Supplementary Information

Perfluoroalkyl bile esters: A new class of efficient gelators of organic and aqueous- organic media

Supratim Banerjee, V.M. Vidya, A.J. Savyasachi and Uday Maitra*

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Table S1: *CGC* and T_{gel} of **$DC_{24}CH_2C_2F_5$**, **$LC_{24}CH_2C_2F_5$** and **$C_{24}CH_2C_9F_{19}$**

Compound	Solvent	CGC (% w/v)	T_{gel} (°C)
$DC_{24}CH_2C_2F_5$	2:1 DMSO-H_2O	0.25	56
	3:1 DMSO-H_2O	0.5	41
$LC_{24}CH_2C_2F_5$	2:1 DMF-H_2O	0.1	65
	6:1 DMF-H_2O	0.9	42
$C_{24}CH_2C_9F_{19}$	2:1 DMF-H_2O	0.9	32
	3:1 DMF-H_2O	0.15	64

Table S2: Lack of gelation of the pentadecafluorooctyl esters (**1d-f**)

Solvent	**$C_{24}CH_2C_7F_{15}$**	**$DC_{24}CH_2C_7F_{15}$**	**$LC_{24}CH_2C_7F_{15}$**
1. Toluene	S (1.5)	S (1.5)	S (1.5)
2. 1-Propanol	S (1.5)	S (1.5)	S (1.5)
3. DMSO	S (1.5)	S (1.5)	S (1.5)
4. DMF	S (1.5)	S (1.5)	S (1.5)
5. DMSO/H_2O			
1:1	N	P (0.75)	P (1.5)
2:1	VS (1.0)	S (1.0)	WG (1.0)
3:1	N	N	WG (2.0)
4:1	S (1.2)	N	N
5. DMF/H_2O			
1:1	N	N	WG (2.0)
2:1	GP(1.0)	P (1.0)	WG (1.0)
3:1	N	N	PG (2.0)

S: solution; P: precipitate; WG: weak gel; VS: viscous solution; GP: gelatinous precipitate; PG: partial gel; N: not checked (the numbers in the parentheses are the concentrations (in % w/v) in which the observations were made).

Table S3: Lack of gelation of **$C_{23}C_9H_{19}$**, **$DC_{23}C_9H_{19}$** and **$LC_{23}C_9H_{19}$** in different organic solvents

Solvent	$C_{23}C_9H_{19}$	$DC_{23}C_9H_{19}$	$LC_{23}C_9H_{19}$
1. Toluene	S	S	S
2. DMSO	S	TS	P
3. DMF	S	TS	S
4. EtOH	S	S	S
5. n-Butanol	S	S	S
6. n-Octanol	S	S	S

S: solution; P: precipitate; TS: turbid solution (all the observations were made at 2.0 % w/v).

Experimental section

Gelation tests

Gelation tests were carried out by dissolving a known amount of the gelator in the respective solvent in a test tube (*d*. 8 mm, *l*. 10 cm) by heating followed by keeping the hot solution at room temperature. If the liquid did not flow upon inverting the test tube, it was termed as a gel.

Gel-sol transition temperature

Gels were prepared in glass tubes (*d*. 8 mm, *l*. 10 cm) after sealing the open end and after stabilization for 12 h, the tubes were kept upside down in a thermostated paraffin oil bath. The temperature of the bath was increased in a controlled manner (~ 2°C/min) and the temperature at which the gel fell under gravity was note as the T_{gel}.

Imaging

Scanning Electron Microscopy

A drop of the hot sol (~ 20μL) was added on the carbon tape of a SEM sample stub. The sample was initially dried in air for 3-4 hours and followed by drying under high vacuum

for 5-6 hours. Before recording the images, the samples were gold coated using sputtering (50 Å) for 38 sec and examined using either QUANTA 200 or SIRION scanning electron microscopes.

Transmission Electron Microscopy

A thin layer of a gel was made on a glass slide. Then a carbon coated copper grid was touched over the surface of the gel so as to make a very thin layer of the gel on the grid. The grid was subsequently dried first in air for 2-3 hours followed by drying under high vacuum for a further 4-5 hours. Then the grids were stained with an aqueous 0.1 % uranyl acetate solution, and dried again under high vacuum for 5-6 hours.

Rheology

A serrated (only the rotor was serrated) plate-plate geometry (diameter 20 mm) was used in all the measurements. The temperature of the plate was controlled at 25 °C (± 0.1 °C). The gels were loaded as hot sols (~0.5 mL) on the bottom plate and were allowed to form gels. After 5 min, the geometry (rotor) was brought down to a 500 μm geometry gap in several steps and the excess sample was trimmed. The experimental gap of 400 μm was then set and the gels were stabilized in the geometry gap for 2 h. The solvent evaporation was kept minimized by placing a metallic cover as a solvent trap.

Synthesis of fluorinated bile acid derivatives with the spacer –(*CO*)-*OCH*$_2$-

2,2,3,3,3,-Pentafluoro-1-propyl 4-toluenesulfonate (4):

In a 10 mL round bottom flask equipped with a dry $CaCl_2$ guard tube, 2.4 mL of dry pyridine was taken and 2,2,3,3,3-pentafluoropropanol (400 μL, 4 mmol) was added. The solution was stirred at 0°C by keeping in an ice-bath and tosyl chloride (0.91 g, 4.8 mmol) was added to it in portions. The reaction mixture was stirred at room temperature for 48 h, and then poured into a mixture of 2.8 mL of conc HCl and 4.8 mL of H_2O and cooled in an ice-bath. A white compound started to precipitate out. The white solid was extracted with Et_2O (3×10 mL). The organic layers were combined, washed with water (2×10 mL), dried over anhyd. Na_2SO_4, filtered and rotavaped. Finally the product was dried under high vacuum. Yield 0.81 g (67 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.81 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 4.41 (t, J = 12 Hz, 2H), 2.48 (s, 3H).

IR (KBr, cm^{-1}): 3448, 3014, 2971, 1598, 1377, 1221, 1204, 1149, 1034.

mp: 51-52 °C.

General procedure for the preparation of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octyl 4-toluenesulfonate (5) and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluoro-1-decyl 4-toluenesulfonate (6):

In a typical procedure, tosyl chloride (3.75 mmol) was taken in a 10 mL round bottom flask (equipped with a dry $CaCl_2$ filled guard tube) and dry Et_2O (4 mL) was added to it. This mixture was stirred in an ice-bath. After a few minutes the mixture became homogenous and pentadecafluoro-1-octanol or nonadecafluoro-1-decanol (3.75 mmol) was added. The reaction mixture turned heterogeneous. KOH (9 mmol) was added and it was stirred in an ice-salt bath (~ -4 °C) for 24 h. After that the reaction mixture was poured into ice-water (20 mL) and extracted with EtOAC (3× 20 mL). The organic layers were combined, dried over anhyd. Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by a silica gel column.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-octyl tosylate (5):

Eluent used for the column chromatography was 5 % EtOAc/Petroleum ether.

From 1 g of pentadecafluoro-1-octanol**,** 1.18 g of **5** was obtained as a white solid (85 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.82 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 4.46 (t, J = 12.9 Hz, 2H), 2.47 (s, 3H).

IR (KBr, cm^{-1}): 3448, 3014, 2968, 1599, 1371, 1201 (C-F), 1174, 1154 (C-F), 1034.

mp: 54-55 °C.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluoro-1-decyl tosylate (6):

Eluent used for the column chromatography was 10 % EtOAc/Petroleum ether.

From 0.5 g of nonadecafluoro-1-decanol**,** 0.5 g of **6** was obtained (75 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.82 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 4.46 (t, J = 12.9 Hz, 2H), 2.48 (s, 3H).

IR (KBr, cm^{-1}): 3446, 2984, 1598, 1375, 1215 (C-F), 1197, 1149 (C-F), 1054.

mp: 80-81 °C.

General procedure for the synthesis of fluorinated bile acid derivatives having spacer–(*CO)-OCH$_2$-*

In a 10 mL round bottom flask equipped with a $CaCl_2$ guard tube, a bile acid (1.96 mmol, 1.5 eqv) was taken and dry DMSO (4 mL) was added. The mixture was stirred at 70 °C for 5 min and DBU (1.96 mmol, 1.5 eqv) was added. Stirring was continued for a further 1 h and then **4**, **5** or **6** (1.3 mmol, 1 eqv) was added. The mixture was stirred at 110 °C for 12 h. The reaction mixture was cooled to room temperature and poured into 15 mL of water. A solid precipitated out which was extracted by $CHCl_3$ (3×15 mL). The organic layers were combined, washed with water (15 mL), dried over anhyd. Na_2SO_4, filtered and rotavaped. Finally the crude product was dried under high vacuum and purified on a silica gel coclumn (2 cm×16 cm).

2,2,3,3,3-Pentafluoro-1-propyl 3α, 7α, 12α-trihydroxy-5β-cholan-24-oate ($C_{24}CH_2C_2F_5$-1a):

Eluent used for the column chromatography was 90 % EtOAc/Petroleum ether.

From 0.4 g of **4**, 0.4 g of **$C_{24}CH_2C_2F_5$** was obtained as a white solid (57 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.53 (t, J = 13.2 Hz, 2H), 3.98 (br s, 1H), 3.85 (br s, 1H), 3.49-3.43 (m, 1H), 2.47 (m, 1H), 2.37 (m, 1H), 2.21 (m, 2H), 1.89-1.37 (m, steroidal CH, CH_2), 0.99 (d, J = 6.0 Hz, 3H), 0.89 (s, 3H), 0.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.56, 73.07, 71.81, 68.43, 58.93 (t, J =27.3 Hz), 46.9, 46.37, 41.55, 41.44, 39.42, 35.29, 35.1, 34.72, 34.63, 30.65, 30.21, 28.09, 27.4, 26.26, 23.16, 22.35, 17.14, 12.36.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -84.77 (s), -124.39 (s).

HRMS: Calcd. for $C_{27}H_{41}O_5F_5$+Na: 563.2772; found 563.2768.

IR (KBr, cm^{-1}): 3402, 2939, 2870, 1762, 1206 (C-F), 1150 (C-F).

mp: 55-58 °C.

$[\alpha]_D^{23}$: +21 (c 1.0, $CHCl_3$).

2,2,3,3,3-Pentafluoro-1-propyl 3α, 12α-dihydroxy-5β-cholan-24-oate ($DC_{24}CH_2C_2F_5$-1b):

Eluent used for the column chromatography was 45 % EtOAc/Petroleum ether.

From 0.4 g of **4**, 0.31g of **$DC_{24}CH_2C_2F_5$** was obtained as a white solid (46 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.54 (t, J = 13.2 Hz, 2H), 3.98 (br s, 1H), 3.65-3.58 (m, 1H), 2.51-2.43 (m, 1H), 2.38-2.32 (m, 1H), 1.84-1.01 (m, steroidal CH, CH_2), 0.97 (d, J = 6.4 Hz, 3H), 0.91 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.51, 73.09, 71.71, 58.94 (t, J =27.4 Hz), 48.2, 47.15, 46.45, 42.01, 36.36, 35.98, 35.18, 34.99, 34.07, 33.59, 30.65, 30.56, 30.39, 28.66, 27.37 27.08, 26.08, 23.6, 23.09, 17.12, 12.65.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -84.77 (s), -124.39 (s).

HRMS: Calcd. for $C_{27}H_{41}O_4F_5$+Na: 547.2823; found 547.2791.

IR (KBr, cm^{-1}): 3394, 2938, 2867, 1762, 1206 (C-F), 1150 (C-F).

mp: 61-62°C.

$[\alpha]_D^{23}$: +33 (c 1.0, $CHCl_3$).

2,2,3,3,3-Pentafluoro-1-propyl 3α-hydroxy-5β-cholan-24-oate ($LC_{24}CH_2C_2F_5$-1c):

Eluent used for the column chromatography was 20 % EtOAc/Petroleum ether.

From 0.4 g of **4**, 0.32 g of **$LC_{24}CH_2C_2F_5$** was obtained as a white solid (49 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.53 (t, J = 12.8 Hz, 2H), 3.67-3.59 (m, 1H), 2.44-2.42 (m, 1H), 2.37-2.32 (m, 1H), 2.17-1.07 (m, steroidal CH, CH_2), 0.92 (d and s merged, 6H), 0.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.57, 71.82, 59.94 (t, J =27.5 Hz), 56.44, 55.83, 42.71, 42.04, 40.38, 40.12, 36.40, 35.80, 35.31, 35.20, 34.53, 30.66, 30.60, 30.49, 28.08, 27.15, 26.37, 24.15, 23.33, 20.77, 18.12, 11.97.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -84.77 (s), -124.39 (s).

HRMS: Calcd. for $C_{27}H_{41}O_3F_5$+Na: 531.2874; found 531.2880.

IR (KBr, cm^{-1}): 3312, 2937, 2864, 1764, 1206 (C-F), 1151 (C-F), 1107.

mp: 80-82°C.

$[\alpha]_D^{23}$: +19 (c 1.0, $CHCl_3$).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-octyl 3α, 7α, 12α-trihydroxy-5β-cholan-24-oate ($C_{24}CH_2C_7F_{15}$-1d):

Eluent used for the column chromatography was 95 % EtOAc/Petroleum ether.

From 0.2 g of **5**, 0.14 g of **$C_{24}CH_2C_7F_{15}$** was obtained as a white solid (50 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.59 (t, J = 13.6 Hz, 2H), 3.98 (br s, 1H), 3.85 (br s, 1H), 3.49-3.42 (m, 1H), 2.53-2.36 (m, 2H), 2.25-2.17 (m, 2H), 1.97-1.07 (m, steroidal CH, CH_2), 0.99 (d, J = 6.0 Hz, 3H), 0.89 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.63, 73.08, 71.81, 68.45, 59.26 (t, J =26 Hz), 46.89, 46.36, 41.55, 41.41, 39.41, 35.29, 35.10, 34.71, 34.61, 30.63, 30.17, 28.06, 27.41 26.26, 23.16, 22.33, 17.12, 12.33.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.67 (t, J = 11.2 Hz), -120.38 (s), -122.87 (br s), -123.63 (br s), -124.2 (br s), -127.00 (br s).

HRMS: Calcd. for $C_{32}H_{41}O_5F_{15}$+Na: 813.2612; found 813.2606.

IR (KBr, cm^{-1}): 3434, 2939, 2870, 1762, 1242, 1211 (C-F), 1149 (C-F).

mp: 125-127°C.

$[\alpha]_D^{23}$: +8 (c 1.0, $CHCl_3$).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-octyl 3α, 12α-dihydroxy-5β-cholan-24-oate ($DC_{24}CH_2C_7F_{15}$-1e):

Eluent used for the column chromatography was 50 % EtOAc/Petroleum ether.

From 0.4 g of **5**, 0.13 g of **$DC_{24}CH_2C_7F_{15}$** was obtained as a white solid (48 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.59 (t, J = 13.5 Hz, 2H), 3.98 (br s, 1H), 3.66-3.56 (m, 1H), 2.53-2.32 (m, 2H), 2.17-1.07 (m, steroidal CH, CH_2), 0.98 (d, J = 5.7 Hz, 3H), 0.91 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.54, 73.11, 71.75, 59.3 (t, J =28 Hz), 48.23, 47.19, 46.46, 42.03, 36.39, 35.99, 35.18, 34.99, 34.08, 33.62, 30.67, 30.59, 30.43, 28.69, 27.36 27.08, 26.08, 23.59, 23.09, 17.12, 12.63.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.69 (t, J = 11.2 Hz), -120.38 (br s), -122.89 (br s), -123.62 (br s), -124.22 (br s), -127.00 (br s).

HRMS: Calcd. for $C_{32}H_{41}O_3F_{15}$+Na: 797.2663; found 797.2666.

IR (KBr, cm^{-1}): 3403, 2938, 2867, 1763, 1243, 1212 (C-F), 1149 (C-F).

mp: 68-69°C.

$[\alpha]_D^{23}$: +23 (c 1.0, $CHCl_3$).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-octyl 3α-hydroxy-5β-cholan-24-oate ($LC_{24}CH_2C_7F_{15}$-1f):

Eluent used for the column chromatography was 15 % EtOAc/Petroleum ether.

From 0.4 g of **5**, 0.22 g of **$LC_{24}CH_2C_7F_{15}$** was obtained as a white solid (41 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.58 (t, J = 13.5 Hz, 2H), 3.63 (m, 1H), 2.46-2.31 (m, 2H), 2.17-1.07 (m, steroidal CH, CH_2), 0.92 (d and s merged, 6H), 0.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.62, 71.84, 59.3 (t, J =27 Hz), 56.45, 55.85, 42.72, 42.06, 40.39, 40.13, 36.42, 35.82, 35.31, 35.21, 34.54, 30.68, 30.63, 30.51, 28.09, 27.16, 26.38, 24.15, 23.33, 20.79, 18.11, 11.96.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.69 (t, J = 11.2 Hz), -120.38 (s), -122.89 (br s), -123.62 (br s), -124.2 (br s), -126.99 (br s).

HRMS: Calcd. for $C_{32}H_{41}O_3F_{15}$+Na: 781.2714; found 781.2708.

IR (KBr, cm^{-1}): 3329, 2928, 1763, 1243, 1212 (C-F), 1149 (C-F).

mp: 64-66°C.

$[\alpha]_D^{23}$: +20 (c 1.0, $CHCl_3$).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluoro-1-decyl 3α, 7α, 12α-trihydroxy-5β-cholan-24-oate ($C_{24}CH_2C_9F_{19}$-1g):

Eluent used for the column chromatography was EtOAc.

From 0.3 g of **6**, 0.17 g of **$C_{24}CH_2C_9F_{19}$** was obtained as a white solid (42 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.59 (t, J = 13.6 Hz, 2H), 3.98 (br s, 1H), 3.85 (br s, 1H), 3.46 (m, 1H), 2.53-2.36 (m, 2H), 2.25-2.17 (m, 2H), 1.94-1.07 (m, steroidal CH, CH_2), 0.99 (d, J = 6.0 Hz, 3H), 0.89 (s, 3H), 0.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.62, 73.08, 71.86, 68.45, 59.26 (t, J =26 Hz), 46.92, 46.40, 41.6, 41.45, 39.46, 35.28, 35.11, 34.73, 34.65, 30.63, 30.3, 28.13, 27.41 26.3, 23.17, 22.34, 17.14, 12.33.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.67 (t, J = 11.2 Hz), -120.38 (t, J = 13 Hz), -122.75 (br s), -123.58 (br s), -124.2 (br s), -127.00 (br s).

HRMS: Calcd. for $C_{34}H_{41}O_5F_{19}$+Na: 913.2548; found 913.2542.

IR (KBr, cm^{-1}): 3428, 2939, 2871, 1762, 1242, 1214 (C-F), 1152 (C-F).

mp: 136-138°C.

$[\alpha]_D^{23}$: +11 (c 1.0, $CHCl_3$).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluoro-1-decyl 3α, 12α-dihydroxy-5β-cholan-24-oate ($DC_{24}CH_2C_9F_{19}$-1h):

Eluent used for the column chromatography was 40 % EtOAc/Petroleum ether.

From 0.4 g of **6**, 0.23 g of **$DC_{24}CH_2C_9F_{19}$** was obtained as a white solid (43 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.59 (t, J = 13.5 Hz, 2H), 3.98 (br s, 1H), 3.65 (m, 1H), 2.53-2.32 (m, 2H), 2.17-1.07 (m, steroidal CH, CH_2), 0.98 (d, J = 5.1 Hz, 3H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.55, 73.12, 71.75, 59.3 (t, J =27 Hz), 48.22, 47.19, 46.46, 42.03, 36.37, 35.99, 35.17, 34.98, 34.08, 33.61, 30.66, 30.58, 30.41, 28.67, 27.36 27.07, 26.08, 23.59, 23.08, 17.12, 12.63.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.70 (t, J = 11.3 Hz), -120.39 (t, J = 11.3 Hz), -122.76 (br s), -123.59 (br s), -124.2 (br s), -127.01 (br s).

HRMS: Calcd. for $C_{34}H_{41}O_4F_{19}$+Na: 897.2599; found 897.2589.

IR (KBr, cm^{-1}): 3417, 2926, 2861, 1763, 1242, 1214 (C-F), 1152 (C-F).

mp: 79-80°C.

$[\alpha]_D^{23}$: +13 (c 1.0, $CHCl_3$).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluoro-1-decyl 3α-hydroxy-5β-cholan-24-oate ($LC_{24}CH_2C_9F_{19}$-1i):

Eluent used for the column chromatography was 15 % EtOAc/Petroleum ether.

From 0.4 g of **6**, 0.12 g of **$LC_{24}CH_2C_9F_{19}$** was obtained as a white solid (45%).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.58 (t, J = 13.5 Hz, 2H), 3.63 (m, 1H), 2.46-2.31 (m, 2H), 2.17-1.07 (m, steroidal CH, CH_2), 0.92 (d and s merged, 6H), 0.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.59, 71.85, 59.3 (t, J = 27 Hz), 56.47, 55.89, 42.74, 42.09, 40.43, 40.16, 36.45, 35.84, 35.33, 35.21, 34.56, 30.70, 30.64, 30.54, 28.09, 27.17, 26.39, 24.15, 23.32, 20.80, 18.11, 11.95.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.72 (t, J = 11.2 Hz), -120.36 (t, J = 11.3 Hz), -122.74 (br s), -123.57 (br s), -124.2 (br s), -127.98 (br s).

HRMS: Calcd. for $C_{34}H_{41}O_3F_{19}$+Na: 881.2650; found 881.2649.

IR (KBr, cm^{-1}): 3375, 2936, 2865, 1761, 1241, 1212 (C-F), 1151 (C-F).

mp: 75-77°C.

$[\alpha]_D^{23}$: +8 (c 1.0, $CHCl_3$).

Synthesis of fluorinated bile acid derivatives with spacer *–O-(CO)-*

General procedure

In a 10 mL round bottom flask equipped with a $CaCl_2$ guard tube, a perfluoroacid (0.52 mmol, 1.3 eqv) was taken and dry DMF (2 mL) was added to it. The mixture was stirred at 70 °C to make a homogenous solution. Then DBU (0.52 mmol, 1.3 eqv) was added to it as a solution in dry DMF (prepared by adding 1 volume of DBU to 4 volume of dry DMF) and the stirring was continued for 1 hr at 70 °C. The reaction mixture slowly turned yellowish during this period. Then **7**, **8** or **9** (0.4 mmol, 1 eqv) was added and stirred at this temperature for 12 hr. After that the reaction mixture was cooled to room temperature and poured into 15 mL of water. A solid precipitated out which was extracted by either EtOAc (3×15 mL) for the derivatives of perfluorotetradecanoic and perfluorododecanoic acids or by $CHCl_3$ (3×15 mL) for) the other shorter chain perfluoro acids. The organic layers were

combined, washed with water (15 mL), dried over anhyd. Na_2SO_4, filtered and rotavaped. Finally the crude product was dried under high vacuum and purified by a silica gel column (2 cm×16 cm).

3α, 12α-Dihydroxy-24-nor-5β-cholan-23-yl perfluorooctan-1-oate ($DC_{23}C_7F_{15}$-2a):

Eluent used for the column chromatography was 55% EtOAc/Petroleum ether.

From 300 mg of **8**, 216 mg of **$DC_{23}C_7F_{15}$** was obtained as a white solid (45 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.46-4.39 (m, 2H), 3.98 (br s, 1H), 3.65-3.59 (m, 1H), 1.89-1.06 (m), 1.02 (d, J = 6.4 H z, 3H), 0.92 (s, 3H), 0.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.34 (t, J = 26 Hz), 73.04, 71.73, 66.98, 48.24, 47.31, 46.50, 42.04, 42.03, 36.39, 35.99, 35.17, 34.09, 34.01, 33.62, 32.68, 30.43, 28.78, 27.50, 27.08, 26.08, 23.56, 23.09, 17.43, 12.43.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -80.72 (t, J = 9.4 Hz), -118.39 (t, J= 11.3 Hz), -121.61 (br s), -121.96 (br s), -122.59 (br s), -126.02 (br s).

HRMS: Calcd. for $C_{31}H_{39}O_4F_{15}$+Na: 783.2507; found 783.2502.

IR (KBr, cm^{-1}): 3362, 2939, 2867, 1782, 1217 (C-F), 1151 (C-F).

mp: 44-45 °C.

$[\alpha]_D^{23}$: +45 (c 1.0, $CHCl_3$).

3α-Hydroxy-24-nor-5β-cholan-23-yl perfluorooctan-1-oate ($LC_{23}C_7F_{15}$-2b):

Eluent used for the column chromatography was 20% EtOAc/Petroleum ether.

From 0.3 g of **9**, 0.2 g of **$LC_{23}C_7F_{15}$** was obtained as a white solid (43 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.46-4.38 (m, 2H), 3.66-3.60 (m, 1H), 1.98-1.01 (m), 0.97 (d, J = 6.4 H z, 3H), 0.92 (s, 3H), 0.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.31 (t, J =27 Hz), 71.88, 67.03, 56.45, 56.06, 42.78, 42.05, 40.40, 40.11, 36.37, 35.80, 35.30, 34.54, 34.05, 32.87, 30.47, 28.19, 27.14, 26.37, 24.11, 23.31, 20.77, 18.47, 11.79.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -80.73 (t, J = 9.4 Hz), -118.40 (t, J= 11.3 Hz), -121.61 (br s), -121.96 (br s), -122.60 (br s), -126.02 (br s).

HRMS: Calcd. for $C_{31}H_{39}O_3F_{15}$+Na: 767.2551; found 767.2558.

IR (KBr, cm^{-1}): 3459, 2934, 2866, 1780, 1214 (C-F), 1153 (C-F).

mp: 62-63 °C.

$[\alpha]_D^{23}$: +20 (c 1.0, $CHCl_3$).

3α, 7α, 12α-Trihydroxy-24-nor-5β-cholan-23-yl perfluorodecan-1-oate ($C_{23}C_9F_{19}$-2c):

Eluent used for the column chromatography was EtOAc.

From 0.2 g of **8**, 0.14 g of **$C_{23}C_9F_{19}$** was obtained as a white solid (39 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.46-4.38 (m, 2H), 3.98 (br s, 1H), 3.86 (br s, 1H), 3.47-3.44 (m, 1H), 2.2 (m, 2H), (1.98-1.07 (m), 1.04 (d, J = 6.4 H z, 3H), 0.89 (s, 3H), 0.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.35 (t, J =27 Hz), 73.04, 71.8, 68.42, 67.0, 47.02, 46.39, 41.56, 41.41, 39.39, 35.28, 34.71, 34.62, 34.05, 32.75, 30.16, 29.69, 28.09, 27.52, 26.25, 23.11, 22.29, 17.43, 12.12.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -80.71 (t, J = 9.4 Hz), -118.37 (t, J = 11.3 Hz), -121.7 (br s), -122.57 (br s), -126.03 (br s).

HRMS: Calcd. for $C_{33}H_{39}O_5F_{19}$+Na: 899.2392; found 899.2391.

IR (KBr, cm^{-1}): 3426, 2940, 2858, 1781, 1210 (C-F), 1152 (C-F).

mp: 70-71°C.

$[\alpha]_D^{23}$: +16 (c 1.0, $CHCl_3$).

3α, 12α-Dihydroxy-24-nor-5β-cholan-23-yl perfluorodecan-1-oate ($DC_{23}C_9F_{19}$-2d):

Eluent used for the column chromatography was 60% EtOAc/Petroleum ether.

From 0.15 g of **8**, 0.14 g of $DC_{23}C_9F_{19}$ was obtained as a white solid (51 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.46-4.39 (m, 2H), 3.98 (br s, 1H), 3.67-3.57 (m, 1H), 1.98-1.07 (m), 1.03 (d, J = 6.0 H z, 3H), 0.92 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.35 (t, J =27 Hz), 73.04, 71.76, 66.98, 48.25, 47.34, 46.50, 42.03, 36.39, 36.0, 35.16, 34.09, 34.01, 33.64, 32.65, 30.44, 28.79, 27.48, 27.07, 26.08, 23.55, 23.09, 17.45, 12.45.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.67 (t, J = 11.2 Hz), -119.32 (t, J = 11.2 Hz), -122.74 (br s), -123.57 (br s), -124.2 (br s), -127.98 (br s).

HRMS: Calcd. for $C_{33}H_{39}O_4F_{19}$+Na: 883.2443; found 883.2446.

IR (KBr, cm^{-1}): 3401, 2939, 2867, 1783, 1243, 1210 (C-F), 1148 (C-F).

mp: 46-48°C.

$[\alpha]_D^{23}$: +35 (c 1.0, $CHCl_3$).

3α-Hydroxy-24-nor-5β-cholan-23-yl perfluorodecan-1-oate ($LC_{23}C_9F_{19}$-2e):

Eluent used for the column chromatography was 20% EtOAc/Petroleum ether.

From 0.2 g of **9**, 0.2 g of **$LC_{23}C_9F_{19}$** was obtained as a white solid (55 %).

^{1}H NMR (400 MHz, $CDCl_3$): 4.45-4.38 (m, 2H), 3.65-3.60 (m, 1H), 1.94-1.01 (m), 0.97 (d, J = 6.4 H z, 3H), 0.92 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.31 (t, J =27 Hz), 71.84, 67.03, 56.47, 56.08, 42.79, 42.07, 40.41, 40.14, 36.44, 35,83, 35.32, 34.55, 34.07, 32.88, 30.53, 28.19, 27.15, 26.38, 24.11, 23.31, 20.78, 18.49, 11.79.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.67 (t, J = 9.8 Hz), -119.32 (t, J= 11.2 Hz), -122.54 (br), 122.67 (br), -123.5 (br), -126.99 (br s).

HRMS: Calcd. for $C_{33}H_{39}O_3F_{19}$: 867.2494; found 867.2504.

IR (KBr, cm^{-1}): 3360, 2937, 2865, 1781, 1217 (C-F), 1152 (C-F).

mp: 80-81°C.

$[\alpha]_D^{23}$: +19 (c 1.0, $CHCl_3$).

3α, 12α-Dihydroxy-24-nor-5β-cholan-23-yl perfluoroundecan-1-oate ($DC_{23}C_{10}F_{21}$-2f):

Eluent used for the column chromatography was 60% EtOAc/Petroleum ether.

From 0.3 g of **8**, 0.34 g of **$DC_{23}C_{10}F_{21}$** was obtained as a white solid (60%).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.46-4.42 (m, 2H), 3.98 (br s, 1H), 3.66-3.62 (m, 1H), 1.89-1.1 (m), 1.03 (d, J = 6.3 H z, 3H), 0.92 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.35 (t, J =29 Hz), 73.06, 71.67, 66.98, 48.19, 47.26, 46.52, 42.06, 36.39, 36.0, 35.23, 34.1, 34.03, 33.59, 32.76, 30.41, 28.72, 27.54, 27.11, 26.1, 23.59, 23.01, 17.39, 12.37.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.69 (t, J = 9.0 Hz), -119.34 (br s), -123.5 (br s), -123.58 (br s), 127.01 (br s).

HRMS: Calcd. for $C_{34}H_{39}O_4F_{21}$+Na: 933.2411; found : 933.2411.

IR (KBr, cm^{-1}): 3439, 2935, 2862, 1779, 1213 (C-F), 1152 (C-F).

mp: 58-59°C.

$[\alpha]_D^{23}$: +32 (c 1.0, $CHCl_3$).

3α-Hydroxy-24-nor-5β-cholan-23-yl perfluoroundecan-1-oate ($LC_{23}C_{10}F_{21}$-2g):

Eluent used for the column chromatography was 20% EtOAc/Petroleum ether.

From 0.4 g of **9**, 0.44 g of **$LC_{23}C_{10}F_{21}$** was obtained as a white solid (57 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.45-4.38 (m, 2H), 3.65-3.60 (m, 1H), 1.94-1.01 (m), 0.97 (d, J = 6.4 H z, 3H), 0.92 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.38 (t, J = 27 Hz), 71.84, 67.02, 56.48, 56.09, 42.8, 42.08, 40.42, 40.15, 36.44, 35,83, 35.33, 34.55, 34.07, 32.88, 30.53, 28.19, 27.16, 26.38, 24.22, 24.11, 23.31, 20.78, 18.48, 11.78.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.68 (t, J = 9.8 Hz), -119.32 (t, J= 11.2 Hz), -122.55 (br s), -123.51 (br s), -126.98 (br s).

HRMS: Calcd. for $C_{34}H_{39}O_3F_{21}$+Na: 917.2462; found 917.2459.

IR (KBr, cm^{-1}): 3428, 2929, 2862, 1779, 1212 (C-F), 1152 (C-F).

mp: 87-88 °C.

$[\alpha]_D^{23}$: +7 (c 1.0, $CHCl_3$).

3α, 12α-Dihydroxy-24-nor-5β-cholan-23-yl perfluorododecan-1-oate ($DC_{23}C_{11}F_{23}$-2i):

Eluent used for the column chromatography was 60% EtOAc/Petroleum ether.

From 0.15 g of **8**, 0.16 g of **$DC_{23}C_{10}F_{21}$** was obtained as a white solid (54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.46-4.39 (m, 2H), 3.98 (br s, 1H), 3.65-3.59 (m, 1H), 1.93-1.25 (m), 1.03 (d, J = 6.4H z, 3H), 0.91 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.35 (t, J =29.3 Hz), 73.05, 71.75, 66.96, 48.23, 47.31, 46.48, 42.0, 36.36, 35.98, 35.15, 34.07, 33.99, 33.61, 32.66, 30.40, 28.75, 27.49, 27.06, 26.07, 23.55, 23.06, 17.41, 12.43.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -80.68 (t, J = 11.3 Hz), -118.39 (br s), -121.62 (br s), -122.55 (br s), -126.05 (br s).

HRMS: Calcd. for $C_{35}H_{39}O_4F_{23}$+Na: 983.2379; found : 983.2363.

IR (KBr, cm^{-1}): 3403, 2939, 2868, 1780, 1219 (C-F), 1154 (C-F).

mp: 76-78°C.

$[\alpha]_D^{23}$: +38(c 1.0, $CHCl_3$).

3α-Hydroxy-24-nor-5β-cholan-23-yl perfluorododecan-1-oate ($LC_{23}C_{11}F_{23}$-2j):

Eluent used for the column chromatography was 20% EtOAc/Petroleum ether.

From 0.2 g of **9**, 0.22 g of **$LC_{23}C_{11}F_{23}$** was obtained as a white solid (55 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.45-4.38 (m, 2H), 3.67-3.59 (m, 1H), 1.98-1.01 (m), 0.97 (d, J = 6.3 Hz), 0.92 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.38 (t, J = 29 Hz), 71.84, 67.02, 56.46, 56.07, 42.78, 42.06, 40.41, 40.13, 36.41, 35.81, 35.31, 34.55, 34.06, 32.88, 30.52, 28.19, 27.14, 26.37, 24.11, 23.30, 20.77, 18.47, 11.78.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -80.70 (t, J = 9.5 Hz), -118.38 (br s), -121.7 (br s), -122.54(br s), -126.03 (br s).

HRMS: Calcd. for $C_{35}H_{39}O_3F_{23}$+Na: 967.2430; found : 967.2435.

IR (KBr, cm^{-1}): 3408, 2940, 2866, 1776, 1210 (C-F), 1153 (C-F).

mp: 100-101°C.

$[\alpha]_D^{23}$: +12(c 1.0, $CHCl_3$).

3α, 7α, 12α-Trihydroxy-24-nor-5β-cholan-23-yl perfluorotetradecan-1-oate ($C_{23}C_{13}F_{27}$-2k):

Eluent used for the column chromatography was EtOAc.

From 0.15 g of **7**, 0.13 g of **$C_{23}C_{13}F_{27}$** was obtained as a white solid (41 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.46-4.40 (m, 2H), 3.99 (br s, 1H), 3.85 (br s, 1H), 3.49-3.44 (m, 1H), 1.96-1.25 (m), 1.04 (d, J = 6.0 Hz, 3H), 0.90 (s, 3H), 0.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.29 (t, J =27 Hz), 72.97, 71.8, 68.38, 66.94, 46.99, 46.35, 41.55, 41.31, 39.34, 35.16, 34.65, 34.57, 33.96, 32.69, 30.19, 28.07, 27.47, 26.24, 23.06, 22.26, 17.38, 12.09.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -80.7 (t, J = 11.3 Hz), -118.37 (s), -121.65 (br s), -122.55 (br s), -126.02 (br s).

HRMS: Calcd. for $C_{37}H_{39}O_5F_{27}$+Na: 1099.2264; found : 1099.2261.

IR (KBr, cm^{-1}): 3421, 2938, 2858, 1780, 1211 (C-F), 1150 (C-F).

mp: 78-79°C.

$[\alpha]_D^{23}$: +23 (c 1.0, $CHCl_3$).

3α, 12α-Dihydroxy-24-nor-5β-cholan-23-yl perfluorotetradecan-1-oate ($DC_{23}C_{13}F_{27}$-2l):

Eluent used for the column chromatography was 60% EtOAc/Petroleum ether.

From 0.3 g of **8**, 0.35 g of **$DC_{23}C_{13}F_{27}$** was obtained as a white solid (53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.45-4.41 (m, 2H), 3.98 (br s, 1H), 3.65-3.59 (m, 1H), 1.96-1.07 (m), 1.03 (d, J = 6.0 Hz, 3H), 0.91 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.36 (t, J = 27 Hz), 73.06, 71.79, 66.97, 48.27, 47.38, 46.53, 42.05, 36.43, 36.03, 35.18, 34.10, 34.04, 33.68, 32.66, 30.49, 28.83, 27.48, 27.08, 26.09, 23.56, 23.10, 17.47, 12.47.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.68 (t, J = 9.8 Hz), -119.33 (s), -122.54 (br s), -123.54 (br s), -126.99 (br s).

HRMS: Calcd. for $C_{37}H_{39}O_4F_{27}$+Na: 1083.2315; found : 1083.2379.

IR (KBr, cm^{-1}): 3428, 2932, 2866, 1780, 1212 (C-F), 1154 (C-F).

mp: 90-92°C.

$[\alpha]_D^{23}$: +20 (c 1.0, $CHCl_3$).

3α-Hydroxy-24-nor-5β-cholan-23-yl perfluorotetradecan-1-oate ($LC_{23}C_{13}F_{27}$-2m):

Eluent used for the column chromatography was 20% EtOAc/Petroleum ether.

From 0.3 g of **9**, 0.34 g of **$LC_{23}C_{13}F_{27}$** was obtained as a white solid (55 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.45-4.35 (m, 2H), 3.67-3.58 (m, 1H), 1.98-1.01 (m), 0.97 (d, J = 6.0 Hz), 0.92 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.38 (t, J = 29 Hz), 71.84, 67.02, 56.47, 56.08, 42.79, 42.07, 40.41, 40.14, 36.43, 35.82, 35.32, 34.55, 34.07, 32.88, 30.53, 28.19, 27.15, 26.38, 24.11, 23.30, 20.78, 18.47, 11.78.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -80.68 (t, J = 7.5 Hz), -118.37 (s), -121.61 (br s), -122.57 (br s), -126.05 (br s).

HRMS: Calcd. for $C_{37}H_{39}O_3F_{27}$+Na: 1067.2366; found : 1067.2367.

IR (KBr, cm^{-1}): 3323, 2936, 2865, 1778, 1210 (C-F), 1153 (C-F).

mp: 122-123°C.

$[\alpha]_D^{23}$: +8 (c 1.0, $CHCl_3$).

Synthesis of non-fluorinated bile acid ester derivatives having spacer *–O-(CO)-*

3α, 7α, 12α-Trihydroxy-24-nor-5β-cholan-23-yl decan-1-oate ($C_{23}C_9H_{19}$-3a):

Eluent used for column chromatography was 8% EtOH/ $CHCl_3$.

From 0.26 g of **9**, 0.16 g of **$C_{23}C_9H_{19}$** was obtained as a white sticky material (55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.17-4.03 (m, 2H), 3.96 (br s, 1H), 3.83 (br s, 1H), 3.45-3.40 (m, 1H), 2.28 (t, J = 7.6 Hz, 2 H), 2.2-2.17 (m, 2H), 1.92-1.26 (m), 1.01 (d, J = 6.4 Hz, 3H), 0.88 (s, 3H), 0.86 ( ), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.95, 72.94, 71.75, 68. 31, 62.52, 47.15, 46.35, 41.47, 41.42, 40.77, 39.39, 35.23, 34.70, 34.62, 34.51, 34.35, 33.02, 31.77, 30.29, 29.33, 29.19, 29.17, 29.06, 28.06, 27.59, 26.16, 24.93, 23.13, 22.56, 22.35, 17.64, 14.02, 12.29.

HRMS: Calcd. for $C_{33}H_{58}O_5$+Na: 557.4182; found : 557.4181.

IR (KBr, cm^{-1}): 3400, 2929, 2858, 1735, 771.

$[\alpha]_D^{23}$: +35 (c 1.0, $CHCl_3$).

3α, 12α-Dihydroxy-24-nor-5β-cholan-23-yl decan-1-oate ($DC_{23}C_9H_{19}$-3b):

Eluent used for column chromatography was 50 % EtOAc/ Petroleum ether.

From 0.2 g of **8**, 0.12 g of **$DC_{23}C_9H_{19}$** was obtained as a white semi-solid material (57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.17-4.03 (m, 2H), 3.98 (br s, 1H), 3.63-3.57 (m, 1H), 2.28 (t, J = 7.6 Hz, 2 H), 1.87-1.04 (m), 1.00 (d, J = 6.4 Hz, 3H), 0.90 (s, 3H), 0.88 (t, J = 6.8 Hz, 3 H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.94, 72.99, 71.60, 62.49, 48.13, 47.45, 46.46, 42.03, 36.35, 35.97, 35.20, 34.53, 34.39, 34.06, 33.53, 32.99, 31.80, 30.38, 29.62, 29.36, 29.22, 29.19, 28.58, 27.61, 27.10, 26.07, 24.96, 23.62, 23.06, 22.59, 17.63, 14.03, 12.56.

HRMS: Calcd. for $C_{33}H_{58}O_4$+Na: 541.4233; found : 541.4236.

IR (KBr, cm^{-1}): 3378, 2928, 2860, 1736, 1042.

$[\alpha]_D^{23}$: +39 (c 1.0, $CHCl_3$).

3α-Hydroxy-24-nor-5β-cholan-23-yl decan-1-oate ($LC_{23}C_9H_{19}$-3c):

Eluent used for column chromatography was 15 % EtOAc/ Petroleum ether.

From 0.3 g of **9**, 0.14 g of **$LC_{23}C_9H_{19}$** was obtained as a white semi-solid material (43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.15-4.01 (m, 2H), 3.63-3.57 (m, 1H), 2.28 (t, J = 7.6 Hz, 2 H), 1.87-1.05 (m), 1.00 (d, J = 6.4 Hz, 3H), 0.90 (s, 3H), 0.88 (t, J = 6.8 Hz, 3H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.98, 71.72, 62.50, 56.43, 56.41, 42.7, 42.03, 40.36, 40.09, 36.31, 35.77, 35.30, 34.56, 34.50, 34.40, 33.13, 31.80, 30.41, 29.36, 29.22, 29.20, 29.09, 28.25, 27.13, 26.36, 24.97, 24.12, 23.30, 22.60, 20.74, 18.66, 14.04, 11.89.

HRMS: Calcd. for $C_{33}H_{58}O_3$+Na: 525.4284; found : 525.4280.

IR (KBr, cm^{-1}): 3444, 2928, 2858, 1737, 1465, 769.

$[\alpha]_D^{23}$: +34 (c 1.0, $CHCl_3$)