Journal of Fundamental and Applied Sciences

ISSN 1112-9867

Available online at http://www.jfas.info

Research Article

Special Issue

THE OXIDATION OF ALCOHOLS WITH PICOLINATE METAL COMPLEX AS CATALYST

K. K. Uthumporn*, T. C. Darunee

Department of Chemistry, Faculty of Science, Maejo University Chiang Mai, Thailand

ABSTRACT

The oxidation of alcoholic functionalities is still important both an academic and industrial point of view. The study focused on the development of a catalytic system based on picolinate metal complex to improve the oxidation under mild condition with TBHP. Under these conditions, secondary alcohols were converted smoothly to the corresponding carbonyl compound in high yield with good selectivity. The oxidation of 1-phenyl ethanol was explored to acetophenone with 85.19 % yield in 5 hours. Additionally, the study focused on the oxidation of 2-phenyl alcohol afforded the corresponding aldehyde yield without carboxylic acid.

Keywords: picolinate; oxidation; alcohol

I. INTRODUCTION

The oxidation of abundant raw materials such as hydrocarbons which are derived from petroleum, to produce fine chemicals in the class of carbonyl compounds is still important both an academic and industrial point of view. The transformations generally involve the use of a metal catalyst. Clean oxidants such as O_2 and hydroperoxide are widely used for economic and environmental reasons.

Over recent years (1), the study of chromium-catalyzed oxidations with hydroperoxide has been explored. The oxidation of alcohols to carbonyl products with pyridinium chlorochromate (Collin's reagent) is selective and mild although the reaction utilizes chromyl chloride which is very hazardous and toxic.

Author Correspondence, e-mail: mooeed@hotmail.com

doi: http://dx.doi.org/10.4314/jfas.v10i3s.74

The use of hydroperoxide coupled with CrO_3 as catalyst has been used more recently instead of Collin's reagent to oxidize alcohols in good yield, especially allylic alcohols. (2) The Chromium-catalyzed oxidation with TBHP which involves a peroxometal pathway is more reactive than cumyl hydroperoxide because of steric effects. However, this is negligible in the case of primary alcohol. (3) On the other hand, another method which is less hazardous and affords high yields used anhydrous acetic acid for the first time as catalyst.(4) The first step involved the formation of pyridinium chloride which reacts with Chromium oxide to prevent the formation of Chromyl Chloride. Moreover, the improvement of the chromium complex (Chromium salen) for selective oxidation of alcohol to carbonyl compound, especially primary and secondary alcohols, has been reported.(5)

In the case of oxidation with catalysts other than metal complex such as Gif oxidation was of interest. (6-8) These conditions were used for hydrocarbon oxidation which catalyzed by Fe (III) picolinate. The reaction can be applied to both homogeneous and heterogeneous reaction. In homogeneous condition, the oxidation of cyclohexane in acetronitrile and pyridine as solvent and peroxide as oxidant give the desired product in high yield (based on oxidant) in cyclohexanone and afford cyclohexanol as a minor product. On the other hand, heterogeneous condition in which Fe (III) picolinate supported with an inorganic compound (zeolites) was used to improve the efficiency and was also advantageous due to the case of separation.

The oxidation of some aldoses, amino sugar and methylated sugars by tris (pyridine-2-carboxylato) manganese (III) have been studied. (9) The reaction afforded good result but the catalysts complex is very unstable in acid or alkaline medium it was therefore controlled by a sodium picolinate-picolinic acid buffer in the pH range of 4.22-6.45.

From the afore mentioned literatures, both Cr and picolinate ligands were found to be good in the oxidation, so it was of interest to complex them into a new catalyst. Generally Cr (III) picolinate helps the body burn fat in hepatic lipid oxidation it should therefore be a good catalyst for alcohol oxidation.(10)

In the study, we expect to improve the oxidation of alcohols to carbonyls utilizing a small amount of catalyst and a clean oxidant. The metal complex with picolinate was therefore used as the catalyst and TBHP as an oxidant at 70°C to study the oxidation of primary and secondary alcohols in mild condition.

II. MATERIALS AND METHOD

A. *The FT-IR spectra* were recorded on a Perkin Elmer fourier transform infrared. Solid samples were incorporated to potassium bromide to form a pellet. The ^{1}H spectra were obtained in deuterated chloroform ($CDCl_3$) solution with tetramethylsilane (TMS) as an internal reference on the Varian nuclear magnetic resonance spectrometer, model Mercury plus 400 NMR spectrometer which operated at 399.84 MHz. The chemical shifts (δ) are assigned by comparison with residue solvent protons.

B. *Chemical and Instrumentation*

Analytical grade iso-octane purchased from Merck was used as solvent. All of the chemicals used analytical grade from Merck to test the oxidation (1-phenyl ethanol, 2-phenyl ethanol). The oxidant, TBHP, was purchased from Fluka. Rotary vacuum evaporator (N-10004-W, Rikakikai, Japan) was used to dry the samples.

TLC Aluminum sheet was tested for the purification of the product which was pursed from Merck. Silica gel 60 F_{254} was used for stationary phase.

C. *Synthesis of Cr(III) picolinate*

Picolinic acid (3.75 g, 30.5 mmol) was added to $CrCl_3.6H_2O$ (2.56 g, 9.6 mmol) in deionized water and the resulting mixture was stirred for 24 hours. The product was washed with water and then filtered. The resulting pink solid was collected and dried at 70°C for 3 hours. The pink solid of Cr(III) picolinate was obtained in 2.59 g, 68.3% yield

IR (KBr): 1678 (s), 1606 (s),1158 and 847 (m) cm^{-1}.

D. *Synthesis of Zn(II) picolinate, Cu(II) picolinate and Fe(III) picolinate*

Picolinic acid (2.0 g, 16.3 mmol) was added to $ZnSO_4.7H_2O$ (3.0g, 10.4 mmol) in deionized water and the resulting mixture was stirred for 3 hours. The product was recrytaled with water and filtered. The resulting white solid was collected and dried at 70°C for 3 hours. The white solid of Zn (II) picolinate was obtained

Metal picolinate complex	% yield	physical properties
Chromium (III) picolinate	68.3	pink powder
Zinc (II) picolinate	96.5	white powder
Copper(II) picolinate	88.6	blue powder
Iron (II) picolinate	87.5	orange powder

Cu (II) picolinate and Fe(III) picolinate can be produced in the same way by using $CuSO_4.5H_2O$ and $FeSO_4.7H_2O$ respectively.

E. *The oxidation procedure (11)*

The solution of alcohol (5 mmol) in isooctane (5 mL) containing a catalyst (0.2 mmol) in a round bottom flask with TBHP (18mmol) as oxidant was refluxed at 70 ^{0}C. After the specific time or the reaction was completed (followed by TLC), the reaction mixture was taken and extracted twice with diethyl ether. The combined extracts were washed with distilled water. The organic layer was dried over anhydrous Na_2SO_4 and analyzed by column chromatography.

F. *The seperation of product by column chromatography*

The organic layer was separated by column chromatography using silica gel 60 (GF254) for stationary phase and the ratio between hexane and ethanol 9:1 for the mobile phase. After the separation was completed, the product structure was characterized by FTIR spectroscopy and ^{1}H-NMR spectroscopy.

III. RESULTS AND DISCUSSION

In the study, several transition metal picolinate complexes such as chromium(III), copper(II), iron(III) and Zinc (II) picolinate were prepared. These catalysts were then used for oxidation of alcohols. The metal picolinate complexes were identified by physical properties (Table 1) and IR spectroscopic data (Figure 1).

A. *Syntheses and identification of metal picolinate complexes.*

Table 1 express the properties of metal picolinate complexes. It was found that the color of the solids corresponding to the color of the state of the metal.

Table 1: The Synthesis of Cr(III) picolinate, Zn(II) picolinate, Cu(II) picolinate and Fe(III) picolinate

Metal picolinate complex	IR spectrum data (cm^{-1})
Chromium(III) picolinate	1678 (s), 1606 (s),1396 (s), 1158 (m) and 847 (m)
Zinc (II) Picolinate	1690 (s), 1594 (s),1350 (s), 1172 (m) and 720 (m)
Copper(II) picolinate	1643 (s), 1603 (s),1151 (s), 1150 (m) and 700 (m)
Iron (II) picolinate	1693 (s), 1594 (s),1297 (s), 1171 (m) and 750 (m)

The synthesis of metal complex gave high yeild. The method to prepare the catalyst is very easy and convenient to seperate from the mixture. The characteristic of the synthesis catalyst was done by IR spectroscopy and the result was shown in Figure1-4 and table 2.

Table 2: The IR data of Cr(III) picolinate, Zn(II) picolinate, Cu(II) picolinate and Fe(III) picolinate.

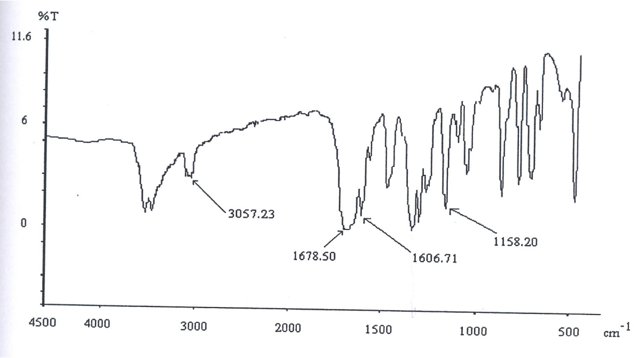

Fig.1. IR spectrum of chromium(III) picolinate complex

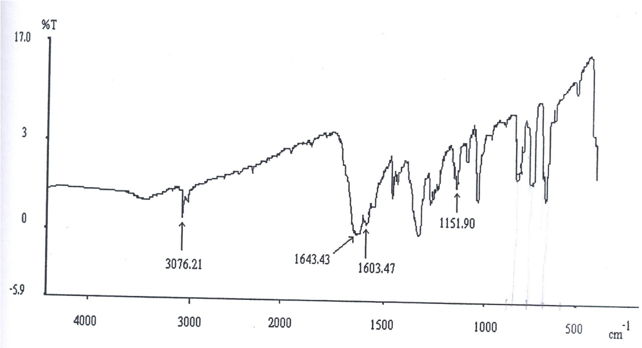

Fig.2. IR spectrum of copper(II) picolinate complex

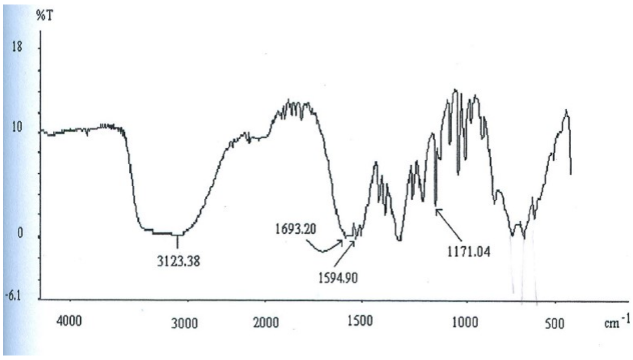

Fig.3. IR spectrum of Ferric (III) picolinate complex

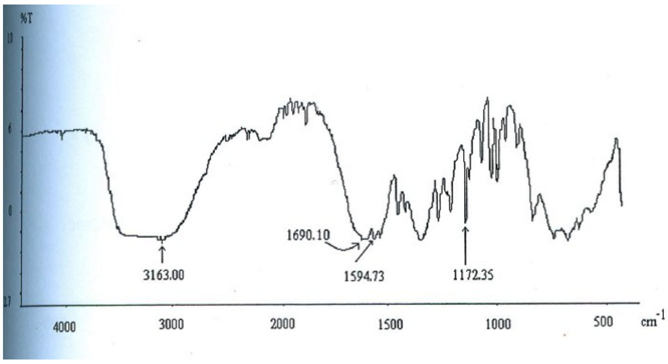

Fig.4. IR spectrum of Zinc (II) picolinate complex

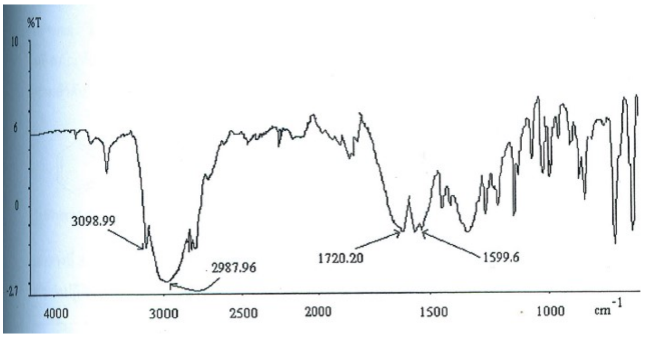

Fig.5. IR spectrum of picolinic acid

From the IR spectrum data, picolinic acid (Figure 5) revealed a broad COOH peak at 2700-3400 cm^{-1}, 1703 cm^{-1} for asymmetric stretching of COO and 1471 cm^{-1} for symmetric stretching of COO. For asymmetric and symmetric stretching of $(COO)^-$ of metal picolinate complex catalysts, the IR spectra of Chromium (III) picolinate, Figure 1 showed C=O bands at 1678 cm^{-1} and 1606,1396 cm^{-1} for the C=C aromatic ring, respectively. The COO peak shifts are the indication of complex formation. Both the free acid and the complexes showed a significant $(CH_2)_n$ skeletal vibration peak at 720 cm^{-1} (12).

The IR spectra of Copper (II) picolinate, Figure 2 showed C=O bands at 1643 cm^{-1} and 1603,1151 cm^{-1} for the C=C aromatic ring, respectively. The IR spectra of Iron (III) picolinate, Figure 3 showed C=O bands at 1693 cm^{-1} and 1594,1297 cm^{-1} for the C=C aromatic ring, respectively. The IR spectra of Zinc (II) picolinate, Figure 4 showed C=O bands at 1690 cm^{-1} and 1594,1350 cm^{-1} for the C=C aromatic ring, respectively.

As shown in table 2, every complex showing the broad peak of OH of COOH of acid around 2700-3400 cm^{-1} was gone but the carbonyl peak at 1600-1700 cm^{-1} and the character of C=C aromatic bond at 1400-1600 cm^{-1} still appeared on every metal complex although the spectrum was shifed because of the formation between metal and ligand. It can be conclude that the metal can form complexity with picolinic acid.

B. *The oxidation of secondary alcohol*

1-phenyl ethanol, one of the structurally simpler secondary alcohols provides the opportunity to study the effects of catalyst lead to preferably benzylic oxidation. The study refers only briefly to recent developments with regard to 1-phenyl ethanol oxidation. One of the most important and current topics of catalysis research has found an efficient catalysts for the benzylic oxidation of secondary alcohol, showing the equation in Figure 2.

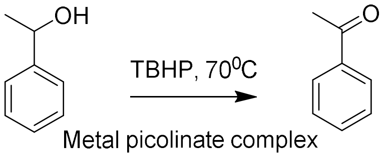

Fig.6. The equation of 1-phenyl ethanol oxidation

The experiments for determining the influence of metal picolinate complexes on the catalytic activities and product selectivity of 1-phenyl ethanol oxidation were performed at temperature of 70°C, using 0.20 mmol of metal picolinate catalysts and 10 mmol of 1-phenyl ethanol. The results were shown in Figure 3.

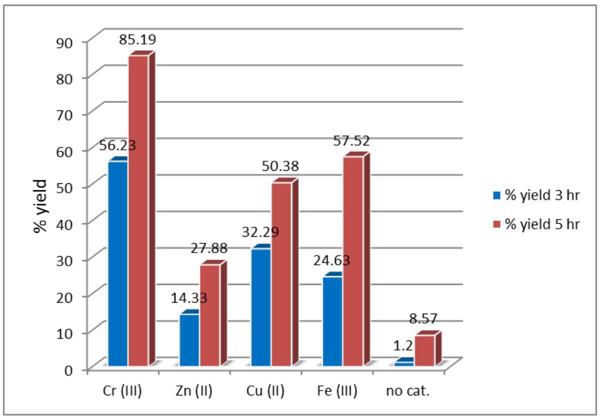

Fig.7. The oxidation of 1-phenyl ethanol

The examination on the influence of metal picolinate catalysts revealed that chromium (III) picolinate was appropriate catalysts for benzylic oxidation of 1-phenyl ethanol with good selectivity and high yield of product (85.19%). Zinc (II), Iron (III) and copper (II) picolinate catalysts also provided high selectivity for benzylic oxidation however the quantity of product was lower than Chromium complex.

From these present experiments, it was found that chromium (III) picolinate presented the very intriguiing catalytic activities, regarding the oxidation of 1-phenyl ethanol being converted to acetrophenone in high yield (85.19%) without by product. This study indicated that the conversion of 1-phenyl ethanol over metal picolinate catalysts investigated followed a sequence of Cr $(pic)_3$>Cu $(pic)_2$~Fe $(pic)_3$>Zn $(pic)_2$.

The experiment took 3 and 5 hours for the reaction. It was found that when the reaction took more time, the product increases. Moreover, the reaction without catalyst gave very low yield. Although it uses longer time, it was found no differences. These preliminarily attractive results prompted for further investigation of the primary alcohol oxidation.

C. *The oxidation of primary alcohol*

From previous results, chromium(III) picolinate provided the excellent selectivity of the desired product and gave high yield. The use of chromium(III) picolinate could be studied to the oxidation of 2-phenul ethanol. One of the structurally simpler primary alcohols provides the opportunity to study the effect of Chromium (III) picolinate for primary alcohol and the equation of the reaction, as showed in Figure 3.

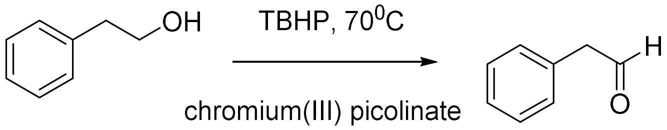

Fig.8. The equation of 2-phenyl ethanol oxidation

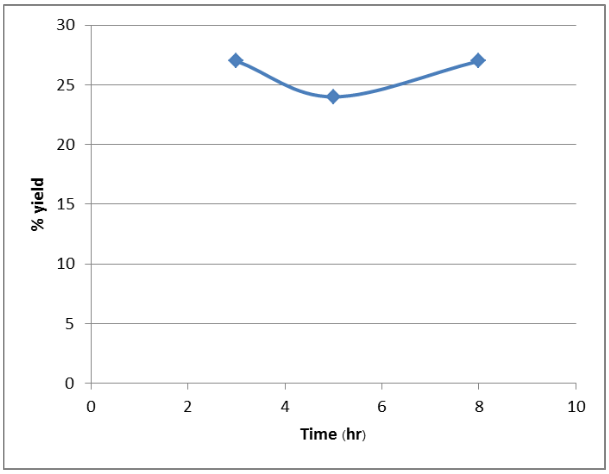

Fig.9. The oxidation of 2-phenyl ethanol

From Figure 4, the catalyst was used to study the primary alcohol. The use of 2-phenyl ethanol 10 mmol, chromium(III) picolinate catalyst and isooctane were added in the reaction. When we increased the time of reaction, the result was found no differences. The result showed that the reaction can produce the product in high selectivity without by product but expressing lower yield than the oxidation of the secondary alcohol.

D. *The selectivity of the primary and secondary alcohol*

The selectivity of catalyst was tested by the reaction mixture of 1-phenyl ethanol and 2-phenyl ethanol and the result was shown in Table3.

Table 3. The oxidation of 1-phenyl ethanol and 2-phenyl ethanol mixture

Time(hr.)	**Acetophenone (%)**	**Benzaldehyde (%)**
3	51.57	0
5	72.32	0

The selectivity catalyst on the oxidation of alcohol was found that the catalyst was selected with the secondary alcohol without the functionalization of primary alcohol.

Previously, we have shown that alcohol is oxidised by TBHP under aerobic conditions used in the present work, and so the data indicated that all metal picolinate complexes examine are indeed active catalysts.With oxidations employing TBHP, heterolytically catalyzed by appropriate metal ion centres (e.g. Cr, Zn, Fe, Cu etc.), with concomitant oxidation of alcohol to corresponding carbonyl compound (Figure5). The chromium(III) complex was transformed to the corresponding high valent(formally) Cr^{V}=O species. This species was then abstracted benzylic hydrogen to form the corresponding benzylic radical and $Cr^{IV}X(OH)$. The benzylic radical was rapidly reacted with O_2 to give hydroperoxyl radical intermediate. Subsequently, it transformed relatively , not stable benzylic hydroperoxide. The decomposition of benzylic hydroperoxide yielded to coreesponding carbonyl compound.

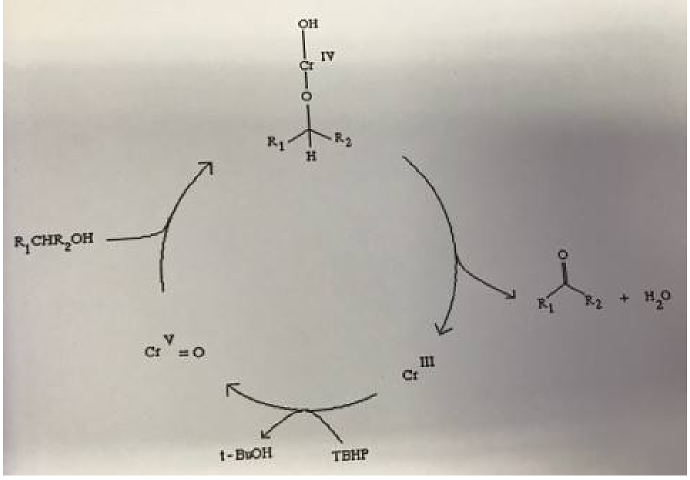

Fig.10. Proposed mechanism for the oxidation of alcohol catalyzed by chromium(III) picolinate

IV. CONCLUSION

The oxidation of secondary alcohols and the primary alcohol were accomplished under mild condition provided moderate to excellent yields of carbonyl compounds. The case of aldehyde oxidation in the same condition also afforded excellent yields of corresponding carboxylic acid.

ACKNOWLEDGMENTS

We would like to acknowledge the Department of Chemistry, Faculty of Science, Maejo University for making the study possible.

REFERENCES

[1] J.C. Collins, W.W. Hes, F.J. Franck, Tetrahedron Lett. (9) (1968) 3363.
[2] E.J. Corey, J.W. Suggs, Tetrahedron Lett. (16) (1975) 2647.
[3] E.J. Corey, G. Schmidt, Tetrahedron Lett. (20) (1979) 399.
[4] M. Hunsen, J. Flu. Chem. (126) (2005) 1356.
[5] J.D. Lou, C.L. Gao, Y.C. Ma, L.H. Huang, L. Li, Tetrahedron Lett. (47) (2006) 311.
[6] J. Muzart, Tetrahedron Lett. (28) (1987) 2133.
[7] R. Abdelkhalek, H. Francoise, M. Jacques, Tetrahedron Lett. (40) (1999) 2303.
[8] S. Agarwal, H.P. Tiwari, J.P.R. Sharma, Tetrahedron. (46) (1990) 4417.
[9] A. Waldemar, G.G. Feyissa, R. Chantu, S. Moller, R.C. Veit, J. Org. Chem. (65) (2000) 1915.

[10] A. Waldemar, S. Hajra, M. Herderich, S. Moller, Org. Lett. (2) (2000) 2773.

[11] Y. Maeda, N. Kakiuchi, S. Matsumura, T. Nishimura, T. Kawamura, S. Uemura J. Org. Chem. (67) (2002) 6718.

[12] S.R. Reddy, S. Das, T. Punniyamurthy, Tetrahedron Lett. (4) (2004) 3561.

[13] T. Iwahama, Y. Yoshino, T. Keitoku, S. Sakaguchi, Y.J. Ishii, J. Org. Chem. (65) (2000) 6502.

[14] R.C. Pratt, T.D.P. Stack, J. Am. Chem. Soc. (125) (2003) 8716.

[15] S. Velusamy, A. Srinivasan, T. Punniyamurthy, Tetrahedron Lett. (47) (2006) 923.

[16] S. Velusamy, M. Ahamed, T. Punniyamurthy, Org. Lett. (6) (2004) 4821.

[17] H. Egami, S. Onitsuka, T. Katsuki, Tetrahedron Lett. (46) (2005) 6049.

[18] H. Egami, S. Shimizu, T. Katsuki, Tetrahedron Lett. (46) (2005) 783.

[19] H. Shimizu, S. Onitsuka, H. Egami, T. Katsuki, J. Am. Chem. Soc. (127) (2005) 5396.

[20] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. (122) (2000) 7144.

[21] I.E. Marko, P.R. Giles, M. Tsukazaki, I. Chelle-Regnaut, C.J. Urch, S.M. Brown, J. Am. Chem. Soc. (119) (1997) 12661.

[22] G. Csjernyik, A.H. Ell, L. Fadini, B. Pugin, J.E.J. Backvall, J. Org. Chem. (67) (2002) 1657.

[23] P. Paraskevopoulou, N. Psaroudakis, S. Koinis, P. Stavropoulos, K. Mertis, J. Mol. Cat. A. (240) (2005) 27.

[24] K. Kaneda, M. Fujii, K. Morioka, J. Org. Chem. (61) (1996) 4502.

[25] T. Nishimura, T. Onoue, K. Ohe, S. Uemura, J. Org. Chem. (64) (1999) 6750.

[26] K.P. Peterson, R.C. Larock, J. Org. Chem. (63) (1998) 3185.

[27] M.J. Schultz, S. S. Hamilton, D. R. Jensen, M. S. Sigman, J. Org. Chem. (70) (2005) 3343.

[28] Iwasawa, M. Tokunaga, Y. Obora, Y. Tsuji, J. Am. Chem. Soc. (126) (2004) 6554.

[29] U.S. Patent 4315927 (Nutrition 21, San Diego,CA).

[30] C.L. Broadhurst, F.S. Walter, B.R. James, M.P. Marilyn, M., G. Kurt, A.A. Richard, J. Inor. Bio. (66) (1997) 119.

How to cite this article:
Uthumporn K K, Darunee T C. The oxidation of alcohols with picolinate metal complex as catalyst. J. Fundam. Appl. Sci., 2018, *10(3S), 855-865.*