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Dielectric and optical anisotropy enhanced by 1,3-dioxolane terminal substitution on tolane-liquid crystals

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Electronic supplementary information

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1. General

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a spectrometer operating at 300 and 75 MHz. Full geometry optimizations have been carried out without imposing any constraints using the Gaussian 09 program package. Spin-restricted DFT calculations were carried out in the framework of the generalized gradient approximation (GGA) using B3LYP exchange-correlation functional and the 6-31G (d, p) basis set.

2. Compound structure characterization

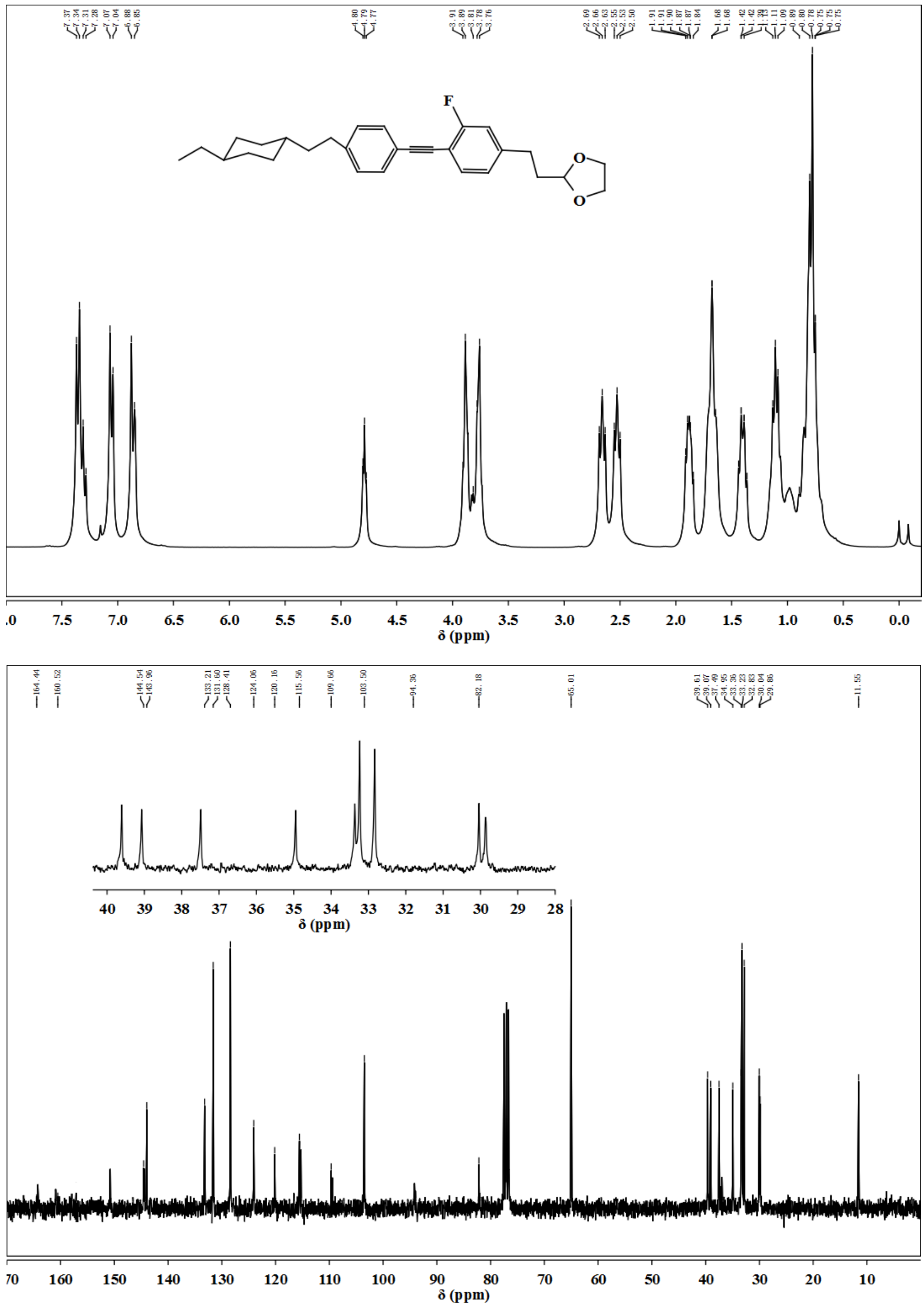
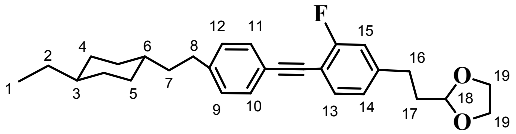
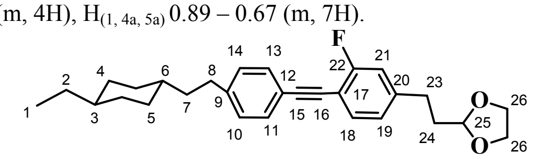


Fig. S1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2TF2** recorded in $CDCl_3$.

2TF2: The yield was 48% of white crystals.



^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): $H_{(10, 11, 13)}$ 7.33 (dd, J = 17.7, 7.8 Hz, 3H), $H_{(9, 12)}$ 7.05 (d, J = 7.9 Hz, 2H), $H_{(14, 15)}$ 6.86 (d, J = 8.0 Hz, 2H), H_{18} 4.86 – 4.71 (m, 1H), H_{19} 3.99 – 3.62 (m, 4H), $H_{(8, 16)}$ 2.78 – 2.42 (m, 4H), H_{17} 1.99 – 1.80 (m, 2H), $H_{(4e, 5e)}$ 1.77 – 1.53 (m, 4H), H_7 1.48 – 1.29 (m, 2H), $H_{(2, 3, 6)}$ 1.21 – 0.95 (m, 4H), $H_{(1, 4a, 5a)}$ 0.89 – 0.67 (m, 7H).

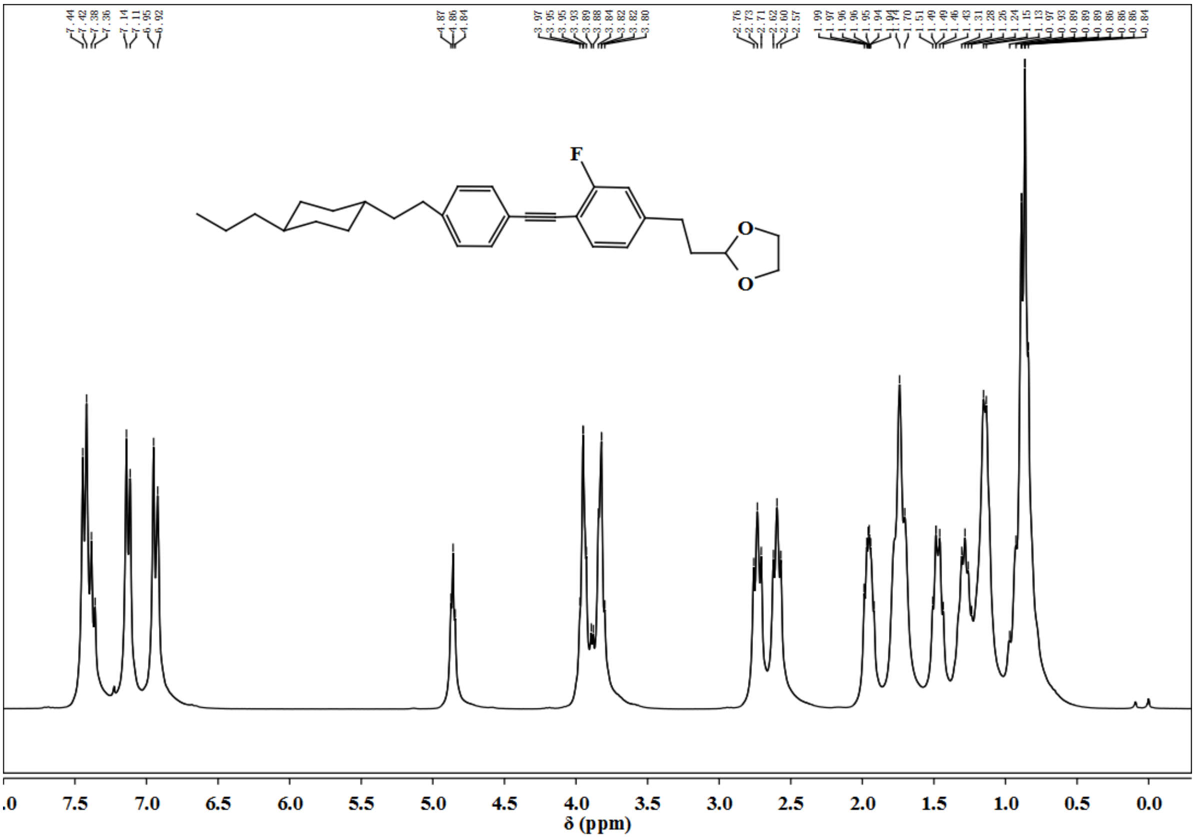


^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): C_{22} 164.4、160.5, C_9 144.5, C_{20} 144.0, C_{18} 133.2, $C_{(11, 13)}$ 131.6, $C_{(10, 14)}$ 128.4, C_{19} 124.1, C_{12} 120.2, C_{21} 115.6, C_{17} 109.7, C_{25} 103.5, C_{16} 94.4, C_{15} 82.2, C_{26} 65.0, C_6 39.6, C_3 39.1, C_8 37.5, C_{24} 35.0, C_4 33.3, C_5 33.3, C_7 32.8, C_{23} 30.0, C_2 30.0, C_1 11.6.

EI-MS *m/z* (rel. int.): 434(M$^+$, 26), 372(15), 309(18), 207(100), 100(73), 73(78).

IR (KBr, pellet, cm^{-1}): 2955, 2912, 2848, 2205, 1907, 1605, 1515, 1438, 1217, 1130, 1038, 886, 812.

Elemental analysis: Calc. for $C_{29}H_{35}FO_2$: C 80.15, H 8.12; Found: C 79.92, H 8.21.



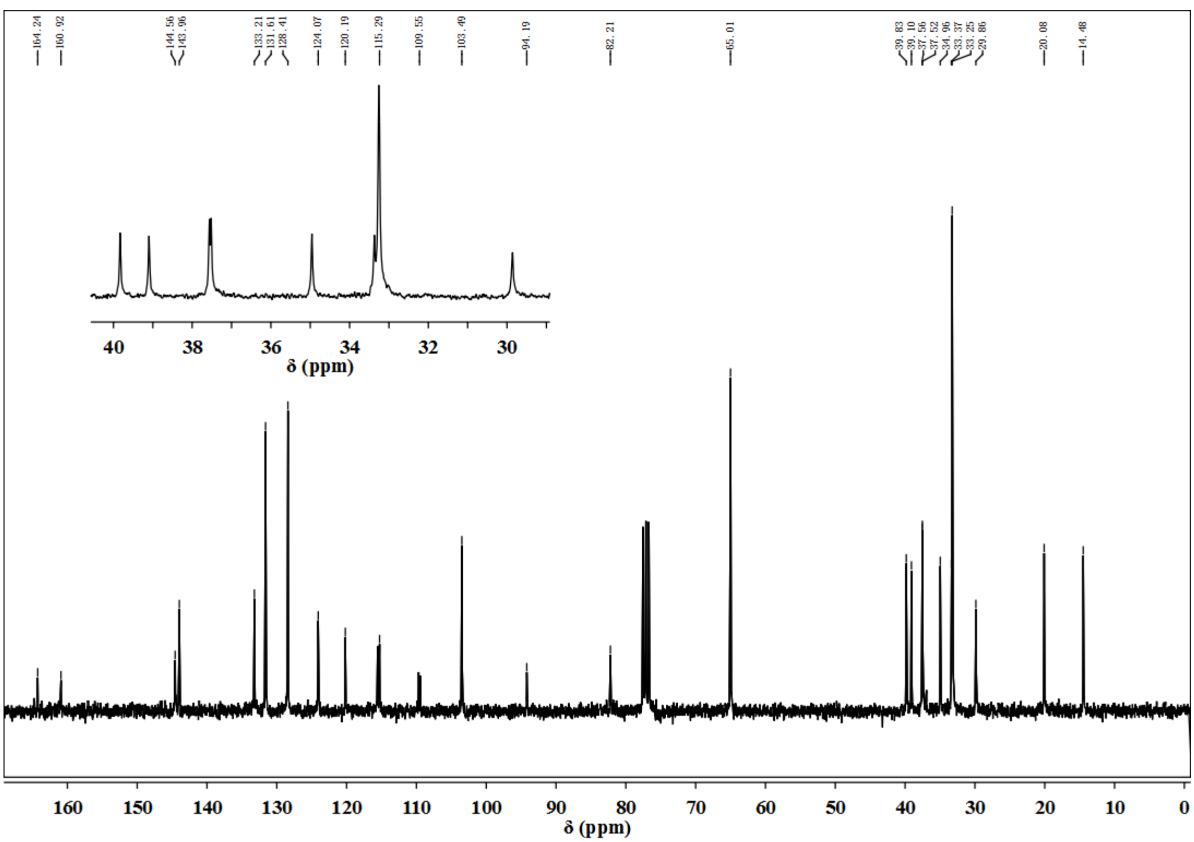
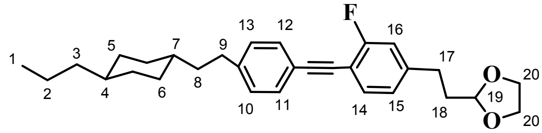
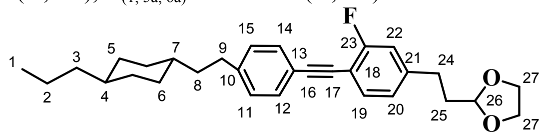


Fig. S2. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3TF2** recorded in $CDCl_3$.

3TF2: The yield was 50% of white crystals.



^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): H$_{(11, 12, 14)}$ 7.40 (dd, J = 18.0, 7.8 Hz, 3H), H$_{(10, 13)}$ 7.13 (d, J = 7.8 Hz, 2H), H$_{(15, 16)}$ 6.94 (d, J = 8.6 Hz, 2H), H$_{19}$ 5.04 – 4.59 (m, 1H), H$_{20}$ 4.04 – 3.72 (m, 4H), H$_{(9, 17)}$ 2.86 – 2.43 (m, 4H), H$_{18}$ 2.09 – 1.87 (m, 2H), H$_{(5e, 6e)}$ 1.84 – 1.60 (m, 4H), H$_8$ 1.56 – 1.42 (m, 2H), H$_{(2, 3, 4, 7)}$ 1.36 – 1.08 (m, 6H), H$_{(1, 5a, 6a)}$ 0.95 – 0.76 (m, 7H).

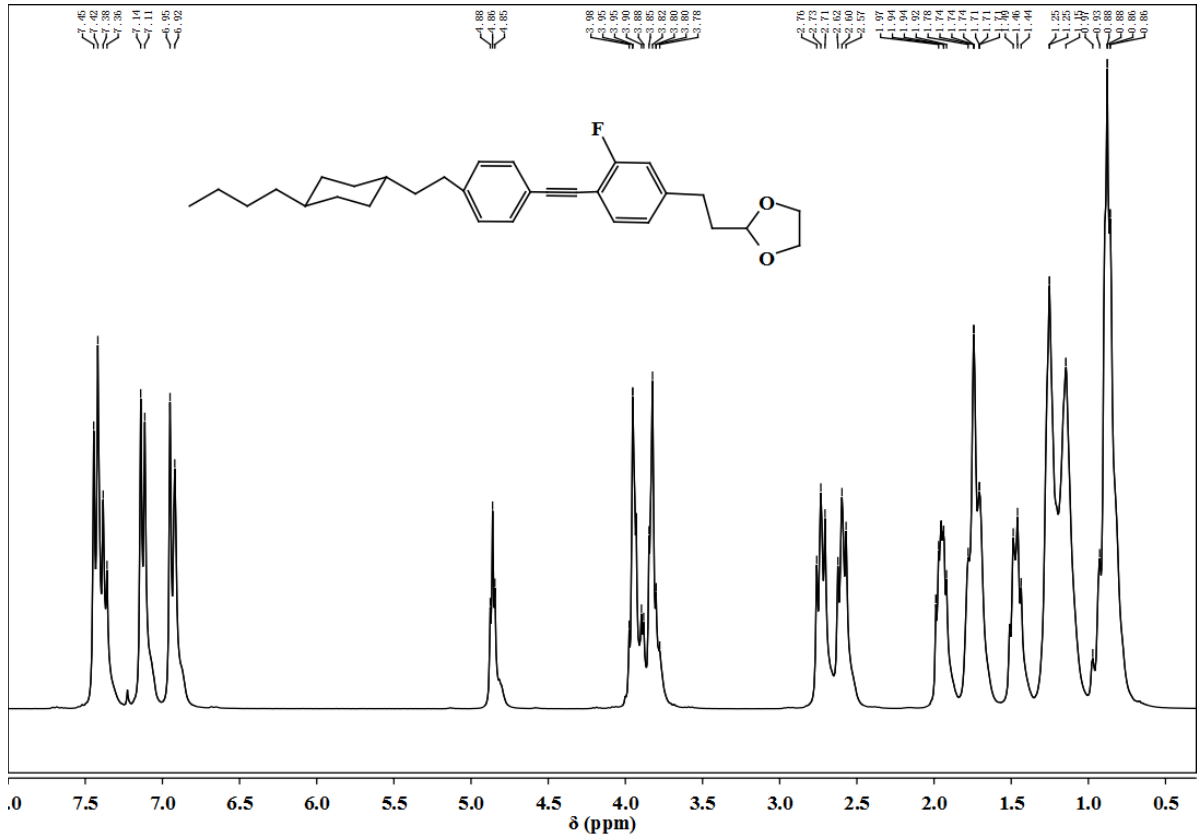


^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): C$_{23}$ 164.2、160.9, C$_{10}$ 144.6, C$_{21}$ 144.0, C$_{19}$ 133.2, C$_{(12, 14)}$ 131.6, C$_{(11, 15)}$ 128.4, C$_{20}$ 124.1, C$_{13}$ 120.2, C$_{22}$ 115.3, C$_{18}$ 109.6, C$_{26}$ 103.5, C$_{17}$ 94.2, C$_{16}$ 82.2, C$_{27}$ 65.0, C$_7$ 39.8, C$_4$ 39.1, C$_9$ 37.5, C$_3$ 37.5, C$_{25}$ 35.0, C$_5$ 33.3, C$_6$ 33.3, C$_8$ 33.3, C$_{24}$ 29.9, C$_2$ 20.1, C$_1$ 14.5.

EI-MS *m/z* (rel. int.): 448(M$^+$, 46), 309(28), 222(28), 207(40), 100(100).

IR (KBr, pellet, cm^{-1}): 2958, 2906, 2848, 2211, 1903, 1613, 1517, 1440, 1221, 1131, 1042, 887, 816.

Elemental analysis: Calc. for $C_{30}H_{37}FO_2$: C 80.32, H 8.31; Found: C 80.26, H 8.52.



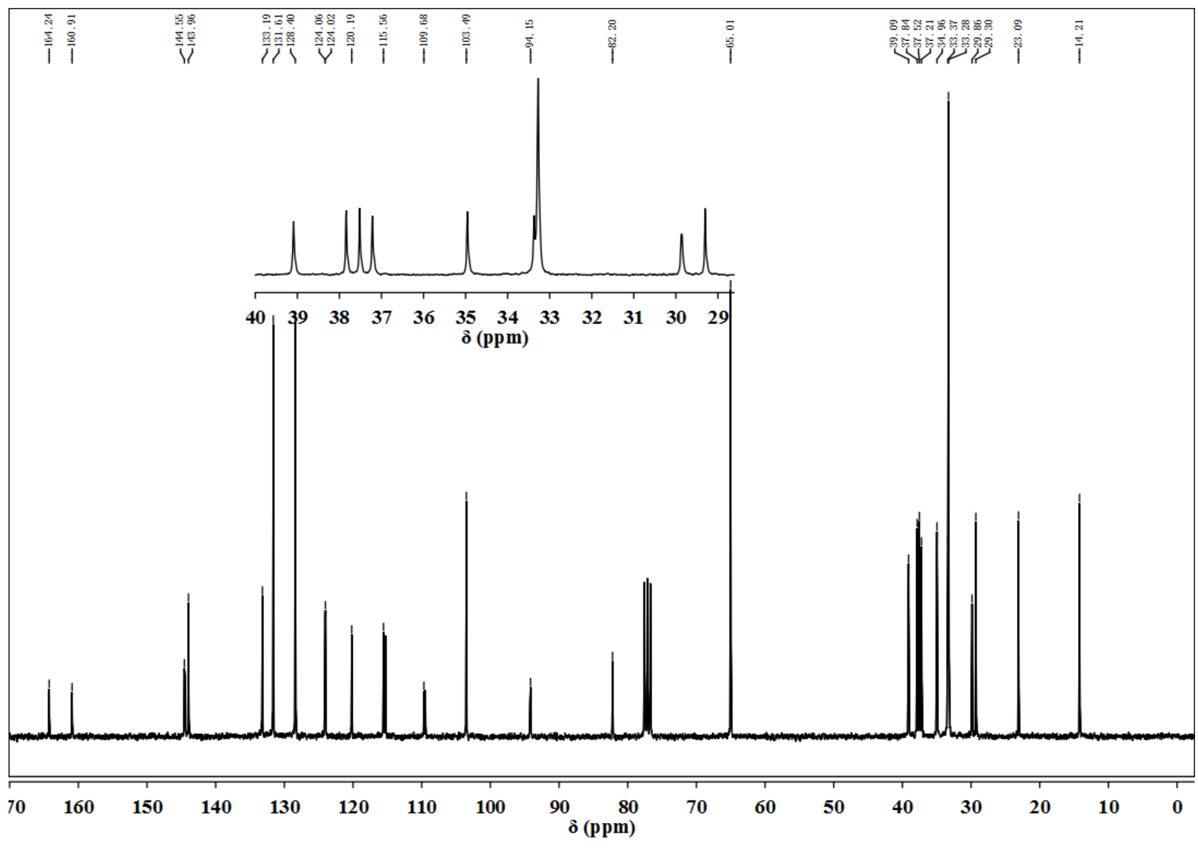
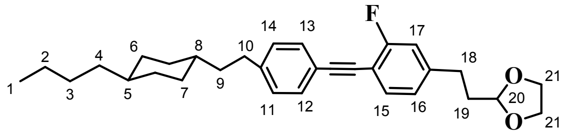
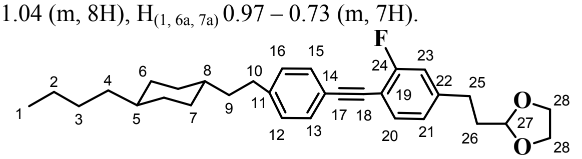


Fig. S3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4TF2** recorded in $CDCl_3$.

4TF2: The yield was 45% of white crystals.



[1]H NMR (300 MHz, $CDCl_3$) δ (ppm): $H_{(12, 13, 15)}$ 7.40 (dd, J = 18.1, 7.8 Hz, 3H), $H_{(11, 14)}$ 7.13 (d, J = 8.0 Hz, 2H), $H_{(16, 17)}$ 6.94 (d, J = 9.2 Hz, 2H), H_{20} 4.93 – 4.77 (m, 1H), H_{21} 4.00 – 3.72 (m, 4H), $H_{(10, 18)}$ 2.78 – 2.49 (m, 4H), H_{19} 2.03 – 1.86 (m, 2H), $H_{(6e, 7e)}$ 1.83 – 1.60 (m, 4H), H_9 1.54 – 1.36 (m, 2H), $H_{(2, 3, 4, 5, 8)}$ 1.34 – 1.04 (m, 8H), $H_{(1, 6a, 7a)}$ 0.97 – 0.73 (m, 7H).

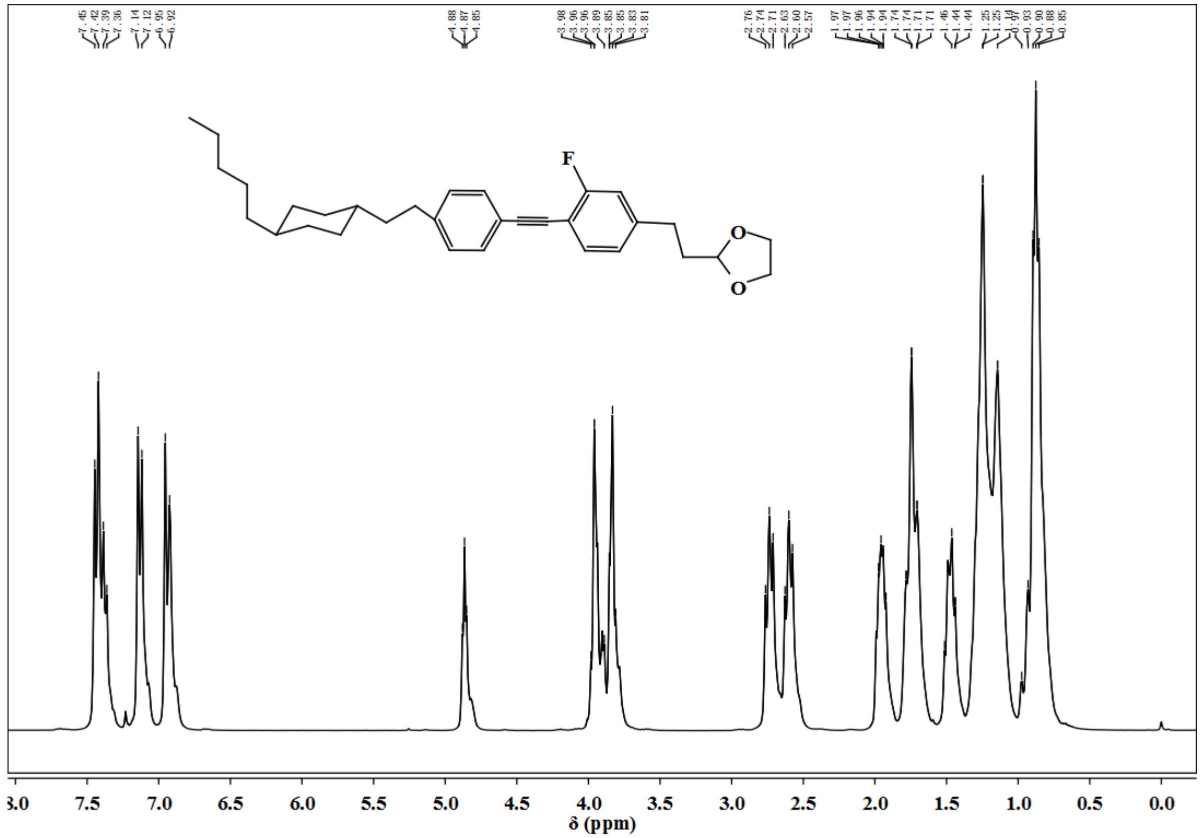


[13]C NMR (75 MHz, $CDCl_3$) δ (ppm): C_{24} 164.2、160.9, C_{11} 144.6, C_{22} 144.0, C_{20} 133.2, $C_{(13, 15)}$ 131.6, $C_{(12, 16)}$ 128.4, C_{21} 124.0, C_{14} 120.2, C_{23} 115.6, C_{19} 109.7, C_{27} 103.5, C_{18} 94.2, C_{17} 82.2, C_{28} 65.0, C_8 39.1, C_5 37.8, C_{10} 37.5, C_4 37.2, C_{26} 35.0, C_6 33.3, C_7 33.3, C_9 33.3, C_{25} 29.9, C_3 29.3, C_2 23.1, C_1 14.2.

EI-MS m/z (rel. int.): 462(M^+, 50), 309(38), 235(30), 100(100), 73(70).

IR (KBr, pellet, cm^{-1}): 2962, 2916, 2848, 2208, 1913, 1617, 1517, 1436, 1217, 1135, 1048, 880, 812.

Elemental analysis: Calc. for $C_{31}H_{39}FO_2$: C 80.48, H 8.50; Found: C 80.28, H 8.66.



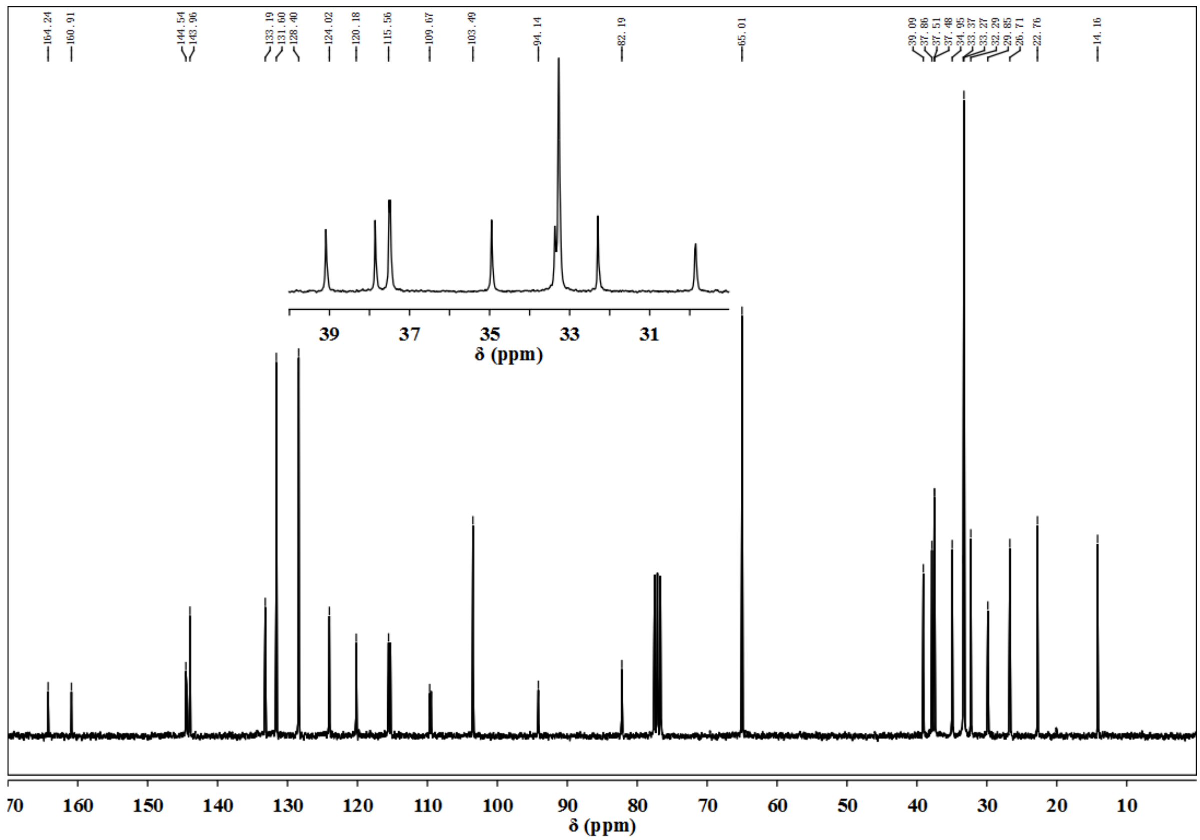
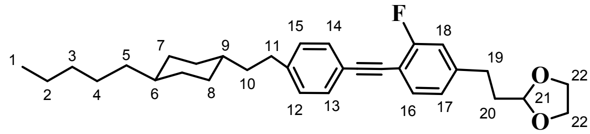
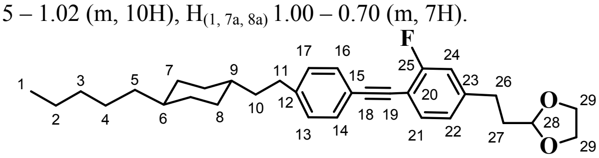


Fig. S4. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **5TF2** recorded in $CDCl_3$.

5TF2: The yield was 52% of white crystals.



^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): $H_{(13, 14, 16)}$ 7.40 (dd, J = 17.7, 7.7 Hz, 3H), $H_{(12, 15)}$ 7.13 (d, J = 7.9 Hz, 2H), $H_{(17, 18)}$ 6.94 (d, J = 9.0 Hz, 2H), H_{21} 4.92 – 4.76 (m, 1H), H_{22} 4.01 – 3.71 (m, 4H), $H_{(11, 19)}$ 2.81 – 2.49 (m, 4H), H_{20} 2.03 – 1.85 (m, 2H), $H_{(7e, 8e)}$ 1.82 – 1.59 (m, 4H), H_{10} 1.55 – 1.37 (m, 2H), $H_{(2, 3, 4, 5, 6, 9)}$ 1.35 – 1.02 (m, 10H), $H_{(1, 7a, 8a)}$ 1.00 – 0.70 (m, 7H).



^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): C_{25} 164.2、160.9, C_{12} 144.5, C_{23} 144.0, C_{21} 133.2, $C_{(14, 16)}$ 131.6, $C_{(13, 17)}$ 128.4, C_{22} 124.0, C_{15} 120.2, C_{24} 115.6, C_{20} 109.7, C_{28} 103.5, C_{19} 94.1, C_{18} 82.2, C_{29} 65.0, C_9 39.1, C_6 37.9, C_{11} 37.5, C_5 37.5, C_{27} 35.0, C_7 33.3, C_8 33.3, C_{10} 33.3, C_3 32.3, C_{26} 29.9, C_4 26.7, C_2 22.8, C_1 14.2.

EI-MS *m/z* (rel. int.): 476(M^+, 55), 309(40), 235(28), 100(100), 73(62).

IR (KBr, pellet, cm^{-1}): 2960, 2909, 2848, 2207, 1903, 1613, 1513, 1440, 1217, 1128, 1049, 886, 816.

Elemental analysis: Calc. for $C_{32}H_{41}FO_2$: C 80.63, H 8.67; Found: C 80.33, H 8.71.

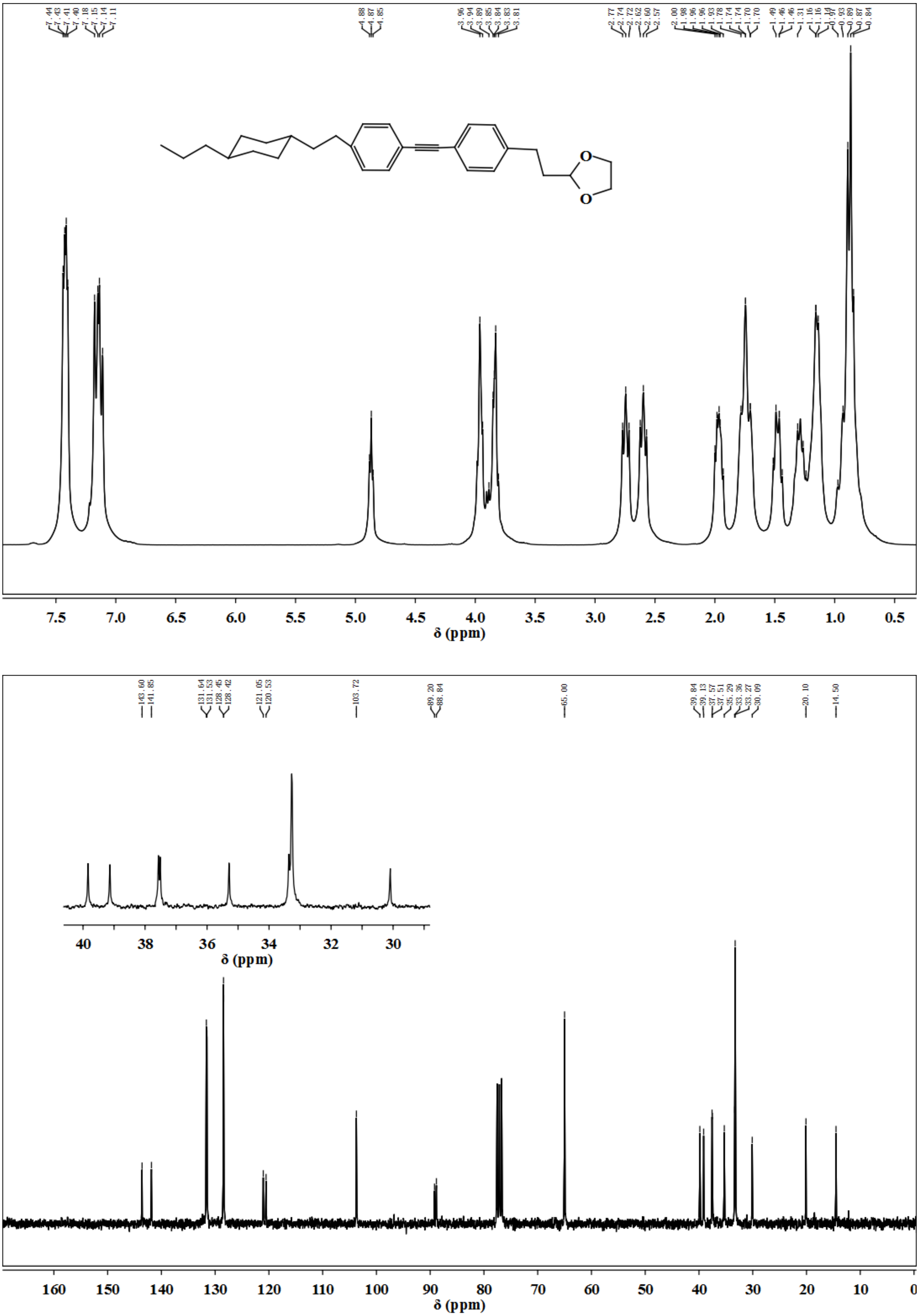
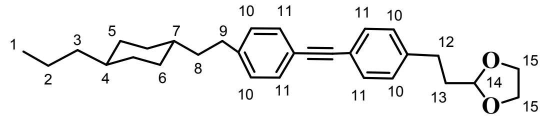
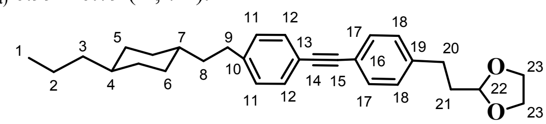


Fig. S5. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3T** recorded in $CDCl_3$.

3T: The yield was 55% of white crystals.



[1]H NMR (300 MHz, $CDCl_3$) δ (ppm): H_{11} 7.42 (dd, J = 7.7, 3.9 Hz, 4H), H_{10} 7.14 (dd, J = 12.1, 8.1 Hz, 4H), H_{14} 5.01 – 4.79 (m, 1H), H_{15} 4.09 – 3.75 (m, 4H), H_{12} 2.87 – 2.67 (m, 2H), H_9 2.67 – 2.47 (m, 2H), H_{13} 2.08 – 1.89 (m, 2H), $H_{(5e, 6e)}$ 1.84 – 1.62 (m, 4H), H_8 1.55 – 1.38 (m, 2H), $H_{(2, 3, 4, 7)}$ 1.36 – 1.08 (m, 6H), $H_{(1, 5a, 6a)}$ 0.99 – 0.79 (m, 7H).



[13]C NMR (75 MHz, $CDCl_3$) δ (ppm): C_{10} 143.6, C_{19} 141.9, C_{17} 131.6, C_{12} 131.5, C_{11} 128.4, C_{18} 128.4, C_{16} 121.1, C_{13} 120.5, C_{22} 103.7, C_{15} 89.2, C_{14} 88.8, C_{23} 65.0, C_7 39.8, C_4 39.1, C_9 37.5, C_3 37.5, C_{21} 35.3, C_5 33.3, C_6 33.3, C_8 33.3, C_{20} 30.1, C_2 20.1, C_1 14.5.

EI-MS *m/z* (rel. int.): 430(M^+, 57), 217(28), 204(30), 100(100), 73(47).

IR (KBr, pellet, cm^{-1}): 2951, 2912, 2848, 2115, 1903, 1607, 1510, 1446, 1408, 1131, 1028, 881, 811.

Elemental analysis: Calc. for $C_{30}H_{38}O_2$: C 83.67, H 8.89; Found: C 83.89, H 9.12.

The characterized data of compounds **nBF1** and **nBF2** are listed below:

2BF1: The yield was 60% of white crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.46 (d, J = 7.1 Hz, 2H), 7.29 (m, 3H), 7.00 - 6.89 (m, 2H), 4.94 - 4.91 (m, 1H), 4.07 – 3.92 (m, 2H), 3.90 – 3.74 (m, 2H), 2.87 – 2.72 (m, 2H), 2.68 – 2.50 (m, 2H), 2.09 – 1.90 (m, 2H), 1.85 – 1.65 (m, 4H), 1.60 – 1.40 (m, 2H), 1.32 – 1.03 (m, 4H), 0.99 – 0.71 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 161.4, 158.1, 144.7, 144.7, 140.8, 133.6, 130.3, 130.3, 129.0, 128.9, 128.5, 126.0, 125.9, 124.3, 124.3, 115.8, 115.5, 103.9, 65.0, 39.6, 39.0, 37.5, 35.5, 33.3, 33.3, 32.8, 30.0, 29.9, 11.6. EI-MS *m/z* (rel. int.): 410(M$^+$, 12), 348(19), 198(19), 100(100), 73(60). IR (KBr, pellet, cm^{-1}): 2964, 2919, 2848, 1916, 1568, 1498, 1446, 1409, 1125, 1035, 861, 816.

3BF1: The yield was 62% of white crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.46 (d, J =7.5 Hz, 2H), 7.30 (m, 3H), 7.00 - 6.87 (m, 2H), 4.94 - 4.91 (m, 1H), 4.02-3.99 (m, 2H), 3.91-3.86 (m, 2H), 2.80-2.77 (m, 2H), 2.64-2.61 (m, 2H), 2.04-2.00 (m, 2H), 1.76-1.73 (m, 4H), 1.57-1.51 (m, 2H), 1.30-1.28 (m, 2H), 1.17-1.13 (m, 4H), 0.92-0.85 (m, 7H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm): 161.3, 158.0, 144.7, 144.7, 140.8, 133.5, 130.3, 130.3, 129.0, 128.9, 128.5, 126.0, 125.9, 124.3, 124.3, 115.9, 115.6, 103.8, 65.0, 39.8, 39.0, 37.5, 37.5, 35.4, 33.2, 33.2, 32.8, 29.9, 20.1, 14.6, EI-MS *m/z* (rel. int.): 424(M$^+$, 8), 362(16), 198(20), 100(100), 73(61). IR (KBr, pellet, cm^{-1}): 2962, 2912, 2848, 1912, 1564, 1496, 1440, 1412, 1122, 1031, 866, 818.

4BF1: The yield was 58% of white crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.38 (d, J = 6.9 Hz, 2H), 7.20 (m, 3H), 6.98 – 6.82 (m, 2H), 4.89 – 4.81 (m, 1H), 3.98 – 3.87 (m, 2H), 3.85 – 3.75 (m, 2H), 2.78 – 2.64 (m, 2H), 2.61 – 2.51 (m, 2H), 2.04 – 1.87 (m, 2H), 1.81 – 1.61 (m, 4H), 1.52 – 1.36 (m, 2H), 1.24 – 1.06 (m, 8H), 0.91 – 0.74 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 161.3, 158.1, 144.7, 144.7, 140.8, 133.6, 130.3, 130.3, 128.9, 128.9, 128.5, 126.0, 125.8, 124.3, 124.3, 115.9, 115.6, 103.8, 65.0, 39.0, 37.8, 37.5, 37.5, 37.2, 35.4, 33.3, 33.3, 32.9, 29.9, 29.3, 23.1, 14.2. EI-MS *m/z* (rel. int.): 438(M$^+$, 7), 376(22), 198(23), 100(100), 73(66). IR (KBr, pellet, cm^{-1}): 2958, 2914, 2846, 1910, 1562, 1494, 1436, 1406, 1117, 1028, 858, 807.

5BF1: The yield was 63% of white crystals.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.45 (d, J = 7.0 Hz, 2H), 7.28 (m, 3H), 6.98 - 6.92 (m, 2H), 4.95 – 4.84 (m, 1H), 4.02 – 3.93 (m, 2H), 3.87 – 3.77 (m, 2H), 2.88 – 2.72 (m, 2H), 2.68 – 2.54 (m, 2H), 2.09 – 1.93 (m, 2H), 1.88 – 1.66 (m, 4H), 1.59 – 1.40 (m, 2H), 1.43 – 1.06 (m, 10H), 1.03 – 0.77 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 161.4, 158.1, 144.7, 144.7, 140.9, 133.6, 130.3, 130.3, 129.0, 129.0, 128.5, 126.0, 125.9, 124.3, 124.3, 116.0, 115.7, 103.9, 65.0, 39.1, 37.9, 37.5, 37.5, 35.5, 33.3, 33.3, 32.9, 32.3, 29.9, 26.8, 22.8, 14.2. EI-MS *m/z* (rel. int.): 452(M$^+$, 8), 390(29), 185(19), 100(100), 73(58). IR (KBr, pellet, cm^{-1}): 2951, 2910, 2848, 1912, 1558, 1488, 1442, 1409, 1115, 1025, 858, 809.

2BF2: The yield was 58% of white crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.33 (d, J = 7.0 Hz, 2H), 7.21 (t, J = 8.1 Hz, 1H), 7.11 (m, 2H), 6.92 - 6.86 (m, 2H), 4.85 – 4.71 (m, 1H), 3.91 – 3.78 (m, 2H), 3.75 – 3.63 (m, 2H), 2.72 – 2.60 (m, 2H), 2.57 – 2.44 (m, 2H), 1.95 – 1.81 (m, 2H), 1.78 – 1.56 (m, 4H), 1.50 – 1.35 (m, 2H), 1.20 – 0.95 (m, 4H), 0.87 – 0.67 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 161.4, 158.2, 143.0, 142.6, 133.1, 130.5, 130.5, 128.8, 128.8, 128.5, 126.6, 126.5, 124.4, 116.1, 115.8, 103.7, 65.0, 39.7, 39.4, 37.7, 35.2, 33.3, 33.2, 32.9, 30.1, 29.6, 11.6. EI-MS *m/z* (rel. int.): 410(M$^+$, 33), 324(30), 211(34), 198(31), 100(100), 73(81). IR (KBr, pellet, cm^{-1}): 2964, 2919, 2848, 1916, 1626, 1492, 1440, 1395, 1273, 1131, 1022, 887, 810.

3BF2: The yield was 62% of white crystals. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.36 (d, J = 7.5 Hz, 2H), 7.26 (t, J = 8.0 Hz, 1H), 7.16 (m, 2H), 6.96 - 6.91 (m, 2H), 4.92 – 4.79 (m, 1H), 3.97 – 3.86 (m, 2H), 3.85 – 3.74 (m, 2H), 2.74 – 2.63 (m, 2H), 2.62 – 2.50 (m, 2H), 1.99 – 1.87 (m, 2H), 1.76 – 1.63 (m, 4H), 1.49 – 1.42 (m, 2H), 1.26 – 1.20 (m, 2H), 1.17 – 1.04 (m, 4H), 0.89 – 0.77 (m, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 160.6, 158.9, 142.9, 142.6, 133.0, 130.5, 130.5, 128.8, 128.8, 128.4, 126.8, 126.6, 124.3, 116.0, 115.9, 103.7, 65.0, 39.8, 39.4, 37.5, 37.5, 35.2, 33.3, 33.3, 33.1, 29.6, 20.1, 14.5. EI-MS *m/z* (rel. int.): 424(M$^+$, 23), 338(25), 211(35), 198(31), 100(100), 73(84). IR (KBr, pellet, cm^{-1}): 2964, 2919, 2848, 1907, 1616, 1489, 1444, 1387, 1270, 1135, 1028, 891, 815.

4BF2: The yield was 60% of white crystals. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.37 (d, J = 7.6 Hz, 2H), 7.27 (t, J = 8.0 Hz, 1H), 7.17 (m, 2H), 6.97 - 6.91 (m, 2H), 4.91 – 4.80 (m, 1H), 3.98 – 3.89 (m, 2H), 3.86 – 3.78 (m, 2H), 2.75 – 2.67 (m, 2H), 2.63 – 2.54 (m, 2H), 1.97 – 1.90 (m, 2H), 1.79 – 1.63 (m, 4H), 1.51 – 1.42 (m, 2H), 1.22 – 1.07 (m, 8H), 0.90 – 0.73 (m, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 160.6, 159.0, 143.0, 142.6, 133.0, 130.5, 130.5, 128.8, 128.8, 128.4, 126.6, 126.5, 124.3, 116.0, 115.8, 103.7, 65.0, 39.4, 37.9, 37.5, 37.5, 37.2, 35.2, 33.3, 33.3, 33.1, 29.6, 29.3, 23.1, 14.2. EI-MS *m/z* (rel. int.): 438(M$^+$, 18), 376(19), 211(34), 198(30), 100(100), 73(82). IR (KBr, pellet, cm^{-1}): 2962, 2910, 2845, 1910, 1616, 1487, 1438, 1392, 1268, 1128, 1022, 887, 813.

5BF2: The yield was 61% of white crystals. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.48 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 8.1 Hz, 1H), 7.22 (m, 2H), 6.97 - 6.92 (m, 2H), 4.96 – 4.85 (m, 1H), 4.05 – 3.92 (m, 2H), 3.92 – 3.81 (m, 2H), 2.82 – 2.75 (m, 2H), 2.70 – 2.51 (m, 2H), 2.05 – 1.97 (m, 2H), 1.83– 1.70 (m, 4H), 1.58 – 1.43 (m, 2H), 1.36 – 1.08 (m, 10H), 1.00 – 0.79 (m, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 163.6, 162.0, 145.8, 142.0, 138.5, 129.6, 129.5, 128.9, 128.7, 128.4, 126.8, 126.8, 124.0, 115.2, 115.0, 103.8, 65.0, 39.4, 37.9, 37.6, 37.5, 35.4, 33.3, 33.3, 33.0, 32.3, 29.8, 26.7, 22.7, 14.1. EI-MS *m/z* (rel. int.): 452(M$^+$, 20), 390(28), 211(33), 207(83), 100(100), 73(97). IR (KBr, pellet, cm^{-1}): 2958, 2919, 2848, 1912, 1622, 1489, 1444, 1387, 1273, 1135, 1017, 890, 810.

3. Table S1 and Fig. S6

Table S1. Types of phase transition, temperatures and corresponding enthalpies obtained by POM and DSC for compounds **nTF2**, **3T**, **nBF1** and **nBF2**.[a]

Compounds	Transition temperature, °C (enthalpy change, kJ mol^{-1})	
	Heating process	Cooling process
2TF2	Cr_1 73.2 (17.8) Cr_2 101.7 (20.1) N 124.9 (1.3) I	I 122.1 (-1.4) N 88.6 (-19.8) Cr
3TF2	Cr_1 83.3 (4.4) Cr_2 117.3 (20.0) N 150.6 (1.5) I	I 146.9 (-1.7) N 94.4 (-19.6) Cr
4TF2	Cr 101.7 (21.9) N 142.8 (1.4) I	I 139.7 (-1.6) N 83.5 (-20.4) Cr
5TF2	Cr_1 83.7 (3.3) Cr_2 115.7 (23.4) N 147.3 (1.5) I	I 143.8 (-1.6) N 99.0 (-15.0) Cr
3T	Cr 130.8 (15.8) N 160.7 (1.1) I	I 155.5 (-0.9) N 108.0 (-9.4) Cr
2BF1	Cr 79.0 (0.5) I	I 76.0 (-0.6) Cr
3BF1	Cr 70.2 (14.1) N 111.8 (1.0) I	I 108.3 (-1.3) N 56.4 (-11.7) Cr
4BF1	Cr 104.3 (0.8) I	I 100.8 (-0.7) Cr
5BF1	Cr 68.1 (32.4) N 112.8 (1.1) I	I 110.3 (-1.4) N 46.0 (-14.6) Cr
2BF2	Cr 71.0 (46.0) I	I 71.4 (-1.3) Cr
3BF2	Cr 82.5 (18.5) N 113.9 (1.5) I	I 110.5 (-1.7) N 58.3 (-17.1) Cr
4BF2	Cr 66.7 (12.9) N 97.4 (0.5) I	I 94.9 (-0.7) N 40.0 (-6.6) Cr
5BF2	Cr 78.1 (21.2) N 110.1 (1.2) I	I 107.1 (-1.3) N 51.5 (-15.2) Cr

[a] Cr_1: crystal 1; Cr_2: crystal 2; N: nematic mesophase phase; I: isotropic liquid.

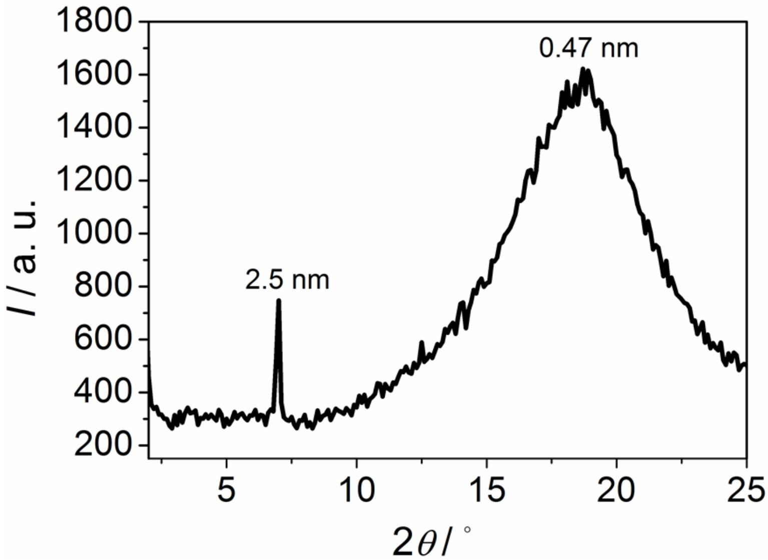


Fig. S6. X-ray scattering diagram (θ - scans over the complete XRD pattern) of **2TF2** obtained at 100 °C on the sample gradually cooled from the isotropic state.

All the nematic phases of target compounds under investigation are evident from the XRD method that was performed for representative compound **2TF2**. As shown in Fig. S6**,** in the XRD pattern of the nematic phase diffuse wide-angle maxima is observed at d = 0.47 nm, which corresponds to the mean lateral distance between the molecules and indicates fluid liquid crystal phase.[S1]

[S1] G. Shanker, M. Prehm, M. Nagaraj, J. K. Vij, M. Weyland, A. Eremin and C. Tschierske, *ChemPhysChem*, 2014, **15**, 1323–1335.

4. Geometric data

Optimized geometry for molecular **2BF2**

C	4.22429400	-0.17494900	-1.34893100
C	2.83676400	-0.18634700	-1.45790900
C	2.01681500	-0.82079400	-0.50744200
C	2.69089900	-1.44297300	0.55179800
C	4.07280200	-1.44278300	0.68137500
C	4.86853000	-0.80248300	-0.27427100
H	4.81718900	0.31637400	-2.11569800
H	2.36524500	0.28427100	-2.31507300
C	0.53772600	-0.80915900	-0.63105400
C	-0.24724100	-1.92949100	-0.30858400
C	-0.12179800	0.33458600	-1.11026800
C	-1.62968200	-1.90211500	-0.46902400
H	0.23034500	-2.82980100	0.05971200
C	-1.50551200	0.35489400	-1.26707600
H	0.45476000	1.22427900	-1.34582200
C	-2.28786700	-0.76228500	-0.94997900
H	-2.21011800	-2.78805100	-0.22193500
H	-1.98714700	1.25680400	-1.63757600
F	1.97733600	-2.07423200	1.51568800
C	6.86712300	0.49411300	0.60700500
H	6.44083600	0.53192600	1.61611400
H	6.54352400	1.39831400	0.08076000
C	-3.79521300	-0.72515100	-1.07703900
H	-4.07219500	-0.03357900	-1.88044200
H	-4.16268700	-1.71555500	-1.37590700
C	-4.49136600	-0.30908400	0.23591100
H	-4.15290600	-0.98370300	1.03338700
H	-4.14416600	0.69342300	0.52273600
C	-6.02975000	-0.32315500	0.19234700
C	-6.61768900	-0.10634900	1.59907800
C	-6.61734400	0.71561700	-0.78066800
H	-6.34916300	-1.32103100	-0.15110000
C	-8.15248800	-0.09908400	1.60125300
H	-6.25012600	0.85314700	1.99256000
H	-6.24487200	-0.88115300	2.28090900
C	-8.15423000	0.72376700	-0.77628100
H	-6.24842100	1.71265700	-0.49611200
H	-6.25917300	0.53344100	-1.80045000
C	-8.73885300	0.94222100	0.63099000
H	-8.52411800	0.08764100	2.61685300
H	-8.52070500	-1.09614700	1.31664400
H	-8.51535600	1.49488400	-1.46620400
H	-8.52292500	-0.23728800	-1.16606400
H	-8.41408700	1.93788000	0.97641100
C	-10.27787600	0.91798200	0.65445500
H	-10.60866800	0.96700600	1.70063300
H	-10.62504200	-0.05337500	0.27418800
C	-10.95501100	2.04612500	-0.13195600
H	-10.73273700	1.99192700	-1.20239500
H	-10.62645000	3.02916500	0.22492400
H	4.51178700	-1.94653400	1.53715200

C	6.37396900	-0.76306100	-0.13404400
H	6.84126700	-0.78756300	-1.12380600
H	6.71773300	-1.65719200	0.40082300
C	8.38025500	0.54050100	0.72629400
O	8.99865800	0.57704000	-0.56407700
H	8.76371100	-0.34826900	1.26191500
C	9.97991300	1.61568400	-0.55970400
C	10.08269800	2.00297300	0.91939700
H	10.92114300	1.23657400	-0.97200900
H	9.63628900	2.45770500	-1.17472700
H	10.83617400	1.39302200	1.44101600
H	10.29367600	3.06039900	1.09277800
O	8.77454800	1.71665700	1.40191700
H	-12.04348100	2.00171400	-0.02213100

Optimized geometry for molecular **2TF2**

C	5.34133500	-1.08044000	-1.44831000
C	3.95412400	-1.07965200	-1.35549800
C	3.30501300	-0.83085900	-0.12938400
C	4.12990200	-0.58404100	0.98153600
C	5.51292800	-0.58381500	0.90071300
C	6.14407900	-0.83431600	-0.32471300
H	5.81156200	-1.28221900	-2.40682000
H	3.34492400	-1.27785500	-2.23101400
C	1.88998200	-0.83980900	-0.00748700
C	0.67726100	-0.85938600	0.08203200
C	-0.74102700	-0.88981600	0.20418100
C	-1.36202700	-0.62477100	1.44080400
C	-1.55628300	-1.19843900	-0.90256500
C	-2.74666600	-0.67288200	1.55854700
H	-0.74503600	-0.38999000	2.30200700
C	-2.93942100	-1.24339100	-0.76854700
H	-1.09137000	-1.40884500	-1.86034800
C	-3.56225300	-0.98416800	0.46100400
H	-3.20583400	-0.47257800	2.52356600
H	-3.55022300	-1.49164100	-1.63320900
F	3.55188700	-0.34514000	2.17453600
C	8.20791900	0.60567400	-0.68498800
H	7.90838500	1.28607800	0.11908100
H	7.80617300	1.00824500	-1.62198300
C	-5.06895600	-1.01107900	0.59024800
H	-5.47300100	-1.77258800	-0.08586000
H	-5.34366100	-1.31892800	1.60726100
C	-5.72411000	0.35337500	0.28785300
H	-5.26992300	1.10841600	0.94293600
H	-5.47248400	0.65403100	-0.73878200
C	-7.25190500	0.38811800	0.47089100
C	-7.78712500	1.82810800	0.35883800
C	-8.00077100	-0.52014300	-0.52199600
H	-7.47723700	0.02884100	1.48861800
C	-9.31057600	1.90257700	0.52978100
H	-7.51214700	2.23278100	-0.62651700
H	-7.29402100	2.46710300	1.10236600
C	-9.52637800	-0.44375400	-0.35367600

H	-7.73266300	-0.21857500	-1.54584100
H	-7.67683000	-1.56165700	-0.41248400
C	-10.06139300	0.99615600	-0.46247200
H	-9.64941800	2.94021500	0.41584200
H	-9.57542000	1.60276600	1.55476100
H	-10.00674900	-1.08923800	-1.09782700
H	-9.80286500	-0.84840100	0.63174500
H	-9.83787000	1.35949000	-1.47921800
C	-11.58372800	1.08957300	-0.25530000
H	-11.86464600	2.15100100	-0.22745200
H	-11.83333300	0.68587700	0.73634900
C	-12.42853900	0.38366800	-1.32181700
H	-12.26299100	-0.69815700	-1.32867700
H	-13.49673600	0.54845000	-1.14696100
H	-12.19557700	0.76089400	-2.32434300
H	6.08765200	-0.39354700	1.80175900
C	7.65237900	-0.80816700	-0.42879400
H	7.97307700	-1.47474400	-1.23894300
H	8.09811200	-1.19402100	0.49373500
C	11.48142500	1.99264600	-0.42991500
O	10.17843300	1.94015000	-1.00107400
C	9.72440200	0.62266300	-0.76970200
C	11.32281300	1.13345000	0.82817900
H	12.22851200	1.56406400	-1.11543500
H	11.73223900	3.03690900	-0.23174900
H	10.08401500	-0.04693000	-1.57350300
H	10.98232600	1.73046500	1.68433300
H	12.23962700	0.60352500	1.10737000
O	10.31556900	0.18916800	0.45954300

5. Vuks equation

$$\frac{n_e^2 - 1}{n^2 + 2} = \frac{N}{3\varepsilon_0}\left[\alpha + \frac{2\Delta\alpha S}{3}\right]$$

$$\frac{n_0^2 - 1}{n^2 + 2} = \frac{N}{3\varepsilon_0}\left[\alpha - \frac{2\Delta\alpha S}{3}\right]$$

$$n^2 = \frac{n_e^2 + 2n_0^2}{3}$$

$$\Delta n = n_e - n_0$$

$$\alpha = \left(\alpha_{//} + 2\alpha_{\perp}\right)/3 = \frac{\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}}{3}$$

$$\Delta\alpha = \alpha_{//} - \alpha_{\perp} = \alpha_{XX} - \left(\frac{\alpha_{YY} + \alpha_{ZZ}}{2}\right)$$

6. The simulated molecular structure of 2BF2V

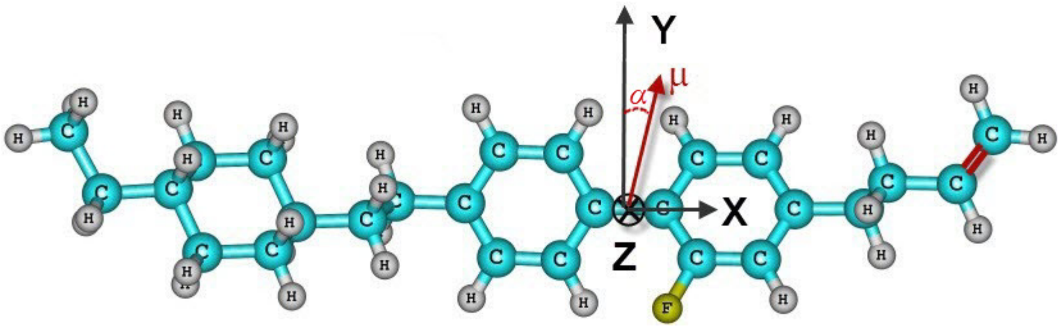


Fig. S7. The simulated molecular structure of **2BF2V**.

μ_x=0.1072, μ_y=0.7320, μ_z=0.3851

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$$

$$\cos\alpha = \frac{\mu_y}{\mu} = 0.88$$

7. Compositions of mixtures SNULC-P01 and SNULC-P02

Table S2. Chemical structures and compositions of mixture SNULC-P01

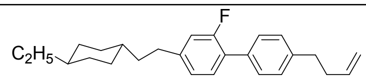
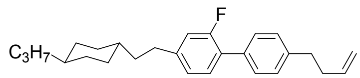
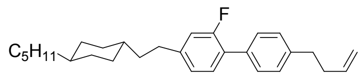
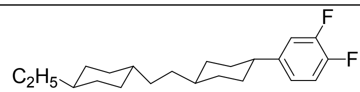
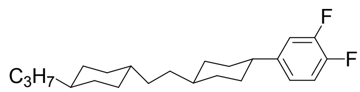
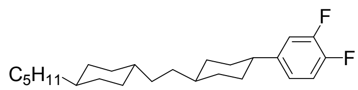
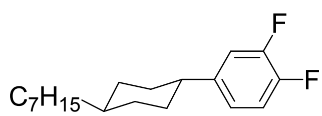
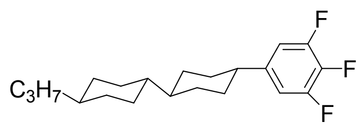
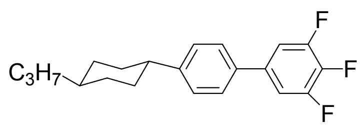
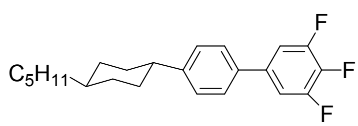
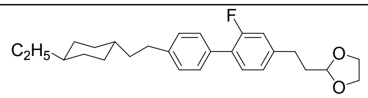
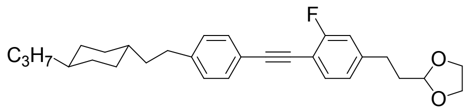
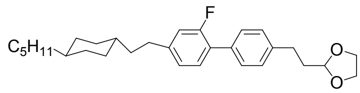
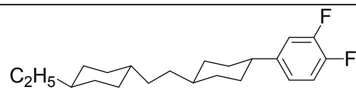
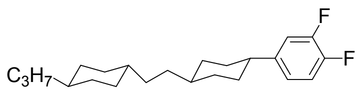
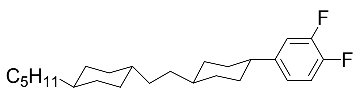
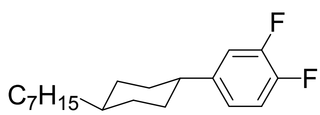
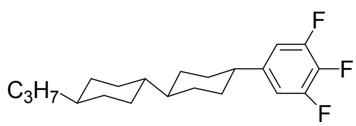
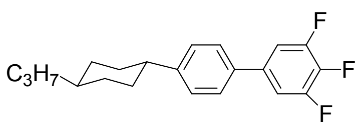
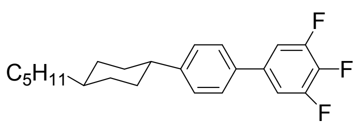
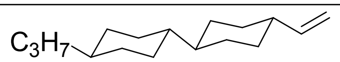
Code	Compound Structures	wt%
2H2BFB2V		8.27
3H2BFB2V		3.51
5H2BFB2V		3.53
2H2HBF2		
3H2HBF2		
5H2HBF2		
7HBF2		49.34
3HHBF3		
3HBBF3		
5HBBF3		
3HHV		35.35

Table S3. Chemical structures and compositions of mixture SNULC-P02

Code	Compound Structures	wt%
2BF2		5.02
3TF2		4.03
5BF1		6.10
2H2HBF2		49.65
3H2HBF2		
5H2HBF2		
7HBF2		
3HHBF3		
3HBBF3		
5HBBF3		
3HHV		35.20