

## Supporting Information

### Targeted Synthesis of 3,3'-, 3,4'- and 3,6'-Phenylpropanoid Sucrose Esters

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#### Table of Contents:

1. Materials and methods	2
2. Synthesis of compounds 2-62	2-33
3. <sup>1</sup> H NMR, <sup>13</sup> C NMR and COSY spectra of compounds 3, 25, 26, 45, 11-17, 33-38, 18-24, 23, 43, and 59	34-58
4. References	59

#### 1. Materials and methods

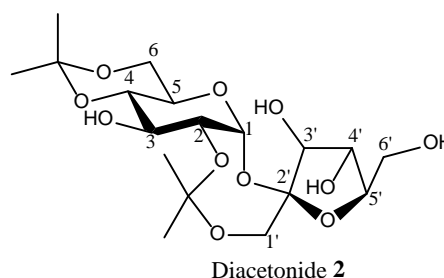
The chemical reagents were purchased from Sigma-Aldrich, Alfa Aesar and Acros and were used as received without further purification. IR spectra were obtained using a Bruker FT-IR spectrometer. <sup>1</sup>H NMR spectra were recorded using a Bruker Avance DPX 300 at 300 MHz. <sup>13</sup>C NMR spectra were recorded using a Bruker Avance DPX 300 at 75.47 MHz. Samples were measured using deuterated chloroform CDCl<sub>3</sub>, unless indicated. <sup>1</sup>H NMR multiplicities were designated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), quartet (q), multiplet (m). Waters Q-TOF Premier mass spectrometer (ESI) was used to obtain high resolution mass spectra. Analytical TLC was performed using Merck 60 F254 precoated silica gel plates (0.2 mm thickness) and visualized using UV at 254 nm or stained using *p*-anisaldehyde solution and heated. *p*-Anisaldehyde staining solution is prepared from scratch with *p*-anisaldehyde, acetic acid, sulfuric acid and ethanol.<sup>1</sup> Column chromatography was performed using Merck silica gel (230-400 mesh).

#### Synthesis of compounds 2-62

##### 2,1':4,6-di-*O*-isopropylidene sucrose 2

The synthesis of 2,1':4,6-di-*O*-isopropylidene sucrose (diacetone 2) was accomplished according to Panda et. al. modified process of Falkenhagen et. al.<sup>2-6</sup>

Drierite® (36.0 g) was added to dry DMF (700 mL) and the mixture der nitrogen atmosphere for an hour. Drierite® was removed by tion and the solvent was collected. Finely grinded sucrose 1 (65.0 g, then added to the filtered dry DMF and the mixture was stirred atmosphere for 30 minutes to ensure dissolution of sucrose. 2-pene (86.0 mL, 898 mmol) and *p*-TsOH (82.0 mg, 0.431 mmol) were mixture which was stirred for a week under inert atmosphere. Sub-reaction mixture was quenched with the addition of NEt<sub>3</sub> (7.00 mL). orated under reduced pressure and the yellow gum obtained was in EtOAc (400 mL). After 10 minutes, the solution was filtered. The filtrate was then dried over anhydrous MgSO<sub>4</sub>, evaporated and the crude product obtained was subjected to purification using column chromatography with pure EtOAc as the eluent. Diace-

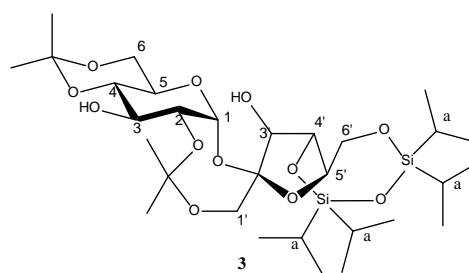


was stirred un-  
vacuum filtra-  
190 mmol was  
under nitrogen  
Methoxypro-  
added to the  
sequently, the  
DMF was evap-  
then suspended

tonide **2** was obtained as the major product in (52 g, 65% yield). Analytical data of diacetone **2** corresponded to the literature values.<sup>2-5</sup>

### Synthesis of 4',6'-O-tetraisopropylidisilyl-2,1':4,6-di-O-isopropylidene sucrose **3**

The synthesis of TIPDS-diacetone **3** was accomplished according to the literature procedure.<sup>3,7</sup> A mixture of diacetone **2** (1.00 g, 2.37 mmol) dichloro-1,1,3,3-tetraisopropylidisiloxane (832  $\mu$ L, 2.61 mmol) in was stirred at room temperature for 6 hours. Pyridine was reduced under pressure and the crude product was purified using silica chromatography using Hexane/EtOAc (3:2) as eluent. TIPDS-diacetone **3** was obtained as white solid (1.18g, 75% yield). Analytical data of diacetone **3** corresponded to the literature values.<sup>3</sup>



ing to the literature and 1,3-pyridine (5.0 ml) moved under a gel column diacetone **3** for TIPDS-

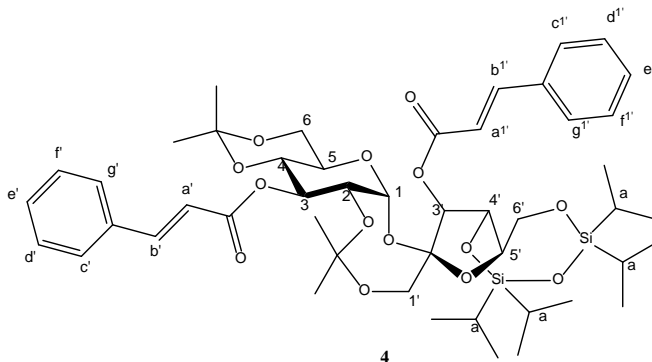
### General procedure for acylation of TIPDS-diacetones **4**, **5**, **6**, **7**, **8**, **9** and **10**

To a stirred solution of TIPDS-diacetone **3** (300 mg, 0.452 mmol) and DMAP (11 mg, 0.09 mmol) in  $\text{CH}_2\text{Cl}_2$  (100 mL) was added (substituted) cinnamic acids (1.81 mmol) and EDC (347 mg, 1.81 mmol) at room temperature. The reaction mixture was left to stir for a period of time. After completion (TLC), it was then washed with distilled water (3 x 30 mL), the organic phase was dried over anhydrous  $\text{MgSO}_4$ , filtered and evaporated under reduced pressure. The crude product was purified using silica gel column chromatography using Hexane/EtOAc (4:1) as eluent. This general procedure was used to prepare compounds **4**, **5**, **6**, **7**, **8**, **9** and **10**, and also gave compounds **11**, **12**, **13**, **14**, **15**, **16** and **17** side products.

### 3,3'-di-O-cinnamoyl-4',6'-O-tetraisopropylidisilyl-2,1':4,6-di-O-isopropylidene sucrose **4**

Following the general procedure, the reaction using cinnamic acid (268 mg, 1.81 mmol) gave the required compound **4** (201 mg, 48%) and along with **11** (126 mg, 35%) as white solids.

**Analytical data for compound **4**:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): TIPDS:  $\delta$  0.82-1.09 (m, 28H, 4 x H-a, 8 x  $(\text{CH}_3)_2\text{CSi}$ ); isopropylidene rings:  $\delta$  1.32-1.42 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ); sucrose = 12 Hz, 1H, H-1'), 3.65- 3.71 (m, 2H), 3.82-3.94 4.16 (m, 1H), 4.65 (t, 1H,  $J$  = 9 Hz, H-4'), 5.18 (d, H-3'), 5.26 (t, 1H,  $J$  = 16.5 Hz, H-3), 5.94 (d, 1H,  $J$  aromatic and alkenyl protons:  $\delta$  6.34 (d, 1H,  $J$  = 6.55 (d, 1H,  $J$  = 16 Hz, H-a'), 7.28-7.59 (m, 11H, H-d', H-d', H-e', H-e', H-f, H-f' H-g', H-g'), 7.77 Hz, H-b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.2, 14.3, 17.1, 17.2, 17.3, 17.6, 17.7, 17.8, 19.2, 22.9, 29.1, 29.2, 29.9, 30.6, 38.9, 62.5, 64.2, 66.2, 66.4, 72.0, 78.9, 81.5, 91.3, 99.8, 101.3, 102.8, 117.3, 128.3, 128.8, 129.0, 129.1, 130.4, 130.6, 131.1, 144.9, 146.8, 166.1, 166.7, 168.0.

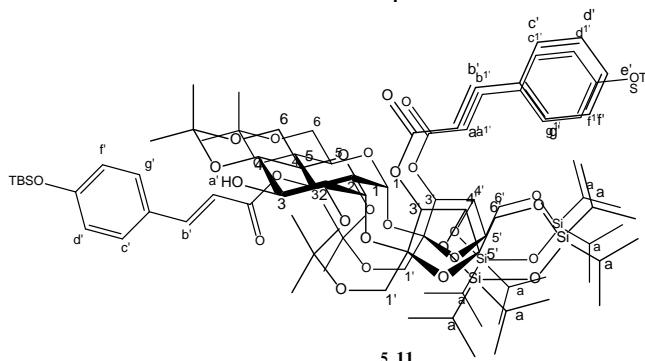


unit:  $\delta$  3.50 (d,  $J$  (m, 7H), 4.12-1H,  $J$  = 8 Hz, = 4 Hz, H-1); 16 Hz, H-a'), H-b', H-c', H-c', (d, 1H,  $J$  = 16 12.6, 13.0, 13.5, 13.9, 24.1, 25.6, 68.4, 71.2, 71.9, 118.3, 128.2, 132.6, 134.6,

**Analytical data for compound **11**:** The  $^1\text{H}$  NMR compound **11** corresponded to our previously obtained confirming the identity of the compound.<sup>3</sup>

### Synthesis of 3,3'-di-O-(4-tert-butylsiloxy-cinnamoyl)-4',6'-O-tetraisopropylidisilyl-2,1':4,6-di-O-isopropylidene sucrose **5**

Following the general procedure, OTBS-coumaric acid (503 mg, 1.81 mmol) was added to the solution, two products, compounds **5** and **12** were obtained as white solid compound in 37% (198 mg) and 49%



data of compound obtained data

### butyldime-tetra-sucrose **5**

acid (synthesized in section 2.2). After purification, two products were obtained as (205 mg) yield

respectively.

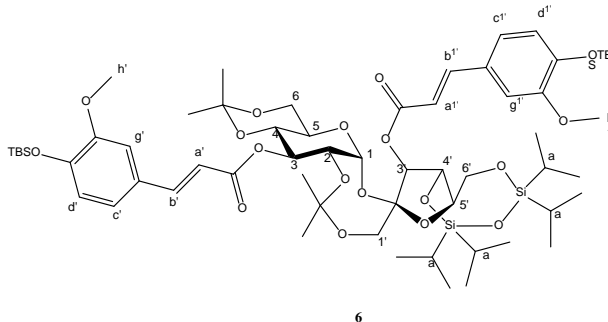
**Analytical data for compound 5:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): TBS protons:  $\delta$  0.19-0.22 (m, 12H), 1.13-1.21 (m, 18H); TIPDS:  $\delta$  0.89-1.09 (m, 28H, 4 x H-a, 8 x  $(\text{CH}_3)_2\text{CSi}$ ); isopropylidene rings:  $\delta$  1.39-1.47 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ); sucrose unit:  $\delta$  3.54 (d,  $J$  = 12 Hz, 1H, H-1'), 3.71-3.78 (m, 2H), 3.85-4.01 (m, 7H), 4.18-4.22 (m, 1H), 4.68 (t, 1H,  $J$  = 14 Hz, H-4'), 5.23 (d, 1H,  $J$  = 8 Hz, H-3'), 5.30 (t, 1H,  $J$  = 18.5 Hz, H-3), 5.97 (d, 1H,  $J$  = 4 Hz, H-1); aromatic and alkenyl protons: 6.26 (d, 1H,  $J$  = 16 Hz, H-a'), 6.46 (d, 1H,  $J$  = 16 Hz, H-a'), 6.80-7.54 (m, 9H, H-b', H-c', H-c', H-d', H-d', H-f, H-f', H-g', H-g'), 7.78 (d, 1H,  $J$  = 16 Hz, H-b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  -4.48, -4.18, 13.0, 13.5, 17.1, 17.2, 17.6, 17.7, 17.8, 18.0, 18.4, 19.2, 23.2, 24.1, 25.6, 25.8, 25.9, 29.1, 29.2, 30.6, 38.9, 62.5, 64.2, 66.3, 66.5, 71.1, 72.0, 81.5, 91.3, 99.8, 101.3, 102.8, 114.9, 116.0, 118.0, 120.7, 128.0, 129.8, 129.9, 130.5, 144.6, 145.1, 146.6, 158.0, 158.2, 166.4, 167.0.

**Analytical data for compound 12:** The  $^1\text{H}$  NMR data of the compound was compared with literature values<sup>3</sup> and confirmed to be 12.

### Synthesis of 3,3'-di-*O*-(4-*tert*-butyldimethylsiloxy-3-methoxycinnamoyl)-4',6'-*O*-tetraisopropylidisilyl-2,1':4,6-di-*O*-isopropylidene sucrose 6

Following the general procedure, OTBS-feru acid (synthesized from the experimental procedure as shown in section 2.2) (557 mg, 1.81 mmol) was added to the solution. After purification, two products, compounds 6 and 13 were obtained as white solid compound in 30% (169 mg) and 35% (151 mg) yield respectively.

**Analytical data for compound 6:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): TBS protons:  $\delta$  0.10-0.13 (m, 12H), 1.18-1.27 (m, 18H); TIPDS:  $\delta$  0.86-1.05 (m, 28H, 4 x H-a, 8 x  $(\text{CH}_3)_2\text{CSi}$ ); isopropylidene rings:  $\delta$  1.33-1.54 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ); methoxy and sucrose unit:  $\delta$  3.50 (d,  $J$  = 12 Hz, 1H), 3.69-3.74 (m, 2H), 3.77-3.84 (m, 6H, h'), 3.94-3.99 (m, 5H), 4.15-4.18 (m, 1H), 4.65 (t, 1H, 3 x H-h', 3 x H- $J$  = 13 Hz, H-4'), 5.20 (d, 1H,  $J$  = 8 Hz, H-3'), 5.30 (t, 1H,  $J$  = 19 Hz, H- = 4 Hz, H-1); aromatic and alkenyl protons:  $\delta$  6.21 H-a'), 6.41 (d, 1H,  $J$  = 16 Hz, H-a'), 6.80-7.12 (m, 6H, H-d', H-g', H-g'), 7.51 (d, 1H,  $J$  = 16 Hz, H-b'), 7.71 H-b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  -4.42, -3.39, 14.3, 17.1, 17.2, 17.6, 17.7, 17.8, 18.7, 19.1, 23.2, 24.2, 30.6, 55.6, 55.7, 64.2, 66.3, 71.0, 72.0, 81.5, 91.3, 99.8, 111.0, 111.5, 115.0, 121.2, 121.3, 122.4, 123.1, 128.6, 147.7, 147.9, 151.4, 166.3, 167.0.

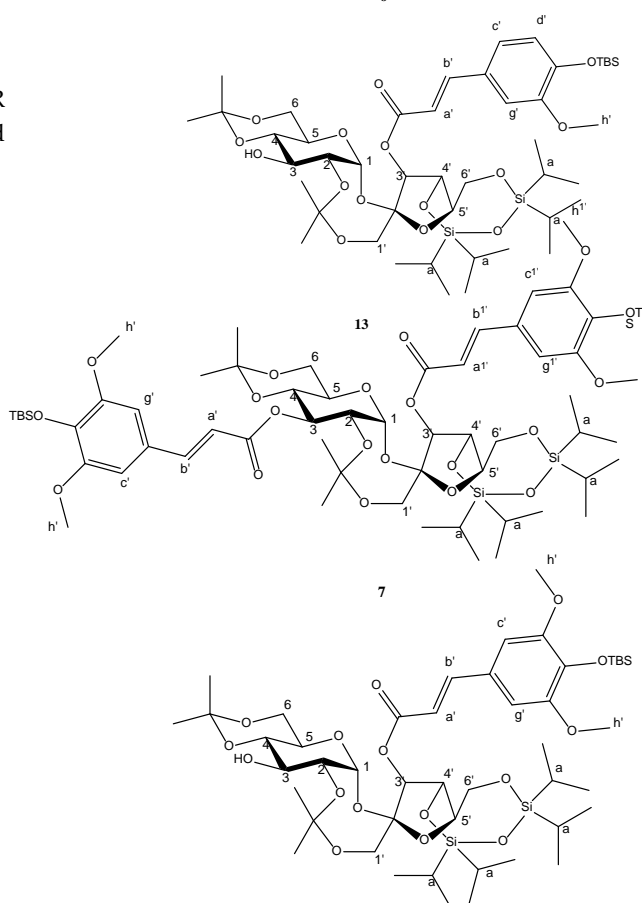


**Analytical data for compound 13:** The  $^1\text{H}$  NMR data of the compound was compared with literature values<sup>3</sup> and confirmed to be 13.

### Synthesis of 3,3'-di-*O*-(4-*tert*-butyldimethylsiloxy-3,5-dimethoxycinnamoyl)-4',6'-*O*-sopropylidisilyl-2,1':4,6-di-*O*-isopropylidene sucrose 7

Following the general procedure, OTBS-sinap acid (synthesized from the experimental procedure as shown in section 2.2) (612 mg, 1.81 mmol) was added to the solution. After purification, two products, compounds 7 and 14 were obtained as white solid compound in 22% (130 mg) and 27% respectively.

**Analytical data for compound 7:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): TBS protons:  $\delta$  0.09-0.12 (m, 12H), 1.06, 1.10, 1.12 TIPDS:  $\delta$  0.86-1.02 (m, 28H, 4 x H-a, 8 x isopropylidene rings:  $\delta$  1.35-1.46 (m, 12H, 2 x methoxy and sucrose unit:  $\delta$  3.52 (d, 1H,  $J$  = 12.5 (m, 2H), 3.74-3.83 (m, 12H, 6 x H-h', 6 x H-h'),



data of the compound confirmed to be

butyldime-tetrai-sucrose 7 acid (synthesized in section 2.2) After purification, obtained as (120 mg) yield

MHz,  $\text{CDCl}_3$ ): (m, 18H);  $(\text{CH}_3)_2\text{CSi}$ );  $(\text{CH}_3)_2\text{C}$ ); Hz), 3.68-3.71 3.85-3.97 (m,

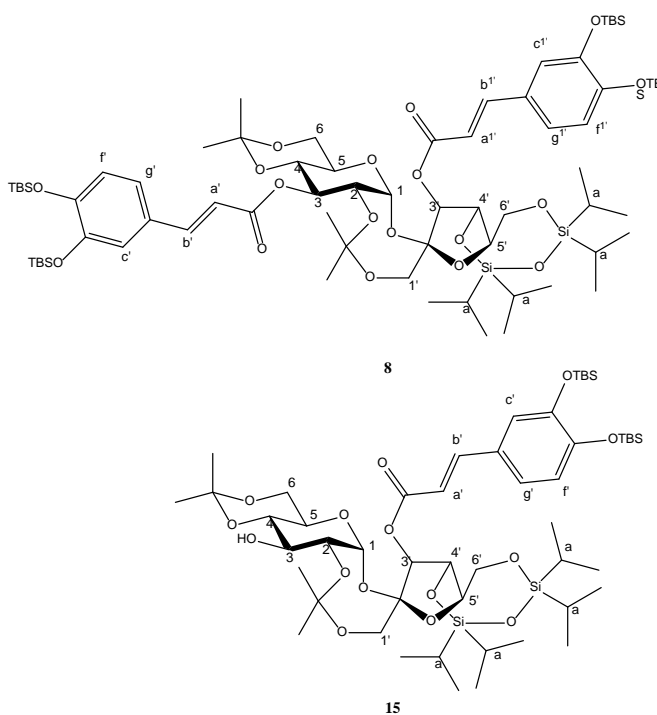
5H), 4.15-4.20 (m, 1H), 4.64 (t, 1H,  $J = 13$  Hz, H-4'), 5.22 (d, 1H,  $J = 8$  Hz, H-3'), 5.33 (t, 1H,  $J = 19$  Hz, H-3), 5.97 (d, 1H,  $J = 4$  Hz, H-1); aromatic and alkenyl protons:  $\delta$  6.24 (d, 1H,  $J = 16$  Hz, H-a'), 6.42 (d, 1H,  $J = 16$  Hz, H-a'), 6.68 (s, 2H, H-c', H-g'), 6.82 (s, 2H, H-c', H-g'), 7.50 (d, 1H,  $J = 16$  Hz, H-b'), 7.70 (d, 1H,  $J = 16$  Hz, H-b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  -4.43, -4.40, 13.6, 17.1, 17.2, 17.3, 17.6, 17.7, 17.8, 18.9, 19.0, 19.1, 24.2, 25.6, 25.9, 26.0, 29.1, 29.2, 30.6, 38.9, 55.9, 56.0, 62.5, 64.1, 66.4, 71.0, 72.0, 81.6, 91.3, 99.8, 101.4, 102.8, 105.5, 106.1, 115.2, 116.0, 127.2, 127.3, 137.1, 137.2, 145.4, 147.2, 151.9, 152.0, 166.3, 166.9.

**Analytical data for compound 14:** The  $^1\text{H}$  NMR data of the compound was compared with literature values<sup>3</sup> and confirmed to be 14.

### Synthesis of 3,3'-di-*O*-(3,4-di-*tert*-butyldimethylsiloxycinnamoyl)-4',6'-*O*-tetraisopropylidisilyl-2,1':4,6-di-*O*-isopropylidene sucrose 8

Following the general procedure, OTBS-caff acid (synthesized from the experimental procedure as shown in section 2.2) (738 mg, 1.81 mmol) was added to the solution. After purification, two products, compounds 8 and 15 were obtained as white solid compound in 34% (222 mg) and 27% (129 mg) yield respectively.

**Analytical data for compound 8:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): TBS:  $\delta$  0.18-0.19 (m, 24H), 0.87-1.12 (m, 36H); 1.12 (m, 28H, 4 x H-a, 8 x  $(\text{CH}_3)_2\text{CSi}$ ); isopropylidene rings:  $\delta$  1.36-1.46 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ); sucrose unit:  $\delta$  12.5 Hz), 3.70-3.73 (m, 2H), 3.85-4.01 (m, 5H), 1H), 4.65 (t, 1H,  $J = 14$  Hz, H-4'), 5.16 (d, 1H,  $J = 8$  Hz, H-3'), 5.33 (t, 1H,  $J = 19$  Hz, H-3), 5.97 (d, 1H,  $J = 4$  Hz, H-1); alkenyl protons:  $\delta$  6.17 (d, 2H,  $J = 16$  Hz, H-a', H-2H, H-g', H-g'), 6.96-7.10 (m, 4H, H-c', H-c', H-f', 1H,  $J = 16$  Hz, H-b'), 7.68 (d, 1H,  $J = 16$  Hz, H-b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  -4.67, -4.11, -4.06, -4.02, 11.1, 12.3, 17.4, 17.5, 17.8, 18.4, 18.5, 22.8, 24.0, 25.7, 25.9, 62.6, 66.8, 68.5, 72.0, 81.1, 91.1, 99.8, 101.0, 103.1, 120.3, 121.1, 122.5, 128.1, 145.2, 147.9, 149.6, 166.4,



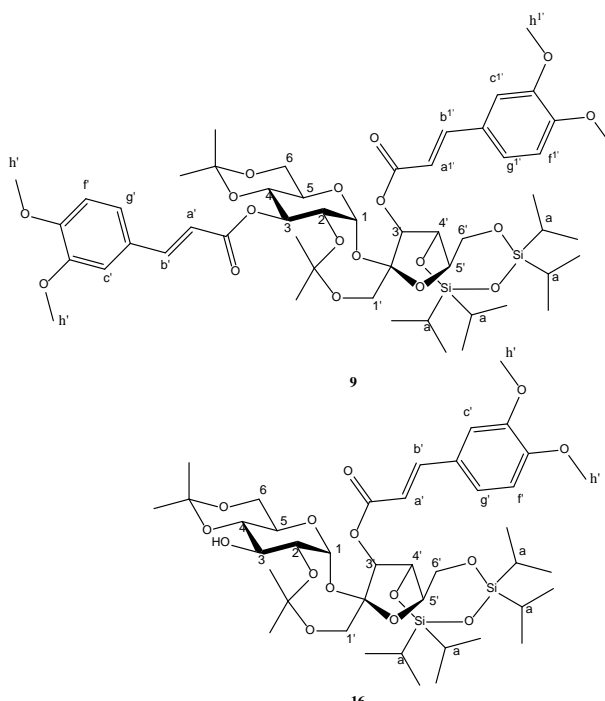
MHz,  $\text{CDCl}_3$ ): TIPDS:  $\delta$  0.87-1.12 (m, 36H); isopropylidene rings:  $\delta$  1.36-1.46 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ); sucrose unit:  $\delta$  12.5 Hz), 3.70-3.73 (m, 2H), 3.85-4.01 (m, 5H), 1H), 4.65 (t, 1H,  $J = 14$  Hz, H-4'), 5.16 (d, 1H,  $J = 8$  Hz, H-3'), 5.33 (t, 1H,  $J = 19$  Hz, H-3), 5.97 (d, 1H,  $J = 4$  Hz, H-1); aromatic and alkenyl protons:  $\delta$  6.17 (d, 2H,  $J = 16$  Hz, H-a', H-2H, H-g', H-g'), 6.96-7.10 (m, 4H, H-c', H-c', H-f', 1H,  $J = 16$  Hz, H-b'), 7.68 (d, 1H,  $J = 16$  Hz, H-b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  -4.67, -4.11, -4.06, -4.02, 11.1, 12.3, 17.4, 17.5, 17.8, 18.4, 18.5, 22.8, 24.0, 25.7, 25.9, 62.6, 66.8, 68.5, 72.0, 81.1, 91.1, 99.8, 101.0, 103.1, 120.3, 121.1, 122.5, 128.1, 145.2, 147.9, 149.6, 166.4,

**Analytical data for compound 15:** The  $^1\text{H}$  NMR data of the compound was compared with literature values<sup>3</sup> and confirmed to be 15.

### Synthesis of 3,3'-di-*O*-(3,4-di-*tert*-butyldimethylsiloxycinnamoyl)-4',6'-*O*-tetraisopropylidisilyl-2,1':4,6-di-*O*-isopropylidene sucrose 9

Following the general procedure, diOMe acid (synthesized from the experimental procedure as shown in section 2.2) (376 mg, 1.81 mmol) was added to the solution. After purification, two products, compounds 9 and 16 were obtained as white solid compound in 29% (137 mg) and 55% (212 mg) yield respectively.

**Analytical data for compound 9:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): TIPDS:  $\delta$  0.88-1.12 (m, 28H, 4 x H-a, 8 x  $(\text{CH}_3)_2\text{CSi}$ ); isopropylidene rings:  $\delta$  1.36-1.46 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ); methoxy and sucrose unit:  $\delta$  3.88-3.90 (m, 12H, 6 x H-h', 6 x H-h'), 3.51 (d, 1H,  $J = 3.76$  Hz, H-4'), 5.23 (d, 1H,  $J = 8$  Hz, H-3'), 5.33 (t, 1H,  $J = 19$  Hz, H-3), 5.97 (d, 1H,  $J = 4$  Hz, H-1); aromatic and alkenyl protons:  $\delta$  6.25 (d, 1H,  $J = 16$  Hz, H-a'), 6.45 (d, 1H,  $J = 16$  Hz, H-a'), 6.80-6.87 (m, 2H, H-g',



dimethoxy-*O*-synthesized from (376 mg, 1.81 mmol) was added to the solution. After purification, two products, compounds 9 and 16 were obtained as white solid compound in 29% (137 mg) and 55% (212 mg) yield respectively.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ): TIPDS:  $\delta$  0.88-1.12 (m, 28H, 4 x H-a, 8 x  $(\text{CH}_3)_2\text{CSi}$ ); isopropylidene rings:  $\delta$  1.36-1.46 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ); methoxy and sucrose unit:  $\delta$  3.88-3.90 (m, 12H, 6 x H-h', 6 x H-h'), 3.51 (d, 1H,  $J = 3.76$  Hz, H-4'), 5.23 (d, 1H,  $J = 8$  Hz, H-3'), 5.33 (t, 1H,  $J = 19$  Hz, H-3), 5.97 (d, 1H,  $J = 4$  Hz, H-1); aromatic and alkenyl protons:  $\delta$  6.25 (d, 1H,  $J = 16$  Hz, H-a'), 6.45 (d, 1H,  $J = 16$  Hz, H-a'), 6.80-6.87 (m, 2H, H-g',

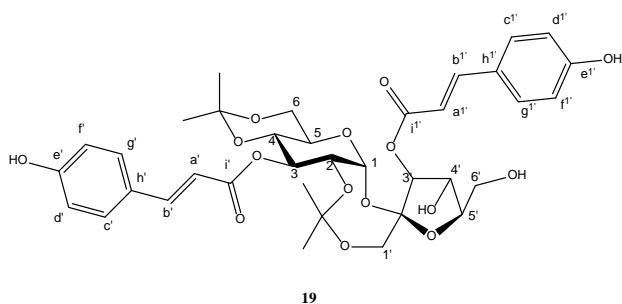
**Analytical data for compound 16:** The <sup>1</sup>H NMR data of the compound was compared with literature values<sup>3</sup> and confirmed to be 16.

protons:  $\delta$  6.43 (d, 1H,  $J$  = 16 Hz, H-a'), 6.62 (d, 1H,  $J$  = 16 Hz, H-a'), 7.36-7.40 (m, 6H, H-d', H-d', H-e', H-e', H-f, H-f'), 7.50-7.70 (m, 5H, H-b', H-c', H-c', H-g', H-g') 7.89 (d, 1H,  $J$  = 16 Hz, H-b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.2, 24.2, 25.5, 29.2 (4 x  $(\text{CH}_3)_2\text{C}$ ), 61.7 (C-6), 62.2 (C-5), 64.6 (C-6'), 66.6 (C-1'), 71.0 (C-3), 71.6 (C-4), 71.8 (C-2), 72.3 (C-4'), 81.5 (C-3'), 85.0 (C-5'), 91.5 (C-1), 100.0, 101.9 (2 x  $(\text{CH}_3)_2\text{C}$ ), 104.0 (C-2'), 116.8, 118.2 (C-a', C-a'), 128.3, 129.1 (C-c', C-c', C-g', C-g', C-d', C-d', C-f', C-f'), 130.5, 131.0 (C-e', C-e'), 134.2, 134.6 (C-h', C-h'), 145.1, 147.8 (C-b', C-b'), 166.1, 168.4 (C-i', C-i'); HRMS (ESI positive mode): found  $m/z$  705.2524  $[\text{M}+\text{Na}]^+$ , calcd. 705.2523 for  $\text{C}_{36}\text{H}_{42}\text{O}_{13}\text{Na}$ .

### Synthesis of 3,3'-di-*O*-coumaroyl-2,1'-di-*O*-isopropylidene sucrose, 3,3'-coum 19

Following the general procedure, deprotection of compound **12** (100 mg, 0.08 mmol) using NEt<sub>3</sub> (24  $\mu\text{L}$ , 0.17 mmol) and 1.56 M 3HF·NEt<sub>3</sub> (163  $\mu\text{L}$ , 0.25 mmol) gave compound **19** as a white solid (33 mg, 58 % yield).

**Analytical data for 3,3'-coum 19:** mp 87-89 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): isopropylidene rings:  $\delta$  1.17-1.46 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ), 3.51-3.55 (m, 1H, H-1'), 3.73-3.86 (m, 5, 2 x H-6', 2 x H-6), 3.98- 4.04 (m, 2H, H-5', H-1'), 14.5 Hz, H-4'), 5.12 (d, 1H,  $J$  = 8 Hz, H-3'), 5.36 (t, H-3), 6.19 (d, 1H,  $J$  = 3.5 Hz, H-1); aromatic and  $\delta$  6.29 (d, 1H,  $J$  = 16 Hz, H-a'), 6.52 (d, 1H,  $J$  = 16 Hz, (m, 9H, H-b', H-c', H-c', H-d', H-d', H-f, H-f' H-g', 1H,  $J$  = 16 Hz, H-b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  x  $(\text{CH}_3)_2\text{C}$ ), 62.4 (C-6), 63.0 (C-5), 64.7 (C-6'), 66.9 (C-1'), 71.1 (C-3), 71.2 (C-4), 71.8 (C-2), 72.4 (C-4'), 73.1, 79.4 (C-3'), 84.5 (C-5'), 91.8 (C-1), 100.1 (2 x  $(\text{CH}_3)_2\text{C}$ ), 104.2 (C-2'), 114.3 (C-a', C-a'), 115.2, 116.5 (C-d', C-d', C-f', C-f'), 126.5 (C-h', C-h'), 130.1, 131.2 (C-c', C-c', C-g', C-g'), 145.3, 146.8 (C-b', C-b'), 160.6, 160.8 (C-e', C-e'), 166.3, 167.4 (C-i', C-i'); HRMS (ESI positive mode): found  $m/z$  737.2457  $[\text{M}+\text{Na}]^+$ , calcd. 737.2421 for  $\text{C}_{36}\text{H}_{42}\text{O}_{15}\text{Na}$ .

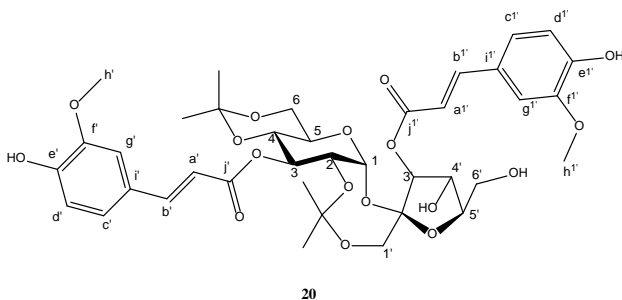


NMR (300 MHz, x  $(\text{CH}_3)_2\text{C}$ ); 7H, H-2, H-4, H-4.61 (t, 1H,  $J$  = 1H,  $J$  = 18 Hz, alkenyl protons: H-a'), 6.85-7.64 H-g'), 7.79 (d, 19.1, 24.1, 25.3 (4

### Synthesis of 3,3'-di-*O*-feruloyl-2,1'-di-*O*-isopropylidene sucrose, 3,3'-feru 20

Following the general procedure, deprotection of compound **13** (100 mg, 0.08 mmol) using NEt<sub>3</sub> (24  $\mu\text{L}$ , 0.17 mmol) and 1.56 M 3HF·NEt<sub>3</sub> (163  $\mu\text{L}$ , 0.25 mmol) gave compound **20** as a white solid (55 mg, 88% yield).

**Analytical data for 3,3'-feru 20:** mp 141-143°C;  $^1\text{H}$  NMR (300 MHz, Acetone- $d_6$ ): isopropylidene rings:  $\delta$  1.26-1.45 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ); methoxy and sucrose unit:  $\delta$  3.91-3.96 (m, H-h'), 3.51-3.55 (m, 1H, H-1'), 3.64-3.76 (m, 7H, H-4, H-2, H-5), 4.07-4.16 (m, 2H, H-5', H-1'), 4.79 (t, 1H,  $J$  = 4 Hz, H-1); aromatic and alkenyl protons:  $\delta$  6.24 H-a'), 6.44 (d, 1H,  $J$  = 16 Hz, H-a'), 6.88-7.26 (m, 6H, H-d', H-g', H-g'), 7.55 (d, 1H,  $J$  = 16 Hz, H-b'), 7.81 H-b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.2, 24.2,  $(\text{CH}_3)_2\text{C}$ ), 56.2, 56.3 (2 x OCH<sub>3</sub>), 61.7 (C-6), 62.2 (C-5), (C-1'), 70.8 (C-3), 71.6 (C-4'), 71.9 (C-2), 72.5 (C-4), (C-5'), 91.5 (C-1), 100.0, 101.9 (2 x  $(\text{CH}_3)_2\text{C}$ ), 104.1 (C-2'), 109.6, 111.2 (C-g', C-g'), 114.2, 114.9 (C-a', C-a'), 115.0, 115.5 (C-d', C-d'), 123.3, 123.6 (C-c', C-c'), 127.1 (C-i', C-i'), 145.2, 147.0 (C-b', C-b'), 147.8 (C-f', C-f'), 148.3, 148.6 (C-e', C-e'), 166.4, 168.7 (C-j', C-j'); HRMS (ESI positive mode): found  $m/z$  775.2818  $[\text{M}+\text{H}]^+$ , calcd. 775.2813 for  $\text{C}_{38}\text{H}_{47}\text{O}_{17}$ .

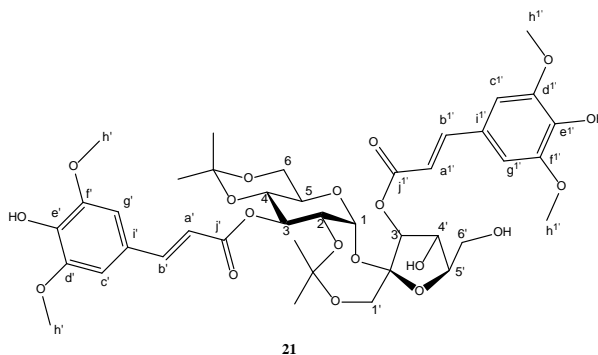


6H, 3 x H-h', 3 x 2 x H-6, 2 x H-6', = 14 Hz, H-4'), H-3), 6.23 (d, 1H, (d, 1H,  $J$  = 15 Hz, H-c', H-c', H-d', (d, 1H,  $J$  = 16 Hz, 25.6, 29.2 (4 x 64.6 (C-6'), 66.6 81.6 (C-3'), 85.1

### Synthesis of 3,3'-di-*O*-sinapoyl-2,1'-di-*O*-isopropylidene sucrose, 3,3'-sinap 21

Following the general procedure, deprotection of compound **14** (100 mg, 0.08 mmol) using NEt<sub>3</sub> (24  $\mu\text{L}$ , 0.17 mmol) and 1.56 M 3HF·NEt<sub>3</sub> (163  $\mu\text{L}$ , 0.25 mmol) gave compound **21** as a white solid (60 mg, 90 % yield).

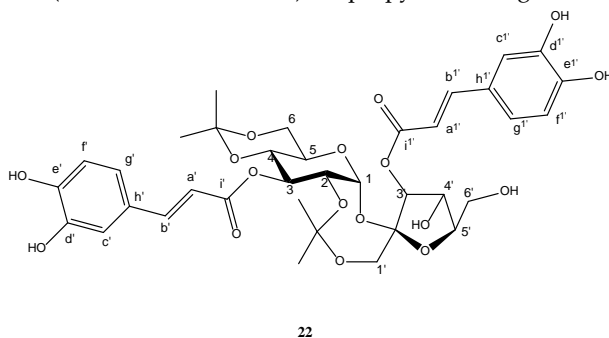
**Analytical data for 3,3'-sinap 21:** mp 142-144 °C; <sup>1</sup>H NMR (300 MHz, Acetone-d<sub>6</sub>): isopropylidene rings: δ 1.26-1.45 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>C); methoxy and sucrose unit: δ 3.90-3.91 (m, 12H), 1H, H-1') 3.64-3.79 (m, 7H, H-4, 2 x H-6, 2 x H-6', H-2, H-5, H-5', H-1'), 4.78 (t, 1H, *J* = 14 Hz, H-4'), 4.93 (d, H-3'), 5.53 (t, 1H, *J* = 18.5 Hz, H-3), 6.23 (d, 1H, *J* = 4 Hz, H-1); aromatic and alkenyl protons: δ 6.27 (d, 1H, *J* = 15.5 Hz, H-a'), 6.74 (s, 2H H-c', H-g'), 6.95 (s, 2H H-7.52 (d, 1H, *J* = 16 Hz, H-b'), 7.80 (d, 1H, *J* = 16 Hz, H-b'); (75.5 MHz, CDCl<sub>3</sub>): δ 19.2, 24.2, 25.6, 29.2 (4 x (CH<sub>3</sub>)<sub>2</sub>C), OCH<sub>3</sub>), 61.8 (C-6), 62.2 (C-5), 64.6 (C-6'), 66.5 (C-1'), 70.8 (C-4'), 71.9 (C-2), 72.7 (C-4), 81.8 (C-3'), 85.2 (C-5'), 91.5 101.9 (2 x (CH<sub>3</sub>)<sub>2</sub>C), 104.2 (C-2'), 105.3, 106.1 (C-c', C-c'), 114.6, 115.7 (C-a', C-a'), 125.9 (C-i', C-i'), 137.5, 137.7 (C-e', C-e'), 145.5, 147.4, 147.5, 148.0 (C-b', C-b', C-d', C-d', C-f', C-f'), 166.3, 168.5 (C-j', C-j'); HRMS (ESI positive mode): found *m/z* 835.3001 [M+H]<sup>+</sup>, calcd.835.3025 for C<sub>40</sub>H<sub>51</sub>O<sub>19</sub>.



### Synthesis of 3,3'-di-*O*-caffeoyl-2,1'-di-*O*-isopropylidene sucrose, 3,3'-caff 22

Following the general procedure, deprotection of compound **15** (100 mg, 0.07 mmol) using NEt<sub>3</sub> (19 μL, 0.14 mmol) and 1.56 M 3HF·NEt<sub>3</sub> (135 μL, 0.21 mmol) gave compound **22** as a yellow solid (28 mg, 54 % yield).

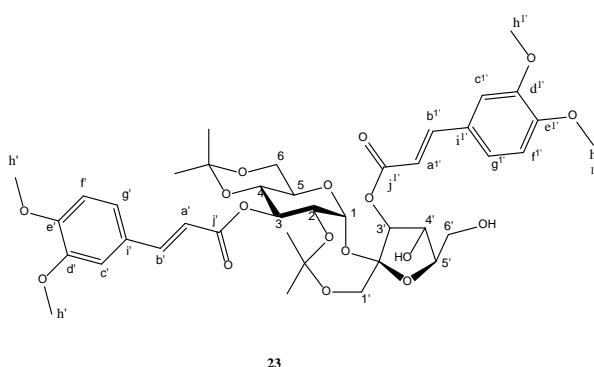
**Analytical data for 3,3'-caff 22:** mp 162-164 °C; <sup>1</sup>H NMR (300 MHz, Acetone-d<sub>6</sub>): isopropylidene rings: δ 1.22-1.47 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>C); sucrose unit: δ 3.51-3.55 (m, 1H, H-1'), H-4, 2 x H-6, 2 x H-6', H-2, H-5), 4.00-4.09 (m, 2H, H-1H, *J* = 15 Hz, H-4'), 5.13 (d, 1H, *J* = 8 Hz, H-3'), 5.39 H-3), 6.21 (d, 1H, *J* = 4 Hz, H-1); aromatic and alkenyl (d, 1H, *J* = 16 Hz, H-a'), 6.43 (d, 1H, *J* = 16 Hz, H-a'), H-f, H-f'), 7.03 (d, 1H, *J* = 8 Hz, H-g'), 7.15-7.16 (m, 7.32 (d, 1H, *J* = 2 Hz, H-c'), 7.52 (d, 1H, *J* = 16 Hz, H-16 Hz, H-b'); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 19.1, (4 x (CH<sub>3</sub>)<sub>2</sub>C), 62.7 (C-6), 63.2 (C-5), 65.1 (C-6'), 67.1 3), 72.4 (C-4'), 72.7 (C-2), 73.1 (C-4), 79.8 (C-3'), 84.9 1), 100.4 (2 x (CH<sub>3</sub>)<sub>2</sub>C), 104.6 (C-2'), 114.7 (C-a', C-a'), 115.6, 116.5 (C-c', C-c', C-f', C-f'), 122.3, 123.5 (C-g', C-g'), 127.6, 127.7 (C-h', C-h'), 146.0, 146.5, 147.5, 149.3 (C-b', C-b', C-d', C-d', C-e', C-e'), 166.6, 167.7 (C-i', C-i'); HRMS (ESI positive mode): found *m/z* 769.2314 [M+Na]<sup>+</sup>, calcd.769.2320 for C<sub>36</sub>H<sub>42</sub>O<sub>17</sub>Na.



### Synthesis of 3,3'-di-*O*-(3,4-dimethoxycinnamoyl)-2,1'-di-*O*-isopropylidene sucrose, 3,3'-diOMe 23

Following the general procedure, deprotection of compound **16** (100 mg, 0.10 mmol) using NEt<sub>3</sub> (28 μL, 0.20 mmol) and 1.56 M 3HF·NEt<sub>3</sub> (192 μL, 0.30 mmol) gave compound **23** as a white solid (52 mg, 65 % yield).

**Analytical data for 3,3'-diOMe 23:** mp 117-119 °C; <sup>1</sup>H NMR (300 MHz, , CDCl<sub>3</sub>): isopropylidene rings: δ 1.25-1.45 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>C); methoxy and sucrose unit: δ 3.89-3.90 (m, x H-h'), 3.51-3.54 (m, 1H, H-1'), 3.63-3.67 (m, 3H, H-4, 3.78 (m, 1H, H-2), 3.83-3.86 (m, 1H, H-6'), 3.93-3.95 (m, 4.10-4.13 (m, 1H, H-5'), 4.14-4.15 (m, 1H, H-1'), 4.80 (t, H-4'), 4.94 (d, 1H, *J* = 7.5 Hz, H-3'), 5.49-5.55 (t, 1H, *J* = 6.24 (d, 1H, *J* = 4 Hz, H-1); aromatic and alkenyl protons: δ 6.27 (d, 1H, *J* = 16 Hz, H-a'), 6.46 (d, 1H, *J* = 16 Hz, H-a'), 6.83-6.87 (m, 2H, H-c', H-f'), 7.02-7.06 (m, 2H, H-c', H-f'), 7.26-7.27 (m, 2H, (d, 1H, *J* = 16 Hz, H-b') 7.82 (d, 1H, *J* = 16 Hz, H-b'); <sup>13</sup>C NMR (75.5 MHz, , CDCl<sub>3</sub>): δ 19.2, 24.2, 25.5, 29.2 (4 x (CH<sub>3</sub>)<sub>2</sub>C), OCH<sub>3</sub>), 61.7 (C-6), 62.2 (C-5), 64.6 (C-6'), 66.5 (C-1'), (C-4'), 71.9 (C-2), 72.4 (C-4), 81.3 (C-3'), 85.0 (C-5'), 91.5 (C-1), 100.0, 101.9 (2 x (CH<sub>3</sub>)<sub>2</sub>C), 104.0 (C-2'), 109.7, 111.2, 111.3 (C-c', C-c',

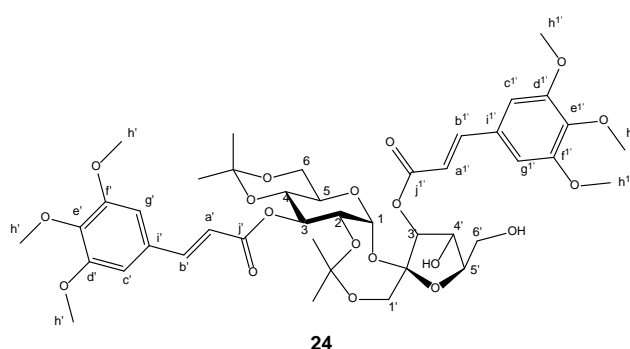


C-f', C-f'), 114.5, 115.7 (C-a', C-a'), 122.9, 123.0 (C-g', C-g'), 127.4, 127.5 (C-i', C-i'), 145.1, 147.6 (C-b', C-b'), 149.3, 149.4 (C-e', C-e'), 151.4, 151.6 (C-d', C-d'), 166.4, 168.6 (C-j', C-j'); HRMS (ESI positive mode): found  $m/z$  803.3152  $[M+H]^+$ , calcd. 803.3126 for  $C_{40}H_{51}O_{17}$ .

### Synthesis of 3,3'-di-*O*-(3,4,5-trimethoxycinnamoyl)-2,1'-di-*O*-isopropylidene sucrose, 3,3'-triOMe **24**

Following the general procedure, deprotection of compound **17** (100 mg, 0.09 mmol) using  $NEt_3$  (25  $\mu$ L, 0.18 mmol) and 1.56 M  $3HF \cdot NEt_3$  (173  $\mu$ L, 0.27 mmol) gave compound **24** as a white solid (75 mg, 97% yield).

**Analytical data for 3,3'-triOMe **24**:** mp 116-118 MHz,  $CDCl_3$ ): isopropylidene rings:  $\delta$  1.25-1.60 ( $(CH_3)_2C$ ); methoxy and sucrose unit:  $\delta$  3.86-3.87 (9 x H-h'), 3.51-3.55 (m, 1H, H-1'), 3.59-3.79 (m, 2 x H-6', H-2, H-5), 4.10-4.16 (m, 2H, H-5', H-1'), Hz, H-4'), 4.95 (d, 1H,  $J = 7$  Hz, H-3'), 5.52 (t, 1H, 6.25 (d, 1H,  $J = 4$  Hz, H-1); aromatic and alkenyl 1H,  $J = 16$  Hz, H-a'), 6.48 (d, 1H,  $J = 16$  Hz, H-a'), H-g'), 6.92 (s, 2H, H-c', H-g'), 7.51 (d, 1H,  $J = 16$  Hz, H-b');  $^{13}C$  NMR (75.5 MHz, , 24.1, 25.5, 29.1, 29.9 (4 x  $(CH_3)_2C$ ), 56.4, 61.1, 61.2 (C-6), 62.1 (C-5), 64.6 (C-6'), 66.5 (C-1'), 70.8 (C-3), 71.5 (C-4'), 71.8 (C-2), 72.4 (C-4), 81.2 (C-3'), 84.9 (C-5'), 91.4 (C-1), 100.0, 101.9 (2 x  $(CH_3)_2C$ ), 104.0 (C-2'), 105.5, 106.2 (C-c', C-c', C-g', C-g'), 116.1, 117.1 (C-a', C-a'), 129.8, 129.9 (C-i', C-i'), 140.4, 140.6 (C-e', C-e'), 145.2, 147.5 (C-b', C-b'), 153.5, 153.6 (C-d', C-d', C-f', C-f'), 166.1, 168.1 (C-j', C-j'); HRMS (ESI positive mode): found  $m/z$  885.3123  $[M+Na]^+$ , calcd. 885.3157 for  $C_{42}H_{54}O_{19}Na$ .

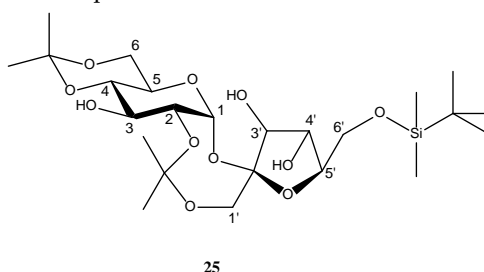


**24**

$^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  19.1, 61.7 (6 x  $OCH_3$ ), 61.7 (m, 12H, 2 x (m, 18H, 9 x H-h', 7H, H-4, 2 x H-6, 4.79 (t, 1H,  $J = 14$   $J = 19$  Hz, H-3), protons:  $\delta$  6.31 (d, 6.72 (s, 2H, H-c', Hz, H-b') 7.80 (d,  $CDCl_3$ ):  $\delta$  19.1, (6 x  $OCH_3$ ), 61.7

### Synthesis of 6'-*O*-tert-butylidimethylsiloxy-2,1':4,6-di-*O*-isopropylidene sucrose, 6'-*O*-TBS **25**

The synthesis of 6'-*O*-TBS **25** was accomplished according to the literature procedure.<sup>3</sup> To a solution of 2,1':4,6-di-*O*-isopropylidene sucrose **2** (1.00 g, 2.37 mmol) and DMAP (28.9 mg, 0.237 mmol) ml,  $NEt_3$  (793  $\mu$ L, 5.68 mmol) and TBSCl (428 mg, 2.84 mmol) room temperature. The reaction mixture was then left to stir for completion (TLC), the reaction mixture was washed with 10% (2 x 15 mL), the organic layer collected, dried over anhydrous  $CH_2Cl_2$  was removed under reduced pressure. The crude mixture was purified using silica gel column chromatography using (1:1) as eluent. 6'-*O*-TBS **25** (1.21 g, 95%) was obtained as white NMR data of the product confirmed with the literature values.<sup>3</sup>

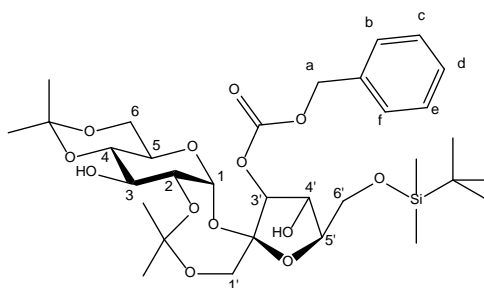


**25**

in  $CH_2Cl_2$  (50.0 were added at 12 hours. Upon  $NH_4Cl$  solution  $MgSO_4$  and ture was purified with EtOAc/hexane solid. The  $^1H$

### Synthesis of 3'-*O*-carboxybenzyl-6'-*O*-tert-butylidimethylsiloxy-2,1'-di-*O*-isopropylidene sucrose, 3'-*O*-Cbz **26**

The synthesis of 3'-*O*-Cbz **26** was accomplished according to the literature procedure.<sup>3</sup> To a stirred solution of 6'-*O*-TBS **25** (500 mg, 0.932 mmol) and DMAP (11.4 mg, 0.0932 mmol) in  $CH_2Cl_2$  (20.0 ml) was added TMEDA (420  $\mu$ L, 2.80 mmol) and CbzCl (199  $\mu$ L, 1.40 mmol) at room temperature. The reaction was left to stir for 12 hours. Upon completion (TLC), the reaction was washed with water (2 x 10 mL), the organic layer dried over anhydrous  $MgSO_4$ , removed and the crude mixture was purified using column chromatography with a gradient of EtOAc/hexane as eluent (starting with then Hexane/EtOAc (6:1) and Hexane/EtOAc (4:1)). 3'-*O*-Cbz **26** white solid (469 mg, 75% yield). The  $^1H$  NMR data of the product confirmed with the literature values.<sup>3</sup>



**26**

$CH_2Cl_2$  was chromatographed with Hex/EtOAc (8:1), was obtained as a white solid. The product was confirmed.

#### 1.2.4.3 General procedure for acylation of 3'-*O*-Cbz **26**



To a stirred solution of 3'-O-Cbz **26** (300 mg, 0.448 mmol) and DMAP (11 mg, 0.09 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added the (substituted) cinnamic acid (1.79 mmol) and EDC (344 mg, 1.79 mmol) at room temperature. The reaction mixture was left to stir for a week, washed with distilled water (2 x 10 mL), the organic phase dried over anhydrous MgSO<sub>4</sub> and the solvent evaporated under reduced pressure. The crude product was purified using silica gel column chromatography using Hexane/EtOAc (8:1) as eluent. The general procedure was used to prepare compounds **27**, **28**, **29**, **30**, **31** and **32** and also gave compounds **33**, **34**, **35**, **36**, **37** and **38** as by products.

### Synthesis of 3,4'-di-O-(4-*tert*-butyldimethylsiloxycinnamoyl)- 3'-O-carboxybenzyl-6'-O-*tert*-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose **27**

Following the general procedure, OTBS-coumaric acid (498 mg, 1.79 mmol) gave compound **27** (192 mg, 36% yield) and by product **33** (258 g, 62% yield) as white solids.

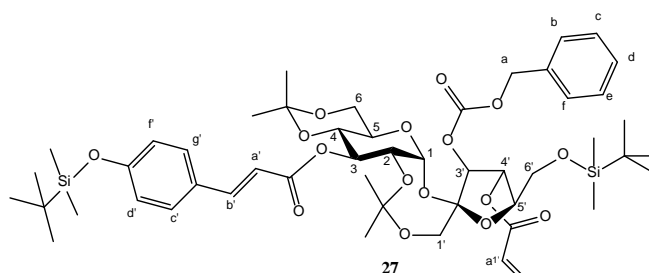
**Analytical data for compound 27:** <sup>1</sup>H NMR (300 TBS groups: δ 0.02 (s, 6H), 0.83 (s, 9H); TBS on royl group: δ 0.18-0.19 (m, 12H), 0.95 (m, 18H); lidene rings: δ 1.22-1.44 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>C); crose unit: δ 3.49 (d, 1H, J = 12 Hz), 3.71-3.90 (m, (m, 2H), 4.89 (d, 1H, J = 4 Hz, H-3'), 5.26-5.41 (m, H-a), 5.52 (t, 1H, J = 7 Hz, H-4'), 6.06 (d, 1H, J = 3.5 OTBS-coumaroyl aromatic and alkenyl protons: δ = 34 Hz, H-a', Ha'), 6.81 (d, 4H, J = 9 Hz, H-d', H-7.23-7.46 (m, 9H, H-c', H-g', Hc', H-g', H-b, H-c, 7.57-7.64 (m, 2H, H-b', H-b'); <sup>13</sup>C NMR (75.5 MHz, -5.12, -4.17, 18.5, 19.3, 24.1, 25.8, 26.1, 29.2, 62.6, 70.9, 71.9, 72.2, 81.7, 83.4, 92.0, 99.9, 101.5, 105.0, 120.7, 120.8, 127.7, 128.1, 128.6, 128.8, 129.9, 130.1, 145.9, 154.7, 158.0, 158.3, 166.0, 166.4.

**Analytical data for compound 33:** The <sup>1</sup>H NMR pound **33** confirmed to the literature values.<sup>3</sup>

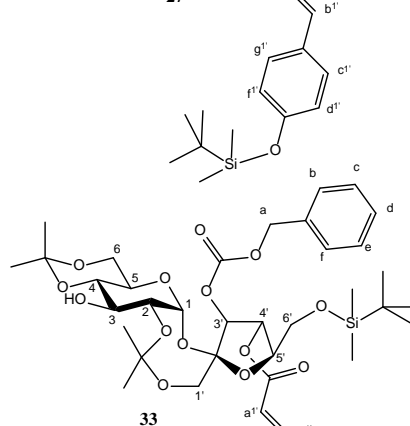
### Synthesis of 3,4'-di-O-(4-*tert*-thylsiloxy-3-methoxycinnamoyl)- 3'-O-zyl-6'-O-*tert*-butyldimethylsiloxy-2,1'-di-O-lidene sucrose **28**

Following the general procedure, OTBS-feru acid mmol) gave compound **28** (140 mg, 25% yield) and by- (151 mg, 35% yield) as white solids.

**Analytical data for compound 28:** <sup>1</sup>H NMR (300 MHz, group: δ 0.03 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>Si), 0.84 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>CSi); feruoyl group: 0.14-0.15 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>Si), 0.97 (m, (CH<sub>3</sub>)<sub>3</sub>CSi); isopropylidene rings: δ 1.23-1.55 (m, 12H, Cbz, methoxy and sucrose unit: δ 3.81-3.83 (m, 6H, 3 x 3.50 (d, 1H, J = 12 Hz), 3.72-3.79 (m, 4H), 3.88-3.91 (m, (m, 2H), 4.89 (d, 1H, J = 4 Hz, H-3'), 5.28-5.42 (m, 3H, 5.53 (t, 1H, J = 7 Hz, H-4'), 6.07 (d, 1H, J = 3.5 Hz, H-1); feruloyl aromatic and alkenyl protons: δ 6.27 (dd, 2H, H-a'), 6.82 (d, 2H, J = 9 Hz, H-c', H-c'), 6.98-7.02 (m, H-d', H-g'), 7.30-7.47 (m, 5H, H-b, H-c, H-d, H-e, H-f), 6 Hz, H-b'), 7.62 (d, 1H, J = 6.5 Hz, H-b'); <sup>13</sup>C NMR CDCl<sub>3</sub>): δ -5.37, -5.33, -4.60, -4.59, 18.3, 18.5, 19.0, 23.9, 62.4, 63.5, 64.1, 66.7, 70.6, 70.7, 71.7, 72.0, 81.5, 83.2, 91.8,



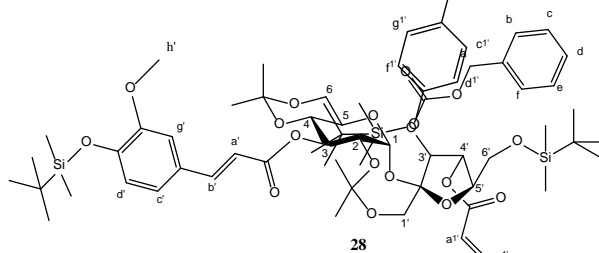
MHz, CDCl<sub>3</sub>): OTBS couma-isopropyl-Cbz and su-7H), 4.15-4.21 3H, H-3, 2 x Hz, H-1); Cbz, 6.26 (dd, 2H, J f', Hd', H-f'), H-d, H-e, H-f), CDCl<sub>3</sub>): δ -5.16, 63.7, 64.3, 70.8, 115.0, 116.1, 135.4, 144.7,



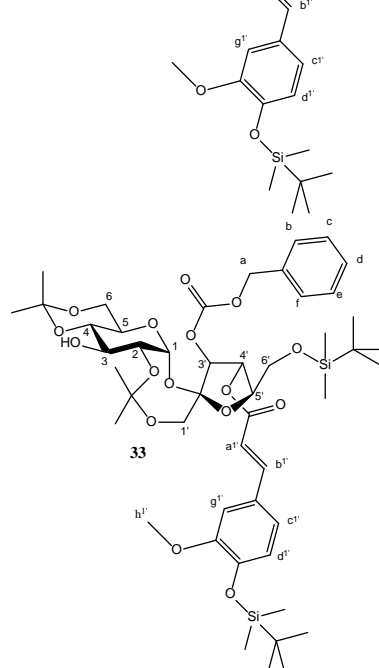
data of com-

butyldime-carboxyben-isopropyl-

(552 mg, 1.79 product **34**



CDCl<sub>3</sub>): TBS TBS on OTBS-18H, 2 x 2 x (CH<sub>3</sub>)<sub>2</sub>C); H-h', 3 x H-h'), 4H), 4.15-4.21 H-3, 2 x H-a), Cbz, OTBS-J = 33 Hz, H-a', 4H, H-d', H-g', 7.57 (d, 1H, J = (75.5 MHz, 25.7, 25.9, 55.5, 99.7, 101.3,



104.8, 110.8, 110.9, 114.8, 115.9, 121.1, 122.2, 122.5, 128.1, 128.4, 128.6, 135.2, 144.8, 146.0, 147.5, 147.8, 151.2, 154.5, 165.7, 166.1.

**Analytical data for compound 34:** The  $^1\text{H}$  NMR data of the compound was compared with literature values<sup>3</sup> and confirmed to be 34.

**Synthesis of 3,4'-di-O-(4-*tert*-butyldimethylsiloxy-3,5-dimethoxycinnamoyl) -3'-O-carboxybenzyl-6'-O-*tert*-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose 29**

Following the general procedure, OTBS-sinapic acid (605 mg, 1.79 mmol) gave compound **29** (182 mg, 31% yield) and by-product **35** (182 mg, 41% yield) as white solids.

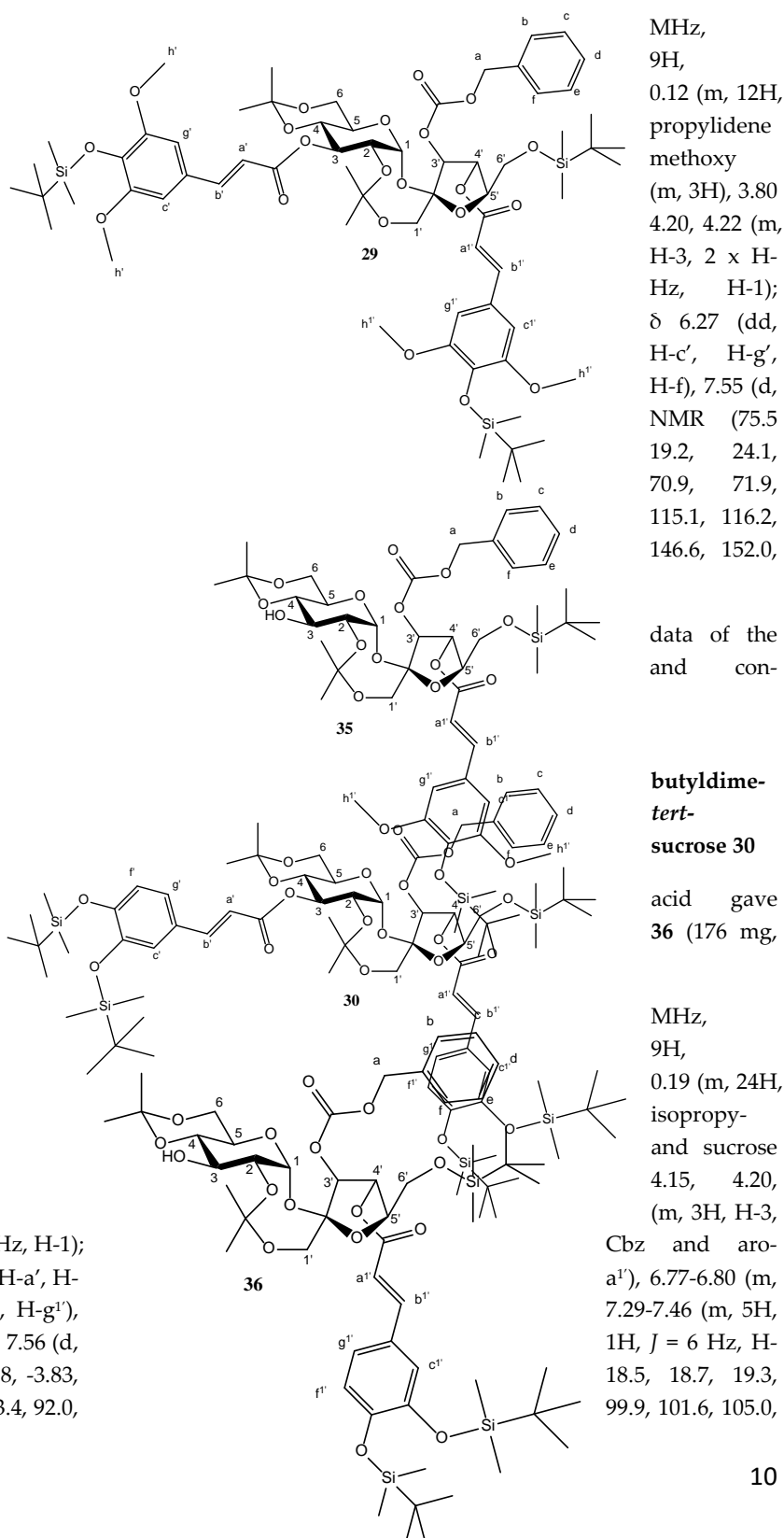
**Analytical data for compound 29:**  $^1\text{H}$  NMR (300  $\text{CDCl}_3$ ): TBS group:  $\delta$  0.03 (s, 6H,  $(\text{CH}_3)_2\text{Si}$ ), 0.85 (s,  $(\text{CH}_3)_3\text{CSi}$ ); TBS on OTBS-sinapoyl groups:  $\delta$  0.11-2  $\times$   $(\text{CH}_3)_2\text{Si}$ , 0.98 (m, 18H, 2  $\times$   $(\text{CH}_3)_3\text{CSi}$ ); isorings:  $\delta$  1.24-1.45 (m, 12H, 2  $\times$   $(\text{CH}_3)_2\text{C}$ ); Cbz, and sucrose unit:  $\delta$  3.51 (d, 1H,  $J = 12$  Hz), 3.72-3.78 (m, 12H, 6  $\times$  H-h', 6  $\times$  h'), 3.89-3.92 (m, 4H), 4.15, 2H), 4.90 (d, 1H,  $J = 4$  Hz, H-3'), 5.29-5.42 (m, 3H, a), 5.53 (t, 1H,  $J = 7.5$  Hz, H-4'), 6.07 (d, 1H,  $J = 4$  Hz, H-a'), 6.27 (dd, 2H,  $J = 32.5$  Hz, H-a', H-a'), 6.71 (d, 4H,  $J = 8$  Hz, H-a', H-g'), 7.30-7.48 (m, 5H, H-b, H-c, H-d, H-e, 1H,  $J = 6$  Hz, H-b'), 7.61 (d, 1H,  $J = 6$  Hz, H-b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.18, -5.14, -4.43, -4.40, 18.5, 18.9, 25.8, 25.9, 26.1, 29.2, 55.9, 62.6, 63.7, 64.3, 66.8, 70.8, 72.1, 81.7, 83.4, 92.0, 99.8, 101.5, 105.0, 105.5, 105.6, 127.0, 127.3, 128.6, 128.8, 135.3, 137.1, 137.3, 145.4, 154.7, 165.8, 166.2.

**Analytical data for compound 35:** The  $^1\text{H}$  NMR compound was compared with literature values<sup>3</sup> confirmed to be 35.

**Synthesis of 3,4'-di-O-(3,4-di-*tert*-thylsiloxy-cinnamoyl) -3'-O-carboxybenzyl-6'-O-butylidimethylsiloxy-2,1'-di-O-isopropylidene**

Following the general procedure, OTBS-cafeic compound **30** (91 mg, 14% yield) and by-product **36** (37% yield) as white solids.

**Analytical data for compound 30:**  $^1\text{H}$  NMR (300  $\text{CDCl}_3$ ): TBS group:  $\delta$  0.18 (s, 6H,  $(\text{CH}_3)_2\text{Si}$ ), 0.83 (s,  $(\text{CH}_3)_3\text{CSi}$ ); TBS on OTBS-cafeoyl groups:  $\delta$  0.18-4  $\times$   $(\text{CH}_3)_2\text{Si}$ , 0.95-0.96 (m, 36H, 4  $\times$   $(\text{CH}_3)_3\text{CSi}$ ); lidene rings:  $\delta$  1.23-1.44 (m, 12H, 2  $\times$   $(\text{CH}_3)_2\text{C}$ ); Cbz unit:  $\delta$  3.51 (d, 1H,  $J = 12$  Hz), 3.65-3.92 (m, 7H), 4.22 (m, 2H), 4.88 (d, 1H,  $J = 4$  Hz, H-3'), 5.27-5.41 (m, 2  $\times$  H-a), 5.51 (t, 1H,  $J = 7$  Hz, H-4'), 6.06 (d, 1H,  $J = 4$  Hz, H-1); matic and alkenyl protons:  $\delta$  6.19 (dd, 2H,  $J = 34$  Hz, H-a', H-2H, H-f', H-f'), 6.96-6.99 (m, 4H, H-c', H-c', H-g', H-g'), H-b, H-c, H-d, H-e, H-f), 7.51 (d, 1H,  $J = 6$  Hz, H-b'), 7.56 (d, b');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.15, -5.12, -3.88, -3.83, 24.1, 26.1, 63.7, 64.3, 66.9, 70.8, 71.0, 71.9, 72.1, 81.7, 83.4, 92.0,



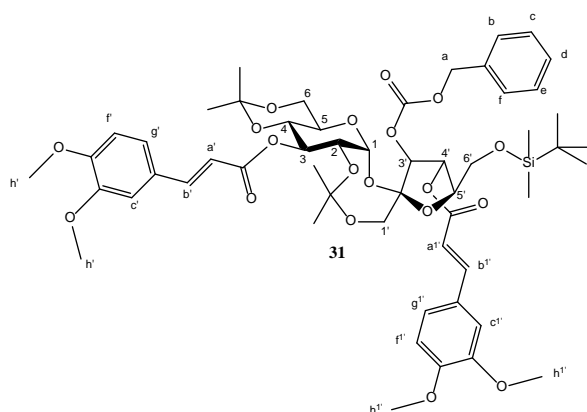
114.9, 116.0, 120.7, 121.4, 122.2, 122.7, 128.6, 128.8, 135.4, 144.9, 146.1, 147.4, 149.6, 149.9, 154.7, 166.0, 166.4.

**Analytical data for compound 36:** The  $^1\text{H}$  NMR data of the compound was compared with literature values<sup>3</sup> and confirmed to be 36.

**Synthesis of 3,4'-di-O-(3,4-dimethoxycinnamoyl) -3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose 31**

Following the general procedure, diOMe acid (373 mg, 1.79 mmol) gave compound 31 (141 mg, 30% yield) and by-product 37 (150 mg, 39% yield) as white solids.

**Analytical data for compound 31:**  $^1\text{H}$  NMR (300 MHz, group:  $\delta$  0.03 (s, 6H,  $(\text{CH}_3)_2\text{Si}$ ), 0.84 (s, 9H,  $(\text{CH}_3)_3\text{CSi}$ ); rings:  $\delta$  1.23-1.45 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ); Cbz, meth-unit:  $\delta$  3.89 (m, 12H, 6 x H-h', 6 x H-h'), 3.50 (d, 1H,  $J$  = 3.83 (m, 7H), 4.15-4.22 (m, 2H), 4.89 (d, 1H,  $J$  = 4 Hz, H-3H, H-3, 2 x H-a), 5.52 (t, 1H,  $J$  = 7.5 Hz, H-4'), 6.07 (d, 1); Cbz and diOMe aromatic and alkenyl protons:  $\delta$  31.5 Hz, H-a', Ha'), 6.83-6.86 (m, 2H, H-f', H-f'), 7.01-c', H-c', H-g', H-g'), 7.29-7.47 (m, 5H, H-b, H-c, H-d, (d, 1H,  $J$  = 7 Hz, H-b'), 7.64 (d, 1H,  $J$  = 6.5 Hz, H-b');  $^{13}\text{C}$  MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.15, -5.11, 14.4, 18.5, 19.3, 24.1, 25.8, 56.2, 60.6, 62.6, 63.7, 64.3, 66.9, 70.8, 71.0, 71.9, 72.2, 81.7, 101.6, 105.0, 109.8, 109.9, 111.2, 115.0, 116.0, 122.9, 123.1, 128.6, 128.8, 135.4, 144.9, 146.1, 149.4, 151.3, 151.6, 154.7,



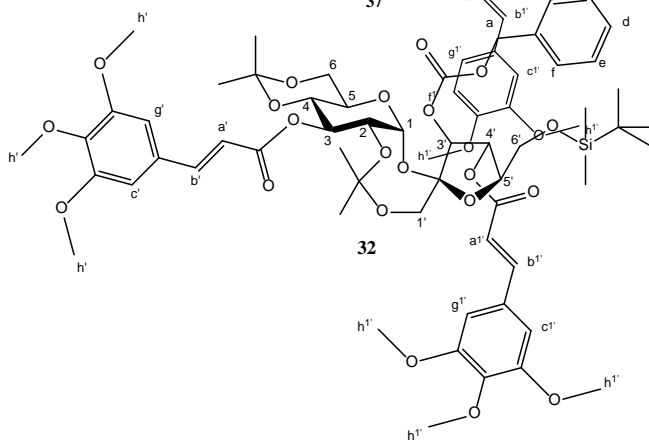
$\text{CDCl}_3$ ): TBS isopropylidene oxy and sucrose 12.5 Hz), 3.69-3'), 5.29-5.41 (m, 1H,  $J$  = 4 Hz, H-6.27 (dd, 2H,  $J$  = 7.10 (m, 4H, H-H-e, H-f), 7.58 NMR (75.5 26.1, 29.2, 56.1, 83.4, 92.0, 99.9, 127.4, 127.7, 165.9, 166.4.

**Analytical data for compound 37:** The  $^1\text{H}$  NMR data pound was compared with literature values<sup>3</sup> and 37.

**Synthesis of 3,4'-di-O-(3,4,5-ycinnamoyl) -3'-O-carboxybenzyl-6'-O-tert-thylsiloxy-2,1'-di-O-isopropylidene sucrose 32**

Following the general procedure, triOMe acid mmol) gave compound 32 (179 mg, 36% yield) 35% yield) as white solids.

**Analytical data for compound 32:**  $^1\text{H}$  NMR (300 TBS group:  $\delta$  0.03 (s, 6H,  $(\text{CH}_3)_2\text{Si}$ ), 0.85 (s, 9H, isopropylidene rings:  $\delta$  1.24-1.46 (m, 12H, 2 x methoxy and sucrose unit:  $\delta$  3.86-3.87 (m, 18H, 9 h'), 3.51 (d, 1H,  $J$  = 12.5 Hz), 3.69-3.76 (m, 6H), 3H), 4.15-4.26 (m, 2H), 4.91 (d, 1H,  $J$  = 4 Hz, H-3'), 3H, H-3, 2 x H-a), 5.55 (t, 1H,  $J$  = 7.5 Hz, H-4'), 4 Hz, H-1); Cbz and triOMe aromatic & alkenyl (dd, 2H,  $J$  = 31 Hz, H-a', H-a'), 6.72-6.75 (m, 4H, H-g'), 7.28-7.48 (m, 5H, H-b, H-c, H-d, H-3, H-f), 6 Hz, H-b'), 7.61 (d, 1H,  $J$  = 6 Hz, H-b');  $^{13}\text{C}$  NMR  $\text{CDCl}_3$ ): -5.16, -5.12, 1.24, 18.5, 19.3, 24.1, 25.8, 26.1, 61.2, 62.6, 63.7, 64.3, 66.9, 70.9, 71.1, 71.9, 72.2, 99.9, 101.6, 105.0, 105.6, 116.6, 117.6, 128.6, 128.8,

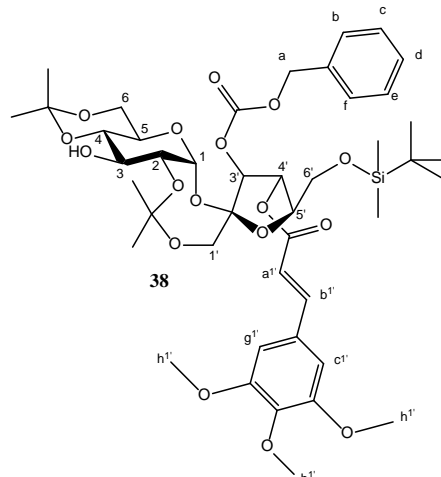


of the com-confirmed to be

**trimethox-butylidime-**

(426 mg, 1.79 and 38 (140 mg,

MHz,  $\text{CDCl}_3$ ):  $(\text{CH}_3)_3\text{CSi}$ ;  $(\text{CH}_3)_2\text{C}$ ); Cbz, x H-h', 9 x H-3.92-3.93 (m, 5.31-5.43 (m, 6.08 (d, 1H,  $J$  = protons:  $\delta$  6.32 H-c', H-c', H-g', 7.56 (d, 1H,  $J$  = (75.5 MHz, 29.2, 56.4, 60.6, 81.7, 83.3, 92.0, 129.9, 130.2,



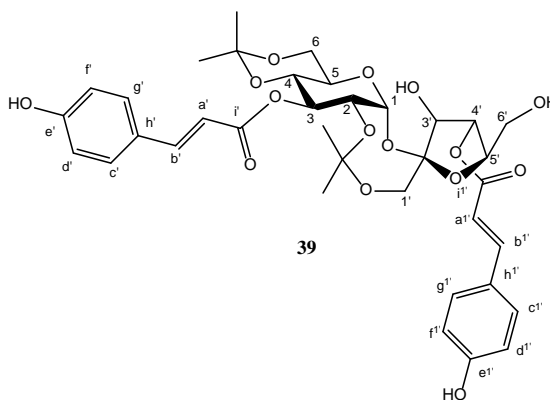
135.3, 140.4, 140.6, 145.0, 146.1, 153.7, 154.7, 165.6, 166.1.

**Analytical data for compound 38:** The  $^1\text{H}$  NMR data of the compound was compared with literature values<sup>3</sup> and confirmed to be 38.

#### Synthesis of 3,4'-di-O-coumaroyl-2,1'-di-O-isopropylidene sucrose, 3,4'-coum 39

To a stirred solution of compound 27 (100 mg, 0.08 mmol) and  $\text{Pd}(\text{OAc})_2$  (1.6 mg, 0.007 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 ml) was added  $\text{NEt}_3$  (1.6  $\mu\text{L}$ , 0.0112 mmol) and  $\text{Et}_3\text{SiH}$  (18  $\mu\text{L}$ , 0.112 mmol) at room temperature and the mixture was left to stir for 12 hours. The reaction mixture was then diluted with  $\text{EtOAc}$  (10.0 ml), washed with water (2 x 10 mL) and the organic layer was dried over anhydrous  $\text{MgSO}_4$  and the solvent evaporated. The crude product obtained was re-dissolved in pyridine (1.0 ml).  $\text{NEt}_3$  (22  $\mu\text{L}$ , 0.16 mmol) and 1.56 M  $3\text{HF}\cdot\text{NEt}_3$  (154  $\mu\text{L}$ , 0.24 mmol) were added to the solution which was left to stir for 12 hours at room temperature. Upon reaction completion (TLC), pyridine was evaporated under reduced pressure and the crude product was subjected to purification using  $\text{EtOAc}/\text{Hexane}$  (3:2) as eluent. 3,4'-coum 39 was obtained as white solid in (28 mg, 49% yield).

**Analytical data for 3,4'-coum 39:** mp 171-173  $^\circ\text{C}$ ;  $^1\text{H}$  Acetone- $d_6$ ): isopropylidene rings:  $\delta$  1.25-1.47 (m, 12H, 2 crose unit:  $\delta$  3.52-3.56 (m, 1H, H-1'), 3.72-3.83 (m, 4H, H-2, 4.00-4.07 (m, 5H, H-5, H-6, H-6', H-1', H-3'), 4.12 (d, 1H, 5.10 (d, 1H,  $J = 11$  Hz), 5.38 (t, 1H,  $J = 19$  Hz, H-3), 5.55 (t, H-4'), 6.21 (d, 1H,  $J = 4$  Hz, H-1); aromatic and alkenyl (dd, 2H,  $J = 31$  Hz, H-a', H-a'), 6.90 (dd, 4H,  $J = 11$  Hz, H-f'), 7.54-7.71 (m, 6H, H-c', H-c', H-g', H-g', H-b', H- (75.5 MHz, Acetone- $d_6$ ):  $\delta$  19.4, 24.5, 25.6 (4 x  $(\text{CH}_3)_2\text{C}$ ), (C-5), 64.1 (C-6'), 64.5, 66.9 (C-1'), 71.5 (C-3), 72.7 (C-4), (C-4'), 78.7 (C-3'), 83.1 (C-5'), 92.4 (C-1), 100.3, 102.1 (2 x (C-2'), 115.0 (C-a', C-a'), 115.8, 116.2, 116.8, 116.9 (C-d', 126.9, 127.1 (C-h', C-h'), 129.5, 130.2, 131.0, 131.2 (C-c', 145.4, 146.5 (C-b', C-b'), 160.8, 161.0 (C-e', C-e'), 166.7, 167.5 (C-i', C-i'); HRMS (ESI positive mode): found  $m/z$  737.2399  $[\text{M}+\text{Na}]^+$ , calcd. 737.2421 for  $\text{C}_{36}\text{H}_{42}\text{O}_{15}\text{Na}$ .

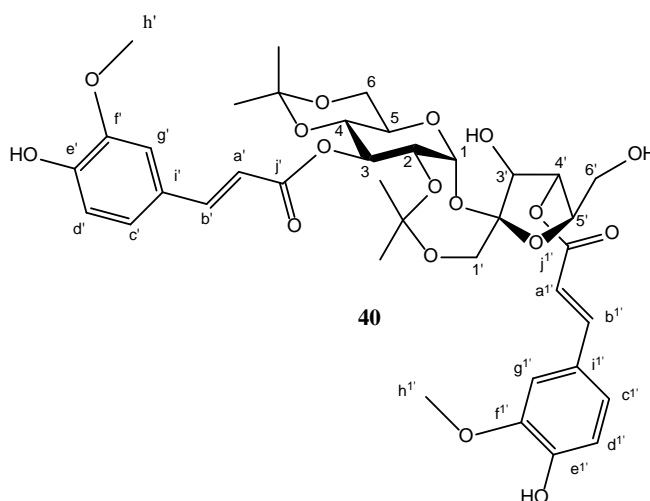


NMR (300 MHz,  $\times (\text{CH}_3)_2\text{C}$ ); su- H-4, H-6, H-6'),  $J = 13$  Hz, H-5'), 1H,  $J = 14.5$  Hz, protons:  $\delta$  6.37 H-d', H-d', H-f', b');  $^{13}\text{C}$  NMR 60.7 (C-6), 62.7 72.9 (C-2), 78.1  $(\text{CH}_3)_2\text{C}$ , 104.7 C-d', C-f', C-f'), C-c', C-g', C-g'),

#### Synthesis of 3,4'-di-O-feruloyl-2,1'-di-O-isopropylidene sucrose, 3,4'-feru 40

To a stirred solution of compound 28 (100 mg, 0.08 mmol) and  $\text{Pd}(\text{OAc})_2$  (1.6 mg, 0.007 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 ml) was added  $\text{NEt}_3$  (1.6  $\mu\text{L}$ , 0.0112 mmol) and  $\text{Et}_3\text{SiH}$  (18  $\mu\text{L}$ , 0.112 mmol) at room temperature and the mixture was left to stir for 12 hours. The reaction was diluted with  $\text{EtOAc}$  (10.0 ml), washed with water (2 x 10 ml) and the organic layer was dried over anhydrous  $\text{MgSO}_4$  and the solvent evaporated. The crude product obtained was re-dissolved in pyridine (1.0 ml).  $\text{NEt}_3$  (22  $\mu\text{L}$ , 0.16 mmol) and 1.56 M  $3\text{HF}\cdot\text{NEt}_3$  (154  $\mu\text{L}$ , 0.24 mmol) were added to the solution which was left to stir for 12 hours at room temperature. Upon reaction completion (TLC), pyridine was evaporated under reduced pressure and the crude mixture was subjected to purification using 3:2  $\text{EtOAc}/\text{Hexane}$  as eluent. 3,4'-feru 40 was obtained as white solid (16 mg, 26% yield).

**Analytical data for 3,4'-feru 40:** mp 131-133  $^\circ\text{C}$ ; MHz,  $\text{CDCl}_3$ ): isopropylidene rings:  $\delta$  1.29-1.46  $(\text{CH}_3)_2\text{C}$ ); methoxy and sucrose unit:  $\delta$  3.86- 3.92 3 x H-h'), 3.49-3.53 (m, 1H, H-1'), 3.69-3.78, (m, H-6, H-6'), 3.98-4.14 (m, 5H, H-5, H-6, H-6', H-1', 1H,  $J = 12.5$  Hz, H-5'), 5.39 (t, 1H,  $J = 19$  Hz, H-3), 14 Hz, H-4'), 6.25 (d, 1H,  $J = 4$  Hz, H-1); aromatic protons:  $\delta$  6.26 (d, 1H,  $J = 4$  Hz, H-a'), 6.31 (d, 1H, 6.91 (d, 2H,  $J = 8$  Hz, H-d', H-d'), 7.01-7.08 (m, H-g', H-g'), 7.63 (dd, 2H,  $J = 28.5$  Hz, H-b', H- (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.1, 22.7, 24.2, 25.4 (4 x 56.2 (2 x  $\text{OCH}_3$ ), 62.1 (C-6), 62.5 (C-5), 64.6 (C-6'),



$^1\text{H}$  NMR (300 (m, 12H, 2 x (m, 6H, 3 x H-h', 4H, H-2, H-4, H-3'), 4.21 (d, 5.54 (t, 1H,  $J =$  and alkenyl  $J = 4$  Hz, H-a'), 4H, H-c', H-c', b');  $^{13}\text{C}$  NMR  $(\text{CH}_3)_2\text{C}$ , 56.1, 66.4 (C-1'), 70.7

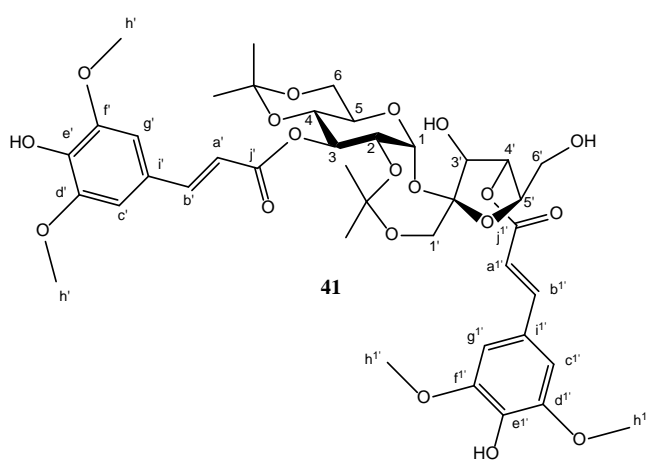
(C-3), 71.6 (C-2), 71.7 (C-4), 78.4 (C-4'), 82.8 (C-3', C-5'), 91.8 (C-1), 100.0, 101.9 (2 x (CH<sub>3</sub>)<sub>2</sub>C), 103.9 (C-2'), 109.7, 109.8 (C-g', C-g<sup>1'</sup>), 114.4, 115.0 (C-a', C-a<sup>1'</sup>), 115.4 (C-d', C-d<sup>1'</sup>), 123.2, 123.5 (C-c', C-c<sup>1'</sup>), 126.9, 127.1 (C-i', C-i<sup>1'</sup>), 145.3 (C-b', C-b<sup>1'</sup>), 146.6, 147.0 (C-f', C-f<sup>1'</sup>), 148.2, 148.5 (C-e', C-e<sup>1'</sup>), 166.5, 167.3 (C-j', C-j<sup>1'</sup>); HRMS (ESI positive mode): found *m/z* 797.2607 [M+Na]<sup>+</sup>, calcd. 797.2633 for C<sub>38</sub>H<sub>46</sub>O<sub>17</sub>Na.

### Synthesis of 3,4'-di-*O*-sinapoyl-2,1'-di-*O*-isopropylidene sucrose, 3,4'-sinap **41**

To a stirred solution of compound **29** (100 mg, 0.08 mmol) and Pd(OAc)<sub>2</sub> (1.6 mg, 0.007 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 ml) was added NEt<sub>3</sub> (1.6 μL, 0.0112 mmol) and Et<sub>3</sub>SiH (18 μL, 0.112 mmol) at room temperature and left to stir for 12 hours. The reaction mixture was then diluted with EtOAc (10.0 ml), washed with water (2 x 10 mL) and the organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent evaporated. The crude product obtained was re-dissolved in pyridine (1.0 ml). NEt<sub>3</sub> (22 μL, 0.16 mmol) and 1.56 M 3HF·NEt<sub>3</sub> (154 μL, 0.24 mmol) were added to the solution and was left to stir for 12 hours at room temperature. Upon reaction completion (TLC), pyridine was removed under reduced pressure and the crude product was subjected to purification using 3:2 EtOAc/Hexane as eluent. 3,4'-sinap **41** was obtained as white solid (17 mg, 26% yield).

**Analytical data for 3,4'-sinap **41**:** mp 143-145 °C;

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): isopropylidene rings: δ 1.29-1.45 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>C); methoxy and sucrose unit: δ 3.91 (m, x H-h'), 3.48-3.52 (m, 1H, H-1'), 3.65-3.77 (m, 4H, H-6'), 3.95-4.23 (m, 6H, H-5, H-6, H-6', H-1', H-3', 1H, *J* = 19 Hz, H-3), 5.56 (t, 1H, *J* = 14 Hz, H-4'), Hz, H-1); aromatic and alkenyl protons: δ 6.25 (d, a'), 6.29 (d, 1H, *J* = 6 Hz, H-a<sup>1'</sup>), 6.75 (d, 4H, *J* = 2 Hz, H-g', H-g<sup>1'</sup>), 7.59 (dd, 2H, *J* = 30 Hz, H-b', H-b<sup>1'</sup>); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 19.1, 23.2, 25.4, 29.1 (4 x (CH<sub>3</sub>)<sub>2</sub>C), OCH<sub>3</sub>, 62.1 (C-6), 62.5 (C-5), 64.5 (C-6'), 66.4 (C-71.6 (C-2), 71.7 (C-4), 77.4 (C-4'), 78.4 (C-3'), 82.7 1), 100.0, 102.0 (2 x (CH<sub>3</sub>)<sub>2</sub>C), 103.9 (C-2'), 105.3, c<sup>1'</sup>, C-g', C-g<sup>1'</sup>), 114.8, 115.8 (C-a', C-a<sup>1'</sup>), 125.8, i<sup>1'</sup>), 126.9, 127.2 (C-e', C-e<sup>1'</sup>), 145.5, 146.8, 147.4 (C-b', C-b<sup>1'</sup>, C-d', C-d<sup>1'</sup>, C-f', C-f<sup>1'</sup>), 166.3, 167.2 (C-j', C-j<sup>1'</sup>); HRMS (ESI positive mode): found *m/z* 857.2885 [M+Na]<sup>+</sup>, calcd. 857.2844 for C<sub>40</sub>H<sub>50</sub>O<sub>19</sub>Na.

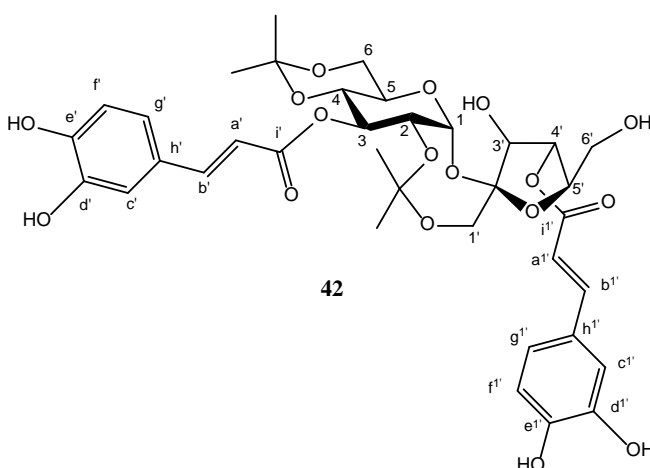


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): (m, 12H, 2 x 12H, 6 x H-h', 6 H-2, H-4, H-6, H-5'), 5.39 (t, 6.24 (d, 1H, *J* = 4 1H, *J* = 6 Hz, H-Hz, H-c', H-c<sup>1'</sup>, <sup>13</sup>C NMR (75.5 56.5, 60.6 (4 x 1'), 70.7 (C-3), (C-5'), 91.8 (C-105.5 (C-c', C-126.0 (C-i', C-

### Synthesis of 3,4'-di-*O*-caffeoyl-2,1'-di-*O*-isopropylidene sucrose, 3,4'-caff **42**

To a stirred solution of compound **30** (100 mg, 0.07 mmol) and Pd(OAc)<sub>2</sub> (1.4 mg, 0.006 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 ml) was added NEt<sub>3</sub> (1.3 μL, 0.0092 mmol) and Et<sub>3</sub>SiH (15 μL, 0.092 mmol) at room temperature and the mixture was left to stir for 12 hours. The reaction mixture was then diluted with EtOAc (10.0 ml), washed with water (2 x 10 mL) and the organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent evaporated. The crude product obtained was re-dissolved in pyridine (1.0 ml). NEt<sub>3</sub> (20 μL, 0.14 mmol) and 1.56 M 3HF·NEt<sub>3</sub> (135 μL, 0.21 mmol) were added to the solution which was left to stir for 12 hours at room temperature. Upon reaction completion (TLC), pyridine was evaporated under reduced pressure and the crude product was subjected to purification using 3:2 EtOAc/Hexane as eluent. 3,4'-caff **42** was obtained as yellow solid (11 mg, 22% yield).

**Analytical data for 3,4'-caff **42**:** mp 165-167 °C; <sup>1</sup>H NMR (300 MHz, Acetone-d<sub>6</sub>): isopropylidene rings: δ 1.24-1.46 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>C); sucrose unit: δ 3.52-3.56 (m, 1H, H-1'), 3.71-3.83 (m, 4H, H-2, H-4, H-6, H-6'), 3.98-4.07 (m, 5H, H-5, H-6, H-6', H-1', H-3'), 4.15 (d, 1H, *J* = 12.5 Hz, H-5'), 5.11 (d, 1H, *J* = 11 Hz, H-3), 5.55 (t, 1H, *J* = 14.5 Hz, H-4'), Hz, H-1); aromatic and alkenyl protons: δ 6.30 Hz, H-a', H-a<sup>1'</sup>), 6.85-6.89 (m, 2H, H-f', H-f<sup>1'</sup>), H-g', H-g<sup>1'</sup>), 7.18 (dd, 2H, *J* = 10 Hz, H-c', H-c<sup>1'</sup>), 37 Hz, H-b', H-b<sup>1'</sup>); <sup>13</sup>C NMR (75.5 MHz, Acetone-d<sub>6</sub>): δ 18.4, 23.6, 24.6 (4 x (CH<sub>3</sub>)<sub>2</sub>C), 61.8 (C-6), 63.1 (C-5), (C-1'), 70.5 (C-3), 71.7 (C-2), 71.9 (C-4), 77.1 (C-82.1 (C-5'), 91.4 (C-1), 99.3, 101.1 (2 x (CH<sub>3</sub>)<sub>2</sub>C),

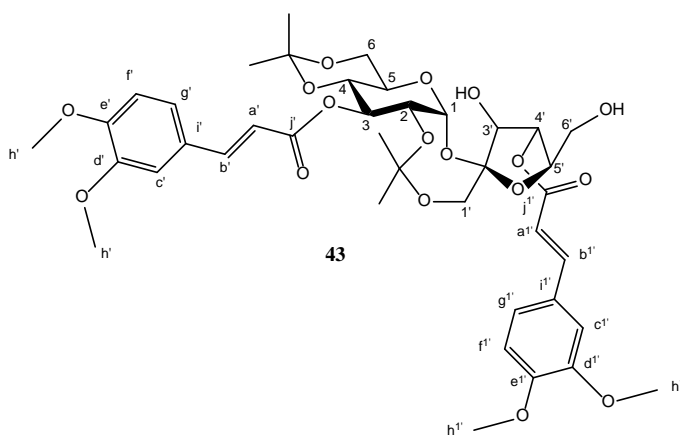


114.0, 114.3, (C-a', C-a''), 114.9, 115.5 (C-c', C-c'', C-f', C-f''), 121.6, 121.9 (C-g', C-g''), 126.6, 126.7 (C-h', C-h''), 144.8, 145.5, 145.8, 147.9, 148.2 (C-b', C-b'', C-d', C-d'', C-e', C-e''), 165.7, 166.5 (C-i', C-i''); HRMS (ESI positive mode): found  $m/z$  747.2499 [M+H]<sup>+</sup>, calcd. 747.2500 for C<sub>36</sub>H<sub>43</sub>O<sub>17</sub>.

### Synthesis of 3,4'-di-O-(3,4-dimethoxycinnamoyl)-2,1'-di-O-isopropylidene sucrose, 3,4'-diOMe **43**

To a stirred solution of compound **31** (100 mg, 0.096 mmol) and Pd(OAc)<sub>2</sub> (1.8 mg, 0.008 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 ml) was added NEt<sub>3</sub> (1.8  $\mu$ L, 0.0128 mmol) and Et<sub>3</sub>SiH (20  $\mu$ L, 0.128 mmol) at room temperature and the mixture was left to stir for 12 hours. The reaction mixture was then diluted with EtOAc (10.0 ml), washed with water (2 x 10 mL) and the organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent evaporated. The crude product obtained was re-dissolved in pyridine (1.0 ml). NEt<sub>3</sub> (27  $\mu$ L, 0.19 mmol) and 1.56 M 3HF·NEt<sub>3</sub> (186  $\mu$ L, 0.29 mmol) were added to the solution and was left to stir for 12 hours at room temperature. Upon reaction completion (TLC), pyridine was evaporated under reduced pressure and the crude product was then subjected to purification using 3:2 EtOAc/Hexane as eluent. 3,4'-diOMe **43** was obtained as white solid (23 mg, 30% yield).

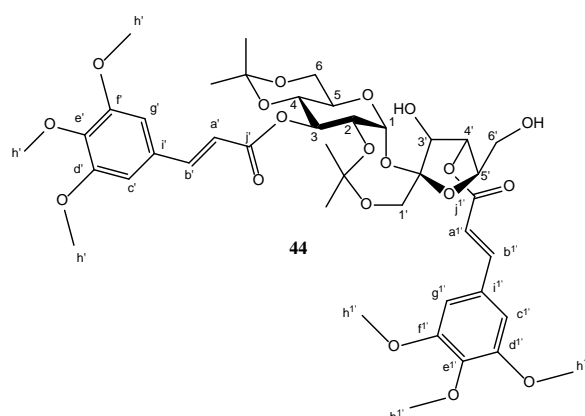
**Analytical data for 3,4'-diOMe **43**:** mp 127-129 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): isopropylidene rings:  $\delta$  1.28-1.44 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>C); methoxy and sucrose unit:  $\delta$  3.88 (m, 12H, 6 x H-h'), 3.47-3.51 (m, 1H, H-1'), 3.67-3.76 (m, 4H, H-2, H-6, H-6'), 3.92-4.11 (m, 5H, H-5, H-6, H-6', H-1', H-3'), 4.20 (d, 1H,  $J$  = 12.5 Hz, H-5'), 5.37 (t, 1H,  $J$  = 14 Hz, H-4'), 6.24 (d, 1H,  $J$  = 4 Hz, H-1'), 6.29 (dd, 2H,  $J$  = 22.5 Hz, H-a', H-a''), 6.82-6.84 (m, 2H, H-f', H-f''), 7.02-7.10 (m, 4H, H-g', H-g''), 7.63 (dd, 2H,  $J$  = 30 Hz, H-b', H-b''); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  19.1, 23.1, 23.9, 25.4 (4 x (CH<sub>3</sub>)<sub>2</sub>C), 56.2, 60.6 (4 x OCH<sub>3</sub>), 62.1 (C-6), 62.5 (C-5), 70.7 (C-3), 71.6 (C-2), 71.7 (C-4), 77.4 (C-1'), 82.8 (C-5'), 91.8 (C-1), 100.0, 101.9 (2 x (C-2')), 109.8, 110.0, 111.2, 111.5 (C-c', C-c'', C-f', C-f''), 115.8 (C-a', C-a''), 122.9 (C-g', C-g''), 127.3, 127.6 (C-i', C-i''), 145.1, 146.4 (C-b', C-b''), 149.4, 149.9 (C-e', C-e''), 151.3, 151.6 (C-d', C-d''), 166.4, 167.2 (C-j', C-j''); HRMS (ESI positive mode): found  $m/z$  825.2903 [M+Na]<sup>+</sup>, calcd. 825.2946 for C<sub>40</sub>H<sub>50</sub>O<sub>17</sub>Na.



### Synthesis of 3,4'-di-O-(3,4,5-trimethoxycinnamoyl)-2,1'-di-O-isopropylidene sucrose, 3,4'-triOMe **44**

To a stirred solution of compound **32** (100 mg, 0.09 mmol) and Pd(OAc)<sub>2</sub> (1.7 mg, 0.0074 mmol) was added NEt<sub>3</sub> (1.7  $\mu$ L, 0.0118 mmol) and Et<sub>3</sub>SiH (19  $\mu$ L, 0.118 mmol) at room temperature and the mixture was left to stir for 12 hours. The reaction mixture was then diluted with EtOAc (10.0 ml), washed with water (2 x 10 mL) and the organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent evaporated. The crude product obtained was re-dissolved in pyridine (1.0 ml). NEt<sub>3</sub> (25  $\mu$ L, 0.18 mmol) and 1.56 M 3HF·NEt<sub>3</sub> (173  $\mu$ L, 0.27 mmol) were added to the solution which was left to stir for 12 hours at room temperature. Upon reaction completion (TLC), pyridine was evaporated under reduced pressure and the crude product was subjected to purification using 3:2 EtOAc/Hexane as eluent. 3,4'-triOMe **44** was obtained as white solid in (24 mg, 31% yield).

**Analytical data for 3,4'-triOMe **44**:** mp 121-123 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): isopropylidene rings:  $\delta$  1.29-1.45 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>C); methoxy and sucrose unit:  $\delta$  3.84-3.86 (m, 18H, 9 x H-h'), 3.48-3.52 (m, 1H, H-1'), 3.67-3.77 (m, 4H, H-2, H-4, H-6, H-6'), 3.93-4.11 (m, 5H, H-5, H-6, H-6', H-1', H-3'), 4.21 (d, 1H,  $J$  = 12.5 Hz, H-5'), 5.40 (t, 1H,  $J$  = 14 Hz, H-4'), 6.24 (d, 1H,  $J$  = 4 Hz, H-1'), 6.33 (dd, 2H,  $J$  = 28.5 Hz, H-a', H-a''), 6.74-6.75 (m, 4H, H-c', H-c'', H-g', H-g''), 7.60 (dd, 2H,  $J$  = 30 Hz, H-b', H-b''); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  19.2, 24.3, 25.5, 29.2 (4 x (CH<sub>3</sub>)<sub>2</sub>C), 56.4, 61.2 (6 x OCH<sub>3</sub>), 62.1 (C-6), 62.5 (C-5), 70.8 (C-3), 71.6 (C-2), 71.7 (C-4), 77.4 (C-4'), 78.4 (C-3'), 82.8 (C-5'), 91.9 (C-1), 100.1, 102.0 (2 x (CH<sub>3</sub>)<sub>2</sub>C), 103.9 (C-2'), 105.5,

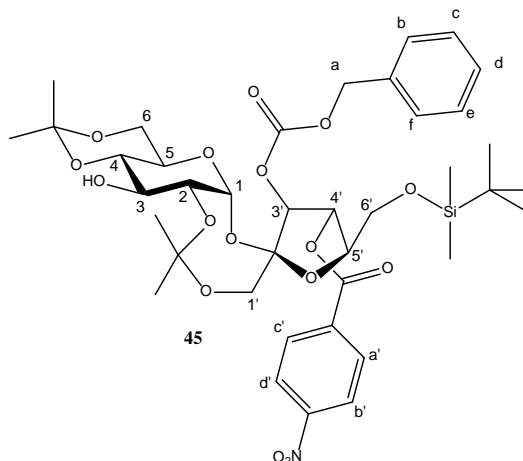


NMR (300 MHz, CDCl<sub>3</sub>): isopropylidene rings:  $\delta$  1.29-1.45 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>C); methoxy and sucrose unit:  $\delta$  3.84-3.86 (m, 18H, 9 x H-h'), 3.48-3.52 (m, 1H, H-1'), 3.67-3.77 (m, 4H, H-2, H-4, H-6, H-6'), 3.93-4.11 (m, 5H, H-5, H-6, H-6', H-1', H-3'), 4.21 (d, 1H,  $J$  = 12.5 Hz, H-5'), 5.40 (t, 1H,  $J$  = 14 Hz, H-4'), 6.24 (d, 1H,  $J$  = 4 Hz, H-1'), 6.33 (dd, 2H,  $J$  = 28.5 Hz, H-a', H-a''), 6.74-6.75 (m, 4H, H-c', H-c'', H-g', H-g''), 7.60 (dd, 2H,  $J$  = 30 Hz, H-b', H-b''); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  19.2, 24.3, 25.5, 29.2 (4 x (CH<sub>3</sub>)<sub>2</sub>C), 56.4, 61.2 (6 x OCH<sub>3</sub>), 62.1 (C-6), 62.5 (C-5), 70.8 (C-3), 71.6 (C-2), 71.7 (C-4), 77.4 (C-4'), 78.4 (C-3'), 82.8 (C-5'), 91.9 (C-1), 100.1, 102.0 (2 x (CH<sub>3</sub>)<sub>2</sub>C), 103.9 (C-2'), 105.5,

C-g', C-g''), 116.4, 117.3 (C-a', C-a''), 129.0, 129.8 (C-i', C-i''), 140.4, 140.6 (C-e', C-e''), 146.5 (C-b', C-b''), 153.7 (C-d', C-d'', C-f', C-f''), 166.2, 167.0 (C-j', C-j''); HRMS (ESI positive mode): found  $m/z$  863.3331  $[M+H]^+$ , calcd. 863.3338 for  $C_{42}H_{55}O_{19}$ .

### Synthesis of 4'-O-para-nitrobenzoyl-3'-O-carboxybenzyl-6'-O-tert-butyldimethylsiloxy-2,1'-di-O-isopropylidene sucrose, 4'-O-PNB 45

The synthesis of 4'-O-PNB was accomplished according to the literature procedure.<sup>3</sup> 3'-O-Cbz 26 (500 mg, 0.746 mmol) and DMAP (9.1 mg, 0.0746 mmol) were dissolved in  $CH_2Cl_2$  (15 mL) and stirred at 4 °C in an ice bath. Subsequently,  $NEt_3$  (312  $\mu L$ , 2.24 mmol) followed by dropwise addition of a solution of PNBCl (208 mg,  $CH_2Cl_2$  (5 mL). The reaction was left to stir for 12 hours. The reaction mixture was evaporated, and the crude product was purified using column chromatography using Hexane/EtOAc (4:1) as eluent (428 mg, 70% yield) was obtained as white solid. The  $^1H$  NMR data of 4'-O-PNB 45 confirmed to the literature data.<sup>3</sup>

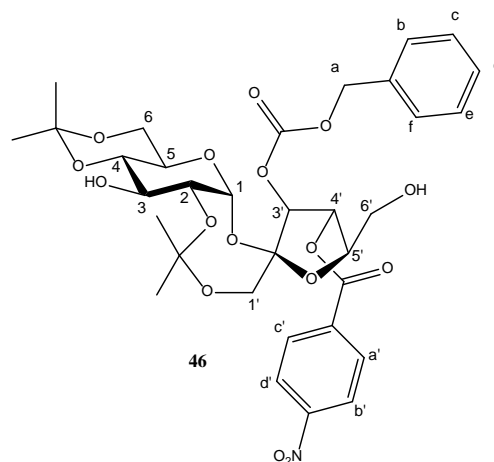


and stirred at 4 °C in an ice bath. Subsequently,  $NEt_3$  (312  $\mu L$ , 2.24 mmol) followed by dropwise addition of a solution of PNBCl (208 mg,  $CH_2Cl_2$  (5 mL). The reaction was left to stir for 12 hours. The reaction mixture was evaporated, and the crude product was purified using column chromatography using Hexane/EtOAc (4:1) as eluent (428 mg, 70% yield) was obtained as white solid. The  $^1H$  NMR data of 4'-O-PNB 45 confirmed to the literature data.<sup>3</sup>

### Synthesis of 3'-O-carboxybenzyl-4'-O-para-nitrobenzoyl - isopropylidene sucrose, 3'-O -Cbz-4'-O-PNB 46

To a stirred solution of 4'-O-PNB 45 (1.00 g, 1.22 mmol) in  $CH_2Cl_2$  (15 mL) was added  $NEt_3$  (339  $\mu L$ , 2.44 mmol) and 1.56 M  $NEt_3$  (2.35 mL, 3.66 mmol) and the reaction was left to stir for 12 hours at room temperature (TLC). Pyridine was removed, and the crude product was subjected to column chromatography purification using EtOAc/Hexane (3:2) as the eluent. 3'-O -Cbz-4'-O-PNB 46 (740 mg, 86% yield) was obtained as white solid.

**Analytical data for 3'-O -Cbz-4'-O-PNB 46:**  $^1H$  NMR (300 MHz,  $CDCl_3$ ): isopropylidene rings:  $\delta$  1.36-1.55 (m, 12H, 2 x  $(CH_3)_2C$ ); sucrose unit:  $\delta$  3.15 (dd, 1H,  $J$  = 15 Hz), 3.54-3.88 (m, 9H), 4.13 (d, 1H,  $J$  = 12.5 Hz), 4.26-4.27 (m, 1H), 5.17-5.19 (m, 1H, H-3'), 5.88 (t, 1H,  $J$  = 12 Hz, 1H,  $J$  = 3.5 Hz, H-1); Cbz group:  $\delta$  5.17-5.19 (m, 2H), 7.30-7.36 (m, 2H); PNB group:  $\delta$  8.20 (dd, 4H,  $J$  = 49 Hz);  $^{13}C$  NMR (75.5 MHz,  $CDCl_3$ ):  $\delta$  25.6, 29.2, 62.0, 64.3, 66.7, 70.1, 70.7, 72.8, 73.7, 76.1, 80.3, 83.1, 91.7, 103.7, 123.9, 128.5, 128.9, 131.2, 134.6, 134.8, 150.1, 151.1, 154.8, 19.3, 24.3, 100.1, 102.3, 164.1.



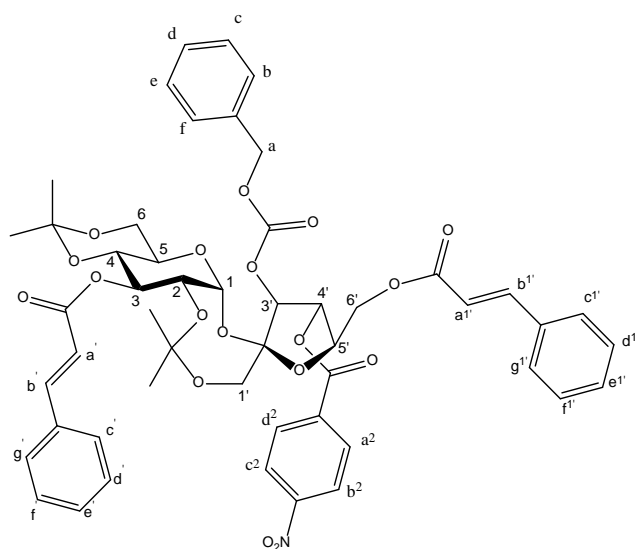
#### 1.2.5.3 General procedure for acylation of 3'-O-Cbz-4'-O-PNB 46

A stirred solution of 3'-O-Cbz-4'-O-PNB 46 (150 mg, 0.218 mmol) (3 mg, 0.02 mmol) in  $CH_2Cl_2$  (15 mL) was heated under reflux for 10 minutes. The (substituted) cinnamic acid (0.872 mmol) and EDC (167 mg, 0.872 mmol) were then added to the refluxing solution which was left under reflux for 2 weeks (TLC). The reaction mixture was then washed with distilled water (3 x 10 mL), the organic phase separated, dried over anhydrous  $MgSO_4$  and the solvent evaporated under vacuum. The crude product was purified using column chromatography using Hexane/EtOAc (8:1) as the eluent. The general procedure was used to prepare compounds 47, 48, 49, 50, 51, 52 and 53. Along with these compounds, a by-product was always obtained, and its analytical data were not recorded.

### Synthesis of 3,6'-di-O-cinnamoyl - 3'-O-carboxybenzyl-4'-O-para-nitrobenzoyl -2,1'-di-O-isopropylidene sucrose 47

Following the general procedure, reaction using cinnamic acid (129 mg, 0.872 mmol) gave compound 47 (135 mg, 64% yield) and a by-product (40 mg, 22% yield) as white solids.

**Analytical data for compound 47:** mp 98-101°C; MHz, MeOD): isopropylidene rings:  $\delta$  1.24-1.45 ( $(\text{CH}_3)_2\text{C}$ ); Cbz and sucrose unit:  $\delta$  3.53-4.52 (m, 1H,  $J = 4$  Hz, H-3'), 5.34 (m, 3H, H-3, 2 x H-a), 5.62 (H-4'), 6.16 (d, 1H,  $J = 4$  Hz, H-1); Cbz and cinnamic and alkenyl protons:  $\delta$  6.41 (dd, 2H,  $J = 32$  7.30-7.52 (m, 15H, H-b, H-c, H-d, H-e, H-f, H-c', H-H-e', H-e', H-f', H-f', H-g', H-g'), 7.65 (dd, 2H,  $J = b'$ ); PNB group:  $\delta$  8.18 (dd, 4H,  $J = 24$  Hz, H-a<sup>2</sup>, H-13C NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.2, 24.1, 25.7, 64.5, 65.0, 66.6, 71.0, 71.2, 71.8, 72.1, 79.4, 79.9, 80.5, 101.8, 105.1, 105.2, 117.6, 118.3, 123.9, 128.3, 128.8, 129.1, 130.5, 130.6, 131.2, 134.3, 134.4, 134.5, 134.7, 145.5, 147.8, 151.0, 154.6, 163.8, 166.0, 166.1, 166.5.



47

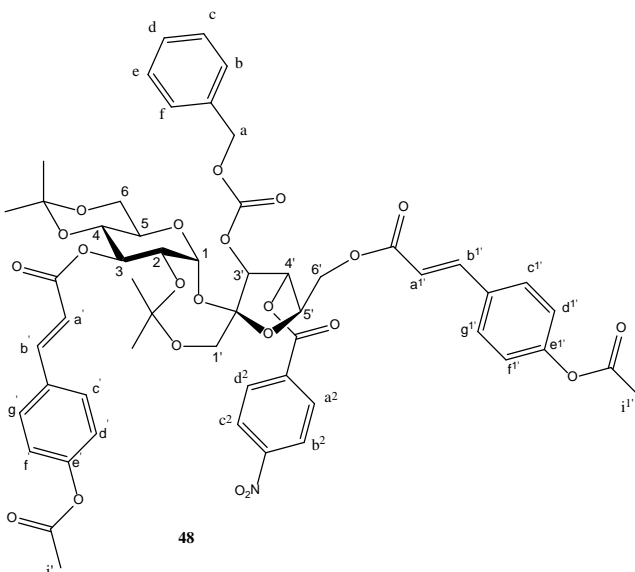
<sup>1</sup>H NMR (300 (m, 12H, 2 x 11H), 5.08 (d, (t, 1H,  $J = 8$  Hz, namoyl aro-Hz, H-a', H-a'), c', H-d', H-d', 15 Hz, H-b', H-b', H-c', H-d'); 29.0, 29.2, 62.3, 81.0, 92.1, 99.9, 128.9, 129.0, 135.0, 145.0,

O-  
O-

### Synthesis of 3,6'-di-O-(4-acetoxycinnamoyl) -3'-carboxybenzyl-4'-O-para-nitrobenzoyl -2,1'-di-isopropylidene sucrose 48

Following the general procedure, reaction using OAc-coum acid (177 mg, 0.872 mmol) gave compound 48 (184 mg, 78% yield) and a by-product (29 mg, 15% yield) as white solids.

**Analytical data for compound 48:** <sup>1</sup>H NMR (300 d6): isopropylidene rings:  $\delta$  1.22-1.49 (m, 12H, 2 x coumaroyl acetoxy & methoxy, Cbz and sucrose (m, 6H, 3 x H-i', 3 x H-i'), 3.64-4.50 (m, 7H), 4.25-4.45-4.50 (m, 1H), 4.52-4.62 (m, 1H), 4.70 (m, 1H), 2 x H-a), 5.37 (d, 1H,  $J = 4$  Hz, H-3'), 5.44 (t, 1H,  $J = 5.77$  (t, 1H,  $J = 7.5$  Hz, H-4'), 6.20 (d, 1H,  $J = 4$  Hz, OAc-coumaroyl aromatic and alkenyl protons:  $\delta$  H-a', H-a'), 7.16-7.50 (m, 9H, H-b, H-c, H-d, H-e, H-f, H-f'), 7.68-7.87 (m, 6H, H-c', H-c', H-g', H-PNB group:  $\delta$  8.35 (dd, 4H,  $J = 26$  Hz, H-a<sup>2</sup>, H-b<sup>2</sup>, NMR (75.5 MHz, Acetone-d<sub>6</sub>):  $\delta$  11.3, 14.3, 19.4, 24.2, 24.3, 24.5, 25.7, 39.7, 55.0, 62.6, 65.2, 65.4, 67.1, 72.4, 80.6, 80.7, 81.8, 92.8, 100.3, 102.2, 118.6, 117.9, 123.2, 123.4, 129.3, 129.4, 129.5, 129.6, 130.2, 130.3, 132.7, 132.8, 132.9, 133.0, 133.5, 136.3, 136.4, 144.5, 153.5, 153.9, 155.1, 164.8, 165.4, 166.3, 166.8, 165.4, 168.0, 169.5, 170.1.



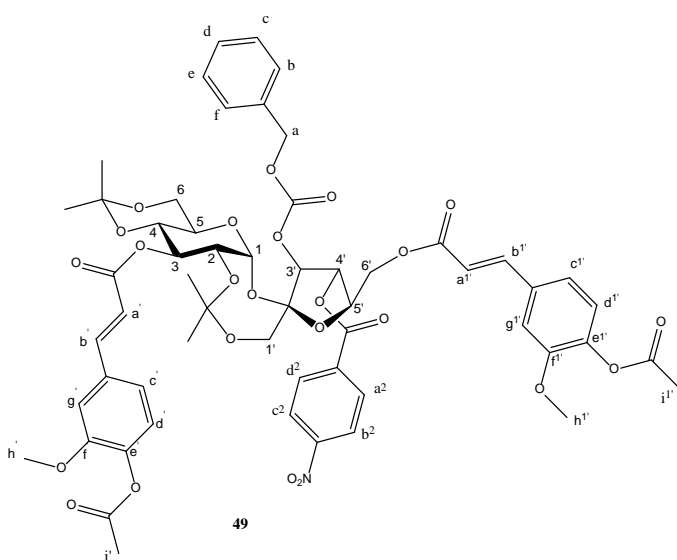
48

MHz, Acetone-( $\text{CH}_3$ )<sub>2</sub>C); OAc-unit:  $\delta$  2.28-2.29 4.32 (m, 1H), 5.29-5.33 (m, 2H, 18.5 Hz, H-3), H-1); Cbz and 6.49-6.59 (m, 2H, H-f, H-d', H-d' g', H-b', H-b'; H-c', H-d'); <sup>13</sup>C 20.9, 21.0, 23.7, 71.2, 71.3, 71.8, 118.6, 119.2, 130.6, 132.0, 144.8, 146.6, 166.3, 166.8,

### Synthesis of 3,6'-di-O-(4-acetoxy-3-ycinnamoyl) -3'-O-carboxybenzyl-4'-O-para-2,1'-di-O-isopropylidene sucrose 49

Following the general procedure, reaction acid (177 mg, 0.872 mmol) gave compound 49 yield) and a by-product (28 mg, 14% yield) as

**Analytical data for compound 49:** <sup>1</sup>H NMR tone-d6): isopropylidene rings:  $\delta$  1.23-1.49 (m, ( $\text{CH}_3$ )<sub>2</sub>C); Cbz, OAc-feru acetoxy, methoxy unit:  $\delta$  2.26-2.27 (m, 6H, 3 x H-i', 3 x Hi'), 3 x H-h', 3 x H-h'), 3.65-4.07 (m, 4H), 4.29-4.33, 4.50 (m, 1H), 4.56-4.62 (m, 1H), 4.68-4.72 (m,



49

methox-  
nitrobenzoyl -

using OAc-feru (149 mg, 60% white solids.

(300 MHz, Ace-12H, 2 x and sucrose 3.89-3.91 (m, 6H, (m, 1H), 4.43-1H), 5.32 (d, 1H,



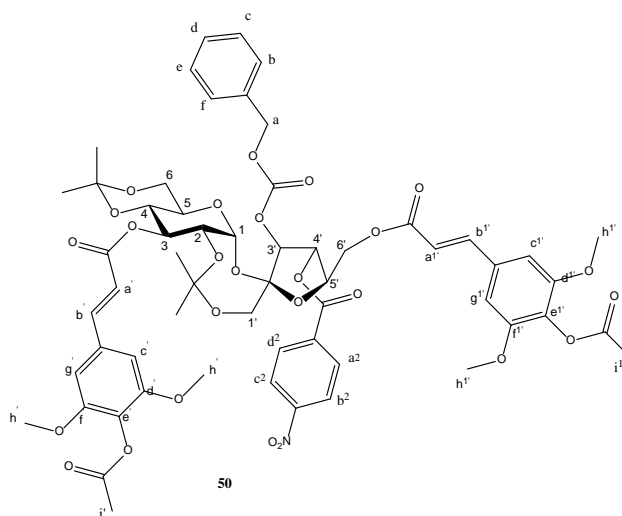
$J = 4$  Hz, H-3'), 5.37- 5.38 (m, 2H, Cbz, 2 x H-a), 5.45 (t, 1H,  $J = 18.5$  Hz, H-3), 5.75 (t, 1H,  $J = 7.5$  Hz, H-4'), 6.20 (d, 1H,  $J = 4$  Hz, H-1); Cbz and OAc- Feru aromatic and alkenyl protons:  $\delta$  6.58 (dd, 2H,  $J = 24.5$  Hz, H-a', H-a''), 7.08-7.13 (m, 2H, H-d', H-d''), 7.20-7.39 (m, 5H, H-b, H-c, H-d, H-e, H-f), 7.45-7.53 (m, 4H, H-c', H-c'', H-g', H-g''), 7.68 (dd, 2H,  $J = 22.5$  Hz, H-b', H-b''); PNB group:  $\delta$  8.34 (dd, 4H,  $J = 26.5$  Hz, H-a<sup>2</sup>, H-b<sup>2</sup>, H-c<sup>2</sup>, H-d<sup>2</sup>); <sup>13</sup>C NMR (75.5 MHz, Acetone-d<sub>6</sub>):  $\delta$  18.5, 19.6, 23.4, 24.8, 55.5, 61.7, 64.3, 64.5, 66.3, 70.4, 70.8, 71.6, 71.8, 79.0, 79.9, 80.9, 91.9, 99.4, 101.3, 105.4, 111.5, 111.7, 117.8, 118.3, 121.5, 123.3, 123.4, 123.6, 128.4, 128.5, 128.6, 128.7, 131.1, 133.3, 134.8, 135.5, 141.8, 144.0, 144.3, 150.9, 151.9, 154.2, 163.9, 165.5, 166.0, 168.0.

### Synthesis of 3,6'-di-O-(4-acetoxy-3,5-dimethoxycinnamoyl) -3'-O-carboxybenzyl-4'-O-para-nitrobenzoyl -2,1'-di-O-isopropylidene sucrose 50

Following the general procedure, reaction using OAc-sinap acid (232 mg, 0.872 mmol) gave compound **50** (173 mg, 66% yield) and a by-product (27 mg, 13% yield) as yellow solids.

#### Analytical data for compound 50: isopropylidene

1.48 (m, 12H, 2 x (CH<sub>3</sub>)<sub>2</sub>C)); OAc-sinap acetoxy, sucrose unit:  $\delta$  2.26 (m, 6H, 3 x H-I', 3 x H-i'), 3.64-3.89 (m, 12H, 6 x H-h', 6 x H-h''), 4.29-4.71 (m, 5H), Hz, H-3') 5.38 (s, 2H, Cbz, 2 x H-a), 5.46 (t, 1H,  $J = 5.74$  (t, 1H,  $J = 8$  Hz, H-4'), 6.20 (d, 1H,  $J = 3.5$  Hz, and alkenyl protons:  $\delta$  6.61 (dd, 2H,  $J = 23.5$  Hz, H-4H,  $J = 16$  Hz, H-c', H-c''), H-g', H-g''), 7.35-7.53 (m, d, H-e, H-f), 7.79 (d, 2H,  $J = 16$  Hz, H-b', H-b''); 8.34 (dd, 4H,  $J = 28$  Hz, H-a<sup>2</sup>, H-b<sup>2</sup>, H-c<sup>2</sup>, H-d<sup>2</sup>); <sup>13</sup>C CDCl<sub>3</sub>): 19.9, 20.7, 21.3, 24.7, 26.2, 29.5, 29.8, 30.1, 57.1, 57.2, 61.0, 65.7, 71.8, 73.0, 80.4, 82.3, 100.8, 106.6, 107.0, 118.5, 119.2, 119.7, 125.0, 129.8, 129.9, 132.7, 133.5, 134.0, 134.1, 136.2, 136.9, 146.2, 149.6, 163.9, 165.3, 166.9, 168.8.



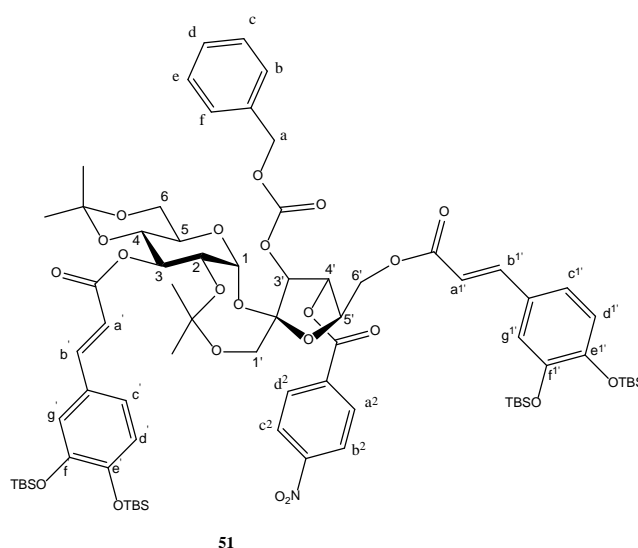
rings:  $\delta$  1.17-methoxy and 3.78 (m, 4H), 5.32 (d, 1H,  $J = 4$  18.5 Hz, H-3), H-1); aromatic a', H-a''), 7.10 (d, 5H, H-b, H-c, H-PNB group:  $\delta$  NMR (75.5 MHz, 30.3, 30.6, 30.8, 102.7, 106.4, 130.0, 132.4, 154.1, 154.2,

### Synthesis of 3,6'-di-O-(3,4-di-tert-butyldimethylsiloxycinnamoyl) -3'-O-carboxybenzyl-4'-O-para-nitrobenzoyl -2,1'-di-O-isopropylidene sucrose, 3,6'-TBS -caff 51

Following the general procedure, reaction using OTBS-caff acid (227 mg, 0.872 mmol) gave compound **51** (198 mg, 61% yield) and a by-product (84 mg, 35% yield) as white solids.

#### Analytical data for compound 51: TBS group: $\delta$

0.98 (m, 36H); isopropylidene rings:  $\delta$  1.20-1.46 (CH<sub>3</sub>)<sub>2</sub>C); sucrose unit:  $\delta$  3.62-4.67 (m, 12H), Hz, H-3'), 5.35 (m, 2H, 2 x H-a), 5.44 (t, 1H,  $J =$  (t, 1H,  $J = 7.5$  Hz, H-4'), 6.18 (d, 1H,  $J = 3.5$  Hz, H-alkenyl protons: 4H, H-a', H-a''), 6.87-6.94 (m, 5H, H-d', H-d''), H-c', H-c'', H-g', H-g''), 7.21-7.74 (m, 13H, H-b, f, H-b', H-b''); PNB group:  $\delta$  8.31 (dd, 4H,  $J = 25$  H-c<sup>2</sup>, H-d<sup>2</sup>); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  -5.32, 10.4, 13.5, 17.5, 17.8, 18.5, 22.8, 23.5, 23.8, 30.4, 66.2, 67.4, 70.3, 71.9, 79.2, 79.9, 80.9, 91.8, 99.5, 115.5, 116.1, 117.7, 118.8, 119.8, 120.6, 120.9, 121.4, 131.1, 132.6, 134.8, 135.5, 144.8, 147.1, 149.2, 151.0, 166.3, 167.2.

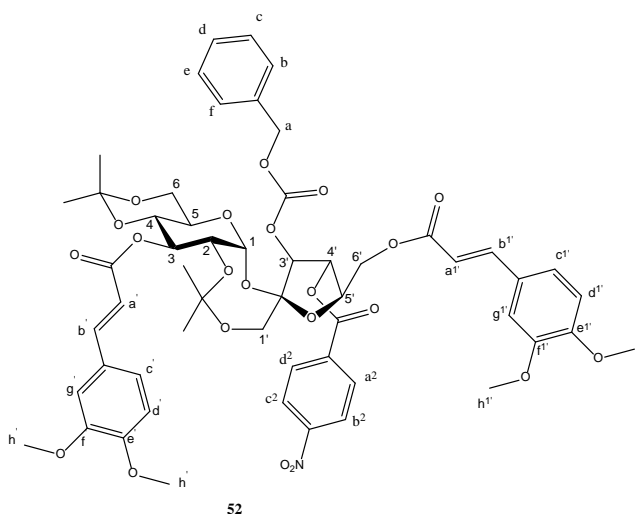


0.22 (m, 24H), (m, 12H, 2 x 5.28 (d, 1H,  $J = 4$  19 Hz, H-3), 5.73 1); aromatic and  $\delta$  6.27-6.38 (m, 7.10-7.19 (m, 9H, H-c, H-d, H-e, H-Hz, H-a<sup>2</sup>, H-b<sup>2</sup>, -4.81, -3.92, 0.63, 38.8, 61.7, 64.4, 101.4, 105.3, 115.0, 122.2, 122.7, 123.6, 154.2, 163.8, 165.7,

### Synthesis of 3,6'-di-O-(3,4-dimethoxycinnamoyl) -3'-O-carboxybenzyl-4'-O-para-nitrobenzoyl -2,1'-di-O-isopropylidene sucrose 52

Following the general procedure, reaction using diOMe acid (181 mg, 0.872 mmol) gave compound **52** (187 mg, 79% yield) and by-product (37 mg, 19% yield) as white solids.

**Analytical data for compound 52:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): isopropylidene rings:  $\delta$  1.23-1.46 (m, 12H, 2 x diOMe methoxy and sucrose unit:  $\delta$  3.89 (m, 13H, 6 x H-h'), 3.54-3.73 (m, 4H), 4.00-4.51 (m, 4H), 5.10 (d, 1H, H-3'), 5.27-5.43 (m, 3H, H-3, 2 x H-a), 5.63 (t, 1H,  $J$  = 7 6.17 (d, 1H,  $J$  = 4 Hz, H-1); aromatic and alkenyl protons:  $\delta$  6.23-6.40 (m, 4H, H-a', H-a''), 6.80-7.17 (m, 12H, H-d', H-c', H-g', H-g''), 7.30-7.47 (m, 5H, H-b, H-c, H-d, H-e, 7.80 (m, 4H, H-b', H-b''); PNB group:  $\delta$  8.19 (dd, 4H,  $J$  H-a<sup>2</sup>, H-b<sup>2</sup>, H-c<sup>2</sup>, H-d<sup>2</sup>);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  29.3, 56.1, 56.2, 56.3, 71.2, 99.9, 101.8, 105.2, 110.1, 111.3, 122.9, 123.8, 127.0, 128.8, 128.9, 131.2, 135.1, 148.7, 149.6, 163.1, 163.9

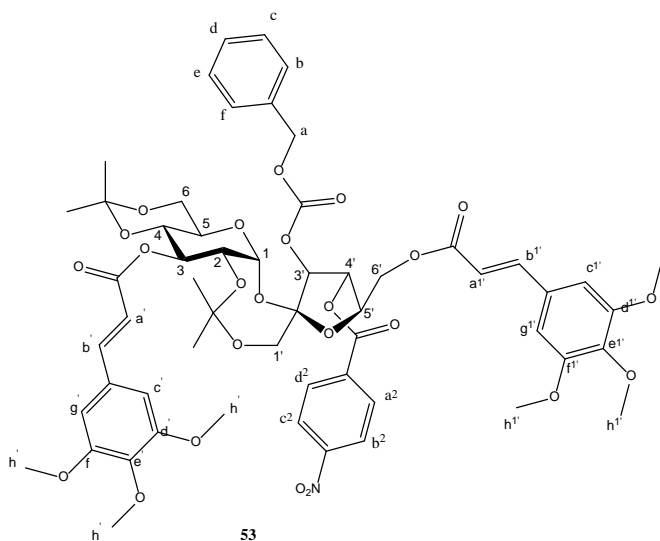


$\text{CDCl}_3$ :  
( $\text{CH}_3$ )<sub>2</sub>C);  
H-h', 6 x  
 $J$  = 4 Hz,  
Hz, H-4'),  
tons:  $\delta$   
H-d', H-c',  
H-f), 7.55-  
= 43 Hz,  
19.3, 25.7,  
114.6,  
152.2,

#### Synthesis of 3,6'-di-O-(3,4,5-trimethoxycinnamoyl) - carboxybenzyl-4'-O-para-nitrobenzoyl -2,1'-di-O-isopropylidene sucrose **53**

Following the general procedure, reaction using triOMe acid (208 mg, 0.872 mmol) gave compound **53** (167 mg, 67% yield) and a by-product (12 mg, 6% yield) as white solids.

**Analytical data for compound 53:**  $^1\text{H}$  NMR (300  $\text{CDCl}_3$ ): isopropylidene rings:  $\delta$  1.26-1.46 (m, 12H, 2 ( $\text{CH}_3$ )<sub>2</sub>C); triOMe methoxy and sucrose unit:  $\delta$  3.85-26H, 9 x H-h', 9 x H-h''), 3.54-3.76 (m, 4H), 3.90-4.50 5.09 (d, 1H,  $J$  = 4 Hz, H-3'), 5.27-5.42 (m, 3H, H-3, 2 x (t, 1H,  $J$  = 7 Hz, H-4'), 6.17 (d, 1H,  $J$  = 4 Hz, H-1); aromatic and alkenyl protons:  $\delta$  6.28-6.43 (m, 3H, H-b', H-b''), (m, 6H H-c', H-c'', H-g', H-g''), 7.28-7.47, (m, 5H, H-b, H-e, H-f), 7.53-7.77 (m, 3H, H-b', H-b''); PNB group: 4H,  $J$  = 43 Hz, H-a<sup>2</sup>, H-b<sup>2</sup>, H-c<sup>2</sup>, H-d<sup>2</sup>);  $^{13}\text{C}$  NMR (75.5  $\text{CDCl}_3$ ):  $\delta$  19.3, 24.1, 25.7, 29.3, 56.4, 61.2, 64.5, 71.2, 80.5, 81.0, 92.1, 99.9, 101.9, 105.2, 105.5, 106.0, 116.0, 117.5, 123.9, 128.8, 128.9, 129.3, 130.0, 131.2, 134.4, 140.4, 145.5, 148.9, 151.1, 153.6, 153.7, 154.6, 162.7, 166.1, 166.4.



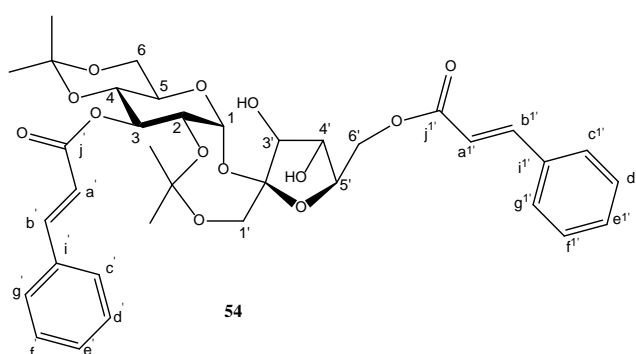
MHz,  
x  
3.88 (m,  
(m, 6H),  
H-a), 5.61  
omatic  
6.69-6.77  
H-c, H-d,  
 $\delta$  8.19 (dd,  
MHz,  
72.1, 79.3,  
116.9,  
135.0,  
163.9,

#### 1.2.5.4 General procedure for the deprotection of PNB, Cbz and acetal groups

To a stirred solution of each of the compounds **47**, **48**, **49**, **50**, **51**, **52**, or **53** in of methanol: THF (1 ml, 9:1) was added  $\text{Mg}(\text{OMe})_2$ . The reaction mixtures were left to stir for 12 hours (TLC) then quenched with 1N HCl. The solvent was evaporated, and the slurries obtained were then dissolved in  $\text{CH}_2\text{Cl}_2$  (15 mL) and washed with water (2 x 10 mL). The organic layer was separated, dried over anhydrous  $\text{MgSO}_4$ , filtered and the solvent evaporated under reduced pressure. Purification using silica gel column chromatography using Hex:EtOAc (1:1) as the eluent gave the desired compounds 3,6'-cinn **54**, 3,6'-coum **55**, 3,6'-feru **56**, 3,6'-diOMe **59**, 3,6'-triOMe **60**, 3,6'-OAc-sinap **61** and 3,6'-OTBS-caff **62**.

#### Synthesis of 3,6'-di-O-cinnamoyl-2,1'-di-O-sucrose, 3,6'-cinn **54**

Following the general procedure, compound **47** (mmol) completely reacted with  $\text{Mg}(\text{OMe})_2$  (158 before quenching the reaction with 1N HCl (104 The product compound **54** (60 mg, 85 % yield)



isopropylidene  
(100 mg, 0.104  
 $\mu\text{L}$ , 0.052 mmol)  
 $\mu\text{L}$ , 0.104 mmol).  
was obtained as

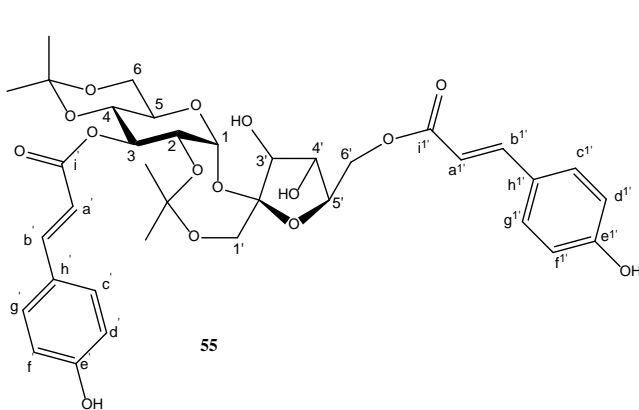
white solid.

**Analytical data for 3,6'-cinn 54:** mp 108-110 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): isopropylidene rings:  $\delta$  1.27-1.45 (m, 12H,  $2 \times (\text{CH}_3)_2\text{C}$ ); sucrose unit:  $\delta$  3.48-3.52 (m, 1H, H-5), 3.71-3.96 (m, 7H,  $2 \times \text{H-1'}$ , H-2, H-4,  $2 \times \text{H-6}$ , H-3'), 4.15-4.34 (m, 3H, H-4', H-5', H-6'), 4.46-4.47 (m, 1H, H-6'), 5.39 (t, 1H,  $J = 19$  Hz, H-3), 6.16 (d, 1H,  $J = 4$  Hz, H-1); aromatic and alkenyl protons:  $\delta$  6.43 (dd, 2H,  $J = 26.5$  Hz, H-a', H-a''), 7.34-7.37 (m, 6H, H-e', H-e''), H-d', H-d'', H-f', H-f''), 7.48-7.53 (m, 4H, H-c', H-c''), H-g', H-g''), 7.68 (dd, 2H,  $J = 22$  Hz, H-b', H-b'');  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.2, 24.3, 25.5, 29.2 ( $4 \times (\text{CH}_3)_2\text{C}$ ), 62.4 (C-6), 64.3 (C-5), 65.9 (C-6'), 66.3 (C-1'), 71.2 (C-3), 71.9 (C-4), 72.0 (C-2), 78.7 (C-4'), 79.9 (C-3'), 80.1 (C-5'), 91.5 (C-1), 100.1, 101.8 ( $2 \times (\text{CH}_3)_2\text{C}$ ), 104.2 (C-2'), 117.9, 118.1 (C-a', C-a''), 128.4, 129.1 (C-c', C-c''), C-g', C-g''), C-d', C-d'', C-f', C-f''), 130.6 (C-e', C-e''), 134.6 (C-h', C-h''), 145.4, 145.5 (C-b', C-b''), 166.6, 167.1 (C-i', C-i''); HRMS (ESI positive mode): found  $m/z$  705.2502  $[\text{M}+\text{Na}]^+$ , calcd. 705.2523 for  $\text{C}_{36}\text{H}_{42}\text{O}_{13}\text{Na}$ .

#### Synthesis of 3,6'-di-O-coumaroyl-2,1'-di-O-isopropylidene sucrose, 3,6'-coum 55

Following the general procedure, compound **48** (100 mg, 0.092 mmol) completely reacted with  $\text{Mg}(\text{OMe})_2$  (140  $\mu\text{L}$ , 0.046 mmol) before quenching the reaction with 1N HCl (92  $\mu\text{L}$ , 0.092 mmol). The product compound **55** (22 mg, 33% yield) was obtained as white solid.

**Analytical data for 3,6'-coum 55:** mp 159-161 °C; isopropylidene rings:  $\delta$  1.16-1.38 (m, 12H,  $2 \times (\text{CH}_3)_2\text{C}$ ); sucrose unit:  $\delta$  3.32-3.37 (m, 1H, H-5), 3.62-3.99 (m, 7H,  $2 \times \text{H-1'}$ , H-2, H-3'), 4.05-4.19 (m, 3H, H-4', H-5', H-6'), 4.32-4.36 (m, 5.34 (t, 1H,  $J = 19$  Hz, H-3), 6.02 (d, 1H,  $J = 4$  Hz, H-1); alkenyl protons:  $\delta$  6.24 (dd, 2H,  $J = 27$  Hz, H-a', H-a''), = 9 Hz, H-d', H-d'', H-f', H-f''), 7.36 (d, 4H,  $J = 8.5$  Hz, H-g', H-g''), 7.52 (dd, 2H,  $J = 29$  Hz, H-b', H-b'');  $^{13}\text{C}$  NMR (75.5 MHz, MeOD):  $\delta$  21.1, 24.5, 25.4, 29.6 ( $4 \times (\text{CH}_3)_2\text{C}$ ), 64.9 (C-5), 65.0 (C-6'), 67.1 (C-1'), 67.7 (C-3), 72.6 (C-78.1 (C-4'), 80.2 (C-3'), 81.4 (C-5'), 92.6 (C-1), 101.1, ( $\text{CH}_3)_2\text{C}$ ), 105.5 (C-2'), 115.1 (C-a', C-a''), 115.4, 117.0 C-f', C-f''), 127.3 (C-h', C-h''), 131.3, 131.4 (C-c', C-c''), C-g', C-g''), 146.8, 146.9 (C-b', C-b''), 161.5 (C-e', C-e''), 168.9, 169.1 (C-i', C-i''); HRMS (ESI positive mode): found  $m/z$  737.2454  $[\text{M}+\text{Na}]^+$ , calcd. 737.2421 for  $\text{C}_{36}\text{H}_{42}\text{O}_{15}\text{Na}$ .

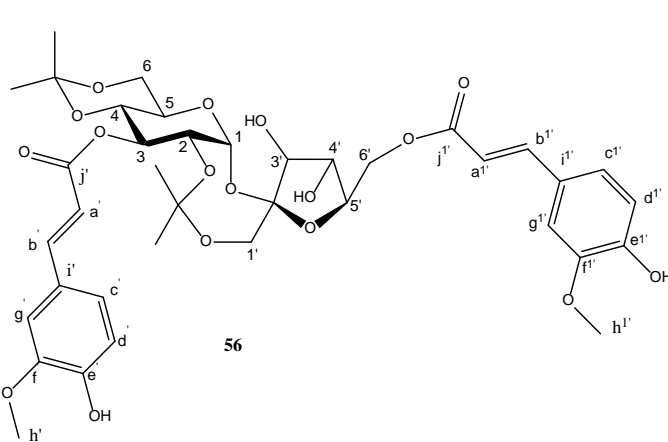


isopropylidene rings:  $\delta$  1.16-1.38 (m, 12H,  $2 \times (\text{CH}_3)_2\text{C}$ ); sucrose unit:  $\delta$  3.32-3.37 (m, 1H, H-5), 3.62-3.99 (m, 7H,  $2 \times \text{H-1'}$ , H-2, H-3'), 4.05-4.19 (m, 3H, H-4', H-5', H-6'), 4.32-4.36 (m, 5.34 (t, 1H,  $J = 19$  Hz, H-3), 6.02 (d, 1H,  $J = 4$  Hz, H-1); alkenyl protons:  $\delta$  6.24 (dd, 2H,  $J = 27$  Hz, H-a', H-a''), = 9 Hz, H-d', H-d'', H-f', H-f''), 7.36 (d, 4H,  $J = 8.5$  Hz, H-g', H-g''), 7.52 (dd, 2H,  $J = 29$  Hz, H-b', H-b'');  $^{13}\text{C}$  NMR (75.5 MHz, MeOD):  $\delta$  21.1, 24.5, 25.4, 29.6 ( $4 \times (\text{CH}_3)_2\text{C}$ ), 64.9 (C-5), 65.0 (C-6'), 67.1 (C-1'), 67.7 (C-3), 72.6 (C-78.1 (C-4'), 80.2 (C-3'), 81.4 (C-5'), 92.6 (C-1), 101.1, ( $\text{CH}_3)_2\text{C}$ ), 105.5 (C-2'), 115.1 (C-a', C-a''), 115.4, 117.0 C-f', C-f''), 127.3 (C-h', C-h''), 131.3, 131.4 (C-c', C-c''), C-g', C-g''), 146.8, 146.9 (C-b', C-b''), 161.5 (C-e', C-e''), 168.9, 169.1 (C-i', C-i''); HRMS (ESI positive mode): found  $m/z$  737.2454  $[\text{M}+\text{Na}]^+$ , calcd. 737.2421 for  $\text{C}_{36}\text{H}_{42}\text{O}_{15}\text{Na}$ .

#### Synthesis of 3,6'-di-O-feruloyl-2,1'-di-O-isopropylidene sucrose, 3,6'-feru 56

Following the general procedure, compound **49** (100 mg, 0.088 mmol) completely reacted with  $\text{Mg}(\text{OMe})_2$  (134  $\mu\text{L}$ , 0.044 mmol) before quenching the reaction with 1N HCl (88  $\mu\text{L}$ , 0.088 mmol). The product compound **56** (14 mg, 21% yield) was obtained as white solid.

**Analytical data for 3,6'-feru 56:** mp 140-142 °C;  $^1\text{H}$  NMR (300 MHz, Acetone- $d_6$ ): isopropylidene rings: 12H,  $2 \times (\text{CH}_3)_2\text{C}$ ); methoxy and sucrose unit: 6H,  $3 \times \text{H-h'}$ ,  $3 \times \text{H-h''}$ , 3.43-3.48 (m, 1H, H-5),  $2 \times \text{H-1'}$ , H-2, H-4,  $2 \times \text{H-6}$ , H-3'), 4.47-4.50 (m, H-6'), 4.72-4.77 (m, 1H, H-6') 5.31 (t, 1H,  $J =$  (d, 1H,  $J = 4$  Hz, H-1'); aromatic and alkenyl (dd, 2H,  $J = 30$  Hz, H-a', H-a''), 6.98 (dd, 2H,  $J$  H-d''), 7.20 (dd, 2H,  $J = 15$  Hz, H-c', H-c''), 14 Hz, H-g', H-g''), 7.61 (dd, 2H,  $J = 25$  Hz, H-NMR (75.5 MHz, Acetone- $d_6$ ):  $\delta$  19.3, 20.8, ( $\text{CH}_3)_2\text{C}$ ), 55.0, 56.4 ( $2 \times \text{OCH}_3$ ), 62.8 (C-6), 64.2 67.2 (C-1'), 71.5 (C-3), 72.7 (C-2), 72.9 (C-4), (C-3'), 81.1 (C-5'), 92.0 (C-1), 100.1, 101.9 ( $2 \times (\text{CH}_3)_2\text{C}$ ), 105.1 (C-2'), 111.2 (C-g', C-g''), 115.7 (C-a', C-a''), 116.0, 116.1 (C-d', C-d''), 124.0, 124.2 (C-c', C-c''), 127.5 (C-i', C-i''), 145.6, 145.9 (C-b', C-b''), 148.8 (C-f', C-f''), 150.1, 150.2 (C-e', C-e''), 166.7, 167.4 (C-j', C-j''); HRMS (ESI positive mode): found  $m/z$  797.2598  $[\text{M}+\text{Na}]^+$ , calcd. 797.2633 for  $\text{C}_{38}\text{H}_{46}\text{O}_{17}\text{Na}$ .



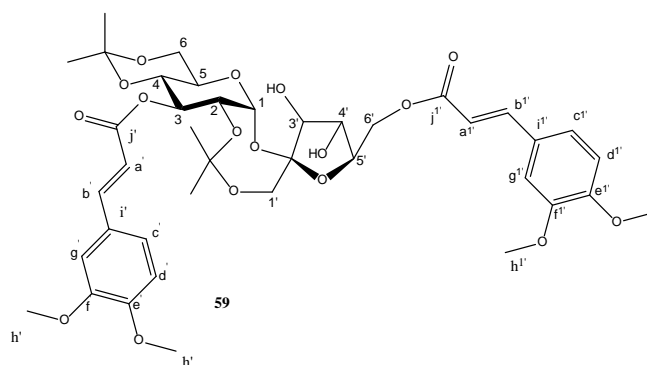
°C;  $^1\text{H}$  NMR  $\delta$  1.24-1.46 (m,  $\delta$  3.93-3.94 (m, 3.65-4.28 (m, 7H, 3H, H-4', H-5', 19 Hz, H-3), 6.10 protons:  $\delta$  6.44 = 10.5 Hz, H-d', 7.35 (d, 2H,  $J =$  b', H-b'') ;  $^{13}\text{C}$  20.9, 24.5 ( $4 \times$  (C-5), 66.8 (C-6'), 78.1 (C-4'), 80.4

#### Synthesis of 3,6'-di-O-(3,4-dimethoxycinnamoyl)-2,1'-di-O-isopropylidene sucrose, 3,6'-diOMe 59

Following the general procedure, compound **52** (100 mg, 0.092 mmol) completely reacted with  $\text{Mg}(\text{OMe})_2$  (140  $\mu\text{L}$ , 0.046 mmol) before quenching the reaction with 1N HCl (92  $\mu\text{L}$ , 0.092 mmol). The product compound **59** (66 mg, 90% yield) was obtained as white solid.

**Analytical data for 3,6'-diOMe 59:** mp 132-134

(300 MHz, Acetone- $d_6$ ): isopropylidene rings:  $\delta$  12H, 2 x  $(\text{CH}_3)_2\text{C}$ ; methoxy and sucrose unit:  $\delta$  12H, 6 x H-h', 6 x H-h<sup>1'</sup>, 3.48-3.51 (m, 1H, H-5), 2 x H-1', H-2, H-4, 2 x H-6, H-3'), 4.18-4.32 (m, H-6'), 4.48-4.52 (m, 1H, H-6'), 5.40 (t, 1H,  $J$  = 6.16 (d, 1H,  $J$  = 4 Hz, H-1'); aromatic and alkenyl (dd, 2H,  $J$  = 30 Hz, H-a', H-a<sup>1'</sup>) 6.81 (dd, 2H,  $J$  = d<sup>1'</sup>), 7.02 (dd, 2H,  $J$  = 18 Hz, H-c', H-c<sup>1'</sup>), 7.07 (d, g', H-g'), 7.60 (dd, 2H,  $J$  = 24 Hz, H-b', H-b<sup>1'</sup>); MHz, Acetone- $d_6$ ):  $\delta$  19.3, 24.5, 25.6, 26.2 (4 x 56.2 (4 x OCH<sub>3</sub>), 62.8 (C-6), 64.2 (C-5), 66.8 (C-6'), (C-3), 72.7 (C-2), 72.9 (C-4), 78.0 (C-4'), 80.4 (C-3'), 81.1 (C-5'), 92.0 (C-1), 100.1, 101.9 (2 x  $(\text{CH}_3)_2\text{C}$ ), 105.1 (C-2'), 111.0, 112.3 (C-c', C-c<sup>1'</sup>, C-f', C-f<sup>1'</sup>), 116.3, 116.6 (C-a', C-a<sup>1'</sup>), 123.7, 123.8 (C-g', C-g<sup>1'</sup>), 128.3 (C-i', C-i<sup>1'</sup>), 145.4, 145.7 (C-b', C-b<sup>1'</sup>), 150.7 (C-e', C-e<sup>1'</sup>), 152.6 (C-d', C-d<sup>1'</sup>), 166.6, 167.4 (C-j', C-j<sup>1'</sup>); HRMS (ESI positive mode): found  $m/z$  803.3154 [M+H]<sup>+</sup>, calcd.803.3126 for C<sub>40</sub>H<sub>51</sub>O<sub>17</sub>.



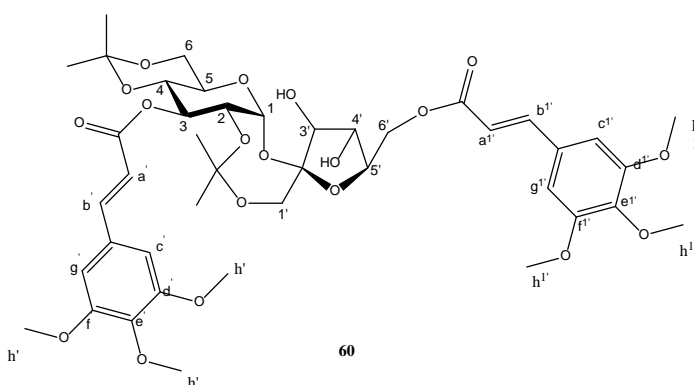
$^{\circ}\text{C}$ ;  $^1\text{H}$  NMR 1.27-1.44 (m, 3.87-3.88 (m, 3.70-4.18 (m, 7H, 3H, H-4', H-5', 18.5 Hz, H-3), protons:  $\delta$  6.29 11 Hz, H-d', H-2H,  $J$  = 16 Hz, H- $^{13}\text{C}$  NMR (75.5 (CH<sub>3</sub>)<sub>2</sub>C), 56.1, 67.2 (C-1'), 71.6

**Synthesis of 3,6'-di-O-(3,4,5-trimethoxycinnamoyl)-2,1'-di-O-isopropylidene sucrose, 3,6'-triOMe 60**

Following the general procedure, compound **53** (100 mg, 0.087 mmol) completely reacted with  $\text{Mg}(\text{OMe})_2$  (134  $\mu\text{L}$ , 0.044 mmol) before quenching the reaction with 1N HCl (87  $\mu\text{L}$ , 0.087 mmol). The product compound **60** (47 mg, 63% yield) was obtained as white solid.

**Analytical data for 3,6'-triOMe 60:** mp 125-

(300 MHz, CDCl<sub>3</sub>): isopropylidene rings:  $\delta$  12H, 2 x  $(\text{CH}_3)_2\text{C}$ ; methoxy and sucrose unit: 18H, 9 x H-h', 9 x H-h<sup>1'</sup>, 3.49- 3.53 (m, 1H, H-7H, 2 x H-1', H-2, H-4, 2 x H-6, H-3'), 4.17-4', H-5', H-6'), 4.50-4.54 (m, 1H, H-6') 5.34 (t, H-3), 6.17 (d, 1H,  $J$  = 4 Hz, H-1'); aromatic protons:  $\delta$  6.35 (dd, 2H,  $J$  = 31 Hz, H-a', H-a<sup>1'</sup>), 6 Hz, H-c', H-c<sup>1'</sup> H-g', H-g<sup>1'</sup>), 7.58 (dd, 2H,  $J$  = b<sup>1'</sup>);  $^{13}\text{C}$  NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  19.2, 21.3, (CH<sub>3</sub>)<sub>2</sub>C), 56.4, 60.6 (6 x OCH<sub>3</sub>), 61.2 (C-6, C-1'), 71.3 (C-3), 71.8 (C-4), 72.0 (C-2), 77.4 (C-80.3 (C-5'), 91.5 (C-1), 100.1, 101.8 (2 x (C-2'), 105.5, 105.6 (C-c', C-c<sup>1'</sup>, C-g', C-g<sup>1'</sup>), a<sup>1'</sup>), 130.0, 130.1 (C-i', C-i<sup>1'</sup>), 140.4, 140.5 (C-(C-b', C-b<sup>1'</sup>), 153.6, 153.7 (C-d', C-d<sup>1'</sup>, C-f', 167.0 (C-j', C-j<sup>1'</sup>); HRMS (ESI positive mode): 885.3162 [M+Na]<sup>+</sup>, calcd.885.3157 for

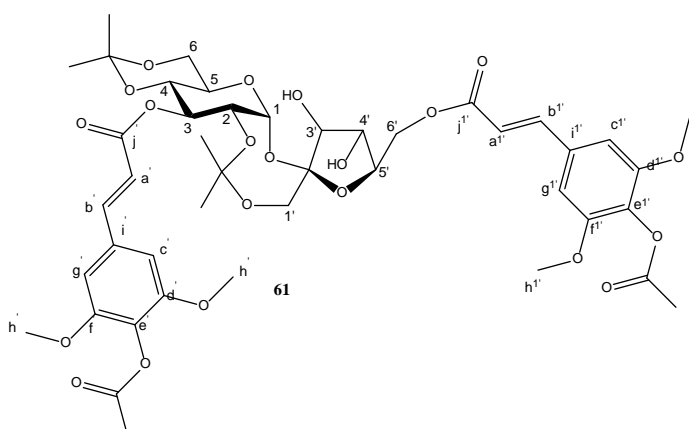


127  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR 1.23-1.45 (m,  $\delta$  3.85-3.89 (m, 5), 3.71-4.11 (m, 4.52 (m, 3H, H-1H,  $J$  = 19 Hz, and alkenyl 6.74 (d, 4H,  $J$  = 19 Hz, H-b', H-24.3, 25.5 (4 x 5), 66.0 (C-6', C-4'), 79.9 (C-3'), (CH<sub>3</sub>)<sub>2</sub>C), 104.3 117.2 (C-a', C-e', C-e<sup>1'</sup>), 145.4 C-f<sup>1'</sup>), 166.9, found  $m/z$  C<sub>42</sub>H<sub>54</sub>O<sub>19</sub>Na.

**Synthesis of 3,6'-di-O-acetoxy-sinapoyl-isopropylidene sucrose, 3,6'-OAc-sinap 61**

Following the general procedure, compound **50** (100 mg, 0.083 mmol) completely reacted with  $\text{Mg}(\text{OMe})_2$  (128  $\mu\text{L}$ , 0.042 mmol) before quenching the reaction with 1N HCl (83  $\mu\text{L}$ , 0.083 mmol). The product compound **61** (40 mg, 53% yield) was obtained as white solid.

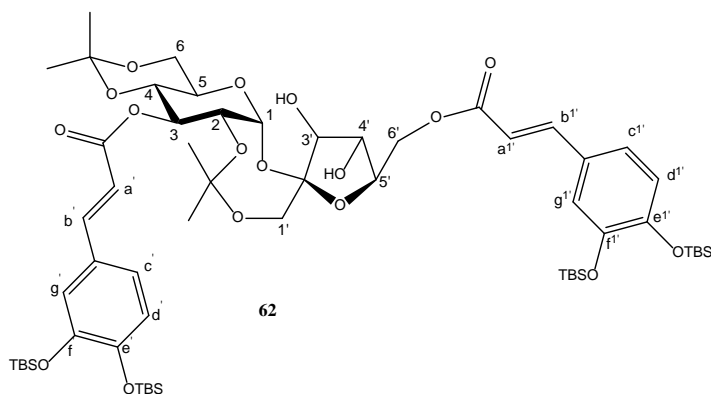
**Analytical data for 3,6'-OAc-sinap 61:** mp 136-138  $^{\circ}\text{C}$ ; isopropylidene rings:  $\delta$  1.25-1.43 (m, 12H, 2 x  $(\text{CH}_3)_2\text{C}$ ); OAc-sinap acetoxy and methoxy sucrose unit:  $\delta$  2.27-2.30 (m, 7H, 3 x H-I', 3 x H-i<sup>1'</sup>), 3.79-3.80 (m, 12H, 6 x H-h', 6 x H-h<sup>1'</sup>), 3.47-4.03 (m, 8H), 4.18-4.54



**2,1'-di-O-**  
pound **50** (100  $\text{Mg}(\text{OMe})_2$  (128 tion with 1N

### Synthesis of 3,6'-di-*O*-(3,4-di-*tert*-butyldimethylsiloxycinnamoyl)-2,1'-di-*O*-isopropylidene sucrose, 3,6'-OTBS-caff 62

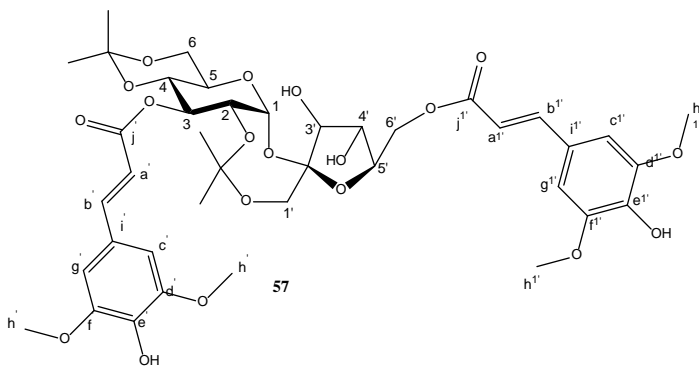
**Analytical data for 3,6'-OTBS-caff 62:**  $^1\text{H}$  CDCl<sub>3</sub>): TBS groups:  $\delta$  0.20 (m, 24H), 0.97, isopropylidene rings:  $\delta$  1.24-1.45 (m, 12H, 2 crose unit:  $\delta$  3.36 (m, 2H), 3.51 (d, 1H,  $J$  = 3.78 (m, 4H), 3.88-3.95 (m, 4H), 4.18- 4.22 4.33 (m, 1H), 4.48 (d, 1H,  $J$  = 11.5 Hz), 5.38 H-3), 6.18 (d, 1H,  $J$  = 4 Hz, H-1'); aromatic protons:  $\delta$  6.26 (dd, 2H,  $J$  = 30 Hz, H-a', H- $J$  = 10 Hz, H-d', H-d'), 6.97-7.04 (m, 4H H-H-g'), 7.57 (dd, 2H,  $J$  = 25.5 Hz, H-b', H- (75.5 MHz, Acetone-d<sub>6</sub>):  $\delta$  -4.8, -4.7, -1.2, 24.6, 25.3, 25.4, 63.3, 63.8, 70.8, 71.8, 79.5, 104.2, 115.9, 120.6, 120.8, 121.3, 122.3, 126.5, 128.5, 144.1, 144.4, 147.1, 149.3, 165.6, 166.4.



NMR (300 MHz, 0.98 (m, 36H); x (CH<sub>3</sub>)<sub>2</sub>C); su- 12.5 Hz), 3.71- (m, 3H), 4.27- (t, 1H, J = 19 Hz, and alkenyl a<sup>1</sup>'), 6.80 (dd, 2H, c', H-c<sup>1</sup>, H-g', b<sup>1</sup>); <sup>13</sup>C NMR 18.2, 18.4, 23.6, 91.1, 99.2, 101.0, 128.0, 128.4,

A mixture of compound **61** (100 mg, 0.108 mmol) and piperidine (42.7  $\mu$ L, 0.432 mmol) in EtOH/THF (1 ml, 5:1) was stirred for 12 hours at room temperature. Upon reaction completion (TLC), the crude mixture was subjected to purification using silica gel column chromatography using EtOAc/Hexane (3:2) using as the eluent. Compound **57** (41 mg, 45 % yield) was obtained as white solid.

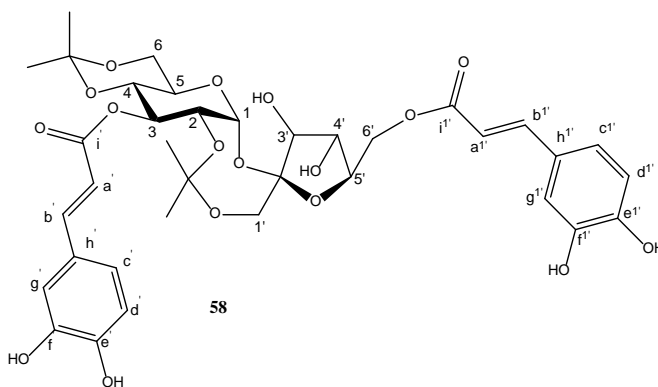
**Analytical data for 3,6'-sinap 57:** mp 136-137 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ isopropylidene 1.43 (m, 12H, 2 × (CH<sub>3</sub>)<sub>2</sub>C); sinapoyl methine unit: δ 3.85-3.86 (m, 14H, 6 × H-h', 6 × H-h''), H-5, 2 × H-1', H-2, H-4, 2 × H-6, H-3'), 3.94-4.04 (m, 2 × H-6'), 5.41 (t, 1H, J = 19 Hz, H-3), 5.42 (t, 1H, J = 19 Hz, H-1'); aromatic and alkenyl protons: δ 6.75 (d, 4H, J = 7.5 Hz, H-a', H-a''), 7.54 (dd, 2H, J = 18 Hz, H-b', H-b''); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 19.7, 24.9, 26.0 (4 × (CH<sub>3</sub>)<sub>2</sub>C), 63.2 (C-6), 64.6 (C-5), 67.2 (C-6'), 67.6 (C-1'), 68.2 (C-2), 73.3 (C-4), 78.4 (C-4'), 80.9 (C-3'), 81.5 (C-3), 116.4, 116.7 (C-a', C-a''), 126.6 (C-i', C-i''), 130.1 (C-j'), 130.2 (C-j''); HRMS (ESI positive mode): found *m/z*



138 °C; <sup>1</sup>H  
rings: δ 1.23-  
oxy and sucrose  
3.32-3.71 (m, 8H,  
4.54 (m, 4H, H-  
6.16 (d, 1H, *J* = 4  
6.27 (dd, 2H, *J* =  
c', H-c1', H-g',  
<sup>13</sup>C NMR (75.5  
57.1 (4 x OCH<sub>3</sub>),  
71.9 (C-3), 73.2

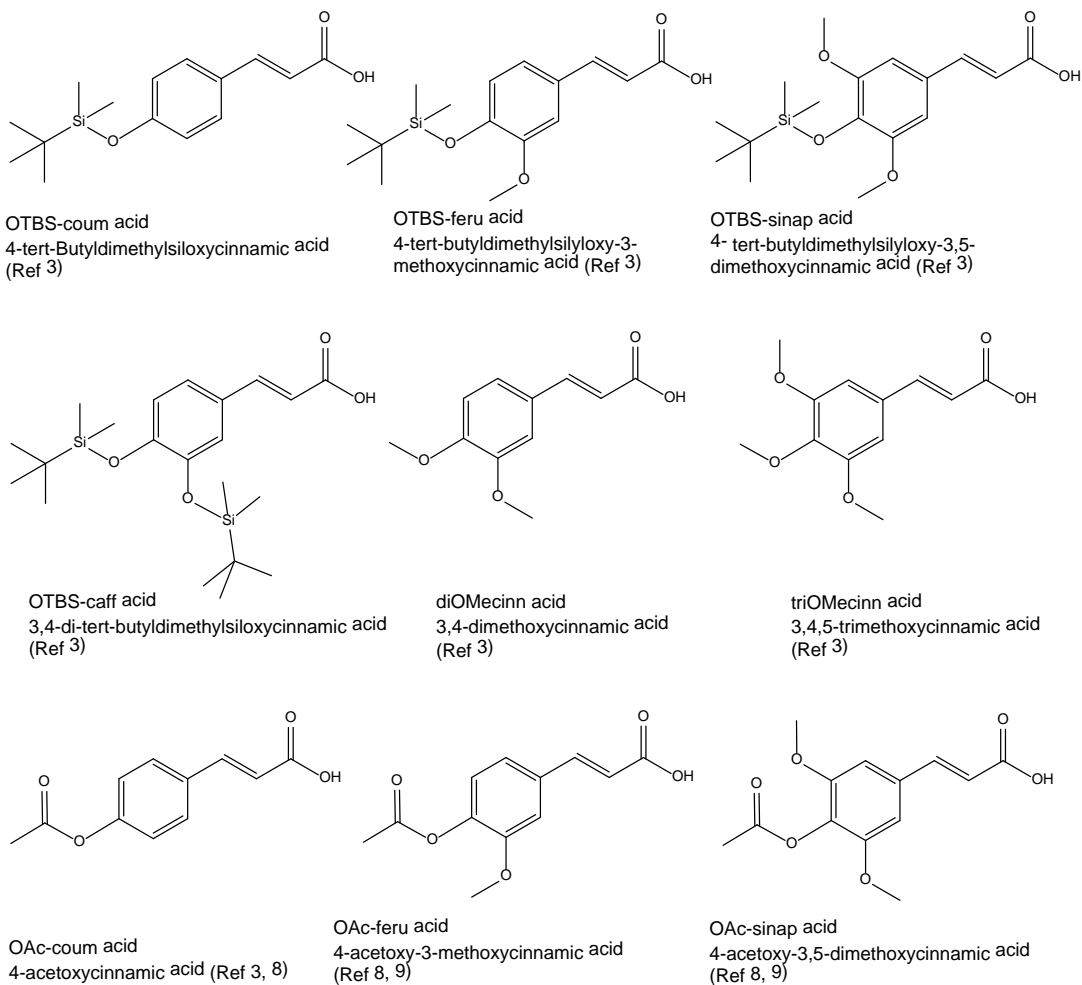
To a stirred solution of 3,6'-OTBS-caff **62** (100 mg, 0.083 mmol) in pyridine (10.0 ml) was added NEt<sub>3</sub> (24  $\mu$ L, 0.17 mmol) and 1.56 M 3HF-NEt<sub>3</sub> (161  $\mu$ L, 0.25 mmol) and the reaction mixture was left to stir for 12 hours at room temperature (TLC). Upon reaction completion, pyridine was removed under reduced pressure and the crude product was then subjected to silica gel column chromatography purification using EtOAc/Hexane (3:2) as the eluent. 3,6'-Caff **58** (58 mg, 94% yield) was obtained as yellow solid.

**Analytical data for 3,6'-caff 58:** mp 110-112 °C; MHz, CDCl<sub>3</sub>): isopropylidene rings:  $\delta$  1.23-1.46 (CH<sub>3</sub>)<sub>2</sub>C; sucrose unit:  $\delta$  3.45-3.49 (m, 1H, H-5), 2 x H-1', H-2, H-4, 2 x H-6, H-3'), 4.05-4.52 (m, x H-6'), 4.72-4.76 (m, 1H, H-6'), 5.30 (t, 1H,  $J$  = (d, 1H,  $J$  = 4 Hz, H-1'); aromatic and alkenyl (dd, 2H,  $J$  = 30 Hz, H-a', H-a'), 6.88 (dd, 2H,  $J$  = d'), 7.06-7.07 (m, 2H, H-c', H-c'), 7.17 (dd, 2H, H-g'), 7.57 (dd, 2H,  $J$  = 26 Hz, H-b', H-b'); <sup>13</sup>C Acetone-d<sub>6</sub>):  $\delta$  18.4, 19.6, 23.6, 24.6 (4 x (C-6), 63.3 (C-5), 65.8 (C-6'), 66.3 (C-1'), 70.7 (C-72.0 (C-2), 77.2 (C-4'), 79.5 (C-3'), 80.2 (C-5'), 101.0 (2 x (CH<sub>3</sub>)<sub>2</sub>C), 104.2 (C-2'), 114.2, 114.3 (C-a', C-a'), 114.6, 115.0 (C-c', C-c', C-f', C-f'), 121.6, 121.7 (C-g', C-g'), 126.8 (C-h', C-h'), 144.9, 145.2, (C-b', C-b'), 145.7, (C-d', C-d'), 148.4, 148.5 (C-e', C-e'), 165.8, 166.5 (C-i', C-i'); HRMS (ESI positive mode): found  $m/z$  769.2323 [M+Na]<sup>+</sup>, calcd. 769.2320 for C<sub>36</sub>H<sub>42</sub>O<sub>17</sub>Na.



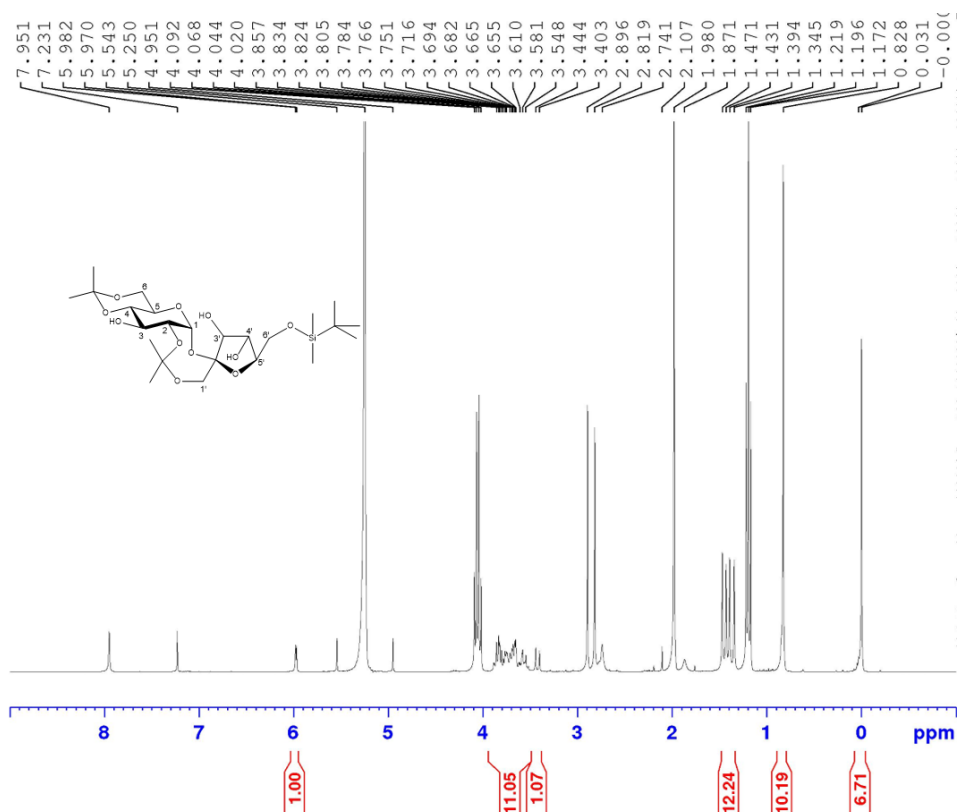
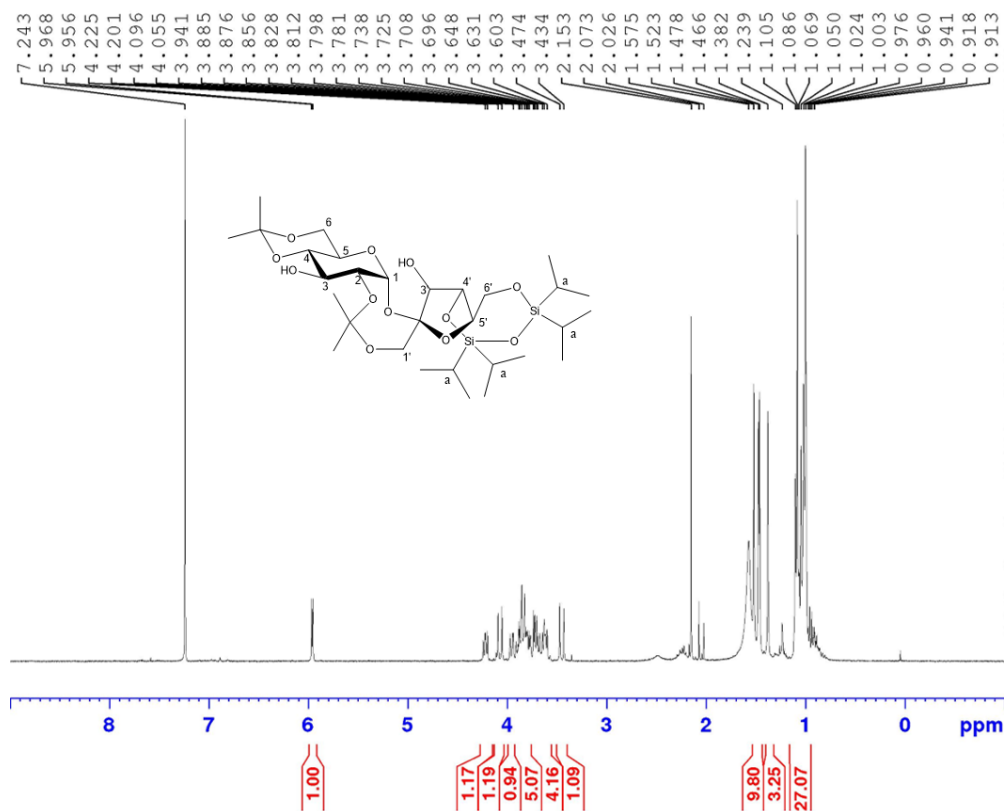
<sup>1</sup>H NMR (300 (m, 12H, 2 x 3.68-3.97 (m, 7H, 3H, H-4', H-5', 2 19 Hz, H-3), 6.11 protons:  $\delta$  6.29 10 Hz, H-d', H-  $J$  = 10 Hz, H-g', NMR (75.5 MHz, (CH<sub>3</sub>)<sub>2</sub>C), 61.9 3), 71.8 (C-4), 91.1 (C-1), 99.2,

The synthesis of the below protected cinnamic acids was accomplished according to the literature as shown in the below figure.



NMR spectra of compounds 3, 25, 26, 45, 11-17, 33-38, 18-24, 23, 43, and 59

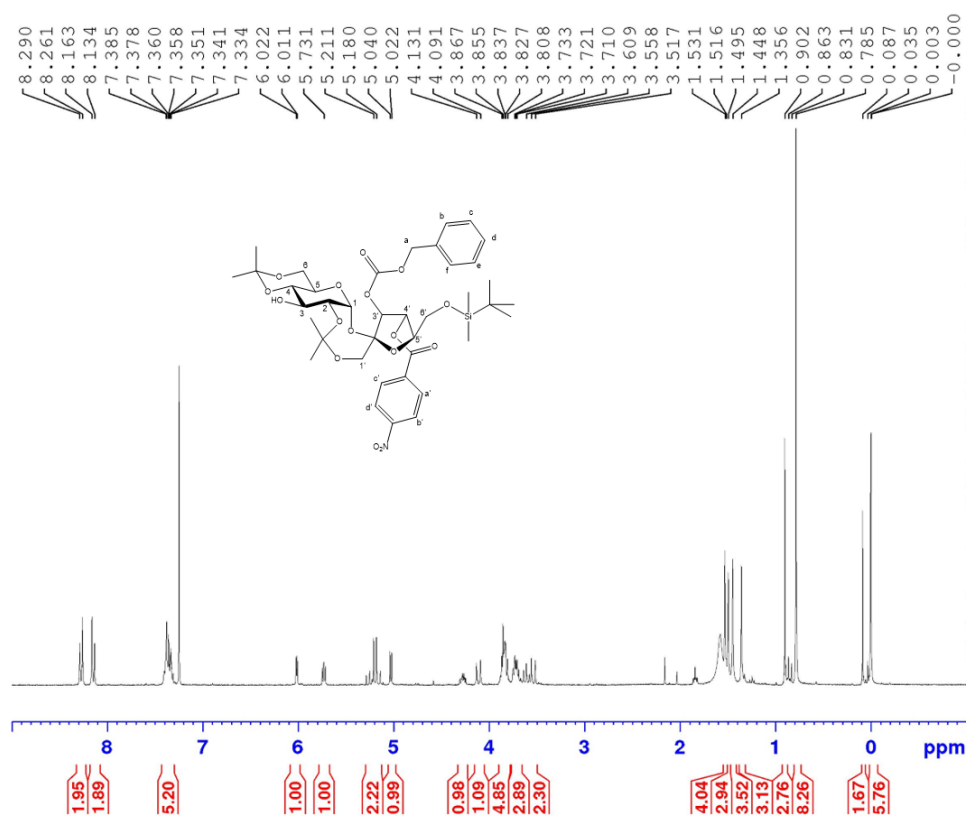
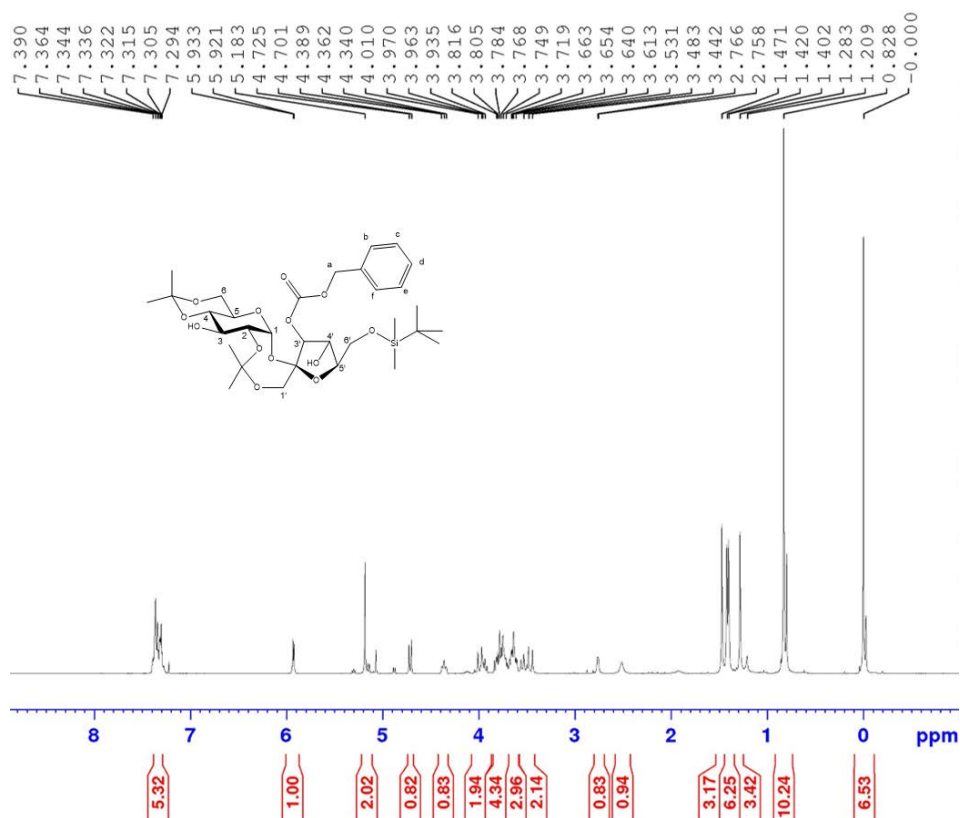
Spectra of compound 3



Spectra of compound 25

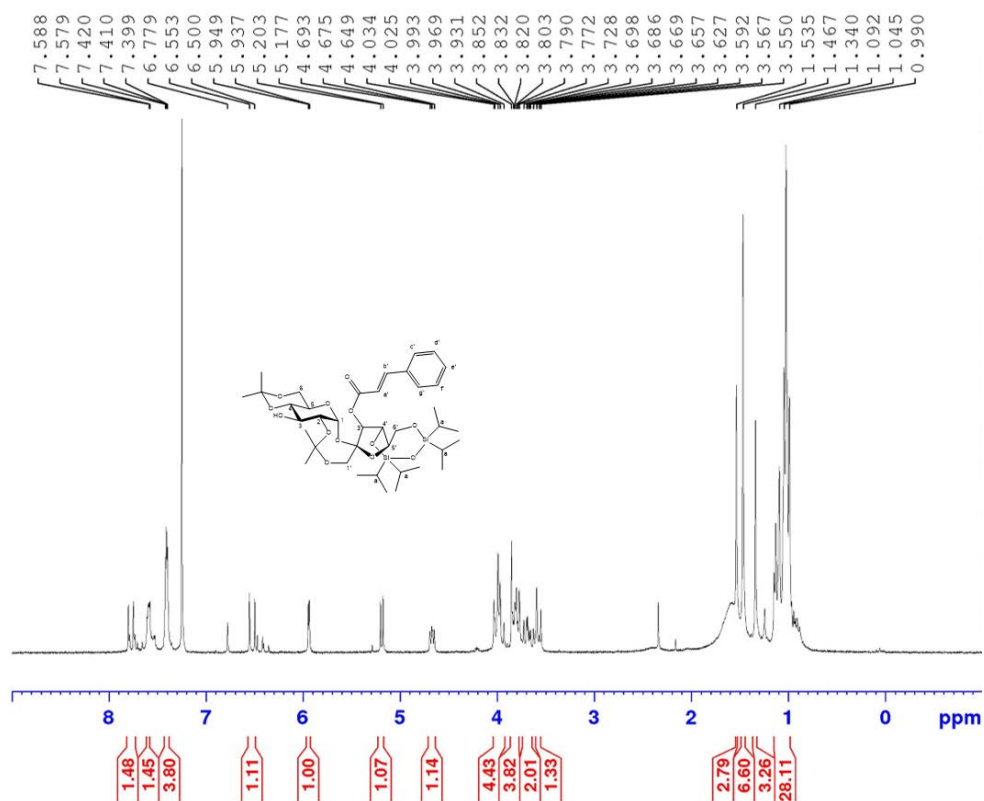
Spectra of compound 26



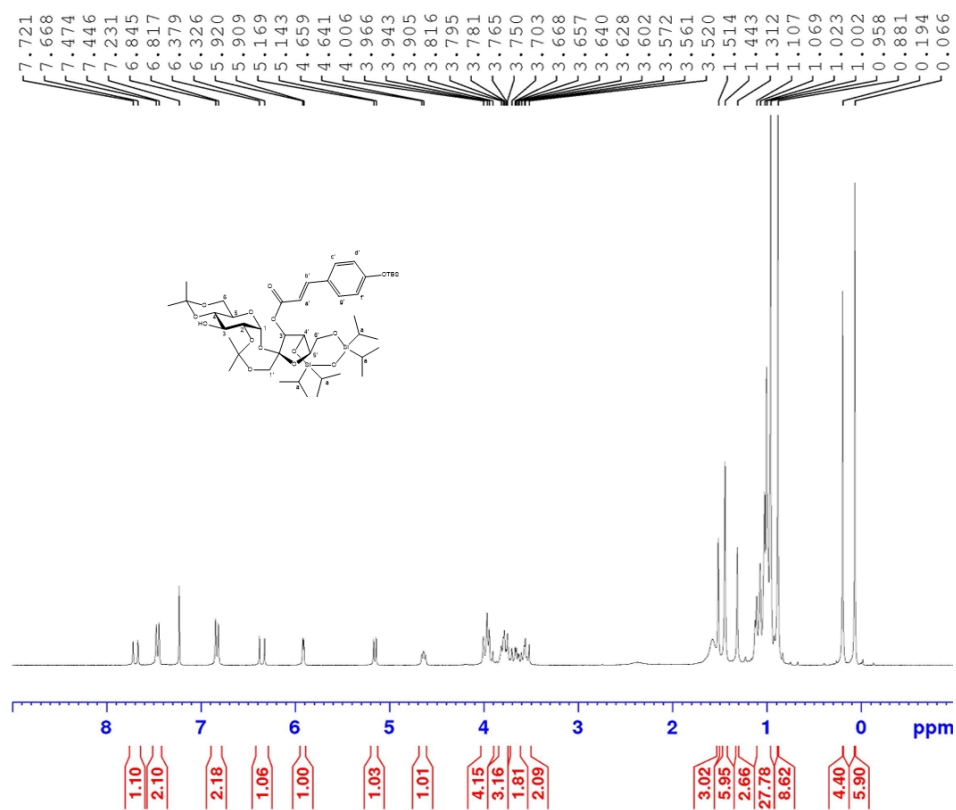


Spectra of compound 45

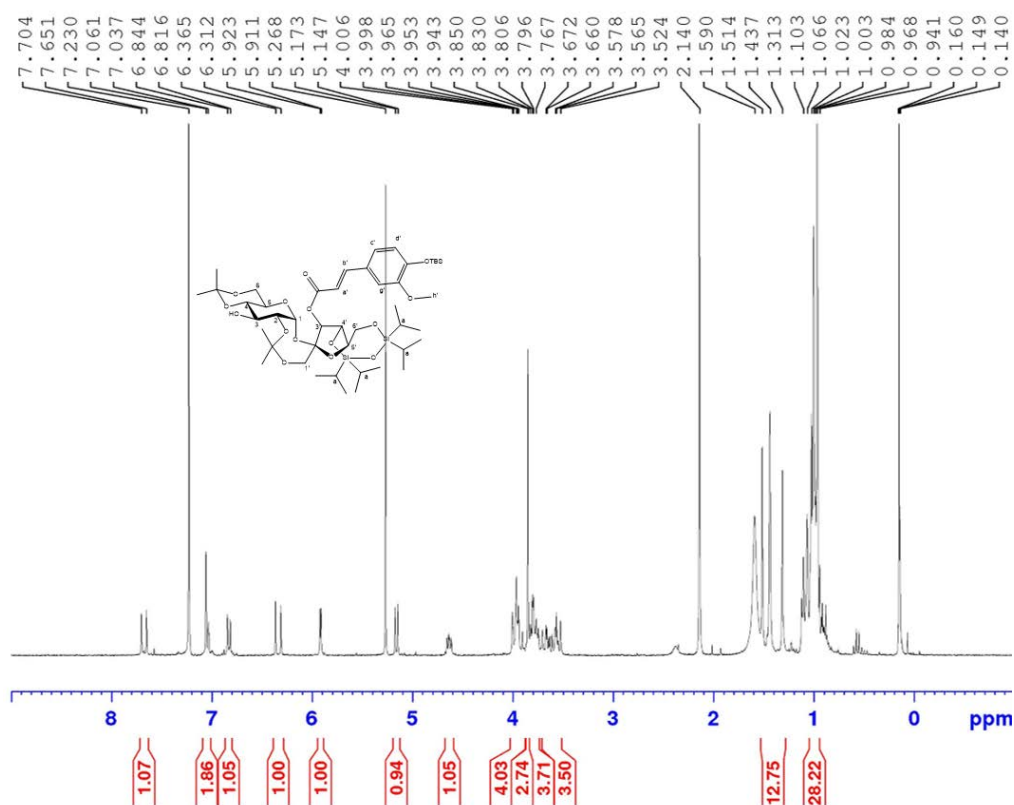
Spectra of compound 11



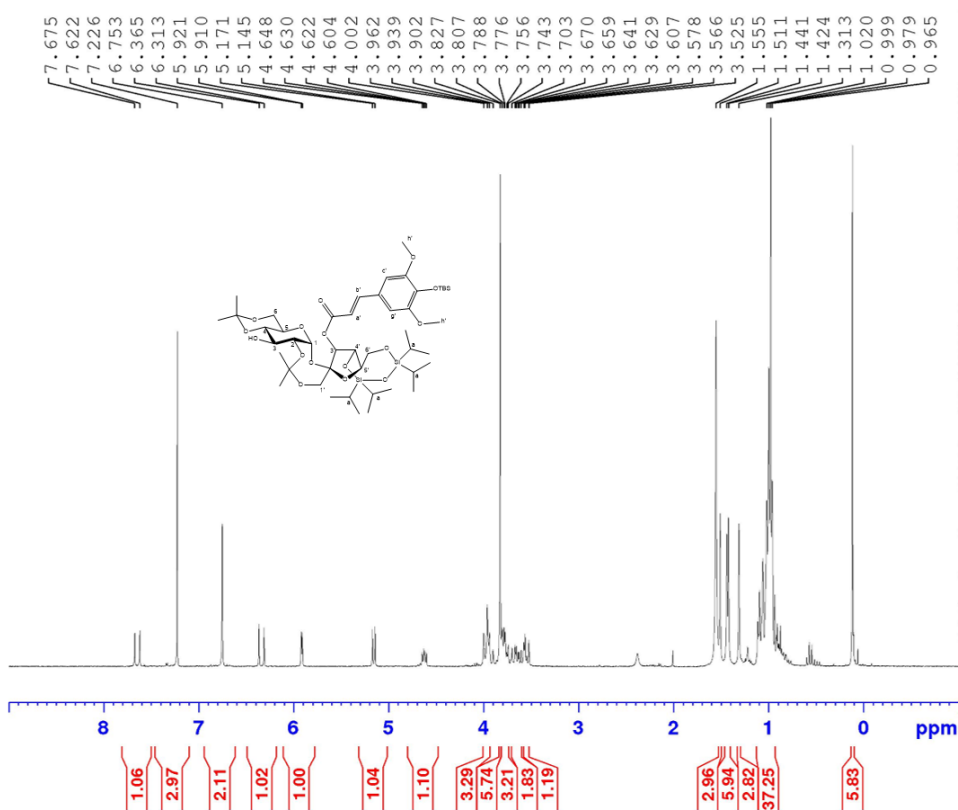
Spectra of compound 12



Spectra of compound 13

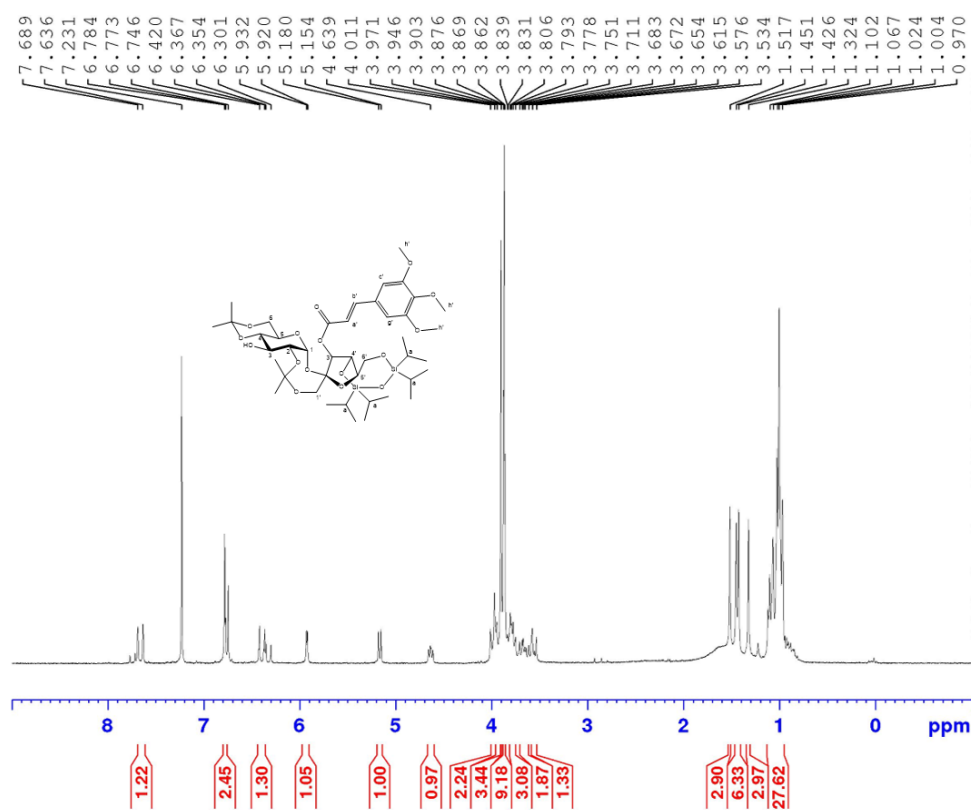


Spectra of compound 14

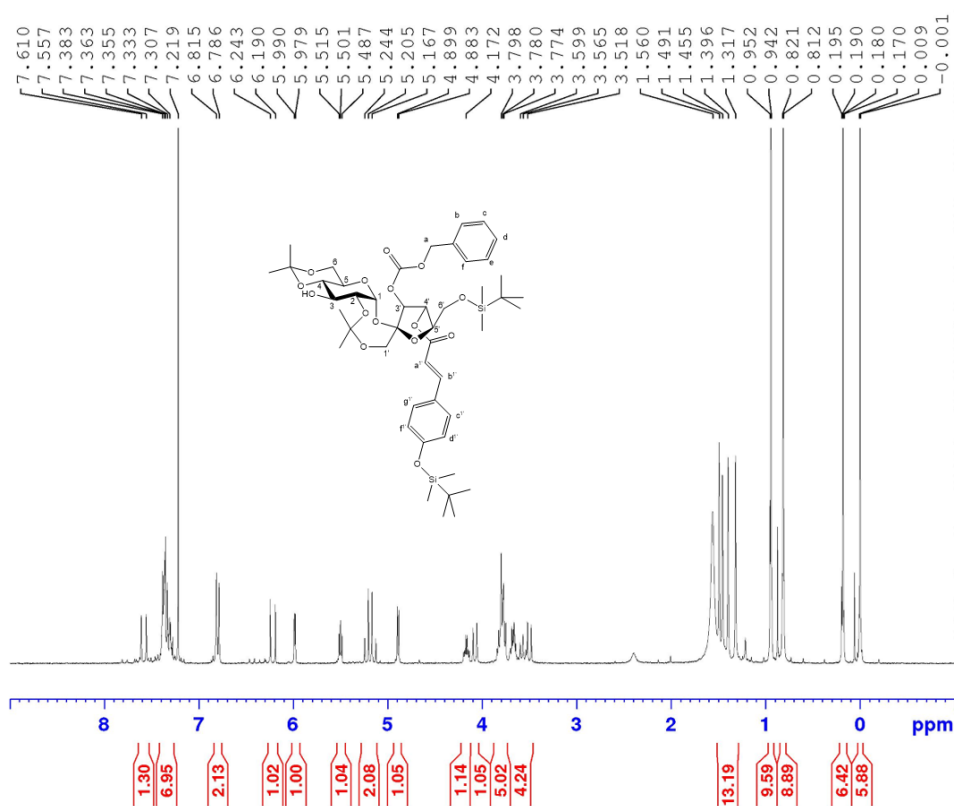


Spectra of compound 15

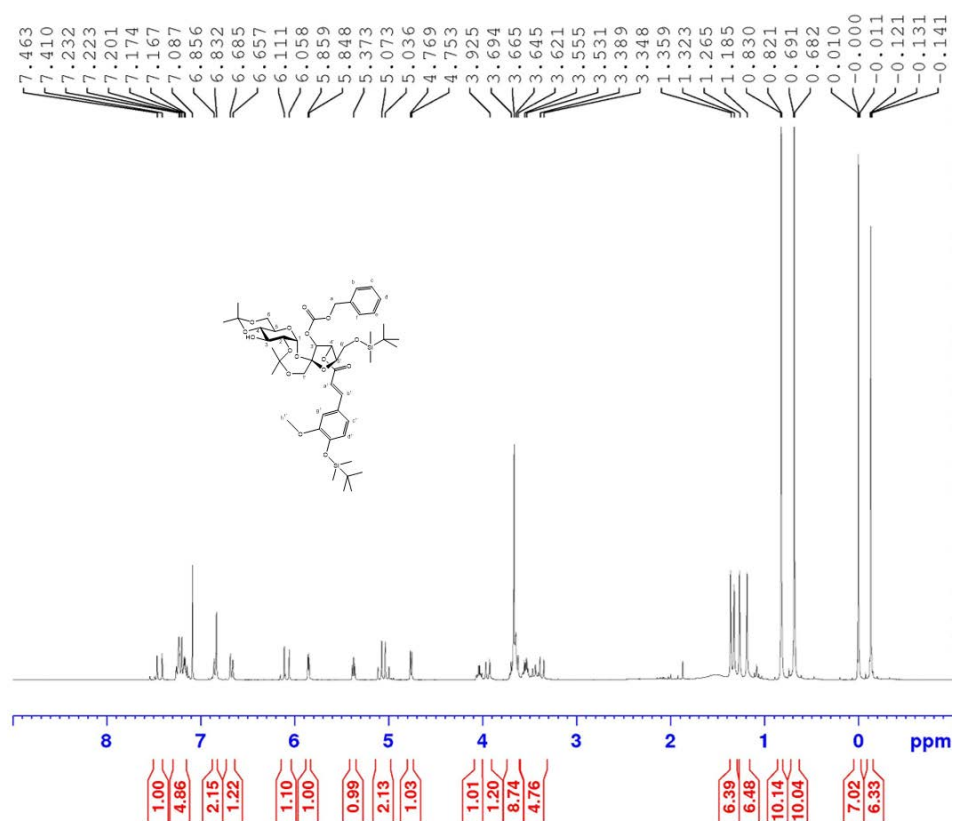




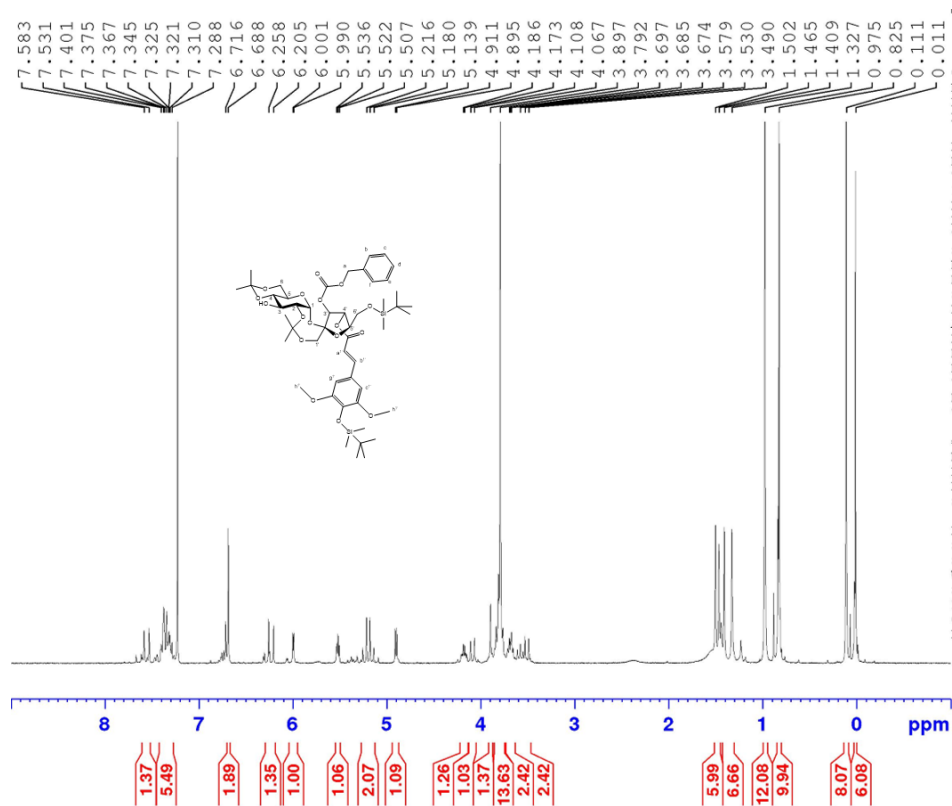
Spectra of compound 33



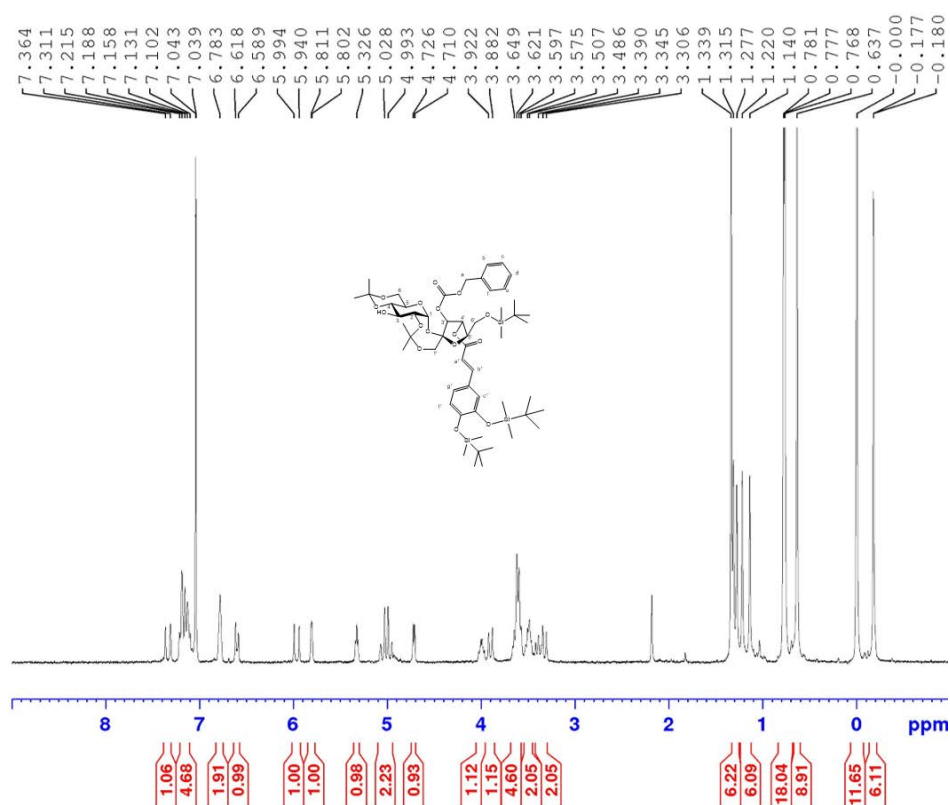
Spectra of compound 34



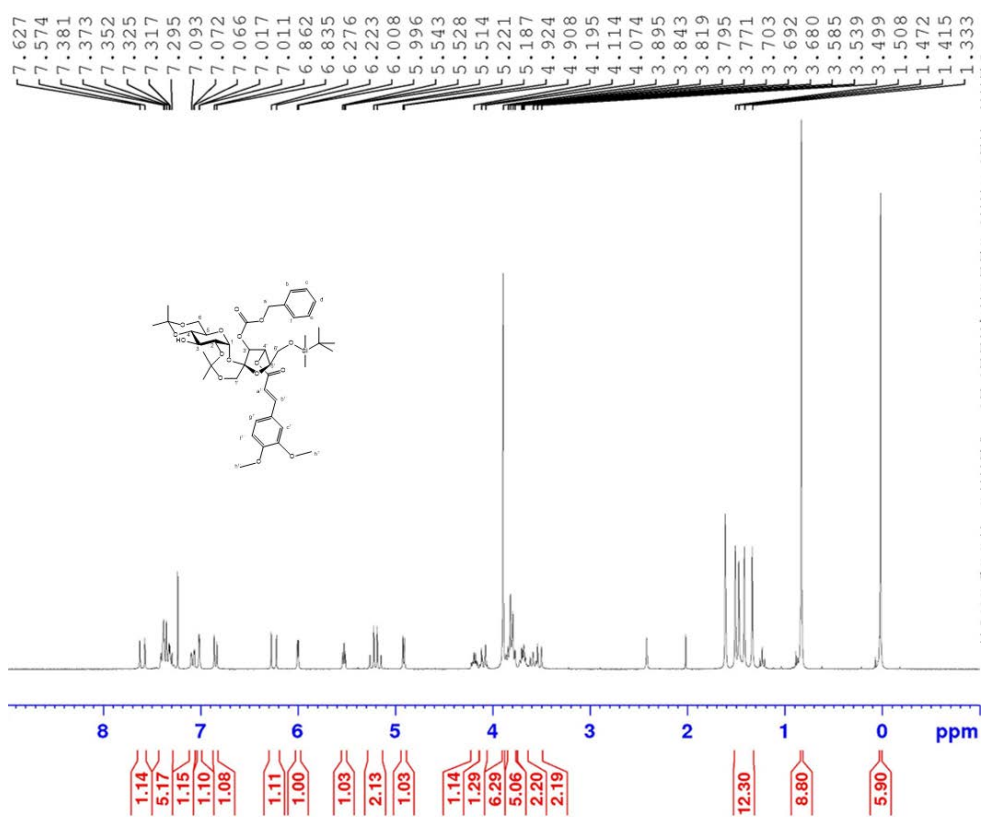
Spectra of compound 35



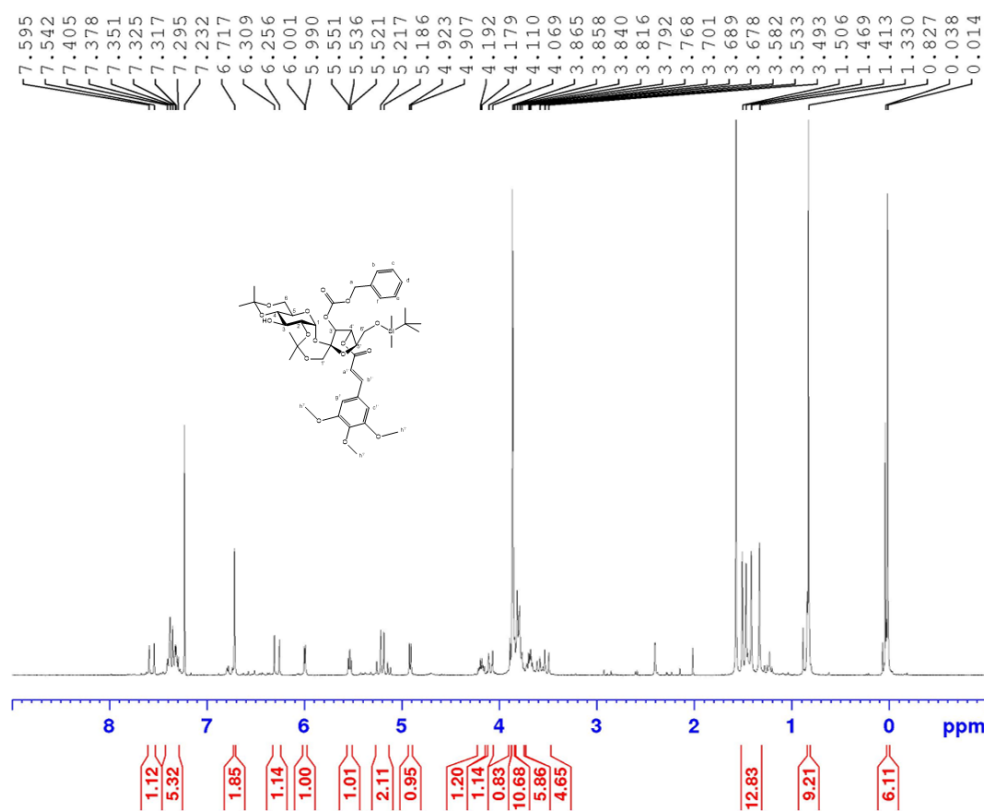
Spectra of compound 36



Spectra of compound 37

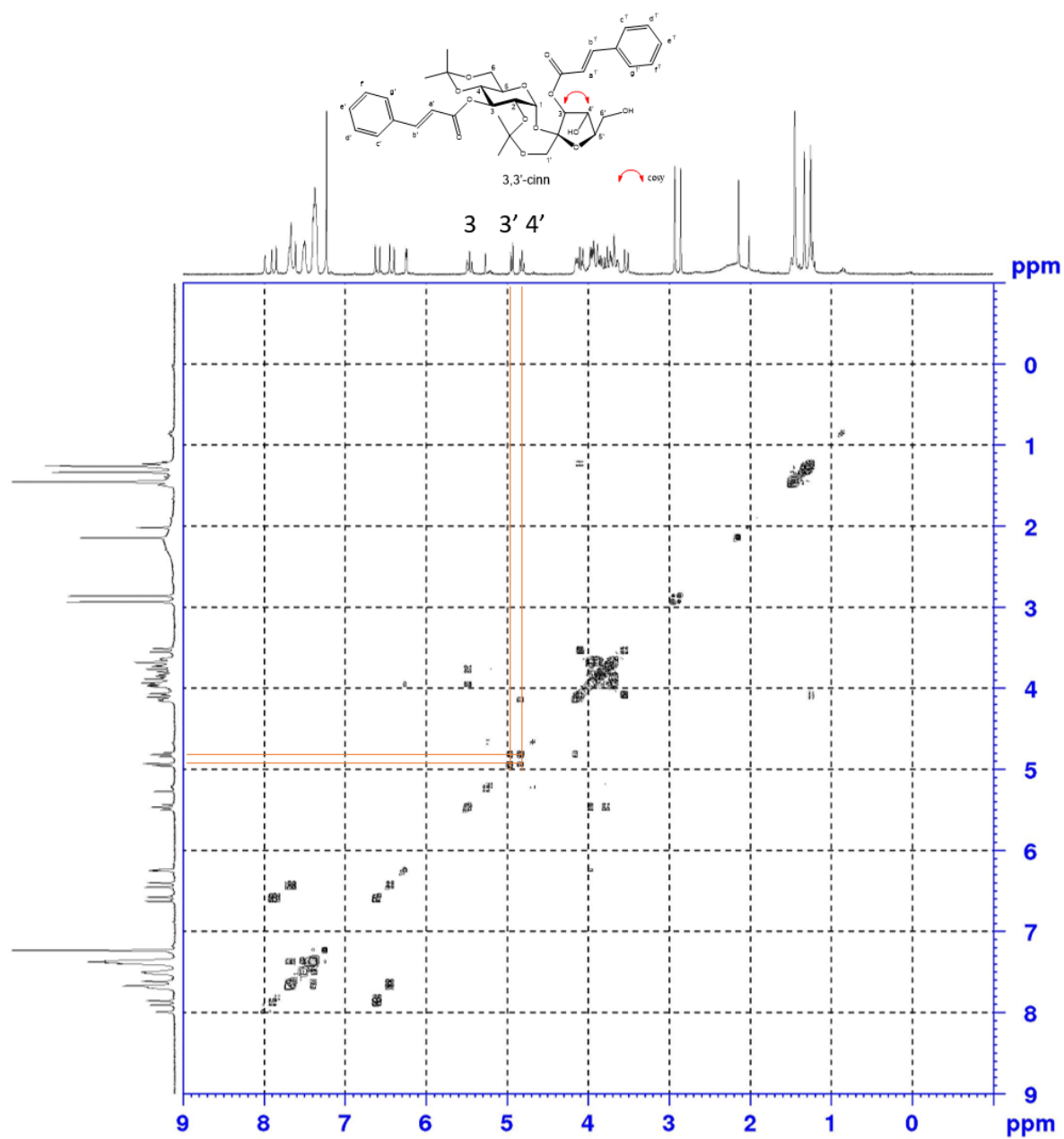


Spectra of compound 38

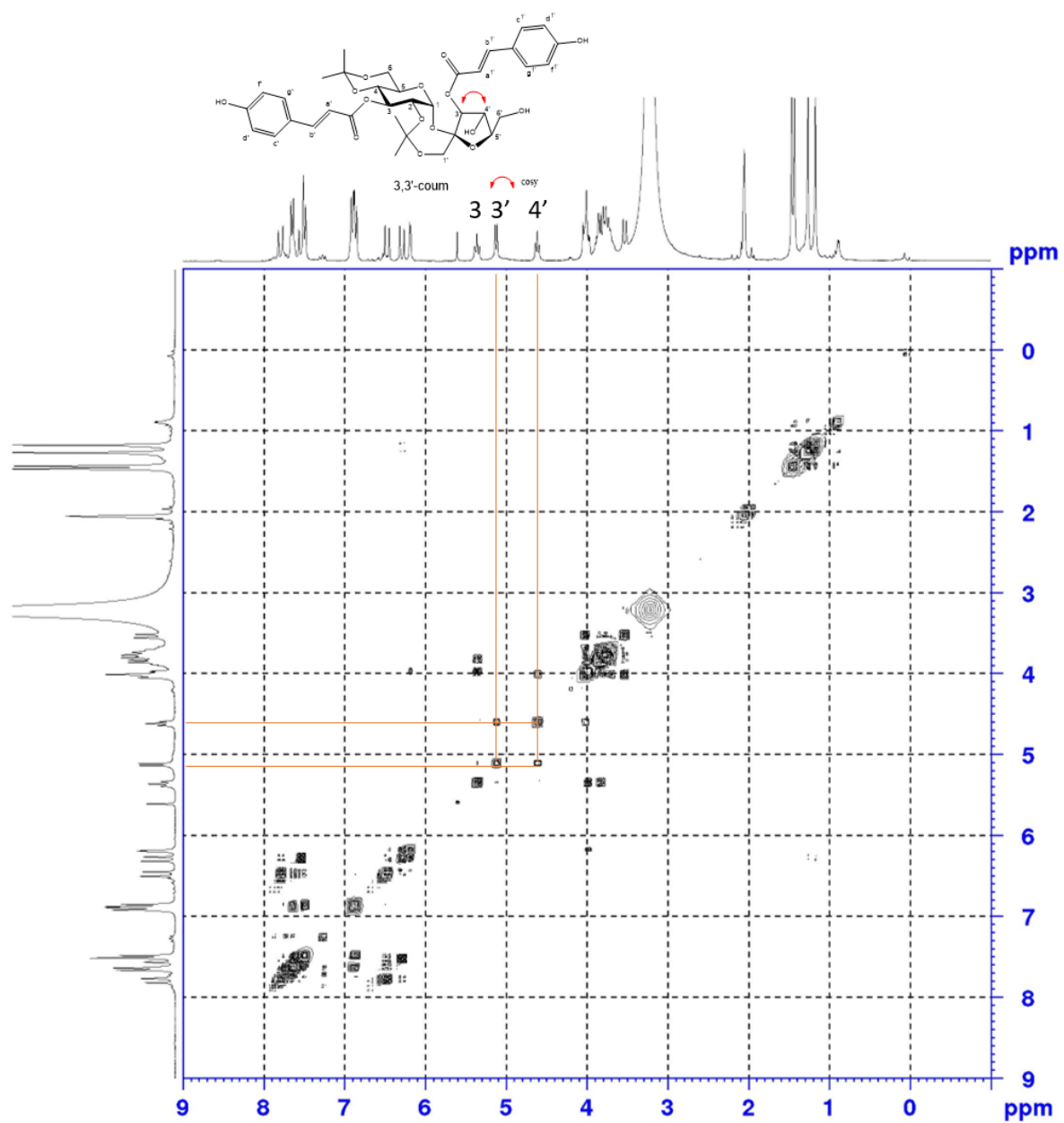


COSY spectra of **18**

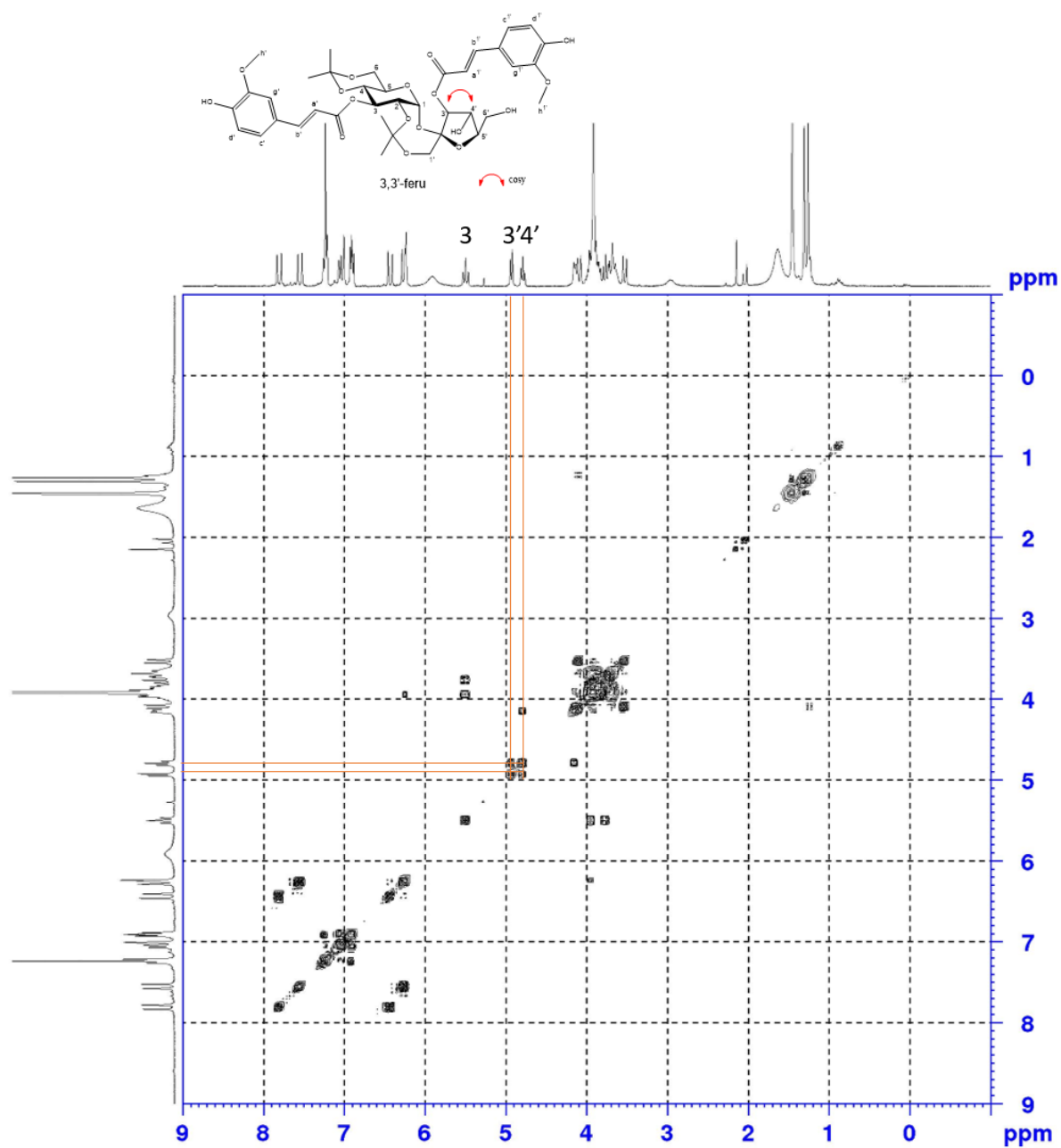




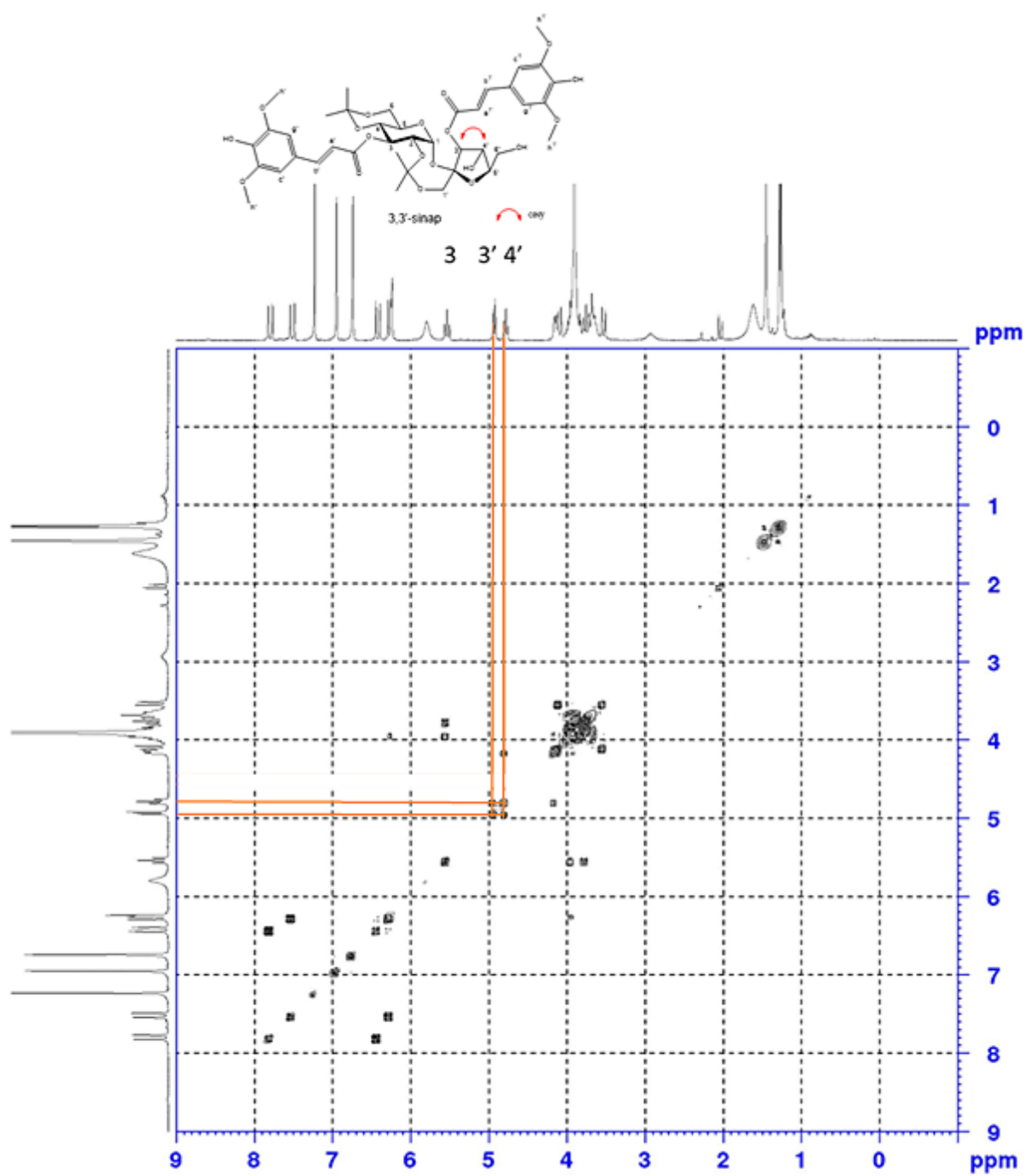
COSY spectra of 19



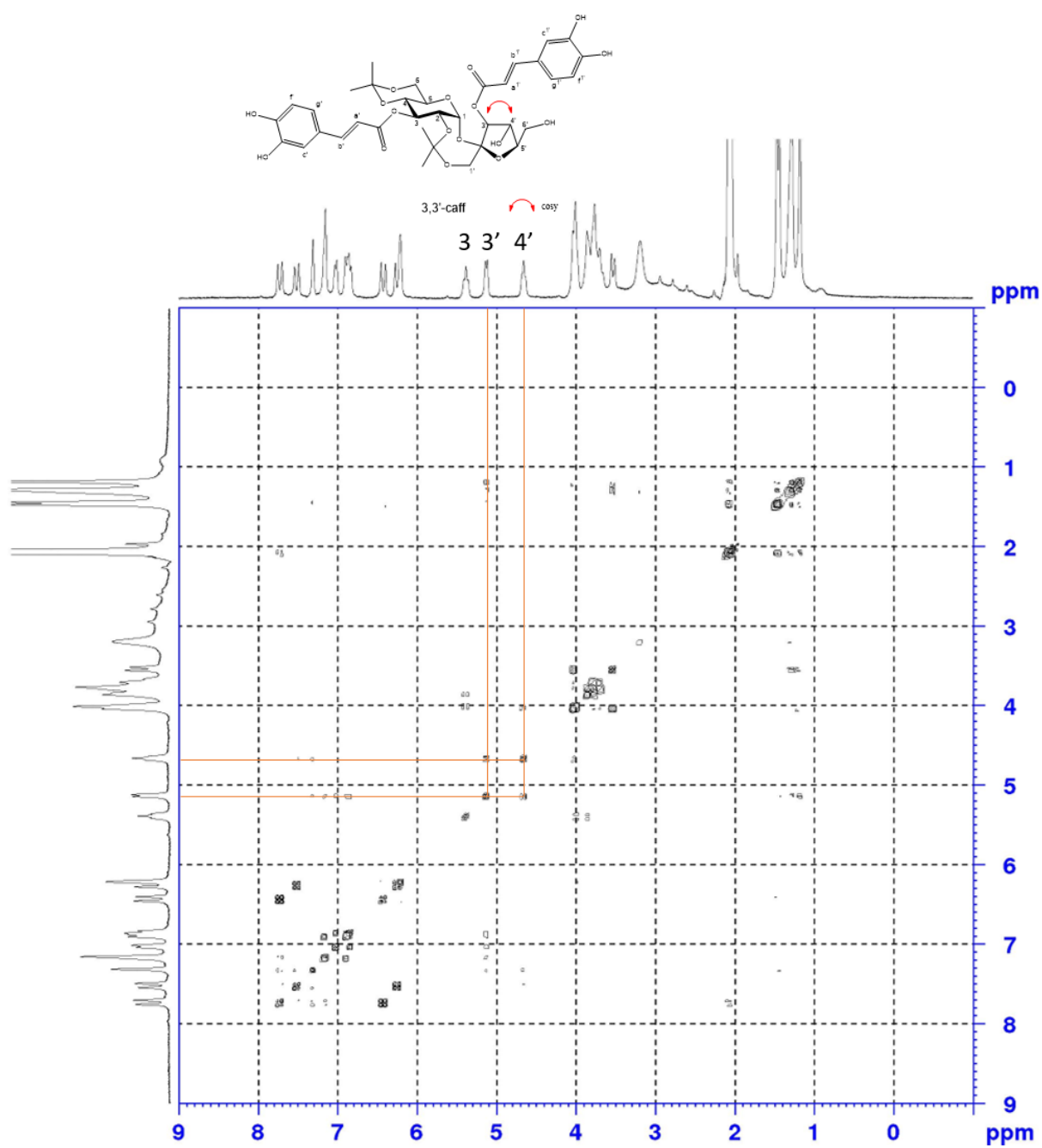
COSY spectra of **20**



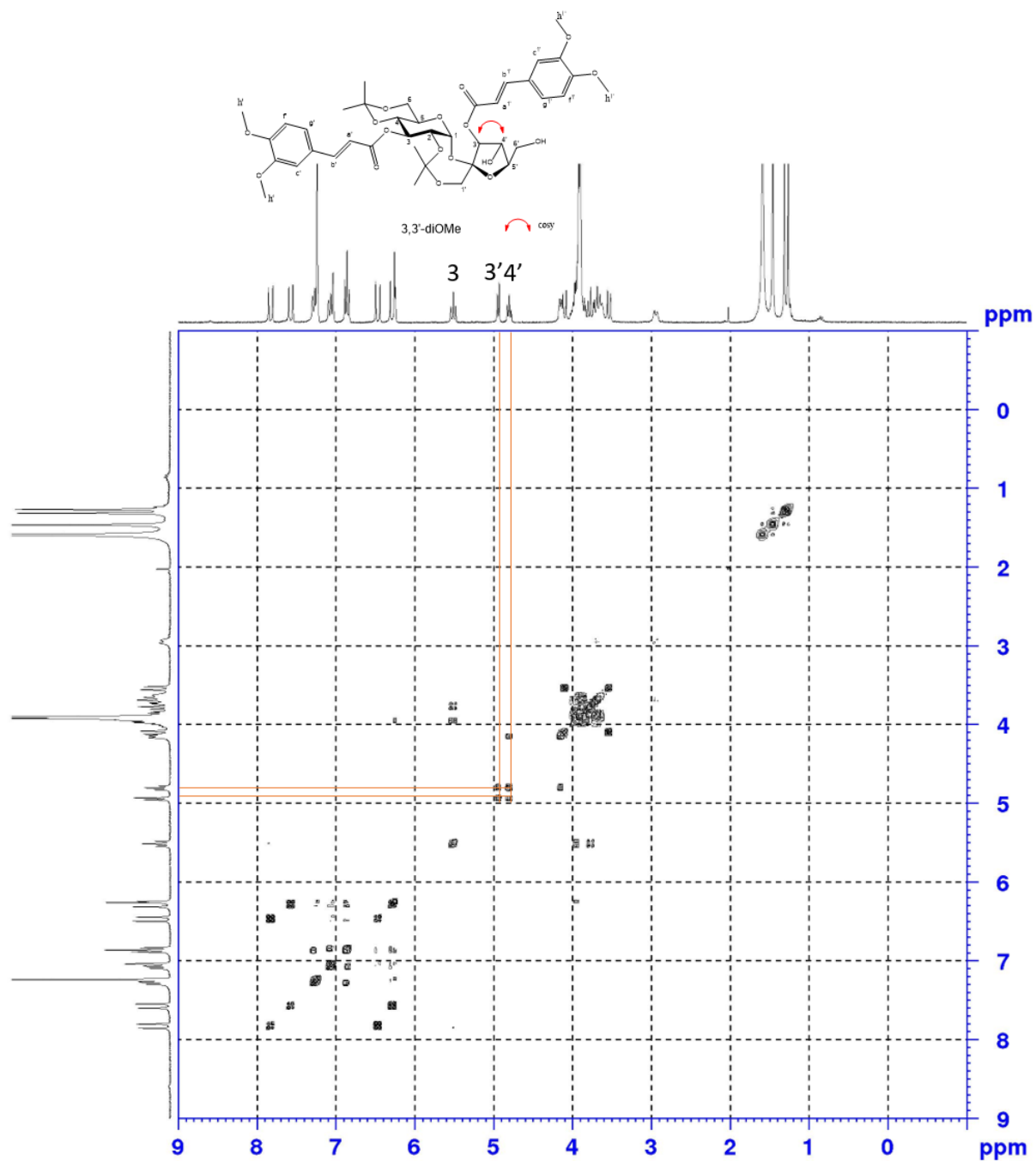
COSY spectra of 21



COSY spectra of 22



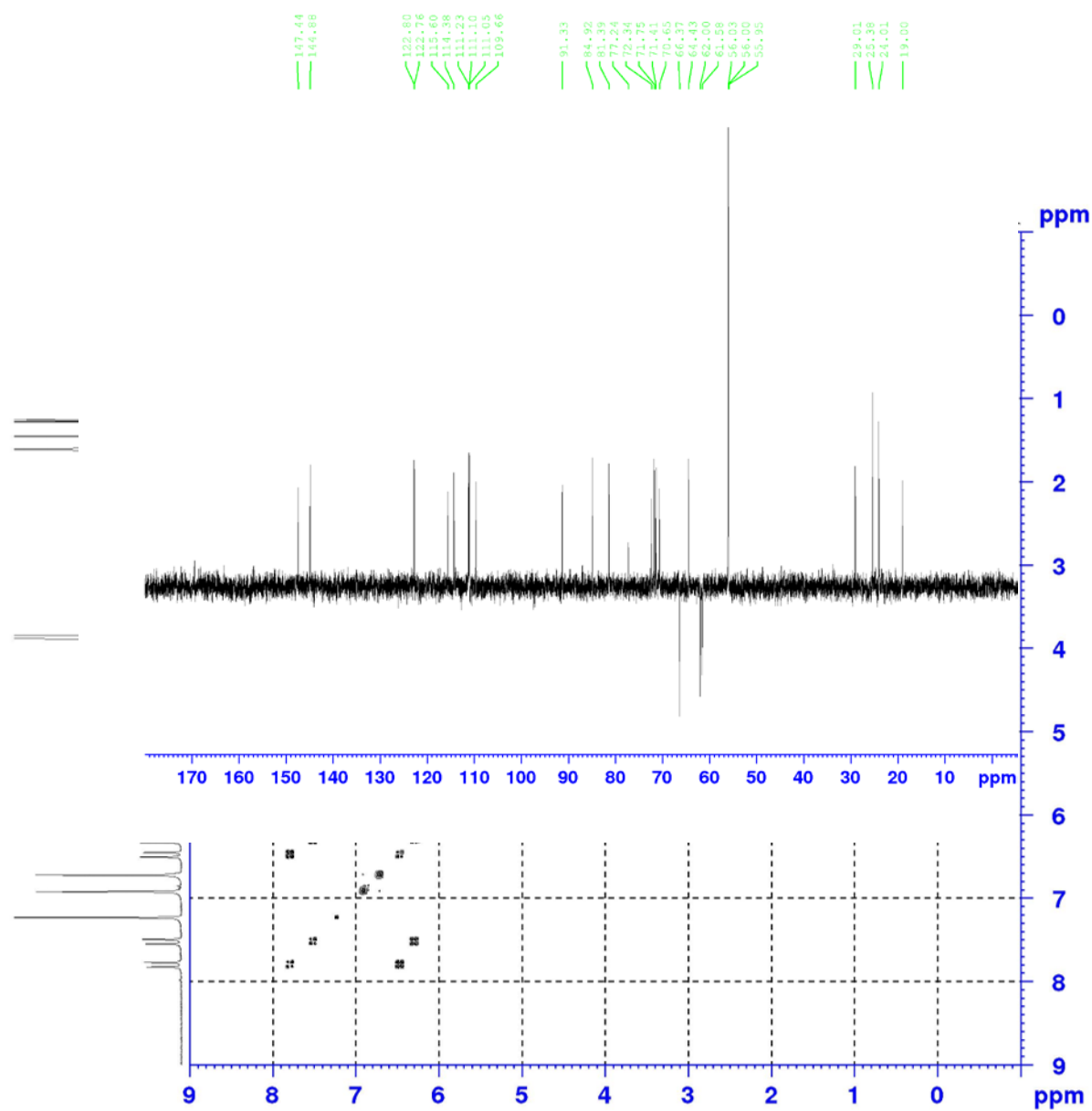
COSY spectra of 23



COSY spectra of 24

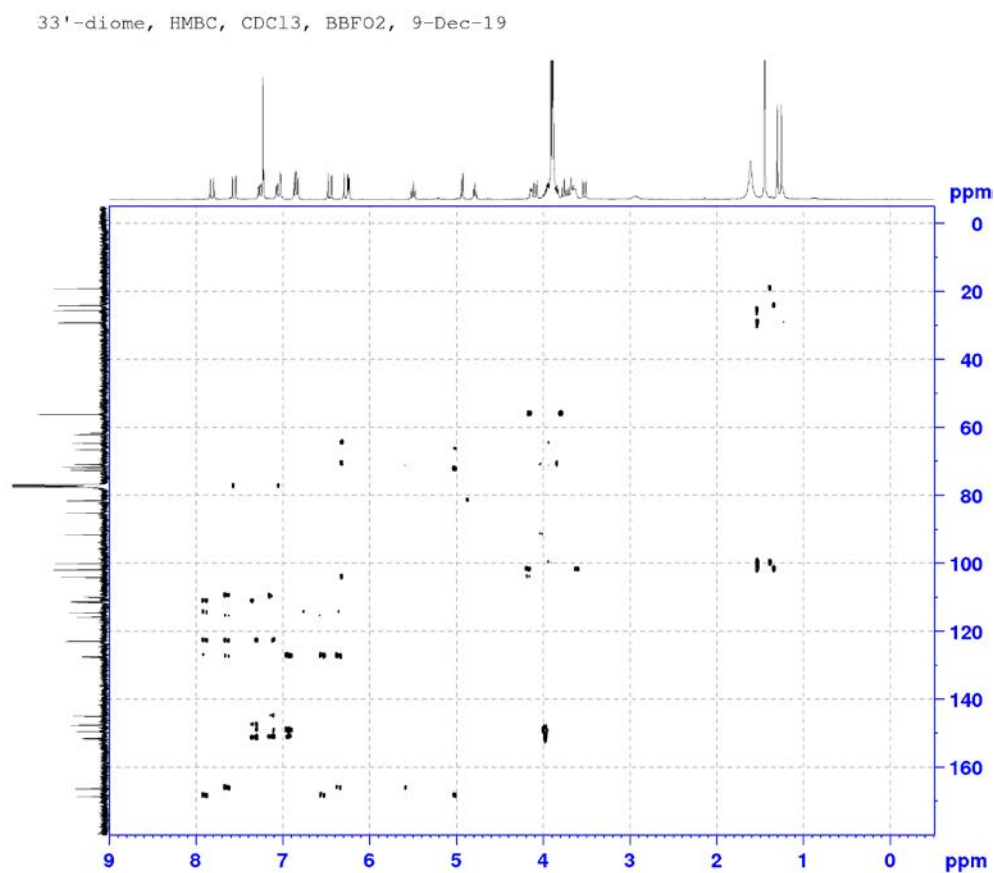


33'-diome, Dept135, CDC13, BBF02, 9-Dec-19



Dept135 spectra of 23

## HMBC spectra of **23**



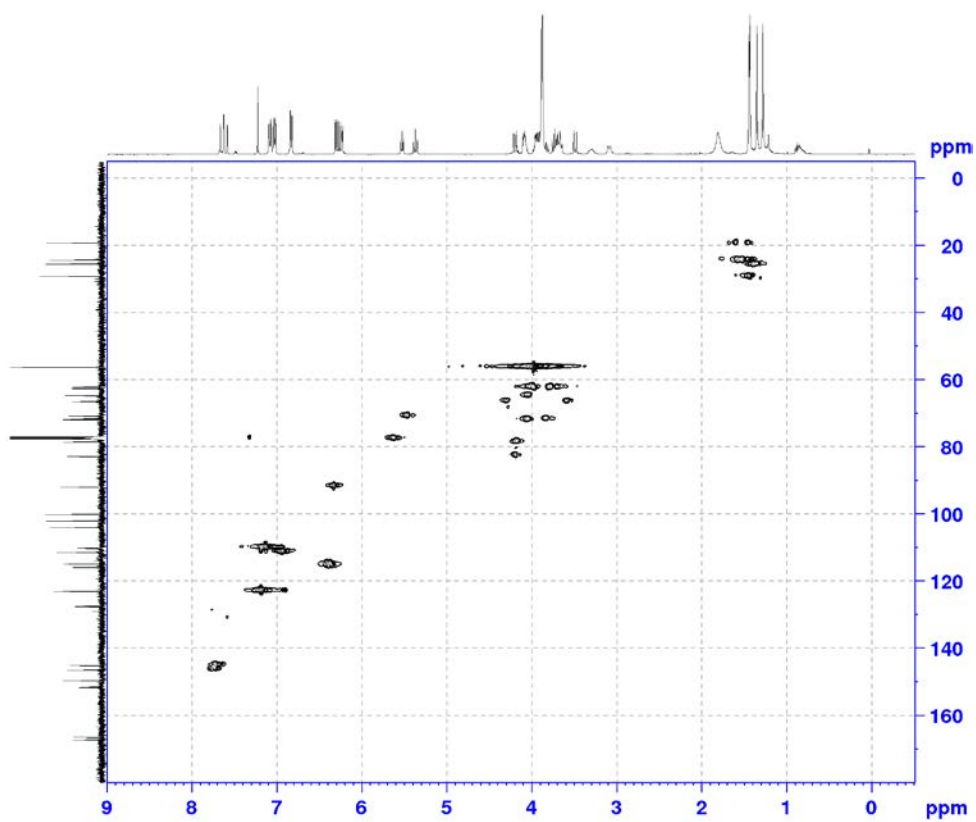
## HSQC spectra of **23**

## Dept135 spectra of **43**

## HMBC spectra of **43**

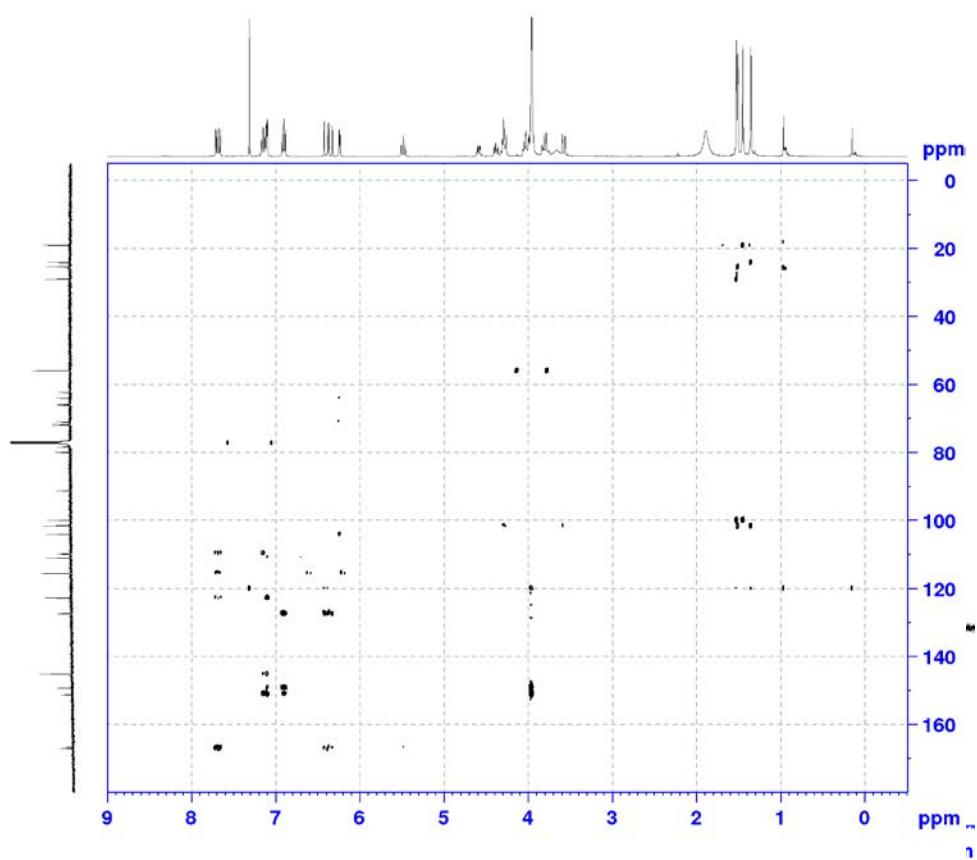


34'-diome, HSQC, CDCl<sub>3</sub>, BBFO2, 9-Dec-19



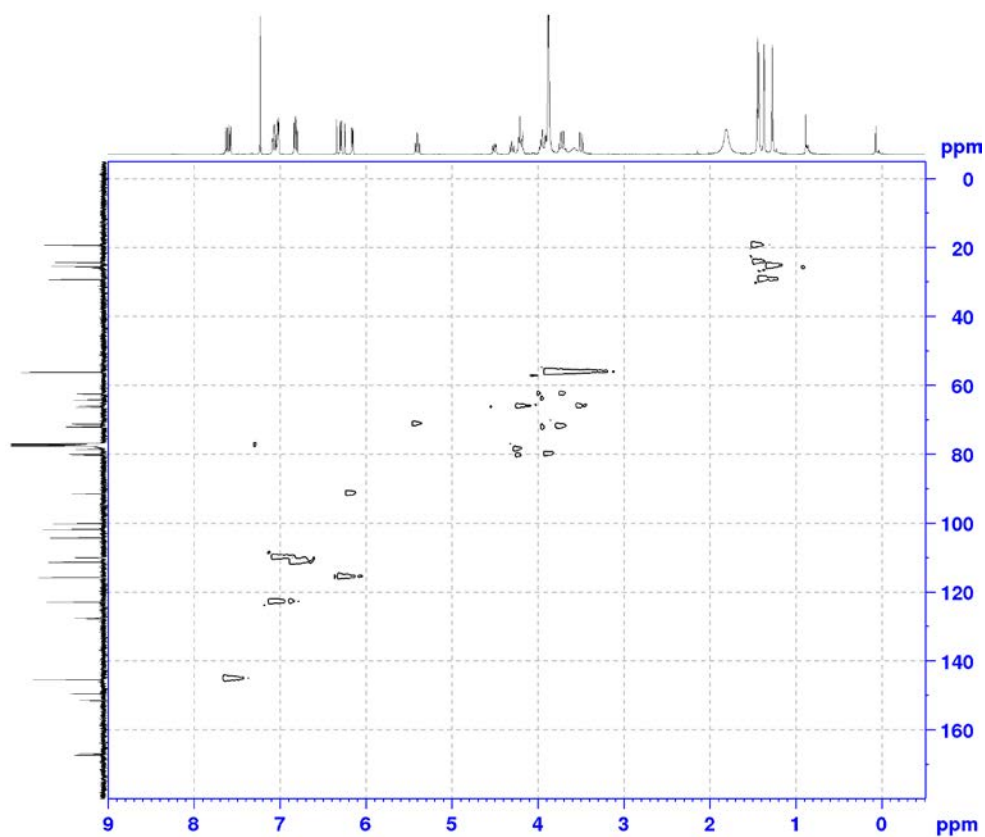
Dept135 spectra of **59**

36'-diome, HMBC, CDCl<sub>3</sub>, BBFO2, 2-Dec-19



HMBC spectra of **59**

36'-diome, HSQC, CDCl<sub>3</sub>, BBFO2, 6-Dec-19



HSQC spectra of **59**

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