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Graphical Abstract

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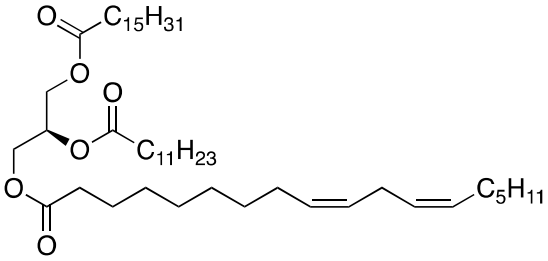

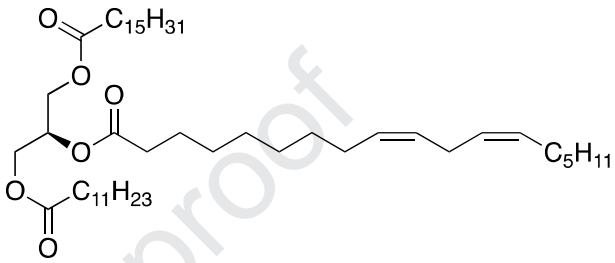

Synthesis of enantiopure ABC-type triacylglycerols

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Keywords

ABC type structured triacylclycerols; *Candida antarctica* lipase; chemoenzymatic synthesis; enantiopure triacylglycerols; enantiospecific TAG analysis.

This paper is dedicated to Professor Steve Davies in recognition of his outstanding contribution to the area of asymmetric and stereoselective synthesis and the Founder and Editor in Chief for Tetrahedron Asymmetry.

Abstract

The synthesis of twelve enantiopure structured triacylglycerols (TAGs) of the ABC type possessing three different fatty acids is described by a six-step chemoenzymatic approach starting from (*S*)-solketal. Eight of the TAGs possess two different saturated fatty acyl groups located in the *sn*-1 and *sn*-2 positions with an unsaturated fatty acyl group in the remaining *sn*-3 position of the glycerol skeleton, whereas the remaining four possess two different saturated acyl groups in the terminal *sn*-1 and *sn*-3 positions with an unsaturated acyl group in the *sn*-2 position. The former group was synthesized by a six-step chemoenzymatic route involving a highly regioselective immobilized *Candida antarctica* lipase. The second group was prepared by a similar six-step approach, that required two separate lipase steps. Such enantiopure TAGs are strongly demanded as standards for enantiospecific analysis of intact TAGs in fats and oils.

1. Introduction

Triacylglycerols (TAGs) are by far the largest class of nonpolar lipids that occur widely in fats and oils of plant and animal origin.[1-3] They consist of a glycerol skeleton to which three fatty acyl groups are attached as carboxylate esters. In fats and oils the variety and number of TAG molecular species is immense as a result of the great number of different fatty acids that differ in length, saturation and location of the carbon-carbon double bonds in unsaturated and polyunsaturated fatty acids (PUFAs). The location of the fatty acids within the glycerol backbone adds further to the diversity in terms of regio- and stereoisomerism.

In the human and animal diet TAGs are of importance, not only as a source of energy but also for supplying bioactive fatty acids for various biological roles. That includes the n-6 and n-3 PUFAs serving as precursors to various potent mediators including eicosanoids and docosanoids. [4-6] The TAGs in animals and plants are known to differ significantly from species to species in terms of their fatty acid compositions as well as their non-random distribution within the glycerol backbone. Classical examples of such positionally structured TAGs and their major role in physical properties and biological function, include cocoa butter[7] used in chocolate manufacturing and human milk TAGs.[8] In fish oil TAGs the n-3 PUFAs show a clear preference for the mid-position, whereas in marine mammals this is the other way around.[9]

The glycerol molecule is prochiral, meaning that when two different fatty acids are attached to its terminal 1,3-positions, a chiral centre is generated at the 2-position. The consequence of that is an increased number of isomers due to the presence of enantiomers, as pairs or with one of them predominating. A stereospecific numbering designated by the prefix *sn*- is used to distinguish between the two enantiotopic terminal positions of the glycerol backbone.[3] The *pro-S*

hydroxymethyl group refers to the *sn*-1 position and the *pro-R* group to the *sn*-3 position with the remaining stereogenic carbon at the mid-position referred to as the *sn*-2 position. There are numerous reports on the enantiospecific location of fatty acids in animals and plants.[10-12]

A proper chemical analysis of TAGs is quite a challenge. Their total fatty acid composition is readily available by routine GC analysis after converting their fatty acids into volatile methyl esters,[13] but all information with regard to their positional distribution within the glycerol backbone is lost. The composition of the most abundant or selected abundant regioisomers is available, for example from atmospheric pressure chemical ionization mass spectrometry (APCI MS)[14, 15] or ammonia negative ion tandem mass spectrometry (NICI-MS/MS).[16,17] However, these methods do not distinguish between the enantiomeric *sn*-1 and *sn*-3 positions. That type of information is available by enantiospecific analyses, where multi-step procedures are combined with chromatography. That includes 1,3-regioselective lipase[18] or Grignard reagents[19] to form a mixture of diacylglycerols (DAGs) and monoacylglycerols (MAGs) undergoing further treatments involving enantioselective phospholipase A2,[10,20] chiral derivatization[21] or chiral-phase HPLC.[22,23] The reliability of the stereospecific analysis is affected by the tedious multi-step procedures and acyl migration[24,25] side reaction where acyl groups migrate from one position to another within the glycerol backbone.

The limitation of the stereospecific analyses described above is that they provide an insight into the overall fatty acid composition of the individual stereospecific *sn*-1/2/3 positions for all TAG molcular species present in a mixture rather than information on individual TAG enantiomers. Obviously, stereospecific analysis of intact TAGs in a natural oil mixture is far more of a challenge. Nonaqueous reversed phase and silver-ion HPLC/MS are the most commonly used analytical techniques for separation and characterization of natural TAG molecular species,[14,26] but these

methods do not allow separation of TAG enantiomers. Consequently, there is an urgent need for a non-destructive enantiospecific analysis of such intact TAGs. That important challenge has been addressed in a few recent reports based on chiral HPLC in attempts to separate TAG enantiomers.[11,12,27,28]

Despite the variation in methods of chromatography and ionization, current MS- and MS/MS-based methods for resolving the regioisomers of intact TAGs in natural oils and fats rely on the difference in the energy required for dissociation of fatty acids between the *sn*-2 and *sn*-1/3 positions. For a specific TAG, the fragmentation pattern depends on both the fatty acid combination and positional distribution. Therefore, it is of crucial importance to have access to regiopure TAGs as reference compounds in order to quantify accurately the regioisomer composition of TAGs.[29,30] For sterespecific separation of enantiomers, chiral chirochromatographic analysis has proven to be a promising method, where enantiopure TAG compounds are needed for identification of separated enantiomers.[28]

Natural oils and fats are complex mixtures of a large number of molecular species of TAGs, of which human milk fat and fish oil are excellent examples with significant nutritional importance.[29,31] Separation, identification, and quantification of the enantiomers would be of crucial importance, for example in studies on gene – lipid composition interactions,[32] as well as in studies on composition of human milk and subsequent development of human milk formulas and dietary supplements.[29,33] A major obstacle hindering the development of the methodologies is the lack of appropriate TAG enantiomers to serve as standards for establishing calibration curves to quantify regioisomers and for distinguishing between the intact TAG enantiomers in such analyses.[11,12,28]

In a recent report the preparation of nine enantiopure (*S*)-TAG enantiomers was described by chemical and chemoenzymatic synthesis starting from enantiomerically pure (*R*)-solketal by use of an immobilized *Candida antarctica* lipase (CAL-B) to secure the regiocontrol.[34] They were all of the AAB type possessing two different fatty acids, one saturated and one unsaturated, and representing TAG species commonly present in plant oils and fats. They were intended and used as standards for enantiospecific separation and recognition of individual enantiomers by a recently developed double chiral column sample recycling HPLC system.[28] In the current report the synthesis of twelve enantiopure ABC type TAGs possessing three different fatty acids, two saturated and one unsaturated, representing TAG molecular species commonly found in plant and animal fats, such as human milk, is addressed by a similar chemoenzymatic approach. The synthesised compounds are of high value as reference compounds for further development of regio- and stereospecific analysis of TAGs. Their structures are illustrated in Figure 1.

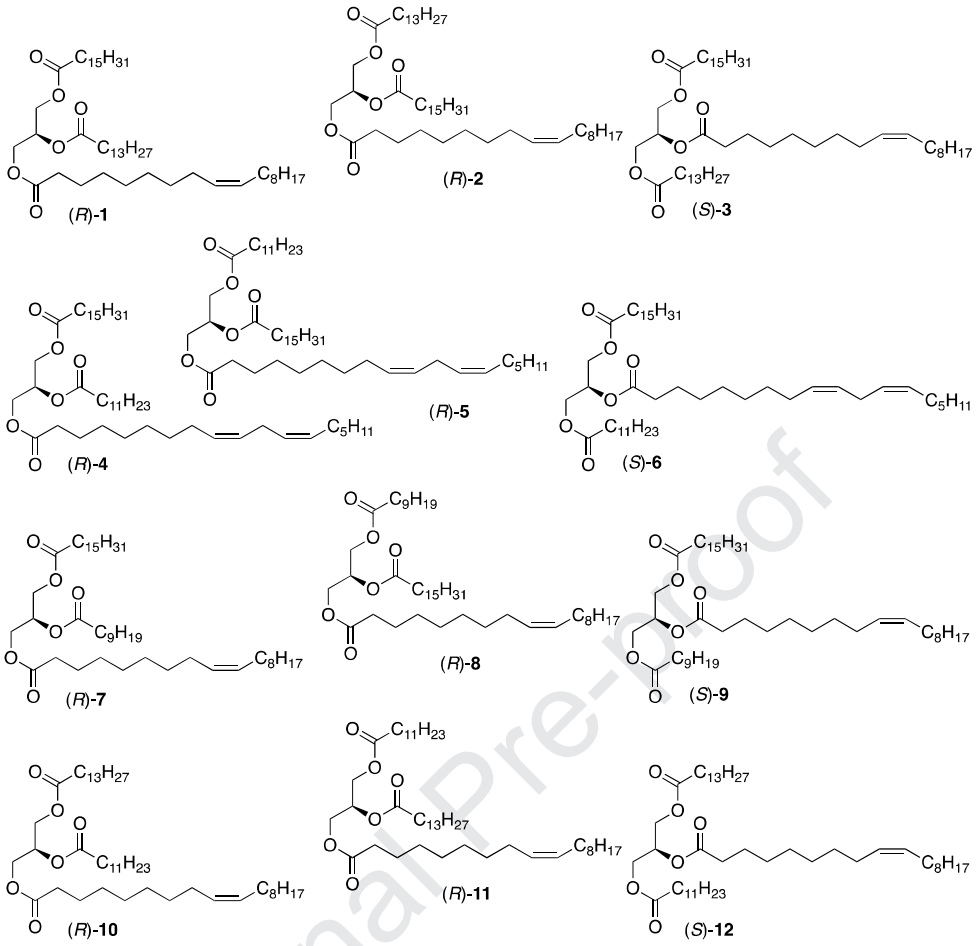


Figure 1. The structures of the twelve enantiostructured TAG products synthesised.

2. Results and Discussion

All the enantiopure structured TAGs addressed in the current study are of the ABC type, thus constituting three different fatty acids. Two of them are saturated, with the third unsaturated, which enables their detection by a UV detector in combination with the intended chiral HPLC analysis. As previously described, the term structured TAG[35,36] refers to selected fatty acids accommodating predetermined positions of the TAG glycerol skeleton. Accordingly, enantiostructured TAG refers to the fatty acids being located in the enantiospecific positions of the glycerol backbone. Four different saturated fatty acids were used in these studies, including hexadecanoic acid (C16:0; palmitic acid), tetradecanoic acid (C14:0; myristic acid), dodecanoic acid (C12:0; lauric acid) and

decanoic acid (C10:0; capric acid), and two unsaturated fatty acids, the monounsaturated *cis*-octadec-9-enoic acid (C18:1; oleic acid) and the diunsaturated *cis*-octadec-9,12-dienoic acid (C18:2; linoleic acid).

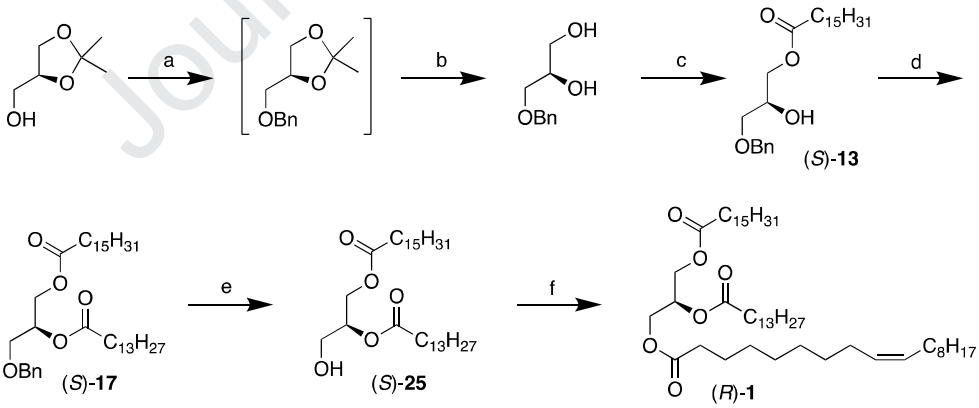
From a synthetic organic chemistry point of view the TAGs may be divided into two categories: (a) Those possessing the two different saturated fatty acyl groups located in the *sn*-1 and *sn*-2 positions, with the unsaturated fatty acyl group in the remaining *sn*-3 position of the glycerol backbone, thus all being of the *R*-configuration; (b) Those possessing the two different saturated acyl groups in the terminal *sn*-1 and *sn*-3 positions, with the unsaturated acyl group in the *sn*-2 position, all of the *S*-configuration. The preparation of the TAGs belonging to each of the two categories requires two different synthetic approaches. A total of twelve such enantiostructured TAGs were prepared, eight belonging to the first category and four belonging to the second one. The structures of these TAGs are illustrated in Figure 1 with compounds (*R*)-**1**, **2**, **4**, **5**, **7**, **8**, **10** and **11** belonging to the first category and (*S*)-**3**, **6**, **9** and **12** belonging to the second one.

In fact this is a set of four TAG fatty acid compositions commonly found in human milk.[29,33] The first is comprised of palmitic, myristic and oleic acids. We were interested in both combinations of TAGs belonging to the first category (TAGs (*R*)-**1** and **2**), and one belonging to the second (TAG (*S*)-**3**). Since only one of the two enantiomers is needed as a standard to determine the separation order of the two TAG enantiomers in their enantiospecific TAG analysis, it was of no relevance which one was prepared, provided that the absolute configuration was known. Therefore, to make the synthetic work simpler, and to reduce the number of intermediates involved, it was decided to base the syntheses on the use of (*S*)-solketal as the sole chiral precursor rather than using both the (*R*)- and (*S*)-solketals. Therefore, we ended up with *R*-configuration of the first category TAGs and the *S*-configuration of those belonging to the second category. This is simply determined by the

Cahn-Ingold-Prelog priority rules rather than being of any scientific necessity. Three more TAG fatty acid compositions were then included in the current task, namely those constituting palmitic, lauric and linoleic acids (TAGs (*R*)-**4**, **5** and (*S*)-**6**), palmitic, capric and oleic acids (TAGs (*R*)-**7**, **8** and (*S*)-**9**), and myristic, lauric and oleic acids (TAGs (*R*)-**10**, **11** and (*S*)-**12**).

2.1 *Synthesis of the first category TAGs*

The synthetic route to the TAGs (*R*)-**1**, **2**, **4**, **5**, **7**, **8**, **10** and **11** belonging to the first category is illustrated in Scheme 1 for (*R*)-**1**. It was based on a six-step chemoenzymatic process starting from enantiomerically pure 1,2-isopropylidene-*sn*-glycerol, (*S*)-solketal, as a chiral precursor. In the first three steps a previously reported approach towards synthesis of (*R*)-**13** obtained from (*R*)-solketal was followed.[34] In the current work (*S*)-solketal was benzylated at the *sn*-3 position and the resulting benzylated adduct subsequently deprotected without purification to remove the isopropylidene moiety (see Scheme 1). The enantiomerically pure key intermediate 3-*O*-benzyl-*sn*-glycerol was obtained in 92% overall yield after purification.



Scheme 1. Chemoenzymatic synthesis of the first category of TAGs (*R*)-**1**, **2**, **4**, **5**, **7**, **8**, **10** and **11** (shown for (*R*)-**1**). *Reagents and conditions*: (a) NaH, THF, then BnBr; (b) 1 M HCl, H_2O/EtOH, reflux 30 min. (92% overall); (c) Vinyl hexadecanoate, CAL, CH_2Cl_2, r.t. (87%); (d) Tetradecanoic acid, EDCI, DMAP, CH_2Cl_2, r.t. (95%); (e) H_2, 10% Pd/C, THF, r.t. (71%); (f) *cis*-Hexadec-9-enoic acid, EDCI, DMAP, CH_2Cl_2, r.t. (93%).

The benzylated glycerol adduct was subsequently acylated with palmitic, myristic, lauric and capric acids, all activated as vinyl esters, by use of the highly regioselective immobilised *Candida antarctica* lipase (CAL-B from Novozymes) in dichloromethane at room temperature. Under these conditions, and in accordance with numerous previous reports,[35-37] the enzymatic reaction took place exclusively at the terminal *sn*-1 position with no occurrence of the acyl migration side-reaction. It took the reaction only 90 minutes to proceed to completion. The resulting acylated benzyl ether adducts (*S*)-**13**, **14**, **15** and **16** were all prepared in very high to excellent yields (see Table 1) after purification by column chromatography using boric acid impregnated silica gel[10] to prevent acyl migration.

The second saturated fatty acyl group was introduced to the free hydroxyl groups at the *sn*-2 position of (*S*)-**13**-**16** using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) as a chemical coupling agent in the presence of dimethylaminopyridine (DMAP) following a previously described procedure.[35,36] The resulting diacylated adducts (*S*)-**17**-**24** were all obtained in very high to excellent yields (82-96%) after crystallisation from hot ethanol. They were all subjected to catalytic hydrogenolysis using Pd/C catalyst in THF under atmospheric pressure at room temperature to remove the benzyl protective group under which no acyl migration was observed to take place. The resulting 1,2-DAGs (*S*)-**25**-**32** were all obtained in moderate to good yields after crystallisation from hot hexane, except (*S*)-**30** that was obtained as a brownish wax and used as such without further purification. Table 1 shows the yields obtained for these intermediate adducts along with their specific optical rotation values. These intermediates were all obtained in excellent chemical and regiopurity as was firmly established by ^{1}H NMR spectroscopy at 400 MHz.[35,36]

Table 1. Structural information based on the stereospecific numbering (*sn*-1/2/3), yields and specific rotation of the benzylated 1-MAG and 1,2-DAG, and the 1,2-DAG intermediates obtained in accordance with the reactions described in Scheme 1 for the synthesis of the first category of TAGs

Entry	*sn*-1	*sn*-2	*sn*-3	Yield (%)	$[\alpha]_D^{25}$
(*S*)-**13**	$C_{15}H_{31}COO$-	-OH	-OBn	87	+1.11
(*S*)-**14**	$C_{13}H_{27}COO$-	-OH	-OBn	94	+3.64
(*S*)-**15**	$C_{11}H_{23}COO$-	-OH	-OBn	96	+1.31
(*S*)-**16**	$C_9H_{19}COO$-	-OH	-OBn	97	+1.48
(*S*)-**17**	$C_{15}H_{31}COO$-	$C_{13}H_{27}COO$-	-OBn	95	+4.28
(*S*)-**18**	$C_{13}H_{27}COO$-	$C_{15}H_{31}COO$-	-OBn	89	+4.32
(*S*)-**19**	$C_{15}H_{31}COO$-	$C_{11}H_{23}COO$-	-OBn	96	+8.11
(*S*)-**20**	$C_{11}H_{23}COO$-	$C_{15}H_{31}COO$-	-OBn	84	+5.73
(*S*)-**21**	$C_{15}H_{31}COO$-	$C_9H_{19}COO$-	-OBn	90	+5.34
(*S*)-**22**	$C_9H_{19}COO$-	$C_{15}H_{31}COO$-	-OBn	82	+4.53
(*S*)-**23**	$C_{13}H_{27}COO$-	$C_{11}H_{23}COO$-	-OBn	86	+4.81
(*S*)-**24**	$C_{11}H_{23}COO$-	$C_{13}H_{27}COO$-	-OBn	82	+4.69
(*S*)-**25**	$C_{15}H_{31}COO$-	$C_{13}H_{27}COO$-	-OH	71	-2.20
(*S*)-**26**	$C_{13}H_{27}COO$-	$C_{15}H_{31}COO$-	-OH	74	-3.19
(*S*)-**27**	$C_{15}H_{31}COO$-	$C_{11}H_{23}COO$-	-OH	74	-2.94
(*S*)-**28**	$C_{11}H_{23}COO$-	$C_{15}H_{31}COO$-	-OH	68	-3.15
(*S*)-**29**	$C_{15}H_{31}COO$-	$C_9H_{19}COO$-	-OH	83	-3.10
(*S*)-**30**	$C_9H_{19}COO$-	$C_{15}H_{31}COO$-	-OH	62	*
(*S*)-**31**	$C_{13}H_{27}COO$-	$C_{11}H_{23}COO$-	-OH	82	-3.17
(*S*)-**32**	$C_{11}H_{23}COO$-	$C_{13}H_{27}COO$-	-OH	58	-2.92

*Not purified by crystallisation

In accordance with Scheme 1 and Table 1 both the benzylated adducts (*S*)-**17**-**24** and their derived 1,2-DAGs (*S*)-**25**-**32** are intermediates for the synthesis of the first category of TAGs (*R*)-**1**, **2**, **4**, **5**,

7, **8**, **10** and **11**, respectively. Information on the structures of all these intermediates is provided in Table 1 showing the enantiospecific positioning of the acyl groups and other substituents on the glycerol skeleton for each of these compounds.

Finally, the unsaturated oleic or linoleic acids were introduced to the free hydroxyl group at the *sn*-3 position of (*S*)-**25**-**32** using EDCI as a chemical coupling agent in the presence of DMAP following the same procedure as described above. The resulting first category products (*R*)-**1**, **2**, **4**, **5**, **7**, **8**, **10** and **11** were all obtained in high, and in most cases, excellent yields (77-98%) after purification by flash chromatography on silica gel. No acyl migration was observed to take place during this reaction as had been firmly established in previous studies.[35-37] Table 2 shows the type of products and the yields obtained along with their specific optical rotation values. As may be observed these values are extremely low and a question emerges as to whether this may possibly be an indication of losses in enantiopurity. That possibility, on the other hand, can by ruled out by the absence of any noticeable acyl migration as will be described below.

Table 2. Structural information based on the stereospecific numbering (*sn*-1/2/3), yields[a)] and specific rotation of the first category of TAG products (*R*)-**1**, **2**, **4**, **5**, **7**, **8**, **10** and **11** and the second category of TAG products (*S*)-**3**,**6**,**9** and **12** obtained in accordance with Schemes 1 and 2, respectively

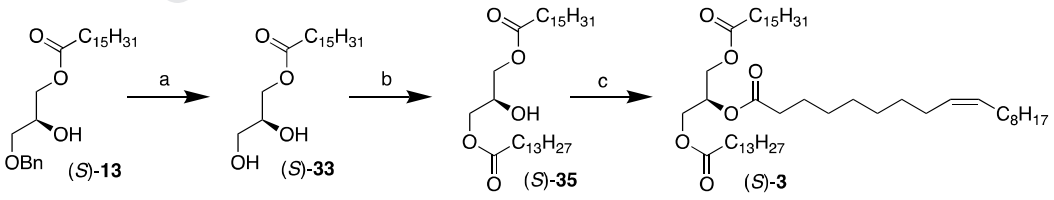
Entry	*sn*-1	*sn*-2	*sn*-3	Yield (%)	$[\alpha]_D^{25}$
(*R*)-**1**	$C_{15}H_{31}COO$-	$C_{13}H_{27}COO$-	$C_{17}H_{33}COO$-	93	+0.10
(*R*)-**2**	$C_{13}H_{27}COO$-	$C_{15}H_{31}COO$-	$C_{17}H_{33}COO$-	96	+0.11
(*S*)-**3**	$C_{15}H_{31}COO$-	$C_{17}H_{33}COO$-	$C_{13}H_{27}COO$-	79	+0.07
(*R*)-**4**	$C_{15}H_{31}COO$-	$C_{11}H_{23}COO$-	$C_{17}H_{31}COO$-	91	+0.03
(*R*)-**5**	$C_{11}H_{23}COO$-	$C_{15}H_{31}COO$-	$C_{17}H_{31}COO$-	94	+0.30

(*S*)-**6**	$C_{15}H_{31}COO$-	$C_{17}H_{31}COO$-	$C_{11}H_{23}COO$-	93	+0.17
(*R*)-**7**	$C_{15}H_{31}COO$-	$C_{9}H_{19}COO$-	$C_{17}H_{33}COO$-	84	+0.14
(*R*)-**8**	$C_{9}H_{19}COO$-	$C_{15}H_{31}COO$-	$C_{17}H_{33}COO$-	77	+0.11
(*S*)-**9**	$C_{15}H_{31}COO$-	$C_{17}H_{33}COO$-	$C_{9}H_{19}COO$-	99	+0.26
(*R*)-**10**	$C_{13}H_{27}COO$-	$C_{11}H_{23}COO$-	$C_{17}H_{33}COO$-	98	+0.09
(*R*)-**11**	$C_{11}H_{23}COO$-	$C_{13}H_{27}COO$-	$C_{17}H_{33}COO$-	95	+0.32
(*S*)-**12**	$C_{13}H_{27}COO$-	$C_{17}H_{33}COO$-	$C_{11}H_{23}COO$-	97	+0.17

[a] Yields are based on the final acylation in Schemes 1 and 2

2.2 *Synthesis of the second category TAGs*

The second category products (*S*)-**3**, **6**, **9** and **12** were synthesised by the synthetic route illustrated in Scheme 2 for (*S*)-**3**. It is a three-step chemoenzymatic route based on the benzylated acylglycerol adduct (*S*)-**13** as a precursor, shared with the synthesis of the first category TAG products, that already involved an enzymatic step. This time a second enzymatic step was required to secure the regiocontrol in introducing the second saturated fatty acyl group exclusively to the *sn*-3 position of the glycerol skeleton, after removal of the benzyl protective group, leaving the *sn*-2 position free for an unsaturated fatty acid.



Scheme 2. Chemical synthesis of the second category of TAGs (*S*)-**3**,**6**,**9** and **12** (shown for (*S*)-**3**). *Reagents and conditions*: (a) H_2, 10% Pd/C, THF, r.t. (87%); (b) Vinyl tetradecanoate, CAL, CH_2Cl_2, r.t. (83%); (c) *cis*-Hexadec-9-enoic acid, EDCI, DMAP, CH_2Cl_2, r.t. (79%).

The benzylated acylglycerol adducts (*S*)-**13** and **14**, obtained from the synthesis of the first category TAGs in accordance with Scheme 1, were subjected to the catalytic hydrogenolysis deprotection of

the benzyl protective group. The resulting 1-MAGs (*S*)-**33** and **34** were obtained in very good yields after crystallisation from hot hexane (see Table 3). A previous synthesis of (*R*)-**33** inolved a similar two-step overall process taking place without purification of the corresponding (*R*)-**13** prior to the deprotection.[34] The second step involved a highly regioselective acylation of (*S*)-**33** and **34** with myristic, lauric and capric acids activated as vinyl esters by use of the immobilised *Candida antarctica* lipase. As in a previous report[37] the acylations took place exclusively at the terminal *sn*-3 position in only 90 minutes, and the resulting 1,3-DAGs (*S*)-**35**-**38** were accomplished in good to very high yields after crystallisation from hot hexane (see Table 3). Their excellent regio- and hence enantiopurity was established by the fact that no acyl migration was observed to take place during these reactions. Also, the use of the activated vinyl esters and the consequent rapid reaction should rule out any side reactions involving the lipase to act on the acyl group already present in the 1-MAGs (*S*)-**33** and **34** to affect the enantiocontrol in the second step. The 1,3-DAGs (*S*)-**35**-**38** served as intermediates for the synthesis of the second category of TAGs (*S*)-**3**, **6**, **9** and **12**, respectively. Their structural information along with yields and specific rotation is provided in Table 3.

Table 3. Structural information based on the stereospecific numbering (*sn*-1/2/3), yields and specific rotation of the 1-MAG and 1,3-DAG intermediates obtained in accordance with the reactions described in Scheme 2 for the synthesis of the second category of TAGs

Entry	*sn*-1	*sn*-2	*sn*-3	Yield (%)	$[\alpha]_D^{25}$
(*S*)-**33**	$C_{15}H_{31}COO$-	-OH	-OH	87	-0.32
(*S*)-**34**	$C_{13}H_{27}COO$-	-OH	-OH	73	-0.40
(*S*)-**35**	$C_{15}H_{31}COO$-	-OH	$C_{13}H_{27}COO$-	83	+0.24
(*S*)-**36**	$C_{15}H_{31}COO$-	-OH	$C_{11}H_{23}COO$-	84	+0.61

(*S*)-**37**	$C_{15}H_{31}COO$-	-OH	$C_9H_{19}COO$-	86	+0.79
(*S*)-**38**	$C_{13}H_{27}COO$-	-OH	$C_{11}H_{23}COO$-	62	+0.68

The asymmetric 1,3-DAG intermediates were subsequently acylated with the unsaturated fatty acids using the same chemical coupling method as before, (*S*)-**35**, **37** and **38** with oleic acid and (*S*)-**36** with linoleic acid, to prepare the corresponding TAGs belonging to the second category, (*S*)-**3**, **9**, **12** and **6**, respectively. These products were accomplished in high and most cases excellent yields (79-99%) after flash chromatography purification as noted in Table 2. The specific optical rotation values for these enantiopure TAGs remain of low magnitude, comparable to those described above (see Table 2).

As reported earlier,[34,37] the specific optical activity of chiral TAGs remains extremely low and that warrants a remark. Enantiopure TAGs are generally known for their extremely low optical activity as was reported by Baer and Fischer in the late 1930s.[38,39] Such compounds are known to display cryptochirality[40] or cryptoactivity,[41,42] terms referring to their optical rotation remaining close to zero and hardly measurable. As can be noticed from the results in Table 2 the specific optical rotation values for all the enantiopure TAGs of both categories are all of positive sign and range from +0.03 to +0.32. The specific optical activity values for the asymmetric MAG and DAG intermediates displayed in Tables 1 and 3 were significantly higher, or roughly two orders of magnitude, which is consistent with previous reports.[34,37]

2.3 *Regio- and enantiocontrol*

All individual partial acylglycerols possibly involved in the reactions described herein, 1-MAGs, 2-MAGs, 1,3-DAGs and 1,2-DAGs, as well as their benzylated adducts and the TAGs, display

characteristic ^{1}H NMR spectra in their glyceryl skeleton proton region.[34-37] This makes it quite straightforward to spot individual acylglycerol constituents present in a reaction mixture and to quantify them with reasonable or good accuracy.[36] Therefore, this is an excellent tool to monitor both the progress of the reactions as they proceed as well as their regiocontrol in terms of acyl migration. The ^{13}C NMR spectroscopy is also of use in supporting the regiocontrol of the reactions.[35,36]

The limit of quantification as detected by 400 MHz ^{1}H NMR spectroscopy for a possible acyl-migration of 1,3-DAGs into 1,2-DAGs as well as 1-MAGs to 2-MAGs has been determined by thorough intensive studies (0.25 mol% for a practical concentration level).[36] In that context it may be borne in mind that an equilibrium composition involving 1(3)-MAGs and 2-MAGs is roughly 10% 2-MAGs and 90% 1(3)-MAGs,[43] whereas the corresponding equilibrium composition for 1,3-DAGs and 1(3),2-DAGs is roughly 70% 1,3-DAGs and 30% 1(3),2-DAGs.[25] It may be further added that the activation of the fatty acids involved in the lipase promoted reactions as vinyl esters not only allows the lipase to act very fast under very mild room temperature conditions, under which no acyl migration takes place, but also a very fast irreversible reaction is promoted, strongly reducing the risk of any side-reactions taking place, including acyl migration. From all this it is beyond doubt that losses of enantiocontrol in these reactions caused by acyl migration can be ruled out in the current work.

All intermediates including the asymmetric MAGs and DAGs and the final TAG products were obtained in high chemical purity and were all fully characterized by traditional synthetic organic chemistry methods including ^{1}H (400 MHz) and ^{13}C NMR and IR spectroscopy methods as well as satisfactory high-resolution accurate mass spectrometry analyses. Specific optical rotation was determined for all chiral compounds involved. A full regiocontrol, and therefore enantiocontrol, in

all the reactions involved was established as based on detailed studies by the ^{1}H and ^{13}C NMR spectroscopy in accordance with previous reports.[35-37] That is anticipated in due time to be unequivocally confirmed in the intended reversed phase chiral HPLC analysis, as certainly was the case regarding our enantiopure AAB type TAGs previously prepared by comparable methods.[28,34] In that case we had access to commercially available TAGs as racemic mixtures, unlike in the current work. It should be emphasised that most natural chiral TAGs are not separable into enantiomers without the use of more sophisticated techniques based on double chiral column and recycling HPLC systems.[11,12,27,28] Hence, the determination of the enantiopurity of the current TAGs must await synthesis of the opposite enantiomers or a racemic mixture of the TAGs and cannot take place until that has been accomplished.

The synthetic strategy that was followed is suitable for preparing enantiopure structured TAGs of the ABC type possessing three different fatty acids with the prerequisite that not more than one of them being unsaturated. This relates to the use of catalytic hydrogenolysis to bring about disconnection of the protective group from the mono- and diacylated benzyl protected intermediates that essentially need to be saturated in terms of the fatty acids. TAGs belonging to the two ABC type categories addressed in the current report, possessing two different saturated and one unsaturated fatty acids, are readily accessible by the current synthetic approach.

It is of interest that despite the superb regioselectivity offered by the CAL to acylate glycerol and 1-*O*-alkylglycerols exclusively at the terminal primary alcohol positions, the same lipase is known to exhibit no detectable preference for one enantiomer of such substrates over the other in these reactions. This has been demonstrated in our previous acylation of (*S*)-1-*O*-benzylglycerol with vinyl esters of both palmitic and capric acids taking place with the same rate and efficiency as described above for the *R*-enantiomer.[34] Similar behavior was also observed in the acylation of 1-

O-alkylglycerol enantiomers in structured ether lipid synthesis[44-46] as well as enantiomers of 1-MAGs in the synthesis of asymmetric 1,3-DAGs (Kristinsson and Haraldsson, unpublished results). From this it may be concluded that the methodology described herein can be used to synthesise both enantiomers of the ABC type enantiostructured TAGs addressed in the current work.

3. Conclusion

A major obstacle in enantiospecific analysis of intact TAGs in fats and oils of plant and animal origin is a shortage of enantiopure structured TAG enantiomers to serve as standards to determine the separation order of two TAG enantiomers in such analysis. That impediment has been addressed to somewhat extent, in a previous report[34] and the current report, describing the synthesis of twelve enantiopure ABC type structured TAGs, this time possessing three different fatty acids. Eight of them possess two different saturated fatty acyl groups located in one of the terminal positions and the mid position, with an unsaturated fatty acyl group in the remaining terminal position of the glycerol backbone. They were synthesised by a six-step chemoenzymatic route involving a highly regioselective immobilised *Candida antarctica* lipase, starting from an enantiopure solketal. The four remaining TAGs constitute two different saturated fatty acyl groups in the terminal 1,3-positions and an unsaturated acyl group in the 2-position and were prepared by a similar six-step approach based on the same chiral precursor, this time requiring two enzymatic steps with the same lipase. This highly efficient synthetic strategy should prove of high use to synthesise a variety of similar and related enantiopure ABC type structured TAGs to serve as standards in stereospecific analysis of intact TAGs in fats and oils.

4. Experimental

4.1 *General*

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Bruker Avance 400 spectrometer in deuterated chloroform as a solvent at 400.12 and 100.61 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) in Hertz (Hz). The following abbreviations are used to describe the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; dd, doublet of doublets; m, multiplet. Infrared spectra were conducted on a Thermo Nicolet FT-IR iS10 Spectrophotometer on a KBr pellet (crystalline material) or as a neat liquid (oils). Melting points were determined on a Büchi 520 melting point apparatus and are uncorrected. The high-resolution mass spectra (HRMS) were acquired on a Bruker micrOTOF-Q mass spectrometer. All data analysis was done on Bruker software. Optical activity measurements were performed on an Autopol^{R} V Automatic Polarimeter from Rudolph Research Analytical using a 40T-2.5-100-0.7 Temp Trol™ polarimetric cell with 2.5 mm inside diameter, 100 mm optical path length and 0.7 mL volume with c referring to g sample/100 mL.

The immobilised *Candida antarctica* lipase (Novozym 435; CAL-B) was supplied as a gift from Novozymes A/S (Bagsvaerd, Denmark). All chemicals and solvents were used without further purification unless otherwise stated. (*S*)-(+)-2,2-Dimethyl-1,3-dioxolane-4-methanol, (*S)*-solketal, (98% purity and 99% ee) were purchased from Sigma-Aldrich (Steinheim, Germany). EDCI (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, 98%) was obtained commercial grade from Sigma-Aldrich (Steinheim, Germany) and 4-dimethylaminopyridine (DMAP, 99%) from Acros Organics (Geel, Belgium). Benzyl bromide (98%), sodium hydride (60% dispersion in mineral oil) and 10% palladium on carbon catalyst were from Sigma-Aldrich (Steinheim). Linoleic, oleic, palmitic, myristic, lauric and capric acids were all obtained as free acids in high (>99%) purity from Larodan Fine Chemicals (Malmö, Sweden). Vinyl palmitate (96%), vinyl myristate (99%), vinyl laurate (99%) and vinyl caprate (99%) were all obtained from TCI Europe

(Zwinderecht, Belgium). Dichloromethane and ethyl acetate were obtained HPLC grade from Sigma-Aldrich (Steinheim, Germany), *n*-hexane as p.a. from Merck (Darmstadt, Germany), petroleum ether, boiling range 40-60 °C, and ethanol (99.8%) from Honeywell (Seelze, Germany). Dichloromethane was dried over CaH_2 under dry nitrogen atmosphere. Tetrahydrofuran for analysis was obtained from Acros Organics (Geel, Belgium) and dried over Na wire in presence of benzophenone under dry nitrogen atmosphere. Column chromatography was performed on Silica gel 60 (Silicycle, Ontario). Reactions were monitered by TLC on Silica gel 60 F254 (Silicycle, Ontario), with detection by quenching of fluorescence and/or with phosphomolybdic acid in ethanol.

4.2 3-*O*-Benzyl-*sn*-glycerol

To a suspension of NaH (9.08 g, 60 wt% dispersion in mineral oil, 227 mmol, 3.0 equiv.) in THF (189 mL) at 0 °C was added (*S*)-solketal (9.43 mL, 75.7 mmol, 1.0 equiv.) dropwise *via* syringe. The cooling bath was removed, and the resulting suspension was stirred at room temperature for 1 h before being cooled back to 0 °C followed by dropwise addition of benzyl bromide (10.8 mL, 90.8 mmol, 1.2 equiv.). The resulting mixture was brought to reflux and stirred for 4 h after which it was cooled to 0 °C, diluted carefully with EtOH (116 mL), followed by addition of a 2.0 M aqueous solution of HCl (114 mL). After stirring at 80 °C for 1 h, the resulting mixture was cooled to room temperature and quenched by addition of a saturated aqueous solution of $NaHCO_3$ (250 mL). The organic layer was separated and the aqueous layer further extracted with EtOAc (3 × 150 mL), the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product which was purified *via* column chromatography (petroleum ether / EtOAc (50%) → petroleum ether / EtOAc (80%)) to give 3-*O*-benzyl-*sn*-glycerol (12.7 g, 69.8 mmol, 92%) as a yellow oil;

$[\alpha]_D^{24}$ +5.10 (*c* 19.6, $CHCl_3$); $\mathbf{R_f}$ 0.20 (petroleum ether / EtOAc (70%)); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.40-7.27 (5H, m, Ar*H*), 4.56 (2H, s, OCH_2Ar), 3.95-3.85 (1H, m, C*H*OH), 3.77-3.69 (1H, m, CH_2OH), 3.67-3.62 (1H, m, CH_2'OH), 3.59 (1H, dd, *J* = 9.5 and 4.0 Hz, CH_2OBn), 3.55 (1H, dd, *J* = 9.5 and 6.0 Hz, CH_2'OBn), 2.57 (1H, d, *J* = 4.5 Hz, O*H*), 2.06 (1H, app. t, *J* = 6.0 Hz, O*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 137.7, 128.5, 127.9, 127.8, 73.6, 71.8, 70.6, 64.1.

Spectroscopic data in agreement with that reported for the *R*-enantiomer by Kristinsson *et al*.[34]

4.3 General Procedure A: Enzymatic Acylation Procedure

To a mixture of benzyl protected glycerol (1.0 equiv.) and vinyl ester of the appropriate saturated fatty acid (1.05-1.3 equiv.) in CH_2Cl_2 (3.5 mL / mmol of substrate) was added immobilized *Candida antarctica* lipase B (CAL) (4-10 wt% of total combined mass of substrates). The resulting suspension was stirred at room temperature at a rate not to imperil the solid supported lipase. After stirring for 1.5 h (or until full consumption of starting material as indicated by TLC) the lipase was separated by filtration and the filtrate concentrated *in vacuo* to give the crude product which was purified by either flash column chromatography or recrystallisation (where appropriate). **Note:** 1-Acyl-3-*O*-alkylglycerols should be purified *via* column chromatography using 4% boric acid impregnated silica gel as they are prone to acyl migration.

4.4 3-*O*-Benzyl-1-hexadecanoyl-*sn*-glycerol, (*S*)-13

(*S*)-**13** was prepared using General Procedure A, with 3-*O*-benzyl-*sn*-glycerol (100 mg, 0.55 mmol, 1.0 equiv.), vinyl palmitate (117 mg, 0.63 mmol, 1.15 equiv.) and CAL (18 mg) in CH_2Cl_2 (2.0 mL), with a 1.5 h reaction time. Purification *via* column chromatography (4% boric acid impregnated silica gel, petroleum ether / EtOAc (40%)) gave (*S*)-**13** (90 mg, 0.48 mmol, 87%) as a colourless oil;

$[\alpha]_D^{25}$ +1.11 (*c* 9.0, CH_2Cl_2); **IR** (NaCl, ν_{max} / cm^{-1}) 3459, 3064, 3031, 2924, 2853, 1739, 1174; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.39-7.27 (5H, m, Ar*H*), 4.56 (2H, s, OCH_2Ar), 4.19 (1H, dd, *J* = 11.5 and 4.5 Hz, CH_2OCO), 4.14 (1H, dd, *J* = 11.5 and 6.0 Hz, CH_2'OCO), 4.07-4.00 (1H, m, C*H*OCO), 3.56 (1H, dd, *J* = 9.5 and 4.5 Hz, CH_2OBn), 3.50 (1H, dd, *J* = 9.5 and 6.0 Hz, CH_2'OBn), 2.51 (1H, bs, O*H*), 2.32 (2H, t, *J* = 7.5 Hz, CH_2COO), 1.67-1.56 (2H, m, CH_2CH$_2$COO), 1.38-1.24 (24H, m, 12 × CH_2), 0.88 (3H, t, *J* = 6.5 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 174.1, 137.8, 128.6, 128.0, 127.9, 73.7, 71.0, 69.1, 65.5 34.3, 32.1, 29.83, 29.80, 29.75, 29.6, 29.5, 29.4, 29.3, 25.1, 22.8, 14.3; **HRMS** (ESI+) calc. for $C_{26}H_{44}O_4Na$ $[M+Na]^+$ 443.3132, found 443.3127.

4.5 3-*O*-Benzyl-1-tetradecanoyl-*sn*-glycerol, (*S*)-14

(*S*)-**14** was prepared using General Procedure A, with 3-*O*-benzyl-*sn*-glycerol (50 mg, 0.27 mmol, 1.0 equiv.), vinyl myristate (0.091 mL, 0.31 mmol, 1.15 equiv.) and CAL (6 mg) in CH_2Cl_2 (1.0 mL), with a 1.5 h reaction time. Purification *via* column chromatography (4% boric acid impregnated silica gel, petroleum ether / EtOAc (40%)) gave (*S*)-**14** (100 mg, 0.25 mmol, 94%) as a colourless oil;

$[\alpha]_D^{25}$ +3.64 (*c* 5.0, CH_2Cl_2); **IR** (NaCl, ν_{max} / cm^{-1}) 3458, 3064, 3031, 2925, 2854, 1739, 1174; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.28 (5H, m, Ar*H*), 4.56 (2H, s, OCH_2Ar), 4.19 (1H, dd, *J* = 11.5 and 4.5 Hz, CH_2OCO), 4.14 (1H, dd, *J* = 11.5 and 6.0 Hz, CH_2'OCO), 4.06-4.00 (1H, m, C*H*OCO), 3.56 (1H, dd, *J* = 9.5 and 4.5 Hz, CH_2OBn), 3.50 (1H, dd, *J* = 9.5 and 6.0 Hz, CH_2'OBn), 2.48 (1H, bs, O*H*), 2.32 (2H, t, *J* = 7.5 Hz, CH_2COO), 1.66-1.58 (2H, m, CH_2CH$_2$COO), 1.32-1.26 (20H, m, 10 × CH_2), 0.89 (3H, t, *J* = 6.5 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 174.1, 137.8, 128.6, 128.0, 127.9, 73.6, 71.0, 69.1, 65.5 34.3, 32.1, 29.8, 29.7, 29.6,

29.5, 29.4, 29.3, 25.1, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{24}H_{40}O_4Na$ $[M+Na]^+$ 415.2819, found 415.2806.

4.6 3-*O*-Benzyl-1-dodecanoyl-*sn*-glycerol, (*S*)-15

(*S*)-**15** was prepared using General Procedure A, with 3-*O*-benzyl-*sn*-glycerol (103 mg, 0.57 mmol, 1.0 equiv.), vinyl laurate (0.19 mL, 0.72 mmol, 1.26 equiv.) and CAL (20 mg) in CH_2Cl_2 (2.0 mL), with a 1.5 h reaction time. Purification *via* column chromatography (4% boric acid impregnated silica gel, petroleum ether / EtOAc (40%)) gave **(*S*)-15** (199 mg, 0.55 mmol, 96%) as a colourless oil;

$[\alpha]_D^{25}$ +1.31 (*c* 4.70, CH_2Cl_2); **IR** (NaCl, ν_{max} / cm^{-1}) 3459, 3031, 2925, 2854, 1739, 1174; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.27 (5H, m, Ar*H*), 4.56 (2H, s, OCH_2Ar), 4.19 (1H, dd, *J* = 11.5 and 4.5 Hz, CH_2OCO), 4.14 (1H, dd, *J* = 11.5 and 6.0 Hz, CH_2'OCO), 4.06-4.00 (1H, m, C*H*OCO), 3.56 (1H, dd, *J* = 9.5 and 4.5 Hz, CH_2OBn), 3.50 (1H, dd, *J* = 9.5 and 6.0 Hz, CH_2'OBn), 2.48 (1H, bs, O*H*), 2.32 (2H, t, *J* = 7.5 Hz, CH_2COO), 1.65-1.57 (2H, m, CH_2CH$_2$COO), 1.32-1.26 (16H, m, 8 × CH_2), 0.88 (3H, t, *J* = 6.5 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 174.1, 137.8, 128.6, 128.0, 127.9, 73.6, 71.0, 69.1, 65.5 34.3, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 25.1, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{22}H_{35}O_4Na$ $[M+Na]^+$ 387.2506, found 387.2498.

4.7 3-*O*-Benzyl-1-decanoyl-*sn*-glycerol, (*S*)-16

(*S*)-**16** was prepared using General Procedure A, with 3-*O*-benzyl-*sn*-glycerol (250 mg, 1.37 mmol, 1.0 equiv.), vinyl caprate (0.28 mL, 1.76 mmol, 1.28 equiv.) and CAL (24 mg) in CH_2Cl_2 (4.0 mL), with a 1.5 h reaction time. Purification *via* column chromatography (4% boric acid impregnated silica gel, petroleum ether / EtOAc (40%)) gave (*S*)-**16** (447 mg, 1.33 mmol, 97%) as a colourless oil;

$[\alpha]_D^{25}$ +1.48 (*c* 10.0, CH_2Cl_2); **IR** (NaCl, ν_{max} / cm^{-1}) 3459, 3031, 2926, 2855, 1739, 1173; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.28 (5H, m, Ar*H*), 4.56 (2H, s, OCH_2Ar), 4.19 (1H, dd, *J* = 11.5 and 4.5 Hz, CH_2OCO), 4.14 (1H, dd, *J* = 11.5 and 6.0 Hz, CH_2'OCO), 4.06-4.01 (1H, m, C*H*OCO), 3.55 (1H, dd, *J* = 9.5 and 4.5 Hz, CH_2OBn), 3.49 (1H, dd, *J* = 9.5 and 6.0 Hz, CH_2'OBn), 2.57 (1H, bs, O*H*), 2.32 (2H, t, *J* = 7.5 Hz, CH_2COO), 1.66-1.57 (2H, m, CH_2CH$_2$COO), 1.35-1.26 (12H, m, 6 × CH_2), 0.87 (3H, t, *J* = 6.5 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 174.1, 137.8, 128.6, 128.0, 127.9, 73.6, 71.0, 69.1, 65.5 34.3, 32.0, 29.5, 29.4, 29.3, 24.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{20}H_{32}O_4Na$ $[M+Na]^+$ 359.2193, found 359.2193.

4.8 General Procedure B: Chemical Acylation Procedure

To a flask containing glycerol (1.0 equiv.), the appropriate fatty acid (1.10 equiv.), EDCI (1.20 equiv.) and DMAP (0.20 equiv.) was added CH_2Cl_2 (2.5 mL / mmol substrate). After stirring at room temperature for 16 h, the reaction mixture was concentrated *in vacuo* and purified *via* column chromatography.

4.9 3-*O*-Benzyl-1-hexadecanoyl-2-tetradecanoyl-*sn*-glycerol, (*S*)-17

(*S*)-**17** was prepared using General Procedure B, with (*S*)-**13** (436 mg, 1.04 mmol, 1.0 equiv.), myristic acid (260 mg, 1.14 mmol, 1.1 equiv.), EDCI (237 mg, 1.24 mol, 1.2 equiv.) and DMAP (25 mg, 0.21 mmol, 0.20 equiv.) in CH_2Cl_2 (2.6 mL) with a reaction time of 16 h. Purification *via* recrystallisation from hot ethanol gave (*S*)-**17** (620 mg, 0.983 mmol, 95%) as a colourless wax;

m.p. 37.7-39.8 °C; $[\alpha]_D^{25}$ +4.28 (*c* 1.94, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 2915, 1721, 1646, 1298; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.26 (5H, m, Ar*H*), 5.28-5.20 (1H, m, C*H*OCO), 4.56 (1H, d, *J* = 12.0 Hz, OCH_2Ar), 4.52 (1H, d, *J* = 12.0 Hz, OCH_2'Ar), 4.35 (1H, dd, *J* = 12.0 and 4.0 Hz, CH_2OCO), 4.19 (1H, dd, *J* = 12.0 and 6.5 Hz, CH_2'OCO), 3.63-3.55 (2H, m, CH_2OBn), 2.32 (2H,

t, *J* = 7.5 Hz, C*H*$_2$COO), 2.28 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 1.68-1.55 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.38-1.18 (44H, m, 22 × C*H*$_2$), 0.88 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.6, 173.3, 137.9, 128.6, 127.9, 127.8, 73.5, 70.2, 68.4, 62.8, 34.5, 34.3, 32.1, 29.84, 29.81, 29.78, 29.63, 29.50, 29.44, 29.28, 29.24, 25.1, 25.0, 22.8, 14.4; **HRMS** (ESI+) calc. for $C_{40}H_{70}O_5Na$ $[M+Na]^+$ 653.5115, found 653.5094.

4.10 3-*O*-Benzyl-2-hexadecanoyl-1-tetradecanoyl-*sn*-glycerol, (*S*)-18

(*S*)-**18** was prepared using General Procedure B, with (*S*)-**14** (496 mg, 1.26 mmol, 1.0 equiv.), palmitic acid (356 mg, 1.39 mmol, 1.1 equiv.), EDCI (291 mg, 1.52 mol, 1.2 equiv.) and DMAP (31 mg, 0.25 mmol, 0.20 equiv.) in CH_2Cl_2 (3.0 mL) with a reaction time of 16 h. Purification *via* recrystallisation from hot ethanol gave (*S*)-**18** (710 mg, 1.26 mmol, 89%) as a colourless solid;

m.p. 31.3-33.9 °C; $[\alpha]_D^{25}$ +4.32 (*c* 2.0, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 2915, 1721, 1646, 1298; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.26 (5H, m, Ar*H*), 5.28-5.20 (1H, m, C*H*OCO), 4.56 (1H, d, *J* = 12.0 Hz, OC*H*$_2$Ar), 4.52 (1H, d, *J* = 12.0 Hz, OC*H*$_2$'Ar), 4.35 (1H, dd, *J* = 12.0 and 4.0 Hz, C*H*$_2$OCO), 4.19 (1H, dd, *J* = 12.0 and 6.5 Hz, C*H*$_2$'OCO), 3.63-3.55 (2H, m, C*H*$_2$OBn), 2.32 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 2.28 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 1.68-1.55 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.38-1.18 (44H, m, 22 × C*H*$_2$), 0.88 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.6, 173.3, 137.9, 128.6, 127.9, 127.8, 73.5, 70.2, 68.4, 62.8, 34.5, 34.3, 32.1, 29.84, 29.81, 29.78, 29.64, 29.51, 29.44, 29.28, 29.24, 25.1, 25.0, 22.8, 14.3; **HRMS** (ESI+) calc. for $C_{40}H_{70}O_5Na$ $[M+Na]^+$ 653.5115, found 653.5111.

4.11 3-*O*-Benzyl-2-dodecanoyl-1-hexadecanoyl-*sn*-glycerol, (*S*)-19

(*S*)-**19** was prepared using General Procedure B, with (*S*)-**13** (460 mg, 1.09 mmol, 1.0 equiv.), lauric acid (241 mg, 1.20 mmol, 1.1 equiv.), EDCI (250 mg, 1.31 mol, 1.2 equiv.) and DMAP (27

mg, 0.22 mmol, 0.20 equiv.) in CH_2Cl_2 (2.7 mL) with a reaction time of 16 h. Purification *via* recrystallisation from hot ethanol gave (*S*)-**19** (633 mg, 1.05 mmol, 96%) as a colourless wax; $[\alpha]_D^{25}$ +8.11 (*c* 1.75, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 2915, 1721, 1646, 1298; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.26 (5H, m, Ar*H*), 5.28-5.20 (1H, m, C*H*OCO), 4.56 (1H, d, *J* = 12.0 Hz, OC*H*$_2$Ar), 4.52 (1H, d, *J* = 12.0 Hz, OC*H*$_2$'Ar), 4.35 (1H, dd, *J* = 12.0 and 4.0 Hz, C*H*$_2$OCO), 4.19 (1H, dd, *J* = 12.0 and 6.5 Hz, C*H*$_2$'OCO), 3.63-3.55 (2H, m, C*H*$_2$OBn), 2.32 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 2.28 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 1.68-1.55 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.38-1.18 (40H, m, 20 × C*H*$_2$), 0.88 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.6, 173.3, 137.9, 128.6, 127.9, 127.8, 73.5, 70.2, 68.4, 62.8, 34.5, 34.3, 32.06, 32.05, 29.84, 29.80, 29.77, 29.62, 29.50, 29.48, 29.43, 29.27, 29.24, 25.1, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{38}H_{66}O_5Na$ $[M+Na]^+$ 625.4802, found 625.4801.

4.12 3-*O*-Benzyl-1-dodecanoyl-2-hexadecanoyl-*sn*-glycerol, (*S*)-20

(*S*)-**20** was prepared using General Procedure B, with (*S*)-**15** (501 mg, 1.37 mmol, 1.0 equiv.), palmitic acid (388 mg, 1.51 mmol, 1.1 equiv.), EDCI (316 mg, 1.65 mol, 1.2 equiv.) and DMAP (34 mg, 0.27 mmol, 0.20 equiv.) in CH_2Cl_2 (3.5 mL) with a reaction time of 16 h. Purification *via* recrystallisation from hot ethanol gave (*S*)-**20** (700 mg, 1.16 mmol, 84%) as a colourless solid; $[\alpha]_D^{25}$ +5.73 (*c* 2.06, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 2915, 1721, 1646, 1298; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.26 (5H, m, Ar*H*), 5.28-5.20 (1H, m, C*H*OCO), 4.56 (1H, d, *J* = 12.0 Hz, OC*H*$_2$Ar), 4.52 (1H, d, *J* = 12.0 Hz, OC*H*$_2$'Ar), 4.35 (1H, dd, *J* = 12.0 and 4.0 Hz, C*H*$_2$OCO), 4.19 (1H, dd, *J* = 12.0 and 6.5 Hz, C*H*$_2$'OCO), 3.63-3.55 (2H, m, C*H*$_2$OBn), 2.32 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 2.28 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 1.68-1.55 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.38-1.18 (40H, m, 20 × C*H*$_2$), 0.88 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.6, 173.3, 137.9, 128.6, 127.9, 127.8, 73.5, 70.2, 68.4, 62.8, 34.5, 34.3, 32.06, 32.05, 29.84, 29.80,

29.77, 29.62, 29.50, 29.48, 29.43, 29.27, 29.24, 25.1, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{38}H_{66}O_5Na$ $[M+Na]^+$ 625.4802, found 625.4799.

4.13 3-*O*-Benzyl-2-decanoyl-1-hexadecanoyl-*sn*-glycerol, (*S*)-21

(*S*)-**21** was prepared using General Procedure B, with (*S*)-**13** (460 mg, 1.09 mmol, 1.0 equiv.), capric acid (207 mg, 1.20 mmol, 1.1 equiv.), EDCI (250 mg, 1.31 mol, 1.2 equiv.) and DMAP (27 mg, 0.22 mmol, 0.20 equiv.) in CH_2Cl_2 (2.7 mL) with a reaction time of 16 h. Purification *via* recrystallisation from hot ethanol gave (*S*)-**21** (564 mg, 0.981 mmol, 90%) as a colourless wax; $[\alpha]_D^{25}$ +5.34 (*c* 2.81, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 2915, 1721, 1646, 1298; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.26 (5H, m, Ar*H*), 5.28-5.20 (1H, m, C*H*OCO), 4.56 (1H, d, *J* = 12.0 Hz, OC*H*$_2$Ar), 4.52 (1H, d, *J* = 12.0 Hz, OC*H*$_2$'Ar), 4.35 (1H, dd, *J* = 12.0 and 4.0 Hz, C*H*$_2$OCO), 4.19 (1H, dd, *J* = 12.0 and 6.5 Hz, C*H*$_2$'OCO), 3.63-3.55 (2H, m, C*H*$_2$OBn), 2.32 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 2.28 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 1.68-1.55 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.38-1.18 (36H, m, 18 × C*H*$_2$), 0.88 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.5, 173.2, 137.9, 128.5, 127.9, 127.8, 73.4, 70.1, 68.4, 62.8, 34.5, 34.3, 32.1, 32.0, 29.83, 29.79, 29.76, 29.62, 29.57, 29.49, 29.42, 29.26, 29.22, 25.1, 25.0, 22.82, 22.80, 14.23, 14.23; **HRMS** (ESI+) calc. for $C_{36}H_{62}O_5Na$ $[M+Na]^+$ 597.4489, found 597.4476.

4.14 3-*O*-Benzyl-1-decanoyl-2-hexadecanoyl-*sn*-glycerol, (*S*)-22

(*S*)-**22** was prepared using General Procedure B, with (*S*)-**16** (403 mg, 1.20 mmol, 1.0 equiv.), palmitic acid (338 mg, 1.32 mmol, 1.1 equiv.), EDCI (276 mg, 1.44 mol, 1.2 equiv.) and DMAP (29 mg, 0.24 mmol, 0.20 equiv.) in CH_2Cl_2 (3.0 mL) with a reaction time of 16 h. Purification *via* recrystallisation from hot ethanol gave (*S*)-**22** (567 mg, 0.986 mmol, 82%) as a colourless wax;

$[\alpha]_D^{25}$ +4.53 (*c* 2.19, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 2915, 1721, 1646, 1298; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.26 (5H, m, Ar*H*), 5.28-5.20 (1H, m, C*H*OCO), 4.56 (1H, d, *J* = 12.0 Hz, OC*H*$_2$Ar), 4.52 (1H, d, *J* = 12.0 Hz, OC*H*$_2$'Ar), 4.35 (1H, dd, *J* = 12.0 and 4.0 Hz, C*H*$_2$OCO), 4.19 (1H, dd, *J* = 12.0 and 6.5 Hz, C*H*$_2$'OCO), 3.63-3.55 (2H, m, C*H*$_2$OBn), 2.32 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 2.28 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 1.68-1.55 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.38-1.18 (36H, m, 18 × C*H*$_2$), 0.88 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.6, 173.3, 137.9, 128.6, 127.9, 127.8, 73.5, 70.2, 68.4, 62.8, 34.5, 34.3, 32.1, 32.0, 29.83, 29.81, 29.78, 29.6, 29.5, 29.4, 29.3, 29.2, 25.1, 25.0, 22.83, 22.80 14.25, 14.24; **HRMS** (ESI+) calc. for $C_{36}H_{62}O_5Na$ $[M+Na]^+$ 597.4489, found 597.4487.

4.15 3-*O*-Benzyl-2-dodecanoyl-1-tetradecanoyl-*sn*-glycerol, (*S*)-23

(*S*)-**23** was prepared using General Procedure B, with (*S*)-**14** 492 mg, 1.25 mmol, 1.0 equiv.), lauric acid (276 mg, 1.38 mmol, 1.1 equiv.), EDCI (288 mg, 1.50 mol, 1.2 equiv.) and DMAP (31 mg, 0.25 mmol, 0.20 equiv.) in CH_2Cl_2 (3.0 mL) with a reaction time of 16 h. Purification *via* recrystallisation from hot ethanol gave (*S*)-**23** (620 mg, 1.08 mmol, 86%) as a colourless wax;

$[\alpha]_D^{25}$ +4.81 (*c* 2.94, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 2915, 1721, 1646, 1298; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.26 (5H, m, Ar*H*), 5.28-5.20 (1H, m, C*H*OCO), 4.56 (1H, d, *J* = 12.0 Hz, OC*H*$_2$Ar), 4.52 (1H, d, *J* = 12.0 Hz, OC*H*$_2$'Ar), 4.35 (1H, dd, *J* = 12.0 and 4.0 Hz, C*H*$_2$OCO), 4.19 (1H, dd, *J* = 12.0 and 6.5 Hz, C*H*$_2$'OCO), 3.63-3.55 (2H, m, C*H*$_2$OBn), 2.32 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 2.28 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 1.68-1.55 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.38-1.18 (36H, m, 18 × C*H*$_2$), 0.88 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.6, 173.3, 137.9, 128.6, 127.9, 127.8, 73.4, 70.2, 68.4, 62.8, 34.5, 34.3, 32.1, 29.82, 29.79, 29.77, 29.62, 29.49, 29.48, 29.43, 29.26, 29.23, 25.1, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{36}H_{62}O_5Na$ $[M+Na]^+$ 597.4489, found 597.4484.

4.16 3-*O*-Benzyl-1-dodecanoyl-2-tetradecanoyl-*sn*-glycerol, (*S*)-24

(*S*)-**24** was prepared using General Procedure B, with (*S*)-**15** (490 mg, 1.34 mmol, 1.0 equiv.), myristic acid (338 mg, 1.48 mmol, 1.1 equiv.), EDCI (309 mg, 1.61 mol, 1.2 equiv.) and DMAP (33 mg, 0.27 mmol, 0.20 equiv.) in CH_2Cl_2 (3.5 mL) with a reaction time of 16 h. Purification *via* recrystallisation from hot ethanol gave (*S*)-**24** (630 mg, 1.10 mmol, 82%) as a colourless wax; $[\alpha]_D^{25}$ +4.69 (*c* 1.80, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 2915, 1721, 1646, 1298; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.38-7.26 (5H, m, Ar*H*), 5.28-5.20 (1H, m, C*H*OCO), 4.56 (1H, d, *J* = 12.0 Hz, OC*H*$_2$Ar), 4.52 (1H, d, *J* = 12.0 Hz, OC*H*$_2$'Ar), 4.35 (1H, dd, *J* = 12.0 and 4.0 Hz, C*H*$_2$OCO), 4.19 (1H, dd, *J* = 12.0 and 6.5 Hz, C*H*$_2$'OCO), 3.63-3.55 (2H, m, C*H*$_2$OBn), 2.32 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 2.28 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 1.68-1.55 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.38-1.18 (36H, m, 18 × C*H*$_2$), 0.88 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.6, 173.3, 137.9, 128.6, 127.9, 127.8, 73.5, 70.2, 68.4, 62.8, 34.5, 34.3, 32.1, 29.83, 29.80, 29.77, 29.76, 29.73, 29.63, 29.48, 29.43, 29.42, 29.27, 29.24, 25.1, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{36}H_{62}O_5Na$ $[M+Na]^+$ 597.4489, found 597.4480.

4.17 General Procedure C: Catalytic Hydrogenolysis Procedure

A round-bottom flask, equipped with a stirrer bar, was charged with benzyl protected glycerol (1.0 equiv.) and Pd/C (10 wt% Pd, 10.0 mol%). The flask was evacuated, filled with nitrogen, the appropriate volume of THF (3-10 mL / mmol substrate) added followed by purging of the flask with hydrogen. Hydrogenation (H_2 balloon) was conducted at room temperature with vigorous stirring until completion (monitored by TLC, usually 16 h). The reaction mixture was then diluted with THF, filtered through Celite and concentrated *in vacuo* to give the crude product which was purified *via* recrystallisation.

4.18 1-Hexadecanoyl-2-tetradecanoyl-*sn*-glycerol, (*S*)-25

(*S*)-**25** was prepared using General Procedure C, with (*S*)-**17** (631 mg, 1.00 mmol, 1.0 equiv.), Pd/C (106 mg, 10 wt% Pd, 0.100 mmol. 10.0 mol%) in THF (10 mL), with a reaction time of 16 h. Purification *via* recrystallisation from hot hexane gave (*S*)-**25** (386 g, 0.714 mmol, 71%) as a colourless solid;

m.p. 64.5-68.2 °C; $[\alpha]_D^{25}$ –2.20 (*c* 1.88, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.08 (1H, quin, *J* = 5.0 Hz, C*H*OCO), 4.32 (1H, dd, *J* = 12.0 and 4.5 Hz, CH_2OCO), 4.24 (1H, dd, *J* = 12.0 and 5.5 Hz, CH_2'OCO), 3.76-3.70 (2H, m, CH_2OH), 2.38-2.27 (4H, m, 2 × CH_2COO), 2.16 (1H, bs, O*H*), 1.68-1.57 (4H, m, 2 × CH_2CH$_2$COO), 1.37-1.19 (44H, m, 22 × CH_2), 0.88 (6H, t, *J* = 6.5 Hz, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.9, 173.6, 72.3, 62.2, 61.7, 34.4, 34.2, 32.1, 29.83, 29.79, 29.76, 29.62, 29.50, 29.41, 29.26, 29.24, 25.1, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{33}H_{64}O_5Na$ $[M+Na]^+$ 563.4646, found 563.4638.

4.19 2-Hexadecanoyl-1-tetradecanoyl-*sn*-glycerol, (*S*)-26

(*S*)-**26** was prepared using General Procedure C, with (*S*)-**18** (675 mg, 1.07 mmol, 1.0 equiv.), Pd/C (114 mg, 10 wt% Pd, 0.107 mmol. 10.0 mol%) in THF (11 mL), with a reaction time of 16 h. Purification *via* recrystallisation from hot hexane gave (*S*)-**26** (429 g, 0.793 mmol, 74%) as a colourless solid;

m.p. 54.2-58.8 °C; $[\alpha]_D^{25}$ –3.19 (*c* 2.31, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.08 (1H, quin, *J* = 5.0 Hz, C*H*OCO), 4.32 (1H, dd, *J* = 12.0 and 4.5 Hz, CH_2OCO), 4.24 (1H, dd, *J* = 12.0 and 5.5 Hz, CH_2'OCO), 3.76-3.70 (2H, m, CH_2OH), 2.38-2.27 (4H, m, 2 × CH_2COO), 2.15 (1H, bs, O*H*), 1.68-1.57 (4H, m, 2 × CH_2CH$_2$COO), 1.37-1.19 (44H, m, 22 × CH_2), 0.88 (6H, t, *J* = 6.5 Hz, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.9,

173.6, 72.3, 62.2, 61.7, 34.4, 34.2, 32.1, 29.83, 29.79, 29.76, 29.62, 29.50, 29.41, 29.26, 29.24, 25.1, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{33}H_{64}O_5Na$ $[M+Na]^+$ 563.4646, found 563.4633.

4.20 2-Dodecanoyl-1-hexadecanoyl-*sn*-glycerol, (*S*)-27

(*S*)-**27** was prepared using General Procedure C, with (*S*)-**19** (633 mg, 1.05 mmol, 1.0 equiv.), Pd/C (112 mg, 10 wt% Pd, 0.105 mmol. 10.0 mol%) in THF (11 mL), with a reaction time of 16 h. Purification *via* recrystallisation from hot hexane gave (*S*)-**27** (399 mg, 0.778 mmol, 74%) as a colourless solid;

m.p. 58.3-61.0 °C; $[\alpha]_D^{25}$ –2.94 (*c* 1.31, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.08 (1H, quin, *J* = 5.0 Hz, C*H*OCO), 4.32 (1H, dd, *J* = 12.0 and 4.5 Hz, CH_2OCO), 4.24 (1H, dd, *J* = 12.0 and 5.5 Hz, CH_2'OCO), 3.76-3.70 (2H, m, CH_2OH), 2.38-2.27 (4H, m, 2 × CH_2COO), 2.06 (1H, bs, O*H*), 1.68-1.57 (4H, m, 2 × CH_2CH$_2$COO), 1.37-1.19 (40H, m, 20 × CH_2), 0.88 (6H, t, *J* = 6.5 Hz, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.9, 173.6, 72.3, 62.1, 61.7, 34.4, 34.3, 32.07, 32.06, 29.84, 29.80, 29.76, 29.62, 29.50, 29.48, 29.41, 29.27, 29.24, 25.1, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{31}H_{60}O_5Na$ $[M+Na]^+$ 535.4333, found 535.4336.

4.21 1-Dodecanoyl-2-hexadecanoyl-*sn*-glycerol, (*S*)-28

(*S*)-**28** was prepared using General Procedure C, with (*S*)-**20** (640 mg, 1.06 mmol, 1.0 equiv.), Pd/C (113 mg, 10 wt% Pd, 0.106 mmol. 10.0 mol%) in THF (11 mL), with a reaction time of 16 h. Purification *via* recrystallisation from hot hexane gave (*S*)-**28** (369 mg, 0.720 mmol, 68%) as a colourless solid;

m.p. 43.9-45.9 °C; $[\alpha]_D^{25}$ –3.15 (*c* 1.88, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.08 (1H, quin, *J* = 5.0 Hz, C*H*OCO), 4.32 (1H, dd, *J* = 12.0 and

4.5 Hz, C*H*$_2$OCO), 4.24 (1H, dd, *J* = 12.0 and 5.5 Hz, C*H*$_2$'OCO), 3.76-3.70 (2H, m, C*H*$_2$OH), 2.38-2.27 (4H, m, 2 × C*H*$_2$COO), 2.11 (1H, bs, O*H*), 1.68-1.57 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.37-1.19 (40H, m, 20 × C*H*$_2$), 0.88 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.9, 173.6, 72.3, 62.2, 61.7, 34.4, 34.2, 32.06, 32.05, 29.83, 29.79, 29.75, 29.61, 29.49, 29.47, 29.41, 29.26, 29.23, 25.1, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{31}H_{60}O_5Na$ $[M+Na]^+$ 525.4333, found 535.4330.

4.22 2-Decanoyl-1-hexadecanoyl-sn-glycerol, (*S*)-29

(*S*)-**29** was prepared using General Procedure C, with (*S*)-**21** (564 mg, 0.981 mmol, 1.0 equiv.), Pd/C (104 mg, 10 wt% Pd, 0.098 mmol. 10.0 mol%) in THF (10 mL), with a reaction time of 16 h. Purification *via* recrystallisation from hot hexane gave (*S*)-**29** (394 g, 0.813 mmol, 83%) as a colourless solid;

m.p. 39.9-44.4 °C; $[\alpha]_D^{25}$ –3.10 (*c* 1.94, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.08 (1H, quin, *J* = 5.0 Hz, C*H*OCO), 4.32 (1H, dd, *J* = 12.0 and 4.5 Hz, C*H*$_2$OCO), 4.24 (1H, dd, *J* = 12.0 and 5.5 Hz, C*H*$_2$'OCO), 3.76-3.70 (2H, m, C*H*$_2$OH), 2.38-2.27 (4H, m, 2 × C*H*$_2$COO), 1.68-1.57 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.37-1.19 (36H, m, 18 × C*H*$_2$), 0.88 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.9, 173.6, 72.3, 62.2, 61.7, 34.4, 34.2, 32.1, 31.9, 29.83, 29.80, 29.76, 29.61, 29.57, 29.41, 29.27, 29.23, 29.0, 25.1, 25.0, 22.83, 22.80, 14.24, 14.23; **HRMS** (ESI+) calc. for $C_{29}H_{56}O_5Na$ $[M+Na]^+$ 507.4020, found 507.4021.

4.23 1-Decanoyl-2-hexadecanoyl-*sn*-glycerol, (*S*)-30

(*S*)-**30** was prepared using General Procedure C, with (*S*)-**22** (515 mg, 0.896 mmol, 1.0 equiv.), Pd/C (95 mg, 10 wt% Pd, 0.090 mmol. 10.0 mol%) in THF (9.0 mL), with a reaction time of 16 h.

Crude (*S*)-**30** (267 g, 0.551 mmol, 62%) was obtained as a brown wax which was used in the next reaction without further purification;

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.08 (1H, quin, *J* = 5.0 Hz, C*H*OCO), 4.32 (1H, dd, *J* = 12.0 and 4.5 Hz, CH_2OCO), 4.24 (1H, dd, *J* = 12.0 and 5.5 Hz, CH_2'OCO), 3.76-3.70 (2H, m, CH_2OH), 2.38-2.27 (4H, m, 2 × CH_2COO), 1.68-1.57 (4H, m, 2 × CH_2CH$_2$COO), 1.37-1.19 (36H, m, 18 × CH_2), 0.88 (6H, t, *J* = 6.5 Hz, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.9, 173.6, 72.2, 62.2, 61.6, 34.4, 34.1, 32.0, 29.82, 29.77, 29.72, 29.52, 29.48, 29.37, 29.24, 25.0, 22.81, 22.78, 14.23, 14.21.

4.24 2-Dodecanoyl-1-tetradecanoyl-*sn*-glycerol, (*S*)-31

(*S*)-**31** was prepared using General Procedure C, with (*S*)-**23** (563 g, 0.979 mmol, 1.0 equiv.), Pd/C (104 mg, 10 wt% Pd, 0.098 mmol. 10.0 mol%) in THF (10 mL), with a reaction time of 16 h. Purification *via* recrystallisation from hot hexane gave (*S*)-**31** (387 mg, 0.798 mmol, 82%) as a colourless solid;

m.p. 53.4-57.3 °C; $[\alpha]_D^{25}$ –3.17 (*c* 1.38, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.08 (1H, quin, *J* = 5.0 Hz, C*H*OCO), 4.32 (1H, dd, *J* = 12.0 and 4.5 Hz, CH_2OCO), 4.24 (1H, dd, *J* = 12.0 and 5.5 Hz, CH_2'OCO), 3.76-3.70 (2H, m, CH_2OH), 2.38-2.27 (4H, m, 2 × CH_2COO), 2.09 (1H, bs, O*H*), 1.68-1.57 (4H, m, 2 × CH_2CH$_2$COO), 1.37-1.19 (36H, m, 18 × CH_2), 0.88 (6H, t, *J* = 6.5 Hz, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.9, 173.6, 72.3, 62.2, 61.7, 34.4, 34.2, 32.1, 29.80, 29.79, 29.75, 29.61, 29.49, 29.48, 29.41, 29.27, 29.23, 25.1, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{29}H_{56}O_5Na$ $[M+Na]^+$ 507.4020, found 507.4027.

4.25 1-Dodecanoyl-2-tetradecanoyl-*sn*-glycerol, (*S*)-32

(*S*)-**32** was prepared using General Procedure C, with (*S*)-**24** (589 mg, 1.02 mmol, 1.0 equiv.), Pd/C (109 mg, 10 wt% Pd, 0.102 mmol. 10.0 mol%) in THF (10 mL), with a reaction time of 16 h. Purification *via* recrystallisation from hot hexane gave (*S*)-**32** (289 mg, 0.596 mmol, 58%) as a colourless solid;

m.p. 42.5-46.0 °C; $[\alpha]_D^{25}$ –2.92 (*c* 1.81, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.08 (1H, quin, *J* = 5.0 Hz, C*H*OCO), 4.32 (1H, dd, *J* = 12.0 and 4.5 Hz, CH_2OCO), 4.24 (1H, dd, *J* = 12.0 and 5.5 Hz, CH_2'OCO), 3.76-3.70 (2H, m, CH_2OH), 2.38-2.27 (4H, m, 2 × CH_2COO), 1.68-1.57 (4H, m, 2 × CH_2CH$_2$COO), 1.37-1.19 (36H, m, 18 × CH_2), 0.88 (6H, t, *J* = 6.5 Hz, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.9, 173.6, 72.3, 62.2, 61.7, 34.4, 34.2, 32.1, 29.82, 29.79, 29.75, 29.61, 29.49, 29.47, 29.41, 29.26, 29.23, 25.1, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{29}H_{56}O_5Na$ $[M+Na]^+$ 507.4020, found 507.4008.

4.26 1-Hexadecanoyl-*sn*-glycerol, (*S*)-33

(*S*)-**33** was prepared using General Procedure C, with (*S*)-**13** (2.15 g, 5.11 mmol, 1.0 equiv.), Pd/C (544 mg, 10 wt% Pd, 0.511 mmol. 10.0 mol%) in THF (17 mL), with a 16 h reaction time. Purification *via* recrystallisation from hot hexane gave (*S*)-**33** (1.46 g, 4.43 mmol, 87%) as a colourless solid;

m.p. 68.2-73.8 °C; $[\alpha]_D^{25}$ –0.32 (*c* 0.63, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3319, 2918, 1735, 1473, 1463; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.21 (1H, dd, *J* = 12.0 and 4.5 Hz, CH_2OCO), 4.15 (1H, dd, *J* = 12.0 and 6.0 Hz, CH_2'OCO), 3.97-3.89 (1H, m, C*H*OH), 3.70 (1H, dd, *J* = 11.5 and 4.0 Hz, CH_2OH), 3.60 (1H, dd, *J* = 11.5 and 5.5 Hz, CH_2'OH), 2.50 (1H, bs, O*H*), 2.35 (2H, t, *J* = 7.5 Hz, CH_2COO), 2.16 (1H, bs, O*H*), 1.68-1.55 (2H, m, CH_2CH$_2$COO), 1.37-1.19 (24H, m, 12 × CH_2), 0.88 (3H, t, *J* = 6.5 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 174.5, 70.4, 65.3, 63.5, 34.3, 32.1,

29.83, 29.82, 29.80, 29.79, 29.74, 29.59, 29.50, 29.39, 29.28, 25.1, 22.8, 14.3; **HRMS** (ESI+) calc. for $C_{19}H_{38}O_4Na$ $[M+Na]^+$ 353.2662, found 353.2659.

4.27 1-Tetradecanoyl-*sn*-glycerol, (*S*)-34

(*S*)-**34** was prepared using General Procedure C, with (*S*)-**14** (835 mg, 2.13 mmol, 1.0 equiv.), Pd/C (226 mg, 10 wt% Pd, 0.212 mmol. 10.0 mol%) in THF (7.0 mL), with a 16 h reaction time. Purification *via* recrystallisation from hot hexane gave (*S*)-**34** (471 mg, 1.56 mmol, 73%) as a colourless solid;

m.p. 62.5-65.2 °C; $[\alpha]_D^{25}$ –0.40 (*c* 1.0, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3319, 2918, 1735, 1473, 1463; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.21 (1H, dd, *J* = 12.0 and 4.5 Hz, C*H*$_2$OCO), 4.15 (1H, dd, *J* = 12.0 and 6.0 Hz, C*H*$_2$'OCO), 3.97-3.89 (1H, m, C*H*OH), 3.70 (1H, dd, *J* = 11.5 and 4.0 Hz, C*H*$_2$OH), 3.60 (1H, dd, *J* = 11.5 and 5.5 Hz, C*H*$_2$'OH), 2.51 (1H, bs, O*H*), 2.35 (2H, t, *J* = 7.5 Hz, C*H*$_2$COO), 2.08 (1H, bs, O*H*), 1.68-1.55 (2H, m, C*H*$_2$CH$_2$COO), 1.37-1.19 (20H, m, 10 × C*H*$_2$), 0.88 (3H, t, *J* = 6.5 Hz, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 174.5, 70.4, 65.3, 63.5, 34.3, 32.1, 29.81, 29.78, 29.74, 29.59, 29.50, 29.39, 29.27, 25.1, 22.8, 14.3; **HRMS** (ESI+) calc. for $C_{17}H_{34}O_4Na$ $[M+Na]^+$ 325.2349, found 325.2350.

4.28 1-Hexadecanoyl-3-tetradecanoyl-*sn*-glycerol, (*S*)-35

(*S*)-**35** was prepared using General Procedure A, with (*S*)-**33** (430 mg, 1.30 mmol, 1.0 equiv.), vinyl myristate (0.40 mL, 1.37 mmol, 1.05 equiv.) and CAL (78 mg) in CH_2Cl_2 (3.3 mL), with a 1.5 h reaction time. Purification *via* recrystallisation from hot hexane gave (*S*)-**35** (582 mg, 1.08 mmol, 83%) as a colourless solid;

m.p. 60.1-63.3 °C; $[\alpha]_D^{25}$ +0.24 (*c* 1.81, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.23-4.02 (5H, m, C*H*$_2$C*H*C*H*$_2$), 2.50 (1H, bs, O*H*), 2.34 (4H, app.

t, *J* = 7.5 Hz, 2 × C*H*$_2$COO), 1.70-1.53 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.37-1.17 (44H, m, 22 × C*H*$_2$), 0.87 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 174.1, 68.5, 65.2, 34.2, 32.1, 32.0, 29.81, 29.74, 29.59, 29.49, 29.39, 29.26, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{33}H_{64}O_5Na$ $[M+Na]^+$ 563.4646, found 563.4631.

4.29 3-Dodecanoyl-1-hexadecanoyl-*sn*-glycerol, (*S*)-36

(*S*)-**36** was prepared using General Procedure A, with (*S*)-**33** (430 mg, 1.30 mmol, 1.0 equiv.), vinyl laurate (0.36 mL, 1.37 mmol, 1.05 equiv.) and CAL (73 mg) in CH_2Cl_2 (3.3 mL), with a 1.5 h reaction time. Purification *via* recrystallisation from hot hexane gave (*S*)-**36** (560 mg, 1.09 mmol, 84%) as a colourless solid;

m.p. 55.3-60.6 °C; $[\alpha]_D^{25}$ +0.61 (*c* 1.75, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.23-4.02 (5H, m, C*H*$_2$C*H*C*H*$_2$), 2.47 (1H, bs, O*H*), 2.34 (4H, app. t, *J* = 7.5 Hz, 2 × C*H*$_2$COO), 1.70-1.53 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.37-1.17 (40H, m, 20 × C*H*$_2$), 0.87 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 174.1, 68.5, 65.2, 34.2, 32.1, 32.0, 29.83, 29.79, 29.74, 29.59, 29.50, 29.47, 29.39, 29.27, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{31}H_{60}O_5Na$ $[M+Na]^+$ 535.4333, found 535.4335.

4.30 3-Decanoyl-1-hexadecanoyl-*sn*-glycerol, (*S*)-37

(*S*)-**37** was prepared using General Procedure A, with (*S*)-**33** (380 mg, 1.15 mmol, 1.0 equiv.), vinyl decanoate (0.27 mL, 1.21 mmol, 1.05 equiv.) and CAL (62 mg) in CH_2Cl_2 (3.0 mL), with a 1.5 h reaction time. Purification *via* recrystallisation from hot hexane gave (*S*)-**37** (482 mg, 0.994 mmol, 86%) as a colourless solid;

m.p. 55.0-60.0 °C; $[\alpha]_D^{25}$ +0.79 (*c* 2.65, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.23-4.02 (5H, m, C*H*$_2$C*H*C*H*$_2$), 2.51 (1H, bs, O*H*), 2.34 (4H, app.

t, *J* = 7.5 Hz, 2 × C*H*$_2$COO), 1.70-1.53 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.37-1.17 (36H, m, 18 × C*H*$_2$), 0.87 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 174.0, 68.5, 65.2, 34.2, 32.1, 32.0, 29.82, 29.78, 29.73, 29.59, 29.53, 29.49, 29.38, 29.26, 25.0, 22.82, 22.79, 14.24, 14.23; **HRMS** (ESI+) calc. for $C_{29}H_{56}O_5Na$ $[M+Na]^+$ 507.4020, found 507.4001.

4.31 3-Dodecanoyl-1-tetradecanoyl-*sn*-glycerol, (*S*)-38

(*S*)-**38** was prepared using General Procedure A, with (*S*)-**34** (393 mg, 1.30 mmol, 1.0 equiv.), vinyl laurate (0.36 mL, 1.37 mmol, 1.05 equiv.) and CAL (70 mg) in CH_2Cl_2 (3.3 mL), with a 1.5 h reaction time. Purification *via* recrystallisation from hot hexane gave (*S*)-**38** (390 mg, 0.804 mmol, 62%) as a colourless solid;

m.p. 54.3-58.0 °C; $[\alpha]_D^{25}$ +0.68 (*c* 1.63, $CHCl_3$); **IR** (NaCl, ν_{max} / cm^{-1}) 3504, 2956, 1732, 1708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.23-4.02 (5H, m, C*H*$_2$C*H*C*H*$_2$), 2.48 (1H, bs, O*H*), 2.34 (4H, app. t, *J* = 7.5 Hz, 2 × C*H*$_2$COO), 1.70-1.53 (4H, m, 2 × C*H*$_2$CH$_2$COO), 1.37-1.17 (36H, m, 18 × C*H*$_2$), 0.87 (6H, t, *J* = 6.5 Hz, 2 × C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 174.1, 68.5, 65.2, 34.2, 32.1, 32.0, 29.81, 29.78, 29.73, 29.59, 29.49, 29.38, 29.27, 25.0, 22.8, 14.2; **HRMS** (ESI+) calc. for $C_{29}H_{56}O_5Na$ $[M+Na]^+$ 507.4020, found 507.4480.

4.32 1-Hexadecanoyl-3-[(9*Z*)-octadeca-9-enoyl]-2-tetradecanoyl-*sn*-glycerol, (*R*)-1

(*R*)-**1** was prepared using General Procedure B, with (*S*)-**25** (200 mg, 0.370 mmol, 1.0 equiv.), oleic acid (0.129 mL, 0.407 mmol, 1.1 equiv.), EDCI (85 mg, 0.443 mol, 1.2 equiv.) and DMAP (9 mg, 0.074 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*R*)-**1** (277 mg, 0.344 mmol, 93%) as a colourless wax;

$[\alpha]_D^{25}$ +0.10 (*c* 5.0, $CHCl_3$); $\mathbf{R_f}$ 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.41-5.30 (2H, m, =C*H*), 5.30-5.22 (1H, m, C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.37-2.26 (6H, m, 3 × CH_2COO), 2.07-1.94 (4H, m, 2 × =CC$H_2$$CH_2$), 1.69-1.53 (6H, m, 3 × C$H_2$$CH_2$COO), 1.42-1.17 (64H, m, 32 × CH_2), 0.88 (9H, t, *J* = 6.5 Hz, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.43, 173.40, 173.0, 130.2, 129.9, 69.0, 62.3, 34.4, 34.21, 34.19, 32.07, 32.06, 32.02, 29.92, 29.85, 29.81, 29.68, 29.65, 29.63, 29.51, 29.47, 29.45, 29.42, 29.33, 29.27, 29.24, 27.4, 27.37, 27.32, 25.06, 25.02, 24.50, 22.8, 14.3; **HRMS** (ESI+) calc. for $C_{51}H_{96}O_6Na$ $[M+Na]^+$ 827.7099, found 827.7091.

4.33 2-Hexadecanoyl-3-[(9*Z*)-octadeca-9-enoyl]-1-tetradecanoyl-*sn*-glycerol, (*R*)-2

(*R*)-**2** was prepared using General Procedure B, with (*S*)-**26** (200 mg, 0.370 mmol, 1.0 equiv.), oleic acid (0.129 mL, 0.407 mmol, 1.1 equiv.), EDCI (85 mg, 0.443 mol, 1.2 equiv.) and DMAP (9 mg, 0.074 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*R*)-**2** (285 mg, 0.354 mmol, 96%) as a colourless wax;

$[\alpha]_D^{25}$ +0.11 (*c* 2.5, $CHCl_3$); $\mathbf{R_f}$ 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.41-5.30 (2H, m, =C*H*), 5.30-5.22 (1H, m, C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.37-2.26 (6H, m, 3 × CH_2COO), 2.07-1.94 (4H, m, 2 × =CC$H_2$$CH_2$), 1.69-1.53 (6H, m, 3 × C$H_2$$CH_2$COO), 1.42-1.17 (64H, m, 32 × CH_2), 0.88 (9H, t, *J* = 6.5 Hz, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.41, 173.38, 172.0, 130.1, 129.8, 69.0, 62.2, 34.4, 34.20, 34.18, 32.07, 32.05, 32.02, 29.91, 29.85, 29.80, 29.77, 29.67, 29.65, 29.62, 29.50, 29.47, 29.44, 29.41, 29.32,

29.26, 29.23, 27.4, 27.3, 25.05, 25.01, 24.50, 22.8, 14.3; **HRMS** (ESI+) calc. for $C_{51}H_{96}O_6Na$ $[M+Na]^+$ 827.7099, found 827.7090.

4.34 1-Hexadecanoyl-2-[(9*Z*)-octadeca-9-enoyl]-3-tetradecanoyl-*sn*-glycerol, (*S*)-3

(*S*)-**3** was prepared using General Procedure B, with (*S*)-**35** (200 mg, 0.370 mmol, 1.0 equiv.), oleic acid (0.129 mL, 0.407 mmol, 1.1 equiv.), EDCI (85 mg, 0.443 mol, 1.2 equiv.) and DMAP (9 mg, 0.074 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*S*)-**3** (234 mg, 0.291 mmol, 79%) as a colourless wax;

$[\alpha]_D^{25}$ +0.07 (*c* 2.06, $CHCl_3$); $\mathbf{R_f}$ 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.41-5.30 (2H, m, =C*H*), 5.30-5.22 (1H, m, C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.37-2.26 (6H, m, 3 × CH_2COO), 2.07-1.94 (4H, m, 2 × =CCH_2CH$_2$), 1.69-1.53 (6H, m, 3 × CH_2CH$_2$COO), 1.42-1.17 (64H, m, 32 × CH_2), 0.88 (9H, t, *J* = 6.5 Hz, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.4, 173.0, 130.2, 129.8, 69.0, 62.2, 34.3, 34.2, 32.07, 32.06, 29.92, 29.84, 29.81, 29.77, 29.67, 29.63, 29.51, 29.47, 29.42, 29.35, 29.27, 29.20, 27.4, 27.3, 25.03, 25.01, 22.8, 14.3; **HRMS** (ESI+) calc. for $C_{51}H_{96}O_6Na$ $[M+Na]^+$ 827.7099, found 827.7094.

4.35 2-Dodecanoyl-1-hexadecanoyl-3-[(9*Z*,12*Z*)-octadeca-9,12-dienoyl]-*sn*-glycerol, (*R*)-4

(*R*)-**4** was prepared using General Procedure B, with (*S*)-**27** (200 mg, 0.390 mmol, 1.0 equiv.), linoleic acid (0.133 mL, 0.429 mmol, 1.1 equiv.), EDCI (90 mg, 0.468 mol, 1.2 equiv.) and DMAP (10 mg, 0.078 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*R*)-**4** (274 mg, 0.353 mmol, 91%) as a colourless wax;

$[\alpha]_D^{25}$ +0.03 (*c* 4.0, $CHCl_3$); **R_f** 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.46-5.20 (5H, m, 2 × =C*H* and C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.76 (2H, app. t, *J* = 6.5 Hz, =CCH_2C=), 2.37-2.23 (6H, m, 3 × CH_2COO), 2.11-1.97 (4H, m, 2 × =CC$H_2$$CH_2$), 1.70-1.52 (6H, m, 3 × C$H_2$$CH_2$COO), 1.48-1.07 (54H, m, 27 × CH_2), 0.94-0.79 (9H, m, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.4, 173.3, 173.0, 130.3, 130.1, 128.2, 128.3, 69.0, 62.2, 34.3, 34.18, 34.15, 32.1, 31.7, 29.83, 29.79, 29.75, 29.62, 29.49, 29.48, 29.42, 29.41, 29.31, 29.25, 29.21, 27.4, 25.8, 25.04, 25.00, 24.97, 22.8, 22.7, 14.23, 14.19; **HRMS** (ESI+) calc. for $C_{49}H_{90}O_6Na$ $[M+Na]^+$ 797.6630, found 797.6611.

4.36 1-Dodecanoyl-2-hexadecanoyl-3-[(9*Z*,12*Z*)-octadeca-9,12-dienoyl]-*sn*-glycerol, (*R*)-5

(*R*)-**5** was prepared using General Procedure B, with (*S*)-**28** (200 mg, 0.390 mmol, 1.0 equiv.), linoleic acid (0.133 mL, 0.429 mmol, 1.1 equiv.), EDCI (90 mg, 0.468 mol, 1.2 equiv.) and DMAP (10 mg, 0.078 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*R*)-**5** (285 mg, 0.368 mmol, 94%) as a colourless wax;

$[\alpha]_D^{25}$ +0.30 (*c* 1.88, $CHCl_3$); **R_f** 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.46-5.20 (5H, m, 2 × =C*H* and C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.76 (2H, app. t, *J* = 6.5 Hz, =CCH_2C=), 2.37-2.23 (6H, m, 3 × CH_2COO), 2.11-1.97 (4H, m, 2 × =CC$H_2$$CH_2$), 1.70-1.52 (6H, m, 3 × C$H_2$$CH_2$COO), 1.48-1.07 (54H, m, 27 × CH_2), 0.94-0.79 (9H, m, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.42, 173.38, 173.0, 130.4, 130.2, 128.2, 128.0, 69.0, 62.3, 34.4, 34.20, 34.17, 32.1, 31.7, 29.85, 29.82, 29.81, 29.79, 29.76, 29.64, 29.62, 29.51,

29.49, 29.44, 29.41, 29.32, 29.27, 29.23, 27.3, 25.8, 25.06, 25.01, 24.99, 22.8, 22.7, 14.25, 14.21; **HRMS** (ESI+) calc. for $C_{49}H_{90}O_6Na$ $[M+Na]^+$ 797.6630, found 797.6612.

4.37 3-Dodecanoyl-1-hexadecanoyl-2-[(9*Z*,12*Z*)-octadeca-9,12-dienoyl]-*sn*-glycerol, (*S*)-6

(*S*)-**6** was prepared using General Procedure B, with (*S*)-**36** (200 mg, 0.390 mmol, 1.0 equiv.), linoleic acid (0.133 mL, 0.429 mmol, 1.1 equiv.), EDCI (90 mg, 0.468 mol, 1.2 equiv.) and DMAP (10 mg, 0.078 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*S*)-**6** (281 mg, 0.362mmol, 93%) as a colourless wax;

$[\alpha]_D^{25}$ +0.17 (*c* 1.75, $CHCl_3$); $\mathbf{R_f}$ 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.46-5.20 (5H, m, 2 × =C*H* and C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.76 (2H, app. t, *J* = 6.5 Hz, =CCH_2C=), 2.37-2.23 (6H, m, 3 × CH_2COO), 2.11-1.97 (4H, m, 2 × =CCH_2CH$_2$), 1.70-1.52 (6H, m, 3 × CH_2CH$_2$COO), 1.48-1.07 (54H, m, 27 × CH_2), 0.94-0.79 (9H, m, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.4, 173.0, 130.4, 130.1, 128.2, 128.0, 69.0, 62.2, 34.3, 34.2, 32.07, 32.06, 31.7, 29.84, 29.80, 29.77, 29.62, 29.50, 29.48, 29.41, 29.34, 29.26, 29.19, 27.3, 25.8, 25.0, 22.8, 22.7, 14.25, 14.20; **HRMS** (ESI+) calc. for $C_{49}H_{90}O_6Na$ $[M+Na]^+$ 797.6630, found 797.6603.

4.38 2-Decanoyl-1-hexadecanoyl-3-[(9*Z*)-octadeca-9-enoyl]-*sn*-glycerol, (*R*)-7

(*R*)-**7** was prepared using General Procedure B, with (*S*)-**29** (200 mg, 0.413 mmol, 1.0 equiv.), oleic acid (0.144 mL, 0.454 mmol, 1.1 equiv.), EDCI (95 mg, 0.495 mol, 1.2 equiv.) and DMAP (10 mg, 0.083 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*R*)-**7** (259 mg, 0.346 mmol, 84%) as a colourless wax;

$[\alpha]_D^{25}$ +0.14 (*c* 2.13, $CHCl_3$); **R_f** 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.41-5.30 (2H, m, =C*H*), 5.30-5.22 (1H, m, C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.37-2.26 (6H, m, 3 × CH_2COO), 2.07-1.94 (4H, m, 2 × =CCH_2CH$_2$), 1.69-1.53 (6H, m, 3 × CH_2CH$_2$COO), 1.42-1.17 (56H, m, 28 × CH_2), 0.88 (9H, t, *J* = 6.5 Hz, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.42, 173.39, 173.0, 130.2, 129.9, 69.0, 62.3, 34.4, 34.20, 34.18, 32.07, 32.05, 32.02, 29.91, 29.84, 29.81, 29.77, 29.67, 29.62, 29.59, 29.51, 29.47, 29.43, 29.32, 29.27, 29.24, 27.4, 27.3, 25.05, 25.01, 24.99, 22.83, 22.81, 14.3; **HRMS** (ESI+) calc. for $C_{47}H_{88}O_6Na$ $[M+Na]^+$ 771.6473, found 771.6441.

4.39 1-Decanoyl-2-hexadecanoyl-3-[(9*Z*)-octadeca-9-enoyl]-*sn*-glycerol, (*R*)-8

(*R*)-**8** was prepared using General Procedure B, with crude (*S*)-**30** (200 mg, 0.413 mmol, 1.0 equiv.), oleic acid (0.144 mL, 0.454 mmol, 1.1 equiv.), EDCI (95 mg, 0.495 mol, 1.2 equiv.) and DMAP (10 mg, 0.083 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*R*)-**8** (240 mg, 0.320 mmol, 77%) as a colourless wax;

$[\alpha]_D^{25}$ +0.11 (*c* 1.81, $CHCl_3$); **R_f** 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.41-5.30 (2H, m, =C*H*), 5.30-5.22 (1H, m, C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.37-2.26 (6H, m, 3 × CH_2COO), 2.07-1.94 (4H, m, 2 × =CCH_2CH$_2$), 1.69-1.53 (6H, m, 3 × CH_2CH$_2$COO), 1.42-1.17 (56H, m, 28 × CH_2), 0.88 (9H, t, *J* = 6.5 Hz, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.42, 173.39, 173.0, 130.2, 129.9, 69.0, 62.3, 34.4, 34.20, 34.18, 32.07, 32.05, 32.02, 29.91, 29.84, 29.81, 29.77, 29.67, 29.62, 29.59, 29.51, 29.47, 29.43, 29.32, 29.27,

29.24, 27.4, 27.3, 25.05, 25.01, 24.99, 22.83, 22.81, 14.3; **HRMS** (ESI+) calc. for $C_{47}H_{88}O_6Na$ $[M+Na]^+$ 771.6473, found 771.6447.

4.40 3-Decanoyl-1-hexadecanoyl-2-[(9*Z*)-octadeca-9-enoyl]-*sn*-glycerol, (*S*)-9

(*S*)-**9** was prepared using General Procedure B, with (*S*)-**37** (200 mg, 0.413 mmol, 1.0 equiv.), oleic acid (0.144 mL, 0.454 mmol, 1.1 equiv.), EDAC (95 mg, 0.495 mol, 1.2 equiv.) and DMAP (10 mg, 0.083 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*S*)-**9** (307 mg, 0.410 mmol, 99%) as a colourless wax;

$[\alpha]_D^{25}$ +0.26 (*c* 1.81, $CHCl_3$); $\mathbf{R_f}$ 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.41-5.30 (2H, m, =C*H*), 5.30-5.22 (1H, m, C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.37-2.26 (6H, m, 3 × CH_2COO), 2.07-1.94 (4H, m, 2 × =CCH_2CH$_2$), 1.69-1.53 (6H, m, 3 × CH_2CH$_2$COO), 1.42-1.17 (56H, m, 28 × CH_2), 0.88 (9H, t, *J* = 6.5 Hz, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.42, 173.39, 173.0, 130.2, 129.9, 69.0, 62.3, 34.4, 34.20, 34.18, 32.07, 32.05, 32.02, 29.91, 29.84, 29.81, 29.77, 29.67, 29.62, 29.59, 29.51, 29.47, 29.43, 29.32, 29.27, 29.24, 27.4, 27.3, 25.05, 25.01, 24.99, 22.83, 22.81, 14.3; **HRMS** (ESI+) calc. for $C_{47}H_{88}O_6Na$ $[M+Na]^+$ 771.6473, found 771.6456.

4.41 2-Dodecanoyl-3-[(9*Z*)-octadeca-9-enoyl]-1-tetradecanoyl-*sn*-glycerol, (*R*)-10

(*R*)-**10** was prepared using General Procedure B, with (*S*)-**31** (200 mg, 0.413 mmol, 1.0 equiv.), oleic acid (0.144 mL, 0.454 mmol, 1.1 equiv.), EDCI (95 mg, 0.495 mol, 1.2 equiv.) and DMAP (10 mg, 0.083 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*R*)-**10** (302 mg, 0.403 mmol, 98%) as a colourless wax;

$[\alpha]_D^{25}$ +0.09 (*c* 1.38, $CHCl_3$); **R_f** 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.41-5.30 (2H, m, =C*H*), 5.30-5.22 (1H, m, C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.37-2.26 (6H, m, 3 × CH_2COO), 2.07-1.94 (4H, m, 2 × =CCH_2CH$_2$), 1.69-1.53 (6H, m, 3 × CH_2CH$_2$COO), 1.42-1.17 (56H, m, 28 × CH_2), 0.88 (9H, t, *J* = 6.5 Hz, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.43, 173.39, 173.0, 130.2, 129.9, 69.0, 62.3, 34.37, 34.20, 34.18, 32.1, 29.92, 29.85, 29.83, 29.80, 29.79, 29.77, 29.67, 29.64, 29.63, 29.50, 29.47, 29.44, 29.42, 29.33, 29.27, 29.34, 27.4, 27.3, 25.06, 25.01, 25.00, 22.8, 14.3; **HRMS** (ESI+) calc. for $C_{47}H_{88}O_6Na$ $[M+Na]^+$ 771.6473, found 771.6462.

4.42 1-Dodecanoyl-3-[(9*Z*)-octadeca-9-enoyl]-2-tetradecanoyl-*sn*-glycerol, (*R*)-11

(*R*)-**11** was prepared using General Procedure B, with (*S*)-**32** (200 mg, 0.413 mmol, 1.0 equiv.), oleic acid (0.144 mL, 0.454 mmol, 1.1 equiv.), EDCI (95 mg, 0.495 mol, 1.2 equiv.) and DMAP (10 mg, 0.083 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*R*)-**11** (292 mg, 0.390 mmol, 95%) as a colourless wax;

$[\alpha]_D^{25}$ +0.32 (*c* 1.56, $CHCl_3$); **R_f** 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.41-5.30 (2H, m, =C*H*), 5.30-5.22 (1H, m, C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.37-2.26 (6H, m, 3 × CH_2COO), 2.07-1.94 (4H, m, 2 × =CCH_2CH$_2$), 1.69-1.53 (6H, m, 3 × CH_2CH$_2$COO), 1.42-1.17 (56H, m, 28 × CH_2), 0.88 (9H, t, *J* = 6.5 Hz, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.43, 173.40, 173.0, 130.2, 129.9, 69.0, 62.3, 34.37, 34.20, 34.19, 32.1, 29.92, 29.84, 29.81, 29.77, 29.67, 29.65, 29.62, 29.51, 29.48, 29.45, 29.42, 29.33, 29.27, 29.24,

27.4, 27.3, 25.06, 25.02, 25.00, 22.8, 14.3; **HRMS** (ESI+) calc. for $C_{47}H_{88}O_6Na$ $[M+Na]^+$ 771.6473, found 771.6472.

4.43 3-Dodecanoyl-2-[(9*Z*)-octadeca-9-enoyl]-1-tetradecanoyl-*sn*-glycerol, (*S*)-12

(*S*)-**12** was prepared using General Procedure B, with (*S*)-**38** (200 mg, 0.413 mmol, 1.0 equiv.), oleic acid (0.144 mL, 0.454 mmol, 1.1 equiv.), EDCI (95 mg, 0.495 mol, 1.2 equiv.) and DMAP (10 mg, 0.083 mmol, 0.20 equiv.) in CH_2Cl_2 (1.0 mL) with a reaction time of 16 h. Purification *via* column chromatography (petroleum ether / EtOAc (5%) gave (*S*)-**12** (305 mg, 0.401 mmol, 97%) as a colourless wax;

$[\alpha]_D^{25}$ +0.17 (*c* 1.75, $CHCl_3$); $\mathbf{R_f}$ 0.70 (petroleum ether / EtOAc (10%)); **IR** (NaCl, ν_{max} / cm^{-1}) 2920, 1740, 723; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.41-5.30 (2H, m, =C*H*), 5.30-5.22 (1H, m, C*H*OCO), 4.29 (2H, dd, *J* = 12.0 and 4.0 Hz, 2 × CH_2OCO), 4.14 (2H, dd, *J* = 12.0 and 6.0 Hz, 2 × CH_2'OCO), 2.37-2.26 (6H, m, 3 × CH_2COO), 2.07-1.94 (4H, m, 2 × =CCH_2CH$_2$), 1.69-1.53 (6H, m, 3 × CH_2CH$_2$COO), 1.42-1.17 (56H, m, 28 × CH_2), 0.88 (9H, t, *J* = 6.5 Hz, 3 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 173.4, 173.0, 130.2, 129.8, 69.0, 62.2, 34.4, 34.2, 32.1, 29.91, 29.87, 29.83, 29.80, 29.77, 29.68, 29.62, 29.50, 29.48, 29.42, 29.35, 29.27, 29.21, 27.4, 27.3, 25.04, 25.02, 22.8, 14.3; **HRMS** (ESI+) calc. for $C_{47}H_{88}O_6Na$ $[M+Na]^+$ 771.6473, found 771.6469.

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Highlights

- Twelve enantiostructured ABC type triacylglycerols (TAGs) were synthesised
- Unique TAGs as standards for chiral separation
- Facile methodology to synthesise both enantiomers of ABC type TAGs
- Highly regioselective lipase

Declaration of interest statement

The authors declare no competing financial interest