Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supporting Information (ESI†)

Separation of phenolic compounds by centrifugal partition chromatography

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Table S1: Recovery of phenolic compounds towards the PEG-8000-rich phase (Rec_{Top} %) by applying polymer-based ABS using inorganic salts or ionic liquids as electrolytes.

Electrolyte	**Rec_{Top}CA ± σ (%)**	**Rec_{Top}PA ± σ (%)**	**Rec_{Top}FA ± σ (%)**	**Rec_{Top}SA ± σ (%)**	**Rec_{Top}VN ± σ (%)**
NaCl	89.6 ± 1.8	53.92 ± 0.35	45.69 ± 0.27	60.20 ± 3.01	54.68 ± 2.73
Na_2SO_4	62.0 ± 1.9	64.31 ± 0.10	51.8 ± 6.7	59.52 ± 2.98	58.52 ± 2.93
$[C_2mim]Cl$	57.3 ± 3.2	51.75 ± 0.22	44.6 ± 1.1	59.21 ± 2.96	57.85 ± 2.89
$[C_2mim][CF_3SO_3]$	57.8 ± 3.0	85.5 ± 1.7	46.8 ± 2.5	58.20 ± 2.91	56.25 ± 2.81
$[C_2mim][CH_3SO_3]$	73.28 ± 0.48	48.5 ± 1.6	39.40 ± 0.13	59.25 ± 2.95	58.98 ± 2.95
$[C_2mim][TOS]$	56.3 ± 2.1	61.2 ± 2.1	25.4 ± 5.8	59.75 ± 2.99	58.87 ± 2.94
$[C_2mim][N(CN)_2]$	56.65 ± 0.32	7.44 ± 0.60	21.62 ± 0.95	59.95 ± 3.00	56.25 ± 2.81

Table S2: GHG emission factors used in the calculation of the carbon footprint and name of the processes taken from Ecoinvent version 3.4.

Input	**Reference unit**	**GHG emissions (kg CO_{2eq}/reference unit)[a]**	**Name of the process in Ecoinvent**
PEG 8000	kg	1.841	Ethylene glycol production, Europe[b]
NaPA 8000	kg	1.988	Acrylic acid production, Europe[c]
NaCl	kg	0.184	Sodium chloride production, powder, Europe
Water	kg	8.1E-04	-
Electricity	kWh	0.413	Market for electricity, low voltage, Portugal

[a] Global warming potentials for converting the mass of each GHG into mass of CO_{2eq} are those recommended by the Intergovernmental Panel on Climate Change (IPCC)[1] for a time horizon of 100 years. [b] In the absence of data for the production of polyethylene glycol, this process was selected as the most similar. [c] In the absence of data for the production of sodium polyacrylate, this process was selected as the most similar.

Table S3: Partition coefficient of the ionic liquids as electrolytes in PEG/NaPA 8000 ABS.[2]

Electrolyte	**$K_{IL} \pm \sigma$ (%)**
$[C_2mim]Cl$	0.77 ± 0.01
$[C_2mim][CF_3SO_3]$	0.44 ± 0.01
$[C_2mim][CH_3SO_3]$	0.34 ± 0.02
$[C_2mim][TOS]$	0.69 ± 0.04
$[C_2mim][N(CN)_2]$	0.98 ± 0.03

Table S4: Partition coefficient (K) of phenolic compounds, namely ferulic (FA), protocatechuic (PA), caffeic (CA) acids, vanillin (VN) and syringaldehyde (SA), using inorganic salts or ionic liquids as electrolytes in polymer-based ABS. The pH values and volume ratio (V_R) of each ABS are also given.

Electrolyte	**K_{CA} ± σ**	**K_{PA} ± σ**	**K_{FA} ± σ**	**K_{SA} ± σ**	**K_{VN} ± σ**	**pH (± 0.1)**		**V_R ± σ**
						Top	**Bottom**	
NaCl	2.78 ± 0.2	0.44 ± 0.04	0.23 ± 0.01	1.23 ± 0.02	1.12 ± 0.05	6.7	6.6	3.0 ± 0.1
Na_2SO_4	1.8 ± 0.3	1.69 ± 0.02	0.9 ± 0.3	1.18 ± 0.02	1.17 ± 0.04	6.9	6.8	1.00 ± 0.06
[C_2mim]Cl	0.48 ± 0.04	0.41 ± 0.04	0.39 ± 0.01	1.21 ± 0.10	1.21 ± 0.04	7.4	7.4	2.7 ± 0.2
[C_2mim][CF_3SO_3]	0.63 ± 0.01	1.9 ± 0.23	0.40 ± 0.08	1.20 ± 0.04	1.25 ± 0.08	7.3	7.2	2.9 ± 0.2
[C_2mim][CH_3SO_3]	0.92 ± 0.08	0.337 ± 0.003	0.239 ± 0.002	1.24 ± 0.09	1.24 ± 0.05	6.9	6.7	2.7 ± 0.2
[C_2mim][TOS]	0.6 ± 0.1	0.57 ± 0.02	0.57 ± 0.04	1.24 ± 0.07	1.23 ± 0.07	7.4	7.2	2.5 ± 0.1
[C_2mim][$N(CN)_2$]	0.57 ± 0.02	0.0339 ± 0.0001	0.120 ± 0.003	1.23 ± 0.02	1.19 ± 0.05	7.6	7.4	2.3 ± 0.1

Table S5: Recovery experimental data obtained for each phenolic compound after the dialysis process and identification of the techniques used to analyse the isolation of the phenolic compounds from the polymeric-rich phases.

Phenolic compound extract	**Rec ± σ (%)**	**Isolation analysis**
FA	84 ± 2	^{1}H NMR*
CA	87 ± 3	UV-Vis*
PA	65 ± 4	^{1}H NMR*
VN and SA	82 ± 3	UV-Vis*

Note: * in all cases, ATR-FTIR was used to analyse the polymeric fractions obtained after the dialysis step, proving the absence of phenolic compounds in the PEG 8000 and NaPA 8000-rich phases, thus attesting the high purity of the polymeric phases after dialysis.

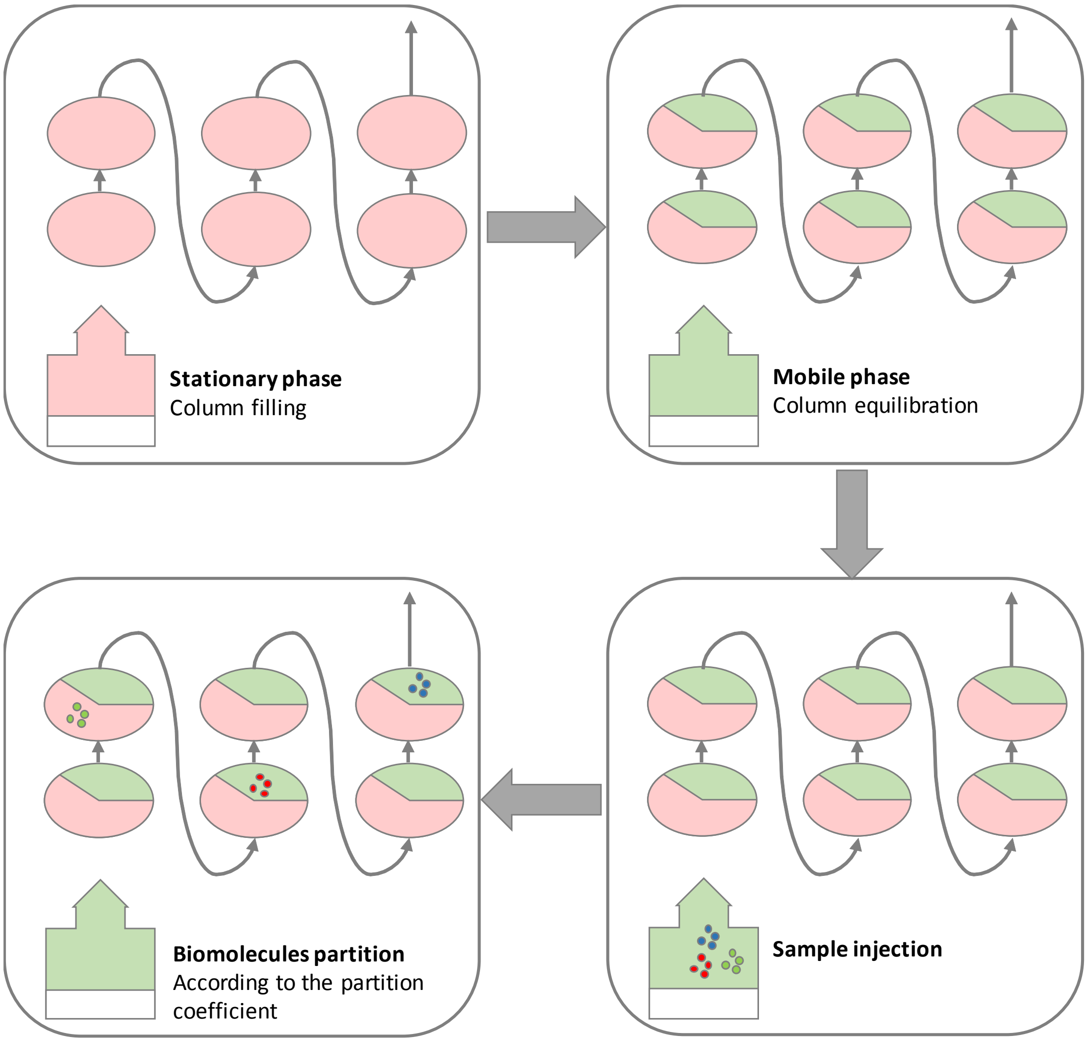


Fig. S1: Schematic representation of the CPC operation.

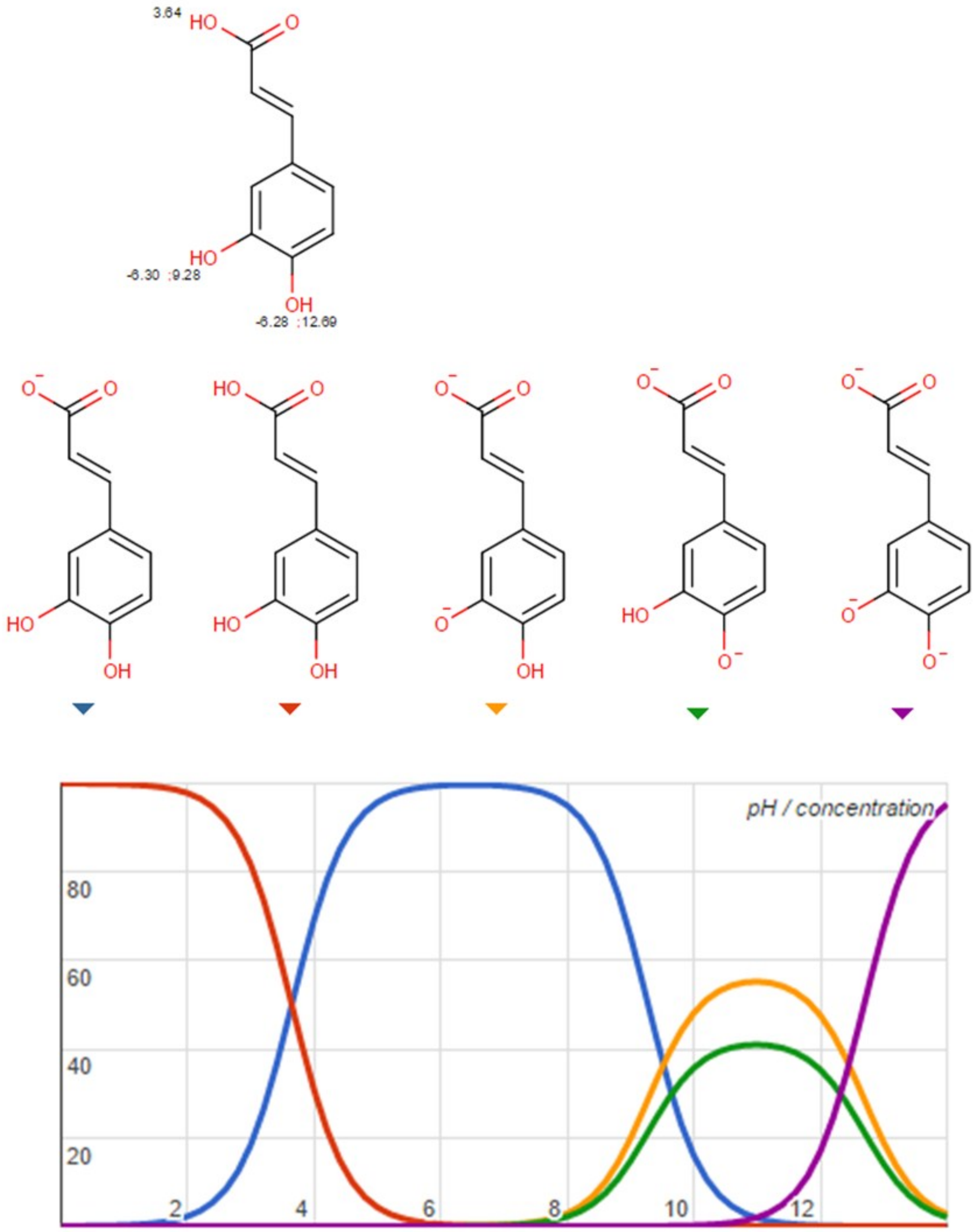


Fig. S2: Speciation of caffeic acid as a function of pH (ChemSpider database, accessed at August 24th 2017).

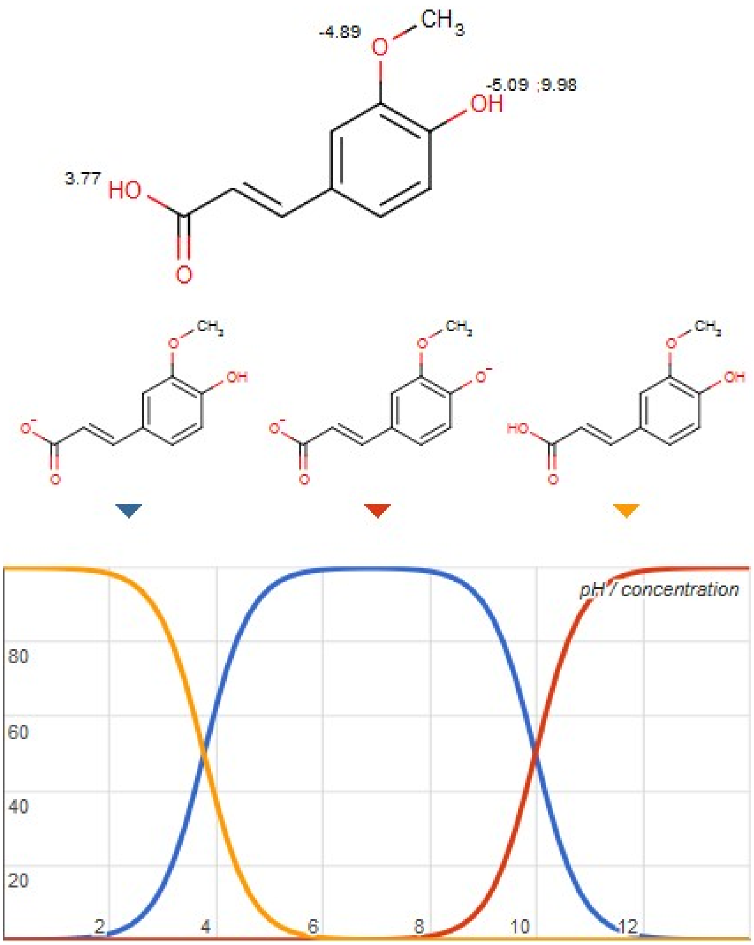


Fig. S3: Speciation of ferulic acid as a function of pH (ChemSpider database, accessed at August 24th 2017).

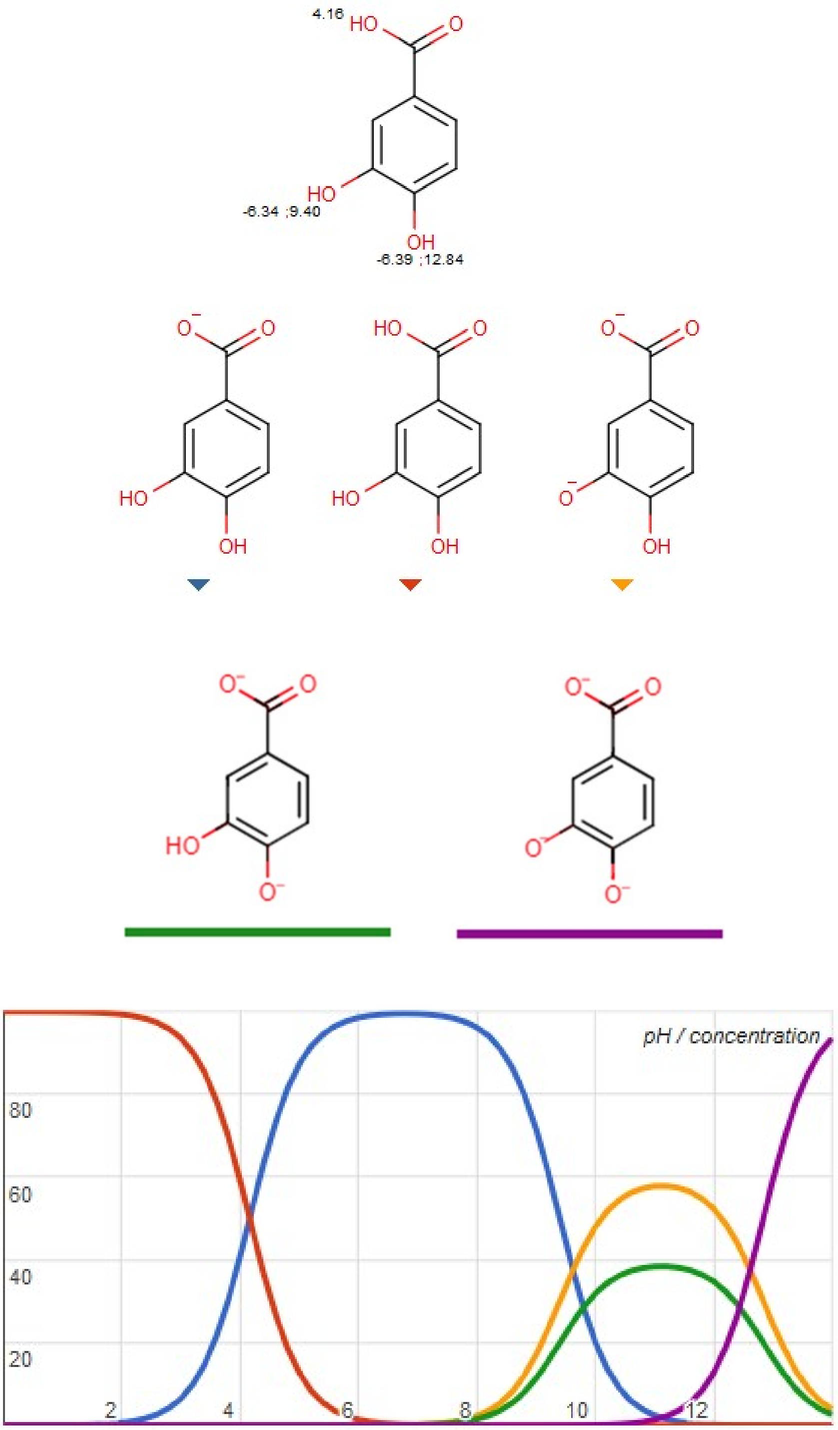


Fig. S4: Speciation of protocatechuic acid as a function of pH (ChemSpider database, accessed at August 24th 2017).

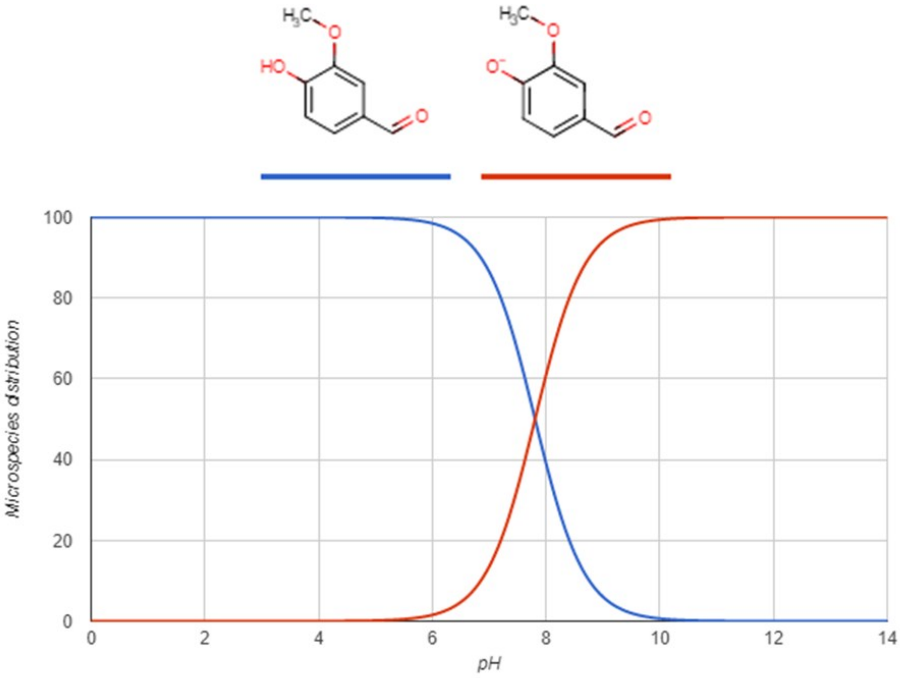


Fig. S5: Speciation of vanillin as a function of pH (ChemSpider database, accessed at January 9th 2018).

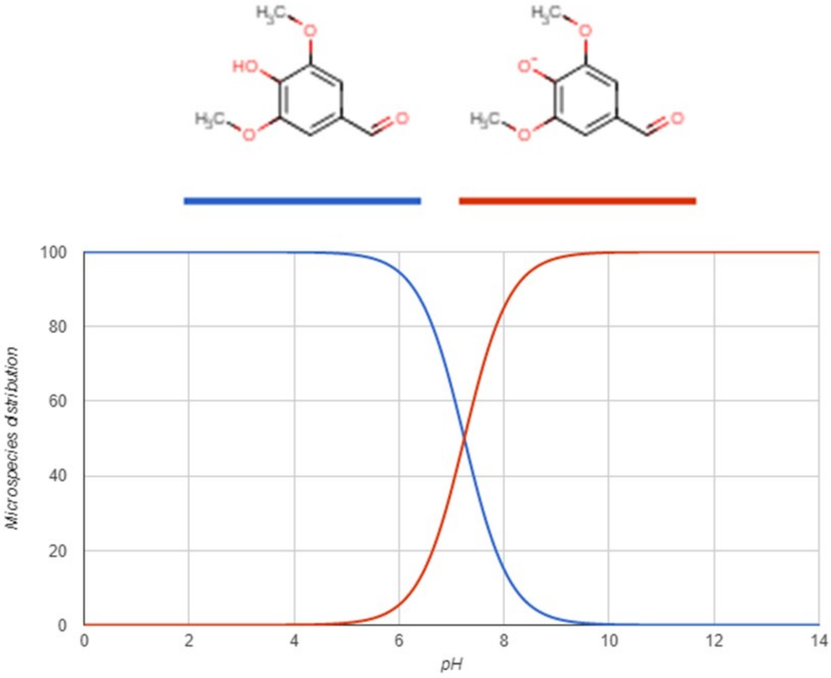


Fig. S6: Speciation of syringaldehyde as a function of pH (ChemSpider database, accessed at January 9th 2018).

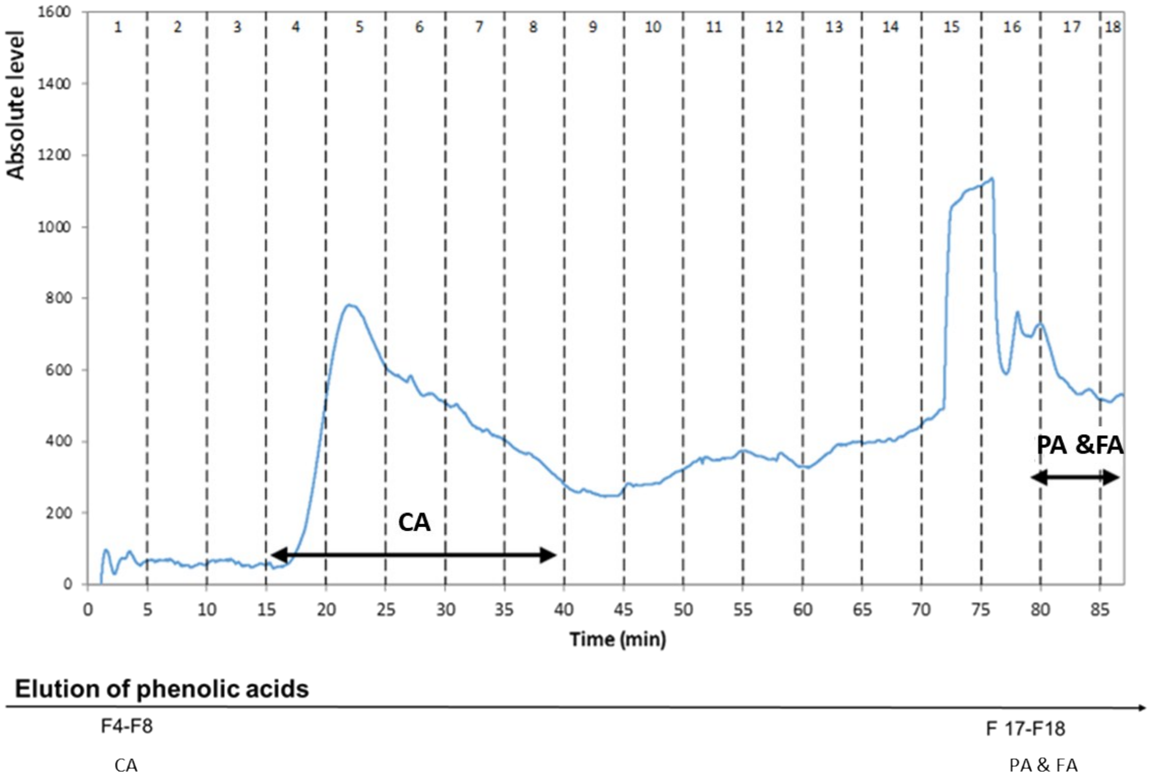
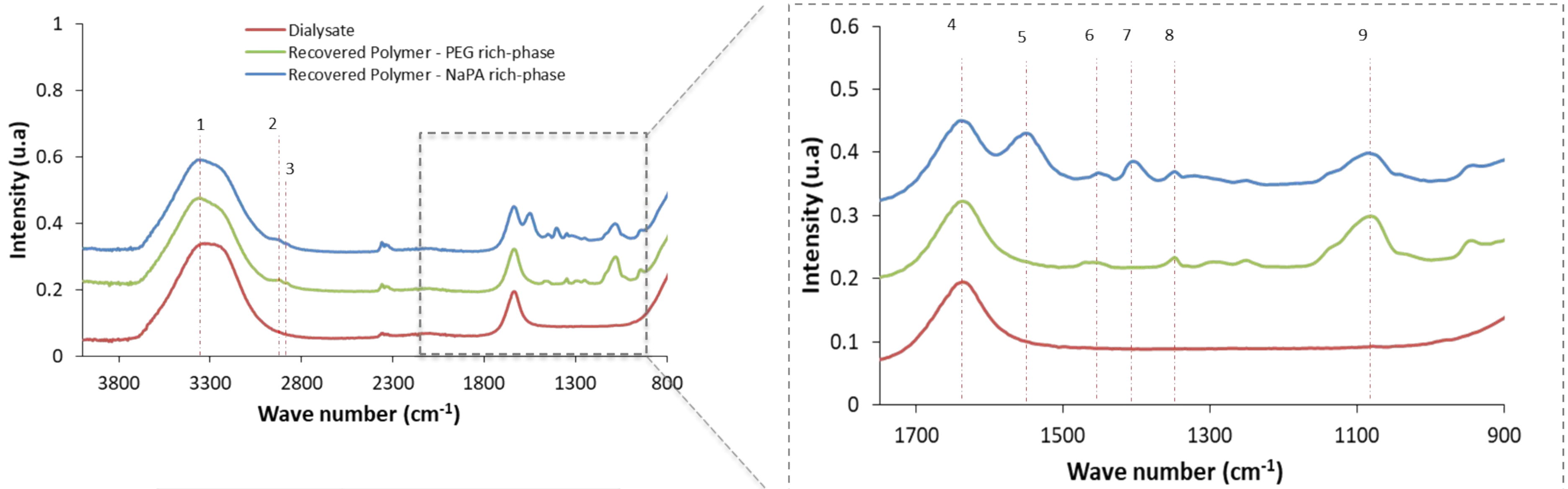


Figure S7: Separation of phenolic acids by CPC using the ABS composed of 15 wt% of PEG 8000 + 4.5 wt% of NaPA 8000 + 75.5 wt% of water + 5 wt% of NaCl. Experimental conditions: rotation speed of 2000 rpm.min^{-1}; flow-rate of 1.0 mL.min^{-1}; S_f = 20 %; P ≈ 24 bar; detection wavelength of 280 nm.



	Wave number (cm^{-1})	Assignments
1	3400-3200	**Water:** O-H stretch
2	2890	**Polymers:** CH_2 asym. stretch
3	2860	**Polymers:** CH_2 sym. stretch
4	1625	**Water:** H-O-H bend
5	1539	**NaPA:** $-COO^-$ sym. stretch
6	1445	**Polymers:** C-H bend
7	1400	**NaPA:** $-COO^-$ sym. stretch
8	1342	**PEG:** O-H bend
9	1070	**PEG:** C-O-C

Fig. S8: ATR-FTIR spectra and respective assignment table of the dialysate and both polymeric fractions obtained after the isolation steps experimentally carried to both polymeric fractions.

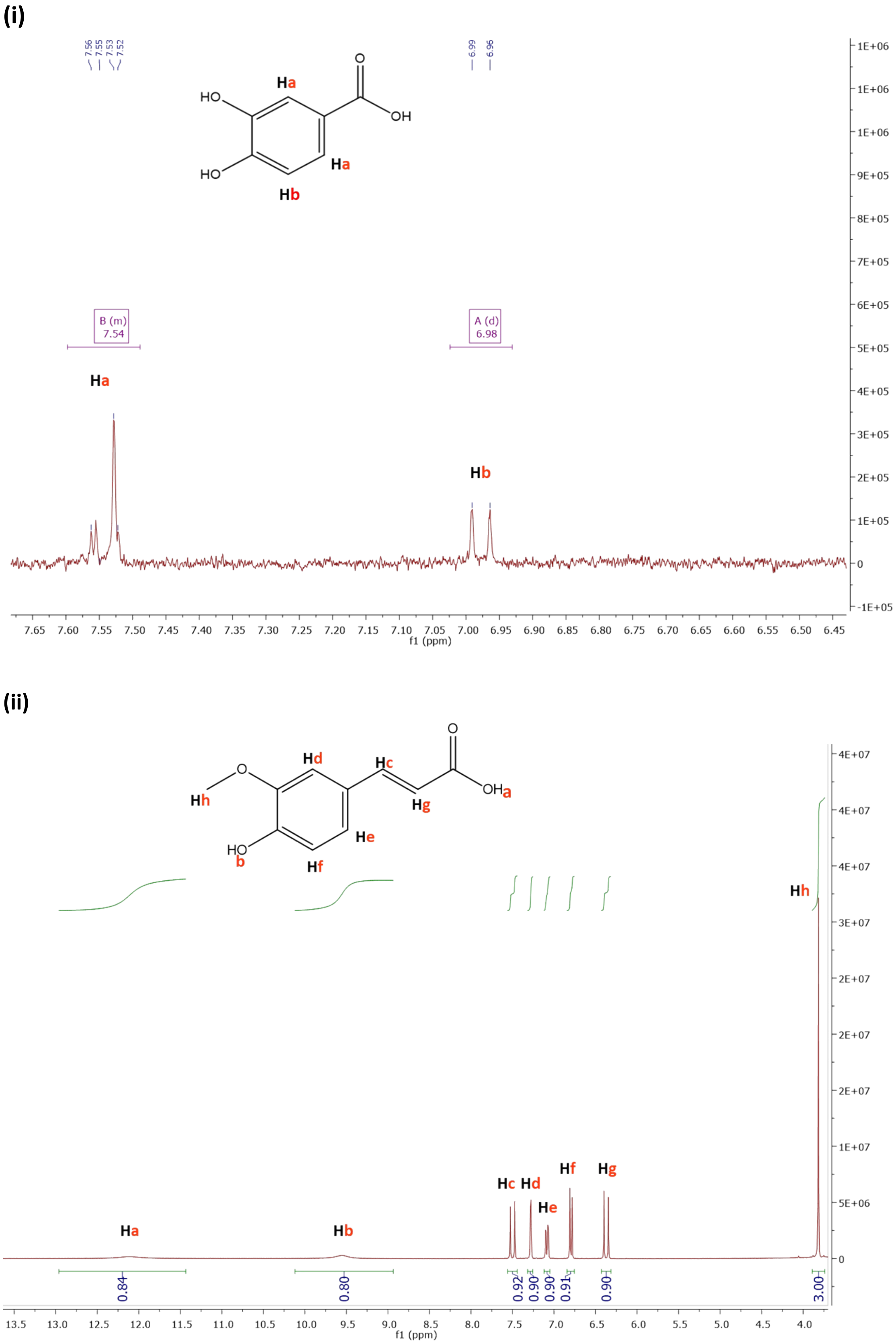
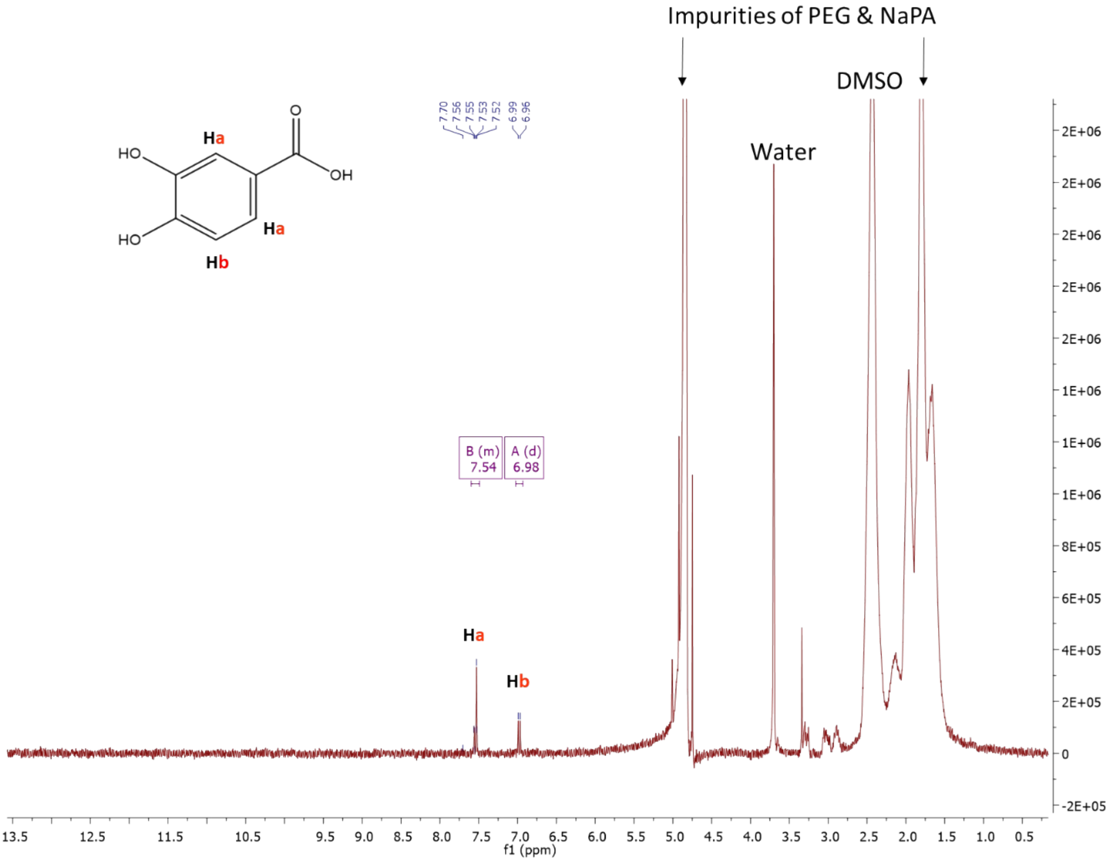


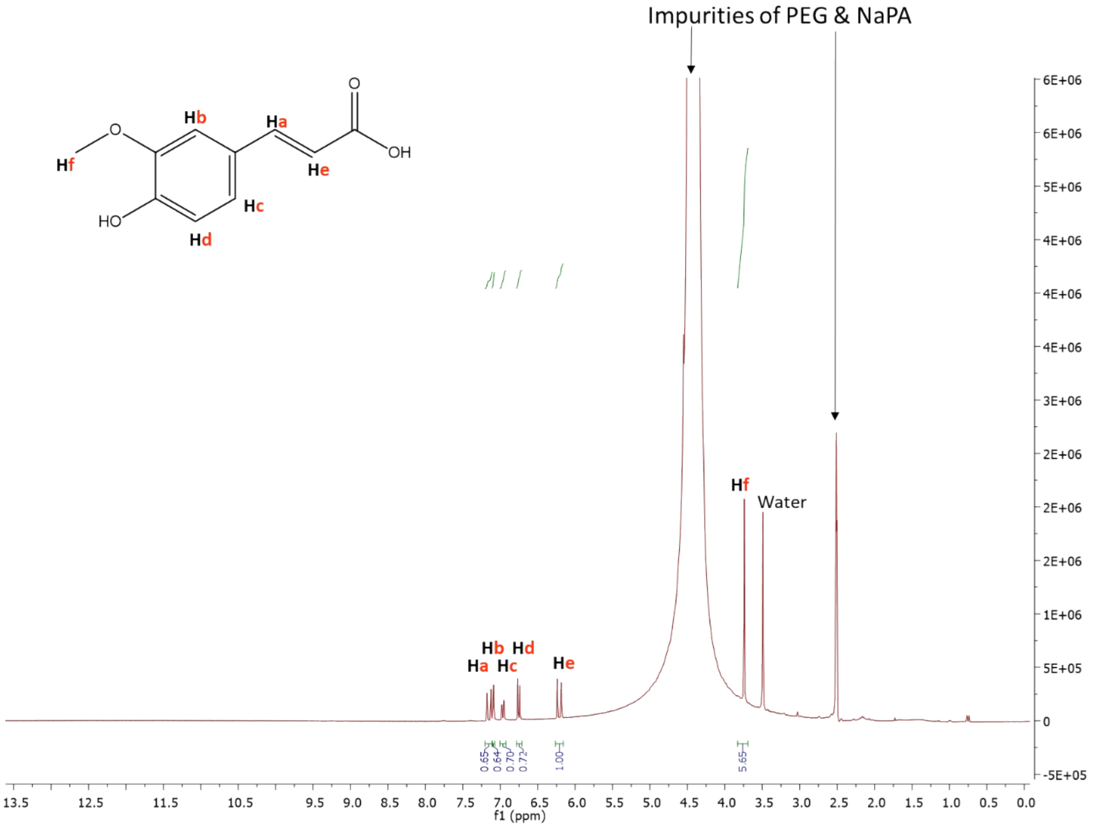
Fig. S9: ^{1}H NMR spectrum of **(i)** protocatechuic acid and **(ii)** ferulic acid in DMSO-d$_6$, after its purification by CPC.

Before the dialysis process

(i)

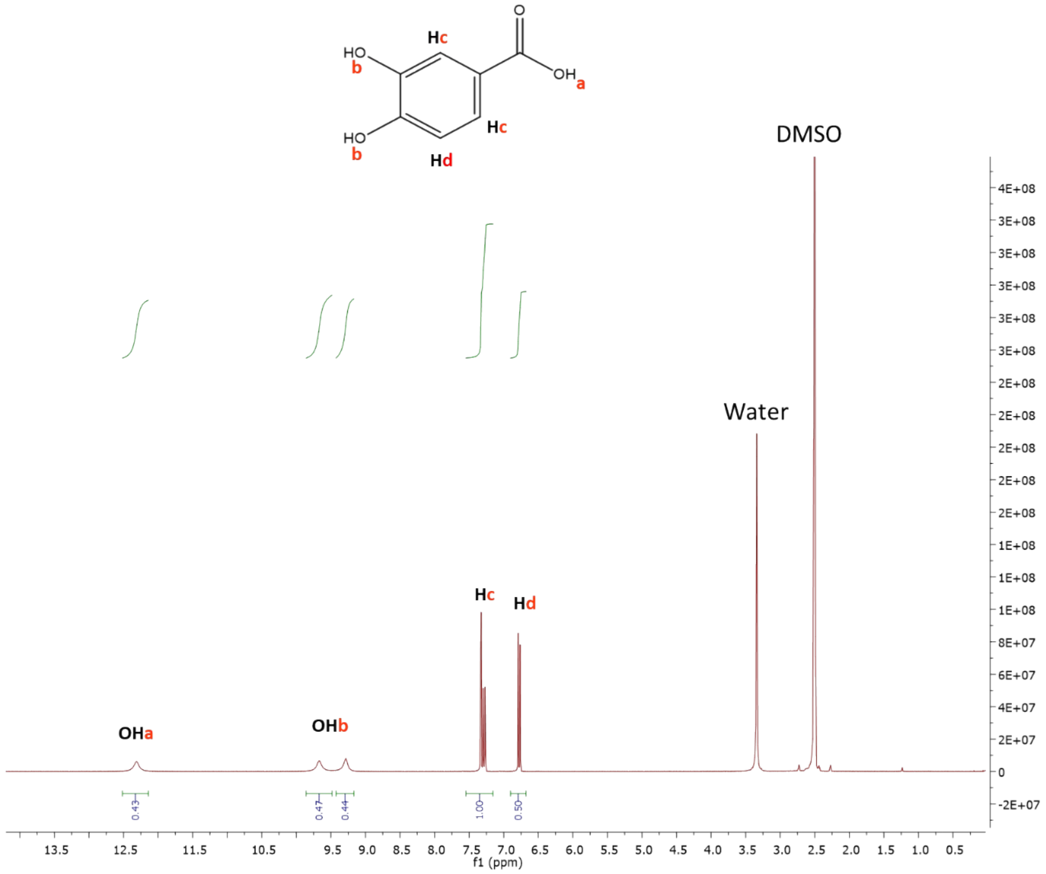


(ii)



After the dialysis process

(iii)



(iv)

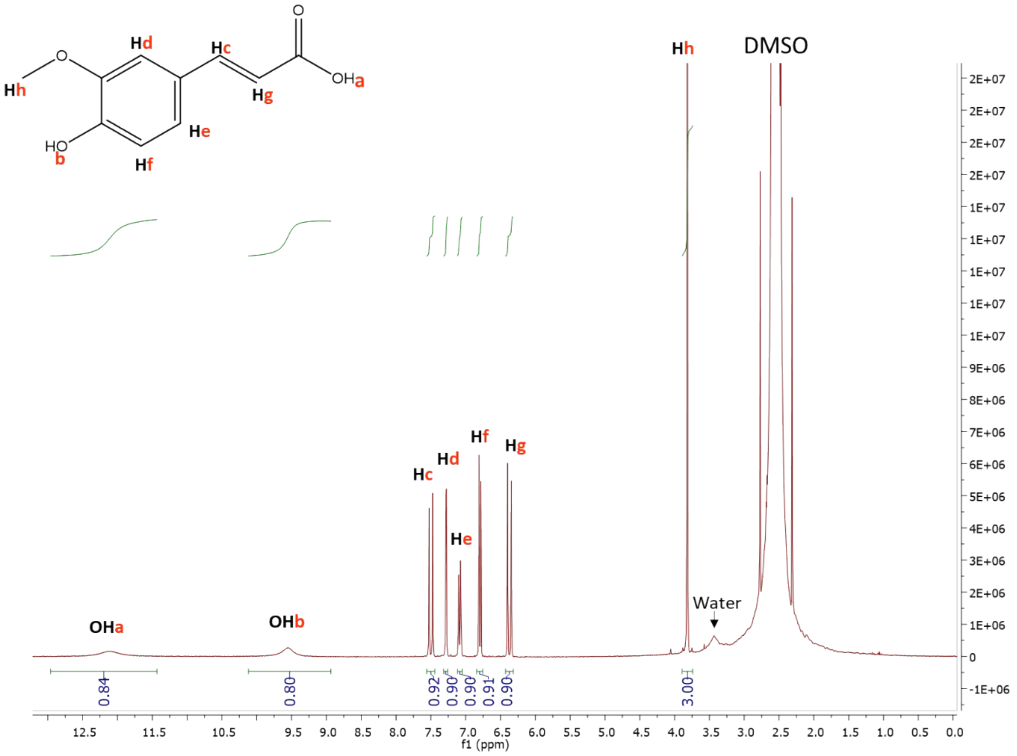


Fig. S10: ^{1}H NMR spectrum in whole ^{1}H region (0-13 ppm) of protocatechuic **(i, iii)** and ferulic acid **(ii, iv)** in DMSO-d_6, before and after dialysis, respectively.

References:

(1) G. Myhre, D. Shindell, F.-M. Bréon, W. Collins, J. Fuglestvedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G. Stephens, T. Takemura and H. Zhang, in *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, 2013, pp. 659-740.

(2) J. H. P. M. Santos, F. A. e Silva, J. A. P. Coutinho, S. P. M. Ventura and A. Pessoa, *Process Biochem*., 2015, **50**, 661-668.