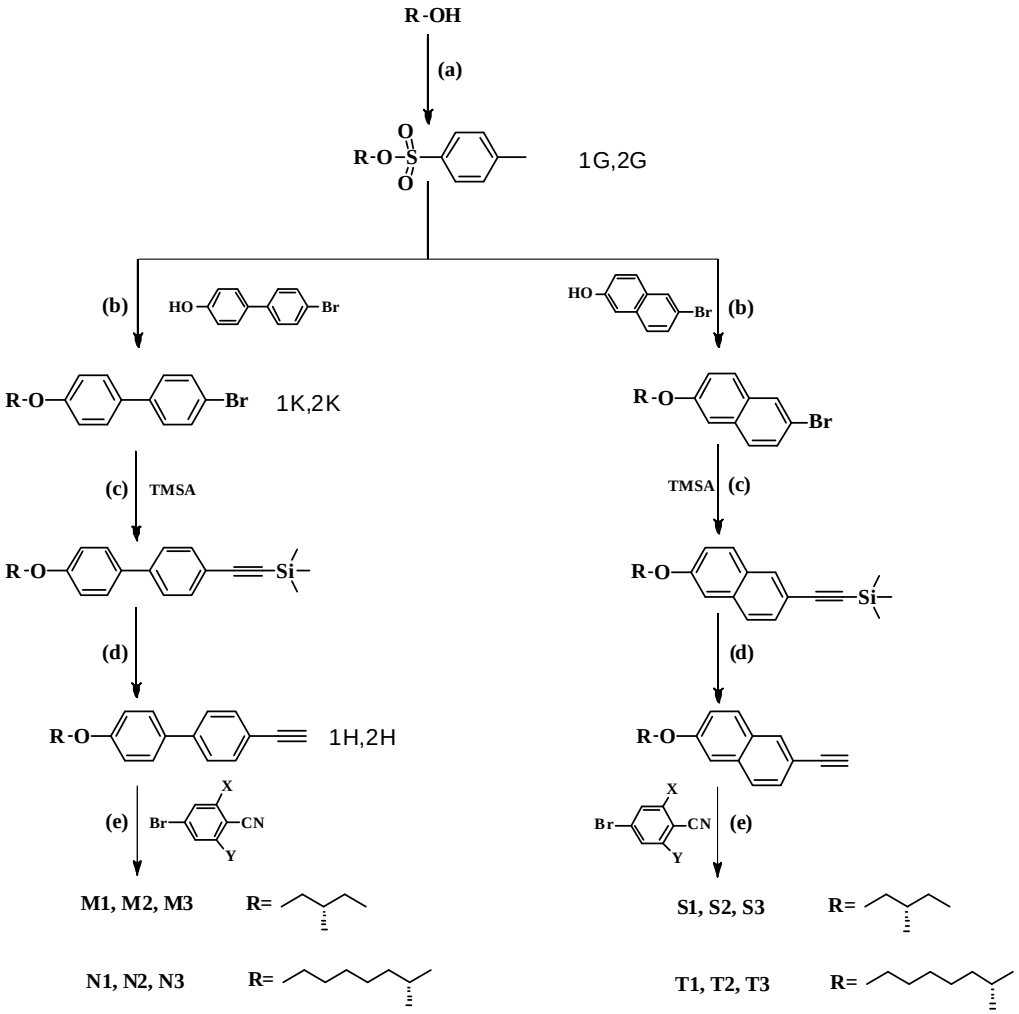
# Effect of lateral fluoro substituents of rodlike tolane cyano mesogens on blue phase temperature ranges

**Birong Li,[a] Wanli He,[a] Ling Wang,[a] Xia Xiao,[c] and Huai Yang[*a, b]**

## Expermental

### General procedures for the synthesis of M1-M3, N1-N3, S1-S3, T1-T3.




**Scheme 1** Synthetic route to the target compounds. Reagents and conditions: (a) TsCl, pyridine, 0-5°C; (b) $K_2CO_3$, DMF, reflux; (c) TMSA, $PdCl_2(PPh_3)_2$, CuI, THF, TEA, 80 °C, Ar; (d) $K_2CO_3$, $CH_3OH$, THF, rt; (e) $PdCl_2(PPh_3)_2$, CuI, THF, TEA, 80 °C, Ar.

### (S)-2-methylbutyl-4-methylbenzenesulfonate (1G)

4-methylbenzene-1- sulfonyl chloride (28.0g, 0.150mol) was added to stirred solution of (S)-2-methylbutan-1-ol (10.0g, 0.110mol) in 100ml pyridine at 0-5℃, and the reaction mixture was stirred for 5h. Then the sovent was evaporated, and the rest yellow liquid was diluted in 300ml ethyl acetate, washed with brine(3×200ml), then dried with magnesium sulfate. The solvent was evaporated after filtering. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate: petroleum ether, 5:1) to give 1G as a colourless oil. Yield: 72%, 19.2g. $^1$H-NMR (300MHz, $CDCl_3$, TMS)

$\delta_H$/ppm:7.74(d, J=6.3Hz, 2H), 7.31 (d, J=6.0Hz, 2H), 3.82-3.85(m, 1H), 3.75-3.79 (m, 1H), 2.41(s, 3H), 1.64-1.70(m, 1H), 1.33-1.34(m, 1H), 1.08-1.13(m, 1H), 0.76-0.84(m, 6H); $\nu_{max}$(KBr)/$cm^{-1}$: 2968, 1603, 1365, 1179, 967.

**(S)-octan-2-yl, 4-methylbenzenesulfonate (2G)**

The same procedure as described for compound 1G using (S)-octan-2-ol was carried out to yield a colourless oil. Yield: 60%, 18.7g. $^1$H-NMR (300 MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.94(d, J=6.80 Hz, 2H), 7.41 (d, J=6.3 Hz, 2H), 3.83-3.88 (m, 1H), 3.74-3.82 (m, 1H), 2.45 (s, 3H), 1.67-1.70 (m, 1H), 1.31-1.34 (m, 1H), 1.08-1.15(m, 1H), 0.74-0.86 (m, 6H); $\nu_{max}$ (KBr)/$cm^{-1}$: 2930, 2859, 1598, 1461, 1349, 1188, 1162, 1096, 896, 815, 721, 664, 577, 556.

**4-((S)-2-methylbutoxy)-4'-bromobiphenyl (1K)**

4-bromo-4'-hydroxybiphenyl (16.4g, 0.066mol) was add to a stirred solution of compound 1G (14.5g, 0.060mol), potassium carbonate (27.6g, 0.150mol) in 300ml DMF. The stirred mixture was heated at 90°C for 10h, then the mixture was diluted in 500ml ethyl acetate and washed with water. The organic layer was dried with magnesium sulfate and then filtered, The solvent was removed into vacuo and the residue was purified by column chromatography (petroleum ether: $CH_2Cl_2$, 10:1) to give 1k as a white solid. Yield: 70%, 13.4g. $^1$H-NMR (300MHz, $CDCl_3$, TMS) δH/ppm: 7.51(d, J=6.3Hz, 2H), 7.45(d, J=6.6Hz, 2H), 7.39(d, J=6.3Hz, 2H), 6.94(d, J=6.3Hz, 2H), 3.82-3.85(m, 1H), 3.73-3.77(m, 1H), 1.84-1.91(m, 1H), 1.52-1.62(m, 1H), 1.20-1.31(m, 1H), 1.02(d, J=5.1Hz, 3H), 0.94(t, J=5.5Hz, 3H); $\nu_{max}$ (KBr) /cm-1: 2968, 2926, 1629, 1585, 1490, 1458, 1390, 1254, 1212, 1026, 856.

**4-((S)-octan-2-yloxy)-4'- bromobiphenyl (2K)**

The same procedure as described for compound 1K using 2G and 4-bromo-4'-hydroxybiphenyl was carried out to yield a white solid. Yield: 60%, 13.0g. $^1$H-NMR (300MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.50(d, J=6.3Hz, 2H), 7.44(d, J=6.3Hz, 2H), 7.39(d, J=6.3Hz, 2H), 6.92(d, J=6.3Hz, 2H), 4.33-4.41(m, 1H), 1.71-1.77(m, 1H), 1.53-1.55(m, 1H), 1.21-1.31(m, 11H), 0.86(t, J=4.5Hz, 3H); $\nu_{max}$ (KBr) /$cm^{-1}$: 2929, 2857, 1626, 1590, 1497, 1464, 1386, 1259, 1205, 1123, 1063, 876, 849, 472.

**4-((S)-2-methylbutoxy)-4'-ethynylbiphenyl (1H)**

1K(10g, 0.031mol) was dissolved in the mixed solvent of 100 mL TEA and 100 mL THF in a round bottom flask. The solution was purged for 30 min with bubbling Ar followed by addition of $Pd(PPh_3)_2Cl_2$ (0.42g, 0.6 mmol) and CuI (0.66 g, 0.6 mmol). The addition of TMSA (9.8 g, 0.100 mol) occurred via injection after Ar purging. The reaction mixture was then stirred at 80ºC for 10h under Ar atmosphere. Upon completion, the mixture was concentrated, rediluted with $CH_2Cl_2$, filtered through a plug of silica gel, after concentrating the crude product was purified by chromatography of silica gel (petroleum ether: $CH_2Cl_2$, 7:1). The solvent was removed in vacuo and then dissolved in THF: MeOH (7:3, 200 mL), added $K_2CO_3$ (3 equiv per silyl group). The reaction mixture was stirred at room temperature for 4h. Upon completion, the solvent was removed in vacuo and the crude product was purified by chromatography of silica gel (petroleum ether: $CH_2Cl_2$, 2:1) to give 1h as a yellowish solid. Yield: 49.5%, 4.1g. 1H-NMR (300 MHz, $CDCl_3$, TMS) δH/ppm: 7.37-7.48(m, 6H), 6.83(d, J=6.6Hz, 2H), 4.03(d, J=6.4Hz, 2H), 3.06(s, 1H), 2.16(m, 1H), 1.29(m, 2H), 1.06(m, 3H), 0.96(m, 3H); $\nu_{max}$(KBr) /$cm^{-1}$: 3289, 2972, 2961, 2911, 2105, 1908, 1605, 1494, 1249, 1050, 1009, 841, 666, 630.

**4-((S)-octan-2-yloxy)-4'-ethynylbiphenyl (2H)**

The same procedure as described for compound 1H using 2K was carried out to yield a white solid. Yield: 45%, 4.3g. $^1$H-NMR (300 MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.36-7.49(m , 6H), 6.83(d, J = 6.5Hz, 2H),3.86(m, 1H), 3.06(s, 1H), 1.67(m, 2H), 1.43(d, J=6.6Hz, 3H),1.29-1.33(m, 8H), 0.95(m, 3H); $\nu_{max}$(KBr) /$cm^{-1}$: 3339, 2956, 2919, 2849, 2131, 1690, 1469, 1260, 1101, 720, 624.

**4-[(4'-(S)-2-methylbutoxy-biphenyl-4-yl)-1-ethynyl]-benzonitrile (M1)**

1H (1.3g, 4.9mmol) and 4-bromo-benzonitrile (0.82g, 4.5mmol) were dissolved in the mixed solvent of 15 mL triethylamine and 15 mL tetrahydrofuran in a round bottom flask. The solution was purged for 30 min with bubbling Ar followed by addition of $Pd(PPh_3)_3Cl_2$ (0.069g, 0.10mmol) and CuI (1.09 mg, 0.10 mmol). The reaction mixture then stirred at 80ºC for 10h under an Ar atmosphere. Upon completion, the mixture was concentrated, rediluted with $CH_2Cl_2$. The solvent was removed into vacuo and the crude product was purified by chromatography of silica gel (petroleum ether: $CH_2Cl_2$, 2:1) to give 1h as a yellowish solid. Yield: 65%, 1.07g. $^1$H-NMR (300 MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.63(dd, J=6.0, 4.2HZ, 4H), 7.57(dd, J=7.5Hz, 4H), 7.52(d, J=6.3Hz, 2H), 6.97(d, J=6.3Hz, 2H), 3.83-3.87(m, 1H), 3.74-3.78(m, 1H), 1.83-1.91(m, 1H), 1.61-1.57(m, 1H), 1.18-1.30(m, 1H), 1.01-1.02(d, J=4.8Hz, 3H), 0.93-0.96(t, J=5.6Hz, 3H); $\nu_{max}$ (KBr) /cm$^{-1}$: 2968, 2926, 2221, 2203, 1629, 1585, 1490, 1458, 1390, 1254, 1212, 1026, 856.

**2-fluoro-4-[(4'-(S)-2-methylbutoxy-biphenyl-4-yl)-1-ethynyl]-benzonitrile (M2).**

The same procedure as described for compound M1 using 1H and 4-bromo-2-fluorobenzonitrile was carried out to yield a white solid. Yield: 62%, 1.03g. $^1$H-NMR (300 MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.59(dd, J=6.0Hz，4H), 7.56(s, 1H), 7.52(d, J=6.3Hz, 2H), 7.36(d, J=6.3Hz, 2H), 6.97(d, J=6.3Hz, 2H), 3.83-3.87 (m, 1H), 3.74-3.78(m, 1H), 1.85-1.90(m, 1H), 1.54(m, 1H), 1.23-1.30(m, 1H), 1.01(d, J=5.1Hz, 3H), 0.94(t, J=5.6Hz, 3H); $\nu_{max}$ (KBr) /cm$^{-1}$: 2968, 2926, 2238, 2210, 1629, 1585, 1490, 1458, 1390, 1254, 1212, 1026, 856.

**2,6-difluoro-4-[(4'-(S)-2-methylbutoxy-biphenyl-4-yl)-1-ethynyl]-benzonitrile (M3).**

The same procedure as described for compound M1 using 1H and 4-bromo-2, 6-difluorobenzonitrile was carried out to yield a white solid. Yield: 58%, 1.05g. $^1$H-NMR (300 MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.56(s, 2H), 7.52(dd, J=6.3Hz, 4H), 7.16(d, J=6.0Hz, 2H), 6.97(d, J=6.3Hz, 2H), 3.83-3.87(m, 1H), 3.74-3.78(m, 1H), 1.83-1.92(m, 1H), 1.57-1.63(m, 1H), 1.21-1.28(m, 1H), 1.02(d, J=5.1Hz, 3H), 0.94(t, J=5.6Hz, 3H); $\nu_{max}$(KBr) /cm$^{-1}$: 2968, 2926, 2223, 2219, 1629, 1585, 1490, 1458, 1390, 1254, 1212, 1026, 856.

**[(4'-(S)-octan-2-yloxy-biphenyl-4-yl)-1-ethynyl]-benzonitrile (N1).**

The same procedure as described for compound M1 using 2H and 4-bromo-benzonitrile was carried out to yield a white solid, Yield: 62%, 1.14g. $^1$H-NMR (300 MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.51 (dd, J=5.1Hz, 4H), 7.51 (dd, J=8.1Hz, 4H), 7.51 (d, J=6.6Hz, 2H), 6.95 (d, J=6.6Hz, 2H), 4.36-4.41 (m, 1H), 1.73-1.75(m, 1H), 1.54-1.56 (m, 1H), 1.27-1.32 (m, 11H), 0.86 (t, J=4.5Hz, 3H); $\nu_{max}$(KBr) /cm$^{-1}$: 2931, 2858, 2215, 2206, 1595, 1504, 1288, 1255, 838, 822, 553, 523.

**2-fluoro-4-[(4'-(S)-octan-2-yloxy-biphenyl-4-yl)-1-ethynyl]-benzonitrile (N2).**

The same procedure as described for compound M1 using 2H and 4-bromo-2-fluorobenzonitrile was carried out to yield a white solid, Yield: 55%, 1.05g. $^1$H-NMR (300 MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.53-7.6 (d, 5H), 7.51 (d, J=6.6Hz, 2H), 7.36 (d, J=6.6Hz, 2H), 6.95 (d, J=6.6Hz, 2H), 4.35-4.41 (m, 1H), 1.72-1.77(m, 1H), 1.56-1.60 (m, 1H), 1.42-1.45 (m, 1H), 1.27-1.32 (m,10H), 0.86 (t, J=5.1Hz, 3H); $\nu_{max}$(KBr) /cm$^{-1}$: 3051, 2927, 2856, 2229, 2142, 1604, 1488, 1246, 1180, 1020, 810, 747.

**2,6-difluoro-4-[(4'-(S)-octan-2-yloxy-biphenyl-4-yl)-1-ethynyl]-benzonitrile (N3).**

The same procedure as described for compound M1 using 2H and 4-bromo-2,6-difluorobenzonitrile was carried out to yield a white solid, Yield: 51%, 1.02g. $^1$H-NMR (300MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.56(sd, 4H), 7.51(d, J=6.6Hz, 2H), 7.16(d, J=5.7Hz, 2H), 6.95(d, J=6.6Hz, 2H), 4.35-4.43(m, 1H), 1.72-1.75(m, 1H), 1.54-1.56(m, 1H), 1.42-1.43(m, 1H), 1.27-1.32 (m, 10H), 0.86(t, J=4.3Hz, 3H); $\nu_{max}$(KBr) /cm$^{-1}$: 2954, 2929, 2239, 2208, 1597, 1442, 1249, 825.

**4-(2-(2-(2(S)-methylbutoxy)naphthalen-6-yl)ethynyl)benzonitrile (S1)**

The same procedure described for compound M1 was carried out to yield a white solid, Yield: 67%, 1.82g. $^1$H-NMR (300MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.97(s, 1H), 7.70(d, J=6.9Hz, 2H),

7.67(d, J=6.9Hz, 2H), 7.54(d, J=5.7Hz, 2H), 7.49(d, J=6.6Hz, 2H), 7.16(d, J=5.1Hz, 1H), 7.09(s, 1H), 3.88(m, 2H), 1.93(m, 1H), 1.61(m, 1H), 1.46(m, 1H), 1.36(d, J=4.5HZ, 3H), 0.86(t, J=5.0Hz, 3H); $\nu_{max}$(KBr) /cm$^{-1}$: 2960, 2919, 2229, 2203, 1602, 1396, 1261, 856.

**2-fluoro-4-(2-(2-(2(S)-methylbutoxy)naphthalen-6-yl)ethynyl)benzonitrile (S2)**

The same procedure described for compound M1 was carried out to yield a white solid, Yield: 61%, 1.64g.$^{1}$H-NMR (300MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 8.02(s, 1H), 7.75(d, J=6.9Hz, 2H), 7.61(d, J=5.1Hz, 1H), 7.53(d, J=5.4Hz, 1H), 7.42(d, J=4.8Hz, 2H), 7.21(d, J=4.8Hz, 1H), 7.14(s, 1H), 3.93(m, 2H), 1.96(m, 1H), 1.64(m, 1H), 1.34(m, 1H), 1.09(d, J=5.7HZ, 3H), 1.01(t, J=5.7Hz, 3H); $\nu_{max}$(KBr) /cm$^{-1}$: 2963, 2920, 2233, 2201, 1621, 1419, 1224, 847.

**2,6-difluoro-4-(2-(2-(2(S)-methylbutoxy)naphthalen-6-yl)ethynyl)benzonitrile (S3)**

The same procedure described for compound M1 was carried out to yield a white solid, Yield: 55%, 1.32g.$^{1}$H-NMR (300MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.98(s, 1H), 7.70(d, J=6.6Hz, 2H), 7.48(d, J=5.1Hz, 1H), 7.19(d, J=6.3Hz, 2H), 7.16(d, J=5.1Hz, 1H), 7.10(s, 1H), 3.89(m, 2H), 1.92(m, 1H), 1.60(m, 1H), 1.32(m, 1H), 1.05(d, J=4.8Hz, 3H), 1.01(t, J=5.7Hz, 3H); $\nu_{max}$(KBr) /cm$^{-1}$: 2970, 2920, 2237, 2207, 1623, 1429, 1235, 848.

**4-(2-(2-((S)-octan-2-yloxy)naphthalen-6-yl)ethynyl)benzonitrile (T1)**

The same procedure described for compound M1 was carried out to yield a white solid, Yield: 65%, 1.52g. $^{1}$H-NMR (300MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.97(s, 1H), 7.71(d, J=6.9Hz, 2H), 7.64(d, J=6.9Hz, 4H), 7.50(d, J=6.6Hz, 1H), 7.13(d, J=4.8Hz, 1H), 7.09(s, 1H), 4.51(m, 1H), 1.73(m, 1H), 1.55(m, 1H), 1.42 (m, 1H), 1.27-1.32 (m, 10H), 0.86(t, J=5.0Hz, 3H); $\nu_{max}$(KBr) /cm$^{-1}$: 2931, 2857, 2226, 2202, 1600, 1477, 1272, 859.

**2-fluoro-4-(2-(2-((S)-octan-2-yloxy)naphthalen-6-yl)ethynyl)benzonitrile (T2)**

The same procedure described for compound M1 was carried out to yield a white solid, Yield: 61%, 1.32g. $^{1}$H-NMR (300MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.97(s, 1H), 7.69(d, J=6.9Hz, 2H), 7.57(d, J=5.1Hz, 1H), 7.49(d, J=4.8Hz, 1H), 7.38(d, J=4.8Hz, 2H), 7.14(d, J=4.8Hz, 1H), 7.09(s, 1H), 4.51(m, 1H), 1.73(m, 1H), 1.55(m, 1H), 1.42 (m, 1H), 1.27-1.30(m, 10H), 0.86(t, J=5.0Hz, 3H); $\nu_{max}$(KBr) /cm$^{-1}$: 2931, 2857, 2233, 2208, 1612, 1476, 1259, 966, 870.

**2,6-difluoro-4-(2-(2-((S)-octan-2-yloxy)naphthalen-6-yl)ethynyl)benzonitrile (T3)**

The same procedure described for compound M1 was carried out to yield a white solid, Yield: 56%, 1.20g. $^{1}$H-NMR (300MHz, $CDCl_3$, TMS) $\delta_H$/ppm: 7.97(s, 1H), 7.69(d, J=6.6Hz, 2H), 7.48(d, J=4.8Hz, 1H), 7.49(d, J=4.8Hz, 1H), 7.17(d, J=6.0(Hz, 2H), 7.14(d, J=4.8Hz, 1H), 7.09(s, 1H), 4.51(m, 1H), 1.78(m, 1H), 1.55(m, 1H), 1.42 (m, 1H), 1.28-1.35 (m, 10H), 0.85(t, J=5.0Hz, 3H); $\nu_{max}$(KBr) /cm$^{-1}$: 2926, 2855, 2237, 2206, 1621, 1474, 1241, 1041, 845.

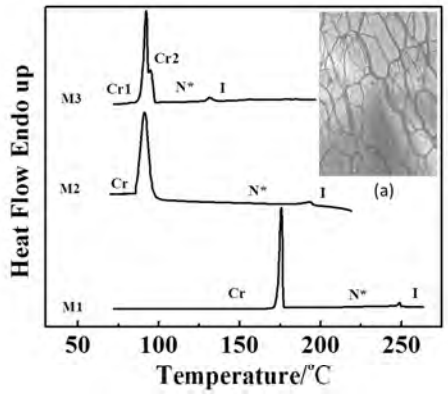



**Fig. 1** The DSC measurements of compounds M1-M3 on cooling recycles and the POM texture for compound M3 at 135°C.

Various phase behaviors of compound N1 were documented by DSC and POM measurements. Fig. 2 shows the DSC thermogram for N1. It could be obviously seen that four clear peaks were obtained at 171.9°C, 162.9°C, 157.3°C, 107.1°C. However, the enthalpy changes at the transition from I-BP and N*-TGBA* were too small to be detected. Fig. 3 shows the optical photomicrographs of each mesophase on cooling from the isotropic phase. A platelet texture of BP (Fig.3a) was observed initially, followed by a common oily-streaks texture of N*(Fig.3b) phases, then a filament texture of TGBA* phase (Fig.3c), subsequently a pseudo isotropic SmB* phase (Fig.3e), and a mosaic texture phase of CrB* phase (Fig.3g).

The phase assignment of compound N1 was also confirmed by XRD measurements. Fig. 4 presents the thermal-dependent XRD patterns obtained from the powder sample of N1 at 190℃, 167℃, 160℃, 153℃ and 120℃ (Fig. 5). The X-ray pattern obtained for N1 at 167 °C exhibits two sharp reflection at 16.2 Å in the low-angle region and 4.4 Å in the wide-angle region to a N* phase. A typical X-ray pattern recorded for the SmB* phase shows a sharp reflection in (001) and (002) in the low-angle region and a sharp reflection in (110). The curve in Fig. 5 reveals a sharp reflection at about 4.62 Å, and a sharp first- and second-order reflection of 44.05 Å, which verifies the formation of a highly ordered CrB* phase.

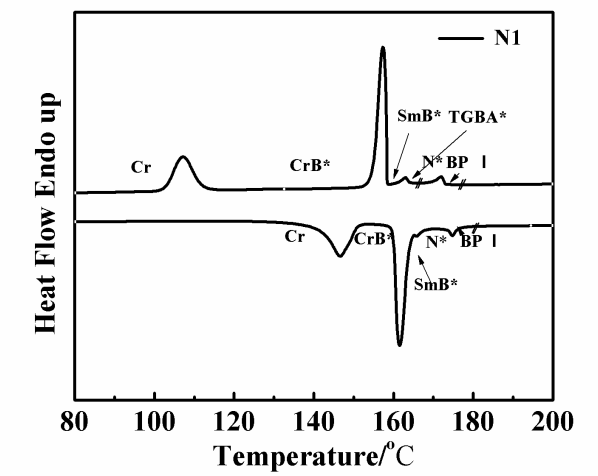



**Fig. 2** DSC measurement for N1 on heating and cooling recycles.

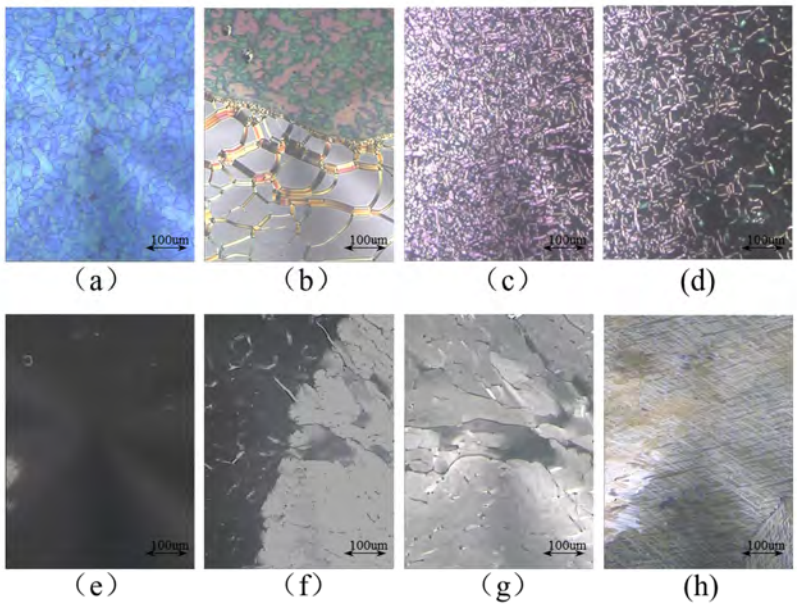



**Fig. 3** Microphotographs of compound N1 observed under the POM: (a) platelet texture of BPs at 172.2°C; (b) the BP-N*phase transition at 171.7°C in a homogeneously aligning substrate; (c) the filament texture of the TGBA* phase at 167.8°C; (d) the TGBA*-SmB* phase transition at 167.2°C; (e) the optic isotropic phase transition at 165.8°C (free standing film). (f) SmB*-CrB* transition at 163.5°C; (g) the mosaic texture of the CrB* phase at 162.2°C; (h) crystalline texture at 112.5°C.

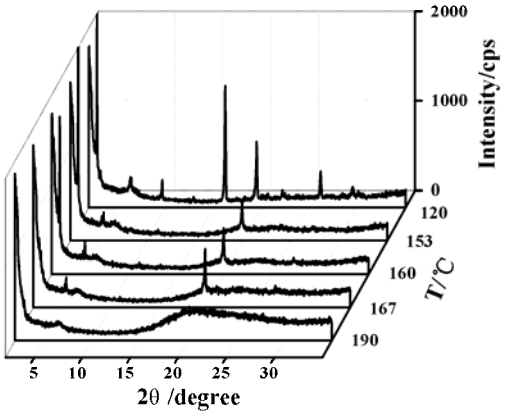



**Fig. 4** The thermal-dependent XRD measurements of compound N1.

## Measurements of Helical Pitch and Helical Twisting Power of the chiral dopant M1-M3 by Cano's Wedge method.

Cano's wedge method is a conventional technique for pitch measurement. When a N*-LC sample was inserted into a wedge-type cell with gradient thickness, the discontinuity lines named Cano lines appeared on the surface of the cell under crossed nicols. The helical pitch (p) was evaluated by measuring the distance (a) between Cano lines as follows:

$$p = 2a \tan\theta$$

where θ is the angle of the wedge of the cell. The twisting power ($\beta_M$) of the chiral dopant was evaluated with the following equation:

$$\beta_M = 1/(pcr)$$

where c is the molar concentration of the chiral dopant and r is the enantiometric purity of the chiral dopant.

In this experiment, the cell angle θ is 0.03874, the concentration of the chiral dopant c is 5%, r is assumed to be 1.

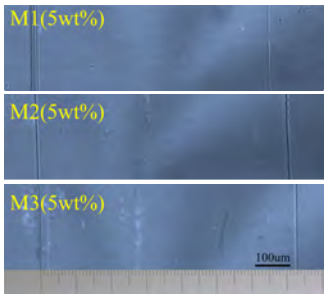



**Fig. 5** Cano's Wedge Method to measure the helical pitch of N*-LCs (a N-LC 1717 and 5.0 wt% of each chiral compound M1-M3

**Tab. 1** Cano's Wedge Method for the Helical Pitch (p) and Helical Twisting Power ($\beta_M$) of the chiral dopant M1-M3 in N*-LC.

| Compound | Helical Pitch (um) | HTP ($um^{-1}$) |
|---|---|---|
| M1 | 52.6 | 0.38 |
| M2 | 55.6 | 0.36 |
| M3 | 57.1 | 0.35 |

Helical pitch (um) in the N* phase for chiral nematic mixtures of 1717 and 5.0 wt% of each chiral compound M1-M3 were observed at room temperature.

A molecular simulation software was used to estimate the breadths and lengths of compounds

S1 and M1. The results reveal that the molecule breadth increases from 4.3 Å to 5.6 Å and the molecule length in the rigid part decreases from 17.4 Å to 15.4 Å by comparing compound M1 to S1.

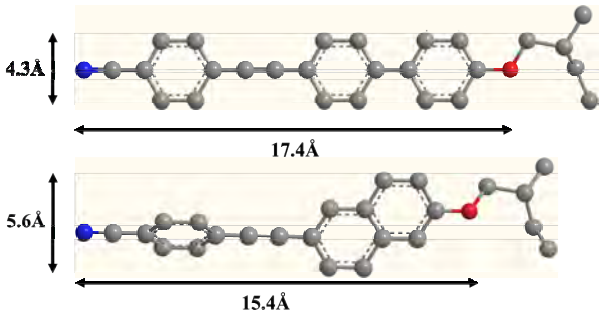



**Fig. 6** The molecular model for estimating the breadths and lengths of compounds S1 and M1.