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Orthogonal Approach for the Precise Synthesis of Phenylpropanoid Sucrose Esters

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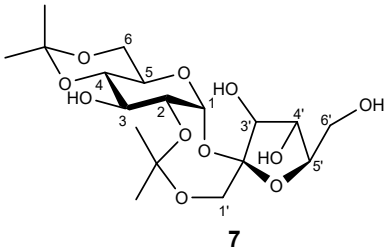
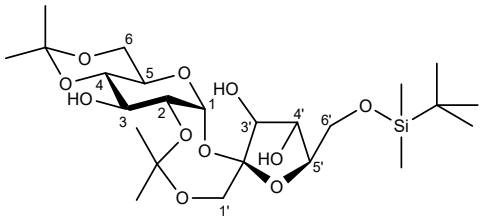
1. Preparation of compounds **7**, **15-33** and **41-61**



7

2,1':4,6-di-O-isopropylidene sucrose 7: The synthesis of **7** was accomplished following the literature procedure[1] with a slight modification. Dry DMF (700 ml) was stirred over Drierite (36.0 g) under a nitrogen atmosphere overnight and then filtered. Finely ground sucrose (65.0g, 190 mmol) was added to the filtered DMF and the mixture was stirred. 2-Methoxypropene (86.0 ml, 898 mmol) and *p*-TsOH (82.0 mg, 0.476 mmol) were added to the stirred mixture under a nitrogen atmosphere. The solution was left to stir for a week before adding NEt_3 (7.0 ml, 50.1 mmol) to quench the reaction. DMF was evaporated off under reduced pressure and the syrup obtained was stirred with EtOAc (400 ml) for 10 minutes. The solution was then filtered, and the filtrates were dried over anhydrous $MgSO_4$. Finally, the yellow syrup obtained was subjected to flash chromatography using EtOAc as the eluent to give 2,1' :4,6-di-*O*-isopropylidene sucrose **7** as **a** white solid in 65% yield. Comparison of ^1H and ^{13}C NMR data with the literature values[1] confirmed the product to be 2,1′:4,6-di-*O*-isopropylidene sucrose **7**.

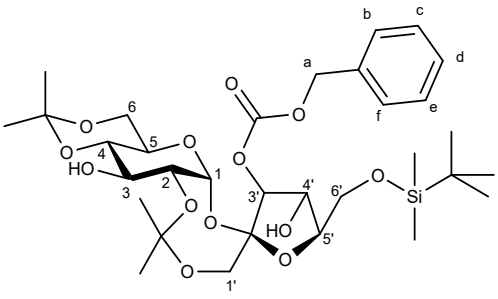


15

6'-O-tert-butyldimethylsiloxy-2,1':4,6-di-O-isopropylidene sucrose, 6'-*O*-TBS ***15***: A solution of 4,6-di-*O*-isopropylidene sucrose **7** (1.00 g, 2.37 mmol) and DMAP (28.9 mg, 0.237 mmol) was stirred in CH_2Cl_2 (50.0 ml) at room temperature. Subsequently, NEt_3 (793 µL, 5.68 mmol) and TBSCl (428 mg, 2.84 mmol) were also added and the reaction was then left to stir for 12 hours. The reaction mixture was then washed twice with 10% NH_4Cl solution and the organic layer separated, dried over anhydrous $MgSO_4$ and evaporated. The crude product was purified using silica gel column chromatography with 1:1 EtOAc/hexane as eluent. Finally **15** was obtained in 95% yield as white solid. mp 81.5-83.6˚C; ^1H NMR (300 MHz, $CDCl_3$): δ TBS group: 0.02 (s, 6H, $(CH_3)_2Si$), 0.85 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.20, 1.27, 1.43, 1.48 (4 x s, 12H, 2 x $(CH_3)_2C$); sucrose unit: δ 3.44 (d, 1H, J = 12 Hz, H-5), 3.49-3.59 (m, 2H, 2 x H-1'), 3.61-370 (m, 3H, H-2, H-6, H-6'), 3.73-3.88 (m, 6H, H-3, H-4, H-6, H-3', H-6', H-3'), 4.04-4.08 (m, 2H, H-4', H-5'), 6.09 (d, 1H, H-1'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.43, -5.22, 18.4, 19.1, 24.2, 25.3, 26.0, 29.0, 62.4, 63.6, 66.0, 66.0, 69.4, 73.3, 73.9, 78.5, 78.8, 81.5, 90.8, 100.0, 102.0, 103.2; HRMS (ESI-positive mode): m/z calcd. for $C_{24}H_{45}O_{11}Si$ 537.2731; found 537.2734 $[M+H]^+$.

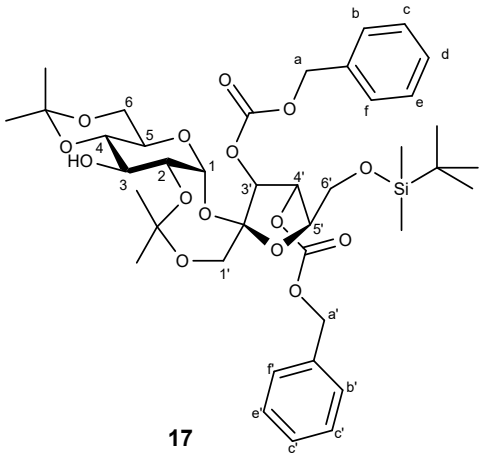
*3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose, 3'-O-Cbz **16:*** 6'-*O*-TBS **15** (500 g, 0.932 mmol) and DMAP (11.4 mg, 0.0932 mmol) were dissolved in CH_2Cl_2 and stirred at room temperature. After which, CbzCl (199 µL, 1.40 mmol) and TMEDA (420 µL, 2.80 mmol) were added to the stirring solution and the reaction was left to stir for 12 hours. Upon completion, the reaction was washed twice with water and the organic layer was collected and dried with anhydrous

$MgSO_4$. CH_2Cl_2 was removed and the crude mixture was subjected to chromatographic purification using a gradient of EtOAc/hexane as eluent (starting from 8:1 Hexane /EtOAc, to 6:1 Hexane/EtOAc then to 4:1 Hexane/EtOAc). In the end, white solid product 3'-*O*-Cbz **16** was obtained in 75% yield. This reaction also gave 3',4'-di-*O*-carboxybenzyl-6'-*tert*-butyldimethylsiloxy-2,1': 4,6-di-*O*-isopropylidene sucrose, di-*O*-Cbz **17** as a white solid in 20% yield.



16

*Analytical data for 3'-O-Cbz **16**:* mp 73.3-74.9˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.02 (s, 6H, $(CH_3)_2Si$), 0.86 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.21, 1.29, 1.41, 1.43 (4 x s, 12H, 2 x $(CH_3)_2C$); sucrose unit: δ 3.47 (d, 1H, *J* = 12 Hz, H-5), 3.54-3.66 (m, 3H, H-2, 2 x H-1'), 3.68-3.85 (m, 5H, H-4, 2 x H-6, 2 x H-6') 3.94-4.01 (m, 2H, H-3, H-5'), 4.38 (t, 1H, *J* = 3 Hz, H-4'), 4.72 (d, 1H, *J* = 6 Hz, H-3'), 5.93 (d, 1H, *J* = 3 Hz, H-1); Cbz group: 5.19 (s, 2H, 2 x H-a), 7.30-7.40 (m, 5H, H-b, H-c, H-d, H-e, H-f); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.5, -5.3, 18.3, 19.1, 24.1, 25.5, 25.7, 25.9, 29.1, 62.3, 63.5, 65.1, 66.2, 70.0, 70.4, 73.0, 73.8, 82.0, 82.3, 90.8, 99.8, 101.6, 103.4, 128.4, 128.7, 128.7, 134.7, 155.2; HRMS (ESI-positive mode): *m*/z calcd. for $C_{32}H_{51}O_{13}Si$ 671.3099; found 671.3102 $[M+H]^+$.

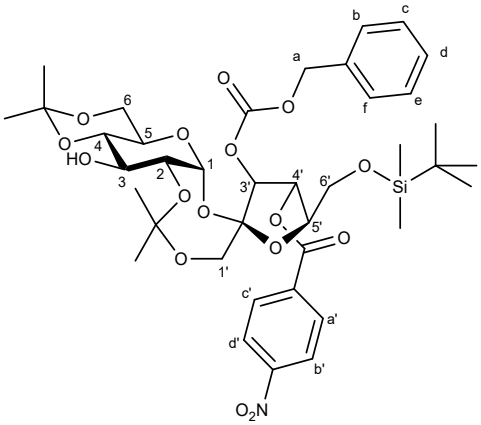


17

*Analytical data for di-O-Cbz **17**:* mp 80.0-82.5˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.83 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.30, 1.32, 1.43, 1.45 (s, 12H, 2 x $(CH_3)_2C$); sucrose unit: δ 3.48 (d, 1H, *J* = 12 Hz, H-5), 3.56 (d, 1H, *J* = 12 Hz, H-1'), 3.61-3.69 (m, 2H, H-2, H-1'), 3.71-3.84 (m, 5H, H-4, 2 x H-6, 2 x H-6'), 4.05 (d, 1H, J = 12 Hz, H-3), 4.12-4.18 (m, 1H, H-5'), 4.91 (d, 1H, I = 6 Hz, H-3'), 5.33 (t, 1H, *J* = 4.5 Hz, H-4'), 5.97 (d, 1H, J = 3 Hz, H-1); Cbz groups: δ 5.17 (s, 2H, 2 x H-a), 5.12 (d, 2H, *J* = 15 Hz, 2 x H-a'), 7.32-7.39 (m, 10H, H-b, H-c, H-d, H-e, H-f, H-b', H-c', H-d', H-e', H-f'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.6, -5.4, 18.2, 19.1 62.3, 63.7, 63.8, 66.2, 70.0, 70.1, 70.3, 72.9, 73.9, 80.8, 81.1, 81.5, 91.2, 99.9, 101.6, 104.1, 128.3, 128.4, 128.6, 128.7, 134.8, 134.8, 154.0, 154.5; HRMS (ESI-positive mode): *m*/z calcd. for $C_{40}H_{57}O_{15}Si$ 805.3467; found 805.3452 $[M+H]^+$.

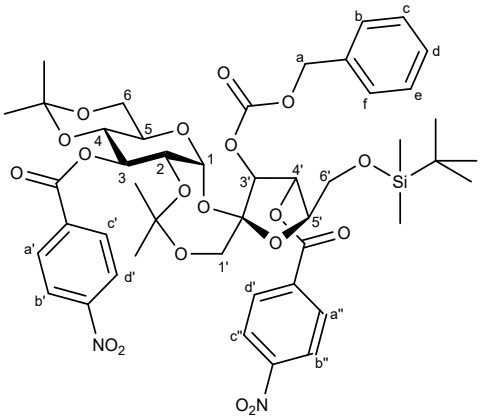
*4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose, 4'-O-PNB **18***: 3'-*O*-Cbz **16** (500 mg, 0.746 mmol) and DMAP (9.1 mg, 0.0746 mmol) were dissolved in CH_2Cl_2 and stirred at 4 ˚C using an ice bath. Subsequently, NEt_3 (312 µL, 2.24 mmol) was added to the stirring solution. Then PNBCl (208 mg, 1.12 mmol) was dissolved in CH_2Cl_2 and added to the stirring solution dropwise. The reaction was left to stir for 12 hours. Upon completion, CH_2Cl_2 was removed and the crude product was purified with column chromatography using 4:1

Hexane/EtOAc as eluent. White solid 4'-*O*-PNB **18** was obtained in 70% yield. This reaction also gave white solid *3,4'-di-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose (di-O-PNB)* **19** in 19% yield and *3-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose (3-O-PNB*) **20** in 10% yield.



18

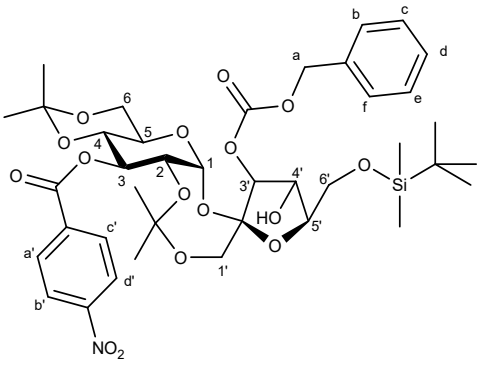
*Analytical data for 4'-O-PNB **18**:* mp 87.1-88.9˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.82 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.36-1.53 (4 x S, 12H, 2 x $(CH_3)_2C$); sucrose unit: δ 3.54 (d, 1H, *J* = 15 Hz, H-5), 3.60 (d, 1H, *J* = 9 Hz, H-1'), 3.64-3.74 (m, 3H, H-2, H-1', H-6'), 3.80-3.86 (m, 3H, H-4, 2 x H-6, H-6'), 4.11 (d, 1H, *J* = 12 Hz, H-3), 4.22-4.27 (m, 1H, H-5'), 5.03 (d, 1H, *J* = 6 Hz, H-3'), 5.73 (t, 1H, *J* = 4.5 Hz, H-4'), 6.02 (d, 1H, *J* = 3 Hz, H-1); Cbz group: δ 5.14-5.25 (m, 2H, 2 x H-a), 7.31-7.38 (m, 5H, H-b, H-c, H-d, H-e, H-f); PNB group: δ 8.22, 8.24 (2 x d, 4H, *J* = 30, 9 Hz, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.46, -5.42, 18.2, 19.1, 25.7, 29.1, 70.0, 70.4, 72.9, 73.9, 78.9, 80.8, 81.7, 99.9, 101.7, 104.2, 123.6, 128.2, 128.6, 128.7, 130.9, 134.7, 151.0, 154.6; HRMS (ESI-positive mode): *m*/z calcd. for $C_{39}H_{54}NO_{16}Si$ 820.3212; found 820.3218 $[M+H]^+$.



19

*Analytical data for di-O-PNB **19**:* mp 95.0-96.7˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.02 (s, 6H, $(CH_3)_2Si$), 0.82 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.17-1.43 (4 x S, 12H, 2 x $(CH_3)_2C$); sucrose unit: δ 3.50 (d, 1H, *J* = 12 Hz, H-5), 3.71-3.74 (m, 2H, 2 x H-1'), 3.81-3.87 (m, 4H, H-2, 2 x H-6, H-6'), 3.97-4.01 (2H, m, H-4, H-6'), 4.08 (d, 1H, *J* = 6 Hz, H-5'), 4.99 (d, 1H, *J* = 3 Hz, H-3'), 5.35 (t, 1H, *J* = 12 Hz, H-4'), 5.72 (t, 1H, *J* = 4.5 Hz, H-3), 6.10 (d, 1H, *J* = 3 Hz, H-1); Cbz group: δ 5.32 (dd, 2H, *J* = 18, 12 Hz, 2 x H-a), 7.29-7.31 (m, 3H, H-c, H-d, H-e), 7.42-7.45 (m, 2H, H-b, H-f); PNB group: δ 8.11-8.18 (m, 4H, H-a', H-b', H-c', H-d'), 8.24-8.28 (m, 4H, H-a", H-b", H-c", H-d"); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.4, -5.3, 14.1, 18.3, 18.4, 19.0, 19.1, 24.0, 25.4, 25.8, 29.0, 29.7, 29.7, 30.9, 31.9, 62.3, 63.8, 64.6, 64.9, 70.6, 71.5, 71.6, 71.8, 72.6, 82.5, 91.1, 92.0, 99.7, 99.8, 101.3, 103.7, 103.9, 123.5, 123.6, 123.7, 123.9, 127.4, 128.4, 128.5, 128.6, 128.6, 128.7, 130.7, 130.9, 131.3, 134.9, 135.7, 135.9, 150.5, 150.6, 154.6 155.2, 163.7, 164.6, 167.1; HRMS (ESI-positive mode): *m*/z calcd. for $C_{46}H_{57}N_2O_{19}Si$ 969.3325; found 969.3352 $[M+H]^+$.

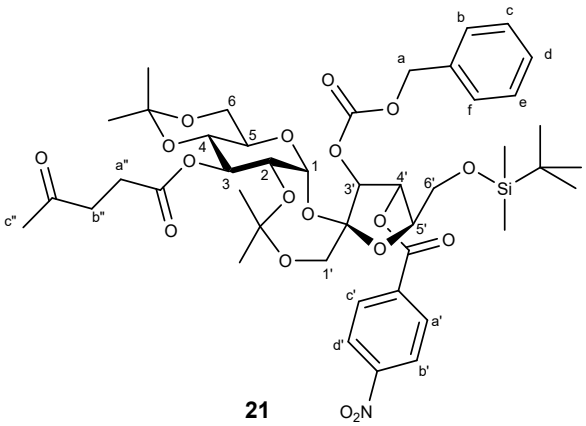
*Analytical data for 3-O-PNB **20**:* mp 85.8-86.9˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.83 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.10-1.40 (4 x S, 12H, 2 x $(CH_3)_2C$); sucrose unit: δ 3.66 (d, 1H, *J* = 9 Hz, H-5), 3.69-3.78 (m, 2H, 2 x H-1'), 3.82-3.89 (m, 4H, H-2, H-6', 2 x H-6), 3.92-3.96 (m, 2H, H-4, H-6'), 4.06 (d, 1H, *J* = 12 Hz, H-5'), 4.41 (t, 1H, *J* = 3 Hz, H-4'), 4.73 (d, 1H, *J* = 6 Hz, H-3'), 5.47 (t, 1H, *J* = 10.5 Hz, H-3), 6.02 (d, 1H, *J* = 3 Hz, H-1); Cbz group: δ 5.27-5.32 (m, 2H, 2 x H-a), 7.30-7.35 (m, 3H, H-c, H-d, H-e), 7.42-7.45 (m, 2H, H-b, H-f); PNB group: δ 8.20 (2 x d, 4H, *J* = 24, 9 Hz, H-a', H-b', Hc', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.4, -5.3, 14.1, 18.3, 18.4, 19.0, 19.1, 24.0, 25.4, 25.8, 29.0, 29.7, 29.7, 30.9, 31.9, 62.3, 63.8, 64.6, 64.9, 70.6, 71.5, 71.6, 71.8, 72.6, 82.5, 91.1, 92.0, 99.7, 99.8, 101.3, 103.7, 103.9, 123.5, 123.6, 123.9, 127.4, 128.4, 128.5, 128.6, 128.6, 128.7, 130.7, 130.9, 134.9, 135.7, 135.9, 150.5, 155.2, 163.7, 164.6; HRMS (ESI-positive mode): *m*/z calcd. for $C_{39}H_{54}NO_{16}Si$ 820.3212; found 820.3216 $[M+H]^+$.



20

*4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **18***: This compound was also prepared as follows: Compound **21** (200 mg, 0.218 mmol) was dissolved in 1,4-dioxane (5.0 ml) and $NaBH_4$ (18.1 mg, 0.480 mmol) was added to it. The reaction was left stirring for 4 hours and upon completion, 1,4-dioxane was removed. The crude mixture was subjected to purification via column chromatography using 3:2 Hexane/EtOAc as eluent to give compound **18** as a white solid in 72% yield. The analytical data matched.

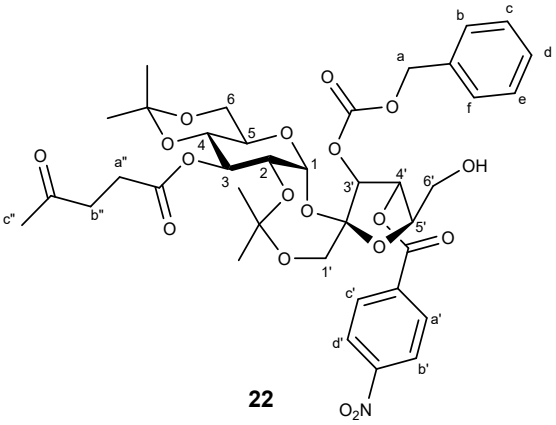
*3-O-(4-oxopentanoyl)-4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **21**:* 4'-*O*-PNB **18** (500 mg, 0.610 mmol) and DMAP (7.5 mg, 0.0610 mmol) were dissolved in CH_2Cl_2 and stirred at room temperature. Subsequently, LevOH (75.0 µL, 0.732 mmol) and DCC (151 mg, 0.732 mmol) were added to the stirring solution and the reaction was left to stir for 12 hours. Upon completion, CH_2Cl_2 was removed and the crude mixture was re-dissolved in cold diethyl ether. After which, the mixture was filtered. After removing diethyl ether, the remaining crude residue was purified by column chromatography using 3:1 Hexane/EtOAc as eluent. White solid **21** was obtained in 85% yield. mp 96.1-98.9˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.82 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.23-1.46 (4 x s, 12H, 2 x $(CH_3)_2C$); Lev group: 2.15 (s, 3H, 3 x H-c"), 2.59-2.61 (m, 2H, 2 x H-b"), 2.73-2.74 (m, 2H, 2 x H-a"); Cbz and sucrose unit: δ 3.49 (d, 1H, *J* = 12 Hz, H-5), 3.65-3.68 (m, 2H,



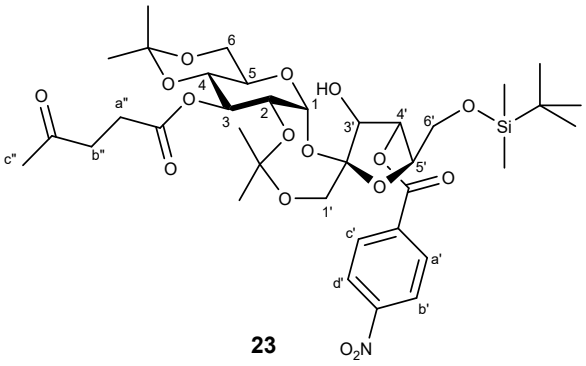
21

H-4, H-1'), 3.81-3.86 (m, 5H, H-2, 2 x H-6, H-1', H-6'), 4.18 (d, 1H, *J* = 12 Hz, H-6'), 4.22-4.27 (m, 1H, H-5'), 4.99 (d, 1H, *J* = 6 Hz, H-3'), 5.23-5.29 (m, 3H, H-3, 2 x H-a), 5.71 (t, 1H, *J* = 3 Hz, H-4'), 6.04 (d, 1H, *J* = 3 Hz, H-1), 7.30-7.32 (m, 3H, H-c, H-d, H-e), 7.39-7.42 (m, 2H, H-b, H-f); PNB group: δ 8.20, 8.22 (2 x d, 4H, *J* = 30, 7.5 Hz, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.45, -5.41, 5.79, 6.59, 18.2, 19.0, 23.8, 25.4, 25.8, 28.0, 29.0, 29.9, 38.1, 62.3, 63.5, 64.0, 66.4, 70.6, 71.0, 71.5, 71.8, 79.1, 81.0, 82.2, 91.7, 99.7, 101.5, 104.6, 123.6, 128.5, 130.9, 134.7, 134.9, 150.7, 154.5, 163.4, 171.6, 206.4; HRMS (ESI-positive mode): *m*/z calcd. for $C_{44}H_{60}NO_{18}Si$ 918.3580; found 918.3589 $[M+H]^+$.

*3-O-(4-oxopentanoyl)-4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-2,1'-di-O-isopropylidene sucrose **22**:* Compound **21** (200 mg, 0.218 mmol) was dissolved in pyridine (1.0 ml) and stirred at room temperature. 1.56 M $3HF{\cdot}NEt_3$ (419 µL, 0.654 mmol) and NEt_3 (60.9 µL, 0.436 mmol) were added to the stirring solution and the reaction was left to stir for 12 hours. Upon completion, pyridine was removed, and the crude mixture was subjected to chromatographic purification using 3:2 Hexane/EtOAc as eluent. White solid compound **22** was obtained in 86%. mp 85.1-87.9˚C; ^{1}H NMR (300 MHz, $CDCl_3$): isopropylidene rings: δ 1.25-1.43 (4 x s, 12H, 2 x $(CH_3)_2C$); Lev group: 2.11 (s, 3H, 3 x H-c"), 2.55-2.57 (m, 2H, 2 x H-b"), 2.68-2.70 (m, 2H, 2 x H-a"); Cbz and sucrose unit: δ 3.50 (d, 1H, *J* = 12 Hz, H-5), 3.61-3.66 (m, 2H, H-2, H-1'), 3.80-3.86 (m, 5H, H-4, 2 x H-6, H-1', H-6'), 4.16 (d, 1H, *J* = 3 Hz, H-6'), 4.19-4.20 (m, 1H, H-5'), 5.10 (d, 1H, *J* = 6 Hz, H-3'), 5.15-5.23 (m, 3H, H-3, 2 x H-a), 5.72 (t, 1H, *J* = 3 Hz, H-4'), 6.18 (d, 1H, *J* = 6 Hz, H-1), 7.24-7.26 (m, 3H, H-c, H-d, H-e), 7.34-7.37 (m, 2H, H-b, H-f), PNB group: δ 8.06, 8.22 (2 x d, 4H, *J* = 15, 9 Hz, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.0, 23.9, 24.9, 25.3, 28.0, 29.0, 29.9, 30.9, 34.0, 38.0, 61.8, 61.9, 70.7, 70.8, 71.2, 71.4, 80.4, 83.4, 91.8, 99.8, 101.9, 103.9, 123.7, 128.5, 128.6, 131.0, 134.3, 134.,8, 150.8, 154.4, 163.8, 171.6, 206.4; HRMS (ESI-positive mode): *m*/z calcd. for $C_{38}H_{45}NO_{18}Na$ 826.2534; found 826.2546 $[M+Na]^+$.

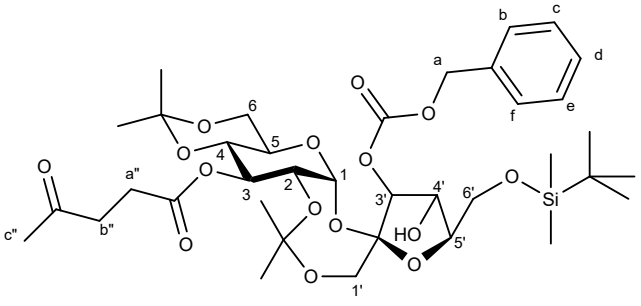


*3-O-(4-oxopentanoyl)-4'-O-para-nitrobenzoyl-6'-O-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **23***: Compound **21** (200 mg, 0.218 mmol) and $Pd(OAc)_2$ (4.1 mg, 0.0182 mmol) were dissolved in CH_2Cl_2 (5.0 ml) and stirred at room temperature. After which, Et_3SiH (46.4 mg, 0.291 mmol) and NEt_3 (4.06 µL, 0.0291 mmol) were added and the reaction was left to stir for 12 hours. Upon completion, CH_2Cl_2 was removed, and the crude mixture was subjected to purification using



column chromatography. 2:1 Hexane/EtOAc were used as eluent and white solid compound **23** was obtained in 68% yield. mp 84.3-85.9˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.78 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.30-1.50 (4 x s, 12H, 2 x $(CH_3)_2C$); Lev group: 2.20 (s, 3H, 3 x H-c"), 2.59-2.65 (m, 2H, 2 x H-b"), 2.73- 2.82 (m, 2H, 2 x H-a"); sucrose unit: δ 3.52 (d, 1H, *J* = 12 Hz, H-5), 3.68-3.94 3.94 (m, 7H, H-2, H-4, 2 x H-6, 2 x H-1', H-6'), 4.11 (d, 1H, *J* = 9 Hz, H-6'), 4.17-4.22 (m, 2H, H-3', H-5'), 5.27 (t, 1H, *J* = H-4'), 5.55 (t, 1H, *J* = 6 Hz, H-3), 6.12 (d, 1H, *J* = 6 Hz, H-1'); PNB group: δ 8.22, 8.28 (2 x d, 4H, *J* = 15, 9 Hz, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -6.98, 0.6.93, -6.91, -6.85, 4.30, 5.11, 16.7, 16.8, 16.8, 17.5, 17.5, 22.4, 23.7, 24.2, 24.3, 24.3, 24.3, 24.5, 26.6, 26.9, 27.5, 28.2, 28.4, 28.4, 29.5, 36.5, 60.8, 62.5 63.6, 69.4, 69.9, 70.2, 78.8, 79.4, 79.9, 89.2, 89.9, 98.3, 98.3, 100.1, 102.6, 103.3, 103.7, 122.0, 122.1, 129.5, 133.4, 133.5, 133.6 149.2, 162.5, 170.6, 206.7; HRMS (ESI-positive mode): *m*/z calcd. for $C_{36}H_{53}NO_{16}NaSi$ 806.3031; found 806.3079 $[M+Na]^+$.

*3-O-(4-oxopentanoyl)-3'-O-carboxybenzyl-6'-O-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **24**:* Compound **21** (200 mg, 0.218 mmol) was treated with $Mg(OMe)_2$ (65.4 µL, 0.0218 mmol) in 8:2 MeOH/THF (5.0 ml) at 4 ˚C (ice bath). The reaction was closely monitored with TLC and quenched immediately with 1N HCl (43.6 µL, 0.0436 mmol) after all starting material was consumed (usually within 1 hour). MeOH/THF were removed and the crude mixture was subjected to purification via column chromatography. 2:1 Hexane/EtOAc was used as eluent and two products – compounds **24** and **25** were obtained as white solid in 70% and 15 % yield respectively. Since compound **25** is an undesired by-product, its analytical data was not included. mp 85.0-86.9˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.83 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.23-1.43 (4 x s, 12H, 2 x $(CH_3)_2C$); Lev group: 2.14 (s, 3H, 3 x H-c"), 2.56-2.58 (m, 2H, 2 x H-b"), 2.69-2.72 (m, 2H, 2 x H-a"); Cbz and sucrose unit: δ 3.44 (d, 1H, *J* = 12 Hz, H-5), 3.60-3.66 (m, 3H, H-2, 2 x H-1'), 3.77-3.85 (m, 4H, H-4, 2 x H-6, H-6'), 3.91-3.97 (m, 1H, H-6'), 4.04 (d, 1H, *J* = 12 Hz, H-5'), 4.36 (t, 1H, *J* = 4.5, H-4') 4.72 (d, 1H, *J* = 9 Hz, H-3'), 5.16-5.24 (m, 3H, H-3, 2 x H-a), 5.96 (d, *J* = 6 Hz, 1H, H-1'), 7.29-7.43 (m, 5H, H-b, H-c, H-d, H-e, H-f); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.44, -5.34, 18.3, 19.0, 23.9, 25.4, 28.1, 29.0, 29.9, 38.1, 62.3, 63.7, 64.9, 66.2, 70.5, 71.2, 71.5, 82.1, 82.4, 91.1, 99.6, 101.3, 103.6, 128.5, 128.7, 134.9, 155.2, 171.6, 206.4; HRMS (ESI-positive mode): *m*/z calcd. for $C_{37}H_{57}NO_{15}Si$ 769.3467; found 769.3460 $[M+H]^+$.



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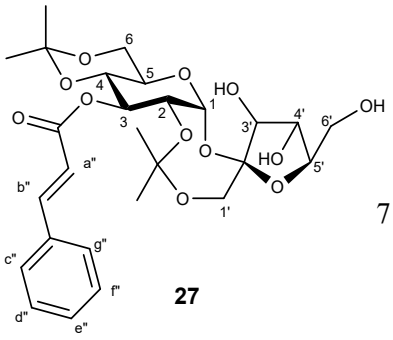
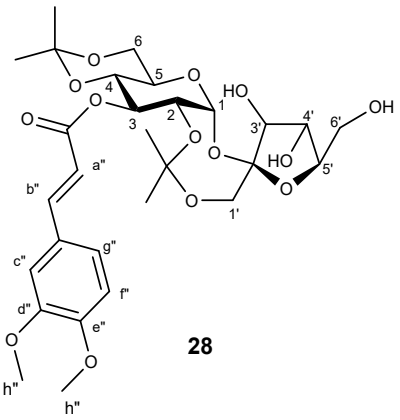
*3-O-cinnamoyl-2,1'-di-O-isopropylidene sucrose, 3-cinn **27**:* Compound **41** (300 mg, 0.316 mmol) was treated with $Mg(OMe)_2$ (47.4 µL, 0.158 mmol) in 8:2 MeOH/THF at room temperature for



27

12 hours. The reaction was quenched with 1N HCl (316 µL, 0.316 mmol) and then evaporated to dryness. The crude mixture obtained was then re-dissolved in pyridine (1.0 ml) and stirred with a solution of 1.56 M $3HF{\cdot}NEt_3$ (608 µL, 0.948 mmol) and NEt_3 (88.2 µL, 0.632 mmol) at room temperature for another 12 hours. The mixture was evaporated to dryness and purified using column chromatography using 2:1 EtOAc/Hexane as eluent. Compound **27** was obtained as a white solid in 70% yield. mp 70.1-70.9˚C; ^{1}H NMR (300 MHz, $CDCl_3$): isopropylidene rings: δ 1.34 (s, 3H, $(CH_3)_2C$), 1.43 (s, 3H, $(CH_3)_2C$), 1.50 (2 x S, 6H, $(CH_3)_2C$); sucrose unit: δ 3.51-3.57 (m, 1H, H-5), 3.68-4.04 (m, 9H, H-2, 2 x H-6, 2 x H-1', H-3', H-4', 2 x H-6'), 4.26 (d, 1H, *J* = 12 Hz, H-5'), 4.58-4.64 (m, 1H, H-4), 5.44 (t, 1H, *J* = 9 Hz, H-3), 6.30 (d, 1H, *J* = 3 Hz, H-1); *trans*-alkenyl and aromatic protons: δ 6.47 (d, 1H, *J* = 15 Hz, H-a"), 7.40-7.42 (m, 3H, H-d", H-e", H-f"), 7.55-7.58 (m, 2H, H-c", H-g"), 7.71 (d, 1H, *J* = 15 Hz, H-b"); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.0, 24.13, 25.2, 26.0, 28.9, 61.2, 62.0, 64.1, 66.3, 71.4, 71.5, 73.3, 79.3, 83.0, 91.3, 100.1, 101.8, 103.4, 117.9, 128.2, 128.9, 130.4, 134.4, 145.2, 166.3; HRMS (ESI-positive mode): *m*/z calcd. for $C_{27}H_{37}O_{12}$ 553.2285; found 553.2278 $[M+H]^+$.

*3-O-(3,4-dimethoxycinnamoyl)-2,1'-di-O-isopropylidene sucrose, 3-diOMe **28**:* Compound **42** (300 mg, 0.297mmol) was treated with $Mg(OMe)_2$ (44.6 µL, 0.149 mmol) in 8:2 MeOH/THF at room temperature for 12 hours. The reaction was quenched using 1N HCl (29.7 µL, 0.297 mmol) and then evaporated to dryness. The residue was re-dissolved in pyridine (1.0 ml) and stirred with 1.56 M $3HF{\cdot}NEt_3$ (572 µL, 0.892 mmol) and NEt_3 (83.0 µL, 0.594 mmol) at room temperature for 12 hours. Upon completion, the reaction was evaporated to dryness, and the crude mixture was purified using column chromatography with 2:1 EtOAc/Hexane as eluent. Compound **30** was obtained as white solid in 76% yield. mp 82.2-83.5˚C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$): isopropylidene rings: δ 1.18-1.42 (4 x s, 12H, 2 x $(CH_3)_2C$); methoxy and sucrose unit: δ 3.44 (d, 1H, *J* = 12 Hz, H-5), 3.66-3.88 (m, 13H, H-2, H-6, 2 x H-1', H-3', 2 x H-6', 6 x H-h"), 3.94-3.98 (m, 2H, H-6, H-4'), 4.09 (d, 1H, *J* = 12 Hz, H-5'), 4.39 (t, 1H, *J* = 6 Hz, H-4), 5.31 (t, 1H, *J* = 6 Hz, H-3), 6.15, 6.16 (d, 1H, *J* = 3 Hz, H-1'); *trans*-alkenyl and aromatic protons: δ 6.41 (d, 1H, *J* = 15 Hz, H-a"), 6.98 (d, 1H, *J* = 9 Hz, H-g"), 7.18 (d, 1H, *J* = 3 Hz, H-f"), 7.31 (s, 1H, H-c"), 7.60 (d, 1H, *J* = 15 Hz, H-b"); ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$): δ 23.6, 24.9, 28.8, 29.8, 33.4, 60.4, 60.5, 66.9, 67.3, 68.6, 71.3, 73.7, 75.7, 76.8, 77.0, 79.0, 84.5, 88.9, 96.3, 104.5, 106.3, 108.7, 115.3, 116.6, 120.9, 128.1, 132.6, 149.8, 154.9, 156.9, 170.9; HRMS (ESI-positive mode): *m*/z calcd. for $C_{29}H_{41}O_{14}$ 613.2496; found 613.2468 $[M+H]^+$.



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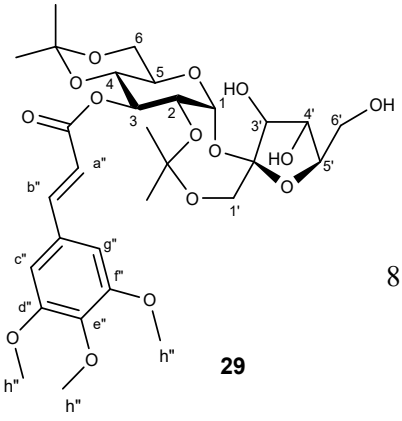
*3-O-(3,4,5-trimethoxycinnnamoyl)-2,1'-di-O-isopropylidene sucrose, 3-triOMe **29**:* Compound **43** (300 mg, 0.289 mmol) was treated with $Mg(OMe)_2$ (43.3 µL, 0.144 mmol) in 8:2 MeOH/THF at room temperature for 12 hours. Upon completion, the reaction was quenched with 1N HCl (28.9 µL, 0.289 mmol) and evaporated



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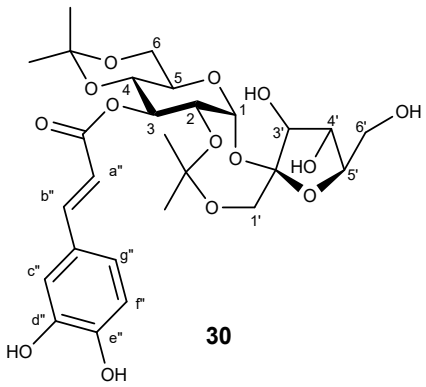
to dryness. The mixture was re-dissolved in pyridine (1.0 ml) and stirred with 1.56 M $3HF{\cdot}NEt_3$ (555 µL, 0.866 mmol) and NEt_3 (80.6 µL, 0.577 mmol) at room temperature for 12 hours. Upon completion, the reaction was evaporated to dryness, and the crude mixture was purified using column chromatography with 2:1 EtOAc/Hexane as eluent. Compound **31** was obtained as white solid in 79% yield. mp 99.0-100.2˚C; ^{1}H NMR (300 MHz, $CDCl_3$): isopropylidene rings: δ 1.21-140 (4 x s, 12H, 2 x $(CH_3)_2C$); methoxy and sucrose unit: δ 3.42 (d, 1H, *J* = 12 Hz, H-5), 3.61-3.72 (m, 3H, H-1', 2 x H-6'), 3.80-3.89 (m, 12H, 2 x H-6, H-1', 9 x H-h"), 4.02-4.12 (m, 4H, H-4, H-3', H-4', H-5'), 5.31 (t, 1H, *J* = 10.5 Hz, H-3), 6.03 (d, 1H, *J* = 3 Hz, H-1); *trans*-alkenyl and aromatic protons: δ 6.29 (d, 1H, *J* = 15 Hz, H-a"), 6.71 (s, 2H, H-c", H-g"), 7.55 (d, 1H, *J* = 15 Hz, H-b"); ^{13}C NMR (75.5 MHz, MeOD): δ 24.5, 26.8, 29.3, 31.0, 61.7, 63.8, 69.4, 71.7, 74.6, 75.8, 77.5, 79.4, 84.2, 93.7, 105.8, 107.2, 118.9, 131.9, 146.5, 155.0, 169.1; HRMS (ESI-positive mode): *m*/z calcd. for $C_{30}H_{42}O_{15}Na$ 665.2421; found 665.2444 $[M+Na]^+$.

*3-O-caffeoyl-2,1'-di-O-isopropylidene sucrose, 3-caff **30**:* Compound **44** (200 mg, 0.301 mmol) was treated with $Mg(OMe)_2$ (24.8 µL, 0.0827 mmol) in 8:2 MeOH/THF at room temperature for 12 hours. Upon completion, the reaction was quenched with 1N HCl (165 µL, 0.165 mmol) and the mixture evaporated to dryness. The crude mixture was re-dissolved in pyridine (1.0 mL) and stirred with 1.56 M $3HF{\cdot}NEt_3$ (318 µL, 0.496 mmol) and NEt_3 (46.2 µL, 0.331 mmol) at room temperature for 12 hours. Upon completion, the reaction was evaporated to dryness, and the crude mixture was purified using column chromatography with 2:1 EtOAc/Hexane as eluent. Compound **32** was obtained as white solid in 62% yield. mp 106.0-107.4˚C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$): isopropylidene rings: δ 1.13-1.32 (4 x s, 12H, 2 x $(CH_3)_2C$); sucrose unit: δ 3.46-3.80 (m, 7H, H-5, 2 x H-6, 2 x H-1', 2 x H-6'), 3.82-3.87 (m, 2H, H-2, H-3'), 3.99 (d, 2H, *J* = 12 Hz, H-4', H-5'), 4.26 (t, 1H, *J* = 6 Hz, H-4), 5.19 (t, 1H, *J* = 9 Hz, H-3), 6.05 (d, 1H, *J* = 3 Hz, H-1); *trans*-alkenyl and aromatic peaks: δ 6.15 (d, 1H, *J* = 18 Hz, H-a"), 6.75 (d, 1H, *J* = 9 Hz, H-f"), 6.90 (d, 1H, *J* = 6 Hz, H-g"), 7.05 (s, 1H, H-c"), 7.42 (d, 1H, *J* = 15 Hz, H-b"); ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$) : δ 23.6, 24.6, 35.4, 46.4, 61.7, 62.2, 63.4, 70.5, 71.6, 71.8, 73.9, 70.3, 83.3, 91.4, 99.3, 101.1, 103.5, 114.3, 114.7, 115.5, 121.6, 126.6, 144.9, 145.6, 148.1 162.2, 165.9; HRMS (ESI-positive mode): *m*/z calcd. for $C_{27}H_{36}O_{14}Na$ 607.2003; found 607.2007 $[M+Na]^+$.



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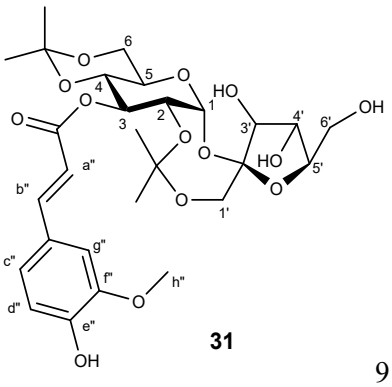
*3-O-feruloyl-2,1'-di-O-isopropylidene sucrose, 3-feru **31**:* Compound **45** (200 mg, 0.180 mmol) was treated with $Mg(OMe)_2$ (27.0 µL, 0.0901 mmol) in 8:2 MeOH/THF at room temperature for 12 hours. Upon completion, the reaction was quenched with 1N HCl (180 µL, 0.180 mmol) and evaporated to dryness. The crude mixture was re-dissolved in pyridine (1.0 mL) and stirred with 1.56



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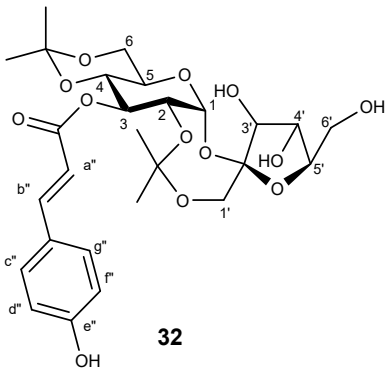
M 3HF·NEt_3 (347 µL, 0.541 mmol) and NEt_3 (50.3 µL, 0.361 mmol) at room temperature for 12 hours. Upon completion, the reaction was evaporated to dryness, and the crude mixture was purified using column chromatography with 2:1 EtOAc/Hexane as eluent. Compound **31** was obtained as white solid in 80% yield. mp 80.1-82.3˚C; ^{1}H NMR (300 MHz, $CDCl_3$): isopropylidene rings: δ 1.23-1.32 (4 x s, 12H, 2 x $(CH_3)_2C$); methoxy and sucrose unit: δ 3.43 (d, 1H, *J* = 9 Hz, H-5), 3.58-3.67 (m, 2H, 2 x H-6'), 3.70-3.90 (m, 10H, H-2, H-3', H-4, 2 x H-6, 2 x H-1', 3 x H-h"), 4.14 (d, 1H, H-5'), 4.48-4.51 (m, 1H, H-4), 5.31(t, 1H, J = 9 Hz, H-3); anomeric, *trans*-alkenyl and aromatic protons: δ 6.17-6.23 (m, 2H, H-1, H-a"), 6.87 (d, 1H, *J* = 9 Hz, H-c"), 6.97-7.02 (m, 2H, H-d", H-g"), 7.54 (d, 1H, *J* = 15 Hz, H-b"); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.0, 24.1, 25.2, 28.9, 46.4, 56.0, 61.9, 63.9, 70.7, 71.5, 71.6, 73.2, 79.2, 83.0, 91.2, 99.9, 101.7, 103.5, 109.6, 114.9, 115.1, 123.1, 126.8, 145.2, 146.9, 148.2, 166.5; HRMS (ESI-positive mode): *m*/z calcd. for $C_{28}H_{38}O_{14}Na$ 621.2159; found 621.2175 $[M+Na]^+$.

*3-O-coumaroyl-2,1'-di-O-isopropylidene sucrose, 3-coum **32**:* Compound **46** (200 mg, 0.301 mmol) was treated with $Mg(OMe)_2$ (24.8 µL, 0.0827 mmol) in 8:2 MeOH/THF at room temperature for 12 hours. Upon completion, the reaction was quenched with 1N HCl (165 µL, 0.165 mmol) and evaporated to dryness. The crude mixture was re-dissolved in pyridine (1.0 mL) and stirred with 1.56 M 3HF·NEt_3 (318 µL, 0.496 mmol) and NEt_3 (46.2 µL, 0.331 mmol) at room temperature for 12 hours. Upon completion, the reaction was evaporated to dryness, and the crude mixture was purified using column chromatography with 2:1 EtOAc/Hexane as eluent. Compound **32** was obtained as white solid in 81% yield. mp 79.5-80.9˚C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$): isopropylidene rings: δ 1.24-143 (4 x s, 12H, 2 x $(CH_3)_2C$); sucrose unit: δ 3.44 (d, 1H, *J* = 12 Hz, H-5), 3.59-3.83 (m, 6H, H-2, 2 x H-1', H-3', 2 x H-6'), 3.94-3.98 (m, 2H, H-4', 2 x H-6), 4.09 (d, 1H, J = 12 Hz, H-5'), 4.38 (t, 1H, *J* =7.5 Hz, H-4), 5.30 (t, 1H, *J* = 9 Hz, H-3), 6.15 (d, 1H, *J* = 6 Hz, H-1); *trans*-alkenyl and aromatic protons: δ 6.33 (d, 1H, *J* = 15 Hz, H-a"), 6.88 (d, 2H, *J* = 9 Hz, H-d", H-f"), 7.53 (d, 2H, *J* = 6 Hz, H-c", H-g"), 7.59 (d, 1H, *J* = 18 Hz, H-b"); ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$): δ 18.4, 23.6, 24.6, 25.4, 25.4, 61.7, 62.1, 63.4, 66.1, 70.5, 71.6, 71.8, 73.8, 79.3, 83.4, 91.1, 99.3, 101.1, 103.5, 114.8, 115.8, 116.2, 126.1, 130.1, 144.5, 159.8, 165.8; HRMS (ESI-positive mode): *m*/z calcd. for $C_{27}H_{37}O_{13}$ 569.2234; found 569.2232 $[M+H]^+$.



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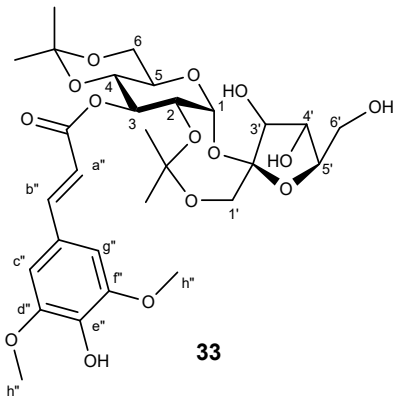
*3-O-sinapoyl-2,1'-di-O-isopropylidene sucrose, 3-sinap **33**:* Compound **47** (200 mg, 0.269 mmol) was dissolved in pyridine (1.0 ml) and stirred at room temperature. 1.56 M 3HF·NEt_3 (518 µL, 0.808 mmol) and NEt_3 (75.2 µL, 0.539 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, the mixture was evaporated to dryness, and the residue was purified using column chromatography using 2:1 EtOAc/Hexane as eluent. Compound **33** was obtained as white



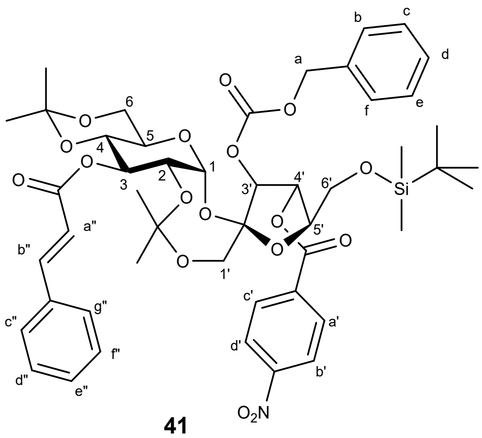
33

solid in 80% yield. mp 85.2-86.4˚C; ^{1}H NMR (300 MHz, $CDCl_3$): isopropylidene rings: δ 1.23-1.38 (4 x s, 12H, 2 x $(CH_3)_2C$); methoxy and sucrose unit: δ 3.43 (d, 1H, *J* = 12 Hz, H-5), 3.52-3.70 (m, 2H, 2 x H-6'), 3.74-4.03 (m, 13H, H-2, 2 x H-6, 2 x H-1', H-3', H-4', 6 x H-h"), 4.16 (d, 1H, *J* = 15 Hz, H-5'), 4.51 (t, 1H, *J* = 7.5 Hz, H-4), 5.34 (t, 1H, *J* = 9 Hz, H-3), 6.18 (d, 1H, *J* = 3 Hz, H-1); *trans*-alkenyl and aromatic protons: δ 6.29 (d, 1H, *J* = 15 Hz, H-a"), 6.70 (s, 2H, H-c", H-g"), 7.53 (d, 1H, *J* = 15 Hz, H-b"); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.3, 23.4, 24.4, 28.2, 55.5, 61.2, 61.5, 63.3, 65.6, 68.1, 68.1, 72.3, 72.8, 81.4, 90.6, 99.1, 101.6, 101.7, 102.5, 102.5, 104.4, 104.4, 113.7, 136.6, 136.6, 145.7, 146.4, 146.4, 166.3; HRMS (ESI-positive mode): *m*/z calcd. for $C_{29}H_{40}O_{15}Na$ 651.2265; found 651.2281 $[M+Na]^+$.

General procedure for the acylation of compound 18: Synthesis of compounds 41-47

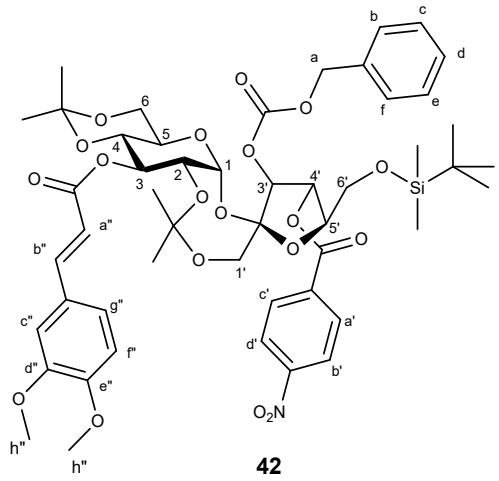
To a stirred solution of Compound **18** (500 mg, 0.610 mmol) and DMAP (7.5 mg, 0.0610 mmol) in CH_2Cl_2 (10 ml) was added the respective (substituted) cinnamic acid (0.610 mmol) and DCC (252 mg, 1.22 mmol) at room temperature. After 24 hours (TLC), CH_2Cl_2 was removed under vacuum and the residue was triturated with cold diethyl ether (20 ml) and filtered. Diethyl ether was then removed under vacuum, and the crude product was purified using column chromatography using 8:1 Hexane/EtOAc as eluent.

*3-O-cinnamoyl-4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **41:*** Following general procedure 1, reaction with cinnamic acid **34** (181 mg, 1.22 mmol) gave **41** in as white solid in 76% yield. mp 90.3-90.9˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.01 (s, 6H, $(CH_3)_2Si$), 0.79 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.23-147 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz and sucrose unit: δ 3.50 (d, 1H, *J* = 12 Hz, H-5), 3.69-3.95 (m, 7H, H-2, H-4, 2 x H-6, 2 x H-1', H-6'), 4.21-4.26 (m, 2H, H-5', H-6'), 4.99 (d, 1H, *J* = 3 Hz, H-3'), 5.25-5.41 (m, 3H, H-3, 2 x H-a), 5.71 (t, 1H, *J* = 3 Hz, H-4'), 6.07 (d, 1H, *J* = 3 Hz, H-1'); Cbz and cinnamoyl protons: δ 6.44 (d, 1H, *J* = 15 Hz, H-a"), 7.29-7.37 (m, 6H, H-b, H-c, H-d, H-e, H-f, H-e"), 7.45 (d, 2H, *J* = 9 Hz, H-d", H-f"), 7.50-7.53 (m, 2H, H-c", H-g"), 7.68 (d, 1H, *J* = 15 Hz, H-b"); PNB group: δ 8.20, 8.22 (2 x d, 4H, *J* = 27, 9 Hz, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.43, -5.39, 18.2, 19.0, 23.8, 25.5, 25.8, 29.0, 63.5, 66.5, 70.8, 71.7, 71.9, 79.2, 81.1, 82.3, 91.8, 99.7, 101.4, 104.7, 118.1, 123.6, 128.0, 128.1, 128.5, 128.6, 128.9, 130.9, 134.5, 135.0, 144.8, 154.5, 163.4, 165.9; HRMS (ESI-positive mode): *m*/z calcd. for $C_{48}H_{59}NO_{17}NaSi$ 972.3450; found 972.3431 $[M+Na]^+$.



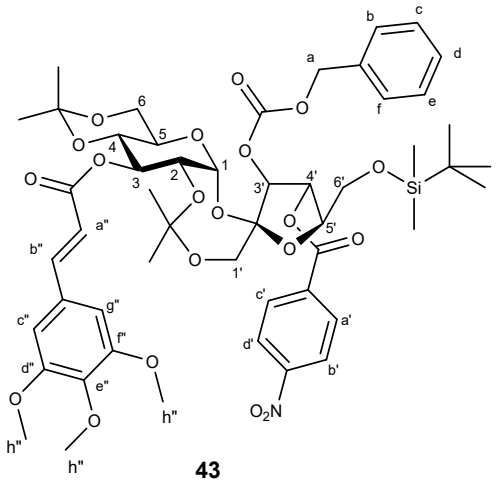
41

3-O-(3,4-dimethoxycinnamoyl)-4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose ***42:*** Following the general procedure 1, diOMe-cinnamic acid **35** (254 mg, 1.22 mmol) gave compound **42** as white solid in 80% yield. mp 86.7-87.7˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.01 (s, 6H, $(CH_3)_2Si$), 0.84 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.20-1.46 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz, methoxy and sucrose unit: δ 3.47 (t, 1H, *J* = 7.5 Hz, H-5), 3.70-3.77 (m, 3H, H-2, 2 x H-1'), 3.82-3.89 (m, 11H, 6 x H-h", H-4, 2 x H-6, 2 x H-6') 4.05-4.25 (m, 1H, H-5'), 5.10 (d, 1H, *J* = 3 Hz, H-3'), 5.29-5.38 (m, 3H, H-3, 2 x H-a), 5.70 (t, 1H, *J* = 6 Hz, H-4'), 6.04 (d, 1H, *J* = 3 Hz, H-1'); Cbz and dimethoxycinnamoyl peaks: δ 6.30 (d, 1H, *J* = 15 Hz, H-a"), 6.84 (d, 1H, *J* = 6 Hz, H-g"), 7.04-7.07 (m, 2H, H-c", H-f"), 7.20-7.25 (m, 3H, H-c, H-d, H-e), 7.30-7.34 (m, 2H, H-b, H-f), 7.44 (d, 1H, *J* = 6 Hz, H-b"); PNB peaks: δ 8.20-8.23 (2 x d, 4H, *J* = 27, 9 Hz, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.43, -5.38, 18.2, 19.0, 23.5, 25.0, 25.6, 25.8, 25.8, 28.0, 56.1, 61.0, 62.2, 64.2, 66.5, 70.7, 70.8, 71.7, 71.9, 76.6, 78.2, 81.2, 82.9, 91.7, 99.7, 101.3, 101.4, 104.7, 105.3, 117.3, 121.6, 126.5, 128.5, 128.6, 128.7, 130.0, 130.8, 134.9, 135.0, 140.2, 144.9, 150.8, 153.4, 153.9, 154.5, 165.4, 165.6; HRMS (ESI-positive mode): *m*/z calcd. for $C_{50}H_{63}NO_{19}NaSi$ 1032.3661; found 1032.3684 $[M+Na]^+$.



42

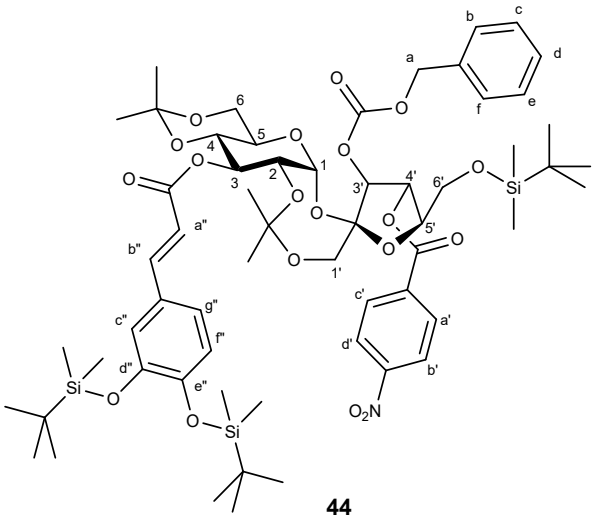
3-O-(3,4,5-trimethoxycinnamoyl)-4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose ***43****:* Following the general procedure 1, triOMe-cinnamic acid **36** (291 mg, 1.22 mmol) gave compound **43** as white solid in 81% yield. mp 109.7-110.7˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.80 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.21-1.25 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz, methoxy and sucrose unit: δ 3.48 (d, 1H, *J* = 15 Hz, H-5), 3.73-3.78 (m, 4H, H-2, 2 x H-1', H-6'), 3.82-3.90 (m, 12H, 9 x H-h", H-4, 2 x H-6), 4.28 (m, 2H, H-5', H-6'), 4.99 (d, 1H, *J* = 6 Hz, H-3'), 5.27-5.40 (m, 3H, H-3, 2 x H-a), 5.70 (t, 1H, *J* = 7.5 Hz, H-4'), 6.04 (d, 1H, *J* = 6 Hz, H-1'); Cbz and trimethoxycinnamoyl peaks: δ 6.34 (d, 1H, *J* = 15 Hz, H-a"), 6.74 (s, 2H, H-c", H-g"), 7.31-7.34 (m, 3H, H-c, H-d, H-e), 7.43-7.46 (m, 2H, H-b, H-f), 7.55 (d, 1H, H-b"); PNB group: δ 8.20-8.22 (2 x d, 4H, *J* = 27, 9 Hz, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.43, -5.38, 14.2, 18.2, 19.0, 23.8, 25.5, 25.8, 29.0, 56.2, 61.0, 62.4, 63.5, 64.2, 66.5, 70.7, 70.8, 71.7, 71.9, 79.2, 81.1, 82.3, 91.8, 99.7, 101.4, 104.7, 105.3, 117.3, 123.6, 128.5, 128.6,



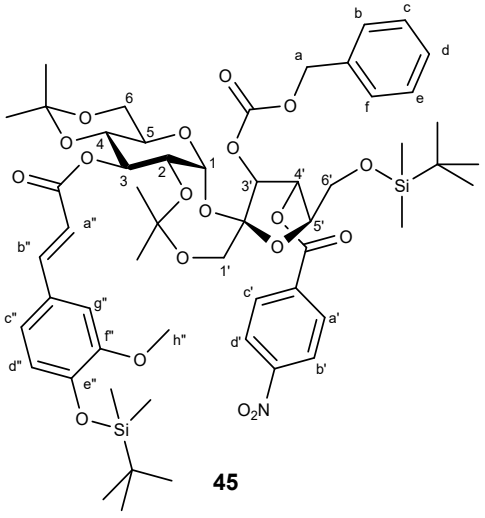
43

128.6, 130.0, 130.9, 134.7, 135.0, 140.1, 144.8, 150.8, 153.5, 164.5, 163.4, 165.8; HRMS (ESI-positive mode): *m*/z calcd. for $C_{51}H_{65}NO_{20}NaSi$ 1062.3767; found 1062.3792 $[M+Na]^+$.

*3-O-(3,4-di-tert-butyldimethylsiloxycinnmoyl)-4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **44**:* Following the general procedure 1, OTBS-caff acid **37** (498 mg, 1.22 mmol) gave compound **44** as yellowish solid in 80% yield. mp 100.6-101.3˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ -0.18 (s, 6H, $(CH_3)_2Si$), 0.61 (s, 9H, $(CH_3)_3CSi$); TBS on OTBS-caffeoyl group: δ 0.01 (s, 12H, 2 x $(CH_3)_2Si$), 0.78 (s, 18H, 2 x $(CH_3)_3CSi$); isopropylidene rings: δ 1.05-1.27 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz and sucrose unit: δ 3.31 (d, 1H, *J* = 12 Hz, H-5), 3.47-3.59 (m, 2H, H-2, H-1'), 3.63-3.77 (m, H-4, 2 x H-6, H-1', H-6'), 4.02-4.06 (m, 2H, H-5', H-6'), 4.81 (d, 1H, *J* = 3 Hz, H-3'), 5.06-5.20 (m, 3H, H-3, 2 x H-a), 5.53 (t, 1H, *J* = 6 Hz, H-4'), 5.88 (d, 1H, *J* = 3 Hz, H-1); Cbz and OTBS caffeoyl peaks: δ 6.04 (d, 1H, *J* = 15 Hz, H-a"), 6.61 (d, 1H, *J* = 6 Hz, H-c"), 6.82 (m, 2H, H-f", H-g"), 7.09-7.17 (m, 3H, H-c, H-d, H-e), 7.24-7.28 (m, 2H, H-b, H-f), 7.37 (d, 1H, *J* = 15 Hz, H-b"); PNB peaks: δ 8.02-8.10 (2 x d, 4H, *J* = 27, 10.5, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.43, -5.39, -4.10, -4.05, 18.2, 18.5, 18.5, 19.0, 25.5, 25.8, 25.9, 25.9, 29.0, 48.2, 51.7, 63.5, 65.8, 66.7, 70.7, 71.7, 72.0, 81.1, 92.0, 99.7, 101.4, 104.7, 120.7, 123.6, 128.4, 128.6, 130.9, 135.0, 147.3, 154.5, 163.3; HRMS (ESI-positive mode): *m*/z calcd. for $C_{60}H_{87}NO_{19}NaSi_3$ 1232.5078; found 1232.5082 $[M+Na]^+$.

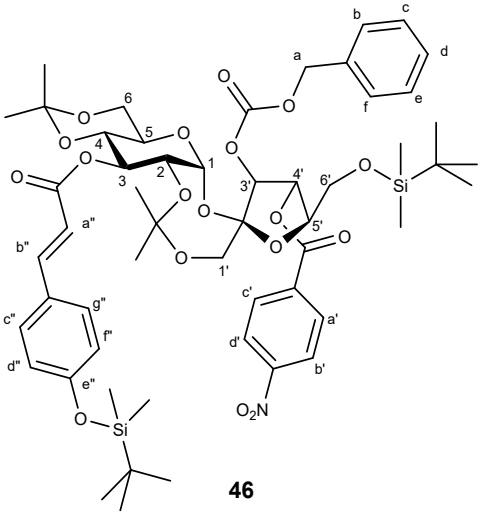

44

*3-O-(4-tert-butyldimethylsilyloxy-3-methoxycinnamoyl)-4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **45**:* Following the general procedure 1, OTBS-feru acid **38** (376 mg, 1.22 mmol) gave compound **45** as white solid in 89% yield. mp 85.0-86.2˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ -0.13 (s, 6H, $(CH_3)_2Si$), 0.66 (s, 9H, $(CH_3)_3CSi$); TBS on OTBS-feruloyl group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.83 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.10-1.40 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz, methoxy and sucrose unit: δ 3.57 (d, 1H, *J* = 12 Hz, H-5), 3.67-3.72 (m, 3H, 2 x H-1', H-6'), 3.75 (s, 3H, 3 x H-h"), 3.76-3.81 (m, H-2, 4H, 2 x H-6, H-6'), 4.10-4.11 (m, 2H, H-4, H-5'), 4.86 (d, 1H, *J* = 3 Hz, H-3'), 5.15-5.24 (m, 3H, H-3, 2 x H-a), 5.58 (t, 1H, *J* = 3 Hz, H-4'), 5.93 (d, 1H, *J* = 3 Hz, H-1); Cbz and OTBS-feruloyl peaks: δ 6.158 (d, 1H, *J* =15.9, H-a"), 6.68 (d, 1H,


45

J = 6 Hz, H-d"), 6.87-6.88 (m, 2H, H-c", H-g"), 7.16-7.19 (m, 3 H, H-c, H-d, H-e), 7.29-7.31 (m, 2H, H-b, H-f), 7.47 (d, 1H, *J* = 15 Hz, H-b"); PNB group: δ 8.06-8.11 (2 x d, 4H, *J* = 27, 9 Hz, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.5, -5.4, -4.6, 18.2, 18.5, 19.0, 23.8, 25.5, 25.7, 25.8, 29.0, 55.5, 62.4, 63.5, 64.2, 66.5, 70.6, 70.7, 71.7, 71.9, 79.2, 81.1, 82.3, 91.8, 99.7, 101.4, 104.7, 110.8, 115.8, 121.1, 122.3, 123.6, 128.4, 128.5, 128.6, 128.6, 128.6, 130.9, 134.8, 135.0, 144.9, 147.5, 150.7, 151.2, 154.5, 163.4, 166.1; HRMS (ESI-positive mode): *m*/z calcd. for $C_{55}H_{75}NO_{19}NaSi_2$ 1132.4370; found 1132.4365 $[M+Na]^+$.

*3-O-(4-tert-butyldimethylsilyloxy)-4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **46**:* Following the general procedure 1, OTBS-coum acid **39** (339 mg, 1.22 mmol) gave compound **46** as white solid in 80% yield. mp 84.6-85.6˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ 0.02 (s, 6H, $(CH_3)_2Si$), 0.80 (s, 9H, $(CH_3)_3CSi$); TBS on OTBS-coumaroyl group: δ 0.20 (s, 6H, $(CH_3)_2Si$), 0.96 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.24-1.46 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz and sucrose unit: δ 3.72 (d, 1H, *J* = 10.5 Hz, H-5), 3.83-3.86 (m, 2H, 2 x H-1'), 3.90-4.01 (m, 5H, H-2, 2 x H-6, 2 x H-6'); 4.25-4.26 (m, 2H, H-4, H-5'), 5.00 (d, 1H, *J* = 3 Hz, H-3'), 5.30-5.40 (m, 3H, H-3, 2 x H-a), 5.72 (t, 1H, *J* = 3 Hz, H-4'), 6.07 (d, 1H, *J* = 3.6, H-1); Cbz and OTBS-coumaroyl peaks: δ 6.31 (d, 1H, *J* = 15.9, H-a"), 6.83 (d, 2H, *J* = 8.4 Hz, H-d", H-f"), 7.31-7.33 (m, 3H, H-c, H-d, H-e), 7.40-7.46 (m, 4H, H-b, H-f, H-c", H-g"), 7.64 (d, 1H, *J* = 15.9, H-b"); PNB group: δ 8.05-8.21 (2 x d, 4H, *J* = 27, 9 Hz, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.5, -5.4, -4.4, 18.2, 18.3, 19.0, 25.5, 2.6, 25.8, 29.0, 64.2, 70.7, 99.7, 101.4, 104.7, 120.5, 123.6, 127.8, 128.5, 128.6, 128.6, 129.7, 130.9, 134.8, 135.0, 150.7, 157.8; HRMS (ESI-positive mode): *m*/z calcd. for $C_{54}H_{73}NO_{18}NaSi_2$ 1102.4232; found 1102.4264 $[M+Na]^+$.



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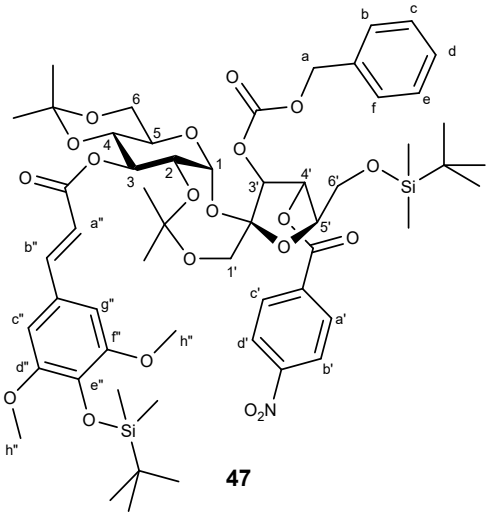
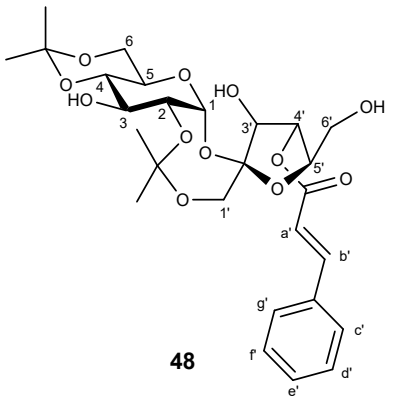
*3-O-(4-tert-butyldimethylsilyloxy-3,5-dimethoxycinnamoyl)-4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **47**:* Following the general procedure, OTBS-sinap acid **40** (413 mg, 1.22 mmol) gave compound **47** as white solid in 80% yield. mp 105.5-106.2˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS group: δ -0.10 (s, 6H, *J* = 2.1 Hz, $(CH_3)_2Si$), 0.69 (s, 9H, $(CH_3)_3CSi$); TBS on OTBS-sinapoyl group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.87 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.14-1.35 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz, methoxy and sucrose unit: δ 3.40 (d, 1H, *J* = 9 Hz, H-5), 3.59-3.69 (m, 4H, H-6, H-6', 2 x H-1') 3.70-3.71 (m, 6H, 6 x H-h"), 3.73-3.79 (m, 3H, H-2, H-



47

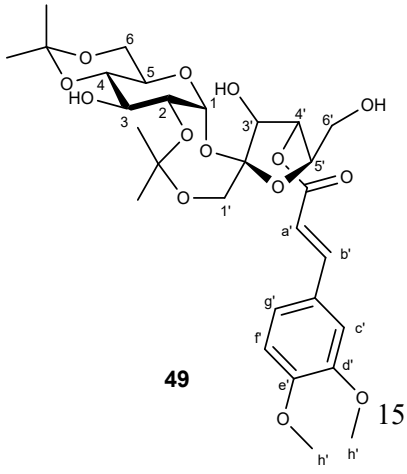
6, H-6'), 4.14-4.15 (m, 2H, H-4, H-5'), 4.89 (d, 1H, *J* = 3 Hz, H-3'), 5.24-5.27 (m, 3H, H-3, 2 x H-a), 5.61 (t, 1H, *J* = 3 Hz, H-4'), 5.96 (d, 1H, *J* = 3.6 Hz, H-1); Cbz and OTBS-sinapoyl peaks: δ 6.19 (d, 1H, *J* = 15.9 Hz, H-a"), 6.55-6.61 (m, 2H, H-c", H-g"), 7.13-7.22 (m, 3H, H-c, H-d, H-e), 7.32-7.35 (m, 2H, H-b, H-f), 7.48 (d, 1H, *J* = 15 Hz, H-b"); PNB group: δ 8.06-8.22 (2 x d, 4H, *J* = 27, 9 Hz, H-a', H-b', H-c', H-d'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.5, -5.4, -4.6, -4.5, -3.6, 18.0, 18.2, 18.8, 19.0, 23.9, 24.7, 25.4, 25.5, 25.7, 25.7, 25.9, 26.3, 29.0, 31.0, 32.8, 55.7, 55.8, 55.9, 62.4, 63.5, 64.1, 70.6, 70.7, 721.7, 71.9, 79.2, 81.1, 82.3, 91.8, 99.7, 101.4, 104.7, 105.2, 105.4, 115.9, 117.4, 123.6, 127.1, 127.4, 128.5, 128.6, 128.6, 130.9, 134.7, 135.0, 136.9, 143.9, 145.3, 150.7, 151.8, 154.5, 163.4, 166.1; HRMS (ESI-positive mode): *m*/z calcd. for $C_{56}H_{77}NO_{20}NaSi_2$ 1162.4475; found 1162.4419 $[M+Na]^+$

*4'-O-cinnamoyl-2,1'-di-O-isopropylidene sucrose, 4'-cinn **48**:* Compound **55** (200 mg, 0.250 mmol) and $Pd(OAc)_2$ (4.7 mg, 0.0208 mmol) were dissolved in CH_2Cl_2 (5.0 ml) and stirred at room temperature. Subsequently, Et_3SiH (53.2 µL, 0.333 mmol) and NEt_3 (4.65 µL, 0.0333 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, the reaction was diluted with EtOAc (30.0 ml). The reaction mixture was washed twice with H_2O and the organic layer was collected and dried over anhydrous $MgSO_4$. After removal of EtOAc, the crude product obtained was re-dissolved in pyridine (1.0 ml) and stirred at room temperature. Subsequently, 1.56 M $3HF{\cdot}NEt_3$ (481 µL, 0.750 mmol) and NEt_3 (69.8 µL, 0.500 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, pyridine was removed. The crude product was then subjected to purification using 3:2 EtOAc/Hexane as eluent. Compound **48** was obtained as white solid in 88% yield. mp 88.1-89.2˚C; ^{1}H NMR (300 MHz, $CDCl_3$): isopropylidene rings: δ 1.38-1.45 (4 x s, 12H, 2 x $(CH_3)_2C$); sucrose unit: δ 3.44-3.48 (m, 2H, H-5, H-1'), 3.52-3.67 (m, 2H, H-2, H-1'), 3.72-3.90 (m, 6H, H-3, H-4, 2 x H-6, 2 x H-6'), 3.93-4.02 (m, 1H, H-5'), 4.19 (d, 1H, *J* = 3 Hz, H-3'), 5.43 (t, 1H, *J* = 7.5 Hz, H-4'), 6.19 (d, 1H, *J* = 3 Hz, H-1); *trans*-alkenyl and aromatic protons: δ 6.65 (d, 1H, *J* = 30 Hz, H-a'), 7.15-7.21 (m, 3H, H-d', H-e', H-f'), 7.23-7.26 (m, 3H, H-b', H-c', H-g'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 17.1, 22.2, 23.2, 27.0, 28.8, 33.7, 5,9,9, 62.1, 64.2, 67.3, 70.9, 71.4, 80.0, 89.4, 98.0, 100.3, 101.3, 124.4, 126.3, 126.5, 138.0, 170.9; HRMS (ESI-positive mode): *m*/z calcd. for $C_{27}H_{36}O_{12}Na$ 575.2104; found 575.2088 $[M+Na]^+$.



48

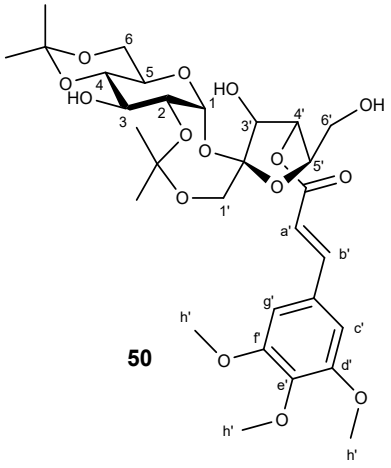
*4'-O-(3,4-dimethoxycinnamoyl)-2,1'-di-O-isopropylidene sucrose, 4'-diOMe **49**:* Compound **56** (200 mg, 0.232 mmol) and $Pd(OAc)_2$ (4.3 mg, 0.0193 mmol) were dissolved in CH_2Cl_2 (5.0 ml) and stirred at room temperature. Subsequently, Et_3SiH (49.5 µL, 0.310 mmol) and NEt_3 (4.35 µL, 0.0193 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, the reaction was diluted with EtOAc (30.0 ml). The



49

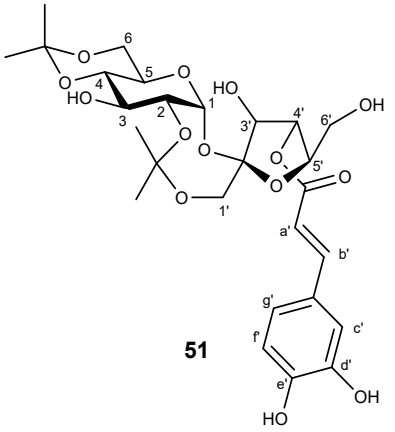
reaction mixture was washed twice with H_2O and the organic layer was collected and dried over anhydrous $MgSO_4$. After removal of EtOAc, the crude product obtained was re-dissolved in pyridine (1.0 ml) and stirred at room temperature. Subsequently, 1.56 M $3HF{\cdot}NEt_3$ (447 µL, 0.697 mmol) and NEt_3 (64.9 µL, 0.465 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, pyridine was removed. The crude product was then subjected to purification using 3:2 EtOAc/Hexane as eluent. Compound **49** was obtained as white solid in 85% yield. mp 82.1-83.6˚C; ^{1}H NMR (300 MHz, $CDCl_3$): isopropylidene rings: δ 1.41-1.46 (4 x s, 12H, 2 x $(CH_3)_3C$); sucrose unit: δ 3.47 (d, 1H, *J* = 15 Hz, H-5), 3.53-3.66 (m, 3H, H-2, 2 x H-1'), 3.72-3.79 (m, 1H, H-6'), 3.81-3.91 (m, 9H, H-4, 2 x H-6, 6 x H-h'), 3.96-4.06 (m, 3H, H-3, H-5', H-6'), 4.22 (d, 1H, *J* = 12 Hz, H-3'), 5.52 (t, 1H, *J* = 7.5 Hz, H-4'), 6.20 (d, 1H, *J* = 3 Hz, H-1); *trans*-alkenyl and aromatic protons: δ 6.25 (d, 1H, *J* = 18 Hz, H-a'), 6.79 (d, 1H, *J* = 9 Hz, H-g'), 6.95 (s, 1H, H-f'), 6.99-7.02 (m, 1H, H-c'), 7.58 (d, 1H, *J* = 15 Hz, H-b'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.0, 17.4, 18.7, 19.1, 24.2, 25.3, 29.0, 41.9, 53.6, 55.9, 56.0, 64.2, 82.4, 91.4, 100.0, 102.2, 103.6, 114.5, 123.0, 127.0, 149.3, 151.5, 167.2; HRMS (ESI-positive mode): *m*/z calcd. for $C_{29}H_{40}O_{14}Na$ 635.2316; found 635.2296 $[M+Na]^+$.

*4'-O-(3,4,5-trimethoxycinnamoyl)-2,1'-di-O-isopropylidene sucrose, 4'-triOMe **50**:* Compound **57** (200 mg, 0.225 mmol) and $Pd(OAc)_2$ (4.2 mg, 0.0187 mmol) were dissolved in CH_2Cl_2 (5.0 ml) and stirred at room temperature. Subsequently, Et_3SiH (47.8 µL, 0.229 mmol) and NEt_3 (4.18 µL, 0.0229 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, the reaction was diluted with EtOAc (30.0 ml). The reaction mixture was washed twice with H_2O and the organic layer was collected and dried over anhydrous $MgSO_4$. After removal of EtOAc, the crude product obtained was re-dissolved in pyridine (1.0 ml) and stirred at room temperature. Subsequently, 1.56 M $3HF{\cdot}NEt_3$ (432 µL, 0.674 mmol) and NEt_3 (62.7 µL, 0.449 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, pyridine was removed. The crude product was then subjected to purification using 3:2 EtOAc/Hexane as eluent. Compound **50** was obtained as white solid in 85% yield. mp 87.1-88.3˚C; ^{1}H NMR (300 MHz, $CDCl_3$): isopropylidene rings: δ 1.38-1.44 (4 x s, 12H, 2 x $(CH_3)_3C$); methoxy and sucrose: δ 3.44 (d, 1H, *J* = 12 Hz, H-5), 3.49-3.70 (m, 4H, H-2, 2 x H-1', H-6'), 3.71-3.83 (m, 12H, H-4, 2 x H-6, 9 x H-h'), 3.92-4.08 (m, 3H, H-3, H-5', H-6'), 4.27 (d, 1H, *J* = 12 Hz, H-3'), 5.53 (t, 1H, *J* = 7.5 Hz, H-4'), 6.20 (d, 1H, *J* = 3 Hz, H-1); *trans*-alkenyl and aromatic protons: δ 6.25 (d, 1H, *J* = 18 Hz, H-a'), 6.59 (s, 2H, H-c', H-g'), 7.47 (d, 1H, *J* = 15 Hz, H-b'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.2, 24.2, 25.2, 25.6, 25.9, 29.0, 56.1, 56.2, 61.0, 62.0, 62.3, 64.2, 66.4, 69.0, 73.2, 73.6, 82.2, 91.5, 99.9, 100.0, 102.4, 102.5, 103.4, 105.4, 116.2, 128.2, 129.6, 140.3, 146.3, 153.2, 153.4, 167.0.



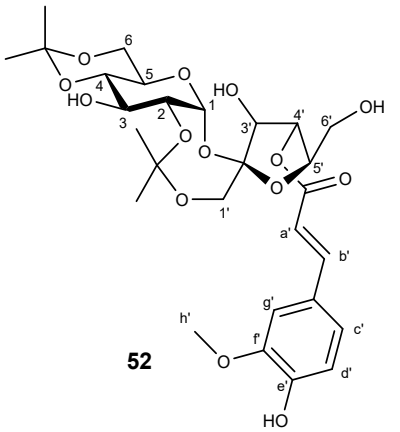
50

4'-O-caffeoyl-2,1'-di-O-isopropylidene sucrose, 4'-caff ***51****:* Compound **58** (200 mg, 0.189 mmol) and $Pd(OAc)_2$ (3.5 mg, 0.0157 mmol) were dissolved in CH_2Cl_2 (5.0 ml) and stirred at room temperature. Subsequently, Et_3SiH (40.2 µL, 0.251 mmol) and NEt_3 (3.51 µL, 0.0251 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, the reaction was diluted with EtOAc (30.0 ml). The reaction mixture was washed twice with H_2O and the organic layer was collected and dried over anhydrous $MgSO_4$. After removal of EtOAc, the crude product obtained was re-dissolved in pyridine (1.0 ml) and stirred at room temperature. Subsequently, 1.56 M $3HF{\cdot}NEt_3$ (363 µL, 0.566 mmol) and NEt_3 (52.6 µL, 0.377 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, pyridine was removed. The crude product was then subjected to purification using 3:2 EtOAc/Hexane as eluent. Compound **51** was obtained as white solid in 84% yield. mp 69.5-70.6˚C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$): isopropylidene rings: δ 1.16-1.32 (4 x s, 12H, 2 x $(CH_3)_3C$); sucrose: δ 3.35-3.49 (m, 3H, H-5, 2 x H-1'), 3.51-3.69 (m, 4H, H-2, 2 x H-6, H-6'), 3.72-3.77 (m, 2H, H-4, H-6'), 3.82-3.89 (m, 2H, H-3, H-5'), 4.00 (d, 1H, *J* = 15 Hz, H-3'), 5.38 (t, 1H, *J* = 7.5 Hz, H-4'), 5.99 (d, 1H, *J* = 15 Hz, H-1); *trans*-alkenyl and aromatic protons: δ 6.16 (d, 1H, *J* = 15 Hz, H-a'), 6.72 (d, 1H, *J* = 9 Hz, H-f'), 6.90 (d, 1H, *J* = 9 Hz, H-g'), 7.03 (d, 1H, *J* = 3 Hz, H-c'), 7.44 (d, 1H, *J* = 18 Hz, H-b'); ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$): δ 19.4, 24.5, 25.5, 62.7, 63.8, 64.3, 65.4, 66.8, 70.1, 71.5, 73.7, 74.3, 75.0, 77.7, 78.6, 82.8, 92.2, 93.9, 99.9, 100.0, 102.0, 102.2, 104.3, 104.4, 105.9, 114.9, 115.2, 116.1, 116.4, 120.4, 122.8, 127.4, 146.4, 146.7, 129.1, 167.2, 167.4; HRMS (ESI-positive mode): *m*/z calcd. for $C_{27}H_{37}O_{14}$ 585.2183; found 585.2163 $[M+H]^{+\cdot}$



51

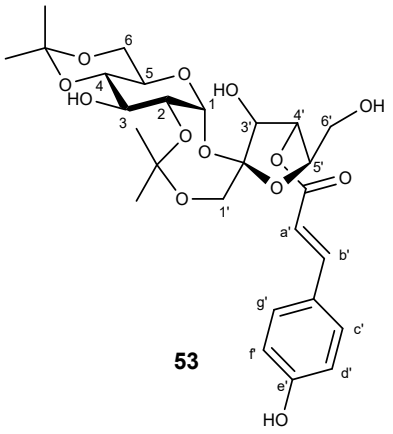
4'-O-feruloyl-2,1'-di-O-isopropylidene sucrose, 4'-feru ***52****:* Compound **59** (200 mg, 0.208 mmol) and $Pd(OAc)_2$ (3.9 mg, 0.0174 mmol) were dissolved in CH_2Cl_2 (5.0 ml) and stirred at room temperature. Subsequently, Et_3SiH (44.3 µL, 0.278 mmol) and NEt_3 (3.88 µL, 0.0278 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, the reaction was diluted with EtOAc (30.0 ml). The reaction mixture was washed twice with H_2O and the organic layer was collected and dried over anhydrous $MgSO_4$. After removal of EtOAc, the crude product obtained was re-dissolved in pyridine (1.0 ml) and stirred at room temperature. Subsequently, 1.56 M $3HF{\cdot}NEt_3$ (400 µL, 0.625 mmol) and NEt_3 (58.1 µL, 0.416 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, pyridine was removed. The crude product was then subjected to purification using 3:2 EtOAc/Hexane as eluent. Compound **52** was obtained as white solid in 82% yield. mp 77.8-79.0˚C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$): isopropylidene rings: δ 1.31-1.46 (4 x s, 12H, 2 x $(CH_3)_3C$); methoxy and sucrose unit: δ 3.49-3.58 (m,



52

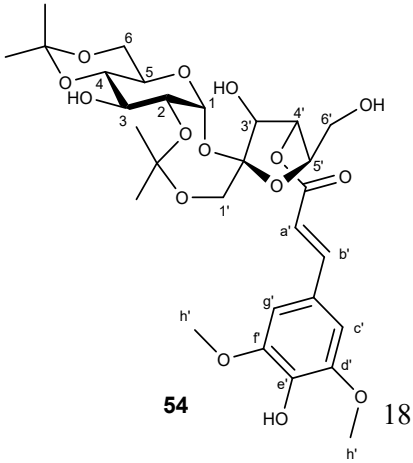
2H, H-5, H-1'), 3.62-3.77 (m, 5H, H-2, 2 x H-6, H-1', H-6'), 3.82-3.88 (m, 2H, H-4, H-6'), 3.91 (s, 3H, 3 x H-h'), 3.97-4.02 (m, 2H, H-3, H-5'), 4.14 (d, 1H, *J* = 12 Hz, H-3'), 5.52 (t, 1H, *J* = 7.5 Hz, H-4'), 6.13 (d, 1H, *J* = 3 Hz, H-1); aromatic and *trans*-alkenyl protons: δ 6.42 (d, 1H, *J* = 15 Hz, H-a'), 6.86 (d, 1H, *J* = 6 Hz, H-c'), 7.13 (d, 1H, *J* = 3 Hz, H-d') 7.15 (s, 1H, H-g'), 7.34 (d, 1H, *J* = 3 Hz, H-b'); ^{13}C NMR (75.5 MHz, $(CD_3)CO$): δ 18.5, 23.6, 24.6, 25.3, 55.5, 61.8, 63.0, 63.4, 65.8, 69.2, 73.4, 74.1, 76.9, 77.6, 81.9, 91.3, 99.2, 101.4, 103.5, 105.0, 110.6, 114.1, 115.3, 123.3, 126.3, 145.9, 148.0, 149.6, 166.5, 166.7; HRMS (ESI-positive mode): *m*/z calcd. for $C_{28}H_{39}O_{14}$ 599.2340; found 599.2333 $[M+H]^+$

*The synthesis of 4'-O-coumaroyl-2,1'-di-O-isopropylidene sucrose, 4'-coum **53**:* Compound **60** (200 mg, 0.215 mmol) and $Pd(OAc)_2$ (4.0 mg, 0.0179 mmol) were dissolved in CH_2Cl_2 (5.0 ml) and stirred at room temperature. Subsequently, Et_3SiH (45.8 µL, 0.287 mmol) and NEt_3 (4.00 µL, 0.0286 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, the reaction was diluted with EtOAc (30.0 ml). The reaction mixture was washed twice with H_2O and the organic layer was collected and dried over anhydrous $MgSO_4$. After removal of EtOAc, the crude product obtained was re-dissolved in pyridine (1.0 ml) and stirred at room temperature. Subsequently, 1.56 M $3HF{\cdot}NEt_3$ (413 µL, 0.645 mmol) and NEt_3 (60.0 µL, 0.430 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, pyridine was removed. The crude product was then subjected to purification using 3:2 EtOAc/Hexane as eluent. In the end, 4'-coum **53** was obtained as white solid in 84% yield. mp 75.5-76.9˚C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$): isopropylidene rings: δ 1.08-1.31 (4 x s, 12H, 2 x $(CH_3)_3C$); sucrose unit: δ 3.35-3.43 (m, 2H, H-5, H-1'), 3.51-3.60 (m, 6H, H-2, H-4, 2 x H-6, H-1', H-6'), 3.68-3.77 (m, 2H, H-3, H-6'), 3.82-3.89 (m, 1H, H-5'), 3.99 (d, 1H, *J* = 12 Hz, H-3'), 5.39 (t, 1H, *J* = 7.5 Hz, H-4'), 5.99 (d, 1H, *J* = 3 Hz, H-1); *trans*-alkenyl and aromatic protons: δ 6.22 (d, 1H, *J* = 18 Hz, H-a'), 6.76 (d, 2H, *J* = 9 Hz, H-d', H-f'), 7.41 (d, 2H, *J* = 9 Hz, H-c', H-g'), 7.51 (d, 1H, *J* = 15 Hz, H-b'); ^{13}C NMR (75.5 MHz, $(CD_3)CO$): δ 25.8, 62.5, 62.9, 64.1, 71.5, 73.0, 74.4, 74.6, 78.4, 78.9, 83.3, 93.4, 106.4, 114.8, 116.8, 126.7, 131.2, 146.5, 161.0, 167.2; HRMS (ESI-positive mode): *m*/z calcd. for $C_{27}H_{37}O_{13}$ 569.2234; found 569.2239 $[M+Na]^+$



53

4'-*O*-sinapoyl-2,1'-di-*O*-isopropylidene sucrose, 4'-sinap **54**: Compound **61** (200 mg, 0.202 mmol) and $Pd(OAc)_2$ (3.8 mg, 0.0168 mmol) were dissolved in CH_2Cl_2 (5.0 ml) and stirred at room temperature. Subsequently, Et_3SiH (43.0 µL, 0.269 mmol) and NEt_3 (3.76 µL, 0.0269 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, the reaction was diluted with EtOAc (30.0 ml). The reaction mixture



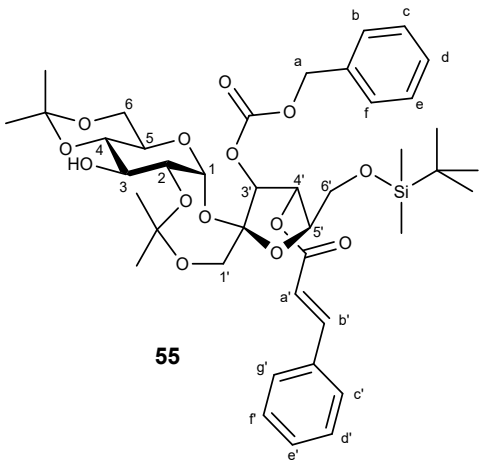
54

was washed twice with H_2O and the organic layer was collected and dried over anhydrous $MgSO_4$. After removal of EtOAc, the crude product obtained were dissolved in pyridine (1.0 ml) and stirred at room temperature. Subsequently, 1.56 M $3HF{\cdot}NEt_3$ (388 µL, 0.606 mmol) and NEt_3 (56.4 µL, 0.404 mmol) were added to the solution and the reaction was left to stir for 12 hours. Upon completion, pyridine was removed. The crude product was then subjected to purification using 3:2 EtOAc/Hexane as eluent. Compound **54** was obtained as white solid in 88% yield. mp 84.8-86.2˚C; ^{1}H NMR (300 MHz, $CDCl_3$): isopropylidene rings: δ 1.46-1.52 (4 x s, 12H, 2 x $(CH_3)_3C$); methoxy and sucrose: δ 3.50-3.79 (m, 5H, H-2, H-5, 2 x H-1', H-6'), 3.81-3.91 (m, 8H, 2 x H-6, 6 x H-h'), 4.01-4.14 (m, 4H, H-3, H-4, H-5', H-6'), 4.37 (d, 1H, *J* = 12 Hz, H-3'), 5.59 (t, 1H, *J* = 7.5 Hz, H-4'), 5.96 (s, 1H, H-1); *trans*-alkenyl and aromatic protons: δ 6.24-6.29 (m, 1H, H-a'), 6.66 (s, 2H, H-c', H-g'), 7.51 (d, 1H, *J* = 15 Hz, H-b'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.3, 23.4, 24.4, 28.2, 55.5, 61.2, 61.4, 63.3, 65.6, 68.1, 68.1, 72.3, 72.8, 81.4, 90.6, 99.1, 101.6, 101.7, 102.5, 102.5, 104.4, 104.4, 113.7, 124.7, 136.6, 136.6, 145.7, 146.4, 146.4 166.3; HRMS (ESI-positive mode): *m*/z calcd. for $C_{29}H_{40}O_{15}Na$ 651.2265; found 651.2245 $[M+Na]^+$

General procedure 2 for acylation of 3'-*O*-Cbz 16: Synthesis of compounds 55-61

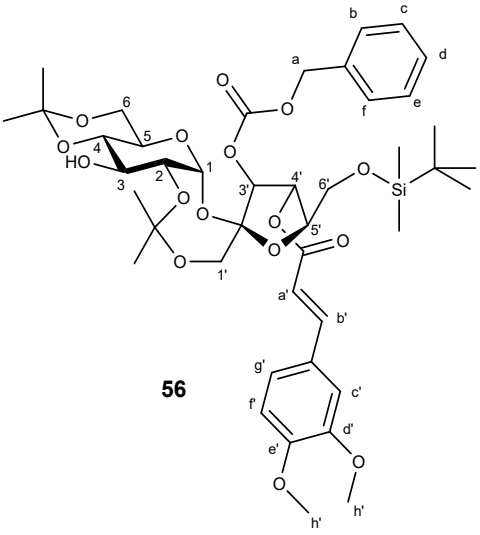
The (Substituted) cinnamic acid (1.12 mmol) and DCC (231 mg, 1.12 mmol) were added to a stirred solution of 3'-*O*-Cbz **16** (500, 0.746 mmol) and DMAP (9.2 mg, 0.0746 mmol) in CH_2Cl_2 (10 ml) at room temperature. After 12 hours (TLC), CH_2Cl_2 was removed under vacuum and the crude residue was triturated in cold diethyl ether (20 mL) and filtered. Diethyl ether was then removed under vacuum and the residue was purified using column chromatography using 4:1 Hexane/EtOAc as eluent. This procedure was used to synthesize compounds **55-61**.

*4'-O-cinnamoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **55**:* Following the general procedure 2, cinnamic acid **34** (166 mg, 1.12 mmol) was added to the solution. After purification, compound **55** was obtained as white solid in 82% yield. mp 88.0-89.5°C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS: δ 0.02 (s, 6H, $(CH_3)_2Si$), 0.83 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.33-1.51 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz and sucrose unit: δ 3.50-3.59 (m, 2H, H-5, H-1'), 3.62-3.69 (m, 2H, H-2, H-1'), 3.71-3.86 (m, 5H, H-4, 2 x H-6, 2 x H-6'), 4.10 (d, 1H, *J* = 12 Hz, H-3), 4.18-4.20 (m, 1H, H-5'), 4.93 (d, 1H, *J* = 3 Hz, H-3'), 5.15-5.26 (m, 2H, 2 x H-a), 5.54 (t, 1H, *J* = 4.5. Hz, H-4'), 6.01 (d, 1H, *J* = 3 Hz, H-1); Cbz and cinnamoyl protons: δ 6.38 (d, 1H, *J* = 18 Hz, H-a'), 7.31-7.49 (m, 8H, H-c', H-d', H-e', H-f', H-g', H-c, H-d, H-e), 7.51 (d, 2H, *J* = 3 Hz, H-b, H-f), 7.66 (d, 1H, *J* = 18 Hz, H-b'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.20,

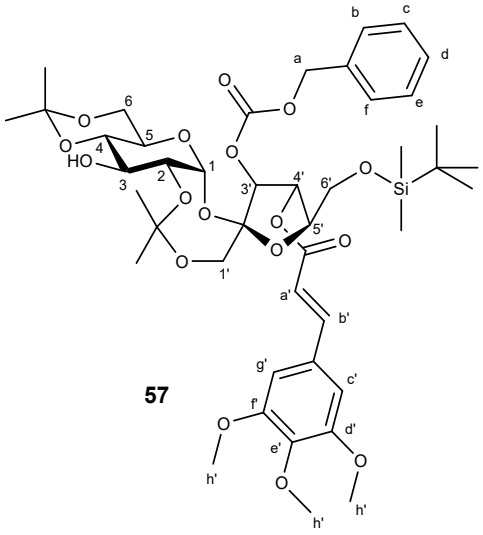


-5.18, 18.5, 19.3, 24.2, 25.7, 25.8, 26.0, 29.3, 63.9, 70.3, 70.5, 73.1, 74.1, 81.2, 82.6, 91.5, 100.0, 101.8, 104.5, 117.3, 128.4, 128.5, 128.7, 128.9, 129.1, 130.8, 134.4, 135.0, 146.2, 145.8, 165.7; HRMS (ESI-positive mode): *m*/z calcd. for $C_{41}H_{57}O_{14}Si$ 801.3518; found 801.3481 $[M+H]^+$

*4'-O-(3,4-dimethoxycinnamoyl)-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **56**:* Following the general procedure 2, diOMe acid **35** (233 mg, 1.12 mmol) was added to the solution. After purification, compound **56** was obtained as white solid in 81% yield. mp 91.7-92.7˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.82 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.32-1.49 (4 x s, 12H, 2 x $(CH_3)_3C$); Cbz, methoxy and sucrose unit: δ 3.50 (d, 1H, *J* = 12 Hz, H-5), 3.57-3.60 (m, 1H, H-1'), 3.65-3.79 (m, 2H, H-2, H-1'), 3.75-3.84 (m, 5H, H-4, 2 x H-6, 2 x H-6'); 3.87 (s, 6H, 6 x H-h'), 4.08 (d, 1H, *J* = 12 Hz, H-3), 4.16-4.18 (m, 1H, H-5'), 4.90 (d, 1H, *J* = 6 Hz, H-3'), 5.13-5.25 (m, 2H, 2 x H-a), 5.51 (t, 1H, *J* = 4.5 Hz, H-4'), 5.99 (d, 1H, *J* = 3 Hz, H-1); Cbz and dimethoxycinnamoyl protons: δ 6.24 (d, 1H, *J* = 15 Hz, H-a'), 6.84 (d, 1H, *J* = 9 Hz, H-g'), 6.99 (s, 1H, H-f'), 7.07 (s, 1H, H-c'), 7.26-7.37 (m, 5H, H-b, H-c, H-d, H-e, H-f), 7.58 (d, 1H, *J* = 15 Hz, H-b'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.4, -5.3, 18.3, 19.2, 24.0, 25.6, 25.9, 29.1, 55.9, 56.0, 63.7, 63.9, 70.1, 70.3, 72.9, 73.9, 82.8, 82.6, 91.3, 99.8, 101.6, 104.3, 109.7, 111.0, 114.7, 122.9, 127.2, 128.2, 128.5, 128.7, 134.9, 145.9, 149.3, 151.4, 154.6, 165.7; HRMS (ESI-positive mode): *m*/z calcd. for $C_{43}H_{61}O_{16}Si$ 861.3729; found 861.3700 $[M+H]^+$

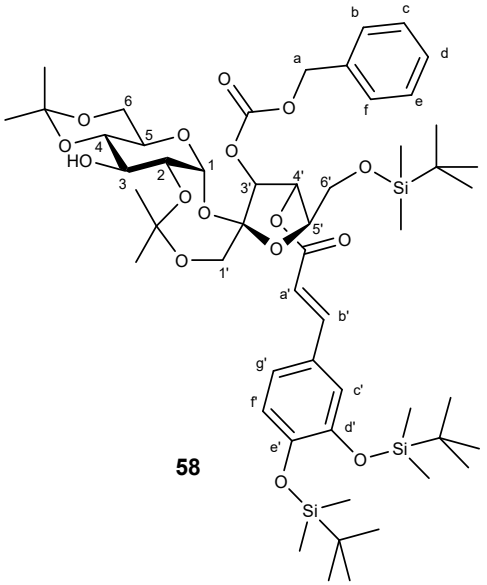


*4'-O-(3,4,5-trimethoxycinnamoyl)-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **57**:* Following the general procedure 2, triOMe acid **36** (266 mg, 1.12 mmol) was added to the solution. After purification, compound **57** was obtained as white solid in 87% yield. mp 92.0-93.1˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.81 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.29-1.49 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz, methoxy and sucrose unit: δ 3.45-3.60 (m, 4H, H-2, H-5, 2 x H-1'), 3.63-3.83 (m, 4H, H-4, 2 x H-6, H-6'), 3.85 (s, 9H, 9 x H-a), 3.92-4.10 (m, 2H, H-6', H-3), 4.15-4.18 (m, 1H, H-5'), 4.90 (d, 1H, *J* = 6 Hz, H-3'), 5.13-5.24 (m, 2H, 2 x H-a), 5.52 (t, 1H, *J* = 4.5 Hz, H-4'), 5.92-5.99 (m, 1H, H-1'); Cbz and trimethoxycinnamoyl protons: δ 6.27 (d, 1H, *J* = 15 Hz, H-a'), 6.70 (s, 2H, H-c', H-g'), 7.28-7.37 (m, 5H, H-b, H-c, H-d, H-e, H-f); 7.56 (d, 1H, *J* = 15 Hz, H-b'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.5, -5.4, -5.3, -5.2, 18.3, 19.1, 19.1, 24.0, 25.5, 25.6, 25.7, 25.9, 25.9, 29.1, 29.7, 30.9, 56.2, 61.0, 62.3, 63.5,

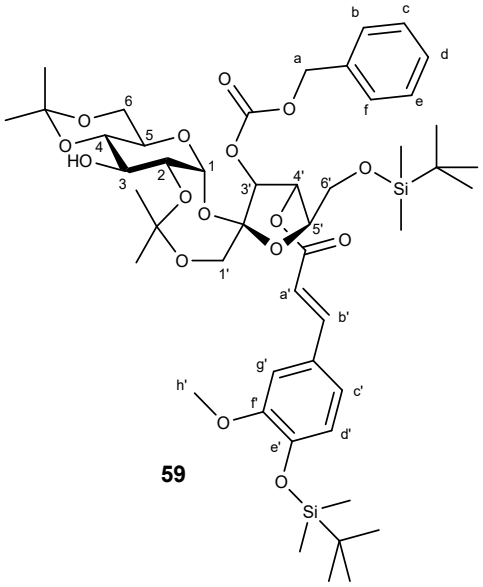


63.7, 63.9, 70.0, 70.1, 70.3, 72.9, 73.0, 81.0, 82.0, 82.3, 82.5, 90.8, 91.3, 99.8, 99.8, 101.6, 103.4, 104.3, 105.3, 116.3, 128.2, 128.5, 128.7, 128.7, 129.6, 134.7, 134.8, 140.3, 145.9, 153.5, 154.6, 165.5; HRMS (ESI-positive mode): *m*/z calcd. for $C_{44}H_{62}O_{17}NaSi$ 913.3654; found 913.3663 $[M+H]^+$

*4'-O-(3,4-di-tert-butyldimethylsiloxylcinnamoyl)-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **58**:* Following the general procedure 2, OTBS-caff acid **37** (457 mg, 1.12 mmol) was added to the solution. After purification, compound **58** was obtained as white solid in 86% yield. mp 69.0-70.1˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS: δ -0.18 (s, 6H, $(CH_3)_2Si$), 0.65 (s, 9H, $(CH_3)_3CSi$); TBS on OTBS-caffeoyl group: δ 0.00 (s, 12H, 2 x $(CH_3)_2Si$), 0.77-0.78 (2 x s, 18H, 2 x $(CH_3)_3CSi$); isopropylidene rings: δ 1.14 (s, 3H, $(CH_3)_2C$), 1.22 (s, 3H, $(CH_3)_2C$), 1.30 (d, 6H, *J* = 12 Hz, $(CH_3)_2C$); Cbz and sucrose unit: δ 3.31-3.42 (m, 2H, H-5, H-1'), 3.49-3.53 (m, 2H, H-2, H-1'), 3.58-3.65 (m, 5H, H-4, 2 x H-6, 2 x H-6'), 3.90 (d, 1H, *J* = 12 Hz, H-3), 3.99-4.00 (m, 1H, H-5'), 4.72 (d, 1H, *J* = 6 Hz, H-3'), 4.95-5.07 (m, 2H, 2 x H-a), 5.33 (t, 1H, *J* = 4.5 Hz, H-4'), 5.81 (d, 1H, *J* = 3 Hz, H-1); Cbz group: δ 7.10-7.22 (m, 5H, H-b, H-c, H-d, H-e, H-f); Cbz and OTBS-caffeoyl protons: δ 5.97 (d, 1H, *J* = 15 Hz, H-a'), 6.61 (d, 1H, *J* = 9 Hz, H-f'), 6.78 (s, 2H, H-c', H-g'), 7.34 (d, 1H, *J* = 15 Hz, H-b'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.4, -5.3, -4.1, -4.0, 18.3, 18.5, 18.5, 19.2, 24.0, 25.6, 25.9, 25.9, 25.9, 29.1, 62.3, 63.7, 63.8, 66.5, 70.1, 70.2, 73.0, 74.0, 76.6, 81.1, 82.6, 91.4, 99.8, 101.6, 104.3, 114.6, 120.5, 121.2, 122.5, 127.8, 128.2, 128.5, 128.7, 134.9, 145.9, 147.2, 149.8, 154.6, 165.8; HRMS (ESI-positive mode): *m*/z calcd. for $C_{53}H_{85}O_{16}Si_3$1061.5145; found 1061.5159 $[M+H]^+$

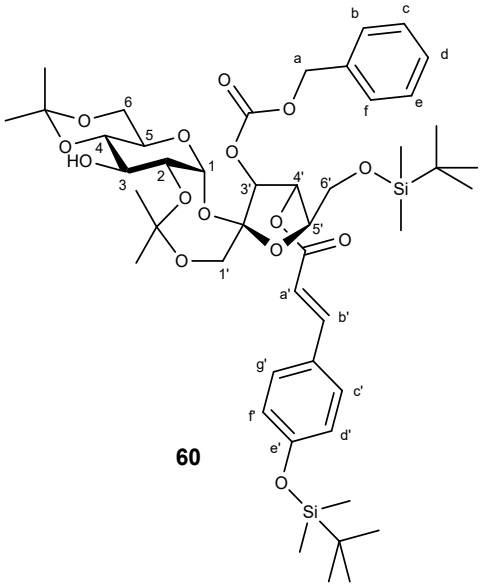


*4'-O-(4-tert-butyldimethylsiloxyl-3-methoxycinnamoyl)-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **59**:* Following the general procedure 2, OTBS-feru acid **38** (345 mg, 1.12 mmol) was added to the solution. After purification, compound **59** was obtained as white solid in 83% yield. mp 61.8-62.8˚C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS: δ -0.13 (s, 6H, $(CH_3)_2Si$), 0.68 (s, 9H, $(CH_3)_3CSi$); TBS on OTBS-feruloyl group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.82 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.19-1.34 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz, methoxy and sucrose unit: δ 3.43 (d, 1H, *J* = 9 Hz, H-5), 3.47-3.57 (m, 3H, H-2, 2 x H-1'), 3.62-3.71 (m, 7H, H-4, 2 x H-6, H-6', 3 x H-h'), 3.95 (d, 1H, *J* = 12 Hz, H-6'), 4.02-4.04 (m, 2H, H-3, H-5'), 4.76 (d, 1H, *J* = 6 Hz, H-3'), 5.04-5.11 (m, 2H, 2 x

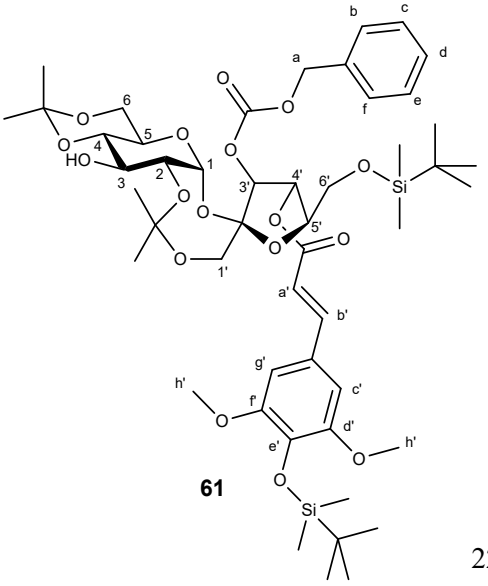


H-a), 5.37 (t, 1H, *J* = 4.5 Hz, H-4'), 5.86 (d, 1H, *J* = 3 Hz, H-1); Cbz group and OTBS-feruloyl protons: δ 6.08 (d, 1H, *J* = 15 Hz, H-a'), 6.68 (d, 1H, *J* = 9 Hz, H-c'), 6.83-6.86 (m, 2H, H-d', H-g'), 7.15-7.27 (m, 5H, H-b, H-c, H-d, H-e, H-f), 7.44 (d, 1H, *J* = 15 Hz, H-b'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.4, -5.3, -4.6, 18.3, 18.5, 19.2, 24.0, 25.6, 25.7, 25.9, 29.1, 55.5, 63.7, 63.9, 66.5, 70.1, 70.3, 72.9, 73.9, 76.6, 81.1, 82.6, 91.3, 99.8, 101.6, 104.3, 110.9, 114.7, 121.1, 122.5, 128.0, 128.2, 128.5, 128.7, 134.9, 146.1, 147.8, 151.2, 154.6, 165.8; HRMS (ESI-positive mode): *m*/z calcd. for $C_{48}H_{73}O_{16}Si_2$ 961.4437; found 961.4446 $[M+H]^+$

*4'-O-(4-tert-butyldimethylsiloxylcinnamoyl)-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **60**:* Following the general procedure 2, OTBS-coum acid **39** (311 mg, 1.12 mmol) was added to the solution. After purification, compound **60** was obtained as white solid in 87% yield. mp 91.7-92.7°C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS: δ -0.18 (s, 6H, $(CH_3)_2Si$), 0.63 (s, 9H, $(CH_3)_3CSi$); TBS on OTBS-coumaroyl group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.76 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.14-1.31 (4 x s, 12H, 2 x $(CH_3)_2C$); Cbz and sucrose unit: δ 3.30-3.48 (m, 4H, H-2, H-5, 2 x H-1'); 3.50-3.66 (m, 5H, H-4, 2 x H-6, 2 x H-6'), 3.90 (d, 1H, *J* = 12 Hz, H-3), 3.96-4.01 (m, 1H, H-5'), 4.71 (d, 1H, *J* = 6 Hz, H-3'), 4.95-5.07 (m, 2H, 2 x H-a), 5.32 (t, 1H, *J* = 4.5 Hz, H-4'), 5.81 (d, 1H, *J* = 3 Hz, H-1'); Cbz and OTBS-coumaroyl protons: δ 6.04 (d, 1H, *J* = 15 Hz, H-a'), 6.63 (d, 2H, *J* = 9 Hz, H-d', H-f'), 7.10-7.23 (m, 7H, H-b, H-c, H-d, H-e, H-f, H-c', H-g'), 7.41 (d, 1H, *J* = 15 Hz, H-b'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.4, -5.3, -4.4, 18.2, 18.3, 19.2, 24.0, 25.6, 25.6, 25.9, 29.1, 63.7, 63.8, 70.1, 70.3, 72.9, 73.9, 76.6, 81.1, 82.6, 91.3, 99.8, 101.6, 104.3, 114.7, 120.6, 120.6, 127.5, 128.2, 128.5, 128.7, 129.9, 130.0, 134.9, 141.3, 145.7, 154.6, 158.1, 165.8; HRMS (ESI-positive mode): *m*/z calcd. for $C_{47}H_{71}O_{15}Si_2$ 931.4332; found 931.4323 $[M+H]^+$

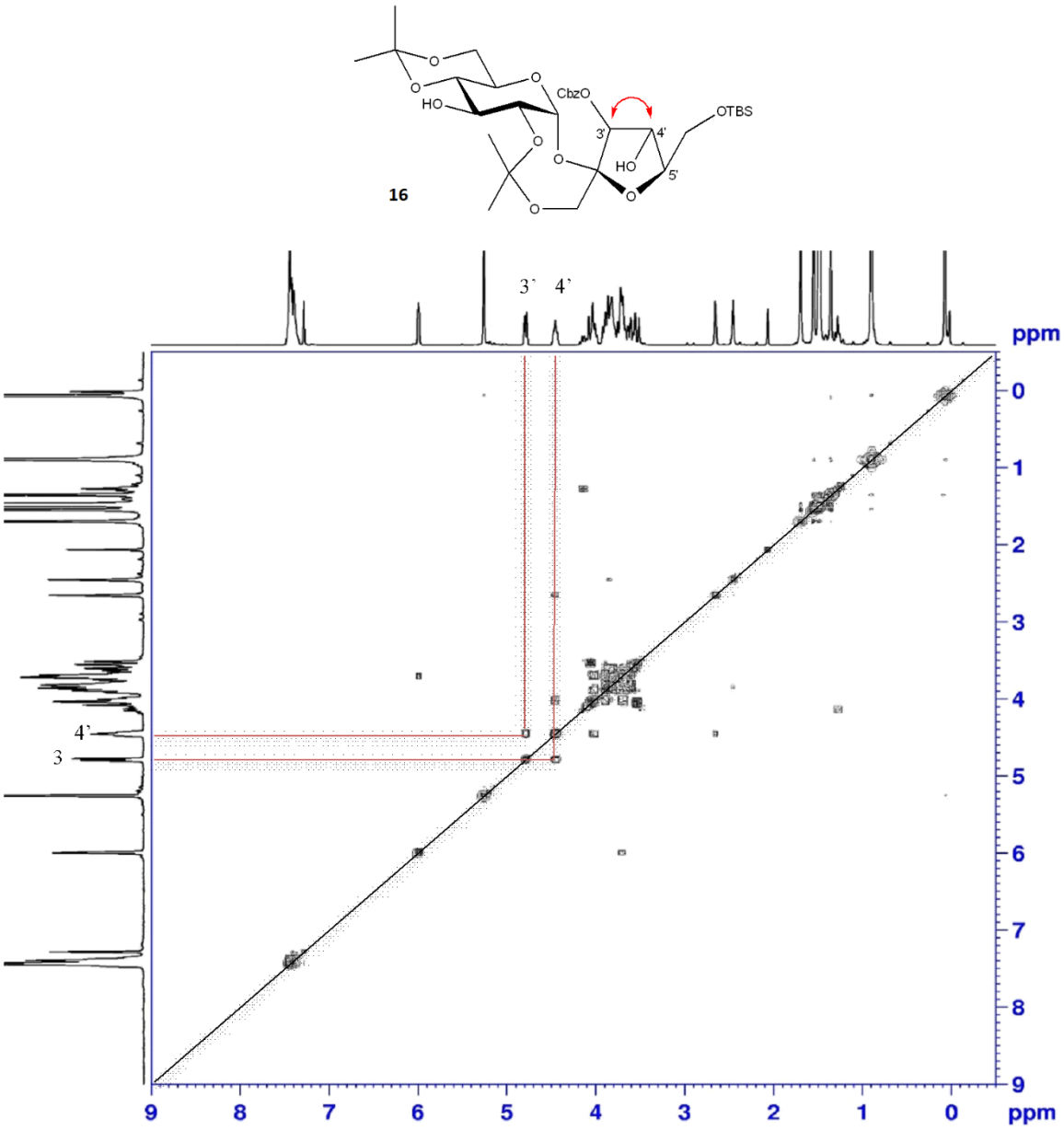


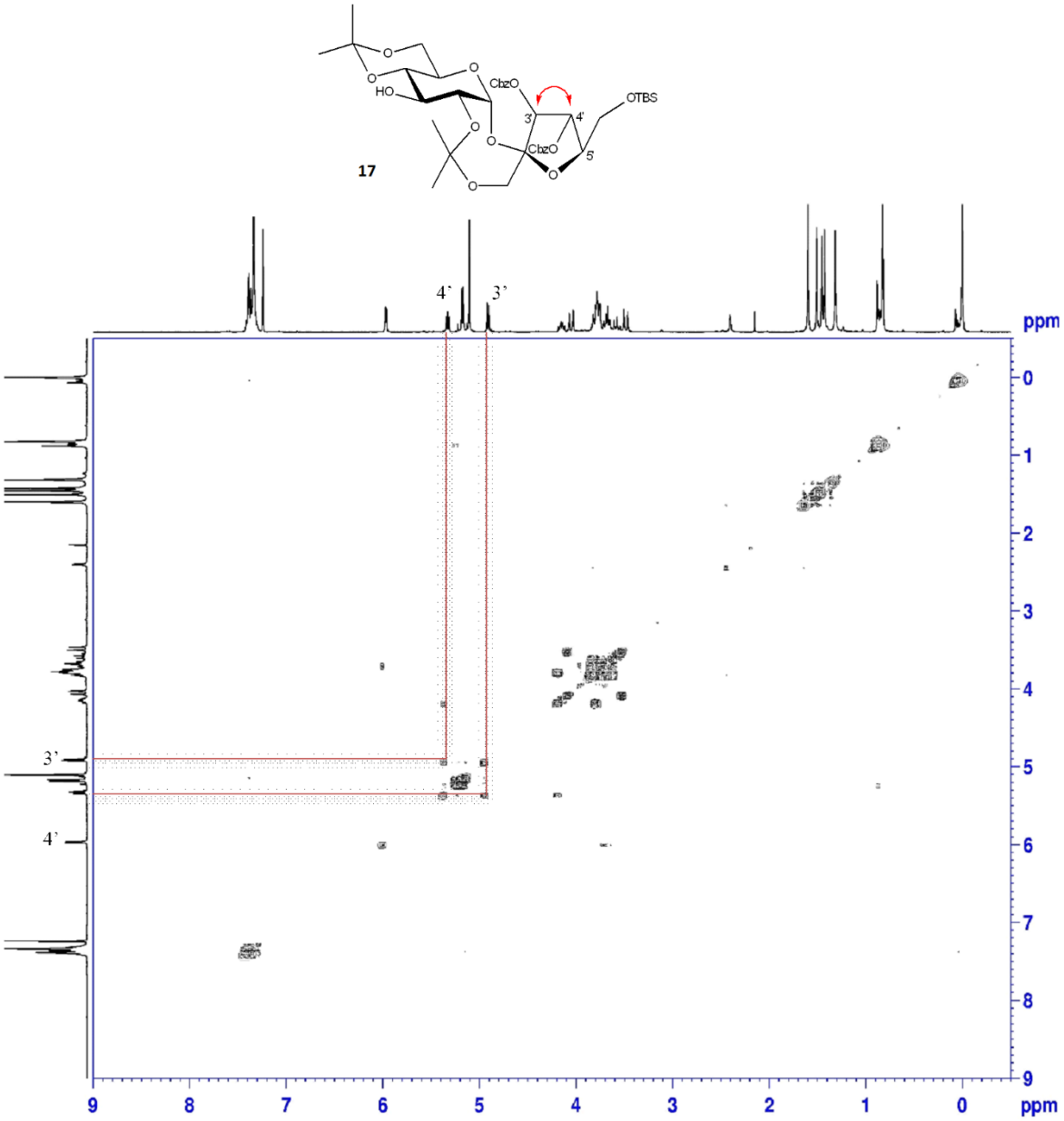
*4'-O-(4-tert-butyldimethylsiloxyl-3,5-dimethoxycinnamoyl)-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **61**:* Following the general procedure 2, OTBS-sinap acid **40** (378 mg, 1.12 mmol) was added to the solution. After purification, compound **61** was obtained as white solid in 84% yield. mp 94.0-94.7°C; ^{1}H NMR (300 MHz, $CDCl_3$): TBS: δ -0.10 (s, 6H, $(CH_3)_2Si$), 0.72 (s, 9H, $(CH_3)_3CSi$); TBS on OTBS-sinapoyl group: δ 0.00 (s, 6H, $(CH_3)_2Si$), 0.86 (s, 9H, $(CH_3)_3CSi$); isopropylidene rings: δ 1.22-1.39



(4 x s, 12H, 2 x $(CH_3)_2C$); Cbz, methoxy and sucrose: δ 3.40 (d, 1H, *J* = 12 Hz, H-5), 3.47 (t, 1H, *J* = 9 Hz, H-1'), 3.55-3.60 (m, 2H, H-2, H-1'), 3.65-3.74 (m, 10H, H-4, 2 x H-6, H-6', 6 x H-h'), 3.98 (d, 1H, *J* = 12 Hz, H-6'), 4.04-4.10 (m, 2H, H-3, H-5'), 4.79 (d, 1H, *J* = 6 Hz, H-3'), 5.03-5.16 (m, 2H, 2 x H-a), 5.41 (t, 1H, *J* = 3 Hz, H-4'), 5.89 (d, 1H, *J* = 3 Hz, H-1); Cbz group and OTBS-sinapoyl protons: δ 6.09, 6.15 (d, 1H, *J* = 18 Hz, H-a'), 6.58 (s, 2H, H-c', H-g'), 7.18-7.29 (m, 5H, H-b, H-c, H-d, H-e, H-f), 7.45 (d, 1H, *J* = 15 Hz, H-b'); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ -5.4, -4.6, 18.3, 18.8, 19.1, 24.0, 25.6, 25.7, 25.9, 55.8, 62.5, 63.9, 70.3, 73.0, 83.0, 91.3, 99.8, 101.6, 104.3, 105.5, 126.8, 128.2, 128.5, 128.7, 134.9, 137.2, 146.4, 151.7, 156.6, 165.9; HRMS (ESI-positive mode): *m*/z calcd. for $C_{49}H_{75}O_{17}Si_2$ 991.4543; found 991.4542 $[M+H]^+$

2. ^{1}H NMR and COESY spectra

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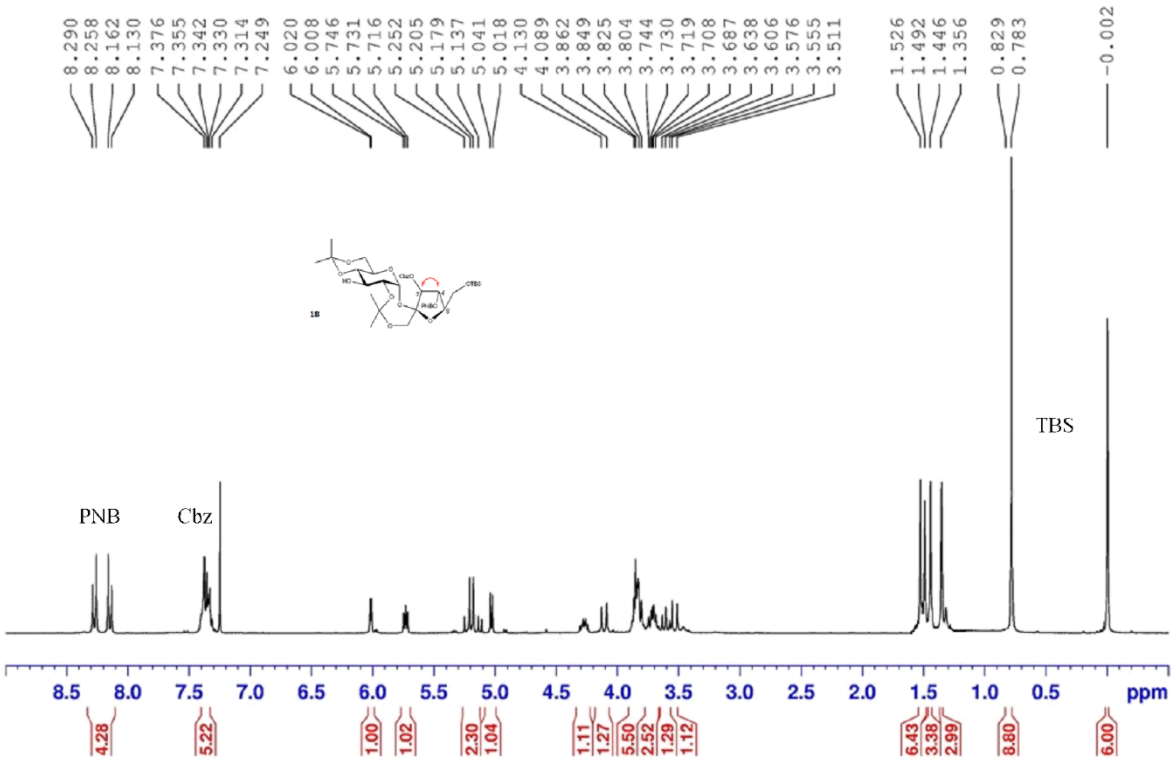
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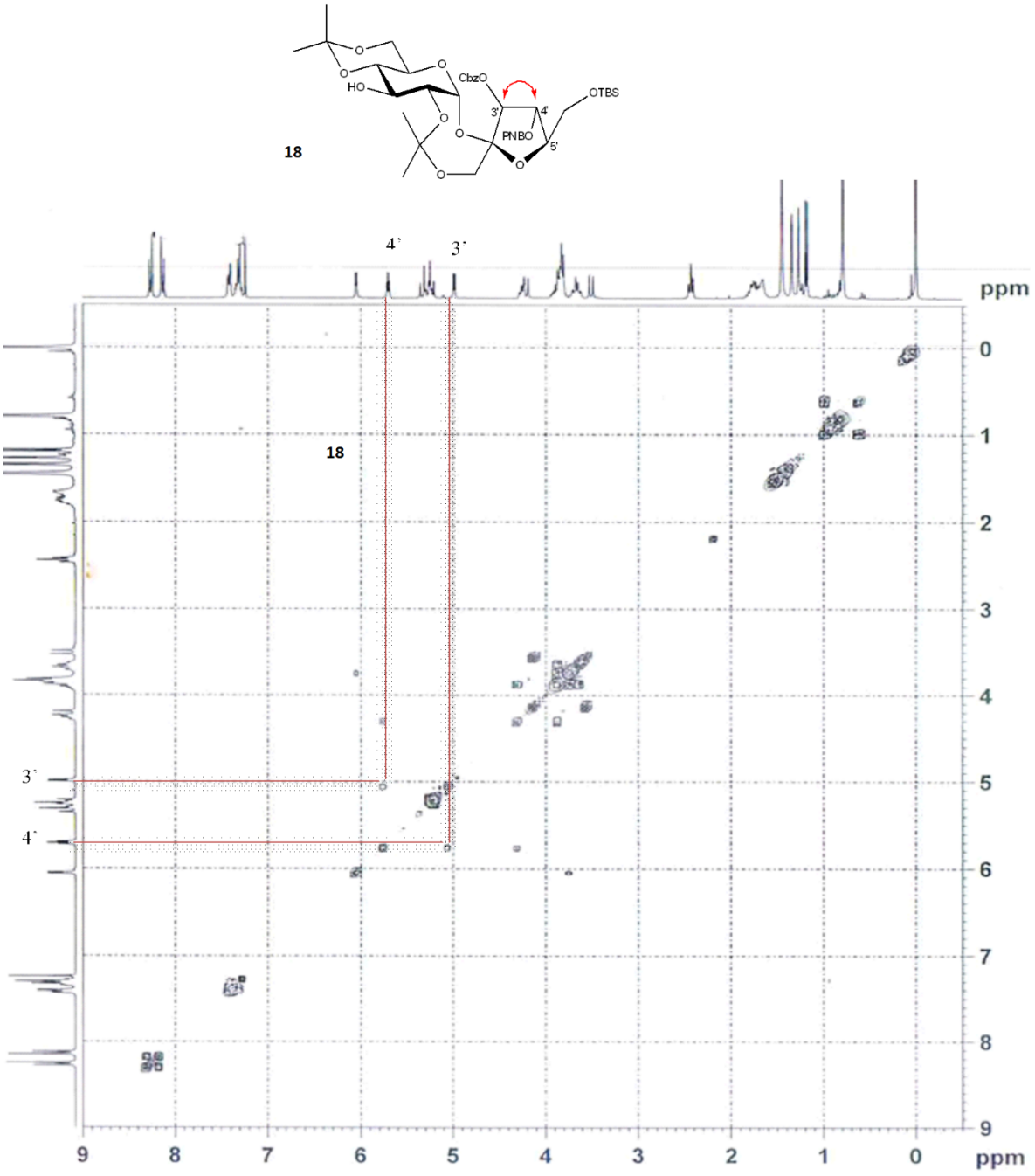
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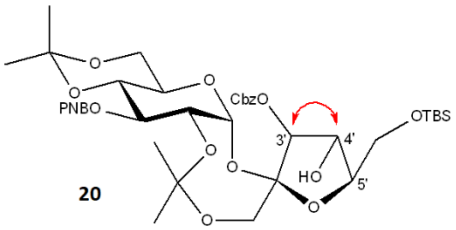

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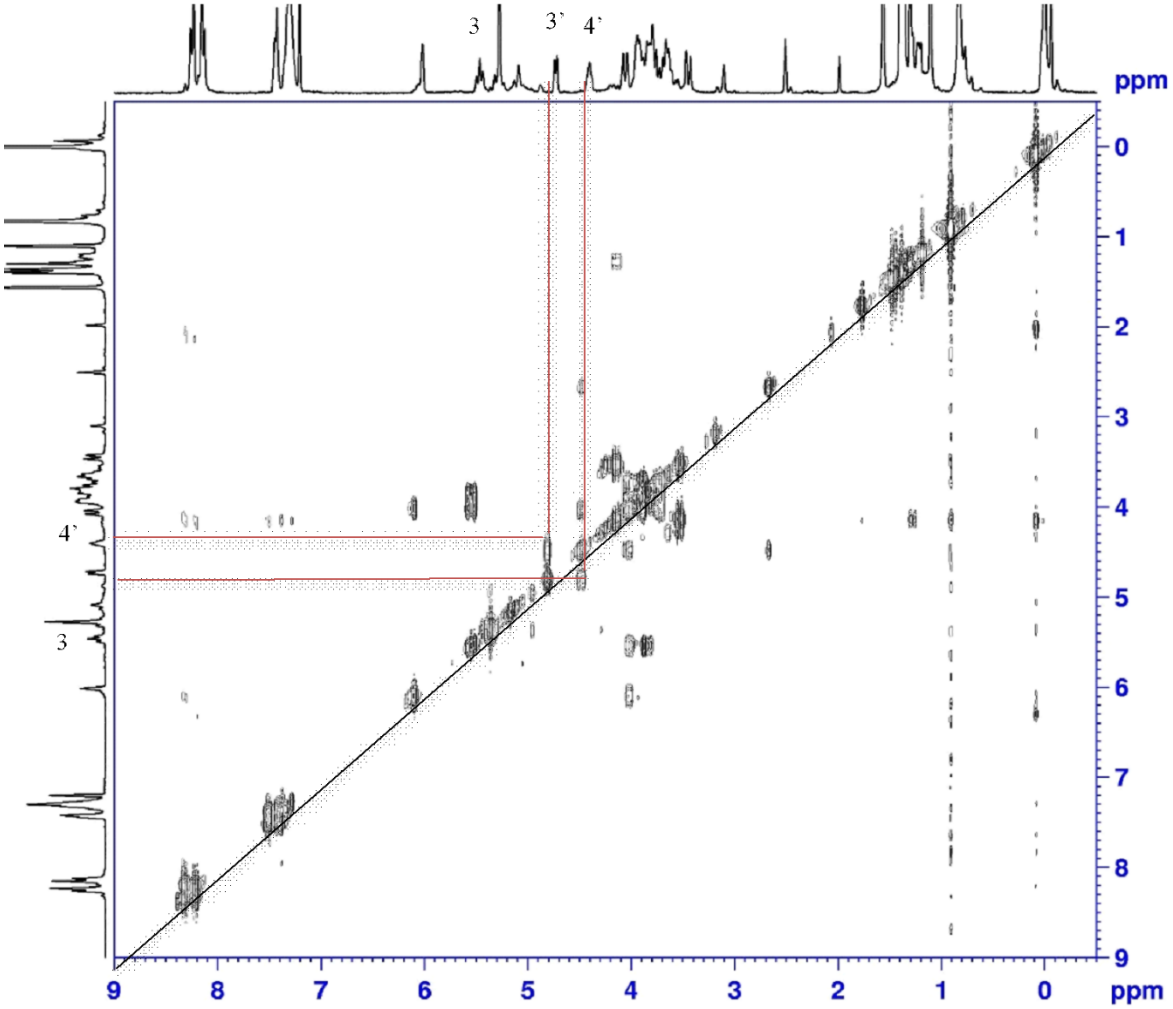

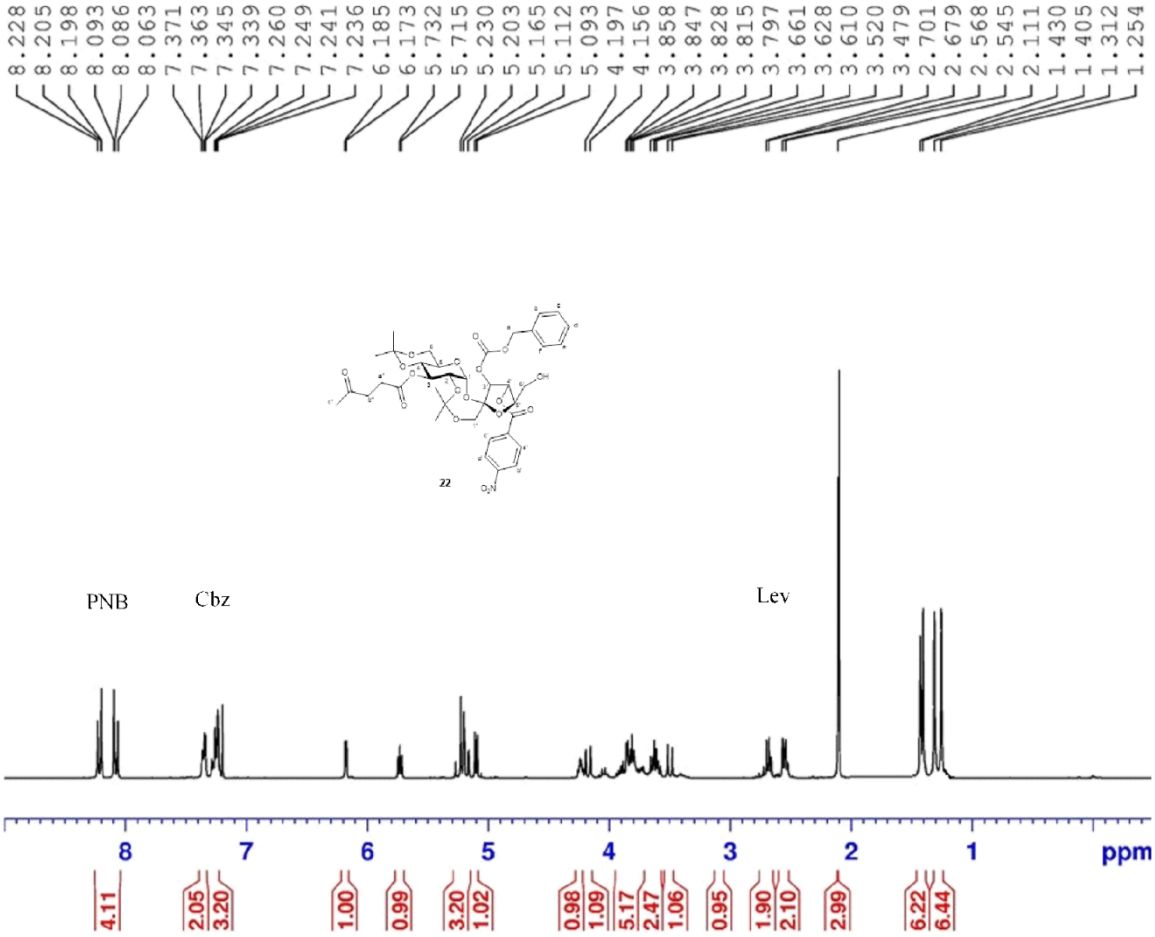
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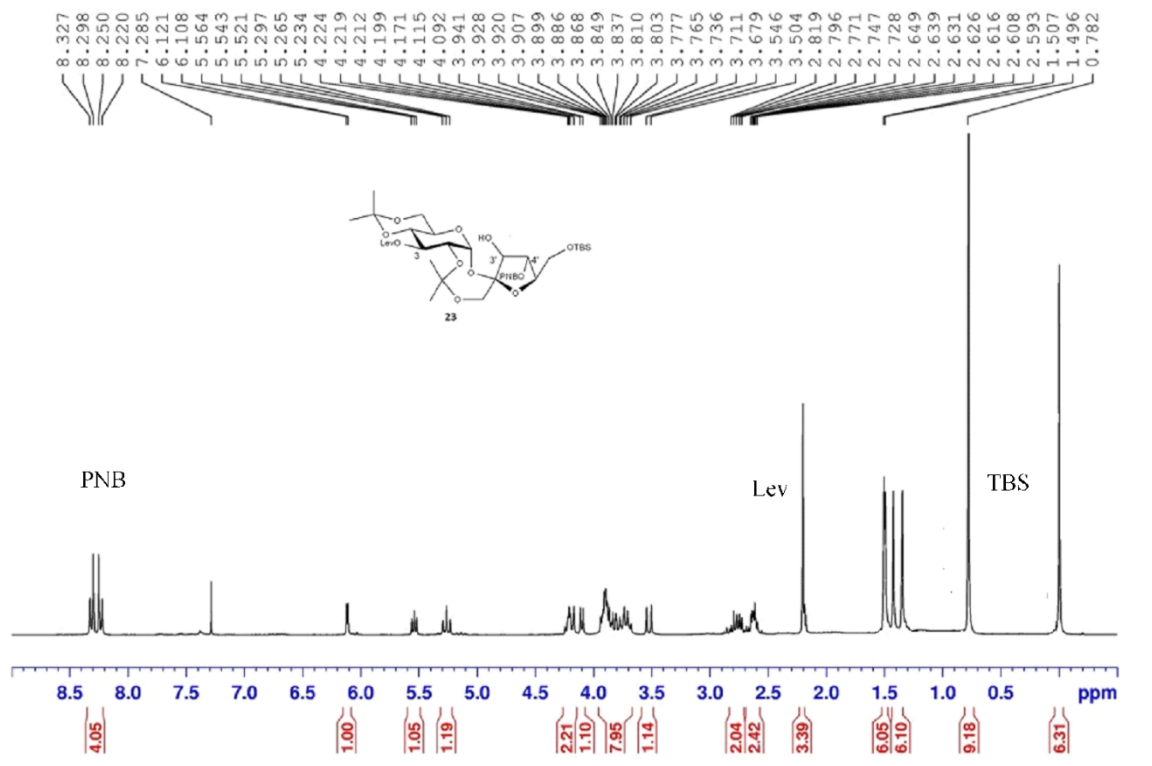
5.230
5.203
5.165
5.112
5.093
4.197
4.156
3.858
3.847
3.828
3.815
3.797
3.661
3.628
3.610
3.520
3.479
2.701
2.679
2.568
2.545
2.111
1.430
1.405
1.312
1.254
22
PNB
Cbz
Lev
8
7
6
5
4
3
2
1
ppm
4.11
2.05
3.20
1.00
0.99
3.20
1.02
0.98
1.09
5.17
2.47
1.06
0.95
1.90
2.10
2.99
6.22
6.44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8.298
8.250
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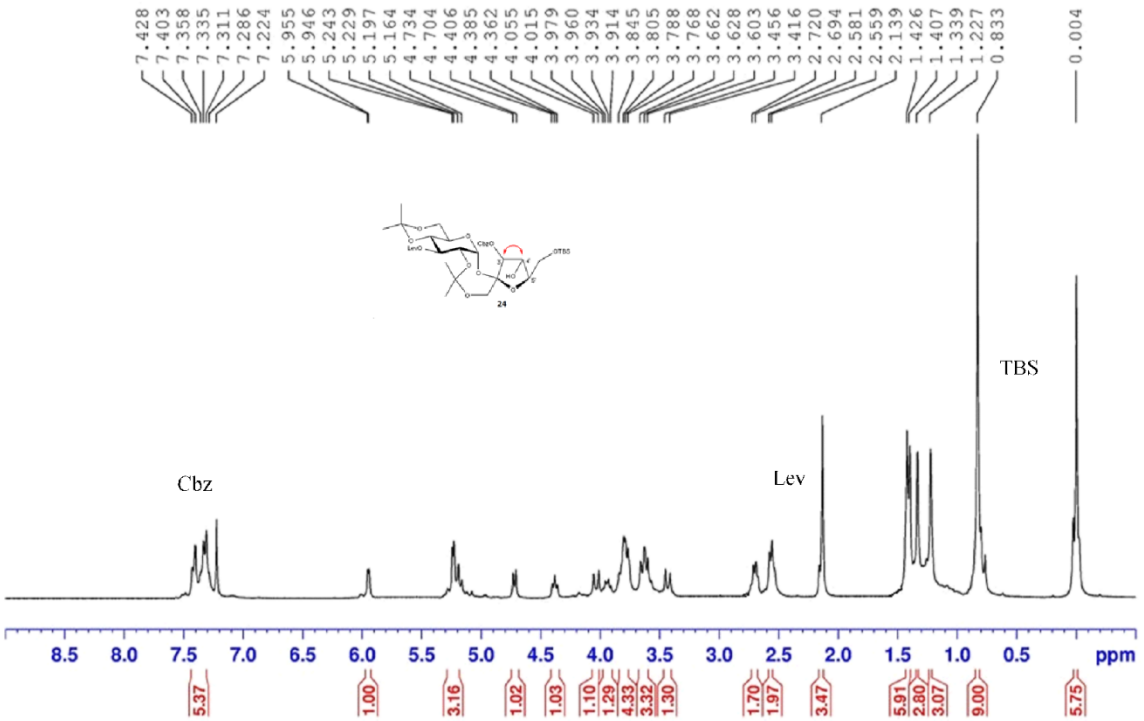
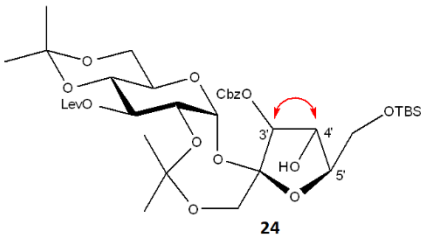
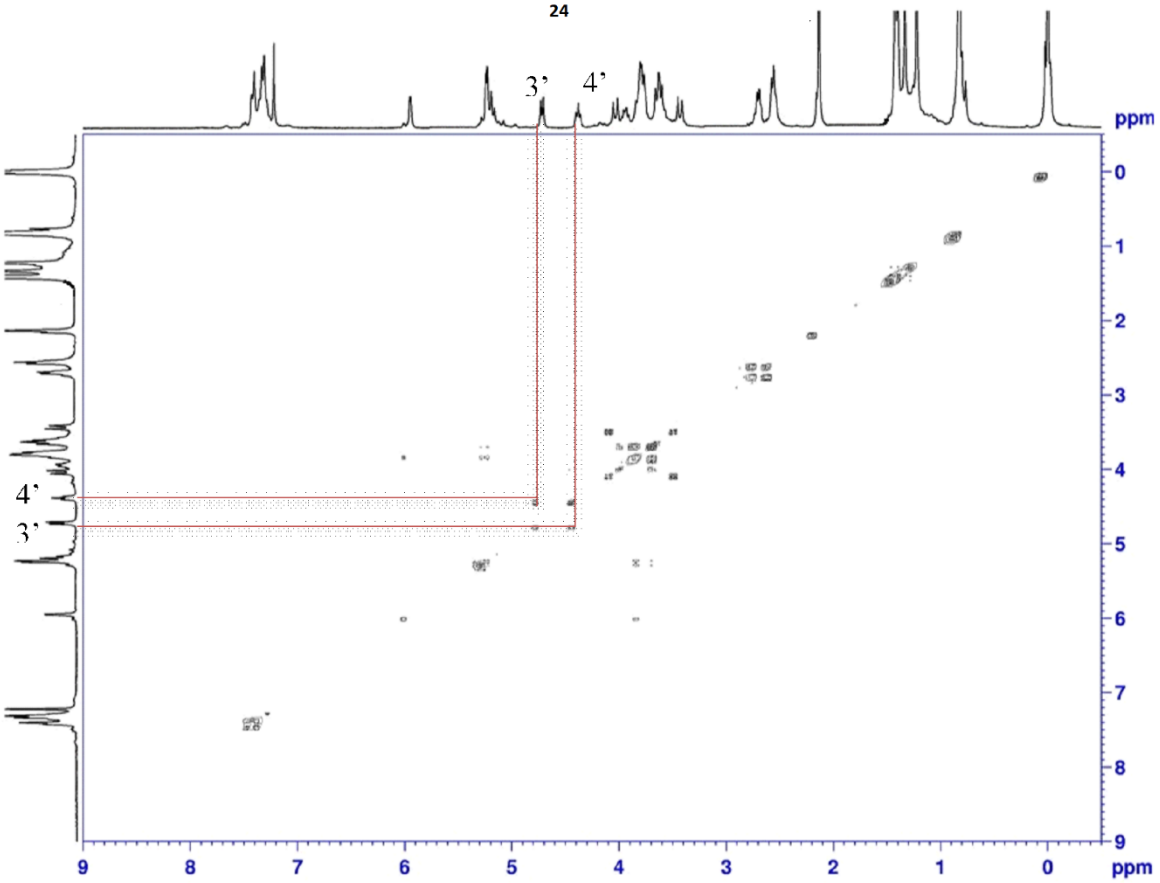
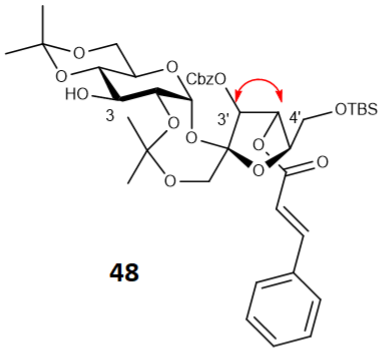
7.285
6.121
6.108
5.564
5.543
5.521
5.297
5.265
5.234
4.224
4.219
4.212
4.199
4.171
4.115
4.092
3.941
3.928
3.920
3.907
3.899
3.886
3.868
3.849
3.837
3.810
3.803
3.777
3.765
3.736
3.711
3.679
3.546
3.504
2.819
2.796
2.771
2.747
2.728
2.649
2.639
2.631
2.626
2.616
2.608
2.593
1.507
1.496
0.782
23
PNB
Lev
TBS
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.05
1.00
1.05
1.19
2.21
1.10
7.95
1.14
2.04
2.42
3.39
6.05
6.10
9.18
6.31


7.428
7.403
7.358
7.335
7.311
7.286
7.224
5.955
5.946
5.243
5.229
5.197
5.164
4.734
4.704
4.406
4.385
4.362
4.055
4.015
3.979
3.960
3.934
3.914
3.845
3.805
3.788
3.768
3.662
3.628
3.603
3.456
3.416
2.720
2.694
2.581
2.559
2.139
1.426
1.407
1.339
1.227
0.833
0.004
Cbz
Lev
TBS
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.37
1.00
3.16
1.02
1.03
1.10
1.29
4.33
3.32
1.30
1.70
1.97
3.47
5.91
2.80
3.07
9.00
5.75

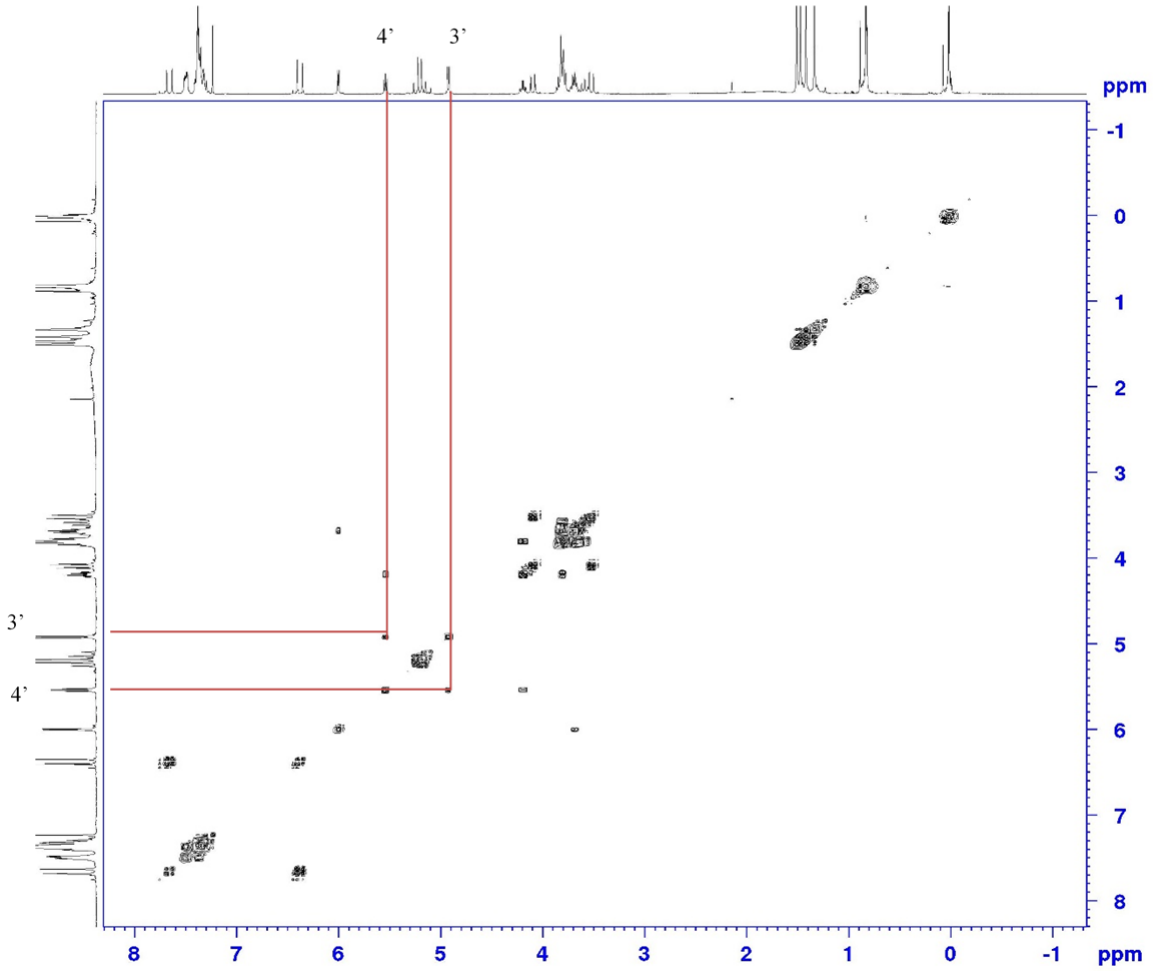

LevO
CbzO
OTBS
3'
4'
HO
5'
O

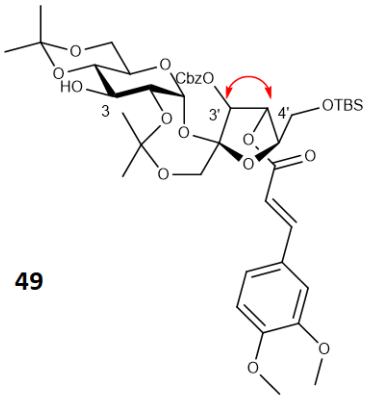
24


3'
4'
4'
3'
ppm
0
1
2
3
4
5
6
7
8
9
9
8
7
6
5
4
3
2
1
0
ppm

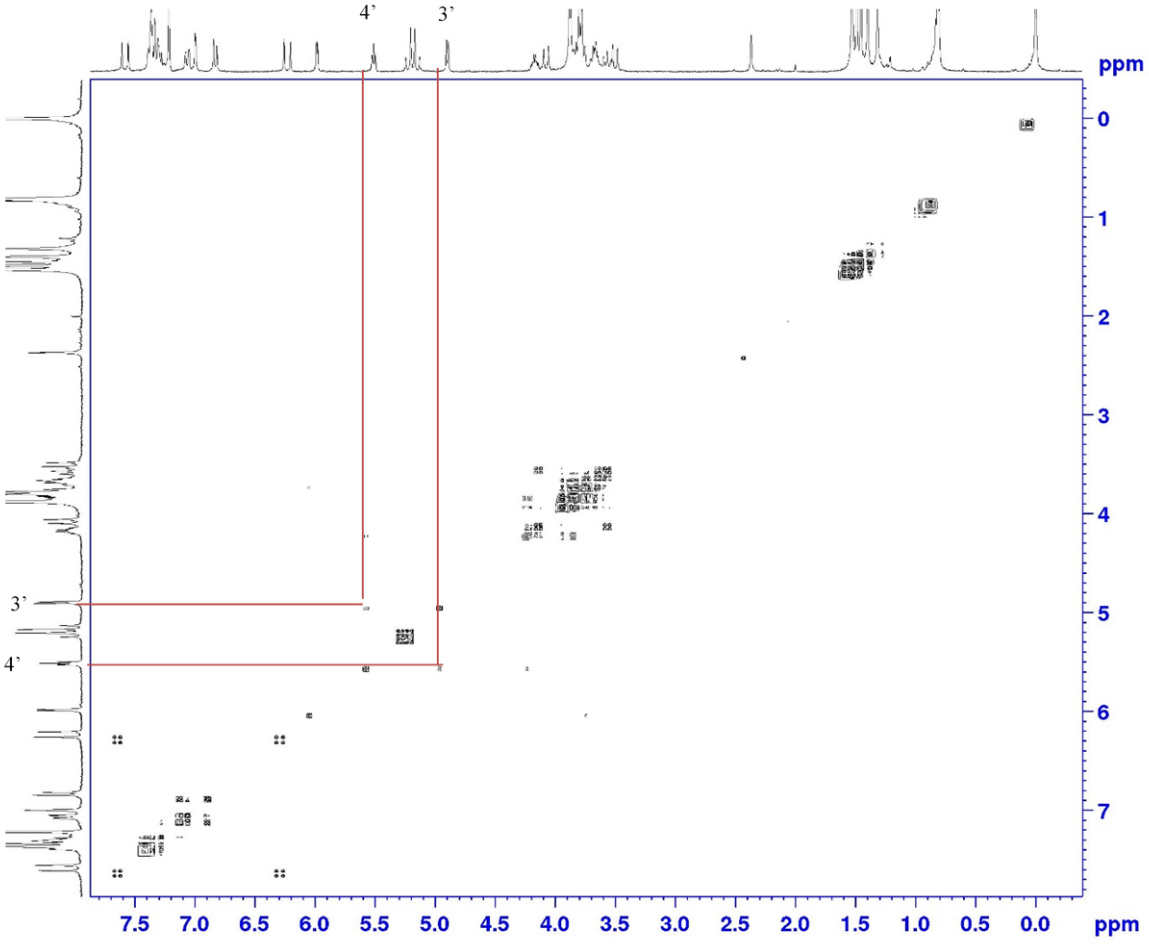


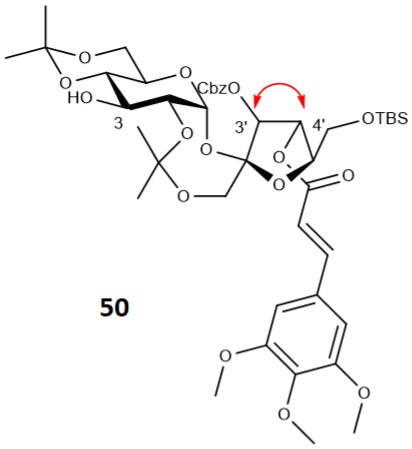
48



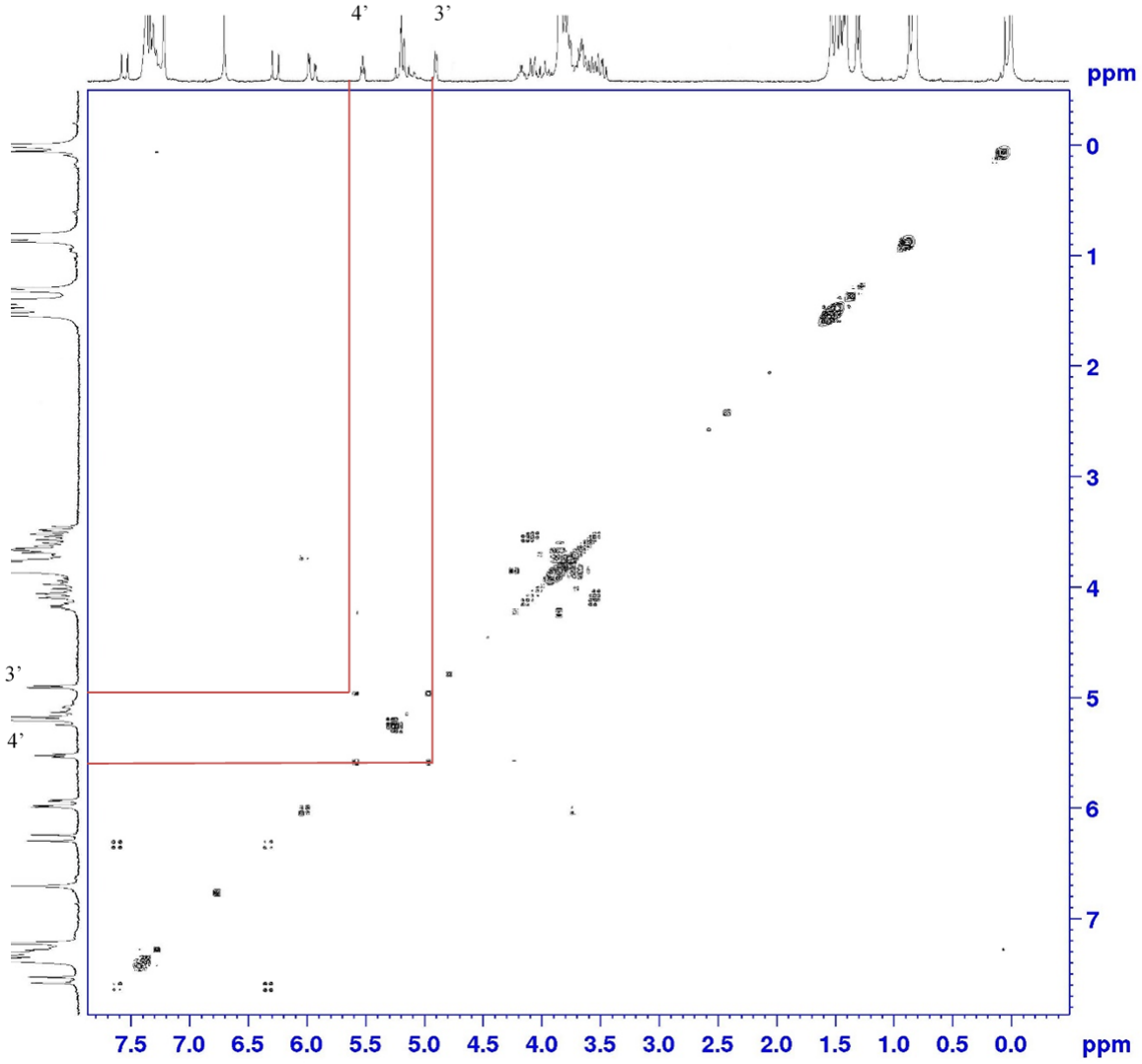

HO
CbzO
OTBS
3
3'
4'
O

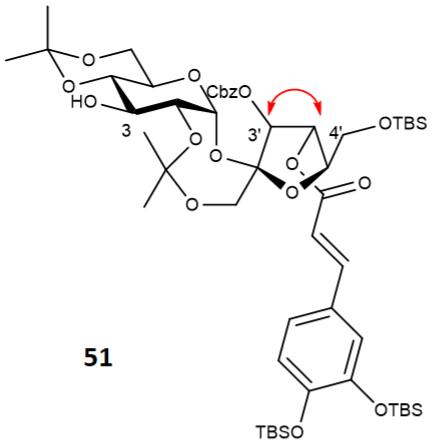
49


4'
3'
ppm
0
1
2
3
4
5
6
7
3'
4'
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

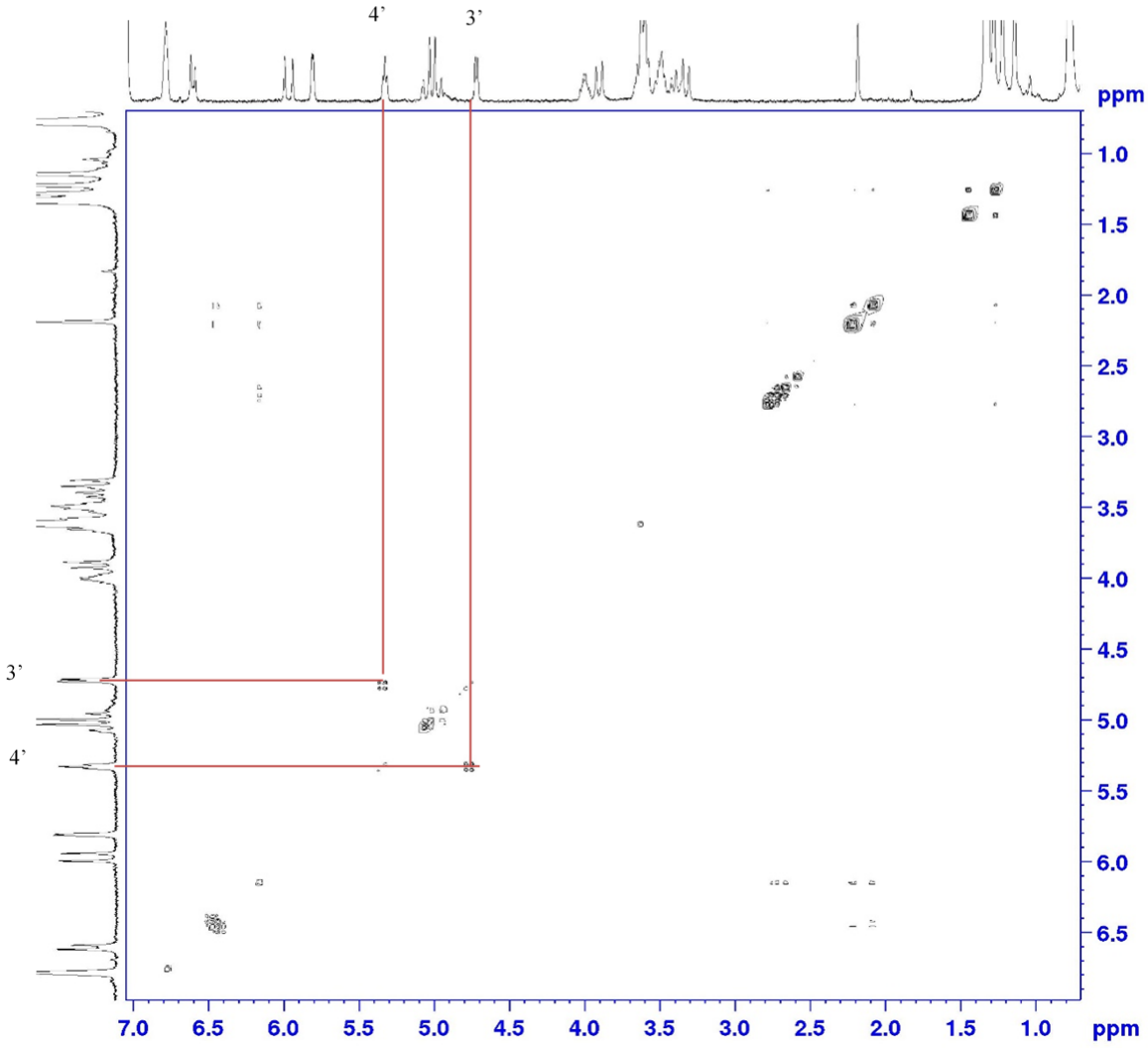

CbzO
HO
3
3'
4'
OTBS
O

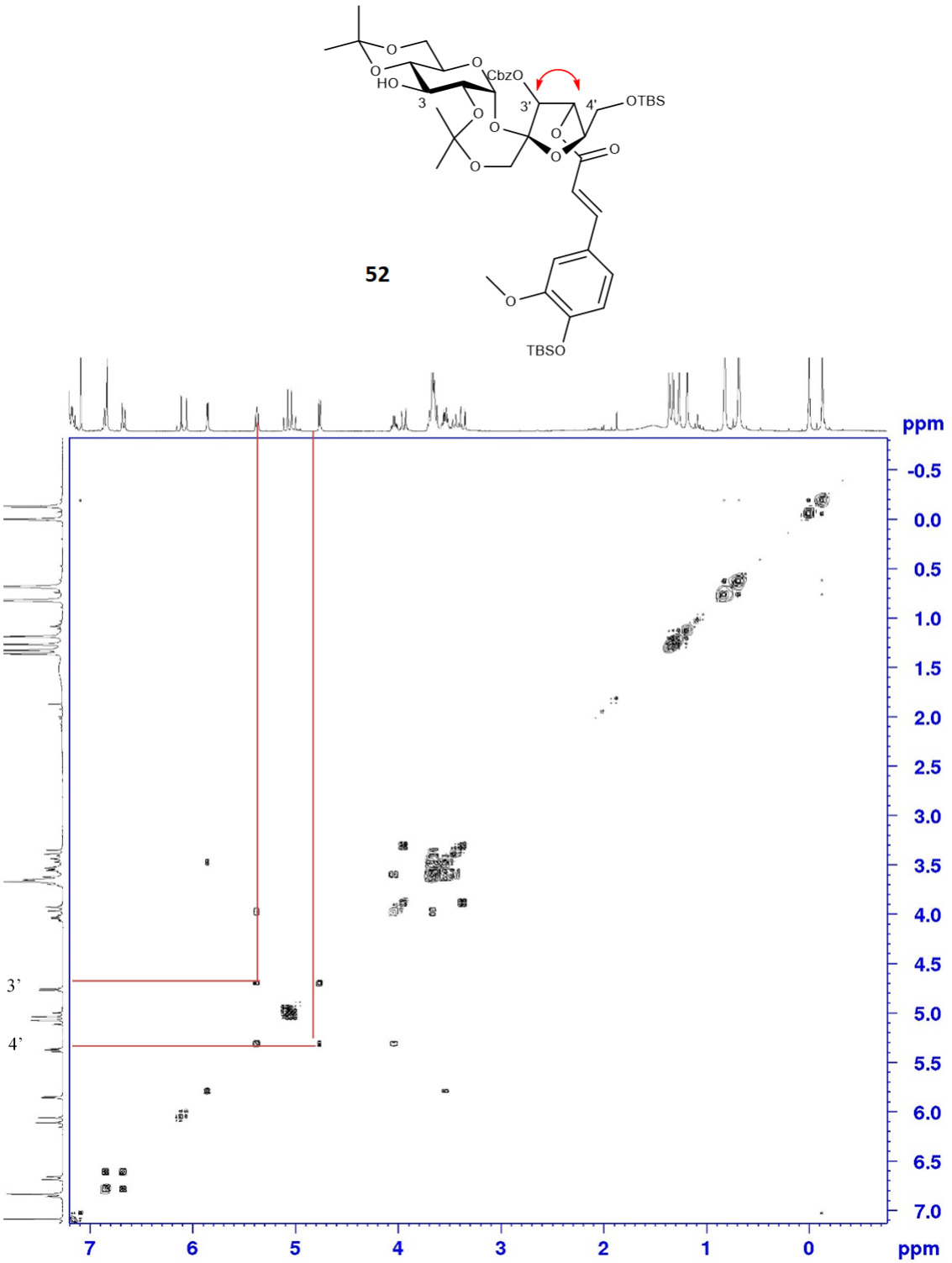
50

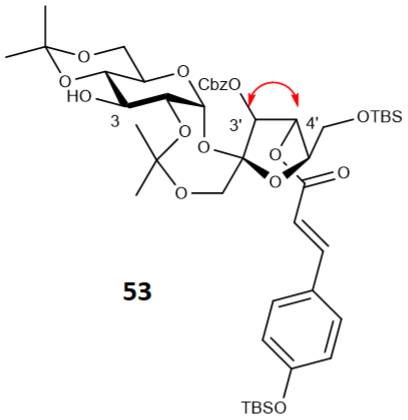

4'
3'
ppm
3'
4'
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


CbzO
HO
3
3'
4'
OTBS
TBSO
OTBS

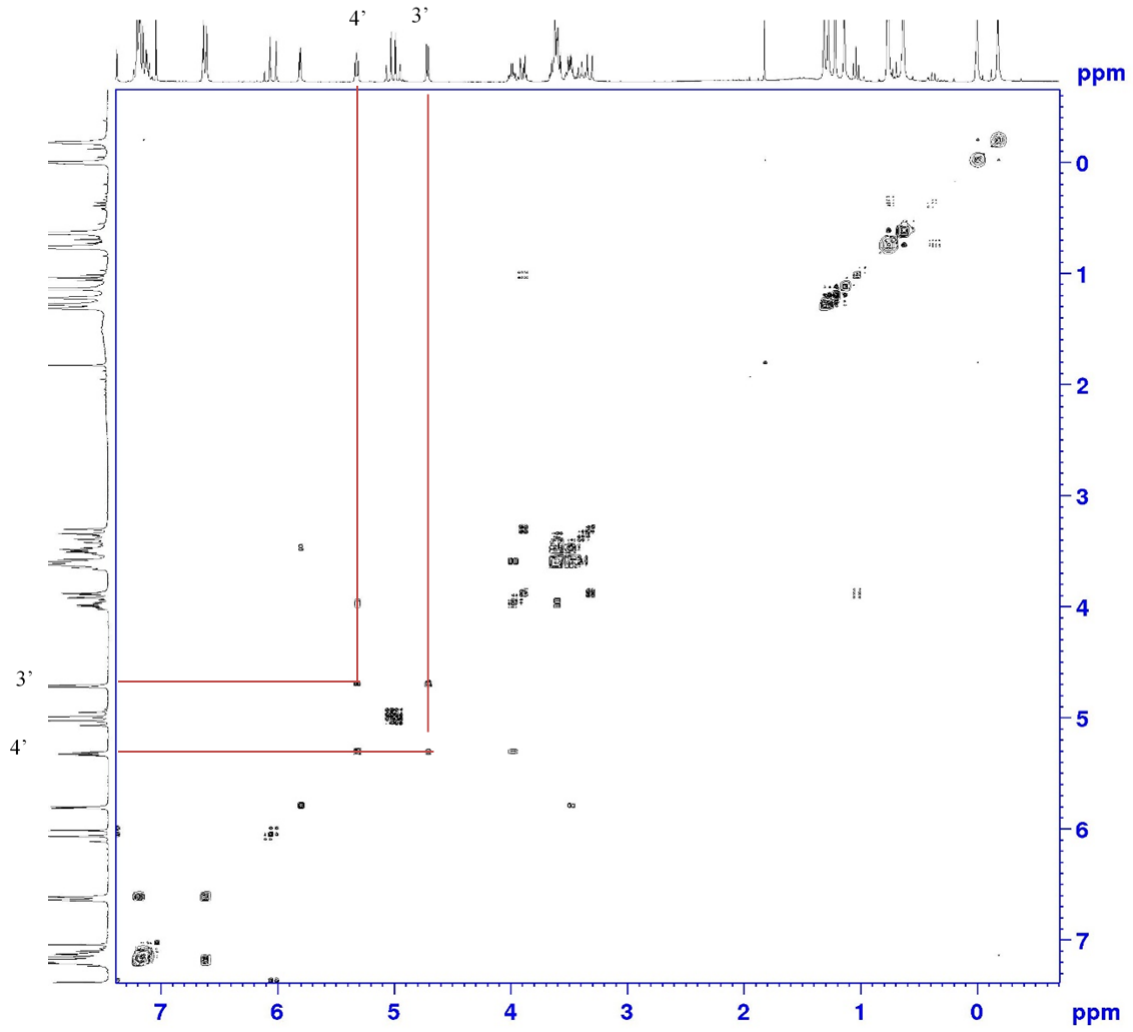
51

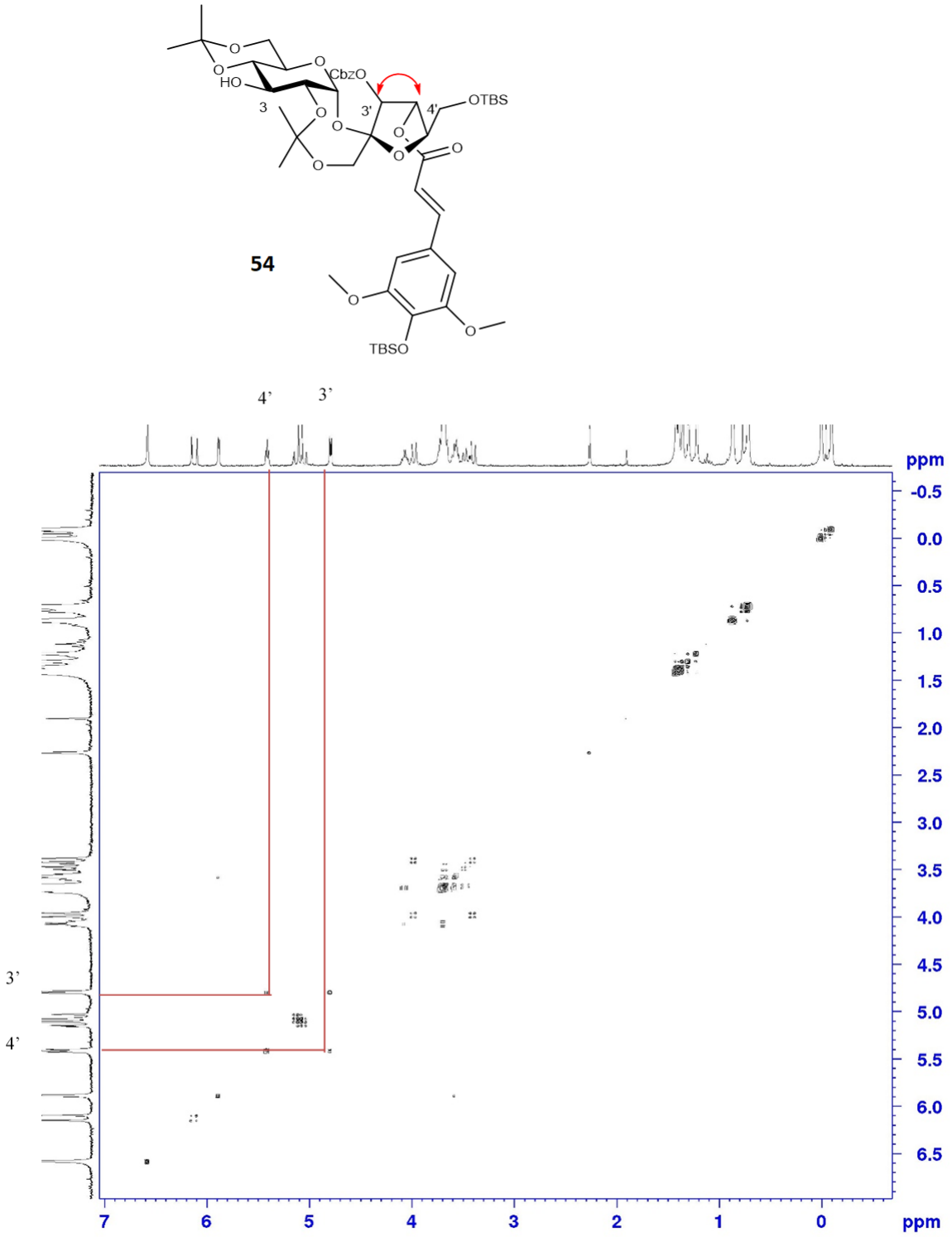

4'
3'
3'
4'
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


HO
CbzO
OTBS
TBSO
3
3'
4'
52
3'
4'
ppm
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7
6
5
4
3
2
1
0
ppm



53





3. References

1. Panda, P.; Appalashetti, M.; Natarajan, M.; Mary, C.-P.; Venkatraman, S. S.; Judeh, Z. M. A., Synthesis and antiproliferative activity of helonioside A, 3′,4′,6′-tri-O-feruloylsucrose, lapathoside C and their analogs. *Eur. J. Med. Chem.* **2012**, *58*, 418-430.