CHINESE JOURNAL OF CHEMISTRY **2003**, *21*, 1—3

Communication

A New Approach on the Active Treatment for Electroless Plating on Glass

LIU, Zheng-Chun(刘正春) **HE, Quan-Guo**(贺全国) **TANG, Jian-Xin**(汤建新)
XIAO, Peng-Feng(肖鹏峰) **HE, Nong-Yue***(何农跃) **LU, Zu-Hong***(陆祖宏)
Key Laboratory for Molecular and Bio-molecular Electronics of Ministry of Education, Southeast University, N 210096, China

A new method is described for the electroless deposition of copper onto glass. Commercially available glass slide was modified with γ-aminopropyltrimethoxysilane to form self-assembled monolayer (SAM) on it. Then it was dipped directly into $PdCl_2$ solution in-

growth of copper deposit was inhibited.[1,6] Th portant to develop a tin-free process in the e industry to avoid the side effect of tin atoms

Communication

A New Approach on the Active Treatment for Electroless Copper Plating on Glass

LIU, Zheng-Chun(刘正春) **HE, Quan-Guo**(贺全国) **TANG, Jian-Xin**(汤建新)
XIAO, Peng-Feng(肖鹏峰) **HE, Nong-Yue***(何农跃) **LU, Zu-Hong***(陆祖宏)
Key Laboratory for Molecular and Bio-molecular Electronics of Ministry of Education, Southeast University, Nanjing, Jiangsu 210096, China

A new method is described for the electroless deposition of copper onto glass. Commercially available glass slide was modified with γ-aminopropyltrimethoxysilane to form self-assembled monolayer (SAM) on it. Then it was dipped directly into $PdCl_2$ solution instead of the conventional $SnCl_2$ sensitization followed by $PdCl_2$ activation. Experimental results showed that the Pd^{2+} ions from $PdCl_2$ solution were coordinated to the amino groups on the glass surface resulting in the formation of N—Pd complex. In an electroless copper bath containing a formaldehyde reducing agent, the N—Pd complexes were reduced to Pd^0 atoms, which then acted as catalysts and initiated the deposition of copper metal. Although the copper deposition rate on SAM-modified glass was slow at the beginning, it reached to that of conventional method in about 5 min.

Keywords self-assembled monolayer, electroless copper plating, activation

Electroless plating of metal is an important industrial coating technique for metallizing insulators (*e.g.*, plastics, glass) and objects with geometries that are difficult to coat by electroplating.[1,2] In contrast to electroplating, where an applied current supplies electrons to reduce a high-oxidation-state metal precursor, the basis of electroless plating is an autocatalytic redox reaction. The important material prerequisite for initiating metal deposition is the presence of an appropriate catalytic surface. For many materials (*e.g.*, insulators), the surface is not inherently catalytic and must be activated prior to electroless plating. The metal, usually Cu or Ni, was deposited on the catalytic sites formed on the object surface. These sites usually contain palladium nuclei chemisorbed from solution. Different methods have been proposed to perform this chemisorption. Historically, the most widely used methods were the "two-step" process and "one-step" process. In the two-step method, the object was successively immersed in a $SnCl_2$ solution and then in a $PdCl_2$ solution.[3,4] The one-step process, on the other hand, used a mixed $SnCl_2/PdCl_2$ solution.[5] Since $SnCl_2$ was used in both methods, the palladium particle was surrounded by a tin chloride shell after the Pd^{2+} ion was reduced to Pd^0 by $SnCl_2$.[6] However, tin chloride is not an active catalyst for electroless plating. As a result, the growth of copper deposit was inhibited.[1,6] Therefore, it is important to develop a tin-free process in the electroless plating industry to avoid the side effect of tin atoms.

Recently, some authors have showed that nitrogen-containing polymers can coordinate with Pd^{2+} through N-Pd complex formation.[7-10] The N-Pd complex is reduced to Pd^0 in an electroless plating bath prior to the electroless deposition of metal. Glass surface does not possess any polar groups that can form a complex with Pd^{2+}. In this paper, a new method for initiating electroless copper deposition onto glass is described. Commercially available glass slides are modified using γ-aminopropyltrimethoxysilane to form self-assembled monolayers (SAMs) on them. Then the modified glass is immersed into $PdCl_2$ solution. The amino groups of SAM will coordinate with the Pd^{2+} ions resulting in N-Pd complex. No acceleration step is required. Immersion of this modified glass into an electroless plating bath containing formaldehyde reducing agent, spontaneously reduces the Pd^{2+} to Pd^0, which is an active catalyst for electroless copper deposition. We have also compared our process with the conventional two-step process.

For the preparation of self-assembled monolayer of γ-aminopropyltrimethoxysilane (APTES), a modified protocol from the literature was used.[11] Glass slides were immersed for 15 min in 1% APTES solution of 95% acetone/water. Afterwards, the glass slides were washed five times (5 min each) with acetone, dried for 45 min at 110 ℃ and weighed.

Surface activations for electroless plating of copper on glass slides were done by the two following methods. (i) The pristine glass slide was sensitized in a solution containing 10 g/L $SnCl_2 \cdot 10H_2O$ and 40 mL/L HCl (37%) for 5 min, rinsed with distilled water, immersed in a solution containing 0.25 g/L $PdCl_2$ and 10 mL/L HCl (37%) for 10 min and rinsed thoroughly with distilled water. (ii) The SAM-modified glass slides were directly immersed in a solution containing 0.25 g/L $PdCl_2$ and 10 mL/L HCl (37%) for 10 min and rinsed thoroughly with distilled water. The surface-activated glass slides were finally placed in an electroless plating

* E-mail: nyhe@seu.edu.cn; zhlu@seu.edu.cn
Received June 28, 2002; revised September 23, 2002; accepted October 18, 2002.
Project supported by the National Natural Science Foundation of China (No. 60071001).

bath. The composition of the plating bath was as follows:[12] 26 g/L $CuSO_4 \cdot 5H_2O$, 43 g/L potassium sodium tartrate, ($KNaC_4H_4O_6 \cdot 4H_2O$), 21 g/L sodium hydroxide, (NaOH), 17.5 ml/L formaldehyde (37%), and 10 mg/L 2,2′-bipyridine. The bath was used at room temperature during plating. The Cu-deposited glass slides were then rinsed thoroughly with copious amounts of doubly distilled water and dried, followed by weighing to calculate the amount deposited.

Surface chemical modifications were determined by X-ray photoelectron spectrometry (XPS) and Auger electron spectroscopy using a Perner Elemer PHI 550 multi-technique spectrometer equipped with a nonmonochromatic Al Kα excitation source run at 250 W. The binding energy scale was calibrated to 285.0 eV for the main C1s (C—C bond) feature. The operating pressure was less than 1.3×10^{-6} Pa.

In Fig. 1, spectra (a) and (b) illustrate the elemental analysis of XPS measurement for the SAM modified glass surface and that after treatment with $PdCl_2$ solution, respectively. Peak at binding energy of about 400 eV represents nitrogen content on the surface of glass, which suggests the formation of self-assembled monolayer of γ-aminopropyltrimethoxysilane (APTES) on glass surface. At the same time, five points on the modified glass were randomly chosen for AES analysis. The results revealed the same content of nitrogen component for these five points, indicating that the self-assembly of APTES on the glass surface produced a homogenous film.

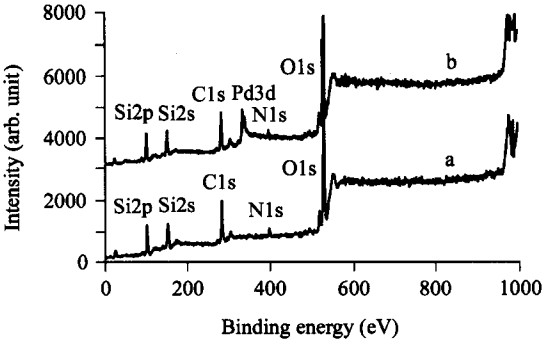


Fig. 1 XPS elemental analysis spectra for the SAM modified glass surface (a) and that after treatment with $PdCl_2$ solution (b).

Compared with spectrum (a) in Fig.1, (b) shows additional Pd3d peaks. It suggests that Pd species have been anchored onto the SAM modified glass.

In Fig. 2, spectra (a) and (b) show N1s core-level spectra of the SAM modified glass surface and that after activation in $PdCl_2$ solution for 10 min, respectively. In spectrum (a), the N1s peak was about 398.9 eV which is the typical peak of nitrogen in amino group (NH_2).[13] After activation, a distinct new peak component at the higher binding energy of about 400.1 eV is discernible. The appearance of this high binding energy component is consistent with the formation of Pd-N complex. Fig. 3 represents four spectra. Spectra (b) and (a) correspond to the SAM-modified glass surface after activation in $PdCl_2$ solution for 10 min and that after immersion in plating bath for 5 min, respectively. For comparison, Pd3d core-level spectra of metallic palladium and $PdCl_2$ are presented as spectra (c) and (d), respectively. In spectra (b), the binding energies for the $Pd3d_{5/2}$ and $Pd3d_{3/2}$ peaks are about 336.5 and 341.5 eV, respectively, which are assigned to the Pd complex.[14]

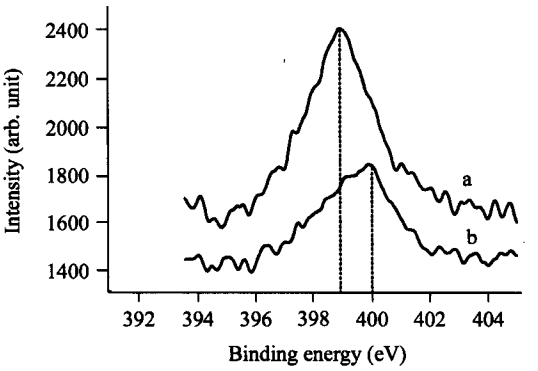


Fig. 2 N1s core-level spectra of the SAM modified glass surface (a) and that after activation in $PdCl_2$ solution for 10 min (b).

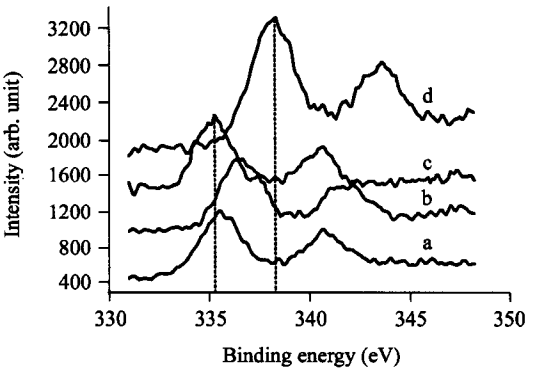


Fig. 3 Pd3d core-level spectra of the SAM-modified glass surface after activation in $PdCl_2$ solution for 10 min (b), that after immersion in plating bath for 5 min (a), metallic palladium (c) and $PdCl_2$ (d).

Pd^0 is a well-known catalyst that initiates electroless copper deposition. In this system, the Pd-N complex is reduced to Pd^0 in electroless plating bath. This process was shown by the color change of glass surface, from colorless to gray, observed upon immersion of the Pd-N complex in electroless plating bath. Pd3d core-level spectra of the SAM-modified glass surface after activation in $PdCl_2$ solution immersed in plating bath for 5 min, as shown as spectrum (a) in Fig. 3, also confirmed this process, where the binding energies for the $Pd3d_{5/2}$ and $Pd3d_{3/2}$ peaks lying at about 335.5 and 340.7 eV, respectively, are nearly the same as those of metallic palladium [spectrum (c)].[15]

Fig. 4 shows the amount of Cu deposition versus plating time. The SAM modified glass, after treatment with $PdCl_2$ solution, was directly immersed into electroless plating bath. The copper deposition rate was slow at the beginning, and then approached that of the conventional method. The time delay is about 5 min due to the transition of Pd-N complex to Pd^0. The delay time can be eliminated, if $PdCl_2$ solution

treated SAM-modified glass is reduced with HCHO solution before immersion in electroless plating bath, as shown in Fig. 4 (curve ●). There is no significant difference in deposition amount and rate between the two methods.

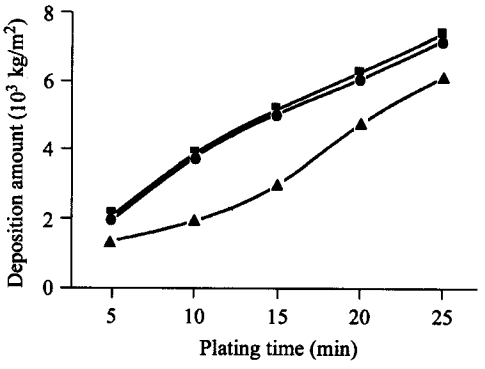


Fig. 4 Amount of Cu deposition versus plating time. ■—conventional method; ▲—Pd-N complex immersed directly in electroless plating bath; ●—Pd-N complex firstly reduced then immersed in electroless plating bath.

In addition, when conventional $SnCl_2$ sensitized glass is activated with $PdCl_2$ solution, due to stripping some of tin compounds will dissolve in solution and catalyze the reduction of Pd^{2+} ions, which decrease Pd^{2+} concentration and accordingly reduce the lifetime of the activation solution. Whereas, since APTES SAM adheres covalently to glass, the $PdCl_2$ activation solution will not be affected during the activation of the SAM-modified glass. Consequently, the useful-time of $PdCl_2$ activation solution is prolonged and the utilization of $PdCl_2$ activation solution is improved.

In summary, a new method for initiating the electroless deposition of copper onto glass has been described. γ-Aminopropyltrimethoxysilane (APTES) was successfully used to form SAM on glass surface. XPS studies showed that the amino groups of SAM formed a complex with Pd^{2+}, which was reduced to Pd^0 by the reducing reagent in electroless copper plating bath, and then catalyzed the deposition of copper onto the glass. The copper deposition amount experiments proved that the copper deposition rate on SAM-modified glass would reach to that of conventional method in about 5 min.

References

1 Riedel, W. *Electroless Nickel Plating*, Finishing Publications, Metals Park, **1991**, Chapters 1, 3 and 9.

2 Yosi, S. D.; Valery, D.; Matthew, A. *Thin Solid Films* **1995**, *262*, 93.

3 Muller, G.; Baudrand, D. W. *Plating on Plastics: a Practical Handbook*, Robert Draper Ltd., Teddington, **1971**.

4 Ebneth, H. In *Metallizing of Plastics. Handbook of Theory and Practice*, Ed.: Suchentrunk, R., 30th ASM International, Materials Part, Finishing Publications Ltd. and ASM International, Chicago **1993**, p. 30.

5 Meek, R. L. *J. Electrochem. Soc.* **1975**, *122*, 1478.

6 Jackson, R. L. *J. Electrochem. Soc.* **1990**, *137*, 95.

7 Charbonnier, M.; Alami, M.; Romand, M. *J. Electrochem. Soc.* **1996**, *143*, 472.

8 Yang, G. H.; Kang, E. T.; Neoh, K. G. *Langmuir* **2001**, *17*, 211.

9 Yen, P. C. *Polymer* **1995**, *36*, 3399.

10 Warshawsky, A. W.; Upson, D. A. *Polymer* **1989**, *30*, 972.

11 Guo, Z.; Guiltoyle, R. A.; Thile, A. J.; Wang, R.; Smith, L. M. *Nucleic Acid Res.* **1994**, *22*, 5456.

12 Niino, H.; Yabe, A. *Appl. Phys. Lett.* **1993**, *60*, 2697.

13 Hercules, D. M.; Cox, L. E.; Onisick, S.; Nichols, G. D.; Carver, J. C. *Anal. Chem.* **1973**, *45*, 1973.

14 Dressick, W. J.; Dulcey, C. S.; George, J. H.; Calabrese, G. S.; Calvert, J. M. *J. Electrochem. Soc.* **1994**, *141*, 210.

15 Mance, A. M.; Waldo, R. A.; Dow, A. A. *J. Electrochem. Soc.* **1989**, *136*, 1667.

(E0206281 LI, L. T.; FAN, Y. Y.)

Communication

Lipases-Catalyzed Alcoholysis for the Preparation of Chiral 1- or 2-Hydroxyalkanephosphonates†

ZHANG, Yong-Hui(张永辉) **LI, Jin-Feng**(李晋峰) **WANG, Ke**(王科) **YUAN, Cheng-Ye***(袁承业)
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

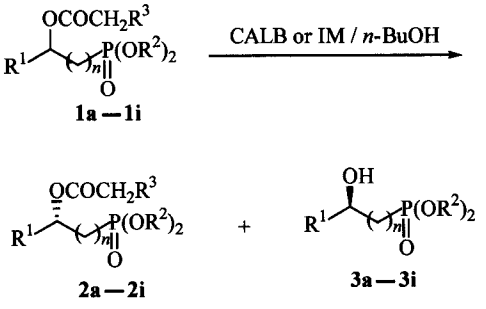
Enzymatic alcoholysis has been developed for the preparation of some chiral 1- and 2-hydroxyalkanephosphonates with high optical purity. This method ensures the convenient access to the optically pure phosphocarnitine, phosphogabob and phosphomycin.

Keywords lipase, alcoholysis, hydroxyalkanephosphonate

Chiral 1- or 2-hydroxyalkanephosphonates show intriguing properties in biology and organic chemistry.[1] The traditional synthetic route leading to such compounds sometimes has drawbacks such as harsh reaction conditions, expensive reagents and low chemical yields.[2] To explore new and convenient procedure is therefore of importance. The utility of lipases for efficient resolution of alcohols and related compounds has shown great importance in organic synthesis.[3] Hammerschmidt has exploited such hydrolases for enantioselective hydrolysis of a series of 1-acyloxyphosphonates in an organic-buffer biphase system.[4] It is known that lipase-catalyzed kinetic resolution of secondary alcohols in organic media can overcome the limitations of the conventional method, such as instability of enzymes, time consuming experimental procedures, relatively lower selectivity, *etc*. We have developed *Candida antarctica* lipase B (CALB)-catalyzed acetylation[2] and crude *Candida rugosa* lipase (CRL)-catalyzed hydrolysis[5] in isopropyl ether for preparing optically active 1- or 2-hydroxyalkanephosphonates. Continuing our study on enzymatic reactions in organic media, we herein wish to report enzymatic resolution of various functionalized acyloxyalkanephosphonates catalyzed by CALB or immobilized *Mucor miehei* lipase (IM).

The optically active 1- or 2-hydroxyalkanephosphonates bearing trifluoromethyl moiety aroused our interest. Though we have developed CALB-catalyzed enantioselective acetylation of hydroxyalkanephosphonates, the method failed to resolve the trifluoromethyl containing substrates. There was no trace of the corresponding acetate detected after one week. We ascribe the poor reactivity to the strong electron-withdrawing effect of the trifluoromethyl moiety, which greatly decreases the nucleophility of the alcohol oxygen. To circumvent this problem, we attempted enzymatic alcoholysis of acyloxyalkanephosphonates (Scheme 1).

Scheme 1



R^1 = Me, Et, vinyl, CF_3; $ClCH_2$, N_3CH_2; R^2 = Et, *n*-Pr, *i*-Pr; R^3 = $ClCH_2$, *n*-Pr; *n* = 0, 1

We have found that the acyl component has profound effect on the reactivity. As to CALB-catalyzed alcoholysis, electron-withdrawing chloroacetyl facilitated the reaction, while acetyl or butyryl group led to poor conversion. For example, some 1- and 2-chloroacetyloxyalkanephosphonates were efficiently alcoholyzed by CALB. This method also provided a convenient access to nearly optically pure hydroxyalkanephosphonates bearing a trifluoromethyl moiety. It should be noted that, however, those substrates containing another chlorine atom could not be resolved successfully by CALB, which may be due to the non-steric effect.[6] Hammerschmidt has reported the resolution of 2-azido-1-hydroxyethylphosphonates using lipase SP524 (*mucor miehei* lipase).[7] Among lipases screened, we also found that IM served as an effective biocatalyst for enantioselective alcoholysis of some 1, or 2-acyloxyalkanephosphonates including azido- or chlorine-bearing ones. It is interesting to note that IM could resolve both 1-chloroacetyloxy and 1-butyryloxyalkanephosphonates efficiently with the later giving much better enantioselectivity. When 2-hydroxyalkanephosphonates were

* E-mail: yuancy@pub.sioc.ac.cn; Fax: +86-21-64166128
Received October 11, 2002; revised and accepted November 25, 2002.
Project supported by the National Natural Science Foundation of China (Nos. 20072052 and 29832050).
† Studies on organophosphorus compounds 119.

used as substrates, however, only their chloroacetyl derivatives were alcoholyzed using butanol as a nucleophile .

Compound **3f** and its (*R*)-isomer underwent dealkylation with Me_3SiBr/MeOH to afford the corresponding hydroxyphosphonic acids, which could be easily converted to both isomers of phosphorus analogues of Carnitine which was prepared by Michalski's group via traditional synthetic method.[8]

Both isomers of phosphorus analogues of Gabob could also be obtained from Pd/C hydrogenation of **3n** and of its (*S*)-isomer, followed by dealkylation in the usual manner.[9]

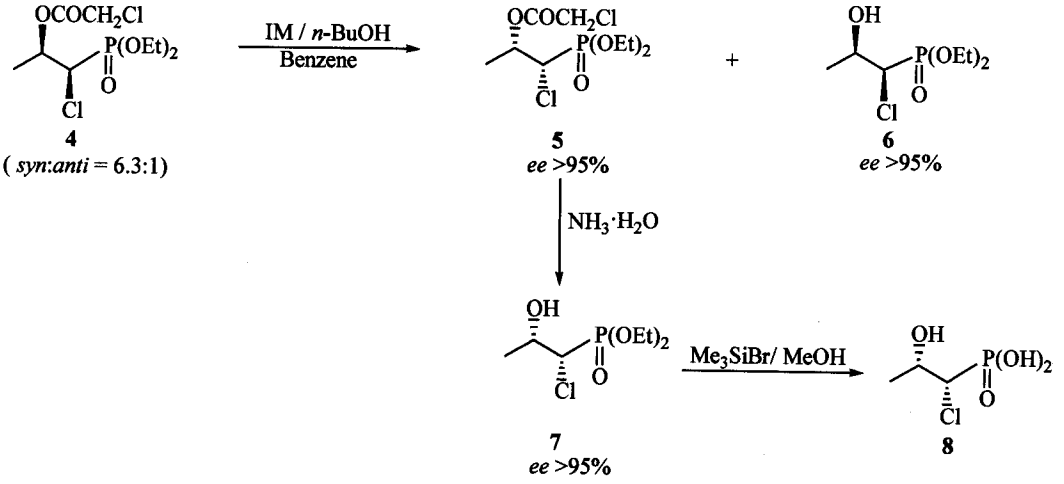
Additionally, this methodology also ensured the preparation of optically pure *syn*-1-chloro-2-hydroxypropanephosphonates (**7**), which underwent dealkylation to afford the key precursor **8** of phosphomycin (Scheme 2).[10]

Table 1 CALB and IM catalyzed enantioselective alcoholysis of 1- and 2-acyloxyalkanephosphonates [a,b]

Entry	Sub	*n*	R^1	R^2	R^3	Lipase	Time (h)	Yield of **2** (%)	*ee* of **2** (%)[d]	Yield of **3** (%)	*ee* of **3** (%)[c]	*E*[e]
1	**1a**	0	Me	*i*-Pr	$ClCH_2$	CALB	40	41	> 95	42	> 95	> 100
2	**1b**	0	Et	Et	$ClCH_2$	CALB	42	42	> 95	41	> 95	> 100
3	**1c**	0	Et	*i*-Pr	$ClCH_2$	CALB	40	43	> 95	41	> 95	> 100
4	**1d**	0	vinyl	Et	$ClCH_2$	CALB	55	42	> 95	41	91	> 100
5[f]	**1e**	0	$ClCH_2$	Et	$ClCH_2$	CALB	58	—	—	—	28	< 10
6	**1f**	0	$ClCH_2$	*n*-Pr	*n*-Pr	IM	49	43	> 95	42	> 95	> 100
7	**1g**	0	CF_3	Et	$ClCH_2$	CALB	33	38	94	44	79	30
8	**1h**	0	CF_3	*n*-Pr	$ClCH_2$	CALB	49	39	> 95	43	82	> 37
9[g]	**1i**	0	CF_3	*n*-Pr	*n*-Pr	IM	30	41	—	40	> 95	—
11	**1j**	1	Me	*i*-Pr	$ClCH_2$	IM	42	43	> 95	44	> 95	> 100
12	**1k**	1	Et	Et	$ClCH_2$	IM	78	36	> 95	45	> 95	> 100
13	**1l**	1	vinyl	Et	$ClCH_2$	CALB	40	43	> 95	44	> 95	> 100
14	**1m**	1	$ClCH_2$	Et	$ClCH_2$	IM	50	45	90	44	94	100
15	**1n**	1	N_3CH_2	Et	$ClCH_2$	CALB	55	44	> 95	48	92	> 89
16	**1n**	1	N_3CH_2	Et	$ClCH_2$	IM	29	45	70	38	94	67
17	**1o**	1	CF_3	Et	$ClCH_2$	CALB	40	43	93	44	> 95	> 100
18	**1p**	1	CF_3	*i*-Pr	$ClCH_2$	IM	43	44	75	40	> 95	> 88
19	**1q**	1	CF_3	*n*-Pr	$ClCH_2$	CALB	35	44	94	39	> 95	> 100

[a] Reactions were generally performed on 1 mmol of scale, 1.5—2 mL of solvent, 0.3—0.5 mL of *n*-BuOH, 100 mg of lipase, 30 ℃. [b] The configurations of **2** and **3**, determinded by refined Mosher's method, are depicted in Scheme 1. [c] *ee* value was determined by ^{19}F NMR or ^1H NMR of its Mosher's ester; some of them were confirmed by ^{19}F NMR or ^{31}P NMR using quinine as the chiral solvating agent. [d] The *ee* value of ester was determined after its chemical conversion to alcohols. [e] The enantiomeric ratio, $E = \ln[(1-c)(1-ees)] / \ln[(1-c)(1+ees)] = \ln[1-c(1+eep)]/\ln[1-c(1-eep)]$, $c = ees/(ees+eep)$.[11] [f] *E* was calculated according to the conversion and the *ee* of **3e** based on the ^{31}P NMR (adding quinine) of reaction mixture. [g] *ee* value of **3i** was not determined.

Scheme 2



4 (*syn*:*anti* = 6.3:1)

5 *ee* >95%

6 *ee* >95%

7 *ee* >95%

8

In summary, we have developed a convenient enzymatic route to some optically active 1- and 2-hydroxyalkanephosphonates. The scope and limitations of this method are under investigation.

References

1 (a) Patel, D. V.; Rielly-Gauvin, K.; Ryono, D. E. *Tetrahedron Lett*. **1990**, *31*, 5587.
(b) Sikorski, J. A.; Miller, M. J.; Braccolino, D. S.; Cleary, D. G.; Corey, S. D.; Font, J. L.; Gruys, K. J.; Han, C. Y.; Lin, K. C.; Pansegram, P. D.; Rean, J. E.; Schnur, D.; Shah, A.; Walker, M. C. *Phosphorus, Sulfur Silicon Relat. Elem*. **1993**, *76*, 375.
(c) Maier, L. *Phosphorus Sulfur* **1983**, *14*, 295.
(d) Kitamura, M.; Tokunaga, M.; Noyori, R. *J. Am. Chem. Soc*. **1995**, *117*, 2931.

2 Zhang, Y.-H.; Yuan, C.-Y., Li, Z.-Y. *Tetrahedron* **2002**, *58*, 2973.

3 (a) Wong, C. H.; Whitesides, G. M. *Enzymes in Synthetic Organic Chemistry*, Tetrahedron Organic Series, Pergamon, **1994**.
(b) Dranz, Y.; Waldman, H. *Enzyme Catalysis in Organic Synthesis*, VCH, New York, **1995**.
(c) Faber, K. *Biotransformations in Organic Chemistry*, 3 rded., Spriger-Verleg, Berlin, **1997**.

4 Frank, W.; Hammerschmidit, F. *Monatsh. Chem*. **1998**, *129*, 423 and references cited herein.

5 Zhang, Y.-H.; Yuan, C.-Y.; Li, Z.-Y. *Tetrahedron Lett*. **2002**, *43*, 3247.

6 Rotticci, D.; Orrenius, C.; Hult, K.; Norin, T. *Tetrahedron: Asymmetry* **1997**, *8*, 359.

7 Hammerschmidt, F.; Lindner, W.; Wuggenig, F.; Zarbl, E. *Tetrahedron: Asymmetry* **2000**, *14*, 2955.

8 Tadeusiak, E.; Krawiecka, B.; Michalski, J. *Tetrahedron Lett*. **1999**, *40*, 1791.

9 Wang, K.; Li, J.-F.; Yuan, C.-Y.; Li, Z.-Y. *Phosphorus, Sulfur Silicon Relat. Elem*., in press.

10 Girotra, N. N.; Wendler, N. L. *Tetrahedron Lett*. **1969**, *53*, 4647.

11 Chen, Ç.-S.; Fujimoto, Y.; Girdaukas, G.; Sih, C. J. *J. Am. Chem. Soc*. **1982**, *104*, 7294.

(E0210114 ZHAO, X. J.)