Selective hydrogenation of *trans*-cinnamaldehyde and hydrogenolysis-free hydrogenation of benzyl cinnamate in imidazolium ILs

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***trans*-Cinnamaldehyde is selectively hydrogenated to hydrocinnamaldehyde using a commercially available palladium catalyst in novel imidazolium ILs. The selective hydrogenation extends to benzyl cinnamate, in which the ester is protected from hydrogenolysis under similar conditions.**

Introduction

One of the principal present day problems facing the field of transition metal catalysis is inefficient recycling and reuse of costly catalysts. Even with cost-effective catalysts, selectivity can be poor and elaborate poisons or conditions may be needed to improve the results.[1] ILs have been shown to extend catalyst lifetime in heterogeneous hydrogenations[2] and facilitate product isolation by simple extraction with non-polar solvents or facile distillation. Many common ILs have been investigated as alternative solvents for catalytic hydrogenations. Of these studies, the greater part focus on the commercially available ILs of the form $Rmim^+$ (R = alkyl chain) X^-.[3]

While it is easy to achieve selective olefin reduction in α,β-unsaturated ketones using simple Pd/C reduction, with α,β-unsaturated aldehydes the situation is more challenging and product mixtures often arise.[4,5] *trans*-Cinnamaldehyde is widely used as a model substrate because the products of its hydrogenation are extensively used in the fine chemical industry.[4,6,7] The selectivity varies due to the possibility of reduction of either the olefin moiety, to give hydrocinnamaldehyde, or the aldehydic moiety, to give cinnamyl alcohol. Owing to the thermodynamically favoured reduction of the C=C bond over the C=O bond,[4,8] the selectivity towards cinnamyl alcohol is generally poor. This can be frustrating as cinnamyl alcohol is used widely in the flavouring and perfume industries. Hydrocinnamaldehyde is also an important chemical and has uses in the perfumery industry and in the synthesis of anti-HIV compounds.[9] In the field of metal catalysed hydrogenation ruthenium complexes generally lead to hydrogenation of the carbonyl moiety,[10] whereas rhodium complexes lead to hydrogenation of the olefin moiety but typically high pressures of hydrogen are required.[11–13]

Herein we present the results obtained for the hydrogenation of *trans*-cinnamaldehyde and benzyl cinnamate using the commercially available Pd/C catalyst at 1 atmosphere hydrogen pressure with the use of alternative green solvents (**1–10**). Palladium on carbon is well known as a universal catalyst for olefin hydrogenation. However its efficient catalytic activity may lead to poor selectivity. Furthermore, the product ratio of unsaturated alcohol to saturated aldehyde depends on many factors, including the nanostructure of the metal catalyst,[14,15] the degree of polarisation of the carbonyl group[12] and the phase-distribution of reagent, substrate and catalyst.[13,16] The Pd-H bond is also amphipolar and can transfer hydrogen as either $Pd^{\delta-}$–$H^{\delta+}$ or $Pd^{\delta+}$–$H^{\delta-}$, the latter being favoured by catalyst poisons, such as quinoline, and the Lindlar catalyst.[17] With so many factors influencing selectivity it is not surprising that some of the solutions to the problem have been elaborate. Tessonier *et al.*,[14] for instance, calcined hydrated palladium(I) nitrate at 350 °C (which had previously been added to carbon nanotubes and distilled water) for 2 hours to generate Pd nanoparticles. 100% conversion was achieved, resulting in 90% hydrocinnamaldehyde and 10% undesired 3-phenylpropanol. This compares very favourably with a commercial Pd-C catalyst that gave a 1:1 ratio of hydrocinnamaldehyde to 3-phenyl-1-propanol.[14] Tessonier suggested that the improvement in selectivity with carbon nanotubes stemmed from the absence of either an oxygenated surface, or the micropores typically present on a conventional activated carbon support. Additionally an 'electronic modification through electron transfer between the metal and the support, which in turn modifies the absorption and selectivity of the products[18,19] was hypothesized to explain the simultaneous hydrogenation of C=C and C=O bonds on activated carbon, compared with the rapid desorption of C=C reduced product from the nanotubes. Notably, in neither case is reduction observed if hydrocinnamaldehyde is the substrate, indicating that it is not an intermediate in the reaction.

A more selective process, also involving a palladium catalyst, was developed by Ledoux *et al.*[15] After first impregnating a carbon nanofibre support with the palladium salt, palladium(I) nitrate was dried overnight at 110 °C and reduced under a flow of hydrogen for 2 hours. This support was the major difference from Tessonier's procedure, with the nanofibres, prepared by a gas phase deposition using ethane and hydrogen over a nickel catalyst (from Al_2O_3, $Ni(NO_3)_2$/glycerol), followed by sonication of the fibres and cleaning with acid at 650 °C. In this case the hydrogenation was 98% selective for the C=C double bond of cinnamaldehyde, compared with a commercial Pd–C catalyst that gave mixtures of C=C hydrogenation, C=O hydrogenation, and complete reduction to 3-phenyl-1-propanol. Ledoux suggested that presence of residual acid on the charcoal, as well as the property that commercial Pd–C is covered with micropores to the extent of 60%, could explain the poor selectivity of palladium on ordinary activated carbon.

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Our research effort is directed by the development of biodegradable, low toxicity solvents which can also offer performance advantages over established methods. This work began with Gathergood and Scammells in 2002[20] where the same principles that are used in the synthesis of biodegradable surfactants, were applied to the design of environmentally friendly ILs. Subsequent studies showed the presence of an ester linkage in the side chain of the IL cation (**1**) promoted biodegradation.[21] The counterion was also a significant factor, with the octyl sulfate present in examples (**3**) which were readily biodegradable. We recently reported that key features which improve biodegradation and reduce antimicrobial toxicity were also required for improved catalyst performance in the selective hydrogenation of phenoxyocta-2,7-diene.[22] Herein, we present our work studying the changes in conversion and selectivity in the hydrogenation reactions of cinnamaldehydes and benzyl cinnamate using novel biodegradable and/or low toxicity ILs and comparison with conventional ILs and common organic solvents. (Fig. 1). Recycling of the catalyst/IL media is also investigated.

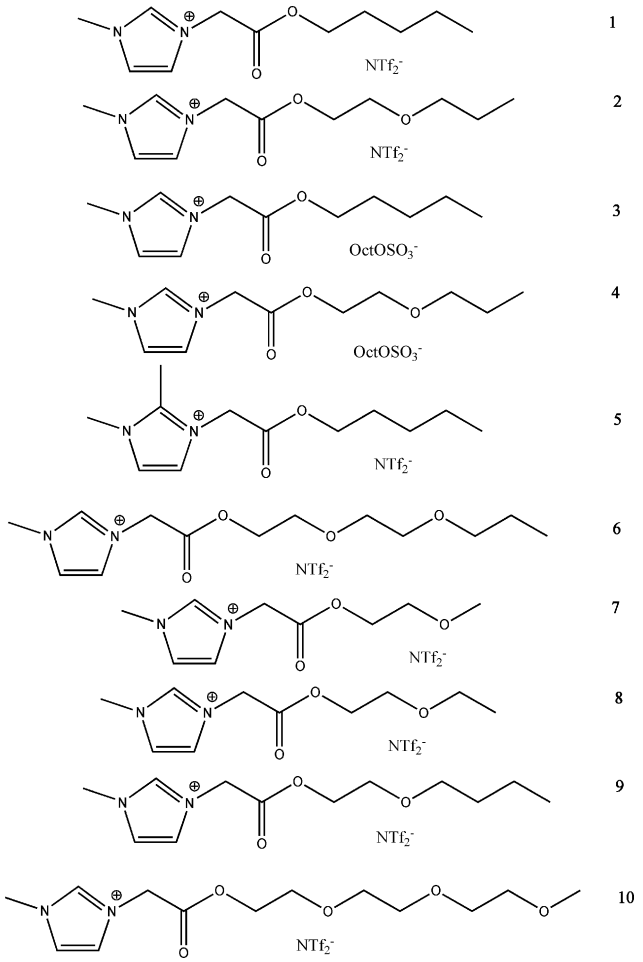


Fig. 1 Ionic liquids used as reaction solvents.

Results

Synthesis of designer ILs for selective catalytic hydrogenation

Novel ILs (**2**,**4–10**) have been prepared containing ester and ether moieties in the side chain (Fig. 2).[20,21] The ILs were readily synthesised from inexpensive alcohols and glycols, thus leading to imidazolium ILs with oxygen in the side chain of the cation.

trans-Cinnamaldehyde

The selective formation of hydrocinnamaldehyde is of both academic interest and of interest to the fine chemical industry (Fig. 3).[23]

Using the pentyl derivative of imidazolium ILs **1** and **5**, selectivity towards hydrocinnamaldehyde generally ranged from 90 to 100%. The most impressive results obtained were achieved using the dimethyl derivative of the ILs, where under 1 atm. H_2 pressure 100% conversion and selectivity were reached at 24 h upon the 1st recycle (Table 1). Although slight variations in conversion and selectivity occurred during the recycling procedure, almost the same reaction efficiency can be seen upon the fourth recycle (conversion 97%, selectivity 100%) (Table 1).

When the side chain length is increased, and also contains an oxygen atom (**2**), the result obtained does not vary significantly; the conversion remains consistent at 100% and the selectivity still does not decrease below 90%. Thus, the method is shown to be still applicable when an oxygen atom is present in the side chain of the IL (Table 2).

Upon increasing the number of oxygen atoms in the side chain from one to two, the selectivity is only slightly negatively affected. There is however a significant drop in conversion by the 3rd recycle (to 64%) (Table 3).

In order to compare the novel ILs with commercially available solvents, *trans*-cinnamaldehyde was hydrogenated using [Bmim][NTf_2] as well as [Bmim][$OctOSO_3$] and the results can be seen in Table 4. The results show that under 1 atm. H_2 pressure [Bmim][$OctOSO_3$] exhibits essentially the same selectivity as toluene, while [Bmim][NTf_2] gives a higher selectivity of 87%,

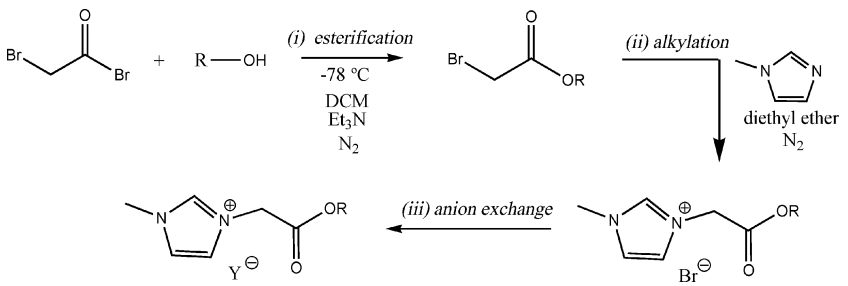


Fig. 2 Synthesis of novel ILs.

Table 1 Results from reactions using solvent **5** and **1**

Solvent	Experiment (E)/Recycle (R)	Time (h)	% conversion	% selectivity **8**
5	E1	24	8	100
		48	36	100
	R1	24	100	100
		48	100	93
	R2	24	48	73
		48	97	98
	R3	24	79	99
		48	100	96
	R4	24	89	100
		48	97	100
1	E1	48	98	94
	R1	48	100	93

Table 2 Results from reactions using solvent **2**

Solvent	Experiment (E)/Recycle (R)	Time (h)	% conversion	% selectivity **8**
2	E1	48	100	93[a]

[a] Isolated yield = 87%.

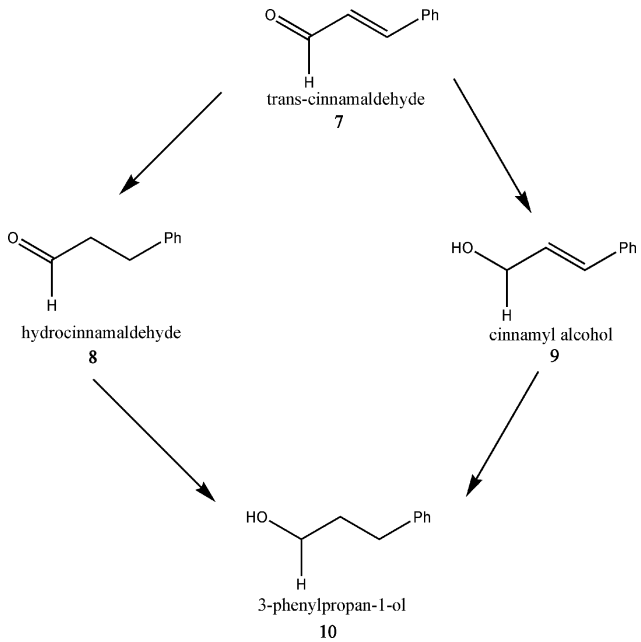


Fig. 3 Reduction pathway of cinnamaldehyde.

which is still lower than the selectivities of 93% achieved with ILs **1** and **2**, or 100% obtained with ILs **5** and **6**.

Nuithitikul and Winterbottom[24] selectively reduced the olefin moiety of cinnamaldehyde using an aqueous solution of a rhodium (I) complex (chlorotris(*meta*-trisulfonato triphenylphosphine). The reactions were carried out in a batch reactor (10–40 atm. H_2, 50–90 °C) and up to 99.9% selectivity towards the saturated aldehyde was observed using a biphasic system (water/toluene). Reductions of cinnamaldehyde based on ruthenium catalysts were carried out by Hajek *et al.*[25] and Qiu *et al.*[26] At 50 atm. H_2 using a 5% Ru/Y catalyst (Y: alumosilicate zeolite used in petrochemistry), Hajek *et al.*[25] achieved selectivity up to 70% towards the unsaturated alcohol. Qiu *et al.*[26] achieved similar selectivity (79.1%), also towards the reduction of the carbonyl moiety, using a carbon nanotubes-supported Pd-Ru catalyst at 120 °C and 50 atm. H_2 pressure. Better results were obtained using the combined metal system than with each metal alone, speculated by the group to be due to a synergic effect or a promoting effect exerted by ruthenium. Our investigations using recyclable Pd/C catalysts in ILs at 1 atm. H_2 pressure to give selective reduction of the double bond in cinnamaldehdyde represent a significant result.

Table 3 Results from reactions using solvent **6**

Solvent	Experiment (E)/Recycle (R)	Time (h)	% conversion	% selectivity **8**
6	E1	24	32	100
		48	97	88[a]
	R1	24	100	100
		48	100	88
	R2	24	31	100
		48	85	91
	R3	24	34	90
		48	64	93

[a] Isolated yield = 77%.

Factors influencing selectivity

Selective reductions using imidazolium ILs have been rationalised on the basis of three parameters of the IL cation: 1) the presence or absence of a methyl group on the C_2 position of the imidazolium moiety, 2) the terminal alkyl chain length and, 3) the presence of oxygen atoms in the side chain. During their investigation into asymmetric hydrogenation in ILs, Jessop *et al.*[27] demonstrated that side chain length and substitution at the C_2 position of the imidazolium cation influenced enantioselectivity. Among their results, a comparison between ILs [emim][NTf_2] and [dmpim][NTf_2] ([dmpim]: 1,2-dimethyl-3-propylimidazolium) displayed differences in %ee obtained for the hydrogenation of tiglic and atropic acids. The %ee obtained when using ILs as reaction solvents was shown to be solvent-dependent. Chandrasekhar *et al.*[28] compared hydrogenation reactions using Adams′ catalyst in poly(ethylene glycol) (400) and [emim][BF_4] and found that the yield dropped

Table 4 Hydrogenation of *trans*-cinnamaldehyde with commercially available solvents

Solvent	Experiment (E)/Recycle (R)	Time (h)	% conversion	% selectivity **8**
[Bmim][NTf_2]	E1	24	100	87
[Bmim][$OctOSO_3$]	E1	24	100	69
Toluene	E1	24	100	67

by as much as 78% when [emim][BF_4] was used in place of PEG 400. An investigation of the quantitative adsorption of hydrogen on the catalyst in both solvents showed PEG 400 to allow superior adsorption, compared to the IL. The presence of repeated oxygen atoms in the PEG solvent was shown to affect the results obtained. Berger *et al.*[29] found the anion also had a significant effect on hydrogen solubility in ILs. [Bmim][BF_4] was found to solubilise hydrogen four times more effectively than [bmim][PF_6]. Our results also demonstrated that it was only possible to achieve highly selective hydrogenation of *trans*-cinnamaldehyde in the presence of the NTf_2 anion. We tentatively propose that steric effects around the cation (substitution at the C_2 position and the presence of ether oxygens in the cation side-chain) together with a subtle alteration in the uptake of hydrogen (influenced by the choice of anion) either in solution or at the catalyst surface, may be contributing to the superior selectivity exhibited by our novel ILs.

Benzyl cinnamate

In order to achieve the selective hydrogenation of the olefin moiety of benzyl cinnamate without hydrogenolysis of the benzyl ester (Fig. 4), elaborate conditions are often required.[30]

The effect of catalyst loading, as well as the solvent effect was investigated during hydrogenations of benzyl cinnamate (Table 5).

The least amount of catalyst effective in inducing 100% conversion under 1 atm. H_2 pressure was 0.005g. Using half this value, only 32% conversion was achieved after 24h with IL **2**. The octylsulfate ILs (**3** and **4**) gave promising results in terms of selectivity; however this was only achieved when conversion was low for IL **3**, but with optimal conversion for IL **4**. The most compelling results from this data set are obtained using ILs **2** and **4**. Using 0.005 g catalyst, after 24 h, 100% conversion and selectivity were obtained under 1 atm. H_2 pressure. More surprising is that the selectivity was retained up to 48h, thus suggesting that hydrogenolysis of this compound in this IL system only occurs with the unsaturated ester. More evidence of this is observed when the non-hydrogenolysed reduced product **12** is further subjected to hydrogenation conditions using an increased amount of catalyst, under 1 atm. H_2 pressure, no hydrogenolysis is observed (Table 6). The significance of this result is that IL **2** completely prevents hydrogenolysis of the benzyl ester.

The system used to obtain 100% selectivity using IL **2** was recycled 4 times with no loss in activity (Table 7). After the fourth recycle, the selectivity remains constant, but the conversion decreases slightly to 91% upon recycle 7. Only on recycle 8 was a small drop in conversion observed (81%). This represents an improvement on previous recycling experiments using $Pd(acac)_2$ in IL **3** to selectively reduce phenoxyocta-2,7-diene, where a decrease in yield from 85 to 55% was observed on the first recycle.[22]

Varying catalytic amounts were tested for the hydrogenation of benzyl cinnamate using IL **4**. As can be seen from the results displayed in Table 8, the increasing amount of catalyst favours

Table 5 Effect of catalyst loading on hydrogenation

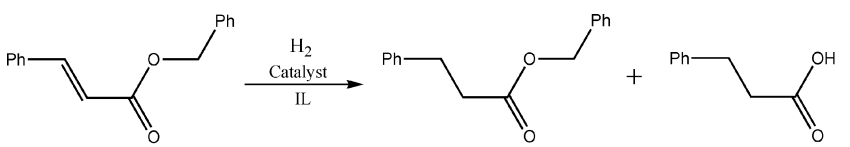
Solvent	Catalyst loading (g)	Time (h)	% conversion	% selectivity **12**
1	0.01	24	100	0
	0.005	24	100	0
2	0.01	24	100	0
	0.005	24	100	100
	0.005	24	100	100
	0.005	48	100	100
	0.0025	24	32	100
3	0.01	24	100	53
	0.0025	24	5	100
	0.005	24	10	100
	0.005	48	19	100
	0.0025	48	0	0
4	0.005	24	11	100
	0.01	48	100	56
	0.005	48	100	100
	0.0025	48	0	0
[Bmim][NTf_2]	0.005	24	100	0
[Bmim][$OctOSO_3$]	0.005	24	100	0
THF	0.005	24	100	0
Ethyl acetate	0.005	24	100	0
Methanol	0.005	24	100	0

Table 6 Hydrogenation of benzyl 3-phenylpropanoate (**12**)

Solvent	Catalyst loading (g)	Time (h)	No reaction
2	0.01	24	

Table 7 Recycling of IL **2** system

Solvent	Experiment (E)/Recycle (R)	% conversion	% selectivity **12**
2	E1	100	100
	R1	100	100
	R2	100	100
	R3	100	100
	R4	100	100
	R5	97	100
	R6	91	100
	R7	91	100
	R8	81	100



benzyl cinnamate 11 — benzyl 3-phenylpropanoate 12 — 3-phenylpropanoic acid 13

Fig. 4 Reduction of benzyl cinnamate.

Table 8 Varying catalytic amount for the hydrogenation of benzyl cinnamate in IL **4**

Solvent	Catalyst loading (g)	Time (h)	% conversion	% selectivity **12**
4	0.005	24	100	100
	0.006		100	68
	0.007		100	55
	0.008		100	26
	0.009		100	25

Table 9 Effect of ILs of differing cation on the selective reduction of benzyl cinnamate

Solvent	Catalyst loading (g)	Time (h)	% conversion	% selectivity **12**
6	0.005	24	100	44
7	0.005	24	100	7
8	0.005	24	100	0
9	0.005	24	100	34
10	0.005	24	100	0

hydrogenolysis, optimum conditions being observed with 0.005 g catalyst.

The effect of cation chain length and the number of oxygens in the side chain was investigated to determine whether only the cation from ILs **2** and **4** gave the best selectivity (Table 9).

It is evident from the results obtained that any difference in the length of the side chain or the number of oxygen atoms contained within, negatively affects the selectivity of the reaction. This reaction is therefore sensitive to many changes in IL composition concerning the IL cation.

Based on the conditions from the result obtained using ILs **2** and **4** and 0.005 g catalyst, this system was used to test other compounds comprising hydrogenolysable functionalities.

Allyl cinnamate

The hydrogenation of allyl cinnamate can lead to the reduction either of the olefinic bonds, or even hydrogenolysis of the allyl functionality may be observed (Fig. 5).

Using both ILs **2** and **4** under 1 atm. H_2 pressure, impressive selectivities were reached in comparison with common organic solvents and classic ILs displaying no selectivity (Table 10).

Table 10 Hydrogenation of allyl cinnamate

IL	% conversion	% selectivity **15**
2	100	84
4	100	71
[Bmim][NTf_2]	100	0
[Bmim][$OctOSO_3$]	100	0
Ethyl acetate	100	0

Table 11 Hydrogenation of vinyl cinnamate

IL	% conversion	% selectivity
2	100	0
4	100	49
Ethyl acetate	100	0

Vinyl cinnamate

Vinyl cinnamate was also used as a test-substrate in order to evaluate the selectivity obtained using the novel ILs in comparison with other more frequently used solvents (Fig. 6).

Only 49% selectivity was obtained using the octylsulfate IL, **4**, in comparison with no selectivity for IL **2** and ethyl acetate (Table 11).

Conclusion

We have demonstrated that novel imidazolium ILs display superior selectivity in olefin hydrogenation compared with conventional organic solvents and classic ILs. Hydrogenolysis-free hydrogenation of benzyl cinnamate was achieved using novel ILs without the need for a catalyst poison, under 1 atm. H_2 pressure. Furthermore *trans*-cinnamaldehyde was selectively reduced to hydrocinnamaldehyde with little or no over-reduction of the aldehydic moiety. The reactions were performed with only the use of the IL, substrate, a simple heterogeneous catalyst and under H_2 at 1 atm. pressure. Successful recycling of the systems was achieved without significant loss of activity. Overall, the novel ILs were found to be robust media for hydrogenation reactions as a replacement for harmful VOCs.

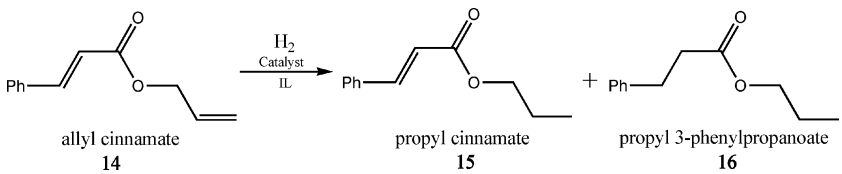


Fig. 5 Reduction of allyl cinnamate.

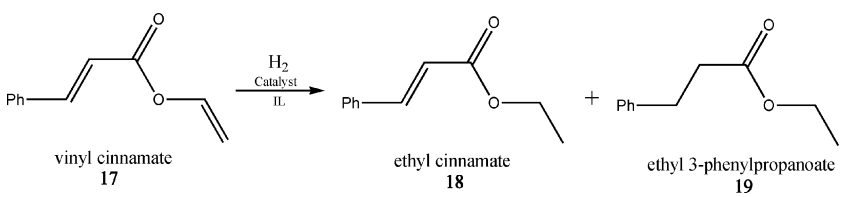


Fig. 6 Reduction of vinyl cinnamate.

Experimental

Hydrogenation

Typical procedure. 10% Pd/C (5.0 mg unless otherwise stated) was weighed into a dry 2-neck round bottom flask. The pre-dried IL (2.0 mL) was then added to the flask, followed by the desired substrate (4 mmol) and 3 N_2/vacuum cycles were performed. The reaction mixture was allowed to stir for 10 minutes or until reaching the desired reaction temperature, or until all the substrate had dissolved in the IL. Hydrogen was then introduced to the reaction *via* a balloon, and the progress of the reaction was monitored by ^{1}H NMR at 24 and 48 hour intervals. Quantitative analysis of the reaction products was carried out by measuring the integration ratio of the peaks from the crude NMR spectrum. These values were then verified by purification of the product by column chromatography and thus the calculation of isolated yields. Upon termination of the reaction, the products were extracted using hexane (10 × 3 mL). The mass recovery after extraction from the IL was always > 98%. In the case of reactions carried out in octylsulfate ILs, the product was either distilled from the IL using high vacuum or a brief column was prepared to separate product from IL. These procedures generally led to a lower mass recovery (> 80%), due to product being lost on the column or lost during the distillation procedure. All reactions carried out in the NTf_2 ILs were carried out at 55 °C and 65 °C in the octylsulfate ILs.

Recycle procedure. Following extraction of the products from the IL, the IL (containing the catalyst) was dried and analysed by ^{1}H NMR. Following confirmation that the IL was substrate/product-free and had not degraded, fresh substrate was then added to the system and the reactions recommenced as described.

Benzyl 3-phenylpropanoate. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.29-7.09 (m, 10H), 5.03 (s, 2H), 2.91 (t, J = 7.8 Hz, 2H), 2.62 (t, J = 7.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.80, 140.44, 135.94, 128.60, 128.56, 128.46, 128.36, 128.27, 126.33, 66.34, 35.21, 30.74.

Data consistent with literature.[31]

3-Phenylpropanoic acid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 11.00 (br s, 1H), 7.23-7.19 (m, 2H), 7.14-7.11 (m, 3H), 2.89 (t, J = 7.8 Hz, 2H), 2.69 (t, J = 7.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 178.97, 140.16, 128.59, 128.29, 126.40, 35.59, 30.58.

Data consistent with literature.[32]

Hydrocinnamaldehyde. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.85 (t, J = 1.4 Hz, 1H), 7.35-7.31 (m, 2H), 7.26-7.22 (m, 3H), 2.99 (t, J = 7.4 Hz, 2H), 2.83-2.79 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 203.49, 141.32, 128.01, 127.99, 127.89, 40.33, 29.63.

Data consistent with literature.[33]

3-Phenylpropan-1-ol. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.23-7.18 (m, 2H), 7.14-7.10 (m, 3H), 3.62 (t, J = 6.6 Hz, 2H), 2.62 (t, J = 7.4 Hz, 2H), 1.82 (tt, J = 6.6, 7.4 Hz, 2H), 1.55 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 141.20, 129.01, 128.93, 126.50, 62.33, 34.30, 33.67.

Data consistent with literature.[34]

Propyl cinnamate. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.74 (d, J = 16 Hz, 1H), 7.56-7.54 (m, 2H), 7.42-7.38 (m, 3H), 6.50 (d, J = 16 Hz, 1H), 4.21 (t, J = 6.7 Hz, 2H), 1.79 (tq, J = 6.7, 7.8 Hz, 2H), 1.04 (t, J = 7.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.25, 143.20, 131.70, 129.29, 129.26, 129.00, 118.03, 61.52, 22.83, 17.01.

Data consistent with literature.[35]

Propyl 3-phenylpropanoate. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34-7.30 (m, 2H), 7.25-7.22 (m, 3H), 4.09 (t, J = 7.0 Hz, 2H), 3.02 (t, J = 7.8 Hz, 2H), 2.69 (t, J = 7.8 Hz, 2H), 1.71 (tq, J = 7.0, 7.3 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 173.06, 140.60, 128.50, 128.32, 126.25, 66.29, 37.43, 31.03, 21.98, 10.40.

Data consistent with literature.[36]

Ethyl cinnamate. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.73 (d, J = 16 Hz, 1H), 7.55-7.52 (m, 2H), 7.42-7.38 (m, 3H), 6.48 (d, J = 16 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.99, 144.93, 134.74, 130.55, 128.58, 128.06, 118.64, 60.50, 14.53.

Data consistent with literature.[35]

Ethyl 3-phenylpropanoate. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34-7.30 (m, 2H), 7.25-7.23 (m, 3H), 4.19 (q, J = 7.2 Hz, 2H), 3.01 (t, J = 7.8 Hz, 2H), 2.67 (t, J = 7.8 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.92, 140.62, 128.51, 128.34, 126.26, 60.43, 35.98, 31.01, 14.24.

Data consistent with literature.[37]

IL preparation

ILs **1** and **3** were synthesised in accordance with the literature.[21]

Representative procedure for the preparation of α-bromoesters (2-propoxyethyl 2-bromoacetate). To a stirred solution of dichloromethane (350 mL), propoxyethanol (47.84 mL, 460 mmol), and triethylamine (69.3 mL, 500 mmol), under a nitrogen atmosphere at −78 °C was added dropwise bromoacetyl bromide (92.92 g, 460 mmol). After stirring at −78 °C for 3 h, the reaction mixture was allowed warm up to −20 °C and quenched by addition of water (50 mL). The organic phase was washed with distilled water (3 × 25 mL), saturated ammonium chloride (3 × 25 mL), saturated sodium bicarbonate (3 × 25 mL) and brine (2 × 25 mL). The organic phase was then dried over magnesium sulfate, filtered and solvents removed *via* rotary evaporation. The crude product was distilled (bp 100–102 °C) to give a pale yellow liquid in 83% yield (85.91 g, 382 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.34 (t, J = 4.6 Hz, 2H), 3.88 (s, 2H), 3.67 (t, J = 4.6 Hz, 2H), 3.47 (t, J = 6.9 Hz, 2H), 1.66 (tq, J = 6.9, 7.3 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.31, 73.07, 68.10, 65.42, 25.90, 22.81, 10.52.

Representative method for the preparation of bromide salts (3-Methyl-1-(propoxyethoxycarbonylmethyl)imidazolium bromide). To a stirred solution of 1-methylimidazole (65.0 mmol, 5.33 g) in diethyl ether (60 mL) at −15 °C under a nitrogen atmosphere was added dropwise propoxyethyl 2-bromoacetate (78.0 mmol, 17.55 g). The reaction mixture was stirred vigorously at −15 °C for 1 h, then at RT for 24 h. The diethyl ether top phase was decanted and the IL washed with diethyl ether (2 × 20 mL), then residual solvent removed on the rotary evaporator. The product was dried under high vacuum for 8 h yielding a pale yellow solid in 88% yield (17.59 g, 57.3 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.25 (s, 1H), 7.48 (t, J = 1.8 Hz, 1H), 7.35 (t, J = 1.8 Hz, 1H), 5.46 (s, 2H), 4.30 (t, J = 4.8 Hz, 2H), 4.02 (s, 3H), 3.61 (t, J = 4.8 Hz, 2H), 3.37 (t, J = 6.8 Hz, 2H), 1.54 (tq, J = 6.8, 7.5 Hz, 2H), 0.85 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.12, 138.74, 123.68, 122.77, 73.08, 67.89, 65.87, 50.28, 36.93, 22.75, 10.50.

M (°C) 25–27 °C.

IR (cm^{-1}) 3099, 2967, 2927, 1751, 1578, 1568, 1558, 1539, 1495, 1452, 1216, 1176.

MS m/z, Found 227.1410 $[M\text{-}Br^-]^+$, Calcd. $C_{11}H_{19}N_2O_3$ 227.1396.

Representative method for the preparation of NTf_2 salts (3-Methyl-1-(propoxyethoxycarbonylmethyl)imidazolium NTf_2) (2). A flask was charged with 3-Methyl-1-(propoxyethoxycarbonylmethyl) imidazolium bromide (3.55 g, 7.00 mmol) and distilled water (20 mL). $LiNTf_2$ (2.15 g, 7.50 mmol) in distilled water (3 mL) was added in one portion and the suspension was stirred vigorously for 6 h at RT. The top aqueous layer was removed and the IL was washed with distilled water (3 × 10 mL). The solvent was then removed on the rotary evaporator and the product was dried under high vacuum for 3 h to give a yellow viscous oil in 68% yield (2.43 g, 4.79 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.78 (s, 1H), 7.39 (t, J = 1.8 Hz, 1H), 7.36 (t, J = 1.8 Hz, 1H), 5.04 (s, 2H), 4.37 (t, J = 4.8 Hz, 2H), 3.95 (s, 3H), 3.67 (t, J = 4.8 Hz, 2H), 3.43 (t, J = 6.7 Hz, 2H), 1.61 (tq, J = 6.7, 7.3 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.76, 137.50, 123.82, 123.34, 119.60 (q, J = 319 Hz), 72.99, 67.79, 65.91, 49.87, 56.49, 22.68, 10.37.

IR (cm^{-1}) 3164, 3117, 2968, 2927, 2862, 1751, 1569, 1558, 1539, 1495, 1452, 1353, 1198, 1135.

MS m/z, 227.2 $[M\text{-}NTf_2^-]^+$; MS: m/z, 280.0 $[NTf_2^-]$.

2,3 Dimethyl-1-(pentoxycarbonylmethyl) imidazolium NTf_2 (5). The title compound was prepared from 2,3-dimethyl-1-(pentoxycarbonylmethyl)imidazolium bromide[21] (3.36 g, 11.0 mmol) and $LiNTf_2$ (4.59 g, 16.0 mmol) according to the general procedure in 95% yield (5.30 g, 10.5 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28 (d, J = 2.2 Hz, 1H), 7.26 (d, J = 2.2 Hz, 1H), 4.93 (s, 2H), 4.21 (t, J = 6.8 Hz, 2H), 3.82 (s, 3H), 2.56 (s, 3H), 1.68-1.60 (m, 2H), 1.34-1.27 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.78, 145.45, 122.38, 122.37, 119.70 (q, J = 319 Hz), 67.21, 49.17, 35.48, 27.93, 27.75, 22.18, 13.85, 9.75.

IR (cm^{-1}) 3154, 2962, 2930, 2862, 1751, 1595, 1558, 1546, 1539, 1495, 1452, 1354, 1197, 1137.

MS m/z, 225.2 $[M\text{-}NTf_2^-]^+$; MS: m/z, 280.0 $[NTf_2^-]$.

3-Methyl-1-(methoxyethoxycarbonylmethyl)imidazolium NTf_2 (7). The title compound was prepared from 3-methyl-1-(methoxyethoxyoxycarbonylmethyl)imidazolium bromide (1.74 g, 6.26 mmol) and $LiNTf_2$ (2.16 g, 7.51 mmol) according to the general procedure in 91% yield (2.73 g, 5.70 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.85 (s, 1H), 7.39 (t, J = 1.8 Hz, 1H), 7.33 (t, J = 1.8 Hz, 1H), 5.07 (s, 2H), 4.40 (t, J = 4.6 Hz, 2H), 3.98 (s, 3H), 3.66 (t, J = 4.6 Hz, 2H), 3.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.73, 137.75, 123.78, 123.18, 119.70 (q, J = 319 Hz), 69.75, 65.72, 63.24, 58.89, 49.93.

IR (cm^{-1}) 2926, 2855, 1750, 1636, 1558, 1539, 1495, 1452, 1365, 1204, 1129.

MS m/z, 199.1 $[M\text{-}NTf_2^-]^+$; MS: m/z, 280.0 $[NTf_2^-]$.

3-Methyl-1-(ethoxyethoxycarbonylmethyl)imidazolium NTf_2 (8). The title compound was prepared from 3-methyl-1-(ethoxyethoxycarbonylmethyl)imidazolium bromide (2.93 g, 10.0 mmol) and $LiNTf_2$ (4.59 g, 16.0 mmol) according to the general procedure in 90% yield (4.42 g, 8.97 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.82 (s, 1H), 7.39 (t, J = 1.8 Hz, 1H), 7.34 (t, J = 1.8 Hz, 1H), 5.06 (s, 2H), 4.38 (t, J = 4.6 Hz, 2H), 3.97 (s, 3H), 3.68 (t, J = 4.6 Hz, 2H), 3.56 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.76, 137.63, 123.80, 123.25, 119.70 (q, J = 319 Hz), 67.62, 66.67, 65.97, 49.92, 36.56, 15.01.

IR (cm^{-1}) 3169, 3116, 2967, 2927, 2859, 1751, 1581, 1569, 1558, 1495, 1452, 1352, 1196, 1135.

MS m/z, 213.1 $[M\text{-}NTf_2^-]^+$; MS: m/z, 280.0 $[NTf_2^-]$.

3-Methyl-1-(butoxyethoxycarbonylmethyl)imidazolium NTf_2 (9). The title compound was prepared from 3-methyl-1-(butoxyethoxycarbonylmethyl)imidazolium bromide (1.85 g, 5.77 mmol) and $LiNTf_2$ (1.99 g, 6.92 mmol) according to the general procedure in 84% yield (2.73 g, 4.82 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.71 (s, 1H), 7.38 (t, J = 1.8 Hz, 1H), 7.36 (t, J = 1.8 Hz, 1H), 5.00 (s, 2H), 4.32 (t, J = 4.8 Hz, 2H), 3.91 (s, 3H), 3.64 (t, J = 4.8 Hz, 2H), 3.44 (t, J = 6.7 Hz, 2H), 1.54 (tt, J = 6.7, 7.2 Hz, 2H), 1.34 (tq, J = 7.2, 7.5 Hz, 2H), 0.89 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.78, 137.32, 123.83, 123.40, 122.33 (q, J = 319 Hz), 71.09, 67.78, 65.81, 49.78, 36.37, 31.50, 19.11, 13.78.

IR (cm^{-1}) 3164, 3123, 2959, 2934, 2864, 1756, 1582, 1569, 1558, 1495, 1453, 1354, 1197, 1135.

MS m/z, 241.2 $[M\text{-}NTf_2^-]^+$; MS: m/z, 280.0 $[NTf_2^-]$.

3-Methyl-1-(propoxyethoxyethoxycarbonylmethyl)imidazolium NTf_2 (6). The title compound was prepared from 3-methyl-1-(methoxyethoxyethoxycarbonylmethyl)imidazolium bromide (1.91 g, 5.45 mmol) and $LiNTf_2$ (1.88 g, 6.54 mmol) according to the general procedure in 82% yield (2.46 g, 4.46 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.92 (s, 1H), 7.40 (t, J = 1.7 Hz, 1H), 7.31 (t, J = 1.7 Hz, 1H), 5.08 (s, 2H), 4.41 (t, J = 4.8 Hz, 2H), 4.00, (s, 3H), 3.77 (t, J = 4.8 Hz, 2H), 3.67

(t, J = 4.8, 2H), 3.61 (t, J = 4.8 Hz, 2H), 3.44 (t, J = 6.8 Hz, 2H), 1.61 (tq, J = 6.8, 7.2 Hz, 2H), 0.93 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.71, 137.92, 123.80, 123.07, 122.00 (q, J = 319 Hz), 73.09, 70.58, 69.89, 68.42, 65.86, 50.02, 36.66, 22.76, 10.47.

IR (cm^{-1}) 3164, 3119, 2966, 2927, 2865, 1751, 1568, 1558, 1495, 1452, 1353, 1198, 1135.

MS m/z, 271.3 [M-NTf_2^-]$^+$; MS: m/z, 280.0 [NTf_2^-].

3-Methyl-1-(methoxyethoxyethoxyethoxycarbonylmethyl)-imidazolium NTf_2 (10). The title compound was prepared from 3-methyl-1-(methoxyethoxyethoxyethoxycarbonylmethyl)imidazolium bromide (2.20 g, 6.00 mmol) and $LiNTf_2$ (2.01 g, 7.00 mmol) according to the general procedure in 93% yield (3.17 g, 5.60 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.78 (s, 1H), 7.37 (t, J = 1.6 Hz, 1H), 7.26 (t, J = 1.6 Hz, 1H), 4.99 (s, 2H), 4.31 (t, J = 4.6 Hz, 2H), 3.89 (s, 3H), 3.66 (t, J = 4.6 Hz, 2H), 3.57-3.54 (m, 6H), 3.49-3.47 (m, 2H), 3.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.78, 137.75, 123.96, 123.18, 119.70 (q, J = 319 Hz), 71.79, 70.42, 70.38, 70.32, 68.35, 65.57, 58.82, 49.92, 36.53.

IR (cm^{-1}) 3161, 3116, 2925, 2859, 1751, 1569, 1558, 1539, 1495, 1452, 1354, 1198, 1135.

MS m/z, 287.2 [M-NTf_2^-]$^+$; MS: m/z, 280.0 [NTf_2^-].

Representative method for the preparation of $OctOSO_3$ salts (3-Methyl-1-(propoxyethoxycarbonylmethyl)imidazolium $OctOSO_3$) (4). To a solution of 3-Methyl-1-(propoxyethoxycarbonylmethyl)imidazolium bromide (3.68 g, 12.0 mmol) in distilled water (20 mL) was added in one portion sodium octyl sulfate (2.09 g, 9.00 mmol) and stirred at 60 °C for 2 h. The water was then slowly removed under vacuum. The precipitate was dissolved in DCM (5 mL) and washed with distilled water (2 × 3 mL). The product remaining was dried on the rotary evaporator and then under high vacuum for 8 h to give a pale yellow grease in 85% yield (3.33 g, 7.62 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.45 (s, 1H), 7.48 (t, J = 1.6 Hz, 1H), 7.41 (t, J = 1.6 Hz, 1H), 5.25 (s, 2H), 4.36 (t, J = 4.7 Hz, 2H), 4.01 (m, 5H), 3.67 (t, J = 4.7 Hz, 2H), 3.43 (t, J = 6.8 Hz, 2H), 1.63-1.58 (m, 4H), 1.56-1.29 (m, 10H), 0.92-0.86 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.45, 138.89, 123.71, 123.06, 73.04, 67.92, 67.89, 65.67, 49.91, 36.58, 31.83, 29.50, 29.36, 29.26, 25.87, 22.73, 22.66, 14.13, 10.47.

IR (cm^{-1}) 3118, 2958, 2927, 2855, 1750, 1569, 1558, 1539, 1495, 1455, 1217, 1178, 1108.

MS m/z, 227.1 [M-$OctSO_4^-$]$^+$; MS: m/z, 209.0 [$OctSO_4^-$].

References

1 (*a*) Y. Kume, K. Qiao, D. Tomida and C. Yokoyama, *Catalysis Communications*, 2008, **9**, 369; (*b*) Y. Kanazawa and H. Nishiyama, *Synlett*, 2006, **19**, 3343; (*c*) F. Lopez-Linares, G. Agrifolio, A. Labrador and A. Karam, *Journal of Molecular Catalysis A*, 2004, **207**, 115; (*d*) A. Mori, T. Mizusaki, Y. Miyakawa, E. Ohashi, T. Haga, T. Maegawa, Y. Monguchi and H. Sajiki, *Tetrahedron*, 2006, **62**, 11925; (*e*) T. Ikawa, H. Sajiki and K. Hirota, *Tetrahedron*, 2005, **61**, 2217.

2 (*a*) Boxwell, P. Dyson, D. Ellis and T. Welton, *J. Am. Chem. Soc*, 2002, **124**, 9334; (*b*) Dupont, G. Fonseca, A. Umpierre, P. Fichtner and S. Teixeira, *J. Am. Chem. Soc.*, 2002, **124**, 4228.

3 (*a*) P. Dyson, D. Ellis, W. Henderson and G. Laurenczy, *Adv. Synth. Catal.*, 2003, 345; (*b*) P. Dyson, G. Laurenczy, C. Andre Ohlin, J. Vallance and T. Welton, *Chem. Commun.*, 2003, 2418; (*c*) L. Rossi, G. Machado, P. Fichtner, S. Teixeira and J. Dupont, *Catalysis Letters*, 2004, **92**(3–4), 149–255; (*d*) M. Steffan, M. Lucas, A. Brandner, M. Wollny, N. Oldenburg and P. Claus, *Chem. Eng. Technol.*, 2007, **30**, 481; (*e*) K. Anderson, P. Goodrich, C. Hardacre and D. Rooney, *Green Chemistry*, 2003, **5**, 448.

4 P. Gallezot and D. Richard, *Catal. Rev.–Sci. Eng.*, 1998, **40**, 81.

5 H. Miura, *Shokubai*, 2007, **49**, 232.

6 X. Cheng, L. Hexing, D. Weilin, W. Jie, R. Yong and Q. Minghua, *Applied Catalysis A: General*, 2003, **253**, 359.

7 P. Maki-Arvela, J. Haje, T. Salmi and D. Murzin, *Applied Catalysis A: General*, 2005, **292**, 1.

8 U. Singh and M. Vannice, *Applied Catalysis A: General*, 2001, **213**, 1.

9 (*a*) A. Muller, J. Bowers, J. Eubanks, C. Geiger, J. Santobianco, 1999, *WO/1999/008989*; (*b*) F. Bennett, A. Ganguly, V. Girijavallabhan, N. Patel, 1993, *EP0533342*; (*c*) P. Jadhav and H.-W. Man, *Tetrahedron Lett.*, 1996, **37**, 1153.

10 P. Kluson and L. Cerveny, *Applied Catalysis A: General*, 1995, **128**, 13.

11 I. Kostas, *Journal of Organometallic Chemistry*, 2001, **634**, 90.

12 K. Nuithitikul and M. Winterbottom, *Catalysis Today*, 2007, **128**, 74.

13 K. Nuithitkul and M. Winterbottom, *Chemical Engineering Science*, 2006, **61**, 5944.

14 J. P. Tessonnier, L. Pesant, G. Ehret, M. Ledoux and C. Pham-Huu, *Applied Catalysis A: General*, 2005, **288**, 203.

15 C. Pham-Huu, N. Keller, L. Charbonniere, R. Ziessel and M. Ledoux, *Chem. Commun.*, 2000, 1871.

16 M. Bhor, A. Panda, S. Jagtap and B. Bhanage, *Catal. Lett.*, 2008, **124**, 157.

17 T. Mallet and A. Baiker, *Applied Catalysis A: General*, 2000, **200**, 3.

18 R. Schlogl, Surface composition and structure of active carbon, in: F. Schuth, K. S. W. Sing and J. Weitkamp, (Eds.), *Handbook of Porous Solids*, Wiley-VCH, 2002, 1863.

19 C. Pham-Huu, N. Keller, G. Ehret and M. Ledoux, *J. Cataly.*, 2001, **200**, 400.

20 N. Gathergood and P. J. Scammells, *Aust. J. Chem.*, 2002, **55**, 557.

21 (*a*) N. Gathergood, M. T. Garcia and P. J. Scammells, *Green Chemistry*, 2004, **6**, 166; (*b*) M. T. Garcia, N. Gathergood and P. J. Scammells, *Green Chemistry*, 2004, **7**, 9; (*c*) N. Gathergood, P. J. Scammells and M. T. Garcia, *Green Chemistry*, 2006, **8**, 156.

22 S. Bouquillon, T. Courant, D. Dean, N. Gathergood, S. Morrissey, B. Pegot, P. J. Scammells and R. Singer, *Aust. J. Chem.*, 2007, **60**, 843.

23 (*a*) F. Benvenuti, C. Carlini, M. Marchionna, A. M. Galletti and G. Sbrana, *Journal of Molecular Catalysis A*, 1999, **145**, 221; (*b*) Y. Kume, K. Qiao, D. Tomida and C. Yokoyama, *Catalysis Communications*, 2008, **9**, 369; (*c*) Y. Kanazawa and H. Nishiyama, *Synlett*, 2006, **19**, 3343; (*d*) F. Lopez-Linares, G. Agrifoglio, A. Labrador and A. Karam, *Journal of Molecular Catalysis A*, 2004, **207**, 115; (*e*) Y. Zhang, S. Liao, Y. Xu and D. Yu, *Applied Catalysis A*, 2000, **192**, 247.

24 K. Nuithitikul and M. Winterbottom, *Chem. Eng. Sci.*, 2004, **59**, 5439.

25 J. Hajek, N. Kumar, P. Maki-Arvela, T. Salmi and D. Murzin, *Journal of Molecular Catalysis A: Chemical*, 2004, **217**, 145.

26 J. Qui, H. Zhang, X. Wang, H. Han, C. Liang and C. Li, *React. Kinet. Catal. Lett.*, 2006, **88**, 269.

27 P. Jessop, R. Stanley, R. Brown, C. Eckert, C. Liotta and T. P. Ngo, Pollet, *Green. Chem.*, 2003, **5**, 123.

28 S. Chandrasekhar, S. Prakash and C. Rao, *J. Org. Chem.*, 2006, **71**, 2196.

29 A. Berger, R. de Souza, M. Delgado and J. Dupont, *Tetrahedron: Asymmetry*, 2001, **12**, 1825.

30 (*a*) A. Mori, T. Mizusaki, Y. Miyakawa, E. Ohashi, T. Haga, T. Maegawa, Y. Monguchi and H. Sajiki, *Tetrahedron*, 2006, **62**, 11925; (*b*) J. Le Bras, D. K. Mukherjee, S. Gonzalez, M. Tristany, B. Ganchegui, M. Moreno-Manas, R. Pleixats, F. Henin and J. Muzart, *New J. Chem.*, 2004, **28**, 1550; (*c*) H. Sajiki, T. Ikawa and K. Hirota, *Tetrahedron Lett.*, 2003, **44**, 8437; (*d*) T. Ikawa, H. Sajiki and

K. Hirota, *Tetrahedron*, 2005, **61**, 2217; (*e*) D. Belotti, G. Cantagrel, C. Combellas, J. Cossy, F. Kanoufi and S. Nunige, *New J. Chem.*, 2005, **29**, 761.
31 P. Black, G. Cami-Kobeci, M. Edward, P. Slatford, M. Whittlesey and J. Williams, *Org. Biomol. Chem.*, 2006, **4**, 116.
32 (*a*) Sigma Aldrich, NMR W288918; (*b*) Beil., **9**, III, 2382.
33 (*a*) Sigma Aldrich, NMR 56660; (*b*) Beil., **7**, IV, 692.
34 (*a*) Sigma Aldrich, NMR 140856; (*b*) Beil., **6**, IV, 3198.
35 S. Yan-mei, L. Jing, Z. Ping, S. Zhi-guang, L. Ye-zhi and H. Hua-min, *Chem. Res. Chinese U.*, 2007, **23**, 669.
36 S. Kiyooka, Y. Wada, M. Ueno, T. Yokoyama and R. Yokoyama, *Tetrahedron*, 2007, **63**, 12695.
37 S. Chandrasekhar, G. Reddy, C. Nagesh and C. Reddy, *Tetrahedron Lett.*, 2007, **48**, 1269.

