

# Visible-Light-Induced Di- $\pi$ -Methane Rearrangement of Dibenzobarrelene Derivatives

Julika Schlosser,<sup>[a]</sup> Radek Cibulka,<sup>[b]</sup> Philipp Groß,<sup>[a]</sup> Heiko Ihmels,<sup>\*[a]</sup> and Christian J. Mohrschladt<sup>[c]</sup>

It is demonstrated that the di- $\pi$ -methane (DPM) rearrangement of carbonyl-substituted dibenzobarrelene (9,10-dihydro-9,10-ethenoanthracene) derivatives is induced by visible-light-induced triplet photosensitization with Ir(ppy)<sub>3</sub>, Ir(dFppy)<sub>3</sub> or 1-

butyl-7,8-dimethoxy-3-methylalloxazine as catalysts, whereas derivatives that lack carbonyl substituents are photoinert under these conditions. Notably, the products are formed almost quantitatively.

## 1. Introduction

The investigation and exploitation of reactions that are induced with visible-light are presently among the most topical research areas in organic chemistry.<sup>[1]</sup> As visible light is easily accessed with simple equipment, specifically commercially available domestic appliance LED lamps, or even provided by daylight, it offers a convenient stimulus to induce an organic reaction. At the same time, UV light is absorbed by several different functionalities and therefore might cause unwanted side reactions and secondary reactions in multiply functionalized substrates that do not occur upon exposure to visible light. Therefore, photocatalysts have been established that absorb efficiently in the visible range and that have the ability to induce a reaction from their excited state by an electron or energy transfer with the substrate.<sup>[1]</sup> With this method in hand, several efficient and highly selective photocatalyzed reactions have been discovered and developed that can be performed by application of visible light, most of which have been known only as ground-state reactions, so far. In addition, established photoreactions, that used to be induced by UV light, have been improved by photocatalysis with visible light. For example, the well-established photodimerization reaction of alkenes to give the synthetically useful cyclobutane products was significantly

optimized by using tailor-made photocatalysts.<sup>[2]</sup> In this context, it is interesting to note that the combination of visible-light photocatalysis with the di- $\pi$ -methane (DPM) rearrangement (Zimmerman rearrangement)<sup>[3]</sup> has been neglected so far,<sup>[4]</sup> although this photoreaction is an established and very useful tool in organic synthesis, especially for the construction of complex structures in one reaction step.<sup>[3e,f,5]</sup> Moreover, this reaction has attracted also considerable attention with regard to theoretical aspects of photoreactions.<sup>[6]</sup> It is therefore desirable to be able to perform this versatile photoreaction under milder conditions with visible light. To this end, we started to investigate the propensity of the DPM rearrangement to be photocatalyzed under visible-light irradiation. As a model reaction, the DPM rearrangement of dibenzobarrelene to dibenzosemibullvalene was chosen (Scheme 1), because this particular reaction is already well investigated,<sup>[7]</sup> thus allowing good comparison with the UV light-induced reaction, and because substrates with a broad variation of substitution pattern are available. Moreover, the photoreactivity of dibenzobarrelene derivatives is multiplicity-dependent. Upon direct irradiation, the parent compound **1a** reacts from the first excited singlet state to give dibenzocyclooctatetraenes, whereas triplet sensitization leads to the formation of the dibenzose-

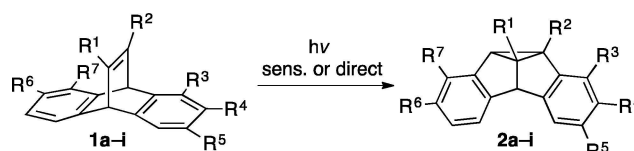
[a] J. Schlosser, P. Groß, Prof. Dr. H. Ihmels  
Department of Chemistry-Biology  
University of Siegen  
Adolf-Reichwein-Str. 2, 57068 Siegen (Germany)  
E-mail: ihmels@chemie.uni-siegen.de

[b] Prof. Dr. R. Cibulka  
Department of Organic Chemistry  
University of Chemistry and Technology, Prague  
Technická 5, 16628 Prague (Czech Republic)

[c] Dr. C. J. Mohrschladt  
Institute of Organic Chemistry  
University of Würzburg  
Am Hubland 2, 97074 Würzburg (Germany)

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cptc.201900221>

© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA.  
This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.



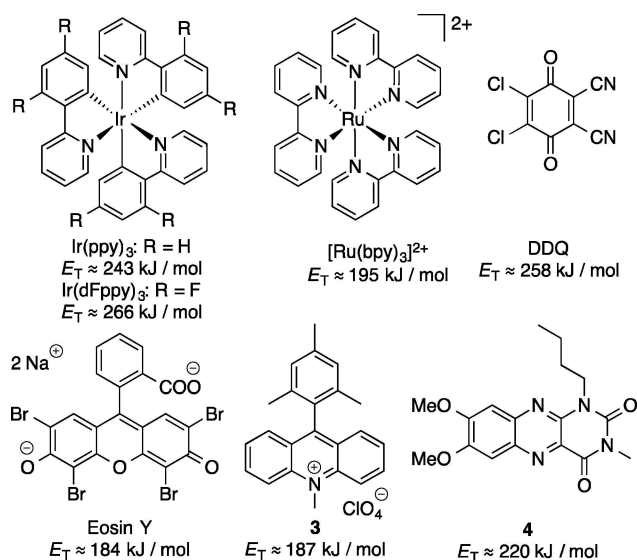
- a: R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = R<sup>6</sup> = R<sup>7</sup> = H (sens.)  
b: R<sup>1</sup> = R<sup>2</sup> = CH<sub>2</sub>OH, R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = R<sup>6</sup> = R<sup>7</sup> = H (sens.)  
c: R<sup>1</sup> = R<sup>2</sup> = CH<sub>2</sub>NEt<sub>2</sub>, R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = R<sup>6</sup> = R<sup>7</sup> = H (sens.)  
d: R<sup>1</sup> = R<sup>2</sup> = CO<sub>2</sub>Me, R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = R<sup>6</sup> = R<sup>7</sup> = H (direct)  
e: R<sup>1</sup> = CHO, R<sup>2</sup> = CH<sub>3</sub>, R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = R<sup>6</sup> = R<sup>7</sup> = H (direct)  
f: R<sup>1</sup> = R<sup>2</sup> = R<sup>5</sup> = CO<sub>2</sub>Me, R<sup>3</sup> = R<sup>4</sup> = R<sup>6</sup> = R<sup>7</sup> = H (direct)  
g: R<sup>1</sup> = R<sup>2</sup> = R<sup>5</sup> = CO<sub>2</sub>Me, R<sup>6</sup> = OMe, R<sup>3</sup> = R<sup>4</sup> = R<sup>7</sup> = H (direct)  
h: R<sup>1</sup> = R<sup>2</sup> = CO<sub>2</sub>Me, R<sup>3</sup>-R<sup>4</sup> = -(C<sub>4</sub>H<sub>4</sub>)-, R<sup>5</sup> = R<sup>6</sup> = R<sup>7</sup> = H (direct)  
i: R<sup>1</sup> = R<sup>2</sup> = CO<sub>2</sub>Me, R<sup>3</sup>-R<sup>4</sup> = R<sup>6</sup>-R<sup>7</sup> = -(C<sub>4</sub>H<sub>4</sub>)-, R<sup>5</sup> = H (direct)

**Scheme 1.** Di- $\pi$ -methane rearrangement of dibenzobarrelene derivatives **1a-i** (sens. = triplet sensitized; in **2e-i** only one possible regioisomer shown).

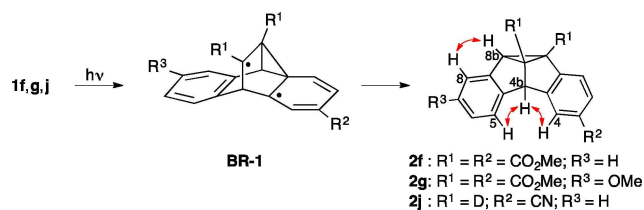
tribullvalene **2a** in a DPM rearrangement (Scheme 1). The latter may also be induced by direct irradiation if the dibenzobarrelene chromophore carries carbonyl substituents, such as in derivative **2d** (Scheme 1). With this in mind, we submitted a selection of dibenzobarrelene derivatives **1a–i** to visible-light irradiation in the presence of established photocatalysts, namely Ir(ppy)<sub>3</sub>,<sup>[8]</sup> Ir(dFppy)<sub>3</sub>,<sup>[9]</sup> [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>,<sup>[10]</sup> DDQ, eosin Y,<sup>[11]</sup> 9-mesityl-10-methylacridinium (**3**, “Fukuzumi dye”)<sup>[12]</sup> and the flavin derivative **4**<sup>[13]</sup> (Figure 1). Based on these experiments, we demonstrate herein that indeed the DPM rearrangement of particular dibenzobarrelene derivatives may be photocatalyzed with visible light; and we will discuss the scope and limits of this type of reaction.

## 2. Results and Discussion

The known dibenzobarrelene derivatives **1a–e** and the additionally annelated barrelene derivatives **1h–i** were available according to literature protocols.<sup>[14]</sup> The unknown derivatives **1f** and **1g** were synthesized in 83% and 72% yield, respectively, by the Diels-Alder reaction of the corresponding anthracene derivatives<sup>[15]</sup> with dimethyl acetylene dicarboxylate. As the dibenzobarrelene derivatives **1f** and **1g** were not known, so



**Figure 1.** Structures and triplet energies,  $E_T$ , of photocatalysts used in this study (data taken from Refs. [1a], [1b], [2a] and [13b]).



**Scheme 2.** Di- $\pi$ -methane rearrangement of dibenzobarrelene derivatives **1f**, **g**, **j**; red arrows indicate NOE contacts in photoproducts **1f**, **g**, **j** as determined by ROESY NMR experiments.

far, their photoreactivity upon direct irradiation was firstly investigated. Thus, upon irradiation ( $\lambda > 280$  nm) of the derivatives **1f** and **1g** in benzene solution, the photoproducts **2f** and **2g** were formed almost exclusively (>90%), as shown by <sup>1</sup>H-NMR spectroscopic analysis of the reaction mixtures (Scheme 2). However, small amounts of the other regioisomers were formed as well, which could not be separated, so that the photoproducts **2f** and **2g** could not be obtained as pure samples. Their structural assignment is based on the NMR-spectroscopic data, especially the NOE effects between the protons 4b-H and 4-H, 4b-H and 5-H, and 8b-H and 8-H as determined by ROESY NMR spectroscopy (Scheme 2; see also the Supporting Information). These highly regioselective DPM reactions are in agreement with results from Zimmerman et al.<sup>[3d]</sup> who have shown that the irradiation of dibenzobarrelene **1j** leads to the selective formation of the biradical intermediate **BR1** and subsequent reaction to the dibenzosemibullvalene **2j**. This remarkable regioselectivity has been rationalized in terms of a selective stabilization of one of the four conceivable biradicals, i.e. **BR1**, by the electron-accepting substituent on the benzene rings. Thus, the stabilization of the intermediate cyclohexadienyl radical moiety in **BR1** is most efficient with the acceptor function in the *meta* position relative to the radical center leading to the formation of products **1f**, **g**, **j**. It is important to note that the methoxy substituent cannot compete with the stabilization of the acceptor under these conditions, because even in the case of substrate **1g** the photoproduct **2g** is selectively formed in favor of the other possible regioisomeric semibullvalene products.

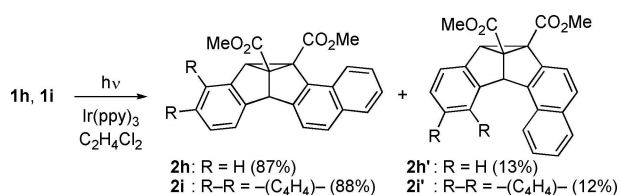
The results of the visible light-induced reactions of the different dibenzobarrelene derivatives **1a–i** are summarized in Table 1 (see also the Supporting Information). If not stated otherwise the samples were irradiated with a commercially available household appliance LED lamp with emission bands from ca. 489–750 ( $\lambda_{\text{max}} = 577$  nm) and 410–470 nm (weaker band,  $\lambda_{\text{max}} = 420$  nm, see Supporting Information for emission profile). As the dibenzobarrelene substrates as well as the dibenzosemibullvalene photoproducts were already known and fully characterized by NMR spectroscopy (except for **2d**, **e**, see above), the product mixtures were analyzed by <sup>1</sup>H-NMR spectroscopy and comparison with authentic samples or literature data. The parent dibenzobarrelene **1a** was irradiated with visible-light LED for 22 h in the presence of Ir(ppy)<sub>3</sub>, *fac*-[Ir(dFppy)<sub>3</sub>], in 1,2-dichloroethane solution, respectively, or the flavin catalyst **4** in 1,2-dichloroethane or acetonitrile solution. The latter irradiation was also performed with a 420 nm LED source. In all these cases, only a very small (<1%) or no conversion of the substrate to the dibenzosemibullvalene **2a** was observed (Table 1, entries 1–4). Likewise, the hydroxymethyl- and aminomethyl-substituted derivatives **1b** and **1c** were photoinert upon irradiation with visible light in the presence of Ir(ppy)<sub>3</sub> or *fac*-[Ir(dFppy)<sub>3</sub>]. In contrast, the photoinduced DPM-rearrangement of the carbonyl-substituted dibenzobarrelene derivatives **1d–i** to the products **2d–i** was catalyzed by Ir(ppy)<sub>3</sub> in dichloroethane solution, as clearly shown by the development of the characteristic <sup>1</sup>H NMR shifts of the methine protons at the semibullvalene unit (see also the Supporting Informa-

Entry	Substrate	t [h]	Catalyst [mol%] <sup>[a]</sup>	Conversion <sup>[b]</sup>	Product <sup>[c]</sup>
1	1a	22	Ir(ppy) <sub>3</sub> (4)	< 3%	–
2	1a	22	Ir(dFppy) <sub>3</sub> (5)	< 3%	–
3	1a	22	4 (4)	< 3%	–
4	1b	48	Ir(ppy) <sub>3</sub> (3)	< 3%	–
5	1b	45	Ir(dFppy) <sub>3</sub> (3)	< 3%	–
6	1b	46	Ir(dFppy) <sub>3</sub> (3) <sup>[d]</sup>	< 3%	–
7	1c	48	Ir(ppy) <sub>3</sub> (5)	< 3%	–
8	1d	24	Ir(ppy) <sub>3</sub> (3)	> 97%	2d
9	1d	22	Ir(dFppy) <sub>3</sub> (3)	> 97%	2d
10	1d	48	4 (3)	21%	2d
11	1d	24	4 (3) <sup>[d]</sup>	76%	2d
11	1d	22	4 (3) <sup>[d,e]</sup>	> 97%	2d
13	1d	48	DDQ (3)	< 3%	–
14	1d	48	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> (3)	< 3%	–
15	1d	48	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> , NEt(iPr) <sub>2</sub> (2)	< 3%	–
16	1d	48	Eosin Y (2)	< 3%	–
17	1d	48	3 (3)	< 3%	–
18	1d	24	no catalyst	< 3%	–
19	1e	120	Ir(ppy) <sub>3</sub> (5)	> 97%	2e
20	1f	95	Ir(ppy) <sub>3</sub> (3)	95%	2f
21	1g	96	Ir(ppy) <sub>3</sub> (2)	95%	2g
22	1h	23	Ir(ppy) <sub>3</sub> (3)	> 97%	2h/2h' 87:13
23	1i	46	Ir(ppy) <sub>3</sub> (3)	> 97%	2i/2i' 88:12

[a] Unless stated otherwise: in 1,2-dichloroethane solution, irradiation with broadband LED (489–750 nm, λ<sub>max</sub> = 577 nm; and 410–470 nm, λ<sub>max</sub> = 420 nm). [b] The conversion was determined by integration of <sup>1</sup>H NMR signals, estimated error: ± 3% of given value. [c] The product ratios were determined by integration of <sup>1</sup>H NMR signals of bridgehead protons, error: ± 3% of given value. [d] In CH<sub>3</sub>CN. [e] Irradiation with 420 nm.

tion). Depending on the substrate, the conversions were complete (> 97%) after irradiation times of 24 h (1d), 120 h (1e), 95 h (1f), 96 h (1g), 23 h (1h), and 46 h (1i). Notably, with the substrates 1e–i, that may result different regioisomeric products in the DPM rearrangement, the same products and product ratios were obtained as with direct irradiation with UV light. Thus, the photoreaction of 1e–1g in the presence of Ir(ppy)<sub>3</sub> gave also the products 2e–2g with the same high regioselectivity as the direct irradiation (Schemes 1 and 2). Similarly, the photocatalyzed DPM rearrangement of the naphtho-annulated barrelene derivatives 1h and 1i gave mixtures of the regioisomers 2h/2h' and 2i/2i' in a ratio of 87:13 and 88:12 (Scheme 3), that essentially match the reported ones for direct irradiation (88:12).<sup>[14c]</sup>

To demonstrate that a catalyst is needed in order to induce the photoreactions with the LED light, solutions of the dibenzobarrelenes 1d, 1e and 1h were exemplarily irradiated



Scheme 3. Regioselective di- $\pi$ -methane rearrangement of dibenzobarrelene derivatives 1h and 1i.

in the absence of the catalyst. In the case of 1d and 1h, the formation of the corresponding dibenzosemibullvalenes was not observed; however, with substrate 1e small amounts (< 3%) of the semibullvalene 2d were detected after 120 h of irradiation.

The diester-substituted dibenzobarrelene 1d was chosen for further examination of the reaction conditions, because the photochemical behavior of this type of substrate has been investigated already in much detail so that sufficient reference data is available from the literature.<sup>[16]</sup> The reactions were performed in dichloroethane as this solvent has been reported to be suitable for photocatalyzed reactions of alkene derivatives. In other solvents such as acetonitrile, the photoreactions were significantly slower. Furthermore, the irradiation of the dibenzobarrelene 1d with visible light in the presence of other commonly employed photocatalysts, namely DDQ, Eosin Y, acridinium 3 or [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> – the latter in the absence or presence of Hünig's base as cocatalyst –, did not induce the formation of the dibenzobarrelene 2d even at long irradiation times. In contrast, with the flavin derivative 4 as catalyst, the photoreaction of 1d gave the dibenzobarrelene 2d with 21% conversion in dichloroethane solution and with 76% conversion in acetonitrile solution after 24 h of visible-light irradiation. On irradiation with a 420 nm LED the flavin-catalyzed reaction was complete (> 95%) after 24 h. Furthermore, it was shown exemplarily with derivative 2d that the photocatalyzed reaction with Ir(ppy)<sub>3</sub> as catalyst can be performed in preparative scale (100 mg substrate, 81% yield).

Overall, our results indicate that the DPM rearrangement of dibenzobarrelene derivatives, that carry at least one carbonyl functionality at the etheno bridge, may be conducted with visible-light irradiation from LED sources. In contrast, dibenzobarrelene derivatives that lack this functionality, namely 1a–c, are photoinert under these conditions. To explain this different behavior of dibenzobarrelene derivatives and to clarify the mechanism of the observed photoreactions, some general trends from the experimental results shall be accentuated and interpreted.

The employed catalysts may induce a photoreaction through an initial electron transfer between the excited catalyst and the substrate or through triplet-sensitization. But based on our results with the representative substrate 1d, an electron-transfer reaction can be excluded because the DPM rearrangement of this compound, like the parent compound, is not induced by those catalysts that are known to generate intermediate radical ions upon photoinduced electron transfer process, such as DDQ [ $E^0(\text{DDQ}^*/\text{DDQ}^-) \approx 3.1 \text{ V}$ ], 3 [ $E^0(3^{+*}/3^-) \approx 2.9 \text{ V}$ ], Eosin Y [ $E^0(\text{EY}^*/\text{EY}^-) \approx 0.8 \text{ V}$ ], and [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> [ $E^0(\text{Ru II}^*/\text{Ru III}) \approx -0.8 \text{ V}$ ;  $E^0(\text{Ru II}^*/\text{Ru I}) = +0.77 \text{ V}$ ].<sup>[1c]</sup> In contrast, the catalysts Ir(ppy)<sub>3</sub> [ $E^0(\text{Ir III}^*/\text{Ir IV}) \approx -1.7 \text{ V}$ ], Ir(dFppy)<sub>3</sub> [ $E^0(\text{Ir III}^*/\text{Ir IV}) \approx -1.4 \text{ V}$ ]<sup>[9]</sup> and flavin 4 [ $E^0(4^*/4^-) \approx 1.0 \text{ V}$ ,  $E^0(4^*/4^+) = -0.6 \text{ V}$ ],<sup>[13b]</sup> that have been shown already to be efficient photosensitizers for olefins, e.g. in [2 + 2] photocycloadditions or E–Z isomerizations, also turned out to sensitize the DPM rearrangement of dibenzobarrelene 1d. Although the catalysts Ir(ppy)<sub>3</sub> ( $E_T = 243 \text{ kJ/mol}$ ), 4 ( $E_T = 220 \text{ kJ/mol}$ ) and Ir(dFppy)<sub>3</sub> ( $E_T = 266 \text{ kJ/mol}$ ; Figure 1), have somewhat lower triplet ener-

gies,  $E_T$ , than those sensitizers that are commonly applied for UV-light induced DPM rearrangements, i.e. benzophenone ( $E_T = 287$  kJ/mol) or thioxanthen-9-one ( $E_T = 265$  kJ/mol), they are apparently still able to act as triplet sensitizer for this reaction, indicating a triplet energy of **1d** in this energy range. In contrast, triplet energies below 200 kJ/mol as in [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> ( $E_T = 195$  kJ/mol), Eosin Y ( $E_T = 184$  kJ/mol), and **3** ( $E_T = 187$  kJ/mol; Figure 1) are obviously too low for an efficient triplet-triplet energy transfer with dibenzobarrelene derivatives, which is in agreement with the observation that these reagents do not catalyze the DPM rearrangement.

Along the same lines, the photoreluctance of the dibenzobarrelene derivatives **1a–c** is also consistent with a triplet-photosensitization pathway. Although the triplet energies of the dibenzobarrelene derivatives **1a** and **1d** have not been reported, it is well known that acceptor substituents at a given chromophore lower the triplet energies.<sup>[17]</sup> Therefore, it is proposed that the dibenzobarrelene derivatives without acceptor substituent, **1a–c**, have significantly higher triplet energies than the ones with ester or formyl substituents, **1e–i**, so that a triplet-sensitization with the catalysts Ir(ppy)<sub>3</sub>, Ir(dFppy)<sub>3</sub> and the flavin **4** is energetically not favorable. This proposal is consistent with the observation that the DPM rearrangement of **1a** is not sensitized by thioxanthen-9-one ( $E_T = 265$  kJ/mol), either under otherwise identical conditions (see Table S1 in the Supporting Information). Moreover, these results parallel recent findings on the flavin-catalyzed [2+2] photocycloaddition of different aromatic diene derivatives.<sup>[18]</sup> In that study, it has been shown that the [2+2] photocycloaddition could not be accomplished with simple dienes, such as 1-phenylpropene, whereas the lowering of the triplet-energy of the substrates by electron-acceptor substituents at the diene highly facilitated the photoreaction.

Most notably, the Ir(ppy)<sub>3</sub>-photosensitized DPM rearrangement of the derivatives **1e–i** resulted in the same regioselective formation of products as their triplet photoreactions induced by direct irradiation with UV light (Table 1, entries 19–23). This regioselectivity of the DPM rearrangement is commonly explained by the selective stabilization of the initially formed cyclopropyldicarbonyl (1,4-biradical), as exemplarily shown with **BR1** (Scheme 2). Therefore, the same regioselectivities under different irradiation conditions indicate that the same intermediates are formed in photocatalysis as with direct irradiation, which also supports a common triplet-sensitized DPM rearrangement of dibenzobarrelene derivatives in the presence of the Ir(ppy)<sub>3</sub>, [Ir(dFppy)<sub>3</sub>] and the flavin catalyst **4**.

### 3. Conclusions

In summary, we have demonstrated that the DPM rearrangement of dibenzobarrelene derivatives may be induced by visible-light-induced triplet photosensitization, as long as the substrate is acceptor-substituted. Notably, the products are formed almost quantitatively. Considering the usefulness and importance of the DPM rearrangement as well as the oxa- and aza-DPM rearrangement in organic synthesis we propose that

the application of visible-light catalysts may constitute a reasonable alternative to perform these reactions under milder conditions and with fewer side and secondary reactions.

## Experimental Section

### General Instrumentations and Materials

<sup>1</sup>H NMR and <sup>13</sup>C NMR: Bruker AC 200 (<sup>1</sup>H NMR: 200 MHz; <sup>13</sup>C NMR: 50.3 MHz); Bruker Advance 400 (NOESY <sup>1</sup>H NMR: 400 MHz); Jeol ECZ 500 (<sup>1</sup>H NMR: 500 MHz), or Bruker DMX 600 (ROESY <sup>1</sup>H NMR: 600 MHz). <sup>1</sup>H and <sup>13</sup>C chemical shifts refer to  $\delta_{TMS} = 0.0$ . Chemical shifts are given in ppm relative to the residual signal of the solvent (CDCl<sub>3</sub>:  $\delta_H = 7.27$  ppm, benzene-*d*<sub>6</sub>:  $\delta_H = 7.16$  ppm). The signals of quat. C, CH, CH<sub>2</sub> and CH<sub>3</sub> were assigned with the DEPT pulse sequence. Melting points were determined with a Büchi B545 melting point apparatus and are not corrected. The photoreactions were carried out in a home-built LED-reactor. UV: Hitachi U-3200 spectrophotometer; spectra were taken from solutions in spectral grade solvents. MS: Finnigan MAT 8200 for electron impact ionization (70 eV); Finnigan MAT 90 for high-resolution MS. Melting points: Büchi B-545. Elemental analyses were performed by Mr. C. P. Kneis, University of Würzburg Preparative photoreactions were performed with a high-pressure mercury lamp (150 W, Heraeus TQ 150) at room temp. (ca. 20 °C); the sample was placed ca. 5 cm in front of the cooling mantle of the light source. A cut-off filter (Schott WG 280;  $\lambda > 280$  nm) was placed between the lamp and the sample. Solutions were purged with argon for at least 0.5 h prior to irradiation.

Commercially available reagents were used without further purification unless stated otherwise. Chemicals were obtained from the following companies: Alfa Aesar GmbH & Co. KG (Karlsruhe, D); DDQ, Eosin Y, [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> × 6 H<sub>2</sub>O, Merck KGaA (Darmstadt, D); 9-Mesityl-10-methylacridinium perchlorate, Ir(ppy)<sub>3</sub>, Anhydrous methanol was obtained by stirring over Mg chips (11 g/L) and I<sub>2</sub> (0.71 g/L) under reflux for 2 h. The solvent was removed by decantation and subsequently distilled under reduced pressure. Methanol was stored over molecular sieves (3 Å). DMSO was distilled from CaH<sub>2</sub> (10 g/L) under reduced pressure (76 °C, 16 mbar). K<sub>2</sub>CO<sub>3</sub> was dried in a desiccator over CaCl<sub>2</sub>.

### Synthesis

#### General Procedure (GP1) for the Synthesis of Dibenzobarrelene Derivatives

Under argon-gas atmosphere, a stirred mixture of the corresponding anthracene derivative and dimethyl acetylenedicarboxylate was slowly heated to 230 °C for 30 min. After cooling to room temperature, the resulting reaction mixture was purified by column chromatography and the product was further recrystallized from an appropriate solvent.

#### Trimethyl-6-methoxy-9,10-dihydro-9,10-ethenoanthracene-2,11,12-tricarboxylate (**1g**)

According to the *General Procedure (GP1)*, methyl 6-methoxyanthracene-2-carboxylate (125 mg, 0.47 mmol) and dimethyl acetylenedicarboxylate (115 mg, 0.81 mmol) were allowed to react and purified by chromatography (SiO<sub>2</sub>, *n*-hexane/ethyl acetate 3:1,  $R_f = 0.21$ ) and subsequent crystallization from methanol to give **1g** as colorless solid (140 mg, 0.34 mmol, 72%), mp 71–74 °C. – UV

(hexane):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ) = 234 (4.46), 275 (3.62), 295 (3.48); (CH<sub>3</sub>CN): 234 (4.46), 294 (3.47). – <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  = 3.74 (s, 3 H, OCH<sub>3</sub>), 3.78 (s, 3 H, OCH<sub>3</sub>), 3.79 (s, 3 H, OCH<sub>3</sub>), 3.87 (s, 3 H, OCH<sub>3</sub>), 5.46 (s, 1 H, CH), 5.49 (s, 1 H, CH), 6.53 (dd,  $J$  = 8 Hz,  $J$  = 2 Hz, 1 H, Ar–H), 7.01 (d,  $J$  = 2 Hz, 1 H, Ar–H), 7.27 (d,  $J$  = 8 Hz, 1 H, Ar–H), 7.43 (d,  $J$  = 8 Hz, 1 H, Ar–H), 7.76 (dd,  $J$  = 8 Hz,  $J$  = 2 Hz, 1 H, Ar–H), 8.01 (d,  $J$  = 2 Hz, 1 H, Ar–H). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  = 51.5 (CH), 52.1 (CH<sub>3</sub>), 52.3 (CH), 52.4 (CH<sub>3</sub>), 52.5 (CH<sub>3</sub>), 55.4 (CH<sub>3</sub>), 109.7 (CH), 111.4 (CH), 123.6 (CH), 124.2 (CH), 124.4 (CH), 127.4 (C<sub>q</sub>), 127.5 (CH), 135.1 (C<sub>q</sub>), 144.4 (C<sub>q</sub>), 144.5 (C<sub>q</sub>), 145.4 (C<sub>q</sub>), 147.8 (C<sub>q</sub>), 148.6 (C<sub>q</sub>), 157.6 (C<sub>q</sub>), 165.4 (C<sub>q</sub>), 165.7 (C<sub>q</sub>), 166.7 (C<sub>q</sub>). – MS (EI, 70 eV);  $m/z$  (%): 408 (79) [M<sup>+</sup>], 349 (100). – El. Anal. C<sub>23</sub>H<sub>20</sub>O<sub>7</sub> (408.4) calcd C: 67.64, H: 4.94; found C: 67.19, H: 5.00.

#### Trimethyl-9,10-dihydro-9,10-ethenoanthracene-2,11,12-tricarboxylate (1f)

According to the *General Procedure (GP1)*, methyl anthracene-2-carboxylate (54.0 mg, 0.23 mmol) and dimethyl acetylenedicarboxylate (100 mg, 0.70 mmol) were allowed to react and purified by chromatography (SiO<sub>2</sub>, *n*-hexane/ethyl acetate 3:1,  $R_f$  = 0.28) and subsequent crystallization from methanol to give **1f** as colorless solid (71.0 mg, 0.19 mmol, 83%), mp 138–140 °C. – UV (MeOH):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ) = 221 (4.52), 254 (3.97); (hexane): 221 (4.54), 251 (3.96); (CH<sub>3</sub>CN): 222 (4.52), 253 (3.94). – <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  = 3.78 (s, 3 H, OCH<sub>3</sub>), 3.79 (s, 3 H, OCH<sub>3</sub>), 3.86 (s, 3 H, OCH<sub>3</sub>), 5.55 (s, 1 H, CH), 5.55 (s, 1 H, CH), 7.03, 7.40 (AA'BB' System, 4 H, Ar–H), 7.44 (d,  $J$  = 8 Hz, 1 H, Ar–H), 7.76 (dd,  $J$  = 8 Hz,  $J$  = 2 Hz, 1 H, Ar–H), 8.04 (d,  $J$  = 2 Hz, 1 H, Ar–H). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  = 52.1 (CH), 52.1 (CH), 52.3 (CH<sub>3</sub>), 52.5 (CH<sub>3</sub>), 123.7 (CH), 124.0 (CH), 124.1 (CH), 124.6 (CH), 125.7 (CH), 125.8 (CH), 127.4 (C<sub>q</sub>), 127.7 (CH), 142.7 (C<sub>q</sub>), 143.1 (C<sub>q</sub>), 144.1 (C<sub>q</sub>), 146.1 (C<sub>q</sub>), 147.1 (C<sub>q</sub>), 148.8 (C<sub>q</sub>), 165.6 (C<sub>q</sub>), 165.7 (C<sub>q</sub>), 166.7 (C<sub>q</sub>). – MS (EI, 70 eV);  $m/z$  (%): 408 (79) [M<sup>+</sup>], 349 (100). – El. Anal. C<sub>22</sub>H<sub>18</sub>O<sub>6</sub> · 0.5H<sub>2</sub>O (387.4) calcd C: 68.21, H: 4.94; found C: 68.59, H: 4.60.

#### Trimethyl-4b,8b-dihydro-7-methoxy-dibenzo[a,f]cyclopropa[c,d]pentalen-3,8c,8e-tricarboxylate (2g)

A solution of **1g** (75.0 mg, 0.18 mmol) in benzene (10 ml) was irradiated at  $\lambda > 320$  nm for 5 h at 20 °C. The solvent was removed in vacuo and the remaining residue was submitted to column chromatography (SiO<sub>2</sub>, *n*-hexane/ethyl acetate 2:1,  $R_f$  = 0.29) to give product **2g** (66.0 mg, 0.16 mmol, 89%) as colorless solid. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  = 3.11 (s, 3 H, OCH<sub>3</sub>), 3.26 (s, 3 H, OCH<sub>3</sub>), 3.44 (s, 3 H, OCH<sub>3</sub>), 3.50 (s, 3 H, OCH<sub>3</sub>), 4.64 (s, 1 H, 8b-H), 4.92 (s, 1 H, 4b-H), 6.46 (dd,  $J$  = 8.3 Hz,  $J$  = 3 Hz, 1 H, Ar–H), 6.59 (d,  $J$  = 3 Hz, 1 H, Ar–H), 6.65 (d,  $J$  = 8 Hz, 1 H, Ar–H), 7.21 (d,  $J$  = 8 Hz, 1 H, Ar–H), 7.85 (dd,  $J$  = 8 Hz,  $J$  = 2 Hz, 1 H, Ar–H), 7.93–7.95 (m, 1 H, Ar–H). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  = 49.7 (CH), 52.1 (OCH<sub>3</sub>), 52.4 (OCH<sub>3</sub>), 52.9 (OCH<sub>3</sub>), 55.5 (CH), 57.2 (C<sub>q</sub>), 68.1 (C<sub>q</sub>), 121.5 (CH), 122.6 (CH), 125.5 (CH), 125.9 (CH), 127.2 (CH), 127.9 (CH), 128.6 (CH), 129.8 (C<sub>q</sub>), 134.4 (C<sub>q</sub>), 138.5 (C<sub>q</sub>), 149.5 (C<sub>q</sub>), 150.1 (C<sub>q</sub>), 166.7 (C<sub>q</sub>), 168.0 (C<sub>q</sub>), 169.0 (C<sub>q</sub>).

#### Trimethyl-4b,8b-dihydro-dibenzo[a,f]cyclopropa[c,d]pentalen-3,8c,8e-tricarboxylate (2f)

A solution of **1f** (95.0 mg, 0.25 mmol) in benzene (5 ml) was irradiated at  $\lambda > 280$  nm for 11 h at 20 °C. The solvent was removed in vacuo and the remaining residue was submitted to column chromatography (SiO<sub>2</sub>, *n*-hexane/ethyl acetate 5:2,  $R_f$  = 0.41) to give product **2f** (38.0 mg, 0.10 mmol, 40%) as colorless solid. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  = 3.29 (s, 3 H, OCH<sub>3</sub>), 3.44 (s, 3 H, OCH<sub>3</sub>), 3.50 (s, 3 H, OCH<sub>3</sub>), 4.67 (s, 1 H, 8b-H), 4.95 (s, 1 H, 4b-H), 6.76–6.82

(m, 3 H, Ar–H), 6.97 (dd,  $J$  = 7 Hz,  $J$  = 1 Hz, 1 H, Ar–H), 7.18 (d,  $J$  = 8 Hz, 1 H, Ar–H), 7.80 (dd,  $J$  = 8 Hz,  $J$  = 2 Hz, 1 H, Ar–H), 7.91 (d,  $J$  = 2 Hz, 1 H, Ar–H). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  = 49.8 (CH), 52.1 (OCH<sub>3</sub>), 52.4 (OCH<sub>3</sub>), 52.9 (OCH<sub>3</sub>), 54.7 (CH), 55.3 (OCH<sub>3</sub>), 57.0 (C<sub>q</sub>), 66.4 (C<sub>q</sub>), 111.3 (CH), 113.6 (CH), 122.1 (CH), 122.3 (CH), 125.9 (CH), 128.4 (CH), 129.7 (C<sub>q</sub>), 135.6 (C<sub>q</sub>), 138.4 (C<sub>q</sub>), 141.7 (C<sub>q</sub>), 150.5 (C<sub>q</sub>), 159.4 (C<sub>q</sub>), 166.7 (C<sub>q</sub>), 168.0 (C<sub>q</sub>), 169.0 (C<sub>q</sub>). – MS (EI, 70 eV);  $m/z$  (%): 408 (53) [M<sup>+</sup>], 349 (100).

#### General Procedure (GP2) for Photoreactions with Visible Light

In a Duran test tube equipped with a rubber septum a solution ( $c = 5.0 \times 10^{-3}$  mol/L) of the dibenzobarrelene and the catalyst in dichloroethane or acetonitrile was bubbled with argon gas for 30 min. The solution was irradiated with visible light LED (see the Supporting Information for emission profile). After the irradiation the solvent was evaporated and the residue was analyzed by <sup>1</sup>H-NMR spectroscopy (500 MHz). The signals for the catalysts were not detected due to the low amounts that were used. The <sup>1</sup>H-NMR spectra were analyzed by comparison with literature data or with authentic samples.

#### Synthesis of Dimethyl-4b,8c-dihydro-dibenzo[a,f]cyclopropa[c,d]pentalen-8b,8e-dicarboxylate (2d) on a Preparative Scale

According to the *General Procedure (GP2)*, a solution of **1d** (100 mg, 0.31 mmol) and Ir(ppy)<sub>3</sub> (5.1 mg, 7.8  $\mu$ mol) in dichloroethane (62 mL) was irradiated for 72 h. The solvent was removed in vacuo and the remaining residue was submitted to column chromatography (SiO<sub>2</sub>, *n*-hexane/ethyl acetate, 3:2,  $R_f$  = 0.9) to give product **2d** (81.5 mg, 0.25 mmol, 81%) as colorless highly viscous oil.

#### Acknowledgements

This work was generously supported by the University of Siegen and the University of Würzburg. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank Mr. Rouven Kreienmeier for technical assistance.

#### Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** dibenzosemibullvalenes · di- $\pi$ -methane rearrangement · ethenoanthracenes · photocatalysis · photosensitization

- [1] a) Q.-Q. Zhou, Y.-Q. Zou, L.-Q. Lu, W.-J. Xiao, *Angew. Chem.* **2019**, *131*, 1600–1619; b) F. Strieth-Kalthoff, M. J. James, M. Teders, L. Pitzer, F. Glorius, *Chem. Soc. Rev.* **2018**, *47*, 7190–7202; c) L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem.* **2018**, *130*, 10188–10228; d) B. Qiao, Z. Jiang, *ChemPhotoChem* **2018**, *2*, 703–714; e) *Visible Light Photocatalysis in Organic Chemistry*, (Eds.: C. R. J. Stephenson, T. P. Yoon, D. W. C. MacMillan) Wiley-VCH, Weinheim, **2018**; f) O. Boubertakh, J.-P. Goddard, *Eur. J. Org. Chem.* **2017**, 2072–2084; g) D. Menigaux, P. Belmont, E. Brachet, *Eur. J. Org. Chem.* **2017**, 2008–2055; h) S. Roslin, L. R. Odell, *Eur. J. Org. Chem.* **2017**, 1993–2007; i) D. Ravelli, S. Protti, M. Fagnoni, *Chem. Rev.* **2016**, *116*, 9850–9913; j) M. Oelgemöller, *Chem. Rev.* **2016**, *116*, 9664–9682; k) S. P. Pitre, C. D. McTiernan, J. C. Scaiano, *Acc. Chem. Res.*

- 2016, 49, 1320–1330; l) R. A. Angnes, Z. Li, C. R. D. Correia, G. B. Hammond, *Org. Biomol. Chem.* **2015**, 13, 9152–9167.
- [2] a) T. P. Yoon, *ACS Catal.* **2013**, 3, 895–902; b) T. P. Yoon, *Acc. Chem. Res.* **2016**, 49, 2307–2315; c) J. Du, T. P. Yoon, *J. Am. Chem. Soc.* **2009**, 131, 14604–14605; d) M. Riener, D. A. Nicewicz, *Chem. Sci.* **2013**, 4, 2625–2629; e) A. E. Hurtley, Z. Lu, T. P. Yoon, *Angew. Chem.* **2014**, 126, 9137–9140; f) Z. Lu, T. P. Yoon, *Angew. Chem.* **2012**, 124, 10475–10478; g) N. Vallavoju, S. Selvakumar, B. C. Pemberton, S. Jockusch, M. P. Sibi, J. Sivaguru, *Angew. Chem.* **2016**, 128, 5536–5541; h) T. R. Blum, Z. D. Miller, D. M. Bates, I. A. Guzei, T. P. Yoon, *Science* **2016**, 354, 1391–1395; i) Z. D. Miller, B. J. Lee, T. P. Yoon, *Angew. Chem.* **2017**, 129, 12053–12057; j) X. Huang, T. R. Quinn, K. Harms, R. D. Webster, L. Zhang, O. Wiest, E. Meggers, *J. Am. Chem. Soc.* **2017**, 139, 9120–9123; k) S. K. Pagire, A. Hossain, L. Traub, S. Kerres, O. Reiser, *Chem. Commun.* **2017**, 53, 12072–12075; l) J. Zhao, J. L. Brosmer, Q. Tang, Z. Yang, K. N. Houk, P. L. Diaconescu, O. Kwon, *J. Am. Chem. Soc.* **2017**, 139, 9807–9810; m) C. Wang, Z. Lu, *Org. Lett.* **2017**, 19, 5888–5891; n) T. Lei, C. Zhou, M.-Y. Huang, L.-M. Zhao, B. Yang, C. Ye, H. Xiao, Q.-Y. Meng, V. Ramamurthy, C.-H. Tung, L.-Z. Wu, *Angew. Chem.* **2017**, 129, 15609–15612; o) R. Martínez-Haya, L. Marzo, B. König, *Chem. Commun.*, **2018**, 54, 11602–11605; p) F. M. Hörmann, T. S. Chung, E. Rodríguez, M. Jakob, T. Bach, *Angew. Chem.* **2018**, 130, 835–839; q) L.-M. Mohr, T. Bach, *Synlett* **2017**, 28, 2946–2950; r) R. Alonso, T. Bach, *Angew. Chem.* **2014**, 126, 4457–4460; s) T. R. Blum, Z. D. Miller, D. M. Bates, I. A. Guzei, T. P. Yoon, *Science* **2016**, 354, 1391–1395; t) M. Jirásek, K. Straková, T. Neveselý, E. Svobodová, Z. Rottnerová, R. Cibulka, *Eur. J. Org. Chem.* **2017**, 2139–2146; u) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, 116, 10075–10166.
- [3] a) H. E. Zimmerman, G. L. Grunewald, *J. Am. Chem. Soc.* **1966**, 88, 183–184; b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, M. A. Sherwin, *J. Am. Chem. Soc.* **1967**, 89, 3932–3933; c) S. S. Hixson, P. S. Mariano, H. E. Zimmerman, *Chem. Rev.* **1973**, 73, 531–551; d) H. E. Zimmerman, H. M. Sulzbach, M. B. Tollefson, *J. Am. Chem. Soc.* **1993**, 115, 6548–6556; e) H. E. Zimmerman, D. Armesto, *Chem. Rev.* **1996**, 96, 3065–3112; f) D. Armesto, M. J. Ortiz, A. R. Agarrabeitia in *Molecular and Supramolecular Photochemistry, Vol. 12* (Eds.: A. Griebbeck, J. Mattay), Marcel Dekker, New York, **2005**, pp 161–181.
- [4] For visible-light-induced DPM rearrangements, see: a) A. Tröster, A. Bauer, C. Jandl, T. Bach, *Angew. Chem.* **2019**, 131, 3576–3579; b) A. Sygula, R. Sygula, P. W. Rabideau, *Tetrahedron Lett.* **2005**, 46, 1189–1192.
- [5] D. Ramaiah, M. C. Sajimon, J. Joseph, M. V. George, *Chem. Soc. Rev.* **2005**, 34, 48–57.
- [6] a) R. A. Matute, P. Pérez, E. Chamorro, N. Villegas-Escobar, D. Cortés-Arriagada, B. Herrera, S. Gutiérrez-Oliva, A. Toro-Labbé, *J. Org. Chem.* **2018**, 83, 5969–5974; b) X. Li, T. Liao, L. Wa Chung, *J. Am. Chem. Soc.* **2017**, 139, 16438–16441; c) R. A. Matute, M. A. Garcia-Garibay, K. N. Houk, *Org. Lett.* **2014**, 16, 5232–5234; d) Z. Zuo, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2014**, 136, 5257–5260; e) R. A. Matute, K. N. Houk, *Angew. Chem.* **2012**, 124, 13274–13277.
- [7] a) J. R. Scheffer, J. Yang in *CRC Handbook of Organic Photochemistry and Photobiology, Vol. 1* (Eds.: W. M. Horspool, P.-S. Song), CRC Press, New York, **1995**, pp. 204–221; b) J. Chen, J. R. Scheffer, J. Trotter, *Tetrahedron* **1992**, 48, 3251–3274; c) W. Adam, O. De Lucchi, K. Peters, E.-M. Peters, H. G. von Schnering, *J. Am. Chem. Soc.* **1982**, 104, 5747–5753; d) H. E. Zimmerman, H. M. Sulzbach, M. B. Tollefson, *J. Am. Chem. Soc.* **1993**, 115, 6548–6556.
- [8] H.-W. Shih, M. N. Vander Wal, R. L. Grange, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2010**, 132, 13600–13603.
- [9] Z. Zuo, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2014**, 136, 5257–5260.
- [10] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, 113, 5322–5363.
- [11] D. P. Hari, B. König, *Chem. Commun.* **2014**, 50, 6688–6699.
- [12] S. Fukuzumi, K. Ohkubo, *Chem. Sci.* **2013**, 4, 561–574.
- [13] a) V. Mojir, E. Svobodová, K. Straková, T. Neveselý, J. Chudoba, H. Dvořáková, R. Cibulka, *Chem. Commun.* **2015**, 51, 12036–12039; b) V. Mojir, G. Pitrová, K. Straková, D. Prukala, S. Brazevic, E. Svobodová, I. Hoskovcová, G. Burdzinski, T. Slanina, M. Sikorski, R. Cibulka, *ChemCatChem* **2018**, 10, 849–858.
- [14] a) H. P. Figeys, A. Dralants, *Tetrahedron* **1972**, 28, 3031–3036; b) M. Benitez, G. Bringmann, M. Dreyer, H. Garcia, H. Ihmels, M. Waidelich, K. Wissel, *J. Org. Chem.* **2005**, 70, 2315–2321; c) J. Luo, H. Ihmels, H.-J. Deiseroth, M. Schlosser, *Can. J. Chem.* **2009**, 87, 619–626; d) A. Anantanarayan, H. Hart, *J. Org. Chem.* **1991**, 56, 991–996.
- [15] a) H. Ihmels, *Eur. J. Org. Chem.* **1999**, 1595–1600; b) F. A. McCormick, D. J. Marquardt, *Tetrahedron Lett.* **1994**, 35, 5169–5172.
- [16] a) C. V. Kumar, B. A. R. C. Murty, S. Lahiri, E. Chackachery, J. C. Scaiano, M. V. George, *J. Org. Chem.* **1984**, 49, 4923–4929; b) C. V. Asokan, S. A. Kumar, S. Das, N. P. Rath, M. V. George, *J. Org. Chem.* **1991**, 56, 5890–5893; c) P. R. Pokkuri, J. R. Scheffer, J. Trotter, *J. Am. Chem. Soc.* **1990**, 112, 3676–3677; d) J. Chen, J. R. Scheffer, J. Trotter, *Tetrahedron* **1992**, 48, 3251–3274; e) M. C. Sajimon, D. Ramaiah, C. H. Suresh, W. Adam, F. D. Lewis, M. V. George, *J. Am. Chem. Soc.* **2007**, 129, 9439–9445.
- [17] a) Z.-P. Lin, W. A. Aue, *Spectrochim. Acta Part A* **1999**, 56, 111–117; b) Y. Ito, H. Nishimura, Y. Umehara, Y. Yamada, M. Tone, T. Matsuura, *J. Am. Chem. Soc.* **1983**, 105, 1590–1597.
- [18] J. Špačková, E. Svobodová, T. Hartman, I. Stibor, J. Kopecká, J. Cibulková, J. Chudoba, R. Cibulka, *ChemCatChem* **2017**, 9, 1177–1181.

---

 Manuscript received: September 3, 2019

Revised manuscript received: October 26, 2019

Accepted manuscript online: October 28, 2019

Version of record online: November 12, 2019