**Supporting Information**

# Neuraminidase inhibition of dietary chlorogenic acids and derivatives – Potential antivirals from dietary sources

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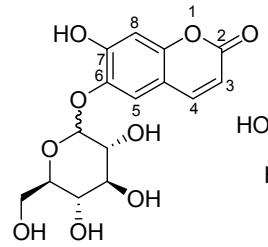
**References**



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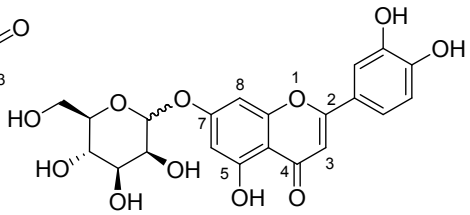

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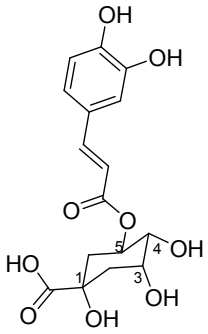

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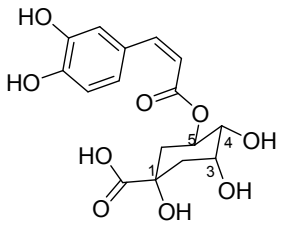

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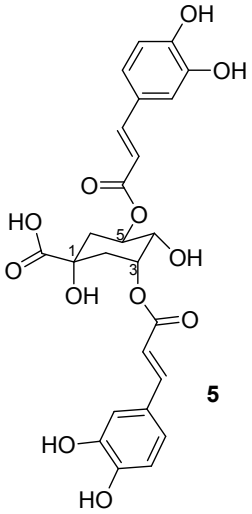

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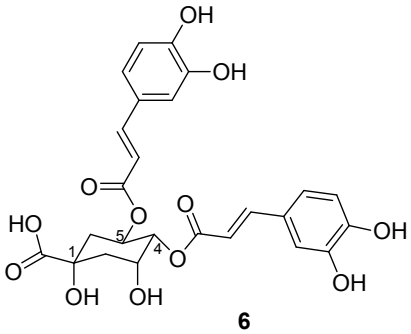

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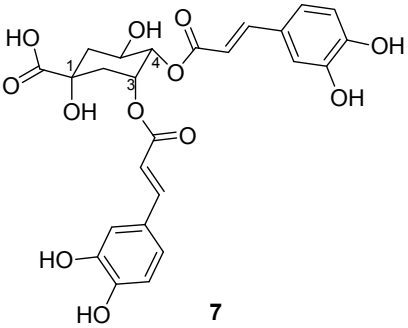

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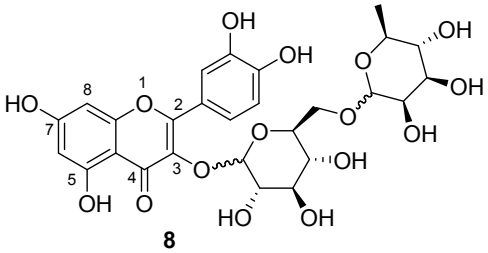

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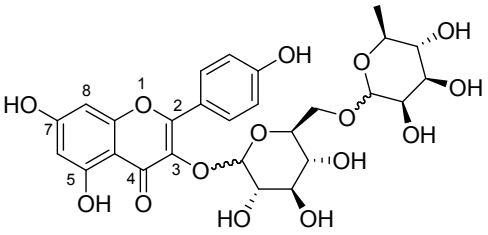

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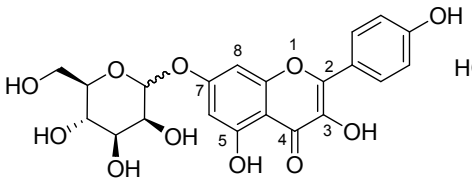

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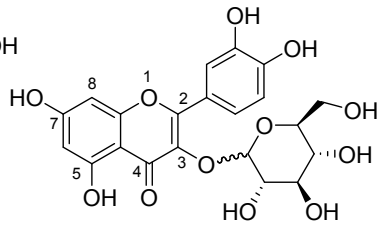

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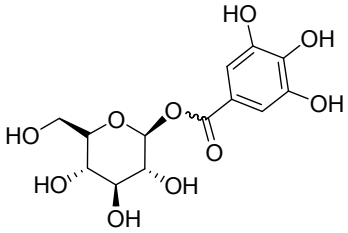

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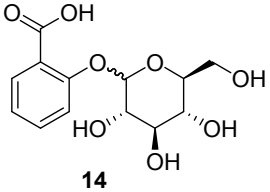

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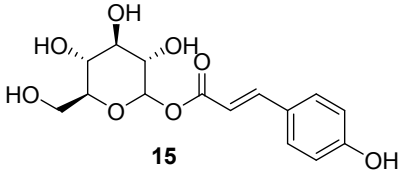

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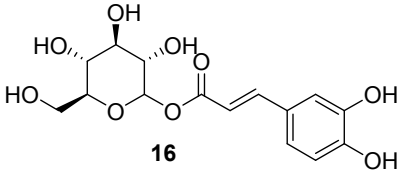

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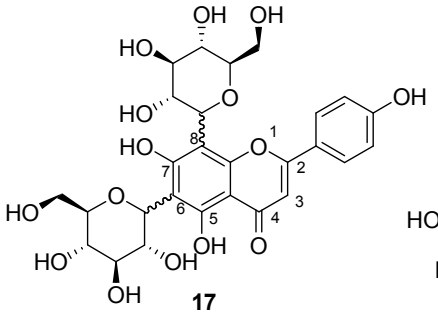

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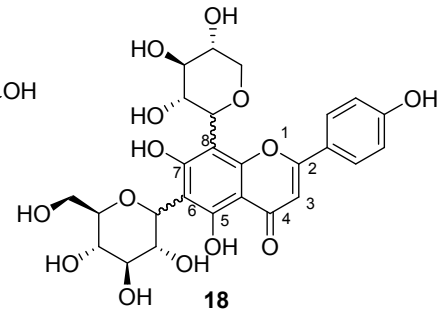

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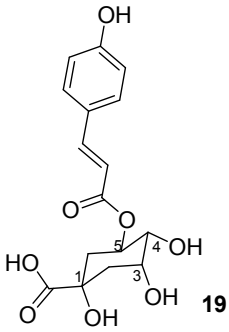

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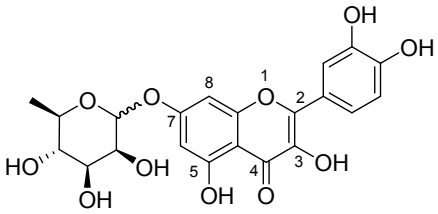

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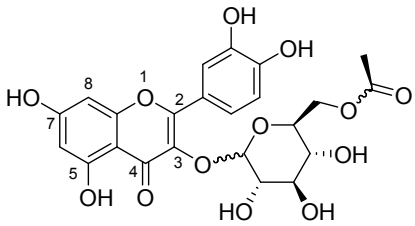

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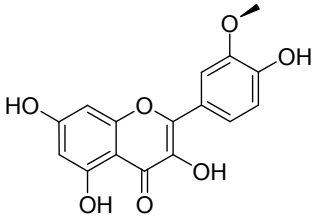

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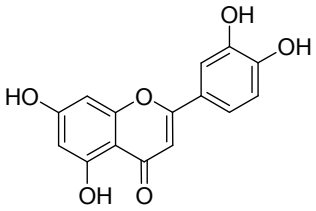

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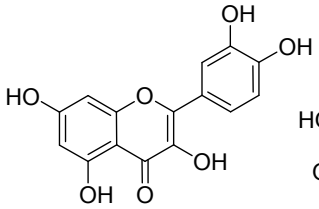

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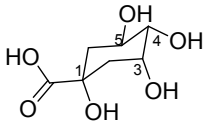

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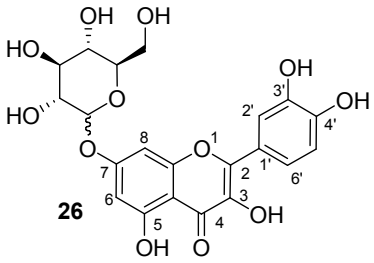

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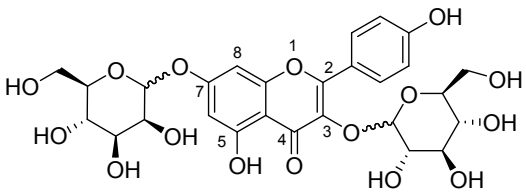

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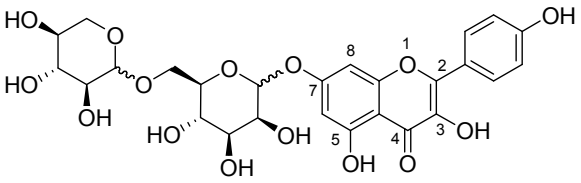

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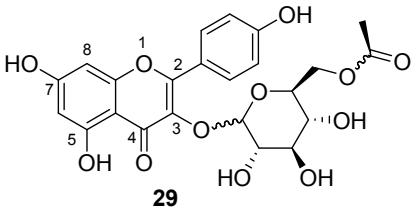

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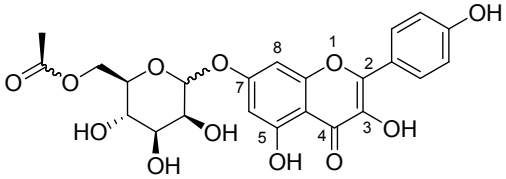

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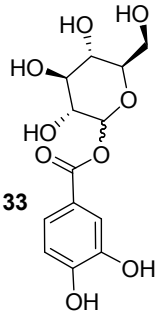

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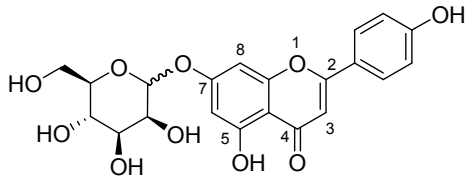

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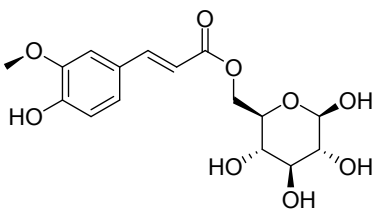

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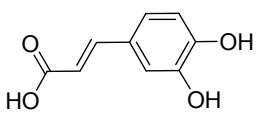

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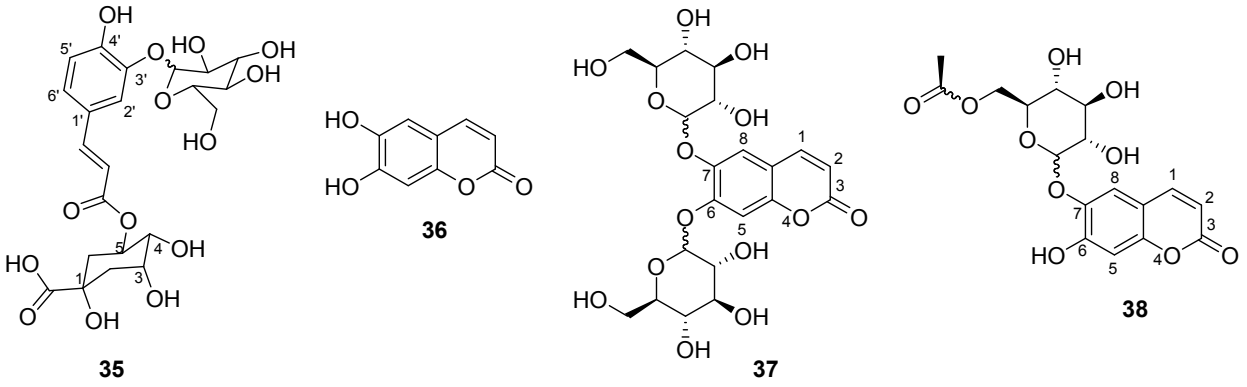


**Figure S1**. Representative structures of *A. maritima* and *S. oleraceus* phenolics.

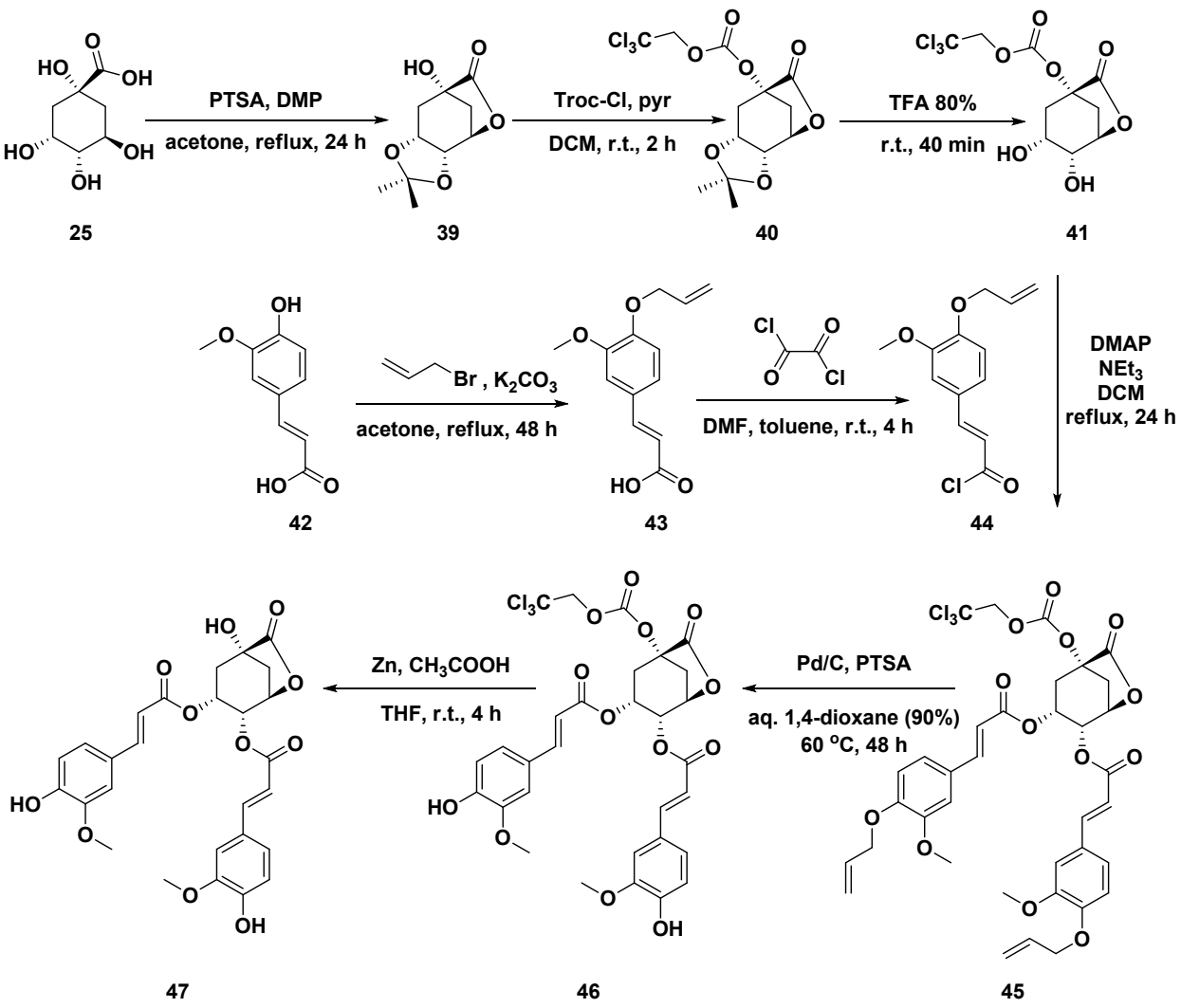


**Figure S2**. Synthetic path to 3,4-di-*O*-feruloyl-1,5-quinide.

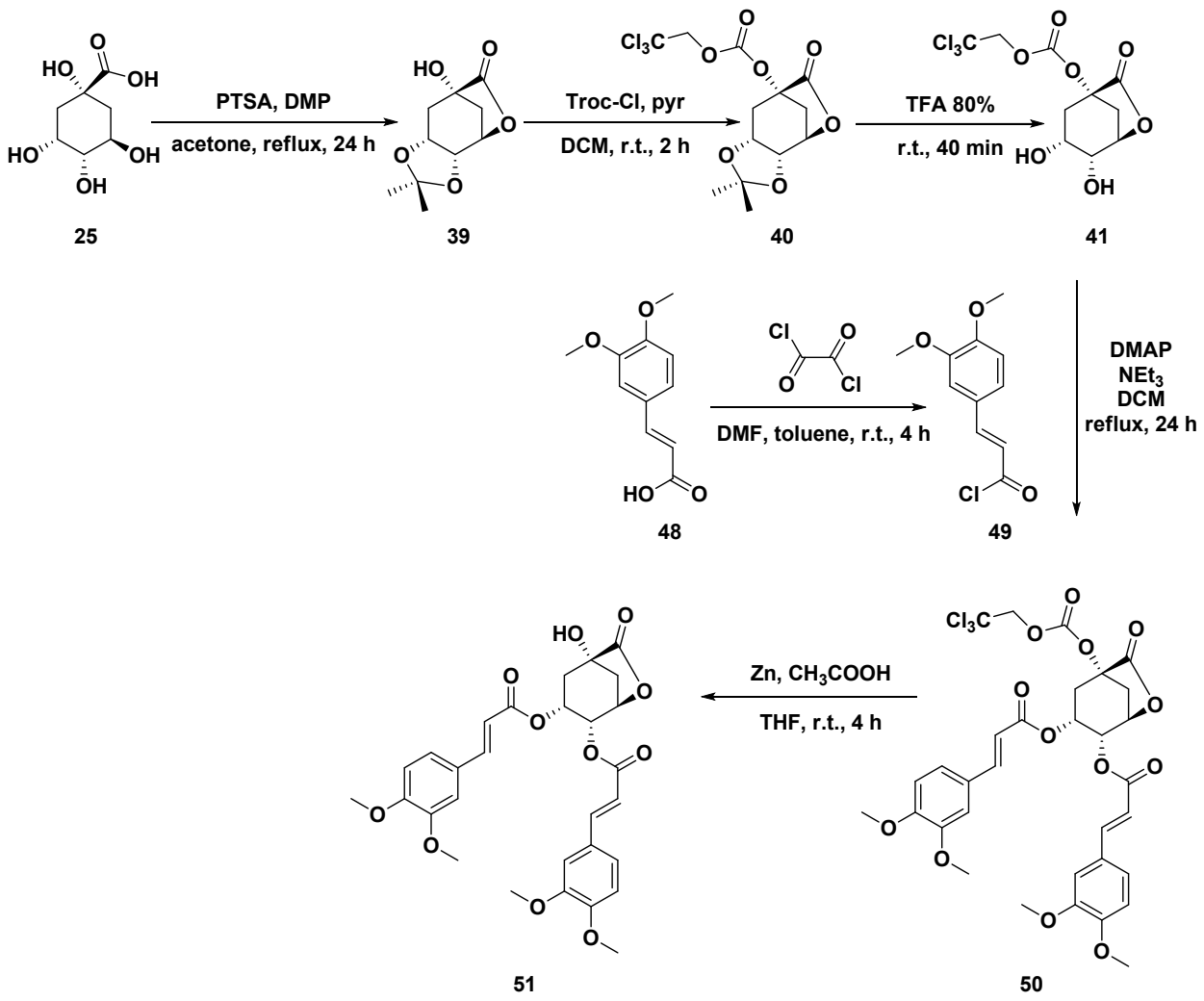


**Figure S3**. Synthetic path to 3,4-di-*O*-dimethoxycinnamoyl-1,5-quinide.

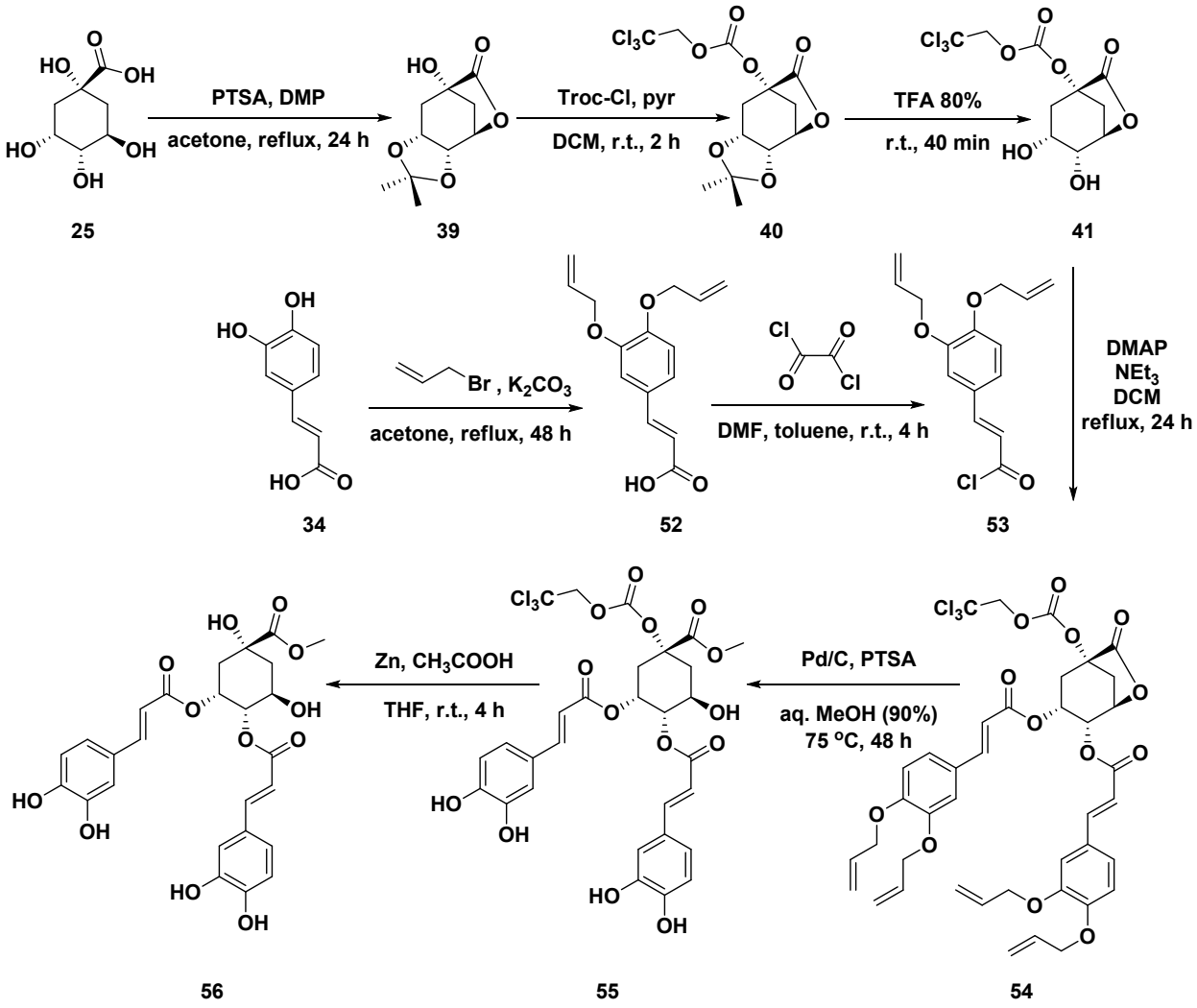


**Figure S4**. Synthetic path to methyl 3,4-di-*O*-caffeoylquinate.

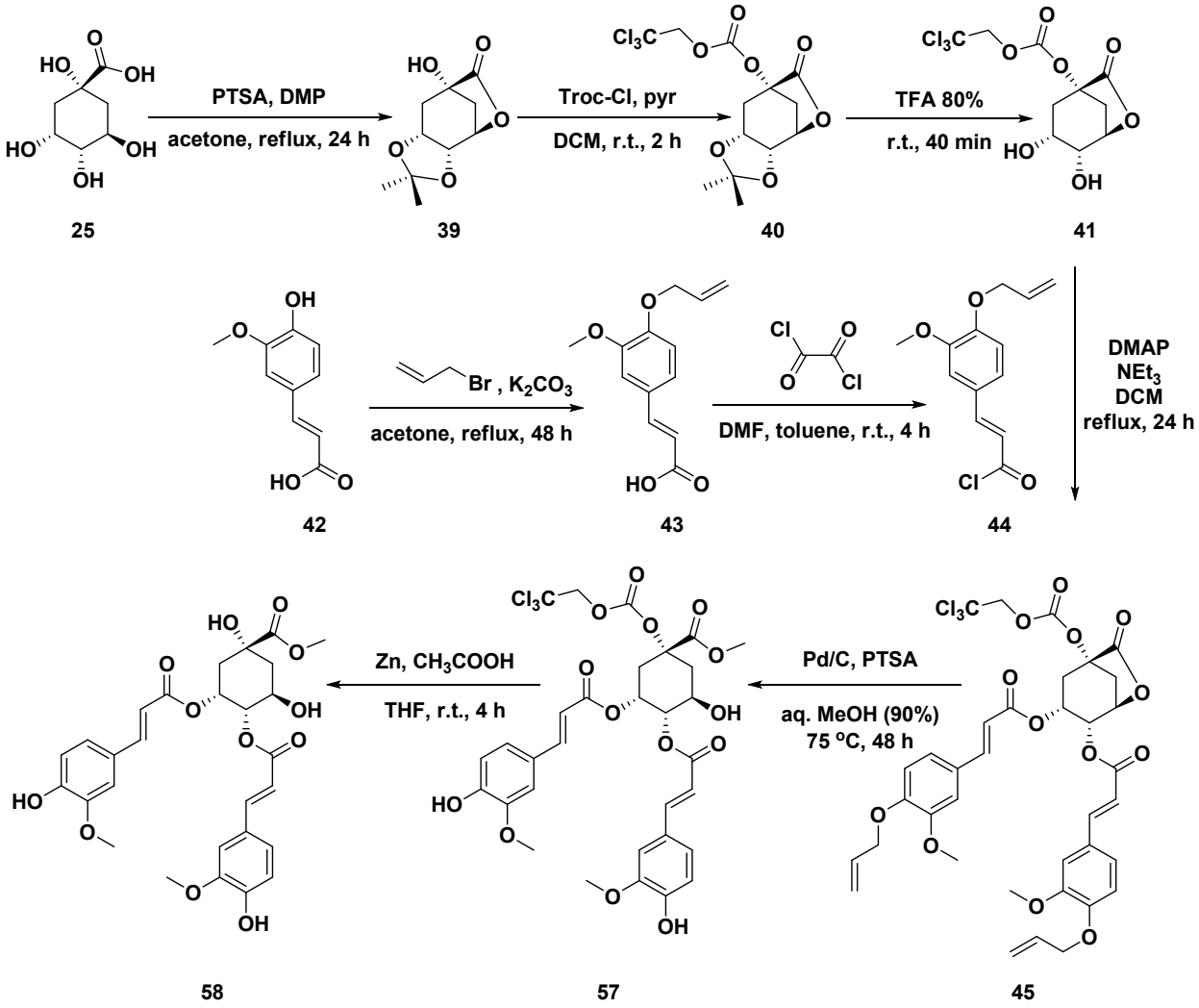


**Figure S5**. Synthetic path to methyl 3,4-di-*O*-feruloylquinate.

**Synthesis of 3,4-di-*O*-feruloyl-1,5-quinide (3,4-diFQL), 47.**

**3,4-*O*-Isopropylidene-1,5-quinide, 39:** To a solution of 10.00 g (52.04 mmol) of quinic acid in 50 mL acetone, a quantity of 200 mg (1.05 mmol) of *p*-toluenesulfonic acid monohydrate (PTSA·$H_2O$) was added, followed by addition of 22.4 mL of 2,2-dimethoxypropane (DMP) to give a white suspension. The reaction was then refluxed for 24 h to give a clear red solution which was cooled to 50 ºC and neutralized with a solution of NaOEt (71.5 mg) in EtOH (5 mL) to give a yellow clear solution. The solvents were removed under reduced pressure and to the resulting orange viscous liquid a volume of 100 mL of EtOAc was added. The organic phase was washed with 50 mL of $H_2O$ and the aqueous phase was back-extracted with 30 mL EtOAc. The combined organic layers were washed with a half-saturated $NaHCO_3$ solution, dried on $Na_2SO_4$, filtered and evaporated. The resulting yellow solid was recrystallized successively from a 1:1 n-heptane:EtOAc solution to afford white crystals of **39** (6.13 g, 28.62 mmol, 55%); (Rohloff et al., 1998; Matei et al., 2012) mp 142 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 4.71 (dd, 1H, $J$ = 2.5, 6.2 Hz), 4.48 (td, 1H, $J$ = 2.8, 7.3 Hz), 4.29 (ddd, 1H, $J$ = 1.4, 2.3, 6.4 Hz), 2.96 (br, 1H), 2.63 (d, 1H, $J$ = 11.9 Hz), 2.39-2.32 (ddd, 1H, $J$ = 2.3, 7.8, 14.7 Hz), 2.32-2.26 (m, 1H), 2.16 (dd, 1H, $J$ = 2.8, 14.7 Hz), 1.51 (s, 3H), 1.31 (s, 3H); $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 178.95 (COOR), 109.88 (*C*-$(CH_3)_2$), 75.94 (C-4), 72.18 (C-1), 71.59 (C-3), 71.59 (C-5), 38.27 (C-6), 34.35 (C-2), 27.06 ($CH_3$), 24.38 ($CH_3$).

**1-*O*-Troc-3,4-*O*-isopropylidene-1,5-quinide, 40:** Pyridine (5.66 mL) was added to a solution of 3,4-*O*-isopropylidene-1,5-quinide, **39** (4070 mg, 19.00 mmol) in DCM (40 mL). The mixture was then cooled to 0 ºC and a solution of 2,2,2-trichloroethylchloroformate (4282 mg, 20.21 mmol) in 6.5 mL DCM was added drop-wise. After stirring for 2 h at r.t. a volume of 40 mL DCM was added and the mixture was washed with HCl 1M (2x40 mL) followed by water

(40 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated in vacuo to 20 mL. Addition of EtOH (40 mL) precipitated the desired white product **40** (5625 mg, 14.44 mmol, 76%); (Frank et al., 2006) mp 165-166 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 4.81 (d, 1H, *J* = 11.9 Hz), 4.79 (m, 1H), 4.71 (d, 1H, *J* = 11.9 Hz), 4.55 (td, 1H, *J* = 3.2, 7.8 Hz), 4.31 (ddd, 1H, *J* = 1.4, 2.3, 6.4 Hz), 3.05 (m, 1H), 2.65 (d, 1H, *J* = 11.0 Hz), 2.54 (ddd, 1H, *J* = 2.3, 7.8, 14.6 Hz), 2.40 (dd, 1H, *J* = 2.8, 14.6 Hz), 1.52 (s, 3H), 1.32 (s, 3H). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 172.30 (COOR), 151.55 (O*C*OOCH$_2$), 109.96 (*C*-(CH$_3$)$_2$), 93.97 ($CCl_3$), 78.98 (C-1), 77.12 (*C*H$_2$-CCl$_3$), 75.22 (C-4), 72.43 (C-3), 71.19 (C-5), 35.37 (C-6), 30.18 (C-2), 27.05 ($CH_3$), 24.32 ($CH_3$).

**1-*O*-Troc-1,5-quinide, 41:** A quantity of 1000 mg (2.567 mmol) of 1-*O*-Troc-3,4-*O*-isopropylidene-1,5-quinide, **40** and a solution of TFA 80% (21 mL) were cooled to 0 ºC. The acid solution was then added drop-wise at the same temperature to the quinide. The ice bath was removed and the reaction was stirred for 40 min at r.t., then the solvents were removed in vacuum to give 897 mg (quantitative yield) of the white product **41**; (Frank et al., 2006) mp 123-125 ºC; $^1$H-NMR (acetone-D6): $\delta_H$ 4.90 (m, 3H), 4.07 (t, 1H, *J* = 4.6 Hz), 3.81 (td, 1H, *J* = 4.6, 8.7 Hz), 2.98 (m, 1H), 2.66 (d, 1H, *J* = 11.4 Hz), 2.16 (d, 1H, *J* = 9.2 Hz), 2.15 (d, 1H, *J* = 8.2 Hz). $^{13}$C-NMR (acetone-D6): $\delta_C$ 172.12 (COOR), 151.21 (O*C*OOCH$_2$), 95.00 ($CCl_3$), 79.99 (C-1), 77.13 (*C*H$_2$-CCl$_3$), 76.60 (C-3), 65.90 (C-4), 65.57 (C-5), 36.63 (C-6), 32.94 (C-2).

**4-*O*-allylferulic acid, 43:** A mixture of ferulic acid, **42** (1000 mg, 5.15 mmol) and anhydrous potassium carbonate (4270 mg, 30.90 mmol) in acetone (50 mL) was stirred at room temperature for 30 min. To the mixture was added a solution of allyl bromide (1250 mg, 10.30 mmol) in acetone (10 mL) and the entire mixture was refluxed for 48 h. The reaction was cooled to r.t., filtered and the filtrate was dried in vacuo. The residue was suspended in ethanol (30 mL) and a NaOH 2M solution (20 mL) was added. The mixture was refluxed for 2 h. The solution

was cooled to r.t., poured into a beaker and acidified (pH=2) with 3M HCl. The suspension was stirred at r.t. for 30 min and the solid was filtered off and washed successively with a 1:1 mixture of ethanol/water (200 mL). The solid was dried overnight in vacuum to yield a white powder of **43** (1025 mg, 4.38 mmol, 85%); (Barros and Silva, 2006; Jaiswal et al., 2012) $^{1}$H-NMR ($CDCl_3$): $\delta_H$ 7.72 (d, 1H, *J* = 16.0 Hz), 7.14 (dd, 1H, *J* = 1.8, 8.7 Hz), 7.08 (d, 1H, *J* = 1.8 Hz), 6.87 (d, 1H, *J* = 8.7 Hz), 6.28 (d, 1H, *J* = 16.0 Hz), 6.05 (m, 1H), 5.41 (d, 1H, *J* = 16.9 Hz), 5.31 (d, 1H, *J* = 10.5 Hz), 4.65 (d, 2H, *J* = 5.5 Hz), 3.91 (s, 3H). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 169.22 (COOH), 149.96 ($C_{Ar}$-$OCH_3$), 149.52 ($C_{Ar}$-$OCH_2$), 144.66 (*C*H-$C_{Ar}$), 132.81 (*C*H=$CH_2$), 127.76 ($C_{Ar}$-CH), 122.36 ($C_{Ar}$), 118.35 (*C*$H_2$=CH), 116.58 (*C*H-COOH), 112.94 ($C_{Ar}$), 110.11 ($C_{Ar}$), 69.73 ($C_{Ar}$-O*C*$H_2$), 55.95 ($CH_3$).

**4-*O*-allylferuloyl chloride, 44:** 4-*O*-allylferulic acid, **43** (1025 mg, 4.38 mmol) was added to a solution of 20 mL toluene containing 100 µL of DMF. A volume of 2 mL (2912 mg, 22.93 mmol) oxalyl chloride was added drop-wise at 0 ºC. The reaction mixture was stirred at r.t. for 4 h and the resulting yellow solution was transferred slowly to a new round bottom flask (dark color viscous residues remaining on the bottom of the reaction vessel). The toluene and the unreacted oxalyl chloride were removed under the rotary evaporator to give a yellow solid of **44** (1040 mg, 4.12 mmol, 94%); (Jaiswal et al., 2012; Sefkow, 2001) $^{1}$H-NMR ($CDCl_3$): $\delta_H$ 7.76 (d, 1H, *J* = 15.6 Hz), 7.14 (dd, 1H, *J* = 1.8, 8.2 Hz), 7.06 (d, 1H, *J* = 1.8 Hz), 6.89 (d, 1H, *J* = 8.2 Hz), 6.49 (d, 1H, *J* = 15.6 Hz), 6.07 (m, 1H), 5.42 (d, 1H, *J* = 17.4 Hz), 5.32 (d, 1H, *J* = 10.5 Hz), 4.66 (d, 2H, *J* = 5.5 Hz), 3.92 (s, 3H). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 166.12 (COCl), 151.80 ($C_{Ar}$-$OCH_3$), 150.91 ($C_{Ar}$-$OCH_2$), 149.83 (*C*H-$C_{Ar}$), 132.45 (*C*H=$CH_2$), 126.22 ($C_{Ar}$-CH), 124.46 ($C_{Ar}$), 119.85 (*C*$H_2$=CH), 118.81 (*C*H-COCl), 112.85 ($C_{Ar}$), 110.61 ($C_{Ar}$), 69.84 ($C_{Ar}$-O*C*$H_2$), 56.10 ($CH_3$).

**1-*O*-Troc-3,4-di-*O*-(4-*O*-allylferuloyl)-1,5-quinide, 45:** To a solution of 1-*O*-Troc-1,5-quinide, **41** (800 mg, 2.29 mmol) in 50 mL DCM, a quantity of 112 mg (0.92 mmol, 2x20% mol) DMAP was added and a volume of 14 mL of $NEt_3$. A quantity of 1556 mg (6.87 mmol) 4-*O*-allylferuloyl chloride, **44** was then added and the mixture was refluxed for 24 h. It was then allowed to cool to r.t., acidified (pH=2) with a HCl 2M solution and extracted 3 times with DCM (3x30 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and evaporated in vacuo. The product was purified by column chromatography (20-30% EtOAc/petroleum ether) to afford 1535 mg (1.96 mmol, 86%) of white solid **45**; (Sefkow, 2001) mp 85-87 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 7.65 (d, 1H, *J* = 15.8 Hz), 7.55 (d, 1H, *J* = 15.8 Hz), 7.05 (dd, 1H, *J* = 1.8, 8.2 Hz), 7.04 (d, 1H, *J* = 1.8 Hz), 6.95 (dd, 1H, *J* = 1.8, 8.2 Hz), 6.92 (d, 1H, *J* = 1.8 Hz), 6.85 (d, 1H, *J* = 8.2 Hz), 6.75 (d, 1H, *J* = 8.2 Hz), 6.35 (d, 1H, *J* = 15.8 Hz), 6.18 (d, 1H, *J* = 15.8 Hz), 6.03 (m, 2H), 5.68 (t, 1H, *J* = 4.6 Hz), 5.43-5.25 (m, 5H), 5.00 (dd, 1H, *J* = 5.5 Hz), 4.82 (d, 1H, *J* = 11.9 Hz), 4.72 (d, 1H, *J* = 11.9 Hz), 4.63 (d, 2H, *J* = 5.3 Hz), 4.58 (d, 2H, *J* = 5.3 Hz), 3.88 (s, 3H), 3.76 (s, 3H), 3.18 (m, 1H), 2.73 (d, 1H, *J* = 11.9 Hz), 2.54 (m, 1H), 2.46 (t, 1H, *J* = 11.9 Hz). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 170.22 (OC-*C*OOR), 165.47 (CH-*C*OOR), 165.19 (CH-*C*OOR), 151.50 (O*C*OOCH$_2$), 150.80 (*C*$_{Ar}$-OCH$_3$), 150.46 (*C*$_{Ar}$-OCH$_3$), 149.74 (*C*$_{Ar}$-OCH$_2$), 149.57 (*C*$_{Ar}$-OCH$_2$), 146.92 (*C*H-C$_{Ar}$), 146.30 (*C*H-C$_{Ar}$), 132.73 (*C*H=CH$_2$), 132.64 (*C*H=CH$_2$), 127.23 (*C*$_{Ar}$-CH), 127.02 (*C*$_{Ar}$-CH), 123.09 (C$_{Ar}$), 122.74 (C$_{Ar}$), 118.61 (*C*H$_2$=CH), 118.50 (*C*H$_2$=CH), 114.31 (*C*H-COOR), 113.97 (*C*H-COOR), 112.88 (C$_{Ar}$), 112.84 (C$_{Ar}$), 110.31 (C$_{Ar}$), 110.16 (C$_{Ar}$), 94.02 ($CCl_3$), 78.88 (C-1), 77.06 (*C*H$_2$-CCl$_3$), 73.88 (C-3), 69.81 (C$_{Ar}$-O*C*H$_2$), 69.77 (C$_{Ar}$-O*C*H$_2$), 65.81 (C-4), 64.74 (C-5), 56.07 ($CH_3$), 55.92 ($CH_3$), 33.88 (C-6), 33.81 (C-2).

**1-*O*-Troc-3,4-di-*O*-feruloyl-1,5-quinide, 46:** To a solution of 534 mg (0.68 mmol) of 1-*O*-Troc-3,4-di-*O*-(4-*O*-allylferuloyl)-1,5-quinide, **45** in 35 mL of aqueous 1,4-dioxane (90%), a

quantity of 25 mg (0.13 mmol) of PTSA·$H_2O$ was added. The reaction mixture was put under a nitrogen atmosphere, Pd/C (267 mg) was slowly added at r.t. and it was then heated to 60 ºC for 48 h. The mixture was cooled to r.t., filtered and dioxane removed in vacuo. The aqueous reaction mixture was extracted with EtOAc (3x30 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and the solvent was removed under low pressure. The crude product was purified by column chromatography on silica gel (30-40% EtOAc/petroleum ether) to give 1-*O*-Troc-3,4-di-*O*-feruloyl-1,5-quinide, **46** as a white powder (143 mg, 0.20 mmol, 30%); (Li et al., 2005) mp 88-90 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 7.65 (d, 1H, *J* = 16.0 Hz), 7.54 (d, 1H, *J* = 16.0 Hz), 7.08 (dd, 1H, *J* = 1.8, 8.2 Hz), 7.00 (d, 1H, *J* = 1.8 Hz), 6.96 (dd, 1H, *J* = 1.8, 8.2 Hz), 6.92 (d, 1H, *J* = 8.2 Hz), 6.91 (d, 1H, *J* = 1.8 Hz), 6.82 (d, 1H, *J* = 8.2 Hz), 6.34 (d, 1H, *J* = 16.0 Hz), 6.17 (d, 1H, *J* = 16.0 Hz), 6.02 (br, 1H), 5.94 (br, 1H), 5.70 (t, 1H, *J* = 4.6 Hz), 5.35 (m, 1H), 5.02 (t, 1H, *J* = 5.5 Hz), 4.84 (d, 1H, *J* = 11.9 Hz), 4.74 (d, 1H, *J* = 11.9 Hz), 3.91 (s, 3H), 3.80 (s, 3H), 3.19 (m, 1H), 2.74 (d, 1H, *J* = 11.9 Hz), 2.56 (m, 1H), 2.47 (t, 1H, *J* = 11.9 Hz). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 170.24 (OC-*C*OOR), 165.57 (CH-*C*OOR), 165.26 (CH-*C*OOR), 151.52 (O*C*OOCH$_2$), 148.71 (*C*$_{Ar}$-OCH$_3$), 148.36 (*C*$_{Ar}$-OCH$_3$), 147.14 (*C*H-C$_{Ar}$), 146.99 (*C*H-C$_{Ar}$), 146.82 (C$_{Ar}$-OH), 146.49 (C$_{Ar}$-OH), 126.64 (*C*$_{Ar}$-CH), 126.46 (*C*$_{Ar}$-CH), 123.51 (C$_{Ar}$), 123.30 (C$_{Ar}$), 114.98 (C$_{Ar}$), 114.80 (C$_{Ar}$), 113.94 (*C*H-COOR), 113.62 (*C*H-COOR), 109.72 (C$_{Ar}$), 109.72 (C$_{Ar}$), 94.00 ($CCl_3$), 78.88 (C-1), 77.13 (*C*H$_2$-$CCl_3$), 73.89 (C-3), 65.79 (C-4), 64.75 (C-5), 56.08 ($CH_3$), 55.94 ($CH_3$), 33.90 (C-6), 33.83 (C-2).

**3,4-di-*O*-feruloyl-1,5-quinide (3,4-diFQL), 47:** A quantity of 80 mg (0.11 mmol) of 1-*O*-Troc-3,4-di-*O*-feruloyl-1,5-quinide, **46** was suspended in THF (0.75 mL) and an equal volume of glacial acetic acid was added, followed by addition of 54 mg (0.83 mmol, 7.2 eq.) of Zn powder. The grey suspension was stirred at r.t. for 4 h and then the solvents were removed under reduced

pressure. A volume of 15 mL EtOAc was added to the flask and the new suspension was cooled to 0 ºC and extracted with aqueous HCl 0.5M (2x10mL) followed by brine (10 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated in vacuo to yield the white solid product **47** (60 mg, quantitative yield); (Frank et al., 2006) mp 125-127 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 7.65 (d, 1H, *J* = 16.0 Hz), 7.54 (d, 1H, *J* = 16.0 Hz), 7.09 (dd, 1H, *J* = 1.8, 8.2 Hz), 7.01 (d, 1H, *J* = 1.8 Hz), 6.96 (dd, 1H, *J* = 1.8, 8.2 Hz), 6.93 (d, 1H, *J* = 8.2 Hz), 6.91 (d, 1H, *J* = 1.8 Hz), 6.82 (d, 1H, *J* = 8.2 Hz), 6.35 (d, 1H, *J* = 16.0 Hz), 6.17 (d, 1H, *J* = 16.0 Hz), 5.94 (br, 1H), 5.86 (br, 1H), 5.67 (t, 1H, *J* = 4.6 Hz), 5.28 (m, 1H), 4.94 (t, 1H, *J* = 5.5 Hz), 3.92 (s, 6H), 3.80 (s, 3H), 3.00 (br, 1H), 2.64 (d, 1H, *J* = 11.9 Hz), 2.50 (m, 1H), 2.34 (m, 1H), 2.24 (t, 1H, *J* = 11.9 Hz). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 176.91 (OC-*C*OOR), 165.71 (CH-*C*OOR), 165.53 (CH-*C*OOR), 148.63 ($C_{Ar}$-$OCH_3$), 148.27 ($C_{Ar}$-$OCH_3$), 146.96 (*C*H-$C_{Ar}$), 146.92 (*C*H-$C_{Ar}$), 146.80 ($C_{Ar}$-OH), 146.26 ($C_{Ar}$-OH), 126.72 ($C_{Ar}$-CH), 126.53 ($C_{Ar}$-CH), 123.44 ($C_{Ar}$), 123.27 ($C_{Ar}$), 114.97 ($C_{Ar}$), 114.77 ($C_{Ar}$), 114.21 (*C*H-COOR), 113.86 (*C*H-COOR), 109.74 ($C_{Ar}$), 109.69 ($C_{Ar}$), 74.12 (C-1), 72.13 (C-3), 66.23 (C-4), 64.65 (C-5), 56.09 ($CH_3$), 55.94 ($CH_3$), 37.55 (C-6), 37.11 (C-2).

**Synthesis of 3,4-di-*O*-(3,4-dimethoxycinnamoyl)-1,5-quinide (3,4-diDQL), 51.**

**3,4-dimethoxycinnamoyl chloride, 49:** 3,4-dimethoxycinnamic acid, **48** (7000 mg, 33.62 mmol) was added to a solution of 170 mL toluene containing 150 µL of DMF. A volume of 6 mL (8754 mg, 68.96 mmol) oxalyl chloride was added drop-wise at 0 ºC. The reaction mixture was stirred at r.t. for 4 h and the resulting yellow solution was transferred slowly to a new round bottom flask (dark color viscous residues remaining on the bottom of the reaction vessel). The toluene and the unreacted oxalyl chloride were removed under the rotary evaporator to give a yellow solid of **49** (7532 mg, 33.23 mmol, 99%); (Sefkow, 2001) $^1$H-NMR ($CDCl_3$): $\delta_H$ 7.77 (d, 1H, *J* = 15.6 Hz), 7.17 (d, 1H, *J* = 8.2 Hz), 7.05 (d, 1H, *J* = 2.3 Hz), 6.89 (dd, 1H, *J* = 2.3, 8.2

Hz), 6.49 (d, 1H, *J* = 15.6 Hz), 3.93 (s, 3H), 3.92 (s, 3H); $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 166.11 (COCl), 152.97 ($C_{Ar}$-$OCH_3$), 150.93 (*C*H-$C_{Ar}$), 149.67 ($C_{Ar}$-$OCH_3$), 126.15 ($C_{Ar}$-CH), 124.89 ($C_{Ar}$), 119.82 (*C*H-COCl), 111.31 ($C_{Ar}$), 110.12 ($C_{Ar}$), 56.04 ($CH_3$), 55.99 ($CH_3$).

**1-*O*-Troc-3,4-di-*O*-(3,4-dimethoxycinnamoyl)-1,5-quinide, 50:** To a solution of 1-*O*-Troc-1,5-quinide, **41** (1025 mg, 2.86 mmol) in 50 mL DCM, a quantity of 105 mg (0.86 mmol, 30% mol) DMAP was added and a volume of 15 mL of $NEt_3$. A quantity of 1945 mg (8.58 mmol) 3,4-dimethoxycinnamoyl chloride, **49** was then added and the mixture was refluxed for 24 h. It was then allowed to cool to r.t., acidified (pH=2) with a HCl 2M solution and extracted 3 times with DCM (3x30 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and evaporated in vacuo. The product was purified by column chromatography (20-30% EtOAc/petroleum ether) to afford 983 mg (1.35 mmol, 47%) of white solid **50**; (Sefkow, 2001) $^1$H-NMR ($CDCl_3$): $\delta_H$ 7.67 (d, 1H, *J* = 16.0 Hz), 7.57 (d, 1H, *J* = 16.0 Hz), 7.10 (dd, 1H, *J* = 2.3, 8.2 Hz), 7.04 (d, 1H, *J* = 2.3 Hz), 7.00 (dd, 1H, *J* = 2.3, 8.2 Hz), 6.94 (d, 1H, *J* = 2.3 Hz), 6.86 (d, 1H, *J* = 8.2 Hz), 6.77 (d, 1H, *J* = 8.2 Hz), 6.36 (d, 1H, *J* = 16.0 Hz), 6.19 (d, 1H, *J* = 16.0 Hz), 5.71 (t, 1H, *J* = 4.6 Hz), 5.36 (m, 1H), 5.02 (t, 1H, *J* = 5.5 Hz), 4.84 (d, 1H, *J* = 11.9 Hz), 4.73 (d, 1H, *J* = 11.9 Hz), 3.91 (s, 3H), 3.90 (s, 3H), 3.87 (s, 3H), 3.79 (s, 3H), 3.20 (m, 1H), 2.74 (d, 1H, *J* = 11.9 Hz), 2.56 (m, 1H), 2.48 (t, 1H, *J* = 11.9 Hz). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 170.18 (OC-*C*OOR), 165.49 (CH-*C*OOR), 165.21 (CH-*C*OOR), 151.83 (O*C*OOCH$_2$), 151.52 ($C_{Ar}$-$OCH_3$), 151.50 ($C_{Ar}$-$OCH_3$), 149.44 ($C_{Ar}$-$OCH_3$), 149.26 ($C_{Ar}$-$OCH_3$), 146.96 (*C*H-$C_{Ar}$), 146.35 (*C*H-$C_{Ar}$), 127.06 ($C_{Ar}$-CH), 126.86 ($C_{Ar}$-CH), 123.32 ($C_{Ar}$), 123.00 ($C_{Ar}$), 114.24 (*C*H-COOR), 113.91 (*C*H-COOR), 111.15 ($C_{Ar}$), 111.04 ($C_{Ar}$), 109.86 ($C_{Ar}$), 109.73 ($C_{Ar}$), 94.00 ($CCl_3$), 78.88 (C-1), 77.35 (*C*H$_2$-$CCl_3$), 73.87 (C-3), 65.81 (C-4), 64.78 (C-5), 56.12 ($CH_3$), 56.04 ($CH_3$), 56.04 ($CH_3$), 55.88 ($CH_3$), 33.90 (C-6), 33.83 (C-2).

**3,4-di-*O*-(3,4-dimethoxycinnamoyl)-1,5-quinide (3,4-diDQL), 51:** A quantity of 263 mg (0.42 mmol) of 1-*O*-Troc-3,4-di-*O*-(3,4-dimethoxycinnamoyl)-1,5-quinide, **50** was suspended in THF (1.75 mL) and an equal volume (1.75 mL) of glacial acetic acid was added, followed by addition of 87 mg (1.51 mmol, 3.6 eq.) of Zn powder. The grey suspension was stirred at r.t. for 4 h and then the solvents were removed under reduced pressure. A volume of 20 mL EtOAc was added to the flask and the new suspension was cooled to 0 ºC and extracted with aqueous HCl 0.5M (2x15mL) followed by brine (15 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated in vacuo to yield the white solid product **51** (216 mg, 0.39 mmol, 93%); (Frank et al., 2006) mp 101-103 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 7.63 (d, 1H, *J* = 16.0 Hz), 7.50 (d, 1H, *J* = 16.0 Hz), 7.06 (dd, 1H, *J* = 2.3, 8.2 Hz), 7.02 (d, 1H, *J* = 2.3 Hz), 6.92 (dd, 1H, *J* = 2.3, 8.2 Hz), 6.89 (d, 1H, *J* = 2.3 Hz), 6.81 (d, 1H, *J* = 8.2 Hz), 6.70 (d, 1H, *J* = 8.2 Hz), 6.35 (d, 1H, *J* = 16.0 Hz), 6.16 (d, 1H, *J* = 16.0 Hz), 5.64 (t, 1H, 4.6), 5.24 (m, 1H), 4.88 (t, 1H, *J* = 5.5 Hz), 3.86 (s, 6H), 3.80 (s, 3H), 3.72 (s, 3H), 2.59 (d, 1H, *J* = 11.9 Hz), 2.50 (m, 1H), 2.36 (m, 1H), 2.22 (t, 1H, *J* = 11.9 Hz). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 177.15 (OC-*C*OOR), 165.78 (CH-*C*OOR), 165.63 (CH-*C*OOR), 151.69 ($C_{Ar}$-$OCH_3$), 151.36 ($C_{Ar}$-$OCH_3$), 149.35 ($C_{Ar}$-$OCH_3$), 149.17 ($C_{Ar}$-$OCH_3$), 146.73 (*C*H-$C_{Ar}$), 146.11 (*C*H-$C_{Ar}$), 127.07 ($C_{Ar}$-CH), 126.93 ($C_{Ar}$-CH), 123.23 ($C_{Ar}$), 122.93 ($C_{Ar}$), 114.49 ($C_{Ar}$), 114.17 ($C_{Ar}$), 111.14 (*C*H-COOR), 111.00 (*C*H-COOR), 109.85 ($C_{Ar}$), 109.85 ($C_{Ar}$), 74.05 (C-1), 72.21 (C-3), 66.37 (C-4), 64.69 (C-5), 56.06 ($CH_3$), 56.00 ($CH_3$), 55.97 ($CH_3$), 55.82 ($CH_3$), 37.53 (C-6), 36.66 (C-2).

**Synthesis of methyl 3,4-di-*O*-caffeoylquinate (3,4-diCQM), 56.**

**3,4-Di-*O*-allylcaffeic acid, 52:** A mixture of caffeic acid, **34** (5 g, 27.75 mmol) and anhydrous potassium carbonate (55.3 g, 401 mmol) in acetone (250 mL) was stirred at room temperature for 30 min. To the mixture was added a solution of allyl bromide (6.23 g, 51.5

mmol) in acetone (50 mL) and the entire mixture was refluxed for 48 h. The reaction was cooled to r.t., filtered and the filtrate was dried in vacuo. The residue was suspended in ethanol (150 mL) and a NaOH 2M solution (100 mL) was added. The mixture was refluxed for 2 h. The solution was cooled to r.t., poured into a beaker and acidified (pH 2) with conc. HCl. The suspension was stirred at r.t. for 30 min and the solid was filtered off and washed successively with a 1:1 mixture of ethanol/water (200 mL). The solid was dried overnight in vacuum to yield a white powder of **52** (6.16 g, 23.59 mmol, 85%); (Matei et al., 2012; Barros and Silva, 2006; Jaiswal et al., 2012) mp 155-157 ºC; $^{1}$H-NMR ($CDCl_3$): $\delta_H$ 7.70 (d, 1H, *J* = 16.0 Hz), 7.11 (dd, 1H, *J* = 1.8, 8.2 Hz), 7.09 (d, 1H, *J* = 1.8 Hz), 6.88 (d, 1H, *J* = 8.2 Hz), 6.28 (d, 1H, *J* = 16.0 Hz), 6.07 (m, 2H), 5.43 (d, 1H, *J* = 16.9 Hz), 5.42 (d, 1H, *J* = 16.9 Hz), 5.31 (d, 1H, *J* = 10.5 Hz), 5.30 (d, 1H, *J* = 10.5 Hz), 4.64 (m, 4H). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 172.53 (COOH), 151.11 ($C_{Ar}$-$OCH_2$), 148.56 ($C_{Ar}$-$OCH_2$), 147.06 ($C$H-$C_{Ar}$), 133.11 ($C$H=$CH_2$), 132.89 ($C$H=$CH_2$), 127.24 ($C_{Ar}$-CH), 123.26 ($C_{Ar}$), 118.16 ($CH_2$=CH), 118.09 ($CH_2$=CH), 114.86 ($C$H-COOH), 113.42 ($C_{Ar}$), 112.85 ($C_{Ar}$), 70.05 ($C_{Ar}$-O$CH_2$), 69.80 ($C_{Ar}$-O$CH_2$).

**3,4-Di-*O*-allylcaffeoyl chloride, 53:** 3,4-di-*O*-allylcaffeic acid, **52** (6.16 g, 23.59 mmol) was added to a solution of 100 mL toluene containing 150 µL of dimethylformamide (DMF). A volume of 6.8 mL (9.90 g, 77.98 mmol) oxalyl chloride was added drop-wise at 0 ºC. The reaction mixture was stirred at r.t. for 4 h and the resulting brown solution was transferred slowly to a new round bottom flask (dark color viscous residues remaining on the bottom of the reaction vessel). The toluene and the unreacted oxalyl chloride were removed under rotary evaporator to give a light brown solid of **53** (6.05 g, 21.70 mmol, 92%); (Matei et al., 2012; Jaiswal et al., 2012; Sefkow, 2001) mp 67-68 ºC; $^{1}$H-NMR ($CDCl_3$): $\delta_H$ 7.74 (d, 1H, *J* = 15.6 Hz), 7.14 (dd, 1H, *J* = 1.8, 8.2 Hz), 7.07 (d, 1H, *J* = 1.8 Hz), 6.89 (d, 1H, *J* = 8.2 Hz), 6.45 (d, 1H, *J* = 15.6 Hz),

6.07 (m, 2H), 5.44 (d, 1H, *J* = 16.9 Hz), 5.43 (d, 1H, *J* = 16.9 Hz), 5.32 (d, 1H, *J* = 10.5 Hz), 5.31 (d, 1H, *J* = 10.5 Hz), 4.65 (m, 4H). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 166.12 (COCl), 152.33 ($C_{Ar}$-$OCH_2$), 150.90 ($C_{Ar}$-$OCH_2$), 148.81 ($C$H-$C_{Ar}$), 132.90 ($C$H=$CH_2$), 132.58 ($C$H=$CH_2$), 126.16 ($C_{Ar}$-CH), 124.68 ($C_{Ar}$), 119.85 (COCl), 118.36 ($C$H$_2$=CH), 118.22 ($C$H$_2$=CH), 113.33 ($C_{Ar}$), 113.19 ($C_{Ar}$), 70.10 ($C_{Ar}$-O$C$H$_2$), 69.78 ($C_{Ar}$-O$C$H$_2$).

**1-*O*-Troc-3,4-di-*O*-(3,4-di-*O*-allylcaffeoyl)-1,5-quinide, 54:** To a solution of 1-*O*-Troc-1,5-quinide, **41** (1770 mg, 5.06 mmol) in 100 mL DCM, a quantity of 242 mg (1.98 mmol, 40% mol) DMAP was added and a volume of 20 mL of $NEt_3$. A quantity of 6000 mg (21.53 mmol) 3,4-di-*O*-allylcaffeoyl chloride, **53** was then added and the mixture was refluxed for 72 h. It was then allowed to cool to r.t., acidified (pH=2) with a HCl 2M solution and extracted 3 times with DCM (3x50 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and evaporated in vacuo. The product was purified by column chromatography (20-30% EtOAc/petroleum ether) to afford 3075 mg (3.69 mmol, 73%) of white solid **54**; (Sefkow, 2001) mp 104-105 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 7.64 (d, 1H, *J* = 16.0 Hz), 7.55 (d, 1H, *J* = 16.0 Hz), 7.08 (dd, 1H, *J* = 1.8, 8.2 Hz), 7.08 (d, 1H, *J* = 1.8 Hz), 6.98 (dd, 1H, *J* = 1.8, 8.2 Hz), 6.98 (d, 1H, *J* = 8.2 Hz), 6.87 (d, 1H, *J* = 8.2 Hz), 6.79 (d, 1H, *J* = 8.2 Hz), 6.32 (d, 1H, *J* = 16.0 Hz), 6.16 (d, 1H, *J* = 16.0 Hz), 6.13-5.95 (m, 4H), 5.70 (t, 1H, *J* = 4.6 Hz), 5.46-5.22 (m, 9H), 5.01 (t, 1H, *J* = 5.5 Hz), 4.84 (d, 1H, *J* = 11.4 Hz), 4.73 (d, 1H, *J* = 11.4 Hz), 4.66-4.59 (m, 6H), 4.51 (d, 2H, *J* = 5.5 Hz), 3.20 (m, 1H), 2.73 (d, 1H, *J* = 11.4 Hz), 2.56 (m, 1H), 2.47 (t, 1H, *J* = 11.9 Hz). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 170.19 (OC-*C*OOR), 165.49 (CH-*C*OOR), 165.22 (CH-*C*OOR), 151.52 ($C_{Ar}$-$OCH_2$), 151.35 ($C_{Ar}$-$OCH_2$), 151.01 (O*C*OO$CH_2$), 148.75 ($C_{Ar}$-$OCH_2$), 148.60 ($C_{Ar}$-$OCH_2$), 146.86 ($C$H-$C_{Ar}$), 146.30 ($C$H-$C_{Ar}$), 133.05 ($C$H=$CH_2$), 133.00 ($C$H=$CH_2$), 132.87 ($C$H=$CH_2$), 132.78 ($C$H=$CH_2$), 127.22 ($C_{Ar}$-CH), 126.99 ($C_{Ar}$-CH), 123.36 ($C_{Ar}$), 123.05 ($C_{Ar}$), 118.20 ($C$H$_2$=CH), 118.13

($CH_2$=CH), 118.11 ($CH_2$=CH), 117.99 ($CH_2$=CH), 113.96 (CH-COOR), 113.41 (CH-COOR), 111.38 ($C_{Ar}$), 111.38 ($C_{Ar}$), 112.88 ($C_{Ar}$), 112.78 ($C_{Ar}$), 94.00 ($CCl_3$), 78.88 (C-1), 77.32 ($CH_2$-$CCl_3$), 73.86 (C-3), 70.10 ($C_{Ar}$-O$CH_2$), 69.98 ($C_{Ar}$-O$CH_2$), 69.78 ($C_{Ar}$-O$CH_2$), 69.78 ($C_{Ar}$-O$CH_2$), 65.79 (C-4), 64.78 (C-5), 33.89 (C-6), 33.84 (C-2).

**Methyl 1-*O*-Troc-3,4-di-*O*-caffeoylquinate, 55:** To a solution of 833 mg (1.00 mmol) of 1-*O*-Troc-3,4-di-*O*-(3,4-di-*O*-allylcaffeoyl)-1,5-quinide, **54** in 50 mL of aqueous MeOH (90%), a quantity of 76 mg (0.40 mmol) of PTSA·$H_2O$ was added. The reaction mixture was put under a nitrogen atmosphere, Pd/C (781 mg) was slowly added at r.t. and it was then heated to 80 ºC for 48 h. The mixture was cooled to r.t., filtered and the solvents removed in vacuo. The crude product was purified by column chromatography on silica gel (n-heptane/acetone/MeOH = 60/35/5) to give methyl 1-*O*-Troc-3,4-di-*O*-caffeoylquinate, **55** as a white powder (212 mg, 0.30 mmol, 30%); (Barros and Silva, 2006) mp 128-130 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 8.30 (br, 4H), 7.57 (d, 1H, *J* = 16.0 Hz), 7.50 (d, 1H, *J* = 16.0 Hz), 7.12 (d, 1H, *J* = 2.3 Hz), 7.11 (d, 1H, *J* = 2.3 Hz), 7.02 (dd, 1H, *J* = 2.3, 8.2 Hz), 6.94 (dd, 1H, *J* = 2.3, 8.2 Hz), 6.85 (d, 1H, *J* = 8.2 Hz), 6.79 (d, 1H, *J* = 8.2 Hz), 6.23 (d, 1H, *J* = 16.0 Hz), 6.22 (d, 1H, *J* = 16.0 Hz), 5.67 (q, 1H, *J* = 3.7, 7.3 Hz), 5.05 (dd, 1H, *J* = 3.7, 9.2 Hz), 4.93 (d, 1H, *J* = 12.4 Hz), 4.63 (d, 1H, *J* = 12.4 Hz), 4.42 (td, 1H, *J* = 3.7, 10.1 Hz), 3.73 (s, 3H), 3.11 (br, 1H), 2.73 (dt, 1H, *J* = 3.7, 15.6 Hz), 2.63 (dd, 1H, *J* = 3.7, 15.6 Hz), 2.54 (m, 1H), 2.10 (m, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 170.08 ($COOCH_3$), 166.07 (CH-COOR), 165.60 (CH-COOR), 152.37 (O$COOCH_2$), 148.08 ($C_{Ar}$-OH), 148.02 ($C_{Ar}$-OH), 145.54 (CH-$C_{Ar}$), 145.54 (CH-$C_{Ar}$), 145.47 ($C_{Ar}$-OH), 145.33 ($C_{Ar}$-OH), 126.71 ($C_{Ar}$-CH), 126.67 ($C_{Ar}$-CH), 121.95 ($C_{Ar}$), 121.95 ($C_{Ar}$), 115.58 ($C_{Ar}$), 115.54 ($C_{Ar}$), 114.56 (CH-COOR), 114.56 (CH-COOR), 114.52 ($C_{Ar}$), 114.27 ($C_{Ar}$), 94.64 ($CCl_3$), 82.97 (C-1), 76.45 ($CH_2$-$CCl_3$), 74.70 (C-3), 68.02 (C-4), 64.04 (C-5), 52.45 ($CH_3$), 39.50 (C-6), 31.94 (C-2).

**Methyl 3,4-di-*O*-caffeoylquinate (3,4-diCQM), 56:** A quantity of 100 mg (0.14 mmol) of methyl 1-*O*-Troc-3,4-di-*O*-caffeoylquinate, **55** was suspended in THF (1.00 mL) and an equal volume of glacial acetic acid was added, followed by addition of 67 mg (1.02 mmol, 7.2 eq.) of Zn powder. The grey suspension was stirred at r.t. for 4 h and then the solvents were removed under reduced pressure. A volume of 20 mL EtOAc was added to the flask and the new suspension was cooled to 0 ºC and extracted with aqueous HCl 0.5M (2x10mL) followed by brine (10 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated in vacuo to yield the white solid product **56** (75 mg, quantitative yield); (Frank et al., 2006) mp 131-133 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 7.53 (d, 1H, *J* = 16.0 Hz), 7.52 (d, 1H, *J* = 16.0 Hz), 7.01 (d, 1H, *J* = 2.3 Hz), 7.00 (d, 1H, *J* = 2.3 Hz), 6.88 (dd, 1H, *J* = 2.3, 8.2 Hz), 6.86 (dd, 1H, *J* = 2.3, 8.2 Hz), 6.73 (d, 1H, *J* = 8.2 Hz), 6.71 (d, 1H, *J* = 8.2 Hz), 6.24 (d, 1H, *J* = 16.0 Hz), 6.23 (d, 1H, *J* = 16.0 Hz), 5.60 (m, 1H), 5.01 (dd, 1H, *J* = 3.2, 8.5 Hz), 4.30 (td, 1H, *J* = 4.6, 8.5 Hz), 3.73 (s, 3H), 2.33 (dd, 1H, *J* = 3.7, 14.7 Hz), 2.19-2.06 (m, 3H). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 174.81 (*C*$OOCH_3$), 167.19 (CH-*C*OOR), 167.12 (CH-*C*OOR), 148.31 ($C_{Ar}$-OH), 148.27 ($C_{Ar}$-OH), 146.04 (*C*H-$C_{Ar}$), 146.04 (*C*H-$C_{Ar}$), 145.45 (*C*H-$C_{Ar}$), 145.45 (*C*H-$C_{Ar}$), 126.42 (*C*$_{Ar}$-CH), 126.34 (*C*$_{Ar}$-CH), 121.92 ($C_{Ar}$), 121.81 ($C_{Ar}$), 115.14 (*C*H-COOR), 115.14 (*C*H-COOR), 113.84 ($C_{Ar}$), 113.74 ($C_{Ar}$), 113.66 ($C_{Ar}$), 113.53 ($C_{Ar}$), 74.29 (C-1), 73.85 (C-3), 68.52 (C-4), 64.71 (C-5), 51.65 ($CH_3$), 40.01 (C-6), 35.48 (C-2).

**Synthesis of methyl 3,4-di-*O*-feruloylquinate (3,4-diFQM), 58.**

**Methyl 1-O-Troc-3,4-di-O-feruloylquinate, 57:** To a solution of 450 mg (0.58 mmol) of 1-*O*-Troc-3,4-di-*O*-(4-*O*-allylferuloyl)-1,5-quinide, **45** in 30 mL of aqueous MeOH (90%), a quantity of 23 mg (0.11 mmol) of PTSA·$H_2O$ was added. The reaction mixture was put under a nitrogen atmosphere, Pd/C (225 mg) was slowly added at r.t. and it was then heated to 80 ºC for

48 h. The mixture was cooled to r.t., filtered and MeOH removed in vacuo. The aqueous reaction mixture was extracted with EtOAc (3x25 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and the solvent was removed under low pressure. The crude product was purified by column chromatography on silica gel (30-40% EtOAc/petroleum ether) to give methyl 1-*O*-Troc-3,4-di-*O*-feruloylquinate, **57** as a white powder (203 mg, 0.28 mmol, 48%); (Barros and Silva, 2006) mp 120-121 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 7.61 (d, 1H, *J* = 16.0 Hz), 7.57 (d, 1H, *J* = 16.0 Hz), 7.05 (dd, 1H, *J* = 1.8, 8.2 Hz), 6.98 (d, 1H, *J* = 1.8 Hz), 6.97 (dd, 1H, *J* = 1.8, 8.2 Hz), 6.92 (d, 1H, *J* = 1.8 Hz), 6.88 (d, 1H, *J* = 8.2 Hz), 6.83 (d, 1H, *J* = 8.2 Hz), 6.27 (d, 1H, *J* = 16.0 Hz), 6.22 (d, 1H, *J* = 16.0 Hz), 5.97 (br, 2H), 5.72 (q, 1H, *J* = 3.7, 7.3 Hz), 5.03 (dd, 1H, *J* = 3.4, 9.2 Hz), 4.76 (d, 1H, *J* = 11.9 Hz), 4.53 (d, 1H, *J* = 11.9 Hz), 4.50 (m, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 2.85 (m, 1H), 2.64 (m, 1H), 2.51 (dd, 1H, *J* = 3.4, 15.8 Hz), 2.05 (m, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 170.54 (*C*OOCH$_3$), 166.88 (CH-*C*OOR), 166.16 (CH-*C*OOR), 152.33 (O*C*OOCH$_2$), 148.36 ($C_{Ar}$-OCH$_3$), 148.31 ($C_{Ar}$-OCH$_3$), 146.92 (*C*H-$C_{Ar}$), 146.82 (*C*H-$C_{Ar}$), 146.39 ($C_{Ar}$-OH), 145.95 ($C_{Ar}$-OH), 126.74 (*C*$_{Ar}$-CH), 126.74 (*C*$_{Ar}$-CH), 123.53 ($C_{Ar}$), 123.40 ($C_{Ar}$), 114.86 (*C*H-COOR), 114.82 (*C*H-COOR), 114.82 ($C_{Ar}$), 114.35 ($C_{Ar}$), 109.65 ($C_{Ar}$), 109.49 ($C_{Ar}$), 94.27 ($CCl_3$), 82.70 (C-1), 77.11 (*C*H$_2$-CCl$_3$), 75.20 (C-3), 67.73 (C-4), 64.98 (C-5), 56.10 ($C_{Ar}$-O*C*H$_3$), 55.95 ($C_{Ar}$-O*C*H$_3$), 53.34 (COO*C*H$_3$), 39.31 (C-6), 32.14 (C-2).

**Methyl 3,4-di-*O*-feruloylquinate (3,4-diFQM), 58:** A quantity of 109 mg (0.15 mmol) of 1-*O*-Troc-3,4-di-*O*-feruloylquinate, **57** was suspended in THF (1.00 mL) and an equal volume of glacial acetic acid was added, followed by addition of 70 mg (1.07 mmol, 7.2 eq.) of Zn powder. The grey suspension was stirred at r.t. for 4 h and then the solvents were removed under reduced pressure. A volume of 15 mL EtOAc was added to the flask and the new suspension was cooled to 0 ºC and extracted with aqueous HCl 0.5M (2x10mL) followed by brine (10 mL). The organic

layer was dried over $Na_2SO_4$, filtered and concentrated in vacuo to yield the white solid product **58** (83 mg, quantitative yield); (Frank et al., 2006) mp 121-123 ºC; $^1$H-NMR ($CDCl_3$): $\delta_H$ 7.62 (d, 1H, *J* = 16.0 Hz), 7.61 (d, 1H, *J* = 16.0 Hz), 7.05 (dd, 1H, *J* = 1.8, 8.2 Hz), 7.01 (dd, 1H, *J* = 1.8, 8.2 Hz), 7.00 (d, 1H, *J* = 1.8 Hz), 6.96 (d, 1H, *J* = 1.8 Hz), 6.89 (d, 1H, *J* = 8.2 Hz), 6.86 (d, 1H, *J* = 8.2 Hz), 6.31 (d, 1H, *J* = 16.0 Hz), 6.27 (d, 1H, *J* = 16.0 Hz), 5.90 (br, 2H), 5.66 (q, 1H, *J* = 3.7, 7.3 Hz), 5.02 (dd, 1H, *J* = 3.2, 9.2 Hz), 4.51 (td, 1H, *J* = 4.6, 10.1 Hz), 3.91 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 3.28 (br, 1H), 2.30 (dd, 2H, *J* = 3.2, 15.1 Hz), 2.21 (dt, 1H, *J* = 3.2, 15.1 Hz), 2.11 (m, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta_C$ 175.37 (*C*OOCH$_3$), 167.00 (CH-*C*OOR), 166.41 (CH-*C*OOR), 148.27 ($C_{Ar}$-OCH$_3$), 148.24 ($C_{Ar}$-OCH$_3$), 146.87 (*C*H-$C_{Ar}$), 146.81 (*C*H-$C_{Ar}$), 146.26 ($C_{Ar}$-OH), 145.89 ($C_{Ar}$-OH), 126.91 (*C*$_{Ar}$-CH), 126.82 (*C*$_{Ar}$-CH), 123.45 ($C_{Ar}$), 123.45 ($C_{Ar}$), 115.07 (*C*H-COOR), 114.79 (*C*H-COOR), 114.79 ($C_{Ar}$), 114.57 ($C_{Ar}$), 109.57 ($C_{Ar}$), 109.47 ($C_{Ar}$), 75.73 (C-1), 74.50 (C-3), 68.96 (C-4), 65.38 (C-5), 56.09 ($C_{Ar}$-O*C*H$_3$), 55.99 ($C_{Ar}$-O*C*H$_3$), 53.47 (COO*C*H$_3$), 41.34 (C-6), 36.46 (C-2).

**Table S1**. High resolution (UPLC-QTOF-MS) data of *A. maritima* and *S. oleraceus* phenolics

| No. | Compound identity | Rt (min) | Mol. formula | The. *m/z* (M−H) | Exp. *m/z* (M−H) | Error (ppm) | MS/MS fragments | Ref./Std. |
|---|---|---|---|---|---|---|---|---|
| 1 | Esculin [a,s] | 14.9 | $C_{15}H_{16}O_9$ | 339.0722 | 339.0720 | 0.6 | 177.0192 | Std. |
| 2 | Luteolin 7-*O*-glucoside [a,s] | 37.2 | $C_{21}H_{20}O_{11}$ | 447.0933 | 447.0930 | 0.6 | 285.0400 | Std. |
| 3 | 5-*O*-Caffeoylquinic acid [a,s] | 18.5 | $C_{16}H_{18}O_9$ | 353.0878 | 353.0879 | -0.3 | 191.0560, 179.0358, 133.0303 | Std. |
| 4 | *cis*-5-*O*-Caffeoylquinic acid [a,s] | 23.2 | $C_{16}H_{18}O_9$ | 353.0878 | 353.0878 | -0.1 | 191.0565, 133.0299, 173.0455, 85.0297 | (Karar et al., 2013) |
| 5 | 3,5-di-*O*-Caffeoylquinic acid [a,s] | 45.3 | $C_{25}H_{24}O_{12}$ | 515.1195 | 515.1199 | -0.9 | Not fragmented | Std. |
| 6 | 4,5-di-*O*-Caffeoylquinic acid [a,s] | 46.8 | $C_{25}H_{24}O_{12}$ | 515.1195 | 515.1190 | 1.0 | Not fragmented | Std. |
| 7 | 3,4-di-*O*-Caffeoylquinic acid [a] | 45.4 | $C_{25}H_{24}O_{12}$ | 515.1195 | 515.1107 | -2.4 | 353.0858, 191.0569, 179.0331, 173.0447, 143.1081 | Std. |
| 8 | Quercetin 3-*O*-(6-*O*-rhmanosyl-glucoside) (rutin) [a,s] | 41.4 | $C_{27}H_{30}O_{16}$ | 609.1461 | 609.1441 | 3.2 | 301.0338, 209.0798, 112.9850 | Std. |
| 9 | Kaempferol 3-*O*-(6-*O*-rhamnosyl-galactoside) [a] | 45.1 | $C_{27}H_{30}O_{15}$ | 593.1512 | 593.1497 | 2.5 | 112.9845, 96.9703 | (Jaiswal et al., 2014) |
| 10 | Kaempferol 3-*O*-(6-*O*-rhamnosyl-glucoside) [a] | 46.0 | $C_{27}H_{30}O_{15}$ | 593.1512 | 593.11496 | 2.7 | 285.0408, 112.9858, 96.9675, 159.1047 | Std. |
| 11 | Kaempferol 7-*O*-glucoside [a] | 50.2 | $C_{21}H_{20}O_{11}$ | 447.0933 | 447.0916 | 3.7 | 285.0357, 174.9541, 112.9840 | Std. |
| 12 | Quercetin 3-*O*-glucoside [a] | 42.0 | $C_{21}H_{20}O_{12}$ | 463.0882 | 463.0871 | 2.3 | 301.0337, 178.9980 | Std. |
| 13 | Gallic acid *O*-hexoside [a] | 7.9 | $C_{13}H_{16}O_{10}$ | 331.0671 | 331.0655 | 4.6 | 169.0153 | (Barros et al., 2013) |
| 14 | Salicylic acid *O*-glucoside [a,s] | 12.8 | $C_{13}H_{16}O_8$ | 299.0772 | 299.0773 | -0.3 | 137.0247 | (Abu-Reidah et al., 2012) |
| 15 | *p*-Coumaric acid *O*- | 17.4 | $C_{15}H_{18}O_8$ | 325.0929 | 325.0929 | 0.1 | 163.0403, 119.0504 | (Abu-Reidah et al., |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | hexoside [a] | | | | | | | 2012; Jaiswal and Kuhnert, 2014) |
| 16 | Caffeic acid *O*-glucoside [a] | 17.5 | $C_{15}H_{18}O_9$ | 341.0878 | 341.0876 | 0.6 | 179.0351, 135.0439 | (Abu-Reidah et al., 2012) |
| 17 | Apigenin 6,8-di-*C*-glucoside [a] | 27.1 | $C_{27}H_{30}O_{15}$ | 593.1512 | 593.1506 | 1.0 | Not fragmented | (Karar et al., 2013) |
| 18 | Apigenin 6-*C*-pentosyl-8-*C*-hexoside [a,s] | 31.5 | $C_{26}H_{28}O_{14}$ | 563.1406 | 563.1307 | -0.2 | Not fragmented | (Ernst, 2009; Ferreres et al., 2003) |
| 19 | 5-*p*-Coumaroylquinic acid [a] | 27.7 | $C_{16}H_{18}O_8$ | 337.0929 | 337.0938 | -2.8 | 191.0565, 163.0384, 93.0350 | (Clifford et al., 2006; Clifford et al., 2008) |
| 20 | Quercetin 7-*O*-rhamnoside [a] | 44.4 | $C_{21}H_{20}O_{11}$ | 447.0933 | 447.0916 | 3.8 | Not fragmented | (Jaiswal et al., 2014) |
| 21 | Quercetin *O*-acetyl hexoside [a] | 47.7 | $C_{23}H_{22}O_{13}$ | 505.0988 | 505.0977 | 2.1 | Not fragmented | (Tusevski et al., 2013; Banos et al., 2012) |
| 22 | Isorhamnetin [a] | 67.2 | $C_{16}H_{12}O_7$ | 315.0510 | 315.0510 | 2.4 | 300.0262, 251.1648, 217.0825, 112.9833 | (Rauha et al., 2001) |
| 23 | Luteolin [a,s] | 69.7 | $C_{15}H_{10}O_6$ | 285.0405 | 285.0399 | 2.0 | 255.0288, 241.0506, 151.0336, 217.0525 | Std. |
| 24 | Quercetin [a] | 51.7 | $C_{15}H_{10}O_7$ | 301.0354 | 301.0363 | -3.1 | 273.0446, 151.0044, 178.9996 | Std. |
| 25 | Quinic acid [a,s] | 3.0 | $C_7H_{12}O_6$ | 191.0561 | 191.0561 | 0.3 | 173.0453, 127.0400, 85.0294 | Std. |
| 26 | Quercetin 7-*O*-glucoside [s] | 34.0 | $C_{21}H_{20}O_{12}$ | 463.0982 | 463.0885 | -0.6 | 301.0337, 112.9845 | (Zhao et al., 2014) |
| 27 | Kaempferol 3,7-di-*O*-hexoside [s] | 29.7 | $C_{27}H_{30}O_{16}$ | 609.1461 | 609.1461 | 0.1 | Not fragmented | (Ferreres et al., 2008) |
| 28 | Luteolin 7-*O*-pentosyl-hexoside [s] | 36.3 | $C_{26}H_{28}O_{15}$ | 579.1355 | 579.1367 | -2.0 | 285.0384, 112.9851 | (Lin and Harnly, 2010) |
| 29 | Kaempferol 3-*O*-acetylhexoside [s] | 48.2 | $C_{23}H_{22}O_{12}$ | 489.1038 | 489.1029 | 2.0 | Not fragmented | (Abad-Garcia et al., 2009; Kajdzanoska et al., 2010) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 30 | Kaempferol 7-*O*-acetylhexoside [s] | 43.7 | $C_{23}H_{22}O_{12}$ | 489.1038 | 489.1030 | 1.8 | 285.0404, 112.9853 | (Banos et al., 2012; Abad-Garcia et al., 2009) |
| 31 | Apigenin 7-*O*-galactoside [s] | 41.9 | $C_{21}H_{20}O_{10}$ | 431.0984 | 431.0988 | -1.0 | 269.0448, 147.3070 | Std. |
| 32 | 6-*O*-Feruloyl-glucose [s] | 13.9 | $C_{16}H_{20}O_9$ | 355.1035 | 355.1033 | 0.5 | Not fragmented | (Abu-Reidah et al., 2012; Jaiswal and Kuhnert, 2014) |
| 33 | Protocatechuic acid *O*-hexoside [s] | 6.8 | $C_{13}H_{16}O_9$ | 315.0722 | 315.0723 | -0.4 | 153.0188, 109.0298, 107.0488 | (Brannan et al., 2015) |
| 34 | Caffeic acid [s] | 11.6 | $C_9H_8O_4$ | 179.0350 | 179.0353 | -2.0 | 135.0454, 133.0280, 105.0348 | Std. |
| 35 | 5-*O*-(3'-*O*-Caffeoyl glucosyl)quinic acid [s] | 15.8 | $C_{22}H_{28}O_{14}$ | 515.1406 | 515.1410 | -0.7 | Not fragmented | (Jaiswal et al., 2014; Jaiswal et al., 2014) |
| 36 | Esculetin [s] | 20.4 | $C_9H_6O_4$ | 177.0193 | 177.0193 | 0.1 | 133.0294, 105.0348, 89.0329 | (Whitehill et al., 2012) |
| 37 | Esculetin 6,7-di-*O*-glucopyranoside [s] | 17.2 | $C_{21}H_{26}O_{14}$ | 501.1250 | 501.1250 | -0.1 | 177.093, 164.0715 | (Lin et al., 2007; Zhao et al., 2008) |
| 38 | Esculetin *O*-acetylglucoside [s] | 25.2 | $C_{17}H_{18}O_{10}$ | 381.0827 | 381.0830 | -0.7 | 177.0194, 112.9838 | NA |

a: present in *A. maritima*; s: present in *S. oleraceus*; Std.: Compounds identified after comparison with their commercial standards; NA: No literature data available

resent in *S. oleraceus*)

**Table S2**. HPLC-$MS^n$ fragmentation of *A. maritima* and *S. oleraceus* phenolics (a: present in *A. maritima*; s: present in *S. oleraceus*)

| No. | Compound name | Parent ion (M−H) | Characteristic *m/z* of ions in negative ion mode |
|---|---|---|---|
| 1 | Esculin [a,s] | 339 | $MS^2$ → 177 (100); $MS^3$ → 133 (100), 105 (14) |
| 2 | Luteolin 7-*O*-glucoside [a,s] | 447 | $MS^2$ → 285 (100); $MS^3$ → 199 (100), 217 (48), 175 (61), 151 (31), 241 (43); $MS^4$ → 169 (30) |
| 3 | 5-*O*-Caffeoylquinic acid [a,s] | 353 | $MS^2$ → 191 (100); $MS^3$ → 85 (100), 167 (99), 173 (65) |
| 4 | *cis*-5-*O*-Caffeoylquinic acid [a,s] | 353 | $MS^2$ → 191 (100); $MS^3$ → 127 (100), 173 (30), 145 (31), 111 (24), 94 (73), 72 (42) |
| 5 | 3,5-di-*O*-Caffeoylquinic acid [a,s] | 515 | $MS^2$ → 353 (100); $MS^3$ → 191 (100), 179 (43); $MS^4$ → 127 (100), 173 (89), 155 (33), 111 (51), 85 (81), 71 (67) |
| 6 | 4,5-di-*O*-Caffeoylquinic acid [a,s] | 515 | $MS^2$ → 353 (100); $MS^3$ → 173 (100), 191 (31), 179 (53), 135 (13); $MS^4$ → 93 (100), 111 (29), 115 (20), 59 (11) |
| 7 | 3,4-di-*O*-Caffeoylquinic acid [a] | 515 | $MS^2$ → 353 (100); $MS^3$ → 173 (100), 179 (77), 191 (47), 135 (15); $MS^4$ → 93 (100), 155 (53), 111 (60), 83 (53), 71 (77), 60 (20) |
| 8 | Quercetin 3-*O*- (6-*O*-rhmanosyl-glucoside) (rutin) [a,s] | 609 | $MS^2$ → 301 (100), 300 (18); $MS^3$ → 151 (100), 179 (82), 255 (49), 27 (51); $MS^4$ → 107 (100), 139 (20), 169 (26) |
| 9 | Kaempferol 3-*O*-(6-*O*-rhamnosyl-galactoside) [a] | 593 | $MS^2$ → 285 (100), 284 (41), 255 (17); $MS^3$ → 284 (100), 257 (30), 255 (25)241 (13) |
| 10 | Kaempferol 3-*O*-(6-*O*-rhamnosyl-glucoside) [a] | 593 | $MS^2$ → 285 (100); $MS^3$ → 257 (100), 267 (30), 241 (28), 229 (40); $MS^4$ → 255 (100), 229 (62), 212 (38), 185 (43), 163 (49) |
| 11 | Kaempferol 7-*O*-glucoside [a] | 447 | $MS^2$ → 285 (100), 284 (77), 255 (30); $MS^3$ → 255 (100), 284 (20) ; $MS^4$ → 255 (100) |
| 12 | Quercetin 3-*O*-glucoside [a] | 463 | $MS^2$ → 301 (100); $MS^3$ → 179 (100), 271 (39), 151 (90), 255 (16 ); $MS^4$ → 151 (100) |
| 13 | Gallic acid *O*-hexoside [a] | 331 | $MS^2$ → 169 (100); $MS^3$ → 125 (100), 150 (15), 82 (20) |
| 14 | Salicylic acid *O*-glucoside [a,s] | 299 | $MS^2$ → 137 (100); $MS^3$ → 93 (100) |
| 15 | *p*-Coumaric acid *O*-hexoside [a] | 325 | $MS^2$ → 193 (100), 163 (45); $MS^3$ → 149 (100), 178 (65), 134 (79) |
| 16 | Caffeic acid *O*-glucoside [a] | 341 | $MS^2$ → 179 (100), 135 (15); $MS^3$ → 135 (100) |

| | | | |
|---|---|---|---|
| 17 | Apigenin 6,8-di-*C*-glucoside [a] | 593 | $MS^2$ → 473 (100), 503 (30), 383 (40), 353 (70); $MS^3$ → 353 (100), 383 (23); $MS^4$ → 325 (100), 353 (50), 297 (62) |
| 18 | Apigenin 6-*C*-pentosyl-8-*C*-hexoside [a,s] | 563 | $MS^2$ → 383 (100), 503 (80), 473 (95), 433 (73), 353 (93), 323 (10), 545 (25); $MS^3$ → 365 (100), 355 (18), 337 (28), 325 (11), 284 (13); $MS^4$ → 308 (100), 337 (69), 365 (56) |
| 19 | 5-*p*-Coumaroylquinic acid [a] | 337 | $MS^2$ → 191 (100), 163 (05); $MS^3$ → 85 (100), 173 (45), 155 (22), 127 (22) |
| 20 | Quercetin 7-*O*-rhamnoside [a] | 447 | $MS^2$ → 301 (100); $MS^3$ → 179 (100), 151 (83), 273 (15); $MS^4$ → 151 (100) |
| 21 | Quercetin *O*-acetyl hexoside [a] | 505 | $MS^2$ → 301 (100); $MS^3$ → 300 (100), 151 (44), 271 (16), 179 (45); $MS^4$ → 107 (100) |
| 22 | Isorhamnetin [a] | 315 | $MS^2$ → 300 (100); $MS^3$ → 300 (100), 214 (02); $MS^4$ → 241 (100), 188 (65), 158 (57) |
| 23 | Luteolin [a,s] | 285 | $MS^2$ → 285 (100), 241 (46), 175 (39), 199 (22), 217 (15); $MS^3$ → 241 (100), 199 (79), 226 (12), 215 (12); $MS^4$ → 199 (100), 215 (68) |
| 24 | Quercetin [a] | 301 | $MS^2$ → 179 (100), 151 (93), 273 (19), 257 (14) |
| 25 | Quinic acid [a,s] | 191 | $MS^2$ → 85 (100), 127 (70), 173 (71); $MS^3$ → 83 (100), 109 (23) |
| 26 | Quercetin 7-*O*-glucoside [s] | 463 | $MS^2$ → 301 (100); $MS^3$ → 151 (100), 251 (14), 239 (34), 215 (32), 257 (23), 107 (13); $MS^4$ → 107 (100), 169 (36), 83 (12) |
| 27 | Kaempferol 3,7-di-*O*-hexoside [s] | 609 | $MS^2$ → 447 (100), 285 (9); $MS^3$ → 285 (100); $MS^4$ → 217 (100), 241 (56), 199 (73), 175 (32) |
| 28 | Luteolin 7-*O*-pentosyl-hexoside [s] | 579 | $MS^2$ → 285 (100); $MS^3$ → 217 (100), 214 (20), 199 (78), 197 (65), 175 (57); $MS^4$ → 170 (100), 186 (23) |
| 29 | Kaempferol 3-*O*-acetylhexoside [s] | 489 | $MS^2$ → 285 (100); $MS^3$ → 241 (100), 217 (56), 199 (92), 175 (97), 151 (32), 133 (12), 107 (11); $MS^4$ → 198 (100), 215 (29), 173 (22), 133 (64) |
| 30 | Kaempferol 7-*O*-acetylhexoside [s] | 489 | $MS^2$ → 285 (100); $MS^3$ → 175 (100), 241 (68), 217 (73), 199 (64), 151 (22), 133 (12), 107 (17) |
| 31 | Apigenin 7-*O*-galactoside [s] | 431 | $MS^2$ → 269 (100); $MS^3$ → 225 (100), 267 (46), 197 (31), 183 (42), 169 (22), 149 (51); $MS^4$ → 197 (100), 183 (47), 169 (60), 155 (20) |
| 32 | 6-*O*-Feruloyl-glucose [s] | 355 | $MS^2$ → 193 (100); $MS^3$ → 191 (100), 175 (24), 165 (23), 149 (61), 121 (40) |
| 33 | Protocatechuic acid *O*-hexoside [s] | 315 | $MS^2$ → 153 (100), 109 (16), 195 (15), 225 (06), 255 (07); $MS^3$ → 109 |

| | | | |
|---|---|---|---|
| | | | (100) |
| 34 | Caffeic acid [s] | 179 | $MS^2$ → 135 (100), 133 (49) |
| 35 | 5-*O*-(3'-*O*-Caffeoyl glucosyl)quinic acid [s] | 515 | $MS^2$ → 323 (100), 341 (17), 353 (37), 191 (38), 179 (21); $MS^3$ → 161 (100), 133 (10); $MS^4$ → 133 (100) |
| 36 | Esculetin [s] | 177 | $MS^2$ → 133 (100), 105 (15) |
| 37 | Esculetin 6,7-di-*O*-glucopyranoside [s] | 501 | $MS^2$ → 177 (100); $MS^3$ → 133 (100), 150 (10) |
| 38 | Esculetin *O*-acetylglucoside [s] | 381 | $MS^2$ → 177 (100); $MS^3$ → 133 (100), 105 (15) |

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