

Res Chem Intermed (2014) 40:2811–2822  
DOI 10.1007/s11164-013-1130-3

# Oxidation of benzoin to benzil in the presence of porphyrin sensitizers by air and sunlight or visible light

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Received: 24 December 2012 / Accepted: 1 March 2013 / Published online: 17 March 2013  
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**Abstract** In this work, two new aerobic routes are introduced for the oxidation of a variety of benzoin to benzil by using molecular oxygen in the presence of porphyrins as sensitizers, using white light or sunlight in acetonitrile under mild conditions. The methods have a wide range of applications, do not involve cumbersome work-up, exhibit chemoselectivity and proceed under mild reaction conditions. The resulting products are obtained in good yields in a reasonable time.

**Keywords** Photooxidation · Benzoin · Benzil · Visible light · Sunlight

## Introduction

Among the important structures that are found in many bioactive compounds [1, 2], and applications in organic synthesis are 1,2-diketones [3]. 1,2-Diketones are utilized as intermediates in the synthesis of chiral ligands, pharmaceuticals, and biologically active compounds [4–6], photoinitiators [7–10], precursors of porphyrins [11–13], preparation of variety of heterocycles [14–21], and natural products [22, 23]. 1,2-Diketones are found in selective inhibitors of carboxylesterases, acid corrosion of mild steel inhibitors, and in photocurable coatings as photosensitive agents [24–26].

Because of the above-mentioned properties of 1,2-diketones, various synthetic methods have been reported by different research groups, such as direct oxidation of  $\alpha$ -hydroxyketones by using nitric acid [27], ammonium nitrate-copper(II) acetate [28], thallium(III) nitrate [29], iodoxybenzene [30], oxone-alumina [31], bis-muth(III) nitrate-copper(II) acetate [32], iron(III) nitrate [33], tert-butyl

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hydroperoxide-titanium(IV) chloride [34], sodium hydride [35], and porphyrin [36]. 1,2-Diketones have been synthesized with different reagents, such as oxidation of 1,2-diols [37, 38], oxidation of alkynes [39–49], oxidation of alkenes [50], oxidation of  $\alpha$ -methylene ketones [51], rearrangement of  $\alpha,\beta$ -epoxyketones [52–54], oxidation of vicinal dihaloalkenes [55], oxidation of epoxides [56], oxidation of 1,3-diols [57], and oxidation with molecular oxygen. They have been catalyzed by trichloroxyvanadium [58], nickel-aluminum hydrotalcite [59], and chiral cobalt complex [60], while palladium-catalyzed oxidation of benzoin to benzil was achieved by using CsOH or  $K_2CO_3$  as a base [61–63]. Porphyrins and metalloporphyrin complexes have been used in numerous biological systems [64]. Various synthetic metalloporphyrins have been studied such as the cytochrome P-450 model and as the catalyst for oxidation of alcohols, hydrocarbons and epoxidation of alkenes using molecular oxygen and various oxygen transfer reagents [65–69]. Iron porphyrins are well known, and many studies have been devoted to elucidating and using catalysts for alkane hydroxylation, oxidation of alkanes to alcohols or ketones, and oxidation of hydrocarbons [70–73]. Stoichiometric amounts of a strong oxidant are needed for the generation of metalloporphyrins [74]. The photosensitized production of singlet oxygen has significance in the photooxidation of organic compounds, DNA damage, and photodynamic therapy [75–77], such that a variety of these photosensitizers have been developed and extensively studied [78–83].

## Experimental

### General procedure for the synthesis of porphyrins

$H_2TPP$  (Tetraphenylporphyrin),  $H_2TMP$  (Tetramesitylporphyrin),  $H_2TPFPFPP$  (Tetra(pentafluorophenyl) porphyrin),  $ClFeTMP$ ,  $ClFeTPP$ ,  $ClFeTPFPFPP$  and  $ZnTMP$  were synthesized and purified using Lindsey's Method and metallated according to Adler [84–86]. Metallated and non-metallated sensitizers were characterized by UV–Vis and  $^1H$  NMR spectra.

### General procedure for the synthesis of benzoin

To a solution of aldehydes (15 mmol) in EtOH (8 mL) was added a solution of NaCN (6.3 mmol) in  $H_2O$  (1.5 mL). After stirring at reflux (80 °C) for 2 h, the reaction mixture was cooled to room temperature, concentrated in vacuo, and extracted with  $CH_2Cl_2$  and saturated aqueous  $NaHCO_3$ . The combined organic layers were dried over  $Na_2SO_4$  and concentrated in vacuo. The residue was purified by flash column chromatography to give benzoin substrates [87–89].

### General procedure for the synthesis of benzil

The benzoin (1.0 mmol) and a 1 mL  $CH_2Cl_2$  solution of the porphyrins ( $1.0 \times 10^{-3}$  mmol) were dissolved in 14 mL of  $CH_3CN$  in a quartz tube. Air was bubbled through the solution and the samples were irradiated using visible light

or sunlight for 24 h. The solvent was removed under vacuum, and the residue was separated by column chromatography (silica gel, *n*-hexane/EtOAc, 3:1) to give the corresponding benzil.

## Spectral data

### Benzil

Yellow solid, Mp: 95–96 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 7.50 (t,  $J = 8.0$  Hz, 4H); 7.69 (t,  $J = 7.2$  Hz, 2H); 7.90–8.00 (4H, m).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 129.0; 130.0; 133.1; 135.0; 194.7. Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{O}_2$ : C, 79.98; H, 4.79; found C, 79.95; H, 4.69.

### 1,2-Dip-tolyethane-1,2-dione

Yellow solid. Mp: 103–104 °C  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 2.33 (6H, s); 7.20 (4H, d,  $J = 8.1$  Hz); 7.77 (4H, d,  $J = 8.1$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 22.1; 129.8; 130.2; 130.8; 146.0; 194.6. Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_2$ : C, 80.65; H, 5.92; found C, 80.65; H, 5.92.

### 1,2-Bis(3-Methoxyphenyl)ethane-1,2-dione

Yellow solid, Mp: 82 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 3.80 (6H, s); 7.10–7.20 (2H, m); 7.40 (2H, t,  $J = 8.0$  Hz); 7.45–7.50 (2H, m); 7.50–7.50 (2H, m).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 55.4; 113.8; 122.1; 123.3; 130.0; 134.5; 160.4; 194.0. Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_4$ : C, 71.10; H, 5.22; found C, 71.08; H, 5.12.

### 1,2-Bis(4-Chlorophenyl)ethane-1,2-dione

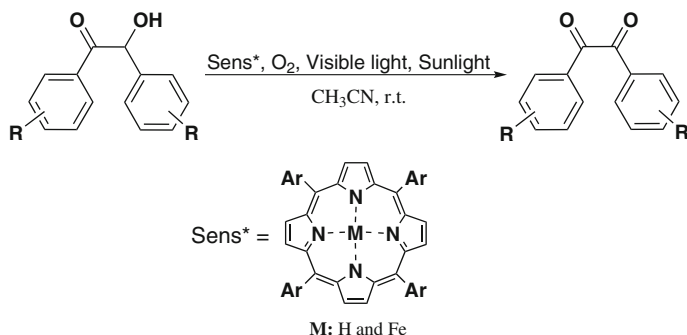
Yellow solid, Mp: 195–196 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 7.50 (4H, d,  $J = 8.6$ ); 7.92 (4H, d,  $J = 8.6$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 129.7; 131.3; 131.4; 142.0, 192.5. Anal. Calcd. for  $\text{C}_{14}\text{H}_8\text{Cl}_2\text{O}_2$ : C, 60.24; H, 2.89; found C, 60.20; H, 2.85.

### 1,2-Bis(4-Bromophenyl)ethane-1,2-dione

Yellow solid, Mp: 224–226 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 7.65 (4H, d,  $J = 8.0$  Hz); 7.80 (4H, d,  $J = 8.0$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 130.9; 131.4; 131.7; 132.7; 192.7. Anal. Calcd. for  $\text{C}_{14}\text{H}_8\text{Br}_2\text{O}_2$ : C, 45.69; H, 2.19; found C, 45.60; H, 2.09.

### 1,2-Di(Naphthalen-2-yl)ethane-1,2-dione

Yellow solid, Mp: 156–158 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 7.50–7.58 (2H, m); 7.63 (2H, m); 7.86–7.97 (6H, m); 8.17 (2H, m); 8.49 (2H, s).  $^{13}\text{C}$  NMR (75 MHz,



**Scheme 1** Oxidation of benzoin to benzils

$\text{CDCl}_3$ ):  $\delta$ : 123.5; 127.3; 128.0; 129.2; 129.7; 130.1; 130.5; 132.4; 133.7; 136.4; 194.7. Anal. Calcd. for  $\text{C}_{22}\text{H}_{14}\text{O}_2$ : C, 85.14; H, 4.55; found C, 85.04; H, 4.45.

## Results and discussion

Many investigations for the preparation of benzils such as the reaction of oxalyl chloride with organostannanes, oxidation of alkynes, aldehyde condensation, and oxidation of alcohols have been documented. In view of significant drawbacks, such as the use of toxic and expensive reagents, high temperature, stoichiometric amounts of reagents, and low yield of these methods [90–94], a more efficient catalytic system is in high demand.

In continuation, here we would like to report a highly efficient catalytic system for the aerobic oxidation of benzoin derivatives using porphyrins as catalyst, which can be smoothly oxidized to corresponding benzils. Photooxygenation was performed in solutions of acetonitrile under visible light or sunlight in the presence of porphyrins under 1 atm pressure of air at room temperature (Scheme 1).

The catalytic activity of different metalloporphyrins and structurally different free base porphyrins for the oxidation of benzoin to benzil compounds by molecular oxygen were investigated by using 2-hydroxy-1,2-diphenylethanone as a model substrate. The engaged metals for the oxidation reactions were Fe, Mn, and Zn, and ( $\text{H}_2\text{TPP}$ ), ( $\text{H}_2\text{TMP}$ ), and ( $\text{H}_2\text{TPFPP}$ ) were employed to cover different electronic properties. The results are summarized in Table 1. The oxidation of 2-hydroxy-1,2-diphenylethanone catalyzed by these catalysts produced benzil as the product. The catalytic activity of metalloporphyrins for oxidation appears to be dependent on the nature of the central ions.  $\text{ClFeTMP}$  porphyrin showed the best activity among the three simple structure metalloporphyrin catalysts, and presented an excellent catalytic performance for the oxidation of 2-hydroxy-1,2-diphenylethanone in mild conditions. The catalytic activation of the four metalloporphyrins were in the sequence:  $\text{ClFeTMP} > \text{ClMnTMP} > \text{Mn(TDCPP)Cl} > \text{Mn(TDFPP)Cl} > \text{Mn(TPFPP)Cl} = \text{ZnTMP}$ . The order for reactivity of the free base ligands was  $\text{H}_2\text{TMP} > \text{H}_2\text{TPP} > \text{H}_2\text{TPFPP}$ , showing that electron donation to the porphyrin rings facilitates the conversion of

**Table 1** Effect of porphyrins on the photooxidation of 2-hydroxy-1,2-diphenylethanone to benzil

Entry	Catalyst	Yield of benzil (%)
1	H <sub>2</sub> TMP	90
2	H <sub>2</sub> TPP	55
3	H <sub>2</sub> TPFPP	Trace
4	ClFeTMP	87
5	ClFeTPP	22
6	ClFeTPFPP	23
7	ClMnTMP	60
8	Mn(TDCPP)Cl	10
9	Mn(TDFPP)Cl	5
10	Mn(TPFPP)Cl	Trace
11	ZnTMP	Trace
12	–	0

$1 \times 10^{-6}$  mol porphyrins,  $1 \times 10^{-3}$  mol 2-hydroxy-1,2-diphenylethanone after 24 h irradiation, air (1 atm) and fluorescent circular lamp, in the CH<sub>3</sub>CN solvent

2-hydroxy-1,2-diphenylethanone in our reaction condition. Safari and et al. reported oxidations of alcohols with paramagnetic metals and free base ligands in high yields (Fe and Mn) [95, 96].

In order to obtain the best conditions, various solvents were used for the aerobic oxidation of 2-hydroxy-1,2-diphenylethanone, and the results are summarized in Table 2. Acetonitrile is a good solvent for oxidation reactions, since it is relatively inert toward oxidation, and its tendency toward coordination and interaction with coordination compound is low. In addition, acetonitrile is usually polar enough to dissolve the substrates, products, and the catalyst. For the *m*-THPC (5,10,15,20-tetra(*m*-hydroxyphenyl)chlorin) sensitizer, the singlet oxygen lifetime in DMSO is 19 μs compared to 65 μs in CH<sub>3</sub>CN [97]. According to the literature, DMSO, H<sub>2</sub>O, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH and DMF are singlet oxygen quenchers [98–100]. In addition, it is confirmed that the lifetime of <sup>1</sup>O<sub>2</sub> in acetonitrile is high. The main mechanism which takes place in our reaction conditions may be the generation of singlet oxygens and their reaction with the substrates. Further evidence for a <sup>1</sup>O<sub>2</sub> mechanism was obtained by performing the photooxygenation in the presence of N<sub>3</sub><sup>−</sup>, which is known as a singlet oxygen scavenger [95, 96, 101]. Entry 4 in Table 2 shows that the yield of free base porphyrin was considerably reduced under these conditions. In the presence of N<sub>3</sub><sup>−</sup>, degradation of the porphyrin sensitizers was also inhibited.

The effect of light sources on the aerobic oxidation of 2-hydroxy-1,2-diphenylethanone to benzil catalyzed by H<sub>2</sub>TMP and ClFeTMP was investigated. As shown in Table 3, it seems that the conversion of 2-hydroxy-1,2-diphenylethanone was closely related with sunlight or white light. However, the reaction rate is considerably increased with the UV light.

It occurred to us that this reaction might proceed under solar irradiation because the spectral distribution curves of a fluorescent lamp and visible light were similar

**Table 2** Effect of solvent on the photooxidation of 2-hydroxy-1,2-diphenylethanone to benzil

Entry	Solvent	Yield (%)	
		H <sub>2</sub> TMP	ClFeTMP
1	Acetonitrile	90	87
2	Dimethyl formamide	Trace	Trace
3	Dimethyl sulfoxide	Trace	Trace
4	NaN <sub>3</sub> /Na <sub>2</sub> SO <sub>3</sub> /acetonitrile	–	85
5	H <sub>2</sub> O	Trace	Trace
6	CH <sub>3</sub> OH	Trace	Trace
7	C <sub>2</sub> H <sub>5</sub> OH	Trace	Trace

$1 \times 10^{-6}$  mol porphyrins,  $1 \times 10^{-3}$  mol 2-hydroxy-1,2-diphenylethanone after 24 h irradiation

**Table 3** Effect of light on the photooxidation of 2-hydroxy-1,2-diphenylethanone

Entry	Source	Time (h)	Yield for H <sub>2</sub> TMP (%)	Yield for ClFeTMP (%)
1	White light	24	90	87
2	Sunlight	20	90	87

$1 \times 10^{-6}$  mol porphyrins,  $1.0 \times 10^{-3}$  mol 2-hydroxy-1,2-diphenylethanone

to that of sunlight. Furthermore, in accordance with the concept of ‘green chemistry’, solar radiation is an infinite source of clean energy. In continuation, we checked the generality of the method, in which a variety of benzoin s were oxidized to benzil compounds with H<sub>2</sub>TMP and ClFeTMP in moderate to excellent yields at room temperature with sunlight irradiation. The reactions were performed in a tube without any particular precautions. As shown in Table 4, this catalytic system was applicable to a wide range of benzoin substrates.

A possible mechanism for the formation of products with H<sub>2</sub>TMP and ClFeTMP porphyrin is shown in Scheme 2. Thus, in the presence of H<sub>2</sub>TMP formation singlet oxygen, there may be a new photochemical pathway that involves the overall insertion of molecular oxygen into the C–H bond of the alcohols **1** to form benzoin s **2**. Furthermore, independent photolysis of 2-hydroperoxy-2-hydroxy-1,2-diphenylethanone **2** in CH<sub>3</sub>CN results in the formation of **3**, which is the only product [95, 96, 102]. Compound **3** decomposes further to the final product **4** and hydrogen peroxide which is a by-product. In the presence of ClFeTMP as a catalyst and oxygen, formation of intermediate **5** from photo-homolysis of **5** was formed through the reaction of Fe(II)TMP. The existence of Iron (II) comes from the homolysis of ClFeTMP [80, 95, 96, 103]. Iron(IV)–oxo intermediates activate alcohols exclusively by H-atom abstraction from the R-CH group of alcohol and result in the formation of **7**. Formation of **4** possibly occurred by a dual hydrogen abstraction mechanism as previously proposed [95, 96, 103–105]. Safari et al. have proven these mechanisms [95, 96].

**Table 4** Oxidation of benzoin to benzil in the presence of H<sub>2</sub>TMP and ClFeTMP under visible light irradiation or sunlight

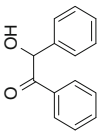
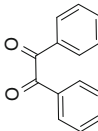
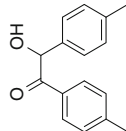
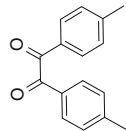
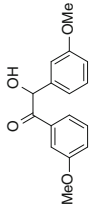
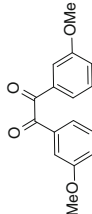
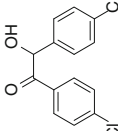
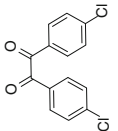
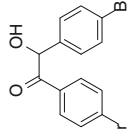
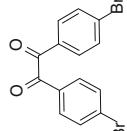
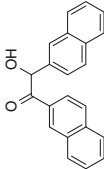
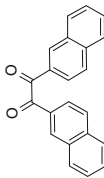
Entry	Benzoin	Benzil	Time (h)	Yield (%)		Mp °C		Reported[97]	
				H <sub>2</sub> TMP <sup>a</sup>		ClFeTMP <sup>b</sup>			Found
				Visible light	Sunlight	Visible light	Sunlight		
1			24	90	91	87	89	95–96	94–95
2			24	89	90	85	85	103–104	103–105
3			24	90	91	87	85	82	82–83
4			24	82	83	80	83	195–196	195–198
5			24	85	89	82	85	224–226	224–226

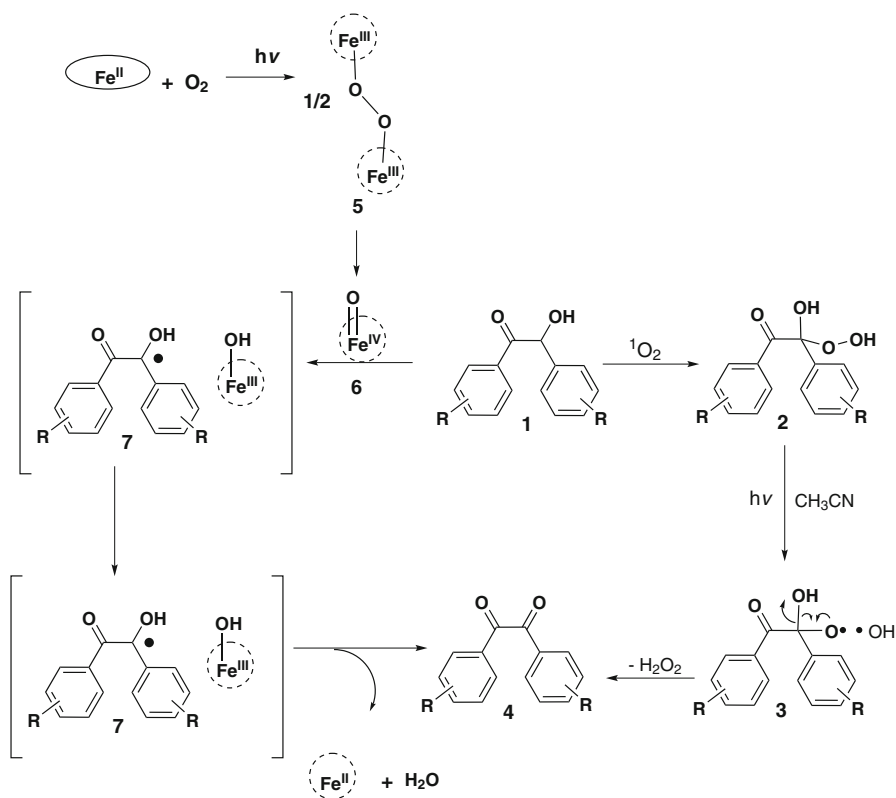
Table 4 continued

Entry	Benzoin	Benzil	Time (h)	Yield (%)		Mp °C			
				H <sub>2</sub> TMP <sup>a</sup>		Found	Reported[97]		
				Visible light	Sunlight			Visible light	Sunlight
6			24	75	75	70	71	156–158	156–157

<sup>a</sup>  $1.0 \times 10^{-6}$  mol H<sub>2</sub>TMP and  $1.0 \times 10^{-3}$  mol benzoin as substrates, air (1 atm) and fluorescent circular lamp or sunlight

<sup>b</sup>  $1.0 \times 10^{-6}$  mol ClFeTMP and  $1.0 \times 10^{-3}$  mol benzoin as substrates, air (1 atm) and fluorescent circular lamp or sunlight





**Scheme 2** Proposed mechanism

## Conclusion

We have developed a very simple and efficient aerobic photooxidation reaction for the conversion of benzoin to benzil using a catalytic amount of a nonmetallated and metallated porphyrins in the presence of visible light irradiation of a fluorescent lamp or sunlight and air in  $\text{CH}_3\text{CN}$ . This novel method is thought to be convenient, green in view of the use of the catalyst, and environmentally friendly. This method is of great value from the perspectives green chemistry and organic synthesis due to its use of inexpensive and harmless visible light irradiated from a general purpose fluorescent lamp or sunlight, and molecular oxygen as terminal oxidant. Further application of this photooxidation to other reactions is now in progress in our laboratory.

**Acknowledgment** We gratefully acknowledge financial support from the Research Council of Islamic Azad University of Karaj.

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## References

1. K.C. Nicolaou, D.L.F. Gray, J. Tae, *J. Am. Chem. Soc.* **126**, 613 (2004)
2. M.R. Angelstro, S. Mehdi, J.P. Burkhart, N.P. Peet, P. Bey, *J. Med. Chem.* **33**, 11 (1990)
3. E.S. Krongauz, *Russ. Chem. Rev.* **46**, 59 (1977)
4. E.J. Corey, D.H. Lee, S. Sarshar, *Tetrahedron Asymmetry* **6**, 3 (1995)
5. A. Ryoda, N. Yajima, T. Haga, T. Kumamoto, W. Nakanishi, M. Kawahata, K. Yamaguchi, T. Ishikawa, *J. Org. Chem.* **73**, 133 (2008)
6. L.R. Hillis, R.C. Ronald, *J. Org. Chem.* **50**, 470 (1985)
7. D.H.S. Yu, J.M. Torkelson, *Macromolecules* **21**, 852 (1988)
8. F. Catalina, C. Peinado, M. Blanco, A. Alonso, N.S.J. Allen, *Photochem. Photobiol. A* **131**, 141 (2000)
9. P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary, *Polym. Degrad. Stab.* **90**, 577 (2005)
10. Z. Szablan, T.M. Lovestead, T.P. Davis, M.H. Stenzel, C. Barner-Kowollik, *Macromolecules* **40**, 26 (2007)
11. M. Friedman, *J. Org. Chem.* **30**, 859 (1965)
12. K.M. Kadish, E. Van Caemelbecke, F. DSouza, M. Lin, D.J. Nurco, C.J. Medforth, T.P. Forsyth, B. Krattinger, K.M. Smith, S. Fukuzumi, I. Nakanishi, J. Shelnut, A. Inorg. Chem. **38**, 2188 (1999)
13. G. Du, G.A. Mirafzal, L.K. Woo, *Organometallics* **23**, 4230 (2004)
14. A.S. Kiselyov, *Tetrahedron Lett.* **36**, 493 (1995)
15. M.H. Nantz, D.A. Lee, D.M. Bender, A.H. Roohi, *J. Org. Chem.* **57**, 6653 (1992)
16. E.C. Taylor, J.E.L.G. Macor, J. French, *Org. Chem.* **56**, 1807 (1991)
17. I. Flament, M. Stoll, *Helv. Chim. Acta* **50**, 1754 (1967)
18. T.E. Barta, M.A. Stealey, P.W. Collins, R.M. Weier, *Bioorg. Med. Chem. Lett.* **8**, 3443 (1998)
19. Z. Zhao, D.D. Wisnoski, S.E. Wolkenberg, W.H. Leister, Y. Wang, C.W. Lindsley, *Tetrahedron Lett.* **45**, 4873 (2004)
20. I. Held, S.J. Xu, H. Zipse, *Synthesis* **8**, 1185 (2007)
21. F. Rong, S. Chow, S. Yan, G. Larson, Z. Hong, Wu, J. *Bioorg. Med. Chem. Lett.* **17**, 1663 (2007)
22. W.G. Dauben, K.L. Lorenz, D.W. Dean, G. Shapiro, I. Farkas, *Tetrahedron Lett.* **39**, 7079 (1998)
23. S. Danishefsky, R. Zamboni, M. Kahn, S.J. Etheredge, *J. Am. Chem. Soc.* **103**, 3460 (1981)
24. J.L. Hyatt, V. Stacy, R.M. Wadkins, K.J.P. Yoon, M. Wierdl, C.C. Edwards, M. Zeller, A.D. Hunter, M.K. Danks, G. Crundwell, P.M. Potter, *J. Med. Chem.* **48**, 5543 (2005)
25. B.I. Ita, O.E. Offiong, *Mater. Chem. Phys.* **70**, 330 (2001)
26. M.R. Ams, C.S. Wilcox, *J. Am. Chem. Soc.* **129**, 3966 (2007)
27. N. Zinin, *Ann. Chem. Pharm.* **34**, 186 (1840)
28. M. Weiss, M. Appel, *J. Am. Chem. Soc.* **70**, 3666 (1948)
29. A. McKillop, B.P. Swann, M.E. Ford, E.C. Taylor, *J. Am. Chem. Soc.* **95**, 3641 (1973)
30. S. Ranganathan, D. Ranganathan, P.V. Ramachandran, *Tetrahedron* **40**, 3145 (1984)
31. M. Hirano, M. Oose, T. Morimoto, *Bull. Chem. Soc. Jpn.* **64**, 1046 (1991)
32. S.A. Tymonko, B.A. Nattier, R.S. Mohan, *Tetrahedron Lett.* **40**, 7657 (1999)
33. V.V. Namboodiri, V. Polshettiwar, R.S. Varma, *Tetrahedron Lett.* **48**, 8839 (2007)
34. C.T. Shei, H.L. Chien, K. Sung, *Synlett* **7**, 1021 (2008)
35. C. Joo, S. Kang, S.M. Kim, H. Han, J.W. Yang, *Tetrahedron Lett.* **51**, 6006 (2010)
36. G. Du, L.K. Woo, J. Porphyrins Phthalocyanines **9**, 206 (2005)
37. S.L. Jain, V.B. Sharma, B. Sain, *Tetrahedron Lett.* **45**, 1233 (2004)
38. J.M. Khurana, B.M. Kandpal, *Tetrahedron Lett.* **44**, 4909 (2003)
39. J.N. Moorthy, N. Singhal, K. Senapati, *Tetrahedron Lett.* **47**, 1757 (2006)
40. R. Zibuck, D. Seebach, *Helv. Chim. Acta* **71**, 237 (1988)
41. H. Gopal, A.J. Gordon, *Tetrahedron Lett.* **12**, 2941 (1971)
42. D.G. Lee, V.S. Chang, *J. Org. Chem.* **44**, 2726 (1979)
43. S. Wolfe, W.R. Pilgrim, T.F. Garrard, P. Chamberlain, *Can. J. Chem.* **49**, 1099 (1971)
44. A. McKillop, O.H. Oldenzel, B.P. Swann, E.C. Taylor, R.L. Robey, *J. Am. Chem. Soc.* **95**, 1296 (1973)
45. W. Ren, Y. Xia, S. Ji, Y. Zhang, X. Wan, J. Zhao, *Org. Lett.* **11**, 1841 (2009)
46. K. J. Tan, U. Wille, *Chem. Commun.* 6239 (2008)
47. M. Niu, H. Fu, Y. Jiang, Y. Zhao, *Synthesis* **18**, 2879 (2008)

48. S. Dayan, I. Ben-David, S. Rozen, *J. Org. Chem.* **65**, 8816 (2000)
49. Y. Sawaki, H. Inoue, Y. Ogata, *Bull. Chem. Soc. Jpn.* **56**, 1133 (1983)
50. Yusubov, V.D. Filimonov, V.P. Vasilyeva, *Synthesis* **10**, 1234 (1995)
51. N. Rabjohn, *Org. React.* **24**, 261 (1976)
52. C.L. Chang, M.P. Kumar, R.S. Liu, *J. Org. Chem.* **69**, 2793 (2004)
53. T.B. Rao, J.M. Rao, *Synth. Commun.* **23**, 1527 (1993)
54. K. Suda, K. Baba, S. Nakajima, T. Takanami, *Chem. Commun.* 2570 (2002)
55. F.A. Khan, B. Prabhudas, J. Dash, N. Sahu, *J. Am. Chem. Soc.* **122**, 9558 (2000)
56. S. Antonioti, E. Dunach, *Chem. Commun.* 2566 (2001)
57. J.S. Yadav, S.K. Biswas, R. Srinivas, *Synthesis* **24**, 4237 (2006)
58. M. Kirihara, Y. Ochiai, S. Takizawa, H. Takahata, H. Nemoto, *Chem. Commun.* 1387 (1999)
59. B.M. Choudary, M.L. Kantam, A. Rahman, C.V. Reddy, K.K. Rao, *Angew. Chem. Int. Ed.* **40**, 763 (2001)
60. S.K. Alamsetti, P. Muthupandi, G. Sekar, *Chem. Eur. J.* **15**, 5424 (2009)
61. C. Qin, J. Chen, H. Wu, J. Cheng, Q. Zhang, B. Zuo, W. Su, J. Ding, *Tetrahedron Lett.* **49**, 1884 (2008)
62. W. Zhang, M. Liu, H. Wu, J. Ding, J. Cheng, *Tetrahedron Lett.* **49**, 5336 (2008)
63. Q. Zhang, C.M. Xu, J.X. Chen, X.-L. Xu, J.C. Ding, H.Y. Wu, *Appl. Organomet. Chem.* **23**, 524 (2009)
64. G.J. Abhilash, J. Bhuyan, P. Singh, S. Maji, K. Pal, S. Sarkar, *Inorg. Chem.* **48**, 1790 (2009)
65. G.J. Abhilash, J. Bhuyan, P. Singh, S. Maji, K. Pal, S. Sarkar, *Inorg. Chem.* **48**, 1790 (2009)
66. M. Haranaka, A. Hara, W. Ando, T. Akasaka, *Tetrahedron Lett.* **50**, 3585 (2009)
67. G. Huang, S.Y. Liu, Y.A. Guo, A. Wang, J. Luo, C.C. Cai, *Appl. Catal. A* **350**, 173 (2009)
68. M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork, H. kargar, *Molecular Catalysis A* **288**, 116 (2008)
69. M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, A.A. Abbasi-Larki, *Applied Catalysis A* **349**, 177 (2008)
70. A.R. Han, Y.J. Jeong, Y. Kang, J.Y. Lee, M.S. Seo, W. Nam, *Chem. Commun.* **9**, 1076 (2008)
71. J.E.L. Ellis, *Coord. Chem. Rev.* **105**, 181 (1990)
72. A. Maldotti, C. Bartocci, G. Varani, A. Molinari, *Inorg. Chem.* **35**, 1126 (1996)
73. H.R. Khavasi, N. Safari, *J. Mol. Catal. A* **220**, 127 (2004)
74. V.N. Korotchenko, K. Severin, M.R. Gagn, *Org. Biomol. Chem.* **6**, 1961 (2008)
75. M.C. Derosa, R.J. Crutchley, *Coord. Chem. Rev.* **351**, 233 (2002)
76. A. Greer, *Acc. Chem. Res.* **39**, 797 (2006)
77. M. Hajimohammadi, F. Bahadoran, S.S.H. Davarani, N. Safari, *React. Kinet. Mech. Catal.* **99**, 243 (2010)
78. R.W. Redmond, J.N. Gamlin, *Photochem. Photobiol.* **70**, 391 (1999)
79. R. Bonnett, *Chem. Soc. Rev.* **24**, 19 (1995)
80. L. Weber, R. Hommel, J. Behling, G. Haufe, H. Hennig, *J. Am. Chem. Soc.* **116**, 2400 (1994)
81. R.K. Pandey, G. Zheng, in *The Porphyrin Handbook*, ed. by K.M. Kadish, K.M. Smith, R. Guilard (Academic Press, New York, 2000), p. 157
82. S.K. Pushpan, S. Venkatraman, V.G. Anand, J. Sankar, D. Parmeswaran, S. Ganesan, T.K. Chandrashekar, *Curr. Med. Chem. Anticancer Agents.* **2**, 187 (2002)
83. E.S. Nyman, P.H. Hynninen, *J. Photochem. Photobiol. B* **73**, 1 (2004)
84. J.S. Lindsey, R.W. Wagner, *J. Org. Chem.* **54**, 828 (1989)
85. J. Adler, *Inorg. Nucl. Chem.* **32**, 2443 (1970)
86. B. Boens, P.A. Faugeras, J. Vergnaud, R. Lucas, K. Teste, R. Zerrouki, *Tetrahedron* **66**, 1994 (2010)
87. P. Singh, A. Mittal, S. Kumar, *Bioorg. Med. Chem.* **15**, 3990 (2007)
88. P. Hoyos, G. Sansottera, M. Fernández, F. Molinari, J.V. Sinisterra, A.R. Alcantara, *Tetrahedron* **64**, 7929 (2008)
89. Y. Shimakawa, T. Morikawa, S. Sakaguchi, *Tetrahedron Lett.* **51**, 1786 (2010)
90. T. Kashiwabara, M. Tanaka, *J. Org. Chem.* **74**, 3958 (2009)
91. A. Giraud, O. Provot, J. Franç, O. Peyrat, M. Alami, J.D. Brion, *Tetrahedron* **62**, 7667 (2006)
92. Y. Shimakawa, T. Morikawa, S. Sakaguchi, *Tetrahedron Lett.* **51**, 1786 (2010)
93. C. Joo, S. Kang, S.M. Kim, H. Han, J.W. Yang, *Tetrahedron Lett.* **51**, 6006 (2010)
94. J.M. Khurana, B.M. Kandpal, *Tetrahedron Lett.* **44**, 4909 (2003)
95. M. Hajimohammadi, N. Safari, H. Mofakham, F. Deyhimi, *Green Chem.* **13**, 991 (2011)
96. M. Hajimohammadi, N. Safari, H. Mofakham, A. Shaabani, *Tetrahedron Lett.* **51**, 4061 (2010)

97. Y. Chen, S. Xu, L. Li, M. Zhang, J. Shen, T. Shen, *Dye. Pigment.* **51**, 63 (2001)
98. I. Kruk, A.E. Hassan, T. Michalska, K. Ichszteld, K. Kubasik-Kladna, S. Olgen, *Luminescence* **22**, 379 (2007)
99. A. Ogunsipe, J.Y. Chen, T. Nyokong, *New J. Chem.* **28**, 822 (2004)
100. S. He, L. Jiang, B. Wu, Y. Pan, C. Sun, *Biochem. Biophys. Res. Commun.* **379**, 283 (2009)
101. J.R. Harbour, S.L. Issler, *J. Am. Chem. Soc.* **104**, 903 (1982)
102. P. Wan, S. Muralidharaina, I. Cauley, C.A. Babbage, *Can. J. Chem.* **65**, 1775 (1987)
103. W. Nam, *Acc. Chem. Res.* **40**, 522 (2007)
104. Y.-M. Lee, S. Hong, Y. Morimoto, W. Shin, S. Fukuzumi, W.J. Nam, *Am. Chem. Soc.* **132**, 10668 (2010)
105. N.Y. Oh, Y. Suh, M.J. Park, M.S. Seo, J. Kim, W. Nam, *Angew. Chem. Int. Ed.* **117**, 4307 (2005)