Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

1,2,4-Tris(5-aryl-1,3,4-oxadiazolyl)-benzenes: Novel ⍰-shaped Fluorescent Liquid Crystals

Vincent Graschtat, Igor Proz, Matthias Lehmann, and Heiner Detert

Experimental

General Information: ^{1}H and ^{13}C NMR spectra: Bruker AC 300 (300 MHz), Bruker AV 400 (400 MHz), and Bruker ARX 400 (400 MHz), solvents were $CDCl_3$, DMSO-d_6. Chemical shifts are expressed as δ values in ppm, coupling constants are given in Hz. Melting points: Büchi HWS SG 200, Stuart Scientific SMP3. DSC: TA Instruments DSC250, IR: JASCO 4100 FT-IR (ATR), FD-MS: Mat 95 (Finnigan); HR-ESI: Agilent 6545 QTOF-HRAM-MS. UV-vis: Perkin-Elmer Lambda 16. Fluorescence: Perkin-Elmer LS 50B. Polarized optical microscopy: Olympus BX51, ColorView Olympus camera, heattable Linkam LTS 350 for temperature regulation. The temperature-dependent middle angle X-ray scattering MAXS (sample-detector distance 28 cm; 2θmax = 11.5°) and wide angle X-ray scattering WAXS (sampledetector distance 13 cm; 2θmax = 25° or with by 14° tilted detector, sample-detector distance 21 cm, 2θmax = 28.5°) investigations were performed on a Bruker Nanostar (Detector Vantec2000, Microfocus copper anode X-ray tube Incoatec). The samples were prepared by fibre extrusion using a mini-extruder. The mini-extruder consisted of a cylindrical stainless steel container of 2 mm diameter with a nozzle of 0.7 mm diameter. The container was heated to the temperature range of the liquid crystal and the fibre was extruded manually via the nozzle with a cylindrical steel pistil. The measurements were carried out in Mark capillaries (Hilgenberg) positioned perpendicular to the incident X-ray beam. All X-ray data was processed and evaluated with the program datasqueeze (http://www.datasqueezesoftware.com/) Silver behenate was used as calibration standard for MAXS and WAXS studies.

Synthesis

General procedure A: 1,2,4-TOB

Trimellitic anhydride (1 eq.) was dissolved in 2 mL of thionylchloride and a few drops of dimethylformamide where added. The mixture was heated under reflux for 4 hours. The excess of thionylchloride was removed by addition of 10 mL of dry toluene and subsequent distillation.

The crude acid chloride was dissolved in abs. toluene under nitrogen and was treated with the appropriate alkoxyaryl-tetrazole (3 eq.) and DIPEA (5 eq.). The resulting mixture was heated under reflux for 48 h. The solvent was removed under reduced pressure and the residue was recrystallized from ethyl acetate. The resulting solid was filtrated with suction and washed with cold ethyl acetate, toluene and then methanol to yield the corresponding TOB.

If the resulting product wasn't pure (^{1}H-NMR and TLC) it was further purified by column chromatography (SiO_2) using toluene/ethyl acetate (9/1) as the eluent.

General procedure B: Tetrazoles from nitriles

3,4-Bis(alkyloxy)benzonitrile (1.0 eq.), sodium azide (1.0 eq.) and $AlCl_3$ (0.1 eq.) were added to 5 mL of NMP and stirred at 170 °C overnight. The reaction progress was monitored by thin layer chromatography and, if needed, more NaN_3 and $AlCl_3$ was added. 50 mL of 2 N HCl was added to the cooled solution and the precipitated solid was filtrated by suction. The crude product was recrystallized from acetonitrile or ethanol.

General procedure C: Alkylation of hydroxybenzonitriles

3,4-Dihydroxybenzonitrile was dissolved in ACN and 3.0 eq. of K_2CO_3 and 2.1 eq. of the corresponding alkyl bromide or alkyl mesylate were added under a nitrogen atmosphere. The reaction mixture was stirred for 2 hours at room temperature and then stirred at 80 °C over night. The reaction progress was monitored by thin layer chromatography. If necessary, further alkyl bromide or alkyl mesylate was added and stirring continued. After the reaction was complete, 2 N HCl was added and the precipitated solid was filtered by suction or, in case the crude product didn't crystallize, the aqueous layer was extracted tree times with ethyl acetate. The combined organic phases were washed with brine and dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by recrystallization from petroleum ether. If the product didn't crystallize it was purified by column chromatography (SiO_2) using petroleum ether/ethyl acetate (20/1) as eluent.

1,2,4-Tris(2-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7a)

According to general procedure A: 63 mg (0.33 mmol, 1 eq.) of trimellitic anhydride and 400 mg (1 mmol, 3 eq.) (3,4-bis(octyloxy)phenyl)-tetrazole **(6a)** as well as 0.13 mL DIPEA were dissolved in 10 mL abs. toluene. **Yield:** 123 mg (0.1 mmol; 29 %) brown solid. **T_m:** 120 – 134 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 8.81 (d, *J* = 1.7 Hz, 1H), 8.51 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 7.72 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.52 – 7.38 (m, 4H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.81 (t, *J* = 8.5 Hz, 2H), 4.16 – 4.06 (m, 4H), 4.04 – 3.91 (m, 8H), 1.95 – 1.73 (m, 12H), 1.64 – 1.18 (m, 62H), 0.94 – 0.83 (m, 18H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ [ppm] = 165.96, 165.82, 162.53, 162.33, 152.62, 149.57, 149.44, 131.47, 129.02, 127.25, 124.57, 120.99, 120.73, 115.71, 115.47, 115.40, 112.98, 112.87, 111.75, 111.35, 77.58, 77.16, 76.73, 69.63, 69.38, 69.20, 31.97, 29.55, 29.50, 29.41, 29.30, 29.20, 26.18, 26.11, 22.82, 14.25. **IR (ATR):** $\tilde{\nu}$ [cm^{-1}] = 3014, 2926, 2855, 2365, 2357, 1719, 1605, 1558, 1496, 1466, 1391, 1267, 1214, 1139, 1022, 910, 867, 807, 752, 680, 666, 653. **FD-MS:** calculated for $C_{78}H_{114}N_6O_9$: 1278.86, found: 1279.00.

1,2,4-Tris(2-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7b)

According to general procedure A: 50 mg (0.26 mmol, 1 eq.) of trimellitic anhydride and 350 mg (0.76 mmol, 3 eq.) (3,4-bis(decyloxy)phenyl)-tetrazole **(6b)** as well as 0.13 mL DIPEA were dissolved in 10 mL abs. toluene. **Yield:** 86 mg (0.06 mmol; 23 %) yellow solid. **T_m:** 122 – 136 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 8.81 (d, *J* = 1.7 Hz, 1H), 8.51 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.50 – 7.38 (m, 4H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.81 (t, *J* = 8.6 Hz, 2H), 4.11 (m, 4H), 4.04 – 3.90 (m, 8H), 1.95 – 1.72 (m, 12H), 1.57 – 1.15 (m, 87H), 0.96 – 0.80 (m, 18H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ [ppm] = 165.83, 162.20, 152.50, 149.32, 125.77, 124.44, 120.60, 115.26, 112.86, 112.76, 111.24, 77.46, 77.04, 76.61, 69.51, 69.25, 69.08, 31.94, 29.68, 29.64, 29.60, 29.48, 29.43, 29.37, 29.18, 29.08, 26.07, 26.00, 22.71, 14.14. **IR (ATR):** ṽ [cm^{-1}] = 2919, 2850, 1717, 1606, 1561, 1507, 1496, 1464, 1409, 1391, 1332, 1265, 1218, 1136, 1054, 1019, 985, 940, 863, 846, 806, 771, 747, 735, 722, 697, 681, 673, 656. **FD-MS:** calculated for $C_{90}H_{138}N_6O_9$: 1447.05, found: 1447.31.

1,2,4-Tris(2-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7c)

According to general procedure A: 63 mg (0.33 mmol, 1 eq.) of trimellitic anhydride and 510 mg (1 mmol, 3 eq.) (3,4-bis(dodecyloxy)phenyl)-tetrazole **(6c)** as well as 0.13 mL DIPEA were dissolved in 10 mL abs. toluene. **Yield:** 142 mg (0.09 mmol; 27 %) brown solid. **T_m:** 123 – 135 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 8.81 (d, *J* = 1.7 Hz, 1H), 8.51 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 7.78 – 7.62 (m, 2H), 7.51 – 7.38 (m, 4H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.81 (t, *J* = 8.6 Hz, 2H), 4.16 – 4.05 (m, 4H), 4.04 – 3.90 (m, 8H), 1.84 (m, 12H), 1.65 – 1.20 (m, 114H), 0.93 – 0.82 (m, 18H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ [ppm] = 196.06, 170.83, 165.70, 162.21, 152.50, 149.33, 130.54, 120.87, 115.35, 112.82, 111.23, 77.46, 77.04, 76.61, 69.26, 69.08, 31.96, 29.74, 29.70, 29.65, 29.49, 29.45, 29.40, 29.19, 29.08, 26.07, 26.01, 22.72, 14.15. **IR (ATR):** ṽ [cm^{-1}] = 2918, 2849, 2365, 2359, 1740, 1606, 1561,1508, 1496,1465, 1391,1332, 1264,1218,1136,1067, 1055, 1012, 969,916, 886, 865, 807, 771, 747, 735, 722, 699, 688, 674, 657. **FD-MS:** calculated for $C_{102}H_{162}N_6O_9$: 1615.25, found: 1615.89.

1,2,4-Tris(2-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7d)

According to general procedure A: 63 mg (0.33 mmol, 1 eq.) of trimellitic anhydride and 460 mg (1 mmol, 3 eq.) 5-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1H-tetrazole **(6d)** as well as 0.13 mL DIPEA were dissolved in 10 mL of abs. toluene. **Yield:** 112 mg (0.08 mmol; 24 %) brown solid. **T_m:** 66 – 87 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 8.80 (d, *J* = 1.7 Hz, 1H), 8.51 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 7.77 – 7.64 (m, 2H), 7.52 – 7.38 (m, 4H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.83 (t, *J* = 8.3 Hz, 2H), 4.21 – 4.09 (m, 4H), 4.08 – 3.94 (m, 8H), 1.91 (m, 6H), 1.78 – 1.45 (m, 24H), 1.41 – 1.08 (m, 36H), 0.96 (m, 18H), 0.87 (m, 36H).**^{13}C NMR (75 MHz, $CDCl_3$):** δ [ppm] = 165.84, 165.71, 162.42, 152.49, 149.33, 129.45, 125.83, 124.51, 120.58, 112.65, 111.12, 77.46, 77.03, 76.61, 67.84, 67.46, 39.26, 37.39, 36.13, 35.99, 29.96, 28.01, 24.75, 22.73, 22.63, 19.77, 19.69. **IR (ATR):** ṽ [cm^{-1}] = 2952, 2926, 2868, 1719, 1605, 1558, 1496, 1466, 1383, 1365, 1325, 1266, 1217, 1139, 1114, 1047, 1018, 977, 905, 861, 809, 770, 736, 700, 694, 673, 668, 655. **FD-MS:** calculated for $C_{90}H_{138}N_6O_9$: 1447.05, found: 1447.05.

1,4-bis(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (11)

According to general procedure A: 51 mg (0.25 mmol, 1 eq.) of terephthalic acid and 243 mg (0.5 mmol, 3 eq.) (3,4-bis(decyloxy)phenyl)-tetrazole **(6b)** as well as 0.13 mL DIPEA were dissolved in 10 mL of abs. toluene. Isolation of target compound via column chromatography. **Yield:** 171 mg (0.17 mmol; 69 %) yellow solid. **T_m:** ~136 °C (decomposition). **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 8.29 (s, 2H), 7.71 – 7.65 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 4.10 (dt, *J* = 12.9, 6.6 Hz, 4H), 1.92 – 1.83 (m, 4H), 1.73 – 1.59 (m, 2H), 1.56 – 1.45 (m, 4H), 1.44 – 1.20 (m, 25H), 0.94 – 0.83 (m, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ [ppm] = 165.21, 163.36, 152.53, 149.39, 127.40, 126.61, 120.62, 115.91, 112.87, 111.69, 69.49, 69.16, 31.94, 29.66, 29.64, 29.61, 29.60, 29.45, 29.42, 29.38, 29.22, 29.11, 26.04, 26.01, 22.71, 14.14. **IR (ATR):** ṽ [cm^{-1}] = 2918, 2848, 1603, 1509, 1466, 1271, 1220, 1139, 1045, 1014, 987, 856, 808, 723, 668, 657. **FD-MS:** calculated for $C_{62}H_{94}N_4O_6$: 990.72, found: 990.33.

5-(3,4-Bis(octyloxy)phenyl)-1*H*-tetrazol (6a)[1]

According to general procedure B: 5.08 g 3,4-bis(octyloxy)benzonitrile **(5a)** (14 mmol, 1 eq.) 0.19 g $AlCl_3$ (1.4 mmol, 0.1 eq.) and 0,91 g NaN_3 (14 mmol, 1 eq.) were suspended in 15 mL NMP. Aqueous work-up and recrystallization from acetonitrile. **Yield:** 4.75 g (11.8 mmol; 84 %) beige solid. **T_m:** 164 – 168 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 7.62 – 7.47 (m, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 4.03 – 3.93 (m, 1H), 1.77 (m, 1H), 1.50 – 1.15 (m, 20H), 0.89 – 0.77 (m, 6H). **IR (ATR):** ṽ [cm^{-1}] = 2920, 2850, 1606, 1510, 1464, 1269, 1233, 1135, 1067, 1038, 873, 810,759, 745, 724, 659.

5-(3,4-Bis(decyloxy)phenyl)-1*H*-tetrazol (6b)[1]

According to general procedure B: 16 g 3,4-bis(decyloxy)benzonitrile **(5b)** (35 mmol, 1 eq.) 0.46 g $AlCl_3$ (3.5 mmol, 0.1 eq.) and 2.3 g NaN_3 (35 mmol, 1 eq.) were suspended in 15 mL NMP. Aqueous work-up and recrystallization from acetonitrile. **Yield:** 13.76 g (30 mmol; 85 %) beige solid. **T_m:** 158 – 159 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 7.64 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 4.07 – 3.95 (m, 4H), 1.82 (m, 4H), 1.52 – 1.18 (m, 28H), 0.91 – 0.80 (m, 6H).

5-(3,4-Bis(dodecyloxy)phenyl)-1*H*-tetrazol (6c)[1]

According to general procedure B: 3.93 g 3,4-bis(dodecyloxy)benzonitrile **(5c)** (8.3 mmol, 1 eq.) 0.11 g $AlCl_3$ (0.8 mmol, 0.1 eq.) and 1.35 g NaN_3 (8.3 mmol, 1 eq.) were suspended in

15 mL NMP. Aqueous work-up and recrystallization from acetonitrile. **Yield:** 13.76 g (30 mmol; 85 %) brown solid. **T_m:** 153 – 157 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 7.53 (d, *J* = 2.0 Hz, 1H), 7.49 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 3.93 (m, 4H), 1.71 (m, 4H), 1.43 – 1.05 (m, 36H), 0.80 – 0.70 (m, 6H). **IR (ATR):** $\tilde{\nu}$ [cm^{-1}] = 2920, 2849, 1606, 1510, 1465, 1270, 1235, 1131, 1038, 875, 810, 745, 723, 715, 682, 669.

5-(3,4-Di((3,7-dimethyloctyl)oxy)phenyl)-1H-tetrazole (6d)[1]

According to general procedure B: 3.0 g 3,4-bis((3,7-dimethyloctyl)oxy)benzonitrile **(5d)** (6.54 mmol, 1 eq.) 0.09 g $AlCl_3$ (0.65 mmol, 0.1 eq.) and 0.425 g NaN_3 (6.54 mmol, 1 eq.) were suspended in 10 mL NMP. Aqueous work-up and recrystallization from acetonitrile. **Yield:** 2.13 g (4.65 mmol; 65 %) beige solid. **T_m:** 94 – 95 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 7.71 (d, *J* = 7.2 Hz, 2H), 7.02 – 6.96 (m, 1H), 4.09 (m, 4H), 1.87 (m, 2H), 1.75 – 1.43 (m, 6H), 1.40 – 1.04 (m, 12H), 0.95 (d, *J* = 6.3 Hz, 3H), 0.91 (d, *J* = 6.3 Hz, 3H), 0.86 (t, *J* = 6.6 Hz, 12H).

3,4-Bis(octyloxy)benzonitrile (5a)[1]

According to general procedure A: 2.7 g (20 mmol, 1.0 eq) 3,4-dihydroxybenzonitrile, 8.3 g (60 mmol, 3 eq.) K_2CO_3 and 7,3 mL (42 mmol, 2.1 eq.) octylbromide were suspended in 50 mL ACN. Aqueous work-up and recrystallization from petroleum ether. **Yield:** 5.1 g (14,2 mmol; 71 %) colorless solid. **T_m:** 73 – 74 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 7.23 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.07 (d, *J* = 1.9 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 4.06 – 3.99 (m, 4H), 1.88 – 1.77 (m, 4H), 1.51 – 1.22 (m, 20H), 0.91 – 0.86 (m, 6H). **IR (ATR):** $\tilde{\nu}$ [cm^{-1}] = 2952, 2917, 2871, 2849, 2219, 1595, 1579, 1517, 1468, 1421, 1395, 1335, 1274, 1243, 1168, 1137 1058, 1012, 997,984, 957, 943, 914, 855, 836, 810, 805, 753, 736, 722, 695, 653.

3,4-Bis(decyloxy)benzonitrile (5b) [1]

According to general procedure A: 3.4 g (25 mmol, 1.0 eq) 3,4-dihydroxybenzonitrile, 10.4 g (75 mmol, 3 eq.) K_2CO_3 and 11 g (50 mmol, 2 eq.) decylbromide were suspended in 50 mL ACN. Aqueous work-up and recrystallization from petroleum ether. **Yield:** 7.9 g (19 mmol; 76 %) colorless solid. **T_m:** 78 – 79 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 7.23 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.07 (d, *J* = 1.9 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.04 – 3.97 (m, 4H), 1.87 – 1.78 (m, 4H), 1.50 – 1.27 (m, 28H), 0.90 – 0.86 (m, 6H).

3,4-Bis(dodecyloxy)benzonitrile (5c) [1]

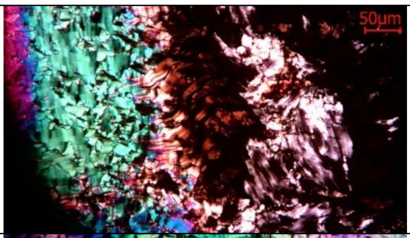
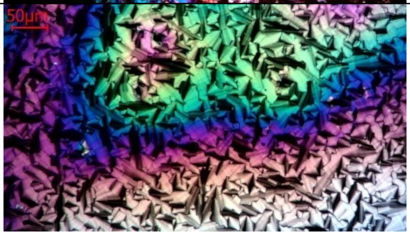
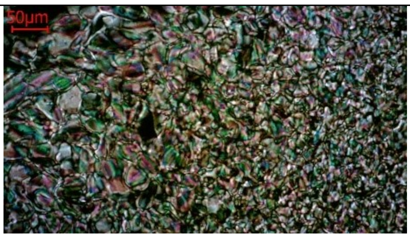
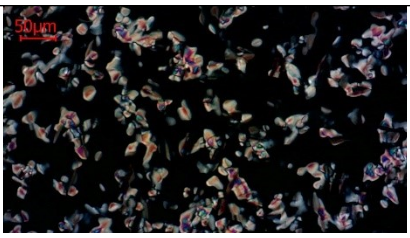
According to general procedure A: 2.7 g (20 mmol, 1.0 eq) 3,4-dihydroxybenzonitrile, 8.3 g (60 mmol, 3 eq.) K_2CO_3 and 10.1 mL (42 mmol, 2.1 eq.) dodecylbromide were suspended in 50 mL ACN. Aqueous work-up and recrystallization from petroleum ether. **Yield:** 3.9 g (19 mmol; 42 %) colorless solid. **T_m:** 83 – 84 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 7.23 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.07 (d, *J* = 1.9 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.04 – 3.97 (m, 4H), 1.87 – 1.78 (m, 4H), 1.50 – 1.27 (m, 28H), 0.90 – 0.86 (m, 6H). **IR (ATR):** ṽ [cm^{-1}] = 2953, 2915, 2872, 2848, 2220, 1596, 1580, 1519, 1468, 1422, 1396, 1336, 1277, 1242, 1169, 1138, 1069, 1030, 992, 955, 905, 854, 810, 721, 664, 658.

3,4-Bis((3,7-dimethyloctyl)oxy)benzonitrile (5d)[1]

According to general procedure A: 1.2 g (9 mmol, 1.0 eq) 3,4-dihydroxybenzonitrile, 5 g (36 mmol, 4 eq.) K_2CO_3 and 5.2 g (20 mmol, 2.1 eq.) 3,7-dimethyloctyl mesylate were suspended in 25 mL ACN. Aqueous work-up and column chromatography. **Yield:** 2.13 g (4.65 mmol; 52 %) beige solid. **T_m:** 94 – 95 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 7.71 (d, *J* = 7.2 Hz, 2H), 7.02 – 6.96 (m, 1H), 4.09 (tt, *J* = 6.4, 3.1 Hz, 4H), 1.87 (h, *J* = 7.4 Hz, 2H), 1.75 – 1.43 (m, 6H), 1.40 – 1.04 (m, 12H), 0.95 (d, *J* = 6.3 Hz, 3H), 0.91 (d, *J* = 6.3 Hz, 3H), 0.86 (t, *J* = 6.6 Hz, 12H).

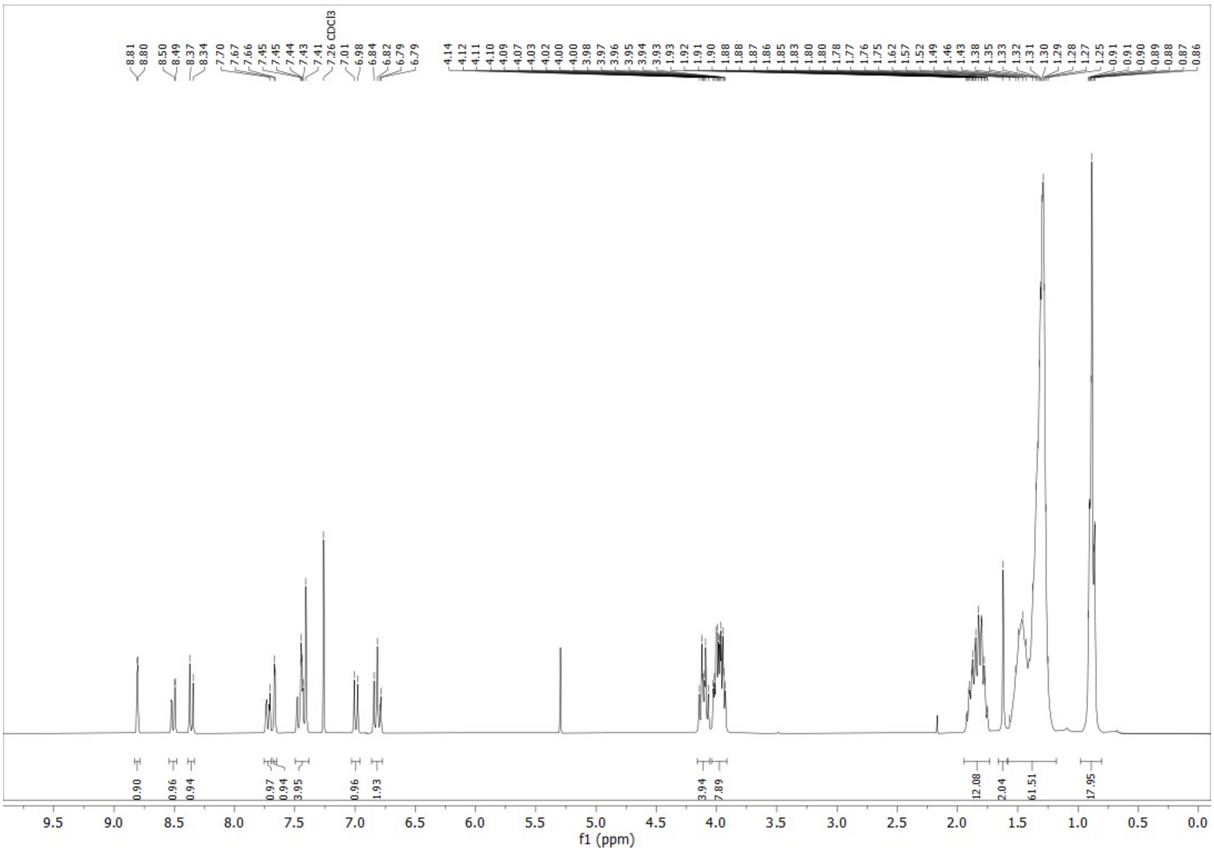
Textures POM:

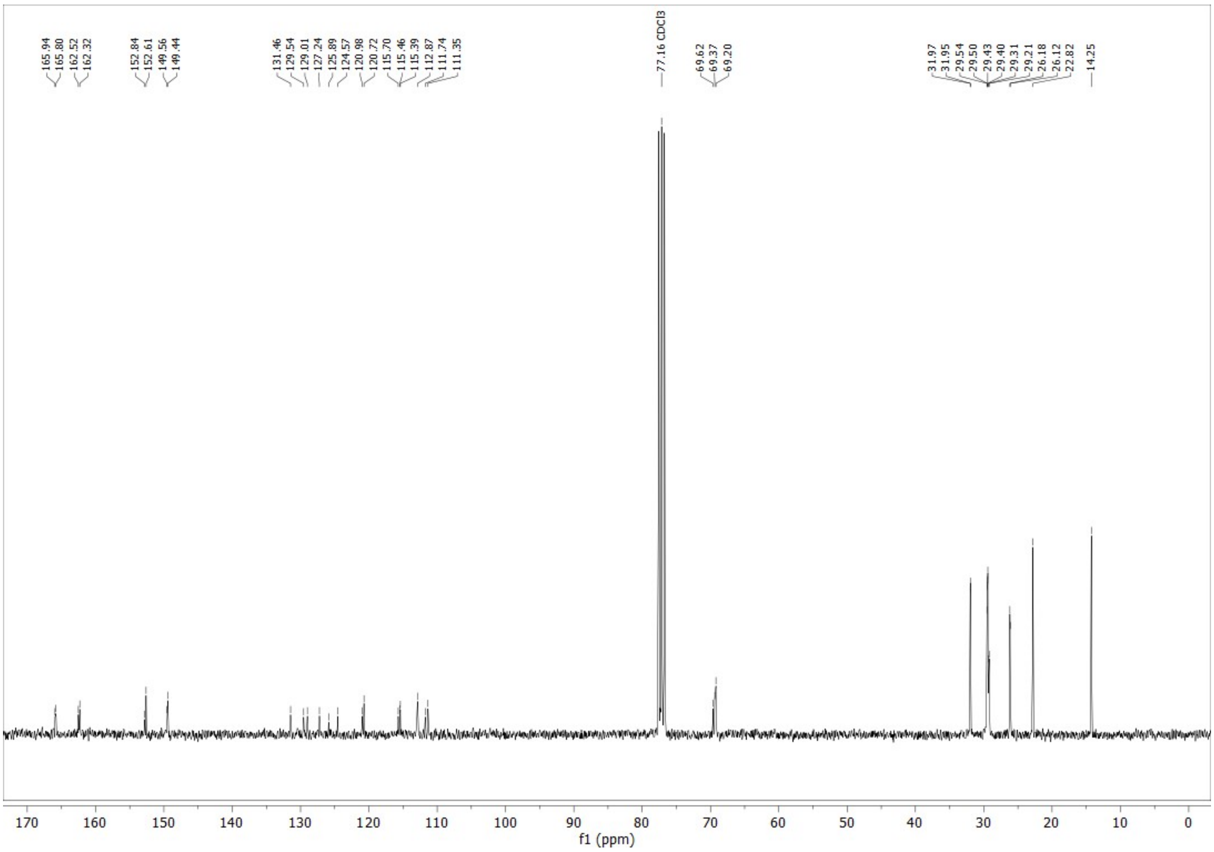
Table S1: Textures

Compound	Texture	T / °C	Texture
7a		130	mosaic texture
7b		130	Pseudo focal conic fans
7c		130	Mosaic texture
7d		75	Pseudo focal conic fans

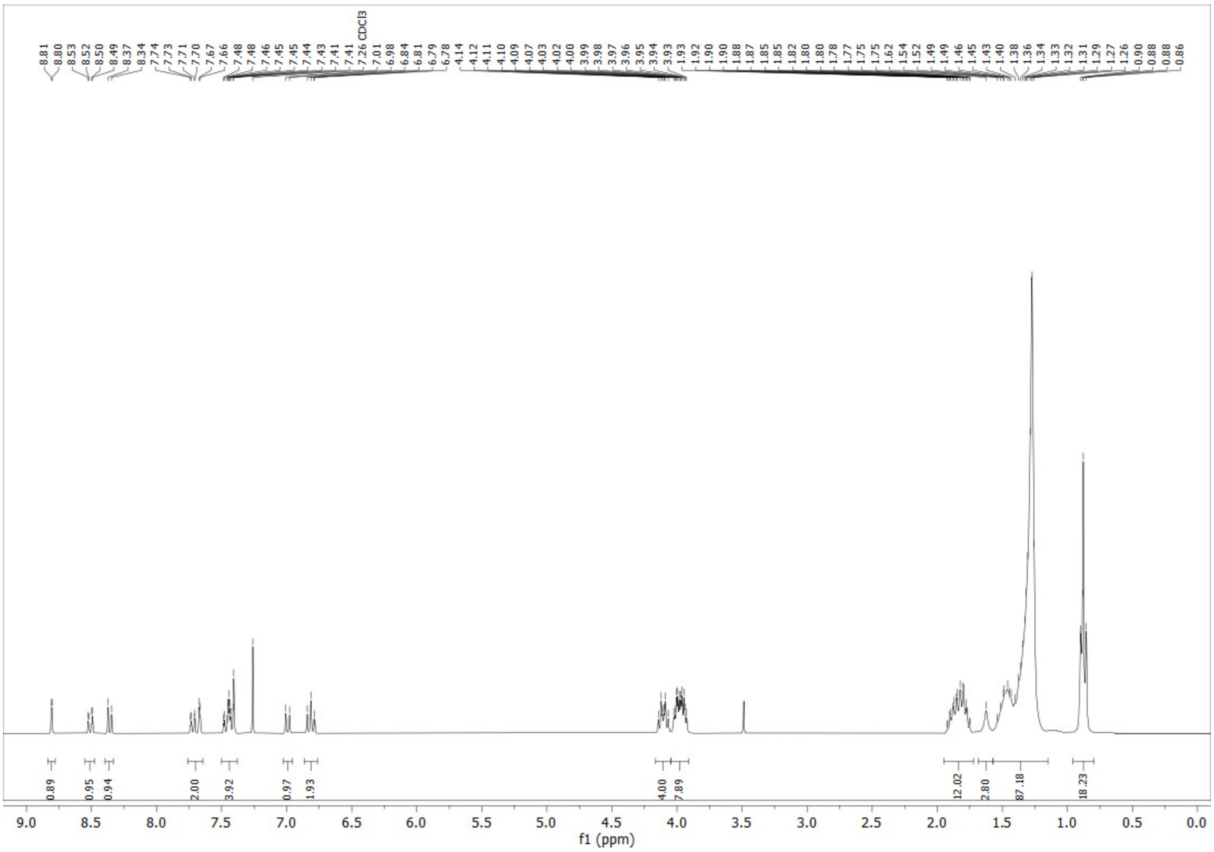
^{1}H- and ^{13}C-spectra:

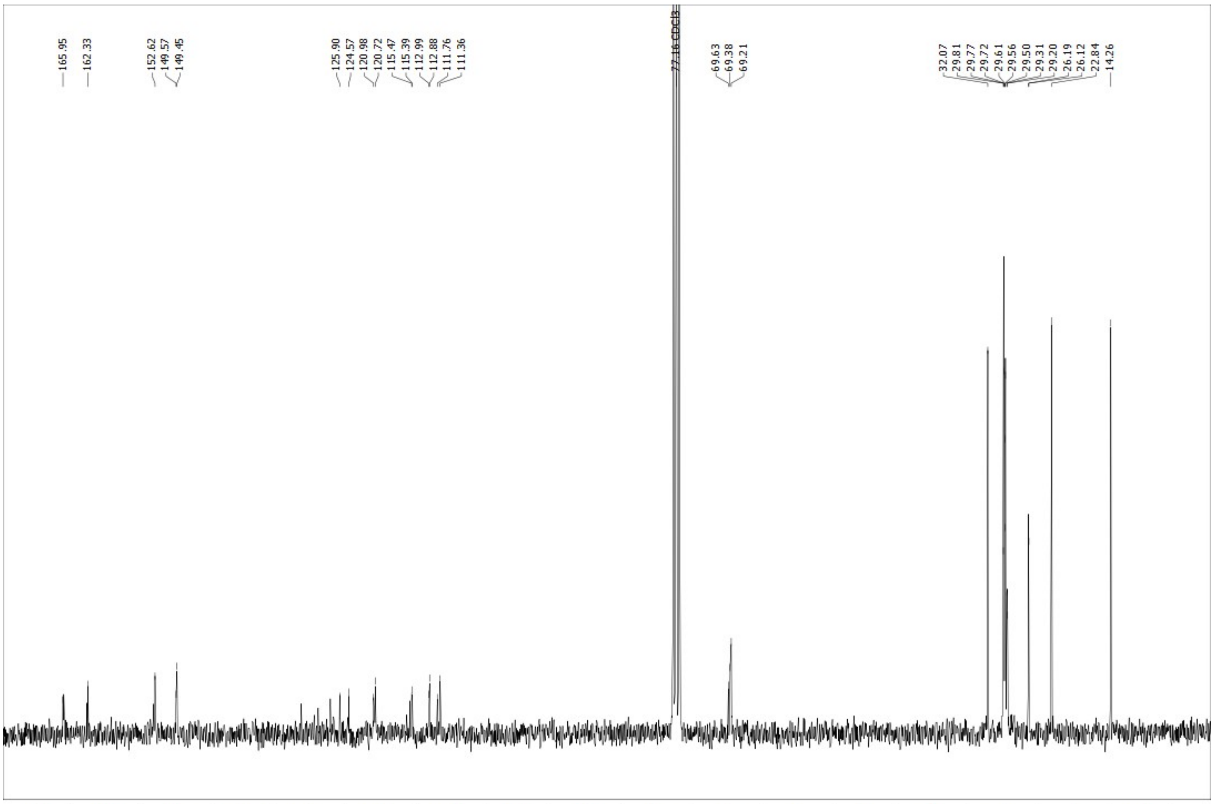
1,2,4-Tris(2-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7a) in $CDCl_3$



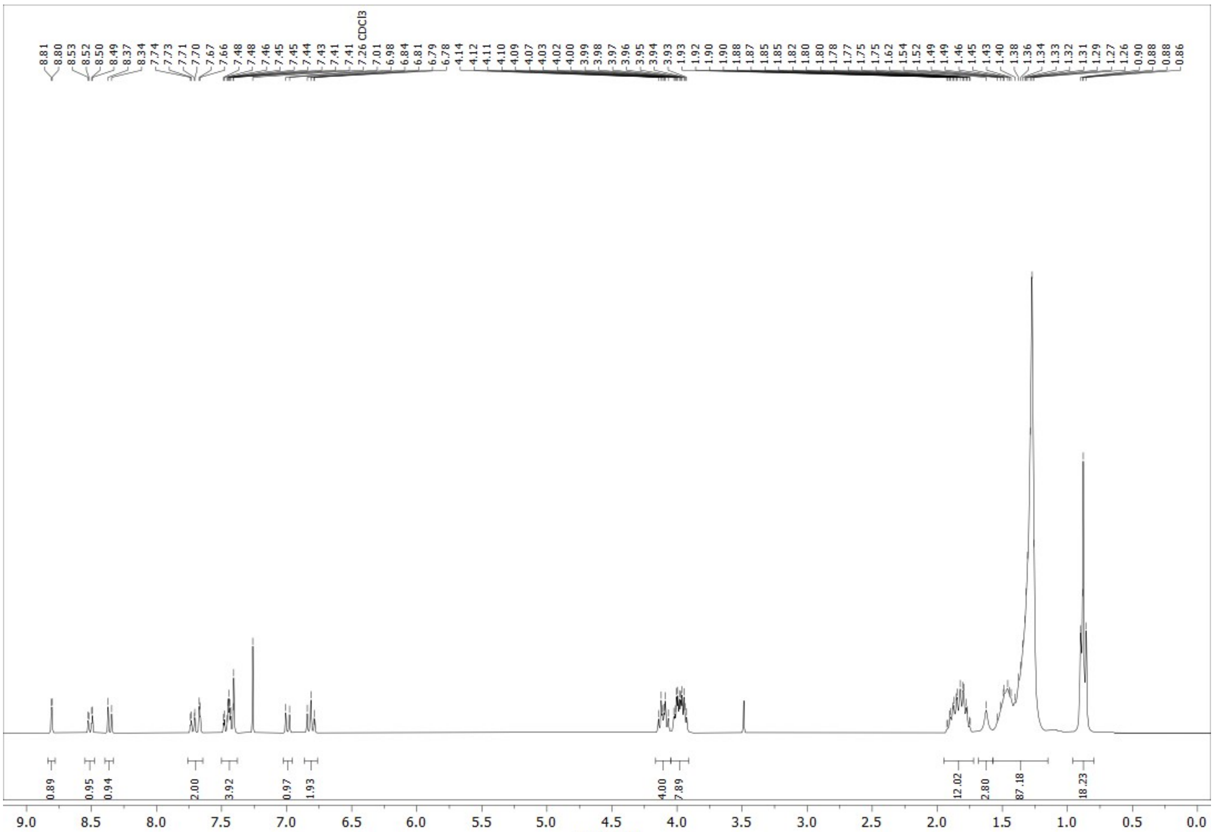


1,2,4-Tris(2-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7b) in $CDCl_3$

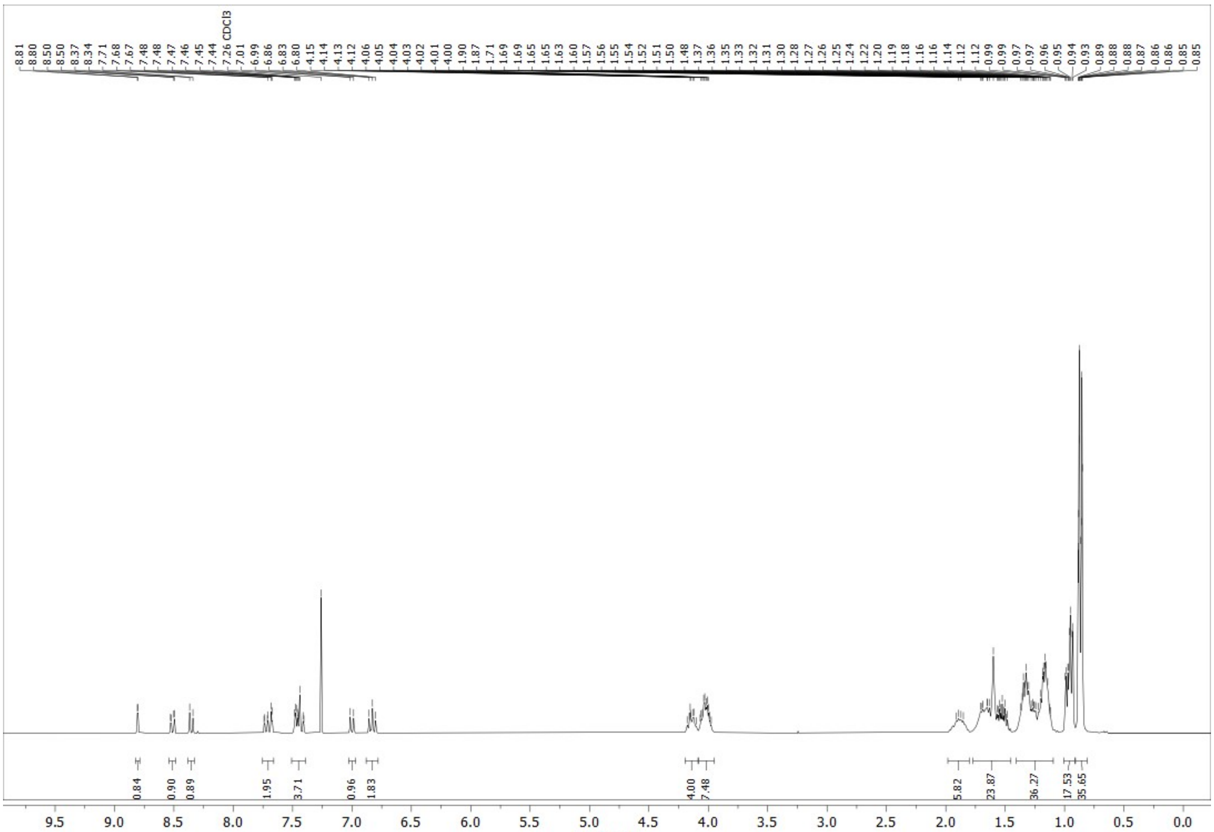


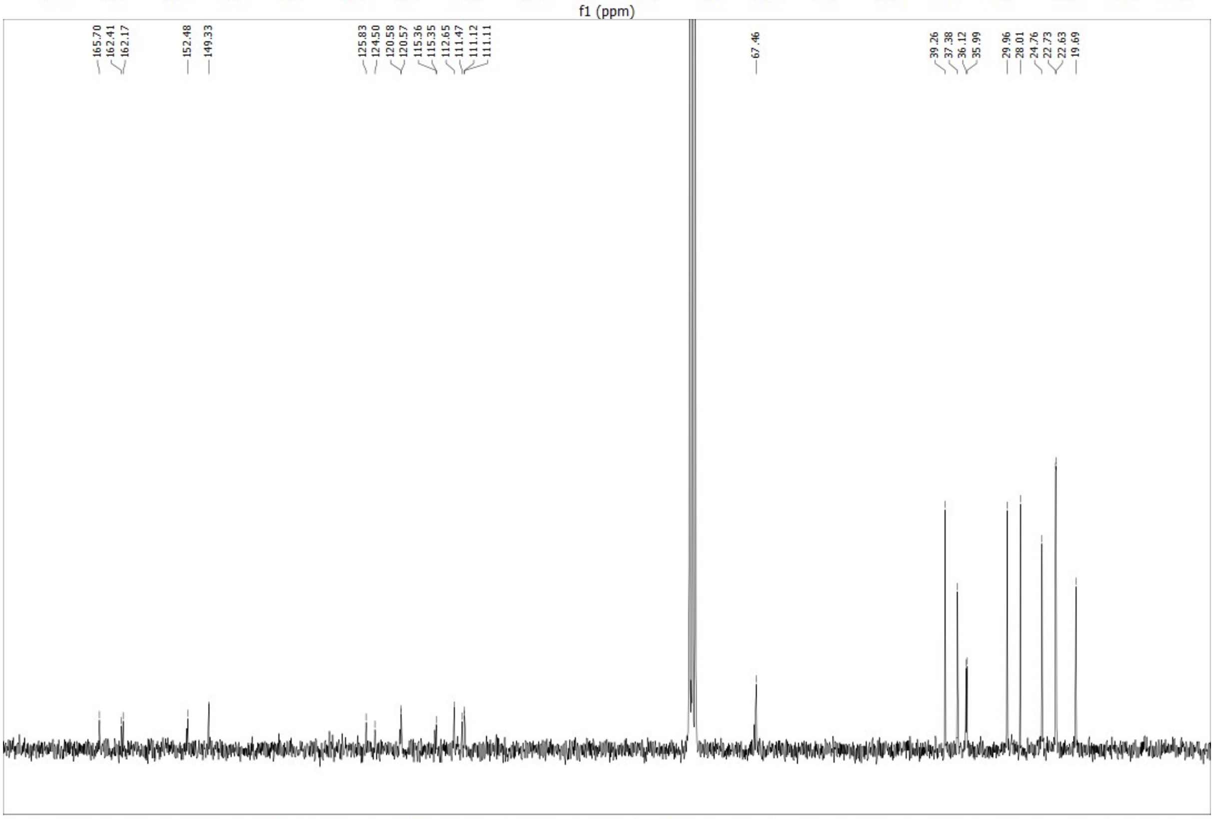


1,2,4-Tris(2-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7c) in $CDCl_3$

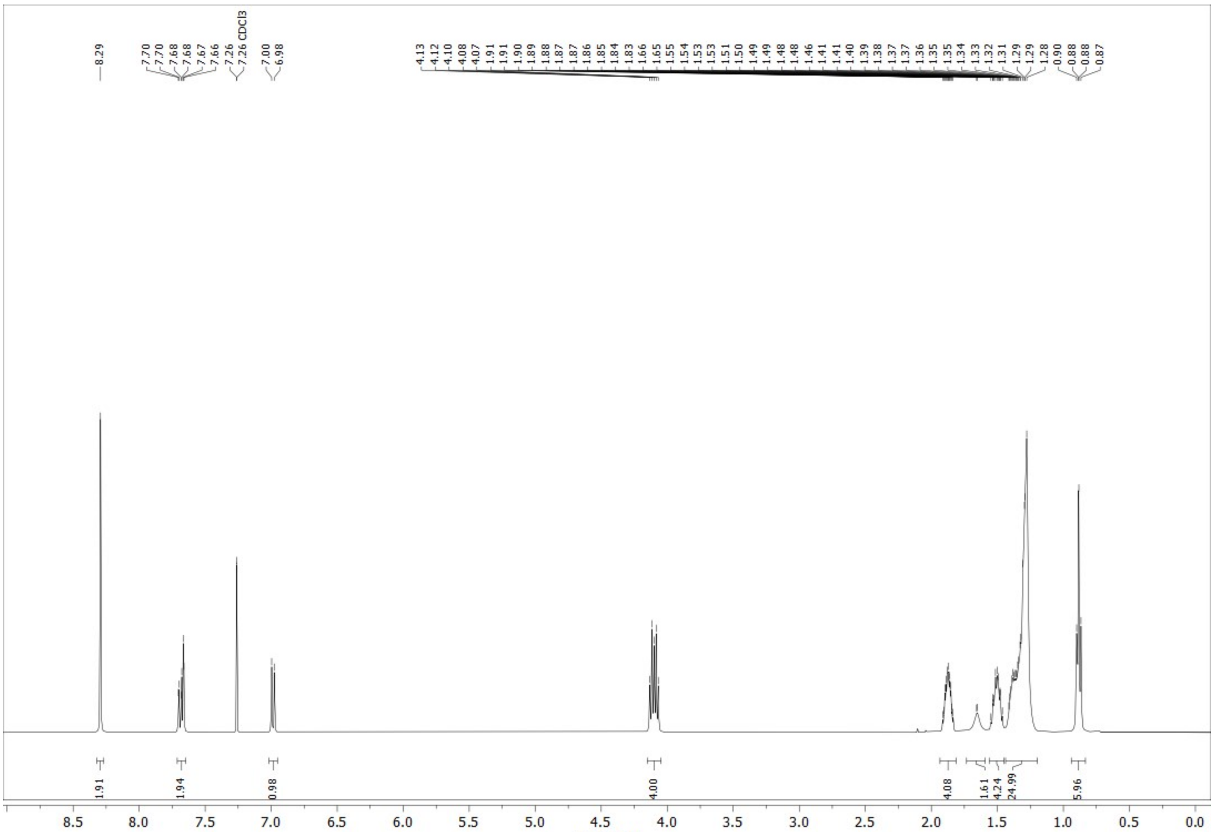


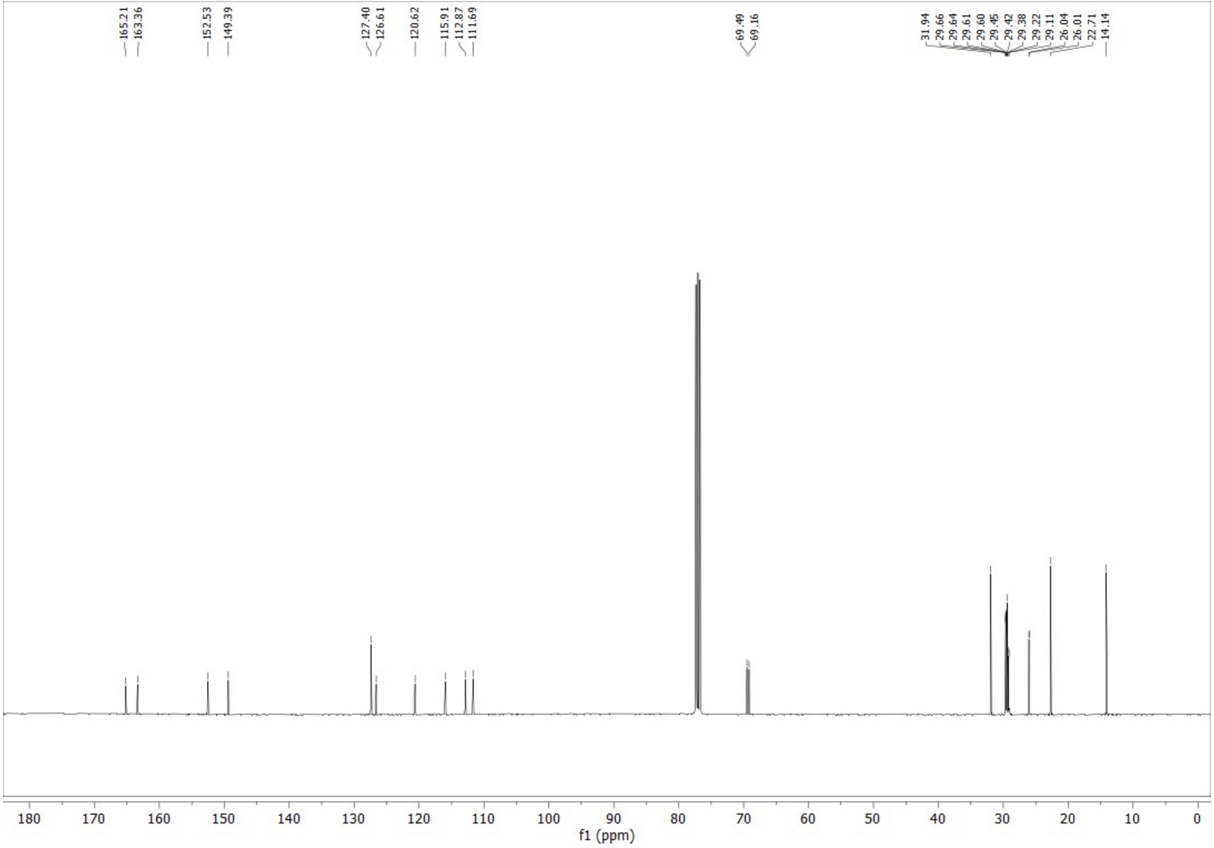
1,2,4-Tris(2-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7d) in $CDCl_3$



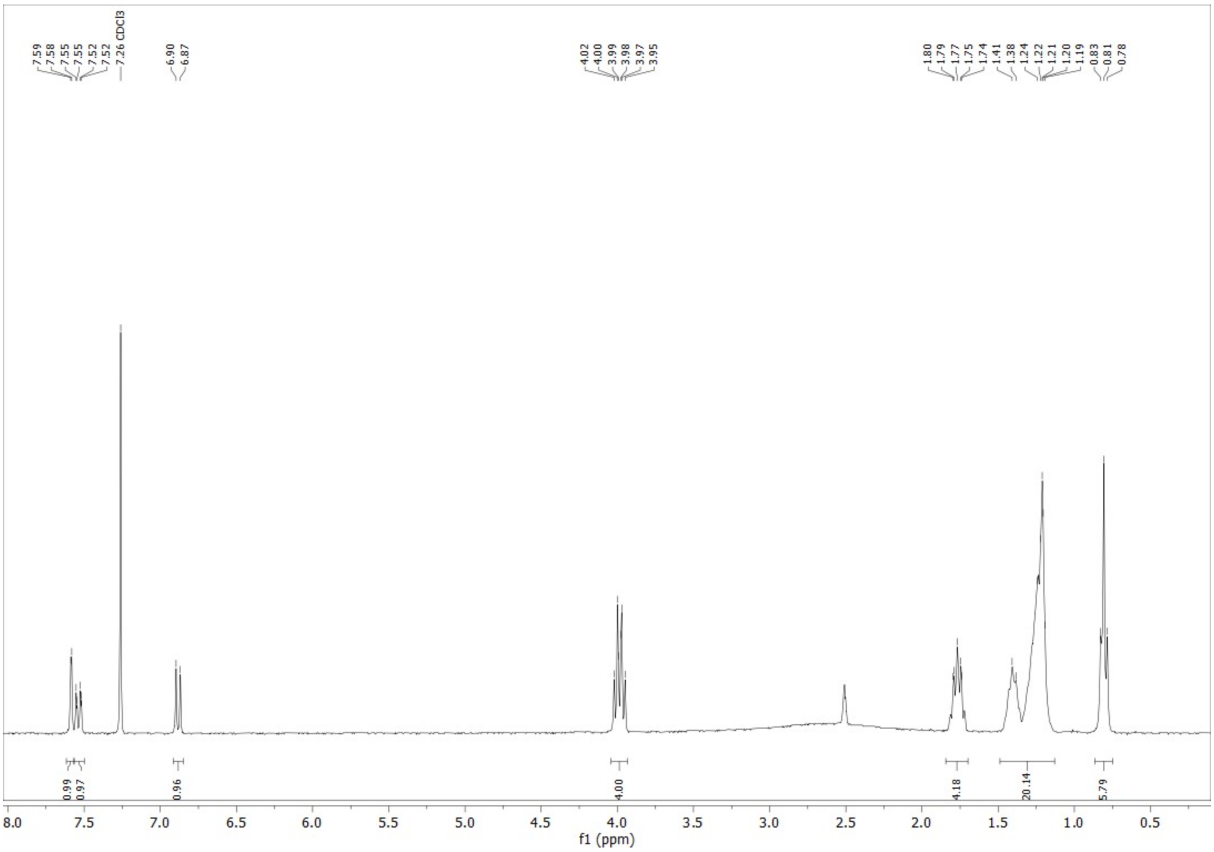


1,2,4-Tris(2-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (11) in $CDCl_3$

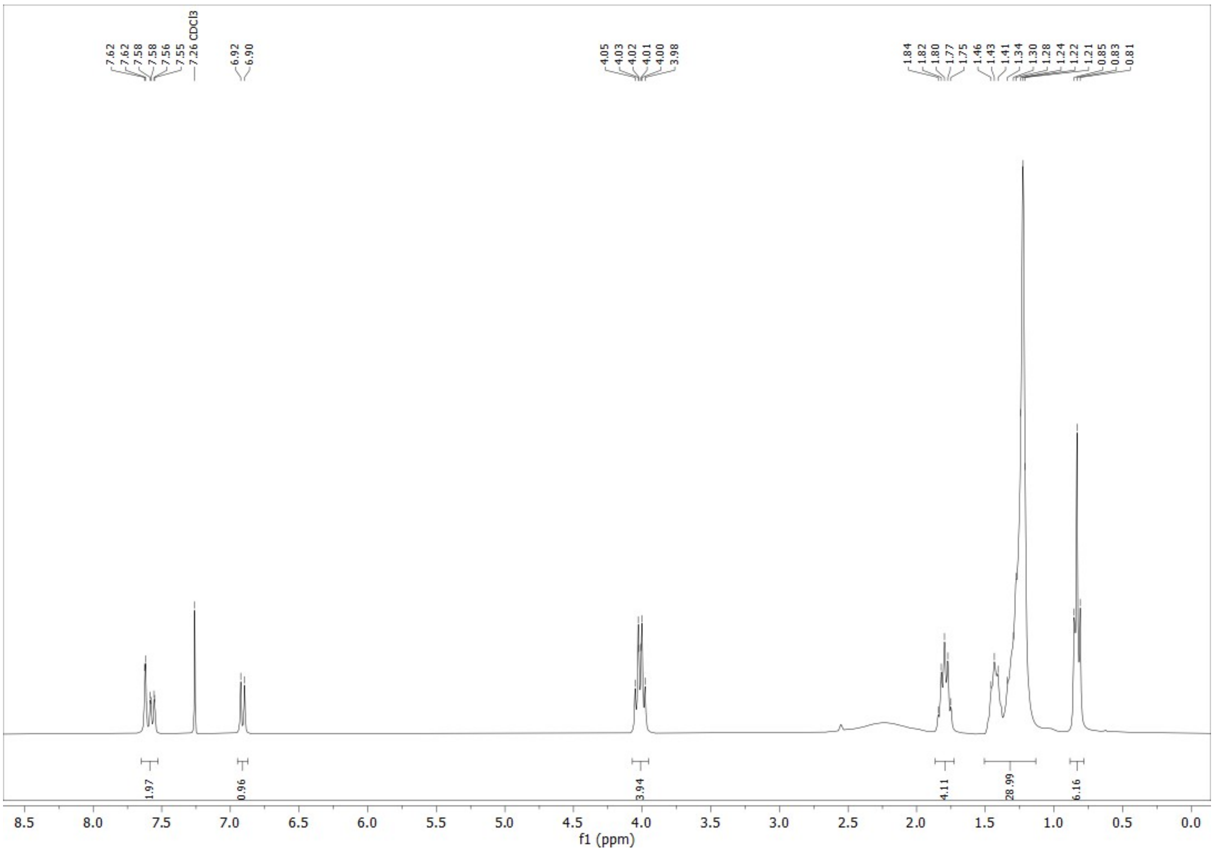




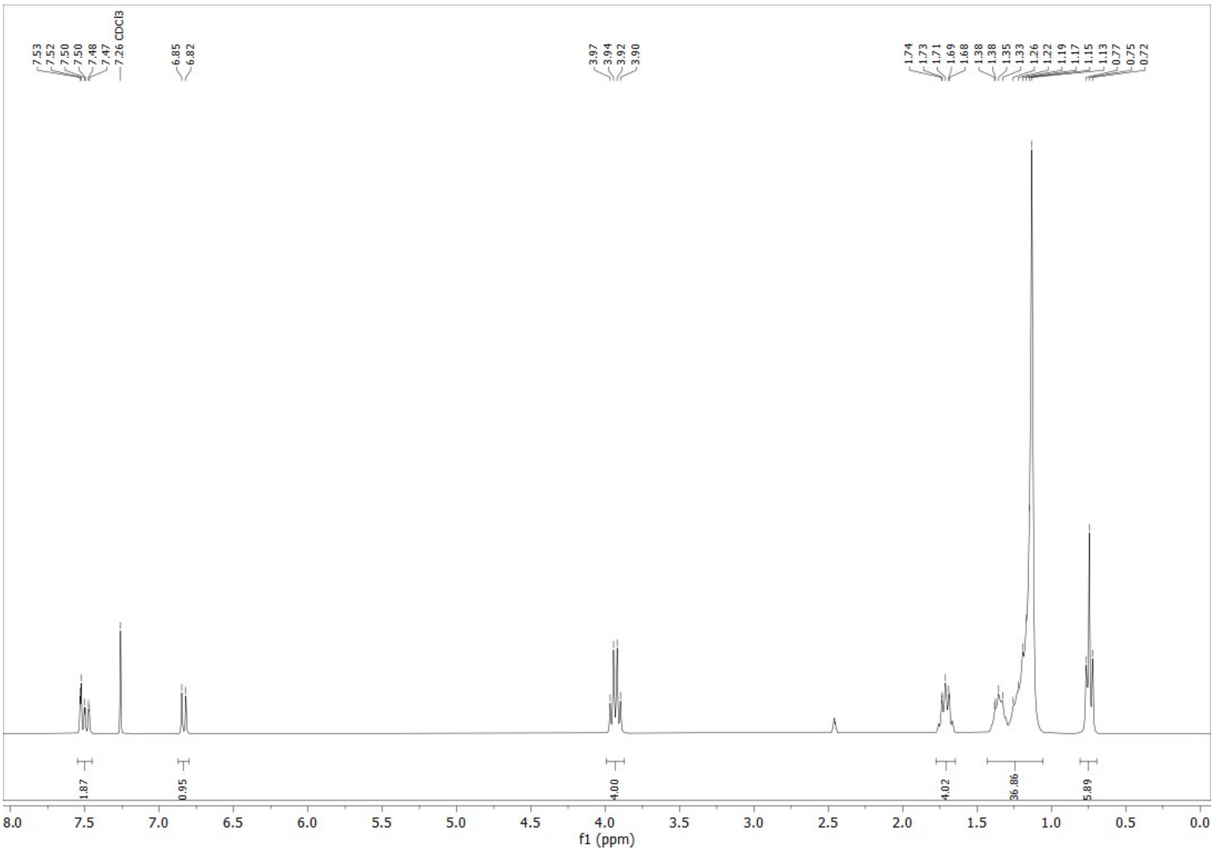
5-(3,4-Bis(octyloxy)phenyl)-1H-tetrazol (6a) in $CDCl_3$/DMSO-d_6 (50/1)



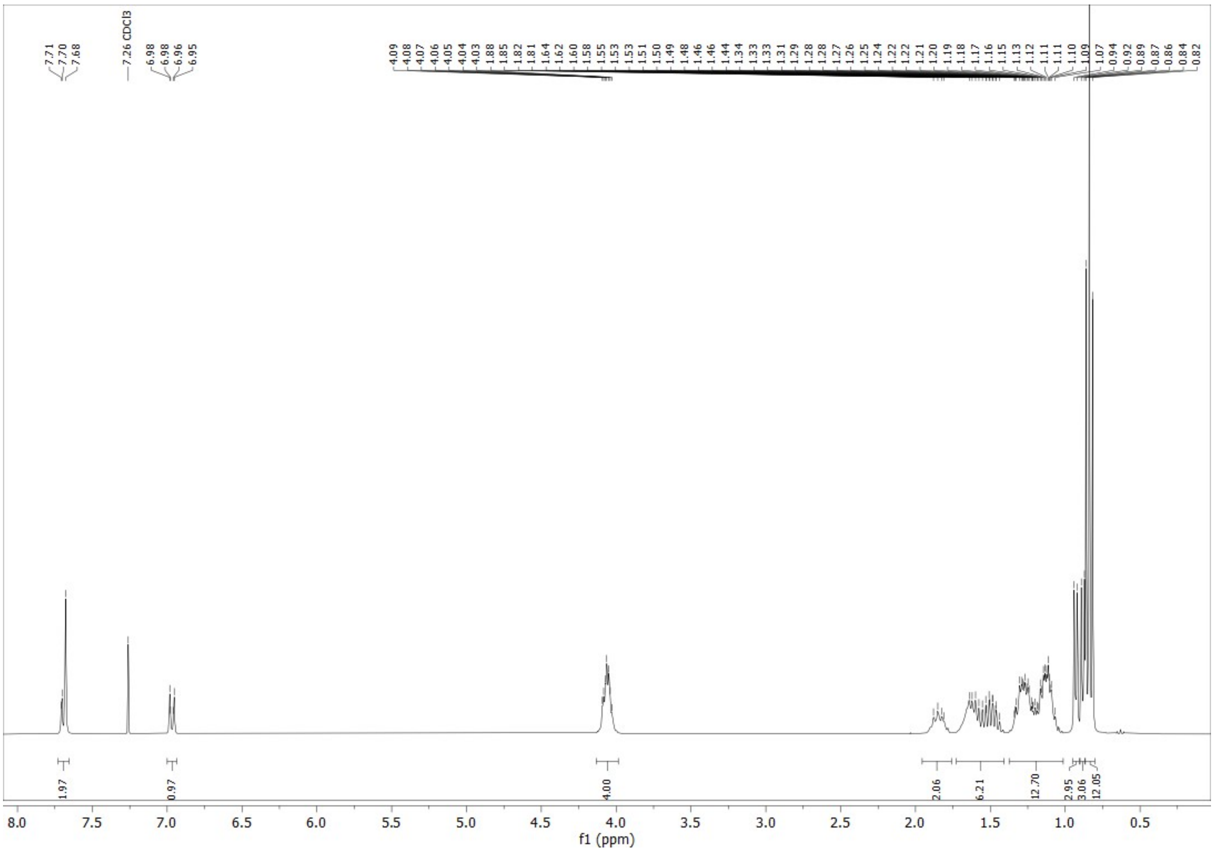
^{1}H-spectra: **5-(3,4-Bis(decyloxy)phenyl)-1H-tetrazol (6b) in $CDCl_3$/DMSO-d_6 (50/1)**



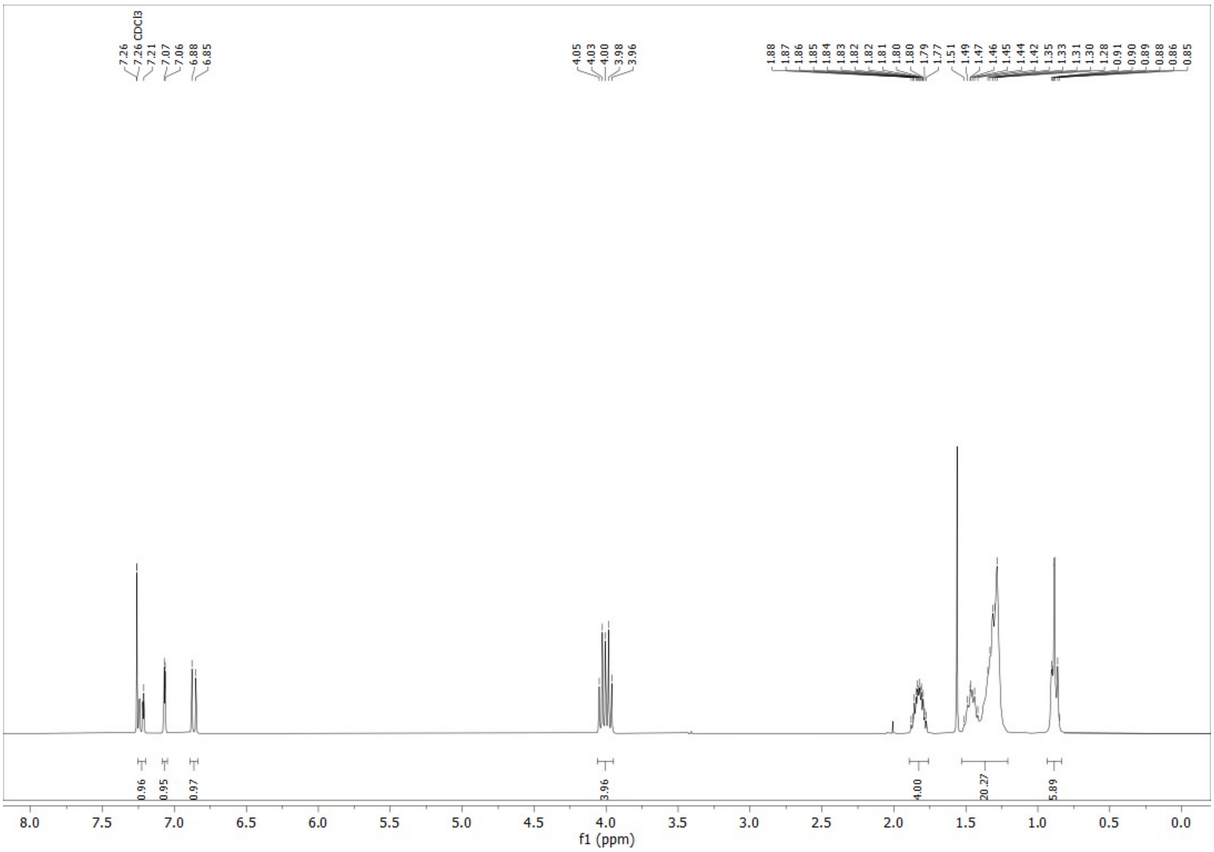
5-(3,4-Bis(dodecyloxy)phenyl)-1H-tetrazol (6c) in $CDCl_3$/DMSO-d_6 (50/1) in $CDCl_3$



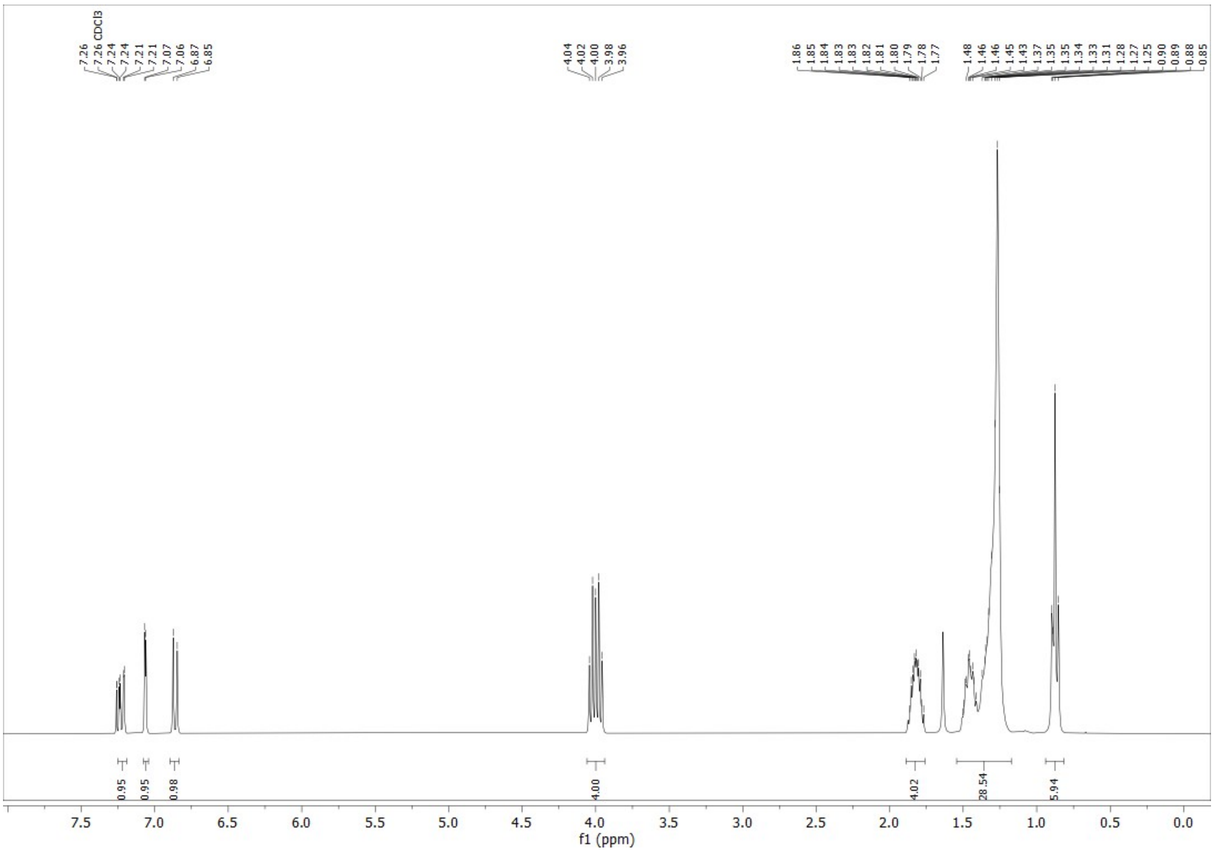
5-(3,4-Di((3,7-dimethyloctyl)oxy)phenyl)-1H-tetrazole (6d) in $CDCl_3$



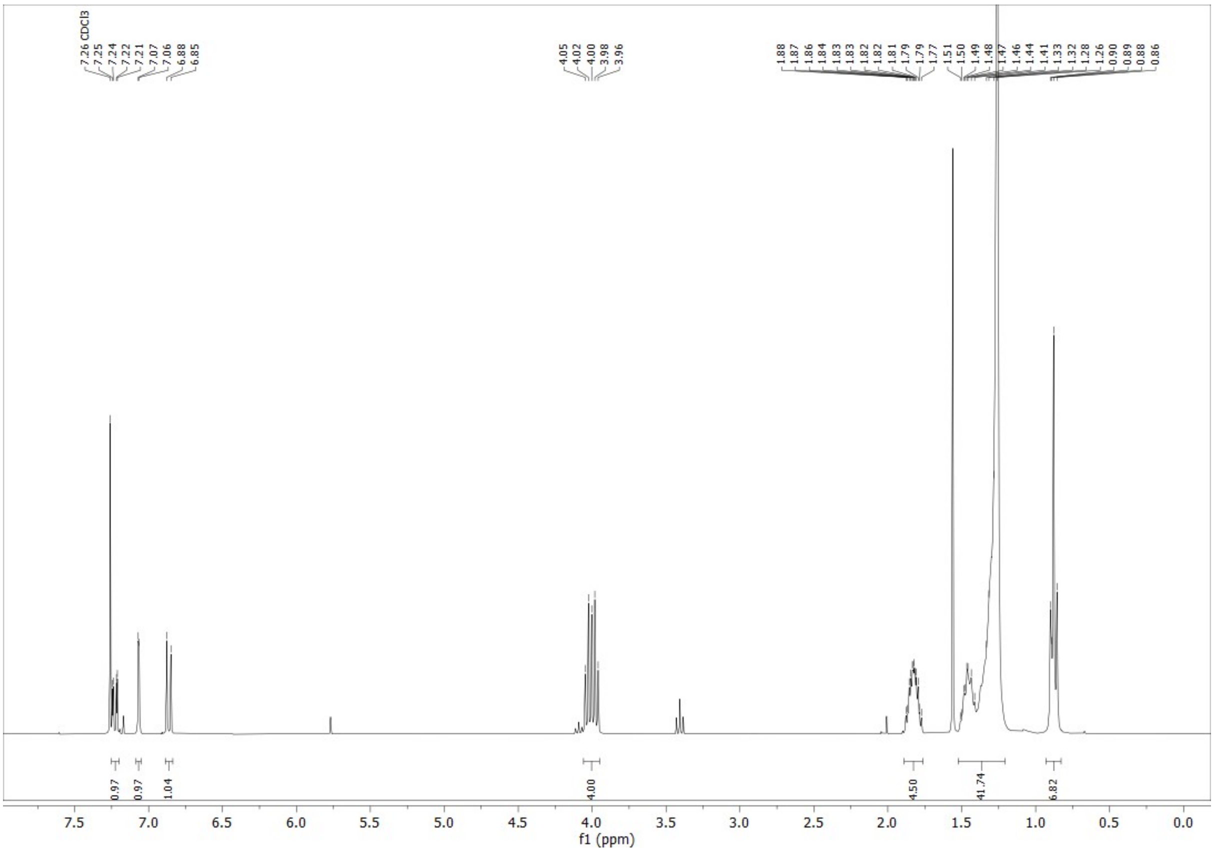
3,4-bis(octyloxy)benzonitrile (5a) in $CDCl_3$



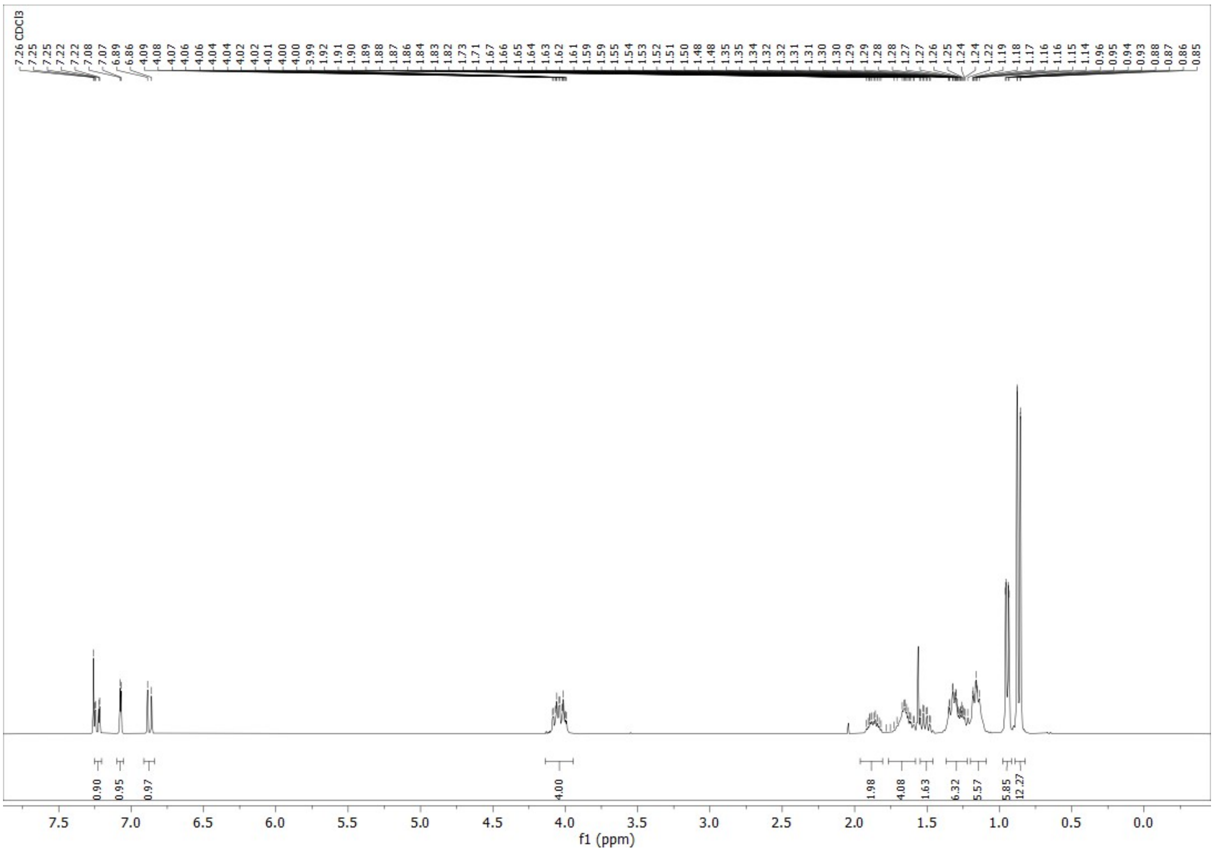
3,4-bis(decyloxy)benzonitrile (5b) in $CDCl_3$



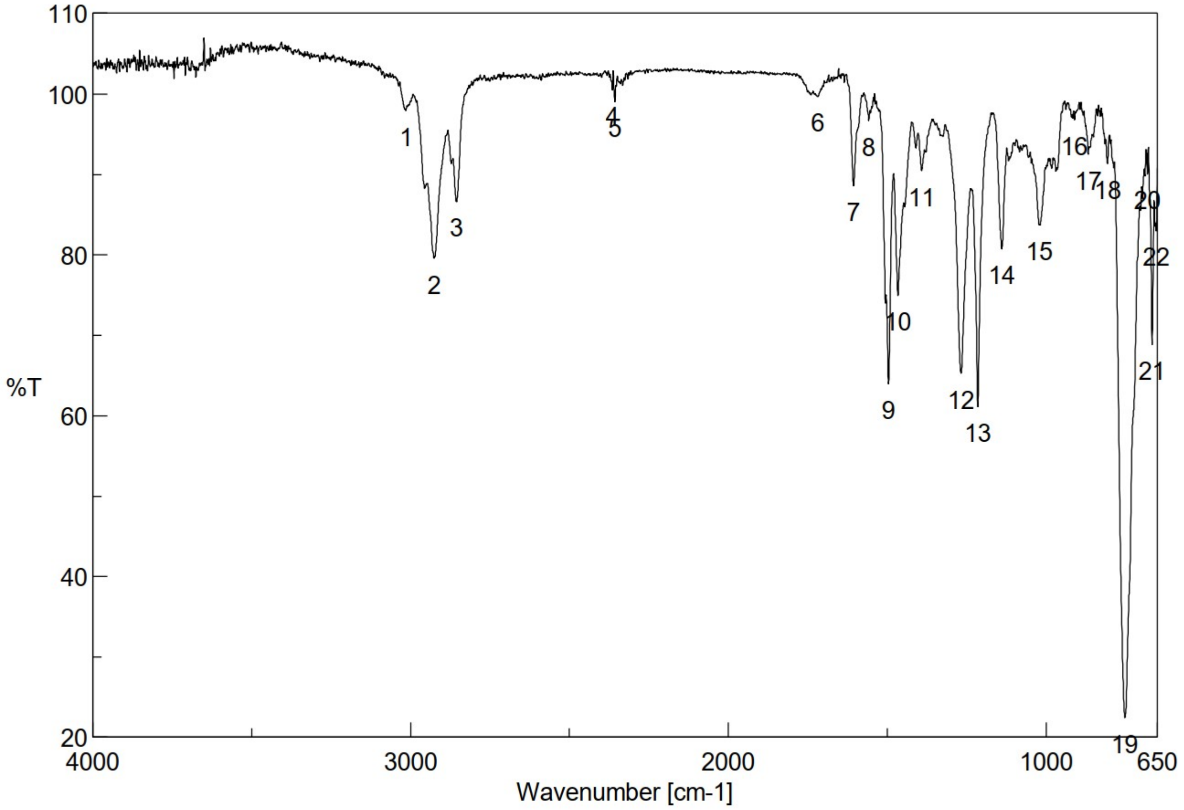
3,4-bis(dodecyloxy)benzonitrile (5c) in $CDCl_3$



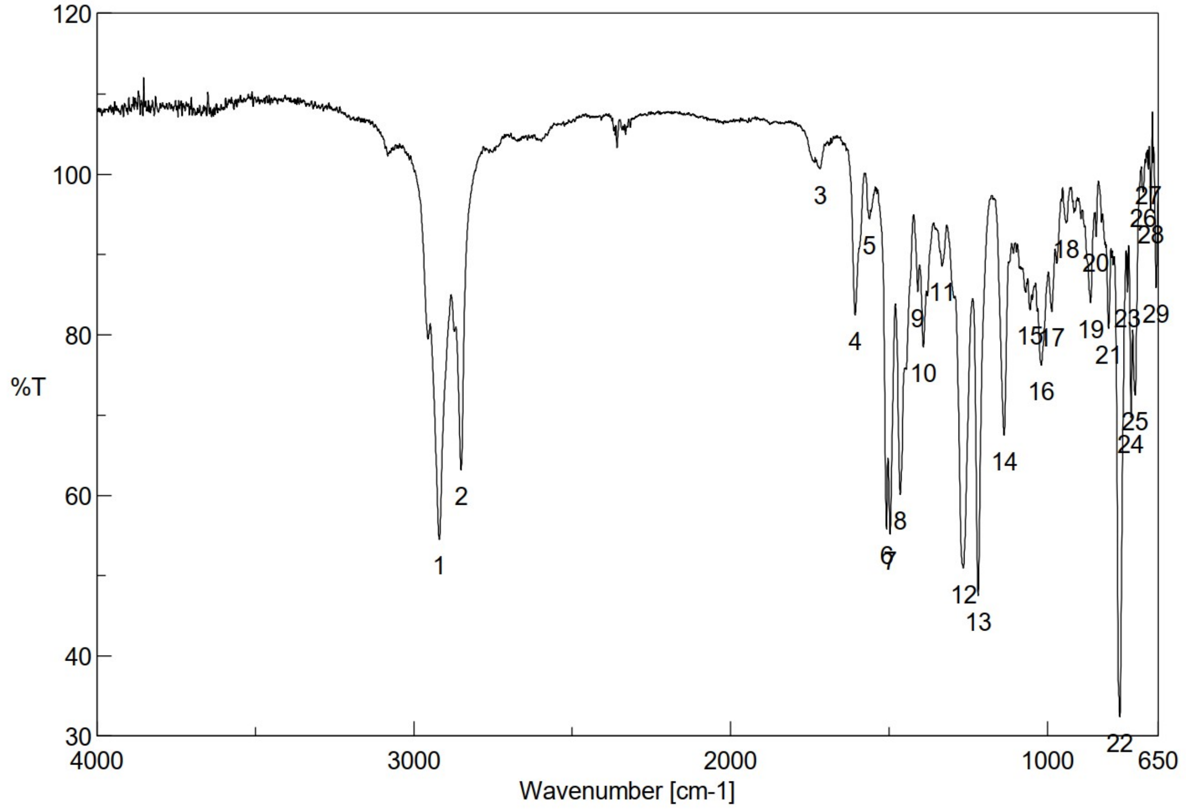
3,4-bis((3,7-dimethyloctyl)oxy)benzonitrile (5d) in $CDCl_3$



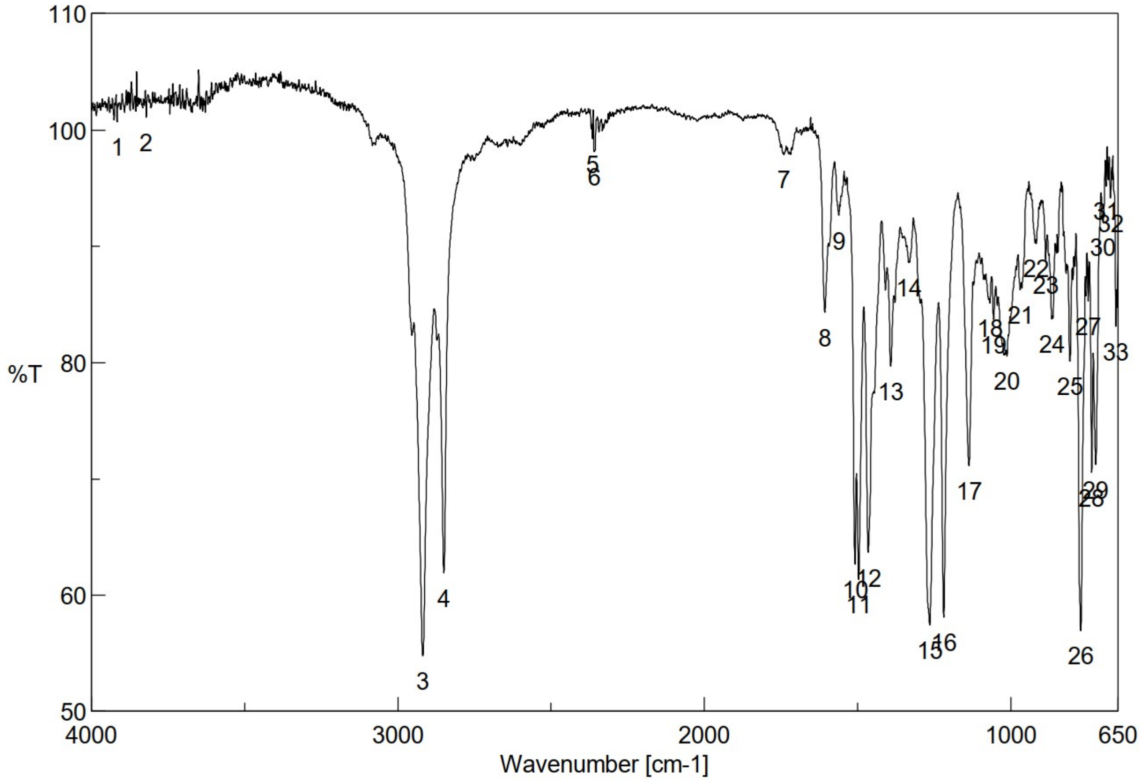
IR-Spectra1,2,4-Tris(2-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7a)



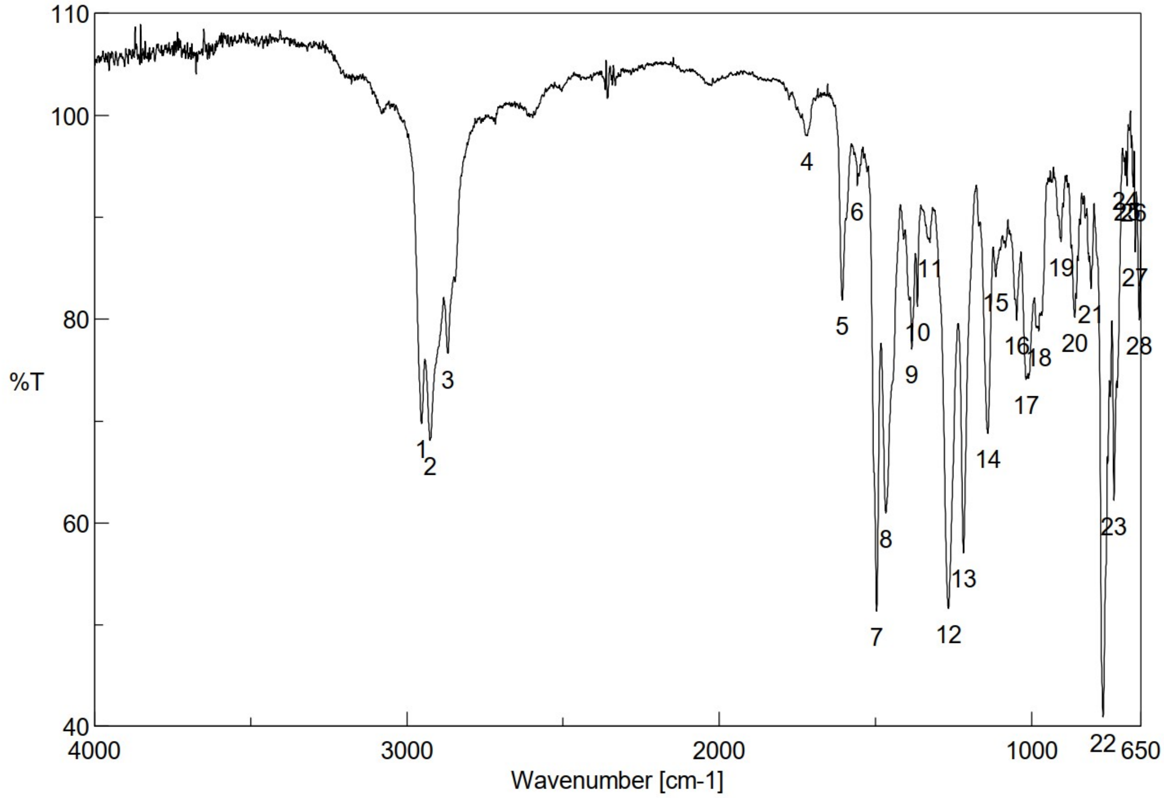
1,2,4-Tris(2-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7b)



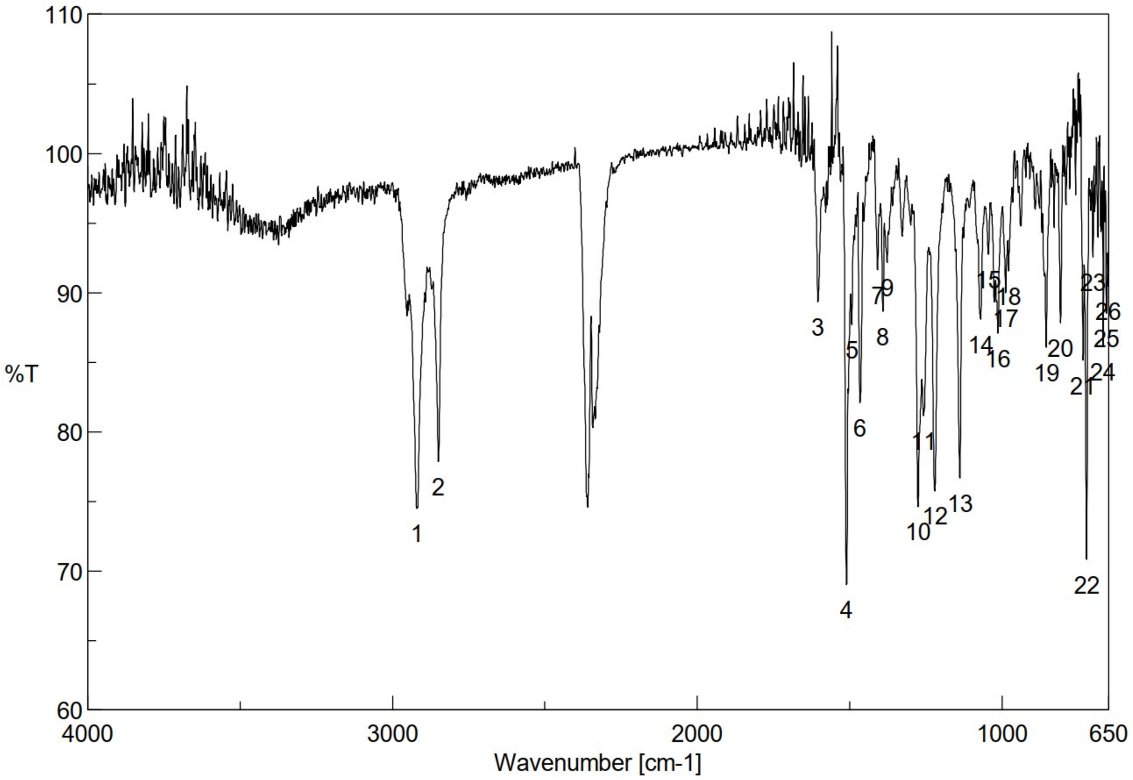
1,2,4-Tris(2-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7c)



1,2,4-Tris(2-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7d)

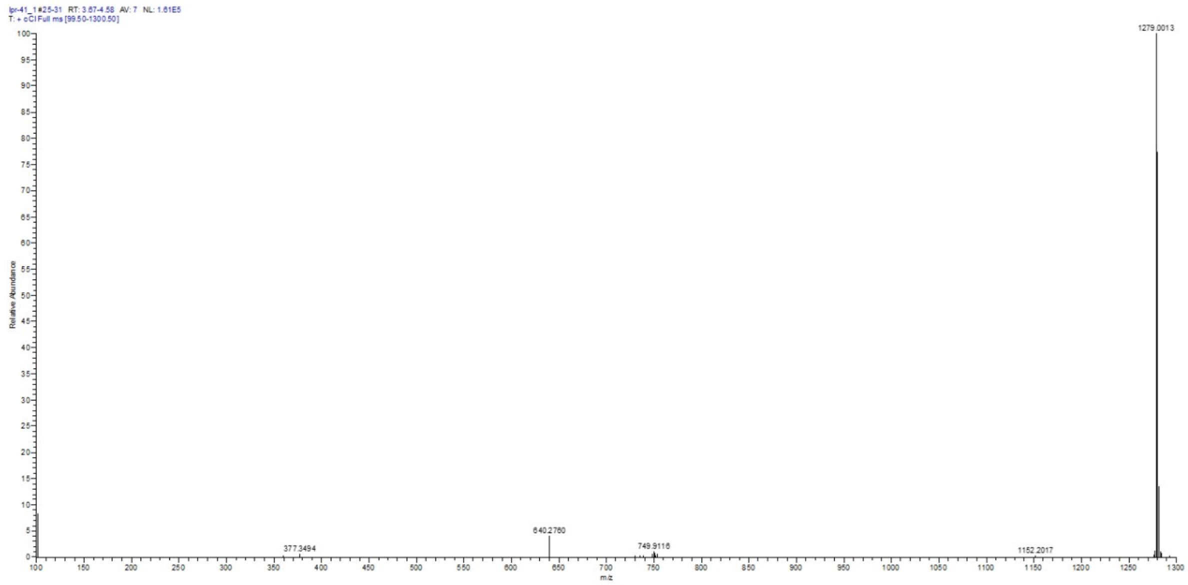


1,4-bis(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (11)

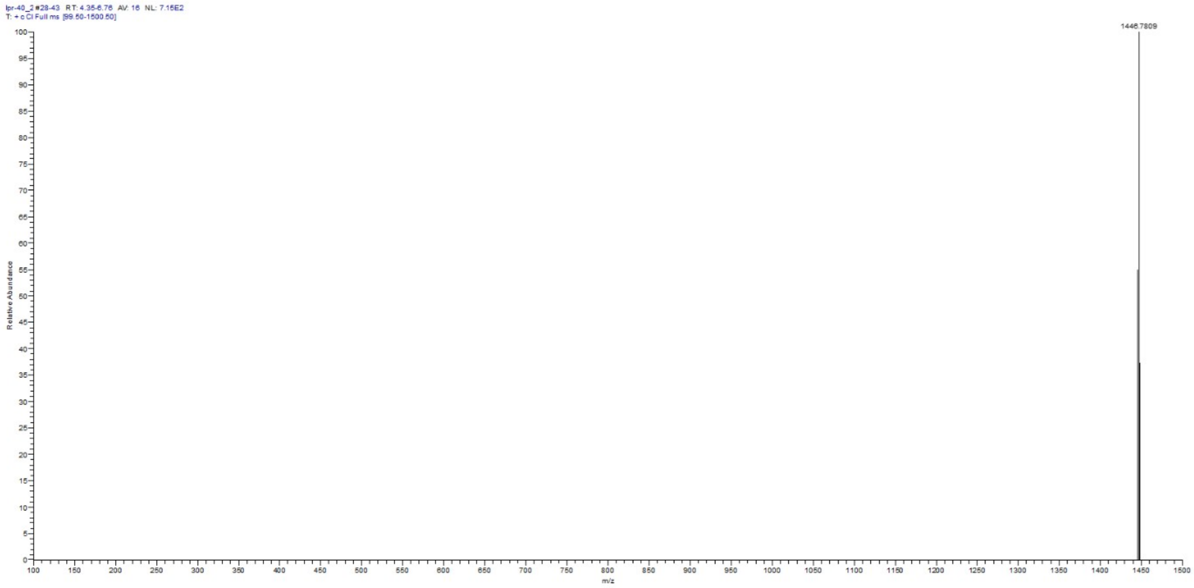

110
100
90
%T
80
70
60
4000
3000
2000
1000
650
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26

FD-Mass Spectra

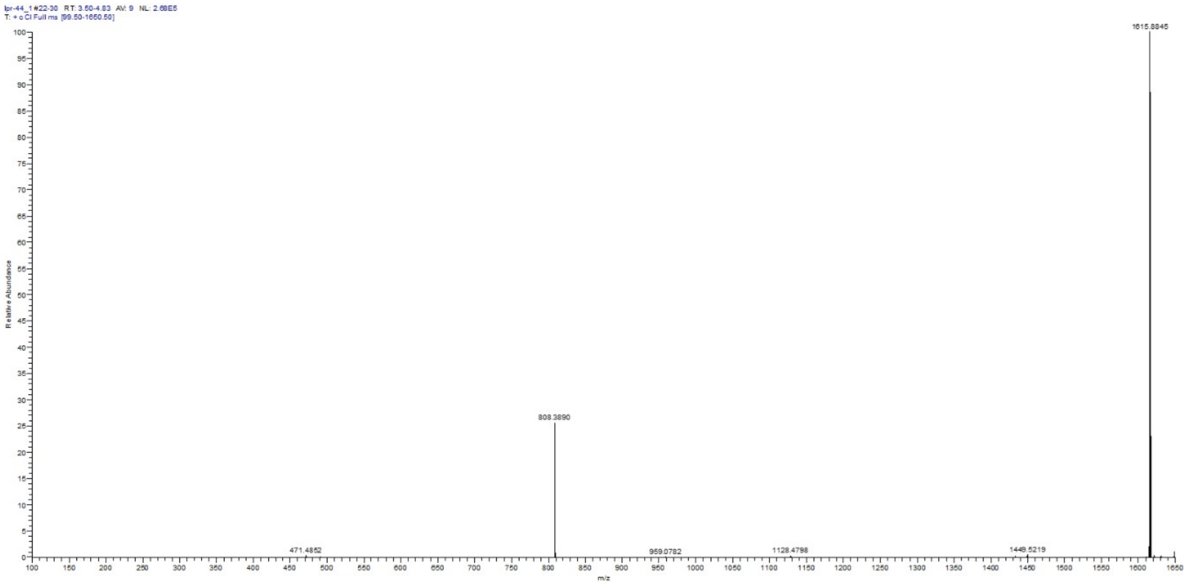
1,2,4-Tris(2-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7a)



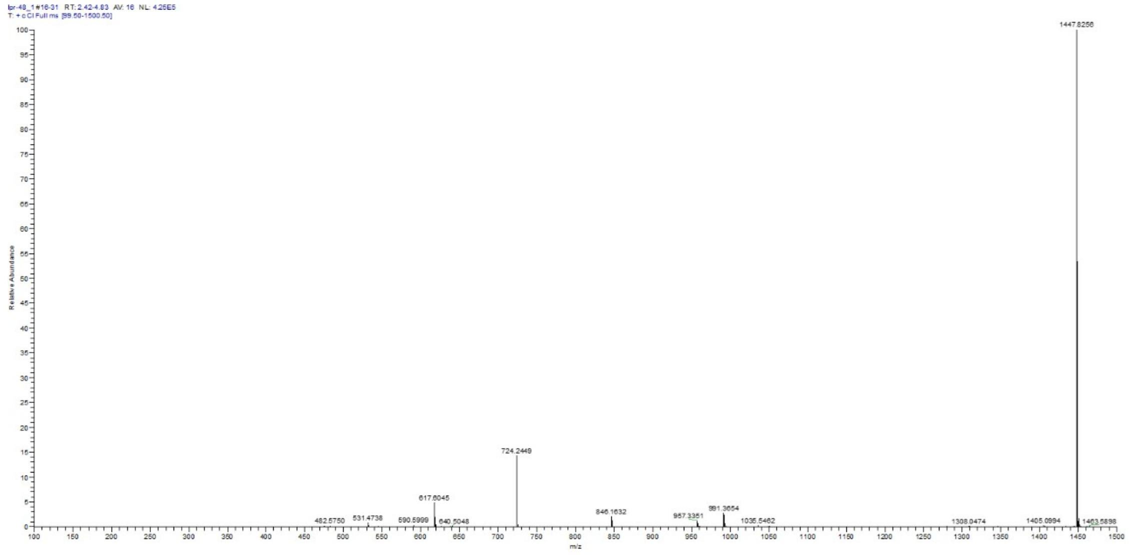
1,2,4-Tris(2-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7b)



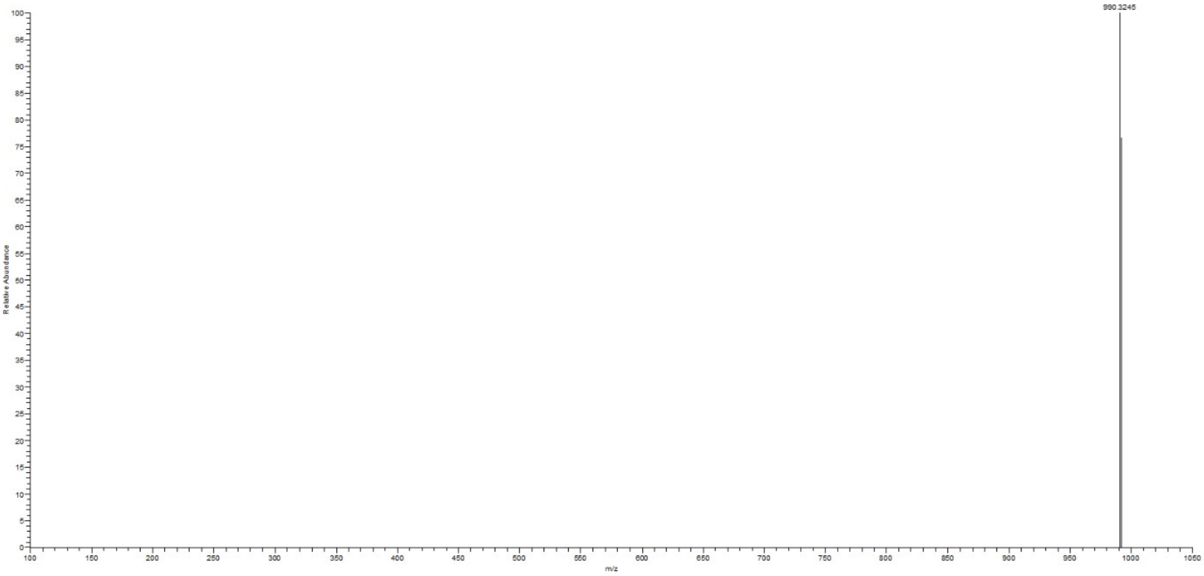
1,2,4-Tris(2-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7c)



1,2,4-Tris(2-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7d)



1,4-bis(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (11)


990.3245
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
m/z

Phase Transition Temperatures and Enthalpies:

Table S2: Phase Transition Temperatures and Enthalpies

Compound	*T* (melting)* [°C]	*ΔH* [J/g]	*T* (clearing)* [°C]	*ΔH* [J/g]
7a	120,55	41,15	135,6	5,12
7b	122,25	51,1	136,76	4,87
7c	122,95	45,46	136,12	4,32
7d	46,35	4,80	84,41	2,46

*onset signals of first cooling curve

DSC-Curves:

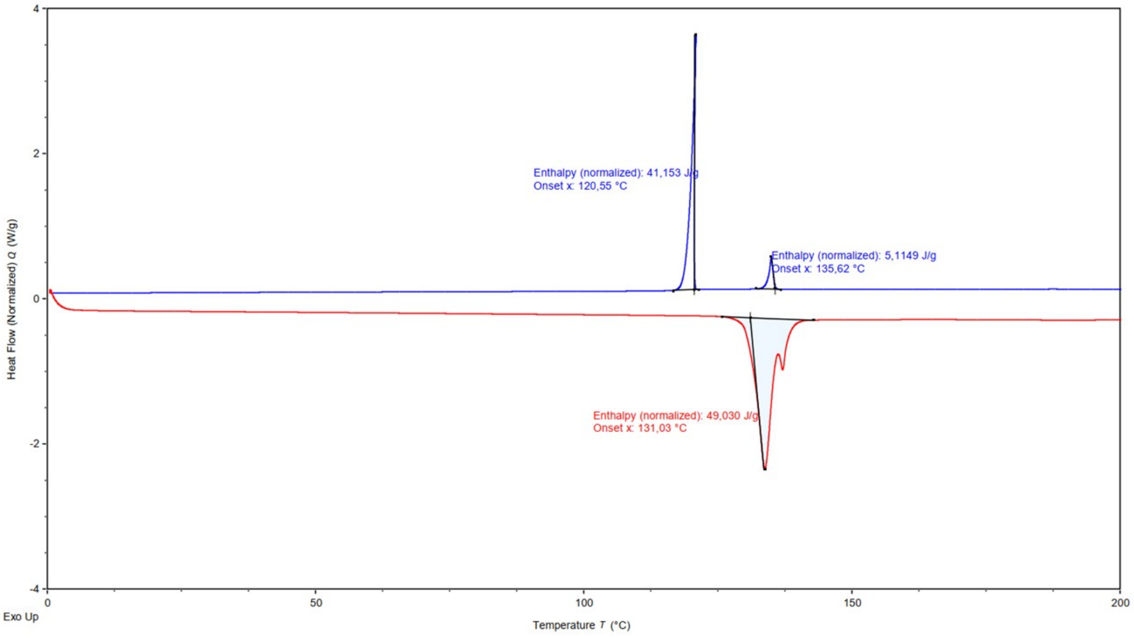


Figure S1: 1,2,4-Tris(2-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7a)

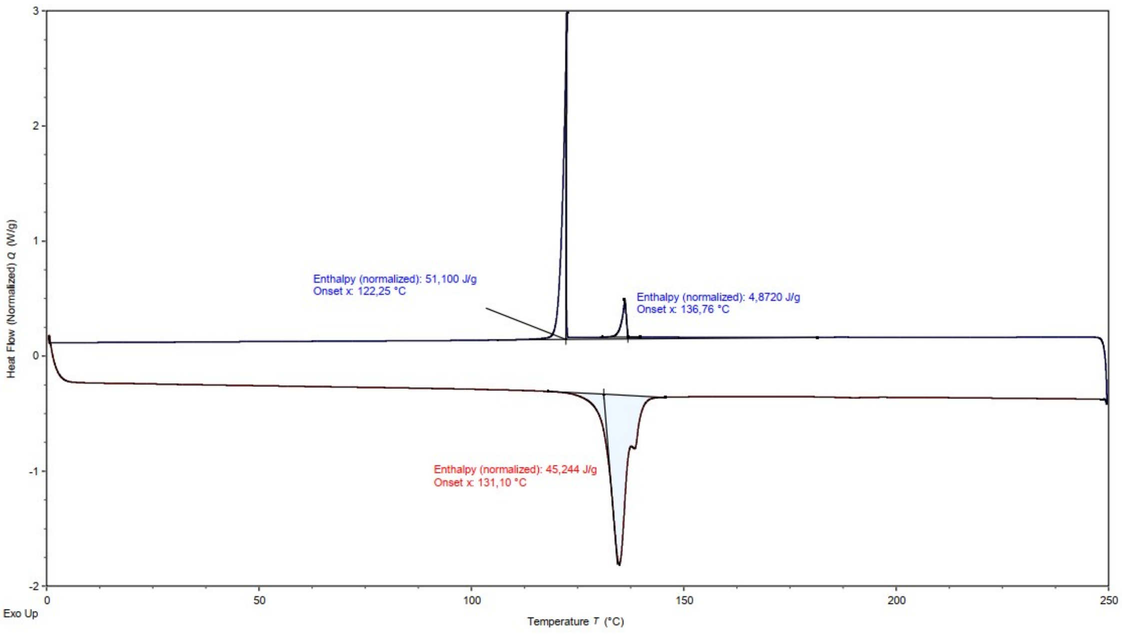


Figure S2: 1,2,4-Tris(2-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7b)

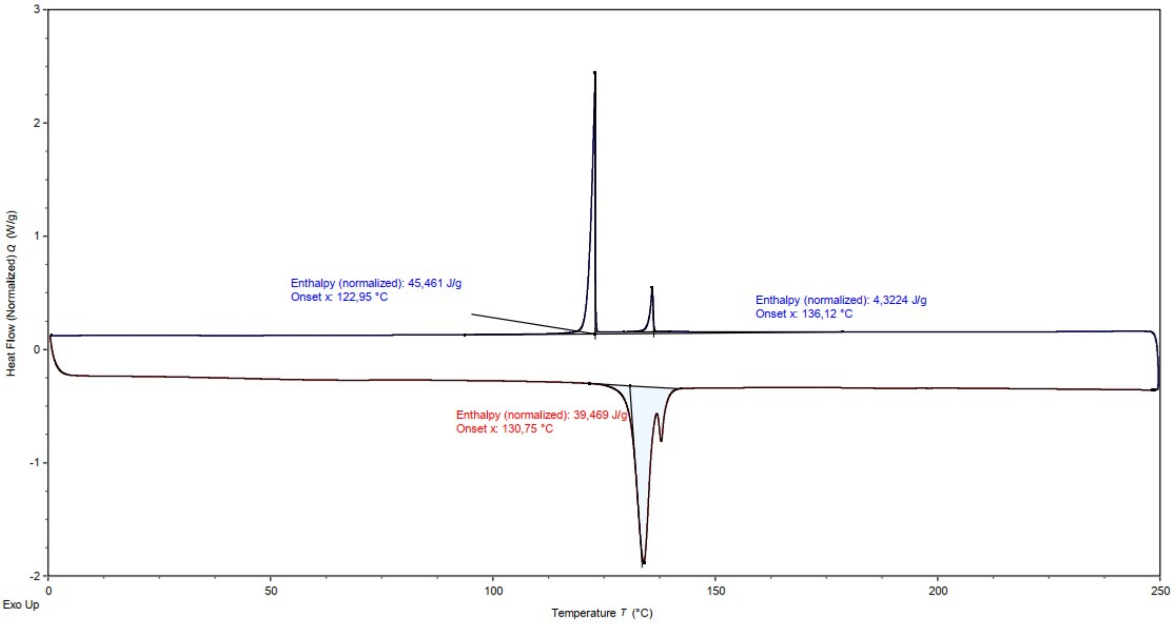


Figure S3:1,2,4-Tris(2-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7c)

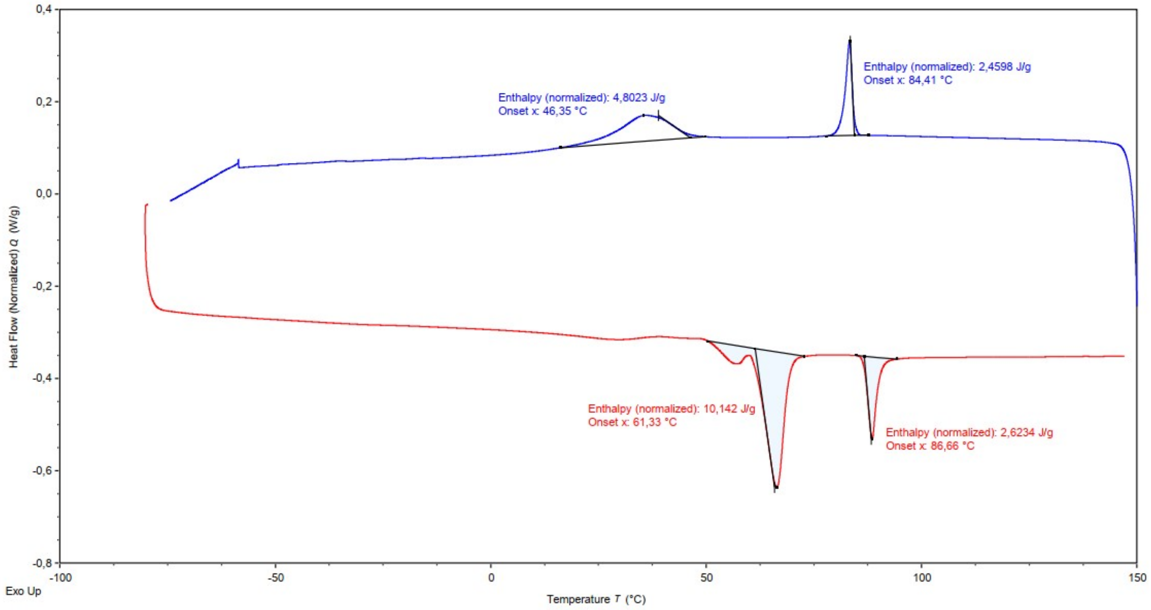


Figure S4: 1,2,4-Tris(2-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (7d)

UV-Vis and Fuorescence Spectroscopy

Table S3: UV-Vis- and Fluorescence Spectroscopy in solution of compound 7a

solvent	λ_{max}^{abs} [nm]	ε [L · mol^{-1} ·cm^{-1}]	λ_{max}^{Fl} [nm]	$\lambda_{max}^{Fl\ Abs}$ [nm]	$\Delta\bar{\nu}^{St}$ [cm^{-1}]	ΦF [%]
dichloromethane	340	2,57 · 10^4	474	341	8315	39
chloroform	343	2,90 · 10^4	459	341	7368	40
toluene	341	2,93 · 10^4	440	342	6598	39
benzene	343	2,87 · 10^4	441	344	6479	39
cyclohexane	341	2,10 · 10^4	421	338	5573	26

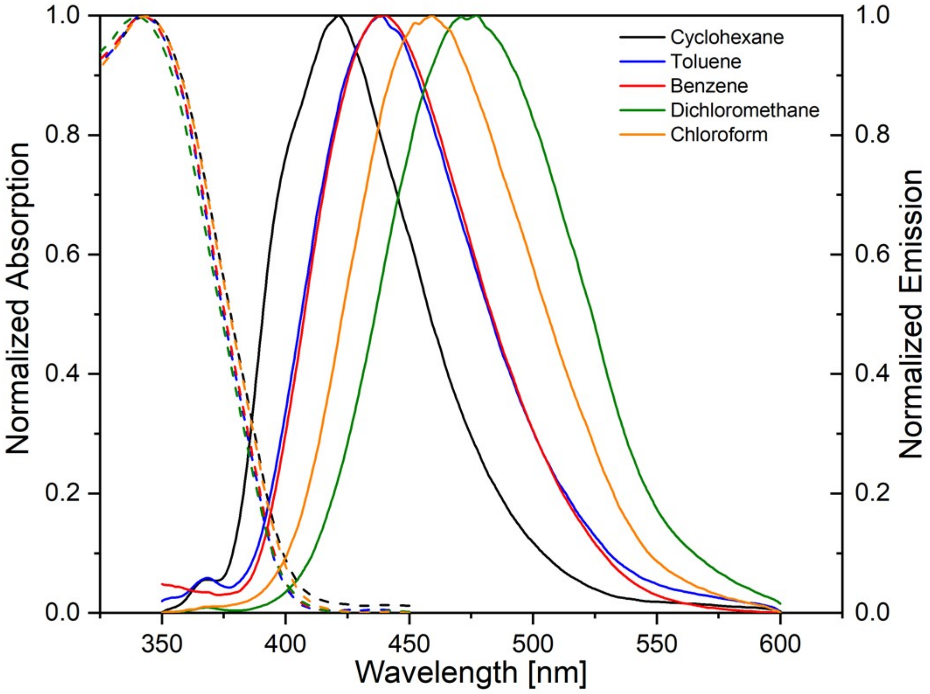


Figure S5: Absorption (dashed) and fluorescence spectra (solid) of compound 7a in various solvents.

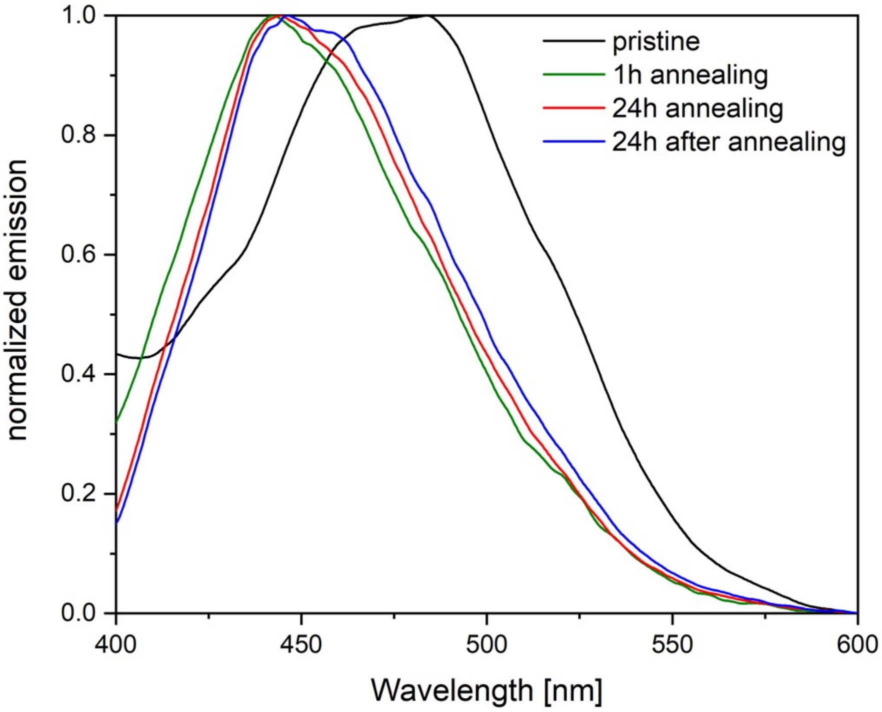


Figure S6: Absorption (dashed) and fluorescence spectra (solid) of compound 11 in various solvents.

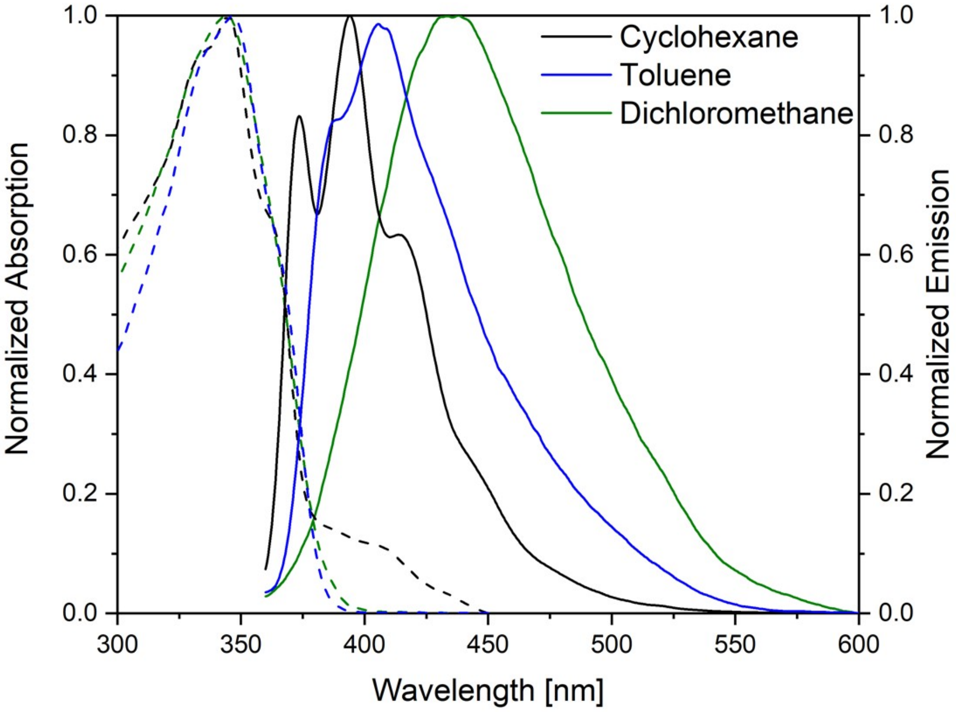


Figure S7: Absorption (dashed) and fluorescence spectra (solid) of compound 11 in various solvents.

2D-Scattering on oriented fiber:

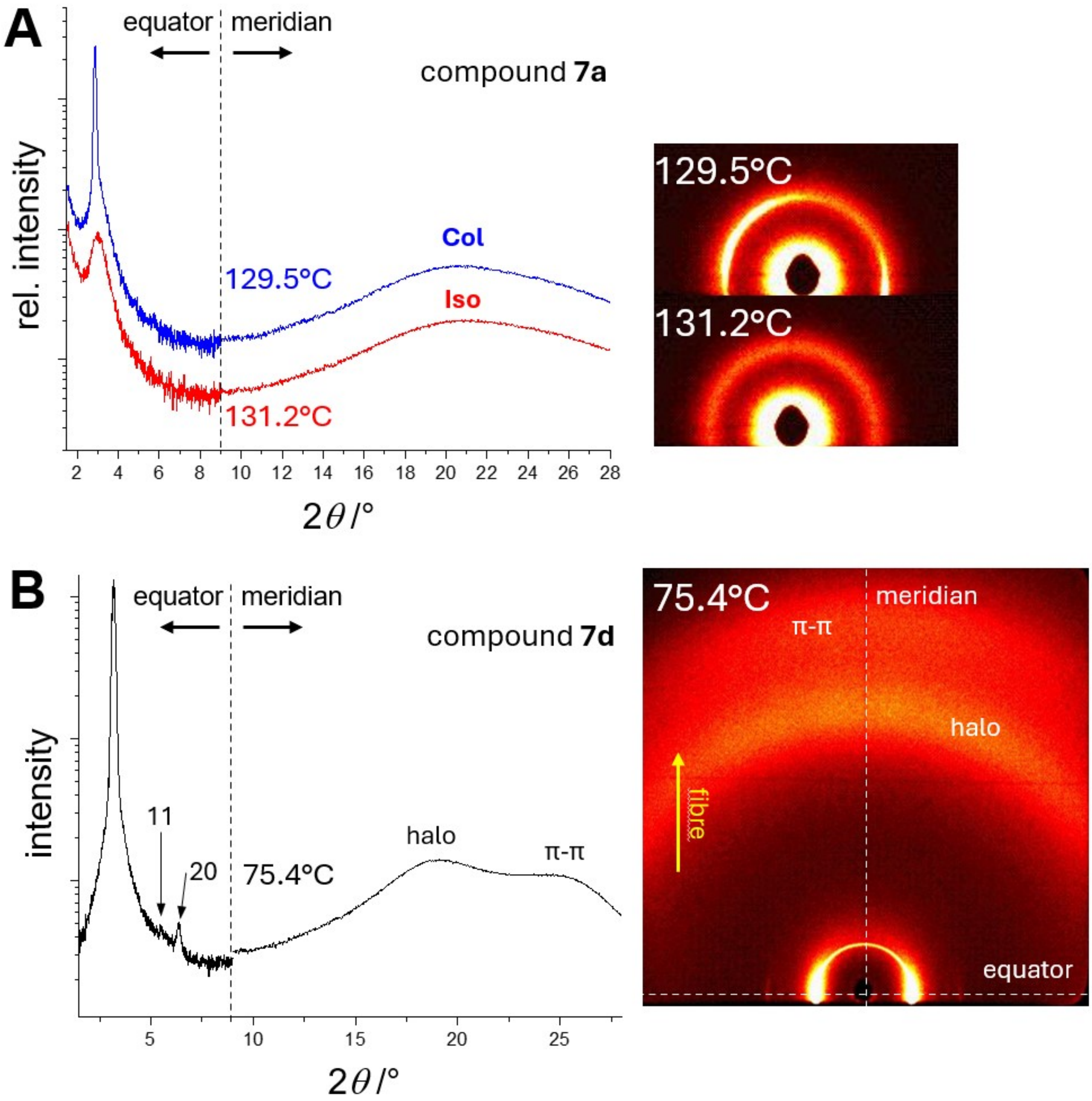


Figure S8: Diffraction Patterns with integration for compounds 7a and 7d.

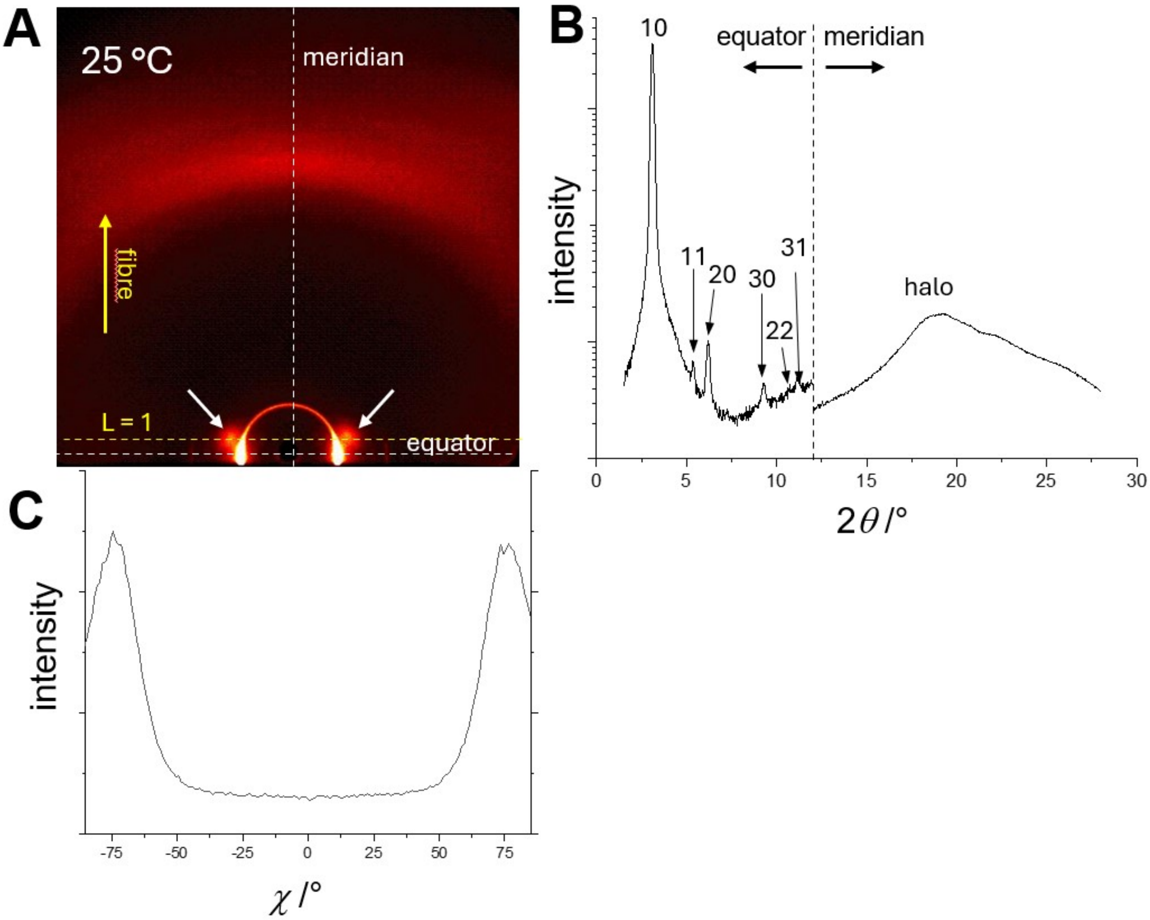


Figure S9: X-ray results for the soft crystal of 7d at 25 °C. A 2D diffraction pattern. B integrated diffraction pattern along the equator and the meridian. The small angle reflections can be indexed to a hexagonal symmetry with a = 3.29 nm. On the meridian sever

The X-ray results for the room temperature phase of **7d** confirm a columnar hexagonal phase. This is the reason why the alignment is maintained when reheating to the LC phase range. Interestingly the pattern does not show anymore a signal reminiscent for the π-π-stacking. However, the broad signals highlighted with the white arrows indicate a helical self-assembly with a pitch of 8.94 nm. The correlation length calculated with the Scheerer formula amounts only to two repeating units, which rationalizes why there are no furthervisible signals related with the helical packing. Assuming a density of 1 g/cm^3 35 mesogens form the helical column.

References

[1] T. Rieth, N. Tober, D. Limbach, T. Haspel, M. Sperner, N. Schupp, P. Wicker, S. Glang, M. Lehmann, H. Detert, *Molecules (Basel, Switzerland)* **2020**, *25*.