Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting information for: Excited-state dynamics of cinnamate-based UV filters: bringing decay pathways to light by photoelectron velocity map imaging

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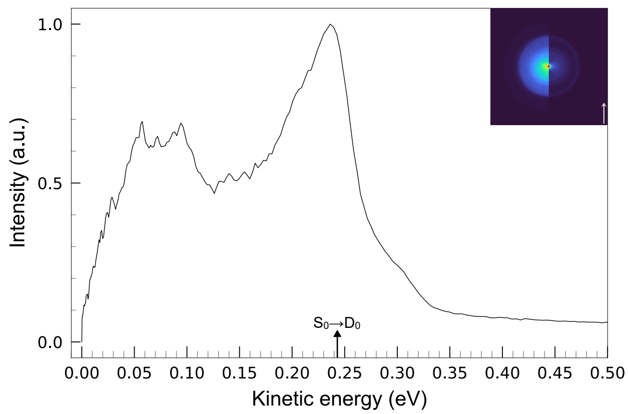

Figure S1: PE spectrum of the *anti/cis* conformer of methyl sinapate obtained after one-colour (1+1) R2PI via the $S_1 \leftarrow S_0$ 0-0 transition at 31170.1 cm^{-1}. The inset shows in the left half the recorded image while the right half presents the reconstructed slice through the centre of the original 3D distribution with the arrow indicating the electric field polarisation of the counter-propagating excitation and ionization laser pulses. The kinetic energy associated with adiabatic $D_0 \leftarrow S_0$ ionization as determined in ZEKE-PFI studies[1] is indicated with the black arrow.

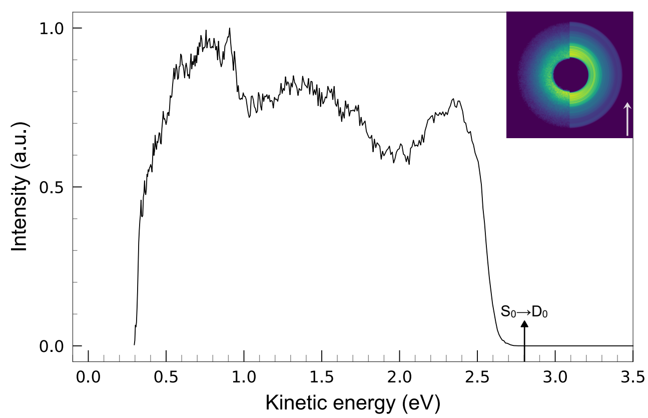

Figure S2: PE spectrum of the *anti/cis* conformer of methyl sinapate obtained after two-colour (1+1') R2PI via the $S_1 \leftarrow S_0$ 0-0 transition at 31170.1 cm^{-1} and using a 193 nm photon for ionization. The inset shows in the left half the recorded image while the right half presents the reconstructed slice through the centre of the original 3D distribution with the arrow indicating the electric field polarisation of the counter-propagating excitation and ionization laser pulses. The kinetic energy associated with adiabatic $D_0 \leftarrow S_0$ ionization at 7.486 eV as determined in ZEKE-PFI studies[1] is indicated with the black arrow. Due to the very poor signal to noise ratio of the experiment a somewhat poorer agreement is observed between this value and the value as it appears from the spectrum.

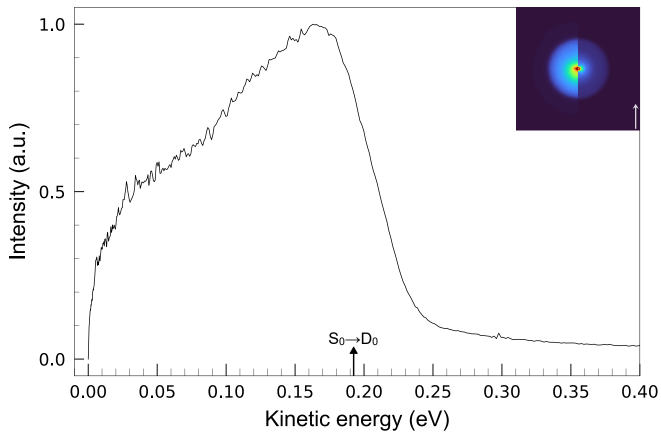

Figure S3: PE spectrum of the *anti/cis* conformer of sinapoyl methyl lactate obtained after one-colour (1+1) R2PI probed via the $S_1 \leftarrow S_0$ b_0^1 transition at 30894 cm^{-1}. The inset shows in the left half the recorded image while the right half presents the reconstructed slice through the centre of the original 3D distribution with the arrow indicating the electric field polarisation of the counter-propagating excitation and ionization laser pulses. The determined kinetic energy associated with adiabatic $D_0 \leftarrow S_0$ ionization is indicated with the black arrow. The determined adiabatic ionisation energy is 7.47 eV.

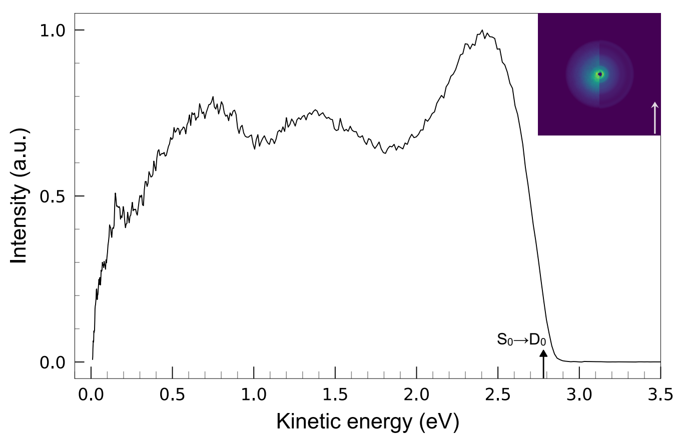

Figure S4: PE spectrum of the *anti/cis* conformer of sinapoyl methyl lactate obtained after two-colour (1+1') R2PI probed via $S_1 \leftarrow S_0$ b_0^1 transition at 30894 cm^{-1} and using a 193 nm photon for ionization. The inset shows in the left half the recorded image while the right half presents the reconstructed slice through the centre of the original 3D distribution with the arrow indicating the electric field polarisation of the counter-propagating excitation and ionization laser pulses. The determined kinetic energy associated with adiabatic $D_0 \leftarrow S_0$ ionization is indicated with the black arrow.

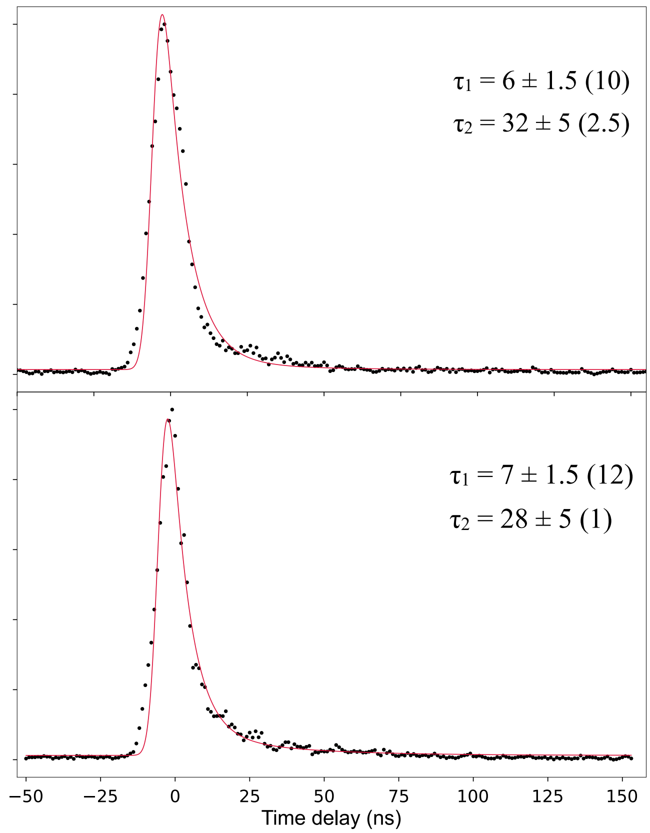

Figure S5: Time-resolved (1+1') R2PI curves of the *syn/cis* (top) and *anti/cis* (bottom) conformers of synapoyl methyl lactate after excitation via the $S_1 \leftarrow S_0$ 0-0 transitions at 30713 and 30847 cm^{-1}, respectively. The solid lines are biexponential fits convoluted with a Gaussian profile, with decay times in nanoseconds, and the relative amplitude of each component given in parentheses.

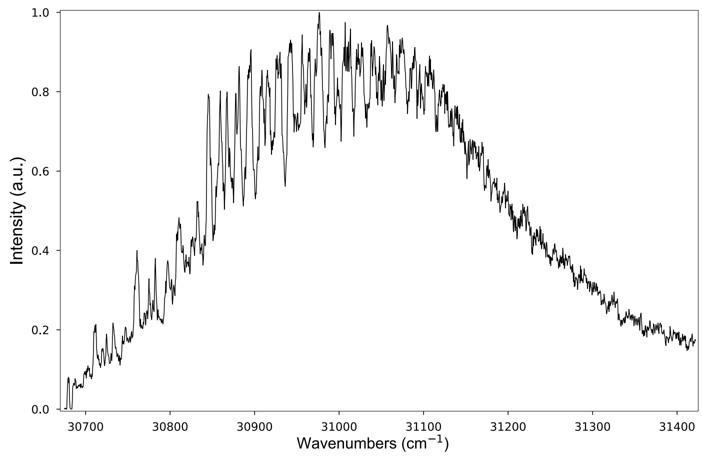

Figure S6: (1+1) R2PI excitation spectrum of SML.

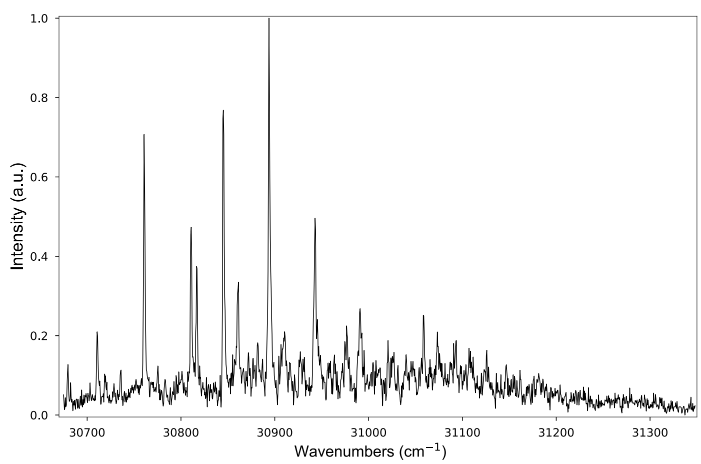

Figure S7: (1+1') R2PI excitation spectrum of SML.

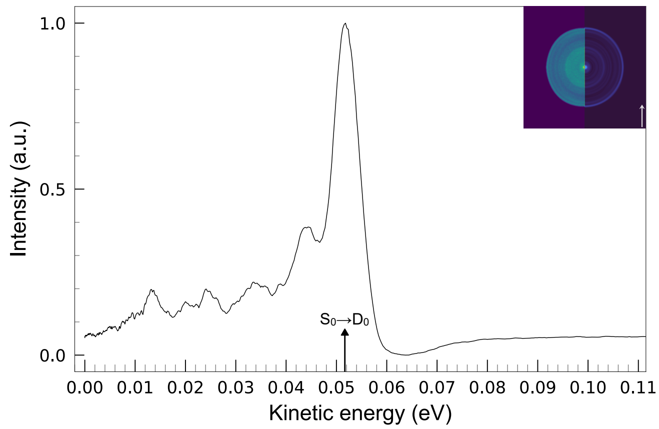

Figure S8: PE spectrum of the *syn/trans* conformer of methyl ferulate obtained after one-colour (1+1) R2PI obtained via the $S_1 \leftarrow S_0$ 0-0 transition at 31659.6 cm^{-1}. The inset shows in the left half the recorded image while the right half presents the reconstructed slice through the centre of the original 3D distribution with the arrow indicating the electric field polarisation of the counter-propagating excitation and ionization laser pulses. The determined kinetic energy associated with adiabatic $D_0 \leftarrow S_0$ ionization is indicated with the black arrow. The determined adiabatic ionisation energy is 7.799 eV.

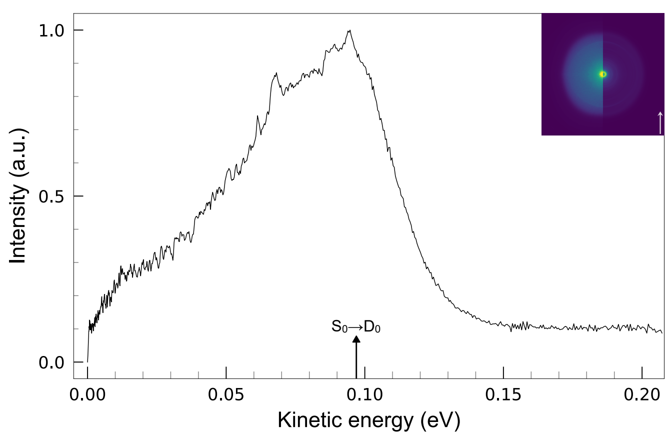

Figure S9: PE spectrum of the *anti/trans* conformer of methyl ferulate obtained after one-colour (1+1) R2PI obtained via the $S_1 \leftarrow S_0$ 0-0 transition at 32083.7 cm^{-1}. The inset shows in the left half the recorded image while the right half presents the reconstructed slice through the centre of the original 3D distribution with the arrow indicating the electric field polarisation of the counter-propagating excitation and ionization laser pulses. The determined kinetic energy associated with adiabatic $D_0 \leftarrow S_0$ ionization is indicated with the black arrow. The determined adiabatic ionisation energy is 7.86 eV.

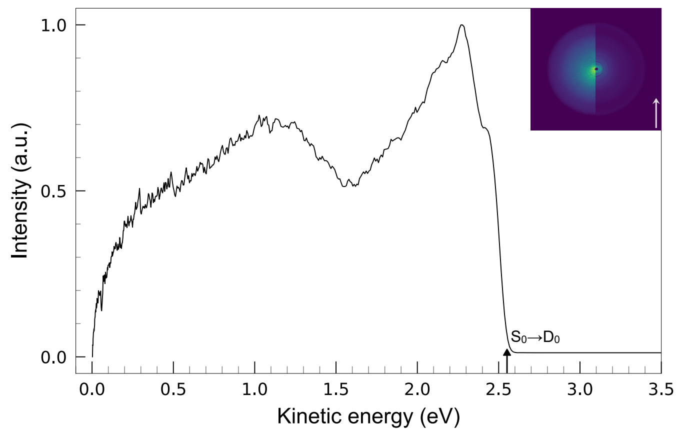

Figure S10: PE spectrum of the *syn/trans* conformer of methyl ferulate obtained after two-colour (1+1') R2PI via the $S_1 \leftarrow S_0$ 0-0 transition at 31659.6 cm^{-1} and using a 193 nm photon for ionization. The inset shows in the left half the recorded image while the right half presents the reconstructed slice through the centre of the original 3D distribution with the arrow indicating the electric field polarisation of the counter-propagating excitation and ionization laser pulses. The kinetic energy associated with adiabatic $D_0 \leftarrow S_0$ ionization is indicated with the black arrow.

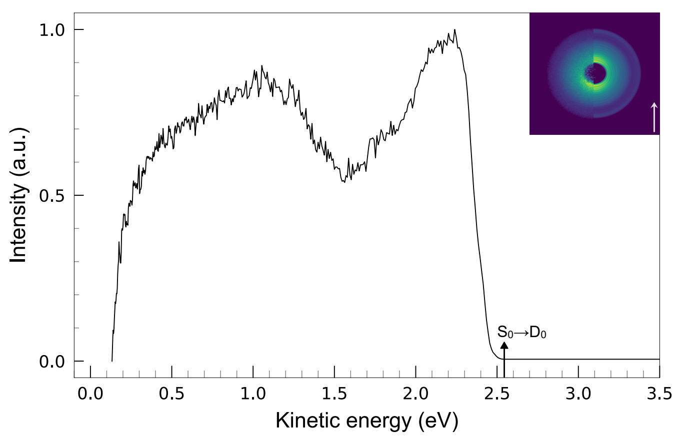

Figure S11: PE spectrum of the *anti/trans* conformer of methyl ferulate obtained after two-colour (1+1') R2PI via the $S_1 \leftarrow S_0$ 0-0 transition at 32083.7 cm^{-1} and using a 193 nm photon for ionization. The inset shows in the left half the recorded image while the right half presents the reconstructed slice through the centre of the original 3D distribution with the arrow indicating the electric field polarisation of the counter-propagating excitation and ionization laser pulses. The kinetic energy associated with adiabatic $D_0 \leftarrow S_0$ ionization is indicated with the black arrow.

References

(1) Fan, J.; Finazzi, L.; Jan Buma, W. Elucidating the photoprotective properties of natural UV screening agents: ZEKE–PFI spectroscopy of methyl sinapate. *Phys. Chem. Chem. Phys.* **2022**, *24*, 3984–3993.