

**EGE UNIVERSITY GRADUATE SCHOOL OF
NATURAL AND APPLIED SCIENCES**

(PhD THESIS)

**IMPROVING CATALYTIC SYSTEMS
IN IONIC LIQUIDS**

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ÖZET

İYONİK SIVILARDA KATALİTİK SİSTEMLERİN
GELİŞTİRİLMESİ

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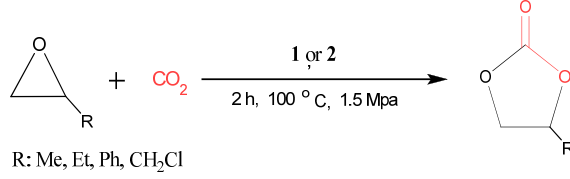
Eylül 2011, 141 sayfa

İyonik sıvıların organik sentezlerde kullanılması ilgi çeken bir konudur. Katalizör geri kazanımını ve ürün saflaştırma işlemini kolaylaştırmasından dolayı iyonik sıvılar ve metallerle olan kombinasyonları, karbon dioksitin kimyasal ürünlere dönüşümü tepkimesinde katalizör olarak kullanılmaktadır. CO₂ ucuz, yeşil ve bol bulunan C1 kaynağı olarak değerli kimyasal bileşiklerin üretiminde önemli bir başlangıç maddesidir. Karbon dioksitin kimyasal ürünlere dönüştürülmesinde araştırılan proseslerden biri karbon dioksit ve epoksitlerden yola çıkarak halkalı karbonat sentez yöntemidir. Bu tezin amacı **1** ve **2** tipi bileşiklerin karbon dioksitin halkalı karbonatlara dönüşümündeki katalitik etkilerini araştırmaktır.

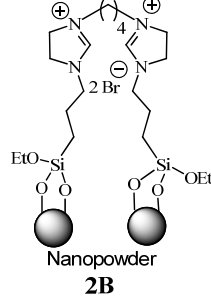
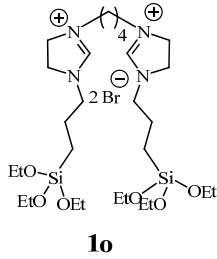
İyonik sıvılarla yapılan araştırmalar kolay sentezlenebilmesi, hava ve neme karşı kararlı olmasından dolayı imidazolyum yapısı üzerine yoğunlaşmıştır. Sürekli akışkan yatak reaktörler için aktif ve seçici katalizörlerin katı destek üzerine immobilizasyonu istenen bir yöntemdir. Trialkoksisilil grubu içeren iyonik sıvılar heterojen bileşik hazırlamak için kullanılmaktadır ancak literatürde **imeo** [1-(3-triethoxysilylpropyl)imidazolin] kullanarak yapılmış çok az çalışma bulunmaktadır.

Bu tez dört kısımdan oluşmaktadır. İlk kısım iyonik sıvılar, immobilize iyonik sıvılar ve bunların katalitik ve endüstriyel uygulamalarına yönelik genel bir derlemeden oluşmaktadır. İkinci kısım karbon dioksitin çevreye etkisi ve kimyasal tepkimelerine ilişkin bir derleme mahiyetindedir. Üçüncü kısımda deneysel ayrıntılar ve imidazolinyum tuzlarının (**1**) ve tutundurulmuş imidazolinyum bileşiklerinin (**2**) sentez yöntemlerinden bahsedilmiştir. Dördüncü kısımda, silisyum temelli imidazolinyum tuzlarının (**1**) ve tutundurulmuş bileşiklerin (**2**)

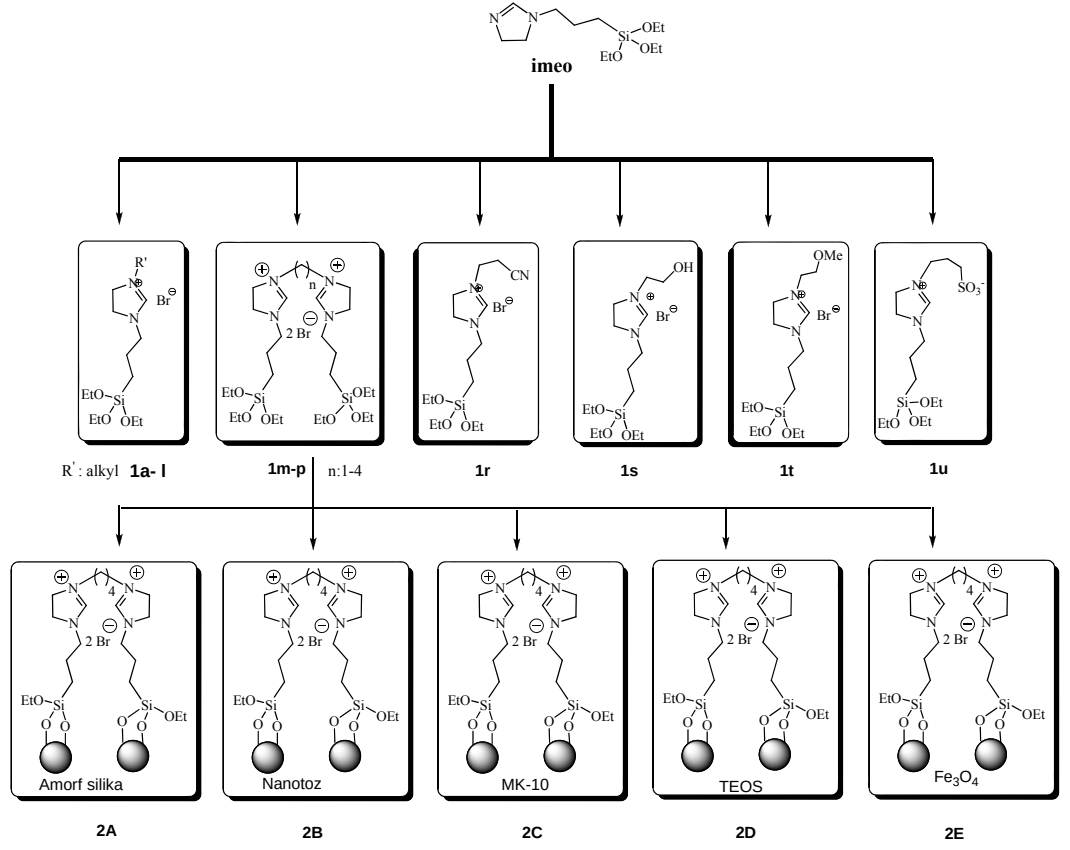
karakterizasyonu ayrıntılı bir şekilde açıklanmıştır. Bu bileşiklerin epoksit ve karbon dioksitten halkalı karbonat sentezi tepkimesine katalitik etkinlikleri bu kısımda tartışılmıştır. Zincir uzunluğunun, fonksiyonel grupların, anyonun ve farklı destek maddelerinin katalizör yapısına ve katalitik aktivite üzerine etkisi araştırılmıştır.



Katalitik denem sonuçlarına göre en iyi katalitik etkinliği homojen fazda **1o** bileşiği [1,4-(3-triethoxysilylpropil)bütan dibromür] (92% PC verim); heterojen fazda ise **2B** bileşiğinin (75% PC verim) sergilediği görülmüştür.



Katalitik sistemin optimizasyonunda sıcaklık, basınç, süre, epoksit türü ve katalizör miktarı gibi çeşitli parametreler denenmiştir. Optimizasyon denemeleri sonucunda 120 °C sıcaklık, 1.5 MPa karbon dioksit basıncı, 0.5 mol % katalizör (**1o** veya **2B**) ve 3 saatlik tepkime süresi optimum koşullar olarak belirlenmiştir.



Tez deney şeması

Anahtar Kelimeler: İyonik sıvı, immobilize iyonik bileşikler, immobilizasyon, CO₂ dönüşümü, Halkalı karbonat

ABSTRACT

IMPROVING CATALYTIC SYSTEMS IN IONIC LIQUIDS

TAŞCI, ZEYNEP

Ph.D. Thesis in Chemistry

Supervisor: Prof. Dr. Mehmet BALCAN

Co-Supervisor: Prof. Dr. Nurgün BEŞÜN

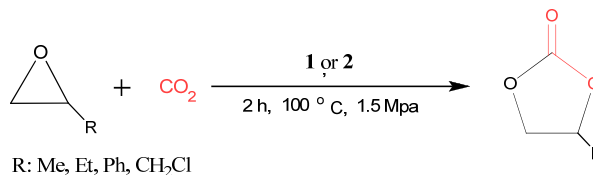
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The utilization of ionic liquids as reaction media is a current topic of interest in organic synthesis. Due to the ease of catalyst recovery and product purification, ionic liquids or their combination with metal salts have been investigated as catalyst for the chemical fixation of CO₂. This is important since CO₂ is cheap, green and abundant C1 source of producing lots of valuable chemicals. One of the most investigated process in this area is the synthesis of five-membered cyclic carbonates via the coupling of CO₂ and epoxides. The aim of this thesis is transformation of CO₂ into cyclic carbonates using **1** and **2** compounds as catalysts.

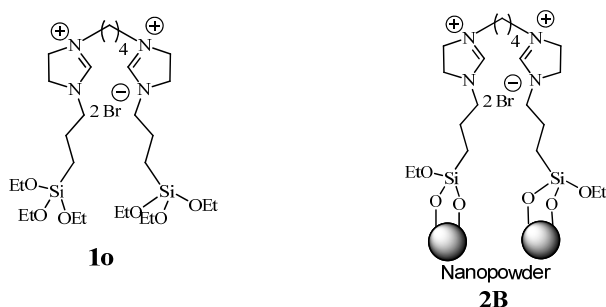
The recent researches focused on ionic liquids which have imidazolium structure due to ease of synthesis, air and moisture stability. The immobilization of the catalyst onto a solid support is most promising methodology for an efficient continuous flow process based on active and selective catalysts. Trialkoxysilyl functionalized ionic liquids are used for the preparation of supported compounds but there is a few study related to **imeo** [1-(3-triethoxysilyl)propylimidazoline] based compounds.

This thesis consist of four parts. The first part is a general review about ionic liquids, supported ionic liquids and their catalytic and industrial application. The second part is a concise review about the effect of carbon dioxide to environment and chemical fixation of it. In part III, the experimental details and synthesis of imidazolinium salts (**1**) and immobilized imidazolinium (**2**) compounds were given. In part IV, the characterization of silisium-based imidazolinium salts (**1**) and supported imidazolinium compounds (**2**) were described in detail. Using these compounds as catalyst, the synthesis of cyclic

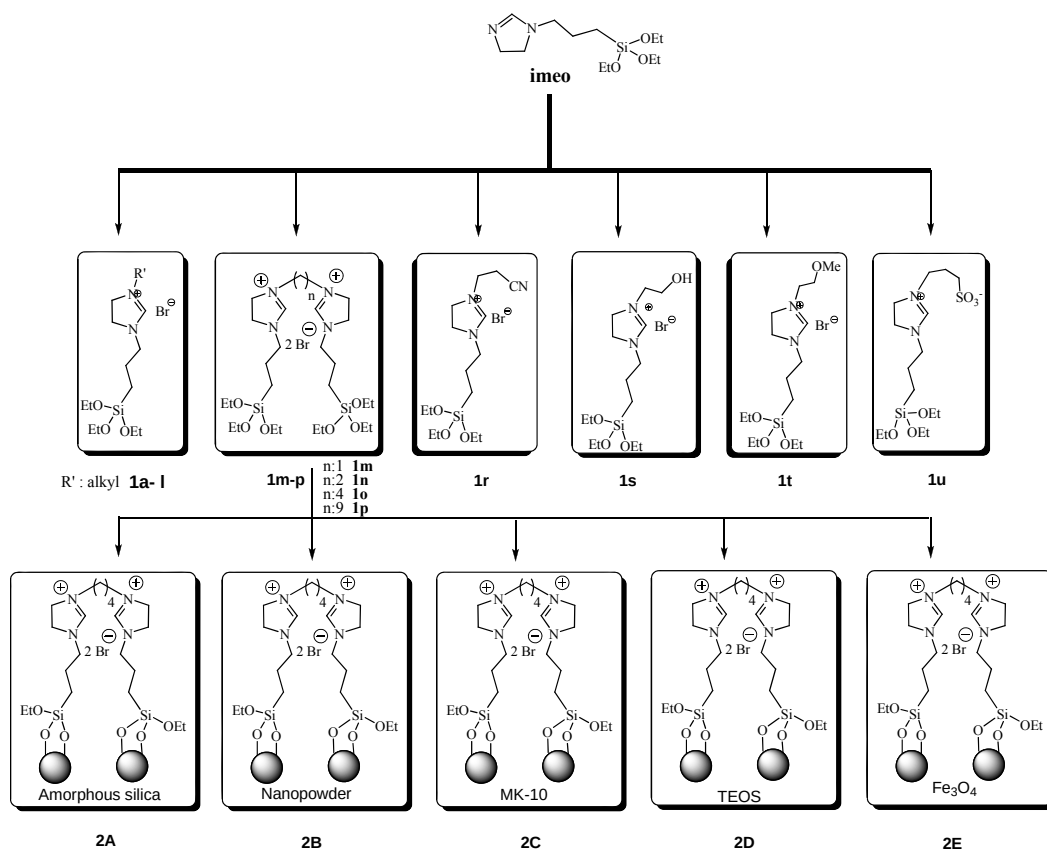
carbonates from carbon dioxide and terminal epoxides were also mentioned in this part. The effect of the length of chain, functional group and anion on the homogeneous structure and the effect of different type of supporting materials on the heterogeneous structure and catalytic activity were investigated. The optimization studies on the catalytic system were also performed.



According to catalytic experiment results, the most active catalysts for the **1** type complexes **1o** [1,4-(3-triethoxysilylpropyl)butane dibromide] (92%); for the **2** type complexes **2B** (75%) was found.



The optimization of the catalytic system was performed changing the parameters such as the amount of catalyst, temperature, pressure, time and epoxide. According to the optimization experiments, 120 °C, 1.5 MPa carbon dioxide pressure, 0.5 mol % catalyst(**1o** or **2B**) and 3 h was determined to be optimum conditions.



Experimental scheme of the thesis

Keywords: Ionic liquid, supported ionic compound, immobilization, CO₂ fixation, Cyclic carbonate.

DEDICATION

Dedicated to my dear husband Şamil TAŞCI

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ABBREVIATIONS

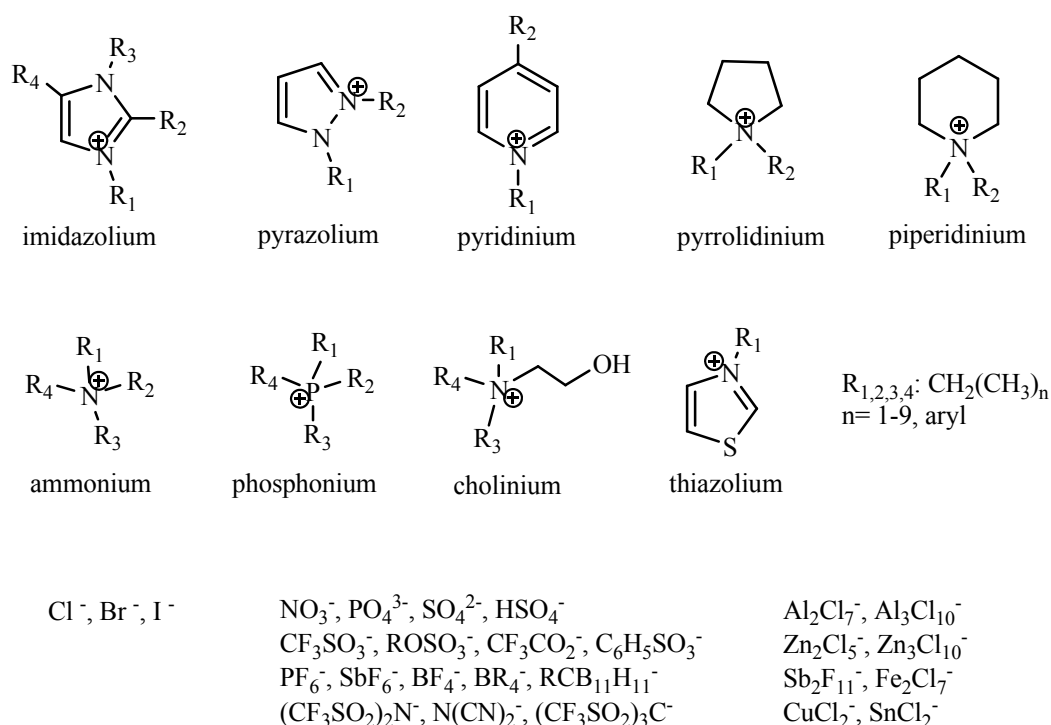
<u>Abbreviation</u>	<u>Explanation</u>
<i>BPA</i>	Bisphenol-A
<i>CILs</i>	Chiral Ionic Liquids
<i>DMAP</i>	4-dimethylaminopyridine
<i>DMC</i>	Dimethylcarbonate
<i>DMF</i>	Dimethylformamide
<i>DPC</i>	Diphenylcarbonate
<i>EC</i>	Ethylene Carbonate
<i>EG</i>	Ethylene Glycol
<i>FTIR</i>	Fourier Transform Infrared
<i>GPE</i>	Glycidyl Phenyl Ether
<i>ILs</i>	Ionic liquids
<i>MK10</i>	Montmorillonit K10
<i>Mt</i>	Megatones
<i>MTO</i>	Methyltrioxorhenium
<i>NMP</i>	N-methylpyrrolidone
<i>NMR</i>	Nuclear Magnetic Resonance

ABBREVIATIONS (CONTINUE)

<u>Abbreviation</u>	<u>Explanation</u>
<i>PC</i>	Propylene Carbonate
<i>PDI</i>	Polydispersity Index
<i>PEG</i>	Poly(ethylene glycol)
<i>PO</i>	Propylene Oxide
<i>PPNCl</i>	Bis(triphenylphosphoran-ylidene)ammonium chloride
<i>PS</i>	Polystyrene
<i>RTILs</i>	Room Temperature Ionic Liquids
<i>scCO₂</i>	Super Critic Carbon Dioxide
<i>SILP</i>	Supported Ionic Liquid Phase
<i>SILs</i>	Supported Ionic Liquids
<i>TBAB</i>	Tetrabutylammonium Bromide
<i>TBD</i>	1,5,7-triazabicyclo[4,4,0]-dec-5-ene
<i>TBHP</i>	tert-Butylhydroperoxide
TGA	Thermogravimetric Analyses
<i>TOF</i>	Turnover Frequence
<i>TON</i>	Turnover Number
<i>UHP</i>	Urea Hydrogen Peroxide

1. IONIC LIQUIDS

Ionic liquids (ILs) are defined as pure compounds, consisting only of cations and anions (i.e., salts), which melt at or below 100 °C (Wasserscheid and Keim, 2000). Many ILs are liquid at 25 °C (and are occasionally named room temperature ionic liquids or RTILs). Structures and for commonly studying cations and anions are given in Scheme 1.1.



Scheme 1.1. Main cations and anions for ILs described in literature.

Besides their advantages with respect to environmental impact, ILs have an interesting medium for chemical synthesis due to their some properties. The large number of cations and anions permit a wide range of physical and chemical properties to be accomplished, including volatile and involatile systems, and as a result the terms “designer” and “task-specific” ILs have been developed (Paczal and Kotschy, 2007; Binnemans, 2007; Han and Armstrong, 2007). This enables both control over processing of the reaction and control over solvent-solute interactions. The other important aspect that these solvents are ionic and highly structured.

There is a comparison of organic solvents and ILs in Table 1.1 (Plechkovaa and Seddon, 2008)

Table 1.1. Comparison of organic solvents with ionic liquids

Property	Organic solvents	Ionic liquids
<i>Number of solvents</i>	>1000	>1,000,000
<i>Applicability</i>	Single function	Multi function
<i>Catalytic ability</i>	Rare	Common and tuneable
<i>Chirality</i>	Rare	Common and tuneable
<i>Solvation</i>	Weakly solvating	Strongly solvating
<i>Tuneability</i>	Limited range of solvents available	Virtually unlimited range means "designer solvents"
<i>Recyclability</i>	Green imperative	Economic imperative
<i>Flammability</i>	Usually flammable	Usually nonflammable
<i>Polarity</i>	Conventional polarity concepts apply	Polarity concept questionable
<i>Vapour pressure</i>	Obeys Classius-Clapeyron equation	Negligible vapour pressure under normal conditions
<i>Viscosity(cP)</i>	0.2-100	22-40,000
<i>Density(gcm⁻³)</i>	0.6-1.7	0.8-3.3
<i>Refractive index</i>	1.3-1.6	1.5-2.2
<i>Cost</i>	Normally cheap	Typically between 2 and 100 times the cost of organic solvents

1.1 Properties of ILs

Considering the broad range of ILs and applications (Majewski et al., 2003), it is hard to generalise their properties and to report general tendencies. Only a list of their important properties is mentioned below:

Melting point: Melting point of many ILs may be indefinite because they can undergo supercooling and have impurities (Olivier-Bourbigou et al., 2010).

Volatility: For typical ILs, normal boiling temperatures (T_b), which correlate with their vapour pressure at 1 atmosphere, cannot be experimentally determined since they decompose before T_b . It has nevertheless been reported that ILs can be distilled at 200–300 °C but under significantly reduced pressure and at very low distillation rate ($<0.01 \text{ g h}^{-1}$) (Earle et al., 2006). The ionic nature (or ionicity) of ILs can partially explain their negligible vapour pressure in the liquid state, which separates them from molecular solvents. (Tokuda et al., 2006)

Non flammability: Main interest of ILs has been focused on their possible use as “green” alternatives to volatile organic solvents, because of considering ILs as non-volatile and accordingly non-flammable at ambient and higher temperatures. The main interest area for ILs has been centered on their potential usage. For

instance they can be fine-tuned for energetic content and substitute for hydrazine and its derivatives (Smiglak et al., 2006; Schneider et al., 2008)

Thermal and chemical stability: Many ILs indicate high thermal stability measuring with thermogravimetric analyses (TGA), a thermal decomposition generally occurs over 350 °C. However, lower values are found for long-term stability which is important to deliberate when ILs are used in catalytic processes. Phosphonium ILs with $[\text{NTf}_2]^-$ or $[\text{N}(\text{CN})_2]^-$ anions decompose completely to volatile products in a single step. Inversely, ILs based on nitrogen cations do not decompose completely (cyano groups are prone to polymerization) (Bhatt et al., 2006).

Conductivity and electrochemical window: ILs conductivity is an interesting property because of their dual role of solvent and electrolyte in electrochemical reactions. ILs have broad range of conductivities between 0.1 and 20 mS cm^{-1} . Usually higher conductivities are reported for imidazolium-based ILs in comparison with the ammonium ones. Many factors such as viscosity, density, ion size, anionic charge delocalization, aggregations and ionic motions can influence their conductivity (Hapiot and Lagrost, 2008). On the subject of their electrochemical window, it is typically measured in the range 4.5–5 V, which is similar to conventional organic solvents, but larger than aqueous electrolytes. In reduction reactions, quaternary ammonium is generally more stable than imidazolium which can occur the formation of N-heterocyclic carbenes.

Density: ILs are generally denser than either organic solvents or water, with typical density values ranging from 1 to 1.6 g cm^{-3} . Jacquemin et al. has also been modelled the density of ionic liquids correlating with temperature and pressure (Jacquemin et al., 2008). A noticeable amount of data on the density of ILs have been reported in the literature (Mantz et al., 2005).

Viscosity: In the view of engineering, the viscosity of ILs is important for transport properties such as diffusion and may be a subject in catalytic applications. It plays a major role in stirring, mixing and pumping operations. The viscosity of many ILs is relatively high compared to conventional solvents, one to three orders of magnitude higher. In ambient conditions viscosity range of ILs are between 66 and 1110 cP (Fröba et al., 2008).

Polarity: The polarity is one of the most important properties for characterizing the solvent effect in chemical reactions (Chiappe et al., 2009). There is no single parameter and direct measurement that can characterize IL polarity. The difficulty in the case of ILs is to find a suitable soluble probe which measures the polarity parameters as independently as possible of the other influences of the solvent (Reichardt, 2005; Bright and Baker, 2006)

Toxicity and biodegradability (Smiglak et al., 2006; Wang et al., 2007): The first claims ILs could exhibit low toxicity and biodegradability, however their negligible vapour pressure is not realistic. It has been authorized that commonly used ionic liquids are not easily biodegradable.

Surface tension: ILs have relatively moderate surface tensions compared to organic solvents (Martino et al., 2006). A screening of some properties such as compressibility has been examined under long-term conditions and under high pressure (Wasserscheid et al., 2007). Figure 1.1 gives a tentative qualitative description of ILs compared to alternative solvents, in terms of polarity and volatility.

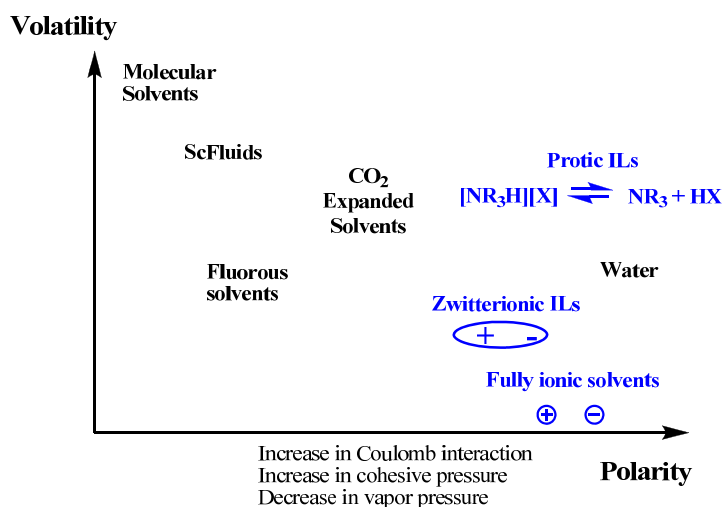


Figure 1.1. Typical polarity and volatility characteristics of alternative solvents

1.2 Evolution of IL Generation

Ionic liquids have attracted rising interest in the last decades with a varied range of applications (Figure. 1.2).

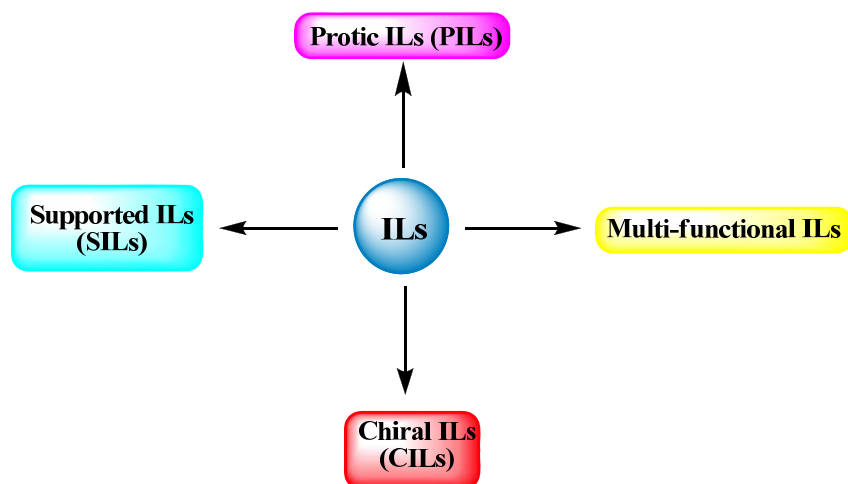
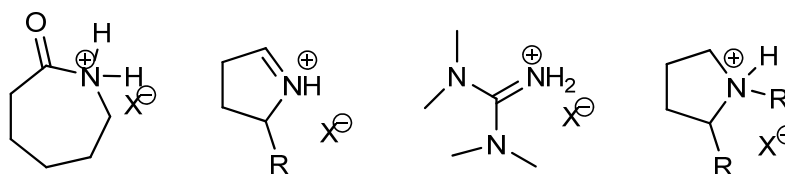


Figure 1.2. Evolution of IL generations.

1.2.1. Protic ionic liquids (PILs)

Protic ILs has been a renewal interest because of their great potential for proton transfer applications in fuel cell technologies. Poole has reported a review in 2004 about the application of protic ILs in chromatography (Poole, 2004). Some of these ILs demonstrate low melting points (well below 100 °C) and high conductivities (over 10^{-2} S cm⁻¹ at 130 °C) (Huang et al., 2006). Protic ILs are formed through direct proton transfer from a Brønsted acid to a base (or a Brønsted base). They represent the advantage of being cost-effective and easy-prepared. Examples of Protic ILs are given in Scheme 1.2 (Fericola et al., 2007; Guo, 2006).

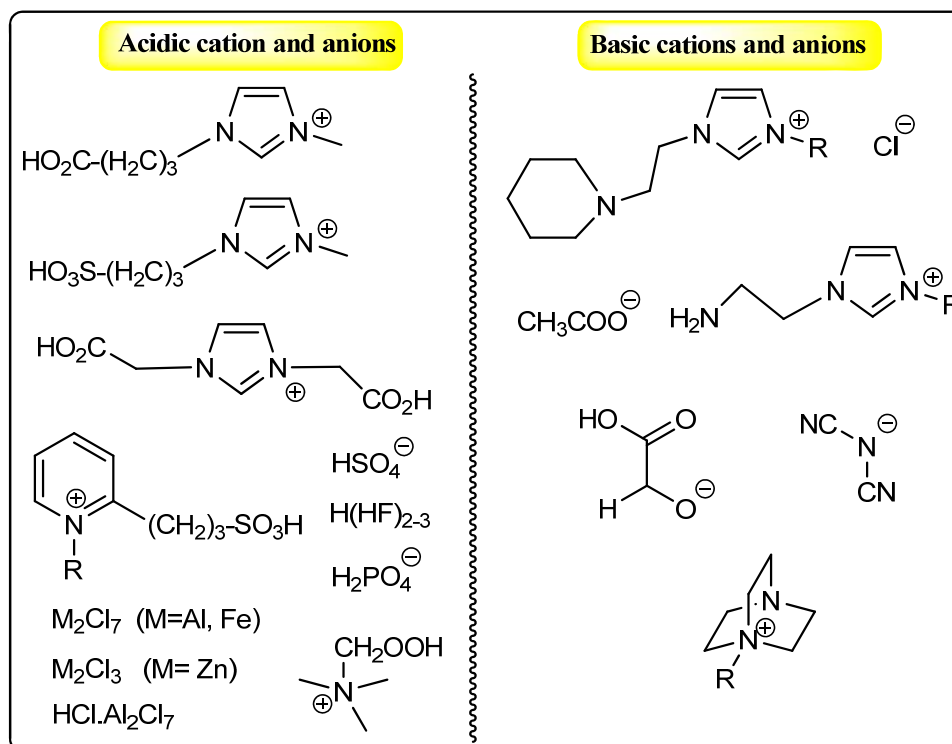


Scheme 1.2. Protic ILs synthesized by direct protonation (X^- =[NTf₂]⁻, [CF₃SO₃]⁻[CF₃CO₂]⁻, [CH₃SO₃]⁻, [HCOO]⁻, [HSO₄]⁻, [H₂PO₃]⁻).

1.2.2. Multi-functional ionic liquids

Acidic and basic ILs define new classes of ILs (Scheme 1.3). Either anion and/or cation could have acidic or basic function (MacFarlane et al., 2006). Owing to their potential Lewis acidity and superacidity in the presence of protons, chloroaluminates have been known for a long time. They have been outspread to

other polynuclear anions that are stable towards moisture (e.g chloroferrate or chlorozincate). Basic ILs have been less developed than acidic ones. Amine organic bases have been fastened to IL cations. Synthesis of basic functional ILs were firstly designed to capture CO₂ (Bates et al., 2002; Zhang et al., 2006).

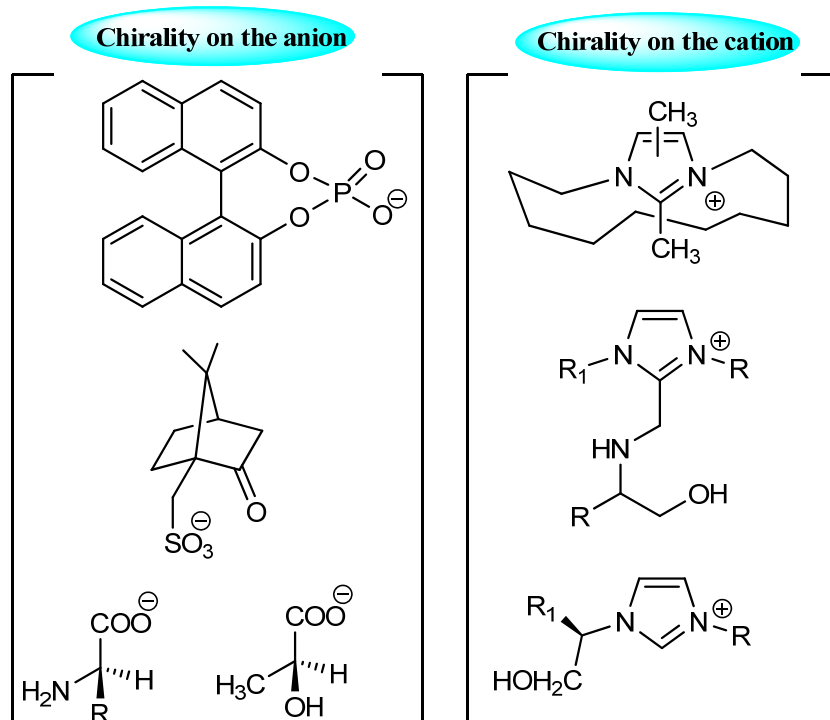


Scheme 1.3. Acidic and basic ILs.

1.2.3. Chiral ILs (CILs)

The source of chirality can be located either on the cation, on the anion or both on anion and cation (Scheme 1.4).

A great majority of CILs have been synthesized based on chiral aminoacids anions and ammonium, imidazolium and phosphonium cations (Ohno and Fukumoto, 2006; 2007). In conjunction with imidazolium, guanidinium cations a new family of chiral ILs based on natural chiral anions have been prepared. The applications of these CILs are not only asymmetric catalysis, and also spectroscopic and chromatographic areas. In asymmetric synthesis, it is often believed that CILs can be used as chiral solvents and as inducer of chirality due to their polymer-like behaviour and potential high degree of organisation. However, very few results are reported exhibiting a potential.



Scheme 1.4 Examples of chiral ILs.

1.2.4. Supported ILs (SILs)

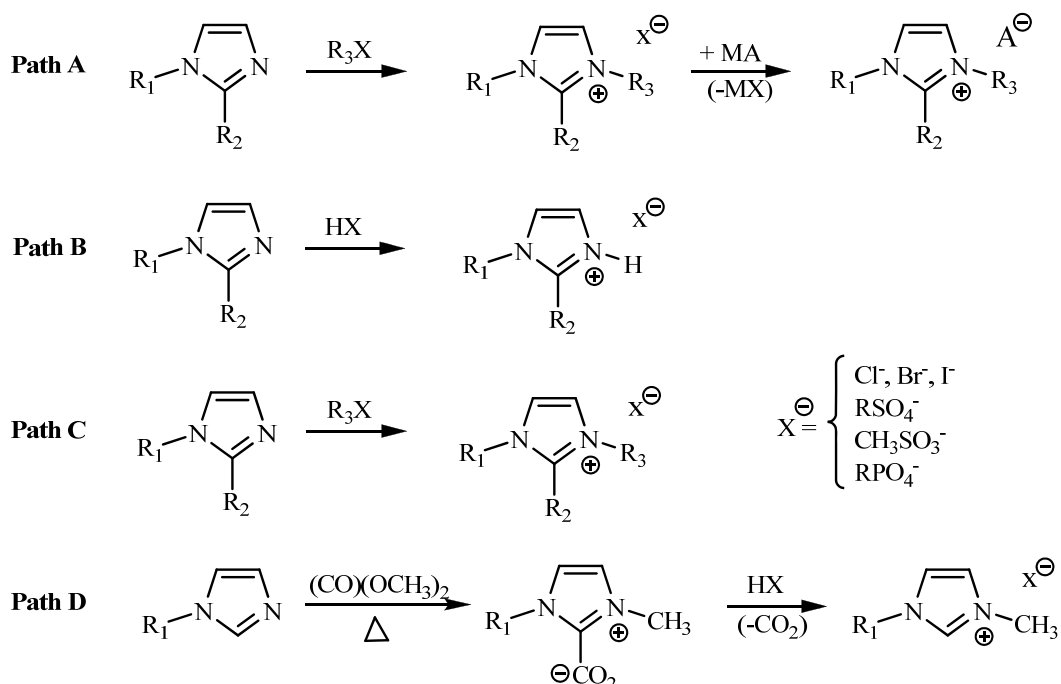
For application of ionic liquids to fixed-bed reactors, to solve mass transport limitation of viscous ILs and to enable catalyst separation and recycling ionic liquids had been supported onto high surface area supports (Riisager et al., 2003; 2006). The use of SILs in catalysis has been reviewed recently Friedel–Crafts reactions, hydroformylations (Rh-catalysed), hydrogenation (Rh-catalysed), Heck reactions (Pd-catalysed), and hydroaminations (Rh-, Pd-, and Zn-catalysed) (Mehnert, 2005; deCastro et al., 2000; Mehnert et al., 2002a; 2002b; Hagiwara et al., 2004; Breitenlechner et al., 2004).

1.3 Preparation of ILs

Different routes for the synthesis of ILs are described, each of them having advantages and disadvantages (Scheme 1.5):

(1) *Metathetic exchange of anion (path A)*: This is possibly the most used pathway for the synthesis of ILs. The production of alkylimidazole is industrial. In the metathetic exchange of anions, halide by-products (MX) are produced which could be difficult to remove by filtration remarkably for hydrophilic ILs.

(2) *Neutralization of base with Brønsted acids (path B) or direct alkylation of alkylimidazole (path C)*: This route worthwhile because it prevents the presence of halide (atom efficiency). Nonetheless, while direct reaction of Brønsted acid (HX), it may be difficult to get ILs with high purity. The final ILs may be conclude traces of alkylimidazole or acid. The alkylation reaction is limited to the reactivity and availability of the alkylating agents. This method has been outlined for the preparation of sulfate, phosphate or sulfonate based ILs.



Scheme 1.5 General route for ILs synthesis: (path A) metathetic exchange of anion, (path B) neutralisation of base with Brønsted acids, (path C) direct alkylation of alkylimidazole, (path D) the carbonate method.

(3) *The carbonate route (path D)*: The use of dimethylcarbonate (DMC) as a clean methylating agent to replace alkyl halides has verified to be a new interesting route to obviate formation of halide and other by-products (Smiglak et al., 2007).

1.4 Structure and self-organisation of ILs

Solvents are usually qualified by macroscopic physical constants (“bulk properties”) such as density, vapour pressure, surface tension, boiling point, cohesive pressure, refractive index, relative permittivity or (“dielectric constants”). In Figure 1.3, a normalized solvent polarity scale is illustrated for conventional solvents and ILs.

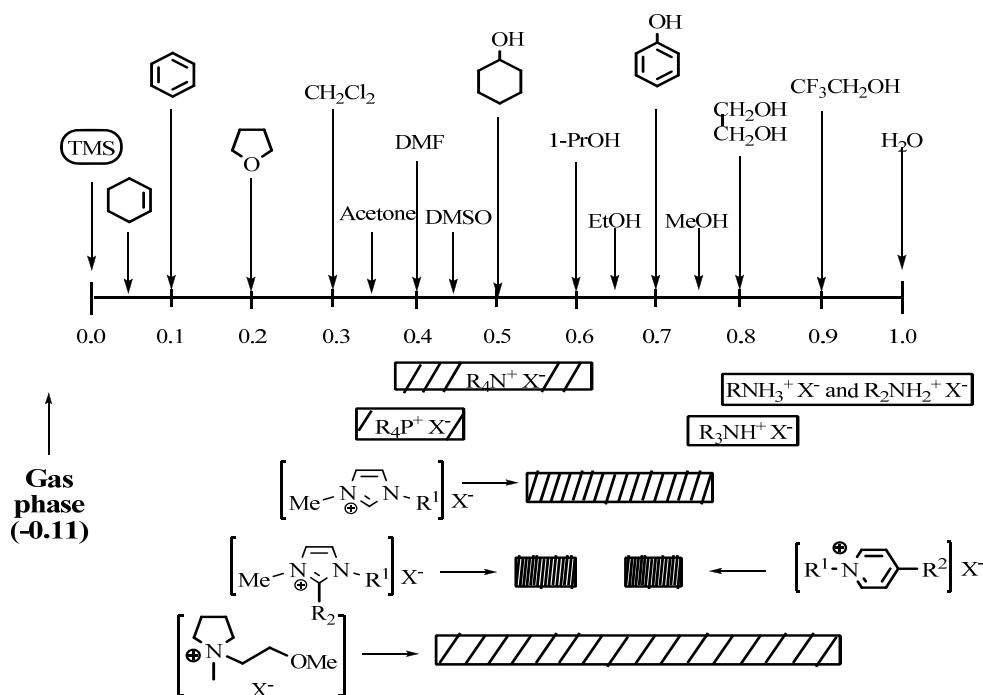
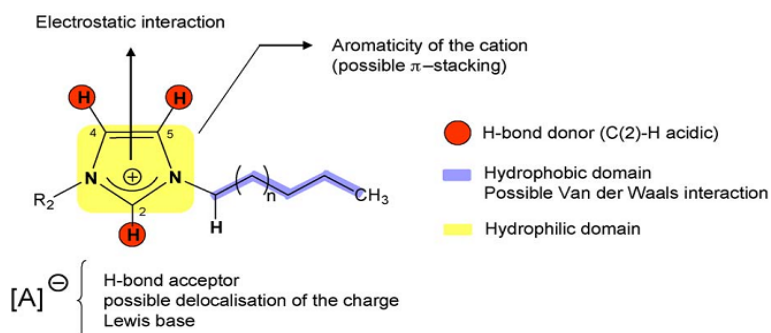


Figure 1.3. Normalised solvent polarity scale

Between the ions, there are coulombic and molecular interactions (such as H bonding, π - π stacking, van der Waals interactions). Coulombic interactions are the dominant one. For the comparison the strength of the different energies: the energy of H-bonds are generally around 40 kJ/mol (for water), the van der Waals forces around 40 kJ/mol (for n-pentane), whereas coulombic interactions (ion/ion) in ILs can be up to 600 kJ/mol (Reichardt, 2005).

For imidazolium based ILs, probable interactions is drawn in Scheme 1.6.



Scheme 1.6 Schematic representation of the different type of interactions present in imidazolium based ILs (Reichardt, 2005).

1.5 Catalysis via ILs

Catalytic reactions in ionic liquids (ILs) have been studied for at least 20 years; for example in 1986, for the first time the use of an IL as a catalyst in Friedel-Crafts acylation was reported. By the way, in the past decade number of publication increased rapidly in their usage of catalytic and stoichiometric reactions and other applications (Pervulescu and Hardacre, 2007).

In chemical industry, molecular catalysis is widely applied as for example in metathesis, oxidation, oligomerisation, hydroformylation carbonylation, and hydrocyanation. However, usage of homogeneous counterpart is limited (e.g. hydroformylation, hydrocyanation). Nonetheless, homogeneous catalysis have advantages of high selectivity and activity, the separation and recycling of the catalyst suffer it. Therefore, there is a need for systems that can associate the advantages of homogeneous catalysis with straightforward separation, recovery and reuse of the catalyst (Baker, 2006). In this point ILs have proved a new area which have been used immobilization strategies for the roles such as “liquid supports” in multiphase catalysis or in heterogeneous systems (SILP).

1.5.1 Multiphasic IL systems

In homogeneous catalysis, the catalyst separation and reuse are important problems. The recycling can be performed by chemical transformation or by direct distillation, depending on the catalyst and its stability. Its recycling can also be manipulated using a biphasic liquid/liquid system (Cornils et al., 2005).

In the case of working with the ILs, the ideal situation is obtained when the IL displays partial miscibility with the substrates and when the products have trivial miscibility with the IL (Figure 1.4). Separation is then acquired by decantation, thus the process scheme gets easier and the threats of catalyst decomposition restricts during distillation.

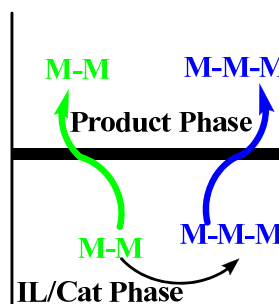


Figure 1.4. The IL-liquid/liquid-biphase concept (M = monomer, M-M= dimer, M-M-M = trimer).

To extract the reaction products using a co-solvent poorly miscible with the IL (water or organic solvent) decreases the whole simplification of the reuse and avoid contaminating the IL. The use of supercritical fluids in particular CO_2 (scCO_2) demonstrated to be an interesting alternative to common organic solvent because of its nontoxic nature, recoverability and ease of separation (Figure 1.5). ScCO_2 dissolves quite well in ILs while ILs cannot dissolve in scCO_2 , which provides ILs recycling without product contamination. The first report using continuous-flow catalytic systems based on the combination of IL $[\text{BMI}][\text{PF}_6]$ and scCO_2 was published in 2001 for Rh-catalysed 1-octene hydroformylation using ionic phosphine (Sellin et al., 2001). ILs/ scCO_2 system has been extended to other reactions such as hydrogenation, hydrovinylation, as well as to bio-catalysed reactions (Damen et al., 2009; Jessop et al., 2003; Bösmann et al., 2001; Reetz et al., 2003).

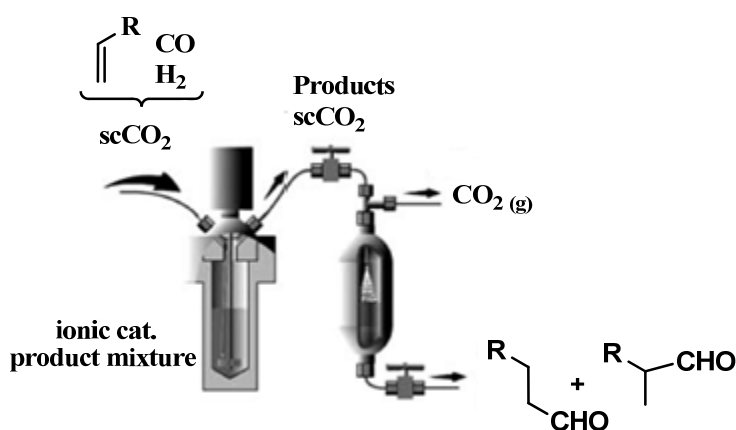


Figure 1.5. Continuous flow homogeneous catalysis using a supercritical fluid–ionic liquid biphasic system

1.5.2 Supported ionic liquid phase system (SILP)

In parallel to the improvement of ILs for multiphasic catalysis, immobilization strategies of ILs onto a solid support have been addressed. This concept was developed, in the meantime to diminish the amount of expensive ILs and to give an opportunity for application of ILs in continuous-flow-operated fixed-bed processing.

Acidic chloroaluminates were first supported on solid inorganic material (Figure 1.6). The immobilization of the IL was performed by the addition of a pre-formed chloroaluminate IL to a support which was dried and calcinated at 500 °C for 3 h. The excess of IL on the support was then extracted with dichloromethane (Webb et al., 2005). In continuous mode, some catalyst deactivation observed when the supported IL system was operated. It is assumed to be the effect of heavy products that block the active sites of the solid material from further reaction, and as a result of this deactivation, loss of conversion with time observed.

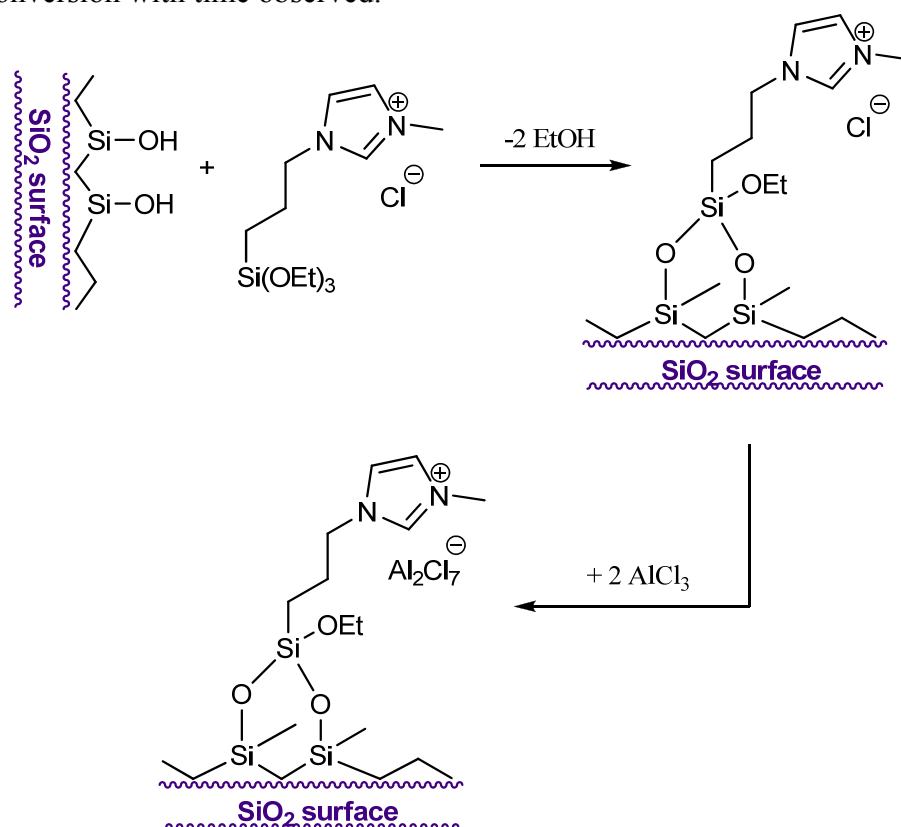


Figure 1.6. Preparation of acidic IL anchored on silica

In 2002, C. P. Mehnert at ExxonMobil used a similar approach for olefin hydroformylation. For the immobilization they used a support material (silica gel) that is modified with a monolayer of covalently anchored fragments of 1-n-butyl-3-[3-(triethoxysilanyl)propyl]-4,5-dihydroimidazolium. After the treatment of this surface with additional ionic liquid, formation of a multiple layer of free ionic liquid occurred (Figure 1.7).

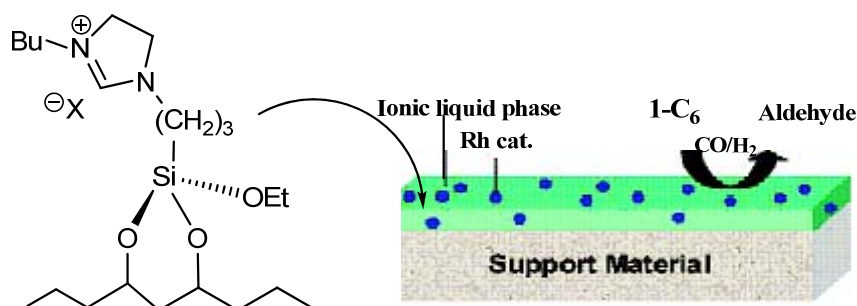


Figure 1.7. Supported Ionic Liquid Phase (SILP) catalysis concept for olefin hydroformylation.

In the study of Gadenne, hybrid organic–inorganic silica materials including covalently bonded imidazolium and Si–C covalently bonded moiety have been synthesised according to conventional sol–gel procedures in the presence of a surfactant and tetraethylorthosilicate (Gadenne et al., 2004)

Instead of silica, other supports, especially the use of a polystyrene functionalised resins was also investigated (Kim et al., 2006). These supported ILs were prepared by Merrifield resins. These types ILs have many opportunities for change the structure such as the derivation of the linker length, the loading level of the IL portion and the nature of the IL anion (Figure 1.8).

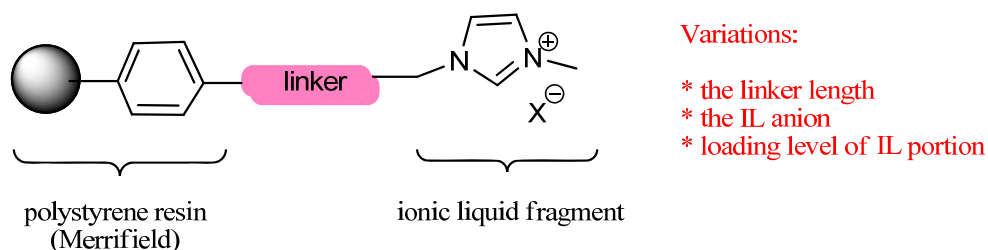


Figure 1.8. Polystyrene supported ionic liquids (PSIL)

Poly(ethylene glycol) (PEG) polymers have received rising interest as a reusable solvent medium for organic synthesis and catalytic process. The

combination of PEG with ILs was fulfilled by the synthesis of PEG-functionalised ILs (Fraga-Dubreuil et al., 2002).

1.5.3 Phase transfer catalysis

One of the essential roles of classical phase transfer catalyst is to displace an inorganic reagent from the aqueous phase into the organic phase, thus enabling the organic substrate to react with the transferred anion and form the product in the organic phase reaction (Figure 1.9). a [BMIm][PF₆]/water biphasic system was reported by Wang for the phase transfer epoxidation of electron-deficient α/β unsaturated carbonyl compounds (Zhang, 2006; , Wang et al., 2003). Under the mild conditions, the [BMIm][PF₆]/water system was more efficient than the traditional CH₂Cl₂/water system. By optimising the reaction conditions, including temperature, reaction time, the amount of oxidant and sodium hydroxide, 100% conversion and 98% selectivity could be succeeded in the epoxidation of mesityl oxide.

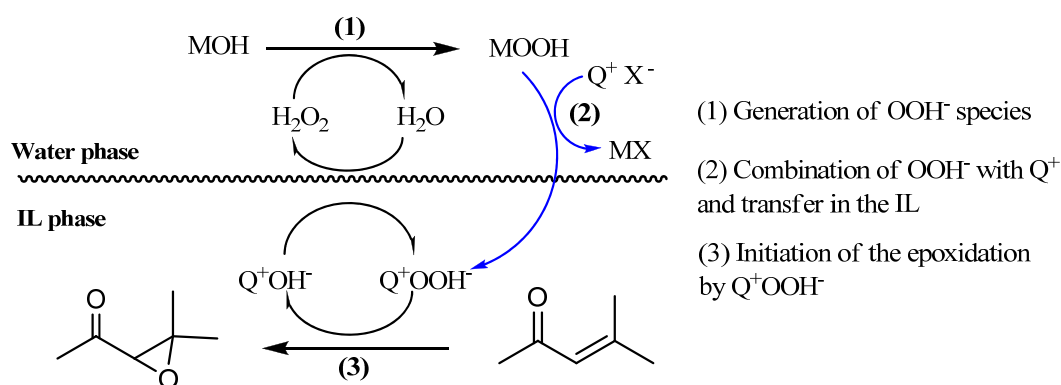


Figure 1.9. Mass transfer model for epoxidation in [BMI][PF₆]/water PTC system (Q = dialkylimidazolium cation; M = sodium; X = hexafluorophosphate anion)

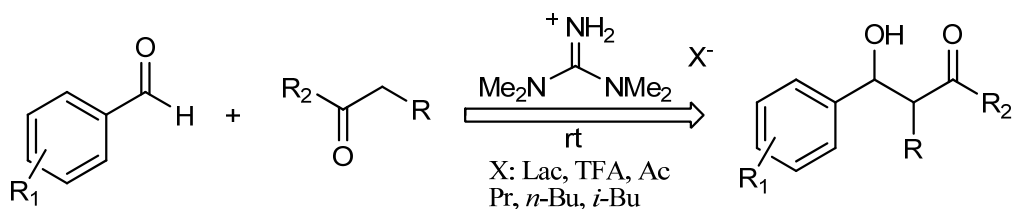
1.5.4 Chemical reactions catalyzed directly by ionic liquids

Usage of acidic or basic ILs in chemical reactions is an interesting topic, due to ILs' dual role as solvent and catalyst. In this part, some of the examples utilizing ILs as catalyst have been mentioned (Jiang and Han, 2009).

1.5.4.1 Direct Aldol reaction

Aldol reactions are effective C-C bond forming reactions and the products of β -hydroxy ketones are usually found in complex polyol structures of natural

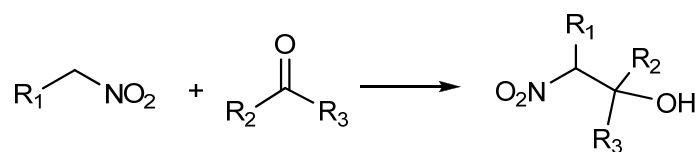
products. These reactions have been investigated extensively. organic or inorganic bases can be used for Aldol reactions. Studying by inorganic bases are not desired due to the fact that control of the reaction is serious drawback and the dehydration of the product is frequently unavoidable. Zhu et al examined basic guanidine based IL to catalyze aldol reaction in solventless conditions (Zhu et al, 2006) (Scheme 1.7).



Scheme 1.7 Aldol reaction catalyzed by basic ILs

1.5.4.2 Henry reaction

The most useful carbon-carbon bond forming reaction is Henry reaction that has wide synthetic applications in organic synthesis. In the presence of a basic catalyst, the treatment of nitroalkanes and carbonyl derivatives results the formation 2-nitroalcohols (Scheme 1.8). different types of catalysts can be applied for Henry reactions such as organic and inorganic bases, quaternary ammonium salts, etc. Utilization [TMG][Lac] (1,1,3,3- tetramethylguanidinium lactate) as a catalyst in Henry reaction proved advantages of studying under milder reaction condition and shorter reaction time (Jiang et al., 2004).

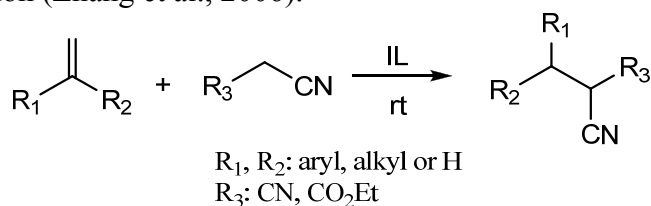


Scheme 1.8 Henry reaction

1.5.4.3 Knoevenagel condensation

The Knoevenagel condensation reaction is an effective C=C formation reaction between carbonyl or heterocarbonyl compounds and any compound having an active methylene group (Scheme 1.9). This reaction is widely used in the preparation of natural products, functional polymers, fine chemicals, etc. Generally, the reaction is performed in the presence of bases, such as piperidine,

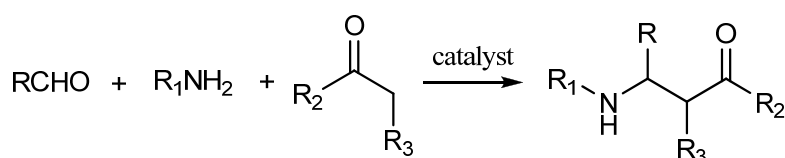
pyridine or their salts. Some researchers have used ILs as the catalysts in Knoevenagel reaction (Zhang et al., 2006).



Scheme 1.9 Knoevenagel condensation reaction

1.5.4.4. Mannich reaction

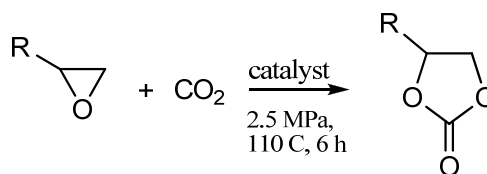
Mannich reaction provides one of the most basic and useful methods for the synthesis of natural molecules, pharmaceuticals and other nitrogenous biologically active compounds. In such a reaction, an amine, two carbonyl compounds and acid (or base) catalysts are used to produce beta-amino-carbonyl compounds (Scheme 1.10). The acid catalysts usually used involve organic and mineral acids. As ionic liquid, acidic compounds such as 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim][HSO₄]), 1-butyl-3-methylimidazolium dihydrogen phosphate ([Bmim][H₂PO₄]), 1-methylimidazolium trifluoroacetic acid ([Hmim][Tfa]) was operated in the literature (Zhao et al., 2004). [Hmim][Tfa] showed the highest catalytic activity (yield 83%).



Scheme 1.10 Mannich reaction

1.5.4.5 Synthesis of cyclic carbonates from carbon dioxide and epoxides

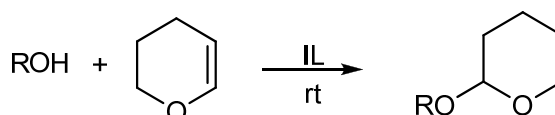
Conversion of CO₂ to useful chemicals and intermediates is of significance but is still a challenge. The formation of cyclic carbonates via cycloaddition of CO₂ with epoxides (Scheme 1.11) is one of the attractive routes for chemical fixation of CO₂. As discussed in Section 2.2.3 for the first time, Peng and Deng has used ILs in this reaction process (Peng and Deng, 2001).



Scheme 1.11 Cycloaddition reaction of CO₂ and terminal epoxides.

1.5.4.6 Tetrahydropyranilation reaction

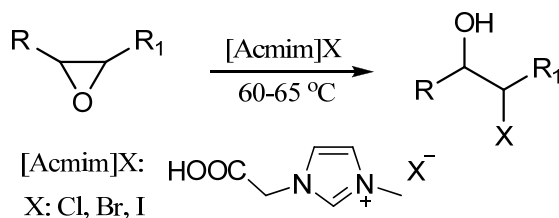
The tetrahydropyranilation of a variety of alcohols has been carried out in a series of Brønsted-acidic ionic liquids (Scheme 1.12). The best results were obtained with [Hmim][BF₄] and [Hmim][TSO] (Duan et al., 2005)



Scheme 1.12 Tetrahydropyranilation reaction

1.5.4.7 Conversion of epoxides to halohydrins

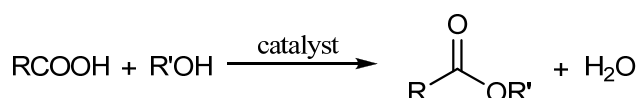
The generation of halohydrins from epoxides may be achieved with ionic liquids such as in Scheme 1.13. The method is quite versatile and a wide variety of epoxides can be converted to the corresponding halohydrin in good yields (Ranu and Banerjee, 2005).



Scheme 1.13 Halohydrin formation from epoxides

1.5.4.8 Esterification reaction

Carboxylic esters as important intermediates for the synthesis of dopes, adhesives, flavors, pharmaceuticals and plasticizers had attracted much attention. Generally as illustrated in Scheme 1.14 they were synthesized by Fischer esterification of carboxylic acids and alcohols (Otera, 2001). Recently PS-supported acidic ionic liquid catalyst PS-CH₂-[SO₃H-pIM][HSO₄] was used for the synthesis of carboxylic esters and achieved high catalytic activity (Xu et al, 2010).



Scheme 1.14 Esterification reaction via alcohol and acid.

1.6 Industrial Applications of ILs

The patents (and publications) often describe numerous applications such as catalysis with increased rates and yields, recovery of catalytic systems, use of ILs as solvents that can reduce environmental impacts and that lead to more energy-efficient separation. ILs are novel solutions to the chemical industry. By the way, despite these significant advantages, their translation into viable industrial processes is far from being apparent and the industrialization of IL technologies is rather slow, notably in the field of catalysis. For the industrial application of ILs, some major points must be covered such as IL synthesis scale-up, purity, stability, toxicity, recycling, saving and price. Selected examples of industrial scale applications of ILs are summarized below.

1.6.1 Dimerization and oligomerisation of olefins

1.6.1.1 The Difasol process (IFP (Institut Français du Pétrole)–Axens)

The Dimersol-XTM fabricates mixtures of low branched octenes which are good starting materials for isononanol production (intermediates in the plasticizer industry). Using a Ziegler-type catalyst based on nickel and activated with an alkyl-aluminium co-catalyst the reaction is performed without a solvent in a single liquid phase (Chauvin et al., 2000). The DifasolTM process can be evaluated as the

biphasic analogue of the Dimersol-XTM process (Figure 1.10). With the same Ni catalyst precursor and chloroaluminate ionic liquids as the solvent reaction takes place (Eq. (1)). When connected with a chloroalkylaluminium activator like EtAlCl₂, the mixture can react to form ionic liquids having mixed anions (Eq. (2)) (Gilbert et al., 2007; 1991). The ionic liquid can then act as both solvent and co-catalyst (Eq. (3)). The best results were succeeded from [BMI][Cl]/AlCl₃/EtAlCl₂ (1:1.2:0.11) mixtures.

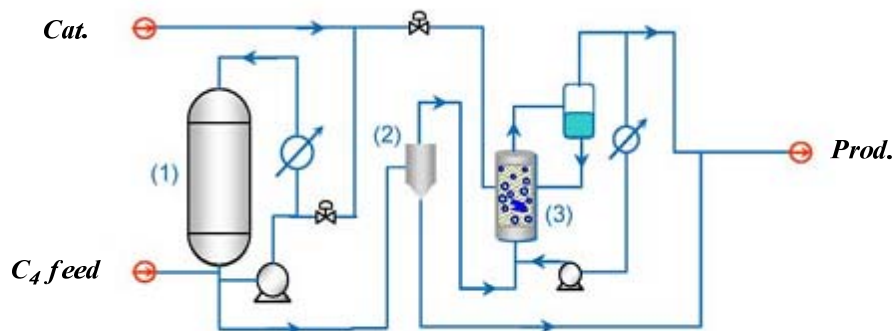
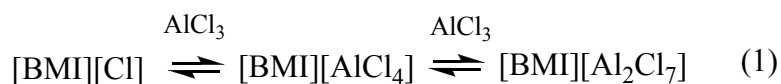


Figure 1.10. Dimersol + Difasol package reaction: (1) Dimersol reactor(s), (2) Vaporisation–condensation, (3) Difasol reactor.

The main DifasolTM advantages can be concluded as follows;

- the total yield can be 10% higher than in the homogeneous process in C8 octenes;
- the nickel consumption is less than in the homogeneous process;
- no ionic liquid contamination can be noticed in the products;

1.6.1.2 Oligomerisation of olefins for synthetic lubricants production

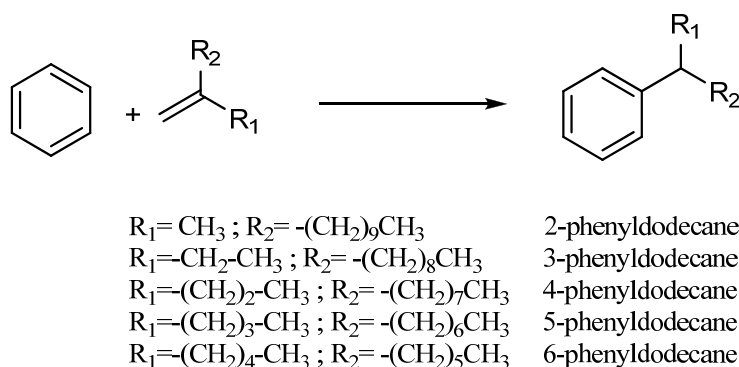
Synthetic lubricating oil base stocks which have desirable lubricating properties such as a low pour point and a high viscosity index could be prepared by oligomerization of α -olefins. In 1997, BP Chemicals developed a process for the oligomerisation of a mixture of α -olefins (typically C6-C10) using acidic ionic liquids (Atkins et al., 1997). [EMI][Cl]/AlCl₃ in a 1:2 molar ratio is used. Chevron company also performed [HNMe₃][Cl]/AlCl₃ in a 1:2 molar ratio at a pilot scale

starting from 1-decene and produced commercial amounts of over 450 tons of polyalphaolefins (Maase et al., 2008).

1.6.2 Friedel-Crafts alkylation and acylation of aromatic hydrocarbons

1.6.2.1 LAB production

In the industrial application it is successfully established that alkylation of benzene with linear olefins (C10–C14) (Scheme 1.15). The produced linear alkylbenzenes (LABs) are employed as intermediates in the production of surfactants and detergents. In the traditional processes used acid catalysts (such as AlCl_3 and HF) have some issues such as poor catalyst separation and recycling.



Scheme 1.15. LAB production.

Akzo-Nobel company improved specific ILs based on triethylamine hydrochloride and aluminium chloride ($2\text{AlCl}_3 + [\text{HNMe}_3][\text{Cl}] \rightleftharpoons [\text{HNMe}_3][\text{Al}_2\text{Cl}_7]$). As a cheaper alternative to imidazolium-based salts and applicability in a similar manner these ILs can be good candidates (Hope et al., 2004). Their special application is the alkylation of benzene with 1-dodecene (Sherif et al., 1998). The higher 2-dodecylbenzene yields were taken with the IL than the standart HF process. In this process, in view of biodegradability of the compounds, linearity of the alkylbenzenes is an important parameter.

1.6.2.2 Friedel-Crafts acylation of aromatic hydrocarbons

ILs have been largely known as catalyst-solvents or solvents to operate acylation reactions (Liu et al., 2009). Using ILs have some advantages, the mains are increased reaction rates, conversion and higher selectivity. Owing to high

solvation properties of ILs, reactants can be soluble which can diminish the number of steps in synthesis.

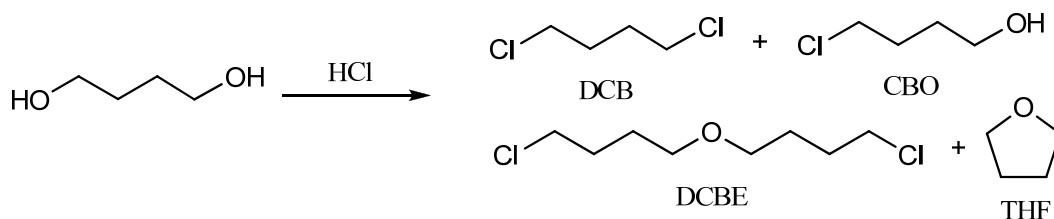
1.6.3 Alkylation of olefins with isobutane: IL as solvent and acid catalyst

Isobutane alkylation is one of the most significant processes for producing reformulated gasoline. In commercial alkylation plants, either sulphuric acid or hydrogen fluoride is used as catalyst. Both of them suffer from some restrictions considering productivity, safety factors, alkylation quality and operating costs (Albright, 1990; Olivier-Bourbigou et al., 2005b). IFP utilized acidic chloroaluminates for the alkylation of isobutane with 2-butene or ethylene (Chauvin et al., 1994). Petrochina evolved a process called “Ionikylation” for the alkylation reaction (Liu et al., 2006). The ionic liquid used including a mixture of chloroaluminate-IL with CuCl. During the pilot test period, olefin conversion was more than 99%. This retrofit increased both the yield of the process (compared to sulfuric acid), and the process units capacity by 40% (to 248 tonnes per day).

1.6.4 Chlorination and fluorination reactions

1.6.4.1 Chlorination.

For safety aspects, the substitution of phosgene is a subject of major interest. In 2005, BASF described the chlorination of diols (ex: 1,4-butanediol, Scheme 1.16 using HCl as the chlorinated agent in conjunction of an IL (Stegmann and Massonne, 2005). When compared with direct chlorination of diol with HCl, the IL system gives virtually pure 1,4-dichlorobutane (98% selectivity). In the presence of IL, it appears enhancing HCl reactivity. Additionally, meanwhile the reaction continues, the initial homogeneous single phase system (butanediol wholly soluble in the IL) changes through a biphasic mixture as formation of the 1,4-dichlorobutane in the upper phase. The product separation and recycling can be easier with this process.



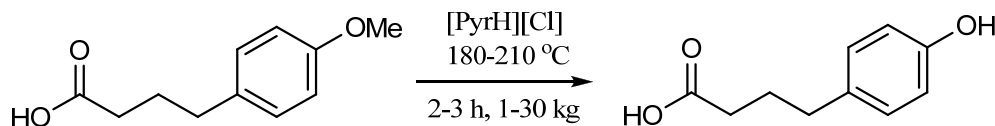
Scheme 1.16. Chlorination of 1,4-butanediol

1.6.4.2 The liquid-phase HF fluorination

Chlorofluorocarbons, still used as refrigerants in the air-conditioning and refrigeration industry, will have to be put in place of chloride-free hydrofluorocarbons (HFCs). These HFCs can be synthesized by reaction of chlorinated hydrocarbons with HF through an acid catalysed reaction. The acid catalysts usually used for this chlorine/fluorine substitution are super acids based on antimony Lewis acid, such as SbX_5 ($\text{X} = \text{F}$ or Cl) connected with Brønsted acids. Nevertheless, these catalytic systems suffer from a reductive deactivation with formation of Sb(III) species. In industrial processes, this drawback can be defeated by the addition of Cl_2 in order to re-oxidize Sb(III) , but this leads to a significant reduction of the yield in the desired products due to back chlorination of the fluorinated products. Arkema company used ILs based on $[\text{SbF}_6]^-$ anion at a pilot reactor as liquid catalyst phase in presence of HF (Bonnet et al., 2001). The pilot reaction has been performing more than 400 h for the liquid fluorination of trichloroethylene, this process also demonstrates exceptional selectivities (99.5% for 1,2-dichloro-2,2-difluoroethane and 1-chloro-2,2,2-trifluoroethane) without any observable deactivation.

1.6.5 Ether cleavage

In the report of Eli Lilly company, they used pyridinium hydrochloride $[\text{PyrH}][\text{Cl}]$ as IL for the demethylation of 4-methoxyphenylbutyric acid (Scheme 1.17), a key feedstock for the synthesis of a medicine (LY518674) (Schmid et al., 2004). For preclinical evaluation, by kilograms of this compound are needed. It has no use for the classical demethylation reactants (BBr_3 , $\text{BBr}_3/\text{Me}_2\text{S}$, BCl_3 and many others) each of them having undesirable features.



Scheme 1.17 Demethylation of 4-methoxyphenylbutyric acid.

1.6.6 Acid scavenging

Alkoxyphenylphosphines are recognized as important crude materials for the manufacture of photo-initiators substances (BASF's Lucirines). The reaction of chlorophenylphosphines with alcohols gives alkoxyphenylphosphines. In the

original process, triethylamine was used to clean the acid that was formed during reaction progress, but this made the reaction mixture difficult to handle as the waste by-product, insoluble and dense triethylammonium chloride formed. Replacing triethylamine with 1-methylimidazole results in the formation of 1-methylimidazolium chloride, an ionic liquid, which separates out of the reaction mixture as a individual phase (Freemantle, 2003; Rogers and Seddon, 2003) (Figure 1.11). In this new process, much smaller reactor is used than the initial process; the space-time yield is increased from $8 \text{ kg m}^3 \text{ h}^{-1}$ to $690,000 \text{ kg m}^3 \text{ h}^{-1}$, and the yield increased from 50% to 98%. This reaction process has been carried out at a multi-ton scale.

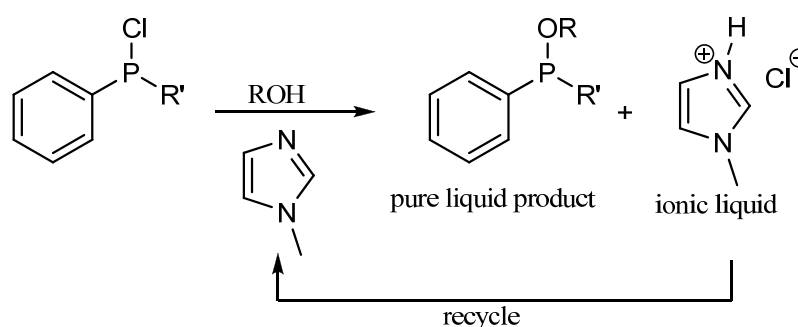
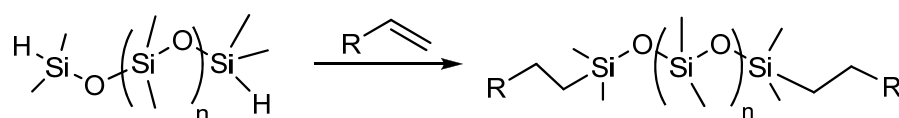


Figure 1.11. The BASIL™ process.

1.6.7 Hydrosilylation: IL as solvent and nanoparticle stabiliser



Scheme 1.18 Hydrosilylation of polydimethylsiloxane

The hydrosilylation reaction is usually operated in a single phase homogeneous system (Scheme 1.18). As a result, catalyst and product separation problem is ongoing. To overtake this restriction, Degussa innovated the use of ionic liquid as a way for catalyst heterogenisation (Weyershausen et al., 2005a; 2005b; 2005c). The catalyst (ionic) is dissolved in the ionic liquid in which the product is insoluble thus it has not observed any leaching (Figure 1.12).

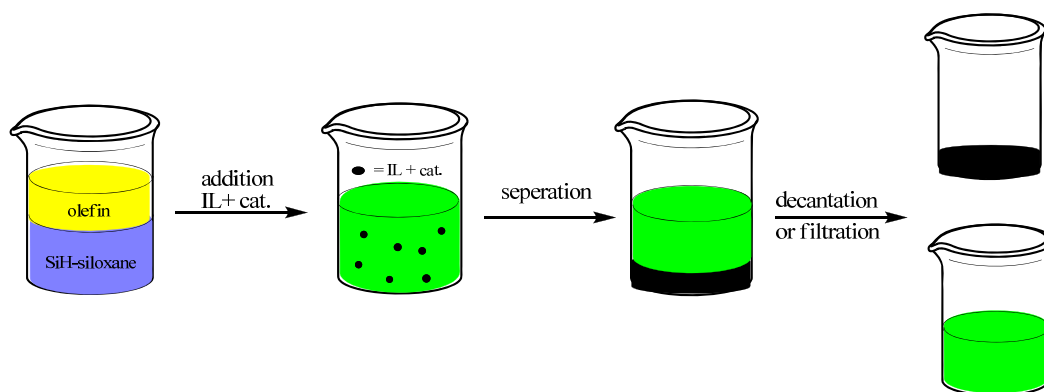
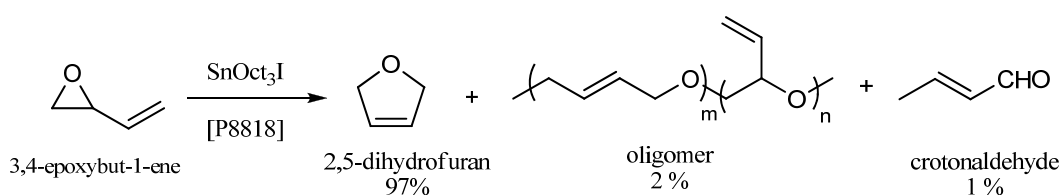


Figure 1.12. Schematic for the hydrosilylation process (yellow = alkene; blue = silane; green = product; black = catalyst dissolved in ionic liquid phase).

1.6.8 Isomerisation: IL as a solvent

As known in literature, the production of tetrahydrofuran has involved isomerisation of 3,4-epoxybut-1-ene to 2,5-dihydrofuran as a reaction step. This isomerisation process requires simultaneous activation by a Lewis base and by Lewis acid being an organotin compounds. The Eastman Chemical Company occupied this reaction at an industrial scale using phosphonium iodide ionic liquid (Scheme 1.19). This ionic liquid was chosen due to its high thermal stability, its high hydrophobic character, and its limited cost with respect to ammonium analogues. Simplified product separation, milder reaction conditions, and the ability to remove and replenish the catalyst system are the advantages provided by this process (Fallinget al., 1993; Phillips et al., 1994).



Scheme 1.19 Isomerisation of 3,4-epoxybut-1-ene to 2,5-dihydrofuran

1.6.9 Methanol carbonylation

Methanol carbonylation are still operated in liquid phase using homogeneous catalyst systems commonly based on rhodium metal in the industrial processes. In liquid phase, the precipitation of rhodium during the flashing step is a serious problem. Catalyst stabilisation and recycling problems

can be solved using ionic liquids which have been introduced as solvents of the anionic active rhodium species $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ (Commereuc et al., 2004).

1.6.10 Other examples

Some of the examples are listed in Table 3 using ILs as electrolytes for electroplating, as hydraulic or cleaning fluids, or entrainers for breaking azeotropes (Olivier-Bourbigou et al., 2010).

Table 1.2. Other examples of industrial/pilot scale applications of IL

	Company	Scale	Ionic Liquid	Role of IL
<u>Storage of gases</u>	Air products	Commercial	$[\text{RMI}][\text{BF}_4]$	Liquid support
<u>Separation/ storage</u> EtOH/H ₂ O or EtOH/THF separation	BASF	Pilot	$[\text{RMI}][\text{BF}_4]$	Entrainer for breaking azeotropes
<u>Energy</u> Dye Synthesized Solar Cells (Gratzel cells)	G24i	Commercial	-	Electrolyte
<u>Engineering fluids</u> Hydraulic liquids	Linde	Pilot	-	Liquid piston
Cleaning fluids	Iolitec/Wanders	Pilot	-	Cleaning agent
<u>Analytical chemistry</u> Commercial GC-stationary phase	Supelco	Commercial	A	GC stationary phase
<u>Electrochemistry</u> Electroplating of Cr	Scionix	Pilot (1200L)	B	Electrolyte
Electropolishing of stainless steel	Scionix	Pilot (50L)	-	Electrolyte

A: $[1,9\text{-di}(3\text{-vinylimidazolium})\text{nonane}][\text{NTf}_2]$

B: $[\text{OH}(\text{CH}_2)_2\text{NMe}_3][\text{Cl}]$

2. CARBON DIOXIDE

Carbon dioxide is a colourless, odourless gas. Amounts above 5,000 ppm are considered very unhealthy, and those above about 50,000 ppm (equal to 5% by volume) are considered dangerous to animal life.

At standard temperature and pressure, the density of carbon dioxide is around 1.98 kg/m^3 , about 1.5 times that of air. The carbon dioxide molecule ($\text{O}=\text{C}=\text{O}$) contains two double bonds and has a linear shape. It has no electrical dipole, and as it is fully oxidized, it is moderately reactive and is non-flammable.

At -78.51°C carbon dioxide changes directly from a solid phase to a gaseous phase through sublimation, or from gaseous to solid through deposition. Solid carbon dioxide is normally called "dry ice", a generic trademark. Liquid carbon dioxide forms only at pressures above 5.1 atm; the triple point of carbon dioxide is about 518 kPa at -56.6°C (Figure 2.1). The critical point is 7.38 MPa (73.8 atm) at 31.1°C .

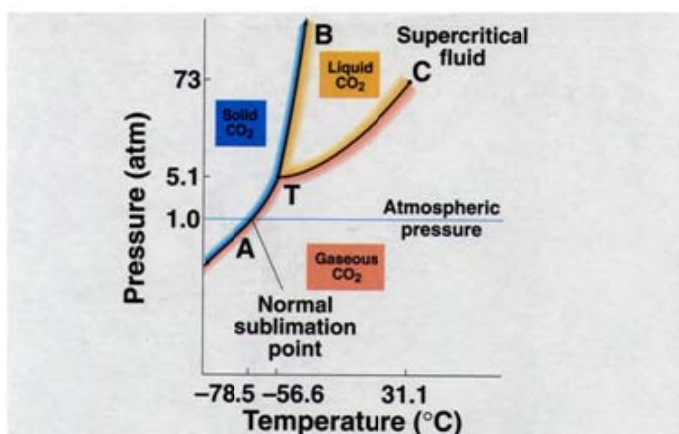
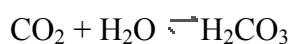


Figure 2.1 CO_2 pressure-temperature phase diagram.

CO_2 is an acidic oxide: an aqueous solution turns litmus from blue to pink. It is the anhydride of carbonic acid, an acid which is unstable in aqueous solution, from which it cannot be concentrated. In organisms carbonic acid production is catalysed by the enzyme, carbonic anhydrase.



CO_2 is toxic in higher concentrations: 1% (10,000 ppm) will make some people feel drowsy. Concentrations of 7% to 10% cause dizziness, headache, visual and

hearing dysfunction, and unconsciousness within a few minutes to an hour (Carbon dioxide, 2011)

2.1 Carbon Dioxide in the Earth's Atmosphere

Carbon dioxide is known as a major greenhouse gas in the atmosphere, responsible for 50-55% of global warming, along with methane for 15-18%, nitrous oxide for 6% (Holder J.V., 2002).

Carbon dioxide forms approximately 0.04% of the Earth's atmosphere. It is essential to photosynthesis in plants and other photoautotrophs, and is also a prominent greenhouse gas. The CO₂ concentration in Earth's atmosphere was about 0.0392% by volume as 2011, or 392 parts per million by volume (ppmv). This is 100 ppmv (35%) above the 1832 ice core levels of 292 ppmv (Figure 2.2) (Atmospheric carbon dioxide, 2011). The upper safety limit for atmospheric CO₂ is 350 ppm. Atmospheric CO₂ levels have stayed higher than 350 ppm since early 1988.



Figure 2.2 Atmospheric CO₂ values (ppmv)

2.2. Carbon Dioxide in the oceans

There is about 50 times as much carbon dioxide dissolved in the oceans in the form of CO₂ and carbonic acid, bicarbonate and carbonate ions as exists in the atmosphere. The oceans act as an enormous carbon sink, having "absorbed about one-third of all human-generated CO₂ emissions to date." Generally, gas solubility

decreases as water temperature increases. Accordingly the rate of uptake from the atmosphere decreases as ocean temperatures rise.

Most of the CO_2 taken up by the ocean forms carbonic acid in equilibrium with bicarbonate and carbonate ions. Some is consumed in photosynthesis by organisms in the water, and a small proportion of that sinks and leaves the carbon cycle. Increased CO_2 in the atmosphere has led to increasing acidity (strictly, decreasing alkalinity) of seawater and there is some concern that this may adversely affect organisms living in the water.

2.3 Global warming and greenhouse effect

Global warming is the increase in the average temperature of Earth's near-surface air and oceans since the mid-20th century and its projected continuation. During the 20th century, global surface temperature increased by 0.74 ± 0.18 °C (1.33 ± 0.32 °F). Most of the observed temperature increase since the middle of the 20th century has been caused by increasing concentrations of greenhouse gases, which result from human activities such as the burning of fossil fuel and deforestation (Global warming, 2011).

The greenhouse effect is the process by which absorption and emission of infrared radiation by gases in the atmosphere warm a planet's lower atmosphere and surface. Greenhouse effect schematic showing energy flows between space, the atmosphere, and earth's surface is given in Figure 2.3. Naturally occurring greenhouse gases have a mean warming effect of about 33 °C (59 °F). The major greenhouse gases are water vapor, which causes about 36–70 percent of the greenhouse effect; carbon dioxide (CO_2), which causes 9–26 percent; methane (CH_4), which causes 4–9 percent; and ozone (O_3), which causes 3–7 percent. Clouds also affect the radiation balance, but they are composed of liquid water or ice and so have different effects on radiation from water vapor.

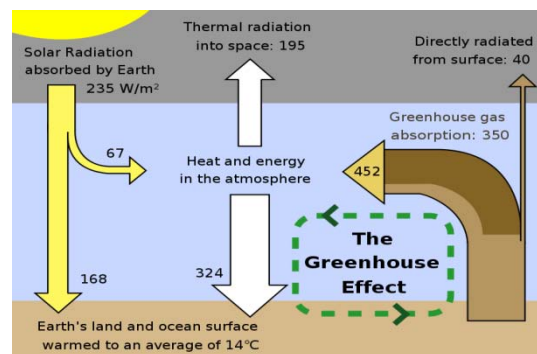


Figure 2.3 Schematic Greenhouse effect

Since about 1750 human activity has increased the concentration of carbon dioxide and other greenhouse gases. Measured atmospheric concentrations of carbon dioxide are currently 100 ppm higher than pre-industrial levels. Figure 2.4 shows the relative fraction of man-made greenhouse gases coming from each of eight categories of sources. This consists of 72% carbon dioxide, 18% methane, 8% nitrous oxide and 1% other gases (Greenhouse gas, 2011)

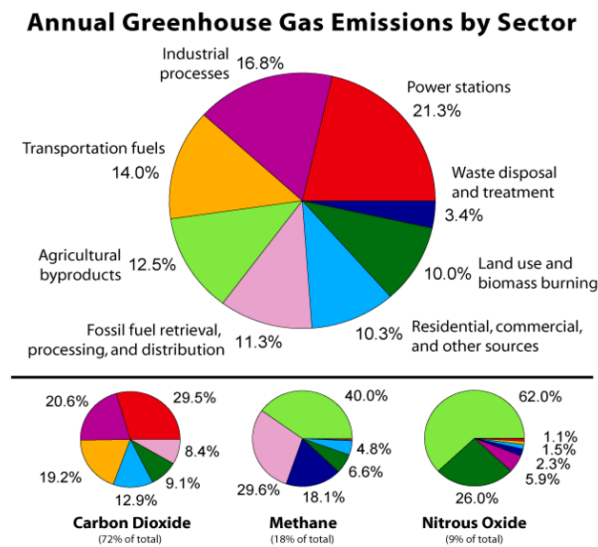


Figure 2.4. Greenhouse gas emissions by sector

Water vapor accounts for the largest percentage of the greenhouse effect, between 36% and 66% for clear sky conditions and between 66% and 85% when including clouds. Water vapor concentrations fluctuate regionally, but human activity does not significantly affect water vapor concentrations except at local scales, such as near irrigated fields. The atmospheric concentration of vapor is highly variable, from less than 0.01% in extremely cold regions up to 2% in warm, humid regions.

Figure 2.5 shows the absorption bands in the Earth's atmosphere (middle panel) and the effect that this has on both solar radiation and upgoing thermal radiation (top panel). Individual absorption spectrum for major greenhouse gases plus Rayleigh scattering are shown in the lower panel. Both the Earth and the Sun emit electromagnetic radiation (e.g. light) that closely follows a blackbody spectrum, and which can be predicted based solely on their respective

temperatures. For the sun, these emissions peak in the visible region and correspond to a temperature of ~ 5500 K. Emissions from the Earth vary following variations in temperature across different locations and altitudes, but always peak in the infrared.

The position and number of absorption bands are determined by the chemical properties of the gases present. In the present atmosphere, water vapor is the most significant of these greenhouse gases, followed by carbon dioxide and various other minor greenhouse gases. In addition, Rayleigh scattering, the physical process that makes the sky blue, also disperses some incoming sunlight. Collectively these processes capture and redistribute 25-30% of the energy in direct sunlight passing through the atmosphere. By contrast, the greenhouse gases capture 70-85% of the energy in upgoing thermal radiation emitted from the Earth surface.

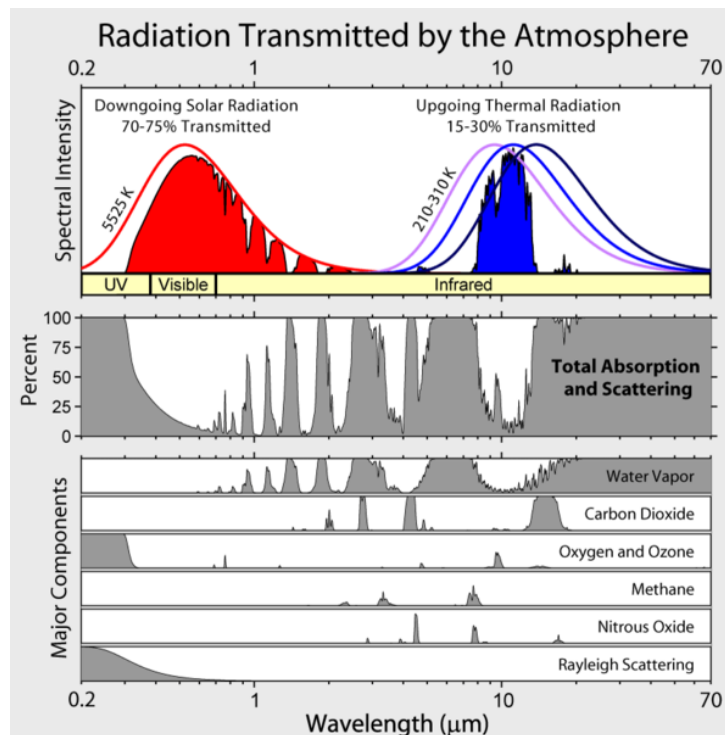


Figure 2.5 Atmospheric absorption of gases and scattering at different electromagnetic wavelengths

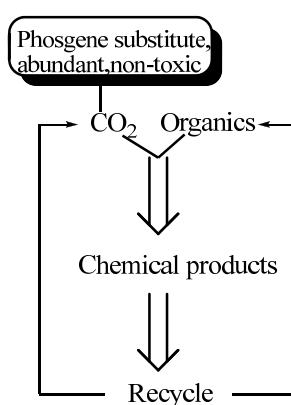
Avoiding the currently ongoing climate change caused by CO_2 and other greenhouse gases requires the long-term or permanent storage of several Gt of CO_2 annually. Using CO_2 as a chemical feedstock gives only a marginal yet not irrelevant contribution to the CO_2 mitigation. The size of the markets of the products produced using industrially produced CO_2 and their lifetime before again releasing the fixed CO_2 are limited, being of the order of 120 megatonnes (Mt)

annually at the moment (urea stands for 60% of this) and 100 years (for polyurethanes used in building insulation), respectively.

Nonetheless, financial, legal, social and environmental factors promote the development of markets and technologies that make use of industrially produced (more generally: anthropogenic) CO₂ as a chemical feedstock. Since the 1990s increasing amounts of fuels, polymers and other organic products, and inorganic products have been produced using new or alternative routes. Besides a small contribution to CO₂ emissions reduction, such processes often have the benefit of higher energy efficiency, lower fossil fuel consumption, less pollution or the use of less toxic chemicals (Xiaoding *et al*, 1996).

2.2 Transformation of CO₂ to Organic Products

As well as being nontoxic, abundant, and economical, carbon dioxide (CO₂), is one of the simply available renewable carbon source (Scheme 2.1). CO₂ is also engaging as an environmentally-conscious chemical agent and is remarkably applicable as a phosgene substitute. However, utilization of CO₂ as a raw material is very limited in the industrial processes. Because CO₂ is the most oxidized state of carbon, it has low energy level, a high energy input is lacking to transform CO₂ (Sakakura *et al.*, 2007).



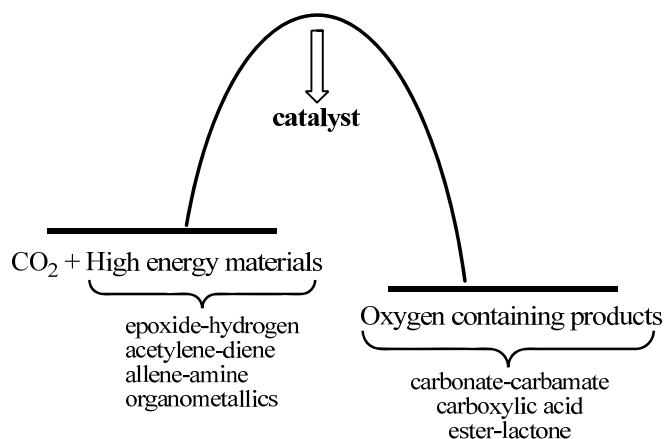
Scheme 2.1 CO₂ as a Green Carbon Resource

There are four fundamental methodologies to transform CO₂ into useful chemicals:

- (i) To apply high-energy starting materials for instance hydrogen, unsaturated compounds, small-membered ring compounds, and organometallics.

- (ii) To select oxidized low-energy synthetic goals such as organic carbonates.
- (iii) To lead the equilibrium to the product side by moving out a particular compound.
- (iv) To contribute physical energy such as light or electricity.

To get a negative Gibbs free energy suitable reactions can be selected (Scheme 2.2).



Scheme 2.2. Organic Synthesis Using CO₂

Using CO₂ as a crude material, a great deal of research has been directed reactions as exemplified in Scheme 2.3, e.g. CO₂ reductions under photoirradiation, or electrolytic conditions, or manufacturig of synthesis gas by reforming natural gas with CO₂. Otherwise, lots of these reactions produce quite simple molecules such as carbon monoxide and formic acid.

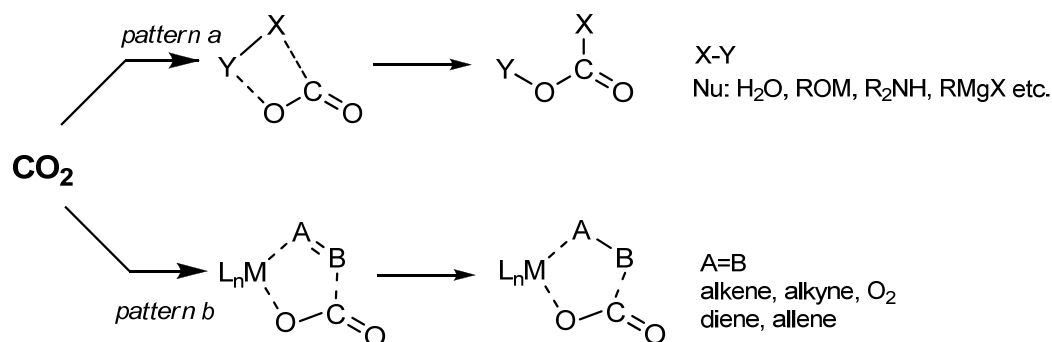
CO₂ transformation

Category	Products
Chemical	Carbonates, carbamates, hydrocarbons, MeOH, EtOH etc.
Photochemical	CO, HCO ₂ H, CH ₄
Electrochemical	CO, HCO ₂ H, CH ₃ OH
Biological	EtOH, Sugar, CH ₃ CO ₂ H
Inorganic	Carbonates:M ₂ CO ₃
Reforming	CO + H ₂

Scheme 2.3 Scope of CO₂

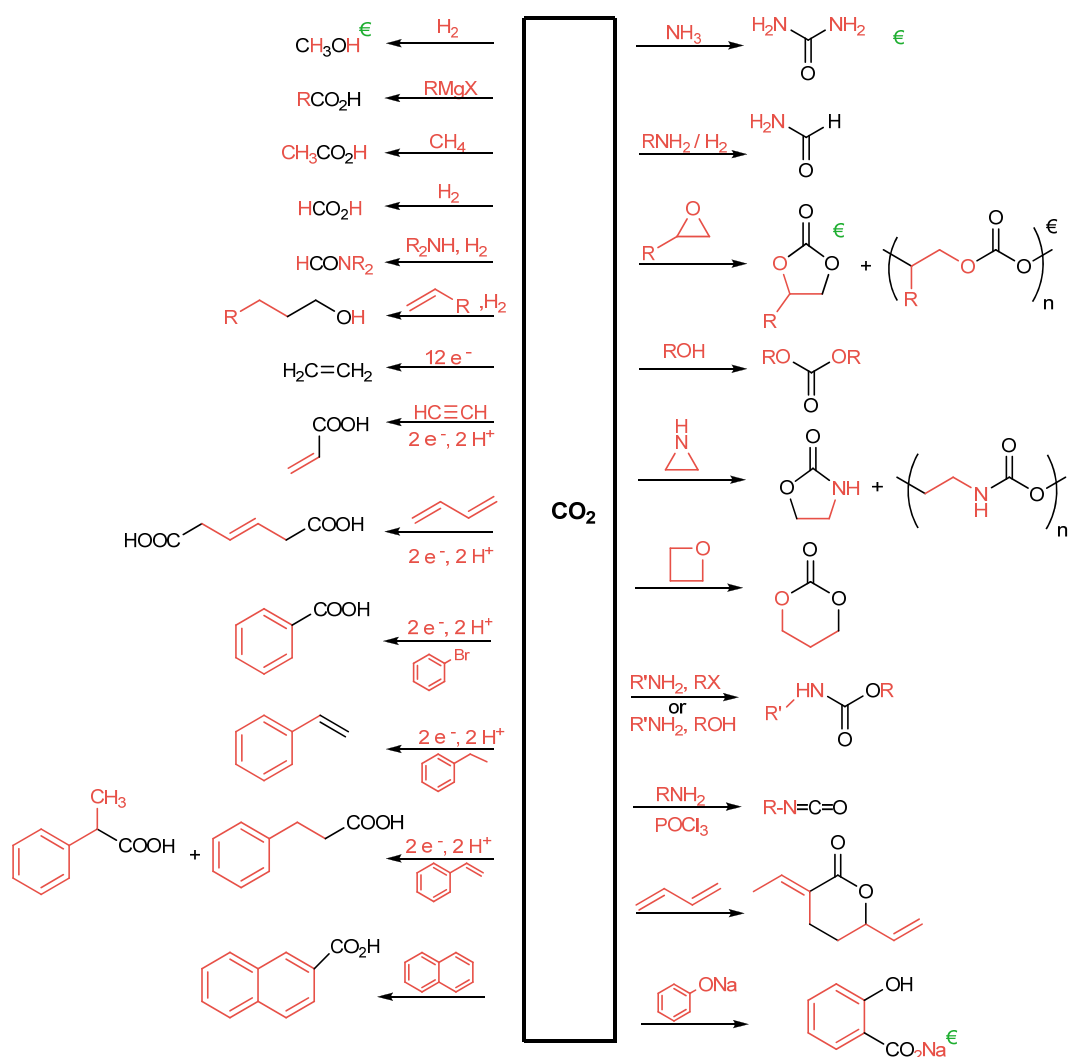
A widely accepted idea is that CO_2 is so thermodynamically and kinetically stable because of the fact that it is rarely utilized its fullest potential. Even though, due to the electron deficiency of the carbonyl carbons, CO_2 has a strong affinity toward nucleophiles and electron-donating reagents. In other words, seeing that CO_2 is an “anhydrous form of carbonic acid”, it gives reaction easily with basic compounds. As an example, organometallic reagents such as Grignard reagents smoothly react with CO_2 even at a low temperature. In similar procedures, to produce compounds which have carboxyl or carboxylate group water, alkoxides, and amines also add to CO_2 . With these reactions carbonic and carbamic acids produce readily (Scheme 2.4). Additional reactions of these species with electrophiles directed to the formation of organic carbonates and carbamates. Nevertheless, reactions of low valent metal complexes (mainly nickel(0) and palladium(0)) with CO_2 and unsaturated compounds result the formation of five-membered metallalactones (Behr, 1988). This type of reaction is called an “oxidative cycloaddition”, because the valence of the metal increases. In view of the fact that, reactions covering CO_2 can be classified into two patterns:

- (1) generation of a carboxyl group via nucleophilic attack (pattern a)
- (2) formulation of a five-membered ring via oxidative cycloaddition (pattern b).



Scheme 2.4 Typical Transformations of Carbon Dioxide

Scheme 2.5 summarizes examples of organic synthesis starting from CO_2 .



€: Industrialized

Scheme 2.5 Organic compounds derived from carbon dioxide

2.4.1 Organic Carbonates

There are three outstanding reasons to determined organic carbonates as synthetic goals (Sakakura and Kohno, 2009).

- (1) *Thermodynamics* The energy difference between the product and CO_2 is significant impact in view of selecting synthetic targets. CO_2 is the most oxidized state of carbon, for this reason, synthetic targets having high oxidation states, in other words heavily oxygenated molecules, would be most opportune. Organic carbonates, the four chemical bonds of the carbonyl carbon are connected to oxygen is rather suitable for this target.

(2) *Environmental demand*: Phosgene is a quite reactive and easily available reagent for manufacturing organic carbonates and isocyanates. In any case, a substitute for phosgene is highly found desirable because, it is not only being highly toxic and corrosive and also raw material for the chemical weapons. On the contrary, CO₂ is safe (non-toxic and non-flammable), economical and abundant.

(2) *Market share*: Organic carbonates are further classified into low-molecular weight carbonates and polymeric examples. Both are industrially valuable. Especially, aromatic polycarbonates are quite prominent as engineering plastics. The world annual production of aromatic polycarbonates is about two million tons.

2.4.1.1 General utilization of organic carbonates

Four value-added organic carbonates are dimethyl carbonate (DMC), diphenyl carbonate (DPC), ethylene carbonate (EC) and propylene carbonate (PC). DMC and DPC have open chain structures, whereas EC and PC are cyclic

The main usage areas of organic carbonates are summarized here:

(i) *The manufacturing of engineering plastics* (a crude material for polycarbonates and polyurethanes): Polycarbonates are highly impact-resistant and optically transparent chemicals, owing to the fact that they have wide scope of application consistig of CDs, DVDs, eyeglasses, aircraft windows, etc. Additionally, in the synthetic procesure of aromatic polycarbonates, dimethyl and diphenyl carbonates are being potential phosgene substitutes. Polyurethanes are presently manufactured via a reaction of diols and isocyanates, however, phosgene is used for the synthesis of the isocyanates. Substituting phosgene with organic carbonates is sought-after in terms of environmental impact.

(ii) *Electrolyte solvents for lithium ion batteries*: The request for rechargeable batteries, particularly lithium ion batteries which is essential in the growth of mobile electric equipments, involving camcorders, laptop PCs, cell phones and electric vehicles has been increasing. Organic carbonates are characteristic solvents for dissolving electrolytes in batteries.

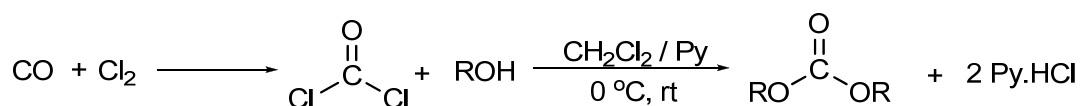
(iii) *Organic solvents*: Organic carbonates typically have a high solubilizing power, relatively low toxicity and suitable boiling point to be eliminated by vaporization. Accordingly, their use as a toluene substitute in painting processes will create an enormous new market. On the other hand, as an environmentally friendly reaction solvent has also been suggested (Schaffner et al., 2008; Bayardon et al., 2007).

(iv) *Fuel additives*: The addition of organic carbonates to gasoline lead to an improved octane value. Moreover, their addition to light oil remarkably minimized carbon particulates. This has importance due to their application as fuel additives which has a huge market (Pacheco and Marshall, 1997)

(v) *Green reagents*: Organic carbonates are a good substitution agents instead of many toxic chemicals. As an example, DMC have been used as a substitute for dimethyl sulfate, methyl chloroformate, and so on (Tundo and Selva, 2002; Tundo et al., 2000). Inoue et al. discovered aliphatic polycarbonate synthesis by alternating the copolymerization of CO₂ and oxiranes (Scheme 19), is an important issue involving CO₂ usage (Inoue, 2005). Industrial production of poly(aliphatic carbonates) in China and the US, has been actualized to reach large scale commercialization, the polymeric features and catalytic activity may require to be further advanced (Tullo, 2008).

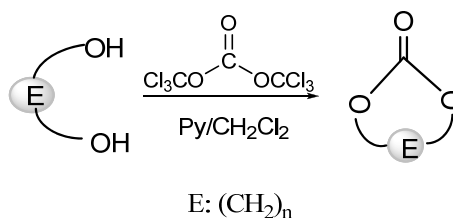
2.4.1.2 Synthesis of acyclic carbonates from CO₂

In the traditional synthesis of acyclic carbonates, a two-step process including phosgene formation from CO and Cl₂, followed by reaction with alcohols (Scheme 2.6). With this process, only moderate yields is obtained. The high toxicity of the starting materials and hydrogen chloride as byproduct are the major problems (Muskat and Strain, 1945).



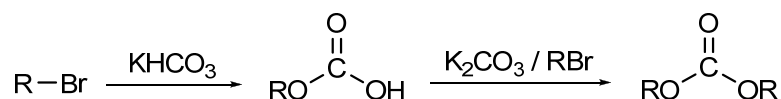
Scheme 2.6 Synthesis of organic carbonates by phosgenation method

Burk et al. reported the preparation of carbonates using chloroformic acid trichloromethyl ester (diphosgene) or bis(trichloromethyl) carbonate instead of phosgene. Cyclic carbonates were also synthesized easily using diols with triphosgene in CH_2Cl_2 and pyridine at 70°C (Burk et al., 1993) (Scheme 2.7).



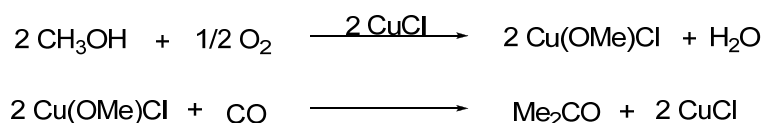
Scheme 2.7 Synthesis organic carbonates using diols

In 1921, it is the first time, synthesis of organic carbonates via transformation of inorganic carbonates starting alkyl halide (Scheme 2.8) (Beilstein, 1921). In Fujinami et al. report, hexabutyldistannoxane or chlorotributylstannane was used as catalyst in the presence of solid potassium carbonate, alkyl bromide in dimethylformamide or dimethyl sulfoxide (Fujinami et al., 1981). The drawback of this methode is salt wastes.



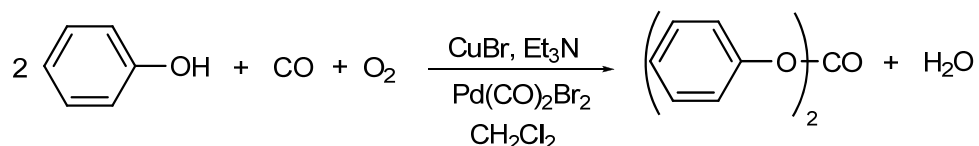
Scheme 2.8 Synthesis organic carbonates via alkylation of metal carbonates

In 1990, ENIChem described a one-pot synthesis by oxidative carbonylation of methanol over a CuCl catalyst (Scheme 2.9) (Tundo and Selva, 2002). At the same period, the Japanese company UBE commercialized a similar transformation based on a Pd -nitric oxide system (Pacheco and Marshall, 1997). Good conversion for dimethyl carbonate is succeeded with high selectivity.



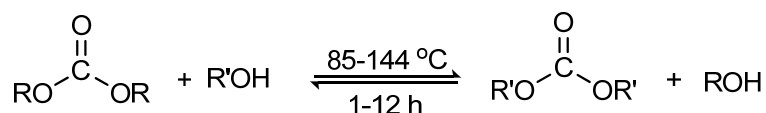
Scheme 2.9 Synthesis of organic carbonates via oxidative carbonylation of alcohols

Synthesis of diaryl carbonate by direct oxidative coupling of phenols with carbon monoxide illustrated in Scheme 2.10. According to this route, the yield of diphenyl carbonate is found 4-30% with 90-96% selectivity (Hallgren J. E., 1978; Chang T. C. T, 1990; Kezuka et al., 1993). The drawbacks of oxidative carbonylation process are usage of toxic, flammable and corrosive chemicals.



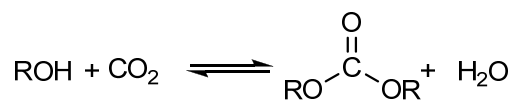
Scheme 2.10 Synthesis of diphenyl carbonate via oxidative carbonylation

An alternative route to acyclic carbonates involves the reaction of a cyclic carbonate (usually ethylene carbonate) with an alcohol (Scheme 2.11). In 1986, Texaco investigated the commercialization of this process, despite the drawbacks associated with the multi-step synthesis, formation of ethylene glycol as by-product and the hazards due to the utilization of ethylene oxide as a starting material. The Japanese company Asahi Kensei also commercialized the same process several years later (Knifton, 1986; 1987; 1988; Asahi, 1991).



Scheme 2.11. Synthesis of organic carbonates via transesterification reaction

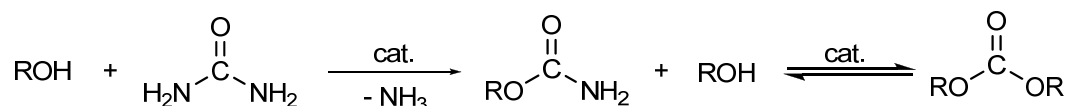
Direct formation of dimethyl carbonate (DMC) from CO₂ and methanol is potentially the most straightforward process for the synthesis of organic carbonates (Scheme 2.12) (Sakakura et al., 2007; Shaikh and Sivaram, 1996; Sakakura and Kohno, 2009). The reaction usually requires high temperatures and an organostannane catalyst, though more recently new titanium and tin/acid catalysts have shown enhanced activity (Choi et al., 2008).



Scheme 2.12. Dehydrative condensation reaction of CO₂ and alcohol

Despite the attempts to improve this process, drawbacks are still related to catalyst decomposition and poor conversions due to product hydrolysis side-reactions. The use of more efficient dehydrating agents such as zeolites, orthoesters or Mitsunobu reagents has been investigated and shown significant improvements to the conversions, though the high cost of these dehydrating agents was not practical at an industrial level (Chaturvedi et al., 2007). At the present time, dehydrative condensation of methanol and CO₂ does appear to be the most efficient system for the synthesis of DMC (Sakakura and Kohno, 2009). The transformation is carried out at 180 °C and up to 300 atm pressure, using acetals as dehydrating agents and tin, titanium or zirconium alkoxides catalysts. The process can give 720 kg day⁻¹ m³ of production.

Starting from urea and alcohol, after two step reaction linear organic carbonates can be obtained (Scheme 2.13). Zinc acetate and lead acetate was used by Paquin who discovered this methode (Fukuoka et al., 1990). Other catalyst such as dibutyltin oxide, dibutyltin dimethoxide and triphenyltin chloride have exhibited high yields. The drawback of this process is unfavorable equilibrium.



Scheme 2.13. Synthesis of organic carbonates with urea.

In Figure 2.6 a summary for the formation of organic carbonates is illustrated.

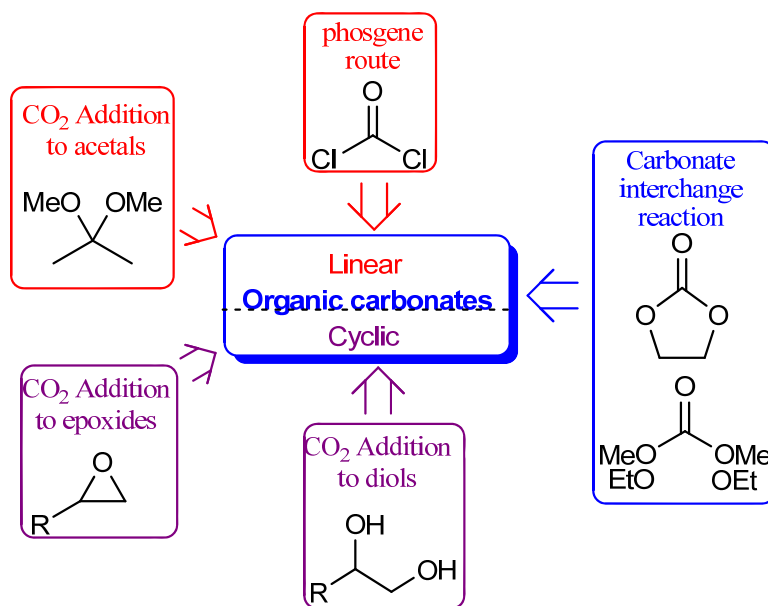
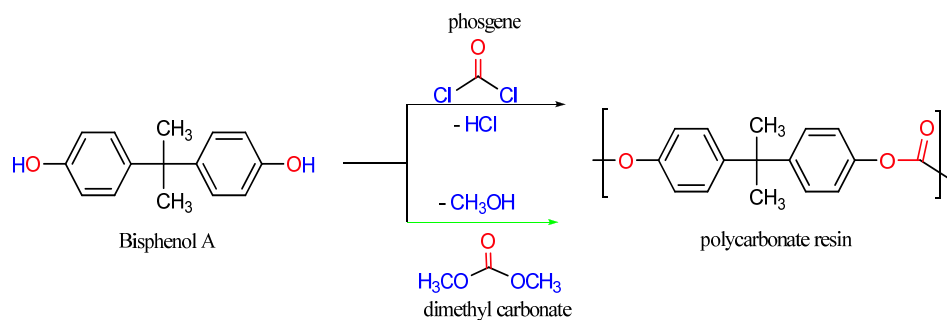


Figure 2.6 Commonly used building blocks in the synthesis and modification of organic carbonates

2.4.2 Copolymerization of epoxides and CO₂

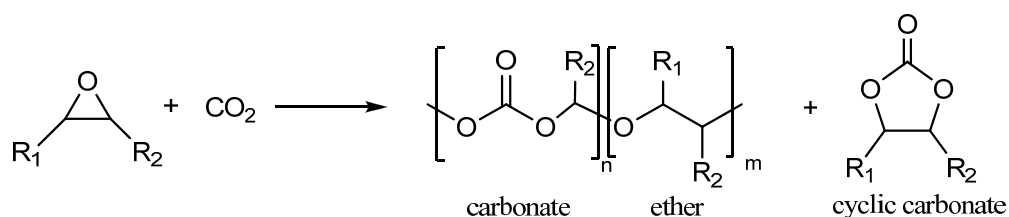
The first aromatic polycarbonates were prepared in the late 1890s by reacting hydroquinone or resorcinol with phosgene in pyridine but the crystalline polymers produced were brittle and difficult to process. In 1941, PPG company introduced a crosslinked resin prepared by a peroxide initiated radical polymerisation of the bisallyl carbonate of diethylene glycol. The colourless, transparent plastic was the first available polycarbonate (Polycarbonate Production and Manufacturing Process, 2011).

However, the use of polycarbonate took off in the late 1950s when Bayer and General Electric (GE) companies separately commercialised processes based on bisphenol-A (BPA). Early production was based on reacting phosgene with phenol to produce diphenyl carbonate (DPC), which was then reacted with BPA to produce the polymer and liberate phenol for reuse. However, this approach suffered from slow reaction rates and the need for several small-scale batch reactors (Scheme 2.14) (Greener Industry, 2011).



Scheme 2.14 The route of polycarbonates in the industry (greener industry, 2011)

The alternating copolymerization of epoxides and CO₂ to generate biodegradable polycarbonates has been a subject of much interest. Polycarbonates has important properties which include strength, lightness, durability, heat resistance and good electrical insulation (Brunelle *et al*, 2005). Scheme 2.15 illustrates the general copolymerization reaction of CO₂ and epoxides.



Scheme 2.15 Copolymerization reaction of CO₂ and epoxides

In 1969, the first example of propylene oxide/CO₂ copolymerization was discovered by Inoue. Using CO₂ as a C1 building block and heterogeneous catalyst system involving 1:1 Et₂Zn/H₂O, very low TOF (0.12 h⁻¹) value is obtained at 50–60 atm pressure and 80 °C (Inoue *et al.*, 1969). Comparable results were also observed with other substrates such as ethylene oxide, epichlorohydrin and styrene oxide. Kobayashi investigated different hydroxyl sources including resorcinol and pyrogallol as the substrate, even though any noticeable improvements were attained for the Et₂Zn catalyst (Kobayashi *et al.*, 1971). To get more efficient catalysts for epoxide/CO₂ copolymerization, various system has developed involving a metal source such as ZnEt₂, Zn(OAc)₂, Zn(OH)₂, and ZnO that is reacted with either a trihydric phenol or one of a variety of carboxylic acids. During the 90's homogeneous zinc catalysts were developed with the most notable being Darensbourgs' zinc bis(phenoxide) and Coates' zinc β-diimine

catalyst (Figure 2.7) (Darensbourg *et al*, 1995a; Cheng *et al*, 1998; Darensbourg *et al*, 1999; Darensbourg *et al*, 2000; Moore *et al*, 2002).

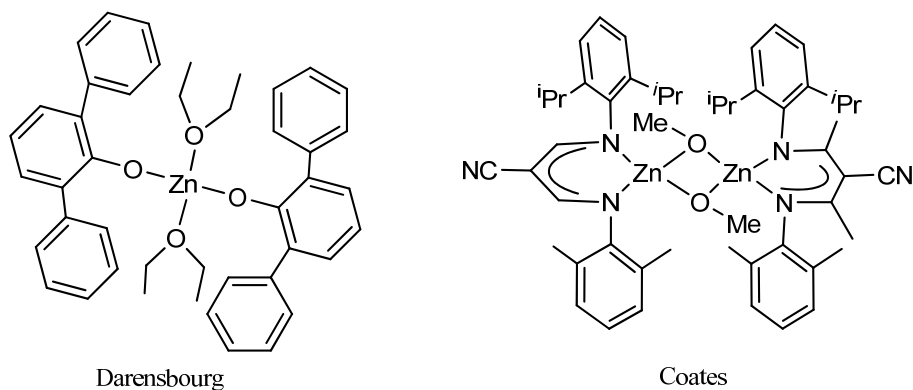


Figure 2.7 Examples of Darensbourg' zinc bis(phenoxide) catalyst and Coates' zinc β -diimine catalyst.

The high Lewis acidity of zinc can cause the consecutive ring opening of epoxides without CO₂ insertion. Both catalysts are highly active for towards the synthesis of poly(cyclohexene carbonate).

With the diethyl zinc / water system, a lack of molecular weight control or a high polydispersity index (PDI > 6) were the major problems for the application of this system in the industry. Despite the apparent infancy of this chemistry, it demonstrated that CO₂ could serve as a viable source of C1 feedstock and that further research might lead to a system that is more industrially useful. The following years of research into this process focused on bulk studies of these heterogeneous catalysts, replaced water with other di- and tri-protic sources, however, only modest advances were attained in the process, while the problems associated with Inoue's system have still being proceeded (Inoue *et al*, 1969b; Kobayashi *et al*, 1973; Kuran *et al*, 1976a; Soga *et al*, 1977; Soga *et al*, 1981).

In the literature proposed copolymerization mechanism is illustrated as Figure 2.8. According to the suggested mechanism, it is necessary to have one vacant site on the catalyst for epoxide binding. On the other hand, more than one vacant site can lead to polyether formation. In the reaction, the first step is binding the epoxide to catalyst and then ring of cyclohexene oxide opens by mitigation of alkoxide. In the latter step, carbon dioxide inserts into the Zn-O bond to produce the desired carbonate species. The high molecular weight copolymers are formed by repeating the cycle scores of times.

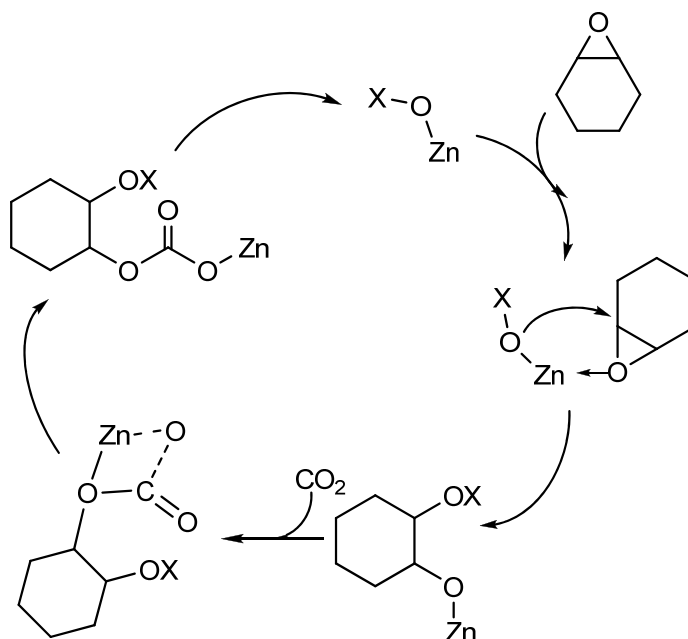


Figure 2.8. Proposed copolymerization mechanism.

A key aspect in copolymerization reaction is the need of a cocatalyst. The most studied cocatalysts are nitrogen donor Lewis bases such as *N*-methylimidazole (N-MeIm), 4-dimethylaminopyridine (DMAP) or bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) (Figure 2.9).

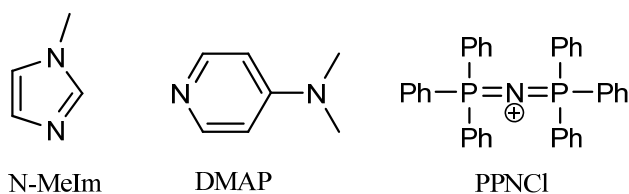
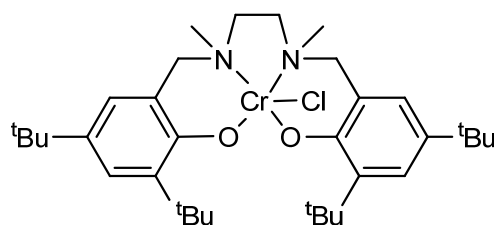


Figure 2.9. Used co-catalyst in copolymerization reactions.

Many other catalysts have since been developed for polycarbonate synthesis including zinc-based complexes, solid supported zinc catalysts, rare earth metals, metal macrocycles and salen complexes (Darensbourg et al., 1995; 2000; 2005; Cheng et al., 2001; 2002; 2003; Yu and Jones, 2003; Shen et al., 1990; Aida et al., 1986)

Ulusoy et al. studied with a salen Cr(III) complex for the copolymerization and block copolymerization of epoxides (Darensbourg et al., 2009). PDI values

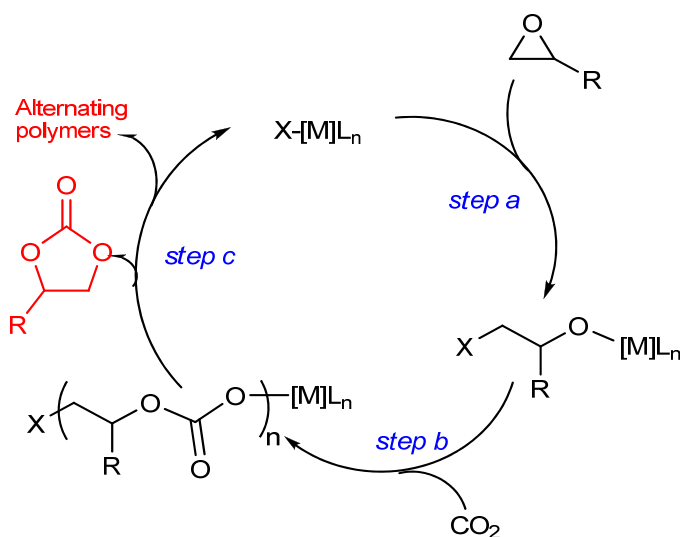
was narrow as desired and surprisingly the product, poly(cyclohexylene carbonate) was obtained as clean and white product after methanol precipitation (M_n : 11.9-27.2 kgmol⁻¹) whereas using salen Cr(III) complex, yellow product was obtained due to the presence of metal contamination (Scheme 2.16).



Scheme 2.16 The structure of Cr-III(salan) complex

2.4.3 The synthesis of cyclic carbonates

The reaction of oxiranes with CO₂ produces cyclic or polymeric carbonates (Scheme 2.17) (Coates and Moore, 2004; Darensbourg, 2007). Cyclic carbonates are valuable either as synthetic intermediates as mentioned in section 2.2.1.1. In addition, the importance of cyclic carbonates has increasing attention due to the fact that the synthetic pathway of aromatic polycarbonates from EC via DMC has recently been commercialized. On account of production of two million tons of polycarbonate is currently requiring phosgene, the utilization of CO₂ as a phosgene substitute is demanding.



Scheme 2.17 Reaction of oxiranes with CO₂

2.4.3.1 Reactions with oxiranes

Cyclic carbonates are currently produced via CO_2 and oxiranes (eqn (4), step a). On the contrary the dehydrative condensation of diols and CO_2 , the reaction easily proceeds owing to the high energy level of the starting oxiranes (Darensbourg et al., 2003) (Figure 2.10).

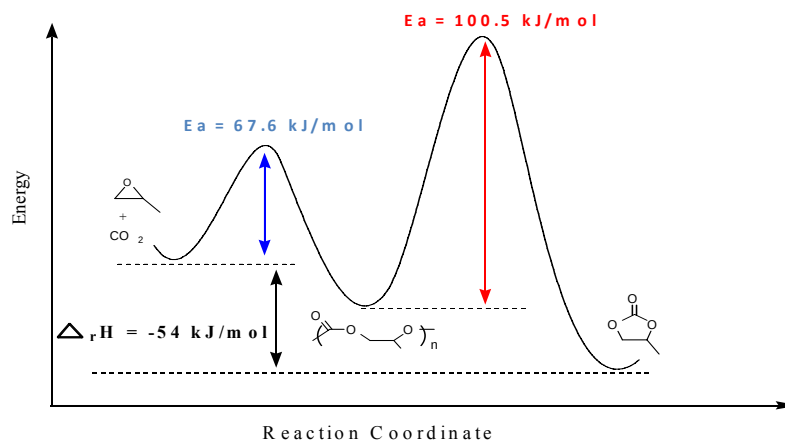
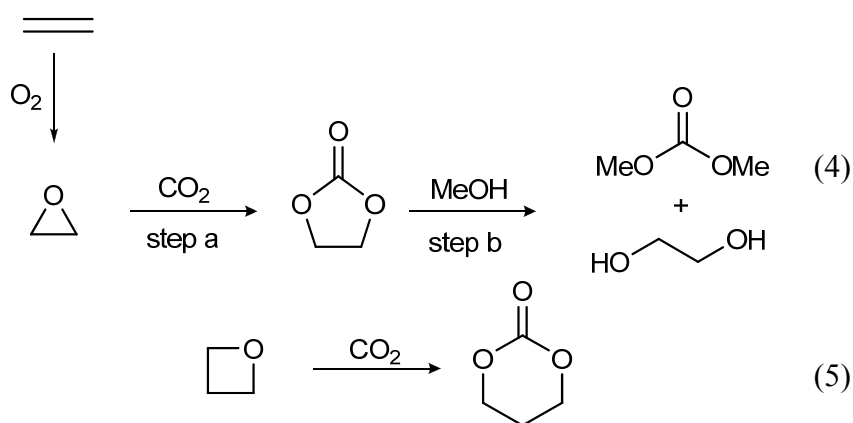


Figure 2.10. Reaction coordinate diagram for the coupling reaction of CO_2 and propylene oxide. $\Delta_r H$ is estimated to be -54 kJ/mol

For the synthesis of dry ethylene glycol and DMC, the transesterification of the cyclic carbonates with MeOH (eqn (4), step b) is significant. Since CO_2 cyclization (eqn (4), step a) usually have occurred in high yield and selectivity, the reaction is appropriate as a vitrine of new reaction methodologies.



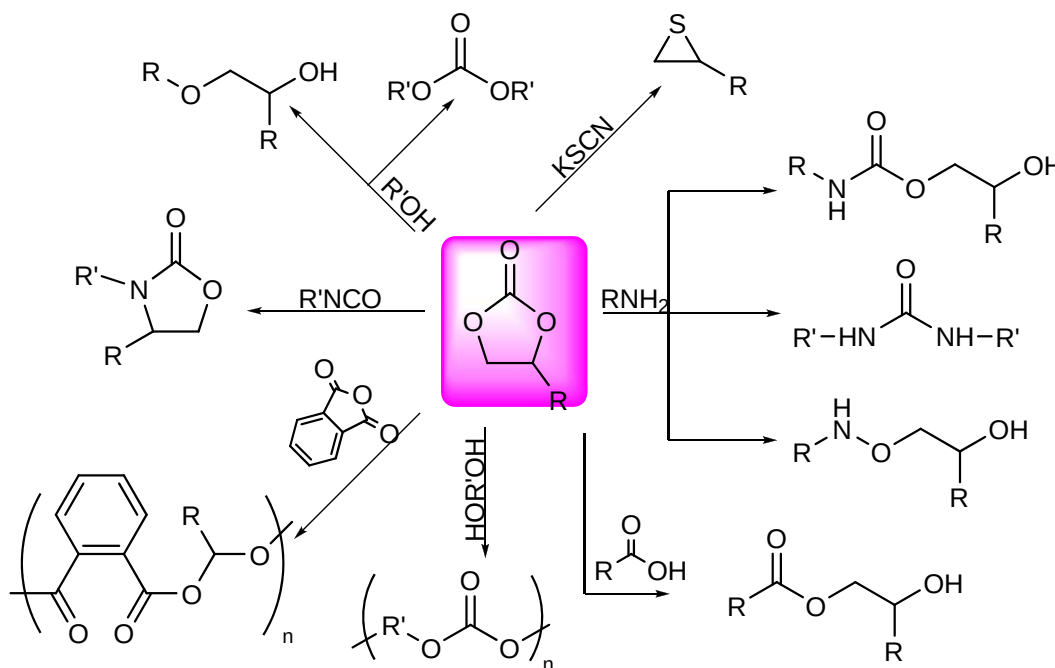
For developing the step a, next research topics are:

- (1) The further improvement of highly active catalysts.
- (2) To research halogen-free catalysts (e.g. metal oxides).

- (3) Catalyst recycling by employing phase separation (scCO_2 , ionic liquids, PEG, etc.).
- (4) For continuous flow processes, to prepare solid or immobilized catalysts.
- (5) Different substrates, e.g. oxetanes (see eqn (5)).

In order to spotlight their high catalytic activity, reactions at low temperature (below 100 °C) are often considered. Nonetheless, such conflicts are not very logical for the reason that it is an exothermic reaction and temperature control below 100 °C is hard.

Economically valuable compounds (pharmaceuticals, fine chemicals etc.) could be synthesized via chemical reaction of cyclic carbonates. Some reactions utilizing cyclic carbonates are given in Scheme 2.18.



Scheme 2.18 Some organic reactions using cyclic carbonates.

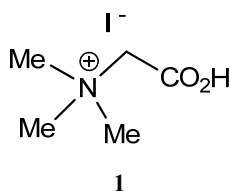
Simple metal salts such as K_2CO_3 , KCl , KI , LiBr and NaOH catalysed propylene carbonate formation with quantitative yields, particularly when used in conjunction with crown ethers although (TOF: 30h^{-1} , 50 atm, 120 °C) (Rokicki et al., 1984). A moderate TOF of 24h^{-1} for reactions carried out under 40 atm pressure at 120 °C in the presence of $\text{NaI}/\text{PPh}_3/\text{PhOH}$ (Huang and Shi, 2003). Under the same reaction conditions, a CaCl_2 / $\text{octyl}_3(\text{Me})\text{NCl}$ catalyst system also

exhibited high yields (TOF: 52 h^{-1} for PC) (Kossev et al., 2003). A catalyst system based on $\text{NiCl}_2/\text{PPh}_3$ in the presence of TBAB and zinc powder as a reducing agent, produced an excellent yield ($>99\%$) and TOF (3544 h^{-1}) at 25 atm pressure and 120°C (Li et al., 2003). Work by Gonz'alez et al. demonstrated high catalytic activity (TOF 293 h^{-1}), in the presence of solid supported RuCl_3 (with SiO_2 , or tetraethylammonium bromide as the support), at 80°C and under supercritical conditions (Gomes et al., 2008). Conversely, when polyphosphotungstic acid (HPW) was used as the support, polycarbonate products were obtained with the same TOF. Differences in the solid supports were suggested to influence the relative hardness of the electrophilic ruthenium sites, resulting in the formation of a single- or multi-site catalyst; thus, cyclic carbonate or polycarbonate was formed selectively (Darensbourg and Holtcam, 1996). Sakakura et al. reported the use of samarium oxychloride as a catalyst for the addition of CO_2 to propylene oxide, obtaining quantitative yields in DMF at 200°C under supercritical conditions (Yashuda et al., 2002).

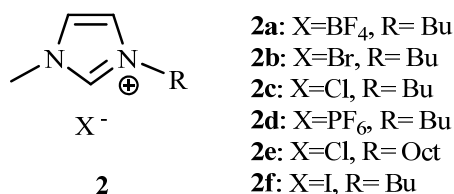
Caló et al. studied with molten tetrabutylammonium bromide (TBAB) to catalyse the synthesis of styrene carbonate from CO_2 and styrene oxide (Caló et al., 2002). The yield of styrene carbonate was 83% (120°C , atmospheric pressure, TOF 1.3 h^{-1}). In 2008, Park et al. also investigated the addition of CO_2 to butyl glycidyl ether in the presence of tetraalkylammonium salts. The catalytic activity improved as the length of the alkyl groups increased, though substituents longer than C8 did not produce any beneficial effect (Ju et al., 2008).

Tetraalkylammonium and phosphonium halides combined with organotin halides were successfully used by Baba et al. for the synthesis of cyclic carbonates. Using $n\text{-Bu}_3\text{SnI}$ with $n\text{-Bu}_4\text{PI}$ gave excellent yields (100% with propylene oxide, one hour, 40°C , 49 atm CO_2) (Baba et al., 1987). When tetraalkylammonium and phosphonium halides used alone, yields were lower ($17\text{--}100\%$, TOF's are $0.85\text{--}5 \text{ h}^{-1}$) for the reaction of CO_2 with phenylglycidol in N-methylpyrrolidone (NMP) (100% with $5\text{mol}\%$ benzyltrimethylammonium chloride) (Peppel, 1958; Kihara et al., 1993).

A series of betaine-based solid catalysts prepared by Han et al. showed moderate activity (Zhou et al., 2008). Propylene carbonate was obtained in 98% yield in the presence of the betaine hydroiodide catalyst **1** (140°C , 80 atm CO_2 , TOF 4.9 h^{-1}).



It is first time reported that utilization of water as an additive in the chemical fixation of propylene oxide and CO₂, with ionic liquids (Sun et al., 2009). Excellent isolated yields were achieved using quaternary ammonium salts Bu₄NBr (86%), Bu₄NI (88%), ionic liquids [BMIm]Br **2b** (87%), [BMIm]I **2f** (90%) and phosphonium salts Ph₃PBuBr (88%), Ph₃PBuI (95%), Ph₃PEtBr (85%), Ph₃PHexBr (89%). The reactions were carried out under 20 atm pressure of CO₂ with 0.5 mol% of catalyst at 125 °C for one hour. The highest TOF was 194 h⁻¹ using Ph₃PBuI. Compared to anhydrous condition, this value was four times higher. Ph₃PBuI was recyclable and it is not detected any decrease after being reused ten times. The role of the water was supposed to increase initial activation of the epoxide and stabilization of the ring-opened and carbonate intermediates.



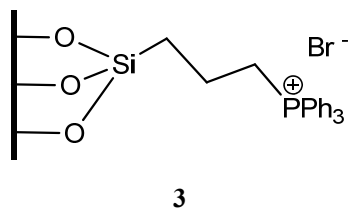
Scheme 2.19 General representation of methylimidazolium ILs

In 2010, Li et al. disclosed the role of water depending on conductivity working under identical conditions. In this study, it is revealed that yield of PC was proportional to conductivity of the reaction medium (Li et al., 2010).

He et al. used CO₂ under scCO₂ with a silica-supported tetrabutylammonium salt catalyst for the synthesis of cyclic carbonates (Wang et al., 2006). The reaction conditions was 80 atm pressure of CO₂, 1 mmol % catalyst at 150 °C for 10 h. All of the four silica supported salts exhibited high yields with the bromide and iodide anions (96-97 %). Unsupported TBAB showed almostly similar result. Even though with the other halide salts, moderate yields was obtained especially fluoride salt was the lowest (66 %).

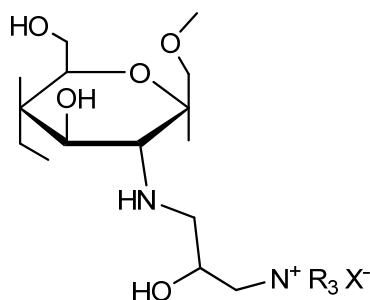
3-(Triethoxysilyl)propyltriphenylphosphonium bromide supported on mesoporous silica, **3**, was reported by Sakai et al. Using 1,2-epoxyhexane as the

substrate, product was attained with 99% conversion at 90 °C and 10 atm pressure with a TOF of 8.2 h⁻¹ (Sakai et al., 2008). Complex **3** could be reused over 10 runs, without any significant loss in the activity.



For the synthesis of cyclic carbonates, Nishikubo experimented polystyrene bound onium salts. In this report, moderate results were obtained. The best of which was with (PS)-CH₂-P⁺(Bu)₃Cl⁻ which catalysed the addition of CO₂ to phenylglycidol, with 62% yield. Reactions were performed using 1 mol% of catalyst with atmospheric pressure CO₂ at 60 °C in toluene. There was a proportion between the length of the supporting tether and observed yields. Up to seven times, the catalyst could be reused (Nishikubo et al. 1993; 1995).

Zhou also studied trimethylammonium iodide supported on chitosan (chitosan-NMe₃I) as a catalyst for the synthesis of propylene carbonate and achieved 100% yield with high selectivity (Zhao et al., 2007). The reaction was performed at 140 °C and at 40 atm pressure with a TOF of 9.8 h⁻¹.

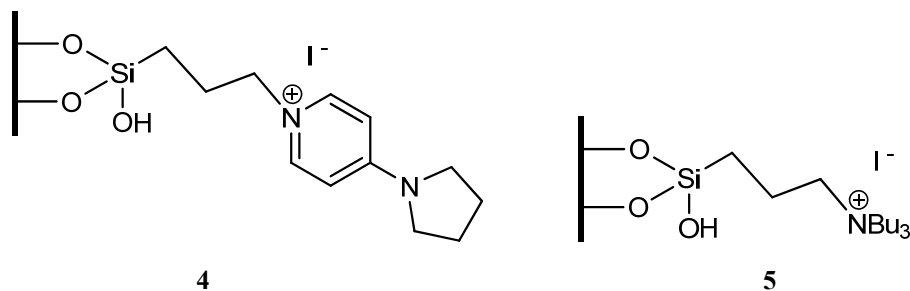


Scheme 2.20 Structure of Chitosan NMe₃X

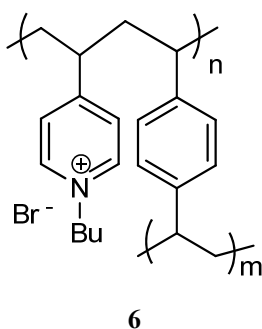
Syntheses of various cyclic carbonates were also experimented in the presence of triphenylphosphonium bromide bonded to polyethylene glycol (Br-Ph₃P⁺-PEG600-P⁺Ph₃Br⁻) at 100 °C and 27 atm pressure (Patil et al., 2008). Whereas styrene carbonate exhibited high yield (98%), propylene carbonate gave just 60% yield even though the reaction temperature was 120 °C.

Motokura et al. reported the use of silica-supported ammonium and aminopyridinium halides as catalysts (Motokura et al., 2009). Using styrene oxide

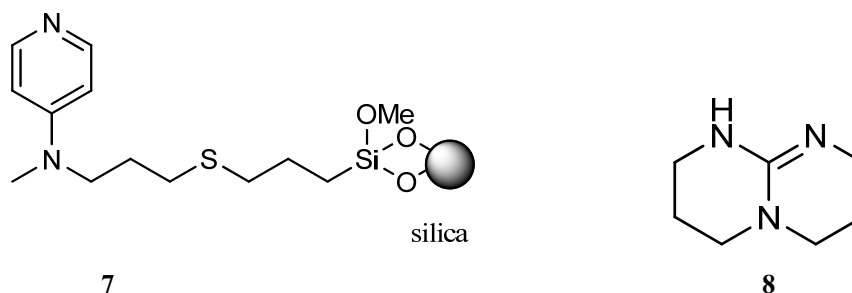
as substrate with one atmosphere CO_2 at 100 °C, 0.9 mol% of catalysts **4** and **5** gave the best yields of styrene carbonate (both 89%). When catalyst **4** could be reused four times without loss of activity, whereas with catalyst **5** yield decreased by 20% after just one reuse. Increasing the amount of catalyst **4** to 3.6 mol % , an 86 % yield was recorded at 30 °C, one atmosphere pressure and 32 h.



Pyridinium salts attached to polystyrene support were also investigated to catalyse the synthesis of cyclic carbonates. After 6 h reaction at 80 °C in N-methylpyrrolidone (NMP) at one atmosphere pressure, poly(4-vinyl-n-butylpyridinium bromide) **6** catalysed the addition of CO_2 to glycidyl phenyl ether (GPE) in quantitative yield. Catalyst **6** was easily removed from the reaction mixture by centrifugation and recycled without remarkable decrease in catalytic activity (Ochiai and Endo, 2007).

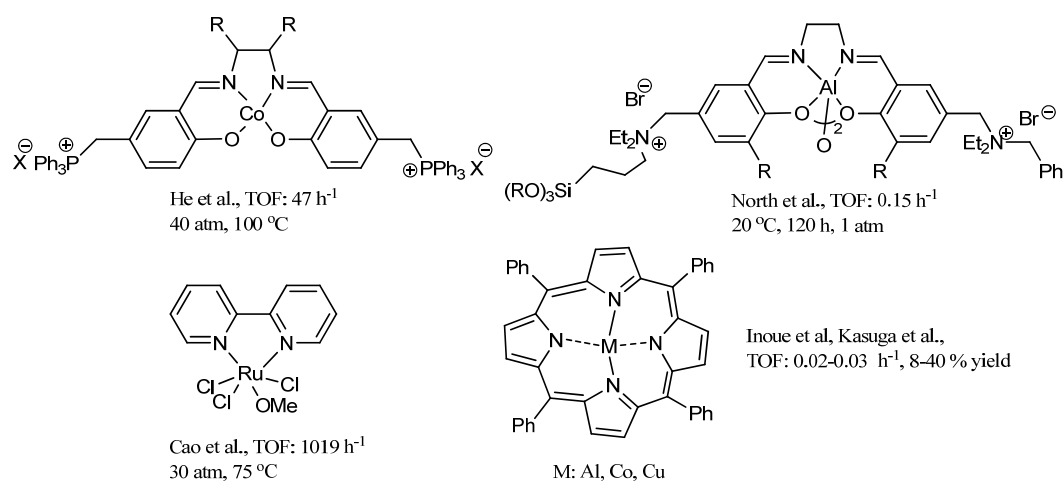


Jones and Shiels studied the use of DMAP and its heterogeneous derivatives immobilized onto silica as catalyst for propylene carbonate formation (Shiels and Jones, 2007). Using 0.4 mol% of DMAP, 85% of conversion was obtained after 4 h at 120 °C under 17 atm of CO_2 . Supported DMAP derivative **7** displayed a conversion of 81% under the optimized conditions.



The use of silica supported and non-supported amines for the synthesis of cyclic carbonates have recently reported by Tsang et al. Under the conditions of 150 °C, 50 atmosphere CO₂ pressure, 24 h and using an excess of 1,5,7-triazabicyclo[4,4,0]-dec-5-ene (TBD) **8** was able to catalyze propylene carbonate formation with 100% yield. TBD covalently attached to silica also catalyze the reaction with 100% yield. To form a carbamate it is essential ring-opening of the epoxide, therefore, amine group was proposed to activate carbon dioxide giving carbamate intermediate (Yu et al., 2010).

Porphyrin and salen complexes are often referred to as highly active catalysts (Scheme 2.21), although the addition of halide salts or amines is usually necessary to realize high activities. Al and Cr are very active central metals, followed by Zn, Co, Ru, etc. (North et al, 2010).



Scheme 2.21 Some porphyrin and salen complexes used for cyclic carbonate formation

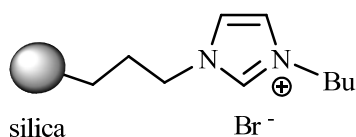
The usage of ionic liquids as reaction media is a current topic of interest in organic synthesis. CO₂ cyclization with oxiranes occurs smoothly in ionic liquids

to succeed higher TONs. This is not surprising because typical ionic liquids are derivatives of quaternary ammonium halides, which are highly effective catalysts for CO₂ cyclization. Furthermore, because some ionic liquids are not soluble in scCO₂, product/catalyst separation through scCO₂ extraction of the product from the reaction mixture is favorable (Ji et al., 2000).

Ionic liquids, or their combination with different metal salts have been studied for the synthesis of cyclic carbonates owing to a simple method for catalyst recovery and product purification. Peng and Deng experimented for the first time, quantitative synthesis of propylene carbonate in the presence of 2.5 mol% of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF₄) **2a**, under the reaction condition of 25 atm pressure of CO₂, 110 °C, 6 h obtained TOF was 6.6 h⁻¹ (Zhang et al., 2006; Sun et al., 2005; Peng and Deng, 2001). Moreover, Kim et al. reported the role of Lewis acid species such as ZnBr₂ with ionic liquids as catalysts and large improvements in the yields was observed, however, high-pressure conditions were still necessary (Kim et al., 2003).

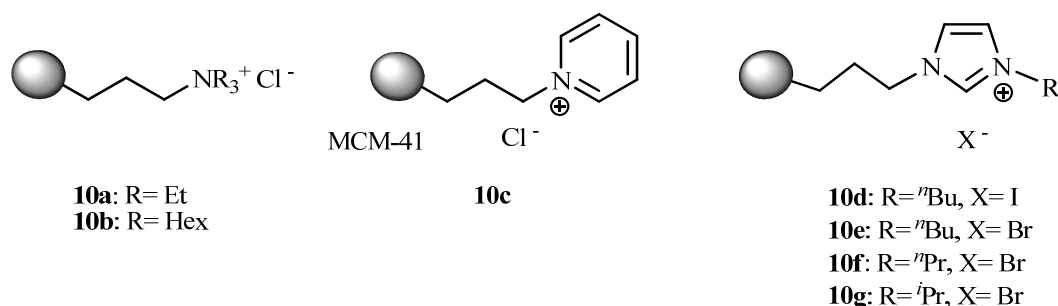
Xia et al. used a similar system combining zinc salts with [BMIm]X (X = Cl, Br, BF₄, PF₆) **2a–d** for the addition of CO₂ to propylene oxide (Li et al., 2004). Reactions were carried out at 100 °C, 1 hour applying a CO₂ pressure of 15 atm. High TOF values (5410–5580 h⁻¹) were observed with catalyst **2b**. Using BF₄ or PF₆ as the ionic liquid counterion (**2a,d**) resulted in minimal catalytic activity, therefore analysing that the nucleophilic nature of the anion is decisive for the formation of the reaction.

In 2006, the same group investigated an immobilized catalytic system consist of ionic liquid and zinc salts (Xiao et al., 2006). Silica supported ionic liquid **9** was prepared via a sol–gel method and used as a catalyst (with ZnCl₂) for the addition of CO₂ to propylene oxide. Standard reaction conditions utilized 10 mL of propylene oxide with CO₂ pressurized to 15 atm and a temperature of 110 °C for one hour. With only zinc chloride as catalyst, no reaction occurred. The effects of amount of ionic liquid, reaction temperature and pressure have significant impact on the yield of propylene carbonate.

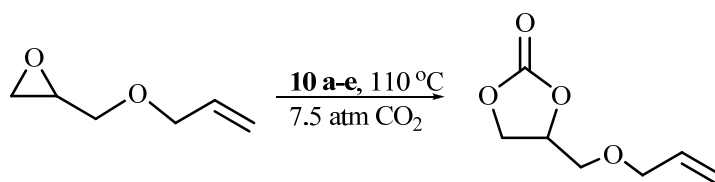


9

Instead of covalently linking the ionic liquid to silica, methylimidazolium derivatives **2a,b,d** were adsorbed onto amorphous silica to form supported ionic liquid catalysts by He and coworkers. (Wang et al., 2007). Selecting PO as substrate, the optimal conditions were found to be 160 °C, 4 h, 80 atm pressure of CO₂ using 1.8 mmol% of **2a,b,d**. Under these conditions, catalysts **2a** and **2a**/silica displayed good yields (>99 and 96% respectively) with >99% selectivity for formation of the cyclic carbonate. It was found that catalyst **2a**/silica could be removed from the reaction by filtration and reused up to four runs.



In 2008, Udayakumar et al. reported quaternary ammonium salts which were covalently bonded via an organic linker to MCM-41 to get catalysts **10a–c**. (Udayakumar et al., 2008). The immobilized salts were promoted the reaction of CO₂ with allylglycidol (Scheme 2.22). The best result was 70% conversion, with 89% selectivity, using 1.0 g of catalyst **10a** in solvent-free conditions at 7.5 atm pressure of CO₂ for 10 h at 110 °C. The use of solvents (dichloromethane or acetonitrile) had a negative impact on the reaction, giving conversions of just 45% and 52% respectively.



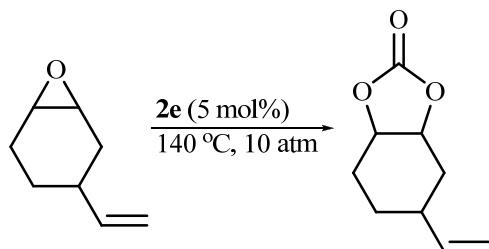
Scheme 2.22. Reaction of CO₂ with allylglycidol catalysed by immobilized catalysts **10a–e**

The same group reported the synthesis of allylglycidyl carbonate using immobilized imidazolium-based ionic liquids, with different forms of silica as support. Likewise, TOFs (4.4 h⁻¹ to 5.3 h⁻¹) were low at 16.5 atm pressure and 110 °C to allylglycidyl ether using compounds **10e–g** supported on MCM-41. If used support was amorphous silica, better TOFs of 13.0 h⁻¹ (for **10d** and **10f**) and 16.2

h^{-1} (**10e**) were obtained. Compound **10e** supported on mesoporous silica exhibited the highest TOF of 32.6 h^{-1} at 35 atm CO_2 pressure (15.5 h^{-1} at 8.6 atm) (Udayakumar et al, 2009a; 2009b; 2009c; 2009d).

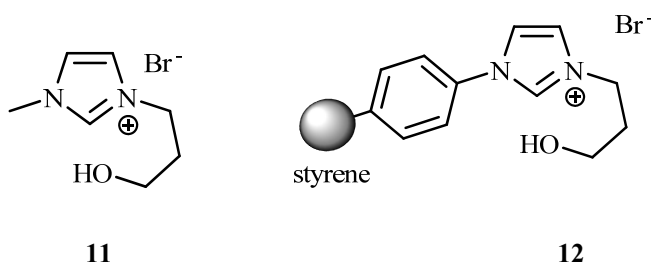
Park et al. worked similar silica-grafted imidazolium-based ionic liquids for the cyclization of epoxides and CO_2 (Han et al., 2009). After three hours, catalyst **10e** gave a 77% yield (TOF: 8 h^{-1}) of allylglycidyl carbonate (Scheme 2.22) at 110°C , 7.5 atm CO_2 pressure and solventless condition. The catalytic system was recyclable up to five times with no significant loss in activity.

Lee et al. investigated the addition of CO_2 to 4-vinyl-cyclohexene oxide in the presence of 1-n-octyl-3-methylimidazolium chloride [OMIm]Cl **2e**, the yield of corresponding cyclic carbonate was recorded as 62% (Scheme 2.23) (Lee et al., 2008).



Scheme 2.23. Addition of CO_2 to epoxide **4** catalysed by [OMIm]Cl **2e**

The recent work of Zhang et al. involved a new series of hydroxyl-functionalized imidazolium-based ionic liquids as active catalysts for the synthesis of propylene carbonate (Sun et al., 2008). 1-(2-Hydroxyethyl)-3-methylimidazoliumbromide **11** [HeMIm]Br was the most active catalyst, giving propylene carbonate in 99% yield at 125°C and 20 atm pressure, resulting a moderate TOF (62 h^{-1}). A supported type (**12**) of the same catalyst system was also improved as a copolymer using styrene (Sun et al., 2009). At a CO_2 pressure of 25 atm and 120°C with 1.6 mol% of catalyst **12**, conversion of 98% was recorded after 4 h. The obtained results were comparable with catalyst **11** and **12**. Hence, due to advantage of catalyst recyclability (six times), catalyst **12** was found more favorable.



The acidic and basic properties of metal oxides make them enable to interact with polarizable species such as CO₂. The adsorption of CO₂ onto metal oxides is a known process with several examples reported in the literature including infrared studies on MgO, CaO, TiO₂, ZnO, and BeO. Activation of CO₂ by metal oxides has been used to catalyse the synthesis of cyclic carbonates has encouraged much work on the improvement of metal oxide catalysts (Dai et al., 2009; Fukuda and Tanabe, 1973; Yates, 1961; Matsushita and Nakata, 1962; Stuart and Whateley, 1965; Yano et al., 1997; Yamaguchi et al., 1999)

MgO was found to convert propylene and styrene oxides into the corresponding cyclic carbonates in 41% and 47% yield respectively at 135 °C and 20 atm pressure; performing moderate TOFs of 14 h⁻¹ and 15 h⁻¹ respectively (Yano et al., 1997).

Several smectite materials containing Mg–Ni mixtures and alkali metals, such as Na, K and Li, were also discovered for propylene carbonate synthesis, exhibiting high activity (81% yield) and selectivity (94%) at 150 °C and 80 atm pressure (Fujita et al., 2002). In 2008, Yuan et al. developed a heterogeneous magnesium-based catalyst system, using a combination of magnesium hydroxychloride [Mg(OH)Cl] and potassium iodide (Yuan et al., 2008). Propylene carbonate was yielded in 98% ratio at 130 °C and 60 atm pressure (TOF : 17 h⁻¹) whereas styrene carbonate was resulted in 75% yield with a lower TOF (8.0 h⁻¹).

Work carried by Davis et al. on ethylene carbonate synthesis experimented many solid catalysts, involving modified zeolites and magnesia (Dorskocil et al., 1999). When the reaction was performed at 150 °C and 100 atm pressure in the presence of a Cs-zeolite catalyst, only 33% of ethylene carbonate formed. Later results showed that at 80 atm pressure the yield dropped further to 19% (Dorskocil and Davis, 1999). On the contrary, in the Sakakura's work cesium-phosphorous-silicon mixed oxide (Cs–P–Si) resulted in quantitative yields for propylene carbonate synthesis at 80 atm pressure and 200 °C (Yasuda et al., 2006). Moreover, in a flow reactor, the Cs–P–Si catalyst also exhibited greater than 50% yields and quantitative selectivity.

Titanosilicate molecular sieves have been applied as catalysts in combination with TBAB or DMAP, and high yields (71–85%) of epichlorohydrin carbonate were recorded at 120 °C and 7 atm pressure; this catalyst system demonstrated moderate to high TOFs (168–790 h⁻¹) (Srivastava et al., 2003). Conversely, using mesoporous ordered silicates, such as titanium-MCM-41, gave

high catalytic activity for propylene carbonate synthesis (yield 90%), despite only a moderate TOF (36 h^{-1}) was achieved in the identical conditions (Srivastava et al., 2006). However, changing terminal epoxides, the product selectivity decreased because the reaction gave a mixture of cyclic carbonate, diols and ethers.

In 2007, Bhanage investigated that silica supported-poly(4-vinylpyridine) ($\text{SiO}_2\text{-PVP}$) could be used to catalyse the addition of CO_2 to terminal epoxides. Propylene carbonate was obtained 93% yield at 150°C and 54 atm pressure, with a moderate TOF (17 h^{-1}). Even though this was dependent on the degree of pyridine association into the support. Styrene and epichlorohydrin carbonate were also synthesized with yields greater than 84% (Jagtap et al., 2007).

A zinc-based hydroxyapatite catalyst exhibited high yields of styrene carbonate (89%), in the presence of DMAP as a cocatalyst; the process was performed at 100 atm pressure and 100°C and TOF was calculated 308 h^{-1} (Mori et al., 2005) (Figure 2.11). Baiker et al. discovered the use of zinc-based catalysts supported on silica combination with TBAB as cocatalyst for the synthesis of propylene carbonate under solvent-free conditions (Ramin et al., 2006).

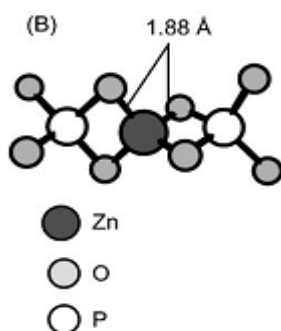


Figure 2.11 Schematic representation of Zn-based hydroxyapatite

Dai and Au have recently demonstrated that a composite oxide material composed of zinc, aluminium and a third metal could be used for the synthesis of cyclic carbonates from CO_2 and epoxides (Dai et al., 2010). The highest yield (89%) for the reaction of CO_2 with propylene oxide was achieved after 12 h using Zn-Mg-Al-O under 25 atm pressure of CO_2 at 120°C with triethylamine as an cocatalyst. This catalyst was reused five times. The method of catalyst preparation (temperature and pH) were determined important factors for its subsequent activity. It was proposed that catalyst has to involve active sites contain both

Lewis acidic (Al) and basic (ZnMg) groups, essential for the concurrent activation of epoxide and carbon dioxide.

Catalyst/product separation is assisted by utilizing phase separation. Despite the fact that, the starting materials (oxirane and scCO_2) form a homogeneous mixture, the resultant carbonate is not soluble in scCO_2 . Therefore, the product is automatically separated from the reaction mixture by preserving supercritical conditions in the upper phase (Fig. 2.12). As a consequence, the development of a scCO_2 -soluble catalyst would result in facile catalyst/product separation. Perfluorinated phosphonium salts is applicable due to the remaining in the upper CO_2 phase and recyclability.

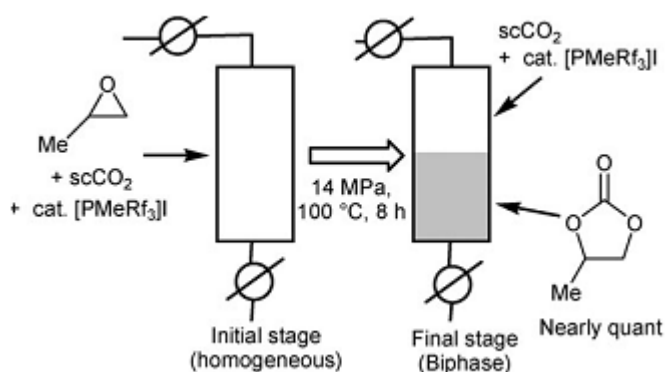
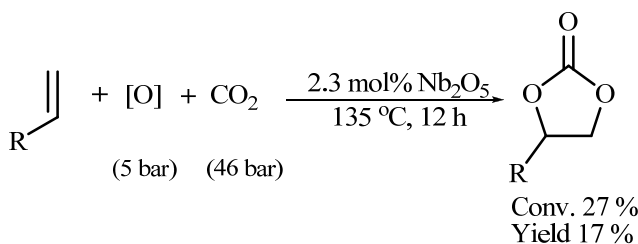


Figure 2.12. Catalyst-product separation by phase separation.

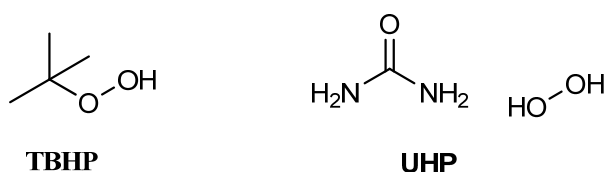
2.4.3.2 Reactions with olefins and oxidants

Oxidative addition of CO_2 to olefins is an alternative single-step route for the synthesis of cyclic carbonates (Scheme 2.24). In the presence of molecular oxygen, niobium oxide catalysts performed limited activity for styrene carbonate synthesis, otherwise, the process needed DMF as the solvent, and the selectivity for the carbonate was rather low. In addition, high pressures and temperatures were demanded (50 atm, 125 °C, 5 h, 27% conversion) (Aresta et al., 2000; Eghbali and Li, 2007).



Scheme 2.24 Synthesis of cyclic carbonates via olefins and oxidants

The oxidative carboxylation of styrene described by Arai et al carrying out in an ionic liquid in the presence of TBAB and tert-butylhydroperoxide (TBHP) as the oxidizing agent, nonetheless, pressurized CO₂ and an elevated temperature were still required to succeed in the transformation (10 atm, 80 °C, 6 h, 38% yield) (Sun et al., 2005).



Scheme 2.25 The chemical structure of TBHP and UHP

Arai et al. also depicted a second system for the direct synthesis of styrene carbonate from styrene without isolation of the intermediate epoxide (Sun et al., 2005b). By using a one-pot catalytic system consisting of gold on silica, with zinc bromide and TBAB, and TBHP as oxidant, styrene carbonate could be successfully formed in the presence of 80 atm pressure of CO₂ at 80 °C for 4 h. With 2.5 mol% of ZnBr₂ and 5 mol% of TBAB, 31–37% of styrene carbonate could be obtained using 1–8 weight % loading of gold on silica. In addition, some styrene oxide and benzaldehyde were consisted.

Former work from the same group highlighted the same oxidation/addition process instead of the zinc salt, TBHP used as oxidant and TBAB as catalyst (Sun et al., 2004). A yield of 38% of styrene carbonate was reported after six hours at 10 atm pressure of CO₂ and 80 °C. with 11.6 mol% TBAB. Extending the reaction time did not multiply the yields. On the contrary, at a higher pressure (15 atm) of CO₂, yields were lowered,. Using either hydrogen peroxide or oxygen in place of

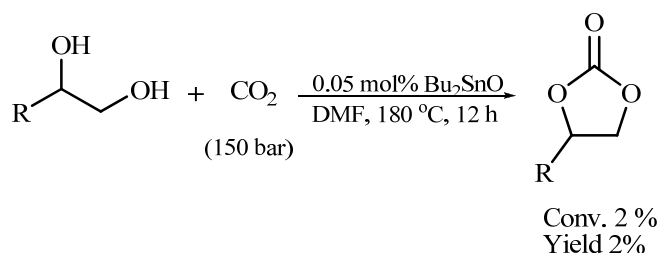
TBHP significantly decreased the amount of styrene carbonate and increased the amount of benzaldehyde.

Qiao and Yokoyama established a multi-step one-pot synthesis of styrene carbonate starting from styrene under a pressurized CO₂ atmosphere in an ionic liquid medium ([BMIm]BF₄, **2a**) with urea hydrogen peroxide (UHP) as oxidant and methyltrioxorhenium (MTO) as oxidation catalyst (Ono et al., 2007). The highest yield of styrene carbonate was 83% (the remainder consisting of styrene oxide), succeeded by using 30 atm CO₂ at 110 °C in the ionic liquid with 2 mol% MTO in the presence of a zinc-based cocatalyst (Zn[EMIm]₂Br₄) and UHP.

2.4.3.3 Reactions with diols (Du et al., 2005; Huang et al., 2007; 2008)

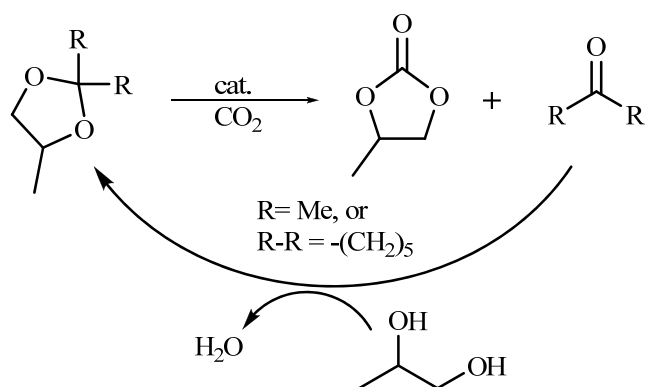
The synthesis of cyclic carbonates from diols and urea using metal oxides as catalysts was reported by Sun et al (Zhang et al., 2006). When zinc oxide used as catalyst, 93% yield of ethylene carbonate was obtained at 150 °C under a CO₂ atmosphere and 3 h. With other diols were also observed satisfactory results under the same conditions. Prolonging the reaction time gave higher yields of ethylene carbonate, whilst diminished reaction times formed higher levels of cyclic carbamate which was therefore concluded to be an intermediate in the mechanism.

Using CO₂ and 1,2-propylene glycol, Wei et al. examined the synthesis of propylene carbonate in the presence of anhydrous zinc acetate as catalyst (Huang et al., 2007). The reaction conditions were 170 °C and 100 atm pressure, using acetonitrile as solvent however, calculated TOF value was very low, 0.8 h⁻¹. The reason to select acetonitrile as the reaction solvent was its applicability as dehydrating agent. Consequently, formed water is absorbed by the solvent during the reaction.



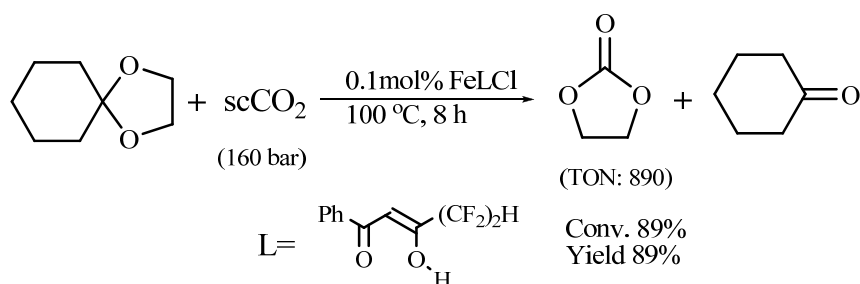
Scheme 2.26 Synthesis of cyclic carbonate from propylene glycol

He et al. studied with tin catalysts in supercritical CO₂ for the synthesis of propylene carbonate directly from propylene glycol (Scheme 2.26). When dibutyltin oxide or dibutyltin dimethoxide is used in the presence of DMF, low propylene carbonate conversion is reported after 12 h at 180 °C under 150 atm pressure of CO₂. In this study, the formation of propylene carbonate was usually low (no greater than 2%) with the best result described for 0.05 mmol% dibutyltin dimethoxide, which gave only 5.7 h⁻¹ TOF. To get highest yield used 5 mol% of the acetal derived from cyclohexanone and propylene glycol was added as a dehydrated form of propylene glycol. Scheme 2.27 illustrates a suggested catalytic cycle in which the acetal reacts with CO₂ in the presence of the tin catalyst to form the cyclic carbonate and reform the ketone which constitute cyclic carbonate via joining to another propylene glycol molecule (Du et al., 2005).



Scheme 2.27. Reaction of CO₂ with propylene glycol derived acetals

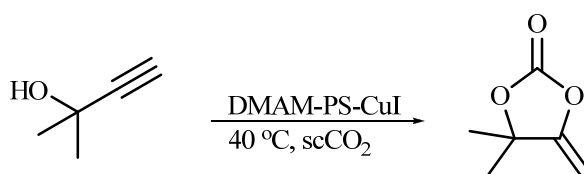
2.4.3.4 Reactions with cyclic ketals (Aresta et al., 2003)



Scheme 2.28 Synthesis of cyclic carbonates via cyclic ketals

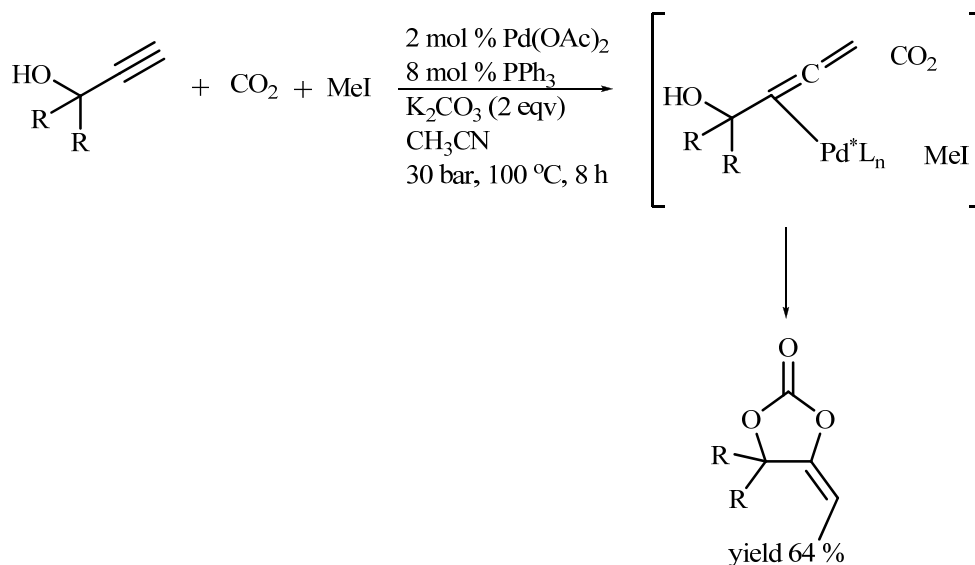
2.4.3.4 Reactions with propargyl alcohols

In 2008, Jiang et al. used a solid supported copper iodide catalyst (CuI-[(dimethylamino)methyl-polystyrene; DMAM-PS) for the carboxylative cyclization of propargylic alcohols in supercritical CO₂ (Scheme 2.29) (Jiang et al., 2008). High yield (99%) was obtained at 40 °C and 14 atm pressure, whereas TOF value was low, 1.4 h⁻¹. Recycling studies indicated that the supported CuI catalyst could be reused without significant loss of activity over five reactions.



Scheme 2.29. Synthesis of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one catalysed by solid-supported (DMAM-PS) CuI catalyst.

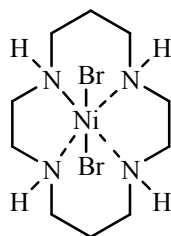
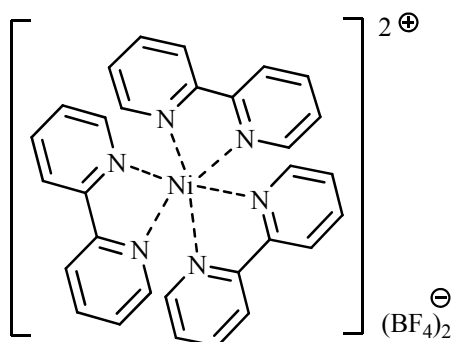
The synthesis of alkene carbonates are depicted by Pd catalyst with propargyl alcohols in the presence of methyl iodide (Scheme 2.30) (Yamada et al., 2007; Kayaki et al., 2007).



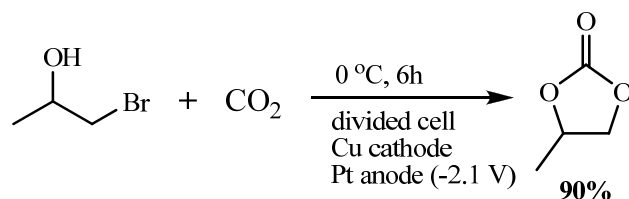
Scheme 2.30 Synthesis of cyclic carbonates from propargylic alcohol

2.4.3.5 Electrochemical synthesis of cyclic carbonates

At room temperature and atmospheric pressure, the electrochemical coalescence of CO₂ into epoxides in the presence of Ni catalyst, **13**, has been described (Tascadda and Dunăch, 1995). The reaction was performed in a single-division electrolysis cell, using DMF as solvent and potassium bromide as supporting electrolyte. Catalyst **13** exhibited a TOF of 1.3 h⁻¹ for the synthesis of styrene carbonate, applying a magnesium rod for the anode and stainless-steel as the cathode. For ortho-halo-substituted styrene oxides, the other Ni complex has bipyridine ligands, **14**, was demonstrated comparable results for the electrochemical addition of CO₂ to under the same reaction conditions (Tascadda and Dunăch, 2000). Yuan et al. used a 0.05 M solution of TBAB in DMF as electrolyte in a cell at room temperature and under 40 atm CO₂ pressure (Wang, et al., 2007). It is noticeable that the electrodes has significant effect to get good results. Depending on the electrodes, obtained yields were between 67-98%. Other terminal epoxides also gave admirable yields of cyclic carbonates under the same conditions.

**13****14**

The synthesis of cyclic carbonates from primary and secondary alcohols via leaving group at the β-position have been reported by Rossi et al. using an electrochemical process to activate CO₂ (Scheme 2.31). The yield of propylene carbonate was 90%, using a divided cell system with a copper cathode and a palladium anode (Rossi et al, 1997).

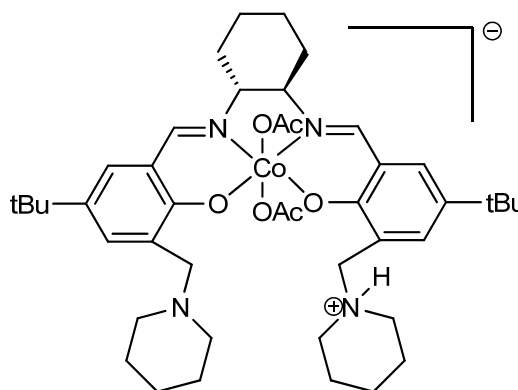


Scheme 2.31 Synthesis of propylene carbonate using electrochemically activated CO_2

Deng et al. demonstrated that ionic liquids could also be used for the electrochemical synthesis of cyclic carbonates from CO_2 and epoxides (Yang et al., 2002; Zhang et al., 2006). With this method, propylene carbonate was isolated by 92% conversion in the presence of $[\text{BMIm}][\text{BF}_4]$, **2a** at room temperature and atmospheric pressure.

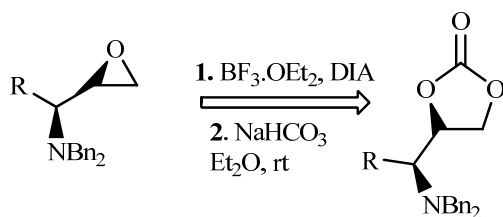
2.4.3.6 Asymmetric reactions

Optically active Co–salen complexes can catalyze asymmetric carbonate synthesis (Scheme 2.32). The reaction is carried out by the kinetic resolution of racemic oxiranes. Reactions of substrates having functional groups, such as amino-epoxides, conclude the higher enantiomeric excesses (ee).



Scheme 2.32 An active ionic Salen Co complex for the synthesis asymmetric carbonates

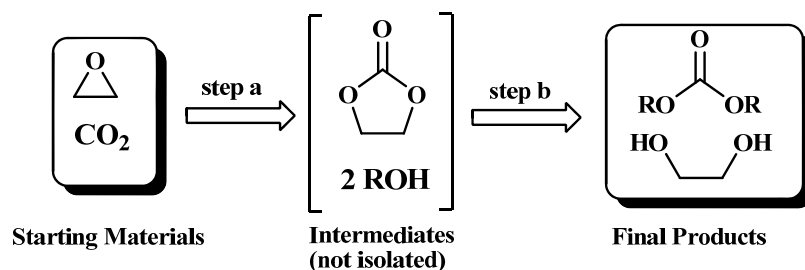
The highest ee has been obtained (92%) using N-carbazoylmethyloxirane as a substrate (92) (Concellon et al., 2007) (Scheme 2.33).



Scheme 2.33 Synthesis of (4R,1S)-4-(1-Aminoalkyl)-2-oxo-1,3-dioxolanes from N-carbazoyl-methyloxirane.

2.5 DMC synthesis via cyclic carbonates (EG and DMC synthesis)

The reaction proceeds over cyclic carbonates as intermediate, and then an ester exchange with alcohols is occurred (Scheme 2.34). In general, basic compounds catalyze both step **a** and step **b**. The advantages of this one-pot procedure, by comparison with the direct synthesis of DMC from MeOH and CO₂, is that eliminating to use drying agents. Conversely, the disadvantages are that requiring excess alcohol and the possibility of side reactions (such as ethylene glycol, EG) between the oxirane and the alcohol (Kishimoto and Ogawa, 2004).



Scheme 2.34 DMC synthesis from cyclic carbonates

2.6 Aim of the Study

As can be seen from the above examples, chemical fixation of CO₂ in the presence of ionic liquids as catalysts, have been receiving increased attention in literature, since CO₂ is green, abundant and cheap C1 source of producing lots of valuable chemicals. Instead of metal complexes using ionic liquids is more advantage in the view of environmental aspects. Since use of metal complexes as catalyst needs generally an additional base to activate the reaction. For the chemical conversion of CO₂ to cyclic carbonate it is known from the literature that

the reaction proceeds with a Lewis acid center and a base (nucleophile). However ionic liquids have two parts: cationic and anionic sides. In the ionic liquid structure cationic side acts as a Lewis acid center and anionic side acts as a Lewis base. Therefore without any additional cocatalyst the reaction could be proceed.

The recent researches focused on ionic liquids which have imidazolium structure due to ease of synthesis, air and moisture stability. The immobilization of the catalyst onto a solid support is most promising methodology for an efficient continuous flow process based on active and selective catalysts. Trialkoxysilyl functionalized ionic liquids are used for the preparation of supported compounds but there is a few study related to **imeo** [1-(3-triethoxysilyl)propylimidazoline] based compounds.

In order to gain a better understanding of the effect the length of chain, functional group and anion on the structure and the reactivity of the ionic liquids, we synthesized the new type of ionic compounds. Also immobilization of the catalyst is an important aspect from the standpoint of industrial usage. We prepared heterogeneous catalytic systems using ionic liquids to investigate the effect of different type of supporting materials on the structure and catalytic activity. These ionic compounds were evaluated as catalysts for the coupling of epoxides with CO₂.

3. EXPERIMENTAL

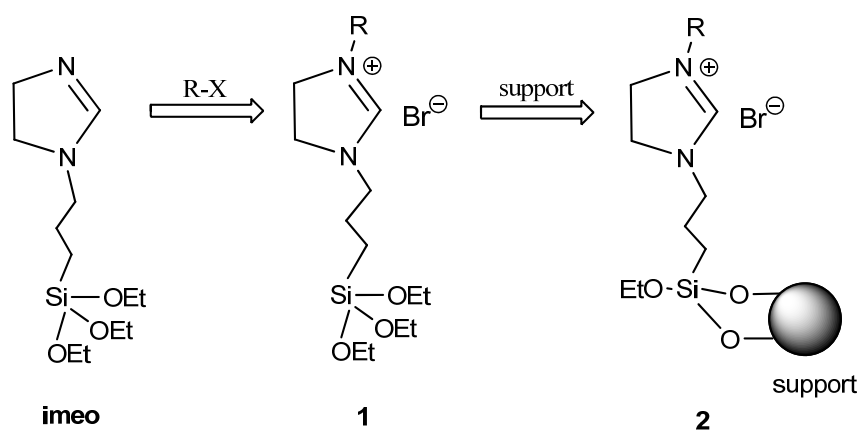
Reactions involving air-sensitive components were performed by using Schlenk-type flasks under argon atmosphere and high vacuum-line techniques. The glass equipment was heated under vacuum in order to remove oxygen and moisture and then they were filled with argon. The solvents were analytical grade and distilled under argon atmosphere from sodium (toluene, diethyl ether, hexane, tetrahydrofuran), (diphosphor pentaoxide) P_2O_5 (dichloromethane).

Reagents: 1-[3-(triethoxysilyl)propyl]-2-imidazoline (imeo) was purchased from ABCR and used after distillation. Alkyl bromides (ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, 2-methyl propyl, 2-hydroxyethyl, propionitrile, methoxyethyl), dibromoethane, 1,4-dibromobutane, 1,9-dibromononane, 1,3-propanesultone were purchased from Alfa Aesar. Epoxides (propylene oxide, epoxy butane, epichlorohydrine, styrene oxide and cyclohexene oxide), DMAP (dimethylaminopyridine), 1,1-diiodomethane, ammonium tetrafluoroborate, ammonium hexafluorophosphate, potassium iodide, tetraethoxysilane, silica (Davisil), silica nanopowder, montmorillonite-K10 (MK-10) were purchased from Aldrich and used as received. Toluene, tetrahydrofuran, hexane, dichloromethane, ethanol, and isopropylalcohol were obtained from Merck.

Instruments: ^1H and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer. J values are given in Hz. X-ray diffractograms were recorded on a Phillips X'Pert Pro diffractometer. Nitrogen adsorption-desorption isotherms were obtained at 77 °K using Micromeritics ASAP 2010 apparatus. TG measurements were performed on a Perkin Elmer Diamond TG/DTA Instrument. FTIR Spectra were recorded on a Perkin Elmer Spectrum 100 series. AFM measurements were carried out at room temperature and ambient conditions by using Ambios Q-Scope 250 instrument. SEM observations were performed using Phillips XL-30S FEG microscope. Elemental analysis of samples were done using on a LECO CHNS model 932 elemental analyzer. AAS determinations of metals carried out Solaar AA Spectrometer Thermo Elemental. Catalytic tests performed in a PARR 4843 50 mL stainless pressure reactor.

3.1 Synthesis of imidazolinium salts (1a-1u)

Imeo (2 mL, 7.3 mmol) and alkyl bromide (7.3 mmol) were heated at 75 °C for 24 h under Ar atmosphere. After the reaction, the mixture was cooled to room temperature and the viscous liquid obtained was washed with dry n-hexane and/or dry diethyl ether (10 mL $\times$ 3) and the volatiles were removed under reduced pressure (Yamaguchi et al., 2005).



Scheme 3.1 Experimental route for the preparation **1** and **2** type compounds

Table 3.1 Yield of the synthesized **1** type compounds.

R	Comp.	Yield	R	Comp.	Yield ^a
-C ₂ H ₅	1a	90	-C ₁₂ H ₂₅	1k	65
-C ₃ H ₇	1b	95	-C ₄ H ₉ (iso-propyl)	1l	77
-C ₄ H ₉	1c	87	-(CH ₂) ₉ -(imeo)	1m	53
-C ₅ H ₁₁	1d	78	-(CH ₂) ₂ -(imeo)	1n	60
-C ₆ H ₁₃	1e	80	-(CH ₂) ₄ -(imeo)	1o	50
-C ₇ H ₁₅	1f	75	-(CH ₂) ₉ -(imeo)	1p	64
-C ₈ H ₁₇	1g	82	-(CH ₂) ₂ CN	1r	86
-C ₉ H ₁₉	1h	74	-(CH ₂) ₂ OH	1s	77
-C ₁₀ H ₂₁	1i	70	-(CH ₂) ₂ OMe	1t	82
-C ₁₁ H ₂₃	1j	71	-(CH ₂) ₃ SO ₃ ⁻	1u	93

3.2 Synthesis of immobilized ILs (2A-2E)

For immobilization experiments 1,4-[3-triethoxysilylpropyl]butane dibromide (**1o**) was used because of the fact that **1o** exhibited higher catalytic activity for the chemical fixation of CO₂ and terminal epoxides to cyclic carbonate. Five different supporting material was chosen for immobilization studies (**2A-E**).

3.2.1 Preparation of 2A:

Amorphous silica (Davisil grade, surface area: 480 m²/g; pore size: 0.75 cm³/g; particle size: 35-60 mesh) (3g) treated with 50 mL 0.01 M acetic acid solution in ultrasonic bath for 1 h at ambient temperature. Then pre-treated silica was washed with ultra pure water until a pH of 7 was obtained and dried under vacuo at 200 °C for 2 days (Horniakova et al., 2004).

Pretreated SiO₂ (3.0 g) was vigorously stirred with a chloroform solution of **1o** (0.24 M, 50 mL) for 24 h under reflux conditions (bath temp. 353 K) (Yamaguchi et al., 2005). The solid was separated by the filtration, washed with n-heptane (50 mL) and acetonitrile (50 mL), and then dried in vacuo to afford **2A** as a white solid. Elemental analysis of **2A** revealed that 228 µmol of ionic liquid fragments per gram of **2A** existed. IR: (KBr disk) 2942, 2892 cm⁻¹ ν(C-H); 1658 cm⁻¹ ν(C=N). Elemental anal. Found (%) C :11.13, H: 2.319, N: 3.00.

3.2.2 Preparation of 2B:

Silica nanopowder (3 g) was vigorously stirred with a chloroform solution of **1o** (0.24 M, 50 mL) for 24 h under reflux conditions (bath temp. 353 K). The solid was separated by the filtration, washed with dichloromethane (30 mL), acetonitrile (30 mL) and n-heptane (50 mL); then dried in vacuo to afford **2B** as a white solid. Elemental analysis of **2B** revealed that 661 µmol of ionic liquid fragments per gram of **2B** existed. IR: (KBr disk) 2939, 2874 cm⁻¹ ν(C-H); 1657 cm⁻¹ ν(C=N). Elemental anal. found (%) C 13.09, H: 2.91, N: 3.69.

3.2.3 Preparation of 2C:

The same method used for the preparation of **2B** was applied. Instead of silica nanopowder MK-10 was used as a supporting material. Elemental analysis of **2C** revealed that 391 μmol of ionic liquid fragments per gram of **2C** existed. IR: (KBr disk) 2940 cm^{-1} $\nu(\text{C-H})$; 1655 cm^{-1} $\nu(\text{C=N})$. Elemental anal. found (%) C: 10.18, H: 2.64, N: 2.19.

3.2.4 Preparation of 2D:

Synthesis of silica-gel-confined ionic-liquid catalysts: A mixture of tetraethoxysilane (TEOS, 20 mL), EtOH (5 mL) and water (6mL) was heated to $60\text{ }^{\circ}\text{C}$ and then ionic liquids (5 g) were immediately transferred into the TEOS. After the formation of a clear and homogeneous liquid mixture, hydrochloric acid (5m, 5 mL) was added and the mixture gradually coagulated. After aging at $60\text{ }^{\circ}\text{C}$ for 12 h, the resultant solid material was dried in vacuo at $150\text{ }^{\circ}\text{C}$ for 3 h and 8 g of solid sample was obtained. IR: (KBr disk) $2984, 2962\text{ cm}^{-1}$ $\nu(\text{C-H})$; 1659 cm^{-1} $\nu(\text{C=N})$. Elemental anal. found (%) C : 10.36, H: 2.97, N: 2.55.

3.2.5 Preparation of 2E:

The magnetite nanoparticles were prepared according to Massart's method (Massart , 1981). Briefly, 11.6 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 4.3 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were mixed in 400 mL of degassed water. The mixture was heated at $85\text{ }^{\circ}\text{C}$, and then 15 mL of concentrated ammonia (28%) were added quickly. The heating was continued for another 30 min. After cooling to room temperature, the solution was decanted and the black precipitate was washed five times with 200 mL water. The black magnetite nanoparticles were suspended in 500 mL of ethanol (95%) and sonicated for 60 min. The resulted suspension was mechanically stirred and a solution of 100 mL ethanol (95%) containing 6 mmol of the desired functionalized ionic liquid and 2 mL of concentrated ammonia (28%) were added. Stirring under N_2 was continued for 36 h. The modified magnetite nanoparticles were magnetically separated and washed three times with 100 mL of ethanol (95%) and then dissolved in 400 mL of methanol and stirred mechanically for 30

min. 100 mL of ether were added and the modified nanoparticles were magnetically separated, washed with 100 mL of ether and dried under a vacuum of 0.2 mmHg for 24 h. Brownish-black powder was obtained (Abu-Reziq et al., 2007). Elemental analysis of **2E** revealed that 132 μmol of ionic liquid fragments per gram of **2E** existed. IR: (KBr disk) 2974, 2929 cm^{-1} $\nu(\text{C-H})$; 1651 cm^{-1} $\nu(\text{C=N})$. Elemental Anal. found (%) C : 3.13, H: 1.04, N: 0.74.

3.3 General Procedure for the Cycloaddition of Epoxides to CO_2

A 50 mL stainless pressure reactor was charged with ionic compound **1** or supported ionic compound **2** (0.2 mmol), epoxide (20 mmol). The reaction vessel was placed under a constant pressure of carbon dioxide for 1 min. to allow the system to equilibrate and CO_2 was charged into the autoclave with desired pressure then heated to the desired temperature. The vessel was then cooled to 5-10 $^{\circ}\text{C}$ in ice bath after the expiration of the desired time of reaction. The pressure was released, then, the excess gases were vented. The yields of epoxides to corresponding cyclic carbonates were determined by comparing the ratio of product to substrate in the ^1H NMR spectrum of an aliquot of the reaction mixture.

4 RESULT AND DISCUSSION

4.1 Synthesis and Characterization of the Compounds

As can be seen from chapter 2 the chemical fixation of carbon dioxide is very important from point of chemistry and environmental considerations. Production of cyclic carbonates from the carbon dioxide as carbon source is very attractive because there are a number of usages of these products. On the other hand, carbon dioxide is thermodynamically stable and inert molecule for the fixation, but this aspect can be altered using various catalysts for the activation of it.

Up to now, several catalytic systems have been developed for this coupling reaction. A greater knowledge of the catalytic cycle has facilitated the design of new catalysts including the ILs. By increasing the electron density around the cationic center $-(C_2)$ the rate of the reaction can enhance. Therefore we are interested in extending this investigation by studying the differences in catalytic activity between the saturated imidazolium systems, in other words 1-(3-triethoxysilylpropyl)imidazoline derived salts were chosen. Therefore, the main aim was to synthesize active compounds in either homogeneous and heterogeneous phases.

The synthetic route used for the preparation of ionic liquids and supported ionic liquids derived from **imeo**, **1** and **2** are shown in Scheme 3.1.

In this context, ionic liquids from **imeo** (**1**) have been prepared and screened for the chemical fixation of CO₂ with epoxides then the most active compound (**1o**) was immobilized to five different supporting materials.

4.1.1 Synthesis and characterization of imidazolinium salts, (**1**).

Imidazolinium salts **1** were prepared in moderate to good yields (*ca.* 50%-96%) by quarternization of the **imeo** using alkyl bromides as the reactant at 75 °C. The crude oils **1** were washed with dry diethyl ether and dry hexane to remove traces of the unreacted reactants.

The salts (**1**) have been fully characterized by ^1H and ^{13}C NMR spectroscopy and detailed NMR data were given in Figure 4.1-4.19. ^1H NMR spectra of the salts showed sharp signals for the characteristic signals of imidazolinium C2-*H* in the region of 9.50 ppm. The ^{13}C NMR data for **1** are consistent with the proposed structures. In the ^{13}C NMR (CDCl_3) the central (NCHN-) imidazolinium carbon resonances in the region of 158 ppm. Details of the synthesis and product characterization are given in the experimental section.

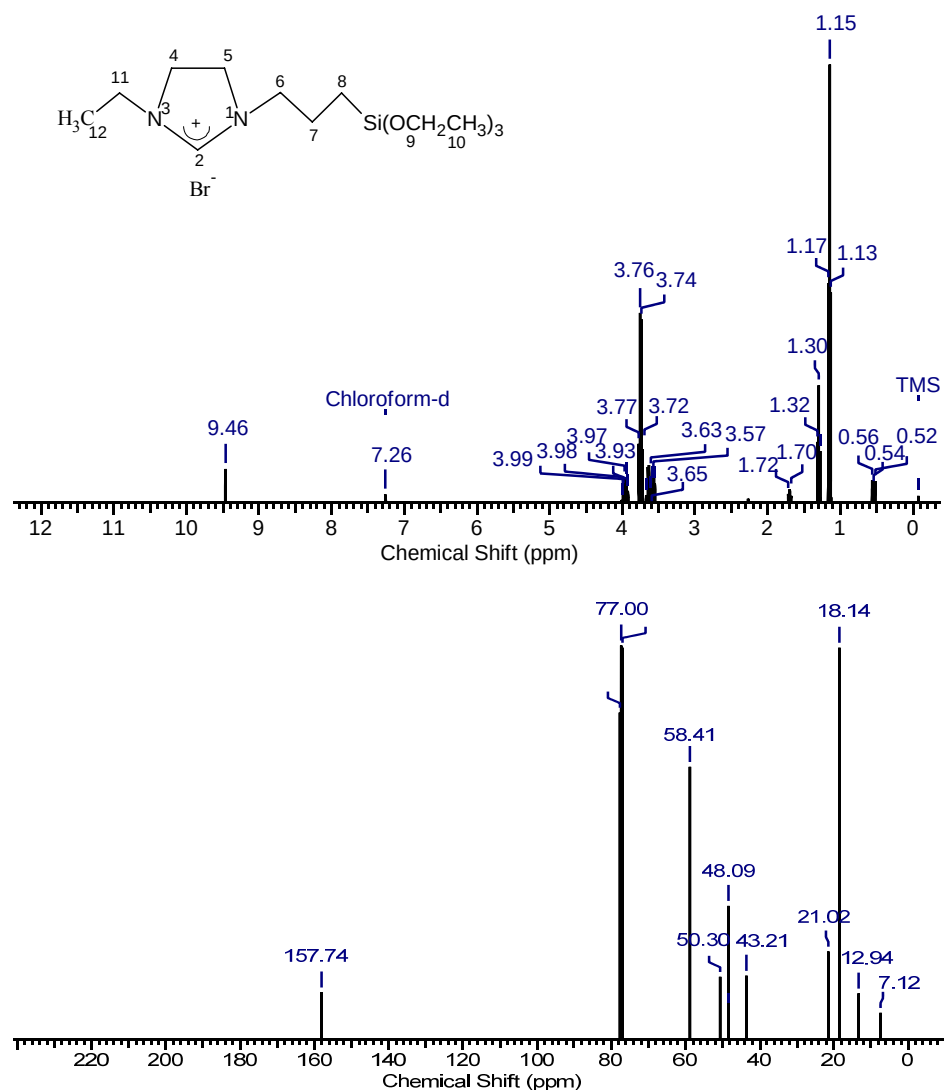


Figure 4.1 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1a**.

Table 4.1 Selected ^1H and ^{13}C NMR data of **1a**.

<i>Numbers of atoms</i>	<i>^1H NMR (δ ppm)</i>	<i>J (Hz)</i>	<i>^{13}C NMR (δ ppm)</i>
2	9.46 (1H, s)	-	157.7
4, 5	3.95 (4H, m)	-	48.1, 48.2
6	3.63 (2H, t)	7.4	50.3
7	0.54 (2H, m)	-	12.9
8	1.71 (2H, m)	-	21.0
9	3.75 (6H, m)	-	58.4
10	1.15 (9H, m)	-	18.1
11	3.57 (2H, k)	7.2	43.2
12	1.37 (3H, m)	-	7.1

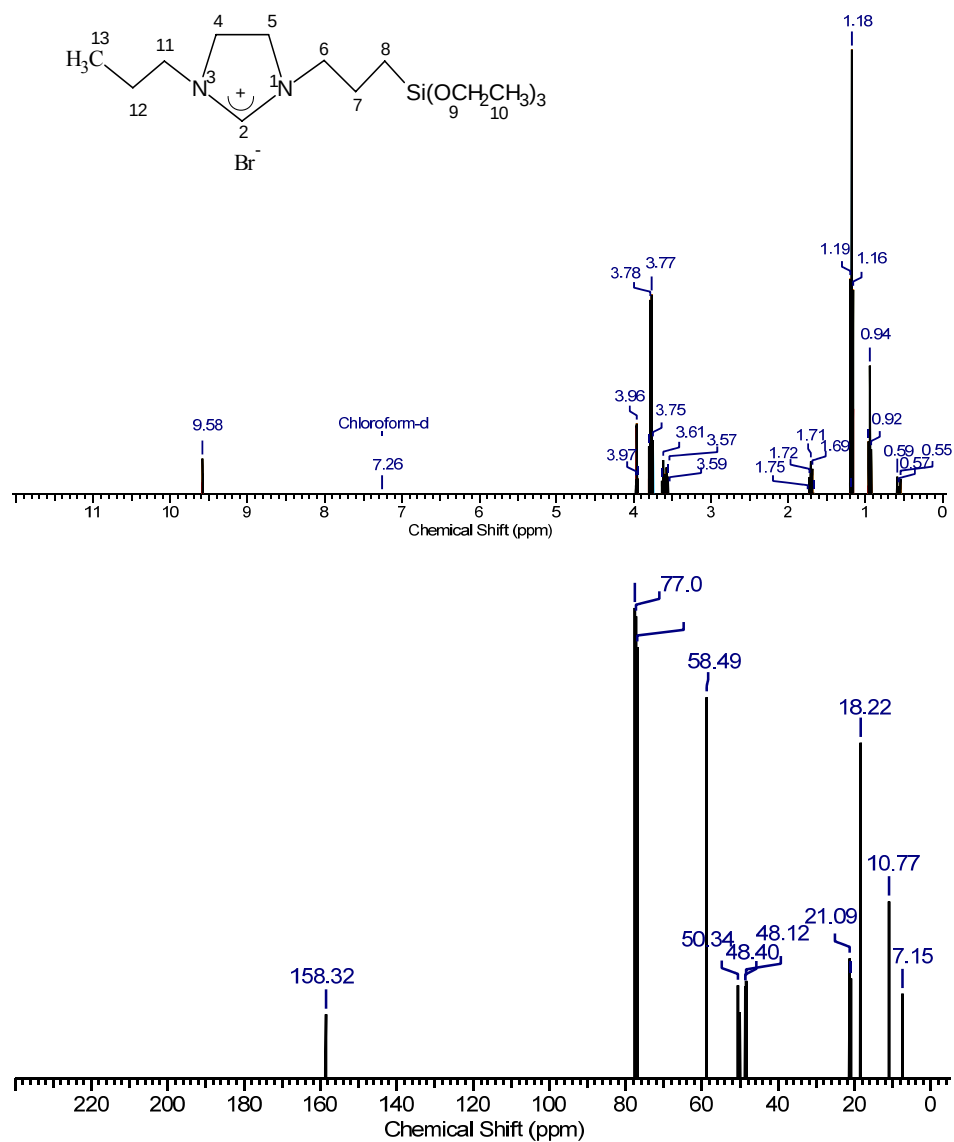


Figure 4.2 (a) ¹H NMR, (b) ¹³C NMR spectra of **1b**

Table 4.2 Selected ¹H and ¹³C NMR data of **1b**

Numbers of atoms	¹ H NMR (δ ppm)	J (Hz)	¹³ C NMR (δ ppm)
2	9.58 (1H, s)	-	158.3
4, 5	3.96 (4H, m)	-	49.8, 50.3
6, 11	3.60 (4H, m)	-	48.1, 48.4
7, 12	1.71 (4H, m)	-	20.9, 21.1
8	0.57 (2H, m)	-	7.2
9	3.78 (6H, k)	6.9	58.5
10	1.18 (9H, m)	-	18.2
13	0.94 (3H, t)	7.6	10.8

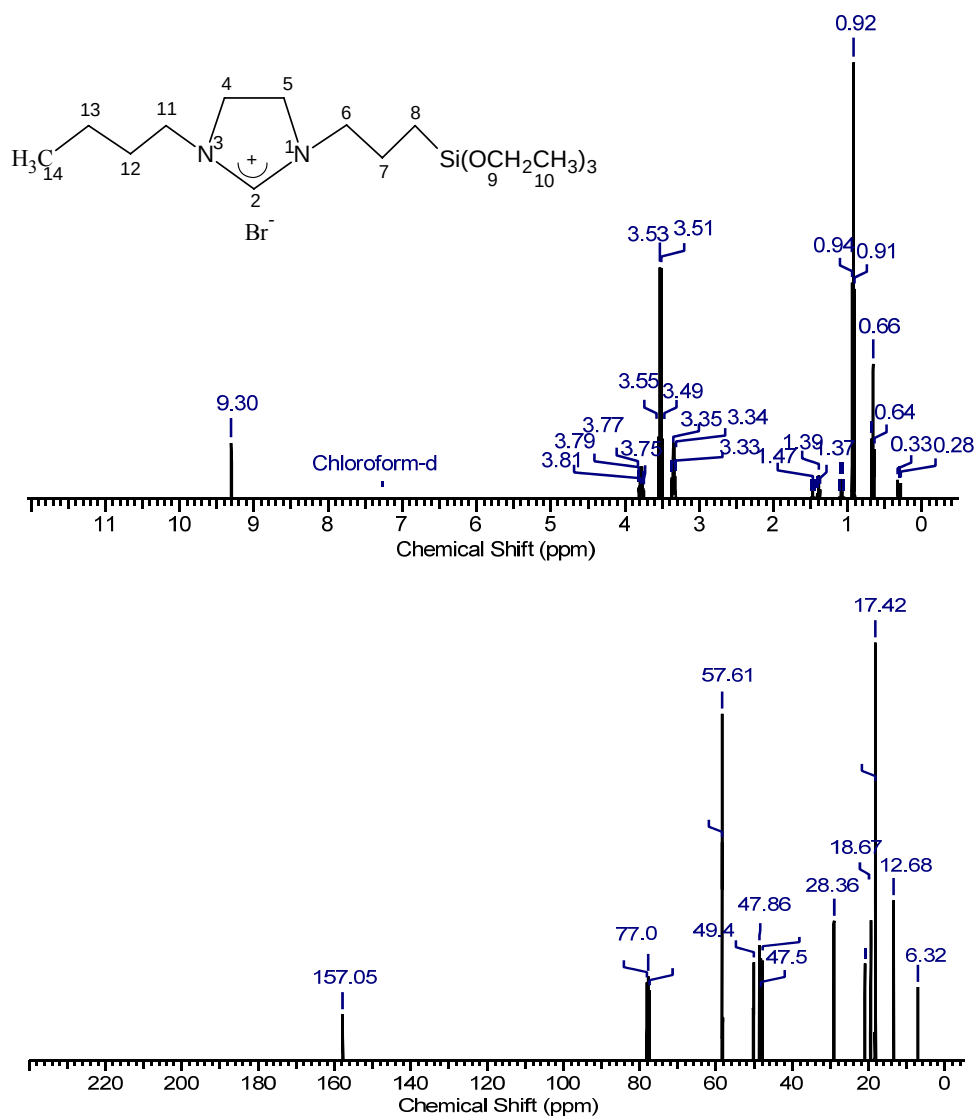


Figure 4.3(a) ¹H NMR, (b) ¹³C NMR spectra of **1c**

Table 4.3 Selected ¹H and ¹³C NMR data of **1c**.

Numbers of atoms	¹ H NMR (δ ppm)	J (Hz)	¹³ C NMR (δ ppm)
2	9.30 (1H, s)	-	157.1
4, 5	3.78 (4H, m)	-	47.1, 47.5
6, 11	3.34 (4H, m)	-	49.4, 47.9
7, 12	1.42 (4H, m)	-	20.3, 28.4
8	0.30 (2H, t)	8.4	18.7
9	3.52 (6H, m)	-	57.6
10	0.92 (9H, m)	-	17.4
13	1.08 (2H, m)	-	12.7
14	0.65 (3H, t)	7.4	6.3

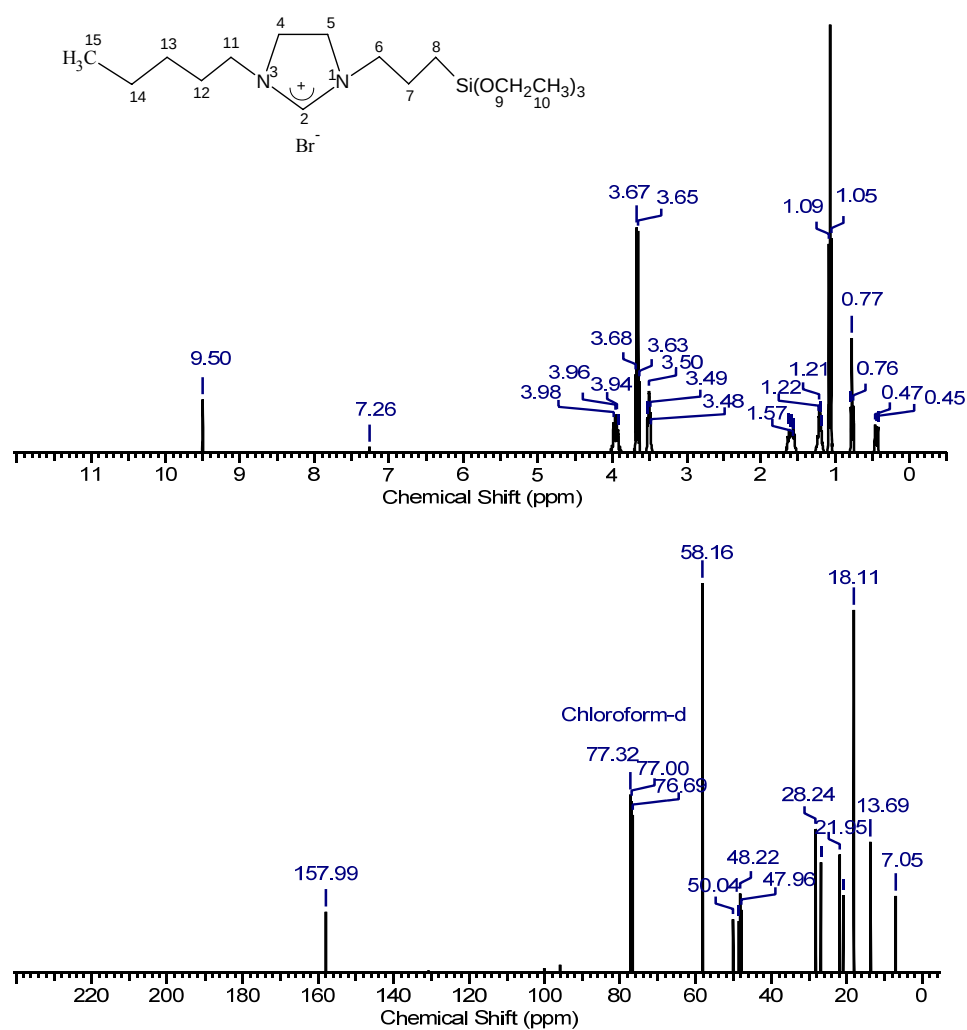


Figure 4.4 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1d**

Table 4.4 Selected ^1H and ^{13}C NMR data of **1d**

Numbers of atoms	^1H NMR (δ ppm)	J (Hz)	^{13}C NMR (δ ppm)
2	9.50 (1H, s)	-	158.0
4, 5	3.96 (4H, m)	-	48.2, 48.0
6, 11	3.49 (4H, k)	7.3	48.6, 50.0
7, 12	1.57 (4H, m)	-	28.2, 26.8
8	0.46 (2H, t)	8.2	13.7
9	3.65 (6H, m)	-	58.2
10	1.70 (13H, m)	-	18.1
13, 14	1.21 (4H, m)		21.9, 20.9
15	0.77 (3H, t)	7	7.1

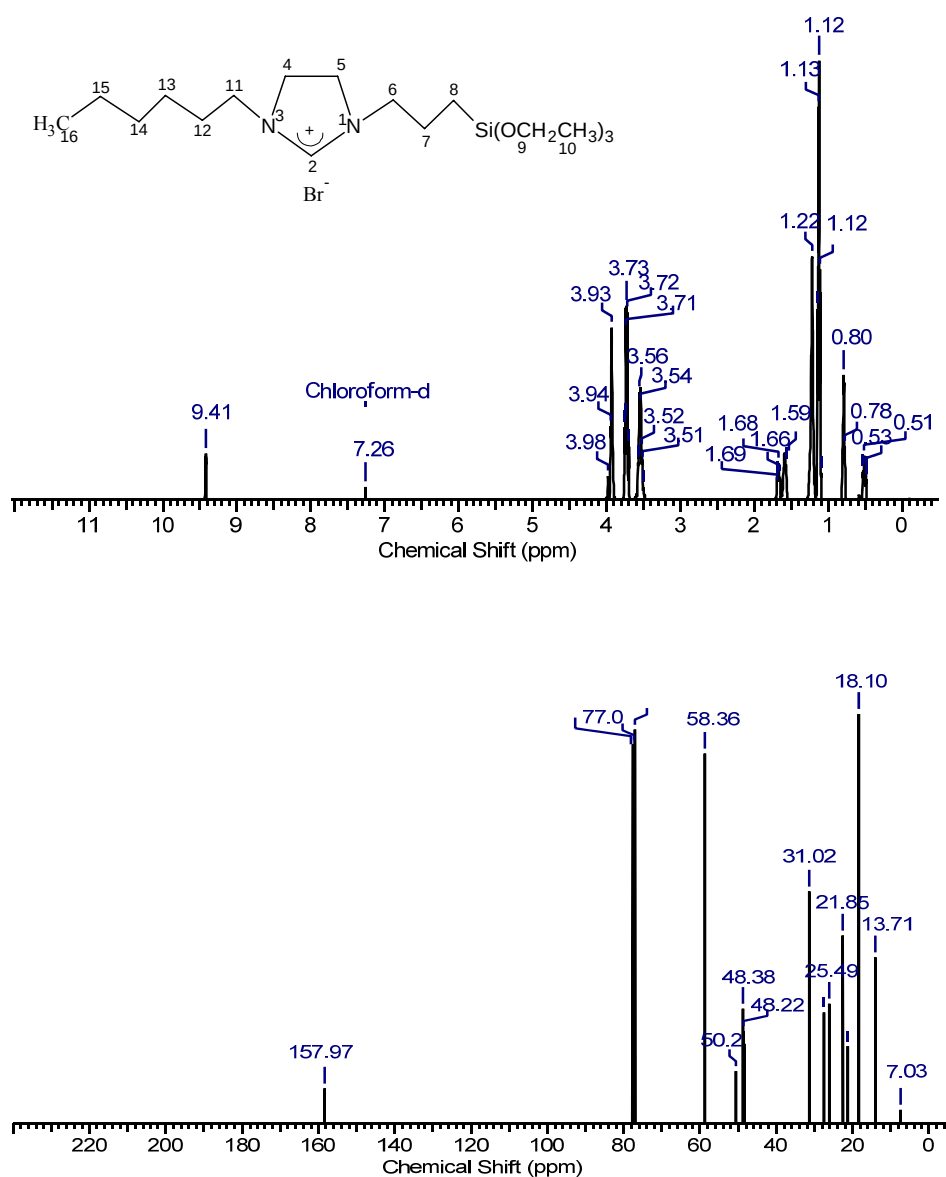


Figure 4.5 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1e**

Table 4.5 Selected ^1H and ^{13}C NMR data of **1e**

Numbers of atoms	^1H NMR (δ ppm)	J (Hz)	^{13}C NMR (δ ppm)
2	9.41 (1H, s)		158.0
4, 5	3.94 (4H, m)		48.2, 48.1
6, 11	3.54 (4H, q))	5	50.2, 48.4
7, 12	1.64 (4H, m)		31.0, 27.2
8	0.53 (2H, t)	8	13.7
9	3.72 (6H, q)	4	58.4
10	1.12 (9H, t)		18.1
13, 14	1.22 (4H, m)		22.2, 25.9
15	0.80 (3H, t)	8	7.0

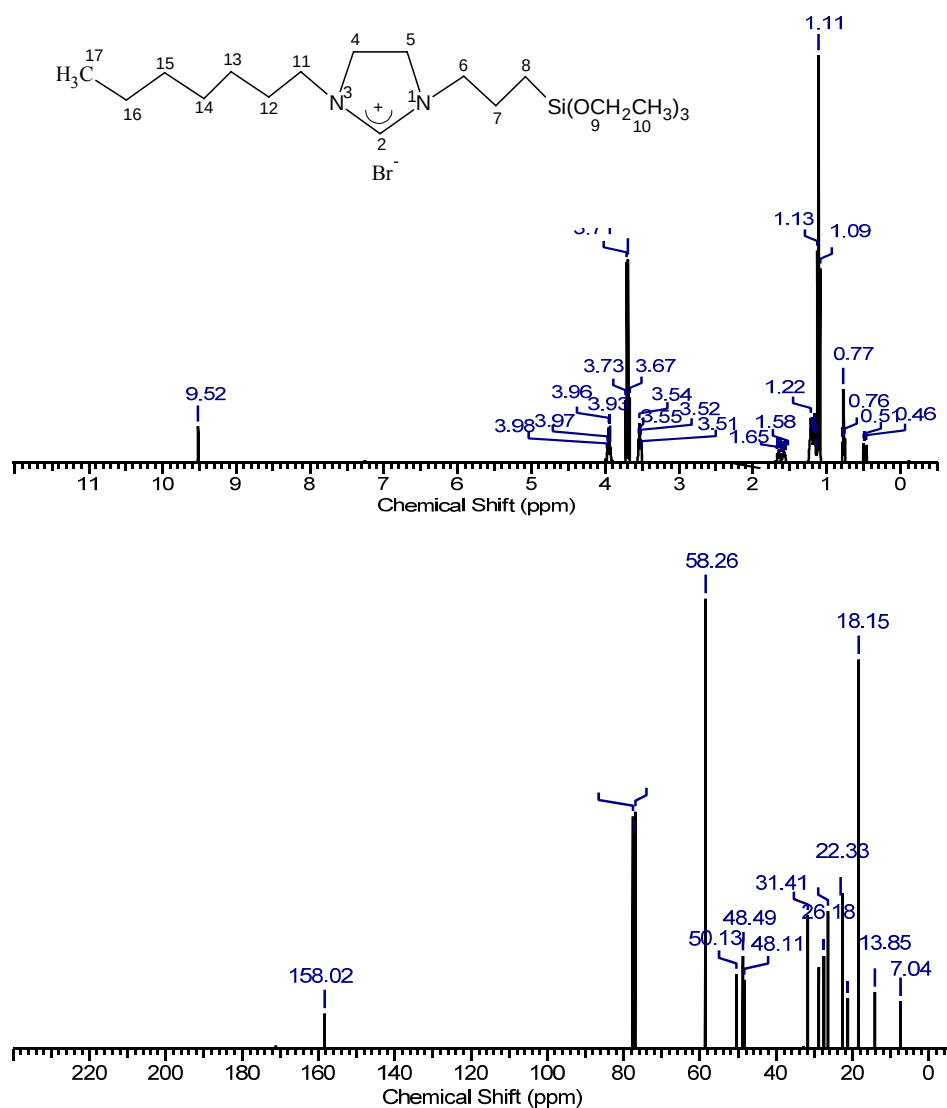


Figure 4.6 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1f**

Table 4.6 Selected ^1H and ^{13}C NMR data of **1f**

Numbers of atoms	^1H NMR (δ ppm)	J (Hz)	^{13}C NMR (δ ppm)
2	9.52 (1H, s)	-	158.0
4, 5	3.95 (4H, m)	-	48.5, 50.1
6, 11	3.54 (4H, m)	-	48.0, 48.1
7, 12	1.63 (4H, m)	-	28.6, 31.4
8	0.48 (2H, t)	8.4	27.2
9	3.71 (6H, m)	-	58.3
10	1.12 (9H, m)	-	18.2
13, 14, 15, 16	1.18 (8H, m)	-	13.9, 21.0, 22.3, 26.1
17	0.77 (3H, t)	6.8	7.0

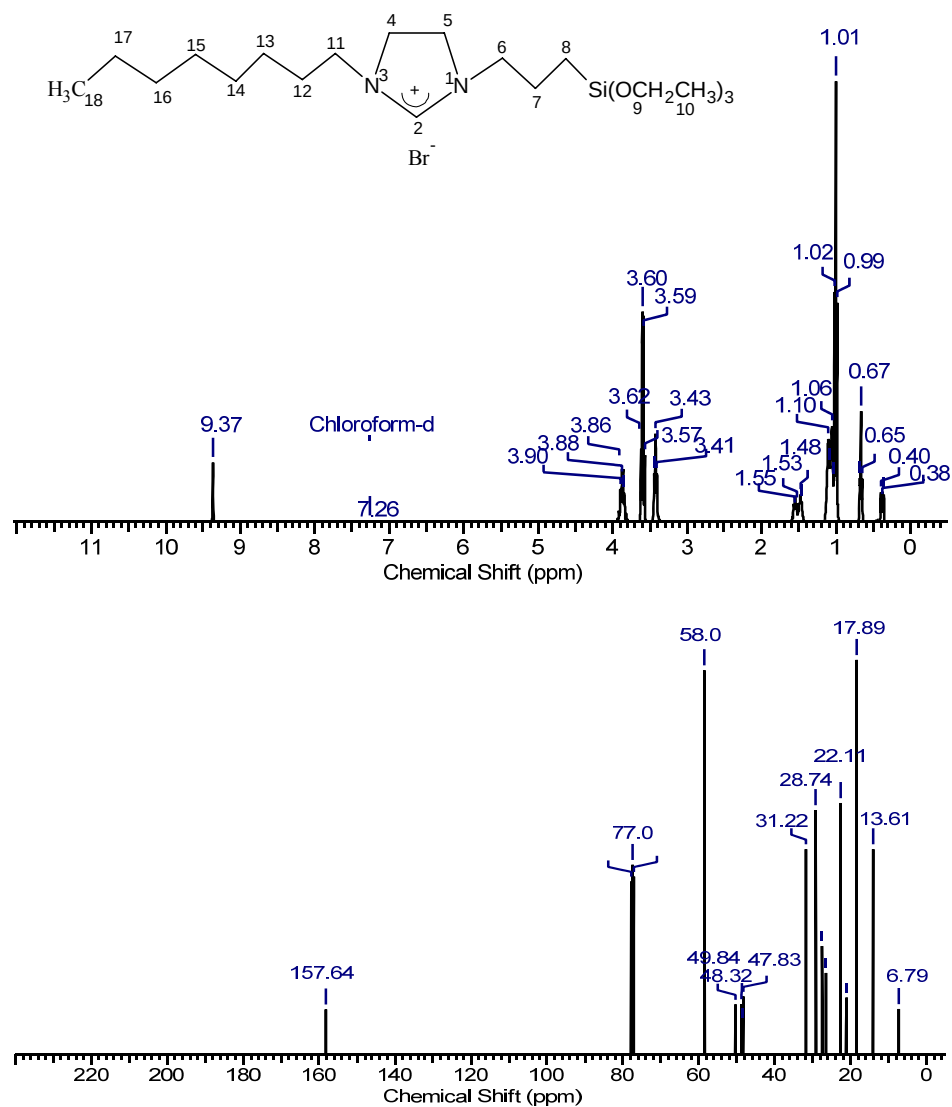


Figure 4.7 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1g**

Table 4.7 Selected ^1H and ^{13}C NMR data of **1g**

Numbers of atoms	^1H NMR (δ ppm)	J (Hz)	^{13}C NMR (δ ppm)
2	9.37 (1H, s)	-	157.6
4, 5	3.88 (4H, m)	-	48.3, 49.9
6, 11	3.43 (4H, t)	7.2	48.0, 47.8
7, 12	1.53 (4H, m)	-	28.7, 31.2
8	0.40 (2H, t)	8.2	29.2
9	3.60 (6H, q)	4.4	58.0
10	1.0 (9H, t)	8	17.9
13, 14, 15, 16, 17	1.08 (10H, m)	-	13.6, 20.7, 22.1, 26.0, 27.0
18	0.40 (3H, t)	6.8	6.8

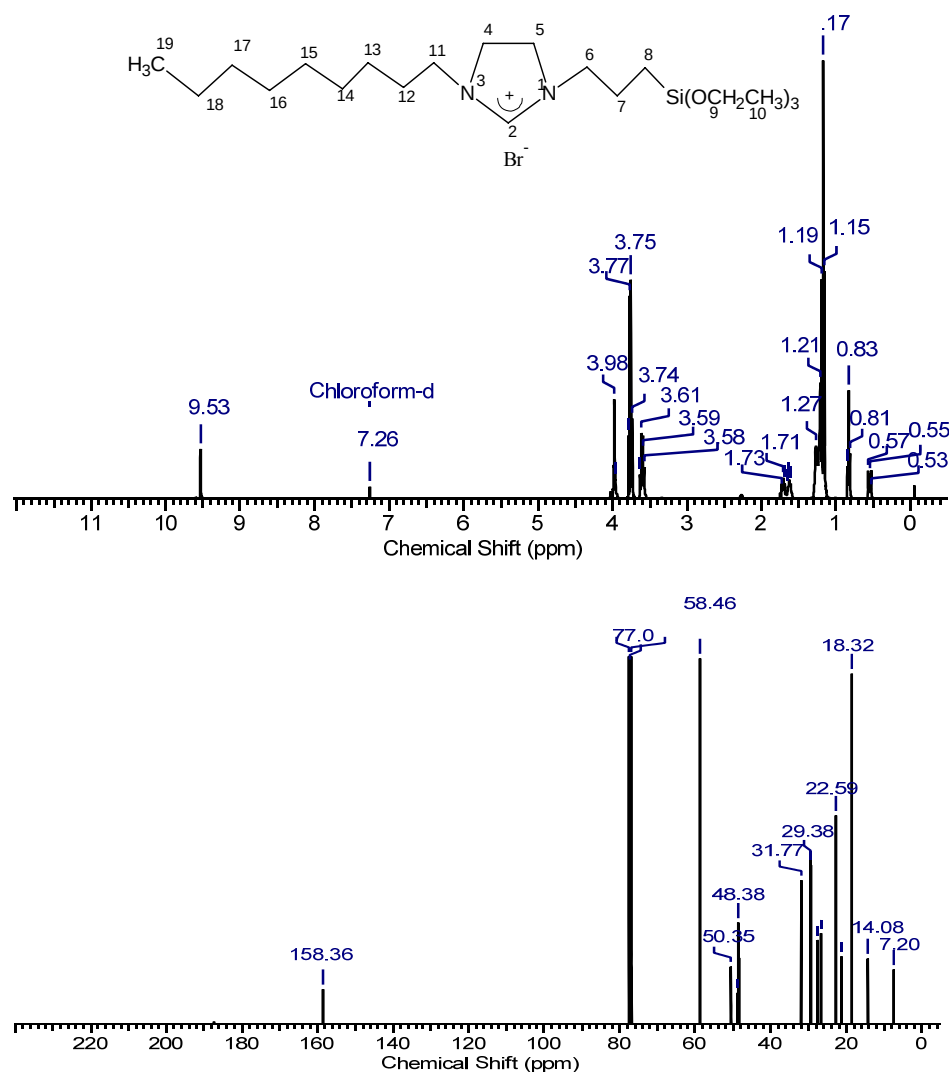


Figure 4.8 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1h**

Table 4.8 Selected ^1H and ^{13}C NMR data of **1h**

<i>Numbers of atoms</i>	<i>^1H NMR (δ ppm)</i>	<i>J (Hz)</i>	<i>^{13}C NMR (δ ppm)</i>
2	9.53 (1H, s)	-	158.4
4, 5	3.98 (4H, m)	-	50.4, 48.4
6, 11	3.59 (4H, m)	-	48.3, 48.4
7, 12	1.72 (4H, m)	-	31.8, 29.4
8	0.55 (2H, t)	8.2	7.2
9	3.76 (6H, q)	7.2	58.5
10	1.17 (9H, t)	3.2	18.3
13, 14, 15, 16, 17, 18	1.27 (12H, m)	-	29.2, 29.2, 27.4, 26.5, 22.6, 21.1
19	0.83 (3H, t)	6.8	14.1

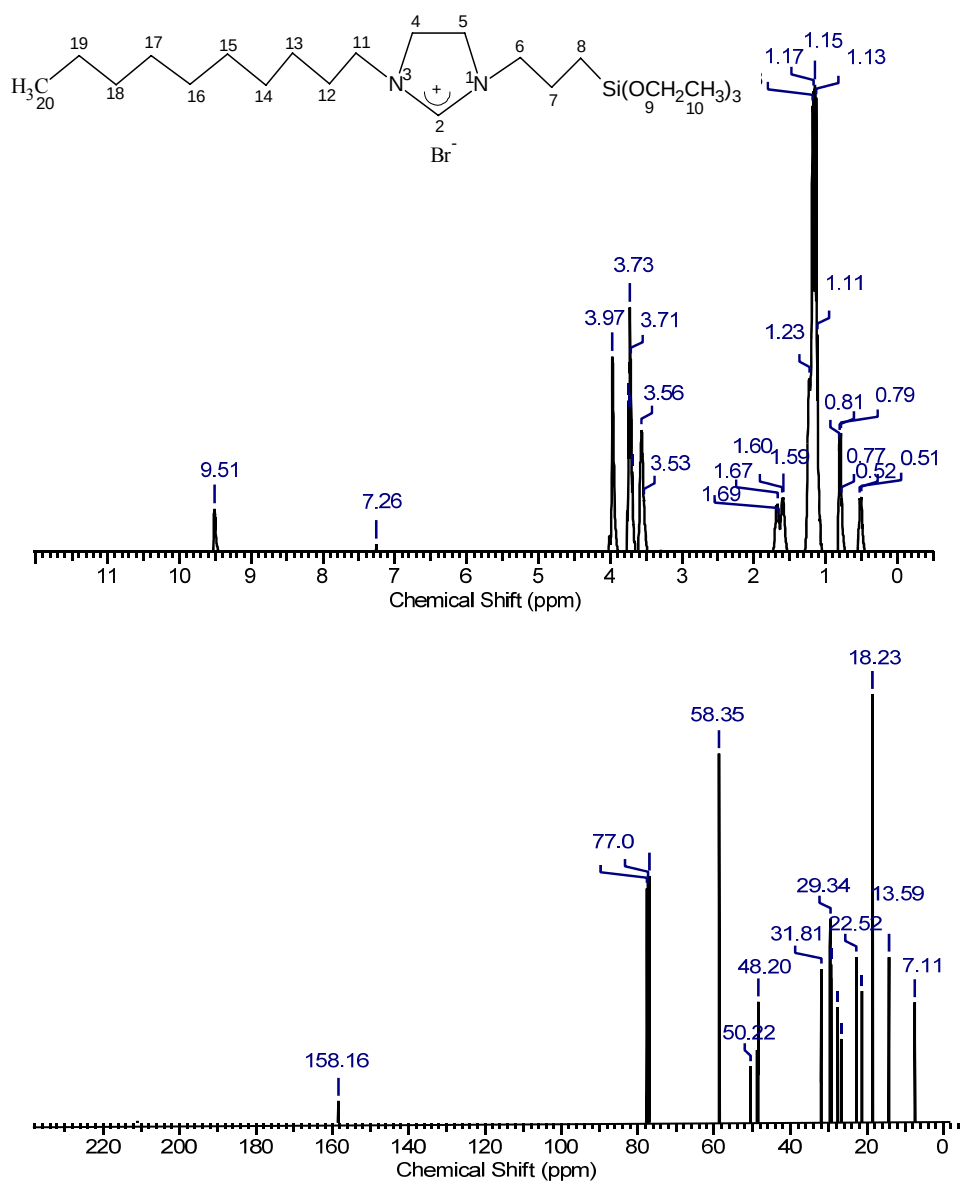


Figure 4.9 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1i**

Table 4.9 Selected ^1H and ^{13}C NMR data of **1i**

<i>Numbers of atoms</i>	<i>^1H NMR (δ ppm)</i>	<i>J (Hz)</i>	<i>^{13}C NMR (δ ppm)</i>
2	9.51 (1H, s)	-	158.2
4, 5	3.97 (4H, d)	17.2	50.2, 48.2
6, 11	3.73 ((4H, m)	-	48.3, 48.2
7, 12	1.65 (4H, m)		31.8, 29.4
8	0.52 (2H, t)	4.0	7.1
9	3.56 (6H, m)		58.4
10	1.15 (9H, t)	8.0	18.2
13-19	1.23 (14 H, m)		29.3, 29.1, 26.4, 22.5, 21.0
20	0.81 (3H, t)	8.0	13.6

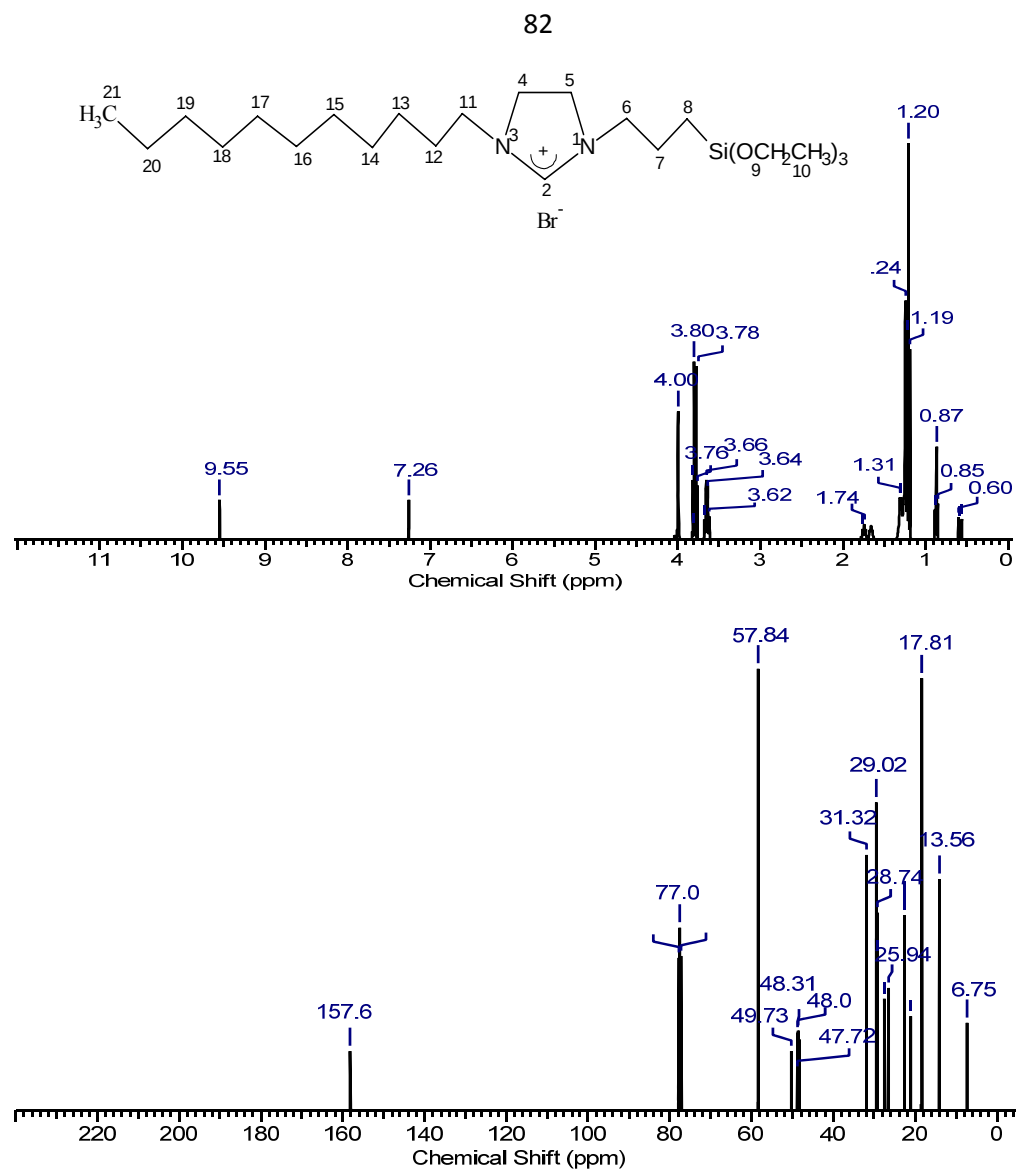


Figure 4.10 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1j**

Table 4.10 Selected ^1H and ^{13}C NMR data of **1j**

Numbers of atoms	^1H NMR (δ ppm)	J (Hz)	^{13}C NMR (δ ppm)
2	9.55 (1H, s)	-	157.6
4, 5	4.00 (4H, s)		49.7, 48.3
6, 11	3.64 (4H, q)	7.3	48.0, 47.7
7, 12	1.69 (4H, m)		31,3, 29.0
8	0.60 (2H, t)	8.2	6.8
9	3.78 (6H, q)	8.6	57.9
10	1.20 (9H, t)	6.6	17.8
13-20	1.28 (14 H, m)		28.7,28.5, 25.9, 25.7, 23.6, 22.1,
21	0.87 (3H, t)	7.0	13.6

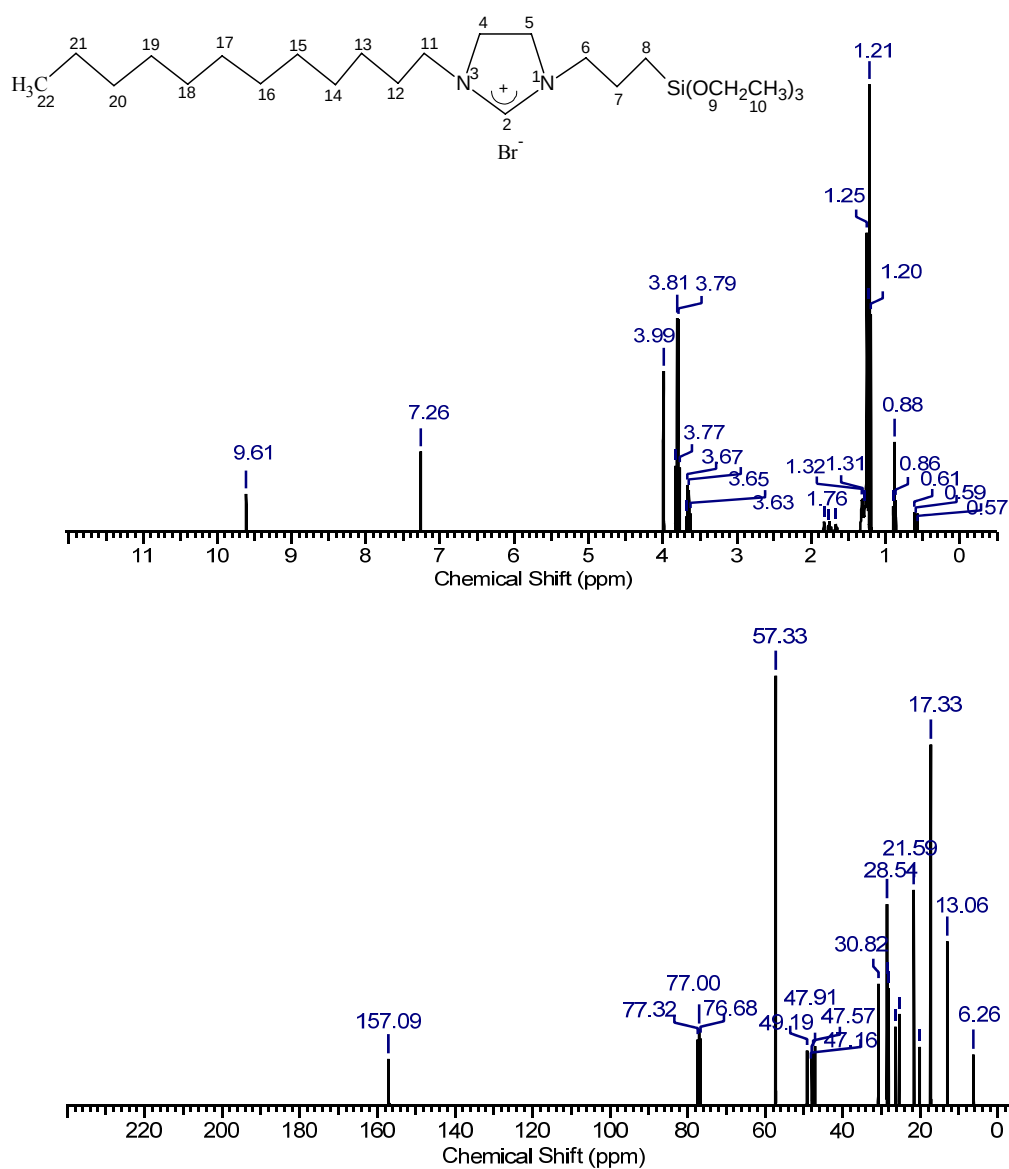


Figure 4.11 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1k**

Table 4.11 Selected ^1H and ^{13}C NMR data of **1k**

<i>Numbers of atoms</i>	<i>^1H NMR (δ ppm)</i>	<i>J (Hz)</i>	<i>^{13}C NMR (δ ppm)</i>
2	9.61 (1H, s)	-	157.1
4, 5	3.99 (4H, s)	-	49.2, 47.9
6, 11	3.66 (4H, q)	7.7	47.6, 47.2
7, 12	1.74 (4H, m)	-	30.8, 28.6
8	0.59 (2H, t)	8.2	6.3
9	3.81 (6H, q)	7.0	57.3
10	1.22 (9H, t)	7.2	17.3
13-21	1.31 (18H, m)	-	28.5, 28.5, 28.4, 28.2, 29.0, 28.4, 26.4, 25.4, 21.6
22	0.88 (3H, t)	7.2	13.1

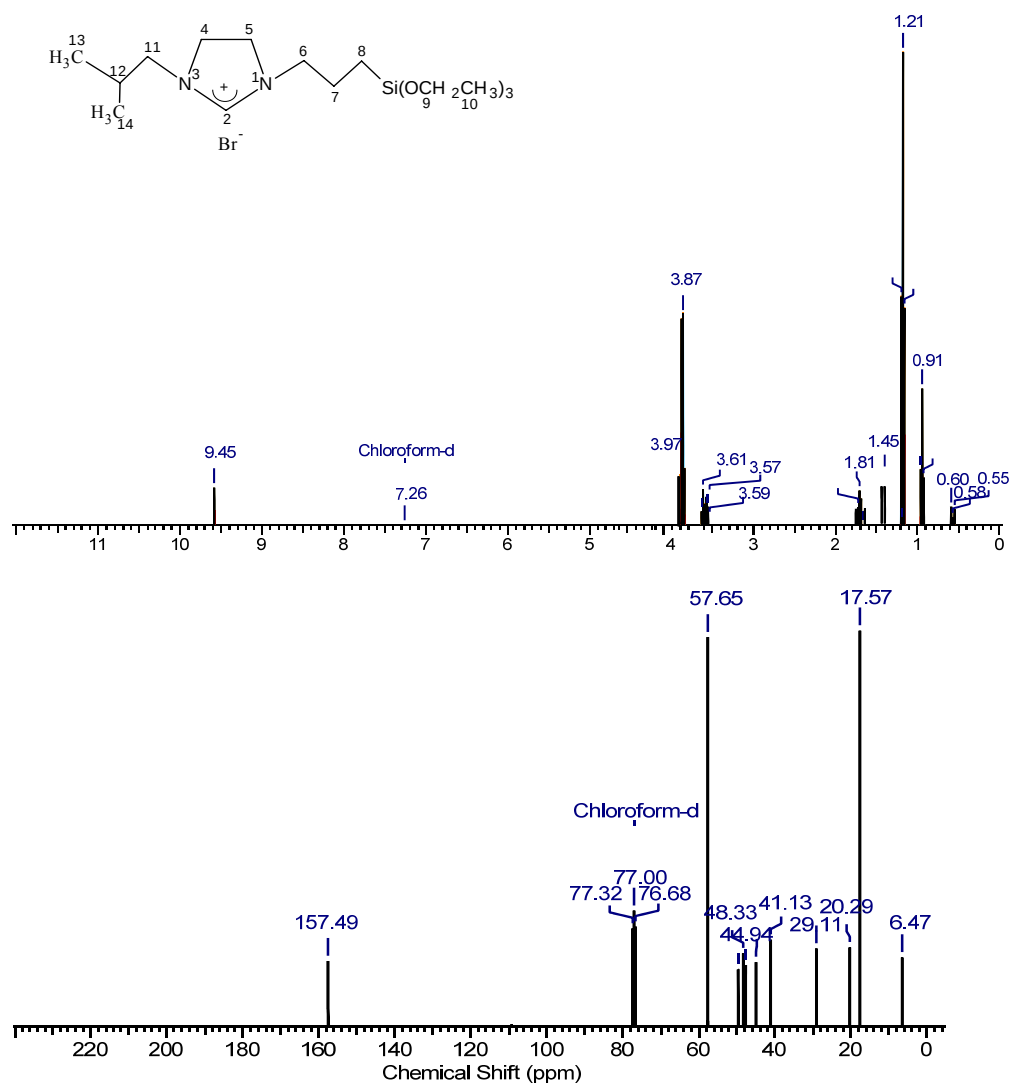


Figure 4.12 (a) ^1H NMR, (b) ^{13}C NMR spectra of **11**

Table 4.12 Selected ^1H and ^{13}C NMR data of **11**

Numbers of atoms	^1H NMR (δ ppm)	J (Hz)	^{13}C NMR (δ ppm)
2	9.45 (1H, s)	-	157.5
4, 5	3.97 (4H, m)	-	49.3, 47.8
6, 11	3.59 (4H, t)	6.5	49.7
7	0.91 (2H, t)	7	41.9
8	0.58 (2H, t)	8	6.5
9	3.87 (6H, k)	6.9	57.7
10	1.21 (9H, m)	-	17.6
12	1.81 (1H, m)	-	41.1
13, 14	1.45 (6H, d)	7.2	20.3, 29.1

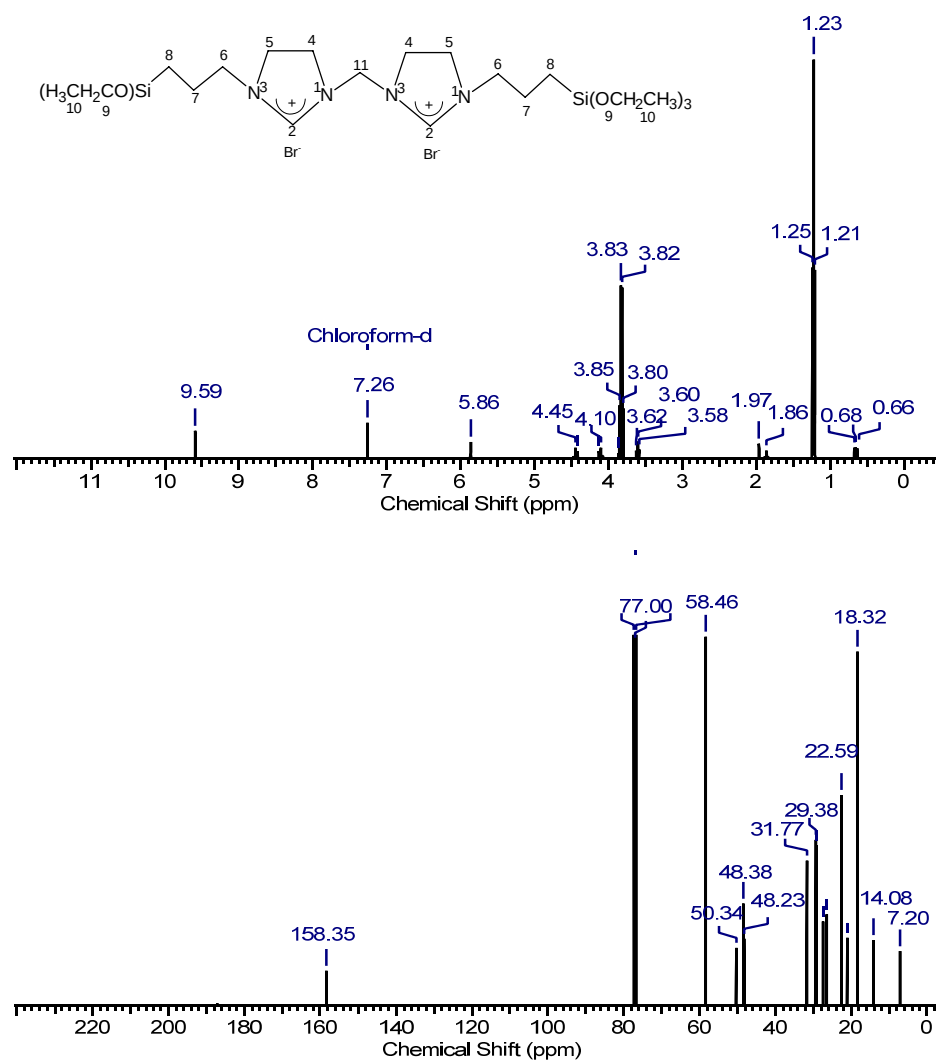


Figure 4.13 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1m**.

Table 4.13 Selected ^1H and ^{13}C NMR data of **1m**.

Numbers of atoms	^1H NMR (δ ppm)	J (Hz)	^{13}C NMR (δ ppm)
2	9.59 (2H, s)	-	158.4
4, 5	4.45 (4H, t), 4.1 (4H, t)	10.6, 10.8	48.2, 48.4
6	3.60 (4H, t)	7.4	31.8, 29.4
7	1.86 (4H, t)	7.6	14.1
8	0.66 (4H, t)	8.2	7.2
9	3.81 (12H, q)	7	58.5
10	1.23 (18H, t)	7.2	18.3
11	5.86 (2H, s)	-	50.3

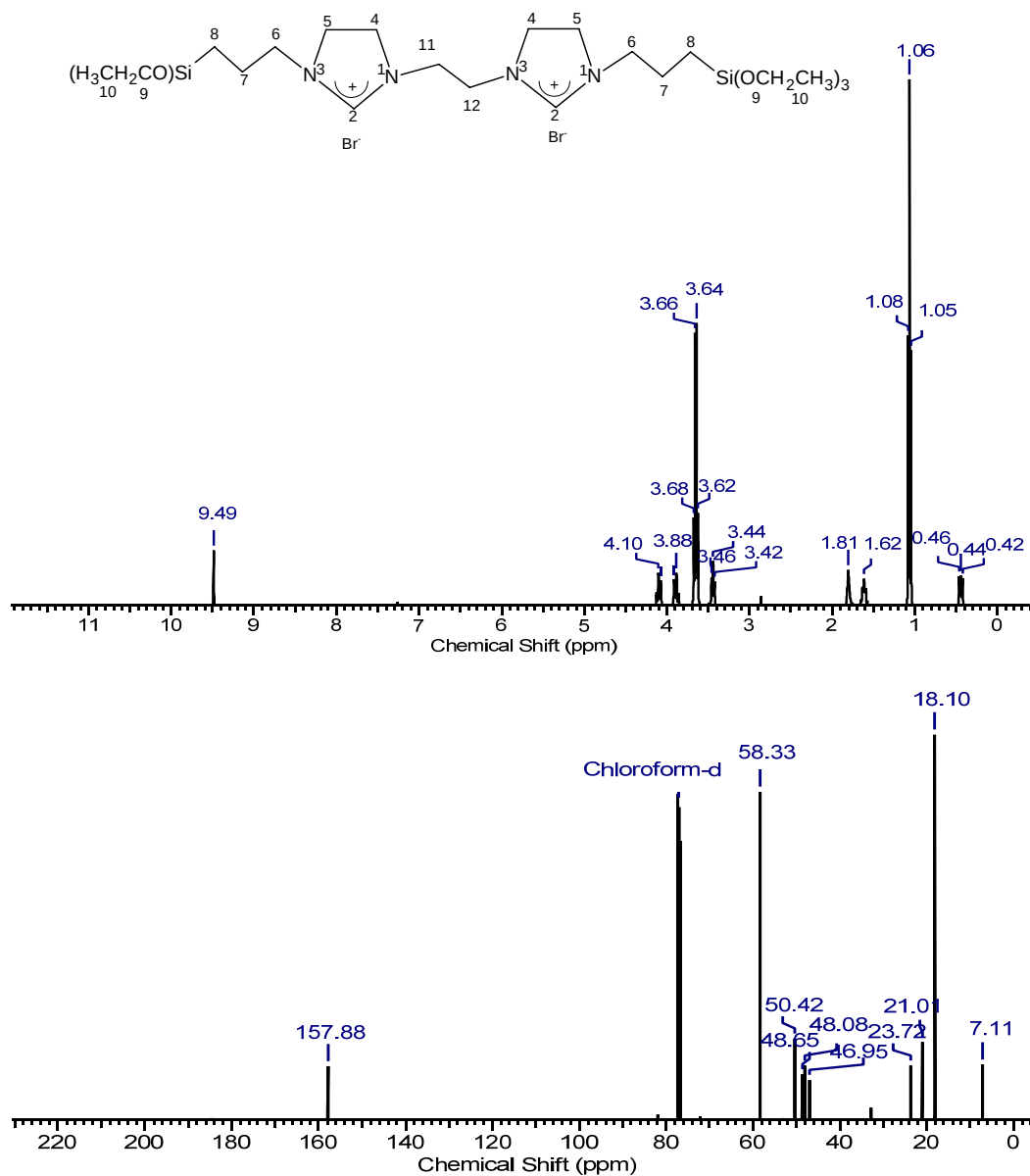


Figure 4.14(a) ¹H NMR, (b) ¹³C NMR spectra of **1n**.

Table 4.14 ¹H and ¹³C NMR data of **1n**.

Numbers of atoms	¹ H NMR (δ ppm)	J (Hz)	¹³ C NMR (δ ppm)
2	9.49 (2H, s)	-	157.9
4, 5	4.11 (4H, t), 3.91 (4H, t)	10.6, 10.8	48.1, 47.0
6	3.44 (4H, t)	7.2	50.4
7	1.62 (4H, m)	-	48.7
8	0.51 (4H, t)	8.2	7.1
9	3.64 (12H, q)	14	58.3
10	1.13 (18H, t)	7.2	18.1
11, 12	1.81 (4H, s)	-	23.7, 21.0

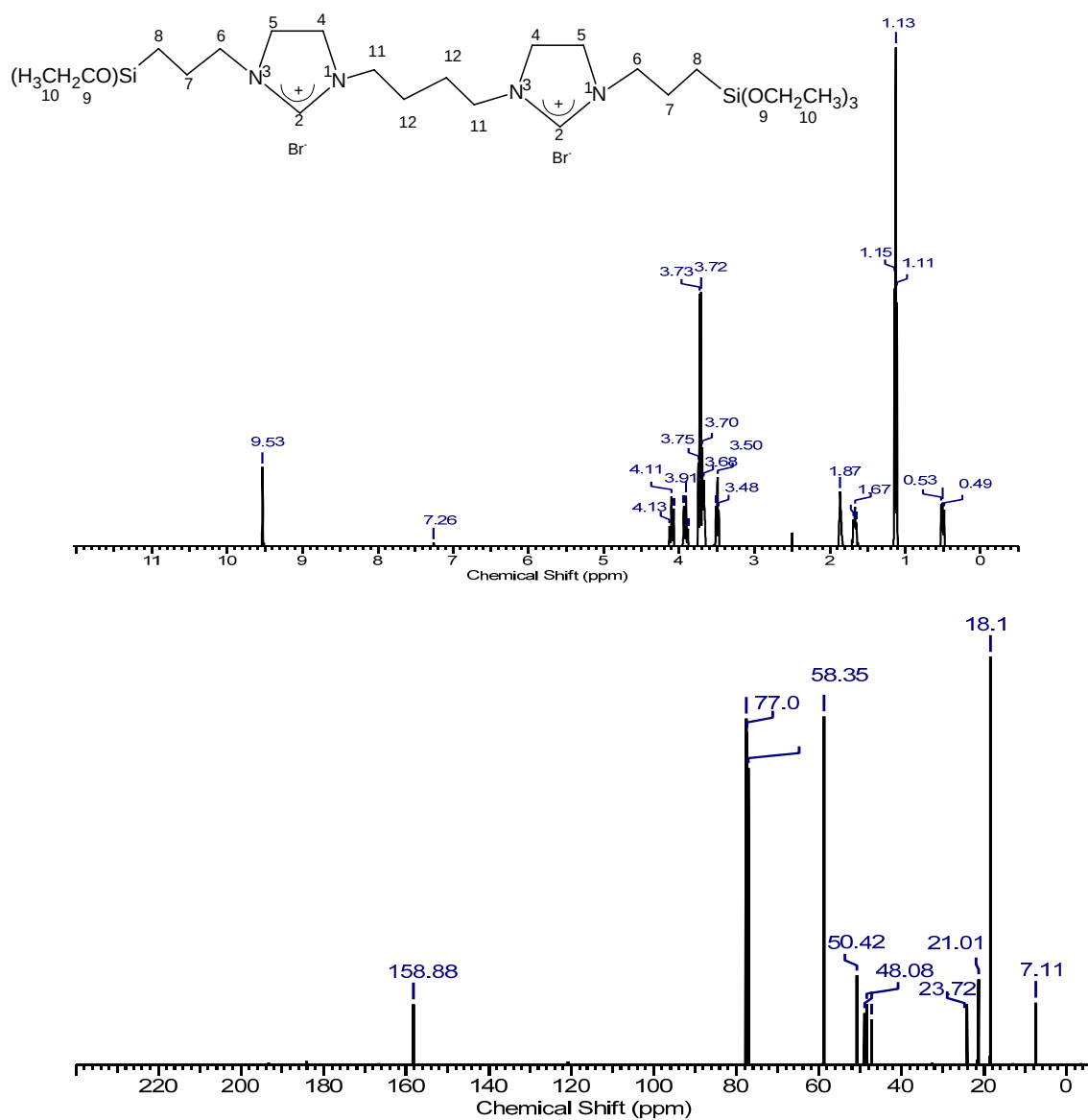


Figure 4.15 (a) ^1H NMR, (b) ^{13}C NMR spectra of **10**.

Table 4.15 ^1H and ^{13}C NMR data of **10**.

<i>Numbers of atoms</i>	<i>^1H NMR (δ ppm)</i>	<i>J (Hz)</i>	<i>^{13}C NMR (δ ppm)</i>
2	9.53 (2H, s)	-	158.9
4, 5	4.11 (4H, t), 3.91 (4H, t)	10.6, 10.8	48.1, 47.0
6	3.50 (4H, t)	7.2	50.4
7	1.67 (4H, m)	-	48.7
8	0.51 (4H, t)	8.2	7.1
9	3.72 (12H, q)	14	58.4
10	1.13 (18H, t)	7.2	18.1
11,12	1.87 (4H, s)	-	23.7, 21.0

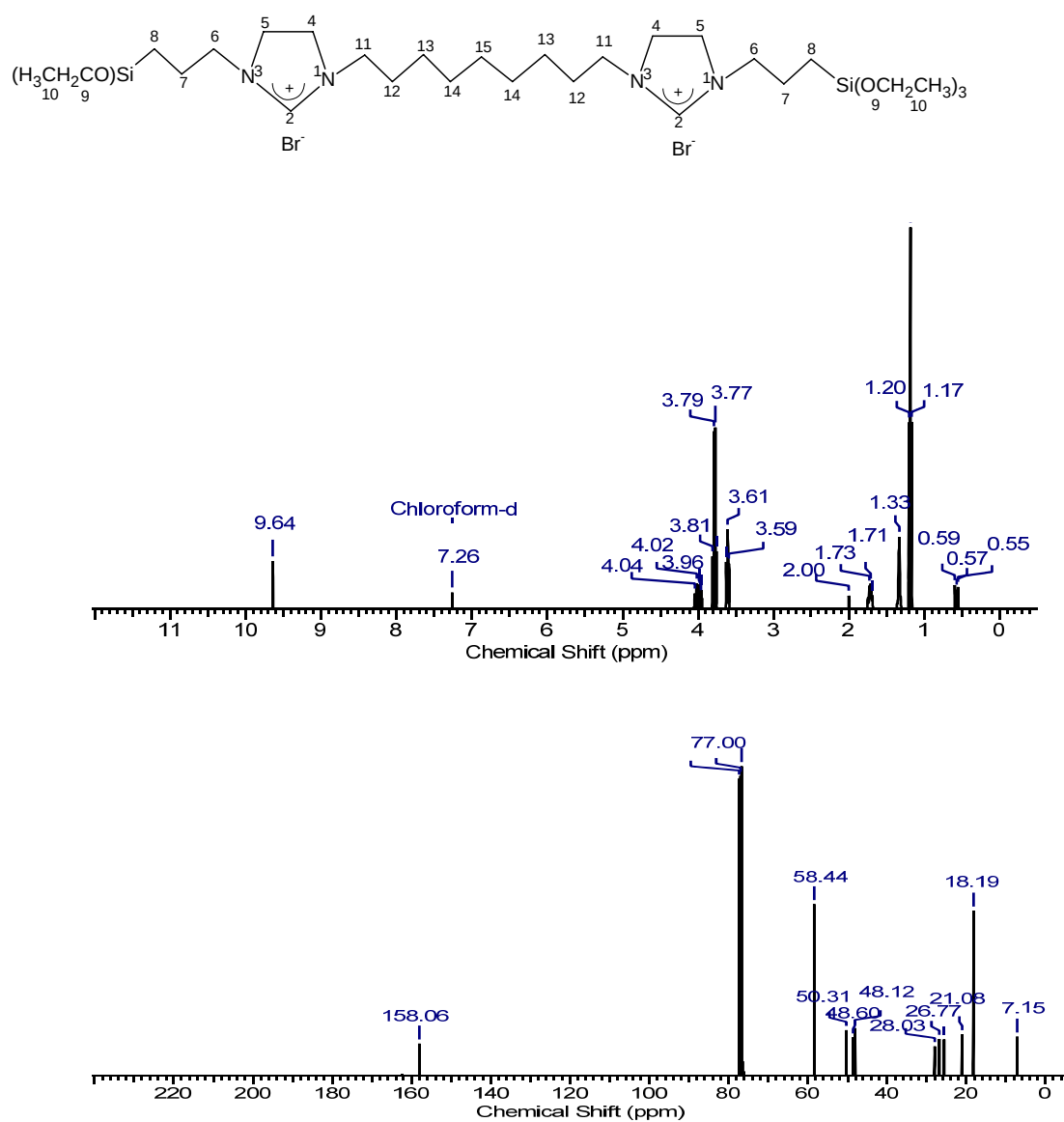


Figure 4.16 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1p**.

Table 4.16. Selected ^1H and ^{13}C NMR data of **1p**

<i>Numbers of atoms</i>	<i>^1H NMR (δ ppm)</i>	<i>J (Hz)</i>	<i>^{13}C NMR (δ ppm)</i>
2	9.64 (2H, s)	-	158.1
4, 5	4.00 (8H, m)	-	50.3
6, 11	3.60 (8H, t)	7.2	48.1, 48.6
7, 12	1.72 (8H, m)	-	21.1, 28.0, 28.4
8	0.57 (4H, t)	8.2	7.2
9	3.78 (12H, q)	7.1	58.4
10	1.19 (18H, t)	7.2	18.2
13, 14, 15	1.33 (10H, d)	12.4	25.6, 26.8

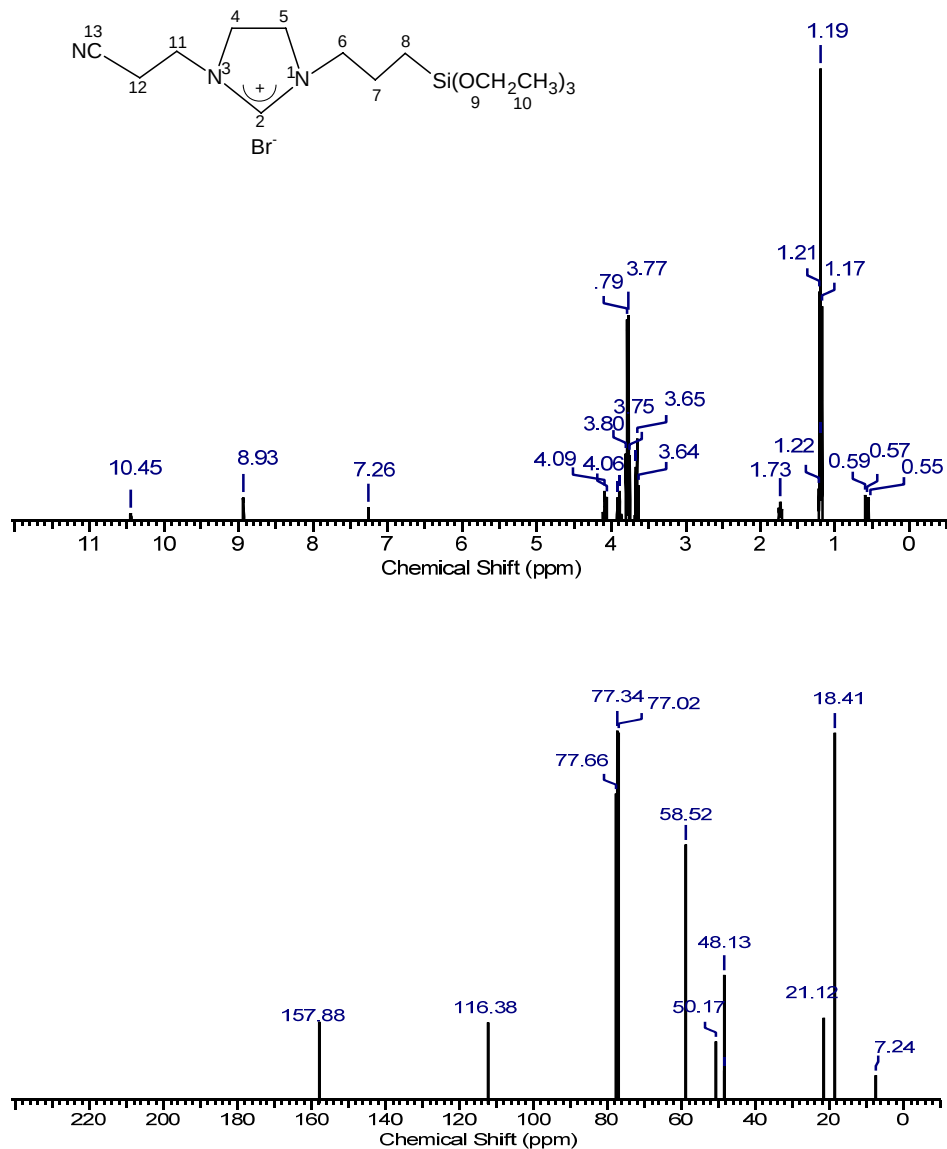


Figure 4.17 (a) ¹H NMR, (b) ¹³C NMR spectra of **1r**.

Table 4.17 Selected ¹H and ¹³C NMR data of **1r**

<i>Numbers of atoms</i>	<i>¹H NMR (δ ppm)</i>	<i>J (Hz)</i>	<i>¹³C NMR (δ ppm)</i>
2	8.93 (1H, s)	-	157.9
4, 5	3.99 (4H, m)	-	50.2
6, 11	3.66 (4H, t)	7.2	48.1
7, 10	1.2 (11H, m)	-	21.1, 18.4
8	0.57 (2H, t)	8.2	7.2
9	3.79 (6H, q)	14, 25.2	58.5
12	1.73 (2H, m)	-	44.7
13	-	-	116.4

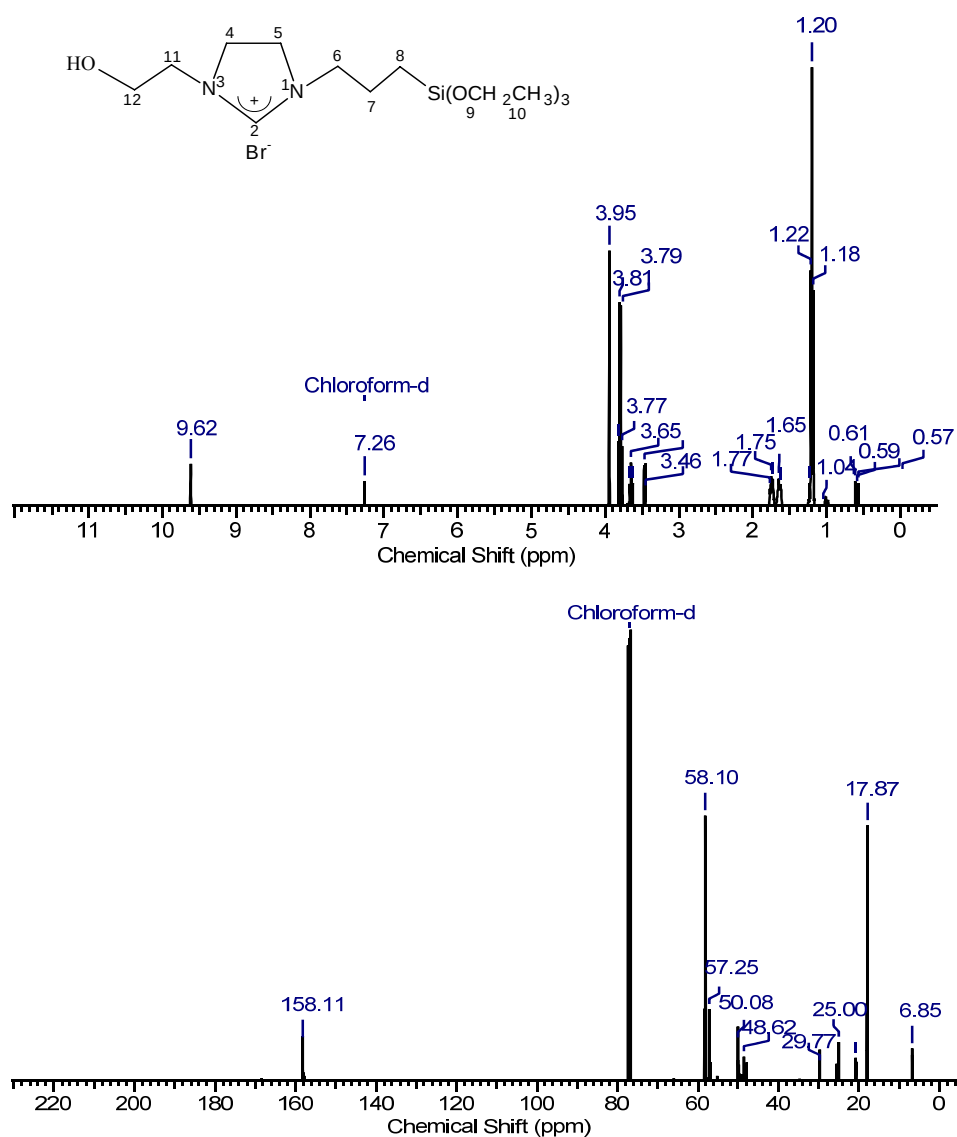


Figure 4.18 (a) ^1H NMR, (b) ^{13}C NMR spectra of **1s**.

Table 4.18 Selected ^1H and ^{13}C NMR data of **1s**

Numbers of atoms	^1H NMR (δ ppm)	J (Hz)	^{13}C NMR (δ ppm)
2	9.62 (1H, s)	-	158.1
4, 5	3.95 (4H, s)	-	30.0, 48.6
6	3.47 (2H, d)	6.8	57.3
7	1.00 (2H, m)	-	20.8
8	0.59 (2H, t)	8.2	6.9
9	3.81 (6H, q)	14, 20.8	58.1
10	1.20 (9H, t)	12.8	17.9
11	3.70 (2H, m)	-	50.1
12	1.74 (2H, m)	-	25.0

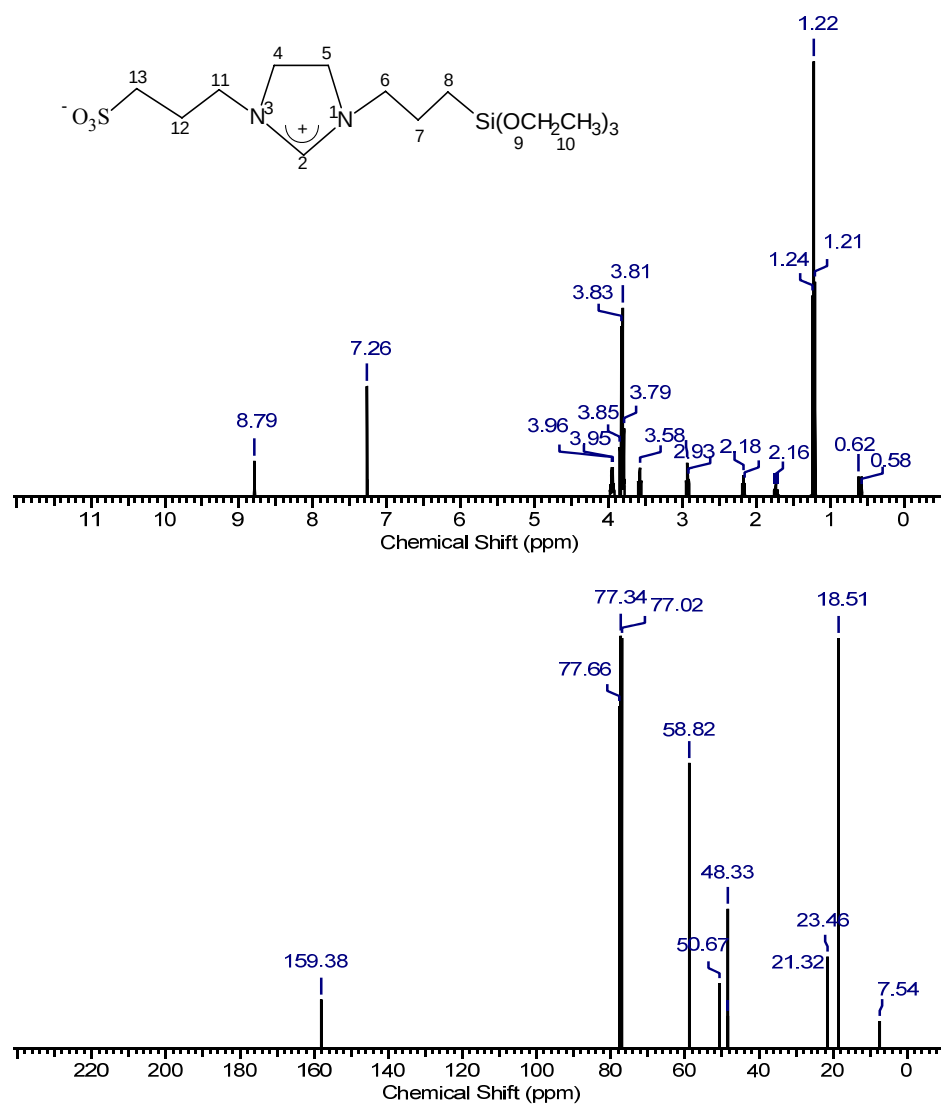


Figure 4.19(a) ^1H NMR, (b) ^{13}C NMR spectra of **1u**.

Table 4.19. Selected ^1H and ^{13}C NMR data of **1u**

<i>Numbers of atoms</i>	<i>^1H NMR (δ ppm)</i>	<i>J (Hz)</i>	<i>^{13}C NMR (δ ppm)</i>
2	8.79 (1H, s)	-	159.4
4, 5	3.95 (4H, m)	-	48.3, 48.2
6	3.58 (2H, t)	7.2	48.1
7	1.74 (2H, t)	7.6	21.3
8	2.93 (2H, t)	6.8	7.5
9, 11	3.81 (8H, m)	-	58.8, 50.7
10	1.22 (9H, m)	-	18.5
12	2.18 (2H, t)	7.2	23.5
13	0.6 (2H, t)	8.4	47.2

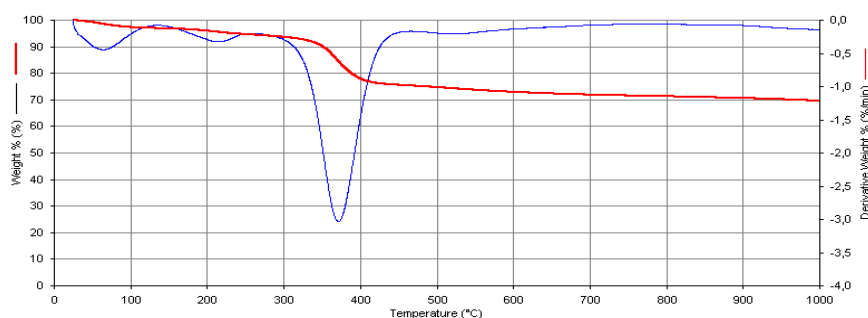
4.1.2 Synthesis and characterization of supported imidazolinium compounds, (2).

Supported imidazolinium compounds (2) were prepared using 1,4(3-triethoxysilylpropyl)butane dibromide (10) because of having the most effective compound for the chemical transformation of CO₂ and epoxide. Preparation methods of supported ionic compounds were given in detail in experimental section.

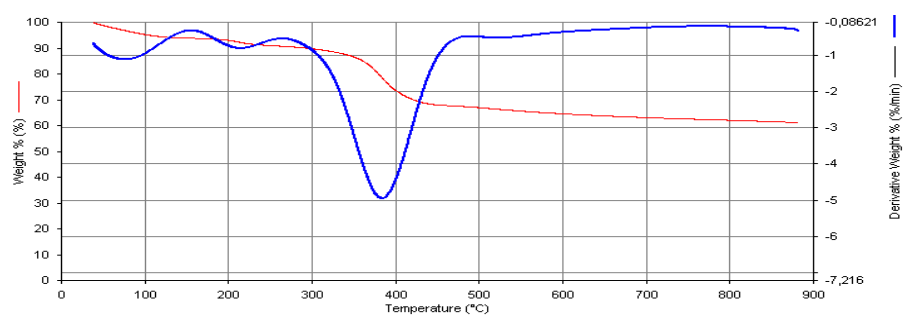
The synthesized heterogeneous compounds (2) were characterized by X-ray diffraction (XRD), sorption measurement (BET), FT-IR spectroscopy, atomic force microscopy (AFM), scanning electron micrograph (SEM), thermal and elemental analysis.

Elemental analysis and TG/DTA were used to determine the amount of supported organic ligands. Elemental analysis and TG data were compatible with calculated amount of supported ligand. TG/DTA profile is shown in Figure 4.20. It appears that immobilized compound decomposes in three temperature region. The first decomposition occurs between 30 °C and 100 °C due to the loss of loosely bound water. The second decomposition was observed during heating from 100 °C to 250 °C. The third decomposition was between 250 °C and 600 °C possibly owing to corresponding to covalently bonded organic group

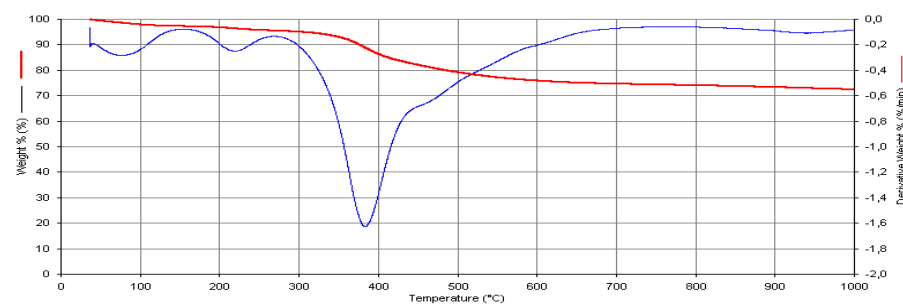
a) 2A



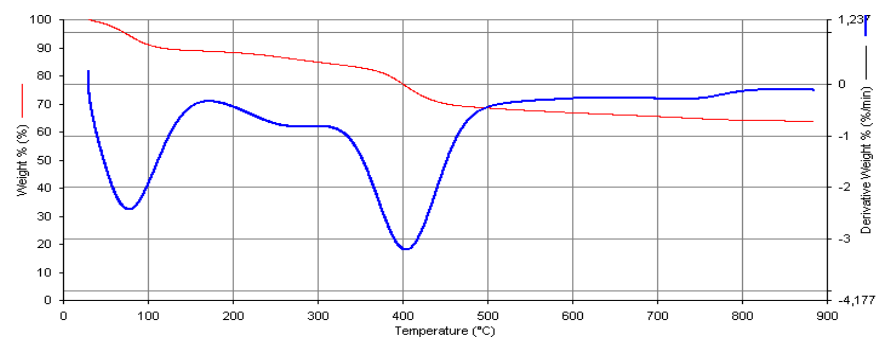
b) 2B



c) 2C



d) 2D



e) 2E

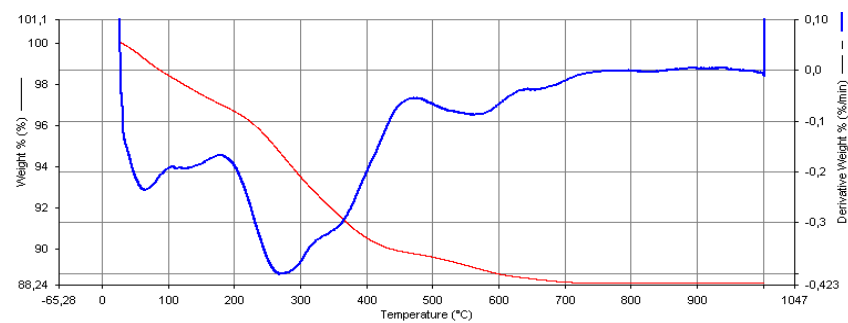
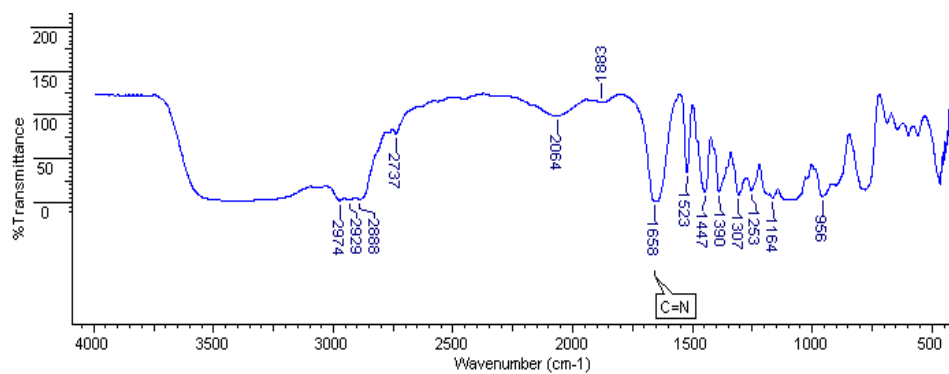
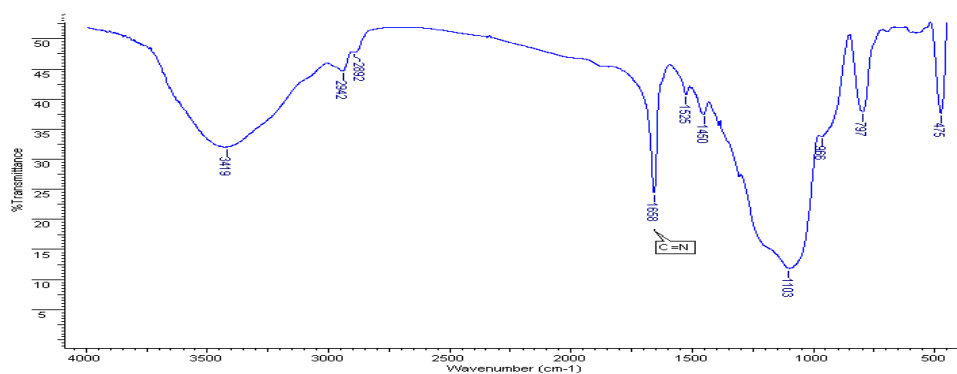
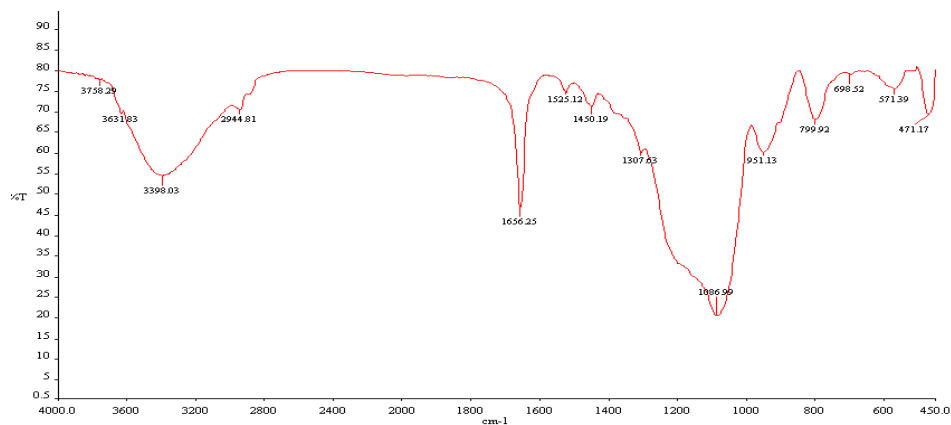
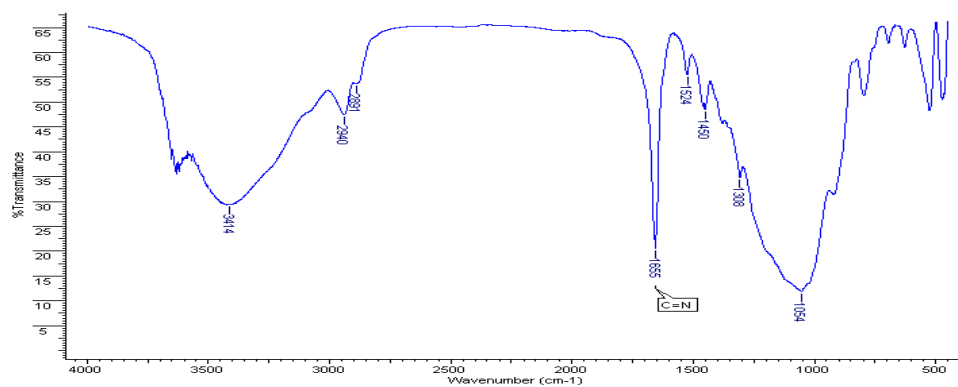


Figure 4.20 TG/DTA profile of 2 compounds.

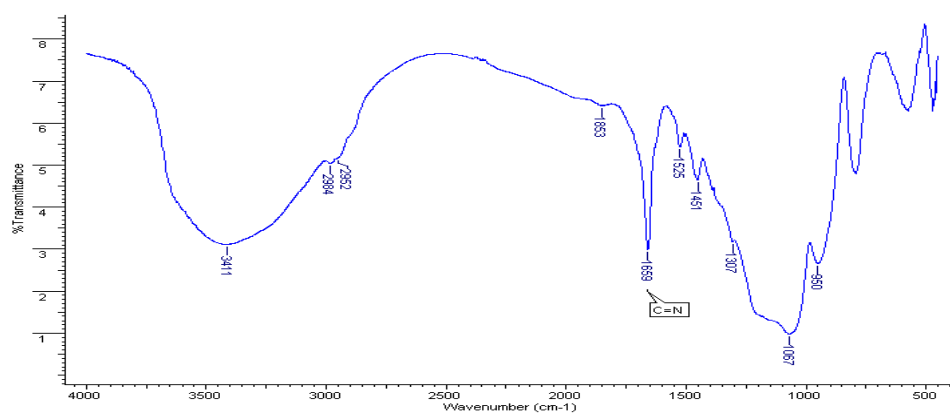
The IR spectra of imidazolinium salts **2** showed peaks for the C=N stretching frequency region at 1658 cm^{-1} . The bands at $2800\text{--}2950\text{ cm}^{-1}$ are due to the C-H stretching as shown in Figure 4.21.

a) **1o**b) **2A**c) **2B**

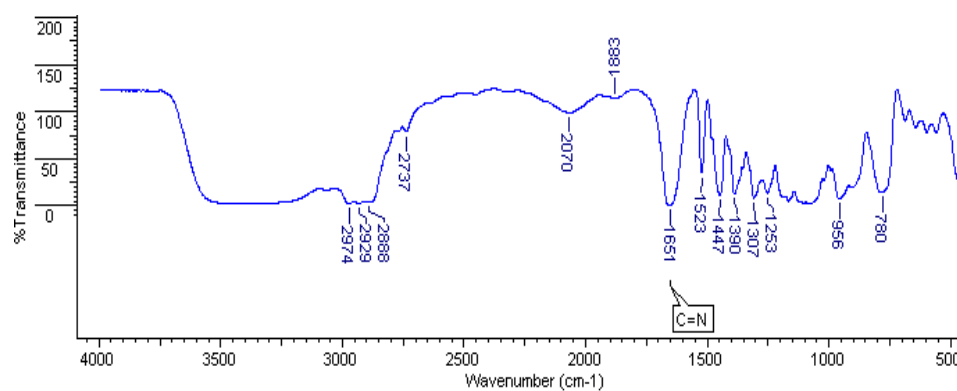
d) 2C



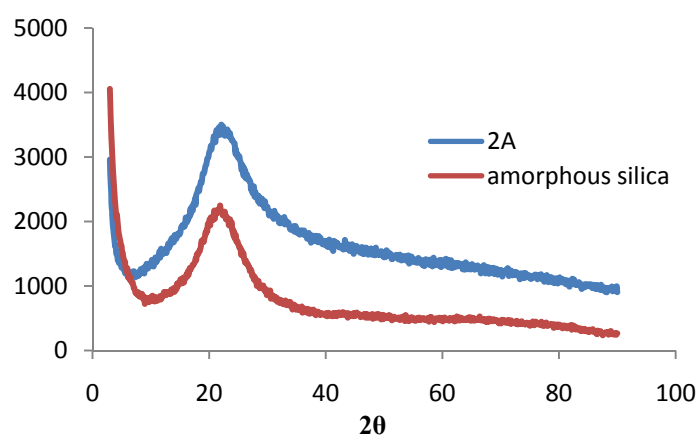
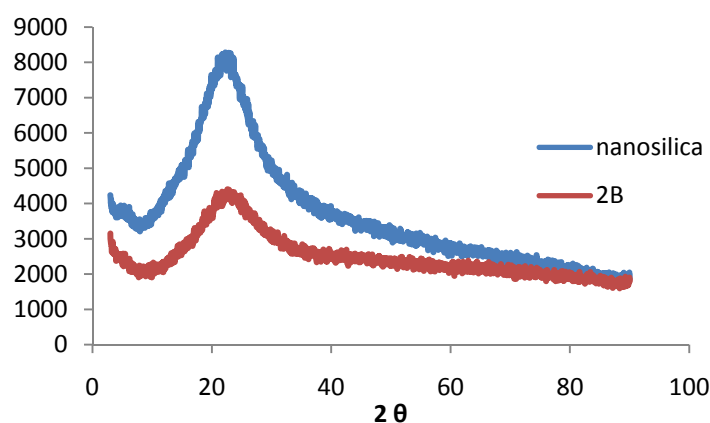
e) 2D



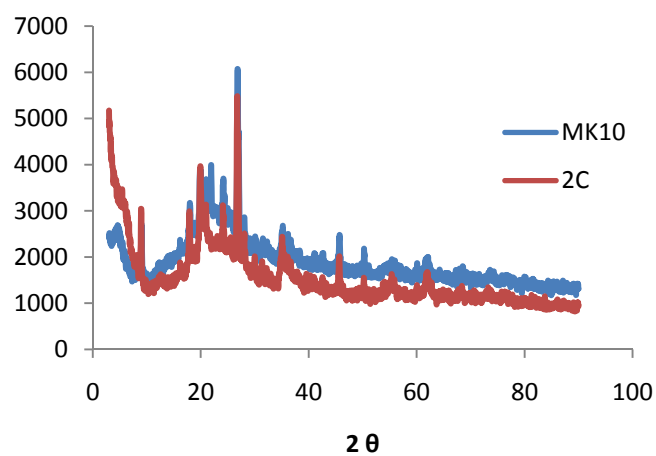
f) 2E

**Figure 4.21** IR spectra of 2 type compounds

The powder XRD patterns of supporting materials and **2** are shown in Figure 4.22. X-ray diffraction pattern for amorphous silica and nanopowder silica show characteristic low angle peaks attributed to nonhomogeneous structure. Immobilized **2A**, **2B**, **2D** compounds also has low angle peaks and they have characteristic amorphous silica structure. Due to their more uniform structure, **2C** and **2E** demonstrated 2 θ peaks. **2C** has characteristic clay structure and **2E** has Fe₃O₄ structure due to the analyzing the peaks. For comparison, MK-10 and **2C** has been showed the same signals. In addition, Fe₃O₄ and **2E** has also exhibited the same 2 θ values. This indicates that the morphology of supporting material did not change during the immobilization process. Thus, immobilization of **1o** compound on different supports did not significantly affect the structure of supporting material.

a) **2A**b) **2B**

c) 2C and MK-10



d) 2D

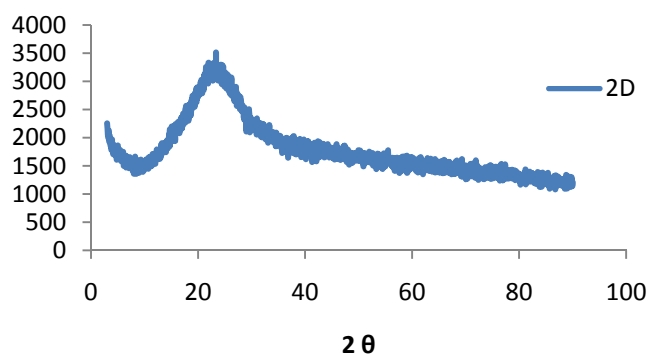
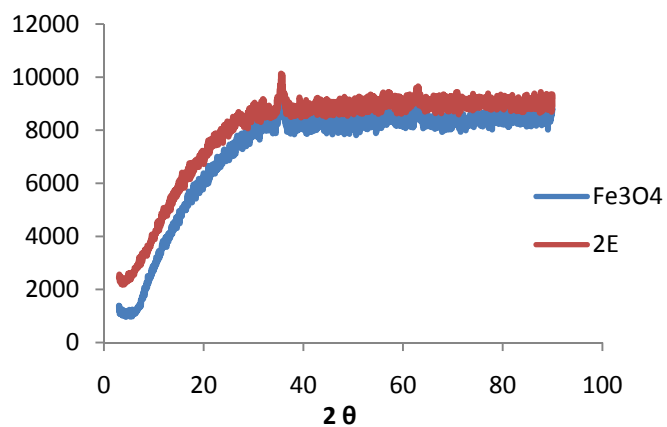
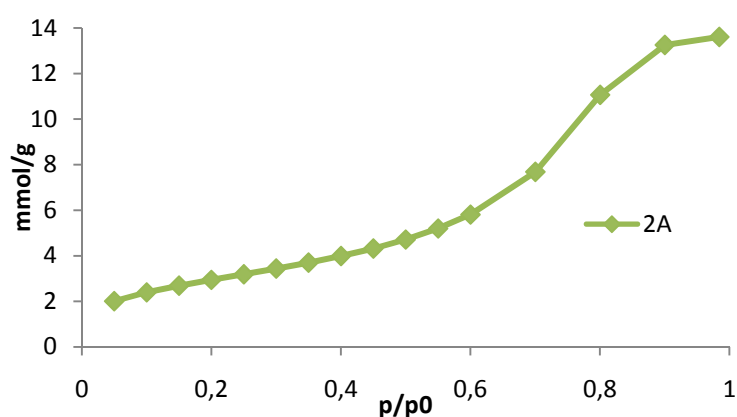
e) 2E and Fe_3O_4 

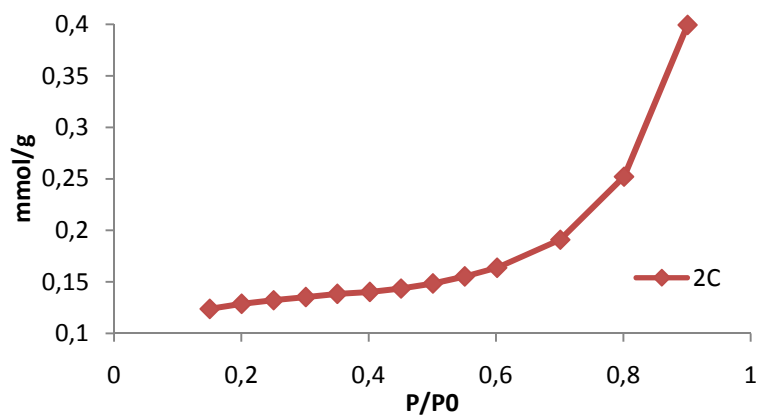
Figure 4.22 XRD-powder patterns of 2 type compounds and their supporting materials.

Nitrogen isotherms of compounds of type **2**, except **2D** are of the type II that indicates formation of multimolecular adsorption (Figure 4.23). **2D** exhibited a type I adsorption isotherm that corresponds to Langmuir isotherm and it tends to monotonically to the limiting adsorption, probably attained on completion of the monomolecular layer.

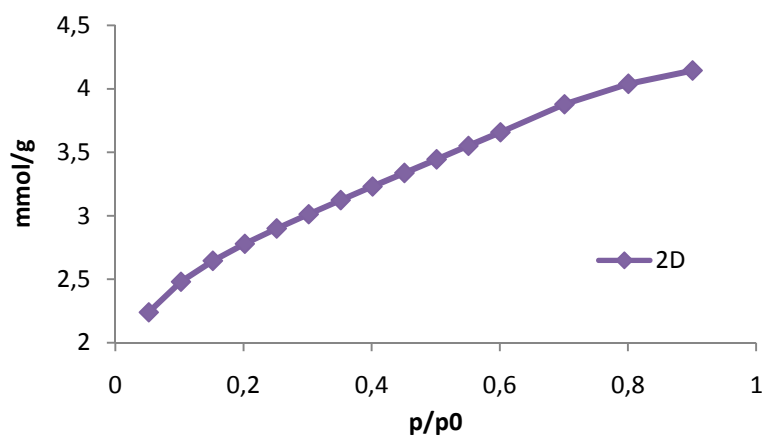
a) **2A**



b) **2C**



c) 2D



d) 2E

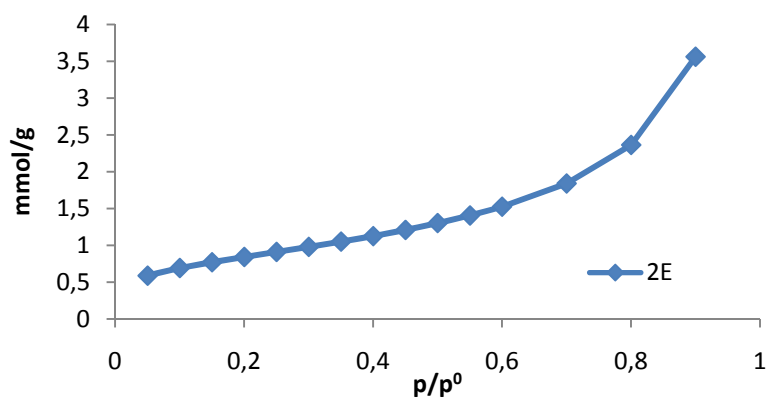


Figure 4.23 N₂ adsorption measurements of **2** type compounds and their supporting materials.

From the nitrogen adsorption (BET) analysis data, physicochemical properties of supported compounds (**2A-E**) are listed in Table 4.20. When compared with supporting materials, the decrease in the surface area and the pore volume of supported compounds (**2A-E**) is explained by the surface modification. The highest loading of ionic compound (**1o**) was found at compound **2B** and compound **2E** showed the lowest ionic compound loading.

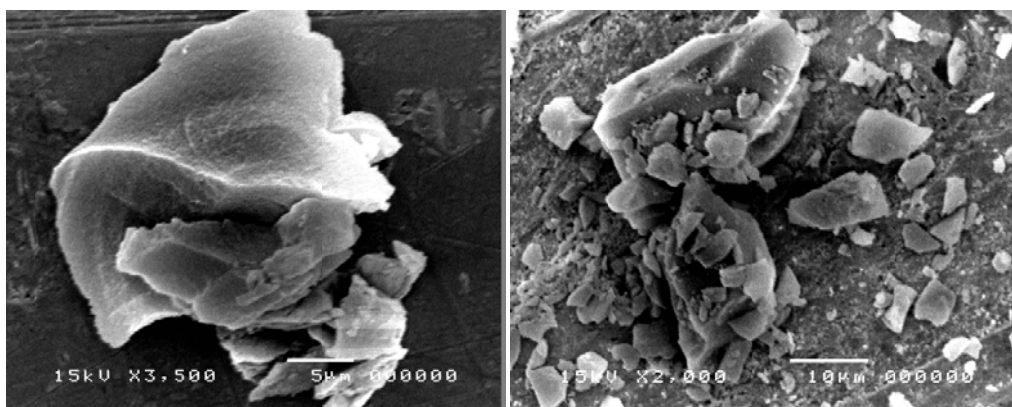
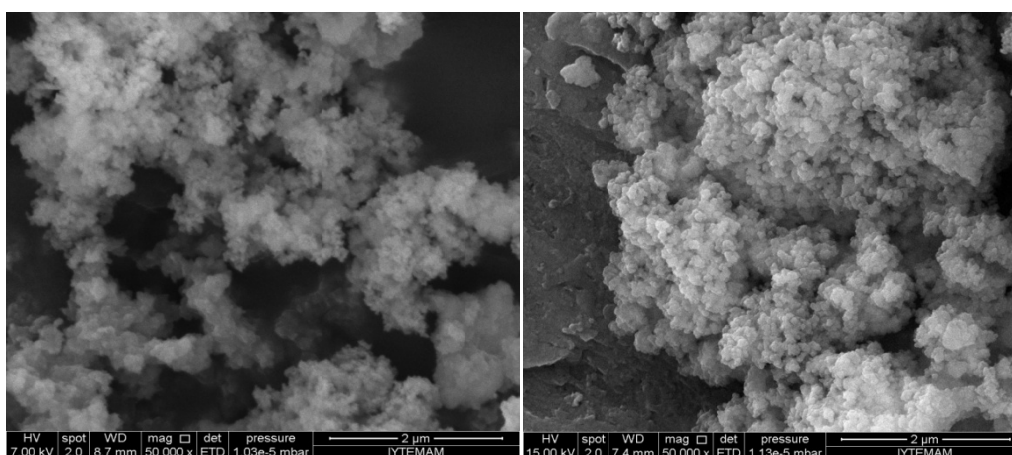
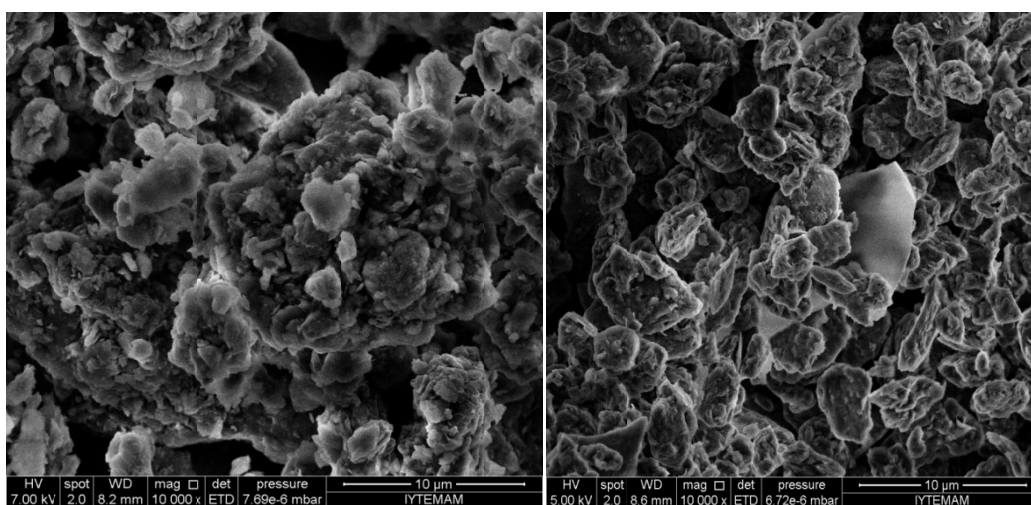
Table 4.20. Physicochemical properties of **2** type compounds and their supporting materials.

Compound	Surface area ^a (m ² g ⁻¹)	Pore volume ^b V (cm ³ g ⁻¹)	Pore size ^c (Å)	Ligand ^d (mmolg ⁻¹)
Amorphous silica	400	0.75	48.7	-
2A	244.64	0.472	77.13	0.54
Nanopowder silica	179.29	0.206	55.36	-
2B	-*	-*	-*	0.66
MK-10	125.26	0.293	25.13	-
2C	4.85	0.012	30.43	0.39
2D	68.34	0.110	45.45	0.46
Fe ₃ O ₄	55.02	0.148	19.96	-
2E	45.13	0.121	18.07	0.13

^a Calculated from BET isotherm ^b Calculated from BET isotherm (4V/A)

^c BET analysis ^d Calculated from elemental analysis * Cannot be measured due to having microporous structure.

Surface morphology and particle size distribution were analyzed by AFM and SEM. Only **2E** compound could be analyzed by AFM because of its nanoscale particle size. According to SEM images of supporting materials and compounds of type **2** (Figure 4.24), the particles appear nonuniform size in the range of 1-200 micrometer for **2A** and 2-50 micrometer for amorphous silica; 0.05-0.25 micrometer for nanopowder silica and 0.1-0.4 micrometer for **2B**; 2-15 micrometer for MK-10 and 2-10 micrometer for **2C**; 0.1-1 micrometer for **2D**; 0.025-0.3 micrometer for Fe₃O₄ and **2E**. AFM image of **2E** is consistent with its SEM image (Figure 4.25). It seems that grain size is nonhomogeneous. AFM and SEM images are convenient with sorption measurements and it can be seen that particle size of supporting materials decreased during modification with organic ligands.

a) (Left:Amorphous silica; right: **2A**)b) (left: NP; right: **2B**)c) Left: MK-10; right: **2C**

d) 2D

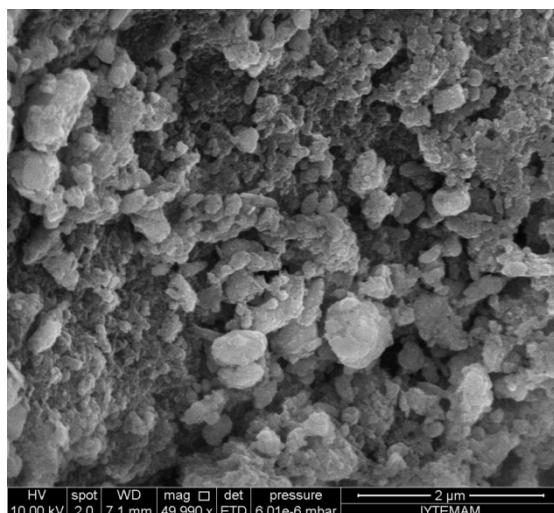
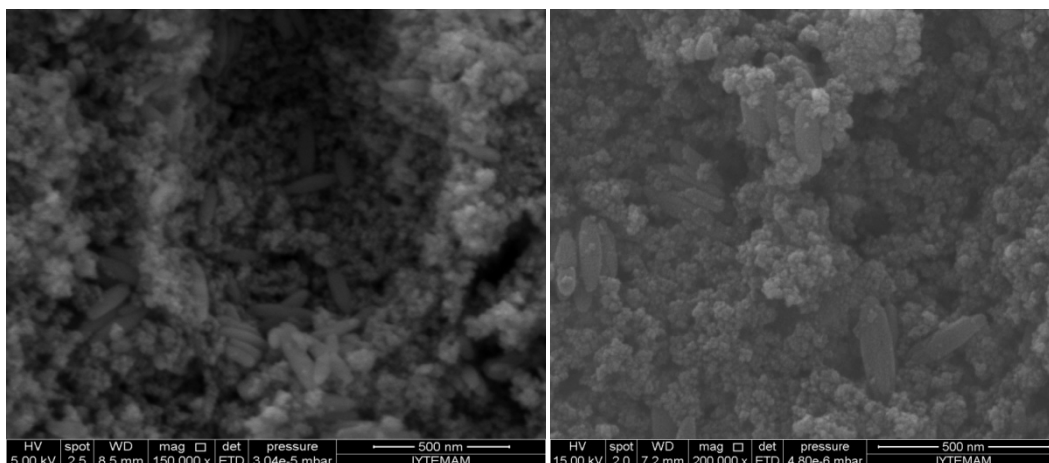
e) Left: Fe_3O_4 ; right: 2E

Figure 4.24 SEM micrographs of 2 type compounds

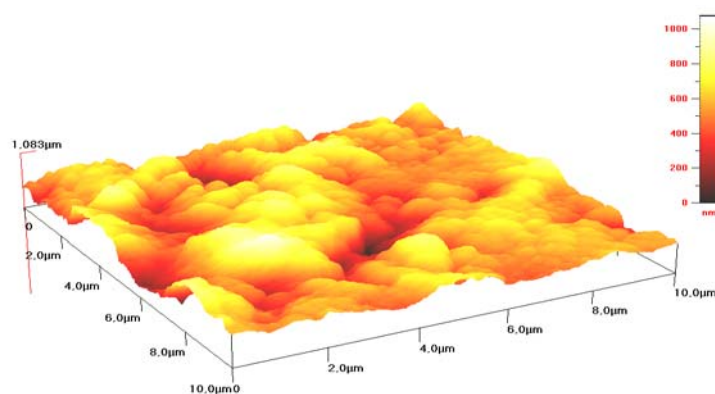
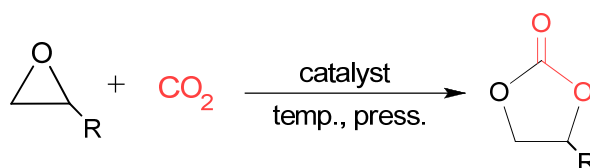


Figure 4.25 AFM image of 2E

4.2 Results of the Catalytic Studies

From the point of CO₂ fixation, one of the most common process is transformation of carbon dioxide to cyclic carbonates. Because the cyclic carbonates are widely used as organic synthetic intermediates, aprotic polar solvents, precursors for biomedical applications, and as raw materials for engineering plastics. Furthermore imidazolinium moiety and immobilized compounds of type **2** have not been used as catalysts system for chemical fixation of carbon dioxide.

In this study both imidazolinium bromides (**1**) and immobilized ionic structures (**2**) were synthesized and tested as catalysts for the transformation of from CO₂ and liquid epoxides (propylene oxide, epichlorohydrine, 1,2-epoxybutane and styrene oxide) which served as both reactant and solvent to five membered cyclic carbonates.



Scheme 4.1 General representation of cyclic carbonates formation from epoxides. R = Me, propylene oxide (PO); Et, 1,2-epoxybutane (EB); CH₂Cl, epichlorohydrin (EC); phenyl, styrene oxide (SO).

The cycloaddition reaction of carbon dioxide with epoxides in the presence of 1% **1** was conducted as a model reaction for testing and the results were compiled in Table 4.21. It is clear that the nature of the cation and anion is influencing the yield of the cyclic carbonate. Ligand structure has a marked influence on the catalytic activity.

Table 4.21 Synthesis of propylene carbonate from epoxides and CO₂ catalyzed by **1**(**1a-1r**)^a.

Entries	Cat.	Yield ^a	Entries	Cat.	Yield ^b
1	-	-	14	1l	55
2	imeo	3	15	1m	75
3	1a	54	16	1n	82
4	1b	56	17	1o	92
5	1c	59	18	1p	88
6	1d	62	19	1r	85
7	1e	63	20	1s	80
8	1f	65	21	1t	30
9	1g	67	22	1u	0
10	1h	69	23	1r-I	94
11	1i	70	24	1r-BF₄	40
12	1j	72	25	1r-PF₆	5
13	1k	75			

^a Conditions; 100 °C, 1.5 MPa, 2 h, 1 %mol **1**. ^b Determined by ¹H NMR.

Of great importance to detailed product characterization was performed with readily available ¹H NMR techniques (Figure 4.26). The yields of epoxides to corresponding cyclic carbonates were determined by comparing the ratio of product area to substrate area in the ¹H NMR spectrum of an aliquot of the reaction mixture.

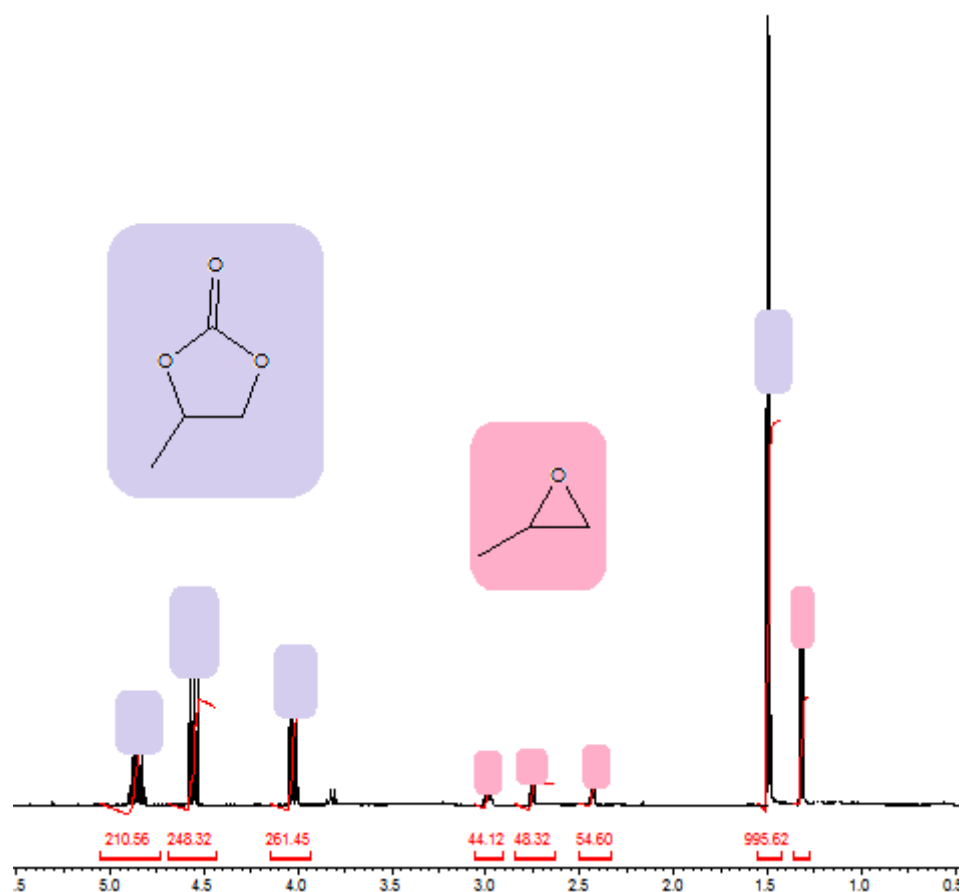


Figure 4.26. A typical ^1H NMR spectra of the reaction mixture.

In the absence of a catalyst, the reaction did not work at all and gave 1,2-propandiol as by-product (12% yield). Moreover imeo alone exhibited 3% yield of PC, 34% 1,2-propandiol, 7% propanal and 3% acetone. Therefore, **imeo** by itself gave 1,2-propandiol instead of cyclic carbonate. Using ionic liquids as catalyst that have short to long chain (**1a-l**) it can be seen that the yield of the PC increased with the chain length and only cyclic carbonate occurs selectively (Figure 4.27). The yield of PC were 54% for **1a** and 75% for **1k**. When compared **1c** (R: butyl) and **1l** (R: iso-propyl) which are isomers of each other, their influence of the cyclic carbonate formation were tested; **1c** exhibited 59% PC yield and **1l** gave lower yield (55 %).

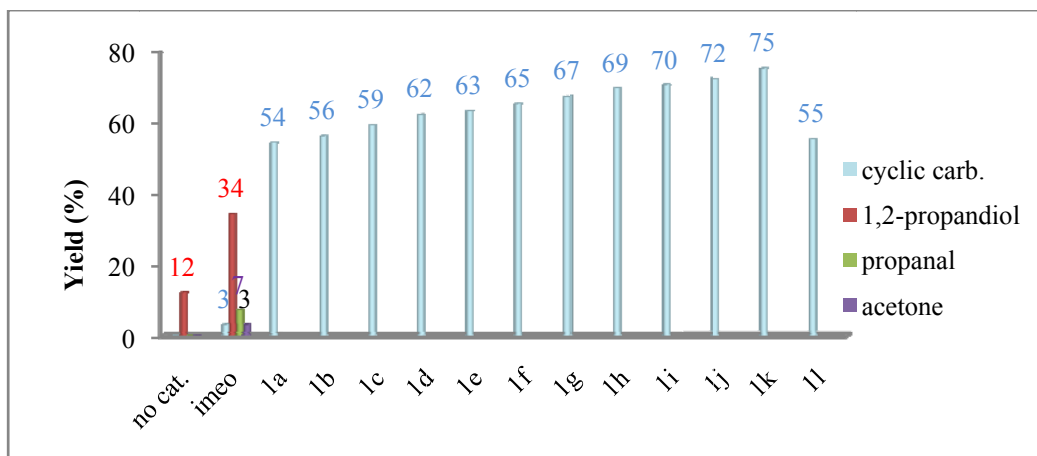


Figure 4.27 The comparison of ionic liquids that have short to long chain (100 °C, 1.5 MPa, 2 h) .

When biimidazolinium bromides (**1m-p**) used, the highest PC yield obtained with **1o** [1,4-(3-triethoxysilylpropyl)imidazolinium]butane dibromide] (Figure 4.28). Compared with monomeric ionic liquids (**1a-l**) biimidazolinium compounds are more efficient than monomeric ionic compounds.

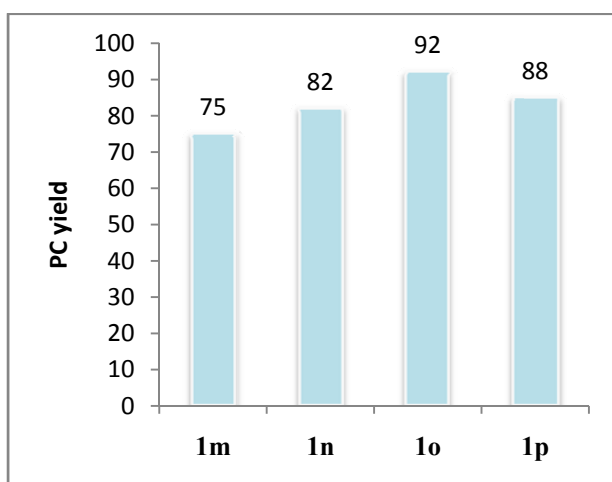


Figure 4.28. Yield of PC using dimeric ionic liquids (100 °C, 1.5 MPa, 2 h)

Ionic liquids containing functional groups on the tip of the alkyl chain (-CN, -OH, -OMe or -SO₃⁻), **1r-1u**, have also been tested as catalyst for the formation of PC from CO₂ and PO (Figure 4.29). Hydroxyl and nitrile group increased the catalytic activity, on the contrary, with sulfonate group the expected reaction did not work at all. This is reasonable according to proposed reaction mechanism; absence of a free anion the yield can be decreased. Because of having

the same chain length the comparison of **1b** with **1r** and **1t** for the formation of PC, yields are respectively 56% (**1b**), 80% (**1r**) and 85 % (**1t**).

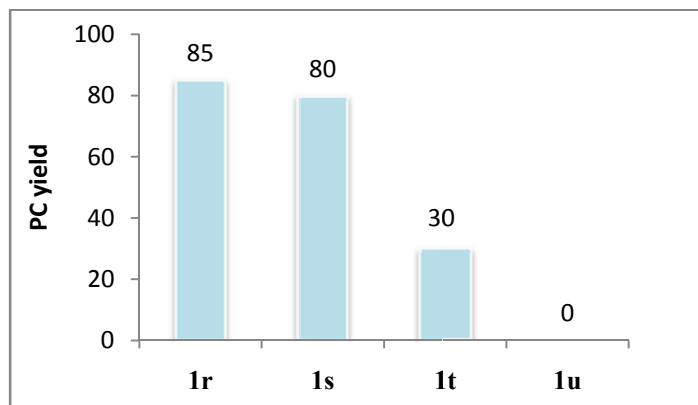


Figure 4.29 Yield of PC using ionic liquids have functional group (100 °C, 1.5 Mpa, 2 h)

The influence of the anion was tested with **1r** ionic liquid and its anion exchanged derivatives (**1r-I**, **1r-BF₄**, **1r-PF₆**). PC yield was found in the order of **1r-I** > **1r-Br** > **1r-BF₄** > **1r-PF₆** (Table 4.21).

From the results in Figure 4.27-4.29 **1o** was found to be as the most active catalyst. Therefore, for the optimization of catalytic conditions and immobilization studies to the supporting materials, **1o** has been chosen as catalyst precursor.

The most efficient ionic liquid, **1o**, immobilized into five different supporting materials. Preparation and characterization of **2** is given above. According to elemental analysis results the amount of **1o** (mmol) per gram of supporting material was calculated. For the comparison the same amount of **1o** and **2A-E** were tested under the same condition with homogeneous counterpart (**1o**). In Figure 4.30 results are given. It is clear that the catalytic activity of all heterogeneous compounds (**2A-E**) were lower than their homogeneous counterpart. **2B** that has nanopowder silica as supporting material was the most efficient immobilized catalyst probably due to its high surface area. **2E** exhibited very low catalytic activity this could be explained with acidic nature of Fe₃O₄ and low immobilization ratio of **1o** into Fe₃O₄.

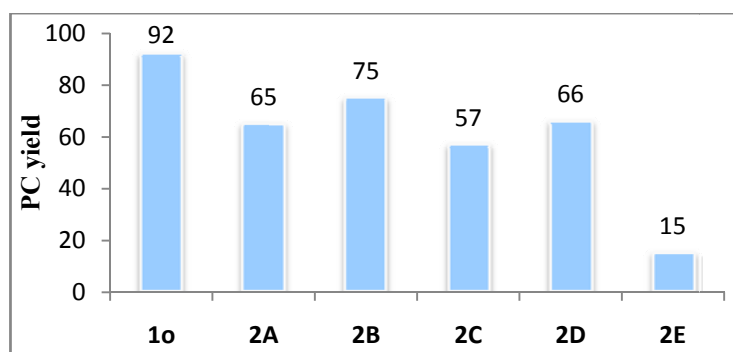


Figure 4.30 The comparison of immobilized compounds and their homogeneous counterpart (100 °C, 1.5 MPa, 2 h, 0.5 mol % cat.)

The yield of PC was increased using type **2** catalyst with increasing temperature and time of the reaction (120 °C, 3 h). It is clear that almost quantitative PC yield was achieved using **2B** as catalyst and under the same condition blank reaction did not work at all (Figure 4.31).

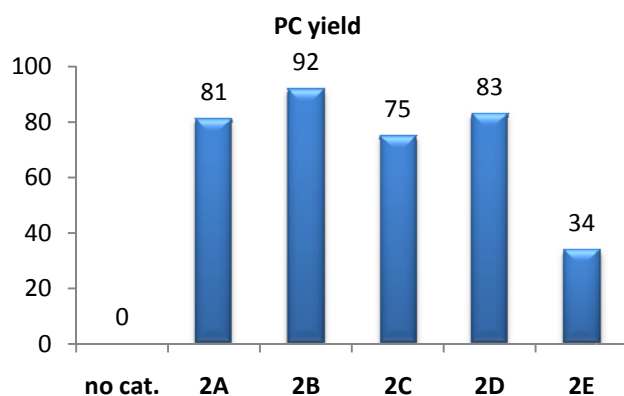


Figure 4.31. The yield of PC using type **2** compounds at 120 °C, 1.5 MPa, 3 h.

The amount of the catalyst, reaction time, reaction temperature and pressure of CO₂ are also important parameters on the yield of cyclic carbonates. For comparison using **1o** (Figure 4.32) and **2B** (Figure 4.35), optimization conditions were determined.

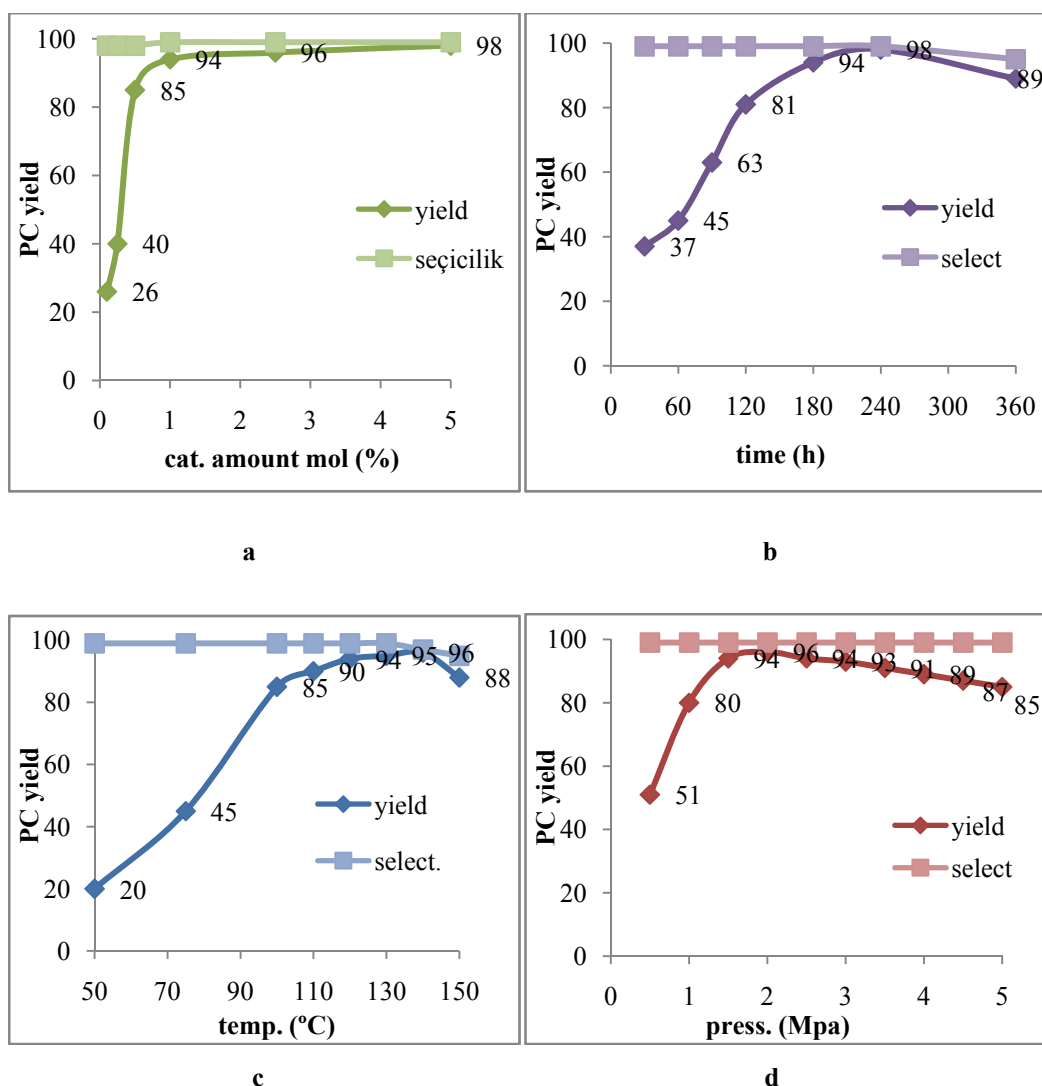


Figure 4.32. The effect of **a)** cat. amount; **b)** time; **c)** temperature; **d)** pressure on the yield of PC using **1o** as catalyst (120 °C, 1.5 MPa, 3 h).

Figure 4.32a shows the effect of catalyst loading on the yield of propylene carbonate using **1o** as a catalyst. The yield of PC was 26% using 0.05% mol catalyst but it increases sharply with the 0.5% catalyst loading (85%) then the yield slightly increase. From the environmental aspects 0.5% mol catalyst loading seems optimum.

Figure 4.32b shows the variation of PO conversion as a function of reaction time. The results indicate that the reaction progress within first 2 h, 81% PC yield could be attained after 2 h at 120 °C under 1.5 MPa CO₂ pressure. At the end of 3 h, the yield of PC reached to 94% with 99% selectivity. After 4 h the yield was almost quantitative. However, after 5 h, unexpectedly, the yield of PC decreased to 89% and selectivity decreased to 95%. This can not be explained but

decomposition of catalyst which may be responsible because, the catalyst (**1o**) was isolated as a insoluble, polymeric material. Therefore, 3 h is chosen for optimum reaction time.

Temperature effect on PC yield was illustrated in Figure 4.32c. The yield of PC increases sharply with the temperature from 50 °C to 100 °C and then slight increase up to 140 °C. However in the higher temperature, at 150 °C, the yield and selectivity of PC decreases, probably as a result of side reactions such as diol formation. Therefore the optimum temperature range was chosen as 110-120 °C.

The influence of CO₂ pressure on the yield of cyclic carbonates was studied at 120 °C and 3 h with **1o** as the catalyst (Figure 4.32d). In the low pressure region (0.5-2.0 MPa), PC yield and selectivity was in proportion to pressure but in the high pressure region (3.0-5.0 MPa) there was inverse relation between PC yield and CO₂ pressure. Similar effect of CO₂ pressure on catalytic activity has been relayed in other catalytic systems (Ulusoy et al., 2009; 2010; Addock and Nguyen, 2001; Peng and Deng, 2001; Sun et al., 2006). According to these reports, in too high CO₂ pressure medium, the molar ratio of CO₂ to epoxide would be very high, so epoxide could not play as a substrate role. The maximum yield of PC was observed at around 1.5-2.0 MPa pressure regio.

To survey the scope of different epoxides, under the optimized conditions (120 °C, 1.5 MPa, 3 h); **1o** compound was experimented and results given in Figure 4.33.

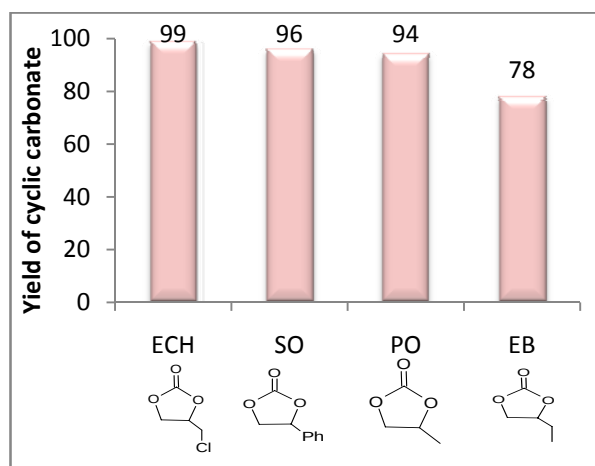


Figure 4.33 The scope of different epoxides using **1o** as catalyst ((120 °C, 1.5 MPa, 3 h, 0.5 mol % **1o**)

As can be seen from the data given in Figure 4.33, all epoxides converted into corresponding cyclic carbonates in good yields. Among the epoxides surveyed, epichlorohydrin was the most reactive epoxide. According to the proposed reaction mechanism (Mori et al., 2005) base attacks to the less sterically hindered carbon atom. Thus, if 2-position of the epoxide has an electron withdrawing group, C atom in the 3-position will be more electrophile therefore this epoxide will be more reactive.

Compound **1o** was also tested for recycling; the reaction was catalyzed up to seven times with slight decrease of the yield (Figure 4.34).

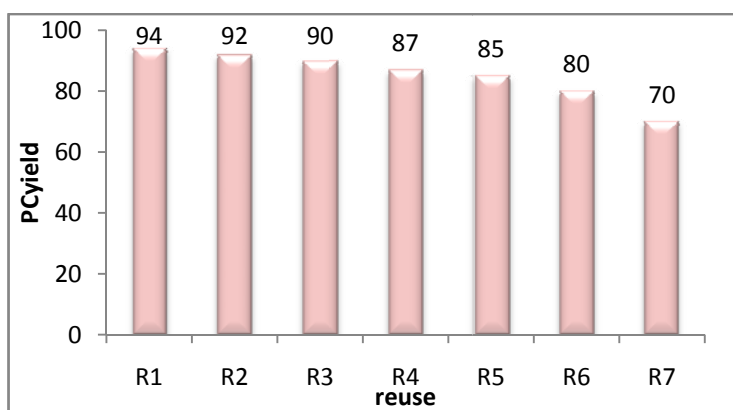


Figure 4.34 Reuse ability of **1o** compound (120 °C, 1.5 MPa, 3 h, 0.5 mol % **1o**)

Recycle experiments were examined with propylene oxide as substrate which is available for many applications and easier to separate propylene carbonate from the reaction mixture by vacuum distillation. In each cycle, **1o** catalyst were separated from the reaction mixture by vacuum distillation at 80 °C. After distillation of the propylene carbonate and propylene oxide, **1o** stayed in the reaction pot. After adding the same amount of PO, the second reuse was performed. After seven cycle the yield decreased slowly from 94% to 70% at 120 °C, 1.5 MPa and 3 h. Accordingly, the catalyst could be reused at least seven times with a slight decrease on the PC yield.

To compare homogeneous compound (**1o**) with its immobilized counterpart, the optimization conditions of PC synthesis was experimented using **2B** as heterogeneous compound. The effects of catalyst amount, reaction time, temperature, and CO₂ pressure were investigated (Figure 4.35).

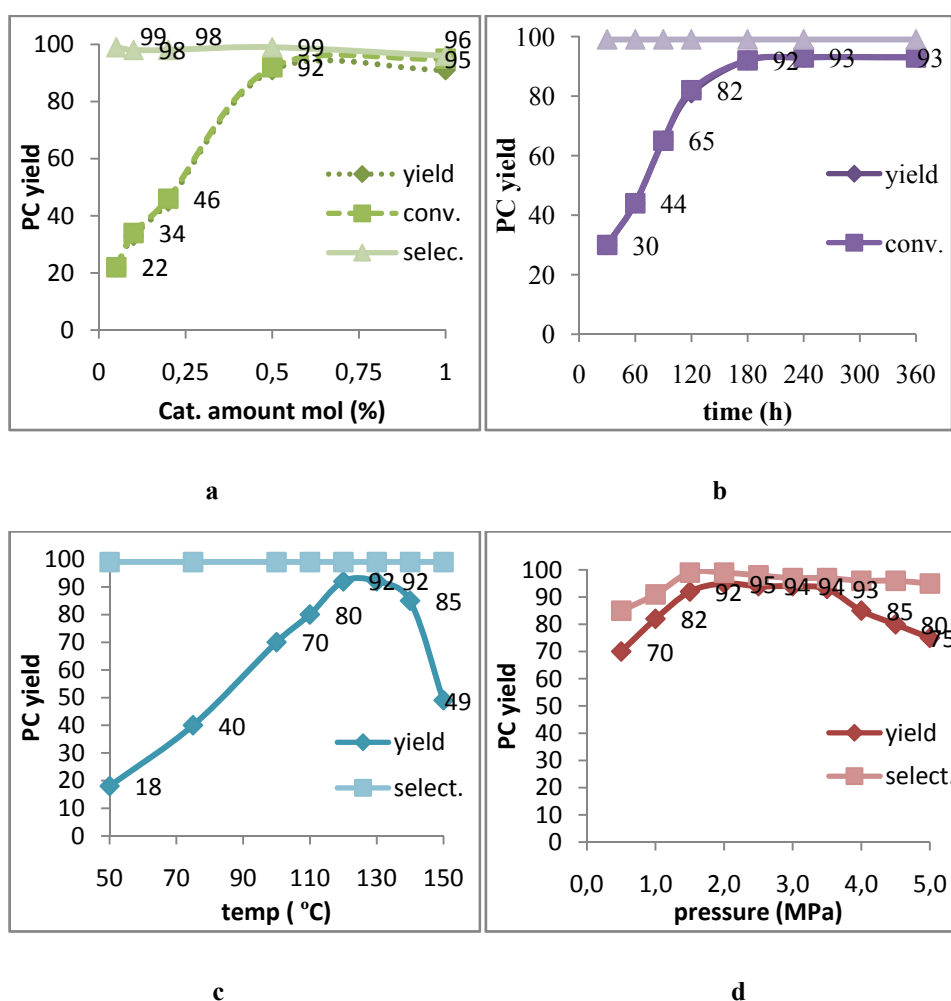


Figure 4.35. The effect of **a)** cat. amount; **b)** time; **c)** temperature; **d)** pressure on the yield of PC yield

Figure 4.35a shows the influence of catalyst loading on the yield of propylene carbonate using **2B** as catalyst. The yield of PC was 22% using 0.05% mol catalyst but it increases sharply with the 0.5% catalyst amount (92%) then slight increase on the yield was observed. From the environmental aspects 0.5% mol catalyst amount is optimum.

Figure 4.35b shows the variation of PO conversion as a function of reaction time. The results indicate that the reaction progress within first 3 h and 92% PC yield could be attained at 120 °C under 1.5 MPa CO₂ pressure. At the end of 4 h, the yield of PC reached to only 93% , the yield could not increase with time after 3 h. Therefore optimum time was determined to be 3 h for **2B**.

In Figure 4.35c, the influence of temperature on PC yield was illustrated. The yield of PC increases rapidly with the temperature from 50 °C to 120 °C and

then it became constant between 120 and 130 °C. However in the higher temperature (140 - 150 °C), the yield of PC decreases even though selectivity remains the same. Therefore the optimum temperature was chosen as 120 °C.

The influence of CO₂ pressure on the yields of cyclic carbonates was experimented at 120 °C and 3h with **2B** as the catalyst (Figure 4.35d). In the low pressure region (0.5-1.5 MPa), PC yield and selectivity was in proportion to pressure, however in the high pressure region (3.5-5.0 MPa) there was inverse relationship between PC yield and CO₂ pressure. Between 1.5 and 3.5 MPa CO₂ pressure, the yield of PC almostly quantitative. From the standpoint of safety, low pressure ,1.5 MPa CO₂ is optimum.

Compound **2B** was studied for surveying the scope of different epoxides. It can be seen in Figure 4.36, the catalyst was efficient for different epoxides at 120 °C, 3 h and 1.5 MPa CO₂ pressure). Similar affinity with **1o** compound was obtained by **2B**. Epichlorohydrine was the most reactive epoxide for the formation of cyclic carbonate from CO₂.

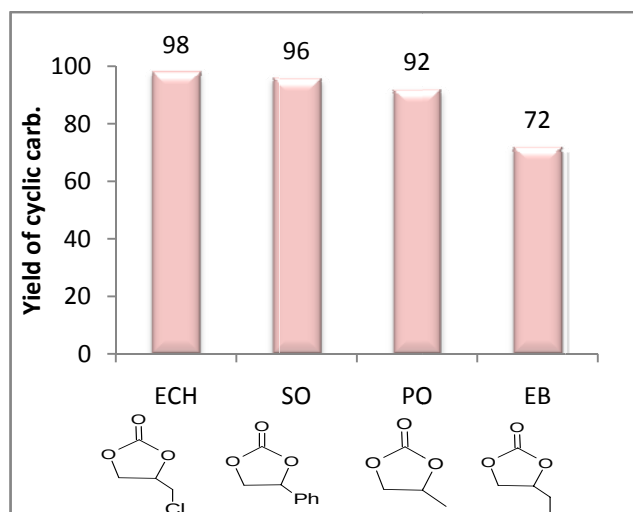


Figure 4.36 The yields of different epoxides using compound **2B**

The reuse ability of **2B** compound was investigated. It was given in Figure 4.37. From the results, **2B** catalyst was effective for the formation of cyclic carbonate.

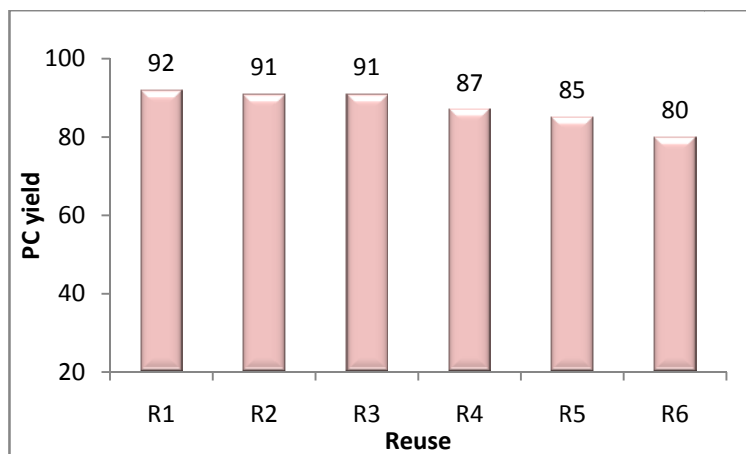


Figure 4.37 The reuse ability of **2B** compound.

After six recycle, whether any changes in catalyst structure, **2B'** was characterized by IR, TG and elemental analysis. It can be seen from IR diagrams of starting **2B** and **2B'** reused for six times (Figure 4.38), there was not significant changes at the structure of immobilized compound after recycle reactions.

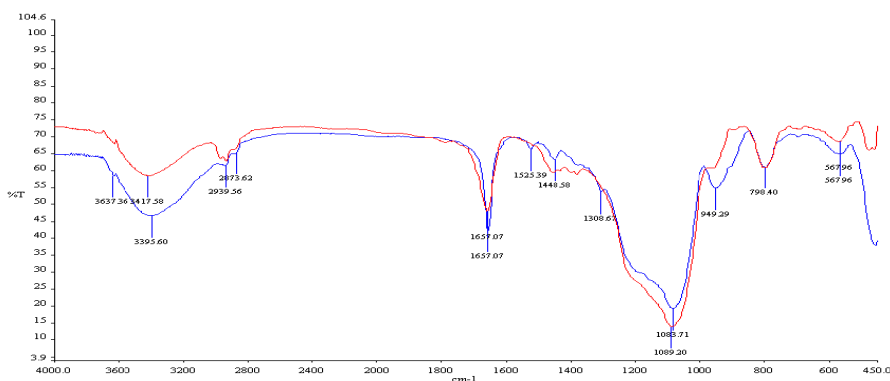


Figure 4.38 IR diagram of **2B** (blue line) and **2B'** (red line)

TGA diagram of **2B'** has also similar behavior with **2B** (Figure 4.39). Elemental analysis data is also convenient with TGA. According to the elemental analysis measurement, the amount of supported ionic liquid was calculated as 0.59 mmol ionic compound/g supporting material. This indicates that only 0.07 mmol/g ionic liquid was leached during the six cycle because of the fact that the amount of ionic compound per gram of nanopowder silica was calculated as 0.66 mmol/g from the elemental analysis of **2B** (Table 4.21).

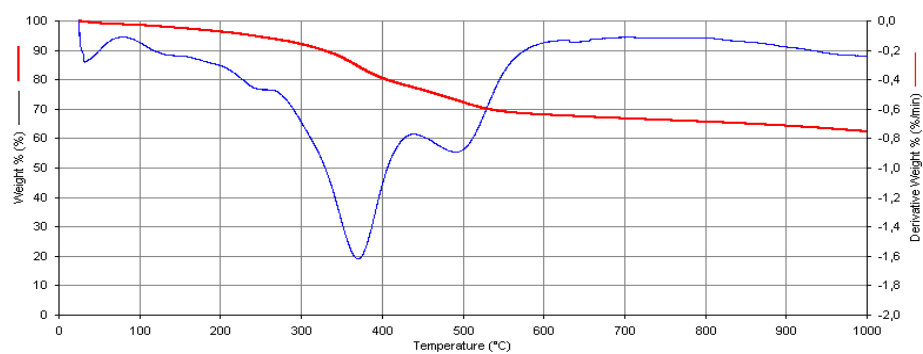


Figure 4.39 TG/DTG profile **2B'** after 6 cycle.

5 CONCLUSION

The utilization of ionic liquids as reaction media is a current topic of interest in organic synthesis. Due to the ease of catalyst recovery and product purification, ionic liquids or their combination with metal salts have been investigated

Chemical fixation of CO₂ is of great interest in connection with the development of a truly environmentally benign process, since there are many possibilities for CO₂ to be used as a safe and cheap C1 building block in organic synthesis.

CO₂ has been used in the synthesis of organic compounds such as urea, cyclic carbonates and salicylic acid. One of the most investigated process in this field is the synthesis of five-membered cyclic carbonates via the coupling of CO₂ and epoxides. These carbonates can be used as aprotic polar solvents and as precursors for polycarbonates and other polymeric materials.

Imidazolium salts mostly used as catalysts for the chemical fixation of CO₂, but using imidazolinium salts especially starting from **imeo** [1-(3-triethoxysilylpropyl) imidazoline] has not reported for the coupling of carbon dioxide with epoxides. The main aim of this thesis was to compare **imeo** derived IL with previously known ILs.

The structures of the synthesized compounds (**1a-u**) were determined by spectroscopic techniques. The one-pot reaction of these salts afforded in high yields. From the elemental analysis of supported compounds (**2A-E**) it can be seen immobilization experiments has succeeded except **2E** that is including a few amount of **1o**. TGA graphs have also proved the elemental analysis. Organic group decomposition starts after 300 °C, this enables to study with these supported compounds up to 300 °C temperature.

FT-IR measurements have demonstrated that all supported ionic compounds and their homogeneous counterpart **1o** have C=N and C-H peaks at around 1650

and 2900 cm^{-1} . These demonstrates that there has not any deformation on the structure of ionic compound (**1o**) during immobilization process.

The effect of the length of chain, functional group and anion on the structure and the effect of different type of supporting materials on the structure and catalytic activity were investigated. The yield of PC increased with increasing the alkyl length. Ionic liquids that have functional group has showed catalytic activities as supposed. According to reaction mechanism in the literature, the Lewis acidity of cation is proportion with the yield of cyclic carbonate. The highest PC yield was obtained by using **1r** that has cyano group owing to have higher Lewis acidity. The lowest PC yield was observed when used **1u**, a zwitterionic compound that includes sulfonate group. The absence of free anion can be concluded this result.

According to results of the catalytic experiment, the most active catalysts for the type **1** homogeneous compound was found **1o** (92%); and for the type **2** supported compound was **2B** (75%).

The optimization studies on the catalytic system were performed by changing parameters such as the amount of the catalyst, reaction temperature, pressure of CO_2 and reaction time. The optimum conditions were chosen as 120°C , 15 atm CO_2 pressure, 3h and 0.5 mol % the amount of catalyst.

Recycling experiments were carried out under the optimized conditions using **1o** and **2B** as catalyst. The catalysts were effective for the cycloaddition of propylene oxide up to six times without significant decrease on the PC yield. It can be declined that it was observed decomposition of catalyst during the reuse experiment of homogeneous compound, **1o**.

6 REFERENCES

- Abbott, A. P., Boothby, D., Capper, G., Davies, D. L., and Rasheed, R. K.,** 2004, Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids, *J. Am. Chem. Soc.*, 126, 9142p.
- Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K. and Tambyrajah, V.,** 2003, Novel solvent properties of choline chloride/urea mixtures, *Chem. Comm.*, 70p.
- Abu-Reziq, R., Wang, D., Post, M. and Alper, H.,** 2007, Platinum Nanoparticles Supported on Ionic Liquid-Modified Magnetic Nanoparticles: Selective Hydrogenation Catalysts, *Adv. Synth. Catal.*, 349, 2145p.
- Albright, L. F.,** 1990, Alkylation will be key process in reformulated gasoline era, *Oil Gas J.*, 88, 79p.
- Aresta, M., Dibenedetto, A., Dileo, C., Tommasi, I. and Amodio, E.,** 2003, The first synthesis of a cyclic carbonate from a ketal in Sc-CO₂, *J. Supercrit. Fluids*, 2003, 25, 177p.
- Aresta, M., Dibenedetto, A. and Tommasi, I.,** 2000, Direct synthesis of organic carbonates by oxidative carboxylation of olefins catalyzed by metal oxides: developing green chemistry based on carbon dioxide, *Appl. Organomet. Chem.*, 14, 799p.
- Asahi, JP Pat. 3,109,358, 1991
- Atkins, M. P., Smith, M. R. and Ellis, B.,** 1997, BP Chemicals, EP 0 791 643
- Baba, A., Nozaki, T. and Matsuda, H. ,** 1987, Carbonate Formation from Oxiranes and Carbon Dioxide Catalyzed by Organotin Halide-Tetraalkylphosphonium Halide Complexes, *Bull. Chem. Soc. Jpn.*, 60, 1552p.
- Baker, T., Kobayashi, S. and Leitner, W.,** 2006, Divide et Impera-Multiphase, Green Solvent and Immobilization Strategies for Molecular Catalysis, *Adv. Synth. Catal.* 48, 1337p.
- Bates, E. D., Mayton, R. D., Ntai, I. and Davis, J. H.,** 2002, CO Capture by a Task-Specific Ionic Liquid, *J. Am. Chem. Soc.*, 124, 926p.
- Bayardon, J., Holz, J., Schäffner, B., Andrushko, V., Verevki, S., Preetz, A. and Börner, A.,** 2007, Propylene Carbonate as a Solvent for Asymmetric Hydrogenations, *Angew. Chem., Int. Ed.*, 46, 5971p.

REFERENCES (CONTINUED)

- Behr, A.**, 1988, Carbon Dioxide as an Alternative C₁ Synthetic Unit: Activation by Transition-Metal Complexes, *Angew. Chem., Int. Ed. Engl.*, 27, 661p.
- Bhatt, A.I., Bond, A.M., MacFarlane, D.R., Zhang, J., Scott, J.L., Strauss, C.R., Iotov, P.I. and Kalcheva, S.V.**, 2006, A critical assessment of electrochemistry in a distillable room temperature ionic liquid, DIMCARB, *Green Chem.*, 8, 161p.
- Binnemans, K.**, 2007, Lanthanides and Actinides in Ionic Liquids, *Chem. Rev.* 107, 2592p.
- Beilstein** Handbuch der Organischen Chemie; 1921, Springer-Verlag: Berlin, Vol. III, 3p.
- Bonnet, P., Lacroix, E. and Schirmann, J.-P.**, 2001, ATOFINA, WO 01/81353 A1.
- Bourbigou, H. O., Magna ,L. and Morvan, D.**, 2010, Ionic liquids and catalysis: Recent progress from knowledge to applications ,*Applied Catalysis A: General*, 373, 1p.
- Bösmann, A., Franciò, G., Janssen, E., Solinas, M., Leitner, W. and Wasserscheid, P.**, 2001, Activation, Tuning and Immobilisation of homogeneous catalysts in an ionic liquid/compressed CO₂ continuous flow system, *Angew. Chem. Int. Ed.*, 40, 2697p.
- Breitenlechner, S., Fleck, M., Müller, T. E. and Suppan, A.**, 2004, Solid Catalyst on the Basis of Supported Ionic Liquids and Their Use in Hydroamination Reactions, *J. Mol. Catal. A*, 214, 175p.
- Bright, F. V., and Baker, G., J.** 2006, Comment on “How Polar Are Ionic Liquids? Determination of the Static Dielectric Constant of an Imidazolium-based Ionic Liquid by Microwave Dielectric Spectroscopy”, *Phys. Chem. B* 110, 5822p.
- Bu, Z., Qin, G. and Cao, S.**, 2007, *J.Mol.Catal.A:Chem.*, 277, 35p.
- Caló, V., Nacci, A., Monopoli, A. and Fanizzi, A.**, 2002, Cyclic Carbonate Formation from Carbon Dioxide and Oxiranes in Tetrabutylammonium Halides as Solvents and Catalysts, *Org. Lett.*, 4, 2561p.
- Casadei, M. A., Inesi, A and Rossi, L.**, 1997, Electrochemical activation of Carbon Dioxide: Synthesis of Organic Carbonates, *Tetrahedron Lett.*, 38, 3565p.

REFERENCES (CONTINUED)

- Chang, T. C. T.**, (General Electric Co.) EP-A 3 50 700, 1988; *Chem. Abstr.* 1990, 113, 40168u.
- Chaturvedi, D., Mishra, N. and Mishra, V.**, 2007, A high yielding, one-pot synthesis of dialkyl carbonates from alcohols using Mitsunobu's reagent, *Tetrahedron Lett.*, 48, 5043p.
- Chauvin, Y., Hirschauer, A., Olivier, H.**, 1994, Alkylation of isobutane with 2-butene using 1-butyl-3-methylimidazolium chloride-aluminium chloride molten salts as catalysts, *J. Mol. Catal.*, 92, 155p.
- Chauvin, Y., Olivier, H., Cornils, B. and Herrmann W. A.** (Eds.), 2000, *Applied Homogeneous Catalysis with Organometallic Compounds*, WILEY-VCH Verlag GmbH, Weinheim, pp. 258p.
- Chiappe, C., Malvaldi, M. and Pomelli, C.S.**, 2009, Ionic liquids: Solvation ability and polarity, *Pure Appl. Chem.* 81, 767p.
- Choi, J. C., Kohno, K., Ohshima, Y., Yasuda, H. and Sakakura, T.**, 2008, Tin- or titanium-catalyzed dimethyl carbonate synthesis from carbon dioxide and methanol: Large promotion by a small amount of triflate salts, *Catal. Commun.*, 9, 1630p.
- Coates, G. W. and Moore, D. R.**, 2004, Discrete Metal-Based Catalysts for the Copolymerization of CO₂ and Epoxides: Discovery, Reactivity, Optimization, and Mechanism, *Angew. Chem., Int. Ed.*, 43, 6618p.
- Commereuc, D., Harry, S., Magna, L. and Olivier-Bourbigou, H.**, 2004, Process for carbonylating alcohols, employing a catalyst based on rhodium or iridium in a non-aqueous ionic liquid, with efficient catalyst recycling, Institut Francais du Petrole, US2004059153.
- Concellon, J. M., del Solar, V., Granda, S. G. and Diaz, M. R.**, 2007, Totally Selective Reaction of CO₂ with Enantiopure Amino Epoxides under Mild Reaction Conditions. Synthesis and Synthetic Applications of Enantiopure (4R,1'S)- or (4S,1'S)-4-(1-Aminoalkyl)-2-oxo-1,3-dioxolanes *J. Org. Chem.*, 72, 7567p.
- Cornils, B., Herrmann, W. A., Horvath, I. T., Leitner, W., Mecking, S., Bourbigou, H. O. and Vogt., D.**, 2005, *Multiphase Homogeneous Catalysis*, Wiley-VCH Verlag GmbH & Co. kGaA, Weinheim.

REFERENCES (CONTINUED)

- Dai, W.-L., Yin, S.-F., Guo, R., Luo, S.-L., Du, X. and Au, C.-T.,** 2010, Synthesis of Propylene Carbonate from Carbon Dioxide and Propylene Oxide Using Zn-Mg-Al Composite Oxide as High-efficiency Catalyst, *Catal. Lett.*, 136, 35p.
- Dai, W.-L., Luo, S.-L., Yin, S.-F. and Au, C. T,** 2009, The direct transformation of carbon dioxide to organic carbonates over heterogeneous catalysts *Appl. Catal., A*, 366, 2p.
- Damen, M. R., Brand, R. W., Bloem, S. C., Pinggen, E., Steur, K., Peters, C. J., Witkamp, G. J. and Kroon, M. C.,** 2009, Process intensification by combining ionic liquids and supercritical carbon dioxide applied to the design of levadopa production, *Chem. Eng. Process*, 48, 549p.
- Darensbourg, D. J. and Holtcamp, M. W.,** 1996, Catalysts for the reactions of epoxides and carbon dioxide, *Coord. Chem. Rev.*, 153, 155p.
- Darensbourg, D. J.,** 2007, Making Plastics from Carbon Dioxide: Salen Metal Complexes as Catalysts for the Production of Polycarbonates from Epoxides and CO₂, *Chem. Rev.*, 107, 2388p.
- Darensbourg, D. J., Ulusoy, M., Karroonnirum, O., Poland, R. R., Reibenspies, J. H. and Çetinkaya, B.,** 2009, Highly Selective and Reactive (salen)CrCl Catalyst for the Copolymerization and Block Copolymerization of Epoxides with Carbon Dioxide, *Macromolecules*, 42, 6992p.
- DeCastro, C., Sauvage, E., Valkenberg, M. H. and Hölderich, W. F.,** 2000, Immobilised Ionic Liquids as Lewis Acid Catalysts for the Alkylation of Aromatic Compounds with Dodecene, *J.Catal.*, 196, 86p.
- Doskocil, E. J. and Davis, R. J.,** 1999, Spectroscopic Characterization and Catalytic Activity of Zeolite X Containing Occluded Alkali Species, *J. Catal.*, 188, 353p.
- Doskocil, E. J.,** 2004, Ion-exchanged ETS-10 catalysts for the cycloaddition of carbon dioxide to propylene oxide, *Microporous Mesoporous Mater.*, 76, 177p.
- Doskocil, E. J.,** 2005, Effect of Water and Alkali Modifications on ETS-10 for the Cycloaddition of CO₂ to Propylene Oxide *J. Phys. Chem. B*, 109, 2315p.

REFERENCES (CONTINUED)

- Doskocil, E. J., Bordaweakar, S. V., Kaye, B. G. and Davis, R. J.,** 1999, UV-Vis Spectroscopy of Iodine Adsorbed on Alkali-Modified Zeolite Catalysts for Addition of Carbon Dioxide to Ethylene Oxide, *J. Phys. Chem. B*, 103, 6277p.
- Du, Y., Kong, D.-L., Yang, H.-Y., Cai, F., Tian, J.-S., Wang, J.-Q. and He, L.-N.,** 2005, Sn-catalyzed synthesis of propylene carbonate from propylene glycol and CO₂ under supercritical conditions, *J. Mol. Catal. A: Chem.*, 241, 233p.
- Duan, Z., Gu, Y. and Deng, Y.,** 2005, Brønsted Acidic Ionic Liquids: Fast, Mild, and Efficient Catalysts for Solvent-Free Tetrahydropyranylation of Alcohols, *Synth. Commun.*, 35, 1939p.
- Earle, M.J., Esperanca, J., Gilea, M.A., Lopes, J.N.C., Rebelo, L.P.N., Magee, J.W., Seddon, K.R. and Widegren, J.A.,** 2006, The distillation and volatility of ionic liquids, *Nature* 439, 831p.
- Eghbali, N. and Li, C. J.,** 2007, Conversion of carbon dioxide and olefins into cyclic carbonates in water *Green Chem.*, 9, 213p.
- Falling, S. N., Godleski, S. A. and McGarry, L. W.,** 1993, Process for the separation of oligomeric materials from a catalyst mixture, Eastmann Kodak Company, US 5,238,889.
- Fernicola, A., Panero, S., Scrosati, B., Tamada, M. and Ohno, H.,** 2007, New Types of Brønsted Acid–Base Ionic Liquids-Based Membranes for Applications in PEMFCs *ChemPhysChem*, 8, 1103p.
- Fraga-Dubreuil, J., Famelart, M. H. and Bazureau, J. P.,** 2002, Ecofriendly Fast Synthesis of Hydrophilic Poly(ethyleneglycol)-Ionic Liquid Matrices for Liquid-Phase Organic Synthesis, *Org. Process. Res. Dev.*, 6, 374p.
- Freemantle, M.,** 2003, BASF's Smart Ionic Liquid, Process Scavenges Acid On A Large Scale Without Producing Solids, *Chem. Eng. News*, 81, (13), 9p.
- Fröba, A.P., Kremer, H. And Leipertz, A.,** 2008, Density, Refractive Index, Interfacial Tension, and Viscosity of Ionic Liquids [EMIM][EtSO₄], [EMIM][NTf₂], [EMIM][N(CN)₂], and [OMA][NTf₂] in Dependence on Temperature at Atmospheric Pressure, *J. Phys. Chem. B.*, 112, 12420p.

REFERENCES (CONTINUED)

- Fujinami, T., Sato, S. and Sakai, S.**, 1981, A facile preparation of dialkyl carbonates from potassium carbonate and alkyl bromides by using organostannyl compound as a catalyst, *Chem. Lett.* 749p.
- Fujita, S.-i., Bhanage, B. M., Ikushima, Y., Shirai, M., Torii, K. and Arai, M.**, 2002, Chemical Fixation of Carbon Dioxide to Propylene Carbonate Using Smectite Catalysts with High Activity and Selectivity, *Catal. Lett.*, 79, 95p.
- Fukuda, Y. and Tanabe, K.**, 1973, Infrared Study of Carbon Dioxide Adsorbed on Magnesium and Calcium Oxides *Bull. Chem. Soc. Jpn.*, 46, 1616p.
- Fukumoto, K. and Ohno, H.**, 2006, Design and synthesis of hydrophobic and chiral anions from amino acids as precursor for functional ionic liquids, *Chem. Comm.*, 3081p.
- Fukuoka, S., Ogawa, H., Watanabe, T.**, 1990, (Asahi Chem. Ind. Co. Ltd.) *Jap. Pat.* 01 16 551, 1989; *Chem. Abstr.* 112, 76618p.
- Gadenne, B., Hesemann, P. and Moreau, J. J. E.**, 2004, Supported ionic liquids: ordered mesoporous silicas containing covalently linked ionic species, *Chem. Comm.*, 1768p.
- Geldbach, T. J.**, 2008, Organometallics in ionic liquids: catalysis and coordination chemistry, *Organomet. Chem.*, 34, 58p.
- Gilbert, B., Chauvin, Y., and Guibard, I.**, 1991, Investigation by Raman spectrometry of a new room-temperature organochloroaluminate molten salt, *Vibr. Spectrosc.*, 299p.
- Gilbert, B., Olivier-Bourbigou, H. and Favre, F.**, 2007, Chloroaluminate Ionic Liquids: from their Structural Properties to their Applications in Process Intensification, *Oil Gas Sci. Technol.*, 62, 745p.
- Guo S., Du, Z., Zhang, S., Li, D., Li, Z. and Deng, Y.**, 2006, Clean Beckmann rearrangement of cyclohexanone oxime in caprolactam- based Brønsted acidic ionic liquids, *Green Chem.*, 8, 296p.
- Guo, L., Wang, C., Luo, X., Cui, G. and Li, H.**, 2010, Probing catalytic activity of halide salts by electrical conductivity in the coupling reaction of CO₂ and propylene oxide, *Chem. Comm.*, 46, 5960p.
- Han, X. And Armstrong, D.W.**, 2007, Ionic Liquids in Separations, *Acc. Chem. Res.* 40, 1079p.

REFERENCES (CONTINUED)

- Hagiwara, H., Sugawara, Y., Isobe, K., Hoshi, T. and Suzuki, T.,** 2004, Immobilization of Pd(OAc)₂ in Ionic Liquid on Silica: Application to Sustainable Mizoroki-Heck Reaction, *Organic Lett.*, 2325p.
- Hallgren, J. E.,** 1978, (General Electric Co.) U.S. Pat. 4,096,168, 1978; *Chem. Abstr.* 89, 42830p.
- Hapiot, P. and Lagrost, C.,** 2008, Electrochemical Reactivity in Room-Temperature Ionic Liquids, *Chem. Rev.* 108, 2238p.
- Hope, K. D., Stern, D. A. and Twomey, D. W.,** 2004, Method for manufacturing high viscosity polyalphaolefins using ionic liquid catalysts, Akzo Nobel, US 2004 0005985
- Horniakova, J., Raja, T., Kubota, Y. And Sugi, Y.,** 2004, Pyridine-derived palladium complexes immobilized on ordered mesoporous silica as catalysts for Heck-type reactions, *J. Mol. Cat. A*, 217, 73p.
- Hou, Y., Gu, Y., Zhang, S., Yang, F., Ding, H. and Shan, Y.,** 2008, Novel binary eutectic mixtures based on imidazole, *J. Mol. Liquids*, 143, 154p.
- Carbon dioxide,** 10 September 2011, <http://en.wikipedia.org/wiki/CO2>
- Global warming,** 10 September 2011, http://en.wikipedia.org/wiki/Global_warming
- Greenhouse gas,** 10 September 2011, http://en.wikipedia.org/wiki/Greenhouse_gas
- Greener Industry,** 10 September 2011, http://www.greener-industry.org.uk/pages/safer/safer_4_reactions.htm
- Huang, J. W. and Shi, M.,** 2003, Chemical Fixation of Carbon Dioxide by NaI/PPh₃/PhOH, *J. Org. Chem.*, 68, 6705p.
- Huang, J.-F., Baker, G.A, Luo, H., Hong, K, Li, Q.-F., Bjerrum N.J, Dai S.,** 2006, Brønsted acidic room temperature ionic liquids derived from *N,N*-dimethylformamide and similar protophilic amides, *Green Chem.*, 8, 599p.
- Huang, S. Y., Liu, S. G., Li, J. P., Zhao, N., Wei, W. and Sun, Y. H.,** 2007, Modified Zinc Oxide for the Direct Synthesis of Propylene Carbonate from Propylene Glycol and Carbon dioxide *Catal. Lett.*, 118, 290p.
- Huang, S. Y., Ma, J., Li, J. P., Zhao, N., Wei, W. and Sun, Y. H.,** 2008, Efficient propylene carbonate synthesis from propylene glycol and carbon dioxide via organic bases, *Catal. Commun.*, 9, 276p.

REFERENCES (CONTINUED)

- Huang, S.-Y., Liu, S.-G., Li, J.-P., Zhang, N., Wei, W. and Sun, Y.-H.**, 2007, Synthesis of cyclic carbonate from carbon dioxide and diols over metal acetates, *J. Fuel Chem. Technol.*, 35, 701p.
- Inoue, S.**, 2005, *Gendai Kagaku*, 408, 42
- Inoue, S., Koinuma, H. and Tsuruta, T.**, 1969, Copolymerization of carbon dioxide and epoxide, *J. Polym. Sci., Part B: Polym. Lett.*, 7, 287p.
- Inoue, S., Koinuma, H. and Tsuruta, T.**, 1969, Copolymerization of carbon dioxide and epoxide with organometallic compounds, *Makromol. Chem.*, 130, 210p.
- Jacquemin, J., Nancarrow, P., Rooney, D.W., Gomes, M. F. C., Husson, P., Majer, V., Padua, A. A. H. and Hardacre, C.**, 2008, Prediction of Ionic Liquid Properties. II. Volumetric Properties as a Function of Temperature and Pressure, *J. Chem. Eng. Data* 53, 2133p.
- Jagtap, S. R., Raje, V. P., Samant, S. D. and Bhanage, B. M.**, 2007, Silica supported polyvinyl pyridine as a highly active heterogeneous base catalyst for the synthesis of cyclic carbonates from carbon dioxide and epoxides, *J. Mol. Catal. A: Chem.*, 266, 69p.
- Jessop, P. G., Stanley, R. R., Brown, R. A., Eckert, C. A., Liotta, C. L., Ngo, T. T. and Pollet, P.**, 2003, Neoteric solvents for asymmetric hydrogenation: supercritical fluids, ionic liquids, and expanded ionic liquids, *Green Chem.*, 5, 123p.
- Jiang, H. F., Wang, A.-Z., Liu, H.-L. and Qi, C.-R.**, 2008, Reusable Polymer-Supported Amine-Copper Catalyst for the Formation of α -Alkylidene Cyclic Carbonates in Supercritical Carbon Dioxide, *Eur. J. Org. Chem.*, 2309p.
- Jiang, T. and Han, B.**, 2009, Ionic Liquid Catalytic Systems and Chemical Reactions, *Current Org. Chem.*, 13, 1278p.
- Jiang, T., Gao, H.X., Han, B.X., Zhao, G.Y., Chang, Y.H., Wu, W.Z. and Yang, G.Y.**, Ionic liquid catalyzed Henry reactions. *Tetrahedron Lett.*, 2004, 45, 2699p.
- Ju, H.-Y., Manju, M.-D., Kim, K.-H., Park, S.-W. and Park, D.-W.**, 2008, Catalytic performance of quaternary ammonium salts in the reaction of butyl glycidyl ether and carbon dioxide, *J. Ind. Eng. Chem.*, 14, 157p.

REFERENCES (CONTINUED)

- Kasuga, K., Nagao, S., Fukumoto, T. and Handa, M.,** 1996, Cycloaddition of carbon dioxide to propylene oxide catalysed by tetra-*t*-butylphthalocyaninatoaluminium(III) chloride, *Polyhedron*, 15, 69p.
- Kayaki, Y., Yamamoto, M. and Ikariya, T.,** 2007, Stereoselective Formation of *r*-Alkylidene Cyclic Carbonates via Carboxylative Cyclization of Propargyl Alcohols in Supercritical Carbon Dioxide, *J. Org. Chem.*, 72, 647p.
- Kezuka, H. and Okuda, F.,** 1993, (Idemitsu Kosan Co. Ltd.) EP 508,340, 1991; *Chem. Abstr.* 118, 101660a.
- Kihara, N., Hara, N. and Endo, T.,** 1993, Catalytic Activity of Various Salts in the Reaction of 2,3-Epoxypropyl Phenyl Ether and Carbon Dioxide under Atmospheric Pressure, *J. Org. Chem.*, 58, 6198p.
- Kim, D. W., Hong, D. J., Jang, K. S. and Chi, D. Y.,** 2006, Structural Modification of Polymer-Supported Ionic Liquids as Catalysts for Nucleophilic Substitution Reactions Including Fluorination, *Adv. Synth. Catal.*, 348, 1719p.
- Kim, H. S., Kim, J. J., Kim, H. and Jang, H. G.,** 2003, Imidazolium zinc tetrahalide-catalyzed coupling reaction of CO₂ and ethylene oxide or propylene oxide, *J. Catal.*, 220, 44p.
- Kishimoto, Y. and Ogawa, I.,** 2004, Amine-Catalyzed, One-Pot Coproduction of Dialkyl Carbonates and 1,2-Diols from Epoxides, Alcohols, and Carbon Dioxide, *Ind. Eng. Chem. Res.*, 43, 8155p.
- Knifton, J. F.,** 1986, Process for Production of Ethylene Glycol and Dimethyl Carbonate, US Pat. 4,734,518.
- Knifton, J. F.,** 1987, Process for Co-Synthesis of Ethylene Glycol and DMC, US Pat. 4,661609.
- Knifton, J. F.,** 1988, Process for Co-Synthesis of Ethylene Glycol and DMC, US Pat. 4, 734, 518.
- Koshev, K., Koseva, N. and Troev, K.,** 2003, Calcium chloride as co-catalyst of onium halides in the cycloaddition of carbon dioxide to oxiranes, *J. Mol. Catal. A: Chem.*, 194, 29.

REFERENCES (CONTINUED)

- Lecocq, V., Graille, A., Santini, C. C., Baudouin, A., Chauvin, Y., Basset, J. M., Arzel, L., Bouchu, D. and Fenet, B.,** 2005, Synthesis and characterization of ionic liquids based upon 1-butyl-2,3-dimethylimidazolium chloride/ ZnCl_2 , *New J. Chem.*, 29, 700p.
- Lee, E.-H., Ahn, J.-Y., Dharman, M.M., Park, D.-W., Park, S.-W. and Kim, I.,** 2008, Synthesis of cyclic carbonate from vinyl cyclohexene oxide and CO_2 using ionic liquids as catalysts *Catal. Today*, 131, 130p.
- Li, F., Xiao, L., Xia, C. and Hu, B.,** 2004, Chemical fixation of CO_2 with highly efficient ZnCl_2 /[BMIm]Br catalyst system, *Tetrahedron Lett.*, 45, 8307p.
- Li, Q., Zhang, W., Zhao, N., Wei, W. and Sun, Y.,** 2006, Synthesis of cyclic carbonates from urea and diols over metal oxides, *Catal. Today*, 115, 111p.
- Lin, I. J. B. and Vasam, C. S.,** 2005, Metal-containing ionic liquids and ionic liquid crystals based on imidazolium moiety, *J. Organomet. Chem.* 690, 3498p.
- Liu, Z. C., Meng, X. H., Zhang, R. and Xu, C. M.,** 2009, Friedel-Crafts Acylation of Aromatic Compounds in Ionic Liquids, *Pet. Sci. Technol.*, 27, 226p.
- Liu, Z., Zhang, R., Xu, C. and Xia, R.,** 2006, Ionic liquid alkylation process produces high-quality gasoline, *Oil Gas J.*, 104, 52p.
- M. Smiglak, J.D. Holbrey, S.T. Griffi, W.M. Reichert, R.P. Swatloski, A.R. Kattartzky, H. Yang, D. Zhang, K. Kirichenko, R.D. Rogers,** 2007, Ionic liquids *via* reaction of the zwitterionic 1,3-dimethylimidazolium-2-carboxylate with protic acids. Overcoming synthetic limitations and establishing new halide free protocols for the formation of ILs, *Green Chem.*, 9, 90p.
- Maase, M., Wasserscheid, P. and Welton, T. (Eds.),** 2008, *Ionic Liquids in Synthesis*, WILEY-VCH Verlags GmbH & Co. KGaA, Weinheim, pp. 663–687.
- MacFarlane, D. R., Pringle, J. M., Johansson, K. M., Forsyth, S. A. and Forsyth, M.,** 2006, Lewis base ionic liquids, *Chem. Commun.*, 1905p.
- Majewski, P., Pernak, A., Grzymislowski, M., Iwanik, K. and Pernak, J.,** 2003, Ionic liquids in embalming and tissue preservation. Can traditional formalin-fixation be replaced safely?, *Acta Histochem.* 105, 135p.

REFERENCES (CONTINUED)

Man, M. L., Lam, K. C., Sit, W. N., Ng, S. M., Zhou, Z. Y., Lin, Z. Y. and Lau, C. P., 2006, Synthesis of Heterobimetallic Ru_Mn Complexes and the Coupling Reactions of Epoxides with Carbon Dioxide Catalyzed by these Complexes, *Chem. Eur. J.*, 12, 1004p.

Mantz, R.A., Trulove, P.C., Wasserscheid, P., Welton, T., 2005, *Ionic Liquids in Synthesis*, Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim, pp. 72p.

Martino, W., Mora F. F., Yoshida, Y., Saito, G. and Wilkes, J., 2006, Surface tension measurements of highly conducting ionic liquids, *Green Chem.*, 8, 390p.

Massart, R., 1981, Preparation of aqueous magnetic liquids in alkaline and acidic media, *IEEE Trans. Magn.*, 17, 1247p.

Matsuda, H., Ninagawa, A. and Nomura, R., 1979, Reaction of Carbon Dioxide With Epoxides in The Presence of Pentavalent Organoantimony Compounds, *Chem. Lett.*, 1261p.

Matsushita, S. and Nakata, T., 1962, Infrared Absorption of Zinc Oxide and of Adsorbed CO₂. II, *J. Chem. Phys.*, 36, 665p.

Mecking, S., Olivier-Bourbigou, H., Vogt, D. (Eds.), 2005, *Multiphase Homogeneous Catalysis*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 511p.

Mehnert, C. P., 2005, Supported Ionic Liquid Catalysis, *Chem. Eur. J.*, 11, 50p.

Mehnert, C. P., Cook, R. A., Dispenziere, N. C. and Afeworki, M., 2002, Supported Ionic Liquid Catalysis A New Concept for Homogeneous Hydroformylation Catalysis, *J. Am. Chem. Soc.* 124, 12932p.

Mehnert, C. P., Mozeleski, E. J. and Cook, R. A., 2002, Supported Ionic Liquid Catalysis Investigated for hydrogenation reaction, *Chem. Comm.*, 3010p.

Miao, C.-X., Wang, J.-Q., Wu, Y., Duand and He, Y.L.-N., 2008, *ChemSusChem*, 1, 236p.

Mori, K., Mitani, Y., Hara, T., Mizugaki, T., Ebitani, K. and Kaneda, K., 2005, A single-site hydroxyapatite-bound zinc catalyst for highly efficient chemical fixation of carbon dioxide with epoxides, *Chem. Commun.*, 3331p.

REFERENCES (CONTINUED)

- Motokura, K., Itagaki, S., Iwasawa, Y., Miyaji, A. and Baba, T.,** 2009, Silica-supported aminopyridinium halides for catalytic transformations of epoxides to cyclic carbonates under atmospheric pressure of carbon dioxide, *Green Chem.*, 11, 1876p.
- Muskat, E. and Strain, F.,** 1945, Preparation of Carbonic Acid Esters, US Patent 2,379,250I.
- Nishikubo, T, Kameyama, A., Yamashita, J., Fukumitsu, T., Maejima, C. and Tomoi, M.,** 1995, Soluble polymer-supported catalysts containing pendant quaternary onium salts for the addition reaction of oxiranes with carbon dioxide, *J. Polym. Sci., Part A: Polym. Chem.*, 33, 1011p.
- Nishikubo, T., Kameyama, A., Yamashita, J., Tomoi, M. and Fukuda, W.,** 1993, Insoluble polystyrene-bound quaternary onium salt catalysts for the synthesis of cyclic carbonates by the reaction of oxiranes with carbon dioxide, *J. Polym. Sci., Part A: Polym. Chem.*, 31, 939p.
- Noda, A., Hayamizu, K. and Watanabe, M.,** 2001, Pulsed-Gradient Spin-Echo ^1H and ^{19}F NMR Ionic Diffusion Coefficient, Viscosity, and Ionic Conductivity of Non-Chloroaluminate Room-Temperature Ionic Liquids, *J. Phys. Chem. B*, 105, 4603p.
- North, M., Villuendas, P. and Young, C.,** 2009, A Gas-Phase Flow Reactor for Ethylene Carbonate Synthesis from Waste Carbon Dioxide, *Chem.–Eur. J.*, 15, 11454p.
- Ochiai, B. and Endo, T.,** 2007, Polymer-Supported Pyridinium Catalysts for Synthesis of Cyclic Carbonate by Reaction of Carbon Dioxide and Oxirane, *J. Polym. Sci., Part A: Polym. Chem.*, 45, 5673p.
- Ohno, H. and Fukumoto K.,** 2007, Amino Acid Ionic Liquids, *Acc. Chem. Res.*, 40, 1122p.
- Olivier-Bourbigou, H., Cornils, B., Herrmann, W., Horvath, I. T., Leitner, W. and Mecking, S.,** Olivier-Bourbigou, H., Vogt, D. (Eds.), 2005, Multiphase Homogeneous Catalysis, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 511–524.
- Ono, F., Qiao, K., Tomida, D. and Yokoyama, C.,** 2007, Direct preparation of styrene carbonates from styrene using an ionic-liquid-based one-pot multistep synthetic process *Appl. Catal., A*, 333, 107p.

REFERENCES (CONTINUED)

- Otera, J.**, 2001, In search of Practical Esterification, *Angew. Chem. Int. Ed.*, 40, 2044p.
- Pacheco, M. A. and Marshall, C. L.**, 1997, Review of Dimethyl Carbonate (DMC) Manufacture and Its Characteristics as a Fuel Additive, *Energy Fuels*, 11, 2p.
- Paczal, A. And Kotschy, A.**, 2007, Asymmetric Synthesis in Ionic Liquids, *Monatsh. Chem.* 138, 1115p.
- Pârvulescu, V. I. and Hardacre, C.**, 2007, Catalysis in Ionic Liquids, *Chem. Rev.* 107, 2615p.
- Patil, Y. P., Tambade, P. J., Jagtap, S. R. and Bhanage, B. M.**, 2008, Synthesis of 2-oxazolidinones/2-imidazolidinones from CO₂, different epoxides and amino alcohols/alkylene diamines using Br⁻Ph₃⁺P-PEG₆₀₀-P⁺Ph₃Br⁻ as homogenous recyclable catalyst, *J. Mol. Catal. A: Chem.*, 289, 14p.
- Peng, J. and Deng, Y.**, 2001, Cycloaddition of carbon dioxide to propylene oxide catalyzed by Ionic Liquids, *New J. Chem.*, 25, 639p.
- Peppel, W. J.**, 1958, Preparation and Properties of the Alkylene Carbonates, *Ind. Eng. Chem.*, 50, 767p.
- Phan, L., Andreatta, J. R., Horvey, L. K., Edie, C. F., Luco, A. L., Mirchandani, A., Darensbourg, D. J. and Jessop P. G.**, 2008, Switchable-Polarity Solvents Prepared with a Single Liquid Component, *J. Org. Chem.*, 73, 127p.
- Phillips, G. W., Falling, S. N., Godleski, S. A. and Monnier, J. R.**, 1994, Continuous process for the manufacture of 2,5-dihydrofurans from .gamma., .delta.-epoxybutenes , Eastmann Kodak Company, US 5,315,019.
- Plechkovaa, N. V. and Seddon, K. R.**, 2008, Applications of ionic liquids in the chemical industry , *Chem. Soc. Rev.*, 37, 123p.
- Poole, C.F.**, 2004._Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids, *J. Chromatogr A*, 1037, 49p.
- Predel, T., Wasserscheid, P., Gerhard, D. and Arlt, W.**, 2007, Ionic liquids as operating fluids in high pressure applications, *Chem. Eng. Technol.*, 30, 1475p.

REFERENCES (CONTINUED)

- Ramin, M., van Vegten, N., Grunwaldt, J.-D. and Baiker, A.,** 2006, Simple preparation routes towards novel Zn-based catalysts for the solventless synthesis of propylene carbonate using dense carbon dioxide, *J. Mol. Catal. A: Chem.*, 258, 165p.
- Ranu, B. C. and Banerjee, S.,** 2005, Ionic Liquid as Reagent. A Green Procedure for the Regioselective Conversion of Epoxides to *Vicinal*-Halohydrins Using [AcMIm]X under Catalyst- and Solvent-Free Conditions, *J. Org. Chem.* 70, 4517p.
- Reetz, M. T., Wiesenhöfer, W., Franciò, G. and Leitner, W.,** 2003, Continuous flow enzymatic kinetic resolution and enantiomer separation using ionic liquid/supercritical carbon dioxide media, *Adv. Synth. Catal.*, 345, 1221p.
- Reichardt, C.,** 2005, Polarity of ionic liquids determined empirically by means of solvatochromic pyridinium *N*-phenolate betaine dyes, *Green Chem.* 7, 339p.
- Riisager, A., Fehrmann, R., Haumann, M. and Wasserscheid, P.,** 2006, Supported Ionic Liquids: Versatile Reaction and Separation Media, *Topics in Catalysis*, 40, 91p.
- Riisager, A., Wasserscheid, P., van Hal, R. and Fehrmann, R.,** 2003, Continuous Fixed-Bed Gas Phase Hydroformylation Using Supported Ionic Liquid Phase (SILP) Rh catalysts, *J. Catal.*, 219, 252p.
- Rogers, R. D. and Seddon, K. R.,** 2003, Ionic Liquids-Solvents of the Future?, *Science*, 302, 792p.
- Rokicki, G., Kuran, W. and Pogorzelska-Marciniak, B.,** 1984, Cyclic carbonates from carbon dioxide and oxiranes, *Monatsh. Chem.*, 115, 205p.
- Sakai, T., Tsutsumi, Y. and Ema, T.,** 2008, Highly active and robust organic-inorganic hybrid catalyst for the synthesis of cyclic carbonates from carbon dioxide and epoxides, *Green Chem.*, 10, 337p.
- Sakakura, T., Choi, J.-C. and Yasuda, H.,** 2007, Transformation of Carbon Dioxide, *Chem. Rev.*, 107, 2365p.
- Sakakura, T. and Kohno, K.,** 2009, The synthesis of organic carbonates from carbon dioxide, *Chem. Commun.*, 1312p.

REFERENCES (CONTINUED)

- Schäffner, B., Holz, J., Verevkin, S. P. and Börner, A.**, 2008, Organic carbonates as alternative solvents for palladium-catalyzed substitution reactions, *ChemSusChem*, 1, 249p.
- Schmid, C. R., Beck, C. A., Cronin, J. S., Staszak, M. A.**, 2004, Demethylation of 4-Methoxyphenyl-butyric Acid Using Molten Pyridinium Hydrochloride on Multikilogram Scale, *Org. Process Res. Dev.*, 8, 670p.
- Schneider, S., Hawkins, T., Rosander, M., Vaghjiani, G., Chambreau, S. and Drake, G.**, 2008, Ionic Liquids as Hypergolic Fuels, *Energy Fuels*, 22, 2871p.
- Sellin, M. F., Webb, P. B. and Cole-Hamilton, D. J.**, 2001, Continuous flow homogeneous catalysis: hydroformylation of alkenes in supercritical fluid–ionic liquid biphasic mixtures, *Chem. Comm.*, 781p.
- Shaikh, A.-A. G. and Sivaram, S.**, 1996, Organic carbonates, *Chem. Rev.*, 96, 951p.
- Sherif, F. G., Greco, C., Shyu, L. J., Talma, A. G. and Lacroix, C.**, 1998, Process For The Production Of Irones, Akzo Nobel, W0 1998/03454.
- Shiels, R. A. and Jones, C. W.**, 2007, Homogeneous and heterogeneous 4-(*N,N*-dialkylamino)pyridines as effective single component catalysts in the synthesis of propylene carbonate, *J. Mol. Catal. A: Chem.*, 261, 160p.
- Shim, H.-L., Udayakumar, S., Yu, J.-I., Kim, I. and Park, D.-W.**, 2009, Synthesis of cyclic carbonate from allyl glycidyl ether and carbon dioxide using ionic liquid-functionalized amorphous silica, *Catal. Today*, 148, 350p.
- Smiglak, M., Reichert, W.M., Holbrey, J.D., Wilkes, J.S., Sun, L.Y., Thrasher, J.S., Kirichenko, K., Singh, S., Katritzky, A.R. and Rogers, R.D.**, 2006, Combustible ionic liquids by design: is laboratory safety another ionic liquid myth?, *Chem. Commun.*, 2554p.
- Srivastava, R., Srinivas, D. and Ratnasamy, P.**, 2005, CO₂ activation and synthesis of cyclic carbonates and alkyl/aryl carbamates over adenine-modified Ti-SBA-15 solid catalysts, *J. Catal.*, 233, 1p.

REFERENCES (CONTINUED)

- Srivastava, R., Srinivas, D. and Ratnasamy, P.,** 2006, Syntheses of polycarbonate and polyurethane precursors utilizing CO₂ over highly efficient, solid as-synthesized MCM-41 catalyst, *Tetrahedron Lett.*, 47, 4213p..
- Srivastava, R., Srinivas, D. and Ratnsamy, P.,** 2003, Synthesis of Polycarbonate Precursors over Titanosilicate Molecular Sieves, *Catal. Lett.*, 91, 133p.
- Stegmann, V. and Massonne, K.,** 2005, Method For Producing Haloalkanes From Alcohols, BASF, WO 2005/026089 A2
- Stuart, W. I. and Whateley, T. L.,** 1965, Adsorption of water and carbon dioxide on beryllium oxide, *Trans. Faraday Soc.*, 61, 2763p.
- Sun, J., Chen, W., Fan, W., Wang, Y., Meng, Z. and Zhang, S.,** 2009, Reusable and efficient polymer-supported task-specific ionic liquid catalyst for cycloaddition of epoxide with CO₂ *Catal. Today*, 148, 361p.
- Sun, J., Fujita, S.-I. and Arai, M.,** 2005, Development in the Green Synthesis of Cyclic Carbonate from Carbon Dioxide Using Ionic Liquids, *J. Organomet. Chem.*, 690, 3490p.
- Sun, J., Fujita, S.-I. and Arai, M.,** 2005, Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids *J Organomet. Chem.*, 690, 3490p.
- Sun, J., Fujita, S.-I., Bhanage B. M. and Arai, M.,** 2004, One-pot synthesis of styrene carbonate from styrene in tetrabutylammonium bromide, *Catal. Today*, 93–95, 383p.
- Sun, J., Fujita, S.-I., Zhao, F., Hasegawa, M. and Arai, M.,** 2005, A direct synthesis of styrene carbonate from styrene with the Au/SiO₂–ZnBr₂/Bu₄NBr catalyst system *J. Catal.*, 230, 398p.
- Sun, J., Ren, J., Zhang, S. and Cheng, W.,** 2009, Water as an efficient medium for the synthesis of cyclic carbonate, *Tetrahedron Lett.*, 50, 423p.
- Sun, J., Zhang, S., Cheng, W. and Ren, J.,** 2008, Hydroxyl-functionalized ionic liquid: a novel efficient catalyst for chemical fixation of CO₂ to cyclic carbonate, *Tetrahedron Lett.*, 49, 3588p.

REFERENCES (CONTINUED)

- Takeda, N. and Inoue, S.**, 1978, Activation of Carbon Dioxide by Tetraphenylporphinatoaluminium Methoxide. Reaction with Epoxide, *Bull. Chem. Soc. Jpn.*, 51, 3564p.
- Tascedda P. and Duñach E.**, 1995, Novel Electrochemical Reactivity of Ni(cyclam)Br₂: Catalytic Carbon Dioxide Incorporation into Epoxides, *J. Chem. Soc., Chem. Commun.*, 43p.
- Tascedda P. and Duñach E.**, 2000, Electrosynthesis of benzolactones by nickel-catalyzed carboxylation of epoxide-functionalized aromatic halides, *Synlett*, 245p.
- Tokuda, H., Tsuzuki, S., Susan, M. A. B. H., Hayamizu, K. and Watanabe, M.**, 2006, How Ionic Are Room-Temperature Ionic Liquids? An Indicator of the Physicochemical Properties, *J. Phys. Chem. B* 110, 19593p.
- Tu, M. and Davis, R. J.**, 2001, Cyclo-addition of CO₂ to Epoxides over Solid Base Catalysts *J. Catal.*, 199, 85p.
- Tullo, A.**, 2008, Capturing Carbon, Novomer aims to turn carbon dioxide into something useful, *Chem. Eng. News*, 86, (25), 21p.
- Tundo, P. and Selva, M.**, 2002, The Chemistry of Dimethyl Carbonate, *Acc. Chem. Res.*, 35, 706p.
- Tundo, P., Selva M. and Memoli, S.**, 2000, Dimethylcarbonate as a Green Reagent, *ACS Symp. Ser.*, 767, 87p.
- Udayakumar, S., Lee, M.-K., Shim, H.-L. and Park, D.-W.**, 2009, Functionalization of organic ions on hybrid MCM-41 for cycloaddition reaction: The effective conversion of carbon dioxide *Appl. Catal., A*, 365, 88p.
- Udayakumar, S., Lee, M.-K., Shim, H.-L., Park, S.-W. and Park, D. W.**, 2009, Imidazolium derivatives functionalized MCM-41 for catalytic conversion of carbon dioxide to cyclic carbonate *Catal. Commun.*, 10, 659p.
- Udayakumar, S., Park, S.-W., Park, D.-W. and Choi, B.-S.**, 2008, Immobilization of ionic liquid on hybrid MCM-41 system for the chemical fixation of carbon dioxide on cyclic carbonate, *Catal. Commun.*, 9, 1563p.

REFERENCES (CONTINUED)

- Udayakumar, S., Raman, V., Shimand, H.-L., Park, D.-W.,** 2009, Cycloaddition of carbon dioxide for commercially-imperative cyclic carbonates using ionic liquid-functionalized porous amorphous silica *Appl. Catal., A*, 368, 97p.
- Wang, B., Kang, Y.-R., Yang, L.-M. and Suo, J.-S.,** 2003, Epoxidation of α,β -unsaturated carbonyl compounds in ionic liquid/water biphasic system under mild conditions, *J. Mol. Catal. A: Chem.*, 203, 29p.
- Wang, J.-Q., Kong, D.-L., Chen, J.-Y., Cai, F. and He, L.-N.,** 2006, Synthesis of cyclic carbonates from epoxides and carbon dioxide over silica-supported quaternary ammonium salts under supercritical conditions, *J. Mol. Catal. A: Chem.*, 249, 143p.
- Wang, J.-Q., Yue, X.-D., Cai, F. and He, L.-N.,** 2007, Solventless synthesis of cyclic carbonates from carbon dioxide and epoxides catalyzed by silica-supported ionic liquids under supercritical conditions, *Catal. Commun.*, 8, 167p.
- Wang, X., Ohlin, C.A., Lu, Q., Fei, Z. F., Hu, J. and Dyson P. J.,** 2007, Cytotoxicity of ionic liquids and precursor compounds towards human cell line HeLa, *Green Chem.*, 9, 1191p.
- Wang, Y., Yuan, G.-Q., Zeng Y.-C. and Jiang, 2007 H.-F.,** Electrochemical Synthesis of Cyclic Carbonates from CO₂ with Epoxides at Room Temperature, *Chin. J.Org. Chem.*, 27, 1397p.
- Wasserscheid, P. and Keim, W.,** 2000, Ionic Liquids-New “Solutions” for Transition Metal Catalysis, *Angew. Chem. Int. Ed.*, 39, 3772p.
- Webb, P. B., Kunene, T. E. and Cole-Hamilton, D. J.,** 2005, Continuous flow homogeneous hydroformylation of alkenes using supercritical fluids, *Green Chem.* 7, 373p.
- Weyershausen, B., Hell, K. and Hesse, U.,** 2005, Industrial application of ionic liquids as process aid, *Green Chem.*, 7, 283p.
- Weyershausen, B., Hell, K. and Hesse, U.,** 2005, Ionic liquids at Degussa: Catalyst heterogenization in an industrial process, *ACS Sympos. Ser.* 902, 133p.
- Weyershausen, B., Hell, K. and Hesse, U.,** *Organosilicon Chemistry VI: From Molecules To Materials, Hydrosilylation Using Ionic Liquids*, 2nd, Munich, Germany, Sept. 11–12, 2003.1 (2005) 424. WILEY-VCH Verlags GmbH & Co. KGaA, Weinheim, pp. 663–687.

REFERENCES (CONTINUED)

- Xiao, L.-F., Li, F.-W., Peng, J.-J. and Xia, C.-G.**, 2006, Immobilized ionic liquid/zinc chloride: Heterogeneous catalyst for synthesis of cyclic carbonates from carbon dioxide and epoxides, *J. Mol. Catal. A: Chem.*, 253, 265p.
- Xu, Z., Wan, H., Miao, J., Han, M., Yang, C. and Guan, G.**, 2010, Reusable and efficient polystyrene-supported acidic ionic liquid catalyst for esterification, *J. Mol. Catal. A*, 332, 152p.
- Yamada, W., Sugawara, Y., Cheng, H. M., Ikeno, T. and Yamada, T.**, 2007, Silver-Catalyzed Incorporation of Carbon Dioxide into Propargylic Alcohol, *Eur. J. Org. Chem.*, 2604p..
- Yamaguchi, K., Ebitani, K., Yoshida, T., Yoshida, H. and Kaneda, K.**, 1999, Mg-Al mixed oxides as highly active acid-base catalysts for cycloaddition of carbon dioxide to epoxides, *J. Am. Chem. Soc.*, 121, 4526p.
- Yamaguchi, K., Yoshida, C., Uchida, S. and Mizuno N.**, 2005, Peroxotungstate Immobilized on Ionic Liquid-Modified Silica as a Heterogeneous Epoxidation Catalyst with Hydrogen Peroxide., *J. Am. Chem. Soc.*, 127, 530p.
- Yang, H., Gu, Y., Deng, Y. and Shi, F.**, 2002, Electrochemical activation of carbon dioxide in ionic liquid: synthesis of cyclic carbonates at mild reaction conditions, *Chem. Commun.*, 274p.
- Yano, T., Matsui, H., Koike, T., Ishiguro, H., Fujihara, H., Yoshihara, M. and Maeshima, T.**, 1997, Magnesium oxide-catalysed reaction of carbon dioxide with anepoxide with retention of stereochemistry, *Chem. Commun.*, 1129p.
- Yashuda, H., He, L.-N. and Sakakura, T.**, 2002, Cyclic Carbonate Synthesis from Supercritical Carbon Dioxide and Epoxide over Lanthanide Oxychloride, *J. Catal .*, 209, 547p.
- Yasuda, H., He, L.-N., Takahashi, T. and Sakakura, T.**, 2006, Non-halogen catalysts for propylene carbonate synthesis from CO₂ under supercritical conditions, *Appl. Catal., A*, 298, 177p.
- Yates, D.J.C.**, 1961, Infrared Studies of the Surface Hydroxyl Groups on Titanium Dioxide, and of the Chemisorption of Carbon Monoxide and Carbon Dioxide, *J. Phys. Chem.*, 65, 746p.
- Yuan, G.-Q., Shan, Y.-J., Jiang, H.-F. and Qi, C. R.**, 2008, Mg(OH)Cl/KI as a Highly Active Heterogeneous Catalyst for the Synthesis of Cyclic Carbonates from CO₂ and Epoxides under Solvent-Free Conditions, *Chin. J. Chem.*, 26, 947p.

REFERENCES (CONTINUED)

- Zhang, J.C., Jiang, T., Han, B.X., Zhu, A.L. and Ma, X.M.** Knoevenagel condensation catalyzed by 1,1,3,3-tetramethylguanidine lactate. *Synth. Commun.*, 2006, 36, 3305p.
- Zhang, J. M., Zhang, F. J., Dong, K., Zhang, Y. Q., Shen, Y. Q., Lv X. M.,** 2006, Supported Absorption of CO₂ by Tetrabutylphosphonium Amino Acid Ionic Liquids, *Chem. Eur. J.*, 12, 4021p.
- Zhang, S., Chen, Y., Li, F., Lu, X., Dai, W. and Mori, R.,** 2006, Fixation and conversion of CO₂ using ionic liquids, *Catal. Today*, 115, 61p.
- Zhang, Z. C.,** 2006, Catalysis in Ionic Liquids, *Adv. Catal.*, 49, 153-237p.
- Zhao, G.Y., Jiang, T., Han, B.X., Chang, Y.H., Gao, H.X., Huang, J. and Sun, D.H.** Mannich reaction using acidic ionic liquids as catalysts and solvents. *Green Chem.*, 2004, 6, 75p.
- Zhao, Y., Tian, J.-S., Qi, X.-H., Han, Z.-N., Zhuang, Y.-Y. and He, L.-N.,** 2007, Quaternary ammonium salt-functionalized chitosan: An easily recyclable catalyst for efficient synthesis of cyclic carbonates from epoxides and carbon dioxide, *J. Mol. Catal. A: Chem.*, 271, 284p.
- Zhou, Y., Hu, S., Ma, X., Liang, S., Jiang, T. and Han, B.,** 2008, Synthesis of cyclic carbonates from carbon dioxide and epoxides over betaine-based catalysts, *J.Mol. Catal.A: Chem.*, 284, 52p.
- Zhu, A.L., Jiang, T., Han, B.X., Huang, J., Zhang, J.C. and Ma, X.M.,** Study on guanidine-based task-specific ionic liquids as catalysts for direct aldol reactions without solvent. *New J. Chem.*, 2006, 30, 736p.

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EDUCATION AND PROFESSIONAL KNOWLEDGE

BSc:2000-2005 Ege University, Faculty of Science., Department of Chemistry, İZMİR

PhD, 2005- Ege University, Natural and Applied Science Institute, Chemistry, (Research Assistant) İZMİR

Research student [2008-2009(3 months)] Niigata University, Graduate school of Science and Technology (in the lab. of Prof. Hisahiro Hagiwara), Japan

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SCI EXPANDED PUBLICATIONS:

- 1.) “Hetero- and homo- leptic Ru(II) catalyzed synthesis of cyclic carbonates from CO₂: Synthesis, spectroscopic characterization and electrochemical properties”, *Applied Organomet. Chem.*, **2010**, 24, 446.
- 2.) “Silicon containing new salicylaldimine Pd(II) and Co(II) metal complexes as efficient catalysts in transformation of carbon dioxide (CO₂) to cyclic carbonates”, **J. Organomet. Chem.**, 2011, 696, 1372.

SCIENTIFIC MEETINGS

1. XXII., National Chemistry Congress, Poster session, Gazimağusa, KKTC (2008) Poster title: The influence of heterogenized complexes to the transformation of cyclic carbonates
2. II. National Inorganic Chemistry Congress, Poster session, Elazığ, Turkey (2009) Poster title: “Investigation of dihydroxylation of alkenes in the presence of heterogeneous catalyst”

3. XXIII. National Chemistry Congress, Poster session, Sivas, Turkey (2009) Poster title: "Investigation of the cyclic carbonate formation by the ionic liquid catalyst"
4. Organometallic Chemistry and Catalysis Workshop, Poster session, Malatya, Turkey (2010) Poster title: "Investigation of the cyclic carbonate formation by the ionic liquid containing functional groups"
5. 24. National Chemistry Congress, Poster session, Zonguldak, Turkey (2010) Poster title: "Synthesis of cyclic carbonates from CO₂ using hetero- and homo- leptic Ru(II) complexes: Synthesis, spectroscopic characterization and electrochemical properties"
6. 24. National Chemistry Congress, Oral session, Zonguldak, Turkey (2010) Title: "Silicon containing salicylaldimine Pd(II) and Co(II) metal complexes as efficient catalysts in transformation of carbon dioxide (CO₂) to cyclic carbonates"
7. III. National Inorganic Chemistry Congress, Poster session, Çanakkale, Turkey (2011) Poster title: "Supported rutenium and paladium compounds and their catalytic applications"
8. 25. National Chemistry Congress, Oral session, Erzurum, Turkey, 2011 Oral session title: Conversion of CO₂ to cyclic carbonate by Ag NHC catalyst"

RESEARCH PROJECTS

1. Prof. Dr. Bekir Çetinkaya "Improving Catalytic Systems in Ionic Liquids", ÖYP, 2005-DPT-003/7, 2009-2011.
2. Yard. Doç. Dr. Mahmut Ulusoy, "Conversion of carbon dioxide into organic products using 2-(2-pyridyl)benzimidazole complexes", TÜBİTAK, 110T655, 2011-...

SCHOLARSHIP

2003-2005: Undergraduate scholarship (TUBITAK)

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