Table S1: *Oligopin composition according to Segal et al.*[1]

Oligopin® composition.

Constituents	Average content (%mass)	Method
Procyanidolic oligomers :	67–75	GPC
Dimers:	15–20	
Trimers :	15–20	
Tetramers and higher oligomers:	30–40	
Total polyphenol	> 96	HPLC
Catechin	4-10	
Taxifoliol	0.5-4	
Taxifoliol glucoside	3-8	
Ferrulate glucoside	4-10	
Gallic acid	0.1-1	
Protocatechic acid	0.5-3	
Caffeic acid	0.5-3	
p-coumaric acid	0.3-2	
Ferulic acid	1-5	

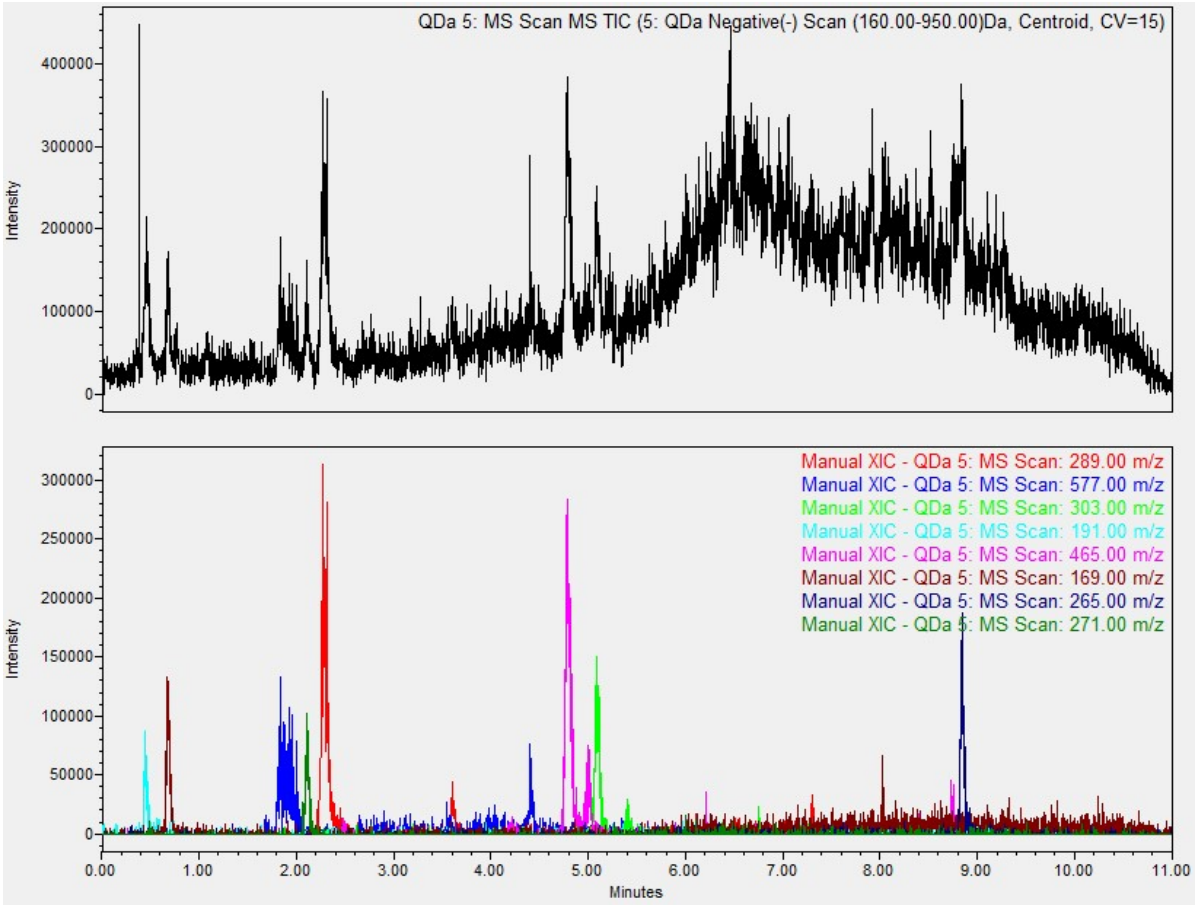

Figure S1: *UPLC-MS analysis of Oligopin. Different m/z values were extracted (below) from the total ion current chromatogram (above). Tentatively identified compounds: catechin, m/z 289; procyanidin B-type dimers, m/z 577; taxifolin glycoside, m/z 465; taxifolin, m/z 303; gallic acid, m/z 169.*

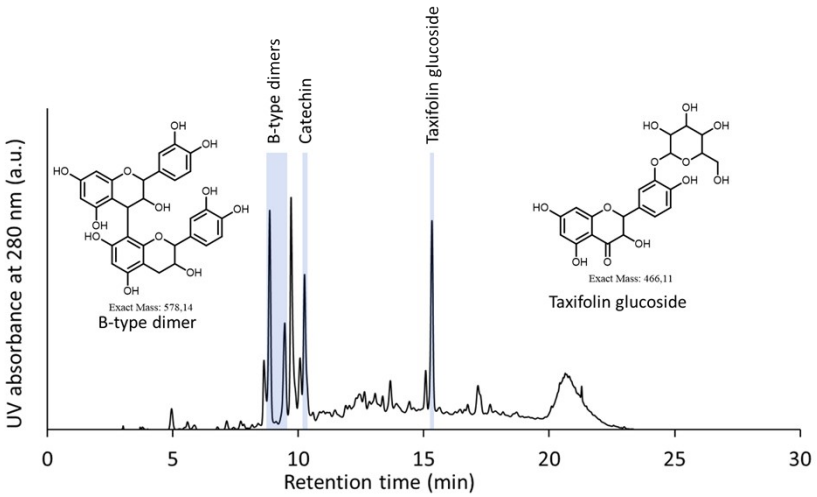

Figure S2: *HPLC-UV analysis of Oligopin. Catechin was identified based on a model compound. Taxifolin glucoside and the different B-type procyanidin dimers were assigned based on UPLC-MS of Oligopin, see fig. S1.*

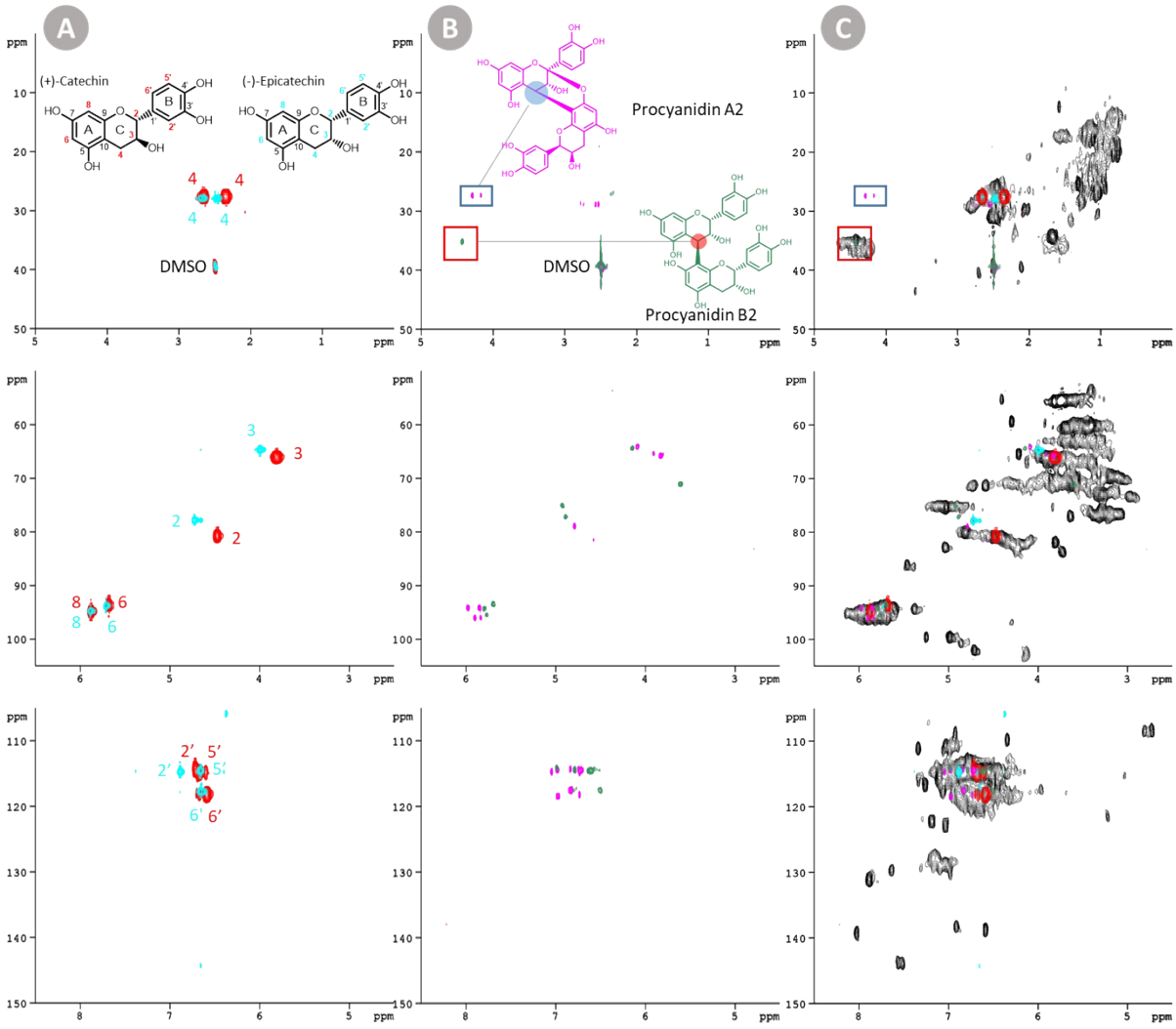

Figure S3: *^{1}H-^{13}C HSQC NMR analysis. (A) catechin (red) and epicatechin (blue), with identification of signals. (B) Procyanidin A2 (pink) and procyanidin B2 (green), with identification of B-type interflavonoid bond in procyanidin B2 (red square) and A-type interflavonoid bond in procyanidin A2 (blue square). (C) Oligopin, with the spectra of (epi)catechin and procyanidin A2 and B2 overlaid. This demonstrates the presence of B-type bonds in Oligopin, whereas A-type bonds are absent. Top: aliphatic region. Middle: oxygenated aliphatic region. Bottom: aromatic region.*

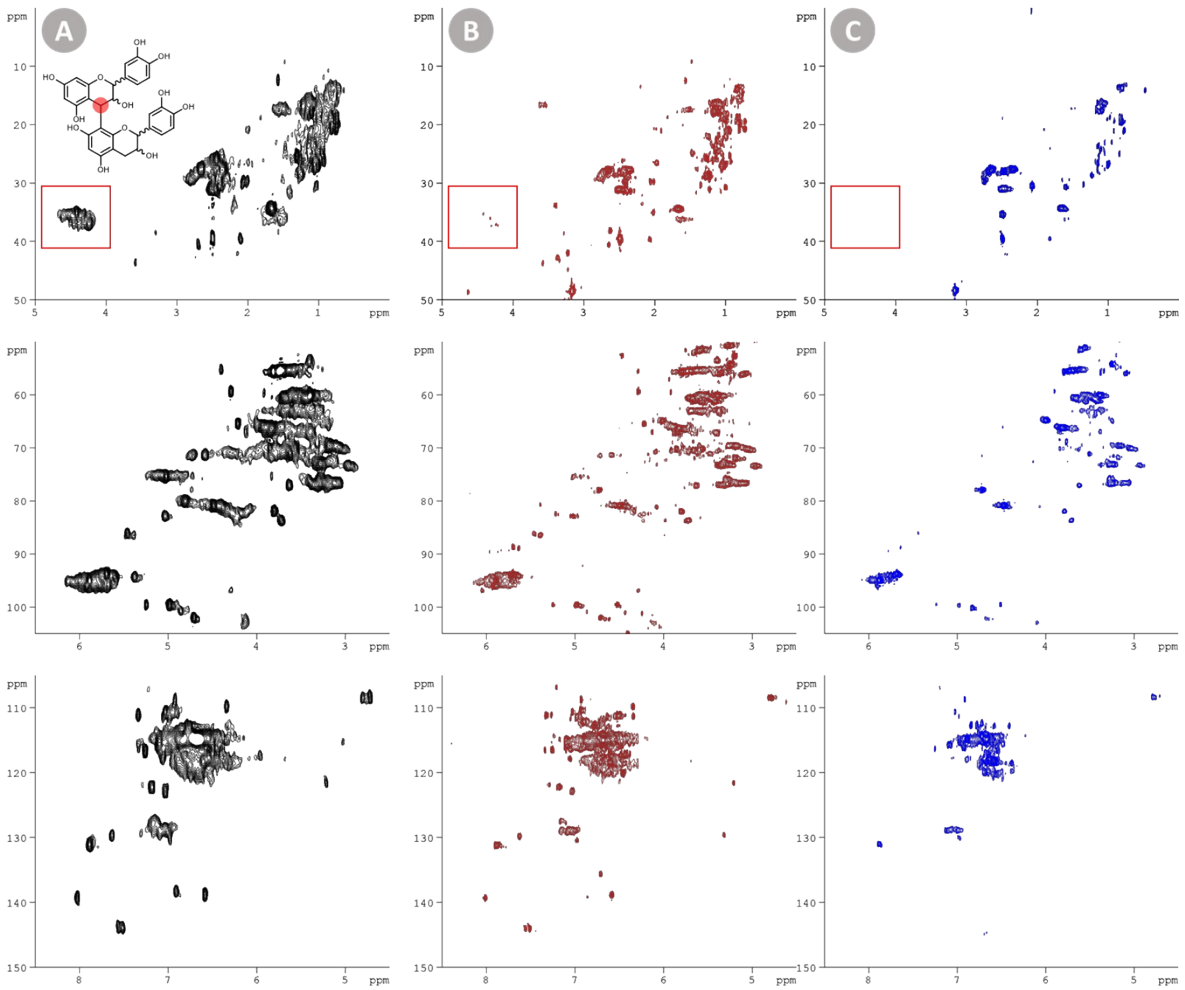

Figure S4: *^{1}H-^{13}C HSQC NMR analysis at different shifts of three samples: (A) Oligopin, (B) after blank reaction and (C) after proof-of-concept catalysed reaction. Reaction conditions: 200 mg Oligopin, 60 mL methanol, 150 °C, 6 bar N_2 and no catalyst (blank reaction) or 30 bar H_2 and 25 mg Pd/C (catalysed reaction). Top: aliphatic region (red square indicates the 4 position with a interflavonoid 4->8 B-type bond). Middle: oxygenated aliphatic region. Bottom: aromatic region.*

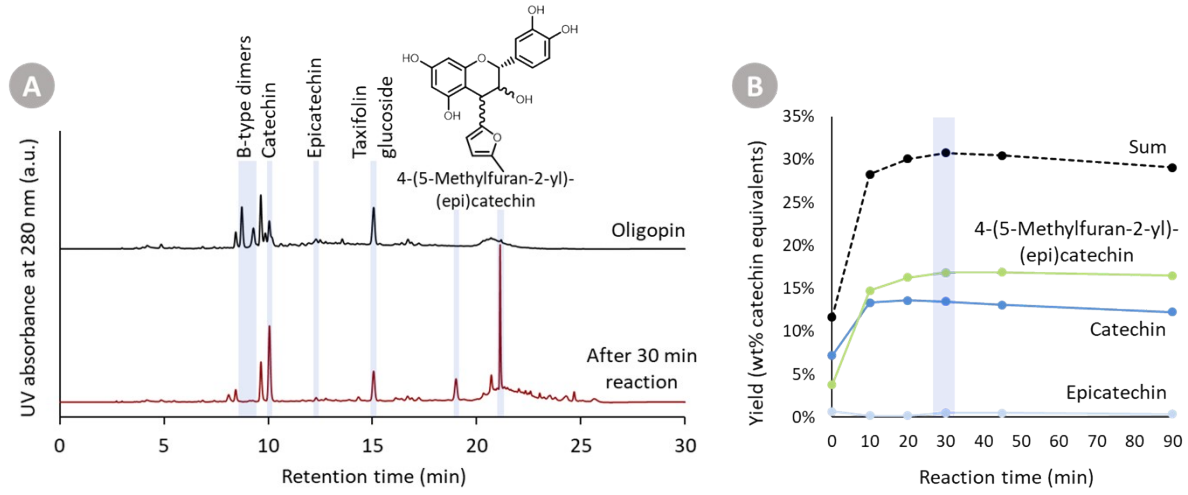

Figure S5: *Depolymerisation - nucleophilic trapping of Oligopin using 2-methyl furan as nucleophile. Reaction conditions: 750 µL methanol, 250 µL 2-methylfuran, 0.1 M HCl, 3.49 mg Oligopin, 30°C, 0-90 min reaction time. (A) HPLC-UV analysis of the Oligopin substrate and product mixture after 30 min of reaction. The chromatogram shows two peaks (isomers) corresponding to the 2-methyl furylated (epi)catechin products. (B) Time evolution of reaction products. Expressed in wt% catechin equivalents, thus omitting the mass contribution of the nucleophile. After 30 min, the highest combined yield of monomers (i.e. (epi)catechin and 2-methyl furylated (epi)catechin products) was achieved.*

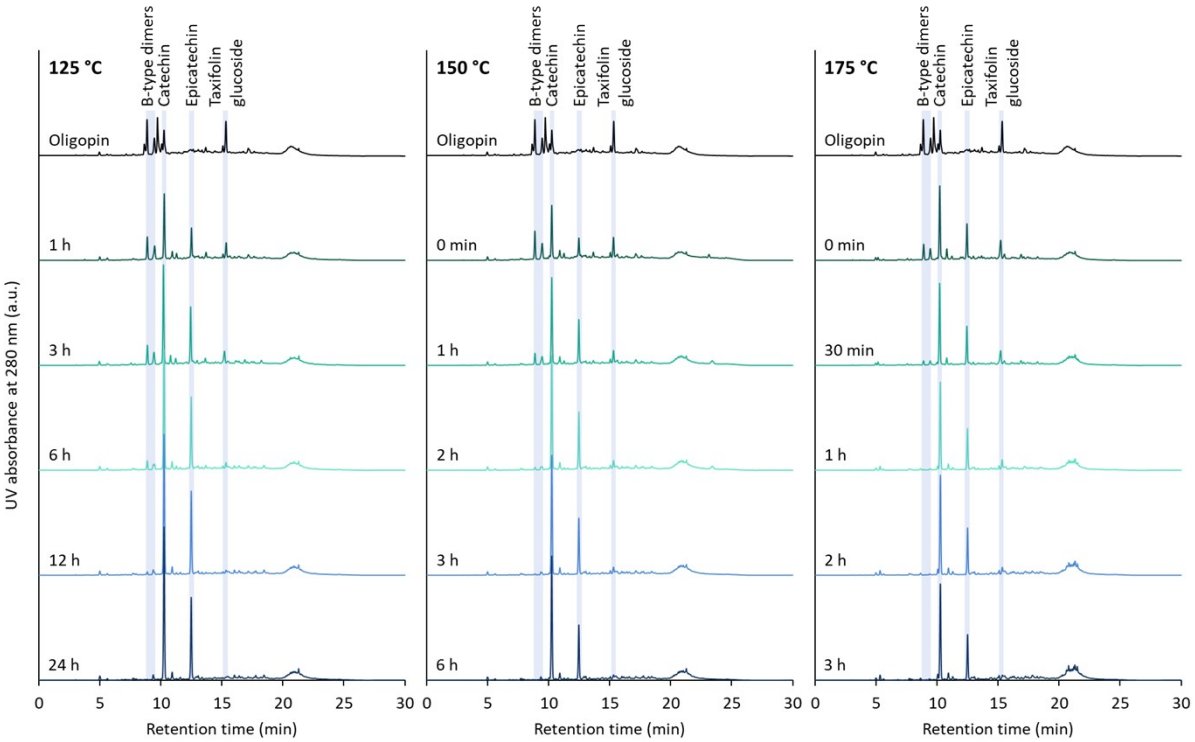

Figure S6: *HPLC-UV analysis of the depolymerisation - hydrogenation of Oligopin at different temperatures (125, 150 and 175 °C) and time intervals. Reaction conditions: 200 mg Oligopin, 60 mL methanol, 30 bar H_2 and 25 mg Pd/C, 20 min heating to reaction temperature.*

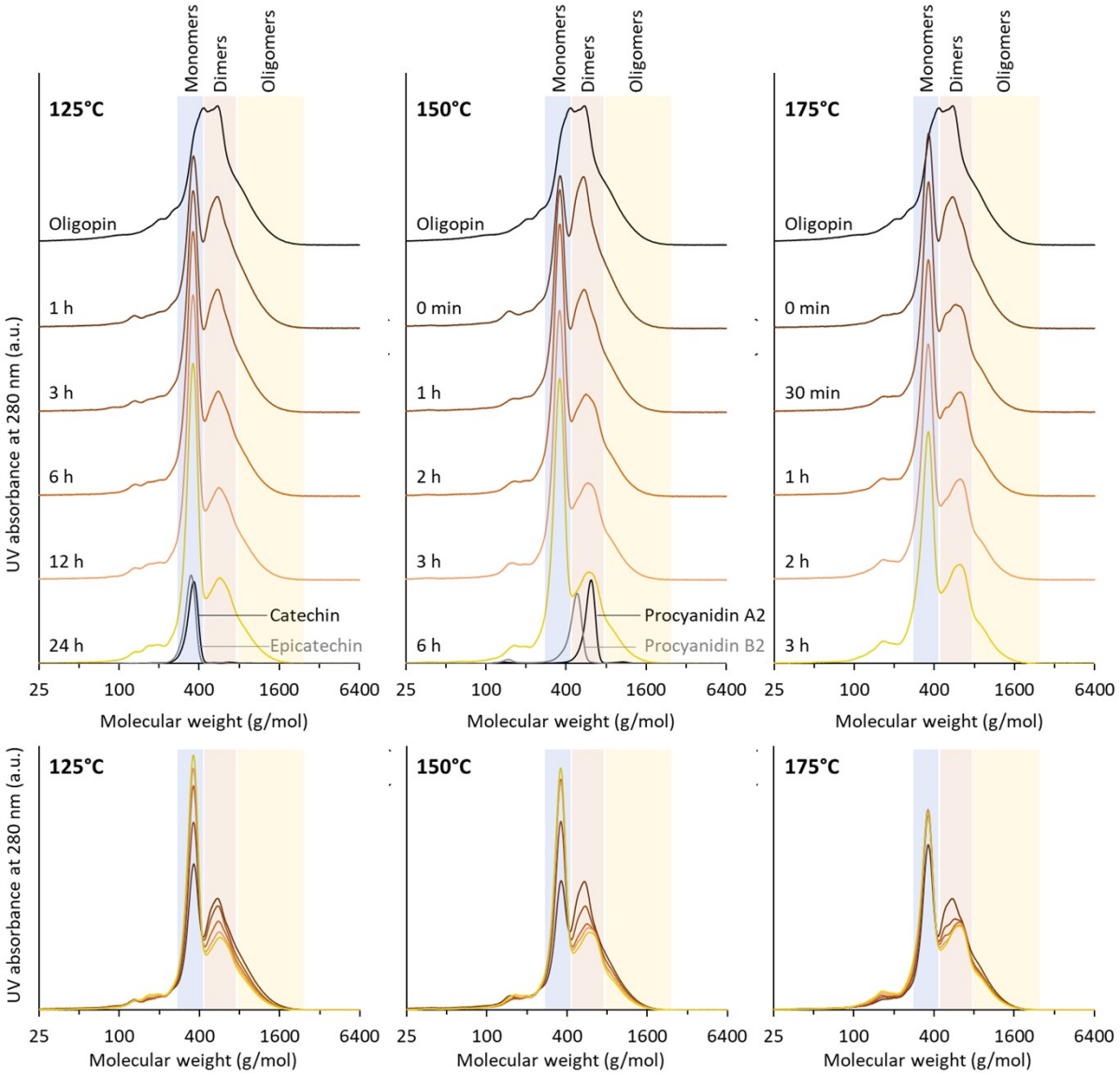

Figure S7: *GPC analysis of the depolymerisation - hydrogenation of Oligopin at different temperatures (125, 150 and 175 °C), and time intervals. Reaction conditions: 200 mg Oligopin, 60 mL methanol, 30 bar H_2 and 25 mg Pd/C, 20 min heating to reaction temperature. Chromatograms are normalised to have the same area under the curve. Model monomers (catechin and epicatechin) and dimers (procyanidin A2 and B2) are additionally shown, to assert the monomer and dimer signal assignment. Below: the same chromatograms as above (except Oligopin) are plotted on top of each other, to visualise the change in MW over time.*

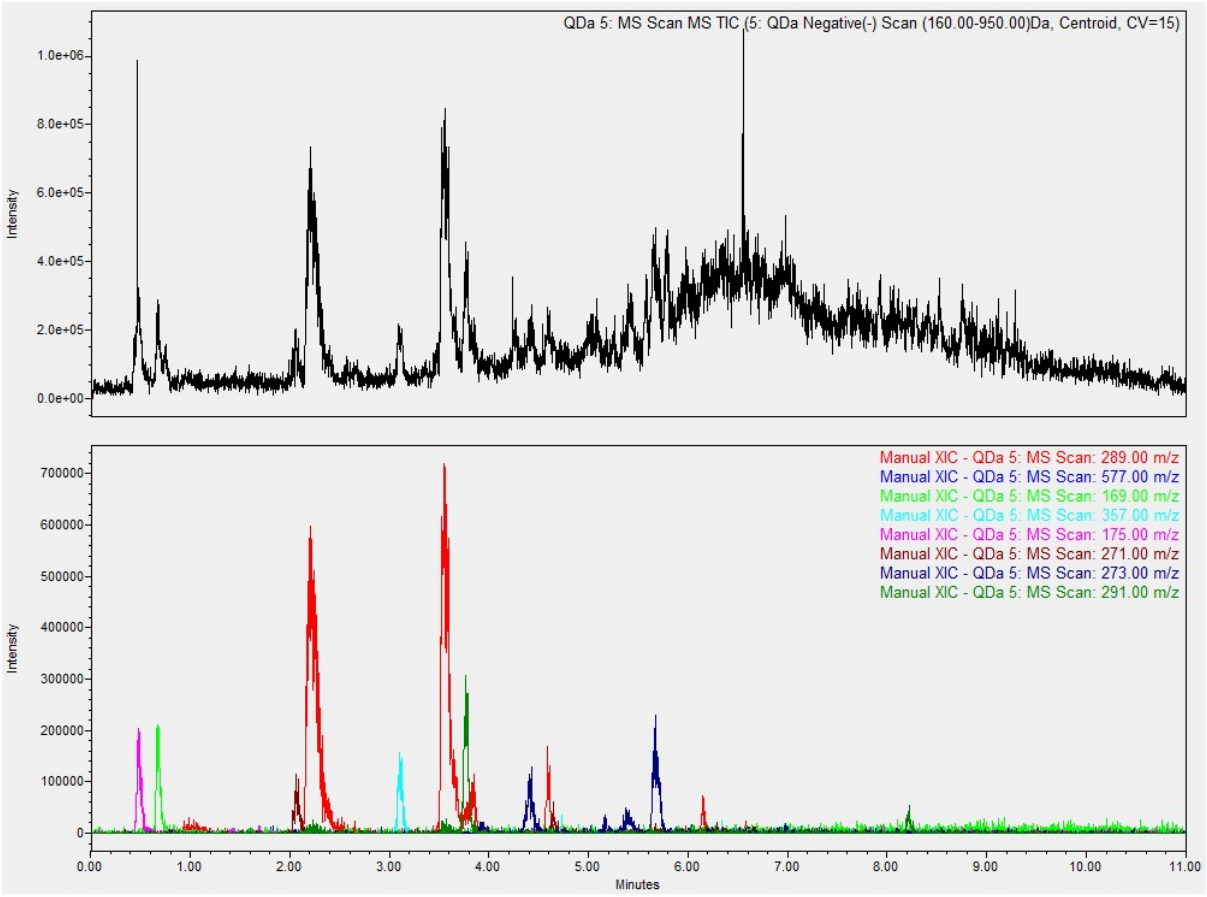

Figure S8: *UPLC-MS analysis after depolymerisation - hydrogenation of Oligopin. Reaction conditions: 200 mg Oligopin, 60 mL methanol, 30 bar H_2 and 25 mg Pd/C, 125°C, 24 h (see also fig. S6). Different m/z values were extracted (below) from the total ion current chromatogram (above). (Tentatively) identified compounds: catechin, m/z 289; gallic acid, m/z 169; compound (1), m/z 291 (see fig. S9-10); compound (2), m/z 273 (see fig. S9-10). Full conversion of the B-type dimers was confirmed because of the complete absence of the m/z 577 (see also fig. S1).*

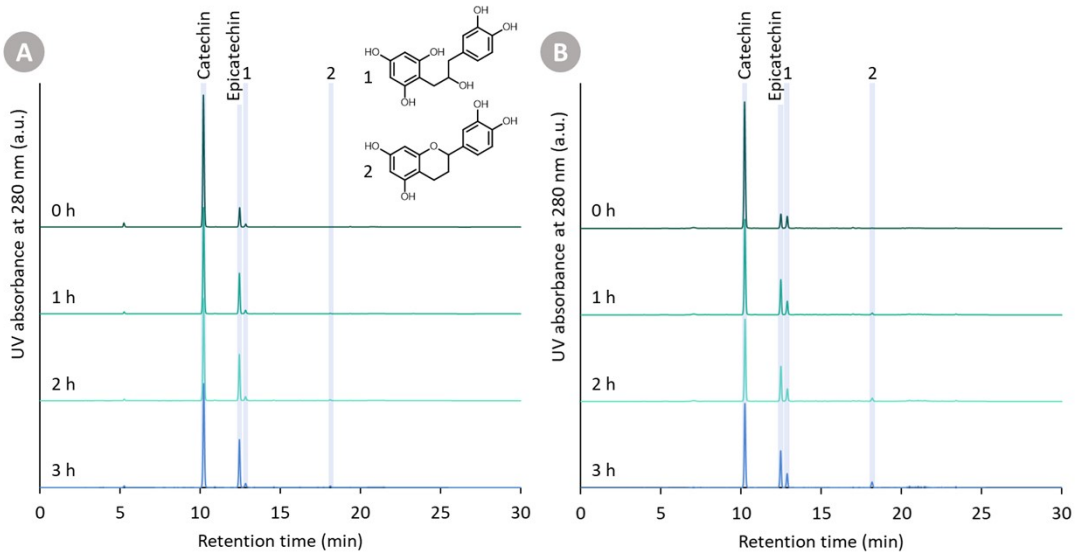

Figure S9: *Hydrogenation of catechin. HPLC-UV analysis after different reaction times and at a catalyst loading (with respect to catechin) of (A) 12.5 wt% or (B) 50 wt%. Reaction conditions: 200 mg catechin, 60 mL methanol, 150 °C, 30 bar H_2 and 12.5 or 100 mg Pd/C, measured at different time intervals.*

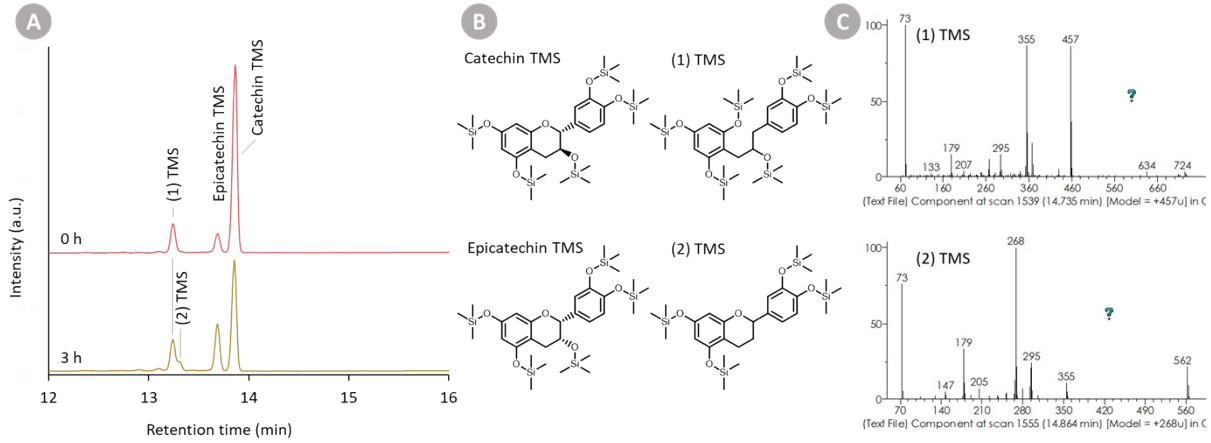

Figure S10: *Identification of compounds (1) and (2) using derivatisation (i.e. trimethylsilylation) in combination with GC(-MS). (A) GC-FID of the product mixture after 0 h and 3 h of reaction at a catalyst loading of 50 wt% (see fig. S9 B). (B) Structures of the TMS derivatised products. (C) Mass spectra of the identified, TMS derivatised products (1) and (2).*

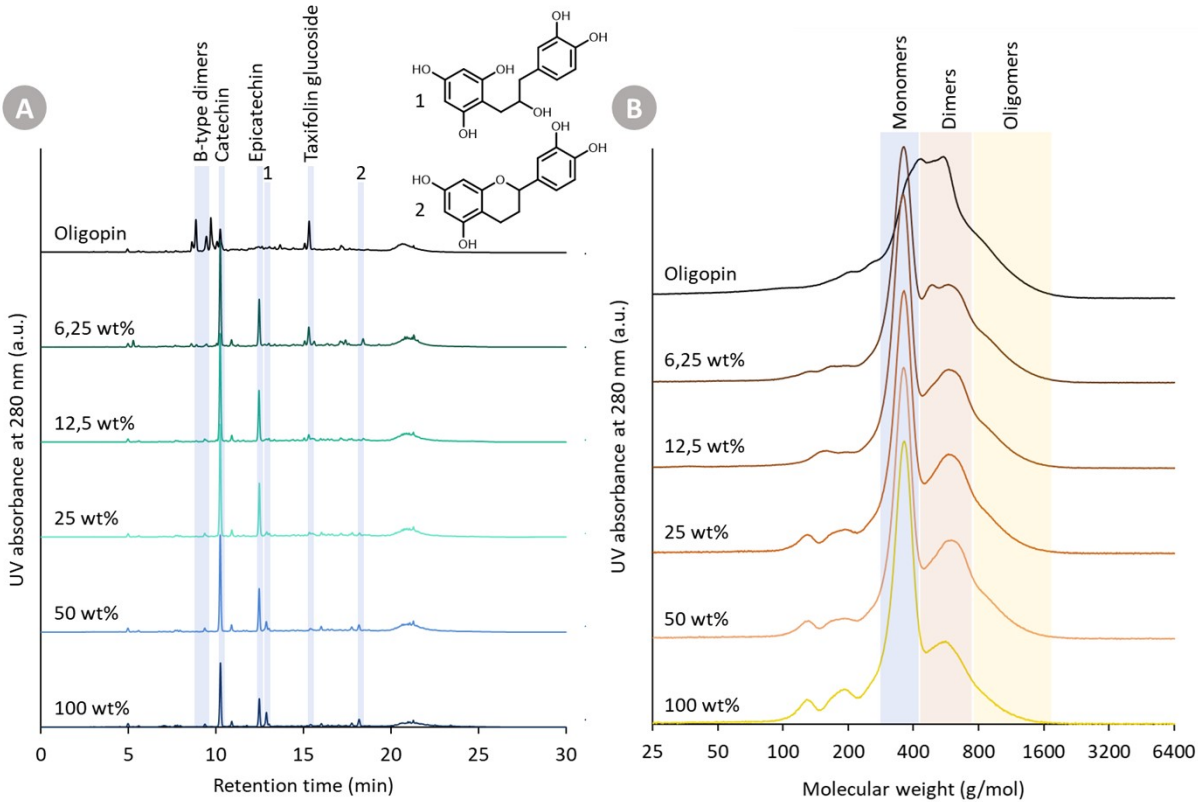

Figure S11: *HPLC-UV (A) and GPC (B) analysis of the depolymerisation - hydrogenation of Oligopin at different catalyst loadings (6.25 wt% to 100 wt%, with respect to the substrate). Reaction conditions: 200 mg Oligopin, 60 mL methanol, 30 bar H_2 and 12.5 - 200 mg Pd/C, 3 h.*

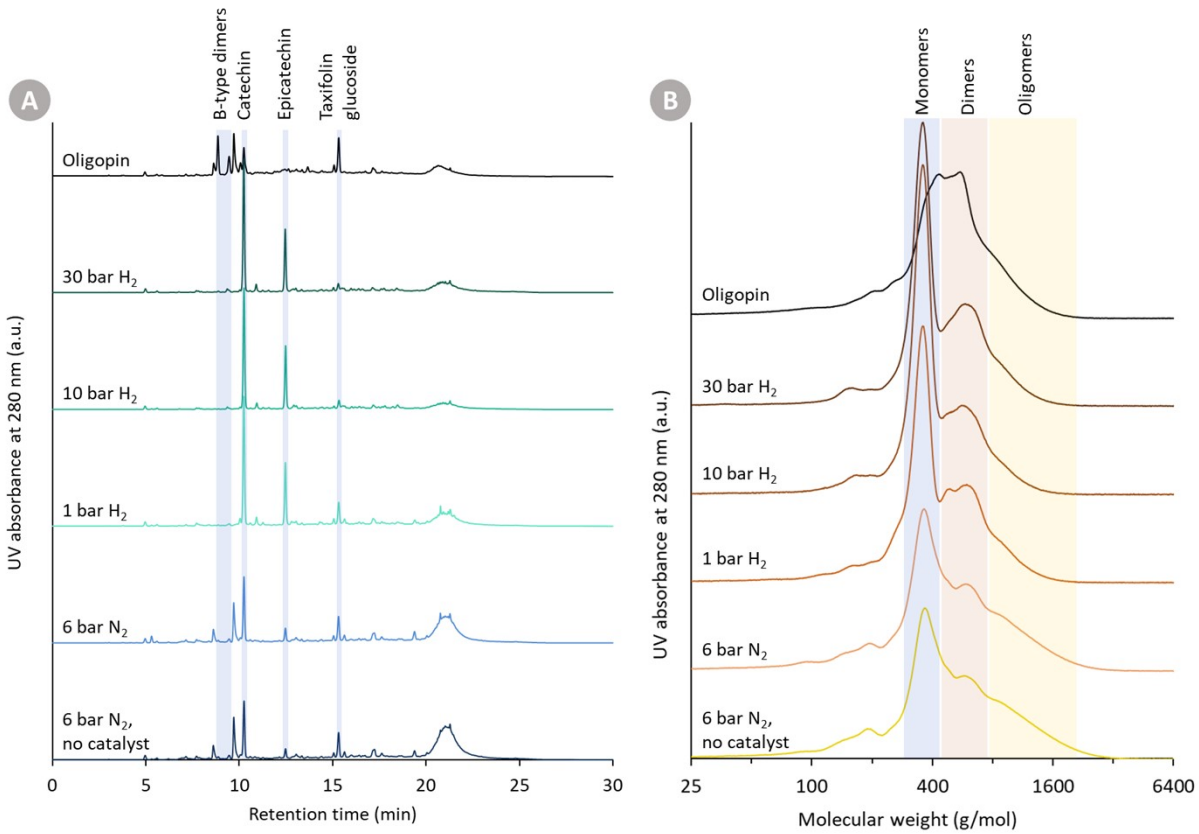

Figure S12: *HPLC-UV (A) and GPC (B) analysis of the depolymerisation - hydrogenation of Oligopin at different H_2 pressures (measured at RT). For comparison, also a reaction with N_2 and a reaction without catalyst and with N_2 were carried out. Reaction conditions: 200 mg Oligopin, 60 mL methanol, 1-30 bar H_2 or 6 bar N_2, 25 mg Pd/C (or no catalyst), 3 h reaction time.*

References

[1] L. Segal, M. Penman, Y. Piriou, Evaluation of the systemic toxicity and mutagenicity of OLIGOPIN®, procyanidolic oligomers (OPC) extracted from French Maritime Pine Bark extract, *Toxicology Reports*, 5 (2018) 531-541.