Catal Lett (2008) 124:105–110
DOI 10.1007/s10562-008-9431-7

The Diels–Alder Reaction in Phosphonium Ionic Liquid Catalysed by Metal Chlorides, Triflates and Triflimides

Ewa Janus · Waldemar Stefaniak

Received: 10 December 2007 / Accepted: 7 February 2008 / Published online: 6 March 2008

Abstract Phosphonium ionic liquid (IL)—trihexyl-tetradecylphosphonium bis(trifluoromethylsulfonyl)imide, has been tested as the medium in the Diels–Alder reaction between cyclopentadiene and dienophiles from the group of α,β-unsaturated esters, aldehydes and ketones. Catalytic activities of a few metal chlorides, triflates and bis-triflimides in this reaction have been compared. The recycling of the catalyst with phosphonium IL was studied.

Keywords Diels–Alder reaction · Lewis acids · Phosphonium ionic liquid

1 Introduction

The Diels–Alder reaction is a powerful tool in organic synthesis and chemical industry as it permits a one-stage formation of six-membered carbocycles of easily accessible unsaturated substrates. The reaction is used in production of such compounds as functionalized norbornenes used in drug delivery [1], biochemical applications [2] as well as luminescent materials and devices [3], liquid crystalline [4], nonlinear optical materials [5]. It has been established that the yield and selectivity of the Diels–Alder reaction are affected by the reaction medium [6].

Recently, ionic liquids have been proposed as an interesting alternative to molecular solvents. They have been shown to lead to higher reaction rates and higher selectivities. Additionally, ionic liquids (ILs) posses negligible vapour pressure and they are nonflammable, therefore are considered as potentially environmentally friendly solvents [7]. Of particular interest has become the use of ionic liquids with catalysts, especially metallic ones, as the ionic liquids are able to dissolve them increasing their activity and stability and first of all they can be recycled many times [8]. Metal compounds include Lewis acids, which are known to catalyse the Diels–Alder reaction.

The most thoroughly tested as media of the Diels–Alder reaction (with and without Lewis acids) were the ionic liquids from the group of imidazolium salts [9], pyridinium salts [10] and ammonium salts [11]. The influence of the imidazolium ionic liquids on the reaction is explained by the solvophobic effect. Moreover, catalytic effect is attributed to the proton at C2 [12] or at the nitrogen of the imidazole ring [13].

Of particular interest among the ionic liquids are the phosphonium ionic liquids. Recently number of reports using phosphonium ILs grows noticeably [14]. Phosphonium ILs tend to be less prone to thermal decomposition than the salts containing a quaternary nitrogen atom (ammonium, imidazolium, pyridinium) [15]. It ensures the stability of a phosphonium ILs when the reaction is conducted at high temperature or when the reaction products are separated by distillation.

In our study we have used phosphonium IL—trihexyltetradecyl bis(trifluoromethylsulfonyl)imide ($P_{6.6.6.14}$ NTf_2), as the medium of the Diels–Alder reaction. The choice of an ionic liquid with the NTf_2^- anion followed from the hydrophobic character of this anion, its resistance to air and moisture and weak coordination character. The ionic liquids containing this anion are known to be more chemically and thermally stable than the ionic liquids with BF_4^- or PF_6^- anions [16], that undergo hydrolysis with formation of hydrogen fluoride [17]. The ionic liquids with

---

E. Janus (✉) · W. Stefaniak
Department of Organic Chemical Technology, Szczecin University of Technology, Pułaski Str. 10, 70-322 Szczecin, Poland
e-mail: ejanus@ps.pl

NTf_2 anion also have low viscosity [18] which considerably facilitates manual operation.

In this study we have tested the reaction of cyclopentadiene with selected dienophiles from the group of α, β-unsaturated esters, aldehydes and ketones (dimethyl maleate (**2a**), methacrolein (**2b**), methyl-vinyl ketone(**2c**)) (Scheme 1). The reaction was conducted in the phosphonium ionic liquid, $P_{6.6.6.14}NTf_2$, either with or without metal catalysts. The catalysts used included chlorides, trifluoromethanesulfonates (triflates) and bis(trifluoromethylsufonyl)imides (bis-triflimides) of different metals starting from alkali metals (Li), through alkaline earth metals (Mg) and transition metals (Zn) to rare earth metals (Sc, Y, Yb) and others (In). According to our best knowledge no data have been reported in the hitherto published literature on the use of these catalysts with the phosphonium ionic liquids. In the group of phosphonium ILs, only phosphonium tosylates [19] have been investigated as solvents for Diels–Alder reaction of cyclopentadiene or isoprene with various dienophiles, in the absence of metal catalysts.

2 Experimental

2.1 Materials

The ionic liquid $P_{6.6.6.14}NTf_2$ was made by Cytec, Canada. Prior to the use in the Diels–Alder reaction it was dried at 60 °C under a pressure of 5 mbar for 24 h. Dicyclopentadiene of 95% purity and metacroleine (95%) were purchased from Fluka. Dimethyl maleate (96%), methyl-vinyl ketone (99%) and all catalysts tested were provided by Aldrich. The catalysts included: scandium triflate (97%), scandium bis-triflimide (97%), lithium triflate (99.995%), lithium bis-triflimide (99.95%), ytterbium triflate (99.99%), ytterbium bis-triflimide (97%), yttrium triflate (98%), anhydrous yttrium chloride (99.99%), anhydrous ytterbium chloride (99.9%), indium chloride (98%), magnesium triflate (97%), zinc triflate (98%).

2.2 Typical Procedure for the Diels–Alder Reaction

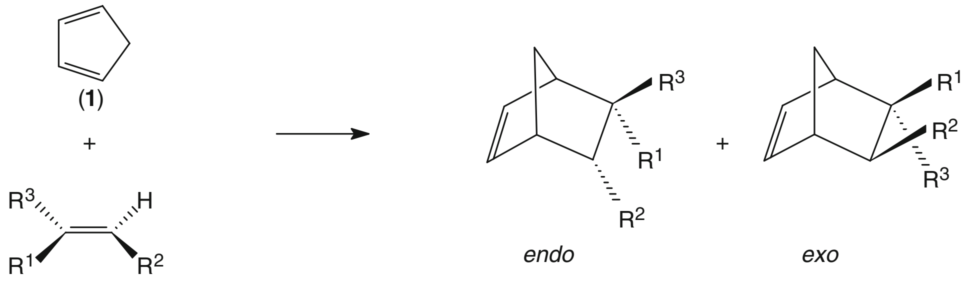
The reaction was conducted in $P_{6.6.6.14}NTf_2$ as follows: 1.0 mL (1.3 mmol) of ionic liquid $P_{6.6.6.14}NTf_2$, cyclohexanone (20 μL) as an internal chromatographic standard, dienophile (4 mmol) and freshly cracked cold cyclopentadiene (6.0 mmol) were added into a 4 mL vial containing a small stirring bar. The reaction was conducted at 25 °C. The progress of the reaction was monitored by GC analysis over the time needed to obtain quantitative yield or over 24 h. The yield of products and endo/exo ratios were calculated based on the GC analysis.

If the reaction was to be performed in the presence of a catalyst, the required portion of the catalyst was weighted first (0.04 mmol) and dissolved in the ionic liquid. All the catalysts used were well soluble in $P_{6.6.6.14}NTf_2$.

2.3 Recycling Experiments

A portion of 0.0432 g (0.08 mmol) of $Y(OTf)_3$ was weighted and introduced into a round-bottomed flask of 5 mL in capacity, equipped with a magnetic stirrer. The catalyst was dissolved in 2 mL of the ionic liquid $P_{6.6.6.14}NTf_2$. About 60μL of cyclohexanone as an internal standard and 1.152 g (8 mmol) of dimethyl maleate were added. Subsequently, cyclopentadiene was introduced in the amount of 0.7920 g (12 mmol). The flask was placed in a thermostated bath heated to 25 °C. The course of the reaction was controlled by the GC analysis. The turnover number (TON) and turnover frequency (TOF) were calculated, based on the GC analysis. Then the reaction flask was connected to distillation apparatus. The product—5-norbornene-2,3-dicarboxylic acid dimethyl ester—was distilled at 98 °C, under a pressure of 3 mbar and the yield of the pure product was found. The purity of the product was assessed based on the GC and NMR analyses.

The residue left in the flask was the ionic liquid and the catalyst and to them, the fresh portions of cyclohexanone,



$R^1 = R^2 = COOCH_3$; $R^3 = H$ dimethyl maleate (**2a**)
$R^1 = CHO$; $R^2 = H$; $R^3 = CH_3$ methacrolein (**2b**)
$R^1 = COCH_3$; $R^2 = R^3 = H$ methyl-vinyl ketone (**2c**)

Scheme. 1 The reaction of cyclopentadiene with dienophiles dimethyl maleate and cyclopentadiene in the amounts as above were added and the reaction was performed as above.

3 Results and Discussion

Diels–Alder cycloadditions (Scheme 1) in the ionic liquid without the catalyst proceeded at 25 °C. The products, as mixtures of endo- and exo-stereoisomers were analyzed by GC.

The yields and selectivities of the reaction in the phosphonium ionic liquid depended on the type of dienophile (Fig. 1). The fastest reaction was between cyclopentadiene and methyl-vinyl ketone (**2c**). The yield of above 90% was obtained within less than 2 h, whereas the selectivity expressed as a ratio of the endo to exo isomer of the product was 83:17. Ludley and Karodia [19], in the same reaction of (**1**) with (**2c**), carried out in the phosphonium tosylates, achieved a slightly lower yield and similar selectivity.

After 24 h of the reaction of (**1**) with the other two dienophiles (dimethyl maleate (**2a**) and methacrolein (**2b**)) the yields were rather moderate in a range of 60–70%.

At the subsequent stage of the study, the activities of the catalysts from the groups of metal chlorides (Y, Yb, In), triflates (Li, Mg, Sc, Y, Yb, Zn) and bis-triflimides (Li, Sc, Yb) were determined in the reaction between cyclopentadiene and each dienophile studied (Table 1). Metal chlorides are the most commonly used Lewis acids, although often they show very poor solubility in organic solvents and corrosion inducing properties. In the hitherto reported studies the following chlorides were used in combination with ionic liquids: $AlCl_3$, $ZnCl_2$, $SnCl_4$ [10, 11]. They showed catalytic activity when the molar ratio of the metal chlorides to the chloride ionic liquids was greater than 0.5. We have chosen to examine three metal chlorides: YCl_3, $YbCl_3$ and $InCl_3$.

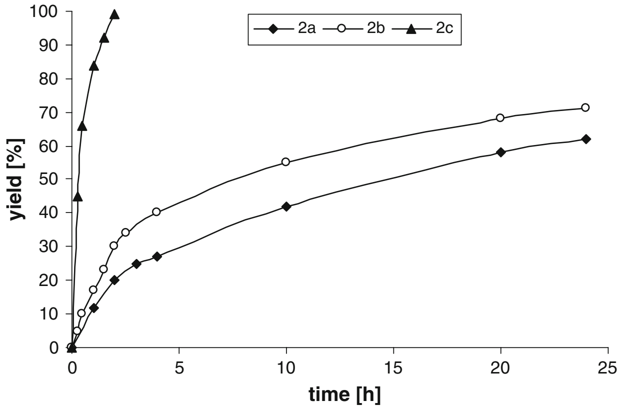


Fig. 1 The product yield versus the time of the cyclopentadiene reaction with dienophiles (**2a–c**), in a phosphonium ionic liquid as a medium. (1 mL of $P_{6.6.6.14}NTf_2$; 4 mmol of dienophile; 6 mmol of cyclopentadiene; reaction temperature 25 °C)

Metal tirflates and bis-triflimides [20] have been recently introduced to organic synthesis as representatives of the Lewis acid type catalysts. Their main advantage over metal chlorides is much better solubility in organic solvents. Activities of some of these catalysts has been determined in the Diels–Alder reaction carried out in imidazolium ionic liquids [9a, b].

The majority of the catalysts used facilitated the reaction of cyclopentadiene with dimethyl maleate (**2a**) and increased the yield of the reaction relative to that obtained in the ionic liquid $P_{6.6.6.14}NTf_2$ without any catalyst (Table 1). Addition of each of the above-mentioned catalysts in a concentration of 1% with respect to that of dienophile also led to an increase in the selectivity of the endo-isomer of the product relative to the selectivity achieved in the ionic liquid $P_{6.6.6.14}NTf_2$ alone. However, the increase in selectivity depended on the type of metal and its salt. Not always the increase in selectivity was accompanied by an increase in the yield. For $Sc(OTf)_3$, $Sc(NTf_2)_3$ and $Zn(OTf)_2$ used as catalysts the selectivity of the reaction increased relative to that without the catalysts, however, the yield increased for the first 2–3 h of the reaction, reaching a value of about over 40% and further increase in the reaction time did not change it. The cessation of the cycloaddition was a consequence of the parallel reaction of cyclopentadiene polymerisation in which cyclopentadiene was consumed.

The most active in the reaction of cyclopentadiene with dimethyl maleate (**2a**) were found to be the salts of yttrium YCl_3 and $Y(OTf)_3$, ytterbium $Yb(OTf)_3$ and $Yb(NTf_2)_3$, and magnesium $Mg(OTf)_2$. These catalysts gave almost quantitative yields of product—5-norbornene-2,3-dicarboxylic acid dimethyl ester, in 2–3 h. The highest stereoselectivities of the endo-isomer (90:10 and higher) were achieved in the presence of YCl_3, $Yb(NTf_2)_3$, $Yb(OTf)_3$, $Y(OTf)_3$ and slightly lower (86:12)—in the presence of $Mg(OTf)_2$. The lithium catalysts LiOTf and $Li(NTf_2)$ proved less active and they had to be used in the concentration of 2 mol% to get the yields of 83% and 88%, respectively, in the time of 4 h. An increase in the lithium salts concentration from 1% to 2% also led to an increase in the selectivity towards the endo isomer of the product.

The most active catalysts in the reaction of cyclopentadiene with methacrolein (**2b**) were $Zn(OTf)_2$, $Y(OTf)_3$, $Yb(OTf)_3$, $Yb(NTf_2)_3$, $Sc(OTf)_3$ and $Sc(NTf_2)_3$. The quantitative yields of the product of cycloaddition were obtained in only 30 min. The next active catalyst was $InCl_3$, in whose presence, a yield of 93% was achieved in 90 min. The presence of $Mg(OTf)_2$ only slightly increased the reaction rate and led to the quantitative yields within 24 h, whereas

Table 1 The yields and stereoselectivities of the Diels–Alder cycloaddition between cyclopentadiene and dienophiles (**2a–c**) in $P_{6.6.6.14}NTf_2$ as the reaction medium and in the presence of various metal catalysts

L.p.	Catalyst	(**1**) + (**2a**)			(**1**) + (**2b**)			(**1**) + (**2c**)		
		Yield (%)		endo:exo ratio	Yield (%)		endo:exo ratio	Yield (%)		endo:exo ratio
		2 h	4 h		30 min	90 min		30 min	60 min	
1	LiOTf	54	66 (83)[a]	86:14 (89:11)[a]	11	20	17:83	79	91	85:15
2	$Li(NTf_2)_3$	58	73 (88)[a]	88:12 (90:10)[a]	19	25	17:83	76	92	85:15
3	$Mg(OTf)_2$	88	**>95**	86:14	32	40	19:81	80	**>95**	87:13
4	$Zn(OTf)_2$	43	49	87:13	**>95**	–	20:80	**>95**	–	**92:8**
5	$Y(OTf)_3$	**>95**	–	90:10	**>95**	–	23:77	**>95**	–	**92:8**
6	YCl_3	**>95**	–	92:8	10	15	23:77	60	77	83:17
7	$Yb(OTf)_3$	**>95**	–	90:10	**>95**	–	22:78	**>95**	–	**92:8**
9	$Yb(NTf_2)_3$	**>95**	–	91:9	**>95**	–	23:77	**>95**	–	**92:8**
10	$YbCl_3$	50	58	84:16	9	20	17:83	66	81	85:15
11	$Sc(OTf)_3$	36	42 (58)[a]	87:13(94:6)[a]	**>95**	–	22:78	**>95**	–	92:8
12	$Sc(NTf_2)_3$	38	42 (64)[a]	89:11 (93:7)[a]	**>95**	–	23:77	**>95**	–	**91:9**
13	$InCl_3$	35	45	76:24	61	**>95**	21:79	**>95**	–	**92:8**
14	without	20	27	72:28	8	27	16:84	62	81	83:17

Reaction conditions: temperature 25 °C; 1 mL of $P_{6.6.6.14}NTf2$; 1%mol of catalyst versus dienophile; molar ratio of cyclopentadiene to dienophile 1.5

[a] The value in parenthesis is the yield obtained with the catalyst amount increased to 2% mol versus dimethyl maleate

YCl_3 and $YbCl_3$ as well as LiOTf and $LiNTf_2$ were practically inactive. Each of the catalysts led to a small increase in the selectivity of the reaction towards the product with the formyl group in the endo position.

When the reaction was carried out between cyclopentadiene and methyl-vinyl ketone (**2c**), for the majority of the applied catalysts—$Zn(OTf)_2$, $Y(OTf)_3$, $Yb(OTf)_3$, $Yb(NTf_2)_3$, $Sc(OTf)_3$, $Sc(NTf_2)_3$, $InCl_3$—almost quantitative yields of the cycloaddition product with a considerable selectivity towards the endo-isomer were achieved in 30 min. Slightly less activity was proved for the Li and Mg catalysts. In their presence the yields of about 90% were obtained within 1 h, but the stereoselectivities were only slightly higher than in the ionic liquid alone. YCl_3 and $YbCl_3$ chlorides were proved to be practically inactive.

In summary, the activity of the catalysts depended first of all on the type of metal and structure of the dienophile. No significant differences were observed in the activities of triflates and bis-triflimides of the same metal, while the results obtained with the metal chlorides differed considerably from those obtained in the presence of triflates or bis-triflimides of these metals. It must be emphasized, that each of the applied catalysts was well soluble in the ionic liquid. Therefore solubility or nonsolubility could not be the reason of the differences in the catalysts activity. The differences in the activities of various salts of the same metal (e.g. Y or Yb chlorides and triflates) in the reactions of cyclopentadiene with the same dienophile can suggest the differences in the solvation and complexation of the catalyst by the ionic liquid. It is known that even poorly coordinating anions such as PF_6^- or NTf_2^- can enter the metal coordination sphere. The structure of the complex formed depends on the type of metal, its salt and the cation and anion of the ionic liquid [21]. The solvation and complexation of the catalyst by the ionic liquid could diminish the availability of metal of the catalyst for dienophile.

The most universal catalysts in the Diels–Alder reaction whose presence led to a significant increase in the reaction rate and selectivity for each dienophile used were found to be $Yb(NTf_2)_3$, $Yb(OTf)_3$, $Y(OTf)_3$. The activity of the other metal salts (Zn, Li, Sc, In and Mg) depended on the dienophile structure. In the reaction of methyl-vinyl ketone (**2c**) and methacrolein (**2b**) with cyclopentadiene the activity of $InCl_3$, $Zn(OTf)_2$ and Sc catalysts was found much higher, while that of YCl_3 and $YbCl_3$ practically was negligible, in comparison to their activities in the reaction of dimethyl maleate (**2a**) with the same diene.

An important technological aspect of the use of ionic liquids in the catalysed reactions is the possibility of recycling of the ionic liquid and the catalyst. The relevant studies were performed for the test reaction of cyclopentadiene with dimethyl maleate carried out in $P_{6.6.6.14}NTf_2$ in the presence of $Y(OTf)_3$. When the reaction was completed the product was separated from the ionic liquid by distillation under a reduced pressure. The phosphonium ionic liquid $P_{6.6.6.14}NTf_2$ was stable under distillation and the catalyst was dissolved in the liquid. Six

Table 2 Reaction of cyclopentadiene (**1**) with dimethyl maleate (**2a**) in $P_{6.6.6.14}NTf_2$ in the presence of $Y(OTf)_3$; recycling experiments

Turn	TOF[a] (mol h^{-1} mol^{-1})	TON[b] (mol mol^{-1})	Yield[c] (%)	endo:exo ratio
0	96	96	81	90:10
1	97	97	88	89:11
2	97	97	86	91:9
3	95	95	87	90:10
4	96	96	84	91:9
5	95	95	81	90:10
6	44	96	74	91:9
		Σ TON = 672		

Molar ratio of (**2a**)/$Y(OTf)_3$ = 100; molar ratio of (**1**)/(**2a**) = 1.5; reaction time 1 h; temperature 25 °C

[a] Turnover frequency (TOF) in mol of (**2a**) converted per mol of $Y(OTf)_3$ per hour. [b] Turnover number (TON) in mol of (**2a**) converted per mol of $Y(OTf)_3$ over the complete reaction time. [c] yield of the pure product

testing cycles were performed and the results are presented in Table 2.

Although the catalysts used are expensive, their use in the ionic liquid $P_{6.6.6.14}NTf_2$ increases the total efficiency of the catalysts and its lifetime.

4 Conclusions

The above-discussed results have shown that in the phosphonium ionic liquid $P_{6.6.6.14}NTf_2$ and in the presence of catalysts, the Diels–Alder reaction between cyclopentadiene and dienophiles in the form of α,β-unsaturated esters, aldehydes and ketones at room temperature occurs smoothly, with high yield and high stereoselectivity. There is no need to heat or cool the reaction mixture. The time of the reaction needed to get quantitative yields of the product is relatively short and varies from 30 to 120 min. The catalysts from the group of metal chlorides, triflates and bis-triflimides are well soluble in the phosphonium ionic liquid used. The universal catalysts in the Diels–Alder reaction, leading to a significant increase in the rate and stereoselectivity of the reaction for each dienophile used proved to be $Yb(NTf_2)_3$, $Yb(OTf)_3$, $Y(OTf)_3$. It was proved that, the activity of the other catalysts depended on the structure of the dienophile used. Bis-triflimides and triflates of the same metal gave similar yields and stereoselectivities of the reaction. Among the metal chlorides studied, $InCl_3$ was the most active in the reaction of cyclopentadiene with methacrolein and methyl-vinyl ketone, while YCl_3 was the most active in the reaction with dimethyl maleate as a substrate.

Thanks to the high thermal stability of the phosphonium ionic liquid, the product can be isolated by distillation from the ionic liquid and the catalyst, so that there is no use to deal with the ballast organic solvents used in the extraction methods. The catalyst dissolved in the phosphonium ionic liquid can be many times recycled with no loss in activity.

Acknowledgments The research was supported by Polish grant No. N205 055 31/2491.

References

1. Berlin PA, Watson KJ, Nguyen ST (2004) Macromolecules 37:8364–8372
2. (a)Owen RM, Gestwicki JE, Young T, Kiessling LL (2002) Org Lett 4:142293–142296; (b) Gestwicki JE, Strong LE, Cairo CW, Boehm FJ, Kiessling LL (2002) Chem Biol 2:163–169; (c)Maynard HD, Okada SY, Grubbs RH (2001) J Am Chem Soc 123:1275–1279
3. (a) Buchmeiser MR (2000) Chem Rev 100:1565–1604 and references therein; (b) Meyers A, South C, Weck M (2004) Chem Commun 1176; (c) Meyers A, Weck M (2004) Chem Mater 16:1183; (d) Meyers A, Weck M (2003) Macromolecules 36:1766
4. (a) Arehart SV, Pugh C (1997) J Am Chem Soc 119:3027; (b) Weck M, Mohr B, Maughon BR, Grubbs RH (1997) Macromolecules 30:6430; (c) Wewerka K, Wewerka A, Stelzer F, Gallot B, Andruzzi L, Galli G (2003) Macromol Rapid Commun 24:906
5. Raimundo J-M, Lecomte S, Edelman MJ, Consilio S, Biaggio I, Bosshard C, Guenter P, Diederich F (2004) J Mater Chem 14:292
6. (a) Rideout DC, Breslow R (1980) J Am Chem Soc 102:7816; (b) Grieco PA, Yoshida K, Garner P (1983) J Org Chem 48:3137; (c) Breslow R, Maitra U (1984) Tetrahedron Lett 25:1239; (d) Pindur U, Luft G, Otto C (1993) Chem Rev 93:741–761; (e) Kumar A (2001) Chem Rev 101:1
7. (a) Holbrey JD, Seddon KR (1999) Clean Prod Process 1:223–236; (b) Clark JH, Tavener SJ (2007) Org Process Res Dev 11:149–155
8. (a) Welton T (1999) Chem Rev 99:2071–2083; (b) Welton T (2004) Coordin Chem Rev 248:2459–2477
9. (a) Lopez I, Silvero G, Arevalo MJ, Babiano R, Palacios JC, Bravo JL (2007) Tetrahedron 63:2901–2906; (b) Silvero G,

Arevalo MJ, Bravo JL, Avalos M, Jimenez JL, Lopez I (2005) Tetrahedron 61:7105–7111; (c) Fu F, Teo Y-Ch, Loh T-P (2006) Org Lett 8:5999–6001; (d) Yadav JS, Reddy BVS, Kondaji G, Sowjanya S, Nagaiah K (2006) J Mol Catal A: Chem 258:361–366; (e) Dramska A, Antoszczyszyn M, Janus E (2006) Przem Chem 85/1:47–49; (f) Earle MJ, McCormac PB, Seddon KR (1999) Green Chem 1:23–25

10. Lee CW (1999) Tetrahedron Lett 40:2461–2464
11. Abbott AP, Capper G, Davies DL, Rasheed RK, Tambyrajah V (2002) Green Chem 4:24–26
12. Aggarwal A, Lancaster NL, Sethi AR, Welton T (2002) Green Chem 4:517–520
13. Janus E, Goc-Maciejewska I, Łożyński M, Pernak J (2006) Tetrahedron Lett 47:4079–4083
14. (a) McNulty J, Cheekoori S, Nair JJ, Larichev V, Capretta A, Robertson Al J (2005) Tetrahedron Lett 46:3641–3644; (b) Cieniecka-Rosłonkiewicz A, Pernak J, Kubis-Feder J, Ramani A, Robertson AJ, Seddon K (2005) Green Chem 7:855–862; (c) McNulty J, Nair JJ, Cheekoori S, Larichev V, Capretta A, Robertson Al J (2006) Chem Eur J 12:9314–9322; (d) Bonnet LG, Kariuki BM (2006) Eur J Inorg Chem 437–446; (e) McNulty J, Cheekoori S, Bender TP, Coggan JA (2007) Eur J Org Chem 1423–1428; (f) Fergusson L, Scovazzo P (2007) Ind Eng Chem Res 46:1369–1374
15. (a) Bradaric CJ, Downard A, Kennedy C, Robertson AJ, Zhou Y (2003) Green Chem 5:143–152; (b) Tsunashima K, Sugiya M (2007) Electrochem Commun 9:2353–2358; (c) Chowdhury S, Mohan RS, Scott JL (2007) Tetrahedron 63:2363–2389
16. (a) Hagiwara R, Ito Y (2000) Fluorine Chem 105:221; (b) Matsumoto H, Yanagida M, Tanimoto K, Nomura M, Kitagawa Y, Miyazaki Y (2000) Chem Lett 29:922
17. Swatloski RP, Holbrey JD, Rogers RD (2003) Green Chem 5:361–363
18. Ferguson L, Scovazzo P (2007) Ind Eng Chem Res 46:1369–1374
19. (a) Ludley P, Karodia N (2001) Tetrahedron Lett 42:2011–2014; (b) Ludley P, Karodia N (2002) ARKIVOC (iii) 172–175
20. (a) Kobayashi S, Morikawa M, Ishitani H (1995) Synlett 1153–1154; (b) Kobayashi S, Sugiura M, Kitagawa H, Lam WW-L (2002) Chem Rev 102:2227–2302; (c) Kobayashi H, Nie J, Sonoda T (1995) Chem Lett 24:307
21. Binnemans K (2007) Chem Rev 107:2592–2614 and references therein