Tetrahedron 70 (2014) 650–657

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Wavelength-selective cleavage of *o*-nitrobenzyl and polyheteroaromatic benzyl protecting groups

Ana M. Piloto, Susana P.G. Costa, M. Sameiro T. Gonçalves *

Centre of Chemistry, University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal

ARTICLE INFO

Article history:
Received 26 September 2013
Received in revised form 27 November 2013
Accepted 28 November 2013
Available online 4 December 2013

Keywords:
Photolabile protecting groups
Selective cleavage
o-Nitrobenzyl group
Acridine
Coumarin

ABSTRACT

Evaluation of the wavelength-selective cleavage of five photolabile protecting groups from two different families has been performed. Alanine, as a model bifunctional target molecule was masked at the amino terminal with *o*-nitrobenzyl group and at the carboxylic terminal with benzyl-type nitrogen and oxygen polyheteroaromatics, namely acridine, (thioxo)benzocoumarin and a coumarin built on the julolidine nucleus. The photosensitivity of the corresponding alanine conjugates was studied at selected wavelengths with HPLC/UV and ^{1}H NMR monitoring. The release of the fully deprotected molecule could be achieved by sequential irradiation in variable irradiation times, which were dependent on the heteroaromatic group used.

1. Introduction

Photoremovable protecting groups (PPGs) defined as systems that contain a chromophore, which is sensitive to light, but relatively stable to most chemical reagents, have been used to mask various functional groups. Their importance has been proved by their potential applications in synthetic organic chemistry,[1–3] biochemistry[4–6] and materials science.[4,7]

In the last two decades, the intense development of fluorescence techniques along with fluorescent reagents and strategies for various purposes, including bioapplications, has also evolved the research concerning PPGs to include fluorescent molecules. Fluorescent photoremovable protecting groups present advantages over non-fluorescent groups, since in addition to releasing molecules of interest at the desired location for a specific period of time, they also allow the visualisation, quantification and monitoring of the spatial distribution, localisation and depletion of the released molecules.[8] Such groups are particularly useful if the released molecule has higher fluorescence in its free form when compared to the conjugated form, providing a means to monitor the photorelease process. Depending on the application, the use of fluorescent protecting groups can sometimes difficult the photoactivation because it provides an alternative deactivation pathway to the intended photoreaction.

The above strategy of using fluorescent PPGs has been successfully employed on the temporally and spatially controlled delivery of bioactive molecules in the study of numerous processes in biological and medical research fields. Also, in organic synthetic methodologies, the use of fluorescent PPGs is important, since it can facilitate the follow up of experimental procedures involved in synthesis and deprotection reaction steps.

Among the fluorescent PPGs, polyaromatics including (anthracen-9-yl)methyl,[9] (pyren-1-yl)methyl,[10–12] (perylen-3-yl)methyl[13] and (phenanthren-9-yl)methyl[10] have been introduced. Heteroaromatics that can also be considered analogues of the benzyl protecting group have emerged in the last years, following the report on (coumarin-4-yl)methyl group photosensitivity in the release of phosphate ester by Givens in 1984,[14] and includes quinolines,[15,16] quinolones,[17,18] thiocoumarins and thioquinolones,[18] fused oxazoles[19,20] and acridine.[21,22]

Structural modifications at the coumarin ring by the introduction of substituents, particularly at C-6 and C-7 resulted in an improvement of photochemical and photophysical properties increasing the range of applications of this class of protecting groups.[23] An extension of the aromatic ring of coumarins, resulting in polyaromatic analogues has led to the enhancement of fluorophoric properties.[24–27] Also the exchange of the carbonyl function to thiocarbonyl affording the corresponding thioxo(benzo)coumarin resulted in an increase in the photosensitivity.[18,28]

* Corresponding author. E-mail address: msameiro@quimica.uminho.pt (M.S.T. Gonçalves).

0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.11.100

The advantages of fluorescent protecting groups mentioned do not diminish the importance of the remaining groups, including the most well-known *o*-nitrobenzyl group and its derivatives, which have been widely used in the caging of different molecules.[3]

The variety of PPGs, working by different mechanisms and possessing different types of chromophores/fluorophores, allows the possibility for wavelength-selective deprotection, a type of orthogonality referred to as chromatic orthogonality. This concept has been considered in certain research works, including in peptide solid phase synthesis with selective release using the nitroveratryl/pivaloylglycol pair.[29,30] Also, in bioapplications, some examples have been reported, involving amino acids,[31,32] peptides[33] and (poli)nucleotides,[34,35] using different pairs of protecting groups, such as coumarins, nitrophenethyl, 6-nitroveratryl and *p*-methoxyphenacyl groups. These studies involved photolysis of mixtures of the caged molecules bearing in each case only one photolabile protecting group, whereas a single report[33] refers to the use of two different groups in the same molecule.

Considering these facts and taking advantage of our knowledge in fluorescent PPGs, especially benzyl-based heteroaromatic groups, the present work aims to evaluate the possibility of wavelength-selective photolysis between four heteroaromatic photolabile protecting groups, previously introduced by our research team, and *o*-nitrobenzyl group. Given our promising earlier findings with (acridin-9-yl)methyl, (9-methoxy-3-oxo-3*H*-naphtho[2,1-*b*]pyran-1-yl)methyl (trivially named benzocoumarin), [11-oxo-2,3,5,6,7,11-hexahydro-1*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-9-yl]methyl (commonly called coumarin, based on the julolidine nucleus) and (9-methoxy-3-thioxo-3*H*-naphtho[2,1-*b*]pyran-1-yl)methyl (trivially designated (thioxo)benzocoumarin) groups, these systems were selected for the present study. Alanine was used as model of a bifunctionalised molecule, possessing different functional groups, an amine and a carboxylic acid. Conjugates were prepared bearing the *o*-nitrobenzyl and the heterocyclic group as protections of the N- and C-terminus through carbamate and ester linkages, respectively. Photolysis of these conjugates at selected wavelengths was carried out and the process course was monitored by HPLC/UV and ^{1}H NMR.

2. Results and discussion

2.1. Synthesis of alanine conjugates 1,2 and 6–9

(2-Nitrophenyl)methanol was reacted with L-alanine methyl ester via a *N*,*N*′-carbonyldiimidazole (CDI) mediated carbonyl transfer reaction in *N*,*N*-dimethylformamide, at room temperature to give *N*-(2-nitrobenzyloxycarbonyl)-L-alanine methyl ester **1**. Subsequent basic hydrolysis of the methyl ester with aqueous sodium hydroxide in 1,4-dioxane, at low temperature gave *N*-(2-nitrobenzyloxycarbonyl)-L-alanine **2**. This carbamate conjugate was used in the reaction with bromo- or chloromethylated heterocycles, namely 9-(bromomethyl)acridine **3**, 1-chloromethyl-9-methoxy-3-oxo-3*H*-naphtho[2,1-*b*]pyran[36] **4** and 9-(chloromethyl)-2,3,6,7-tetrahydro-1*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-11(5*H*)-one[37] **5**, in the presence of potassium fluoride in *N*,*N*-dimethylformamide, at room temperature (Scheme 1, Table 1),[38] to afford the corresponding conjugates **6**–**8**. In order to exchange the carbonyl by a thiocarbonyl group at the naphtho[2,1-*b*]pyran conjugate **7**, this compound was reacted with Lawesson's reagent in toluene, under reflux conditions,[39] yielding the corresponding thionaphthopyran conjugate **9** (Scheme 1, Table 1).

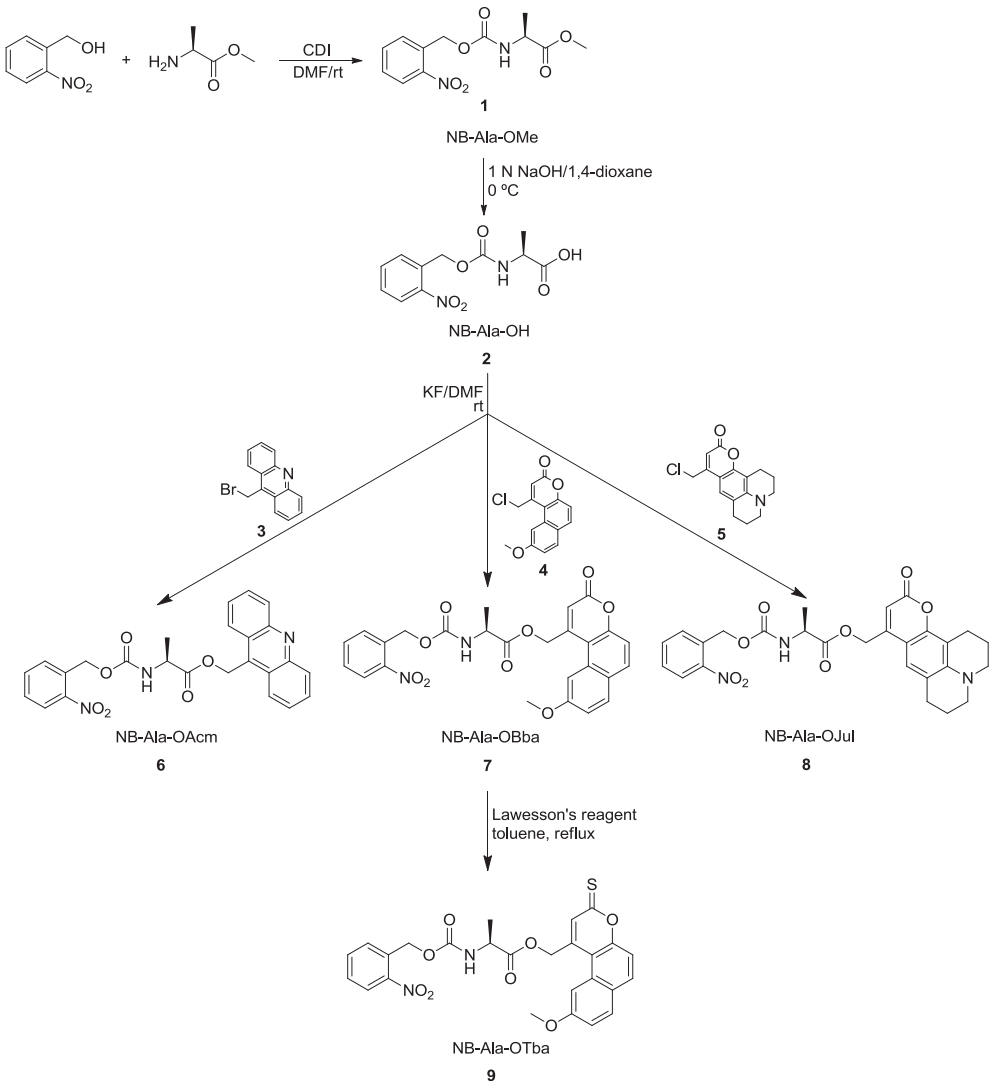
For simplicity of naming the various conjugates in this report, the photocleavable protecting groups will be designated by a two- or three-letter code, as follows: 2-nitrobenzyloxycarbonyl (NB), acridin-9-yl methylene (Acm), (9-methoxy-3-oxo-3*H*-naphtho[2,1-*b*]pyran-1-yl)methylene (Bba), (11-oxo-2,3,5,6,7,11-hexahydro-1*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-9-yl)methylene (Jul) and (9-methoxy-3-thioxo-3*H*-naphtho[2,1-*b*]pyran-1-yl)methylene (Tba), as indicated in Schemes 1 and 2 and Tables 1 and 2.

All new compounds were fully characterised by high resolution mass spectrometry, IR, ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR spectra showed signals of the alanine residue, such as the α-CH (δ 3.50–4.60 ppm) and β-CH_3 (δ 1.17–1.54 ppm). The 2-nitrobenzyloxycarbonyl (conjugates **1**, **2**, **6**–**9**) and heterocycle (conjugates **6**–**9**) methylene groups were also visible (δ 5.32–5.60 ppm, and δ 5.17–6.20 ppm, respectively). The confirmation of the presence of the carbamate bond linking the N-terminal of alanine to 2-nitrobenzyl group, as well as the ester linkage between the C-terminal of *N*-(2-nitrobenzyloxycarbonyl)-L-alanine and the heterocyclic moieties were also supported by ^{13}C NMR spectra signals at δ 154.46–155.55 ppm, and δ 172.17–172.69 ppm, respectively.

In order to evaluate the possibility of wavelength-selective photolysis and to obtain the parameters required for monitoring the processes, fundamental UV/vis photophysical characterisation was carried out. The UV/vis absorption and emission spectra of degassed 10^{-5} or 10^{-6} M solutions in absolute ethanol and in a methanol/HEPES buffer (80:20) solution of conjugates **2** and **6**–**9** were measured; absorption and emission maxima, molar absorption coefficients and relative fluorescence quantum yields are also reported (Table 1). Relative fluorescence quantum yields were calculated using naphthalene (Φ_F=0.23 in cyclohexane),[40] 9,10-diphenylanthracene (Φ_F=0.95 in ethanol),[41] or a 0.05 M solution of quinine in sulfuric acid (Φ_F=0.54)[42] as standards. For the Φ_F determination, the fluorescence standard was excited at the wavelengths of maximum absorption found for each one of the compounds to be tested and in all fluorimetric measurements the absorbance of the solution did not exceed 0.1.

Regarding the absorption data of conjugates **6**–**9**, in both solvents, it was found that all conjugates displayed two maximum absorption wavelengths (λ_{abs}), one of them at about 260 nm, which is related to the presence of 2-nitrobenzyloxycarbonyl group, as it was confirmed by the spectra of *N*-(2-nitrobenzyloxycarbonyl)-L-alanine **2** (λ_{abs} about 260 nm), and the other associated to the heterocycle moiety, which differs accordingly to its structure. Conjugate **6** bearing the nitrogen heterocycle acridine displayed absorption maxima at about 360 nm in both solvents. Concerning conjugate **7**, possessing the naphtho[2,1-*b*]pyran skeleton showed the lowest value of the set (λ_{abs} about 347 nm), but the replacement of the carbonyl group at the pyran ring by a thiocarbonyl (conjugate **9**) resulted in a bathochromic shift, tuning absorption maxima to values in the visible region (λ_{abs} 400 or 414 nm). In addition, it was observed that for conjugate **8** with a 3*H*-benzopyran fused julolidine, the maximum absorption wavelengths were at about 400 nm in both solvents (λ_{abs} 395 or 403 nm). For easier comparison, Fig. 1 shows the UV/vis spectra of the photosensitive compounds **2**, **6**–**9** in methanol/HEPES buffer (80:20) solutions.

Concerning the fluorescence spectra, in both tested solvents, it was observed that emission maxima (λ_{em}) of conjugates **6**–**9** occurred in the range (412–496 nm), being the conjugate possessing 3*H*-benzopyran fused julolidine **8** associated to the longer wavelengths, and the *N*-(2-nitrobenzyloxycarbonyl)-L-alanine **2** displaying the lowest value (λ_{em} at 304 nm), as expected due to its less conjugated structure. As for the fluorescence quantum yields, naphtho[2,1-*b*]pyran **7** was the most emissive (Φ_F 0.44 and 0.22, depending on the solvent). The emission of thiocarbonyl conjugate **9** was bathochromically shifted in ethanol with lower fluorescent quantum yields, in comparison with the corresponding carbonyl precursor (compound **7**). Stokes' shifts ($\Delta\lambda$) occurred in a broad range (41–130 nm), being the lowest values associated to conjugate **2**, and the highest values corresponding to conjugates **7** and **8**, bearing coumarin moieties.



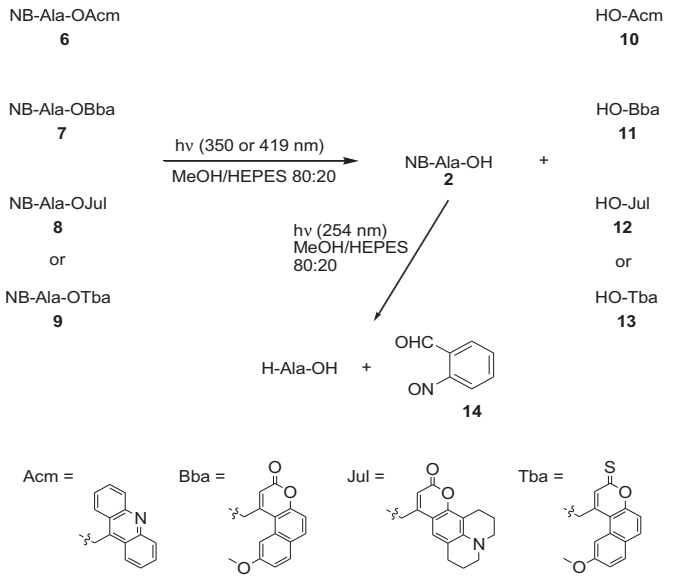
Scheme 1. Synthesis of photosensitive conjugates **2** and **6**–**9**.

Table 1
Yields, UV/vis and fluorescence data for conjugates **2**, **6**–**9** in absolute ethanol and methanol/HEPES buffer (80:20) solution

Compound		Yield/%	Ethanol					Methanol/Hepes (80:20)				
			λ_{abs}/nm	log ε	λ_{em}/nm	Φ_F	$\Delta\lambda$/nm	λ_{abs}/nm	log ε	λ_{em}/nm	Φ_F	$\Delta\lambda$/nm
2	NB-Ala-OH	92	257	3.91	304	0.064	47	263	3.78	304	0.073	41
6	NB-Ala-OAcm	32	254	5.61				254	5.42			
			354	4.46	412	0.113	58	362	4.60	413	0.157	51
7	NB-Ala-OBba	55	259	4.65				257	4.96			
			347	4.59	466	0.439	119	350	4.92	480	0.222	130
8	NB-Ala-OJul	44	254	4.68				259	4.66			
			395	4.50	486	0.184	91	403	4.67	496	0.207	93
9	NB-Ala-OTba	28	250	4.48				261	4.65			
			307	3.98				309	4.11			
			400	3.96	475	0.012	75	414	4.09	480	0.003	66

2.2. Photolysis studies of alanine conjugates 2 and 6–9

The possibility of selective deprotection of either terminus of a bifunctionalised molecule by choosing the appropriate wavelength was the main goal of the present work. As mentioned before, alanine was chosen as model target, and protected at its N-terminal with the well-known *o*-nitrobenzyl group via a carbamate linkage, and at its C-terminal with benzyl-type nitrogen and oxygen polyheteroaromatics, namely acridine, (thioxo)benzocoumarin and a coumarin built on the julolidine nucleus, through an ester bond. The later groups were selected from the collection of photoremovable protecting groups developed by our research group taking into consideration the photophysical properties, namely the wavelengths of maximum absorption displayed when linked to



Scheme 2. Photocleavage reactions of conjugates **2** and **6**–**9**.

properties of the selected groups and the *o*-nitrobenzyl group together in the same molecule.

Overall, owing to the wavelengths of maximum absorption of conjugates **6**–**9** in MeOH/HEPES buffer (80:20), it was found that photolysis at 350 nm would probably be suitable for the deprotection of the C-terminal of alanine in conjugates **6** and **7**, whereas irradiation at 419 nm would be adequate in the case of conjugates **8** and **9**. In order to check this and also to verify the stability to other nearby wavelengths, solutions of conjugates **2** and **6**–**9** were irradiated at different wavelengths (254, 300, 350 and 419 nm) in a Rayonet RPR-100 reactor (Scheme 2, Table 2). The photolysis reaction was monitored by reverse phase HPLC with UV detection, peak areas of the starting material (*A*, average of three runs for each compound) revealing a gradual decrease with time and plots of *A* versus irradiation time were obtained for each compound, at the considered wavelengths. The determined irradiation time represents the time necessary for the consumption of the starting materials until less than 5% of the initial area was detected (Table 2). For each compound and based on HPLC data, the plot of ln *A* versus irradiation time showed a linear correlation for the disappearance of the starting material, which suggested a first order reaction, obtained by the linear least squares methodology for a straight line. The photochemical quantum yields (Φ_{Phot}) were calculated based on half-lives ($t_{1/2}$), molar extinction coefficients (ε) and the incident photon flux (I_0), which was determined by potassium ferrioxalate actinometry.[43]

Conjugates **6** and **7** were exposed to light at 350 nm and results revealed that cleavage of the ester bond with release of *N*-(2-nitrobenzyloxycarbonyl)-L-alanine **2** occurred with an irradiation

Table 2
Irradiation times, t_{irr}, and photochemical quantum yields, Φ_{Phot}, for the photolysis of conjugates **2**, **6**–**9** at 254, 300, 350 and 419 nm in methanol/HEPES buffer (80:20) solution

Compound		254 nm		300 nm		350 nm		419 nm	
		t_{irr}/min	Φ_{Phot}	t_{irr}/min	Φ_{Phot}	t_{irr}/min	Φ_{Phot}	t_{irr}/min	Φ_{Phot}
2	NB-Ala-OH	153	1.17×10^{-4}	256	3.33×10^{-5}	469	1.72×10^{-5}	647	1.29×10^{-5}
6	NB-Ala-OAcm	25	2.28×10^{-4}	35	1.04×10^{-4}	18	7.90×10^{-5}	108	1.32×10^{-4}
7	NB-Ala-OBba	48	3.53×10^{-5}	98	6.38×10^{-6}	60	1.01×10^{-5}	243	2.51×10^{-6}
8	NB-Ala-OJul	12	1.94×10^{-4}	13	8.53×10^{-5}	21	5.20×10^{-5}	17	6.25×10^{-5}
9	NB-Ala-OTba	38	1.09×10^{-4}	41	3.63×10^{-5}	51	6.89×10^{-5}	31	1.11×10^{-5}

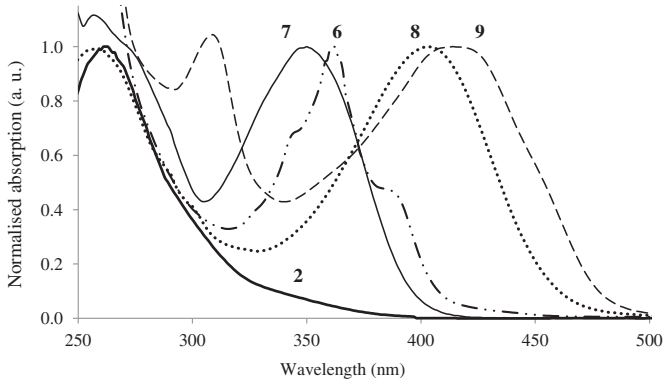


Fig. 1. Normalised UV/vis absorption spectra of conjugates **2**, **6**–**9** in methanol/HEPES buffer (80:20).

amino acid residues or butyric acid,[17–21,24–28,36,37] and also the promising photolytic results especially at longer wavelengths, which provided potential orthogonal behaviour to the *o*-nitrobenzyl group. Nevertheless, the fundamental photophysical studies of conjugates **2** and **6**–**9** were obviously essential to ascertain the time (t_{irr}) of 18 and 60 min, respectively. On the other hand, irradiation at 419 nm of conjugates **8** and **9** cleaved the carboxylic protecting group in 17 and 31 min, respectively (Scheme 2, Table 2). Conjugates **6**–**9** possess benzyl-type nitrogen and oxygen heterocycles connected through an ester bond, which have been found to cleave by formation of an ion pair that can recombine or proceed to the products after nucleophilic attack by the solvent molecules.[3] In this case, the formation of the corresponding heterocyclic alcohols **10**–**13** as by-products, respectively, was expected.

In order to estimate the stability of 2-nitrobenzyloxycarbonyl group in the above conditions, *N*-(2-nitrobenzyloxycarbonyl)-L-alanine **2** was irradiated at 350 and 419 nm. The results showed that 2-nitrobenzyloxycarbonyl group cleaved in 11% (after 18 min), 31% (after 60 min) at 350 nm, and in 9% (after 17 min), 15% (after 31 min) at 419 nm. Considering these results, the tested protecting groups cannot be considered totally orthogonal but rather quasi-orthogonal since selective cleavage can only be achieved in a particular order of irradiation: in order to minimise simultaneous cleavage at both terminals, the molecule should always be irradiated first at the longer wavelength of irradiation.

Considering that after deprotection of the C-terminal, cleavage of protecting group of N-terminal is required, *N*-(2-nitrobenzyloxycarbonyl)-L-alanine **2** was exposed to light of

254 nm, and it was found that cleavage of the carbamate linkage occurred in 153 min. The photolytic process performed at 300, 350 and 419 nm with conjugate **2**, revealed that the irradiation times increased considerably (t_{irr} between 256 and 647 min), thus confirming the expected behaviour, with 254 nm being the most adequate wavelength for the cleavage of *o*-nitrobenzyl group. This group is known to cleave by an intramolecular proton abstraction mechanism yielding the released product (in the present case involving a carbamate linkage, accompanied by spontaneous decarboxylation to the free amine) and a nitroso compound **14**.[3]

Bearing in mind the above findings, the release of the fully deprotected alanine residue by sequential irradiation was attempted, by irradiating first at the longer wavelength of irradiation (350 or 419 nm, depending on the heteroaromatic group) followed by the shorter wavelength of irradiation (254 nm). It was found that the release was possible in irradiation times very similar to the sum of the irradiation times presented in Table 2 (relative to the cleavage of each individual group), revealing that the by-products of the first photolysis (which remained in the solution being irradiated) did not influence the overall outcome of the second photolysis.

Additionally to monitoring the photolysis process by HPLC/UV detection, the photolysis of conjugates **2** (NB-Ala-OH) and **8** (NB-Ala-OJul), as representative examples of the tested set of compounds, was also followed by ^{1}H NMR in a methanol-d_4/D_2O (80:20) solution. In the case of conjugate **2**, upon irradiation at 254 nm, the signals related to the alanine α-CH and β-CH_3 in the conjugated form at about δ 4.20 and 1.45 ppm, gave rise to a close set of signals corresponding to alanine in its free form at about δ 3.75 and 1.50 ppm, respectively (Fig. 2). This conversion was also accompanied by the decrease with time of the integration of the signal due to the benzylic CH_2 at about δ 5.5 ppm. In the case of conjugate **8**, irradiation was carried out first at 419 nm, to cleave the heterocyclic C-terminal protecting group (the coumarin built on the julolidine nucleus). The alanine α-CH and β-CH_3 signals in the conjugated form, at about δ 4.35 and 1.50 ppm, were replaced by the new set of signals corresponding to the released compound, *N*-(2-nitrobenzyloxycarbonyl)-L-alanine **2**, at about δ 4.20 and 1.45 ppm, respectively (Fig. 3). The multiplets corresponding to the benzylic CH_2 of the N- and C-termini protecting groups of conjugate **8**, between δ 5.30–5.50 ppm, were substituted by a singlet due to the remaining *N*-(2-nitrobenzyloxycarbonyl) group. After irradiation at 419 nm for 11 h, ensuring almost complete conversion of conjugate **8** to conjugate **2**, the same solution was further irradiated at 254 nm to cleave the N-terminal nitrobenzyl protecting group. The same observations were made concerning the shifts of the alanine α-CH and β-CH_3 signals, as in the above referred photolysis for the pure conjugate **2**.

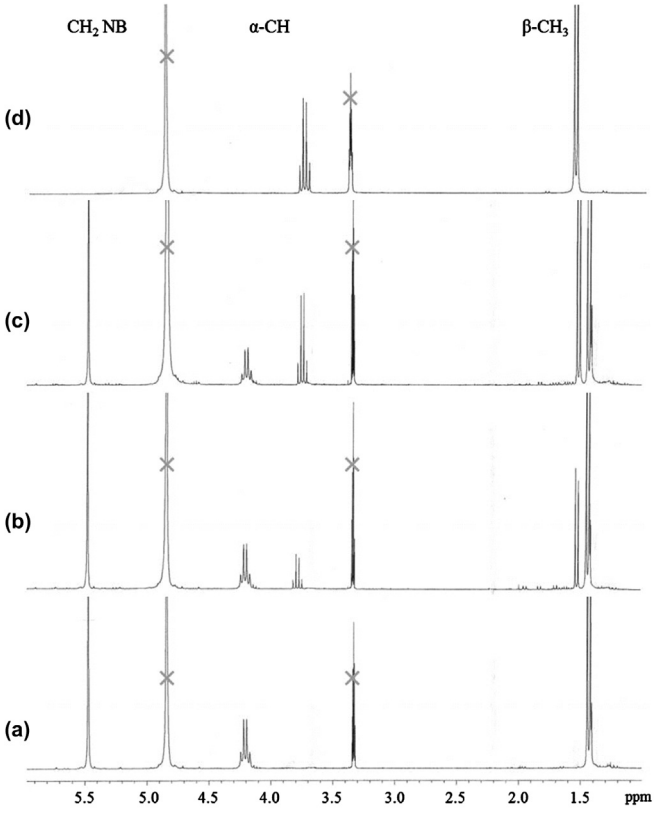


Fig. 2. Partial ^{1}H NMR spectra in methanol-d_4/D_2O (80:20) of the photolysis of conjugate **2**, NB-Ala-OH (C=2×10^{-2} M) at 254 nm: (a) before irradiation; (b) after irradiation for 18 h; (c) after irradiation for 34 h; (d) free H-Ala-OH.

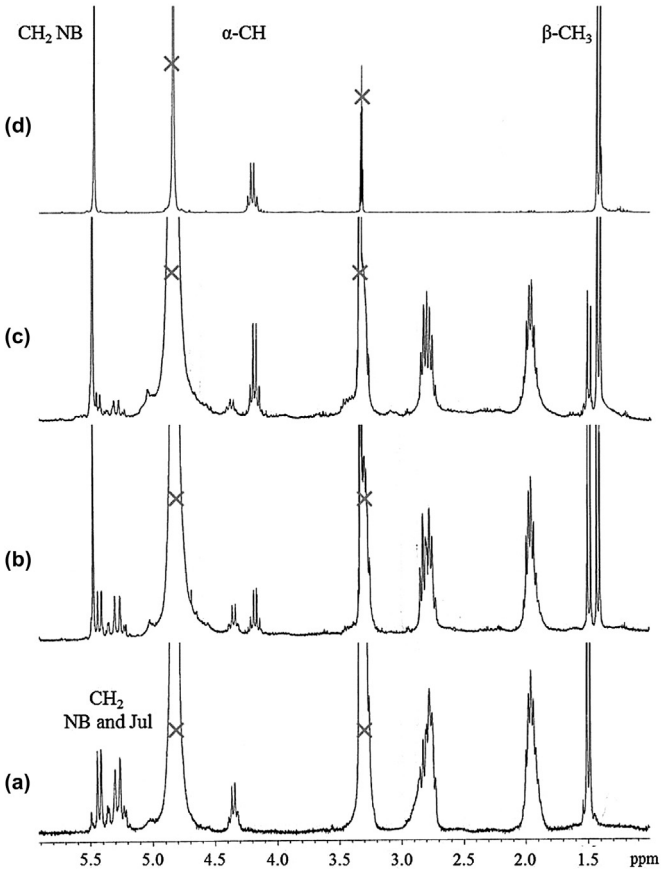


Fig. 3. Partial ^{1}H NMR spectra in methanol-d_4/D_2O (80:20) of the photolysis of conjugate **8**, NB-Ala-OJul (C=2×10^{-2} M) at 419 nm: (a) before irradiation; (b) after irradiation for 2 h; (c) after irradiation for 10 h; (d) free NB-Ala-OH **2**.

The NMR monitoring was carried out with a 2×10^{-2} M solution, which led to an expected increase in the photolysis time for the complete release of the molecule, when compared to the irradiation times in Table 2 obtained with dilute solutions.

3. Conclusions

It was investigated the photolysis of four conjugates bearing in the same molecule two photolabile groups, the *o*-nitrobenzyloxycarbonyl and a benzyl-type polyheteroaromatics, namely acridine, (thioxo)benzocoumarin and a coumarin built on the julolidine nucleus, and identified the wavelengths where the chromophores show different sensitivities. It was demonstrated

that selective cleavage of the photolabile groups was possible by choosing the most appropriate wavelength, being for the tested heterocyclic chromophores 350 and 419 nm, and for the *o*-nitrobenzyl group 254 nm. Overall, the results showed that the combinations of photolabile protecting groups used in conjugates **6**–**9** are wavelength-selective; however, a specific irradiation sequence is required, meaning that the heterocyclic chromophore should always be cleaved before the *o*-nitrobenzyl group.

The possibility of using other classes of photolabile protecting group, together with other photolysis conditions, and even the use of two-photon excitation are possibilities under study in our research group.

4. Experimental section

4.1. General

All melting points were measured on a Stuart SMP3 melting point apparatus. TLC analyses were carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel 60F_{254}) and spots were visualised under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (230–240 mesh). IR spectra were determined on a BOMEM MB 104 spectrophotometer using KBr discs. UV/vis absorption spectra (200–700 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^{1}H or a Bruker Avance III 400 at an operating frequency of 400 MHz for ^{1}H and 100.6 MHz for ^{13}C using the solvent peak as internal reference at 25 °C. All chemical shifts are given in parts per million using δ_H Me_4Si=0 ppm as reference and *J* values are given in hertz. Assignments were made by comparison of chemical shifts, peak multiplicities and *J* values and were supported by spin decoupling-double resonance and bidimensional heteronuclear correlation techniques. Mass spectrometry analyses were performed at the 'C.A.C.T.I.—Unidad de Espectrometria de Masas', at University of Vigo, Spain. Fluorescence spectra were collected using a FluoroMax-4 spectrofluorometer. Photolysis was carried out using a Rayonet RPR-100 chamber reactor equipped with 10 lamps of 254, 300, 350 and 419±10 nm. HPLC analyses were performed using a Licrospher 100 RP18 (5 μm) column in a JASCO HPLC system composed by a PU-2080 pump and a UV-2070 detector with ChromNav software. All reagents were used as received.

4.2. Synthesis of compounds 1, 2 and 6–9

4.2.1. N-(2-Nitrobenzyloxycarbonyl)-L-alanine methyl ester, ***1****. N,N′*-Carbonyldiimidazole (1.078 g, 6.65×10^{-3} mol) was stirred with (2-nitrophenyl)methanol (1.018 g, 6.65×10^{-3} mol) in dry DMF (4 mL) at 0 °C for 30 min. L-Alanine methyl ester hydrochloride (0.928 g, 6.65×10^{-3} mol), previously treated with triethylamine (1.01 mL, 7.32×10^{-3} mol) in dry DMF (2 mL) was added to the reaction mixture and the mixture was kept stirring for 18 h. The precipitate was filtered, the solvent was removed by rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using ethyl acetate and light petroleum, with mixtures of increasing polarity as eluent. Compound **1** was obtained as a pink oily solid (0.430 g, 23%). R_f=0.48 (ethyl acetate/light petroleum, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.44 (d, *J* 7.2 Hz, 3H, β-CH_3), 3.76 (s, 3H, OCH_3), 4.30–4.44 (m, 1H, α-CH), 5.49 (broad s, 1H, α-NH), 5.53 (s, 2H, CH_2), 7.47 (dt, *J* 7.4 and 1.6 Hz, 1H, H-4), 7.62 (dd, 1H, *J* 7.2 and 1.2 Hz, H-6), 7.65 (dt, *J* 6.8 and 0.8 Hz, 1H, H-5), 8.10 (dd, *J* 8.0 and 0.8 Hz, 1H, H-3). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ=18.54 (β-CH_3), 49.63 (α-CH), 52.49 (OCH_3), 63.41 (CH_2), 124.92 (C-3), 128.49 (C-4), 128.56 (C-6), 132.98 (C-1), 133.74 (C-5), 147.22 (C-2), 155.01 (C=O carbamate), 173.32 (C=O ester). IR (KBr 1%, cm^{-1}): ν=3345, 3113, 3044, 2991, 2956, 2880, 1729, 1613, 1578, 1526, 1453, 1344, 1302, 1250, 1216, 1177, 1151, 1117, 1086, 1071, 980, 859, 816, 791, 733, 703, 672. HRMS (EI): calcd for $C_{12}H_{14}N_2O_6$ [M^+]: 282.08522; found: 282.08543.

4.2.2. N-(2-Nitrobenzyloxycarbonyl)-L-alanine, ***2****.* To a suspension of compound **1** (0.403 g, 1.44×10^{-3} mol) in 1,4-dioxane (4.0 mL) at 0 °C, 1 M aqueous sodium hydroxide (1.44 mL, 1.44×10^{-3} mol) was added. The solution was stirred at low temperature for 18 h and acidified to pH 2–3 with 1 M aqueous potassium hydrogensulfate. The reaction mixture was reduced to half the initial volume in a rotary evaporator and extracted with dichloromethane (3×10 mL). The organic extracts were combined, dried with anhydrous magnesium sulfate and after solvent evaporation, compound **2** was obtained as a colourless oil (0.355 g, 92%). R_f=0.39 (ethyl acetate). ^{1}H NMR (DMSO-d_6, 400 MHz): δ=1.17 (d, *J* 6.8 Hz, 3H, β-CH_3), 3.50–3.59 (m, 1H, α-CH), 5.32 (s, 2H, CH_2), 6.64 (d, *J* 6.0 Hz, 1H, α-NH), 7.58 (dt, *J* 7.6 and 1.2 Hz, 1H, H-4), 7.68 (dd, 1H, *J* 7.6 and 0.8 Hz, H-6), 7.77 (dt, *J* 7.2 and 0.8 Hz, 1H, H-5), 8.08 (dd, *J* 8.4 and 1.2 Hz, 1H, H-3). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ=19.41 (β-CH_3), 51.40 (α-CH), 61.76 (CH_2), 124.73 (C-3), 128.74 (C-6), 128.86 (C-4), 133.22 (C-1), 134.20 (C-5), 147.12 (C-2), 154.46 (C=O carbamate), 174.33 (C=O acid). IR (film, cm^{-1}): ν=3369, 2987, 1692, 1614, 1576, 1533, 1451, 1343, 1295, 1264, 1215, 1120, 1067, 1020, 982, 936, 896, 860, 802, 738, 704. HRMS (EI): calcd for $C_{11}H_{12}N_2O_6$ [M^+]: 268.06956; found: 268.06986.

4.2.3. N-(2-Nitrobenzyloxycarbonyl)-L-alanine (acridin-9-yl)methyl ester, ***6****.* To a solution of compound **2** (0.073 g, 2.73×10^{-4} mol) in dry DMF (3 mL), potassium fluoride (0.047 g, 8.16×10^{-4} mol) and 9-(bromomethyl)acridine **3** (0.074 g, 2.72×10^{-4} mol) were added. The reaction mixture was stirred at room temperature for 30 h. Potassium fluoride was removed by filtration, the solvent was removed by rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using mixtures of ethyl acetate and light petroleum of increasing polarity as eluent. Compound **6** was obtained as light brown oil (0.040 g, 32%). R_f=0.51 (ethyl acetate/light petroleum, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.33 (d, *J* 7.2 Hz, 3H, β-CH_3), 4.30–4.40 (m, 1H, α-CH), 5.45 (s, 2H, CH_2 NB), 5.58 (d, *J* 7.6 Hz, 1H, NH), 6.08 (d, *J* 6.8 Hz, 1H, CH_2 OAcm), 6.20 (d, *J* 6.8 Hz, 1H, CH_2 OAcm), 7.35–7.45 (m, 1H, H-4′), 7.46–7.55 (m, 2H, H-5′and H-6′), 7.56–7.62 (m, 2H, H-2 and H-7), 7.73–7.79 (m, 2H, H-3 and H-6), 8.043 (dd, *J* 6.4 and 1.6 Hz, 1H, H-3′), 8.20–8.30 (m, 4H, H-1, H-8, H-4 and H-5). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ=18.14 (β-CH_3), 49.77 (α-CH), 58.57 (CH_2 OAcm), 63.37 (CH_2 NB), 123.74 (C-1 and C-8), 124.83 (C-3′), 125.16 (C-8a and C-9a), 126.82 (C-2 and C-7), 128.34 (C-4′), 128.41 (C-5′), 129.85 (C-4 and C-5), 130.11 (C-3 and C-6), 132.78 (C-1′), 133.65 (C-6′), 136.49 (C-9), 147.06 (C-2′), 148.32 (C-4a and C-10a), 155.04 (C=O carbamate), 172.69 (C=O ester). IR (film, cm^{-1}): ν=3420, 3331, 3056, 2985, 2941, 2878, 1727, 1630, 1611, 1579, 1526, 1452, 1421, 1344, 1305, 1266, 1209, 1170, 1115, 1068, 966, 910, 897, 859, 819, 790, 738, 704, 674, 642. HRMS (EI): calcd for $C_{25}H_{21}N_3O_6$ [M^+]: 459.14313; found: 459.14292.

4.2.4. N-(2-Nitrobenzyloxycarbonyl)-L-alanine [(9-methoxy-3-oxo-3H-naphtho[2,1-b]pyran-1-yl)]methyl ester, ***7****.* To a solution of compound **2** (0.134 g, 4.99×10^{-4} mol) in dry DMF (3 mL), potassium fluoride (0.087 g, 1.49×10^{-3} mol) and 1-chloromethyl-9-methoxy-3-oxo-3*H*-naphtho[2,1-*b*]pyran **4** (0.137 g, 4.99×10^{-4} mol) were added. The reaction mixture was stirred at room temperature for 48 h. Potassium fluoride was removed by filtration, the solvent was removed by rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using ethyl acetate and light petroleum, with mixtures of increasing polarity as eluent. Compound **7** was obtained as a light yellow solid (0.139 g, 55%); mp 145.0–146.6 °C. R_f=0.40 (ethyl acetate/light petroleum,

1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.54 (d, *J* 7.6 Hz, 3H, β-CH_3), 3.96 (s, 3H, OCH_3), 4.52–4.58 (m, 1H, α-CH), 5.53 (s, 2H, CH_2 NB), 5.55 (broad s, 1H, α-NH), 5.60–5.79 (m, 2H, CH_2 OBba), 6.64 (s, 1H, H-2), 7.22 (dd, *J* 8.8 and 2.0 Hz, 1H, H-8), 7.30 (d, *J* 9.2 Hz, 1H, H-5), 7.36–7.42 (m, 1H, H-10), 7.45 (dt, *J* 7.2 and 2.0 Hz, 1H, H-4′), 7.55–7.69 (m, 2H, H-5′and H-6′), 7.82 (d, *J* 8.8 Hz, 1H, H-7), 7.90 (d, *J* 8.8 Hz, 1H, H-6), 8.08 (d, *J* 8.0 Hz, 1H, H-3′). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ=18.12 (β-CH_3), 49.86 (α-CH), 55.46 (OCH_3), 63.64 (CH_2 NB), 64.98 (CH_2 OBba), 105.72 (C-10), 111.70 (C-4b), 112.93 (C-2), 115.23 (C-5), 116.53 (C-8), 124.93 (C-3′), 126.32 (C-6a), 128.60 (C-4′), 128.74 (C-5′), 130.48 (C-6b), 131.35 (C-7), 132.66 (C-1′), 133.75 (C-6′), 133.86 (C-6), 147.28 (C-2′), 150.25 (C-1), 155.15 (C-4a), 155.55 (C=O carbamate), 159.71 (C-9), 160.07 (C-3), 172.17 (C=O ester). IR (KBr 1%, cm^{-1}): ν=3406, 3057, 2987, 2959, 2942, 1718, 1624, 1579, 1553, 1523, 1460, 1425, 1345, 1232, 1214, 1171, 1142, 1121, 1073, 1026, 983, 946, 894, 862, 844, 822, 789, 731, 703, 674, 608. HRMS (EI): calcd for $C_{26}H_{22}N_2O_9$ [M^+]: 506.13256; found: 506.13268.

4.2.5. N-(2-Nitrobenzyloxycarbonyl)-L-alanine [11-oxo-2,3,5,6,7,11-hexahydro-1H-pyrano[2,3-f]pyrido[3,2,1-ij]quinolin-9-yl]methyl ester, ***8****.* To a solution of compound **2** (0.027 g, 1.01×10^{-4} mol) in dry DMF (3 mL), potassium fluoride (0.017 g, 3.02×10^{-4} mol) and 9-(chloromethyl)-2,3,6,7-tetrahydro-1*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-11(5*H*)-one **5** (0.029 g, 1.01×10^{-4} mol) were added. The reaction mixture was stirred at room temperature for 46 h. Potassium fluoride was removed by filtration, the solvent was removed by rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using ethyl acetate and light petroleum, with mixtures of increasing polarity as eluent. Compound **8** was obtained as brown oil (0.023 g, 44%). R_f=0.44 (ethyl acetate/light petroleum, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.52 (d, *J* 7.2 Hz, 3H, β-CH_3), 1.90–2.00 (m, 4H, H-2 and H-6), 2.73–2.78 (m, 2H, H-7), 2.83–2.89 (m, 2H, H-1), 3.20–3.30 (m, 4H, H-3 and H-5), 4.45–4.55 (m, 1H, α-CH), 5.17–5.32 (m, 2H, CH_2 Jul), 5.40–5.50 (m, 1H, α-NH), 5.51–5.60 (m, 2H, CH_2 NB), 6.06 (s, 1H, H-10), 6.86 (s, 1H, H-8), 7.47 (dt, *J* 7.2 and 1.6 Hz, 1H, H-4′), 7.59–7.68 (m, 2H, H-5′and H-6′), 8.10 (dd, *J* 8.4 and 0.8 Hz, 1H, H-3′). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ=18.34 (β-CH_3), 20.36 (C-2), 20.47 (C-1), 21.37 (C-6), 27.63 (C-7), 49.47 (C-3), 49.82 (α-CH), 49.89 (C-5), 62.49 (CH_2 Jul), 63.53 (CH_2 NB), 105.66 (C-10), 105.90 (C-8a), 106.97 (C-12b), 118.35 (C-7a), 120.48 (C-8), 124.93 (C-3′), 128.52 (C-4′), 128.57 (C-5′), 132.88 (C-1′), 133.81 (C-6′), 145.99 (C-7b), 147.19 (C-2′), 148.70 (C-9), 151.19 (C-12a), 155.08 (C=O carbamate), 162.01 (C-11), 172.27 (C=O ester). IR (film, cm^{-1}): ν=3318, 3060, 2940, 2851, 1717, 1603, 1556, 1524, 1440, 1381, 1343, 1312, 1255, 1206, 1177, 1122, 1071, 1015, 960, 885, 858, 820, 790, 732, 700. HRMS (EI): calcd for $C_{27}H_{27}N_3O_8$ [M^+]: 521.17991; found: 521.17989.

4.2.6. N-(2-Nitrobenzyloxycarbonyl)-L-alanine [(9-methoxy-3-thioxo-3H-naphtho[2,1-b]pyran-1-yl)]methyl ester, ***9****.* Lawesson's reagent (0.172 g, 4.26×10^{-4} mol) was added to a solution of compound **7** (0.072 g, 1.42×10^{-4} mol) in toluene (5 mL). The reaction mixture was refluxed for 9 h and the process was followed by TLC (ethyl acetate/light petroleum, 1:4). The solvent was removed by rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using dichloromethane and light petroleum, with mixtures of increasing polarity as eluent. Compound **9** was obtained as an orange oil (0.021 g, 28%). R_f=0.67 (ethyl acetate/light petroleum, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.54 (d, *J* 7.2 Hz, 3H, β-CH_3), 3.97 (s, 3H, OCH_3), 4.50–4.60 (m, 1H, α-CH), 5.35–5.45 (m, 1H, α-NH), 5.54 (s, 2H, CH_2 NB), 5.65–5.80 (m, 2H, CH_2 OTba), 7.25 (d, *J* 2.0 Hz, 1H, H-2), 7.41–7.53 (m, 4H, H-4′, H-10, H-5 and H-8), 7.54–7.70 (m, 2H, H-5′and H-6′), 7.85 (d, *J* 8.8 Hz, 1H, H-7), 7.96 (d, *J* 8.8 Hz, 1H, H-6), 8.03 (d, *J* 8.0 Hz, 1H, H-3′). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ=18.21 (β-CH_3), 49.87 (α-CH), 55.55 (OCH_3), 63.70 (CH_2 NB), 64.79 (CH_2 OTba), 106.29 (C-10), 114.17 (C-4b), 114.93 (C-5), 117.17 (C-2), 124.97 (C-3′), 126.61 (C-6a), 127.39 (C-8), 128.62 (C-4′), 128.77 (C-5′), 130.23 (C-6b), 131.49 (C-7), 132.68 (C-1′), 133.77 (C-6′), 134.42 (C-6), 141.34 (C-1), 147.32 (C-2′), 155.12 (C=O carbamate), 158.81 (C-4a), 159.97 (C-9), 172.21 (C=O ester), 195.12 (C-3). IR (film, cm^{-1}): ν=3338, 3065, 2938, 2852, 1727, 1622, 1591, 1535, 1453, 1343, 1297, 1231, 1174, 1141, 1096, 1069, 1024, 976, 858, 840, 790, 732, 700, 688, 671. HRMS (EI): calcd for $C_{26}H_{22}N_2O_8S$ [M^+]: 522.10976; found: 522.10995.

4.3. General photolysis procedure

A 1×10^{-4} M methanol/HEPES (80:20) solution of compounds **2** and **6**–**9** (5 mL) was placed in a quartz tube and irradiated in a Rayonet RPR-100 reactor at the desired wavelength. The lamps used for irradiation were of 254, 300, 350 and 419±10 nm.

Aliquots of 100 μL were taken at regular intervals and analysed by RP-HPLC. The eluent was acetonitrile/water, 75:25 with 0.1% trifluoroacetic acid, at a flow rate of 0.8 mL/min, previously filtered through a Millipore, type HN 0.45 μm filter and degassed by ultrasound for 30 min. The chromatograms were traced by detecting UV absorption at the wavelength of maximum absorption for each compound (retention time: **2**, 3.5; **6**, 5.0; **7**, 6.3; **8**, 7.5 and **9** 9.5 min).

Acknowledgements

Thanks are given to the *Fundação para a Ciência e Tecnologia* (FCT, Portugal) for financial support to the NMR Portuguese network (PTNMR, Bruker Avance III 400-Univ. Minho), FCT and FEDER (European Fund for Regional Development)-COMPETE-QREN-EU for financial support to the research centre CQ/UM [PEst-C/QUI/UI0686/2011 (FCOMP-01-0124-FEDER-022716)] and for a Ph.D. grant to A.M.P. (SFRH/BD/61459/2009).

References and notes

1. Pillai, V. N. R. *Synthesis* **1980**, 1–26.
2. Greene, T. W.; Wuts, G. M. *Protective Groups in Organic Chemistry*, 3rd ed.; John Wiley: New York, NY, 1999.
3. Klan, P.; Solomek, T.; Bochet, C. G.; Blanc, A.; Givens, R.; Rubina, M.; Popik, V.; Kostikov, A.; Wirz, J. *Chem. Rev.* **2013**, *113*, 119–191.
4. Abelson, J.; Simon, M.; Marriott, G. *Caged Compounds*; Academic: New York, NY, London, 1998.
5. Shigeri, Y.; Tatsu, Y.; Yumoto, N. *Pharmacol. Ther.* **2001**, *91*, 85–92.
6. Pelliccioli, A. P.; Wirz, J. *Photochem. Photobiol. Sci.* **2002**, *1*, 441–458.
7. San Miguel Arnanz, V.; Bochet, C. G.; del Campo, A. *J. Am. Chem. Soc.* **2011**, *133*, 5380–5388.
8. Mayer, G.; Heckel, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4900–4921.
9. Singh, A. K.; Khade, P. K. *Tetrahedron Lett.* **2005**, *46*, 5563–5566.
10. Furuta, T.; Hirayama, Y.; Iwamura, M. *Org. Lett.* **2001**, *3*, 1809–1812.
11. Fernandes, M. J. G.; Gonçalves, M. S. T.; Costa, S. P. G. *Tetrahedron* **2007**, *63*, 10133–10139.
12. Fernandes, M. J. G.; Costa, S. P. G.; Gonçalves, M. S. T. *New J. Chem.* **2013**, 2369–2376.
13. Jana, A.; Ikbal, M.; Singh, N. D. P. *Tetrahedron* **2012**, *68*, 112811–112836.
14. Givens, R. S.; Matuszewski, B. *J. Am. Chem. Soc.* **1984**, *106*, 6860–6861.
15. Fedoryak, O. D.; Dore, T. M. *Org. Lett.* **2002**, *4*, 3419–3422.
16. Ma, J. N.; Cheng, S. C.; An, H. Y.; Li, M. D.; Ma, C. S.; Rea, A. C.; Zhu, Y.; Nganga, J. L.; Dore, T. M.; Phillips, D. L. *J. Phys. Chem. A* **2011**, *115*, 11632–11640.
17. Fonseca, A. S. C.; Gonçalves, M. S. T.; Costa, S. P. G. *Amino Acids* **2010**, *39*, 699–712.
18. Fonseca, A. S. C.; Soares, A. M. S.; Gonçalves, M. S. T.; Costa, S. P. G. *Tetrahedron* **2012**, *68*, 7892–7900.
19. Soares, A. M. S.; Costa, S. P. G.; Gonçalves, M. S. T. *Tetrahedron* **2010**, *66*, 8189–8195.
20. Soares, A. M. S.; Piloto, A. M.; Hungerford, G.; Costa, S. P. G.; Gonçalves, M. S. T. *Eur. J. Org. Chem.* **2012**, 922–930.
21. Piloto, A. M.; Hungerford, G.; Costa, S. P. G.; Gonçalves, M. S. T. *Photobiol. Sci.* **2013**, *12*, 339–347.
22. Jana, A.; Saha, B.; Karthik, S.; Barman, S.; Ikbal, M.; Ghosh, S. K.; Singh, N. D. P. *Photochem. Photobiol. Sci.* **2013**, *12*, 1041–1052.
23. Givens, R. S.; Rubina, M.; Wirz, J. *Photochem. Photobiol. Sci.* **2012**, *11*, 472–488.
24. Fernandes, M. J. G.; Gonçalves, M. S. T.; Costa, S. P. G. *Tetrahedron* **2008**, *64*, 11175–11179.

25. Soares, A. M. S.; Costa, S. P. G.; Gonçalves, M. S. T. *Amino Acids* **2010**, *39*, 121–133.
26. Fernandes, M. J. G.; Costa, S. P. G.; Gonçalves, M. S. T. *Tetrahedron* **2011**, *67*, 2422–2426.
27. Piloto, A. M.; Soares, A. M. S.; Hungerford, G.; Costa, S. P. G.; Gonçalves, M. S. T. *Eur. J. Org. Chem.* **2011**, 5447–5451.
28. Piloto, A. M.; Soares, A. M. S.; Costa, S. P. G.; Gonçalves, M. S. T. *Amino Acids* **2012**, *42*, 2275–2282.
29. Kessler, M.; Glatthar, R.; Giese, B.; Bochet, C. G. *Org. Lett.* **2003**, *5*, 1179–1181.
30. Ladlow, M.; Legge, C. H.; Neudeck, T.; Pipe, A. J.; Sheppard, T.; Yang, L. Q. L. *Chem. Commun.* **2003**, 2048–2049.
31. Kantevari, S.; Matsuzaki, M.; Kanemoto, Y.; Kasai, H.; Ellis-Davies, G. C. R. *Nat. Methods* **2010**, *7*, 123–125.
32. Stanton-Humphreys, M. N.; Taylor, R. D. T.; McDougall, C.; Hart, M. L.; Brown, C. T. A.; Emptage, N. J.; Conway, S. J. *Chem. Commun.* **2012**, 657–659.
33. Kotzur, N.; Briand, B.; Beyermann, M.; Hagen, V. *J. Am. Chem. Soc.* **2009**, *131*, 16927–16931.
34. Schafer, F.; Joshi, K. B.; Fichte, M. A. H.; Mack, T.; Wachtveitl, J.; Heckel, A. *Org. Lett.* **2011**, *13*, 1450–1453.
35. Priestman, M. A.; Sun, L.; Lawrence, D. S. *ACS Chem. Biol.* **2011**, *6*, 377–384.
36. Piloto, A. M.; Costa, S. P. G.; Gonçalves, M. S. T. *Tetrahedron Lett.* **2005**, *46*, 4757–4760.
37. Piloto, A. M.; Hungerford, G.; Costa, S. P. G.; Gonçalves, M. S. T. *Eur. J. Org. Chem.* **2013**, 7715–7723.
38. Tjoeng, F. S.; Heavner, G. A. *Synthesis* **1981**, 897–899.
39. Jesberger, M.; Davis, T. P.; Barner, L. *Synthesis* **2003**, *13*, 1929–1958.
40. Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic: London, 1971.
41. Morris, J. V.; Mahaney, M. A.; Huber, J. R. *J. Phys. Chem.* **1976**, *80*, 969–974.
42. Montalti, L.; Credi, A.; Prodi, T.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; Taylor and Francis: Boca Ratón, 2006.
43. Muller, C.; Even, P.; Viriot, M.-L.; Carré, M.-C. *Helv. Chim. Acta* **2001**, *84*, 3735–3741.