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Ionic liquid-functionalized salen Mn(III) complexes as tunable separation catalysts for enantioselective epoxidation of styrene

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Abstract

A series of novel chiral salen Mn(III) complexes functionalized by ionic liquid (IL) of 1-propylamine-3-methylimidazolium tetrafluoroborate were synthesized through the reaction of amino group ($-NH_2$) of the IL with chloromethyl ($-CH_2Cl$) in the salen ligand at one side of the 5 position (complex **2**) and at two sides of the 5, 5′ position (complex **3**), as well as by direct axial coordination between $-NH_2$ of the IL and metal center of the salen Mn(III) complex (complex **4**). All of the synthesized complexes were well characterized, and their performance in the enantioselective epoxidation of styrene was investigated systematically. Under optimum reaction conditions, a 99% styrene epoxide yield with 50% enantiometric excess (ee) could be obtained over the complex **2**. Furthermore, the IL-functionalized chiral salen Mn(III) complexes of **2** and **3** could be conveniently separated from the reaction system by simple precipitation in hexane and subsequently used without significant loss of activity and enantioselectivity.

Keywords: Chiral salen Mn(III) complex; Ionic liquid; Styrene; Enantioselective epoxidation

1. Introduction

Catalytic enantioselective epoxidation of alkenes presents a powerful strategy for the synthesis of enantiometrically enriched epoxides, which are used as the important building blocks in the synthesis of many pharmaceuticals and fine chemicals. Of several catalytic methods, the enantioselective epoxidation of unfunctionalized alkenes catalyzed by homogeneous chiral salen Mn(III) complexes developed by Zhang et al. is one of the most relevant methods [1–3]. However, separation and recycling of the homogeneous catalysts often prove difficult. Recently, much effort has been aimed at overcoming this difficulty by heterogenizing the homogeneous chiral salen Mn(III) complexes (e.g., immobilization of salen Mn(III) complex on mesoporous materials [4,5], activated carbon [6,7], zeolite Y [8], poly-system [9], clay compounds [10], and inorganic membranes [11]), thereby creating chiral heterogeneous catalyst that can be readily recovered from reaction mixtures. Unfortunately, despite their excellent performance in easy separation, the heterogenized catalysts often suffer from decreased catalytic efficiency, likely due to the leaching of salen Mn(III) complexes during reaction and/or the inaccessibility of the reagents to the reactive centers [12]. Therefore, it is highly desirable to develop a novel method to make the salen Mn(III)-type catalyst effective and recoverable. More recently, we have synthesized a polymeric chiral salen Mn(III) complex with chiral diamine bridging [13]. The complex can be used as solvent-regulated phase-transfer catalyst in the enantioselective epoxidation of styrene and shows both facile separation and high catalytic efficiency, bearing comparison with the corresponding homogeneous chiral salen Mn(III) complex. Such a tunable separation catalyst gives rise to an alternative approach to the heterogenization of homogeneous catalysts.

Ionic liquids (ILs) with intriguing physical and chemical properties have received considerable attention in several scientific disciplines over the last several years [14]. They gen-

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erally are used as green solvents and/or catalysts in various organic transformations [15]. Specifically, attempts have been made to use ILs as reaction media for improving the activity and separation of the catalysts in the enantioselective epoxidation of olefins [16]; for example, Song and Roh [17] investigated the performance of a homogeneous chiral salen Mn(III) catalyst for enantioselective epoxidation of alkenes in a [bmim][PF_6]-containing reaction medium and found that the use of [bmim]PF_6 gave an elevated yield and ee value. Likewise, we found that some ILs are conducive to the epoxidation of cyclohexene catalyzed by homogeneous salen Mn(III) complexes [18]. However, disregarding the tunable dissolvability of ILs determined by the structure of cation and the type of anion, the bonding of ILs onto the structure of salen Mn(III) complex to prepare tunable separation catalysts has not been reported to date.

Based on our previous work [13,15,18] and the concept of "one-phase catalysis and two-phase separation" [19], in the present study, an IL of 1-propylamine-3-methylimidazolium tetrafluoroborate that is miscible with dichloromethane and immiscible with hexane was synthesized and successively bonded onto a chiral salen Mn(III) complex. Different strategies have been used to attach the IL onto different positions of the chiral salen Mn(III) complex. All IL-functionalized chiral salen Mn(III) complexes show particular properties of tunable separation in the enantioselective epoxidation of styrene, and their catalytic performance depends strongly on the location of the attachment of chiral salen Mn(III) complex and the IL.

2. Experimental

2.1. Materials and methods

L(+)-tartaric acid, 1,2-diaminocyclohexane, 3-chloroperoxybenzoic acid (m-CPBA), 3-bromopropylamine, 4-phenylpyridine *N*-oxide (4-PhPyNO), 4-methylmorpholine-*N*-oxide (NMO), and 1-methylimidazole were purchased from Acros. Pyridine *N*-oxide (PyNO) and sodium tetrafluoroborate were obtained from Fluka. 2-*tert*-butyl phenol and 4-(3-phenylpropyl) pyridine *N*-oxide (4-PPPyNO) were purchased from Alfa Aesar and Aldrich, respectively. Other commercially available chemicals were laboratory-grade reagents from local suppliers. (*R*, *R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt, 3-*tert*-butyl-2-hydroxybenzaldehyde, and 3-*tert*-butyl-5-(chloromethyl)-2-hydroxybenzaldehyde were synthesized according to the procedures described previously [3,20,21].

FT-IR spectra were obtained as potassium bromide pellets with a resolution of 4 cm^{-1} and 32 scans in the range of 400–4000 cm^{-1} using an AVATAR 370 Thermo Nicolet spectrophotometer. The ultraviolet–visible light (UV–vis) spectra were recorded on a UV–vis Agilent 8453 spectrophotometer. The solution of samples in dichloromethane (ca. 1.0 mM) was poured into a 1-cm quartz cell for UV–vis adsorption with dichloromethane as the reference. ^{1}H NMR spectra of the samples were recorded with a Varian-400 spectrometer using tetramethylsilane (TMS) as an internal reference. Mass spectrometry analyses were performed using an API 3000 tandem mass spectrometer (Applied Biosystems) with an electrospray interface (ESI-MS/MS in MeOH). The operating conditions in positive ionization mode were optimized using a +5500 V ion spray voltage, 8 psi for curtain gas, 8 psi for drying gas heated to 100 °C, and 7 psi for nebulizing gas. Elemental analyses of C, H, and N were carried out on a Vario EL III elemental analyzer. The optical rotation of catalysts was measured in dichloromethane on a WZZ-2A automatic polarimeter. The Mn ion content was measured by the complexiметry method with ethylenediamine tetraacetic acid (EDTA) as described previously [22]. The ee value for styrene epoxide and the product analysis were determined using an Agilent Technologies 6890N gas chromatograph equipped with 19091G-B213 chiral capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID).

2.2. Preparation of ionic liquid

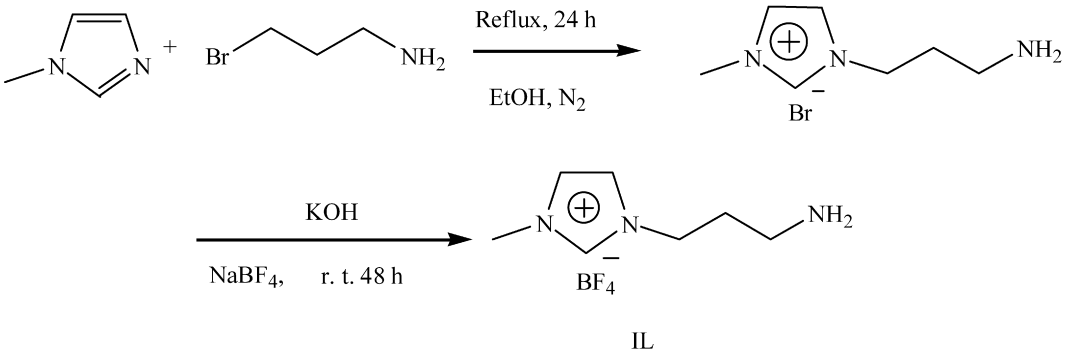
The IL of 1-propylamine-3-methylimidazolium tetrafluoroborate was synthesized as described previously [23] (see Scheme 1). First, 100 mmol of 1-methylimidazole and 100 mmol of 3-bromopropylamine were dissolved in 50 mL of dry ethanol under stirring. The resulting mixture was refluxed for 24 h under nitrogen protection. After removal of ethanol in vacuum, the solid residue was dissolved in water. Then the pH value of the solution was adjusted to 10 by the addition of potassium hydroxide. The obtained solution was concentrated under vacuum and then extracted with ethanol–tetrahydrofuran. Subsequently, ion exchange with sodium tetrafluoroborate (110 mmol) in ethanol/water was performed for 48 h at ambient temperature. After the solvent was removed, the resulting mixture was filtered, after which the filtrate was dried under vacuum at 80 °C to give a pale-yellow viscous liquid of 1-propylamine-3-methylimidazolium tetrafluoroborate (IL) (13.85 g, yield of 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 8.77 (s, 1 H), 7.50 (d, 1 H), 7.42 (d, 1 H), 4.31 (t, 2 H), 4.17 (t, 2 H), 2.70 (m, 2 H), 0.86 (t, 3 H). FT-IR (KBr): 3426, 3143, 2955, 2739, 2643, 2504, 2015, 1574, 1506, 1457, 1339, 1285, 1232, 1169, 1085, 1021, 831, 756, 621 cm^{-1}.

2.3. Preparation of IL-functionalized chiral salen ligand 1 (IL-CL1) and IL-functionalized chiral salen ligand 2 (IL-CL2)

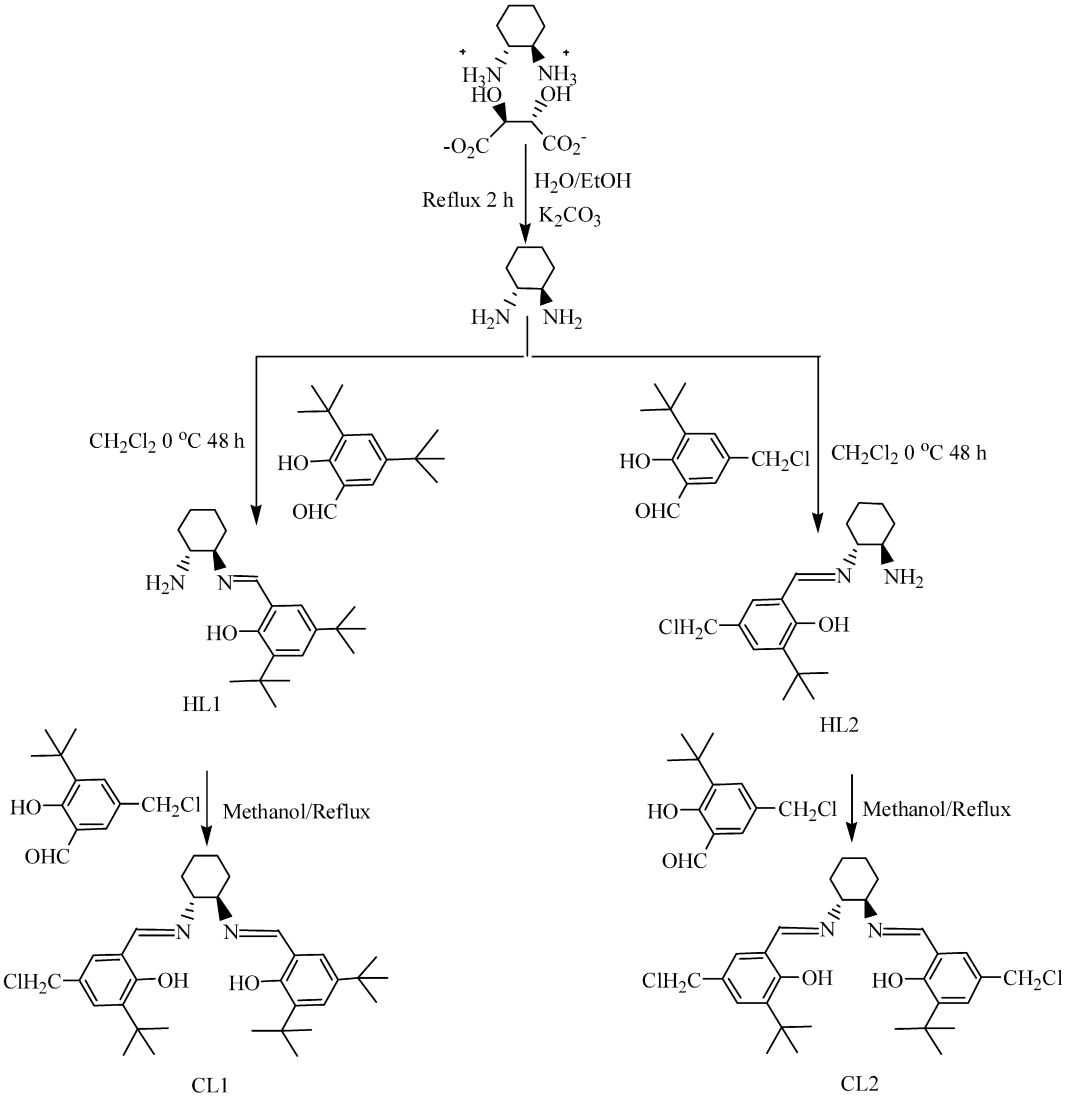
The preparation of IL-CL1 and IL-CL2 is outlined in Scheme 2.

2.3.1. Synthesis of chiral half-unit of ligand 1 (HL1) and chiral half-unit of ligand 2 (HL2)

In this procedure, 11.2 mmol of (*R*, *R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt and 22.5 mmol of potassium carbonate were dissolved in 15 mL of distilled water, followed by the addition of 6 mL of dry ethanol under vigorous stirring. The resulting cloudy mixture was refluxed for another 2 h. The liberated diamine was extracted with chloroform (4 × 5 mL). Then 20 mL of chloroform containing 11.2 mmol of 3,5-di-*tert*-butyl salicylaldehyde (for synthesis of the compound HL1) or 3-*tert*-butyl-5-(chloro-methyl)-

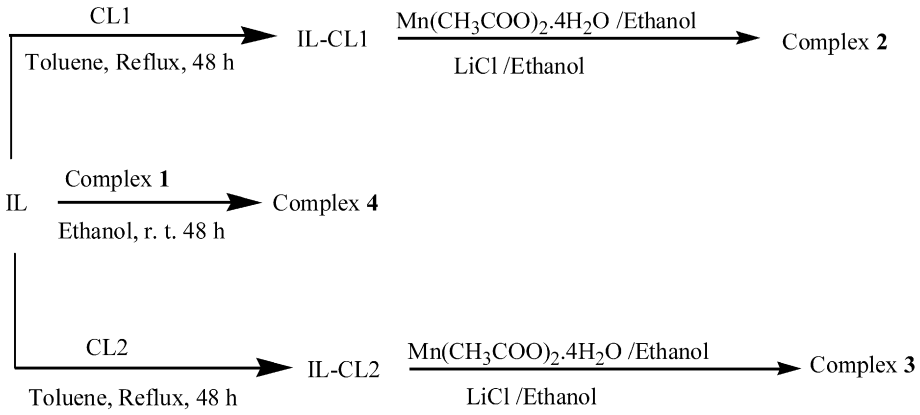


Scheme 1. Synthesis of the ionic liquid (IL) containing primary amine.



Scheme 2. Synthesis of chiral salen ligand CL1 and chiral salen ligand CL2.

2-hydroxybenzaldehyde (for synthesis of the compound HL2) was added dropwise to the solution of diamine at 0 °C under stirring for 48 h. On filtration, precipitate was collected and recrystallized from ethanol to give a pale-yellow powder of HL1 (3.52 g, 95%) or HL2 (3.23 g, 89%). HL1: Calc. for $C_{21}H_{34}N_2O$: C, 76.31; H, 10.37; N, 8.48. Found: C, 76.43; H, 10.32; N, 8.41%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 13.74 (s, 1 H), 8.30 (s, 1 H), 7.21 (s, 1 H), 7.00 (s, 1 H), 3.34 (s, 1 H), 1.95–1.46 (m, 10 H), 1.40 (s, 9 H), 1.24 (s, 9 H). FT-IR (KBr): 3440, 2953, 2864, 1630, 1593, 1469, 1439, 1391, 1361, 1325, 1270, 1252, 1240, 1202, 1174, 1135, 1085, 1063, 1037, 981, 939, 879, 862, 828, 803, 772, 731, 711, 644 cm^{-1}. HL2: Calc.



Scheme 3. Synthesis of the IL-functionalized chiral salen Mn(III) complexes **2**, **3**, and **4**.

for $C_{18}H_{27}ClN_2O$: C, 66.96; H, 8.43; N, 8.68. Found: C, 66.89; H, 8.52; N, 8.57%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 13.78 (s, 1 H), 8.29 (s, 1 H), 7.28 (s, 1 H), 7.11 (s, 1 H), 4.58 (s, 2 H), 3.32 (s, 1 H), 2.05–1.44 (m, 10 H), 1.42 (s, 9 H). FT-IR (KBr): 3449, 2956, 2858, 1630, 1582, 1547, 1480, 1468, 1442, 1386, 1351, 1340, 1325, 1291, 1270, 1240, 1224, 1200, 1173, 1153, 1081, 1054, 1043, 942, 859, 823, 798, 717, 646 cm^{-1}.

2.3.2. Synthesis of chiral salen ligand 1 (CL1) and chiral salen ligand 2 (CL2)

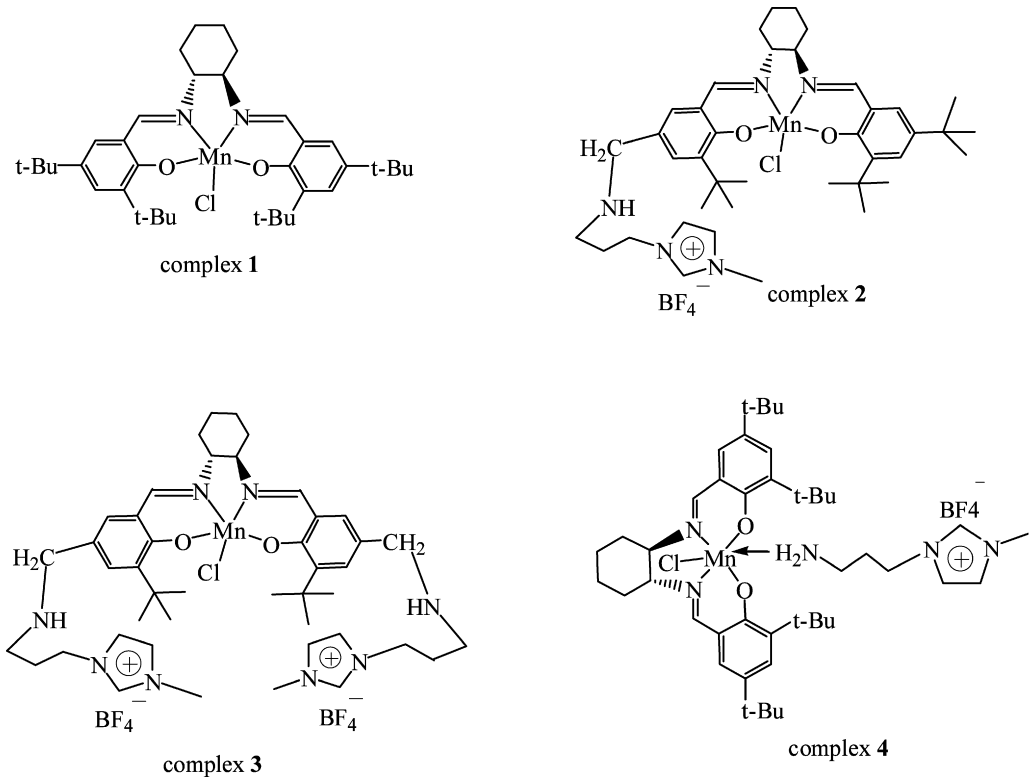
In this procedure, 8 mmol of the previously obtained HL1 (for the synthesis of CL1) or HL2 (for the synthesis of CL2) was dissolved in 20 mL of dry ethanol. The solution was added dropwise to 20 mL of dry ethanol containing 8 mmol of 3-*tert*-butyl-5-(chloro-methyl)-2-hydroxybenzaldehyde at ambient temperature. The resulting mixture was gradually heated to 60 °C and stirred for 8 h. The slurry thus obtained was cooled in ice-water bath over 3 h. Then the solid obtained was filtered and recrystallized from ethanol to give pale-yellow powder of CL1 (3.55 g, 85%) or CL2 (3.38 g, 82%). CL1: Calc. for $C_{33}H_{47}ClN_2O_2$: C, 73.51; H, 8.79; N, 5.20. Found: C, 73.58; H, 8.75; N, 5.13%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 14.29 (s, 1 H), 13.67 (s, 1 H), 8.44 (s, 1 H), 8.31 (s, 1 H), 7.30 (d, 1 H), 7.26 (d, 1 H), 6.99 (d, 1 H), 6.89 (d, 1 H), 4.43 (s, 2 H), 3.55–3.32 (m, 2 H), 1.97–1.46 (m, 8 H), 1.40 (s, 9 H), 1.23 (s, 18 H). FT-IR (KBr): 3446, 2954, 2865, 1630, 1591, 1479, 1468, 1439, 1391, 1362, 1271, 1253, 1241, 1202, 1174, 1135, 1085, 1037, 982, 939, 879, 828, 803, 772, 731, 711, 644 cm^{-1}. CL2: Calc. for $C_{30}H_{40}Cl_2N_2O_2$: C, 67.79; H, 7.58; N, 5.27. Found: C, 67.71; H, 7.69; N, 5.32%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 13.68 (s, 2 H), 8.42 (s, 2 H), 7.31 (d, 2 H), 7.26 (d, 2 H), 4.58 (s, 4 H), 3.55–3.30 (m, 2 H), 1.89–1.44 (m, 8 H), 1.42 (s, 18 H). FT-IR (KBr): 3449, 2952, 2866, 1630, 1594, 1545, 1466, 1439, 1390, 1361, 1308, 1266, 1229, 1200, 1167, 1142, 1091, 1030, 974, 930, 871, 778, 753, 669 cm^{-1}.

2.3.3. Synthesis of IL-CL1 and IL-CL2

First, 15 mL of dry toluene containing 5 mmol of the CL1 (for the synthesis of IL-CL1) or the chiral salen ligand CL2 (for the synthesis of IL-CL2) was added to equiv. of IL. The resulting mixture was refluxed for 48 h under nitrogen protection. After cooling to 5 °C overnight, the complex thus obtained was collected by removal of toluene, washed completely with hexane for several times, and dried in vacuum to obtain a deep-yellow solid of IL-CL1 (2.26 g, 91%) or IL-CL2 (3.89 g, 82%). IL-CL1: Calc. for $C_{40}H_{63}BF_4N_5O_2$: C, 65.56; H, 8.67; N, 9.56. Found: C, 65.50; H, 8.74; N, 9.73%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 14.25 (s, 1 H), 13.68 (s, 1 H), 8.93 (s, 1 H), 8.45 (s, 1 H), 8.29 (s, 1 H), 7.58 (d, 1 H), 7.47 (d, 1 H), 7.30 (d, 1 H), 7.26 (d, 1 H), 6.99 (d, 1 H), 6.89 (d, 1 H), 4.56 (s, 2 H), 4.32 (m, 2 H), 4.17 (t, 2 H), 3.60–3.34 (m, 2 H), 2.70 (m, 2 H), 2.4 (s, 1 H), 1.88–1.49 (m, 8 H), 1.40 (s, 9 H), 1.28 (s, 18 H), 0.88 (t, 3 H). FT-IR (KBr): 3443, 3144, 2956, 2864, 2013, 1630, 1547, 1530, 1468, 1439, 1390, 1363, 1313, 1269, 1252, 1240, 1204, 1173, 1135, 1084, 1037, 982, 939, 879, 828, 772, 731, 712, 642, 621 cm^{-1}. IL-CL2: Calc. for $C_{44}H_{72}B_2F_8N_8O_2$: C, 57.52; H, 7.90; N, 12.20. Found: C, 57.41; H, 7.97; N, 12.32%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 13.68 (s, 2 H), 8.91 (s, 2 H), 8.42 (s, 2 H), 7.60 (d, 2 H), 7.49 (d, 2 H), 7.31 (d, 2 H), 7.23 (d, 2 H), 4.58 (s, 4 H), 4.29 (m, 4 H), 4.15 (t, 4 H), 3.55–3.30 (m, 2 H), 2.70 (m, 4 H), 2.4 (s, 2 H), 1.89–1.44 (m, 8 H), 1.32 (s, 18 H), 0.85 (t, 6 H). FT-IR (KBr): 3448, 3146, 3089, 2953, 2861, 2013, 1630, 1547, 1530, 1471, 1438, 1390, 1363, 1339, 1313, 1272, 1246, 1204, 1174, 1089, 1031, 874, 830, 772, 712, 642, 621 cm^{-1}.

2.4. Preparation of IL-functionalized chiral salen Mn(III) complexes *2*, *3*, and *4*

The preparation of complexes **2**, **3**, and **4** is outlined in Scheme 3. Under vigorous stirring, 15 mL of dry ethanol containing 8 mmol of manganese acetate was added dropwise to 15 mL of dry ethanol solution containing 4 mmol of chiral salen ligand IL-CL1 (for the synthesis of complex **2**) or IL-CL2 (for the synthesis of complex **3**) at 50 °C under nitrogen protection. The mixture was refluxed for 5 h, then cooled to ambient temperature. Then 10 mL of ethanol containing 24 mmol of lithium chloride was added to the mixture under stirring for 3 h. After bubbling with a gentle stream of air for another 2 h, the mixture was exposed to air overnight. The resulting slurry was cooled to 5 °C for 2 h, filtered, and washed with 50 mL of water. The solid thus obtained was dried under vacuum at 40 °C to



Scheme 4. Molecular structure of chiral salen Mn(III) complexes **1**, **2**, **3**, and **4**.

give a brown powder of IL-functionalized chiral salen Mn(III) complex **2** (3.02 g, 87%) or **3** (3.65 g, 89%). Complex **2**: FT-IR (KBr): 3408, 3147, 2953, 2864, 2013, 1613, 1558, 1538, 1458, 1437, 1390, 1361, 1339, 1310, 1270, 1251, 1200, 1171, 1085, 1027, 877, 836, 772, 750, 645, 621, 568 cm^{-1}; UV–vis (CH_2Cl_2): 508, 434, 326 nm; Calc. for $C_{40}H_{61}BClF_4MnN_5O_2$: C, 58.51; H, 7.49; N, 8.53. Found: C, 58.43; H, 7.61; N, 8.46%; Mn ion content: 1.19 mmol/g (theoretical value: 1.25 mmol/g); ESI-MS, $m/z = 822$ $(M+H)^+$, 543 $(M\text{-}CH_2\text{-IL-}Cl)^+$; $[\alpha]_D^{33} = +562$ ($C = 0.04$, CH_2Cl_2). Complex **3**: FT-IR (KBr): 3408, 3143, 3087, 2953, 2861, 2013, 1613, 1586, 1547, 1538, 1461, 1442, 1390, 1358, 1308, 1198, 1169, 1087, 1044, 930, 871, 832, 751, 626, 621, 568 cm^{-1}; UV–vis (CH_2Cl_2): 508, 433, 325 nm; Calc. for $C_{44}H_{70}B_2ClF_8MnN_8O_2$: C, 52.48; H, 7.01; N, 11.13. Found: C, 52.54; H, 7.05; N, 11.06%; Mn ion content: 1.02 mmol/g (theoretical value: 1.04 mmol/g); ESI-MS, $m/z = 1008$ $(M+H)^+$, 487 $[M\text{-}2(CH_2+IL)\text{-}Cl]^+$; $[\alpha]_D^{33} = +545$ ($C = 0.04$, CH_2Cl_2).

The IL-functionalized chiral salen Mn(III) complex **4** was prepared as follows. First, 1 mmol of neat salen Mn(III) complex **1** synthesized as described previously [2] and 1 mmol of IL were dissolved in 15 mL of dry ethanol at ambient temperature, after which the mixture was stirred vigorously for another 48 h. After the removal of ethanol, the resulting solid was washed with hexane several times and dried under vacuum to get the complex **4** (0.7 g, 86%). FT-IR (KBr): 3408, 2956, 2865, 1613, 1575, 1538, 1462, 1433, 1390, 1361, 1340, 1311, 1271, 1252, 1172, 1087, 1028, 928, 837, 780, 749, 659, 621, 569 cm^{-1}; UV–vis (CH_2Cl_2): 520, 447, 327 nm; Calc. for $C_{43}H_{69}BClF_4MnN_5O_2$: C, 59.69; H, 8.04; N, 8.09. Found: C, 59.62; H, 8.11; N, 8.13%; Mn ion content: 1.21 mmol/g (theoretical value: 1.23 mmol/g); ESI-MS, $m/z = 866$ $(M+H)^+$, 599 $(M\text{-IL-}Cl)^+$; $[\alpha]_D^{33} = +544$ ($C = 0.04$, CH_2Cl_2).

2.5. Enantioselective epoxidation of styrene

The enantioselective epoxidation of styrene was typically performed according to the following procedure. First, 0.5 mmol of styrene and a desirable amount of axial base were added to 1 mL of dichloromethane containing 0.02 mmol of catalyst under stirring. The mixture was precooled to the specified temperature, after which 1 mmol of m-CPBA was added in five equal portions over 5-min periods. The reaction products were analyzed by Agilent Technologies 6890N gas chromatography (FID, 19091G-B213 chiral capillary column [30 m × 0.32 mm × 0.25 μm]) using nitrogen as a carrier gas with a flow rate of 30 mL/min. The injector temperature, detector temperature, and oven temperature were 250, 250, and 100 °C, respectively. The retention times of styrene, *R*-configuration styrene epoxide, and *S*-configuration styrene epoxide were 3.37, 10.1, and 10.5 min, respectively. The authentic sample of *R*- or *S*-configuration styrene epoxide was used as the standard product to determine the yields through comparison of peak height and area. After completion of the reaction, the catalyst was precipitated from the reaction system by the addition of hexane and subsequently used without further purification.

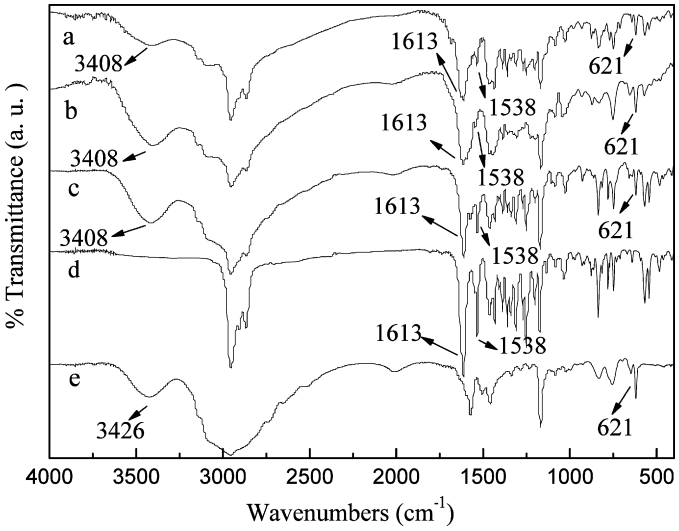


Fig. 1. FT-IR spectra of the IL-functionalized chiral salen Mn(III) complexes **2** (a), **3** (b), and **4** (c), the neat chiral salen Mn(III) complex **1** (d), and the ionic liquid **A** (e).

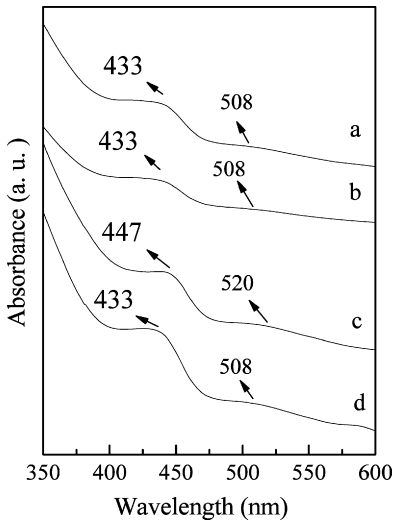


Fig. 2. UV–vis spectra of the IL-functionalized chiral complexes **2** (a), **3** (b), and **4** (c), as well as the neat chiral salen Mn(III) complex **1** (d).

3. Results and discussion

3.1. Characterization of samples

The synthesized IL-functionalized chiral salen Mn(III) complexes **2**, **3**, and **4** were characterized by FT-IR (see Fig. 1). All of the IL-functionalized chiral salen Mn(III) complexes displayed major characteristic bands around 1613, 1538, 1463, 1432, 1390, 1361, 1252, 1175, 836, and 568 cm^{-1} (Figs. 1a, 1b, and 1c), which are similar to the neat chiral salen Mn(III) complex **1** (Fig. 1d). The results indicated the identity of the IL-functionalized chiral salen Mn(III) complexes **2**, **3**, and **4** with the neat chiral salen Mn(III) complex **1**. Furthermore, the IL-functionalized samples exhibited an additional feature at 3408 and 621 cm^{-1} assigned to the stretching vibration of N–H groups [24] and characteristic peaks of imidazole fragment [25], respectively. These observations suggest that the IL has been successfully bonded with the chiral salen Mn(III) complex. ^{1}H NMR further characterized the IL-CL1. Compared with CL1, some new peaks at 2.4 ppm originated from the secondary amine (–NH) proton, and also at 8.93, 7.58, 7.47, 4.32, 4.17, 2.70, and 0.88 ppm originated from the protons of imidazole were observed in the ^{1}H NMR spectrum of IL-CL1. It is proposed that the secondary amine group in the IL-CL1 resulted from the reaction between chloromethyl group (–CH_2Cl) at the 5-position of the salen ligand and the amino group (–NH_2) of the IL.

The UV–vis electronic spectra of the neat chiral salen Mn(III) complex **1** and the IL-functionalized complexes **2**, **3**, and **4** are shown in Fig. 2. It can be seen that complexes **2** and **3** demonstrate broad peaks at near 433 nm and at around 508 nm, which were identical with those of complex **1**. The peak at 433 nm was assigned to charge-transfer transitions between the metal and ligand, and the peak at 508 nm was assigned to the d–d transitions in the salen Mn(III) complex [26], respectively. The observation implies that the active site of the IL-functionalized salen Mn(III) complexes **2** and **3** is maintained, provided that the IL is bonded onto the salen ligand. But complex **4**, in which the IL was attached via direct axial coordination of the metal center with IL, exhibited a red shift in the wavelength from 433 to 447 nm and from 508 to 520 nm due to strong coordination between the metal center and the amino group of the IL. These findings suggest that the electronic properties of the active site for chiral salen Mn(III) complex **4** should change slightly. Therefore, the different attachment locations of IL with salen Mn(III) complex should have crucial effects on their catalytic performance in the epoxidation of alkene.

3.2. Catalytic performances

Table 1 summarizes the catalytic performance of the synthesized complexes **2**, **3**, and **4** and the neat chiral salen Mn(III) complex **1** in the enantioselective epoxidation of styrene. In comparison with the neat chiral salen Mn(III) complex **1**, complexes **2** and **3** showed comparable catalytic activity (TOF) and enantioselectivity (ee). This is because complexes **2** and **3**, which can dissolve in dichloromethane, act as homogeneous catalysis in the reaction system presented here, thus leading to excellent catalytic activity. Furthermore, Table 1 shows that different attachment positions of chiral salen Mn(III) complex with the amino group in the IL had crucial effects on the catalytic performance of the corresponding IL-functionalized chiral salen Mn(III) complex. Clearly, complex **3** demonstrated similar catalytic activity and ee value as the neat complex **1**, due to the fact that the IL was bonded onto two sides of 5, 5′ position of complex **3**, which imparts the same C_2-symmetric structure as in complex **1**. In complex **2,** with the IL bonded onto one side of the 5 position, the non-C_2-symmetric structure gave rise to an elevated ee value (40%) under the same reaction conditions. It is believed that the electronic and steric features of the non-C_2-symmetric chiral salen Mn(III) complex **2** improve the enantioselectivity collectively [27,28]; however, when complex **4** was used as catalyst, an ee value of only 21% with a 75% yield

Table 1
The results of the asymmetry epoxidation of styrene over different chiral salen Mn(III) complexes

Catalyst	Run times	Yield (%)[b]	ee (%)[c]	TOF[d] × 10^{-3} (s^{-1})
No		32	0 (R)	–
Complex **1**[a]	Fresh	92	35 (R)	3.19
Complex **2**[a]	Fresh	99	40 (R)	3.44
	2nd	98	38 (R)	3.41
	3rd	98	38 (R)	3.41
	5th	98	38 (R)	3.41
	10th	98	38 (R)	3.41
Complex **3**[a]	Fresh	98	35 (R)	3.42
	2nd	98	35 (R)	3.42
	10th	98	34 (R)	3.42
Complex **4**[a]	Fresh	75	21 (R)	2.60
	2nd	55	8 (R)	1.91
	3rd	38	0	1.32

[a] Catalyst (4% of styrene), styrene (0.5 mmol), PyNO (1 mmol), m-CPBA (1 mmol), 1 mL CH_2Cl_2, 2 h, 0 °C.
[b] Yield of the isolated epoxide.
[c] Determined by GC.
[d] Turnover frequency (TOF) is calculated by the expression of [product]/[catalyst] × time (s^{-1}).

of the styrene epoxide was obtained. A possible explanation for this finding might be that axial ligation has a critical influence on the catalytically active species [29]; an overly strong coordination between the metal center of the chiral salen Mn(III) complex and the amino group of the IL results in occupation of most of the coordination sites, eventually leading to decreased formation of the active oxygen transfer species (Mn(V)–oxo) in the enantioselective epoxidation of styrene [30].

We also found that the synthesized IL-functionalized chiral salen Mn(III) complexes **2**, **3**, and **4** were immiscible with hexane and thus could be readily separated from the reaction system by the addition of hexane for the subsequent catalytic runs. Table 1 characterizes the recovery and reusability of these complexes. Obviously, complexes **2** and **3** could be reused at least 10 times with no significant loss of activity and enantioselectivity, whereas the recycling of complex **4** led to an apparent drop in both activity and enantioselectivity. This finding may indicate that the strong coordination of amino group (–NH_2) in the IL with the metal center of the chiral salen Mn(III) complex led to an increase in electron density of the metal center, making complex **4** less resistant to oxidative degradation [31,32]. In addition, the undesirable axial coordination may have led to a distortion of the coordination sphere of the manganese in the triplet state, decreasing the stability of the complex [29].

The reuse properties of the three new complexes were further confirmed by UV–vis (Fig. 3) and FT-IR spectra (Fig. 4). No significant changes were seen in the UV–vis and FT-IR spectra of complexes **2** and **3** even after 10 reuses; however, complex **4** lost the characteristic absorbance peaks in UV–vis spectra completely after 3 reuses (see Fig. 3), implying that complex **4** is destroyed during the oxidative reaction. Nevertheless, the novel complexes **2** and **3** showed high efficiency in the enantioselective epoxidation of styrene. More importantly, they had the property of tunable separation, facilitating their recycling and reuse. In the goal to gain a better understanding of this unique

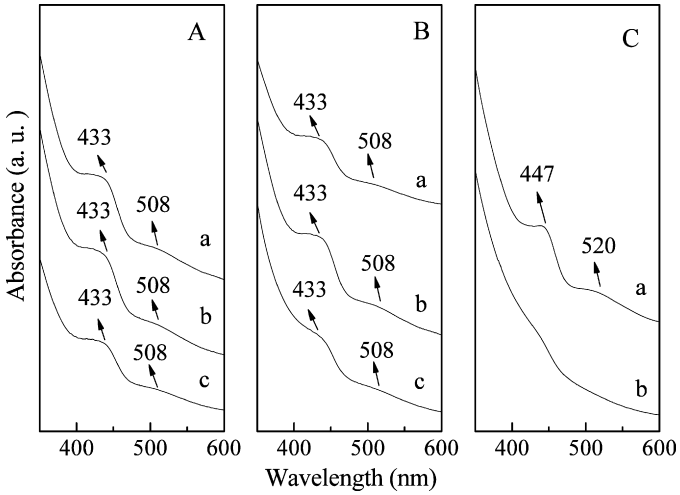


Fig. 3. UV–vis spectra of the fresh complex **2** (A-a), the complex **2** after the first reaction (A-b), and the complex **2** after the 10th reaction (A-c); the fresh complex **3** (B-a), the complex **3** after the first reaction (B-b), and the complex **3** after the 10th reaction (B-c); the fresh complex **4** (C-a), the complex **4** after the third reaction (C-b).

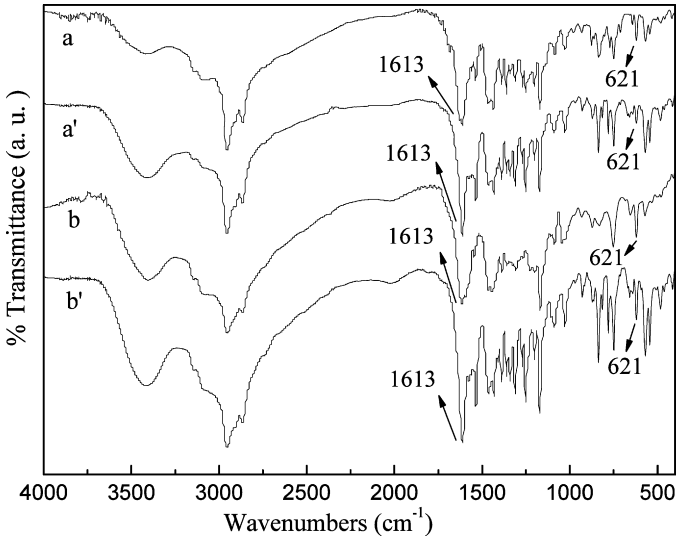


Fig. 4. FT-IR spectra of the fresh complex **2** (a) and the complex **2** after the 10th reaction (a′); the fresh complex **3** (b) and the complex **3** after the 10th reaction (b′).

catalytic system, complex **2** was selected as the typical catalyst to investigate the effects of various solvents, axial bases, and reaction temperatures on the enantioselective epoxidation of styrene.

3.3. Effect of solvent

Table 2 summarizes the results of a comparative study of the enantioselective epoxidation of styrene over the catalyst of complex **2** in various solvents. As expected, the catalytic activity and enantioselectivity were related to the solvent. If the IL-functionalized chiral salen Mn(III) complex **2** could be dissolved completely in the reaction system, then the yield of epoxide and the ee value should be high. It was found that only a 33% yield with a 12% ee value was obtained when

Table 2
The results of the enantioselective epoxidation of styrene in different solvent over the complex **2**[a]

Solvent	Yield (%)[b]	ee (%)[c]	TOF[d] × 10^{-3} (s^{-1})
n-Hexane	33	12 (R)	1.15
Dichloromethane	99	40 (R)	3.44
Ethyl acetate	98	35 (R)	3.41
Acetone	96	35 (R)	3.34
Acetonitrile	87	27 (R)	3.02

[a] Catalyst (4% in 1 mL solvent), styrene (0.5 mmol), PyNO (1 mmol), m-CPBA (1 mmol), 2 h, 0 °C.
[b] Same as in Table 1.
[c] Same as in Table 1.
[d] Same as in Table 1.

Table 3
The results of the enantioselective epoxidation of styrene catalyzed by the complex **2** in the presence of different axial base

Axial base	Yield (%)[b]	ee (%)[c]	TOF[d] × 10^{-3} (s^{-1})
–	52	0	1.80
PyNO[a]	99	40 (R)	3.44
4-PPPyNO[a]	99	39 (R)	3.44
4-PhPyNO[a]	98	39 (R)	3.41
NMO[e]	99	44 (R)	3.44

[a] Catalyst (4% in 1 mL CH_2Cl_2), styrene (0.5 mmol), axial base (1 mmol), m-CPBA (1 mmol), 2 h, 0 °C.
[b] Same as in Table 1.
[c] Same as in Table 1.
[d] Same as in Table 1.
[e] Catalyst (4% in 1 mL CH_2Cl_2), styrene (0.5 mmol), NMO (2 mmol), m-CPBA (1 mmol), 2 h, 0 °C.

the reaction was performed in hexane, due to the immiscibility of the complex **2** with hexane. For dichloromethane, ethyl acetate, and acetone, a yield of >96% and ee of 35% could be obtained, because complex **2** can be miscible with these solvents. The enantioselectivity was lower in ethyl acetate and acetone than in dichloromethane, possibly indicating that the solvent containing oxygen or nitrogen atoms with a lone electron pair can induce coordination with the metal center of the chiral salen Mn(III) complex, suppressing formation of the active oxygen transfer species (Mn(V)–oxo) in the epoxidation of styrene [30]. In particular, a yield of only 87% with an ee of 27% was obtained in acetonitrile, due to the strong coordination of nitrogen atoms with manganese ions, even though complex **2** was miscible with acetonitrile. Therefore, dichloromethane is considered a suitable solvent for the catalytic enantioselective epoxidation presented here, giving the highest epoxide yield (99%) and ee value (40%).

3.4. Effect of axial bases

Axial bases, which are only weakly bound to the manganese center, have remarkable effects on both the activity and enantioselectivity of the enantioselective epoxidation by activating and stabilizing the catalyst [33–35]. Table 3 summarizes the comparative results of the enantioselective epoxidation of styrene in the presence of various axial bases of PyNO, 4-PhPyNO, 4-PPPyNO, and NMO using complex **2** as the catalyst. Rather low activity (52% yield) and only racemic styrene epoxides were obtained in the absence of an axial base even at low reaction temperatures, suggesting that the axial base plays a very important role in improving catalytic activity and enantioselectivity. As expected, significant increases in the yield and enantioselectivity of the epoxide could be obtained by adding the axial base PyNO, 4-PhPyNO, 4-PPPyNO, or NMO, demonstrating that the addition of axial base is essential to the enantioselective epoxidation of styrene presented here. The axial base of NMO gave the highest enantioselectivity (44% ee) for the large steric hindrance on the N atom. In addition, Pietikiinen observed that in CH_2Cl_2, a salt is generated between NMO and m-CPBA that oxidizes the salen Mn(III) catalyst even at low temperature to form the catalytically active species Mn(V)–oxo complexes [35], thereby giving a high yield of the styrene epoxide (99%).

Table 4
The results of the enantioselective epoxidation of styrene at different temperature over the complex **2**[a]

Temperature (°C)	Yield (%)[b]	ee (%)[c]	TOF[d] × 10^{-3} (s^{-1})
−78	94	35 (R)	3.27
−40	99	50 (R)	3.44
−10	99	47 (R)	3.44
0	99	44 (R)	3.44
20	93	37 (R)	3.22
30	89	34 (R)	3.08

[a] Catalyst (4% in 1 mL CH_2Cl_2), styrene (0.5 mmol), NMO (2 mmol), m-CPBA (1 mmol), 2 h.
[b] Same as in Table 1.
[c] Same as in Table 1.
[d] Same as in Table 1.

3.5. Effect of reaction temperature

Table 4 summarizes the catalytic performance of the complex **2** at different reaction temperatures. The tables shows that the yield and enantioselectivity to the styrene epoxide with an *R*-configuration increased with decreasing reaction temperature from 30 to −40 °C. It is known that the enantiofacial selectivity in the initial C–O bond-forming step will be enhanced and that the trans-pathway in the second C–O bond-forming step will be suppressed when the epoxidation reaction is performed at low temperature [36]. Moreover, the second C–O bond-forming step provides an enantiometric leakage pathway for terminal olefins [37,38]. Therefore, the ee value can be increased with decreasing reaction temperature. Table 4 also shows that the yield of styrene epoxide decreased with an increase of reaction temperature from 0 to 30 °C; this is because the decomposition of the oxidant of m-CPBA increased, decreasing the catalytic efficiency of complex **2**. But further attempts to decrease reaction temperature from −40 to −78 °C resulted in decreases in epoxide yield and ee value. The solubility of the IL-functionalized chiral salen Mn(III) complex **2** likely was decreased at −78 °C in the reaction system; indeed, some granules of catalyst could be observed after the reaction. After optimizing the reaction conditions, a 99% epoxide yield with an ee of 50% could be

obtained when the reaction was performed at −40 °C using complex **2** as the catalyst and NMO as the axial base.

4. Conclusion

In this work, novel IL-functionalized chiral salen Mn(III) complexes were synthesized and used as catalysts in the enantioselective epoxidation of styrene. FT-IR, UV–vis spectra, elemental analyses, and mass spectra analyses indicated that the IL of 1-propylamine-3-methylimidazolium tetrafluoroborate can be successfully bonded onto the chiral salen Mn(III) complexes. The attachment position of chiral salen Mn(III) complex with IL has significant effects on catalytic activity and enantioselectivity. The chiral salen Mn(III)complex **2** prepared through covalent linkage of the amino group in the IL with the salen ligand at one side of the 5 position exhibited the best catalytic performance in the epoxidation reaction. Moreover, the synthesized IL-functionalized chiral salen Mn(III) complexes could be conveniently separated from the reaction system through simple hexane extraction. Among these, the complexes of **2** and **3** are stable and can be readily recovered for reuse. These observations suggested that the tunable separation complexes presented here are promising chiral catalysts for the enantioselective epoxidation of nonfunctional olefins.

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