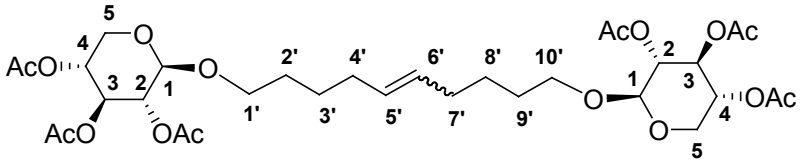
Supplementary data (deleu et al.)

Synthesis conditions for the different xylose-based bolaforms and their chemical characterization

1',10'-bis-dec-5-enyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside 1ββ

A solution of Grubbs I catalyst (13.8 mg, 0.0167 mmol, 0.1 eq.) in CH_2Cl_2 (2 mL) is added through a canula to a solution of hex-5'-enyl (2,3,4-tri-O-acetyl)-b-D-xylopyranoside (60 mg, 0.167 mmol) in CH_2Cl_2 (2 mL) . After stirring for 24 h, the solvent is evaporated under reduced pressure, the residue is then dissolved in diethylether (3 mL) and stirred on charcoal for 2 h and filtered on Celite. After evaporation of the solvent, the residue obtained is purified by column chromatography (silica gel, 10% ethyl acetate in petroleum ether) to give the 1,10-bis-dec-5'enyl(2,3,4-tri-*O*-acétyl)-β-D-xylopyranoside as a yellow oil (42.7 mg, 74%).



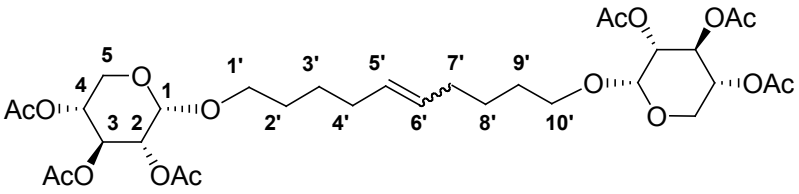
(*Z*/*E* = 22/78) (688 g/mol)

IR (Film): 2939, 2864, 1755, 434,1371,1224, 1047, 985, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.38-1.49 (m, 4H; $H_{3'}$, $H_{8'}$), 1.51-1.68 (m, 4H; $H_{2'}$, $H_{9'}$), 1.97-2.13 (m, 13H; H_4, H_7, 3 CH_3), 3.36 (dd, 2H, J = 8.8 Hz, J = 11.8 Hz; H_{5a}), 3.46 (dt, 2H, J = 3.2 Hz, J = 9.6 Hz; $H_{1'}$, $H_{10'}$), 3.82 (dt, 2H, J = 3.3 Hz, J = 9.6 Hz; $H_{1'}$, $H_{10'}$), 4.12 (dd, 2H, J = 5.1 Hz, J = 11.8 Hz; H_{5e}), 4.40 (d, 2H, J = 6.8 Hz; $H_{1\beta}$), 4.80-5.95 (m, 4H; H_2, H_4), 5.16 (t, 2H, J = 8.6 Hz, H_3), 5.22-5.34 (m, 2H; $H_{5'}$, $H_{6'}$) ppm; ^{13}C NMR ($CDCl_3$, 250 MHz): δ = 21.3, 21.4, 21.5 (6 CH_3), 26.5, 26.6 ($C_{3'}$, $C_{8'}$), 27.5 ($C_{4'Z}$, $C_{7'Z}$), 29.6, 29.7 ($C_{2'}$, $C_{9'}$), 33.8 ($C_{4'E}$, $C_{7'E}$), 62.7

(C_5), 69.6 (C_4), 70.2 ($C_{1'}$, $C_{10'}$), 71.5 (C_2), 72.2 (C_3), 101.3 ($C_{1\beta}$), 130.4 ($C_{5'Z}$, $C_{6'Z}$), 130.9 ($C_{5'E}$, $C_{6'E}$), 170.0, 170.5, 170.7 (6 C=O) ppm; HRMS calculated for $C_{32}H_{48}O_{16}$ [M+Na^+]: 711.2840 ; found: 711.2819.

1',10'-bis-dec-5'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside 1αα

A solution of Grubbs I catalyst (38.9 mg, 0.047 mmol, 0.1 eq.) in CH_2Cl_2 (3 mL) is added with a shoot-syringe (0.7 mL/h) to a solution of hex-5'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside (165 mg, 0.46 mmol) in CH_2Cl_2 (5 mL) . After stirring for 24h, the solvent is evaporated under reduced pressure, the residue is then dissolved in diethylether (3 mL) and stirred on charcoal for 3 h and filtered on Celite. After evaporation of the solvent, the residue obtained is purified by column chromatography (silica gel, 10% ethyl acetate in petroleum ether) to give the 1,10-bis-dec-5'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside as a yellow oil (142.3 mg, 90%).



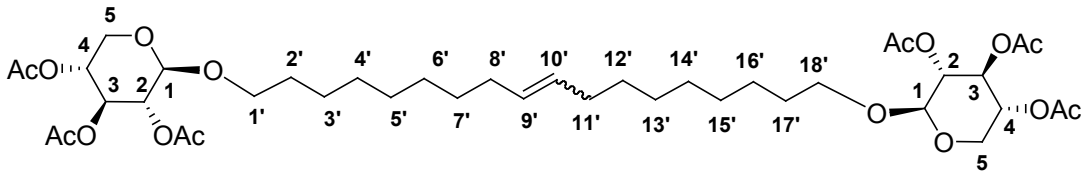
(*Z*/*E* = 26/74) (688 g/mol)

IR (Film): 2938, 2848, 1755, 1434, 1371, 1251, 1146, 1045, 943, 733 cm^{-1}; NMR ^1H ($CDCl_3$, 250 MHz): δ = 1.35-1.44 (m, 4H; $H_{3'}$, $H_{8'}$), 1.50-1.61 (m, 4H; $H_{2'}$, $H_{9'}$), 1.92-2.06 (m, 13H; $H_{4'}$, $H_{7'}$, 6 CH_3), 3.20-3.40 (m, 2H; $H_{1'}$, $H_{10'}$), 3.48-3.63 (m, 4H; H_5), 3.64-3.78 (m, 2H; $H_{1'}$, $H_{10'}$), 4.70 (dd, 2H, J = 3.6 Hz, J = 10.1 Hz; H_2), 4.82-4.89 (m, 2H, H_4), 4.91 (d, 2H, J = 3.4 Hz; $H_{1\alpha}$), 5.23-5.36 (m, 2H; $H_{5'}$, $H_{6'}$), 5.41 (dd, 2H, J = 9.8 Hz, J = 9.9 Hz; H_3) ppm; NMR ^{13}C ($CDCl_3$, 250 MHz): δ = 21.2, 21.3 (6 CH_3), 26.5, 26.7 ($C_{3'}$, $C_{8'}$), 27.6 ($C_{4'Z}$, $C_{7'Z}$), 29.3, 29.5 ($C_{2'}$, $C_{9'}$), 32.7 ($C_{4'E}$, $C_{7'E}$), 58.8 (C_5), 68,9 ($C_{1'}$, $C_{10'}$), 70.0 (C_4), 70.3 (C_3), 71.7 (C_2),

96.2 ($C_{1\alpha}$), 130.4 ($C_{5'Z}$, $C_{6'Z}$), 130.9 ($C_{5'E}$, $C_{6'E}$), 170.5, 170.6, 170.7 (6 C=O) ppm; HRMS calculated for $C_{32}H_{48}O_{16}$ [M+Na^+]: 711.2840 ; found: 711.2855.

1',18'-bis-octadec-9'-enyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside 2ββ

The same procedure as described for the synthesis of **1ββ** with a solution of dec-9'-enyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside (100 mg, 0.24 mmol) in CH_2Cl_2 (3 mL) and a solution of Grubbs I catalyst (38.9 mg, 0.047 mmol, 0.1 eq.) in CH_2Cl_2 (2 mL) was used. The 1',18'-bis-octadec-9'-enyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside is obtained as a colorless paste (67 mg, 69%).

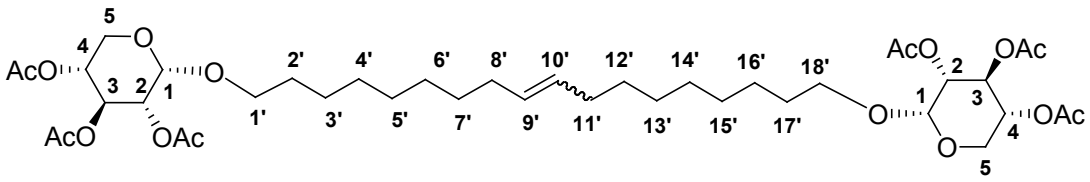


(*Z*/*E* = 19/81*)* (800 g/mol)

IR (Film): 2926, 2854, 1755, 1443, 1370, 1225, 1048 cm^{-1}; NMR ^1H ($CDCl_3$, 250 MHz): δ = 1.30-1.47 (m, 20H; $H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$, $H_{7'}$, $H_{12'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$), 1.39-1.56 (m, 4H; $H_{2'}$, $H_{17'}$), 1.93-2.08 (m, 22H; $H_{8'}$, $H_{11'}$, 6 CH_3), 3.29 (dd, 2H, J = 9.0 Hz, J = 11.7 Hz, H_{5a}), 3.34-3.44 (m, 2H; $H_{1'}$, $H_{18'}$), 3.69-3.79 (m, 2H; $H_{1'}$, $H_{18'}$), 4.04 (dd, 2H, J = 5.1 Hz, J = 11.7 Hz, H_{5e}), 4.39 (d, 2H, J = 6.8 Hz, $H_{1\beta}$), 4.79-4.94 (m, 4H; H_2, H_4), 5.09 (dd, 2H; J = 8.5 Hz, J = 8.6 Hz, H_3), 5.22-5.36 (m, 2H; $H_{9'}$, $H_{10'}$) ppm; NMR ^{13}C ($CDCl_3$, 250 MHz): δ = 21.0, 21.1, 21.2 (6 CH_3), 26.3, 26.4 ($C_{3'}$, $C_{16'}$), 27.4 ($C_{8'Z}$, $C_{11'Z}$), 29.5, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 30.2 ($C_{2'}$, $C_{4'}$, $C_{5'}$, $C_{6'}$, $C_{7'}$, $C_{12'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{17'}$), 32.9 ($C_{8'E}$, $C_{11'E}$), 62.4 (C_5), 69.3 (C_4), 70.1 ($C_{1'}$, $C_{18'}$), 71.3 (C_2), 71.9 (C_3), 101.1 ($C_{1\beta}$), 130.4 ($C_{9'Z}$, $C_{10'Z}$), 130.7 ($C_{9'E}$, $C_{10'E}$), 169.7, 169.8, 170.2 (6 C=O) ppm; HRMS calculated for $C_{40}H_{64}O_{16}$ [M+Na^+]: 823.4092; found: 823.4095.

1',18'-bis-octadec-9'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside 2αα

A solution of Grubbs I catalyst (32.1 mg, 0.039 mmol, 0.1 eq.) in CH_2Cl_2 (3 mL) is added in three times (10.7 mg in CH_2Cl_2 (1 mL) every two hours during 6 hours) to a solution of dec-9'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside (160 mg, 0.386 mmol) in CH_2Cl_2 (3 mL). After stirring for 24 h, the solvent is evaporated under reduced pressure and the metallic residues are precipitated by adding petroleum ether (5 mL) and filtered on cotton. After evaporation of the solvent, the residue obtained is purified by column chromatography (silica gel, 10% ethyl acetate in petroleum ether) to give the 1',18'-bis-octadec-9'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside as a colorless paste (105 mg, 69%).

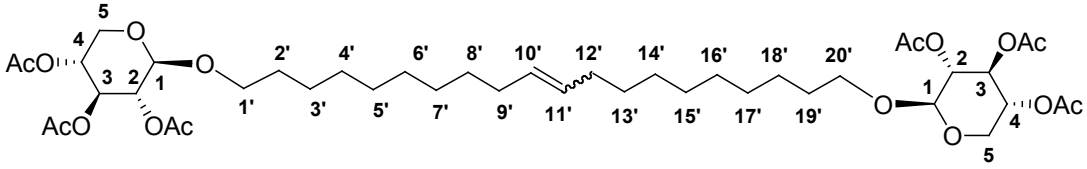


(*Z*/*E* = 15/85) (800 g/mol)

IR (Film): 2828, 2855, 1755, 1434, 1370, 1229, 1145, 1049, 907, 728 cm^{-1}; NMR ^1H ($CDCl_3$, 250 MHz): δ = 1.-1.47 (m, 20H; $H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$, $H_{7'}$, $H_{12'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$), 1.50-1.61 (m, 4H; $H_{2'}$, $H_{17'}$), 1.89-2.11 (m, 22H; $H_{8'}$, $H_{11'}$, 6 CH_3), 3.31-3.46 (m, 2H, $H_{1'}$, $H_{18'}$), 3.53-3.61 (m, 4H; H_5), 3.62-3.78 (m, 2H; $H_{1'}$, $H_{18'}$), 4.70 (dd, 2H, J = 3.3 Hz, J = 10.0 Hz; H_2), 4.82-4.89 (m, 2H; H_4), 4.91 (d, 2H, J = 3.2 Hz, $H_{1\alpha}$), 5.23-5.36 (m, 2H; $H_{9'}$, $H_{10'}$), 5.41 (dd, 2H, J = 9.7 Hz, J = 9.9 Hz, H_3); NMR ^{13}C ($CDCl_3$, 250 MHz): δ = 21.1, 21.2, 21.3 (6 CH_3), 26.4 ($C_{3'}$, $C_{16'}$), 27.6 ($C_{8'Z}$, $C_{11'Z}$), 29.5, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 30.2 ($C_{2'}$, $C_{4'}$, $C_{5'}$, $C_{6'}$, $C_{7'}$, $C_{12'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{17'}$), 32.9 ($C_{8'E}$, $C_{11'E}$), 58.6 (C_5), 68.9 ($C_{1'}$, $C_{18'}$), 69.9 (C_4), 70.1 (C_3), 71.6 (C_2), 96.0 ($C_{1\alpha}$), 130.3 ($C_{9'Z}$, $C_{10'Z}$), 130.7 ($C_{9'E}$, $C_{10'E}$), 170.4, 170.5, 170.6 (6 C=O); HRMS calculated for $C_{40}H_{64}O_{16}$ [$M+Na^+$]: 823.4092; found: 823.4075.

1',20'-bis-eicos-10'-enyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside 3ββ

The same procedure as described for the synthesis of **1ββ** with a solution of undec-10'-enyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside (60 mg, 0.14 mmol) in CH_2Cl_2 (1 mL) and a solution of Grubbs I catalyst (11.5 mg, 0.014 mmol, 0.1 eq.) in CH_2Cl_2 (2 mL) was used. The 1',20'-bis-eicos-10'-enyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside is obtained as a white paste (33 mg, 76%).

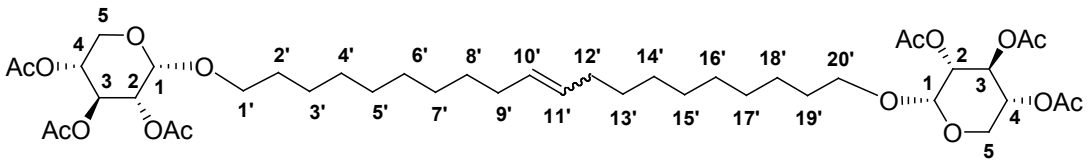


(*Z*/*E* = 18/82) (828 g/mol)

IR (Film): 2926, 2854, 1755, 1432, 1371, 1225, 1047 cm^{-1}; NMR ^1H ($CDCl_3$, 250 MHz): δ = 1.11-1.37 (m, 24H; $H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$, $H_{7'}$, $H_{8'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$, $H_{17'}$, $H_{18'}$), 1.39-1.56 (m, 4H; $H_{2'}$, $H_{19'}$), 1.93-2.08 (m, 22H; $H_{9'}$, $H_{12'}$, 6 CH_3), 3.29 (dd, 2H, J = 8.9 Hz, J = 11.8 Hz; H_{5a}), 3.35-3.45 (m, 2H; $H_{1'}$, $H_{20'}$), 3.67-3.81 (m, 2H; $H_{1'}$, $H_{20'}$), 4.04 (dd, 2H, J = 5.1 Hz, J = 11.8 Hz; H_{5e}), 4.40 (d, 2H, J = 6.8 Hz; $H_{1\beta}$), 4.80-4.94 (m, 4H; H_2, H_4), 5.09 (dd, 2H, J = 8.5 Hz, J = 8.6 Hz; H_3), 5.22-5.36 (m, 2H; $H_{10'}$, $H_{11'}$) ppm; NMR ^{13}C ($CDCl_3$, 250 MHz): δ = 21.0, 21.1, 21.2 (6 CH_3), 26.3, 26.4 ($C_{3'}$, $C_{18'}$), 27.6 ($C_{9'Z}$, $C_{12'Z}$), 29.5, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 30.2 ($C_{2'}$, $C_{4'}$, $C_{5'}$, $C_{6'}$, $C_{7'}$, $C_{8'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{16'}$, $C_{17'}$, $C_{19'}$), 33.0 ($C_{9'E}$, $C_{12'E}$), 62.4 (C_5), 69.3 (C_4), 70.1 ($C_{1'}$, $C_{20'}$), 71.3 (C_2), 71.9 (C_3), 101.1 ($C_{1\beta}$), 130.3 ($C_{10'Z}$, $C_{11'Z}$), 130.7 ($C_{10'E}$, $C_{11'E}$), 169.8, 170.3, 170.5 (6 C=O) ppm; Anal. Calculated for $C_{42}H_{68}O_{16}$: C: 60.85, H: 8.27; found C: 61.12, H: 8.69; HRMS calculated for $C_{42}H_{68}O_{16}$ [$M+Na^+$]: 851.4405; found: 851.4398.

1'-20'-bis-eicos-10'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside 3αα

The same procedure as described for the synthesis of **1ββ** with a solution of undec-10'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside (115 mg, 0.27 mmol) in CH_2Cl_2 (3 mL) and a solution of Grubbs I catalyst (22.2 mg, 0.027 mmol, 0.1 eq.) in CH_2Cl_2 (2 mL) was used. The 1',20'-bis-eicos-10'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside is obtained as a yellow paste (89 mg, 80%).



(*Z*/*E* 16/84) (828 g/mol)

IR (Film): 2827, 2854, 1755, 1433, 1371, 1229, 1145, 1050, 729 cm^{-1}; NMR ^{1}H ($CDCl_3$, 250 MHz): δ = 1.10-1.34 (m, 24H; $H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$, $H_{7'}$, $H_{8'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$, $H_{17'}$, $H_{18'}$), 1.45-1.57 (m, 4H; $H_{2'}$, $H_{19'}$), 1.89-2.01 (m, 22H, $H_{9'}$, $H_{12'}$, 6 CH_3), 3.21-3.37 (m, 2H; $H_{1'}$, $H_{20'}$), 3.47-3.61 (m, 4H; H_5), 3.62-3.76 (m, 2H; $H_{1'}$, $H_{20'}$), 4.70 (dd, 2H, J = 3.6 Hz, J = 10.1 Hz; H_2), 4.82-4.89 (m, 2H; H_4), 4.91 (d, 2H, J = 3.3 Hz, $H_{1\alpha}$), 5.23-5.33 (m, 2H; $H_{10'}$, $H_{11'}$), 5.40 (dd, 2H, J = 9.7 Hz, J = 9.9 Hz; H_3) ppm; NMR ^{13}C ($CDCl_3$, 250 MHz): δ = 21.1, 21.2, 21.3 (6 CH_3), 26.4 ($C_{3'}$, $C_{18'}$), 27.7 ($C_{9'Z}$, $C_{12'Z}$), 29.5, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 30.2 ($C_{2'}$, $C_{4'}$, $C_{5'}$, $C_{6'}$, $C_{7'}$, $C_{8'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{16'}$, $C_{17'}$, $C_{19'}$), 32.9 ($C_{9'E}$, $C_{12'E}$), 58.6 (C_5), 68.9 ($C_{1'}$, $C_{20'}$), 69.9 (C_4), 70.2 (C_3), 71.7 (C_2), 96.1 ($C_{1\alpha}$), 130.3 ($C_{10'Z}$, $C_{11'Z}$), 130.8 ($C_{10'E}$, $C_{11'E}$), 170.4, 170.5, 170.7 (6 C=O) ppm; HRMS calculated for $C_{42}H_{68}O_{16}$ [$M+Na^+$]: 851.4405; found: 851.4400.

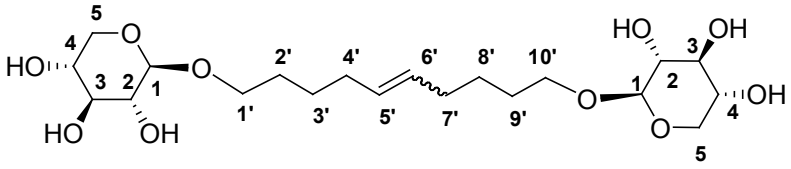
Deacetylation of the homodimers: general procedure

The acetylated compound was dissolved in 1:1 MeOH-CH_2Cl_2 and a 0.5 M solution of NaOMe (1.5 equiv) was then added. After stirring for 24 h at room temperature, the mixture

was neutralized with Amberlite IR120® and filtered to liberate almost quantitatively the unprotected compound.

1',10'-bis-dec-5'-enyl-β-D-xylopyranoside 1'ββ

The general procedure of deacetylation with respectively the 1',10'-bis-dec-5'-enyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside (30 mg, 0.0436 mmol) in a mixture of CH_2Cl_2/MeOH (0.8 mL) and a 0.5 M methanolic solution of sodium methanolate (0.1 mL, 0.131 mmol) is used. The 1',10'-bis-dec-5'-enyl-β-D-xylopyranoside is obtained as a yellow paste (18.3 mg, 95%).



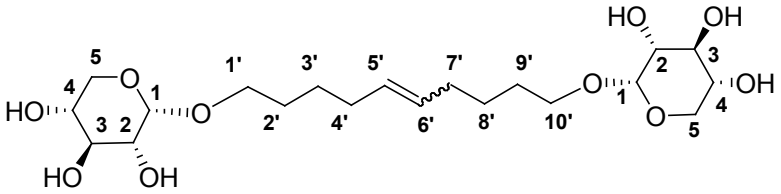
(*Z*/*E* = 22/78) (436 g/mol)

IR (Film): 3373, 2919, 2849, 1591, 1465, 1351, 1048, 970 cm^{-1}; NMR ^1H (MeOD, 250 MHz): δ = 1.28-1.42 (m, 4H; $H_{3'}$, $H_{8'}$), 1.44-1.62 (m, 4H; $H_{2'}$, $H_{9'}$), 1.87-2.05 (m, 4H; $H_{4'}$, $H_{7'}$), 2.85-3.00 (m, 4H, H_2, H_{5a}), 3.01-3.19 (m, 2H, H_3), 3.20-3.40 (m, 6H; $H_{1'}$, $H_{10'}$, H_4), 3.50-3.71 (m, 6H; $H_{1'}$, $H_{10'}$, H_{5e}), 3.98 (d, 2H; J = 7.3 Hz, $H_{1\beta}$), 4.70 (s, 6H, 6 OH), 5.19 (m, 2H; $H_{5'}$, $H_{6'}$) ppm; NMR ^{13}C (MeOD, 250 MHz): δ = 27.5, 27.6 ($C_{3'}$, $C_{8'}$), 28.3 ($C_{4'Z}$, $C_{7'Z}$), 30.7, 30.8 ($C_{2'}$, $C_{9'}$), 33.8 ($C_{4'E}$, $C_{7'E}$), 67.3 (C_5), 71.1 ($C_{1'}$, $C_{10'}$), 71.6 (C_4), 75.3 (C_2), 78.2 (C_3), 105.4 ($C_{1\beta}$), 131.3 ($C_{5'Z}$, $C_{6'Z}$), 131.9 ($C_{5'E}$, $C_{6'E}$) ppm; HRMS calculated for $C_{20}H_{36}O_{10}$ [M+Na^+]: 459.2206; found: 459.2222.

1'-10'-bis-dec-5'-enyl-α-D-xylopyranoside 1'αα

The general procedure of deacetylation with respectively the 1',10'-bis-dec-5'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside (539 mg, 0.783 mmol) in a mixture of CH_2Cl_2/MeOH (26 mL)

and a 0.5 M methanolic solution of sodium methanolate (4.7 mL, 2.35 mmol) was used. The 1',10'-bis-dec-5'-enyl-α-D-xylopyranoside is obtained as a yellow paste (337.9 mg, 99%).

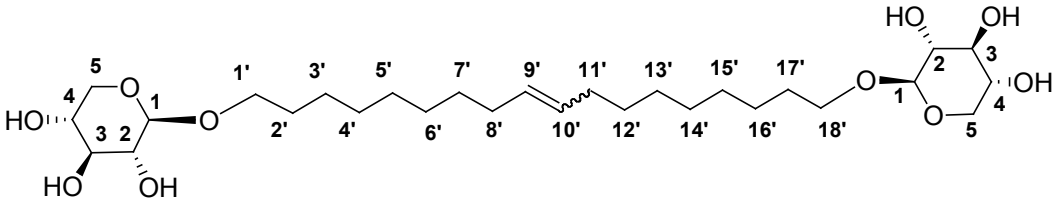


(*Z*/*E* = 26/74) (436 g/mol)

IR (Film): 3373, 2933, 1595, 1437, 1352, 1043, 944 cm^{-1}; NMR ^{1}H (MeOD, 250 MHz): δ = 1.28-1.42 (m, 4H; $H_{3'}$, $H_{8'}$), 1.44-1.62 (m, 4H; $H_{2'}$, $H_{9'}$), 1.87-2.05 (m, 4H; $H_{4'}$, $H_{7'}$), 3.23-3.76 (m, 14H; $H_{1'}$, $H_{10'}$, H_2, H_3, H_4, H_{5a}, H_{5e}), 4.67 (d, 2H; J = 3.4 Hz, $H_{1\alpha}$), 4.84 (s, 6H; 6 OH), 5.31-5.58 (m, 2H; $H_{5'}$, $H_{6'}$) ppm; NMR ^{13}C (MeOD, 250 MHz): δ = 27.7, 27.8 ($C_{3'}$, $C_{8'}$), 28.4 ($C_{4'Z}$, $C_{7'Z}$), 30.5, 30.6 ($C_{2'}$, $C_{9'}$), 33.8 ($C_{4'E}$, $C_{7'E}$), 63.4 (C_5), 69.5 ($C_{1'}$, $C_{10'}$), 72.0 (C_4), 74.0 (C_2), 75.6 (C_3), 100.7 ($C_{1\alpha}$), 131.2 ($C_{5'Z}$, $C_{6'Z}$), 131.9 ($C_{5'E}$, $C_{6'E}$) ppm; HRMS calculated for $C_{20}H_{36}O_{10}$ [$M+Na^{+}$]: 459.2206 ; found: 459.2193.

1'-18'-bis-octadec-9-enyl-β-D-xylopyranoside 2'ββ

The general procedure with respectively the 1',18'-bis-octadec-9-enyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside (51 mg, 0.0637 mmol) in a mixture of CH_2Cl_2/MeOH (2.4 mL) and a 0.5 M methanolic solution of sodium methanolate (0.38 mL, 0.191 mmol) was used. The 1',18'-bis-octadec-9-enyl-β-D-xylopyranoside is obtained as a white paste (33.9 mg, 97%).

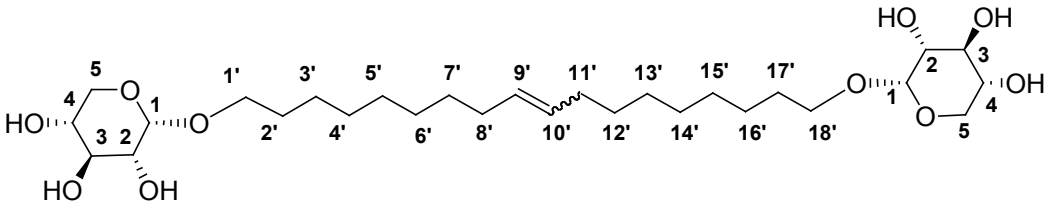


(*Z*/*E* = 19/81) (548 g/mol)

IR (Film): 3383, 2918, 2852, 1589, 1434, 1351, 1049, 980 cm^{-1}; NMR ^{1}H (MeOD, 250 MHz): δ = 1.12-1.38 (m, 20H; $H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$, $H_{7'}$, $H_{12'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$), 1.41-1.58 (m, 4H; $H_{2'}$, $H_{17'}$), 1.81-1.99 (m, 4H; $H_{8'}$, $H_{11'}$), 3.01-3.15 (m, 4H, H_2, H_{5a}), 3.16-3.28 (m, 2H; H_3), 3.32-3.49 (m, 6H; $H_{1'}$, $H_{18'}$, H_4), 3.59-380 (m, 6H; $H_{1'}$, $H_{18'}$, H_{5e}), 4.09 (d, 2H, J = 7.4 Hz, $H_{1\beta}$), 4.80 (s, 6H; 6 OH), 5.22-5.31 (m, 2H, $H_{9'}$, $H_{10'}$) ppm; NMR ^{13}C (MeOD, 250 MHz): δ = 27.5, 27.7 ($C_{3'}$, $C_{16'}$), 28.6 ($C_{8'Z}$, $C_{11'Z}$), 30.6, 30.7, 30.8 30.9, 31.0, 31.1 31.2 ($C_{2'}$, $C_{4'}$, $C_{5'}$, $C_{6'}$, $C_{7'}$, $C_{12'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{17'}$), 34.0 ($C_{8'E}$, $C_{11'E}$), 67.3 (C_5), 71.3 ($C_{1'}$, $C_{18'}$), 71.6 (C_4), 75.2 (C_2), 78.2 (C_3), 105.5 ($C_{1\beta}$), 131.3 ($C_{9'Z}$, $C_{10'Z}$), 131.9 ($C_{9'E}$, $C_{10'E}$) ppm; HRMS calculated for $C_{28}H_{52}O_{10}$ [$M+Na^{+}$]: 571.3458; found: 571.3439.

1'-18'-bis-octadec-9'-enyl-α-D-xylopyranoside 2'αα

The general procedure of deacetylation with respectively the 1',18'-bis-octadec-9'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside (100 mg, 0.125 mmol) in a mixture of CH_2Cl_2/MeOH (4.6 mL) and a 0.5 M methanolic solution of sodium methanolate (0.75 mL, 0.375 mmol) was used. The 1',18'-bis-octadec-9'-enyl-α-D-xylopyranoside is obtained as a yellow paste (67.1 mg, 98%).



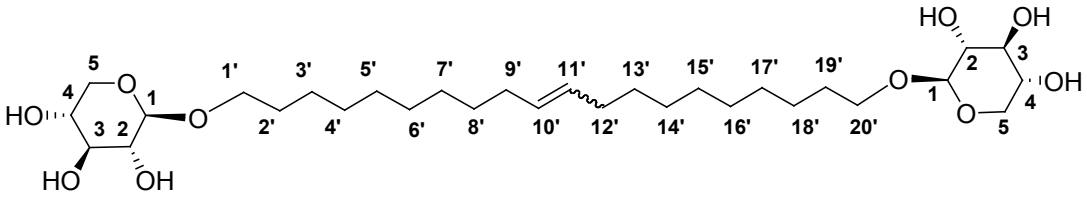
(*Z*/*E* = 15/85) (548 g/mol)

IR (Film): 3385, 2920, 2852, 1592, 1468, 1144, 1043 cm^{-1}; NMR ^{1}H (MeOD, 250 MHz): δ = 1.11-1.29 (m, 20H; $H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$, $H_{7'}$, $H_{12'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$), 1.32-1.53 (m, 4H; $H_{2'}$,

$H_{17'}$), 1.71-1.90 (m, 4H; $H_{8'}$, $H_{11'}$), 3.13-3.58 (m, 14H; $H_{1'}$, $H_{18'}$, H_2, H_3, H_4, H_{5a}, H_{5e}), 4.49 (d, 2H; J = 3.6 Hz, $H_{1\alpha}$), 4.68 (s, 6H; 6 OH), 5.10-5.25 (m, 2H; $H_{9'}$, $H_{10'}$) ppm; NMR ^{13}C (MeOD, 250 MHz): δ = 27.6, 27.7 ($C_{3'}$, $C_{16'}$), 28.6 ($C_{8'Z}$, $C_{11'Z}$), 30.6, 30.7, 30.8 30.9, 31.0, 31.1 31.2 ($C_{2'}$, $C_{4'}$, $C_{5'}$, $C_{6'}$, $C_{7'}$, $C_{12'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{17'}$), 34.1 ($C_{8'E}$, $C_{11'E}$), 63.4 (C_5), 69.7 ($C_{1'}$, $C_{18'}$), 71.9 (C_4), 73.9 (C_2), 75.6 (C_3), 100.7 ($C_{1\alpha}$), 131.3 ($C_{9'Z}$, $C_{10'Z}$), 131.9 ($C_{9'E}$, $C_{10'E}$) ppm; HRMS calculated for $C_{28}H_{52}O_{10}$ [$M+Na^+$]: 571.3458; found: 571.3454.

1'-20'-bis-eicos-10'-enyl-β-D-xylopyranoside 3'ββ

The general procedure of deacetylation with respectively the 1',20'-bis-eicos-10'-enyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside (70 mg, 0.084 mmol) in a mixture of CH_2Cl_2/MeOH (10 mL) and a 0.5 M methanolic solution of sodium methanolate (0.5 mL, 0.253 mmol) was used. The 1',20'-bis-eicos-10'-enyl-β-D-xylopyranoside is obtained as a yellow paste (46.9 mg, 97%).



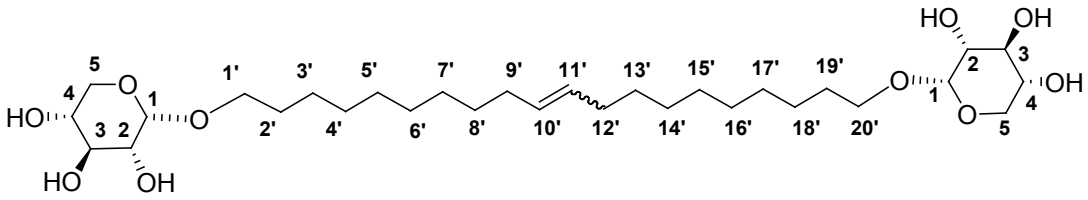
(*Z*/*E* = 18/82) (576 g/mol)

IR (Film): 3383, 2918, 2852, 1589, 1434, 1351, 1049, 980 cm^{-1}; NMR ^1H (MeOD, 250 MHz): δ = 1.12-1.38 (m, 24H; $H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$, $H_{7'}$, $H_{8'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$, $H_{17'}$, $H_{18'}$), 1.41-1.58 (m, 4H; $H_{2'}$, $H_{19'}$), 1.81-1.99 (m, 4H; $H_{9'}$, $H_{12'}$), 3.01-3.15 (m, 4H; H_2, H_{5a}), 3.16-3.28 (m, 2H; H_3), 3.32-3.49 (m, 6H; $H_{1'}$, $H_{20'}$, H_4), 3.59-3.80 (m, 6H; $H_{1'}$, $H_{20'}$, H_{5e}), 4.09 (d, 2H; J = 7.4 Hz, $H_{1\beta}$), 4.80 (s, 6H; 6 OH), 5.22-5.31 (m, 2H; $H_{10'}$, $H_{11'}$) ppm; NMR ^{13}C (MeOD, 250 MHz): δ = 27.5, 27.7 ($C_{3'}$, $C_{18'}$), 28.6 ($C_{9'Z}$, $C_{12'Z}$), 30.6, 30.7, 30.8 30.9, 31.0, 31.1 31.2 ($C_{2'}$, $C_{4'}$, $C_{5'}$, $C_{6'}$, $C_{7'}$, $C_{8'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{16'}$, $C_{17'}$, $C_{19'}$), 34.0 ($C_{9'E}$, $C_{12'E}$), 67.3 (C_5),

71.3 ($C_{1'}$, $C_{20'}$), 71.6 (C_4), 75.2 (C_2), 78.2 (C_3), 105.5 ($C_{1\beta}$), 131.3 ($C_{10'Z}$, $C_{11'Z}$), 131.9 ($C_{10'E}$, $C_{11'E}$) ppm; HRMS calculated for $C_{30}H_{56}O_{10}$ [M+Na^+]: 599.3771; found: 599.3759.

1'-20'-bis-eicos-10'-enyl-α-D-xylopyranoside 3'αα

The general procedure of deacetylation with respectively the 1',20'-bis-eicos-10'-enyl(2,3,4-tri-*O*-acetyl)-α-D-xylopyranoside (89 mg, 0.107 mmol) in a mixture of CH_2Cl_2/MeOH (4.6 mL) and a 0.5 M methanolic solution of sodium methanolate (0.64 mL, 0.321 mmol) was used. The 1',20'-bis-eicos-10'-enyl-α-D-xylopyranoside is obtained as a white paste (58.5 mg, 95%).

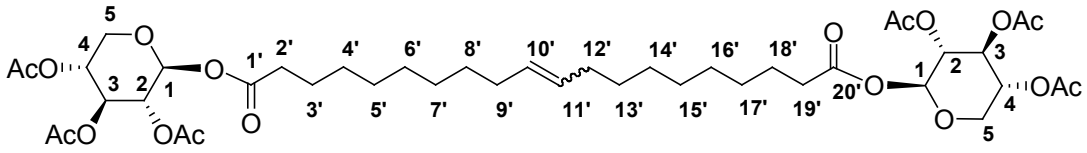


(*Z*/*E* = 16/84) (576 g/mol)

IR (Film): 3380, 2927, 2849, 1593, 1448, 1350, 1043 cm^{-1}; NMR ^1H (D_2O, 250 MHz): δ = 1.01-1.32 (m, 24H; $H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$, $H_{7'}$, $H_{8'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$, $H_{17'}$, $H_{18'}$), 1.33-1.61 (m, 4H; $H_{2'}$, $H_{19'}$), 1.83-2.01 (m, 4H; $H_{9'}$, $H_{12'}$), 3.16-3.67 (m, 14H; $H_{1'}$, $H_{20'}$, H_2, H_3, H_4, H_{5a}, H_{5e}), 4.61 (d, 2H, J = 3,4 Hz; $H_{1\alpha}$), 4.82 (s, 6H; 6 OH), 5.21-5.38 (m, 2H; $H_{10'}$, $H_{11'}$) ppm; NMR ^{13}C (D_2O, 250 MHz): δ = 27.6, 27.7 ($C_{3'}$, $C_{18'}$), 28.6 ($C_{9'Z}$, $C_{12'Z}$), 30.6, 30.7, 30.8, 30.9, 31.0, 31.1, 31.2 ($C_{2'}$, $C_{4'}$, $C_{5'}$, $C_{6'}$, $C_{7'}$, $C_{8'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{17'}$, $C_{19'}$), 34.0 ($C_{9'E}$, $C_{12'E}$), 63.5 (C_5), 69.7 ($C_{1'}$, $C_{20'}$), 71.9 (C_4), 73.9 (C_2), 75.5 (C_3), 100.7 ($C_{1\alpha}$), 131.3 ($C_{10'Z}$, $C_{11'Z}$), 131.9 ($C_{10'E}$, $C_{11'E}$) ppm; HRMS calculated for $C_{30}H_{56}O_{10}$ [M+Na^+]: 599.3771; found: 599.3777.

1',20'-bis-eicos-10'-enedioyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside 4ββ

A solution of Grubbs I catalyst (19 mg, 0.023 mmol, 0.1 eq.) in CH_2Cl_2 (3 mL) is added to a solution of undec-10'-enoyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside (100 mg, 0.23 mmol, 1 eq.) in dichloromethane (3 mL) . After stirring for 20 h at 40°C, the solvent is evaporated under reduced pressure, the residue is then dissolved in diethylether (10 mL) and stirred on charcoal for 2 h and filtered on Celite. After evaporation of the solvent, the residue obtained is purified by flash chromatography (silica gel, 10% ethyl acetate in petroleum ether) to give the 1',20'-bis-eicos-10'-enedioyl(2,3,4-tri-*O*-acetyl)-β-D-xylopyranoside as a white paste (66 mg, 67%).



(*E*/*Z* = 78/22) (857 g/mol)

IR (Film): 2920, 2852, 1752, 1377, 1233, 1089 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.19-1.31 (m, 20H; $H_{4'}$, $H_{5'}$, $H_{6'}$, $H_{7'}$, $H_{8'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$, $H_{17'}$), 1.48-1.69 (m, 4H; $H_{3'}$, $H_{18'}$), 1.99-2.06 (m, 22H; $H_{9'}$, $H_{12'}$, 6 CH_3), 2.32 (td, 4H, J = 1.1 Hz, J = 7.5 Hz; $H_{2'}$, $H_{19'}$), 3.45 (dd, 2H, J = 8.5 Hz, J = 11.9 Hz; H_{5a}), 4.07 (dd, 2H, J = 5.0 Hz, J = 11.9 Hz, H_{5e}), 4.92-5.01 (m, 2H; H_4), 5.02 (t, 2H, J = 8.3 Hz; H_2), 5.19 (t, 2H, J = 8.3 Hz; H_3), 5.82-5.86 (m, 2H; $H_{10'Z}$, $H_{11'Z}$), 5.86-5.89 (m, 2H; $H_{10'E}$, $H_{11'E}$), 5.72 (d, 2H, J = 6.9 Hz; $H_{1\beta}$) ppm; NMR ^{13}C ($CDCl_3$, 250 MHz): δ = 21.0, 21.1, 21.2 (6 CH_3), 24.5, 24,. ($C_{3'}$, $C_{18'}$), 26.1 ($C_{9'Z}$, $C_{12'Z}$), 29.0, 29.1, 29.2, 29.3, 29.5, 29.6, 29.7 ($C_{4'}$, $C_{5'}$, $C_{6'}$, $C_{7'}$, $C_{8'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{16'}$, $C_{17'}$), 32.5 ($C_{9'E}$, $C_{12'E}$), 33.8, 34.3 ($C_{2'}$, $C_{19'}$), 62.7 (C_5), 69.6 (C_4), 71.5 (C_3), 72.2 (C_2), 101.3 ($C_{1\beta}$), 130.4 ($C_{10'Z}$, $C_{11'Z}$), 130.9 ($C_{10'E}$, $C_{11'E}$), 170.0, 170.5, 170.7 (6 C=O), 172.2, 172.5 ($C_{1'}$, $C_{20'}$)

ppm; Anal. Calculated for $C_{42}H_{64}O_{18}$: C: 58.87, H: 7.53; found C: 59.17, H: 7.63; HRMS calculated for $C_{42}H_{64}O_{18}$ [M+Na^+]: 879.3990; found: 879.3974.

1',20'-bis-eicos-10'-enedioyl(2,3,4-tri-*O*-benzyl)-D-xylopyranoside 5

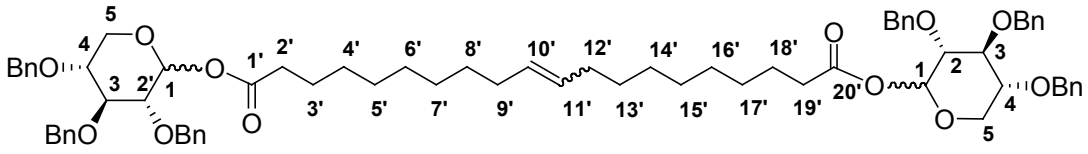
- addition of the catalyst by means of a transfer cannula (M1)

A solution of Grubbs I catalyst (14.1 mg, 0.017 mmol, 0.1 eq.) in CH_2Cl_2 (3 mL) is added under argon at 40°C by mean of a transfer cannula to a solution of undec-10'-enoyl(2,3,4-tri-*O*-benzyl)-D-xylopyranoside (100 mg, 0.17 mmol) in dichloromethane (4 mL). After reaction, the solvent is evaporated under reduced pressure, the residue is then dissolved in diethylether (5 mL) and stirred on charcoal for 2 h and filtered on Celite. After evaporation of the solvent, the residue obtained is purified by chromatography (silica gel, 10% ethyl acetate in petroleum ether) to give the 1',20'-bis-eicos-10'-enedioyl(2,3,4-tri-*O*-benzyl)-D-xylopyranoside as a white paste.

- addition of the catalyst by means of a syringe (M2)

A solution of Grubbs I catalyst (14.1 mg, 0.017 mmol, 0.1 eq.) in CH_2Cl_2 (3 mL) is added under argon drop by drop by means of a syringe to a solution of undec-10'-enoyl(2,3,4-tri-*O*-benzyl)-D-xylopyranoside III.1.f (100 mg, 0.17 mmol) in dichloromethane (4 mL). After reaction, the solvent is evaporated under reduced pressure, the residue is then dissolved in diethylether (5 mL) and stirred on charcoal for 2 h and filtered on Celite. After evaporation of the solvent, the residue obtained is purified by chromatography (silica gel, 10% ethyl acetate in petroleum ether) to give the 1',20'-bis-eicos-10'-enedioyl(2,3,4-tri-*O*-benzyl)-D-xylopyranoside as a white paste.

Entry	Addition conditions	Time (h)	m(mg)	Yield (%)
1	M1	3	35,0	36
2		14	44,7	46
3	M2 (2 x 7 mg, t = 0 h, t = 12 h)	24	70,0	72
4	M2 (3 x 4,7 mg, t = 0 h, t = 9 h, t = 18 h)	51	78,7	81



(*E*/*Z* = 78/22) (1144 g/mol)

IR (Film): 3065, 3031, 2926, 2855, 1738, 1497, 1455, 1274, 1075, 736 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.14-1.42 (m, 40H; $H_{4'}$, $H_{5'}$, $H_{6'}$, $H_{7'}$, $H_{8'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$, $H_{17'}$), 1.52-1.73 (m, 4H; $H_{3'}$, $H_{18'}$), 1.86-2.06 (m, 4H; $H_{9'}$, $H_{12'}$), 2.25-2.32 (m, 4H; $H_{2'}$, $H_{19'}$), 2.36-2.44 (m, 4H; $H_{2'}$, $H_{19'}$), 3.37 (dd, 2H, J = 8.5 Hz, J = 11.9 Hz; $H_{5a\beta}$), 3.49 (t, 2H, J = 8.3 Hz; H_3), 3.56-3.69 (m, 8H; $H_{2\alpha}$, $H_{3\alpha}$, $H_{4\alpha}$, $H_{5a\alpha}$), 3.71-3.76 (m, 2H; $H_{5e\alpha}$), 3.83 (m, 2H; $H_{4\beta}$), 3.94 (dd, 2H, J = 5.0 Hz, J = 11.9 Hz; $H_{5e\beta}$), 4.56-4.94 (m, 12H; 6 CH_2), 5.30-5.33 (m, 2H; $H_{10'Z}$, $H_{11'Z}$), 5.34-5.39 (m, 2H; $H_{10'E}$, $H_{11'E}$), 5.57 (d, 2H; J = 7.9 Hz; $H_{1\beta}$), 6.24 (d, 2H; J = 3.5 Hz, $H_{1\alpha}$), 7.20-7.39 (m, 30H, $H_{arom.}$) ppm; NMR ^{13}C ($CDCl_3$, 500 MHz): δ = 24.5, 24.6, 24.8 ($C_{3'}$, $C_{18'}$), 26.1 ($C_{9'Z}$, $C_{12'Z}$), 29.0, 29.1, 29.2, 29.3, 29.5, 29.6, 29.7 ($C_{4'}$, $C_{5'}$, $C_{6'}$, $C_{7'}$, $C_{8'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{16'}$, $C_{17'}$), 32.5 ($C_{9'E}$, $C_{12'E}$), 33.8, 34.2, 34.3 ($C_{2'}$, $C_{19'}$), 62.0 ($C_{5\alpha}$), 64.5 ($C_{5\beta}$), 73.2, 73.3, 73.7, 75.0, 75.6, 75.7 (CH_2), 77.3 ($C_{4\alpha}$), 77.4 ($C_{4\beta}$), 78.5 ($C_{2\alpha}$), 80.4 ($C_{2\beta}$), 81.1 ($C_{3\alpha}$), 83.6 ($C_{3\beta}$), 89.7 ($C_{1\alpha}$), 94.4 ($C_{1\beta}$), 127.6, 127.7, 127.8, 127.93, 127.9, 128.0, 128.3, 128.4, 128.5 ($CH_{arom.}$), 129.8 ($C_{10'Z}$, $C_{11'Z}$), 130.3 ($C_{10'E}$, $C_{11'E}$), 137.6, 137.9,

138.0, 138.1, 138.3, 138.7 ($C_{arom.}$), 172.2, 172.5 ($C_{1'}$, $C_{20'}$) ppm; HRMS calculated for $C_{72}H_{88}O_{12}$ [M+Na^+]: 1167.6173; found: 1167.6191.