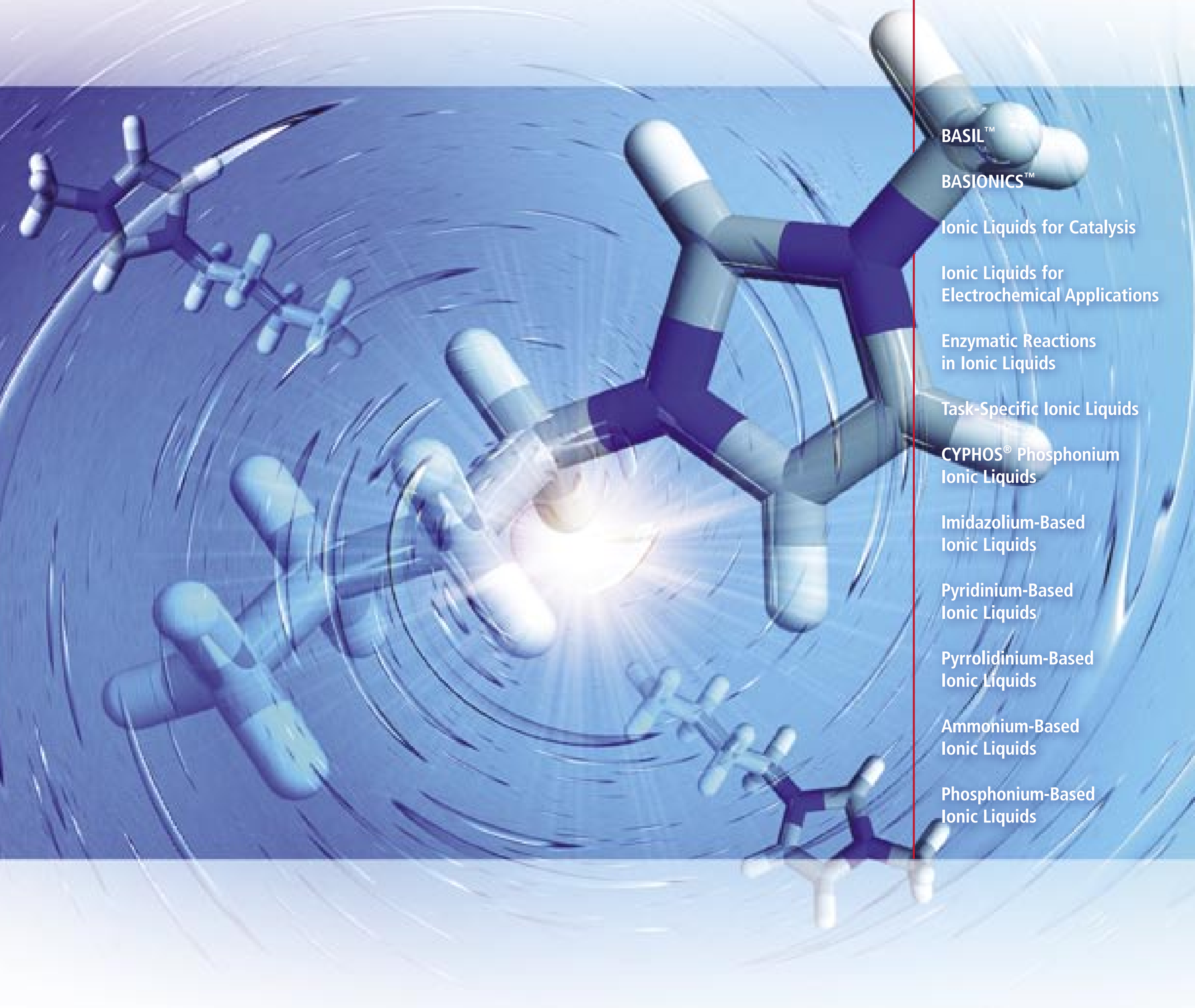
ChemFiles

Vol. 5 No. 6

Enabling Technologies

Ionic Liquids



- BASIL™
- BASIONICS™
- Ionic Liquids for Catalysis
- Ionic Liquids for Electrochemical Applications
- Enzymatic Reactions in Ionic Liquids
- Task-Specific Ionic Liquids
- CYPHOS® Phosphonium Ionic Liquids
- Imidazolium-Based Ionic Liquids
- Pyridinium-Based Ionic Liquids
- Pyrrolidinium-Based Ionic Liquids
- Ammonium-Based Ionic Liquids
- Phosphonium-Based Ionic Liquids

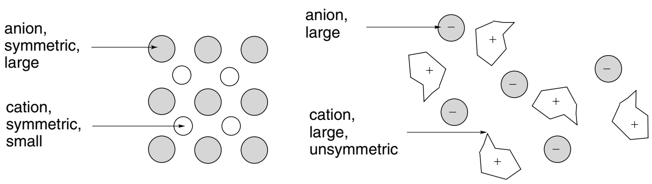
Introduction

Sigma-Aldrich is proud to offer a new series of *ChemFiles*—called Enabling Technologies—to our Chemistry customers. Each piece will highlight enabling products or technologies for chemical synthesis, drug discovery, and other areas of chemistry.

Ionic Liquids have experienced a comet-like boost in the last few years. In this edition of *ChemFiles*, we highlight some current applications of this fascinating class of new materials. We present over 50 new additions to our portfolio of 130+ Ionic Liquids, ranging from well-known imidazolium and pyridinium derivatives to ammonium, pyrrolidinium, phosphonium, and sulfonium derivatives. At Sigma-Aldrich, we are committed to being your preferred supplier for Ionic Liquids. Please visit **sigma-aldrich.com/ionicliquids** for a regular update of the latest Ionic Liquids. If you cannot find a product for your specific research, "please bother us" at **dweibel@europe.sial.com** with new suggestions!

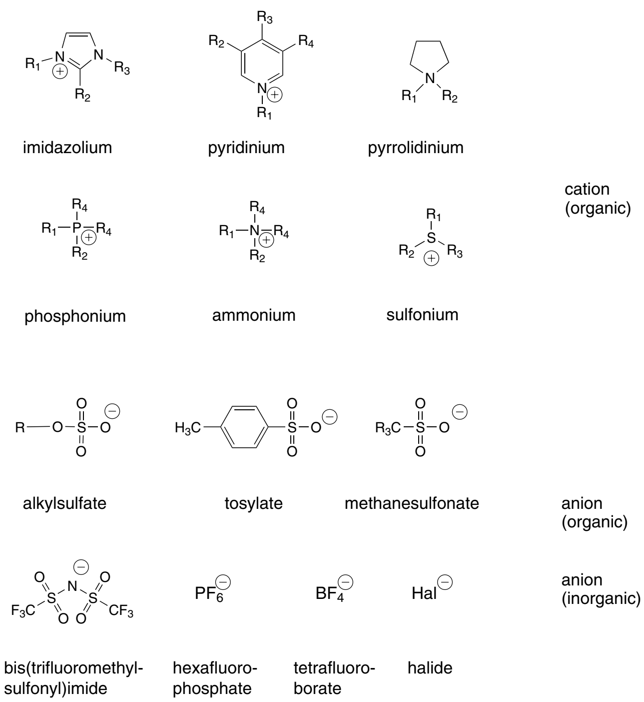
Ionic Liquids are a new class of purely ionic, salt-like materials that are liquid at unusually low temperatures. Currently, the "official" definition of Ionic Liquids uses the boiling point of water as a point of reference: "Ionic Liquids are ionic compounds which are liquid below 100 °C." More commonly, Ionic Liquids have melting points below room temperature; some of them even have melting points below 0 °C. These new materials are liquid over a wide temperature range (300–400 °C) from the melting point to the decomposition temperature of the Ionic Liquid.

If we compare a typical Ionic Liquid, e.g., 1-ethyl-3-methylimidazolium ethylsulfate (m.p. <-20 °C), with a typical inorganic salt, e.g., table salt (NaCl, m.p. 801 °C), it becomes obvious why there is a difference. The Ionic Liquid has a significantly lower symmetry! Furthermore, the charge of the cation as well as the charge of the anion is distributed over a larger volume of the molecule by resonance. As a consequence, the solidification of the Ionic Liquid will take place at lower temperatures. In some cases, especially if long aliphatic side chains are involved, a glass transition is observed instead of a melting point.

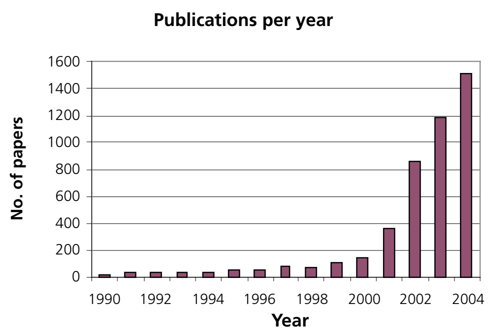


The strong ionic (Coulomb-) interaction within these substances results in a negligible vapor pressure (unless decomposition occurs), a non-flammable substance, and in a high thermally, mechanically as well as electrochemically stable product. In addition to this very interesting combination of properties, they offer other favorable properties: for example, very appealing solvent properties and immiscibility with water or organic solvents that result in biphasic systems.

The choice of the cation has a strong impact on the properties of the Ionic Liquid and will often define the stability. The chemistry and functionality of the Ionic Liquid is, in general, controlled by the choice of the anion. The combination of a broad variety of cations and anions leads to a theoretically possible number of 10^{18} Ionic Liquids. However, a realistic number will be magnitudes lower. Today about 1000 Ionic Liquids are described in the literature, and approximately 300 are commercially available. Typical structures combine organic cations with inorganic or organic anions:

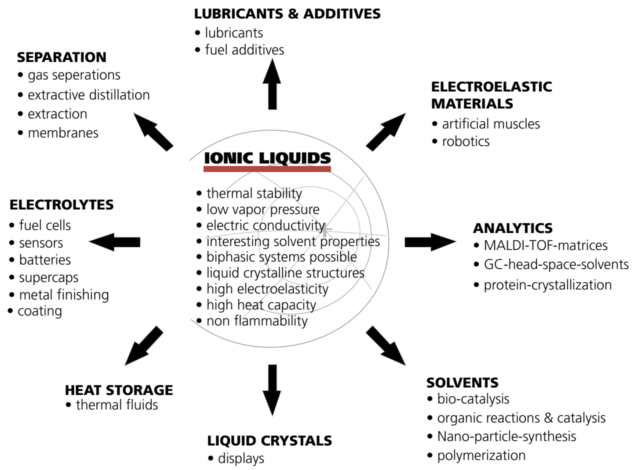


The growing academic and industrial interest in Ionic Liquid technology is represented by the yearly increase in the number of publications (source Sci-Finder™): starting from far below 100 in 1990 to more than 1500 papers published last year.



Use and Applications

The reason for the increase in number of publications can be attributed to the unique properties of these new materials. Ultimately, the possible combinations of organic cations and anions places chemists in the position to design and fine-tune physical and chemical properties by introducing or combining structural motifs and, thereby, making tailor-made materials and solutions possible. The following chart summarizes important properties of Ionic Liquids and their potential and current applications:[1]



The corresponding applications of Ionic Liquids can be divided in their use as process chemicals and performance chemicals. In 1948, this class of electrically conducting materials (1-butylpyridinium chloride/$AlCl_3$) first drew attention for their use as electrolytes for electrodeposition of aluminium.[2] This field is still the subject of current research efforts. Other important applications in this context are their use as electrolytes for batteries and fuel cells.

The major breakthrough came with the advent of less corrosive, air-stable materials in 1992. Wilkes and Zaworotko introduced 1-ethyl-3-methylimidazolium tetrafluoroborate and focused on solvent applications.[3] Although 1-butyl-3-methylimidazolium hexafluorophosphate and -tetrafluoroborate still dominate the current literature, there are better choices with respect to performance and handling. It was demonstrated in aqueous media the hexafluorophosphate anion and the tetrafluoroborate anion will degrade, resulting in the formation of HF, a noxious and aggressive acid.

Over the past five years, other interesting applications were suggested, derived from the unique combination of physical properties. For example, the use of Ionic Liquids as thermal fluids combines their heat capacity with thermal stability and a negligible vapor pressure. It is quite feasible to expect that many more applications will be brought forward by potential users and some of them will be realized in the next couple of years. In order to enable potential users to make use of Ionic Liquids, it will be necessary to give technological support and to make a range of Ionic Liquids available for testing. This support also includes the development of toxicological data and government required notification as well as the implementation of recycling concepts for the Ionic Liquid.

References

1. **Lubricants:** Wang, H.; Lu, Q.; Ye, C.; Liu, W.; Cui, Z. *Wear* **2004**, *256*, 44–48.

   Artificial Muscles: Potential application, personal note.

   MALDI-TOF-Matrices: Armstrong, D. W.; Zhang, L. K.; He, L.; Gross, M. L. *Anal. Chem.* **2001**, *73*, 3679–3686.

   GC-Head-Space-Solvents: Andre, M.; Loidl, J.; Schottenberger, H.; Bentivoglio, G.; Wurst, K.; Ongania, K.-H. *Anal. Chem.* **2005**, *77*, 702–705.

   Protein-Crystallization: Ionic Liquids Technologies, Patent pending.

   Bio-Catalysis: Moriguchi, T.; Yanagi, T.; Kunimori, M. *J. Org. Chem.* **2000**, *65*, 8229–8238.
   Hayakawa, Y.; Kawai, R. Hirata, A. *J. Am. Chem Soc.* **2001**, *123*, 8165–8176.
   Eckstein, M.; Filho, M. V.; Liese, A.; Kragl, U. *Chem. Comm.* **2004**, 1084–1085.
   Liu, Y.; Wang, M.; Li, J.; Li, Z.; He, P; Liu, H.; Li, J. *Chem. Comm.* **2005**, 1778–1780.

   Organic Synthesis & Catalysis: For a general overview see: Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthsis*; Wiley-VCH: Weinheim, 2003.

   Deep Desulfuration: Bösmann, A.; Datsevich, L.; Jess, A.; Lauter, A.; Schmitz, C.; Wasserscheid, P. *Chem. Comm.* **2001**, 2494–2495
   Nakashima, K.; Kubota, F.; Maruyama, T.; Goto, M. *Chem. Mater.* **2003**, *15*, 1825–1829.

   Nano-Particle-Synthesis: Zhou, Y.; Antonietti, M. *J. Am. Chem. Soc.* **2003**, *125*, 14960–14961; *Chem. Mater.* **2004**, *16*, 544–550.

   Liquid Crystals: Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1999**, 2133–2139.
   Haristoy, D.; Tsiourvas, D. *Chem. Mater.* **2003**, *15*, 2079–2083.

   Thermal Fluids: Wu, B.; Reddy, R. G.; Rogers, R. D. Proceedings of Solar Forum, 2001.
   See also: Ionic Liquids Technologies GmbH & Co. KG, http://www.iolitec.de.

   Fuel Cells: Yanes, E. G.; Gratz, S. R.; Baldwin, M. J.; *Anal. Chem.* **2001**, *73*, 3838–3844.

   Sensors: See also: http://www.iolitec.de.

   Supercaps: Sato, T; Masuda, G; Takagi, K. *Electrochim. Acta* **2004**, *49*, 3603–3611.

   Metal Finishing: Zell, C. A.; Freyland, W. *Langmuir* **2003**, *19*, 7445–7450.
   Scheeren, C. W.; Machado, G.; Dupont, J.; Fichtner, P.F.P.; Texeira, S.R. *Inorg. Chem*. **2003**, *42*, 4738–4742.
   Huang, J.-F.; Sun, I.-W. *J. Chromat. A*, **2003**, *1007*, 39–45.

   Gas Separations: Scovazzo, P; Kieft, J.; Finan, D. A.; Koval, C.; DuBios, D.; Noble, R. *J. Membr. Sci.* **2004**, *238*, 57–63.

   Extractive Distillation: Jork, C.; Seiler, M.; Beste, Y.-A.; Arlt, W. *J. Chem. Eng. Data* **2004**, *49*, 852–857.

   Extraction: Uerdingen, M.; *Chem. unserer Zeit* **2004**, *38*, 212–213.

   Membranes: Branco, L. C.; Crespo, J. G.; Afonso, C. A. M. *Angew. Chem.* **2002**, *104*, 2895–2897.
   Fortunato, R.; Afonso, C. A. M.; Reis, M. A. M.; Crespo, J. G. *J. Membr. Sci*. **2004**, *242*, 197–209.

2. Hurley, F. H. U.S. Patent 2,446,331, 1948.
   Wier, T. P.; Hurley, F. S. U.S. Patent 2,446,349, 1948.
   Wier, T. P. U.S. Patent 2,446,350, 1948.

3. Wilkes, J. S.; Zaworotko, M. J. *Chem. Comm.* **1992**, 965–967.

BASIL™—BASF's Processes Based on Ionic Liquids

Dr. Matthias Maase, Dr. Klemens Massonne, Dr. Uwe Vagt, BASF Aktiengesellschaft, 67056 Ludwigshafen, Germany, www.basf.de/new-intermediates.

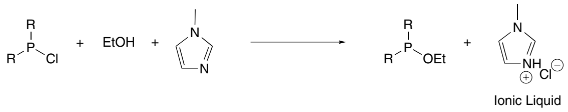
Currently, the most important application of Ionic Liquids described is their use as reaction media for chemical processes. A major breakthrough was reached with BASF's introduction of the first application on a commercial scale: the BASIL™-process, which received the "Innovation for Growth Award 2004" of ECN.

Many chemical processes produce acids as by-products—most commonly hydrochloric acid (HCl). In those cases where the reaction product has to be protected from decomposition or other side reactions, the acid needs to be scavenged. Usually, tertiary amines such as triethylamine are added to the reaction mixture, generating an ammonium salt. In many cases, this ammonium salt can be removed via an aqueous extraction phase. In the case of reaction mixtures that are sensitive to water, the situation is more complicated. The generation of ammonium salts leads to the formation of a slurry during the reaction. The slurry formation results in a number of disadvantages: highly viscous solutions, limited heat transfer, and the ammonium salt has to be separated by filtration.

This was exactly the situation BASF faced in the production of diethoxyphenylphosphine, a photoinitiator intermediate prepared by reaction of dichlorophenylphosphine with ethanol. HCl had to be removed from the reaction mixture or the product would have undergone an unwanted side reaction. An aqueous extraction phase would have led to hydrolysis of the desired product and therefore the reaction had to be carried out in a non-aqueous medium in the presence of equimolar quantities of triethylamine. The resulting mixture was a thick, nearly non-stirrable slurry. While attempting to improve this unfavorable process, the idea came up: "If an acid has to be scavenged with a base, the formation of a salt cannot be avoided; but why not form a liquid salt, an Ionic Liquid?"

Instead of triethylamine, 1-methylimidazole was used as an acid scavenger and immediately led to excellent results. The Ionic Liquid formed in the reaction was methylimidazolium chloride. Methylimidazolium chloride has a melting point of 75 °C and, therefore, is a liquid at the reaction temperature of approx. 80 °C.

After the reaction, there are two clear liquid phases that can easily be worked up by a simple phase separation. The upper phase is the pure product and no reaction solvent is needed. The lower phase is the pure Ionic Liquid and can be deprotonated with sodium hydroxide, regenerating the methylimidazole.



1-Methylimidazole was doing a wonderful job in scavenging the acid, but in the very first lab trials another exciting observation was made. The Ionic Liquid functioned as a nucleophilic catalyst. The combined effect is a tremendous increase in the yield per unit volume time from 8 to 690,000 kg $m^{-3}h^{-1}$. This enabled BASF to carry out the reaction, which previously needed a 20 m^3 batch vessel, in a little jet reactor the size of a thumb. This little reactor is part of a continuously operated plant with a capacity of more than 1000 t/a. The plant went on stream in Q3/2004 at BASF's Ludwigshafen site.

This BASIL™-technology for scavenging acids has been applied for esterifications, acylations, silylations, phosphorylations, sulfurylations, eliminations, deprotonations, and acid removals in general in lab trials. BASF, having gained experience with this process from lab to commercial scale up today, is in a position to offer this process for licensing to others with a full package of services.

An additional process already developed in pilot plant scale at BASF is the chlorination of alcohols with HCl in the presence of methylimidazolium chloride. The chlorination reaction is normally carried out with the use of phosgene or thionyl chloride as chlorinating agents. In the presence of the Ionic Liquid, the Cl^- is apparently a much stronger nucleophile and, therefore, makes it possible to carry out the chlorinations in an easier and more cost-efficient method.

Ionic Liquids also show advantages in separation processes, such as azeotropic or extractive distillations. In separation processes, they are used as entrainers or as solvent for the extraction of phenols.

BASIONICS™—BASF's Portfolio of Ionic Liquids

Under the trade name BASIONICS™, BASF offers a portfolio of Ionic Liquids—mainly based on imidazolium cations. The BASIONICS™ portfolio opens up a broad range of basic properties of Ionic Liquids and is classified into standard, acidic, basic, liquid at RT and low viscosity products and opens up a wide range of possible applications. All of these products are provided by Sigma-Aldrich on kg scale. The BASIONICS™ portfolio is available from BASF in 100 kg or ton scale with the same specification as offered by Sigma-Aldrich on sufficient notice.

Another important part of BASF's concept in bringing Ionic Liquids in commercial quantities to the market is the definition of product quality. It is apparent that for any application the right set of specification parameters needs to be defined. For example, an Ionic Liquid that is used for dye-sensitized solar-cells has to be colorless, but if the same Ionic Liquid is used as a non-aqueous electrolyte in a galvanic process, the color has no relevance. In the non-aqueous electrolyte example, another parameter may have to be clearly defined. Hence, BASF works with the following concept: once a customer (either alone or in cooperation with BASF) has identified an Ionic Liquid suitable for a process or an application, the set of specification parameters (purity, by-products, halogen content, color, viscosity, etc.) will be defined in detail. Based on these specifications, the process for the commercial-scale production is designed.

It is important to note that the BASIONICS™ portfolio of Ionic Liquids is a living portfolio! It will be extended, but even more importantly, driven by customer requests. This is true for the cation as well as for the anion. Both parts of the molecule can be designed to the requirements of the specific application the customer demands. With the given technological expertise in chemical processing as well as existing value chains and raw materials from the "Verbund", BASF is in a position to make a broad portfolio of Ionic Liquids available in commercial quantities and at reasonable prices.

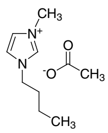
Application Examples

As described above, there are numerous publications on Ionic Liquids. The following are examples that present some applications where BASIONIC™ Ionic Liquids could be used.

Prod. #	Name	Applications
30764 38899	1-Ethyl-3-methylimidazolium chloride (BASIONIC™ ST 80) 1-Butyl-3-methylimidazolium chloride (BASIONIC™ ST 70)	precursors for the preparation of other Ionic Liquids by anion metathesis
29164 30881	1-Ethyl-3-methylimidazolium methanesulfonate (BASIONIC™ ST 35) 1-Butyl-3-methylimidazolium methanesulfonate (BASIONIC™ ST 78)	electrodeposition of metals, e.g., titanium-aluminum or platinum-zinc alloys;[1–3] esterification of starch;[4] dissolution and delignification of lignocellulosic materials;[5] dissolution of silk fibroin[6]
38938	Methyl-tributylammonium methylsulfate (BASIONIC™ ST 62)	electrochemical synthesis of organic compounds[7]
50365	1,2,3-Trimethylimidazolium methylsulfate (BASIONIC™ ST 99)	production of organopolysiloxanes[8]
40477	Methylimidazolium chloride (BASIONIC™ AC 75)	separation of acids from chemical reaction mixtures;[9] halogenating agent and recyclable catalyst;[10] electroplating bath for Tungsten[11] and Molybdenum[12]
59760 56486 57457	Methylimidazolium hydrogensulfate (BASIONIC™ AC 39) 1-Ethyl-3-methylimidazolium hydrogensulfate (BASIONIC™ AC 25) 1-Butyl-3-methylimidazolium hydrogensulfate (BASIONIC™ AC 28)	extraction medium for removing impurities from aprotic solvents;[13] synthesis of coumarins;[14] solvent for GC-headspace;[15] solvent and catalyst for Mannich-reaction,[16] Friedel–Crafts-alkylations,[17] and aromatic sulfonation[18]
51059 55292	1-Ethyl-3-methylimidazolium tetrachloroaluminate (BASIONIC™ AC 09) 1-Butyl-3-methylimidazolium tetrachloroaluminate (BASIONIC™ AC 01)	electrolyte for batteries;[19] synthesis of polyisoolefins;[20] reaction medium for Rh-catalyzed hydrogenations[21] and Diels–Alder-reactions;[22] extractive desulfuration of hydrocarbon fuels;[23] reaction medium for synthesis and catalysis;[24–26] polymerization of ethylene carbonate[27]
51053 39952	1-Ethyl-3-methylimidazolium acetate (BASIONIC™ BC 01) 1-Butyl-3-methylimidazolium acetate (BASIONIC™ BC 02)	electrolytes for non-aqueous capillary electrophoresis[28]
51682 53177	1-Ethyl-3-methylimidazolium ethylsulfate (BASIONIC™ LQ 01) 1-Butyl-3-methylimidazolium methylsulfate (BASIONIC™ LQ 02)	extractive deep desulfuration;[29] extraction of contaminant gases;[30] lipase-catalyzed enantioselective acylation[31]
43437 42254	1-Ethyl-3-methylimidazolium thiocyanate (BASIONIC™ VS 01) 1-Butyl-3-methylimidazolium thiocyanate (BASIONIC™ VS 02)	electrolyte for dye-sensitized solar cells;[32] electrolyte for dye-sensitized semiconductor-particles;[33] solvent for the dissolution of cellulose with Ionic Liquids[34]
05338	1-Ethyl-2,3-dimethylimidazolium ethyl sulfate (BASIONIC™ ST 67)	

1-Butyl-3-methylimidazolium acetate, BASF quality, ≥95% NEW

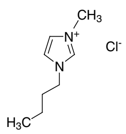
$C_{10}H_{18}N_2O_2$
FW: 198.26
mp: <-20 °C
[*284049-75-8*]



39952-100G	100 g	
39952-1KG	1 kg	

1-Butyl-3-methylimidazolium chloride, BASF quality, ≥95% NEW

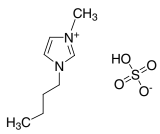
$C_8H_{15}ClN_2$
FW: 174.67
mp: 41 °C
[*79917-90-1*]



38899-100G	100 g	
38899-1KG	1 kg	

1-Butyl-3-methylimidazolium hydrogen sulfate, BASF quality, ≥95% NEW

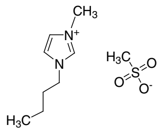
$C_8H_{16}N_2O_4S$
FW: 236.29
mp: 28 °C
[*262297-13-2*]



57457-100G	100 g	
57457-1KG	1 kg	

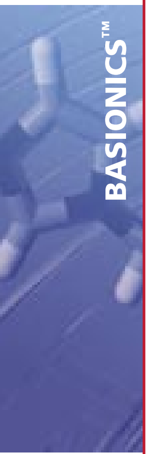
1-Butyl-3-methylimidazolium methanesulfonate, BASF quality, ≥95% NEW

$C_9H_{18}N_2O_3S$
FW: 234.32
mp: 75–80 °C
[*342789-81-5*]



30881-100G	100 g	
30881-1KG	1 kg	

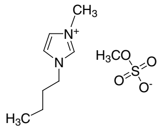
Ready to scale up? For competitive quotes on larger quantities or custom synthesis, contact SAFC™ at 1-800-244-1173 (USA), or visit www.safcglobal.com.



1-Butyl-3-methylimidazolium methyl sulfate, BASF quality, ≥95%

NEW

$C_9H_{18}N_2O_4S$
FW: 250.32
mp: <-20 °C
[*401788-98-5*]

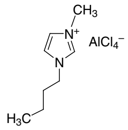


53177-100G	100 g	
53177-1KG	1 kg	

1-Butyl-3-methylimidazolium tetrachloroaluminate, BASF quality, ≥95%

NEW

$C_8H_{15}AlCl_4N_2$
FW: 308.01
mp: -10 °C
[*80432-09-3*]

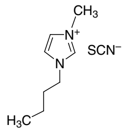


55292-100G	100 g	
55292-1KG	1 kg	

1-Butyl-3-methylimidazolium thiocyanate, BASF quality, ≥95%

NEW

$C_9H_{15}N_3S$
FW: 197.30
mp: <-20 °C
[*344790-87-0*]

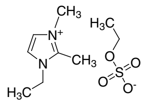


42254-100G	100 g	
42254-1KG	1 kg	

1-Ethyl-2,3-dimethylimidazolium ethyl sulfate, BASF quality, ≥95%

NEW

$C_9H_{18}N_2O_4S$
FW: 250.32
mp: 67 °C
[*516474-08-1*]

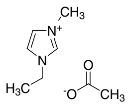


05338-100G	100 g	
05338-1KG	1 kg	

1-Ethyl-3-methylimidazolium acetate, BASF quality, ≥90%

NEW

$C_8H_{14}N_2O_2$
FW: 170.21
mp: <-20 °C
[*143314-17-4*]

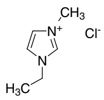


51053-100G	100 g	
51053-1KG	1 kg	

1-Ethyl-3-methylimidazolium chloride, BASF quality, ≥95%

NEW

$C_6H_{11}ClN_2$
FW: 146.62
mp: 80 °C
[*65039-09-0*]

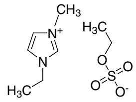


30764-100G	100 g	
30764-1KG	1 kg	

1-Ethyl-3-methylimidazolium ethyl sulfate, BASF quality, ≥95%

NEW

$C_8H_{16}N_2O_4S$
FW: 236.29
mp: <-20 °C
[*342573-75-5*]

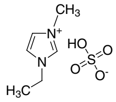


51682-100G	100 g	
51682-1KG	1 kg	

1-Ethyl-3-methylimidazolium hydrogen sulfate, BASF quality, ≥95%

NEW

$C_6H_{12}N_2O_4S$
FW: 208.24
[*412009-61-1*]

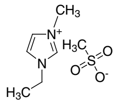


56486-100G	100 g	
56486-1KG	1 kg	

1-Ethyl-3-methylimidazolium methanesulfonate, BASF quality, ≥95%

NEW

$C_7H_{14}N_2O_3S$
FW: 206.26
mp: 35 °C
[*145022-45-3*]

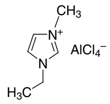


29164-100G	100 g	
29164-1KG	1 kg	

1-Ethyl-3-methylimidazolium tetrachloroaluminate, BASF quality, ≥95%

NEW

$C_6H_{11}AlCl_4N_2$
FW: 279.96
mp: 9 °C
[*80432-05-9*]

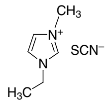


51059-100G	100 g	
51059-1KG	1 kg	

1-Ethyl-3-methylimidazolium thiocyanate, BASF quality, ≥95%

NEW

$C_7H_{11}N_3S$
FW: 169.25
mp: -6 °C
[*331717-63-6*]

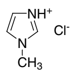


43437-100G	100 g	
43437-1KG	1 kg	

1-Methylimidazolium chloride, BASF quality, ≥95%

NEW

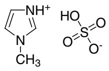
$C_4H_6N_2 \cdot HCl$
FW: 118.56
mp: 75 °C
[*35487-17-3*]



40477-100G	100 g	
40477-1KG	1 kg	

1-Methylimidazolium hydrogen sulfate, BASF quality, ≥95% NEW

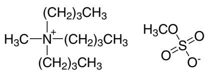
$C_4H_6N_2 \cdot H_2SO_4$
FW: 180.18
mp: 39 °C
[*681281-87-8*]



59760-100G	100 g	
59760-1KG	1 kg	

Tributylmethylammonium methyl sulfate, BASF quality, ≥95% NEW

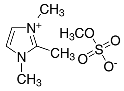
$C_{14}H_{33}NO_4S$
FW: 311.48
mp: 62 °C
[*13106-24-6*]



38938-100G	100 g	
38938-1KG	1 kg	

1,2,3-Trimethylimidazolium methyl sulfate, BASF quality, ≥95% NEW

$C_7H_{14}N_2O_4S$
FW: 222.26
mp: 113 °C
[*65086-12-6*]



50365-100G	100 g	
50365-1KG	1 kg	

References

1. Tsuda, T.; Hussey, C.L.; Stafford, G.R. *Electrochem. Soc.* **2002**, 2002–19 (Molten Salts XIII), 650–659.
2. Huang, J.-F.; Sun, I.-W. *Electrochim. Acta* **2004**, *49*, 3251–3258.
3. Endres, F.; Bukowski, M.; Hempelmann, R.; Natter, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 3428–3430.
4. Myllymaeki, V.; Aksela, R. *PCT Int. Appl.* **2005**, 25 pp. CODEN: PIXXD2 WO 2005023873.
5. Myllymaeki, V.; Aksela, R. *PCT Int. Appl.* **2005**, 25 pp. CODEN: PIXXD2 WO 2005017001.
6. Phillips, D. M.; Drummy, L. F.; Conrady, D. G.; Fox, D. M.; Naik, R. R.; Stone, M. O.; Trulove, P. C.; De Long, H. C.; Mantz, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 14350–14351.
7. Griesbach, U.; Quaiser, C.; Hermeling, D.; Bottke, N.; Schubert, M.; Urtel, H. *PCT Int. Appl.* **2004**, 23 pp. CODEN: PIXXD2 WO 2004106316.
8. Hell, K.; Hesse, U.; Weyershausen, B. *Eur. Pat. Appl.* **2004**, 13 pp. CODEN: EPXXDW EP 1382630.
9. Volland, M.; Seitz, V.; Maase, M.; Flores, M.; Papp, R.; Massonne, K.; Stegmann, V.; Halbritter, K.; Noe, R.; Bartsch, M.; Siegel, W.; Becker, M.; Huttenloch, O. *PCT Int. Appl.* **2003**, 111 pp. CODEN: PIXXD2 WO 2003062251.
10. Wu, H.-H.; Sun, J.; Yang, F.; Tang, J.; He, M.-Y. *Chin. J. Chem.* **2004**, *22*, 619–621.
11. Takahashi, S.; Akimoto, K.; Saeki, I.; Akama, R.; Oku, K. *Jpn. Kokai Tokkyo Koho* **1990**, 5 pp. CODEN: JKXXAF JP 02080589.
12. Takahashi, S.; Akimoto, K.; Saeki, I.; Akama, R.; Oku, K. *Jpn. Kokai Tokkyo Koho* **1990**, 5 pp. CODEN: JKXXAF JP 02097691.
13. Maase, M.; Budich, M.; Grossmann, G.; Szarvas, L. *PCT Int. Appl.* **2005**, 31 pp. CODEN: PIXXD2 WO 2005019137.
14. Singh, V.; Kaur, S.; Sapehiyia, V.; Singh, J.; Kad, G. L. *Catal. Commun.* **2005**, *6*, 57–60.
15. Andre, M.; Loidl, J.; Laus, G.; Schottenberger, H.; Bentivoglio, G.; Wurst, K.; Ongania, K.-H. *Anal. Chem.* **2005**, *77*, 702–705.
16. Zhao, G.; Jiang, T.; Gao, H.; Han, B.; Huang, J.; Sun, D. *Green Chem.* **2004**, *6*, 75–77.
17. Wasserscheid, P.; Sesing, M.; Korth W. *Green Chem.* **2002**, *4*, 134–138.
18. Earle, M.J.; Katdare, S.P. *PCT Int. Appl.* **2002**, 20 pp. CODEN: PIXXD2 WO 2002030878.
19. Carlin, R.T.; De Long, H.C.; Fuller, J.; Trulove, P.C. *J. Electrochem. Soc.* **1994**, *141*, L73–L76.
20. Murphy, V. *PCT Int. Appl.* **2000**, 36 pp. CODEN: PIXXD2 WO 2000032658.
21. Mann, B.E.; Guzman, M.H. *Inorg. Chim. Acta* **2002**, *330*, 143–148.
22. (a) Acevedo, O.; Evanseck, J.D. *ACS Symposium Series* **2003**, *856* (Ionic Liquids as Green Solvents), 174–190. (b) C.W. Lee, *Tetrahedron Lett.* **1999**, *40,* 2461–2464.
23. (a) Schoonover, R.E. U.S. Pat. Appl. **2003**, 10 pp. CODEN: USXXCO US 2003085156. (b) Boesmann, A.; Datsevich, L.; Jess, A.; Lauter, A.; Schmitz, C.; Wasserscheid, P. *Chem. Commun*. **2001**, 2494–2495.
24. Qiao, C.-Z.; Zhang, Y.-F.; Zhang, J.-C.; Li, C.-Y. *Appl. Catal. A: General*, **2004**, *276*, 61–66.
25. Mohile, S.S.; Potdar, M.K.; Salunkhe, M.M. *Tetrahedron Lett.* **2003**, *44*, 1255–1258.
26. Olivier, H.; Chauvin, Y. *Chemical Industries (Dekker)* **1996**, *68* (Catalysis of Organic Reactions), 249–263.
27. Kadokawa, J.-I.; Iwasaki, Y.; Tagaya, H. Macromol. *Rap. Comm.* **2002**, *23*, 757–760.
28. Vaher, M.; Koel, M.; Kaljurand, M. *Electrophoresis* **2002**, *23*, 426–430.
29. Eßer, J.; Wasserscheid, P.; Jess, A. *Green Chem.* **2004**, *6*, 316–322.
30. Brennecke, J. F.; Maginn, E. J. *U.S. Pat. Appl.* **2002**, 17 pp. CODEN: USXXCO US 2002189444.
31. Itoh, T.; Ouchi, N.; Hayase, S.; Nishimura, Y. *Chem. Lett.* **2003**, *32*, 654–655.
32. (a) Meng, Q. B.; Takahashi, K; Zhang, X. T.; Sutanto, I.; Rao, T. N.; Sato, O.; Fujishima, A.; Watanabe, H.; Nakamori, T.; Uragami, M. *Langmuir* **2003**, *19*, 3572–3574. (b) Wang, P.; Zakeeruddin, S. M.; Humphry-Baker, R.; Graetzel, M. *Chem. Mater*. **2004**, *16*, 2694–2696.
33. Tsukahara, J.; Shiratsuchi, K.; Kubota, T.; Sen, S. *Eur. Pat. Appl.* **2001**, 36 pp. CODEN: EPXXDW EP 1107333.
34. Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975.

Ionic Liquids for Catalysis

Annegret Stark and Bernd Ondruschka, Friedrich-Schiller-University, Institute for Technical Chemistry and Environmental Chemistry, Lessingstr. 12, 07743 Jena, Germany; annegret.stark@uni-jena.de.

Ionic Liquids have been thoroughly investigated as solvents in most types of catalytic reactions.[1–4] Their merit lies in the ease with which their physical–chemical properties can be tuned by varying either the anion, the cation, or its substitution pattern. By this means, an Ionic Liquid with optimal properties (viscosity, solubility of substrates and products, etc.) for a given application can be designed (i.e, designer solvents).[5] In catalysis, this feature can be favorably exploited by rendering a homogeneous reaction mixture bi-phasic, thus combining the advantages of homogeneous and heterogeneous catalysis. An alternative to phase separation is the removal of products by thermal means; because of the negligibly low vapor pressure of Ionic Liquids, the solvent and catalyst can be retained quantitatively during distillation processes.

The following examples illustrate that many catalysts possess a high activity in the Ionic Liquid solvent, and product separation is achieved by facile phase separation.

As early as 1995, Chauvin et al. demonstrated that high conversions and selectivities are obtained in the rhodium-catalyzed hydrogenation, isomerization, or hydroformylation of alkenes in the presence of Ionic Liquids. Specifically, Ionic Liquids based on anions with modest coordination ability, such as 1-butyl-3-methylimidazolium hexafluoroantimonate (BMIM SbF_6, Prod. # **51027**), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6), and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM BF_4), gave better results when compared to mono-phasic molecular solvents.[6]

Scandium- or platinum(II)-catalyzed Diels–Alder reactions in either BMIM PF_6, BMIM SbF_6, 1-butyl-3-methylimidazolium trifluoromet hanesulfonate (BMIM CF_3SO_3), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM $N(CF_3SO_2)_2$) were also investigated. Very high endo/exo ratios (>99/1) and improved reaction rates were achieved when compared to dichloromethane. Efficient recycling was demonstrated for ten cycles on the example of the reaction of methyl vinyl ketone and 2,3-dimethylbuta-1,3-diene.[7,8]

Ionic Liquids also have been studied as solvents in bio-catalysis. For example, high enantiomeric excesses were obtained in the lipase-catalyzed trans-esterification of various substrates[4,9–11] in Ionic Liquids based on the 1-alkyl-3-methylimidazolium or 4-methyl-*N*-alkylpyridinium cation and anions such as tetrafluoroborate, hexafluorophosphate, trifluoromethanesulfonate, etc. This finding was attributed to interactions of the Ionic Liquid with the enzyme, altering the selectivity of a biocatalytic reaction. Additionally, both the Ionic Liquid and enzyme were recyclable after extraction of the products from the Ionic Liquid phase with diethyl ether.[10]

Several researchers have found that impurities in Ionic Liquids exhibit an influence on the reaction outcome in catalysis.[4,6,12–22] Nevertheless, the quantitative specification of each batch of Ionic Liquid used is seldom reported, and the comparison of results from different laboratories is thus hampered.

Impurities, such as water, unreacted amine (e.g., 1-methylimidazole), and traces of halides most frequently stem from the preparation of Ionic Liquids. In the example of the metathesis of 1-octene catalyzed by Grubbs' 1st generation catalyst, Sigma-Aldrich's high purity 1-butyl-3-methylimidazolium tetrafluoroborate (Prod. # **39931**) or 1-ethyl-3-methylimidazolium tetrafluoroborate (Prod. # **39736**, were spiked with known amounts of either of these impurities (water <200 ppm, halogens (Cl^-) <10 ppm) to demonstrate the importance of the quality of Ionic Liquids employed in catalysis.

Figure 1 shows that the catalyst is relatively resistant to the presence of water, and even a 100-fold excess of water over catalyst (2.04 mol % water in Ionic Liquid) does not inhibit the reaction significantly.

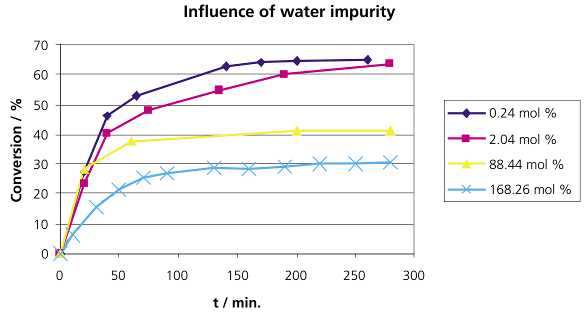


Figure 1. Influence of added increments of water to pure BMIM BF_4 on the conversion of the metathesis of 1-octene at room temperature, as a function of time. Reaction conditions: 0.02 mol % catalyst precursor (relative to 1-octene), Ionic Liquid:1-octene = 1:1 (vol.)

However, the presence of traces of chloride exhibits a much more pronounced effect, as shown in **Figure 2**. A ratio of chloride:catalyst of 2.3 (0.07 mol % chloride in Ionic Liquid, corresponding to only 100 ppm) reduced the turn-over frequency from 820 to 700 h^{-1}.

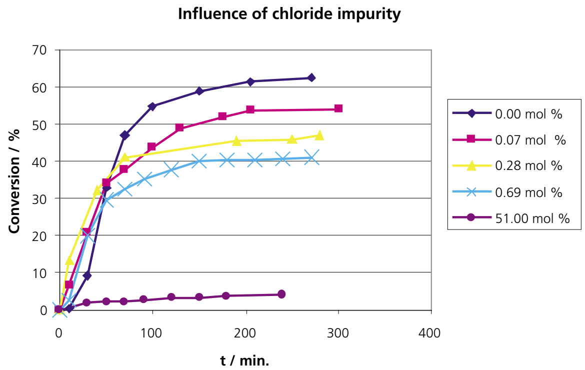


Figure 2. Influence of added increments of 1-hexyl-3-methylimidazolium chloride (HMIM Cl) to pure BMIM BF_4 on the conversion of the metathesis of 1-octene at room temperature, as a function of time. Reaction conditions: 0.03 mol % catalyst precursor (relative to 1-octene), Ionic Liquid:1-octene = 1:1 (vol.).

Interestingly, the catalyst precursor is most sensitive to the presence of traces of 1-methylimidazole. **Figure 3** shows that residual 1-methylimidazole in an Ionic Liquid deactivates the catalyst fully at a ratio of 6.3:1 1-methylimidazole:catalyst, which corresponds to traces of 0.18 mol % (600 ppm) of 1-methylimidazole in the Ionic Liquid.

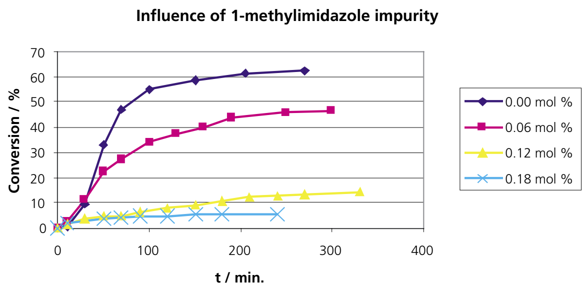
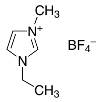


Figure 3. Influence of added increments of 1-methylimidazole to pure BMIM BF_4 on the conversion of the metathesis of 1-octene at room temperature as a function of time. Reaction conditions: 0.03 mol % catalyst precursor (relative to 1-octene), Ionic Liquid:1-octene = 1:1 (vol.).

Sigma-Aldrich is pleased to introduce a new set of highly purified Ionic Liquids for catalysis with water contents below 200 ppm and halogen content (Cl^-) below 10 ppm.

1-Ethyl-3-methylimidazolium tetrafluoroborate for catalysis, ≥98.5% T
NEW

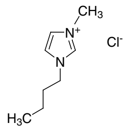
$C_6H_{11}BF_4N_2$
FW: 197.97
mp: 11 °C
[*143314-16-3*]



39736-5ML	5 mL	
39736-50ML	50 mL	

1-Butyl-3-methylimidazolium chloride, dry, ≥99% AT
NEW

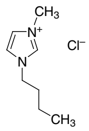
$C_8H_{15}ClN_2$
FW: 174.67
mp: 41 °C
[*79917-90-1*]



55509-5G	5 g	
55509-25G	25 g	

1-Butyl-3-methylimidazolium chloride, puriss., dry, ≥99% AT
NEW

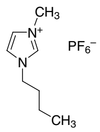
$C_8H_{15}ClN_2$
FW: 174.67
mp: 41 °C
[*79917-90-1*]



04129-5G	5 g	
04129-25G	25 g	

1-Butyl-3-methylimidazolium hexafluorophosphate for catalysis, ≥98.5% T
NEW

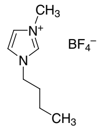
$C_8H_{15}F_6N_2P$
FW: 284.18
mp: 11 °C
[*174501-64-5*]



18122-5G	5 g	
18122-50G	50 g	

1-Butyl-3-methylimidazolium tetrafluoroborate for catalysis, ≥98.5% T
NEW

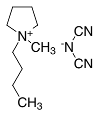
$C_8H_{15}BF_4N_2$
FW: 226.02
mp: -71 °C
[*174501-65-6*]



39931-5G	5 g	
39931-50G	50 g	

1-Butyl-1-methylpyrrolidinium dicyanamide, ≥99%
NEW

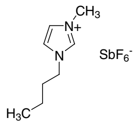
$C_{11}H_{20}N_4$
FW: 208.30
[*370865-80-8*]



50893-5G	5 g	
50893-50G	50 g	

1-Butyl-3-methylimidazolium hexafluoroantimonate, ≥98%
NEW

$C_8H_{15}F_6N_2Sb$
FW: 374.97
mp: -1 °C
[*174645-81-9*]



51027-5G	5 g	
51027-50G	50 g	

References

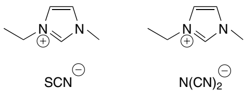
1. Holbrey, J. D.; Seddon, K. R. *Clean Prod. Proc.* **1999** *1*, 223.
2. Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000** *3*, 3772.
3. Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459.
4. Sheldon, R. A.; Madeira, R.; Lau, R. M.; Sorgedrager, M. J.; van Rantwijk, F.; Seddon, K. R. *Green Chem.* **2002**, *4*, 147.
5. Freemantle, M. *Chem. Eng. News* **1998**, *76*, 32.
6. Chauvin, Y.; Olivier-Bourbigou, H. *Chemtech.* **1995**, *26*, 26.
7. Song, C. E.; Shim, W. H.; Roh, E. J.; Lee, S. C.; Choi, J. H. *Chem. Commun*. **2001**, 1122.
8. Doherty, S.; Goodrich, P.; Hardacre, C.; Luo, H. K.; Rooney, D. W.; Seddon, K. R.; Styring, P. *Green Chem.* **2004**, *6*, 63.
9. Schöfer, S. H.; Kaftzik, N.; Wasserscheid, P.; Kragl, U. *Chem. Commun*. **2001**, 425.
10. Itoh, T.; Akasaki, E.; Kudo, K.; Shirakami, S. *Chem. Lett.* **2001**, 262.
11. Lozano, P.; de Diego, T.; Carrie, D.; Vaultier, M.; Iborra, J. L. *Chem. Commun*. **2002**, 692.
12. Chauvin, Y.; Mussmann, L.; Olivier, H. *Angew. Chem. Int. Ed.* **1996**, *34*, 2698.
13. Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; de Souza, R. F.; Dupont, J. *Inorg. Chim. Acta* **1997**, *255*, 207.
14. Monteiro, A. L.; Zinn, F. K.; de Souza, R. F.; Dupont, J. *Tetrahedron: Asymmetry* **1997**, *8*, 177.
15. Dyson, P. J.; Ellis, D. J.; Parker D. G.; Welton, T. *Chem. Commun*. **1999**, 25.
16. Ellis, B.; Keim, W.; Wasserscheid, P. *Chem. Commun*. **1999**, 337.
17. Carmichael, A. J.; Earle, M. J.; Holbrey, J. D.; McCormac, P. B.; Seddon, K. R. *Org. Lett.* **1999**, *1*, 997.
18. Dyson, P. J.; Ellis, D. J.; Lincoln, R.; Russel, K.; Smith, P. J.; Welton, T. *Electrochem. Soc. Proc.* **2000**, *99-41*, 161.
19. Song, C. E.; Roh, E. J. *Chem. Commun*. **2000**, 837.
20. Seddon, K. R.; Stark, A. *Green Chem*. **2002**, 119.
21. de Souza, R. F.; Rech,; V. Dupont, J. *Adv. Synth. Catal*. **2002**, *344*, 153.
22. Klingshirn, M. A.; Broker, G. A.; Holbrey, J. D.; Shaughnessy, K. H.; Rogers, R. D. *Chem. Commun*. **2002**, 1394.

Ionic Liquids for Electrochemical Applications

Over the past decade, Ionic Liquids have attracted much interest for their use as non-aqueous electrolytes in electrochemical applications. In this context, their conductivity as well as their electrochemical stability are the most important physical properties. Together with other interesting properties such as their negligible vapor pressure and their non-flammability, they appear to be ideal electrolytes for many interesting applications as already described and discussed in a growing number of publications.[1]

Conductivity

As mentioned above, one very interesting property is their conductivity. Typical values are in the range from 1.0 mS/cm to 10.0 mS/cm. Recently, interesting materials with conductivities above 20 mS/cm based on the imidazolium-cation were described: 1-ethyl-3-methylimidazolium thiocyanate (Prod. # **07424**) and 1-ethyl-3-methylimidazolium dicyanamide (Prod. # **00796**).



Of course, a solution of a typical inorganic salt such as sodium chloride in water shows a higher conductivity. But if we compare other properties of this solution with an Ionic Liquid, significant disadvantages become obvious: aqueous electrolytes are liquid over a smaller temperature range and the solvent water is volatile!

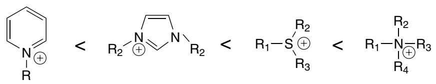
Electrochemical Stability

Another very important property of Ionic Liquids is their wide electrochemical window, which is a measure for their electrochemical stability against oxidation and reduction processes:

$$\text{Cation}^{\oplus} + e^{\ominus} \longrightarrow \text{neutral species}$$
$$\text{Anion}^{\ominus} \longrightarrow \text{neutral species} + e^{\ominus}$$

Obviously, the electrochemical window is sensitive to impurities: halides are oxidized much easier than molecular anions (e.g., stable fluorine-containing anions such as bis(trifluoromethylsulfonyl)imide), where the negative charge is delocalized over larger volume. As a consequence, contamination with halides leads to significantly lower electrochemical stabilities.

Cation stability:



Anion stability:

$$\text{Hal}^{\ominus} < \text{AlCl}_4^{\ominus} < \text{PF}_6^{\ominus}, \text{BF}_4^{\ominus} < {}^{\ominus}\text{N(SO}_2\text{CF}_3)_2$$

Conductivities and Electrochemical Windows of Selected Materials

Ionic Liquid	Conductivity	Electrochemical Window
a) Highly Conductive		
1-Ethyl-3-methylimidazolium dicyanamide	27 mS/cm	2.9 V
1-Ethyl-3-methylimdazolium thiocyanate	21 mS/cm	2.3 V
b) Electrochemically Stable		
Triethylsulphonium bis(trifluoromethylsulfonyl)imide	8.2 mS/cm	5.5 V
N-Methyl-*N*-trioctylammonium bis(trifluoromethylsulfonyl)imide	2.2 mS/cm	5.7 V
N-Butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	2.1 mS/cm	6.6 V
c) Combined Properties		
1-Ethyl-3-methylimidazolium tetrafluoroborate	12 mS/cm	4.3 V
1-Ethyl-3-methylimidazolium trifluoromethylsulfonate	8.6 mS/cm	4.3 V

Applications

a) High Conductivity

The materials showing the highest conductivities, 1-ethyl-3-methylimidazolium thiocyanate and dicyanamide exhibited the lowest electrochemical stabilities. Nevertheless, these materials are good candidates for use in any application where a high conductivity combined with thermal stability and non-volatility is necessary, e.g., 1-dodecyl-3-methylimidazolium iodide (Prod. # **18289**) in dye-sensitized solar cells.[2]

b) High Stability

The electrochemically most stable materials having comparable small conductivities (*N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Prod. # **40963**), triethylsulphonium bis(trifluoromethylsulfonyl)imide (Prod. # **08748**), and *N*-methyl-*N*-trioctylammonium bis(trifluoromethylsulfonyl)imide (Prod. # **00797**). These materials are good electrolytes for use in batteries,[3] fuel cells,[4] metal deposition,[5] and electrochemical synthesis of nano-particles.[6]

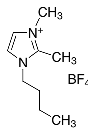
c) Combined Properties

For applications where conductivity and electrochemical stability are needed (e.g., supercapacitors[7] or sensors[8]), imidazolium-based Ionic Liquids with stable anions (e.g., tetrafluoroborate or trifluoromethylsul fonate) are the materials of choice.

Sigma-Aldrich now offers a set of Ionic Liquids especially useful for your electrochemical applications.

1-Butyl-2,3-dimethylimidazolium tetrafluoroborate for electrochemistry, ≥99% NEW

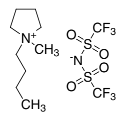
$C_9H_{17}BF_4N_2$
FW: 240.05
mp: 37 °C
[*402846-78-0*]



04383-5G	5 g	
04383-50G	50 g	

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide for electrochemistry, ≥99.5% NEW

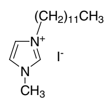
$C_{11}H_{20}F_6N_2O_4S_2$
FW: 422.41
mp: -50 °C



40963-5G	5 g	
40963-50G	50 g	

1-Dodecyl-3-methylimidazolium iodide NEW

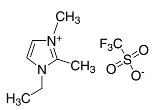
$C_{16}H_{31}IN_2$
FW: 378.34
[*81995-09-7*]



18289-5G	5 g	
18289-50G	50 g	

1-Ethyl-2,3-dimethylimidazolium trifluoromethanesulfonate for electrochemistry, ≥99% NEW

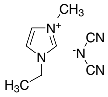
$C_8H_{13}F_3N_2O_3S$
FW: 274.26
[*174899-72-0*]



00765-5G	5 g	
00765-50G	50 g	

1-Ethyl-3-methylimidazolium dicyanamide for electrochemistry, ≥99% NEW

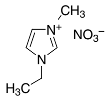
$C_8H_{11}N_5$
FW: 177.21
mp: -21 °C
[*370865-89-7*]



00796-5G	5 g
00796-50G	50 g

1-Ethyl-3-methylimidazolium nitrate, purum, ≥99% NT

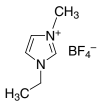
$C_6H_{11}N_3O_3$
FW: 173.17
mp: 38 °C
[*143314-14-1*]



04363-1G	1 g
04363-5G	5 g

1-Ethyl-3-methylimidazolium tetrafluoroborate for electrochemistry, ≥99% NEW

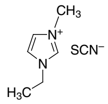
$C_6H_{11}BF_4N_2$
FW: 197.97
mp: 11 °C
[*143314-16-3*]



00768-5G	5 g
00768-50G	50 g

1-Ethyl-3-methylimidazolium thiocyanate for electrochemistry, ≥98% NEW

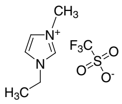
$C_7H_{11}N_3S$
FW: 169.25
mp: -6 °C
[*331717-63-6*]



07424-5G	5 g
07424-50G	50 g

1-Ethyl-3-methylimidazolium trifluoromethane sulfonate for electrochemistry, ≥99% NEW

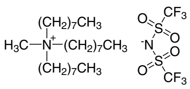
$C_7H_{11}F_3N_2O_3S$
FW: 260.23
mp: -9 °C
[*145022-44-2*]



00738-5G	5 g
00738-50G	50 g

Methyl-trioctylammonium bis(trifluoromethyl-sulfonyl)imide for electrochemistry, ≥99% NEW

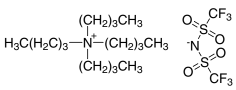
$C_{27}H_{54}F_6N_2O_4S_2$
FW: 648.85
mp: -50 °C
[*375395-33-8*]



00797-5G	5 g
00797-50G	50 g

Tetrabutylammonium bis(trifluoromethylsulfonyl)imide, puriss., for electronic purposes, ≥99% T

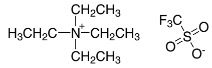
$C_{18}H_{36}F_6N_2O_4S_2$
FW: 522.61
mp: 94–96 °C
[*210230-40-3*]



86838-1G	1 g
86838-5G	5 g

Tetraethylammonium trifluoromethanesulfonate, purum, ≥98% T

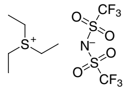
$C_9H_{20}F_3NO_3S$
FW: 279.32
mp: 161–163 °C
[*35895-69-3*]



86651-5G	5 g
86651-25G	25 g

Triethylsulfonium bis(trifluoromethylsulfonyl)imide for electrochemistry, ≥99% NEW

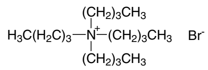
$C_8H_{15}F_6NO_4S_2$
FW: 367.26



08748-5G	5 g
08748-50G	50 g

Tetrabutylammonium bromide puriss., electrochemical grade, ≥99% T

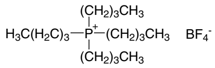
$C_{16}H_{36}BrN$
FW: 322.37
mp: 102–104 °C
[*1643-19-2*]



86836-10G	10 g
86836-50G	50 g

Tetrabutylphosphonium tetrafluoroborate, puriss., electrochemical grade, ≥99% T

$C_{16}H_{36}BF_4P$
FW: 346.24
mp: 96–99 °C
[*1813-60-1*]

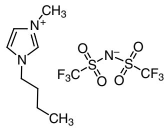


86934-5G	5 g
86934-25G	25 g

Sigma-Aldrich offers, in collaboration with Covalent Associates, Inc., a set of hydrophobic Ionic Liquids exhibiting excellent thermal stabilities and resistance to water and oxygen.

1-Butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide, purum, ≥98% NMR NEW

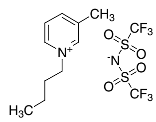
$C_{10}H_{15}F_6N_3O_4S_2$
FW: 419.36
[*174899-83-3*]



77896-1G	1 g
77896-5G	5 g

1-Butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide purum, ≥97% H-NMR

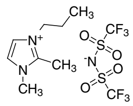
$C_{12}H_{16}F_6N_2O_4S_2$
FW: 430.39
[*344790-86-9*]



14654-1G	1 g
14654-5G	5 g

1,2-Dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide purum, ≥97% H-NMR

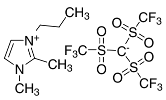
$C_{10}H_{15}F_6N_3O_4S_2$
FW: 419.36
mp: 15 °C
[*169051-76-7*]



50807-1G	1 g	
50807-5G	5 g	

1,2-Dimethyl-3-propylimidazolium tris(trifluoromethylsulfonyl)methide purum, ≥97% H-NMR

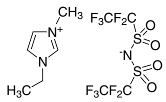
$C_{12}H_{15}F_9N_2O_6S_3$
FW: 550.44
[*169051-77-8*]



74305-1G	1 g	
74305-2.5G	2.5 g	

1-Ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide purum, ≥97% H-NMR

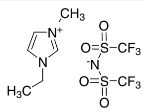
$C_{10}H_{11}F_{10}N_3O_4S_2$
FW: 491.33
mp: -1 °C
[*216299-76-2*]



39056-1G	1 g	
39056-5G	5 g	

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide purum, ≥97% H-NMR

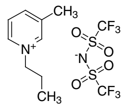
$C_8H_{11}F_6N_3O_4S_2$
FW: 391.31
mp: -17 °C
[*174899-82-2*]



11291-1G	1 g	
11291-5G	5 g	

3-Methyl-1-propylpyridinium bis(trifluoromethylsulfonyl)imide, purum

$C_{11}H_{14}F_6N_2O_4S_2$
FW: 416.36
mp: 0 °C



30565-1G	1 g	
30565-5G	5 g	

References

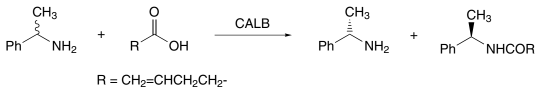
1. For a general overview: Trulove, C.; Mantz, R. A. "Ionic Liquids in Synthesis", Chapter 3.6: Electrochemical Properties of Ionic Liquids, (P. Wasserscheid, T. Welton eds.), Wiley-VCH, Weinheim, **2003**.
2. Yamanaka, N.; Kawano, R.; Kubo, W.; Kitamura, T.; Wada, Y.; Watanabe, M.; Yanagida, S. *Chem. Commun.* **2005**, 740–742.
3. Wilkes, J. S.; Levisky, J. A.; Wilson, R. A. *Inorg. Chem.* **1982**, *21*, 1263–1264. Garcia, B.; Lavallée, S.; Perron, G.; Michot, C.; Armand, M. *Electrochim. Acta* **2004**, *49*, 4583–4588.
4. Yanes, E. G.; Gratz, S. R.; Baldwin, M. *J. Anal. Chem.* **2001**, *73*, 3838–3844.
5. (a) Zell, C. A.; Freyland, W. *Langmuir* **2003**, *19*, 7445–7450. (b) Scheeren, C. W.; Machado, G.; Dupont, J.; Fichtner, P. F. P.; Texeira, S. R. *Inorg. Chem.* **2003**, *42*, 4738–4742. (c) Huang, J.-F.; Sun, I.-W. *J. Chromat. A* **2003**, *1007*, 39–45.
6. (a) Zhou, Y.; Antonietti, M. *J. Am. Chem. Soc.* **2003**, *125*, 14960–14961. (b) Zhou, Y.; Antonietti, M. *Chem. Mater.* **2004**, *16*, 544–550.
7. Sato, T.; Masuda, G.; Takagi, K. *Electrochim. Acta* **2004**, *49*, 3603–3611.
8. See: http://www.iolitec.de.

Enzymatic Reactions in Ionic Liquids

Dr. F. Bordusa, Max Planck Research Unit for Enzymology of Protein Folding, Weinbergweg 22, 06120 Halle/Saale, Germany.

During the last years, a number of enzyme-mediated synthesis reactions in Ionic Liquids were established. In comparison to reactions in classical organic solvents, they showed usually higher enzyme activities and stabilities. Furthermore, the regio-, stereo-, and enantio-selectivites were improved.

Recently, lipases showed the most promising results in Ionic Liquids. One of the most popular lipase for synthetic use is the *candida antarctica* lipase (CALB). CALB catalyzes the enantioselective acylation of 1-phenylethylamine with 4-pentenoic acid (**Scheme 1**).

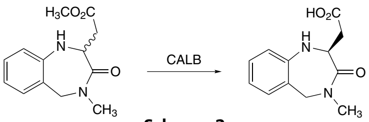


Scheme 1

In Ionic Liquids, the enantiomeric excess of the resulting amide is over 99%. In a solvent-free system, only 59% ee was achieved.[1] The highest conversion rates are reached in 1-butyl-2,3-dimethylimidazolium trifluoromethanesulfonate (Prod. # **00765**) and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (Prod. # **04367**).[2]

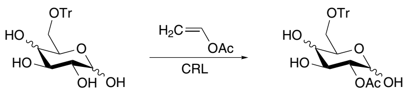
Similarly, in CALB-mediated trans-esterification reactions with ethyl butanoate, higher conversion rates were observed in 1-butyl-3-methylimidazolium hexafluorophosphate (Prod. # **70956**) than in classical organic solvents.[3]

Because of the stabilizing effect of Ionic Liquids, enzymatic resolution of a Lotrafiban-precursor with CALB allows an increase of the reaction temperature up to 75 °C if 1-butyl-3-methylimidazolium hexafluorophosphate is used as solvent (**Scheme 2**). This leads to a four-fold enhancement of the initial rate of product formation compared to *t*-butanol.[4]



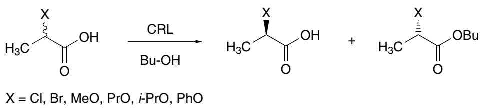
Scheme 2

Also, *candida rugosa* lipase (CRL) shows activity in Ionic Liquids. Methyl-6-*O*-trityl-glucosides and galactosides can be acylated enzymatically by CRL (**Scheme 3**). The regioselectivity of this reaction is increased from 80% in THF to over 98% in 1-butyl-3-methylimidazolium hexafluorophosphate as solvent.[5]



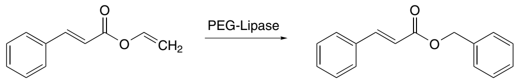
Scheme 3

CRL similarly mediates the esterification of 2-substituted propanoic acids with butanol (**Scheme 4**). The enantioselectivity of this reaction is enhanced by using 1-methyl-3-octylimidazolium hexafluorophosphate (Prod. # **69230**). In this solvent, CRL can be recycled five times without appreciable decrease of activity or enantioselectivity.[6]



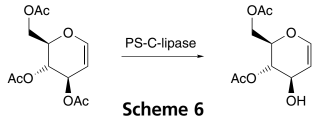
Scheme 4

The PEG-lipase PS from *Pseudomonas cepacia* can catalyze the alcoholysis between vinyl cinnamate and benzyl alcohol (**Scheme 5**). This reaction proceeds with an eight-fold higher enzyme activity in 1-octyl-4-methylimidazolium hexafluorophospate than in an organic solvent system.[7]



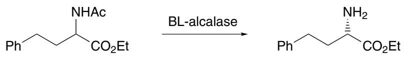
Scheme 5

The PS-C lipase from *Pseudomonas cepacia* hydrolyzes 3,4,6-tri-*O*-acetyl-D-glucal (**Scheme 6**). In 1-butyl-3-methylimidazolium hexafluorophosphate, the regioselectivity is increased up to 80%, whereas the regioselectivity in THF is lower than 20%.[8]



Scheme 6

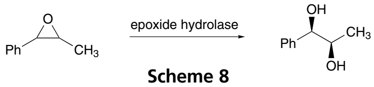
The serine-protease α-*chymotrypsin* mediates the synthesis of *N*-acetyl-L-tyrosine propyl ester through a trans-esterification reaction in Ionic Liquids starting from the ethyl ester. In 1-butyl-3-methylimidazolium hexafluorophosphate and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Prod. # **11291**), α-*chymotrypsin* shows a clear enhancement in enzyme stability and conversion rates in comparison to propanol.[9] BL-alcalase, a commercially available serine-type endoproteinase from *Bacillus licheniforms*, can catalyse the enzymatic resolution of a homophenylalanine ester in Ionic Liquids (**Scheme 7**). In 1-ethyl-3-methylimidazolium tetrafluoroborate (Prod. # **04365**) and 4-ethylpyridinium tetrafluoroborate, high optical purity and yields are achieved.[10]



Scheme 7

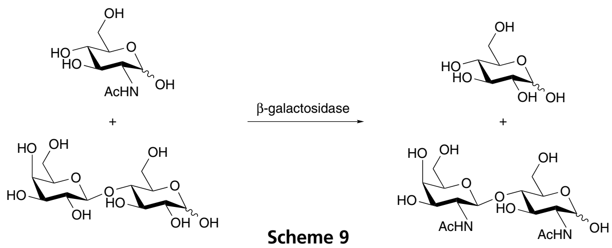
Metalloproteases are applicable in Ionic Liquids. The zinc-protease thermolysin is used for the enzymatic synthesis of (*Z*)-aspartame. Thermolysin activity in 1-butyl-3-methylimidazolium hexafluorophosphate reaches the same order of magnitude as in conventional organic solvents. The enzymatic stability is as good as the stability of immobilized enzymes.[11]

Etherhydrolases also work in Ionic Liquids. The enzyme (recombinant soluble epoxide hydrolase)[12] hydrolyzes trans-β-methylstyrene oxide through a stereoconvergent process to give the corresponding optically active (1*S*,2*R*)-*erythro*-1-phenylpropane-1,2-diol (**Scheme 8**). In 1-butyl-3-methylimidazolium hexafluorophosphate, an enantiomeric excess of 90% is achieved.[13]



Scheme 8

The β-galactosidase from *Bacillus circulans* is able to catalyze the synthesis of *N*-acetyllactosamine in a trans-glycosylation reaction (**Scheme 9**). The addition of 25% 1,3-dimethylimidazolium dimethylsulfate suppresses the secondary hydrolysis of the product, which doubles the yield of the reaction to almost 60% compared to conventional organic media.[14]

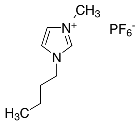


Scheme 9

Sigma-Aldrich offers a collection of Ionic Liquids suitable for bioorganic transformations and enzyme-mediated reactions.

1-Butyl-3-methylimidazolium hexafluorophosphate purum, ≥96% T

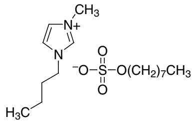
$C_8H_{15}F_6N_2P$
FW: 284.18
mp: 11 °C
[*174501-64-5*]



70956-5G	5 g	
70956-50G	50 g	
70956-250G	250 g	

1-Butyl-3-methylimidazolium octyl sulfate, purum, ≥95% T

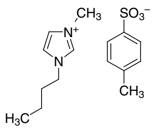
$C_{16}H_{32}N_2O_4S$
FW: 348.50
mp: 33 °C
[*445473-58-5*]



75059-5G	5 g	
75059-50G	50 g	

1-Butyl-3-methylimidazolium tosylate, ≥98.5% NEW

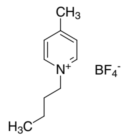
$C_{15}H_{22}N_2O_3S$
FW: 310.41



00806-5G	5 g	
00806-50G	50 g	

1-Butyl-4-methylpyridinium tetrafluoroborate, purum, ≥97% T

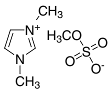
$C_{10}H_{16}BF_4N$
FW: 237.05
mp: <30 °C
[*343952-33-0*]



73261-5G	5 g	
73261-50G	50 g	

1,3-Dimethylimidazolium methyl sulfate, purum, ≥97% NMR

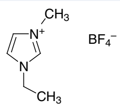
$C_6H_{12}N_2O_4S$
FW: 208.24
[*97345-90-9*]



93607-5G	5 g	
93607-50G	50 g	

1-Ethyl-3-methylimidazolium tetrafluoroborate, purum, ≥97% T

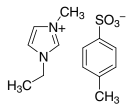
$C_6H_{11}BF_4N_2$
FW: 197.97
mp: 11 °C
[*143314-16-3*]



04365-1ML	1 mL	
04365-5ML	5 mL	
04365-50ML	50 mL	

1-Ethyl-3-methylimidazolium tosylate, purum, ≥98% T

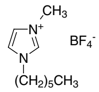
$C_{13}H_{18}N_2O_3S$
FW: 282.36
mp: 25–35 °C
[328090-25-1]



89155-5G	5 g	
89155-50G	50 g	

1-Hexyl-3-methylimidazolium tetrafluoroborate, purum, ≥97% NMR

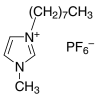
$C_{10}H_{19}BF_4N_2$
FW: 254.08
mp: -81 °C
[*244193-50-8*]



73244-5G	5 g	
73244-50G	50 g	

1-Methyl-3-octylimidazolium hexafluorophosphate, purum, ≥95% T NEW

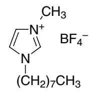
$C_{12}H_{23}F_6N_2P$
FW: 340.29
mp: <-40 °C
[*304680-36-2*]



69230-5G	5 g	
69230-25G	25 g	

1-Methyl-3-octylimidazolium tetrafluoroborate, purum, ≥97% AT NEW

$C_{12}H_{23}BF_4N_2$
FW: 282.13
mp: -88 °C
[*244193-52-0*]



96324-5G	5 g	
96324-50G	50 g	

References:

1 Irimescu, R. et al. *Tetrahedron Lett.* **2004**, *45*, 523.
2. Irimescu, R. et al. *J. Mol. Catal. B: Enzym.* **2004**, *30*, 189.
3. Lau, R. M et al. *Org. Lett.* **2000**, *2*, 4189.
4. Roberts, N. J. et al. *Green Chem.* **2004**, *6*, 475.
5. Kim, M.-J. et al. *J. Mol. Catal. B: Enzym.* **2003**, *26*, 115.
6. Ulbert, O. et al. *J. Mol. Catal. B: Enzym.* **2004**, *31*, 39.
7. Maruyama, T. et al. *Biotechnol. Lett.*, **2002**, *24*, 1341.
8. Nara, S. J. et al. *J. Mol. Catal. B: Enzym.* **2004**, *28*, 39.
9. Lozano, P. et al. *Biotechnol. Bioeng.* **2001**, *75*, 563.
10. Zhao, H. et al. *Biotechnol. Prog.* **2003**, *19*, 1016.
11. Erbeldinger, M. et al. *M. Biotechnol. Prog.* **2000**, *16*, 1129.
12. Morissea, C. et al. *Arch. Biochem. Biophys.* **2000**, *378*, 321.
13. Chiappe et al. *J. Mol. Catal. B: Enzym.* **2004**, *27*, 243.
14. Kaftzik, N. et al. *Org. Process Res. Dev.* **2002**, *6*, 553.

CYPHOS® Phosphonium Ionic Liquids

The phosphonium cation, with the generic formula $[PR_3R']^+$ and with a judicious selection of the appropriate anion, forms many phosphonium salts that are liquid at room temperature and many have melting points below 100 °C.

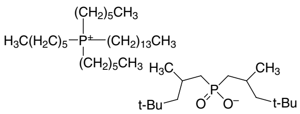
Phosphonium-based Ionic Liquids offer the following advantages:

- Phosphonium salts are thermally more stable than the corresponding ammonium salts and imidazolium salts. This is very important for processes which operate at temperatures higher than 100 °C (e.g., removal of reaction products by distillation). Furthermore, prevention of contaminations by decomposition products is a prerequisite for multiple recycle use of solvents.
- Phosphonium cations lack acidic protons. Thus, they are stable under basic conditions, which can be problematic for several imidazolium-based Ionic Liquids (carbene formation).
- Phosphonium salts are, in general, less dense than water, which might be beneficial in product work-up steps.

Sigma-Aldrich offers, in collaboration with Cytec Industries, Inc., a new class of Ionic Liquids based on phosphonium cations.

Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate, purum NEW

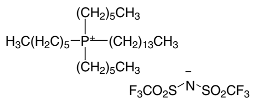
$C_{48}H_{102}O_2P_2$
FW: 773.27
mp: -71 °C



28612-5G	5 g
28612-50G	50 g

Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide, purum NEW

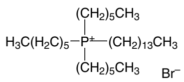
$C_{34}H_{68}F_6NO_4PS_2$
FW: 764.00
mp: -50 °C
[*460092-03-9*]



50971-5G	5 g
50971-50G	50 g

Trihexyltetradecylphosphonium bromide, purum NEW

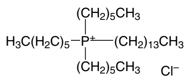
$C_{32}H_{68}BrP$
FW: 563.76
mp: 45–47 °C



96662-5G	5 g
96662-50G	50 g

Trihexyltetradecylphosphonium chloride, purum NEW

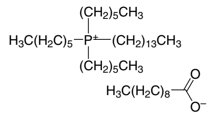
$C_{32}H_{68}ClP$
FW: 519.31
mp: -70 °C
[*258864-54-9*]



89744-5G	5 g
89744-50G	50 g

Trihexyltetradecylphosphonium decanoate, purum NEW

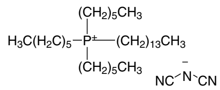
$C_{42}H_{87}O_2P$
FW: 655.11
mp: -9 °C



50826-5G	5 g
50826-50G	50 g

Trihexyltetradecylphosphonium dicyanamide, purum NEW

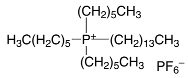
$C_{34}H_{68}N_3P$
FW: 549.90
mp: -50 °C



56776-5G	5 g
56776-50G	50 g

Trihexyltetradecylphosphonium hexafluorophosphate, purum NEW

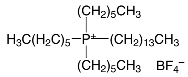
$C_{32}H_{68}F_6P_2$
FW: 628.82
[*374683-44-0*]



40573-5G	5 g
40573-50G	50 g

Trihexyltetradecylphosphonium tetrafluoroborate, purum NEW

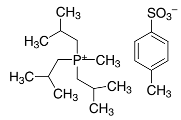
$C_{32}H_{68}BF_4P$
FW: 570.66
mp: 17 °C
[*374683-55-3*]



15909-5G	5 g
15909-50G	50 g

Triisobutylmethylphosphonium tosylate, purum NEW

$C_{20}H_{37}O_3PS$
FW: 388.54
mp: -50 °C
[*344774-05-6*]



90145-5G	5 g
90145-50G	50 g

References

1. Bradaric, C. J.; Downard, A.; Kennedy, C.; Robertson A. J.; Zhou, Y. *Green Chem*. **2003**, *5*, 143

Ionic MALDI Matrices—Improve Your Performance

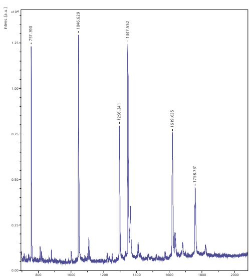
The striking advantages of MALDI (matrix-assisted laser desorption/ ionization)-MS for characterization of mainly large molecules result from the embedding of sample in a chemical matrix that greatly facilitates the production of intact gas-phase ions from large, non-volatile, and thermally labile compounds, such as peptides, proteins, or oligonucleotides. The matrix plays a key role in this technique by absorbing the laser light energy and causing a small part of the target substrate to vaporize.

The commonly used matrix substances offer highly effective ionization and low vapor pressure. One of their main disadvantages is that the analytes cannot be dispersed throughout the solid matrix in a homogeneous manner. The target substance as well as other components of the sample (impurities) typically segregate, resulting in heterogeneous preparations and limited reproducibility. Heterogeneity of analyte distribution within the sample spots is a serious problem, especially for the use of MALDI-MS for quantitative determinations.[1] Liquid matrices would provide homogeneous preparations and other advantages, but typically suffer from their volatility, which results in an altering, uncontrolled matrix. With low mass resolution, poor ionization efficiency, and high chemical background, they have restricted use in UV-MALDI-MS.

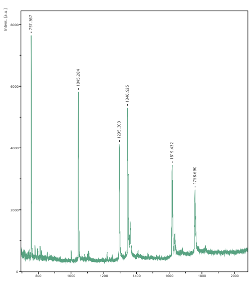
Ionic matrix substances are a new class of matrices composed of organic acids (classical matrices, others turned out to be unsuitable) and organic bases. Ionic matrices, especially the low-melting ones, provide several striking advantages. These matrix systems have excellent solubilizing properties compared to other commonly used matrices. They allow a homogeneous sample preparation with a thin Ionic Liquid layer having negligible vapour pressure.[2] This leads to facilitated qualitative and quantitative measurements compared to classical matrices.

It has been shown that ionic matrices yield a very homogeneous drop, so that performance of a single shot is much more reproducible and search for a "hot spot" is not required. Ionic matrices are specially suitable for qualitative and quantitative analyses of small molecules.[3]

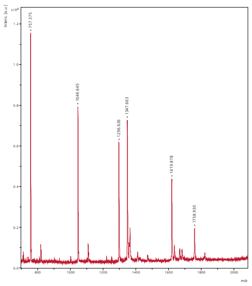
Sigma-Aldrich offers ionic matrices with the highest purity: α-cyano-4-hydroxycinnamic acid diethyl amine (HCCA diethylamine, Prod. # **55341**) and α-cyano-4-hydroxycinnamic acid butyl amine (HCCA butylamine, Prod. # **67336**). The use of these highly purified matrices may result in high signal-to-noise ratios and, especially, improved resolution.



a) Angiotensin II (M = 1046.5); S/N = 74; Res. (M/ΔM) = 341



b) Angiotensin II (M = 1046.5), S/N = 63, Res. (M/ΔM) = 764



c) Angiotensin II (M = 1046.5), S/N = 104, Res. (M/ΔM) = 1218

The graphs show a comparison of mass spectra using a) HCCA, b) HCCA butylamine matrix, and c) HCCA diethylamine matrix. The ionic matrices show improved resolution. These matrices also show modified peak pattern compared to the standard matrix, which may be advantageous for analyzing complex mixtures of peptides. The analyzed peptide mix contains: Bradykinin 1-7, $[M+H]^+$ = 757.411; Angiotensin II, $[M+H]^+$ =1046.504; Angiotensin I, $[M+H]^+$ = 1296.623; Substance P, $[M+H]^+$ = 1347.673; Bombesin, $[M+H]^+$ =1619.741; Renin-Substrate, $[M+H]^+$ =1758.832.

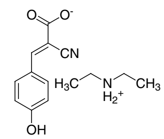
Ionic Matrices: Features and Benefits

- Improved Resolving Power
- Reproducibility
- High Signal-to-Noise Ratio
- Suitable for Quantification

α-Cyano-4-hydroxycinnamic acid Diethylamine salt, puriss. p.a., matrix substance for MALDI-MS, ≥99% HPLC

NEW

$C_{10}H_7NO_3 \cdot C_4H_{11}N$
FW: 262.30
[*355011-52-8*]

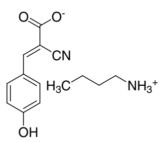


55341-100MG	100 mg	
55341-1G	1 g	
55341-10X10MG	10 × 10 mg	

α-Cyano-4-hydroxycinnamic acid Butylamine salt, puriss. p.a., matrix substance for MALDI-MS, ≥99% HPLC

NEW

$C_{10}H_7NO_3 \cdot C_4H_{11}N$
FW: 262.30
[*355011-53-9*]



67336-100MG	100 mg	
67336-1G	1 g	
67336-10X10MG	10 × 10 mg	

References

1. Garden, R. W.; Swedler, J. V. *Anal. Chem.* **2000**, *72*, 30.
2. Armstrong, D. W.; Zhang, L.-K.; He, L.; Gross, M. L. *Anal. Chem.* **2001**, *73*, 3679.
3. Zabet-Moghaddam, M.; Heinzle, E.; Tholey, A. *Rapid Commun. Mass Spectrom*. **2004**, *18*, 141.

Task-Specific Ionic Liquids

Roland St. Kalb and Michael J. Kotschan, proionic Production of Ionic Substances GmbH, Leoben, Austria.

Task-Specific Ionic Liquids (TSILs) for the selective liquid/liquid extraction of heavy metals from aqueous systems were first published by Robin D. Rogers et al. in the year 2001.[1] Functionalized imidazolium cations with thioether, urea, or thiourea derivatized side chains act as metal ligating moieties, whereas the PF_6^- anions provide the desired water immiscibility (**Figure 1**). Nernst distribution ratios were reported for Cd^{2+} and Hg^{2+} to be ≤380.

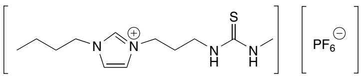


Figure 1: Thiourea derivatized Ionic Liquid

These Ionic Liquids were the first to contain specific functionalities to enable well defined chemical properties and therefore undoubtedly be called "designer solvents."

However, these pioneering Ionic Liquids show some major drawbacks: the hexafluorophosphate anion is known to be quite unstable toward hydrolysis and produces toxic and corrosive HF or fluorides. The toxicity of the imidazolium cation is difficult to be estimated; an expensive toxicological study is risky. The disposal of these fluorous compounds is expensive and problematic. The synthesis at larger scale is complicated; starting materials are expensive.

Trioctylmethylammonium thiosalicylate (TOMATS): A Novel, High Performance, Ionic Liquid for the Extraction of Heavy Metals from Aqueous Solutions

To overcome the aforementioned drawbacks—especially in consideration of a possible industrial application at larger scales—and to enhance the performance, proionic Production of Ionic Substances GmbH developed a new Ionic Liquid in their laboratories: Trioctylmethylammonium thiosalicylate ("TOMATS," Prod. # **08354**, **Figure 2**).

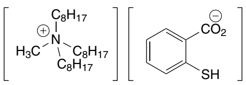


Figure 2: TOMATS

TOMATS contains no fluorine and is absolutely stable to any hydrolysis. It therefore does not release HF or fluorides, is not corrosive, and is much easier to dispose. The toxicity of the cation is known from common compounds like trioctylammonium chloride (a phase-transfer catalyst). The toxicity of the anion is known from thiosalicylic acid and its salts; they are found to be irritants. The distribution coefficients of heavy metals typically show values in the range of 1500 to more than 5000, which may be explained by the chelating effect of the ortho-positioned carboxylate group additional to the known formation of metal-thiolates. The synthesis of TOMATS is simple and can be done at industrial scales.

Application of TOMATS

Figure 3 shows the extraction of copper out of a blue-colored aqueous Cu^{2+}-tetramine phase (left test tube). After addition of the TOMATS Ionic Liquid and before shaking, nice diffusion zones can be seen (middle test tube), showing a copper-free, uncolored region and a dark copper-containing upper region. After shaking and waiting for the separation of the phases, all the copper is extracted into the upper phase, forming an organic, dark-colored copper compound (right test tube).

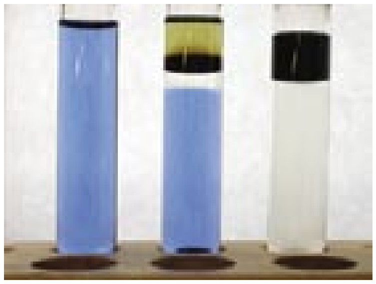


Figure 3: Extraction of Copper

Phase separation sometimes can last a long period of time because of the relative high viscosity of TOMATS of 1500 mPa.s at 20 °C. This drawback can be overcome by either adding some percent of a water-immiscible organic solvent like ethyl acetate or dichloromethane (decreasing the viscosity down to hundred mPa.s), or by heating.

Phase separation can be optimized using a centrifuge and adding some sodium sulfate to the aqueous phase before shaking. If the aqueous phase still looks turbid, it can be filtered through a common membrane filter (µm pore size).

Characterization of TOMATS

Appearance: olive green, viscous liquid

Solubility:
- Soluble in alcohols, ethyl acetate, THF, acetonitrile, acetone, dichloromethane, DMSO
- Insoluble in water, hexane

Nernst distribution coefficients:[1] Cd^{2+} >1500; Cu^{2+} >3000; Pb^{2+}, Hg^{2+} >5000

Refractive index: n_D^{20} = 1.5185

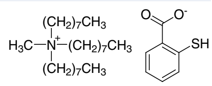
Leaching into aqueous phase: <0.5%

Density, Viscosity:

	TOMATS 100%		TOMATS 95% (5% ethyl acetate)	
T [°C]	d [g/cm³]	η [mPa.s]	d [g/cm³]	η [mPa.s]
20	0.9556	1.500	0.9534	509
40	0.9445	352	0.9424	158
60	0.9325	119	0.9300	63
80	0.9213	50	0.9185	30

Methyltrioctylammonium thiosalicylate, purum NEW

$C_{32}H_{59}NO_2S$
FW: 521.88
m.p.: <10 °C



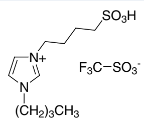
08354-1G	1 g
08354-5G	5 g

Other Task-Specific Ionic Liquids

Recently, zwitterionic, sulfonic acid-functionalized Ionic Liquids have been used as alternatives to conventional acids in acid-catalyzed reactions.[2] Sigma-Aldrich now offers several Task Specific Ionic Liquids for this application.

4-(3-Butyl-1-imidazolio)-1-butanesulfonic acid triflate NEW

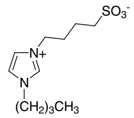
$C_{12}H_{21}F_3N_2O_6S_2$
FW: 410.43
[*439937-63-0*]



19597-5G	5 g
19597-50G	50 g

4-(3-Butyl-1-imidazolio)-1-butanesulfonate NEW

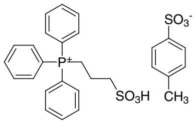
$C_{11}H_{20}N_2O_3S$
FW: 260.35
[*439937-61-8*]



51131-5G	5 g	
51131-50G	50 g	

3-(Triphenylphosphonio)propane-1-sulfonic acid tosylate NEW

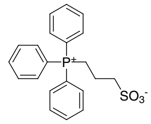
$C_{28}H_{29}O_6PS_2$
FW: 556.63
[*439937-65-2*]



07349-5G	5 g	
07349-50G	50 g	

3-(Triphenylphosphonio)propane-1-sulfonate NEW

$C_{21}H_{21}O_3PS$
FW: 384.43
[*116154-22-4*]



53166-5G	5 g	
53166-50G	50 g	

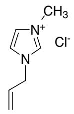
References

1. Aqueous phase with 5 to 50 ppm metal, 1:1 extraction. Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Rogers, R. D.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis Jr., J. H. *Chem. Commun*. **2001**, 135.
2. (a) Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T; Weaver, K. J.; Forbes, D. C.; Davis, Jr., J. H. *J. Am. Chem. Soc.* **2002**, *124*, 5962–5963. (b) Gu, Y.; Shi, F.; Deng, Y. *Catalysis Communications* **2003**, *4*, 597–601.

Imidazolium-Based Ionic Liquids

1-Allyl-3-methylimidazolium chloride NEW

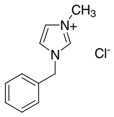
$C_7H_{11}ClN_2$
FW: 158.63
mp: 55 °C
[*65039-10-3*]



43961-5G	5 g	
43961-50G	50 g	

1-Benzyl-3-methylimidazolium chloride NEW

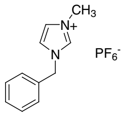
$C_{11}H_{13}ClN_2$
FW: 208.69
mp: 70 °C
[*36443-80-8*]



49914-5G	5 g	
49914-50G	50 g	

1-Benzyl-3-methylimidazolium hexafluorophosphate NEW

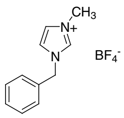
$C_{11}H_{13}F_6N_2P$
FW: 318.20
mp: 136 °C
[*433337-11-2*]



39447-5G	5 g	
39447-50G	50 g	

1-Benzyl-3-methylimidazolium tetrafluoroborate NEW

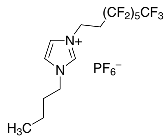
$C_{11}H_{13}BF_4N_2$
FW: 260.04
mp: 77 °C
[*500996-04-3*]



40819-5G	5 g	
40819-50G	50 g	

1-Butyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-imidazolium hexafluorophosphate, purum, ≥97% NMR NEW

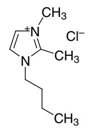
$C_{15}H_{16}F_{19}N_2P$
FW: 616.24
mp: 120–121 °C
[*313475-52-4*]



94049-1G	1 g	
94049-5G	5 g	

1-Butyl-2,3-dimethylimidazolium chloride, ≥97% AT NEW

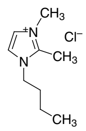
$C_9H_{17}ClN_2$
FW: 188.70
mp: 89 °C
[*98892-75-2*]



19122-5G	5 g	
19122-50G	50 g	

1-Butyl-2,3-dimethylimidazolium chloride, purum, ≥97% AT NEW

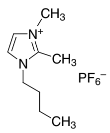
$C_9H_{17}ClN_2$
FW: 188.70
mp: 89 °C
[*98892-75-2*]



78194-5G	5 g	
78194-50G	50 g	

1-Butyl-2,3-dimethylimidazolium hexafluoro-phosphate, purum, ≥97% T NEW

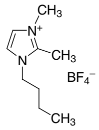
$C_9H_{17}F_6N_2P$
FW: 298.21
[*227617-70-1*]



70869-5G	5 g	
70869-50G	50 g	

1-Butyl-2,3-dimethylimidazolium tetrafluoroborate purum, ≥98% T
NEW

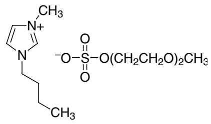
$C_9H_{17}BF_4N_2$
FW: 240.05
mp: 37 °C
[*402846-78-0*]



70863-5G	5 g	
70863-50G	50 g	

1-Butyl-3-methylimidazolium 2-(2-methoxyethoxy)-ethyl sulfate, purum, ≥95% T

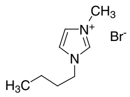
$C_{13}H_{26}N_2O_6S$
FW: 338.42



67421-5G	5 g	
67421-50G	50 g	

1-Butyl-3-methylimidazolium bromide, purum, > 97% T

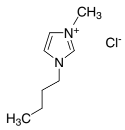
$C_8H_{15}BrN_2$
FW: 219.12
mp: 77 °C
[*85100-77-2*]



95137-5G	5 g	
95137-50G	50 g	

1-Butyl-3-methylimidazolium chloride, purum, ≥95% AT

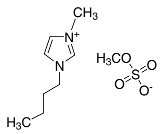
$C_8H_{15}ClN_2$
FW: 174.67
mp: 41 °C
[*79917-90-1*]



94128-5G	5 g	
94128-50G	50 g	
94128-250G	250 g	

1-Butyl-3-methylimidazolium methyl sulfate, purum, ≥97% NMR

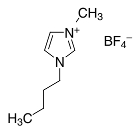
$C_9H_{18}N_2O_4S$
FW: 250.32
mp: 25 °C
[*401788-98-5*]



83086-5G	5 g	
83086-50G	50 g	

1-Butyl-3-methylimidazolium tetrafluoroborate, purum, ≥97% T

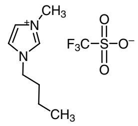
$C_8H_{15}BF_4N_2$
FW: 226.02
mp: -71 °C
[*174501-65-6*]



91508-5G	5 g	
91508-50G	50 g	
91508-250G	250 g	

1-Butyl-3-methylimidazolium trifluoromethane-sulfonate, purum, ≥95% NMR
NEW

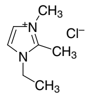
$C_9H_{15}F_3N_2O_3S$
FW: 288.29
mp: 13 °C
[*174899-66-2*]



76420-5G	5 g	
76420-25G	25 g	

1-Ethyl-2,3-dimethylimidazolium chloride, purum, ≥97% T
NEW

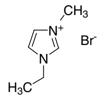
$C_7H_{13}ClN_2$
FW: 160.64
mp: 181 °C
[*92507-97-6*]



78151-5G	5 g	

1-Ethyl-3-methylimidazolium bromide, purum, ≥97% T

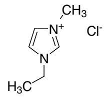
$C_6H_{11}BrN_2$
FW: 191.07
mp: 53 °C
[*65039-08-9*]



89483-5G	5 g	
89483-50G	50 g	

1-Ethyl-3-methylimidazolium chloride, purum, Ionic solvent, ≥97% AT

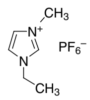
$C_6H_{11}ClN_2$
FW: 146.62
mp: 89 °C
[*65039-09-0*]



72924-5G	5 g	
72924-50G	50 g	

1-Ethyl-3-methylimidazolium hexafluorophosphate purum, ≥97% CE

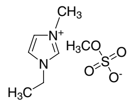
$C_6H_{11}F_6N_2P$
FW: 256.13
mp: 62 °C
[*155371-19-0*]



46093-1G	1 g	
46093-5G	5 g	
46093-50G	50 g	

1-Ethyl-3-methylimidazolium methyl sulfate, ≥99%
NEW

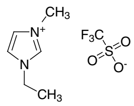
$C_7H_{14}N_2O_4S$
FW: 222.26
[*516474-01-4*]



18086-5G	5 g	
18086-50G	50 g	

1-Ethyl-3-methylimidazolium trifluoromethanesulfonate, purum, ≥98% T

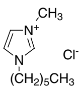
$C_7H_{11}F_3N_2O_3S$
FW: 260.23
mp: -9 °C
[*145022-44-2*]



04367-1ML	1 mL	
04367-5ML	5 mL	
04367-25ML	25 mL	

1-Hexyl-3-methylimidazolium chloride, purum, ≥97% AT

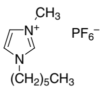
$C_{10}H_{19}ClN_2$
FW: 202.72
mp: -75 °C
[*171058-17-6*]



87929-5G	5 g	
87929-50G	50 g	

1-Hexyl-3-methylimidazolium hexafluorophosphate, purum, ≥97% T — NEW

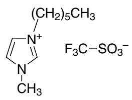
$C_{10}H_{19}F_6N_2P$
FW: 312.24
mp: -80 °C
[*304680-35-1*]



89320-5G	5 g	
89320-50G	50 g	

1-Hexyl-3-methylimidazolium trifluoromethanesulfonate, ≥95% T — NEW

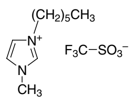
$C_{12}H_{21}F_3N_2O_3S$
FW: 330.37
mp: <30 °C
[*460345-16-8*]



49980-5G	5 g	
49980-25G	25 g	

1-Hexyl-3-methylimidazolium trifluoromethanesulfonate, purum, ≥95% T — NEW

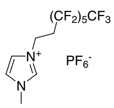
$C_{12}H_{21}F_3N_2O_3S$
FW: 330.37
[*460345-16-8*]



67476-5G	5 g	
67476-25G	25 g	

1-Methyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium hexafluorophosphate, purum, ≥97% NMR — NEW

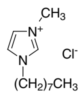
$C_{12}H_{10}F_{19}N_2P$
FW: 574.16
mp: 80 °C
[*313475-50-2*]



44979-1G	1 g	

1-Methyl-3-octylimidazolium chloride, purum, ≥97% AT

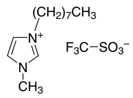
$C_{12}H_{23}ClN_2$
FW: 230.78
mp: <0 °C
[*64697-40-1*]



95803-5G	5 g	
95803-50G	50 g	

1-Methyl-3-octylimidazolium trifluoromethanesulfonate, ≥97% T — NEW

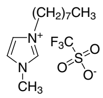
$C_{13}H_{23}F_3N_2O_3S$
FW: 344.39
[*403842-84-2*]



42471-5G	5 g	
42471-25G	25 g	

1-Methyl-3-octylimidazolium trifluoromethanesulfonate, purum, ≥97% T — NEW

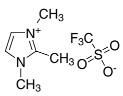
$C_{13}H_{23}F_3N_2O_3S$
FW: 344.39
[*403842-84-2*]



68902-5G	5 g	
68902-25G	25 g	

1,2,3-Trimethylimidazolium trifluoromethanesulfonate, ≥98.5% — NEW

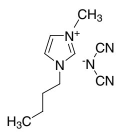
$C_7H_{11}F_3N_2O_3S$
FW: 260.23



05942-5G	5 g	
05942-50G	50 g	

1-Butyl-3-methylimidazolium dicyanamide, ≥99% — NEW

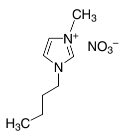
$C_{10}H_{15}N_5$
FW: 205.26
mp: -6 °C
[*448245-52-1*]



55220-5G	5 g	
55220-50G	50 g	

1-Butyl-3-methylimidazolium nitrate, purum, ≥98.5% — NEW

$C_8H_{15}N_3O_3$
FW: 201.22
[*179075-88-8*]

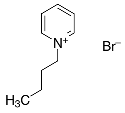


07319-5G	5 g	
07319-50G	50 g	

Pyridinium-Based Ionic Liquids

1-Butylpyridinium bromide, ≥99% NEW

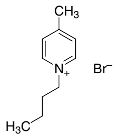
$C_9H_{14}BrN$
FW: 216.12
mp: 105 °C
[*874-80-6*]



00285-5G	5 g	
00285-50G	50 g	

1-Butyl-4-methylpyridinium bromide, purum, ≥98% AT NEW

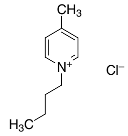
$C_{10}H_{16}BrN$
FW: 230.14
mp: 135 °C
[*65350-59-6*]



94349-5G	5 g	
94349-50G	50 g	

1-Butyl-4-methylpyridinium chloride, purum, ≥97% AT NEW

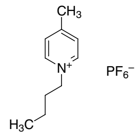
$C_{10}H_{16}ClN$
FW: 185.69
mp: 158 °C
[*112400-86-9*]



88482-5G	5 g	
88482-50G	50 g	

1-Butyl-4-methylpyridinium hexafluorophosphate, purum, ≥97% NMR

$C_{10}H_{16}F_6NP$
FW: 295.20
mp: 41 °C
[*401788-99-6*]

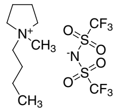


88458-5G	5 g	
88458-50G	50 g	

Pyrrolidinium-Based Ionic Liquids

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, ≥99% NEW

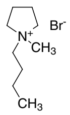
$C_{11}H_{20}F_6N_2O_4S_2$
FW: 422.41



38894-5G	5 g	
38894-50G	50 g	

1-Butyl-1-methylpyrrolidinium bromide, ≥99% NEW

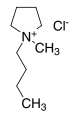
$C_9H_{20}BrN$
FW: 222.17
mp: >160 °C
[*93457-69-3*]



04275-5G	5 g	
04275-50G	50 g	

1-Butyl-1-methylpyrrolidinium chloride, ≥99% NEW

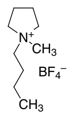
$C_9H_{20}ClN$
FW: 177.71
mp: 114 °C
[*479500-35-1*]



07326-5G	5 g	
07326-50G	50 g	

1-Butyl-1-methylpyrrolidinium tetrafluoroborate, ≥99% NEW

$C_9H_{20}BF_4N$
FW: 229.07
mp: 152 °C
[*345984-11-4*]

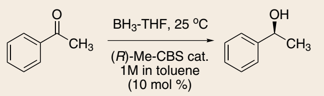


92409-5G	5 g	
92409-50G	50 g	

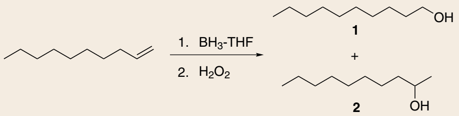
NEW Safer, Amine-Stabilized BH_3-THF Solutions for Hydroboration and Reduction

Product Highlights:

- Enhanced safety
- Shipment for all pack sizes at room temperature providing greater cost savings
- Excellent reactivity and selectivity vs. BH_3-THF (**17,619-2**; $NaBH_4$-stabilized)



65,039-0: 98%; 96.1%ee
65,041-2: 98%; 96.2%ee
17,619-2: 97%; 90.3%ee



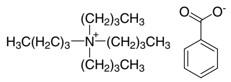
65,039-0: 90%; 93:7 (**1**:**2**)
65,041-2: 93%; 94:6 (**1**:**2**)
17,619-2: 92%; 94:6 (**1**:**2**)

NEW	**65,039-0**	BH_3THF, 1.0M solution in THF, 1,2,2,6,6-Pentamethylpiperidine (PMP)-stabilized
NEW	**65,041-2**	BH_3THF, 1.0M solution in THF, *N*-Isopropyl-*N*-methyl-*tert*-butylamine (NIMBA)-stabilized
	17,619-2	BH_3THF, 1.0M solution in THF, $NaBH_4$-stabilized

Ammonium-Based Ionic Liquids

Tetrabutylammonium benzoate, purum, ≥98% NT

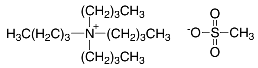
$C_{23}H_{41}NO_2$
FW: 363.58
mp: 64–67 °C
[*18819-89-1*]



86850-5G	5 g	
86850-25G	25 g	

Tetrabutylammonium methanesulfonate, purum, ≥97% T

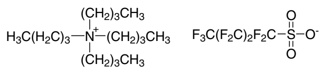
$C_{17}H_{39}NO_3S$
FW: 337.56
mp: 78–80 °C
[*65411-49-6*]



86877-10G	10 g	
86877-50G	50 g	

Tetrabutylammonium nonafluorobutanesulfonate, purum, ≥98% T

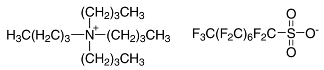
$C_{20}H_{36}F_9NO_3S$
FW: 541.56
mp: 50–53 °C
[*108427-52-7*]



86909-5G	5 g	
86909-25G	25 g	

Tetrabutylammonium heptadecafluorooctanesulfonate technical, ≥90 % T

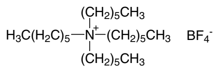
$C_{24}H_{36}F_{17}NO_3S$
FW: 741.59
mp: <5 °C
[*111873-33-7*]



86911-5ML	5 mL	
86911-25ML	25 mL	

Tetrahexylammonium tetrafluoroborate, purum, ≥97% T

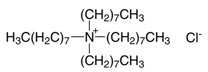
$C_{24}H_{52}BF_4N$
FW: 441.48
mp: 90–92 °C
[*15553-50-1*]



87315-10G	10 g	
87315-50G	50 g	

Tetraoctylammonium chloride, purum, ≥97% AT

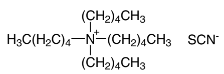
$C_{32}H_{68}ClN$
FW: 502.34
mp: 50–54 °C
[*3125-07-3*]



87991-5G	5 g	
87991-25G	25 g	

Tetrapentylammonium thiocyanate, purum, ≥99% AT

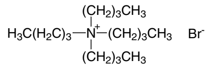
$C_{21}H_{44}N_2S$
FW: 356.65
mp: 46–49 °C
[*3475-60-3*]



88009-5G	5 g	
88009-25G	25 g	

Tetrabutylammonium bromide, puriss., ≥99% AT

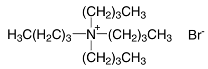
$C_{16}H_{36}BrN$
FW: 322.37
mp: 102–106 °C
[*1643-19-2*]



86860-25G	25 g	
86860-100G	100 g	
86860-500G	500 g	

Tetrabutylammonium bromide, purum, ≥98% AT

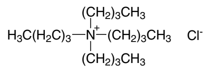
$C_{16}H_{36}BrN$
FW: 322.37
mp: 102–106 °C
[*1643-19-2*]



86861-50G	50 g	
86861-250G	250 g	
86861-1KG	1 kg	

Tetrabutylammonium chloride, purum, ≥97% AT

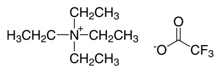
$C_{16}H_{36}ClN$
FW: 277.92
[*1112-67-0*]



86870-25G	25 g	
86870-100G	100 g	
86870-500G	500 g	

Tetraethylammonium trifluoroacetate, purum, ≥98% NT

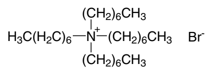
$C_{10}H_{20}F_3NO_2$
FW: 243.27
mp: 74–76 °C
[*30093-29-9*]



86647-5G	5 g	
86647-25G	25 g	

Tetraheptylammonium bromide, purum, ≥99% AT

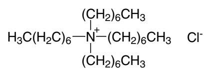
$C_{28}H_{60}BrN$
FW: 490.69
mp: 89–91 °C
[*4368-51-8*]



87301-10G	10 g	
87301-50G	50 g	

Tetraheptylammonium chloride, purum, ≥98% AT

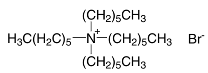
$C_{28}H_{60}ClN$
FW: 446.24
mp: 38–41 °C
[*10247-90-2*]



87292-1G	1 g	
87292-5G	5 g	

Tetrahexylammonium bromide, purum, ≥99% AT

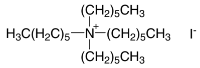
$C_{24}H_{52}BrN$
FW: 434.58
mp: 97 °C
[*4328-13-6*]



87302-10G	10 g	
87302-50G	50 g	

Tetrahexylammonium iodide, puriss., ≥99% AT

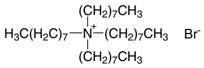
$C_{24}H_{52}IN$
FW: 481.58
mp: 99–101 °C
[*2138-24-1*]



87307-10G	10 g
87307-50G	50 g

Tetraoctylammonium bromide, purum, ≥98% AT

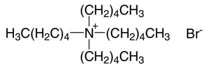
$C_{32}H_{68}BrN$
FW: 546.79
mp: 95–98 °C
[*14866-33-2*]



88000-10G	10 g
88000-50G	50 g

Tetrapentylammonium bromide, purum, ≥99% AT

$C_{20}H_{44}NBr$
FW: 378.47
mp: 99–102 °C
[*866-97-7*]

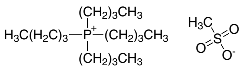


88001-25G	25 g
88001-100G	100 g

Phosphonium-Based Ionic Liquids

Tetrabutylphosphonium methanesulfonate, purum, ≥98% NT

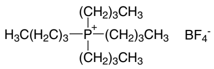
$C_{17}H_{39}O_3PS$
FW: 354.53
mp: 59–62 °C
[*98342-59-7*]



86929-5G	5 g
86929-25G	25 g

Tetrabutylphosphonium tetrafluoroborate, purum, ≥97% T

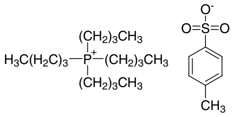
$C_{16}H_{36}BF_4P$
FW: 346.24
mp: 96–99 °C
[*1813-60-1*]



86932-10G	5 g
86932-50G	50 g

Tetrabutylphosphonium *p*-toluenesulfonate, purum, ≥98% NT

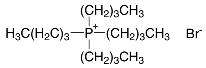
$C_{23}H_{43}O_3PS$
FW: 430.62
mp: 54–57 °C
[*116237-97-9*]



86933-5G	5 g
86933-25G	25 g

Tetrabutylphosphonium bromide, purum, ≥98% AT

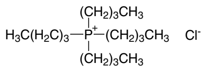
$C_{16}H_{36}BrP$
FW: 339.33
mp: 102–104 °C
[*3115-68-2*]



86917-100G	100 g
86917-500G	500 g

Tetrabutylphosphonium chloride, purum, ≥97% AT

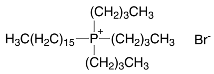
$C_{16}H_{36}ClP$
FW: 294.88
mp: 62–66 °C
[*2304-30-5*]



86919-10G	10 g
86919-50G	50 g

Tributylhexadecylphosphonium bromide, purum, ≥95% AT

$C_{28}H_{60}BrP$
FW: 507.65
mp: 57–62 °C
[*14937-45-2*]



52353-25G	25 g
52353-100G	100 g

Argentina
SIGMA-ALDRICH DE ARGENTINA, S.A.
Tel: 54 11 4556 1472
Fax: 54 11 4552 1698

Australia
SIGMA-ALDRICH PTY., LIMITED
Free Tel: 1800 800 097
Free Fax: 1800 800 096
Tel: 612 9841 0555
Fax: 612 9841 0500

Austria
SIGMA-ALDRICH HANDELS GmbH
Tel: 43 1 605 81 10
Fax: 43 1 605 81 20

Belgium
SIGMA-ALDRICH NV/SA.
Free Tel: 0800-14747
Free Fax: 0800-14745
Tel: 03 899 13 01
Fax: 03 899 13 11

Brazil
SIGMA-ALDRICH BRASIL LTDA.
Tel: 55 11 3732-3100
Fax: 55 11 3733-5151

Canada
SIGMA-ALDRICH CANADA LTD.
Free Tel: 800-565-1400
Free Fax: 800-265-3858
Tel: 905-829-9500
Fax: 905-829-9292

China
SIGMA-ALDRICH CHINA INC.
Tel: 86-21-6386 2766
Fax: 86-21-6386 3966

Czech Republic
SIGMA-ALDRICH s.r.o.
Tel: +420 246 003 200
Fax: +420 246 003 291

Denmark
SIGMA-ALDRICH DENMARK A/S
Tel: 43 56 59 10
Fax: 43 56 59 05

Finland
SIGMA-ALDRICH FINLAND
Tel: (09) 350 9250
Fax: (09) 350 92555

France
SIGMA-ALDRICH CHIMIE S.à.r.l.
Tel appel gratuit: 0800 211 408
Fax appel gratuit: 0800 031 052

Germany
SIGMA-ALDRICH CHEMIE GmbH
Free Tel: 0800-51 55 000
Free Fax: 0800-649 00 00

Greece
SIGMA-ALDRICH (O.M.) LTD
Tel: 30 210 9948010
Fax: 30 210 9943831

Hungary
SIGMA-ALDRICH Kft
Tel: 06-1-235-9054
Fax: 06-1-269-6470
Ingyenes zöld telefon: 06-80-355-355
Ingyenes zöld fax: 06-80-344-344

India
SIGMA-ALDRICH CHEMICALS
PRIVATE LIMITED
Telephone
Bangalore: 91-80-5112-7272
New Delhi: 91-11-5165 4255
Mumbai: 91-22-2570 2364
Hyderabad: 91-40-5584 5488
Fax
Bangalore: 91-80-5112-7473
New Delhi: 91-11-5165 4266
Mumbai: 91-22-2579 7589
Hyderabad: 91-40-5584 5466

Ireland
SIGMA-ALDRICH IRELAND LTD.
Free Tel: 1800 200 888
Free Fax: 1800 600 222
Tel: 353 1 4041900
Fax: 353 1 4041910

Israel
SIGMA-ALDRICH ISRAEL LTD.
Free Tel: 1-800-70-2222
Tel: 08-948-4100
Fax: 08-948-4200

Italy
SIGMA-ALDRICH S.r.l.
Telefono: 02 33417310
Fax: 02 38010737
Numero Verde: 800-827018

Japan
SIGMA-ALDRICH JAPAN K.K.
Tokyo Tel: 03 5796 7300
Tokyo Fax: 03 5796 7315

Korea
SIGMA-ALDRICH KOREA
Tel: 031-329-9000
Fax: 031-329-9090

Malaysia
SIGMA-ALDRICH (M) SDN. BHD
Tel: 603-56353321
Fax: 603-56354116

Mexico
SIGMA-ALDRICH QUÍMICA, S.A. de C.V.
Free Tel: 01-800-007-5300
Free Fax: 01-800-712-9920

The Netherlands
SIGMA-ALDRICH CHEMIE BV
Tel Gratis: 0800-0229088
Fax Gratis: 0800-0229089
Tel: 078-6205411
Fax: 078-6205421

New Zealand
SIGMA-ALDRICH PTY., LIMITED
Free Tel: 0800 936 666
Free Fax: 0800 937 777

Norway
SIGMA-ALDRICH NORWAY AS
Tel: 23 17 60 60
Fax: 23 17 60 50

Poland
SIGMA-ALDRICH Sp. z o.o.
Tel: +4861 829 01 00
Fax: +4861 829 01 20

Portugal
SIGMA-ALDRICH QUÍMICA, S.A.
Free Tel: 800 202180
Free Fax: 800 202178
Tel: 21 9242555
Fax: 21 9242610

Russia
SIGMA-ALDRICH RUSSIA
OOO SAF-LAB
Tel: +7 (095) 975-1917/3321
Fax: +7 (095) 975-4792

Singapore
SIGMA-ALDRICH PTE. LTD.
Tel: 65-6779-1200
Fax: 65-6779-1822

South Africa
SIGMA-ALDRICH
SOUTH AFRICA (PTY) LTD.
Free Tel: 0800 1100 75
Free Fax: 0800 1100 79
Tel: 27 11 979 1188
Fax: 27 11 979 1119

Spain
SIGMA-ALDRICH QUÍMICA S.A.
Free Tel: 900 101376
Free Fax: 900 102028
Tel: 91 661 99 77
Fax: 91 661 96 42

Sweden
SIGMA-ALDRICH SWEDEN AB
Tel: 020-350510
Fax: 020-352522
Outside Sweden Tel: +46 8 7424200
Outside Sweden Fax: +46 8 7424243

Switzerland
FLUKA CHEMIE GmbH
Swiss Free Call: 0800 80 00 80
Tel: +41 81 755 2828
Fax: +41 81 755 2815

United Kingdom
SIGMA-ALDRICH COMPANY LTD.
Free Tel: 0800 717181
Free Fax: 0800 378785
Tel: 01747 833000
Fax: 01747 833313
SAFC (UK): 01202 712305

United States
SIGMA-ALDRICH
P.O. Box 14508
St. Louis, Missouri 63178
Toll-free: 800-325-3010
Call Collect: 314-771-5750
Toll-Free Fax: 800-325-5052
Tel: 314-771-5765
Fax: 314-771-5757

Internet:
sigma-aldrich.com

ALDRICH®
P.O. Box 355
Milwaukee, WI 53201
USA

Order/Customer Service 1-800-325-3010 • Fax 1-800-325-5052
Technical Service 1-800-325-5832 • sigma-aldrich.com/techservice

Development/Bulk Manufacturing Inquiries SAFC™ 1-800-244-1173

World Headquarters • 3050 Spruce St., St. Louis, MO 63103 • (314) 771-5765

SIGMA-ALDRICH

We are committed to the success of our Customers, Employees and Shareholders through leadership in ***Life Science, High Technology*** *and* ***Service.***

The SIGMA-ALDRICH Family SIGMA ALDRICH Fluka Riedel-deHaën SUPELCO ISOTEC

IAX
02159-040517
0065