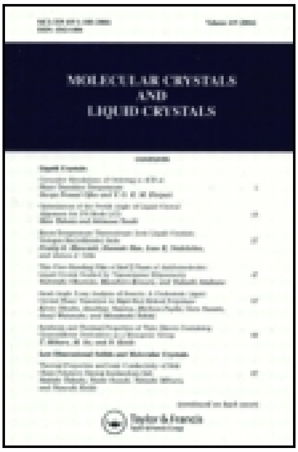

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The Chiral Pool as Valuable Natural Source: New Chiral Mesogens Made From Lactic Acid

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The Chiral Pool as Valuable Natural Source: New Chiral Mesogens Made From Lactic Acid

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Twenty new enantiopure chiral materials have been synthesized, showing liquid crystalline phases of smectic (SmA), twisted grain boundary (TGB) and cholesteric (N*) type. The central ester-linkage as well as the length of the attached alkyl-chains were varied in a systematic way and the effects of these structural changes on the liquid crystalline properties have been studied. The liquid crystalline phases were characterized by means of differential scanning calorimetry, polarisation microscopy as well as small angle X-ray diffraction (SAXS).*

Keywords Chiral pool; chirality; cholesteric phase; liquid crystals; smectic phase; synthesis

1. Introduction

Chiral liquid crystalline (LC) materials have gained increasing importance over the last few decades. Especially mesophases with a chiral tilt pattern of the mesogens have attracted the attention of physicists and chemists worldwide due to their importance for ferroelectric LC-displays, but also the chiral nematic (i.e., cholesteric) and SmA*-phase show interestung features (flexoelectric or electroclinic effect, respectively) which possibly could be applied in electro-optic devices [1–3]. A somewhat more exotic example of an application of chiral LC-phases is the movement of macroscopic objects on a liquid crystalline film [4].

In many mesogens of this kind the chirality is allocated in the aliphatic side-chain which is connected to the core via an ester or ether function. As starting materials for the syntheses of such esters or ethers most commonly enantiomerically pure secondary alkyl alcohols are used which have the disadvantage that they are comparatively expensive due to their difficult production. Therefore a reasonable approach for synthesizing chiral, enantiomerically pure low-cost materials is the use of chiral-pool materials like naturally occurring alcohols, amino-acids or the bifunctional lactic-acid. The latter is the approach which we follow here. The principal use of lactic acid in mesogenic structures is not completely new [5–7], but still the field is wide open and interesting to be explored.

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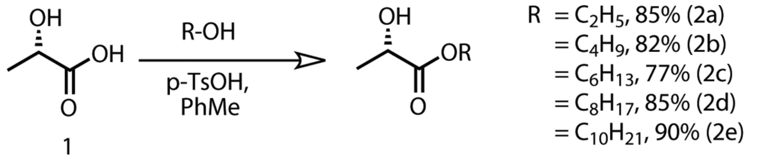


Figure 1. Fischer esterification of lactic acid with alcohols to yield the lactates **2a-e**.

2. Synthesis

The syntheses of the chiral homologue side chains started from commercially available (S)-lactic-acid (**1**) which was esterified under acid catalyzed conditions to yield the alkyl-lactates **2a-e** in enantiomerically pure form (Fig. 1).

The syntheses towards the stiff mesogen cores are shown in Figure 2. These core systems were synthesized via Steglich or acid chloride esterification reactions. For the synthesis of **13** the Steglich esterification failed. Instead, esterification with the respective acid chloride was successful (which previously was prepared from the carboxylic acid with $SOCl_2$). Afterwards, the resulting benzaldehydes were oxidized with Jones reagent to yield the carboxylic acids **5**, **7**, **10** and **13**. For all products, except for **13**, no extensive workup was required. Each precursor **5**, **7**, **10** and **13** was isolated and purified by a single recrystallisation in excellent purities. All these intermediates, the aldehydes resulting after the first step and the carboxylic acids **5**, **7**, **10** and **13** show thermotropic liquid crystalline behavior which will be reported elsewhere together with their detailed synthetic and analytic description.

By combining the five chiral alkyl-lactates **2a-e** with the four carboxylic acids **5**, **7**, **10** and **13** twenty new mesogens were synthesized using a modified Mitsunobu protocol in which di-*tert*-butyl azodicarboxylate (DTBAD) was used to simplify the purification of the final products: DTBAD decomposes in strong acids [8]. An example for this type of reaction is given in Figure 3. Details about the likewise syntheses of all the new chiral liquid crystalline compounds **14-17** are compiled in Table 1.

3. Thermomesomorphic Properties

The characterization of the mesophases of **14-17** was performed by means of polarization microscopy, differential scanning calorimetry and X-ray diffraction measurements.

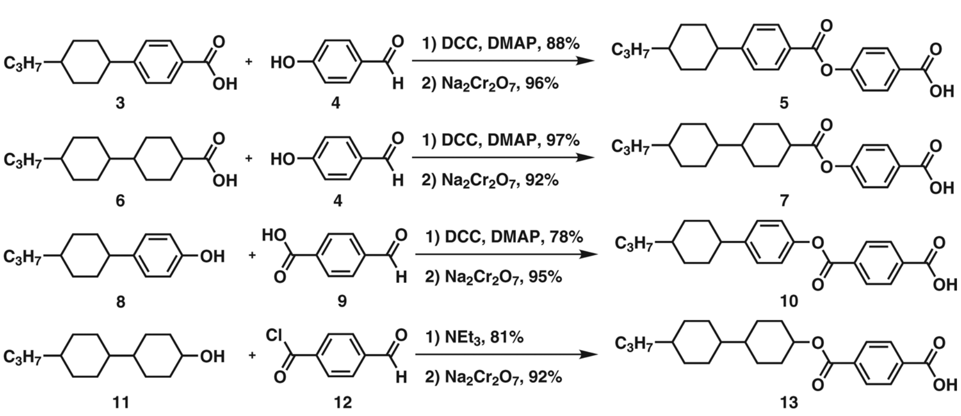


Figure 2. Synthesis of the four rigid core systems **5**, **7**, **10** and **13**.

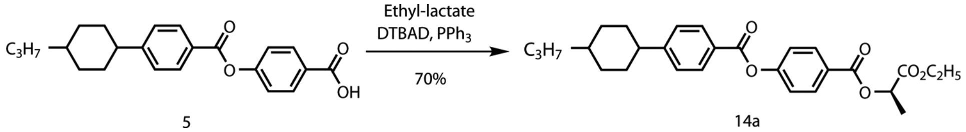


Figure 3. Modified Mitsunobu esterification on the example of **14a**. This principal method was used here to build all the target compounds **14-17**. The yield of 70% was obtained for this exemplified reaction; in general up to 88% of the desired product was isolated (cf. Table 1).

Instrumental details are given in the experimental part. The mesogenic properties of the synthesized new chiral mesogens are summarized in Table 2. Most interestingly, despite of its influence on the π-system of the mesogens, the orientation of the central ester linkage is not that much important for the thermotropic behavior of the compounds, but the nature of the bicyclic structure of the core system is. In case of the cyclohexyl phenyl core (series **14** and **16**), a cholesteric mesophase is found. Furthermore, the clearing temperatures of series **14** and **16** decrease with increasing chain length while the melting temperatures are comparable between both series. For the bicyclohexyl derivatives (series **15** and **17**) the clearing temperatures decrease with increasing chain length. The same trend is observed for the melting temperatures of **17**, except for n = 6 which is an outlier. In contrast to the cyclohexyl phenyl core mesogens (series **14** and **16**) all of the bicyclohexyl core mesogens (series **15** and **17**) developed smectic phases additionally to the cholesteric phase. In some cases

Table 1. Synthesized, chiral liquid crystalline compounds

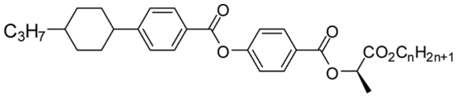
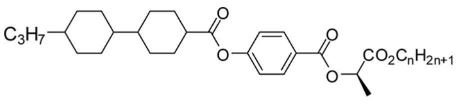
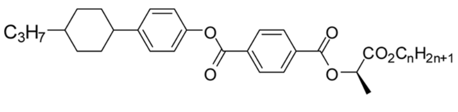
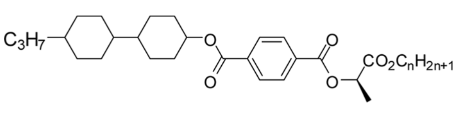
Carboxylic acid	Alcohol	Product	Yield (%)	
5	**2a**	**14a**	70	
5	**2b**	**14b**	76	
5	**2c**	**14c**	65	
5	**2d**	**14d**	54	
5	**2e**	**14e**	60	
7	**2a**	**15a**	52	
7	**2b**	**15b**	71	
7	**2c**	**15c**	75	
7	**2d**	**15d**	57	
7	**2e**	**15e**	68	
10	**2a**	**16a**	88	
10	**2b**	**16b**	48	
10	**2c**	**16c**	66	
10	**2d**	**16d**	45	
10	**2e**	**16e**	66	
13	**2a**	**17a**	75	
13	**2b**	**17b**	40	
13	**2c**	**17c**	50	
13	**2d**	**17d**	47	
13	**2e**	**17e**	35	

Table 2. Thermal data of the new chiral tricyclic ester series 14–17

	n	Cr		M1		SmA*		TGB[b]		Ch		I
14a	2	●	74/74.9 (17.0)	–		●	104/-	●	105/103.3 (0.8)	●	124/126.9 (0.2)	●
14b	4	●	81/82.1 (27.1)	–		–		–		●	106/108.7 (0.3)	●
14c	6	●	58/56.2 (23.0)	–		–		–		●	91/94.5 (0.1)	●
14d	8	●	53/53.6 (23.1)	–		–		–		●	78/81.0 (0.2)	●
14e	10	●	53/52.5 (21.1)	Sm[c]	62/60.4 (2.6)	–		–		●	71/72.5 (1.2)	●
15a	2	●	38/37.9 (12.4)	Sm[c]	120/118.8 (2.2)	●	129/127.2 (1.6)	–		●	144/146.0 (0.3)	●
15b	4	●	76/74.8 (32.6)	Sm[c]	97/95.3 (1.7)	●	112/109.3 (1.1)	–		●	130/130.1 (0.4)	●
15c	6	●	38/37.5 (14.6)	Sm[c]	71/69.0 (1.3)	●	92/90.8 (0.4)	–		●	115/113.3 (0.2)	●
15d	8	●	39/38.2 (14.0)	Sm[c]	49/47.9 (0.9)	●	77/-	●	78/76.0 (0.3)	●	102/103.5 (0.3)	●
15e	10	●	39/37.4 (31.9)	–		●	60/-	●	61/60.6 (0.2)	●	91/92.2 (0.4)	●
16a	2	●	87/85.5 (16.8)	Sm[c]	102/100.2 (5.0)	–		–		●	131/133.5 (0.3)	●
16b	4	●	65/68.1 (22.3)	–		–		–		●	115/116.7 (0.2)	●
16c	6	●	54/53.7 (22.1)	–		–		–		●	101/103.7 (0.3)	●
16d	8	●	43/41.8 (23.0)	–		–		–		●	95/93.3 (0.1)	●
16e	10	●	63/60.5 (43.0)	–		–		–		●	85/87.1 (0.4)	●
17a	2	●	93/92.2 (27.6)	Sm[c]	102/101.7 (1.7)	●	115/114.5 (0.8)	–		●	142/143.2 (0.3)	●
17b	4	●	65/65.3 (26.0)	Sm[c]	72/71.3 (1.0)	●	91/-	●	93/91.4 (0.3)	●	127/127.4 (0.3)	●
17c	6	●	35/47.9 (20.8)	–		●	68/-	●	69/67.0 (0.1)	●	117/115.8 (0.3)	●
17d	8	●	54/54.5 (21.8)	–		–		–		●	104/104 (0.2)	●
17e	10	●	49/49.7 (47.1)	Sm[c]	60/59.2 (0.9)	–		–		●	91/90.6 (0.2)	●

[a] PM/DSC [°C] (ΔH [kJ/mol]), Sm: smectic mesophase without subtype assignment, SmA*: chiral smectic A mesophase, TGB: twisted grain boundary mesophase without subtype assignment, Ch: cholesteric mesophase.

[b] Detected by PM only.

[c] Most likely a highly ordered smectic phase.

Table 3. Measured layer thicknesses in the SmA*-phase, calculated molecular length and intralayer molecular distances

Substance	Measured layer distance	Calculated molecular length	Intralayer molecular distance
15b	27.6 Å	26.9 Å	4.8 Å
15c	29.5 Å	29.0 Å	4.8 Å
15e	32.3 Å	33.7 Å	4.7 Å

(**14a**, **15d**, **15e**, **17b** and **17c**) a TGB phase could be observed between the SmA* and the cholesteric phase.

For compounds **15b**, **15c** and **15e** SAXS measurements were performed to determine the layer spacing of the SmA* phase. To compare these results with the respective molecular structure, the molecular length was estimated by simple force field simulations using Macromodel 9.0 with the implemented MM3 force field [9]. The results of these studies are listed in Table 3. In addition to the small angle X-ray diffraction studies also wide angle measurements were performed. When the samples were cooled below the temperature range of the SmA*-phase the broad, diffuse halo in the wide angle region sharpened and split up to give narrower circles which corresponds to the formation of order within the smectic layers.

4. Single Crystal X-Ray Structure and Circular Dichroism

Some single crystals for X-ray analysis could be grown from compound **16e.** However, the quality of the crystals was somewhat poor due to their sensitivity to mechanical stress. Although the obtained R-values of 15% for R1 and 12% for R2 are too large to meet crystallographic quality standards, the molecular structure could be clearly identified and the obtained crystal structure of **16e** is shown in Figure 4. Interestingly, the carbonyl oxygens of the central terephthalic acid unit have a dihedral-angle of 0.7° with respect to each other (and not of 180°) which is a rather uncommon feature in crystals for terephthalic acid derivatives. The absolute configuration of the stereogenic center could not be confirmed directly by these X-ray investigations due to the lack of heavier atoms than oxygen, but the expected retention of stereochemistry could be proven by the combination of the X-ray structure with circular dichroism (CD) measurements.

The CD spectrum of **16e** is depicted in Figure 5 and shows a negative Cotton effect at 240 nm. Putting the crystal structure of **16e** into the model of the octant rule, the negative sign of the Cotton effect could be rationalized (Fig. 6) and proves the expected retention of the (S)-configured stereo center throughout the synthesis.

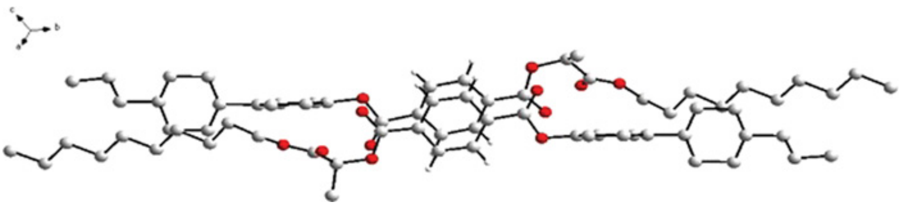


Figure 4. Two molecules of **16e** in their crystalline packing. (Figure appears in color online.)

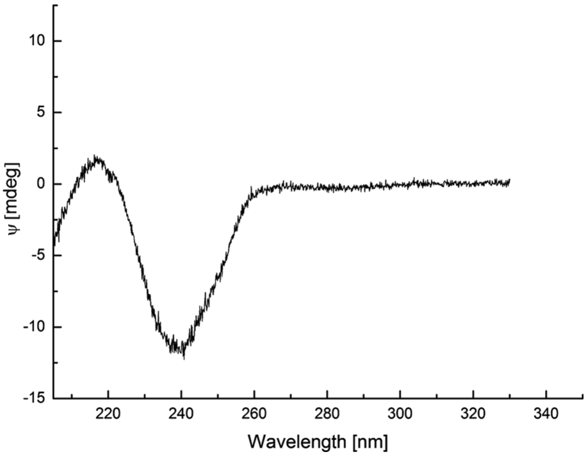


Figure 5. Circular dichroism spectrum of **16e**.

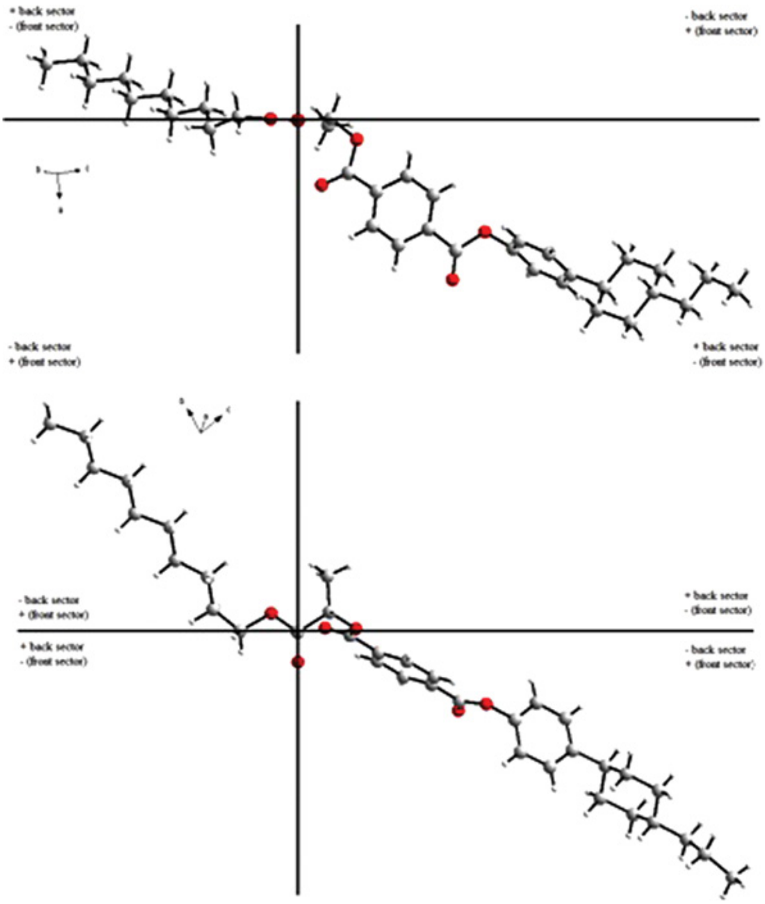


Figure 6. Carbonyl octant rule applied to **16e**, view along the C=O bond (upper part), view from the top (lower part). (Figure appears in color online.)

Quantum chemical calculations in order to separate the contribution of each of the two carbonyl chromophores in the vicinity of the stereocenter to the CD spectrum are in progress.

5. Summary and Perspectives

Twenty new enantiomerically pure thermomesomorphic compounds were synthesized (series **14-17**), each in three linear synthetic steps from commercially available building blocks with their chirality originating from cheap lactic acid. With these compounds the influence of the reversion of the central ester linkage as well as the changes in the mesomorphic properties in cases of either a bicyclohexyl or cyclohexylphenyl core substructure have been investigated. Especially the mesogens **15c** and **17c** with medium long aliphatic chains show melting temperatures close to room temperature and a broad temperature range of their SmA* phase. For all compounds a short pitch cholesteric phase was found, partly accompanied with smectic or TGB phases.

Currently we are investigating the influence of replacing the central phenyl ring of the terephthalic acid or hydroxybenzoic acid substructures, respectively, with a biphenyl system. With these systems we expect a stabilization of smectic phases but also higher melting points.

6. Experimental

6.1. *Instruments*

^{1}H-NMR. The ^{1}H-NMR spectra were recorded on Bruker AC 300, Bruker DPX 300 or on Bruker DRX 500 instruments. Chemical shifts are reported as δ in ppm, coupling constants J in Hz. DMSO-d6 ($\delta = 2.49$ ppm) or $CDCl_3$ ($\delta = 7.24$ ppm) were used as solvents, respectively, and the peaks of their undeuterated parts were used as internal standard. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet).

^{13}C-NMR. The ^{13}C-NMR spectra were recorded as APT spectra either on a Bruker AC 300 or on a Bruker DRX 500 instrument.

Mass Spectrometry. (HR-MS) were recorded on a *Finnigan* MAT 900S. The method of ionization is given individually with each spectrum in parentheses.

Elemental Analysis. Elementar Vario EL.

Differential Scanning Calorimetry (DSC). Mettler DSC TA3000, heating rate 5 K/min, cooling rate 10 K/min.

Polarization Microscopy (PM). Leitz Laborlux 12 Pol.

Small and Wide Angle X-Ray Scattering (SAXS and WAXS). X-Ray measurements were performed using aligned samples (filled in 0.7 mm Mark capillars) with a Bruker AXS NanoSTAR with a 2D-detector.

6.2. *Synthetic Precursors*

The aldehydes and carboxylic acids **5**, **7**, **10** and **13** were synthesized according to Figure 2 by using standard procedures. Exact reaction conditions as well as analytical data of these substances are available from the author on request.

6.3. *General Procedure for the Mitsunobu Esterification*

Under Argon-Atmosphere a Schlenck-flask was charged with 1 mmol of carboxylic acid **5**, **7**, **10** or **13**, respectively, and 1 mmol of PPh_3. Afterwards dry THF and 1 mmol of the corresponding alcohol **2a-e** were added. To this solution 1 equivalent of DTBAD was added in small portions. The progress of the reaction was followed by TLC. After completion of the reaction the solvent was removed and the target compound was isolated via flash-chromatography with ethylacetate/cyclohexane as mobile phase and silica gel as stationary phase.

6.4. *Analytical Data*

The atom numbers in the structure drawings apply to the assignments given in the spectra and do not follow the IUPAC scheme used for the naming of the compounds. IR and LR-MS of all compounds are available from the authors on request.

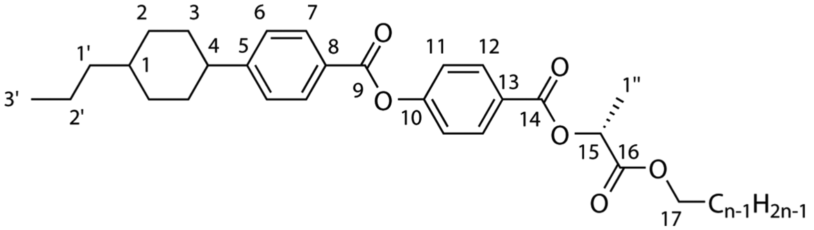


Figure 7.

4-({[(2R)-1-Ethoxy-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4-(4-propylcyclohexyl)benzoate ***14a***, *n = 2.* δ_H (300 MHz; $CDCl_3$) = 8.12 (m, 4H; 7-H, 12-H), 7.30 (m, 4H; 6-H, 11-H), 5.31 (q, *J* = 7.0 Hz, 1H; 15-H), 4.23 (q, *J* = 7.1 Hz, 2H; 17-H), 2.55 (m, 1H; 4-H), 1.89 (m, 4H), 1.34 (m, 18H). δ_C(75 MHz; $CDCl_3$) = 170.3 (C16), 164.8 (C14), 164.2 (C9), 154.6 (C10), 154.1 (C5), 131.0 (C7/C12), 130.0 (C7/C12), 126.8 (C6), 126.6 (C8/C13), 126.2 (C8/C13), 121.4 (C11), 68.8 (C15), 61.0 (C17), 44.4 (C4), 39.2, 36.5, 33.6 (2C), 32.9 (2C), 19.6, 16.7, 13.9, 13.7. HR-MS (EI, 70 eV); *m/z*: 466.236 (calc. 466.2355). EA: Found: C, 72.077; H, 7.3424. $C_{28}H_{34}O_6$ calculated C, 72.08; H, 7.35%.

4-({[(2R)-1-Butoxy-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4-(4-propylcyclohexyl)benzoate ***14b***, *n = 4.* δ_H (300 MHz; $CDCl_3$) = 8.12 (m, 4H; 7-H, 12-H), 7.30 (m, 4H; 6-H, 11-H), 5.31 (q, *J* = 7.0 Hz, 1-H; 15-H), 4.16 (m, 2H; 18-H), 2.55 (m, 1H; 4-H), 1.89 (m, 4H; 3-H), 1.34 (m, 22H). δ_C(75 MHz; $CDCl_3$) = 170.8 (C16), 165.2 (C14), 164.6 (C9), 155.0 (C10), 154.5 (C5), 131.4 (C7/C12), 130.4 (C7/C12), 127.2 (C6), 127.0 (C8/C13), 126.6 (C8/C13), 121.8 (C11), 69.3 (C15), 65.2 (C17), 44.9 (C4), 39.6, 36.9, 34.0 (2C), 33.4 (2C), 30.5, 20.0, 19.0, 17.1, 14.4, 13.6. HR-MS (EI, m/z): 494.267 (calc. 494.2668). EA: Found: C, 72.652; H, 7.7572. $C_{30}H_{38}O_6$ calculated C, 72.85; H, 7.74%.

4-({[(2R)-1-Hexyloxy-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4-(4-propylcyclohexyl)benzoate ***14c***, *n = 6.* δ_H(300 MHz; $CDCl_3$) = 8.12 (m, 4H; 7-H, 12-H), 7.30 (m, 4H; 6-H, 11-H), 5.31 (q, *J* = 7.0 Hz, 1-H; 15-H), 4.16 (m, 2H; 18-H), 2.55 (m, 1H; 4-H), 1.89 (m, 4H; 3-H), 1.34 (m, 26H). δ_C(75 MHz; $CDCl_3$) = 170.8 (C16), 165.2 (C14), 164.6 (C9), 155.0 (C10), 154.5 (C5), 131.4 (C7/C12), 130.4 (C7/C12), 127.2 (C6), 127.0 (C8/C13), 126.6 (C8/C13), 121.8 (C11), 69.3 (C15), 65.6 (C17), 44.9 (C4), 44.9, 39.7, 37.0, 34.0 (2C), 33.4 (2C), 31.4, 28.5, 25.4, 22.5, 20.0, 17.1, 14.4, 13.6. HR-MS (EI, 70 eV); *m/z*: 522.297 (calc. 522.2981). EA: Found: C, 73.561; H 8.0388,. $C_{32}H_{42}O_6$ calculated C, 73.53; H, 8.10%.

4-({[(2R)-1-Octyloxy-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4-(4-propylcyclohexyl)benzoate ***14d****, n = 8.* δ_H(300 MHz; $CDCl_3$) = 8.12 (m, 4H; 7-H, 12-H), 7.30 (m, 4H; 6-H, 11-H), 5.31 (q, *J* = 7.0 Hz, 1-H; 15-H), 4.16 (m, 2H; 18-H), 1.34 (m, 30H). δ_C(75 MHz; $CDCl_3$) = 170.8 (C16), 165.2 (C14), 164.6 (C9), 155.0 (C10), 154.5 (C5), 131.4 (C7/C12), 130.4 (C7/C12), 127.2 (C6), 127.0 (C8/C13), 126.6 (C8/C13), 121.8 (C11), 69.3 (C15), 65.5 (C17), 44.9 (C4), 44.9, 39.6, 36.9, 34.0 (2C), 33.4 (2C), 31.7, 29.1 (2C), 28.5, 25.8, 22.6, 20.0, 17.1, 14.4, 14.1. HR-MS (ESI, 70 eV; MeOH); *m/z*: 573.319 (calc. 573.3192) $[M+Na]^+$. EA: Found: C, 74.259; H, 8.4967. $C_{34}H_{46}O_6$ calculated C, 74.15; H, 8.42%.

4-({[(2R)-1-Decyloxy-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4-(4-propylcyclohexyl)benzoate ***14e****, n = 10.* δ_H(300 MHz; $CDCl_3$) = 8.12 (m, 4H; 7-H, 12-H), 7.30 (m, 4H; 6-H, 11-H), 5.31 (q, *J* = 7.0 Hz, 1-H; 15-H), 4.16 (m, 2H; 18-H), 1.34 (m, 34H). δ_C(75 MHz; $CDCl_3$) = 170.8 (C16), 165.2 (C14), 164.6 (C9), 155.0 (C10), 154.5 (C5), 131.4 (C7/C12), 130.4 (C7/C12), 127.2 (C6), 127.0 (C8/C13), 126.6 (C8/C13), 121.8 (C11), 69.3 (C15), 65.5 (C17), 44.8 (C4), 39.6, 36.9, 34.0 (2C), 33.4 (2C), 31.8, 29.5 (2C), 29.2, 29.1, 28.4, 25.7, 22.6, 19.9, 17.1, 14.3, 14.1. HR-MS (ESI, 70 eV; MeOH); *m/z*: 601.351 (calc. 601.3505) $[M+Na]^+$. EA: Found: C, 74.716; H, 8.7780. $C_{36}H_{50}O_6$ calculated C, 74.71; H, 8.71%.

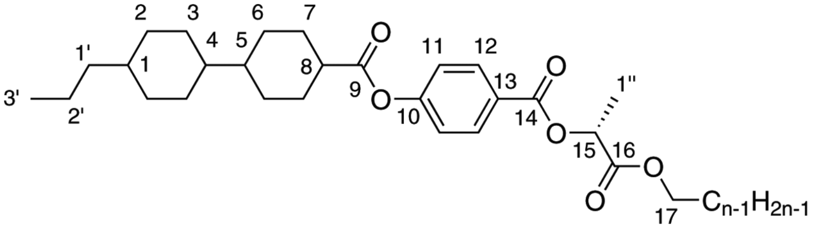


Figure 8.

4-({[(2R)-1-Ethoxy-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4-(4-propylcyclohexyl) cyclohexane-1-carboxylate ***15a****, n = 2.* δ_H(300 MHz; $CDCl_3$) = 8.08 (d, *J* = 8.7 Hz, 2H; 12-H), 7.13 (d, *J* = 8.7 Hz, 2H; 11-H), 5.28 (q, *J* = 7.0 Hz, 1H; 15-H), 4.21 (q, *J* = 7.1 Hz, 2H; 17-H), 2.45 (m, 1H; 8-H), 2.14 (d, *J* = 12.1 Hz, 2H; 7-H), 1.50 (m, 30H). δ_C(75 MHz; $CDCl_3$) = 174.1 (9-C), 170.7 (16-C), 165.2 (14-C), 154.9 (10-C), 131.4 (12-C), 126.8 (13-C), 121.6 (11-C), 69.2 (15-C), 61.4 (17-C), 43.7, 43.2, 42.5, 39.8, 37.6, 33.5 (2C), 30.0 (2C), 29.2 (2C), 29.1 (2C), 20.0, 17.1, 14.4, 14.1. HR-MS (EI, 70 eV); *m/z*: 472.283 (calc. 472.2825). EA: Found: C,71.054 ; H, 8.5263. $C_{28}H_{40}O_6$ calculated C, 71.16; H, 8.53%.

4-({[(2R)-1-Butoxy-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4-(4-propylcyclohexyl) cyclohexane-1-carboxylate ***15b****, n = 4.* δ_H(300 MHz; $CDCl_3$) = 8.08 (d, *J* = 8.6 Hz, 2H; 12-H), 7.13 (d, *J* = 8.6 Hz, 2H; 11-H), 5.28 (q, *J* = 7.0 Hz, 1H; 15-H), 4.15 (m, 2H, 17-H), 2.45 (m, 1H; 8-H), 2.14 (d, $J = 12.1$ Hz, 2H; 7-H), 1.50 (m, 34H). δ_C(75 MHz; $CDCl_3$) = 174.1 (9-C), 170.7 (16-C), 165.2 (14-C), 154.9 (10-C), 131.4 (12-C), 126.8 (13-C), 121.6 (11-C), 69.2 (15-C), 65.3 (17-C), 43.7, 43.2, 42.5, 39.8, 37.6, 33.5 (2C), 30.5, 30.0 (2C), 29.3 (2C), 29.1 (2C), 20.0, 19.0, 17.1, 14.4, 13.7. HR-MS (EI, 70 eV); m/z: 500.313 (calc. 500.3138). EA: Found: C, 72.186; H, 8.8348. $C_{30}H_{44}O_6$ calculated C, 71.97; H, 8.86%.

4-({[(2R)-1-Hexyloxy-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4-(4-propylcyclohexyl) cyclohexane-1-carboxylate ***15c****, n = 6.* δ_H(300 MHz; $CDCl_3$) = 8.08 (d, $J = 8.6$ Hz, 2H; 12-H), 7.13 (d, $J = 8.7$ Hz, 2H; 11-H), 5.29 (q, $J = 7.0$ Hz, 1H; 15-H), 4.13 (m, 2H; 17-H), 2.45 (m, 1H; 8-H), 2.14 (d, $J = 12.2$ Hz, 2H; 7-H), 1.50 (m, 38H). δ_C(75 MHz; $CDCl_3$) = 174.1 (9-C), 170.7 (16-C), 165.2 (14-C), 154.9 (10-C), 131.4 (12-C), 126.8 (13-C), 121.6 (11-C), 69.2 (15-C), 65.5 (17-C), 43.7, 43.2, 42.5, 39.8, 37.6, 33.5 (2C), 31.3, 30.0 (2C), 29.3 (2C), 29.1 (2C), 28.4, 25.4, 22.5, 20.0, 17.1, 14.4, 13.7. HR-MS (EI, 70 eV); m/z: 528.345 (calc. 528.3451). EA: Found: C, 72.672; H, 9.1451. $C_{32}H_{48}O_6$ calculated C, 72.69; H, 9.15%.

4-({[(2R)-1-Octyloxy-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4-(4-propylcyclohexyl) cyclohexane-1-carboxylate ***15d****, n = 8.* δ_H(300 MHz; $CDCl_3$) = 8.08 (d, $J = 8.6$ Hz, 2H; 12-H), 7.13 (d, $J = 8.7$ Hz, 2H; 11-H), 5.29 (q, $J = 7.0$ Hz, 1H; 15-H), 4.13 (m, 2H; 17-H), 2.45 (m, 1H; 8-H), 2.14 (d, $J = 12.2$ Hz, 2H; 7-H), 1.50 (m, 42H). δ_C(75 MHz; $CDCl_3$) = 174.1 (9-C), 170.7 (16-C), 165.2 (14-C), 154.9 (10-C), 131.4 (12-C), 126.8 (13-C), 121.6 (11-C), 69.2 (15-C), 65.5 (17-C), 43.7, 43.2, 42.5, 39.8, 37.6, 33.5 (2C), 31.7, 30.0 (2C), 29.2 (2C), 29.1 (2C), 29.0 (2C), 28.5, 25.7, 22.6, 20.0, 17.1, 14.4, 14.1. HR-MS (EI, 70 eV); m/z: 556.3766 (calc. 556.3764). EA: Found: C, 73.405; H, 9.4615. $C_{34}H_{52}O_6$ calculated C, 73.34; H, 9.41%.

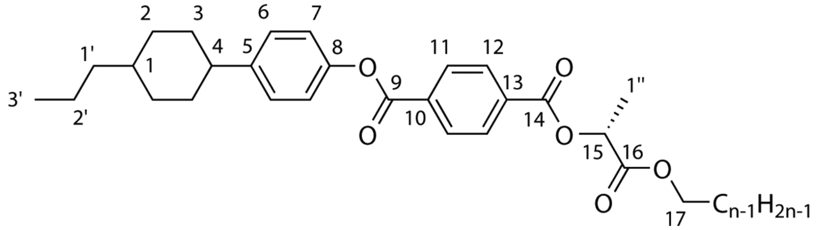


Figure 9.

4-({[(2R)-1-Decyloxy-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4-(4-propylcyclohexyl) cyclohexane-1-carboxylate ***15e****, N = 10.* δ_H(300 MHz; $CDCl_3$) = 8.08 (d, $J = 8.7$ Hz, 2H; 12-H), 7.13 (d, $J = 8.7$ Hz, 2H; 11-H), 5.28 (q, $J = 7.1$ Hz, 1H; 15-H), 4.15 (m, 2H, 17-H), 2.45 (m, 1H; 8-H), 2.14 (d, $J = 12.3$ Hz, 2H; 7-H), 1.50 (m, 46H). δ_C(75 MHz; $CDCl_3$) = 174.1 (9-C), 170.7 (16-C), 165.2 (14-C), 154.9 (10-C), 131.4 (12-C), 126.8 (13-C), 121.6 (11-C), 69.2 (15-C), 65.5 (17-C), 43.7, 43.2, 42.5, 39.8, 37.6, 33.5 (2C), 31.9, 30.0 (2C), 29.5, 29.3 (2C), 29.2 (2C), 29.1 (2C), 28.5, 26.9, 25.7, 22.7, 20.0, 17.1, 14.4, 13.7. HR-MS (EI, 70 eV); m/z: 584.407 (calc. 584.4077). EA: Found: C, 73.725; H, 9.6296. $C_{36}H_{56}O_6$ calculated C, 73.93; H, 9.65%.

4-(4-Propylcyclohexyl)phenyl 4-({[(2R)-1-ethoxy-1-oxopropan-2-yl]oxy}carbonyl)benzoate ***16a****, n = 2.* δ_H(300 MHz; $CDCl_3$) = 8.22 (m, 4H; 11-H, 12-H), 7.25 (d, $J = 6.9$ Hz, 2H; 6-H), 7.12 (d, $J = 8.5$ Hz, 2H; 7-H) 5.34 (q, 1H, $J = 7.1$ Hz; 15-H), 4.21 (q,

$J = 7.1$ Hz, 2H; 17-H), 2.48 (m, 1H; 4-H), 1.88 (t, $J = 11.4$ Hz, 4H; 3-H), 1.64 (d, $J = 7.1$ Hz, 3H; 1″-H), 1.28 (m, 12H), 0.89 (t, $J = 6.9$ Hz, 3H; 3′-H). δ_C(75 MHz; $CDCl_3$) = 170.5 (C-16), 165.1 (C-9/C-13), 164.5 (C-9/C-13), 148.6 (C-8), 145.7 (C-5), 133.8 (C-13, C-10), 130.1 (C-11/C-12), 129.9 (C-11/C-12), 127.8 (C-6), 121.1 (C-7), 69.6 (C-1″), 61.5 (C-17), 44.1 (C-4), 39.7 (C-1′), 37.0 (C-1), 34.4 (C-2/C-3), 33.5 (C-2/C3), 20.0 (C-2′), 17.0 (C-3), 14.4 (C-18), 14.1 (C-3′). HR-MS (EI, 70 eV); m/z: 466.235 (calc. 466.2355). EA: Found: C, 71.995; H, 7.3788. $C_{28}H_{34}O_6$ calculated C, 72.08; H, 7.35%.

4-(4-Propylcyclohexyl)phenyl 4-({[(2R)-1-butoxy-1-oxopropan-2-yl]oxy}carbonyl)benzoate ***16b****, n = 4.* δ_H(300 MHz; $CDCl_3$) = 8.22 (m, 4H; 11-H, 12-H), 7.25 (d, $J = 6.9$ Hz, 2H; 6-H), 7.12 (d, $J = 8.5$ Hz, 2H; 7-H), 5.34 (q, $J = 7.1$ Hz, 1H; 15-H), 4.18 (t, $J = 6.4$ Hz, 2H; 17-H), 2.48 (m, 1H; 4-H), 1.88 (t, $J = 11.5$ Hz, 4H; 3-H), 1.64 (d, $J = 7.1$ Hz, 3H; 1”-H), 1.28 (m, 19H). δ_C(75 MHz; $CDCl_3$) = 170.5 (C-16), 165.1 (C-9/C-13), 164.5 (C-9/C-13), 148.6 (C-8), 145.7 (C-5), 133.8 (C-13, C-10), 130.1 (C-11/C-12), 129.9 (C-11/C-12), 127.8 (C-6), 121.1 (C-7), 69.6 (C-1″), 65.3, 44.0, 39.6, 36.9, 34.3 (2C), 33.5 (2C), 30.4, 20.0, 18.9, 17.0, 14.3, 13.6. HR-MS (EI, 70 eV); m/z: 494.266 (calc. 494.2668). EA: Found: C, 72.781; H, 7.7700. $C_{30}H_{38}O_6$ calculated C, 72.85; H, 7.74%.

4-(4-Propylcyclohexyl)phenyl 4-({[(2R)-1-hexyloxy-1-oxopropan-2-yl]oxy}carbonyl)benzoate ***16c****, n = 6.* δ_H(300 MHz; $CDCl_3$) = 8.22 (m, 4H; 11-H, 12-H), 7.25 (d, $J = 6.9$ Hz, 2H; 6-H), 7.12 (d, $J = 8.5$ Hz, 2H; 7-H), 5.34 (q, $J = 7.0$ Hz, 1H; 15-H), 4.15 (m, 2H; 17-H), 2.48 (m, 1H; 4-H), 1.88 (t, $J = 11.5$ Hz, 4H; 3-H), 1.64 (d, $J = 7.1$ Hz, 3H; 1″-H), 1.28 (m, 23H). δ_C(75 MHz; $CDCl_3$) = 170.5 (C-16), 165.1 (C-9/C-13), 164.5 (C-9/C-13), 148.6 (C-8), 145.7 (C-5), 133.7 (C-13, C-10), 130.1 (C-11/C-12), 129.9 (C-11/C-12), 127.8 (C-6), 121.1 (C-7), 69.6 (C-1″), 65.6, 44.0, 39.6, 36.9, 34.3 (2C), 33.5 (2C), 31.3, 28.4, 25.4, 22.4, 20.0, 17.0, 14.3, 13.9. HR-MS (EI, 70 eV); m/z: 522.298 (calc. 522.2981). EA: Found: C, 73.466; H, 8.1220. $C_{32}H_{42}O_6$ calculated C, 73.53; H, 8.10%.

4-(4-Propylcyclohexyl)phenyl 4-({[(2R)-1-octyloxy-1-oxopropan-2-yl]oxy}carbonyl) benzoate ***16d****, n = 8.* δ_H(300 MHz; $CDCl_3$) = 8.22 (m, 4H; 11-H, 12-H), 7.25 (d, $J = 6.9$ Hz, 2H; 6-H), 7.12 (d, $J = 8.5$ Hz, 2H; 7-H), 5.34 (q, $J = 7.0$ Hz, 1H; 15-H), 4.15 (m, 2H; 17-H), 2.48 (m, 1H; 4-H), 1.88 (t, $J = 11.5$ Hz, 4H; 3-H), 1.64 (d, $J = 7.1$ Hz, 3H; 1″-H), 1.28 (m, 27H). δ_C(75 MHz; $CDCl_3$) = 170.5 (C-16), 165.1 (C-9/C-13), 164.5 (C-9/C-13), 148.6 (C-8), 145.7 (C-5), 133.8 (C-13, C-10), 130.1 (C-11/C-12), 129.9 (C-11/C-12), 127.8 (C-6), 121.1 (C-7), 69.7 (C-1″), 65.7, 44.0, 39.6, 36.9, 34.3 (2C), 33.5 (2C), 31.8, 29.2, 31.3, 28.4, 25.4, 22.4, 20.0, 17.0, 14.3, 13.9. HR-MS (EI, 70 eV); m/z: 550.329 (calc. 550.3294). EA: Found: C, 74.021; H, 8.4327. $C_{34}H_{46}O_6$ calculated C, 74.15; H, 8.42%.

4-(4-Propylcyclohexyl)phenyl 4-({[(2R)-1-decyloxy-1-oxopropan-2-yl]oxy}carbonyl)benzoate ***16e****, n = 10.* δ_H(300 MHz; $CDCl_3$) = 8.22 (m, 4H; 11-H, 12-H), 7.25 (d, $J = 6.9$ Hz, 2H; 6-H), 7.12 (d, $J = 8.5$ Hz, 2H; 7-H), 5.34 (q, $J = 7.0$ Hz, 1H; 15-H), 4.15 (m, 2H; 17-H), 2.48 (m, 1H; 4-H), 1.88 (t, $J = 11.5$ Hz, 4H; 3-H), 1.64 (d, $J = 7.1$ Hz, 3H; 1″-H), 1.28 (m, 31H). δ_C(75 MHz; $CDCl_3$) = 170.5 (C-16), 165.1 (C-9/C-13), 164.5 (C-9/C-13), 148.6 (C-8), 145.7 (C-5), 133.8 (C-13, C-10), 130.1 (C-11/C-12), 129.9 (C-11/C-12), 127.8 (C-6), 121.1 (C-7), 69.6 (C-1″), 65.6, 44.0, 39.6, 36.9, 34.3 (2C), 33.5 (2C), 31.8, 29.4 (2C), 29.2, 29.1, 28.4, 25.7, 22.6, 20.0, 17.0, 14.4, 14.1. HR-MS (EI, 70 eV); *m*/*z*: 578.360 (calc. 578.3607). EA: Found: C, 74.225; H, 8.6944. $C_{36}H_{50}O_6$ calculated C, 74.71; H, 8.71%.

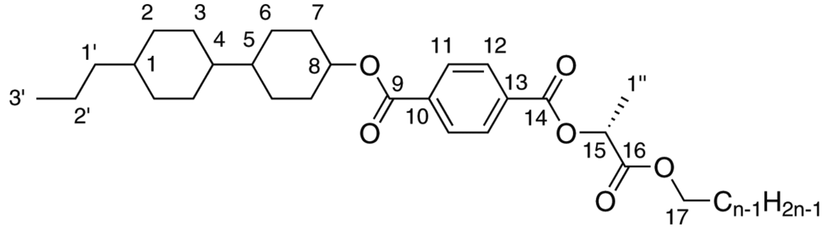


Figure 10.

4-(4-Propylcyclohexyl)cyclohexyl 4-({[(2R)-1-ethoxy-1-oxopropan-2-yl]oxy}carbonyl) benzoate ***17a**, n = 2.* δ_H(300 MHz; $CDCl_3$) = 8.09 (m, 4H; 11-H, 12-H), 5.31 (q, *J* = 7.0 Hz, 1H; 15-H), 4.88 (m, 1H; 8-H), 4.23 (q, *J* = 7.1 Hz, 2H; 17-H), 2.11 (m, 2H; 7-H), 1.20 (m, 30H). δ_C(75 MHz; $CDCl_3$) = 170.5 (C-16), 165.2 (C-9, C-14), 135.0 (C-10/C-13), 132.9 (C-10/C-13), 129.6 (C-11/C-12), 129.4 (C-11/C-12), 74.9 (C-8), 69.5 (C-15), 61.4 (C-17), 42.7, 42.2, 39.7, 37.5, 33.4 (2C), 31.9 (2C), 30.1 (2C), 27.9 (2C), 20.0, 17.0 (C-1′), 14.4 (C-18), 14.0 (C-3′). HR-MS (ESI, 70 eV; MeOH); *m*/*z*: 495.272 (calc. 495.2722) $[M+Na]^+$. EA: Found: C, 71.136; H, 8.5667. $C_{28}H_{40}O_6$ calculated C, 71.16; H, 8.53%.

4-(4-Propylcyclohexyl)cyclohexyl 4-({[(2R)-1-butoxy-1-oxopropan-2-yl]oxy}carbonyl) benzoate ***17b**, n = 4.* δ_H(300 MHz; $CDCl_3$) = 8.09 (m, 4H; 11-H, 12-H), 5.31 (q, *J* = 7.0 Hz, 1H; 15-H), 4.16 (m, 2H; 17-H), 2.11 (m, 2H; 7-H), 1.20 (m, 34H). δ_C(75 MHz; $CDCl_3$) = 170.6 (C-16), 165.2 (C-14, C-9), 135.0 (C10/C13), 133.0 (C10/C13), 129.7 (C-12/C-11), 129.5 (C-12/C-11), 75.0 (C-8), 69.6 (C-15), 65.3 (C-17), 42.8 (C-5/C-4), 42.3 (C-5/C-4), 39.8 (C-1′), 37.6, 33.5 (2C), 32.0 (2C), 30.5, 30.2 (2C), 28.0 (2C), 20.1, 19.0, 17.1, 14.4, 13.6. HR-MS (EI, 70 eV); *m*/*z*: 500.314 (calc. 500.3138). EA: Found: C, 71.793; H, 8.8316. $C_{30}H_{44}O_6$ calculated C, 71.97; H, 8.86%.

4-(4-Propylcyclohexyl)cyclohexyl 4-({[(2R)-1-hexyloxy-1-oxopropan-2-yl]oxy}carbonyl) benzoate ***17c**, n = 6.* δ_H(300 MHz; $CDCl_3$) = 8.09 (m, 4H; 11-H, 12-H), 5.31 (q, *J* = 7.0 Hz, 1H; 15-H), 4.14 (m, 2H; 17-H), 2.11 (m, 2H; 7-H), 1.20 (m, 38H). δ_C(75 MHz; $CDCl_3$) = 170.6 (C-16), 165.2 (C-14, C-9), 135.0 (C10/C13), 133.0 (C10/C13), 129.7 (C-12/C-11), 129.5 (C-12/C-11), 75.0 (C-8), 69.5 (C-15), 65.6 (C-17), 42.7 (C-5/C-4), 42.2 (C-5/C-4), 39.8 (C-1′), 37.5, 33.5(2C), 31.9 (2C), 31.3, 30.2 (2C), 28.4, 27.9 (2C), 25.4, 22.5, 20.0, 17.1, 14.4, 13.9. HR-MS (ESI, 70 eV; MeOH); *m*/*z*: 551.335 (calc. 551.3349) $[M+Na]^+$. EA: Found: C, 72.595; H, 9.1522. $C_{32}H_{48}O_6$ calculated C, 72.69; H, 9.15%.

4-(4-Propylcyclohexyl)cyclohexyl 4-({[(2R)-1-octyloxy-1-oxopropan-2-yl]oxy}carbonyl) benzoate ***17d**, n = 8.* δ_H(300 MHz; $CDCl_3$) = 8.09 (m, 4H; 11-H, 12-H), 5.32 (q, *J* = 7.0 Hz, 1H; 15-H), 4.88 (m, 1H; 8-H), 4.14 (m, 2H; 17-H), 2.11 (m, 2H; 7-H), 1.26 (m, 42H). δ_C(75 MHz; $CDCl_3$) = 170.6 (C-16), 165.2 (C-14, C-9), 135.0 (C10/C13), 133.0 (C10/C13), 129.7 (C-12/C-11), 129.5 (C-12/C-11), 75.0 (C-8), 69.5 (C-15), 65.6 (C-17), 42.7 (C-5/C-4), 42.2 (C-5/C-4), 39.8 (C-1′), 37.5, 33.5 (2C), 31.9 (2C), 31.7, 30.2 (2C), 29.1 (2C), 28.5, 27.9 (2C), 25.8, 22.6, 20.0, 17.1, 14.1, 14.0. HR-MS (ESI, 70 eV; MeOH, CH_2Cl_2); m/z: 579.365 (calc. 579.3661) $[M+Na]^+$. EA: Found: C, 73.193; H, 9.3013. $C_{34}H_{52}O_6$ calculated C, 73.34; H, 9.41%.

*4-(4-Propylcyclohexyl)cyclohexyl 4-({[(2R)-1-decyloxy-1-oxopropan-2-yl]oxy}carbonyl) benzoate **17e**, n = 10.* δ_H(300 MHz; $CDCl_3$) = 8.09 (m, 4H; 11-H, 12-H), 5.32 (q, J = 7.0 Hz, 1H; 15-H), 4.88 (m, 1H; 8-H), 4.14 (m, 2H; 17-H), 2.11 (m, 2H; 7-H), 1.26 (m, 46H). δ_C(75 MHz; $CDCl_3$) = 170.6 (C-16), 165.2 (C-14, C-9), 135.0 (C10/C13), 133.0 (C10/C13), 129.7 (C-12/C-11), 129.5 (C-12/C-11), 75.0 (C-8), 69.5 (C-15), 65.6 (C-17), 42.7 (C-5/C-4), 42.2 (C-5/C-4), 39.8 (C-1′), 37.5, 33.5 (2C), 31.9 (2C), 31.9, 30.2 (2C), 29.5 (2C), 29.3, 29.1, 28.5 (2C), 27.9, 25.8, 22.7, 20.0, 17.1, 14.1, 14.0. HR-MS (ESI, 70 eV; MeOH); m/z: 607.397 (calc. 607.3975) $[M+Na]^+$. EA: Found: C, 73.755; H, 9.5130. $C_{36}H_{56}O_6$ calculated C, 73.93; H, 9.65%.

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