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IRA-200 resin-supported platinum(II) complex for photooxidation of olefins

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Abstract—Cyclometalated platinum(II) 4,6-diphenyl-2,2′-bipyridine complex is supported on a commercially available cationic ion-exchange resin (amberlite IRA-200). Photophysical and ESR determinations indicate that the combined photosensitized system is able to generate singlet oxygen with high quantum yield upon irradiation of light in the visible region. The platinum(II) complex loaded on IRA-200 resin is stable and the photooxidation occurs in an environmentally friendly way. Only a simple filtration is needed to recycle the expensive metal catalyst.

1. Introduction

Though singlet oxygen ($^1O_2$) is a versatile reagent for oxidation reactions including cycloaddition reactions to produce endoperoxides and ene reactions to provide allylic hydroperoxides,[1–4] the reactivity of molecular oxygen toward most organic molecules is inhibited by its spin restriction. Over the past decades, chemists have made tremendous efforts to realize an effective oxidation reaction by using molecular oxygen as oxidized reagent, and photosensitized processes have been demonstrated to be very promising.[1–4]

Square-planar platinum(II) polypyridyl complexes are appealing from photochemical perspective due to the unique properties of open axial coordination site, high population of triplet state and strong visible absorption.[5–13] In the course of exploring the photochemical reactivity, we recently found that platinum(II) polypyridyl complexes can operate the energy transfer process with molecular oxygen to generate singlet oxygen under visible light.[14–17] However, the high costs and low stability in solution render their synthetic application impractical. In this regard, we have incorporated platinum(II) polypyridyl complexes into Nafion[14,15] and mesoporous silica SBA-15[17] by the virtue of noncovalent interaction to accomplish the photosensitized oxidation. As an extension of the previous works, we are interested in resin-supported platinum(II) complex for photooxidation of olefins because ion-exchange resin[18,19] (1) is much cheaper than Nafion and SBA-15; (2) IRA-200 resin has same functional sulfonic group as that in Nafion, and therefore may simplify the surface modification in mesoporous silica systems.

In the present work, we shall report that cyclometalated platinum(II) 4,6-diphenyl-2,2′-bipyridine complex can be loaded on a commercial cationic ion-exchange resin—amberlite IRA-200. The combined system with relatively low cost is able to generate singlet oxygen upon irradiation of light in the visible region, and photosensitized oxidation occurs in an environmentally friendly way. The quantum yield for the product formation in this system is slightly lower than that in SBA-15, but much higher than that in Nafion case. The platinum(II) complex loaded on IRA-200 resin is also more stable than that in homogenous solution; only a simple filtration is needed to recycle the expensive metal catalyst.

2. Results and discussion

The loading of cyclometalated platinum(II) complex Pt(L)Cl onto the commercial cationic ion-exchange resin IRA-200 was achieved by introducing the resin into the solution of Pt(L)Cl. As depicted in Scheme 1, an appropriate amount of the IRA-200 resin (200 mg) was added to a Pt(L)Cl acetonitrile solution at a suitable concentration (0.20 mM, 10 mL). The mixture was stirred for 3 h until the color of platinum(II) complex solution faded. After the resin was filtered, rinsed, and dried, the loading level of 0.54 wt % resin powder was obtained. With a similar approach, a series loadings of platinum(II) complex (0.27,

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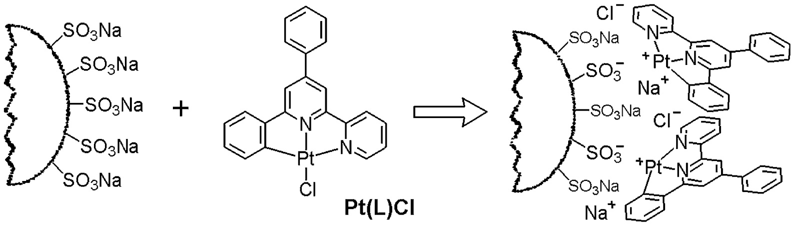


Scheme 1. The loading of platinum(II) complex on amberlite IRA-200 resin.

0.54, 1.07, 2.15, 3.22, 4.30 wt %) were prepared for further experimental use.

Figure 1 shows the absorption profiles of platinum(II) complex in acetonitrile solution and on IRA-200 resin. Pt(L)Cl in acetonitrile exhibits intense vibronic-structured absorption bands at wavelengths below 320 nm with extinction coefficients of the order of 10^4 dm^3 mol^{-1} cm^{-1}, which is assigned to the intraligand (IL) character of the cyclometalated polypyridyl ligand, and a less intense band at 380–480 nm with extinction coefficients of the order of 10^3 dm^3 mol^{-1} cm^{-1}, which is ascribed to $d\pi(Pt) \rightarrow \pi^*$ metal-to-ligand charge transfer (MLCT) state. The diffusion reflectance UV–vis spectroscopy (UV-DRS) is quite similar to those absorption bands of IL state and MLCT state of Pt(L)Cl in solution, suggesting that the platinum(II) complex was immobilized onto the IRA-200 resin.

The emission spectrum of platinum(II) complex-loaded IRA-200 resin shows the emissive band in the range of 500–700 nm with the maximum at 538 nm (Fig. 2). The lifetime of 2.15 wt % platinum(II) complex-loaded IRA-200 powder was determined to be 2.25 μs. With reference to spectroscopic work on the Pt(L)Cl in Nafion and SBA-15, the emissive state was assigned as a typical ^{3}MLCT state of platinum(II) complex.

To assess the $^1O_2$ generation ability of platinum(II) complex-loaded IRA-200 sample, electron spin resonance (ESR) spectroscopy was used to examine the reactive oxygen species. As we know, the stable free radical nitroxide (2,2,6,6-tetramethylpiperidine oxide, TMPO) arising from the reaction of 2,2,6,6-tetramethylpiperidine (TMP) and singlet oxygen can be easily detected by ESR spectroscopy.[20] Therefore, we introduced TMP into acetonitrile solution, in which platinum(II) complex-loaded resin was suspended. Figure 3 shows the ESR spectrum of the sample. Obviously, nitroxide radicals TMPO were generated when oxygen

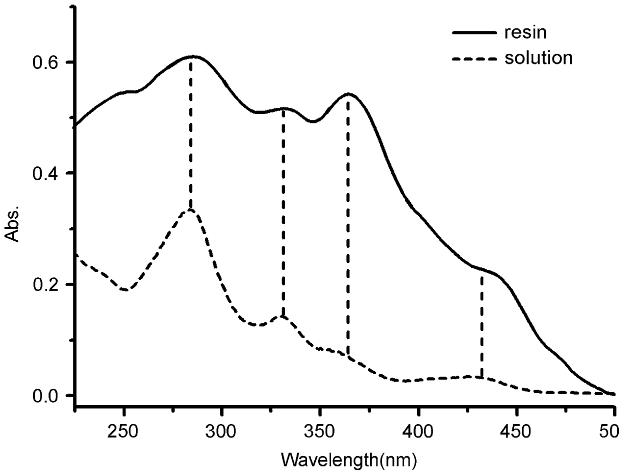


Figure 1. The absorption profile of platinum(II) complex in acetonitrile solution and on IRA-200 resin. The loading level of 2.15 wt % was used.

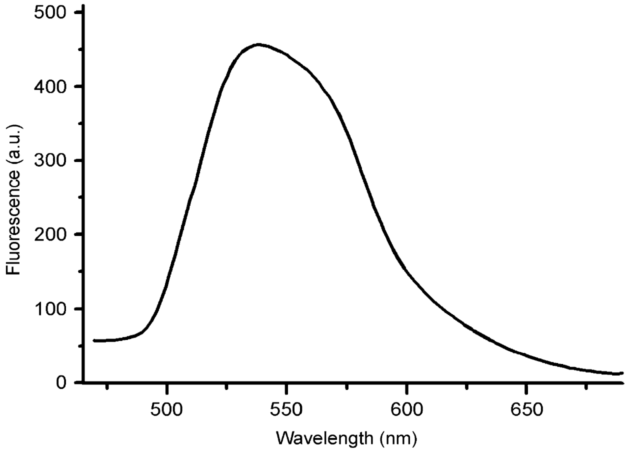


Figure 2. The emission spectrum of platinum(II) complex-loaded IRA-200 powder with loading level of 2.15 wt %.

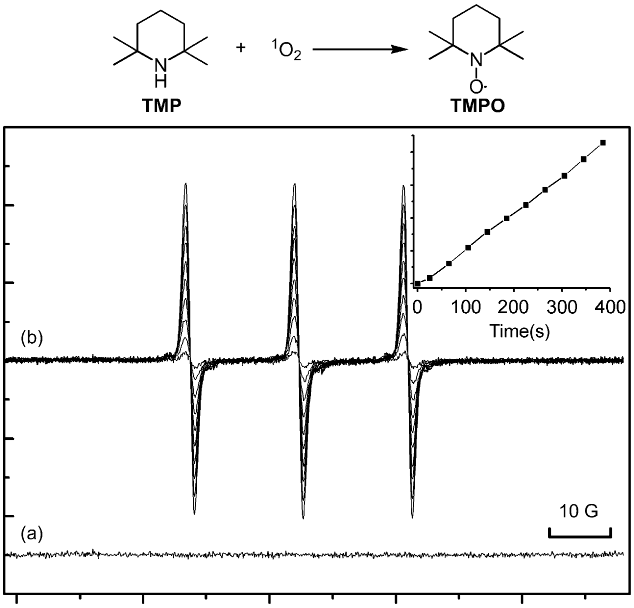


Figure 3. ESR spectra of nitroxide radical generated by irradiation of platinum(II) complex-loaded IRA-200 powder suspended in an oxygen saturated acetonitrile solution of TMP. (a) In the dark; (b) the sample was continuously scanned for 10 cycles under irradiation; the inset shows the intensity's increasing trend of the third peak in a scale of ca. 400 s.

saturated TMP acetonitrile solution was irradiated under the laser beam. The signal intensity was increased gradually as the irradiation time was prolonged. Control experiments reveal that light, platinum(II) complex, oxygen, and TMP are all essential for the production of the ESR signal. Apparently, the emissive ^{3}MLCT excited state of platinum(II) complex on IRA-200 operates the energy transfer process with molecular oxygen to generate $^1O_2$ efficiently and persistently in this combined system.

Photosensitized oxidation of olefins was performed at room temperature. Three types of $^1O_2$ reactions, [2+2], [4+2] cycloaddition, and ene reaction,[4] were involved (Scheme 2). A small amount (5 mg) of 0.54 wt % platinum(II) complex-loaded IRA-200 powder was added into the reaction vessel that contains 5 mL of substrates **1** or **3** solution (1.0 mM). The mixed solution was irradiated with a 500 W Hg lamp with oxygen bubbled in. A quartz jacket with water circulation was used to cool the lamp. A light filter was placed outside to cut off light below 450 nm and guarantee irradiation with visible light. After irradiation, the mixture was centrifuged under 3000 rpm for 15 min, and the upper liquid was separated for further gas chromatograph (GC) detection. These two rich electron stilbene derivatives **1** and **3** underwent [2+2] cycloaddition to afford the dioxetane intermediates, which were quickly converted to their corresponding aldehyde **2** and ester **4**. The GC results indicated that the activities of the reactions are very high. Both the conversion and yields were close to 100%. The oxidation of olefins under fixed ratio of resin to substrate [5 mg/5 mL (1.0 mM)] was also undertaken, which exhibited a nearly linear relationship with the loading level of IRA-200. This observation indicated that the oxidation rate of photooxidation depended on the loading level of platinum(II) complex on IRA-200 resin. Despite of this, a certain extent of photosensitizer leaching was detected in the reaction vessel as the loading level was increased to 4.30 wt %. In this situation, 0.54 wt % platinum(II) complex-loaded IRA-200 was employed as the photosensitizer for all reactions.

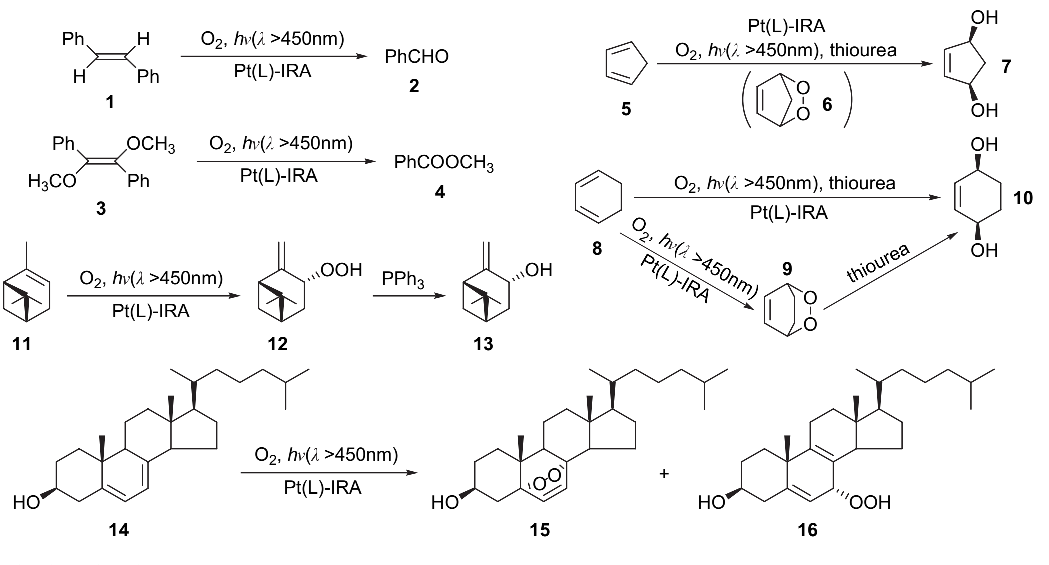
Cyclodienes **5** and **8** underwent [4+2] cycloaddition with $^1O_2$ to yield endoperoxides, which could be reduced by thiourea to give corresponding *cis*-cyclodiols **7** and **10**.[21] The endoperoxy intermediate **9**[22] could be directly observed at room temperature if no thiourea was added into the system. ^{1}H NMR spectrum indicated that the conversion of **8** at high concentration (0.1 M) was 70% and the yield of **9** was about 100%. At the same time, (1*S*,5*S*)-(−)-α-pinene (**11**) underwent ene reaction to exclusively afford **12**. Subsequent reduction with triphenylphosphine, (1*S*,3*S*,5*R*)-(+)-*trans*-3-hydroxypin-2(10)-ene [(+)-*trans*-pinocarveol, (+)-**13**][23] was obtained as an unique product with 25% conversion monitored by GC detection. The photooxidation of 7-dehydrocholesterol (**14**) afforded products **15** and **16**,[24,25] a mixture of [4+2] cycloaddition and ene reaction, the molar ratio of 3:1 could be directly validated from ^{1}H NMR spectroscopy. Product **15** could be separated by column chromatography on silica, while product **16** could not endure such treatment. All the above results were summarized in Table 1 and the mass balance was greater than 95%.

Substrate **3** was selected to study reaction kinetics and recycle of the catalyst. Time course study revealed that the photooxidation was completed in about 90 min (Fig. 4). Almost no decrease in efficiency of the combined photosensitizer

Table 1. Conversion and yield for $^1O_2$ photooxidation of olefins

Substrate[a]	Solvent	Irradiation time (h)	Product	Convt. (%)	Yield (%)
1	CH_3CN	2	**2**	~100[b]	~100[b]
3	CH_3CN	1.5	**4**	~100[b]	~100[b]
5	CH_3CN	3	**7**	—	>95[c,d,e]
8	CH_3CN	3	**10**	—	>95[c,d]
	CH_3CN	3	**9**	—	>95[c,d]
	CD_3CN[g]	2	**9**	70[f]	~100[f]
11	CH_3CN	3	**13**	22[c]	~100[c]
14	CH_3CN	4	**15**, **16**	—	95, —[c,d]
	CD_3CN[g]	2	**15**, **16**	>95[c]	72, 28[c]

[a] The loading level of catalyst was 0.54 wt %.
[b] Concentration of the substrates was about 1.0 mM.
[c] Concentration of the substrates was about 0.01 M.
[d] Yields were calculated based on the consumption of the substrates.
[e] Oligomers of cyclopentadiene were excluded.
[f] Concentration of the substrates was about 0.1 M.
[g] Tetramethylsilane was used as the internal standard.



Scheme 2. Photooxidation of olefins.

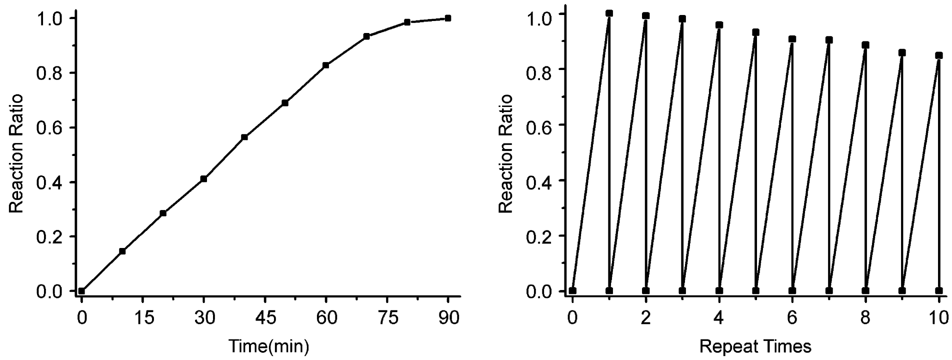


Figure 4. Kinetic plot and repeating reaction of substrate **3**.

was observed in the first three runs, though in the next three runs the conversion decreased to 90% and in the final run the conversion was 85%. The platinum(II) complex-loaded on IRA-200 resin is much stable than that in solution. Only a simple filtration is needed for the separation and recycle of the expensive metal catalysts. Compared with the heterogenous systems in our previous work, the quantum yield[26] for the product formation (0.24) in IRA-200 resin system is slightly lower than that of SBA-15 (0.33); while both systems are much more efficient than that in Nafion case.

3. Conclusion

Cyclometalated platinum(II) 4,6-diphenyl-2,2′-bipyridine complex was successfully supported on a commercial available cationic ion-exchange resin IRA-200. Photophysical and ESR determinations demonstrate that the IRA-200 resin-supported platinum(II) complex is able to generate singlet oxygen with high quantum yield upon irradiation of light in the visible region. Cycloaddition and ene reactions of singlet oxygen with a range of substrates could occur efficiently upon introduction of platinum(II) complex-loaded IRA-200 resin into the reaction vessel. The IRA-200 resin-supported platinum(II) complex is a mild and recyclable alternative to solution-phase photooxidation sensitizer. Only a simple filtration is needed for the separation and recycle of the expensive metal catalyst.

4. Experimental section

4.1. Materials

All solvents and olefin substrates used in the reactions are of analytical grade and used as received. The complex Pt(L)Cl was prepared according to the literature method.[27] Amberlite IRA-200 resin (Alfa Aesar Co. ~1.0 mmol/g saturated loading) was ground entirely. The resin particles were washed with alcohol, 1 M HCl, 1 M NaOH, and deionized water in sequence to remove any possible contaminants. After drying, the resin material was prepared for further experimental use.

4.2. Instrumentation

UV–vis spectra were measured by Shimadzu UV-1601 PC spectrophotometer. Fluorescence spectra were run on Hitachi F-4500. UV-DRS spectra were measured on JASCO UV-550. Solid state luminescent decay profiles of IRA-200 resin-supported platinum(II) complex were obtained by Edinburgh LP 920 at 538 nm using the third harmonic (355 nm) of a pulse Nd: YAG laser as excitation resource. Gas chromatograph was monitored on Shimadzu GC-14B. ESR spectroscopic experiments were carried out at room temperature (298 K) with a Bruker ESP 300E spectrometer.

Acknowledgements

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References and notes

1. Greer, A. *Tetrahedron* **2006**, *62*.
2. Margaros, I.; Montagnon, T.; Tofi, M.; Pavlakos, E.; Vassilikogiannakis, G. *Tetrahedron* **2006**, *62*, 5308–5317.
3. Chen, Y.-Z.; Wu, L.-Z.; Peng, M.-L.; Zhang, D.; Zhang, L.-P.; Tung, C.-H. *Tetrahedron* **2006**, *62*, 10688–10693.
4. Clennan, E. *Tetrahedron* **2000**, *56*, 9151–9179.
5. Lai, S.-W.; Che, C.-M. *Top. Curr. Chem.* **2004**, *241*, 27–63.
6. McMillin, D. R.; Moore, J. J. *Coord. Chem. Rev.* **2002**, *229*, 113–121.
7. Che, C. M.; Fu, W. F.; Lai, S. W.; Hou, Y. J.; Liu, Y. L. *Chem. Commun.* **2003**, 118–119.
8. Lu, W.; Mi, B.-X.; Chan, M. C. W.; Hui, Z.; Che, C.-M.; Zhu, N.; Lee, S.-T. *J. Am. Chem. Soc.* **2004**, *126*, 4958–4971.
9. Yang, Q.-Z.; Wu, L.-Z.; Wu, Z.-X.; Zhang, L.-P.; Tung, C.-H. *Inorg. Chem.* **2002**, *41*, 5653–5655.
10. Sun, W.; Wu, Z.-X.; Yang, Q.-Z.; Wu, L.-Z.; Tung, C.-H. *Appl. Phys. Lett.* **2003**, *82*, 850–852.
11. Yang, Q.-Z.; Wu, L.-Z.; Zhang, H.; Chen, B.; Wu, Z.-X.; Zhang, L.-P.; Tung, C.-H. *Inorg. Chem.* **2004**, *43*, 5195–5197.
12. Yang, Q.-Z.; Tong, Q.-X.; Wu, L.-Z.; Zhang, L.-P.; Tung, C.-H. *Eur. J. Inorg. Chem.* **2004**, 1948–1954.
13. Zhang, D.; Wu, L.-Z.; Zhou, L.; Han, X.; Yang, Q.-Z.; Zhang, L.-P.; Tung, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 3440–3441.
14. Li, X.-H.; Wu, L.-Z.; Zhang, L.-P.; Tung, C.-H.; Che, C.-M. *Chem. Commun.* **2001**, 2280–2281.

15. Zhang, D.; Wu, L.-Z.; Yang, Q.-Z.; Li, X.-H.; Zhang, L.-P.; Tung, C.-H. *Org. Lett.* **2003**, *5*, 3221–3224.
16. Yang, Y.; Zhang, D.; Wu, L.-Z.; Chen, B.; Zhang, L.-P.; Tung, C.-H. *J. Org. Chem.* **2004**, *69*, 4788–4791.
17. Feng, K.; Zhang, R.-Y.; Wu, L.-Z.; Tu, B.; Peng, M.-L.; Zhang, L.-P.; Zhao, D.-Y.; Tung, C.-H. *J. Am. Chem. Soc.* **2006**, *128*, 14685–14690.
18. Ma, W.; Li, J.; Tao, X.; He, J.; Xu, Y.; Yu, J. C.; Zhao, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 1029–1032.
19. Gelbard, G. *Ind. Eng. Chem. Res.* **2005**, *44*, 8468–8498.
20. Zang, L. Y.; Frederik, J. G. M. K.; Bibhu, R. M.; Hara, P. M. *Biochem. Mol. Biol. Int.* **1995**, *37*, 283–293.
21. Compound **7**: MS: m/z 100 (M$^+$), 82 (M−18)$^+$; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.54 (dt, J=15 and 4 Hz, 1H), 2.70 (dt, J=15 and 7 Hz, 1H), 4.65 (dd, J=7 and 4 Hz, 2H), 6.03 (s, 2H). Compound **10**: MS: m/z 114 (M$^+$); ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.74 (m, 4H), 4.09 (br s, 2H), 5.75 (s, 2H).
22. Compound **9**: MS: m/z 112 (M$^+$); ^{1}H NMR (300 MHz, CD$_3$CN) δ: 1.43 (br d, J=10 Hz, 2H), 2.26 (br d, J=10 Hz, 2H), 4.60 (br s, 2H), 6.64 (dd, J=3 and 3 Hz, 2H).
23. Compound **13**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.65 (s, 3H), 1.28 (s, 3H), 1.63–2.55 (m, 6H), 4.42 (d, J=7 Hz, 1H), 4.82 and 5.00 (m, 2H, C=CH$_2$).
24. Compound **15**: MS: m/z 416 (M$^+$); ^{1}H NMR (400 MHz, CD$_3$CN) δ: 0.80 (s, 3H, 13-CH$_3$), 0.90 (s, 3H, 10-CH$_3$), 3.71 (m, 1H, 3α-H), 6.21 (d, J=8.5 Hz, 1H, 6-H) and 6.47 (d, J=8.5 Hz, 1H, 7-H). Compound **16**: MS: m/z 416 (M$^+$); ^{1}H NMR (400 MHz, CD$_3$CN) δ: 0.66 (s, 3H, 18-CH$_3$), 3.45 (m, 1H, 3α-H), 4.55 (br s, 1H, 7-H), 5.66 (d, 1H, 6-H), 8.88 (s, 1H, 7-peroxide-H).
25. Albro, P. W.; Corbett, J. T.; Schroeder, J. L. *Photochem. Photobiol.* **1994**, *60*, 310–315.
26. The quantum yield for the product formation was calculated using the amount of product formed in the first 15 min of irradiation. As the generation of ^{1}O$_2$ is a single-photon process, the corresponding luminous flux taking part in the oxidation can be determined. The total absorbed luminous fluxes can be measured by a photometer. The ratio of two luminous fluxes gave the correlated quantum yield.
27. Lai, S. W.; Chan, M. C. W.; Cheung, T. C.; Peng, S. M.; Che, C. M. *Inorg. Chem.* **1999**, *38*, 4046–4055.