THE STEREOCHEMICAL IMPACT

OF

CHIRAL IONIC LIQUIDS ON

[2+2] PHOTOCHEMICAL CYCLOADDITIONS AND ALDOL REACTONS

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ABSTRACT

THE STEREOCHEMICAL OUTCOME
OF
CHIRAL IONIC LIQUIDS IN
[2+2] PHOTOCHEMICAL CYCLOADDITIONS AND ALDOL REACTIONS

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Eight chiral ionic liquids have been prepared for use as solvents to test whether they can induce enantioselectivity in both photochemical [2+2] cycloadditions and aldol reactions using a variety of starting materials. The chiral ionic liquids include 1-butyl-3-methylimidazolium L-lactate (chiral anion), 1-butyl-3-methylimidazolium camphorsulfonate (*R* and *S* chiral anions), 2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate (*R* and *S* chiral cations), 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide (chiral cation), 1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide (chiral cation), and 1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide (chiral cation). The stability of each chiral ionic liquid was tested to ensure they were well suited for both reaction types. To date, the eight chiral ionic liquids have been used as solvents to impart enantioselectivity in 28 photoadditions and 22 aldol reactions. Specific rotations of the purified products have been obtained. Enhanced optical activity was seen when switching from the achiral environment that utilized classical

organic solvents to the chiral environment that utilized chiral ionic liquids as the solvent. Enantiomeric excesses could not be calculated. All products have been characterized by gas chromatography (GC), infrared (IR) spectrometry, mass spectrometry (MS), and most of them by ^{1}H NMR spectroscopy.

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$[\alpha]$	Specific rotation
CIL	Chiral ionic liquid
DMF	*N,N*-Dimethylformamide
ee	Enantiomeric excess
FID	Flame ionization detector
GC	Gas chromatography
IL	Ionic liquid
IR	Infrared spectroscopy
MS	Mass spectrum
NMR	Nuclear magnetic resonance
TLC	Thin-layer chromatography
VOCs	Volatile organic compounds

Chapter One: Chiral Ionic Liquid Review

1.1 Introduction

Ionic liquids (ILs) are organic salt-like materials that are liquid under 100℃ due to poorly coordinated ions. They are typically constituted by large nonasymmetric cations with weakly coordinating organic or inorganic anions. [1] Examples of frequently used cations include imidazolium, pyridinium, pyrrolidinium, ammonium, and phosphonium. Examples of frequently used coordinating anions include tetrafluoroborate, hexafluorophosphate, lactate, camphorsulfonate, and bistriflateimide. This unique interaction allows ILs to function as an attractive medium for many synthetic and chemical processes. [2]

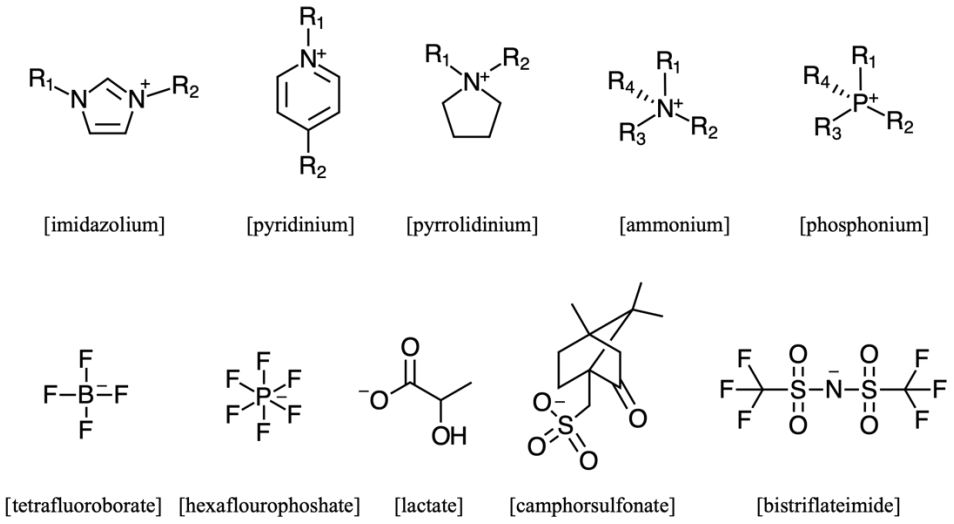


Figure 1. Common cations and anions in ILs. [2]

A novel property of ILs is that they are "designer solvents" allowing them to be modulated to suit specific reaction conditions. Their physical properties can be tuned to optimize yield, substrate solubility, product separation and even enantioselectivity. Altering either the cation, anion, or their substituents, allows for manipulation of properties such as polarity, hydrophobicity, viscosity, and solvent miscibility. [3] For instance, it was demonstrated that an IL consisting of the cation 1-alkyl-3-alkylimidazolium and the anion PF_6^- can be made more

soluble in water by replacing the anion with BF_4^-. Conversely, replacement of the anion with Tf_2N^- dramatically decreases the solubility of the IL in water. Another example demonstrated that hydrophobicity may be altered in an IL by changing the chain length of the cation or the identity of the anion. By changing the 1-alkyl chain on 1-alkyl-3-methyl-imidazolium hexafluorophosphate from one carbon in length to nine carbons results in the IL changing from being soluble in water to very insoluble. [4] A decrease in the IL melting point can be achieved in two ways. First, asymmetry can be introduced on the cation of the IL by adding longer or shorter chains. Second, the longer chains of the IL can be branched, which results in poorer packing of the material, therefore, lower melting points. [5]

The history of ILs dates back to the early 1900s. The first low-melting salt, ethylammonium nitrate, was proposed by Walden in 1914. [6] It had a low melting point of 12℃. During the 1970s and 1980s, ILs were mostly studied for their applications in electrochemistry. [4] These studies focussed on their properties such as good ionic conductivity, a wide electrochemical potential window, high viscosities, high thermal stabilities, and tunable solvent properties. [7] Their application to organic synthesis was first proposed by Fry and Pienta, and Boon et al. [8,9] In the 1990s, the name room-temperature ILs was assigned to describe these molten salts. It was estimated by Earle and Seddon that the number of possible ILs must be in the order of 1 billion. [4] In 1992, ILs became a trending topic when Wilkes and Zaworotko reported the synthesis of imidazolium-based salts, which demonstrated unique and desirable properties. Using imidazolium as the cation in ILs provides salts with low melting points, good chemical and thermal stabilities, and favourable viscosities. These properties directly improve the ILs reusability and thus, make imidazolium a frequently used cation. [10]

1.2 ILs as Green Solvents

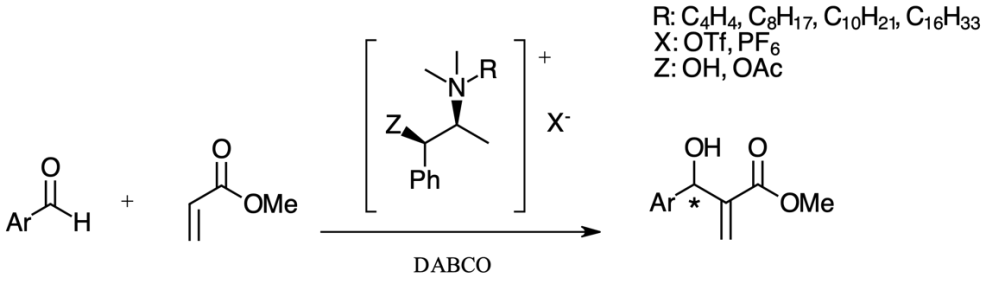
ILs have attracted increasing interest recently for their application in green chemistry due to an increase in environmental consciousness in chemical research and industry. ILs have emerged as a promising, environmentally friendly alternative to traditional organic solvents. Traditional solvents are volatile and pose many negative health effects and environmental concerns such as atmospheric emissions and contamination of water effluents. [11,12] ILs have a negligible vapour pressure and thus, do not contribute volatile organic compounds (VOCs) into the atmosphere. This property alone characterizes them as environmentally friendly solvents. Other properties such as their non-flammability, and good chemical and thermal stability also contribute to their environmentally friendly nature. [13] ILs are also advantageous over traditional solvents as they contain a high liquid range up to more than 300 K, they have a density greater than water and can dissolve a wide range of substances. [4,14] As it is an ionic interaction between the cations and anions in the salt that define the properties of these solvents, they are very miscible with a large range of substances with different polarities. Traditional organic solvents have interactions such as hydrogen-bonding, dipole-dipole and van der Waals interactions and thus, contain a limited liquid range and miscibility. [4] Therefore, some processes that can be achieved with ILs are not possible with traditional organic solvents.

Another property of ILs that classifies them as green solvents is their recyclability. This desirable property allows ILs to be recycled and reused a number of times without losing their functionality. The organic components in the flask can be extracted from the IL by the use of a non-polar organic solvent. This property of recyclability can be attributed to their negligible vapour pressure. In research applications, the recycling process of ILs varies from quite poor to very good. [2] The first enantioselective Diels-Alder reaction performed by Doherty at al. in 2007

reported that their imidazolium tagged bis(oxazoline) chiral ionic liquid (CIL) could be reused up to 10 times without losing its functionality. [15] In another Diels-Alder reaction performed by Wang and coworkers in 2010 reported that their 2-pyrrolidinecarboxylic acid-derived CIL could be reused six times without losing its functionality. [16]

1.3 CILs in Asymmetric Synthesis

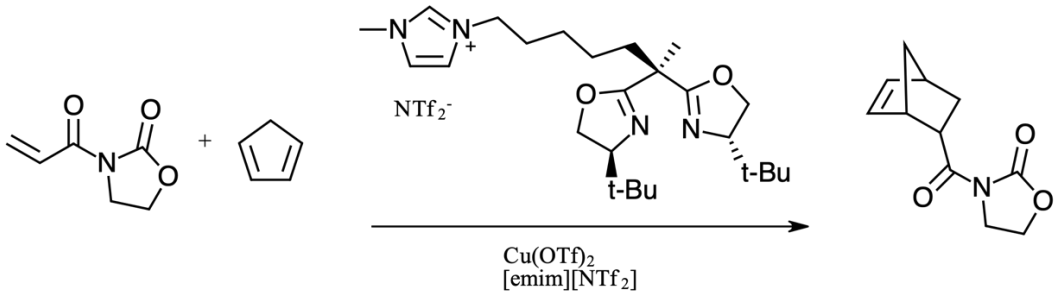
Chiral ionic liquids are ILs that contain a chiral cation and/or a chiral anion. When used as solvents they were found to give unique selectivities and have the potential for chiral discrimination capabilities. The first CIL was synthesized in 1996 by Herrmann et al. during their synthesis of N-heterocyclic carbenes of imidazoles. [17] During these reactions, an imidazolium chloride CIL was produced as an intermediate. The first successful application using a CIL to show selectivity in a reaction was in 2004 by Vo-Thanh and coworkers (**Scheme 1**). [18] They were able to achieve 44% enantiomeric excess in a Baylis-Hillman reaction using an ephedrinium CIL with benzaldehyde and methyl acrylate. The reaction was catalyzed by 1,4-diazabicyclo[2.2.2]octane (DABCO). This was the largest reported enantiomeric excess using CILs in any asymmetric synthesis before 2005.



Scheme 1. Asymmetric Baylis-Hillman reaction using an ephedrinium CIL.

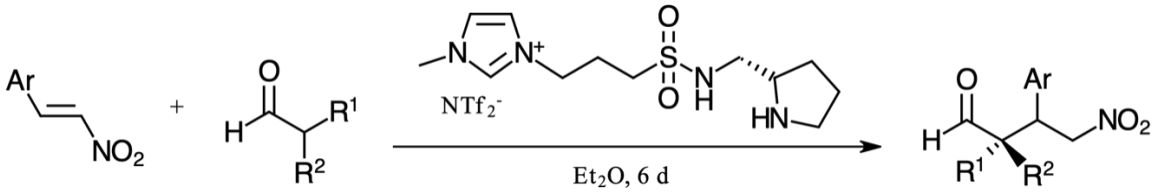
In 2007, Doherty et al. reported the first enantioselective Diels-Alder reaction of *N*-acryloyl- and *N*-crotonyloxazolidinones with cyclopentadiene and 1,3-cyclohexadiene using an imidazolium tagged bis(oxazoline) CIL. Specifically, in a reaction with 3-acryloyl-1,3-oxazolidin-2-one and

cyclopentadiene they were able to achieve 84% enantiomeric excess and endo:exo ratio of 88:12 (Scheme 2). [15]



Scheme 2. Asymmetric Diels-Alder reaction with an imidazolium tagged bis(oxazoline).

In 2007, Headey and coworkers synthesized a pyrrolidine based CIL that successfully induced enantioselectivity in a Michael addition between aldehydes and nitrostyrenes (Scheme 3). They achieved good enantioselectivities of 82% enantiomeric excess and high diastereoselectivies of syn:anti ratio of 97:3. [19]



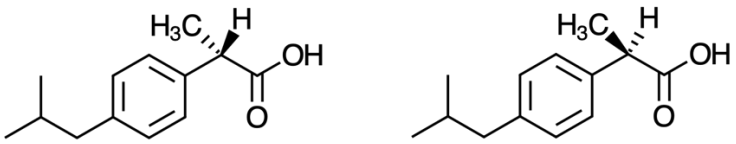
Scheme 3. Asymmetric Michael addition using a pyrrolidine based CIL.

Many other reactions have been reported in literature that used CILs to induce enantioselectivity successfully. These reactions include the asymmetric aldol reaction, enantioselective hydrogenation and the Bignelli reaction. [10]

1.4 Importance of Controlling Stereochemistry

Controlling stereochemistry is very important in drug design. Currently, more than half the drugs in clinical use are chiral. The pharmacological activity of a drug depends mainly on its interaction with the biological target. Although enantiomers have the same physical properties, most enantiomeric pairs of drugs exhibit great differences in their pharmacology. [1] For

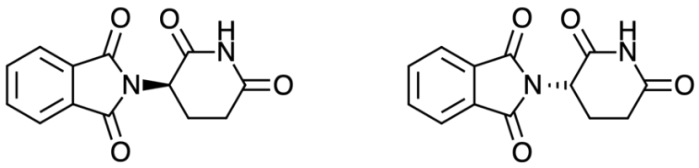
example, it is common that the undesired enantiomer can be biologically inactive. This is exhibited with the well-known painkiller, ibuprofen, where the *S*-enantiomer demonstrates the desired anti-inflammatory and pain-killing effects while the *R*-enantiomer is biologically inactive. [2]



(S)-ibuprofen (R)-ibuprofen

Figure 2. The enantiomers of ibuprofen.

Moreover, the undesired enantiomer can be toxic or have undesirable side-effects. A classic example to illustrate this is the thalidomide disaster in the early 1960's. Thalidomide was a sedative introduced into the market as a racemic mixture. A large population of pregnant women took thalidomide and gave birth to babies with deformities. When taken orally, even if a single enantiomer was present, it epimerized under the acidic conditions in the stomach. It was later discovered the *R*-enantiomer produced the desired sedative effects while the *S*-enantiomer produced the undesired embryo-toxic effects. [3]



(R)-thalidomide (S)-thalidomide

Figure 3. The enantiomers of thalidomide.

Today, it is very difficult to obtain drug approval for a racemic mixture. Typically, only the active enantiomer can be present for the drug to be approved. Racemic mixtures are no longer put out on the market unless both enantiomers are proven safe. Therefore, finding an

efficient way to synthesize only one, or predominately one, enantiomer is very important. Further, being capable of synthesizing only one enantiomer is a greener process, as half of the sample is wasted as the undesired isomer must be removed from the racemic product mixture and discarded.

This literature review demonstrates that enantioselectivity can successfully be imparted on various chemical reactions through the use of CILs as green solvents. The objective of this thesis is to synthesize suitable CILs for use as a solvent to impart enantioselectivity in both photochemical [2+2] cycloadditions and aldol reactions. The synthesis and stability of the chosen CILs will be discussed in Chapter Two. Additionally, two reaction types of interest, photochemical [2+2] cycloadditions and aldol reactions, will be discussed in Chapters Three and Four, respectively.

Chapter Two: Synthesis and Stability of CILs

2.1 Introduction

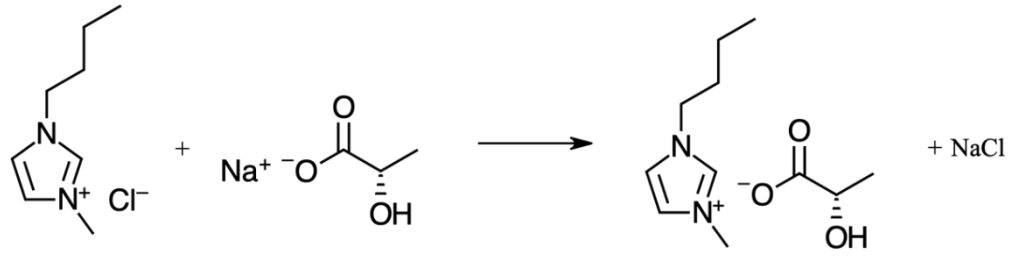
The presence of CILs in the reactions is intended to have multiple roles. The CILs will function as the reaction solvent to provide a recyclable, low volatility alternative to classical organic solvents. The CILs are also being tested for their ability to transfer the solvent chirality to the achiral starting materials, resulting in chiral products. In this capacity they are functioning in place of a chiral catalyst. With this function in mind, the CIL cannot undergo any permanent change during the course of the reaction. Although it is possible the CIL may function to speed up the rate of the reaction, this will not be considered during the course of the study.

The CILs chosen for use were selected by using specific criteria to ensure that they are stable to the different reaction conditions to which they will be subjected. The two reaction types being studied in this thesis are photochemical [2+2] cycloadditions and aldol reactions. Photochemical [2+2] cycloadditions proceed when the reagents are subjected to UV light and, thus, when selecting the CILs for these reactions they must have a UV_{max} value below the transmission cut off for Pyrex (275 nm). This ensures they will not interfere with the [2+2] photochemical reaction being studied by decreasing the light energy available for photoabsorption by the reagents. Furthermore, if the CILs do absorb UV light, their chirality cannot be impacted. Moreover, the aldol reaction requires the use of a base to facilitate the reaction. Optically active compounds containing an acidic hydrogen at the chiral center can be epimerized in the presence of a base. With the optical activity destroyed, the CIL will lose one of its functions. Thus, CILs without an acidic hydrogen at the chiral center were chosen for the aldol reaction. Chiral stability tests were performed on all chiral ionic liquids and are discussed in Chapter 2.2.2.

2.2 Results & Discussion

2.2.1 Synthesis of CILs

Eight chiral ionic liquids have been prepared for use as solvents to test whether they can induce enantioselectivity in both photochemical [2+2] cycloadditions and aldol condensations. Each CIL was synthesized according to literature procedures. The CILs include 1-butyl-3-methylimidazolium L-lactate (**1**, chiral anion) [20] , 1-butyl-3-methylimidazolium camphorsulfonate (**2R** and **2S,** *R* and *S* chiral anions) [20], 2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate (**3R** and **3S**, *R* and *S* chiral cations) [21], 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide (**4**, chiral cation) [22], 1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide (**5**, chiral cation) [23], and 1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide (**6**, chiral cation) [23]. Their respective reaction schemes are as follows:



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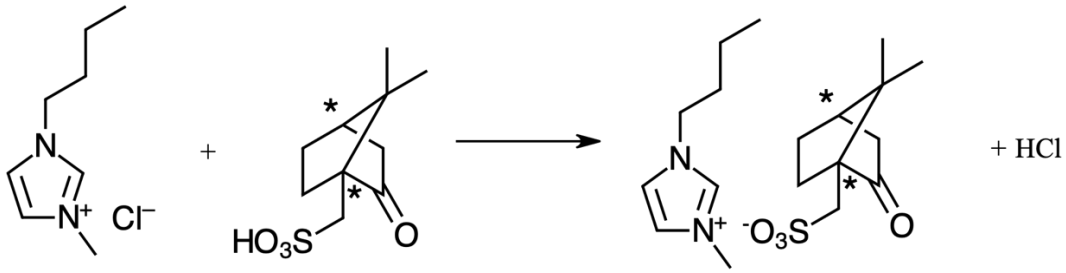
Scheme 4. Reaction scheme of the synthesis of 1-butyl-3-methylimidazolium L-lactate.



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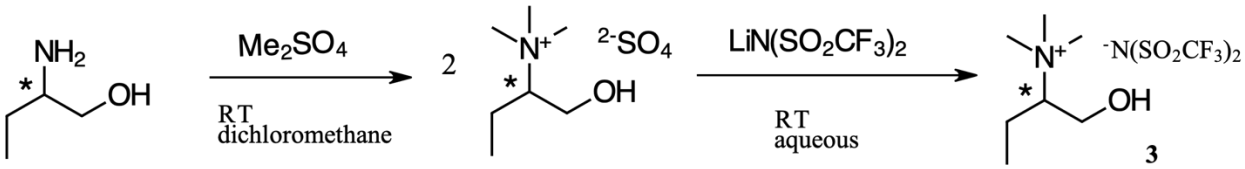
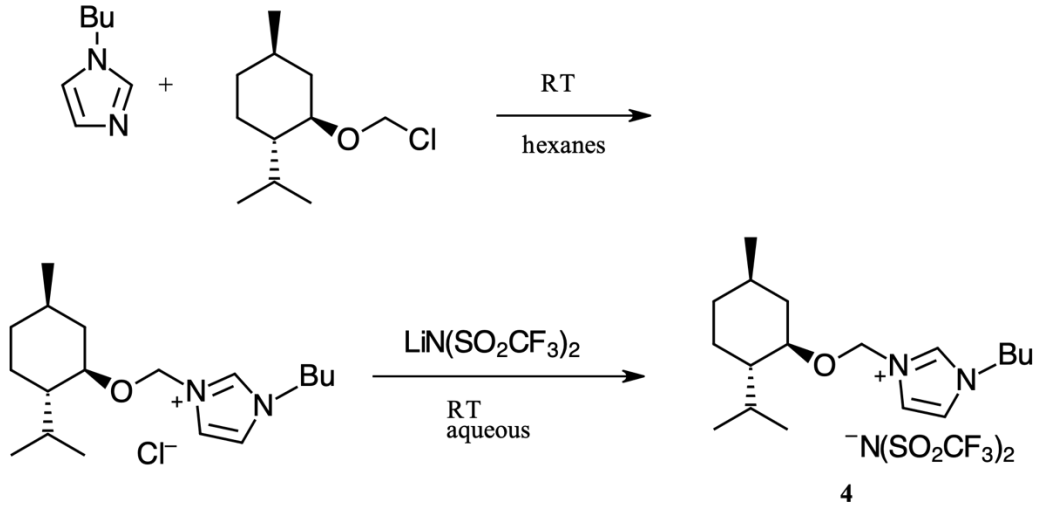
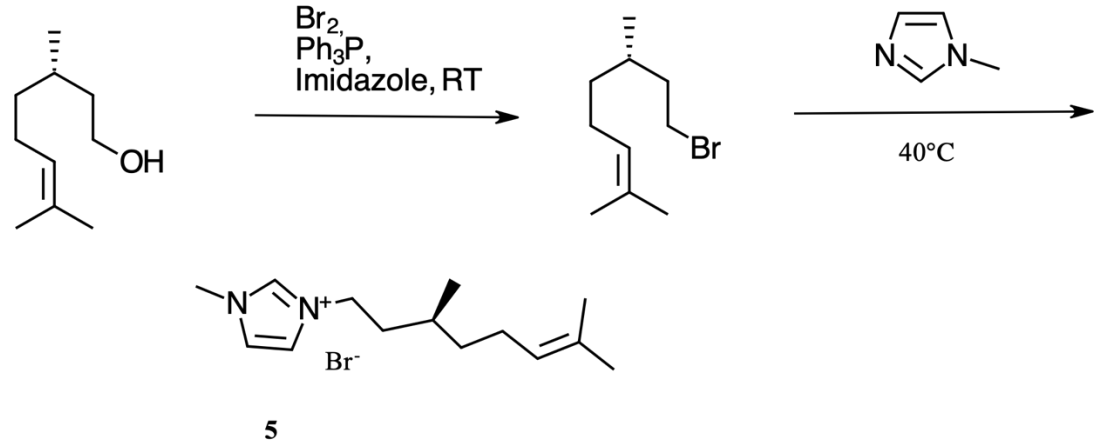
Scheme 5. Reaction scheme of the synthesis of 1-butyl-3-methylimidazolium camphorsulfonate.



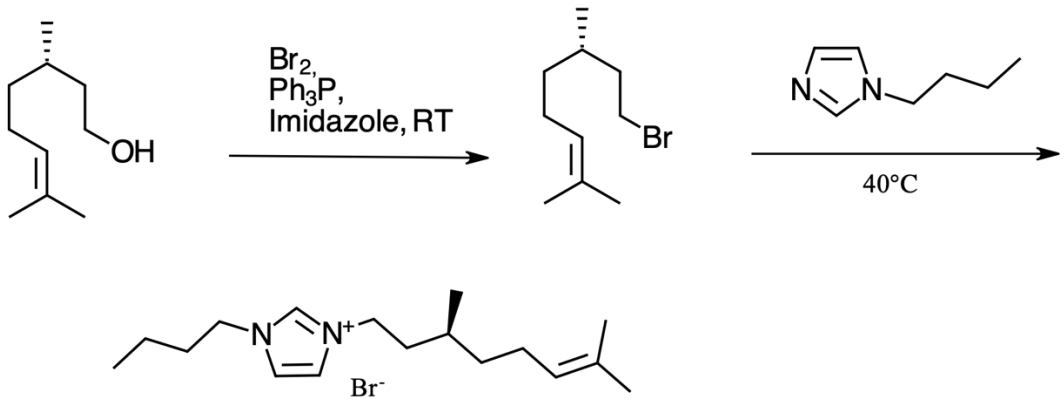
Scheme 6. Reaction scheme of the synthesis of 2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate.



Scheme 7. Reaction scheme of the synthesis of 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide.



Scheme 8. Reaction scheme of the synthesis of 1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide.



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Scheme 9. Reaction scheme of 1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide.

To ensure each CIL was successfully synthesized, the specific rotation of each CIL was measured and compared to literature values (**Table 1**). The specific rotations of each synthesized CILs were very close to literature values and thus, the CILs were successfully synthesized.

Table 1. Experimental and literature specific rotation values for each synthesized CIL.

	CIL	$[\alpha]$	$[\alpha]_{lit}$
1	1-butyl-3-methylimidazolium L-lactate [24]	-5.17°	-4° to -6°
2R	1-butyl-3-methylimidazolium (*R*)-camphorsulfonate [20]	-20.24°	-22°
2S	1-butyl-3-methylimidazolium (*S*)-camphorsulfonate [20]	19.71°	22°
3R	(*R*)-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate [25]	-9.36°	-10°
3S	(*S*)-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate [26]	7.80°	10°
4	1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide [22]	53.43°	54°
5	1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide [23]	1.29°	1.4°
6	1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide [23]	2.21°	2.2°

Additionally, each chiral ionic liquid was characterized via infrared (IR) spectroscopy, mass spectrometry (MS) and compared to the literature values. All of the characterization data was in keeping with the literature values.

2.2.2 Stability of CILs

Two chiral stability tests were performed on each CIL to ensure that they would not react under either the photochemical or aldol addition reaction conditions. To examine their suitability for the photochemical reaction conditions, 1 mL of each CIL was placed into a Pyrex irradiation tube and irradiated with a Hg-vapor lamp for 24 hours. The specific rotation after the chiral stability test showed little to no change with each synthesized CIL and thus, each CIL is stable to use for the photochemical [2+2] cycloadditions. The specific rotations are reported in **Table 2**. To examine their suitability for the aldol reactions, 1 mmol of the base, pyrroldine, was added to 1 mL of each CIL and the mixture was allowed to stir overnight. The base was removed by the rotatory evaporator and the specific rotations were taken. The specific rotations after the chirality stability test showed little to no change with each synthesized CIL except for 1-butyl-3-methylimidazolium L-lactate. Therefore, almost all of the CILs are stable for use. 1-butyl-3-methylmidazolium L-lactate will not be used for the aldol reactions. It contains an acidic hydrogen at its chiral center and thus, was partially racemized by the base pyrrolidine. The specific rotations are reported in **Table 2**.

Table 2. Specific rotations of each synthesized CIL before and after both chiral stability tests.

		Photochemical		Aldol	
Entry	CIL	$[\alpha]^a$	$[\alpha]^b$	$[\alpha]^a$	$[\alpha]^c$
1	1-butyl-3-methylimidazolium L-lactate (**1**)	-5.17°	-5.39°	-3.94°	-0.210°
2	1-butyl-3-methylimidazolium (*R*)-camphorsulfonate (**2R**)	-20.02°	-18.32°	-19.04°	-22.91°
3	1-butyl-3-methylimidazolium (*S*)-camphorsulfonate (**2S**)	18.30°	18.14°	19.71°	19.24°
4	(*R*)- 2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate (**3R**)	-9.36°	-9.19°	-10.52°	-10.48°
5	(*S*)- 2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate (**3S**)	7.80°	7.63°	7.80°	7.46°
6	1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide (**4**)	53.43°	50.83°	53.43°	49.28°
7	1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide (**5**)	1.29°	1.21°	1.29°	1.13°
8	1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide (**6**)	2.21°	2.17°	2.21°	2.09°

[a]: reference optical rotation
[b]: specific rotation after photochemical chiral stability test.
[c]: specific rotation after aldol chiral stability test.

It is important to note that the starting CILs for the stability testing came from different synthetic batches which explains the different starting rotations. It was found, particularly with the camphor sulfonate ionic liquids, that the removal of the reaction solvent, acetone, proved to be difficult and resulted in minor variations in the rotations of the CILs used in the experiments, as their level of purity was different. For each chiral stability test, the reported starting rotation relates to the specific batch of CIL used.

Additionally, to ensure that the CIL would not interfere with the photoaddition, the UV_{max} of each CIL was measured (**Table 3**). Each CIL had a UV_{max} value below the transmission value of Pyrex (275 nm). Thus, all chosen CILs will not interfere with the photoaddition.

Table 3. UV_{max} of each synthesized CIL.

CIL	UV_{max} (nm)
1-butyl-3-methylimidazolium L-lactate	229
1-butyl-3-methylimidazolium (*R*)-camphorsulfonate	225
1-butyl-3-methylimidazolium (*S*)-camphorsulfonate	225
1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide	228
R-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate	214
S-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate	214
1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide	229
1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide	231

All eight CILs that were prepared are suitable for use under the reaction conditions for photochemical [2+2] cycloadditions and will be used as solvents to test whether or not they can impart enantioselectivity in the products. This will be discussed in Chapter Three. With regards to the aldol additions, seven CILs were suitable for use under the reaction conditions and will be used as solvents to test whether or not they can impart enantioselectivity in the products. The exception is 1-butyl-3-methylimidazolium L-lactate, which was partially racemized by the base and thus, will not be used in the aldol additions. The aldol reactions will be discussed in Chapter Four.

Chapter Three: Photochemical [2+2] Cycloadditions

3.1 Introduction

The photochemical [2+2] addition is the most important and frequently used photochemical reaction. It is a cycloaddition that usually occurs between an enone and an alkene that proceeds via a non-concerted mechanism. The conjugated enone absorbs UV light that will promote a π electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), now termed the excited state (HOMO*). The photoexcitation of the enone results in it entering a very short-lived singlet excited state in which intersystem crossing to the triplet state will occur. The enone in its excited triplet state will combine with an alkene leading to a 1,4-biradical intermediate to form cyclobutane. [27]

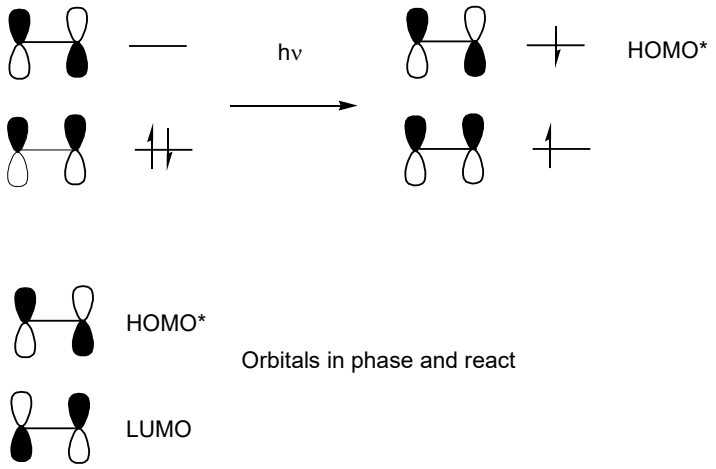


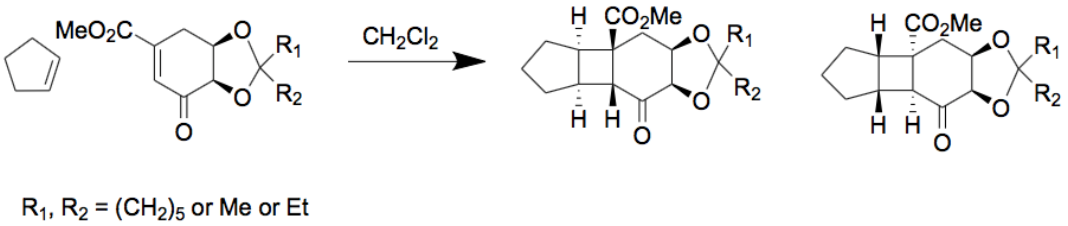
Figure 4. Molecular orbital depiction of a photochemical [2+2] addition.

Stereochemistry in this reaction is controlled by steric interactions in the transition state. Cyclobutane is strained and thus, a trans ring fusion will be less likely to occur. Further, cis-anti-cis products will be more likely to occur due to steric interactions. Regiochemistry is controlled by a number of factors. The original hypothesis, known as “Corey’s Exciplex Theory” stated that the excitation reversed the ground state polarity of the molecule and thus, the molecules would react based on their relative dipoles. However, subsequent investigations have shown a solvent

and ring size dependence. The stability of biradical intermediate explains the regiochemistry favouring the most resonance stable intermediate. If both the alkene and the enone are substituted, then there is the possibility of 16 products. [28]

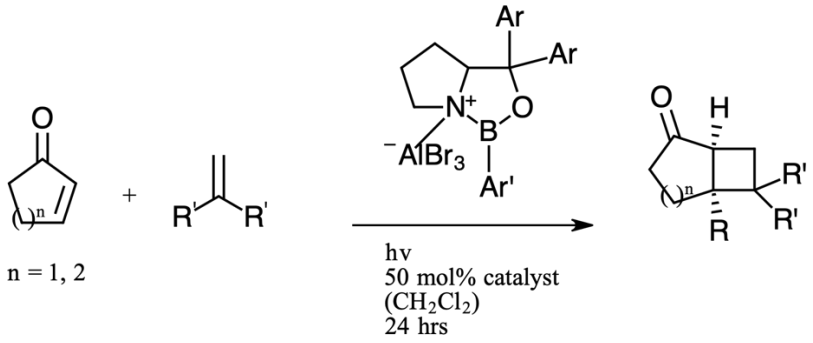
Photochemical [2+2] cycloadditions are an exceptionally powerful tool for synthetic organic chemists. Four-membered rings are almost exclusively formed in these reactions. As well, these photoadditions provide access to the formation of larger ring systems via facile ring expansion/fragmentation of the strained cyclobutane ring. This ability to further react under controlled conditions has allowed them to become a key intermediate in syntheses involving multiple ring systems of structurally complex molecules. A drawback of this reaction is that it suffers from relatively poor regio- and stereocontrol and asymmetric induction is rarely reported in literature for this reaction. Having an efficient method of influencing the stereochemical outcome of these reactions would make them a more useful synthetic tool in organic synthesis. [28]

There are few enantioselective photochemical reactions presented in the literature utilizing a chiral auxiliary, chiral catalyst or CILs. In 2002, Lange at al. presented an enantioselective [2+2] photoaddition using a chiral auxiliary. The researchers used cyclopentene and three different chiral synthons with different ketal auxiliaries in dichloromethane to perform the reaction. The reaction produced cis-anti-cis diastereomers with stereoselectivities up to 6:1, diastereomeric excess greater than 95% and yields greater than 90% (**Scheme 10**). [29]



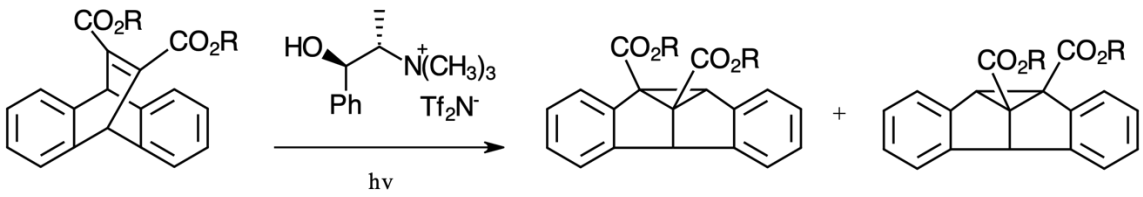
Scheme 10. Diastereoselective [2+2] photoaddition using a chiral ketal auxiliary.

Another example was demonstrated in 2018 by Bach and Poplata. They performed a photochemical [2+2] addition with cyclic enones and alkenes using a chiral oxazaborolidine-$AlBr_3$ Lewis acid catalyst. Their results showed moderate to good yields ranging between 42-82% and they had good levels of enantiocontrol from 82-96% enantiomeric excess. [30]



Scheme 11. Enantioselective photochemical [2+2] addition using a Lewis acid catalyst.

The last example is a photochemical reaction presented in a CIL. Armstrong et al. employed a variety of CILs to induce enantioselectivity in a photoisomerization of dibenzobicyclo[2.2.2]octatrienes. They achieved yields from 60-97% and had low enantiomeric excess that ranged between 3-12%. [31]



Scheme 12. Enantioselective photoisomerization using a CIL.

Photochemical [2+2] cycloadditions are a very important synthetic tool for organic chemists. Although few enantioselective photochemical reactions exist in literature, controlling the chiral outcome of the product would be extremely useful, and the use of CILs to impose enantioselectivity in this reaction needs to be explored.

3.2 Results & Discussion

3.2.1 Photochemical [2+2] Cycloadditions

Nine photochemical [2+2] cycloadditions have been performed in an achiral environment using the traditional organic solvent dichloromethane. A variety of different enones and alkenes have been chosen for use. The structures of the reagents are as follows:

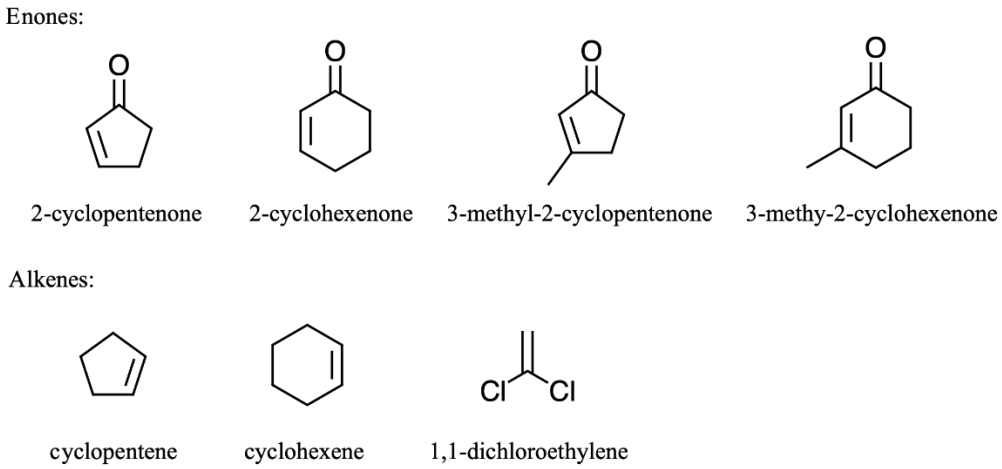


Figure 5. The name and structure of the various enones and alkenes used.

Each enone was reacted separately with the alkenes, cyclopentene and cyclohexene. Further, 2-cyclohexenone was reacted with an additional alkene, 1,1-dichloroethylene. The name and structures of the products are as follows:

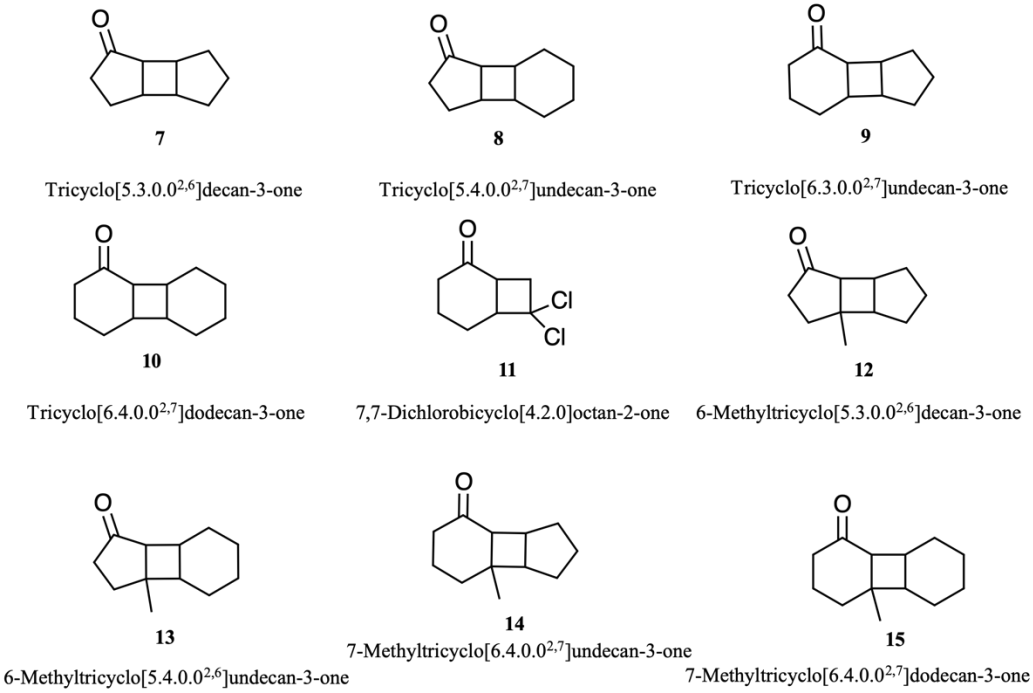


Figure 6. The name and structure of each photoadduct.

These reactions were completed successfully. Each reaction was characterized via gas chromatography (GC), infrared (IR) spectroscopy, mass spectrometry (MS), ^{1}H NMR spectroscopy and the data were compared to the literature values.

Additionally, the specific rotations of each reaction were taken to ensure that they were not optically active as they were completed in an achiral environment. The specific rotations are presented in **Table 4**.

Table 4. Specific rotations of each photochemical [2+2] addition product obtained using dichloromethane as the solvent.

Entry	Product	Specific Rotation
1	**7**	-0.74 $\pm$ 0.562
2	**8**	-1.55 $\pm$ 1.56
3	**9**	-0.40 $\pm$ 0.403
4	**10**	-0.17 $\pm$ 0.341
5	**11**	-3.47 $\pm$ 3.71
6	**12**	0 $\pm$ 0
7	**13**	-1.01 $\pm$ 0.997
8	**14**	-0.79 $\pm$ 0.80
9	**15**	-1.05 $\pm$ 0.959

Using error analysis taking into consideration the error associated with the polarimeter (Appendix), volumetric flask, and balance, most of the specific rotations can be seen as 0. The exceptions include products **7**, **13**, and **15** and their specific rotations after taking error analysis into account are 0.177, 0.013, and 0.09, respectively. These values are extremely close to 0 and the products are assumed to not be optically active.

In conclusion, the specific rotations in **Table 4** confirms that every reaction completed in the achiral environment is not optically active and in turn, guarantees that any degree of rotation exhibited by the reactions completed in the CILs is a result of the chiral environment.

3.2.2 Asymmetric Photochemical [2+2] Cycloadditions

Twenty-eight photochemical [2+2] cycloadditions were performed using seven different CILs as solvents in an attempt to induce enantioselectivity. The same combination of reagents from the photochemical [2+2] cycloadditions in the achiral environment using dichloromethane were used. All reactions were completed with 1-butyl-3-methylimidazolium L-lactate (**1**) and 1-butyl-3-methylimidazolium *R*-camphorsulfonate (**2R**). Two additional reactions were each completed using 1-butyl-3-methylimidazolium *S*-camphorsulfonate (**2S)**, *R*-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate (**3R**), 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide (**4**), 1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide (**5**), and 1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide (**6**) as the reaction solvents. The specific rotations and associated error of the products from each reaction can be seen in **Table 5**.

Table 5. Specific rotations of each photochemical [2+2] addition product obtained using seven CILs as the solvents.

		CIL						
Entry	Product	**1**	**2R**	**2S**	**3R**	**4**	**5**	**6**
1	**7**	-12.86 ± 3.06	-1.08 ± 0.442	-1.21 ± 0.419	-2.23 ± 0.438	29.13 ± 1.74	-10.87 ± 4.83	-2.53 ± 0.688
2	**8**	-5.45 ± 1.01	-3.27 ± 0.999	-1.18 ± 0.303	-2.73 ± 0.665	3.97 ± 0.103	-2.29 ± 0.601	-2.94 ± 0.522
3	**9**	-2.00 ± 0.279	-15.0 ± 4.10	-	-	-	-	-
4	**10**	-2.29 ± 1.23	-4.46 ± 2.39	-	-	-	-	-
5	**11**	-4.45 ± 1.08	-3.30 ± 1.00	-	-	-	-	
6	**12**	-3.38 ± 0.944	-2.73 ± 0.825	-	-	-	-	-
7	**13**	-1.55 ± 0.535	-0.94 ± 0.272	-	-	-	-	-
8	**14**	-1.36 ± 0.467	-0.97 ± 0.246	-	-	-	-	-
9	**15**	-1.47 ± 0.299	-1.52 ± 0.231	-	-	-	-	-

Comparing these specific rotations to the photoadditions completed in the achiral environment, enhanced optical activity is seen. All CILs used with the exception of 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide (**4**) yielded products with negative specific rotations. Interestingly, both *R*- and *S*- enantiomers of 1-butyl-3-methylimidazolium camphorsulfonate (**2R, 2S**) yielded products with negative specific rotations. Both 1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide (**5**) and 1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide (**6**) have positive specific rotations and yielded products with negative specific rotations. It is important to note that this ensures the CIL was fully removed from the product and any optical activity displayed did not come from residual CIL as the *S*-enantiomers produced products with negative rotations. A limited number

of reagent combinations were investigated (**Table 5**, entries 3-9) and these reaction combinations need to be completed to provide a larger number of data points.

Generally, there is no specific trend that can be seen between the CILs and the specific rotations, although, a few single reactions can be highlighted. When 1-butyl-3-methylimidazolium L-lactate (**1**) was used as solvent to impart enantioselectivity on product **7**, the specific rotation was calculated to be -12.86 $\pm$ 3.06. Also, when 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide (**4**) was used as a solvent to impart enantioselectivity on product **7**, the specific rotation was calculated to be 29.13 $\pm$ 1.74. Also, when 1-butyl-3-methylimidazolium *R*-camphorsulfonate (**2R**) was used as a solvent to impart enantioselectivity on product **9**, the specific rotation was calculated to be -15.0 $\pm$ 4.10. Last, when 1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide (**5**) was used to impart enantioselectivity on product **7**, the specific rotation was calculated to be -10.87 $\pm$ 4.83. These specific rotations are of significantly higher magnitude than any of the others when performed in the respective CIL. For more reliable data, these reactions should have been repeated more than once. This was not completed due to time constraints. Replication would allow for better visualization of any patterns or general trends that exists between the CILs used and the optical activity of the products.

A chiral column for GC was purchased to measure the enantiopurity of each product but due to time constraints (COVID-19), no samples were analyzed. Compound **11** is the only product that has an optical rotation provided in the literature for comparison. [30] The researchers used a GC with a chiral column to analyze their product which gave a reported specific rotation of $[\alpha]_D^{25}$ = +112 (1*S*,6*S*)-7,7-dichlorobicyclo[4.2.0]octan-2-one) and a calculated enantiomeric excess of 83%. Using their values, calculated ee of 3.3% and 2.4% were obtained for 1-butyl-3-

methylimidazolium L-lactate (**1**) and 1-butyl-3-methylimidazolium *R*-camphorsulfonate (**2R**), respectively. Their product is the (+)-(1*S*,6*S*) and based on our negative rotations we assign the product to be (–)-(1*R*,6*R*).

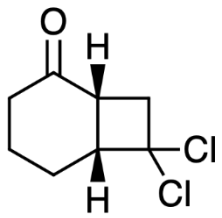


Figure 7. The product (–)-(1*R*,6*R*)-7,7-dichlorobicyclo[4.2.0]octan-2-one.

Asymmetric photochemical [2+2] cycloadditions have the potential to produce up to 8 enantiomeric pairs if either the alkene or enone is substituted, as there can be up to 4 new stereocenters produced. Enantiomers rotate plane-polarized light in equal and opposite directions. If any product contains an unequal mixture of enantiomers, this will affect the magnitude of the optical rotation. Therefore, although some of the specific rotations appear to have a small magnitude, this may be due to the product containing an enantiomeric pair in unequal concentrations.

After column chromatography, few products were collected in very low yields and in combination with the soon to be decommissioned NMR, favourable ^{1}H NMR spectra were difficult to obtain. These products include **7** (with CILs **1**, **2R**, and **3R**), **8** (with CILs **1** and **2R**), **9** (with CIL **2R**), **10** (with CIL **1**), **11** (with CILs **1** and **2R**) and **15** (with CIL **2R**). These products could not be characterized via ^{1}H NMR spectroscopy due to weak signals in their spectra. As their GC retention times, MS, and IR data matched their corresponding products completed in the achiral environment, they are assumed to be successfully synthesized.

3.2.3 Future work

Photochemical [2+2] cycloadditions show promising results for optically active compounds induced by chiral ionic liquids. Future work would include fully completing **Table 5** with each CIL to get a better understanding on how they may impose enantioselectivity on the products, as well as repeating the reactions a few times to achieve replicable results.

Further, ^{1}H NMR must be repeated on the products that were not fully characterized. Also, ^{13}C NMR must be completed on all products to get a more accurate confirmation on the structure of each product. ^{13}C NMR was not completed as the NMR instrument available exhibited numerous problems with the shimming and obtaining spectra with a good signal-to-noise ratio. This NMR instrument will soon to be decommissioned as a new one was purchased, but due to the pandemic, it has not been installed yet.

As well, GC with a chiral column should be additionally used to characterize each reaction product. As mentioned above, photochemical [2+2] cycloadditions have potential to produce up to 8 enantiomeric pairs if the alkene and the enone are both substituted. This method would be a very important step to analyze and provide more accurate information on any enantiomeric pairs found it the samples, and in turn, the specific rotations.

Furthermore, the reusability of each CIL needs to be investigated to see how many times they can be reused and remain effective for in these specific reaction conditions. This can be completed by extracting the CIL and then measuring its own optical rotation and the products optical rotation. Next, it will be reused in the same reaction and the process will be repeated. As long as there is no significant change between the specific rotations of the product and CIL itself, it is still effective and may be reused again.

In conclusion, enhanced optical activity was seen when switching from an achiral environment using dichloromethane as the solvent to the chiral environment using the CILs as the solvent. More research must be completed on CILs to see whether they can impart enantioselectivity on these reactions as they show very promising potential. The photochemical [2+2] addition is a powerful reaction for synthetic chemists and controlling chirality in these reactions would make them an even better synthetic tool.

Chapter Four: Asymmetric Aldol Reaction

4.1 Introduction

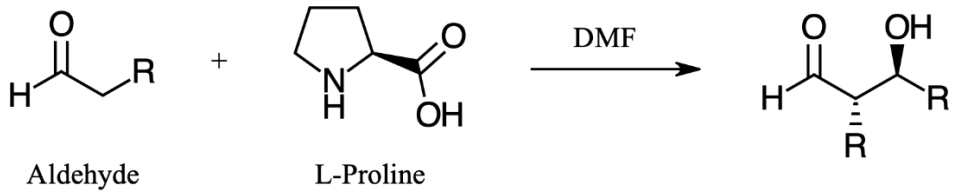
The aldol reaction is one of the most effective and versatile methods for the formation of new carbon-carbon bonds in organic synthesis. [32] This reaction occurs between two aldehydes/ketones in which they react through an enolate or enol to produce a β-hydroxy carbonyl. The reaction proceeds as a self-condensation reaction when the enolate of the aldehyde/ketone attacks a molecule of the same un-enolized aldehyde/ketone to give the product. The aldol reaction is a reversible and is performed by either using acid or base catalysis. When the reaction is performed between two molecules of the same aldehyde, the equilibrium of the reaction lies to the right and is generally successful. On the other hand, when performed between two molecules of the same ketone, the equilibrium lies to the left and unsatisfactory yields may be achieved. [32]

The aldol reaction has the potential to produce up to two new chiral centers and thus, two diastereomeric pairs of enantiomers may be formed. This presents numerous challenges in controlling regio-, diastereo-, and stereocontrol. If there is no effective form of chiral induction, then the enantiomers will be obtained as a racemic mixture. [33]

The formation of new carbon-carbon bonds with complete stereocontrol is of great importance in organic synthesis. The aldol reaction is one of the most powerful transformations in organic synthesis and the products of these reactions may be used for the preparation of key intermediates in the synthesis of important and complex natural products. Further, the carbonyl and hydroxyl groups generated by the aldol reaction can be converted selectively to other functional groups. Asymmetric aldol reactions produce chiral β-hydroxy carbonyl systems that serve as building blocks for antibiotics as well as precursors for antihypertensive drugs and

calcium antagonists. Current methods to control chirality in these reactions include the use of a chiral catalyst paired with an organic solvent. Although proven effective, organic solvents are volatile and pose negative health and environmental effects, and thus, alternative methods need to be researched. There are a handful of examples in the literature in which CILs have worked successfully to induce enantioselectivity in aldol reactions and thus they may provide a green, effective alternative to current approaches. [34]

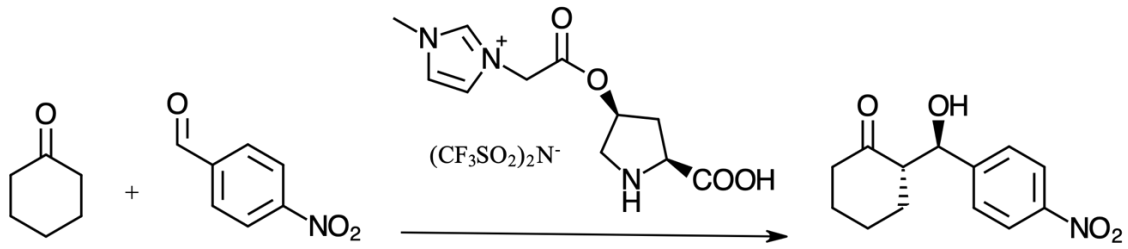
The first direct enantioselective aldol reaction of an aldehyde was presented by Northrup and MacMillan in 2002. The researchers used an L-proline based catalyst and a variety of different aldehydes and the solvent dimethylformamide (DMF). Using these reaction conditions, they were able to achieve good yields (80%) and high levels of enantiocontrol (99% ee). The relationship between the two chiral centers is 4:1 anti:syn. [35]



Aldehyde L-Proline

Scheme 13. Enantioselective aldol reaction using a L-proline based catalyst.

There are a series of publications by Lombardo et al. that presented a handful of cross-aldol reactions in chiral ionic liquids with excellent enantioselectivies (>99% ee) and good yields (80-90%). They used an L-proline based CILs to induce enantioselectivity in their reactions and as the base to catalyze the reaction. Their reactions had no organic solvent but contained water and excess amounts of the ketone, which acted as the nucleophile. The diastereoselectivies were anti:syn up to 95:5. [36]



Scheme 14. Enantioselective cross-aldol reactions using a CIL.

The first counter anion they used for their chiral cation in their IL was BF_4^- where they achieved results of 64% yield and 85% enantiomeric excess. They later observed a higher efficiency with the lipophilic bis(trifluoromethylsulfonyl)imide (NTf_2^-) counter anion. Here, they achieved yields of 37% and enantiomeric excess greater than 99%. Another improvement was made when they used aqueous biphasic conditions instead of only the CIL alone as the solvent. Further, another advancement was observed when they switched from using trans-geometry to cis-geometry of the imidazolium 4-hydroxyproline ionic moiety. This improved the product yield from 37% to 87%. [10]

Aldol reactions are extremely important for synthetic organic chemists as they provide an effective method for the formation of new carbon-carbon bonds. These reactions are regularly used to construct the carbon frameworks of complex biologically active compounds that contain many stereocenters. Controlling enantioselectivity in these reactions with an effective green approach is integral and the use of CILs to do so must be explored.

4.2 Results & Discussion

4.2.1 Aldol Reactions

Twelve aldol reactions have been performed in an achiral environment using the traditional organic solvent, DMF. A variety of different aldehydes and ketones have been chosen for use. Each of these reagents were reacted separately with two bases, morpholine and pyrrolidine. The structures of the reagents are as follows:

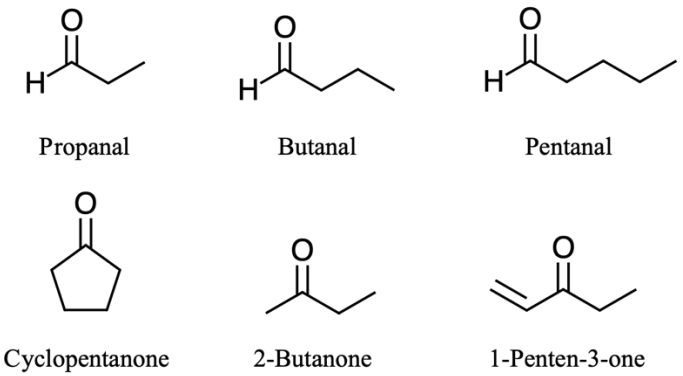


Figure 8. The name and structure of the various aldehydes and ketones used.

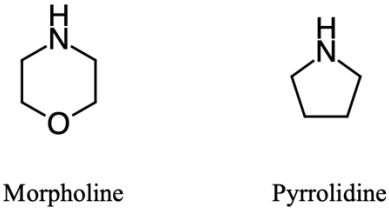


Figure 9. The structure of morpholine and pyrrolidine.

DMF was chosen as the solvent as the procedure was derived from the research completed by Northrup and MacMillan, "The first Direct Enantioselective Cross-aldol Reaction of Aldehydes". [35] The researchers experimented with a variety of different solvents and noted that the best reaction efficiency was seen with DMF. The structure of each aldol addition product is as follows:

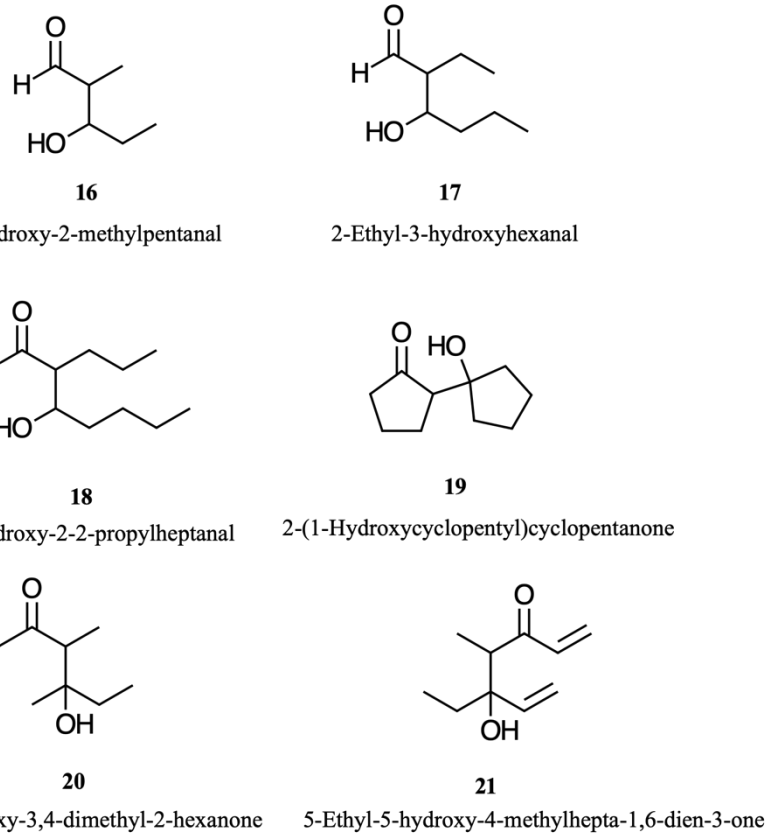


Figure 10. The name and structure of each aldol addition product.

These reactions were completed successfully. Each reaction was characterized via gas chromatography (GC), infrared (IR) spectrometry, mass spectrometry (MS), ^{1}H NMR spectroscopy and compared to the literature values. The exceptions are products **20** and **21** that could not be characterized via ^{1}H NMR. Compound **20A** was produced in an unpurified yield of about 3.2% which amounted to 10.5 mg. This reaction was repeated 3 times and each time produced a similar low yield. This amount of material was too low for purification and thus, no characterization at all was completed. However, its GC retention time was compared to compound **20** when completed in the CILs and they were the same. Thus, it was assumed that the correct product was synthesized. Further, products **19A, 20B**, **21A** and **21B** gave yields of 11.4 mg (2.7%), 8.9 mg (2.5%), 31.5 mg (7.4%), and 16.3 mg (3.8%), respectively. These are very low and in combination with the soon to be decommissioned NMR instrument, no useable NMR

spectra were produced. The spectra had very weak signals and thus, these products could not be characterized. As their GC retention times, MS, and IR data matched their corresponding products completed in the chiral environment, they are assumed to be successfully synthesized.

Additionally, the specific rotations of each reaction were taken to ensure that they were not optically active as they were completed in an achiral environment. The specific rotations are presented in **Table 6**.

Table 6. Specific rotations of each aldol reaction product obtained using DMF as the solvent.

Entry	Product	Base Used	Specific Rotations
1	**16**	**A**	-1.48 $\pm$ 1.24
2		**B**	-1.36 $\pm$ 1.42
3	**17**	**A**	-0.249 $\pm$ 0.251
4		**B**	0 $\pm$ 0
5	**18**	**A**	0 $\pm$ 0
6		**B**	-0.38 $\pm$ 0.383
7	**19**	**A**	0 $\pm$ 0
8		**B**	-1.77 $\pm$ 1.47
9	**20**	**A**	No product isolated
10		**B**	0 $\pm$ 0
11	**21**	**A**	0 $\pm$ 0
12		**B**	0 $\pm$ 0

A: Reaction was completed using morpholine as the base.
B: Reaction was completed using pyrrolidine as the base.

Again, using error analysis by taking into consideration the error associated with the polarimeter, volumetric flask, and balance, most of the specific rotations can be seen as 0. The exceptions are products **16A** and **19B**, and their specific rotations after taking error analysis into account are 0.24 and 0.30, respectively. These values are extremely close to zero and should be assumed to have no optical activity.

In conclusion, this confirms that every reaction completed in the achiral environment is not optically active and in turn, guarantees that any degree of rotation exhibited by the reactions completed in the CILs is a result of the chiral environment.

4.2.2 Asymmetric Aldol Reactions

Twenty-two aldol reactions have been completed using seven different CILs as solvents to induce enantioselectivity. The same combination of reagents from the aldol reactions in the achiral environment using DMF were used. All reactions were completed with 1-butyl-3-methylimidazolium *S*-camphorsulfonate (**2S**). Two additional reactions were completed with 1-butyl-3-methylimidazolium *R*-camphorsulfonate (**2R**), 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide (**4**), 1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide (**5**), and 1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide (**6**). One additional reaction with both *R*-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate (**3R**) and *S*-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate (**3S**) were completed. The reaction done with **3S** was supposed to be completed with the R-enantiomer but as the starting material for the R-enantiomer ran out, **3S** was synthesized for use. The specific rotations and associated error of the products from each reaction can be seen in **Table 7.**

Table 7. Specific rotations of each aldol reaction product obtained using seven CILs as the solvents.

			CIL						
Entry	Product		**2R**	**2S**	**3R**	**3S**	**4**	**5**	**6**
1	**16**	**A**	-4.90 ± 1.43	-2.40 ± 0.704	-1.37 ± 0.479	-	32.42 ± 1.03	-0.295 ± 0.066	-1.73 ± 0.612
2		**B**	-5.24 ± 1.06	-3.50 ± 1.04	-	-1.34 ± 0.277	85.99 ± 0.931	-1.94 ± 1.03	-3.04 ± 0.840
3	**17**	**A**	-	-3.01 ± 0.623	-	-	-	-	-
4		**B**	-	-6.42 ± 1.96	-	-	-	-	-
5	**18**	**A**	-	-6.06 ± 1.61	-	-	-	-	-
6		**B**	-	-3.49 ± 1.21	-	-	-	-	-
7	**19**	**A**	-	-9.74 ± 1.56	-	-	-	-	-
8		**B**	-	-1.85 ± 0.769	-	-	-	-	-
9	**20**	**A**	-	No yield	-	-	-	-	-
10		**B**	-	-3.00 ± 1.06	-	-	-	-	-
11	**21**	**A**	-	-4.77 ± 1.58	-	-	-	-	-
12		**B**	-	-1.38 ± 0.569	-	-	-	-	-

A: Reaction was completed using morpholine as the base.
B: Reaction was completed using pyrrolidine as the base.

Comparing these specific rotations to the aldol additions completed in the achiral environment, enhanced optical activity is seen. Similar to the photochemical [2+2] cycloadditions, all CILs used in the aldol reactions with the exception of 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide (**4**) yielded products with negative specific rotations. Again, both *R*- and *S*- enantiomers of 1-butyl-3-methylimidazolium camphorsulfonate (**2R, 2S**) and 2-amino-*N,N,N*-trimethyl-1-butanol-

bis(trifluoromethanesulfon)imidate (**3R, 3S)** yielded products with negative specific rotations. Both 1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide (**5**) and 1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide (**6**) have positive specific rotations and yielded products with negative specific rotations. It is important to note that this provides additional evidence the CIL is fully removed from the product and any optical activity displayed does not come from residual CIL as *S*-enantiomers produced products with negative rotations. Further, 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide (**4**) has a positive literature specific rotation and also yielded products with a positive specific rotation. The magnitude of rotation exhibited in product **16B** is significantly larger than the CILs rotation and thus, this further confirms that the optical activity displayed is not solely from any residual CIL.

Again, there is no specific trend that can be seen between the CILs and the specific rotations. A few single reactions that can be highlighted include when 1-butyl-3-methylimidazolium *S*-camphorsulfonate (**2S**) was used in conjunction with morpholine to impart enantioselectivity on the product **19A**. The specific rotation of this product is -9.74 $\pm$ 1.56. As well, when 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide (**4**) was used in conjunction with morpholine and pyrroldine to impart enantioselectivity on the product **16A** and **16B.** The specific rotation of both products are 32.42 $\pm$ 1.03 and 85.99 $\pm$ 0.931, respectively. CIL **4** consistently gave products a specific rotation with a larger magnitude. For more reliable data, these reactions should be repeated. These replicate reactions were not completed due to time constraints. Replication would allow for better visualization of any patterns or general trends that exists between the CILs used and the optical activity of the products.

Using the optical rotations found in the literature, [35] it was possible to determine ee values for product **16** (entries 1 and 2, **Table 7**). The researchers used a GC with a chiral column to analyze their product which gave a reported specific rotation of $[\alpha]_D$ = -14.7 (2*S*, 3*S*)-3-hydroxy-2-methylpentanal and a calculated enantiomeric excess of 99%. The specific rotations for CIL **4** are well above the specific rotations for the pure enantiomer given in the literature and therefore, this data needs to be verified through repeating experiments. With those entries not being taken into consideration (CIL **4**), the reactions resulted in the preparation of 3-hydroxy-2-methylpentanal with ee of 9-35% with pyrrolidine as the base. Based on their assignment and our negative rotations we assign the product to be (2*S*, 3*S*)-3-hydroxy-2-methylpentanal.

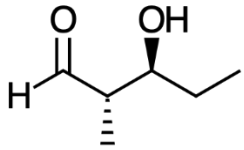


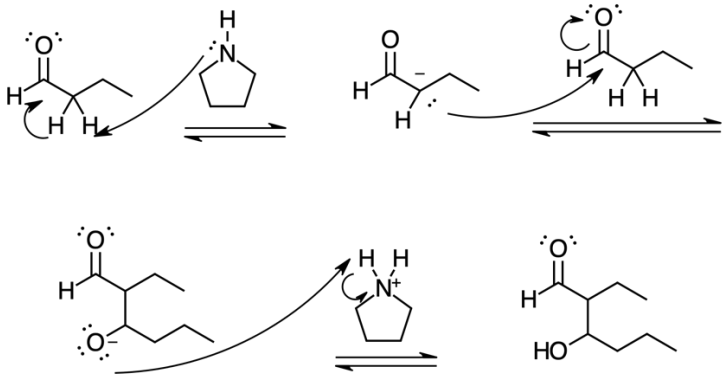
Figure 11. The product (2*S*, 3*S*)-3-hydroxy-2-methylpentanal.

Looking at the effect of CILs **5** and **6** in **Table 7** (entries 1 and 2), it is evident that they produced products with a smaller magnitude of optical activity compared to the other CILs. Both CILs **5** and **6** have a small magnitude of rotation, with literature values of 1.4 and 2.2, respectively. Therefore, it is reasonable that the magnitude of enantioselectivity imparted on these products is small. In contrast, CIL **4** has a literature rotation of 54.0, and it can be seen in **Table 7** (entries 1 and 2), that it imparted a larger magnitude of enantioselectivity on these products. With the few reactions completed, it is plausible that the magnitude of enantioselectivity imposed on the products may be related to the degree in which the chiral center of the CIL impacts the overall optical activity of the liquid.

Again, due to time constraints, the enantiopurity of each product was not measured. In asymmetric aldol reactions, up to two new chiral centers can be formed. This has the potential to

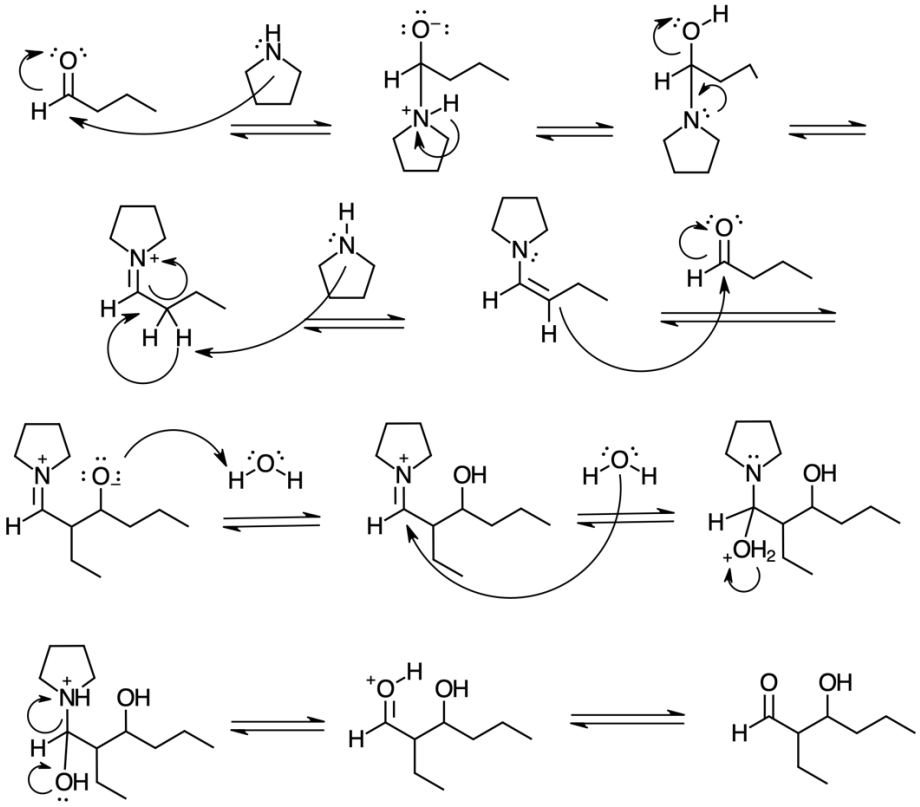
produce 2 enantiomeric pairs. GC with a chiral column would be an accurate method to distinguish if the product contains enantiomers. Enantiomers rotate plane-polarized light in equal and opposite directions. If any product contains an unequal mixture of enantiomers, this will affect the magnitude of the optical rotation. Therefore, although some of the specific rotations appear to have a small magnitude, this may be due to the product containing an enantiomeric pair in unequal concentrations. Moreover, if a product has a large magnitude of rotation, it may be due to the reaction greatly favouring one enantiomer over the other. Furthermore, it is recognized that diastereomeric pairs are formed in aldol reactions and until GC with the chiral column is complete, it is unknown what ratio of the four diastereomeric products we have.

The mechanism of the aldol reaction can occur through a base-catalyzed or enamine-forming amine mechanism. The mechanism of the base-catalyzed reaction begins with the base removing a α-hydrogen of the carbonyl to form an enolate that will attack the second molecule of the carbonyl. This results in an ionic species that will then remove a proton from the protonated base to form the product.



Scheme 15. Base catalyzed aldol reaction mechanism.

In the enamine-forming amine mechanism the 2° amine will react with the aldehyde/ ketone to form an enamine. Next, the enamine performs a nucleophilic attack to form an iminium, followed by hydrolysis to reform the carbonyl.



Scheme 16. Enamine forming amine aldol reaction mechanism.

It was evident that the aldol reactions were proceeding via the enamine mechanism after characterization. MS showed that we were not able to remove the enamine as there were no M+ peaks corresponding to the desired product but fragment peaks that corresponded to the mass of the product with the enamine attached. IR confirmed this as well by displaying N-H stretching in the amine frequency range. The workup for the aldol reactions completed in the CILs involved first the removal of the CIL through extraction with a non-polar organic solvent and second the use of a SPE silica gel filter to ensure any residual CIL was removed. The original reactions completed in the achiral environment included a work-up that used water and brine. After realizing that the enamine was still attached, this work-up was applied to the reactions performed in the CILs. This resulted in removing the enamine through hydrolysis in most aldol products. The exceptions were with the reactions completed with propanal. Unfortunately, the enamine

could not be fully removed via hydrolysis as MS still displayed fragment peaks corresponding to the mass of the product with the enamine still attached.

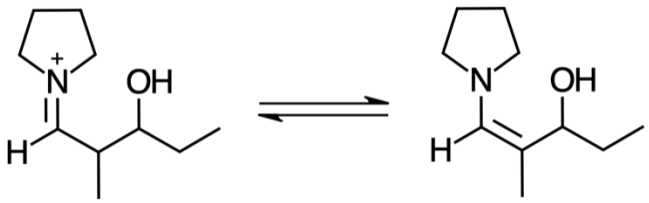


Figure 12. The product 3-hydroxy-2-methylpentanal with the enamine attached.

Although, after hydrolysis for most of the propanal products, ^{1}H NMR spectroscopy produced spectra that corresponded to the correct aldol product (3-hydroxy-2-methylpentanal, **16**). Thus, it is evident that there is a mixture of the correct aldol product and product with the enamine still attached. The exceptions are **16A** completed in CIL **3R** and **16B** completed in CIL **1** in which the product only contained the attached enamine. It is important to note that in the case of a mixture of the correct product and the product with the enamine attached, the reported MS corresponds to possible fragments of the enamine product. This includes product **16A** (completed in CILs **2R**, **2S**, **3R**, **5** and **6**) and **16B** (completed in CILs **2R**, **2S**, **3S**, **4**, **6**). Product **16A** (completed in CIL **4**) in the only product in which the enamine was successfully removed after hydrolysis.

With the mechanism of the aldol reaction in mind, there is a possibility of two different enamines to form with each product as two structurally different bases were used. For the CIL to impart chirality onto the product, it will interact with molecules of itself and possibly other reagents to form a chiral pocket that the product will fit into. With a structurally different base, it is possible that this will affect the optical activity of the products. Comparing the specific rotations of the same product when different bases are used, no evident difference is seen in most cases.

After column chromatography, few products were collected in very low yields and in combination with the soon to be decommissioned NMR, reliable ^{1}H NMR spectra could not be obtained. These products include **16B** (with CIL **6**) and **18B** (with CIL **2S**). These products could not be characterized via ^{1}H NMR spectroscopy due to weak signals in their spectra. As their GC retention times, MS, and IR data matched their corresponding products completed in the achiral environment, they are assumed to be successfully synthesized.

4.2.3 Future Work

Aldol reactions show promising results for optically active compounds induced by CILs. Future work would include fully completing **Table 7** with each CIL to get a better understanding on how these CILs may impose enantioselectivity on the products. As well as repeating each reaction a few times to ensure reproducible results.

Further, ^{1}H NMR must be repeated on the products that could not be fully characterized. Also, ^{13}C NMR must be completed on all products to get a more accurate confirmation on the structure of each product. Furthermore, GC with a chiral column should additionally be used to characterize each reaction product. As mentioned above, the aldol reaction has the potential to produce two enantiomeric pairs and this method would be an important step to analyze and provide more accurate information on any enantiomeric pairs found in the samples, and in turn, their specific rotations. Furthermore, the reusability of each CIL needs to be investigated to see how many times they can be reused and remain effective for in these specific reaction conditions.

In conclusion, enhanced optical activity was demonstrated when switching from the achiral environment using DMF as the solvent to the chiral environment using the CILs as the solvent. More research must be completed on using CILs to induce enantioselectivity in aldol

reactions as they show a very promising alternative to harmful traditional organic solvents paired with chiral catalysts.

Chapter 5: Experimental

5.1 Experimental

5.1.1 General Experimental Techniques, Instrumentations and Materials

Analytical gas chromatography was performed on a Hewlett Packard 5890 equipped with a flame ionization detector (FID) using a 30 m by 0.25 mm DB-5HT capillary column of (5% phenyl)methylpolysiloxane. There was a flow rate of 2.0 mL/min with the carrier gas nitrogen and a column pressure of 21 psi. The instrument was programmed at: initial temperature = 80 °C, initial time = 2.0 minutes, rate = 8.0 °C/minute final temp = 150 °C, final time = 3 minutes.

Analytical thin layer column chromatography (TLC) was performed on TLC Silica gel 60 F_{254} with a thickness of 175-225 μm. The TLC plates are visualized using a handheld UV lamp and stained with p-anisaldehyde followed by heating with a heat gun. Column chromatography was used to purify products using a 230-400 mesh silica gel with a particle size of 40-63 μm. The solvent system for the column consisted of varying concentrations of hexanes and ethyl acetate using a gradient technique.

All photochemical reactions were performed using an immersion 7825 mercury-vapour lamp purchased from Hanovia. Each photochemical reaction was run for 24 hours.

Optical rotations were measured on a Perkin Elmer Model 343 polarimeter with a sodium spectral lamp 93 122E and a 1 dm cell. All measurements were taken at room temperature. All samples were diluted with dichloromethane unless otherwise noted. All specific rotation concentrations are reported in g/100 mL.

Infrared (IR) spectra were measured on a Perkin Elmer 1320 IR Spectrometer with a resolution of 1 cm^{-1}. All spectra were determined without solvent (neat) in the transmission mode using KBr and are reported as wavenumbers.

Mass spectra (MS) were measured on an Advion Expression-L CMS using atmospheric-pressure chemical ionization (APCI). All spectra were determined without solvent (neat) using a direct Atmospheric Solids Analysis Probe (ASAP).

Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured on a Varian AS500 using the UNITYINOVA NMR spectrometer system, VNMR 6.1C software at room temperature. The solvent used was $CDCl_3$. Chemical shifts are reported in parts per million (ppm) from an internal standard of tetramethylsilane (TMS). The NMR data are reported as follows: chemical shift multiplicity, coupling constant in Hertz, integration). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were also recorded at 125 MHz using $CDCl_3$ as the solvent.

Each reaction was run under nitrogen in flasks that were oven or flame dried. Reagents were transferred using a syringe and introduced into the flask though a rubber septum. Excess water was removed from the organic extracts using the drying agent anhydrous magnesium sulfate ($MgSO_4$), and then filtered by gravity. Excess solvents were removed from the flask using a Buchi rotatory evaporator under reduced pressure obtained by the water aspirator. Dimethylformamide (DMF) was dried by storing over molecular sieves. All other solvents were used as received. All chemicals for which procedures are not listed were purchased from Sigma Aldrich.

5.2 Preparations

5.2.1 Experimental for Chapter Two

General Procedure for the Synthesis of 1-butyl-3-methylimidazolium L-Lactate (**1**)

Equimolar amounts 1-butyl-3-methylimidazolium chloride (8.8 mmol, 1.54 g) and sodium (L)-lactate (8.8 mmol, 0.99 g) were combined in a heavy wall flask with a small amount

of acetone (2.5 mL). The flask was degassed with nitrogen for 30 seconds. The sealed mixture was heated to 50°C in an oil bath for approximately 24 hours. The liquid was filtered by vacuum to remove the salt. Excess solvent was removed using the rotatory evaporator to result in 1.82 g (90%) of the chiral ionic liquid.

[α]: -5.09 (c = 1.06, dichloromethane); IR(neat) ν_{max} (cm^{-1}): 3712.25, 3480.7, 2967.9, 2938.7, 2877.6, 1718.1; MS m/z: $[M+H]^+$ calculated for $C_8H_{15}N_2$: 139.12, found 139.1. $[M-H]^-$ calculated for $C_3H_5O_3^-$: 89.03, found 89.1.

General Procedure for the Synthesis of 1-butyl-3-methylimidazolium Camphorsulfonate (**2R, 2S**)

Equimolar amounts of 1-butyl-3-methylimidazolium chloride (10.2 mmol, 1.78 g) and (1*S*)- or (1*R*)-10- camphorsulfonic acid (10.2 mmol, 2.37 g) were combined in a heavy wall flask with a small amount of acetone (2.5 mL). The flask was degassed with nitrogen for 30 seconds. The mixture was heated to 50°C in an oil bath for approximately 24 hours. Excess solvent was removed using the rotatory evaporator to result in 3.77 g (>99%) of the *R*-enantiomer and 3.47 g (94%) of the *S*-enantiomer.

R-enantiomer: [α]: -20.24 (c = 0.420, dichloromethane); IR(neat) ν_{max} (cm^{-1}): 3460, 3149, 3103, 2960, 1741, 1374; MS m/z: $[M+H]^+$ calculated for $C_8H_{15}N_2$: 139.12, found 139.1. $[M+2]^+$ calculated for $C_{10}H_{15}O_4S$ + 2H: 233.08, found 233.1.

S-enantiomer: [α]: 19.71 (c = 0.695, dichloromethane); IR(neat) ν_{max} (cm^{-1}): 3462, 3148, 3102, 2961, 1739, 1374; MS m/z: $[M+H]^+$ calculated for $C_8H_{15}N_2$: 139.12, found 139.2. $[M+2]^+$ calculated for $C_{10}H_{15}O_4S$ + 2H: 233.08, found 233.1.

General Procedure for the Synthesis of 2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate (**3R, 3S**)

(*R*)- or (*S*)-2-amino-1-butanol (1 mmol, 89.1 mg) was dissolved in dichloromethane (10 mL) and Me_2SO_4 (1 mmol, 126 mg) was added dropwise (30 minutes). The solvent was removed by a rotatory evaporator. The residue was dissolved in water (2 mL). Addition of N-lithiotrifluoromethanesulfonimide (1.1 mmol, 315 mg) in water (1 mL) led to the preparation of the product. The product was washed with water (3 x 5 mL) and dried under vacuum at 100℃ (5 hrs) to give 0.156 g (37%) of the R-enantiomer and 0.144 (35%) of the S-enantiomer.

R-enantiomer: [α]: -9.36 (c = 0.114, methanol); IR(neat) ν_{max} (cm^{-1}): 3537, 3176, 2982, 2891, 1196, 1058; MS m/z: $[M+H]^+$ calculated for $C_7H_{18}NO^+$ + H: 132.14, found: 131.9. $[M-H]^-$ calculated for $C_2F_6NO_4S_2^-$: 279.9, found 279.8.

S-enantiomer: [α]: 7.80 (c = 0.141, methanol); IR(neat) ν_{max} (cm^{-1}): 3507, 3170, 2982, 2894, 1190, 1052; MS m/z: $[M+H]^+$ calculated for $C_7H_{18}NO^+$ + H: 132.14, found: 131.9. $[M-H]^-$ calculated for $C_2F_6NO_4S_2^-$: 279.9, found 279.8.

General Procedure for the Synthesis of 1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide[22] (**4**)

(+)-Chloromethyl menthyl ether (12.2 mmol, 2.50 g) was added dropwise over 30 minutes to a vigorously stirred solution of 1-butylimidazole (12.2 mmol, 1.51 g) in dry hexanes (15 mL) in a 3-neck round bottom flask equipped with a stir bar and reflux condenser that was capped with a nitrogen filled balloon. The mixture was stirred for 30 minutes at room temperature and then evaporated to dryness on the rotatory evaporator. The resulting white powder was dissolved in distilled water (50 mL). N-lithiotrifluoromethanesulfonimide (12.2 mmol, 3.5 g) was added. The

solution was washed with water (3 x 15mL). The final product was heated under pressure (100℃) to remove water to give 4.35 g (62%) of the chiral ionic liquid.

[α]: 53.43 (c = 0.812, dichloromethane); IR(neat) ν_{max} (cm^{-1}): 3146, 3085, 2961, 2874, 1459, 1354, 1201, 1138; MS m/z: $[M+H]^+$ calculated for $C_{18}H_{33}N_2O^+$: 293.25, found 292.2. $[M-H]^-$ calculated for $C_2F_6NO_4S_2^-$: 279.9, found 279.8.

General Procedure for the Synthesis of (S)-citronellyl bromide

In a round bottom flask triphenyl phosphine (19.2 mmol, 5.036 g), imidazole (19.2 mmol, 1.307 g) and bromine (19.2 mmol, 0.983 mL) were combined with anhydrous dichloromethane (75.0 mL). S-(-)-citronellol (16 mmol, 2.92 mL) in anhydrous dichloromethane (5 mL) was added to the stirring solution. The flask was back filled with nitrogen and to stirred for 3.0 hrs at room temperature, then concentrated. Flash column chromatography (90% hexanes, 10% ethyl acetate) yielded the 2.4614 g (71%) product as a clear liquid.

IR (neat) ν_{max} (cm^{-1}): 2965, 2923, 1451 and 1378; 1H NMR (500 MHz, CDCl3) δ (ppm): 5.10 (1H, t, J = 7.0 Hz), 3.43 (2H, m), 1.99 (2H, m), 1.89 (1H, m), 1.70 (3H,s), 1.62 (3H, s), 1.35 (2H, m), 1.20 (2H, m), 0.913 (3H, d, J = 6.0 Hz); MS m/z: $[M+H]^+$ calculated for $C_{10}H_{19}Br$ + H: 220.065, found 220.0.

General Procedure of 1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide (**5**)

Equimolar amounts of S-citronellyl bromide (14 mmol, 1.1494 g, 1.12 mL) and 1-methylimidazole (14 mmol, 3.0682 g) were combined into a heavy wall flask filled with nitrogen, sealed and heated at 40 ℃ for 5 days. The product was dried under vacuum at 40 ℃ for 2 days to give 3.0689 g (90%) of the product as a light brown viscous oil.

[α]: 1.29 (c = 0.459 M, dichloromethane)

General Procedure of 1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide (**6**)

Equimolar amounts of S-citronellyl bromide (14 mmol, 3.0682 g) and 1-butylimidazole (14 mmol, 1.1739, 1.84 mL) were combined into a heavy wall flask filled with nitrogen, sealed and heated at 40 ℃ for 5 days. The product was dried under vacuum at 40 ℃ for 2 days to give 2.6612 g (83%) of the product as a light brown viscous oil.

$[\alpha]$: 2.21 (c = 0.473 M, dichloromethane)

5.2.2 Experimental for Chapter Three

General Method for Achiral Reactions

The alkene (15 equivalents) and the enone (1 equivalent) were dissolved in CH_2Cl_2 (2 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Excess solvent was removed by the rotatory evaporator to result in the product.

Tricyclo[5.3.0.$0^{2,6}$]decan-3-one (**7**)

2-Cyclopentenone (0.08 mL, 1 mmol) and cyclopentene (1.32 mL, 15 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Excess solvent was removed by the rotatory evaporator to result in 24.5 mg (17.1 %) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 2922.7, 2849.4, 1703.9; MS m/z: 148.9, 123.0, 81.0. $[M+H]^+$ calculated for $C_{10}H_{14}O$ + H: 151.11, found 151.0; ^{1}H NMR(500 MHz, $CDCl_3$) δ (ppm): 2.22 (1H, m), 1.90 (1H, m), 1.67 (1H, m), 1.56 (1H, m), 1.56 (1H, m), 1.43 (1H, m), 1.38 (1H, m), 1.31 (1H, m), 1.30 (1H, m), 1.28 (1H, m), 1.19 (2H, m), 0.87 (1H, m), 0.83 (1H, m); $[\alpha]$: -0.74 $\pm$ 0.562 (c = 0.204, dichloromethane)

Tricyclo[5.4.0.$0^{2,6}$]undecan-3-one (**8**)

2-Cyclopentenone (0.08mL, 1 mmol) and cyclohexene (1.52 mL, 15 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Excess solvent was removed by the rotatory evaporator to result in 36.7 mg (22%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 2926.8, 2854.6, 1729.3; MS m/z: 149.1, 137.0 $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.9; ^{1}H NMR(500 MHz, $CDCl_3$) δ (ppm): 2.95 (1H, m), 2.81 (1H, m), 2.72 (1H, m), 2.69 (1H, m), 2.59 (1H, m), 2.45 (1H, m), 2.24 (1H, m), 2.23 (1H, m), 2.06 (1H, m), 1.90 (1H, m), 1.82 (1H, m), 1.74 (1H, m), 1.63 (1H, m), 1.45 (1H, m), 1.37 (1H, m), 1.25 (1H, m); [α]: -1.55 $\pm$ 1.56 (c = 0.058, dichloromethane)

Tricyclo[6.3.0.$0^{2,7}$]undecan-3-one (**9**)

2-Cyclohexenone (0.097 mL, 1 mmol) and cyclopentene (1.32 mL, 15 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Excess solvent was removed by the rotatory evaporator to result in 29.3 mg (17.8%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 2940.4, 2862.3, 1702.1; MS m/z: 148.9, 97.0 $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 164.9; ^{1}H NMR(500 MHz, $CDCl_3$) δ (ppm): 2.65 (1H, m), 2.45 (1H, m), 2.29 (1H, m), 2.20 (1H, m), 2.15 (1H, m), 1.80 (1H, m), 1.77 (1H, m), 1.75 (1H, m), 1.72 (1H, m), 1.60 (1H, m), 1.58 (1H, m), 1.40 (1H, m), 1.38 (1H, m), 1.24 (2H, m), 0.92 (1H, m); [α]: -0.40 $\pm$ 2.40 (c = 0.249, dichloromethane)

Tricyclo[6.4.0.$0^{2,7}$]dodecan-3-one (**10**)

2-Cylohehexenone (0.097 mL, 1 mmol) and cyclohexene (1.52 mL, 15 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24

hours. Excess solvent was removed via rotatory evaporator to result in 39.9 mg (22.4%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 2931.7, 2854.1, 1701.6; MS m/z: 162.9,148.9 $[M+H]^+$ calculated for $C_{12}H_{18}O$ + H: 179.14, found 178.9; ^1H NMR(500 MHz, $CDCl_3$) δ (ppm): 2.41 (1H, m), 2.31 (1H, m), 2.25 (1H, m), 2.19 (1H, m), 2.07 (1H, t, J = 4.6), 1.92 (1H, m), 1.84 (1H, m), 1.76 (2H, m), 1.64 (1H, m), 1.60 (1H, m), 1.59 (1H, m), 1.54 (1H, m), 1.52 (1H, m), 1.46 (1H, m), 1.39 (1H, m), 1.31 (2H, m); $[\alpha]$: -0.17 $\pm$ 0.341 (c = 0.287, dichloromethane)

7,7-Dichlorobicyclo[4.2.0]octan-2-one (**11**)

2-Cyclohexenone (0.097 mL, 1 mmol) and 1,1-Dichloroethylene (1.2 mL, 15 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Excess solvent was removed via rotatory evaporator to result in 51.3 mg (28.6%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 3056.6, 2918.9, 2871.1, 2848.5, 1705.8, 736.6, 702.9; MS m/z: 156.9, 148.9, 174.9 $[M+H]^+$ calculated for $C_8H_{12}Cl_2$ + H: 192.01, found 192.9; ^1H NMR(500 MHz, $CDCl_3$) δ (ppm): 3.20 (1H, m), 3.12 (1H, d, J = 8.0), 3.04 (1H, m), 2.81 (1H, m), 2.67 (1H, t, J = 7.5), 2.38 (1H, t, J = 3.5), 2.27 (1H, m), 1.99 (1H, m), 1.87 (1H, m), 1.70 (1H, m), 1.52 (1H, t), 1.49 (1H, t); $[\alpha]$: -3.47 $\pm$ 3.71(c = 0.144, dichloromethane)

6-Methyltricyclo[5.3.0.$0^{2,6}$]decan-3-one (**12**)

3-Methyl-2-cyclopentenone (0.1 mL, 1 mmol) and cyclopentene (1.32 mL, 15 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Excess solvent was removed by the rotatory evaporator to result in 15.2 mg (9.3%) of the product after purification by column chromatography. Product determined by comparing its GC retention time to compound **12** completed in the CILs.

IR(neat) ν_{max} (cm^{-1}): 2947.7, 2860.5, 1734.6; MS m/z: 149.1, 137.1, 121.1 $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.9; ^{1}H NMR(500 MHz, $CDCl_3$) δ (ppm): 2.68 (1H, m), 2.50 (1H, m), 2.25 (1H, m), 1.99 (1H, m), 1.82 (1H, m), 1.78 (1H, m), 1.71 (1H, m), 1.69 (1H, m), 1.67 (1H, m), 1.63 (1H, m), 1.60 (1H, m), 1.40 (1H, m), 1.32 (1H, m), 0.94 (3H, s); $[\alpha]$: 0 $\pm$ 0 (c = 0.151, dichloromethane)

6-Methyltricyclo[5.4.0.$0^{2,6}$]undecan-3-one (**13**)

3-Methyl-2-cyclopentenone (0.1 mL, 1 mmol) and cyclohexene (1.52 mL, 15 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Excess solvent was removed by the rotatory evaporator to result in 41.5 mg (23.2%) of the product.

IR(neat) ν_{max} (cm^{-1}): 2928.1, 2857.5, 1729.0; MS m/z: 149.8, 135.0, 81.0 $[M+H]^+$ calculated for $C_{12}H_{18}O$ + H: 179.14, found 178.9.; ^{1}H NMR(500 MHz, $CDCl_3$) δ (ppm): 2.62 (1H, m), 2.50 (1H, m), 2.44 (1H, m), 2.23 (1H, m), 2.05 (1H, m), 1.97 (1H, m), 1.85 (1H, m), 1.79 (1H, m), 1.68 (1H, m), 1.63 (1H, m), 1.58 (1H, m), 1.51 (1H, m), 1.41(1H, m), 1.33 (1H, m), 1.31 (1H, m), 0.97 (3H, s); $[\alpha]$: -1.01 $\pm$ 0.997 (c = 0.089, dichloromethane)

7-Methyltricyclo[6.4.0.$0^{2,7}$]undecan-3-one (**14**)

3-Methyl-2-cyclohexenone (0.11 mL, 1 mmol) and cyclopentene (1.32 mL. 15 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Excess solvent was removed by the rotatory evaporator to result in 104 mg (58.3%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 2947.5, 2864.1, 1718.7; MS m/z: 149.9, 121.1, 93.1, 81.0 $[M+H]^+$ calculated for $C_{12}H_{18}O$ + H: 179.14, found 178.9; ^{1}H NMR(500 MHz, $CDCl_3$) δ (ppm): 3.16 (1H, d, J = 3.4 Hz), 2.69 (1H, dd, J = 8.7, 1.25), 2.51 (1H, m), 2.36 (1H, m), 2.19 (1H, m), 2.07

(2H, m), 1.94 (1H, m), 1.82 (2H, m), 1.67 (2H, m), 1.51 (1H, m), 1.43 (1H, m), 1.31 (1H, m), 0.94 (3H, s); [α]: -0.79 $\pm$ 0.80 (c = 0.502, dichloromethane)

7-Methyltricyclo[6.4.0.$0^{2,7}$]dodecan-3-one (**15**)

3-Methyl-2-cyclohexenone (0.11 mL, 1 mmol) and cyclohexene (1.52 mL, 15 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Excess solvent was removed by the rotatory evaporator to result in 80.3 mg (41.8%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 2986.8, 2931.1, 1655.4; MS m/z: 165.7, 149.8, 81.0 $[M+H]^+$ calculated for $C_{13}H_{20}O$ + H: 193.16, found 193.5; ^{1}H NMR(500 MHz, $CDCl_3$) δ (ppm): 2.49 (1H, m), 2.31 (1H, td), 2.15 (1H, m), 2.10 (1H, m), 2.04 (1H, m), 1.83 (1H, m), 1.77 (1H, m), 1.72 (1H, m), 1.68 (2H, m), 1.59 (1H, m), 1.51 (2H, m), 1.34 (2H, m), 1.32 (2H, m), 0.88 (3H, s); [α]: -1.05 $\pm$ 0.959 (c = 0.521, dichloromethane)

General Method for Chiral Reactions

The alkene (15 equivalents) and the enone (1 equivalent) were added to the chiral ionic liquid (1 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Diethyl ether (5 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product mixture which was purified by column chromatography. The CIL used for each case is listed followed by the characterization of the product.

Tricyclo[5.3.0.$0^{2,6}$]decan-3-one (**7**)

2-Cyclopentenone (0.04 mL, 0.5 mmol) and cyclopentene (0.66 mL, 7.5 mmol) were dissolved in the chiral ionic liquid (1 mL) in a Pyrex irradiation tube and irradiated with a Hg

lamp for 24 hours. Diethyl ether (5 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product after purification by column chromatography.

1-butyl-3-methylimidazolium L-Lactate: $[\alpha]$ = -5.00 (c = 0.349, dichloromethane)

Product determined by comparing its GC retention time with product **7** completed in the achiral environment.

Yield: 15.8 mg (10.5%); IR(neat) ν_{max} (cm^{-1}): 2986.3, 2926.5, 2854.3, 1728.3; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{14}O$ + H: 151.11, found 150.9; $[\alpha]$ = -12.86 $\pm$ 3.06 (c = 0.093, dichloromethane)

1-butyl-3-methylimidazolium *R*-camphorsulfonate: $[\alpha]$ = 17.99 (c = 0.478, dichloromethane)

Product determined by comparing its GC retention time with product **7** completed in the achiral environment.

Yield: 23.1 mg (22.6%); IR(neat) ν_{max} (cm^{-1}): 2927.2, 2867.9, 1736.2; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{14}O$ + H: 151.11, found 150.9; $[\alpha]$ = -1.08 $\pm$ 0.442 (c = 0.462 M, dichloromethane)

1-butyl-3-methylimidazolium *S*-camphorsulfonate: $[\alpha]$ = 18.21 (c = 0.494, dichloromethane)

Yield: 15.0 mg (10.5%); IR(neat) ν_{max} (cm^{-1}): 2928.1, 2865.1, 1734.2; MS m/z: 123.4 $[M+H]^+$ calculated for $C_{10}H_{14}O$ + H: 151.11, found 151.8; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.22 (1H, m), 2.17 (1H, m), 2.04 (1H, m), 1.93 (1H, m), 1.67 (1H, m), 1.56 (1H, m), 1.51 (1H, m), 1.41 (1H, m), 1.38 (1H, m), 1.30 (2H, m), 1.15 (1H, m), 0.96 (1H, m), 0.82 (1H, m); $[\alpha]$ = -1.21 $\pm$ 0.419 (c = 0.352, dichloromethane)

R-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate: $[\alpha]$ = -8.33 (c = 0.108 M, dichloromethane)

Product determined by comparing its GC retention time with product **7** completed in the achiral environment.

Yield: 20.1 mg (13.4%); IR(neat) ν_{max} (cm^{-1}): 2960.1, 2924.3, 2850.9, 1733.66; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{14}O$ + H: 151.11, found 151.0; $[\alpha]$ = -2.23 $\pm$ 0.438 (c = 0.493 M, dichloromethane)

1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide: $[\alpha]$ = 49.68 (c = 0.471, dichloromethane)

Yield: 30.4 mg (20.2%); IR(neat) ν_{max} (cm^{-1}): 2955.4, 2924.4, 2869.9, 1734.24

MS m/z: $[M+H]^+$ calculated for $C_{10}H_{14}O$ + H: 151.11, found 152.0. Fragments: 137.1, 55.0; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.16 (1H, m), 2.04 (1H, m), 1.62 (1H, M), 1.56 (1H, m), 1.39 (1H, m), 1.36 (1H, m), 1.32 (1H, m), 1.30 (1H, m), 1.26 (2H, m), 1.91 (1H, m), 0.96 (1H, m), 0.90 (1H, m), 0.82 (1H, m); $[\alpha]$ = 29.13 $\pm$1.74 (c = 0.230, dichloromethane)

1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide: $[\alpha]$ = 1.29 (c = 0.459, dichloromethane)

Yield: 18.4 mg (12.2%); IR(neat): 2933.7, 2855.9, 1729.1; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{14}O$ + H: 151.11, found 150.9; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.22 (1H, m), 2.17 (1H, m), 2.04 (1H, m), 1.90 (1H, m), 1.67 (1H, m), 1.55 (1H, m), 1.51 (1H, m), 1.41 (1H, m), 1.38 (1H, m), 1.35 (2H, m), 1.15 (1H, m), 0.94 (1H, m), 0.85 (1H, m); $[\alpha]$ = -10.87 $\pm$ 4.83 (c = 0.046, dichloromethane)

1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide: $[\alpha]$ = 2.21 (c = 0.473, dichloromethane)

Product determined by comparing its GC retention time with product **7** completed in the achiral environment.

Yield: 18.1 mg (12.1%); IR(neat) ν_{max} (cm^{-1}): 2961.1, 2926.9, 2855.1, 1727.9; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{14}O$ + H: 151.11, found 150.9. Fragments: 149, 55; $[\alpha]$ = -2.53 $\pm$ 0.688 (c = 0.316, dichloromethane)

6-Methyltricyclo[5.4.0.$0^{2,6}$]undecan-3-one (**8**)

2-Cyclopentenone (0.04 mL, 0.5 mmol) and cyclohexene (0.76 mL, 7.5 mmol) were dissolved in the chiral ionic liquid (1 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Diethyl ether (5 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product after purification by column chromatography.

1-butyl-3-methylimidazolium L-Lactate: $[\alpha]$ = -5.00 (c = 0.799, dichloromethane)

Product determined by comparing its GC retention time to compound **8** completed in the achiral environment.

Yield: 16.4 mg (10%); IR(neat) ν_{max} (cm^{-1}): 2926.8, 2854.3, 1730.6; MS m/z: $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.1; $[\alpha]$ = -5.45 $\pm$ 1.01 (c = 0.220, dichloromethane)

1-butyl-3-methylimidazolium *R*-camphorsulfonate: $[\alpha]$ = -20.14 (c = 0.849, dichloromethane)

Product determined by comparing its GC retention time to compound **8** completed in the achiral environment.

Yield: 17.4 mg (10.6%); IR(neat) = ν_{max} (cm^{-1}): 2907.8, 2868.0, 1694.6; MS m/z: $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.9; $[\alpha]$ = -3.27 $\pm$ 0.999 (c = 0.107, dichloromethane)

1-butyl-3-methylimidazolium *S*-camphorsulfonate: $[\alpha]$ = 18.21 (c = 0.494, dichloromethane)

Yield: 33.9 mg (20.6%); IR(neat) ν_{max} (cm^{-1}): 2926.6, 2854.3, 1730.0

MS m/z: $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.1. Fragments: 311.3, 83.1; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.94 (1H, m), 2.84 (1H, m), 2.69 (1H, m), 2.59 (1H, m), 2.45 (1H, m), 2.32 (1H, m), 2.20 (1H, m), 2.04 (1H, m), 1.96 (1H, m),1.84 (1H, m), 1.73 (1H, m), 1.62 (1H, m), 1.55 (1H, m), 1.45 (1H, m), 1.37 (1H, m), 1.22 (1H, m); $[\alpha]$ = -1.18 $\pm$ 0.303 (c = 0.678, dichloromethane)

R-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate: $[\alpha]$ = -8.33 (c = 108, dichloromethane)

Product determined by comparing its GC retention time to compound **8** completed in the achiral environment.

Yield: 20.9 mg (12.7%); IR(neat) ν_{max} (cm^{-1}): 2927.3, 2855.0, 1728.7; MS m/z: $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.1; $[\alpha]$ = -2.73 $\pm$ 0.665 (c = 0.330, dichloromethane)

1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide: $[\alpha]$ = 49.68 (c = 0.471, dichloromethane)

Yield: 208.9 mg (>99%); IR(neat) ν_{max} (cm^{-1}): 2927.0, 2855.1, 1731.3; MS m/z: $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.1. Fragments: 83.1; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.93 (1H, m), 2.77 (1H, m), 2.70 (1H, m), 2.60 (1H, m), 2.45 (1H, m), 2.34 (1H, m), 2.21 (1H, m), 2.06 (1H, m), 1.96 (1H, m), 1.86 (1H, m), 1.74 (1H, m), 1.63

(1H, m), 1.54 (1H, m), 1.48 (1H, m), 1.39 (1H, m), 1.26 (1H, m); $[\alpha] = 3.97 \pm 0.103$ (c = 0.208, dichloromethane)

1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide: $[\alpha] = 1.29$ (c = 0.459, dichloromethane)

Yield: 17.4 mg (10.6%); IR(neat) ν_{max} (cm^{-1}): 2926.8, 2854.9, 1732.6

MS m/z: $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.1; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.94 (1H, m), 2.77 (1H, m), 2.71 (1H, m), 2.61 (1H, m), 2.50 (1H, m), 2.33 (1H, m), 2.20 (1H, m), 2.02 (1H, m), 1.96 (1H, m), 1.87 (1H, m), 1.72 (1H, m), 1.62 (1H, m), 1.55 (1H, m), 1.40 (1H, m), 1.38 (1H, m), 1.26 (1H, m); $[\alpha] = -2.29 \pm 0.601$ (c = 0.348, dichloromethane)

1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide: $[\alpha] = 2.21$ (c = 0.473, dichloromethane)

Yield: 20.4 mg (12.4%); IR(neat) ν_{max} (cm^{-1}): 2926.9, 2854.4, 1730.4; MS m/z: $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.1. Fragments: 83.1, 55; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.94 (1H, m), 2.76 (1H, m), 2.70 (1H, m), 2.59 (1H, m), 2.46 (1H, m), 2.36 (1H, m), 2.29 (1H, m), 2.20 (1H, m), 2.04 (1H, m), 1.96 (1H, m), 1.88 (1H, m), 1.76 (1H, m), 1.62 (1H, m), 1.48 (1H, m), 1.38 (1H, m), 1.25 (1H, m); $[\alpha] = -2.94 \pm 0.522$ (c = 0.408, dichloromethane)

Tricyclo[6.3.0.$0^{2,7}$]undecane-3-one (**9**)

2-Cyclohexenone (0.05 mL, 0.5 mmol) and cyclopentene (0.66 mL, 7.5 mmol) were dissolved in the chiral ionic liquid (1 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Diethyl ether (5 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica

gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product after purification by column chromatography.

1-butyl-3-methylimidazolium L-Lactate: $[\alpha]$ = -5.25 (c = 0.990, dichloromethane)

Yield: 48.5 mg (30%); IR(neat) ν_{max} (cm^{-1}): 2928.3, 2854.3, 1700.6; MS m/z: $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.0. Fragments: 97.1; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.62 (1H, m), 2.58 (1H, m), 2.45 (1H, m), 2.19 (1H, m), 2.05 (1H, m), 1.90 (1H, m), 1.85 (1H, m), 1.80 (1H, m), 1.75 (1H, m), 1.72 (1H, m), 1.66 (1H, m), 1.60 (1H, m), 1.58 (1H, m), 1.37 (1H, m), 1.30 (1H, m), 1.28 (1H, m); $[\alpha] = -2.00 \pm 0.279$ (c = 0.204, dichloromethane)

1-butyl-3-methylimidazolium *R*-camphorsulfonate: $[\alpha]$ = -20.02 (c = 1.029, dichloromethane)

Product determined by comparing its GC retention time to compound **9** completed in the achiral environment.

Yield: 8.9 mg (5%); IR(neat) ν_{max} (cm^{-1}): 2924.6, 2853.4, 1740.1; MS m/z: $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.0; $[\alpha] = -15 \pm 4.10$ (c = 0.053, dichloromethane)

Tricyclo[6.4.0.$0^{2,7}$]dodecan-3-one (**10**)

2-Cyclohexenone (0.05 mL, 0.5 mmol) and cyclohexene (0.76 mL, 7.5 mmol) were dissolved in the chiral ionic liquid (1 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Diethyl ether (5 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product after purification by column chromatography.

1-butyl-3-methylimidazolium L-Lactate: [α] = -5.25 (c = 0.990, dichloromethane)

Product determined by comparing its GC retention time to compound **10** completed in the achiral environment.

Yield: 4.1 mg (2.30%); IR(neat) ν_{max} (cm^{-1}): 2986.8, 2845.8, 1702.1; MS m/z: $[M+H]^+$ calculated for $C_{12}H_{18}O$ + H: 179.14, found 178.9. Fragments: 150.8; [α] = -2.29 $\pm$ 1.23 (c = 0.136, dichloromethane)

1-butyl-3-methylimidazolium *R*-camphorsulfonate: [α] = -20.02 (c = 1.029, dichloromethane)

Yield: 18.9 mg (11%); IR(neat) ν_{max} (cm^{-1}): 2924.1, 2854.3, 1743.9; MS m/z: $[M+H]^+$ calculated for $C_{12}H_{18}O$ + H: 179.14, found 179.1. Fragments: 150.0; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.41 (1H, m), 2.36 (1H, m), 2.25 (1H, m), 2.18 (1H, m), 1.06 (1H, m), 1.92 (1H, m), 1.85 (1H, m), 1.74 (1H, m), 1.64 (1H, m), 1.76 (1H, m) 1.64 (1H, m), 1.62 (1H, m), 1.58 (1H, m), 1.55 (1H, m), 1.51 (1H, m), 1.46 (1H, m), 1.39 (1H, m), 1.33 (1H, m); [α] = -4.46 $\pm$ 2.39 (c = 0.112, dichloromethane)

7,7-dichlorobicyclo[4.2.0]octan-2-one (**11**)

2-Cyclohexenone (0.05 mL, 0.5 mmol) and 1,1-dichloroethylene (0.6 mL, 7.5 mmol) were dissolved in the chiral ionic liquid (1 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Diethyl ether (5 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product after purification by column chromatography.

1-butyl-3-methylimidazolium L-Lactate: [α] = -5.24 (c = 0.955, dichloromethane)

Product determined by comparing its GC retention time to compound **11** completed in the achiral environment.

Yield: 10.1 mg (5.64%); IR(neat) ν_{max} (cm^{-1}): 2926.3, 2854, 1725.4, 740.0, 705.5

MS m/z: $[M+H]^+$ calculated for $C_8H_{12}Cl_2$ + H: 179.04, found 179.8. Fragments: 144.6, 109.0; $[\alpha]$ = -4.45 $\pm$ 1.08 (c = 0.202, dichloromethane), ee = 3.3%.

1-butyl-3-methylimidazolium *R*-camphorsulfonate: $[\alpha]$ = -17.08 (c = 0.562, dichloromethane)

Product determined by comparing its GC retention time to compound **11** completed in the achiral environment.

Yield: 74.8 mg (41.8%); IR(neat) ν_{max} (cm^{-1}): 2930.6, 2870.8, 1734.1, 870.1, 814.6; MS m/z: $[M+H]^+$ calculated for $C_8H_{12}Cl_2$ + H: 179.04, found 179.8. Fragments: 144.5, 109.0; $[\alpha]$ = -3.30 $\pm$ 0.100 (c = 0.212, dichloromethane), ee = 2.4%.

6-Methyltricyclo[5.3.0.$0^{2,6}$]decan-3-one (**12**)

3-Methyl-2-cyclopentenone (0.05 mL, 0.5 mmol) and cyclopentene (0.66 mL, 7.5 mmol) were dissolved in the chiral ionic liquid (1 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Diethyl ether (5 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product after purification by column chromatography.

1-butyl-3-methylimidazolium L-Lactate: $[\alpha]$ = -5.24 (c = 0.955, dichloromethane)

Yield: 7.7 mg (4.3%); IR(neat) ν_{max} (cm^{-1}): 2958.7, 2925.2, 2855.6, 1734.6; MS m/z: 149.9 $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.9; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.68 (1H, m), 2.52 (1H, m), 2.24 (1H, m), 2.01 (1H, m), 1.82 (1H, m), 1.76 (1H, m), 1.72 (1H, m), 1.69 (1H, m), 1.68 (1H, m), 1.64 (1H, m), 1.60 (1H, m), 1.42 (1H, m), 1.38 (1H, m), 0.89 (3H, s); $[\alpha]$ = -3.38 $\pm$ 0.944 (c = 0.236, dichloromethane)

1-butyl-3-methylimidazolium *R*-camphorsulfonate: [α] = -20.24 (c = 0.420, dichloromethane)

Yield: 16.7 mg (10.2%); IR(neat) ν_{max} (cm^{-1}): 2963.7, 2926.6, 1733.4; MS m/z: $[M+H]^+$ calculated for $C_{11}H_{16}O$ + H: 165.13, found 165.1; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.92 (1H, m), 2.50 (1H, m), 2.29 (1H, m),1.97 (1H, m), 1.81 (1H, m), 1.78 (1H, m), 1.72 (1H, m), 1.69 (1H, m), 1.67 (1H, m), 1.64 (1H, m), 1.60 (1H, m), 1.41 (1H, m), 1.30 (1H, m), 0.97 (3H, s); [α] = -2.73 $\pm$ 0.825 (c = 0.256, dichloromethane)

6-Methyltricyclo[5.4.0.$0^{2,6}$]undecane-3-one (**13**)

3-Methyl-2-cyclopentenone (0.05 mL, 0.5 mmol) and cyclohexene (0.76 mL, 7.5 mmol) were dissolved in the chiral ionic liquid (1 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Diethyl ether (5 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product after purification by column chromatography.

1-butyl-3-methylimidazolium L-Lactate: [α] = -5.09 (c = 1.060, dichloromethane)

Yield: 19.4 mg (10.9%); IR(neat) ν_{max} (cm^{-1}): 2929.3, 2856.4, 1730.7; MS m/z: 164.9, 137.1 $[M+H]^+$ calculated for $C_{12}H_{18}O$ + H: 179.14, found 179.1; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.62 (1H, m), 2.52 (1H, m), 2.41 (1H, m), 2.31 (1H, m), 2.19 (1H, m), 2.02 (1H, m), 1.97 (1H, m), 1.86 (1H, m), 1.76 (1H, m), 1.67 (1H, m), 1.62 (1H, m), 1.58 (1H, m), 1.51 (1H, m), 1.41 (1H, m), 1.38 (1H, m), 0.88 (3H, s); [α] = -1.55 $\pm$ 0.534 (c = 0.388, dichloromethane)

1-butyl-3-methylimidazolium *R*-camphorsulfonate: [α] = -20.24 (c = 0.420, dichloromethane)

Yield: 74.8 mg (41.9%); IR(neat) ν_{max} (cm^{-1}): 2930.6, 2857.6, 1731.5; MS m/z: $[M+H]^+$ calculated for $C_{12}H_{18}O$ + H: 179.14, found 179.1; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm):

2.61 (1H, m), 2.50 (1H, m), 2.41 (1H, m), 2.33 (1H, m), 2.18 (1H, m), 2.04 (1H, m), 1.90 (1H, m), 1.87 (1H, m), 1.76 (1H, m), 1.66 (1H, m), 1.60 (1H, m), 1.57 (1H, m), 1.55 (1H, m), 1.46 (1H, m), 1.38 (1H, m), 0.88 (3H, s); $[\alpha]$ = -0.94 $\pm$ 0.272 (c = 0.748, dichloromethane)

7-Methyltricyclo[6.3.0.0^{2,7}]undecane-3-one (**14**)

3-Methyl-2-cyclohexenone (0.057 mL, 0.5 mmol) and cyclopentene (0.66 mL, 7.5 mmol) were dissolved in the chiral ionic liquid (1 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Diethyl ether (5 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product after purification by column chromatography.

1-butyl-3-methylimidazolium L-Lactate: $[\alpha]$ = -5.81 (c = 0.930, dichloromethane)

Yield: 22.1 mg (12.4%); IR(neat) ν_{max} (cm^{-1}): 2930.6, 2855.4, 1698.7; MS m/z: 164.9 $[M+H]^+$ calculated for $C_{12}H_{18}O$ + H: 179.14, found 179.1; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.21 (1H, dddd, J = 1.5, 6.5), 2.71 (1H, d, J = 9.4), 2.66 (1H, m), 2.51 (1H, m), 2.36 (1H, m), 2.20 (1H, m), 2.17 (1H, m), 2.08 (1H, m), 1.96 (1H, m), 1.84 (1H, m), 1.81 (1H, m), 1.67 (1H, m), 1.56 (1H, m), 1.43 (1H, m), 1.31 (1H, m), 0.94 (3H, s); $[\alpha]$ = -1.36 $\pm$ 0.467 (c = 0.442, dichloromethane)

1-butyl-3-methylimidazolium *R*-camphorsulfonate: $[\alpha]$ = -20.24 (c = 0.420, dichloromethane)

Yield: 82.1 mg (46.1%); IR(neat) ν_{max} (cm^{-1}): 2950.2, 2869.9, 1685.7; MS m/z: 165.0 $[M+H]^+$ calculated for $C_{12}H_{18}O$ + H: 179.14, found 179.9; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.10 (1H, m), 2.80 (1H, m), 2.66 (1H, m), 2.51 (1H, m), 2.36 (1H, m), 2.29 (1H, m), 2.19 (1H, m), 2.08 (1H, m), 2.01 (1H, m), 1.94 (1H, m), 1.84 (1H, m), 1.76 (1H, m),

1.67 (1H, m), 1.55 (1H, m), 1.30 (1H, m), 0.94 (3H, s); $[\alpha]$ = -0.97 $\pm$ 0.246 (c = 0.821, dichloromethane)

7-Methyltricyclo[6.4.0.$0^{2,7}$]dodecan-3-one (**15**)

3-Methyl-2-cyclohexenone (0.057 mL, 0.5 mmol) and cyclohexene (7.5 mmol) were dissolved in the chiral ionic liquid (1 mL) in a Pyrex irradiation tube and irradiated with a Hg lamp for 24 hours. Diethyl ether (5 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product after purification by column chromatography.

1-butyl-3-methylimidazolium L-Lactate: $[\alpha]$ = -5.81 (c = 0.930, dichloromethane)

Yield: 68.1 mg (35.4%); IR(neat) ν_{max} (cm^{-1}): 2930.5, 2855.3, 1698.6; MS m/z: $[M+H]^+$ calculated for $C_{13}H_{20}O$ + H: 193.16, found 193.1; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.67 (1H, m), 2.61 (1H, d, J = 10.3), 2.53 (1H, d, J = 9.0), 2.41 (2H, m), 2.37 (1H, m), 2.28 (2H, m), 2.06 (2H, m), 1.95 (1H, m), 1.89 (2H, m), 1.60 (1H, m), 1.53 (1H, m), 1.47 (1H, m), 1.38 (1H, m), 0.88 (3H, s); $[\alpha]$ = -1.47 $\pm$ 0.299 (c = 0.681, dichloromethane)

1-butyl-3-methylimidazolium *R*-camphorsulfonate: $[\alpha]$ = -20.24 (c = 0.420, dichloromethane)

Product determined by comparing its GC retention time to compound **15** completed in the achiral environment.

Yield: 21.5 mg (11%); IR(neat) ν_{max} (cm^{-1}): 2929.5, 2857.1, 2835.5, 16.48.5; MS m/z: 165.7 $[M+H]^+$ calculated for $C_{13}H_{20}O$ + H: 193.16, found 193.4; $[\alpha]$ = -1.52 $\pm$ 0.231 (c = 0.521, dichloromethane)

5.2.3 Experimental for Chapter Four

General Method for Achiral Reactions

Two equivalents of the aldehyde/ketone and one equivalent of the base were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product after purification by column chromatography. The CIL used for each case is listed followed by the characterization of the product.

3-Hydroxy-2-methylpentanal (**16**)

A. Propanal (0.36 mL, 5 mmol) and morpholine (0.22 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 31.0 mg (10.7%) of the product after purification by column chromatography.

   IR(neat) ν_{max} (cm^{-1}): 3421.4, 2962.27, 2878.9, 1654.1; MS m/z: 89.7 $[M+H]^+$ calculated for $C_6H_{12}O_2$ + H: 117.09, found 117.1; ^{1}H NMR(500MHz, $CDCl_3$) δ (ppm): 9.20 (1H, s), 3.70 (1H, m), 2.59 (1H, m), 1.59 (2H, m), 1.45 (1H, m), 0.93 (3H, t, J = 7.5), 0.83 (3H, d, J = 7); $[\alpha]$: -1.48 $\pm$ 1.24 (c = 0.203, dichloromethane)

B. Propanal (0.36 mL, 5 mmol) and pyrroldine (0.21 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was

added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 16.8 mg (5.8%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 3433.1, 2960.11, 2925.9, 1684.1; MS m/z: $[M+H]^+$ calculated for $C_6H_{12}O_2$ + H: 117.09, found 117.9; ^{1}H NMR(500 MHz, $CDCl_3$) δ (ppm): 9.25 (1H, s), 4.10 (1H, td), 3.71 (1H, bs), 2.19 (1H, m), 1.65 (2H, m), 0.98 (3H, t, J = 7.5), 0.87 (3H, d, J = 7); $[\alpha]$: -1.36 $\pm$ 1.42 (c = 0.086, dichloromethane)

2-Ethyl-3-hydroxyhexanal (**17**)

A. Butanal (0.45 mL, 5 mmol) and morpholine (0.22 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL) and brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 24.1 mg (6.7%) the product after purification by column chromatography.

   IR(neat) ν_{max} (cm^{-1}): 3405.7, 2961.8, 2932.9, 2874.0, 1718.2; MS m/z: $[M+H]^+$ calculated for $C_8H_{16}O_2$ + H: 145.12, found: 145.0; ^{1}H NMR(500 MHz, $CDCl_3$) δ (ppm): 9.64 (1H, s), 3.87 (1H, bs), 3.64 (1H, m), 2.47 (1H, m), 1.98 (2H, m), 1.70 (2H, m), 1.25 (3H, m), 1.10 (2H, m), 0.88 (3H, m); $[\alpha]$: -0.249 $\pm$ 0.251 (c = 0.482, dichloromethane)

B. Butanal (0.45 mL, 5 mmol) and pyrrolidine (0.21 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was

added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 32.1 mg (8.9%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 3446.9, 2962.7, 2874.0, 1716.8; MS m/z: 72.2 $[M+H]^+$ calculated for $C_8H_{16}O_2$ + H: 145.12, found: 145.0; ^{1}H NMR(500 MHz, $CDCl_3$) δ (ppm): 9.64 (1H, s), 4.13 (1H, bs), 3.89 (1H, m), 2.25 (1H, m), 1.64 (2H, m), 1.36 (2H, m), 1.24 (3H, m), 1.01 (2H, m), 0.86 (3H, m); [α]: 0 $\pm$ 0 (c = 0.492, dichloromethane)

3-Hydroxy-2-2-propylheptanal (**18**)

A. Pentanal (0.27 mL, 5 mmol) and morpholine (0.22 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 13.7 mg (3.2%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 3439.0, 2957.4, 2931.6, 2871.6, 1759.1; MS m/z: 156.1, 72.2 $[M+H]^+$ calculated for $C_{10}H_{20}O_2$ + H: 173.15, found: 173.0; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.19 (1H, s), 3.64 (1H, m), 2.59 (2H, m), 2.30 (1H, m), 1.92 (2H, m), 1.82 (1H, bs), 1.69 (2H, m), 1.46 (2H, m), 1.32 (2H, m), 0.94 (3H, m), 0.80 (3H, m); [α]: 0 $\pm$ 0 (c = 0.274, dichloromethane)

B. Pentanal 0.27 mL, 5 mmol) and pyrroldine (0.21 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 26.1 mg (6.1%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 3496.2, 2960.6, 2933.6, 2873.9, 1756.7; MS m/z: 156.1, 88.2 $[M+H]^+$ calculated for $C_{10}H_{20}O_2$ + H: 173.15, found: 173.0; ^{1}H NMR(500MHz, $CDCl_3$) δ (ppm): 9.49 (1H, s), 4.21 (1H, m), 2.33 (1H, m), 2.27 (2H, m), 1.72 (2H, m), 1.59 (2H, m), 1.46 (2H, m), 1.33 (2H, m), 1.24 (1H, s), 0.96 (3H, m), 0.90 (3H, m); [α]: -0.380 $\pm$ 0.383 (c = 0.402, dichloromethane)

2-(1-Hydroxycyclopentyl)cyclopentanone (**19**)

A. Cyclopentanone (0.44 mL, 5 mmol) and morpholine (0.22 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 11.4 mg (2.7%) of the product after purification by column chromatography.

Product determined by comparing its GC retention time to compound **19A** completed in the CIL **2S.**

IR(neat) ν_{max} (cm^{-1}): 3421.5, 2922.5, 2850.0, 1705.8; MS m/z: 153.1, 84.1, 72.2 $[M+H]^+$ calculated for $C_{10}H_{16}O_2$ + H: 169.12, found: 168.9; [α]: 0 $\pm$ 0 (c = 0.228, dichloromethane)

B. Cyclopentanone (0.44 mL, 5 mmol) and pyrrolidine (0.21 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 25.5 mg (6.1%) of the product after purification by column chromatography.

   Product determined by comparing its GC retention time to compound **19B** completed in the CIL **2S.**

   IR(neat) ν_{max} (cm^{-1}): 3455.1, 2959.2, 2872.0, 1706.3; MS m/z: 153.1, 72.2 $[M+H]^+$ calculated for $C_{10}H_{16}O_2$ + H: 169.12, found: 168.9; [α]: -1.77 $\pm$ 1.47 (c = 0.282, dichloromethane)

4-Hydroxy-3,4-dimethyl-2-hexanone (**20**)

A. 2-Butanone (0.45 mL, 5 mmol) and morpholine (0.22 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 10.5 mg the crude product.

B. 2-Butanone (0.45 mL, 5 mmol) and pyrroldine (0.21 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the 8.9 mg (2.5%) product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 3447.2, 2963.8, 2928.5, 1700.6; MS m/z: $[M+H]^+$ calculated for $C_8H_{16}O_2$ + H: 145.12, found: 145.1; $[\alpha]$: 0 $\pm$ 0 (c = 0.178, dichloromethane)

5-Ethyl-5-hydroxy-4-methylhepta-1,6-dien-3-one (**21**)

A. 1-Penten-3-one (0.25 mL, 5mmol) and morpholine (0.22 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 31.5 mg (7.4%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 2968.3, 2936.9, 2851.1, 1718.9; MS m/z: 72.2 $[M+H]^+$ calculated for $C_{10}H_{16}O_2$ + H: 169.12, found: 168.9; $[\alpha]$: 0 $\pm$ 0 (c = 0.630, dichloromethane)

B. 1-Penten-3-one (0.25 mL, 5mmol) and pyrrolidine (0.21 mL, 2.5 mmol) were added to DMF (5 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (5 mL) was added to the mixture and then the mixture was washed with distilled water (5 mL), brine (5 mL). The aqueous layers were back extracted with dichloromethane (3 × 5

mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in 16.3 mg (3.8%) of the product after purification by column chromatography.

IR(neat) ν_{max} (cm^{-1}): 2966.8, 2938.8, 2850.3, 1720.6; MS m/z: 72.2 $[M+H]^+$ calculated for $C_{10}H_{16}O_2$ + H: 169.12, found: 168.9; $[\alpha]$: 0 $\pm$ 0 (c = 0.326, dichloromethane)

General Method for Chiral Reactions

Two equivalents of the aldehyde/ketone and one equivalent of the base were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product.

3-Hydroxy-2-methylpentanal (**16**)

A. Propanal (0.18 mL, 2.5 mmol) and morpholine (0.11 mL, 1.25 mmol) were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to

result in the product. Excess solvent was removed by the rotatory evaporator to result in the product.

1-butyl-3-methylimidazolium *R*-Camphorsulfonate: [α] = -20.24 (c = 0.420, dichloromethane)

Yield: 27.7 mg (19.1%) of product and product with the enamine attached. IR(neat) ν_{max} (cm^{-1}): 3373.34, 2960.0, 2924.5, 2855.5, 1725.2; MS m/z: $[M+H]^+$ calculated for $C_7H_{14}NO$ + H: 128.10, found 128.1. $[M+H]^+$ calculated for $C_{10}H_{18}NO$ + H: 168.13, found 168.13; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.20 (1H, s), 3.69 (1H, m), 3.17 (1H, m), 2.62 (1H, m), 1.59 (1H, m), 1.40 (1H, m), 0.95 (3H, t, J = 7), 0.88 (3H, d, J = 6.5); [α] = -4.89 $\pm$ 1.43 (c = 0.163, dichloromethane), 33% ee.

1-butyl-3-methylimidazolium *S*-Camphorsulfonate: [α] = 18.21 (c = 0.494, dichloromethane)

Yield: 111.5 mg (76.8%) of the product and product with enamine still attached; IR(neat) ν_{max} (cm^{-1}): 3416.7, 2964.9, 2877.9, 1736.6; MS m/z: $[M+H]^+$ calculated for $C_7H_{14}NO$ + H: 128.10, found 128.1. $[M+H]^+$ calculated for $C_{10}H_{18}NO$ + H: 168.13, found 168.13. $[M+H]^+$ calculated for $C_{10}H_{20}NO_2$ + H: 186.14, found 186.1; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.21 (1H, s), 3.69 (1H, m), 2.58 (1H, m), 1.61 (2H, m), 1.45 (1H, m), 0.93 (3H, t, J = 7.5), 0.82 (3H, d, J = 7); [α] = -2.40 (c = 0.293, dichloromethane), 16% ee.

R-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate: [α] = -10.52 (c = 0.812, dichloromethane)

Yield: 24.6 (16%) of the product with the enamine attached; IR(neat) ν_{max} (cm^{-1}): 3452.7, 2961.8, 2932.4, 1637.1; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{18}NO$ + H: 168.13, found 168.13; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.32 (1H, m), 6.02 (1H, m), 4.85 (1H, m), 4.68 (1H, m), 3.69 (4H, m), 3.33 (1H, m), 2.46 (2H, m), 1.86 (3H, m), 1.70 (1H, m), 1.51 (1H, m), 0.93 (3H, m); [α] = -1.37 $\pm$ 0.479 (c = 0.436, dichloromethane), 9% ee.

1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide: [α] = 50.37 (c = 0.812, dichloromethane)

Yield: 25.6 mg (17.6%) of the product; IR(neat) ν_{max} (cm^{-1}): 3421.2, 2955.3, 2722.6, 1736.9; MS m/z: $[M+H]^+$ calculated for $C_6H_{12}O_2$ + H: 117.09, found 117.1; ^1H NMR (500MHz, $CDCl_3$) δ (ppm): 9.20 (1H, s), 4.02 (1H, t), 3.28 (1H, td), 2.16 (1H, m), 1.64 (1H, m), 1.36 (1H, m), 0.95 (3H, t, J = 7.5), 0.88 (3H, d, J = 7); [α] = 32.42 $\pm$ 1.03 (c = 0.330, dichloromethane)

1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide: [α] = 1.29 (c = 0.459, dichloromethane)

Yield: 91.6 mg (64.3%) of the product and product with the enamine attached; IR(neat) ν_{max} (cm^{-1}): 3447.0, 2965.7, 2852.0, 1683.8; MS m/z: $[M+H]^+$ calculated for $C_7H_{14}NO$ + H: 128.10, found 128.1. $[M+H]^+$ calculated for $C_{10}H_{18}NO$ + H: 168.13, found 168.13; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.20 (1H, s), 3.69 (1H, m), 3.11 (1H, td, J_t = 3.11, J_d = 2.45), 2.62 (1H, m), 1.63 (1H, m), 1.43 (1H,

m), 0.95 (3H, t, J = 7), 0.88 (3H, d, J = 6.5); [α] = -0.295 $\pm$ 0.066 (c = 0.915, dichloromethane), 2% ee.

1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide: [α] = 2.21 (c = 0.473, dichloromethane)

Yield: 22.0 mg (15.2%) of the product and product with the enamine attached; IR(neat) ν_{max} (cm^{-1}): 3439.4, 2964.9, 2853.9, 1700.4; MS m/z: $[M+H]^+$ calculated for $C_7H_{14}NO$ + H: 128.10, found 128.1. $[M+H]^+$ calculated for $C_{10}H_{18}NO$ + H: 168.13, found 168.13; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.51 (1H, s), 4.45 (1H, m), 3.74 (1H, m), 2.05 (1H, bs), 1.63 (2H, m), 0.92 (3H, t), 0.81 (3H, d); [α] = -1.73 $\pm$ 0.612 (c = 0.340, dichloromethane), 12% ee.

B. Propanal (0.18 mL, 2.5 mmol) and pyrroldine (0.11 mL, 1.25 mmol) were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product. Excess solvent was removed by the rotatory evaporator to result in the product.

1-butyl-3-methylimidazolium *R*-Camphorsulfonate: [α] = -20.24 (c = 0.420, dichloromethane)

Yield: 14.8 mg (10.3%) of the product and product with the enamine attached; IR(neat) ν_{max} (cm^{-1}): 3390.3, 2963.8, 2931.3, 2875.2, 1734.7; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{18}N$ + H: 152.14, found 152.1; ^1H NMR (500 MHz, $CDCl_3$); δ (ppm): 9.20 (1H, s), 3.69 (1H, m), 2.16 (1H, m), 1.65 (2H, m), 1.38 (1H, bs), 0.94 (3H, t, J = 7.5), 0.80 (3H, d, J = 7); [α] = -5.24 $\pm$ 1.06 (c = 0.210, dichloromethane), 35% ee.

1-butyl-3-methylimidazolium *S*-Camphorsulfonate: [α] =19.71 (c = 0.695, dichloromethane)

Yield: 84.3 mg (58.1%) of the product and product with the enamine attached.

IR(neat) ν_{max} (cm^{-1}): 3447.0, 2966.1, 2934.0, 2876.4, 1718.4

MS m/z: $[M+H]^+$ calculated for $C_{10}H_{18}N$ + H: 152.14, found 152.1; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.28 (1H, s), 4.10 (1H, m), 3.69 (1H, m), 2.80 (1H, m), 1.65 (1H, m), 1.36 (1H, m), 0.94 (3H, t, J = 7.5), 0.88 (3H, d, J = 7); [α] = 32.42 $\pm$ 1.03; [α] = -3.50 $\pm$ 1.04 (c = 0.200, dichloromethane), 9% ee.

S-2-amino-*N,N,N*-trimethyl-1-butanol-bis(trifluoromethanesulfon)imidate: [α] = 7.80 (c = 0.141, dichloromethane)

Yield: 37.3 mg (25.7%) of the product and product with the enamine attached.

IR(neat) ν_{max} (cm^{-1}): 3458.6, 2961.8, 2932.4, 2854.4, 1637.1; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{18}N$ + H: 152.14, found 152.1; ^1H NMR ($CDCl_3$) δ (ppm): 9.20 (1H, s), 4.02 (1H, m), 3.69 (1H, m), 2.62 (1H, m), 1.65 (1H, m), 1.23 (1H, m),

0.97 (3H, t, J = 7.5), 0.88 (3H, d, J = 7); $[\alpha]$ = -1.34 $\pm$ 0.277 (c = 0.746, dichloromethane)

1-butyl-3-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)amide: $[\alpha]$ = 50.37 (c = 0.812, dichloromethane)

Yield: 25.7 mg (17.7%) of the product and product with the enamine attached; IR(neat) ν_{max} (cm^{-1}): 3401.3, 2956.5, 2923.2, 2870.4, 1680.2; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{18}N$ + H: 152.14, found 152.0; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.21 (1H, s), 3.26 (1H, td, J_t = 10 Hz, J_d = 4.05 Hz), 2.16 (1H, m), 1.62 (2H, m), 1.36 (1H, bs), 0.90 (3H, t, J = 7.5 Hz), 0.76 (3H, d, J = 7 Hz); $[\alpha]$ = 85.99 $\pm$ 0.931 (c = 0.514, dichloromethane)

1-[(3*R*)-3,7-dimethyloct-6-enyl]-3-methyl-1H-imidazolium bromide: $[\alpha]$ = 1.29 (c = 0.459, dichloromethane)

Yield: 14.9 (10.3%) of the product with the enamine attached; IR(neat) ν_{max} (cm^{-1}): 3387.9, 2927.4, 2854.3, 1718.4; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{18}N$ + H: 152.14, found 152.1; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 10.1 (1H, s), 4.19 (1H, s), 3.87 (1H, s), 2.62 (1H, m), 1.97 (2H, m), 0.95 (3H, t, J = 7.5), 0.87 (3H, d, J = 7); $[\alpha]$ = -1.94 $\pm$ 1.03 (c = 0.206, dichloromethane), 13% ee.

1-butyl-3-[(3*R*)-3,7-dimethyl-6-enyl]-1H-imidazolium bromide: $[\alpha]$ = 2.21 (c = 0.473, dichloromethane)

Product determined by comparing its GC retention time with compound **16B** completed in CIL **5**.

Yield: 7.9 mg (5.4%) of the product and product with the enamine attached.

IR(neat) ν_{max} (cm^{-1}): 3418.7, 2963.63, 2853.21, 1670.0; MS m/z: $[M+H]^+$ calculated for $C_{10}H_{18}N$ + H: 152.14, found 152.0; $[\alpha]$ = -3.04 $\pm$ 0.840 (c = 0.263, dichloromethane), 21% ee.

2-Ethyl-3-Hydroxyhexanal (**17**)

A. Butanal (0.23 mL, 2.5 mmol) and morpholine (0.11 mL, 1.25 mmol) were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product. Excess solvent was removed by the rotatory evaporator to result in the product.

   1-butyl-3-methylimidazolium *S*-Camphorsulfonate: $[\alpha]$ = 19.71 (c = 0.695, dichloromethane)

   Yield: 33.2 mg (18.4%); IR(neat) ν_{max} (cm^{-1}): 3416.7, 2960.8, 2934.1, 2873.9, 1685.1; MS m/z: 88.2 $[M+H]^+$ calculated for $C_8H_{16}O_2$ + H: 145.12, found: 145.0; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.41 (1H, s), 3.67 (1H, bs), 2.62 (1H, m), 2.33 (1H, m), 1.89 (2H, m), 1.58 (2H, m), 1.39 (2H, m), 1.25 (3H, m), 0.88 (3H, m); $[\alpha]$ = -3.01 $\pm$ 0.623 (c = 0.332, dichloromethane)

B. Butanal (0.23 mL, 2.5 mmol) and pyrroldine (0.11 mL, 1.25 mmol) were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component

from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product. Excess solvent was removed by the rotatory evaporator to result in the product.

1-butyl-3-methylimidazolium *S*-Camphorsulfonate: $[\alpha]$ = 19.71 (c = 0.695, dichloromethane)

Yield: 36.1 mg (20.0%); IR(neat) ν_{max} (cm^{-1}): 3481.4, 2960.7, 2874.1, 1718.4; ; MS m/z: 88.2 $[M+H]^+$ calculated for $C_8H_{16}O_2$ + H: 145.12, found: 145.1; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.20 (1H, s), 4.10 (1H, bs), 2.69 (1H, m), 2.33 (1H, m), 1.80 (2H, m), 1.64 (2H, m), 1.39 (2H, m), 1.25 (3H, m), 0.88 (3H, m); $[\alpha]$ = -6.42 $\pm$ 1.96 (c = 0.109, dichloromethane)

3-Hydroxy-2-propylheptanal (**18**)

A. Pentanal (0.27 mL, 2.5 mmol) and morpholine (0.11 mL, 1.25 mmol) were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to

result in the product. Excess solvent was removed by the rotatory evaporator to result in the product.

1-butyl-3-methylimidazolium *S*-Camphorsulfonate: [α] = 18.53 (c = 0.804, dichloromethane)

Product determined by comparing its GC retention time to compound **18A** completed in the achiral environment.

Yield: 51.6 mg (24.0%); IR(neat) ν_{max} (cm^{-1}): 3490.1, 2965.1, 2873.4, 1782.2; MS m/z: 156.1 $[M+H]^+$ calculated for $C_{10}H_{20}O_2$ + H: 173.15, found: 173.0; [α] = -6.06 $\pm$ 1.61 (c = 0.132, dichloromethane)

B. Pentanal (0.27 mL, 2.5 mmol) and pyrroldine (0.11 mL, 1.25 mmol) were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product. Excess solvent was removed by the rotatory evaporator to result in the product.

1-butyl-3-methylimidazolium *S*-Camphorsulfonate: [α] =18.53 (c = 0.804, dichloromethane)

Product determined by comparing its GC retention time to compound **18B** completed in the achiral environment.

Yield: 52.0 mg (24.2%); IR(neat) ν_{max} (cm^{-1}): 3468.0, 2958.0, 2872.1, 1690.7; MS m/z: 72.2, 156.1 $[M+H]^+$ calculated for $C_{10}H_{20}O_2$ + H: 173.15, found: 173.1; $[\alpha]$ = -3.49 $\pm$ 1.21 (c = 0.172, dichloromethane)

2-(1-Hydroxycyclopentyl)cyclopentanone (**19**)

A. Cyclopentanone (0.22 mL, 2.5 mmol) and morpholine (0.11 mL, 1.25 mmol) were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. Excess solvent was removed by the rotatory evaporator to result in the product.

   1-butyl-3-methylimidazolium *S*-Camphorsulfonate: $[\alpha]$ = 18.53 (c = 0.804, dichloromethane)

   Yield: 12.2 mg (5.8%); IR(neat) ν_{max} (cm^{-1}): 3447.0, 2958.4, 2924.6, 2855.0, 1735.5; MS m/z: 153.1, 84.1, 72.2 $[M+H]^+$ calculated for $C_{10}H_{16}O_2$ + H: 169.12, found: 168.9; ^{1}H NMR (500Mhz, $CDCl_3$) δ (ppm): 5.12 (1H, m), 3.75 (2H, m), 3.52 (2H, m), 3.22 (1H, bs), 3.01 (2H, m), 2.78 (2H, m), 2.62 (2H, m), 2.15 (2H, m), 1.88 (2H, m); $[\alpha]$ = -9.74 $\pm$ 1.56 (c = 0.154, dichloromethane)

B. Cyclopentanone (0.22 mL, 2.5 mmol) and pyrrolidine (0.11 mL, 1.25 mmol) were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24

hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product. Excess solvent was removed by the rotatory evaporator to result in the product.

1-butyl-3-methylimidazolium *S*-Camphorsulfonate: $[\alpha]$ = 18.53 (c = 0.804, dichloromethane)

Yield: 13.5 mg (6.4%); IR(neat) ν_{max} (cm^{-1}): 3424.9, 2922.5, 1700.5; MS m/z: 153.1 $[M+H]^+$ calculated for $C_{10}H_{16}O_2$ + H: 169.12, found: 168.9; ^1H NMR (500Mhz, $CDCl_3$) δ (ppm): 5.12 (1H, m), 3.69 (2H, m), 3.45 (2H, m), 3.22 (1H, bs), 2.99 (2H, m), 2.78 (2H, m), 2.59 (2H, m), 2.14 (2H, m), 1.89 (2H, m); $[\alpha]$ = -1.85 $\pm$ 0.769 (c = 0.270, dichloromethane)

4-Hydroxy-3,4-dimethylhexan-3-one (**20**)

A. 2-Butanone (0.23 mL, 2.5 mmol) and morpholine (0.11 mL, 1.25 mmol) were added to chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were

dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product. Excess solvent was removed by the rotatory evaporator to result in 15.0 mg of the crude product.

B. 2-Butanone (0.23 mL, 2.5 mmol) and pyrrolidine (0.11 mL, 1.25 mmol) were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product. Excess solvent was removed by the rotatory evaporator to result in the product.

1-butyl-3-methylimidazolium *S*-Camphorsulfonate: $[\alpha]$ = 18.56 (c = 0.726, dichloromethane)

Yield: 10.0 mg (5.6%); IR(neat) ν_{max} (cm^{-1}): 2959.5, 2925.7, 2854.6, 1772.86; MS m/z: $[M+H]^+$ calculated for $C_8H_{16}O_2$ + H: 145.12, found: 145.0; $[\alpha]$ = -3.00 $\pm$ 1.06 (c = 0.200, dichloromethane)

5-Ethyl-5-hydroxy-4-methylhepta-1,6-dien-3-one (**21**)

A. 1-Penten-3-one (0.25 mL, 2.5 mmol) and morpholine (0.11 mL, 1.25 mmol) were added to the chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE

silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product. Excess solvent was removed by the rotatory evaporator to result in the product.

1-butyl-3-methylimidazolium *S*-Camphorsulfonate: $[\alpha]$ = 18.56 (c = 0.726, dichloromethane)

Yield: 10 mg (4.7%); IR(neat) ν_{max} (cm^{-1}): 2965.0, 2925.0, 1717.9; MS m/z: 72.2 $[M+H]^+$ calculated for $C_{10}H_{16}O_2$ + H: 169.12, found: 168.9; $[\alpha]$ = -4.77 $\pm$ 1.58 (c = 0.146, dichloromethane)

B. 1-Penten-3-one (0.25 mL, 2.5 mmol) and pyrrolidine (0.11 mL, 1.25 mmol) were added to chiral ionic liquid (1 mL). The mixture was stirred at room temperature for 24 hours. Diethyl ether (3 × 1 mL) was added to the mixture to remove the organic component from the chiral ionic liquid. The organic mixture was injected through an SPE silica gel filter to remove any excess chiral ionic liquid. The product was dissolved in diethyl ether (3 mL) and washed with water (3mL) followed by brine (3 mL). The aqueous layers were back extracted with dichloromethane (3× 3 mL) and the combined organic products were dried over magnesium sulfate. Excess solvent was removed by the rotatory evaporator to result in the product. Excess solvent was removed by the rotatory evaporator to result in the product.

1-butyl-3-methylimidazolium *S*-Camphorsulfonate: $[\alpha]$ =18.56 (c = 0.726, dichloromethane)

Yield: 18.1 mg (8.5%); IR(neat) ν_{max} (cm^{-1}): 2962.21, 2923.9, 1700.44; MS m/z: 72.2 $[M+H]^+$ calculated for $C_{10}H_{16}O_2$ + H: 169.12, found: 168.9; $[\alpha]$ = -1.38 $\pm$ 0.569 (c = 0.362, dichloromethane)

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Appendix

Error analysis sample calculation for entry 3 from table 4:

$A \div B \div C \pm [A \div B \div C (\frac{a}{A} + \frac{b}{B} + \frac{c}{C})]$

$= -0.002 \div 0.0249\ g \div 5\ mL \pm [0.002 \div 0.0249\ g \div 5\ mL (\frac{0.002}{0.002} + \frac{0.0002}{0.0249} + \frac{0.005}{5})]$

$= -0.40 \pm 0.403$