



Synthetic Communications An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: https://www.tandfonline.com/loi/lsyc20

Synthesis and characterization of novel chiral imidazolium and pyridinium ionic liquids derived from tartaric acid and 2-oxazolidinone

Sagar P. Nehate, Himanshu M. Godbole, Girij P. Singh, Jessy E. Mathew & Gautham G. Shenoy

To cite this article: Sagar P. Nehate, Himanshu M. Godbole, Girij P. Singh, Jessy E. Mathew & Gautham G. Shenoy (2019): Synthesis and characterization of novel chiral imidazolium and pyridinium ionic liquids derived from tartaric acid and 2-oxazolidinone, Synthetic Communications, DOI: 10.1080/00397911.2019.1591455

To link to this article: https://doi.org/10.1080/00397911.2019.1591455



View supplementary material 🕝

4	1	1	1
E			H

Published online: 02 Apr 2019.



Submit your article to this journal



View Crossmark data 🗹



Check for updates

Synthesis and characterization of novel chiral imidazolium and pyridinium ionic liquids derived from tartaric acid and 2-oxazolidinone

Sagar P. Nehate^a, Himanshu M. Godbole^a, Girij P. Singh^a, Jessy E. Mathew^b, and Gautham G. Shenoy^b

^aChemical Research and Development, Lupin Limited, Pune, MH, India;^bDepartment of Chemistry, Manipal Academy of Higher Education, Manipal, KA, India

ABSTRACT

Novel chiral imidazolium and pyridinium ionic liquids based on tartaric acid and 2-oxazolidinone were designed. Symmetrical dicationic ionic liquids based on tartaric acid have been synthesized and characterized. These chiral ionic liquids were designed by employing very short and simple methods. Incorporation of alkyl halide over tartaric acid and 2-oxazolidinone is an important step. N-methyl imidazole and pyridine were used for preparation of quaternary salts. These ionic liquids have been evaluated for the asymmetric sulfide oxidation. Chiral ionic liquids based on tartaric acid showed superior chiral inducing property as compare to 2-oxazolidinone based chiral ionic liquids.

GRAPHICAL ABSTRACT



 $\mathbf{R} = N$ -methyl imidazolium $\mathbf{R} = Pyridinium$



 $\mathbf{R} = i$ -Pr, Ph, Bz $\mathbf{R}_1 = N$ -methyl imidazolium/Pyridinium

ARTICLE HISTORY Received 20 December 2018

KEY WORDS

Chiral ionic liquids; tartaric acid; imidazolium; pyridinium; 2-oxazolidinone

Introduction

Ionic liquids (ILs) have been described as molten salts that are entirely ionic in nature having a melting point below $100 \,^{\circ}C.^{[1]}$ Ionic liquids that are liquid at room temperature are referred as room temperature ionic liquids (RTILs).^[2] RTILs are thermally stable up to $300 \,^{\circ}C$. Generally ionic liquids have a large organic cation and an organic or inorganic anion. Ionic liquids have a unique physicochemical property as compared to the conventional organic solvents. The cations and anions in the ionic liquids made a

B Supplemental data for this article is available online at on the publisher's website.

CONTACT Sagar P. Nehate 🖾 sagarnehate@lupin.com 🗈 Lupin Limited, 46 and 47A, Nande Village, Mulshi Taluka, Pune 412115, India.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lsyc.

^{© 2019} Taylor & Francis Group, LLC



Figure 1. Starting materials.

large impact on their physical properties. Properties of ionic liquids can be altered by modifying the structure of the cations or anions of ionic liquids in order to influence the outcomes of reactions. Hydrogen bonding, charge distribution on the anions, polarity, and dispersive interactions also influence the physical properties of ionic liquids. Miscibility of ionic liquids with water depends on the nature of the anion. At room temperature, ionic liquids having $[PF_6]^-$ and $[Tf_2N]^-$ anions are insoluble in water while ionic liquids with nitrate, acetate, halides, etc are fully miscible with water. Chiral ionic liquids are useful for the stereoselective polymerization, as a chiral stationary phase in chromatography and chiral shift reagent in NMR spectroscopy.^[3] Chiral ionic liquids showed chiral introducing property in many reactions.^[4] Various types of asymmetric reactions have been reported using chiral ionic liquids as a catalyst or reaction media like aldol reaction,^[5] Baylis-Hillmann reaction,^[6] Diels Alder reaction,^[7] Michael addition,^[8] hydrogenation,^[9] and asymmetric alkylation.^[10] Chiral ionic liquids can be recycled many times without affecting the reactivity.^[5] Ionic liquids can be useful as electrolytes for batteries, nuclear fuel reprocessing, solar thermal energy, and waste recycling. ^[11] In view of the emerging importance of the ionic liquids as a chiral catalyst or reaction media in organic synthesis, we designed and synthesized a novel imidazolium as well as pyridinium ionic liquid from D-tartaric acid and 2-oxazolidinone (Fig. 1).

Derivatives of tartaric acid and oxazolidine were reported as chiral axillaries.^[12] Kagan and group reported the metal-catalyzed asymmetric sulfide oxidation using diethyl tartrate in 1984.^[13] Similar oxidation method was reported by Modena in 1984.^[14] Both asymmetric oxidation methods reported by Kagan and Modena were based on the Sharpless asymmetric epoxidation.^[15] Therefore, we designed ionic liquids structurally similar to diethyl tartrate. We have synthesized symmetrical di-cationic ionic liquids from D-tartaric acid. Recently, we have published the synthesis of novel chiral ionic liquids derived from 2-oxazolidinone.^[16] In continuation with this, herein, we report the synthesis of novel chiral ionic liquids through N-acylation of 2-oxazolidinone.

Results and discussion

Symmetrical di-cationic imidazolium and pyridinium ionic liquids 4 and 5 were prepared from D-tartaric acid 1. D-tartaric acid reacted with an excess amount of 2-chloroethanol in presence of catalytic para-toluene sulfonic acid to afford Bis (chloroethyl)-D-tartrate 3. Compound 3 is a low melting, off-white color solid. After quaternization reaction of 3 with N-methyl imidazole and pyridine gives imidazolium 4 and pyridinium 5 ionic liquid as pale-yellow color oil. Higher temperature (90–100 °C) is



Reagent and reaction condition: i) 2-chloroethanol, pTSA, toluene, reflux, 6-8 h ii) N-methyl imidazole or pyridine, 90-100°C, 48h

Scheme 1. Preparation of symmetrical di-cationic ionic liquids.



Reagents and reaction condition: i) chloro acetyl chloride, THF, NaH, 0-10°, 2-3h, ii) N-methyl inidazole, acetonitrile, 50-50°, 5-6h iii) Water, potassium hexafluorophosphate, 1h

Scheme 2. Preparation of imidazolium ionic liquids from 2-oxazolidinone.

required for completion of quaternization reaction (Scheme 1). Presence of hydroxyl and ester functional groups is the major difference between these ionic liquids and earlier reported ionic liquids from tartaric acid.^[17]

Furthermore, we synthesized some imidazolium and pyridinium ionic liquids supported on 2-oxazolidinone **2**. In this case, **2** reacted with 2-chloro acetyl chloride in tetrahydrofuran and sodium hydride as a base to afford **6a–c**. Then **7a–c** were prepared by quaternization reaction of **6a–c** with N-methyl imidazole at 50–60 °C (Scheme 2).

Intermediates 7a-c are the solid compounds, therefore, the melting point of these ionic liquids was recorded. Intermediate ionic liquids 7a-c have melting point more than 100 °C. Therefore, these solid intermediate ionic liquids were subjected to anion exchange reaction with potassium hexafluorophosphate. The new imidazolium ionic liquids bearing hexafluorophosphate anion 8a-c have melting points below 100 °C.

Similarly, **6a–c** was reacted with pyridine to afford intermediate ionic salts which were directly subjected to anion exchange to form ionic pyridinium liquids bearing hexafluorophosphate anion 9a-c (Scheme 3).

Similar to imidazolium ionic liquids, these pyridinium ionic liquids derived from 2-oxazolidinone are also low melting solids except **9b** (m.p. = 110-114 °C) and hydrophobic. Ionic liquids having hexafluorophosphate anion are soluble in acetone, dichloromethane, and dimethyl sulfoxide while insoluble in water and alcohols.

4 🕳 S. P. NEHATE ET AL.



Scheme 3. Preparation of pyridinium ionic liquids from 2-oxazolidinone.



Reagents and reaction condition: DCM, $Ti(O^{i}Pr)_{4}$, Water, Tert butyl hydroperoxide **Scheme 4.** Oxidation of sulfide to sulfoxide using ionic liquids.

Chiral inducing property of these ionic liquids was evaluated for sulfide oxidation of sulfide **10**. In the Kagan asymmetric sulfide oxidation method diethyl tartrate was used as a chiral auxiliary. We tried titanium metal-catalyzed asymmetric sulfide oxidation of sulfide **10** to sulfoxide **11** by replacing diethyl tartrate with ionic liquids (Scheme 4).

Chiral ionic liquids 4 and 5 are, therefore, liquids that were used as solvents for the reaction. Ionic liquids 4 and 5 were also evaluated for sulfide oxidation with co-solvent. Almost same enantiomeric excess was observed using ionic liquids 4 or 5 with and without co-solvent. Other ionic liquids 8a-c and 9a-c are solid compounds; therefore, co-solvent is necessary along with these ionic liquids to allow reaction mixture to stir smoothly. Solvents like dichloromethane, toluene, and acetonitrile were evaluated as cosolvents along with ionic liquids. Based on the solubility of ionic liquids dichloromethane was used as co-solvent along with the TBHP as an oxidant for the reaction. Initially, we carried out the oxidation reaction without a metal catalyst to evaluate the catalytic property of the chiral ionic liquid. But racemic sulfoxide was obtained without metal catalyst. The influence of the mole ratio of ionic liquids with respect to 10 was evaluated for sulfide oxidation keeping other parameters constant. Ionic liquids with 10 moles% and 20 moles% have been explored for this reaction. There is a significant change in the enantiomeric of sulfoxide using 10 moles% and 20 moles% of ionic liquid. The results are summarized in Table 1. Form the table it is clear that enantiomeric excess of sulfoxide obtained using tartaric acid based ionic liquids is higher (up to 81%

lonic liquids	Co- solvent	R=H			R=CH ₃		
		Yield (%)	ee ^a (%)	[α] ²² D	Yield (%)	ee ^a (%)	[α] ²² _D
4	_	73	77	-101.9	76	81	-115.6
5	-	75	75	-98.5	79	78	-111.2
4	DCM	76	76	-101.2	73	79	-113.4
5	DCM	73	74	-98.1	75	78	-112.7
8a	DCM	69	18	-23.9	71	21	-31.5
8b	DCM	71	15	-19.8	75	16	-22.2
8c	DCM	68	12	-16.8	66	12	-18.1
9a	DCM	70	20	-25.7	68	24	-33.8
9b	DCM	72	18	-23.5	73	21	-29.7
9c	DCM	75	18	-23.8	73	20	-27.6

 Table 1. Summary of sulfide oxidation reaction.

DCM: Dichloromethane; ^aenantiomeric excess measured by chiral HPLC.

ee) than that obtained from 2-oxazolidinone. It has been also observed that enantiomeric excess is slightly higher when $R=CH_3$.

Experimental

Procedure for the synthesis of ionic liquid 4

Bis (chloroethyl) tartrate 3 (10 g, 36 mmol) and N-methyl imidazole (12 g, 146 mmol) were added to the round bottom flask at room temperature. The reaction mixture was slowly heated to 90–100 °C and stirred for 24–48 h. The progress of the reaction was monitored on thin layer chromatography. The reaction mixture was cool to room temperature. Water (30 ml) and dichloromethane (60 ml) were added to the reaction mixture. The reaction mixture was stirred at room temperature for 15 min. The aqueous layer was separated and washed with dichloromethane (20 ml \times 2). Then, the aqueous layer was concentrated on the laboratory rotavapor under reduced pressure at 50–55 °C. Concentrated mass was purified on column chromatography using 30% methanol in ethyl acetate. Pure compound was dried under reduced pressure at 50–55 °C for 48 h on laboratory rotavapor to get 4.

1,1'-((((**2S**,**3S**)-**2**,**3**-**dihydroxysuccinyl)bis(oxy**))**bis(ethane-2**,**1**-**diyl**))**bis(3-methyl-1H-imidazol-3-ium). bis chloride (4):** Pale yellow colour oil, (Yield: 14.3 g, 93%); $[\alpha]^{22}_{D} = -31.0^{\circ}$ (c = 1.0, Methanol); Density $\rho = 1.21 \text{ g/cm}^3$; ¹H NMR (500 MHz, DMSO-d6): δ , 3.87 (s, 6H), 4.40–4.54 (m, 10H), 5.90–5.92 (d, 2H), 7.73–7.74 (t, 2H), 7.85–7.86 (t, 2H), 9.36 (s, 1H); ¹³C NMR (125 MHz, DMSO-d₆): 171.0, 137.3, 123.7, 122.6, 72.3, 62.8, 48.2, 35.9 IR (neat), ν /cm-1: 3382, 1755, 1634; Anal. Calcd. for C₁₆H₂₄Cl₂N₄O₆: C, 43.75; H, 5.51; N, 12.75. Found: C, 43.7; H, 5.50; N, 12.77.

Procedure for the synthesis of ionic liquid 7a

Acetonitrile (20 ml) and **6a** (10 g, 48.6 mmol) were added in a round bottom flask at room temperature. N-methyl imidazole (4.4 g, 53.4 mmol) was added to the above reaction mixture and raised the temperature of reaction mixture to 50-55 °C. Then temperature of reaction was to maintained 50-55 °C for 4–5 h. Progress of the reaction monitored on thin layer chromatography. Then after completion of reaction ethyl acetate (80 ml) was added slowly to the reaction mixture and cooled to room temperature.

Reaction mixture was stirred at room temperature for 1 h. Filter the solid and washed with ethyl acetate (20 ml). Solid was dried under reduced pressure to get the **7a**.

(S)-3-(2-(4-isopropyl-2-oxooxazolidin-3-yl)-2-oxoethyl)-1-methyl-1H-imidazol-3-ium chloride(7a); (Yield: 13 g, 93%); $[\alpha]^{22}{}_{\rm D}$ = +39.2° (c = 1.0, Methanol); mp: 127–129 °C; ¹H NMR (500 MHz, MeOD): δ , 0.92–0.96 (d, 6H), 2.30–2.35 (m, 1H), 4.01 (s, 3H), 4.44–4.50 (m, 3H), 5.71–5.79 (q, 2H), 7.62–7.66 (d, 2H), 8.98(s, 1H); ¹³C NMR (125 MHz, CDCl₃): 167.1, 155.9, 139.5, 125.4, 124.4, 66.3, 60.2, 53.6, 36.6, 30.0 17.7, 15.1; IR (neat), ν /cm-1: 3099, 1779, 1713; Anal. Calcd. for C₁₂H₁₈ClN₃O₃: C, 50.09; H, 6.31; N, 14.60. Found: C, 50.10; H, 6.34; N, 14.58.

Procedure for preparation of 8a

In a round bottom flask, **7a** (5 g, 17.4 mmol) and water (50 ml) were added at room temperature. Potassium hexafluorophosphate (3.2 g, 17.4 mmol) added to above reaction mixture and stirred at room temperature for 1 h. Filter the solid and washed with water (20 ml \times 2). Solid was dried under reduced pressure at 40 °C to get **8a**.

(S)-3-(2-(4-isopropyl-2-oxooxazolidin-3-yl)-2-oxoethyl)-1-methyl-1H-imidazol-3-ium hexafluorophosphate (8a); (Yield: 6.5 g, 95%); $[\alpha]^{22}{}_{\rm D} = +58.5^{\circ}$ (c = 1.0, Acetone); mp: 68–70 °C; ¹H NMR (500 MHz, DMSO-d₆): δ , 0.86–0.88 (dd, 6H), 2.16–2.19 (m, 1H), 3.92 (s, 3H), 4.37–4.45 (m, 3H), 5.60–5.78 (dd, 2H), 7.63–7.71 (d, 2H), 8.99 (s, 1H); ¹³C NMR (125 MHz, DMSO-d₆): 166.0, 154.1, 137.8, 123.9, 123.1, 64.9, 58.2, 52.2, 35.9, 28.5, 17.2, 14.8; IR (neat), ν /cm-1: 3170, 1774, 1709, 1391; Anal. calcd for C₁₂H₁₈F₆N₃O₃P: C, 36.28; H, 4.57; N, 10.58. Found: C, 36.25; H, 4.61; N, 10.60.

General procedure for sulfide oxidation

In a round bottom flask, dichloromethane (10 ml) and sulfide **10a** (2 g, 16 mmol) were added at room temperature. Added **4** (0.7 g, 1.6 mmol), titanium isopropoxide (0.22 g, 0.8 mmol) and water (15 μ l, 0.8 mmol) to above reaction mixture. Then the reaction mixture was stirred at room temperature for 1 h. Tertiary butyl hydroperoxide (4.2 ml, 32 mmol) was slowly added to the reaction mixture at room temperature. Then the reaction mixture was stirred at room temperature for 16 h. water was added (20 ml) to the reaction mixture and stirred for 0.5 h. Filter the reaction mixture to remove the solid precipitate. The organic layer separated from the filtrate and concentrated on laboratory rotavapor to get the oily residue. The residue purified on column chromatography using ethyl acetate-cyclohexane to get the pure methyl phenyl sulfoxide. HPLC: The enantiomeric ratio was measured by HPLC (DAICEL OB-H, heptane/isopropanol 70:30, flow rate: 0.5 mL/min, 254 nm, Ret Time for R-isomer = 13.5 min and Ret Time for S-isomer = 21.8 min).

Methyl phenyl sulfoxide (**11a**): (Yield: 1.65 g, 73%); $[\alpha]_{D}^{22} = -101.9^{\circ}$ (c = 1.1, Acetone); ee = 77%; ¹H NMR (500 MHz, CDCl3): δ , 2.74 (s, 3H), 7.50–7.67 (m, 5H); ¹³C NMR (125 MHz, CDCl3): 145.6, 131.0, 129.3, 123.5, 43.9; IR (ν /cm-1) 2920, 1478, 1090, 1040; Anal. Calcd. for C₇H₈OS: C, 59.97; H, 5.75; Found: C, 60.1; H, 5.78.

Conclusion

D- Tartaric acid and 2-oxazolidinone based imidazolium and pyridinium chiral ionic liquids have been synthesized. All these functionalized ionic liquids characterized by ¹H NMR, ¹³C NMR, and FTIR. Physical properties like melting point, density and specific optical rotation of these ionic liquids have also been recorded. Ionic liquids based on tartaric acid are liquids while the ionic liquids based on N-acylation of 2-oxazolidinone with hexafluorophosphate anion are low melting solids. Tartaric acid based ionic liquids produces more optically active sulfoxide.

Full experimental details, 1H and 13C NMR spectra can be found via the "Supplementary Content" section of this article's webpage.

Acknowledgments

The authors are thankful to the M/S Lupin Limited and the authorities of Manipal Academy of Higher Education for the research program. We also acknowledge the valuable guidance, support, and suggestions from Dr. P. R. Upadhaya, and Dr. Vijaya Desai.

References

- [1] Lewandowski, A.; Galiński, M. Carbon-Ionic Liquid Double-Layer Capacitors. J. Phys. Chem. Sol. 2004, 65, 281-286. DOI: 10.1016/j.jpcs.2003.09.009.
- [2] Walden, P.; Die, U. Molekulargrösse and Elektrische Leitfähigkeit Einiger Geschmolzenen Salze. *Bull. Acad. Imper. Sci. St. Petersburg* 1914, *8*, 405–422.
- [3] (a) Bwambok, D. K., Marwani, H. M.; Fernand, V. E.; Fakayode, S. O.; Lowry, M.; Negulescu, I.; Strongin, R. M.; Warner, I. M.. Synthesis and Characterization of Novel Chiral Ionic Liquids and Investigation of their Enantiomeric Recognition Properties. *Chirality* 2008, 20, 151–158. DOI: 10.1002/chir.20517. (b) Laura, G.; Belén, A.; Michael, B.; Isabel, B.; Eduardo, G. -V.; Santiago, V. L. Synthesis of Chiral Room Temperature Ionic Liquids from Amino Acids – Application in Chiral Molecular Recognition. *Eur. J. Org. Chem.* 2012, 4996–5009. DOI: 10.1002/ejoc.201200607. (c) Ding, J.; Welton, T.; Armstrong, D. W. Chiral Ionic Liquids as Stationary Phases in Gas Chromatography. *Anal. Chem.* 2004, 76, 6819–6822. DOI: 10.1021/ac049144c.
- [4] (a) González, L.; Escorihuela, J.; Altava, B.; Burguete, M. I.; Luis, S. V. Chiral Room Temperature Ionic Liquids as Enantioselective Promoters for the Asymmetric Aldol Reaction. Eur. J. Org. Chem. 2014, 2014, 5356. DOI: 10.1002/ejoc.201402436. (b)Beltrán, A.; Isabel Burguete, M.; Abánades, D. R.; Pérez-Sala, D.; Luis, S. V.; Galindo, F. Luis and Francisco Galindo. Turn-on fluorescent probes for nitric oxide sensing based on the ortho-hydroxyamino structure showing no interference with dehydroascorbic acid. Chem. Commun. 2014, 50, 3579-3581. DOI: 10.1039/C3CC49555H. (c) Soumen, P.; Arijit, S.; Subhash, B. Chiral Ionic Liquids: Synthesis and Role as Efficient Green Catalyst in Asymmetric Synthesis. Curr. Organocatal. 2017, 4, 4-32. DOI: 10.2174/ 2213337203666160524143221.
- [5] Miao, W.; Chan, T. H. Ionic-Liquid-Supported Organocatalyst: Efficient and Recyclable Ionic-Liquid-Anchored Proline for Asymmetric Aldol Reaction. Adv. Synth. Catal. 2006, 348, 1711–1718. DOI: 10.1002/adsc.200606059.
- [6] (a) Buskens, P.; Klankermayer, J.; Leitner, W. Bifunctional Activation and Racemization in the Catalytic Asymmetric Aza-Baylis–Hillman Reaction. *J. Am. Chem. Soc.* 2005, 127, 16762–16763. DOI: 10.1021/ja0550024. (b) Gausepohl, R.; Buskens, P.; Kleinen, J.; Bruckmann, A.; Lehmann, C. W.; Klankermayer, J.; Leitner, W. Highly Enantioselective

aza-Baylis-Hillman Reaction In A Chiral Reaction Medium. Angew. Chem. Int. Ed. Engl. 2006, 45, 3689–3692. DOI: 10.1002/anie.200600327.

- [7] Fischer, T.; Sethi, A.; Welton, T.; Woolf, J. Diels-Alder Reactions in Room-Temperature Ionic Liquids. *Tetrahedron Lett.* **1999**, *40*, 793–796. DOI: 10.1016/S0040-4039(98)02415-0.
- [8] Wang, Z.; Wang, Q.; Zhang, Y.; Bao, W. Synthesis of New Chiral Ionic Liquids from Natural Acids and their Applications in Enantioselective Michael Addition. *Tetrahedron Lett.* 2005, 46, 4657–4660. DOI: 10.1016/j.tetlet.2005.04.134.
- [9] Geldbach, T. J.; Dyson, P. J. A Versatile Ruthenium Precursor for Biphasic Catalysis and its Application in Ionic Liquid Biphasic Transfer Hydrogenation: Conventional vs Task-Specific Catalysts. J. Am. Chem. Soc. 2004, 126, 8114. DOI: 10.1021/ja048886k.
- [10] Gadenne, B.; Hesemann, P.; Moreau, J. J. E. Ionic Liquids Incorporating Camphorsulfonamide Units for the Ti-Promoted Asymmetric Diethylzinc Addition to Benzaldehyde. *Tetrahedron Lett.* 2004, 45, 8157–8160. DOI: 10.1016/j.tetlet.2004.09.038.
- [11] (a) Diaw, M.; Chagnes, A.; Carre, B.; Willmann, P.; Lemordant, D. Mixed Ionic Liquid as Electrolyte for Lithium Batteries. *J. Power Sources* 2005, *146*, 682–684. DOI: 10.1016/j.jpowsour.2005.03.068. (b) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. Dialkylimidazolium Chloroaluminate Melts: A New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy and Synthesis. *Inorg.Chem.* 1982, *21*, 1263–1264. DOI: 10.1021/ic00133a078.
- [12] Dal, W.; Li, J.; Chen, B.; Li, G.; Lv, Y.; Wang, L.; Shang, G. Asymmetric Oxidation Catalysis by a Porphyrin-Inspired Manganese Complex: Highly Enantioselective Sulfoxidation with a Wide Substrate Scope. Org. Lett. 2013, 15, 5658. DOI: 10.1021/ ol402612x.
- [13] (a) Pitchen, P.; Kagan, H. B. An Efficient Asymmetric Oxidation of Sulfides to Sulfoxides. *Tetrahedron Lett.* 1984, 25, 1049. DOI: 10.1016/S0040-4039(01)80097-6. (b) Pitchen, P.; Dunach, E.; Deshmukh, M. N.; Kagan, H. B. An Efficient Asymmetric Oxidation of Sulfides to Sulfoxides. *J. Am. Chem. Soc.* 1984, 106, 8188. DOI: 10.1021/ja00338a030.
- [14] Di Furia, F.; Modena, G. Seraglia, R. A New Synthesis of Diaryl Sulfones. Synthesis 1984, 4, 323–325. DOI: 10.1055/s-1984-30828.
- [15] Katsuki, T.; Sharpless, K. B. The first practical method for asymmetric epoxidation. J. Am. Chem. Soc 1980, 102, 5974. DOI: 10.1021/ja00538a077.
- [16] Nehate, S. P.; Godbole, H. M.; Singh, G. P.; Jessy E, M.; Gautham G, S. Synthesis of Novel Class of 2-oxazolidinone Based Chiral Ionic Liquids. *Synth. Comm.* 2018, 48, 2435–2440. DOI: 10.1080/00397911.2018.1496260.
- [17] (a) Machado, M. Y.; Dorta, R. Synthesis and Characterization of Chiral Imidazolium Salts. *Synthesis* 2005, *15*, 2473. DOI: 10.1055/s-2005-872102. (b) Wang, Z.; Wang, Q.; Zhang, Y.; Bao, W. Synthesis of New Chiral Ionic Liquids from Natural Acids and Their Applications in Enantioselective Michael Addition. *Tetrahedron Lett.* 2005, *46*, 4657. DOI: 10.1016/j.tetlet.2005.04.134.