Supporting Information

Anionic surfactants based on intermediates of carbohydrate conversion

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Experimental

1-(tetrahydrofuran-2-yl)alkane-1-ol (2)

1-(furan-2-yl)alkane-1-ol (1) (20 g) was dissolved in ethanol (100 mL). After addition of Ni/SiO2 (10 wt%) the reaction mixture was transferred into a stainless steel autoclave and heated to 100 °C for 3 h with a hydrogen pressure of 150 bar. The catalyst was removed and the solvent evaporated to yield the product as colourless liquid. m(product) = 19.1 g, 96%

(2a)

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.82 (t, 3H, H₁₈), 1.19 (m, 18H, H₉₋₁₇), 1.35-1.83 (m, 8H, H_{2,3,7,8}), 2.67 (s, 1H, OH), 3.32 (q, 1H, H₅), 3.61(q, 1H, H₄) 3.70 (m, 2H, H₁). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.09 (s, 1C, C₁₈), 22.71 (s, 1C, C₁₇), 25.87 (s, 1C, C₈), 26.07 (d, 1C, C₂), 26.25–28.03 (d, 1C, C₃), 29.39 (s, 1C, C₁₀), 29.70 (m, 6C, C_{9,11-15}), 31.95 (s, 1C, C₁₆), 32.99 – 33.73 (d, 1C, C₇), 68.06 – 68.45 (d, 1C, C₁), 71.95 – 73.92 (s, 1C, C₅), 82.39–82.56 (s, 1C, C₄).

(2b)



¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.85 (t, 3H, H₂₀), 1.23 (m, 22H, H₉₋₁₉), 1.38-1.84 (m, 8H,H_{2,3,7,8}), 2.39 (s, 1H, OH), 3.35 (q, 1H, H₅), 3.74 (m, 3H, H_{1,4}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.21 (s, 1C, C₂₀), 22.80 (s, 1C, C₁₉), 24.58–25.81 (s, 1C, C₂), 26.38–28.07 (d, 1C, C₃), 29.48 (s, 1C, C₁₀), 29.82 (m, 10C, C₈₋₁₇), 32.04 (s, 1C, C₁₈), 32.99–33.84 (d, 1C, C₇), 68.16–68.57 (d, 1C, C₁), 71.98–74.03 (d, 1C, C₅), 82.38–82.25 (d, 1C, C₄).

Williamson-Etherification of bio-based alcohols to (4), (6), (8), (10), (12)

The alcohol (1.9 eq) was solved in DMF/Acetonitrile and ^tBuONa/NaH (1.7 eq) was added slowly under stirring. Afterwards the haloalkane (1.0 eq) was added and the reaction mixture was stirred at 100 °C/70 °C for 16 h. The reaction mixture was allowed to cool down to room temperature and extracted with water and diethylether. The organic layer was dried using sodium sulfate, filtered and the solvent was evaporated. The residue oil was purified via column chromatography using a mixture of petroleum ether and diethylether. The products were obtained as a yellowish oils.

(4)



¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.88 (t, 3H, H₁₇), 1.25 (m, 18H, H₈₋₁₆), 1.58 (m, 2H, H₇), 3.45 (t, 2H, H₆), 4.43 (s, 2H, H₅), 4.82 (s), 6.31 (dm, 2H, H_{2,3}), 7.40 (m, 1H, H₁). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.26 (s, 1C, C₁₇), 22.83 (s, 1C, C₁₆), 26.24 (s, 1C, C₈), 29.78 (m, 7C, C_{7,9-14}), 32.07 (s, 1C, C₁₅), 64.87 (s, 1C, C₅), 70.59 (s, 1C, C₆), 109.04 (s, 1C, C₃), 110.31 (s, 1C, C₂), 142.74 (s, 1C, C₁), 152.29 (s, 1C, C₄).

(6a) HO $\frac{5}{2}$ $\frac{4}{6}$ $\frac{7}{6}$ $\frac{9}{8}$ $\frac{11}{12}$ $\frac{13}{14}$ $\frac{15}{12}$

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.86 (t, 3H, H₁₅), 1.24–2.04 (m, 22H, H_{2,3,5,7-14}), 2.62 (s, 1H, OH), 3.32 (m, 2H, H₆), 3.98 (dm, 1H, H₄), 4.31 (dm, 1H, H₁). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.22 (s, 1C, C₁₅), 22.79 (s, 1C, C₁₄), 26.35 (s, 1C, C₈), 29.68 (m, 6C, C_{3,7,9-12}), 32.01 (s, 1C, C₁₃), 33.57 (d, 1C, C₂), 41.42 (d, 1C, C₅), 69.09 (d, 1C, C₆), 73.13 (d, 1C, C₁), 80.62 (s, 1C, C₄).

(6b)
HO
$$\frac{1}{2}$$
 $\frac{5}{3}$ $\frac{7}{6}$ $\frac{9}{8}$ $\frac{11}{12}$ $\frac{13}{14}$ $\frac{15}{16}$ $\frac{17}{12}$

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.86 (t, 3H, H₁₇), 1.24–1.98 (m, 26H, H_{2,3,5,7-16}), 2.76 (s, 1H, OH), 3.37 (m, 2H, H₆), 3.95 (m, 1H, H₄), 4.22 (m, 1H, H₁). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.24 (s, 1C, C₁₇), 22.81 (s, 1C, C₁₆), 26.37 (s, 1C, C₈), 29.78 (m, 8C, C_{3,7,9-14}), 32.054 (s, 1C, C₁₅), 34.10 (s, 1C, C₂), 41.33 (s, 1C, C₅), 69.02 (s, 1C, C₆), 73.68 (s, 1C, C₁), 81.21 (s, 1C, C₄).

(6c)
HO
$$1 \xrightarrow{5}{4} 0 \xrightarrow{7}{9} 11 13 15 17 19$$

 $2 \xrightarrow{3}{6} 8 10 12 14 16 18$

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.86 (t, 3H, H₁₉), 1.24-1.94 (m, 30H, H_{2,3,5,7-18}), 2.81 (s, 1H, OH), 3.36 (m, 2H, H₆), 3.94 (m, 1H, H₄), 4.22 (m, 1H, H₁). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.21 (s, 1C, C₁₉), 22.80 (s, 1C, C₁₈), 26.35 (s, 1C, C₈), 29.77 (m, 10C, C_{3,7,9-16}), 32.03 (s, 1C, C₁₇), 34.07 (s, 1C, C₂), 41.32 (s, 1C, C₅), 69.01 (s, 1C, C₆), 73.63 (s, 1C, C₁), 81.18 (s, 1C, C₄).

(8)

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¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.88 (t, 3H, H₁₈), 1.25 (m, 18H, H₉₋₁₇), 1.59 (m, 2H, H₈), 3.46 (t, 2H, H₇), 4.41 (s, 2H, H₆), 4.59 (s, 2H, H₁), 6.25 (q, 2H, H_{3,4}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.26 (s, 1C, C₁₈), 22.83 (s, 1C, C₁₇), 26.24 (s, 1C, C₉), 29.75 (m, 7C, C_{8,10-15}), 32.07 (s, 1C, C₁₆), 57.78 (s, 1C, C₁), 64.98 (s, 1C, C₆), 70.76 (s, 1C, C₇), 108.56 (s, 1C, C₃), 109.92 (s, 1C, C₄), 152.36 (s, 1C, C₅), 154.30(s, 1C, C₅).

(10a)
HO
$$\frac{5}{2}$$
 $\frac{6}{3}$ $\frac{7}{8}$ $\frac{9}{10}$ $\frac{11}{12}$ $\frac{13}{14}$ $\frac{15}{16}$

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.84 (t, 3H, H₁₆), 1.22–2.77 (m, 23H, H_{2-5,8-15}), 3.36–4.30 (m, 5H, H_{1,6,7}). ¹³**C**-NMR (100 MHz, CDCl₃): δ (ppm) = 14.17 (s, 1C, C₁₆), 22.75 (s, 1C, C₁₅), 26.12 (s, 1C, C₉), 26.21 (s, 1C, C₃), 29.65 (m, 5C, C_{8,10-13}), 31.97 (s, 1C, C₁₄), 36.34 (s, 1C, C₂), 37.28 (s, 1C, C₄), 39.13 (s, 1C, C₅), 71.54 (s, 1C, C₇), 73.32 (s, 1C, C₁), 74.63 (s, 1C, C₆).

(10b) HO $\frac{5}{2}$, $\frac{6}{3}$, $\frac{7}{6}$, $\frac{9}{8}$, $\frac{11}{12}$, $\frac{13}{14}$, $\frac{15}{16}$, $\frac{17}{18}$, $\frac{18}{18}$

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.87 (t, 3H, H₁₈), 1.24–2.86 (m, 27H, H_{2-5,8-17}), 3.23–4.19 (m, 5H, H_{1,6,7}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.24 (s, 1C, C₁₈), 22.82 (s, 1C, C₁₇), 26.12 (s, 1C, C₉), 26.26 (s, 1C, C₃), 29.75 (m, 5C, C_{8,10-15}), 32.05 (s, 1C, C₁₆), 36.51 (s, 1C, C₂), 37.31 (s, 1C, C₄), 39.23 (s, 1C, C₅), 71.63 (s, 1C, C₇), 73.44 (s, 1C, C₁), 74.61 (s, 1C, C₆).

(12a) HO 3 4 7 9 118 10

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.84 (t, 3H, H₁₂), 1.25 (m, 6H, H₉₋₁₁), 1.54–1.86 (m, 6H, H_{3,4,8}), 2.68 (s, 1H, OH), 3.36–3.75 (m, 6H, H_{1,6,7}), 4.06 (m, 2H, H_{2,5}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.07 (s, 1C, C₁₂), 22.63 (s, 1C, C₁₁), 25.76 (s, 1C, C₉), 27.44 (s, 1C, C₃), 28.18 (s, 1C, C₄), 29.51 (s, 1C, C₈), 31.68 (s, 1C, C₁₀), 65.51 (s, 1C, C₁), 71.80 (s, 1C, C₇), 73.17 (s, 1C, C₆), 78.70 (s, 1C, C₅), 80.25 (s, 1C, C₂).

12

(12b)
HO
$$3 4$$
 4 7 9 11 13
 8 10 12 14

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.84 (t, 3H, H₁₄), 1.23 (m, 10H, H₉₋₁₃), 1.55–1.88 (m, 6H, H_{3,4,8}), 2.78 (s, 1H, OH), 3.42 (m, 4H, H_{6,7}), 3.54–3.76 (ddd, 2H, H₁), 4.09 (m, 2H, H_{2,5}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.17 (s, 1C, C₁₄), 22.73 (s, 1C, C₁₃), 26.13 (s, 1C, C₉), 27.53 (s, 1C, C₃), 28.26 (s, 1C, C₄), 29.33 (s, 1C, C₁₁), 29.49 (s, 1C, C₁₀), 29.60 (s, 1C, C₈), 31.91 (s, 1C, C₁₂), 65.61 (s, 1C, C₁), 71.85 (s, 1C, C₇), 73.19 (s, 1C, C₆), 78.79 (s, 1C, C₅), 80.24 (s, 1C, C₂).

(12c)

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.83 (t, 3H, H₁₆), 1.22 (m, 14H, H₉₋₁₅), 1.52–1.90 (m, 6H, H_{3,4,8}), 2.20 (s, 1H, OH), 3.41 (m, 4H, H_{6,7}), 3.53–3.75 (ddd, 2H, H₁), 4.09 (m, 2H, H_{2,5}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.15 (s, 1C, C₁₆), 22.73 (s, 1C, C₁₅), 26.10 (s, 1C, C₉), 27.49 (s, 1C, C₃), 28.22 (s, 1C, C₄), 29.64 (m, 5C, C_{8,10-13}), 31.95 (s, 1C, C₁₄), 65.55 (s, 1C, C₁), 71.82 (s, 1C, C₇), 73.17 (s, 1C, C₆), 78.74 (s, 1C, C₅), 80.23 (s, 1C, C₂).



¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.84 (t, 3H, H₁₈), 1.22 (m, 18H, H₉₋₁₇), 1.53–1.88 (m, 6H, H_{3,4,8}), 2.81 (s, 1H, OH), 3.41 (m, 4H, H_{6,7}), 3.53–3.75 (ddd, 2H, H₁), 4.09 (m, 2H, H_{2,5}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.17 (s, 1C, C₁₈), 22.75 (s, 1C, C₁₇), 26.11 (s, 1C, C₉), 27.50 (s, 1C, C₃), 28.24 (s, 1C, C₄), 29.67 (m, 7C, C_{8,10-15}), 31.98 (s, 1C, C₁₆), 65.56 (s, 1C, C₁), 71.83 (s, 1C, C₇), 73.17 (s, 1C, C₆), 78.75 (s, 1C, C₅), 80.23 (s, 1C, C₂).

(12e)
HO
$$3$$
 1 2 0 5 6 7 9 11 13 15 17 19
 8 10 12 14 16 18 20

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.83 (t, 3H, H₂₀), 1.21 (m, 22H, H₉₋₁₉), 1.50–1.87 (m, 6H, H_{3,4,8}), 2.98 (s, 1H, OH), 3.41 (m, 4H, H_{6,7}), 3.53–3.74 (ddd, 2H, H₁), 4.07 (m, 2H, H_{2,5}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.16 (s, 1C, C₂₀), 22.75 (s, 1C, C₁₉), 26.12 (s, 1C, C₉), 27.50 (s, 1C, C₃), 28.22 (s, 1C, C₄), 29.72 (m, 9C, C_{8,10-17}), 31.99 (s, 1C, C₁₈), 65.54 (s, 1C, C₁), 71.82 (s, 1C, C₇), 73.17 (s, 1C, C₆), 78.74 (s, 1C, C₅), 80.23 (s, 1C, C₂).

Catalytic etherification of BHMTHF to (14)

BHMTHF (1 eq), a corresponding olefin (1 eq) and catalyst were heated in a stainless steel autoclave. After the reaction the mixture was homogenized and the catalyst was removed. The residue was extracted with water and petroleum ether and distilled. After purification with column chromatography using petroleum ether and diethylether the product was obtained as a pale-yellow liquid.

(14a)

HO
$$3 4$$
 4 $0 9$ 11 13 15 17 18

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.86 (t, 3H, H₁₈), 1.12 (t, 3H, H₇), 1.24-1.53 (m, 19H, H₉₋₁₇), 1.92 (m, 4H, H_{3,4}), 2.79 (s, 1H, OH), 3.35–3.80 (m, 5H, H_{1.6,8}), 4.11 (m, 2H, H_{2.5}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.22 (s, 1C, C₁₈), 19.48 (d, 1C, C₇), 22.79 (s, 1C, C₁₇), 25.59 (s, 1C, C₁₀), 27.65 (d, 1C, C₃), 28.36 (d, 1C, C₄), 29.73 (m, 5C, C₁₁₋₁₅), 32.02 (s, 1C, C₁₆), 36.40 (d, 1C, C₉), 65.76 (d, 1C, C₁), 70.67 (d, 1C, C₆), 76.34 (d, 1C, C₈), 79.04 (d, 1C, C₅), 80.20 (d, 1C, C₂).

(14b)
HO
$$3 4$$
 7 12 14 16 18 20
 9 11 13 15 17 19

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.85 (t, 3H, H₂₀), 1.11 (t, 3H, H₇), 1.23-1.67 (m, 23H, H₉₋₁₉), 1.92 (m, 4H, H_{3,4}), 2.95 (s, 1H, OH), 3.33–3.79 (m, 5H, H_{1.6,8}), 4.11 (m, 2H, H_{2.5}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.20 (s, 1C, C₂₀), 19.45 (d, 1C, C₇), 22.77 (s, 1C, C₁₉), 25.57 (s, 1C, C₁₀), 27.68 (d, 1C, C₃), 28.33 (d, 1C, C₄), 29.72 (m, 7C, C₁₁₋₁₇), 32.00 (s, 1C, C₁₈), 36.38 (d, 1C, C₉), 65.71 (d, 1C, C₁), 70.59 (d, 1C, C₆), 76.31 (d, 1C, C₈), 78.97 (d, 1C, C₅), 80.22 (d, 1C, C₂).

(14c)

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.82 (t, 3H, H₂₂), 1.08 (t, 3H, H₇), 1.20-1.64 (m, 27H, H₉₋₂₁), 1.87 (m, 4H, H_{3,4}), 3.05 (s, 1H, OH), 3.30–3.74 (m, 5H, H_{1.6,8}), 4.05 (m, 2H, H_{2.5}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.13 (s, 1C, C₂₁), 19.39 (d, 1C, C₇), 22.71 (s, 1C, C₂₁), 25.51 (s, 1C, C₁₀), 27.54 (d, 1C, C₃), 28.26 (d, 1C, C₄), 29.72 (m, 9C, C₁₁₋₁₉), 31.95 (s, 1C, C₂₀), 36.36 (d, 1C, C₉), 65.59 (d, 1C, C₁), 70.63 (d, 1C, C₆), 76.26 (d, 1C, C₈), 78.88 (d, 1C, C₅), 80.15 (d, 1C, C₂).

(14d)

¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 0.84 (t, 3H, H₂₄), 1.11 (t, 3H, H₇), 1.22-1.67 (m, 31H, H₉₋₂₃), 1.91 (m, 4H, H_{3,4}), 2.95 (s, 1H, OH), 3.33–3.76 (m, 5H, H_{1.6,8}), 4.07 (m, 2H, H_{2,5}). ¹³**C-NMR** (100 MHz, CDCl₃): δ (ppm) = 14.19 (s, 1C, C₂₄), 19.45 (d, 1C, C₇), 22.78 (s, 1C, C₂₃), 25.57 (s, 1C, C₁₀), 27.63 (d, 1C, C₃), 28.27 (d, 1C, C₄), 29.72 (m, 11C, C₁₁₋₂₁), 32.02 (s, 1C, C₂₂), 36.39 (d, 1C, C₉), 65.70 (d, 1C, C₁), 70.66 (d, 1C, C₆), 76.30 (d, 1C, C₈), 78.99 (d, 1C, C₅), 80.22 (d, 1C, C₂).

Sulfatation of bio-based ethers and alcohols to (3) (5), (7), (9), (11), (13), (15)

The ether/alcohol (1 eq) was dissolved in acetonitrile and sulfur trioxide pyridine complex (1.5 eq) was added. After the mixture was stirred at 70°C for 6h, water (0.5 eq) was added. The solvent was evaporated and the residue oil dried in vacuo. The dried product was solved in ethanol, sodium carbonate or NaOH (2 eq) was added and the mixture was stirred for 2 h at 50°C. The solution was filtered over silica and the solvent was evaporated. After addition of petroleum ether the product precipitated as a white solid which was isolated via centrifugation and washed with petroleum ether.

(3a) OSO₃Na $1 \xrightarrow{0}_{2} \xrightarrow{6}_{3} \xrightarrow{7}_{6} \xrightarrow{9}_{11} \xrightarrow{13}_{12} \xrightarrow{15}_{17}$ $1 \xrightarrow{10}_{2} \xrightarrow{6}_{3} \xrightarrow{8}_{10} \xrightarrow{12}_{14} \xrightarrow{14}_{16} \xrightarrow{17}_{17}$

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.91 (t, 3H, H₁₈), 1.19–1.95 (m, 26H, H_{2,3,7-17}), 3.67–4.44 (m, 4H, H_{1,4,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 13.84 (s, 1C, C₁₈), 22.69 (s, 1C, C₁₇), 24.60–25.19 (d, 1C, C₂), 25.52 (s, 1C, C₈), 26.17–27.19 (s, 1C, C₃), 29.59–30.90 (m, 8C, C_{7,9-15}), 32.05 (s, 1C, C₁₆), 68.16–26.65 (d, 1C, C₁), 79.17–79.67 (s, 1C, C₄), 81.31 (s, 1C, C₅).

HRMS (ESI): m/z calcd for C₁₇H₃₃O₅S⁻: 349.20542 [M⁻]; found: 349.20416.

(3b)
OSO₃Na

$$1 \xrightarrow{0}{4} 5 \xrightarrow{7}{9} 11 \xrightarrow{13}{15} 17 \xrightarrow{19}{10} 12 \xrightarrow{14}{16} 18$$

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.89–1.93 (m, 35H, H_{2,3,7-20}), 3.63–4.41 (m, 4H, H_{1,4,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.45 (s, 1C, C₂₀), 23.73 (s, 1C, C₁₉), 25.81 (s, 1C, C₈), 26.51 (s, 1C, C₂), 26.89 (s, 1C, C₃), 28.87 (s, 1C, C₉), 28.45 (s, 1C, C₁₀), 30.69 (m, 7C, C₁₁₋₁₇), 32.13 (s, 1C, C₇), 33.08 (s, 1C, C₁₈), 69.49 (d, 1C, C₁), 80.65 (d, 1C, C₄), 81.65 (d, 1C, C₅).

HRMS (ESI): m/z calcd for C₁₉H₃₇O₅S⁻: 377.23672 [M⁻]; found: 377.23602.

(5)

$$PyO_{3}S_{2} \xrightarrow{1}_{3} \xrightarrow{0}_{3} \xrightarrow{7}_{5} \xrightarrow{9}_{11} \xrightarrow{13}_{13} \xrightarrow{15}_{17}_{17}$$

¹**H-NMR** (400 MHz, Pyridine): δ (ppm) = 0.98 (m, 3H, H₁₇), 1.38 (m, 18H, H₈₋₁₆), 1.64 (m, 2H, H₇), 3.54 (m, 2H, H₆), 4.53 (s, 2H, H₅), 6.50 (s, 2H, H_{2,3}). ¹³**C-NMR** (100 MHz, APT, Pyridine): δ (ppm) = 14.81 (s, 1C, C₁₇), 23.64 (s, 1C, C₁₆), 27.13 (s, 1C, C₈), 30.58 (m, 7C, C₉₋₁₅), 32.59 (s, 1C, C₁₅), 65.39 (s, 1C, C₅), 71.06 (s, 1C, C₆), 110.14 (s, 1C, C₃), 111.53 (d, 1C, C₂).

MS (ESI): m/z calcd for C₁₇H₂₉O₅S⁻: 345 [M⁻]; found: 345.

(7a)

NaO₃SO
$$1 \xrightarrow{5} 4 \xrightarrow{6} 8 \xrightarrow{7} 9 \xrightarrow{911} 13 \xrightarrow{15} 2 \xrightarrow{2} 3 \xrightarrow{6} 8 \xrightarrow{10} 12 \xrightarrow{14} 15$$

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.91 (t, 3H, H₁₅), 1.30 (m, 14H, H₈₋₁₄), 1.51-2.37 (m, 8H, H_{2,3,5,7}), 3.39 (m, 2H, H₆), 3.94 (dm, 1H, H₄), 4.83 (dm, 1H, H₁). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.23 (s, 1C, C₁₅), 23.73 (s, 1C, C₁₄), 27.33 (s, 1C, C₈), 30.74 (m, 7C, C_{2,3,7,9-12}) 33.06 (s, 1C, C₁₃), 40.41 (d, 1C, C₅), 70.06 (d, 1C, C₆), 80.20 (d, 1C, C₄), 80.86 (d, 1C, C₁).

HRMS (ESI): m/z calcd for C₁₅H₂₉O₅S⁻: 321.17412 [M⁻]; found: 321.17291.

(7b)

NaO₃SO
$$-1$$
 -5 -7 -9 -11 -13 -15 -17
 -6 -8 -10 -12 -14 -16 -17

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.92 (t, 3H, H₁₇), 1.31 (m, 18H, H₈₋₁₆), 1.51-2.38 (m, 8H, H_{2,3,5,7}), 3.40 (m, 2H, H₆), 3.98 (dm, 1H, H₄), 4.84 (dm, 1H, H₁). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.44 (s, 1C, C₁₇), 23.73 (s, 1C, C₁₆), 27.33 (s, 1C, C₈), 30.74 (m, 9C, C_{2,3,7,9-14}) 33.06 (s, 1C, C₁₅), 40.97 (d, 1C, C₅), 70.05 (d, 1C, C₆), 79.87 (d, 1C, C₄), 80.83 (d, 1C, C₁).

HRMS (ESI): m/z calcd for C₁₇H₃₃O₅S⁻: 349.20542 [M⁻]; found: 349.20416.

(7c)
NaO₃SO
$$\underbrace{1}_{2}$$
, 5 , 7 , 9 , 11 , 13 , 15 , 17 , 19
 6 , 8 , 10 , 12 , 14 , 16 , 18

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.90 (t, 3H, H₁₉), 1.29 (m, 22H, H₈₋₁₈), 1.50-2.36 (m, 8H, H_{2,3,5,7}), 3.39 (m, 2H, H₆), 3.88 (m, 1H, H₄), 4.75 (m, 1H, H₁). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.44 (s, 1C, C₁₉), 23.74 (s, 1C, C₁₈), 27.33 (s, 1C, C₈), 30.75 (m, 11C, C_{2,3,7,9-16}) 33.08 (s, 1C, C₁₇), 40.15 (s, 1C, C₅), 70.18 (s, 1C, C₆), 79.83 (s, 1C, C₄), 80.53 (s, 1C, C₁).

HRMS (ESI): m/z calcd for C₁₉H₃₇O₅S⁻: 377.23672 [M⁻]; found: 377.23599.

NaO₃SO
$$1 = 0.5 = 6$$
 $7 = 9 = 11 = 13 = 15 = 17$
NaO₃SO $3 = 10 = 12 = 14 = 16 = 18$

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.91 (t, 3H, H₁₈), 1.30 (m, 18H, H₉₋₁₇), 1.56 (m, 2H, H₈), 3.47 (t, 2H, H₇), 4.42 (s, 2H, H₆), 4.94 (s, 2H, H₁), 6.33 (d, 1H, H₄), 6.42 (s, 1H, H₃). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.44 (s, 1C, C₁₈), 23.74 (s, 1C, C₁₇), 27.17 (s, 1C, C₉), 30.76 (m, 7C, C_{8,10-15}), 33.08 (s, 1C, C₁₆), 62.69 (s, 1C, C₁), 65.78 (s, 1C, C₆), 71.30 (s, 1C, C₇), 111.08 (s, 1C, C₃), 112.02 (s, 1C, C₄), 151.49 (s, 1C, C₂), 154.19 (s, 1C, C₅).

(11a)

14461

NaO₃SO
$$1 \xrightarrow{5} 4 \xrightarrow{6} 7 \xrightarrow{9} 11 \xrightarrow{13} 15$$

2 3 0 8 10 12 14 16

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.94 (t, 3H, H₁₆), 1.34–2.21 (m, 23H, H_{2-5,8-15}), 3.41–3.96 (m, 4H, H_{6,7}) 4.84 (m, 1H, H₁). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.42 (s, 1C, C₁₆), 23.71 (s, 1C, C₁₅), 27.25 (s, 1C, C₉), 28.18 (s, 1C, C₃), 30.73 (m, 5C, C_{8,10-13}), 33.04 (s, 1C, C₁₄), 33.76 (s, 1C, C₂), 37.46 (s, 1C, C₅), 38.99 (s, 1C, C₄), 72.12 (s, C, C₇), 76.73 (s, 1C, C₆), 81.97 (s, 1C, C₁).

HRMS (ESI): m/z calcd for C₁₆H₃₁O₅S⁻: 335.18977 [M⁻]; found: 335.18848.

(110)
NaO₃SO
$$1 \xrightarrow{5} 4 \xrightarrow{6} 7 \xrightarrow{9} 11 \xrightarrow{13} 15 \xrightarrow{17} 17$$

 $2 \xrightarrow{3} 3 \xrightarrow{10} 10 \xrightarrow{12} 14 \xrightarrow{16} 18$

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.93 (t, 3H, H₁₈), 1.32 (m, 18H, H₉₋₁₇), 1.58 (m, 4H, H_{3,8}), 1.83 (m, 2H, H₂), 2.00 (m, 1H, H₄), 2.20 (m, 2H, H₅), 3.40 (d, 2H, H₇), 3.46 (t, 2H, H₆), 4.85 (m, 1H, H₁). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.42 (s, 1C, C₁₈), 23.72 (s, 1C, C₁₇), 27.27 (s, 1C, C₉), 28.21 (s, 1C, C₃), 30.73 (m, 7C, C_{8,10-15}), 33.06 (s, 1C, C₁₆), 33.78 (s, 1C, C₂), 37.48 (s, 1C, C₅), 39.02 (s, 1C, C₄), 72.14 (s, C, C₇), 76.76 (s, 1C, C₆), 81.97 (s, 1C, C₁). **HRMS (ESI)**: m/z calcd for C₁₈H₃₅O₅S⁻ : 363.22107 [M⁻]; found: 363.22025.

(13a)
NaO₃SO
$$1 = 0.5 = 6 = 7 = 9 = 11$$

NaO₃SO $0 = 8 = 10$

4

3

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.94 (t, 3H, H₁₂), 1.36 (m, 6H, H₉₋₁₁), 1.61 (m, 2H, H₈), 1.71–2.09 (m, 4H, H_{3,4}), 3.48 (m, 4H, H_{6,7}), 4.01–4.22 (m, 4H, H_{1,2,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.38 (s, 1C, C₁₂), 23.67 (s, 1C, C₁₁), 26.85 (d, 1C, C₉), 28.58 (s, 1C, C₃), 28.86 (s, 1C, C₄), 30.59 (s, 1C, C₈), 32.83 (s, 1C, C₁₀), 70.88 (s, 1C, C₁), 72.63 (s, 1C, C₇), 74.68 (s, 1C, C₆), 79.09 (s, 1C, C₂), 80.23 (s, 1C, C₅).

12

HRMS (ESI): m/z calcd for C₁₂H₂₃O₆S⁻: 295.12208 [M⁻]; found: 295.12085.



¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.92 (t, 3H, H₁₄), 1.32 (m, 10H, H₉₋₁₃), 1.58 (m, 2H, H₈), 1.69–2.04 (m, 4H, H_{3,4}), 3.45 (m, 4H, H_{6,7}), 3.97–4.21 (m, 4H, H_{1,2,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.29 (s, 1C, C₁₄), 23.71 (s, 1C, C₁₃), 27.21 (d, 1C, C₉), 28.64 (s, 1C, C₃), 28.75 (s, 1C, C₄), 30.42 (s, 1C, C₁₁), 30.56 (s, 1C, C₁₀), 30.68 (s, 1C, C₈), 33.01 (s, 1C, C₁₂), 70.88 (s, 1C, C₇), 72.65 (s, 1C, C₆), 74.71 (s, 1C, C₁), 79.08 (s, 1C, C₂), 80.27 (s, 1C, C₅). **HRMS (ESI)**: m/z calcd for C₁₄H₂₇O₆S⁻: 323.15338 [M⁻]; found: 323.15207.

(9)

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.90 (t, 3H, H₁₆), 1.30 (m, 14H, H₉₋₁₅), 1.56 (m, 2H, H₈), 1.72–2.02 (m, 4H, H_{3,4}), 3.45 (m, 4H, H_{6,7}), 3.95–4.19 (m, 4H, H_{1,2,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.44 (s, 1C, C₁₆), 23.74 (s, 1C, C₁₅), 27.22 (d, 1C, C₉), 28.68 (s, 1C, C₃), 28.79 (s, 1C, C₄), 30.46 (s, 1C, C₁₁), 30.60 (s, 1C, C₁₃), 30.71 (m, 3C, C_{8,10,12}), 33.08 (s, 1C, C₁₄), 70.87 (s, 1C, C₇), 72.67 (s, 1C, C₆), 74.73 (s, 1C, C₁), 79.05 (s, 1C, C₂), 80.29 (s, 1C, C₅). **HRMS (ESI)**: m/z calcd for C₁₆H₃₁O₆S⁻: 351.18468 [M⁻]; found: 351.18359.

(13d)

NaO₃SO
$$3 4$$
 $0 7 9 11 13 15 17$
 $8 10 12 14 16 18$

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.90 (t, 3H, H₁₈), 1.31 (m, 18H, H₉₋₁₇), 1.59 (m, 2H, H₈), 1.69–2.10 (m, 4H, H_{3,4}), 3.49 (m, 4H, H_{6,7}), 3.94–4.25 (m, 4H, H_{1,2,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 13.86 (s, 1C, C₁₈), 22.66 (s, 1C, C₁₇), 26.09 (d, 1C, C₉), 26.91 (s, 1C, C₃), 27.65 (s, 1C, C₄), 27.65 (s, 1C, C₁₅), 29.94 (m, C, C_{8,10-14}), 32.02 (s, 1C, C₁₆), 70.30 (s, 1C, C₇), 71.25 (s, 1C, C₆), 72.93 (s, 1C, C₁), 77.59 (s, 1C, C₂), 78.38 (s, 1C, C₅). **HRMS (ESI)**: m/z calcd for C₁₈H₃₅O₆S⁻: 379.21598 [M⁻]; found: 397.21524.

(13e)

NaO₃SO
$$3 4$$
 $0 7 9 11 13 15 17 19$
 $8 10 12 14 16 18 20$

¹**H-NMR** (400 MHz, MeOD): δ (ppm) 0.87 (t, 3H, H₂₀), 1.29 (m, 22H, H₉₋₁₉), 1.57 (m, 2H, H₈), 1.72–2.08 (m, 4H, H_{3,4}), 3.48 (m, 4H, H_{6,7}), 3.93–4.24 (m, 4H, H_{1,2,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 13.83 (s, 1C, C₂₀), 22.68 (s, 1C, C₁₉), 26.24 (d, 1C, C₉), 26.90 (s, 1C, C₃), 27.76 (s, 1C, C₄), 30.22 (m, 9C, C_{8,10-17}), 32.06 (s, 1C, C₁₈), 70.26 (s, 1C, C₇), 71.25 (s, 1C, C₆), 73.00 (s, 1C, C₁), 77.56 (s, 1C, C₂), 78.33 (s, 1C, C₅).

HRMS (ESI): m/z calcd for $C_{20}H_{39}O_6S$: 407.24728 [M]; found: 407.24585.

(15a)

NaO₃SO
$$3 - 4$$
 4 $0 - 9 - 11 - 13 - 15 - 17$ 16 18 $10 - 12 - 14 - 16 - 18$ $10 - 12 - 14 - 16 - 18$

7

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.90 (t, 3H, H₁₈), 1.17 (d, 3H, H₇), 1.31-1.56 (m, 21H, H₉₋₁₇), 1.78-2.04 (m, 4H, H_{3,4}), 3.32–3.61 (m, 3H, H_{6,8}), 3.93–4.25 (m, 4H, H_{1,2,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 13.86 (s, 1C, C₁₈), 19.13 (s, 1C, C₇), 22.65 (s, 1C, C₁₇), 25.58 (d, 1C, C₁₀), 26.76 (d, 1C, C₃), 27.63 (d, 1C, C₄), 29.14 (m, 5C, C₁₁₋₁₅), 31.99 (s, 1C, C₁₆), 36.25 (s, 1C, C₉), 70.31 (s, 1C, C₁), 70.51 (d, 1C, C₆), 76.22 (d, 1C, C₈), 77.59 (d, 1C, C₂), 78.67 (d, 1C, C₅). **HRMS (ESI)**: m/z calcd for C₁₈H₃₅O₆S⁻: 379.21598 [M⁻]; found: 379.21506.

(15b)



¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.90 (t, 3H, H₂₀), 1.16 (d, 3H, H₇), 1.31 (m, 20H, H₁₀₋₁₉), 1.56–2.04 (m, 6H, H_{3,4,9}), 3.31–3.60 (m, 3H, H_{6,8}), 3.93–4.25 (m, 4H, H_{1,2,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 13.87 (s, 1C, C₂₀), 19.18 (s, 1C, C₇), 22.68 (s, 1C, C₁₉), 25.64 (d, 1C, C₁₀), 26.87 (d, 1C, C₃), 27.78 (d, 1C, C₄), 30.03 (m, 7C, C₁₁₋₁₇), 32.03 (s, 1C, C₁₈), 36.32 (s, 1C, C₉), 70.30 (s, 1C, C₁), 70.55 (d, 1C, C₆), 76.22 (d, 1C, C₈), 77.58 (d, 1C, C₂), 78.66 (d, 1C, C₅). **HRMS (ESI)**: m/z calcd for C₂₀H₃₉O₆S⁻: 407.24728 [M⁻]; found: 407.24585.

$$NaO_{3}SO \underbrace{\begin{smallmatrix} 1 & 2 & 0 & 5 & 6 \\ 3 & 4 & 0 & 9 & 11 & 13 & 15 & 17 & 19 & 21 \\ \hline & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & \\ & &$$

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.93 (t, 3H, H₂₂), 1.14 (d, 3H, H₇), 1.32 (m, 24H, H₁₀₋₂₁), 1.54–2.01 (m, 6H, H_{3,4,9}), 3.37–3.57 (m, 3H, H_{6,8}), 3.98–4.21 (m, 4H, H_{1,2,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.46 (s, 1C, C₂₂), 19.94 (s, 1C, C₇), 23.73 (s, 1C, C₂₁), 26.61 (d, 1C, C₁₀), 28.64 (d, 1C, C₃), 28.87 (d, 1C, C₄), 30.76 (m, 9C, C₁₁₋₁₉), 33.07 (s, 1C, C₂₀), 37.59 (d, 1C, C₉), 70.94 (s, 1C, C₆), 72.38 (d, 1C, C₁), 77.42 (d, 1C, C₈), 79.02 (d, 1C, C₂), 80.47 (d, 1C, C₅). **HRMS (ESI)**: m/z calcd for C₂₂H₄₃O₆S⁻: 435.27858 [M⁻]; found: 435.27646.

(15d)

NaO₃SO
$$3 = 4$$
 7 $8 = 10 = 12 = 14 = 16 = 18 = 20 = 22 = 24$ $9 = 11 = 13 = 15 = 17 = 19 = 21 = 23$

¹**H-NMR** (400 MHz, MeOD): δ (ppm) = 0.91 (t, 3H, H₂₄), 1.14 (d, 3H, H₇), 1.30 (m, 28H, H₁₀₋₂₃), 1.53–2.05 (m, 6H, H_{3,4,9}), 3.35–3.55 (m, 3H, H_{6,8}), 3.96–4.19 (m, 4H, H_{1,2,5}). ¹³**C-NMR** (100 MHz, MeOD): δ (ppm) = 14.45 (s, 1C, C₂₄), 19.93 (s, 1C, C₇), 23.74 (s, 1C, C₂₃), 26.62 (d, 1C, C₁₀), 28.61 (d, 1C, C₃), 28.91 (d, 1C, C₄), 30.79 (m, 11C, C₁₁₋₂₁), 33.08 (s, 1C, C₂₂), 37.64 (d, 1C, C₉), 70.93 (s, 1C, C₆), 72.39 (d, 1C, C₁), 77.44 (d, 1C, C₈), 79.02 (d, 1C, C₂), 80.44 (d, 1C, C₅). **HRMS (ESI)**: m/z calcd for C₂₄H₄₇O₆S⁻: 463.30988 [M⁻]; found: 463.30966.

(15c)

Characterization of FF-Ether (2)

¹H-NMR Spectrum of C₁₃-FF-Ether (2a)



¹H-NMR Spectrum of C₁₅-FF-Ether (2b)



Characterization of FF-Surfactant (3)

¹H-NMR Spectrum of C₁₃-FF-Surfactant (3a)



¹H-NMR Spectrum of C₁₅-FF-Surfactant (3b)



Characterization of FFA-Ether (4)





Characterization of C₁₂-FFA-Surfactant (5)





Characterization of CPD-Ether (6)

¹H-NMR Spectrum of C₁₀-CPD-Ether (6a)



¹H-NMR Spectrum of C₁₂-CPD-Ether (6b)



¹H-NMR Spectrum of C₁₄-CPD-Ether (6c)



Characterization of CPD-Surfactant (7)

¹H-NMR Spectrum of C₁₀-CPD-Surfactant (7a)



¹H-NMR Spectrum of C₁₂-CPD-Surfactant (7b)



¹H-NMR Spectrum of C₁₄-CPD-Surfactant (7c)



Characterization of BHMF-Ether (8)

¹H-NMR Spectrum of C₁₂-BHMF-Ether (8)



Characterization of BHMF-Surfactant (9)





Characterization of HCPO-Ether (10)

¹H-NMR Spectrum of C₁₀-HCPO-Ether (10a)



¹H-NMR Spectrum of C₁₂-HCPO-Ether (10b)



Characterization of HCPO-Surfactant (11)

¹H-NMR Spectrum of C₁₀-HCPO-Surfactant (11a)



¹H-NMR Spectrum of C₁₂-HCPO-Surfactant (11b)



Characterization of lin-BHMTHF-Ether (12)

¹H-NMR Spectrum of C₆-lin-BHMTHF-Ether (12a)



¹H-NMR Spectrum of C₈-lin-BHMTHF-Ether (12b)



¹H-NMR Spectrum of C₁₀-lin-BHMTHF-Ether (12c)



¹H-NMR Spectrum of C₁₂-lin-BHMTHF-Ether (12d)



¹H-NMR Spectrum of C₁₄-lin-BHMTHF-Ether (12e)



Characterization of lin-BHMTHF-Surfactant (13)

¹H-NMR Spectrum of C₆-lin-BHMTHF-Surfactant (13a)



¹H-NMR Spectrum of C₈-lin-BHMTHF-Surfactant (13b)



¹H-NMR Spectrum of C₁₀-lin-BHMTHF-Surfactant (13c)



¹H-NMR Spectrum of C₁₂-lin-BHMTHF-Surfactant (13d)



¹H-NMR Spectrum of C₁₄-lin-BHMTHF-Surfactant (13e)



Characterization of branched-BHMTHF-Ether (14)

¹H-NMR Spectrum of C₁₂-branched-BHMTHF-Ether (14a)



¹H-NMR Spectrum of C₁₄-branched-BHMTHF-Ether (14b)



¹H-NMR Spectrum of C₁₆-branched-BHMTHF-Ether (14c)



¹H-NMR Spectrum of C₁₈-branched-BHMTHF-Ether (14d)



Characterization of branched-BHMTHF-Surfactant (15)

¹H-NMR Spectrum of C₁₂-branched-BHMTHF-Surfactant (15a)



¹H-NMR Spectrum of C₁₄-branched-BHMTHF-Surfactant (15b)



¹H-NMR Spectrum of C₁₆-branched-BHMTHF-Surfactant (15c)



¹H-NMR Spectrum of C₁₈-branched-BHMTHF-Surfactant (15d)



Physico-chemical properties

Surface tension isotherms-measurement of FF-Surfactant (3)



Surface tension isotherms-measurement of CPD-Surfactant (7)



Surface tension isotherms-measurement of HCPO-Surfactant (11)



Surface tension isotherms-measurement of lin-BHMTHF-Surfactant (13)





Interfacial tension towards isopropyl myristate-measurement of CPD-Surfactant (7)





Interfacial tension towards isopropyl myristate-measurement of lin-BHMTHF-Surfactant (13)



Interfacial tension towards isopropyl myristate-measurement of branched-BHMTHF-Surfactant (15)

