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Chiral ionic liquids, a renewal for the chemistry of chiral solvents? Design, synthesis and applications for chiral recognition and asymmetric synthesis

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Abstract—Chiral ionic solvents were almost unexplored before the last five years. This field which is of increasing importance could constitute a renewal for the chemistry of chiral solvents. So far reported examples are designed either from the chiral pool (amino-acids, hydroxyacids, amines, aminoalcohols, terpenes and alkaloids) or by asymmetric synthesis; they can bear central, axial or planar chirality. Modern applications in asymmetric synthesis, enzymatic chemistry, chiral chromatography and NMR are surveyed. Their use in the field of liquid crystals and for stereoselective polymerisation are also discussed. At the end of the article, a series of tables is compiled including all the CILs described to date and their physical properties.

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1. Introduction

Asymmetric induction is mainly achieved by the use of chiral substrates or reagents, chiral catalysts or enzymes. Chiral solvents were also evaluated[1] even if they have been mainly used for NMR determination of the enantiomeric excess of enantioenriched compounds.[2,3] The first use of a chiral solvent in asymmetric synthesis was reported in 1975 by Seebach.[4] Using a chiral aminoether as solvent, modest enantioselectivities were obtained in the electrochemical reduction of ketones. A few reports then appeared in the literature[5] but the difficult syntheses of chiral solvents and their high cost often precluded their use. Recently, few examples of chiral ionic liquids (CILs) have been mentioned in the literature and partial information can be found in some reviews.[6] Due to their ease of synthesis and due to their particular properties, these new chiral solvents should play a central role in enantioselective organic chemistry and hopefully expand the scope of chiral solvents. A significant transfer of chirality in these solvents can be expected due to their high degree of organisation. It has been reported that most of the ILs possess a polymeric behaviour and are highly ordered H-bonded liquids (three-dimensional networks of anions and cations linked together by hydrogen bonds).[7] These specific properties suggest that CILs could outperform the classical chiral solvents for asymmetric induction.

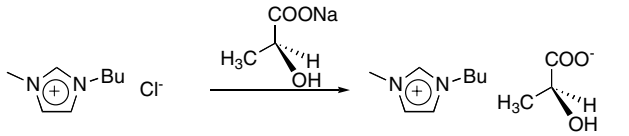
Even though chiral ionic liquids are at a preliminary stage of development, the results obtained in these new media are often promising if not exciting and cover fields as different as asymmetric synthesis (e.g., organic and organometallic catalysis as well as biocatalysis), stereoselective polymerisation, gas chromatography, NMR shift reagents and liquid crystals. The aim of this review is to highlight the recent breakthrough of CILs in chirality transfer or chiral recognition when used as solvent or co-solvent: the case of task specific ionic liquids is beyond the scope of this review. In the first part, the synthesis of CILs will be presented while the second part will be devoted to their use in the field of chirality.

2. Synthesis of chiral ionic liquids (CILs)

The more efficient, economic and simple way to prepare enantiomerically pure ILs is to use precursors derived from the chiral pool either for the generation of the CILs anion or cation or for both. Therefore chiral ionic liquids are mainly compounds having a central chirality. However, some new CILs having an axial or a planar chirality have also been developed.

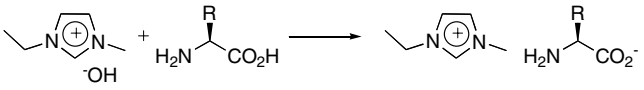
2.1. CILs having a chiral anion

The first example dealing with the preparation of such a chiral ionic liquid was reported by Seddon in 1999. The chirality was brought by the lactate anion.[8] The [bmim][lactate] ionic liquid was simply prepared by anion exchange between [bmim][Cl] and commercially available sodium (*S*)-2-hydroxypropionate in acetone. The CIL was obtained after removal of NaCl by filtration and evaporation of acetone (Eq. 1).



(1)

Recently, Ohno et al. prepared a library of 19 chiral ionic liquids, starting from 1-ethyl-3-methylimidazolium hydroxide and 19 natural aminoacids.[9] The use of an imidazolium hydroxide allowed the direct synthesis of various ionic liquids by neutralisation of the carboxylic acid function, without the need of a metal salt (Eq. 2).



(2)

All 19 compounds are viscous liquids at room temperature, showing a glass transition temperature ranging from −57 °C for [emim][ala] to 6 °C for [emim][glu], and thermal stability over 200 °C, except for [emim][cys] (173 °C). The variety of side chains allowed the authors to draw some correlation between the nature of the aminoacid and the glass transition temperature (Table 1). Increase of the length of the alkyl side chain leads to a small increase of the T_g (entry 1–3): an aromatic side chain induces a larger increase of T_g, presumably due to π-stacking interactions (entry 4). Introduction of very polar units such as carboxyl or amide functional groups induces dramatic increase of the T_g (entries 5–8): carboxyl-containing ILs [emim][glu] and [emim][asp] were also found to be insoluble in chloroform. Despite its relatively long side chain and terminal amino group, [emim][lys] shows a rather low T_g (entry 9).

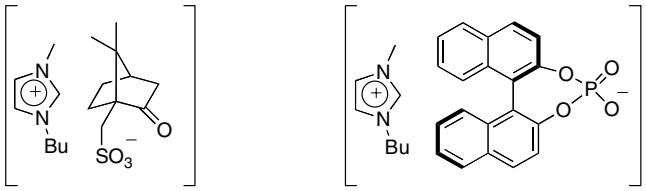
Table 1. Glass transition temperature of imidazolium carboxylates derived from aminoacids

Entry	IL	T_g (°C)
1	[emim][ala]	−57
2	[emim][val]	−52
3	[emim][leu]	−51
4	[emim][phe]	−36
5	[emim][asn]	−16
6	[emim][gln]	−12
7	[emim][asp]	5
8	[emim][glu]	6
9	[emim][lys]	−47

Some interesting trends were also found in the correlation between ionic conductivity and glass transition temperature: whereas most of these salts show a correlation between T_g and σ_i similar to 'usual' imidazolium salts, ILs whose anion moiety comprises a very polar unit present unusual low ionic conductivity, attributed to hydrogen bonding or some other ion interaction through their side chains.

(*S*)-10-Camphorsulfonate and (*R*)-1,1′-binaphthylphosphate were also selected as chiral anions for the design

of new imidazolium based CILs.[10] The salts were prepared on multi-gram scale by simple anion exchange of the commercially available [bmim][Cl] in a CH_2Cl_2/H_2O medium. The camphor derivative proved to be a viscous oil at room temperature while the binaphthyl derivative is a white solid with a melting point of 80 °C. Both salts are highly hygroscopic.



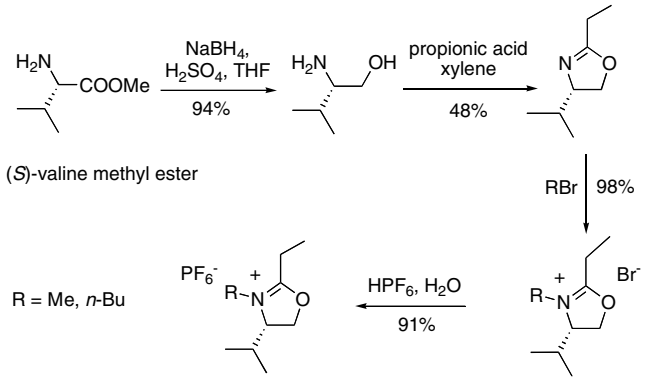
2.2. CILs having a chiral cation

2.2.1. With central chirality from the chiral pool. Most examples of chiral CILs are related to the use of chiral cations, which are designed from various precursors such as aminoacids and aminoalcohols, hydroxyacids, amines and alkaloids or halogenoalkanes.

2.2.1.1. CILs from aminoacids and aminoalcohols. Different chiral ionic liquids were prepared starting from this kind of precursors derived from the chiral pool. Their diversity arises from the nature of the cation: classical cations such as imidazolium and ammonium or more original ones such as oxazolinium or thiazolinium.

- CILs having an oxazolinium cation

These original CILs having an oxazolinium cation derived from aminoacids were reported by Wasserscheid in 2001.[11] The oxazolinium cations were prepared in four steps and 40% overall yield starting from (*S*)-valine (Scheme 1). Reduction of the (*S*)-valine methyl ester following Masamune's protocol using $NaBH_4$–H_2SO_4 in THF afforded the corresponding aminoalcohols. Cyclisation into oxazoline was performed using propionic acid in a classical way. Alkylation of the oxazoline using bromopentane or bromomethane gave the corresponding salts, which after anion metathesis with aqueous HPF_6 afforded the expected CILs. Their melting points

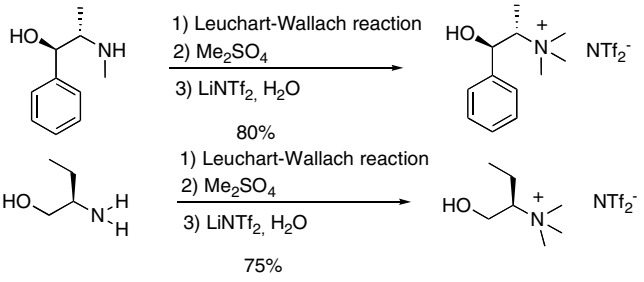


Scheme 1. Oxazolinium ILs from (*S*)-valine.

are comprised between 63 and 79 °C. Despite the fact that the reaction could be performed on a multi-gram scale, the modest overall yield and the low stability of the oxazolinium cation under acidic conditions precluded their use as chiral solvents.

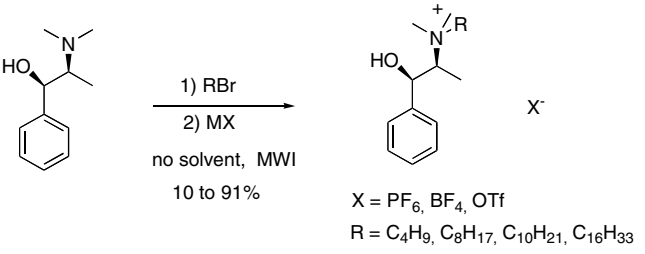
- CILs having an ammonium cation

The same group also prepared, on a kilogram scale, two chiral hydroxyammonium salts starting from (*R*)-2-aminobutan-1-ol and (−)-ephedrine (Scheme 2).[11] These aminoalcohols were converted in three steps (Leuchart–Wallach reaction, alkylation using Me_2SO_4 and anion exchange using $LiNTf_2$ in aqueous solution) into the corresponding CILs with overall yields ranging between 75% and 80%. The ephedrinium salt has a melting point of 54 °C and is insoluble in water. The salt obtained from (*R*)-2-aminobutanol displays a surprisingly low viscosity ($\eta = 0.155$ Pa at 20 °C) and is liquid down to −18 °C. Both salts display a good thermal stability up to 150 °C under vacuum.



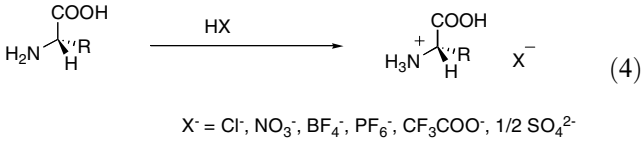
Scheme 2. Ammonium ILs from (−)-ephedrine and (*R*)-2-aminobutan-1-ol.

Other ephedrinium salts having variable alkyl chain lengths on the nitrogen group were prepared in two steps by Vo-Thanh et al.[12] The synthesis was performed using (1*R*,2*S*)-*N*-methylephedrine, previously prepared by reductive amination of ephedrine using an Eschweiler–Clarck procedure. The salt was then alkylated using alkyl halides with different chain lengths and the expected CILs were obtained after anion metathesis. The alkylation step as well as the metathesis was performed in a two-step but one pot procedure under solvent free conditions using a microwave activation (Eq. 3). In most cases, good to excellent yields in ephedrinium salts were obtained in short time using this procedure. All new salts are viscous liquids at room temperature except for $R = C_{16}H_{33}$ and C_4H_9 with $X = PF_6$, which melt, respectively, at 95 and 92 °C.



(3)

Two new families of CILs were simply prepared by a one-step acidification of naturally occurring α-aminoacids and α-aminoacid ester salts.[13] The reactions were performed in water using an equimolar ratio of a strong acid (Eq. 4). This atom-economic reaction allowed a clean preparation of CILs by simple evaporation of the water under vacuum. Due to strong hydrogen bonds involving the carboxylic acid function, most of the salts derived from the α-aminoacid derivatives have high melting points while esters derived salts are viscous oil at room temperature.

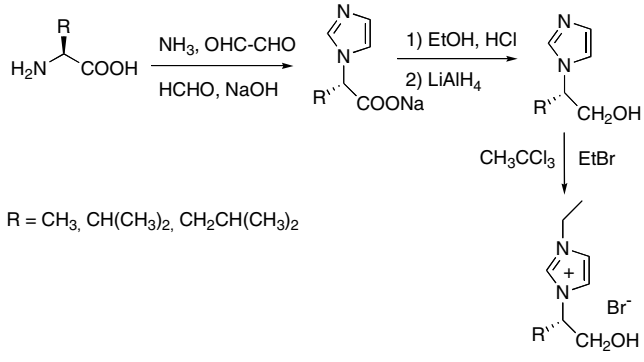


(4)

$X^- = Cl^-, NO_3^-, BF_4^-, PF_6^-, CF_3COO^-, 1/2\ SO_4^{2-}$

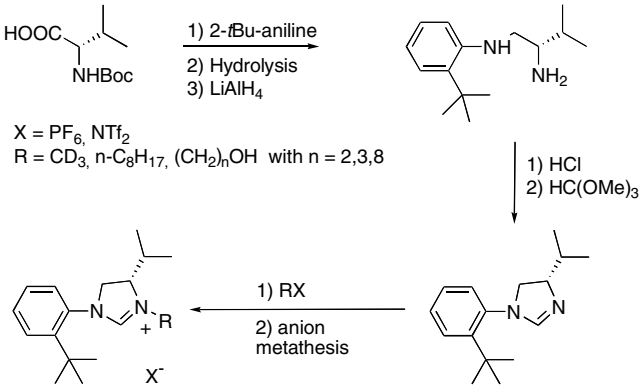
- CILs having an imidazolium or imidazolinium cation

Bao et al. reported the synthesis in four steps of the first chiral imidazolium ILs derived from natural aminoacids [(*S*)-alanine, (*S*)-leucine and (*S*)-valine].[14] The imidazolium ring was formed by condensation of the aminoacid with an aldehyde under basic conditions. Thus by reacting aminoacid, formaldehyde, glyoxal and aqueous ammonia under basic conditions (controlled pH using a NaOH solution), followed by esterification of the acid function, the expected imidazoylalkanoic ester was obtained. Reduction of the ester function using $LiAlH_4$ followed by alkylation using bromoethane in CH_3CCl_3 gave the expected chiral ionic liquid (Scheme 3). The new CILs were obtained after purification by column chromatography with an overall yield ranging between 30% and 33%. They are miscible with water and polar solvent (MeOH, acetone) and immiscible with weakly polar solvent (diethylether, trichloroethane, etc.). They show a good thermal stability (up to 180 °C) and their melting points range from 5 to 16 °C.



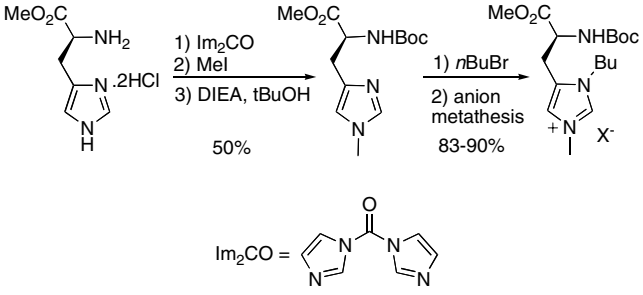
Scheme 3. Imidazolium ILs from aminoacids.

Chiral imidazolinium salts were prepared in five steps by Guillemin et al. starting from *N*-Boc-(*S*)-valine.[15] Reaction of the protected aminoacid with *t*-butylaniline followed by Boc-deprotection under acidic conditions and reduction of the amide function into amine yielded the corresponding diamine. After formation of the diamine chlorohydrate using HCl and condensation with triethylorthoformate, the imidazoline was recovered. The expected imidazolinium salts were obtained after classical alkylation with various alkyl halides and anion exchange ($LiNTf_2$, HPF_6). They were purified by silica gel chromatography (Scheme 4).



Scheme 4. Imidazolinium ILs from (*S*)-valine.

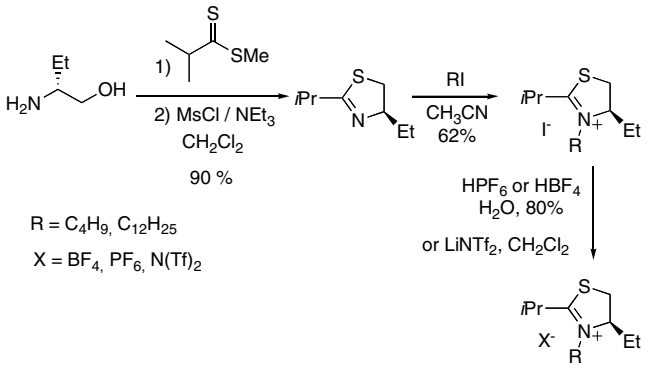
By taking advantage of the pre-existing imidazole ring in histidine, our group recently designed a new family of ionic liquids that retain the amino and carboxyl functions of the original natural aminoacid in a protected form, thus allowing further functional modifications (Scheme 5).[16b] Simultaneous protection of two nitrogen atoms via a cyclic urea, followed by alkylation and subsequent opening of the urea by *t*-butanol afforded the fully protected *N*-(1)-alkylated histidine derivative, which was then selectively alkylated at the *N*-(3) position. Anion metathesis afforded the corresponding NTf_2 or PF_6 salt as a low melting solid and a liquid, respectively.



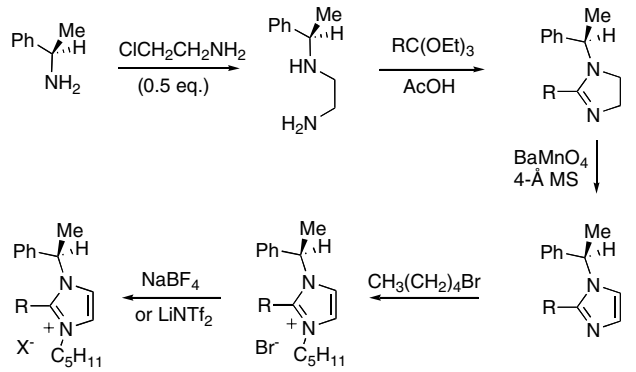
Scheme 5. Imidazolium ILs from histidine.

- CILs having a thiazolinium cation

In 2003, our group proposed a novel class of chiral ionic liquids based on thiazolinium salts.[16] These new chiral ILs were prepared in four steps starting from an aminoalcohol [(*R*)-2 aminobutan-1-ol or (L)-phenylalaninol] with fairly good overall yield (60–68% yield). The key precursors (the thiazolines) were synthesised by reacting a dithioester and the aminoalcohol followed by cyclisa-



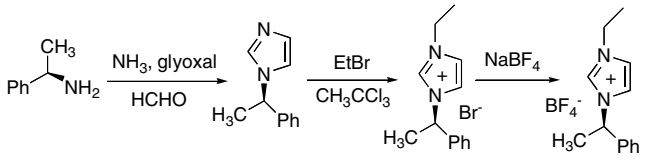
Scheme 6. Thiazolinium ILs from aminoalcohols.



Scheme 8. 2-Alkylimidazolium ILs from 1-phenylethylamine.

tion of the intermediate thioamide in the presence of mesyl chloride and Et_3N.[17] The CILs were obtained after alkylation of the chiral thiazoline with an alkylhalide followed by anion exchange using $LiNTf_2$, HPF_6 or HBF_4 (Scheme 6). Melting points of the new CILs depend on the length of the *N*-alkyl chain and on the nature of the counter anion (from 137 °C to temperatures below 0 °C). The thiazolinium based ILs show a good thermal stability. Moreover, they are stable under basic and even under acidic conditions unlike their oxygen counterparts, the oxazolinium salts.[11]

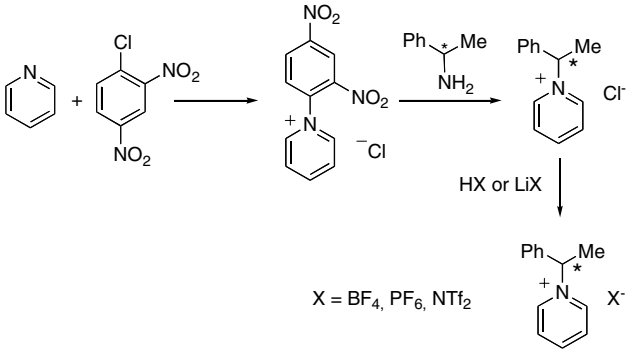
2.2.1.2. From amines and alkaloids. A chiral amine, 1-phenylethylamine, was used as a precursor for the synthesis of a chiral IL having an imidazolium cation.[14] The imidazole ring was formed by reacting formaldehyde, ammonia, glyoxal and the chiral amine under basic conditions. After alkylation and anion exchange, the chiral imidazolium salt was obtained with a low overall yield (30%) (Scheme 7). Its high melting point (90 °C) precluded its use as chiral solvent.



Scheme 7. Imidazolium IL from 1-phenylethylamine.

The 1-phenylethylamine was also used for the synthesis of various other imidazolium derivatives.[18] The imidazole moiety was prepared in three steps: monoalkylation of the amine using 2-chloroethylamine, ring closure of the diamine using an *ortho* ester leading to the corresponding 4,5-dihydroimidazoles and manganese oxidative dehydrogenation of the partially saturated heterocycle leading to various C-2 substituted or unsubstituted imidazole rings. If the yield is excellent for the cyclisation (81–93%), the alkylation and the oxidative dehydrogenation give moderate yields (45% and 58%, respectively). The corresponding CILs were obtained after quaternisation and anion metathesis. BF_4 and NTf_2 salts are liquid below rt and exhibit glass transition temperature at −39 °C and −48 °C, respectively, even if the C-2 position is substituted (Scheme 8). Two salts, having a dihydroimidazolium cation, were also prepared by the same process. These salts show a lower glass transition temperature and a lower viscosity than their imidazolium analogues due probably to disruption of the aromaticity in the heterocycle.

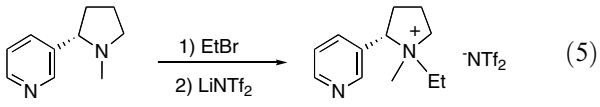
Subsequently, the (*R*)-(+)- or (*S*)-(−)-1-phenylethylamine was used for the preparation of both enantiomeric series of chiral ILs having a pyridinium cation. The chiral pyridinium salts were obtained using the Marazano's route by reacting the Zincke's salt readily obtained from pyridine and 1-chloro-2,4-dinitrobenzene with one or the other enantiomer of the chiral primary amine (Scheme 9).[19] The absence of epimerisation during the process was checked by ^1H NMR in the presence of enantiopure europium salts and confirmed by specific rotation. The new chiral salts are miscible with methanol, dichloromethane and acetone and immiscible with hexane and 1,1,1-trichloroethane. PF_6 and NTf_2 salts are as usual immiscible with water. The melting point depends on the nature of the counter anion (from 125 to −30 °C) going down from chlorine to hexafluorophosphate, tetrafluoroborate and NTf_2. Only the NTf_2 salt is liquid at room temperature. All these new pyridinium salts show good thermal stability.



Scheme 9. Pyridinium ILs from 1-phenylethylamine.

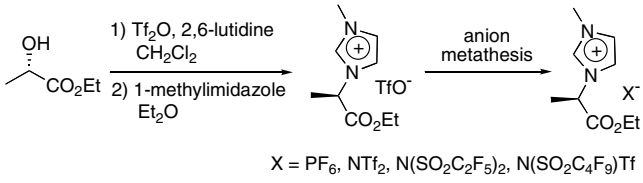
Another amine derived from the chiral pool, (*S*)-nicotine, was used by Kitazume[20] for the synthesis of an ionic liquid. (−)-*N*-Ethylnicotinium-bis(trifluoromethanesulfonyl)amide was prepared by alkylation of nicotine with an ethyl bromide followed by anion

metathesis with $(CF_3SO_2)_2NLi$ (Eq. 5). This optically active ionic liquid was patented in 2001.



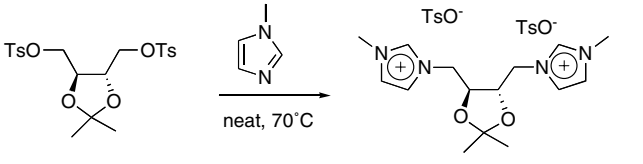
(5)

2.2.1.3. From hydroxyacids. Inexpensive (*S*)-ethyl lactate was also selected as a precursor for the design of a new family of CILs.[21] After transformation into its triflate derivative using triflic anhydride and 2,6-lutidine, the lactate was reacted with 1-methylimidazole in diethylether at −78 °C affording the corresponding salt in excellent yield (92%). The melting point of the salt being rather high (73 °C), anion metathesis using HPF_6, $LiNTf_2$, $LiN(SO_2C_4F_9)Tf$ and $LiN(SO_2C_2F_5)_2$ was performed with good yields (73–94%) (Scheme 10). The advantage of this methodology relies on the fact that no trace of halide, often incompatible with catalytic processes, is present in these CILs. All the new salts are liquid at room temperature showing glass transitions between −50 and −58 °C. Unfortunately, due to the high acidity of the proton adjacent to the carbethoxy group, racemisation of the CILs were observed in the presence of a weak base.



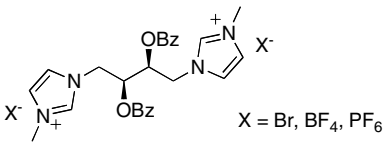
Scheme 10. Imidazolium ILs from (*S*)-ethyl lactate.

The tartrate backbone was used for the design of a dicationic chiral imidazolium salt.[10] Upon reacting the corresponding ditosyl intermediate with methylimidazole at 70 °C for 20 h, the bis-imidazolium salt was obtained in 61% yield after washing off with ether (Eq. 6). The salt has a melting point around 60 °C.

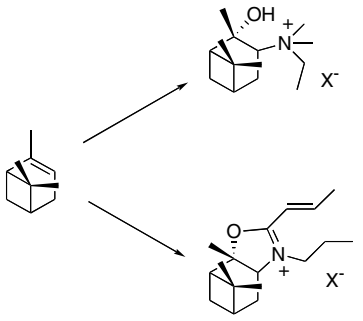


(6)

The tartrate backbone was also used for the synthesis of mono- and bis-imidazolium hexafluorophosphate and tetrafluoroborate salts.[22]

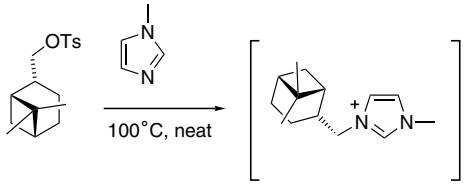


2.2.1.4. From terpenes. Malhotra et al. have designed a series of chiral ionic liquids based on a α-pinene chiral cation and several anions (Scheme 11).[23]



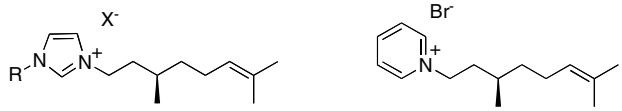
Scheme 11. ILs from α-pinene.

Commercially available (1*S*,2*S*,5*S*)-myrtanol, also accessible starting from α-pinene, was used as a precursor for the synthesis of a new CIL.[10,23] The corresponding tosylate was reacted with neat methylimidazole at 100 °C during 24 h (Eq. 7). The imidazolium tosylate salt was obtained in reasonable yield (60–80%) after washing with CH_2Cl_2/H_2O mixture.



(7)

Imidazolium and pyridinium salts with a chiral side chain derived from (3*R*)-citronellol were prepared from the corresponding citronellyl bromide and alkylimidazole or pyridine.[24] Dialkylation of the starting 1-*H*-imidazole yielded the *C*-2 symmetric derivative. Some examples of the obtained structures were shown to exhibit liquid crystal properties (see Section 3.5).

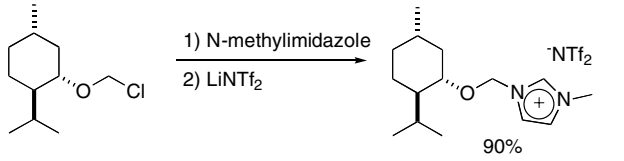


R = Me, Bu, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{18}H_{37}$, (3*R*)-citronellyl

46-94 %

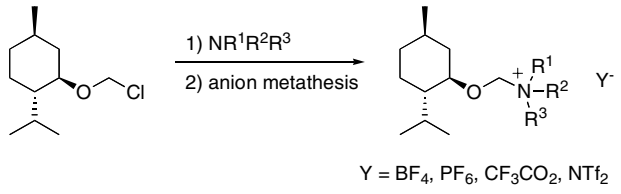
98%

Armstrong et al. described the synthesis of both enantiomers of a chiral imidazolium salt bearing a menthyloxy side chain by alkylation of methylimidazole with the commercially available (+)- or (−)-chloromethylmenthylether, respectively, followed by anion metathesis with $LiNTf_2$ (Eq. 8).[25] The new ILs are obtained in excellent yields (90%) without further purification.



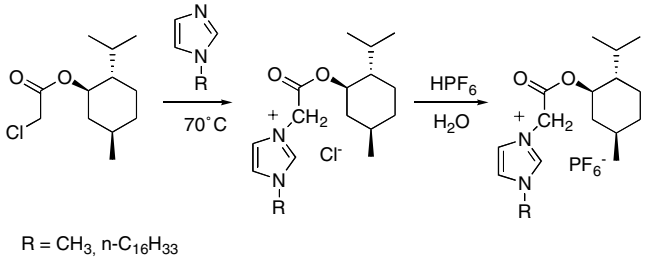
(8)

The same (−)-chloromethylmenthylether was also used for the synthesis of ammonium salts via a Menschutkin reaction with various tertiary amines (Eq. 9).[26] Whereas most chlorides exhibit a rather high melting point (except trimethyl derivative, mp = 31–33 °C), all *N*-bis(triflimide) derivatives obtained after anion metathesis are viscous liquids, showing a glass transition below −30 °C.



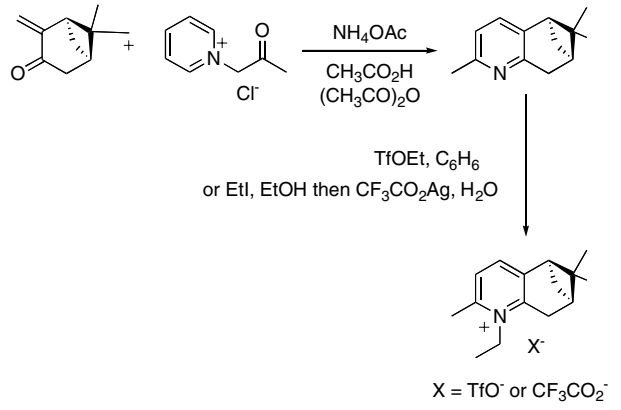
(9)

Two other chiral ILs derived from L-(−)-menthol[27] were prepared in three steps: alkylation of alkylimidazole (R = CH_3, *n*-$C_{16}H_{33}$) with menthylchloroacetate previously formed by esterification of chloroacetylchloride with L-(−)-menthol, and anion exchange using HPF_6 in water (Scheme 12).



Scheme 12. Imidazolium ILs from (−)-menthoxyacetyl chloride.

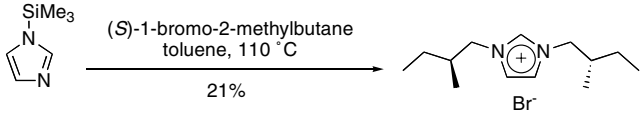
Pinene-fused pyridinium salts[28] were prepared from (+)-pinocarvone by Kröhnke condensation followed by alkylation (Scheme 13). The obtained pyridinium salts



Scheme 13. Pinene-fused pyridinium ILs from (+)-pinocarvone.

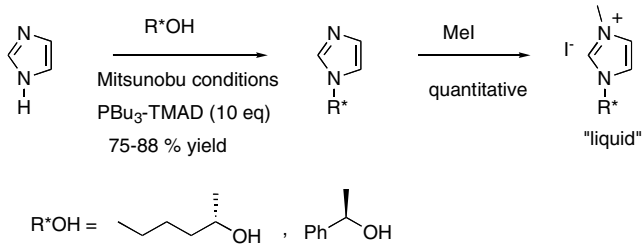
are highly viscous liquids with a glass transition below 0 °C and thermal stability up to 200 °C for the triflate salt and 160 °C for the trifluoroacetate. Both ionic liquids were tested as solvent in a Suzuki cross-coupling reaction and a nickel-catalysed Michael reaction: although good yield of the desired products were obtained, no enantioselectivity was observed.

2.2.1.5. From chiral bromoalkanes and alcohols. By extension of the 'chiral pool' definition (the chiral pool is a term used to include carbohydrates, aminoacids, lipids, terpenes and alkaloids obtained from plant and animal sources, and also synthetic enantiomers that are produced on a large scale), one can say that chiral alkylhalides and chiral alcohols are compounds derived from the chiral pool. As early as 1997, Howarth et al. prepared a moisture stable dialkylimidazolium salt having a chiral alkyl chain arm on each nitrogen.[29] The homochiral 3-bis-((*S*)-2-methyl-butyl)-1*H*-imidazolium bromide was synthesised according to Welton procedure[30] by bis-alkylation of trimethylsilylimidazole with the chiral (*S*)-1-bromo-2-methylbutane (Eq. 10). The yield was quite poor (21%) but the synthesis was straightforward. This chiral IL was not used as a solvent but as a chiral Lewis acid in an enantioselective Diels–Alder reaction.

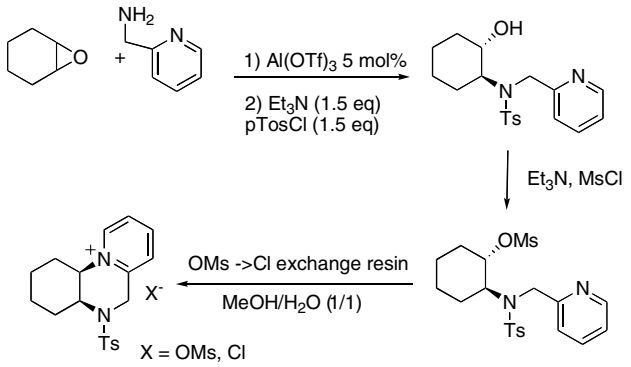


(10)

Two unsymmetrical chiral imidazolium salts were also prepared using in the key step, a Mitsunobu alkylation of the cheap imidazole by a mild electrophile, that is, a chiral alcohol, thus avoiding the bis-alkylation problems and allowing a wide diversity in terms of chirality.[31] The best results (75–88% yields) were obtained using a recent variant of the Mitsunobu reaction using PBu_3–TMAD (*N*,*N*,*N*′,*N*′-tetramethylazodicarboxamide) in large excess (10 equiv of each). The inversion of the stereogenic centre was confirmed by comparison with authentic samples independently prepared using the corresponding chiral amines. However, if the reaction was fully stereoselective with (*S*)-2-hexanol, a lower stereoselectivity (86% ee) was observed when using (*R*)-α-methylbenzylalcohol. The *N*-substituted imidazoles were then



Scheme 14. Imidazolium ILs from chiral alcohols.



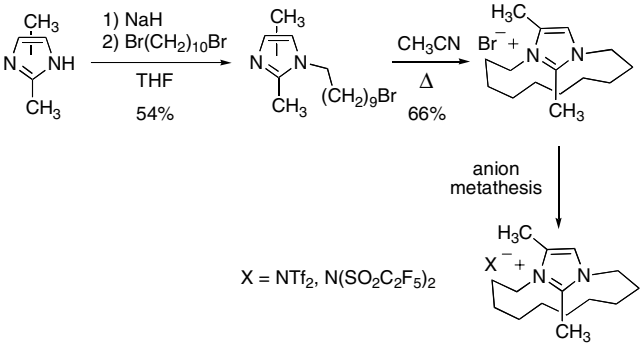
Scheme 15. Pyridinium ILs from an epoxide.

converted to the corresponding imidazolium salts by alkylation with methyliodide (Scheme 14). The two new salts are liquid at room temperature.

Two CILs having a pyridopyrazinium cation were prepared via oxirane ring opening by a bihaptic nucleophile followed by subsequent cyclisation of the resulting product (Scheme 15).[32] The reactions were performed using cyclohexene–oxide and picolylamine. The ring opening occurred at 70 °C in the presence of $Al(OTf)_3$. After tosylation of the amino group, mesylation of the alcohol function at 0 °C in dichloromethane afforded the β-aminomesylate in 70% yield. The cyclisation was extremely slow starting from the mesylate derivative, however after OMs→Cl exchange using a resin, the cyclisation occurred cleanly at 40 °C in a $MeOH/H_2O$ solution affording in 80% yield the corresponding ionic liquids. NOESY and ^{13}C–^{1}H correlations confirmed the expected *cis* stereochemistry.

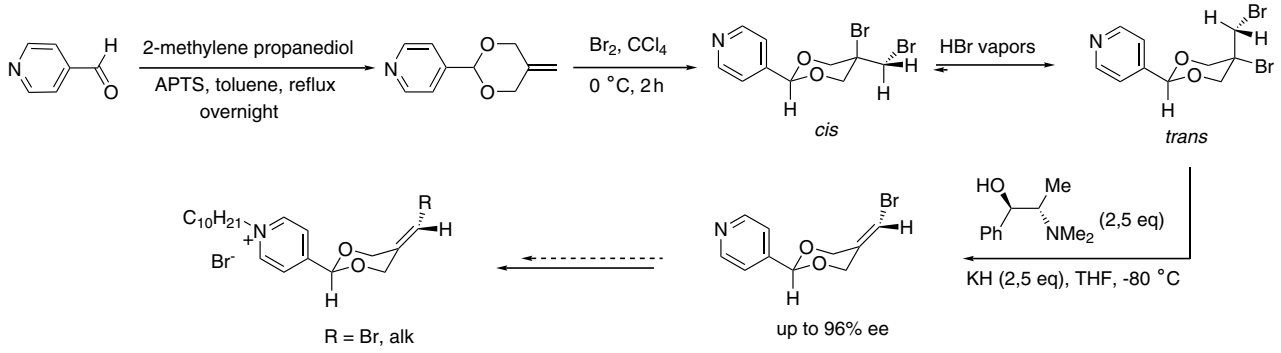
2.2.2. With axial chirality by asymmetric synthesis. Our group proposed for the first time the design and the synthesis of pyridinium ionic liquid crystals with axial chirality.[6a,33] These new pyridinium salts with a 1,3-dioxane ring in their central core were synthesised by enantioselective dehydrohalogenation using chiral alkoxides. It is important to note that these chiral ILs are not obtained from the chiral pool but are synthesised via an enantioselective reaction. The dibrominated cyclic acetals are obtained from the ethylenic precursor, which was prepared by acetalisation. The stereoselective bromination gave exclusively the *cis*-dibrominated acetal, which was isomerised into its *trans* isomer by treatment with hydrobromic acid vapours. Finally, an excess of chiral alkoxide derived from *N*-*N*′-dimethylnorephedrine, yielded the brominated compound bearing a chiral axis in excellent enantioselectivity and yield. The development of a large series of chiral ILs is easy from the obtained chiron. The chiral ILs were obtained directly either by quaternisation or by a two-step sequence (cross-coupling and quaternisation) (Scheme 16). The main advantages of these chiral ILs in asymmetric synthesis are their low melting points (below −20 °C in certain cases), and a high liquid crystal organisation (see Section 1.2.5).

2.2.3. With planar chirality. Only one example using planar chirality was proposed in the literature. Saigo[34] et al. designed chiral imidazolium salts with cyclophane-type planar chirality. The salt was easily prepared in two steps: *N*-alkylation followed by cyclisation (Scheme 17). The yield was however quite low (36%) mainly because of the formation of undesired oligomeric salts. In this structure, the *C*-(4) methyl group is essential to induce the planar chirality and to lower the melting point. The *C*-(2) methyl group is placed to avoid the racemisation of the planar-chiral cyclophane. With the bis-(pentafluoroethanesulfonyl)imide counter ion, a melting point of −20 °C was obtained.



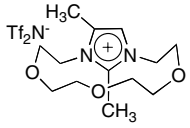
Scheme 17. Synthesis of imidazolium ILs with planar chirality.

Replacement of the alkyl chain by a polyether chain[35] resulted in a better yield of cyclised product (81–82%), at a hundredfold higher substrate concentration and



Scheme 16. Synthesis of pyridinium ILs with axial chirality.

without formation of oligomers. This was explained by the tendency of the vicinal oxygen atoms to adopt a *gauche* conformation, which would impart the polyether chain a curved structure favourable for the cyclisation. Moreover, the racemic bis(trifluoromethanesulfonyl)-imide salt was found to be liquid at room temperature (T_g −42 °C) and insoluble in water.

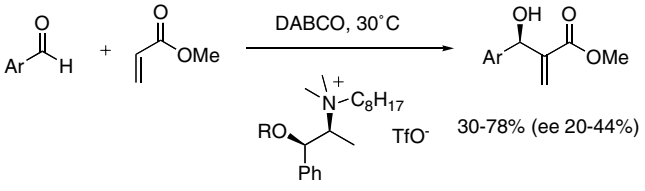


3. Applications

Ionic liquid are highly organised structures.[36] As stated by Dupont:[37] 'pure imidazolium ionic liquid can be described as polymeric hydrogen-bonded supramolecules[38] and in some cases when mixed with other molecules, they should better be regarded as nanostructured materials with polar and non polar regions rather than homogeneous solvent'. With the chiral derivatives, it may be possible to use the solvent structuration, which is the basis for molecular recognition, to devise stereoselective reactions. In Section 3, we will report the preliminary results obtained in the general field of chiral recognition with chiral ionic liquids.

3.1. Chiral solvents for asymmetric synthesis

In 2004, Vo-Thanh et al. reported the first significant asymmetric induction in the use of an enantiomerically pure ionic liquid as solvent and only source of chirality.[39] The Baylis–Hillman reaction of benzaldehyde and methyl acrylate, in the presence of one equivalent of DABCO and a chiral ionic liquid derived from (−)-*N*-methylephedrine,[12] afforded the alkoxyester with up to 44% ee (Eq. 11).



(11)

The presence of the hydroxyl group is necessary to obtain high enantioselectivity: the corresponding acylated ionic liquid gave only 7% ee with a chemical yield similar to the one obtained with the free hydroxyl group (Table 2, entries 1 and 3). The reaction could be extended to other aromatic aldehydes: electron rich *p*-methoxybenzaldehyde gave a higher enantiomeric excess but a lower yield (entry 4), whereas electron deficient aromatic aldehydes afforded slightly higher yields but lowered enantiomeric excesses (Table 2, entries 5–7). Formation of an hydrogen bond between the OH group of the ionic liquid and the nitrogen of pyridine-3-carboxaldehyde or the NO_2 group of the *p*-nitrobenzaldehyde is believed to be responsible for the very low ee observed with these last two substrates.

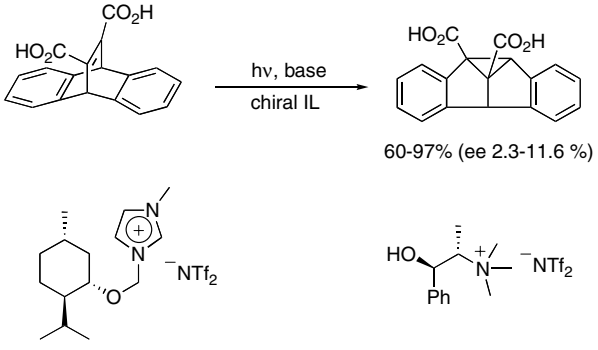
Table 2. Enantioselective Baylis-Hillman reaction

Entry	Ar	R	Yield (%)	ee (%)
1[a]	Ph	H	78 (75)	23 (24)
2[b]	Ph	H	60	44
3	Ph	Ac	77	6
4	*p*-MeOPh	H	36	30
5	*p*-ClPh	H	82	16
6	3-Py	H	83	6
7	*p*-NO_2Ph	H	87	1

Aldehyde–methyl acrylate–DABCO–LI* = 1:1:1:1; temperature = 30 °C; time = 4 days.
[a] Yield and ee obtained with recycled IL is given in brackets.
[b] Aldehyde–methyl acrylate–DABCO–LI* = 1:1:1:3; temperature = 30 °C; time = 7 days.

The chiral ionic liquid could be recycled by dissolving into dichloromethane and washing with water, and reused without loss of either yield or enantiomeric excess (Table 2, entry 1, in brackets). It is worth noting that a control experiment using *N*-methylephedrine as the chiral catalyst gave a low enantiomeric excess of 9% (chemical yield: 75%), ruling out the presence of residual *N*-methylephedrine in the ionic liquid as the source of enantioselectivity.

Recently, Armstrong et al. reported the enantioselective photoisomerisation of dibenzobicyclo[2.2.2]octatriene diacid in chiral ionic liquids.[25] Irradiation at 300 nm of the diacid in a chiral ionic liquid in the presence of an added base afforded the photoisomerised product with ee up to 11% (Eq. 12).



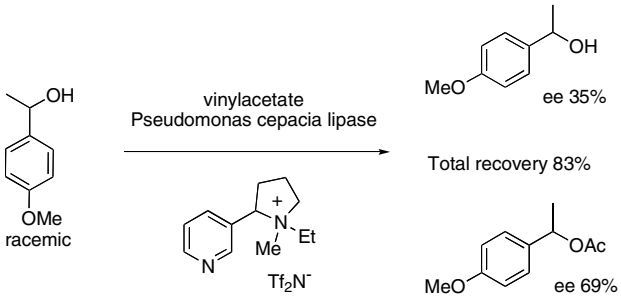
(12)

Various ammonium or imidazolium ionic liquids, as well as different bases, were used in this study: the best ee was obtained with the ammonium salt derived from *N*-methylephedrine, saturated with NaOH. In most ionic liquids no enantioselection occurred in the absence of the added base, as well as when the reaction was conducted on the parent isopropyl or methyl ester. Moreover, the use of either enantiomer of

N-methylephedrine and the chiral ionic liquid showed no significant difference in enantioselectivity. Strong interaction of the carboxylate ion and the ionic liquid is thus believed to be responsible for the observed enantioselectivity, deprotonation of the acid substrate being the only role of the base. A control experiment using *N*-methylephedrine in the achiral ionic liquid [bmim][Cl] did not afford any enantioselectivity in the photoisomerised product.

Chiral menthol-derived imidazolium salts (Eq. 12) induce enantioselectivity without the need of any added base. As expected if the diacid is already largely dissociated in this IL, addition of an amine had only a marginal effect on enantioselectivity.

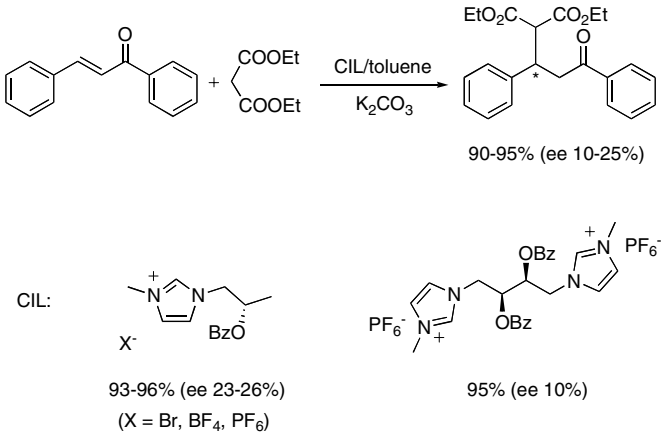
The nicotinium salt prepared by Kitazume (see Section 2.2.1.2) was examined as solvent in the kinetic resolution of 1-(4-methoxyphenyl)-ethanol mediated by the *Pseudomonas cepacia* lipase (Eq. 13).[20] The reaction was carried out at room temperature without any co-solvent. Low enantioselectivities were obtained in this new media.



(13)

In 2003, Brunner et al. reported the use of the chiral IL (*S*)-1-methyl-3-(2-methylbutyl)imidazolium hexafluorophosphate in the palladium catalysed Heck oxyarylation of 3-benzyloxypterocarpan.[40] The CIL was used both as solvent and ligand since imidazolium salts could form a carbene ligand. Although the conversion was fairly good, the selectivities were rather low (Eq. 14). Addition of PPh_3 as ligand increased the yield up to 45% but the chiral induction was completely lost.

observed when varying the counter anion of the lactate-derived imidazolium IL, Br^- giving the best results (96%, ee 25%).

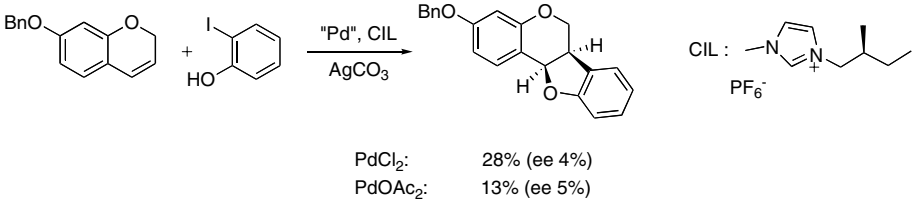


(15)

3.2. Chiral solvents for stereoselective polymerisation

Two applications of chiral ionic liquids as solvent for polymerisation were recently reported. Apart from the fact that the use of ILs allows to considerably reduce the extent of the undesirable side reactions, a clear effect on polymer tacticity was observed when chiral ionic liquids like [mbmim*][PF_6][41] or 3-(2-ethoxy-1-methyl-2-oxoethyl)-1-methylimidazolium hexafluorophosphate or tetrafluoroborate[42] were used for atom transfer radical polymerisation (ATRP) of acrylic monomers.

Wan et al. have used chiral ILs for the free radical polymerisation of vinyl monomers.[27] Two chiral ionic liquids were designed for this purpose, the 1-(−)-menthoxycarbonylmethylene-3-methylimidazolinium hexafluorophosphate and the 1-(−)-menthoxycarbonylmethylene-3-hexadecylimidazolinium hexafluorophosphate were tested. The reverse ATRP (atom transfer radical polymerisation) of MMA was performed in these two CILs at 80 °C using AIBN as an initiator and $CuCl_2$ complexes with bipyridine as a catalyst. The monomer conversion was comparable to the one observed under bulk condition. However, the polydispersity of the polymer



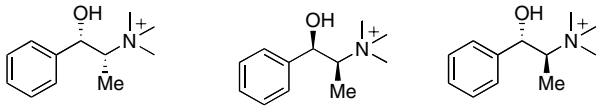
(14)

Mono- and bis-imidazolium CILs were used as chiral co-solvents in enantioselective Michael additions of malonates onto enones (Eq. 15).[22] Toluene was found to be a better co-solvent than DMF or DMSO. Slight differences in chemical yield and enantioselectivity were

was far much better in the CILs ($M_w/M_n < 1.20$) than in the absence of IL ($M_w/M_n = 2.07$). This result could be explained by the good solubility of the catalyst complex in the medium, which would promote a well-controlled polymerisation.

3.3. Chiral phases for gas chromatography

Recently, a chiral ionic liquid was used as a stationary phase for the resolution of organic compounds in gas chromatography.[43] The CIL used is the ephedrinium salt reported by Wasserscheid.[11] The capillary columns used were simply coated using the static method at 40 °C with a 0.25% (w/v) of the CIL stationary phase dissolved in DCM. The chiral IL proved to show enantioselective retention for at least four classes of compounds: alcohols, diols sulfoxides and acetylated amines. The easy access to both enantiomers of the chiral IL allowed the reversal of the enantiomeric elution order, which cannot be done with the more classical chiral selectors such as cyclodextrin. The ephedrinium stationary phase proved to be very stable and a loss of enantioselectivity was only observed with alcohols after several weeks of use at temperature higher than 140 °C.

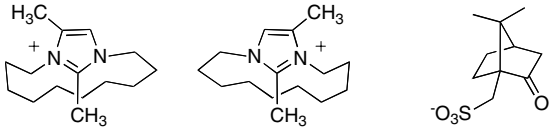


(1*S*,2*R*) (1*R*,2*S*) (1*S*,2*S*)

An example of the separation of two alcohols and a diol using a column coated with the (1*S*,2*S*)-ephedrinium salt is shown in Table 3.

3.4. Chiral shift reagents in NMR

In 2002, Saigo et al. reported[34] diastereomeric interactions between the racemic imidazolium cation and chiral (*S*)-10-camphorsulfonate anion, thus demonstrating the chiral recognition ability of the chiral IL. The ^{1}H NMR spectrum of a chloroform solution of the two salts showed a slight splitting of the doublet for the *C*-(5)–H which can be assigned to the two diastereoisomers. However, before being used as a chiral solvent, this IL salt should be resolved.

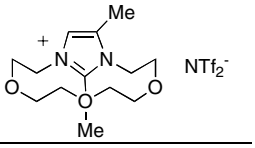


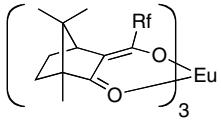
Recently, the same group[35] has modified the structure of this planar ionic liquid by replacing the cyclophane ring, by a polyether bridge. The presence of this pseudo crown-ether moiety allowed a better interaction between the planar chiral ionic liquid and chiral enantiopure europium complexes, allowing a splitting of ca. 13–18 Hz for the *C*-(5)–H imidazolium signals. The larger splitting is attributed to coordination between the oxygen atoms of the polyether unit and the europium salt (see Table 4).

Table 3. Retention times of chiral alcohols using an ephedrinium salt as stationary phase

Alcohol	Retention time (min)	Δt (min)
sec-Phenethylalcohol	7.03 and 4.63	0.60
1-Phenyl-1-butanol	13.2 and 14.13	0.93
trans-1,2-Cyclohexanediol	18.18 and 19.74	1.56

Table 4. NMR splitting of a chiral europium salt with a planar chiral imidazolium IL





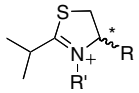
$R^1 = C_3F_7$ $\Delta J = 10.5$ Hz
$R^1 = CF_3$ $\Delta J = 18.6$ Hz

Wasserscheid[11a] and Gaumont[16a] have also probed, by ^{19}F NMR spectroscopy, diastereomeric interactions between a racemic mixture of Mosher's acid salt and, respectively, a chiral ephedrinium and a thiazolinium salt.

For the ephedrinium salt, a study on the influence of the ionic liquid concentration in CD_2Cl_2 on the extend of the signal splitting showed that a minimum concentration of 0.3 mol/L of ionic liquid is required to have a reasonable splitting. Moreover, addition of a small amount of water to the chiral IL resulted in an increase of the signal splitting which amounts to 10 Hz.[11a]

With the thiazolinium salts, the spectra were recorded in C_6D_6. The splitting of the two diastereomeric CF_3 signals depends both on the concentration of the thiazolinium salt and on the structure of the IL cation (Table 5). Replacement in the thiazolinium cation of the ethyl group α to nitrogen by a benzyl group allows a great extend of the CF_3 signal splitting from 1 to 30 Hz without the need of an additional co-solvent (water). In the ^{1}H NMR spectrum, a splitting of the Mosher's acid salt methyl group signal was also observed (5 Hz). With the ethyl, *N*-benzyl derivative, the splitting amounts to 31 Hz. A π-stacking interaction between the two phenyl groups can account for the better interaction between the two salts. The use of various enantioenriched sample of Mosher's acid salts led to the determination of their enantiomeric excess by NMR integration.

Table 5. ^{19}F NMR splitting of Mosher's acid salt signals by thiazolinium ILs

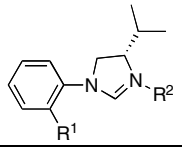


	ΔJ (Hz)	
	1 equiv	5.5 equiv + H_2O
(*S*), R = Et, R′ = Bu	1	11
(*R*), R = Bz, R′ = Bu	30	—
(*R*), R = Bz, R′ = Et	31	—

In 2004, enantiopure imidazolinium salts were reported[15] to have a similar behaviour. Diastereomeric

interactions with the racemic Mosher's acid salt were observed by ^{1}H and ^{19}F NMR. The extent of the splitting depends on the nature of imidazolinium side chains. A bulky group and a hydroxyl one favoured a broad chemical shift difference between the methoxy group and the CF_3 group of the Mosher's acid salt moiety allowing the use of this salt for the determination of enantiomeric excesses (see Table 6).

Table 6. ^{19}F NMR splitting of Mosher's acid salt signals by imidazolinium ILs



R^1	R^2	ΔJ (Hz)[a] ^{1}H	^{19}F
*t*Bu	CH_2CH_2OH	54.7	40.4
*t*Bu	$CH_2CH_2CH_2OH$	60	63
*t*Bu	$(CH_2)_8OH$	12	—
Me	CH_2CH_2OH	7.4	—

[a] Spectra recorded in CD_2Cl_2 in presence of 18C6 crown ether.

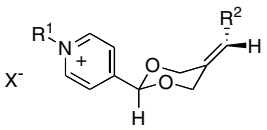
3.5. Chiral liquid crystals

Ionic liquids presenting thermotropic mesophases are attractive new materials because they can be considered as highly structured solvents. They could increase the selectivity in reactions by ordering reactants, or be used as templates for the synthesis of mesoporous materials and ordered thin films. In this context, we have described the first synthesis of a novel family of chiral ionic liquids in which the stereogenic unit is a chiral axis and the 'ionic liquid/liquid crystals' (IL^2Cs) properties are tuned by the constitution of the salts (geometry of the rod-like core and nature of the anion).[6a,33] The construction of chiral precursors was realised as shown in Section 2.2.2 (Scheme 16).

The anionic counterion plays a crucial role for the physical properties of ionic liquids (solubility, viscosity and melting point). Physico-chemical properties of selected examples (either in racemic or enantiomerically pure form) of new IL^2Cs were examined. The presence and the nature of anisotropic phases were checked by polarised microscopy and the transition temperatures were obtained with a Differential Scanning Calorimeter (DSC, heating rate of 10 °C/min) (see Table 7).

Most of these new compounds exhibit the expected properties: low melting or glass transition temperatures and thermal stability up to 150 °C and more. More interestingly, they present liquid crystalline state in a wide range of temperatures. Different phases can be observed depending on the structure of the rod-like cation and the nature of the anion (Table 7). Generally, mesophases can be observed only when the central core bears long chains on both sides. The central core of this molecule is rather small and these two chains are necessary to obtain rod-like calamitic molecules. The transition temperatures (glass transition, melting point and mesomorphic transitions) do not significantly depend on the enantiomeric composition of the chiral material. However, the nature of the mesophase is affected by the enantiomeric purity: cholesteric (**N***) phases are observed for pure (*R*) compounds while nematic or smectic phase is observed for the racemic mixtures. Obtention of liquid crystalline properties is more easily observed with halogen or tetrafluoroborate anions. Such effect of the size of the anion (but also probably charge delocalisation) was already observed in some other series presenting mesomorphic properties.[44] The bigger anions should decrease the packing of the cationic mesomorphic units.

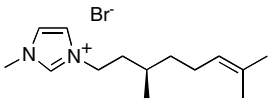
Table 7. Transition temperatures of pyridinium ILs with axial chirality



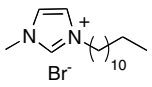
Abs. conf.	R^1	R^2	X	
(***RS***)	$C_{10}H_{21}$	*p*-BuO–C_6H_4	I	**N 47 I**
(***R***)	$C_{10}H_{21}$	*p*-BuO–C_6H_4	I	**N* 39/45 I**
(***RS***)	$C_{10}H_{21}$	*p*-OctO–C_6H_4	I	**G 22 Sm 92 I**
(***RS***)	C_3H_7	$C_{18}H_{37}$	Br	**K 52 Sm 149 I**
(***RS***)	$C_{10}H_{21}$	$C_{18}H_{37}$	I	**Sm 41 N 90 I_{decomp}**
(***R***)	$C_{10}H_{21}$	$C_{18}H_{37}$	I	**Sm_1 50 Sm_2 90 I**
(***RS***)	$C_{10}H_{21}$	C_8H_{17}	I	**Sm 44/55 I**
(***R***)	$C_{10}H_{21}$	C_8H_{17}	I	**N* 35/40 I**
(***RS***)	$C_{10}H_{21}$	C_8H_{17}	Br	**SmC 55 I**
(***RS***)	$C_{10}H_{21}$	C_8H_{17}	BF_4	**G −25 Sm 92 I**
(***RS***)	$C_{10}H_{21}$	C_8H_{17}	PF_6	**G −35 I**
(***RS***)	$C_{10}H_{21}$	C_8H_{17}	$(Tf)_2N$	**G −43 I**

(***RS***): racemic; **K**: crystal, **G**: glass, **N**: nematic, **N***: chiral nematic (cholesteric), **Sm**: smectic, **SmC**: smectic C.

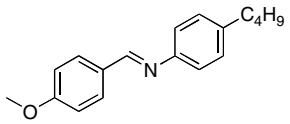
The mesogenic properties of citronellol derived imidazolium and pyridinium salts were studied by Laschat et al.[24] Asymmetric imidazolium bromides with short alkyl chains (i.e., methyl, butyl or hexyl) display only a glass transition (below −50 °C), whereas the dodecyl and octadecyl compounds display a crystal to isotropic liquid transition at 6 °C and 41 °C, respectively. Moreover, tetradecylcitronellylimidazolium bromide displays a crystal to mesogenic phase transition at 9 °C, and a mesogenic to isotropic liquid phase transition at 45 °C. Tetrafluoroborate analogs with a methyl or a dodecyl side chain were shown to have thermal behaviour very



1-methyl-3-citronellylimidazolium bromide



1-methyl-3-dodecylimidazolium bromide



4-butyl-*N*-[(4-methoxyphenyl)-methylene]aniline

similar to bromides. The symmetric bis(citronellyl)imidazolium bromide and citronellylpyridinium bromide display only a glass transition at −56 and −47 °C, respectively. However, examination with a microscope of citronellylpyridinium bromide between cross-polarisers reveals a fan-shaped smectic texture at −56 °C. A study of mixtures of 1-methyl-3-citronellylimidazolium bromide with two known mesogens, smectic 1-methyl-3-dodecylimidazolium bromide and nematic 4-butyl-*N*-[(4-methoxyphenyl)methylene]aniline, was also carried out by this group.

Addition of increasing amounts of the chiral dopant to the achiral imidazolium salt induced a decrease of the width of the smectic A phase, until only melting can be observed, whereas the phase width of the nematic benzylideneaniline liquid crystal remains constant over an extended range of molar fraction of the chiral ionic liquid. However, in neither case could any chiral mesophase be detected.

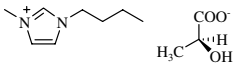
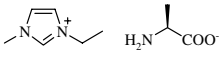
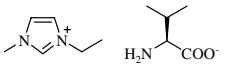
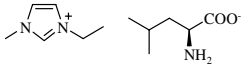
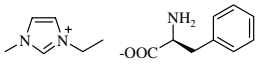
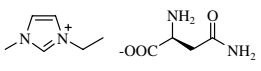
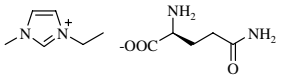
4. Conclusion

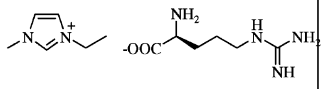
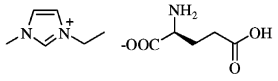
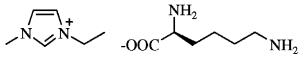
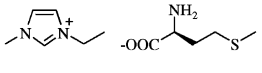
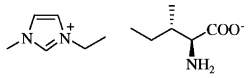
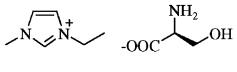
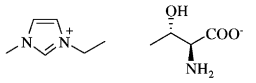
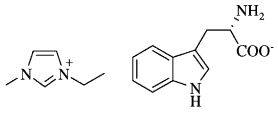
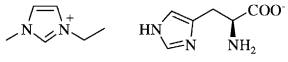
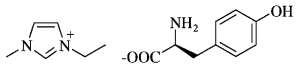
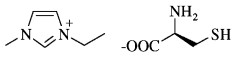
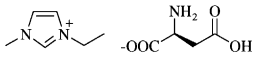
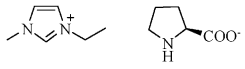
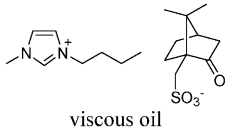
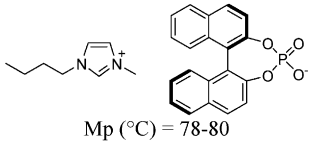
In the present review, the outstanding series of recent work focusing on the synthesis and applications of CILs were highlighted. The increasing interest for these new solvents is, in our opinion, due to chemist's curiosity for a new research area in the field of chirality. Indeed, the concept of 'tailor-made' chiral solvents is rather new, and could afford novel molecular structures and materials, as well as new insights for chiral recognition and chirality transfers. In the latter case, the specific properties of CILs suggest a key role in future asymmetric syntheses, thus giving a 'second souffle' to the chiral solvent topic. A third reason is the broad scope of applications, amplified by the domain of chiral task-specific ionic liquids, which constitutes a related issue even if considered beyond the scope of this review since they cannot be viewed as solvents or co-solvents.

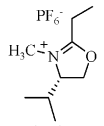
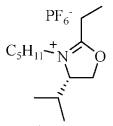
For future design of new CILs, one should think in which manner chirality has to be expressed. Some applications will mainly require a macroscopic effect (chiral solvent role), while the other will necessitate a microscopic one ('pseudo-catalytic' role). Obviously the macroscopic effect would be observed using CIL's including either chiral cations or anions, as well as solvents in which both entities would be chiral. On the other hand, depending on the mechanism of the 'pseudo-catalysed' asymmetric reaction, chiral cations would be preferred when an anionic ('basic') transition state is developed, while use of chiral anions would be worthwhile in the opposite case.

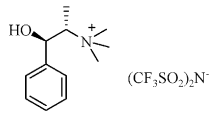
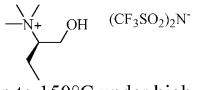
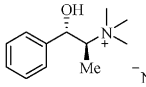
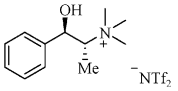
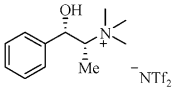
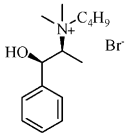
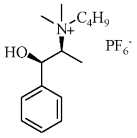
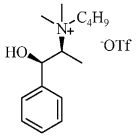
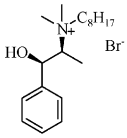
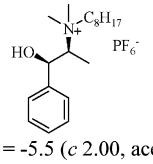
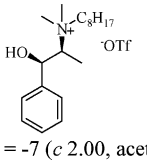
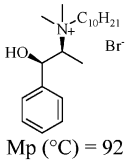
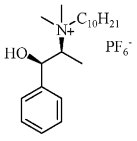
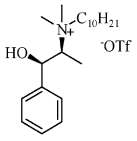
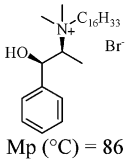
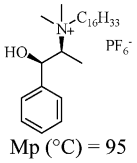
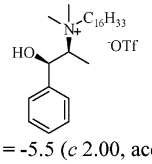
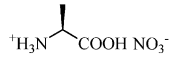
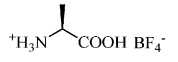
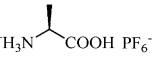
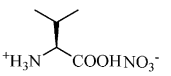
Clearly, the most exciting progress could arise, in our opinion, from future studies dedicated to the exploration of mechanistic aspects, examination of structural features and careful determination of physicochemical data. Indeed, theoretical insights are missing for efficient evaluation of the real potency of these new chiral solvents. Nevertheless, we believe that the use of such solvents will rapidly expand in the fields of chiral chromatography and NMR shift reagents. In these applications, the high cost of CIL's is not a real limitation, and these new tools for chiral recognition will certainly allow chemists to answer hitherto unsolved problems. Later, the better understanding of the specific behaviour of CIL's will give access to promising new materials with unprecedented properties (see for example chiral liquid crystals), and to successful applications in asymmetric syntheses.

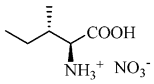
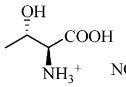
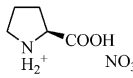
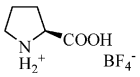
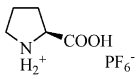
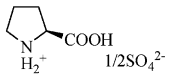
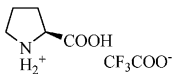
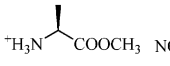
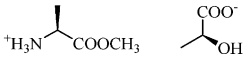
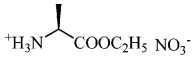
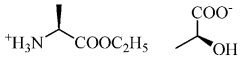
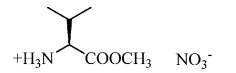
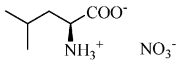
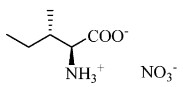
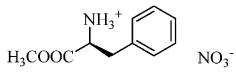
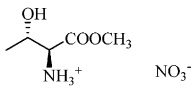
In the following pages are compiled, in a series of Tables, an exhaustive list of CILs described so far and their properties.

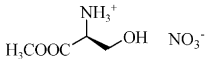
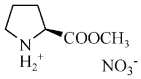
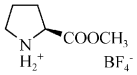
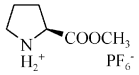
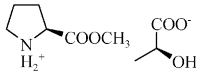
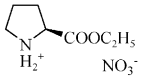
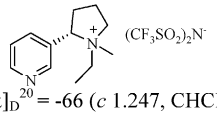
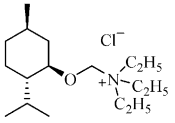
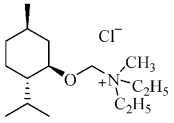
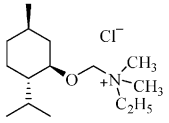
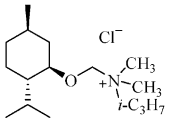
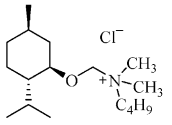
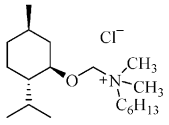
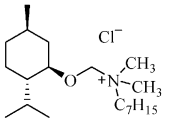
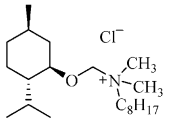
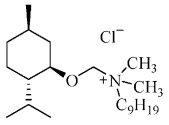
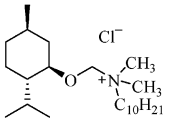
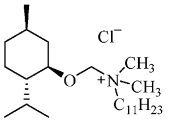
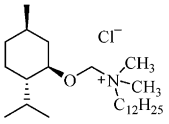
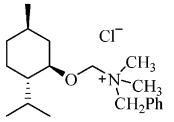
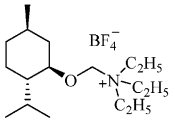
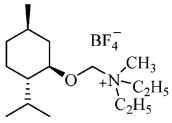
CILs having chiral anion: Imidazolium salts			
Structure			**Ref.**
			8
 [emim][Ala] T_g (°C) = -57 σ_i (S/cm) at 25°C = 6.4×10^{-4} Thermal stability = Up to 200°C	 [emim][Val] T_g (°C) = -52 σ_i (S/cm) at 25°C = 8.8×10^{-5} Thermal stability = Up to 200°C	 [emim][Leu] T_g (°C) = -51 σ_i (S/cm) at 25°C = 8.1×10^{-5} Thermal stability = Up to 200°C	9
 [emim][Phe] T_g (°C) = -36 σ_i (S/cm) at 25°C = 6.0×10^{-5} Thermal stability = Up to 200°C	 [emim][Asn] T_g (°C) = -16 σ_i (S/cm) at 25°C = 1.1×10^{-6} Thermal stability = Up to 200°C	 [emim][Gln] T_g (°C) = -12 σ_i (S/cm) at 25°C = 1.7×10^{-7} Thermal stability = Up to 200°C	9

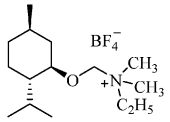
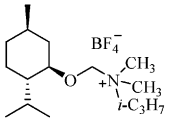
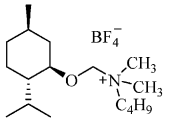
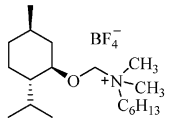
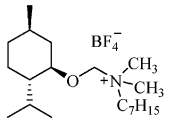
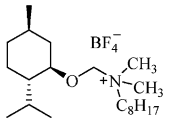
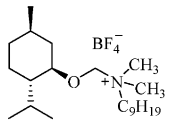
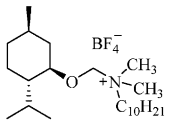
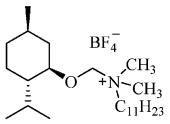
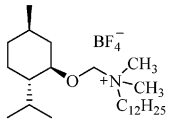
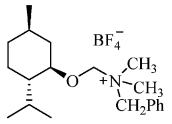
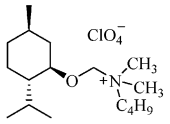
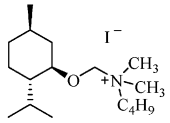
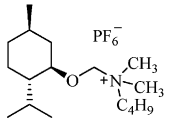
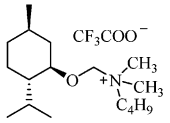
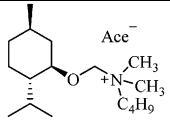
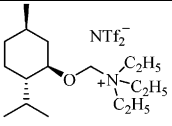
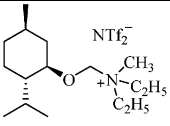
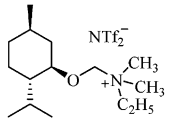
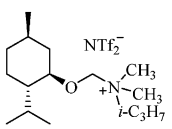
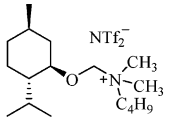
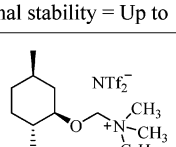
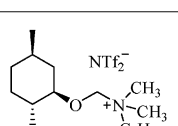
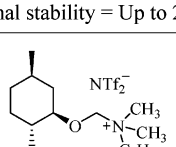
 [emim][Arg] T_g (°C) = -18 σ_i (S/cm) at 25°C = 9.0×10^{-7} Thermal stability = Up to 200°C	 [emim][Glu] T_g (°C) = 6 σ_i (S/cm) at 25°C = 5.0×10^{-7} Thermal stability = Up to 200°C	 [emim][Lys] T_g (°C) = -47 σ_i (S/cm) at 25°C = 7.8×10^{-5} Thermal stability = Up to 200°C	9
 [emim][Met] T_g (°C) = -57 σ_i (S/cm) at 25°C = 2.4×10^{-4} Thermal stability = Up to 200°C	 [emim][Ile] T_g (°C) = -52 σ_i (S/cm) at 25°C = 6.9×10^{-5} Thermal stability = Up to 200°C	 [emim][Ser] T_g (°C) = -49 σ_i (S/cm) at 25°C = 6.5×10^{-4} Thermal stability = Up to 200°C	9
 [emim][Thr] T_g (°C) = -40 σ_i (S/cm) at 25°C = 1.0×10^{-4} Thermal stability = Up to 200°C	 [emim][Trp] T_g (°C) = -31 σ_i (S/cm) at 25°C = 9.1×10^{-9} Thermal stability = Up to 200°C	 [emim][His] T_g (°C) = -24 σ_i (S/cm) at 25°C = 1.0×10^{-7} Thermal stability = Up to 200°C	9
 [emim][Tyr] T_g (°C) = -23 σ_i (S/cm) at 25°C = 4.0×10^{-8} Thermal stability = Up to 200°C	 [emim][Cys] T_g (°C) = -19 σ_i (S/cm) at 25°C = 3.5×10^{-5} Thermal stability = Up to 173°C	 [emim][Asp] T_g (°C) = 5 σ_i (S/cm) at 25°C = 1.7×10^{-9} Thermal stability = Up to 200°C	9
 [emim][Pro] T_g (°C) = -48 σ_i (S/cm) at 25°C = 1.6×10^{-4} Thermal stability = Up to 200°C			9
 viscous oil $[\alpha]_D^{25}$= +39.0 (*c* 1.634, CH_3OH)			10
 Mp (°C) = 78-80			10

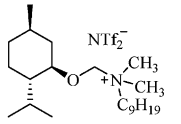
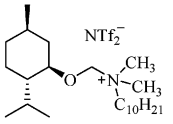
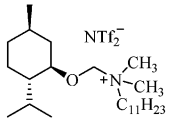
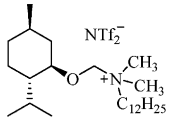
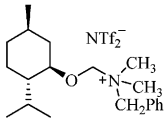
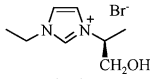
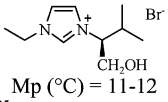
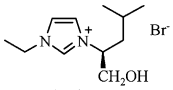
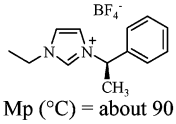
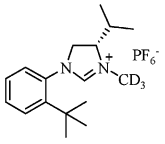
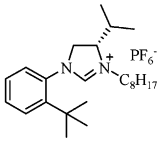
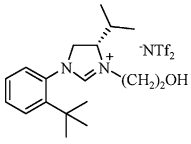
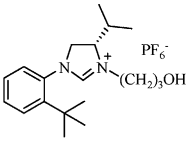
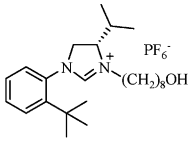
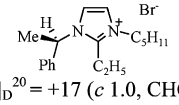
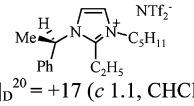
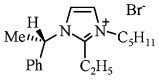
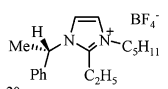
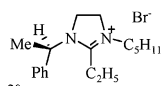
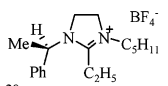
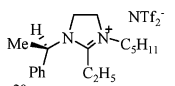
CILs having chiral cation: Oxazolinium salts		
Structure		**Ref.**
 Mp (°C) = 79	 Mp (°C) = 63	11

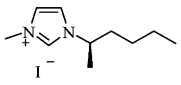
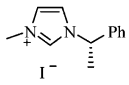
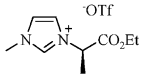
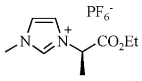
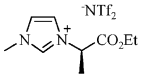
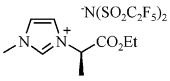
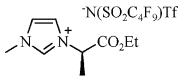
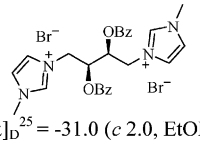
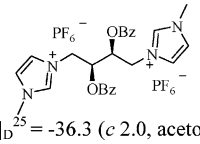
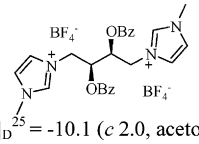
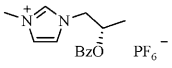
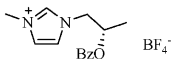
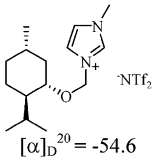
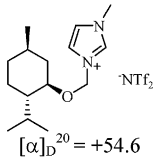
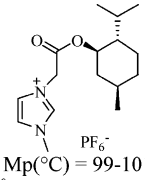
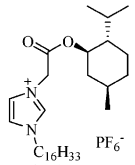
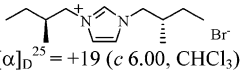
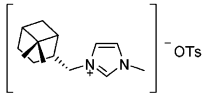
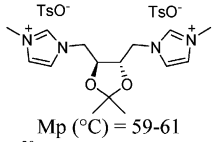
CILs having chiral cation: Ammonium salts			
Structure			**Ref.**
 Mp (°C) = 54 Stable up to 150°C under high vacuum conditions (10^{-3} mbar)		 Stable up to 150°C under high vacuum conditions (10^{-3} mbar) η = 0.155 Pa∗s at 20°C	11
			39
 Mp (°C) = 95-96 $[\alpha]_D^{25}$ = -12.1 (*c* 1.57, $CHCl_3$)	 Mp (°C) = 92 $[\alpha]_D^{25}$ = -10 (*c* 1.00, acetone)	 $[\alpha]_D^{25}$ = -11 (*c* 2.00, acetone)	12
 Mp (°C) = 88 $[\alpha]_D^{25}$ = -13.5 (*c* 2.00, $CHCl_3$)	 $[\alpha]_D^{25}$ = -5.5 (*c* 2.00, acetone)	 $[\alpha]_D^{25}$ = -7 (*c* 2.00, acetone)	12
 Mp (°C) = 92 $[\alpha]_D^{25}$ = -13.5 (*c* 2.00, $CHCl_3$)	 $[\alpha]_D^{25}$ = -9 (*c* 2.00, acetone)	 $[\alpha]_D^{25}$ = -6.5 (*c* 2.00, acetone)	12
 Mp (°C) = 86 $[\alpha]_D^{25}$ = -11 (*c* 2.00, $CHCl_3$)	 Mp (°C) = 95 $[\alpha]_D^{25}$ = -4.5 (*c* 2.00, acetone)	 $[\alpha]_D^{25}$ = -5.5 (*c* 2.00, acetone)	12
 Mp (°C) = 159 $[\alpha]_D^{20}$ = +15.9 (*c* 2.00, MeOH) Thermal stability = Up to 168°C	 Mp (°C) = 78 $[\alpha]_D^{20}$ = +11.6 (*c* 2.00, MeOH) Thermal stability = Up to 241°C	 $[\alpha]_D^{20}$ = +8.4 (*c* 2.00, MeOH) Thermal stability = Up to 176°C	13
 Mp (°C) = 82 $[\alpha]_D^{20}$ = +8.6 (*c* 2.00, MeOH) Thermal stability = Up to 119°C	 Mp (°C) = 141 $[\alpha]_D^{20}$ = +9.1 (*c* 2.00, MeOH) Thermal stability = Up to 193°C	 Mp (°C) = 134 $[\alpha]_D^{20}$ = +27.2 (*c* 2.00, MeOH) Thermal stability = Up to 169°C	13

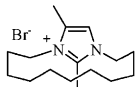
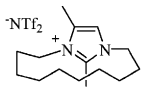
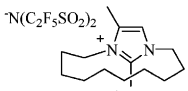
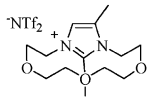
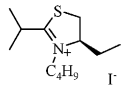
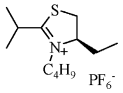
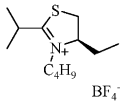
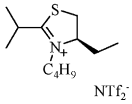
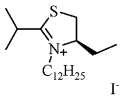
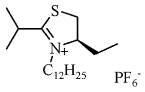
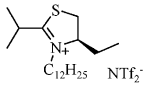
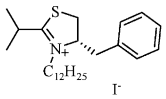
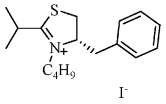
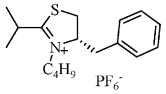
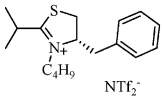
 Mp (°C) = 105 $[\alpha]_D^{20}$ = +40.3 (*c* 2.00, MeOH) Thermal stability = Up to 167°C	 $[\alpha]_D^{20}$ = -10.8 (*c* 2.00, MeOH) Thermal stability = Up to 147°C	 $[\alpha]_D^{20}$ = -29.7 (*c* 2.00, MeOH) Thermal stability = Up to 138°C	13
 Mp (°C) = 76 $[\alpha]_D^{20}$ = -26.8 (*c* 2.00, MeOH) Thermal stability = Up to 236°C	 $[\alpha]_D^{20}$ = -24.0 (*c* 2.00, MeOH) Thermal stability = Up to 168°C	 Mp (°C) = 92 $[\alpha]_D^{20}$ = -38.7 (*c* 2.00, MeOH) Thermal stability = Up to 206°C	13
 Mp (°C) = 78 $[\alpha]_D^{20}$ = -36.1 (*c* 2.00, MeOH) Thermal stability = Up to 192°C	 Mp (°C) = 61 T_g (°C) = -34 $[\alpha]_D^{20}$ = +6.2 (*c* 2.00, MeOH) Thermal stability = Up to 186°C	 Mp (°C) = -18 T_g (°C) = -48 $[\alpha]_D^{20}$ = +5.6 (*c* 2.00, MeOH) Thermal stability = Up to 230°C σ_i (cP) at 30°C = 96	13
 T_g (°C) = -35 $[\alpha]_D^{20}$ = +5.8 (*c* 2.00, MeOH) Thermal stability = Up to 209°C	 Mp (°C) = -17 T_g (°C) = -61 $[\alpha]_D^{20}$ = +5.8 (*c* 2.00, MeOH) Thermal stability = Up to 150°C	 Mp (°C) = 62 T_g (°C) = -38 $[\alpha]_D^{20}$ = +5.2 (*c* 2.00, MeOH) Thermal stability = Up to 139°C σ_i (cP) at 80°C = 103	13
 T_g (°C) = -23 Thermal stability = Up to 172°C	 Mp (°C) = 38 T_g (°C) = -24 $[\alpha]_D^{20}$ = -4.5 (*c* 2.00, MeOH) Thermal stability = Up to 77°C	 Mp (°C) = -17 T_g (°C) = -45 $[\alpha]_D^{20}$ = +4.7 (*c* 2.00, MeOH) Thermal stability = Up to 187°C σ_i (cP) at 30°C = 2030	13
 Mp (°C) = 75 T_g (°C) = -29 $[\alpha]_D^{20}$ = -5.7 (*c* 2.00, MeOH) Thermal stability = Up to 82°C	 Mp (°C) = 74 T_g (°C) = -33 $[\alpha]_D^{20}$ = +22.5 (*c* 2.00, MeOH) Thermal stability = Up to 195°C	 Mp (°C) = 75 T_g (°C) = -31 $[\alpha]_D^{20}$ = +15.4 (*c* 2.00, MeOH) Thermal stability = Up to 210°C σ_i (cP) at 80°C = 1550	13
 Mp (°C) = -14 T_g (°C) = -36 $[\alpha]_D^{20}$ = +32.7 (*c* 2.00, MeOH) Thermal stability = Up to 172°C	 Mp (°C) = 92 T_g (°C) = -32 $[\alpha]_D^{20}$ = +21.1 (*c* 2.00, MeOH) Thermal stability = Up to 224°C	 Mp (°C) = -12 T_g (°C) = -32 $[\alpha]_D^{20}$ = -9.5 (*c* 2.00, MeOH) Thermal stability = Up to 156°C	13

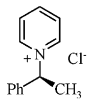
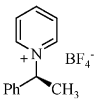
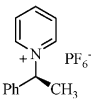
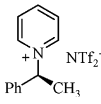
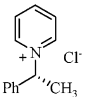
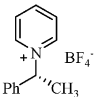
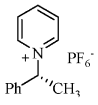
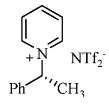
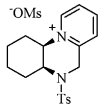
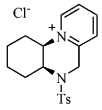
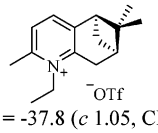
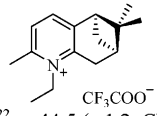
 Mp (°C) = 105 T_g (°C) = -30 $[\alpha]_D^{20}$ = +7.3 (*c* 2.00, MeOH) Thermal stability = Up to 179°C	 Mp (°C) = -16 T_g (°C) = -67 $[\alpha]_D^{20}$ = -36.4 (*c* 2.00, MeOH) Thermal stability = Up to 159°C σ_i (cP) at 30°C = 186	 T_g (°C) = -20 $[\alpha]_D^{20}$ = -20.7 (*c* 2.00, MeOH) Thermal stability = Up to 234°C	13
 T_g (°C) = -22 $[\alpha]_D^{20}$ = -32.2 (*c* 2.00, MeOH) Thermal stability = Up to 221°C	 T_g (°C) = -20 $[\alpha]_D^{20}$ = -23.8 (*c* 2.00, MeOH) Thermal stability = Up to 140°C	 Mp (°C) = -17 T_g (°C) = -50 $[\alpha]_D^{20}$ = -30.9 (*c* 2.00, MeOH) Thermal stability = Up to 183°C	13
 $[\alpha]_D^{20}$ = -66 (*c* 1.247, $CHCl_3$)			20
 M_p (°C) = 31-33 $[\alpha]_D^{20}$ = -57.4 (*c* 1.1, EtOH)	 hygroscopic $[\alpha]_D^{20}$ = -59.5 (*c* 0.7, EtOH)	 M_p (°C) = 87.5-90 $[\alpha]_D^{20}$ = -68.7 (*c* 0.9, EtOH)	26
 M_p (°C) = 158-161 $[\alpha]_D^{20}$ = -71.3 (*c* 0.6, EtOH)	 M_p (°C) = 130-132 $[\alpha]_D^{20}$ = -64.8 (*c* 1.1, EtOH)	 M_p (°C) = 113-116 $[\alpha]_D^{20}$ = -55.7 (*c* 0.7, EtOH)	26
 hygroscopic $[\alpha]_D^{20}$ = -54.1 (*c* 0.7, EtOH)	 M_p (°C) = 74-76 $[\alpha]_D^{20}$ = -54.1 (*c* 1.0, EtOH)	 hygroscopic $[\alpha]_D^{20}$ = -50.3 (*c* 0.5, EtOH)	26
 hygroscopic $[\alpha]_D^{20}$ = -51.5 (*c* 1.4, EtOH)	 hygroscopic $[\alpha]_D^{20}$ = -48.8 (*c* 0.8, EtOH)	 hygroscopic $[\alpha]_D^{20}$ = -48.3 (*c* 1.5, EtOH)	26
 M_p (°C) = 126-129 $[\alpha]_D^{20}$ = -63.5 (*c* 1.1, EtOH)	 M_p (°C) = 125-126.5 $[\alpha]_D^{20}$ = -64.8 (*c* 0.4, EtOH)	 M_p (°C) = 150.5-152 $[\alpha]_D^{20}$ = -61.5 (*c* 1.0, EtOH)	26

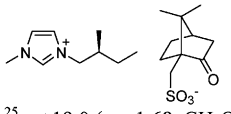
			26
M_p (°C) = 161.5-164 $[\alpha]_D^{20}$ = -63.5 (*c* 1.0, EtOH)	M_p (°C) = 203-206 $[\alpha]_D^{20}$ = -61.2 (*c* 0.8, EtOH)	M_p (°C) = 68.5-71 $[\alpha]_D^{20}$ = -58.3 (*c* 1.1, EtOH)	
			26
M_p (°C) = 42-44 $[\alpha]_D^{20}$ = -52.7 (*c* 1.0, EtOH)	M_p (°C) = 69-72 $[\alpha]_D^{20}$ = -49.1 (*c* 1.0, EtOH)	M_p (°C) = 87.5-88.5 $[\alpha]_D^{20}$ = -48.9 (*c* 1.4, EtOH)	
			26
M_p (°C) = 69-72 $[\alpha]_D^{20}$ = -47.3 (*c* 1.0, EtOH)	M_p (°C) = 55-58 $[\alpha]_D^{20}$ = -44.8 (*c* 1.0, EtOH)	M_p (°C) = 43-48 $[\alpha]_D^{20}$ = -44.4 (*c* 1.0, EtOH)	
			26
M_p (°C) = 42.5-43 $[\alpha]_D^{20}$ = -38.4 (*c* 1.0, EtOH)	M_p (°C) = 97.5-100 $[\alpha]_D^{20}$ = -58.2 (*c* 1.0, EtOH)	M_p (°C) = 77-78.5 $[\alpha]_D^{20}$ = -56.4 (*c* 0.9, EtOH)	
			26
M_p (°C) = 81-83 $[\alpha]_D^{20}$ = -51.3 (*c* 0.9, EtOH)	M_p (°C) = 103-105 $[\alpha]_D^{20}$ = -51.6 (*c* 1.1, EtOH)	M_p (°C) = 72-74 $[\alpha]_D^{20}$ = -52.8 (*c* 1.1, EtOH)	
			26
oil $[\alpha]_D^{20}$ = -51.2 (*c* 0.4, EtOH) Ace : acesulfamate	T_g (°C) = -45.8 $[\alpha]_D^{20}$ = -38.6 (*c* 1.4, EtOH) Thermal stability = Up to 179°C	T_g (°C) = -48.5 $[\alpha]_D^{20}$ = -39.1 (*c* 1.2, EtOH) Thermal stability = Up to 197°C	
			26
T_g (°C) = -49.9 $[\alpha]_D^{20}$ = -40.6 (*c* 1.1, EtOH) Thermal stability = Up to 199°C	$[\alpha]_D^{20}$ = -39.5 (*c* 1.1, EtOH)	T_g (°C) = -50.1 $[\alpha]_D^{20}$ = -38.2 (*c* 0.9, EtOH) Thermal stability = Up to 200°C	
			26
T_g (°C) = -50.2 $[\alpha]_D^{20}$ = -41.6 (*c* 1.0, EtOH) Thermal stability = Up to 200°C	T_g (°C) = -52.8 $[\alpha]_D^{20}$ = -34.8 (*c* 1.2, EtOH) Thermal stability = Up to 202°C	T_g (°C) = -53.0 $[\alpha]_D^{20}$ = -35.6 (*c* 1.4, EtOH) Thermal stability = Up to 200°C	

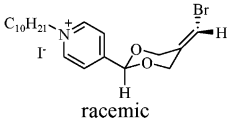
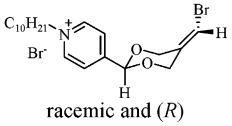
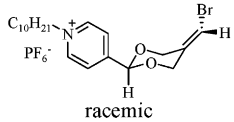
 T_g (°C) = -53.2 $[\alpha]_D^{20}$ = -33.2 (*c* 1.4, EtOH) Thermal stability = Up to 199°C	 T_g (°C) = -54.4 $[\alpha]_D^{20}$ = -37.8 (*c* 1.1, EtOH) Thermal stability = Up to 200°C	 T_g (°C) = -54.3 $[\alpha]_D^{20}$ = -32.7 (*c* 1.6, EtOH) Thermal stability = Up to 206°C	26
 $[\alpha]_D^{20}$ = -31.5 (*c* 1.2, EtOH)	 $[\alpha]_D^{20}$ = -39.1 (*c* 1.0, EtOH)		26
CILs having chiral cation: Imidazolium and imidazolinium salts			
Structure			**Ref.**
 Mp (°C) = 5-6 $[\alpha]_D^{25}$ = +3.7 (*c* 2.00, CH_3OH) Thermal stability = Up to 180°C	 Mp (°C) = 11-12 $[\alpha]_D^{25}$ = -10 (*c* 2.00, CH_3OH) Thermal stability = Up to 180°C		14
 Mp (°C) = 15-16 $[\alpha]_D^{25}$ = +9.2 (*c* 2.00, CH_3OH) Thermal stability = Up to 180°C	 Mp (°C) = about 90		14
			15
			15
 $[\alpha]_D^{20}$ = +17 (*c* 1.0, $CHCl_3$)	 $[\alpha]_D^{20}$ = +17 (*c* 1.1, $CHCl_3$)		18
 $[\alpha]_D^{20}$ = -17 (*c* 1.1, $CHCl_3$)	 $[\alpha]_D^{20}$ = -25 (*c* 1.0, $CHCl_3$)		18
 $[\alpha]_D^{20}$ = -16 (*c* 1.4, $CHCl_3$)	 $[\alpha]_D^{20}$ = -10 (*c* 1.0, $CHCl_3$)	 $[\alpha]_D^{20}$ = -7 (*c* 1.1, $CHCl_3$)	18

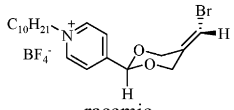
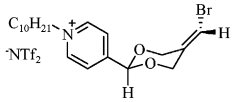
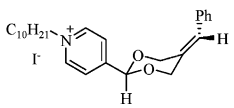
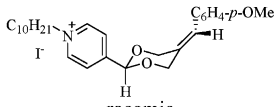
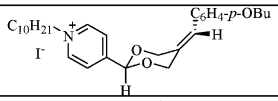
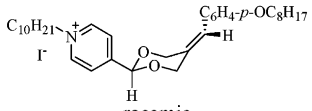
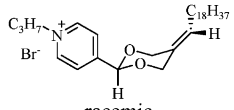
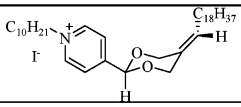
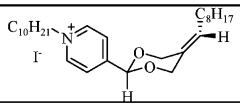
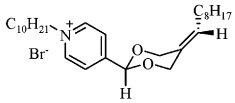
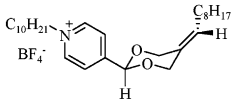
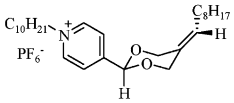
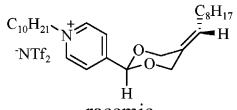
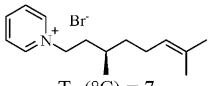
		31
 Mp (°C) = 73 T_g (°C) = -50	 T_g (°C) = -58	 Mp (°C) = 45 T_g (°C) = -57	21
 T_g (°C) = -56	 T_g (°C) = -54	21
 $[\alpha]_D^{25}$ = -31.0 (*c* 2.0, EtOH)	 $[\alpha]_D^{25}$ = -36.3 (*c* 2.0, acetone)	 $[\alpha]_D^{25}$ = -10.1 (*c* 2.0, acetone)	22
 $[\alpha]_D^{25}$ = -30.5 (*c* 2.0, acetone)	 $[\alpha]_D^{25}$ = -19.9 (*c* 2.0, acetone)	22
 $[\alpha]_D^{20}$ = -54.6	 $[\alpha]_D^{20}$ = +54.6	25
 Mp(°C) = 99-101 $[\alpha]_D^{20}$ = +44.3 (*c* 2.00, THF)	 Mp(°C) = 69-71 $[\alpha]_D^{20}$ = -31 (*c* 2.00, THF)	27
 $[\alpha]_D^{25}$ = +19 (*c* 6.00, $CHCl_3$)	29
 Mp (°C) = 102	10
 Mp (°C) = 59-61 $[\alpha]_D^{20}$ = -21 (*c* 2.07, CH_3OH)	10

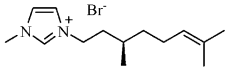
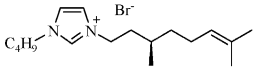
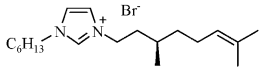
Imidazolium with planar chirality			
Structure			**Ref.**
 racemic	 racemic	 racemic	34
 T_g (°C) = -42			35
CILs having chiral cation: Thiazolinium salts			
Structure			**Ref.**
 Mp (°C) = 137 $[\alpha]_D^{20}$ = -40.7 (*c* 1.00, acetone) Thermal stability = Up to 170°C	 Mp (°C) = 136 $[\alpha]_D^{20}$ = -35.6 (*c* 1.00, acetone) Thermal stability = Up to 170°C	 Mp (°C) = 111 $[\alpha]_D^{20}$ = -32.5 (*c* 1.00, acetone) Thermal stability = Up to 170°C	16
 T_g (°C) = -68 $[\alpha]_D^{20}$ = -29.5 (*c* 1.00, acetone) Thermal stability = Up to 170°C	 Mp (°C) = 38 $[\alpha]_D^{20}$ = -38.8 (*c* 1.00, acetone) Thermal stability = Up to 170°C	 Mp (°C) = 42 $[\alpha]_D^{20}$ = -36.7 (*c* 1.00, acetone) Thermal stability = Up to 170°C	16
 T_g (°C) = -67 $[\alpha]_D^{20}$ = -36.7 (*c* 1.00, acetone) Thermal stability = Up to 170°C		 Mp (°C) = 106	16
 Mp (°C) = 172 $[\alpha]_D^{20}$ = +33 (*c* 1.00, acetone) Thermal stability = Up to 180°C	 Mp (°C) = 115 $[\alpha]_D^{20}$ = +34 (*c* 1.00, acetone) Thermal stability = Up to 180°C	 T_g (°C) = -40 $[\alpha]_D^{20}$ = +29 (*c* 1.00, acetone)	16

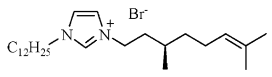
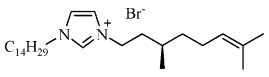
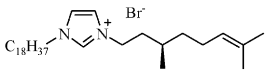
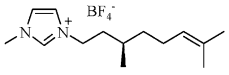
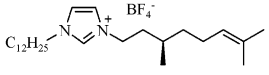
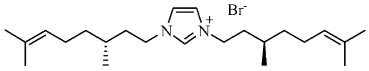
CILs having chiral cation: Pyridinium salts			
Structure			**Ref.**
 T_g (°C) = 125 $[\alpha]_D^{20}$ = -45.2 (*c* 1.00, MeOH) Thermal stability = Up to 200°C	 T_g (°C) = 65 $[\alpha]_D^{20}$ = -11.5 (*c* 1.00, MeOH) Thermal stability = Up to 200°C	 T_g (°C) = 110 $[\alpha]_D^{20}$ = -9.4 (*c* 1.00, MeOH) Thermal stability = Up to 188°C	19
 T_g (°C) = -30 $[\alpha]_D^{20}$ = -22.3 (*c* 1.00, MeOH) Thermal stability = Up to 215°C	 T_g (°C) = 125 $[\alpha]_D^{20}$ = +44.9 (*c* 1.00, MeOH) Thermal stability = Up to 200°C	 T_g (°C) = 65 $[\alpha]_D^{20}$ = +11.5 (*c* 1.00, MeOH) Thermal stability = Up to 200°C	19
 T_g (°C) = 107 $[\alpha]_D^{20}$ = +8.9 (*c* 1.00, MeOH) Thermal stability = Up to 188°C	 T_g (°C) = -30 $[\alpha]_D^{20}$ = +21.5 (*c* 1.00, MeOH) Thermal stability = Up to 215°C		19
			32
 $[\alpha]_D^{22}$ = -37.8 (*c* 1.05, $CHCl_3$) Thermal stability = Up to 160°C	 $[\alpha]_D^{22}$ = -44.5 (*c* 1.2, $CHCl_3$) Thermal stability = Up to 160°C		28

CILs having chiral anion and cation	
Structure	**Ref.**
 $[\alpha]_D^{25}$ = +19.0 (c = 1.68, CH_3OH)	10

Pyridinium salts: Liquid crystals			
Structure			**Ref.**
 racemic G –20 I	 racemic and (*R*) G –23 I	 racemic G –17 I	33

 racemic G –30 I	 racemic G –40 I (*R*) G –39 I	 racemic G –1 I (*R*) G –6 I	33
 racemic G 17 I	 racemic N 47 I (*R*) N* 39/45 I	 racemic G 22 Sm 92 I	33
 racemic K 52 Sm 149 I	 racemic Sm 41 N 90 I_{decomp} (Sm_1 50 Sm_2 90 I	 racemic Sm 44/55 I (*R*) N* 35/40 I $[\alpha]^{25}_{546}$ = 1 (*c* 4, $CHCl_3$)	33
 racemic SmC 55 I	 racemic G -25 Sm 92 I	 racemic G –35 I	33
 racemic G –43 I			33
 T_g (°C) = 7 $[\alpha]_D^{22}$ = -4.7 (*c* 1.00, $CHCl_3$)			24

Imidazolium salts: Liquid crystals			
Structure			**Ref.**
 T_g (°C) = -57 $[\alpha]_D^{22}$ = -1.4 (*c* 1.00, $CHCl_3$)	 T_g (°C) = -52 $[\alpha]_D^{22}$ = -2.2 (*c* 1.00, $CHCl_3$)	 T_g (°C) = -57 $[\alpha]_D^{22}$ = -1.1 (*c* 1.00, $CHCl_3$)	24

 T_g (°C) = -70 T_m(°C) = 6 $[\alpha]_D^{22}$ = -1.0 (*c* 1.00, $CHCl_3$) Cr→I	 T_m(°C) = 9 T_c(°C) = 45 $[\alpha]_D^{22}$ = -0.9 (*c* 1.00, $CHCl_3$) Mesogenic→I	 T_c(°C) = 41 $[\alpha]_D^{22}$ = -0.4 (*c* 1.00, $CHCl_3$) Cr→I	24
 T_g (°C) = -73 $[\alpha]_D^{22}$ = -1.2 (*c* 1.00, $CHCl_3$)		 T_m (°C) = 7 $[\alpha]_D^{22}$ = -1.0 (*c* 1.00, $CHCl_3$)	24
 T_g(°C) = -56			24

References

1. March, J. *Advanced Organic Chemistry*; Mc-Graw-Hill: New York, 1977; pp 106–108.
2. For a review on NMR chiral solvating agents, see: (a) Pirkle, W. H.; Hoover, D. J. *Top. Stereochem.* **1982**, *13*, 263–331; (b) Parker, D. *Chem. Rev.* **1991**, *91*, 1441–1457.
3. (a) Pazos, Y.; Leiro, V.; Seco, J. M.; Quinoa, E.; Rigueira, R. *Tetrahedron: Asymmetry* **2004**, *15*, 1825–1829; For NMR databases in chiral solvents, see: (b) Kobayashi, Y.; Hayashi, N.; Kishi, Y. *Org. Lett.* **2002**, *4*, 411–414, and references cited therein.
4. Seebach, D.; Oei, H. A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 634–636.
5. (a) Ulbert, O.; Szarka, Á; Halasi, S.; Somogyi, B.; Bélafi-Bakó, K.; Gubicza, L. *Biotechnol. Tech.* **1999**, *13*, 299–302; see also (b) March, J.; Smith, M. B. In *Advanced Organic Chemistry*; Wiley Interscience, 2001; p 150; (c) Verbit, L.; Halbert, T. R.; Patterson, R. B. *J. Org. Chem.* **1975**, *40*, 1649–1650.
6. (a) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A.-C.; Plaquevent, J. C. *Tetrahedron: Asymmetry* **2003**, *14*, 3081–3093; (b) Handy, S. T. *Chem. Eur. J.* **2003**, *9*, 2938–2944; (c) Freemantle, M. *Chem. Eng. News* **2004**, *82*, 44–49; (d) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015–1060; (e) Ding, J.; Armstrong, D. W. *Chirality* **2005**, *17*, 281–292.
7. (a) Dupont, J.; Suarez, P. A. Z.; de Souza, R. F.; Burrow, R. A.; Kintzinger, J. P. *Chem. Eur. J.* **2000**, *6*, 2377–2381; (b) Hagiwara, R.; Ito, Y. *J. Fluorine Chem.* **2000**, *105*, 221–227; (c) Schröder, U.; Wadhawan, J. D.; Compton, R. G.; Marken, F.; Suarez, P. A. Z.; Consorti, C. S.; de Souza, R. F.; Dupont, J. *New J. Chem.* **2000**, *24*, 1009–1015.
8. Earle, M. J.; McCormac, P. B.; Seddon, K. R. *Green Chem.* **1999**, *1*, 23–25.
9. Fukumoto, K.; Yoshizawa, M.; Ohno, H. *J. Am. Chem. Soc.* **2005**, *127*, 2398–2399.
10. Machado, M. Y.; Dorta, R. *Synthesis* **2005**, 2473–2475.
11. (a) Wasserscheid, P.; Bösmann, A.; Bolm, C. *Chem. Commun.* **2002**, 200–201; (b) Bösmann, A.; Wasserscheid, P.; Bolm, C.; Keim, W. DE10003708, 2001.
12. Vo-Thanh, G.; Pégot, B.; Loupy, A. *Eur. J. Org. Chem.* **2004**, 1112–1116.
13. Tao, G.-H.; He, L.; Sun, N.; Kou, Y. *Chem. Commun.* **2005**, 3562–3564.
14. Bao, W.; Wang, Z.; Li, Y. *J. Org. Chem.* **2003**, *68*, 591–593.
15. Clavier, H.; Boulanger, L.; Audic, N.; Toupet, L.; Mauduit, M.; Guillemin, J.-C. *Chem. Commun.* **2004**, 1224–1225.
16. (a) Levillain, J.; Dubant, G.; Abrunhosa, I.; Gulea, M.; Gaumont, A.-C. *Chem. Commun.* **2003**, 2914–2915; (b) Brégeon, D.; Levillain, J.; Guillen, F.; Plaquevent, J.-C.; Gaumont, A.-C. *ACS Symposium Series*, in press.; (c) Gaumont, A.-C. cited in *Chem Eng. News*, **2004**, *82*, 44–49.
17. Abrunhosa, I.; Gulea, M.; Levillain, J.; Masson, S. *Tetrahedron: Asymmetry* **2001**, *12*, 2851–2859.
18. Génisson, Y.; Lauth-de Viguerie, N.; André, C.; Baltas, M.; Gorrichon, L. *Tetrahedron: Asymmetry* **2005**, *16*, 1017–1023.
19. Patrascu, C.; Sugisaki, C.; Mintogaud, C.; Marty, J.-D.; Génisson, Y.; Lauth de Viguerie, N. *Heterocycles* **2004**, *63*, 2033–2041.
20. Kitazume, T. U.S. 0,031,875, 2001.
21. Jodry, J. J.; Mikami, K. *Tetrahedron Lett.* **2004**, *45*, 4429–4431.
22. Wang, Z.; Wang, Q.; Zhang, Y.; Bao, W. *Tetrahedron Lett.* **2005**, *46*, 4657–4660.
23. (a) Malhotra, S. et al.; *ACS Symposium Series*, in press; (b) ACS meeting, Philadelphia, August 2004; (c) Malhotra, S. cited in *Chem Eng. News* **2004**, *82*, 44–49; (d) http://www.library.njit.edu/etd/njit-etd2003-103/njit-etd2003-103.html.
24. Tosoni, M.; Laschat, S.; Baro, A. *Helv. Chim. Acta* **2004**, *87*, 2742–2749.
25. Ding, J.; Desikan, V.; Han, X.; Xiao, T. L.; Ding, R.; Jenks, W. S.; Armstrong, D. W. *Org. Lett.* **2005**, *7*, 335–337.
26. Pernak, J.; Feder-Kubis, J. *Chem. Eur. J.* **2005**, *11*, 4441–4449.
27. Ma, H.-Y.; Wan, X.-H.; Chen, X.-F.; Zhou, Q.-F. *Chin. J. Polym. Sci.* **2003**, *21*, 265–270.
28. Drahonovsky, D.; Labat, G. C.; Sevcik, J.; von Zelewsky, A. *Heterocycles* **2005**, *65*, 2169–2179.
29. Howarth, J.; Hanlon, K.; Fayne, D.; McCormac, P. *Tetrahedron Lett.* **1997**, *38*, 3097–3100.
30. Harlow, K. J.; Hill, A. F.; Welton, T. *Synthesis* **1996**, 697–698.

31. Kim, E. J.; Ko, S. Y.; Dziadulewicz, E. K. *Tetrahedron Lett.* **2005**, *46*, 631–633.
32. Fringuelli, F.; Pizzo, F.; Tortoioli, S.; Vaccaro, L. *J. Org. Chem.* **2004**, *69*, 7745–7747.
33. Baudoux, J.; Judeinstein, P.; Cahard, D.; Plaquevent, J. C. *Tetrahedron Lett.* **2005**, *46*, 1137–1140.
34. Ishida, Y.; Miyauchi, H.; Saigo, K. *Chem. Commun.* **2002**, 2240–2241.
35. Ishida, Y.; Sasaki, D.; Miyauchi, H.; Saigo, K. *Tetrahedron Lett.* **2004**, *45*, 9455–9459.
36. See for example: Antonietti, M.; Kuang, D.; Smarsly, B.; Zhou, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 4988–4992.
37. Dupont, J. *J. Braz. Chem. Soc.* **2004**, *15*, 341–350.
38. Elaiwi, A.; Hitchcock, S. B.; Seddon, K. R.; Srinivasan, N.; Tan, Y. M.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1995**, *21*, 3467–3472.
39. Pégot, B.; Vo-Thanh, G.; Loupy, A. *Tetrahedron Lett.* **2004**, *45*, 6425–6428.
40. Kiss, L.; Kurtan, T.; Antus, S.; Brunner, H. *Arkivoc* **2003**, *5*, 69–76.
41. Biedron, T.; Kubisa, P. *Polym. Int.* **2003**, *52*, 1584–1588.
42. Biedron, T.; Kubisa, P. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 3454–3459.
43. Ding, J.; Welton, T.; Armstrong, D. W. *Anal. Chem.* **2004**, *76*, 6819–6822.
44. (a) Abdallah, D. J.; Robertson, A.; Hsu, H.-F.; Weiss, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 3053–3062; (b) Bradley, A. E.; Hardacre, C.; Holbrey, J. D.; Johnston, S.; McMath, S. E.; Nieuwenhuyzen, M. *Chem. Mater.* **2002**, *14*, 629–635.