Supplemental file

Introducing the azocinnamic acid scaffold into bent-core liquid crystal design: a structure–property relationship study

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1. General synthetic procedures

The FTIR spectra were recorded with a Bomem MB series 100 spectrophotometer in the ATR mode. The NMR spectral measurements were performed on a Bruker 300 spectrometer at 400 MHz for the ^{1}H NMR and 100 MHz for the ^{13}C NMR spectra. The spectra were recorded at room temperature in $CDCl_3$ using TMS as the internal standard. The elemental analysis of the synthesized compounds was carried out by standard analytical micromethods using an Elemental Vario EL III microanalyzer. Their results were found to be in good agreement (±0.3%) with the calculated values.

1.1. General procedure for the synthesis of acids (5)

To 30 ml of DMF in a round bottom flask were added potassium carbonate (7.4 mmol), compound **1** (2.48 mmol) and potassium iodide in catalytic amount. After 30 min of stirring at room temperature, 1-bromododecane (2.7 mmol) was added and stirring was continued for 48 h. The reaction mixture was poured into 3 times the amount of water, washed with chloroform, then with 5% solution of sodium hydroxide and at the end with water. Organic layer was dried over $MgSO_4$, filtered and recrystallized from ethanol. Resulting compound **3** was added to a solution of potassium hydroxide (16 mmol) in EtOH (35 ml) and water (5 ml) and reaction mixture was refluxed for 4 hours, followed with TLC using $CHCl_3$ as eluent until the upper point on the chromatogram disappears. The reaction mixture was poured into 3 times the amount of water and acidified with 2 M HCl, precipitate was filtered off and recrystallized from acetic acid.

1.1.1. *4-(4-Dodecyloxyphenylazo)cinnamic acid* (**5a**)

Yield: 93%; FTIR (ATR) υ: 2919, 2849, 2578, 1676, 1622, 1599, 1580, 1499, 1470, 1449, 1426, 1402, 1389, 1328, 1307, 1285, 1245, 1226, 1202, 1150, 1136, 1109, 1021, 988, 953, 841, 807, 786, 721, 706, 639, 546, 527, 514, 478 cm^{-1}; Compound is not soluble in common deuterated solvents; Elemental analysis: for $C_{27}H_{36}N_2O_3$: calculated C 74.28, H 8.31, N 6.42; found: C 74.16, H 8.33, N 6.39%.

1.1.2. *4-(3-Fluoro-4-dodecyloxyphenylazo)cinnamic acid* (**5b**)

Yield: 91%; FTIR (ATR) υ: 2917, 2849, 2679, 2593, 1677, 1624, 1614, 1584, 1511, 1501, 1471, 1424, 1405, 1392, 1321, 1305, 1275, 1215, 1099, 1044, 1020, 1001, 983, 943, 886, 840, 816, 798, 760, 728, 719, 696, 634, 620, 551, 524, 491 cm^{-1}; Compound is not soluble in common deuterated solvents; Elemental analysis: for $C_{27}H_{35}FN_2O_3$: calculated C 71.34, H 7.76, N 6.61; found: C 71.22, H 7.74, N 6.60%.

1.2. General procedure for synthesis of the investigated compounds (**Ia-g**)

To the mixture of 30 ml of toluene and acid **5** (0.92 mmol), oxalyl chloride (4.6 mmol) and DMF in catalytic amount were added. The reaction mixture was stirring overnight at rt. Toluene and oxalyl chloride were removed and the obtained solid was further dried under vacuum for 1 hour. The resulting chloride was dissolved in dichloromethane (10 ml) and added to a solution of resorcinol (0.46 mmol) and triethylamine (1.01 mmol) in dichloromethane (20 ml) and reaction mixture was stirred for 48 h. Afterwards, it was washed with 5% HCl (20 ml), two times with water, dried over $MgSO_4$ and filtered. The crude product was purified by column chromatography ($CHCl_3/CH_3OH$, 200/1).

1.2.1. *1,3-Phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate)* (**Ia**)

Yield: 83%; FTIR (ATR) υ: 2918, 2850, 2160, 1720, 1637, 1600, 1584, 1560, 1473, 1420, 1321, 1246, 1198, 1169, 1107, 1023, 981, 843, 800, 720, 677, 643, 556 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 0.81 (t, 6H, *J* = 7.2 Hz, $–CH_3$), 1.18–1.32 (m, 32H, $–CH_2–$), 1.41 (quin, 4H, *J* = 7.2 Hz, $–CH_2–$), 1.76 (quin, 4H, *J* = 6.8 Hz, $–CH_2–$), 3.98 (t, 4H, *J* = 6.8 Hz, $–CH_2O–$), 6.62 (d, 2H, *J* = 16.0 Hz, –CH=CH–), 6.94 (d, 4H, *J* = 8.8 Hz, Ar-H), 7.05 (d, 3H, *J*=6.4 Hz, Ar-H), 7.38 (t, 1H, *J* = 8.8 Hz, Ar-H), 7.66 (d, 4H, *J* = 8.4 Hz, Ar-H), 7.86 (d, 2H, *J* = 16.0 Hz, –CH=CH–), 7.86 (d, 4H, *J* = 8.4 Hz, Ar-H), 7.87 (d, 4H, *J* = 8.8 Hz, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 29.6, 29.6, 29.7, 31.9, 68.4, 114.8, 117.9, 123.2, 125.1, 129.2, 135.7, 146.0, 146.9, 151.3, 154.0, 162.2, 164.8 ppm; Elemental analysis: for $C_{60}H_{74}N_4O_6$: calculated C 76.08, H 7.87, N 5.91; found: C 76.16, H 7.91, N 5.93%.

1.2.2 *2-Methyl-1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate)* (**Ib**)

Yield: 80%; FTIR (ATR) υ: 2955, 2918, 2871, 2850, 1785, 1721, 1644, 1601, 1582, 1497, 1466, 1418, 1393, 1319, 1303, 1240, 1197, 1147, 1139, 1107, 1071, 1023, 979, 964, 841, 801, 721, 699, 644, 553 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, 6H, *J* = 6.8 Hz, $–CH_3$), 1.18–1.31 (m, 32H, $–CH_2–$), 1.41 (quin, 4H, *J* = 7.2 Hz, $–CH_2–$), 1.76 (quin, 4H, *J* = 6.8 Hz Hz, $–CH_2–$), 2.04 (s, 3H, $–CH_3$), 3.98 (t, 4H, *J* = 6.8 Hz, $–CH_2O–$), 6.67 (d, 2H, *J* = 16 Hz, –CH=CH–), 6.94 (d, 4H, *J* = 8.8 Hz, Ar-H), 7.01 (d, 2H, *J*=8.0 Hz, Ar-H), 7.23 (t, 1H, *J* = 8.2 Hz, Ar-H), 7.67 (d, 4H, *J* = 8.4 Hz, Ar-H), 7.85–7.88 (m, 8H, Ar-H), 7.88 (d, 2H, *J* = 16 Hz, –CH=CH–) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 10.1, 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 29.6, 29.6, 29.7, 31.9, 68.4, 114.8, 117.7, 119.8, 123.2, 123.9, 125.1, 126.6, 129.2, 135.7, 146.0, 146.9, 150.2, 154.0, 162.2, 164.8 ppm; Elemental analysis: for $C_{60}H_{76}N_4O_6$: calculated C 76.22, H 7.97, N 5.83; found: C 76.02, H 7.89, N 5.81%.

1.2.3 *2-Nitro-1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate)* (**Ic**)

Yield: 82%; FTIR (ATR) υ: 2953, 2920, 2849, 1742, 1632, 1602, 1583, 1499, 1467, 1419, 1359, 1315, 1304, 1246, 1191, 1121, 1104, 1021, 1005, 981, 958, 941, 912, 834, 806, 761, 720, 645, 574, 545 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, 6H, *J*=7.2 Hz, $-CH_3$), 1.18–1.31 (m, 32H, $–CH_2–$), 1.41 (quin, 4H, *J* = 7.6 Hz, $–CH_2–$), 1.75 (quin, 4H, *J* = 7.6 Hz, $–CH_2–$), 3.98 (t, 4H, *J* = 6.8 Hz, $–CH_2O–$), 6.58 (d, 2H, *J* = 16.0 Hz, –CH=CH–), 6.94 (d, 4H, *J* = 8.0 Hz, Ar-H), 7.26 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.55 (t, 1H, *J* = 8.4 Hz, Ar-H), 7.65 (d, 4H, *J* = 7.6 Hz, Ar-H), 7.84–7.88 (m, 10H, Ar-H overlapping with –CH=CH–) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 29.6, 29.6, 29.7, 31.9, 68.5, 114.8, 116.2, 121,6, 123.2, 125.2, 129.5, 131.6, 135.3, 137.5, 143.6, 146.9, 147.7, 154.2, 162.3, 163.6 ppm; Elemental analysis: for $C_{60}H_{73}N_5O_8$: calculated C 72.63, H 7.42, N 7.06; found: C 72.46, H 7.20, N 7.03%.

1.2.4. *4-Chloro-1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate)* (**Id**)

Yield: 75%; FTIR (ATR) υ: 2955, 2919, 2851, 1728, 1634, 1602, 1583, 1528, 1497, 1472, 1418, 1393, 1319, 1301, 1243, 1199, 1162, 1151, 1133, 1106, 1055, 1022, 1005, 986, 888, 872, 842, 822, 720, 670, 641, 596, 551, 538 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, 6H, *J* = 6.8 Hz, $–CH_3$), 1.19–1.27 (m, 32H, $–CH_2–$), 1.41 (quin, 4H, *J* = 6.8 Hz, $–CH_2–$), 1.76 (quin, 4H, *J* = 6.8 Hz, $–CH_2–$), 3.98 (t, 4H, *J* = 6.8 Hz, $–CH_2O–$), 6.60 (d, 1H, *J* = 16.0 Hz, –CH=CH–), 6.66 (d, 1H, *J* = 16.0 Hz, –CH=CH–), 6.94 (d, 4H, *J*=8.8 Hz, Ar-H), 7.04 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.8 Hz, Ar-H), 7.13 (d, 1H, *J*= 2.4 Hz, Ar-H), 7.44 (d,

1H, *J* = 8.8 Hz, Ar-H), 7.65 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.67 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.83–7.87 (m, 9H, Ar-H overlapping with –CH=CH–), 7.91 (d, 1H, *J* = 16.0 Hz, –CH=CH–) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 29.6, 29.6, 29.7, 31.9, 68.5, 114.8, 117.0, 117.5, 117.6, 117.6, 123.2, 125.1, 129.2, 129.3, 130.4, 135.6, 146.3, 146.7, 147.0, 149.7, 154.1, 162.2, 163.8, 164.6 ppm; Elemental analysis: for $C_{60}H_{73}ClN_4O_6$: calculated C 73.41, H 7.50, N 5.71; found: C 73.39, H 7.47, N 5.70%.

1.2.5. *4-Bromo-1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate)* (**Ie**)

Yield: 82%; FTIR (ATR) υ: 2920, 2851, 1737, 1724, 1633, 1602, 1583, 1497, 1473, 1465, 1318, 1300, 1244, 1200, 1161, 1151, 1106, 1021, 987, 843, 821, 720, 641, 615, 593, 558, 551 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, 6H, *J* = 6.8 Hz, –CH_3), 1.24–1.40 (m, 32H, –CH_2–), 1.49 (quin, 4H, *J* = 7.2 Hz, –CH_2–), 1.84 (quin, 4H, *J* = 6.8 Hz, –CH_2–), 4.06 (t, 4H, *J* = 6.8 Hz, –CH_2O–), 6.68 (d, 1H, *J* = 16.0 Hz, –CH=CH–), 6.74 (d, 1H, *J* = 16.0 Hz, –CH=CH–), 7.02 (d, 4H, *J* = 8.8 Hz, –C_6H_4–), 7.07 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.6 Hz, –C_6H_3–), 7.20 (d, 1H, *J* = 2.4 Hz, –C_6H_3–), 7.68 (d, 1H, *J* = 8.8 Hz, –C_6H_3–), 7.73 (d, 2H, *J* = 8.8 Hz, –C_6H_4–), 7.76 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.91–7.95 (m, 9H, Ar-H overlapping with –CH=CH–), 8.00 (d, 1H, *J* = 16.0 Hz, –CH=CH–) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 29.6, 29.6, 29.6, 29.7, 31.9, 68.5, 112.9, 114.8, 117.1, 117.5, 117.7, 120.7, 123.2, 125.1, 129.3, 129.3, 133.4, 135.6, 146.4, 146.8, 146.9, 148.7, 150.4, 154.1, 162.2, 163.9, 164.5 ppm; Elemental analysis: for $C_{60}H_{73}BrN_4O_6$: calculated C 70.23, H 7.17, N 5.46; found: C 70.15, H 7.18, N 5.43%.

1.2.6. *4,6-Dichloro-1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate)* (**If**)

Yield: 79%; FTIR (ATR) υ: 2917, 2849, 1727, 1631, 1597, 1581, 1498, 1466, 1382, 1321, 1303, 1242, 1192, 1122, 1090, 1024, 992, 983, 958, 902, 877, 837, 770, 743, 722, 644, 548 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, 6H, *J* = 6.8 Hz, –CH_3), 1.20–1.31 (m, 32H, –CH_2–), 1.41 (quin, 4H, *J* = 6.8 Hz, –CH_2–), 1.76 (quin, 4H, *J* = 6.8 Hz, –CH_2–), 3.98 (t, 4H, *J* = 6.8 Hz, –CH_2O–), 6.64 (d, 2H, *J* = 16.0 Hz, –CH=CH–), 6.94 (d, 4H, *J* = 8.8 Hz, Ar-H), 7.54 (s, 1H, Ar-H), 7.67 (d, 4H, *J*=8.4 Hz, Ar-H), 7.85–7.92 (m, 11H, –CH=CH– overlapping with Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 29.6, 29.6, 29.6, 29.7, 31.9, 68.5, 114.8, 116.6, 119.3, 123.2, 125.0, 125.1, 129.4, 130.8, 135.4, 146.0, 146.9, 147.1, 154.1, 162.3, 163.7 ppm; Elemental analysis: for $C_{60}H_{72}Cl_2N_4O_6$: calculated C 70.92, H 7.14, N 5.51; found: C 70.89, H 7.13, N 5.48%.

1.2.7. *4,6-Dichloro-1,3-phenylene bis(4-(3-fluoro-4-dodecyloxy-phenylazo)cinnamate)* (**Ig**)

Yield: 80%; FTIR (ATR) υ: 2955, 2922, 2850, 1738, 1625, 1571, 1498, 1464, 1405, 1380, 1331, 1317, 1301, 1265, 1208, 1154, 1098, 1088, 1020, 1001, 976, 952, 885, 842, 829, 810, 800, 758, 729, 618, 525 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, 6H, *J* = 7.2 Hz, –CH_3), 1.19–1.32 (m, 32H, –CH_2–), 1.43 (quin, 4H, *J* = 7.2 Hz, –CH_2–), 1.80 (quin, 4H, *J* = 6.8 Hz, –CH_2–), 4.06 (t, 4H, *J* = 6.8 Hz, –CH_2O–), 6.65 (d, 2H, *J* = 16.0 Hz, –CH=CH–), 7.02 (t, 2H, *J* = 8.8 Hz, Ar-H), 7.55 (s, 1H, Ar-H), 7.62–7.74 (m, 9H, Ar-H), 7.83–7.94 (m, 6H, *J*=8.4 Hz, –CH=CH– overlapping with Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.7, 25.9, 29.3, 29.5, 29.6 29.6, 29.6, 29.7, 31.9, 69.6, 107.7, 107.9, 113.5, 116.9, 119.3, 123.4, 123.4, 125.0, 129.4, 130.8, 135.9, 146.0, 146.5, 146.6, 146.9, 150.4, 150.5, 151.7, 153.8, 154.2, 163.6 ppm; Elemental analysis: for $C_{60}H_{70}Cl_2F_2N_4O_6$: calculated C 68.49, H 6.71, N 5.33; found: C 68.51, H 6.68, N 5.34%.

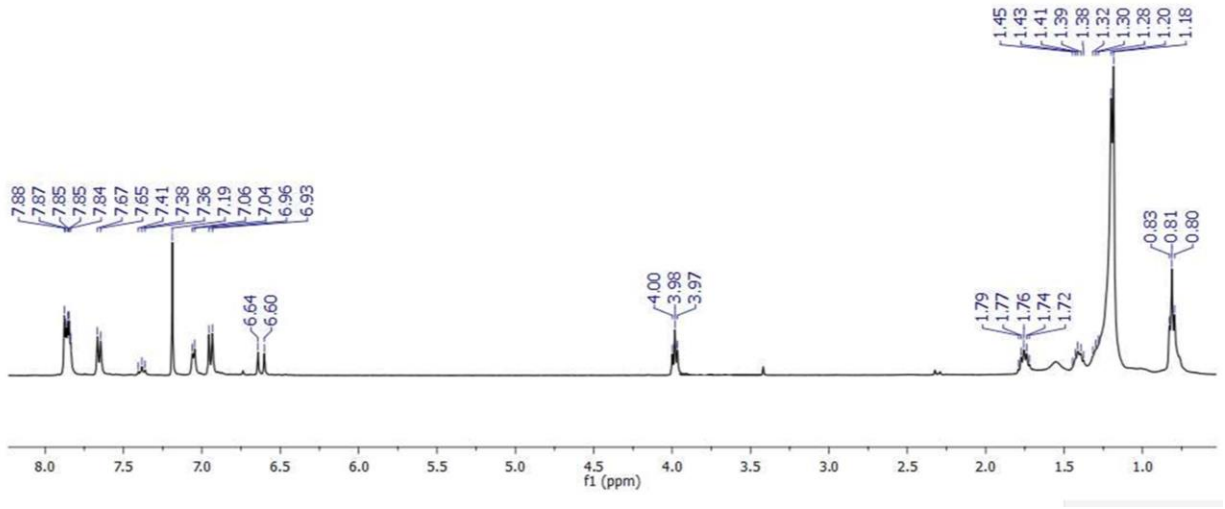

Figure S1. ^{1}H NMR spectrum of 1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate) (**Ia**).

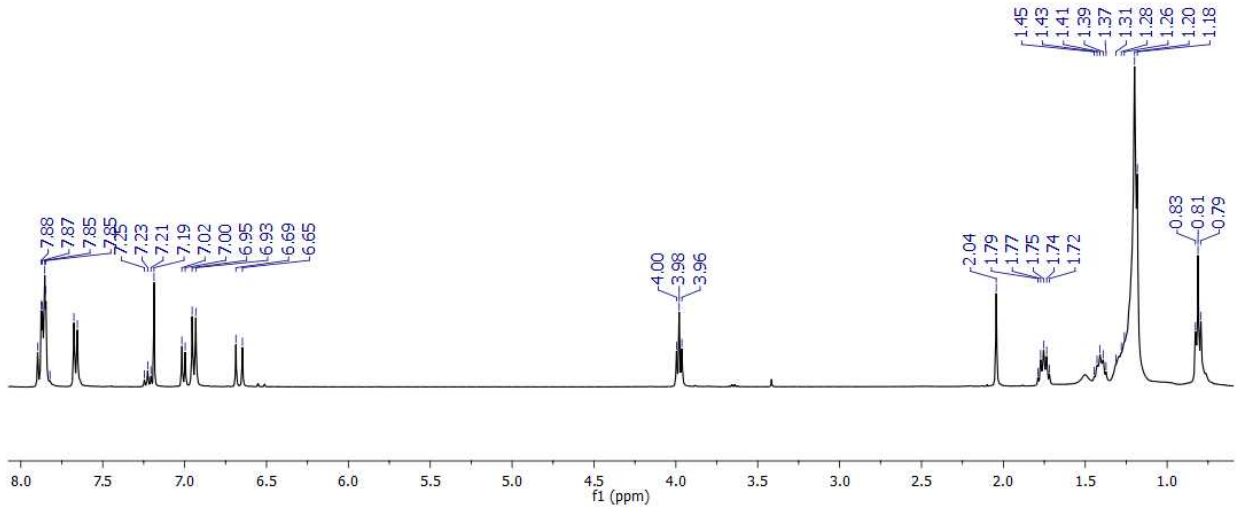

Figure S2. ^{1}H NMR spectrum of 2-methyl-1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate) (**Ib**).

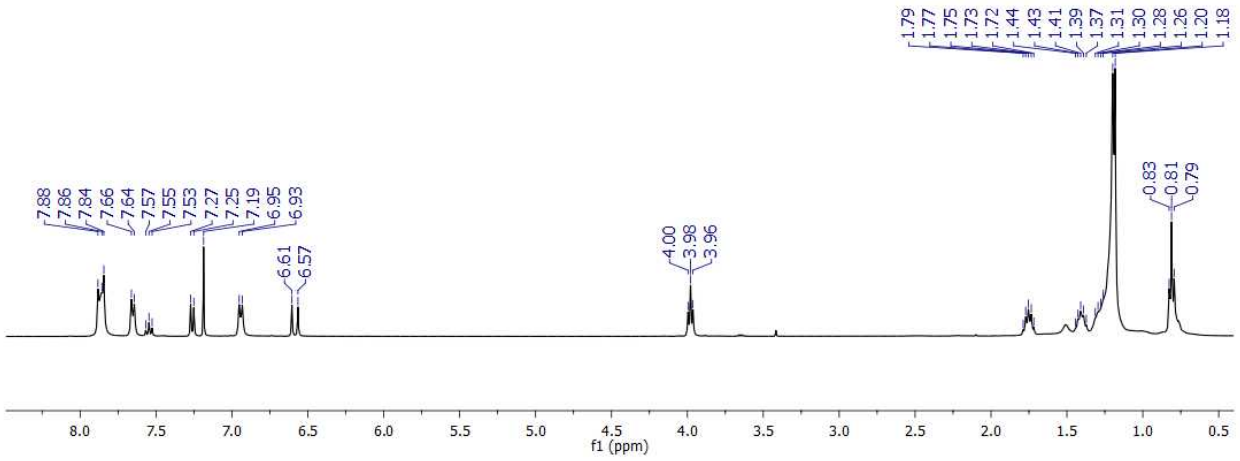

Figure S3. ^{1}H NMR spectrum of 2-nitro-1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate) (**Ic**).

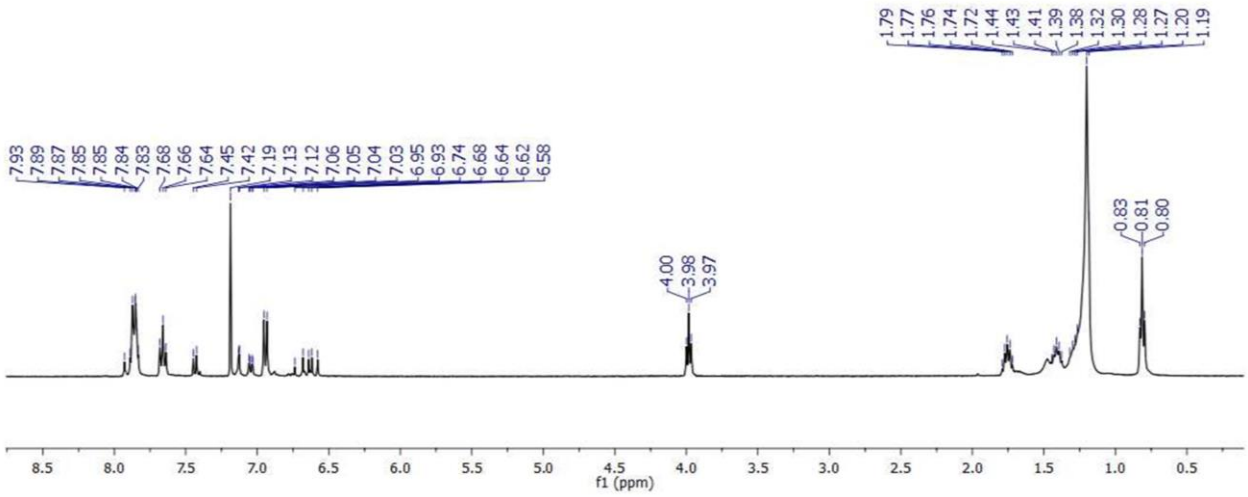

Figure S4. ^{1}H NMR spectrum of 4-chloro-1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate) (**Id**).

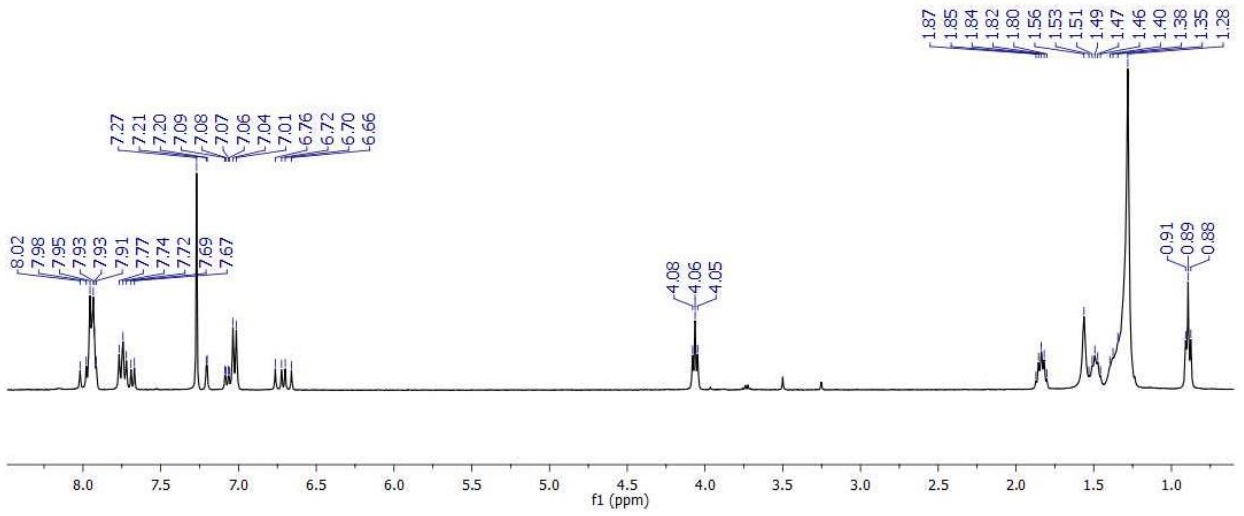

Figure S5. ^{1}H NMR spectrum of 4-bromo-1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate) (**Ie**).

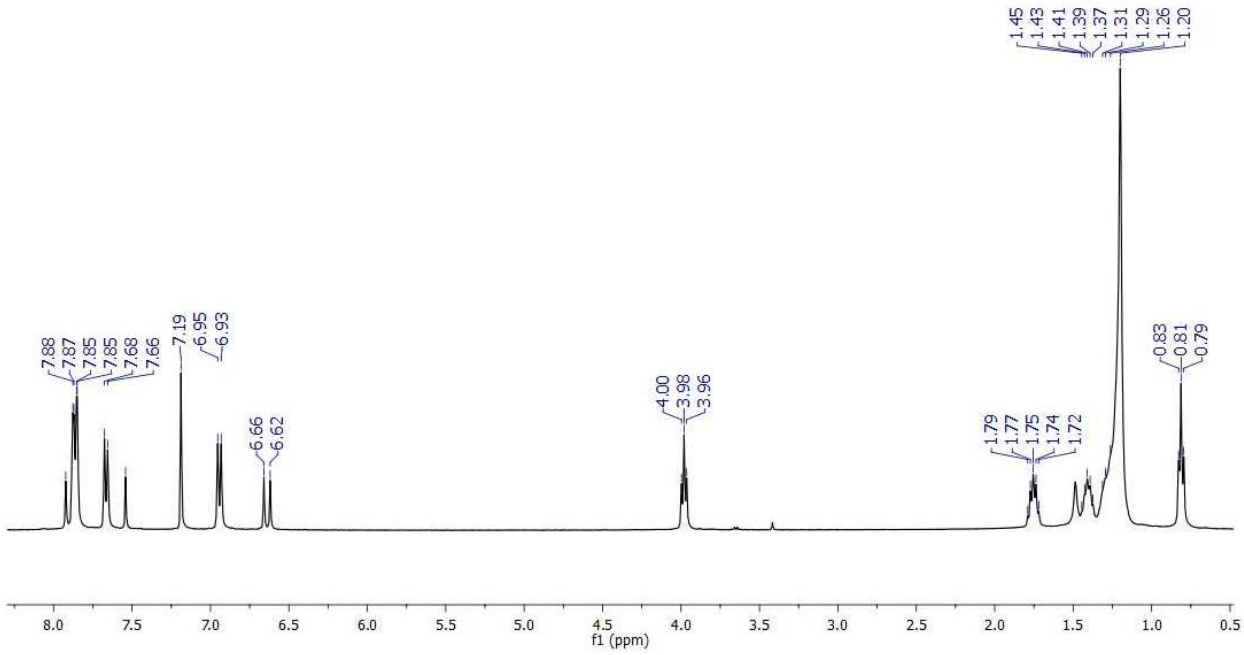

Figure S6. ^{1}H NMR spectrum of 4,6-dichloro-1,3-phenylene bis(4-(4-dodecyloxyphenylazo)cinnamate) (**If**).

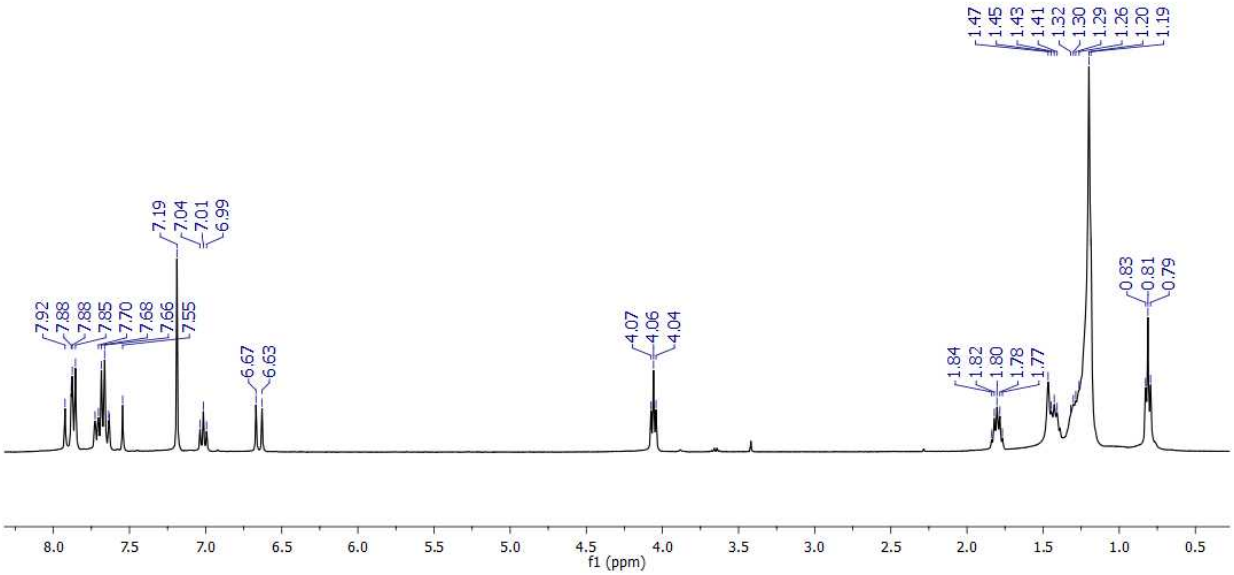

Figure S7. ^{1}H NMR spectrum of 4,6-dichloro-1,3-phenylene bis(4-(3-fluoro-4-dodecyloxy-phenylazo)cinnamate) (**Ig**).

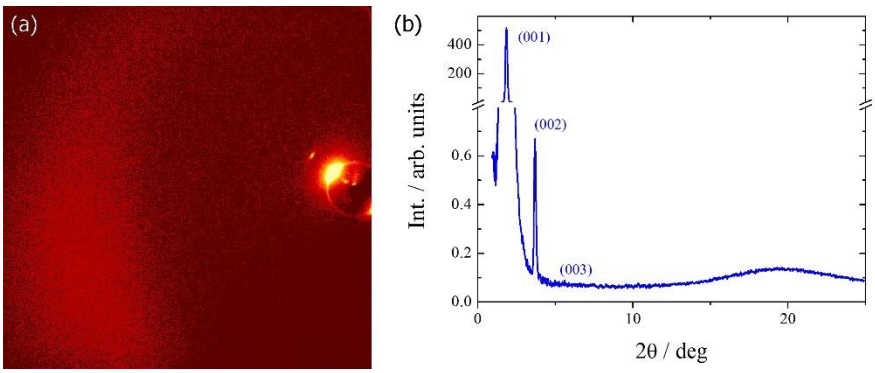

Figure S8. (a) 2D XRD pattern recorded in SmC phase of compound **Ig** at T=150 °C. (b) Diffracted intensity vs. diffraction angle obtained by integration of the pattern given in (a) over azimuthal angle. Diffuse high angle signal centered at ~4.5Å points to liquid-like molecular order within the smectic layers.

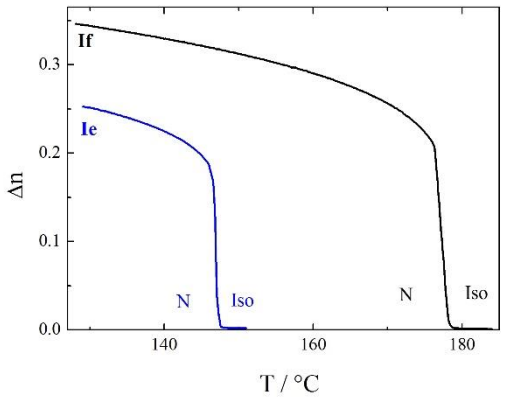

Figure S9. Optical birefringence measured with green light (λ = 532 nm) in nematic phase of compounds **Ie** (blue) and **If** (black).