We, the named authors, hereby retract this Green Chemistry paper.
Signed: Wen-Hua Ou and Zhi-Zhen Huang, Nanjing, China, June 2008.
Retraction endorsed by Sarah Ruthven, Editor. Retraction published 13 June 2008

An efficient and practical synthesis of chiral imidazolium ionic liquids and their application in an enantioselective Michael reaction†

Wen-Hua Ou and Zhi-Zhen Huang*

Received 3rd April 2006, Accepted 13th June 2006
First published as an Advance Article on the web 28th June 2006
DOI: 10.1039/b604801c

We have developed a practical and efficient synthesis of chiral imidazolium ionic liquids by only two or three steps from cheap *N*-methylimidazole with 67-81% overall yields. Some of the new chiral ionic liquids have chiral discrimination (up to 15% ee) when they are used in a Michael reaction as green chiral solvent.

Introduction

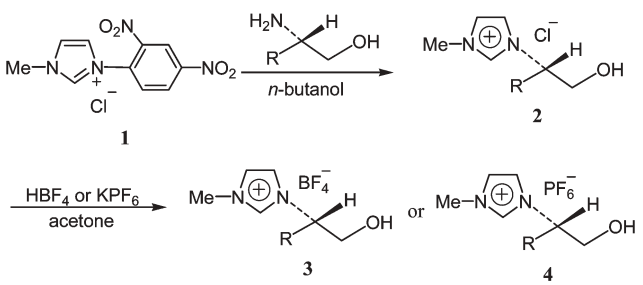
Avoidance of user- and eco-unfriendly organic solvents is a very important subject for chemists. In recent years, more and more attention has been drawn to the syntheses and applications of ionic liquids. This is due to their advantages of nonvolatility, ease of reuse, immiscibility with many organic solvents, good solvating properties for both inorganic and organic compounds *etc*.[1,2] Recently a lot of organic,[1] organometallic[1,2] and bio-catalyzed reactions[2c,3] have been successfully conducted in ionic liquids. Among the various ionic liquids, chiral ionic liquids are particularly attractive and important for their potential applications to chiral recognition, such as asymmetric synthesis and optical resolution of racemates.[4]

There are several synthetic methods for synthesizing chiral imidazolium ionic liquids. In 1997, Howarth *et al.* synthesized a homochiral dialkylimidazolium bromide salt as the first example of a chiral ionic liquid.[5] Although the chiral imidazolium ionic liquids are moisture stable and their synthetic route is short, they are synthesized in low overall yields (21%) by bisalkylation of methylimidazole with expensive chiral (*S*)-1-bromo-2-methylbutane. In 2003, the synthesis of some chiral imidazolium ionic liquids directly from amino acids was revealed,[6] but the synthetic method requires four steps with 30–33% overall yields, which may affect their application on a large scale. In 2005, Bao *et al.*[7] and Machado *et al.*[8] reported the synthesis of some chiral imidazolium ionic liquids from natural tartarate with remarkable chiral discrimination (up to 26% ee). However, the synthetic route also requires five or six steps with 44–60% overall yields, and the chiral unit of these ionic liquids is single. Recently Armstrong *et al.* synthesized some chiral imidazolium ionic liquids with chiral discrimination up to 7% ee.[9] Very recently, it was also reported that chiral ammonium-based ionic liquids containing a (−)-menthyl group can be easily and efficiently synthesized.[10] Also, Machado *et al.*,[8] Tosoni *et al.*,[11] and Ma *et al.*[12] reported the synthesis of a type of myrtanol, citronellol and menthol derived chiral imidazolium ionic liquids, respectively. Herein we wish to present an efficient and practical synthesis of chiral imidazolium ionic liquids from optically pure amino alcohols as the chiral pool, and their application in an enantioselective Michael reaction.

Results and discussion

N-Methylimidazole was employed as a starting material to react with 1-chloro-2,4-dinitrobenzene (Scheme 1), and the desired 1-(2,4-dinitrophenyl)-3-methylimidazolium chloride **1** could be obtained in 22% yield, which is similar to the yield (23%) in the literature[13] and too low for practical use. By changing the reaction conditions, we found that an excellent yield (96%) of 1-(2,4-dinitrophenyl)-3-methylimidazolium chloride **1** could be achieved. In contrast to other cases,[14] the precipitate of imidazolium salt **1**, which was formed in the reaction of 1-chloro-2,4-dinitrobenzene with *N*-methylimidazole, is pure enough to use in successive reactions after just filtration.

Then L-amino alcohols were used to react with 1-(2,4-dinitrophenyl)-3-methylimidazolium chloride **1**, and we found that a reaction similar to the Zincke reaction could be carried out smoothly to give chiral imidazolium salts **2**. As shown in Table 1, by refluxing imidazolium salt **1** with amino alcohols in *n*-butanol for 18–22 h, chiral imidazolium ionic liquids **2** could be obtained in good yields. Consequently, an anion exchange reaction of chiral imidazolium ionic liquids **2** with fluoroboric acid or potassium hexafluorophosphate could be carried out readily to give new chiral imidazolium ionic liquids **3** or **4**,



2a, 3a, 4a: R = CH_3
2b, 3b, 4b: R = $CH(CH_3)_2$
2c, 3c, 4c: R = $CH_2CH(CH_3)_2$

Scheme 1

School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China. E-mail: huangzz@nju.edu.cn
† Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR spectra. See DOI: 10.1039/b604801c

Table 1 Synthesis of chiral imidazolium ionic liquids **2–4**

Entry	Chiral ionic liquid	Yields of Zincke type reaction [a,b](%)	Overall yields of the 2 or 3 steps (%) [a,b]	Melting points/°C	$[\alpha]_D^{25}$
1	**2a**	79	76	9–11	+4.1[c]
2	**3a**		69	59–61	+3.5[d]
3	**4a**		72	65–67	+5.5[d]
4	**2b**	84	81	15–17	+3.4[c]
5	**3b**		77	66–68	+4.4[d]
6	**4b**		78	74–76	+7.9[d]
7	**2c**	78	75	16–18	+6.0[c]
8	**3c**		67	68–70	+4.2[d]
9	**4c**		70	76–78	+5.3[d]

[a] Isolated yields. [b] All products were confirmed by ^{1}H NMR, ^{13}C NMR, IR and EA. [c] c = 2g per 100 ml, MeOH. [d] c = 4g per 100 ml, CH_3CN.

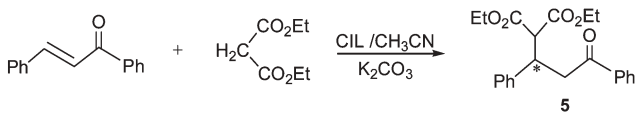
respectively, in excellent yields (90–97%). The overall yields for the chiral ionic liquids **2–4** are 67–81%, and much better than previous methods for the synthesis of similar chiral imidazolium ionic liquids.[6] Moreover the synthetic route requires only two or three steps and few reactants.

Furthermore, we applied the new chiral imidazolium ionic liquids **2–4** to the asymmetric Michael addition. We found that, in the presence of potassium carbonate, 1,3-diphenylprop-2-en-1-one could undergo Michael addition reaction smoothly with ethyl malonate in all of the chiral imidazolium ionic liquids **2–4**, giving diethyl 2-(3-oxo-1,3-diphenylpropyl) malonate in moderate to good yields (Table 2). Although the research on chiral ionic liquids is still at a preliminary stage, the results are promising, if not exciting.[4] The enantioselectivities of chiral ionic liquids are often poor and even zero. We found that most of the new chiral ionic liquids **2–4** have chiral discrimination, and the enantioselective effect of the chiral ionic liquid **3c** could be up to 15% ee in a Michael reaction.

Conclusions

We found that the novel chiral imidazolium ionic liquids **2–4** could be synthesized conveniently by only two or three steps from cheap *N*-methylimidazole with good overall yields. This makes these new chiral ionic liquids **2–4** possibly useful for practical preparation on a large scale. Further study on their application as green chiral solvents in a Michael reaction showed that some of the chiral ionic liquids **2–4** have chiral discrimination (up to 15% ee). It may be expected that some asymmetric reactions with moderate enantioselectivities could be improved to become reactions with excellent enantioselectivities if they are carried out in the new green solvents **2–4**. We are now carrying out the research on this area.

Table 2 Enantioselective Michael addition in chiral ionic liquids **2–4**



5

Entry[a]	Chiral ionic liquid	Reaction time/days	Yields (%)[b]	ee (%)[c]	$[\alpha]_D^{25}$[d]
1	**2a**	5	63	5	+0.32
2	**2b**	5	76	8	+0.50
3	**2c**	5	81	11	+0.64
4	**3a**	5	66	10	+0.58
5	**3b**	4	80	7	+0.41
6	**3c**	4	86	15	+0.92
7	**4a**	3	52	3	+0.19
8	**4b**	3	78	0	0.00
9	**4c**	5	76	5	+0.32

[a] Conditions: diethyl malonate (1.2 mmol), 1,3-diphenylprop-2-en-1-one (1.0 mmol), K_2CO_3 (3.0 mmol) in chiral ionic liquids. (8 mmol, 1.4–2.2 g) and CH_3CN (1.0 mL) at rt. [b] Isolated yields. [c] Enantiomeric excesses were determined by optical rotation mesurements.[15] [d] c = 2 g per 100 ml, C_6H_6

Experimental

1. Typical procedure for the synthesis of imidazolium salt (1)

A solution of 1-methylimidazole (2.5 g, 30.5 mmol) and 2,4-dinitrochlorobenzene (6.2 g, 30.6 mmol) in acetone (20 ml) was refluxed for 6 h. After cooling to room temperature, the resulting mixture was filtered, and the solid residue was washed with acetone and dried under reduced pressure to give the imidazolium salt (**1**).

1-(2,4-Dinitrophenyl)-3-methylimidazolium chloride (1). Yield: 96%; mp 246–247 °C (lit.[13] 244–247 °C). ^{1}H NMR (CD_3OD), δ (ppm) 4.16 (s, 3H), 7.95 (d, J = 2.04 Hz, 1H), 8.05 (d, J = 2.05 Hz, 1H), 8.22–8.87 (m, 3H), 9.18 (d, J = 2.47 Hz, 1H). ^{13}C NMR (CD_3OD), δ (ppm) 36.3, 122.0, 124.5, 124.6, 129.6, 132.1, 132.8, 144.6, 149.6. IR (KBr) ν (cm^{-1}): 3426, 3076, 2927, 1607, 1583, 1536, 1354, 858, 769, 639. Anal. calcd for $C_{10}H_9ClN_4O_4$: C, 42.19; H, 3.19. Found: C, 42.28; H, 3.22.

2. General procedure for the synthesis of chiral imidazolium chloride(2a–c)

To a suspension of 1-(2,4-dinitrophenyl)-3-methylimidazolium chloride (4.0 g, 14.0 mmol) in *n*-butanol (40 ml) was added the solution of amino alcohol (15.4 mmol) in *n*-butanol (1 mL), and the mixture was refluxed for 18–22 h. Removal of solvent under reduced pressure left a residue, which was further purified by column chromatography (methanol–ethyl acetate as eluent) to give chiral imidazolium ionic liquids (**2a–c**).

L-1-Methyl-3-(1′-hydroxy-2′-propanyl)imidazolium chloride(2a). Yield: 79%; mp 9–11 °C. ^{1}H NMR (CD_3OD), δ (ppm) 1.29 (d, J = 6.69 Hz, 3H), 3.32–3.36 (m, 2H), 3.49–3.55 (m, 1H), 3.71–3.80 (m, 1H), 3.87 (s, 3H), 7.27 (s, 1H), 7.36 (s, 1H), 8.28 (s, 1H). ^{13}C NMR (CD_3OD), δ (ppm) 14.2, 34.0, 49.5, 63.0, 122.2, 124.0, 137.0. IR (KBr) ν (cm^{-1}): 3432, 2017, 1596, 1457, 1372, 1063, 659. Anal. calcd for $C_7H_{13}ClN_2O$: C, 47.60; H, 7.42. Found: C, 47.88; H, 7.56.

L-1-Methyl-3-(1′-hydroxy-3′-methyl-2′-butanyl)imidazolium chloride (2b). Yield: 84%; mp 15–17 °C. ^{1}H NMR (CD_3OD), δ (ppm) 1.04 (d, J = 6.90 Hz, 3H), 1.07 (d, J = 6.91 Hz, 3H), 1.96–2.03 (m, 1H), 2.95–3.01 (m, 1H), 3.31–3.36 (m, 1H), 3.60–3.66 (m, 1H), 3.80–3.85 (m, 1H), 3.94 (s, 3H), 7.37 (s, 1H), 7.44 (s, 1H), 8.50 (s, 1H). ^{13}C NMR (CD_3OD), δ (ppm) 17.9, 18.1, 28.2, 34.4, 59.2, 59.7, 122.6, 136.7, 157.9. IR (KBr) ν (cm^{-1}): 3398, 3182, 2866, 1620, 1561, 1233, 672. Anal. calcd for $C_9H_{17}ClN_2O$: C, 52.81; H, 8.37. Found: C, 53.02; H, 8.44.

L-1-Methyl-3-(1′-hydroxy-4′-methyl-2′-pentanyl)imidazolium chloride (2c). Yield: 78%; mp 16–18 °C. ^{1}H NMR (CD_3OD), δ (ppm) 0.94 (d, J = 6.45 Hz, 3H), 0.99 (d, J = 6.54 Hz, 3H), 1.47–1.54 (m, 2H), 1.74–1.83 (m, 1H), 3.31–3.51 (m, 1H), 3.51–3.57 (m, 1H), 3.75–3.90 (m, 5H), 7.32 (s, 1H), 7.40 (s, 1H), 8.39 (s, 1H). ^{13}C NMR (CD_3OD), δ (ppm) 21.6, 21.9, 24.5, 34.2, 38.4, 51.9, 61.4, 122.4, 123.3, 136.8. IR (KBr) ν (cm^{-1}): 3405, 1629, 1468, 1385, 1232, 1059, 659. Anal. calcd for $C_{10}H_{19}ClN_2O$: C, 54.91, H, 8.76. Found: C, 55.12; H, 8.91.

3. Anion exchange for the synthesis of chiral imidazolium tetrafluoroborate (3a–c)

To a solution of chiral imidazolium ionic liquids (**2a–c**) (13.8 mmol) in water (20 ml) was added aqueous fluoroboric acid (50%) (2.4 g, 13.8 mmol). The reaction mixture was stirred for 48 h at room temperature. After the resulting mixture was basified with aluminium oxide to pH 9.5, the mixture was filtered and the filtered residue was washed with water (2 × 10 ml). Evaporation of water from the filtrate under reduced pressure gave new chiral imidazolium ionic liquids (**3a–c**).

L-1-Methyl-3-(1′-hydroxy-2′-propanyl)imidazolium tetrafluoroborate (3a). Yield: 91%; mp 59–61 °C. ^{1}H NMR(CD_3OD), δ (ppm) 1.24 (d, J = 5.53 Hz, 3H), 3.36–3.43 (m, 2H), 3.51–3.56 (m, 1H), 3.77–3.81 (m, 1H), 3.86 (s, 3H), 7.29 (s, 1H), 7.38 (s, 1H), 8.31 (s, 1H). ^{13}C NMR (CD_3OD), δ (ppm) 15.3, 34.2, 50.1, 63.1, 123.2, 124.0, 136.9. IR (KBr) ν (cm^{-1}): 3428, 2014, 1603, 1462, 1369, 1069, 661. Anal. calcd for $C_7H_{13}BF_4N_2O$: C, 36.88; H, 5.75. Found: C, 37.02; H, 5.82.

L-1-Methyl-3-(1′-hydroxy–3′-methyl-2′-butanyl)imidazolium tetrafluoroborate (3b). Yield: 95%; mp 66–68 °C. ^{1}H NMR (CD_3OD), δ (ppm) 1.16 (d, J = 6.23 Hz, 3H), 1.20 (d, J = 6.22 Hz, 3H), 1.84–2.14 (m, 1H), 3.16–3.21 (m, 1H), 3.42–3.47 (m, 1H), 3.64–3.70 (m, 1H), 3.85–3.90 (m, 1H), 4.11 (s, 3H), 7.39 (s, 1H), 7.46 (s, 1H), 8.53 (s, 1H). ^{13}C NMR(CD_3OD), δ (ppm): 17.9, 18.1, 28.3, 34.3, 59.3, 59.8, 122.6, 136.4, 157.6. IR (KBr) ν (cm^{-1}): 3401, 3179, 2876, 1623, 1554, 1231, 673. Anal. calcd for $C_9H_{17}BF_4N_2O$: C, 42.22; H, 6.69. Found: C, 42.76; H, 6.81.

L-1-Methyl-3-(1′-hydroxy-4′-methyl-2′-pentanyl)imidazolium tetrafluoroborate (3c). Yield: 90%; mp 68–70 °C. ^{1}H NMR (CD_3OD), δ (ppm) 0.94 (d, J = 6.45 Hz, 3H), 0.99 (d, J = 6.54 Hz, 3H), 1.47–1.54 (m, 2H), 1.74–1.85 (m, 1H), 3.31–3.51 (m, 1H), 3.51–3.57 (m, 1H), 3.74–3.90 (m, 5H), 7.32 (s, 1H), 7.40 (s, 1H), 8.39 (s, 1H). ^{13}C NMR (CD_3OD), δ (ppm) 19.3, 21.7, 24.7, 33.9, 38.8, 52.0, 61.2, 122.2, 123.4, 136.7. IR (KBr) ν (cm^{-1}): 3402, 2906, 1634, 1463, 1378, 1231, 1064, 664. Anal. calcd for $C_{10}H_{19}BF_4N_2O$: C, 44.47, H, 7.09. Found: C, 44.87; H, 7.23.

4. Anion exchange for the synthesis of chiral imidazolium hexafluorophosphate (4a–c)

To a solution of chiral imidazolium ionic liquids (**2a–c**) (16 mmol) in acetone (40 ml) was added sodium potassium hexafluorophosphate (16 mmol) and the mixture was stirred for 48 h at room temperature. After the resulting mixture was filtered, evaporation of water from the filtrate under reduced pressure gave new chiral imidazolium ionic liquids (**4a–c**).

L-1-Methyl-3-(1′-hydroxy-2′-propanyl)imidazolium hexafluorophosphate (4a). Yield: 95%; mp 65–67 °C. ^{1}H NMR (CD_3OD), δ (ppm) 1.21 (d, J = 6.12 Hz, 3H), 3.32–3.41 (m, 2H), 3.49–3.57 (m, 1H), 3.74–3.81 (m, 1H), 3.85 (s, 3H), 7.24 (s, 1H), 7.41 (s, 1H), 8.35 (s, 1H). ^{13}C NMR (CD_3OD), δ (ppm) 15.3, 34.3, 50.1, 63.2, 123.2, 124.1, 136.8. IR (KBr) ν (cm^{-1}): 3430, 2014, 1603, 1490, 1369, 1069, 661. Anal. calcd for $C_7H_{13}F_6N_2OP$: C, 29.38; H, 4.58. Found: C, 29.89; H, 4.91.

L-1-Methyl-3-(1′-hydroxy-3′-methyl-2′-butanyl)imidazolium hexafluorophosphate (4b). Yield: 97%; mp 74–76 °C. ^{1}H NMR (CD_3OD), δ (ppm) 1.14 (d, J = 4.78 Hz, 3H), 1.20 (d, J = 4.77 Hz, 3H), 1.81–2.13 (m, 1H), 3.13–3.18 (m, 1H), 3.40–3.45 (m, 1H), 3.61–3.67 (m, 1H), 3.83–3.86 (m, 1H), 4.08 (s, 3H), 7.37 (s, 1H), 7.44 (s, 1H), 8.51 (s, 1H). ^{13}C NMR (CD_3OD), δ (ppm) 17.8, 18.1, 28.3, 34.3, 59.3, 59.8, 122.5, 136.5, 157.7. IR (KBr) ν (cm^{-1}): 3398, 3180, 2916, 1665, 1625, 1551, 1232, 672. Anal. calcd for $C_9H_{17}F_6N_2OP$: C, 34.40; H, 5.45. Found: C, 34.91; H, 5.79.

L-1-Methyl-3-(1′-hydroxy-4′-methyl-2′-pentanyl)imidazolium hexafluorophosphate (4c). Yield: 93%; mp 76–78 °C. ^{1}H NMR (CD_3OD), δ (ppm) 0.87 (d, J = 6.23 Hz, 3H), 0.96 (d, J = 6.26 Hz, 3H), 1.24–1.41 (m, 2H), 1.59–1.64 (m, 1H), 3.27–3.46 (m, 1H), 3.48–3.55 (m, 1H), 3.65–3.85 (m, 5H), 7.26 (s, 1H), 7.38 (s, 1H), 8.27 (s, 1H). ^{13}C NMR (CD_3OD), δ (ppm) 19.3, 21.6, 24.7, 33.9, 38.7, 52.1, 61.1, 122.1, 123.36, 136.7. IR (KBr) ν (cm^{-1}): 3400, 2914, 1630, 1459, 1383, 1228, 1054, 657. Anal calcd for $C_{10}H_{19}F_6N_2OP$: C, 36.59, H, 5.83. Found: C, 36.79; H, 6.04.

5. Representative procedure of Michael addition in chiral imidazolium ionic liquids (2–4)

The solution of diethyl malonate (1.2 mmol), 1,3-diphenyl-prop-2-en-1-one (1.0 mmol) and potassium carbonate (3.0 mmol) in chiral imidazolium ionic liquids (**2–4**) (1.4–2.2 g, 8 mmol) and acetonitrile (1 mL) was stirred at room temperature for the time indicated in Table 2. After the reaction was finished, the mixture was filtered. The filtrate was extracted with ethyl ether (3 × 5 ml), and the combined ether layer was evaporated to give a residue, which was purified by column chromatography to afford diethyl 2-(3-oxo-1,3-diphenylpropyl)malonate. At the same time, the ionic liquid can be recovered and reused.

Diethyl-2-(3-oxo-1,3-diphenylpropyl)malonate (5). Yield: 63–86%; mp 65–67 °C (lit.[16] 65–67 °C). ^{1}H NMR ($CDCl_3$), δ (ppm) 7.93–7.18 (m, 10H), 4.24–4.21 (m, 3H), 4.00–3.93 (m, 2H), 3.83 (d, J = 9.76 Hz, 1H), 3.54–3.48 (m, 2H), 1.26 (t, J = 7.12 Hz, 3H), 1.02 (t, J = 7.12 Hz, 3H). ^{13}C NMR ($CDCl_3$), δ (ppm) 14.2, 14.4, 41.2, 43.0, 58.0, 61.8, 62.1, 127.5, 128.5, 128.6, 128.8, 128.9, 133.4, 137.2, 140.8, 168.1, 168.8, 198. IR (KBr) ν (cm^{-1}): 3262, 2947, 1723, 1493, 1097, 764,691. MS (m/z): 368(M, 2), 249(42), 209(52), 105(100), 77(46), 51(6).

Acknowledgements

We thank the National Natural Science Foundation of China for its financial support of the project 20332050 and 20572042.

References

1 (*a*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (*b*) J. Dupont, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667; (*c*) C. Boudequin, J. Baudoux, J. Levillain, D. Cahard, A.-C. Gaumont and J.-C. Plaquevent, *Tetrahedron: Asymmetry*, 2003, **14**, 3081.
2 (*a*) R. Sheldon, *Chem. Commun.*, 2001, 2399; (*b*) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; (*c*) C. M. Gordon, *Appl. Catal., A*, 2001, **222**, 101.
3 R. A. Sheldon, R. M. Lau, M. J. Sorgedrager, F. van Rantwijk and K. R. Seddon, *Green Chem.*, 2002, **4**, 147.
4 C. Baudequin, D. Bregeon, J. Levillain, F. Guillen, J.-C. Plaquevent and A. C. Gaumont, *Tetrahedron: Asymmetry*, 2005, **16**, 3921.
5 J. Howarth, K. Hanlon, D. Fayne and P. McCormac, *Tetrahedron Lett.*, 1997, **38**, 3097.
6 W. Bao, Z. Wang and Y. Li, *J. Org. Chem.*, 2003, **68**, 591.
7 Z. Wang, Y. Zhang and W. Bao, *Tetrahedron Lett.*, 2005, **46**, 4657.
8 M. Y. Machado and R. Dorta, *Synthesis*, 2005, 2473.
9 J. Ding, V. Desikan, X. Han, T. L. Xiao, R. Ding, W. Jenks and D. W. Armstrong, *Org. Lett.*, 2005, **7**, 335.
10 J. Pernak and J. Feder-Kubis, *Chem.–Eur. J.*, 2005, **11**, 4441.
11 M. Tosoni, S. Laschat and A. Baro, *Helv. Chim. Acta*, 2004, **87**, 2742.
12 H.-Y. Ma, X.-H. Wan, X.-F. Chen and Q.-F. Zhou, *Chin. J. Polym. Sci.*, 2003, **21**, 265.
13 E. E. Glover and K. T. Robottom, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2927.
14 (*a*) Y. Genisson, C. Marazano, M. Mehmandoust, D. Gnecco and B. C. Das, *Synlett*, 1992, 431; (*b*) M. Eda, M. J. Kurth and M. H. Nantz, *J. Org. Chem.*, 2000, **65**, 5131.
15 K. Yasuda, M. Shindo and K. Koga, *Tetrahedron Lett.*, 1996, **37**, 6343.
16 A. Garcia-Raso, J. Garcia-Raso, B. Campaner, R. Mestres and J. V. Sinisterra, *Synthesis*, 1982, 1037.

