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Synthesis and characterization of carboxyl-functionalized benzimidazolium based ionic liquids as efficient and recyclable catalysts

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Abstract

A series of Task specific novel COOH-functionalized benzimidazolium-based ionic liquids (CFBILs), N-alkyl-N'-carboxyethyl benzimidazolium bromide ([N-Cn, N'-$CH_2CH_2CO_2H$-Bim] Br, n=2,3,4,6,8), was successfully synthesized and characterized by FT-IR, NMR and HR-MS. All these Task-specific benzimidazolium based ionic liquids was synthesized by simple neutralization process at moderate condition possessing Bronsted acid site i.e. COOH. A series of benzimidazolium based ionic liquids with varying alkyl chain on nitrogen terminal showing the different thermal stability. When the alkyl chain on the benzimidazolium cation were longer like octyl, decomposing temperature and solubility in aqueous solvent goes on decreasing compare to lower alkyl chains like ethyl, propyl, butyl, hexyl. From the literature it reveal that all the these Carboxyl functionalized ionic liquids can be useful for variety of applications like organic transformation, tribological performance, photocatalytic application, solubilizing and extraction of lanthanide and actinides metals, electrochemistry for sensing ATP and enzyme immobilization, selective separation of proteins, micelle formation etc.

Keywords: Synthesis, Functionalized, Benzimidazolium, Ionic liquids, Efficient, Recyclable catalysts.

Introduction

From the last three to four decades Ionic Liquids (ILs) have expanded as an environmental friendly substitute solvents to be used for catalysis, organic synthesis, electrochemistry applications and separations of many inorganic and organic compounds. ILs have unique character i.e. nonexplosive, nonvolatile, thermally robust, simple to handle and recyclable. Hence, ILs are look upon as a “green solvents.” Some of them also called “designer solvents” as they can manipulate by varying the cation/anion for required chemical and physical properties. Therefore, the covalent binding of a functional group either it may on cation or anion of ILs can permit the outcome salt with an ability to interact with dissolved substrate in definite ways. Moreover these ILs have found that magnifying applications such as synthesis, separations, catalysis, and electrochemistry etc.[1,2] hence these titled as Task-Specific Ionic Liquids (TSILs).

Due to the remarkable features like miniature vapor pressure, easy to handle, thermal stability and several others; ILs are attracted increasing awareness. Many of the ionic liquids applied in organic synthesis as catalysts or solvents[3]. In the last few decades, many researchers have focused on the syntheses as well as catalytic application of TSILs[4] such as containing hydroxyl[5], amino[6], carboxyl[7] and many others[8]. However, the physicochemical properties of these TSILs were not examined systematically, due to which limit to specific applications.

In our previous work, we focused on the synthesis of numerous number of Bronsted acidic ionic liquids with varying anions and successful application for few organic transformations, such as esterfication, Beckmann rearrangement, oxidation, amidoalkyl napthol, and tribological performance[3,9-11]. Here we have described the synthesis and characterization of TSILs i.e. Carboxyl Functionalized Benzimidazolium based Ionic Liquids CFBILs. These all CFBILs are characterized with ^{1}H-NMR, ^{13}C-NMR, Mass Spectrometry and Fourier Transform Infrared Spectroscopy (FTIR).

Materials and methods

Benzimidazole was procured from Sigma Aldrich (India). Sodium hydride (60%), 1-Bromoethane, 1-Bromopropane, 1-Bromobutane, 1-Bromohexane, 1-Bromooctane, Tetrahydrofuran (specially dried) and toluene (special dried) were purchased from Merck & Co. 1-bromopropionic acid, diethyl ether, ethyl acetate, $CHCl_3$ and sodium sulphate (anhydrous) were obtained from SD Fine Chemicals, Mumbai, India. Monochloroacetic acid and TLC plate Silica gel GF-254 were procured from Merck & Co. All the reagents and solvents were used as received unless it is specified.

Characterization techniques: ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6, $CDCl_3$ on a Bruker Spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from Tetramethyl silane (δ= 0.00 ppm). HR-MS were analyzed on a JEOL GC MATE II HRMS (EI) and ESI-MS spectrometer while FT-IR spectra were from IR affinity-1 Shimadzu FT_IR spectrophotometer using KBr pellets.

General Procedures for the Synthesis of CFBILs: The carboxyl functionalized benzimidazolium Ionic Liquids (CFBILs) were synthesized in two step (Scheme-1). Initially in the first step benzimidazole treated with 1-Bromoalkane and followed by the reaction of N-alkylated benzimidazole with 1-bromo propionic acid.

Preaparation of alkyl Benzimidazole (2): Benzimidazole (0.1 mol) solution in Tetrahydrofuran (50 mL) was added drop-wise to oil free suspension of Sodium Hydride (0.11 mol) in Tetrahydrofuran (150 mL) and allowed to stir for 2 h at 60ºC. To this reaction mixture 1-Bromoalkane (0.11 mol in 100 mL Tetrahydrofuran) was added drop-wise for 30 min. the reaction mixture was stirred for 48 h at 60ºC until a yellow solution was obtained. Reaction mixture allowed to cool to room temperature, filtered to remove sodium bromide precipitate and Tetrahydrofuran was removed under rotary evaporator to get syrupy liquid to which distilled water was added and extracted with chloroform (3× 100 mL). Organic layer was dried under anhydrous sodium sulphate and $CHCl_3$ was removed under reduced pressure to get yellow 1-alkyl benzimidazole liquid in excellent yield.

Preparation of CFBILs (3): The CFBILs-3 were carried out according to Xiaoquing Wang et al.[12] with slight alteration. Initially alkyl benzimidazole (55 mmol) in 80 mL toluene was stirred for 1 h at 60 ºC. 1-Bromopropionic acid (50 mmol) in toluene was added drop-wise for 30 min to above solution and allowed to stir at 90 ºC for another 14 h. White sticky solid product was obtained which was separated by decantation of toluene directly from the reaction flask. Washed the solid product 3 times with ethyl actetate by (25 mL). followed by with diethyl ether (2× 20 mL). Finally CFBILs-3 were obtained after drying under high vacuum for 3h at 60 ºC. The spectral data of CFBILs are gives as below.

Data: CFBIL-3a (3-(2-carboxyethyl)-1-ethyl-1H-benzo[d] imidazol-3-ium bromide): Yield: 92.01%. FT-IR (KBr/cm^{-1}): 3441, 3147, 3093, 2900, 2684, 1743, 1614, 1568, 1456, 1394, 1336, 1186, 1029, 840, 763, 601. ^{1}H-NMR (400 MHz, DMSO-d$_6$): δ = 12.63 (1H, bs), 9.81 (1H, s), 8.12 (2H, m), 7.70 (2H, m), 4.68 (2H, J = 6.8 Hz, t), 4.52 (2H, J = 7.3 Hz, q), 3.03 (2H, J = 6.8 Hz, t), 1.52 (3H, J = 7.3 Hz, t). ^{13}C-NMR (100 MHz, DMSO-d$_6$): δ = 171.78, 142.39, 131.06, 130.77, 126.55, 126.45, 113.61, 42.50, 42.01, 32.84, 14.20. HR-MS for [$C_{12}H_{15}N_2O_2$][Br], Calculated Mass M-Br (219.1128), found (219.1128).

CFBIL-3b (3-(2-carboxyethyl)-1-propyl-1H-benzo[d]imidazol-3-ium bromide): Yield: 93.21%. FT-IR (KBr, /cm^{-1}): 3440, 3148, 3090, 2907, 2700, 1750, 1610, 1572, 1450, 1396, 1334, 1200, 1030, 843, 761, 608. ^{1}H NMR(400 MHz, DMSO-d$_6$): δ = 12.69 (1H, bs), 9.89 (1H, s), 8.16 (2H, m),7.73 (2H, m), 4.73 (2H, J = 6.7 Hz, t), 4.52 (2H, J = 7.4 Hz, q), 3.05 (2H,J = 6.8 Hz, t), 1.96 (2H, m), 0.95 (3H, J = 7.3 Hz, t). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 171.78, 142.75, 130.97, 126.53, 126.47, 113.84, 113.69, 48.03, 42.59, 32.71, 21.99, 10.59. HRMS for: [$C_{13}H_{17}N_2O_2$][Br], calculated mass M-Br (233.1285), found (233.1285).

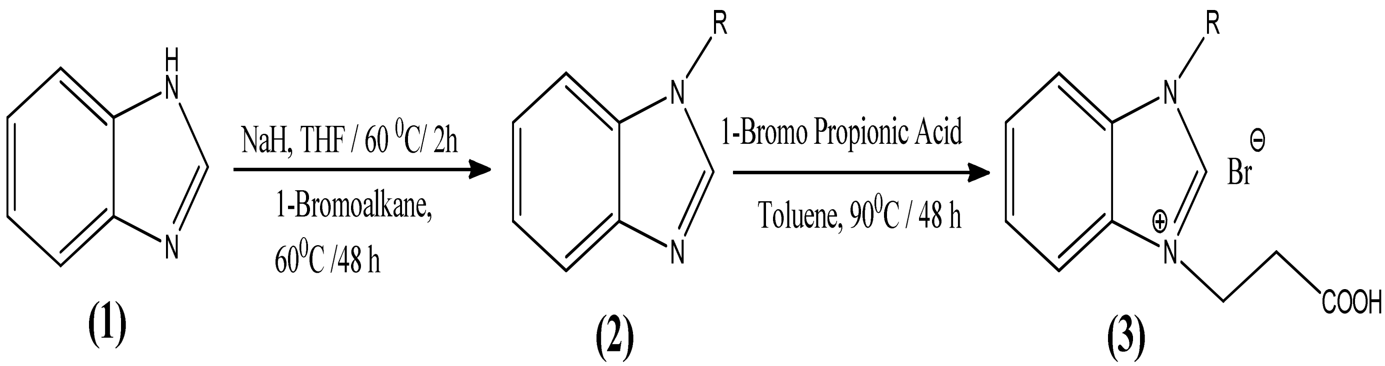
CFBIL-3c (3-(2-carboxyethyl)- 1-butyl-1H-benzo[d]imidazol-3-ium bromide): Yield: 91.93%. FT-IR (KBr, /cm^{-1}): 3444, 3150, 3089, 2898, 2702, 1747, 1612, 1570, 1452, 1395, 1330, 1198, 1036, 844, 762, 607. ^{1}H NMR(400 MHz, DMSO-d$_6$): δ = 12.71 (1H, bs), 9.88 (1H, s), 8.15 (2H, m),7.73 (2H, m), 4.72 (2H, J = 6.8 Hz, t), 4.54 (2H, J = 7.3 Hz, q), 3.04 (2H,J = 6.8 Hz, t), 1.92 (2H, m), 1.37 (2H, m), 0.96 (3H, J = 7.3 Hz, t). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 171.79, 142.71, 130.99, 130.96, 126.54, 126.49, 113.85, 113.68, 46.38, 42.59, 32.72, 30.53, 18.97, 13.37. HRMS for: [$C_{14}H_{19}N_2O_2$][Br], calculated mass M-Br (247.1441), found (247.1440).

CFBIL-3d (3-(2-carboxyethyl)- 1-hexyl-1H-benzo[d]imidazol-3-ium bromide): Yield: 90.92%. FT-IR (KBr, /cm^{-1}): 3440, 3152, 3087, 2899, 2701, 1749, 1616, 1572, 1455, 1399, 1332, 1199, 1038, 840, 764, 608. ^{1}H NMR(400 MHz, $CDCl_3$): δ = 10.34 (1H, s), 7.93 (2H, m),7.68 (2H, m), 4.7 (2H, J = 6.6 Hz, t), 4.55 (2H, J = 7.4 Hz, q), 3.18 (2H,J = 6.8 Hz, t), 1.99 (2H, m), 1.38 (2H, m), 1.27 (4H, m), 0.82 (3H, J = 7.4 Hz, t). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.05, 142.79, 131.42, 131.31, 127.40, 127.13, 113.96, 113.11, 48.03, 43.42, 33.82, 31.26, 29.50, 26.35, 22.51, 14.08. HRMS for: [$C_{16}H_{23}N_2O_2$][Br], calculated mass M-Br (275.1754), found (275.1752).

CFBIL-3e (3-(2-carboxyethyl)- 1-octyl-1H-benzo[d]imidazol-3-ium bromide): Yield: 88.90%. FT-IR (KBr, /cm^{-1}): 3439, 3148, 3092, 2890, 2700, 1746, 1610, 1571, 1453, 1397, 1332, 1199, 1038, 842, 760, 608. ^{1}H NMR(400 MHz, DMSO-d$_6$): δ = 12.73 (1H, bs), 9.92 (1H, s), 8.16 (2H, m),7.73 (2H, m), 4.73 (2H, J = 6.8 Hz, t), 4.53 (2H, J = 7.3 Hz, q), 3.05 (2H,J = 6.8 Hz, t), 1.92 (2H, m), 1.36 (10H, m), 0.87 (3H, J = 7.3 Hz, t). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 171.76, 142.68, 130.97, 130.94, 126.53, 126.47, 113.84, 113.68, 46.61, 42.56, 32.78, 31.14, 28.51, 28.43, 28.37, 25.64, 22.02, 13.92. HRMS for: [$C_{18}H_{27}N_2O_2$][Br], calculated mass M-Br (303.2067), found (303.2066).

Results and discussion

We have prepared several task-specific Carboxyl functionalized benzimidazolium based ionic liquids were synthesized under mild conditions. All TSILs are characterized by ^{1}H-NMR, ^{13}C-NMR, Mass Spectrometry and Fourier Transform Infrared Spectroscopy (FTIR). Form the characterization and fundamental chemistry of TSILs, we can observed that as number of carbon atom on N-benzimidazole increases, the hydrophilic nature of TSILs goes on increasing and water solubility goes on decreasing. Hence higher hexyl and octyl substituted carboxyl functionalized benzimidazolium TSILs can be useful for extraction and separation heavy metal ion, proteins, and micelle formation.



R = C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_8H_{17}

Scheme-1 Synthesis of carboxyl-functionalized benzimidazolium based ionic liquid catalyst (CFBILs).

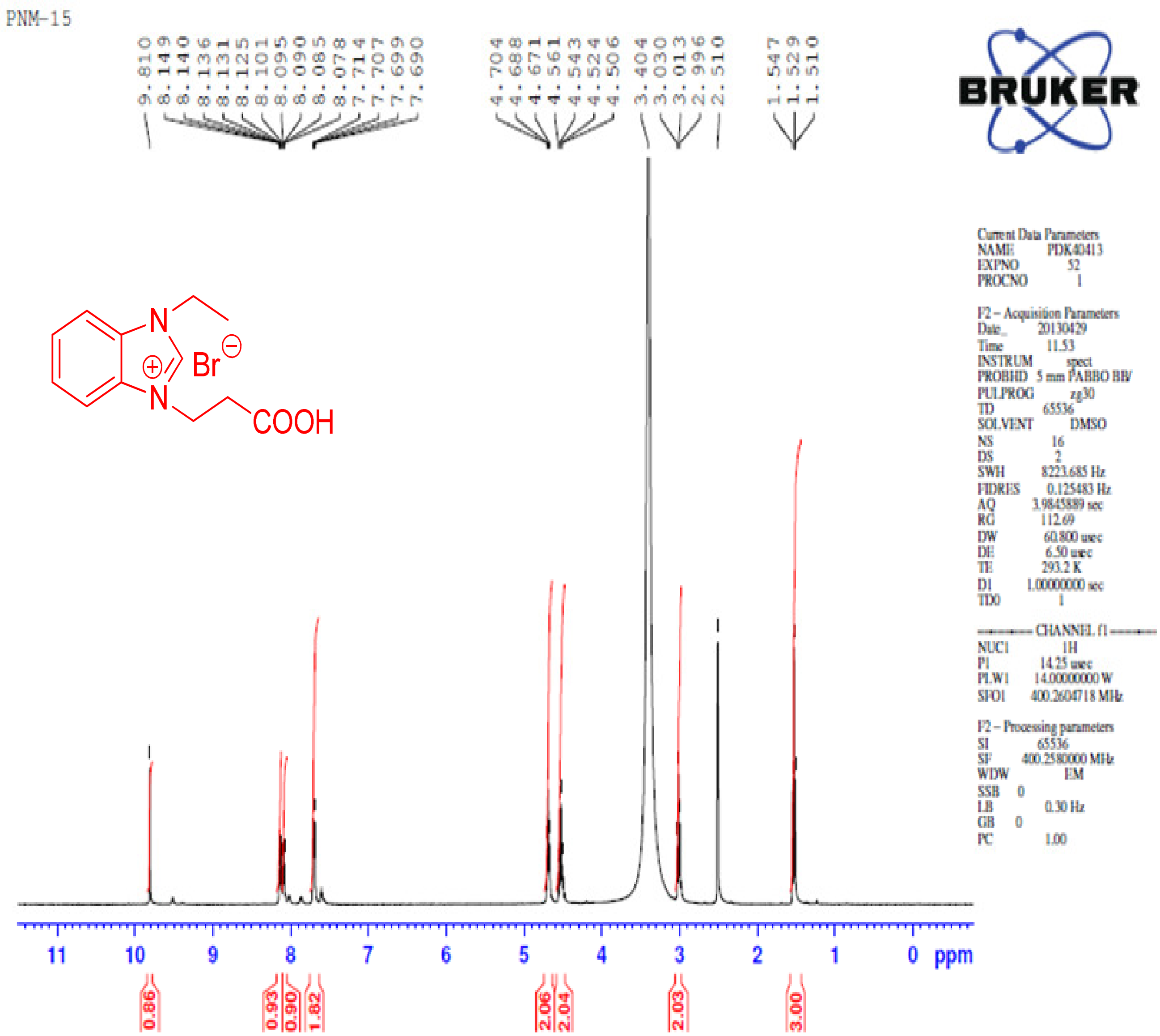


Figure-1: ^{1}H-NMR of CFBIL-3a (3-(2-carboxyethyl)-1-ethyl-1H-benzo[d]imidazol-3-ium bromide)

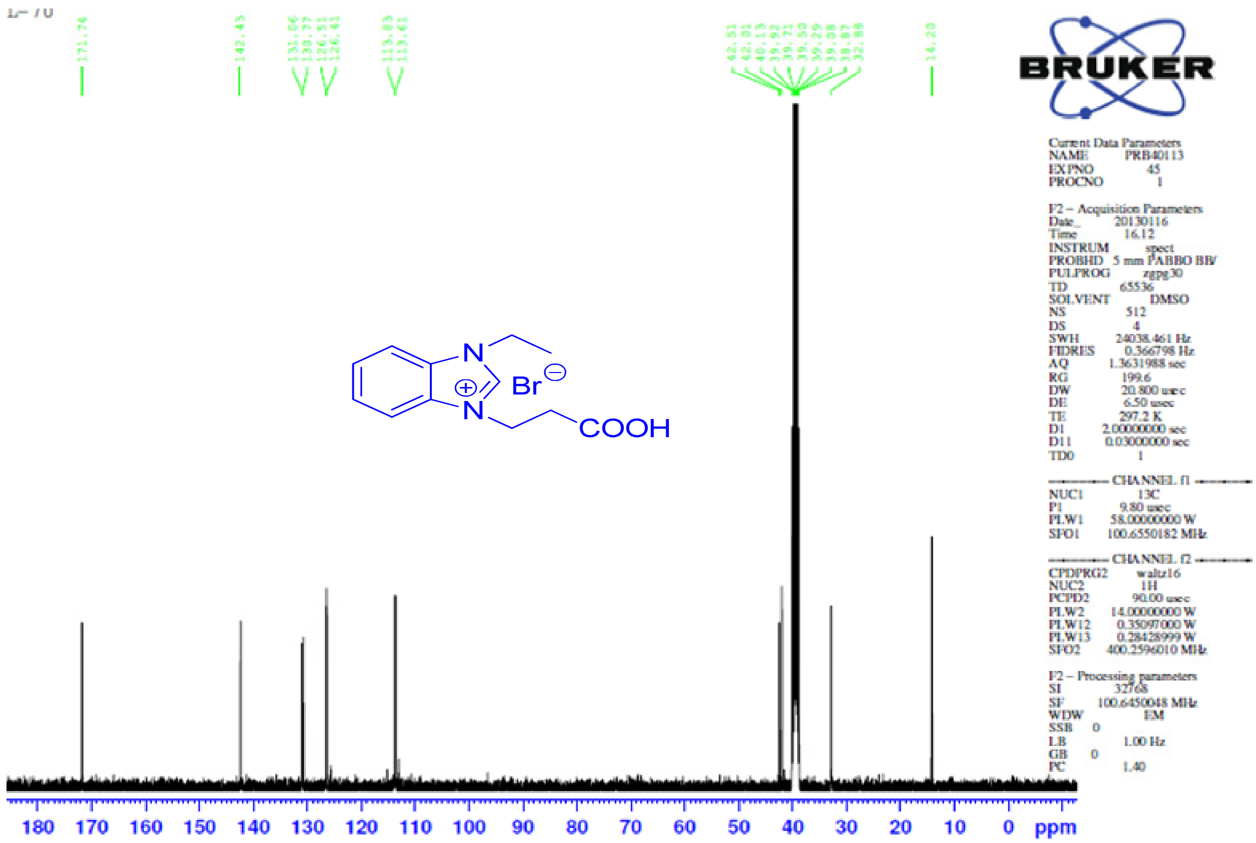


Figure-2: ^{13}C-NMR of CFBIL-3a (3-(2-carboxyethyl)-1-ethyl-1H-benzo[d]imidazol-3-ium bromide)

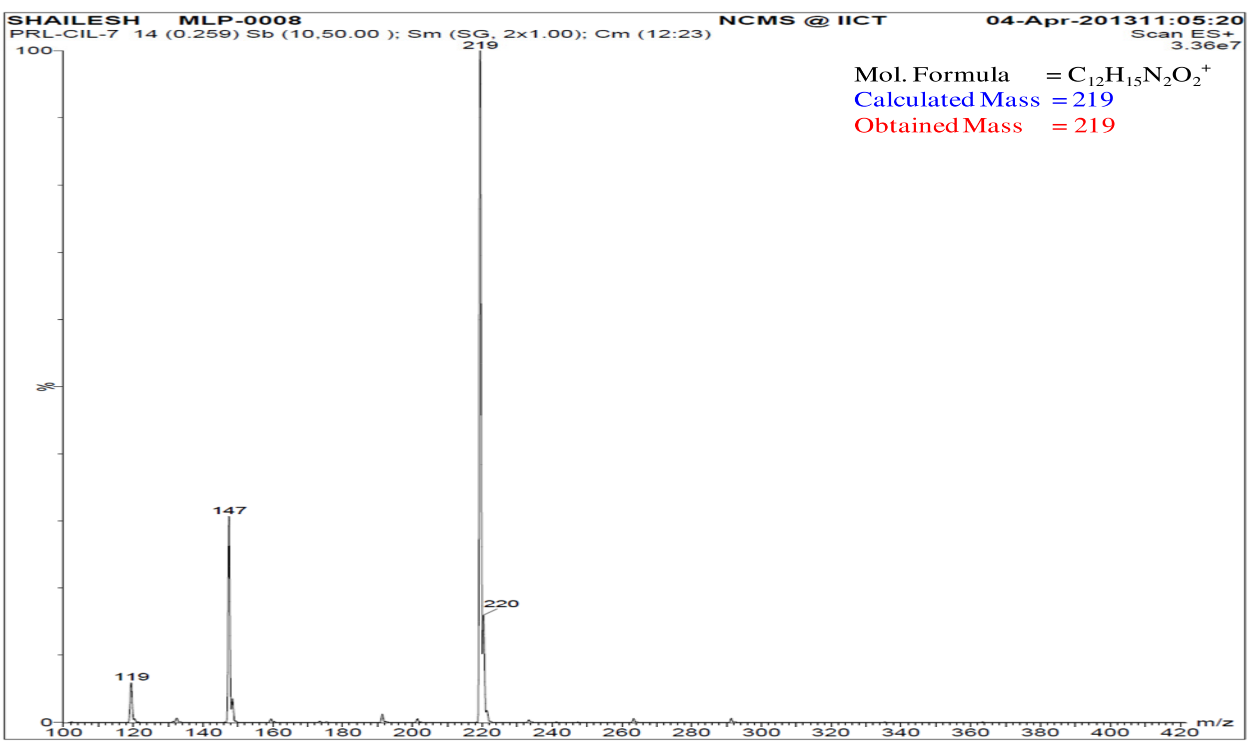


Figure-3: ESI-MS of CFBIL-3a (3-(2-carboxyethyl)-1-ethyl-1H-benzo[d]imidazol-3-ium bromide)

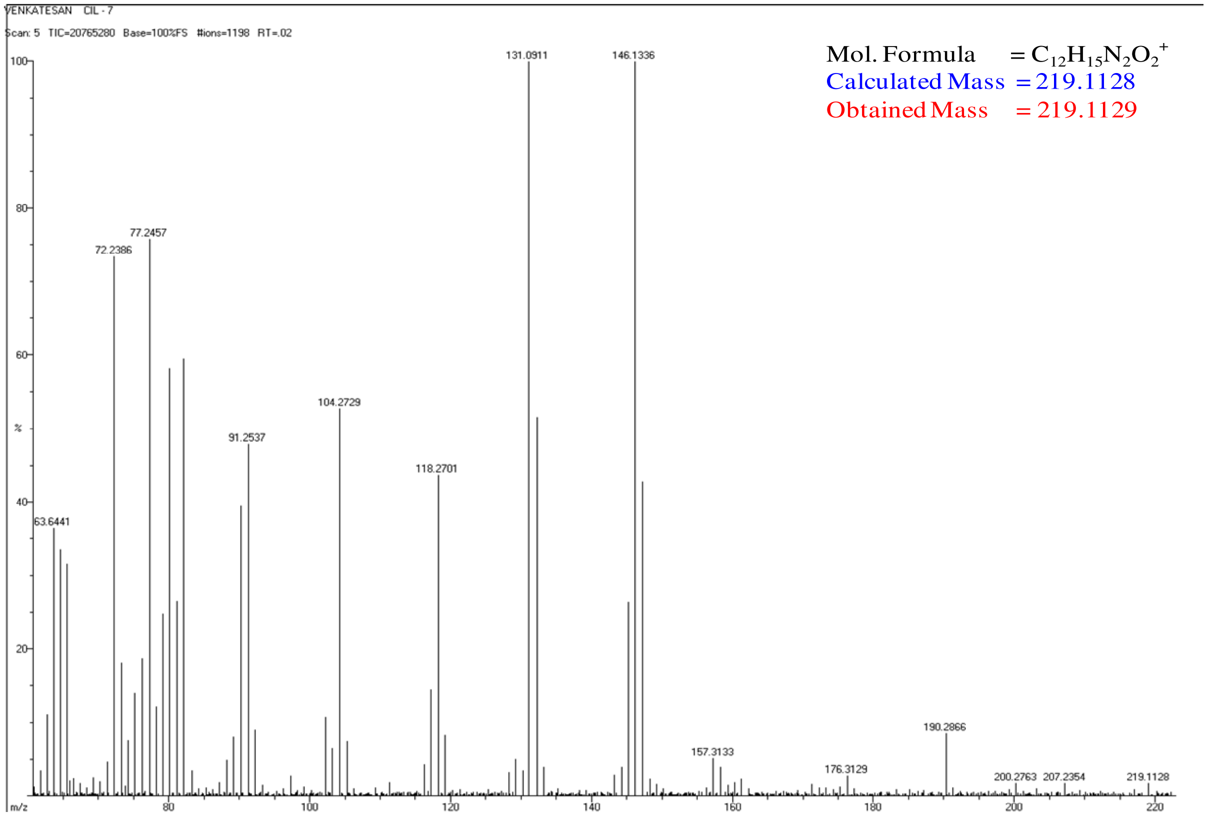


Figure-4: HR-MS of CFBIL-3a (3-(2-carboxyethyl)-1-ethyl-1H-benzo[d]imidazol-3-ium bromide)

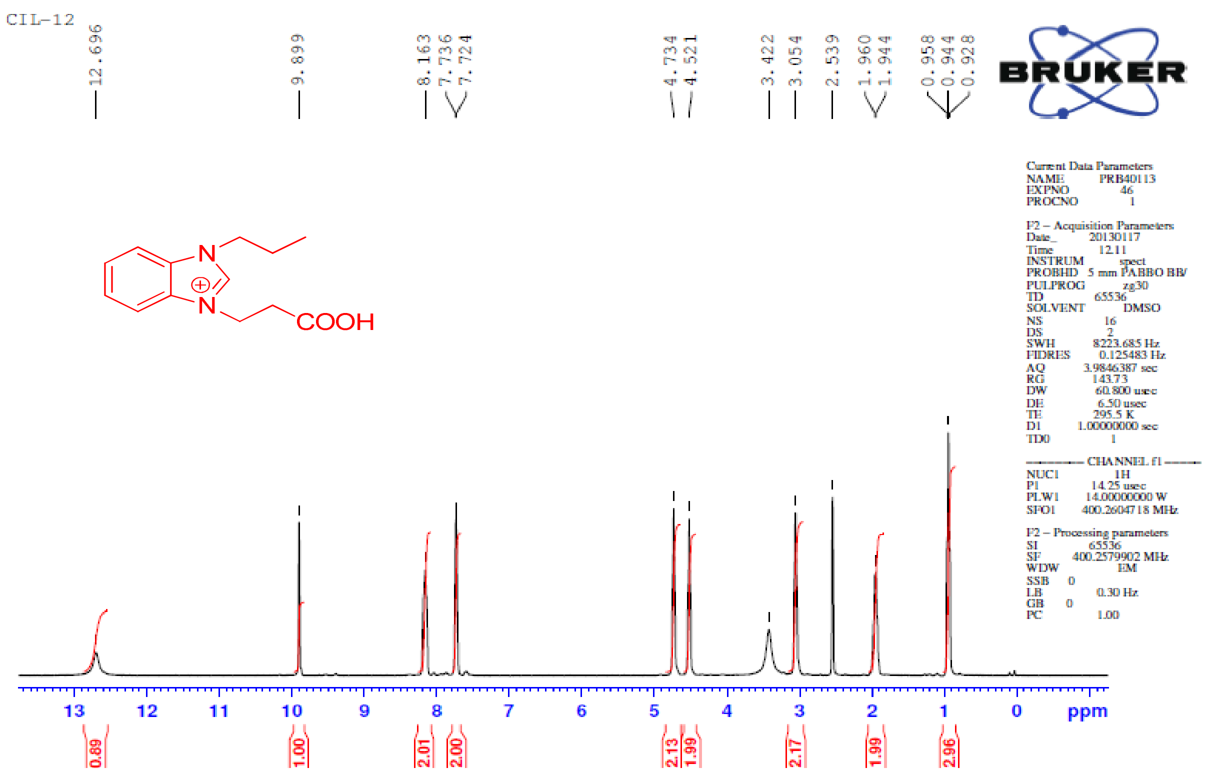


Figure-5: ^{1}H-NMR of CFBIL-3b (3-(2-carboxyethyl)-1-propyl-1H-benzo[d]imidazol-3-ium bromide)

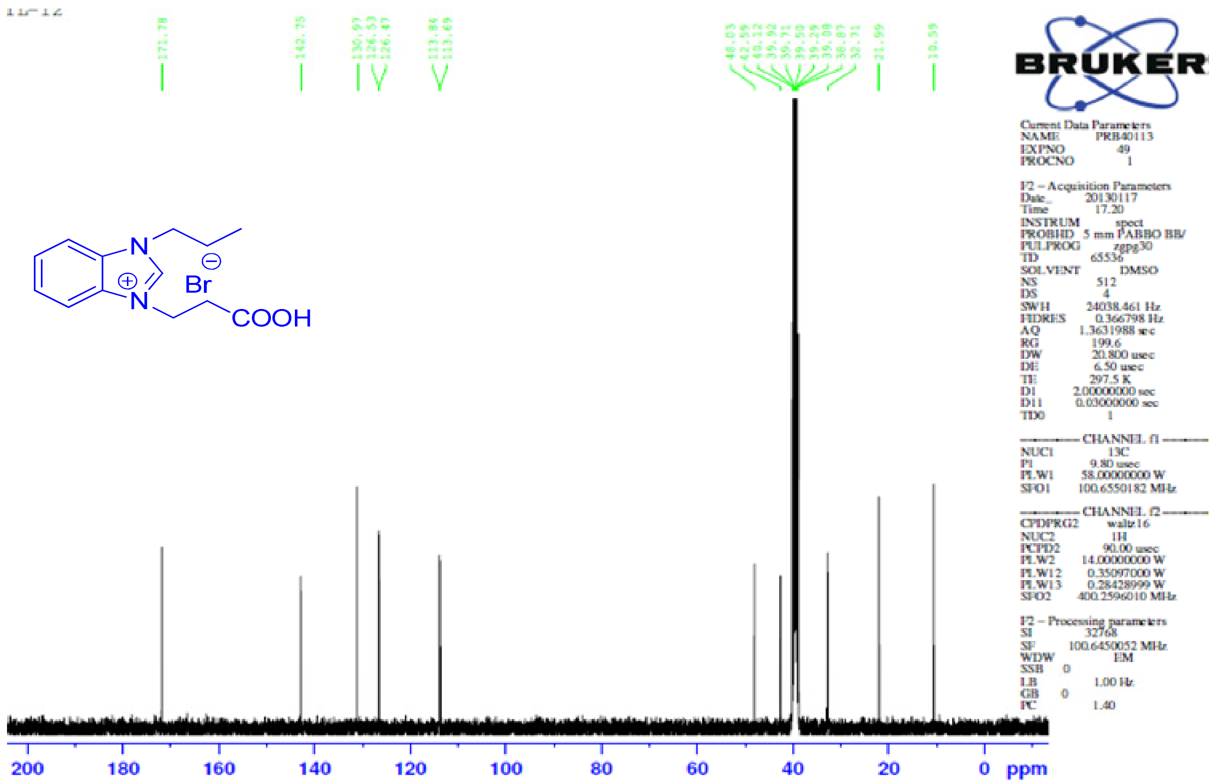


Figure-6: ^{13}C-NMR of CFBIL-3b (3-(2-carboxyethyl)-1-propyl-1H-benzo[d]imidazol-3-ium bromide)

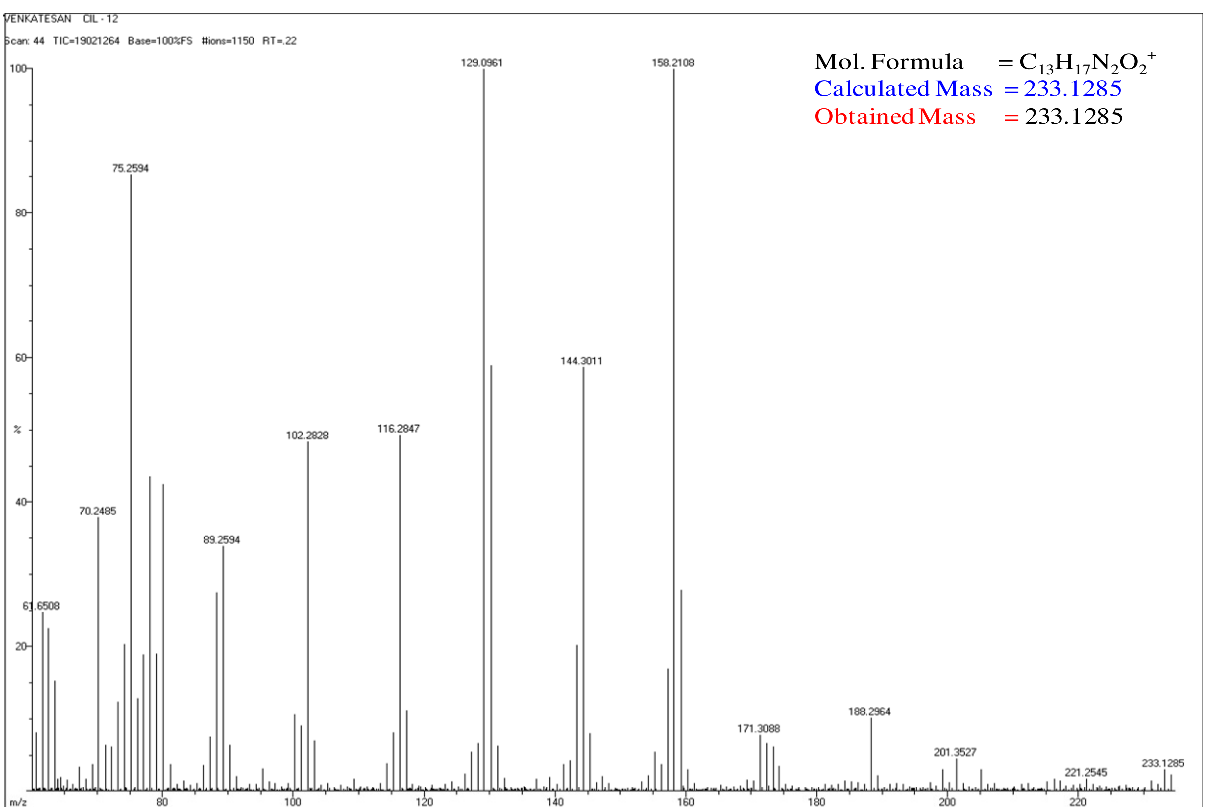


Figure-7: HR-MS CFBIL-3b (3-(2-carboxyethyl)-1-propyl-1H-benzo[d]imidazol-3-ium bromide)

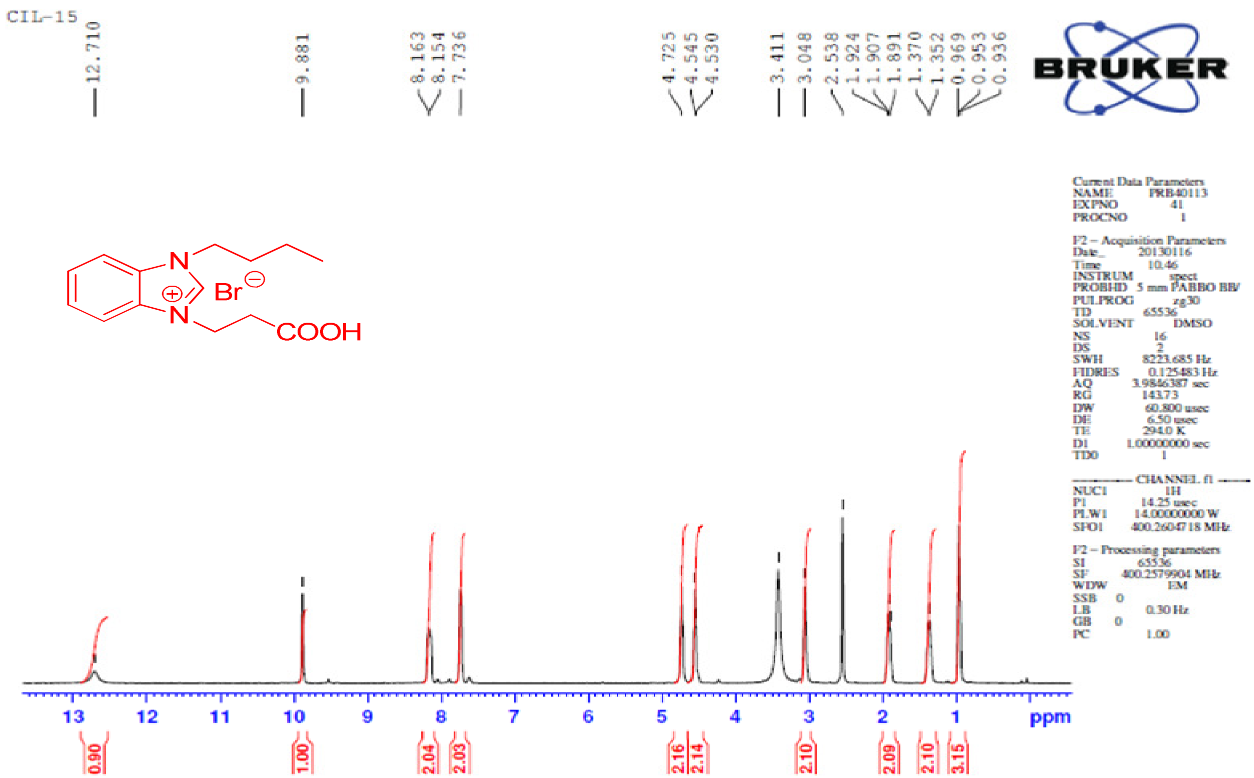


Figure-8: [1]H-NMR of CFBIL-3c (3-(2-carboxyethyl)- 1-butyl-1H-benzo[d]imidazol-3-ium bromide)

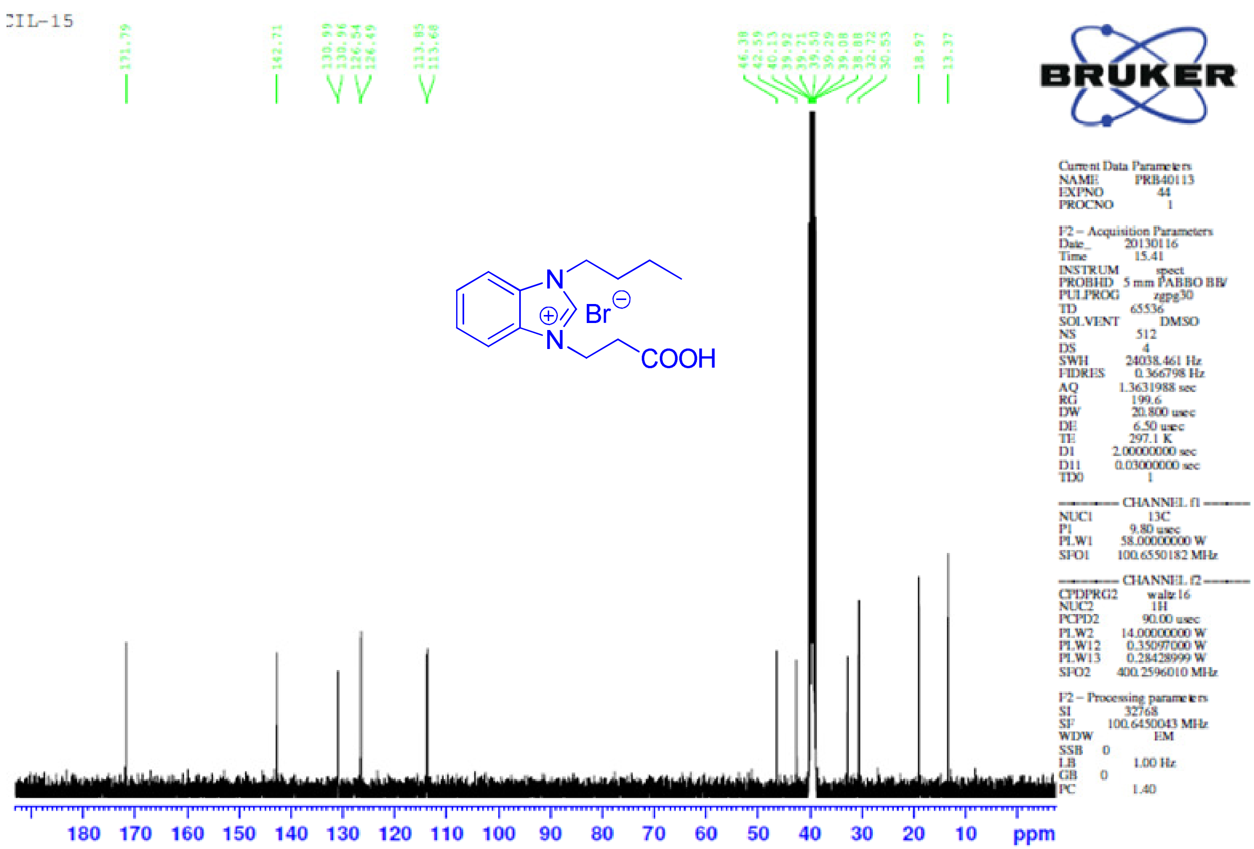


Figure-9: [13]C-NMR of CFBIL-3c (3-(2-carboxyethyl)- 1-butyl-1H-benzo[d]imidazol-3-ium bromide)

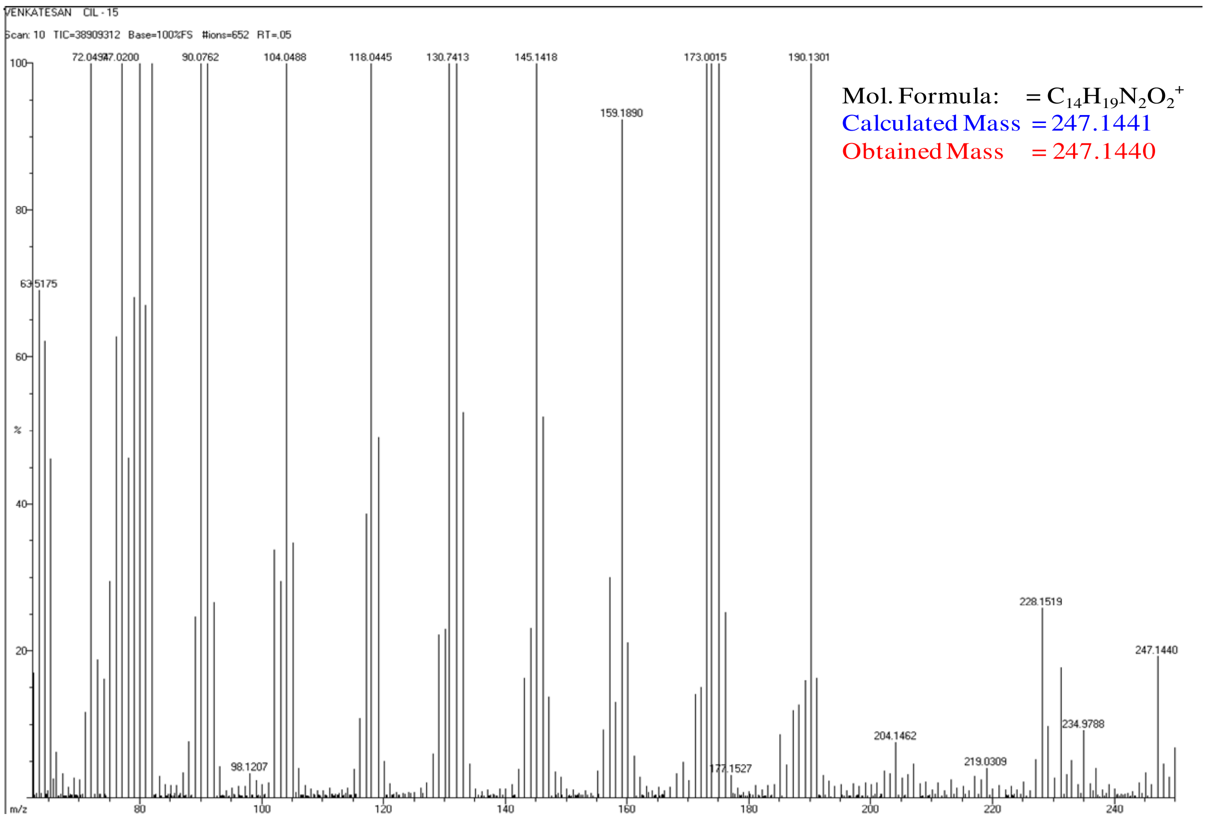


Figure-10: HR-MS of CFBIL-3c (3-(2-carboxyethyl)- 1-butyl-1H-benzo[d]imidazol-3-ium bromide)

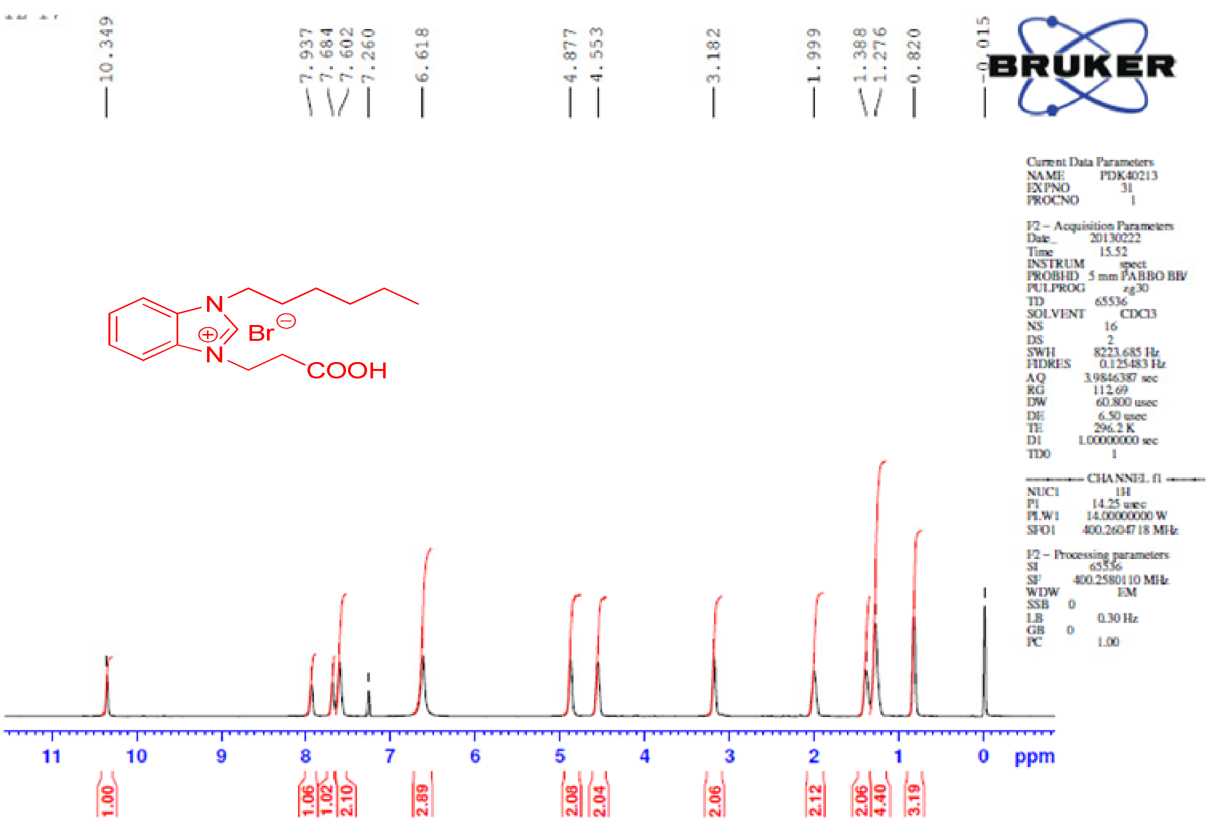


Figure-11: [1]H-NMR of CFBIL-3d (3-(2-carboxyethyl)- 1-hexyl-1H-benzo[d]imidazol-3-ium bromide)

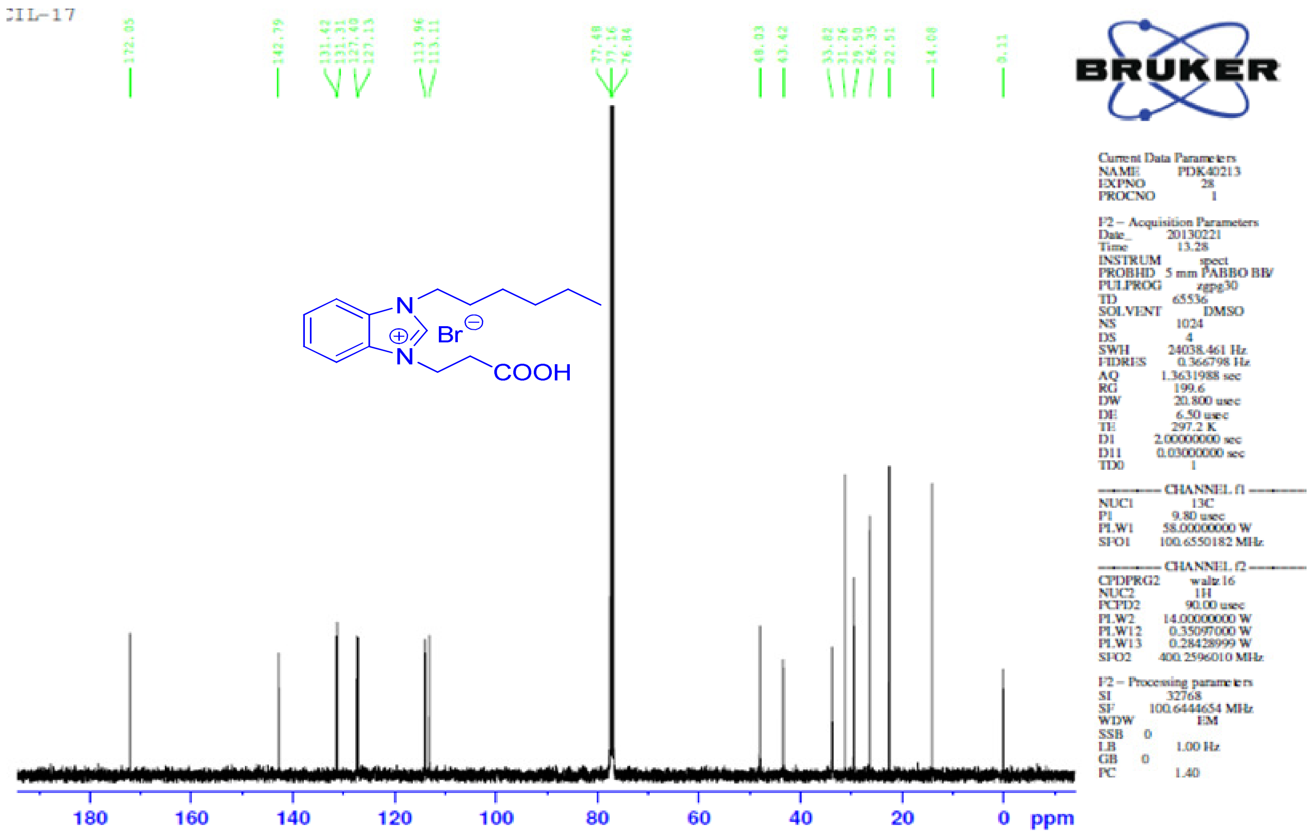


Figure-12: ^{13}C-NMR of CFBIL-3d (3-(2-carboxyethyl)- 1-hexyl-1H-benzo[d]imidazol-3-ium bromide)

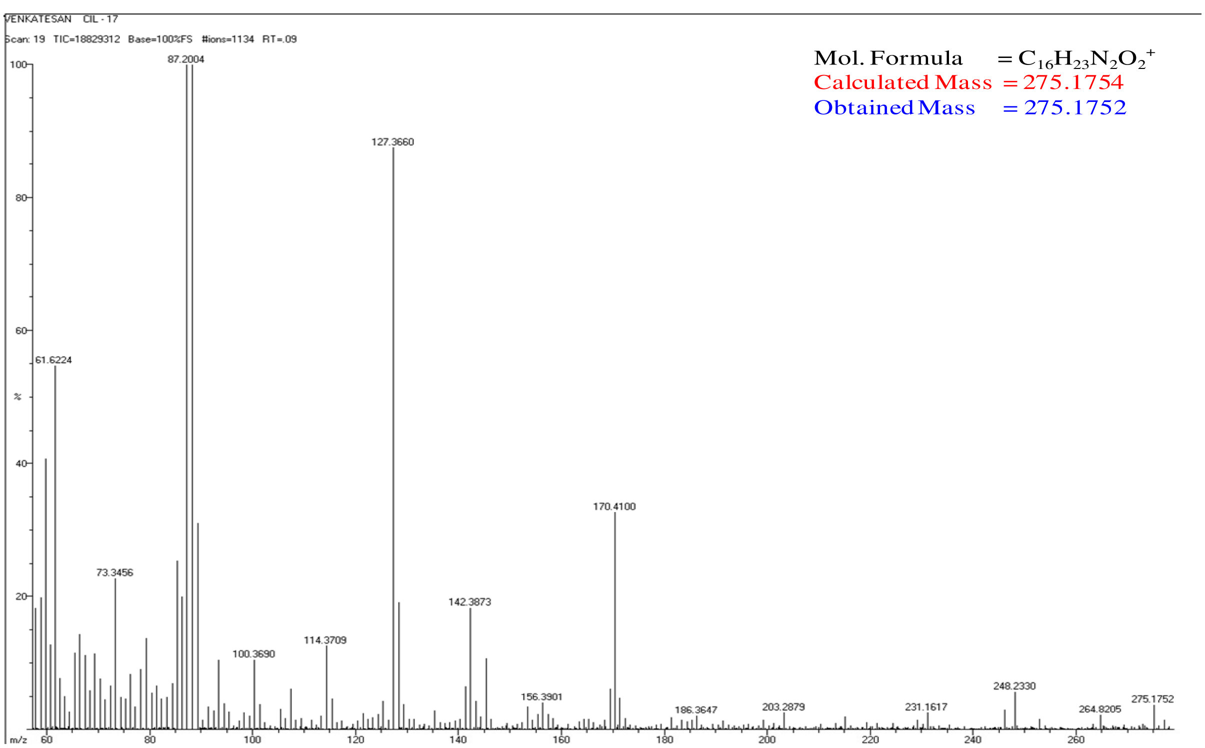


Figure-13: HR-MS of CFBIL-3d (3-(2-carboxyethyl)- 1-hexyl-1H-benzo[d]imidazol-3-ium bromide)

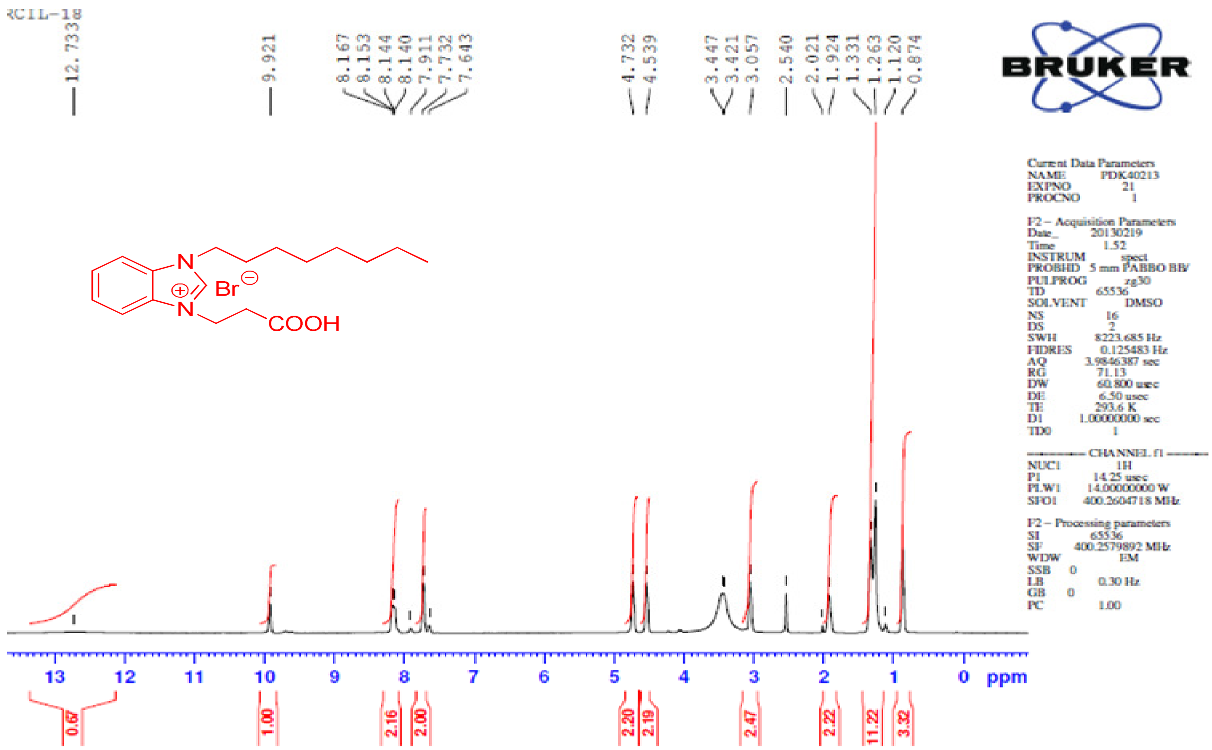


Figure-14: ^{1}H-NMR of CFBIL-3e (3-(2-carboxyethyl)- 1-octyl-1H-benzo[d]imidazol-3-ium bromide)

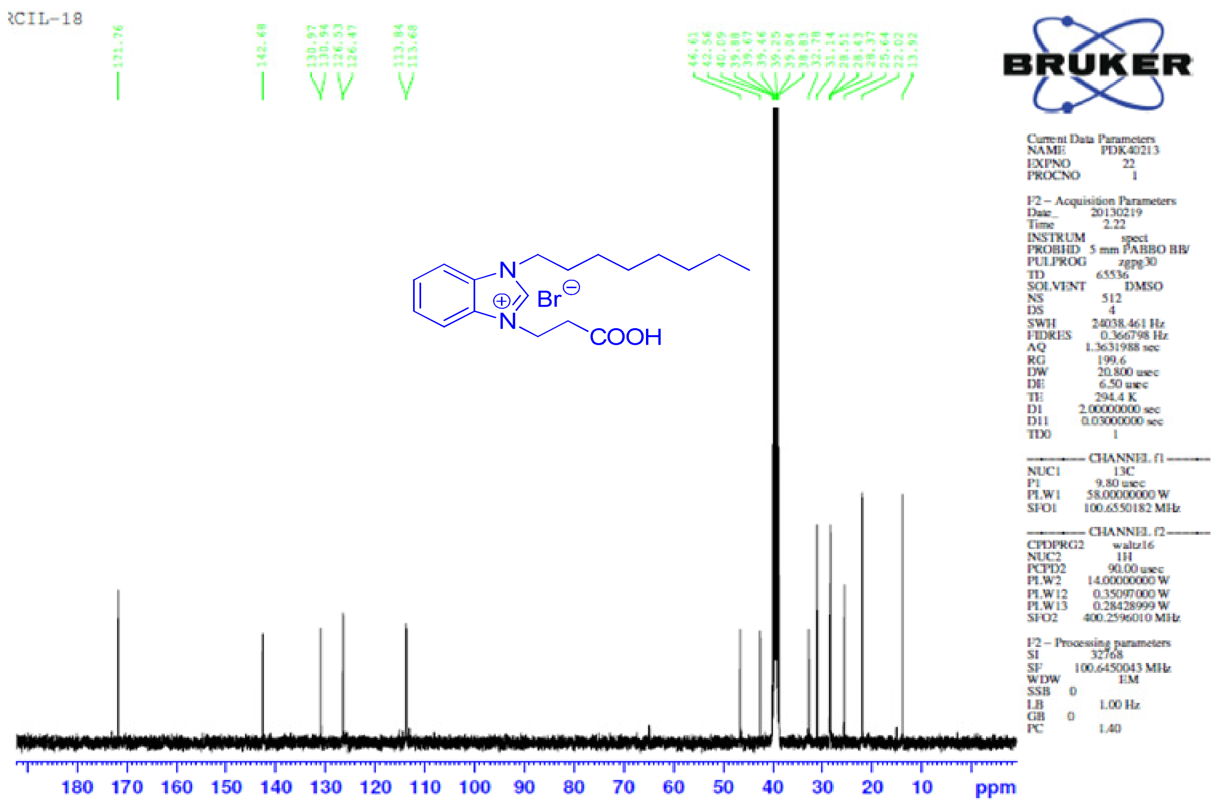


Figure-15: ^{13}C-NMR of CFBIL-3e (3-(2-carboxyethyl)- 1-octyl-1H-benzo[d]imidazol-3-ium bromide)

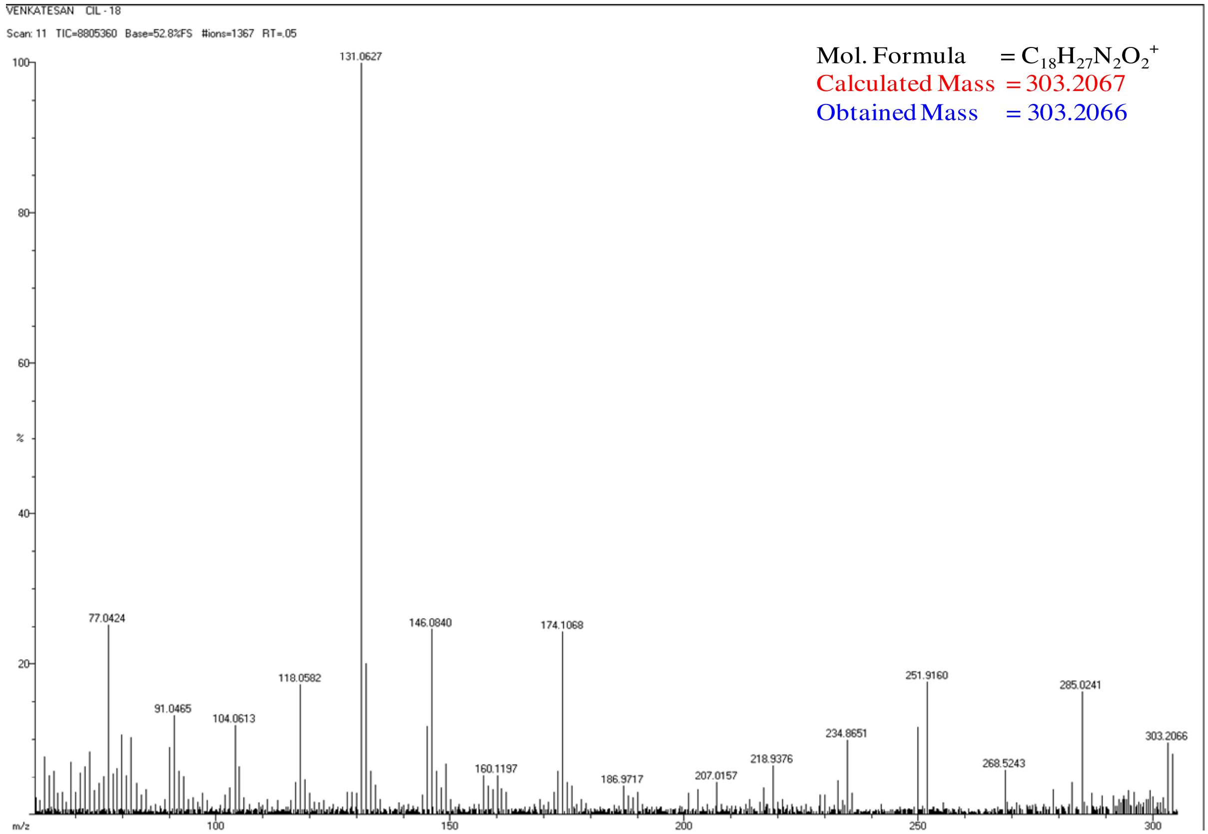


Figure-16: HR-MS of CFBIL-3e (3-(2-carboxyethyl)- 1-octyl-1H-benzo[d]imidazol-3-ium bromide)

Conclusion

Several task-specific Carboxyl functionalized benzimidazolium based ionic liquids were synthesized under mild conditions. These CFBILs can be useful for variety of applications like organic transformation, tribological performance, photocatalytic application, solubilizing and extraction of lanthanide and actinides metals, electrochemistry for sensing ATP and enzyme immobilization, selective separation of proteins, micelle formation etc. Several examinations and possible applications of these TSILs for organic transformations and their acidity-catalytic activity-structure relationships are under exploration in our laboratory.

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References

1. Xue H., Verma R. and Shreeve J.M. (2006). Review of ionic liquids with fluorine containing anions. *J. Fluorine Chem.*, 127, 159–176; (b) Wasserscheid, P., & Welton, T. (2002). Ionic Liquid in Synthesis. Wiley-VCH & CoKGaA: Germany.
2. Buzzeo M.C., Hardacre C. and Compton R.G. (2004). Use of room temperature ionic liquids in gas sensor design. *Anal. Chem.*, 76, 4583–4588.
3. Muskawar P.N., Kumar S.S. Bhagat P.R. (2013). Carboxyl-functionalized ionic liquids based on Benzimidazolium cation: Study of Hammett values and catalytic activity towards one-pot synthesis of 1-amidoalkyl naphthols. *J. Mol. Catal. A: Chem.*, 380, 112–117.
4. Davis Jr. J.H. (2004). Task-Specific Ionic Liquids. *Chem. Lett.*, 33, 1072.
5. Miao W. and Chan T.H. (2003). Exploration of ionic liquids as soluble supports for organic synthesis demonstration with a Suzuki coupling reaction. *Org. Lett.*, 5, 5003.
6. Bates E.D., Mayton R.D., Ntai I. and Davis J.H. (2002). CO2 capture by a task-specific ionic liquid. *J. Am. Chem. Soc.*, 124, 926-929.
7. Li D.M., Shi F., Peng J.J., Guo S. and Deng Y.Q. (2004). Application of functional ionic liquids possessing two adjacent acid sites for acetalization of aldehydes. *J. Org. Chem.,* 69, 3582-3584.

8. Davis Jr. J.H., Forrester K.J.T. and Merrigan J. (1998). Novel organic ionic liquids (OILs) incorporating cations derived from the antifungal drug miconazole. *Tetrahedron Lett.,* 49, 8955-8958.

9. Karthikeyan P., Muskawar P.N., Bhagat P.R. and Senthil Kumar S. (2012). A novel CuCl2/BIL catalyst for direct oxidation of alcohol to acid at ambient temperature. *Cat. Commun*., 26, 189–193.

10. Karthikeyan P., Aswar S.A., Muskawar P.N., Bhagat P.R. and Sythana S.K. (2012). Development of an efficient solvent free one-pot Heck reaction catalyzed by novel palladium (II) complex-via green approach. *J. Mol. Cat. A: Chem.*, 358, 112–120.

11. Karthikeyan P., Aswar S.A., Muskawar P.N., Bhagat P.R., Senthil Kumar S. and Sythana S.K. (2012). Selective oxidation of alcohol to carbonyl compound catalyzed by l-aspartic acid coupled imidazolium based ionic liquid. *J. Mol. Liq.* 173, 180–183.

12. Wang X., Li Yu, Jiao J., Zhang H., Wang R. and Chen H. (2012). Aggregation behavior of COOH-functionalized imidazolium-based surface active ionic liquids in aqueous solution. *J. Mol. Liq*., 173, 103–107.