5 Hz, 2H), 8.30 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 4.0 Hz, 1H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 4H), 2.64 (s, 3H) ppm.

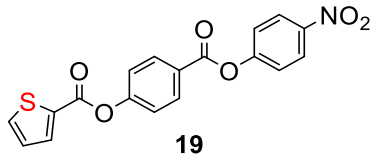
4-((4-Nitrophenoxy)carbonyl)phenyl 3-methoxythiophene-2-carboxylate (**18**)




**18**

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 9.0 Hz, 2H), 7.59 (d, *J* = 5.0 Hz, 1H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 5.0 Hz, 1H), 4.05 (s, 3H) ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{19}H_{13}NNaO_7S$, 422.0305; found, 422.0305.

4-((4-Nitrophenoxy)carbonyl)phenyl thiophene-2-carboxylate (**19**)



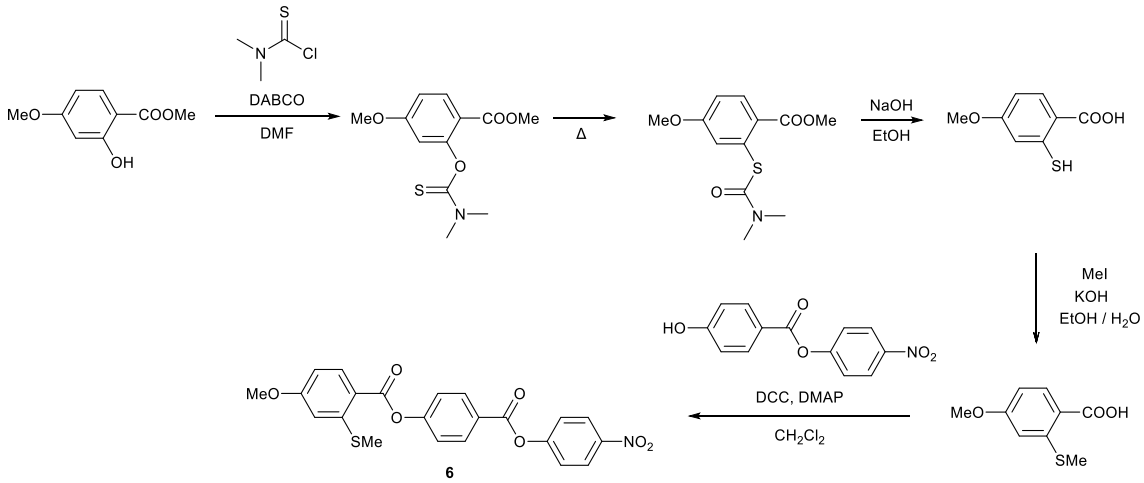

**19**

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.29 (d, *J* = 9.0 Hz, 2H), 8.03 (dd, *J* = 1.5 and 4.0 Hz, 1H), 7.73 (dd, *J* = 1.5 and 5.0 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 2H),

7.43 (d, *J* = 9.0 Hz, 2H), 7.22 (dd, *J* = 4.0 and 5.0 Hz, 1H) ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{18}H_{11}NNaO_6S$, 392.0199; found, 392.0211.

### 1.2. Synthesis of 6

Compound **6** was synthesized as shown in Scheme S2. The synthesis procedures are described below.




Scheme S2. Synthesis of **6**.

Methyl 2-[(dimethylcarbamothioyl)oxy]-4-methoxybenzoate

A mixture of methyl 2-hydroxy-4-methoxybenzoate (4.01 g, 22.0 mmol), dimethylthiocarbamoyl chloride (3.29 g, 26.6 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (3.00 g, 26.7 mmol), and dehydrated dichloromethane (20 mL) was put stirred for 21h at room temperature under an argon atmosphere. The reaction mixture was filtrated off to remove insoluble solids and the volatiles were evaporated. The residue was purified by purified by column chromatography on silica gel with dichloromethane as an eluent to afford 3.01 g of methyl 2-[(dimethylcarbamothioyl)oxy]-4-methoxybenzoate as a pale gray solid. Yield: 51%.$^1$H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.0 Hz, 1H), 6.83 (dd, *J* = 2.5 and 5.0 Hz, 1H), 6.64 (d, *J* = 2.5 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.47 (s, 3H), 3.40 (s, 3H) ppm.

Methyl 2-[(dimethylcarbamoyl)thio]-4-methoxybenzoate

Methyl 2-[(dimethylcarbamothioyl)oxy]-4-methoxybenzoate (3.00 g, 11.1 mmol) was put in a two-necked flask, which was then purged with an argon gas. The mixture was heated to 210°C and kept at the temperature for 4h. The reactant was cooled to room

temperature and purified by silica-gel column chromatography with dichloromethane as an eluent to give 2.36 g of methyl 2-[(dimethylcarbamoyl)thio]-4-methoxybenzoate a brown oil. Yield: 79% yield. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 1H), 7.17 (d, *J* = 2.5 Hz, 1H), 6.91 (d, *J* = 2.5 and 8.5 Hz, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 3.14 (s, 3H), 3.03 (s, 3H) ppm.

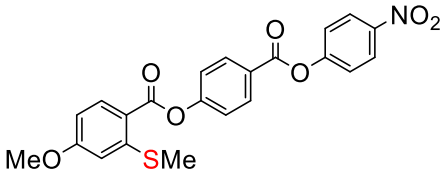
2-Mercapto-4-methoxybenzoic acid

A mixture of methyl 2-[(dimethylcarbamoyl)thio]-4-methoxybenzoate (2.32 g, 8.63 mmol), NaOH (1.04 g, 25.9 mmol), and distilled water (20 ml) was stirred at reflux temperature under an argon atmosphere for 24h. The reaction mixture was acidified with 2M HCl aq. at 0°C on an ice bath, causing solids. The solids were collected through vacuum filtration and washed with a plenty amount of distilled water, to afford 2-mercapto-4-methoxybenzoic acid. Yield: 63%. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 1H), 6.82 (d, *J* = 2.5 Hz, 1H), 6.71 (d, *J* = 2.5 and 8.5 Hz, 1H), 5.10 (s, 1H), 3.85 (s, 3H) ppm.

4-Methoxy-2-(methylthio)benzoic acid

2-Mercapto-4-methoxybenzoic acid (0.303 g, 1.64 mmol) and KOH (1.04 g, 25.9 mmol) dissolved in distilled water (10 mL), and EtOH (4 mL) were put in a flask. Then, iodomethane (MeI) (1 mL, 16.1 mmol) was added into the flask. The mixture was stirred at room temperature overnight and acidified with 2M HCl aq, causing solids. The solids were collected through vacuum filtration and washed with a plenty amount of distilled water, to afford 4-methoxy-2-(methylthio)benzoic acid as a pale yellow solid. Yield: 66%. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 2.0 Hz, 1H), 6.69 (d, *J* = 2.0 and 8.5 Hz, 1H), 3.89 (s, 1H), 2.45 (s, 3H) ppm.

4-((4-Nitrophenoxy)carbonyl)phenyl 4-methoxy-2-(methylthio)benzoate (**6**)

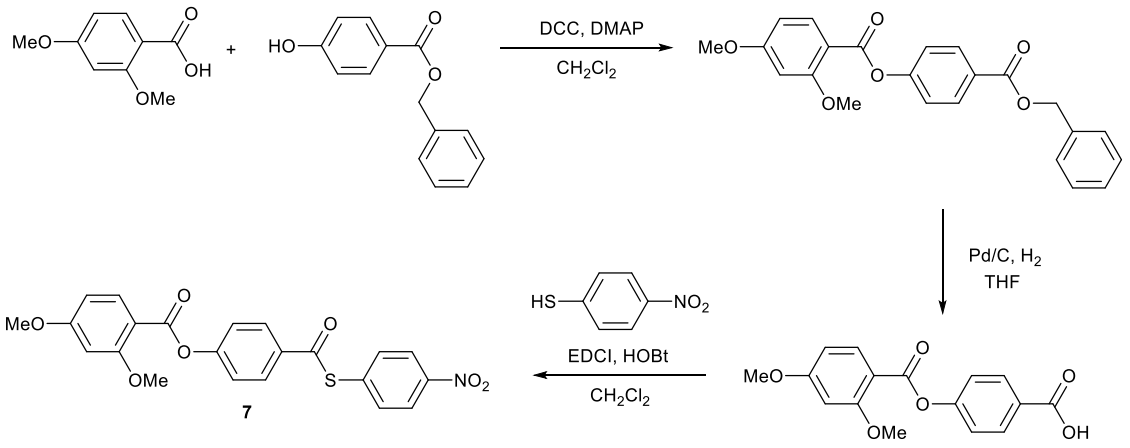



$^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.5 Hz, 2H), 8.27 (brd, *J* = 8.5 Hz, 3H), 7.44 (d, *J* = 9.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 2.5 Hz, 1H), 6.76 (dd, *J* = 2.5 and 5 Hz, 1H) 3.93 (s, 3H), 2.48 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.7, 163.54, 163.49, 155.68, 155.65, 147.7, 145.4, 134.4, 131.9, 125.8, 125.3, 122.6, 122.4, 117.4, 110.6, 108.5, 55.5, 15.6 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for

$C_{22}H_{17}NNaO_7S$, 462.0618; found, 462.0636.

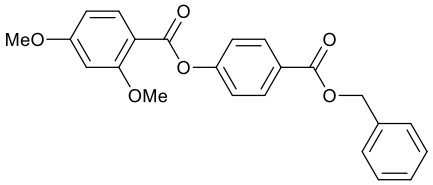
### 1.3. Synthesis of 7

Thioester-based compound **7** was synthesized as shown in Scheme S3. The synthesis procedures are described below.



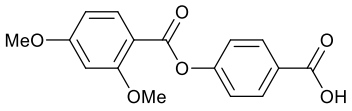

Scheme S3. Synthesis of **7**.

4-[(Benzyloxy)carbonyl]phenyl 2,4-dimethoxybenzoate



This compound was synthesized according to the typical procedure for condensation esterification with DCC. Yield: 92 %. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, $J$ = 8.0 Hz, 2H), 8.07 (d, $J$ = 8.5 Hz, 1H), 7.49-7.22 (m, 7H), 6.56 (dd, $J$ = 2.5 and 9.0 Hz, 1H), 6.53 (d, $J$ = 2.5 Hz, 1H), 5.37 (s, 2H), 3.92 (s, 3H), 3.89 (s, 3H) ppm.

4-[(2,4-Dimethoxybenzoyl)oxy]benzoic acid



4-[(Benzyloxy)carbonyl]phenyl 2,4-dimethoxybenzoate (2.65 g, 6.75 mmol) and 5 wt% of Pd/C (0.132 g) were put in a double-necked round flask, which was then purged with a hydrogen ($H_2$) gas. THF (20 mL) was added into the flask through a syringe and the

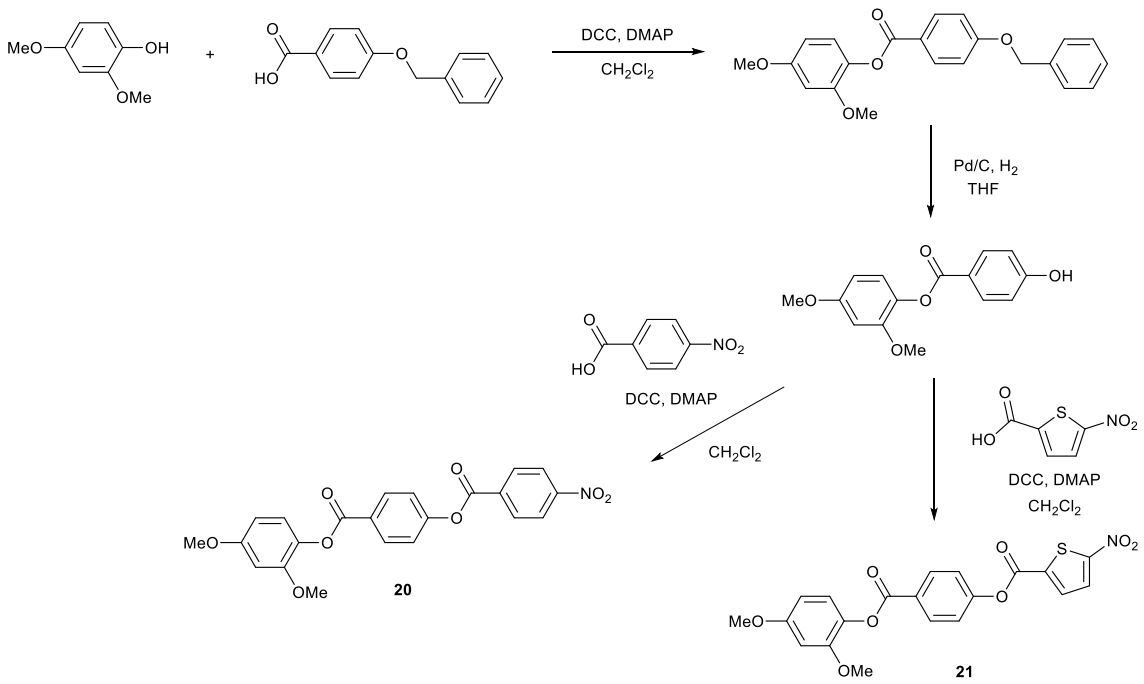
solution was stirred at room temperature. After stirring overnight, the solution was filtrated off through Celite® to remove Pd/C. The volatiles were evaporated to afford 1.85 g of 4-[(2,4-dimethoxybenzoyl)oxy]benzoic acid as a colorless solid. The obtained compound was used for next reactions without further purification. Yield: 91% $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.0 Hz, 2H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.32 (d, *J* = 9.0 Hz, 2H). 6.58 (dd, *J* = 2.5 and 9.0 Hz, 1H), 6.54 (d, *J* = 2.5 Hz, 1H), 6.92 (s, 3H), 3.93 (s, 3H), 3.90 (s, 3H) ppm.

4-(((4-Nitrophenyl)thio)carbonyl)phenyl 2,4-dimethoxybenzoate (**7**)

A mixture of 4-[(2,4-Dimethoxybenzoyl)oxy]benzoic acid (0.30 g, 1.93 mmol), 4-nitrobenzenethiol (0.584 g, 1.93 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) (0.482 g, 2.51 mmol), 1-hydroxybenzotriazole hydrate (HOBt) (0.384 g, 2.51 mmol), and dehydrated dichloromethane (5 mL) in a double-necked flask with an argon atmosphere and stirred at room temperature overnight. The mixture was extracted with dichloromethane and washed with water and brine. The volatiles were evaporated and the residue was purified by column chromatography on silica gel with an eluent of a mixed solvent of dichloromethane/hexane = 3/1 (v/v), which was gradually changed to only dichloromethane, to afford **7**. Yield: 13 %. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.0 Hz, 2H), 8.09 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 2H), 7.73 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 2H), 6.58 (dd, *J* = 2.5 and 9.0 Hz, 1H), 6.55 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 186.9, 165.4, 162.7, 162.5, 156.0, 148.3, 136.0, 135.4, 134.6, 133.0, 129.1, 123.9, 122.6, 110.4, 105.0, 99.0, 56.0, 55.6 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{22}H_{17}NNaO_7S$, 462.0618; found, 462.0627.

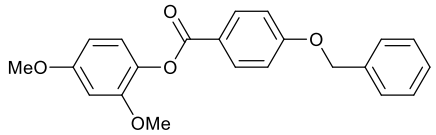
## 1.4. Synthesis of 20 and 21

Compounds **20** and **21** based on inverted ester direction were synthesized as shown in Scheme S4. The synthesis procedures are described below.



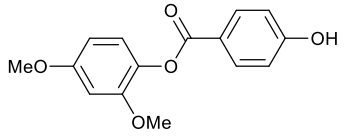

Scheme S4. Synthesis of **20** and **21**.

2,4-Dimethoxyphenyl 4-(benzyloxy)benzoate



This compound was synthesized according to the typical procedure for condensation esterification with DCC. Yield: 100%. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, $J$ = 9.0 Hz, 2H), 7.48–7.32 (m, 5H), 7.08–7.00 (m, 3H), 6.49 (d, $J$ = 2.5 Hz, 1H). 6.48 (dd, $J$ = 2.5 and 9.0 Hz, 1H), 5.16 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H) ppm.

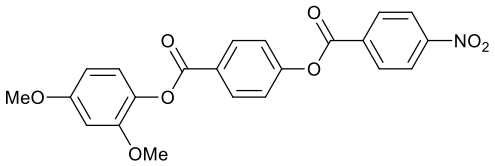
2,4-Dimethoxyphenyl 4-hydroxybenzoate



2,4-Dimethoxyphenyl 4-(benzyloxy)benzoate (1.16 g, 3.18 mmol) and 10 wt% of Pd/C (0.116 g) were put in a double-necked round flask, which was then purged with a

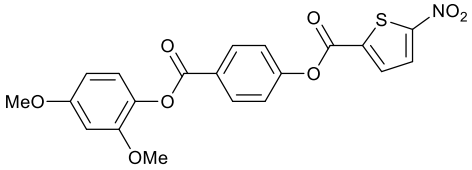
hydrogen ($H_2$) gas. THF (10 mL) was added into the flask through a syringe and the solution was stirred at room temperature. After stirring for 7 h, the solution was filtrated off through Celite® to remove Pd/C. The volatiles were evaporated to afford 0.875 g of 2,4-dimethoxyphenyl 4-hydroxybenzoate as a colorless solid. The obtained compound was used for next reactions without further purification. Yield: 100 %. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 2.5 Hz, 1H). 6.47 (dd, *J* = 2.5 and 8.5 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H) ppm.

4-[(2,4-dimethoxyphenoxy)carbonyl]phenyl 4-nitrobenzoate (**20**)




This compound was synthesized according to the typical procedure for condensation esterification with DCC. Yield: 53%. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 9.5 Hz, 2H), 8.39 (d, *J* = 9.5 Hz, 2H), 8.33 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.60 (d, *J* = 3.0 Hz, 1H), 6.50 (d, *J* = 3.0 and 8.5 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.2, 162.8, 158.6, 154.4, 151.9, 151.1, 134.5, 133.6, 132.1, 131.4, 127.8, 123.8, 122.8, 121.6, 104.0, 100.3, 55.9, 55.6 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{22}H_{17}NNaO_8$, 446.0846; found, 446.0849.

4-[(2,4-Dimethoxyphenoxy)carbonyl]phenyl 5-nitrothiophene-2-carboxylate (**21**)




This compound was synthesized according to the typical procedure for condensation esterification with DCC. Yield: 46 %. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 4.5 Hz, 1H), 7.91 (d, *J* = 4.5 Hz, 1H), 7.38 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 6.50 (d, *J* = 2.5 and 9.0 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.1, 158.6, 156.4, 153.8, 151.9, 137.0, 133.6, 133.2, 132.1, 128.01, 127.96, 122.79, 121.5, 103.9, 100.3, 55.9, 55.6 ppm. HRMS (ESI, m/z): [M+Na]+ calcd. for $C_{20}H_{15}NNaO_8S$, 452.0411; found, 452.0417.

## 2. POM

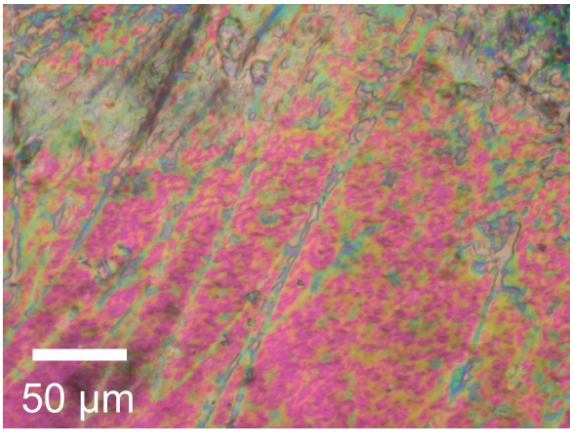



Fig. S1. An optical texture of the N phase taken at 140℃ of **3**.

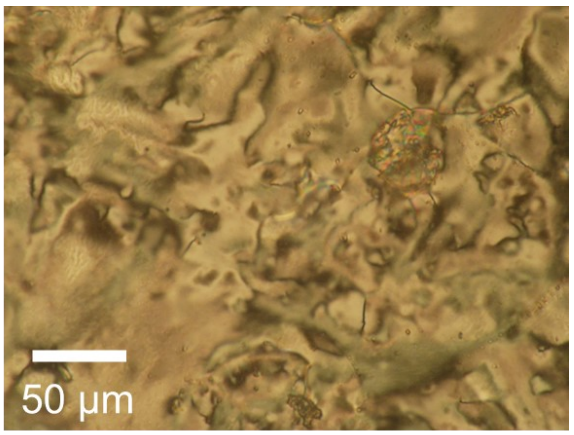



Fig. S2. An optical texture of the N phase taken at 200℃ of **4**.

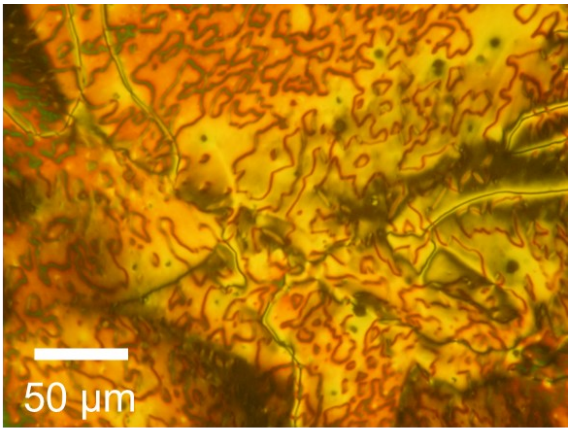



Fig. S3. An optical texture of the N phase taken at 87℃ of **5**.

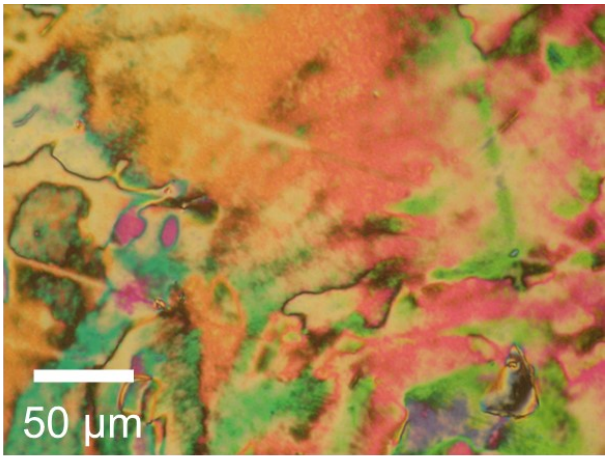



Fig. S4. An optical texture of the N phase taken at 150℃ of **6**.

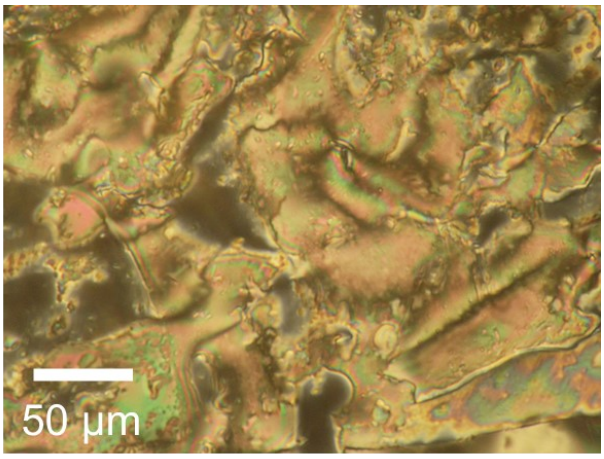



Fig. S5. An optical texture of the N phase taken at 210℃ of **8**.

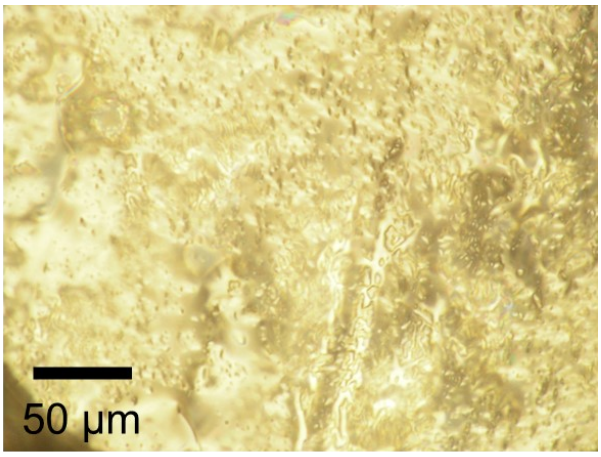



Fig. S6. An optical texture of the N phase taken at 210℃ of **9**.

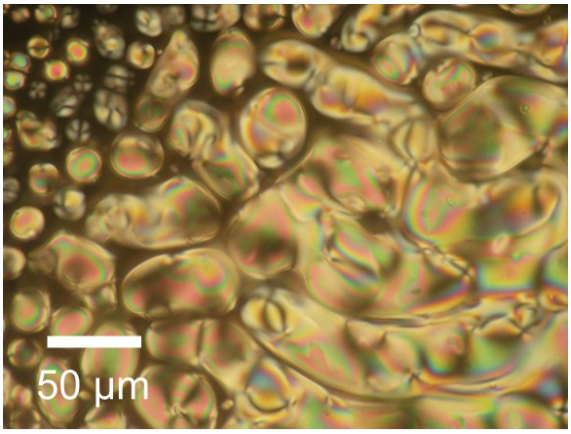



Fig. S7. An optical texture of the N phase (taken at 142°C) of **11**.

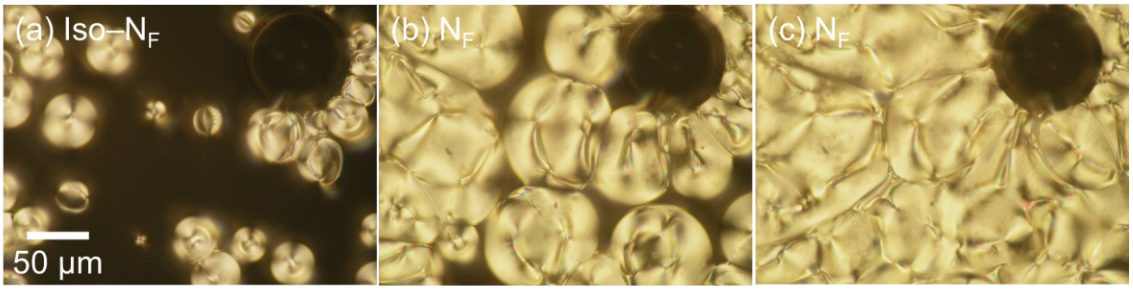



Fig. S8. Optical textures of the direct $N_F$ formation from the Iso phase (taken at 96°C) of **13**.

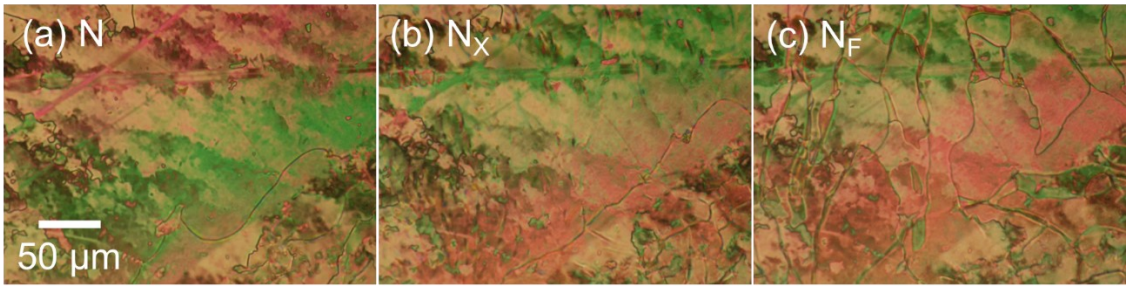



Fig. S9. Optical textures of the (a) N phase (taken at 180°C), (b) $N_X$ phase (taken at 167°C), and $N_F$ phase (taken at 155°C) of **15**.

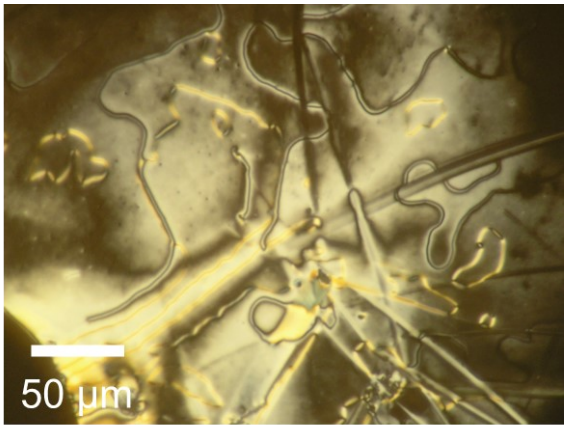



Fig. S10. An optical texture of the N phase (taken at 207°C) of **16**.

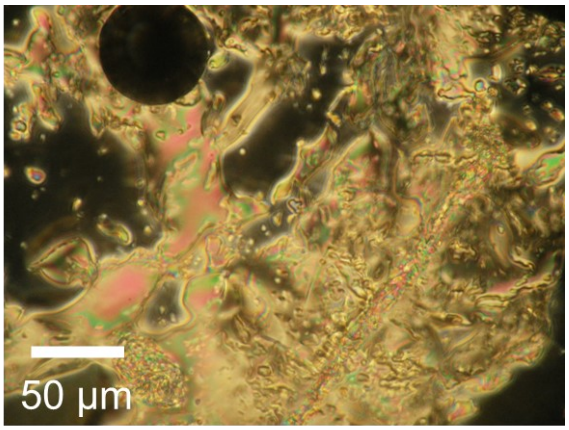



Fig. S11. An optical texture of the N phase (taken at 206°C) of **17**.

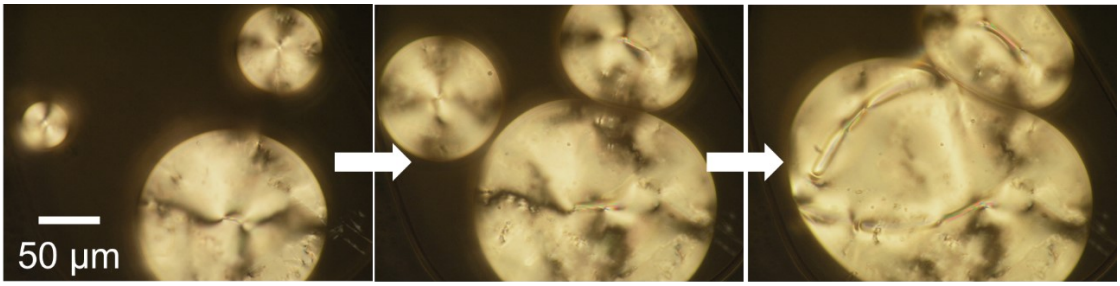



Fig. S12. Optical textures of the direct $N_F$ formation from the Iso phase (taken at 164°C) of **18**.

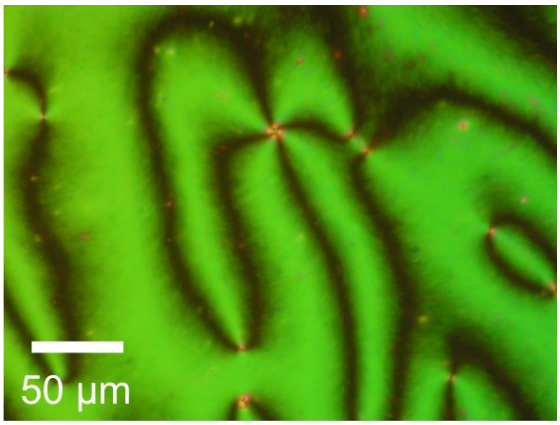



Fig. S13. An optical texture of the N phase (taken at 120°C) of **20.**

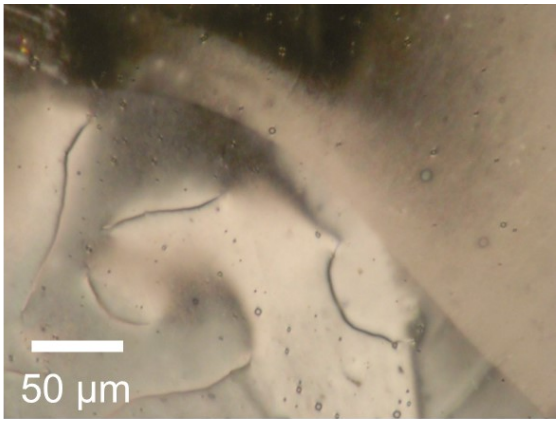



Fig. S14. An optical texture of the N phase (taken at 120°C) of **21.**

## 3. DSC

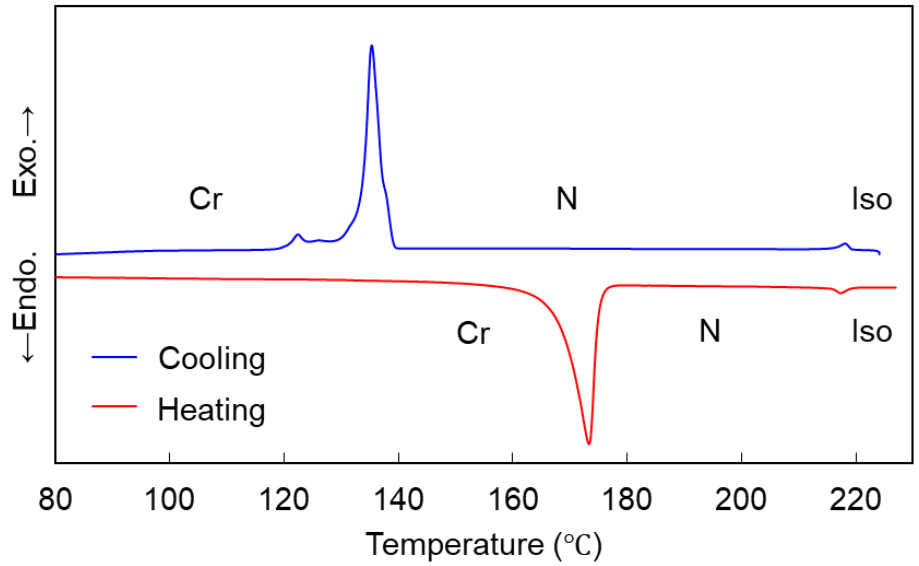



Fig. S15. DSC curves of **7**.

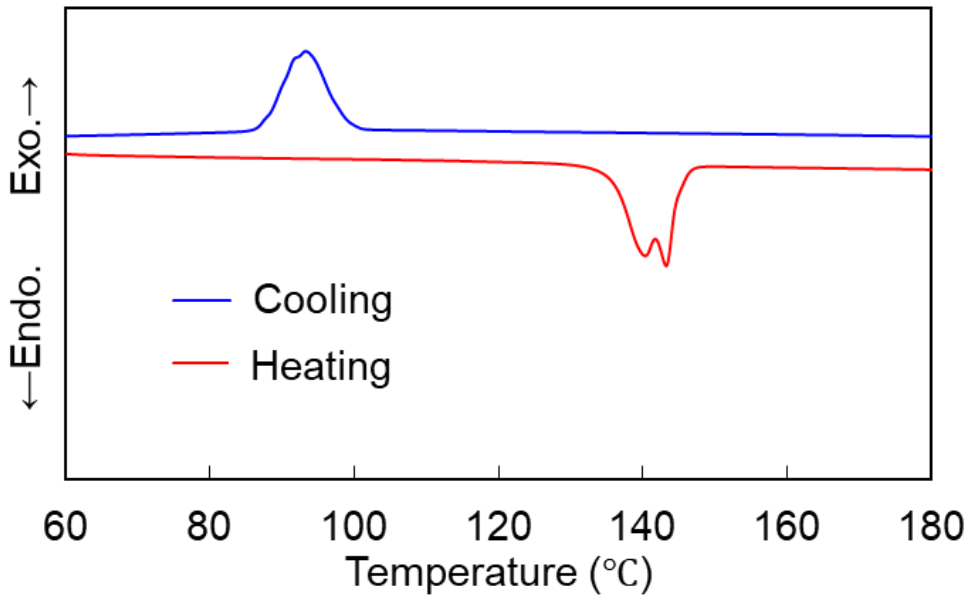



Fig. S16. DSC curves of **13**.

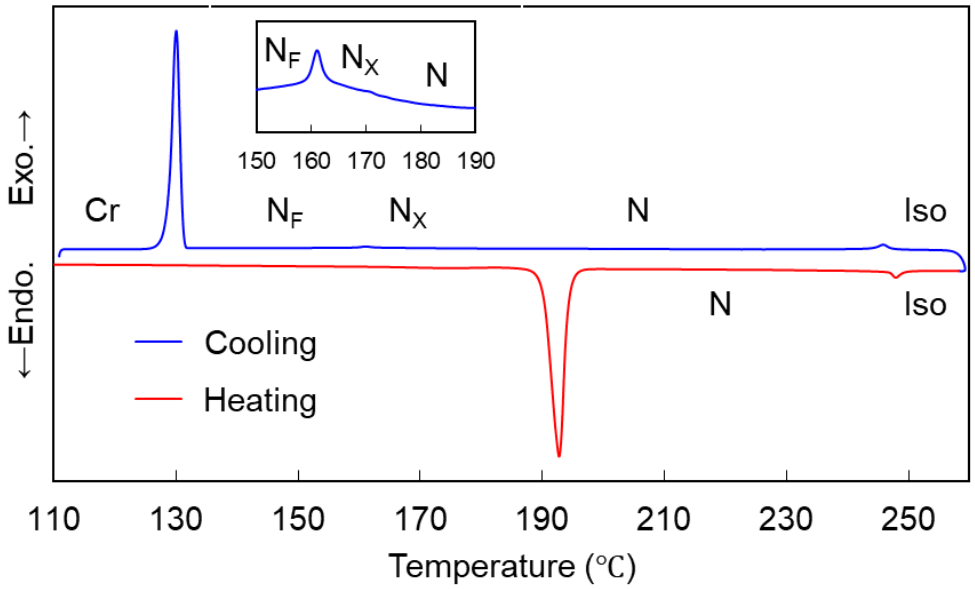



Fig. S17. DSC curves of **15**. The inset is the cooling curve zoomed for $N_X$ and $N_F$ phase transitions.

## 4. SH signals

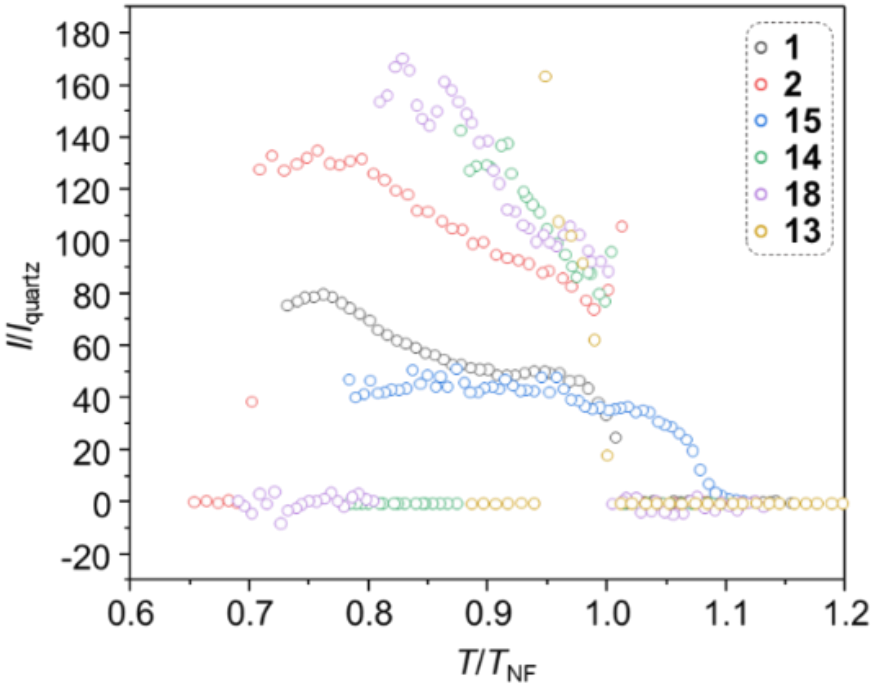



Fig. S18. SH signals ($I$) as a function of reduced temperature ($T/T_{NF}$) for compounds **1**, 2, **13**, **14**, **15**, and **18**. The intensity is scaled with the SH signal of a quartz plate ($I_{quartz}$).

## 5. Birefringence

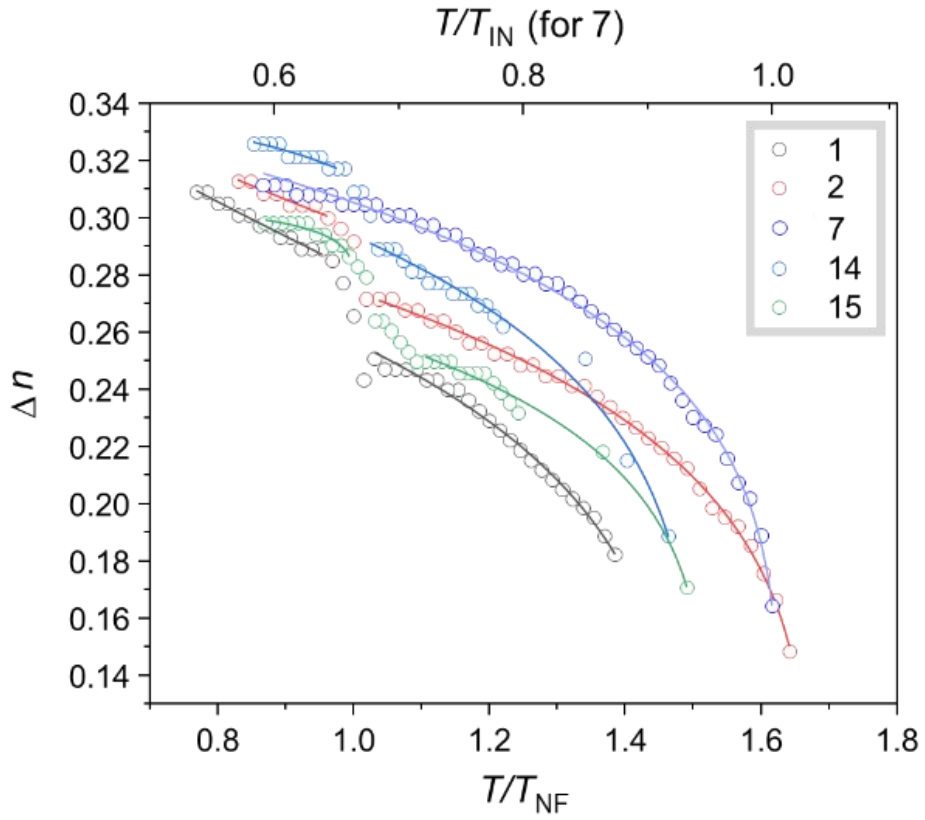



Fig. S19. Birefringence as a function of reduced temperature for compounds **1**, **2**, **7**, **14**, and **15**. Open circles are experimental data. Solid lines are the fitting curves. The measurement is made at λ=550 nm.