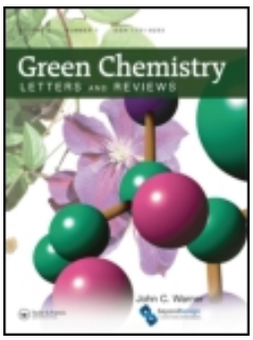


Green Chemistry Letters and Reviews

ISSN: 1751-8253 (Print) 1751-7192 (Online) Journal homepage: http://www.tandfonline.com/loi/tgcl20

Microwave-assisted solvent-free lipase catalyzed transesterification of β-ketoesters

Mariela Risso , Mauro Mazzini , Santiago Kröger , Patricia Saenz-Méndez , Gustavo Seoane & Daniela Gamenara

To cite this article: Mariela Risso , Mauro Mazzini , Santiago Kröger , Patricia Saenz-Méndez , Gustavo Seoane & Daniela Gamenara (2012) Microwave-assisted solvent-free lipase catalyzed transesterification of β-ketoesters, Green Chemistry Letters and Reviews, 5:4, 539-543, DOI: 10.1080/17518253.2012.672596

To link to this article: https://doi.org/10.1080/17518253.2012.672596

Published online: 01 May 2012.

Green Chemistry Letters and Reviews
Vol. 5, No. 4, December 2012, 539–543

Taylor & Francis
Taylor & Francis Group

RESEARCH LETTER

Microwave-assisted solvent-free lipase catalyzed transesterification of β-ketoesters

Mariela Risso[a], Mauro Mazzini[a], Santiago Kröger[a], Patricia Saenz-Méndez[a,b], Gustavo Seoane[a] and Daniela Gamenara[a]*

[a]*Organic Chemistry Department, Facultad de Química, Universidad de la República (UdelaR), Gral, Flores 2124, Montevideo 11800, Uruguay;* [b]*Computational Chemistry and Biology Group, Facultad de Química, Universidad de la República (UdelaR), Gral, Flores 2124, Montevideo 11800, Uruguay*

(Received 13 December 2011; final version received 22 February 2012)

Lipase-catalyzed transesterification was used as an efficient tool for the interconversion of β-ketoesters. Catalytic activity of commercial lipase B from *Candida antarctic*a (Novozym 435) was evaluated in systems involving non activated acyl donors, and enhanced using microwave irradiation. Interestingly, the combination of CAL B in microwave irradiation worked excellent in solvent-free conditions, thus assuring a highly competitive and environment-friendly process with high yields (up to 96%) in competitive times (< 2h). The combination of biocatalysis with solvent-free systems and microwave assistance is currently scarcely used, and may represent a powerful synergy for preparative reactions.

Keywords: solvent-free; microwave; CAL B lipase; biocatalysis

Introduction

β-Ketoesters are versatile starting materials for the preparation of a wide variety of important chiral building blocks. The development of economic and environmentally responsible methodologies for their interconversion remains a challenge, since conventional processes often lead to significant amounts of wastes and/or are performed under strong reaction conditions. We are interested in the development of new green strategies for the synthesis of insect pheromones, since many of them can be furnished starting from β-ketoesters (*1, 2*). Aggregation pheromones of economically important stored grain pests, such as *Sitophilus orizae* (Sitophilure), *S. granarius* (Sitophilate), and *Rhyzopertha dominica* (Dominicalure I and II), can be synthesized from these versatile building blocks (*3–5*).

Microwave irradiation has been used as "green approach" in classical organic synthesis (*6–11*), and a wide variety of reactions were reported in water, organic solvents, or solvent-free conditions, in which microwave heating led to higher conversions and lower reaction times comparing with conventional methods (*12–15*).

The effect of microwave irradiation in organic syntheses is attributed to a combination of thermal effects (heating rate, superheating or "hotspots"), and to the selective absorption of radiation by polar substrates (*16*). These nonthermal effects have been deeply discussed and rationalized according to reaction medium and mechanistic considerations (*17–19*). Furthermore, the use of microwaves in lipase-catalyzed reactions has been increasingly studied during the past decade, leading to improvements in conversion, reaction rates, and stereoselectivities (*20–30*). Moreover, Rejasse and co-workers demonstrated that the stability of immobilized lipase B from *Candida antarctica* (CAL B, Novozym 435) in organic media can be enhanced by using microwave dielectric heating rather than conventional thermal heating, thus explaining the enhancements observed in conversion rate (*31, 32*).

Likewise, Yadav and colleagues highlighted the synergism between lipase activity and microwave irradiation in CAL B-catalyzed transesterifications (*21, 25, 33*). Moderate-to-good conversions at short reaction times compared to conventionally heated reactions were reported. Yet, reactions were conducted in toluene and at low substrate concentrations, with the consequent ecological and economic concerns.

From a practical viewpoint, it would be relevant to provide processes that may gather environmentally friendly aspects with attractive reaction outcomes. For instance, that may be achieved by combining a solvent-free process with microwave irradiation. The use of microwave-assisted approaches with

*Corresponding author. Email: dgamenar@fq.edu.uy

ISSN 1751-8253 print/ISSN 1751-7192 online

http://dx.doi.org/10.1080/17518253.2012.672596
http://www.tandfonline.com

solvent-free processes has been extensively investigated in the past few years (*34–45*). Yet, to the best of our knowledge, the combination of enzyme catalysis with solventless processes under microwave irradiation has been scarcely reported (*31, 32,* 46–48).

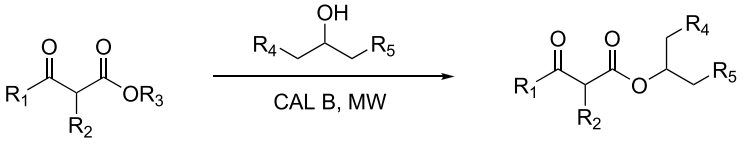
Herein we explore the combination of solvent-free processes and microwave irradiation for the efficient syntheses of β-ketoesters. Thus, an environmentally friendly and efficient methodology for the enzymatic interconversion of structurally related β-ketoesters using 2- and 3-pentanol as nucleophiles is set. CAL B was used as biocatalyst, and its reusability was also studied to assess enzyme stability in the applied reaction conditions.

Results and discussion

As model reaction, we carried out the transesterification of ethyl 3-oxobutanoate (**1**) with 2- and 3-pentanol as nucleophiles and CAL-B as catalyst, under microwave irradiation and in the absence of solvent (Scheme 1). Experiments were conducted at 50°C in a monomode laboratory microwave reactor equipped with an airtight vessel with a mixture of ester and alcohols of 1:2 and 1:1 for the synthesis of compounds **2** and **3** respectively. Reactions reached up to 95% isolated yield (Figure 1, Table 1). Control experiments were performed in the absence of enzyme, and the reactions reached less than 10% yield in 2 hours (Figure 1). Transesterification of **1** with 2- and 3-pentanol were also carried out under conventional heating using a thermostatized orbital shaker, at 30, 40, and 50°C. When reactions were conducted in that way, yields in the range of 80% were only achieved after 48 h (*49*). Consequently, not only the enzyme was active under the reaction conditions, but an enhancement in the activity was achieved under microwave irradiation, consistent with literature reports (*21, 25, 33*). Remarkably, significant higher yields were observed in solvent-free conditions, compared to literature data (*21*). Therefore, by achieving almost full conversion in 2 h, the use of enzymatic reactions combined with microwave-assisted solvent-free system appears to be a very efficient alternative for enzymatic transesterifications. Clearly this approach can be extended to other lipase-based reactions. Likewise, for the production of low-added value products by means of biocatalysis (i.e. biodiesel), the use of competitive solvent-free processes is clearly an important asset.

Triggered by these results, experiments using structurally related acyl donors were conducted, as also shown in Scheme 1. The reactions were run at 50 and 70°C. Results are summarized in Table 1. Excellent yields (higher than 90%) were observed at 50°C for substrates **6** and **7**, namely ethyl 3-oxovalerate and ethyl 4-methyl-3-oxovalerate, using either 2- or 3-pentanol as nucleophile, in addition to already obtained results for substrate **1**. Compounds **2**, **3**, **10–13** were obtained efficiently in two hours under the stated conditions (entries 1, 3, 13, 15, 17, and 19). On the other hand, conversions could not be improved by increasing reaction temperature to 70°C. Moreover, compounds **2**, **3**, **10**, **11**, **12**, and **13** were obtained in considerably lower yields (entries 2, 4, 14, 16, 18, and 20) than when carrying out the biotransformation at 50°C.

Substrate structure definitely has a key influence over the course of the reaction. When *t*-butyl 3-oxobutanoate **5** was used as substrate, conversions were rather low for products **2** and **3** (entries 9–12), presumably due to the steric hindrance conferred by the *t*-butyl substituent. Nevertheless, in these cases, a higher temperature (70°C) led to 2-fold increase of the conversion (entries 10 and 12) over the same reaction time. Furthermore, the methyl substituent in α-position in the β-keto ester leads to a dramatic decrease of enzyme acceptance, achieving very low conversions using either 2- or 3-pentanol as nucleophile, at 50 or 70°C (entries 5–8).



1: $R_1 = CH_3$; $R_2 = H$; $R_3 = Et$
4: $R_1 = R_2 = CH_3$; $R_3 = Et$
5: $R_1 = CH_3$; $R_2 = H$; $R_3 = t$-Bu
6: $R_1 = R_3 = Et$; $R_2 = H$
7: $R_1 = CH(CH_3)_2$; $R_2 = H$; $R_3 = Et$

2: $R_1 = CH_3$; $R_2 = H$; $R_4 = H$; $R_5 = Et$
3: $R_1 = CH_3$; $R_2 = H$; $R_4 = R_5 = CH_3$
8: $R_1 = CH_3$; $R_2 = CH_3$; $R_4 = H$; $R_5 = Et$
9: $R_1 = CH_3$; $R_2 = CH_3$; $R_4 = R_5 = CH_3$
10: $R_1 = Et$; $R_2 = H$; $R_4 = H$; $R_5 = Et$
11: $R_1 = Et$; $R_2 = H$; $R_4 = R_5 = CH_3$
12: $R_1 = CH(CH_3)_2$; $R_2 = H$; $R_4 = H$; $R_5 = Et$
13: $R_1 = CH(CH_3)_2$; $R_2 = H$; $R_4 = R_5 = CH_3$

Scheme 1. Transesterification of **1** and **4–7** with 2- and 3-pentanol as nucleophiles, CAL-B as catalyst, solvent-free conditions, and microwave irradiation.

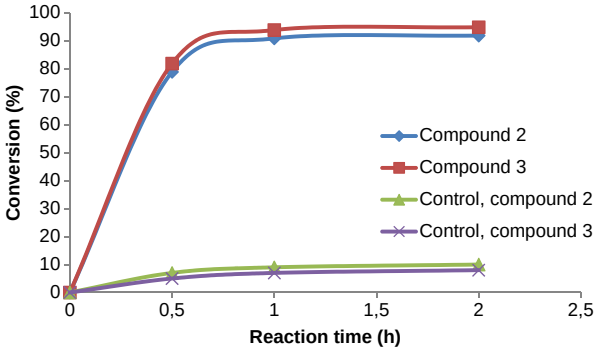


Figure 1. Conversion in transesterification of 3-oxobutanoate with 2- and 3-pentanol, yielding compounds **2** and **3**, respectively. Microwave irradiation in solvent-free conditions. Control experiments performed in the absence of enzyme.

Reactions performed with (*rac*)-2-pentanol as nucleophile (compounds **2**, **8**, **10** and **12**) resulted in a highly stereoselective process, reacting only the (*R*)-isomer, according to Kazlauskas rule (*50*), thus obtaining in all cases the corresponding esters with $>99\%$ *ee*. The reactions were monitored by chiral gas chromatography (GC), and compared to optically pure standards.

In order to test the suitability of this approach for large-scale preparations, the reaction of compounds **1**, **6**, and **7** with 2- and 3-pentanol as nucleophiles were conducted in 10 mmol scale (maximum load allowed by the laboratory monomode reactor used), obtaining yields up to 95%, comparable to those reported in Table 1.

To assure the (economic) competitiveness of the whole process, the reusability of the catalyst was studied and compared in both thermally heated and microwave irradiated reactions. After each reaction cycle, the enzyme was filtered and washed three times with hexane, dried at room temperature for 24 hours and reused as such. Results showed that microwave irradiation does not affect the catalyst stability, compared to thermal heating. We could perform CAL-B-catalyzed transesterification of all substrates without losing any significant enzyme activity even after 10 consecutive cycles. Thus, our system provides a simple and competitive process for lipase-catalyzed transesterification reactions.

Experimental section

Materials and general methods

Lipase Novozym 435 (*C. antarctica* B, CAL B) was obtained from Novozymes. Solvents were purified and dried by conventional methods. Commercial reactants were purchased from Sigma-Aldrich Inc.

The degree of advance of the reactions and the reactants' purity were preliminary monitored using analytical TLC on silica gel (Kieselgel HF254 from Macherey-Nagel) and visualized with UV light (254 nm) and/or *p*-anisaldehyde in acidic ethanolic solution. Further analyses were performed by GC in a Shimadzu 2010 equipment, with FID detector (Flame Ionization Detector) and a Carbowax 20M MEGA column (30 m $\times$ 0.25 mm $\times$ 0.25 μm). Temperature program: 60°C/2°/min/120°C/10°C/min/180°C (5 min). TSPLIT: 220°C, TFID: 250°C. Chiral GC were performed with a MEGADEX DET TBS β (25 m $\times$ 0.25 mm $\times$ 0.25 μm). Temperature ramp was: 38°C (10 min)/1°/min/60°C/10°C/min/200°C (5 min). TSPLIT: 150°C, TFID: 200°C.

Column chromatography was performed using silica gel flash (Kieselgel 60, EM reagent, 230–240 mesh.) from Macherey-Nagel.

NMR spectra (^{1}H and ^{13}C) were carried out in a Bruker Avance DPX 400 MHz equipment. All experiments were taken at 30°C, $CDCl_3$ was used as solvent and TMS as internal standard.

The microwave heating was performed in a laboratory monomode microwave reactor (CEM

Table 1. Conversions obtained by means of transesterification of **1** and **4**–**7** with 2- and 3-pentanol as nucleophiles, CaL-B as catalyst, solvent-free conditions, and microwave irradiation in a monomode laboratory reactor. Reaction time: 2 hours.

Entry	Substrate	Product	Temp. (°C)	Yielda (%)	Entry	Substrate	Product	Temp. (°C)	Yielda (%)
1	**1**	**2**	50	92	**11**	**5**	**3**	50	15
2	**1**	**2**	70	67	**12**	**5**	**3**	70	43
3	**1**	**3**	50	95	**13**	**6**	**10**	50	96
4	**1**	**3**	70	59	**14**	**6**	**10**	70	59
5	**4**	**8**	50	14	**15**	**6**	**11**	50	97
6	**4**	**8**	70	21	**16**	**6**	**11**	70	85
7	**4**	**9**	50	6	**17**	**7**	**12**	50	90
8	**4**	**9**	70	11	**18**	**7**	**12**	70	81
9	**5**	**2**	50	18	**19**	**7**	**13**	50	92
10	**5**	**2**	70	4	**20**	**7**	**13**	70	79

[a]Isolated yield.

corporation, model Discover) with 10 mL Pyrex tubes equipped with septum seal and magnetic stirring. Reactions involving thermal heating were conducted in orbital shaker Thermoforma model 420.

Microwave-assisted synthesis of compounds 2, 3, 8–13

All experiments were carried out in absence of solvent. An amount or 0.5g of the acyl donor was used in each case, the lipase/acyl donor ratio (w/w) was 0.3, and the acyl donor/alcohol ratio (eq/eq) was 0.5 and 1 when using 2- and 3-pentanol as nucleophiles respectively. The enzyme was added to a mixture of the corresponding acyl donor and nucleophile, and the microwave heated experiments were carried out by duplicated in a 10 mL airtight Pyrex vessel, at 50 and 70°C for two hours. Aliquots were taken at 30, 60, and 120 minutes, giving all consistent values. Once the reactions were completed, the enzyme was filtered-off and the products were purified by silica gel flash chromatography (8:2 hexane:EtOAc). **2** (*51*)**:** ^{1}H RMN: δ (ppm) = 5.04–4.96 (m; 1H, CH), 3.44 (s; 2H, CH_2), 2.29 (s; 3H, CH_3), 1.66–1.57 (m; 2H, CH_2), 1.39–1.35 (m; 2H, CH_2), 1.26 (d; $J = 6.3$ Hz, 3H, CH_3), 0.94 (t; $J = 7.3$ Hz, 3H, CH_3). ^{13}C RMN: δ (ppm) = 206.1, 171.2, 72.6, 50.9, 38.3, 30.4, 20.2, 18.9, 14.2. **3:** ^{1}H RMN: δ (ppm) = 4.85–4.79 (m; 1H, CH), 3.46 (s; 2H, CH_2), 2.59 (q; $J = 7.3$ Hz, 2H), 1.63–1.56 (m; 4H, CH_2), 1.11 (t; $J = 7.3$ Hz, 3H), 0.91 (t; $J = 7.3$ Hz, 3H). ^{13}C RMN: δ (ppm) = 203.8, 67.6, 78.5, 49.7, 36.7, 26.7, 9.9, 7.9. **8:** ^{1}H RMN: δ (ppm) = 5.11–5.04 (m; 1H, CH), 3.49 (q; $J = 7.1$ Hz, 1H, CH), 2.25 (s; 3H, CH_3), 1.35 (d; $J = 7.1$ Hz, 3H, CH_3), 1.35–1.33 (m; 2H, CH_2), 1.33–1.28 (m; 2H, CH_2), 1.27 (d; $J = 7.1$ Hz, 3H, CH_3), 0.93 (t; $J = 7.1$ Hz, 3H, CH_3). ^{13}C RMN: δ (ppm) = 204.0, 170.9, 72.5, 54.3, 28.7, 21.9, 14.2, 13.0. **9:** ^{1}H RMN: δ (ppm) = 4.76–4.83 (m, 1H, CH), 3.42 (q, $J = 7.1$ Hz, 1H, CH), 2.17 (s, 3H, CH_3), 1.55–1.62 (m, 4H, CH_2), 1.22 (d, $J = 7.1$ Hz, 3H, CH_3), 0.96 (t, $J = 7.3$ Hz, 6H, CH_3). ^{13}C RMN: δ (ppm) = 204.5, 171.8, 78.6, 55.6, 32.7, 21.7, 9.8, 8.1. **10:** ^{1}H RMN: δ (ppm) = 4.92–5.00 (m; 1H, CH), 3.47 (s; 2H, CH_2), 2.57 (q; $J = 7.2$ Hz, 2H), 1.64–1.55 (m; 2H, CH_2), 1.43–1.37 (m; 2H, CH_2), 1.28 (d, $J = 6.3$ Hz, 3H, CH_3), 1.09 (t; $J = 6.9$ Hz, 3H, CH_3), 0.91 (t; $J = 7.2$ Hz, 3H, CH_3). ^{13}C RMN: δ (ppm) = 203.6, 171.0, 71.4, 48.8, 37.8, 30.3, 19.9, 18.7, 14.3. **11** (*52*)**:** ^{1}H RMN: δ (ppm) = 4.85–4.79 (m; 1H, CH), 3.46 (s; 2H, CH_2), 2.59 (q; $J = 7.3$ Hz, 2H), 1.63–1.56 (m; 4H, CH_2), 1.11 (t; $J = 7.3$ Hz, 3H), 0.91 (t; $J = 7.3$ Hz, 6H). ^{13}C-RMN: δ (ppm) = 203.8, 167.6, 78.5, 49.7, 36.7, 26.7, 9.9, 7.9. **12:** ^{1}H RMN: δ (ppm) = 4.94–5.02 (m, 1H, CH), 3.49 (s, 2H, CH_2), 2.74 (sept, $J = 6.8$ Hz, 1H, CH), 1.57–1.63 (m, 2H, CH_2), 1.42–1.52 (m, 2H, CH_2), 1.25 (d, $J = 6.3$ Hz, 3H, CH_3), 1.15 (d, $J = 6.8$ Hz, 6H, CH_3), 0.93 (t, $J = 7.2$ Hz, 3H, CH_3). ^{13}C RMN: δ (ppm) = 206.8, 167.1, 72.1, 47.5, 41.2, 37.9, 19.9, 18.6, 17.9, 13.9. **13:** ^{1}H RMN: δ (ppm) = 4.82 (tt, $J_1 = 6.9$ Hz, $J_2 = 5.7$ Hz, 1H, CH), 3.52 (s, 2H, CH_2), 2.75 (sept, $J = 6.9$ Hz, 1H, CH), 1.54–1.65 (m, 4H, CH_2), 1.15 (d, $J = 6.9$ Hz, 6H, CH_3), 0.91 (t, $J = 7.5$ Hz, 6H, CH_3). ^{13}C RMN: δ (ppm) = 206.8, 167.3, 78.0, 47.4, 41.2, 26.4, 17.9, 9.6.

Conclusions

CAL B-catalyzed efficient and environmentally friendly transesterifications can be set up by combining microwave-assisted reactions with solvent-free approaches. Competitive reaction times (< 2h, high conversions), together with high substrate concentrations, easier work-up, and largely diminished waste formation, can be achieved. Moreover, the extensive reuse of the biocatalyst is also an important goal achieved by the herein reported strategy, in order to develop not only sustainable but also economically viable processes for the large-scale preparation of useful building blocks.

Acknowledgements

The authors wish to thank Novozymes Inc. for the generous gift of enzymes. Thanks are due to Prof. Peter Wipf (Pittsburgh University) for his kind donation of a laboratory microwave reactor, and to Dr Graciela Mahler for helpful discussions. We also thank OPCW (Organization for the Prohibition of Chemical Weapons), DINACYT (PDT 77/22, Uruguay), ANII (Agencia Nacional de Investigación e Innovación), and PEDECIBA (Programa de Desarrollo de las Ciencias Básicas, Uruguay) for financial support.

References

(1) Mori, K. In *The Total Synthesis of Natural Products*, Vol. 9; ApSimon, J., Ed.; Wiley-Interscience: New York, 1992; p 523.
(2) Mori, K. *Bioorg. Med. Chem.* **2007**, *15*, 7505–7523.
(3) Phillips, J.K.; Chong, J.M.; Andersen, J.F.; Burkholder, W.E. *Entomol. Exp. Appl.* **1989**, *51*, 149–153.
(4) Plarre, R. In *International Working Conference on stored Product Protection*; Highley, E., Wright, E.J., Banks, H.J., Champ, B.R.; CSIRO: Canberra Australia, 1994; pp 570–582.
(5) Williams, H.J.; Silverstein, R.M.; Burkholder, W.E.; Khorramshahi, A. *J. Chem. Ecol.* **1981**, *7*, 759–780.
(6) Leadbeater, N.E. *Microwave Heating as a Tool for Sustainable Chemistry*; CRC Press, Boca Raton, FL, 2010.
(7) Leadbeater, N.E.; McGowan, C.B. *Clean, Fast Organic Chemistry*; CEM Publishing, Matthews, 2006.

(8) Tierney, J.P.; Lidström, P. Microwave Assisted Organic Synthesis Blackwell Publishing: Oxford, 2005.
(9) Bogdal, D. *Microwave Assisted Organic Synthesis*, Vol. 25; Elsevier: Amsterdam, 2005.
(10) Loupy, A. *Microwaves in Organic Synthesis*; Wiley-VCH Verlag Gmbh & Co. KGaA: Weinheim, 2002.
(11) Kappe, C.O.; Dallinger, D. *Mol. Diversity* **2009**, *13*, 71–193.
(12) Dallinger, D.; Kappe, C.O. *Chem. Rev.* **2007**, *107*, 2563–2591.
(13) Lindström, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* **2001**, *57*, 9225–9283.
(14) Kappe, C.O. *Angew. Chem. Int. Ed.* **2004**, *43*, 6250–6284.
(15) Kappe, C.O.; Dallinger, D. *Nat. Rev. Drug Discovery* **2006**, *5*, 51–63.
(16) De la Hoz, A.; Díaz Ortiz, A.; Moreno, A. *Chem. Soc. Rev.* **2005**, *2005*, 164–178.
(17) Kuhnert, N. *Angew. Chem. Int. Ed.* **2002**, *41*, 1863–1866.
(18) Perreux, L.; Loupy, A. *Tetrahedron* **2001**, *57*, 9199–9223.
(19) Obermayer, D.; Gutmann, B.; Kappe, C.O. *Angew. Chem. Int. Ed.* **2009**, *48*, 8321–8324.
(20) Bachu, P.; Gibson, J.S.; Sperry, J.; Brimble, M.A. *Tetrahedron: Asymmetry* **2007**, *18*, 1618–1624.
(21) Yadav, G.D.; Lathi, P.S. *J. Mol. Catal. A: Chem.* **2004**, *223*, 51–56.
(22) Yu, D.; Wang, Z.; Chen, P.; Jin, L.; Cheng, Y.; Zhou, J.; Cao, S. *J. Mol. Catal. B: Enzym.* **2007**, *48*, 51–57.
(23) Yu, D.; Tian, L.; Ma, D.; Wu, H.; Wang, Z.; Wang, L.; Fang, X. *Green Chem.* **2010**, *12*, 844–850.
(24) Yadav, G.D.; Sajgure, A.D.; Dhoot, S.B. *J. Chem. Technol. Biotechnol.* **2008**, *83*, 1145–1153.
(25) Yadav, G.D.; Lathi, P.S. *Synth. Commun.* **2005**, *35*, 1699–1705.
(26) Yadav, G.D.; Borkar, I.V. *Ind. Eng. Chem. Res.* **2009**, *48*, 7915–7922.
(27) Bradoo, S.; Rathi, P.; Saxena, R.K.; Gupta, R. *J. Biochem. Biophys. Methods* **2002**, *51*, 115–120.
(28) Jain, P.; Jain, S.; Gupta, M.N. *Anal. Bioanal. Chem.* **2005**, *381*, 1480–1482.
(29) Yadav, G.D.; Lathi, P.S. *Clean Techn. Environ. Policy* **2007**, *9*, 281–287.
(30) Leadbeater, N.E.; Stencel, L.M.; Wood, E.C. *Org. Biomol. Chem.* **2007**, *5*, 1052–1055.
(31) Rejasse, B.; Lamare, S.; Legoy, M.D.; Besson, T. *Org. Biomol. Chem.* **2004**, *2004*, 1086–1089.
(32) Rejasse, B.; BessonEn, T.; Legoy, M.D.; Lamare, S. *Org. Biomol. Chem.* **2006**, *4*, 3703–3707.
(33) Yadav, G.D.; Sajgure, A.D. *J. Chem. Technol. Biotechnol.* **2007**, *82*, 964–970.
(34) Varma, R.S. *Green Chem.* **1999**, *1*, 43–55.
(35) Andrews, P.C.; Deacon, G.B.; Junk, P.C.; Spiccia, N.F. *Green Chem.* **2007**, *9*, 1319–1327.
(36) Chichetti, S.M.; Ahearn, S.P.; Adams, B.; Rivkin, A. *Tetrahedron Lett.* **2007**, *48*, 8250–8252.
(37) Gupta, N.; Kad, G.L.; Singh, V.; Singh, J. *Synth. Commun.* **2007**, *37*, 3421–3428.
(38) Iida, H.; Hamana, H.; Matsumoto, K. *Synth. Commun.* **2007**, *37*, 1801–1805.
(39) Iida, H.; Moromizato, T.; Hamana, H.; Matsumoto, K. *Tetrahedron Lett.* **2007**, *48*, 2037–2039.
(40) Khurana, J.M.; Arora, R. *Arkivoc* **2008**, *2008*, 211–215.
(41) Liu, F.; You, Q.-D. *Synth. Commun.* **2007**, *37*, 3933–3938.
(42) Öztürk, G.; Gümgüm, B.; Kizil, M.; Emen, S. *Synth. Commun.* **2007**, *37*, 3981–3988.
(43) Ozturk, G.; Petit, A.; Kouklovsky, C. *Synth. Commun.* **2008**, *38*, 2707–2713.
(44) Raghavendra, M.; Naik, H.S.B.; Sherigara, B.S. *Phosphorus, Sulfur Silicon Relat. Elem.* **2008**, *183*, 1229–1235.
(45) Rao, M.L.N.; Awasthi, D.K.; Banerjee, D. *Tetrahedron Lett.* **2007**, *48*, 431–434.
(46) Loupy, A.; Petit, A.; Hamelin, J.; Texier Boullet, F.; Jacquault, P.; Mathé, D. *Synthesis* **1998**, *1998*, 1213–1234.
(47) Huang, W.; Xia, Y.-M.; Gao, H.; Fang, Y.-J.; Wang, Y.; Fang, Y. *J. Mol. Catal. B: Enzym.* **2005**, *35*, 113–116.
(48) Matos, T.D.; King, N.; Simmons, L.; Walker, C.; McClain, A.R.; Mahapatro, A.; Rispoli, F.J.; McDonnell, K.T.; Shah, V. *Green Chem. Lett. Rev.* **2011**, *4*, 73–79.
(49) Ravía, S.; Kröger, S.; Seoane, G.; Vero, S.; Gamenara, D. In *Biotrans 2007. 8th International Symposium on Biocatalysis and Biotransformations*; Oviedo: Spain, 2007.
(50) Kazlauskas, R.J.; Weissfloch, A.; Rappaport, A.T.; Cuccia, L.A. *J. Org. Chem.* **1991**, *56*, 2656–2665.
(51) Reddy, B.M.; Reddy, V.R.; Manohar, B. *Synth. Commun.* **1999**, *29*, 1235–1239.
(52) Chong, J.M. *Tetrahedron* **1989**, *45*, 623–628.