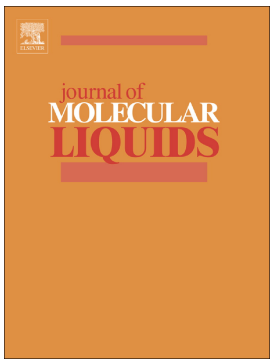

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Synthesis, Characterization and Applications of Some Novel DMAP-based Chiral Ionic Liquids

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Abstract

A convenient and efficient procedure for the synthesis of some novel chiral ionic liquids (CILs) from 4-dimethylaminopyridinium cation has been reported. The synthesis of the CILs includes the treatment of optically active (-)-menthyl ester with 4-dimethylaminopyridine and after that the anion exchange reactions in water. The synthesized ionic salts have been characterized using polarimetry, NMR spectroscopy and EI-MS techniques. The synthesized CIL was used in chiral recognition of Mosher's acid by ^{1}H NMR and also to induce the enantioselectivity in the sodium borohydride reduction of some prochiral ketones.

Keywords: Chiral Ionic Liquids; Asymmetric reduction; Enantiomeric excess; Chirality; Chiral recognition.

1. Introduction

Ionic liquids (ILs), due to their non-volatility, have appeared as the lucrative alternative to the volatile organic compounds [1-3]. These compounds exhibit several peculiar properties such as low vapour pressure, wide electrochemical potential window, solvent and catalytic potential, reusability etc [4-5]. The most commonly synthesized ILs are N,N-dialkyl imidazolium, N-alkyl pyridinium, tetra-alkyl phosphonium and tetra-alkyl ammonium salts. ILs are composed of ions only and are very important in the field of organic synthesis and catalysis [6-7], analytical techniques [8-10], energy storage [11-12] and biotechnology [13] etc.

CILs are the compounds which consist of any sort of chirality in the cation or anion or in both cation and anion. They possess all the above-quoted properties of the ionic liquids and are further important due to their chiral discrimination properties. They exhibit prominent applications in asymmetric synthesis and organocatalysis [14-17], polymerization [18-19], resolution of racemates [20-21] etc. In some cases, CILs provide better results in catalysis than enzyme and transition-metal based catalysts. Their most advantageous property is that they can be recovered and reused in the reaction procedures [22-23]. These can be used as chiral additives and/or chiral stationary phase in advanced analytical methods such as liquid/gas chromatography [24-25] and capillary electrophoresis [26-27]. One can aim at the synthesis of CILs either from the chiral pool or by asymmetric synthetic methods. The chiral pool based synthesis is preferable because of the availability of the inexpensive chiral building blocks.

Chiral recognition is a diastereomeric interaction between a chiral selector and the two enantiomers of the racemate which leads to their enantiodifferentiation. Chiral recognition plays an important role in the determination of absolute configuration and chirality transfer

mechanisms. CILs are also important in chiral recognition of numerous compounds using spectroscopic methods [28-31].

The synthesis and separation of the chiral molecules is an important aspect of chemistry and biology. The chiral secondary alcohols are valuable compounds in pharmaceutics and agrochemicals. Many reports about the synthesis of these scaffolds using metal and biocatalysts can be found in the recent literature [32-34]. CILs are also important in context to the synthesis of these compounds [35-37]. We have already reported the synthesis of some CILs from the natural chiral materials for their application in asymmetric sodium borohydride reduction [38-40].

In this report, we have provided a straightforward method for the synthesis of DMAP-based CILs and also studied their application in chiral molecular recognition and enantioselective sodium borohydride reduction reactions. Although there are some examples about the synthesis of simple ionic liquids from DMAP moiety [41-42], to the best of our knowledge, it is the first report about the synthesis of CILs from DMAP. The easily available and cheap starting materials; very moderate reaction conditions and excellent yields are the advantageous points of these CILs. Moreover, these CILs are also valuable due to their multifaceted applications in chiral recognition and organocatalysis.

2. Experimental

2.1 Materials and methods

All the chemicals were purchased from Sigma-Aldrich, Acros Organics, Alfa Aesar and LOBA Chemie and were used as such unless stated otherwise. The solvents were dried using appropriate drying techniques. The pre-coated Merck TLC silica gel 60 sheets were used to monitor the progress of all the reactions. Optical rotation values were measured on Anton Paar

polarimeter MCP 500 at 589 nm using a cell of length 1 dm at room temperature. Melting points of all the synthesized compounds were determined by using a digital melting point apparatus and are reported as such. The mass spectra were taken on a Shimadzu GCMS-QP 2010 Ultra in electron ionization (EI) mode. ^{1}H, ^{13}C, ^{11}B and ^{31}P NMR spectra of all the salts were taken on a Bruker Advance II, 400 MHz NMR spectrometer. In chiral recognition experiments, ^{1}H NMR spectra were recorded on a 400 MHz JEOL ECS instrument. The enantiomeric excess of the synthesized secondary alcohols has been determined by using GC-FID analysis using a Shimadzu GCMS-QP 2010 Ultra in split mode. Before injection, samples were dissolved in HPLC grade methanol and passed through a 0.22 μm syringe filters.

2.2 Procedure for the quaternization reaction (Synthesis of CIL 2)

The synthesis of (-)-menthyl chloroacetate has been carried out according to our previously reported procedure [38]. Next, to a solution of 4-dimethylaminopyridine (4 mmol, 489 mg), an equimolar quantity of (-)-menthyl chloroacetate was added. The reaction mixture was then refluxed at 70 ^{o}C. The progress of the reaction was checked by TLC (chloroform:methanol). After completion of the reaction, 15 ml of 1 N sulphuric acid was added and the product extraction was carried out using dichloromethane (3×10). The combined dichloromethane layers were then dried over anhydrous Na_2SO_4. Finally, the solvent was removed in vaccuo and the CIL **2** was obtained in good yield (78%).

2.2.1 4-(dimethylamino)-1-(2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-2-oxoethyl)-pyridinium chloride (2)

Produced as white solid in 78% yield, mp: 242-244 ^{o}C, $[\alpha]_D^{25}$= -45.9^{o} (*c* 0.25, MeOH), ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.47-8.45 (d, 2H, J=7.52, Ar), 6.96-6.94 (d, 2H, J=7.52, Ar), 5.57-5.52 (d, 1H, J=17.52, -NCH_2), 5.41-5.36 (d, 1H, J=17.52, -NCH_2), 4.79-4.72 (td, 1H, J=4.44 and J=6.48,

-OCH), 3.28 (s, 6H, -N(CH_3)$_2$), 2.03-2.0 (m, 1H), 1.86-1.82 (m, 1H), 1.70-1.66 (m, 2H), 1.46-1.39 (m, 2H), 1.10-1.01 (m, 2H), 0.91-0.85 (m, 7H, isopropyl group of menthol), 0.75-0.73 (d, 3H, J=6.92 methyl group of the menthol). ^{13}C NMR ($CDCl_3$, 100MHz): δ 166.84, 156.54, 143.86 107.68, 57.56, 46.77, 40.63, 40.52, 33.95, 31.45, 26.07, 23.15, 21.93, 20.85, 16.17. EI-MS: m/z = 319(M^+_{cation}), m/z = 289(M^+_{cation}-2CH_3).

2.3 General procedure for the synthesis of CILs (3-7)

The synthesized chloride salt (2 mmol) was dissolved in 15-20 ml of distilled water and small excess of the various sodium or potassium salts has been added. The reaction mixture was then stirred overnight at room temperature. The products were extracted with dichloromethane and dried over anhydrous Na_2SO_4. The solvent was evaporated using a rotary evaporater to afford excellent yields of the CILs (**3-7**).

2.3.1 4-(dimethylamino)-1-(2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-2-oxoethyl)-pyridinium tetrafluoroborate (3)

Produced as off-white solid in 92% yield. mp: 134-138 ^{o}C, $[\alpha]_D^{25}$= -41.6^o (*c* 0.25, MeOH), ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.96-7.94 (d, 2H, J=7.52, Ar), 6.88-6.86 (d, 2H, J=7.56, Ar), 4.95 (s, 2H, -NCH_2), 4.79-4.73 (td, 1H, J=4.44 and J=6.52, -OCH), 3.24 (s, 6H, -N(CH_3)$_2$), 2.03-2.0 (m, 1H), 1.90-1.81 (m, 1H), 1.70-1.66 (m, 2H), 1.47-1.36 (m, 2H), 1.09-0.98 (m, 2H), 0.91-0.85 (m, 7H, isopropyl group of menthol), 0.75-0.73 (d, 3H, J=6.92, methyl group of the menthol). ^{13}C NMR ($CDCl_3$, 100MHz): δ 166.91, 156.53, 143.07, 107.67, 57.50, 46.80, 40.47, 40.28, 33.95, 31.44, 26.06, 23.18, 21.93, 20.78, 16.12. ^{11}B NMR ($CDCl_3$, 400MHz): δ -1.00 (s). EI-MS: m/z = 319(M^+_{cation}), m/z = 289(M^+_{cation}-2CH_3).

2.3.2 4-(dimethylamino)-1-(2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-2-oxoethyl)-pyridinium hexafluorophosphate (4)

Produced as off-white solid in 89% yield. mp: 126-130 ^{o}C, $[\alpha]_D^{25}$= -39.1^{o} (*c* 0.25, MeOH), ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.86-7.84 (d, 2H, J=7.68, Ar), 6.84-6.82 (d, 2H, J=7.72, Ar), 4.86 (s, 2H, -NCH_2), 4.79-4.73 (td, 1H, J=4.44, and J=6.48, -OCH), 3.23 (s, 6H, -$N(CH_3)_2$), 2.00-1.99 (m, 1H), 1.84-1.80 (m, 1H), 1.71-1.66 (m, 2H), 1.47-1.37 (m, 2H), 1.10-1.01 (m, 2H), 0.91-0.85 (m, 7H, isopropyl group of menthol), 0.75-0.73 (d, 3H, J=6.92, methyl group of the menthol). ^{13}C NMR ($CDCl_3$, 100MHz): δ 166.22, 156.52, 142.76, 107.67, 57.48, 46.78, 40.40, 40.29, 33.93, 31.44, 26.06, 23.17, 21.90, 20.75, 16.07. ^{31}P NMR ($CDCl_3$, 400MHz): δ -131.16-157.56 (hept). EI-MS: m/z = 319(M^+_{cation}), m/z = 289(M^+_{cation}-2CH_3).

2.3.3 4-(dimethylamino)-1-(2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-2-oxoethyl)-pyridinium hexafluoroantimonate (5)

Produced as off-white solid in 86% yield. mp: 104-106 ^{o}C, $[\alpha]_D^{25}$= -30.6^{o} (*c* 0.25, MeOH), ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.88-7.86 (d, 2H, J=7.68, Ar), 6.85-6.83 (d, 2H, J=7.68, Ar), 4.89 (s, 2H, -NCH_2), 4.79-4.73 (td, 1H, J=4.44, and J=6.48, -OCH), 3.22 (s, 6H, -$N(CH_3)_2$), 2.03-2.00 (m, 1H), 1.84-1.80 (m, 1H), 1.70-1.66 (m, 2H), 1.47-1.38 (m, 2H), 1.10-0.98 (m, 2H), 0.93-0.82 (m, 7H, isopropyl group of menthol), 0.75-0.73 (d, 3H, J=6.92, methyl group of the menthol). ^{13}CNMR ($CDCl_3$, 100MHz): δ 166.43, 156.56, 142.84, 107.76, 57.64, 46.78, 40.46, 40.30, 33.93, 31.44, 26.13, 23.18, 21.96, 20.76, 16.10. EI-MS: m/z = 319(M^+_{cation}), m/z = 289(M^+_{cation}-2CH_3).

2.3.4 4-(dimethylamino)-1-(2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-2-oxoethyl)-pyridinium bromoethanesulfonate (6)

Produced as off-white solid in 87% yield. mp: 138-142 ^{o}C, $[\alpha]_D^{25}$= -37.1^{o} (*c* 0.25, Acetone), ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.23-8.21 (d, 2H, J=7.68, Ar), 6.93-6.91 (d, 2H, J=7.68, Ar), 5.24-5.11 (q, 2H, J=17.76 and J=16.56, -NCH_2), 4.80-4.74 (td, 1H, J=4.44 and J=6.48, -OCH), 3.74-3.70 (m, 2H), 3.32-3.28 (m, 2H), 3.27 (s, 6H, -$N(CH_3)_2$), 2.03-2.00 (m, 1H), 1.85-1.81 (m, 1H),

1.71-1.67 (m, 2H), 1.48-1.38 (m, 2H), 1.11-0.99 (m, 2H), 0.93-0.84 (m, 7H, isopropyl group of menthol), 0.76-0.74 (d, 3H, J=6.96, methyl group of the menthol). ^{13}C NMR ($CDCl_3$, 100MHz): δ 166.70, 156.54, 143.70, 107.71, 57.66, 54.58, 46.74, 40.60, 40.43, 33.91, 31.44, 29.69, 26.67, 26.13, 23.17, 21.94, 20.81, 16.18. EI-MS: m/z = 319(M^+_{cation}), m/z = 289(M^+_{cation}-2CH_3).

2.3.5 4-(dimethylamino)-1-(2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-2-oxoethyl)-pyridinium trifluoromethanesulfonate (7)

Produced as semi-solid in 87% yield, $[\alpha]_D^{25}$= -28.6^o (*c* 0.25, MeOH), ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.86-7.84 (d, 2H, J=7.76, Ar), 6.84-6.82 (d, 2H, J=7.40, Ar), 5.04 (s, 2H, -NCH_2), 4.80-4.73 (td, 1H, J=4.44, and J=6.48, -OCH), 3.24 (s, 6H, -$N(CH_3)_2$), 2.02-1.99 (m, 2H), 1.84-1.80 (m, 1H), 1.71-1.67 (m, 2H), 1.45-1.37 (m, 2H), 1.09-1.01 (m, 2H), 0.92-0.85 (m, 7H, isopropyl group of menthol), 0.75-0.73 (d, 3H, J=6.92, methyl group of the menthol). ^{13}C NMR ($CDCl_3$, 100MHz): δ 166.43, 156.57, 143.33, 107.74, 57.66, 46.78, 40.50, 40.44, 33.93, 31.44, 29.71, 26.10, 23.16, 21.91, 20.76, 16.10. EI-MS: m/z = 319(M^+_{cation}), m/z = 289(M^+_{cation}-2CH_3).

2.4 Procedure for the reduction of ketones in the presence of CILs:

The asymmetric sodium borohydride reduction has been carried out according to our previously reported procedure [39]. The GC chromatograms of synthesized secondary alcohols are given in the supplementary information file.

(-)-1-Phenylethanol: GC analysis-Rt-βDEXsm column, split mode, carrier gas helium, makeup gas helium, column oven temperature= 120 ^{o}C, injection temperature 230 ^{o}C, flow rate 0.80 mL/ min, t_{R1} = 11.93 min; t_{R2}= 12.10 min.

(-)-1-(4-Bromophenyl)-ethanol: GC analysis-Rt-βDEXsm column, split mode, carrier gas helium, makeup gas helium, column oven temperature= 120 ^{o}C, injection temperature 230 ^{o}C, flow rate 0.80 mL/min, t_{R1} = 19.60 min; t_{R2}= 19.71 min.

(-)-1-(4-Hydroxyphenyl)-ethanol: GC analysis-Rt-βDEXsm column, split mode, carrier gas helium, makeup gas helium, column oven temperature= 120 ^{o}C, injection temperature 230 ^{o}C, flow rate 0.80 mL/min, t_{R1} = 15.80 min; t_{R2}= 15.89 min.

(-)-1-(4-Methoxyphenyl)-ethanol: GC analysis-Rt-βDEXsm column, split mode, carrier gas helium, makeup gas helium, column oven temperature= 120 ^{o}C, injection temperature 230 ^{o}C, flow rate 1.30 mL/min, t_{R1} = 16.00 min; t_{R2}= 16.07 min.

(-)-1-(4-Chlorophenyl)-ethanol: GC analysis-Rt-βDEXsm column, carrier gas helium, column oven temperature= 120 ^{o}C, injection temperature 230 ^{o}C, flow rate 0.80 mL/min, t_{R1} = 16.64 min; t_{R2}= 16.73 min.

(-)-1-(4-Methylphenyl)-ethanol: GC analysis-Rt-βDEXsm column, split mode, carrier gas helium, makeup gas helium, column oven temperature= 120 ^{o}C, injection temperature 230 ^{o}C, flow rate 0.80 mL/min, t_{R1} = 15.05 min; t_{R2}= 15.21 min.

(-)-1-(2-Hydroxyphenyl)-ethanol: GC analysis-Rt-βDEXsm column, split mode, carrier gas helium, makeup gas helium, column oven temperature= 120 ^{o}C, injection temperature 230 ^{o}C flow rate 1.30 mL/min, t_{R1} = 16.02 min; t_{R2}= 16.09 min.

(-)-2,3-Dihydro-1H-inden-1-ol: GC analysis-Rt-βDEXsm column, split mode, carrier gas helium, makeup gas helium, column oven temperature= 120 ^{o}C, injection temperature 230 ^{o}C, flow rate 0.80 mL/min, t_{R1} = 14.46 min (100% ee).

2.5 Procedure for the enantiomeric recognition using Mosher's acid salt

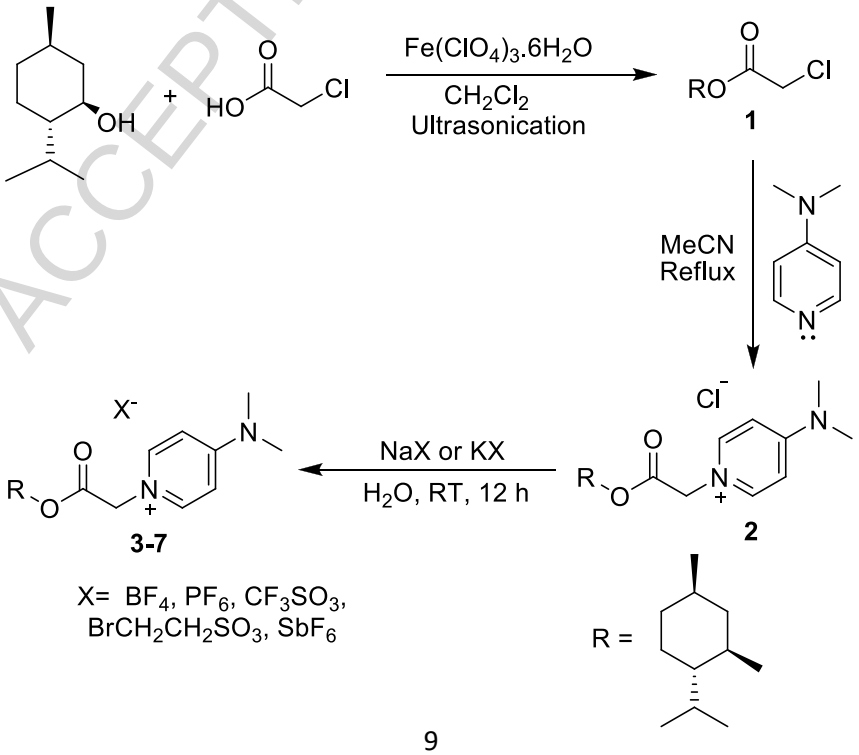
For recognition experiment, 10.2 mg (0.04 equivalent) of racemic Mosher's acid sodium salt was added to 42.6 mg (0.12 equivalent) of CIL **2,** taken in a RBF. Then water was added and the mixture was stirred overnight for anion exchange. After that, water was removed in vacuo and

the resultant solid was dissolved in a mixture of $CDCl_3$ and DMSO-d6 then filtered to take the NMR spectrum.

3. Results and discussion

3.1 Synthesis and characterization of the CILs

In continuation to our efforts towards the synthesis and applications of new CILs from the natural available chiral precursors [14, 38-40, 43]; herein, we have reported the synthesis and applications of (-)-menthyl ester based CILs. These CILs can be synthesized under very mild conditions, as depicted in the **Scheme 1**, from commercially available (-)-menthol. The synthesis of (-)-menthyl ester was carried out under ultrasonication in the presence of Iron(III)perchlorate hexahydrate [38]. After that, quaternization of DMAP was achieved in acetonitrile. The quaternization reaction of DMAP with (-)-menthyl ester occurs by an S_N1 mechanism. In the last step, anion exchange reactions have been performed at room temperature to produce the CIL (3-7) containing different anions. All the CILs were obtained in excellent yields and the physical properties of the CILs are enlisted in **Table 1**.



Scheme 1: Synthesis of DMAP-based CIL

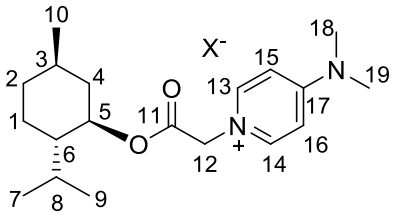
Table 1: Physical properties of the DMAP-based CILs

Entry	CIL	Anion	Physical State	Yield	Mp [^{o}C]	$[\alpha]_D^{25}$(c 0.25)*
1	2	Cl	White solid	78%	242-244	-45.9
2	3	BF_4	Off-white solid	92%	134-138	-41.6
3	4	PF_6	Off-white solid	89%	126-130	-39.1
4	5	SbF_6	Off-white solid	86%	104-106	-30.6
5	6	$BrCH_2CH_2SO_3$	Off-white solid	87%	138-142	-37.1
6	7	CF_3SO_3	Semi-solid	87%	Semi solid	-28.6

*For CIL **6** (entry 5) acetone was used for dilution, for all the other enteries methanol was used

From the above table, it is evident that melting points of these CILs are dependent on the anion size; the salts with larger anions exhibit lower melting points. This can be explained by the fact that with the increase in size, the ions are not closely packed in the lattice thus resulting in the decrease in melting point. The specific rotation values of all the CILs are found to be negative. In the ^{1}H NMR spectra, the downfield signals in case of CIL **2** and **6** reveal the strong coordination of the chloride and bromoethanesulfonate ions with the cationic moieties. An upfield shift of 0.71 and 0.62 ppm has been observed for -NCH_2 protons when Cl^- ion was replaced with PF_6^- and BF_4^- ions respectively. The almost similar trend was seen in the case of CF_3SO_3 and SbF_6 ions. This upfield effect has also been observed in case of the aromatic protons of the DMAP ring and the change in chemical shift is more marked in the case of the protons which are close to the positively charged nitrogen atom of the ring. The effect of various anions on chemical shift values is given in **Table 2.** The similar anion effects have also been reported in the literature [44].

Table 2: Effect of various anions on chemical shift values*

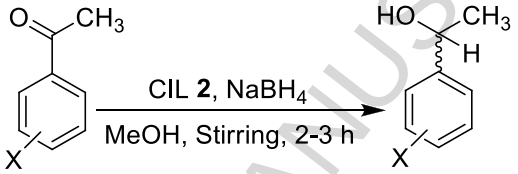


Entry	CIL	Anion	NCH_2 (C12)	Ar-CH (C13, C14)	Ar-CH (C15, C16)
1	2	Cl^-	5.57 (two d)	8.47 (d)	6.96 (d)
2	3	BF_4^-	4.95 (s)	7.96 (d)	6.87 (d)
3	4	PF_6^-	4.86 (s)	7.86 (d)	6.84 (d)
4	5	$CF_3SO_3^-$	5.02 (s)	8.06 (d)	6.90 (d)
5	6	$BrCH_2CH_2SO_3^-$	5.84 (q)	8.23 (d)	6.93 (d)
6	7	SbF_6^-	4.89 (s)	7.88 (d)	6.85 (d)

*chemical shift values in ppm

3.2 Application of the CILs in asymmetric reduction of prochiral ketones

Our previous reports consist of the use of the CILs in asymmetric sodium borohydride reduction of some prochiral substrates to the corresponding enantiopure alcohols [38-40]. Here, we have also employed CIL **2** in the reduction of some acetophenone derivatives (**Scheme 2**).



Scheme 2: Synthesis of optically active alcohols from prochiral ketones using CIL **2**

For the reduction reaction, 1 equivalent of each substrate, 0.1 equivalent of CIL **2** and 1.5 equivalent of sodium borohydride was added and the mixture was stirred at 35 ^oC. The optical purity and percentage yields of the alcohols are mentioned in **Table 3.**

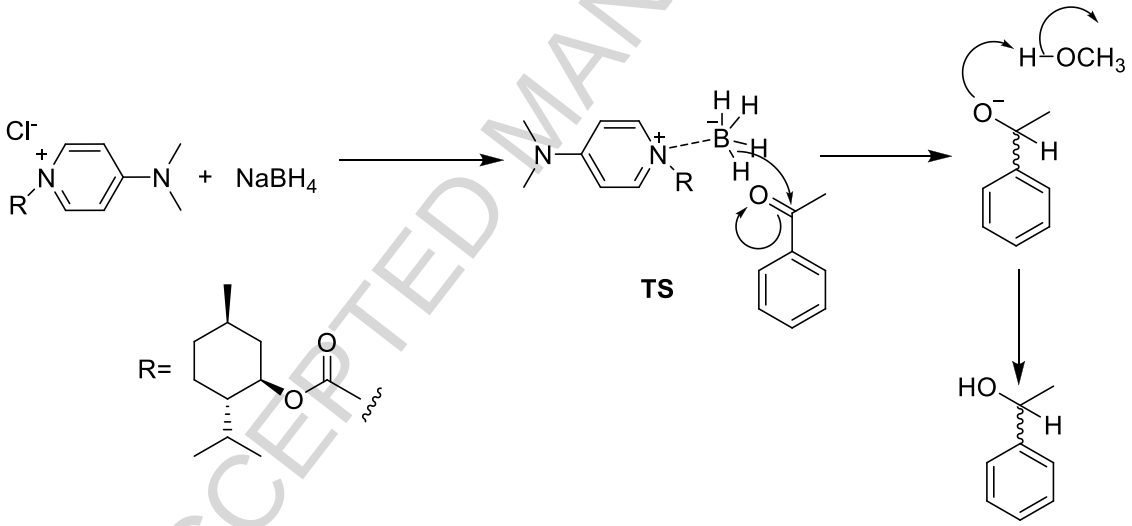
Table 3: Various parameters for the reduction of ketones

Entry	Substrate	Yield (%)	Enantiomeric excess (%)*
1	Acetophenone	76	Rac
2	p-Cl Acetophenone	78	5
3	p-Br Acetophenone	78	10
4	p-OMe Acetophenone	75	13
5	p-OH Acetophenone	72	17
6	p-Me Acetophenone	69	4
7	o-OH Acetophenone	72	8
8	1-Indanone	74	100

*ee values have been determined by GC analysis on a Rt-βDEXsm capillary column

From the **Table 3,** one can find that all the substrates can be converted to the corresponding products in substantial yields. The enantiomeric excess in case of acetophenone, p-methyl acetophenone is very low. For 1-indanone, the enantiomeric excess is very high (100%). The

excellent enantiomeric excess in case of 1-indanone is probably due to the fact that; the carbonyl group in 1-indanone is presnt as a part of the ring system so the hydride attack is favourable from one side only. This favoured attack leads to higher enantiopurity of the corresponding secondary alcohol. The higher enantiomeric excess in case of 1-indanone can also be found in literature reports [36]. In all the other cases moderate enantiomeric excess has been achieved. As shown in **Scheme 3**, we have also proposed a mechanism for the formation of the optically active secondary alcohols. In the proposed transition state (**TS**), there is an interaction between borohydride anion and the quaternary nitrogen atom of the CIL. The hydride transfer from borohydride to the ketonic substrate and subsequent proton abstraction from the solvent yields secondary alcohols.



Scheme 3: Plausible mechanism for the asymmetric reduction

3.3 Application of the CIL 2 in Chiral Recognition by Mosher's acid

Inspired from the induction of chirality in sodium borohydride reduction; we have also employed the CIL **2** in the chiral molecular recognition of Mosher's acid salt. To evaluate the chiral recognition properties of the synthesized CILs sodium salt of Mosher's acid was used. The CILs were treated with Mosher's acid salt to produce diastereomeric complexes. The chiral

recognition mechanism can be explained on the basis of three-point interaction model [45]. As depicted in the Fig. **1** the CILs show different interactions with the enantiomers of Mosher's acid. There is greater possibility of the H-bonding with $–CF_3$ group, in case of *R* enantiomer of the acid than the *S* enantiomer. The selective interactions of the two enantiomers with CILs leads to the recognition of the enantiomers. The splitting of the $–OCH_3$ signal was found to be 12 Hz in case of CIL **2**. The similar results for the splitting of the signal of the $–OCH_3$ group of Mosher's acid have also been reported by Heckel et al using nicotine based CILs [46].

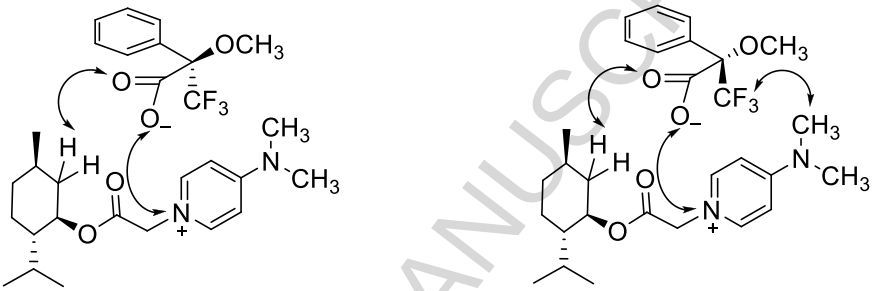


Fig. **1:** Diastereomeric interactions between the two enatiomers of Mosher's acid salt and CILs

4. Conclusions

To summarize, a number of DMAP based CILs have been synthesized in excellent yields under very mild conditions. These CILs have been fully characterized using polarimetry, ^{1}H, ^{13}C, ^{11}B, ^{31}P NMR and EI-MS techniques. The synthesized CIL was successfully employed for the chiral recognition of racemic Mosher's acid salt through NMR spectroscopy. The CIL has also been utilised in the asymmetric reduction of some prochiral ketones using sodium borohydride as a hydrogen source. High yields and low to excellent enantiomeric excess has been obtained in the reduction of the prochiral ketones.

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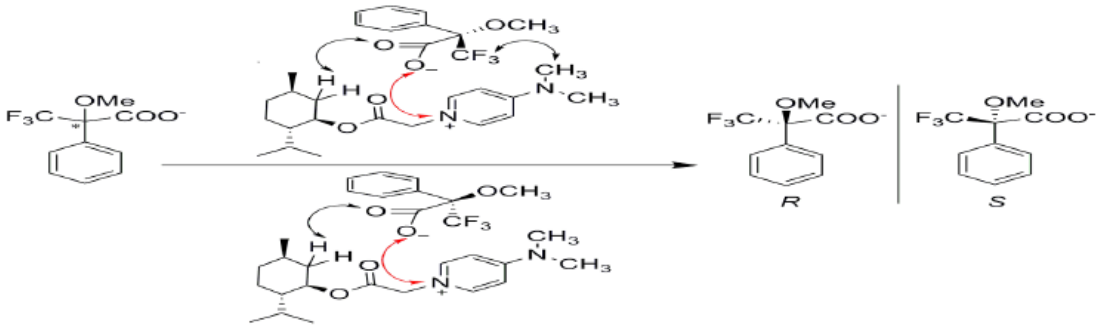

Graphical abstract

Highlights

- Report about the first synthesis of DMAP-based CILs
- A very efficient and simple method for the synthesis of CILs in high yields
- Synthesized CILs were used in enantioselective reductions
- The CILs were also effective in chiral recognition of Mosher's acid salt