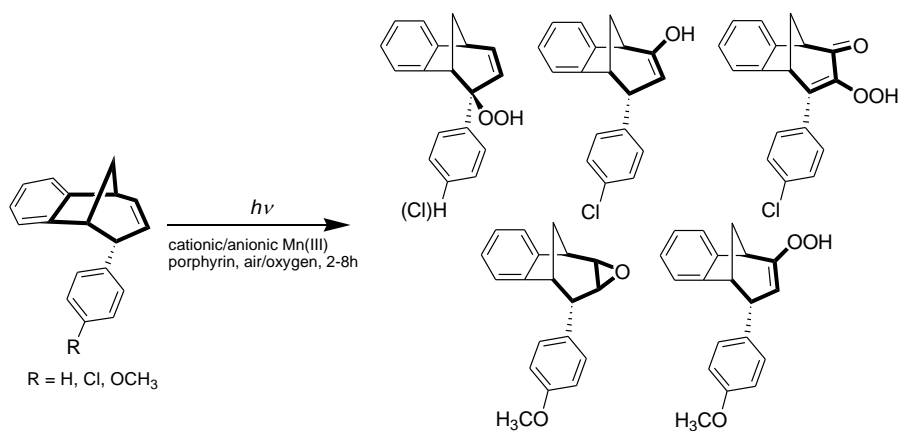1

Functionalization of the benzobicyclo[3.2.1]octadiene skeleton possessing one isolated double bond *via* photocatalytic oxygenation

Dragana Vuk,[a] Ottó Horváth,[b,**] Željko Marinić,[c] Irena Škorić[a,*]

Graphical abstract

---

[*]Corresponding authors. Tel.: +385-1-4597-281; fax: +385-1-4597-260 (I. Škorić), tel.: +36-88-624-159; fax: +36-88-624-548 (O. Horváth)

Functionalization of the benzobicyclo[3.2.1]octadiene skeleton possessing one isolated double bond *via* photocatalytic oxygenation

Dragana Vuk,[a] Ottó Horváth,[b,**] Željko Marinić,[c] Irena Škorić[a,*]

[a]Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10 000 Zagreb, Croatia,
[b]Department of General and Inorganic Chemistry, Institute of Chemistry, Faculty of Engineering, University of Pannonia, P.O.B. 158, Veszprém H-8201, Hungary,
[c]NMR Center, Rudjer Bošković Institute, Bijenička cesta 54, 10 000 Zagreb, Croatia

Abstract

Photocatalytic oxygenation of three phenyl derivatives of a bicyclic skeleton with a free double bond **1a**, **1b** and **1c** were carried out by utilizing a cationic and an anionic manganese(III) porphyrin irradiated in the visible range. While photocatalysis of **1a** and **1b** led to the formation of the corresponding hydroperoxy derivatives **2** and **3**, respectively, (besides unidentified high-molecular-weight products) in the presence of the anionic Mn(III) porphyrin, the cationic photocatalyst proved to be less efficient and less selective with **1a**. In the case of **1b**, also with the cationic porphyrin, the corresponding hydroperoxy derivative (**3**) was the main product at a shorter reaction time (2h), whereas a longer irradiation (4h) led to the significant formation of a keto derivative (**5**) with a hydroperoxy substituent and a free double bond at positions deviating from those in the previous products (**2** and **3**). A dramatic change in the reactivity was observed for the methoxy derivative (**1c**). It gave only traces of identifiable products by using the anionic photocatalyst, while application of the cationic Mn(III) porphyrin resulted in a relatively efficient formation of an epoxy derivative (**6**) due to the reaction of the isolated double bond.

Keywords: benzobicyclo[3.2.1]octadienes, butadiene derivatives, photooxygenation products, spectroscopy, porphyrins

Introduction

Earlier studies[1,2,3] on photocatalytic oxygenations involved reactions of fused furan and thiophene bicyclo[3.2.1]octadiene derivatives with different positions of oxygen or sulfur in the heteroaromatic ring. The results of these experiments showed that the type of the heteroatom and its position in the heteroaromatic ring significantly affect the behavior of these heterocyclic compounds, offering possibilities for preparation of new functionalized bicyclic derivatives. Such oxygenated compounds may have potential bioactivity or may possess the structure of some natural products.

*Corresponding authors. Tel.: +385-1-4597-281; fax: +385-1-4597-260 (I. Škorić), tel.: +36-88-624-159; fax: +36-88-624-548 (O. Horváth)

For photocatalytic oxygenation of various organic compounds, free-base and metalloporphyrins proved to be efficient catalysts. Thus, cycloalkenes[4,5,6] and some unsaturated heteroaromatics[7] were successfully functionalized in these reactions. While free-base porphyrins can be utilized as sensitizers for the generation of singlet oxygen,[7,8,9,10,11] water-soluble metalloporphyrins can offer a wider profile of reaction mechanisms, depending on their charge, the solvent, and the substrate to be oxygenated. Cationic manganese(III) porphyrins proved to be efficient for photocatalytic oxygenation of α-pinene. In aqueous systems, at relatively low substrate: catalyst ratio (S/C = 500) its selective epoxidation took place, considerably deviating from the case of aprotic organic solvents such as benzene or toluene, where allylic hydroxylation products were formed.[4] Anionic and cationic manganese(III) porphyrins were utilized for photocatalytic oxygenation of furan and thiophene derivatives of bicyclo[3.2.1]octadiene structures in acetone/water system.[1,2,3] For a given substrate, the product(s) strongly depended on the charge of the catalyst.

Continuing our study on this field, in order to expand the scope of the research on photocatalytic oxygenation reaction, we have chosen a new bicyclic structure, which possess, for the first time in such investigations, a free double bond in the bicyclic ring.[12,13,14] Three phenyl derivates, 9-phenyl-, 9-(4-chlorophenyl-, and 9-(4-methoxyphenyl)-tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,10-tetraene (**1a**, **1b**, and **1c**, respectively) have been involved in our study: without any substituent (**1a**), containing a chloro (**1b**) or a methoxy substituent (**1c**) in *para* position. Similarly to our earlier experiments, both anionic and cationic manganese(III) porphyrins Mn(III)TSPP^{3-} and Mn(III)TMPyP^{5+}, where H$_2$TSPP^{4-} = 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin and H$_2$TMPyP^{4+} = 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin) were applied in order to study the charge effect, beside the influence of the substituent on the phenyl ring.

Results

The starting compounds **1a-c** were easily synthesized in one step by photochemical ring closure from the corresponding *o*-vinyl-1,4-diphenylbutadienyl derivatives. The proposed mechanism for the formation of the starting substrates involves intramolecular cycloaddition *via* biradical intermediate followed by preferred 1,6-ring closure and subsequent 1,3-H shift.[13] Bicyclic derivatives **1a-c** were obtained as the main products (55-80 % isolated yield) of these reactions.

Photocatalytic oxygenation reactions have been performed in air- or oxygen-saturated acetone/water (50/50%) mixture in the presence of a Mn(III)TMPyP^{5+} or Mn(III)TSPP^{3-} as photocatalysts. In order to obtain the best yield of the isolated products, the reaction time was varied from 2h to 16h, combined with changing the charge of the photocatalyst and the concentration of oxygen.

The most characteristic results obtained under various conditions are demonstrated by Schemes 1, 2, and 3, regarding **1a**, **1b**, and **1c**, respectively. These clearly indicate that the nature of the substituent can drastically affect the reaction course. The lack (Scheme 1) and the type (Schemes 2 and 3) of the substituent on the phenyl ring connecting to the same structure led to significantly deviating types of products, in which oxygenation took place on the unsaturated part of the bicyclic skeleton. The exception is the photocatalytic oxygenation

of starting compounds **1a** and **1b** in the presence of the anionic manganese(III) porphyrin, where the main products were hydroperoxy derivatives **2** and **3**, respectively.
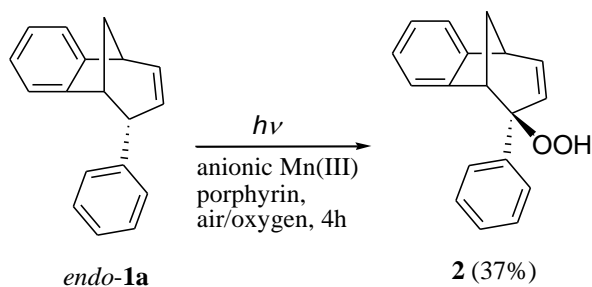
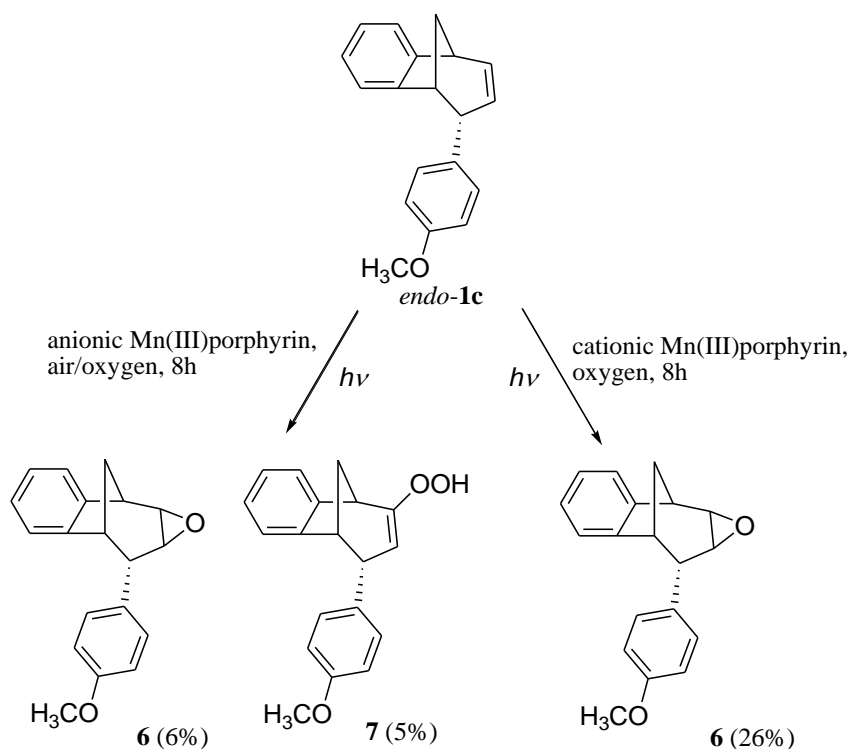**Scheme 1.** Photocatalytic oxygenation of compound **1a**

   Photocatalytic oxygenation reaction of compound **1a** in the presence of the cationic photocatalyst proved to be indiscriminate in comparison with the case of the anionic porphyrin; the analysis of the raw reaction mixture showed only a series of unidentified byproducts, so no further studies has been conducted on under these conditions. On the other hand, starting compound **1b** underwent a more selective reaction in the presence of the cationic catalyst within 2h, and gave compound **3** as the main product, similarly to the case with the anionic manganese(III) porphyrin. Besides product **3**, compounds **4** and **5** have also been isolated after 2h of reaction time, but only in traces. In the case of prolonged irradiation time (4h), photocatalytic oxygenation with the cationic catalyst gave a better result. Photoproduct **5**, which was found only in traces after 2h, was obtained with a higher yield (23%). Besides the photoproducts unambiguously determined both qualitatively and quantitatively, the raw reaction mixture contained also unidentified byproducts, which could not be isolated.

4
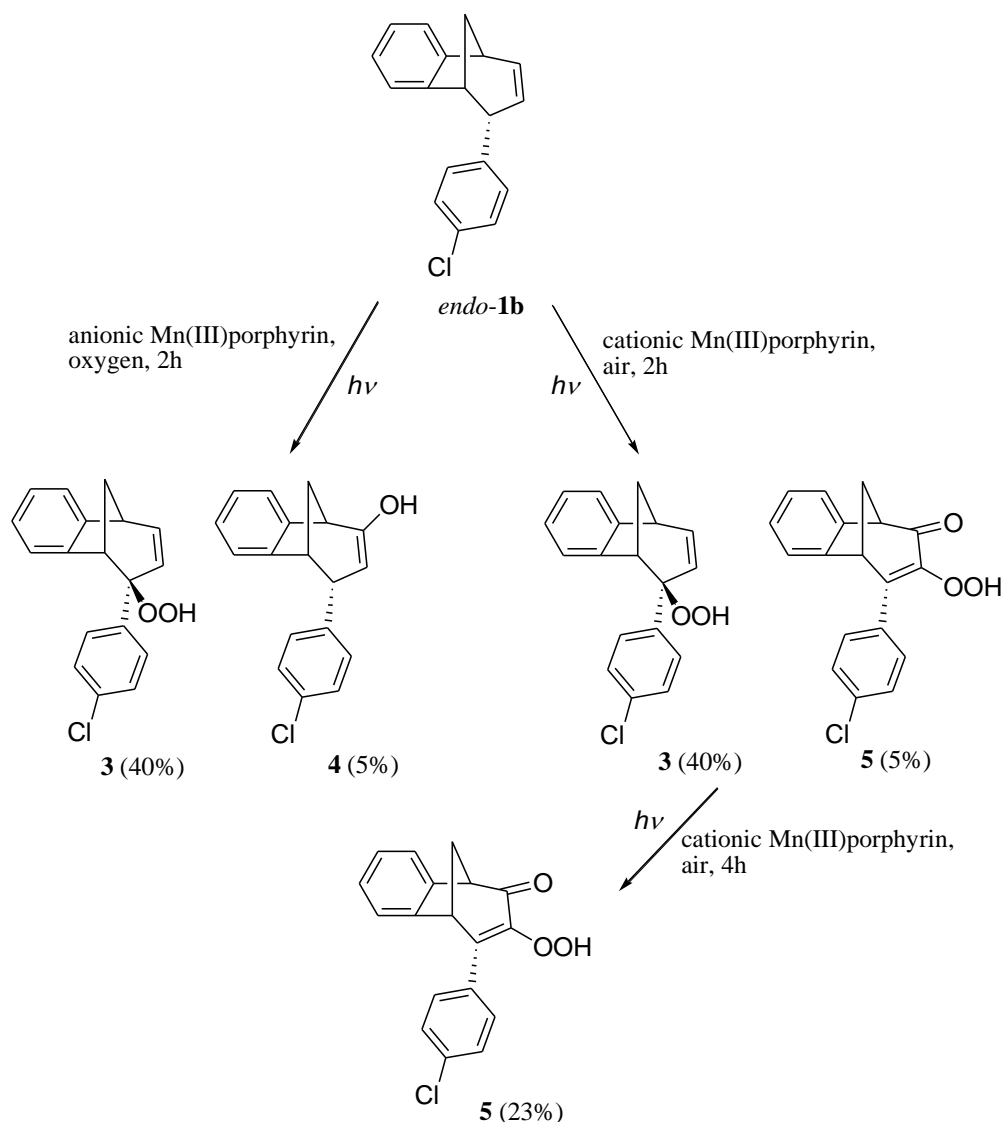
Scheme 2. Photocatalytic oxygenation of compound **1b**

In comparison with the chloro derivative (**1b**), the methoxy derivative (**1c**) reacted in a completely different way. The ^{1}H NMR spectrum of the reaction mixture after 8h irradiation in the presence of the anionic photocatalyst showed only the starting compound **1c**. However, after chromatographic purification two new products, **6** and **7** were found in traces. On the other hand, the reaction with the cationic manganese(III) porphyrin in the stream of oxygen gave a somewhat better result; the epoxy derivative **6** was isolated with a higher yield (26%) than in the previous case. However, at an extended reaction time (16h), deviating from the case of the chloro derivative (**1b**), no appraisable result was obtained. Too long reaction time only caused an additional decomposition and formation of unwanted byproducts.

The new products **2-7** were isolated and completely characterized by spectroscopic methods. From the ^{1}H and ^{13}C NMR spectra and taking as reference the previous results for starting compounds **1a-c**,[12-14] the structures of all the compounds were determined. All the photoproducts have recognizable patterns in their ^{1}H NMR spectra (Figure 1-5) but different

numbers of signals in their aliphatic regions, depending on the structure. These suggested results were confirmed from their ^{13}C NMR spectra which revealed the structures with characteristic epoxy, keto, hydroxy and/or hydroperoxy groups. The IR spectra of **2**-**7** showed characteristic signals for the keto, hydroxy and/or hydroperoxy groups. Compounds **4** and **5** have almost the same spectrum in spite of having something different structures. This fact can be the consequence of the keto-enol equilibria in both cases causes similar signals in IR spectra but somewhat different in NMR spectra (which are for the same noisy).

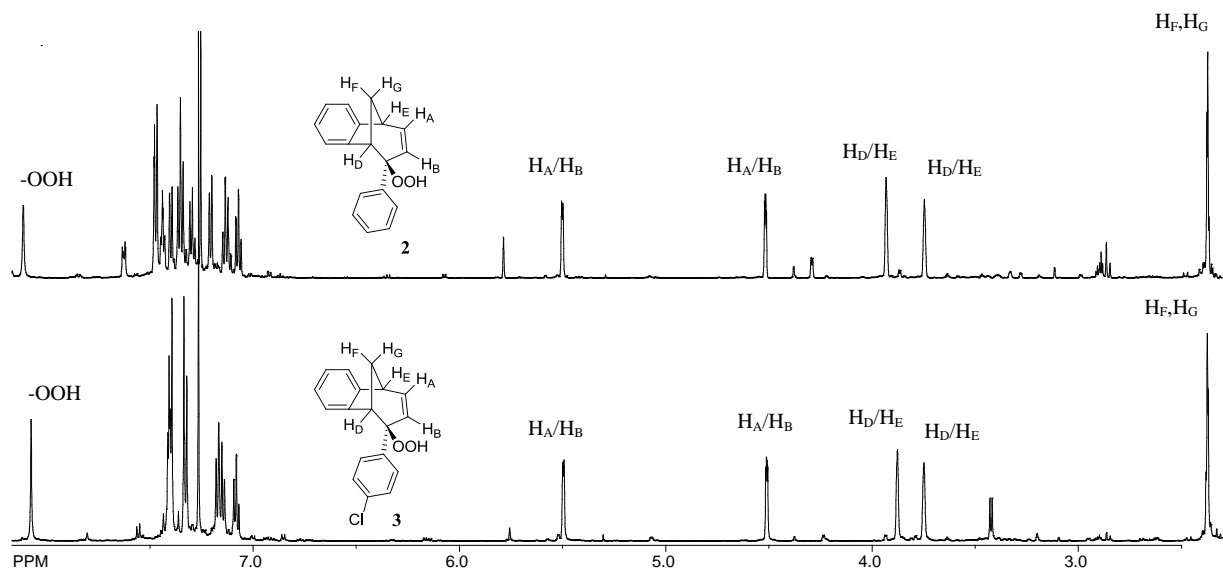**Scheme 3.** Photocatalytic oxygenation of compound **1c**

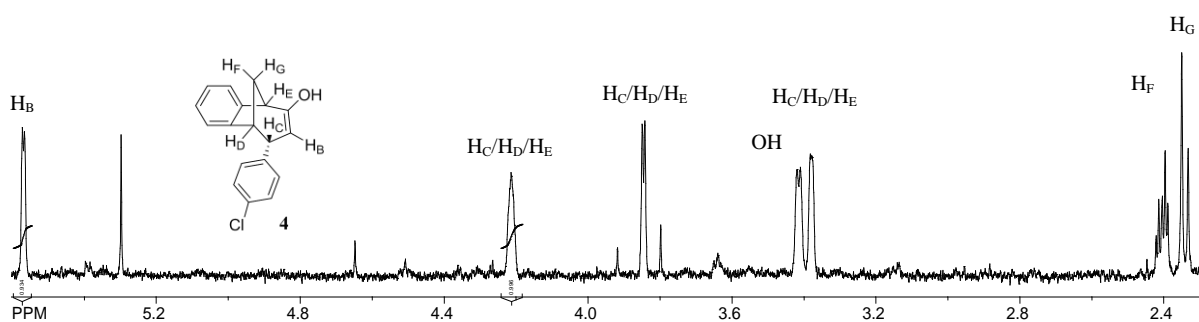**Figure 1.** ^{1}H NMR spectra (CDCl$_3$) of photoproducts **2** and **3**

Figure 2. ^{1}H NMR spectrum (CDCl$_3$, aliphatic part) of photoproduct **4**
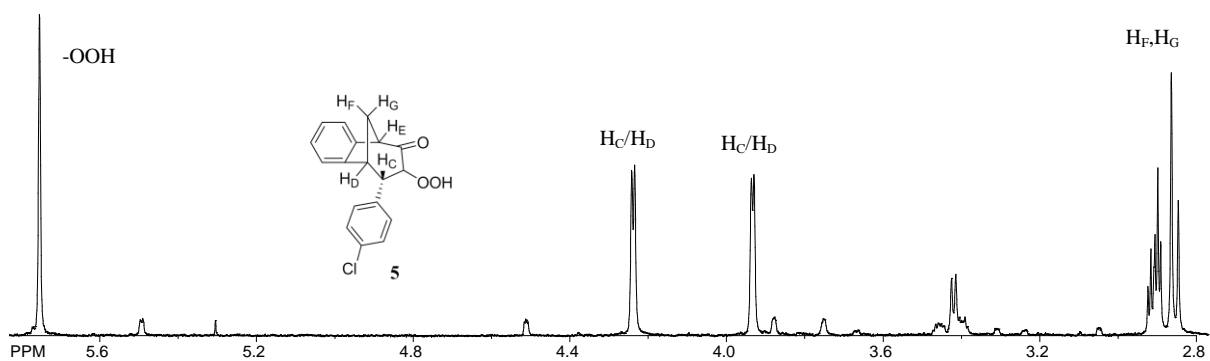

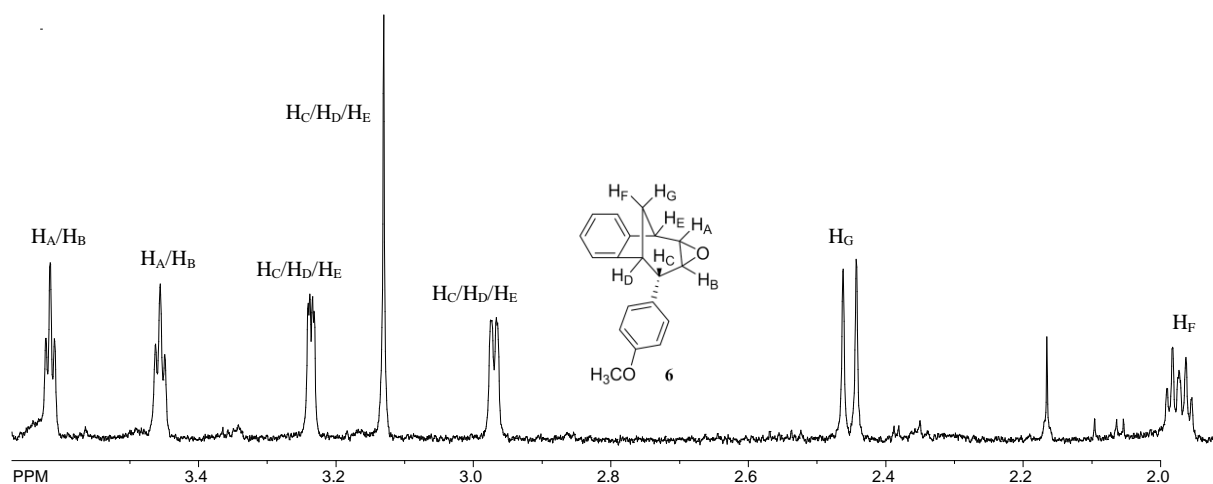**Figure 3.** ^{1}H NMR spectrum (CDCl$_3$, aliphatic part) of photoproduct **5**

Figure 4. ^{1}H NMR spectrum (CDCl$_3$, aliphatic part) of photoproduct **6**
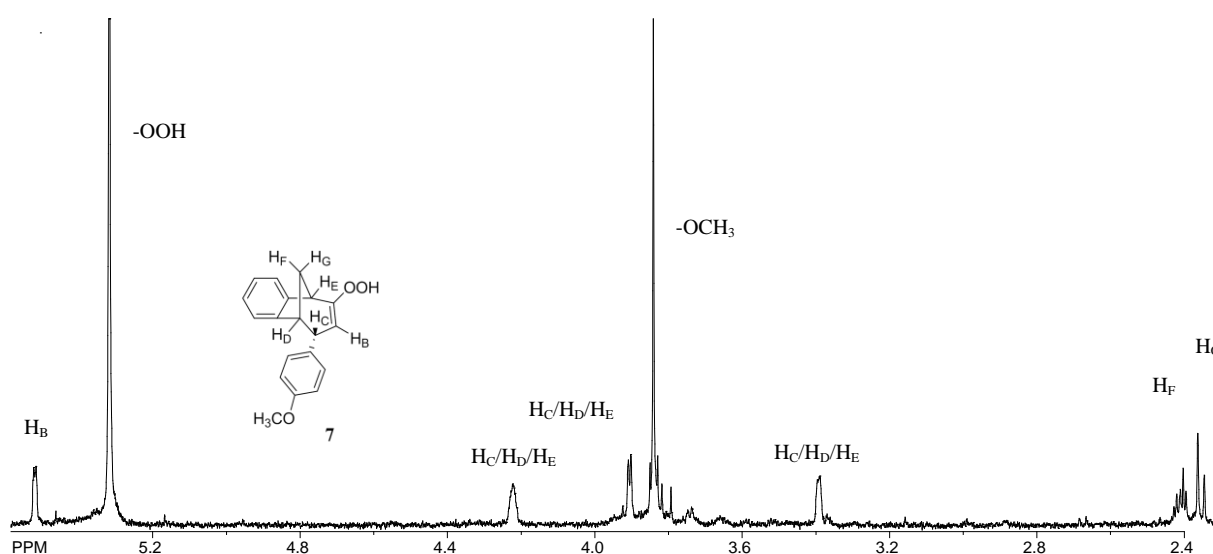

Figure 5. ^{1}H NMR spectrum (CDCl$_3$, aliphatic part) of photoproduct **7**

The yields and the corresponding reaction conditions regarding the characteristic products obtained are summarized in Table 1.

Table 1. Experimental conditions and yields regarding the characteristic products of photocatalytic oxygenation of **1a**, **1b**, and **1c**.

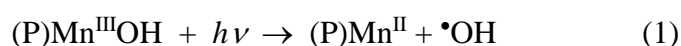| starting compound	product	photocatalyst	oxygen content[*]	yield (%)	time (h)
1a	**2**	anionic	air/O$_2$	37	4
1b	**3**	anionic / cationic	air/O$_2$	40	2
1b	**4**	anionic	O$_2$	5	2
1b	**5**	cationic	air	23	4
1c	**6**	cationic	O$_2$	26	8
1c	**7**	anionic	O$_2$	5	8

[*]Saturation with air or O$_2$.

8

Discussion

As our previous studies on manganese(III)-porphyrin-based oxygenation of various bicyclic derivatives indicated,[1,2,3] in accordance with earlier publications on photocatalytic oxidations utilizing metalloporphyrins,[4,5,6,7,10,11] both steric and electronic effects can influence the efficiency and selectivity of these reactions. Besides, the role of the photocatalyst in these processes can also be a determining factor. Thus, characterization of the excited states of these compounds may provide useful pieces of information for the interpretation of the results obtained in this study. Irradiation of manganese(III) porphyrins, both at the Soret-bands (430-450 nm) and at the Q-bands (500-650 nm) leads to the formation of singlet excited states, S_2 and S_1, respectively. The previous one (S_2) relaxes to the latter one (S_1) within a ps timescale *via* internal conversion. The first singlet excited state can transform to the first triplet state (T_1) of a much longer lifetime, efficiently competing with fluorescence and non-radiative decay to the ground state. The fluorescence lifetime of the manganese(III) porphyrin complexes is in the 1-3 ns range,[15] indicating that singlet excited state of these photocatalysts can only be involved in the oxygenation reactions if they are already coordinated to the substrate in a ground-state equilibrium or if they can produce oxygen-containing reactive intermediates which efficiently attack the substrate molecules. The lifetime of the triplet excited state of these manganese(III) porphyrins is of µs order of magnitude, which may react with the ground-state substrates to be oxygenated.

In the case of both **1a** and **1b** the main products with the anionic photocatalyst were the corresponding hydroperoxy derivatives (**2** and **3**, respectively), where the site of the oxygenation is in the immediate neighborhood of the phenyl ring. This suggests that the aromatic ring can coordinate the manganese(III) complex by a π-π interaction with the porphyrin ligand, providing for it a favorable proximity to the electron-rich site of the substrate. Besides, it is noteworthy that the formation of hydroperoxy derivatives in earlier studies on photocatalytic oxygenations was only observed in the case of manganese(III) porphyrins as catalysts, but not with the corresponding free bases, which can only generate singlet excited-state oxygen molecule ($^1O_2$) as oxidative agent.[1,2] Hence, other oxygen-containing reactive intermediates are involved, the formation of which takes place from the ligands axially coordinated to the manganese(III) center of the metalloporphyrins applied. Thus, both the proximity of the porphyrin to the site of attack and the appropriate metal center coordinating the suitable oxygen-containing ligand are crucial conditions in the respect of the formation of the hydroperoxy derivatives **2** and **3**.

The oxygen-containing reactive intermediates playing role in these processes are generated in the photoinduced reactions of the manganese(III) porphyrins applied. Similarly to the oxygenation of cycloalkenes,[4,6,16,17] $(P)Mn^{IV}=O$ and $(P)Mn^V=O$ intermediates are suggested to the most important *in situ* generated reactive species in these systems. The primary step in this process is a photoinduced LMCT (ligand-to-metal charge transfer) from axially coordinated hydroxide ligands in aqueous systems (Eq. 1).[4,18] The Mn(II) species formed in this way undergoes an oxidation with the dissolved O_2 (Eq. 2).

$$(P)Mn^{III}OH \; + \; h\nu \; \rightarrow \; (P)Mn^{II} + \,^\bullet OH \qquad (1)$$

$$2\,(P)Mn^{II} + O_2 \rightarrow 2\,(P)Mn^{IV}=O \qquad (2)$$

In Eq. 2 several steps are comprised.[18] In water-acetone solvent mixture (applied in our experiments), hydroxyl radicals produced in the primary photochemical step most probably react with the organic solvent. Disproportionation of the Mn(IV) complexes formed generates highly reactive manganese(V)-oxo species (Eq. 3).[16,17]

$$2 \ (P)Mn^{IV}=O + H^+ \rightleftharpoons (P)Mn^V=O + (P)Mn^{III}OH \qquad (3)$$

In this equilibrium system, disproportionation is much faster than the reversed reaction. Besides, a polar solvent also promotes the previous process, hence it is nearly diffusion-controlled.[16] Moreover, manganese(V)-oxo porphyrins react several orders of magnitude faster in oxygenation processes than the corresponding Mn(IV) species. Accordingly, $(P)Mn^V=O$ can be considered as the major oxidizing agent in our systems.

At shorter (2- or 4-hour) periods of irradiation the predominant products were the hydroperoxy derivatives (**2** and **3**) functionalized at the carbon atom connecting to the phenyl ring. These results can be attributed to a considerable π-stacking interaction between the aromatic ring and the porphyrin ligand.[19,20] Due to this interaction, the connecting manganese(III) porphyrin is in a very close proximity of the indicated carbon atom, promoting its attack by an oxidative species formed in the photoinduced reactions of the coordinated complex. Although the charge of the porphyrin ligand may affect the strength of the π-stacking interaction, no significant difference could be observed between the yields of **3** obtained with cationic or anionic complex from **1b**. However, compared to the case of **1a**, where 4-hour irradiation was needed for almost the same yield of **2** (37%) as for **3** (40%), the latter was reached within 2 hours. The reason for this phenomenon may be that the chloro substituent increases the electron density on the carbon atom attacked, due to a positive mesomer effect, promoting its oxidation. A longer (4h) irradiation of the system containing **1b** and the cationic catalyst resulted in the appreciable (23%) formation of a more oxidized (keto-hydroperoxy) derivative (**5**), indicating that the positive charge on the ligand more effectively favor the formation of the oxidizing intermediates than the negative one does.

Reactivity of **1c** strongly deviated from those of **1a** and **1b**. Application of the anionic photocatalyst, even after a longer (8h) irradiation period, resulted in the formation of only traces of identifiable products (an epoxy (**6**) and a hydroperoxy (7) derivative), while almost 100% of the starting material did not react at all. This phenomenon clearly indicates that **1c** is much less reactive than the other two substrates. Although from the viewpoint of electronic effect on the phenyl ring the methoxy group does not significantly differ from the chloro substituent, in the respect of steric influence the former one hinders the π-π stacking interaction between the porphyrin and the aromatic ring. Due to the bulkier CH_3O- group decreasing the coordination possibility of the manganese(III) complexes to the phenyl ring, the carbon atom which was efficiently attacked in the case of **1a** and **1b** remained intact in the reactions of **1c**.

The efficacy of oxygenation of **1c** at the free double bond is very low in the presence of the anionic porphyrin as indicated by the small (trace) amounts of the products obtained even after a relatively long irradiation period. However, the cationic photocatalyst proved to be significantly more efficient, demonstrated by the appreciable ratio of product **6**. This phenomenon may be attributed to the electronic interaction between the electron-rich free

double bond and differently charged metalloporphyrins. Regarding this interaction, the positively charged substituents are much more favorable than the anionic complex of higher electron density. This interpretation is in accordance with the mechanism of Jacobsen-Katsuki epoxidation, where the free double bond approaches the metal oxo complexes side-on.[21] Such an approach is promoted by the positive charge on the porphyrin.

Experimental Section

General. The ^{1}H NMR spectra were recorded on a spectrometer at 600 MHz. The ^{13}C NMR spectra were registered at 150 MHz. All NMR spectra were measured in CDCl$_3$ using tetramethylsilane as reference. IR spectra were recorded on a FTIR-ATR (film). HRMS analysis were carried out on a mass spectrometer (MALDI TOF/TOF analyzer), equipped with Nd:YAG laser operating at 355 nm with firing rate 200 Hz in the positive (H$^+$) or negative (H$^-$) ion reflector mode. Silica gel (0.063-0.2 mm) was used for chromatographic purifications. Thin-layer chromatography (TLC) was performed silica gel 60 F$_{254}$ plates. Solvents were purified by distillation.

Typical experimental procedure for the photocatalytic oxygenation of 1a – c

A solution of 50 ml of **1a – c** and the anionic or cationic manganese(III) porphyrins in acetone/water *(50:50)* was irradiated with a 70-W tungsten halogen immersion lamp (Philips, λ_{ir}> 380 nm) in a thermostated 50-ml cylindrical photoreactor. A stream of air or oxygen was passed through the solution at RT during 2h, 4h or 8h, also with vigorously stirring. The following concentrations conditions were: S/C = 100, porphyrin = 0.00111 mmol and **1a – c** = 0.111 mmol. After termination of the photolysis acetone was removed by vacuum distillation. The remaining two phases were separated by standard methods. The water-insoluble oxygenation products remained in the organic phase. The photoproducts **2** (from **1a**, Scheme 1), **3**, **4**, **5** (from **1b**, Scheme 2), **6** and **7** (from **1c**, Scheme 3) were isolated by repeated thin-layer chromatography using dichloromethane /diethylether (9/1) as eluent and characterized by spectroscopic methods.
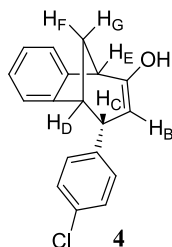

2
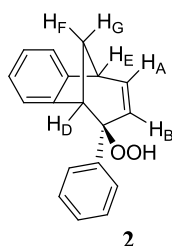
9-phenyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,10-tetraene-9-peroxol (**2**): R$_f$ (dichloromethane: diethylether = 0.95:0.5) = 0.63; colourless oil; δ_H (600 MHz, CDCl$_3$) 8.11 (s, 1H, -OOH), 7.47 (d, *J* = 7.8 Hz, 2H, H$_{ar}$), 7.40 (d, *J* = 7.3 Hz, 1H, H$_{ar}$), 7.35 (d, *J* = 7.8 Hz, 2H, H$_{ar}$), 7.29 (td, *J* = 7.3 Hz, *J* = 1.1 Hz, 1H, H$_{ar}$), 7.21 (d, *J* = 7.3 Hz, 1H, H$_{ar}$), 7.13 (td, *J* = 7.3 Hz, 1H, H$_{ar}$), 7.07 (td, *J* = 7.3 Hz, 1H, H$_{ar}$), 7.52 − 7.48 (m, 1H, H$_A$/H$_B$), 7.42 (dd, *J* = 4.0; 2.1 Hz, 1H, H$_A$/H$_B$), 3.93 (s, 1H, H$_E$/H$_D$), 3.75 (s, 1H, H$_E$/H$_D$), 2.39 − 2.36 (m, 2H, H$_F$, H$_G$); δ_C (150 MHz, CDCl$_3$) 151.77 (s), 151.29 (s), 142.64 (s), 138.92 (s), 127.98 (2d), 127.54 (d), 125.94 (2d), 124.99 (2d), 124.18 (d), 121.10 (d), 114.95 (d), 81.77 (d), 44.26 (d), 42.25 (d), 37.84 (t); IR

ν_{max}/cm^{-1} (evaporated from CHCl$_3$ film): 3419, 1651, 1446, 1250, 999, 753; HRMS M$^+$, found 264.1213. C$_{18}$H$_{16}$O$_2$ requires 264.1224.
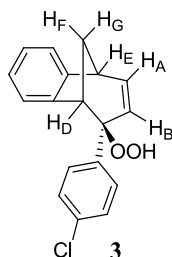

9-(4-chlorophenyl)tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,10-tetraene-9-peroxol **(3)**: R$_f$ (dichloromethane: diethylether = 0.95:0.5) = 0.57; colourless oil; δ_H (600 MHz, CDCl$_3$,) 8.07 (s, 1H, -OOH), 7.40 (d, J = 7,3 Hz, 1H, H$_{ar}$), 7.39 (d, J = 8.6 Hz, 2H, H$_{ar}$), 7.32 (d, J = 8.6 Hz, 2H, H$_{ar}$), 7.17 (d, J = 7.3 Hz, 1H), 7.15 (td, J = 7.3; 0.9 Hz, 1H, H$_{ar}$), 7.08 (td, J = 7.3; 0.9 Hz, 1H, H$_{ar}$), 5.49 (d, J = 3.7 Hz, 1H, H$_A$/H$_B$), 4.49 − 4.51 (m, 1H, H$_A$/H$_B$), 3.87 (s, 1H, H$_D$/H$_E$), 3.74 (s, 1H, H$_D$/H$_E$), 2,35 − 2,38 (m, 1H, H$_F$, H$_G$); δ_C (150 MHz, CDCl$_3$) 151.5 (s), 151.2 (s), 143.0 (s), 137.8 (s), 133.9 (s), 128.7 (2d), 126.8 (2d), 126.6 (d), 126.5 (d), 124.8 (d), 121.5 (d), 116.0 (d), 82.1 (d), 44.7 (d), 42.6 (d), 38.3 (t); IR ν_{max}/cm^{-1} (evaporated from CHCl$_3$ film): 3429, 1649, 1491, 1092, 753; HRMS M$^+$, found 298.0802. C$_{18}$H$_{15}$ClO$_2$ requires 282.0811.
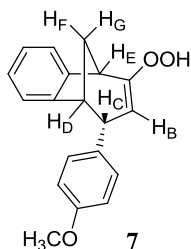

11-(4-chlorophenyl)tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraen-9-ol **(4)**: R$_f$ (dichloromethane: diethylether = 0.95:0.5) = 0.38; colourless oil; δ_H (600 MHz, CDCl$_3$) 7.39 (d, J = 8.6 Hz, 2H, H$_{ar}$), 7.37 (d, J = 7.3 Hz, 1H, H$_{ar}$), 7.32 (d, J = 8.6 Hz, 2H, H$_{ar}$), 7.15 (d, J = 7.3 Hz, 1H, H$_{ar}$), 7.13 (td, J = 7.3; 0.8 Hz, 1H, H$_{ar}$), 7.06 (td, J = 7.3; 0.8 Hz, 1H, H$_{ar}$), 5.57 (d, J = 3.4 Hz, 1H, H$_B$), 4.19 − 4.24 (m, 1H, H$_C$/H$_D$/H$_E$), 3.84 (d, J = 4.2 Hz, 1H, H$_C$/H$_D$/H$_E$), 3.41 (m, 1H, H$_C$/H$_D$/H$_E$), 3.36 − 3.39 (s, 1H, -OH), 2.38 − 2.42 (m, 1H, H$_F$), 2.34 (d, J = 10.6 Hz, 1H, H$_G$); HRMS M$^+$, found 282.0742. C$_{18}$H$_{15}$ClO requires 282.0728.
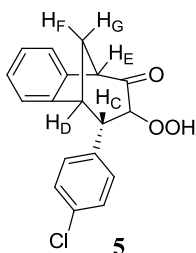
11-(4-chlorophenyl)-10-hydroxytricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,10-tetraen-9-one (**5**): R_f (dichloromethane:diethylether = 0.95:0.5) = 0.54; colourless oil; δ_H (600 MHz, CDCl$_3$) 7.56 (d, J = 8.5 Hz, 2H, H$_{ar}$), 7.44 (d, J = 7.0 Hz, 1H, H$_{ar}$), 7.43 (d, J = 8.5 Hz, 2H, H$_{ar}$), 7.30 (d, J = 7.0 Hz, 1H, H$_{ar}$), 7.15 (td, J = 7.0; 1.1 Hz, 1H, H$_{ar}$), 7.12 (td, J = 7.0; 1.1 Hz, 1H, H$_{ar}$), 5.75 (s, 1H, -OOH), 4.24 (d, J = 4.4 Hz, 1H, H$_C$/H$_D$), 3.93 (d, J = 3.9 Hz, 1H, H$_C$/H$_D$) 2.88 – 2.93 (m, 1H, H$_F$), 2.85 (d, J = 10.6 Hz, 1H, H$_G$); δ_C (150 MHz, CDCl$_3$) 197.5 (s), 162.5 (s), 147.2 (s), 141.0 (s), 135.9 (s), 134.8 (s), 128.7 (2d), 127.0 (2d), 126.6 (d), 126.5 (d), 124.8 (d), 122.3 (d), 118.2 (d), 56.7 (d), 49.2 (t), 45.5 (d); IR ν_{max}/cm^{-1} (evaporated from CHCl$_3$ film): 3435, 2091, 1651, 1491, 1249, 1093, 1010; HRMS M$^+$, found 311.1128. C$_{18}$H$_{12}$ClO$_3$ requires 311.0469.
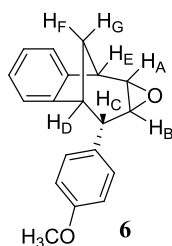
12-(4-methoxyphenyl)-10-oxatetracyclo[6.4.1.0^{2,7}.0^{9,11}]trideca-2,4,6-triene (**6**): R_f (dichloromethane: diethylether = 0.95:0.5) = 0.34; colourless oil; δ_H (600 MHz, CDCl$_3$) 7.22 – 7.30 (m, 1H, H$_{ar}$), 7.13 (td, J = 7.4; 0.9 Hz, 1H, H$_{ar}$), 6.89 (td, J = 7.4; 0.9 Hz, 1H, H$_{ar}$), 6.84 (d, J = 8.8 Hz, 2H, H$_{ar}$), 6.75 (d, J = 8.8 Hz, 2H, H$_{ar}$), 6.14 (d, J = 7.4 Hz, 1H, H$_{ar}$), 3.79 (s, 3H, -OCH$_3$), 3.61 (t, J = 3.8 Hz, 1H), 3.45 (t, J = 4.1 Hz, 1H), 3.22 – 3.25 (m, 1H), 3.13 (s, 1H), 2.97 (d, J = 5.0 Hz, 1H), 2.45 (d, J = 11.6 Hz, 1H), 1.94-2.00 (m, 1H); δ_C (75 MHz, CDCl$_3$) 158.6 (s), 144.8 (s), 143.4 (s), 135.6 (s), 127.1 (d), 127.0 (2d), 126.9 (d), 126.1 (d), 122.4 (d), 112.6 (2d), 71.4 (q), 57.5 (d), 56.4 (d), 55.2 (d), 54.1 (d), 40.3 (d), 32.1 (t); IR ν_{max}/cm^{-1} (evaporated from CHCl$_3$ film): 2916, 2373, 1709, 1513, 1215, 750; HRMS M$^+$, found 277.1211. C$_{19}$H$_{17}$O$_2$ requires 277.1223.

11-(4-methoxyphenyl)tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,10-tetraene-9-peroxol (**7**): Rf = 0.28 (dichloromethane: diethylether = 0.95:0.5); colourless oil; δ_H (600 MHz, CDCl$_3$) 7.44 (d, 2H, J = 8.8 Hz, H$_{ar}$), 7.38 (d, 1H, J = 7.2 Hz, H$_{ar}$), 7.18 (d, 1H, J = 7.2 Hz, H$_{ar}$), 7.13 (td, 1H, J = 7.2; 0.9 Hz, H$_{ar}$), 7.06 (td, 1H, J = 7.2; 0.9 Hz, H$_{ar}$), 6.91 (d, 2H, J = 8.8 Hz, H$_{ar}$), 5.52 (d, 1H,

J = 3.8 Hz, H_B), 5.29 (s, 1H, -OOH) 4.20 – 4.25 (m, 1H, $H_C/H_D/H_E$), 3.90 (d, 1H, J = 4.0 Hz, $H_C/H_D/H_E$), 3.84 (s, 3H, -OCH$_3$), 3.38 – 3.40 (m, 1H, $H_C/H_D/H_E$), 2.39 – 2.43 (m, 1H, H_F), 2.35 (d, 1H, J = 10.6 Hz, H_G); IR ν_{max}/cm^{-1} (evaporated from CHCl$_3$ film) 3430, 2917, 1602, 1511, 1248, 1174, 1031; HRMS M$^+$, found 294.1333. C$_{19}$H$_{18}$O$_3$ requires 294.1320.

Conclusion

Continuing our study on photocatalytic oxygenations of various bicyclic organic compounds, in this work, for the first time, three derivatives with an isolated/free double bond were investigated. Connecting to the parent bicyclic structure, these compounds also contained a phenyl group (unsubstituted or substituted) close to the free double bond, which significantly affected the mechanism of their manganese(III) porphyrin-based photocatalytic oxygenation. A considerable π-stacking interaction between that phenyl ring and the porphyrin catalyst may promote the functionalization of the carbon atom, to which the aromatic is connected, resulting the formation of the suitable hydroperoxy derivatives (**2** and **3**) in the case of **1a** and **1b**. While no effect of the porphyrin charge was observed in these cases, the main oxygenation reaction of the methoxy derivative (**1c**), i.e, the epoxidation, proved to be efficient only with the cationic complex, probably due to its interaction with the electron-rich free double bond. These results clearly indicate that both steric and electronic effects govern the mechanisms of the photocatalytic oxygenations of these compounds. Our observations may help plan the preparation of new functionalized bicyclic derivatives of potential bioactivity. Accordingly, the continuation of our systematic study will focus on other aryl/heteroaryl derivatives of such bicyclic structures in order to elucidate the role of the position of the aryl/heteroaryl substituent in the mechanism of the photocatalytic oxygenation of these compounds.

Generally, the continual research of interest in the chemistry of this framework (functionalized bicyclo[3.2.1] skeleton) is mainly due to its ubiquity in numerous families of biologically active natural products coupled with its versatile reactivity, making it a very useful building block with a valuable impact in modern organic synthesis.[22] Moreover, our specific synthetic approach, photochemical cycloaddition followed by photooxygenation, for the preparation of this framework is connected directly with the important applications to the total synthesis of some natural products.

1. Kikaš, I.; Horváth, O.; Škorić, I. *Tetrahedron Lett.* **2011**, 52, 6255.
2. Kikaš, I.; Horváth, O.; Škorić, I. *J. Mol. Struct.* **2013**, 1034, 62.

3. Vuk, D.; Kikaš, I.; Molčanov, K.; Horváth, O.; Škorić, I. *J. Mol. Struct.* **2014**, 1063, 83.

4. Hennig, H. *Coord. Chem. Rev.* **1999**, 182, 101. and references therein.

5. Maldotti, A.; Andreotti, L.; Molinari, A.; Varani, G.; Cerichelli, G.; Chiarini, M. *Green Chem.* **2001**, 3, 42.

6. Hajimohammadi, M.; Bahadoran, F.; Davarani, S. S. H.; Safari, N. React. Kinet. *Mech. Cat.* **2010**, 99, 243.

7. Gollnick, K.; Griesbeck, A. *Tetrahedron* **1985**, 41, 2057.

8. Turro, N. J. In *Modern Molecular Photochemistry*; University Science Books: Sausalito, 1991. pp. 587–593.

9. Iesce, M. R.; Cermola, F.; Guitto, A.; Scarpati, R.; Graziano, M. L. *J. Org. Chem.* **1995**, 60, 5324.

10. Monteiro, C. J. P.; Pereira, M. M.; Azenha, M. E.; Burrows, H. D.; Serpa, C.; Arnaut, L. G.; Tapia, M. J.; Sarakha, M.; Wong-Wah-Chung, P.; Navaratnam, S. *Photochem. Photobiol. Sci.* **2005**, 4, 617.

11. Montagnon, T.; Tofi, M.; Vissilikoginnakis, G. Acc. *Chem. Res.* **2008**, 41, 1001.

12. Škorić, I.; Šmehil, M.; Marinić, Ž.; Molčanov, K.; Kojić-Prodić, B.; Šindler-Kulyk, M. *J. Photochem. Photobiol. A* **2009**, 207, 190.

13. Vuk, D.; Potroško, D.; Šindler-Kulyk, M.; Marinić, Ž.; Molčanov, K.; Kojić-Prodić, B.; Škorić, I. *J. Mol. Struct.* **2013**, 1051, 1.

14. Vuk, D.; Marinić, Ž.; Škorić, I. *Croat.. Chem. Acta* **2014**, 87, 465.

15. Fodor M. A., Diploma Thesis, University of Pannonia, Veszprém, 2013.

16. Zhang, R.; Horner, J. H.; Newcomb, M. *J. Am. Chem. Soc*. **2005**, 127, 6573.

17. Newcomb, M.; Zang, R.; Pan, Z.; Harischandra, D. N.; Chandrasena, R. E. P.; Horner, J. H.; Martinez E. *Catal. Today* **2006**, 117, 98.

18. Hennig, H.; Behling, J.; Meusinger, R.; Weber L. *Chem. Ber.* **1995**, 128, 229.

19. Hunter, C.A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, 112, 5525.

20. Wheeler, S. E.; Bloom, J. W. G. *J. Phys. Chem. A* **2014**, 118, 6133.

21. Linker, T. *Angew. Chem. Int. Ed*. **1997**, *36*, 2060.

22. Presset, M.; Coquerel, Y.; Rodriguez, J. *Chem. Rev.* **2013**, 113, 525 and references therein.