Electronic Supplementary Material (ESI) for Soft Matter

Electronic Supporting Information

Effects of Chain Branching and Chirality on Liquid Crystalline Phases of Bent-core Molecules: Blue Phases, de Vries Transitions and Switching of Diastereomeric States

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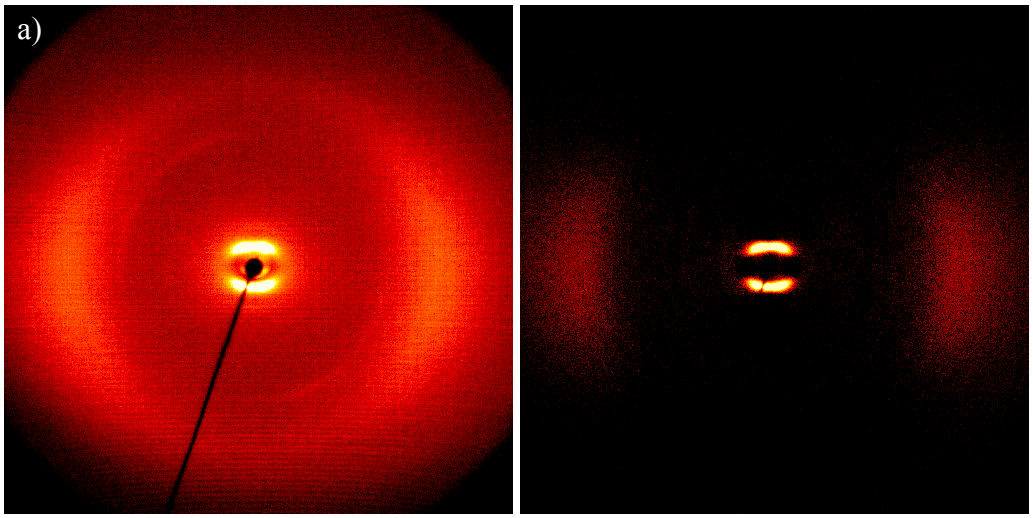
1. Additional X-ray data



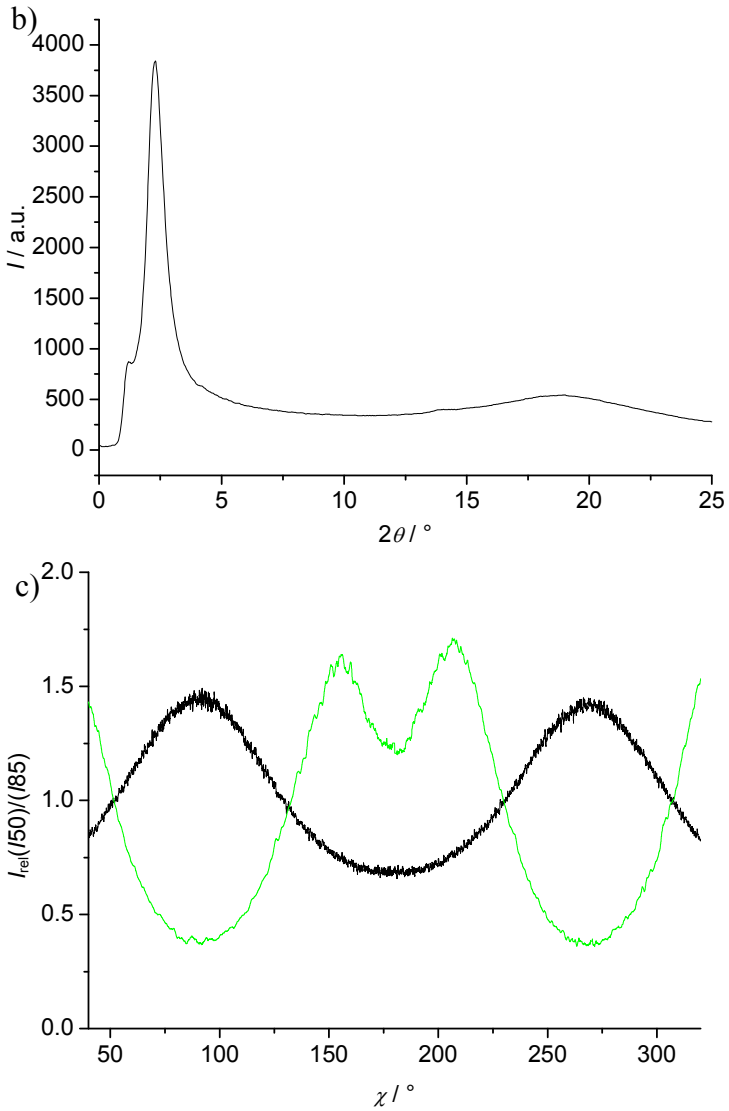
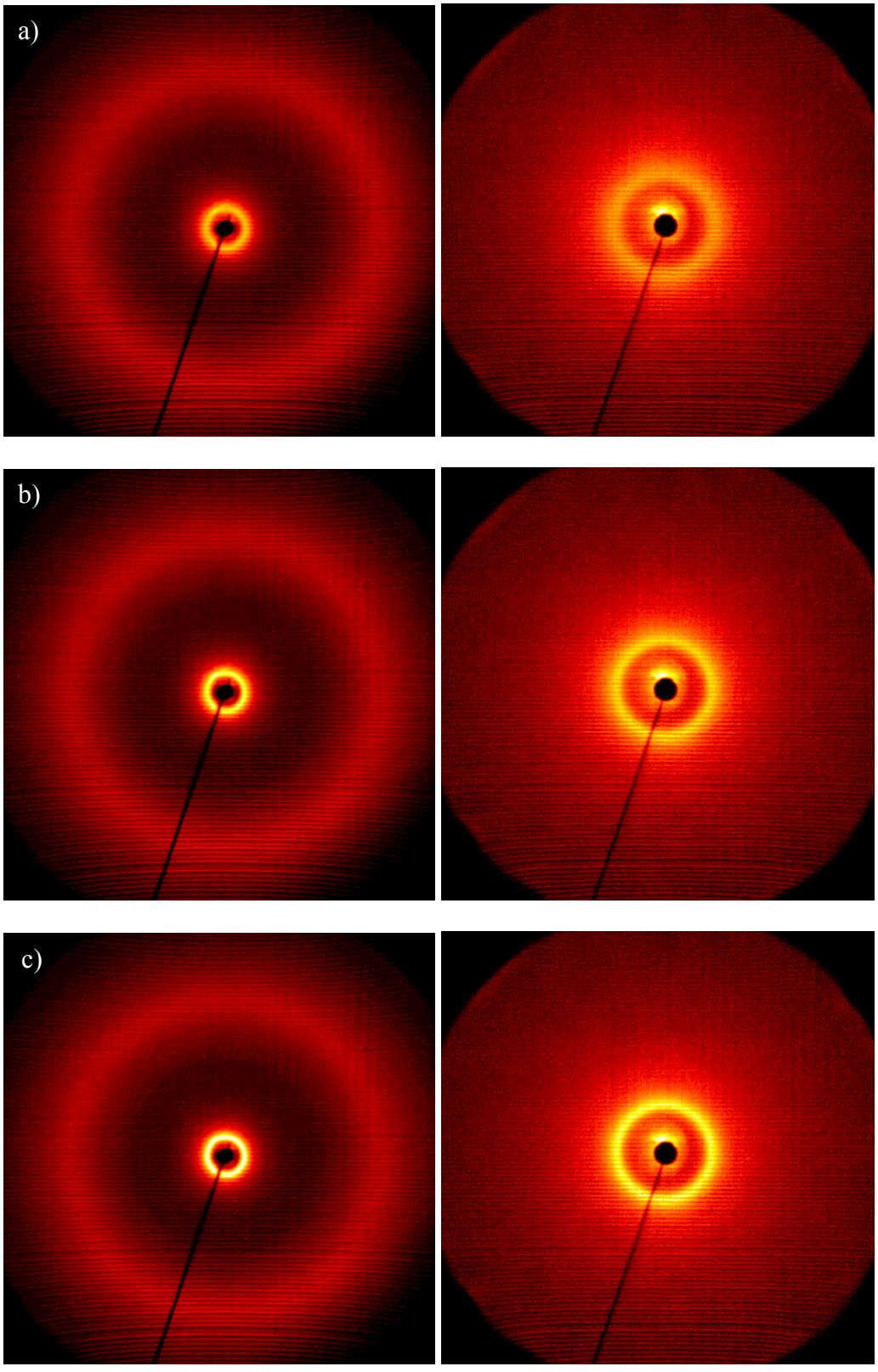


Figure S1. X-ray diffraction patterns of a magnetically aligned sample of compound *rac*-**4:** a) N_{cybC} phase at T = 50 ºC; the left picture shows the original wide angle patterns, the right picture shows the same patterns after subtraction of the scattering in the isotropic liquid state at T = 85 °C. b) θ-scan over the small angle and wide angle scattering at different temperatures; c) χ-scan over the small angle (green line) and wide angle scattering (black line) at T = 50 ºC.



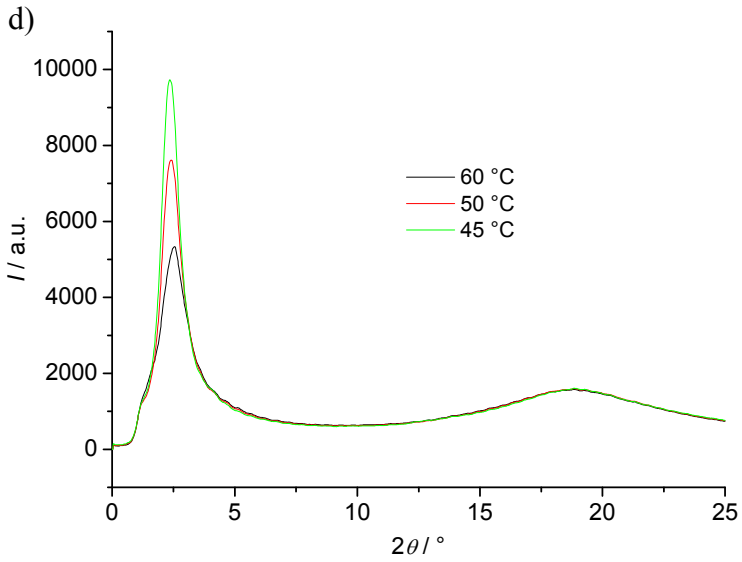
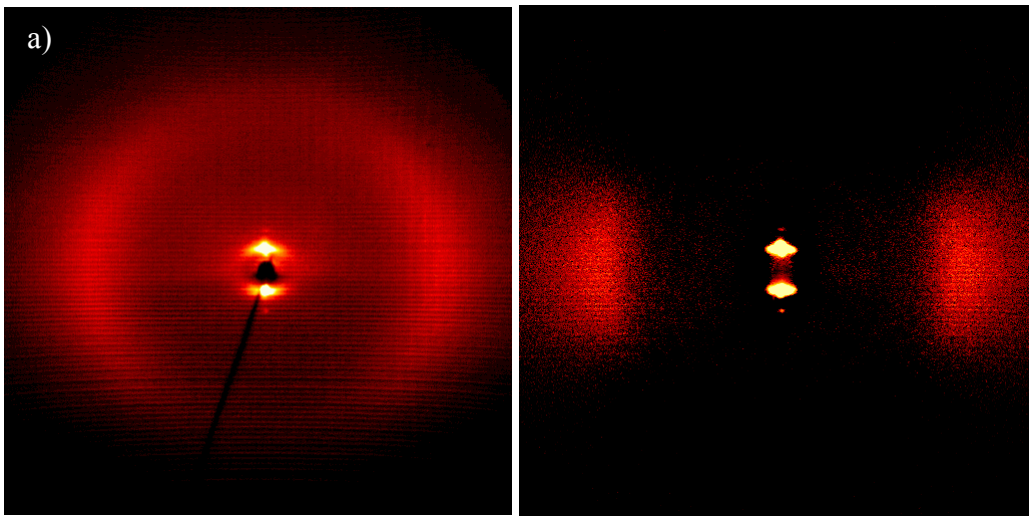
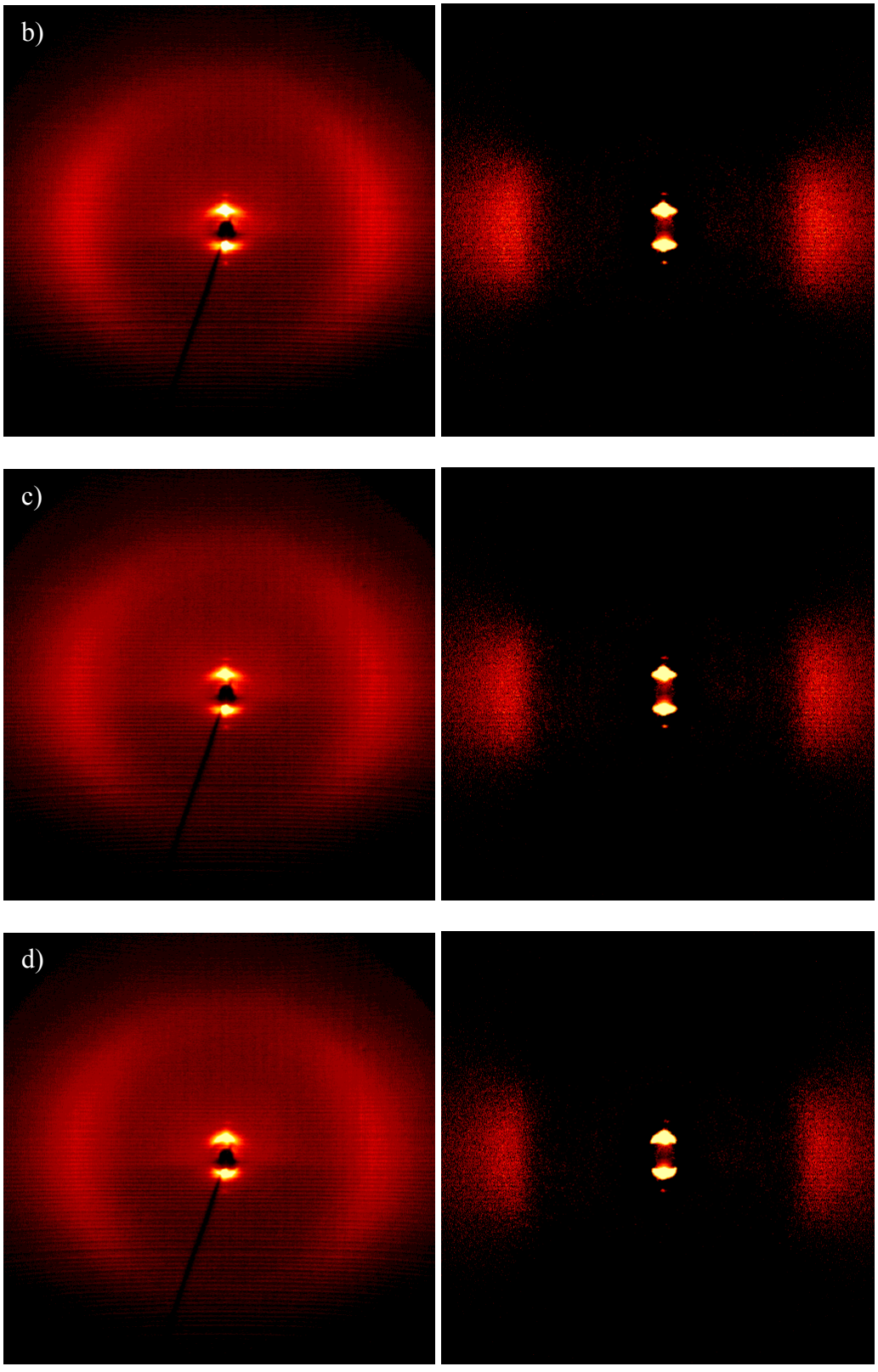


Figure S2. X-ray diffraction patterns of a sample of compound *(S)*-**4** under a magnetic field: a) $BPIII_{cybC}$* phase at T = 60 ºC; b) at T = 50 ºC; c) at T = 45 ºC; the left row shows the original wide angle patterns, the right row shows the small angle patterns; d) θ-scan over the small angle and wide angle scattering at different temperatures.





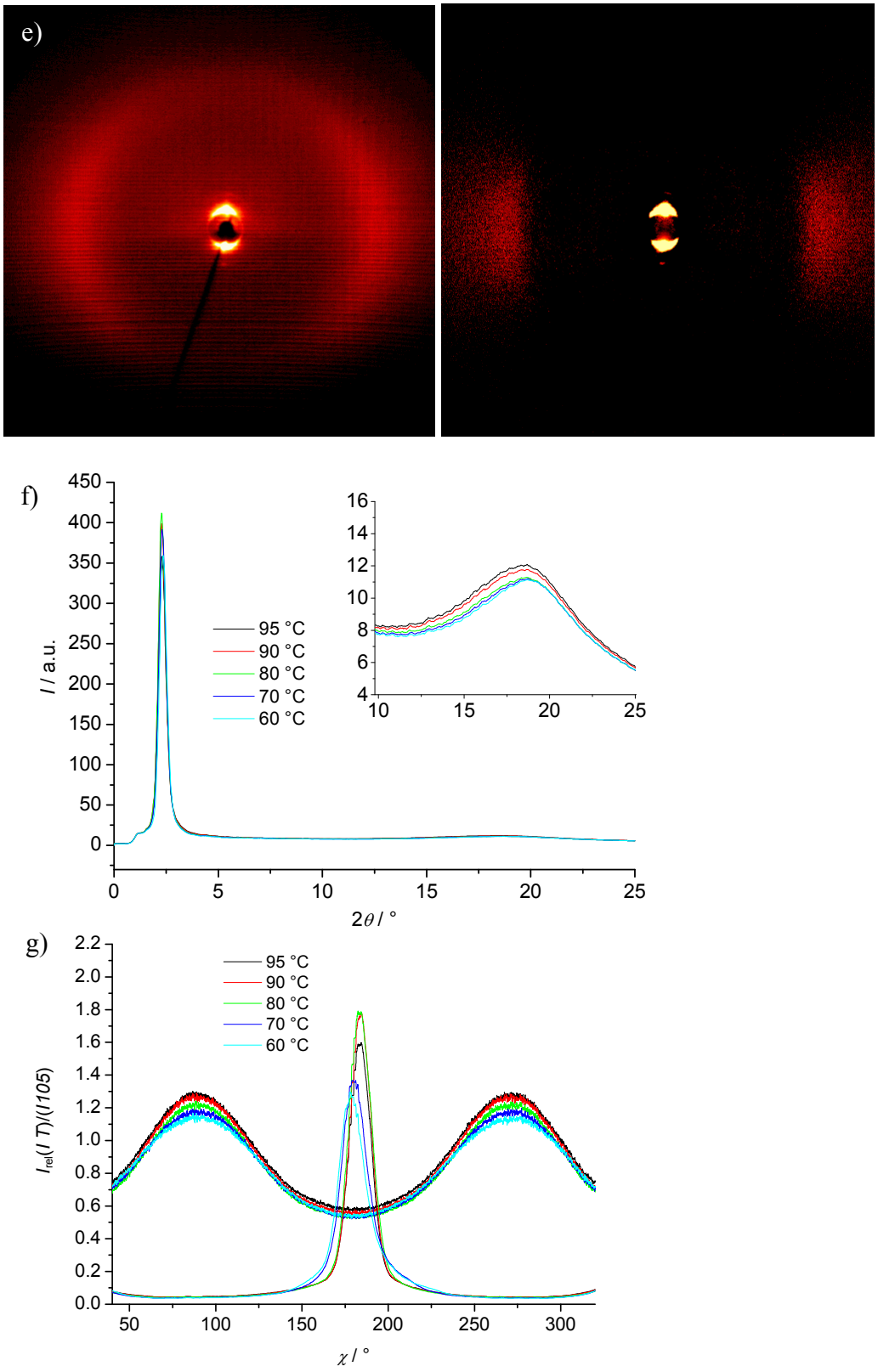
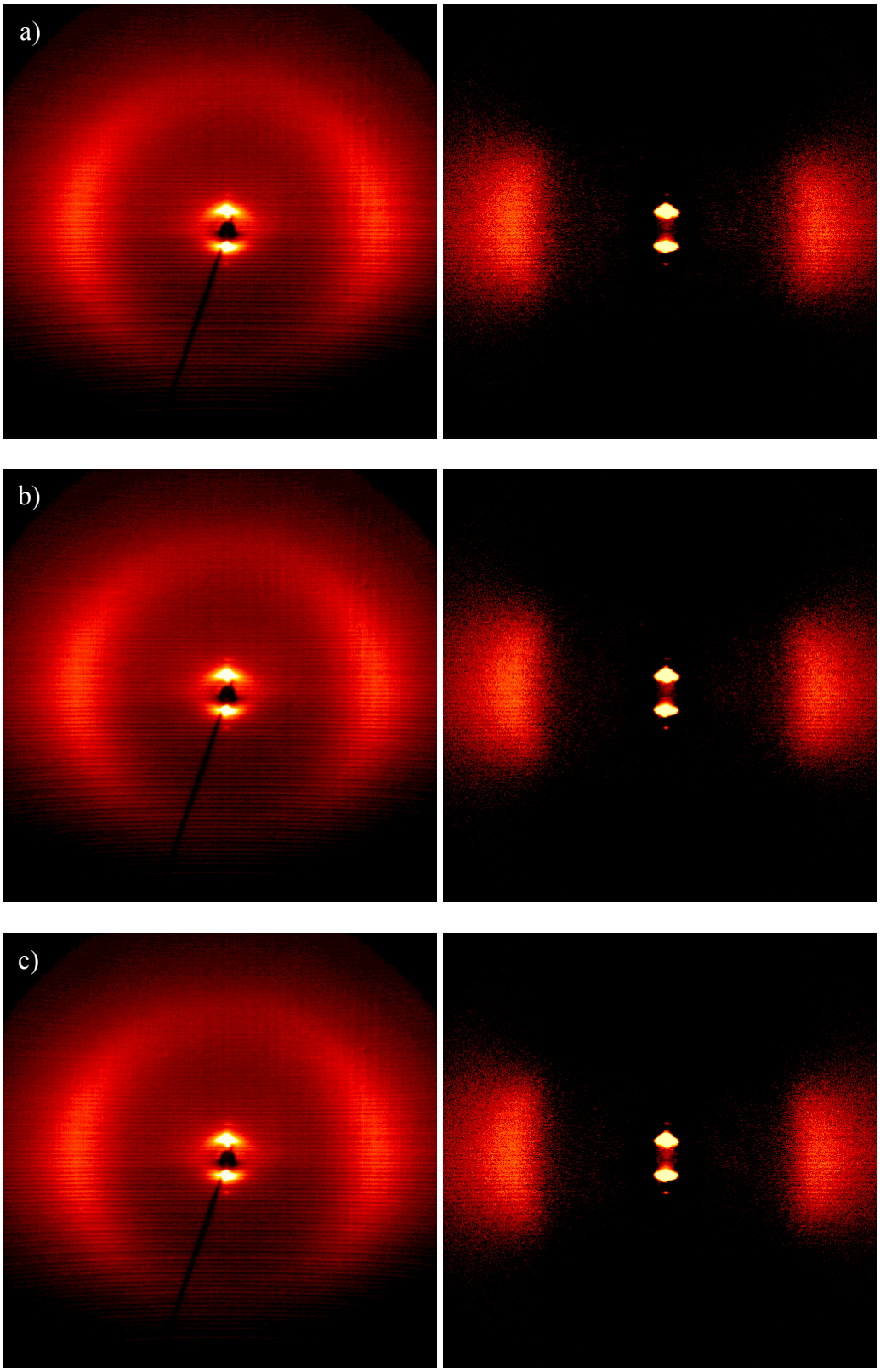
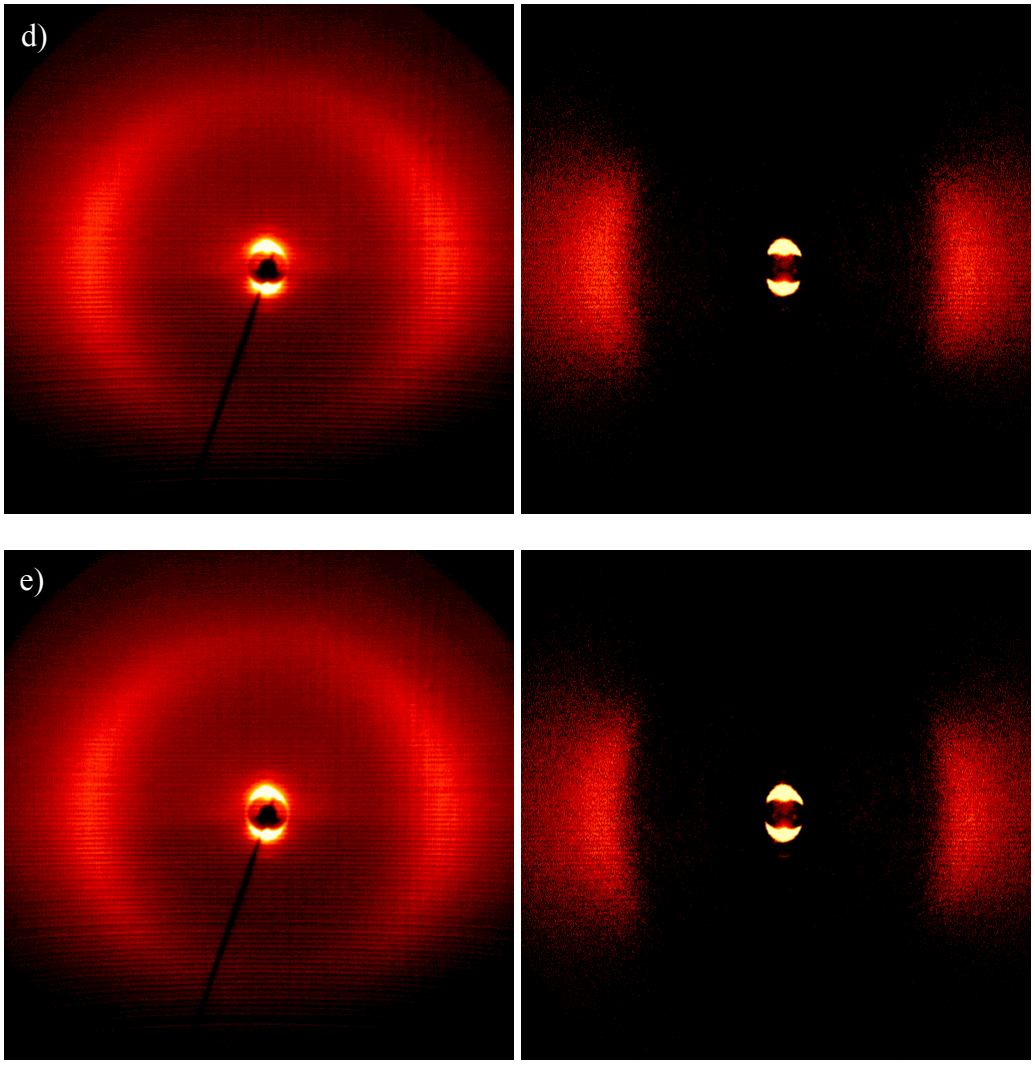


Figure S3. X-ray diffraction patterns of a surface aligned sample of compound *rac*-**5:** a) SmA phase at $T = 95$ ºC; b) SmA phase at $T = 90$ ºC; c) SmA phase at $T = 80$ ºC; d) SmC phase at $T = 70$ ºC and e) SmC phase at $T = 60$ ºC; the left row shows the original wide angle patterns, the right row shows the same patterns after subtraction of the scattering in the isotropic liquid

state at T = 105 °C; f) θ-scan over the small angle and wide angle scattering at different temperatures; g) χ-scan over the small angle and wide angle scattering at different temperatures.





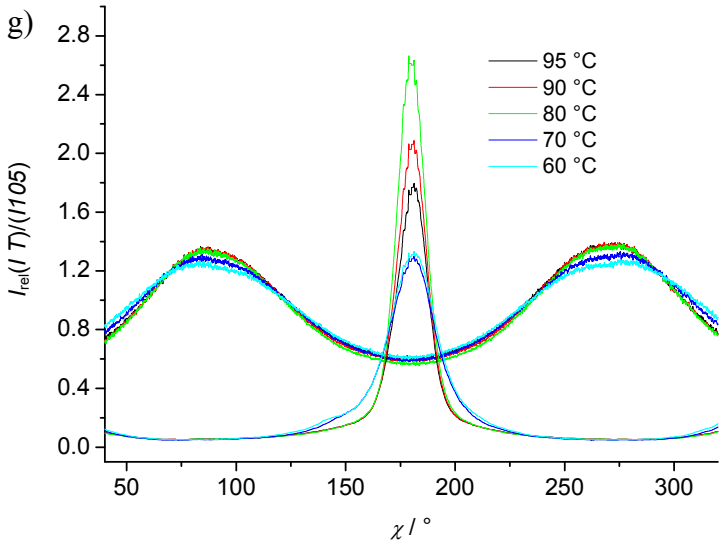


Figure S4. X-ray diffraction patterns of a surface aligned sample of compound *(S)*-**5:** a) SmA* phase at $T = 95$ ºC; b) SmA* phase at $T = 90$ ºC; c) SmA* phase at $T = 80$ ºC; d) SmC* phase at $T = 70$ ºC and e) SmC* phase at $T = 60$ ºC; the left row shows the original wide angle patterns, the right row shows the same patterns after subtraction of the scattering in the isotropic liquid state at $T = 105$ °C. f) θ-scan over the small angle and wide angle scattering at different temperatures; g) χ-scan over the small angle and wide angle scattering at different temperatures.

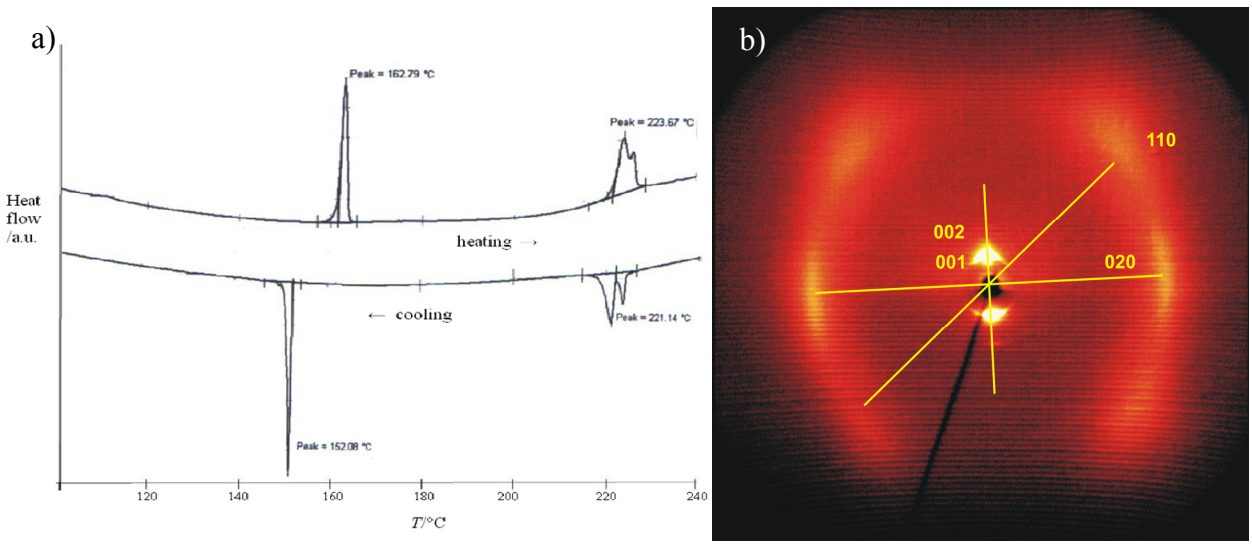


Figure S5. Compound *rac*-**2b:** a) DSC scan (first heating and first cooling, rate 10 K min^{-1}) and b) 2D X-ray diffraction patterns of compound *rac*-**2b** in the SmI phase ($a = 0.79$ nm; $b = 0.98$ nm; $c = 2.82$ nm, $\beta = 139°$) at $T = 170$ °C.

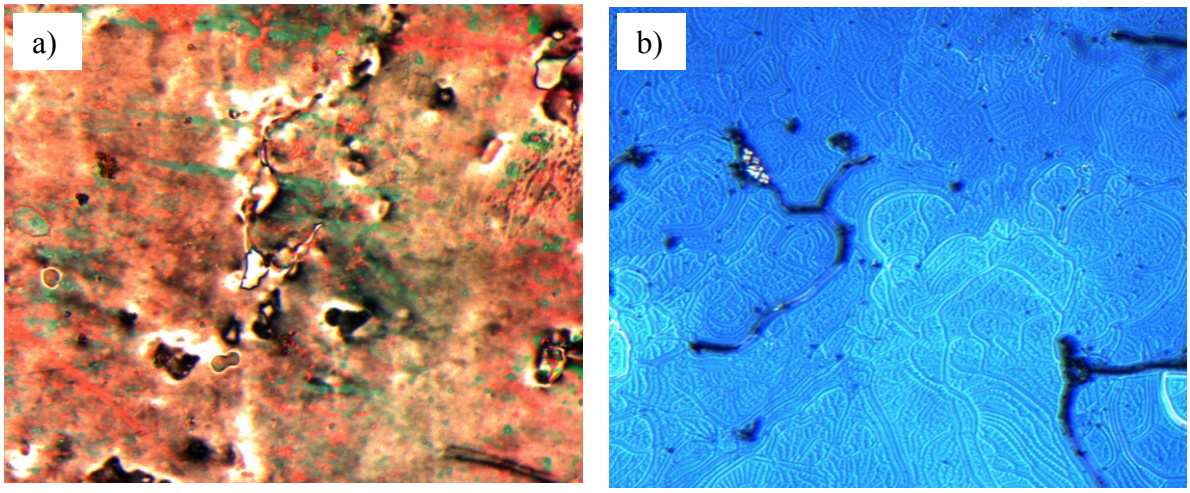


Figure S6. Polarised light optical photomicrograph a) of the N phase of *rac*-**2b** and b) of the N^* phase of *(S)*-**2b**, both recorded at $T = 224$ °C (magnification x 200).

2. Synthesis and analytical data

The characterization of the synthesized compounds is based on ^{1}H-, ^{13}C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions, with tetramethylsilane as internal standard), MS [AMD 402 (electron impact, 70 eV)]. Microanalyses were performed using a Leco CHNS-932 elemental analyzer. ^{1}H-NMR and ^{13}C-NMR spectra of compounds **3- 5** carrying terminal groups in the racemic form and chiral form are shown in Figures S7-S18 as an example for the proof of being same structure completely.

Transition temperatures were measured using a Leitz Laborlux 12 Pol polarizing microscope, equipped with a Linkam THMS 600 hot stage and a Linkam TMS93 temperature controller or a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing microscope. DSC-thermograms were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10 K min^{-1}. The electro-optical switching characteristics were examined using a triangular-wave method or under a DC field using polyimide coated ITO cells, EHC Japan.

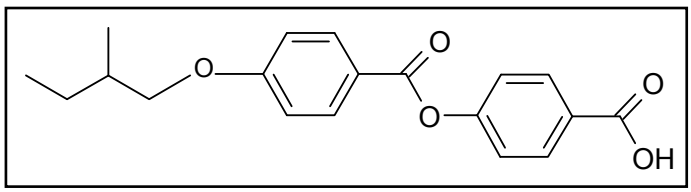
2D XRD patterns of aligned samples were recorded using quartz-monochromatized CuKα radiation (30 to 60 min exposure time) with a HI-STAR 2D detector, Siemens. Alignment was obtained by slow cooling (rate 0.1 K min^{-1}) a drop of the material on a glass substrate on a temperature controlled heating stage, leading to domains fiber-like disordered around an axis perpendicular to the surfaces; the X-ray beam was parallel to the glass substrate.

Materials: Resorcinol, 4-chlororesorcinol, 4-bromoresorcinol, 4,6-dichlororesorcinol, 2-methylresorcinol, 2-nitroresorcinol and 3,5-dihydroxybenzonitrile are commercial materials. 2,4-dihydroxybenzonitrile was synthesized according to the procedured described in Ref.[S1] (*S*)-(-)-2-Methyl-1-butanol (Fluka, 95.0%, $[\alpha]_D^{20}$ -6.3 ± 0.5°, *c* = 10 in EtOH), (+/-)-2-Methyl-1-butanol (Fluka, ≥98.0%), (*S*)-(-)-β-Citronellol (Aldrich, ≥99.0%, $[\alpha]_D^{20}$ -5.3°, neat), 3,7-Dimethyl-1-octanol (Aldrich, 99.0%) were purchased commercially. The optical rotation of (+/-)-2-Methyl-1-butanol and 3,7-Dimethyl-1-octanol was also measured using a Perkin-Elmer polarimeter 341 Serial No. 7146 and found $[\alpha]_{589}^{20}$ 0.7° (*c* = 0.5 in MeOH) and $[\alpha]_{589}^{20}$ -1.5° (neat) respectively. As the stereogenic center of chiral alcohols is not touched during the synthesis it can be assumed that the optical purity of the final products corresponds to the starting material.

2.1 Preparation procedures and spectroscopic data for *alkoxybenzoyloxybenzoic acids* and *alkoxybiphenylcarboxylic acids*

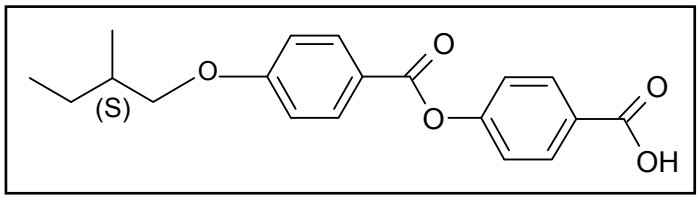
(S)-(-)-β-Citronellol was reduced to *(S)*-3,7-dimethyl-1-octanol under catalytic hydrogenation conditions (H_2, Pd/C in MeOH) in the first reaction step of the corresponding 4-(4-alkoxybenzoyloxy)benzoic acid *(S)*-**1b** and 4'-alkoxy-4-biphenylcarboxylic acid *(S)*-**2b**.
The preparation procedures for 4-(4-alkoxybenzoyloxy)benzoic acids (**1a** and **1b**) are given in Ref.[S2,S3] The compounds *rac*-**1a,** *(S)*-**1a** and *(S)*-**1b** were first reported by Luo et al.[S4], Xie et al.[S5] and Barbera et al.[S6], respectively.

4-[4-(2-Methylbutoxy)benzoyloxy]benzoic acid *($C_{19}H_{20}O_5$; 328.36 g/mol)*



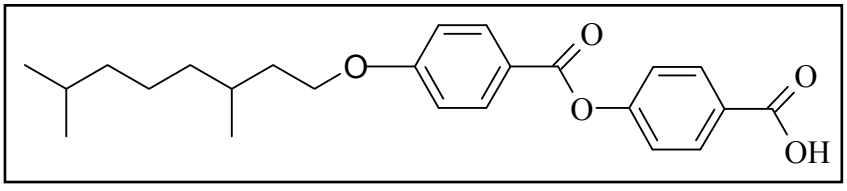
rac-**1a:** Yield: 92%, white crystals. **^{1}H-NMR:** δ (ppm) = 8.17 (d, $J \approx 8.9$ Hz; 2 Ar-H), 8.12 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.32 (d, $J \approx 8.9$ Hz; 2 Ar-H), 6.97 (d, $J \approx 8.9$ Hz; 2 Ar-H), 3.91, 3.83 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2), 1.92-1.85 (m; 1H, CH), 1.61-1.52, 1.33-1.24 (2m; 2H, CH_2), 1.03 (d, $J \approx 6.6$ Hz; 3H, CH_3), 0.96 (t, $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR:** δ (ppm) = 169.77 (COOH), 164.26 (CO), 163.95, 155.46, 126.55, 120.97 (Ar-C), 132.36, 131.80, 121.95, 114.44 (Ar-CH), 73.19 (OCH_2), 34.68 (CH), 26.14 (CH_2), 16.52, 11.31 (CH_3). **MS** (**EI**): m/z (%) = 328 (2) [M^+], 191 (76) [M^+-$C_7H_5O_3$], 121 (100) [C_5H_{11}]. Phase transitions (*T*/°C): Cr 168 N 183 Iso.

4-[4-(S)-2-Methylbutoxybenzoyloxy]benzoic acid *($C_{19}H_{20}O_5$; 328.36 g/mol)*



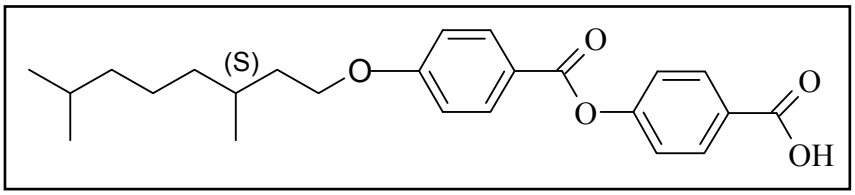
(S)-**1a:** Yield: 64%, white crystals. **^{1}H-NMR:** δ (ppm) = 8.16 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.12 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.31 (d, $J \approx 8.7$ Hz; 2 Ar-H), 6.97 (d, $J \approx 8.9$ Hz; 2 Ar-H), 3.90, 3.82 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2), 1.94-1.85 (m; 1H, CH), 1.61-1.52, 1.35-1.24 (2m; 2H, CH_2), 1.03 (d, $J \approx 6.9$ Hz; 3H, CH_3), 0.95 (t, $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR:** δ (ppm) = 169.96 (COOH), 164.35 (CO), 163.97, 155.37, 126.84, 120.97 (Ar-C), 132.39, 131.80, 121.94, 114.43 (Ar-CH), 73.16 (OCH_2), 34.63 (CH), 26.08 (CH_2), 16.47, 11.28 (CH_3). **MS** (**EI**): m/z (%) = 328 (2) [M^+], 191 (76) [M^+-$C_7H_5O_3$], 121 (100) [C_5H_{11}]. Phase transitions (*T*/°C): Cr 168 N* 184 Iso

4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoic acid *($C_{24}H_{30}O_5$; 398.49 g/mol)*



rac-**1b:** Yield: 78%, white crystals. **^{1}H-NMR:** δ (ppm) = 8.17 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.13 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.31 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 6.97 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 4.12-4.05 (m; 2H, OCH_2), 1.92-1.81 (m; 1H, CH), 1.70-1.47, 1.38-1.13 (2m; 9H, CH, 4 CH_2), 0.95 (d, *J* ≈ 6.4 Hz; 3H, CH_3), 0.86 (d, *J* ≈ 6.4 Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) = 169.95 (COOH), 164.31 (CO), 163.80, 155.49, 126.53, 120.98 (Ar-C), 132.41, 131.85, 121.99, 114.43 (Ar-CH), 66.74 (OCH_2), 39.22 (CH_2), 37.25, 35.98 (CH), 29.83, 27.97, 24.64 (CH_2), 22.68, 22.59, 19.63 (CH_3). **MS** (**EI**): m/z (%) = 398 (1) [M^+], 261 (100) [M^+-$C_7H_5O_3$], 121 (57) [$C_{10}H_{21}$]. Phase transitions (*T*/°C): Cr 99 SmC 169 N 197 Iso.

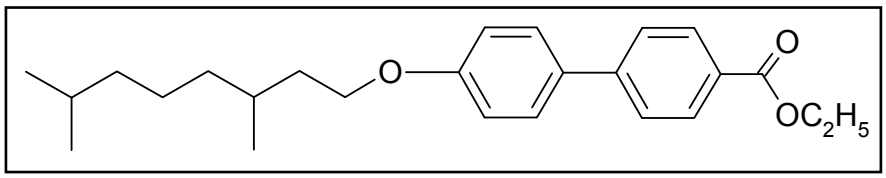
4-[4-(S)-3,7-Dimethyloctyloxybenzoyloxy]benzoic acid *($C_{24}H_{30}O_5$; 398.49 g/mol)*



(S)-**1b:** Yield: 90%, white crystals. **^{1}H-NMR:** δ (ppm) = 8.16 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 8.13 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.32 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.97 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 4.10-4.05 (m; 2H, OCH_2), 1.88-1.81 (m; 1H, CH), 1.72-1.49, 1.35-1.13 (2m; 9H, CH, 4 CH_2), 0.95 (d, *J* ≈ 6.4 Hz; 3H, CH_3), 0.86 (d, *J* ≈ 6.6 Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) = 169.08 (COOH), 164.15 (CO), 163.67, 155.36, 126.39, 120.96 (Ar-C), 132.31, 131.74, 121.91, 114.39 (Ar-CH), 66.79 (OCH_2), 39.31 (CH_2), 37.35, 36.09 (CH), 29.96, 28.06, 24.75 (CH_2), 22.78, 22.69, 19.76 (CH_3). **MS** (**EI**): m/z (%) = 398 (1) [M^+], 261 (100) [M^+-$C_7H_5O_3$], 121 (57) [$C_{10}H_{21}$]. Phase transitions (*T*/°C): Cr 98 SmC* 167 N* 194 Iso.

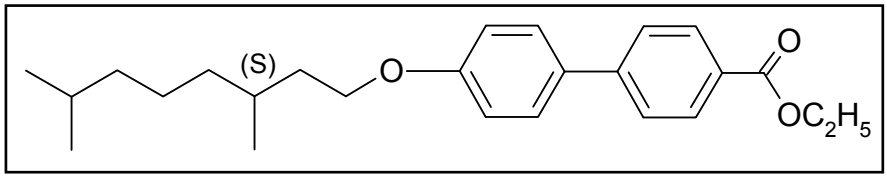
The synthesis of 4'-alkoxy-4-biphenylcarboxylic acids *rac*-**2b** and *(S)*-**2b** was carried out by using known procedures[S7]. Firstly, Ethyl 4'-alkoxy-4-biphenylcarboxylates having 3,7-dimethyloctyloxy group in the racemic and chiral forms were obtained by the reaction of Ethyl 4'-hydroxy-4-biphenylcarboxylate (10 mmol) with the appropriate alkyl bromides (15 mmol), using K_2CO_3 (15 mmol) as base and 2-Butanone (60 ml) as solvent. The compounds were purified by column chromatography (silica gel; eluent was hexane/ethyl acetate). Then, the hydrolysis reaction of the corresponding compounds (7 mmol) in EtOH (10 ml) with KOH (14 mmol) as base gave the 4'-alkoxy-4-biphenylcarboxylic acids (*rac*-**2b** and *(S)*-**2b**).

Ethyl 4'-(3,7-dimethyloctyloxy)-4-biphenylcarboxylates *($C_{25}H_{34}O_3$; 382.54 g/mol)*



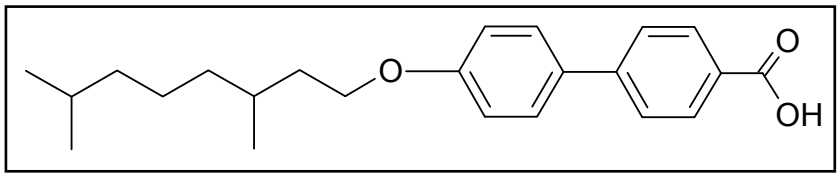
Yield: 2.48 g (65%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.05 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 7.59 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 7.54 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 6.96 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 4.37 (q, *J* ≈ 7.1 Hz; 2H, COOC$\underline{H}_2$), 4.07-3.98 (m; 2H, OCH_2), 1.87-1.79 (m; 1H, CH), 1.68-1.45, 1.35-1.14 (2m; 9H, CH, 4 CH_2), 1.39 (t, *J* ≈ 7.1 Hz; 3H, $OCH_2C\underline{H}_3$), 0.94 (d, *J* ≈ 6.4 Hz; 3H, CH_3), 0.86 (d, *J* ≈ 6.4 Hz; 6H, 2 CH_3).

Ethyl 4'-(S)-3,7-dimethyloctyloxy-4-biphenylcarboxylates *($C_{25}H_{34}O_3$; 382.54 g/mol)*



Yield: 3.59 g (94%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.06 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 7.59 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 7.54 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 6.96 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 4.37 (q, *J* ≈ 7.1 Hz; 2H, COOC$\underline{H}_2$), 4.05-4.00 (m; 2H, OCH_2), 1.86-1.79 (m; 1H, CH), 1.67-1.49, 1.35-1.14 (2m; 9H, CH, 4 CH_2), 1.39 (t, *J* ≈ 7.1 Hz; 3H, $OCH_2C\underline{H}_3$), 0.94 (d, *J* ≈ 6.4 Hz; 3H, CH_3), 0.86 (d, *J* ≈ 6.4 Hz; 6H, 2 CH_3).

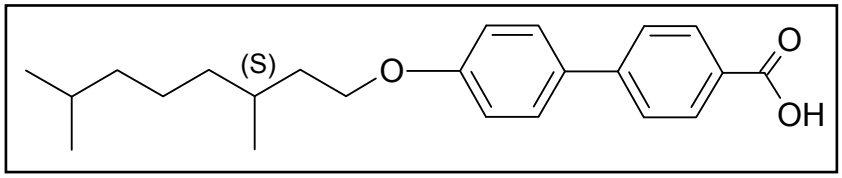
4'-(3,7-Dimethyloctyloxy)-4-biphenylcarboxylic acid *($C_{23}H_{30}O_3$; 354.49 g/mol)*



rac-**2b:** Yield: 2.33 g (94%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.13 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.64 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.56 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 6.98 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 4.06-4.01 (m; 2H, OCH_2), 1.87-1.82 (m; 1H, CH), 1.68-1.48, 1.35-1.14 (2m; 9H, CH, 4 CH_2), 0.95 (d, *J* ≈ 6.4 Hz; 3H, CH_3), 0.86 (d, *J* ≈ 6.6 Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) = 170.27 (COOH), 159.45, 146.03, 131.96, 126.98 (Ar-C), 130.64, 128.29, 126.46, 114.97 (Ar-CH), 66.56 (OCH_2), 39.34 (CH_2), 37.39, 36.29 (CH), 30.00, 28.08, 24.76 (CH_2), 22.79, 22.69,

19.79 (CH_3). **MS** (**EI**): m/z (%) = 354 (57) [M^+], 214 (100) [M^+-$C_{10}H_{21}$], 197 (11) [OH]. *T*/°C [Δ*H* kJ/mol]: Cr 163 [14.1] Sm I 223 N 225 [12.2] Iso (phase transition enthalpies SmI-N-Iso not resolved).).

4'-(S)-3,7-Dimethyloctyloxy-4-biphenylcarboxylic acid *($C_{23}H_{30}O_3$; 354.49 g/mol)*



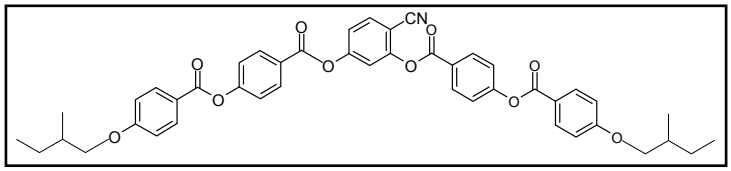
(S)-**2b:** Yield: 2.36 g (95%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.13 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.64 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.56 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 6.98 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 4.06-4.01 (m; 2H, OCH_2), 1.87-1.82 (m; 1H, CH), 1.68-1.48, 1.35-1.14 (2m; 9H, CH, 4 CH_2), 0.95 (d, *J* ≈ 6.4 Hz; 3H, CH_3), 0.86 (d, *J* ≈ 6.6 Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) = 170.29 (COOH), 159.45, 146.03, 131.96, 127.06 (Ar-C), 130.64, 128.29, 126.46, 114.97 (Ar-CH), 66.56 (OCH_2), 39.34 (CH_2), 37.39, 36.29 (CH), 30.00, 28.07, 24.76 (CH_2), 22.79, 22.69, 19.78 (CH_3). **MS** (**EI**): m/z (%) = 354 (98) [M^+], 214 (100) [M^+-$C_{10}H_{21}$], 197 (29) [OH]. *T*/°C [Δ*H* kJ/mol]: Cr 163 [12.5] Sm I* 224 N* 226 [11.5] Iso (phase transition enthalpies SmI-N-Iso not resolved).

2.2 Synthesis and analytical data of the bent-core compounds

The mixture of 1.2 mmol of the related resorcinols, 2.4 mmol of the corresponding 4-(4-alkoxybenzoyloxy)benzoic acids or 4'-alkoxy-4-biphenylcarboxylic acids, 2.4 mmol of dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) as catalyst in 40 ml of dry dichloromethane was stirred at room temperature under an argon atmosphere for 24 h. The precipitate was filtered, the solvent was evaporated. The crude products were purified by column chromatography on silica gel using dichloromethane as eluent and crystallized from ethanol.

4- Cyano-1,3-phenylene bis[4-(4-(2-methylbutoxy)benzoyloxy)-benzoate]

($C_{45}H_{41}NO_{10}$; 755.82 g/mol)



rac-**3:** Yield: 0.43 g (47%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.32 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 8.25 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 8.14 (d, *J* ≈ 9.0 Hz; 4 Ar-H), 7.78 (d, *J* ≈ 8.6 Hz; 1 Ar-H), 7.52 (d, *J* ≈ 2.1 Hz; 1 Ar-H), 7.39 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.38 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.31 (dd, *J* ≈ 8.6 Hz and *J* ≈ 2.1 Hz; 1 Ar-H), 6.98 (d, *J* ≈ 9.0 Hz; 4 Ar-H), 3.91, 3.82 (2dd, , *J* ≈ 9.0 Hz and *J* ≈ 6.0 Hz each; 4H, 2 OCH_2), 1.93-1.87 (m; 2H, 2 CH), 1.60-1.52, 1.33-1.26 (2m; 4H, 2 CH_2), 1.03 (d, *J* ≈ 6.9 Hz; 6H, 2 CH_3), 0.96 (t, *J* ≈ 7.5 Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) = 164.21, 164.05, 164.01, 162.89 (CO), 164.16, 163.27, 156.05, 155.91, 154.77, 153.46, 125.69, 125.30, 120.81, 120.75, 104.24 (Ar-C), 133.94, 132.42, 132.41, 132.24, 131.98, 122.38, 122.33, 120.01, 117.38, 114.45, 114.44 (Ar-CH), 114.75 (CN), 73.15, 73.14 (OCH_2), 34.61 (CH), 26.05 (CH_2), 16.45, 11.26 (CH_3). **MS (EI) :** m/z (%) = 311 (3) [M^+-$C_{26}H_{22}O_6N$], 191 (100) [$C_7H_4O_2$], 121 (71) [C_5H_{11}].

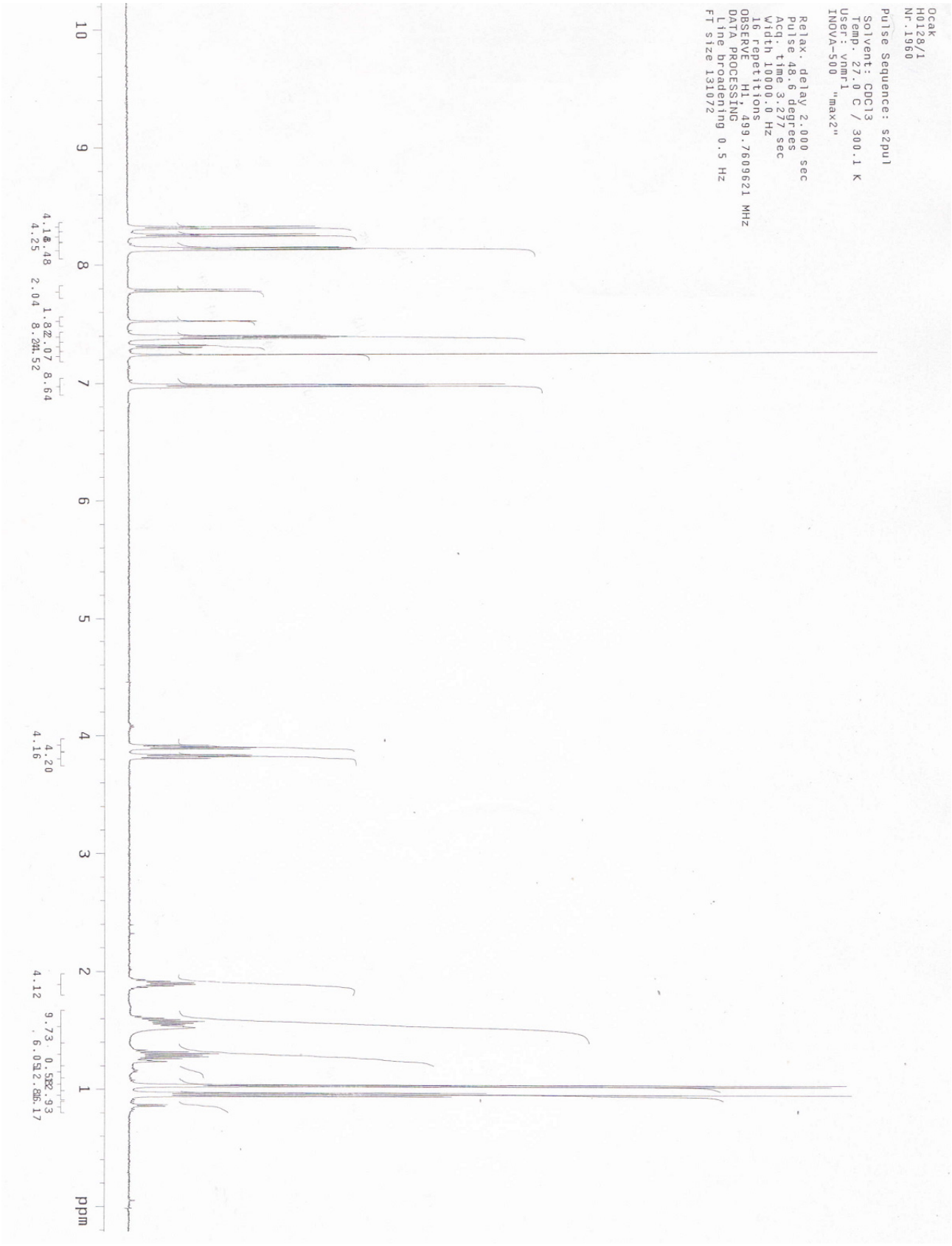


Figure S7. ^{1}H-NMR spectrum of compound *rac*-**3**.

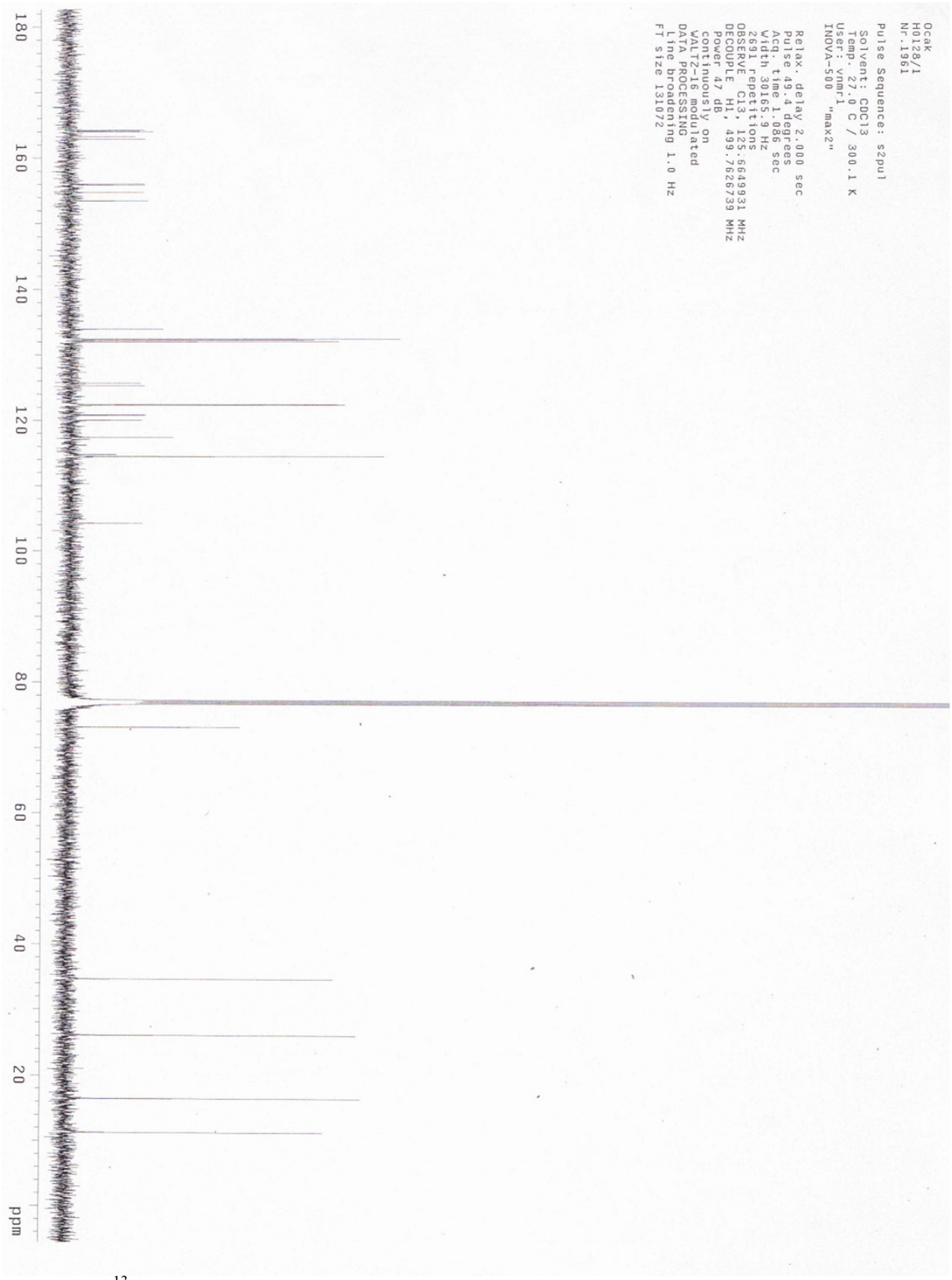
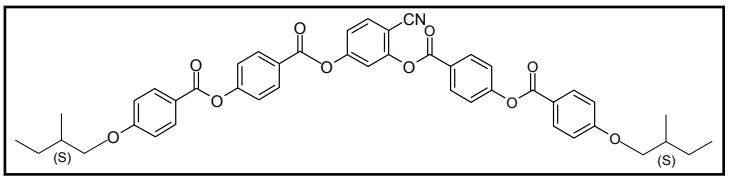


Figure S8. ^{13}C-NMR spectrum of compound *rac*-**3**.

4- Cyano-1,3-phenylene bis[4-(4-(S)-2-methylbutoxybenzoyloxy)-benzoate]

($C_{45}H_{41}NO_{10}$; 755.82 g/mol)



(S)-**3:** Yield: 0.54 g (60%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.33 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.26 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.15 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 7.80 (d, *J* ≈ 8.5 Hz; 1 Ar-H), 7.54 (d, *J* ≈ 2.1 Hz; 1 Ar-H), 7.41 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.40 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.33 (dd, *J* ≈ 8.5 Hz and *J* ≈ 2.1 Hz; 1 Ar-H), 6.99 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 3.92, 3.84 (2dd, , *J* ≈ 9.0 Hz and *J* ≈ 6.0 Hz each; 4H, 2 OCH_2), 1.96-1.87 (m; 2H, 2 CH), 1.63-1.55, 1.35-1.25 (2m; 4H, 2 CH_2), 1.05 (d, *J* ≈ 6.8 Hz; 6H, 2 CH_3), 0.97 (t, *J* ≈ 7.5 Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) = 164.20, 164.04, 164.01, 162.89 (CO), 164.16, 163.27, 156.05, 155.91, 154.77, 153.46, 125.69, 125.30, 120.82, 120.76, 104.24 (Ar-C), 133.94, 132.42, 132.41, 132.24, 131.99, 122.38, 122.33, 120.00, 117.38, 114.46, 114.44 (Ar-CH), 114.75 (CN), 73.16 (OCH_2), 34.61 (CH), 26.06 (CH_2), 16.45, 11.26 (CH_3). **MS (EI) :** m/z (%) = 311 (10) [M^+-$C_{26}H_{22}O_6N$], 191 (100) [$C_7H_4O_2$], 121 (60) [C_5H_{11}].

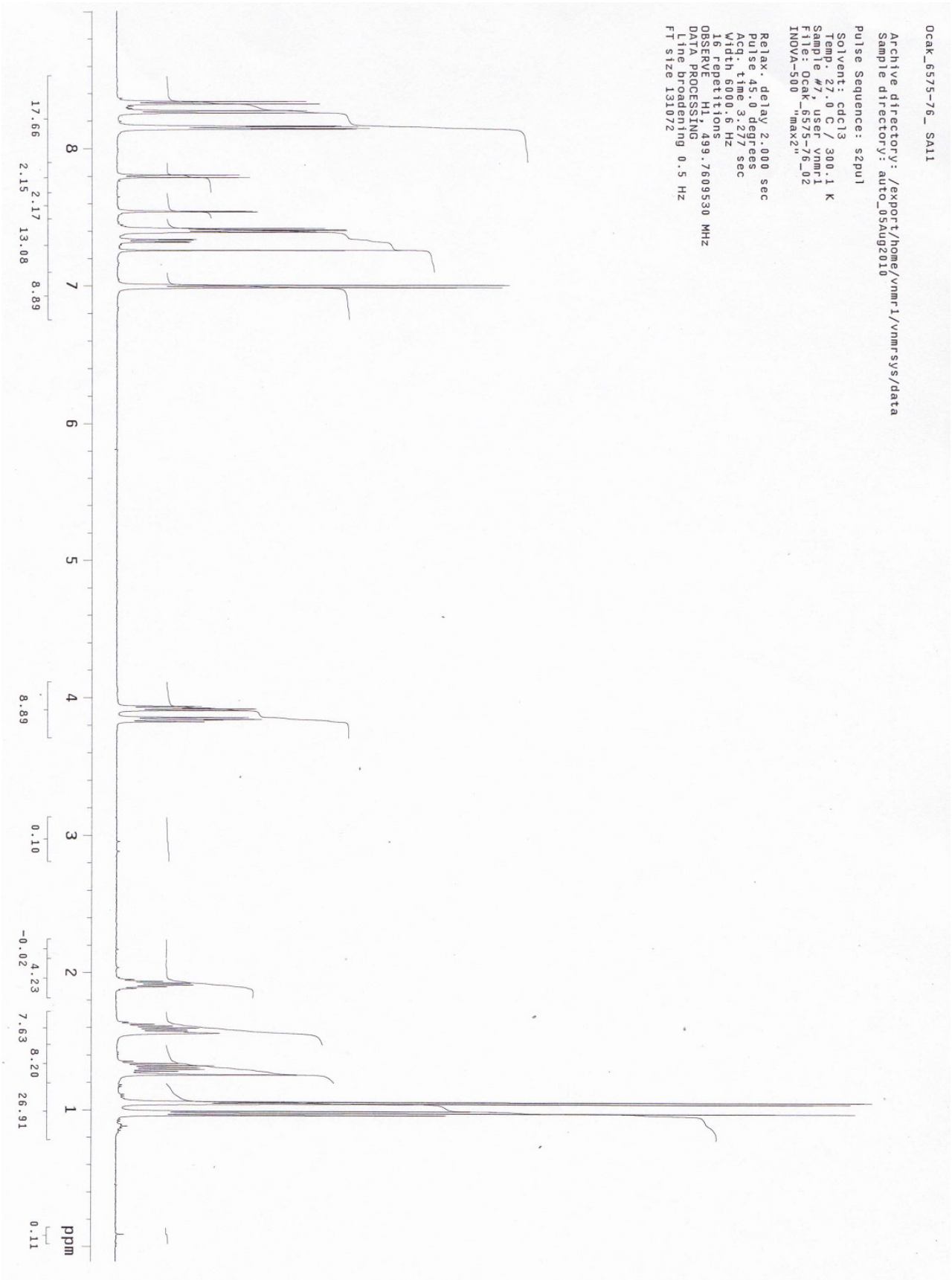


Figure S9. ^{1}H-NMR spectrum of compound *(S)*-**3**.

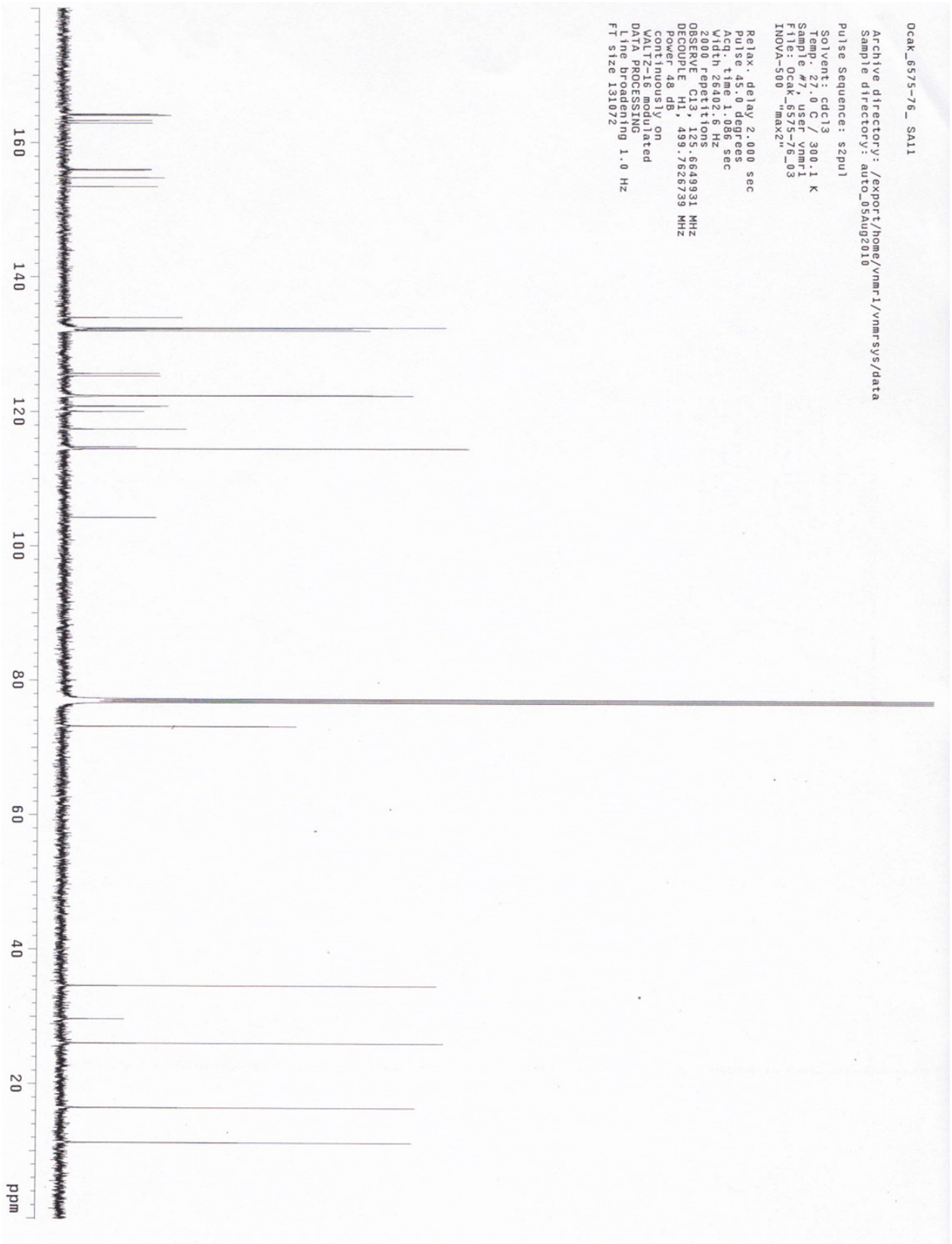
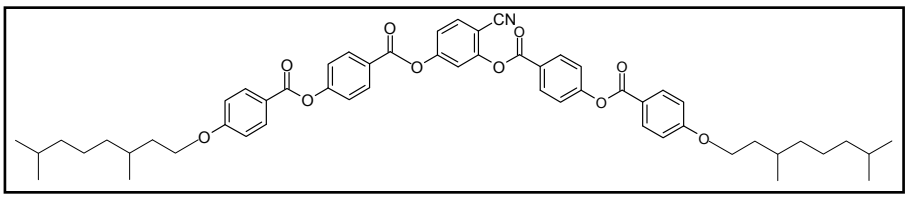


Figure S10. ^{13}C-NMR spectrum of compound *(S)*-**3**.

4-Cyano-1,3-phenylene bis[4-(4-(3,7-dimethyloctyloxy)benzoyloxy)-benzoate]

($C_{55}H_{61}NO_{10}$; 896.08 g/mol)



rac-**4:** Yield: 0.47 g (44%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.33 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.27 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.16 (d, *J* ≈ 9.0 Hz; 4 Ar-H), 7.80 (d, *J* ≈ 8.6 Hz; 1 Ar-H), 7.54 (d, *J* ≈ 2.1 Hz; 1 Ar-H), 7.41 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.40 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.33 (dd, *J* ≈ 8.6 Hz and *J* ≈ 2.1 Hz; 1 Ar-H), 6.99 (d, *J* ≈ 9.0 Hz; 4 Ar-H), 4.14-4.06 (m; 4H, 2 OCH_2), 1.91-1.84 (m; 2H, 2 CH), 1.71-1.52, 1.39-1.13 (2m; 18H, 2 CH, 8 CH_2), 0.97 (d, *J* ≈ 6.4 Hz; 6H, 2 CH_3), 0.88 (d, *J* ≈ 6.6 Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 164.20, 163.86, 163.83, 162.88 (CO), 164.15, 163.27, 156.04, 155.90, 154.77, 153.46, 125.69, 125.31, 120.86, 120.80, 104.24 (Ar-C), 133.94, 132.44, 132.42, 132.24, 131.99, 122.37, 122.32, 120.00, 117.38, 114.45, 114.43 (Ar-CH), 114.75 (CN), 66.73 (OCH_2), 39.20 (CH_2), 37.23, 35.96 (CH), 29.81, 27.94, 24.62 (CH_2), 22.67, 22.57, 19.61 (CH_3). **MS (EI) :** m/z (%) = 381 (7) [M^+-$C_{31}H_{32}O_6N$], 261 (100) [$C_7H_4O_2$], 121 (50) [$C_{10}H_{21}$]. **$C_{55}H_{61}NO_{10}$** (896.08); Anal. Calc.: C, 73.72; H, 6.86; N, 1.56. Found: C, 73.51; H, 6.69; N, 1.51%.

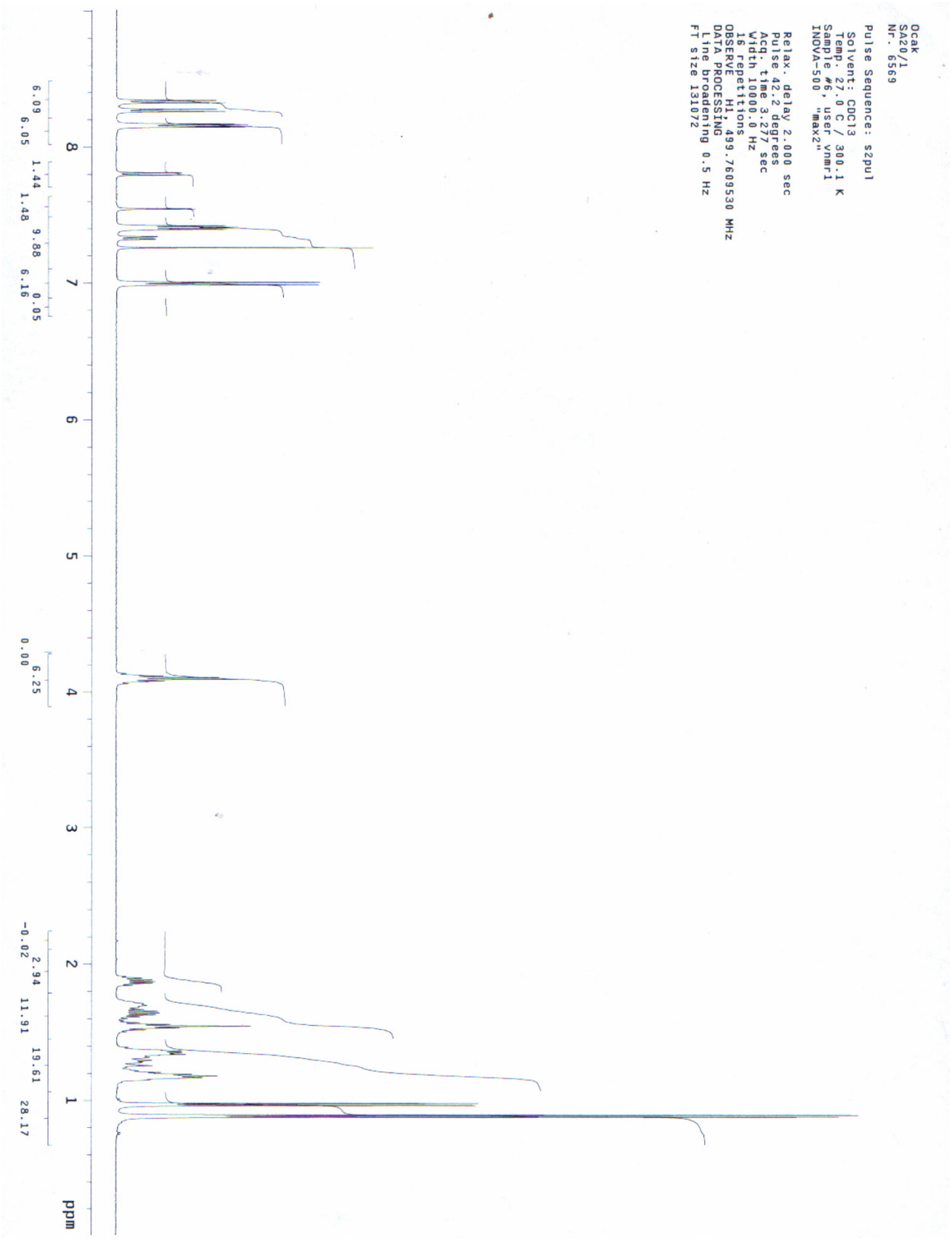


Figure S11. [1]H-NMR spectrum of compound *rac*-**4**.

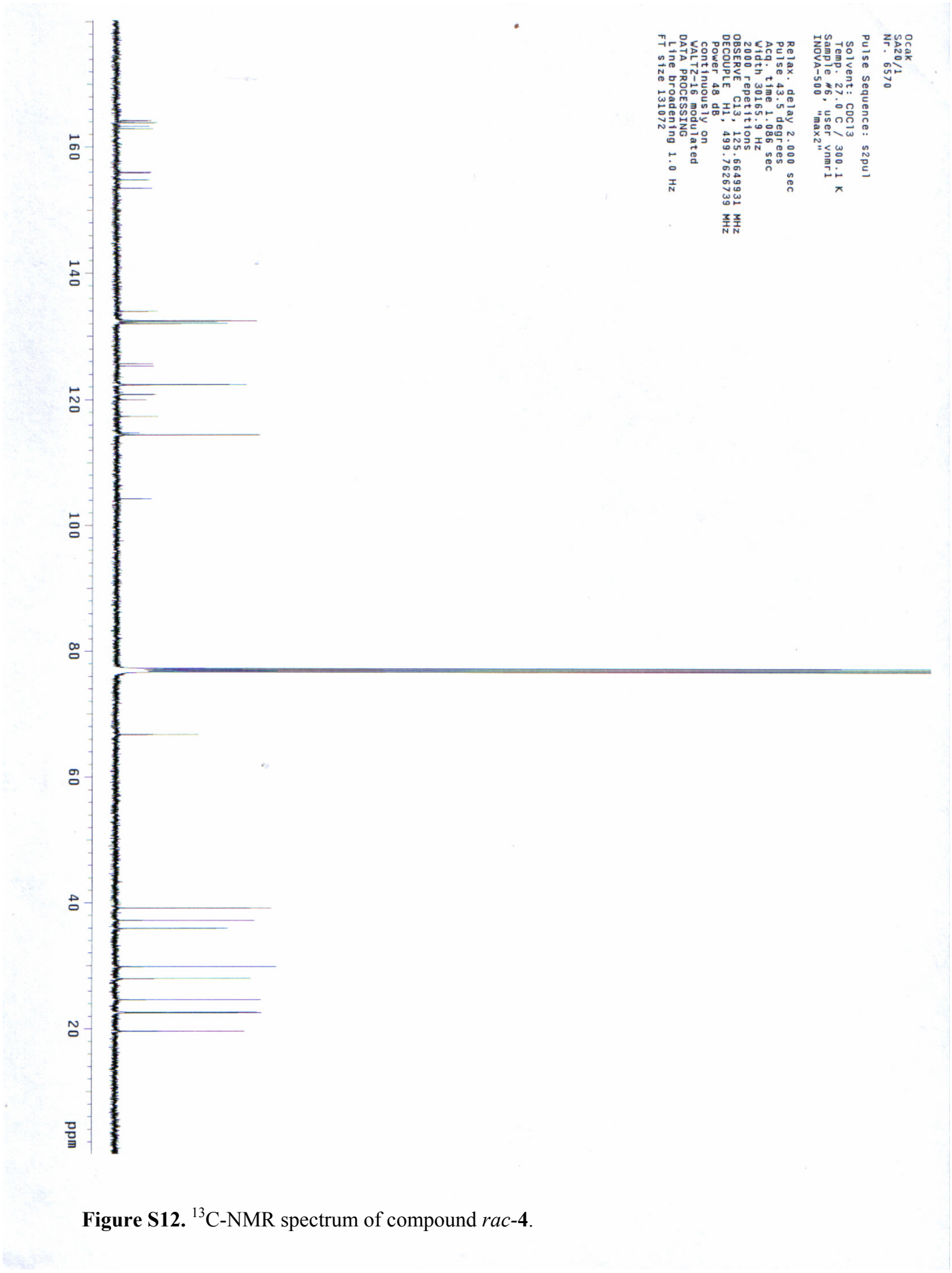
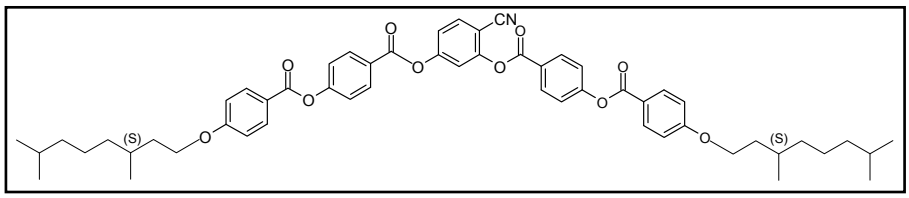


Figure S12. ^{13}C-NMR spectrum of compound *rac*-**4**.

4-Cyano-1,3-phenylene bis[4-(4-(S)-3,7-dimethyloctyloxybenzoyloxy)-benzoate]

($C_{55}H_{61}NO_{10}$; 896.08 g/mol)



(S)-4: Yield: 0.44 g (41%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.33 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.27 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.16 (d, *J* ≈ 9.0 Hz; 4 Ar-H), 7.80 (d, *J* ≈ 8.6 Hz; 1 Ar-H), 7.54 (d, *J* ≈ 2.1 Hz; 1 Ar-H), 7.41 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.40 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.33 (dd, *J* ≈ 8.6 Hz and *J* ≈ 2.1 Hz; 1 Ar-H), 6.99 (d, *J* ≈ 9.0 Hz; 4 Ar-H), 4.14-4.06 (m; 4H, 2 OCH_2), 1.91-1.84 (m; 2H, 2 CH), 1.71-1.52, 1.39-1.13 (2m; 18H, 2 CH, 8 CH_2), 0.97 (d, *J* ≈ 6.4 Hz; 6H, 2 CH_3), 0.88 (d, *J* ≈ 6.6 Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 164.20, 163.86, 163.83, 162.88 (CO), 164.15, 163.26, 156.04, 155.90, 154.77, 153.46, 125.69, 125.31, 120.85, 120.79, 104.24 (Ar-C), 133.94, 132.44, 132.42, 132.24, 131.99, 122.37, 122.32, 120.01, 117.38, 114.45, 114.43 (Ar-CH), 114.75 (CN), 66.74 (OCH_2), 39.20 (CH_2), 37.23, 35.96 (CH), 29.81, 27.94, 24.62 (CH_2), 22.67, 22.57, 19.61 (CH_3). **MS (EI) :** m/z (%) = 381 (10) [M^+-$C_{31}H_{32}O_6N$], 261 (100) [$C_7H_4O_2$], 121 (47) [$C_{10}H_{21}$].

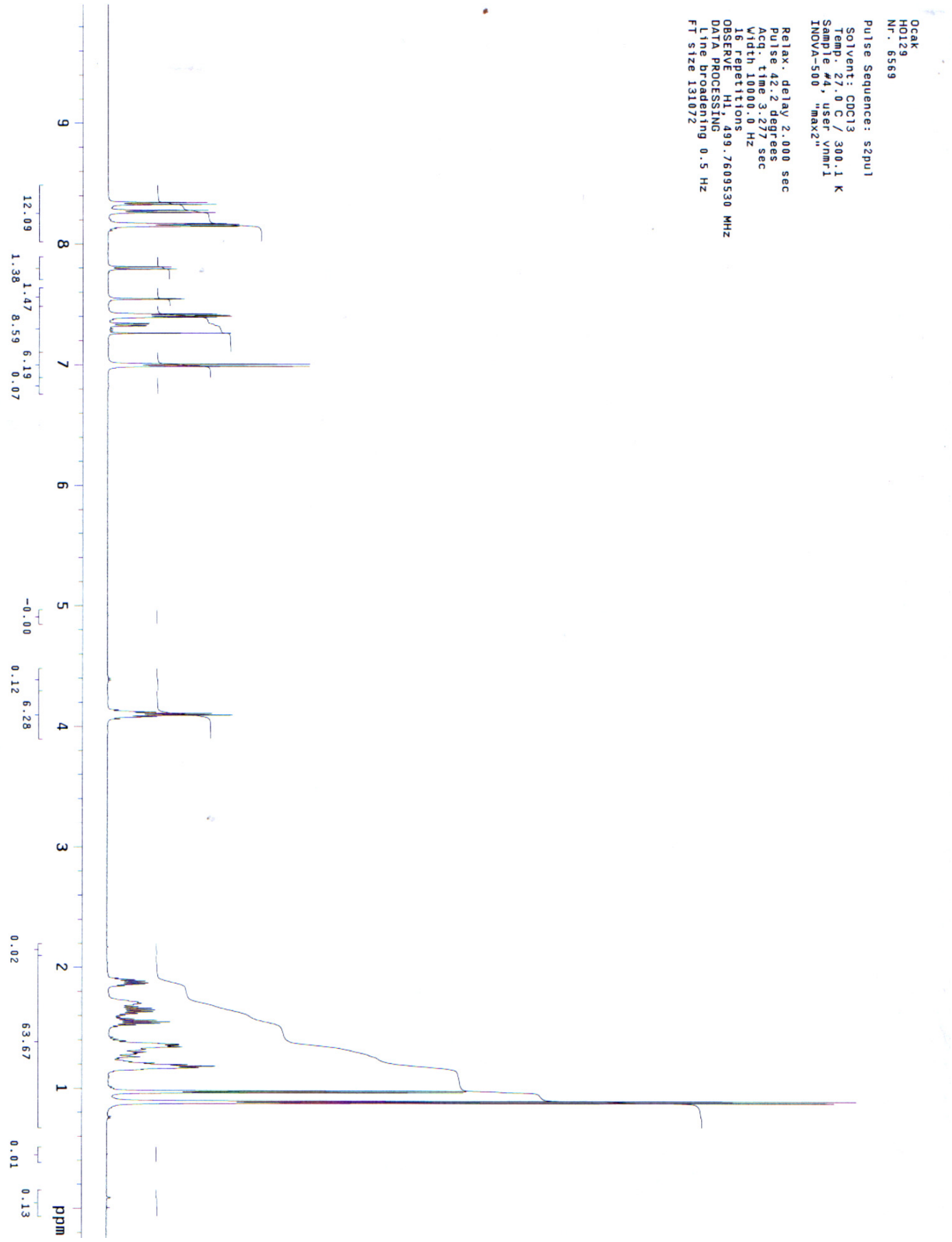


Figure S13. ^{1}H-NMR spectrum of compound *(S)*-**4**.

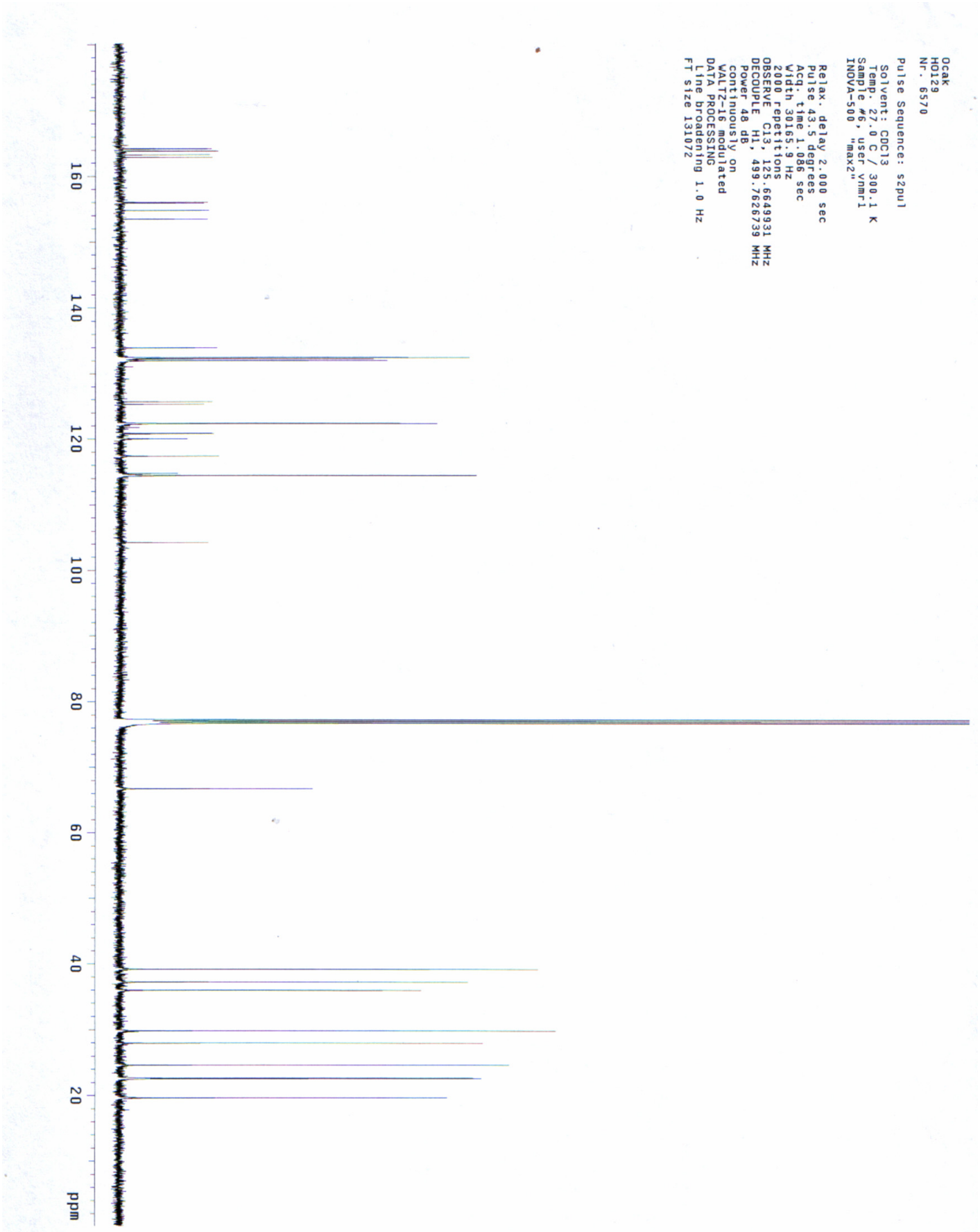
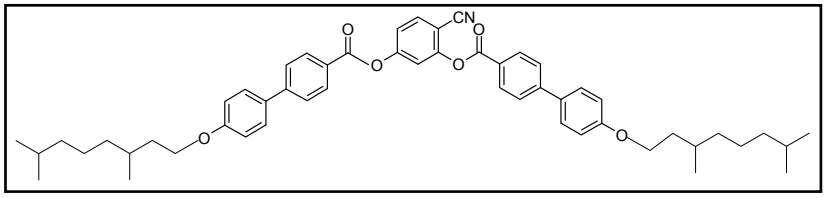


Figure S14. ^{13}C-NMR spectrum of compound (S)-**4**.

4-Cyano-1,3-phenylene bis[4'-(3,7-dimethyloctyloxy)-4-biphenylcarboxylate]

($C_{53}H_{61}NO_6$; 808.07 g/mol)



rac-**5:** Yield: 0.37 g (38%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.27 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 8.20 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 7.77 (d, *J* ≈ 8.6 Hz; 1 Ar-H), 7.70 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 7.69 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.58 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 7.54 (d, *J* ≈ 2.1 Hz; 1 Ar-H), 7.31 (dd, *J* ≈ 8.6 Hz and *J* ≈ 2.1 Hz; 1 Ar-H), 6.99 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 4.06-4.01 (m; 4H, 2 OCH_2), 1.88-1.80 (m; 2H, 2 CH), 1.70-1.47, 1.35-1.14 (2m; 18H, 2 CH, 8 CH_2), 0.95 (d, *J* ≈ 6.4 Hz; 6H, 2 CH_3), 0.86 (d, *J* ≈ 6.4 Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 163.86, 163.49 (CO), 159.69, 159.66, 154.91, 153.62, 146.80, 146.64, 131.77, 131.68, 126.34, 125.97, 104.17 (Ar-C), 133.84, 131.09, 130.86, 128.41, 128.38, 126.81, 126.72, 119.90, 117.43, 115.09 (Ar-CH), 114.88 (CN), 66.63 (OCH_2), 39.39 (CH_2), 37.44, 36.33 (CH), 30.06, 28.13, 24.81 (CH_2), 22.84, 22.75, 19.84 (CH_3). **MS (EI) :** m/z (%) = 808 (22) [M^+], 337 (100) [M^+-$C_{30}H_{32}O_4N$], 197 (18) [$C_{10}H_{21}$].

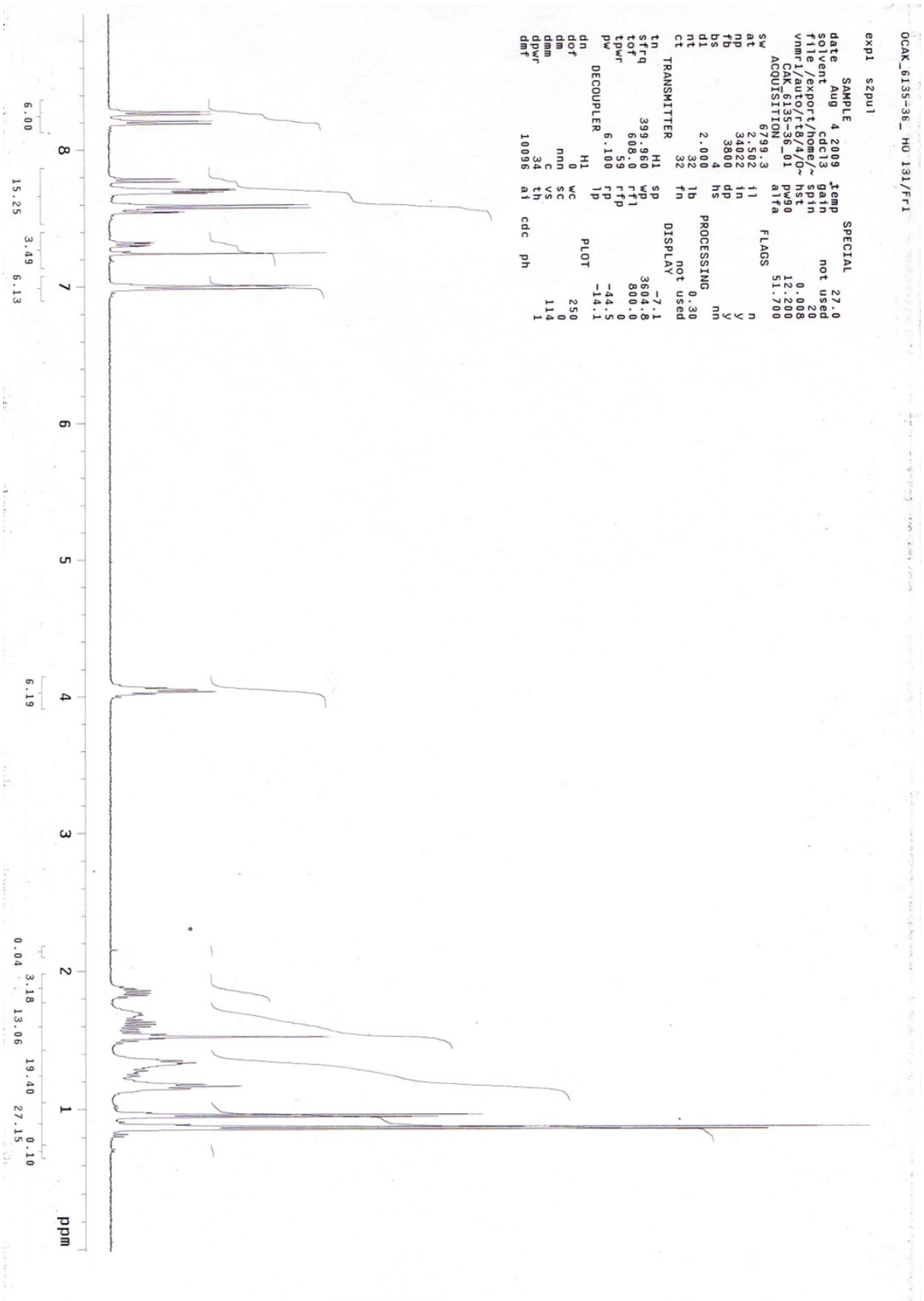


Figure S15. ^{1}H-NMR spectrum of compound *rac*-**5**.

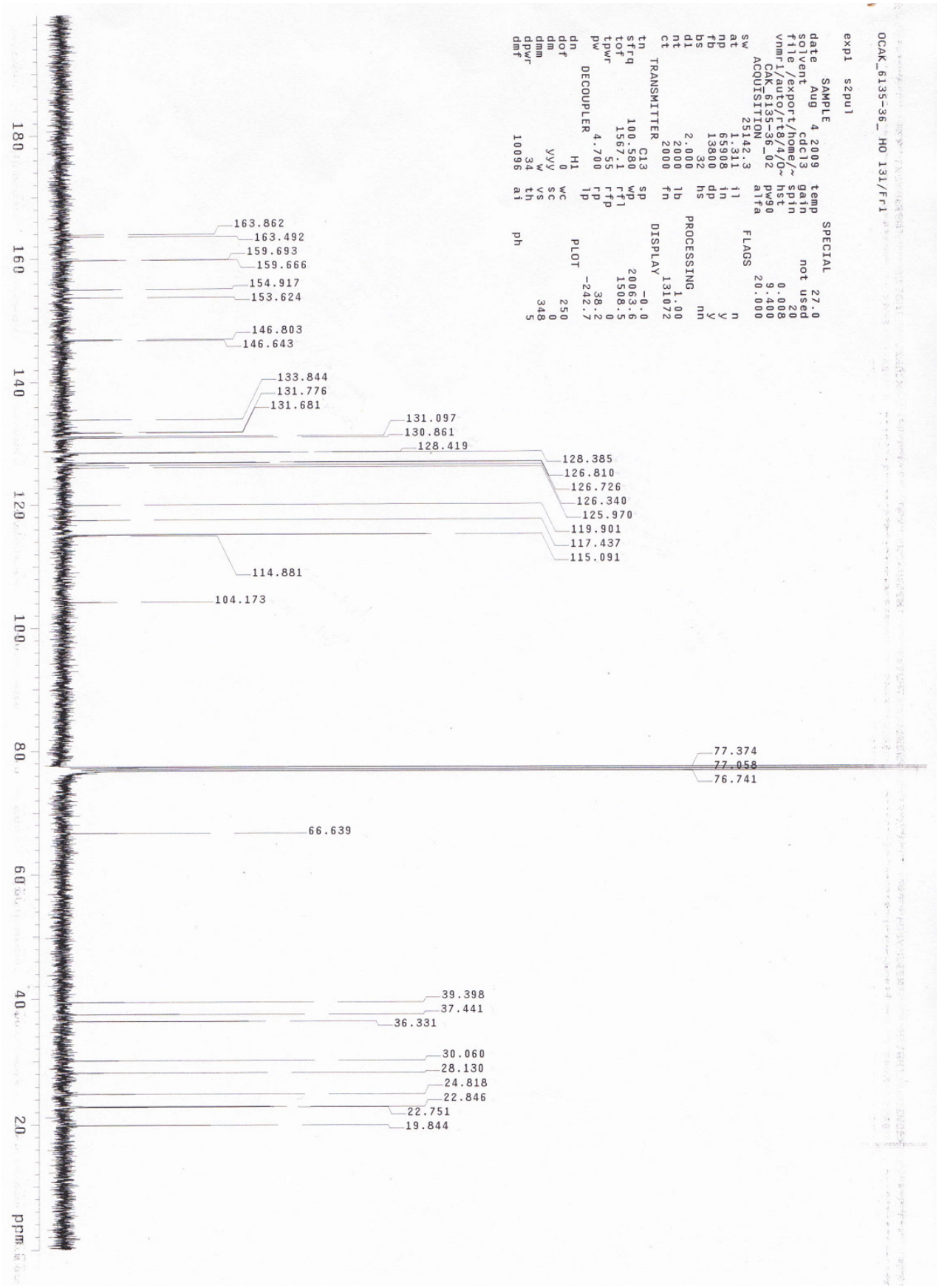
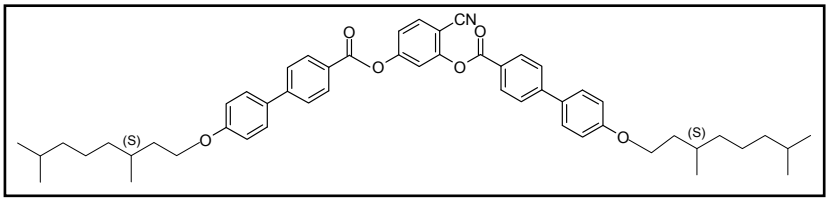


Figure S16. ^{13}C-NMR spectrum of compound *rac*-**5**.

4-Cyano-1,3-phenylene bis[4'-(S)-3,7-dimethyloctyloxy-4-biphenylcarboxylate]

($C_{53}H_{61}NO_6$; 808.07 g/mol)



(S)-**5:** Yield: 0.34 g (35%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.28 (d, *J* ≈ 8.4 Hz; 2 Ar-H), 8.21 (d, *J* ≈ 8.4 Hz; 2 Ar-H), 7.79 (d, *J* ≈ 8.5 Hz; 1 Ar-H), 7.72 (d, *J* ≈ 8.4 Hz; 2 Ar-H), 7.71 (d, *J* ≈ 8.4 Hz; 2 Ar-H), 7.60 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 7.56 (d, *J* ≈ 2.1 Hz; 1 Ar-H), 7.32 (dd, *J* ≈ 8.5 Hz and *J* ≈ 2.1 Hz; 1 Ar-H), 7.01 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 4.10-4.02 (m; 4H, 2 OCH_2), 1.89-1.83 (m; 2H, 2 CH), 1.71-1.49, 1.39-1.14 (2m; 18H, 2 CH, 8 CH_2), 0.96 (d, *J* ≈ 6.6 Hz; 6H, 2 CH_3), 0.88 (d, *J* ≈ 6.6 Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 163.94, 163.56 (CO), 159.72, 159.70, 154.94, 153.64, 146.82, 146.65, 131.75, 131.65, 126.29, 125.92, 104.10 (Ar-C), 133.88, 131.11, 130.88, 128.43, 128.39, 126.80, 126.72, 119.92, 117.44, 115.04 (Ar-CH), 114.89 (CN), 66.49, 66.48 (OCH_2), 39.23 (CH_2), 37.27, 36.14 (CH), 29.85, 27.95, 24.64 (CH_2), 22.68, 22.58, 19.64 (CH_3). **MS (EI) :** m/z (%) = 808 (31) [M^+], 337 (100) [M^+-$C_{30}H_{32}O_4N$], 197 (17) [$C_{10}H_{21}$]. **$C_{53}H_{61}NO_6$** (808.07); Anal. Calc.: C, 78.77; H, 7.61; N, 1.73. Found: C, 78.55; H, 7.42; N, 1.69%.

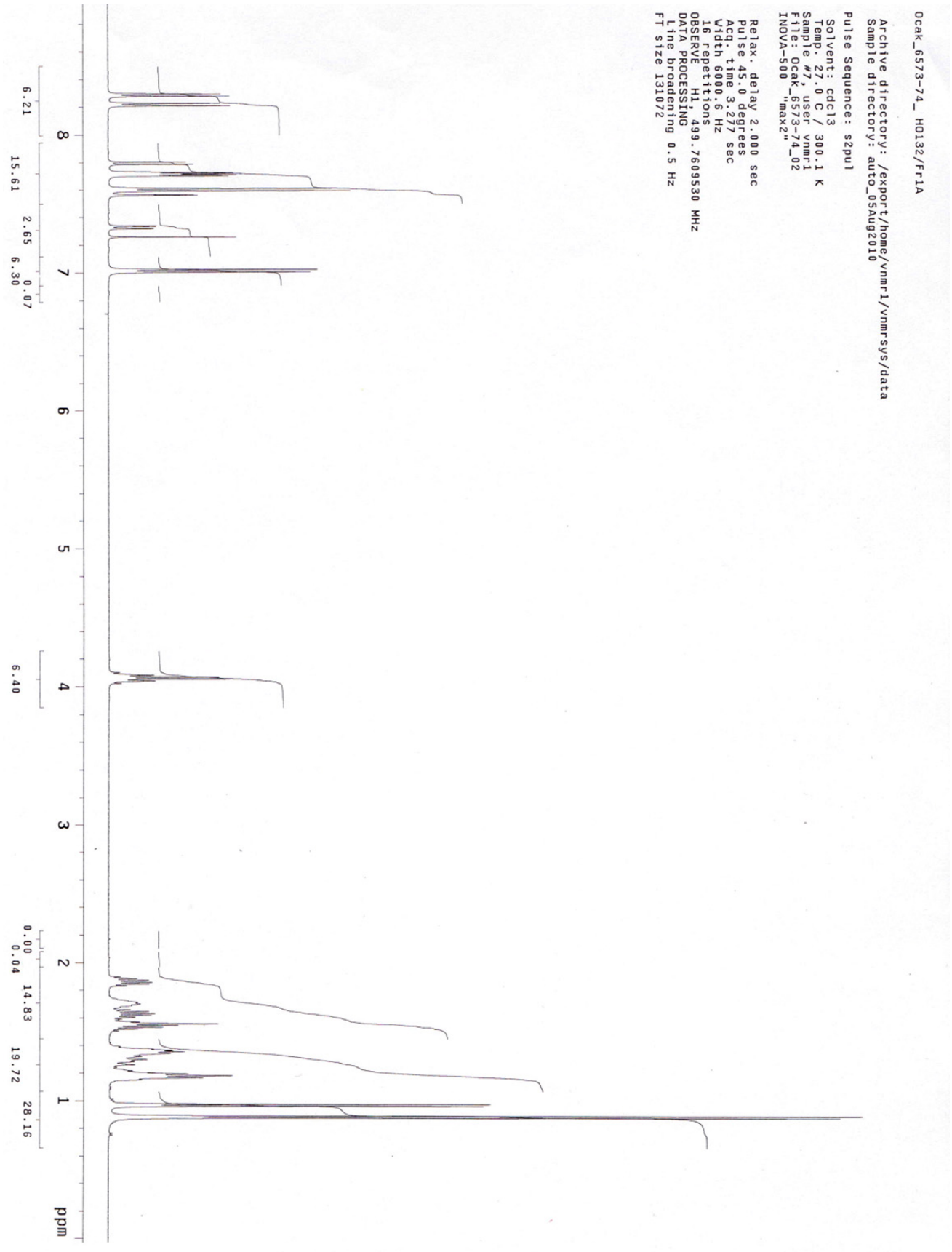


Figure S17. [1]H-NMR spectrum of compound *(S)*-**5**.

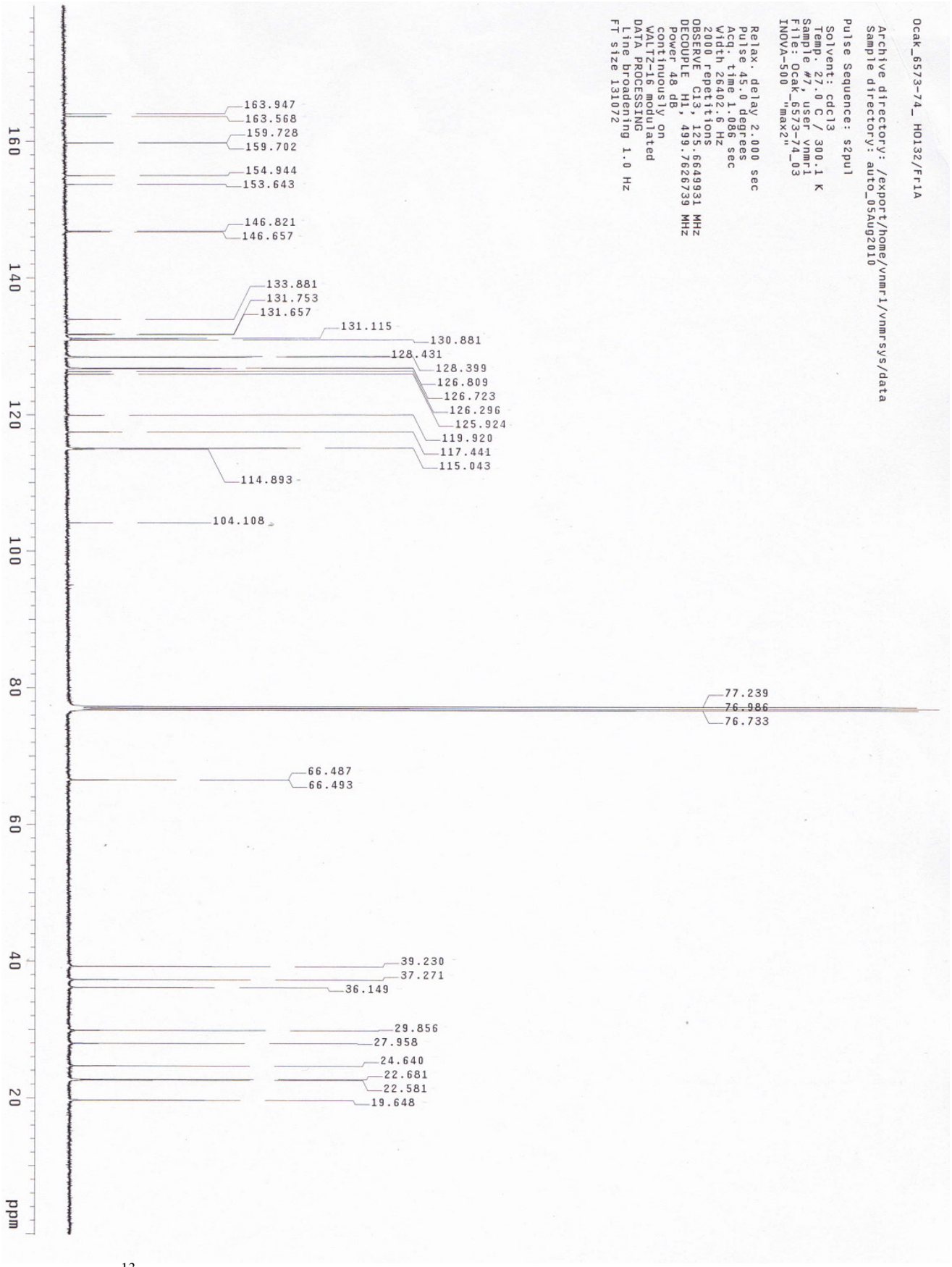
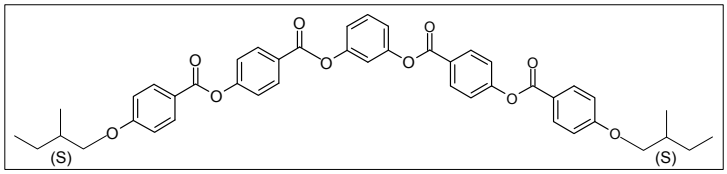


Figure S18. ^{13}C-NMR spectrum of compound *(S)*-**5**.

1,3-Phenylene bis[4-(4-(S)-2-methylbutoxybenzoyloxy)-benzoate]

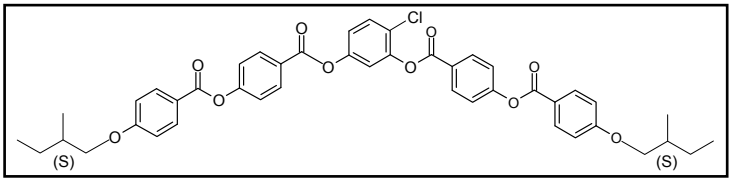
($C_{44}H_{42}O_{10}$; 730.80 g/mol)



(S)-**6:** Yield: 0.54 g (62%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.26 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 8.13 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 7.48 (dd, *J* ≈ 8.3 Hz and *J* ≈ 8.3 Hz, 1 Ar-H), 7.36 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 7.19-7.15 (m; 3 Ar-H), 6.97 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 3.90, 3.82 (2dd, *J* ≈ 9.0 Hz and *J* ≈ 6.0 Hz each; 4H, 2 OCH_2), 1.95-1.82 (m; 2H, 2 CH), 1.65-1.52, 1.40-1.24 (2m; 4H, 2 CH_2), 1.03 (d, *J* ≈ 6.9 Hz; 6H, 2 CH_3), 0.96 (t, *J* ≈ 7.5 Hz; 6H, 2 CH_3). **^{13}C-NMR**: δ (ppm) = 164.17, 163.36 (CO), 163.24, 155.10, 151.36, 127.07, 120.28 (Ar-C), 132.59, 132.03, 130.05, 122.33, 119.92, 116.94, 114.65 (Ar-CH), 73.61 (OCH_2), 35.07 (CH), 26.06 (CH_2), 16.04, 11.15 (CH_3). **MS (EI) :** m/z (%) = 311 (10) [M^+-$C_{25}H_{23}O_6$], 191 (100) [$C_7H_4O_2$], 121 (60) [C_5H_{11}]. **$C_{44}H_{42}O_{10}$** (730.80); Anal. Calc.: C, 72.31; H, 5.79. Found: C, 72.05; H, 5.52%.

4-Chloro-1,3-phenylene bis[4-(4-(S)-2-methylbutoxybenzoyloxy)-benzoate]

($C_{44}H_{41}ClO_{10}$; 765.25 g/mol)

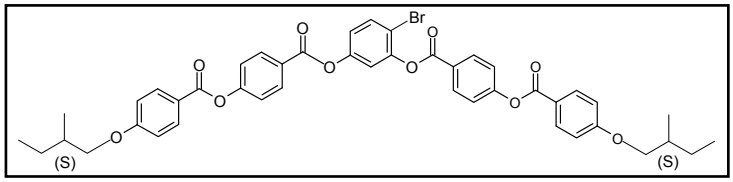


(S)-**7:** Yield: 0.48 g (52%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.29 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.24 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.14 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 7.53 (d, *J* ≈ 8.7 Hz; 1 Ar-H), 7.39 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.35 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.28 (d, *J* ≈ 2.6 Hz; 1 Ar-H), 7.16 (dd, *J* ≈ 8.7 Hz and *J* ≈ 2.6 Hz; 1 Ar-H), 6.97 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 3.89, 3.84 (2dd, *J* ≈ 9.0 Hz and *J* ≈ 6.0 Hz each; 4H, 2 OCH_2), 1.92 -1.82 (m; 2H, 2 CH), 1.65-1.54, 1.36-1.24 (2m; 4H, 2 CH_2), 1.03 (d, *J* ≈ 6.6 Hz; 6H, 2 CH_3), 0.96 (t, *J* ≈ 7.4 Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) = 164.25, 163.99, 163.86 (CO), 163.18, 155.69, 155.61, 149.73, 147.45, 126.25, 125.93, 124.26, 120.87, 120.86 (Ar-C), 132.40, 132.39, 132.07, 131.86, 130.46, 122.20, 122.18, 120.47, 117.84, 114.43 (Ar-CH), 73.14 (OCH_2), 34.61 (CH), 26.06 (CH_2), 16.45,

11.26 (CH_3). **MS (EI) :** m/z (%) = 311 (10) [M^+-$C_{25}H_{22}ClO_6$], 191 (100) [$C_7H_4O_2$], 121 (60) [C_5H_{11}]. **$C_{44}H_{41}ClO_{10}$** (765.25); Anal. Calc.: C, 69.06; H, 5.40. Found: C, 68.76; H, 5.33%.

4- Bromo-1,3-phenylene bis[4-(4-(S)-2-methylbutoxybenzoyloxy)-benzoate]

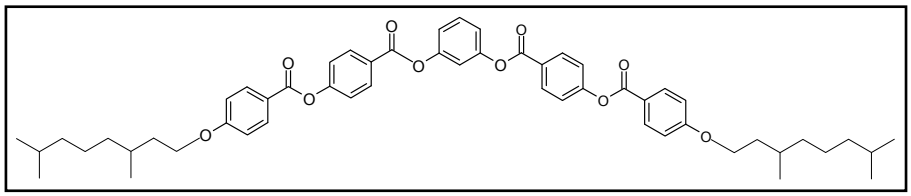
($C_{44}H_{41}BrO_{10}$; 809.70 g/mol)



(S)-**8:** Yield: 0.48 g (49%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.30 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.24 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.15 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 8.11 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.69 (d, *J* ≈ 8.7 Hz; 1 Ar-H), 7.39 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.35 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.28 (d, *J* ≈ 2.6 Hz; 1 Ar-H), 7.10 (dd, *J* ≈ 8.7 Hz and *J* ≈ 2.6 Hz; 1 Ar-H), 6.97 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 3.89, 3.84 (2dd, *J* ≈ 9.0 Hz and *J* ≈ 6.0 Hz each; 4H, 2 OCH_2), 1.98-1.82 (m; 2H, 2 CH), 1.65-1.52, 1.36-1.24 (2m; 4H, 2 CH_2), 1.03 (d, *J* ≈ 6.6 Hz; 6H, 2 CH_3), 0.96 (t, *J* ≈ 7.4 Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) = 164.26, 163.99, 163.79 (CO), 163.18, 155.69, 155.62, 150.48, 148.75, 128.71, 126.24, 126.02, 120.87, 120.85 (Ar-C), 133.44, 132.40, 132.39, 132.09, 131.86, 122.21, 122.18, 120.48, 117.90, 114.44 (Ar-CH), 73.15 (OCH_2), 34.61 (d; CH), 26.06 (CH_2), 16.45, 11.26 (CH_3). **MS (EI) :** m/z (%) = 311 (10) [M^+-$C_{25}H_{22}BrO_6$], 191 (100) [$C_7H_4O_2$], 121 (60) [C_5H_{11}]. **$C_{44}H_{41}BrO_{10}$** (809.70); Anal. Calc.: C, 65.26; H, 5.10. Found: C, 65.11; H, 5.07%.

1,3-Phenylene bis[4-(4-(3,7-dimethyloctyloxy)benzoyloxy)-benzoate]

($C_{54}H_{62}O_{10}$; 871.07 g/mol)

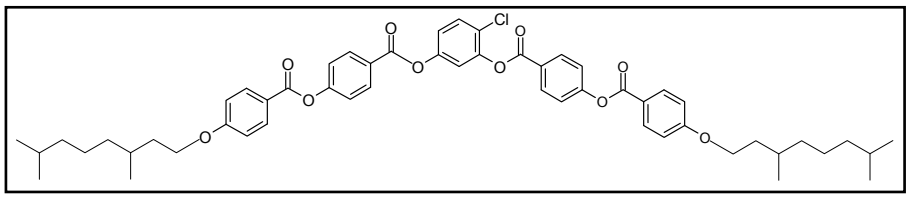


rac-**9:** Yield: 0.59 g (57%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.27 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 8.15 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 7.49 (dd, *J* ≈ 8.2 Hz and *J* ≈ 8.2 Hz; 1 Ar-H), 7.37 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 7.19-7.17 (m; 3 Ar-H), 6.98 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 4.13-4.05 (m; 4H, 2 OCH_2), 1.89-1.85 (m; 2H, 2 CH), 1.69-1.51, 1.36-1.15 (2m; 18H, 2 CH, 8 CH_2), 0.96 (d, *J* ≈ 6.6 Hz;

6H, 2 CH_3), 0.88 (d, $J \approx 6.6$ Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 164.27, 164.06 (CO), 163.87, 155.46, 151.40, 126.60, 120.93 (Ar-C), 132.37, 131.82, 129.85, 122.11, 119.25, 115.78, 114.41 (Ar-CH), 66.72 (OCH_2), 39.19 (CH_2), 37.22, 35.96 (CH), 29.80, 27.94, 24.62 (CH_2), 22.66, 22.56, 19.61 (CH_3). **MS (EI) :** m/z (%) = 381 (7) [M^+-$C_{30}H_{33}O_6$], 261 (100) [$C_7H_4O_2$], 121 (50) [$C_{10}H_{21}$]. **$C_{54}H_{62}O_{10}$** (871.07); Anal. Calc.: C, 74.45; H, 7.17. Found: C, 74.20; H, 7.13%.

4-Chloro-1,3-phenylene bis[4-(4-(3,7-dimethyloctyloxy)benzoyloxy)-benzoate]

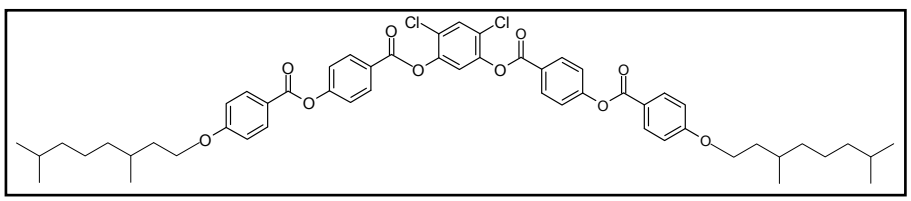
($C_{54}H_{61}ClO_{10}$; 905.52 g/mol)



rac-**10:** Yield: 0.63 g (58%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.30 (d, $J \approx 8.9$ Hz; 2 Ar-H), 8.25 (d, $J \approx 8.9$ Hz; 2 Ar-H), 8.14 (d, $J \approx 8.9$ Hz; 4 Ar-H), 7.55 (d, $J \approx 8.7$ Hz; 1 Ar-H), 7.39 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.34 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.28 (d, $J \approx 2.5$ Hz; 1 Ar-H), 7.16 (dd, $J \approx 8.7$ Hz and $J \approx 2.5$ Hz; 1 Ar-H), 6.97 (d, $J \approx 8.9$ Hz, 4 Ar-H), 4.11-4.05 (m; 4H, 2 OCH_2), 1.88-1.79 (m; 2H, 2 CH), 1.65-1.46, 1.33-1.17 (2m; 18H, 2 CH, 8 CH_2), 0.95 (d, $J \approx$ 6.4 Hz; 6H, 2 CH_3), 0.86 (d, $J \approx 6.6$ Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 164.25, 163.99, 163.85 (CO), 163.18, 155.69, 155.61, 149.73, 147.45, 126.25, 125.93, 124.26, 120.87, 120.86 (Ar-C), 132.40, 132.39, 132.07, 131.86, 130.46, 122.20, 122.18, 120.47, 117.84, 114.43 (Ar-CH), 66.72 (OCH_2), 39.22 (CH_2), 37.25, 35.99 (CH), 29.83, 27.97, 24.65 (CH_2), 22.69, 22.59, 19.64 (CH_3). **MS (EI) :** m/z (%) = 381 (7) [M^+-$C_{30}H_{32}ClO_6$], 261 (100) [$C_7H_4O_2$], 121 (50) [$C_{10}H_{21}$]. **$C_{54}H_{61}ClO_{10}$** (905.52); Anal. Calc.: C, 71.62; H, 6.79. Found: C, 71.85; H, 6.71%.

4,6-Dichloro-1,3-phenylene bis[4-(4-(3,7-dimethyloctyloxy)benzoyloxy)-benzoate]

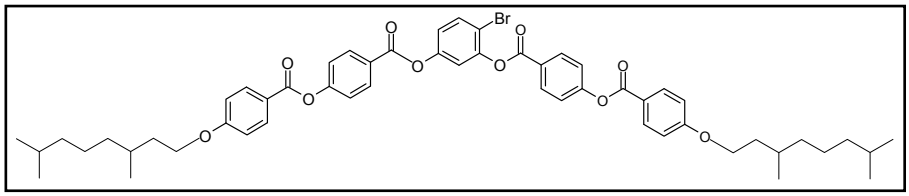
($C_{54}H_{60}Cl_2O_{10}$; 939.96 g/mol)



rac-**11:** Yield: 0.63 g (56%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.28 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 8.14 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 7.63 (s, 2 Ar-H), 7.38 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 6.97 (d, *J* ≈ 8.9 Hz, 4 Ar-H), 4.10-4.06 (m; 4H, 2 OCH_2), 1.88-1.84 (m; 2H, 2 CH), 1.68-1.49, 1.35-1.15 (2m; 18H, 2 CH, 8 CH_2), 0.95 (d, *J* ≈ 6.4 Hz; 6H, 2 CH_3), 0.87 (d, *J* ≈ 6.6 Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 164.08, 163.73, 162.86 (CO), 155.74, 145.98, 125.61, 125.05, 120.88, 119.41 (Ar-C), 132.35, 132.03, 130.71, 122.21, 114.43 (Ar-CH), 66.82 (OCH_2), 39.32 (CH_2), 37.35, 36.09 (CH), 29.97, 28.07, 24.75 (CH_2), 22.78, 22.69, 19.76 (CH_3). **$C_{54}H_{60}Cl_2O_{10}$** (939.96); Anal. Calc.: C, 69.00; H, 6.43. Found: C, 68.75; H, 6.21%.

4- Bromo-1,3-phenylene bis[4-(4-(3,7-dimethyloctyloxy)benzoyloxy)-benzoate]

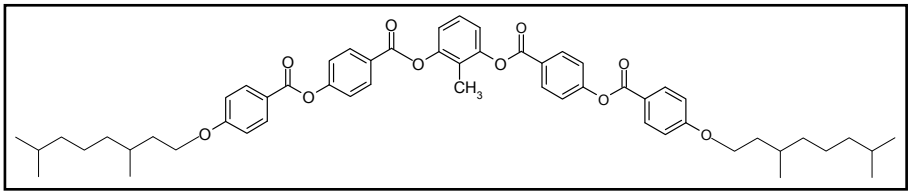
($C_{54}H_{61}BrO_{10}$; 949.97 g/mol)



rac-**12:** Yield: 0.69 g (61%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.30 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.24 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.14 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 7.69 (d, *J* ≈ 8.7 Hz; 1 Ar-H), 7.39 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.35 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.28 (d, *J* ≈ 2.7 Hz; 1 Ar-H), 7.10 (dd, *J* ≈ 8.7 Hz and *J* ≈ 2.7 Hz; 1 Ar-H), 6.97 (d, *J* ≈ 8.7 Hz, 4 Ar-H), 4.11-4.05 (m; 4H, 2 OCH_2), 1.88-1.79 (m; 2H, 2 CH), 1.65-1.46, 1.33-1.17 (2m; 18H, 2 CH, 8 CH_2), 0.95 (d, *J* ≈ 6.2 Hz; 6H, 2 CH_3), 0.86 (d, *J* ≈ 6.4 Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 164.24, 163.81, 163.78 (CO), 163.18, 155.69, 155.61, 150.48, 148.75, 128.71, 126.25, 126.03, 120.91, 120.89 (Ar-C), 133.44, 132.42, 132.41, 132.10, 131.86, 122.21, 122.18, 120.84, 117.90, 114.93 (Ar-CH), 66.73 (OCH_2), 39.20 (CH_2), 37.23, 35.97 (CH), 29.81, 24.95, 24.62 (CH_2), 22.67, 22.57, 19.62 (CH_3). **MS (EI) :** m/z (%) = 381 (7) [M^+- $C_{30}H_{32}BrO_6$], 261 (100) [$C_7H_4O_2$], 121 (50) [$C_{10}H_{21}$]. **$C_{54}H_{61}BrO_{10}$** (949.97); Anal. Calc.: C, 68.27; H, 6.47. Found: C, 68.06; H, 6.45%.

***2-Methyl-1,3-phenylene bis[4-(4-(3,7-dimethyloctyloxy)benzoyloxy)-benzoate*]**

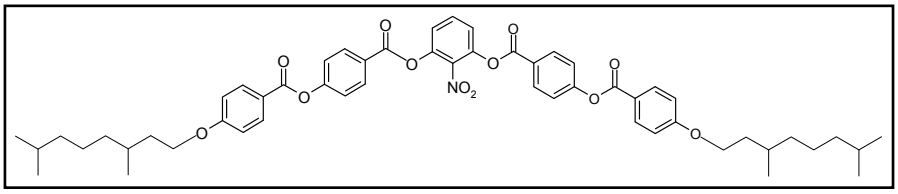
($C_{55}H_{64}O_{10}$; 885.10 g/mol)



rac-**13:** Yield: 0.55 g (52%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.29 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 8.14 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 7.37 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 7.34-7.29 (m, 1 Ar-H), 7.12 (d, *J* ≈ 8.2 Hz; 2 Ar-H), 6.97 (d, *J* ≈ 8.9 Hz, 4 Ar-H), 4.13-4.04 (m; 4H, 2 OCH_2), 2.11 (s, 3H, CH_3), 1.88-1.82 (m; 2H, 2 CH), 1.66-1.49, 1.35-1.15 (2m; 18H, 2 CH, 8 CH_2), 0.95 (d, *J* ≈ 6.4 Hz; 6H, 2 CH_3), 0.87 (d, *J* ≈ 6.6 Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 163.84, 163.79 (CO), 155.47, 150.27, 126.57, 120.98, 119.93 (Ar-C), 132.40, 131.83, 122.17, 114.45 (Ar-CH), 66.80 (OCH_2), 39.28 (CH_2), 37.31, 36.05 (CH), 29.91, 28.02, 24.70 (CH_2), 22.73, 22.64, 19.70, 10.17 (CH_3). **$C_{55}H_{64}O_{10}$** (885.10); Anal. Calc.: C, 74.63; H, 7.28. Found: C, 74.38; H, 7.07%.

2-Nitro-1,3-phenylene bis[4-(4-(3,7-dimethyloctyloxy)benzoyloxy)-benzoate]

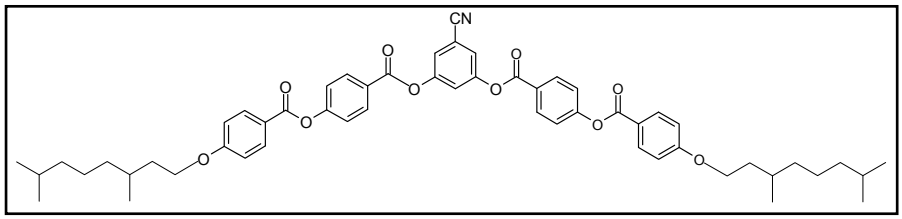
($C_{54}H_{61}NO_{12}$; 916.07 g/mol)



rac-**14:** Yield: 0.49 g (45%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.21 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 8.13 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 7.67-7.63 (m, 1 Ar-H), 7.40 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 7.37 (d, *J* ≈ 8.7 Hz; 4 Ar-H), 6.97 (d, *J* ≈ 8.9 Hz, 4 Ar-H), 4.10-4.04 (m; 4H, 2 OCH_2), 1.88-1.82 (m; 2H, 2 CH), 1.68-1.48, 1.35-1.15 (2m; 18H, 2 CH, 8 CH_2), 0.95 (d, *J* ≈ 6.4 Hz; 6H, 2 CH_3), 0.87 (d, *J* ≈ 6.6 Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 164.12, 163.82, 162.92 (CO), 155.98, 143.74, 125.21, 122.21, 121.71, 120.90 (Ar-C), 132.42, 132.22, 131.91, 122.31, 114.46 (Ar-CH), 66.79 (OCH_2), 39.27 (CH_2), 37.30, 36.04 (CH), 29.91, 28.01, 24.69 (CH_2), 22.72, 22.63, 19.69 (CH_3). **$C_{54}H_{61}NO_{12}$** (916.07); Anal. Calc.: C, 70.80; H, 6.71; N, 1.53. Found: C, 70.52; H, 6.42; N, 1.37%.

5-Cyano-1,3-phenylene bis[4-(4-(3,7-dimethyloctyloxy)benzoyloxy)-benzoate]

($C_{55}H_{61}NO_{10}$; 896.08 g/mol)



rac-**15:** Yield: 0.41 g (38%) of white crystals. **^{1}H-NMR:** δ (ppm) = 8.25 (d, $J \approx 8.7$ Hz; 4 Ar-H), 8.13 (d, $J \approx 8.9$ Hz; 4 Ar-H), 7.51-7.46 (m, 3 Ar-H), 7.38 (d, $J \approx 8.7$ Hz; 4 Ar-H), 6.97 (d, $J \approx 8.9$ Hz, 4 Ar-H), 4.13-4.01 (m; 4H, 2 OCH_2), 1.90-1.82 (m; 2H, 2 CH), 1.69-1.49, 1.35-1.13 (2m; 18H, 2 CH, 8 CH_2), 0.95 (d, $J \approx 6.4$ Hz; 6H, 2 CH_3), 0.87 (d, $J \approx 6.6$ Hz; 12H, 4 CH_3). **^{13}C-NMR:** δ (ppm) = 164.14, 163.85, 163.42 (CO), 155.91, 151.70, 125.64, 122.99, 121.04, 120.85 (Ar-C), 132.48, 132.41, 131.95, 122.32, 117.08, 114.48 (Ar-CH), 114.55 (CN), 66.81 (OCH_2), 39.27 (CH_2), 37.30, 36.04 (CH), 29.91, 28.00, 24.69 (CH_2), 22.72, 22.62, 19.69 (CH_3). **$C_{55}H_{61}NO_{10}$** (896.08); Anal. Calc.: C, 73.72; H, 6.86; N, 1.56. Found: C, 73.47; H, 6.84; N, 1.78%.

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