

SUPPORTING INFORMATION

Design and Synthesis of Photoactive Ionic Liquids

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General Methods and Experimental procedures

^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100MHz respectively using a Bruker AMX400 in CDCl_3 referenced to the solvent for both proton and carbon spectra. Elemental analyses (EA) were performed using a ThermoFinnigan Flash EA 112 Series.

Spectroscopic experiments were carried out in HPLC grade acetonitrile. UV/Vis absorption spectra were carried out in a Cary 100 spectrophotometer.

Irradiations were done using a 200 W Xe/Hg Arc lamp coupled with a Thorlabs UG11 Colored Glass UV-Passing Filter, 275 - 375 nm (for concentrated solutions) or a Horiba Jobin Yvon H10 UV monochromator (for diluted solutions). Lamp light fluxes were determined by chemical actinometry using the classical ferrioxalate actinometer.¹ Photochemical quantum yields were determined by ^1H NMR spectroscopy for concentrated solutions and by UV-Vis spectroscopy for dilute solutions.

ESI-MS spectra were recorded with an microTOF (Bruker) using electrospray positive mode (ESI+) or negative modes (ESI-), flow injection analysis (FIA) and time-of-flight (TOF) analyzer.

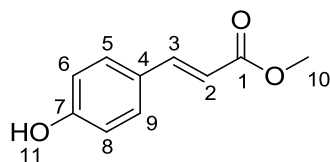
Rheology measurements were performed in a Bohlin Gemini HR^{nano} rotational rheometer, using a standard cone and plate geometry. A cone with diameter of 20 mm, angle of 2°, and a gap of 70 μm was used. The viscosity curves of both samples were recorded at 25 °C prior to and after irradiation.

Full details about the hyper-Rayleigh scattering (HRS) procedure for pure liquids can be found in reference (10). Last HRS experimental details are given in reference (11). The HRS experiments for the pure ILs (3a and 3b) were performed at 90-100°C in order to sufficiently decrease the viscosity of the liquids and minimize extra scattering from dust particles and air bubbles. HRS experiment with 4-methyl-7-hydroxycoumarin were done in chloroform and a high concentration (0.20 M) was required to obtain a signal distinguishable from the one of the solvent.

Synthesis

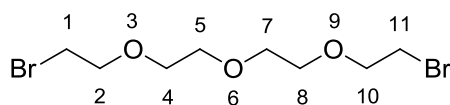
Acetonitrile was dried by standing 48h in 3Å molecular sieves under Argon atmosphere.² 1-Methylimidazole was distilled under vacuum before use. All other chemicals were used as obtained from supplier.

Methyl *p*-coumarate.



To a solution of 5 g (30 mmol) of *p*-coumaric acid in methanol (50 mL), a drop of conc. sulphuric acid was added. The resulting mixture was refluxed while stirring for 5 hours. After cooling down to room temperature, dichloromethane (100 mL) and water (100 mL) were added. The organic phase was collected and the aqueous phase washed twice with dichloromethane (100 mL). The combined organic extracts were washed with NaHCO_3 1%, brine and dried with anhydrous MgSO_4 . The solvent was removed by rotatory evaporation to yield 5.0 g (94%) of white solid, requiring no further purification. m.p. 135-137 °C; ^1H NMR (CDCl_3) δ (ppm): 7.64 (d, J = 15.9 Hz, 1H, H_3), 7.43 (d, J = 7.9 Hz, 2H, H_5 , H_9), 6.85 (d, J = 8.0 Hz, 2H, H_6 , H_8), 6.30 (d, J = 15.9 Hz, 1H, H_2), 5.69 (s, 1H, H_{11}), 3.80 (s, 3H, H_{10}). ^{13}C NMR (CDCl_3) δ (ppm): 168.3, 158.0, 144.9, 130.0, 127.0, 115.9, 115.0, 51.8 c. EA calculated for $\text{C}_{10}\text{H}_{10}\text{O}_3$: C 67.41; H 5.66; found: C 67.66; H 5.37

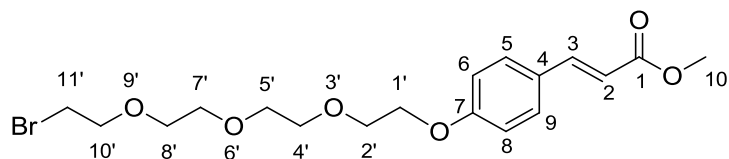
1,11-dibromo-3,6,9-trioxaundecane (1).



To a suspension of 15.72 g (62 mmol) of triphenylphosphine in dry acetonitrile at 0° C, 9.6 g (62 mmol) of bromine were added dropwise under inert atmosphere during 30 minutes. To the resulting mixture, a solution of 6.0 g (31 mmol) of tetraethylene glycol in acetonitrile was added dropwise. The reaction was allowed to warm up to room temperature and stirred for 48 hours. The white

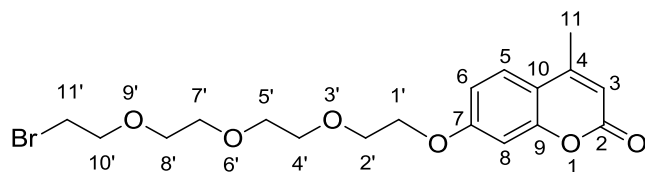
precipitate was removed by filtration and the solvent was removed by rotatory evaporation, resulting in an orange-colored residue, which was extracted several times with hexane. The combined extracts were concentrated in vacuo and 8.52 g (87%) of colorless oil were obtained. For analytical purposes, further purification was achieved by silica gel flash column chromatography (dichloromethane as eluent). ^1H NMR (CDCl_3) δ (ppm): 3.82 (t, $J = 6.34$ Hz, 4H, H_2 , H_{10}), 3.68 (s, 8H, H_{4-8}), 3.48 (t, $J = 6.34$ Hz, 4H, Br-H_1 , H_{11}); ^{13}C NMR (CDCl_3) δ (ppm): 71.2, 70.7, 70.5, 30.4; EA calculated for $\text{C}_8\text{H}_{16}\text{BrO}_3 \cdot 0.1 \text{ CH}_2\text{Cl}_2$: C 29.61; H 4.97; found: C 29.84; H 4.68

(E)-Methyl p-(11-bromo-3,6,9-trioxaundecanoxy)cinnamate (2a).



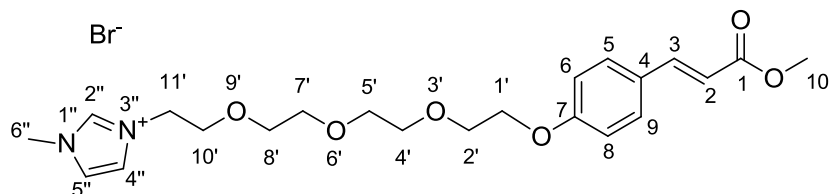
To a solution of 1.0 g (5.6 mmol) of methyl *p*-coumarate in dry acetone, 5.4 g (16.9 mmol) of compound **1** were added. To the resulting mixture, 1.55 g (11.2 mmol) of potassium carbonate were added in one portion and the reaction was refluxed overnight while stirring. The white solid was removed by filtration and the solvent was removed by rotatory evaporation. The residue was purified by silica gel flash column chromatography (hexanes/ethyl acetate eluent) and 2.1 g (91%) of dark yellow oil were obtained. After dissolution in chloroform and filtration through a pad of activated charcoal a pale yellow oil was obtained. ^1H NMR (CDCl_3) δ (ppm): 7.64 (d, $J = 16.0$ Hz, 1H, H_3), 7.46 (d, $J = 8.6$ Hz, 2H, H_5 , H_9), 6.92 (d, $J = 8.7$ Hz, 2H, H_6 , H_8), 6.31 (d, $J = 16.0$ Hz, 1H, H_2), 4.16 (t, $J = 4.7$ Hz, 2H, $\text{H}_{1'}$), 3.87 (t, $J = 4.8$ Hz, 2H, H_2), 3.79-3.82 (m, 5H, H_{10} , $\text{H}_{10'}$), 3.73 (m, 2H, H_4), 3.69 (m, 2H, H_5), 3.67 (s, 4H, H_7 , H_8), 3.46 (t, $J = 6.3$ Hz, 2H, $\text{H}_{11'}$); ^{13}C NMR (CDCl_3) δ (ppm): 167.8, 160.6, 144.5, 129.7, 127.3, 115.4, 115.0, 71.2, 70.9, 70.7, 70.6, 70.5, 67.6, 51.6, 30.4, 30.3; EA calculated for $\text{C}_{18}\text{H}_{25}\text{BrO}_6 \cdot 0.35 \text{ CHCl}_3$: C 48.01; H 5.57; found: C 48.09; H 5.57

4-methyl-7-(11-bromo-3,6,9-trioxaundecanoxy)coumarin (2b).



4-methyl-7-hydroxy coumarin (1.0 g, 5.7 mmol) and compound **1** (5.5 g, 17.1 mmol) were dissolved in dry acetonitrile. Potassium carbonate (1.6 g, 11.4 mmol) was added in one portion and the reaction mixture was heated to reflux overnight while stirring. The white solid was removed by filtration and the solvent was removed by rotatory evaporation. The residue was purified by silica gel flash column chromatography (hexanes/ethyl acetate eluent) to yield 2.0 g (86%) of pale yellow oil. ^1H NMR (CDCl_3) δ (ppm): 7.48 (d, $J = 8.8$ Hz, 1H, H_5), 6.88 (dd, $J_1 = 2.2$ Hz, $J_2 = 8.8$ Hz, 1H, H_6), 6.82 (d, $J = 2.2$ Hz, 1H, H_8), 6.12 (s, 1H, H_3), 4.18 (t, $J = 4.7$ Hz, 2H, $\text{H}_{1'}$), 3.89 (t, $J = 4.6$ Hz, 2H, H_2), 3.80 (t, $J = 6.3$ Hz, 2H, $\text{H}_{10'}$), 3.67-3.73 (m, 8H, H_{4-8}), 3.46 (t, $J = 6.2$ Hz, 2H, $\text{H}_{11'}$), 2.39 (s, 3H, H_{11}); ^{13}C NMR (CDCl_3) δ (ppm): 161.6, 161.1, 155.2, 152.4, 125.6, 113.7, 112.3, 112.0, 101.5, 71.2, 70.7, 70.5, 30.4, 18.6; EA calculated for $\text{C}_{18}\text{H}_{23}\text{BrO}_6$: C 52.06; H 5.58; found: C 52.13; H 5.50

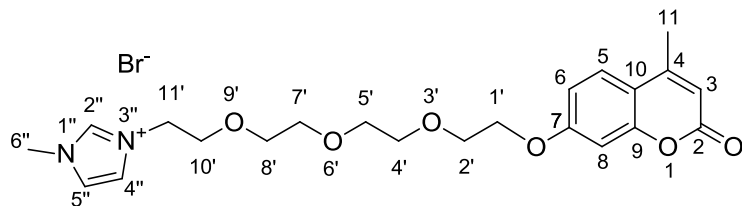
(E)-3-(11-(p-(3-methoxy-3-oxoprop-1-enyl)phenoxy)3,6,9-trioxaundecanoxy)-1-N-methyl-imidazol-3-ium bromide (3a)



To a solution of compound **2a** (1.0 g, 2.4 mmol) in acetonitrile, 197 mg (2.4 mmol) of *N*-methylimidazole were added dropwise. The reaction was refluxed overnight and allowed to cool down to room temperature. The solvent was removed by rotatory evaporation and the residue was washed with boiling diethyl ether, yielding 1.1 g (91%) of a pale yellow oil. For analytical purposes further purification was achieved by filtration in chloroform solution through a pad of activated charcoal and removal of solvent *in vacuo*.

^1H NMR (CDCl_3) δ (ppm): 10.37 (s, 1H, $\text{H}_{2''}$), 7.61-7.65 (m, 2H, H_3 , $\text{H}_{4''}$), 7.47 (d, $J = 8.7$ Hz, 2H, H_5 , H_9), 7.13 (t, $J = 1.7$ Hz, 1H, $\text{H}_{5''}$), 6.88 (d, $J = 8.7$ Hz, 2H, H_6 , H_8), 6.31 (d, $J = 16.4$ Hz, 1H, H_2), 4.58 (t, $J = 4.5$ Hz, 2H, $\text{H}_{11'}$), 4.14 (t, $J = 4.4$ Hz, 2H, $\text{H}_{1'}$), 3.95 (s, 3H, $\text{H}_{6''}$), 3.85-3.90 (m, 4H, H_2 , $\text{H}_{10'}$), 3.79 (s, 3H, H_{10}), 3.71-3.73 (m, 2H, H_8), 3.60-3.67 (m, 6H, H_4 , H_5 , H_7); ^{13}C NMR (CDCl_3) δ (ppm): 167.5, 160.3, 144.1, 137.3, 129.7, 127.2, 123.4, 123.2, 122.7, 115.4, 114.8, 70.6, 70.3, 70.2, 70.1, 69.4, 68.8, 67.5, 51.5, 49.6, 36.4. EA calculated for $\text{C}_{22}\text{H}_{31}\text{BrN}_2\text{O}_6 \cdot 0.2 \text{CHCl}_3$: C 50.96; H 6.01, N 5.35; found: C 50.71, H 5.96, N 5.43

3-(11-(4-methyl-7-coumarinoxy)-3,6,9-trioxaundecanoxy)-1-*N*-methylimidazol-3-ium bromide (3b).



Compound **2b** (1.0 g, 2.4 mmol) and *N*-methylimidazole (197 mg, 2.4 mmol) were dissolved in dry acetonitrile. The reaction was refluxed overnight and allowed to cool down to room temperature. The solvent was removed by rotatory evaporation and the residue was washed with boiling diethyl ether, yielding 1.1 g (91%) of pale yellow oil. For analytical purposes further purification was achieved by filtration in chloroform solution through a pad of activated charcoal and removal of solvent *in vacuo*. ^1H NMR (CDCl_3) δ (ppm): 10.17 (s, 1H, $\text{H}_{2''}$), 7.67 (s, 1H, $\text{H}_{4''}$), 7.50 (d, $J = 8.8$ Hz, 1H, H_5), 7.37 (s, 1H, $\text{H}_{5''}$), 6.83 (dd, $J_1 = 2.4$ Hz, $J_2 = 8.8$ Hz, 1H, H_6), 6.78 (d, $J = 2.4$ Hz, 1H, H_8), 6.10 (s, 1H, H_3), 4.57 (t, $J = 4.4$ Hz, 2H, $\text{H}_{11'}$), 4.18 (t, $J = 4.4$ Hz, 2H, $\text{H}_{1'}$), 4.01 (s, 3H, $\text{H}_{6''}$), 3.85-3.88 (m, 4H, H_2 , $\text{H}_{10'}$), 3.70-3.72 (m, 2H, H_8), 3.60-3.65 (m, 6H, H_4 , H_5 , H_7), 2.38 (s, 3H, H_{11}); ^{13}C NMR (CDCl_3) δ (ppm): 161.6, 161.1, 155.2, 152.4, 137.3, 125.6, 123.4, 123.2, 122.7, 113.7, 112.3, 112.0, 101.5, 70.6, 70.3, 70.2, 70.1, 69.4, 68.8, 67.5, 18.6; EA calculated for $\text{C}_{22}\text{H}_{29}\text{BrN}_2\text{O}_6$: C 53.13; H 5.88; N 5.63; found: C 53.25; H 5.82; N 5.85.

NMR spectra of synthesized compounds

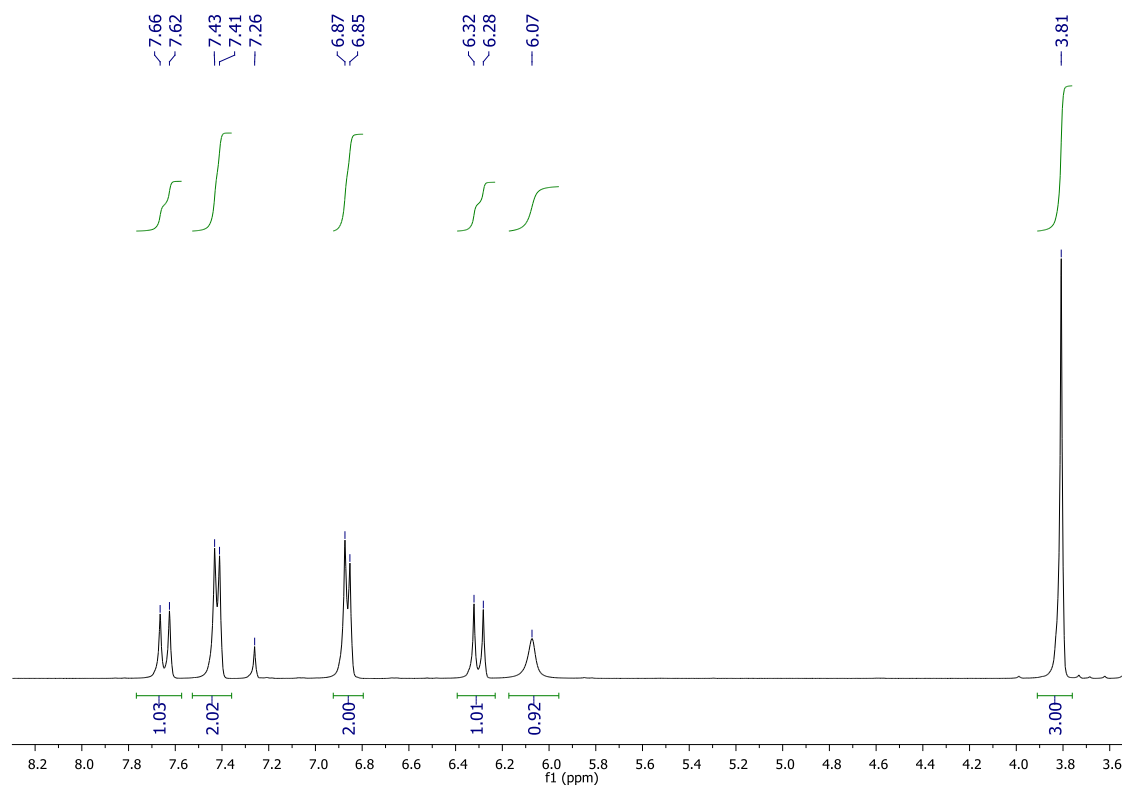


Figure S 1 - ¹H NMR spectrum of methyl *p*-coumarate

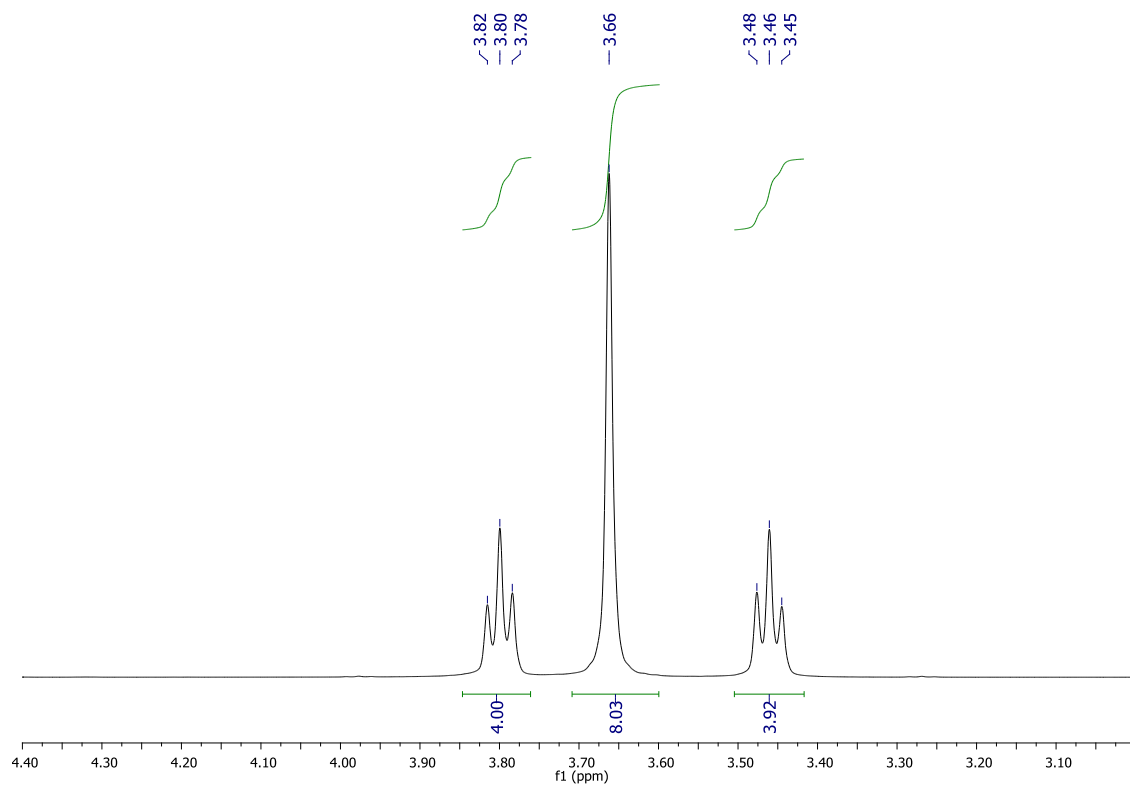


Figure S 2 - ¹H NMR spectrum of compound 1

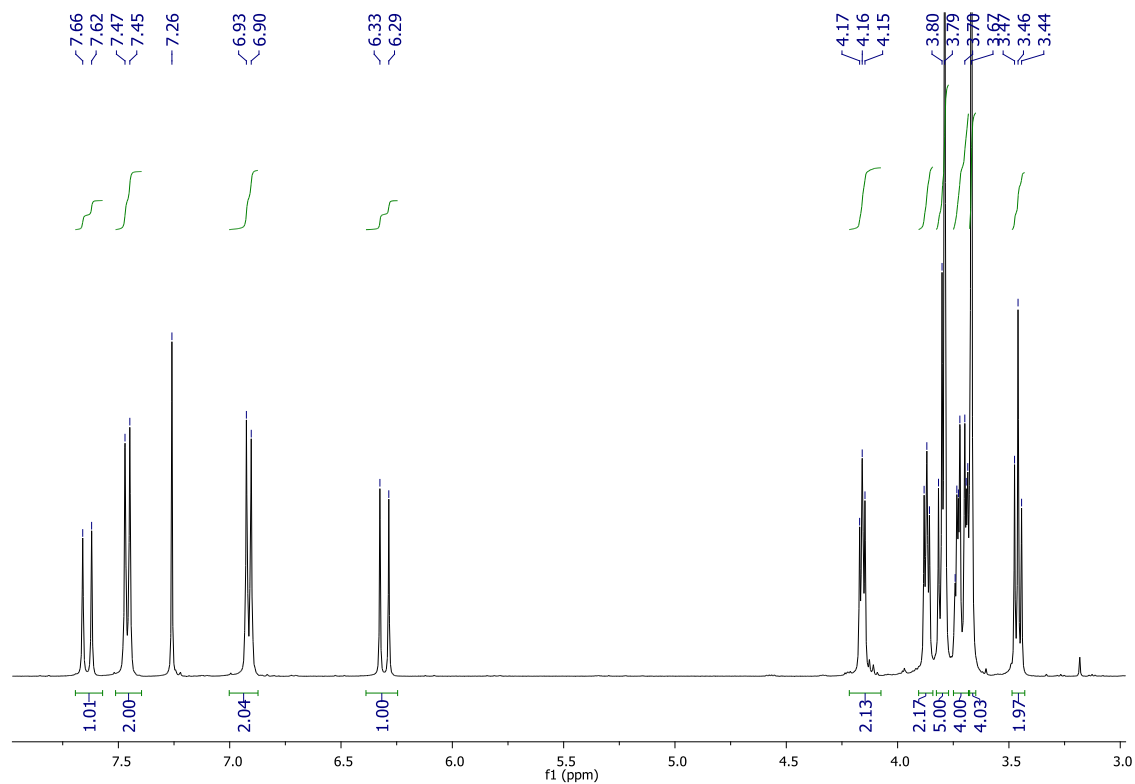


Figure S 3 - ¹H NMR spectrum of compound 2a

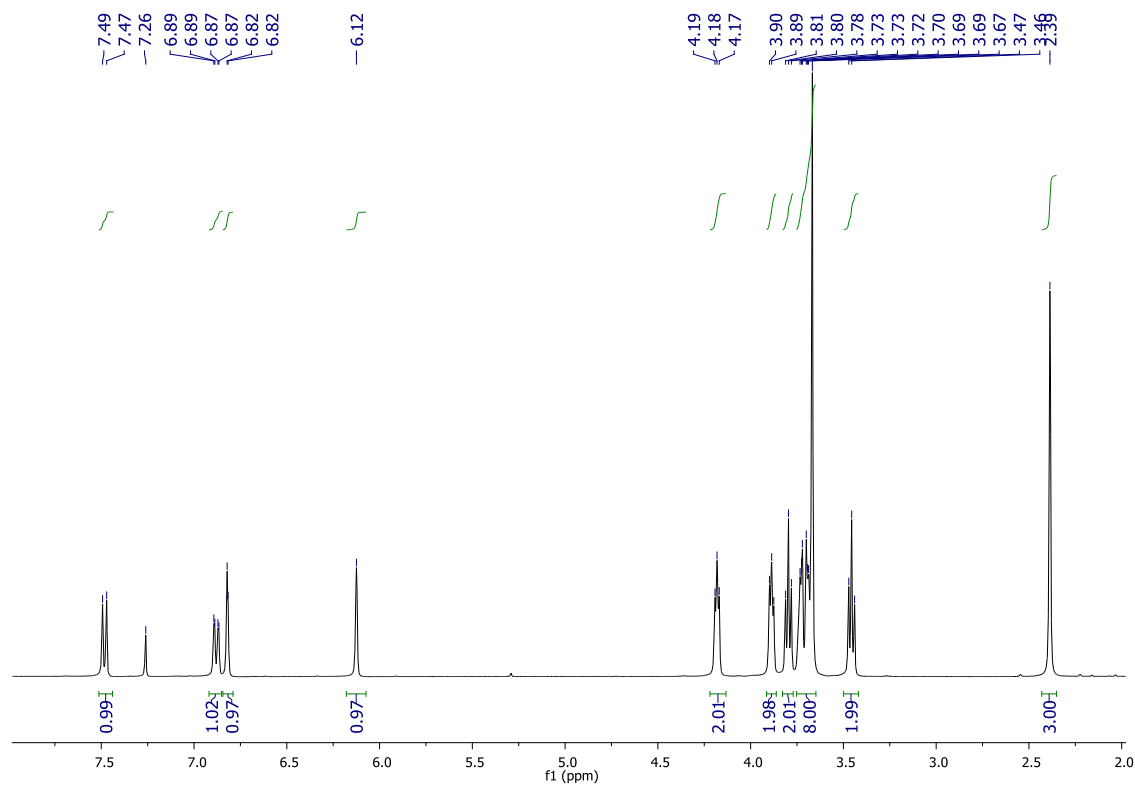


Figure S 4 - ¹H NMR spectrum of compound 2b

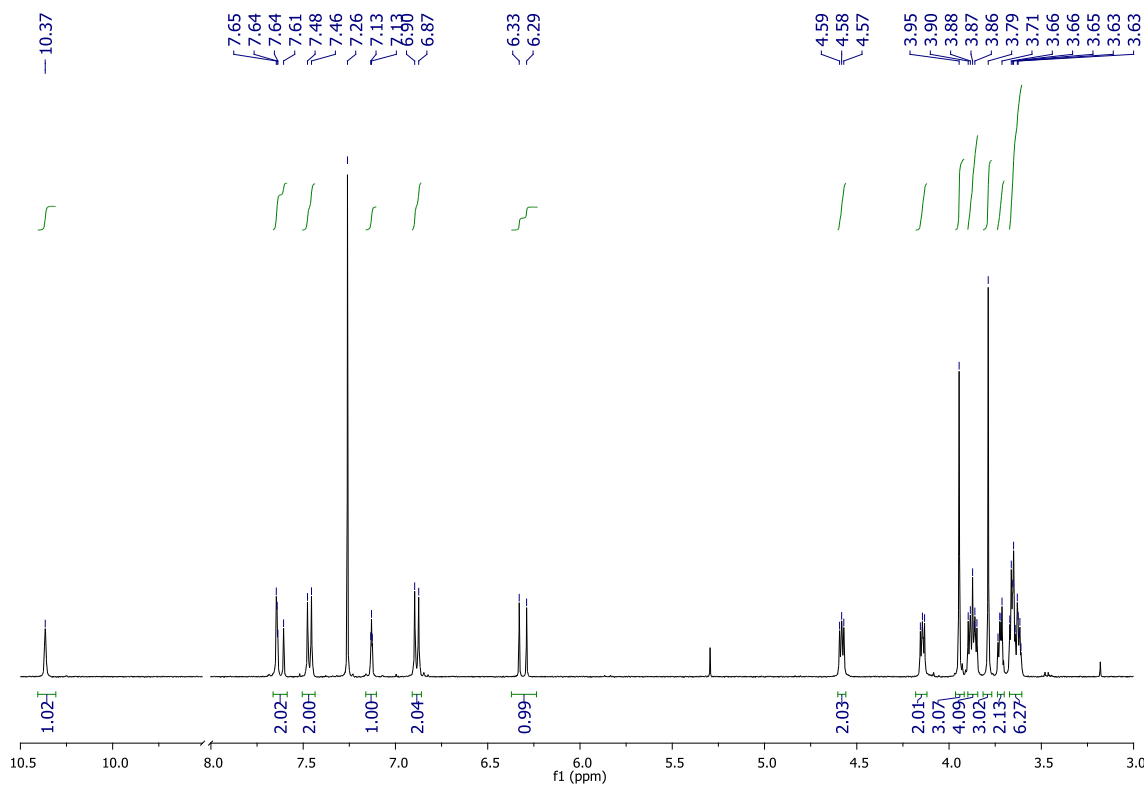


Figure S 5 – ¹H NMR spectrum of compound 3a

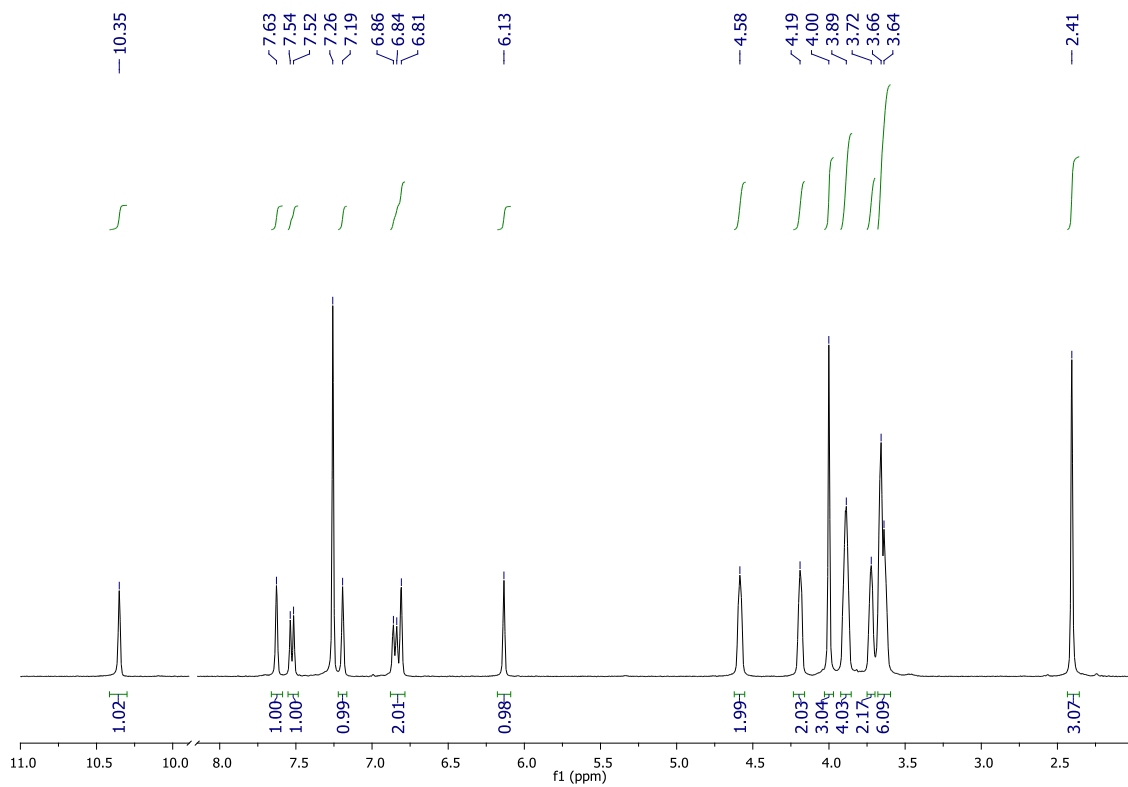


Figure S 6 - ¹H NMR spectrum of compound 3b

NMR spectra of irradiated ionic liquids

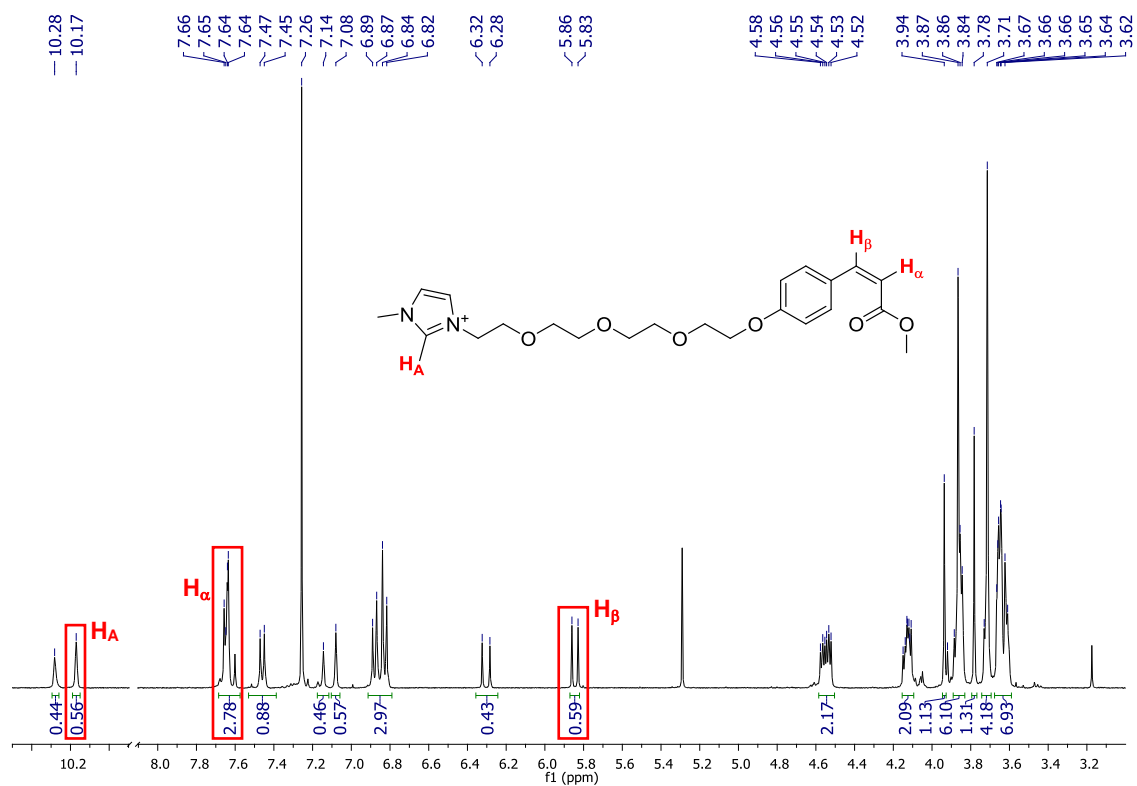


Figure S7 – ¹H NMR spectrum of compound 3a after irradiation in acetonitrile solution at 300 nm. Total irradiation time is 20 min

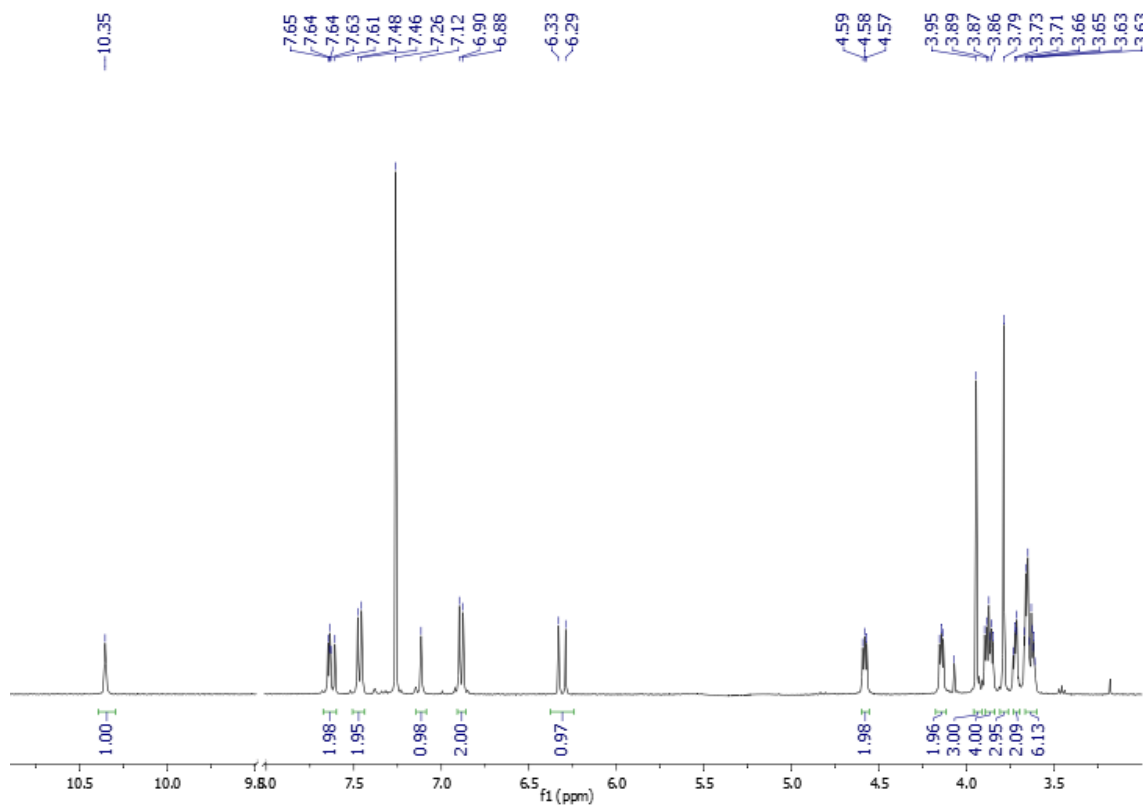


Figure S8 - ¹H NMR spectrum of compound 3a after initial irradiation in acetonitrile solution at 300 nm followed by recovery irradiation at 240 nm. Total irradiation time is 600 min

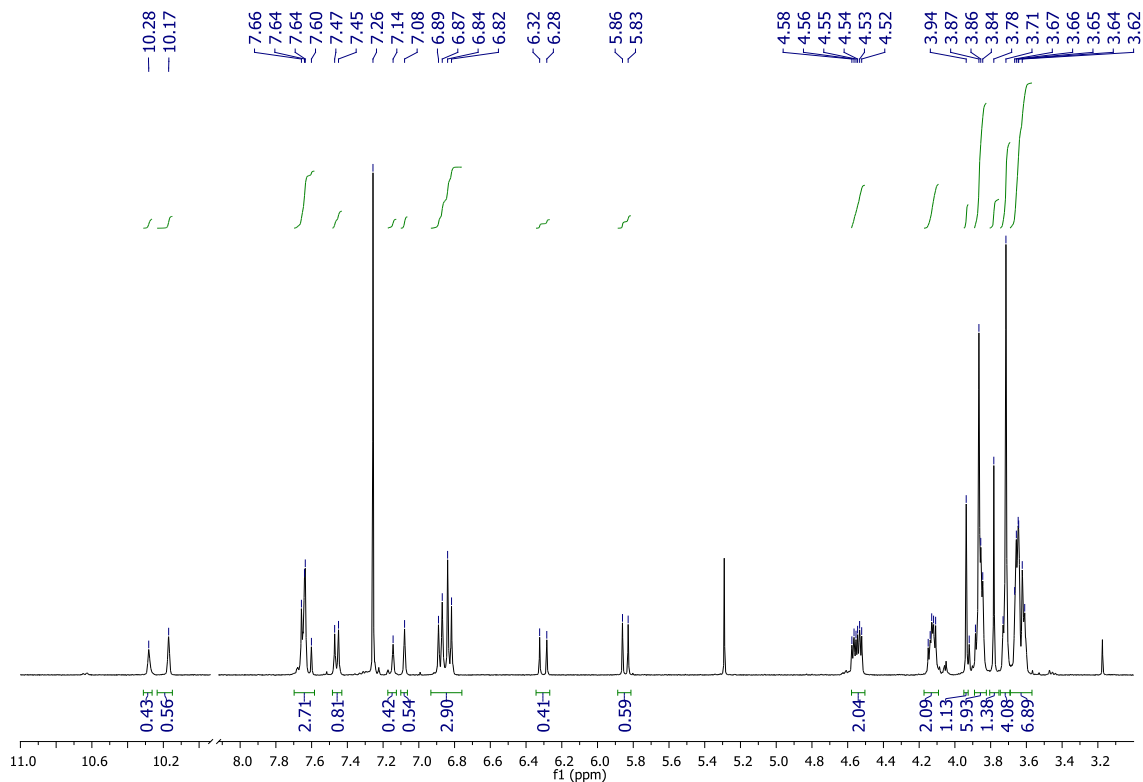


Figure S9 – ¹H NMR spectrum of compound 3a after irradiation in neat conditions under inert atmosphere at 300 nm. Total irradiation time is 120 min

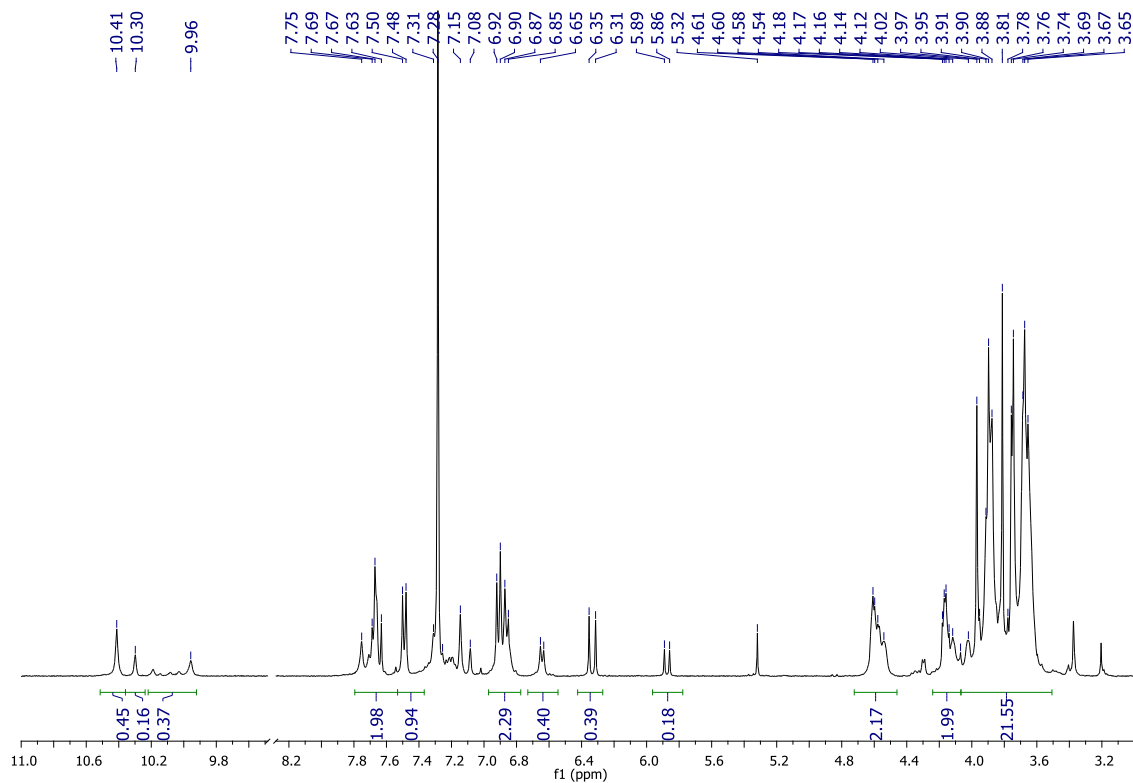


Figure S10 – ¹H NMR spectrum of compound 3a irradiated in neat conditions in open air at 300 nm. Total irradiation time is 120 min

From ^1H NMR spectra of compound **3a** before (Figure S5) and after irradiation in acetonitrile solution (Figure S7), it is evidenced that photoisomerization is the only photochemical reaction taking place upon irradiation. This conclusion is supported by the doublet at 5.84 ppm, corresponding to the β -proton of (*Z*)-isomer of the cinnamate moiety. Also, the intensities of (*E*)- H_β and (*Z*)- H_β peaks add to the same value of H_α peaks (imidazolium ring protons, with chemical shifts of 10.2 ppm), indicating that (*E*) and (*Z*) isomers are the only species bearing an imidazolium cation. The ^1H NMR spectra depicted in figures S8 and S9 evidence the effect of the atmospheric control on the photochemical products resulting from irradiation of **3a** in neat conditions. Whilst irradiation in open air yields a variety of products (ca. 37%), indicated by the large variety of peaks at 9.8-10.5 ppm corresponding to imidazolium moiety protons, irradiation under inert atmosphere yields exclusively a mixture of *trans* and *cis* isomers, similarly to what was observed in acetonitrile solution.

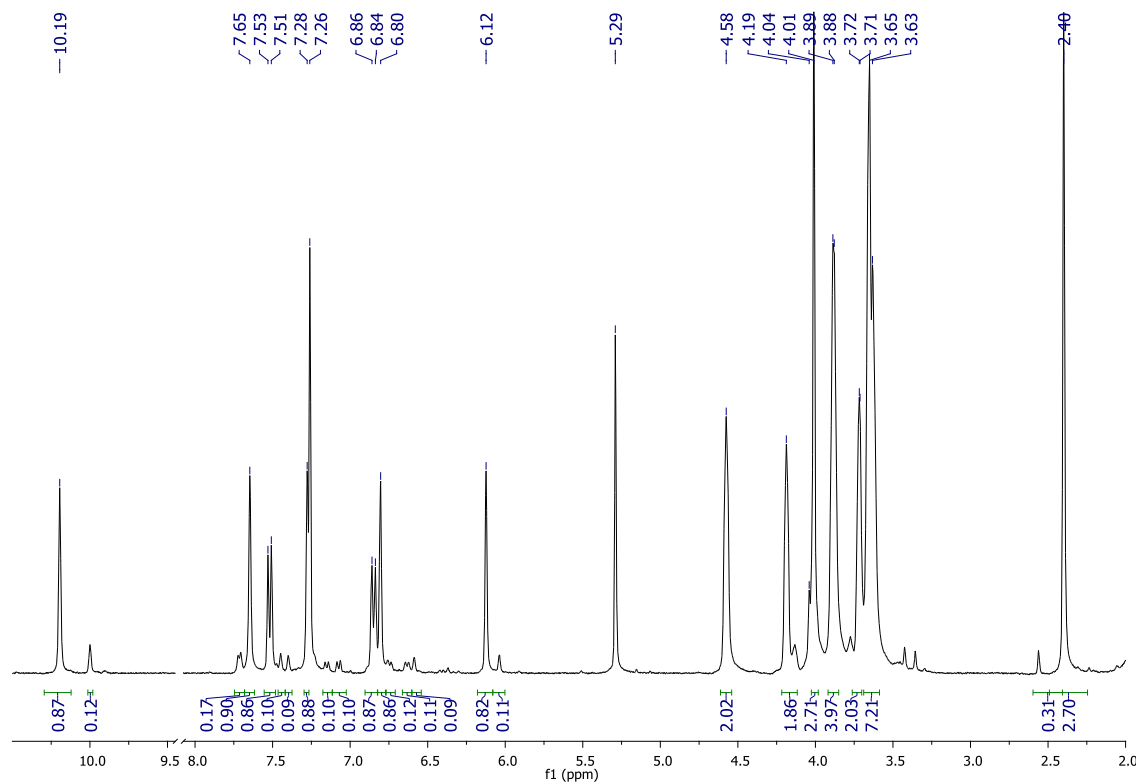


Figure S11 – ^1H NMR spectrum of compound **3b** after irradiation in acetonitrile solution at 330 nm. Total irradiation time is 120 min.

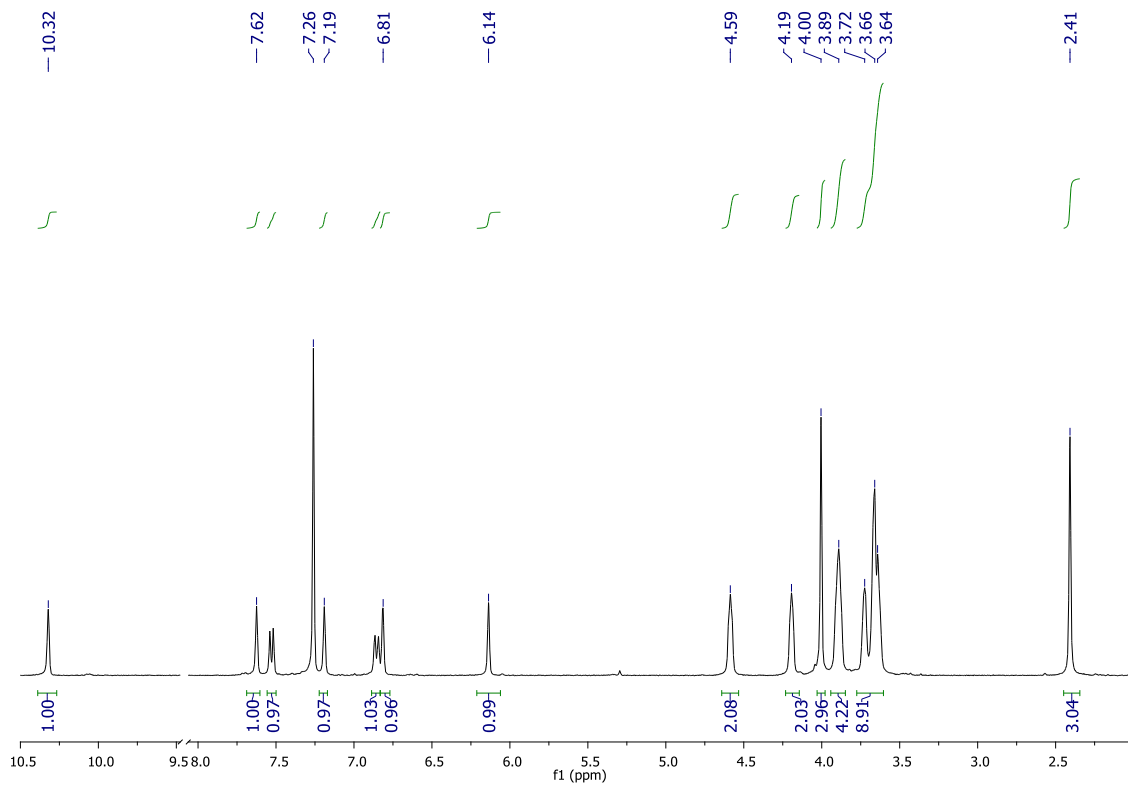


Figure S12 - ¹H NMR spectrum of compound 3b after irradiation in neat conditions under inert atmosphere at 330 nm. Total irradiation time is 120 min.

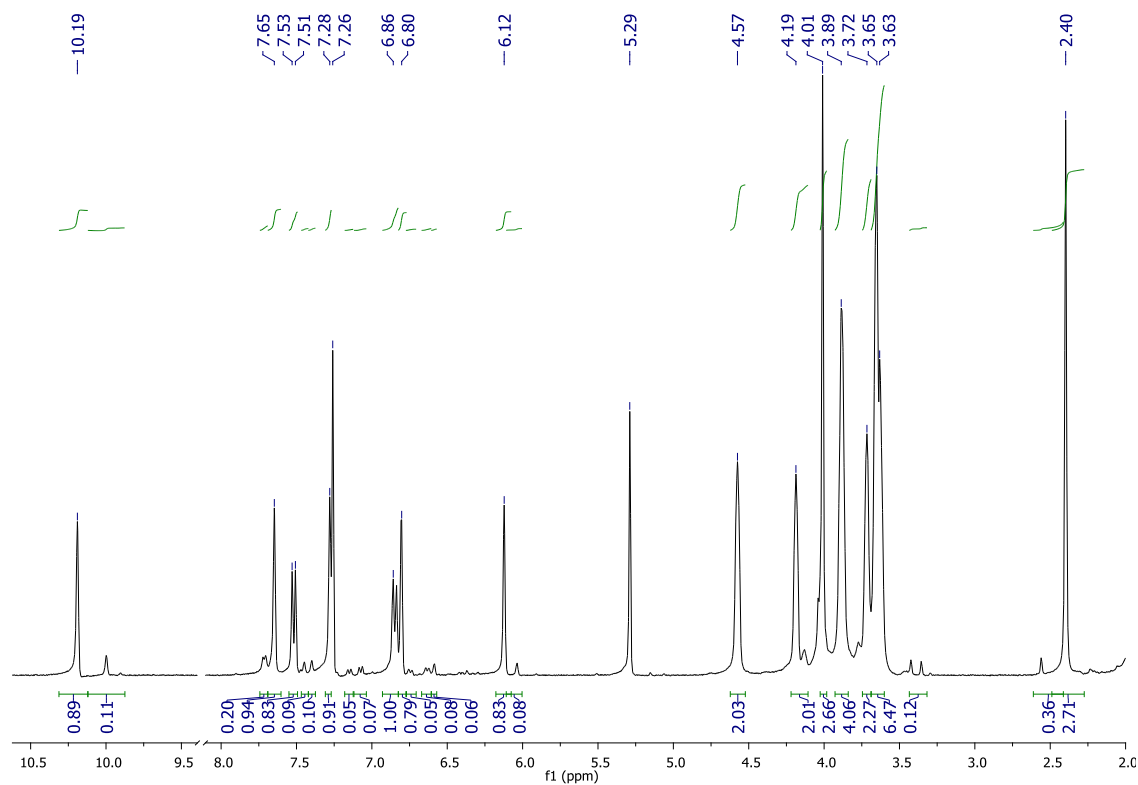


Figure S13 - ¹H NMR spectrum of compound 3b after irradiation in neat conditions in open air at 330 nm. Total irradiation time is 120 min.

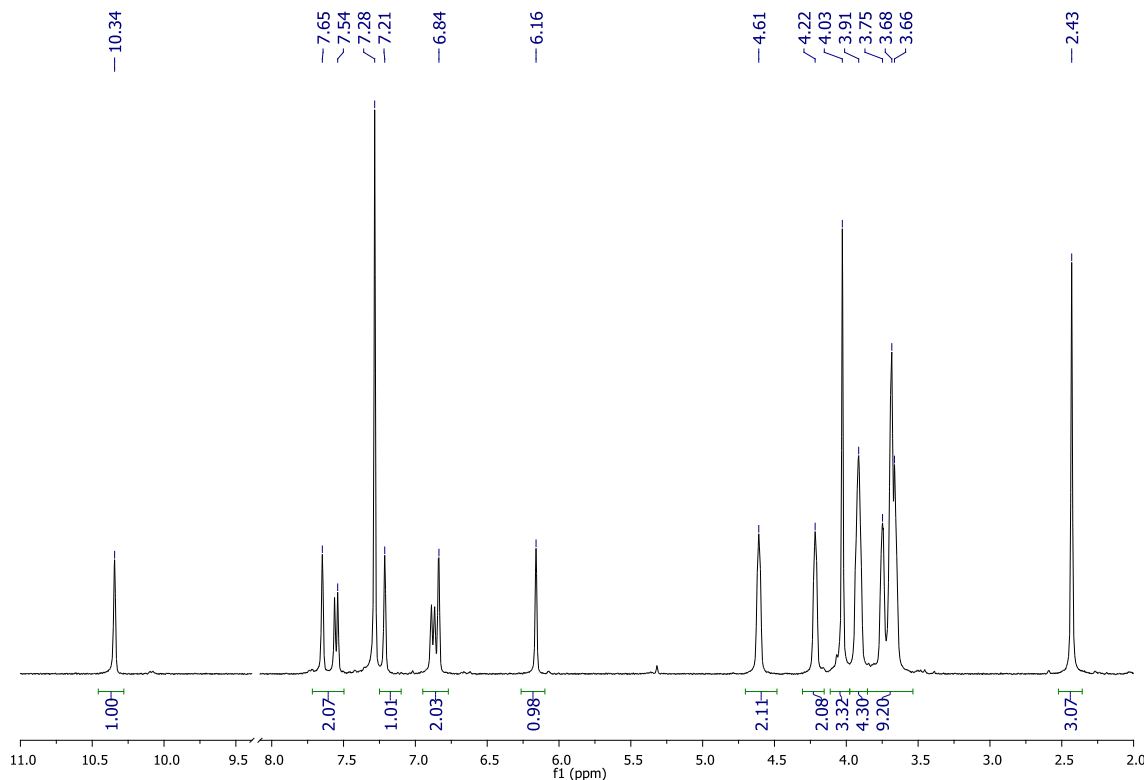


Figure S14 - ^1H NMR spectrum of compound **3b after irradiation in dry acetonitrile at 330 nm. Total irradiation time is 120 min**

From ^1H NMR spectra of compound **3b** before (Figure S6) and after irradiation in acetonitrile solution (Figure S11) or in neat conditions (Figure S12), it is demonstrated that the coumarin ionic liquid undergoes a photochemical reaction, which is evidenced by the appearance of several low intensity peaks in the aromatic region (6.0-10.0 ppm).

In particular, the singlets at ca. 6.0 ppm and 10.0 ppm with the same relative intensity point to the formation of a imidazolium-bearing product with a double bond conjugated with the aromatic ring, which suggests that an alternative photochemical reaction is occurring upon irradiation instead of photodimerization. In addition, the quantum yield does not vary with increasing concentration of **3b** (table S1), suggesting that the photochemical process is unimolecular. Several studies on the alternate photoreactivity of coumarins show that these chromophores may undergo photolytical reactions when isolated in solid matrixes or in gaseous state.^{3,4} In addition, coumarins are known to undergo hydrolysis and/or oxidation reactions that give rise to a variety of photoproducts, such as coumaric acid, benzaldehydes or benzophenones. Furthermore, 4-methyl substituent is prone to oxidation to its hydroxyl or carboxyl counterpart.⁵⁻⁸ Thus, it is proposed that **3b** undergoes photoactivated hydrolysis/oxidation with the concomitant formation of hydroxyl, carbonyl and carboxyl moieties. Although isolation of the photoproducts was not possible, due to the low extension of the photochemical reaction and the ionic nature of the system, this hypothesis is consistent with the obtained ^1H NMR spectrum after irradiation. Furthermore, when **3b** is irradiated in dry acetonitrile, as well as under inert atmosphere in neat conditions, no transformations are observed (Figures S13 and S14), evidencing that water is required in order to the photoreaction to occur.

Photochemical quantum yield

Table S1 - Photochemical quantum yield of IL **3b** in acetonitrile solution at 1×10^{-5} to 1×10^{-2} M upon irradiation at absorption maximum.

compound	λ_{max} (nm)	conc. (M)	Φ_R	PSS <i>cis</i> fraction
3b	330	10^{-2}	0.014	0.47
		10^{-3}	0.012	
		10^{-4}	0.013	
		10^{-5}	0.014	

Mass spectrometry results

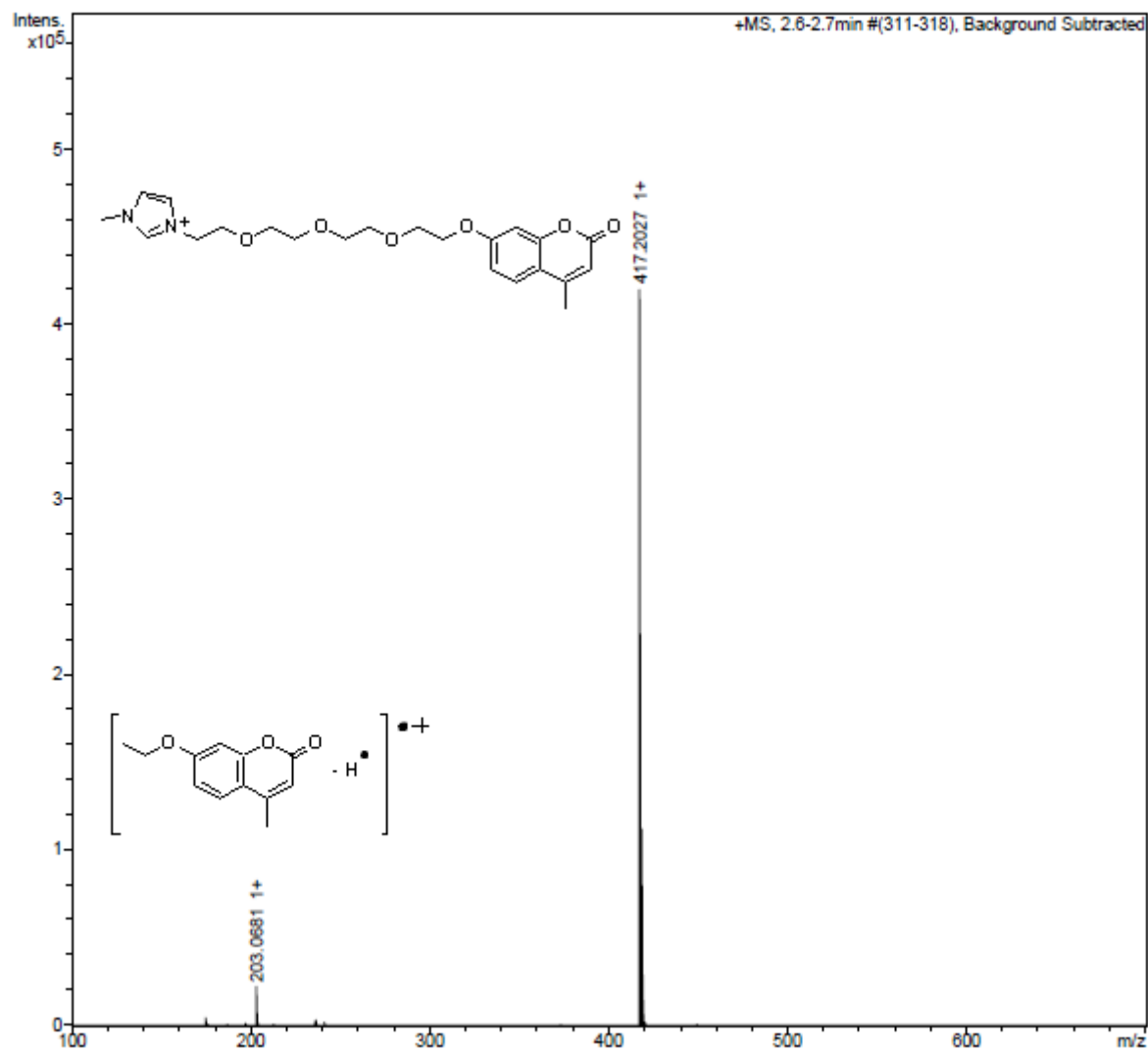


Figure S15 – Mass spectrum (ESI+MS) of compound **3b** before irradiation.

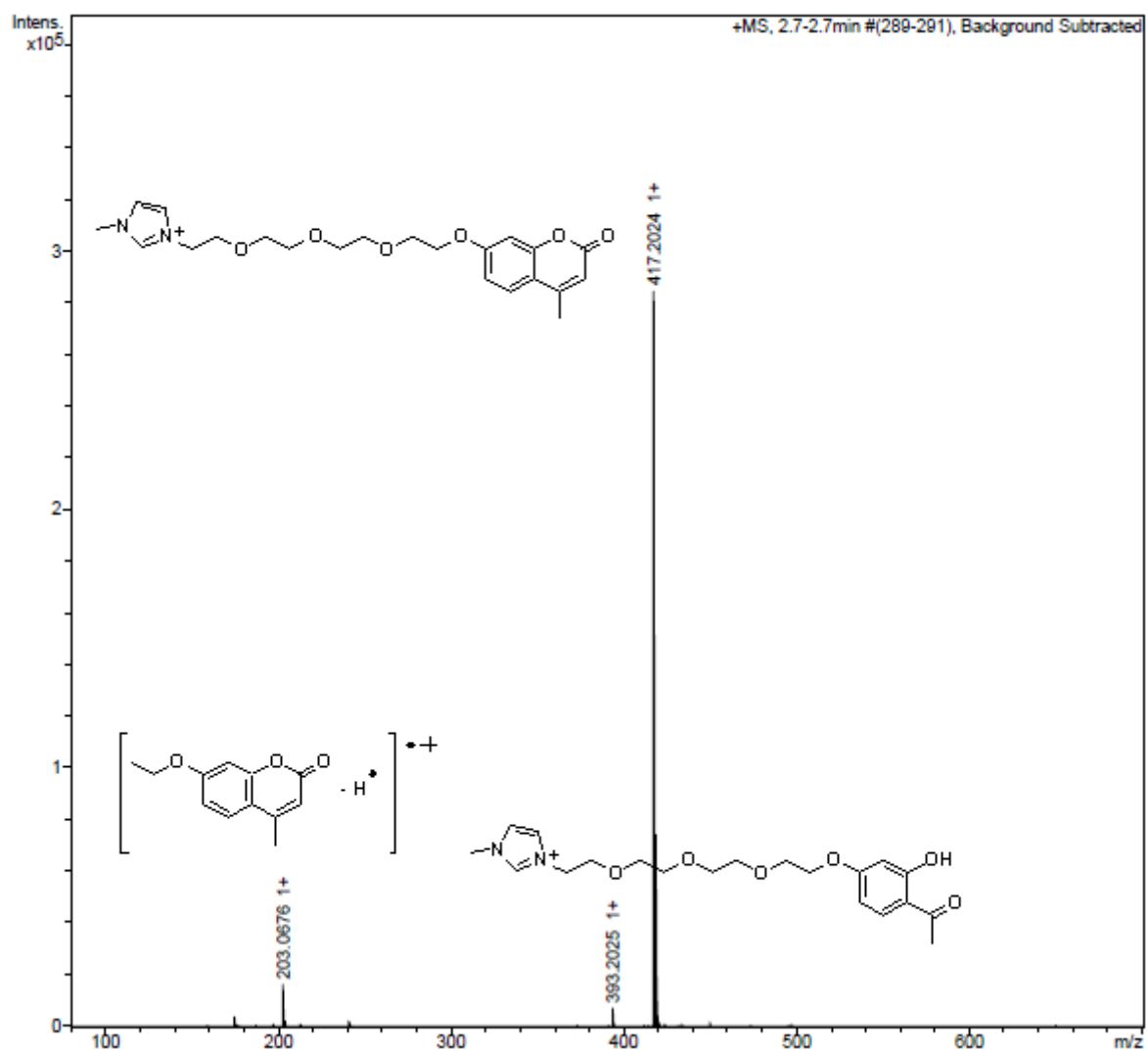


Figure S16 - Mass spectrum (ESI+MS) of compound 3b after irradiation at 330 nm in neat conditions. Total irradiation time is 120 min. 203.0676

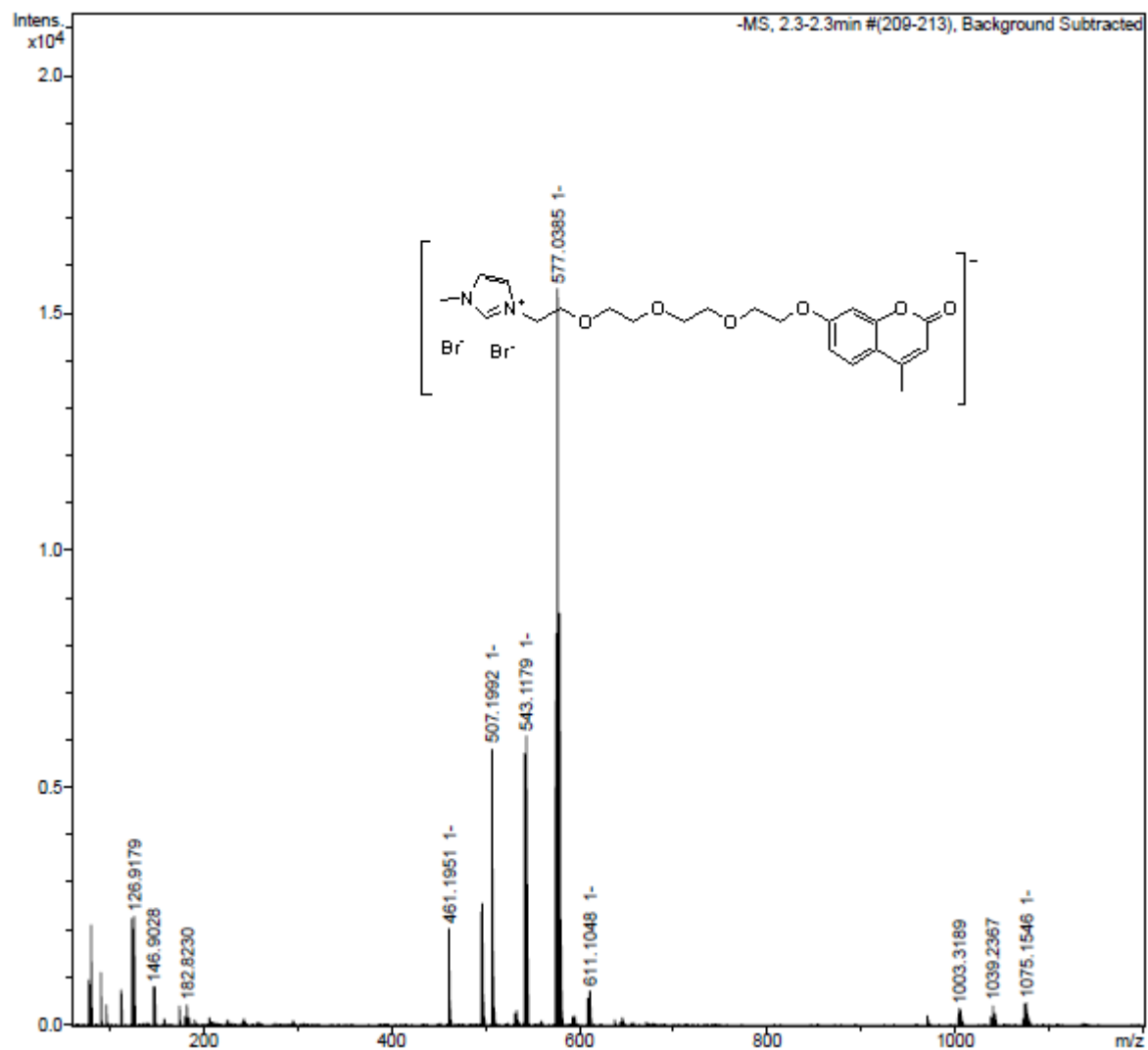


Figure S17 – Mass spectrum (ESI-MS) of compound 3b before irradiation.

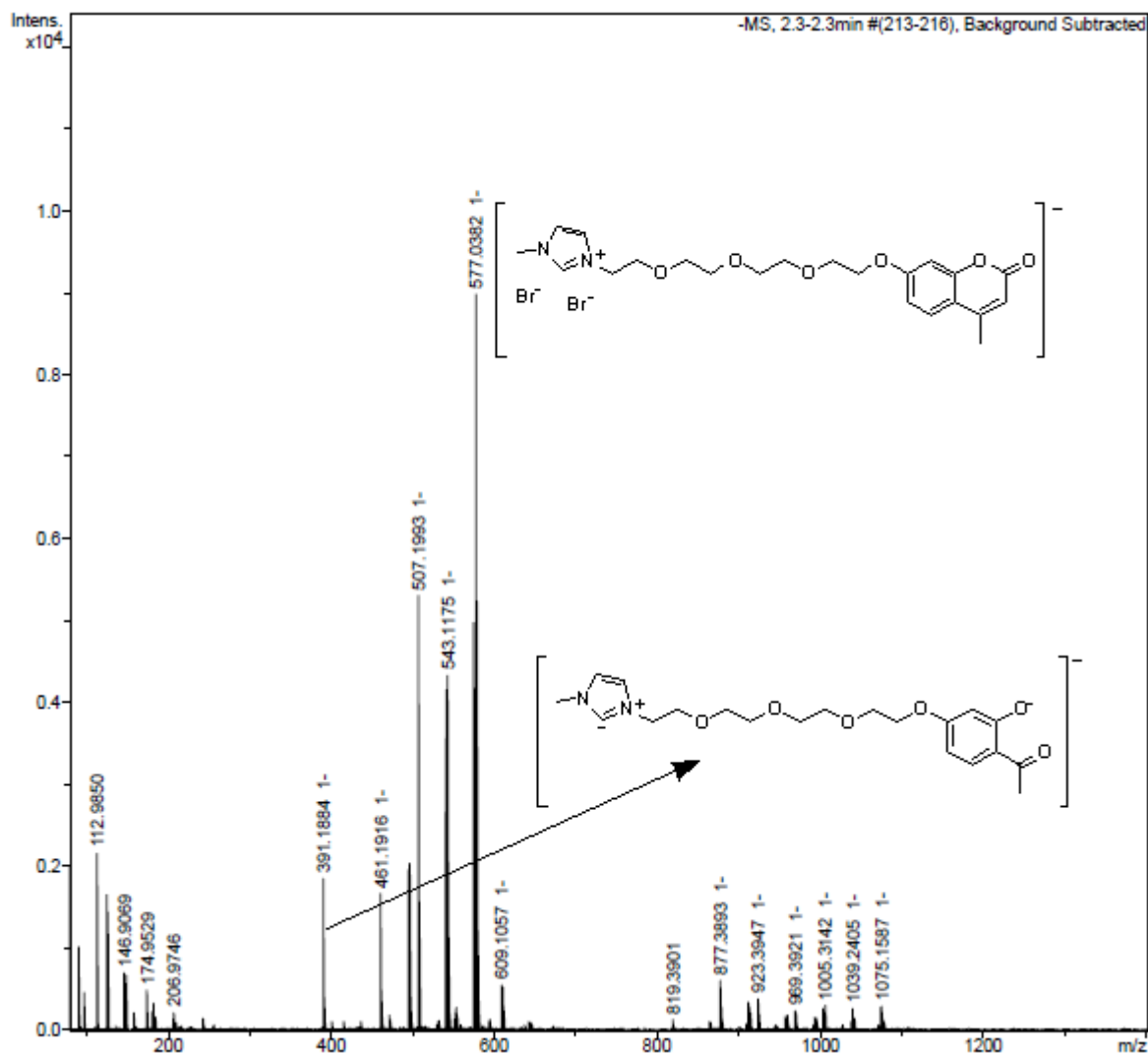
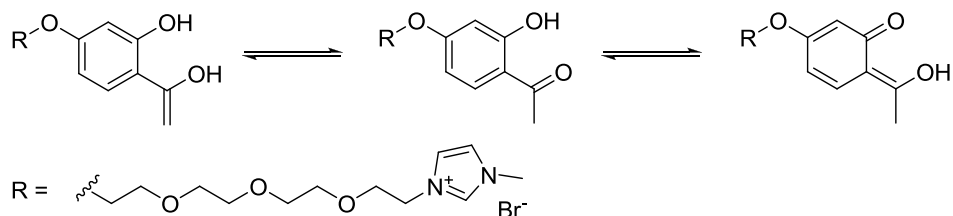


Figure S18 - Mass spectrum (ESI-MS) of compound **3b** after irradiation at 330 nm in neat conditions. Total irradiation time is 120 min.

The mass spectra obtained for **3b** before (Figure S15) and after (Figure S16) irradiation show that the photochemical reaction leads to the formation of a single major product, indicated by the emergence of a peak at $m/z = 393$. This result is consistent with the formation of an acetophenone derivative, which has been previously described for coumarin analogs.⁸ These results are corroborated by the ESI- mass spectra obtained for the same samples, where a significant peak at $m/z = 391$ appears after irradiation, which corresponds to the same acetophenone derivative upon loss of two protons.

Through mass spectroscopy it was possible to identify the major photoproduct arising from the irradiation of **3b**. However, NMR results suggest that a variety of compounds is present in solution. This discrepancy can be explained by the tautomerization of the acetophenone compound that may give rise to extra peaks in the NMR spectrum (Scheme S1).⁹

Scheme S1 – Proposed tautomerization for the major photoproduct of **3b**



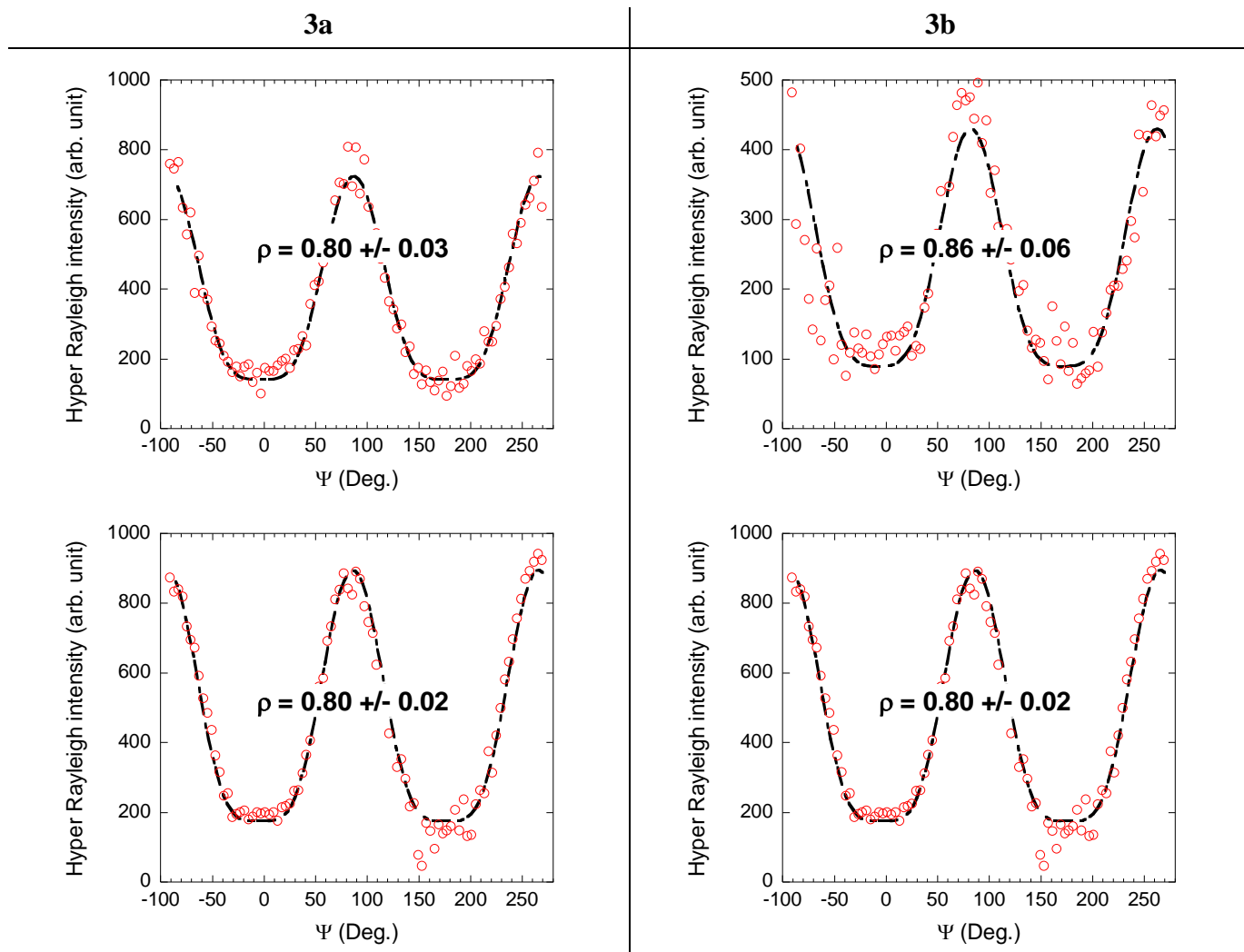


Figure S19 – HRS extracted polarization curves of non-irradiated 3a and 3b (Top) and irradiated 3a and 3b (Bottom).

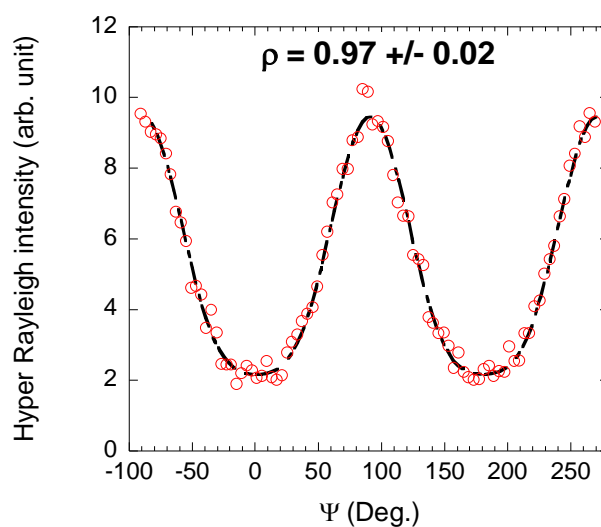
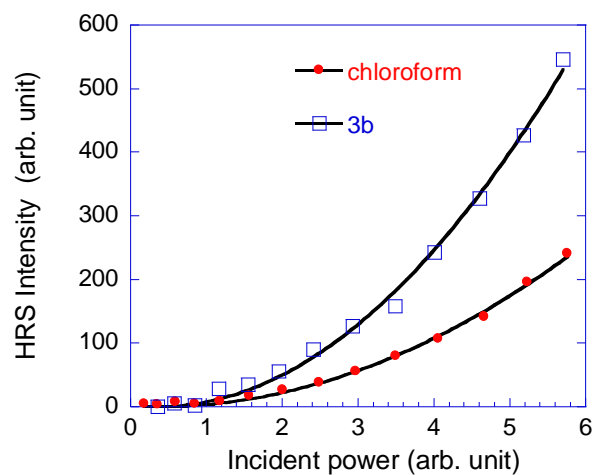
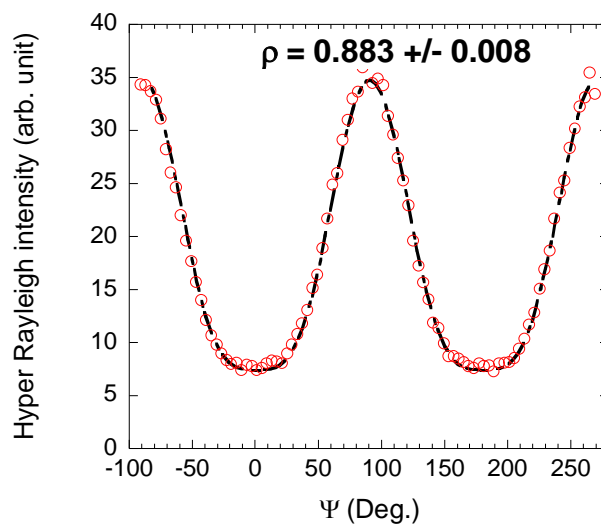
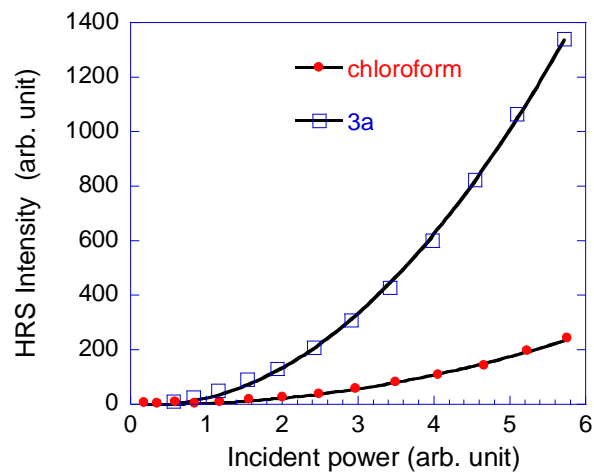


Figure S20 - HRS quadratic dependence (left) and extracted polarization curves (right) of 3a (24.5mM) and 3b (32.0mM).

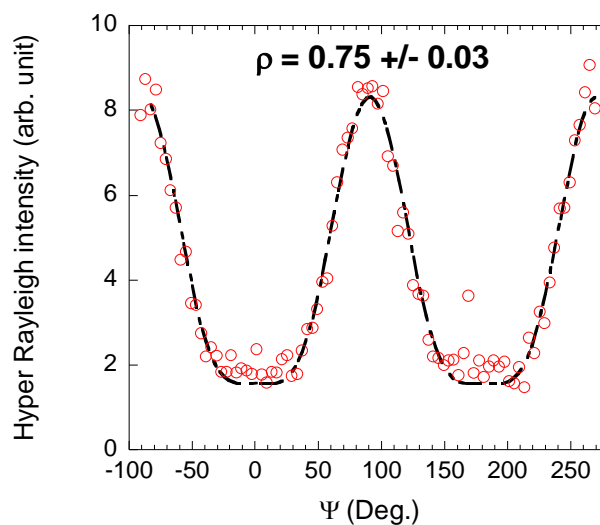
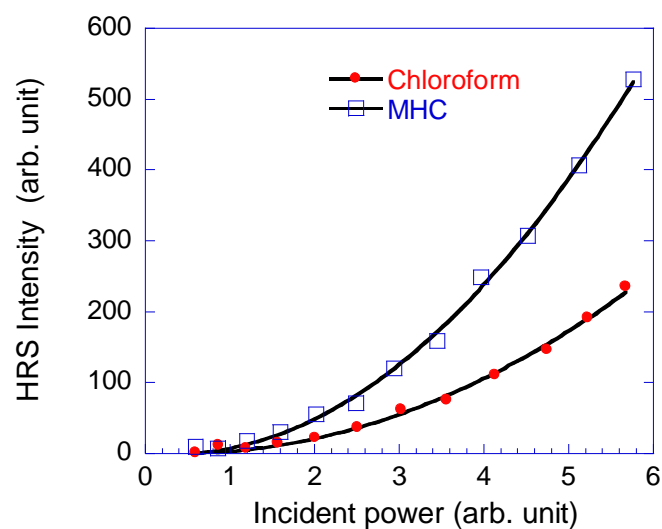


Figure S21 - HRS quadratic dependence (left) and extracted polarization curves (right) of coumarine (0.20 M) solvated in chloroform

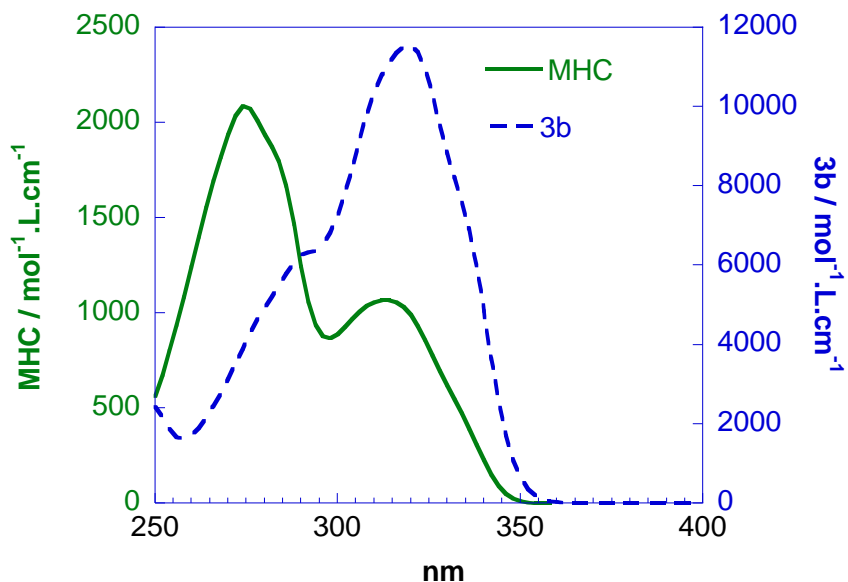


Figure S22 - UV-Vis absorption coefficient of coumarin in chloroform (green solid curve) and 3b (blue dotted curve).

Table S2 - Mean refractive indices (n) with Lorentz-Lorenz local field correction and molarity C for the various ILs and chloroform.

	n	f_L^2	C (M/l)
3a	1.53	9.29	2.70
3a Irradiated			2.70
3b	1.55	5.789	2.74
3b Irradiated			2.75
Chloroform	1.44	6.2	12.5

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