Tetrahedron Letters 52 (2011) 1325-1328

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Mandelate and prolinate ionic liquids: synthesis, characterization, catalytic and biological activity

Jacek Cybulski^a, Anna Wiśniewska^a, Anna Kulig-Adamiak^a, Zbigniew Dąbrowski^a, Tadeusz Praczyk^b, Alicja Michalczyk^c, Filip Walkiewicz^d, Katarzyna Materna^d, Juliusz Pernak^{d,*}

^a Industrial Chemistry Research Institute, ul. Rydygiera 8, 01-793 Warsaw, Poland

^b Institute of Plant Protection, ul. W. Wegorka 20, 60-318 Poznan, Poland

^c The Institute of Industrial Organic Chemistry, ul. Annopol 6, 03-236 Warsaw, Poland

^d Poznan University of Technology, Faculty of Chemical Technology, pl. M. Sklodowskiej-Curie 2, 60-965 Poznan, Poland

ARTICLE INFO

Article history: Received 28 October 2010 Revised 23 December 2010 Accepted 14 January 2011 Available online 20 January 2011

Keywords: Ionic liquids Mandelates Prolinates Biological activity Catalysis Phytotoxicity

ABSTRACT

A group of quaternary ammonium mandelates and L-prolinates, as ionic liquids, were synthesized and characterized. The prepared salts were soluble in water and showed high surface activity. The described synthesis of L-prolinate was simple and the obtained ionic liquid contained a chiral anion. L-Prolinate in CH_2Cl_2 was employed for the asymmetric Michael addition of a ketone to nitrostyrene. A yield of 60%, enantioselectivity (upto 50% ee), and good diastereoselectivity (*syn/anti* ratio of up to 90:10) were obtained for the asymmetric addition of cyclohexanone. These novel ionic liquids proved to be very effective anti-microbial and anti-fungal agents, especially didecyldimethylammonium L-prolinate. Additionally, it was found that phytotoxicity can be a useful tool in assessing the optical forms of ionic liquids. © 2011 Elsevier Ltd. All rights reserved.

Ionic liquids (ILs) are salts that are generally liquid at ambient temperatures or melt at <100 °C, have long liquid ranges, and have low vapor pressures. They have received considerable attention in recent years due to their potential applications.¹ The huge number of cation–anion combinations permits the design of appropriate ILs for a particular application. They have been used in many areas of chemistry including organic² and polymer synthesis,³ biphasic catalysis,⁴ biocatalysis,⁵ battery systems, electrochemical deposition, and electrochemistry.⁶ Consequently, the properties of ILs have led to a multitude of uses in industry [e.g., BASIL (Biphasic Acid Scavenging utilizing Ionic Liquids)].⁷ Recently, ILs as active pharmaceutical ingredients have been discussed.⁸

Amino acids represent a very useful class of starting materials for construction of ionic liquids, especially chiral examples (CILs). This is the result of their availability in both enantiomeric forms at reasonable cost. Numerous groups⁹ have elected to include either a chiral anion, a chiral cation, or both in the IL.

The main strategy to prepare economic CILs is via substrates derived from the chiral pool. Our research with (1R, 2S, 5R)-(-)-menthol showed that this compound was very suitable for the synthesis of CILs.¹⁰ L-Proline in combination with ILs has proved to be an efficient system for direct asymmetric α -aminoxylation of aldehydes and ketones¹¹ as well as Mannich reactions.¹² Also, prolinamide derivatives modified with IL moieties were synthesized and studied as organocatalysts in asymmetric aldol reactions in water.¹³

etrahedro

Here, we report the synthesis, characterization, properties, and potential application of novel organic salts based on didecyldimethylammonium, benzalkonium, and domiphen cations combined with mandelate (two enantiomers and the racemic mixture) and the L-prolinate anion.

Long chain alkyl quaternary ammonium mandelates and prolinates were obtained by metathesis reactions. The structures of the cations are shown in Scheme 1, and those of the anions in Scheme 2. Salts with chiral anions were prepared from (R)-(-)-mandelic and (S)-(+)-mandelic acids and L-proline. The racemic mixture was also synthesized when mandelic acid was used. The products were dried and the potassium chloride by-product was







^{*} Corresponding author. Tel.: +48 61 665 3682; fax: +48 61 665 3649. *E-mail address:* juliusz.pernak@put.poznan.pl (J. Pernak).

^{0040-4039/\$ -} see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.tetlet.2011.01.069



removed using anhydrous methanol. This metathesis reaction was simple and the products were obtained in good yields over 86%.

In the case of L-proline we did not use an anion exchange resin in contrast to the method of Ohno and co-workers.^{9a} The properties of the synthesized salts, which contain large ammonium cations (didecyldimethylammonium [**DDA**], benzalkonium with $C_{12}H_{25}$ and $C_{14}H_{29}$ alkyl groups equal to 60% and 40%, respectively, [**BA**], and domiphen [*N*,*N*-dimethyl-*N*-(2-phenoxyethyl)-1-dodecanaminium] [**DOM**]) are summarized in Table 1.

All mandelates with the **[DOM]** cation **(9, 10, and 11)** and **[BA]**[**L-PRO]** were obtained as waxes and the remainder were liquid. The results obtained allow the synthesized eleven salts to be classified as ILs. Eight are chiral ionic liquids (CILs) with the specific rotations listed in Table 1. The synthesized ILs are air and moisture stable and soluble in water and organic solvents: methanol, dichloromethane (except 8), toluene (except 8), acetone (except 4 and 8), and THF (except 4, 8, 9, 10 and 11).

The water content of the ILs, determined by Karl–Fischer measurements, was found to be less than 500 ppm. The salts were characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis.

The ammonium mandelates begin to decompose at about 155 °C (Table 2). ILs with the prolinate anion were less stable: **[DDA]**[**L**-**PRO]** and **[BA]**[**L**-**PRO]** decomposed at 166 °C and 128 °C, respectively. A glass transition was found for all the studied ILs, but a melting point at -21.3 °C was observed only for **[BA]**[**L**-**PRO]**. In the case of the pure enantiomers and racemic mixtures of **[DDA]** and **[BA]** mandelates it was observed that pure *R* and *S* forms showed higher glass transitions in comparison to those of racemic mixtures (Table 2). This phenomenon could be explained by better and faster packing of the system in the case of pure enantiomers, which was also observed by Pham.¹⁴ This phenomenon is not observed in the **[DOM]** mandelates because the differences in glass transition temperature values are small.

The ionic liquids obtained were also studied as possible surface active compounds. Surface excess concentrations Γ_{max} were calculated from the slope of the linear portion of the $\gamma - \log c$ plots using the Gibbs isotherm:

$$\Gamma_{max} = -\frac{1}{RT} \cdot \frac{d\gamma}{d(\ln c)}$$

Table 1				
Properties	of	the	prepared	ILs

Table 2Thermal stabilities of the ILs

IL	T_{g} (°C)	$T_{\rm m}$ (°C)	$T_{\text{onset5\%}}$ (°C)	$T_{\text{onset50\%}}$ (°C)
1	-57.1	_	204	232
2	-46.1	-	156	226
3	-48.9	-	212	273
4	-60.5	-	166	253
5	-49.5	-	175	207
6	-32.1	-	202	210
7	-35.9	-	187	238
8	-51.0	-21.3	128	194
9	-22.4	-	210	286
10	-26.1	-	205	267
11	-22.1	_	204	266

 $T_{\rm g}$ -glass transition temperature, $T_{\rm m}$ -melting point, $T_{\rm onset}$ -decomposition temperature.

where: Γ_{max} is the surface excess concentration at the saturated interface, *R* is the gas constant and *T* the absolute temperature, *c* is the concentration of the salt.

From Γ_{max} , the minimum surface occupied by a molecule at the interface A_{min} can be calculated from the equation:

$$A_{min}=\frac{1}{\Gamma_{max}N_{\rm A}},$$

where: N_A is the Avogadro number.

The critical micelle concentration (*CMC*) and the corresponding surface tension (γ_{CMC}), the surface excess Γ_{max} and area per molecule A_{min} , are summarized in Table 3.

For the studied IL aqueous solutions, the surface tension decreased from the water value to a minimum located between 26.1 and 36.4 mN m⁻¹. After this point the surface tension reached a plateau region. In the case of [**BA**] and [**DOM**] the solutions manifested the highest γ_{CMC} values of 36.4 and 36.2 mN m⁻¹, respectively. This demonstrated that [**DDA**] exhibited more pronounced intermolecular hydrophobic interactions, making it easier to form aggregates in water than was the case for [**BA**] and [**DOM**]. The *CMC* locations obtained with the plots of [**DDA**][*R*-MAN], [**DDA**][*S*-MAN], and [**DDA**][MAN] were almost identical. A similar situation was observed for [**BA**][*R*-MAN], [**BA**][*S*-MAN], and [**BA**]-[MAN] solutions.

As far as the γ_{CMC} values are concerned, they are dependent mainly on the cationic form of the IL, but the anion is also important. The area per molecule A_{min} of **[DDA]** forms with **[MAN]** was higher than that of the corresponding [L-PRO] form, indicating that the molecules of ILs containing [L-PRO] were more tightly packed at the water–air interface. **[DDA]**[**MAN**] has a lower *CMC* value and a lower γ_{CMC} , resulting in better surface properties than **[BA]**-[**MAN**]. The *CMC* values of aqueous solutions of **[DDA]** and **[DOM]**

-						
IL	Cation	Anion	Yield (%)	Specific rotation ^a $[\alpha]_D^{20}$	Density ^b (g mL ⁻¹)	Viscosity ^c (cP)
1	[DDA]	[MAN]	92	_	0.952	$\textbf{5.73}\times \textbf{10}^{3}$
2	[DDA]	[<i>R</i> -MAN]	86	-31.1	0.952	3.68×10^3
3	[DDA]	[S-MAN]	90	+31.0	0.952	$3.80 imes 10^3$
4	[DDA]	[L-PRO]	95	-26.3	0.938	$12.70 imes 10^3$
5	[BA]	[MAN]	98	_	1.015	18.40×10^3
6	[BA]	[R-MAN]	91	-32.7	1.015	21.20×10^3
7	[BA]	[S-MAN]	98	+32.3	1.015	$22.40\times\mathbf{10^{3}}$
8	[BA]	[L-PRO]	97	-30.6	Wax	-
9	[DOM]	[MAN]	93	_	Wax	-
10	[DOM]	[R-MAN]	97	-30.9	Wax	-
11	[DOM]	[S-MAN]	97	+30.4	Wax	-

^a In MeOH $c \sim 1.0$.

^b At 20 °C.

^c At 25 °C.

Table 3			
CMC, surface tension (γ_{CMC}), surface excess concent	tration (Γ_{max}), and area per m	olecule (A_{min}) of the prepared ILs in	aqueous solution at 25 $^\circ$

IL	$CMC \pmod{L^{-1}}$	$\gamma_{CMC} (mN m^{-1})$	Γ_{max} (µmol m ⁻²)	$A_{min} (10^{-19} \mathrm{m}^2)$
[BA][MAN]	2.399	36.3	7.91	2.10
[BA][<i>R</i> -MAN]	2.512	36.2	6.63	2.51
[BA][S-MAN]	2.510	36.4	7.98	2.23
[BA][L-PRO]	2.818	30.3	5.25	3.16
[DDA][MAN]	0.661	26.4	4.69	3.54
[DDA][<i>R</i> -MAN]	0.708	26.1	5.11	3.25
[DDA][S-MAN]	0.631	26.6	5.06	3.28
[DDA][L-PRO]	2.520	27.5	6.39	2.60
[DOM][MAN]	1.318	36.2	7.40	2.24
[DOM][<i>R</i> -MAN]	1.259	36.0	9.13	1.82
[DOM][S-MAN]	1.247	36.3	8.24	2.12

were lower, or of the same order as the *CMC* values of cationic surfactants.¹⁵ These results indicate that ILs with [**DDA**], [**BA**], and [**DOM**] self-assemble easily in aqueous solutions.

Prolinate ionic liquids were also studied as compounds with catalytic activity. The asymmetric addition of cyclohexanone to *trans*-β-nitrostyrene was investigated using the L-prolinates **[DDA]**[L-**PRO**] and **[BA]**[L-**PRO**] (Scheme 3). The reaction proceeded with the use of benzoic acid as a cocatalyst. The best results obtained were compared with the literature data^{12,16} and are given in Table 4. Asymmetric Michael addition of a catalyst with **[DDA]**[L-**PRO**] was better than with L-proline, and worse than a functionalized IL containing L-proline in the cation. As the synthesis of L-prolinates **[CATION**][L-**PRO**] is simple and is characterized by high efficiency, it is appropriate to seek a cation, which improves the efficiency of the catalytic activity.

Mandelic acid is a well known compound used as an antibacterial, particularly for the treatment of urinary tract infections. L-Proline as an osmoprotectant is popular in many pharmaceutical and biological applications. Didecyldimethylammonium and benzalkonium chlorides are antiseptic/disinfectants and domiphen bromide is a chemical antiseptic. Starting from these active substrates we expected the product to retain high biological activity.

The minimum inhibitory concentration (MIC) and minimum bactericidal and fungicidal concentrations (MBC and MFC) were established and are presented in Table 5. All the studied ILs exhibited high activity against the tested microorganisms. The ILs with **[DDA]** (1–4) and **[DOM]** acted more effectively than the standard, benzalkonium chloride **[BA]**[**CI**]. ILs with the **[BA]** cation also worked effectively, but less so than **[BA]**[**CI**]. The most effective was **[DDA]**[L-PRO]. Evidently no difference in action between racemic and optically pure forms **[***R***-MAN]** and **[***S***-MAN] were observed. However, we noted differences in the biological activity of protic ILs (1-alkylimidazolium and 1-alkoxymethylimidazolium L-lactates and DL-lactates) in our earlier paper.¹⁷**

The impact of ILs toward plants depends on the concentration of substance and plant species. Moreover, the type of anion or cation is also an important factor. Studies on the response of duckweed (*Lemma minor*) to 1-alkyl-3-methylimidazolium compounds showed that the length of the alkyl chain influenced the phytotox-icity.¹⁸ In our research with mandelate and L-prolinate compounds conducted on garden cress (*Lepidium sativum*) the inhibition of plant growth depended both on the cation and anion structure. The ILs with [MAN] anions were generally more phytotoxic than



Scheme 3. Asymmetric Michael addition.

Table 4

The effect of CIL catalysts on the asymmetric Michael addition	
--	--

Catalyst	Solvent	Time (h)	Yield (%)	syn/anti ^a	ee (%)	Ref.
L-Proline	[bmim]BF ₄	55	76	88	33	12
Func. IL ^b	TFA ^c	10	99	99	98 ^d	16
4 ^e	CH_2Cl_2	69	60	94	51 ^d	

^a Determined by ¹H NMR.

^b Functionalized IL = 1-butyl-3-(pyrrolidin-2-yl)imidazolium tetrafluoroborate.

^c Trifluoroacetic acid.

^d Determined by HPLC analysis (Chiralpak AD-H).

^e [DDA][L-PRO], with benzoic acid as the cocatalyst.

those with [L-PRO], but the type of cation used was also important. For example, mandelate with the [**DDA**] cation was more phytotoxic than with the [**BA**] cation in contrast to L-prolinate ILs. Among the tested ILs, mandelate with the [**DDA**] cation inhibited plant growth more than other compounds. In this case the ED_{50} values ranged between 101 and 326 ppm. Compounds with the [**BA**] cation were less toxic, especially with the [**R-MAN**] anion. In the case of mandelates with the [**DOM**] cation, large differences between the phytotoxicity of the compounds with [**R-MAN**] and [**S-MAN**] anions were found: the ED₅₀ values were 412 and 5412 ppm, respectively.

Some mandelates, especially **[DOM]**[*S*-MAN], when used at low concentrations, promoted the growth of garden cress seedlings (Fig. 1). L-Prolinate salts such as **[BA]**[**[L-PRO]** and **[DDA]**[**L-PRO]** were characterized by relatively high ED_{50} values ranging from 1060 to 1400 ppm. Our results showed how strong the impact of the enantiomer structure was on the phytotoxicity. The phytotoxicity of the racemate was probably a result of the phytotoxicity of the individual enantiomers. Figure 1 illustrates that the phytotoxicity of the racemate was between the values of the *R* and *S* forms. The results obtained show that plants are very effective in assessing the optical forms of compounds.

In conclusion, long chain alkyl quaternary ammonium mandelates, (R)-(–)-mandelates, (S)-(–)-mandelates, and L-prolinates were prepared. The reaction conditions were mild, with a simple work-up procedure and high yields. All of the synthesized compounds were classified as ionic liquids with several being chiral ionic liquids. All of the obtained ammonium ionic liquids were air- and moisture stable under ambient conditions. Moreover, the ionic liquids were soluble in water. Our results indicate that ILs with [DDA], [BA], and [DOM] self-assemble easily in aqueous solutions. We noted that the γ_{CMC} values were dependent on the cation form of the IL. Almost the same surface behavior was observed for enantiomers and racemates. The CMC values of the synthesized ILs were similar or lower than those of aqueous solutions of classical cationic surfactants. Furthermore, the chiral ionic liquids were potential solvents and catalysts for asymmetric reactions. L-Prolinates were selective catalysts for asymmetric Michael addition.

Table 5

	MDC 1	1 1 2	C .1			ID A HOU
IVIIC.	WIBC and	WFC values	tor the	prepared	ils and	

Strain		IL							
		1	2	3	4	9	10	11	[BA][Cl] ^b
M. luteus	MIC	<0.1	0.1	0.2	<0.1	0.2	0.1	0.2	0.5
	MBC	<0.1	0.5	0.5	<0.1	0.2	0.2	0.5	4
S. aureus	MIC	0.2	0.5	0.5	0.1	1	1	1	1
	MBC	0.5	0.5	1	0.1	2	1	4	8
S. epidermidis	MIC	0.1	<0.1	0.2	<0.1	0.1	0.1	0.5	0.5
	MBC	0.2	<0.1	0.2	<0.1	0.5	0.2	1	2
E. feacium	MIC	0.5	0.5	1	0.1	1	1	1	2
	MBC	1	1	1	0.2	8	1	1	8
M. catarrhalis	MIC	0.2	0.2	0.5	1	1	1	0.5	0.2
	MBC	0.2	0.2	0.5	1	4	8	1	0.5
E. coli	MIC	0.5	0.5	0.5	<0.1	1	0.5	1	1
	MBC	1	1	2	0.5	1	1	2	1
S. marcescens	MIC	16	31	16	16	31	31	31	62
	MBC	16	62	31	16	31	62	62	62
P. vulgaris	MIC	16	8	8	4	31	16	16	31
	MBC	31	16	31	4	31	62	16	31
P. aeruginosa	MIC	31	16	16	16	16	16	31	62
	MBC	62	31	62	31	62	31	62	62
B. subtilis	MIC	0.1	2	0.2	0.1	1	2	1	1
	MBC	0.1	2	0.5	0.1	1	2	1	1
C. albicans	MIC	1	0.5	1	1	2	1	2	4
	MFC	2	1	1	4	4	1	16	31
R. rubra	MIC	1	1	1	1	2	1	1	8
	MFC	2	2	1	8	4	1	8	31

^a In mg L⁻¹.

^b Benzalkonium chloride.



Figure 1. The influence of mandelate with [BA] cation on the biomass of *Lepidium* sativum: (a) [MAN], (b) [*R*-MAN], (c) [*S*-MAN].

Moreover, the synthesized ionic liquids were strongly effective against bacteria and fungi. Didecyldimethylammonium L-prolinate proved the most active as an anti-bacterial and anti-fungal agent. The measured phytotoxicity indicated how heavily it depends on the type of cation and anion. In the case of chiral ionic liquids, the phytotoxicity depends on the specific rotation and has a significant impact on the phytotoxicity of the racemate. The recognized properties showed that mandelate and prolinate ionic liquids, synthesized from natural, economic, and easy available feedstocks are multifunctional compounds of practical importance.

Acknowledgment

This work was supported by grant BW 32-222/2010 from Poznan University of Technology.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.01.069.

References and notes

- (a) Welton, T. Chem. Rev. 1999, 99, 2071–2084; (b) Wasserscheid, P.; Keim, W. Angew. Chem., Int. Ed. 2000, 39, 3772–3789; (c) Wasserscheid, P.; Welton, T. Ionic Liquids in Synthesis; Wiley-VCH: Weinheim, 2008; (d) Deetlefs, M.; Seddon, K. Green Chem. 2010, 12, 17–30; (e) Kirchner, B. Ionic Liquids; Springer: Berlin Heidelberg, 2009.
- (a) Parvulescu, V. I.; Hardacre, C. Chem. Rev. 2007, 107, 2615–2665; (b) Chowdhury, S.; Mohan, R. S.; Scott, J. L. Tetrahedron 2007, 63, 2363–2389; (c) Greaves, T. L.; Drummond, C. J. Chem. Rev. 2008, 108, 206–237; (d) Martins, M. A. P.; Fizzo, C. P.; Moreira, D. N.; Zanatta, N.; Bonacorso, H. G. Chem. Rev. 2008, 108, 2015–2050; (e) Cybulski, J.; Wišniewska, A.; Kulig-Adamiak, A.; Lewicka, L.; Cieniewska-Rosłonkiewicz, A.; Kita, K.; Fojutowski, A.; Nawrot, J.; Materna, K.; Pernak, J. Chem. Eur. J. 2008, 14, 9305–9311.
- 3. Lu, J.; Yan, F.; Texter, J. Prog. Polym. Sci. 2009, 34, 431-448.
- (a) Haumann, M.; Riisager, A. Chem. Rev. 2008, 108, 1474–1497; (b) Olivier-Bourbigou, H.; Magna, L.; Morvan, D. Appl. Catal. A: Gen. 2010, 373, 1–56.
- 5. van Rantwijk, F.; Sheldon, R. A. Chem. Rev. 2007, 107, 2757-2785.
 - 6. Hapiot, P.; Lagrost, C. Chem. Rev. 2008, 108, 2238-2264.
 - 7. Plechkova, N. V.; Seddon, K. R. Chem. Soc. Rev. 2008, 37, 123-150.
- (a) Hough, W. L.; Rogers, R. D. Bull. Chem. Soc. Jpn. 2007, 80, 2262–2269; (b) Hough, W. L.; Smiglak, M.; Rodriguez, H.; Swatloski, R. P.; Spear, S. K.; Daly, D. T.; Pernak, J.; Grisel, J. E.; Carliss, R. D.; Soutullo, M. D.; Davis, J. H.; Rogers, R. D. New J. Chem. 2007, 31, 1429–1436; (c) Stoimenovski, J.; MacFarlane, D. R.; Bica, K.; Rogers, R. D. Pharm. Res. 2010, 27, 521–526; (d) Bica, K.; Rijksen, C.; Nieuwenhuyzen, M.; Rogers, R. D. Phys. Chem. Chem. Phys. 2010, 12, 2011–2017.
- (a) Fukumoto, K.; Yoshizawa, M.; Ohno, H. J. Am. Chem. Soc. 2005, 127, 2398; (b) Plaquevent, J. C.; Levillain, J.; Guillen, F.; Malhiac, C.; Gaumont, A. C. Chem. Rev. 2008, 108, 5035–5060; (c) Luo, S.; Zhang, L.; Cheng, J. P. Chem. Asian J. 2009, 4, 1184–1195; (d) Winkel, A.; Wilhelm, R. Tetrahedron: Asymmetry 2009, 20, 2344–2350.
- (a) Pernak, J.; Feder-Kubis, J. Chem. Eur. J. 2005, 11, 4441–4449; (b) Pernak, J.; Feder-Kubis, J. Tetrahedron: Asymmetry 2006, 17, 1728–1737; (c) Pernak, J.; Feder-Kubis, J.; Cieniecka-Rosłonkiewicz, A.; Fischmeister, C.; Griffin, S. T.; Rogers, R. D. New J. Chem. 2007, 31, 879–892.
- Guo, H. M.; Niu, H. Y.; Xue, M. X.; Guo, Q. X.; Cun, L. F.; Mi, A. Q.; Jiang, Y. Z.; Wang, J. J. Green Chem. 2008, 8, 682–684.
- (a) Rasalkar, M. S.; Potdar, M. K.; Mohile, S. S.; Salunkhe, M. M. J. Mol. Catal. A: Chem. 2005, 235, 267–270; (b) Zheng, X.; Qian, Y. B.; Wang, Y. Eur. J. Org. Chem. 2010, 515–522.
- 13. Siyutkin, D. E.; Kucherenko, A. S.; Zlotin, S. G. Tetrahedron 2010, 66, 513-518.
- 14. Pham, X. H.; Kim, J. M.; Chang, S. M.; Kim, I.; Kim, W. S. J. Mol. Catal. B: Enzym.
- **2009**, 60, 87–92.
- 15. Beyer, K.; Leine, D.; Blume, A. *Colloids Surf., B* **2006**, 49, 31–39.
- Luo, S.; Mi, X.; Zhang, L.; Liu, S.; Xu, H.; Cheng, J. P. Angew. Chem., Int. Ed. 2006, 45, 3093–3097.
- 17. Pernak, J.; Goc, I.; Mirska, I. Green Chem. 2004, 6, 323-329.
- 18. Pham, T. P. T.; Cho, C. W.; Yun, Y. S. Water Res. 2010, 44, 352-372.