

## Photoinduced reactions of bicycloalkylidenes with isatin and isoquinolinetriene†

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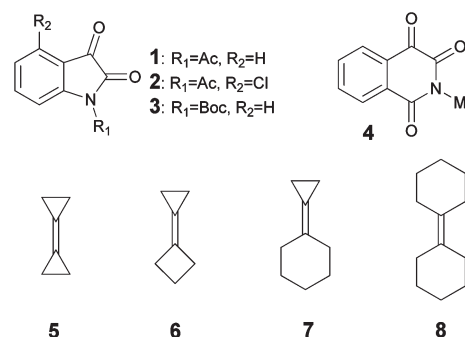
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Photoinduced reactions of isatin and *N*-methyl-1,3,4-isoquinolinetriene with bicycloalkylidenes such as bicyclopropylidene, cyclopropylidenecyclobutane, cyclopropylidenecyclohexane and bicyclohexylidene were investigated. The reactions gave spirooxetanes as the major products derived from the [2 + 2] photocycloaddition pathway via 1,4-biradical recombination. Unusual products including the [4 + 2 + 2] cycloadducts, the oxoisochroman derivatives and other ring-rearranged products were derived from competitive pathways via 1,6-biradical recombination. The presence of oxygen in the reaction solution was found to be relevant to the distribution of different types of products. Mechanisms were proposed to rationalize the chemo- and regioselectivity in the photoreactions and the origin of the different types of products.

## Introduction

Photocycloadditions of carbonyl compounds with C=C containing substrates, along with subsequent cascade reactions, have provided an expeditious way to construct diversified organic frameworks.<sup>1,2</sup> Photoreactions of heterocyclic carbonyl compounds, especially heterocyclic 1,2-dicarbonyl compounds such as isatin and isoquinolinetriene, have been of continuous research interest to us.<sup>3,4</sup> The C3 carbonyl group of *N*-acetylisatin **1** was the reactive site in Paterno–Büchi reactions with C=C or C≡C bonds<sup>3b,e–g</sup> and in hydrogen abstraction reactions.<sup>3c</sup> Photocycloadditions involving the two adjacent carbonyl groups in **1–3** as a 1,4-dioxadiene have only been found in its photoreactions with specific oxazoles via a [4 + 4] cycloaddition pathway.<sup>3a,d</sup> In photoreactions of isoquinolinetrienes such as **4** with alkynes or oxazoles, the C4 carbonyl group on the isoquinoline ring was found to be the only reaction site.<sup>4</sup>



Bicycloalkylidenes such as bicyclopropylidene<sup>5</sup> (5), cyclopropylidenecyclobutane<sup>6</sup> (6), cyclopropylidenecyclohexane<sup>7</sup> (7) and bicyclohexylidene<sup>8</sup> (8), are unconventional alkene species with unusual bonding properties. Theoretical and experimental studies on these bicycloalkylidenes have indicated that the central double bonds in **5** are substantially shorter than the normal C=C bonds with a bond length of 1.304 Å.<sup>9,10</sup> The extra strain caused by the cyclopropyl rings led to many unusual reactivities of **5** in thermal reactions, which have been systematically studied over the past decades.<sup>11,12</sup> It is also known that **5** has a much higher HOMO energy than methylenecyclopropane.<sup>13</sup> The crystal structure of bicyclohexylidene **8** revealed that the two cyclohexane rings were in the chair conformation and the length of the central double bond was 1.332 Å.<sup>14</sup>

Due to the unusual physical and bonding properties of these bicycloalkylidenes, unusual reactivities and applications of cyclopropylidene cycloalkanes<sup>6,7,15</sup> as well as those of

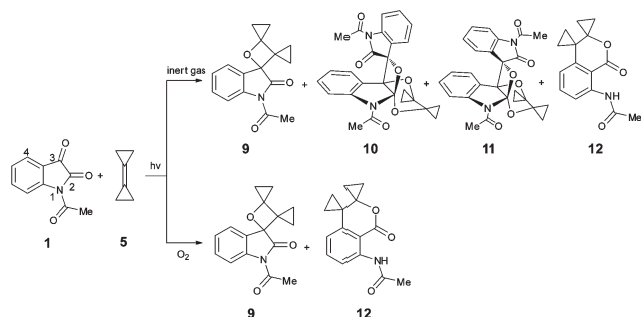
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†Electronic supplementary information (ESI) available: Crystal structure of compounds **12**, **31** and **32**; control experiments; <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all the new compounds. CCDC 838079–838081, 859787, 859788. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob07158d

bicyclohexylidene<sup>16</sup> have been reported. De Meijere *et al.* has systematically investigated the thermal reactions and transformations of bicyclopropylidene **5** in the past decades.<sup>11,12,17</sup> On the other hand, photoreactions involving the bicycloalkylidenes and their synthetic application have rarely been explored except for a few examples of photooxidation<sup>18</sup> and photoinduced conversion in hydroxylic media<sup>19</sup> or rare-gas matrices.<sup>20</sup> Recently we reported the [4 + 2] photocycloaddition of bicycloalkylidenes with 9,10-phenanthrene-9,10-dione followed by photooxidation as a facile and highly atom-economic method for the preparation of biaryl containing bislactones.<sup>21</sup>

Here we report the photoinduced reactions of substituted isatin (**1–3**) and *N*-methyl-1,3,4-isoquinolinetrione (**4**) with four cycloalkylidenes (**5–8**). Comparison of the photoreactions of isatin and isoquinolinetrione with the four bicycloalkylidenes could provide detailed information on electronic and steric effects on the photoreaction pathway partitioning. Besides, the photoreactions could also serve as facile and atom-economic approaches for the preparation of various spirocycloalkyl heterocycles which are otherwise difficult to prepare.



Scheme 1 Photoreaction of **1** with **5**.

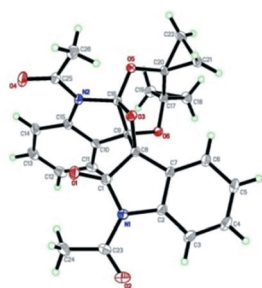


Fig. 1 Crystal structure of compound **10**.

## Results and discussion

### Photoreaction of isatin with **5**

The photoreaction of **1** with **5** proceeded smoothly in benzene and complete conversion of **1** could be achieved after 12 hours of irradiation at wavelengths higher than 400 nm. As shown in Scheme 1, four products **9–12** were obtained from the photolysis during which inert gas was purged. The major product, **9**, was the spirooxetane fused with two spirocyclopropyl which was derived from the common Paterno–Büchi reaction. Products **10** and **11** were a pair of diastereoisomeric [4 + 2 + 2] cycloadducts. The relative configuration of the diastereoisomer **10** was determined by X-Ray crystallographic analysis (Fig. 1). Product **12** was an oxoisochroman derivative fused with two spirocyclopropyl rings whose structure has also been confirmed by X-Ray crystallographic analysis (ESI†). When the reaction mixture was irradiated under an oxygen atmosphere, only **9** and **12** were obtained with a total yield of 86% (Table 1).

The formation of the major [2 + 2] cycloadduct **9** was not sensitive to the atmosphere during photolysis (Table 1). While the formation of the [4 + 2 + 2] cycloadducts (**10**, **11**) and the oxoisochroman **12** seemed to be competitive and the presence of oxygen favored the formation of **12**. Reaction pathways leading to the formation of **9–12** are proposed in Scheme 2. The photo-excited *N*-acetyl isatin **1**\* reacted with **5** to give the biradical intermediate **DR**<sub>1</sub>. The involvement of biradical intermediates in Paterno–Büchi reactions is well established.<sup>3</sup> In the reaction of **1** with **5**, the involvement of biradical species was also confirmed by a control experiment to trap the biradical which eliminated the formation of **9–12** (ESI†).

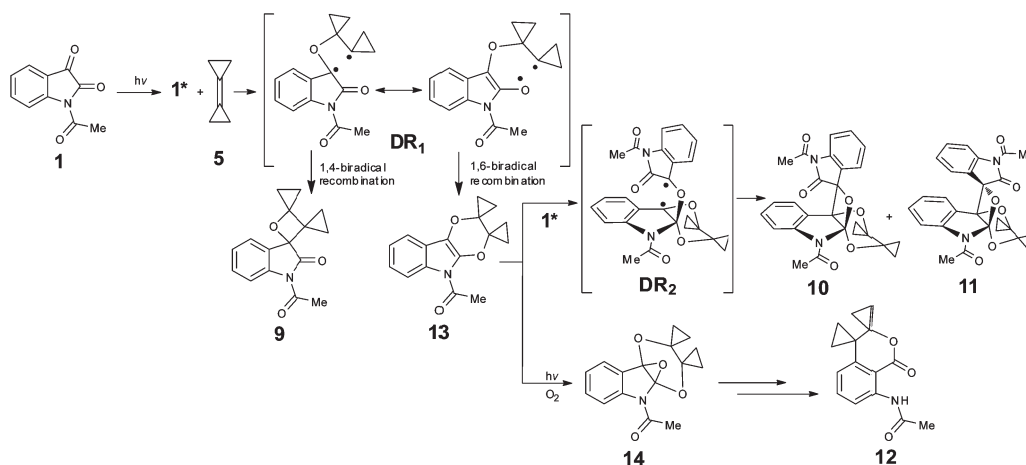
Although cyclopropylcarbonyl radicals are usually prone to undergo ring opening reactions and serve as radical clocks,<sup>22</sup> the radical center at the cyclopropyl carbon in **DR**<sub>1</sub> did not induce ring opening of the other cyclopropane before the radical recombination. This is most likely because the cyclopropyl group at the radical center can efficiently stabilize it, preventing the  $\alpha$ -cyclopropane ring from being opened. Recombination of the 1,4-biradical led to the major spirooxetane product **9**, while 1,6-biradical recombination gave the [4 + 2] cycloadduct **13** which was highly reactive for further reaction with another **1**\* or with O<sub>2</sub>. The thermal hetero-Diels–Alder reaction pathway<sup>23</sup> which could also lead to the formation of **13** has been excluded since HPLC monitoring of a mixture of **5** with **1** in benzene either at room temperature or under reflux did not show any change of the starting material.

Reaction of the intermediate **13** with **1**\* was regioselective to give two diastereoisomeric [4 + 2 + 2] cycloadducts **10** and **11**.

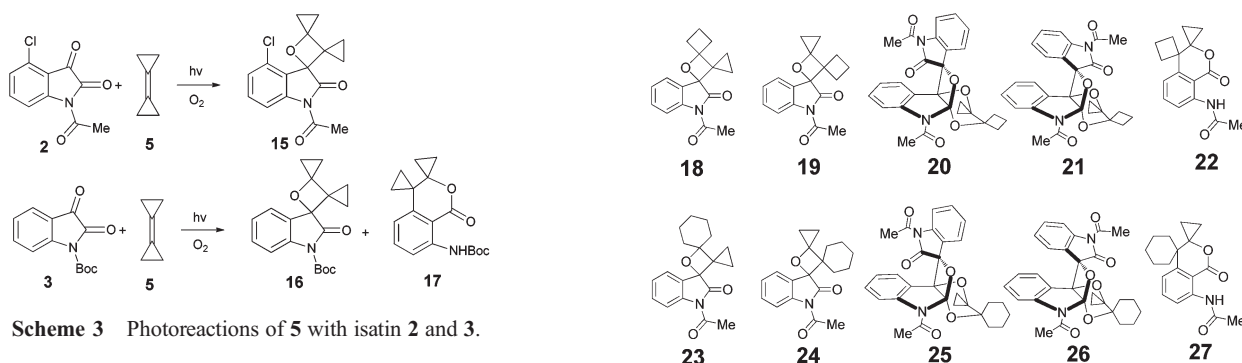
Table 1 Results of photoreactions of **5** with isatin

Entry	Isatin	Atmosphere	Products and yields <sup>a</sup> (%)		
			Spirooxetanes	[4 + 2 + 2] cycloadducts	Oxoisochroman
1	<b>1</b>	inert	<b>9</b> (63)	<b>10</b> (4), <b>11</b> (6)	<b>12</b> (6)
2	<b>2</b>	O <sub>2</sub>	<b>9</b> (62)	— <sup>b</sup>	<b>12</b> (24)
3	<b>2</b>	O <sub>2</sub>	<b>15</b> (84)	— <sup>b</sup>	— <sup>b</sup>
4	<b>3</b>	O <sub>2</sub>	<b>16</b> (35)	— <sup>b</sup>	<b>17</b> (47)

<sup>a</sup> Isolated yields. <sup>b</sup> Undetectable.



**Scheme 2** Reaction pathway proposed for the photoreaction of **1** with **5**.



**Scheme 3** Photoreactions of **5** with isatin **2** and **3**.

**Scheme 4** Products from reactions of **1** with **6** and **7**.

The same regioselectivity was observed in the  $[4 + 4 + 2]$  cycloaddition of **1** with oxazoles.<sup>3a,d</sup> Formation of the oxoisochroman product **12** may result from photooxygenation of the primary product **13**. Since **13** was highly reactive and could not be obtained, the pathway leading to **12** was still quite clear at this stage. However, we have confirmed that **12** was not the secondary product of **9–11** by carrying out a control experiment using **9–11** as the substrate for photoirradiation or thermal decomposition. Besides, the fact that photoreaction of **1** with **5** under an oxygen atmosphere resulted in an increased yield of **12** at the expense of **10** and **11** was in accord with the reaction pathway proposed in Scheme 2.

Substitution groups on **1** also showed influence on the formation of the oxoisochroman type product. As shown in Scheme 3 and Table 1, photoreaction of **5** with **2** with a Cl atom at C4 of the indole ring gave the spirooxetane product exclusively upon photoirradiation under an oxygen atmosphere. Thereby indicating that the ring-rearrangement following the decarbonylation step involved the C–H at the C4 of the indole ring. The substituent at the indole N was also relevant to the relative ratio of the spirooxetane product and the oxoisochroman type product as shown in the reaction of **5** with **3**.

#### Photoreaction of **1** with **6** and **7**

Photoreactions of **1** with the other bicycloalkylidenes including **6** and **7** were then investigated. The unsymmetric feature of **6** and **7** allowed us to explore the regioselectivity of the

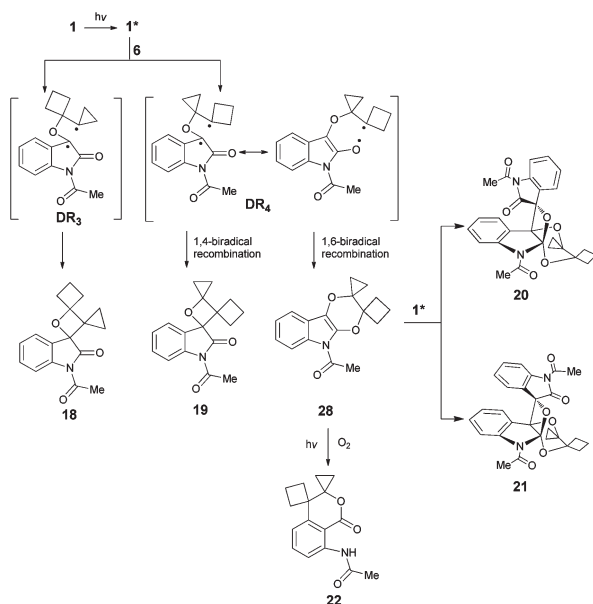
photocycloadditions. Products and yields of the photoreactions are shown in Scheme 4 and Table 2. The reaction of **1** with **6** under an inert atmosphere gave two regioisomeric spirooxetane products (**18** and **19**) and two diastereoisomeric  $[4 + 2 + 2]$  photocycloadducts (**20** and **21**). Formation of the oxoisochroman type product **22** was observed only upon irradiation under an oxygen atmosphere. The reaction pathways leading to these products are shown in Scheme 5.

The two spirooxetane products **18** and **19** were formed *via* radical recombination of the biradical **DR<sub>3</sub>** and **DR<sub>4</sub>** respectively. Chemo- and regioselectivity can be ascribed to the steric hindrance for biradical recombination. The relative ratio of the  $[4 + 2 + 2]$  cycloadducts to the  $[2 + 2]$  cycloadducts was around 1 : 3, which was higher than that found in the reaction of **1** with **5**. It revealed that the 1,6-biradical recombination in **DR<sub>4</sub>** happened more readily as compared with **DR<sub>1</sub>** in Scheme 2. The relative ratio of the two regioisomers **18** to **19** in the final products was over 4 : 1, which revealed that the steric hindrance for the 1,4-biradical recombination in **DR<sub>3</sub>** was less than that in **DR<sub>4</sub>**. The relatively higher steric hindrance for 1,4-biradical recombination in **DR<sub>4</sub>** pushed the less sterically hindered 1,6-biradical recombination to take place preferentially, leading to the formation of **28** and the following  $[4 + 2 + 2]$  cycloadduct or the oxoisochroman type product.

The photoreaction of **1** with **7** proceeded with similar chemo-, regio- and diastereoselectivity. As shown in Table 2, two

**Table 2** Results of photoreactions of **1** with **6** and **7**

Entry	Bicycloalkylidene	Atmosphere	Products and yields <sup>a</sup>		
			Spirooxetane	[4 + 2 + 2] cycloadducts	Oxoisochroman
1	<b>6</b>	Inert	<b>18</b> (48), <b>19</b> (11)	<b>20</b> (3), <b>21</b> (17)	— <sup>b</sup>
2		O <sub>2</sub>	<b>18</b> (54), <b>19</b> (14)	— <sup>b</sup>	<b>22</b> (12)
3	<b>7</b>	Inert	<b>23</b> (25), <b>24</b> (11)	<b>25</b> (9), <b>26</b> (31)	— <sup>b</sup>
4		O <sub>2</sub>	<b>23</b> (31), <b>24</b> (16)	— <sup>b</sup>	<b>27</b> (28)

<sup>a</sup> Isolated yields. <sup>b</sup> Undetectable.**Scheme 5** Proposed pathway for reaction of **1** with **6**.

regioisomeric spirooxetanes (**23** and **24**) and two diastereoisomeric [4 + 2 + 2] cycloadducts (**25** and **26**) were obtained from the photoreaction under an inert atmosphere. Photoreaction under an oxygen atmosphere also gave the corresponding oxoisochroman **27** together with the spirooxetanes **23** and **24**.

### Photoreaction of **1** with **8**

The photoreaction of **1** with **8** proceeded smoothly to give five products (Scheme 6). The spirooxetane product **29** was obtained with a yield of 38%, which was significantly lower than the yield of **1** in the reaction of **1** with **5**. The two bulky cyclohexyl groups might have impeded the [2 + 2] cycloaddition of **1** with **8** even more. The alternative [4 + 2] cycloaddition pathway resulted in tiny amounts of the dioxine type product **30**. Compared to other [4 + 2] intermediates such as **13**, compound **30** was less reactive because the two bulky cyclohexyl groups caused extra steric hindrance for the further formation of [4 + 2 + 2] cycloadduct. Therefore **30** has been isolated and characterized, which provided direct evidence for the involvement of the [4 + 2] cycloadducts in the reaction pathway. Photoirradiation of **30** under an oxygen atmosphere could convert it into **31**. Structure of the ring-rearranged product **31** was confirmed by X-Ray crystallographic analysis (ESI<sup>†</sup>) and the pathway leading to its formation is proposed in Scheme 7.

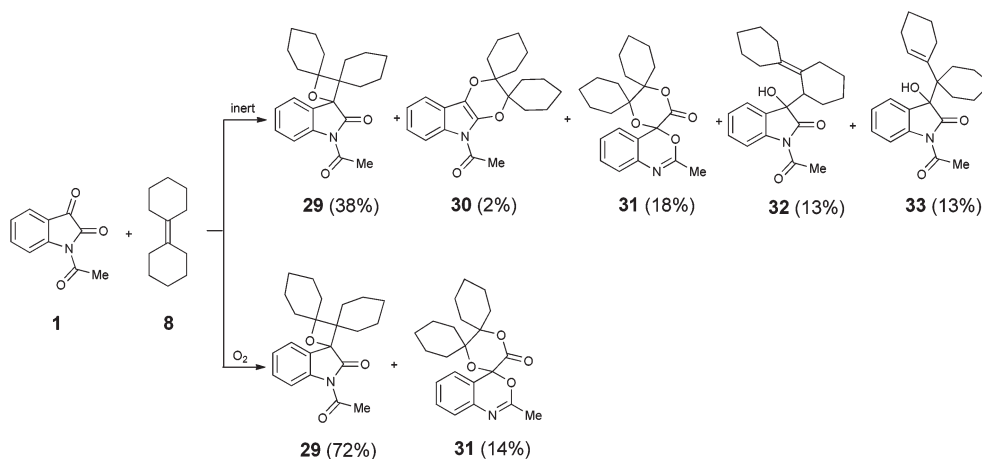
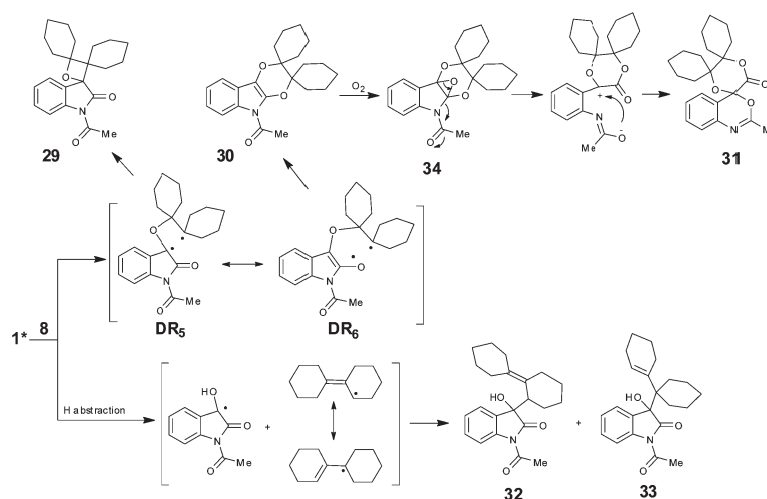
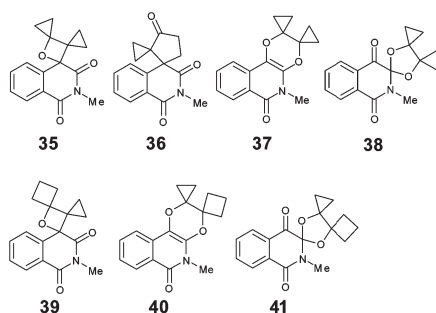
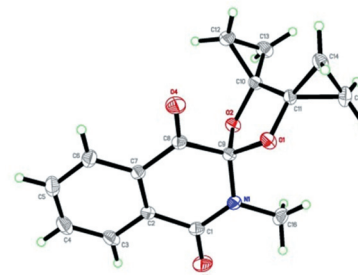
Products **32** and **33** were derived from hydrogen abstraction of **1**\* from the allylic carbon adjacent to the C=C in **8**. The structure of product **32** was confirmed by X-Ray crystallographic analysis (ESI<sup>†</sup>). The formation of hydrogen abstraction products indicated that the two cyclohexyl groups impeded the cycloaddition pathway whilst providing an alternative pathway for consuming the excited **1**. Moreover, photoreaction under an oxygen atmosphere also only gave the spirooxetane **29** and the ring arrangement product **31**.

### Photoreaction of **4** with **5** and **6**

Photoreactions of bicycloalkylidenes with the isoquinolinetrione **4** were then explored. The C4 carbonyl group in **4** has been known as the reactive position for photoreactions with alkynes or oxazoles.<sup>4</sup> As shown in Scheme 8, photolysis of **4** and **5** in acetonitrile under an inert atmosphere gave the spirooxetane **35** and three other minor products **36**, **37** and **38**. Compound **36** was confirmed to be the secondary product of the spirooxetane **35** because photolysis of **35** resulted in the formation of **36**. Product **37** was the [4 + 2] cycloadduct of **4** with **5**. The formation of the spirodioxolane **38** was unexpected since the C4 carbonyl group in **4** remained intact while the less reactive C3 carbonyl group was involved in the reaction. X-Ray crystallographic analysis of **38** confirmed its structure (Fig. 2). The same reaction under an oxygen atmosphere gave **35** and **38** exclusively.

Photolysis of **4** with **6** under an inert atmosphere yielded three products including the spirooxetane **39**, the dioxine **40** and the spirodioxolane **41** (Scheme 8 and Table 3). It was noteworthy that the regioselectivity was high both in the formation of the spirooxetane and in the formation of the dioxine. No regioisomers of **39** or **40** were detected. Moreover, formation of the secondary product of **39** was not observed. Compared with **37**, **40** was more stable and could be purified for characterization. Furthermore, a control experiment using **40** as the substrate for photoirradiation under an oxygen atmosphere resulted in the formation of product **41**.

A mechanism for the photoreactions between **4** and the bicycloalkylidenes is proposed in Scheme 9. The recombination of the 1,4-biradical resulted in the formation of spirooxetanes (**35** or **39**). Further photolysis of **35** resulted in the homolysis of the C–O to give a biradical intermediate with one radical center  $\alpha$  to the cyclopropyl ring. Ring cleavage and biradical recombination give the secondary product **36**. On the other hand, the recombination of the 1,6-biradical led to the formation of the dioxines (**37** or **40**) which could be further photooxidized to give **38** or

Scheme 6 Photoreaction of **1** with **8**.Scheme 7 Proposed pathway for reaction of **1** with **8**.Scheme 8 Photoreaction products of **4** with **5** and **6**.Fig. 2 Crystal structure of compound **38**.

**41** respectively. The mechanism proposed could be well supported by the control experiments described above.

## Conclusions

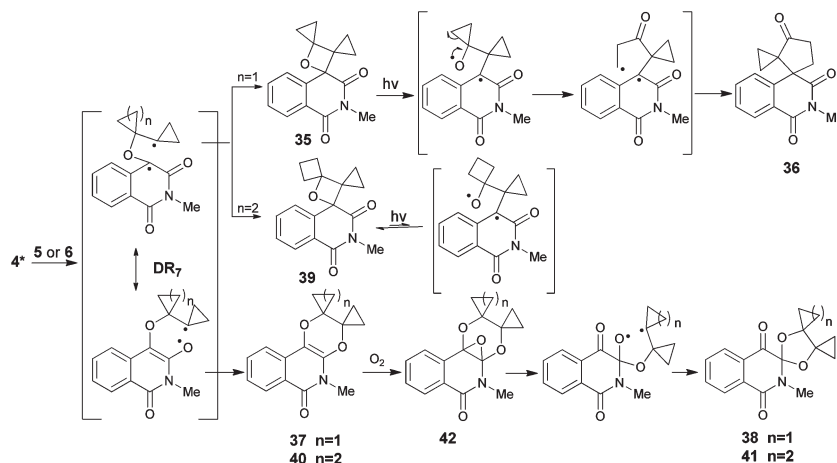
In summary, unusual photoinduced reactions of bicycloalkylidenes **5–8** with isatin **1–3** and isoquinolinetriene **4** have been

reported. Except for the spirooxetane products derived from the conventional Paterno–Büchi reactions of  $C=C$  with  $C=O$ , other unusual products derived from the competitive pathways or secondary reaction of the primary products have been obtained. Photolysis of isatin **1** with the bicycloalkylidenes **5–7** gave  $[4 + 2 + 2]$  cycloadducts and oxoisochroman derivatives other than the spirooxetane products. The presence of oxygen during photolysis favored the formation of oxoisochroman derivatives at



**Table 3** Results of photoreactions of **4** with **5** and **6**

Entry	Bicycloalkylidene	Atmosphere	Products and yields <sup>a</sup>			
			Spirooxetane	Dioxine	Spirodioxolane	Other
1	<b>5</b>	Inert	<b>35</b> (31)	<b>37</b> (18)	<b>38</b> (19)	<b>36</b> (14)
2		O <sub>2</sub>	<b>35</b> (51)	<sup>b</sup>	<b>38</b> (39)	
3	<b>6</b>	Inert	<b>39</b> (39)	<b>40</b> (25)	<b>41</b> (18)	
4		O <sub>2</sub>	<b>39</b> (48)	<sup>b</sup>	<b>41</b> (39)	

<sup>a</sup> Isolated yields. <sup>b</sup> Undetectable.**Scheme 9** Proposed pathway for reaction of **4** with bicycloalkylidenes.

the expense of the [4 + 2 + 2] cycloadducts. Photoreactions of isoquinolinetrione **4** with cyclopropylidenecyclohexanes also proceeded *via* the [2 + 2] and [4 + 2] pathway, leading to spirooxetanes, [4 + 2] cycloadducts and their secondary products. A mechanism leading to different type of products has been proposed and supported by control experiments. These photoreactions not only provided important information on the unusual reactivity of the strained alkenes at their excited states, but also developed a useful approach for the preparation of cyclopropyl annelated heterocyclic compounds which are otherwise difficult to synthesize.

## Experimental

### General procedures for the preparative photolysis of 1,2-dicarbonyl compounds with bicycloalkylidenes

The bicycloalkylidenes were prepared according to reported methods.<sup>5–8</sup> The light source for the photolysis was a medium-pressure mercury lamp (500 W) in a cooling water jacket that was further surrounded by a layer of filter solution (1 cm thick, 20% aqueous sodium nitrite) to cut off light of wavelength shorter than 400 nm. The solution of 1,2-dicarbonyl compounds and an excess amount of bicycloalkylidenes in anhydrous benzene or acetonitrile irradiated with continuous gas (inert gas or oxygen) purging. The reaction course was monitored by TLC. At the end of the reaction, the solvent was removed under reduced pressure and the residue was separated by flash chromatography on a silica gel column.

### Photolysis of **1** with **5** in anhydrous benzene

A solution of **1** (378 mg, 2 mmol) and **5** (320 mg, 4 mmol) in anhydrous benzene (50 mL) was photolyzed with inert gas (oxygen) bubbling for 12 h to reach a complete conversion of **1**. Flash column chromatography on 300–400 mesh silica gel with petroleum ether–ethyl acetate as eluents afforded pure analytical samples of **9–12** (**9** and **12** for oxygen bubbling).

**9**, colorless crystal from acetone–petroleum ether; m.p. 137–139 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.71 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.35 (td, *J* = 7.7, 1.5 Hz, 1H), 7.27 (td, *J* = 7.4, 1.1 Hz, 1H), 2.64 (s, 3H), 1.16–1.07 (m, 1H), 1.02–0.93 (m, 1H), 0.73–0.41 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 175.4, 170.4, 140.6, 131.1, 126.0, 125.9, 125.7, 116.7, 85.2, 73.9, 33.4, 26.5, 8.8, 8.0, 7.0 (2C); IR (KBr) cm<sup>−1</sup>: 2995, 1770, 1701, 1607, 1462, 1171, 1100, 768; MS *m/z* (% base) 269 (M<sup>+</sup>, 9), 241 (6), 227 (47), 199 (40), 171 (100), 143 (26), 115 (21), 90 (9), 43 (68); EA found: C, 71.40; H, 5.79; N, 5.18. Calc. for C<sub>16</sub>H<sub>15</sub>NO<sub>3</sub> C, 71.36; H, 5.61; N, 5.20%.

**10**, the representative diastereoisomer was crystallized from acetone–petroleum ether; m.p. 239–242 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 8.2 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 7.37–7.31 (m, 1H), 7.25–7.19 (m, 1H), 6.93 (t, 1H, *J* = 7.6 Hz), 6.82–6.73 (m, 2H), 6.52 (d, *J* = 7.0 Hz, 1H), 2.73 (s, 3H), 2.43 (s, 3H), 1.75–1.66 (m, 1H), 1.46–1.37 (m, 1H), 0.93–0.80 (m, 2H), 0.63–0.37 (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 171.3, 170.6, 169.8, 144.3, 139.6, 131.3, 131.2, 125.1, 125.0, 124.4, 124.2, 116.8, 116.4, 61.3, 60.3, 26.7, 24.3, 15.0,

12.1, 9.2, 9.0; IR (KBr)  $\text{cm}^{-1}$ : 3021, 1765, 1718, 1686, 1462, 1227, 1172, 935, 761; MS  $m/z$  (% base) 269 (18), 146 (100), 79 (47), 43 (76); **EA** found: C, 67.98; H, 4.90; N, 6.22. Calc. for  $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_6$  C, 68.11; H, 4.84; N, 6.11%.

**11**, white powder; m.p. 217–218 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 (d,  $J$  = 7.4 Hz, 1H), 8.22 (d,  $J$  = 8.1 Hz, 1H), 8.12 (d,  $J$  = 7.1 Hz, 1H), 7.45 (t,  $J$  = 7.8 Hz, 1H), 7.43–7.32 (m, 2 H), 7.05 (d,  $J$  = 7.3 Hz, 1H), 6.97 (d,  $J$  = 7.2 Hz, 1H), 2.40 (s, 3 H), 2.20 (s, 3 H), 1.67–1.60 (m, 1 H), 1.38–1.28 (m, 1 H), 1.00–0.93 (m, 1 H), 0.91–0.82 (m, 1 H), 0.69–0.56 (m, 2 H), 0.48 (dt,  $J$  = 10.9, 6.8 Hz, 1 H), 0.38 (dt,  $J$  = 10.4, 6.5 Hz, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 170.2, 169.5, 146.1, 140.8, 131.8, 131.5, 128.2, 125.1, 124.4, 122.3, 116.9, 116.6, 106.1, 93.5, 60.4, 60.3, 26.2, 24.0, 14.3, 12.5, 8.8, 8.5; MS (ESI)  $m/z$  (%) 459 [ $\text{M} + \text{H}$ ] $^+$ ; **EA** found: C, 68.05; H, 4.88; N, 6.08. Calc. for  $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_6$  C, 68.11; H, 4.84; N, 6.11%.

**12**, colorless crystal from acetone–petroleum ether; m.p. 110–112 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  11.35 (br, 1H), 8.58 (dd,  $J$  = 8.5, 0.7 Hz, 1H), 7.48 (t,  $J$  = 8.2 Hz, 1H), 6.61 (dd,  $J$  = 7.7, 0.6 Hz, 1H), 2.24 (s, 3H), 1.12–1.07 (m, 2H), 1.05–1.00 (m, 2H), 0.96–0.91 (m, 2H), 0.65–0.60 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 168.7, 145.3, 142.7, 135.5, 118.8, 115.7, 111.8, 66.0, 25.8, 22.1, 13.0 (2C), 9.9 (2C); IR (KBr)  $\text{cm}^{-1}$ : 3456, 2927, 1782, 1754, 1718, 1697, 1464, 1373, 1278, 1167, 766; MS  $m/z$  (% base) 257 ( $\text{M}^+$ , 18), 229 (21), 215 (37), 188 (28), 159 (100), 130 (27), 77 (13); **EA** found: C, 70.09; H, 5.80; N, 5.66. Calc. for  $\text{C}_{15}\text{H}_{15}\text{NO}_3$  C, 70.02; H, 5.88; N, 5.44%.

#### Photolysis of **2** with **5** in anhydrous benzene under oxygen atmosphere

A solution of **2** (446 mg, 2 mmol) and **5** (320 mg, 4 mmol) in anhydrous benzene (50 mL) was photolyzed with oxygen bubbling for 12 h to reach a complete conversion of **2**. Flash column chromatography on 300–400 mesh silica gel with petroleum ether–ethyl acetate as eluents afforded pure analytical samples of **15**.

**15**, colorless crystal from acetone–petroleum ether; m.p. 187–189 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d,  $J$  = 7.9 Hz, 1H), 7.31 (t,  $J$  = 8.0 Hz, 1H), 7.23 (d,  $J$  = 8.2 Hz, 1H), 2.67 (s, 3H), 1.12–1.04 (m, 2H), 0.70–0.50 (m, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  174.8, 170.5, 142.1, 133.3, 132.3, 127.1, 122.5, 115.2, 74.5, 31.4, 26.8, 8.8, 8.7, 7.8, 7.6; IR (KBr)  $\text{cm}^{-1}$ : 1770, 1713, 1597, 1443, 1372, 1140, 792; MS  $m/z$  (% base) 303 ( $\text{M}^+$ , 0.04), 261 (9), 233 (38), 205 (100), 43 (83); **EA** found: C, 63.33; H, 4.70; Cl, 11.65; N, 4.66. Calc. for  $\text{C}_{16}\text{H}_{14}\text{ClNO}_3$  C, 63.24; H, 4.65; Cl, 11.67%.

#### Photolysis of **3** with **5** in anhydrous benzene under oxygen atmosphere

A solution of **3** (494 mg, 2 mmol) and **5** (320 mg, 4 mmol) in anhydrous benzene (50 mL) was photolyzed with oxygen bubbling for 12 h to reach a complete conversion of **3**. Flash column chromatography on 300–400 mesh silica gel with petroleum ether–ethyl acetate as eluents afforded pure analytical samples of **16** and **17**.

**16**, colorless crystal from acetone–petroleum ether; m.p. 131–133 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J$  = 7.9 Hz, 1H), 7.67 (d,  $J$  = 8.0 Hz, 1H), 7.35–7.29 (m, 1H), 7.21 (t,  $J$  = 8.0 Hz, 1H), 1.58 (s, 9H), 1.14–1.04 (m, 1H), 0.98–0.88 (m, 1H), 0.65–0.30 (m, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 149.1, 140.2, 130.9, 126.1, 125.6, 124.9, 115.1, 84.3, 73.7, 33.0, 29.7, 28.1 (3C), 8.7, 7.9, 7.0, 6.8; IR (KBr)  $\text{cm}^{-1}$ : 2972, 1799, 1467, 1308, 1146, 750; MS  $m/z$  (% base) 227 (20), 199 (12), 171 (67), 143 (17), 57 (100); **EA** found: C, 69.85; H, 6.53; N, 4.14. Calc. for  $\text{C}_{19}\text{H}_{21}\text{NO}_4$  C, 69.71; H, 6.47; N, 4.28%.

**17**, white powder; m.p. 91–94 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.6 (br, 1H), 8.34 (dd,  $J$  = 8.4, 1.0 Hz, 1H), 7.46 (t,  $J$  = 8.0 Hz, 1H), 6.53 (dd,  $J$  = 7.7, 1.2 Hz, 1H), 1.53 (s, 9H), 1.12–1.07 (m, 2H), 1.06–1.00 (m, 2H), 0.95–0.90 (m, 2H), 0.65–0.60 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 153.1, 145.3, 143.6, 135.2, 117.4, 114.4, 111.4, 80.9, 65.8, 28.5, 22.2, 13.0, 9.9; IR (KBr)  $\text{cm}^{-1}$ : 3266, 1716, 1683, 1584, 1532, 1272, 1245, 1156, 809; MS  $m/z$  (% base) 215 (9), 187 (21), 173 (100), 159 (41), 130 (84), 41 (45); **EA** found: C, 68.58; H, 6.59; N, 4.36. Calc. for  $\text{C}_{18}\text{H}_{21}\text{NO}_4$  C, 68.55; H, 6.71; N, 4.44%.

#### Photolysis of **1** with **6** in anhydrous benzene

A solution of **1** (378 mg, 2 mmol) and **6** (376 mg, 4 mmol) in anhydrous benzene (50 mL) was photolyzed with inert gas (oxygen) bubbling for 4 h (12 h) to reach a complete conversion of **1**. Flash column chromatography on 300–400 mesh silica gel with petroleum ether–ethyl acetate as eluents afforded pure analytical samples of **18–21** (**18**, **19** and **22** for oxygen bubbling).

**18**, colorless crystal from acetone–petroleum ether; m.p. 158–160 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17–8.13 (m, 1H), 7.57–7.53 (m, 1H), 7.37 (td,  $J$  = 7.6, 1.6 Hz, 1H), 7.28 (td,  $J$  = 7.5, 1.0 Hz, 1H), 2.67 (s, 3H), 2.65–2.43 (m, 3H), 2.36–2.29 (m, 1H), 1.79–1.66 (m, 1H), 1.13–1.02 (m, 1H), 0.99–0.80 (m, 2H), 0.57–0.50 (m, 1H), 0.39–0.32 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.3, 170.7, 140.6, 131.2, 126.2, 126.0, 125.8, 116.9, 89.9, 37.1, 35.2, 34.9, 26.7, 11.7, 7.8, 7.6; IR (KBr)  $\text{cm}^{-1}$ : 2972, 1774, 1705, 1466, 1374, 1305, 1170, 756; MS  $m/z$  (% base) 283 ( $\text{M}^+$ , 1.7), 241 (58.8), 213 (41), 185 (76), 171 (61), 146 (66), 43 (100); **EA** found: C, 72.01; H, 6.01; N, 4.93. Calc. for  $\text{C}_{17}\text{H}_{17}\text{NO}_3$  C, 72.07; H, 6.05; N, 4.94%.

**19**, white powder; m.p. 84–87 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (d,  $J$  = 8.2 Hz, 1H), 7.45–7.38 (m, 2H), 7.28–7.22 (m, 1H), 2.66 (s, 3H), 2.62–2.50 (m, 2H), 2.35–2.24 (m, 2H), 1.89–1.76 (m, 1H), 1.41–1.31 (m, 1H), 1.15–1.05 (m, 3H), 0.96–0.91 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 170.6, 141.1, 132.1, 126.0, 125.8, 124.9, 117.2, 84.8, 77.4, 70.7, 34.1, 33.1, 26.7, 13.1, 9.0, 6.9; IR (KBr)  $\text{cm}^{-1}$ : 2925, 1775, 1717, 1464, 1270, 1118, 763; MS  $m/z$  (% base) 201 (4.8), 213 (41.1), 146 (100), 82 (15), 54 (28), 43 (35); **EA** found: C, 72.13; H, 6.08; N, 4.90. Calc. for  $\text{C}_{17}\text{H}_{17}\text{NO}_3$  C, 72.07; H, 6.05; N, 4.94%.

**20**, colorless crystal from acetone–petroleum ether; m.p. 143–146 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J$  = 8.2 Hz, 1H), 8.11 (d,  $J$  = 8.0 Hz, 1H), 7.34–7.28 (m, 1H), 7.22–7.16 (m, 1H), 6.89 (td,  $J$  = 7.5, 0.8 Hz, 1H), 6.77 (td,  $J$  = 7.6, 0.9 Hz, 1H), 6.69 (d,  $J$  = 7.5, 0.8 Hz, 1H), 6.51 (dd,  $J$  = 7.6,

0.8 Hz, 1H), 3.28–3.18 (m, 1H), 3.10–3.00 (m, 1H), 2.71 (s, 3H), 2.56 (s, 3H), 2.27–2.17 (m, 1H), 2.01–1.91 (m, 1H), 1.65–1.52 (m, 2H), 0.98–0.92 (m, 2H), 0.50–0.42 (m, 1H), 0.30–0.22 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  171.2, 170.5, 170.0, 144.5, 139.5, 131.3, 131.1, 125.0, 124.9, 124.8, 124.5, 124.0, 123.6, 116.8, 116.2, 107.3, 87.4, 80.4, 60.3, 35.3, 31.5, 26.7, 24.5, 13.3, 8.6, 8.4; IR (KBr)  $\text{cm}^{-1}$ : 2955, 1778, 1709, 1683, 1462, 1388, 1275, 1241, 1170, 766; MS  $m/z$  (% base) 283 (1.6), 146 (75), 79 (59), 43 (100); EA found: C, 68.67; H, 5.20; N, 5.87. Calc. for  $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_6$  C, 68.63; H, 5.12; N, 5.93%.

**21**, colorless crystal from acetone–petroleum ether; m.p. 123–126 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (d,  $J$  = 8.3 Hz, 1H), 8.18 (d,  $J$  = 7.9 Hz, 1H), 7.91 (d,  $J$  = 7.3 Hz, 1H), 7.45 (t,  $J$  = 7.5 Hz, 1H), 7.38–7.28 (m, 2H), 7.01 (t,  $J$  = 7.3 Hz, 1H), 6.94 (d,  $J$  = 6.9 Hz, 1H), 3.06–3.01 (m, 2H), 2.54 (s, 3H), 2.15–2.11 (m, 5H), 1.77–1.62 (m, 2H), 1.00–0.85 (m, 2H), 0.52–0.40 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 170.0, 169.7, 146.1, 140.5, 131.7, 131.4, 127.9, 125.0, 124.2, 123.8, 122.1, 122.0, 116.9, 116.5, 106.7, 98.4, 87.0, 76.8, 60.7, 34.7, 31.1, 26.0, 24.1, 13.5, 9.0, 8.4; IR (KBr)  $\text{cm}^{-1}$ : 2954, 1768, 1718, 1689, 1462, 1375, 1288, 1240, 1171, 754; MS (ESI)  $m/z$  473  $[\text{M} + \text{H}]^+$ ; EA found: C, 68.77; H, 5.08; N, 5.91. Calc. for  $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_6$  C, 68.63; H, 5.12; N, 5.93%.

**22**, white powder;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  11.27 (br, 1 H), 8.63 (dd,  $J$  = 8.6, 0.9 Hz, 1H), 7.61 (t,  $J$  = 8.0 Hz, 1H), 7.24 (dd,  $J$  = 7.7, 1.0 Hz, 1H), 2.32–2.22 (m, 5 H), 2.17–1.95 (m, 4 H), 1.09–1.04 (m, 2 H), 0.94–0.89 (m, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 168.5, 148.1, 142.6, 135.6, 119.3, 117.6, 109.3, 67.3, 43.0, 29.9, 28.6, 25.7, 15.1, 8.6 (2C); MS (ESI)  $m/z$  (%) 272  $[\text{M} + \text{H}]^+$ ; EA found: C, 70.88; H, 6.23; N, 5.00. Calc. for  $\text{C}_{16}\text{H}_{17}\text{NO}_3$  C, 70.83; H, 6.32; N, 5.16%.

#### Photolysis of **1** with **7** in anhydrous benzene

A solution of **1** (378 mg, 2 mmol) and **7** (488 mg, 4 mmol) in anhydrous benzene (50 mL) was photolyzed with inert gas (oxygen) bubbling for 12 h to reach a complete conversion of **1**. Flash column chromatography on 300–400 mesh silica gel with petroleum ether–ethyl acetate as eluents afforded pure analytical samples of **23**–**26** (**23**, **24** and **27** for oxygen bubbling).

**23**, colorless liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (d,  $J$  = 8.2 Hz, 1H), 7.70 (dd,  $J$  = 7.5, 1.3 Hz, 1H), 7.40 (td,  $J$  = 8.0, 1.5 Hz, 1H), 7.27 (td,  $J$  = 7.5, 1.0 Hz, 1H), 2.69 (s, 3H), 2.47–2.42 (m, 1H), 2.10–2.05 (m, 1H), 1.49–0.69 (m, 12H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.4, 170.5, 139.8, 130.6, 126.1, 125.1, 117.0, 116.6, 87.8, 76.5, 50.4, 31.4, 30.4, 26.6, 25.1, 23.8, 22.5, 7.4, 7.0; IR (KBr)  $\text{cm}^{-1}$ : 2931, 2856, 1774, 1712, 1464, 1371, 1338, 1274, 1169, 1108, 757; MS  $m/z$  (% base) 311 (0.18), 255 (94), 213 (100), 146 (60), 43 (41); EA found: C, 73.38; H, 6.67; N, 4.45. Calc. for  $\text{C}_{19}\text{H}_{21}\text{NO}_3$  C, 73.29; H, 6.80; N, 4.50%.

**24**, colorless liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (d,  $J$  = 8.0 Hz, 1H), 7.47–7.38 (m, 2H), 7.25 (t,  $J$  = 7.5 Hz, 1H), 2.65 (s, 3H), 2.21 (d,  $J$  = 13.6 Hz, 1H), 2.07 (d,  $J$  = 12.8 Hz, 1H), 1.75–1.60 (m, 5H), 1.42–0.87 (m, 6H), 0.72–0.65 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 170.6, 141.1, 131.8, 125.9, 125.4, 124.9, 117.1, 100.9, 83.1, 70.8, 36.2, 33.7, 26.6, 25.6, 22.7, 22.3, 8.9, 6.0; IR (KBr)  $\text{cm}^{-1}$ : 2933, 2860, 1779, 1715, 1466, 1371, 1335, 1268, 1170, 1121, 754; MS  $m/z$  (% base) 310

(15), 85 (27), 43 (84); EA found: C, 73.47; H, 7.06; N, 4.30. Calc. for  $\text{C}_{19}\text{H}_{21}\text{NO}_3$  C, 73.29; H, 6.80; N, 4.50%.

**25**, colorless crystal from acetone–petroleum ether; m.p. 160–162 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (d,  $J$  = 8.2 Hz, 1H), 8.11 (d,  $J$  = 8.3 Hz, 1H), 7.36–7.30 (m, 1H), 7.23–7.17 (m, 1H), 6.90 (td,  $J$  = 7.5, 0.8 Hz, 1H), 6.78 (td,  $J$  = 7.6, 0.9 Hz, 1H), 6.67 (dd,  $J$  = 7.5, 0.7 Hz, 1H), 6.45 (dd,  $J$  = 7.6, 0.7 Hz, 1H), 2.72 (s, 3H), 2.60 (s, 3H), 1.93–1.57 (m, 6H), 1.44–1.13 (m, 3H), 0.90–0.69 (m, 2H), 0.62–0.48 (m, 2H), 0.27–0.20 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  171.6, 170.5, 170.2, 144.6, 139.5, 131.4, 131.2, 124.9, 124.8, 124.7, 124.6, 124.5, 123.6, 116.9, 116.2, 78.7, 62.6, 33.2, 32.9, 26.7, 25.6, 24.5, 21.5, 10.5, 9.4; IR (KBr)  $\text{cm}^{-1}$ : 2932, 1777, 1720, 1684, 1463, 1384, 1269, 1236, 754; MS  $m/z$  (% base) 311 (5), 162 (42), 146 (100), 90 (23), 79 (17), 43 (40); EA found: C, 69.74; H, 5.49; N, 5.61. Calc. for  $\text{C}_{29}\text{H}_{28}\text{N}_2\text{O}_6$  C, 69.59; H, 5.64; N, 5.60%.

**26**, colorless crystal from acetone–petroleum ether; m.p. 150–153 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 (d,  $J$  = 8.4 Hz, 1H), 8.21 (d,  $J$  = 8.1 Hz, 1H), 8.02 (d,  $J$  = 7.7 Hz, 1H), 7.48–7.29 (m, 3H), 7.06–6.95 (m, 2H), 2.57 (s, 3H), 2.17 (s, 3H), 1.92–1.11 (m, 9H), 0.91–0.37 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 170.1, 169.8, 146.0, 140.7, 131.7, 131.4, 128.2, 125.1, 124.2, 124.0, 122.7, 122.2, 117.0, 116.6, 77.3, 62.5, 34.6, 32.8, 26.1, 25.4, 24.2, 21.5, 21.2, 11.2, 9.5; IR (KBr)  $\text{cm}^{-1}$ : 2938, 1768, 1718, 1687, 1462, 1375, 1290, 1235, 756; MS  $m/z$  (% base) 191 (45), 146 (99), 132 (48), 71 (100), 43 (58); EA found: C, 69.59; H, 5.64; N, 5.60. Calc. for  $\text{C}_{29}\text{H}_{28}\text{N}_2\text{O}_6$  C, 69.59; H, 5.64; N, 5.60%.

**27**, colorless liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  11.22 (br, 1 H), 8.60 (dd,  $J$  = 8.5, 1.0 Hz, 1H), 7.53 (t,  $J$  = 8.1 Hz, 1H), 7.29 (dd,  $J$  = 7.9, 0.9 Hz, 1H), 2.23 (s, 3H), 1.88–0.87 (m, 14 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 168.6, 150.0, 142.3, 134.6, 119.8, 119.3, 110.6, 70.1, 38.5, 30.4, 29.9, 25.7, 25.5, 22.8, 9.0; MS (ESI)  $m/z$  300  $[\text{M} + \text{H}]^+$ .

#### Photolysis of **1** with **8** in anhydrous benzene

A solution of **1** (378 mg, 2 mmol) and **8** (656 mg, 4 mmol) in anhydrous benzene (50 mL) was photolyzed with inert gas (oxygen) bubbling for 12 h to reach a complete conversion of **1**. Flash column chromatography on 300–400 mesh silica gel with petroleum ether–ethyl acetate as eluents afforded pure analytical samples of **29**–**33** (**29** and **31** for oxygen bubbling).

**29**, colorless crystal from acetone–petroleum ether; m.p. 241–243 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d,  $J$  = 8.1 Hz, 1H), 7.61 (d,  $J$  = 6.9 Hz, 1H), 7.36 (td,  $J$  = 7.9, 1.3 Hz, 1H), 7.24 (t,  $J$  = 7.6 Hz, 1H), 2.66 (br, 4H), 2.45–2.38 (m, 1H), 2.26–2.09 (m, 2H), 1.73–1.42 (m, 10H), 1.30–1.00 (m, 4H), 0.90–0.77 (m, 2H), 0.30–0.21 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.8, 170.5, 139.7, 130.3, 127.3, 125.9, 125.0, 116.4, 88.1, 52.0, 33.9, 33.2, 29.0, 28.2, 26.6, 25.7, 25.2, 24.2, 22.8, 22.4; IR (KBr)  $\text{cm}^{-1}$ : 2924, 1766, 1712, 1463, 1371, 1274, 1167, 765; MS  $m/z$  (% base) 353 ( $\text{M}^+$ , 13), 191 (56), 163 (75), 149 (53), 81 (100), 67 (86); EA found: C, 74.69; H, 7.58; N, 4.11. Calc. for  $\text{C}_{22}\text{H}_{27}\text{NO}_3$  C, 74.76; H, 7.70; N, 3.96%.

**30**, white powder;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 (dd,  $J$  = 7.3, 1.3 Hz, 1H), 7.39 (dd,  $J$  = 6.9, 1.5 Hz, 1H), 7.26–7.15 (m, 2H), 2.68 (s, 3H), 1.99–1.16 (m, 20H);  $^{13}\text{C}$  NMR (75 MHz,



$\text{CDCl}_3$ )  $\delta$  168.7, 131.9, 128.8, 123.9, 122.8, 122.5, 117.5, 116.6, 114.9, 84.7, 79.4, 25.9, 25.8, 25.6, 21.7, 21.4; MS  $m/z$  (% base) 353 ( $\text{M}^+$ , 19), 191 (57), 163 (91), 149 (100), 81 (96), 67 (85).

**31**, colorless crystal from acetone–petroleum ether; m.p. 141–144 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta$  7.44 (t,  $J = 7.4$  Hz, 1H), 7.29 (t,  $J = 7.1$  Hz, 1H), 7.23 (d,  $J = 8.2$  Hz, 1H), 7.14 (d,  $J = 8.1$  Hz, 1H), 2.34–2.21 (m, 2H), 2.19 (s, 3H), 1.86–1.23 (m, 18H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta$  145.5, 130.4, 126.6, 125.1, 124.3, 78.9, 31.7, 31.6, 31.2, 29.2, 25.1, 24.9, 21.5, 21.2, 20.7, 20.6; IR (KBr)  $\text{cm}^{-1}$ : 3437, 2925, 1772, 1693, 1463, 1379, 1176, 764; MS  $m/z$  (% base) 370 ( $\text{M} - 1^+$ , 0.03), 190 (6), 164 (100), 162 (88), 146 (56), 117 (78), 81 (72); EA found: C, 71.65; H, 7.30; N, 3.74. Calc. for  $\text{C}_{22}\text{H}_{27}\text{NO}_4$  C, 71.52; H, 7.37; N, 3.79%.

**32**, colorless crystal from acetone–petroleum ether; m.p. 101–102 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d,  $J = 8.1$  Hz, 1H), 7.40–7.33 (m, 2H), 7.24 (t,  $J = 7.2$  Hz, 1H), 3.34 (br, 2H), 2.72–2.66 (m, 4H), 2.37–2.14 (m, 5H), 1.82–1.18 (m, 12H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.6, 170.7, 141.0, 140.4, 130.5, 130.0, 125.7, 123.8, 116.4, 78.1, 46.1, 31.6, 31.1, 29.0, 28.9, 27.1, 27.0, 26.7, 25.8, 25.7, 22.5; IR (KBr)  $\text{cm}^{-1}$ : 3481, 2929, 1748, 1721, 1461, 1368, 1270, 1168, 760; MS  $m/z$  (% base) 353 ( $\text{M}^+$ , 1), 335 (18), 292 (27), 162 (55), 146 (78), 119 (96), 91 (100); EA found: C, 74.69; H, 7.57; N, 4.08. Calc. for  $\text{C}_{22}\text{H}_{27}\text{NO}_3$  C, 74.76; H, 7.70; N, 3.96%.

**33**, colorless crystal from acetone–petroleum ether; m.p. 151–153 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J = 8.1$  Hz, 1H), 7.38–7.28 (m, 2H), 7.16 (t,  $J = 7.6$  Hz, 1H), 3.04 (br, 1H), 2.54 (s, 3H), 2.32–2.28 (m, 1H), 2.04–1.07 (m, 18H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  179.9, 170.1, 140.1, 129.8, 129.1, 127.8, 125.6, 124.6, 116.3, 81.2, 51.1, 27.0, 26.4, 26.3, 26.0, 25.8, 23.4, 22.0; IR (KBr)  $\text{cm}^{-1}$ : 3457, 2925, 1748, 1712, 1463, 1370, 1267, 1172, 763; MS  $m/z$  (% base) 353 ( $\text{M}^+$ , 1), 335 (18), 292 (27), 163 (100), 146 (29), 95 (76), 81 (71); EA found: C, 74.85; H, 7.63; N, 4.00. Calc. for  $\text{C}_{22}\text{H}_{27}\text{NO}_3$  C, 74.76; H, 7.70; N, 3.96%.

#### Photolysis of 4 with 5 in anhydrous acetonitrile

A solution of **4** (378 mg, 2 mmol) and **5** (320 mg, 4 mmol) in anhydrous acetonitrile (50 mL) was photolyzed with inert gas (oxygen) bubbling for 12 h to reach a complete conversion of **4**. Flash column chromatography on 300–400 mesh silica gel with petroleum ether–ethyl acetate as eluents afforded pure analytical samples of **35**, **36** and **38**. An impure sample of **37** was obtained. (**35** and **38** for oxygen bubbling).

**35**, colorless crystal from acetone–petroleum ether; m.p. 145–146 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (dd,  $J = 7.9, 0.5$  Hz, 1 H), 8.07 (d,  $J = 7.8$  Hz, 1 H), 7.77 (td,  $J = 7.8, 1.2$  Hz, 1 H), 7.52 (td,  $J = 8.0, 1.1$  Hz, 1 H), 3.37 (s, 3 H), 1.33–1.23 (m, 1 H), 1.13–1.03 (m, 1 H), 0.67–0.30 (m, 5 H), 0.05–0.03 (m, 1 H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 164.0, 138.3, 134.6, 129.3, 128.5, 126.8, 124.4, 73.3, 39.3, 27.3, 8.8, 7.8, 7.7, 7.3; MS  $m/z$  (% base) 269 (0.3), 241 (7.2), 146 (25.2), 104 (68), 76 (71.8); EA found: C, 71.37; H, 5.55; N, 5.25. Calc. for  $\text{C}_{16}\text{H}_{15}\text{NO}_3$  C, 71.36; H, 5.61; N, 5.20%.

**36**, colorless crystal from acetone–petroleum ether; m.p. 163–164 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (dd,  $J =$

8.0, 1.3 Hz, 1 H), 7.69 (td,  $J = 7.9, 1.4$  Hz, 1 H), 7.47 (td,  $J = 7.6, 1.0$  Hz, 1 H), 7.40 (d,  $J = 7.8$  Hz, 1 H), 3.36 (s, 3 H), 3.20 (dt,  $J = 18.3, 10.2$  Hz, 1 H), 2.92–2.82 (m, 1 H), 2.68 (qd,  $J = 9.7, 2.4$  Hz, 1 H), 2.51 (dt,  $J = 13.3, 10.0$  Hz, 1 H), 1.42–1.34 (m, 1 H), 1.23–1.26 (m, 1 H), 0.61–0.53 (m, 1 H), 0.49–0.42 (m, 1 H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  216.1, 776.8, 164.3, 140.6, 134.0, 129.1, 128.2 (2C), 125.4, 53.5, 40.9, 37.1, 36.2, 27.2, 21.0, 16.2; MS  $m/z$  (% base) 241 (100), 213 (36), 128 (13.6); EA found: C, 71.44; H, 5.69; N, 5.10. Calc. for  $\text{C}_{16}\text{H}_{15}\text{NO}_3$  C, 71.36; H, 5.61; N, 5.20%.

**38**, colorless crystal from acetone–petroleum ether; m.p. 100–102 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (d,  $J = 7.7$  Hz, 1 H), 8.04 (dd,  $J = 7.8, 1.0$  Hz, 1 H), 7.77 (td,  $J = 7.6, 1.4$  Hz, 1 H), 7.68 (td,  $J = 7.5, 1.1$  Hz, 1 H), 3.24 (s, 3 H), 1.18–1.02 (m, 4 H), 0.63–0.46 (m, 4 H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  186.1, 162.5, 135.3, 133.1, 131.4, 129.4, 128.9, 126.6, 106.8, 67.1 (2C), 27.5, 8.3 (2C), 7.3 (2C); MS  $m/z$  (% base) 285 (12.1), 187 (37.6), 104 (38.5), 68 (100); EA found: C, 67.33; H, 5.37; N, 4.74. Calc. for  $\text{C}_{16}\text{H}_{15}\text{NO}_4$  C, 7.36; H, 5.30; N, 4.91%.

#### Photolysis of 4 with 6 in anhydrous acetonitrile

A solution of **4** (378 mg, 2 mmol) and **6** (376 mg, 4 mmol) in anhydrous acetonitrile (50 mL) was photolyzed with inert gas (oxygen) bubbling for 12 h to reach a complete conversion of **4**. Flash column chromatography with chloroform as eluent afforded pure analytical samples of **39–41**. (**39** and **41** for oxygen bubbling).

**39**, colorless crystal from acetone–petroleum ether; m.p. 135–137 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 8.0$  Hz, 1H), 7.85 (d,  $J = 7.7$  Hz, 1H), 7.71 (t,  $J = 7.4$  Hz, 1H), 7.48 (t,  $J = 7.5$  Hz, 1H), 3.32 (s, 3H), 2.74 (dd,  $J = 22.3, 10.2$  Hz, 1H), 2.57 (dd,  $J = 21.9, 10.4$  Hz, 1H), 2.50–2.42 (m, 1H), 2.29–2.23 (m, 1H), 1.79–1.67 (m, 1H), 1.09–0.93 (m, 1H), 0.81–0.73 (m, 1H), 0.66–0.58 (m, 1H), 0.51–0.43 (m, 1H), –0.02–0.10 (m, 1H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 164.0, 138.6, 134.5, 129.1, 128.4, 126.5, 124.3, 89.4, 83.5, 42.8, 35.4, 34.7, 27.2, 11.9, 8.2, 7.7; MS  $m/z$  (% base) 282 (6.1), 227 (100), 213 (41.5), 170 (30.0), 128 (91.7); EA found: C, 72.13; H, 5.97; N, 4.98. Calc. for  $\text{C}_{17}\text{H}_{17}\text{NO}_3$  C, 72.07; H, 6.05; N, 4.94%.

**40**, straw yellow powder;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 (d,  $J = 7.7$  Hz, 1H), 7.58 (d,  $J = 3.9$  Hz, 2H), 7.34–7.28 (m, 1H), 3.58 (s, 3H), 2.43–2.32 (m, 2H), 2.20–2.11 (m, 2H), 2.08–1.94 (m, 1H), 1.78–1.62 (m, 1H), 1.14–1.09 (m, 2H), 0.97–0.92 (m, 2H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  160.2, 132.2, 131.6, 128.2, 124.4, 120.8, 118.7, 81.5, 60.8, 31.6 (2C), 31.1, 28.1, 12.9, 9.1 (2C); MS  $m/z$  (% base) 283 (13.9), 215 (100), 190 (10.8), 104 (11.0), 79 (67.0); EA found: C, 71.88; H, 6.03; N, 5.00. Calc. for  $\text{C}_{17}\text{H}_{17}\text{NO}_3$  C, 72.07; H, 6.05; N, 4.94%.

**41**, white powder; m.p. 89–90 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (dd,  $J = 7.6, 0.8$  Hz, 1H), 8.01 (dd,  $J = 7.6, 1.1$  Hz, 1H), 7.77 (td,  $J = 7.6, 1.4$  Hz, 1H), 7.67 (td,  $J = 7.5, 1.1$  Hz, 1H), 3.15 (s, 3H), 2.67–2.51 (m, 2H), 2.33–2.20 (m, 2H), 1.84–1.71 (m, 1H), 1.33–1.18 (m, 1H), 1.06–0.97 (m, 3H), 0.90–0.84 (m, 1H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  186.9, 162.5, 135.3, 133.0, 131.56, 129.5, 128.9, 126.6, 107.1, 84.6, 70.7, 33.9, 33.6, 27.3, 12.8, 9.3, 7.2; MS  $m/z$  (% base) 190 (0.7), 161 (59.7), 104 (100), 76 (61.6).

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