Efficient Biomimetic Oxidative Decarboxylation of Some Carboxylic Acids Catalyzed by a Manganese (III) Schiff Base Complex

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The four dentate N_2O_2 Schiff base ligand of bis(2-hydroxyacetophenone)-1,2-propanediimine (BHAPN) and its manganese (III) complex were synthesized and identified by microanalysis, spectral data (^{1}H NMR, MS, FT-IR and UV-Visible) and molar conductivity measurement. The mild and efficient homogeneous oxidative decarboxylation of some carboxylic acids by catalytic amount of this manganese (III) complex, using tetrabutylamonium periodate as a mild oxidant in chloroform at room temperature is reported. The catalyst used in this study showed good activity for the decarboxylation of the titled compounds.

Key Words: Schiff base, Complex, Catalytic, Decarboxylation, Manganese(III)

Introduction

In the last two decades, some synthetic coordination compounds such as manganese porphyrins and related Schiff base complexes which exhibit similar structural and properties to cytochrome P-450 dependent monooxygenases, have been extensively investigated as effective biomimetic systems for the oxidation of organic compounds.[1-3]

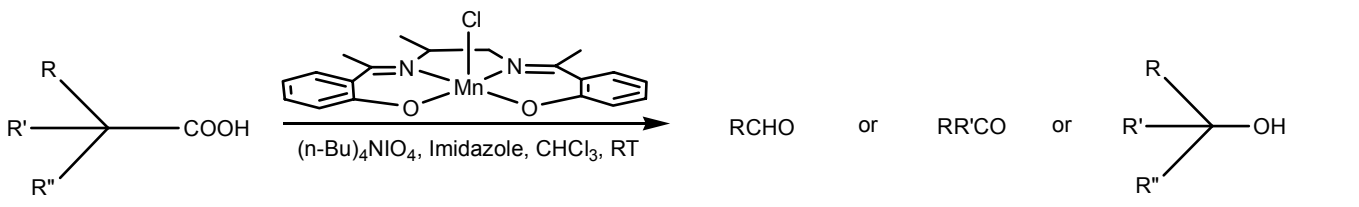
Several oxidants such as iodosylbenzene, hypochlorite, *m*-chloroperbenzoic acid, hydrogen peroxide, and periodates have been have been applied as oxygen source for performance of catalytic role of those compounds to understand the mechanism of cytochrome P-450 monooxygenase enzyme.[4-8] Among the various coordination compounds, especially, metalloporphyrins and the metal Schiff base complexes including salen and salophen ligands aroused the interest of synthetic chemists as model compounds for the active site of cytochrome P-450 due to their electronic structure and catalytic activity. Electronic and steric nature of the metal complex can be tuned by introducing electron-withdrawing, electron-releasing and/or bulky substituents in the ligand. For instance manganese, chromium, nickel, iron and cobalt Schiff base complexes have been extensively used as bio-mimicing catalysts for oxidation of organic compounds such as alkenes, alkanes, alcohols, aldehydes under homogeneous and heterogeneous conditions.[9-18]

Decarboxylation reactions have a key role in some areas of organic synthesis and biochemical processes. Several decarboxylation methods have been reported under thermal,[19-20] photochemical[21-22] and catalytic conditions.[23-25] The oxidative decarboxylation of antiinflammatory drugs such as Indomethacin and Ibuprofen afforded corresponding carbonyl derivatives that have been observed as well as similar pathway during drug metabolism *in vivo*.[26-28]

In continuation of our ongoing research programme on the catalytic oxidation of organic compounds,[29] herein we wish to report the synthesis of a manganese(III) Schiff base complex with a four dentate Schiff base ligand and then investigation of its catalytic activity for the biomimetic oxidative decarboxylation of a variety of carboxylic acids. (Scheme1).

Results and Discussion

The ligand of BHAPN was prepared by condensing of 2-hydroxyacetophenone and 1,2-propanediamine in a 2:1 molar ratio and then was characterized by elemental analysis, FT- IR, ^{1}H NMR and Mass spectral data. In the infra-red spectrum, the vibrational frequencies at 3400 cm^{-1} and 1612 cm^{-1} well assigned to the O-H and the asymmetric iminic vibrational stretching modes as the characteristic stretchings of the free ligand. The ^{1}H NMR spectrum of the ligand in dimethylsulfoxide-d_6 solution showed two singlet peaks at 16.18 and 15.96 ppm for two -OH groups of the ligand. The ^{1}H NMR spectrum also exhibited the expected signals at 7.54 (t, 2H, J = 7.75 Hz), 7.31 (m, 2H), 6.95 (d, 2H, J = 8.25 Hz), 6.84 (d, 1H, J = 7.65 Hz), 6.83 (d, 1H, J = 7.14 Hz) for aromatic protons, 4.35 (sext, 1H, J = 6.35 Hz), 3.85 (dd, 1H, J = 14.20 Hz and J = 7.15 Hz), 3.81 (dd, 1H, J = 14.2 Hz and J = 5.80 Hz), 2.44 (s, 3H),



Scheme 1

2.37 (s, 3H), 1.45 (d, 3H, J = 6.35 Hz) ppm for methylene, methyne (CH_2 and CH) and three methyl ($3CH_3$) groups of the ligand respectively. At the UV-Visible spectrum of the ligand three bands at 210, 247 and 321 nm were observed that two first bands are assigned to π-π* of the phenyl groups and the third band attributed to π-π* of the iminic groups (C=N) of the ligand. Mass spectrum of the ligand showed the molecular ion peak at 310 (M+, $HOC_6H_4C(CH_3)=N(CH_2)_3N=C(CH_3)C_6H_4OH$) together with some other fragments at 295 ($HOC_6H_4C(CH_3)=N(CH_2)_3$-N=$C(CH_3)$-$C_6H_4$-), 278 ($C_6H_4C(CH_3)=N(CH_2)_3N=C(CH_3)C_6H_4$-), 176 ($HOC_6H_4C(CH_3)=N(CH_2)_3$-), 160 ($HOC_6H_4C(CH_3)=N(CH_2)_2$-, 148 ($HOC_6H_4C(CH_3)=N(CH_2$-), 134 ($HOC_6H_4C(CH_3)=N$), 121 ($HOC_6H_4C(CH_3)C=$), 108 ($HOC_6H_4CH$-C=), 96 ($HOC_6H_4CH$-), 83 ($HOC_6H_4$-), 66 (-$C_6H_4$-) *m/z*. The synthesis of manganese(III) Schiff base complex was carried out similar to previously reported method in the literature with a modified conditions.[30-32] Analytical data, FT-IR, UV-Visible spectrum and molar conductivity measurement confirmed the proposed structure. In the Infra-red spectrum, the vibrational frequency at 1583 cm^{-1} was attributed to the asymmetric stretching mode of the coordinated -C=N.[29] In the electronic spectrum of the complex four bands at 219, 260, 380 and 540 nm were observed that the first two bands are assigned to π-π* of the phenyl groups and the third band to the π-π* of iminic groups of the coordinated ligand that shifted to lower energy with respect to free ligand. The fourth band at 540 nm maybe assigned to d-d electronic transition of the complex. The conductivity measurement in DMF solution indicated that the Mn(III) complex is neutral (Ω = 20.75 μS/cm).[30,31] The NMR of the complex could not be recorded due to its paramagnetic property. After the synthesis and characterization of the Mn(III) complex, its catalytic activity was examined for the oxidative decarboxylation of some carboxylic acids according to typical procedure using (n-Bu)$_4NIO_4$ as an oxidant at room temperature. Before every thing to obtain the suitable conditions for catalytic decarboxylation, some parameters such as the kind of solvent and, catalyst, oxidant and auxiliary base amounts must be optimized. At first as shown in Table 1 various solvents such as dichloromethane, chloroform, acetonitrile, acetone and ethanol were used for the choice of a suitable solvent. A typical reaction on phenylacetic acid (1 mmol) was designed using the 10% molar ratio of Mn(III) complex and tetrabutylamonium periodate as oxidant in above solvents. Among the solvents used, the chloroform was found to be a suitable solvent.

Figure 1 illustrates the effect of catalyst molar ratio (%) on the conversion time of phenylacetic acid as typical substrate in chloroform at room temperature. In the absence of the catalyst, the reaction showed very low progress even after prolonged reaction time with increasing the catalyst, the reaction time is decreased up to 10% of catalyst molar ratio that was found to be an optimum amount in current conditions. The higher amount of catalyst was found that have not a notable effect on the reaction time.

Generally catalytic reactions by the Schiff base and/or porphyrin complexes are accelerated by use of auxiliary bases such as imidazole. Therefore similar to others, different molar ratios of imidazole (with respect to substrate) were examined. The decarboxylation rate of phenylacetic acid in the absence of imidazole is low (< 30% conversion within 40 minutes) whereas the conversion reaches to 100% in 40 minutes when 40% imidazole as the auxiliary base is used. In final as shown in Figure 2, among the various ratios of oxidant to substrate, the 1.5/1 ratio of tetrabutylamonium periodate to phenylacetic acid was selected as optimum ratio.

After optimization reactions, some carboxylic acid derivatives were subjected to the Mn(III) complex/imidazole/(n-Bu)$_4$ NIO_4 catalytic system in chloroform that led to decarboxylation in good to high yields at reasonable reaction times at room temperature. Based on the results in Table 2, all carboxylic

Table 1. The solvent effect on the conversion (%) of 1 mmol phenylacetic acid using 1.5 mmol (n-Bu)$_4NIO_4$, 10% and 40% molar ratios of the catalyst and imidazole.

Entry	Solvent	Time (min)	Conversion (%)[a]
1	CH_2Cl_2	60	100
2	$CHCl_3$	40	100
3	CH_3CN	100	50
4	CH_3COCH_3	100	60
5	CH_3CH_2OH	100	45

[a]Based on disappearance and/or recovery of phenylacetic acid.

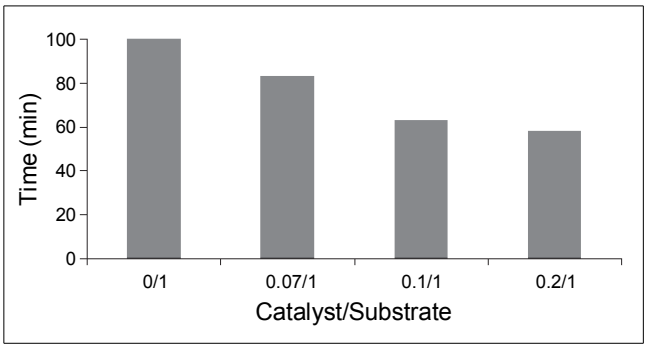


Figure 1. The catalyst amount effect on the conversion time of 1mmol phenylacetic acid using 1.5 mmol (n-Bu)$_4NIO_4$ and 40% molar ratio of imidazole.[a] ([a]Based on disappearance and/or recovery of phenylacetic acid. For 0/1 catalyst to substrate after 100 minutes, the conversion was < 10%).

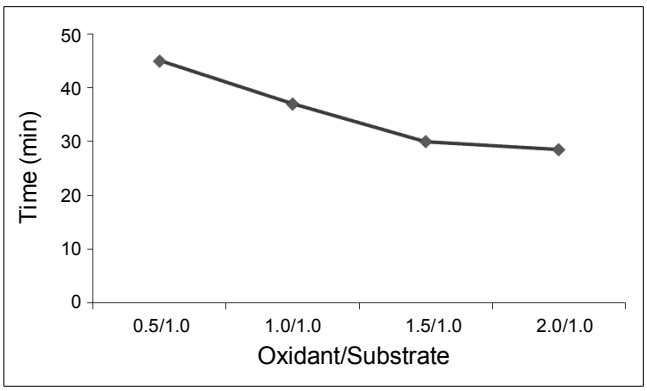
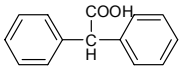
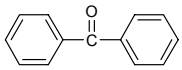
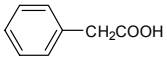
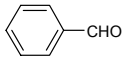
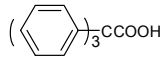
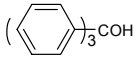
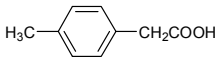
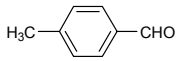
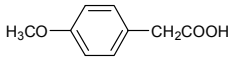
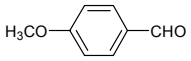
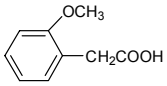
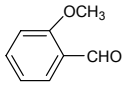
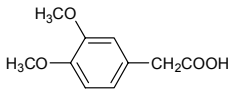
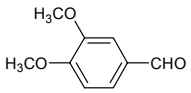
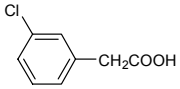
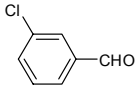
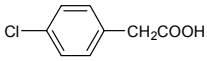
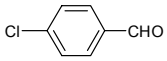
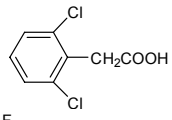
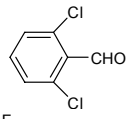
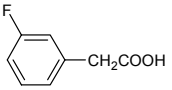
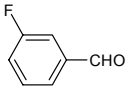
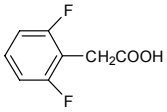
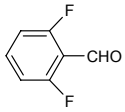
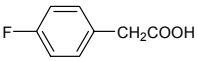
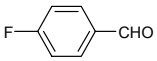
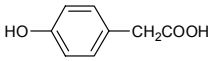
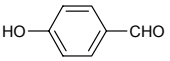
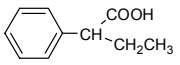
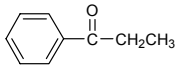
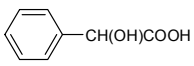
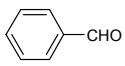
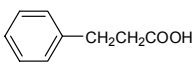
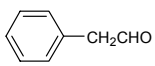
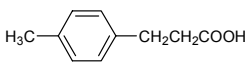
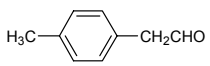
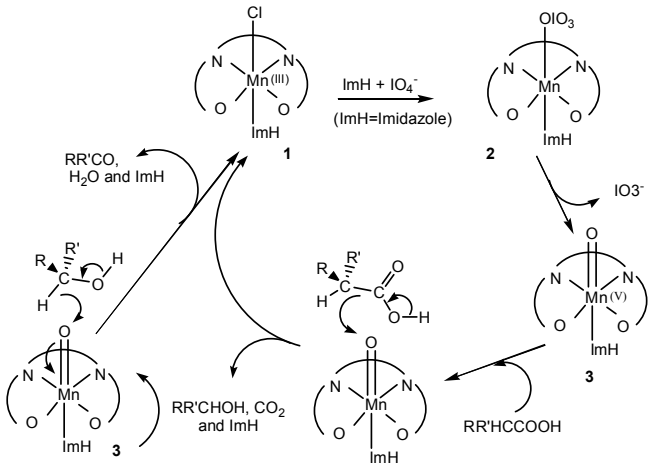


Figure 2. The oxidant amount effect on the conversion time of 1 mmol of phenylacetic acid using 10% and 40% molar ratio of catalyst and imidazole.

Table 2. Oxidative decarboxylation of carboxylic acids using Mn(III) complex/ imidazole/ (n-Bu)$_4$NIO$_4$ catalytic system in chloroform at room temperature.[a]

Entry	Carboxylic acid	Product[b]	Time/min.	Yields[c]/%
1			100	90
2			30	94
3			95	91
4			48	93
5			50	90
6			70	86
7			55	90
8			100	92
9			90	90
10			55	87
11			110	95
12			110	94
13			120	86
14			50	93
15			63	92
16			40	85
17			95	70
18			105	75

[a]Refers to 1 mmol carboxylic acid, 1.5 mmol (n-Bu)$_4$NIO$_4$, 10% and 40% molar ratios of catalyst and imidazole. [b]All products are known and their physical and spectral data of them were compared with authentic samples. [c]Refers to isolated yields.



Scheme 2

acids were converted to carbonyl compounds as major products with yields in 70-94% except for the triphenylacetic acid (entry 3) that was converted to tertiary alcohols.

With regard to the literature,[28] the mechanism in Scheme 2 is proposed for the catalytic oxidative decarboxylation of carboxylic acids by Mn(III)-complex (**1**). At first suggested stage, by treatment of the $(n\text{-Bu})_4NIO_4$ with the Mn(III)- complex, the oxo-intermediate of $[Mn^{V}(O)(L)]$ (**3**) as a direct oxidant is formed. Then the carboxylic acid, $R_1R_2HCCOOH$ approaches *via* its C_1-C_2 to **3** to produce the alcohol of R_1R_2CHOH, CO_2 and **1**. At the second oxidative step, the formed alcohols again are subjected to another oxo-intermediate **3** to give the aldehydes or ketones as major products. To support of the suggested mechanism, two secondary alcohols such as 1-phenyl-1-propanol and benzhydrol were treated by the same catalytic oxidative reactions. The results revealed that they were oxidized to the same products of decarboxylation of carboxylic acids of entries of 1 and 15. In the case of a tertiary carboxylic acid (entry 3), the first step oxidative decarboxylation lead to a tertiary alcohol (triphenylmethanol) that can not be over-oxidized to aldehyde or ketone in our mild conditions. This observation is also in agreement with proposed two oxidation step mechanism for decarboxylation. On the other hand it seems that the mandelic acid (entry 16) with one -OH in α-position is directly decarboxylated to benzaldehyde at one step oxidation. The aliphatic carboxylic acids (entries, 17 and 18) were also subjected to this catalytic system. These acids were decarboxylated to the expected aldehydes but in lower yields at similar reaction times with respect to others. Again these results somewhat supports two suggested steps for decarboxylation of carboxylic acids.

Conclusions

In this paper we have reported a new application of a Mn(III) Schiff base complex as a novel homogeneous catalytic system in a convenient, efficient and practical method for the effective oxidative decarboxylation of some carboxylic acids. The availability of the reagents, facile synthesis of the complex, the easy work-up of products and the high yields make this method as a useful alternative to the literature procedures in this subject.

Experimental

Chemicals and apparatus. Carboxylic acids were purchased from Merck or Fluka and used without further purification. The electronic absorption spectra were recorded with a JASCO UV-570 spectrophotometer. ^{1}H NMR spectra were obtained with a Brucker 500 MHz spectrometer. IR spectra were recorded on a FT-IR JASCO-680 spectrophotometer. Mass spectra were recorded on shimadzu 1800. Molar conductivity of complexes was measured by Metrohm 712 model. Elemental analyses (CNHS) of samples were performed using a CHNS-932 elemental analyzer.

Preparation of bis(2-hydroxyacetophenone)-1,2-propanediimine(BHAPN). A solution of 1,2-propanediamine (0.223 g, 3 mmol) in absolute ethanol (15 mL) was added to a solution of 2-hydroxyacetophenone (0.817 g, 6 mmol) in absolute ethanol (20 mL) and then refluxed for 7 h. The reaction mixture was kept in the refrigerator overnight and three days under air evaporation. The product was obtained as yellow crystalline powder in 85% yields. Elemental analysis, % $C_{19}H_{22}N_2O_2$, calculated: C, 73.52; H, 7.14; N, 9.03; found: C, 73.21; H, 7.18; N, 8.98. IR (KBr, cm^{-1}): 3434 (bs, νOH), 3158 (w, CH-Aromatic), 2922 (w, CH-Aliphatic), 1612 (-C=N), 1571 (C=C), 1506 (m), 1446 (m, C=C), 1382 (m), 1373 (s, C-N), 1298 (m), 1257 (m), 1226 (m), 1157 (s), 1061 (m, C-O), 1029 (m, C-O), 916 (m), 829 (s), 750 (s), 644 (m), 508 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 16.18 (s, 1H), 15.96 (s, 1H), 7.54 (t, 2H, J = 7.75 Hz), 7.31 (m, 2H), 6.95 (d, 2H, J = 8.25 Hz), 6.84 (d, 1H, J = 7.65 Hz), 6.83 (d, 1H, J = 7.14 Hz), 4.35 (sext, 1H, J = 6.35 Hz), 3.85 (dd, 1H, J = 14.20 Hz and J = 7.15 Hz), 3.81 (dd, 1H, J = 14.2 Hz and J = 5.80 Hz), 2.44 (s, 3H), 2.37 (s, 3H), 1.45 (d, 3H, J = 6.35 Hz). UV-Visible (CH_2Cl_2, λ_{max}): 210, 247, 321 nm. Mass spectral data (main fragments): 310, 295, 278, 176, 160, 148, 134, 121, 108, 96, 83, 66 *m*/*z*.

Preparation of Mn(III) complex. Mn(III) complex was achieved by reaction of 5 mmol (1.55 g) of the free ligand and 5 mmol of $MnCl_2{\cdot}4H_2O$ (0.98 g) under reflux and air bobbling, in ethanol during 4 hours according to the literature,[30-32] with modified conditions. After cooling, the solids were collected by filtration and washed twice with a small portion of ethanol and water. $[Mn^{(III)}(L)Cl]{\cdot}H_2O$: IR (KBr, cm^{-1}): 3413 (m, ν(H_2O)), 3059 (w), 2967 (w), 2882 (w), 2918 (m), 1583 (vs, ν(-C=N)), 1533 (s, ν(-C=N)), 1531 (m), 1464 (w), 1439 (m), 1422 (vs), 1373 (w), 1310 (m), 1233 (m), 1154 (w), 1132 (m), 1022 (s), 971 (m), 888 (s), 856 (m), 778 (s), 618 (m). UV-Visible (CH_2Cl_2, λ_{max}): 219, 260, 380 and 540 nm. m.p. = (> 300 °C, dec.). Ω = 20.75 μS/cm.

Typical experimental procedure. To Mn(III) complex (0.1 mmol, 10% molar ratio) in chloroform (20 mL), imidazole (0.4 mole, 40% mmol), 2,6-dichlorophenylacetic acid (1 mmol) and then tetrabutylamonium periodate (1.5 mmol) were added. The reaction mixture was stirred until TLC indicated the reaction was completed at room temperature. The resulting solution was concentrated under reduced pressure to yield a residue, which was passed through a short pad of silica gel using ethyl acetate and *n*-hexane (1:2) as eluent to provide analytically pure product in 87% yield. IR (KBr, cm^{-1}): 3459 (w), 3150 (w), 3091 (m), 2975 (w), 2892 (m), 2777 (w), 1698

(vs), 1577 (s), 1561 (s), 1434 (s), 1402 (m), 1275 (m), 1207 (s), 1186 (m), 1093 (m), 1069 (m), 986 (w), 873 (s), 842 (s), 704 (s). ^{1}H NMR (500 MHz, $CDCl_3$): 10.52 (s, 1H), 7.43 (m, 3H) ppm. Mass spectral data (main fragments): 175, 174, 173(M^+), 145, 138, 110, 87, 75, 61, 50 *m*/*z*.

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References

1. (a) Coon, M. J.; White, R. E. *Dioxygen Binding and Activation by Metal Centers*; Spiro, T. G., Ed.; Wiley: New York, 1980; p 73; (b) White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315; (c) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411;(d) Sono, M.; Roach, M. P. *Chem. Rev.* **1992**, *96*, 2841; (e) Liu, J.; Li, X.; Guo, Z.; Li, Y.; Huang, A.; Chang, W. *J. Mol. Catal. A: Chem.* **2002**, *179*, 27; (f) Woggon, W. D. *Acc. Chem. Res.* **2005**, *38*, 127; (g) Chan, W. K.; Liu, P.; Yu, W. Y.;Wong, M. K.; Che, C. M. *Org. Lett.* **2004**, *6*, 1597; (h) Borocci, S.; Marotti, F.; Mancini, G.; Monti, D.; Pastorini, A. *Langmuir* **2001**, *17*, 7198; (i) Yang, J.; Gabriele, B.; Belvedere, S.; Huang, Y.; Breslow, R. *J. Org. Chem.* **2002**, *67*, 5057; (j) Hata, M.; Hirano, Y.; Hoshino, T.; Tsuda, M. *J. Am. Chem. Soc.* **2001**, *123*, 6410.
2. (a) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411; (b) Bernadou, J.; Fabiano, A. S.; Robert, A.; Meunier, B. *J. Am. Chem. Soc.* **1994**, *116*, 9375; (c) Balahura, R. J.; Sorokin, A.; Bernadou, J.; Meunier, B. *Inorg. Chem.* **1997**, *36*, 3488.
3. Paluki, M.; Finney, N. S.; Pospisil, P. J.; Guller, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 948.
4. Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786.
5. Bortolini, O.; Meunier, B. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1967.
6. Meunier, B.; Guilmet, E.; De Carvalho, M. E.; Poilblanc, R. *J. Am. Chem. Soc.* **1984**, *106*, 6668.
7. Mohajer, D.; Tangestaninejad, S. *J. Chem. Soc., Chem. Commun.* **1993**, 240.
8. Mohajer, D.; Tangestaninejad, S. *Tetrahedron Lett.* **1994**, *35*, 945.
9. (a) Srinivasa, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309; (b) Rihter, B.; Masnovi, J. *J. Chem. Soc., Chem. Commun.* **1988**, 35; (c) Chellamani, A.; Alhaji, N. M. I.; Rajagopal, S.; Sevvel, R.; Srinivasan, C. *Tetrahedron* **1995**, *51*, 12677; (d) Chellamani, A.; Alhaji, N. M. I.; Rajagopal, S. *J. Chem. Soc., Perkin Trans. 2* **1997**, 299; (e) Koola, J.; Kochi, J. K. *Inorg. Chem.* **1987**, *26*, 908.
10. Amatsu, H.; Miyamoto, T. K.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3193.
11. Palucki, M.; McCormick, G. J.; Jacobsen, E. N. *Tetrahedron Lett.* **1995**, *36*, 5457.
12. Adam, W.; Jeco, J.; Levai, A.; Nemes, C.; Patonay, T.; Sebok, P. *Tetrahedron Lett.* **1995**, *36*, 3669.
13. Linker, T. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2060.
14. Irie, R.; Hashihayata, T.; Katasuki, T.; Akita, M.; Moro-oka, M. *Chem. Lett.* **1998**, 1041.
15. (a) Gomes, M. F. T.; Antunes, O. A. C. *Catal. Lett.* **1996**, *42*, 213; (b) Gomes, M. F. T.; Antunes, O. A. C. *Catal. Lett.* **1996**, *38*, 133.
16. Niassary, M. S.; Farzaneh, F.; Ghandi, M.; Turkian, L. *J. Mol. Catal. A: Chem.* **2000**, *157*, 183.
17. Adam, W.; Humpf, H. U.; Roschmann, K. J.; Saha-Moller, C. R. *J. Org. Chem.* **2001**, *66*, 5796.
18. Ganeshpure, P. A.; Satish, S. *J. Chem. Soc., Chem. Commun.* **1988**, 981.
19. Kim, Y. I.; Kim, Y. H. *Tetrahedron Lett.* **1998**, *39*, 639.
20. Mohri, K.; Mamiya, J.; Kasahara, Y.; Isobe, K.; Tsuda,Y. *Chem. Pharm. Bull.* **1996**, *44*, 2218.
21. Habibi, M. H.; Farhadi, S. *Tetrahedron Lett.* **1999**, *40*, 2821.
22. Itoh, A.; Kodama, T.; Masaki, Y.; Inagaki, S. *Chem. Pharm. Bull.* **2006**, *54*, 1571.
23. Mirkhani, V.; Tangestaninejad, S.; Moghadam, M.; Moghbel, M. *Bioorg. Med. Chem.* **2004**, *12*, 4673.
24. Karimipour, Gh.; Montazerozohori, M.; Karami, B. *J. Chem. Res.* **2006**, 605.
25. (a) Karimipour, Gh.; Karami, B.; Montazerozohori, M.; Zakavi, S. *Chin. J. Catal.* **2007**, *28*, 940; (b) Montazerozohori, M.; Habibi, M. H.; Zamani-fradonbe, L.; Musavi, S. A. *Arkivoc* **2008**, *xi*, 238.
26. Komuro, M.; Nagatsu, Y.; Higuchi, T.; Hirobe, M. *Tetrahedron Lett.* **1992**, *33*, 4949.
27. Komuro, M.; Higuchi, T.; Hirobe, M. *Bioorg. Med. Chem.* **1995**, *3*, 55.
28. Mirkhani, V.; Tangestaninejad, S.; Moghadam, M.; Karimian, Z. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3433.
29. (a)Nasr-Esfahani, M.; Moghadam, M.; Tangestaninejad, S.; Mirkhani, V. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3276; (b) Nasr-Esfahani, M.; Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Momeni, A. R. *Bioorg. Med. Chem.* **2006**, *14*, 2720; (c) Moghadam, M.; Nasr-Esfahani, M.; Tangestaninejad, S.; Mirkhani, V.; Zolfigol, M. A. *Can. J. Chem.* **2006**, *84*, 4; (d) Moghadam, M.; Nasr-Esfahani, M.; Tangestaninejad, S.; Mirkhani, V. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 2026; (e) Karami, B.; Montazerozohori, M.; Nasr-Esfahani, M. *Heterocycle* **2005**, *65*, 2181; (f) Nasr-Esfahani, M.; Moghadam, M.; Valipour, G. *J. Iran. Chem. Soc.* **2008**, *5*, 244.
30. (a) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81; (b) Salomao, G. C.; Olsen, M. H. N.; Drago, C.; Fernandes, L.; Cardozo Filho, C.; Antunes, O. A. C. *Catal. Commun.* **2007**, *8*, 69.
31. (a) Miomandre, F.; Audebert, P.; Maumy, M.; Uhl, L. *J. Electroanal. Chem.* **2001**, *516*, 66; (b) Hotchandani, S.; Ozdemir, U.; Nasr, C.; Allakhverdiev, S. I.; Karacan, N.; Klimov, V. V.; Kamat, P. V.; Carpentier, R. *Bioelectrochem. Bioenerg.* **1999**, *48*, 53; (c) Puglisi, A.; Tabbi, G.; Vecchio, G. *J. Inorg. Biochem.* **2004**, *98*, 969.
32. Boucher, L. J.; Herrington, D. R. *Inorg. Chem.* **1974**, *13*, 1105.