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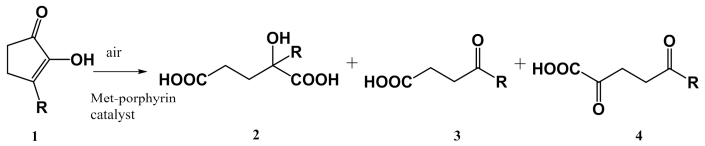

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Aerobic cascade oxidation of substituted cyclopentane-1,2-diones using metalloporphyrin catalysts

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ABSTRACT

A method for the aerobic cascade oxidation of cyclopentane-1,2-diones using metal porphyrins as catalysts, yielding hydroxydiacids **2**, ketoacid **3** and diketoacids **4** which are the intermediates of important biologically active compounds is reported. This method is operationally simple and can be employed under ambient conditions.

1. Introduction

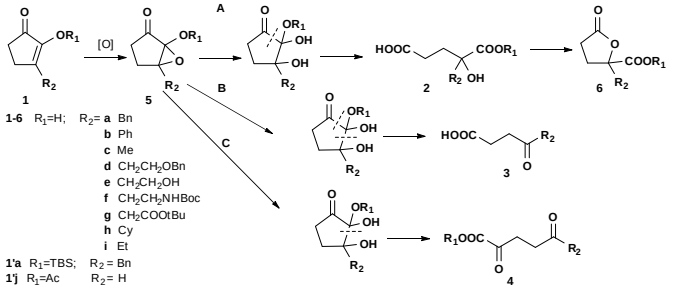
Currently, the development of sustainable chemical processes is one of the major challenges in chemical engineering and applied science. Over the past decades, various transition metal catalysts have been successfully utilized in combination with different oxidizing reagents, such as peroxides, hydroperoxides, peracids and others, to convert alkenes to epoxides or carbonyl compounds.[1,2,3] However, from both economic and ecological points of view, the use of atmospheric oxygen as a terminal oxidant is more attractive due to its high natural abundance (nearly 20% of air is oxygen) and environmental sustainability. The main limitation for wide application of atmospheric oxygen in oxidation reactions is its relatively low reactivity in ambient conditions and lack of selectivity. Therefore, the selection of a catalyst is vital to carry out aerobic oxidations of different substrates in an efficient manner. Among known catalysts for performing aerobic oxidations of organic compounds,[4,5] synthetic metalloporphyrins, mimics of the oxygen carrier and oxidation catalyst in living organisms, are remarkably efficient and prospective.[6,7] In contrast to natural enzymatic systems, the selectivity of artificial catalysts is governed by the careful choice of a transition metal ion and by modifications in the skeleton of the porphyrin catalyst.[6]

Metalloporphyrin-catalyzed air oxidation has so far been used sparsely in organic syntheses to oxidize various compounds and functional groups. For example, it has been used in the oxidation of alkanes,[7-13] alkenes,[7,11,14-16] aromatic hydrocarbons,[7,17,18] steroids,[19,20] and aldehydes.[11] The listed examples represent only oxidation reactions, without considering subsequent transformations. However, in the preparation of pharmaceuticals or complex biologically active compounds, as a rule, a multi-step synthesis is necessary. Therefore, the development of catalytic conditions to assist reaction cascades is of importance.

In the present paper we report the first example of a cascade air oxidation of reactive organic molecules. Substituted cyclopentane-1,2-diones (**1**, Scheme 1) have been chosen as substrates because of their multiple functional groups sensitive to oxidation, allowing the formation of oxidation cascades which result in producing hydroxydiacid **2**. Also, the other oxidation products[21-23] of these structures have demonstrated interesting biological activities (e.g. clionamides[22] and dichotomain B.[23]). Hydroxydiacids **2** have also been used as precursors for the synthesis of nucleoside analogues[24] and HIV-1 protease inhibitors.[25] On the other hand, ketoacid **3** is also a viable substrate for the synthesis of γ-lactones[26], whilst diketoacid **4** is a valuable precursor for the synthesis of heterocycles, including bioactive compounds.[27] Moreover, hydroxydiacid **2** contains an asymmetric center, which may open up additional opportunities for the elaboration of an enantioselective oxidation approach using chiral porphyrin catalysts.[28,29]

We found that enol derivatives **1** can be easily oxidized by air, using a catalytic amount of metalloporphyrin catalyst (1-5 mol%), affording 2-substituted-2-hydroxydiacids **2**, and other ring-cleaved compounds, such as ketoacids **3** and diketoacids **4**. On the basis of our earlier studies,[30,31] we can suggest a following cascade of occurring aerobic oxidation reactions (Scheme 1): in all cases the first reaction is the epoxidation of the enol double bond (formation of intermediate **5**). The second oxidation reaction that may depend on the oxidizing reagent is a Baeyer-Villiger reaction leading to hydroxydiacid **2** (which easily

convers to lactone acid **6**, route A), or the combination of a Bayer-Villiger reaction and diol cleavage resulting in ketoacid **3** (route B), or only a diol cleavage reaction yielding the diketoacid **4** product (route C). The reactions proceed under mild conditions, at ambient temperature and normal air pressure, and the method is operationally simple (see supplementary info).



Scheme 1. Reaction oxidative cascade of **1.**

2. Results and discussion

For initial catalyst screening, conventional 3-benzylsubstituted ketoenol (**1a**) was a selected as a substrate. The most frequently used transition metal complexes (Mn, Fe, and Co) of octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) were used as catalysts (Table 1 and Figure 1).

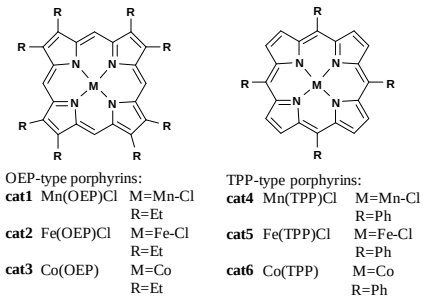


Figure 1. Used TPP- and OEP-type metalloporphyrin metal complexes.

Table 1. Oxidation of 3-benzyl-cyclopentane-1,2-dione **1** (enol form) with air using different porphyrin metal complexes as a catalyst.

No	Catalyst	Loading mol%	Unreacted 1a,%	Products,%		
				2a	3a	4a
1	-	-	81	10	9	-
2	cat1	5	-	33	67	-
3	cat2	5	30	-	30	40
4	cat3	5	49	-	18	33
5	cat4	5	-	54	46	-
6	cat4	1	3	55	42	-
7	cat5	5	31	-	37	32
8	cat6	5	20	8	24	48

Reaction conditions: $CDCl_3$; rt; 5 mol% catalyst; 24 h. Product composition determined by ^1H NMR.

The oxidation of **1a** without presence of catalyst proceeds, as expected, considerably slower (81% of unreacted substrate), without any selectivity (Table 1, No. 1). In reactions with the catalysts, it was found that formation of different products **2a**, **3a** or **4a** was highly dependent on the central metal ion of the porphyrin complex. In the case of the Mn complexes **cat1** and **cat4** (Table 1, No. 2, 5 and 6) mostly diacid **2a** and ketoacid **3a** were formed, while diketoacid **4a** was not observed (route A and route B). However, with Co (**cat3** and **cat6**) and with Fe porphyrin complexes (**cat2** and **cat5**) the reaction yielded mostly diketoacid **4a** and ketoacid **3a** (route C and double oxidation according to route B; Table 1, No. 3, 4, 7 and 8). The yield of hydroxydiacid **2a** was up to 55% in the best case with Mn catalyst (Table 1, No. 6), for ketoacid **3a** the highest yield was 67% (Table 1, No. 2) and for **4a** 48% (Table 1, No. 8).

The substrate was completely consumed in the case of Mn catalysts (**cat1** and **cat4**; Table 1, No. 2 and 5). However, it the case of Fe catalysts (**cat2** and **cat5**) and with Co catalysts **cat3** and **cat6**, a certain amount of substrate remained unreacted (from 20 to 49%; Table 1, No. 3, 4, 7 and 8). From Mn catalysts Mn(TPP)Cl **cat4** was more efficient, affording a considerably higher yield of the target product hydroxyl diacid **2a** than **cat1**; (55% vs 33%; Table 1, No. 2 and 6). It was also found that **cat4** was efficient even with 1 mol% of catalyst (Table 1, No. 6). However, with preliminary results Mn catalysts had poor chemoselectivity: pathways A and B formed an almost equimolecular mixture of compounds **2** and **3** (55% to 42% in the best case). To follow the formation of **2a** and **3a**, the kinetics of these compounds were monitored by ^1H NMR. The obtained curves clearly indicate that hydroxydiacid **2a** and ketoacid **3a** form in parallel reactions (Figure 2).

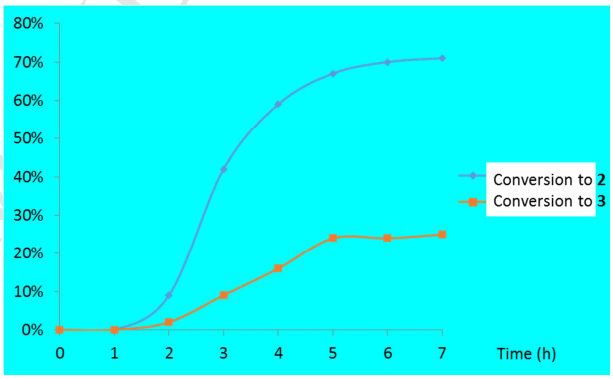


Figure 2 Reaction monitoring results.

An effort was made to affect the relative rates of these reactions by using different solvents and **cat4** because of its highest selectivity towards formation of diacid **2**. The results are presented in Table 2.

Table 2. Solvent and temperature screening with **1a**.

No	Solvent	Temp °C	Time [h]	Additive 10 mol%	Unreacted 1a%	2a,%	3a,%
1	$CDCl_3$	rt	2	-	3	55	42
2	CH_2Cl_2	rt	2	-	-	54	46
3	Benzene	rt	24	-	-	56	44
4	Toluene	rt	18	-	9	75 (63*)	16 (16*)
5	Toluene	5 °C	18	-	11	28	61
6	Toluene	15 °C	18	-	9	61	30
7	Toluene	30 °C	18	-	3	38	59
8	Toluene	40 °C	2	-	6	35	59
9	THF	rt	24	-	100	-	-
10	MeOH	rt	24	-	100	-	-
11	DMC	rt	2	-	69	-	31

12	Toluene	rt	24	pyridine	100	-	-
13	Toluene	rt	24	squaramide	100	-	-
14	Toluene	rt	24	imidazole	12	35	53
15	Toluene	rt	24	BHT	100	-	-
16	Toluene	rt	24	TEMPO**	100	-	-

Catalyst **cat4**; 1 mol%. The composition of the reaction mixtures was determined by ^{1}H NMR.
* Isolated yield.
** 1 equivalent

With the initial chlorinated solvents both transformations were fast but not selective (Table 2, No. 1 and 2). Benzene did not give any improvement in selectivity (Table 2, No. 3). From the investigated solvents the best selectivity for **2** was obtained by using toluene, with a 75/16 ratio of **2a** to **3a** (Table 2, No. 4). The selectivity was very sensitive to temperature- both lowering and increasing of temperature decreased the selectivity towards **2** (Table 2, No. 4-8).

The use of ether solvent (THF) and alcohol (MeOH) completely hindered the reaction (Scheme 2, No. 9 and 10, respectively), while in dimethylcarbonate (DMC) only the formation of 31% of ketoacid **3** was observed (Scheme 2, No. 11).

Previously it has been shown that external ligands are able to accelerate porphyrin-catalyzed oxidation reactions.[33,34] However, in our case the addition of pyridine (10 mol%) or a basic and widely used organocatalyst, squaramide[35] (10 mol%), to the porphyrin complex **cat4** (1 mol%) had a negative impact on the catalytic reaction and no transformation was observed during 24h at rt (Table 2, No. 12 and 13). Another coordination agent, methyl imidazole (10 mol%) redirected the reaction towards the formation of ketoacid **3a** (53%) while the conversion to **2a** was 35% (Table 2, No. 14).

In general, there are several possible mechanisms for metalloporphyrin-catalyzed oxidations, including a radical pathway.[36] Since there are no additional agents, such as oxygen-carriers or reductants in our particular cases, a radical mechanism is the most plausible. In order to support this assumption, the **cat4** mediated reaction was performed in the presence of radical scavengers. It was found that both BHT (10 mol%) and TEMPO (1 eq) blocked the reaction completely (Table 2, No. 15 and 16). This finding supports the radical character of the reaction according to pathway A (see references[37,38]) as a new example of radical Baeyer-Villiger oxidation. The reactivity of other substrates towards oxidation also corroborates our assumption (Table 3).

To elucidate the scope of the reaction, the oxidation of differently substituted enols of cyclopentane-1,2-diones **1** was carried out by using **cat4** as a porphyrin complex. The results are presented in Table 3. First it was found that enols with protected OH are unreactive: the free hydroxyl group is necessary for the oxidation. Thus, substrates **1'a** and **1'j** did not give any products after 24 h. (Table 3, No. 2, 11), which means that the hydroxyl group deprotonation may be the initial step of the reaction. The phenyl group as a substituent at the enol double bond inhibits the reaction. The effect of this substituent on the electron density of the double bond has been studied before.[39] In the case of porphyrin catalysts phenyl substituted substrate **1b** is inert in the oxidation (Table 3, No. 3). At the same time methyl-substituted diketone **1c** afforded tertiary oxidized products in 34% total yield (**2c** in 11% yield, and its *in situ* lactonized derivative **6c** in 23% yield). However, the double oxidation occurred predominantly, affording ketoacid **3c** in 66% yield, after a 24 h reaction (Table 3, No. 4). These results show that the difference in the substituent-dependent electron density on the double bond of substrates and steric hindrance that prevents the formation of catalytic complexes are both important factors for the oxidation reaction catalysed by porphyrins. Indeed, the substrates with electron withdrawing groups and bulky substituents, such as phenyl **1b**, CH_2CH_2NHBoc **1f** and $CH_2COOtBu$ **1g**, make the double-bond too electron-deficient for the reaction to occur or produce the excessive bulkiness which inhibits the oxidation (Table 3, No. 3,7 and 8) whilst with electron-donating and less sterically hindered groups, such as benzyl **1a**, methyl **1c**, CH_2CH_2OBn **1d**, CH_2CH_2OH **1e**, Cy **1h** and ethyl **1i**, the oxidation proceeded more readily (Table 3, No. 1, 4, 5, 6 and 10).

Table 3. Oxidation of substituted substrates **1** with air oxygen in the presence of porphyrin catalyst **cat4**.

No	Substrate	Time	Conversion to **2a-d**	Conversion to **3**/**4**
1	**1a**	18 h	75% (63%*)	16% (16%*) **3a**
2	**1'a**	24 h	-	-
3	**1b**	24 h	-	-
4	**1c**	24 h	11% (and **6c** 23%)	66% **3c**
5	**1d**	48 h	51%*	43%* **3d**
6	**1e**	48 h	33%*	-
7	**1f**	48 h	-	-
8	**1g**	48 h	-	-
9	**1h**	48 h	-	86% **4h**
10	**1i**	48 h	40%*	16%* **3i**
11	**1'j**	24 h	-	-

Catalyst **cat4** (Mn(TPP)Cl); 1 mol%. The composition of the reaction mixtures was determined by ^{1}H NMR.
* Isolated yield

Interestingly, while with most reactive substrates the reaction resulted in diacids **2** and ketoacids **3**, substrate **1h** with bulky Cy group as substituent selectively produced only diketoacid **4h**.

3. Conclusion

The possibility to use environmentally friendly metal complexes of porphyrin for a cascade aerobic oxidation of substituted cyclopentane-1,2-diones was demonstrated. The reactions proceed with moderate to good chemoselectivity to afford the corresponding oxidation products hydroxy diacids **2**, ketoacids **3** and diketoacids **4**. The use of manganese metalloporphyrins affords diacids **2** with up to 75% yield. This method is operationally simple, environmentally benign, does not require the use of harmful oxidants and reductants, and can be used under ambient conditions. Further studies to increase the selectivity, to understand the detail mechanism, and to widen the applicability of this synthetic approach are in progress and will be reported in due course.

4. Experimental section

Full assignment of ^{1}H and ^{13}C chemical shifts is based on the 1D and 2D FT NMR spectra measured on a 400 MHz or 500 MHz instrument. Residual solvent signals were used as internal standards. High resolution mass spectra were recorded by using an Q-TOF LC/MS spectrometer by using ESI ionization. IR spectra were recorded on a Bruker Tensor 27 FT infrared spectrophotometer. Mass spectra were measured on a Shimadzu GCMS – QP 2010 spectrometer using EI (70 eV). Precoated silica gel 60 F254 plates were used for TLC. Column chromatography was performed on a preparative purification

system with silica gel Kieselgel 40-63 µm. Purchased chemicals and solvents were used as received. Petroleum ether has a boiling point of 40-60 °C. The reactions were performed under air atmosphere. The porphyrins used for the reactions were commercially obtained from PorphyChem.

*4.1 Synthesis of diacid **2**.*

A solution of diketone **1a** (18.8 mg, 0.1 mmol) and Mn(TPP)Cl (0.7 mg, 0.001 mmol) in toluene (0.5 mL) is stirred overnight (18 h) at room temperature. The reaction progress is monitored by ^{1}H NMR. After completion, the crude product is purified with column chromatography (CH_2Cl_2:MeOH 100:1-15:1) to afford diacid **2a** (15 mg, 63% isolated yield) and ketoacid **3a** (3 mg, 16% isolated yield) as colourless oils.

*6.2 Synthesis of diketoacid **4**.*

A solution of diketone **1** (18.8 mg, 0.1 mmol) and Fe(TPP)Cl (0.7 mg, 0.001 mmol) in THF (0.5 mL) is stirred overnight (18 h) at room temperature. The reaction progress is monitored by ^{1}H NMR. After completion, the crude product is purified with column chromatography (CH_2Cl_2:MeOH 100:1-15:1) to afford ketoacid **3a** (12 mg, 60% yield) and diketoacid **4a** (3 mg, 20% yield) as unisolable mixture.

2,5-Dioxo-6-phenylhexanoic acid 4a: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 – 7.17 (m, Bn, 5H), 3.75 (s, CH_2-Bn, 2H), 3.14 – 3.06 (m, H-3, 2H), 2.95 – 2.87 (m, H-4, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0 (C-5), 194.4 (C-2), 159.3 (C-1), 133.6 (s-Bn), 129.4 (o or m-Bn), 128.9 (o or m-Bn), 127.3 (p-Bn), 49.6 (C-6), 36.0 (C-4), 31.2 (C-3). HRMS (ESI) calculated for $C_{12}H_{12}O_4$, $[M - H]^-$: 219.0663, found 219.0675. MS (*m/z*): 220, 202, 175, 129, 101, 91, 73, 65, 55. The compound was obtained as a yellow oil.

*4.2 Synthesis of 3-cyclohexyl-2-hydroxycyclopent-2-en-1-one **1h**.*

A 2N HCl solution (0.43 ml) is added to a solution of 2-((tert-butyldimethylsilyl)oxy)-3-cyclohexylcyclopent-2-en-1-one (52 mg, 0.18 mmol) in THF (1 mL). After 5 days, 2 mL of water is added to the reaction mixture and extracted 3x with DCM. The combined organic phase are washed with brine and dried through a phase separator. After column chromatography (Petroleum ether:EtOAc 10:1), compound **1h** is obtained as a yellow oil in 70% yield (25 mg, 0.14 mmol). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.02 – 5.83 (m, 1H), 2.67 (ddd, *J* = 11.5, 8.0, 3.5 Hz, 1H), 2.42 (d, *J* = 5.0 Hz, 2H), 2.40 – 2.36 (m, 2H), 1.84 – 1.67 (m, 5H), 1.46 – 1.28 (m, 5H), 1.28 – 1.15 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 152.3, 147.6, 147.6, 38.1, 31.8, 30.2, 26.2, 26.1, 22.8. HRMS (ESI) calculated for $C_{11}H_{16}O_2$, $[M + H]^+$: 181.1223, found 181.1215.

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References

1. Paju A, Oja K, Matkevitš K, Lumi P, Järving I, Pehk T, Lopp M. *Heterocycles*, 2014;88:981.
2. Chen S, Lui Z, Chen L, Wei W, Li H, Cheng Y, Wan X. *Org. Lett.* 2011;13:2274.
3. Che C-M, Huang J-S. *Chem. Commun.*2009:3996.
4. Punniyamurthy T, Velusamy S, Iqbal J. *Chem. Rev*. 2005;105:2329.
5. Ghogare AA, Greer A. *Chem. Rev*. 2016;116:9994.
6. Meunier B. *Chem. Rev*. 1992;92:1411.
7. G. Jiang, Q. Liu, C. Guo, *Biomimetic Based Applications*, Prof. M. Cavrak, InTech, China, 2011; Vol. 2, pp 32–58.
8. Guo C-C, Liu X-Q, Li Y, Chu M-F, Zhang X-B. *Journal of Molecular Catalysis A: Chem.* 2003;192:289.
9. Zhou W, Hu B, Sun C, Xu S, Liu Z. *Catal Lett*, 2011;141:1709.
10. Xu S, Hu B, Cui Q, Hu T, Huang X, Liu Z. *Advanced Materials Research*, 2011;233-235:1093–1096.
11. Jiang G, Chen J, Thu H-Y, Huang J-S, Zhu N, Che C-M. *Angew. Chem. Int. Ed*, 2008;47:6638.
12. Guo C-C, Liu X-Q, Liu Q, Liu Y, Chu M-F, Lin W-Y. *J. Porphyrins Phthalocyanines* 2009;13:1250.
13. Yang W-Y, Tao N-Y, Guo C-C. *J. Cent. South Univ. Technol.* 2007;14:660.
14. Yan Y, Kang E-H, Yang K-E, Tong S-L, Fang C-G, Liu S-J, Xiao F-S. *Catalysis Communications* 2004;5:387.
15. Li XD, Zhu YC, Yang LJ. *Chinese Chemical Letters* 2012;23:375.
16. Kalajahi SSM, Hajimohammadi M, Safari N. *Reac Kinet Mech Cat* 2014;113:629.
17. Sun C, Hu B, Liu Z. *Chemical Engineering Journal* 2013;232:96.
18. Huang G, Yuan RX, Peng Y, Chen XF, Zhao SK, Wei SJ, Guo WX, Chen X. *RSC Adv*. 2016;6:48571.
19. Borovkov VV, Solovieva AB, Cheremenskaya OV, Belkina NV *J. Mol. Catal. A: Chem.* 1997;120:L1.
20. Solovieva AB, Borovkov VV, Lukashova EA, Grinenko GS. *Chem. Lett.* 1995:441.
21. Ballatore C, Gay B, Huang L, Robinson KH, James MJ, Trojanowski JQ, Lee VM-Y, Brunden KR, Smith III AB. *Bioorg. Med. Chem. Lett.* 2014;24:4171.
22. Hao X, Wu J, Tian H, Shi Y, Lin J, Tian W. *Chin. J. Chem.* 2015;33:1235.
23. Shao L-D, Wu Y-N, Xu J, He J, Zhao Y, Peng L-Y, Li Y, Yang Y-R, Xia C-F, Zhao Q-S. *Nat. Prod. Bioprospect.* 2014;4:181.
24. Jõgi A, Paju A, Pehk T, Kailas T, Müürisepp A-M, Lopp M. *Tetrahedron* 2009;65:2959.
25. Joshi A, Veron J-B, Unge J, Rosenquist Å, Wallberg H, Samuelsson B, Hallberg A, Larhed M. *J. Med. Chem.* 2013;56:8999.
26. Sakai N, Horikawa S, Ogiwara Y. *RSC Adv.* 2016;6:81763.
27. Ju Y, Miao D, Yu R, Koo S. *Org. Biomol. Chem.* 2015;13:2588.
28. Carminati DM, Intrieri D, Caselli A, Le Gac S, Boitrel B, Toma L, Legnani L, Gallo E. *Chem. Eur. J.* 2016; 22:13599.
29. Simonneaux G, Tagliatesta P. *J. Porphyrins Phthalocyanines* 2004;8:1166.
30. Reile I, Paju A, Müürisepp A-M, Pehk T, Lopp M. *Tetrahedron* 2011;67:5942.
31. Paju A, Kanger T, Lindmaa R, Müürisepp A-M, Lopp M. *Tetrahedron: Asymmetry* 2003;14:1565.
32. Wang X, She Y. *Front. Chem. Eng. China* 2009;3:453.
33. Renaud J-P, Battioni P, Bartoli JF, Mansuy D. *J. Chem. Soc. Chem. Commun.* 1985:888.
34. Srour H, Jalkh J, Le Maux P, Chevance S, Kobeissi M, Simonneaux G. *J. Mol. Catal. A: Chem.* 2013;370:75.
35. Rouf A, Tanyeli C. *Current Organic Chemistry* 2016;20:2996.
36. Evans S, Smith JRL. *J. Chem. Soc., Perkin Trans 2*. 2000:1541.
37. Cavani F, Raabova K, Bigi F, Quarantelli C. *Chem. Eur. J.* 2010;16:12962.
38. Robertson JC, Swelim A. *Tetrahedron Lett.* 1967;30:2871.
39. Jõgi A, Paju A, Pehk T, Kailas T, Müürisepp A-M, Kanger T, Lopp M. *Synthesis*, 2006;18:3031.
40. Paju A, Laos M, Jõgi A, Päri M, Jäälaid R, Pehk T, Kanger T, Lopp M. *Tetrahedron Lett.* 2006;47:4491.