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PAPER

Highly efficient and regiospecific photocyclization of 2,2′-diacyl bixanthenylidenes†

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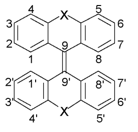
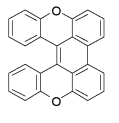
In contrast to the reversible photochemistry of the 2,2′-substituted bixanthenylidenes (**1a–f**), the photocyclization of 2,2′-diacyl bixanthenylidenes (**1g–j**) reveals an irreversible process where the initial cyclic intermediate C(*E*) can undergo a rapid [1,11] hydrogen shift to form stable isomer C′(*E*) in a degassed solution, which cannot revert to the starting compound, so giving a highly efficient and regiospecific photocyclization.

Introduction

Bistricyclic aromatic enes (BAEs) are attractive substrates for the study of the conformational behavior and dynamic stereochemistry of overcrowded polycyclic aromatic enes and for the interplay of strain and delocalization effects.[1] Thermochromic[2] and photochromic[2a,3] BAEs have been extensively investigated, and serve as candidates for chiroptical molecular switches and molecular motors.[4]



BAEs



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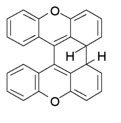
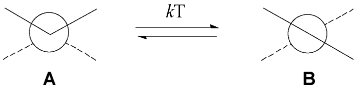


C

The phenomenon of thermochromism in BAEs has been attributed to a unimolecular equilibrium between two distinct and interconvertible conformers:[5] a colorless or yellow ambient-temperature form **A**, and a deep-blue or deep-green high-temperature form **B**, with enthalpy differences between them of 4–30 kJ mol^{-1}. The **B** isomer is formed from the triplet state **A**.[6] The form **A** was identified as the ground state, *anti*-folded or unevenly *anti*-folded conformer, and the form **B** was the thermochromic, a low energy local minimum twisted conformer.



Photochromism resulting from conformational isomerizations of 9,9′-bi-9*H*-xanthen-9-ylidene (X = O, bixanthenylidenes, **1**) has been well established by means of flash photolysis over a wide temperature range and steady-state methods in low temperature, and these conformers are unstable in room temperature.[6b,7] *Z*, *E* isomerization, with a low activation energy of 2,2′-disubstituted bixanthenylidenes, occurs easily at room temperature, and the ratio of *Z*/*E* in solution depends on the bulkiness of the 2 and 2′ substituents.[8] However, few reports on photochemical reactions such as the photocyclization of bixanthenylidenes are found.[7d,9] In the presence of iodine and air, bixanthenylidene can be converted photochemically to helixanthen (**2**) undergoing a photocyclization to generate a labile photoisomer **C**. The dihydro-intermediate can either revert thermally or photochemically to **1**, or be oxidized to **2**.[7d,9] Herein, we report the conclusive mechanism for rationalizing the regioselectivity and efficiency in the photocyclization of synthesized 2,2′-substituted bixanthenylidenes (**1a–j**).

Results and discussion

The bixanthenylidenes in aerated THF solutions were irradiated with a 500 W Xe lamp to generate the corresponding helixanthens **2**, which were one or two regioisomeric helixanthens, **2**(*E*) and **2**(*Z*) (Scheme 1), but another possible kind of regioisomeric product **2**(*Z*′), from cyclization between the 1- and 1′-positions, was not found (*vide infra*).

To investigate the regioselectivity, the crude product mixtures from the photolysis of **1** were analyzed with HPLC chromatography. Fig. 1 clearly shows that the concentration of **1b** decreases and **2b**(*E*, *Z*) increases with photolysis time, and consumption of **1b** is equal to increment of **2b**(*E*, *Z*), and the ratio of **2b**(*E*) : **2b**(*Z*) is a constant (44 : 56) during photolysis. These indicate that the photoconversion is a very clean reaction with no byproducts and the photoproducts **2b**(*E*, *Z*) are stable to irradiation light.

Similar analysis was performed, and the ratio of two regioisomers (**2**(*E*) : **2**(*Z*)) was obtained from HPLC chromatograms of the crude photolysis products in aerated solution, and are listed in Table 1. With increasing the size of 2,2′ substituents, the ratio of **2**(*E*) : **2**(*Z*) increases from 44 : 56 for **1b** (R = F) to 79 : 21 for

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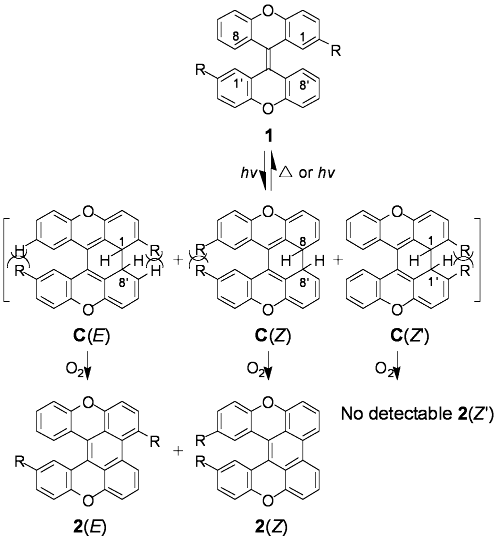
† Electronic supplementary information (ESI) available: Synthesis and characterization data of **4b**, **4d–j**, **1b**, **1d–j**, **2b–e**(*E*, *Z*) and **2f–j**(*E*), UV–Vis spectrum changes of photolysis of **1** recorded at different irradiation times, HPLC chromatograms for photolysis of **1b–j**, and copies of NMR spectra of new compounds. See DOI: 10.1039/c1ob05072a



Scheme 1 Photoconversion of 2,2′-substituted bixanthenylidenes (**1**) to helixanthens (**2**) in aerated solutions.

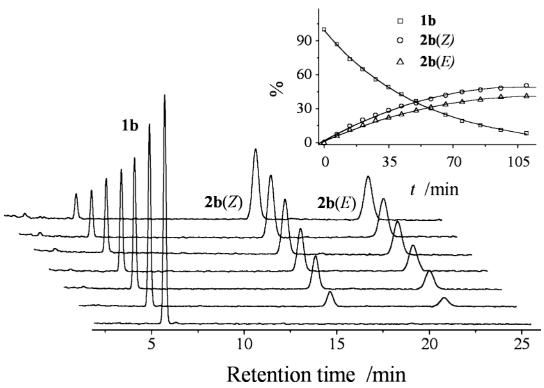


Fig. 1 HPLC chromatograms of the crude products in the photolysis of **1b** in aerated acetonitrile–THF (v/v, 9 : 1) irradiated for different times under 365 nm light. Insert: percentages of **1b**, and **2b**(*E*, *Z*).

1e (R = Et), and photolysis of **1f** and 2,2′-diacylbixanthenylidenes (**1g–j**) give one kind of regioisomeric product, **2**(*E*). Hence, the steric hindrance of the R substituents seems to be responsible for the regioselectivity. The order of the steric strain in the three possible photoisomers would be **C**(*Z*′) > **C**(*Z*) > **C**(*E*), which result in the expected oxidation products **2**(*Z*′), **2**(*Z*) and **2**(*E*), respectively (Scheme 1). No detectable **2**(*Z*′) may be because of a too large a strain between the substituent groups to form **C**(*Z*′) or its formation cannot compete with the more rapid ring opening. The high proportion of **2b**(*Z*) (56%) in the photolysis of **1b** may be because of the small size of fluorine.

The regioselectivity and the efficiency in the photoconversion is determined by the formation rates of the two **C** photoisomers and the relative rates of ring opening and oxidation by O_2. If the difference in the oxidation rate for the **C** intermediates is neglected, the photoconversion rates are determined by the relative rates between the photocyclization rates of **1** and the ring-opening rates of **C**. The rates should be controlled by the steric strains of the **C** intermediates, which depend on the size of the substituent groups R, finally giving different efficiencies and regioslectivity.

Table 1 The regioselectivity (**2**(E) : **2**(Z)) and quantum yields of photoconversion of **1**

Entry	**1**: substituents	**2**(*E*) : **2**(*Z*)[a]	$\Phi_{1\to2}$[b]
1	**1a**: R = H		0.027
2	**1b**: R = F	44 : 56	0.0052
3	**1c**: R = CH_3	61 : 39	0.0042
4	**1d**: R = OCH_3	71 : 29	0.0025
5	**1e**: R = Et	79 : 21	0.0034
6	**1f**: R = CN	100 : 0	0.018
7	**1g**: R = $COCH_3$	100 : 0	0.36
8	**1h**: R = COOH	100 : 0	0.26
9	**1i**: R = COOMe	100 : 0	0.080
10	**1j**: R = $CONEt_2$	100 : 0	0.24

[a] From HPLC chromatograms of photolysis crude in CH_3CN–THF(v/v, 9 : 1) solutions. [b] Measurement in THF solutions, error within 5%.

The photoconversion of **1** to **2** can be observed by a UV–Vis spectrometer. The spectral changes with an isobestic point at about 390 nm clearly show the conversion of **1** to **2** under 370 nm light: the concurrent disappearance of the absorption band (340–390 nm) of **1** and the appearance of the 400–500 nm band of **2** (Fig. 2). Hence, the conversion extent of **1** could be estimated by monitoring the increase in absorbance of **2** at 440 nm. Furthermore, because the absorbance of the two regioisomeric products are very similar in the visible region, the photoconversion efficiency ($\Phi_{1\to2}$) could be measured by monitoring the UV–Vis absorption change of the photolysis systems of **1** under the irradiation of a monochromatic light (370 nm) from a fluorescence spectrometer, and data are listed in Table 1.

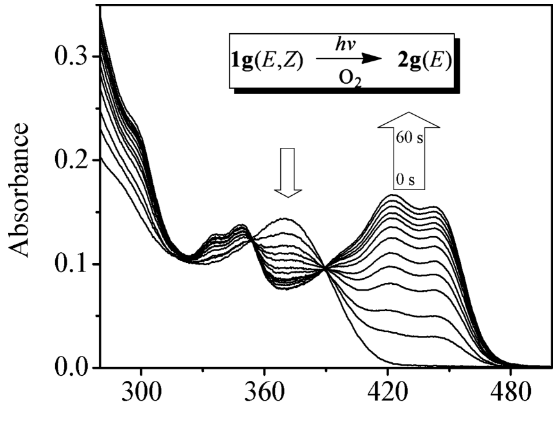


Fig. 2 UV–Vis absorption spectra of the photolysis of **1g** in the aerated THF recorded after each irradiation for 5 s under 365 nm light from a UV lamp.

Data in Table 1 show that 2,2′-diacylbixanthenylidenes (**1g–j**) give much higher values of $\Phi_{1\to2}$ than other bixanthenylidenes (**1a–f**) (*vide infra*), and the values of **1b–f** are lower than that of **1a**. This indicates that the steric hinder of the 2,2′ substituents (R) plays a dominating role in the efficiency of photocyclization of **1b–f**. A highly inefficient photocyclization of 2,2′-di-*tert*-butylbixanthenylidene provided further support.[10]

According to the electronic effects of R (CN, F, CH_3, Et, OCH_3), the values of $\Phi_{1\to2}$ gradually decrease from electron-withdrawing groups (EWGs) to electron-donating groups (EDGs) for **1b–f**.

These results show that the C1-C8′ coupling reactivity of the reagent with EWGs (a positive C1$^{\delta+}$) is higher than that with EDGs (a negative C1$^{\delta-}$) in the photocyclization. In other words, the intermediate **C**(*E*) with EWGs is more stable than that with EDGs. Therefore, besides the steric effects of R, electronic effects also play an important role on the efficiency of the photocyclization.

To understand the highly efficient and regiospecific photocyclization of 2,2′-diacylbixanthenylidenes (**1g–j**), the photolysis of **1g** in degassed benzene-d_6 with a sealed Pyrex tube was monitored by ^{1}H NMR spectroscopy, under irradiation with a hand-held UV lamp (Fig. 3). As shown in Fig. 3, the disappearance of some peaks of **1g** is accompanied by the appearance of a series of new peaks *a–f*, which are assigned to an enol isomer **C′g**(*E*) shown in Chart 1. The concentration of **C′g**(*E*) increases with irradiation time, and the *c*, *d* peaks shift to low field and the *b* peak shifts to high field in NMR spectra. The changing chemical shifts with the amount of **C′g**(*E*) indicate the existence of an interaction between **C′g**(*E*) molecules, such as a hydrogen bond. Comparison of the structures of **C′g**(*E*) and **Cg**(*E*) shows that **Cg**(*E*) undergoes a [1,11] hydrogen shift to generate **C′g**(*E*).

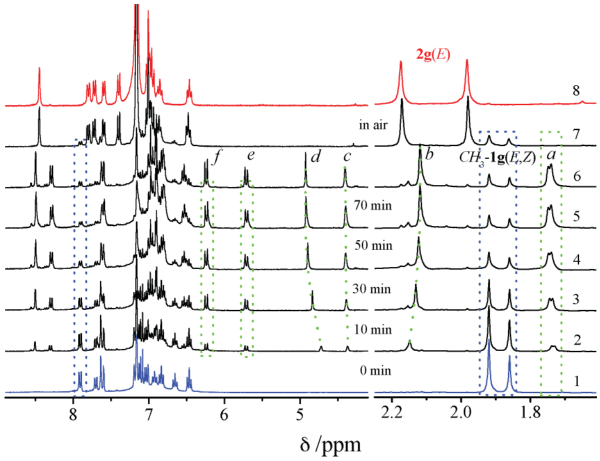
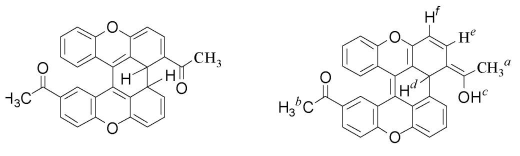


Fig. 3 ^{1}H NMR spectrum change of **1g** in degassed benzene-d_6 before and after irradiation, for times shown (1–5), under a 365 nm light at room temperature; (6) standing at room temperature for 5 h; (7) after opening the sealed tube; (8) neat **2g**(*E*) in benzene-d_6.



Cg(*E*)

C'g(*E*)

Chart 1 Two intermediates, **Cg**(*E*) and **C′g**(*E*), in the photoconversion of **1g** to **2g**(*E*)

In contrast to light yellow and fluorescent **1g** and **2g**(*E*), **C′g**(*E*) is a dark red, non-fluorescent compound with a good stability under room-temperature irradiation conditions in the degassed solution. ^{1}H NMR spectra show no other detectable products besides **C′g**(*E*) during the 70 min irradiation and no change in the irradiated sample after standing at room temperature for 5 h. Furthermore, **1g** could convert completely to **C′g**(*E*) after a sufficient irradiation. Hence, **C′g**(*E*) is very stable in the degassed solution, and cannot revert to **1g** under the irradiation conditions. However, **C′g**(*E*) could be rapidly oxidized to **2g** upon exposure of the degassed solution to air, shown in Fig. 3.

The photoisomer **C**(*E*) was undetectable by steady-state methods (NMR and UV spectrometry) due to its too short half-life at room temperature, and thus the conversion of **Cg**(*E*) to **C′g**(*E*) must be more rapid than its formation. Therefore, the formation of **C′g**(*E*), preventing ring opening of **Cg**(*E*) to revert to **1g**, results in a highly efficient and regiospecific photocyclization. Analogue phenomena have been observed from photocyclization of *cis*-stilbenes in both the absence and presence of catalysts[11] and 3-styrylpyridines in anaerobic conditions.[12]

In addition, relative to the oxidation of **C**(*E*, *Z*), the hydrogen migration in **C**(*E*) would compete more effectively with the ring opening, leading to the regiospecific product **2**(*E*), in the photolysis of the diacylbixanthenylidenes. When the hydrogen migration is a relative slow process, such as the photolysis of **1i**, we observed a minor product **2i**(*Z*) in THF–methanol (v/v 1 : 9) solution (**2i**(*E*) : **2i**(*Z*) = 95 : 5), see Fig. S1 in the ESI.†

Conclusions

In summary, we have demonstrated that the efficiency and regioselectivity in the photocyclization of 2,2′-disubstituted bixanthenylidenes depend on both the steric hindrance effects and electronic effects of the substituent groups. Moreover, we have observed an irreversible photocyclization of 2,2′-diacylbixanthenylidenes (**1g–j**), that is, the intermediate **C**(*E*) generated initially can undergo a rapid thermal [1,11] hydrogen shift to form a stable enol **C′**(*E*) in a degassed solution, which cannot revert to **1**, but can be rapidly oxidized to **2**(*E*) in the presence of oxygen. This implies that the photoconversion efficiency is independent of the oxygen concentration during the irradiation period. It can be expected that the clean photoconversion has a potential application as a convenient chemical actinometry on the radiation measurement in UV wavelength region of 250–400 nm.

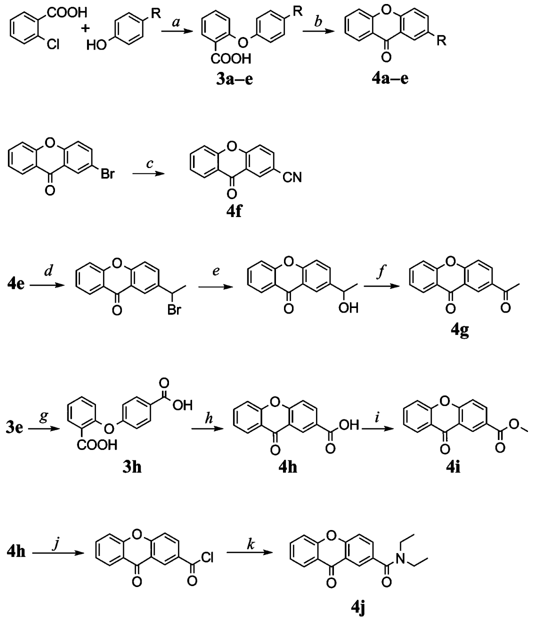
Experimental

General methods

Solvents of chemical quality were distilled prior to use. Melting points are uncorrected. ^{1}H NMR spectra were recorded on Bruker AV spectrometers (300 or 400 MHz). ^{13}C NMR spectra were recorded on Bruker AV spectrometers (75 or 100 MHz). Mass spectra were measured on a Bucker BIFLEX™ III Mass spectrometer. FTIR spectra were acquired on a BRUKER VECTOR22 infrared spectrometer. Fluorescence–emission spectra were carried out on a Perkin–Elmer Instruments LS55 Luminescence Spectrometer. UV–Vis absorption spectra were recorded with a Shimadzu UV–Vis 2450 spectrometer at room temperature. HPLC analysis was performed on an Agilent HPLC system (1200 series) with a Agilent C-18 reverse phase column or a Agilent SIL normal phase column (5 μm × 4.6 mm × 150 mm).

Synthesis of 2,2′-disubstituted dixanthylenes (1)

The 2-substituted xanthones (**4**) were synthesized according to procedures shown in Scheme 2. The substituted *o*-phenoxybenzoic acids (**3a–e**, **a**: R = H, **b**: R = F, **c**: R = CH_3, **d**: OCH_3, **e**:



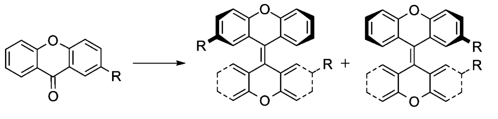
Scheme 2 Reagents and conditions: (a) K_2CO_3, Cu, CuI, anisole, reflux, 5 h; (b) 98% H_2SO_4, rt, 1 h; (c) CuCN, DMF, reflux, 8 h; (d) NBS, CCl_4, reflux, 6 h; (e) NaOH, THF–H_2O, reflux, overnight; (f) MnO_2, CH_2Cl_2, reflux, 2 d; (g) $KMnO_4$, H_2O, reflux, 8 h; (h) polyphosphoric acid, 180 °C, 4 h; (i) $SOCl_2$, CH_3OH, reflux, 1 h; (j) $SOCl_2$, reflux, 0.5 h; (k) diethylamine, $CHCl_3$, reflux, 2 h.

R = Et) were prepared by Ullmann condensations of the appropriately *para*-substituted phenols with *o*-chlorobenzoic acid.[13] Adding concentrated H_2SO_4, cyclization of **3a–e** gave the 2-substituted xanthones **4a–e** in high yields. **4f** could be obtained by refluxing 2-bromoxanthone and CuCN in DMF. Oxidation of 2-(1-hydroxyethyl)xanthone with manganese dioxide in refluxing CH_2Cl_2 for about 48 h afforded 2-acetylxanthone (**4g**) in 90% yield. Xanthone-2-carboxylic acid (**4h**) was obtained by intramolecular Friedel–Crafts acylation of polyphosphoric acid with **3h**, which is from the oxidation of the ethyl group of **3e** with potassium permanganate in an alkaline solution. Reaction of **4h** with $SOCl_2$ in CH_3OH solution leads to xanthone-2-carboxylic acid methyl ester (**4i**) in 95% yield. The carboxamide **4j** could be obtained by first refluxing **4h** with $SOCl_2$ for 0.5 h, removing the $SOCl_2$, and then adding diethylamine and freshly distilled $CHCl_3$ to reflux for 2 h.

The xanthones **4** are converted to 2,2′-disubstituted dixanthylenes **1** according to two conventional methods as follows (Scheme 3). Method A: the xanthones **4** are converted into unstable *gem*-dichlorides by refluxing in oxalyl dichloride to facilitate the subsequent intermolecular coupling by the action of activated Cu powder in refluxing *p*-xylene. Method B is a classical method for the preparation of dixanthylenes, converting by a bimolecular Zn–HCl reduction in glacial acetic acid. Compounds **1a–e** were prepared according to method A in high yields (70–80%). Compounds **1f–j** were obtained following method B in higher yields (60–80%) over method A (only 10%).

Synthesis and characterization of helixanthens 2

Dixanthylene was dissolved in $CHCl_3$ with saturated concentration in a flask. Under an air atmosphere, the solution was irradiated with a 500 W Xe lamp for a certain time. The solvent in the photolysis mixture was removed by rotary evaporation. The residue was subjected to column chromatography on silica gel, and the corresponding helixanthen **2**(*E*) were obtained. **2**(*Z*) was obtained from HPLC of crude photolysis products of **1**.



4 (*E*)-**1** (*Z*)-**1**

Scheme 3 Reagents and conditions: Method A for **1a–e**: (1) $(COCl)_2$, reflux, 10 h; (2) Cu powder, *p*-xylene, reflux, 7 h; method B for **1f–j**: Zn, HCl, CH_3COOH, reflux, 1 h.

Measurements for conversion quantum yields of 1 to 2

3 mL samples in quartz cuvettes were irradiated with 370 nm light from a fluorescence spectrometer with a 20 nm slit for **1b–e** and a 5 nm slit for other compounds. The conversion extent of the 2,2′-disubstituted dixanthylenes (**1**) was monitored by the increase in absorbance at 440 nm of the helixanthens (**2**). After certain time intervals, the absorbance of the irradiated solutions was recorded by a UV–Vis spectrometer. The photoconversion rates of **1a–f** depended on the concentration of oxygen in the solutions. Hence, solvents were saturated sufficiently with air before preparation of the sample solutions in all measurements. Since the photoproducts **2** absorb 370 nm light, in order to avoid the competition of absorbing the irradiated light between reactants **1** and products **2**, the conversion extent of reactants **1** was controlled within 5% in the measurements.

To obtain the quantum yields for photoconversion of compounds **1a–j**, [$\Phi_{1\rightarrow 2}$ = (rate of dixanthylene electrocyclization)/(rate of photons absorbed)], the absorbances at 440 nm (A_{440}, absorption peaks of **2**) and 370 nm (A_{370}) were measured at certain irradiated time intervals. The A_{440} of the irradiated solution depends on the extent of photoconversion of **1** to **2**. The molar extinction coefficient at 440 nm (ε_{440}) was obtained from the UV–Vis absorption spectrum of **2**, and the concentration of **2** in the photolysis system was obtained from $A_{440}/\varepsilon_{440}$. The plot of the concentration against the irradiation time (t/ min) is well fitted as a straight line. The slope of the straight line, B, is a conversion rate of **1** to **2**. The intensity of the incident light I_0 (unit: einstein min^{-1}) was measured using ferrioxalate actinometry.[14] The intensity of light absorbed (I_a) by the solution was calculated in term of Beer's law, $I_a = I_0\ (1–10^{-A_{370}})$. These values allowed the calculation of the quantum yield, $\Phi = BV_0/I_a$, wherein V_0 was the volume of irradiation solution, 3×10^{-3} L.

^{1}H NMR spectra of photolysis of 1 g in degassed benzene-d_6

To obtain information about the mechanism of photocyclization of **1g**, the progress of its irradiation in degassed solution was monitored by NMR spectroscopy. **1g** was dissolved in benzene-d_6 (20 mM) and placed in a Pyrex NMR tube. The solution was degassed by three freeze–pump–thaw cycles, and then sealed under vacuum. The degassed solution of **1g** was irradiated under 365 nm light from a hand-held UV lamp, and the ^{1}H NMR spectra were recorded after several incremental irradiation periods.

Acknowledgements

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