

Electronic Supporting Information

Development of tilt, biaxiality and polar order in bent-core liquid crystals derived from 4'-hydroxybiphenyl-3-carboxylic acid

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1. Additional Data

1.1 Additional textures

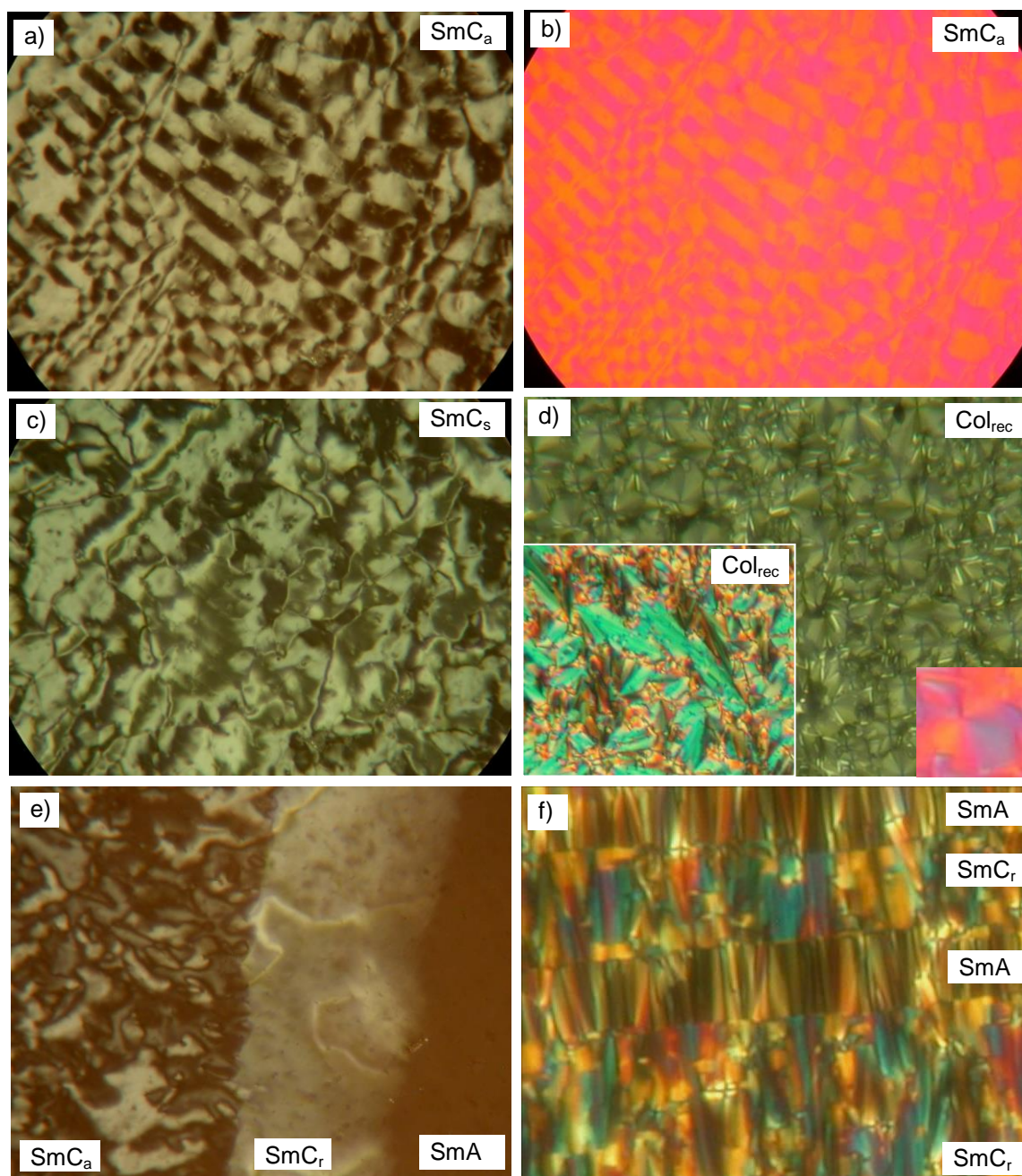


Figure S1. Textures of the LC phases of compound *rac-10* as observed between crossed polarizers (horizontal and vertical) (a-e) between non-treated microscopic glass slides (homeotropic alignment) and (f) in 6 μm ITO cell with planar alignment: (a) SmC_a phase at $T = 148$ °C, (b) with additional λ-retarder plate, indicating the change of the direction of the secondary optical axis in adjacent stripes; (c) SmC_s phase at $T = 144$ °C (same region as (a,b)); (d) Col_{rec} phase at $T = 122$ °C; the inset at the left shows the Col_{rec} phase as grown from a fan-texture (compare with insets in Fig. 3a-d) and the right inset shows the texture with additional λ-retarder plate, indicating an optical positive phase; (e) sample with temperature gradient showing the transition SmA-SmC_r-SmC_a (from left to right; highest temperature at the right) and (f) transition SmC_r-SmA at $T = 153$ °C, observed on heating.

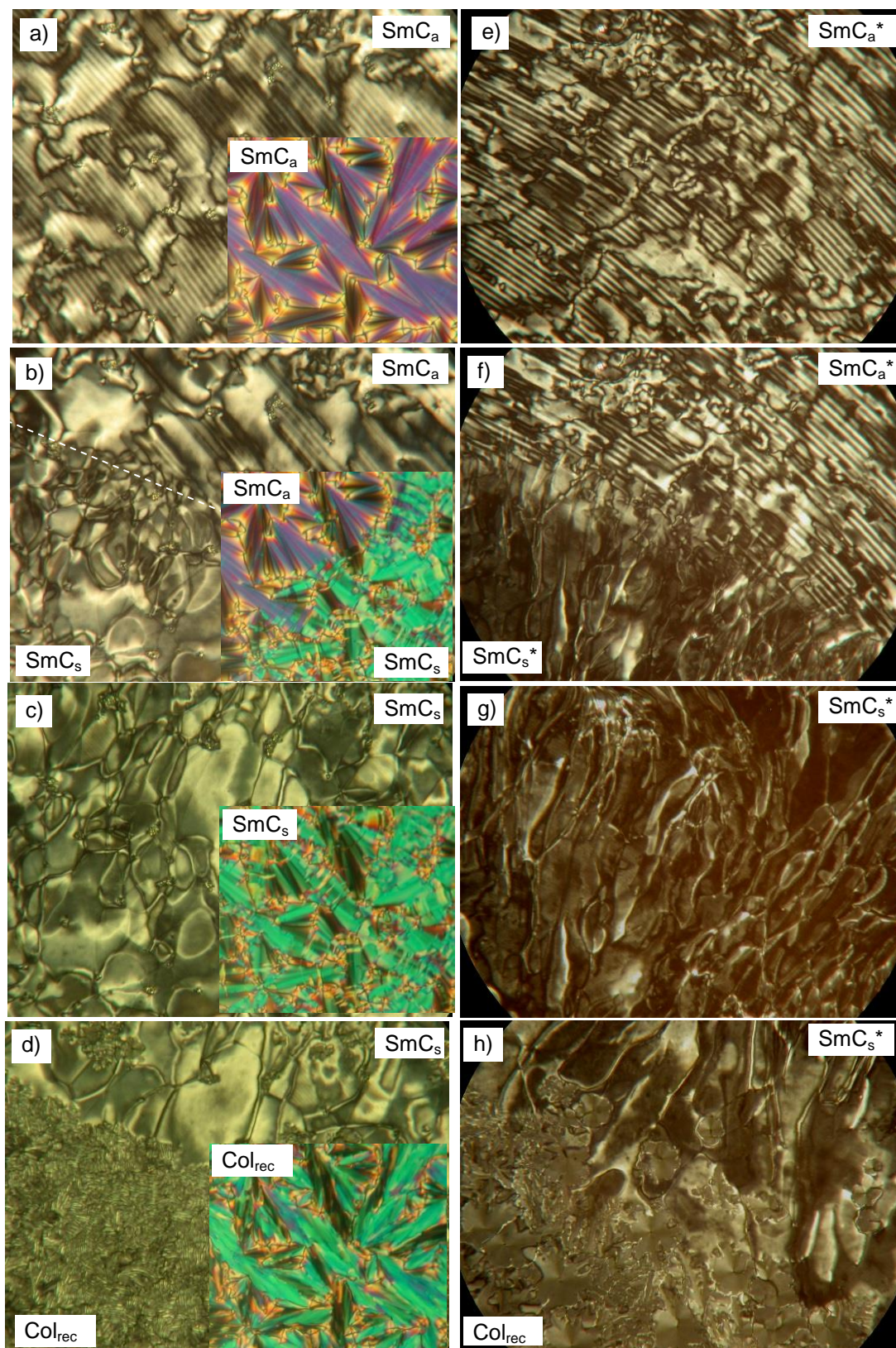


Figure S2. Textures of the LC phases of compound *rac-11* and (*S*)-**11** as observed between crossed polarizers (horizontal and vertical): (a-d) textures of *rac-11* between non-treated microscopic slides (homeotropic alignment); the insets show the corresponding planar fan-like textures as obtained in PI-coated ITO cells with 6 μm cell thickness; (e-h) textures of (*S*)-

11 with homeotropic alignment: (a, e) $\text{SmC}_a/\text{SmC}_a^*$ phase at $T = 151\text{ }^\circ\text{C}$; (b, f) $\text{SmC}_a/\text{SmC}_a^*$ - $\text{SmC}_s/\text{SmC}_s^*$ transition at $T = 146\text{ }^\circ\text{C}$; (c, g) $\text{SmC}_s/\text{SmC}_s^*$ phase at $T = 143\text{ }^\circ\text{C}$; (d) $\text{SmC}_s/\text{SmC}_s^*$ - Col_{rec} transition at $T = 137\text{ }^\circ\text{C}$.

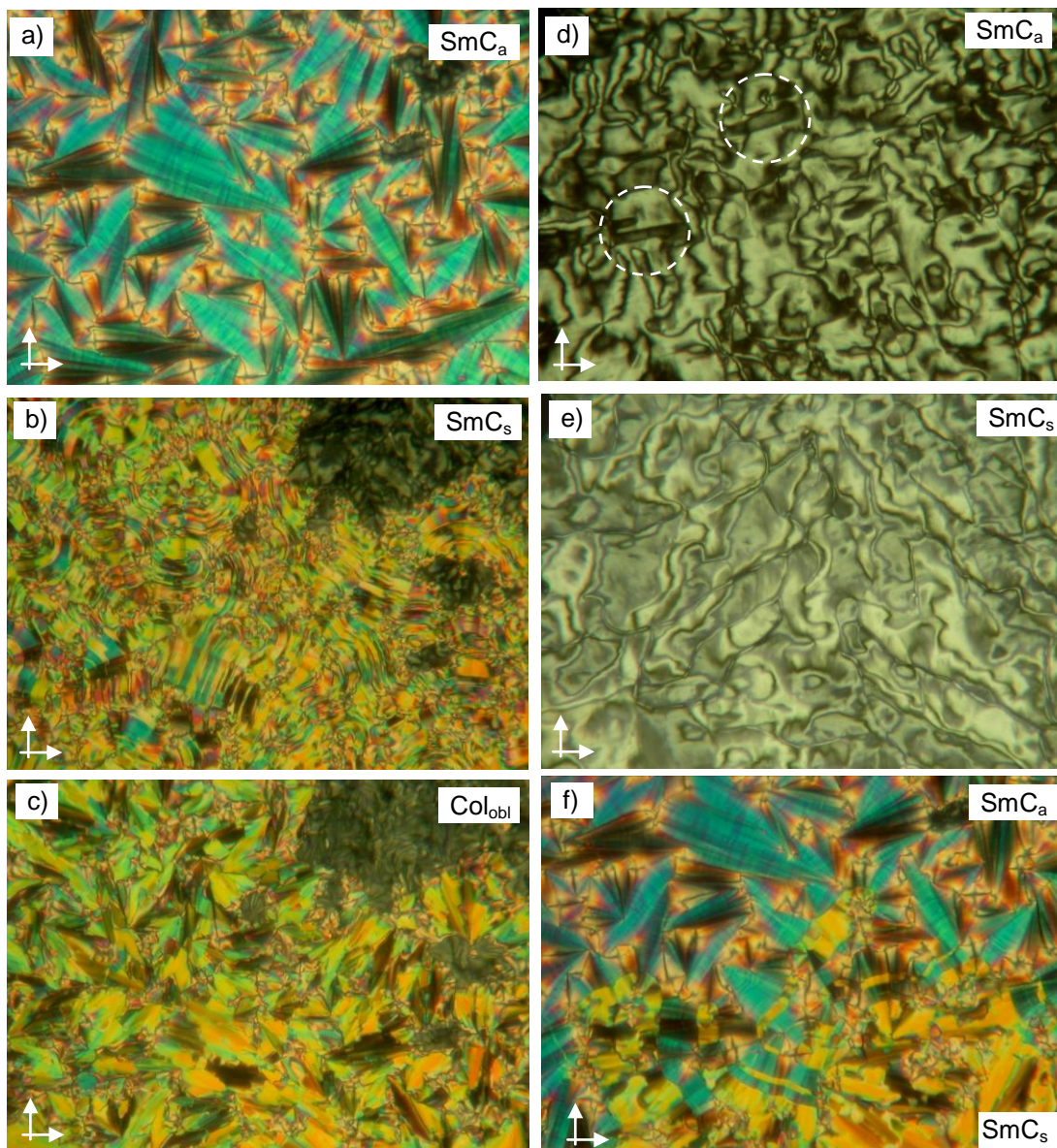


Figure S3. Textures of the LC phases of compound *rac-14* as observed between crossed polarizers (horizontal and vertical): (a-c,f) samples with planar alignment and (d,e) with homeotropic alignment: (a) SmC_a phase at $T = 150\text{ }^\circ\text{C}$; (b) SmC_s phase at $T = 140\text{ }^\circ\text{C}$; (c) Col_{obl} phase at $T = 130\text{ }^\circ\text{C}$; (d) SmC_a phase at $T = 152\text{ }^\circ\text{C}$; the encircled areas indicate residues of the stripe pattern as typically observed for the shorter homologs in this phase; (e) SmC_s phase at $T = 143\text{ }^\circ\text{C}$; series (a)-(d) and (d), (e) were observed on cooling; (f) SmC_s - SmC_a -transition on heating at $T = 145\text{ }^\circ\text{C}$. In planar aligned samples the SmC_a phase has, for the used cell gap, a green fan texture with blue (lower birefringent) stripes (Fig. S3a), which changes to a filament texture with orange/yellow to greenish birefringence color at the transition to SmC_s (Fig. S3b). The filaments fuse to a mosaic-like fan texture at the transition to Col_{obl} (Fig. S3c). The transition of the birefringence colour from bluish green via green to yellow/orange indicates an increase of the birefringence at the transition form SmC_a to SmC_s , as typical for anticlinic to synclinic transitions, whereas no significant birefringence change is observed for the SmC_s - Col_{obl} transition (Fig. S3a-c and f).

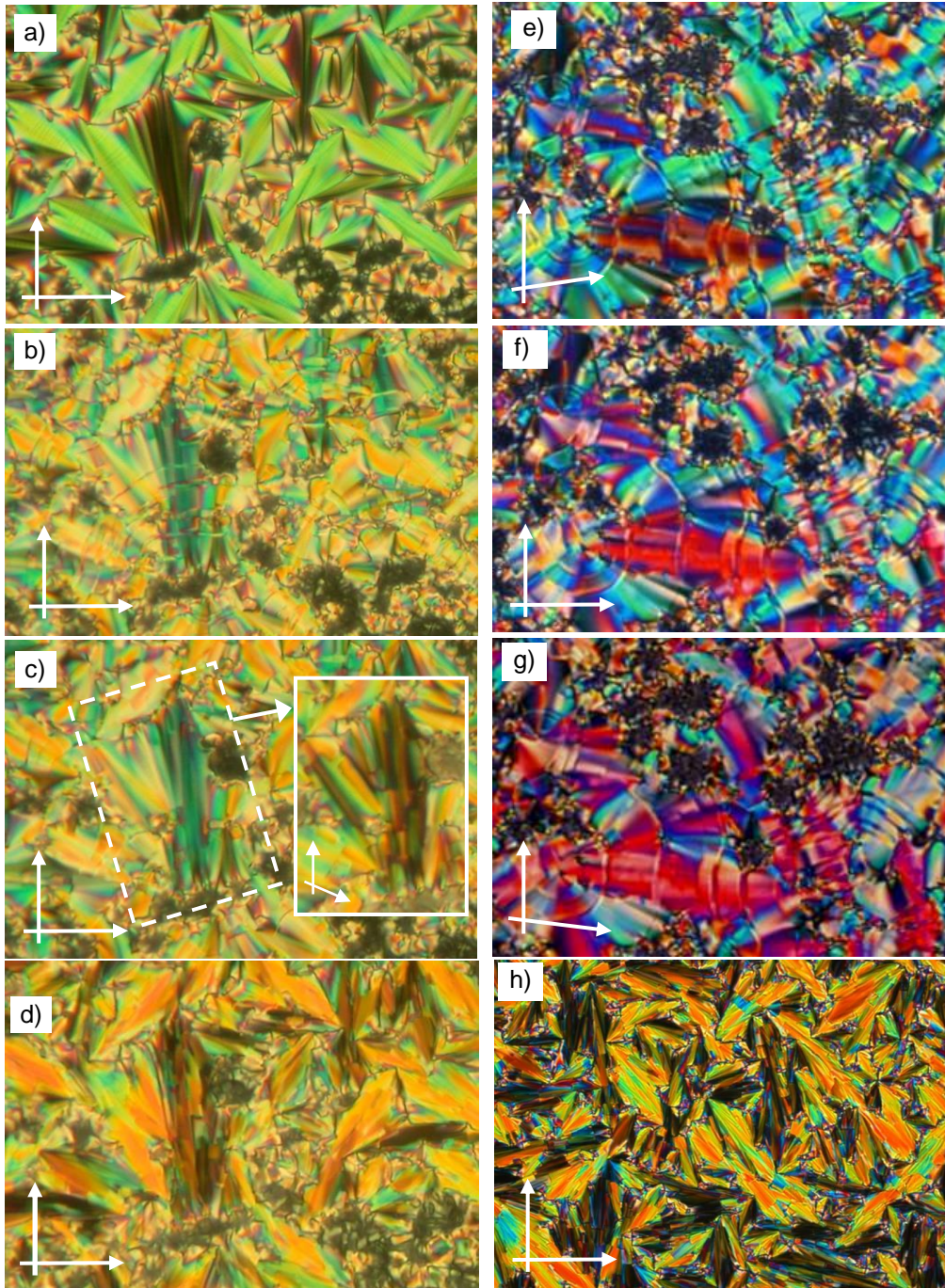


Figure S4. Textures of (*S*)-**11** (a-d) as observed on cooling in a 6 μm PI-coated ITO cell: (a) SmC_a^* phase at $T = 155\text{ }^\circ\text{C}$; (b) SmC_s^* phase at $T = 144\text{ }^\circ\text{C}$ and (c) at $T = 141\text{ }^\circ\text{C}$; the inset shows the texture after uncrossing the polarizers by an angle of 35° ; (d) Col_{rec} phase at $T = 120\text{ }^\circ\text{C}$; (e-h) as observed on cooling in a 5 μm non-coated ITO cell; (e-g) finger-print textures of the SmC_s^* phase at $T = 142\text{ }^\circ\text{C}$ (f) between crossed polarizers and (e, g) between slightly uncrossed polarizers ($\pm 10^\circ$); (h) texture of the columnar phase at $T = 131\text{ }^\circ\text{C}$; the orientation of the dark extinctions with respect to the polarizers indicates an average tilt of $\sim 15^\circ$; orientation of polarizer and analyzer is indicated by arrows.

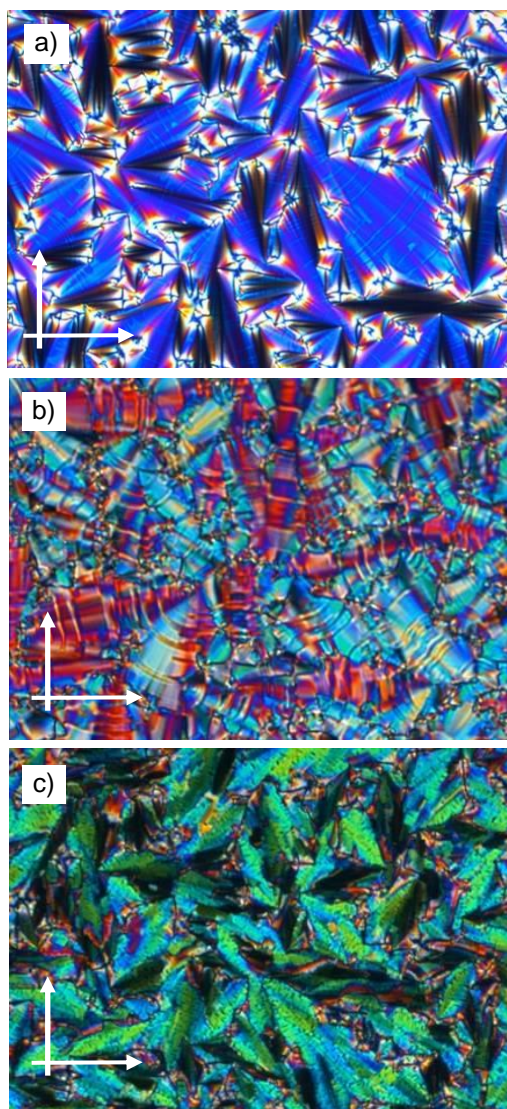


Figure S5. Textures of (*S*)-**12** on cooling in a 5 μm non-coated ITO cell: (a) SmC_aP_R^* phase at $T = 144$ $^\circ\text{C}$; b) SmCs^* phase at $T = 138$ $^\circ\text{C}$; c) Col phase at $T = 128$ $^\circ\text{C}$.

1.2 Additional XRD Data

Table S1. Crystallographic data of compounds *rac-6*, *rac-8*, *rac-10*, *rac-11*, *rac-14* and (*S*)-**11**.^a

Comp.	$T/^\circ\text{C}$	Phase	$2\theta_{\text{obs}}/^\circ$	d_{obs}/nm	hk	$d_{\text{calc}}/\text{nm}$	$d_{\text{obs}}-d_{\text{calc}}$	lattice para.	
<i>rac-6</i>	150	SmA	1.739	5.080	01			$d = 5.08 \text{ nm}$	
			18.92	0.469	diff				
	140	Col _{obl}	1.274	6.934	10;-10	6.937	0.00	$a = 7.14 \text{ nm}$	
			2.034	4.343	01;0-1	4.343	0.00	$b = 4.47 \text{ nm}$	
			2.142	4.124	1-1;-11	4.149	-0.03	$\gamma = 103.8^\circ$	
			2.627	3.363	11;-1-1	3.342	0.02		
			3.965	2.228	1-2;-12	2.228	0.00		
			19.17	0.463	diff				
<i>rac-8</i>	158	SmA	1.804	4.897	01			$d = 4.90 \text{ nm}$	
			18.90	0.470	diff				
	143	Col _{obl}	1.170	7.554	10;-10	7.551	0.00	$a = 7.62 \text{ nm}$	
			1.937	4.561	01;0-1	4.559	0.00	$b = 4.60 \text{ nm}$	
			2.124	4.160	1-1;-11	4.157	0.00	$\gamma = 97.7^\circ$	
			3.885	2.274	02	2.279	-0.01		
			19.09	0.465	diff				
<i>rac-10</i>	140	SmC _s	1.657	5.332	01			$d = 5.33 \text{ nm}$	
			18.89	0.470	diff				
	120	Col _{rec}	1.088	8.119	10	8.390	0.00	$a = 8.50 \text{ nm}$	
			1.753	5.039	01	5.000	0.04	$b = 5.00 \text{ nm}$	
			2.045	4.320	11	4.310	0.01		
			3.614	2.445	02	2.500	-0.05		
			20.09	0.442	diff				
<i>rac-11</i>	140	SmC _s	1.760	5.019	01			$d = 5.02 \text{ nm}$	
			18.38	0.483	diff				
	120	Col _{rec}	1.839	4.804	01	4.800	0.00	$a = 9.57 \text{ nm}$	
			2.058	4.293	11	4.291	0.00	$b = 4.80 \text{ nm}$	
			3.723	2.373	02	2.400	-0.03		
			19.34	0.459	diff				
<i>(S)-11</i>	140	SmC _s	1.772	4.985	01			$d = 4.99 \text{ nm}$	
			18.50	0.480	diff				
	120	Col _{rec}	1.146	7.709	10	7.710	0.00	$a = 7.71 \text{ nm}$	
			1.759	5.022	01	5.020	0.00	$b = 5.02 \text{ nm}$	
			2.089	4.229	11	4.207	0.02		
			3.645	2.424	12	2.387	0.04		
			18.69	0.475	diff				
<i>rac-14</i>	150	SmC _a	1.712	5.160	01			$d = 5.16 \text{ nm}$	
			18.34	0.484	diff				
	120	Col _{obl}	1.107	7.980	10,-10	7.976	0.00	$a = 8.06 \text{ nm}$	
			1.742	5.071	01,0-1	5.066	0.01	$b = 5.12 \text{ nm}$	
			1.925	4.589	1-1,-11	4.578	0.01	$\gamma = 98.3^\circ$	
			3.473	2.544	02,0-2	2.533	0.01		
			3.503	2.522	1-2,-12	2.522	0.00		
			18.64	0.476	diff				

^a (θ_{obs} : experimental scattering angle; d_{obs} : experimental and d_{calc} : calculated d spacing; hk : assigned indices for 2D phases (Col_{rec}, Col_{obl}), Parameter used: Lattice parameters used to calculate d_{calc} with an error of the calculated parameters in the order of 0.1 nm).

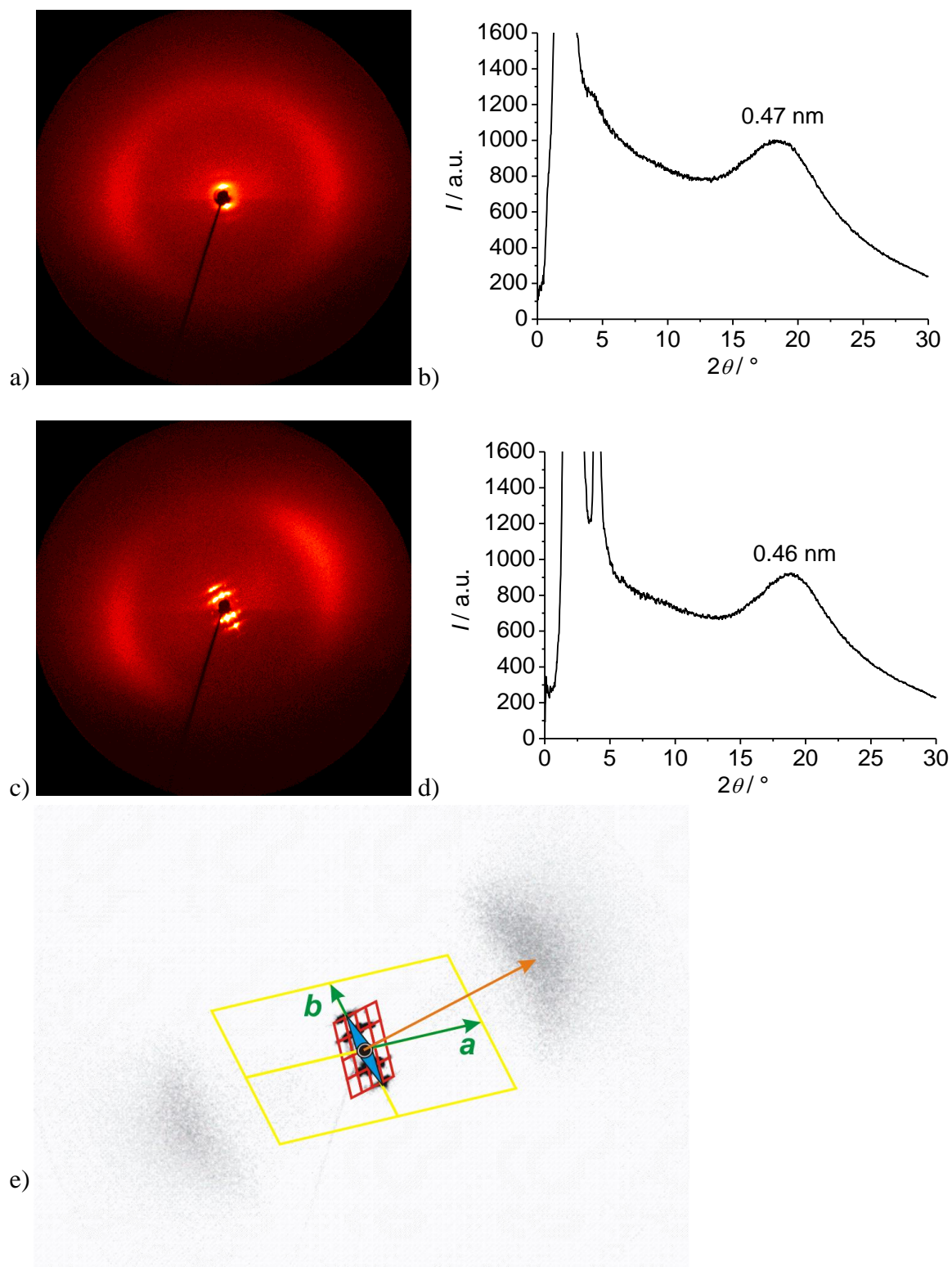


Figure S6. X-ray diffraction patterns of compound *rac-6*: (a) in the SmA phase at $T = 150$ $^\circ\text{C}$; (b) θ -scan of the diffraction pattern; (c) in the Col_{obl} phase at $T = 140$ $^\circ\text{C}$, (d) θ -scan of the diffraction pattern. and (e) 2D XRD pattern at the same temperature with alignment of reciprocal lattice (red) and real lattice (yellow) with respect to the maximum of the diffuse scattering (orange arrow), indicating that the molecules are nearly parallel to the b -axes of the real lattice in the Col_{ob}-phase.

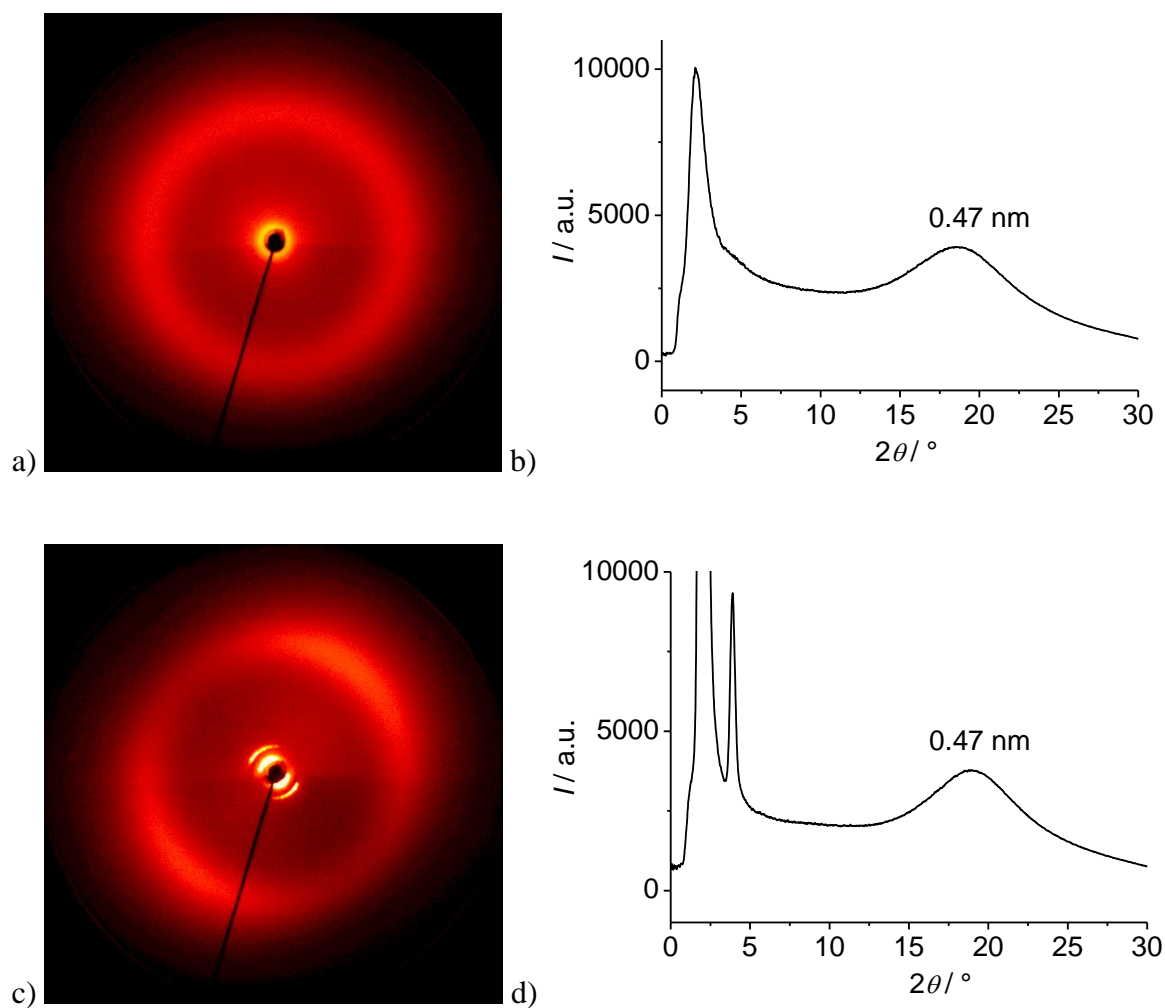


Figure S7. X-ray diffraction patterns of compound *rac-8*: (a) in the SmA phase at $T = 158\text{ }^\circ\text{C}$; (b) θ -scan of the diffraction pattern; (c) in the Col_{obl} phase at $T = 145\text{ }^\circ\text{C}$, (d) θ -scan of the diffraction pattern.

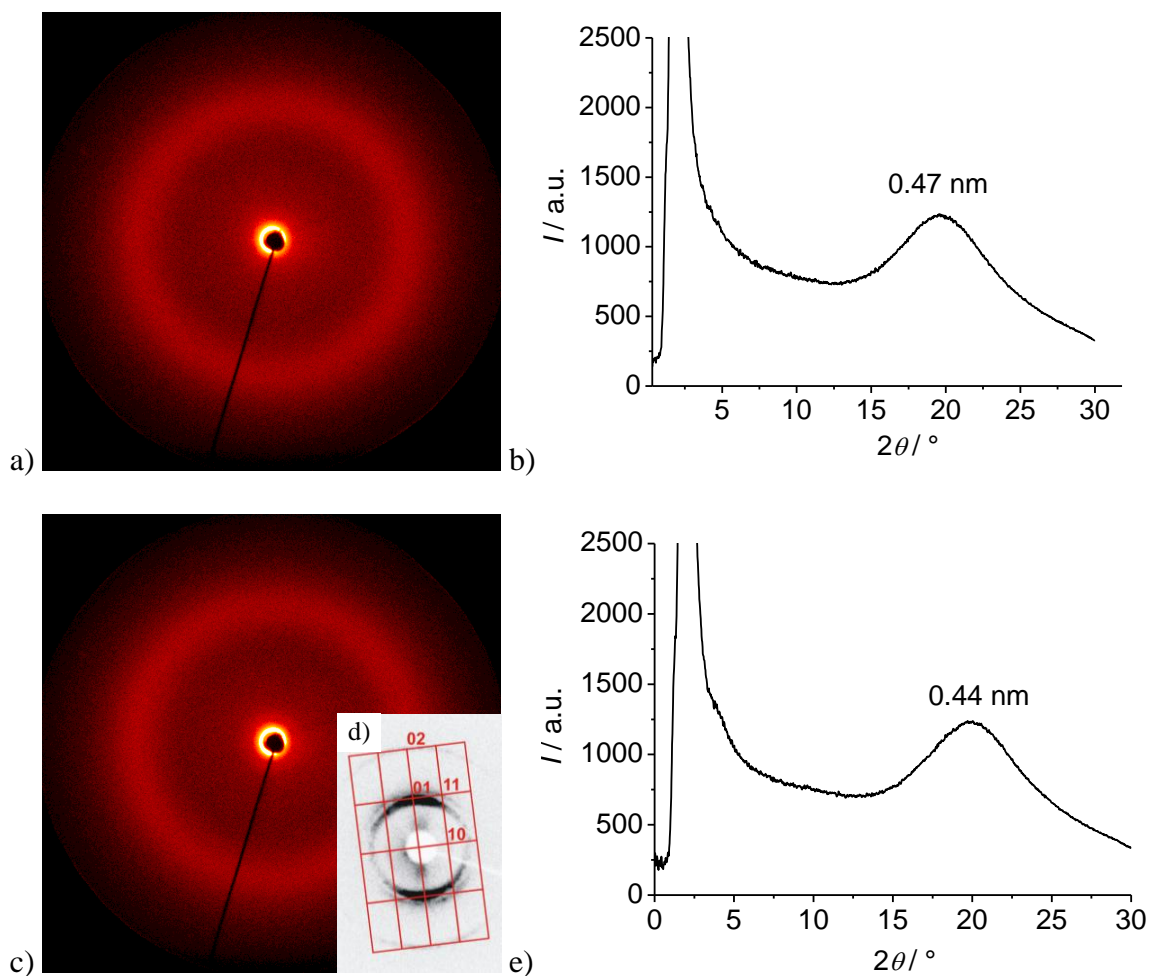


Figure S8. X-ray diffraction patterns of compound *rac-10*: (a) in the SmC_s phase at $T = 140$ °C; (b) θ -scan of the diffraction pattern; (c) in the Col_{rec} phase at $T = 120$ °C; (d) 2D small angle XRD pattern at $T = 120$ °C with indexation to a rectangular $p2mm$ lattice with $a = 8.50$ nm, $b = 5.00$ nm (for details, see Table S1); (e) θ -scan of the diffraction pattern.

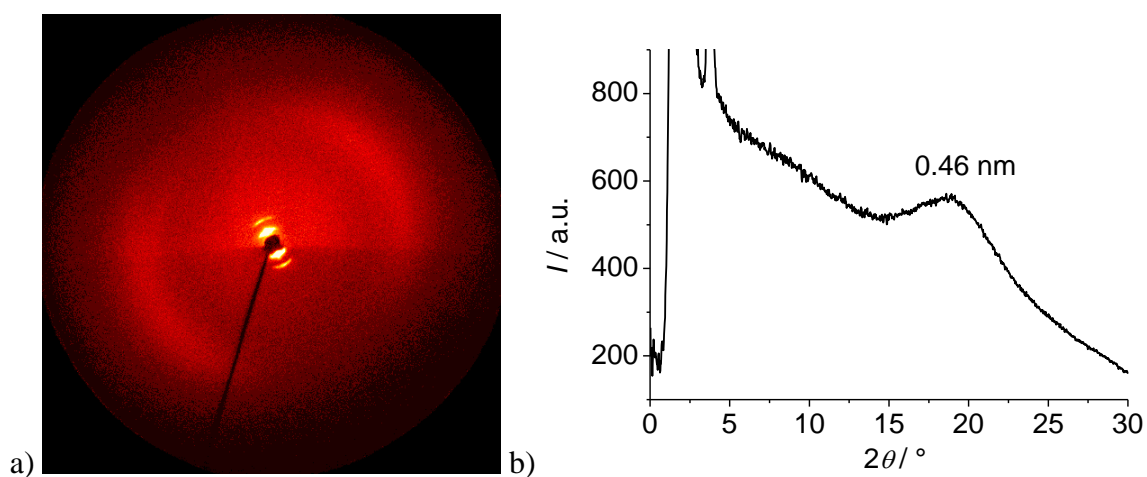


Figure S9. (a) X-ray diffraction patterns of compound *rac-11* in the Col_{rec} phase at $T = 110$ °C; (b) θ -scan of the diffraction pattern.

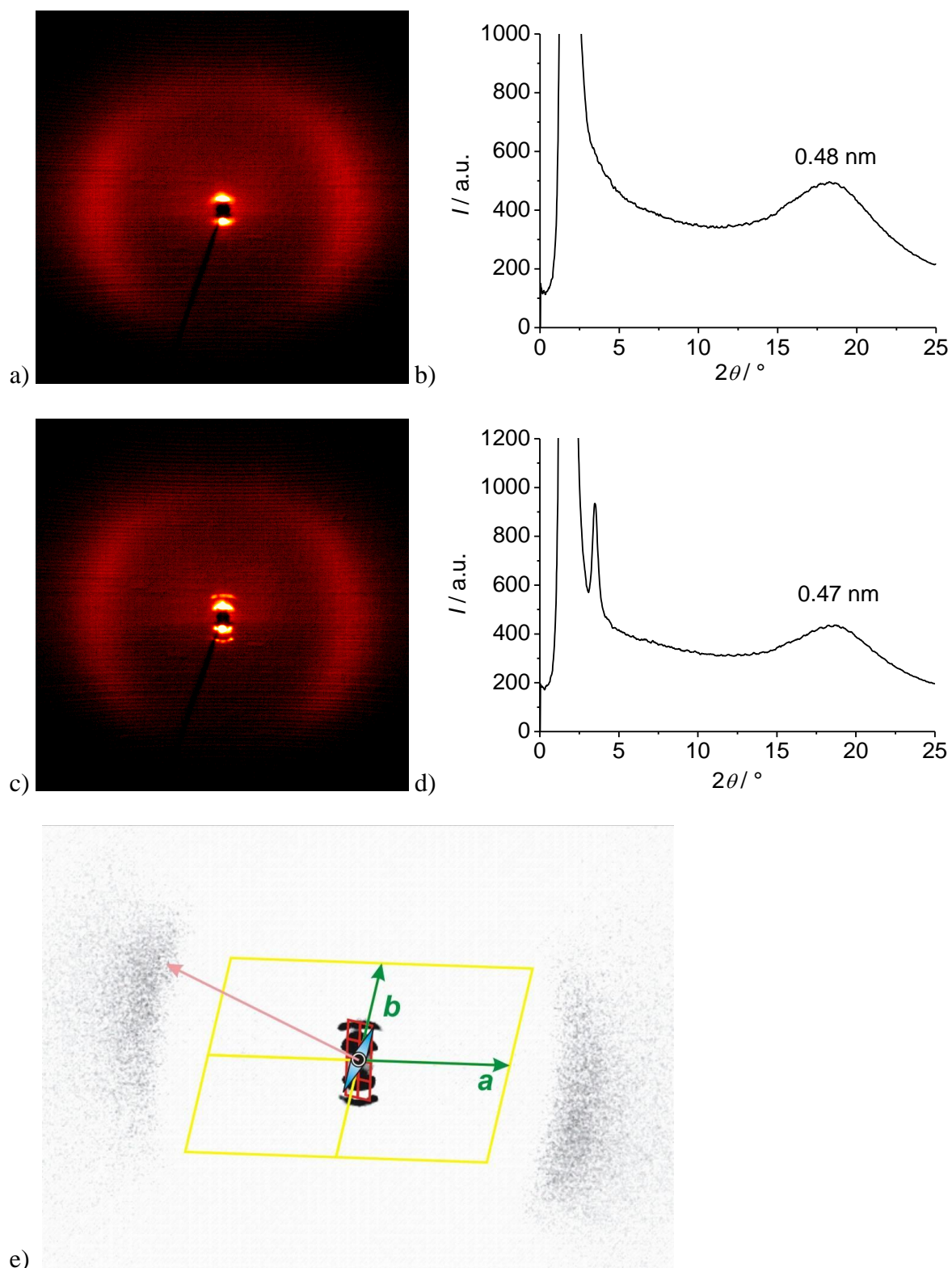


Figure S10. X-ray diffraction patterns of compound *rac-14*: (a) in the SmC_a phase at $T = 150 \text{ }^\circ\text{C}$; (b) θ -scan of the diffraction pattern; (c) in the Col_{obl} phase at $T = 120 \text{ }^\circ\text{C}$, (d) θ -scan of the diffraction pattern and (e) 2D XRD pattern at the same temperature with alignment of reciprocal lattice (red) and real lattice (yellow) with respect to the maximum of the diffuse scattering (orange arrow), indicating that the molecules are tilted about 12° against the b -axes of the real lattice in the Col_{ob} -phase.

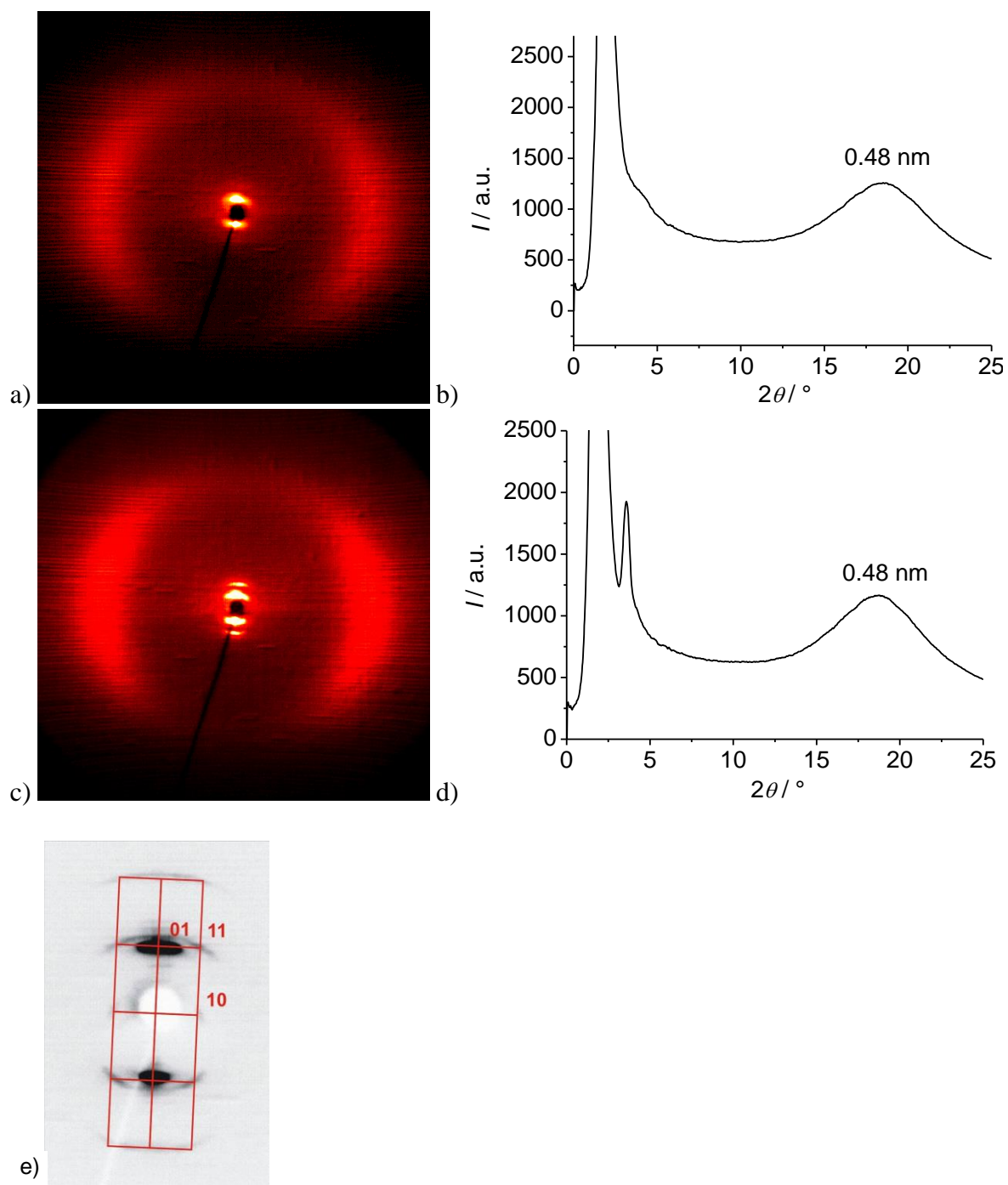


Figure S11. X-ray diffraction patterns of compound (*S*)-**11**: (a) in the SmC_s^* phase at $T = 140$ °C; (b) θ -scan of the diffraction pattern; (c) in the Col_{rec} phase at $T = 120$ °C, (d) θ -scan of the diffraction pattern (e) 2D small angle XRD pattern at $T = 120$ °C with indexation to a rectangular $p2mm$ lattice with $a = 7.7$ nm, $b = 5.0$ nm (for details, see Table S1).

1.3. DSC

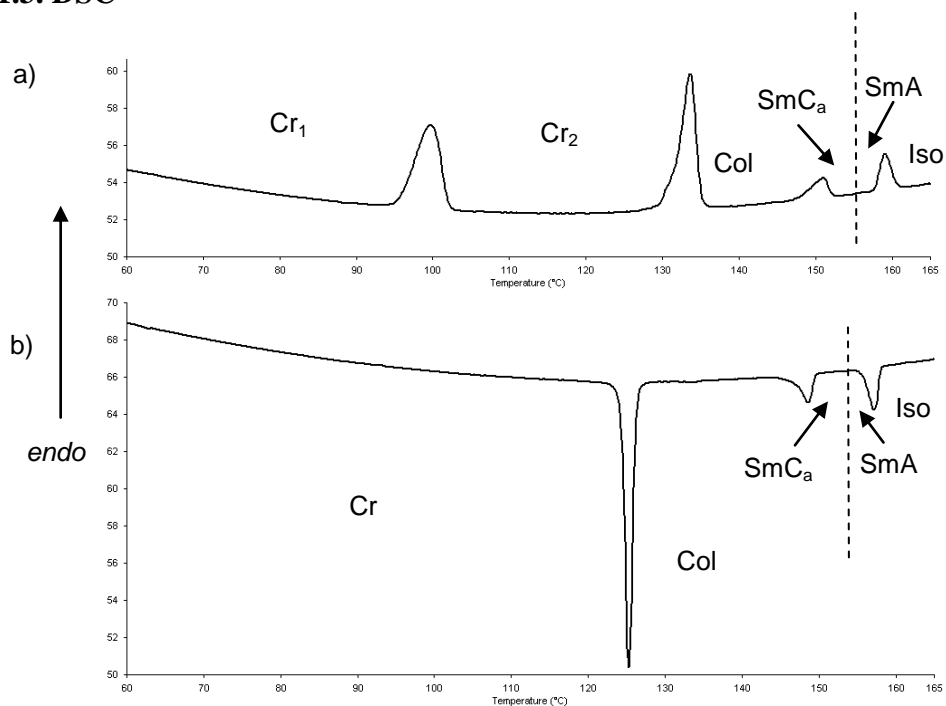


Figure S12. DSC traces of compound *rac*-8: a) on first heating and b) on cooling at 10 K min⁻¹.

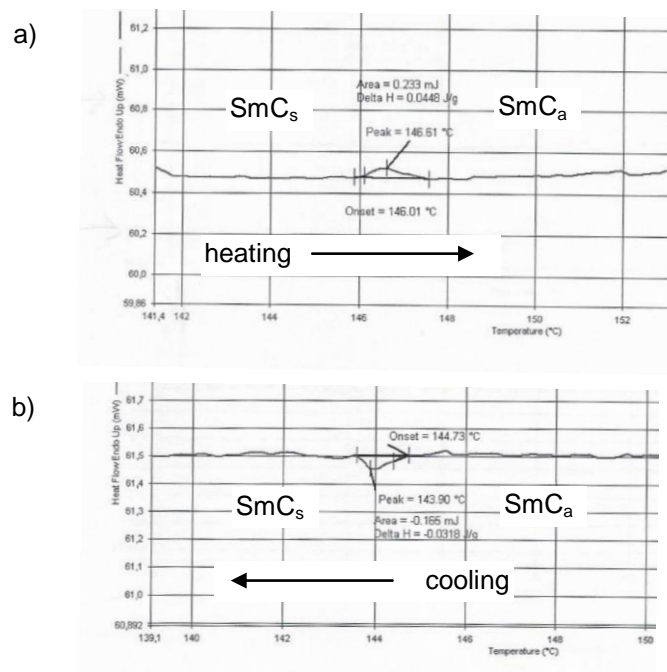


Figure S13. DSC traces of compound (*S*)-11, showing the enlarged region of the SmC_s-SmC_a transition (see Fig. 5), a) on heating and b) on cooling at 10 K min⁻¹.

1.4 Electrooptical investigations

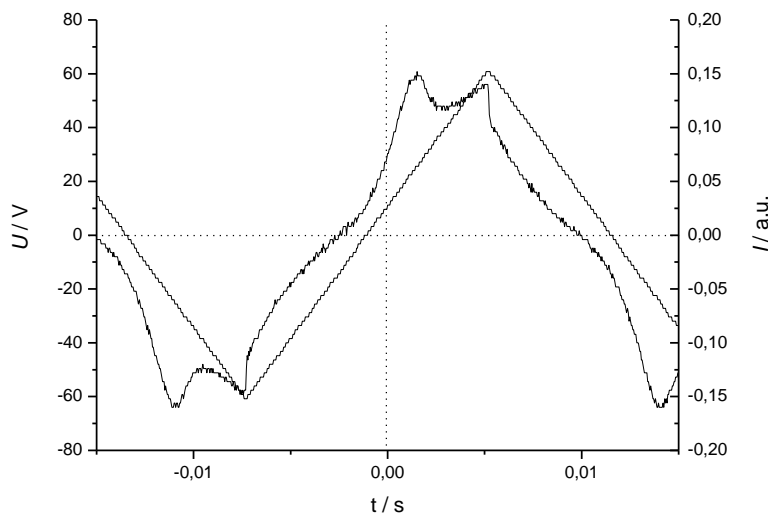


Figure S14. Switching current response obtained for (*S*)-**12** in the SmC_aP_R* phase under a triangular wave field at $T = 150\text{ }^{\circ}\text{C}$ and $U = 120\text{ V}_{pp}$, in a $6\text{ }\mu\text{m}$ PI coated ITO cell ($f = 40\text{ Hz}$).

2. Synthesis and analytical data of compounds

3,7-Dimethyl-1-octanol (Aldrich, 99.0%), (*S*)-(-)- β -citronellol (Aldrich, $\geq 99.0\%$, $[\alpha]_D^{20} -5.3^{\circ}$, neat), methyl 3-bromobenzoate (Alfa Aesar), 4-benzyloxyphenol (ABCR) and tetrakis(triphenylphosphine)palladium(0) (Aldrich, 99.0%), *N,N'*-dicyclohexylcarbodiimide (Merck) and 4-(dimethylamino)pyridine (Merck) were purchased commercially. Solvents were purchased or distilled. 1,2-Dimethoxyethane (Merck), 2-butanone (Merck) and THF (Merck %99) were purchased commercially as dry solvents and were used without further purification. Anhydrous solvent CH_2Cl_2 was dried over di-phosphorus pentoxide (Merck) and distilled under a N_2 atmosphere. Solvents used in the purification step such as crystallization and column chromatography (hexane, ethyl acetate, chloroform, dichloromethane and ethanol) were distilled. Analytical thin-layer chromatography (TLC) was carried out on aluminium plates coated with silica gel 60 F254 (Merck). Column chromatography was performed using silica gel 60 (Merck, pore size 60 \AA , 230-400 mesh particle size).

The optical rotation of (*S*)-3,7-dimethyl-1-octanol (obtained by catalytic hydrogenation of (*S*)-(-)- β -citronellol^{S6}) was found $[\alpha]_{589}^{20} -5.2$ (neat) (Krüss manual polarimeter P1000-LED). The

value of optical rotation was reported by Hameren et al.^{S1} as $[\alpha]_D^{24} = -2.73$ ($c\ 10$, EtOH); a value of $[\alpha]_D^{20} = -3.8$ to -4.8 is given by Takasago Int. Corp.^{S2} The structures of all intermediates were confirmed by NMR and the purity ($> 95\%$) was checked by TLC and indicated by the absence of additional spots based on UV detection and treatment with iodine vapour.

2.1 4'-Benzyloxybiphenyl-3-carboxylic acid A

4'-Benzyloxybiphenyl-3-carboxylic acid^{S3} was obtained by Pd(0)-catalyzed Suzuki cross-coupling reaction^{S4} of methyl 3-bromobenzoate with 4-benzyloxybenzeneboronic acid,

followed by hydrolysis reaction using aqueous KOH and ethanol to yield **A**^{S3}, as described below.

Methyl 4'-benzyloxybiphenyl-3-carboxylate

4-Benzyloxybenzeneboronic acid (4.33 g, 19 mmol) and methyl 3-bromobenzoate (3.44 g, 16 mmol) were dissolved in 1,2-dimethoxyethane (60 ml). To this solution, Pd(PPh₃)₄ (0.92 g, 0.8 mmol) and saturated solution of NaHCO₃ (30 ml) were added and the reaction mixture was refluxed under argon atmosphere for 4h. The end of the reaction was monitored by TLC (hexane: ethyl acetate / 2:1). The solvent was removed under reduced pressure. The mixture was extracted into chloroform (3 x) and the combined organic phases were washed with brine and dried over NaSO₄. The solution was filtered on silicagel to remove the residue of catalyst and the solvent was removed under reduced pressure. The resulting product was purified by crystallization from methanol.

Yield: 65 %, colorless crystals: m.p.: 104 °C, R_f 0.8 (hexane:ethyl acetate / 2:1). ¹H-NMR (400 MHz, CDCl₃): δ = 8.22 (s, broad; 1 Ar-H), 7.96-7.94 (m; 1 Ar-H), 7.73-7.71 (m; 1 Ar-H), 7.54 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 7.48-7.43 (m, 3 Ar-H), 7.40-7.36 (m, 2 Ar-H), 7.34-7.30 (m, 1 Ar-H), 7.05 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 5.11 (s; 2H, OCH₂), 3.92 (s; 3H, OCH₃).

4'-Benzyloxybiphenyl-3-carboxylic acid A^{S3}

Methyl 4'-benzyloxybiphenyl-3-carboxylate (4.13 g, 13 mmol) was dissolved in ethanol (100 ml) and then potassium hydroxide solution (20 ml, 10 wt. % in H₂O) was added to this solution. The reaction mixture was refluxed for 2h. The end of the reaction was monitored by TLC (hexane: ethyl acetate / 2:1). The mixture was poured into 100 ml water and then the aqueous solution was acidified to pH 1 by adding 1 N HCl. The obtained precipitate was filtered, washed with water and purified by crystallization from ethanol.

Yield: 84 %, colorless crystals: m.p.: 226 °C, R_f 0.1 (hexane:ethyl acetate / 2:1). ¹H-NMR (400 MHz, CDCl₃): δ = 8.27 (s, broad; 1 Ar-H), 8.01-7.99 (m; 1 Ar-H), 7.78-7.76 (m; 1 Ar-H), 7.55 (d, *J* ≈ 8.8; 2 Ar-H), 7.52-7.48 (m; 1 Ar-H), 7.45-7.32 (m; 5 Ar-H), 7.06 (d, *J* ≈ 8.8; 2 Ar-H), 5.11 (s; 2H, OCH₂). MS (EI): m/z (%) = 304 (70) [M⁺], 91 (100) [C₇H₇].

2.2 4-(3,7-Dimethyloctyloxy)phenyl 4-hydroxybenzoates *rac*-B and (*S*)-B

In the first step of the synthesis of *rac*-**B** and (*S*)-**B**, 4-benzyloxyphenol was alkylated with 3,7-dimethyloctylosylate^{S5} (prepared from the commercially available 3,7-dimethyl-1-octanol by tosylation^{S6}) and (*S*)-3,7-dimethyloctyl-1-bromide (prepared from (*S*)-3,7-dimethyl-1-octanol by reaction with conc. aqu. HBr/conc. H₂SO₄^{S7}), respectively, followed by hydrogenolytic debenzoylation (H₂, 10 % Pd/C in THF). Esterification of the obtained 4-alkyloxyphenols^{S8,S9} with 4-benzyloxybenzoic acid^{S10} using *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP)^{S11}, followed by hydrogenolytic deprotection of the benzyl group^{S12} leads to final compounds *rac*-**B**^{S13} and (*S*)-**B**. (*S*)-3,7-dimethyl-1-octanol was obtained from (*S*)-(-)-β-citronellol by catalytic hydrogenation (H₂, Pd/C in MeOH) as described previously^{S7}.

4-(3,7-Dimethyloctyloxy)phenyl benzyl ether

The mixture of 3,7-dimethyloctylosylate (7.81 g, 25 mmol), 4-benzyloxyphenol (4.60 g, 23 mmol) and K₂CO₃ (3.45 g, 25 mmol) in 2-butanone (50 ml) was refluxed under argon atmosphere for 5h, and the end of reaction was monitored by TLC (hexane:ethyl acetate /

5:1). The resulting mixture was filtered on silica gel and washed with CHCl_3 . After removing the volatile components in vacuo, the crude product was purified by column chromatography on silica gel eluting with hexane:ethyl acetate / 20:1

Yield: 80 %, light yellow viscous liquid, R_f 0.8 (hexane:ethyl acetate / 5:1). **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ = 7.44-7.33 (m; 5 Ar-H), 6.89 (d, $J \approx 9.1$ Hz; 2 Ar-H), 6.82 (d, $J \approx 9.1$ Hz; 2 Ar-H), 5.01 (s; 2H, OCH_2), 3.96-3.90 (m; 2H, OCH_2), 1.88-1.83 (m; 1H, CH), 1.70-1.49, 1.35-1.13 (2m; 9H, CH, 4 CH_2), 0.93 (d, $J \approx 6.4$ Hz; 3H, CH_3), 0.87 (d, $J \approx 6.4$ Hz; 6H, 2 CH_3). **$^{13}\text{C-NMR}$** (125 MHz, CDCl_3): δ = 153.55, 152.88, 137.39 (Ar-C), 128.47, 127.78, 127.41, 115.87, 115.45 (Ar-CH), 70.80, 67.02 (OCH_2), 39.30, 37.36, 36.40, 24.69 (CH_2), 29.93, 28.04 (CH), 22.72, 22.62, 19.72 (CH_3).

(S)-4-(3,7-Dimethyloctyloxy)phenyl benzyl ether

This compound was prepared similarly to 4-(3,7-dimethyloctyloxy)phenyl benzyl ether from (S)-3,7-dimethyloctyl-1-bromide and 4-benzyloxyphenol.

Yield: 84 %, light yellow viscous liquid, R_f 0.8 (hexane:ethyl acetate / 5:1). **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ = 7.45-7.33 (m; 5 Ar-H), 6.92 (d, $J \approx 9.1$ Hz; 2 Ar-H), 6.85 (d, $J \approx 9.1$ Hz; 2 Ar-H), 5.03 (s; 2H, OCH_2), 3.99-3.91 (m; 2H, OCH_2), 1.88-1.82 (m; 1H, CH), 1.75-1.54, 1.39-1.15 (2m; 9H, CH, 4 CH_2), 0.96 (d, $J \approx 6.6$ Hz; 3H, CH_3), 0.90 (d, $J \approx 6.6$ Hz; 6H, 2 CH_3).

4-(3,7-Dimethyloctyloxy)phenol^{S8}

The mixture of 4-(3,7-dimethyloctyloxy)phenyl benzyl ether (3.40 g, 10 mmol) and Pd/C-10% (0.28 g) in THF (80 ml) was heated in argon-flushed vessel of autoclave with continuous stirring under 5 bar pressure of H_2 gas for 12h. The end of reaction was monitored by TLC (chloroform). The resulting mixture was filtered on silica gel to remove the residue of catalyst and washed with THF. After removing the solvent in vacuo, the crude product was purified by column chromatography on silica gel, eluting with chloroform.

Yield: 80 %, light yellow viscous liquid, R_f 0.4 (CHCl_3). **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ = 6.77 (d, $J \approx 8.9$ Hz; 2 Ar-H), 6.73 (d, $J \approx 8.9$ Hz; 2 Ar-H), 3.96-3.88 (m; 2H, OCH_2), 1.85-1.68 (m; 1H, CH), 1.66-1.45, 1.39-1.06 (2m; 9H, CH, 4 CH_2), 0.91 (d, $J \approx 6.6$ Hz; 3H, CH_3), 0.86 (d, $J \approx 6.6$ Hz; 6H, 2 CH_3).

(S)-4-(3,7-Dimethyloctyloxy)phenol^{S9}

This compound was prepared similarly to 4-(3,7-dimethyloctyloxy)phenol from (S)-4-(3,7-dimethyloctyloxy)phenyl benzyl ether.

Yield: 75 %, light yellow viscous liquid, R_f 0.4 (CHCl_3). **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ = 6.77 (d, $J \approx 8.9$ Hz; 2 Ar-H), 6.72 (d, $J \approx 8.9$ Hz; 2 Ar-H), 3.98-3.87 (m; 2H, OCH_2), 1.83-1.68 (m; 1H, CH), 1.66-1.48, 1.38-1.06 (2m; 9H, CH, 4 CH_2), 0.90 (d, $J \approx 6.6$ Hz; 3H, CH_3), 0.86 (d, $J \approx 6.6$ Hz; 6H, 2 CH_3).

4-(3,7-Dimethyloctyloxy)phenyl 4-benzyloxybenzoate

To a mixture of 4-(3,7-dimethyloctyloxy)phenol (5.50 g, 22 mmol) and 4-benzyloxybenzoic acid (4.79 g, 21 mmol) in dry CH_2Cl_2 (100 ml) *N,N'*-dicyclohexylcarbodiimide (DCC) (5.36 g, 26 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.23 g, 1.9 mmol) were added and this mixture was stirred for 24h at room temperature under argon atmosphere. The end of reaction was monitored by TLC (hexane:ethyl acetate / 5:1) The reaction mixture was filtered on silica

gel with CH₂Cl₂. After removing the solvent in vacuo, the crude product was purified by column chromatography on silica gel, eluting with chloroform and then crystallization from a mixture of chloroform and ethanol.

Yield: 70 %; colorless crystals, *T*/°C: Cr 105 (SmA 84) Iso. R_f 0.6 (hexane:ethyl acetate / 5:1). ¹H-NMR (400 MHz, CDCl₃): δ = 8.13 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.44-7.33 (m; 5 Ar-H), 7.08 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.03 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.90 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 5.14 (s; 2H, OCH₂), 3.99-3.95 (m; 2H, OCH₂), 1.86-1.76 (m; 1H, CH), 1.72-1.47, 1.38-1.12 (2m; 9H, CH, 4 CH₂), 0.93 (d, *J* ≈ 6.8 Hz; 3H, CH₃), 0.86 (d, *J* ≈ 6.8 Hz; 6H, 2 CH₃). ¹³C-NMR (125 MHz, CDCl₃): δ = 165.13 (COO), 162.91, 156.77, 144.38, 136.18, 122.32 (Ar-C), 132.20, 128.67, 128.20, 127.43, 122.39, 115.11, 114.67 (Ar-CH), 70.22, 66.84 (OCH₂), 39.30, 37.34, 36.30, 24.70 (CH₂), 29.94, 28.02 (CH), 22.73, 22.63, 19.71 (CH₃).

***(S)*-4-(3,7-Dimethyloctyloxy)phenyl 4-benzyloxybenzoate**

This compound was prepared similarly to 4-(3,7-dimethyloctyloxy)phenyl 4-benzyloxybenzoate from (*S*)-4-(3,7-dimethyloctyloxy)phenol and 4-benzyloxybenzoic acid.

Yield: 75 %; colorless crystals, *T*/°C: Cr 106 (SmA 83) Iso. R_f 0.6 (hexane:ethyl acetate / 5:1) ¹H-NMR (400 MHz, CDCl₃): δ = 8.13 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.44-7.34 (m; 5 Ar-H), 7.07 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.03 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 6.90 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 5.14 (s; 2H, OCH₂), 4.01-3.92 (m; 2H, OCH₂), 1.84-1.78 (m; 1H, CH), 1.73-1.48, 1.35-1.12 (2m; 9H, CH, 4 CH₂), 0.93 (d, *J* ≈ 6.6 Hz; 3H, CH₃), 0.86 (d, *J* ≈ 6.6 Hz; 6H, 2 CH₃).

4-(3,7-Dimethyloctyloxy)phenyl 4-hydroxybenzoate *rac*-B^{S13}

A mixture of 4-(3,7-dimethyloctyloxy)phenyl 4-benzyloxybenzoate (4.60 g, 10 mmol) and Pd/C-10% (0.28 g) in THF (80 ml) was heated in argon-flushed vessel of autoclave with continuous stirring under 5 bar pressure of H₂ gas for 12h. The end of reaction was monitored by TLC (chloroform). The resulting mixture was filtered on silica gel to remove the residue of catalyst and washed with THF. After removing the solvent in vacuo, the crude product was purified by column chromatography on silica gel, eluting with dichloromethane and then crystallization from a mixture of dichloromethane and ethanol.

Yield: 75 %; colorless crystals, m.p. 161 °C, R_f 0.2 (CHCl₃). ¹H-NMR (400 MHz, CDCl₃): δ = 8.08 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.08 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.90 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.87 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 5.56 (broad s; H, OH), 4.02-3.93 (m; 2H, OCH₂), 1.86-1.77 (m; 1H, CH), 1.65-1.47, 1.37-1.14 (2m; 9H, CH, 4 CH₂), 0.93 (d, *J* ≈ 6.8 Hz; 3H, CH₃), 0.86 (d, *J* ≈ 6.8 Hz; 6H, 2 CH₃). ¹³C-NMR (125 MHz, CDCl₃): δ = 165.27 (COO), 160.20, 156.82, 144.34, 122.25 (Ar-C), 132.51, 122.39, 115.36, 115.16 (Ar-CH), 66.88 (OCH₂), 39.30, 37.34, 36.29, 24.69 (CH₂), 29.95, 28.01 (CH), 22.73, 22.63, 19.70 (CH₃). MS (EI): m/z (%) = 370 (95) [M⁺], 250 (98) [M⁺ - C₇H₄O₂], 121 (100) [C₇H₅O₂], 93 (48) [C₆H₅O].

***(S)*-4-(3,7-Dimethyloctyloxy)phenyl 4-hydroxybenzoate (*S*)-B**

This compound was prepared similarly to 4-(3,7-dimethyloctyloxy)phenyl 4-hydroxybenzoate (*rac*-B) from (*S*)-4-(3,7-dimethyloctyloxy)phenyl 4-benzyloxybenzoate.

Yield: 80 %; colorless crystals, m.p. 161 °C, R_f 0.2 (CHCl₃). ¹H-NMR (400 MHz, CDCl₃): δ = 8.08 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.07 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 6.89 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 6.88

(d, $J \approx 8.7$ Hz; 2 Ar-H), 5.43 (broad s; H, OH), 4.00-3.91 (m; 2H, OCH₂), 1.83-1.77 (m; 1H, CH), 1.67-1.47, 1.34-1.10 (2m; 9H, CH, 4 CH₂), 0.92 (d, $J \approx 6.6$ Hz; 3H, CH₃), 0.85 (d, $J \approx 6.6$ Hz; 6H, 2 CH₃). ¹³C-NMR (125 MHz, CDCl₃): δ = 165.27 (COO), 160.16, 156.82, 144.28, 122.25 (Ar-C), 132.56, 122.43, 115.35, 115.09 (Ar-CH), 66.74 (OCH₂), 39.25, 37.29, 36.22, 24.67 (CH₂), 29.84, 27.98 (CH), 22.72, 22.62, 19.65 (CH₃).

2.3 4'-Benzyloxy-3-{4-[4-(3,7-dimethyloctyloxy)phenoxy-carbonyl]phenoxy-carbonyl}-biphenyls (*rac*-Bz-C, (*S*)-Bz-C) and 3'-{4-[4-(3,7-dimethyloctyloxy)phenoxy-carbonyl]phenoxy-carbonyl}biphenyl-4-ols (*rac*-C, (*S*)-C) :

The synthesis of the *rac*-Bz-C and (*S*)-Bz-C were carried out by the esterification of 4'-benzyloxybiphenyl-3-carboxylic acid **A** with *rac*-B and (*S*)-B, respectively, using *N,N'*-dicyclohexylcarbodiimide (DCC)/DMAP. In the following step, the catalytic hydrogenation of the benzyl ethers *rac*-Bz-C and (*S*)-Bz-C according to procedures described in ref^{S14} leads to compounds *rac*-C and (*S*)-C.

For the synthesis of the *rac*-Bz-C and (*S*)-Bz-C compounds, the mixture 4'-benzyloxybiphenyl-3-carboxylic acid **A** (1.06 g, 3.5 mmol), *rac*-B or (*S*)-B (1.48 g, 4.0 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC) (0.82 g, 4.0 mmol) and 4-(dimethylamino)pyridine (DMAP) as catalyst in dry dichloromethane (50 ml) was stirred at room temperature under an argon atmosphere for 24 h. The end of reaction was monitored by TLC (chloroform). The reaction mixture was filtered on silica gel with CH₂Cl₂ and the solvent was evaporated. The crude products were purified by column chromatography on silica gel using chloroform as eluent and crystallized from ethanol.

In the next step, the compound *rac*-Bz-C or (*S*)-Bz-C (1.64 g, 2.5 mmol) was dissolved in THF (40 ml) and a catalytic amount of Pd/C-10% was added to this solution. The mixture was stirred in argon-flushed vessel of autoclave at 40 °C under 5 bar pressure of H₂ gas for 18h. The end of reaction was monitored by TLC (chloroform). The resulting mixture was filtered on silica gel to remove the residue of catalyst and washed with THF. After removing the solvent in vacuo, the crude product was purified by column chromatography on silica gel, eluting with chloroform.

4'-Benzyloxy-3-{4-[4-(3,7-dimethyloctyloxy)phenoxy-carbonyl]phenoxy-carbonyl}biphenyl *rac*-Bz-C

Yield: 74 %; colorless crystals, m.p.: 113 °C, R_f 0.9 (CHCl₃). ¹H-NMR (400 MHz, CDCl₃): δ = 8.37 (s, broad; 1 Ar-H), 8.28 (d, $J \approx 8.8$ Hz; 2 Ar-H), 8.14-8.12 (m; 1 Ar-H), 7.83-7.81 (m; 1 Ar-H), 7.58 (d, $J \approx 8.8$ Hz; 2 Ar-H), 7.56-7.54 (m; 1 Ar-H), 7.46-7.40 (m; 3 Ar-H), 7.38 (d, $J \approx 8.8$ Hz; 2 Ar-H), 7.37-7.32 (m; 2 Ar-H), 7.11 (d, $J \approx 9.1$ Hz; 2 Ar-H), 7.07 (d, $J \approx 8.8$ Hz; 2 Ar-H), 6.92 (d, $J \approx 9.1$ Hz; 2 Ar-H), 5.12 (s; 2H, OCH₂), 4.01-3.97 (m; 2H, OCH₂), 1.84-1.80 (m; 1H, CH), 1.66-1.49, 1.35-1.13 (2m; 9H, CH, 4 CH₂), 0.94 (d, $J \approx 6.6$ Hz; 3H, CH₃), 0.87 (d, $J \approx 6.6$ Hz; 6H, 2 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 164.66, 164.53 (CO), 158.85, 156.92, 155.07, 144.23, 141.45, 136.84, 132.57, 129.60, 127.37 (Ar-C), 132.02, 131.77, 129.09, 128.60, 128.40, 128.37, 128.25, 128.01, 127.42, 122.32, 121.96, 115.45, 115.20 (Ar-CH), 70.28, 66.95 (OCH₂), 39.41, 37.45, 36.40, 24.82 (CH₂), 30.06, 28.13 (CH), 22.85, 22.75, 19.83 (CH₃). MS (EI): m/z (%) = 656 (5) [M⁺], 407 (45) [M⁺-C₁₆H₂₅O₂], 287 (100) [C₂₀H₁₅O₂], 91 (60) [C₇H₇].

4'-Benzyloxy-3-{4-[4-((*S*)-3,7-dimethyloctyloxy)phenoxy-carbonyl]phenoxy-carbonyl}

biphenyl (S)-Bz-C

Yield: 72 %; colorless crystals, m.p.: 113 °C, R_f 0.9 (CHCl₃). ¹H-NMR (400 MHz, CDCl₃): δ = 8.37 (s, broad; 1 Ar-H), 8.27 (d, $J \approx 8.6$ Hz; 2 Ar-H), 8.13-8.12 (m; 1 Ar-H), 7.83-7.81 (m; 1 Ar-H), 7.58 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.56-7.54 (m; 1 Ar-H), 7.48-7.41 (m; 3 Ar-H), 7.39 (d, $J \approx 8.6$ Hz; 2 Ar-H), 7.37-7.33 (m; 2 Ar-H), 7.10 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.07 (d, $J \approx 8.7$ Hz; 2 Ar-H), 6.91 (d, $J \approx 8.9$ Hz; 2 Ar-H), 5.11 (s; 2H, OCH₂), 4.01-3.97 (m; 2H, OCH₂), 1.84-1.78 (m; 1H, CH), 1.66-1.47, 1.35-1.12 (2m; 9H, CH, 4 CH₂), 0.92 (d, $J \approx 6.6$ Hz; 3H, CH₃), 0.85 (d, $J \approx 6.6$ Hz; 6H, 2 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 164.68, 164.16 (CO), 158.84, 156.95, 155.07, 144.23, 141.43, 136.84, 132.54, 129.53, 127.49 (Ar-C), 132.11, 131.84, 129.15, 128.66, 128.29, 128.37, 128.25, 128.01, 127.42, 122.36, 122.02, 115.36, 115.13 (Ar-CH), 70.12, 66.74 (OCH₂), 39.25, 37.29, 36.21, 24.67 (CH₂), 29.84, 27.98 (CH), 22.72, 22.62, 19.66 (CH₃).

3'-{4-[4-(3,7-Dimethyloctyloxy)phenoxy]phenoxy}biphenyl-4-ol rac-C

Yield: 65 %; colorless crystals, m.p.: 155 °C, R_f 0.4 (CHCl₃). ¹H-NMR (400 MHz, CDCl₃): δ = 8.37 (s, broad; 1 Ar-H), 8.27 (d, $J \approx 8.9$ Hz; 2 Ar-H), 8.14-8.12 (m; 1 Ar-H), 7.83-7.81 (m; 1 Ar-H), 7.56-7.54 (m; 1 Ar-H), 7.53 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.37 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.11 (d, $J \approx 8.9$ Hz; 2 Ar-H), 6.92 (d, $J \approx 8.7$ Hz; 4 Ar-H), 5.03 (broad s; 1H, OH), 4.01-3.96 (m; 2H, OCH₂), 1.84-1.80 (m; 1H, CH), 1.66-1.49, 1.35-1.24, 1.18-1.13 (3m; 9H, CH, 4 CH₂), 0.94 (d, $J \approx 6.6$ Hz; 3H, CH₃), 0.87 (d, $J \approx 6.6$ Hz; 6H, 2 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 164.69, 164.56 (CO), 156.92, 155.63, 155.06, 144.21, 141.43, 132.57, 129.59, 127.37 (Ar-C), 132.02, 131.78, 129.09, 128.46, 128.39, 122.31, 121.96, 115.90, 115.20 (Ar-CH), 66.95 (OCH₂), 39.40, 37.45, 36.39, 24.81 (CH₂), 30.06, 28.12 (CH), 22.84, 22.74, 19.83 (CH₃). MS (EI): m/z (%) = 566 (5) [M⁺], 317 (45) [M⁺-C₁₆H₂₅O₂], 197 (98) [C₁₃H₉O₂], 121 (100) [C₇H₄O₂].

3'-{4-[4-((S)-3,7-Dimethyloctyloxy)phenoxy]phenoxy}biphenyl-4-ol (S)-C

Yield: 85 %; colorless crystals, m.p.: 155 °C, R_f 0.4 (CHCl₃). ¹H-NMR (400 MHz, CDCl₃): δ = 8.37 (s, broad; 1 Ar-H), 8.28 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.14-8.13 (m; 1 Ar-H), 7.83-7.81 (m; 1 Ar-H), 7.58-7.56 (m; 1 Ar-H), 7.53 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.37 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.11 (d, $J \approx 8.7$ Hz; 2 Ar-H), 6.93 (d, $J \approx 8.7$ Hz; 4 Ar-H), 5.04 (broad s; 1H, OH), 4.02-3.94 (m; 2H, OCH₂), 1.85-1.78 (m; 1H, CH), 1.70-1.48, 1.37-1.20, 1.18-1.11 (3m; 9H, CH, 4 CH₂), 0.93 (d, $J \approx 6.6$ Hz; 3H, CH₃), 0.86 (d, $J \approx 6.6$ Hz; 6H, 2 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 164.86, 164.71 (CO), 156.96, 155.70, 155.09, 144.14, 141.43, 132.51, 129.51, 127.60 (Ar-C), 132.10, 131.85, 129.16, 128.50, 128.43, 128.41, 122.36, 122.03, 115.89, 115.14 (Ar-CH), 66.75 (OCH₂), 39.25, 37.29, 36.21, 24.67 (CH₂), 29.84, 27.98 (CH), 22.72, 22.62, 19.65 (CH₃).

2.4 4-(4-n-Alkyloxybenzoyloxy)benzoic acids and 4-[4-(10-undecenyloxy)benzoyloxy]benzoic acid Dn:

4-(4-n-Alkyloxybenzoyloxy)benzoic acids^{S15,S16,S17} Dn ($n = 4, 6, 8, 10, 12, 14$) and 4-[4-(10-undecenyloxy)benzoyloxy]benzoic acid^{S17} were synthesized according to procedures described in the literature^{S18,S19} by alkylation of ethyl 4-hydroxybenzoate with the appropriate alkyl bromides, followed by hydrolysis of the ester group. Esterification^{S11} of the obtained 4-alkyloxybenzoic acids with 4-hydroxybenzaldehyde, followed by NaClO₂ oxidation^{S20} leads

to the 4-(4-*n*-alkyloxybenzoyloxy)benzoic acids. 4-[4-(10-Undecenyloxy)benzoyloxy]benzoic acid was prepared from 10-undecenyl bromide by using same procedures described in ref.^{S18,S19}. Spectroscopic data of the 4-(4-*n*-alkyloxybenzoyloxy)benzoic acids and 4-[4-(10-undecenyloxy)benzoyloxy]benzoic acid were given in ref.^{S21,S22,S23} The transition temperatures and ¹H-NMR spectra of the obtained compounds correspond to those given in the literature.

2.5 Synthesis and analytical data of compounds *rac*-4 - *rac*-14, (*S*)-11 and (*S*)-12

A mixture of *rac*-C or (*S*)-C (1.13 g, 2 mmol) with the appropriate 4-(4-*n*-alkyloxybenzoyloxy)benzoic acid **D4** - **D14** or 4-[4-(10-undecenyloxy)benzoyloxy]benzoic acid **D11** (2 mmol), DCC (0.47 g, 2.3 mmol) and DMAP (48 mg, 0.4 mmol) in dry dichloromethane (20 ml) was stirred at room temperature under an argon atmosphere for 24 h. The precipitate was filtered off, the solvent was evaporated and the crude products were purified by column chromatography on silica gel using chloroform as eluent and recrystallized from ethanol.

4-[4-(3,7-Dimethyloctyloxy)phenoxy]carbonyl]phenyl 4-[4-(4-butyloxybenzoyloxy)-benzoyloxy]biphenyl-3'-carboxylate

rac-4: Yield: 1.36 g (79 %) of colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.48 (s, broad; 1 Ar-H), 8.34 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 8.33 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.25-8.24 (m; 1 Ar-H), 8.19 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.94-7.92 (m; 1 Ar-H), 7.76 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.68-7.64 (m; 1 Ar-H), 7.45-7.41 (m; 4 Ar-H), 7.39 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.17 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 7.03 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.97 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 4.10 (t; *J* ≈ 6.5 Hz; 2H, OCH₂), 4.08-4.01 (m; 2H, OCH₂), 1.96-1.79, 1.78-1.42, 1.39-1.18 (3m; 14H, 2 CH, 6 CH₂), 1.04 (t, *J* ≈ 7.4 Hz; 3H, CH₃), 0.99 (d, *J* ≈ 6.6 Hz; 3H, CH₃), 0.92 (d, *J* ≈ 6.6 Hz; 9H, 2 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.76, 164.49, 164.44, 164.30 (CO), 163.85, 156.95, 155.49, 155.05, 150.87, 144.18, 141.05, 137.65, 129.69, 127.37, 126.72, 120.93 (Ar-C), 132.49, 132.41, 131.84, 131.82, 129.26, 129.10, 128.85, 128.33, 122.33, 122.29, 122.14, 121.98, 115.13, 114.42 (Ar-CH), 68.07, 66.76 (OCH₂), 39.24, 37.35, 36.11, 29.68, 24.74, 22.78 (CH₂), 29.98, 28.06 (CH), 19.76, 19.30, 13.89 (CH₃). C₅₄H₅₄O₁₀ (863.01); Anal. Calc.: C, 75.15; H, 6.31. Found: C, 75.36; H, 6.38%.

4-[4-(3,7-Dimethyloctyloxy)phenoxy]carbonyl]phenyl 4-[4-(4-hexyloxybenzoyloxy)-benzoyloxy]biphenyl-3'-carboxylate

rac-6: Yield: 1.17 g (66 %) of colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.48 (s, broad; 1 Ar-H), 8.34 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 8.33 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 8.26-8.24 (m; 1 Ar-H), 8.19 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.94-7.92 (m; 1 Ar-H), 7.76 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.68-7.64 (m; 1 Ar-H), 7.45-7.41 (m; 4 Ar-H), 7.39 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.17 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 7.03 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.97 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 4.09 (t; *J* ≈ 6.6 Hz; 2H, OCH₂), 4.06-4.01 (m; 2H, OCH₂), 1.89-1.84, 1.72-1.51, 1.42-1.18 (3m; 18H, 2 CH, 8 CH₂), 0.99 (d, *J* ≈ 6.6 Hz; 3H, CH₃), 0.97-0.95 (m; 3H, CH₃), 0.92 (d, *J* ≈ 6.6 Hz; 9H, 2 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.84, 164.57, 164.52, 164.38 (CO), 163.92, 157.03, 155.57, 155.12, 150.96, 144.27, 141.15, 137.79, 129.78, 127.46, 126.81, 121.01 (Ar-C), 132.58, 132.50, 131.93, 131.90, 129.35, 129.19, 128.94, 128.43, 122.37, 122.23, 122.06, 122.02, 115.22, 114.51 (Ar-CH), 68.49, 66.86 (OCH₂), 39.33, 37.37, 36.31, 31.62, 29.77, 25.73, 24.74, 22.78 (CH₂), 29.94, 29.13 (CH), 22.66, 19.72, 14.08 (CH₃). C₅₆H₅₈O₁₀ (891.07); Anal. Calc.: C, 75.48; H, 6.56. Found: C, 75.42; H, 6.27%.

4-[4-(3,7-Dimethyloctyloxy)phenoxy]phenyl 4-[4-(4-octyloxybenzoyloxy)-benzoyloxy]biphenyl-3'-carboxylate

rac-**8**: Yield: 1.45 g (79 %) of colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.48 (s, broad; 1 Ar-H), 8.34 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 8.33 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 8.26-8.24 (m; 1 Ar-H), 8.20 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 7.94-7.92 (m; 1 Ar-H), 7.76 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 7.68-7.64 (m; 1 Ar-H), 7.45-7.41 (m; 4 Ar-H), 7.39 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 7.17 (d, *J* ≈ 9.1 Hz; 2 Ar-H), 7.03 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 6.98 (d, *J* ≈ 9.1 Hz; 2 Ar-H), 4.09 (t; *J* ≈ 6.5 Hz; 2H, OCH₂), 4.06-4.01 (m; 2H, OCH₂), 1.89-1.84, 1.65-1.50, 1.43-1.18 (3m; 22H, 2 CH, 10 CH₂), 0.99 (d, *J* ≈ 6.6 Hz; 3H, CH₃), 0.97-0.95 (m; 3H, CH₃), 0.95-0.91 (m; 9H, 3 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.74, 164.47, 164.42, 164.28 (CO), 163.83, 156.94, 155.48, 155.03, 150.86, 144.17, 141.04, 137.64, 129.68, 127.36, 126.71, 120.91 (Ar-C), 132.48, 132.40, 131.83, 131.81, 129.25, 129.09, 128.83, 128.32, 122.32, 122.28, 122.13, 121.97, 115.12, 114.42 (Ar-CH), 68.39, 66.76 (OCH₂), 39.24, 37.28, 36.21, 31.78, 29.30, 29.20, 29.07, 25.97, 24.65, 22.69 (CH₂), 29.85, 29.07 (CH), 22.64, 19.66, 14.08 (CH₃). C₅₈H₆₂O₁₀ (919.12); Anal. Calc.: C, 75.79; H, 6.80. Found: C, 75.82; H, 6.39%.

4-[4-(3,7-Dimethyloctyloxy)phenoxy]phenyl 4-[4-(4-decyloxybenzoyloxy)-benzoyloxy]biphenyl-3'-carboxylate

rac-**10**: Yield: 1.25 g (66 %) of colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.47 (s, broad; 1 Ar-H), 8.31 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 8.30 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.22-8.21 (m; 1 Ar-H), 8.16 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.91-7.89 (m; 1 Ar-H), 7.73 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.64-7.61 (m; 1 Ar-H), 7.42-7.38 (m; 4 Ar-H), 7.36 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.13 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 6.99 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.94 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 4.06 (t; *J* ≈ 6.6 Hz; 2H, OCH₂), 4.03-3.98 (m; 2H, OCH₂), 1.93-1.80, 1.76-1.46, 1.37-1.16 (3m; 26H, 2 CH, 12 CH₂), 0.96 (d, *J* ≈ 6.6 Hz; 3H, CH₃), 0.91-0.88 (m; 9H, 3 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.76, 164.49, 164.44, 164.30 (CO), 163.84, 156.95, 155.49, 155.04, 150.87, 144.17, 141.05, 137.65, 129.69, 127.37, 126.72, 120.92 (Ar-C), 132.49, 132.41, 131.83, 131.82, 129.26, 129.10, 128.84, 128.33, 122.33, 122.28, 122.14, 121.97, 115.13, 114.42 (Ar-CH), 68.39, 66.75 (OCH₂), 39.23, 37.27, 36.21, 31.87, 29.67, 29.53, 29.52, 29.33, 29.29, 25.96, 24.64, 22.69 (CH₂), 29.84, 27.96 (CH), 22.59, 19.64, 14.09 (CH₃). C₆₀H₆₆O₁₀ (947.18); Anal. Calc.: C, 76.08; H, 7.02. Found: C, 75.86; H, 7.10 %.

4-[4-(3,7-Dimethyloctyloxy)phenoxy]phenyl 4-[4-[4-(10-Undecenyloxybenzoyloxy)-benzoyloxy]biphenyl-3'-carboxylate

rac-**11**: Yield: 1.01 g (53 %) of colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.45 (s, broad; 1 Ar-H), 8.32-8.29 (m, 4 Ar-H), 8.22-8.20 (m; 1 Ar-H), 8.16 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.91-7.89 (m; 1 Ar-H), 7.73 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.64-7.61 (m; 1 Ar-H), 7.42-7.39 (m; 4 Ar-H), 7.36 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.13 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.99 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 6.94 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 5.85-5.80 (m; 1H, CH₂=CH), 5.02-4.93 (m; 2H, CH₂=CH), 4.06 (t; *J* ≈ 6.5 Hz; 2H, OCH₂), 4.03-3.97 (m; 2H, OCH₂), 2.07-2.03 (m; 2H, CH₂=CH-CH₂), 1.87-1.80 (m; 3H, CH₂, CH), 1.71-1.45, 1.39-1.15 (2m; 21H, CH, 10 CH₂), 0.95 (d, *J* ≈ 6.6 Hz; 3H, CH₃), 0.88 (d, *J* ≈ 6.6 Hz; 6H, 2 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.78, 164.50, 164.46, 164.32 (CO), 163.84, 156.95, 155.49, 155.05, 150.87, 144.17, 141.06, 137.67, 128.85, 127.37, 126.73, 120.93 (Ar-C), 132.50, 132.41, 131.84, 131.83, 129.69, 129.26, 129.10, 128.34, 122.33, 122.29, 122.14, 121.98, 115.14, 114.43 (Ar-CH), 139.17 (CH₂=CH), 114.13 (CH₂=CH), 68.38, 66.77 (OCH₂), 39.24, 37.27, 36.21, 33.77,

29.67, 29.46, 29.38, 29.31, 29.08, 28.90, 25.95, 24.64 (CH₂), 29.84, 27.96 (CH), 22.69, 22.58, 19.64 (CH₃). C₆₁H₆₆O₁₀ (959.19); Anal. Calc.: C, 76.38; H, 6.94. Found: C, 74.28; H, 6.98%.

4-[4-((S)-3,7-Dimethyloctyloxy)phenoxy]phenyl 4-[4-(10-Undecenylbenzoyloxy)-benzoyloxy]biphenyl-3'-carboxylate

(S)-**11**: Yield: 1.05 g (55 %) of colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.45 (s, broad; 1 Ar-H), 8.31 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.30 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.22-8.20 (m; 1 Ar-H), 8.16 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 7.91-7.89 (m; 1 Ar-H), 7.73 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.64-7.61 (m; 1 Ar-H), 7.41 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 7.39 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 7.36 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.13 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.99 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 6.94 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 5.86-5.78 (m; 1H, CH₂=CH), 5.01-4.92 (m; 2H, CH₂=CH), 4.06 (t; *J* ≈ 6.6 Hz; 2H, OCH₂), 4.02-3.97 (m; 2H, OCH₂), 2.07-2.03 (m; 2H, CH₂=CH-CH₂), 1.87-1.80 (m; 3H, CH₂, CH), 1.71-1.45, 1.40-1.15 (2m; 21H, CH, 10 CH₂), 0.95 (d, *J* ≈ 6.0 Hz; 3H, CH₃), 0.88 (d, *J* ≈ 6.6 Hz; 6H, 2 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.78, 164.50, 164.46, 164.32 (CO), 163.84, 156.95, 155.49, 155.05, 150.87, 144.17, 141.06, 137.67, 128.85, 127.37, 126.73, 120.93 (Ar-C), 132.50, 132.41, 131.84, 131.83, 129.69, 129.26, 129.10, 128.34, 122.33, 122.29, 122.14, 121.98, 115.14, 114.43 (Ar-CH), 139.17 (CH₂=CH), 114.13 (CH₂=CH), 68.38, 66.77 (OCH₂), 39.24, 37.27, 36.21, 33.77, 29.67, 29.46, 29.38, 29.31, 29.08, 28.90, 25.95, 24.64 (CH₂), 29.85, 27.96 (CH), 22.69, 22.59, 19.64 (CH₃).

4-[4-(3,7-Dimethyloctyloxy)phenoxy]phenyl 4-[4-(4-dodecylbenzoyloxy)-benzoyloxy]biphenyl-3'-carboxylate

rac-**12**: Yield: 1.11 g (57 %) of colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.46 (s, broad; 1 Ar-H), 8.31 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.30 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.22-8.21 (m; 1 Ar-H), 8.16 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.91-7.89 (m; 1 Ar-H), 7.73 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.64-7.61 (m; 1 Ar-H), 7.42-7.38 (m; 4 Ar-H), 7.36 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.13 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 6.99 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.94 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 4.06 (t; *J* ≈ 6.6 Hz; 2H, OCH₂), 4.03-3.97 (m; 2H, OCH₂), 1.87-1.81, 1.70-1.43, 1.39-1.15 (3m; 30H, 2 CH, 14 CH₂), 0.96 (d, *J* ≈ 6.6 Hz; 3H, CH₃), 0.90-0.88 (m; 9H, 3 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.78, 164.51, 164.45, 164.32 (CO), 163.85, 156.95, 155.49, 155.05, 150.87, 144.18, 141.06, 137.66, 129.69, 127.37, 126.72, 120.92 (Ar-C), 132.50, 132.41, 131.84, 131.83, 129.27, 129.10, 128.85, 128.34, 122.33, 122.29, 122.14, 121.98, 115.14, 114.43 (Ar-CH), 68.40, 66.77 (OCH₂), 39.24, 37.27, 36.21, 31.90, 29.64, 29.61, 29.56, 29.53, 29.34, 29.07, 25.96, 24.64, 22.69, 22.67 (CH₂), 29.85, 27.96 (CH), 22.59, 19.64, 14.09 (CH₃). C₆₂H₇₀O₁₀ (975.23); Anal. Calc.: C, 76.36; H, 7.23. Found: C, 76.51; H, 7.73%.

4-[4-((S)-3,7-Dimethyloctyloxy)phenoxy]phenyl 4-[4-(4-dodecylbenzoyloxy)-benzoyloxy]biphenyl-3'-carboxylate

(S)-**12**: Yield: 1.17 g (60 %) of colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.46 (s, broad; 1 Ar-H), 8.32 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.31 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.23-8.22 (m; 1 Ar-H), 8.17 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.92-7.90 (m; 1 Ar-H), 7.74 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.66-7.63 (m; 1 Ar-H), 7.42-7.36 (m; 4 Ar-H), 7.36 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.14 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 7.00 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.95 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 4.06 (t; *J* ≈ 6.5 Hz; 2H, OCH₂), 4.03-3.97 (m; 2H, OCH₂), 1.86-1.81, 1.73-1.44, 1.42-1.14 (3m; 30H, 2 CH, 14 CH₂), 0.96 (d, *J* ≈ 6.6 Hz; 3H, CH₃), 0.91-0.89 (m; 9H, 3 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.78, 164.51, 164.46, 164.32 (CO), 163.85, 156.95, 155.49, 155.05, 150.87, 144.18, 141.06, 137.66, 129.69, 127.37, 126.72, 120.92 (Ar-C), 132.50, 132.41,

131.84, 131.83, 129.26, 129.10, 128.85, 128.34, 122.33, 122.29, 122.14, 121.98, 115.14, 114.43 (Ar-CH), 68.40, 66.77 (OCH₂), 39.24, 37.27, 36.21, 31.90, 29.64, 29.61, 29.56, 29.53, 29.34, 29.07, 25.96, 24.64, 22.69, 22.67 (CH₂), 29.85, 27.96 (CH), 22.59, 19.64, 14.09 (CH₃). **C₆₂H₇₀O₁₀** (975.23); Anal. Calc.: C, 76.36; H, 7.23. Found: C, 76.62; H, 7.77%.

4-[4-(3,7-Dimethyloctyloxy)phenoxy]phenyl 4-[4-(4-tetradecyloxybenzoyloxy)-benzoyloxy]biphenyl-3'-carboxylate

rac-**14**: Yield: 1.04 g (52 %) of colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.46 (s, broad; 1 Ar-H), 8.31 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.30 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.22-8.21 (m; 1 Ar-H), 8.16 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.91-7.89 (m; 1 Ar-H), 7.73 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.64-7.61 (m; 1 Ar-H), 7.42-7.38 (m; 4 Ar-H), 7.36 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.14 (d, *J* ≈ 9.1 Hz; 2 Ar-H), 6.99 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.94 (d, *J* ≈ 9.1 Hz; 2 Ar-H), 4.06 (t; *J* ≈ 6.5 Hz; 2H, OCH₂), 4.03-3.99 (m; 2H, OCH₂), 1.86-1.82 (m; 3H, CH, CH₂), 1.61-1.47, 1.39-1.16 (2m; 31H, CH, 15 CH₂), 0.96 (d, *J* ≈ 6.6 Hz; 3H, CH₃), 0.90-0.88 (m; 9H, 3 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.76, 164.48, 164.44, 164.30 (CO), 163.84, 156.95, 155.49, 155.04, 150.87, 144.18, 141.05, 137.65, 128.84, 127.37, 126.72, 120.92 (Ar-C), 132.49, 132.41, 131.84, 131.82, 129.69, 129.26, 129.10, 128.33, 122.33, 122.28, 122.14, 121.97, 115.13, 114.42 (Ar-CH), 68.39, 66.76 (OCH₂), 39.24, 37.28, 36.21, 31.90, 29.67, 29.65, 29.64, 29.63, 29.57, 29.53, 29.34, 29.07, 25.96, 24.64, 22.69, 22.67 (CH₂), 29.85, 27.96 (CH), 22.59, 19.64, 14.09 (CH₃). **C₆₄H₇₄O₁₀** (1003.28); Anal. Calc.: C, 76.62; H, 7.43. Found: C, 76.38; H, 7.33%.

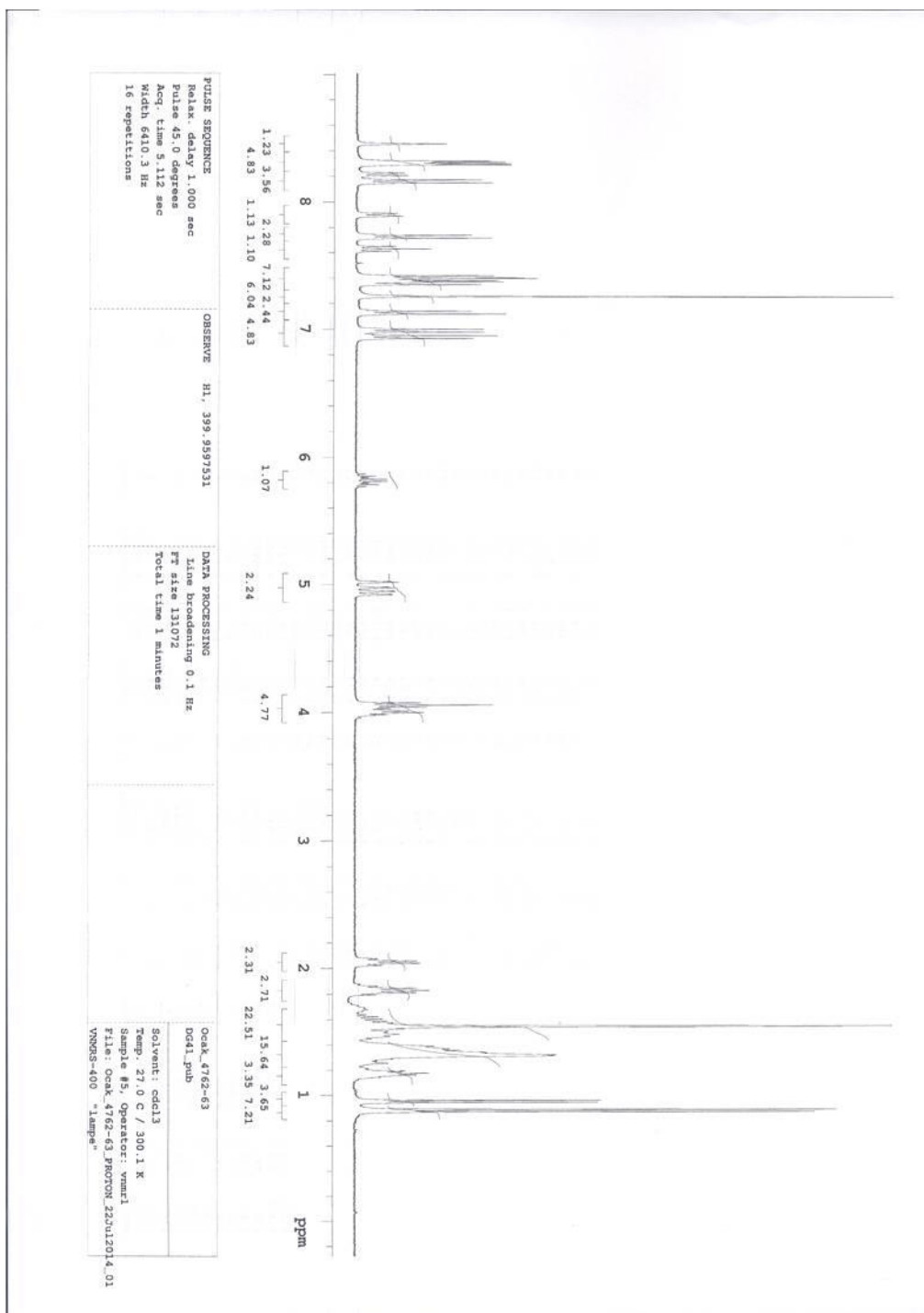


Figure S15. ¹H-NMR spectrum of compound *rac*-11 (CDCl₃).

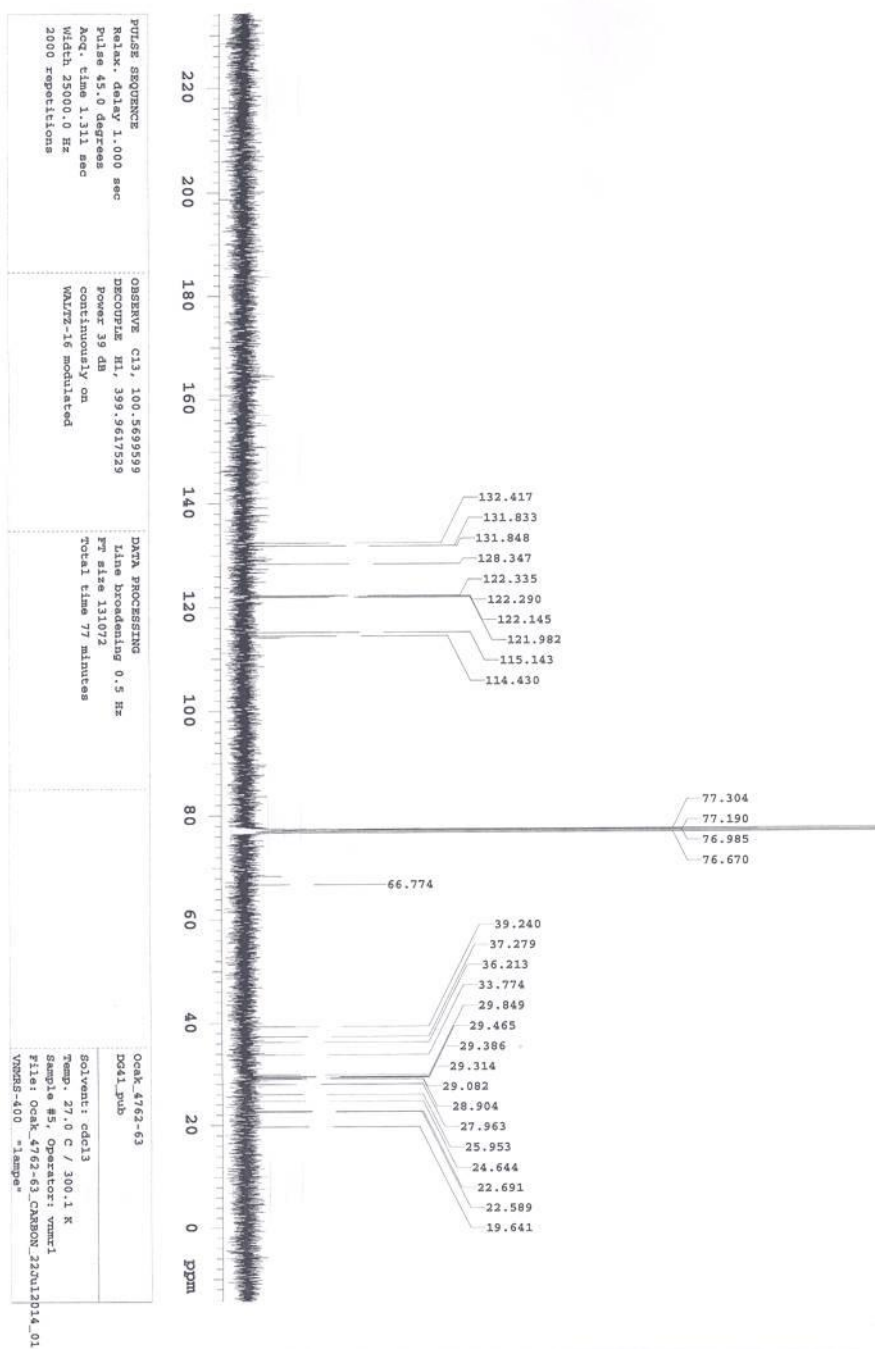


Figure S16. ^{13}C -NMR spectrum of compound *rac*-11 (CDCl_3).

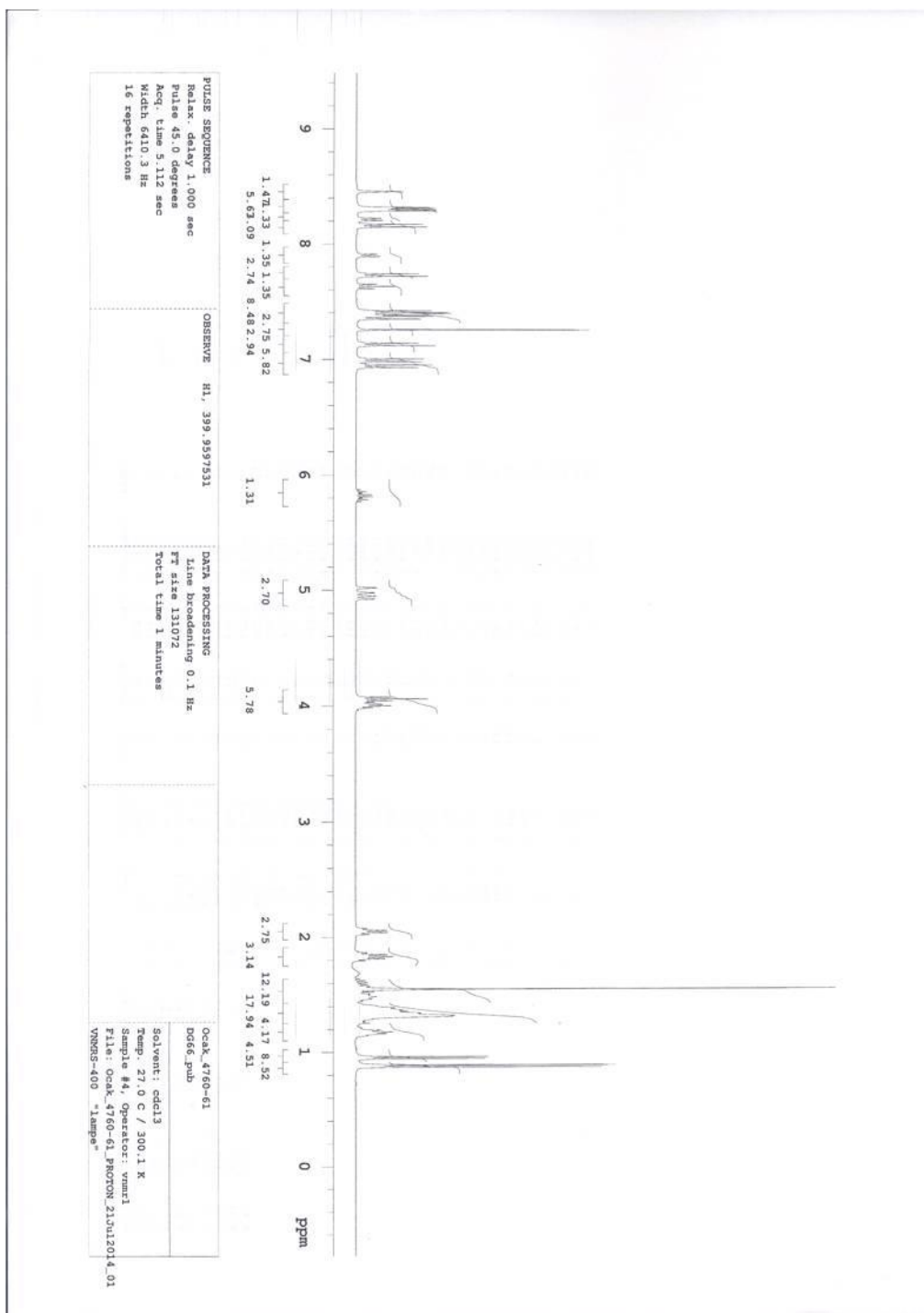


Figure S17. $^1\text{H-NMR}$ spectrum of compound (*S*)-**11** (CDCl_3).

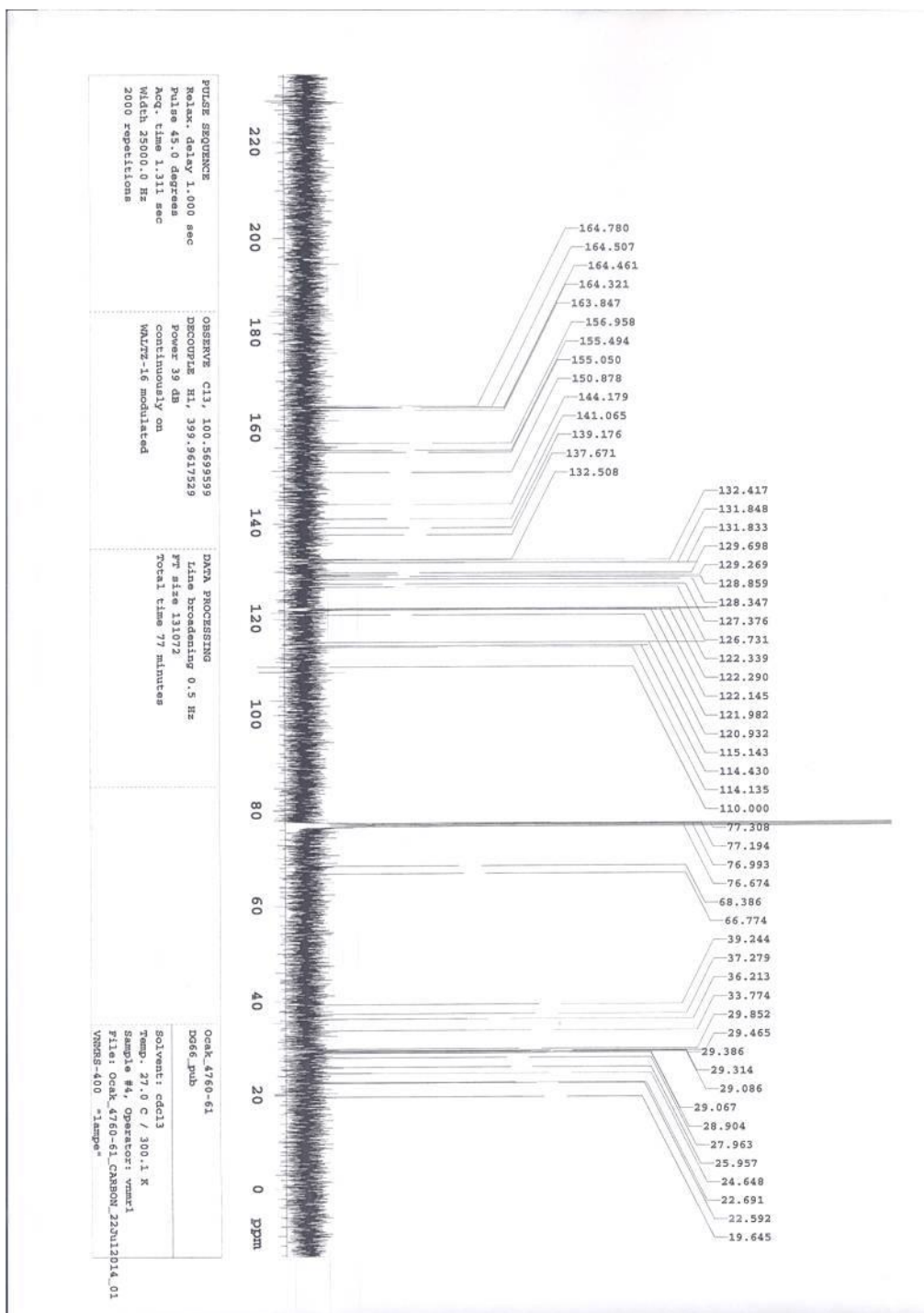


Figure S18. ^{13}C -NMR spectrum of compound (*S*)-**11** (CDCl_3).

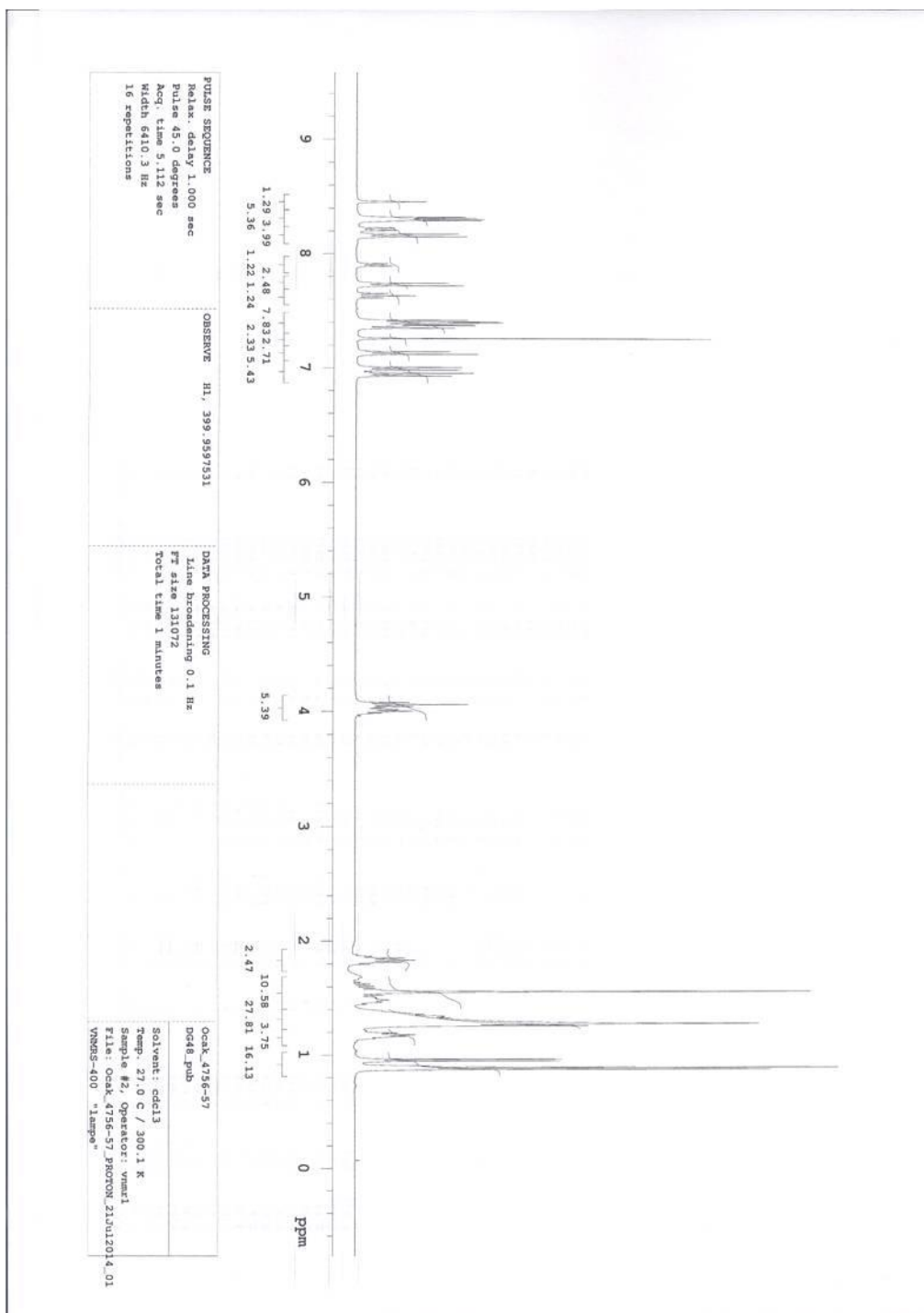


Figure S19. $^1\text{H-NMR}$ spectrum of compound *rac-12* (CDCl_3).

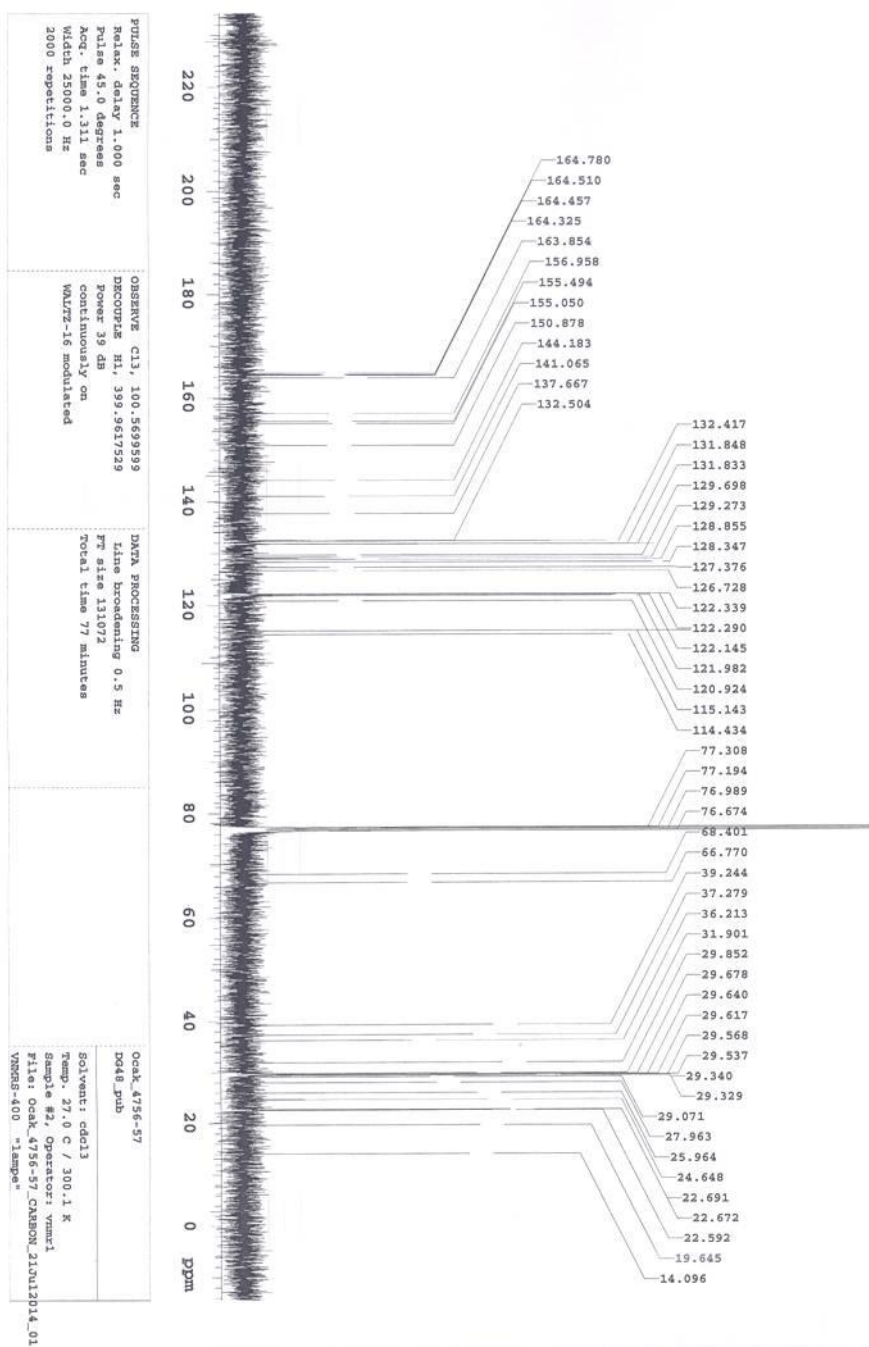


Figure S20. ^{13}C -NMR spectrum of compound *rac*-12 (CDCl_3).

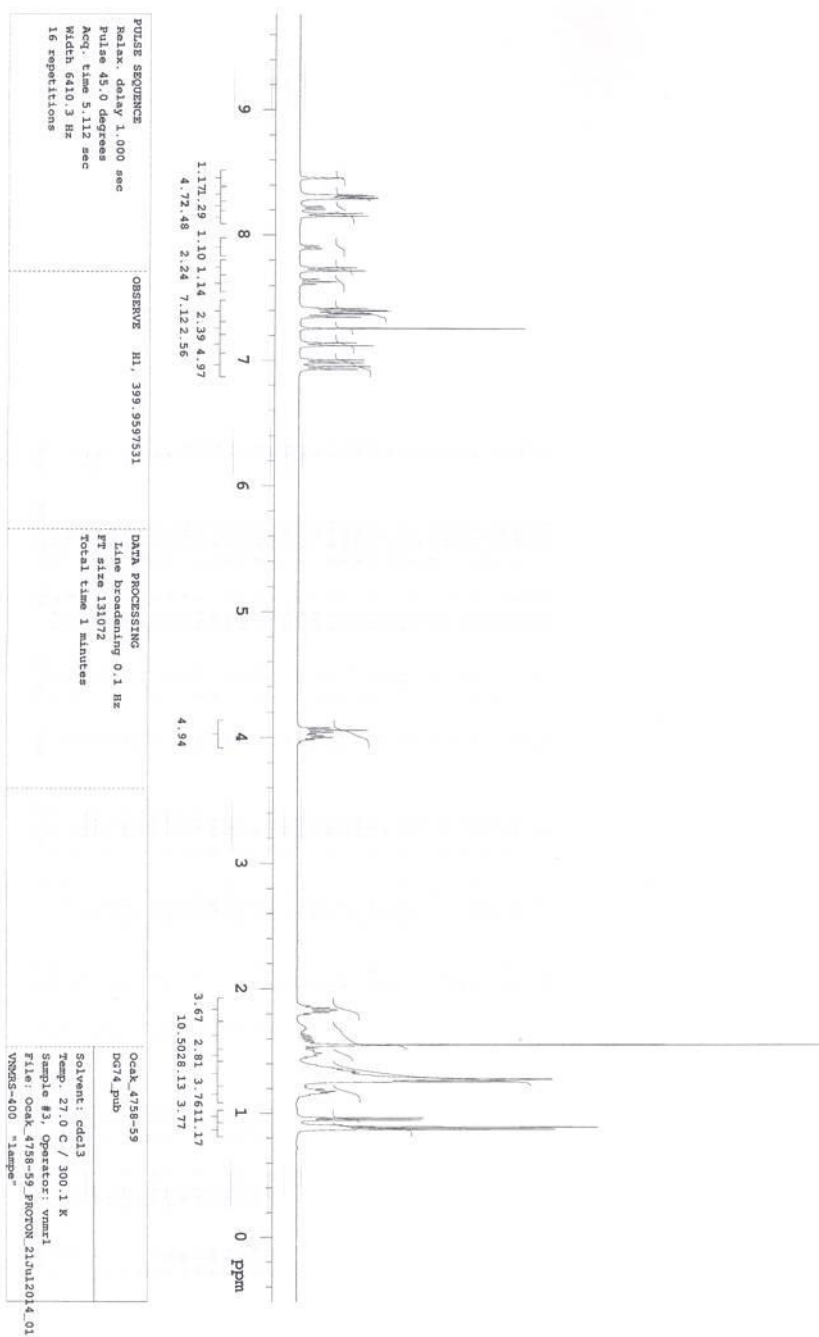


Figure S21. $^1\text{H-NMR}$ spectrum of compound (*S*)-**12** (CDCl_3).

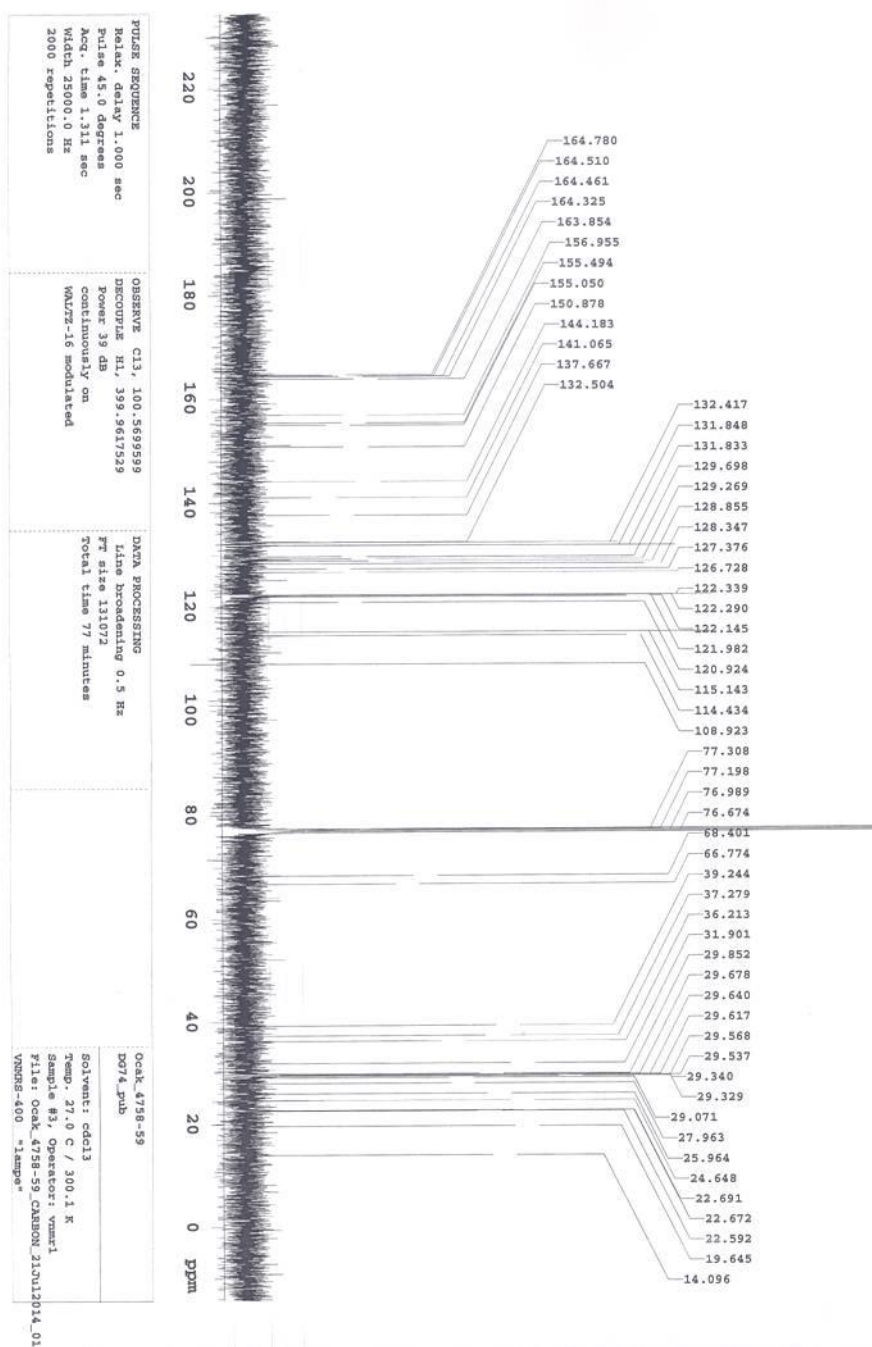


Figure S22. ^{13}C -NMR spectrum of compound (*S*)-12 (CDCl_3).

Oc1k_4359
Oc1k
DG 31/1
Sp.Nr:4359

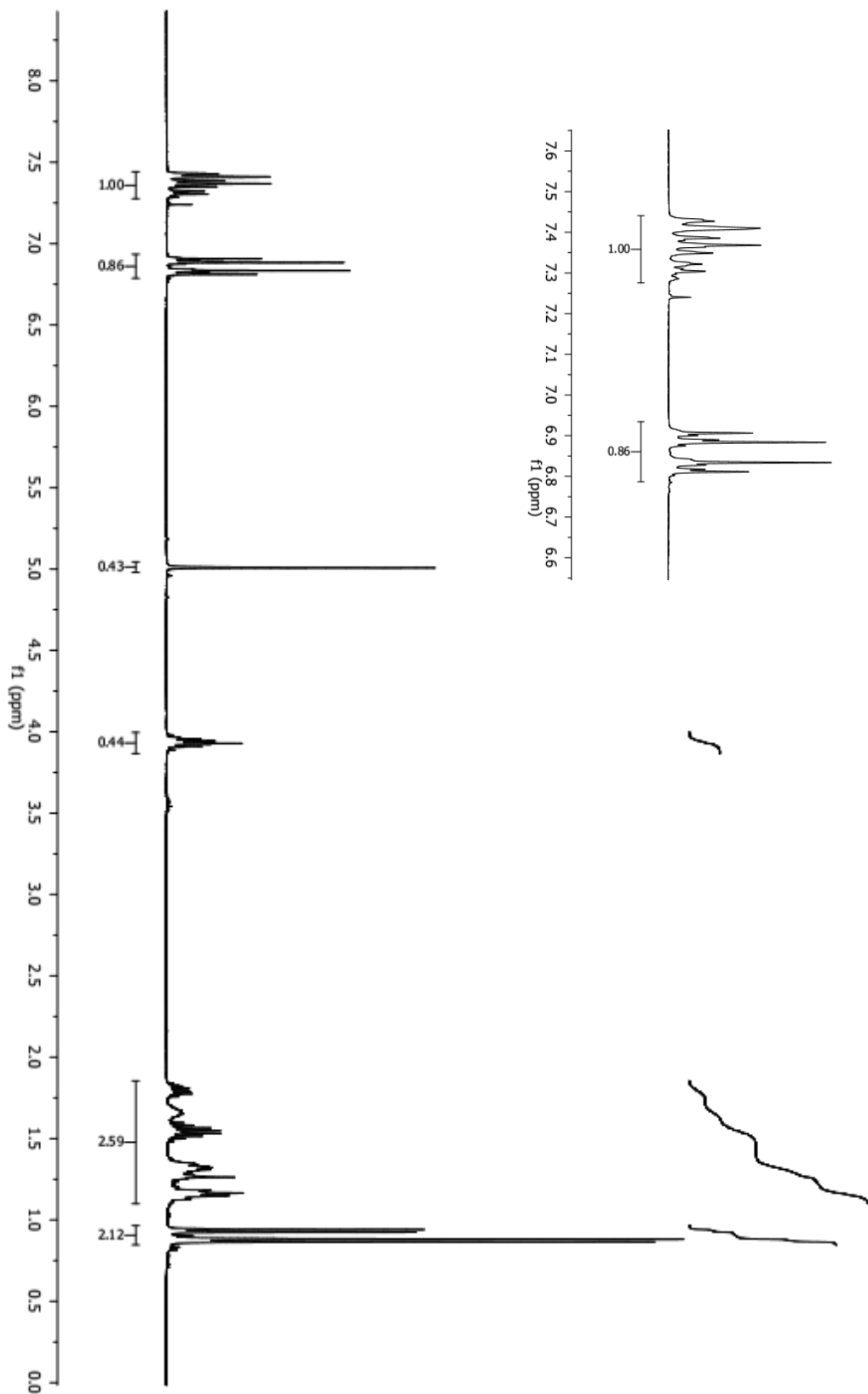


Figure S23. ¹H-NMR spectrum of 4-(3,7-dimethyloctyloxy)phenyl benzyl ether (CDCl₃).

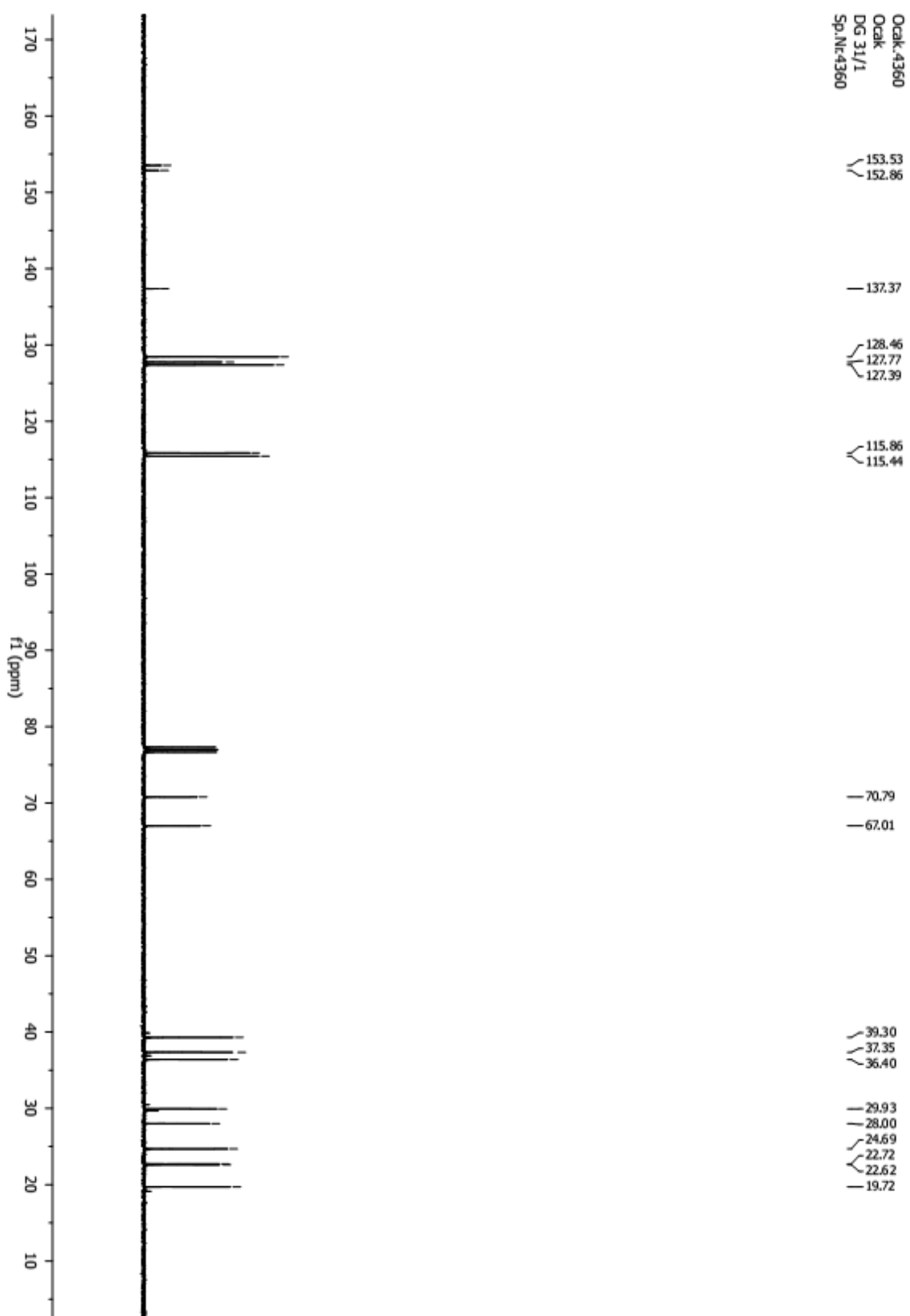


Figure S24. ^{13}C -NMR spectrum of 4-(3,7-dimethyloctyloxy)phenyl benzyl ether (CDCl_3).

Ocak-4361
Ocak
DG 35/1
Sp.Nr:4361

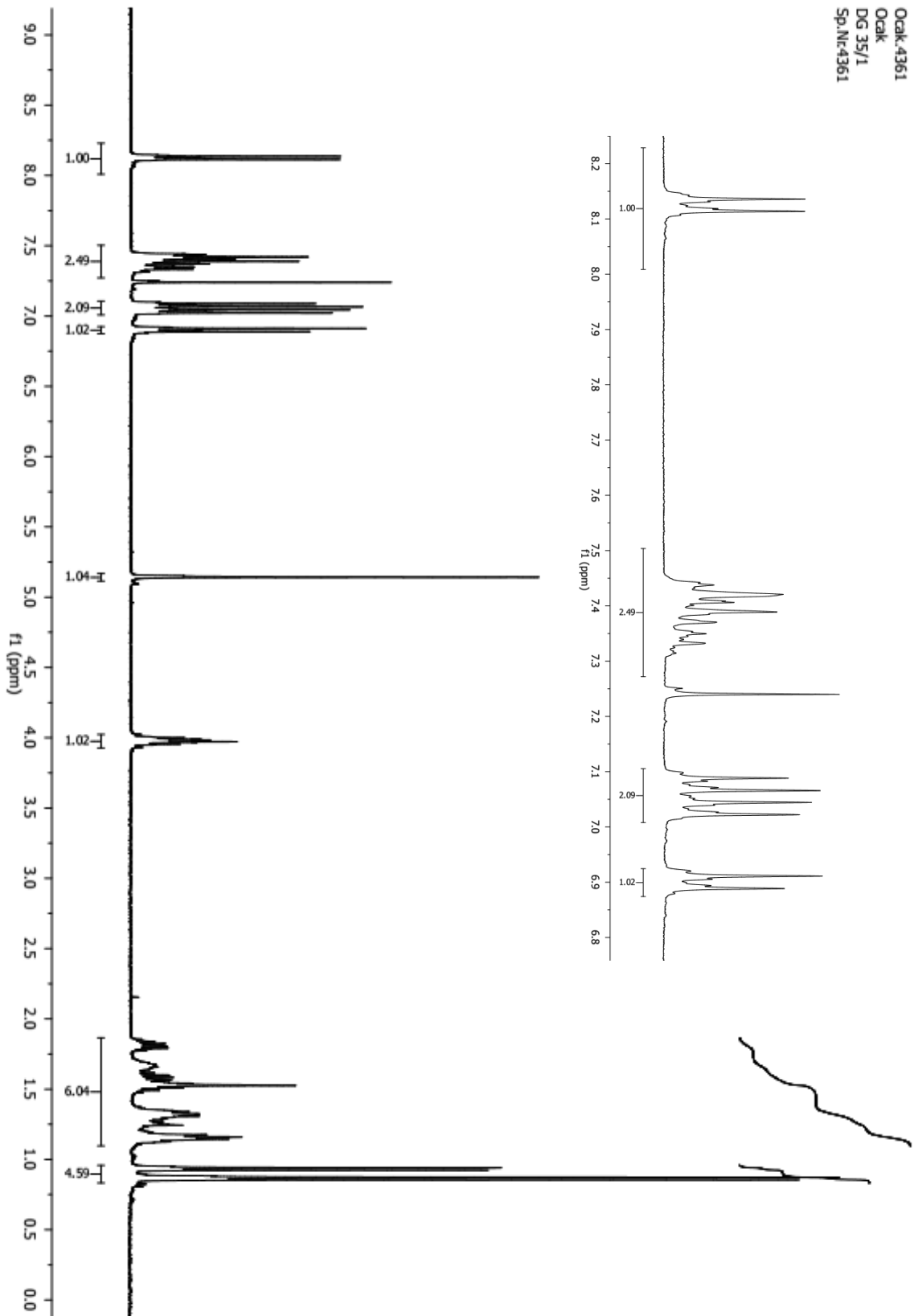


Figure S25. $^1\text{H-NMR}$ spectrum of 4-(3,7-dimethyloctyloxy)phenyl 4-benzyloxybenzoate (CDCl_3)

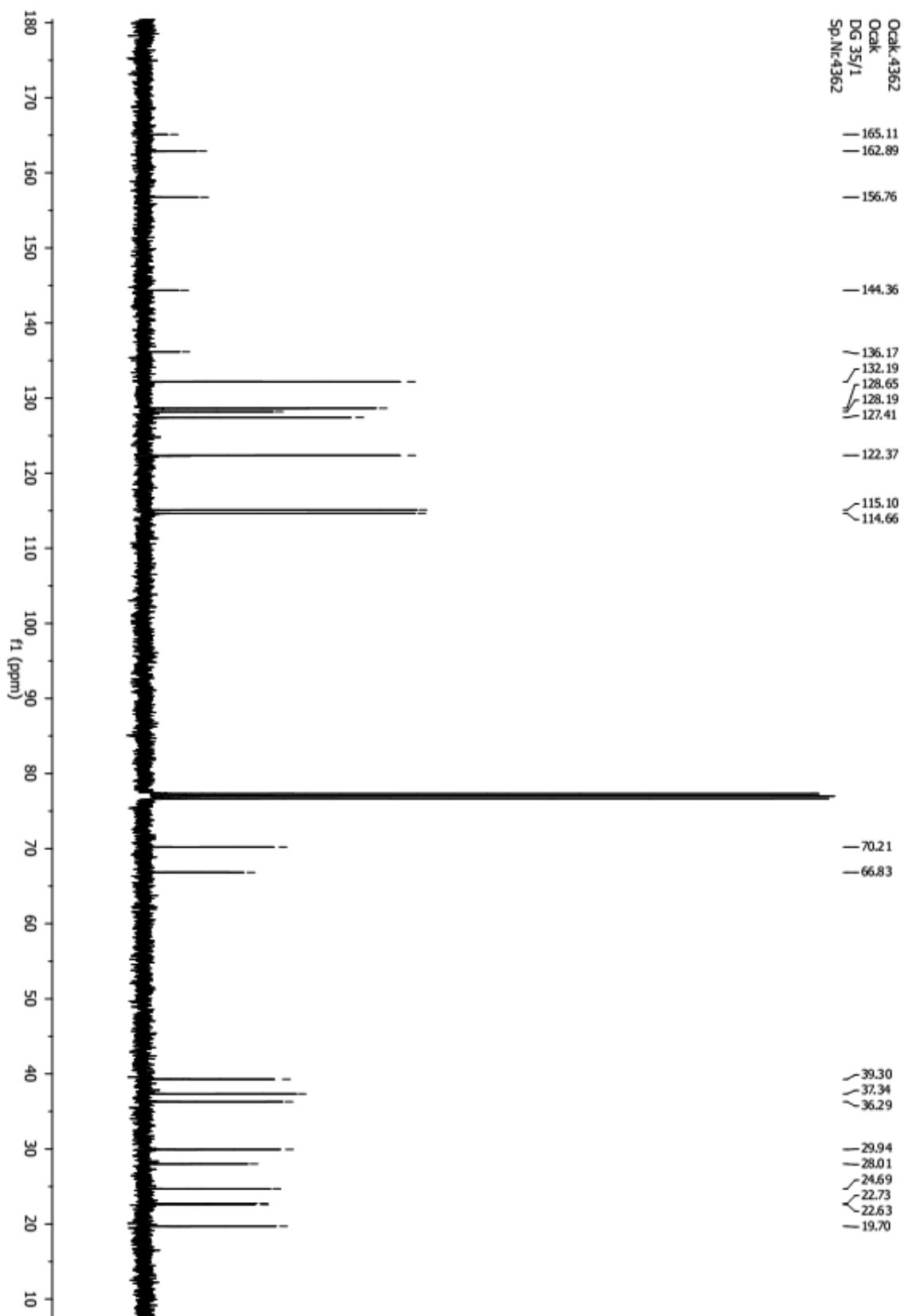


Figure S26. ^{13}C -NMR spectrum of 4-(3,7-dimethyloctyloxy)phenyl 4-benzyloxybenzoate (CDCl_3).

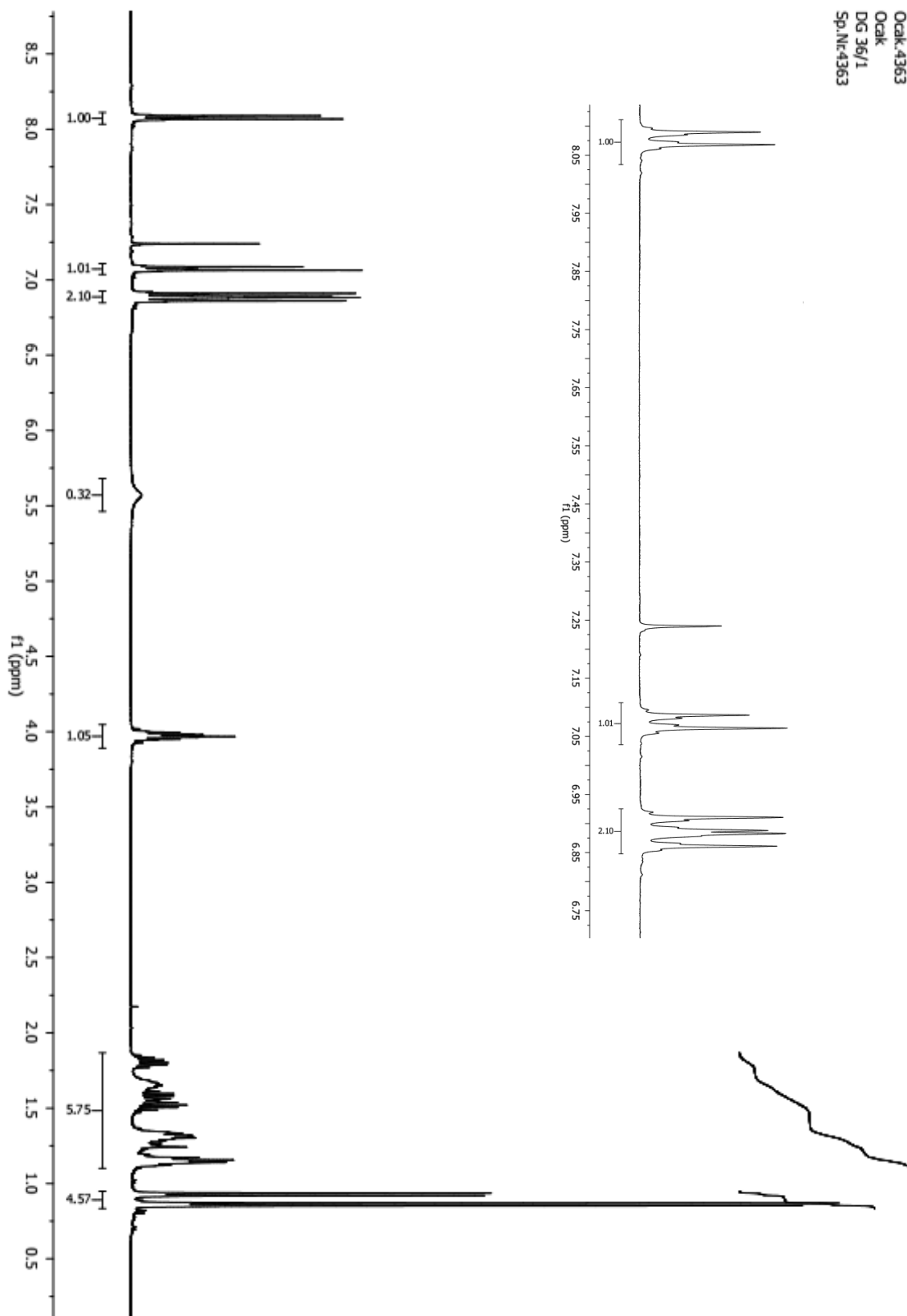


Figure S27. $^1\text{H-NMR}$ spectrum of 4-(3,7-dimethyloctyloxy)phenyl 4-hydroxybenzoate (CDCl_3).

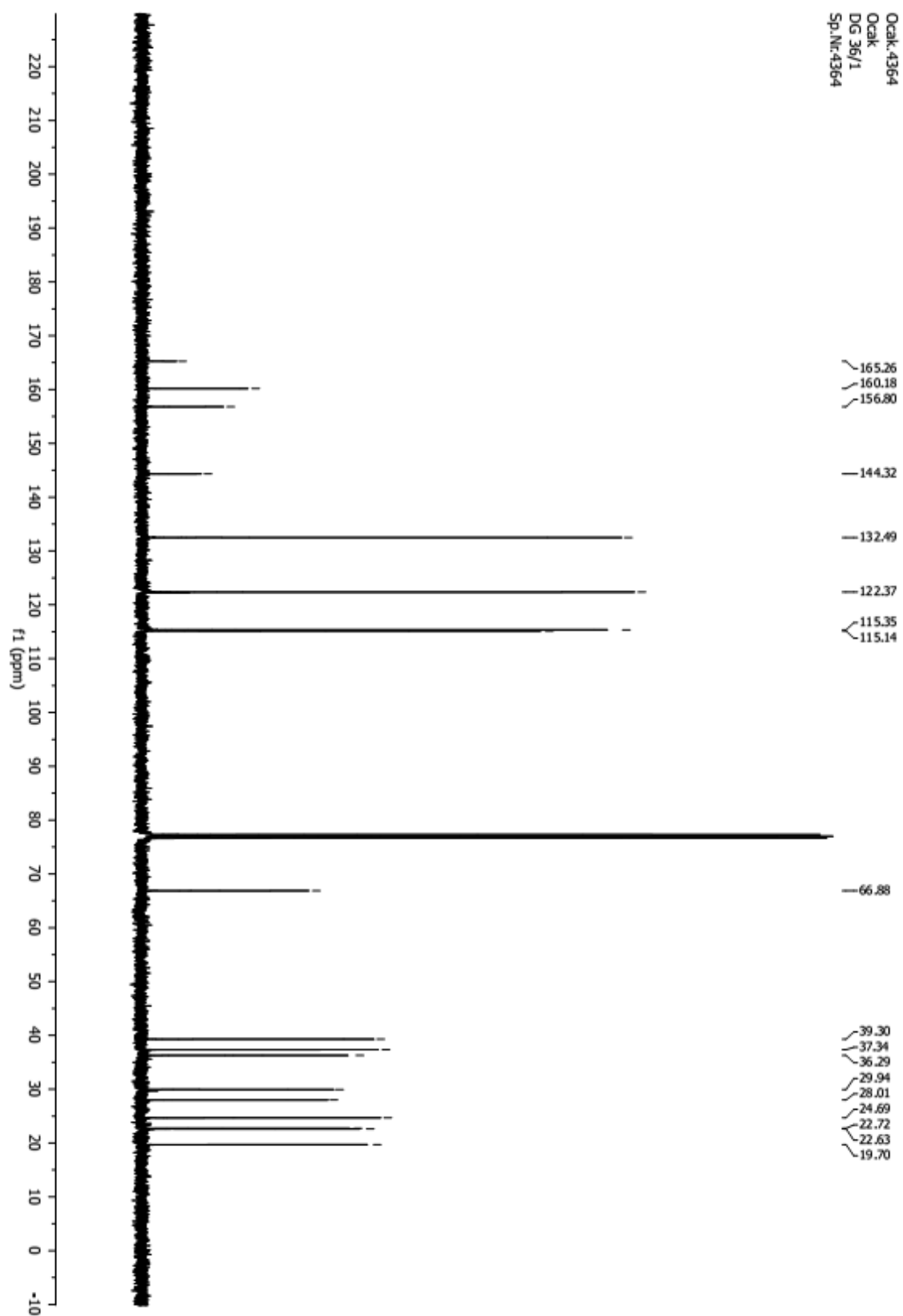


Figure S28. ^{13}C -NMR spectrum of 4-(3,7-dimethyloctyloxy)phenyl 4-hydroxybenzoate (CDCl_3).

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