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Salen Complexes with Bulky Substituents as Useful Tools for Biomimetic Phenol Oxidation Research

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Abstract—The catalytic properties of bulky water-soluble Co-, Cu-, Fe- and Mn-salen complexes in the oxidation of phenolic lignin model compounds have been studied in aqueous water–dioxane solutions (pH 3–10). Mn catalysts were found to oxidize coniferyl alcohol in a same reaction time as horseradish peroxidase (HRP) enzyme and Mn and Co catalysts showed different regioselectivity suggesting a different substrate to catalyst interaction in the oxidative coupling. When the oxidation of material more relevant to plant polyphenolics was studied, the results indicated that the complexes catalyze one- and two-electron oxidations depending on the bulk of the substrate.

Introduction

Plant polyphenols constitute an important source of renewable carbon in the biosphere. Although research on the oxidative bioconversion of lignocellulosic materials has been intensive for decades, our knowledge of either the relevant enzymes participating in such processes or the oxidative mechanisms they induce is still rather limited. At present it is known that at least three enzymes are involved in biodegradation of lignin-like materials, namely lignin peroxidases,[1] manganese peroxidases[2] and laccases.[3] The two former ones are two-electron oxidants using hydrogen peroxide whereas laccases are one-electron oxidants and use dioxygen. Their direct use in the mechanistical studies is, however, problematic. They are difficult to isolate from natural sources in pure form and in biological systems they also seem to use mediators, such as Mn ions or veratryl alcohol, in the oxidative conversions. Therefore, more easily obtainable and readily oxidizing catalysts, especially HRP but also porphyrins, salens and phthalocyanines, have commonly been used in plant phenolic research.[4]

Metal salen compounds have been investigated as catalysts for several different reactions, for example epoxidation[5] and aziridination[5b] of olefins and oxidation of sulphides to sulfoxides.[5b,6] Salen complexes have also been used in medicinal studies for example as mimics for superoxide dismutase[7] and as DNA scission catalysts.[8] One of the great advantages of the salen catalysts is that the structure of the ligand as well as the coordinated metal ion can be easily varied. For example, introducing chiral ligands has provided possibilities for enantioselective epoxidations[5,6] and recently for asymmetric addition of cyanide to aldehydes.[9]

In polyphenol oxidation research, most of the studies involving salen-type catalysts have included the use of structurally simple Co-salens in organic solvents and oxidations are usually performed under an over-pressure of dioxygen.[10] The results have indicated that these conditions lead to a significant formation of quinonoic structures. In biomimetic work, however, the preferred system consists of oxidation in aqueous conditions. Only a few examples of water-soluble salen complexes have been reported and they have mainly been used as DNA cleavage catalysts.[8,11]

Results

In the present work, we have investigated the catalytic properties of salen complexes by chancing the metal

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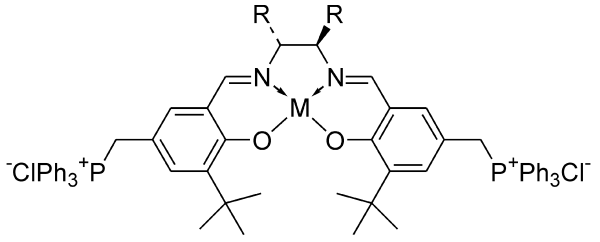
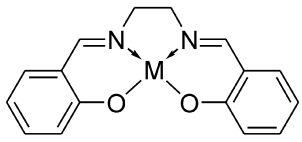
ions in the active center and varying steric demand of the ligand backbone.[12] For this purpose a new set of water-soluble salen complexes containing bulky substituents were prepared (**1**–**8** in Fig. 1) and their reactivity compared to that of unsubstituted salen compounds **9** and **10**. All new ligands and complexes were characterized with ^{1}H NMR, ^{13}C NMR, elemental analysis, MS (ESI-TOF) or crystal structure determination.[13]

The first reaction system studied consisted of a coniferyl alcohol (CA) and hydrogen peroxide in 2:1 buffer–dioxane solution at pH 3, and the activity of different catalysts in CA oxidation was monitored by following the disappearance of CA by TLC. In dilute solutions, the system predominantly gives structures shown in Figure 2. The limited number of reaction products allows a convenient way to study the possible interactions between the catalyst and the substrate simply by following the regioselectivity of the coupling reactions by 1- and 2-D-NMR.

The results indicated that the bulky Mn complexes **4** and **8** catalyzed the oxidation of coniferyl alcohol with hydrogen peroxide giving mixtures of products in about 1:1:1 β-0-4, β-5 and β-β coupling ratios (Table 1). The ratio of the couplings obtained with unsubstituted salen **9** was notably different, about 1:2:3, whereas iron complexes **3** and **7** as well as HRP gave values practically the same as in bulky Mn complexes. The monitoring of the disappearance of CA by TLC showed that Mn complexes catalyzed oxidations proceeded as fast as those catalyzed by HRP. In cases of the iron complexes, the reactions were slightly slower and the unsubstituted Mn catalyst **9** was clearly the least active. The 1-D-NMR studies of the materials revealed that in all cases the oxidation produced similar types of oligomeric materials. The possible enantioselectivity of the coupling was checked by using the chiral manganese complex **8** and analyzing the dimeric β-5 product formed by HPLC equipped with a chiral column. The product was racemic.

The activities of cobalt complexes were studied using a slight overpressure of dioxygen. In cases of bulky cobalt complexes **1** and **5**, the coupling ratios were about 1:2:3 and this was also the case with catalyst **10**. The disappearance of CA in case of complexes **1** and **5** was also





1 R = H, M = Co
2 R = H, M = Cu
3 R = H, M = FeCl
4 R = H, M = Mn(OAc)
5 R = (*R*,*R*)-cyclohexyl, M = Co
6 R = (*R*,*R*)-cyclohexyl, M = Cu
7 R = (*R*,*R*)-cyclohexyl, M = FeCl
8 R = (*R*,*R*)-cyclohexyl, M = Mn(OAc)

9 M = MnCl
10 M = Co

Figure 1. Complexes **1**–**10** used as oxidation catalysts.

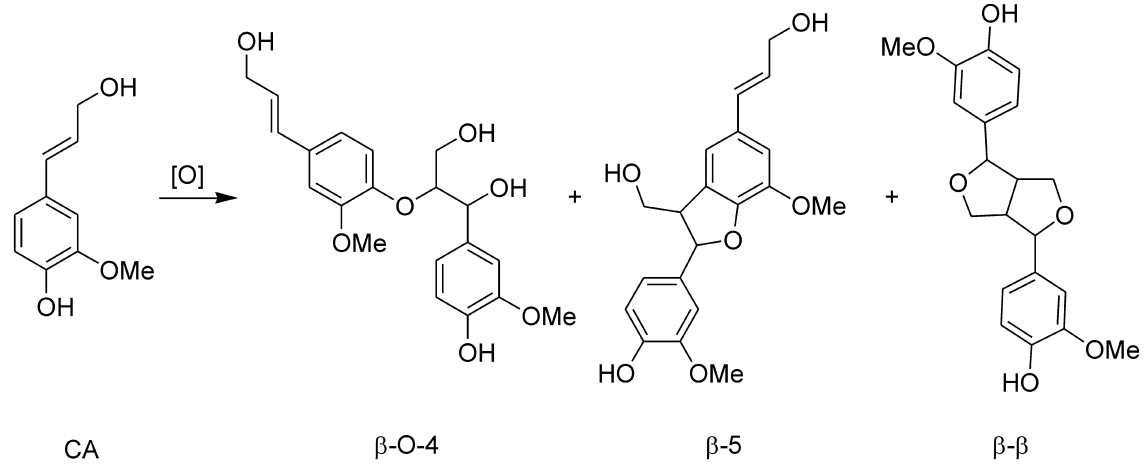


Figure 2. Coupling products obtained on the oxidation of coniferyl alcohol.

faster than in case of simple Co-salen **10**. The copper complexes **2** and **6** were found to be inactive with dioxygen. When the oxidant was changed to hydrogen peroxide, they slowly gave coupling products in a 1:1:1 ratio. With cobalt and copper complexes the material obtained was mainly dimeric.

To mimic the effect of the axially coordinating histidine residue found in the peroxidase enzymes,[14] we also performed the reactions in the presence of imidazole. Imidazole is known to coordinate to the metal ion center of the salen complexes yielding complexes of increased activities in oxidations.[15] We found that imidazole accelerated the oxidation of CA with all Fe- and Mn-complexes, but had no effect on product distribution (Table 2). On the other hand, Co- and Cu-salen catalyzed oxidations with imidazole gave back intact starting material.

To examine the catalysts in the oxidation of the phenolics representative for lignocellulosic material, we then studied the oxidation of monomeric benzyl alcohols **11**, **12** and a dimer **15** (Fig. 3) with complex **4**, which appeared to be the most active catalyst in CA oxidation experiments. The reactions were first performed in 1:1 water–methanol solution at pH 10. In the oxidation of compounds **11** and **12**, we found that they were converted to **13** and **14**, respectively, in a yield of 70%. When the substrate was changed to the more bulky *erythro*-**15,** the reaction gave quantitatively a diastereoisomeric mixture of compound **16**, tetrameric products formed in an oxidative coupling of the dimer **15**. At pH 3, the reactivity pattern was the same but the conversions were lower. When oxidation experiments on **15** were performed using cobalt complexes **1**, **5** or **10** no oxidation products were found, neither at pH 3 nor at pH 10.

Table 1. Results of the oxidations of coniferyl alcohol

Catalyst	Oxidant	β-O-4[a]	β-5[a]	β-β[a]	Reaction time[b]	Polymerization[c]
1 or **5**	O_2	1	2	3	1 h	Dimeric
2 or **6**	H_2O_2	1	1	1	3 d	Dimeric
3 or **7**	H_2O_2	1	1	1	2 h	Oligomeric
4 or **8**	H_2O_2	1	1	1	40 min	Oligomeric
9	H_2O_2	1	2	3	18 h	Oligomeric
10	O_2	1	3	3	12 h	Dimeric
HRP	H_2O_2	1.5	1	1	1 h	Oligomeric

[a]The relative amounts of coupling products were determined by NMR.
[b]Disappearance of coniferyl alcohol (TLC).
[c]The degree of polymerization was estimated from the ^{13}C NMR spectra.

Table 2. The results of the oxidation of coniferyl alcohol with added imidazole

Catalyst	Oxidant	β-O-4[a]	β-5[a]	β-β[a]	Reaction time[b]
1 or **5**	O_2	—	—	—	—[c]
2 or **6**	H_2O_2	—	—	—	—[c]
3 or **7**	H_2O_2	1	1	1	30 min
4 or **8**	H_2O_2	1	1	1	30 min
9	H_2O_2	1	2	3	1 h
10	O_2	—	—	—	—[c]

[a]The relative amounts of coupling products were determined using NMR.
[b]Disappearance of coniferyl alcohol (TLC).
[c]No reaction.

Discussion

Mn-salen catalyzed oxidations are known to occur through a metal–oxo complex[15,16] while cobalt complexes activate dioxygen forming a 1:1 metal to oxygen superoxo or a 2:1 metal to oxygen peroxo complexes as the active oxidant.[10a,17] The oxidative coupling of CA catalyzed by simple manganese and cobalt salens (Table 1) show practically no differences, neither in β-0-4, β-5 and β-β coupling ratios nor in the rate of CA disappearance. However, in cases of bulky Mn (**4** and **8**) and Co catalysts (**1** and **5**) the regiochemistry of couplings is markedly different to those observed with **9** and **10** whereas the rate of CA disappearance was again about the same (Table 1). Interestingly, the oxidations of CA catalyzed by bulky Mn, Cu and Fe complexes show practically the same regiochemistry obtained with HRP. Since HRP oxidations are assumed to proceed without any special interaction between the phenoxy radical and the catalyst during the oxidative coupling,[18] it can be concluded that the bulky catalysts show similar lack of interaction. On the other hand, the different regiochemistry of couplings found with the unsubstituted salens **9** and **10** to that observed with bulky catalysts (and with HRP) suggest a stronger interaction with the phenoxy radicals formed from CA with the catalysts, and that this interaction persists also in the transition state of the coupling.

The beneficial effect of the added imidazole to the Fe- and Mn-salen catalyzed H_2O_2 oxidations is a known phenomenon.[19] The partial crystal structure of the Mn complex **17** with two imidazole ligands at apical positions suggests that the initially formed complex before the addition of oxidant is of the octahedral type (Fig. 4).[20] In the case of Co- and Cu-salen catalysts, on the other hand, imidazole seem to form more stronger octahedral complex and no oxidation is observed. The result further suggest that this interaction of imidazole is different than that of pyridine which is known to facilitate the Co-salen catalyzed oxidations.[10b]

The oxidation of lignin models **11** and **12** yield the respective carbonyl compounds **13** and **14** indicating that in the case of simple benzyl alcohols the oxidation gives two-electron oxidation products. The reactions thus resemble 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) oxidations of phenols, probably involving a hydride abstraction from the benzylic position.[21] One possible reason for the different regioselectivity in oxidations of **11** and CA may be that CA with a low oxidation potential preferentially forms phenoxy radicals prone to rapid coupling reactions. Interestingly, with a dimeric *erythro*-**15** the regioselectivity of the oxidation is markedly different. The reaction gives now quantitatively a diastereoisomeric mixture of coupling product

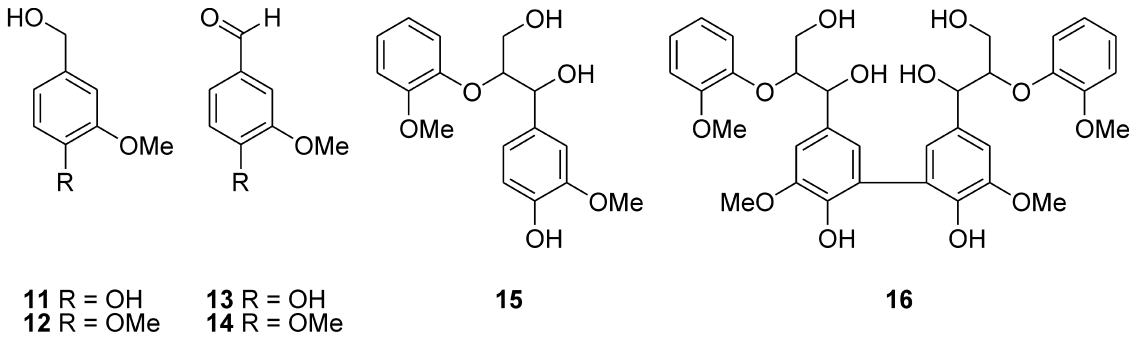


Figure 3. Benzylic alcohols and their oxidation products.

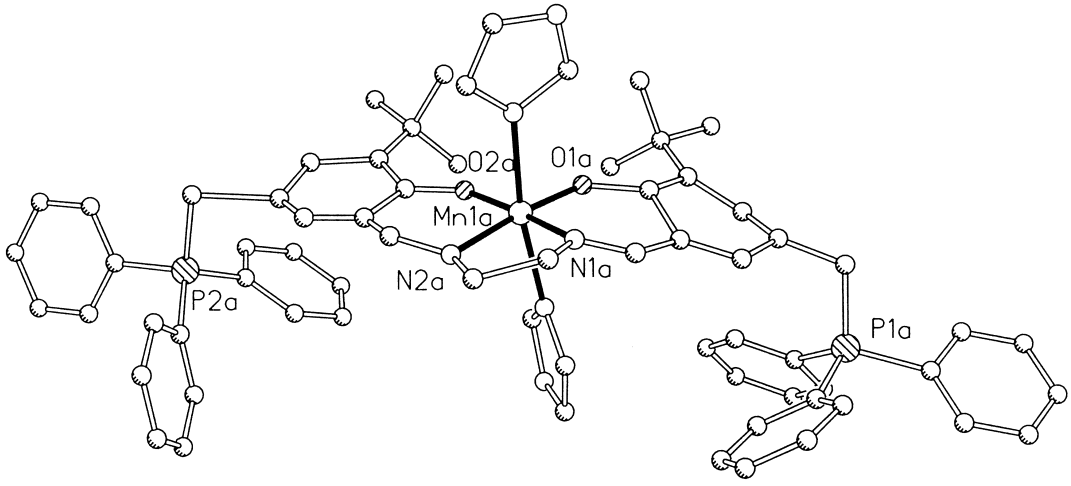


Figure 4. Crystal structure of the complex cation of the imidazole adduct **17**.

16, not a α-carbonyl structure. The DDQ oxidation of lignin models also forms these structures, however, as minor products. The observed preferential formation of coupling products **16** in salen catalyzed oxidation is most probably due to the difficulties of Mn-salen catalyst to form a complex with the bulky substrate that is required for the hydride (or electron) abstraction from the benzylic position.

Conclusion

The present results demonstrate that bulky metal salen compounds are useful biomimetic oxidation catalysts in plant polyphenol research. Our experiments show that the substrate to catalyst interaction may vary substantially between dioxygen and hydrogen peroxide oxidations and that the bulk of the substrate affects dramatically to the regioselectivity of the oxidation. The results also demonstrate that the understanding of the role of water in biomimetic oxidation systems seems to be of the utmost importance.

Experimental

The 1- and 2-D NMR spectra were recorded on Varian Gemini 2000 (200 MHz) and Varian Inova (300 MHz) spectrometers in $CDCl_3$ or acetone-D_6 (for acetylated **16**) using the residual solvent signals (δ 7.27 in ^1H and 77.1 ppm in ^{13}C for $CDCl_3$ and δ 2.04 in ^1H and 29.8 ppm in ^{13}C NMR for acetone-D_6) as references. The mass spectra were recorded using PerSeptive Biosystems Mariner Biospectrometry Workstation ESI-TOF spectrometer. HPLC analysis was carried out using Waters 600 Controller and pump, Waters 996 Photodiode Array Detector and Chiralcel OF column. TLC was conducted on precoated Merck Silica Gel 60 F_{254} plates and visualized with UV light and molybdatophosphoric acid–$Ce(SO_4)_2$–H_2SO_4 with subsequent heating at 120 °C. Solvents were analytical or HPLC grade. Dioxane was distilled from sodium before use. Coniferyl alcohol was synthesized according to the literature procedure.[22] The syntheses of the bulky salen complexes are described elsewhere.[13] The unsubstituted salen complexes were prepared using the literature methods.[23] Lignin model compound *erythro*-**15** was prepared according to the standard literature procedure.[24] The ^{13}C NMR signals for acetylated β-O-4, β-5 and β-β structures used in product characterizations were found at 80.1, 88.0 and 85.0 ppm, respectively. Corresponding ^1H NMR signals were found at 4.69, 5.51 and 4.75 ppm. The degree of the oxidation of the benzyl alcohols **11** and **12** was calculated from ^1H NMR spectra by comparing the characteristic peaks of aldehyde protons and benzylic methylene protons. The diastereoisomeric mixture of compound **16** has similar NMR spectra when compared to **15**, but the peaks are wider. Peracetate of compound **16** gave an identical ^{13}C NMR spectrum to that reported earlier.[25] The identification of

16 was also based on the TLC analysis and comparison with the authentic sample.[26]

General procedure for the oxidation of coniferyl alcohol

Coniferyl alcohol (180 mg, 1.0 mmol) was dissolved in dioxane (1.5 mL). Into this mixture, the catalyst (0.05 mmol, 5 mol%) and imidazole (34 mg, 0.5 mmol, when used) was added followed by the introduction of the buffer (3.5 mL, pH 3, 0.01 M citrate-phosphate). When HRP was used, 5 mg was dissolved in the buffer and added to the CA–dioxane solution. Hydrogen peroxide (1.0 mmol of 10% solution in the buffer) was then added to the resulting mixture in three portions (15 min intervals) or the mixture was stirred under an O_2 atmosphere. After the disappearance of coniferyl alcohol (TLC monitoring, ethyl acetate as the eluent) the mixture was diluted with water (10 mL) and extracted with ethyl acetate (3×15 mL). The combined extracts were washed with 0.01 M HCl (10 mL) and brine (10 mL) and dried with Na_2SO_4. The solvent was evaporated (recoveries in all cases over 90%) and the residue acetylated in 1:1 pyridine–acetic anhydride overnight. The acetylated material was then analyzed by NMR. The degree of polymerization was estimated from the signal widths of the ^1H and ^{13}C NMR together with the information obtained from TLC of the raw materials. HPLC analysis of the non-acetylated material was carried out using hexane–isopropanol (9:1) as an eluent, flow rate 1.0 mL min^{-1}. When the reactions using H_2O_2 or O_2 were performed without the catalyst, no oxidation of CA was evident after 3 days.

General procedure for the oxidation of benzyl alcohols

Substrate (1.0 mmol) and catalyst (0.05 mmol, 5 mol%) were dissolved in 1:1 MeOH–buffer solution (10 mL, pH 10 or 3, 0.01 M carbonate or citrate-phosphate). To the resulting mixture was added hydrogen peroxide (3 mmol, 30% solution) in three portions at 10 min intervals or the mixture was stirred under an O_2 atmosphere. After stirring overnight at room temperature, the mixture was diluted with brine (20 mL) and extracted with ethyl acetate (3×15 mL). The combined extracts were washed with 0.01 M HCl (20 mL) and brine (20 mL). After drying with Na_2SO_4 the solvent was evaporated. Recoveries were always over 90%. The residue was analyzed with NMR spectrometry.

X-ray crystallography

Preparation of 17. Compound **4** was dissolved in CH_2Cl_2. A ten-fold excess of imidazole was added resulting in the change of color from brown to greenish brown. To this mixture was added a solution of an excess of NH_4PF_6 in ethanol-isopropanol. The solution was filtered and allowed to evaporate slowly at room temperature. Crystals of the imidazole adduct $[Mn(C_{62}H_{62}N_2O_2P_2)(C_3H_4N_2)_2]^{3+}\cdot 3PF_6^-\cdot 2(C_3H_8O)$ **17** as a hexafluorophosphate salt were obtained after 2 days.

Crystal data and structure refinement for **17**.[20] Empirical formula $C_{74}H_{86}F_{18}MnN_6O_4P_5$, formula weight = 1675.26, temperature = 193(2) K, wavelength = 0.71073 Å, crystal system: monoclinic, space group: P2(1), unit cell dimensions: $a = 13.017(8)$ Å, $b = 12.631(6)$ Å, $c = 48.72(3)$ Å, $\alpha = 90°$, $\beta = 98.01(5)°$, $\gamma = 90°$, volume = 7932(8) $Å^3$, $Z = 4$, absorption coefficient = 0.353 mm^{-1}, F(000) = 3192.

Due to the limited quality of the data, only a partial structure determination is given here. Bond angles and lengths could not be determined, but the general connectivity was clearly established.

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References

1. (a) Tien, M.; Kirk, T. K. *Science* **1983**, *221*, 661. (b) Hammel, K. E.; Jensen, K. A., Jr.; Mozuch, M. D.; Landucci, L. L.; Tien, M.; Rease, E. A. *J. Biol. Chem.* **1993**, *268*, 12274.
2. (a) Wariishi, H.; Valli, K.; Gold, M. H. *Biochem. Biophys. Res. Commun.* **1991**, *176*, 269. (b) Kishi, K.; Wariishi, H.; Marquez, L.; Dunford, H. B.; Gold, M. H. *Biochemistry* **1994**, *33*, 8694.
3. (a) Morohoshi, N.; Wariishi, H.; Muraiso, C.; Nagai, T.; Haraguchi, T. *Mokuzai Gakkaishi* **1987**, *33*, 218. (b) Ducros, V.; Davies, G. J.; Lawson, D. M.; Wilson, K. S.; Brown, S. H.; Ostergaard, P.; Pedersen, A. H.; Schneider, P.; Yaver, D. S.; Brzozowski, A. M. *Acta Cryst. D* **1997**, *D53*, 605.
4. (a) Joo, H.; Chae, H. J.; Yeo, J. S.; Yoo, Y. J. *Process Biochem.* **1997**, *32*, 291. (b) Kurek, B.; Artaud, I.; Pollet, B.; Lapierre, C.; Monties, B. *J. Agric. Food Chem.* **1996**, *44*, 1953. (c) Okusa, K.; Miyakoshi, T.; Chen, C.-L. *Holzforschung* **1996**, *50*, 15. (d) Dordick, J. S.; Marletta, M. A.; Klibanov, A. M. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 6255. (e) Kurek, B.; Artaud, I.; Pollet, B.; Lapierre, C.; Monties, B. *J. Agric. Food Chem.* **1996**, *44*, 1953. (f) Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1981**, *22*, 4437.
5. (a) Katsuki, T. *Recent Res. Dev. Pure Appl. Chem.* **1997**, *1*, 35. (b) Ito, Y. N.; Katsuki, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 603. (c) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 1993; pp 159–202.
6. (a) Nakajima, K.; Kojima, K.; Fujita, J. *Chem. Lett.* **1986**, 1483. (b) Kokubo, C.; Katsuki, T. *Tetrahedron* **1996**, *52*, 13895. (c) Bunce, S.; Ronald, R. J.; Farrugia, L. J.; Kunchandy, S.; Meason, L. L.; Muir, K. W.; O'Donnel, M.; Peacock, R. D.; Stirling, D.; Teat, S. J. *Polyhedron* **1998**, *17*, 4179.
7. (a) Henke, S. L. *Expert Opin. Ther. Pat.* **1999**, *9*, 169. (b) Baker, K.; Marcus, C. B.; Huffman, K.; Kruk, H.; Malfroy, B.; Doctrow, S. R. *J. Pharmacol. Exp. Ther.* **1998**, *284*, 215. (c) Baudry, M.; Etienne, S.; Bruce, A.; Palucki, M.; Jacobsen, E.; Malfroy, B. *Biochem. Biophys. Res. Commun.* **1993**, *192*, 964.
8. (a) Routier, S.; Vezin, H.; Lamour, E.; Bernier, J.-L.; Catteau, J.-P.; Bailly, C. *Nucleic Acids Res.* **1999**, *27*, 4160. (b) Kumbhar, A. S.; Damle, S. G.; Dasgupta, S. T.; Rane, S. Y.; Kumbhar, A. S. *J. Chem. Res., Synop.* **1999**, 98. (c) Sakamoto, F.; Sumiya, T.; Fujita, M.; Tada, T.; Tan, X. S.; Suzuki, E.; Okura, I.; Fujii, Y. *Chem. Lett.* **1998**, 1127.
9. Belokon, Y. N.; Caveda-Cepas, S.; Green, B.; Ikonnikov, N. S.; Khrustalev, V. N.; Larichev, V. S.; Moscalenko, M. A.; North, M.; Orizu, C.; Tararov, V. I.; Tasinazzo, M.; Timofeeva, G. I.; Yashkina, L. V. *J. Am. Chem. Soc.* **1999**, *121*, 3968.

10. (a) Bolzacchini, E.; Canevali, C.; Morazzoni, F.; Orlandi, M.; Rindone, B.; Scotti, R. *J. Chem. Soc., Dalton Trans*. **1997**, 4695. (b) Bozell, J. J.; Hames, B. R.; Dimmel, D. R. *J. Org. Chem*. **1995**, *60*, 2398.
11. (a) Shearer, J. M.; Rokita, S. E. *Bioorg. Med. Chem. Lett*. **1999**, *9*, 501. (b) Cheng, C.-C.; Lu, Y.-L. *J. Chin. Chem. Soc*. **1998**, *45*, 611. (c) Tanaka, T.; Tsurutani, K.; Komatsu, A.; Ito, T.; Iida, K.; Fujii, Y.; Nakano, Y.; Usui, Y.; Fukuda, Y.; Chikira, M. *Bull. Chem. Soc. Jpn*. **1997**, *70*, 615. (d) Mandal, S. S.; Kumar, N. V.; Varshney, U.; Bhattacharya, S. *J. Inorg. Biochem*. **1996**, *63*, 265. (e) Routier, S.; Bernier, J.-L.; Waring, M. J.; Colson, P.; Houssier, C.; Bailly, C. *J. Org. Chem*. **1996**, *61*, 23262. (f) Botsvali, M.; Evans, D. F.; Missen, P. H.; Upton, M. W. *J. Chem. Soc., Dalton Trans*. **1985**, 1147. (g) Mukherjee, A. J.; Rây, P. *J. Indian Chem. Soc*. **1955**, *32*, 633.
12. Sipilä, J.; Pietikäinen, P.; Haikarainen, A.; Brunow, G. *Poster Presentations*, 9th International Symposium on Wood and Pulping Chemistry, Montreal, Canada, 9–12 June 1997; Marriot Château Champlain Montréal: Québec, Canada, 1997; p105–1.
13. Haikarainen, A.; Sipilä, J.; Pietikäinen, P.; Pajunen, A.; Mutikainen, I. *Dalton Trans*. **2001**, 991.
14. English, A. M.; Tsaprailis, G. *Adv. Inorg. Chem*. **1995**, *43*, 79.
15. Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc*. **1986**, *108*, 2309.
16. Feichtinger, D.; Plattner, D. A. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1718.
17. (a) Floriani, C.; Calderazzo, F. *J. Chem. Soc. (A)* **1969**, 946. (b) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev*. **1979**, *79*, 139. (c) Punniyamurthy, T.; Bhatia, B.; Reddy, M. M.; Maikap, G. C.; Iqbal, J. *Tetrahedron* **1997**, *53*, 7649. (d) Deng, Y.; Busch, D. H. *Inorg. Chem*. **1995**, *34*, 6380.
18. Chioccara, F.; Polia, S.; Rindone, B.; Pilati, T.; Brunow, G.; Pietikäinen, P.; Setälä, H. *Acta Chem. Scand*. **1993**, *47*, 610.
19. Pietikäinen, P. *Tetrahedron Lett*. **1994**, *35*, 941.
20. To be published later.
21. Becker, H.-D.; Björk, A.; Adler, E. *J. Org. Chem*. **1980**, *45*, 1596.
22. Quideau, S.; Ralph, J. *J. Agric. Food Chem*. **1992**, *40*, 1108.
23. (a) Pajunen, A.; Brunow, G.; Haikarainen, A.; Pietikäinen, P.; Sipilä, J. Z. *Kristallogr*. **1998**, *213*, 441. (b) Diehl, H.; Hach, C. C. *Inorg. Synth*. **1950**, *3*, 196.
24. Sipilä, J.; Syrjänen, K. *Holzforschung* **1995**, *49*, 325.
25. Landucci, L. L.; Ralph, S. A.; Hammel, K. E. *Holzforschung* **1998**, *52*, 160.
26. Pew, J. C.; Connors, W. J. *J. Org. Chem*. **1969**, *34*, 580.