Supplementary Information

O-Silylated C3-halohydrins as a novel class of protected building blocks for total, regio- and stereocontrolled syntheses of glycerolipid frameworks

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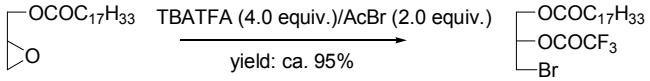
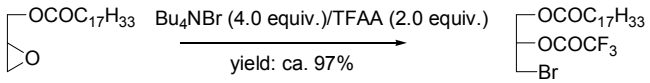
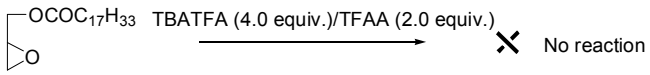
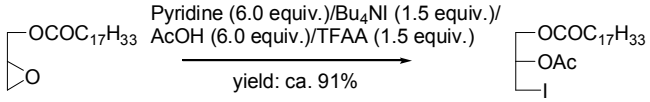
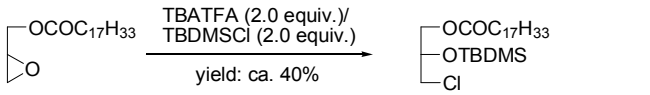
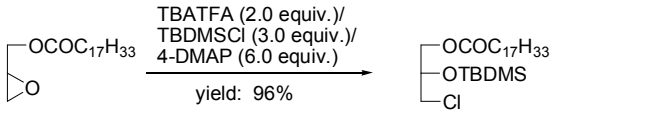
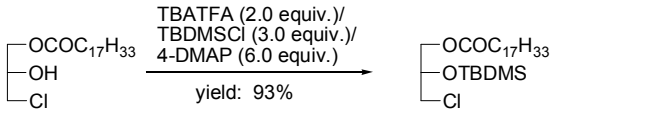
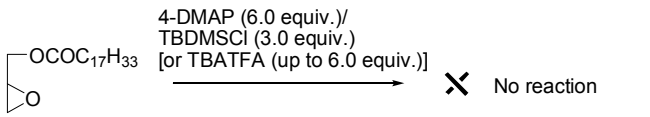
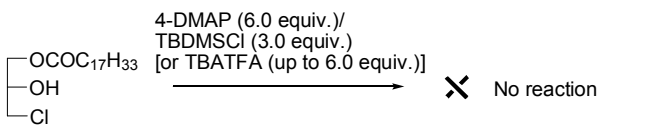
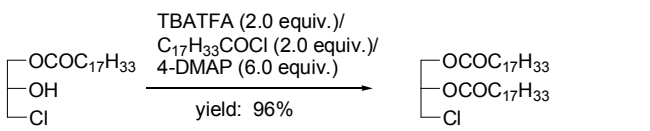
1. Mechanistic insights into a trifluoroacetate anion/4-*N*,*N*-dimethylaminopyridine-assisted synthesis of C2-*O*-acylated- (7-11, 61) and C2-*O*-silylated (12-19) C3-vicinal halohydrins from glycidyls (1-6)

Table S1.

No	Reaction conditions (in $CHCl_3$)[a]:	Temp	Time
1.		r.t.	2 h
2.		r.t.	3 h
3.		r.t.	24 h
4.		80 °C	3 h
5.		r.t. (80 °C)	6 h (4 h)
6.		r.t.	2 h
7.		r.t.	1.5 h
8.		r.t.	3.0 h
9.		r.t.	3.0 h
10.		r.t.	15 min

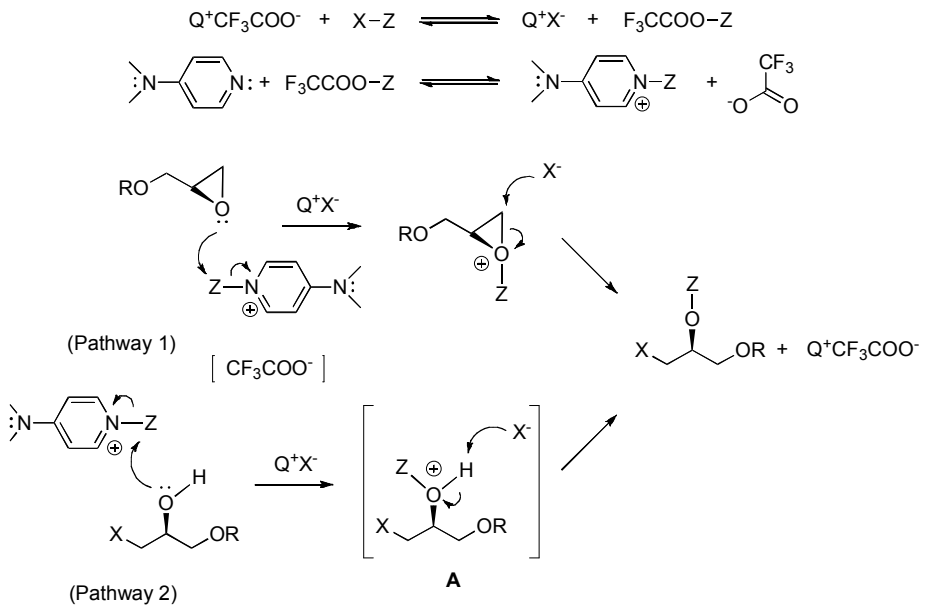
[a] TBATFA = tetra-*n*-butylammonium trifluoroacetate; Bu_4N = tetra-*n*-butylammonium; TFAA = $(CF_3CO)_2O$; TBDMS = *tert*-butyldimethylsilyl.

Preliminary experiments using ^1H and ^{13}C NMR spectroscopy (Table S1) revealed that the transformation of racemic glycidyl oleate (GO) into C2-*O*-trifluoroacetylated

bromohydrin by means of acetyl bromide in the presence of TBATFA, apparently took place via intermediacy of a mixed trifluoroacetyl-anhydride and tetra-*n*-butylammonium bromide generated in situ from these species (entry 1) as evidenced by parallel experiments where either the same conjugate was formed using TFAA along with Bu_4NBr (entry 2), or no reaction could be observed if a bromide anion is replaced by trifluoroacetate (entry 3). As shown in entry 4, however, treatment of a solution of GO, Bu_4NI, and pyridine in chloroform at 80 ^oC (pressure tube) for 3 h with a mixture of AcOH and TFAA prepared in the same solvent, gave the expected C2-*O*-acetylated iodohydrin. Tetra-*n*-butylammonium halides (4.0-6.0 equiv.) alone were completely inert towards the epoxide function of glycidyl oleate.

Quite different from entry 1, the TLC monitoring of a reaction between the model GO and TBDMSCl, in the presence of TBATFA, exposed a gradual disappearance of the starting material with formation of a polar intermediate that remained intact at room temperature for 6 h but it underwent ca. 40% conversion to the target C2-*O*-silylated C3-chlorohydrin after heating the mixture at 80 ^oC (pressure tube) for 4 h (entry 5). Since the generated intermediate had chromatographic mobility identical to that of the reference 1-oleoyl-3-chloro-*rac*-glycerol, we assumed that this was an artifact and arose via hydrolysis on TLC plates of some other reactive species initially present in the reaction system. Thus, to the mixture of GO, TBATFA, and TBDMSCl was added 4-DMAP to increase trapping efficiency of the incipient hydroxyl group that resulted in highly regioselective production of the TBDMS-ether at though room temperature for ca. 2 h (entry 6). Analogous results were obtained when 1-oleoyl-3-chloro-*rac*-glycerol was subjected to silylation in the same way (entry 7). Under conditions equal with those of entries 6 and 7, no reactions occurred when pyridine was used instead. The investigated substrates were also essentially unreactive if a combination of only 4-DMAP and TBDMSCl was applied or such three-component systems have subsequently been treated with TBATFA (entries 8 and 9). Similarly to entry 7, replacement of TBDMSCl by the long-chain oleoyl chloride led to fast production of the corresponding C2-oleate within ca. 15 min (entry 10). In this particular case pyridine (20 equiv.) can act as a substitute for 4-DMAP but the acylation process required about 2 h to go to completion (not shown).

The above data are consistent with a tentative common mechanism where the initial interaction of TBATFA with acyl- or silyl halides (ZX) gives rise to a highly efficient halide donor (i.e. Q^+X^-) and a mixed carboxylic-trifluoroacetic anhydride or silyl trifluoroacetate, respectively, while the next activation of the resulted trifluoroacetyl conjugates by 4-DMAP affords the reactive either *N*-acylpyridinium- or *N*-silylpyridinium cations (Scheme S1).



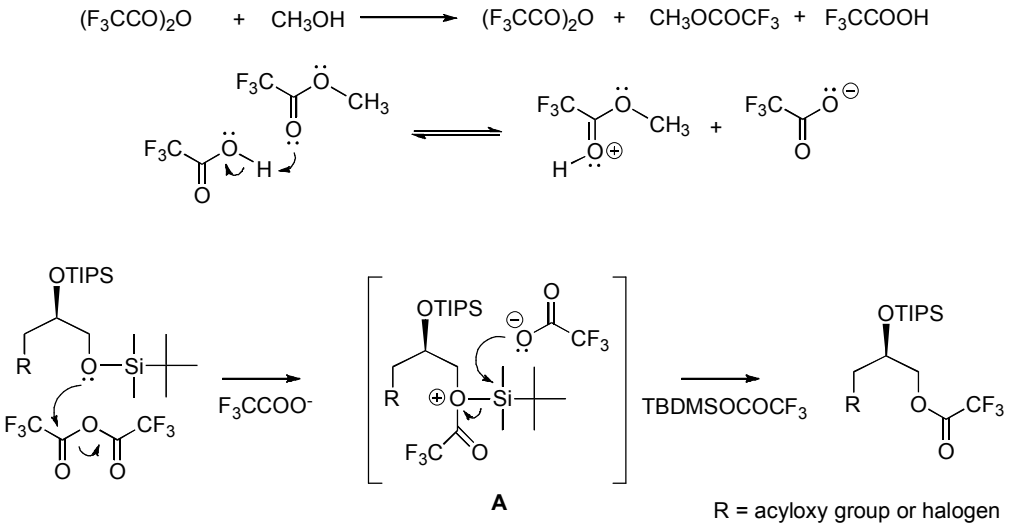
R = $C_{17}H_{33}CO$; Z = acyl or TBDMS; $Q^+ = Bu_4N^+$; X = Cl, Br or I

Scheme S1.

In this context, the oxirane ring-opening of a glycidyl (pathway 1) most likely proceeds via nucleophilic attack of halide from Q^+X^- on the primary carbon center with simultaneous formation of the ester-/or silyl ether bond. As the *N*-acyl- or *N*-silylpyridinium cation is expected to be a powerful electrophilic catalyst that can coordinate to the epoxide oxygen, the nucleophilic fission of the oxirane system and acylation/or silylation of the incipient 2-hydroxyl function could take place in a synchronous manner that ultimately regenerates equimolar amounts of TBATFA. Mechanistically coherent with this is the TBATFA/4-DMAP-mediated conversion of C3-haloalkanols into the same types of compounds (pathway 2) by means of acyl-/silyl chlorides, which probably involves coordination of the corresponding *N*-pyridinium-derived species to the hydroxyl oxygen to give a protonated intermediate of type **A**, followed by nucleophilic attack of the chloride anion on hydrogen. This is apparently the rate-determining step of the process but one cannot exclude that both events (i.e. formation of **A** and deprotonation) might be synchronous, where the presence of 4-DMAP is essential to facilitate the departure of hydrohalide, thus contributing to concerted shaping of the final products. The combination of nucleophile and electrophile catalysis rationalizes the fact that in all instances C2-*O*-functionalized C3-vicinal halohydrins are producible without migration of the terminal acyl moiety. Since no C-O bond breaking takes place at the stereogenic secondary carbon atom, the transformations should be stereospecific and occur with retention of configuration.

A route with *N*-acyl-/or *N*-silylpyridinium cations from acyl-/silyl chlorides seems less plausible on two counts. Firstly, *N*-acylpyridinium chlorides of 4-DMAP in spite of the high degree of carbonyl activation are known to react much slower with nucleophiles than *N*-acylpyridinium carboxylates,[1] which is in agreement with the fast acyl transfer observed in entry 10 (Table S1). Secondly, if preliminary generated from 4-DMAP and TBDMSCl, such a bulky *N*-silylpyridinium chloride was found to be unable to effect silylation even in the presence of TBATFA added to the reaction systems afterwards (entries 8 and 9, Table S1).

2. Selective trifluoroacetylation across *tert*-butyldimethylsilyloxy systems of 1-*O*-*tert*-butyldimethylsilyl-2-*O*-triisopropylsilyl-3-iodo- (13) or -3-*O*-acyl-*sn*-glycerols (26, 27) as mediated by trifluoroacetic anhydride (TFAA) in the presence of methanol



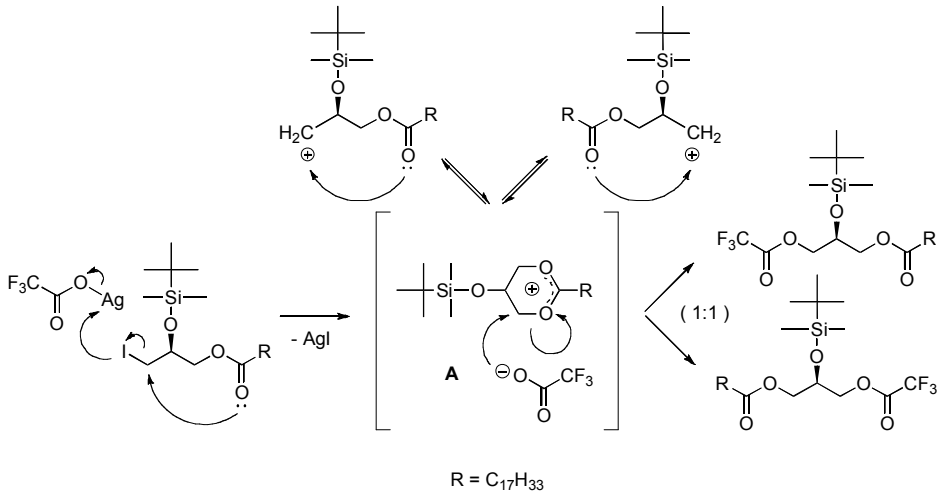
Scheme S2.

According to mechanistic studies supported by ^{1}H and ^{13}C NMR spectroscopy, test substrates (e.g., **13**, **26** and **27** or TBDMS ether of oleyl alcohol) were recovered practically intact where the process was carried out at room temperature (r.t.) for up to 24 h with TFAA (up to 4.0 equiv.) alone, or underwent under the same conditions partial cleavage (~40%) of the TBDMS-protection solely when trifluoroacetic acid (3.0 equiv.) was used alternatively. Treatment of TBDMS ethers at r.t. with an equimolar mixture of TFAA and methanol (6.0 equiv.) in chloroform furnished after ca. 20 h the target trifluoroacetates (60-70%) along with spots (TLC analysis) of more polar products (~30%) having chromatographic mobility identical with the established for the respective deprotected hydroxylates (e.g., oleyl alcohol). Appearance of the latter on the chromatograms was completely suppressed by adding TFAA

(6.0 equiv.) to such systems. A reagent comprising TFAA (9.0 equiv.) and tetra-*n*-butylammonium trifluoroacetate (3.0 equiv.) as a replacement for methanol was just as efficient. In all instances no reaction was observed at 70 ^{o}C (pressure tube) for 3 h employing a combination of TFAA (12.0 equiv.) and methyl trifluoroacetate (4.0 equiv.).

The above findings permitted us to propose a mechanism for a trifluoroacetate-promoted direct acylation of TBDMS ethers with trifluoroacetic anhydride (Scheme S2). The process presumably commences with coordination of a trifluoroacetyl group to the oxygen atom of the silyloxy system to form an intermediate (**A**), with subsequent nucleophilic catalysis exerted by the trifluoroacetate anion, as released via transfer of a proton from the strong trifluoroacetic acid to the carbonyl function of methyl trifluoroacetate. The combination of nucleophile and electrophile assistance provided by this in situ generated, two-component reagent should facilitate the replacement of the TBDMS group by the trifluoroacetyl fragment and prevent acyl migration as apparently no free hydroxyl functionality of the glycerol backbone is exposed. Since none of the reaction steps involve scission of C-O bond extending from an alcohol moiety, the mechanism predicts retention of configuration if the substitution is carried out at a stereogenic molecular center.

3. The incidence of long-range acyloxy migration during silver trifluoroacetate-promoted replacement of halogen in 1-oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-iodo-*sn*-glycerol (15)



Scheme S3.

To explain the observed epimerization during the replacement of iodine in **15** by silver trifluoroacetate, we propose a mechanism depicted in Scheme S3. It involves

electrophilic assistance by Ag^+ of the iodine departure and stabilization of the formed carbocation with the terminal acyl group in the form of 1,3-dioxacarbenium ion. Since the carbenium ion **A** is symmetrical, its interaction with the trifluoroacetate should produce racemic product **54**. Unlike literature precedents describing a 1,3-acyl migration,[2] this process represents the first example of 1,3-long-range acyloxy transfer to the incipient electron-deficient carbon center within a glyceride structure. The smooth acylolysis effected by tetra-*n*-butylammonium acetate instead, indicates that intramolecular group participation by the primary acyloxy functionality is kinetically less important in this reaction, and that the critical role is played by the electrophile catalyst, the silver cation. The mechanism rationalizes the complete racemization of **54** which occurs without breaking bonds at the stereogenic center at C2 in the glycerol unit.

At the mechanistic level, it seems that displacement of iodine atom in 1-*O*-acyl-3-iodohydrins by a carboxylate is very sensitive to the basicity of the carboxylate used and the kind of the counter cation. Weekly basic carboxylates (e.g., trifluoroacetate) in the form of tetra-*n*-butylammonium derivatives cannot effect the transformation, while in the presence of soft Lewis acid (e.g., Ag+), the substitution occurs readily with the terminal acyloxy group migration. This is also consistent with the experimental data for the strictly stereospecific outcome of the preparations involving tetra-*n*-butylammonium salts of fatty acids vs those instances where certain degree of epimerization and other side-reactions have frequently been observed in an attempted esterification of C3-vicinal halohydrins with metal carboxylates.[3]

4. Preparative parameters of transformations and physicochemical characteristics of derivatives not shown in the Experimental section.

Compounds obtained according to general procedure 3.2.

1-Iodo-2-oleoyl-3-*O*-*tert*-butyldiphenylsilyl-*sn*-glycerol 7. Obtained from (*R*)-(+)-2-(*tert*-butyldiphenylsilyloxymethyl)oxirane (**1**; 0.312 g, 1.00 mmol) using Bu_4NI (1.108 g, 3.00 mmol), oleoyl chloride (0.496 mL, 1.50 mmol) and 4-DMAP (reaction times, stage I: 5 min; stage II: 10 min). Yield: 0.648 g (92%, colorless oil); R_f (toluene-pentane = 80:20, v/v) = 0.78; $[\alpha]_D^{20}$= +4.52 (*c* 10.10, $CHCl_3$); Found: C, 62.95; H, 8.20; I, 18.07%. $C_{37}H_{57}IO_3Si$ (704.85) requires C, 63.05; H, 8.15; I, 18.00%.

1-*O*-*tert*-Butyldimethylsilyl-2-acetyl-3-iodo-*rac*-glycerol 11. Obtained from (*rac*)-(±)-2-(*tert*-butyldimethylsilyloxymethyl)oxirane (**4**; 0.188 g, 1.00 mmol) using Bu_4NI (1.108 g, 3.00 mmol), acetyl chloride (0.107 mL, 1.50 mmol) and 4-DMAP (reaction times, stage I: 5 min; stage II: 20 min). Yield: 0.322 g (90%, colorless oil); R_f (pentane-toluene-EtOAc =

40:50:10, v/v/v) = 0.65; Found: C, 37.01; H, 6.31; I, 35.53%. $C_{11}H_{23}IO_3Si$ (358.29) requires C, 36.87; H, 6.47; I, 35.42%.

1-Iodo-2-*O*-tripropylsilyl-3-*O*-*tert*-butyldiphenylsilyl-*sn*-glycerol 12. Obtained from (*R*)-(+)-2-(*tert*-butyldiphenylsilyloxymethyl)oxirane (**1**; 0.312 g, 1.00 mmol) using Bu_4NI (1.108 g, 3.00 mmol), tripropylchlorosilane (0.402 mL, 3.00 mmol) and 4-DMAP (reaction times, stage I: 5 min; stage II: 10 min). Yield: 0.585 g (98%, colorless oil); R_f (toluene) = 0.92; $[\alpha]_D^{20}$= +1.50 (*c* 9.27, $CHCl_3$); Found: C, 56.00; H, 7.70; I, 21.32%. $C_{28}H_{45}IO_2Si_2$ (596.74) requires C, 56.36; H, 7.60; I, 21.27%.

1,2-*O*-Di(*tert*-butyldimethylsilyl)-3-iodo-*rac*-glycerol 14. Obtained from (*rac*)-(±)-2-(*tert*-butyldimethylsilyloxymethyl)oxirane (**4**; 0.188 g, 1.00 mmol) using Bu_4NI (1.108 g, 3.00 mmol), TBDMSCl (0.452 g, 3.00 mmol) and 4-DMAP (reaction times, stage I: 5 min; stage II: 4 h). Yield: 0.400 g (93%, colorless oil); R_f (pentane-toluene = 90:10, v/v) = 0.57; Found: C, 41.79; H, 8.22; I, 29.51%. $C_{15}H_{35}IO_2Si_2$ (430.51) requires C, 41.85; H, 8.19; I, 29.48%.

1-Oleoyl-2-*O*-trimethylsilyl-3-bromo-*sn*-glycerol 17. Obtained from (*S*)-(+)-2-(oleoyloxymethyl)oxirane (**5**; 0.338 g, 1.00 mmol) using Bu_4NBr (0.967 g, 3.00 mmol), trimethylsilyl chloride (0.379 mL, 3.00 mmol) and 4-DMAP (reaction times, stage I: 10 min; stage II: 5 min). Yield: 0.476 g (97%, colorless oil); R_f (pentane-toluene-EtOAc, 40:50:10, v/v/v) = 0.75; $[\alpha]_D^{20}$= +1.96 (*c* 7.07, $CHCl_3$); lit.[4] $[\alpha]_D^{20}$= +1.91 (*c* 13.10, $CHCl_3$); Found: C, 58.59; H, 9.60; Br, 16.29%. $C_{24}H_{47}BrO_3Si$ (491.62) requires C, 58.63; H, 9.64; Br, 16.25%.

1-Oleoyl-2-*O*-triisopropylsilyl-3-chloro-*rac*-glycerol 18. Obtained from (*rac*)-(±)-2-(oleoyloxymethyl)oxirane (**6**; 0.338 g, 1.00 mmol) using Bu_4NCl (0.834 g, 3.00 mmol), TIPSCl (0.636 mL, 3.00 mmol) and 4-DMAP (reaction times, stage I: 1 h; stage II: 24 h). Yield: 0.494 g (93%, colorless oil); R_f (pentane-toluene = 50:50, v/v) = 0.67; Found: C, 67.80; H, 11.22; Cl, 6.65%. $C_{30}H_{59}ClO_3Si$ (531.33) requires C, 67.81; H, 11.19; Cl, 6.67%.

1-Oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-chloro-*rac*-glycerol 19. Obtained from (*rac*)-(±)-2-(oleoyloxymethyl)oxirane (**6**; 0.338 g, 1.00 mmol) using Bu_4NCl (0.834 g, 3.00 mmol), TBDMSCl (0.452 g, 3.00 mmol) and 4-DMAP (reaction times, stage I: 1 h; stage II: 1.5 h). Yield: 0.479 g (98%, colorless oil); R_f (pentane-toluene-EtOAc, 40:50:10, v/v/v) = 0.82; Found: C, 66.33; H, 10.89; Cl, 7.28%. $C_{27}H_{53}ClO_3Si$ (489.25) requires C, 66.28; H, 10.92; Cl, 7.25%.

Compound obtained according to typical procedure 3.3.

1-Oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-acetyl-*sn*-glycerol 49. Obtained from 1-oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-iodo-*sn*-glycerol (**15**; 0.581 g, 1.00 mmol) and tetra-*n*-

butylammonium acetate (0.90 g, 3.00 mmol). Yield: 0.487 g (95%, colorless oil); R_f (pentane-toluene-EtOAc = 40:50:10, v/v/v) = 0.59; $[\alpha]_D^{20}$= -0.29 (*c* 5.11, $CHCl_3$); Found: C, 68.03; H, 11.00%. $C_{29}H_{56}O_5Si$ (512.84) requires C, 67.92; H, 11.01%.

Compounds obtained according to typical procedure 3.5.

1,2-Dioleoyl-3-acetyl-*sn*-glycerol 52. Synthesized from 1-oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-acetyl-*sn*-glycerol (**49**; 0.513 g, 1.00 mmol), oleic anhydride (1.641 g, 3.00 mmol), Bu_4NBr, and TMSBr for 7 h. Yield: 0.590 g (89%, colorless oil); R_f (pentane-toluene-EtOAc = 40:50:10, v/v/v) = 0.58; $[\alpha]_D^{20}$= -0.66 (c, 10.45, $CHCl_3$); lit.[5] $[\alpha]_D^{20}$= -0.68 (c, 7.60, $CHCl_3$); Found: C, 74.20; H, 11.27%. $C_{41}H_{74}O_6$ (663.02) requires C, 74.27; H, 11.25%.

1-Oleoyl-2,3-diacetyl-*sn*-glycerol 53. Acquired from 1-oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-acetyl-*sn*-glycerol (**49**; 0.513 g, 1.00 mmol), acetic anhydride (0.284 mL, 3.00 mmol), Bu_4NBr, and TMSBr for 6 h. Yield: 0.405 g (92%, colorless oil); R_f (pentane-toluene-EtOAc = 40:50:10, v/v/v) = 0.28; $[\alpha]_D^{20}$= -1.28 (c, 9.12, $CHCl_3$); lit.[5] $[\alpha]_D^{20}$= -1.29 (c, 8.93, $CHCl_3$); Found: C, 68.10; H, 10.09%. $C_{25}H_{44}O_6$ (440.61) requires C, 68.15; H, 10.06%.

1-Oleoyl-2-palmitoyl-3-iodo-*sn*-glycerol 61. Acquired alternatively from 1-oleoyl-2-*O*-triethylsilyl-3-iodo-*sn*-glycerol (**16**; 0.581 g, 1.00 mmol), palmitic anhydride (1.484 g, 3.00 mmol), Bu_4NI, and TMSI for 30 min. Yield: 0.662 g (94%, colorless oil); $[\alpha]_D^{20}$= +3.61 (*c* 5.74, $CHCl_3$); all other physicochemical and spectral characteristics were identical with those of the same compound synthesized as described in section **3.2** within the main body text.

Compounds obtained according to typical procedure 3.7.

2-*O*-Triisopropylsilyl-3-acetyl-*sn*-glycerol 36. Acquired from 1-trifluoroacetyl-2-*O*-triisopropylsilyl-3-acetyl-*sn*-glycerol (**34**; 0.386 g, 1.00 mmol) for 30 min. Yield: 0.290 g (100%, colorless oil); R_f (toluene-EtOAc, 80:20, v/v) = 0.35; $[\alpha]_D^{20}$= +10.94 (*c* 13.16, $CHCl_3$); Found: C, 57.94; H, 10.36%. $C_{14}H_{30}O_4Si$ (290.47) requires C, 57.89; H, 10.41%.

1-Oleoyl-2-*O*-*tert*-butyldimethylsilyl-*rac*-glycerol 55. Acquired from 1-oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-trifluoroacetyl-*rac*-glycerol (**54**; 0.567 g, 1.00 mmol) for 30 min. Yield: 0.470 g (100%, colorless oil); R_f (pentane-toluene-EtOAc = 40:50:10, v/v/v) = 0.39; Found: C, 68.99; H, 11.38%. $C_{27}H_{54}O_4Si$ (470.80) requires C, 68.88; H, 11.56%.

1-Oleoyl-3-acetyl-*rac*-glycerol 58. Obtained from 1-oleoyl-2-trichloroacetyl-3-acetyl-*rac*-glycerol (**57**) for 2 h. Yield: 0.398 g (100%, colorless oil); excluding the lack of

optical activity, all other physicochemical and spectral characteristics were identical with those of **32** and **33**.

Compounds obtained according to typical procedure 3.8.

1-Acetyl-2-*O*-triisopropylsilyl-3-iodo-*sn*-glycerol 39. A solution of 1-*O*-*tert*-butyldimethylsilyl-2-*O*-triisopropylsilyl-3-iodo-*sn*-glycerol (**13**; 0.473 g, 1.00 mmol), trifluoroacetic anhydride (1.67 mL, 12.00 mmol) and methanol (0.122 mL, 3.0 mmol) was kept at 70 ºC for 2 h (pressure tube), and the solvents were evaporated under reduced pressure (stage I). The residue was taken in tetrahydofuran (5.0 mL), the solution was treated at room temperature for 30 min with a mixture of pyridine (4.0 mL, 50 mmol) and methanol (20.3 mL, 500 mmol), and volatile products were removed to produce the intermediary 2-*O*-triisopropylsilyl-3-iodo-*sn*-glycerol (**38**) as described in section **3.7** (stage II). The latter compound was dissolved in alcohol-free chloroform (10.0 mL), acetyl chloride (0.14 mL, 2.00 mmol) was added at -20 °C, and the reaction was left at room temperature for 2 h (stage III). The solution was passed through a chloroform-filled silica gel pad (~5 g) and the support was washed with the same solvent (~100 mL). Chloroform was removed under reduced pressure and acetate **39** was isolated in pure state (>99%, ^{1}H NMR spectroscopy) by flash column silica gel chromatography using toluene as the eluent. Yield: 0.384 g (96%, colorless oil); R_f (toluene) = 0.48; $[\alpha]_D^{20}$= +15.66 (*c* 4.65, $CHCl_3$); Found: C, 42.29; H, 7.36; I, 31.95%. $C_{14}H_{29}IO_3Si$ (400.37) requires C, 42.00; H, 7.30; I, 31.70%.

1,3-Dioleoyl-2-acetylglycerol 41. Prepared from 1-oleoyl-2-acetyl-3-trichloroacetyl-*sn*-glycerol (**22**; 0.544 g, 1.00 mmol) via **24** and oleoyl chloride (0.66 mL, 2.00 mmol) (stage I; 2 h; stage II: 2 h). Yield: 0.623 g (94%, colorless oil); R_f (pentane-toluene-EtOAc = 40:50:10, v/v/v) = 0.58; Found: C, 74.20; H, 11.28%. $C_{41}H_{74}O_6$ (663.02) requires C, 74.27; H, 11.25%. ^{1}H and ^{13}C NMR spectra identical with those reported in the literature.[6]

1-Oleoyl-2-acetyl-3-palmitoyl-*sn*-glycerol 42. Acquired from 1-oleoyl-2-acetyl-3-trichloroacetyl-*sn*-glycerol (**22**; 0.544 g, 1.00 mmol) via **24** and palmitoyl chloride (0.61 mL, 2.00 mmol) (stage I; 2 h; stage II: 2 h). Yield: 0.586 g (92%, colorless oil); R_f (pentane-toluene-EtOAc = 40:50:10, v/v/v) = 0.60; Found: C, 73.60; H, 11.30%. $C_{39}H_{72}O_6$ (636.98) requires C, 73.54; H, 11.39%. ^{1}H and ^{13}C NMR spectra identical with those reported in the literature.[5]

1,3-Diacetyl-2-oleoylglycerol 43. Obtained from 1-acetyl-2-oleoyl-3-trichloroacetyl-*sn*-glycerol (**23**; 0.544 g, 1.00 mmol) via **25** and acetyl chloride (0.14 mL, 2.00 mmol) (stage I; 2 h; stage II: 2 h). Yield: 0.418 g (95%, colorless oil); R_f (pentane-toluene-EtOAc =

40:50:10, v/v/v) = 0.24; Found: C, 68.27; H, 10.03%. $C_{25}H_{44}O_6$ (440.61) requires C, 68.15; H, 10.06%. ^{1}H and ^{13}C NMR spectra identical with those reported in the literature.[6]

1-Acetyl-2,3-dioleoyl-*sn*-glycerol 44. Synthesized from 1-acetyl-2-oleoyl-3-trichloroacetyl-*sn*-glycerol (**23**; 0.544 g, 1.00 mmol) via **25** and oleoyl chloride (0.66 mL, 2.00 mmol) (stage I; 2 h; stage II: 2 h). Yield: 0.636 g (96%, colorless oil); $[\alpha]_D^{20}$= +0.70 (c, 5.82, $CHCl_3$); all other physicochemical and spectral characteristics were identical with those of **52** (section **3.5.**).

1-Oleoyl-2-palmitoyl-3-acetyl-*sn*-glycerol 45. Obtained from 1-oleoyl-2-trichloroacetyl-3-acetyl-*sn*-glycerol (**30**; 0.544 g, 1.00 mmol) via **32** and palmitoyl chloride (0.61 mL, 2.00 mmol) (stage I; 2 h; stage II: 3.5 h). Yield: 0.611 g (96%, colorless oil); R_f (pentane-toluene-EtOAc = 40:50:10, v/v/v) = 0.59; $[\alpha]_D^{20}$= -0.63 (*c* 13.15, $CHCl_3$); lit.[5] $[\alpha]_D^{20}$= -0.64 (*c* 8.15, $CHCl_3$); Found: C, 73.59; H, 11.35%. $C_{39}H_{72}O_6$ (636.98) requires C, 73.54; H, 11.39%.

1-Acetyl-2-palmitoyl-3-oleoyl-*sn*-glycerol 46. Obtained from 1-acetyl-2-trichloroacetyl-3-oleoyl-*sn*-glycerol (**31**; 0.544 g, 1.00 mmol) via **33** and palmitoyl chloride (0.61 mL, 2.00 mmol) (stage I; 2 h; stage II: 3.5 h). Yield: 0.598 g (94%, colorless oil); $[\alpha]_D^{20}$= +0.64 (*c* 12.75, $CHCl_3$); all other physicochemical and spectral characteristics were identical with those of **45**.

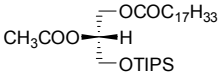
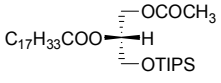
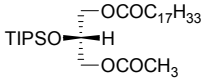
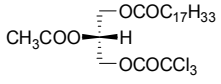
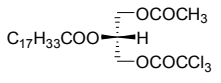
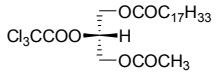
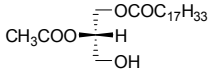
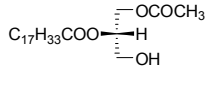
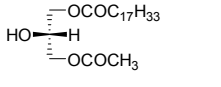
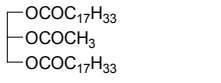
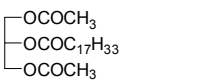
1-Oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-acetyl-*rac*-glycerol 56. Prepared from 1-oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-trifluoroacetyl-*rac*-glycerol (**54**; 0.567 g, 1.00 mmol) via **55** and acetyl chloride (0.14 mL, 2.00 mmol) (stage I; 30 min; stage II: 2 h). Yield: 0.482 g (94%, colorless oil); excluding the lack of optical activity, all other physicochemical and spectral characteristics were identical with those of **49** (section **3.3.**).

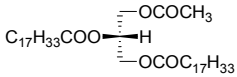
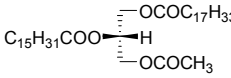
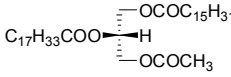
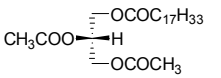
5. Analytical criteria for assessing regiochemistry of the preparations by high-resolution ^{1}H and ^{13}C NMR spectroscopy

Since ^{1}H- and ^{13}C NMR spectrometry have so far been exploited to carry out the regiospecific analysis of triacylglycerols predominantly,[7] little is known about effects on the informative parameters of such techniques, caused by steric-/electronic factors extending from non-lipid substituents or functional groups adjacent to a fatty acid residue within the glycerol backbone. These circumstances persuaded us to present briefly the results of our own studies on the correlation of particular ^{1}H- and ^{13}C NMR spectral characteristics of mixed-acid glycerides to the molecular structure of theirs as summarized in Table S2.

Table S2.

Characteristic ^{1}H (δ_H) and ^{13}C (δ_C) NMR chemical shifts (in ppm, sample concentration: ~mol.10^{-1}.L^{-1}, in $CDCl_3$) of molecular segments within the most representative, intermediary/final products obtained as the spectral means of their assignment to the corresponding regioisomeric structures

Compound		CH_3CO fragment	$C_{17}H_{33}CO$ fragment	$C_{15}H_{31}CO$ fragment	Glycerol fragment	$[\alpha]_D^{20}/c$ ($CHCl_3$)
			Silyl ethers			
	**20**	δ_H 2.05 (C*H*$_3$) δ_C 170.51 (C1) δ_C 21.20 (C2)	δ_C 173.67 (C1)	-	δ_C 62.60 (C1) δ_C 72.30 (C2)	+13.45/3.67
	**21**	δ_H 2.03 (C*H*$_3$) δ_C 170.89 (C1) δ_C 20.98 (C2)	δ_C 173.34 (C1)	-	δ_C 63.02 (C1) δ_C 71.94 (C2)	+15.72/11.38
	**28**	δ_H 2.06 (C*H*$_3$) δ_C 170.96 (C1) δ_C 21.04 (C2)	δ_C 173.78 (C1)	-	δ_C 65.57 (C1) δ_C 65.85 (C3)	-1.20/18.05
			Trichloroacetates			
	**22**	δ_H 2.08 (C*H*$_3$) δ_C 170.07 (C1) δ_C 20.95 (C2)	δ_C 173.36 (C1)	-	δ_C 61.67 (C1) δ_C 68.63 (C2)	-0.41/5.17
	**23**	δ_H 2.00 (C*H*$_3$) δ_C 170.54 (C1) δ_C 20.86 (C2)	δ_C 172.89 (C1)	-	δ_C 62.01 (C1) δ_C 68.33 (C2)	+1.78/10.31
	**30**	δ_H 2.08 (C*H*$_3$) δ_C 170.48 (C1) δ_C 20.77 (C2)	δ_C 173.28 (C1)	-	δ_C 61.61 (C1) δ_C 61.81 (C3)	-0.69/9.15
			Diacylglycerols			
	**24**	δ_H 2.10 (C*H*$_3$) δ_C 170.78 (C1) δ_C 21.21 (C2)	δ_C 174.02 (C1)	-	δ_C 62.17 (C1) δ_C 72.58 (C2) δ_C 61.63 (C3)	-5.47/4.82
	**25**	δ_H 2.07 (C*H*$_3$) δ_C 171.16 (C1) δ_C 20.95 (C2)	δ_C 173.65 (C1)	-	δ_C 62.52 (C1) δ_C 72.26 (C2) δ_C 61.76 (C3)	-1.62/6.53
	**32**	δ_H 2.09 (C*H*$_3$) δ_C 171.26 (C1) δ_C 20.99 (C2)	δ_C 174.12 (C1)	-	δ_C 65.23 (C1) δ_C 68.49 (C2) δ_C 65.46 (C3)	-0.27/10.85
			Triacylglycerols			
	**41**	δ_H 2.07 (C*H*$_3$) δ_C 170.26 (C1) δ_C 21.09 (C2)	δ_C 173.49 (C1) (at C1/C3)	-	δ_C 62.24 (C1) δ_C 69.40 (C2) δ_C 62.24 (C3)	-
	**43**	δ_H 2.06 (C*H*$_3$) δ_C 170.70 (C1) δ_C 20.89 (C2)	δ_C 173.12 (C1)	-	δ_C 62.53 (C1) δ_C 68.95 (C2) δ_C 62.53 (C3)	-

	(at C1/C3)				
 **44**	δ_H 2.06 (C*H*$_3$) δ_C 170.68 (C1) δ_C 20.90 (C2)	δ_C 173.09 (C1) (at *sn*-C2) δ_C 173.47 (C1) (at *sn*-C3)	-	δ_C 62.58 (C1) δ_C 69.03 (C2) δ_C 62.28 (C3)	+0.70/5.82
 **45**	δ_H 2.06 (C*H*$_3$) δ_C 170.68 (C1) δ_C 20.90 (C2)	δ_C 173.47 (C1)	δ_C 173.12 (C1)	δ_C 62.28 (C1) δ_C 69.01 (C2) δ_C 62.58 (C3)	-0.63/13.15
 **50**	δ_H 2.06 (C*H*$_3$) δ_C 170.68 (C1) δ_C 20.90 (C2)	δ_C 173.09 (C1)	δ_C 173.50 (C1)	δ_C 62.27 (C1) δ_C 69.03 (C2) δ_C 62.58 (C3)	-0.74/4.13
 **53**	δ_H 2.07 (C*H*$_3$) δ_C 170.28 (C1) δ_C 21.09 (C2) (at *sn*-C2) δ_H 2.06 (C*H*$_3$) δ_C 170.69 (C1) δ_C 20.89 (C2) (at *sn*-C3)	δ_C 173.49 (C1)	-	δ_C 62.20 (C1) δ_C 69.34 (C2) δ_C 62.50 (C3)	-1.28/9.12

Due to the distinctive chemical shifts of the methyl protons of an acetyl group at the C1(3) vs C2 center in the glycerol moiety,[5] the positional distribution of this fatty acid in the two- or three-component esters examined (e.g., types **20** vs **21**, **41** vs **44**, or vs **50**) can readily be pinpointed by routine ^{1}H NMR spectroscopy (400 MHz instrument, analysis conducted at 25 ^{o}C, spectral width: 5999 Hz, pulse angle: 43^o, line broadening: 0.1 Hz, acquisition time: 2.7 s) alone.

In triacylglycerols (**41**, **43-45**, **50**, **53**), for example, the resonances of a C2-acetyl replacement occurred systematically downfield (δ_H 2.07 ppm) from those of one entered the C1(3)-sites (δ_H 2.06 ppm) of the glyceride framework. These signals are highly intensive singlets, which appeared either as magnetically equivalent- (e.g., in **43**) or as virtually base line-separated peaks in the spectrum of vicinal diacetate **53** and in all instances where mixtures of the corresponding regioisomers (e.g., **20** with **21**, **22** with **23**, etc., at ratios from 9.5:0.5 to 1.0:1.0, w/w) were recorded.

The invariance of the specific chemical shifts for *sn*-2- (2.07 ppm) and *sn*-1(3)-acetates (2.06 ppm) inherent to triesters of types **41**, **43-45**, **50**, and **53**, indicates that the nature of neighboring fatty acids has no appreciable effect as far as the ^{1}H NMR regiospecific analysis is concerned. The observation by itself is important from an analytical point of view in terms that positioning of acetyl groups in any triacylglycerol sample of natural origin could be ascertained by this method even in the absence of information on the structural features of the other one/or two fatty acids incorporated.

Relative to these constant values (i.e. 2.06 ppm and 2.07 ppm) detected for the ordinary TAGs under investigation, the external acetyl moiety in the trichloroacetyl analogue **23** was markedly shielded ($\Delta\delta$ = -0.06 ppm) unlike the much weaker deshielding effect exerted by the trichloroacetyl substituent on that attached to the *sn*-2-position in **22** ($\Delta\delta$ = 0.01 ppm). Downfield relocation with comparable magnitude ($\Delta\delta$ = 0.02 ppm) was observed for the *sn*-3-acetyl fragment vicinal to the secondary trichloroacetyl replacement in **30**. While the chemical shift for *sn*-3-acetate **28** (2.06 ppm) remained practically unaffected by the presence of the C2-*O*-TIPS residue, the latter functionality when at a primary glycerol position induced shielding of both the *sn*-1- and *sn*-2-acetyl resonances, which appeared to be more pronouncedly shifted in the case of terminal acetate **21** ($\Delta\delta$ = -0.03 ppm) than that in its regioisomer **20** ($\Delta\delta$ = -0.02 ppm). Quite opposite deshielding trend was observed upon exposure of either a primary- or secondary hydroxyl group where the shift impact of this particular chemical environment on a *sn*-2-acetyl chain (**24**, $\Delta\delta$ = 0.03 ppm) was commensurable- (**32**, $\Delta\delta$ = 0.03 ppm) or stronger than on the lateral one (**25**, $\Delta\delta$ = 0.01 ppm).

The above deviations, however, obey the same upfield-downfield regularities regarding the chemical shifts of an acetyl residue at the primary vs secondary glycerol positions, which allows structured diglycerides and their isosteric forms to be assigned to the respective regioisomeric acetates (e.g., **20-25**, **28**, **30**, and **32**) in a highly accurate manner as well.

^{13}C NMR spectroscopy (WALTZ proton-decoupled carbon observation at 100 MHz, analysis conducted at 25 ^{o}C, spectral width: 25000 Hz, relaxation delay: 1.0 s, pulse angle: 48^{o}, line broadening: 1.0 Hz, acquisition time: 1.2 s) provided even more detailed evidence in this context.

Thus, the methyl carbons of an acetyl group positioned at *sn*-2 on the glycerol were also found to resonate at higher frequencies (δ_C ~21.11 ppm), as a rule, than if attached to *sn*-1(3)-sites (δ_C ~20.90 ppm). On the examples of model compounds studied, however, these signals followed the realignment tendency of the methyl protons only as to (i) the steady resonances of 21.09 ppm (for *sn*-2) and 20.90 ppm [for *sn*-1(3)] in TAGs bearing naturally occurring fatty acids (**41**, **43-45**, **50**, **53**); and (ii) the downfield shift relative to these values caused by a hydroxyl group with an emphasis upon *sn*-2 (**24**, $\Delta\delta$ = 0.12 ppm) compared to *sn*-1 (**25**, $\Delta\delta$ = 0.05 ppm; **32**, $\Delta\delta$ = 0.09 ppm).

Compared with the ^{1}H NMR shift-pattern, these ^{13}C parameters for silyl ether- **20** ($\Delta\delta$ = 0.11 ppm for *sn*-2), **21** ($\Delta\delta$ = 0.08 ppm for *sn*-1) and **28** ($\Delta\delta$ = 0.14 ppm for *sn*-1), as well as for trichloroacetyl monoacetates **22** ($\Delta\delta$ = -0.14 ppm for *sn*-2), **23** ($\Delta\delta$ = -0.04 ppm for *sn*-1) and **30** ($\Delta\delta$ = -0.13 ppm for *sn*-1), exhibited a clear trend to inversion. This suggests that

the specific shifting introduced by either *O*-TIPS or trichloroacetyl functionalities on the methyl protons of a C2-/C1(3)-acetyl chain (i) is balanced by the opposite effect on the parent carbon nucleus; and (ii) it has most likely an electronic rather than steric origin.

Unlike methyl carbons, the resonances attributable to the carbonyl function of an internal acetyl replacement (Ac) were seen consistently upfield (δ_C ~170.38 ppm) from those of its *sn*-1(3)-external counterpart (δ_C ~170.79 ppm). Similar spectral regularities in the carbonyl region were established for the oleoyl chain (Ol), i.e. (δ_C ~173.20 ppm at *sn*-2) and [δ_C ~173.61 ppm at *sn*-1(3)].

For the rest, there was an analogous drift concerning (i) the fair independence of the chemical shift values, namely Ac: 170.27 (±0.01) ppm/Ol: 173.10 (±0.01) ppm (for *sn*-2) and Ac: 170.69 (±0.01) ppm/Ol: 173.48 (±0.01) ppm [for *sn*-1(3)], from both the molecular symmetry and the positional distribution in triacylglycerols (**41**, **43-45**, **50**, **53**); and relative to these (ii) a deshielding effect decreasing from diglycerides **24/25** (Ac: Δδ = 0.51 ppm/Ol: Δδ = 0.55 ppm for *sn*-2), **25/24** (Ac: Δδ = 0.47 ppm/Ol: Δδ = 0.54 ppm for *sn*-1) and **32** (Ac: Δδ = 0.57 ppm/Ol: Δδ = 0.64 ppm for *sn*-1) to silyl ethers **20/21** [Ac: Δδ = 0.24 ppm/Ol: Δδ = 0.24 ppm for *sn*-2], **21/20** (Ac: Δδ = 0.20 ppm/Ol: Δδ = 0.19 ppm for *sn*-1), and **28** (Ac: Δδ = 0.27 ppm/Ol: Δδ = 0.19 ppm for *sn*-1); along with (iii) an upfield shift detected for trichloroacetates **22/23** (Ac: Δδ = -0.20 ppm/Ol: Δδ = -0.21 ppm for *sn*-2), **23/22** (Ac: Δδ = -0.15 ppm/Ol: Δδ = -0.12 ppm for *sn*-1) and **30** (Ac: Δδ = -0.21 ppm/Ol: Δδ = -0.20 ppm for *sn*-1) only.

At variance with all previous cases, these shift-effects on the carbonyl carbons, exerted discretely by a silyl- (in **20**, **21** or **28**), trichloroacetyl- (in **22**, **23** or **30**) or hydroxyl group (in **24**, **25** or **32**), appeared to be within the same range of magnitude regardless of both an acyl chain-length (e.g., acetyl vs oleoyl) and its attachment to a primary or the secondary position in the glyceride skeleton.

Regioisomeric esters comprising acetic acid can additionally be differentiated by considering the shifts of the glyceryl carbon atoms. For example, an average downfield shift of Δδ = ca. 0.37 (±0.07) ppm for *sn*-*C*2 could be detected upon rearrangement of C2-oleates (**21**, **23**, **25**, **43**, and **44**) into C2-acetyl conjugates (**20**, **22**, **24**, **41**, and **53**). Exchange of a terminal oleoyl moiety for an acetyl one induced a comparable deshielding effect [i.e. Δδ = ca. 0.36 (±0.06) ppm] on the primary carbon atom ($-CH_2CH)_{sn\text{-}1/3}$ where the substitution occurred (e.g., **20**, **22**, **24**, **41**, **44**, and **53** vs **21**, **23**, **25**, **43**, **44**, and **53**, respectively).

The reversed shielding upshot established in this region after exposure of a free hydroxyl function on the glycerol offers a complementary course for assessing configurational homogeneity of the diglycerides **24**, **25** and **32**. Thus, in 1-oleoyl-3-acetyl-*sn*-glycerol (**32**),

the secondary C2 carbon atom was found to resonate at 68.49 ppm vs the downfield signals furnished by the same carbon atom in C2-*O*-acyl isomers **24** (72.58 ppm) and **25** (72.26 ppm). In a similar way, resonances of the primary C3 carbon atom within **24** and **25** were shifted from ~61.7 to ~62.4 ppm upon acylation to triesters **41**, **43**, **44** and **53**. In these instances, however, the chemical shift values of *sn*-*C*2 and *sn*-*C*1(3) were observed to vary to some extent indicating that the phenomenon might be due to alterations in the shape of the glycerol skeleton affected by the nature of either the acid substituent or the neighboring functionalities (e.g., *O*-silyl, etc.) present, as well as by their particular positioning in the molecular construction, as supported by the dependence of optical activity on the regioisomeric profile of the enantiomerically defined acylates under investigation (e.g., **20** vs **21**, **22** vs **23**, **24** vs **25**, etc.).

Taken together, the above findings provide nondestructive analytical means that, within the limits of sensitivity of ^{1}H-/^{13}C NMR spectroscopy and polarimetry, allow the distribution of acetyl- and oleoyl radicals to be also specified toward a third acyl moiety in a glyceride ester, for example, seen upon comparing the corresponding spectral characteristics of vicinal dioleate (**44**) with those of the regioisomeric palmitoyl homologues (**45**) and (**50**).

6. ^{1}H- and ^{13}C NMR data for compounds 7-63

1-Iodo-2-oleoyl-3-*O*-*tert*-butyldiphenylsilyl-*sn*-glycerol 7. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 7.60-7.75 (4H, m, Aryl); 7.30-7.55 (6H, m, Aryl); 5.34 (2H, m, C*H*=C*H*); 4.86 (1H, tt, *J*=5.5, 5.2 Hz, C*H*OCOR); 3.85 (1H, dd, *J*=4.9, 4.9 Hz, $ICH_2CHCH_aH_bOSi$); 3.74 (1H, dd, *J*=5.2, 5.2 Hz, $ICH_2CHCH_aH_bOSi$); 3.50 (1H, dd, *J*=5.5, 5.5 Hz, $SiOCH_2CHCH_aH_bI$); 3.38 (1H, dd, *J*=5.2, 5.5 Hz, $SiOCH_2CHCH_aH_bI$); 2.30 (2H, m, 2-CH_2); 2.02 (4H, m, 8-CH_2, 11-CH_2); 1.62 (2H, m, 3-CH_2); 1.30 (20H, m, 4-7-CH_2, 12-17-CH_2); 1.06 (9H, s, *t-Bu*-Si); 0.88 (3H, br t, 18-CH_3); ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 135.84, 135.76, 133.21, 130.08, 128.02, 127.99 (*C*H, *C*-Si); 26.97 (*C*H_3-); 19.48 (*C*-Si): *tert*-butyldiphenylsilyl fragment; 173.02 (C1); 129.98, 130.23 (C9, C10); 34.54 (C2); 32.13 (C16); 29.33-30.00 (C4-C7, C12-C15); 27.40, 27.45 (C11, C8); 25.15 (C3); 22.91 (C17); 14.35 (C18): oleoyl fragment; 72.72 (C2); 64.39 (C3); 4.20 (C1): glycerol fragment.

1-Iodo-2-acetyl-3-*O*-triisopropylsilyl-*sn*-glycerol 8. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 4.76 (1H, tt, *J*=5.5, 5.5 Hz, C*H*OAc); 3.88 (1H, dd, *J*=4.8, 4.8 Hz, $ICH_2CHCH_aH_bOSi$); 3.78 (1H, dd, *J*=5.5, 5.5 Hz, $ICH_2CHCH_aH_bOSi$); 3.47 (1H, dd, *J*=5.5, 5.5 Hz, $SiOCH_2CHCH_aH_bI$); 3.35 (1H, dd, *J*=5.3, 5.3 Hz, $SiOCH_2CHCH_aH_bI$); 2.08 (3H, s, 2-CH_3); 0.98-1.16 (21H, m, SiC*H*(CH_3)$_2$). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.11

(*C*H_3-);12.09 (*C*H-Si): triisopropylsilyl fragment; 170.32 (C1); 21.21 (C2): acetyl fragment; 73.18 (C2); 63.97 (C3); 4.54 (C1): glycerol fragment.

1-Iodo-2-oleoyl-3-*O*-triisopropylsilyl-*sn*-glycerol 9. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 4.76 (1H, tt, *J*=5.5, 5.5 Hz, C*H*OCOR); 3.88 (1H, dd, *J*=4.9, 4.7 Hz, $ICH_2CHCH_aH_b$OSi); 3.77 (1H, dd, *J*=5.8, 5.8 Hz, $ICH_2CHCH_aH_b$OSi); 3.48 (1H, dd, *J*=5.2, 5.2 Hz, $SiOCH_2CHCH_aH_b$I); 3.36 (1H, dd, *J*=5.5, 5.5 Hz, $SiOCH_2CHCH_aH_b$I); 2.32 (2H, m, 2-CH_2); 2.00 (4H, m, 8-CH_2, 11-CH_2); 1.64 (2H, m, 3-CH_2); 1.30 (20H, m, 4-7-CH_2, 12-17-CH_2); 0.98-1.18 (21H, m, SiC*H*(CH_3)$_2$); 0.88 (3H, t, *J*=6.9 Hz, 18-CH_3). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.14 (*C*H_3-); 12.11 (*C*H-Si): triisopropylsilyl fragment; 173.12 (C1); 129.96, 130.23 (C9, C10); 34.56 (C2); 32.13 (C16); 29.33-30.00 (C4-C7, C12-C15); 27.40, 27.45 (C11, C8); 25.15 (C3); 22.91 (C17); 14.34 (C18): oleoyl fragment; 72.91 (C2); 64.02 (C3); 4.76 (C1): glycerol fragment.

1-*O*-*tert*-Butyldimethylsilyl-2-oleoyl-3-iodo-*sn*-glycerol 10. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 4.73 (1H, tt, *J*=5.2, 5.2 Hz, C*H*OCOR); 3.77 (1H, dd, *J*=4.9, 4.7 Hz, $ICH_2CHCH_aH_b$OSi); 3.66 (1H, dd, *J*=5.8, 5.5 Hz, $ICH_2CHCH_aH_b$OSi); 3.43 (1H, dd, *J*=5.2, 5.2 Hz, $SiOCH_2CHCH_aH_b$I); 3.32 (1H, dd, *J*=5.5, 5.2 Hz, $SiOCH_2CHCH_aH_b$I); 2.33 (2H, m, 2-CH_2); 2.00 (4H, m, 8-CH_2, 11-CH_2); 1.64 (2H, m, 3-CH_2); 1.28 (20H, m, 4-7-CH_2, 12-17-CH_2); 0.82-0.96 (12H, s overlapping with t, *t-Bu*-Si, 18-CH_3); 0.08 (6H, d, *J*=1.1 Hz, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 26.01 (*C*H_3-); 18.42 (*C*-Si); -5.18 (*C*H_3-Si): *tert*-butyldimethylsilyl fragment; 173.10 (C1); 129.96, 130.23 (C9, C10); 34.56 (C2); 32.13 (C16); 29.32-29.99 (C4-C7, C12-C15); 27.39, 27.45 (C11, C8); 25.17 (C3); 22.91 (C17); 14.35 (C18): oleoyl fragment; 72.70 (C2); 63.67 (C1); 4.76 (C3): glycerol fragment.

1-*O*-*tert*-Butyldimethylsilyl-2-acetyl-3-iodo-*rac*-glycerol 11. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 4.73 (1H, tt, *J*=5.3, 5.3 Hz, C*H*OAc); 3.78 (1H, dd, *J*=4.8, 4.8 Hz, $ICH_2CHCH_aH_b$OSi); 3.67 (1H, dd, *J*=5.7, 5.5 Hz, $ICH_2CHCH_aH_b$OSi); 3.43 (1H, dd, *J*=5.3, 5.3 Hz, $SiOCH_2CHCH_aH_b$I); 3.32 (1H, dd, *J*=5.5, 5.3 Hz, $SiOCH_2CHCH_aH_b$I); 2.08 (3H, s, 2-CH_3); 0.88 (9H, s, *t-Bu*-Si); 0.06 (6H, d, *J*=1.6 Hz, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 25.99 (*C*H_3-); 18.43 (*C*-Si); -5.19 (*C*H_3-Si): *tert*-butyldimethylsilyl fragment; 170.29 (C1); 21.21 (C2): acetyl fragment; 72.99 (C2); 63.62 (C1); 4.52 (C3): glycerol fragment.

1-Iodo-2-*O*-tripropylsilyl-3-*O*-*tert*-butyldiphenylsilyl-*sn*-glycerol 12. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 7.60-7.76 (4H, m, Aryl); 7.30-7.54 (6H, m, Aryl); 3.20-3.70 (5H, m, C*H*OSi, $ICH_2CHCH_aH_b$OSi, $SiOCH_2CHCH_aH_b$I); 1.22-1.42 (6H, m, $CH_3CH_2CH_2$-Si); 1.06 (9H, s, *t-Bu*-Si); 0.86-1.00 (9H, m, $CH_3CH_2CH_2$-Si); 0.46-0.58 (6H, m, $CH_3CH_2CH_2$-Si).

^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 135.86, 135.76, 133.62, 133.40, 129.96, 127.95 (*C*H, *C*-Si); 27.03 (*C*H_3-); 19.44 (*C*-Si): *tert*-butyldiphenylsilyl fragment; 18.82 (CH_3*C*H_2CH_2-Si); 18.65 (d, *J*=5.7 Hz, *C*$H_3CH_2CH_2$-Si); 17.00 (m, CH_3*C*H_2*C*H_2-Si): tripropylsilyl fragment; 71.77 (C2); 67.08 (C3); 12.09 (C1): glycerol fragment.

1-*O*-*tert*-Butyldimethylsilyl-2-*O*-triisopropylsilyl-3-iodo-*sn*-glycerol 13. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 3.30-3.70 (5H, m overlapping with m, C*H*OSi, $ICH_2CHCH_aH_bOSi$, $SiOCH_2CHCH_aH_bI$); 1.00-1.20 (21H, m, $SiCH(CH_3)_2$); 0.90 (9H, s, *t-Bu*-Si); 0.07 (6H, d, *J*=3.6, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 26.12 (*C*H_3-); 18.47 (*C*-Si); -5.14, -5.09 (*C*H_3-Si): *tert*-butyldimethylsilyl fragment; 18.30 (*C*H_3-); 12.69 (*C*-Si): triisopropylsilyl fragment; 71.09 (C2); 66.47 (C1); 13.34 (C3): glycerol fragment.

1,2-*O*-Di(*tert*-butyldimethylsilyl)-3-iodo-*rac*-glycerol 14. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 3.42-3.66 (3H, m, overlapping signals of C*H*OSi, $SiOCH_aH_bCHCH_2I$); 3.22-3.38 (2H, m, $SiOCH_2CHCH_aH_bI$); 0.90 (18H, d, *J*=3.8 Hz, *t-Bu*-Si); 0.03-0.15 (12H, d overlapping with d, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 26.12, 26.04 (*C*H_3-); 18.49, 18.32 (*C*-Si); -4.22, -4.36, -5.12 (*C*H_3-Si): both *tert*-butyldimethylsilyl fragments; 71.95 (C2); 66.69 (C1); 12.20 (C3): glycerol fragment.

1-Oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-iodo-*sn*-glycerol 15. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 4.00-4.18 (2H, m, $ICH_2CHCH_aH_bOCOR$); 3.78 (1H, tt, *J*=5.5, 4.7 Hz, C*H*OSi); 3.23 (1H, dd, *J*=5.7, 5.7 Hz, $R(O)COCH_2CHCH_aH_bI$); 3.18 (1H, dd, *J*=4.8, 4.8 Hz, $R(O)COCH_2CHCH_aH_bI$); 2.31 (2H, t, *J*=7.7 Hz, 2-CH_2); 2.00 (4H, m, 8-CH_2, 11-CH_2); 1.62 (2H, m, 3-CH_2); 1.28 (20H, m, 4-7-CH_2, 12-17-CH_2); 0.82-0.96 (12H, s overlapping with t, *t-Bu*-Si, 18-CH_3); 0.11 (6H, d, *J*=8.2 Hz, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 25.93 (*C*H_3-); 18.28 (*C*-Si); -4.41, -4.39 (*C*H_3-Si): *tert*-butyldimethylsilyl fragment; 173.59 (C1); 129.95, 130.23 (C9, C10); 34.40 (C2); 32.13 (C16); 29.31-29.99 (C4-C7, C12-C15); 27.39, 27.44 (C11, C8); 25.12 (C3); 22.91 (C17); 14.34 (C18): oleoyl fragment; 69.66 (C2); 67.34 (C1); 9.18 (C3): glycerol fragment.

1-Oleoyl-2-*O*-triethylsilyl-3-iodo-*sn*-glycerol 16. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 4.02-4.18 (2H, m, $R(O)COCH_aH_bCHCH_2I$); 3.82 (1H, tt, *J*=5.5, 5.5 Hz, C*H*OSi); 3.24 (1H, dd, *J*=5.7, 5.8 Hz, $R(O)COCH_2CHCH_aH_bI$); 3.17 (1H, dd, *J*=4.9, 4.9 Hz, $R(O)COCH_2CHCH_aH_bI$); 2.31 (2H, t, *J*=7.4 Hz, 2-CH_2); 1.90-2.12 (4H, m, 8-CH_2, 11-CH_2); 1.54-1.72 (2H, m, 3-CH_2); 1.20-1.40 (20H, m, 4-7-CH_2, 12-17-CH_2); 0.97 (9H, t, *J*=7.9 Hz, $Si\text{-}CH_2CH_3$); 0.88 (3H, t, *J*= 6.9 Hz, 18-CH_3); 0.64 (6H, q, *J*=8.0 Hz, $Si\text{-}CH_2CH_3$). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 0.43 6.98 ($Si\text{-}CH_2CH_3$); 5.10 ($Si\text{-}CH_2CH_3$): triethylsilyl fragment; 173.63 (C1); 129.95, 130.23 (C9, C10); 34.38 (C2); 32.13

(C16); 29.32-29.99 (C4-C7, C12-C15); 27.39, 27.44 (C11, C8); 25.12 (C3); 22.90 (C17); 14.33 (C18): oleoyl fragment; 69.72 (C2); 67.30 (C1); 9.10 (C3): glycerol fragment.

1-Oleoyl-2-*O*-trimethylsilyl-3-bromo-*sn*-glycerol 17. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 3.96-4.25 (3H, m, overlapping signals of C*H*OSi, R(O)COCH_aH_bCHCH_2Br); 3.40 (1H, dd, *J*=5.3, 5.5 Hz, R(O)COCH_2CHC$H_a$$H_b$Br); 3.31 (1H, dd, *J*=5.5, 5.5 Hz, R(O)COCH_2CHC$H_a$$H_b$Br); 0.88 (3H, t, *J*= 7.1 Hz, 18-CH_3): oleoyl and glycerol fragments; 0.16 (9H, d, *J*= 0.7 Hz, Si-CH_3): trimethylsilyl fragment. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 0.34 (Si-*C*H$_3$): trimethylsilyl fragment; 173.64 (C1); 129.95, 130.24 (C9, C10); 34.38 (C2); 14.33 (C18): oleoyl fragment; 70.30 (C2); 66.15 (C1); 34.25 (C3): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[4]

1-Oleoyl-2-*O*-triisopropylsilyl-3-chloro-*rac*-glycerol 18. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.36 (2H, m, C*H*=C*H*); 4.07-4.30 (3H, m, overlapping signals of C*H*OSi, R(O)COCH_aH_bCHCH_2Cl); 3.48-3.64 (2H, m, R(O)COCH_2CHCH_aH_bCl); 2.31 (2H, t, *J*=7.4 Hz, 2-CH_2); 1.88-2.16 (4H, m, 8-CH_2, 11-CH_2); 1.52-1.74 (2H, m, 3-CH_2); 1.22-1.40 (20H, m, 4-7-CH_2, 12-17-CH_2); 1.03-1.14 (21H, m, SiC*H*(CH_3)$_2$); 0.88 (3H, t, *J*=6.9 Hz, 18-CH_3). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.16 (-*C*H$_3$); 12.59 (Si-*C*): triisopropylsilyl fragment; 173.68 (C1); 129.95, 130.23 (C9, C10); 34.39 (C2); 32.13 (C16); 29.32-29.99 (C4-C7, C12-C15); 27.39, 27.44 (C11, C8); 25.12 (C3); 22.90 (C17); 14.32 (C18): oleoyl fragment; 70.56 (C2); 65.34 (C1); 45.76 (C3): glycerol fragment.

1-Oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-chloro-*rac*-glycerol 19. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 3.90-4.30 (3H, m, overlapping signals of C*H*OSi, R(O)COCH_aH_bCHCH_2Cl); 3.30-3.60 (2H, m, R(O)COCH_2CHCH_aH_bCl); 2.31 (2H, t, *J*=7.4 Hz, 2-CH_2); 1.86-2.14 (4H, m, 8-CH_2, 11-CH_2); 1.52-1.72 (2H, m, 3-CH_2); 1.22-1.38 (20H, m, 4-7-CH_2, 12-17-CH_2); 0.82-0.96 (12H, s overlapping with t, *t-Bu*-Si, 18-CH_3); 0.10 (6H, d, *J*=4.4 Hz, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 25.87 (*C*H$_3$-); 18.27 (*C*-Si); -4.55 (*C*H$_3$-Si): *tert*-butyldimethylsilyl fragment; 173.63 (C1); 129.94, 130.23 (C9, C10); 34.39 (C2); 32.12 (C16); 29.31-29.98 (C4-C7, C12-C15); 27.38, 27.44 (C11, C8); 25.11 (C3); 22.90 (C17); 14.32 (C18): oleoyl fragment; 70.76 (C2); 65.60 (C1); 45.90 (C3): glycerol fragment.

1-Oleoyl-2-acetyl-3-*O*-triisopropylsilyl-*sn*-glycerol 20. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.35 (2H, m, C*H*=C*H*); 5.08 (1H, m, C*H*OAc); 4.37 (1H, dd, *J*=3.8, 3.8 Hz, R(O)COCH_aH$_b$CHCH_2OSi); 4.19 (1H, dd, *J*=6.0, 6.0 Hz, R(O)COC$H_a$$H_bCHCH_2$OSi); 3.81 (2H, d, *J*=5.2 Hz, R(O)COCH_2CHCH_aH_bOSi); 0.87 (3H, t, *J*=7.1 Hz,18-CH_3): oleoyl and glycerol fragments; 2.05 (3H, s, 2-CH_3): acetyl fragment; 1.05 (21H, m, SiC*H*(CH_3)$_2$):

triisopropylsilyl fragment. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.67 (C1); 129.94, 130.22 (C9, C10); 14.31 (C18): oleoyl fragment; 170.51 (C1); 21.20 (C2): acetyl fragment; 18.07 (*C*H$_3$-); 12.08 (*C*H-Si): triisopropylsilyl fragment; 72.30 (C2); 62.60 (C1); 62.01 (C3): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[5]

1-Acetyl-2-oleoyl-3-*O*-triisopropylsilyl-*sn*-glycerol 21. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 5.10 (1H, m, C*H*OCOR); 4.37 (1H, dd, *J*=3.6, 3.6 Hz, SiOCH$_2$CHCH$_a$*H$_b$*OAc); 4.18 (1H, dd, *J*=6.3, 6.6 Hz, SiOCH$_2$CHC*H$_a$*H$_b$OAc); 3.70-3.90 (2H, m, AcOCH$_2$CHC*H$_a$H$_b$*OSi); 2.30 (2H, m, 2-C*H$_2$*); 2.03 (3H, s, 2-C*H$_3$*); 2.00 (4H, m, 8-C*H$_2$*, 11-C*H$_2$*); 1.61 (2H, m, 3-C*H$_2$*); 1.28 (20H, m, 4-7-C*H$_2$*, 12-17-C*H$_2$*); 0.98-1.16 (21H, m, SiC*H*(C*H$_3$*)$_2$); 0.87 (3H, t, *J*=6.9 Hz, 18-C*H$_3$*). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.34 (C1); 129.93, 130.22 (C9, C10); 34.54 (C2); 32.12 (C16); 29.28-29.98 (C4-C7, C12-C15); 27.38, 27.43 (C11, C8); 25.12 (C3); 22.89 (C17); 14.31 (C18): oleoyl fragment; 170.89 (C1); 20.98 (C2): acetyl fragment; 18.07 (-*C*H$_3$); 12.08 (Si-*C*): triisopropylsilyl fragment; 71.94 (C2); 63.02 (C1); 62.05 (C3): glycerol fragment.

1-Oleoyl-2-acetyl-3-trichloroacetyl-*sn*-glycerol 22. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (3H, m, C*H*=C*H*, C*H*OAc); 4.59 (1H, dd, *J*=3.8, 3.8 Hz, R(O)COCH$_2$CHCH$_a$*H$_b$*OCOCCl$_3$); 4.46 (1H, dd, *J*=5.9, 5.7 Hz, R(O)COCH$_2$CHC*H$_a$*H$_b$OCOCCl$_3$); 4.35 (1H, dd, *J*=4.8, 4.8 Hz, R(O)COC*H$_a$*H$_b$CHCH$_2$OCOCCl$_3$); 4.20 (1H, dd, *J*=5.5, 5.5 Hz, R(O)COCH$_a$*H$_b$*CHCH$_2$OCOCCl$_3$); 0.88 (3H, t, *J*= 6.7 Hz, 18-CH$_3$): oleoyl and glycerol fragments; 2.08 (3H, s, 2-C*H$_3$*): acetyl fragment; ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.36 (C1); 129.92, 130.25 (C9, C10); 14.33 (C18): oleoyl fragment; 170.07 (C1); 20.95 (C2): acetyl fragment; 161.87 (C1): trichloroacetyl fragment; 68.63 (C2); 66.61 (C3); 61.67 (C1): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[5]

1-Acetyl-2-oleoyl-3-trichloroacetyl-*sn*-glycerol 23. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.25-5.45 (3H, m, C*H*=C*H*, C*H*OCOR); 4.59 (1H, dd, *J*=4.0, 3.8 Hz, AcOCH$_2$CHCH$_a$*H$_b$*OCOCCl$_3$); 4.46 (1H, dd, *J*=5.7, 5.7 Hz, AcOCH$_2$CHC*H$_a$*H$_b$OCOCCl$_3$); 4.34 (1H, dd, *J*=4.8, 4.9 Hz, CCl$_3$(O)COCH$_2$CHCH$_a$*H$_b$*OAc); 4.20 (1H, dd, *J*=5.7, 5.7 Hz, CCl$_3$(O)COCH$_2$CHC*H$_a$*H$_b$OAc); 2.32 (2H, t, *J*=7.5 Hz, 2-C*H$_2$*); 2.00 (3H, s, 2-C*H$_3$*); 2.02 (4H, m, 8-CH$_2$, 11-C*H$_2$*); 1.61 (2H, m, 3-C*H$_2$*); 1.30 (20H, m, 4-7-C*H$_2$*, 12-17-C*H$_2$*); 0.87 (3H, t, *J*= 6.9 Hz, 18-CH$_3$). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 172.89 (C1); 129.91, 130.26 (C9, C10); 34.28 (C2); 32.12 (C16); 29.23-29.98 (C4-C7, C12-C15); 27.44, 27.37 (C11, C8); 24.98 (C3); 22.89 (C17); 14.33 (C18): oleoyl fragment; 170.54 (C1); 20.86 (C2):

acetyl fragment; 161.86 (C1): trichloroacetyl fragment; 68.33 (C2); 66.70 (C3); 62.01 (C1): glycerol fragment.

1-Oleoyl-2-acetyl-*sn*-glycerol 24. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.33 (2H, m, C*H*=C*H*); 5.06 (1H, tt, *J*=4.9, 4.9 Hz, C*H*OAc); 4.32 (1H, dd, *J*=4.4, 4.4 Hz, R(O)COCH_aH$_b$CHCH$_2$OH); 4.22 (1H, dd, *J*=5.5, 5.7 Hz, R(O)COCH$_a$$H_b$CHCH$_2$OH); 3.72 (2H, m, R(O)COCH$_2$CHC$H_a$$H_b$OH); 0.87 (3H, t, *J*= 6.6 Hz, 18-CH_3): oleoyl and glycerol fragments; 2.10 (3H, s, 2-CH_3): acetyl fragment. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 174.02 (C1); 129.92, 130.25 (C9, C10); 14.32 (C18): oleoyl fragment; 170.78 (C1); 21.21 (C2): acetyl fragment; 72.58 (C2); 62.17 (C1); 61.63 (C3): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[5]

1-Acetyl-2-oleoyl-*sn*-glycerol 25. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.33 (2H, m, C*H*=C*H*); 5.08 (1H, tt, *J*=4.7, 4.7 Hz, C*H*OCOR); 4.31 (1H, dd, *J*=4.4, 4.7 Hz, HOCH$_2$CHCH$_a$$H_b$OAc); 4.22 (1H, dd, *J*=5.8, 5.8 Hz, HOCH$_2$CHCH_aH$_b$OAc); 3.60-3.86 (2H, m, AcOCH$_2$CHC$H_a$$H_b$OH); 2.34 (2H, t, *J*=7.7 Hz, 2-CH_2); 2.07 (3H, s, 2-CH_3); 2.01 (4H, m, 8-CH_2, 11-CH_2); 1.62 (2H, m, 3-CH_2); 1.30 (20H, m, 4-7-CH_2, 12-17-CH_2); 0.87 (3H, t, *J*=6.9 Hz, 18-CH_3). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.65 (C1); 130.26, 129.92 (C9, C10); 34.48 (C2); 32.12 (C16); 29.26-29.98 (C4-C7, C12-C15); 27.44, 27.37 (C11, C8); 25.14 (C3); 22.90 (C17); 14.32 (C18): oleoyl fragment; 171.16 (C1); 20.95 (C2): acetyl fragment; 72.26 (C2); 62.52 (C1); 61.76 (C3): glycerol fragment.

1-*O*-*tert*-Butyldimethylsilyl-2-*O*-triisopropylsilyl-3-acetyl-*sn*-glycerol 26. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 3.90-4.40 (3H, mm overlapping with m, SiOCH$_2$CHC$H_a$$H_b$OAc, C*H*OSi); 3.44-3.74 (2H, m, AcOCH$_2$CHC$H_a$$H_b$OSi); 2.05 (3H, s, 2-C$H_3$); 1.00-1.18 (21H, m, SiC*H*(CH_3)$_2$); 0.88 (9H, s, *t-Bu*-Si); 0.04 (6H, s, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 26.07 (*C*H$_3$-); 18.21, 18.19 (*C*-Si); -5.27, -5.29 (*C*H$_3$-Si): *tert*-butyldimethylsilyl fragment; 18.48 (-*C*H$_3$); 12.64 (Si-*C*): triisopropylsilyl fragment; 171.21 (C1); 21.13 (C2): acetyl fragment; 71.42 (C2); 66.60 (C3); 64.66 (C1): glycerol fragment.

1-*O*-*tert*-Butyldimethylsilyl-2-*O*-triisopropylsilyl-3-oleoyl-*sn*-glycerol 27. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 3.90-4.38 (3H, mm overlapping with m, SiOCH$_2$CHC$H_a$$H_b$OCOR, C*H*OSi); 3.46-3.76 (2H, m, R(O)COCH$_2$CHC$H_a$$H_b$OSi); 2.30 (2H, t, *J*=7.4 Hz, 2-CH_2); 2.00 (4H, m, 8-CH_2, 11-CH_2); 1.62 (2H, m, 3-CH_2); 1.28 (20H, m, 4-7-CH_2, 12-17-CH_2); 1.02-1.12 (21H, m, SiC*H*(CH_3)$_2$); 0.84-0.93 (12H, t overlapping with s, *t-Bu*-Si, 18-CH_3); 0.04 (6H, s, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 26.08 (*C*H$_3$-); 18.23, 18.22 (*C*-Si); -5.25, -5.27 (*C*H$_3$-Si): *tert*-butyldimethylsilyl fragment; 18.50 (-*C*H$_3$); 12.65 (Si-*C*): triisopropylsilyl fragment; 173.98(C1); 129.98, 130.20 (C9, C10); 34.51 (C2); 32.13 (C16); 29.34-29.99 (C4-C7, C12-C15); 27.41, 27.44 (C11, C8);

25.17 (C3); 22.91 (C17); 14.33 (C18): oleoyl fragment; 71.48 (C2); 66.18 (C3); 64.65 (C1): glycerol fragment.

1-Oleoyl-2-*O*-triisopropylsilyl-3-acetyl-*sn*-glycerol 28. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 3.97-4.30 (5H, m, R(O)COCH_aH_bCHCH_aH_bOAc, C*H*OSi); 2.31 (2H, t, *J*=7.4 Hz, 2-CH_2); 2.06 (3H, s, 2-CH_3); 2.00 (4H, m, 8-CH_2, 11-CH_2); 1.61 (2H, m, 3-CH_2); 1.29 (20H, m, 4-7-CH_2, 12-17-CH_2); 1.00-1.14 (21H, m, SiC*H*(CH_3)$_2$); 0.88 (3H, t, *J*=7.1 Hz, 18-CH_3). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.15 (-*C*H$_3$); 12.59 (Si-*C*): triisopropylsilyl fragment; 173.78 (C1); 129.96, 130.23 (C9, C10); 34.39 (C2); 32.13 (C16); 29.33-29.99 (C4-C7, C12-C15); 27.40, 27.44 (C11, C8); 25.10 (C3); 22.90 (C17); 14.33 (C18): oleoyl fragment; 170.96 (C1); 21.04 (C2): acetyl fragment; 68.64 (C2); 65.85 (C3); 65.57 (C1): glycerol fragment.

1-Acetyl-2-*O*-triisopropylsilyl-3-oleoyl-*sn*-glycerol 29. Spectral characteristics identical with those of the previous product.

1-Oleoyl-2-trichloroacetyl-3-acetyl-*sn*-glycerol 30. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.28-5.44 (3H, mm, C*H*=C*H*, C*H*OCOCCl$_3$); 4.20-4.49 (4H, mm, R(O)COCH$_2$CHCH$_a$$H_b$OAc, R(O)COCH$_2CHCH_aH_b$OAc, AcOCH$_2$CHCH$_a$$H_b$OCOR, AcOCH$_2CHCH_aH_b$OCOR); 0.87 (3H, t, *J*=7.1 Hz, 18-CH_3): oleoyl and glycerol fragments; 2.08 (3H, s, 2-CH_3): acetyl fragment. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.28 (C1); 129.93, 130.24 (C9, C10); 34.14 (C2); 14.33 (C18): oleoyl fragment; 170.48 (C1); 20.77 (C2): acetyl fragment; 161.57 (C1): trichloroacetyl fragment; 74.69 (C2); 61.81 (C3); 61.61 (C1): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[5]

1-Acetyl-2-trichloroacetyl-3-oleoyl-*sn*-glycerol 31. Spectral characteristics identical with those of the previous product.

1-Oleoyl-3-acetyl-*sn*-glycerol 32. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.33 (2H, m, C*H*=C*H*); 4.02-4.23 (5H, m, R(O)COCH_aH_bCHCH_aH_bOAc, C*H*OH); 0.87 (3H, t, *J*=7.0 Hz, 18-CH_3): oleoyl and glycerol fragments; 2.09 (3H, s, 2-CH_3): acetyl fragment. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 174.12 (C1); 129.93, 130.24 (C9, C10); 34.29 (C2); 14.32 (C18): oleoyl fragment; 171.26 (C1); 20.99 (C2): acetyl fragment; 68.49 (C2); 65.46 (C3); 65.23 (C1): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[5]

1-Acetyl-3-oleoyl-*sn*-glycerol 33. Spectral characteristics identical with those of **32**.

1-Trifluoroacetyl-2-*O*-triisopropylsilyl-3-acetyl-*sn*-glycerol 34. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 4.22-4.54 (3H, mm overlapping with m, AcOCH$_2$CHCH_aH_bOCOCF$_3$, C*H*OSi); 4.00-4.22 (2H, m, CF$_3$(O)COCH$_2$CHCH_aH_bOAc);

2.07 (3H, s, 2-CH_3); 0.98-1.18 (21H, m, SiCH(CH_3)$_2$). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.02 (-CH$_3$); 12.50 (Si-C): triisopropylsilyl fragment; 170.70 (C1); 20.88 (C2): acetyl fragment; 114.68 (d, J=285.4 Hz, C2): trifluoroacetyl fragment; 68.99 (C1); 67.97 (C2); 64.91 (C3): glycerol fragment.

1-Trifluoroacetyl-2-*O*-triisopropylsilyl-3-oleoyl-*sn*-glycerol 35. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, CH=CH); 4.24-4.52 (3H, mm overlapping with m, R(O)COCH$_2$CHC$H_a$$H_b$OCOCF$_3$, C$H$OSi); 4.02-4.23 (2H, m, CF$_3$(O)COCH$_2$CHC$H_a$$H_b$OCOR); 2.31 (2H, t, J=7.5 Hz, 2-CH_2); 2.00 (4H, m, 8-CH_2, 11-CH_2); 1.62 (2H, m, 3-CH_2); 1.29 (20H, m, 4-7-CH_2, 12-17-CH_2); 1.02-1.12 (21H, m, SiCH(CH_3)$_2$); 0.88 (3H, t, J=7.0 Hz, 18-CH_3). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.05 (-CH$_3$); 12.51 (Si-C): triisopropylsilyl fragment; 173.53 (C1); 129.93, 130.24 (C9, C10); 34.26 (C2); 32.12 (C16); 29.31-29.98 (C4-C7, C12-C15); 27.38, 27.43 (C11, C8); 25.05 (C3); 22.90 (C17); 14.31 (C18): oleoyl fragment; 114.70 (d, J=285.4 Hz, C2): trifluoroacetyl fragment; 69.01 (C1); 68.06 (C2); 64.64 (C3): glycerol fragment.

2-*O*-Triisopropylsilyl-3-acetyl-*sn*-glycerol 36. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 3.94-4.28 (3H, m overlapping with mm, HOCH$_2$CHC$H_a$$H_bOAc, CH$OSi); 3.50-3.78 (2H, m, AcOCH$_2$CHC$H_a$$H_b$OH); 2.06 (3H, s, 2-C$H_3$); 0.96-1.20 (21H, m, SiCH(CH_3)$_2$). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.16, 18.19 (-CH$_3$); 12.56 (Si-C): triisopropylsilyl fragment; 171.16 (C1); 21.06 (C2): acetyl fragment; 70.65 (C2); 65.04 (C3); 63.97 (C1): glycerol fragment.

2-*O*-Triisopropylsilyl-3-oleoyl-*sn*-glycerol 37. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, CH=CH); 3.96-4.30 (3H, mm overlapping with m, HOCH$_2$CHC$H_a$$H_b$OCOR, C$H$OSi); 3.52-3.76 (2H, m, R(O)COCH$_2$CHC$H_a$$H_b$OH); 2.31 (2H, t, J=7.5 Hz, 2-CH_2); 2.00 (4H, m, 8-CH_2, 11-CH_2); 1.61 (2H, m, 3-CH_2); 1.29 (20H, m, 4-7-CH_2, 12-17-CH_2); 1.00-1.18 (21H, m, SiCH(CH_3)$_2$); 0.87 (3H, t, J=7.1 Hz, 18-CH_3). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.18, 18.21 (-CH$_3$); 12.57 (Si-C): triisopropylsilyl fragment; 174.00 (C1); 129.95, 130.23 (C9, C10); 34.41 (C2); 32.13 (C16); 29.31-29.99 (C4-C7, C12-C15); 27.39, 27.44 (C11, C8); 25.11 (C3); 22.90 (C17); 14.32 (C18): oleoyl fragment; 70.71 (C2); 64.74 (C3); 63.96 (C1): glycerol fragment.

2-*O*-Triisopropylsilyl-3-iodo-*sn*-glycerol 38. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 3.83-3.96 (1H, m, CHOSi); 3.66-3.83 (2H, m, ICH$_2$CHC$H_a$$H_b$OH); 3.34 (1H, dd, J=8.2, 8.2 Hz, ICH_aH$_b$CHCH$_2$OH); 3.22 (1H, dd, J=3.3, 3.8 Hz, ICH$_a$$H_b$CHCH$_2$OH); 1.89 (1H, broad s, ICH$_2$CHCH$_2$OH); 1.00-1.20 (21H, m, SiCH(CH_3)$_2$). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.22 (-CH$_3$); 12.60 (Si-C): triisopropylsilyl fragment; 72.30 (C2); 65.13 (C1); 7.94 (C3): glycerol fragment.

1-Acetyl-2-*O*-triisopropylsilyl-3-iodo-*sn*-glycerol 39. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 4.14 (2H, ss, $ICH_2CHCH_aH_bOAc$); 3.75-3.95 (1H, m, C*H*OSi); 3.29 (2H, s and d, *J*=0.8 Hz, $ICH_aH_bCHCH_2OAc$); 2.07 (3H, s, 2-CH_3); 1.00-1.18 (21H, m, $SiCH(CH_3)_2$). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.20 (-*C*H_3); 12.64 (Si-*C*): triisopropylsilyl fragment; 170.83 (C1); 21.06 (C2): acetyl fragment; 69.12 (C2); 67.65 (C1); 9.90 (C3): glycerol fragment.

1-Oleoyl-2-*O*-triisopropylsilyl-3-iodo-*sn*-glycerol 40. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 4.02-4.28 (2H, m, $ICH_2CHCH_aH_bOCOR$); 3.85 (1H, tt, *J*=5.2, 4.9 Hz, C*H*OSi); 3.29 (2H, d, *J*=4.7 Hz, $R(O)COCH_2CHCH_aH_bI$); 2.31 (2H, t, *J*=7.7 Hz, 2-CH_2); 2.00 (4H, m, 8-CH_2, 11-CH_2); 1.62 (2H, m, 3-CH_2); 1.28 (20H, m, 4-7-CH_2, 12-17-CH_2); 1.02-1.14 (21H, m, $SiCH(CH_3)_2$); 0.88 (3H, t, *J*=6.9 Hz, 18-CH_3). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 18.22 (-*C*H_3); 12.64 (Si-*C*): triisopropylsilyl fragment; 173.63 (C1); 129.96, 130.24 (C9, C10); 34.40 (C2); 32.13 (C16); 29.33-29.99 (C4-C7, C12-C15); 27.39, 27.45 (C11, C8); 25.12 (C3); 22.91 (C17); 14.33 (C18): oleoyl fragment; 69.17 (C2); 67.14 (C1); 10.00 (C3): glycerol fragment.

1,3-Dioleoyl-2-acetylglycerol 41. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.35 (4H, m, C*H*=C*H*); 5.24 (1H, m, C*H*OAc); 4.30 (2H, dd, *J*= 4.4, 4.4 Hz, $R(O)COCH_bH_aCHCH_aH_bOCOR$); 4.14 (2H, dd, *J*= 5.9, 5.9 Hz, $R(O)COCH_bH_aCHCH_aH_bOCOR$); 0.87 (6H, t, *J*= 6.9 Hz, 18-CH_3): oleoyl and glycerol fragments; 2.07 (3H, s, 2-CH_3): acetyl fragment. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.49 (C1); 129.93, 130.23 (C9, C10); 14.32 (C18): both oleoyl fragments; 170.26 (C1); 21.09 (C2): acetyl fragment; 69.40 (C2); 62.24 (C1, C3): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[6]

1-Oleoyl-2-acetyl-3-palmitoyl-*sn*-glycerol 42. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 0.87 (6H, t, *J*=7.1 Hz, 16-CH_3, 18-CH_3): oleoyl and palmitoyl fragments; 2.07 (3H, s, 2-CH_3): *sn*-2-acetyl fragment; 5.24 (1H, m, C*H*OAc); 4.30 (2H, dd, *J*=4.4, 4.2 Hz, $R(O)COCH_aH_bCHCH_2OCOR^1$); 4.14 (2H, dd, *J*=5.9, 5.9 Hz, $R(O)COCH_2CHCH_aH_bOCOR^1$): glycerol fragment. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.50, 173.53 (C1); 129.93, 130.23 (C9, C10); 34.25 (C2); 14.33 (C16, C18): oleoyl and palmitoyl fragments; 170.28 (C1); 21.09 (C2): *sn*-2-acetyl fragment; 69.40 (C2); 62.23 (C1, C3): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[5]

1,3-Diacetyl-2-oleoylglycerol 43. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.33 (2H, m, C*H*=C*H*); 5.26 (1H, m, C*H*OCOR); 4.27 (2H, dd, *J*= 4.4, 4.4 Hz, $AcOCH_bH_aCHCH_aH_bOAc$); 4.14 (2H, dd, *J*= 6.0, 6.0 Hz, $AcOCH_bH_aCHCH_aH_bOAc$); 0.87

(3H, t, *J*= 7.0 Hz, 18-CH_3): oleoyl and glycerol fragments; 2.06 (6H, s, 2-CH_3): both acetyl fragments. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.12 (C1); 129.90, 130.25 (C9, C10); 14.32 (C18): oleoyl fragment; 170.70 (C1); 20.89 (C2): both acetyl fragments; 68.95 (C2); 62.53 (C1, C3): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[6]

1-Acetyl-2,3-dioleoyl-*sn*-glycerol 44. Spectral characteristics identical with those of **52**.

1-Oleoyl-2-palmitoyl-3-acetyl-*sn*-glycerol 45. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.33 (2H, m, C*H*=C*H*); 5.26 (1H, m, C*H*OCOR^1); 4.23-4.34 (2H, m, R(O)COCH$_2$CHCH_aH_bOAc); 4.14 (2H, dd, *J*=6.0, 6.2 Hz, AcOCH$_2$CHCH_aH_bOCOR); 0.87 (6H, t, *J*=7.1 Hz, 16-CH_3, 18-CH_3): oleoyl, palmitoyl, and glycerol fragments; 2.06 (3H, s, 2-CH_3): acetyl fragment. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.12, 173.47 (C1); 129.92, 130.23 (C9, C10); 34.25, 34.42 (C2); 14.32 (C16, C18): oleoyl and palmitoyl fragments; 170.68 (C1); 20.90 (C2): acetyl fragment; 69.01 (C2); 62.58 (C3); 62.28 (C1): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[5]

1-Acetyl-2-palmitoyl-3-oleoyl-*sn*-glycerol 46. Spectral characteristics identical with those of **45**.

1-*O*-*tert*-Butyldimethylsilyl-2-oleoyl-3-acetyl-*sn*-glycerol 47. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 5.07 (1H, m, C*H*OCOR); 4.32 (1H, dd, *J*=3.8, 3.7 Hz, SiOCH$_2$CHCH$_a$$H_b$OAc); 4.16 (1H, dd, *J*=6.4, 6.4 Hz, SiOCH$_2$CHCH_aH$_b$OAc); 3.64-3.78 (2H, m, AcOCH$_2$CHCH_aH_bOSi); 2.31 (2H, m, 2-CH_2); 2.05 (3H, s, 2-CH_3); 2.01 (4H, m, 8-CH_2, 11-CH_2); 1.61 (2H, m, 3-CH_2); 1.28 (20H, m, 4-7-CH_2, 12-17-CH_2); 0.84-0.94 (12H, s overlapping with t, *t-Bu*-Si, 18-CH_3); 0.05 (6H, s, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.34 (C1); 129.94, 130.24 (C9, C10); 34.55 (C2); 32.12 (C16); 29.27-29.98 (C4-C7, C12-C15); 27.38, 27.44 (C11, C8); 25.15 (C3); 22.90 (C17); 14.33 (C18): oleoyl fragment; 170.90 (C1); 20.99 (C2): acetyl fragment; 25.96 (*C*H$_3$-); 18.42 (*C*-Si); -5.31, -5.26 (*C*H$_3$-Si): *tert*-butyldimethylsilyl fragment; 71.83 (C2); 62.99 (C3); 61.65 (C1): glycerol fragment.

1-*O*-*tert*-Butyldimethylsilyl-2-oleoyl-3-palmitoyl-*sn*-glycerol 48. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.22-5.45 (2H, m, C*H*=C*H*); 4.94-5.14 (1H, m, C*H*OCOR); 4.33 (1H, dd, *J*=3.8, 3.8 Hz, SiOCH$_2$CHCH$_a$$H_b$OCOR^1); 4.15 (1H, dd, *J*=6.3, 6.3 Hz, SiOCH$_2$CHCH_aH$_b$OCOR^1); 3.60-3.80 (2H, m, ^{1}R(O)COCH$_2$CHCH_aH_bOSi); 2.22-2.36 (4H, m, 2-C$H_{2,\ Palm}$, 2-CH_2); 1.90-2.12 (4H, m, 8-CH_2, 11-CH_2); 1.50-1.70 (4H, m, 3-C$H_{2,\ Palm}$, 3-CH_2); 1.20-1.40 (44H, m, 4-15-C$H_{2,\ Palm}$, 4-7-CH_2, 12-17-CH_2); 0.80-0.96 (15H, s

overlapping with t, *t-Bu*-Si, 16-CH_3, 18-CH_3); 0.05 (6H, s, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.30, 173.65 (C1); 129.94, 130.23 (C9, C10); 34.39, 34.55 (C2); 32.15 (C14); 32.12 (C16); 29.30-29.99 (C4-C13, C4-C7, C12-C15); 27.40, 27.44 (C11, C8); 25.12, 25.15 (C3); 22.90 (C17); 14.32 (C16, C18): oleoyl and palmitoyl fragments; 25.97 (*C*H_3-); 18.42 (*C*-Si); -5.30, -5.26 (*C*H_3-Si): *tert*-butyldimethylsilyl fragment; 71.91 (C2); 62.68 (C3); 61.68 (C1): glycerol fragment.

1-Oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-acetyl-*sn*-glycerol 49. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.33 (2H, m, C*H*=C*H*); 4.20-3.90 (5H, m, AcOCH_2CHC$H_a$$H_b$OCOR, C*H*OSi, R(O)COC$H_2CHCH_a$$H_b$OAc); 2.30 (2H, t, *J*=7.5 Hz, 2-CH_2); 2.06 (3H, s, 2-CH_3); 2.00 (4H, m, 8-CH_2, 11-CH_2); 1.61 (2H, m, 3-CH_2); 1.28 (20H, m, 4-7-CH_2, 12-17-CH_2); 0.93-0.83 (12H, s overlapping with t, *t-Bu*-Si, 18-CH_3); 0.08 (6H, s, CH_3-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 25.84 (*C*H_3-); 18.26 (*C*-Si); -4.62 (*C*H_3-Si): *tert*-butyldimethylsilyl fragment; 173.72 (C1); 129.96, 130.21 (C9, C10); 34.38 (C2); 32.12 (C16); 29.31-29.98 (C4-C7, C12-C15); 27.43, 27.38 (C11, C8); 25.09 (C3); 22.89 (C17); 14.32 (C18): oleoyl fragment; 170.90 (C1); 21.04 (C2): acetyl fragment; 68.60 (C2); 65.82 (C3); 65.53 (C1): glycerol fragment.

1-Palmitoyl-2-oleoyl-3-acetyl-*sn*-glycerol 50. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 5.26 (1H, m, C*H*OCOR); 4.24-4.33 (2H, m, AcOC$H_a$$H_bCHCH_2$OCOR[1]); 4.14 (2H, dd, *J*=6.0, 6.0 Hz, AcOCH_2CHC$H_a$$H_b$OCOR[1]); 2.31 (4H, m, 2-C$H_{2,\ Palm}$, 2-CH_2); 2.06 (3H, s, 2-CH_3); 2.00 (4H, m, 8-CH_2, 11-CH_2); 1.60 (4H, m, 3-C$H_{2,\ Palm}$, 3-CH_2); 1.20-1.40 (44H, m, 4-15-C$H_{2,\ Palm}$, 4-7-CH_2, 12-17-CH_2); 0.87 (6H, t, *J*=7.1 Hz, 16-CH_3, 18-CH_3). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.09, 173.50 (C1); 129.90, 130.24 (C9, C10); 34.26, 34.41 (C2); 32.14 (C16, C14); 29.25-29.98 (C4-C13, C4-C7, C12-C15); 27.38, 27.44 (C11, C8); 25.08 (C3); 22.91 (C17); 14.33 (C16, C18): oleoyl and palmitoyl fragments; 170.68 (C1); 20.90 (C2): acetyl fragment; 69.03 (C2); 62.58 (C3); 62.27 (C1): glycerol fragment.

1-Acetyl-2-oleoyl-3-palmitoyl-*sn*-glycerol 51. Spectral characteristics identical with those of **50**.

1,2-Dioleoyl-3-acetyl-*sn*-glycerol 52. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (4H, m, C*H*=C*H*); 5.26 (1H, m, C*H*OCOR); 4.24-4.33 (2H, m, R(O)COCH_2CHC$H_a$$H_b$OAc); 4.14 (2H, dd, *J*= 5.9, 6.0 Hz, R(O)COC$H_a$$H_bCHCH_2$OAc); 0.88 (6H, t, *J*= 7.1 Hz, 18-CH_3): oleoyl and glycerol fragments; 2.06 (3H, s, 2-CH_3): acetyl fragment. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.09, 173.47 (C1); 129.91, 129.92, 130.24, 130.25 (C9, C10); 14.33 (C18): both oleoyl fragments; 170.68 (C1); 20.90 (C2): acetyl fragment; 69.03 (C2); 62.58

(C3); 62.28 (C1): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[5]

1-Oleoyl-2,3-diacetyl-*sn*-glycerol 53. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.33 (2H, m, C*H*=C*H*); 5.23 (1H, m, C*H*OAc); 4.05-4.37 (4H, mm, R(O)COCH$_2$CHCH$_a$*H$_b$*OAc, R(O)COCH$_2$CHC*H$_a$*H$_b$OAc, R(O)COC*H$_a$*H$_b$CHCH$_2$OAc, R(O)COCH$_a$*H$_b$*CHCH$_2$OAc); 0.87 (3H, t, *J*= 7.0 Hz, 18-CH$_3$): oleoyl and glycerol fragments; 2.07 (3H, s, 2-C*H$_3$*); 2.06 (3H, s, 2-C*H$_3$*): both acetyl fragments. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.49 (C1); 129.92, 130.23 (C9, C10); 14.31 (C18): oleoyl fragment; 170.28, 170.69 (C1); 20.89, 21.09 (C2): both acetyl fragments; 69.34 (C2); 62.50 (C3); 62.20 (C1): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[5]

1-Oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-trifluoroacetyl-*rac*-glycerol 54. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 4.42 (1H, dd, *J*=3.7, 3.8 Hz, R(O)COCH$_2$CHCH$_a$*H$_b$*OCOCF$_3$); 4.26 (1H, *J*=6.2, 6.2 Hz, R(O)COCH$_2$CHC*H$_a$*H$_b$OCOCF$_3$); 4.10-4.18 (1H, m, C*H*OSi); 4.02-4.10 (2H, m, CF$_3$(O)COCH$_2$CHC*H$_a$H$_b$*OCOR); 2.31 (2H, t, *J*=7.5 Hz, 2-C*H$_2$*); 2.00 (4H, m, 8-C*H$_2$*, 11-C*H$_2$*); 1.62 (2H, m, 3-C*H$_2$*); 1.28 (20H, m, 4-7-C*H$_2$*, 12-17-C*H$_2$*); 0.83-0.94 (12H, s overlapping with t, *t-Bu*-Si, 18-C*H$_3$*); 0.09 (6H, d, *J*=5.7 Hz, C*H$_3$*-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 25.71 (*C*H$_3$-); 18.12 (*C*-Si); -4.68, -4.95 (*C*H$_3$-Si): *tert*-butyldimethylsilyl fragment; 173.51 (C1); 129.92, 130.24 (C9, C10); 34.28 (C2); 32.12 (C16); 29.30-29.98 (C4-C7, C12-C15); 27.37, 27.43 (C11, C8); 25.05 (C3); 22.89 (C17); 14.31 (C18): oleoyl fragment; 157.52 (d, *J*=42.7 Hz, C1); 114.69 (d, *J*=285.3 Hz, C2): trifluoroacetyl fragment; 69.06 (C3); 67.97 (C2); 64.66 (C1): glycerol fragment.

1-Oleoyl-2-*O*-*tert*-butyldimethylsilyl-*rac*-glycerol 55. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.33 (2H, m, C*H*=C*H*); 4.16-4.00 (2H, m, HOCH$_2$CHC*H$_a$H$_b$*OCOR); 3.93 (1H, m, C*H*OSi); 3.60 (1H, dd, *J*=4.4, 4.1 Hz, R(O)COCH$_2$CHCH$_a$*H$_b$*OH); 3.54 (1H, dd, *J*=4.7, 4.7 Hz, R(O)COCH$_2$CHC*H$_a$*H$_b$OH); 2.30 (2H, t, *J*=7.4 Hz, 2-C*H$_2$*); 2.00 (4H, m, 8-C*H$_2$*, 11-C*H$_2$*); 1.62 (2H, m, 3-C*H$_2$*); 1.28 (20H, m, 4-7-C*H$_2$*, 12-17-C*H$_2$*); 0.93-0.85 (12H, s overlapping with t, *t-Bu*-Si, 18-C*H$_3$*); 0.10 (6H, d, *J*=1.4 Hz, C*H$_3$*-Si). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 25.94 (*C*H$_3$-); 18.27 (*C*-Si); -4.44, -4.61 (*C*H$_3$-Si): *tert*-butyldimethylsilyl fragment; 173.92 (C1); 129.94, 130.22 (C9, C10); 34.42 (C2); 32.12 (C16); 29.30-29.98 (C4-C7, C12-C15); 27.43, 27.38 (C11, C8); 25.10 (C3); 22.90 (C17); 14.32 (C18): oleoyl fragment; 70.83 (C2); 65.04 (C1); 64.11 (C3): glycerol fragment.

1-Oleoyl-2-*O*-*tert*-butyldimethylsilyl-3-acetyl-*rac*-glycerol 56. Spectral characteristics identical with those of **49**.

1-Oleoyl-2-trichloroacetyl-3-acetyl-*rac*-glycerol 57. Spectral characteristics identical with those of compounds **30** and **31**.

1-Oleoyl-3-acetyl-*rac*-glycerol 58. Spectral characteristics identical with those of **32** and **33**.

1-Oleoyl-2-[*R*-(-)-*α*-methoxy-*α*-trifluoromethylphenylacetyl]-3-acetyl-*rac*-glycerol 59. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 7.60-7.50 (2H, m, *Ar*-ring); 7.45-7.33 (3H, m, *Ar*-ring); 5.53 (1H, m, C*H*OCO-MTPA); 5.34 (2H, m, C*H*=C*H*); 4.42 (1H, mm, R(O)COCH$_2$CHCH$_a$*H$_b$*OAc); 4.33 (1H, mm, R(O)COCH$_2$CHC*H$_a$*H$_b$OAc); 4.05-4.24 (2H, mm, AcOCH$_2$CHC*H$_a$H$_b$*OCOR); 3.56 (3H, s, C*H$_3$*O); 2.29, 2.22 (2H, tt, 1:1, *J*=7.5, 7.1 Hz, 2-C*H$_2$*); 2.05, 1.98 (3H, ss, 1:1, 2-C*H$_3$*); 2.01 (4H, m, 8-C*H$_2$*, 11-C*H$_2$*); 1.57 (2H, m, 3-C*H$_2$*); 1.26 (20H, m, 4-7-C*H$_2$*, 12-17-C*H$_2$*); 0.87 (3H, t, *J*=7.1 Hz, 18-CH$_3$). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.26 (C1); 130.24, 129.94 (C9, C10); 34.13, 34.04 (C2); 32.12 (C16); 29.29-29.98 (C4-C7, C12-C15); 27.44, 27.38 (C11, C8); 24.93, 24.88 (C3); 22.89 (C17); 14.32 (C18): oleoyl fragment; 170.44 (C1); 20.77, 20.68 (C2): acetyl fragment; 166.14 (-*C*(O)-); 132.20, 128.63, 127.52 (C1-C6, Ar-ring); 123.38 (d, *J*=288.4 Hz, F$_3$*C*-); 55.64 (*C*H$_3$O-): MTPA-fragment; 71.56 (C2); 62.31, 62.07 (C3); 62.09, 61.86 (C1): glycerol fragment.

1-Oleoyl-2-acetyl-3-iodo-*rac*-glycerol 60. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 4.99 (1H, m, C*H*OAc); 4.31 (1H, dd, *J*=4.2, 4.2 Hz, R(O)COC*H$_a$*H$_b$CHCH$_2$I); 4.22 (1H, dd, *J*=5.5, 5.5 Hz, R(O)COCH$_a$*H$_b$*CHCH$_2$I); 3.34 (1H, dd, *J*=5.9, 6.0 Hz, R(O)COCH$_2$CHCH$_a$*H$_b$*I); 3.27 (1H, dd, *J*=5.7, 5.7 Hz, R(O)COCH$_2$CHC*H$_a$*H$_b$I); 2.32 (2H, t, *J*=7.5 Hz, 2-C*H$_2$*); 2.10 (3H, s, 2-C*H$_3$*); 2.00 (4H, m, 8-C*H$_2$*, 11-C*H$_2$*); 1.61 (2H, m, 3-C*H$_2$*); 1.28 (20H, m, 4-7-C*H$_2$*, 12-17-C*H$_2$*); 0.87 (3H, t, *J*= 7.0 Hz, 18-C*H$_3$*). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.40 (C1); 129.92, 130.25 (C9, C10); 34.24 (C2); 32.12 (C16); 29.28-29.98 (C4-C7, C12-C15); 27.38, 27.44 (C11, C8); 25.07 (C3); 22.90 (C17); 14.33 (C18): oleoyl fragment; 170.07 (C1); 21.09 (C2): acetyl fragment; 70.53 (C2); 64.25 (C1); 2.29 (C3): glycerol fragment.

1-Oleoyl-2-palmitoyl-3-iodo-*sn*-glycerol 61. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 5.34 (2H, m, C*H*=C*H*); 0.88 (6H, t, *J*=7.1 Hz, 16-C*H$_3$*, 18-C*H$_3$*): oleoyl and palmitoyl fragments; 5.00 (1H, m, C*H*OCOR[1]); 4.31 (1H, dd, *J*=4.2, 4.4 Hz, R(O)COC*H$_a$*H$_b$CHCH$_2$I); 4.21 (1H, dd, *J*=5.7, 5.7 Hz, R(O)COCH$_a$*H$_b$*CHCH$_2$I); 3.34 (1H, dd, *J*=5.7, 5.9 Hz, R(O)COCH$_2$CHCH$_a$*H$_b$*I); 3.27 (1H, dd, *J*=5.7, 5.8 Hz, R(O)COCH$_2$CHC*H$_a$*H$_b$I): glycerol fragment. ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 172.91, 173.38 (C1); 129.92, 130.24 (C9, C10); 34.25, 34.44 (C2); 14.34 (C16, C18): oleoyl and palmitoyl fragments; 70.17 (C2);

64.38 (C1); 2.63 (C3): glycerol fragment. All other ^{1}H and ^{13}C NMR spectral characteristics identical with those reported in the literature.[4]

(±)-*N*-(1-Oleoyl-2-acetyl-3-propyl)pyridinium iodide 62. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 9.42 (2H, d, *J*=5.5 Hz, pyridinium nucleus); 8.59 (1H, t, *J*=7.9 Hz, pyridinium nucleus); 8.16 (2H, t, *J*=6.8 Hz, pyridinium nucleus); 5.67 (1H, dd, *J*=2.7, 2.7 Hz, $R(O)COCH_2CHCH_aH_bN_{py}$); 5.54 (1H, m, C*H*OAc); 5.33 (2H, m, C*H*=C*H*); 5.11 (1H, dd, *J*=9.1, 9.0 Hz, $R(O)COCH_2CHCH_aH_bN_{py}$); 4.51 (1H, dd, *J*=3.8, 3.8 Hz, $R(O)COCH_aH_bCHCH_2N_{py}$); 4.38 (1H, dd, *J*=4.8, 4.8 Hz, $R(O)COCH_aH_bCHCH_2N_{py}$); 2.36 (2H, t, *J*=7.5 Hz, 2-CH_2); 1.92-2.06 (7H, s overlapping m, 2-CH_3, 8-CH_2, 11-CH_2); 1.59 (2H, m, 3-CH_2); 1.20-1.40 (20H, m, 4-7-CH_2, 12-17-CH_2); 0.86 (3H, t, *J*= 6.6 Hz, 18-CH_3). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 173.41 (C1); 129.92, 130.25 (C9, C10); 34.25 (C2); 32.11 (C16); 29.30-29.98 (C4-C7, C12-C15); 27.40, 27.44 (C11, C8); 25.01 (C3); 22.89 (C17); 14.33 (C18): oleoyl fragment; 169.88 (C1); 21.07 (C2): acetyl fragment; 146.59 (C4); 145.98 (C3, C5); 128.57 (C2, C6): pyridinium fragment; 70.44 (C2); 61.92 (C1); 61.63 (C3): glycerol fragment.

(-)-*N*-(1-Oleoyl-2-palmitoyl-3-propyl)pyridinium iodide 63. ^{1}H NMR δ_H (in ppm, $CDCl_3$, 400 MHz) 9.40 (2H, d, *J*=5.7 Hz, pyridinium nucleus); 8.56 (1H, t, *J*=7.7 Hz, pyridinium nucleus); 8.12 (2H, t, *J*=7.1 Hz, pyridinium nucleus); 5.64-5.76 (1H, m, $R(O)COCH_2CHCH_aH_bN_{py}$); 5.53 (1H, m, C*H*OCOR[1]); 5.32 (2H, m, C*H*=C*H*); 5.12 (1H, dd, *J*=9.3, 9.1 Hz, $R(O)COCH_2CHCH_aH_bN_{py}$); 4.50 (1H, dd, *J*=3.7, 3.5 Hz, $R(O)COCH_aH_bCHCH_2N_{py}$); 4.36 (1H, dd, *J*=4.8, 4.8 Hz, $R(O)COCH_aH_bCHCH_2N_{py}$); 2.34 (2H, t, *J*=7.5 Hz, 2-CH_2); 2.13-2.30 (2H, m, 2-C$H_{2,\ Palm}$); 1.90-2.10 (4H, m, 8-CH_2, 11-CH_2); 1.52-1.66 (2H, m, 3-CH_2); 1.39-1.50 (2H, m, 3-C$H_{2,\ Palm}$); 1.10-1.38 (44H, m, 4-15-C$H_{2,\ Palm}$, 4-7-CH_2, 12-17-CH_2); 0.86 (6H, t, *J*=7.0 Hz, 16-CH_3, 18-CH_3). ^{13}C NMR δ_C (in ppm, $CDCl_3$, 100 MHz) 172.71, 173.34 (C1); 129.90, 130.23 (C9, C10); 34.10, 34.25 (C2); 32.11, 32.13 (C14, C16); 29.21-29.96 (C4-C13, C4-C7, C12-C15); 27.41, 27.44 (C11, C8); 24.89, 25.02 (C3); 22.89 (C17); 14.33 (C16, C18): oleoyl and palmitoyl fragments; 146.42 (C4); 146.02 (C3, C5); 128.41 (C2, C6): pyridinium fragment; 70.31 (C2); 62.01 (C1); 61.75 (C3): glycerol fragment.

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