Electronic Supplementary Information for:

Photodynamics of potent antioxidants: ferulic and caffeic acids

Michael D. Horbury,[a] Lewis A. Baker,[a] Wen-Dong Quan,[a] Simon E. Greenough, [a,‡,]* and

Vasilios G. Stavros[a,]*

[a] *Department of Chemistry, University of Warwick, Library Road, Coventry, CV4 7AL, UK.*

[‡] *Current address: Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK.*

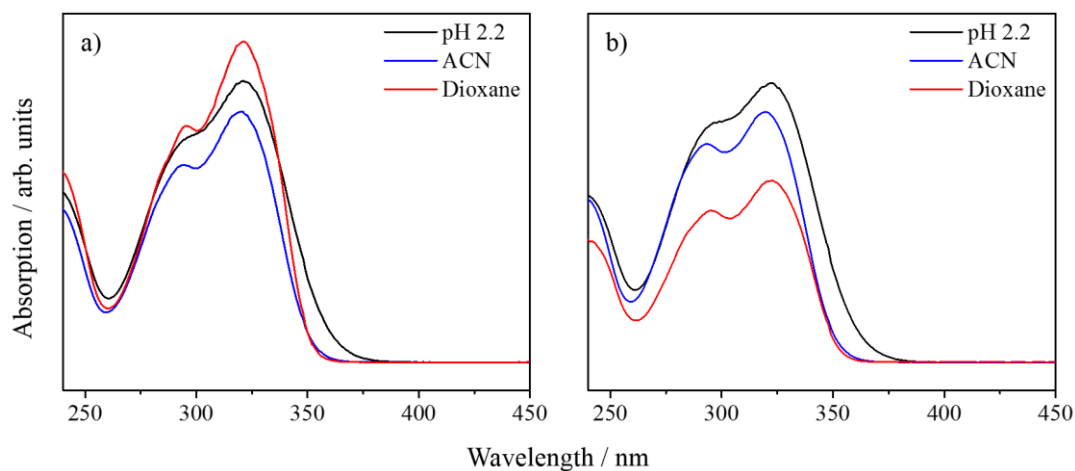### A. Static UV/Vis of ferulic and caffeic acid

Fig. S1: Static UV-visible absorption spectra of ~1 μM ferulic and caffeic acids in pH 2.2 water (black line), acetonitrile (ACN, blue line) and dioxane (red line) were obtained using a Cary 300 UV-vis spectrophotometer. A quartz cuvette with a 1 cm path length was used.
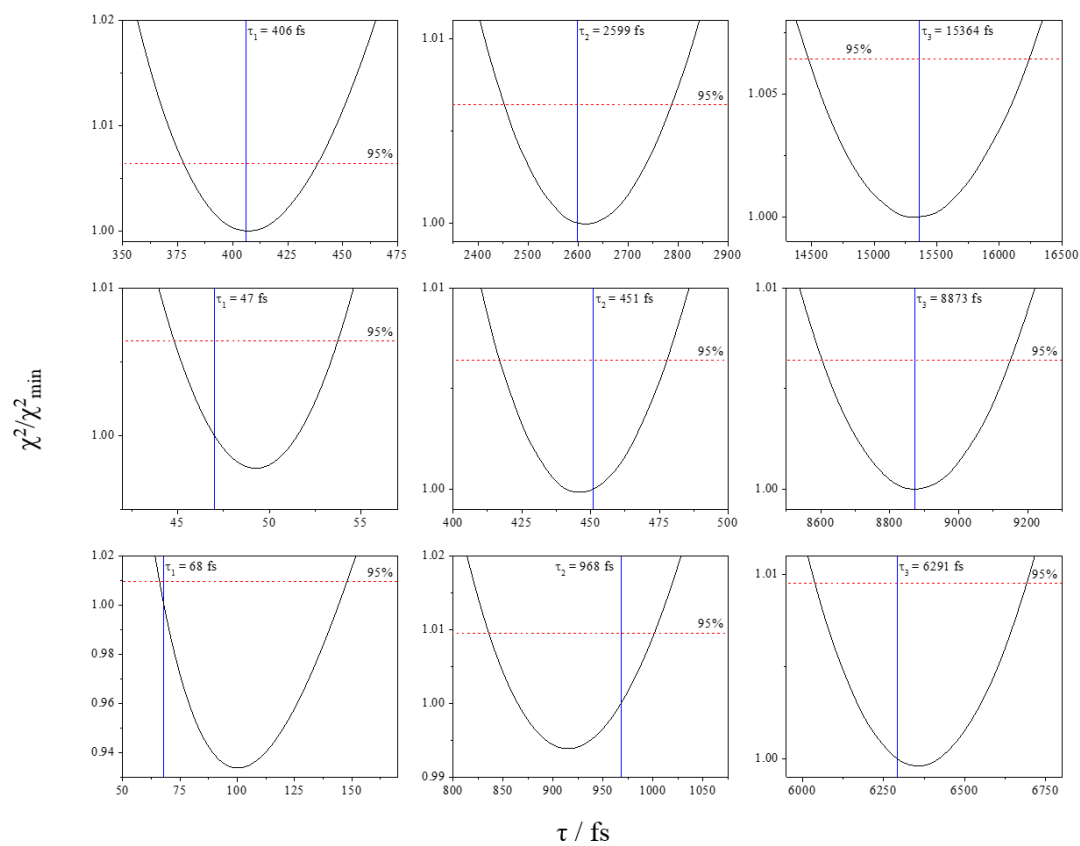
B. Global fitting error analysis

Fig. S2: Errors on the globally fitted lifetimes determined by asymptotic standard error analysis for ferulic acid. (Top) pH 2.2 water, (Middle) acetonitrile and (Bottom) dioxane.
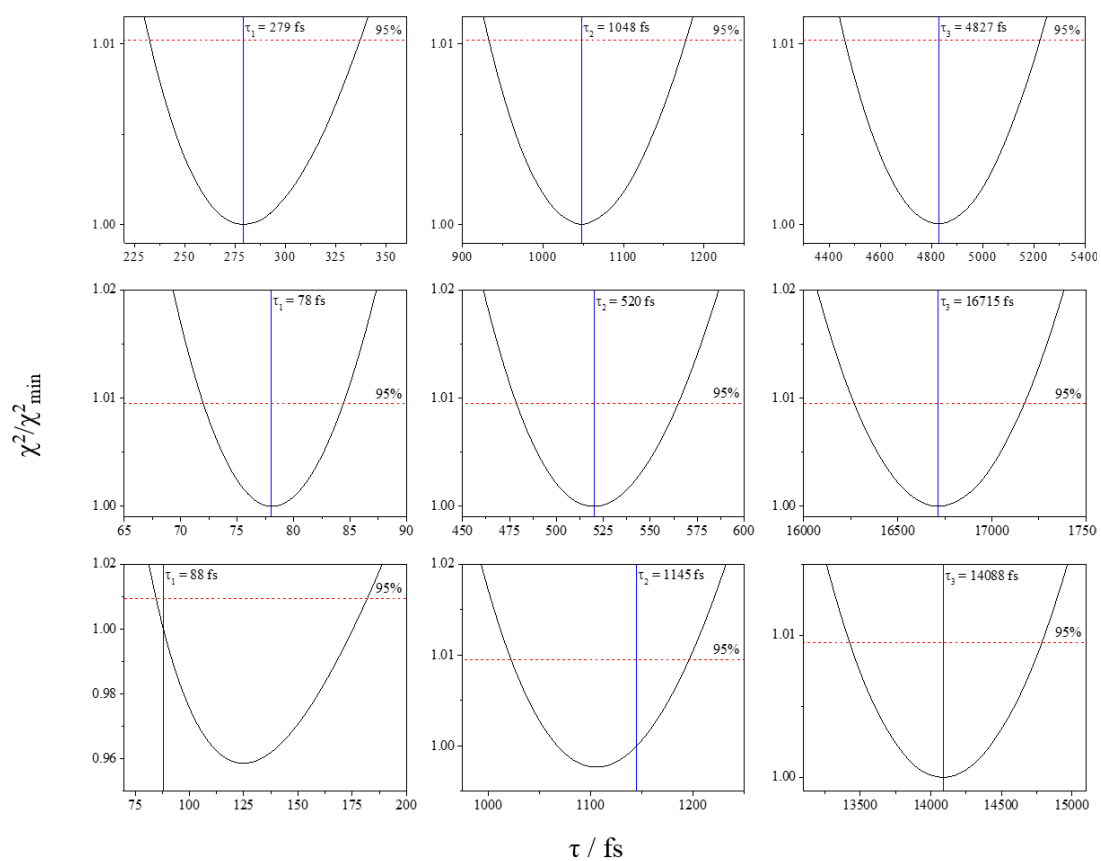
Fig. S3: Errors on the globally fitted lifetimes determined by asymptotic standard error analysis for caffeic acid. (Top) pH 2.2 water, (Middle) acetonitrile and (Bottom) dioxane.
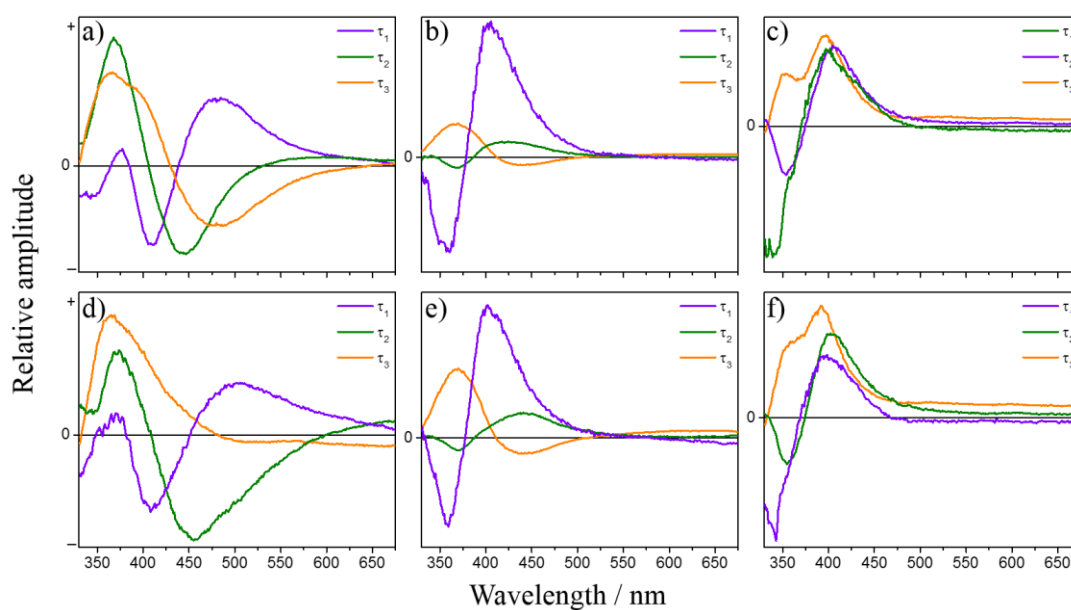
C. Decay associated spectra

Fig. S4: Decay associated spectra provided by the global fitting procedure, a) ferulic acid in pH 2.2 water, b) ferulic acid in acetonitrile, c) ferulic acid in dioxane, d) caffeic acid in pH 2.2 water, e) caffeic acid in acetonitrile and f) caffeic acid in dioxane.

Table. S1: The time constants corresponding to the DAS displayed in Fig. S4

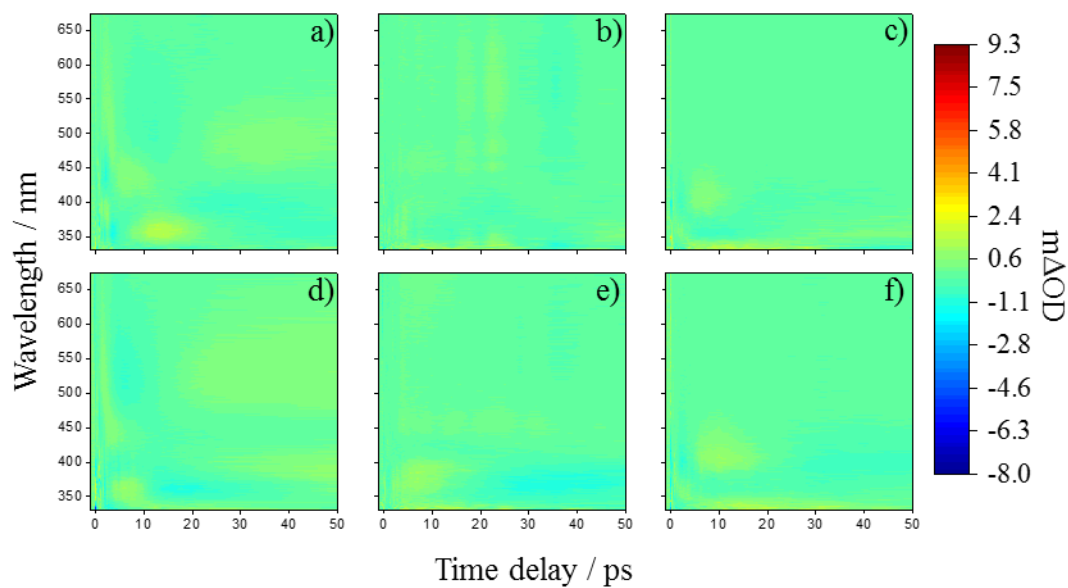|		τ_1 / fs	τ_2 / ps	τ_3 / ps
Ferulic Acid	pH 2.2	406 ± 32	2.60 ± 0.19	15.4 ± 0.9
	Acetonitrile	$47 \,^{+6}_{-2}$	0.45 ± 0.04	8.9 ± 0.3
	Dioxane	$68 \,^{+79}_{-2}$	0.97 ± 0.13	6.3 ± 0.4
Caffeic Acid	pH 2.2	279 ± 58	1.05 ± 0.13	4.8 ± 0.4
	Acetonitrile	78 ± 6	0.52 ± 0.04	16.7 ± 0.5
	Dioxane	$88 \,^{+93}_{-4}$	1.15 ± 0.12	14.1 ± 0.7

D. Global fitting residuals

Fig. S5: Residuals between the fits returned by the global fitter and the raw data, demonstrating the goodness of fit: a) ferulic acid in pH 2.2 water, b) ferulic acid in acetonitrile, c) ferulic acid in dioxane, d) caffeic acid in pH 2.2 water, e) caffeic acid in acetonitrile and f) caffeic acid in dioxane.
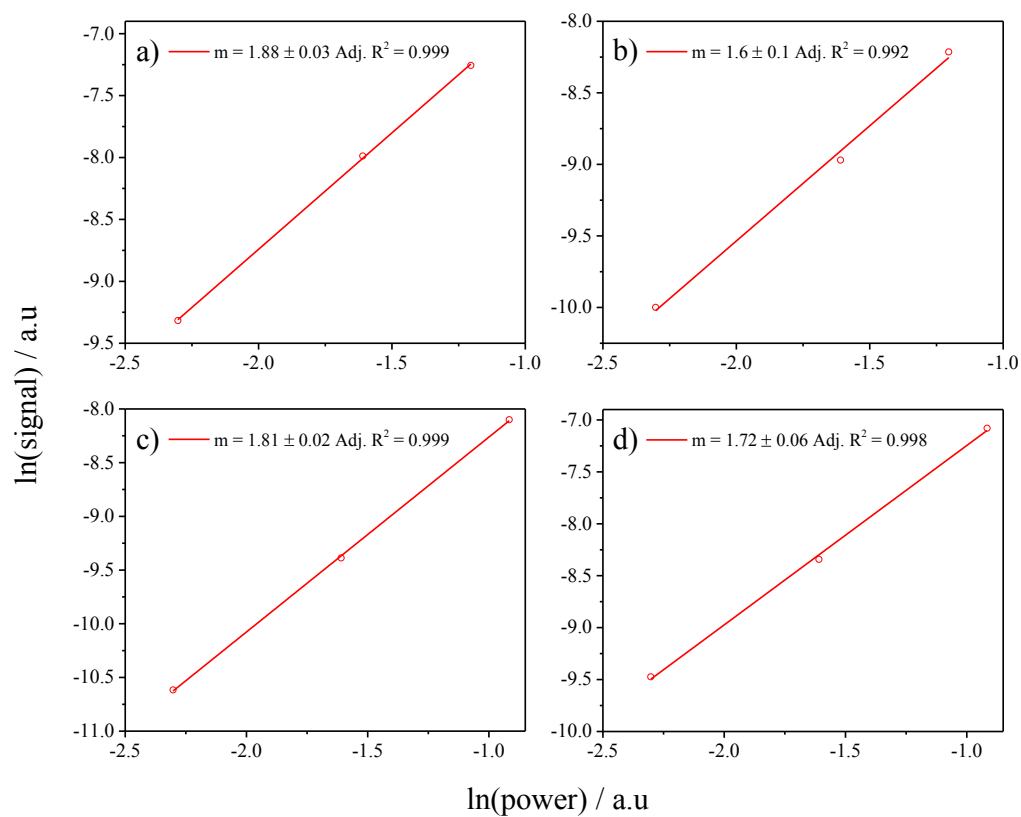
E. Power dependence measurements

Fig. S6: Power dependence of the absorption peak at 360 nm and solvated electron absorption (670 nm) in ferulic acid a) and b) respectively, and caffeic acid c) and d) respectively.
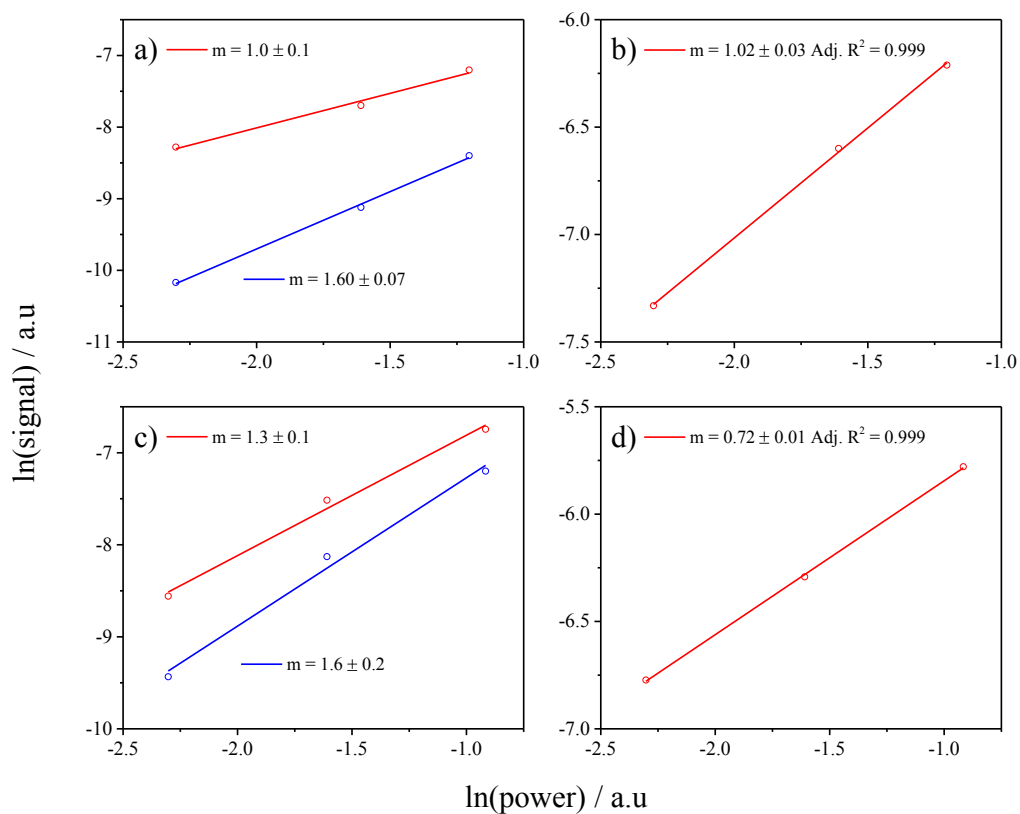
Fig. S7: Power dependence of a) ferulic acid in acetonitrile at 355 nm (red line) and 394 nm (blue line), b) ferulic acid in dioxane at 360 nm, c) caffeic acid in acetonitrile at 357 nm (red line) and 383 nm (blue line), and d) caffeic acid in dioxane at 360 nm.
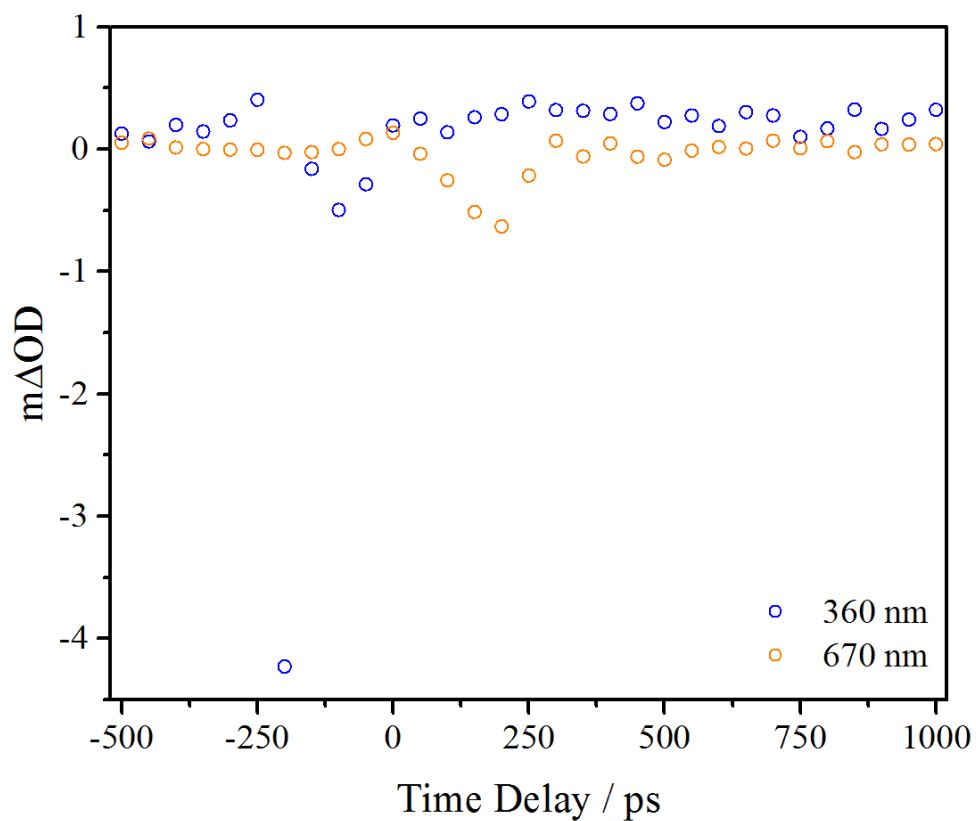
F. Solvent response

Fig. S8: Solvent only transients for water at pH 2.2 with 50 mM Glygly buffer solution. The wavelength slices are taken to demonstrate that the long-lived absorption peak and solvated electron absorption shown in Fig. 3a and 3d of the main manuscript are attributed to the solute.

G. Additional pH levels

Alongside the TEAS measurements in water at pH 2.2, additional studies at various pHs were also performed, in order to determine if the level of deprotonation of ferulic and caffeic acid had any effect on the observed photodynamics. The level of deprotonation is shown in Fig. S9. The additional measurements taken for these pH levels are shown below (Sections H-O) and demonstrate that the photodynamics display a dependence upon the pH level but, as discussed in the main text, no trend is apparent.

The solutions for ferulic acid and caffeic acid at these additional pH levels were made to a concentration of 3 mM in nano-pure water using the following buffers: 50 mM HEPES at pH 7.4, 50 mM Glygly at pH 11 and 50 mM KCl at pH 14. The level of protonation for each O–H bond was calculated using known pKa values for these acids[1] and the (adapted form of the) Henderson-Hasselbalch equation:[2]

$$10^{pH-pka} = [A^-]/[HA]$$

Table. S2: Percentage protonation for each O–H group at the pH levels used in the present studies. The labels O–H$_1$, O–H$_2$ and O–H$_3$ are expanded upon in Fig. S9.

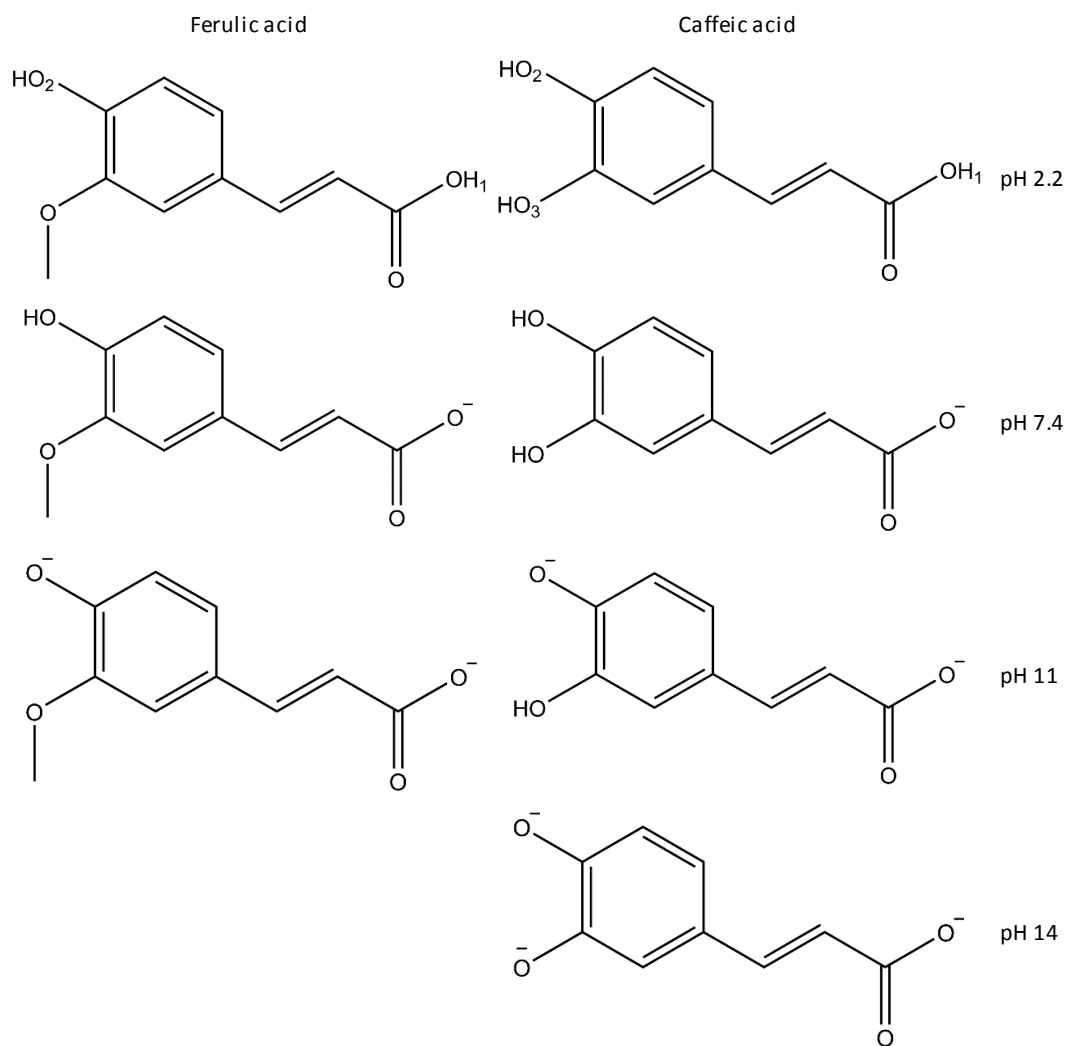|		O–H$_1$	O–H$_2$	O–H$_3$
FERULIC ACID	pKa	4.50	8.92	n/a
	pH 2.2	99.50%	>99.99%	n/a
	pH 7.4	0.13%	96.98%	n/a
	pH 11	<0.01%	0.83%	n/a
CAFFEIC ACID	pKa	4.38	8.58	11.50
	pH 2.2	99.34%	>99.99%	>99.99%
	pH 7.4	0.10%	93.40%	>99.99%
	pH 11	<0.01%	0.38%	68.38%
	pH 14	<0.01%	<0.01%	0.32%

Fig. S9: The level of protonation of the O–H groups of ferulic and caffeic acid at pHs 2.2, 7.4, 11 and 14.
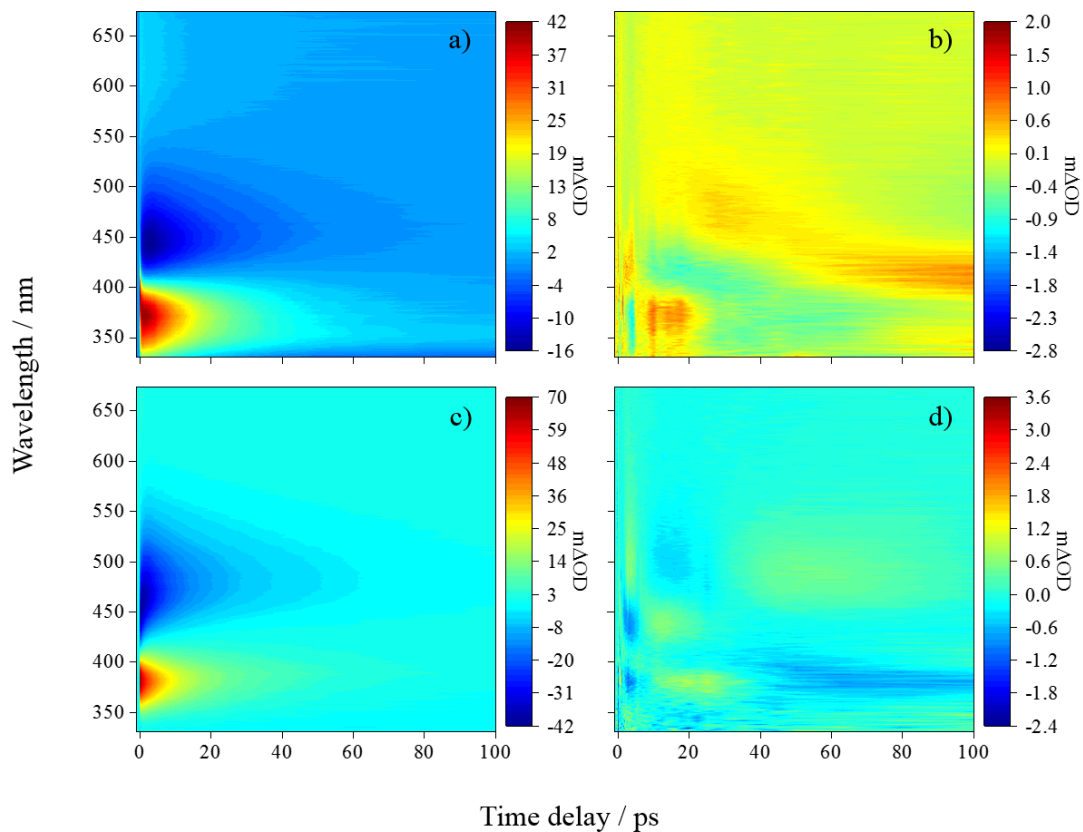
H. TAS of ferulic acid in water at pH 7.4 and 11

Fig. S10: Transient absorption spectra (TAS) and global fit residuals for ferulic acid, a) pH 7.4 water TAS, b) pH 7.4 water residual, c) pH 11 water TAS, and d) pH 11 water residual.

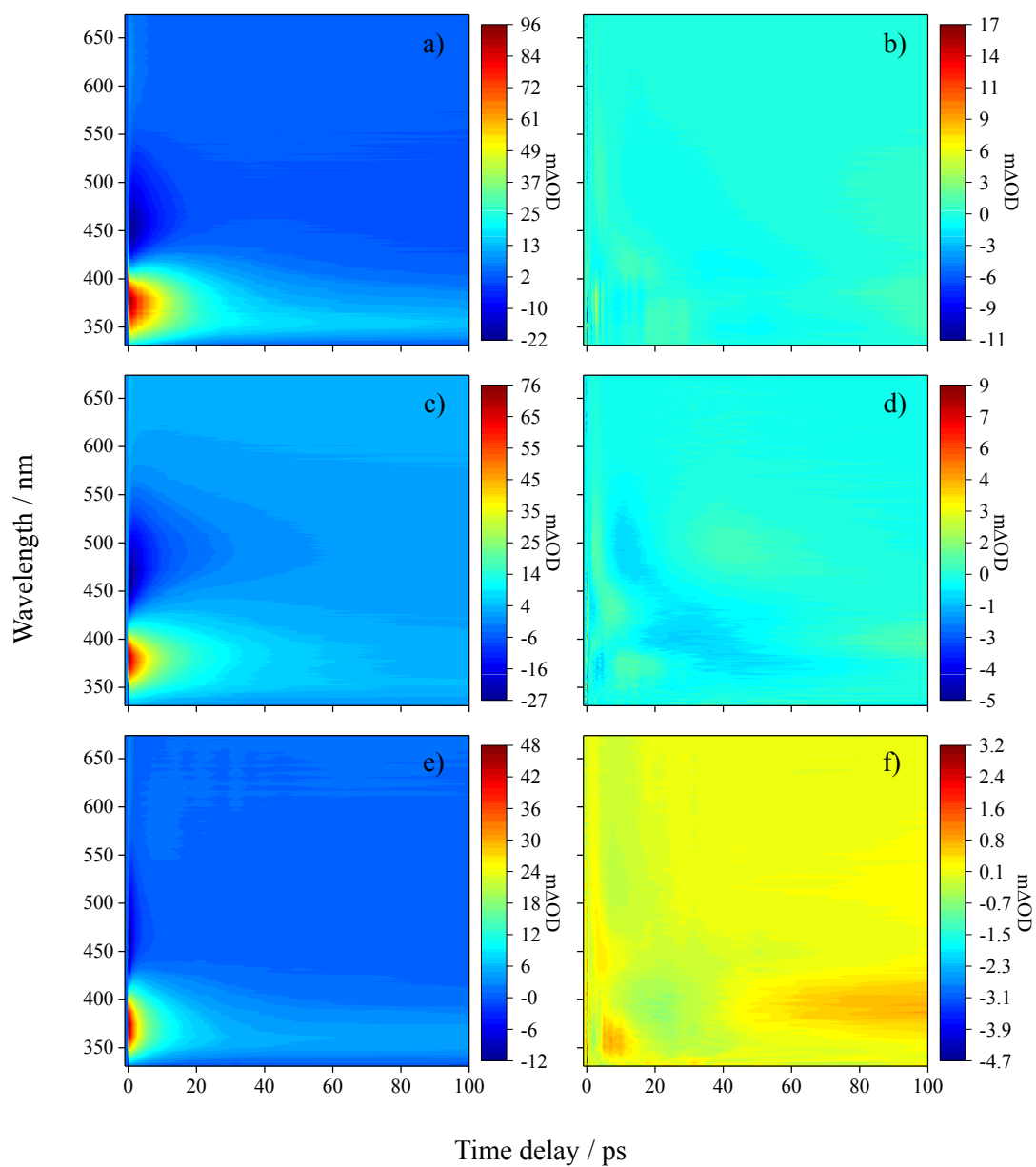# I. TAS of caffeic acid in water at pH 7.4, 11 and 14

Fig. S11: Additional transient absorption spectra (TAS) and global fit residuals for caffeic acid, a) pH 7.4 water TAS, b) pH 7.4 water residual, c) pH 11 water TAS, d) pH 11 water residual, e) pH 14 water TAS and f) pH 14 water residual.

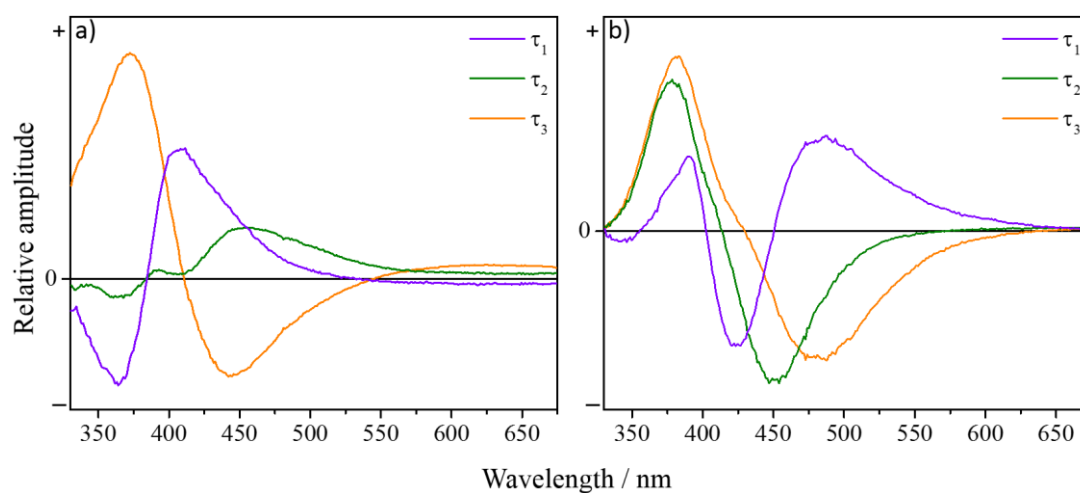## J. Decay associate spectra for ferulic and caffeic acids at higher pH.

Fig. S12: Additional decay associated spectra provided by the global fitting procedure for ferulic acid in a) pH 7.4 water and b) pH 11 water. The corresponding time-constants are shown in Table S2.
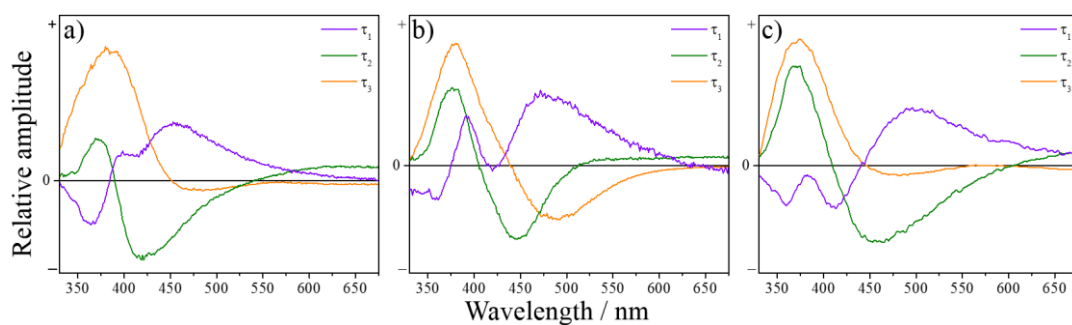

Fig. S13: Additional decay associated spectra provided by the global fitting procedure for caffeic acid in a) pH 7.4 water, b) pH 11 water and c) pH 14 water. The corresponding time-constants are shown in Table S2.

K. Global fit time constants

Table S3: Time constants (τ) for ferulic acid and caffeic acid in varying solvent environments. Values are retrieved from global analysis of the TAS, with the errors calculated using asymptotic standard errors.

		τ_1 / fs	τ_2 / ps	τ_3 / ps
Ferulic Acid	pH 2.2	406 ± 32	2.60 ± 0.19	15.4 ± 0.9
	pH 7.4	275 ± 29	1.13 ± 0.11	17.8 ± 0.5
	pH 11	527 ± 36	4.89 ± 0.33	23.5 ± 1.3
	Acetonitrile	$47\,^{+\,6}_{-\,2}$	0.45 ± 0.04	8.9 ± 0.3
	Dioxane	$68\,^{+\,79}_{-\,2}$	0.97 ± 0.13	6.3 ± 0.4
Caffeic Acid	pH 2.2	279 ± 58	1.05 ± 0.13	4.8 ± 0.4
	pH 7.4	401 ± 76	5.65 ± 1.63	14.6 ± 2.0
	pH 11	286 ± 33	2.90 ± 0.37	15.0 ± 1.2
	pH 14	328 ± 46	1.13 ± 0.11	8.3 ± 0.5
	Acetonitrile	78 ± 6	0.52 ± 0.04	16.7 ± 0.5
	Dioxane	$88\,^{+\,93}_{-\,4}$	1.15 ± 0.12	14.1 ± 0.7

L. Global fitting error analysis on ferulic acid at pH 7.4, and 11
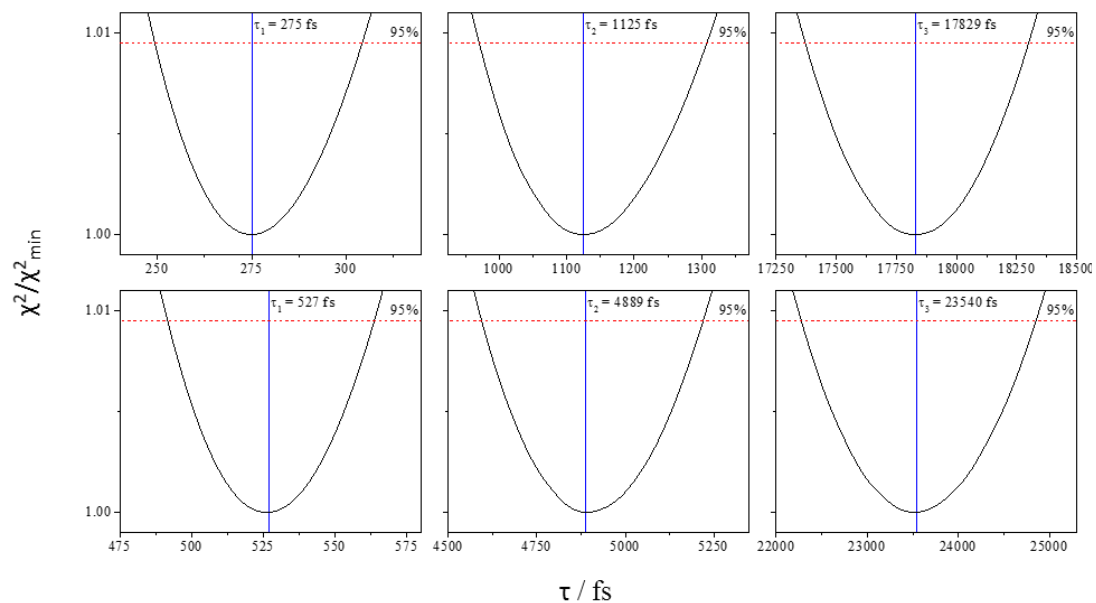

Fig. S15: Errors on the globally fitted lifetimes determined by asymptotic standard error analysis for ferulic acid. (Top) pH 7.4 water and (Bottom) pH 11 water.

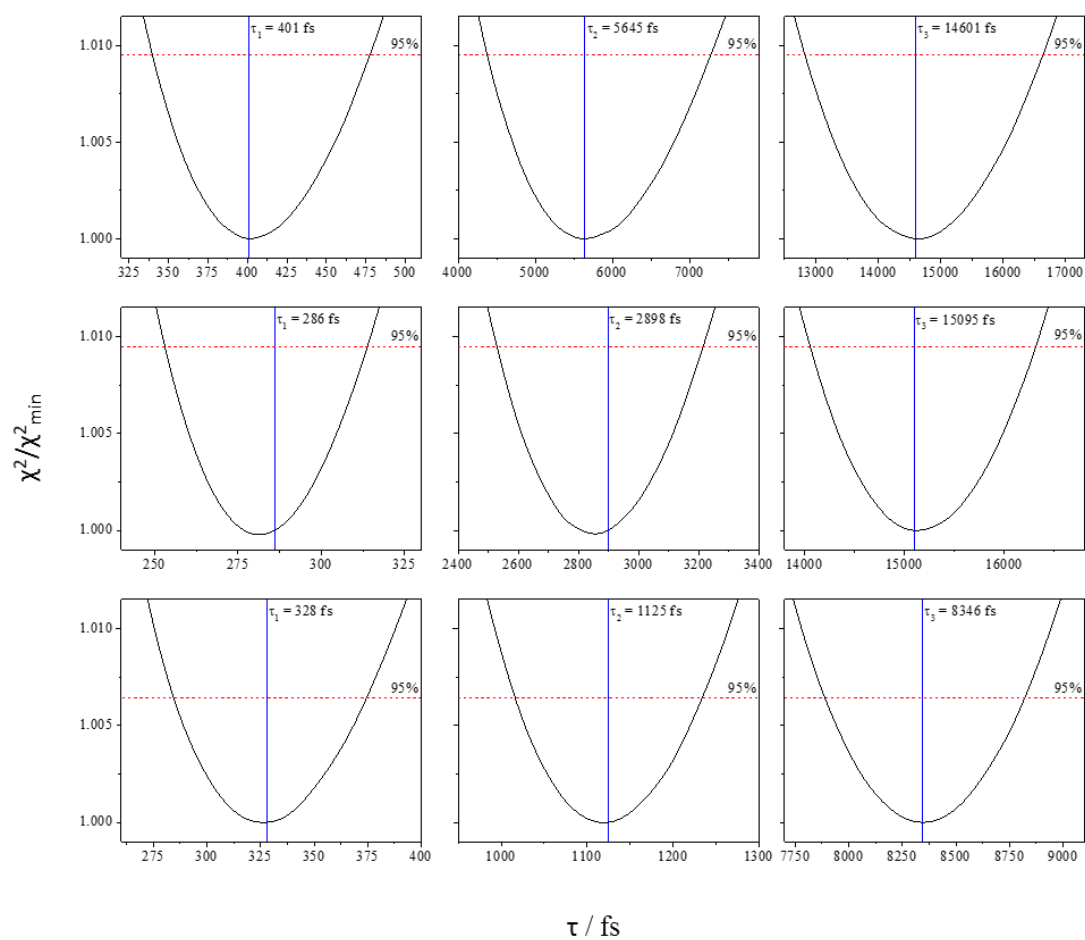## M. Global fitting error analysis on caffeic acid at pH 7.4, 11 and 14

Fig. S14: Errors on the globally fitted lifetimes determined by asymptotic standard error analysis for caffeic acid. (Top) pH 7.4 water, (Middle) pH 11 water and (Bottom) pH14 water.

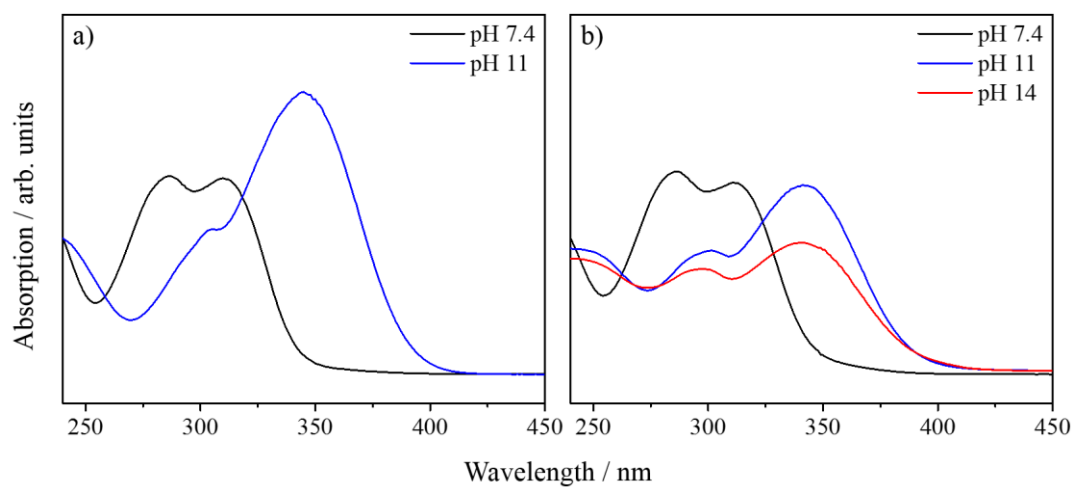## N. Static UV/vis ferulic and caffeic acid at higher pHs

Fig. S16: UV-Vis of a) ferulic acid and b) caffeic acid, in pH 7.4 water (black line), pH 11 water (blue line) and pH 14 water (red line).

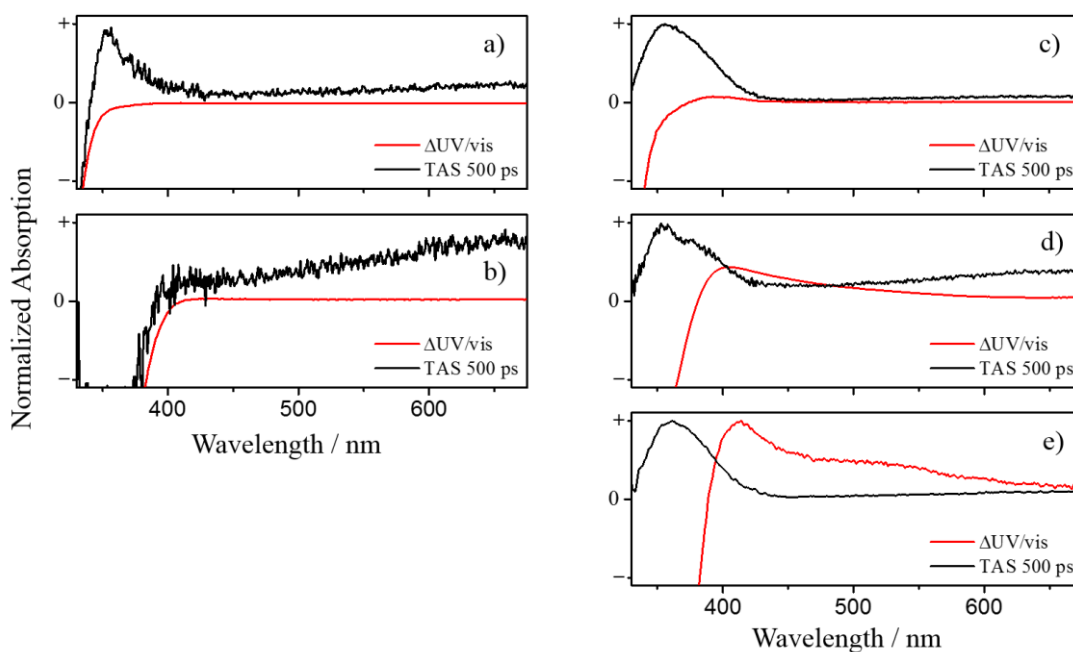## O. ΔUV/vis spectra for ferulic and caffeic acid at higher pHs

Fig. S17: The 500 ps TAS overlaid with ΔUV/vis spectra for ferulic acid in a) pH 7.4 water, and b) pH 11 and for caffeic acid in c) pH 7.4 water, d) pH 11 water, and e) pH 14 water.

We note that in the case of the ΔUV/vis spectra for caffeic acid at pH 11 and 14, a large absorption feature begins to appear that is significantly red-shifted moving it out of the radical's absorption region. Whether this is due to a large spectral-shift in the *cis*-isomer's absorption or the appearance of a new photoproduct is unknown; yet it is absent within the corresponding TAS.

1.   Borges, F.; Lima, J. L.; Pinto, I.; Reis, S.; Siquet, C. Application of a Potentiometric System with Data-Analysis Computer Programs to the Quantification of Metal-Chelating Activity of Two Natural Antioxidants: Caffeic Acid and Ferulic Acid. *Helv. Chim. Acta* **2003,** *86* (9), 3081-3087.
2.   Hasselbalch, K. The calculation of blood pH via the partition of carbon dioxide in plasma and oxygen binding of the blood as a function of plasma pH. *Biochem Z* **1916,** *78*, 112-144.