Electronic Supporting Information

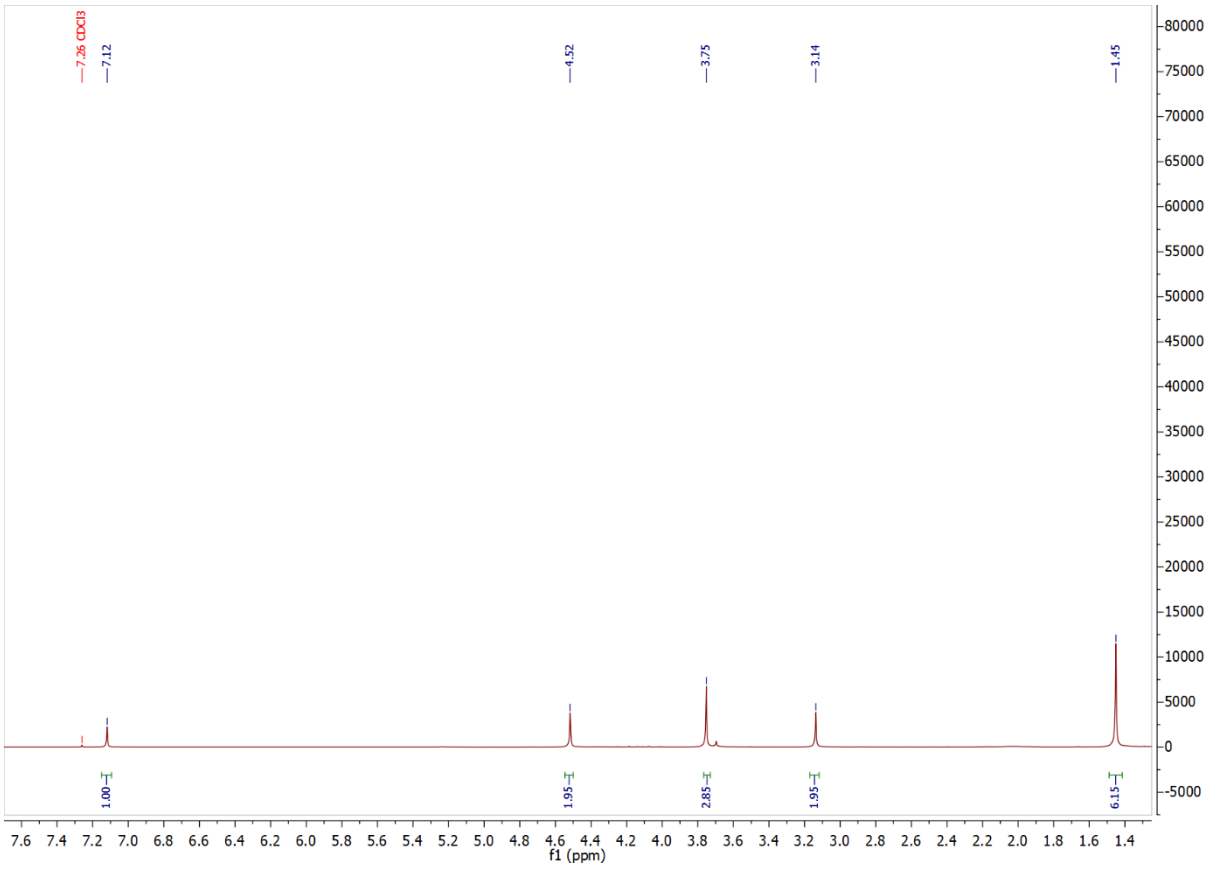
Photosensitised Biphotonic Chemistry of Pyrimidine Derivatives

Ofelia R. Alzueta,[a] Jean Cadet, [b] M. Consuelo Cuquerella[a]* and Miguel A. Miranda[a] *

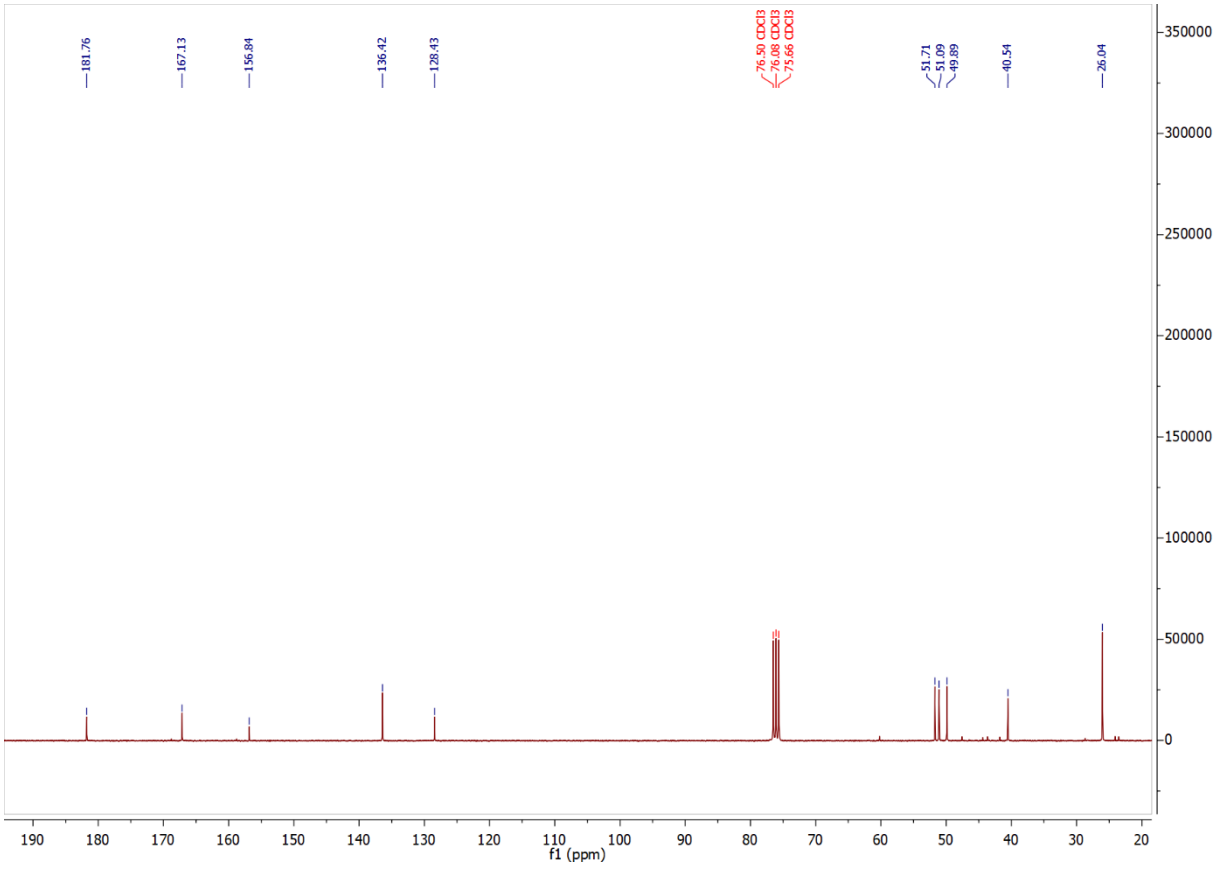
[a]Instituto Universitario Mixto de Tecnología Química (UPV-CSIC), Universitat Politècnica de València, Av. Los Naranjos s/n 46022, Valencia, Spain. e-mail: mmiranda@qim.upv.es, ofrodal@upv.es and mcuquere@itq.upv.es

[b]Département de Médecine Nucléaire et Radiobiologie, Faculté de médecine et des sciences de la santé, Université de Sherbrooke, Sherbrooke, QC, Canada. e-mail: jean.cadet@USherbrooke.ca

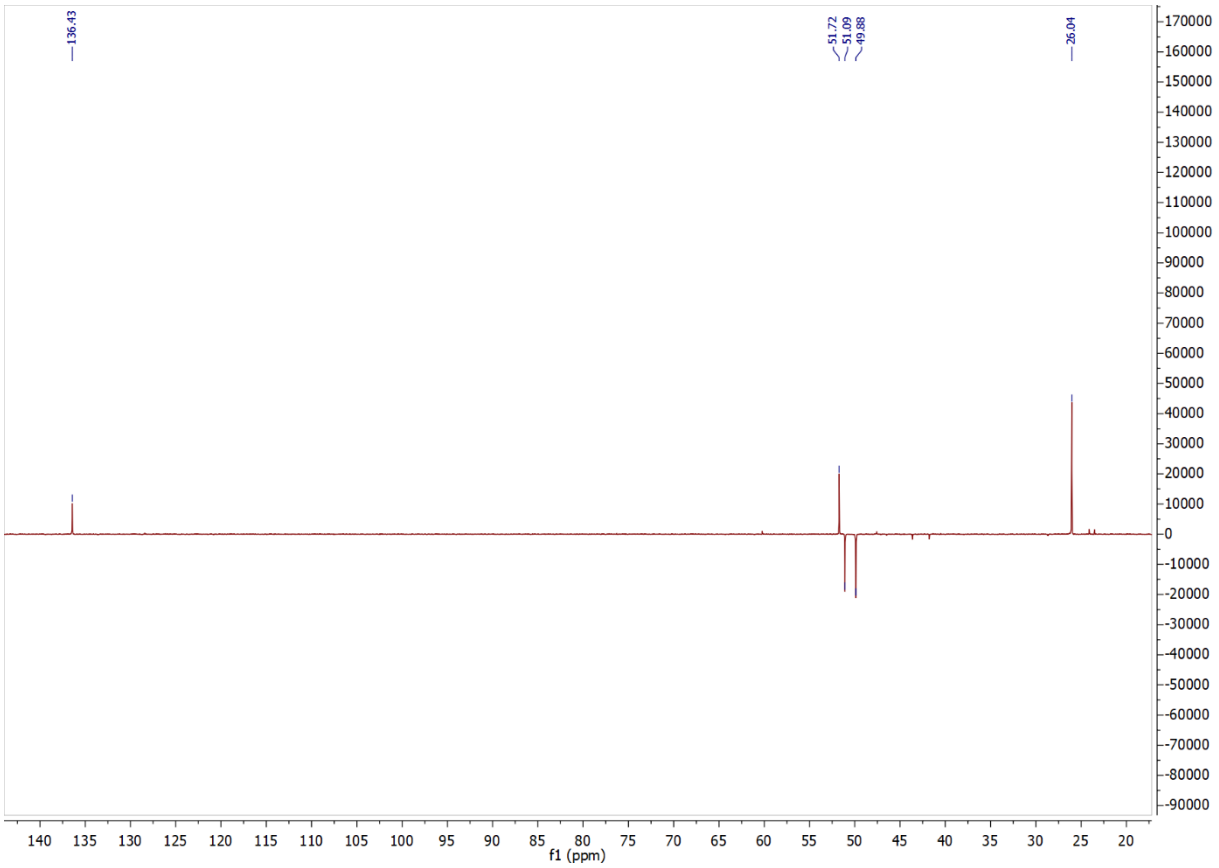
^{1}H Norrish-Yang photoproduct



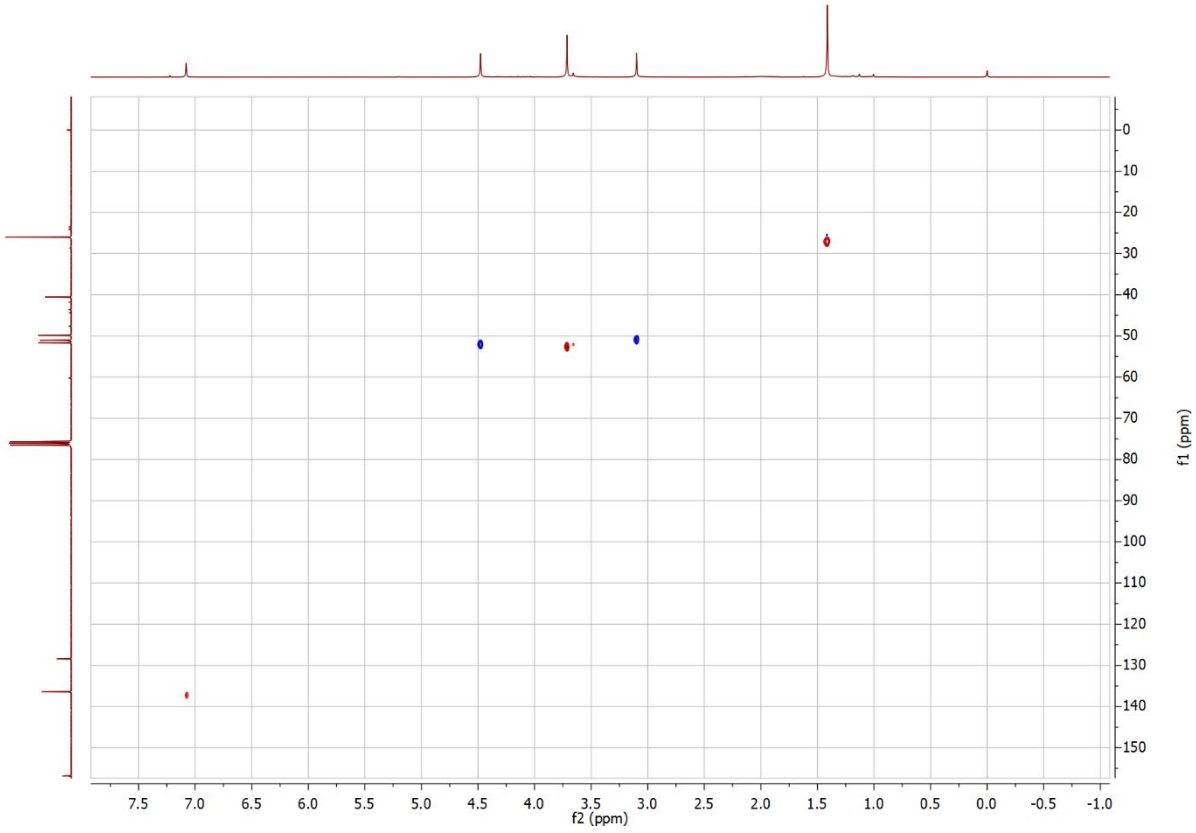
^{13}C Norrish-Yang photoproduct



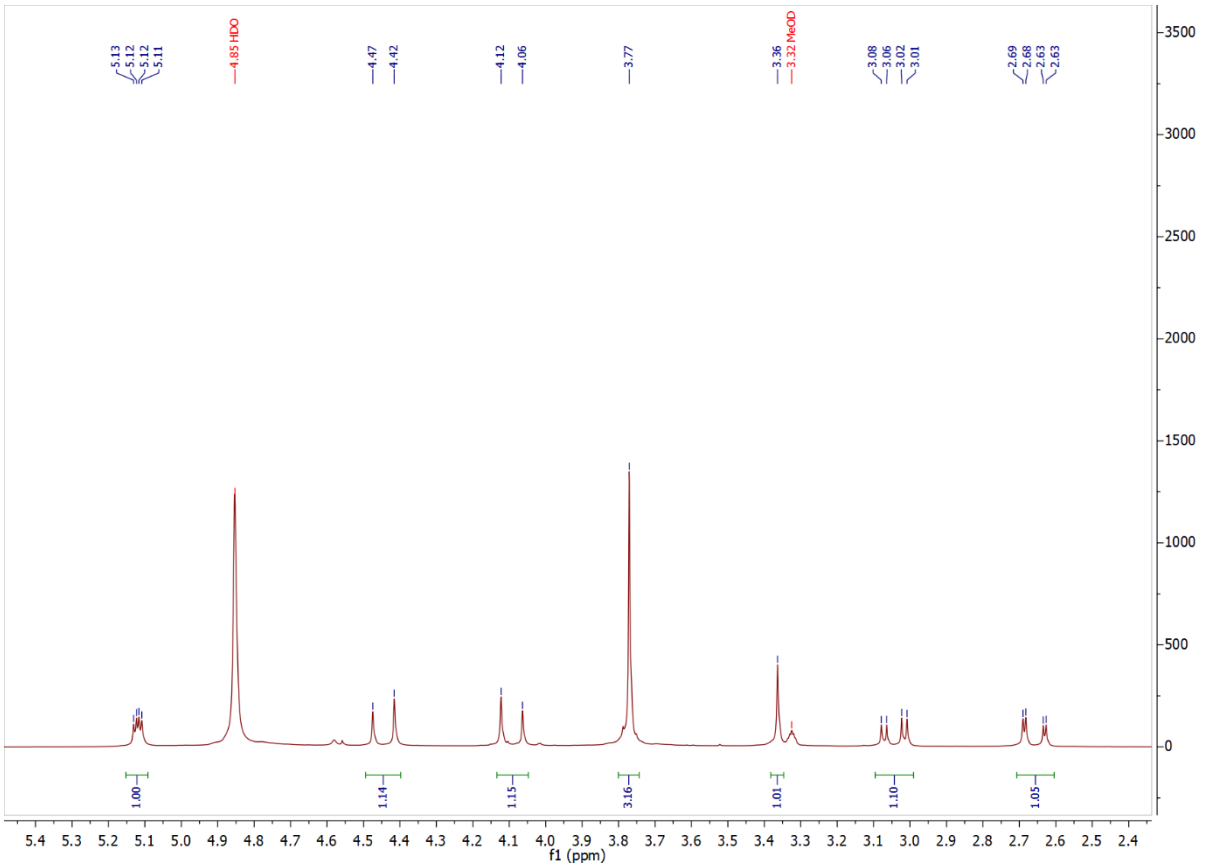
DEPT-135 Norrish-Yang photoproduct



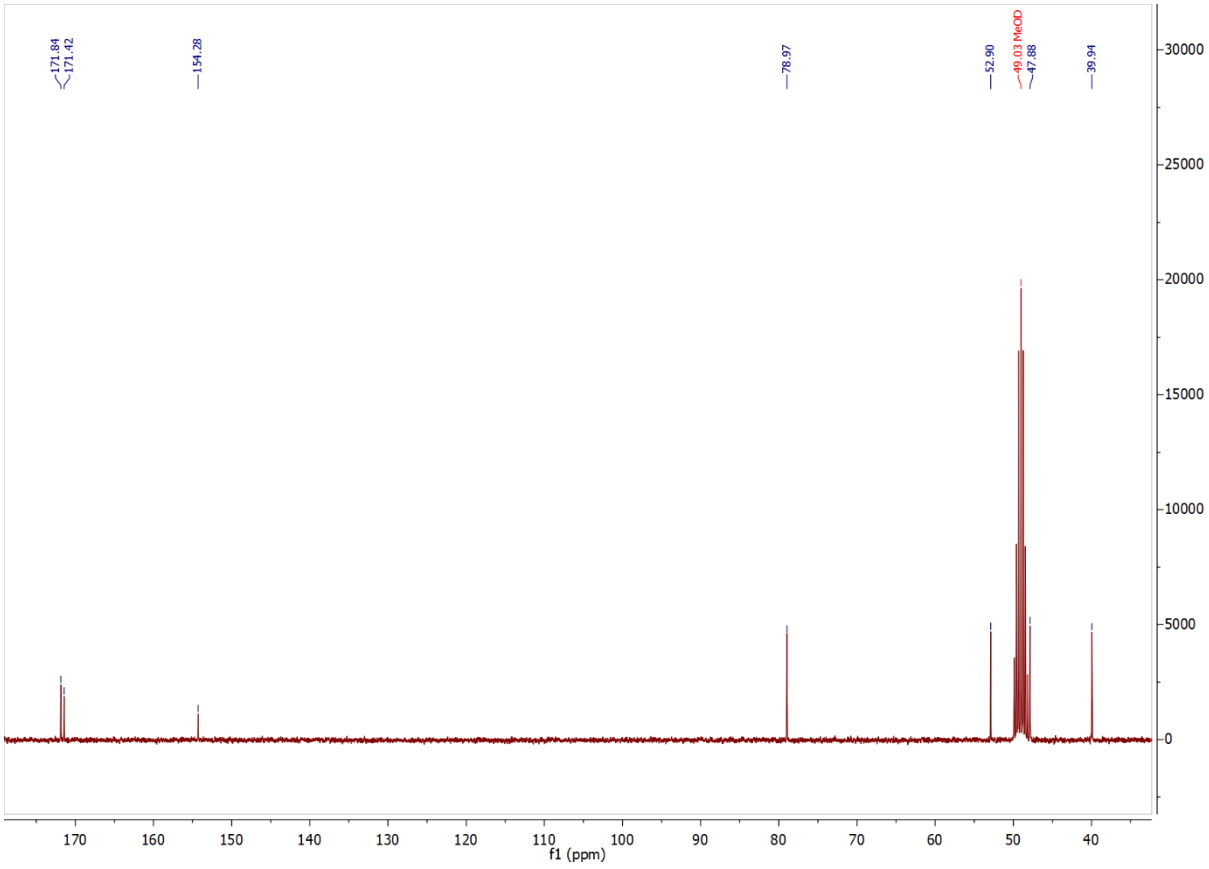
HSQC Norrish-Yang photoproduct



^{1}H Hydrated uracil



^{13}C Hydrated uracil



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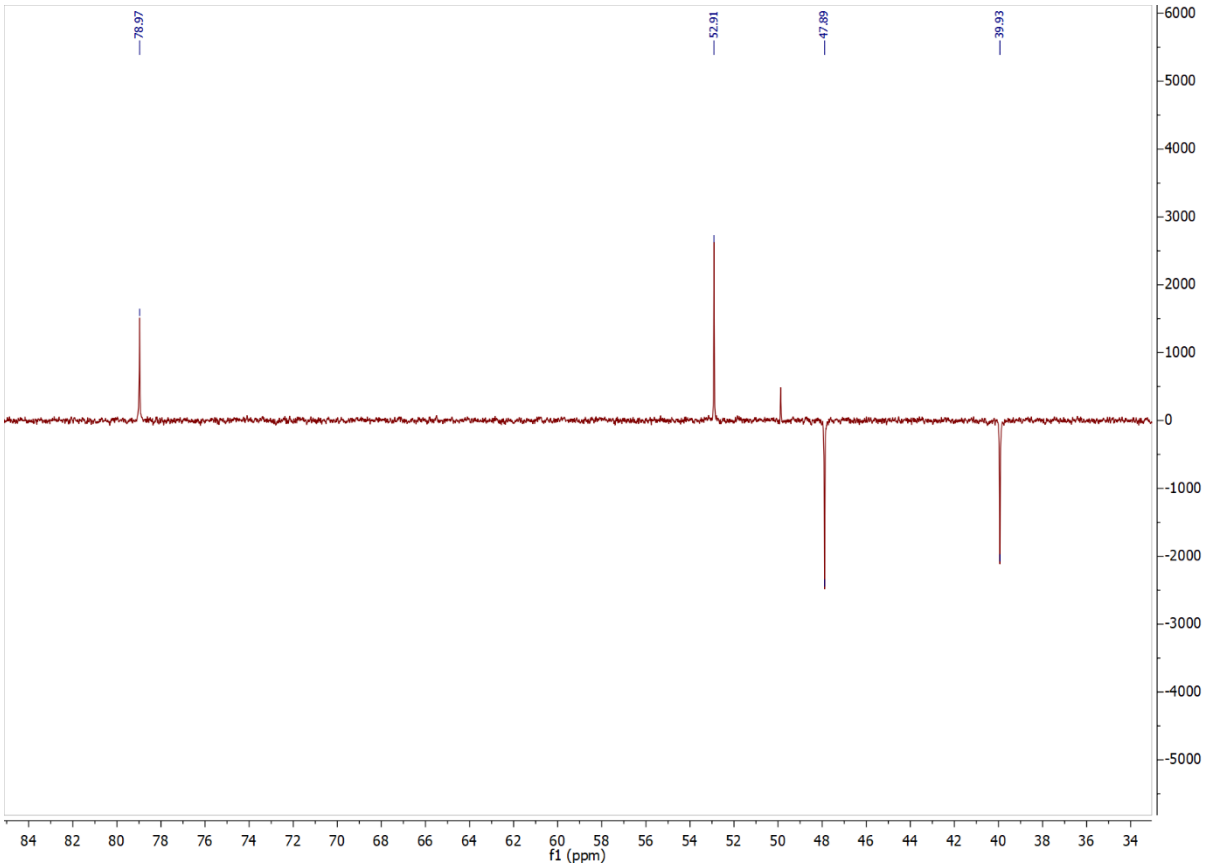
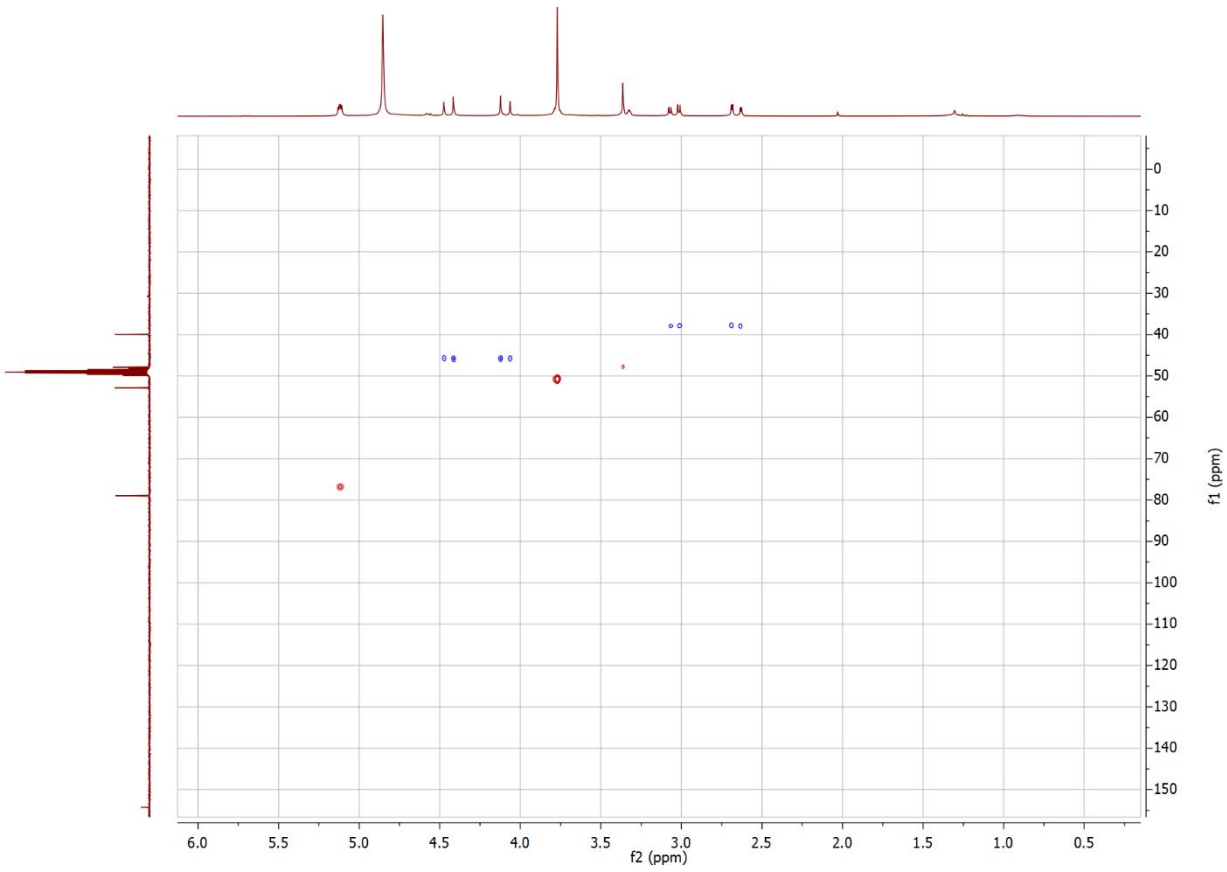


HSQC Hydrated uracil



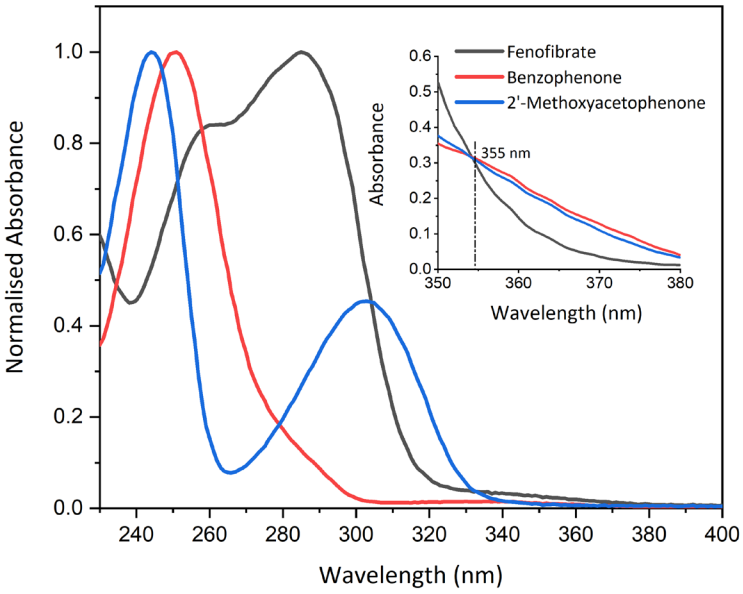
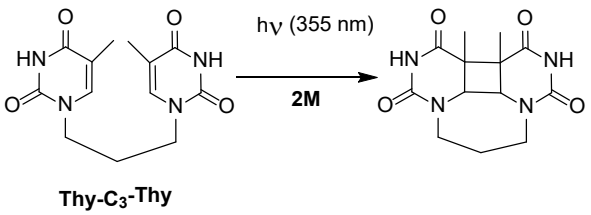


Figure S1. UV spectra of photosensitisers: fenofibrate (black), benzophenone (red) and 2’-methoxyacetophenone (blue). Inset) UV spectra of the mentioned photosensitisers at the biphotonic irradiation concentration, with 0.3 absorbance at 355 nm.

Securing equivalent photon fluxes in the laser and Xe-lamp irradiations

Equivalent photon fluxes must be secured for both laser and Xe-lamp irradiations, in order to make meaningful comparisons. To achieve this goal, **2M** photosensitisation of a dimeric thymine (**Thy-C_3-Thy**) yielding thymine cyclobutane dimers[1] has been chosen as reaction model (Scheme S1).



Scheme S1. 2M photosensitised cyclobutane thymine dimerisation.[1]

A solution containing 0.04 mM of both, **2M** and **Thy-C_3-Thy** in PBS 10 mM was prepared. Then, two aliquots (2 mL) of this solution were treated separately. One of them was irradiated with a laser beam (Nd/YAG, 355 nm, 10 Hz, 45 mJ/pulse) during 1.5 min, and its UV spectrum absorbance registered. The other one was irradiated at 355 nm with a Xenon lamp equipped with a monochromator. The progress of the reaction was periodically monitored by UV spectroscopy. The results are shown in Figure S2.

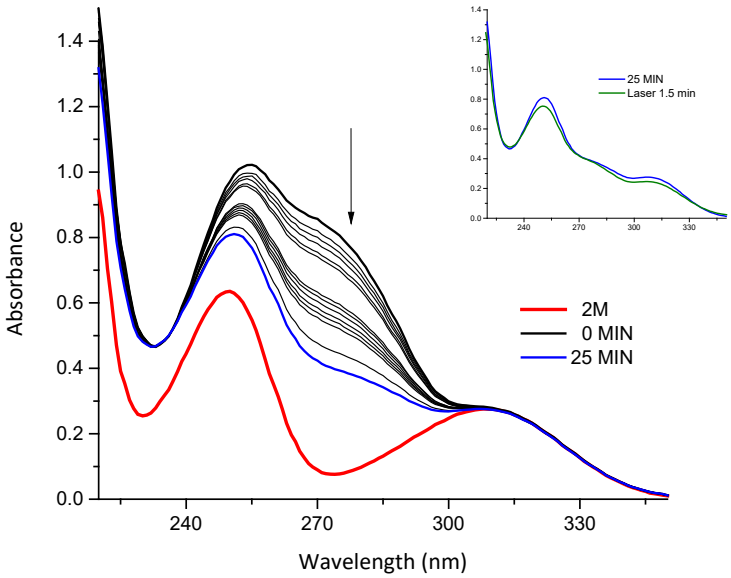


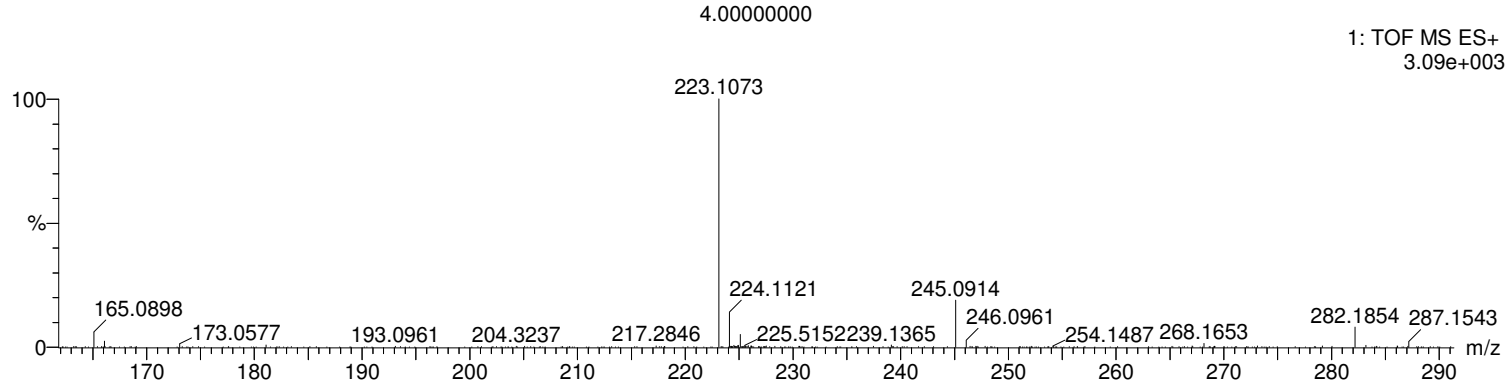
Figure S2. Xe lamp irradiation of a solution containing equimolar quantities of 2M and Thy-C3-Thy (0.04 mM) in PBS 10 mM, monitored by UV spectroscopy. Inset: Comparison of the UV spectra of the sample irradiated with 355 nm laser light (1.5 min) with the 25 min Xe lamp irradiation. Under these conditions, the absorbance of the samples was 0.01 at 355 nm.

[1] a) O. R. Alzueta, M. C. Cuquerella and M. A. Miranda, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2019**, *218*, 191-195; b) O. R. Alzueta, M. C. Cuquerella and M. A. Miranda, *J. Org. Chem.* **2019**, *84*, 13329-13335.

Single Mass Analysis

Tolerance = 6.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
156 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-30 N: 0-2 O: 0-4 Na: 0-1 Cl: 0-1



Minimum:				-1.5			
Maximum:		5.0	6.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
223.1073	223.1083	-1.0	-4.5	5.5	101.1	0.0	C11 H15 N2 O3

Figure S3.- Mass spectra of photoinduced product 1

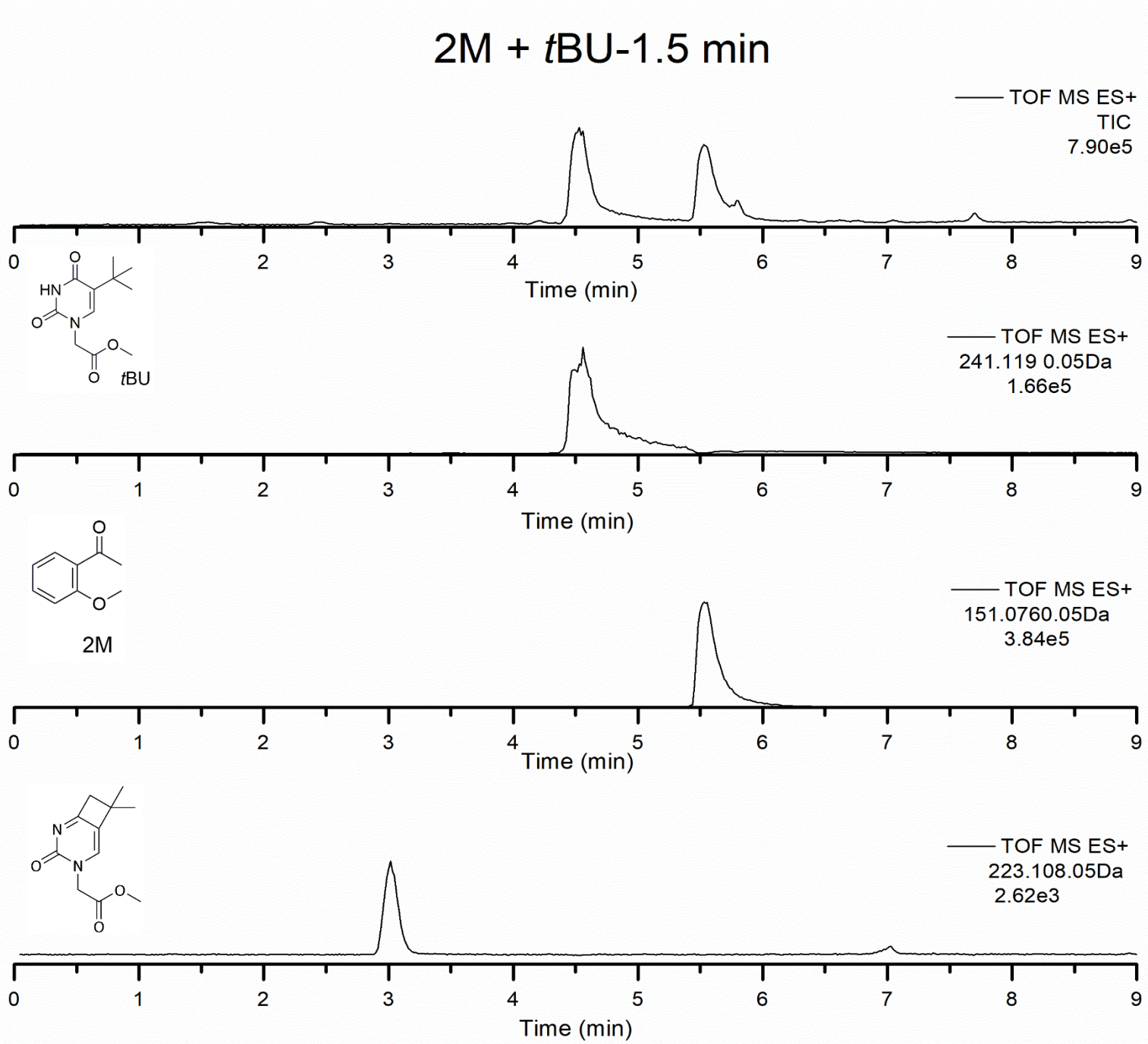


Figure S4. UPLC-MS chromatograms of a **2M** + ***t*BU** mixture irradiated during 1.5 min with a 355 nm[S9] laser beam operating at 10 Hz and 45 mJ