General

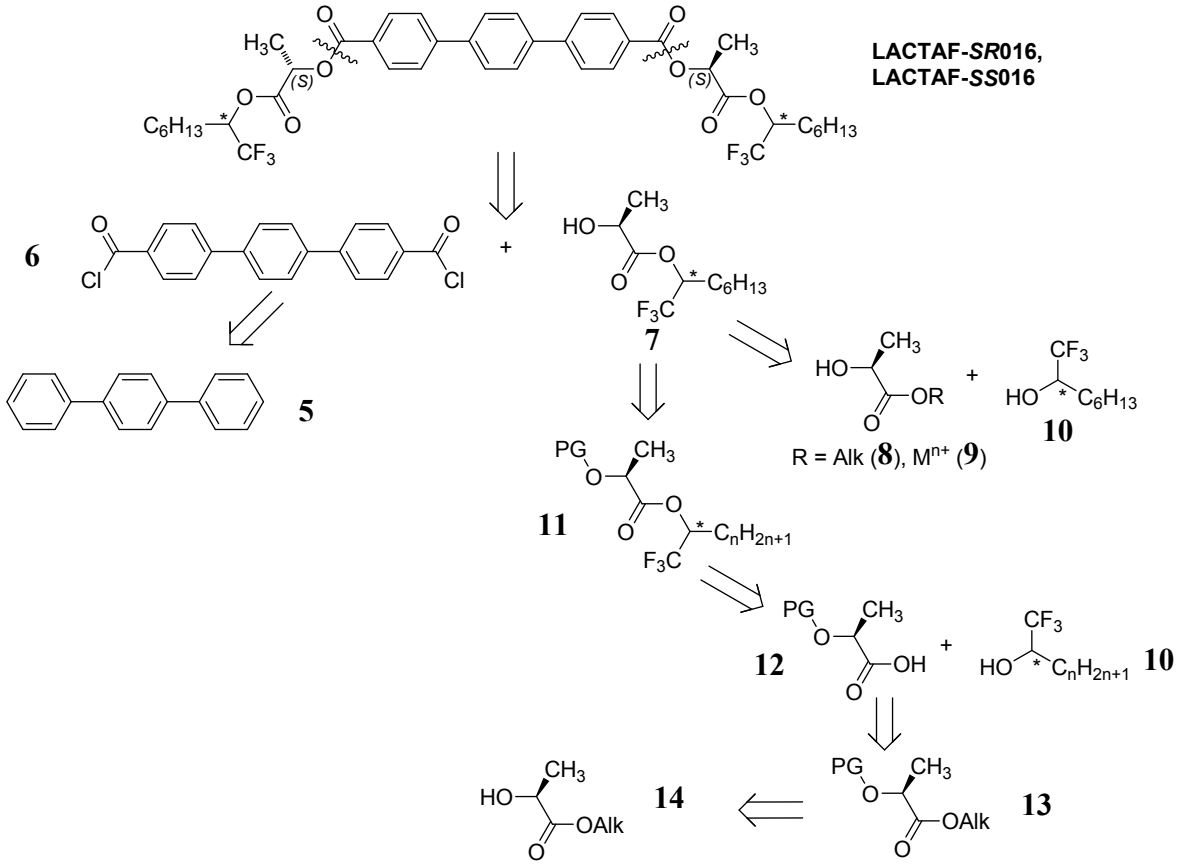
^{1}H NMR spectra were recorded on a Varian Mercury VX-200 (200 MHz) spectrometer in $CDCl_3$ or DMSO-d_6 using the signal of residual protons of undeuterated solvent as the internal standard.[S1] Mass-spectra were recorded with the use of direct exposure probe (DEP) method on a Varian 1200L GC-MS instrument with EI at 70 eV. HPLC analyses were performed at analytical wavelength 254 nm on a Bischoff module chromatograph equipped with a reversed-phase column Prontosil 120-5-C18H (4.0×250 mm) using acetonitrile, acetonitrile/water, or acetonitrile/water/trifluoroacetic acid mixtures as the eluents; or an Ascentis Si column (4.6×250 mm, 5μm) using dichloromethane/hexane mixtures as the eluents.

4-Bromobenzoic acid, (*S*)-benzyl lactate, *N*,*N*-dimethylaminopyridine (DMAP), dicyclohexylcarbodiimide (DCC), 10% Pd/C, 1,4-phenyldiboronic acid, $PdCl_2$dppf (complex with dichloromethane), sodium dodecylsulphate (SDS), and sodium hydrocarbonate ($NaHCO_3$) are commercially available from *Aldrich* and were used as is. Dichloromethane was dried over anhydrous $CaCl_2$ and distilled immediately before use. Pyridine was dried over KOH and distilled immediately before use. *tert*-Butyl alcohol, *n*-butanol, and toluene were distilled immediately before use. Enantiomeric (*R*)- and (*S*)-1,1,1-trifluorooctan-2-ols were synthesized according to Ref. S2.

Syntheses

1. Synthetic approaches toward target compounds SR-LACTAF-6 and *SS-LACTAF-6*

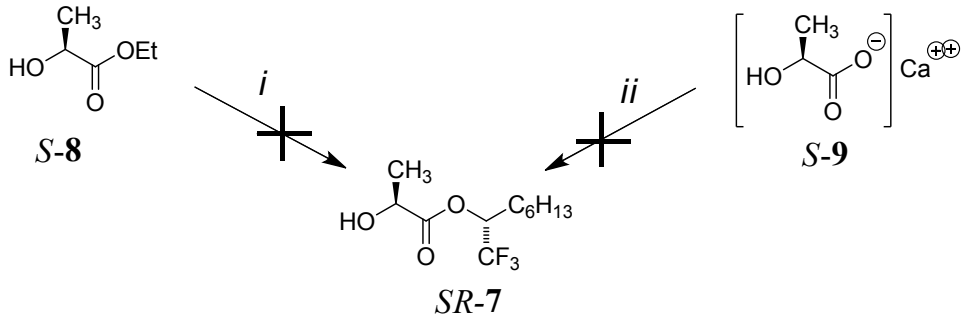
The primarily assumed synthetic approach toward the target compounds **SR-LACTAF-6** and **SS-LACTAF-6** consist of their formation by reaction of terphenyldicarboxylic acid chloride **6** (derived from *p*-terphenyl (**5**) according to Ref. S3) and corresponding alcohols **7** similarly to as described in Ref. S4 (Scheme S1).



Scheme S1. Retro-synthetic scheme of an approach toward target compounds **SR-LACTAF-6** and **SS-LACTAF-6** starting from *p*-terphenyl (**1**).

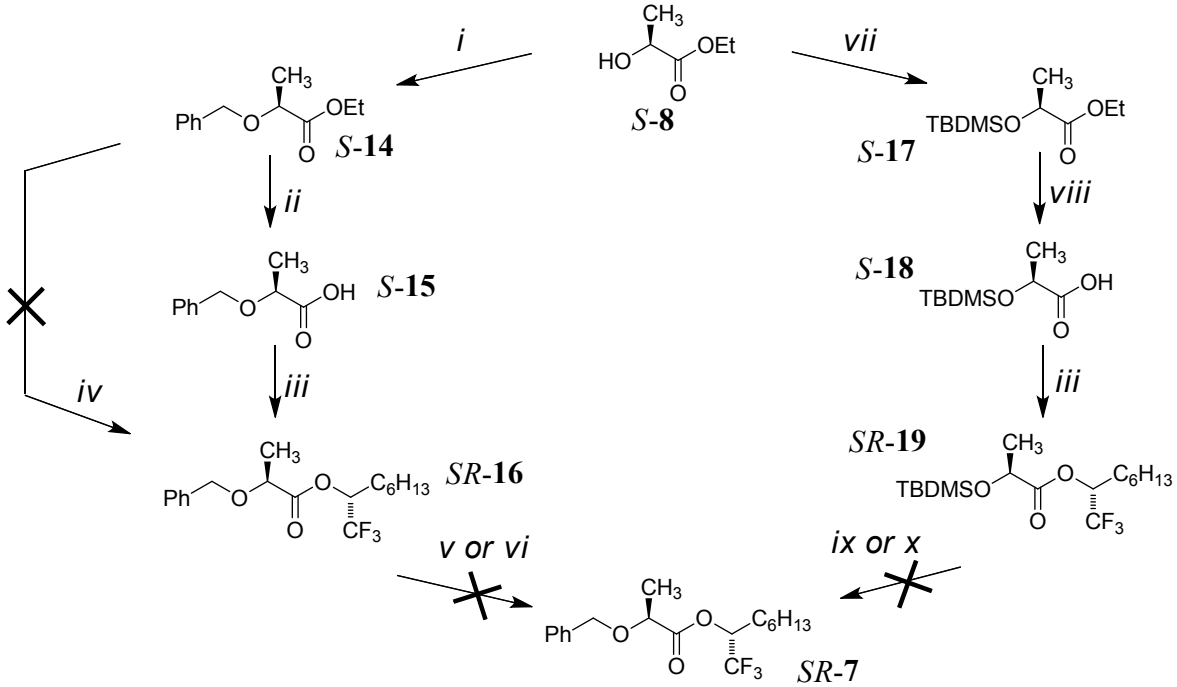
According to this approach, alcohols **7** are to be obtained either by direct reactions of the corresponding lactic esters **8** and/or salts **9** with enantiomeric (*R*)- and (*S*)-1,1,1-trifluoromethyl-octan-2-ols **10** or by reaction sequence consisting of protection of the starting lactic ester **8** (**8**→**13**) followed by transformations **13**→**11** at the carboxylic group and deprotection **13**→**7**.

However, when starting ethyl (*S*)-lactate *S*-**9** (Alk=C_2H_5) was treated with an excess of *R*-**10** in the presence of a catalytic amount of p-toluenesulfonic acid (PTSA) only trace amount of *SR*-**7** is detected in the reaction mixture by GC-MS (Scheme S2). The reaction of calcium (*S*)-lactate *S*-**9** (M=Ca^{2+}) with an excess of *R*-**10** in the presence of a catalytic amount of concentrated sulfuric acid does not result in any detectable amount of the ester *SR*-**7**.



Scheme S2. Direct syntheses of (2*S*)-(*R*)-1,1,1-trifluorooctan-2-yl 2-hydroxypropanoate (*SR*-**7**). *Reagents and conditions*: (i) (*R*)-1,1,1-trifluoromethyloctan-2-ol (*R*-**10**), PTSA (cat.), Δ; (ii) (*R*)-1,1,1-trifluoromethyloctan-2-ol (*R*-**10**), H_2SO_4 (cat.), Δ.

Approaches through protection of a hydroxylic group of *S*-**8** (R=C_2H_5) were tested by using benzylic and silyl protective groups (Scheme S3).



Scheme S3. Syntheses of (2*S*)-(*R*)-1,1,1-trifluorooctan-2-yl 2-hydroxypropanoate (*SR*-**3**) by protection of a hydroxyl group in *S*-**8**. *Reagents and conditions (yields)*: (i) $PhCH_2Br$, Ag_2O, Et_2O, Δ (78%); (ii) KOH (aq.), MeOH, Δ (45%); (iii) (*R*)-1,1,1-trifluoromethyloctan-2-ol (*R*-**10**), DCC, DMAP (cat.), CH_2Cl_2, 0°C→rt; (iv) (*R*)-1,1,1-trifluoromethyloctan-2-ol (*R*-**10**), PTSA (cat.), Δ; (v) H_2 (1 atm.), 10% Pd/C, EtOAc, rt; (vi) H_2 (25 atm.), 10% Pd/C, EtOAc, rt; (vii) TBDMS-Cl, NEt3, DMAP (cat.), THF, rt (75%); (viii) LiOH (aq.), THF, rt (54%); (ix) TBAF, THF, rt; (x) $KHSO_4$, MeOH, H_2O, rt.

Thus, *O*-benzylation of *S*-**8** with benzyl bromide according to Ref. S5 gives corresponding protected lactate *S*-**14** which was saponified to the carboxylic acid *S*-**15**. The acid *S*-**15** was esterified with *R*-**10** under carbodiimide methodology[S6] to give the ester *SR*-**16**. It is worth mentioning that as in the case of the non-protected lactate *S*-**8** (see above discussion on Scheme S2), *O*-benzylated lactate *S*-**14** also cannot be transesterified with *R*-**10** to give *SR*-**16** directly. At last, *SR*-**16** failed to give target *SR*-**7** under hydrogenolysis conditions neither at atmospheric nor at an elevated pressure of hydrogen. Thus, benzylic protection of hydroxyl group in *S*-**8** cannot be used for the synthesis of *SR*-**7**.

Alternatively, *S*-**8** was *O*-silylated with *tert*-butyldimethylsilyl chloride (TBDMS-Cl) according to Ref. S7 (Scheme S3). *O*-silyl ether *S*-**17** was subjected to saponification in mild conditions[8] to give corresponding carboxylic acid *S*-**18** which was esterified with *R*-**10** under carbodiimide methodology[S6] to give the ester *SR*-**19**. However *O*-desilylation *SR*-**19** with tetrabutylammonium fluoride (TBAF) according to Ref. S9 leads to a complex mixture of products according to GC-MS whereas using $KHSO_4$ according to Ref. S10 gives any product. Thus, silylic protection of hydroxyl group in *S*-**8** also cannot be used for the synthesis of *SR*-**7**.

Thus, diastereomeric compounds ***SR-LACTAF-6*** and ***SS-LACTAF-6*** were synthesized according to the scheme referred to in the full-text as Scheme 1 starting from commercially available (*S*)-benzyl lactate followed by transformations at its hydroxylic group, deprotection of the carboxylic group by *O*-debenzylation and formation of the terphenyl core at the last step by palladium catalyzed Suzuki cross-coupling reaction in a microemulsion similarly to the described in Ref. S11.

2. Synthesis of (S)-1-((benzyloxy)carbonyl)ethyl 4-bromobenzoate (S-2)

To the solution of 4-bromobenzoic acid (9.7 g, 48.2 mmol, 1.1 eq.), (*S*)-benzyl lactate (7.8 g, 43.3 mmol) and DMAP (590 mg, 4.8 mmol, 0.11 eq.) in dry dichloromethane (90 ml) a solution of DCC (11.9 g, 57.8 mmol, 1.3 eq.) in dry dichloromethane (60 ml) was added drop wise at 0-5 °C with stirring. The mixture was left warming to room temperature overnight with stirring. Then it was filtered through a short pad of silica and evaporated to dryness. The residue after evaporation was transferred into a column containing silica and extracted with hot heptane giving after evaporation of heptane crude (*S*)-1-((benzyloxy)carbonyl)ethyl 4-bromobenzoate (***S*-2**) as a clear oil which was used further without additional purification.

(S)-1-((benzyloxy)carbonyl)ethyl 4-bromobenzoate (S-2). Yield 21.5 g (78%). Purity 98% (HPLC, reversed phase column, eluent acetonitrile-water azeotrope).

3. Synthesis of (S)-2-(4-bromobenzoyloxy)propanoic acid (S-3)

In a reaction system flushed with argon, freshly distilled *tert*-butyl alcohol (350 ml) was carefully added to 10% Pd/C powder (1.0 g) in counter flow of argon (CAUTION: reverse addition of Pd/C to *tert*-butyl alcohol causes oxidation of the alcohol vapor in air under Pd/C catalysis resulting in flashing!) followed by crude (*S*)-1-((benzyloxy)carbonyl)ethyl 4-bromobenzoate (***S*-2**) (21.5 g, 5.9 mmol) from the previous step and dry pyridine (9.4 g, 11.8 mmol, 2 eq.). The system was flushed with hydrogen three times and left overnight with stirring under a hydrogen atmosphere. The resulted mixture was filtered through a short pad of *Celite* 450 and poured on ice followed by acidification with diluted HCl. The product was extracted into ethyl acetate (3×100 ml). The combined organic extracts were washed (twice) with diluted HCl, thereafter, with water and dried over anhydrous $CaCl_2$. The $CaCl_2$ was filtered off and the solution obtained was evaporated to dryness. The residue after evaporation was suspended in hexane and refuxed followed by drop wise addition of ethyl actetate till complete dissolution. The precipitate formed on cooling was filtered off a dried *in vacuum* to give ***S*-3** as a colourless powder.

(*S*)-2-(4-bromobenzoyloxy)propanoic acid (*S*-3). Yield 10.3 g (64%). Purity 97.5% (HPLC, reversed phase column, eluent 70% acetonitrile/water/0.05% trifluoroacetic acid). NMR (200 MHz, DMSO-d_6), δ, ppm: 7.89—8.07 (m, 2H), 7.53—7.85 (m, 2H), 5.19 (q, 1H), 3.66 (s, 1H) 1.57 (d, 3H).

4. Synthesis of diastereomeric (S)-1-(1,1,1-trifluorooctan-2-yloxy)carbonyl)ethyl 4-bromobenzoates (SR-4 and SS-4) (general procedure)

To the solution of (*S*)-2-(4-bromobenzoyloxy)propanoic acid (***S*-3**) (2.8 g, 10.0 mmol, 1.1 eq.), corresponding (*R*)- or (*S*)-1,1,1-trifluorooctan-2-ol (*R*- or *S*-10; 1,7 g, 9,10 mmol) and DMAP (126 mg, 1.0 mmol, 0.11 eq.) in dry dichloromethane (20 ml) a solution of DCC (2.5 g, 12.3 mmol, 1.35 eq.) in dry dichloromethane (15 ml) was added drop wise at 0—5 °C with stirring. The mixture was left warming to room temperature overnight with stirring. Then it was filtered through a short pad of silica and evaporated to dryness. The residue after evaporation was transferred into a column containing silica and extracted with hot heptane giving after evaporation of heptane crude ***SR*-4** or ***SS*-4** as the colourless oil which was further used without additional purification.

(*S*)-1-(((*R*)-1,1,1-trifluorooctan-2-yloxy)carbonyl)ethyl 4-bromobenzoate (*SR*-4). Yield 4.0 g (100 %). Purity 99.5% (HPLC, reversed phase column, eluent acetonitrile-water azeotrope).

(*S*)-1-(((*S*)-1,1,1-trifluorooctan-2-yloxy)carbonyl)ethyl 4-bromobenzoate (*SS*-4). Yield 3.8 g (95 %). Purity 99.7% (HPLC, reversed phase column, eluent acetonitrile-water azeotrope).

4. Palladium-catalyzed Suzuki cross-coupling reaction of diastereomeric (S)-1-(1,1,1-trifluorooctan-2-yloxy)carbonyl)ethyl 4-bromobenzoates (SR-4 and SS-4) and 1,4-penyldiboronic acid (general procedure)

A mixture of (S)-1-(1,1,1-trifluorooctan-2-yloxy)carbonyl)ethyl 4-bromobenzoate (***SR-4*** or ***SS-4***) (3.6 g, 8.2 mmol), 1,4-phenyldiboronic acid (815 mg, 4.9 mmol, 1.2 eq), $PdCl_2$dppf (267 mg, 0.3 mmol, 0.04 eq.), and SDS (300 mg) in a mixture of toluene (18 ml), *n*-butanol (3 ml), and H_2O (2 ml) was degassed *in vacuo* and flushed with argon for five times followed by heating to reflux with stirring. To the refluxed mixture a solution of $NaHCO_3$ (690 mg, 49.2 mmol, 6 eq.) in H_2O (18 ml) degassed by bubbling argon was added. The resulted mixture was stirred at reflux for an hour, cooled, poured into water (1 l) and acidified with concentrated HCl to pH 1. The organic layer was separated and the water one was extracted with toluene (3×20 ml). The organic extracts were collected, washed with water till neutral reaction and dried over anhydrous Na_2SO_4. Na_2SO_4 was filtered off and the solution was evaporated to dryness. The residue after evaporation was transferred into a column filled with silica and extracted with hot toluene. The extract was evaporated to dryness and the residue was chromatographed on silica with 50% dichloromethane/hexane as eluent to give an analytically pure sample.

Phase diagrams

The phase transitions temperatures were obtained by POM upon cooling the sample from the isotropic liquid, however, the melting point obtained on heating for pre-crystallized samples. The LC phases were assigned according to "natural textures" between untreated glass substrates.

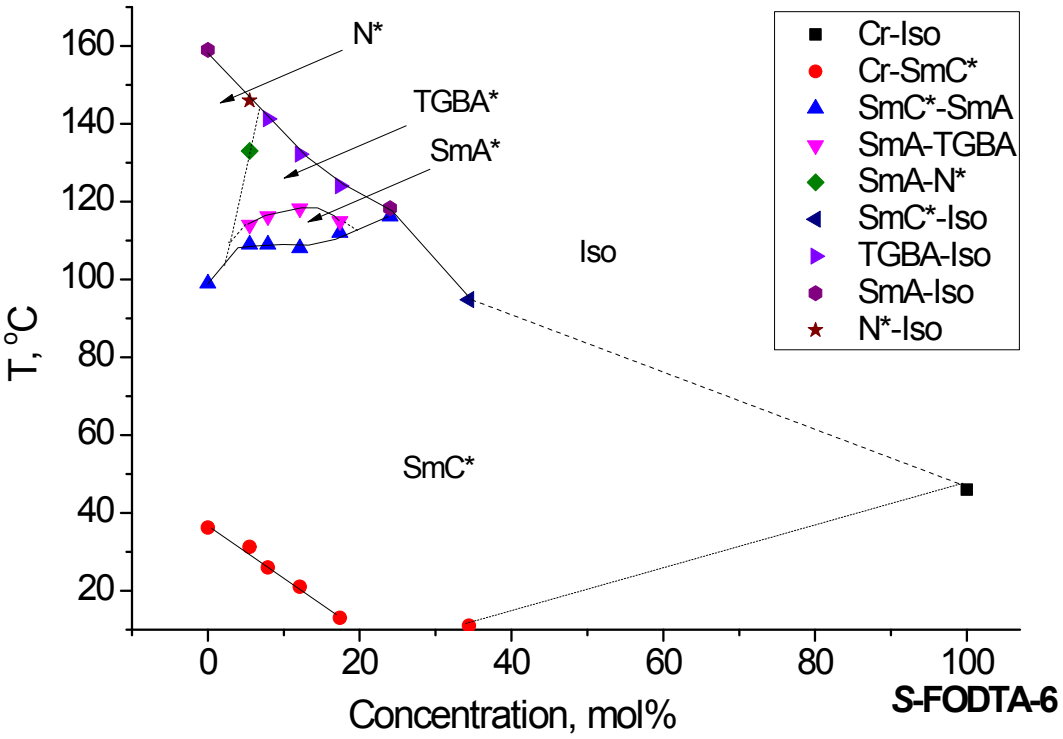


Fig.S1 Phase diagram for ***S*-FODTA** in **M1** host

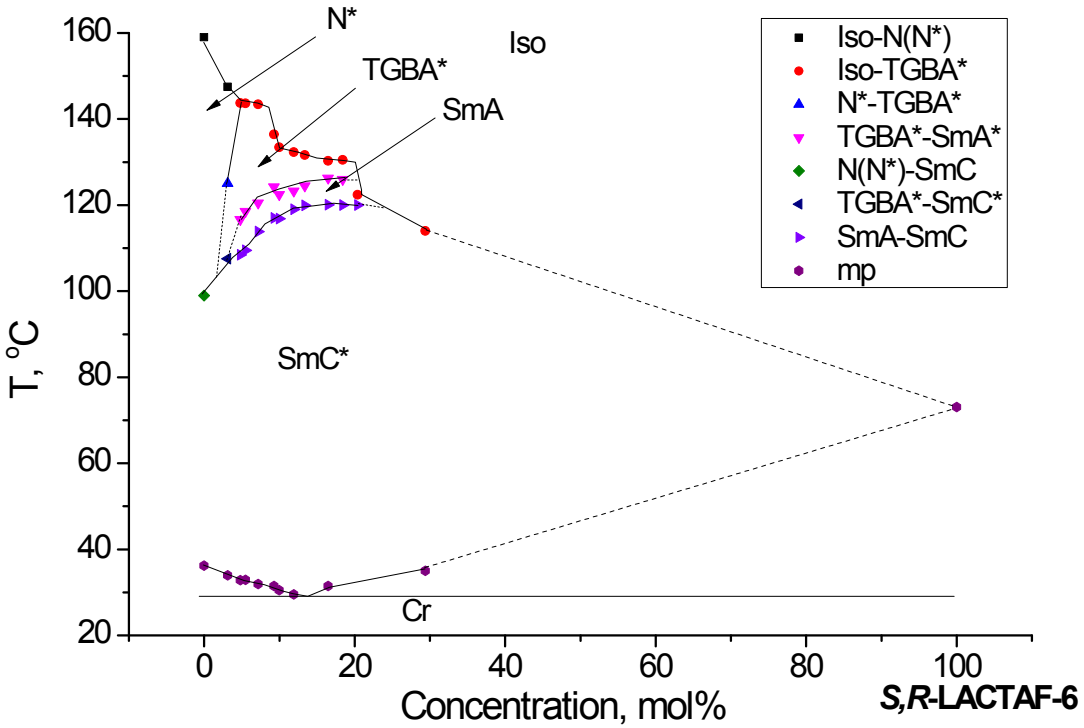


Fig.S2 Phase diagram for ***S,R*-LACTAF-6** in **M1** host

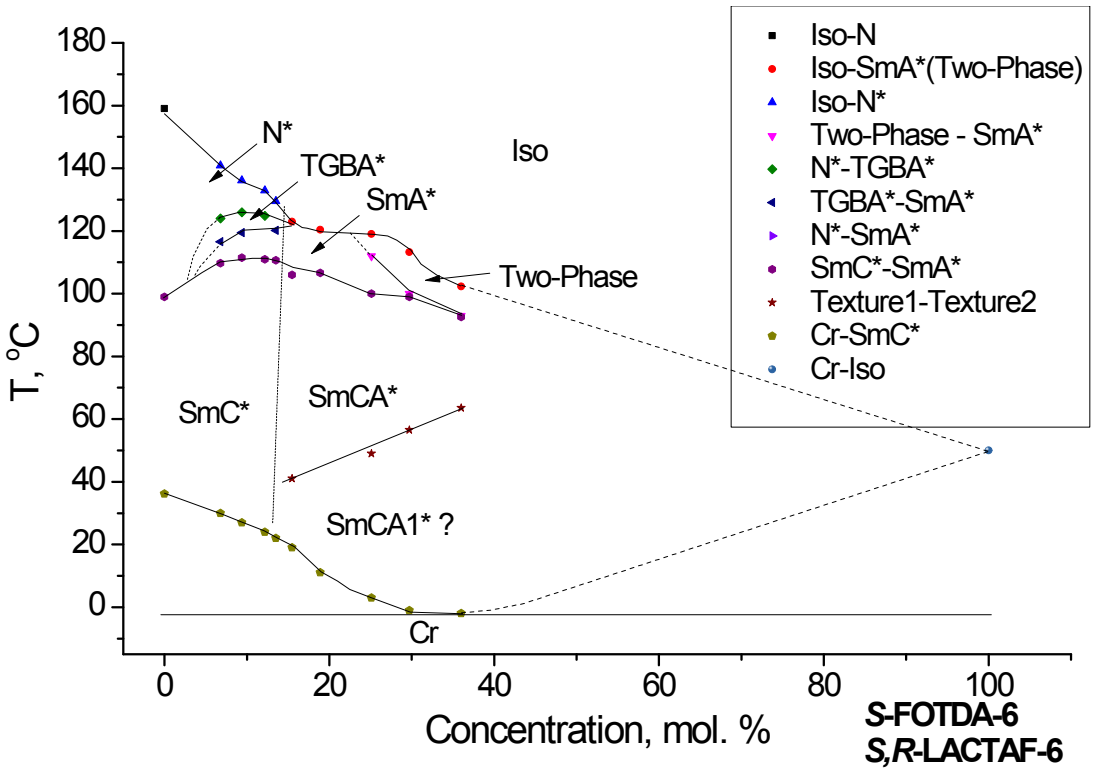


Fig.S3 Phase diagram for mixture of ***S*-FODTA** and ***S,R*-LACTAF-6** (4:3) in **M1** host. For transition Texture 1 – Texture 2 see text below.

For the mixtures within the CD concentration range from 15 to 36 mol%, a transition is observed when one vertical alignment quickly transforms *via* intermediate schlieren texture to another homeotropic area (Texture 1 – Texture 2 transition at Fig. S3). The measurements of selective reflection are only possible at higher temperature region. An example of the texture evolutions, **AFLC-036**, is given in Fig.S4.

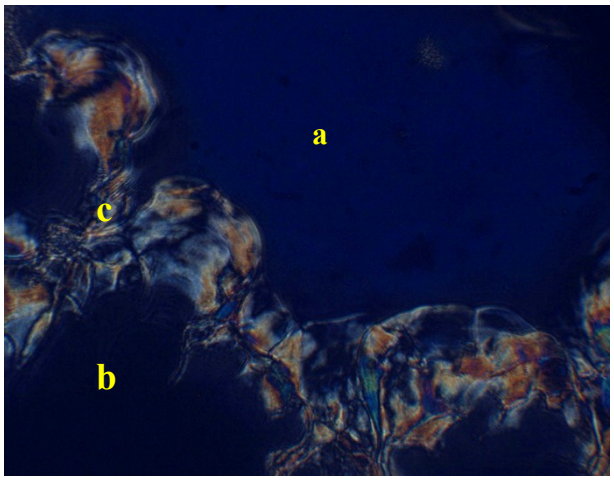


Fig. S4. Change between high- (**a**) and low- temperature (**b**) areas of homeotropic alignment *via* intermediate schlieren texture (**c**) for **AFLC-036** sample. Microphotography was taken by POM at 64.2 °C, polarizers were slightly uncrossed.

Since both DSC curves and optoelectronic dependencies do not show any inflection points within 60—65 °C range, the optical pattern evolution (Fig.S4) should be assigned to textural instability of the highly concentrated mixtures. Thus, it is reasonable to assume that below the textural instability point the helical pitch also continues to decrease throughout the whole temperature range of the smectic phase.

References for Supporting Information

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