GREEN CHEMISTRY

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6 CFU – AA 2017-2018

Green Chemistry 06

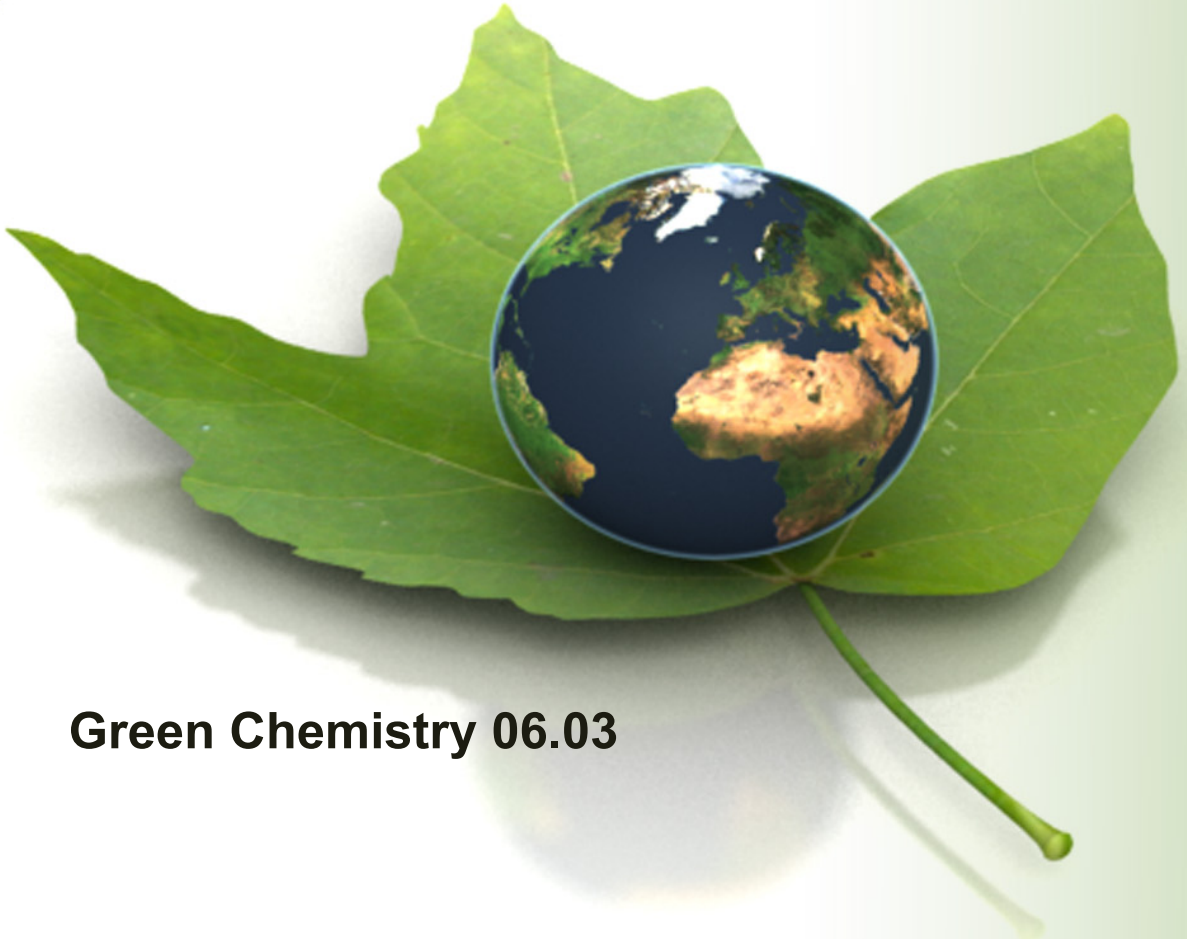
SOLVENTS IN GREEN CHEMISTRY II

Solvents in Green Chemistry

Use safer solvents and auxiliaries

RENEWABLE SOLVENTS AND OTHER ‘GREEN’ VOCS

INTRODUCTION



Green Chemistry 06.03

Introduction

Many solvents can be obtained from renewable feedstocks and they can be used as 'slot-in' alternatives for current VOCs without any need for modification of equipment or procedure.

Introduction

Due to the large number of oxygens in biomass-sourced materials such as cellulose and starch, most renewable solvents have oxygen-containing functional groups: alcohols, esters and ethers being the most common.

Introduction

The most extensively used group of VOC solvents that cannot be biosourced are chlorinated hydrocarbons such as methylene chloride. However, blends of biosolvents can be made and used in many applications where these are normally used.

Introduction

Hydrocarbons including aromatics could potentially be biosourced through transformations of cellulose and lignocellulose.

Introduction

Although biosourced solvents are nominally green through a life-cycle analysis, they are not perfect. They are still VOCs and have associated risks including atmospheric pollution, flammability and user exposure.

Significant amount of energy are used in their production.

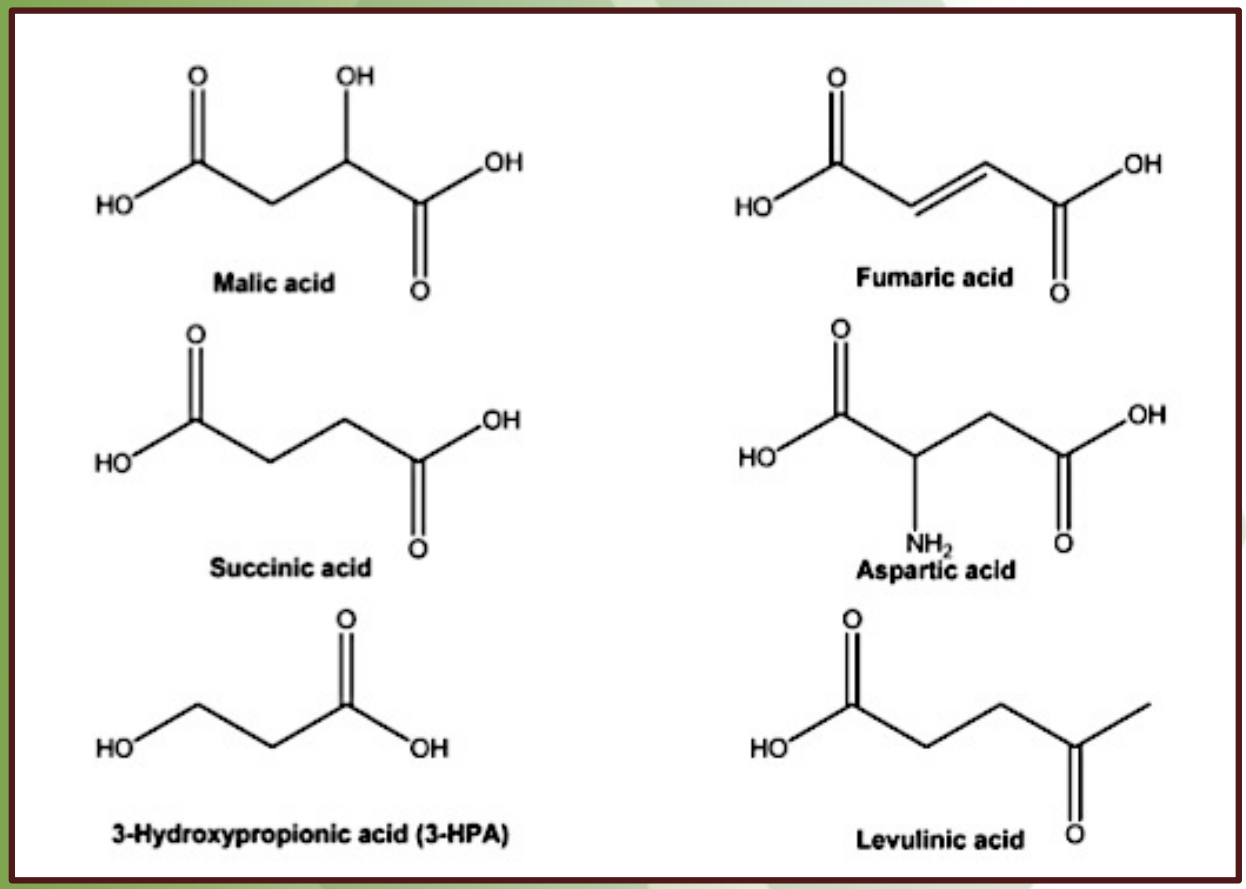
Introduction

Table 6.1 Types of biomass feedstocks.

Waste materials
Agricultural, wood, and urban wastes, crop residues
Forest products
Wood, logging residues, trees, shrubs
Energy crops
Starch crops such as corn, wheat, and barley, sugar crops, grasses, vegetable oils, hydrocarbon plants (*e.g. Pittosporum resiniferum* and *euphorbia lathyris*)
Aquatic biomass
Algae, water weed (including seaweed), water hyacinth

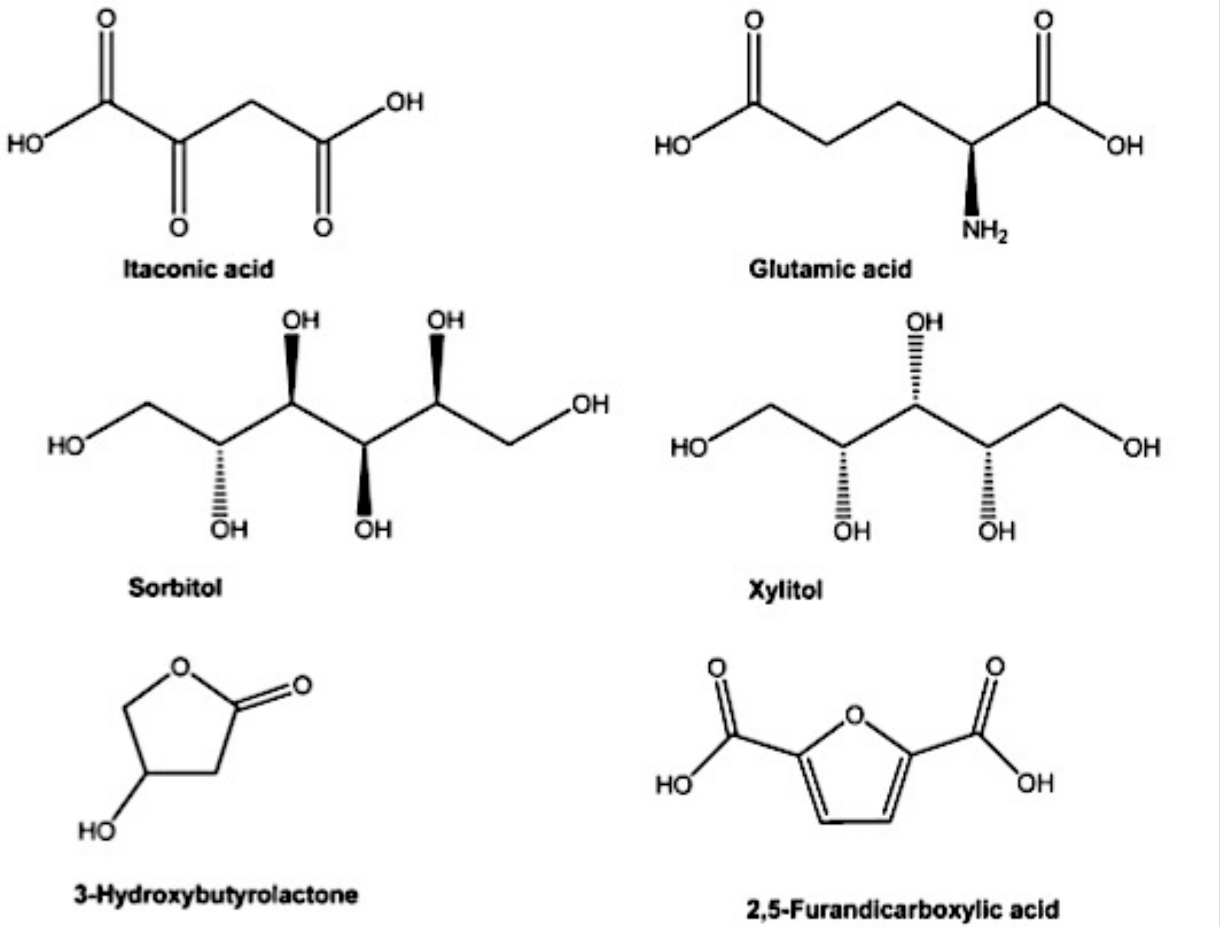
Introduction

Chemicals from natural carbohydrate feedstocks



Introduction

Chemicals from natural carbohydrate feedstocks



Biosolvents

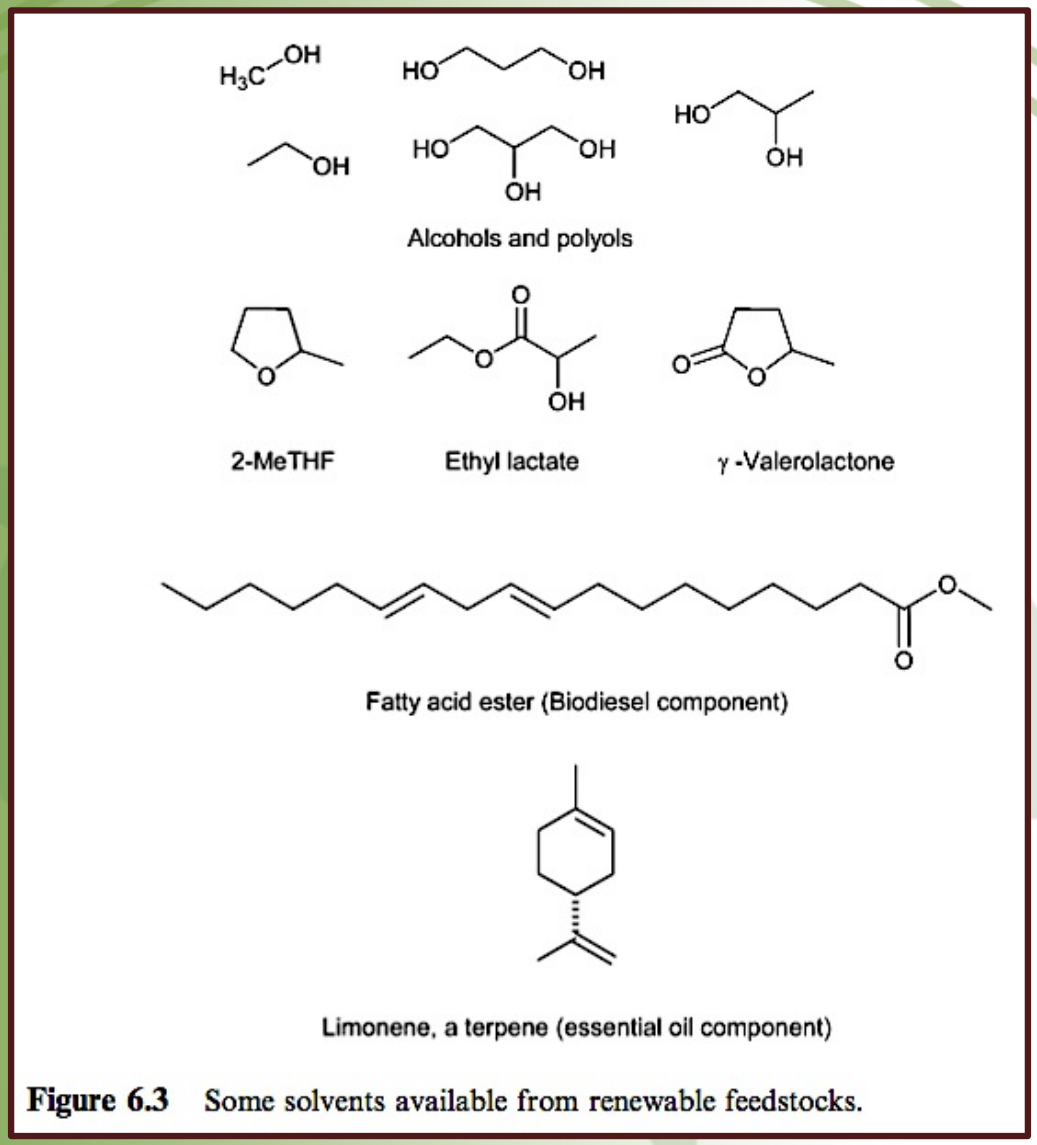


Figure 6.3 Some solvents available from renewable feedstocks.

Biosolvents

Alcohols

- Ethanol is generally produced through fermentation of starch crops or cellulose
- Ethanol has widespread use as a solvent of substances intended for human contact or consumption, including scents, flavourings, colourings, and medicines.
- Ethanol is widely used in the food industry and in the extraction of natural products.
- Ethanol is also used in thermometers.

Biosolvents

Alcohols

- Methanol can be produced from synthesis gas that can be obtained through biomass gasification.
- It is toxic!!
- In synthetic procedures methanol is more commonly used due to its greater volatility and ease of removal under vacuum.

Biosolvents

Alcohols

- Glycerol, is a byproduct of biodiesel production and other processes, is nontoxic and has promising physical and chemical properties as an alternative solvent.
- It has a very high boiling point and negligible vapour pressure and can dissolve many organic and inorganic compounds.

Biosolvents

Alcohols

- It is poorly miscible with water and some ethers and hydrocarbons.
- Simple extractions with solvents such as ether and ethyl acetate are also possible.
- It can be converted to methanol, ethanol, 1-propanol and propanediols through hydrogenolysis reactions, and is therefore a potential feedstock for other solvents.

Biosolvents

Alcohols

Table 6.2 Comparison of solvent properties of methanol, ethanol, glycerol.

Property	*MeOH*	*EtOH*	*Glycerol*
Dielectric constant	32.66	24.3	42.5
Density, g cm^{-3}	0.79	0.79	1.26
Boiling point, °C	64.7	78.4	290
Melting point, °C	−97	−114	18
Viscosity, cP	0.6	1.2	629
pKa	15.5	15.9	14.4
Flash point, °C	12	16	160
Explosion range, lower/upper limit, vol%	6.0/36	3.3/19	Not applicable
Vapour pressure, mm Hg at 20 °C	97	44	<1
Hildebrand, $MPa^{1/2}$	29.7	26.2	36.2
Donor number, kcal mol^{-1}	19	31.5	-

Biosolvents

Esters

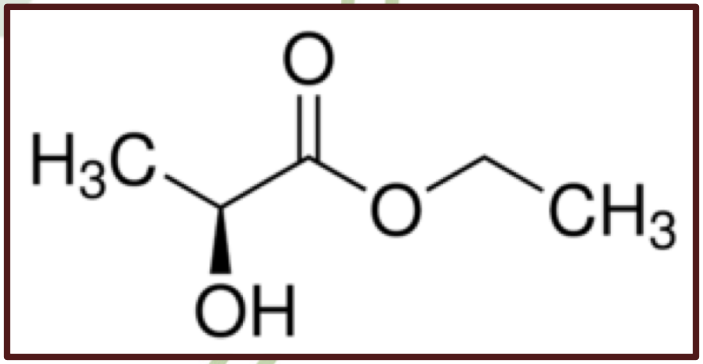
Table 6.3 Industrial uses of some ester 'green' solvents.

Solvent	*Industrial use*
Glycerol carbonate	Nonreactive diluent in epoxy or polyurethane systems
Ethyl lactate	Degreaser
	Photoresist carrier solvent
	Clean-up solvent in microelectronics and semiconductor manufacture
2-Ethylhexyl lactate	Degreaser
	Agrochemical formulations
Fatty acid esters (and related compounds)	Biodegradable carrier oil for green inks
	Coalescent for decorative paint systems
	Agrochemical/pesticide formulations

Biosolvents

Ethyl Lactate

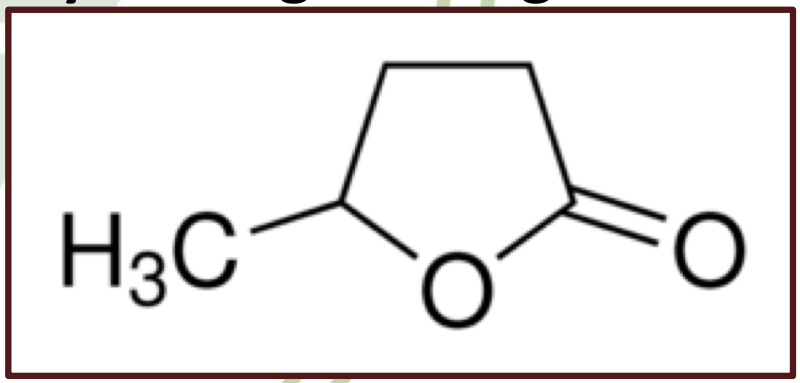
- Ethyl lactate has a boiling point of 154 °C and melting point of –26 °C.
- It has the potential to replace many toxic halogenated solvents.
- It is biodegradable, renewable, noncarcinogenic, noncorrosive, stable in water, has a low vapour pressure and high solvency power.



Biosolvents

γ-Valerolactone

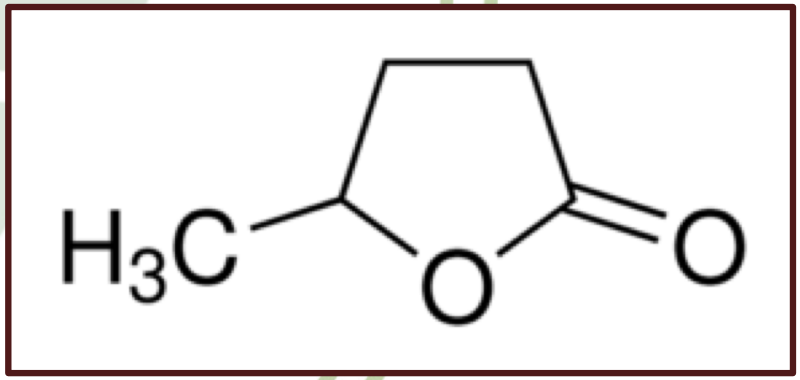
It has a low melting point (–31 °C), high boiling point (207 °C) and high open cup flash point (96 °C).
Its density is 1.05 g/cm^3. It is miscible with water and biodegradable.
Its vapour pressure is very low even at high temperatures, only 3.5 kPa at 80 °C.
It does not form an azeotrope with water, and therefore water can be removed by distillation, as can volatile organic components because of GVL's low volatility and high boiling point.



Biosolvents

γ-Valerolactone

Its high boiling point may also be advantageous in some reaction chemistry by allowing increased rates of reaction.
It is stable in air (no peroxides could be detected after 35 days) and it did not hydrolyze in water.
However, it can be hydrolyzed and ring-opens in the presence of acid to give γ-hydroxy-pentanoic acid and with aqueous sodium hydroxide, it forms γ-hydroxylpentanoate.



Biosolvents

Biodiesel

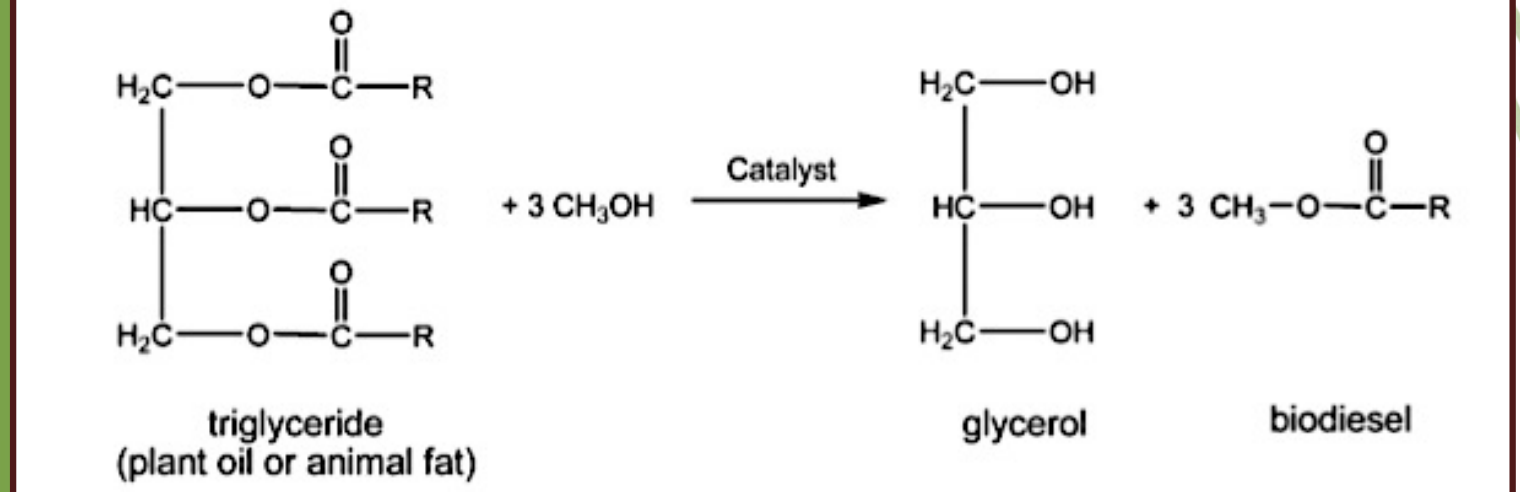


Figure 6.7 Typical synthetic route used in biodiesel production.

Biosolvents

Biodiesel

Table 6.4 Summary of advantageous properties of biodiesels including methyl soyate as solvents.

Safety advantages
Lower toxicity than toluene and methylene chloride, LD_{50} 17.4 g/kg
Low vapour pressure, <0.1 mmHg
High flash point, >182 °C
Reaction and process advantages
Excellent compatibility with other organic solvents, metals and most plastics
Low cost, 0.60 US$ L^{-1}
Environmental advantages
Can be biosourced from a range of feedstocks
Readily biodegradable
Low volatile organic compound level, < 50 g mL^{-1}
Non-ozone-depleting compound
Non-SARA reportable[a]

[a]Superfund Amendments and Reauthorisation Act, http://www.epa.gov/superfund/index.htm

Biosolvents

Biodiesel

Table 6.5 Potential applications of methyl soyate as a solvent.

Industrial parts cleaning and degreasing
Household cleaners, food processing equipment cleaning, asphalt handling
With ethyl lactate, as a cleaner in the aerospace and electronics industries
Resin cleaning and removal
Commercial and military paint strippers (replacing methylene chloride)
Printing ink cleaners/Ink press washers (replacing toluene)
Adhesive removers (replacing acetone)
Graffiti removers (replacing mineral spirits, a mixture of hydrocarbons)
Cleaning up oil spills
Shoreline cleaner[a]
Refinery or tank farm spills
Cleaning reactors and storage tanks
Other
Carrier solvent in paints, stains and anticorrosion coverings
Consumer products including hand cleaners

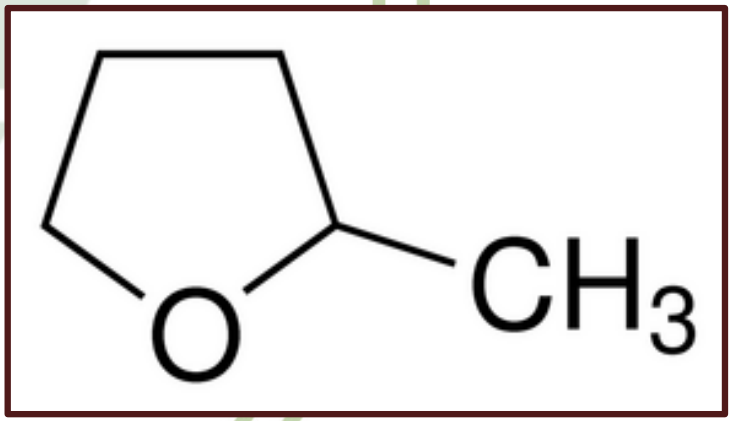
[a]Listed on the EPA's national contingency plan, http://www.epa.gov/OEM/content/lawsregs/ncpover.htm

Biosolvents

2-Methyltetrahydrofuran (2-MeTHF)

2-MeTHF can be made through a two-step hydrogenation of 2-furaldehyde, which can be produced using agricultural waste such as corncobs and bagasse.

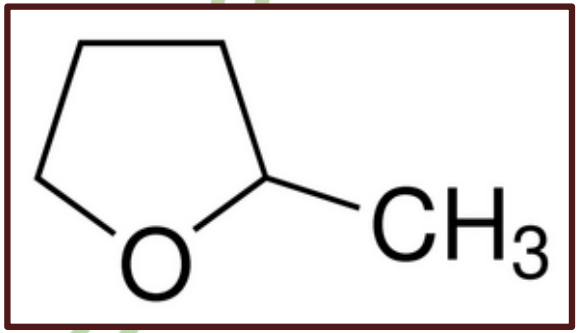
- **2-MeTHF has similar properties to conventional THF, which is used in many organometallic reactions;**
- **as THF is miscible with water this complicates the quenching process in many of these reactions and other organic solvents have to be introduced to aid in the separation of organic and aqueous phases.**



Biosolvents

2-Methyltetrahydrofuran (2-MeTHF)

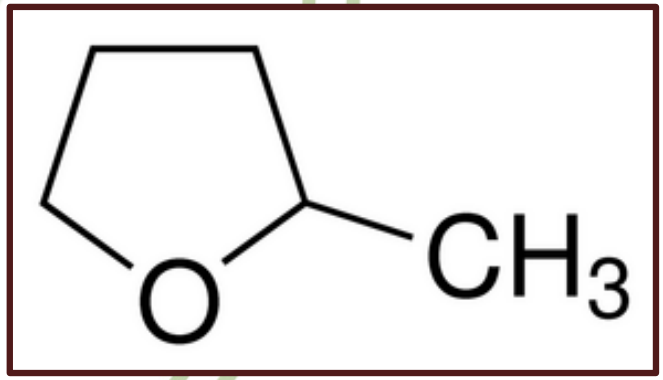
- It forms an azeotrope rich with water and can be more easily dried than THF or dichloromethane;
- It is stable to bases and in degradation studies it has been shown to be more stable towards acids than THF;
- In common with THF and Et_2O, 2-MeTHF is a Lewis base and its polarity (dielectric constant and Hildebrand solubility parameter) is intermediate of these two conventional solvents;



Biosolvents

2-Methyltetrahydrofuran (2-MeTHF)

- It has a higher boiling point than THF and therefore higher reaction temperatures can be used that reduce overall reaction times.
- It has a low heat of vaporization, which means less solvent is lost during reaction reflux and this saves energy during distillation and recovery
- 2-MeTHF will form peroxides when exposed to air if no stabilizer is present.



Biosolvents

2-Methyltetrahydrofuran (2-MeTHF)

Table 6.6 Comparison of solvent properties of 2-MeTHF with other VOC solvents.

Property	*2-MeTHF*	*CPME*	*THF*	*Et_2O*	*CH_2Cl_2*
Dielectric constant	6.97	4.76	7.58	4.42	8.93
Density, g cm^{-3}	0.85	0.86	0.89	0.71	1.32
Boiling point, °C	80	106	65	35	40
Melting point	−136	<−140	−108.5	−116	−95
Viscosity, cP	0.46	0.55	0.55	0.24	0.42
Solubility of water in solvent, g/100 g	4.4	0.3	miscible	1.2	0.2
Azeotropic temperature with water, °C	71	83	64	34	39
Flash point, °C	−11.1	−1	−14.2	−45	na
Explosion range, lower/upper limit, vol%	1.5/8.9	1.1/9.9	1.8/11.8	1.8/48	14/22
Hildebrand, $MPa^{1/2}$	16.9	-	18.7	15.5	20.2
Solvation energy, kcal mol^{-1}	0.6	-	0	2.3	-
Donor number	18	-	20.5	19.2	-

Biosolvents

2-Methyltetrahydrofuran (2-MeTHF)

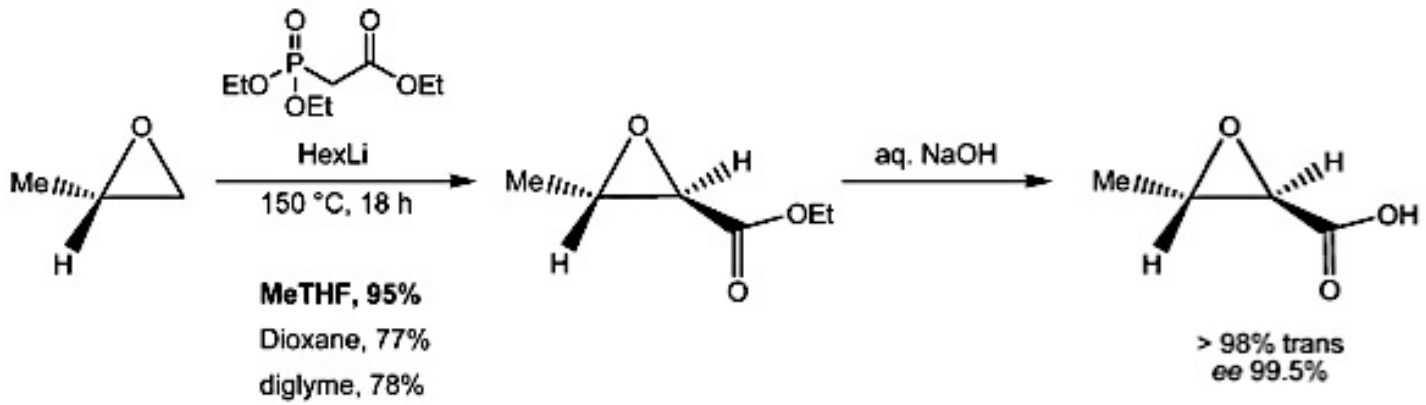


Figure 6.11 Synthesis of (*R*,*R*)-2-methylcyclopropanecarboxylic acid with enhanced yields using 2-MeTHF.

Biosolvents

Carbonates

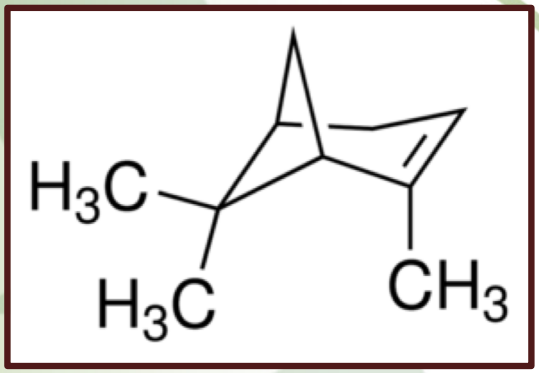
This class of solvent has several favorable features including:

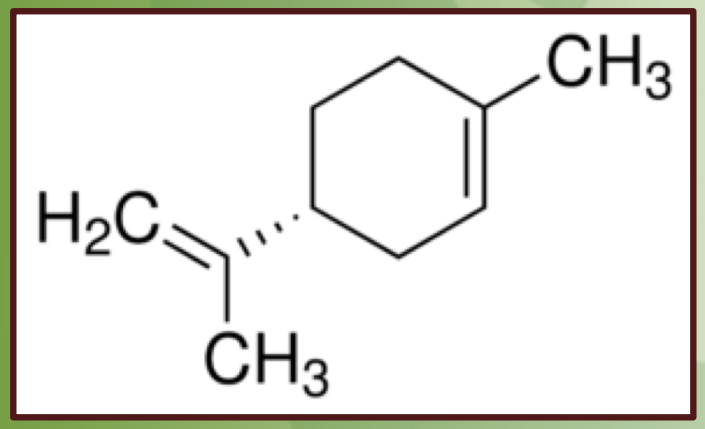
- **low cost and wide availability;**
- **their polarity;**
- **a broad liquid temperature range (e.g., for propylene carbonate, m.p. –49 °C, b.p. 243 °C);**
- **low (eco)toxicity;**
- **biodegradability.**

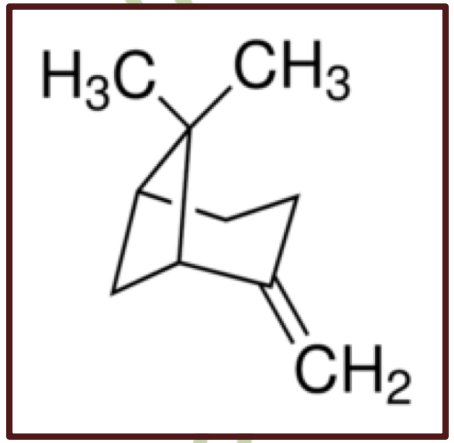
Unfortunately, at present, industrial routes to linear carbonates use phosgene as a starting material, and cyclic carbonates are made using propylene oxide. These two reagents are highly toxic chemicals

Biosolvents

Terpenes and Plant Oils







Turpentine is composed of terpenes, mainly the monoterpenes alpha-pinene and beta-pinene with lesser amounts of carene, camphene, dipentene, and terpinolene.

Biosolvents

Terpenes and Plant Oils

Table 6.7 Some physical properties of D-limonene and turpentine alongside methylene chloride and toluene for comparison.

Property	*D-limonene*	*Turpentine*	*Toluene*	*CH_2Cl_2*
Dielectric constant	2.37	2.2–2.7	2.38	8.93
Density, g cm^{-3}	0.84	0.85–0.87	0.86	1.32
Boiling point, °C	178	150–180	110	40
Melting point	−74	<−50	−95	−95
Viscosity, cP	0.9	1.49	0.59	0.42
Vapour pressure, kPa at 20 °C	0.19	0.25–0.67	3.8	72
Flash point, °C	48	35	7	na
Explosion range, lower/ upper limit, vol%	Not available	0.8/6	1.1/7.1	14/22

Turpentine is composed of terpenes, mainly the monoterpenes alpha-pinene and beta-pinene with lesser amounts of carene, camphene, dipentene, and terpinolene.

Biosolvents

Terpenes and Plant Oils

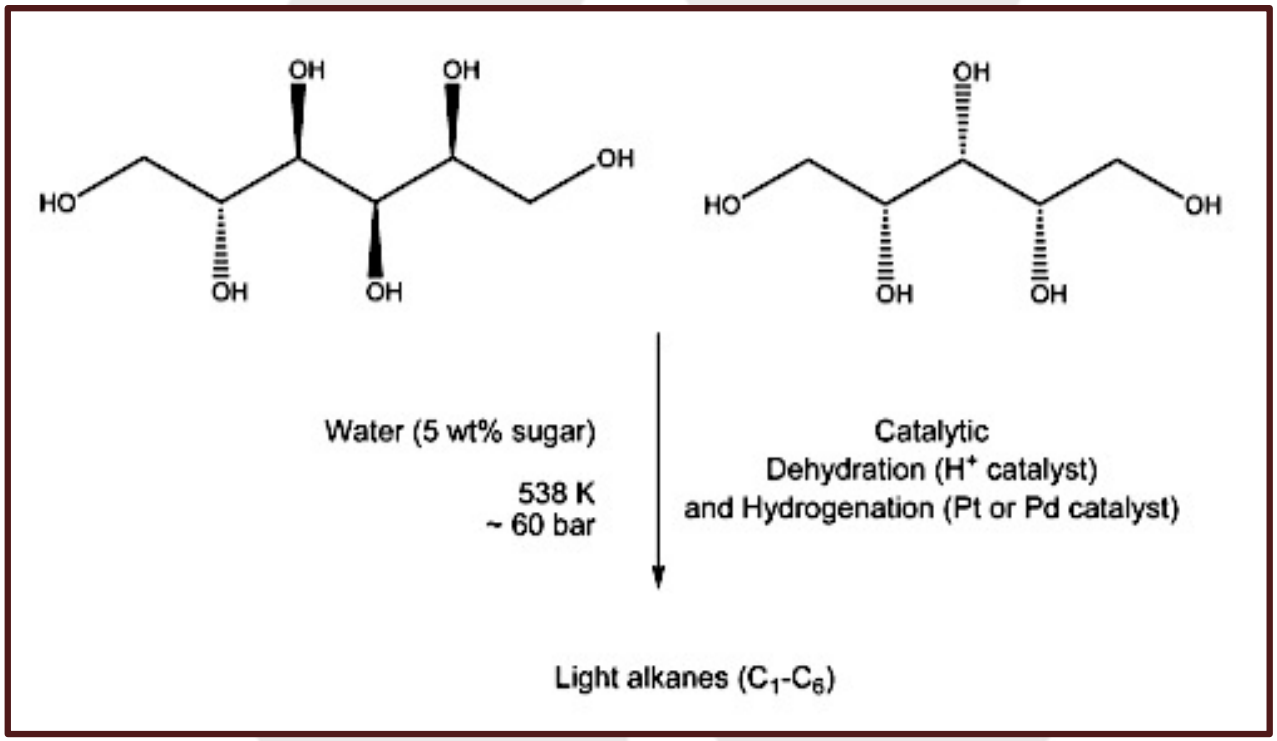
Table 6.8 Summary of advantageous properties of D-limonene.

Safety advantages
Lower toxicity than toluene and methylene chloride, LD_{50} 4.4 g/kg
Relatively low vapour pressure, <1.5 mmHg
No known long-term health effects on humans. It is classified as noncarcinogenic and nonmutagenic. (Short-term effects include being a slight skin and eye irritant)
Reaction and process advantages
Noncaustic and relatively inert
Pricing competitive with conventional solvents. Food-grade limonene is twice the price of hexane.[64]
High boiling point may be advantageous for some processes
Environmental advantages
Can be biosourced from a range of feedstocks
Readily biodegradable
It is not a SARA Title III compound, and it is not regulated by the Clean Air Act[a]

[a]Superfund Amendments and Reauthorisation Act, http://www.epa.gov/superfund/index.htm

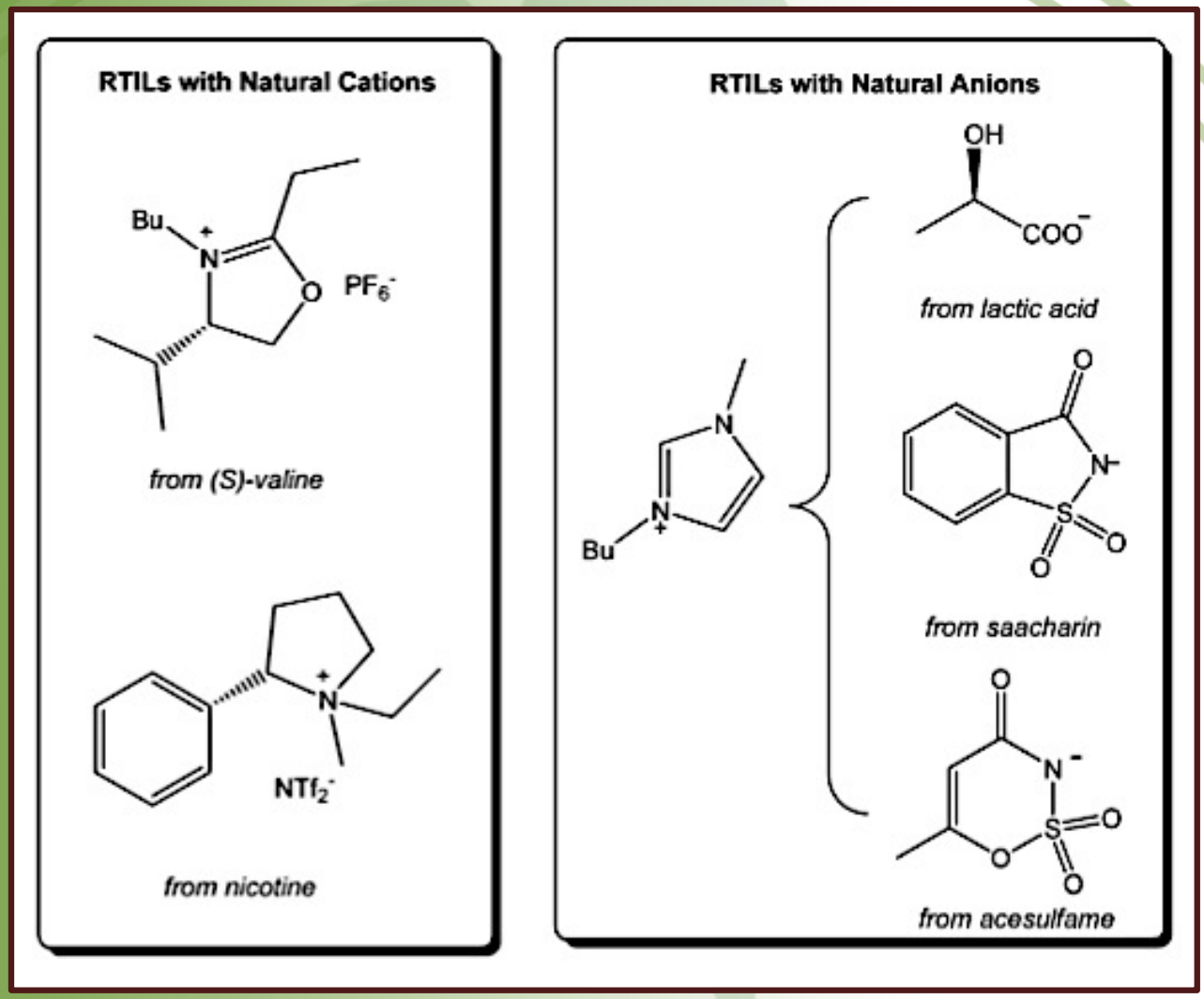
Biosolvents

Renewable Alkanes



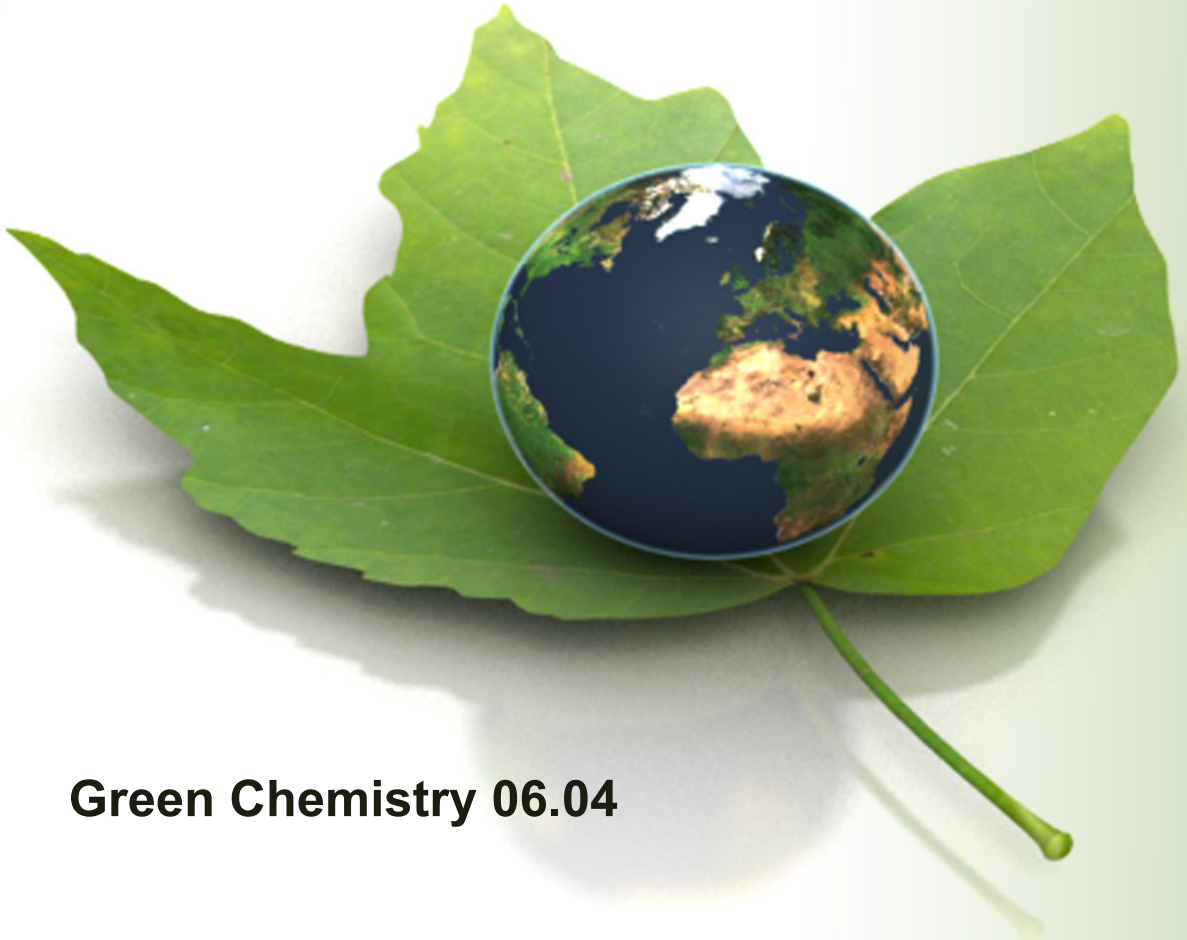
Biosolvents

Ionic Liquids



ROOM-TEMPERATURE IONIC LIQUIDS AND EUTECTIC MIXTURES

INTRODUCTION



Green Chemistry 06.04

Introduction

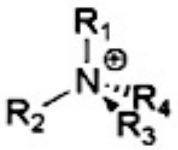
- Ionic liquids are defined as salts with melting points below 100 °C.
- They are of interest to green chemists as alternative solvents because of their inherent low volatility.
- It should be noted that there has been some debate surrounding the green credentials or otherwise of RTILs, particularly regarding their toxicity, environmental persistence

Introduction

- They have no (or exceedingly low) vapor pressure, so volatile organic reaction products can be separated easily by distillation or under vacuum.
- They are thermally stable and can be used over a wide temperature range compared with conventional solvents Their properties can be readily adjusted by varying the anion and cation. (1-butyl-3-methyl-imidazolium (Bmim) tetrafluoroborate (BF_4) is a hydrophilic solvent whereas its hexafluorophosphate (PF_6) analogue is hydrophobic.
- The melting points of the ionic liquids are usually lower for more unsymmetrical cations (e.g. [Mmim][BF_4], 103 °C; [Emim][BF_4], 6 °C and [Bmim][BF_4], –81 °C ([Mmim] is 1,3-dimethyl-imidazolium and [Emim] is 1-ethyl-3-methyl-imidazolium).

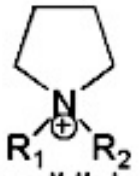
Introduction

Cations

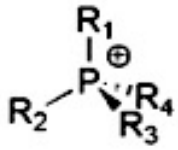


ammonium

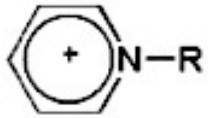
imidazolium



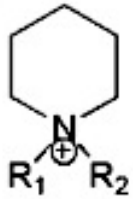
pyrrolidinium



phosphonium



pyridinium



piperidinium

Anions

NO_3^-	BF_4^-	$CF_3SO_3^-$	Cl^-, Br^-, I^-
$Al_2Cl_7^-$	SbF_6^-	$CF_3CO_2^-$	$CH_3CO_2^-$
$Me_2PO_4^-$	PF_6^-	$(CF_3SO_2)_2N^-$	$(CN)_2N^-$

Introduction

Table 7.1 Some physical properties of imidazolium-based ionic liquids.[a]

Cation	*Anion*	*Mp, °C*	*Thermal stability, °C*	*Density, g cm^{-3}*	*Viscosity, cP*	*Conductivity, ohm^{-1} cm^{-1}*
Emim	BF_4^-	6	412	1.24	37.7	1.4
Bmim	BF_4^-	−81	403	1.12	219	0.173
Bmim	$(CF_3SO_2)_2N^-$	−4	439	1.429	52	0.39
Bmim	PF_6^-	−61	349	1.36	450	0.146
Hmim	PF_6^-	−61	417	1.29	585	–

[a]Emim = 1-ethyl-3-methylimidazolium, Bmim = 1-butyl-3-methylimidazolium, Hmim = 1-hexyl-3-methylimidazolium.

Introduction

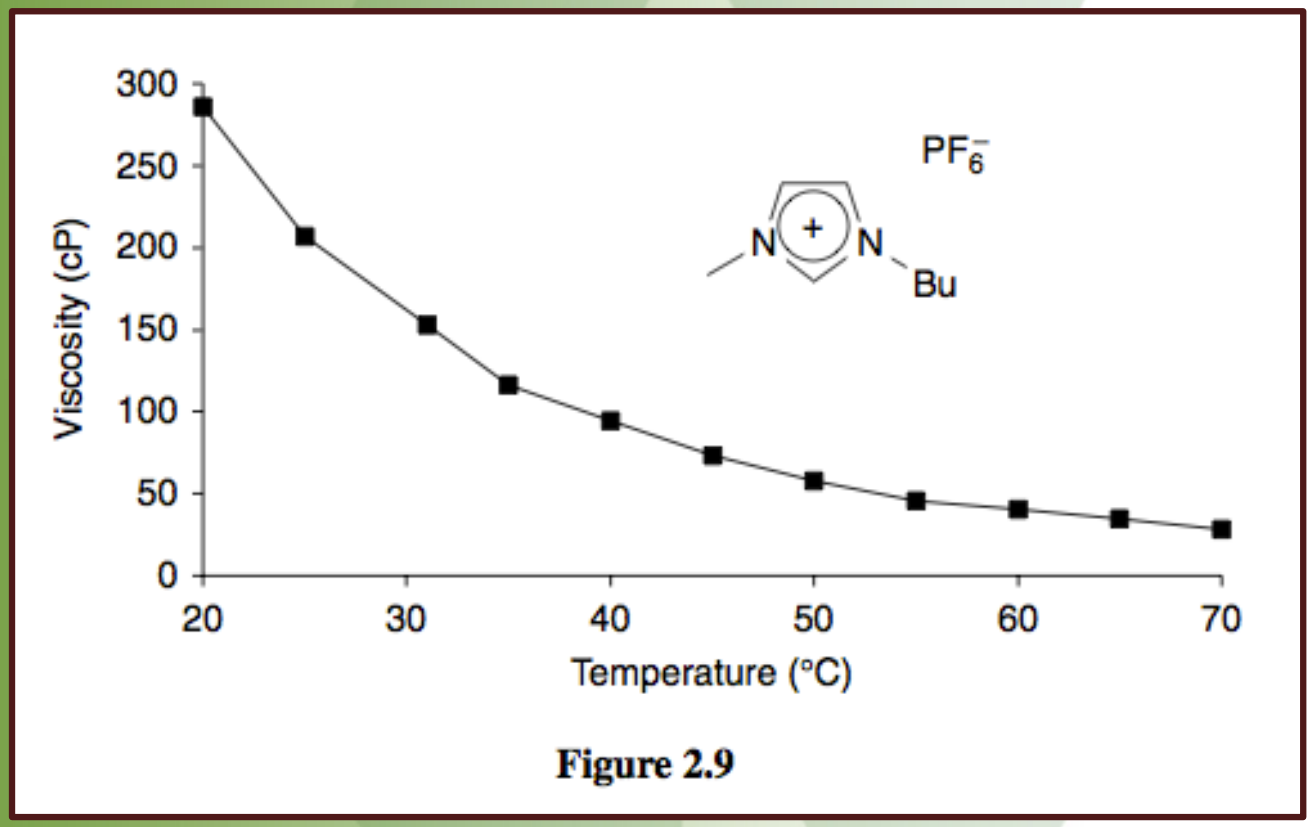


Figure 2.9

Introduction

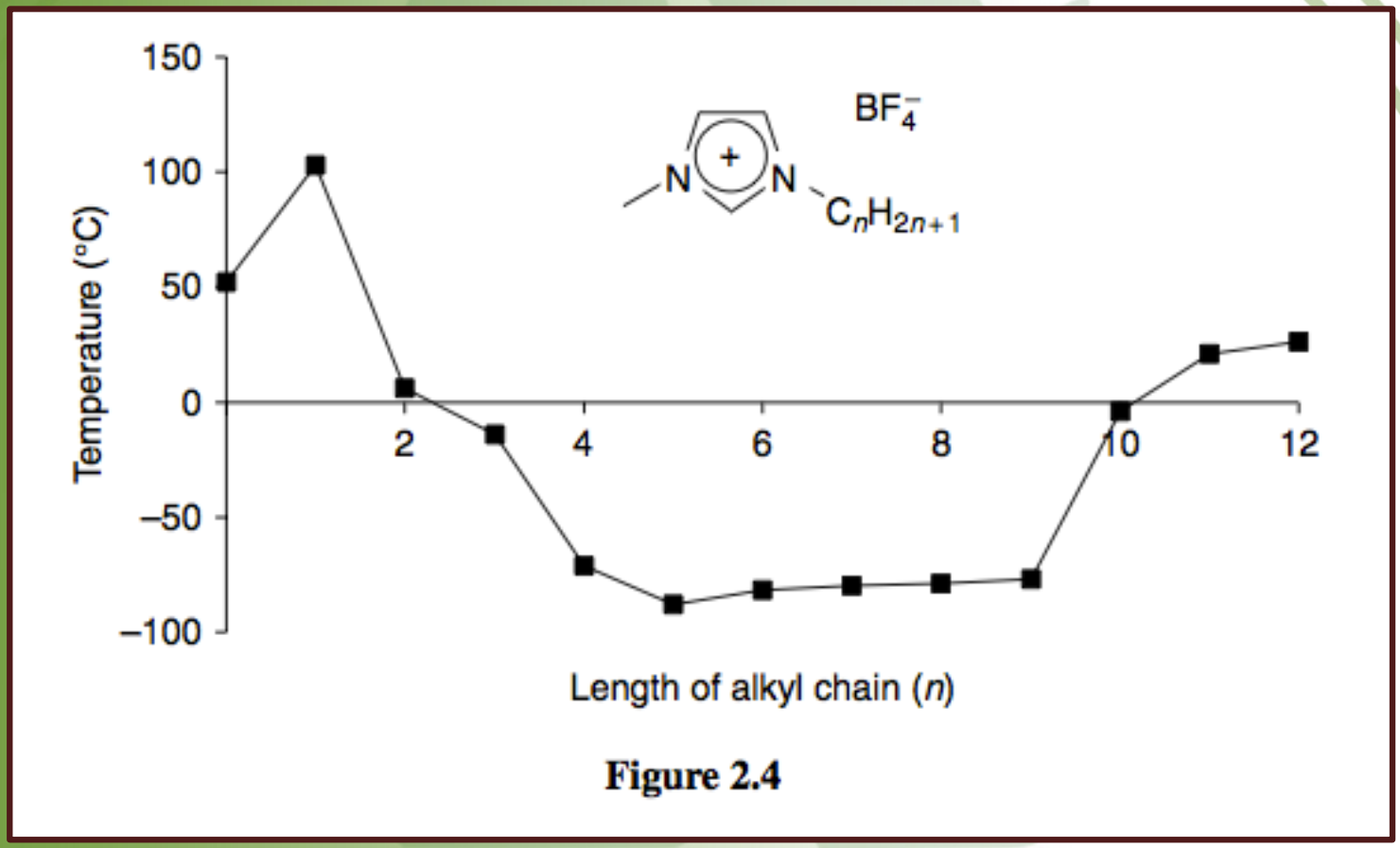
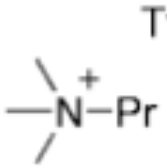
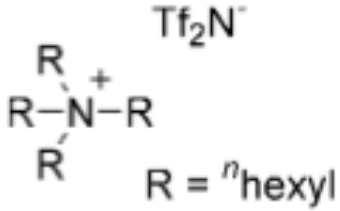
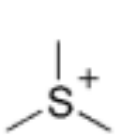
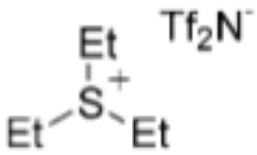


Figure 2.4

Introduction

Table 2.3

			
23	**24**	**25**	**26**
m.p. = 17°C	m.p. = −7°C	m.p. = 45°C	m.p. = −36°C

m.p. = melting point.

Introduction

Deep eutectic solvents or mixtures

A series of these materials based on choline chloride ($HOCH_2CH_2NMe_3Cl$) and metal chlorides, polyols, carboxylic acids or urea have been reported.
The urea–choline chloride material has many of the advantages of better-known ionic liquids (e.g. low volatility) but can be sourced from renewable feedstocks, is nontoxic and readily biodegradable.

It is not an inert solvent

Synthesis

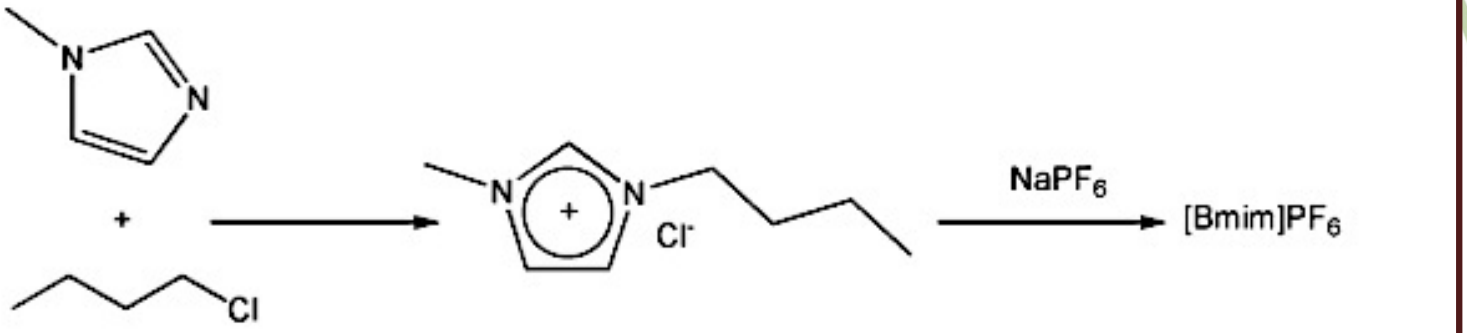


Figure 7.2 Preparation of 1-butyl-3-methylimidazolium chloride and hexafluorophosphate.

Synthesis

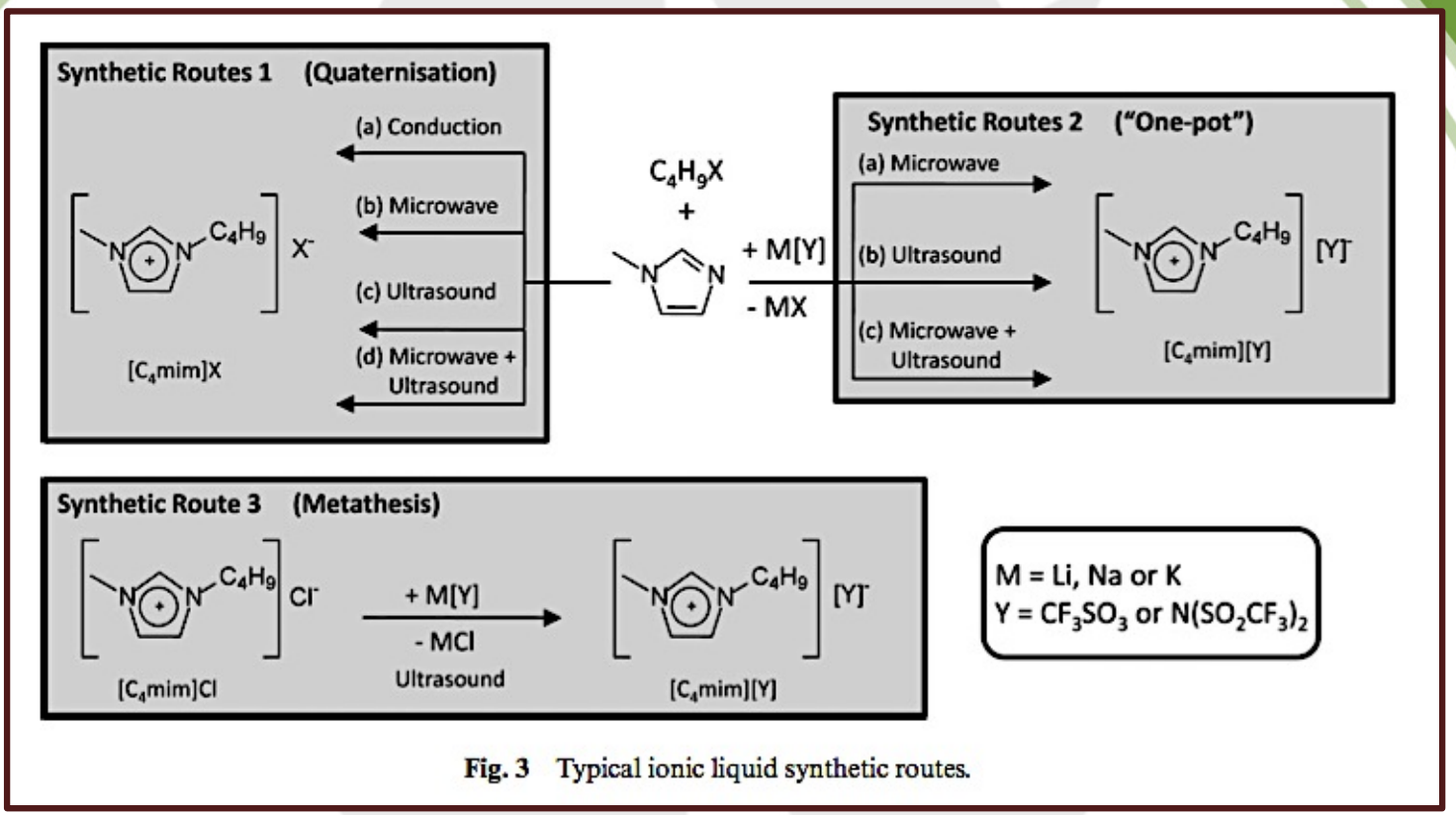


Fig. 3 Typical ionic liquid synthetic routes.

Synthesis

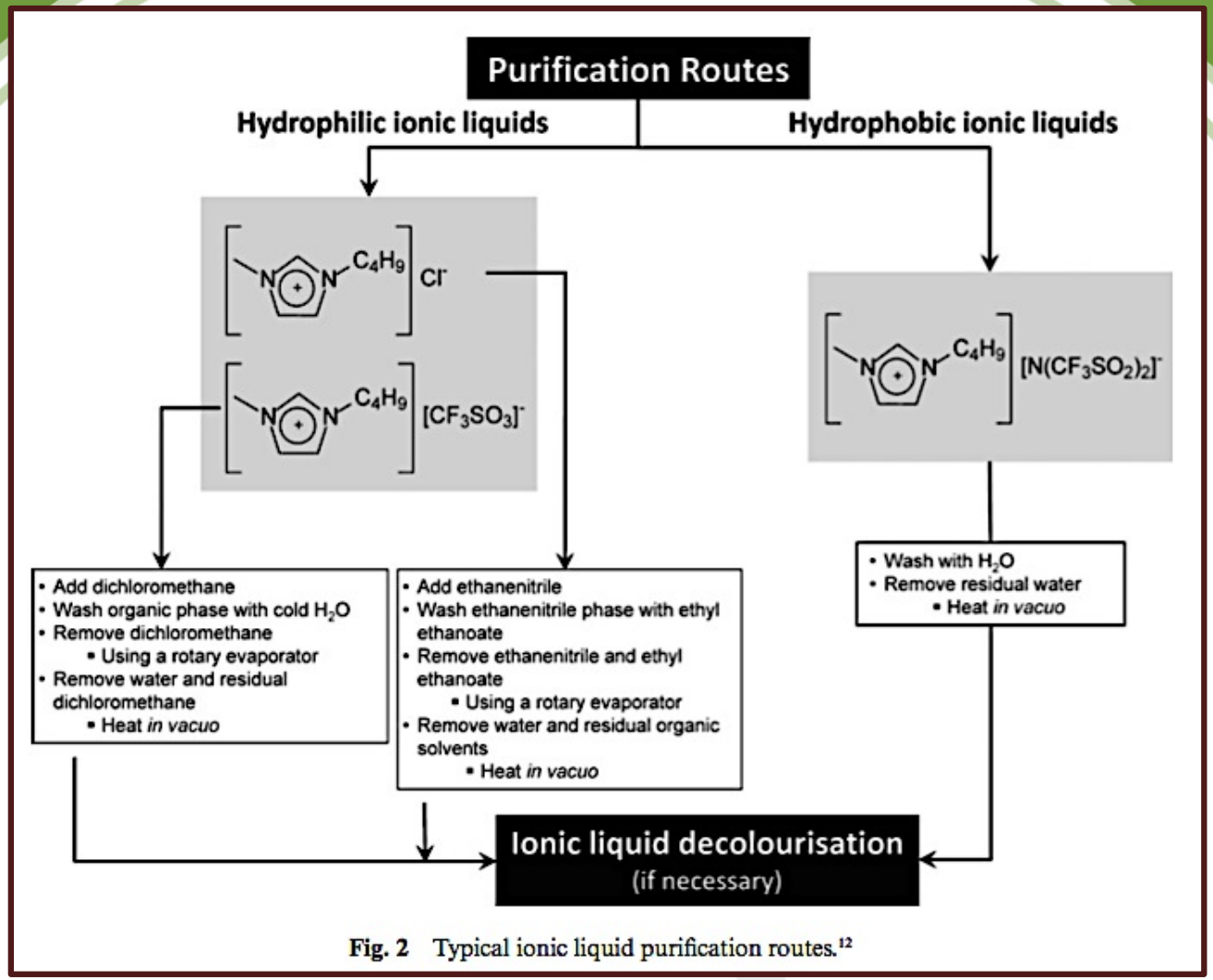


Fig. 2 Typical ionic liquid purification routes.[12]

Properties

Table 7.2 Polarities of some ionic liquids and VOCs using the E_T^N scale.

Solvent	E_T^N
Hexane	0.009
[Omim][PF_6][a]	0.642
[Bmim][$N(CF_3SO_2)_2$]	0.642
Ethanol	0.654
[Bmim][PF_6]	0.667
[Bmim][CF_3SO_3]	0.667
[Bmim][BF_4]	0.673
Methanol	0.762
[$EtNH_3$][NO_3]	0.954
Water	1.000

[a]Omim = 1-octyl-3-methylimidazolium.

Properties

Table 7.3 Miscibility of water and VOCs with [Bmim][PF_6].

Solvent	ε_r	*Miscibility*
Water	78.3	Immiscible
CH_3OH	32.7	Miscible
CH_3CN	35.9	Miscible
Acetone	20.6	Miscible
CH_2Cl_2	8.9	Miscible
THF	7.8	Miscible
Toluene	2.4	Immiscible
Hexane	1.9	Immiscible

Properties

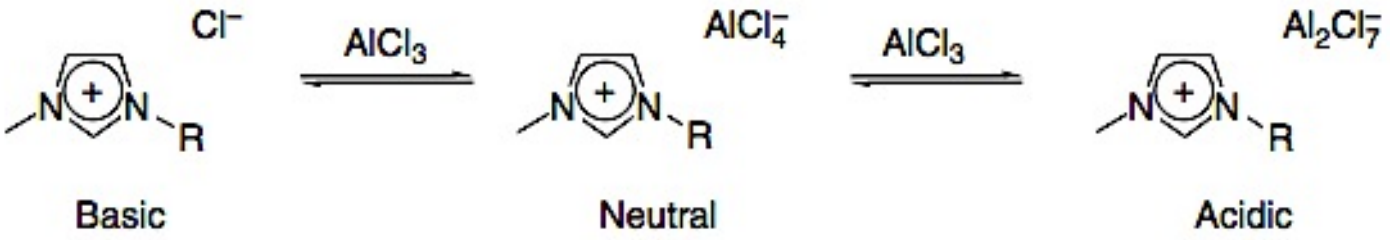
Table 2.7

Salt	H_2O	MeOH	CH_2Cl_2	Et_2O
[bmim][Cl]	Soluble	Soluble	Insoluble	Insoluble
[bmim][BF_4]	Soluble	Soluble	Soluble	Insoluble
[bmim][PF_6]	Insoluble	Soluble	Soluble	Insoluble
[bmim][NTf_2]	Insoluble	Soluble	Soluble	Insoluble
[bmim][$AlCl_4$]	Not compatible	Not compatible	Soluble	Insoluble

Properties

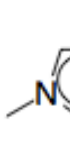
Table 2.9

Basic, strongly coordinating	Neutral, weakly coordinating	Acidic, non-coordinating
$Cl^-/NO_3^-/SO_4^{2-}$	$AlCl_4^-/SbF_6^-/BF_4^-/PF_6^-$	$Al_2Cl_7^-/Cu_2Cl_3^-/Al_3Cl_{10}^-$



Scheme 10

Properties



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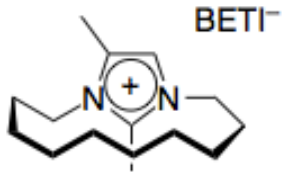

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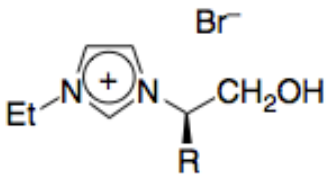
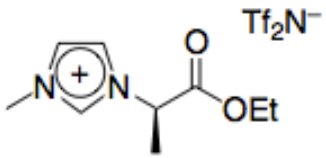


(47)

Figure 2.10



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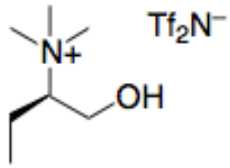

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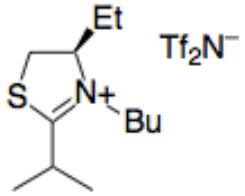

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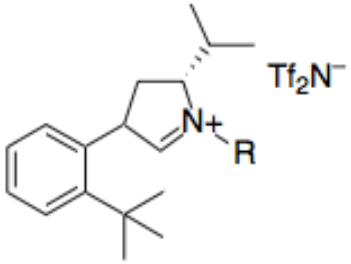
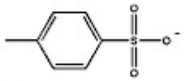
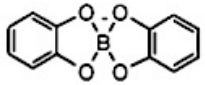
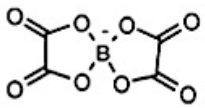


(51)

Figure 2.11

Properties

Table 2 Influence of the anion on the cytotoxicity of $[C_4mim]X$ (IPC-81 cell line). Values, given as EC_{50}, were adapted from the UFT/Merck database[32] (except for the methylpoly(oxy-1,2-ethanediyl)sulfates)[64] and $\log_{10}(K_{ow})$ of the anions were predicted using algorithms available on the ChemSpider website[176]

Anion structure	Name	$EC_{50}/\mu M$	$\log_{10}(K_{ow})$
Cl^-	Chloride	3850	0.00
Br^-	Bromide	2670	0.00
I^-	Iodide	3030	0.00
$[Co(CO)_4]^-$	Tetracarbonylcobaltate(−1)	277	—
$[SCN]^-$	Thiocyanate	2610	0.58
$[N(CN)_2]^-$	Dicyanamide	1420	−0.67
$[HSO_4]^-$	Hydrogen sulfate	1940	−1.03
$[C_1SO_4]^-$	Methylsulfate	1630	−0.595 ± 0.4
$[C_8SO_4]^-$	Octylsulfate	1680	3.27
$[H_3CO(CH_2)_2O(CH_2)_2OSO_3]^-$	2-(2-Methoxyethoxy)ethylsulfate	1440	−0.80
$[H_3C(OCH_2CH_2)_nOSO_3]^-$	Methylpoly(oxy-1,2-ethanediyl)sulfate	1100	—
	4-Methylbenzenesulfonate	1950	0.93
$[CH_3SO_3]^-$	Methanesulfonate	3250	−1.89
$[OTf]^-$ (*i.e.* $[CF_3SO_3]^-$)	Trifluoromethanesulfonate	1050	−0.37
$[BF_4]^-$	Tetrafluoroborate	1030	—
$[PF_6]^-$	Hexafluorophosphate	1250	—
$[SbF_6]^-$	Hexafluoroantimonate	180	—
$[N(CF_3)_2]^-$	Bis(trifluoromethyl)amide	154	3.37
$[NTf_2]^-$ (*i.e.* $[N(SO_2CF_3)_2]^-$)	Bis{(trifluoromethyl)sulfonyl}amide	481	1.49
$[(C_2F_5)_3PF_3]^-$	Tris(pentafluoroethyl)trifluorophosphate	23.7	—
	Bis[1,2-benzenediolato(2−)]borate	10 ($[C_2mim]^+$)	—
	Bis[oxalato(2−)]borate	860 ($[C_2mim]^+$)	—

Extractions and Separations

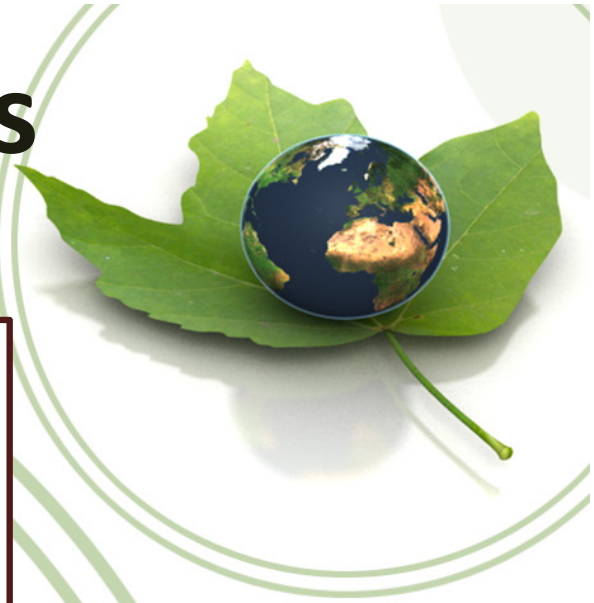


Table 1. Examples of IL extractions of metal ions

	Substances	IL	Extractant/ligand/ metal chelator	Reference
Alkali metals	Li^+, Na^+, K^+, Rb^+, Cs^+	$[C_nMIM][PF_6]$ ($n = 4–9$)	DC18C6	21,37
	Na^+, Cs^+	$[C_nMIM][PF_6]$ ($n = 4, 6, 8$)	18C6, DC18C6, Dtb18C6	18
	Cs^+	$[C_nMIM][Tf_2N]$ ($n = 2, 3, 4, 6, 8$)	BOBCalixC6	38
	Na^+, K^+, Cs^+	$[C_nMIM][Tf_2N]$ ($n = 2, 4, 6, 8$)	DC18C6, *N*-alkyl aza-18-crown-6 ethers	39
Alkaline earth metals	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	$[C_nMIM][PF_6]$ ($n = 4–9$)	DC18C6	37
	Sr^{2+}	$[C_nMIM][PF_6]$ ($n = 4, 6, 8$)	18C6, DC18C6, Dtb18C6	18
	Sr^{2+}	$[R_1R_2MeIM][PF_6]$, $[R_1R_2MeIM][Tf_2N]$	DC18C6	19
	Sr^{2+}	$[C_nMIM][Tf_2N]$ ($n = 2, 4, 6, 8$)	DC18C6, *N*-alkyl aza-18-crown-6 ethers	39
Heavy and radioactive metals	Pb^{2+}	$[C_nMIM][PF_6]$ ($n = 4–9$)	DC18C6	37
	Cu^{2+}, Ag^+, Pb^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}	$[C_4MIM][PF_6]$	Dithizone	23
	Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Hg^{2+}	$[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$	PAN, TAN	20
	Ag^+	$[C_nMIM][PF_6]$ ($n = 4, 6, 8$)	Calyx[4]arene-bearing pyridine	40
	Cu^{2+}, Cr^{6+}, Zn^{2+}	$[C_nMIM][BF_4]$ ($n = 1, 3, 6, 8, 10$) $[C_nMIM][PF_6]$ ($n = 6, 10$)	None	41
	Hg^{2+}, Cd^{2+}	TSILs	None	28,35
	Lanthanides (Nd^{3+}, La^{3+}, Er^{3+}, Ce^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Ho^{3+})	$[C_4MIM][PF_6]$	CMPO	32
	Actinides (Th^{4+}, U^{2+}, Pu^{4+})	$[C_4MIM][PF_6]$, $[C_4MIM][NO_3]$, $[C_4MIM][Tf_2N]$, $[C_6MIM][PF_6]$ $[C_8MIM][PF_6]$	Dtb18C6, CMPO, TBP	29,34
Others	Al^{3+}		n/a	42,43

Note: C_nMIM = 1-alkyl-3-methylimidazolium; DC18C6 = dicyclohexano-18-crown-6; 18C6 = 18-crown-6; Dtb18C6 = 4,4′-(5′)-di-(*tert*-butylcyclohexano)-18-crown-6; BOBCalixC6 = calix[4]arene-bis(*tert*-octylbenzo-crown-6); Tf_2N = bis[(trifluoromethyl)sulfonyl]amide; R_1R_2MeIM = 1-R_1-2-R_2-3-methylimidazolium (R_1 = Bu, Et, or Pr; R_2 = H, or Me); PAN = 1-(2-pyridylazo)-2-naphthol; TAN = 1-(2-thiazolylazo)-2-naphthol; CMPO = octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide; TBP = tri-*n*-butylphosphate.

Extractions and Separations

Table 2. Examples of IL extractions of organic/bio/biofuel molecules

	Substances	IL	Extractant	Reference
Phenolic compounds	phthalic acid, aniline, 4-hydroxybenzoic acid, benzoic acid, *p*-toluic acid, benzene, chlorobenzene, 1,2,4-trichlorobenzene, 1,4-dichlorobenzene, 4,4′-dichlorobiphenyl	$[BMIM][PF_6]$	None	44
	Phenol, tyrosol, *p*-hydroxybenzoic acid	$[C_nMIM][BF_4]$ ($n = 1, 3, 6, 8, 10$) $[C_nMIM][PF_6]$ ($n = 6, 10$)	None	41
	Chlorophenols	$[C_4MIM][PF_6]$, [EMIM][Beti]	None	58
Amino acids	Tryptophan, glycine, alanine, leucine, lysine, arginine	$[BMIM][PF_6]$	DC18C6	45
Carbohydrates	Xylose, fructose, glucose, sucrose	$[C_nMIM][X]$ ($n = 4, 6, 8, 10$; $X = Cl^-, PF_6^-, BF_4^-$)	None	46
	Glucose, sucrose, lactose, cyclodextrin	[BMIM][dca] (carbohydrate solubility is approximately 200 g l^{-1})	None	47
	Cellulose	$[C_nMIM]X$ ($n = 4, 6, 8$)	None	59
Organic acids	Lactic acid, acetic acid, glycolic acid, propionic acid, pyruvic acid, butyric acid	$[C_nMIM][PF_6]$ ($n = 4, 6, 8$)	TBP (in some cases)	48
Biofuels	Butyl alcohol (from fermentation broth)	$[BMIM][PF_6]$, $[C_8MIM][PF_6]$	Pervaporation was used	49
Antibiotic	Erythromycin-A	$[BMIM][PF_6]$	None	50
Hydrocarbons	Olefins (such as ethylene, propylene, and butanes) from paraffins	$[C_nMIM][X]$, $[HPy][X]$ ($n = 4, 6$; $X = BF_4^-, PF_6^-$)	None	54,55
	C_{4-8} diolefin (such as butadiene) from C_{1-18} paraffins	$[BMIM][BF_4]$	None	56

Note: BMIM (or C_4MIM) = 1-butyl-3-methylimidazolium; EMIM = 1-ethyl-3-methylimidazolium; Beti = bis(perfluoroethylsulfonyl)imide; HPy = *N*-hexylpyridinium; dca = dicyanamide.

Extractions and Separations

Table 7.4 Solubility of various metal oxides in a 2:1 urea–choline chloride eutectic at 60 °C.

Metal oxide	*Mp of metal oxide, °C*	*Solubility, ppm*
Al_2O_3	2045	< 1
CaO	2580	6
CuO	1326	470
Cu_2O	1235	8725
Fe_2O_3	1565	49
Fe_3O_4	1538	40
MnO_2	535	493
NiO	1990	325
PbO_2	888	9157
ZnO	1975	8466

Electrochemistry

Table 7.5 Some examples of metals deposited from ionic liquids.

Ionic liquid type		*Metals deposited*
Discrete anions	*e.g.* BF_4^-, PF_6^-, $(CF_3SO_2)_2N^-$	Cd, Cu, In, Sn, Pb, Au, Ag Ag, Ge Li, Mg, Ti, Al, Si, Ta, La, Sm, Cu, Co, Eu, Ag, Cs, Ga
Type-I Eutectics	*e.g.* $AlCl_3$, $ZnCl_2$	Al, Fe, Co, Ni, Cu, Zn, Ga, Pd, Au, Ag, Cd, In, Sn, Sb, Cr, Na, Li, La, Pb Fe, Mn, Ni, Cu, Co, Ti, Cr, Nb, Nd, La, Zn, Sn, Cd
Type-II Eutectics	*e.g.* $CrCl_3 \cdot 6H_2O$[26]	Cr
Type-III Eutectics	*e.g.* Urea, Ethylene glycol	Zn, Sn, Cu, Ag Zn, Sn

Electrochemistry

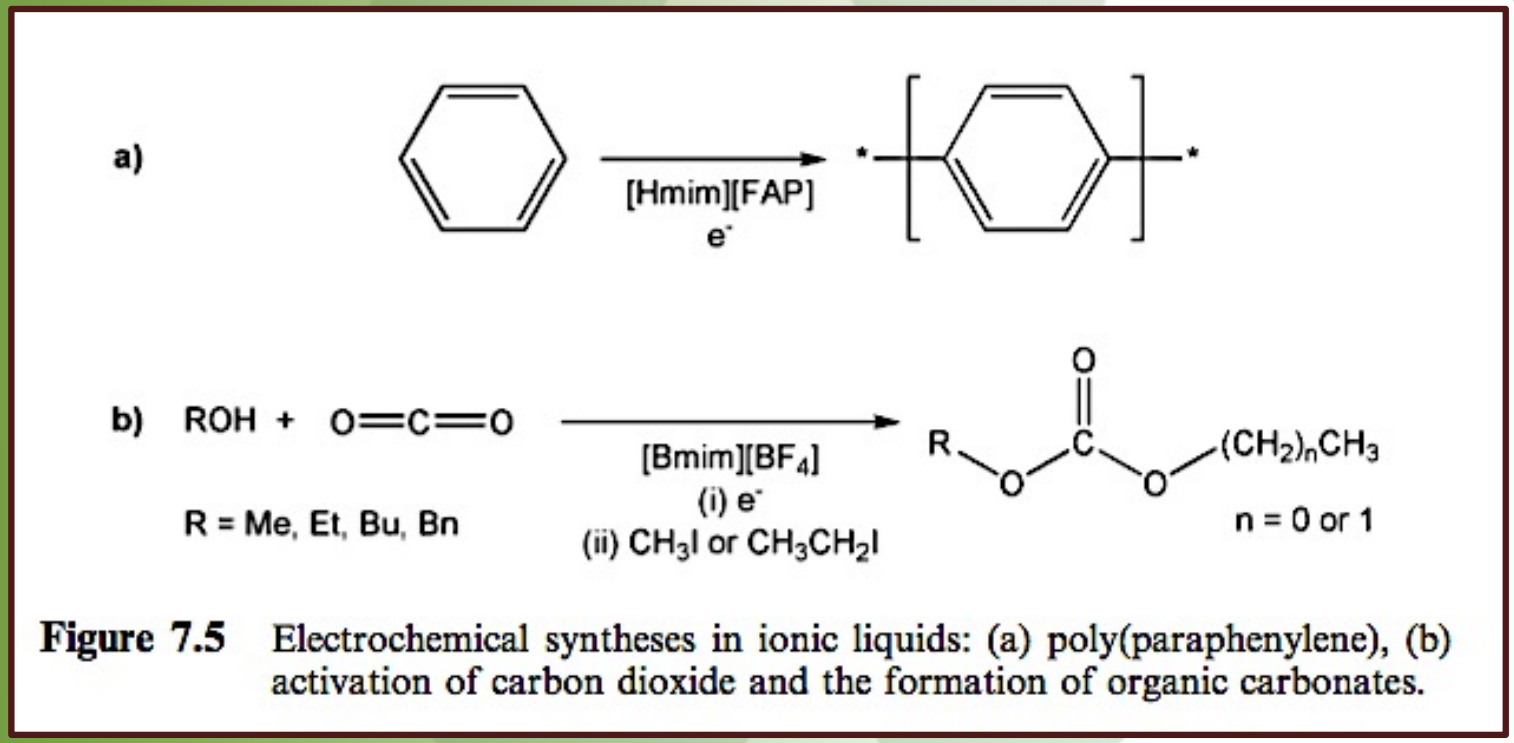
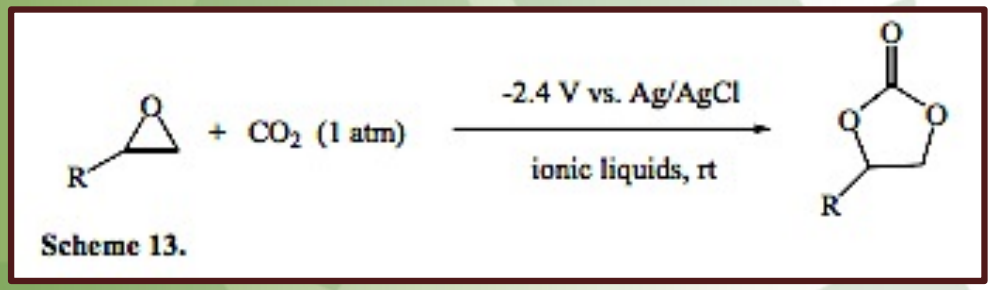
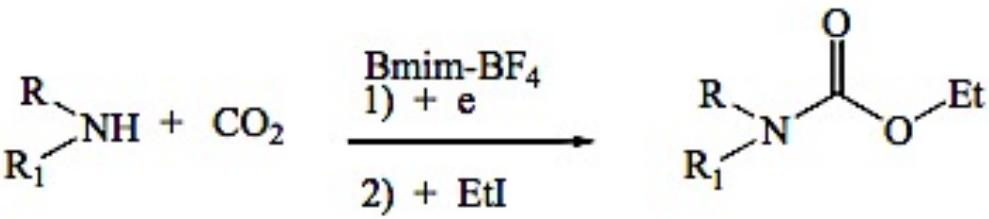


Figure 7.5 Electrochemical syntheses in ionic liquids: (a) poly(paraphenylene), (b) activation of carbon dioxide and the formation of organic carbonates.

Electrochemistry



Scheme 13.



Scheme 14.

Synthesis in RTILs

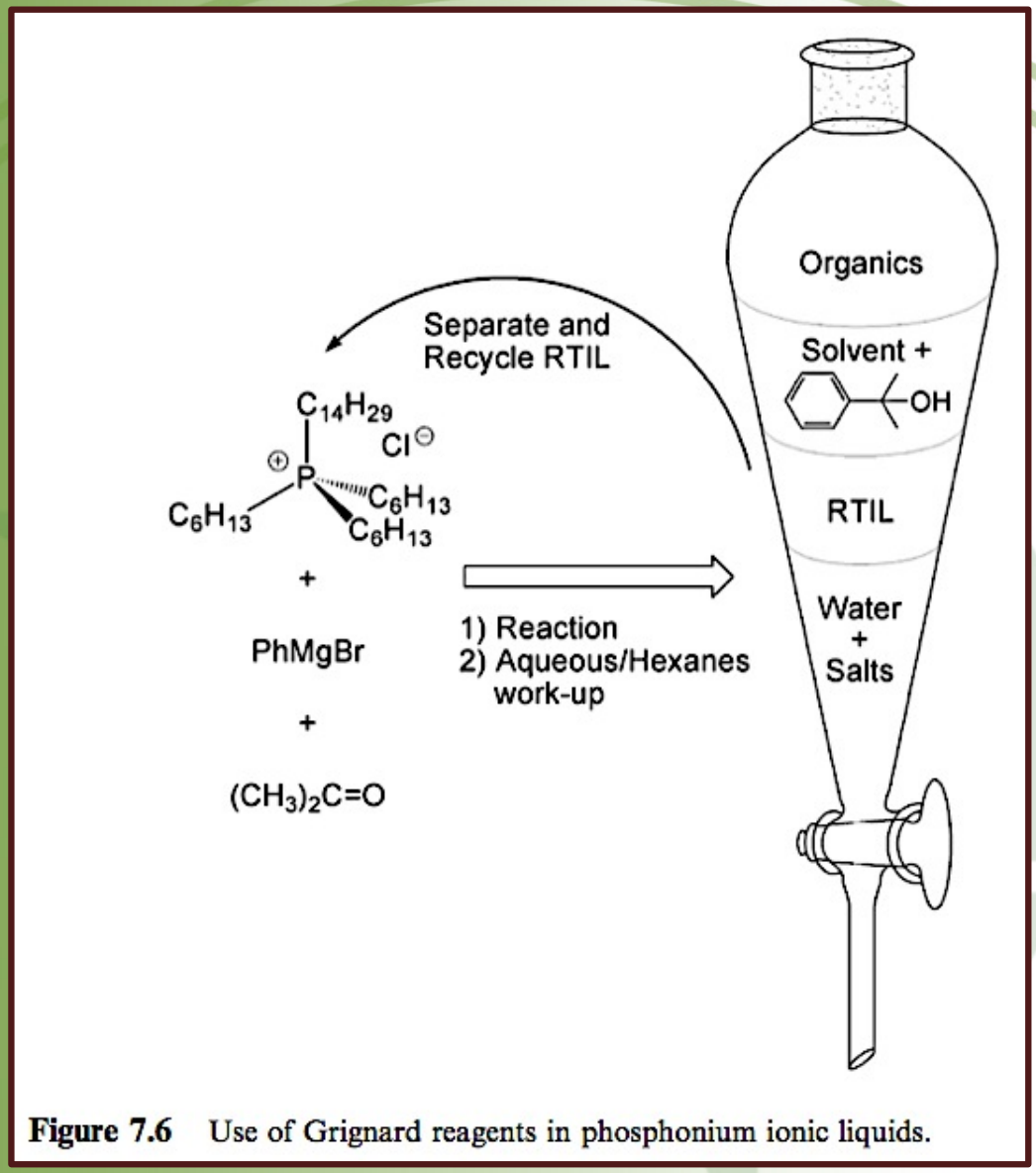
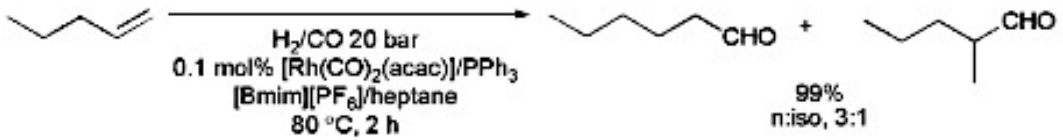


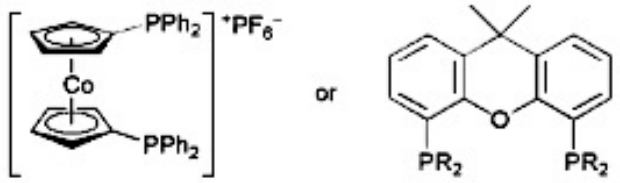
Figure 7.6 Use of Grignard reagents in phosphonium ionic liquids.

Synthesis in RTILs

Hydroformylation

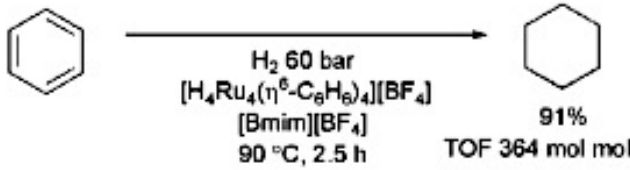


alternative ligands =

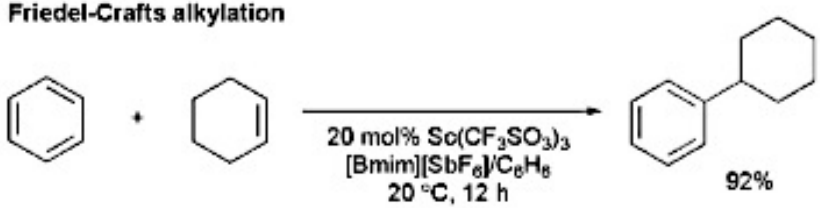


or

Hydrogenation

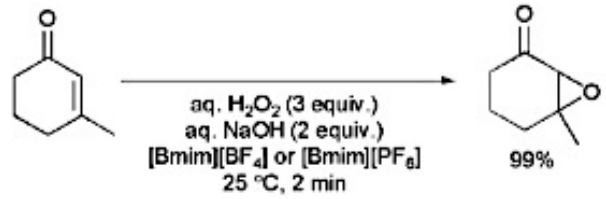


Friedel-Crafts alkylation

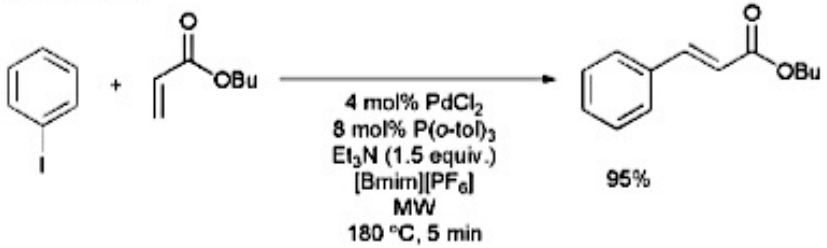


Synthesis in RTILs

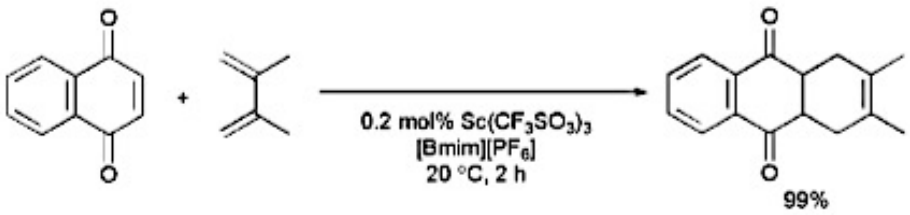
Epoxidation



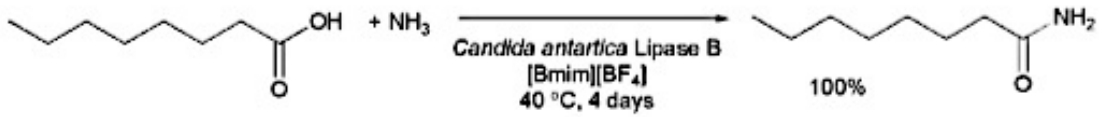
Heck reaction



Diels-Alder reaction

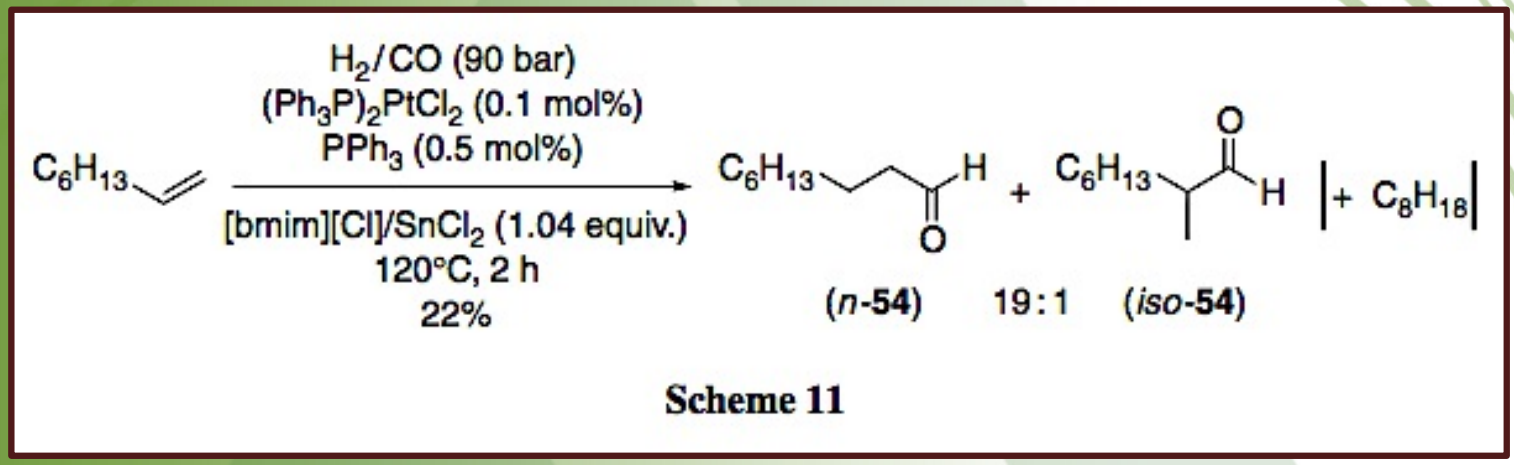


Biocatalytic ammonolysis

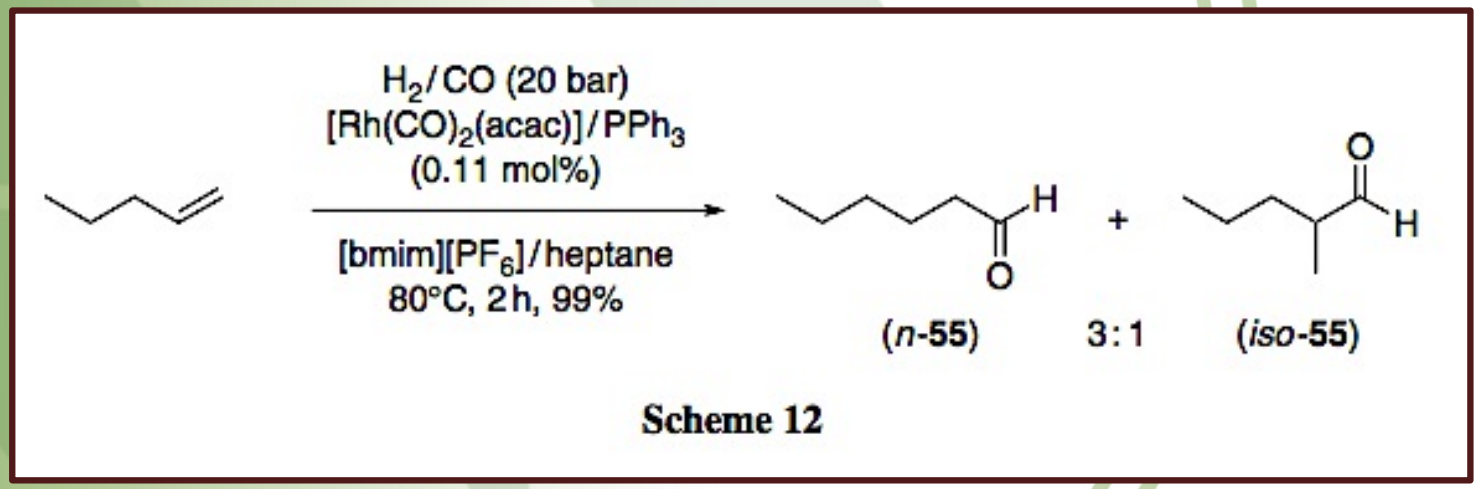


Synthesis in RTILs

Hydroformylation



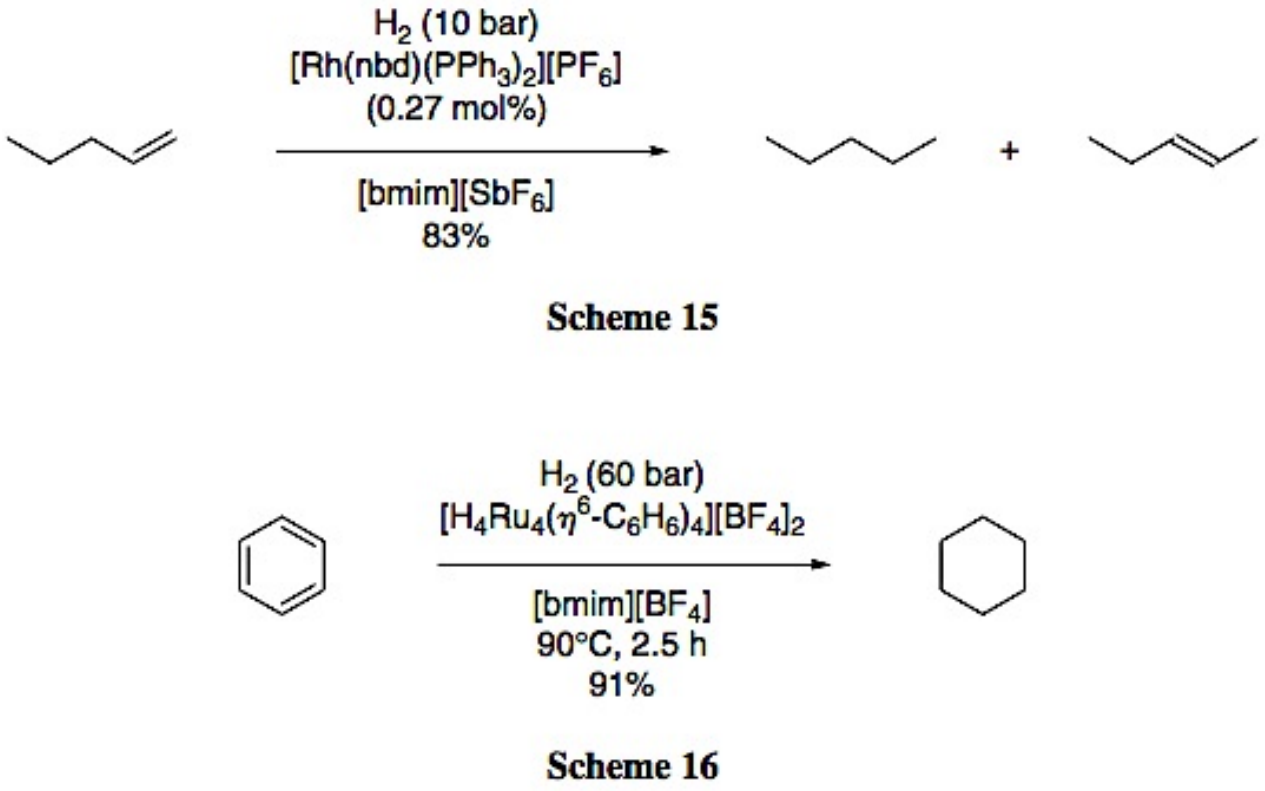
Scheme 11



Scheme 12

Synthesis in RTILs

Hydrogenation

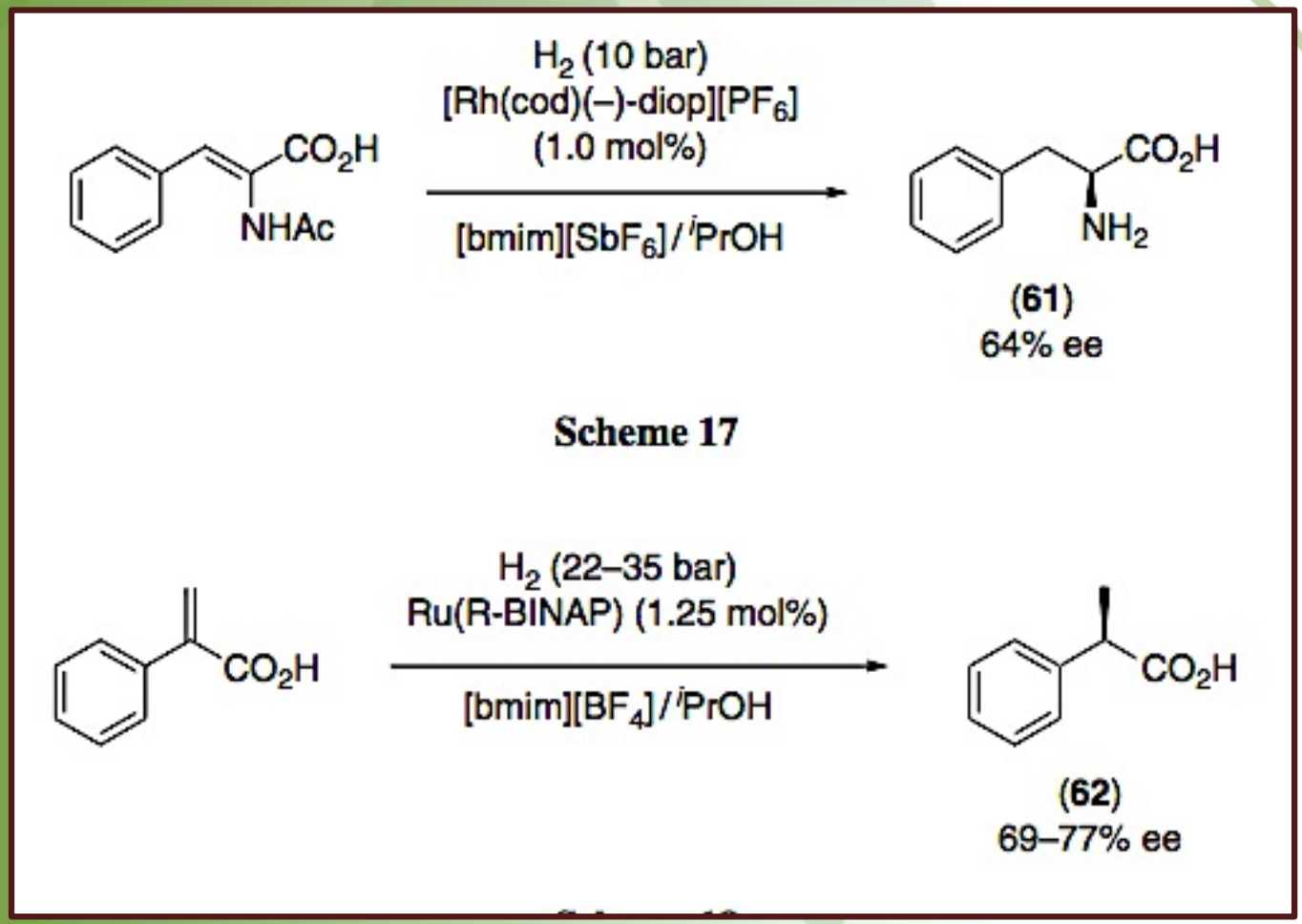


Scheme 15

Scheme 16

Synthesis in RTILs

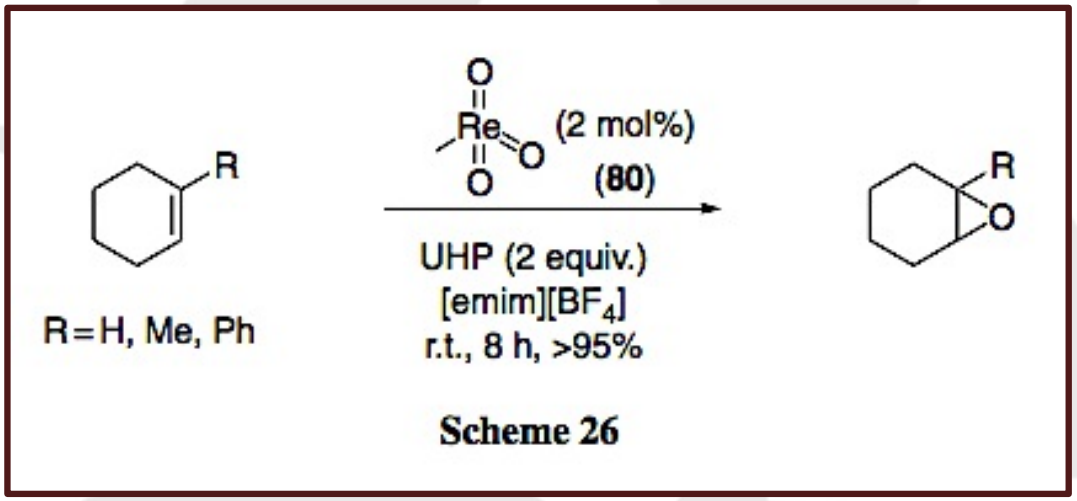
Hydrogenation



Scheme 17

Synthesis in RTILs

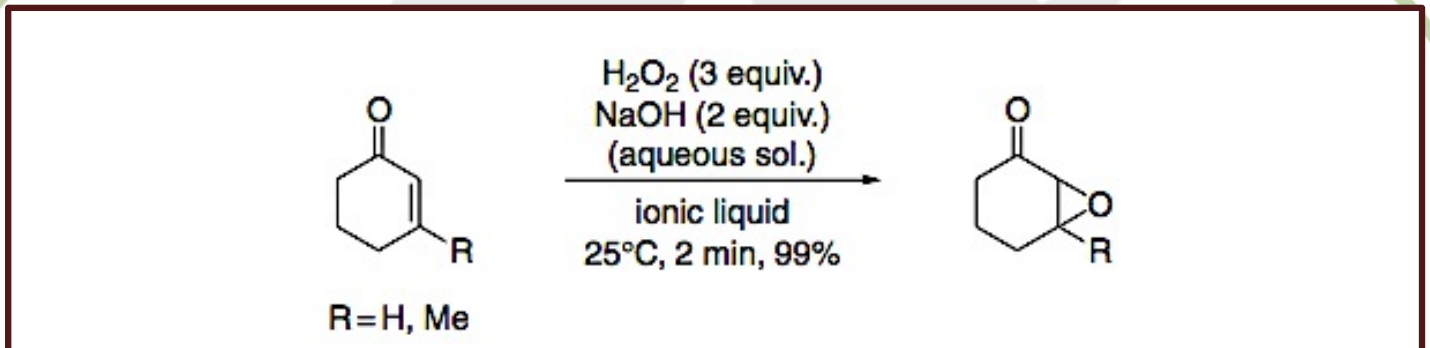
Epoxidation



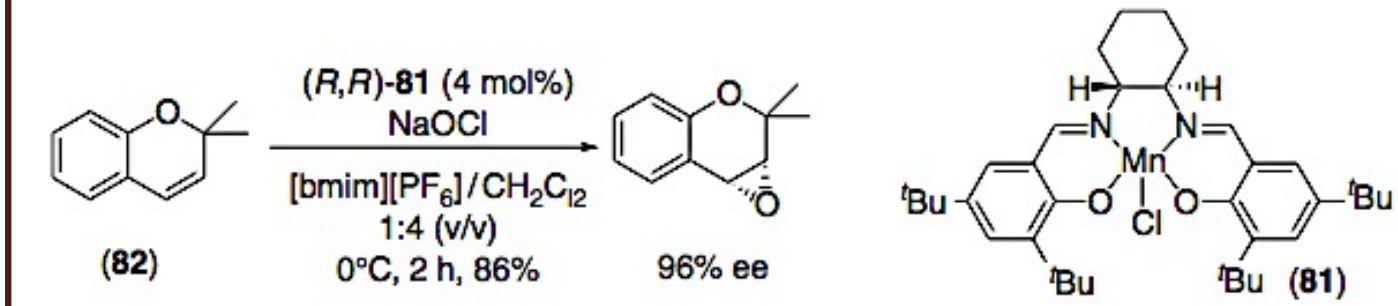
Scheme 26

Synthesis in RTILs

Epoxidation



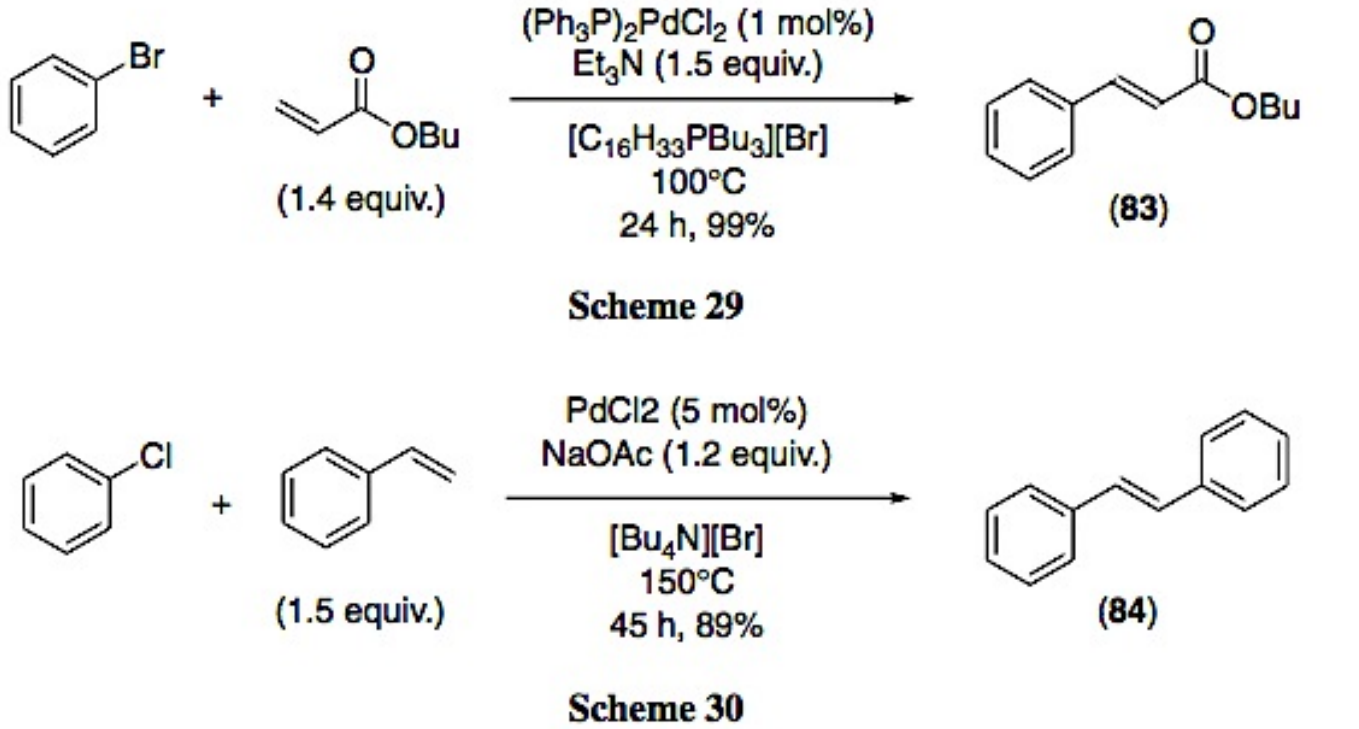
Scheme 27



Scheme 28

Synthesis in RTILs

Mizoroki–Heck reaction

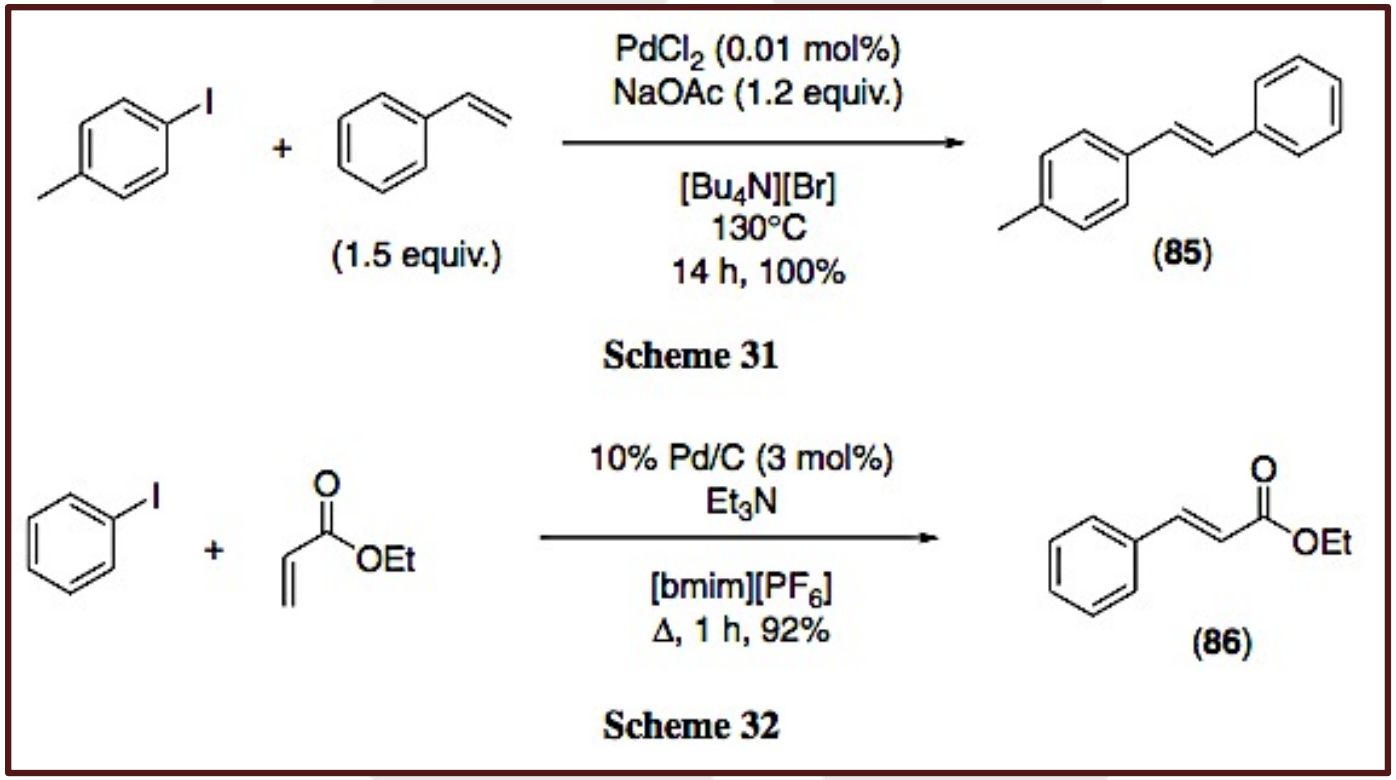


Scheme 29

Scheme 30

Synthesis in RTILs

Mizoroki–Heck reaction

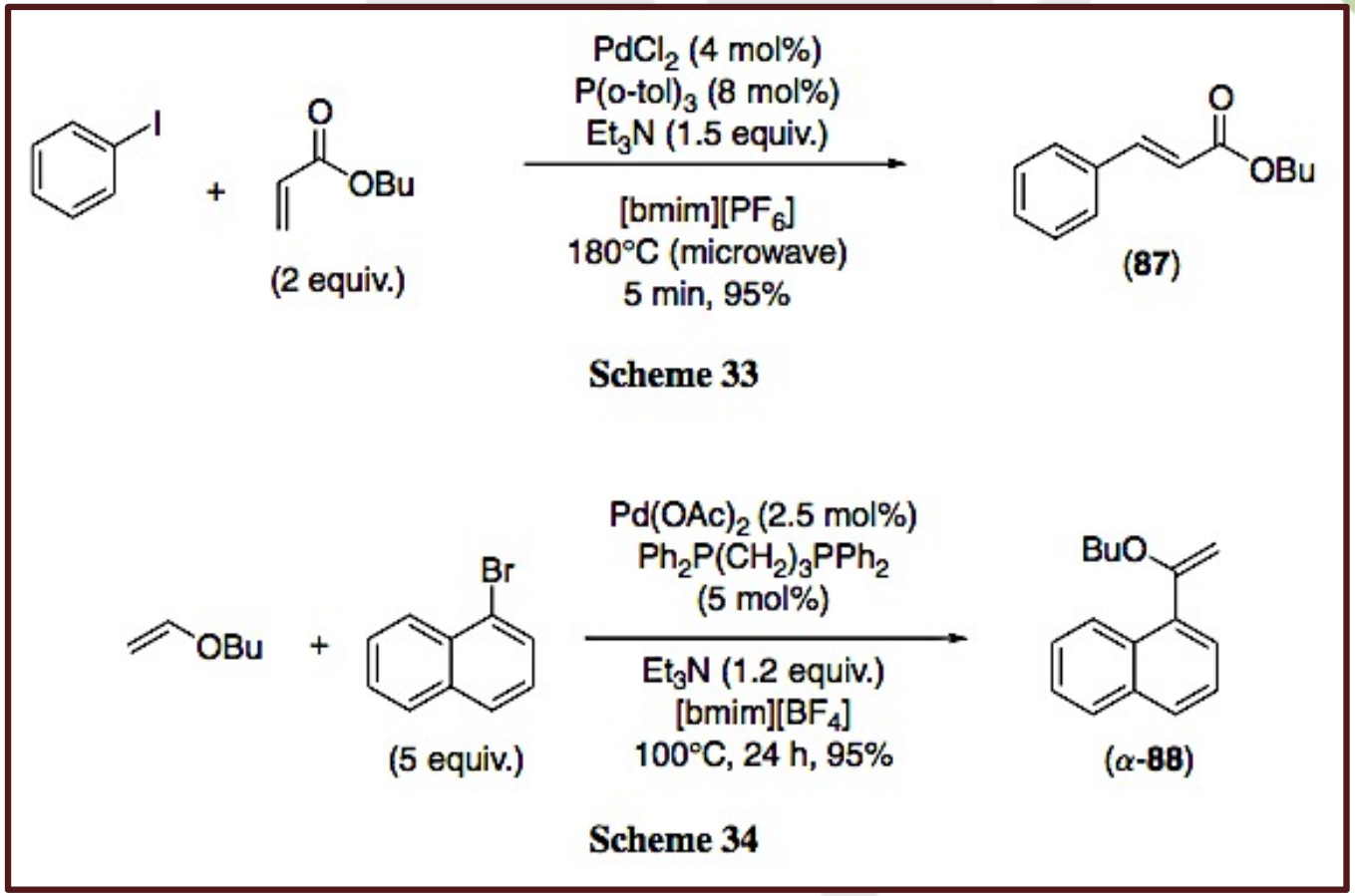


Scheme 31

Scheme 32

Synthesis in RTILs

Mizoroki–Heck reaction

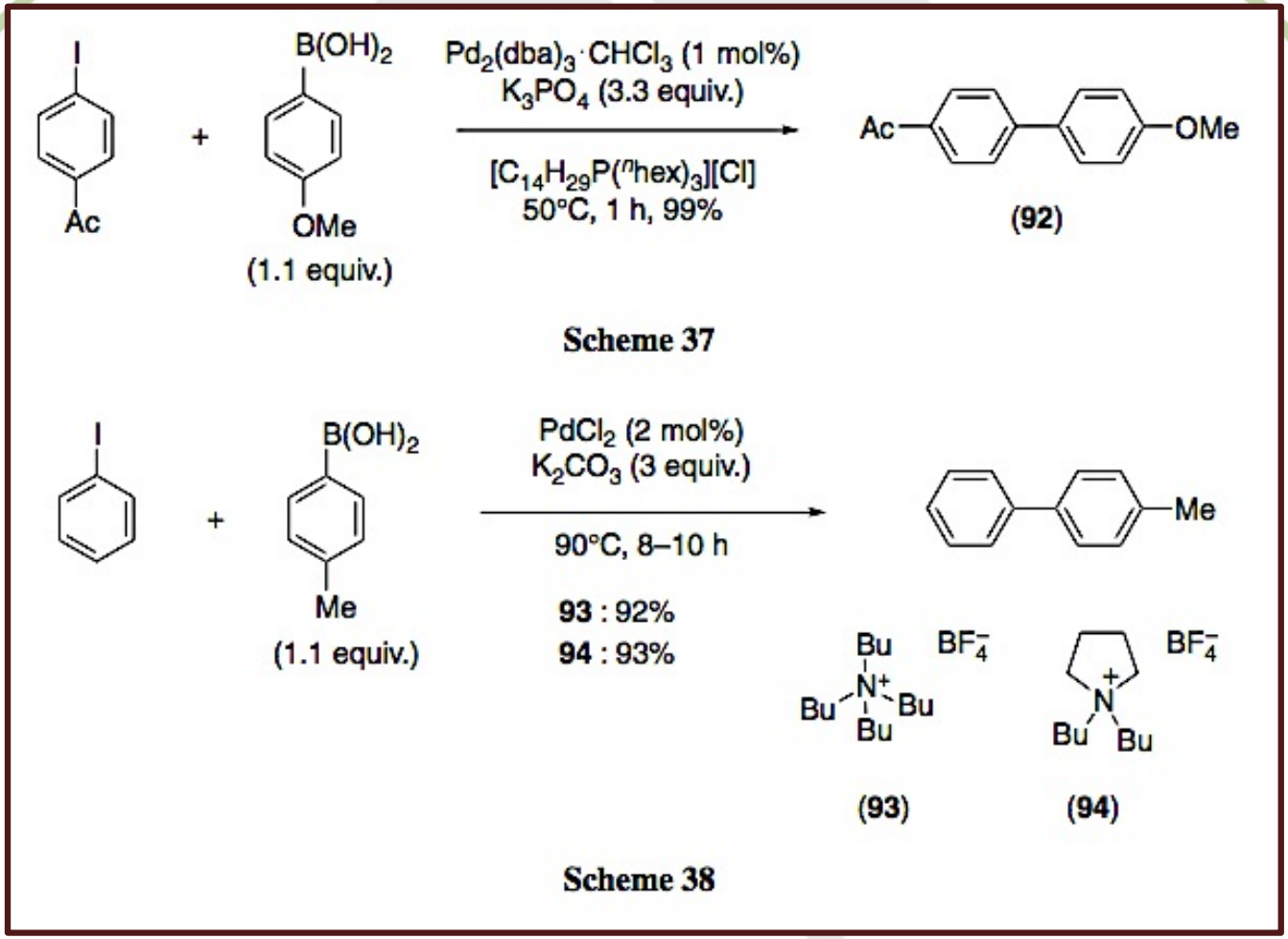


Scheme 33

Scheme 34

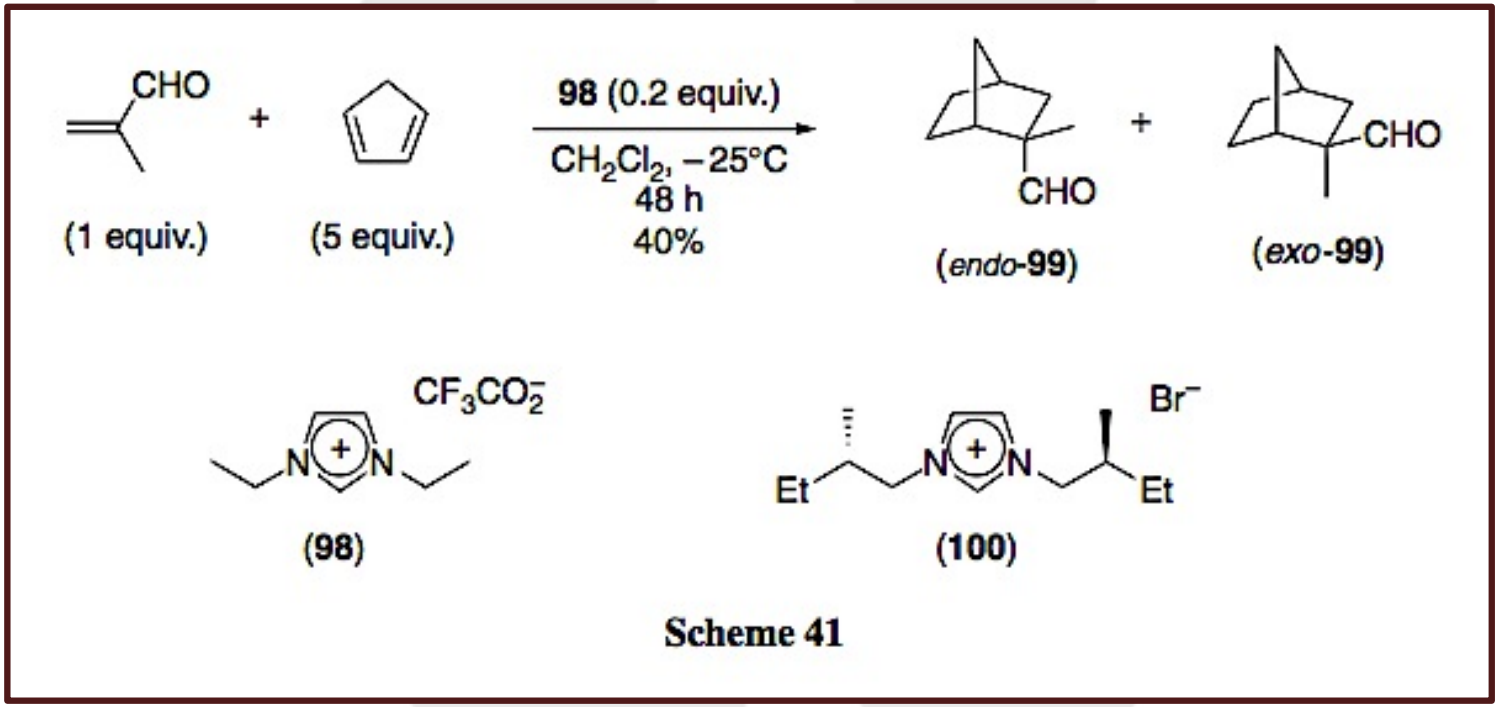
Synthesis in RTILs

Suzuki–Miyaura cross-coupling reaction



Synthesis in RTILs

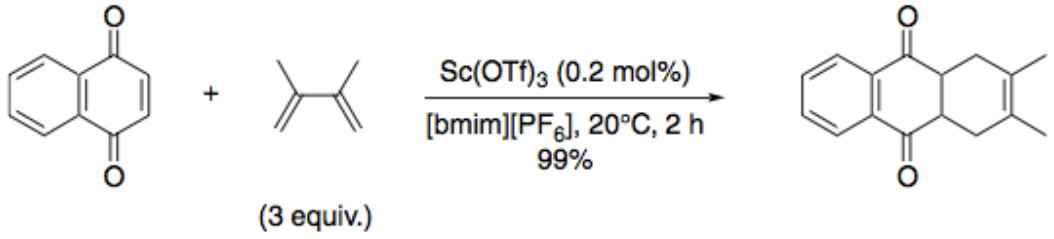
Diels-Alder Reaction



Scheme 41

Synthesis in RTILs

Diels-Alder Reaction



Scheme 43

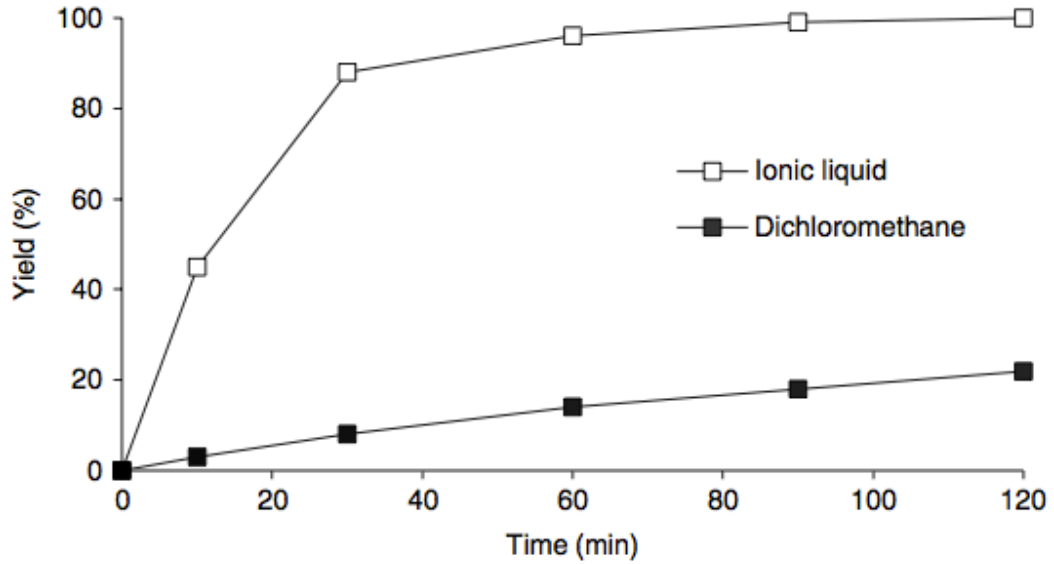


Figure 2.13

Synthesis in RTILs

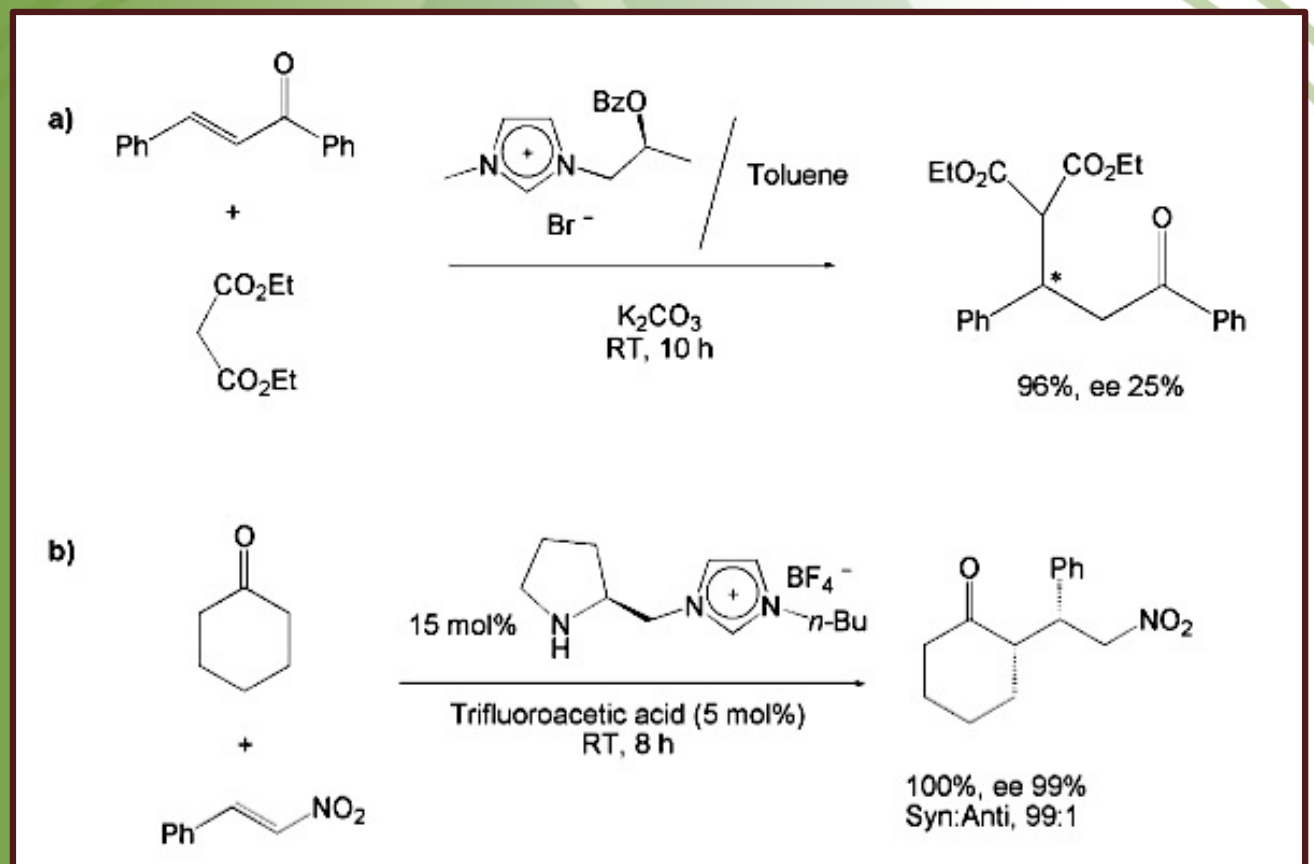


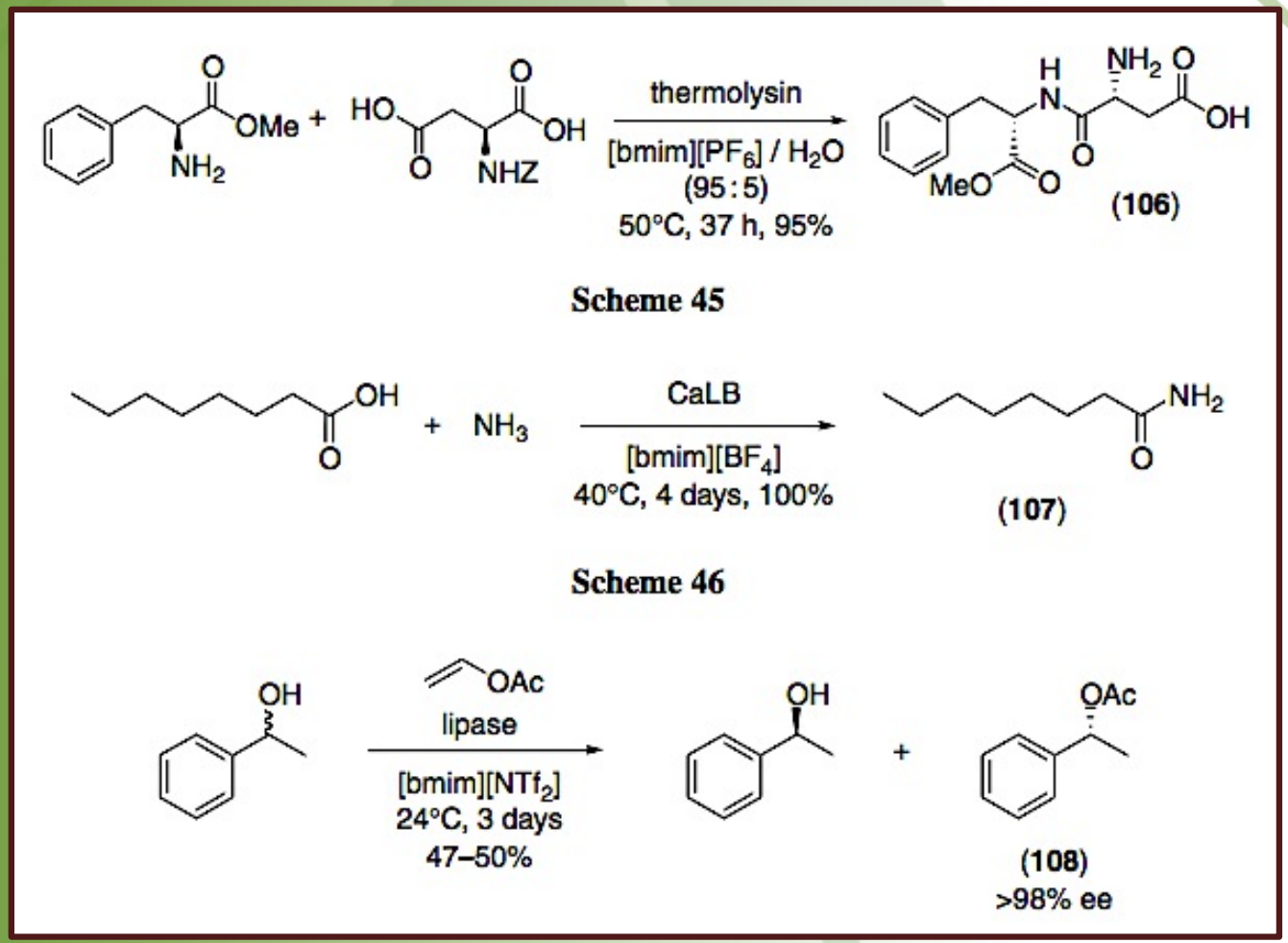
Figure 7.8 Asymmetric Michael addition reactions using chiral ionic liquids: (a) derived from lactate, (b) derived from proline.

Biocatalysis in RTILs

Table 7.6 Some examples of biocatalysed reactions in RTILs.

Enzyme Class	*Reactions*	*Typical comments*
Lipase	Transesterification and direct esterification (incl. polyester synthesis) Ring-opening polymerisation of ε-caprolactone Hydrolysis; Alcoholysis Acetylation	Higher stability of enzyme; greater activity; catalyst recyclable; sometimes higher enantio- and regioselectivity compared with VOCs
Esterase	Transesterification	Higher stability of enzyme; activity and enantioselectivity similar to VOCs
Protease	Transesterification Hydrolysis (incl. stereospecific)	Higher stability of enzyme; rates comparable to buffer solutions and VOCs; enhanced enantioselectivity
Dehydrogenase	Enantioselective reduction of ketone Oxidation of codeine	Faster rate than VOC
Peroxidase	Oxidation of anisoles and thioanisoles	Activity similar to VOC; stereoselectivity similar to water
β-galactosidase (whole cells *e.g.* Baker's yeast)	Reduction of ketones	RTIL recyclable after product distilled; RTILs (alone) do not damage cell membrane

Biocatalysis in RTILs



Polymer Synthesis in RTILs

very high molecular weight polymers

- free-radical polymerizations (including styrene and alkyl methacrylates)
- cationic polymerization of styrene;
- cationic ring-opening polymerization of oxazolines
- reverse atom-transfer radical polymerizations (including methyl methacrylate (MMA) and acrylonitrile)
- ruthenium-catalyzed ring-opening metathesis polymerization of norbornenes;
- palladium-catalyzed copolymerization of propene with carbon monoxide.

Polymer Synthesis in RTILs

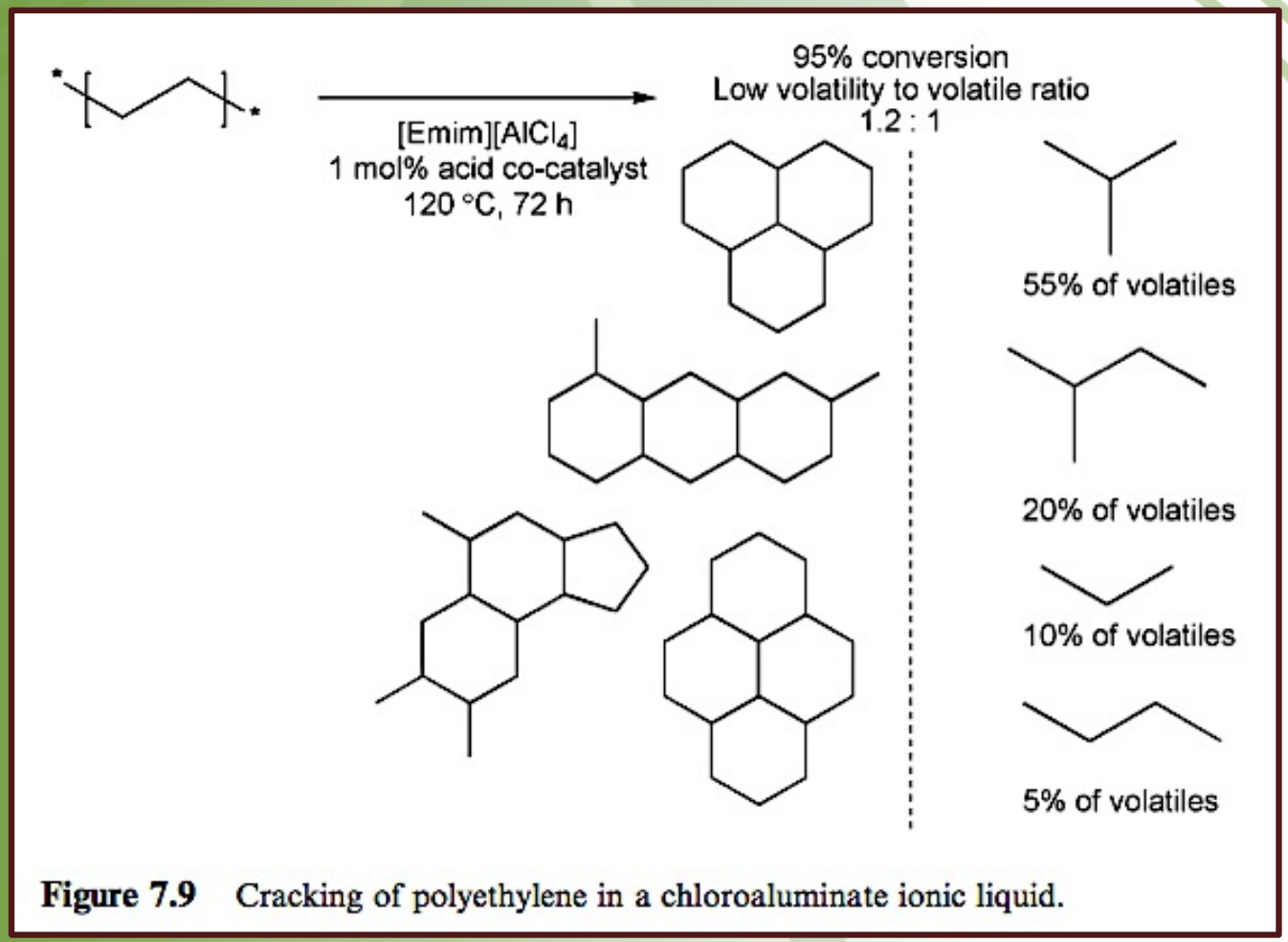
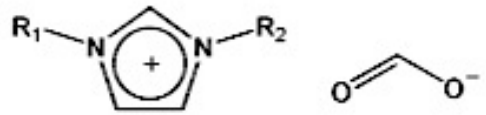
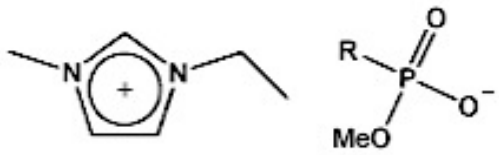


Figure 7.9 Cracking of polyethylene in a chloroaluminate ionic liquid.

Polymer Synthesis in RTILs



1. R_1 = Et, R_2 = Me; T_m = 52 °C, T_d = 212 °C
2. R_1 = Pr, R_2 = Me; T_g = –73 °C, T_d = 213 °C, Viscosity = 117 cP, α = 0.46, β = 0.99, π* = 1.06
3. R_1 = allyl, R_2 = Me; T_g = –76 °C, T_d = 205 °C, Viscosity = 66 cP, α = 0.48, β = 0.99, π* = 1.08
4. R_1 = allyl, R_2 = Et; T_g = –76 °C, T_d = 205 °C, Viscosity = 67 cP, α = 0.47, β = 0.99, π* = 1.06



1. R = H; T_g = –86 °C, T_d = 275 °C, Viscosity = 107 cP, α = 0.52, β = 1.00, π* = 1.06
2. R = Me; T_g = –66 °C, T_d = 262 °C, Viscosity = 510 cP, α = 0.50, β = 1.07, π* = 1.04
3. R = OMe; T_g = –74 °C, T_d = 289 °C, Viscosity = 265 cP, α = 0.51, β = 1.00, π* = 1.06

Figure 7.10 Structures and physical data for next-generation ionic liquids for carbohydrate dissolution.