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Synthesis of novel spiro imidazolium salts as chiral ionic liquids

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Abstract—A library of 13 novel chiral spiro imidazolium salts has been synthesized. The effects of *N*-substituents and counteranions on the melting point of spiro bis(imidazolium) salts are studied in efforts toward the development of room temperature chiral ionic liquids.

1. Introduction

In recent years the use of ionic liquids in environmentally benign chemical processes[1] and chemical analyses[2] has dramatically increased. Chiral ionic liquids are expected to show significant chirality transfer in asymmetric reactions due to their unique physical properties[3] and high degree of organization.[4] Consequently, considerable efforts have been made to synthesize various chiral ionic liquids, which are mainly derived from chiral pools toward potential applications in asymmetric synthesis.[5,6] Although some of these chiral ionic liquids exhibited promising results,[7] difficulties in structural refinement and the inaccessibility of both enantiomers limited their applications for asymmetric induction. Moreover, the structure of the chiral cation plays an important role in various organic reactions. For example, the use of imidazolium derived ionic liquids under basic conditions results in the formation of an undesired side product due to deprotonation at the acidic C(2) hydrogen of the imidazolium ring.[8] On the other hand, such imidazolium salts are excellent precursors for Arduengo-type carbenes.[9] Therefore, structural diversity oriented design and the availability of both enantiomers are the major goals in the synthesis of novel chiral ionic liquids in order for their potential applications in asymmetric synthesis to be realized. Previously, we have demonstrated the effective use of rigid chiral spiro ligands for asymmetric catalysis,[10] spiro compounds as potential phase transfer catalysts,[11] and spiro imidazolium salts as chiral ionic liquids.[12] Herein, we report a detailed study on the design and syntheses of two types of novel chiral spiro imidazolium salt derived ionic liquids.

Keywords: Chiral ionic liquids; Spiro imidazolium salts; Diastereomeric interaction.
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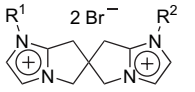
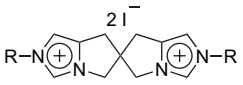
2. Results and discussion



1a: R^1 = Me, R^2= Me,
1b: R^1 = *i*-Pr, R^2 = *i*-Pr
1c: R^1 = Me, R^2= Et
1d: R^1 = *i*-Pr, R^2= Pr

Chiral Spiro
Imidazolium Salt **1**

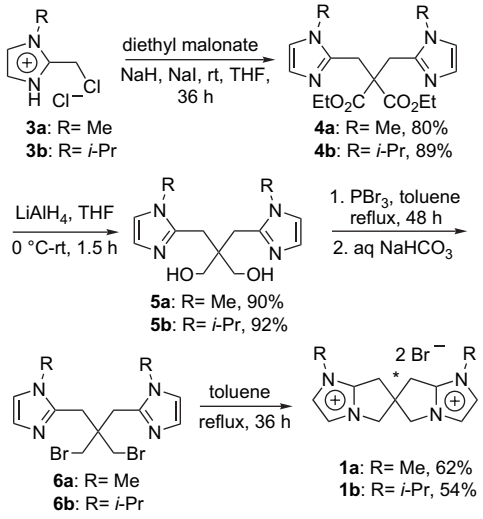


2a: R= *i*-Pr
2b: R= *n*-Bu

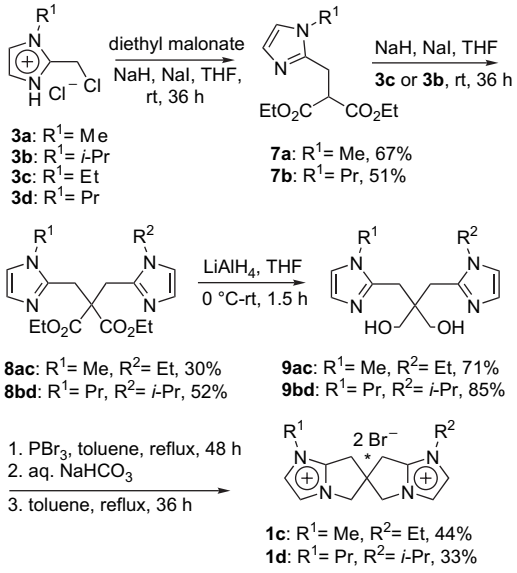
Chiral Spiro
Imidazolium Salt **2**

Two types of chiral spiro imidazolium salts **1** and **2** with a rigid spiro skeleton as the chiral backbone were designed. The present design is concise with a feasible scope for easy structural refinement, e.g., a variety of *N*-substituted chiral spiro ionic liquids can be derived from the common precursors, C(2) position substituted imidazolium salts **1a–d** and C(2) position unsubstituted imidazolium salts **2a**,**b**. Additionally, the chiral spiro imidazolium salt **2**, which contains a relatively acidic hydrogen at the C(2) imidazole position, facilitates the generation of chiral spiro *N*-heterocyclic carbenes. First, a modular approach for the synthesis of various rigid chiral spiro imidazolium salts **1a–d** was developed as depicted in Schemes 1 and 2.

The alkylation of diethyl malonate with 2-chloromethyl-3-methyl-1*H*-imidazolium hydrochloride (**3a**)[13] followed by reduction with LAH, produced diol **5a**, which upon treatment with PBr_3 afforded dibromide **6a**.[14] The intramolecular N-alkylation of **6a** smoothly produced the desired spiro bis(imidazolium) salt **1a**. Similarly, spiro bis(imidazolium) salt **1b** was synthesized starting from 2-chloromethyl-3-(2-propyl)-1*H*-imidazolium hydrochloride (**3b**).[15]



Scheme 1. Synthesis of symmetrical spiro bis(imidazolium) salts **1a**,**b**.



Scheme 2. Synthesis of unsymmetrical spiro bis(imidazolium) salts **1c**,**d**.

We further envisaged the synthesis of unsymmetrical chiral spiro imidazolium salts **1c**,**d**, given the previously established role of unsymmetrical cations in lowering the melting point of imidazolium salts due to crystallographic disorder.[5f,16]

The synthetic route for the preparation of unsymmetrical spiro imidazolium salts **1c**,**d** is depicted in Scheme 2. The monoalkylation of diethyl malonate with **3a** produced compound **7a**, which upon a second alkylation with 2-chloromethyl-3-ethyl-1*H*-imidazolium hydrochloride (**3c**)[15] afforded diester **8ac**. Further reduction of **8ac** with LAH followed by treatment with PBr_3 and intramolecular N-alkylation produced the desired unsymmetrical spiro bis(imidazolium) salt **1c**. The unsymmetrical spiro bis(imidazolium) salt **1d** was prepared from **3b** and **7b** following a similar synthetic protocol described for **1c**.

In order to gain insight into the effects of *N*-substituents and counteranions on melting point, spiro imidazolium salts **1a–d** were subjected to counteranion exchange. The treatment of **1a** with $(CF_3SO_2)_2NLi$ afforded the spiro imidazolium bis(trifluoromethanesulfonyl)imide derivative **1e** in excellent yield. The counteranion exchange of spiro imidazolium salts **1b–d** was carried out by a similar procedure to afford **1f–i**.

The rigid spiro skeleton was unequivocally confirmed by X-ray crystallographic analysis of **1e** (Fig. 1).[17]

The melting points of the spiro imidazolium salts with various *N*-substituents and counteranions are reported in Table 1.

The spiro imidazolium salts **1a–c** with bromide counteranions displayed high melting points (Table 1, entries 1–3), while the melting point of **1d** decreased dramatically (Table 1, entry 4). A considerable decrease in melting point was observed for bis(imidazolium) salts **1e** and **1f** having two $(CF_3SO_2)_2N^-$ counteranions (Table 1, entries 5 and 6). Furthermore, the long fluoroalkyl chain $[CF_3(CF_2)_2SO_2]_2N^-$ counteranion produced a room temperature ionic liquid **1g** with a glass transition temperature (T_g) of −10 °C (Table 1, entry 7). We compared melting points of *N*-methyl-*N*′-ethyl substituted unsymmetrical bis(imidazolium) salt **1h** with its symmetrical analogue **1e** (R^1=R^2=Me), however, no significant difference in the melting point was observed (Table 1, entries 8 and 5).

Notably, the melting point of *N*-isopropyl-substituted symmetrical spiro imidazolium salt **1f** was below 100 °C (Table 1, entry 6) and its unsymmetrical analogue **1i**, with *N*-propyl-*N*′-isopropyl substituents was a liquid at rt (T_g=−20 °C) (Table 1, entry 9). These results are consistent with the hypothesis that unsymmetrical substitution on imidazolium salts causes inefficient crystal packing resulting in lower melting ionic liquids.[5f,16]

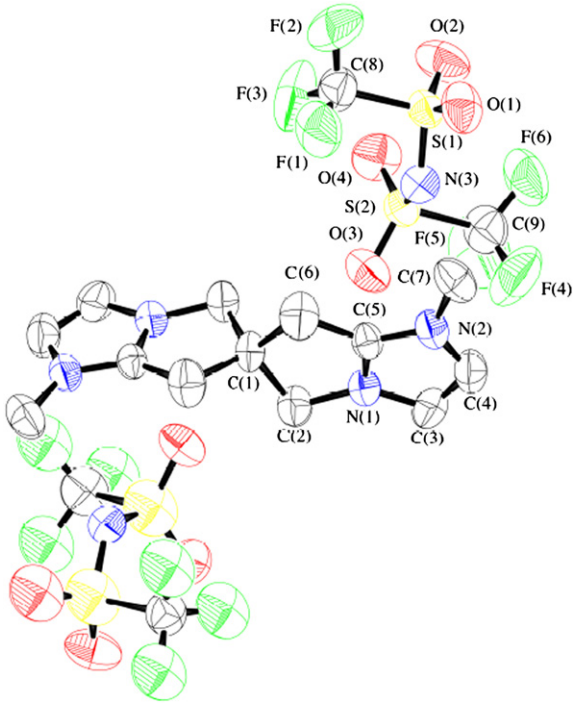
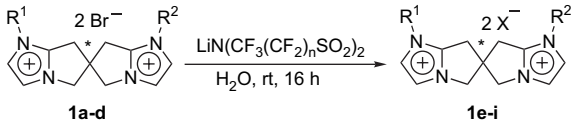


Figure 1. X-ray crystal structure of **1e**.

Table 1. Effects of *N*-substituents and counteranions on melting points



Entry	Imidazolium salt	R^1	R^2	Counteranion (X)	Mp or *Tg* (°C)
1	**1a**	Me	Me	Br	>300[a]
2	**1b**	*i*-Pr	*i*-Pr	Br	>300[a]
3	**1c**	Me	Et	Br	>300[a]
4	**1d**	Pr	*i*-Pr	Br	120[a]
5	**1e**	Me	Me	$N(CF_3SO_2)_2$	112[a]
6	**1f**	*i*-Pr	*i*-Pr	$N(CF_3SO_2)_2$	68[a]
7	**1g**	*i*-Pr	*i*-Pr	$N(CF_3CF_2CF_2SO_2)_2$	−10[b]
8	**1h**	Me	Et	$N(CF_3SO_2)_2$	116[a]
9	**1i**	Pr	*i*-Pr	$N(CF_3SO_2)_2$	−20[b]

[a] Melting point (mp).
[b] Glass transition temperature (T_g).

As a preliminary study on the chiral discrimination ability of the novel spiro imidazolium salts, the diastereomeric interaction between racemic cation **1b** and (*S*)-Mosher's acid[18] as chiral anion was examined. The counteranion exchange was carried out in situ by treating racemic **1b** with the potassium salt of (*S*)-2-methoxy-2-(trifluoromethyl)phenylacetate in the presence of 18-crown-6 (Fig. 2).

The ^{1}H NMR spectrum of racemic spiro imidazolium salt **1b** exhibited two pairs of doublets (Fig. 2a). The upfield doublets at δ 4.09 (Ha) and 4.41 (Hb) correspond to the methylene protons of the spiro skeleton fused to the imidazole ring, whereas the downfield doublets at δ 4.89 (Hc) and 5.02 (Hd) represent the *N*-CH_2 protons. Changing the counteranion from bromide to a chiral anion shows further splitting in the pairs of doublets (Ha–d), suggesting that enantiomers of racemic cation **1b** could sense chirality of anion differently (Fig. 2b). These results demonstrate the potential of spiro imidazolium salts in molecular recognition studies.

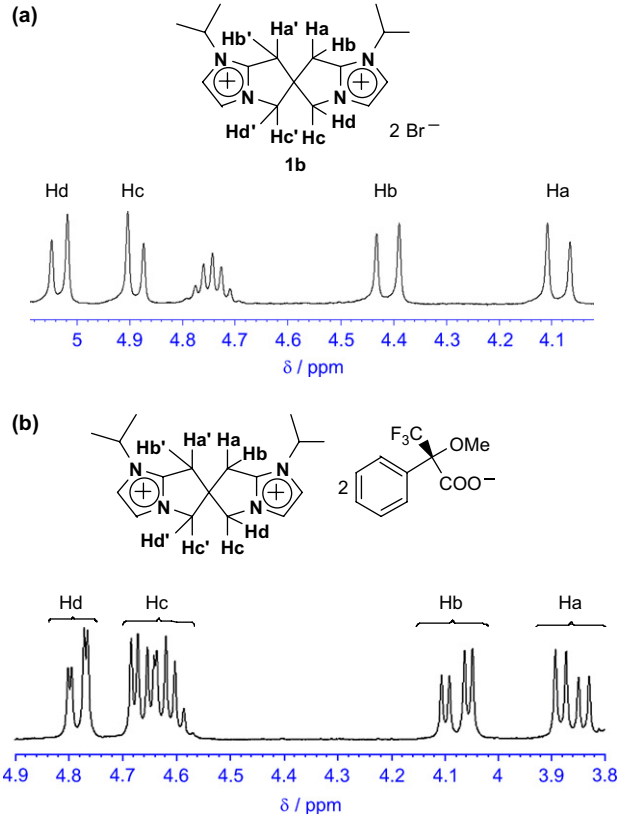


Figure 2. (a) ^{1}H NMR spectrum of **1b** in 20% DMSO-d_6–$CDCl_3$, (b) ^{1}H NMR spectrum of **1b** and potassium salt of (*S*)-Mosher's acid in 20% DMSO-d_6–$CDCl_3$ in the presence of 18-crown-6.

Optical resolution of these novel chiral spiro bis(imidazolium) salts **1a–d** was attempted by diastereomeric salt formation with (1*S*)-(+)-10-camphorsulfonic acid. Thus spiro imidazolium salt **1b** was treated with silver(I) camphorsulfonate in methanol to produce corresponding diastereomeric salt, which showed excellent splitting for methylene and *N*-CH_2 protons of spiro imidazolium cation as observed in Figure 2b. Such splitting arose from the diastereomeric interaction of racemic spiro imidazolium cation and chiral anion, however, repeated recrystallizations of obtained diastereomeric salt failed to afford a single diastereomer. After screening several conditions, the optical resolution of **1b** was achieved by HPLC using a chiral stationary phase column, Sumichiral OA-4500. The enantiomers of **1b** exhibited opposite optical rotations, which upon counteranion exchange using $[CF_3(CF_2)_2SO_2]_2NLi$ produced enantiomerically pure chiral spiro ionic liquids (+)-**1g** and (−)-**1g** with glass transition temperatures (T_g) of −10 and −11 °C, respectively.

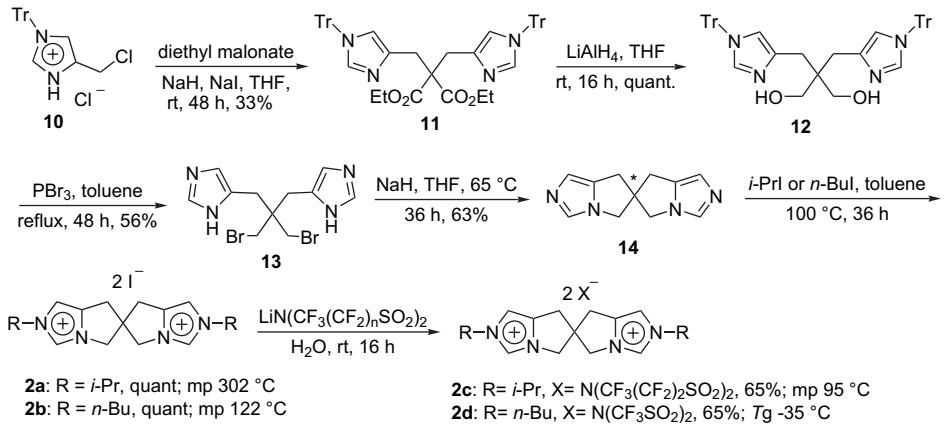
We further extended the protocol for preparation of salts **1** toward the synthesis of a new type of chiral spiro imidazolium salt **2**. The spiro imidazole **14**, an important precursor for the synthesis of imidazolium salt **2**, was prepared starting from 4-(chloromethyl)-1-trityl-1*H*-imidazolium hydrochloride **10**[19] (Scheme 3). Alkylation of diethyl malonate with **10** resulted in the formation of diester **11**, which was transformed into diol **12** upon reduction with LAH. The treatment of diol **12** with PBr_3 and subsequent intramolecular N-alkylation afforded spiro imidazole **14**.

Next, quaternization of chiral spiro imidazole **14** was performed. Based on the results obtained for spiro imidazolium salt **1g** (Table 1, entry 7), spiro imidazole **14** was treated with 2-iodopropane in toluene at 100 °C to afford spiro imidazolium salt **2a** in quantitative yield.

The structure of **2a** was confirmed by X-ray crystallographic analysis (Fig. 3).[20]

Further anion exchange of **2a** with $[CF_3(CF_2)_2SO_2]_2NLi$ produced spiro imidazolium salt **2c**, however, it exhibited a high melting point (mp 95 °C). In order to obtain a low melting imidazolium salt, a long alkyl substituent was introduced on the nitrogen of spiro imidazole **14**. Accordingly, treatment of **14** with *n*-iodobutane followed by counteranion exchange with $(CF_3SO_2)_2NLi$ resulted in room temperature chiral spiro ionic liquid **2d** with a glass transition temperature (T_g) of −35 °C.[21]

The optical resolution of spiro imidazole **14** was achieved by HPLC using a chiral stationary phase column (Daicel Chiralpak IB). Each enantiomer of spiro imidazole **14** obtained using preparative HPLC was subjected to quaternization



Scheme 3. Synthesis of spiro bis(imidazolium) salts **2c**,**d**.

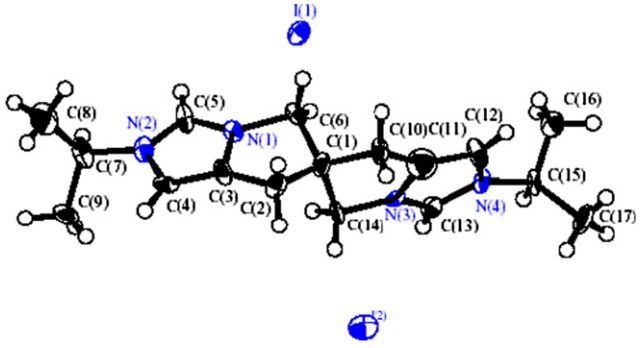


Figure 3. X-ray crystal structure of **2a**.

using *n*-iodobutane to give enantiomers of **2b**. Each enantiomer of spiro imidazolium salt **2b** was subjected to counteranion exchange to afford the corresponding enantiomerically pure room temperature spiro ionic liquids, (+)-**2d** and (−)-**2d**, with glass transition temperatures (T_g) of −30 °C and −33 °C, respectively.

Furthermore, the imidazolium salt **2** is a precursor for the generation of novel chiral spiro *N*-heterocyclic carbenes with potential applications in asymmetric synthesis.[22,23]

3. Conclusion

We have designed and synthesized a library of 13 novel chiral spiro imidazolium salts. Room temperature ionic liquids were produced from both types of spiro imidazolium salts **1** and **2** by appropriately selecting *N*-substituents and counteranions. As a preliminary study, we have also demonstrated the chiral discriminating abilities of spiro imidazolium salts. Further studies on the applications of chiral spiro imidazolium salt derived ionic liquids and *N*-heterocyclic carbenes are in progress.

4. Experimental section

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-EX270 (^{1}H NMR, 270 MHz; ^{13}C NMR, 68 MHz) and JEOL JNM-LA400 (^{1}H NMR, 400 MHz) spectrometers. ^{19}F NMR was recorded on a Bruker ARX400 (^{19}F NMR, 376 MHz) spectrometer. All signals were expressed as parts per million downfield from tetramethylsilane, used as an internal standard (for ^{1}H and ^{13}C NMR) and trifluoroacetic acid, used as an external standard (for ^{19}F NMR). IR spectra were obtained with a Shimadzu FTIR-8300 spectrometer. Elemental analyses were performed on a Perkin–Elmer 2400 elemental analyzer. ESI-HRMS spectra were obtained on a JMS-T100LC mass spectrometer and FAB-HRMS spectra were obtained on a JEOL JMS-700 mass spectrometer. X-ray crystallographic analysis was carried out with a Rigaku AFC-7R diffractometer, and all calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Melting points (mp) were measured with Yanaco micro melting point apparatus model MP-S9 and glass transition temperatures (T_g) by differential scanning calorimetry (DSC) on a Shimadzu DSC-60 (processing software: TA-60WS). Column chromatography was performed using Kanto Silica Gel 60 (40–100 μm). Anhydrous THF and toluene were purchased from Kanto Chemicals, Tokyo.

4.2. Representative procedure for the synthesis of symmetrical spiro bis(imidazolium) salts (1a,b)

4.2.1. Diethyl 2,2-bis(1-methyl-1*H*-imidazol-2-ylmethyl)-malonate (4a). To a stirred solution of diethyl malonate (0.72 mL, 4.5 mmol) in dry THF (20 mL) was added NaH (60% dispersed in mineral oil) (880 mg, 22 mmol) at 0 °C under argon atmosphere. After stirring at rt for 30 min, the reaction mixture was cooled to 0 °C and **3a** (1.8 g, 11 mmol) was added in portions over 10 min, followed by addition of NaI (1.6 g, 11 mmol). The resulting mixture was allowed to stir at rt for 36 h. The reaction mixture was then poured into ice-cold water (100 mL) and extracted with dichloromethane (50 mL×3). The combined organic layer was washed with water, brine and dried over sodium sulfate. The residue obtained on evaporation of solvent was purified by silica gel column chromatography (MeOH/CH_2Cl_2=3:97 as eluent) to give **4a** (1.2 g, 80%) as a pale yellow oil. IR (neat): ν_{max} 1734, 1558, 1541, 1507, 1204, 864, 746 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.16 (t, J=7.0 Hz, 6H), 3.43 (s, 6H), 3.55 (s, 4H), 4.20 (q, J=7.0 Hz, 4H), 6.70 (d, J=1.4 Hz, 2H), 6.88 (d, J=1.4 Hz,

2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 14.0, 28.2, 32.6, 56.4, 61.8, 120.2, 127.05, 144.1, 169.9. Compound **4a** was used directly in further reactions.

4.2.2. Diethyl 2,2-bis[1-(2-propyl)-1*H*-imidazol-2-ylmethyl]malonate (4b). Compound **4b** was obtained in 89% yield (1.6 g) from **3b** (2.14 g, 11 mmol) using a similar procedure as for **4a**.

IR (neat): ν_{max} 1731, 1424, 1212, 870, 740 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.18 (t, J=7.0 Hz, 6H), 1.26 (d, J=6.8 Hz, 12H), 3.64 (s, 4H), 4.22 (q, J=7.0 Hz, 4H), 4.35 (sept, J=6.8 Hz, 2H), 6.85–6.86 (m, 2H), 6.98–6.99 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 14.0, 23.5, 28.4, 47.0, 56.4, 62.0, 114.6, 127.0, 142.8, 169.9; MS (ESI-HRMS) calcd for $C_{21}H_{32}N_4O_4$ $[M]^+$: 404.2424, found: 404.2457.

4.2.3. 2,2-Bis(1-methyl-1*H*-imidazol-2-ylmethyl)propane-1,3-diol (5a). Lithium aluminum hydride (645 mg, 17 mmol) was added to a stirred solution of ester **4a** (1.35 g, 3.9 mmol) in dry THF (20 mL) at 0 °C under argon atmosphere. The resulting reaction mixture was stirred at 0 °C for 30 min and then at rt for 1 h. Excess lithium aluminum hydride was quenched by addition of $MgSO_4\cdot 10H_2O$. The resulting white solid was removed by filtration through Celite and evaporation of the solvent afforded diol **5a** (0.9 g, 90%) as a white gummy material. IR (neat): ν_{max} 2937, 1653, 1527, 1490, 1412, 1282, 1154, 1079, 1044, 935, 741 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.89 (s, 4H), 3.23 (s, 4H), 3.51 (s, 6H), 6.76 (d, J=1.4 Hz, 2H), 6.92 (d, J=1.4 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 29.8, 33.1, 45.8, 65.7, 120.5, 126.2, 146.1; MS (FAB-HRMS) calcd for $C_{13}H_{21}N_4O_2$ $[M+H]^+$: 265.1659, found: 265.1677.

4.2.4. 2,2-Bis[1-(2-propyl)-1*H*-imidazol-2-ylmethyl]propane-1,3-diol (5b). Compound **5b** was obtained in 92% yield (1.15 g) from ester **4b** (1.58 g, 3.9 mmol) by a similar procedure as for **5a**.

Mp 119–122 °C (EtOAc/hexane); IR (neat): ν_{max} 3367, 2971, 1455, 1268 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.28 (d, J=6.7 Hz, 12H), 2.94 (s, 4H), 3.24 (s, 4H), 4.41 (sept, J=6.7 Hz, 2H), 6.85–6.86 (m, 2H), 6.93–6.94 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 23.7, 30.1, 45.4, 47.2, 66.2, 114.6, 126.5, 144.8; MS (ESI-HRMS) calcd for $C_{17}H_{28}N_4O_2$ $[M]^+$: 320.2212, found: 320.2233.

4.2.5. 6,6′-Spirobi(1-methyl-1,5,6,7-tetrahydropyrrolo[1,2-*a*]-imidazolium)dibromide (1a). A solution of diol **5a** (714 mg, 2.7 mmol) and PBr_3 (8 mL) in toluene (20 mL) was stirred at reflux for 48 h under argon atmosphere. The reaction mixture was then allowed to cool and the toluene layer was decanted. The residue was washed three times with toluene and then neutralized with saturated aqueous sodium bicarbonate solution followed by extraction with dichloromethane (50 mL×3). The combined organic layer was washed with water, brine and dried over sodium sulfate. Evaporation of solvent afforded **6a** as a brown oil, which was directly subjected to cyclization without further purification. A solution of **6a** in toluene (10 mL) was refluxed for 36 h under argon atmosphere. Evaporation of toluene and precipitation by adding dichloromethane produced **1a** (653 mg, 62%) as a white solid: mp >300 °C (CH_2Cl_2/MeOH); IR (neat): ν_{max} 2947, 2835, 2520, 2039, 1659, 1555, 1449, 1113, 1026 cm^{-1}; ^{1}H NMR (270 MHz, CD_3OD): δ 3.68 (s, 4H), 3.87 (s, 6H), 4.62 (s, 4H), 7.56–7.57 (m, 4H); ^{13}C NMR (68 MHz, CD_3OD): δ 35.9, 36.8, 57.9, 59.7, 119.3, 128.3, 151.6; MS (ESI-HRMS) calcd for $C_{13}H_{18}BrN_4$ $[M-Br]^+$: 309.0709, found: 309.0699.

4.2.6. 6,6′-Spirobi{1-(2-propyl)-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium}dibromide (1b). Spiro bis(imidazolium) dibromide (**1b**) was obtained in 54% yield (650 mg) from diol **5b** (864 mg, 2.7 mmol) under reaction conditions identical to **1a**.

Mp >300 °C (CH_2Cl_2/MeOH); IR (neat): ν_{max} 2948, 2836, 2518, 2033, 1650, 1024 cm^{-1}; ^{1}H NMR (270 MHz, CD_3OD): δ 1.58 (dd, J=1.8, 6.8 Hz, 12H), 3.71–3.86 (m, 4H), 4.59–4.67 (m, 6H), 7.58–7.59 (m, 2H), 7.73–7.74 (m, 2H); ^{13}C NMR (68 MHz, CD_3OD): δ 22.6, 22.7, 37.6, 54.1, 57.3, 59.3, 119.7, 141.9, 145.0; MS (ESI-HRMS) calcd for $C_{17}H_{26}BrN_4$ $[M-Br]^+$: 365.1341, found: 365.1355.

4.3. Representative procedure for the synthesis of unsymmetrical spiro bis(imidazolium) salts (1c,d)

4.3.1. Diethyl 2-(1-methyl-1*H*-imidazol-2-ylmethyl)malonate (7a). To a stirred solution of diethyl malonate (1.40 mL, 8.8 mmol) in dry THF (25 mL) was added NaH (60% dispersed in mineral oil) (612 mg, 15.3 mmol) at 0 °C under argon atmosphere. This mixture was allowed to stir at rt for 30 min. The reaction mixture was then cooled to 0 °C and **3a** (1.00 g, 5.9 mmol) was added in portions over 10 min, followed by addition of NaI (826 mg, 5.9 mmol). The resulting mixture was allowed to stir at rt for 36 h. The reaction mixture was then poured into ice-cold water (100 mL) followed by extraction with dichloromethane (50 mL×3). The combined organic layer was washed with water, brine and dried over sodium sulfate. The residue obtained on evaporation of solvent was purified by silica gel column chromatography (MeOH/CH_2Cl_2=5:95 as eluent) to give **7a** (1.00 g, 67%) as a pale yellow oil. IR (neat): ν_{max} 2984, 1732, 1525, 1497, 1466, 1417, 1371, 1340, 1281, 1239, 1173, 1096, 1033, 859, 754 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.25 (t, J=7.0 Hz, 6H), 3.21 (d, J=7.6 Hz, 2H), 3.62 (s, 3H), 4.11–4.29 (m, 5H), 6.76 (d, J=1.1 Hz, 1H), 6.91 (d, J=1.1 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 14.0, 25.5, 32.6, 50.1, 61.6, 120.5, 127.1, 144.7, 168.7. MS (FAB-HRMS) calcd for $C_{12}H_{18}N_2O_4$ $[M]^+$: 254.1267, found: 254.1278.

4.3.2. Diethyl 2-[1-(1-propyl)-1*H*-imidazol-2-ylmethyl]-malonate (7b). Similarly, **3d** (1.15 g, 5.9 mmol) produced ester **7b** in 51% yield (848 mg) as an oil.

IR (neat): ν_{max} 2969, 1735, 1272, 1159 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.94 (t, J=7.3 Hz, 3H), 1.24 (t, J=7.1 Hz, 6H), 1.70–1.81 (m, 2H), 3.19 (d, J=7.4 Hz, 2H), 3.85 (t, J=7.3 Hz, 2H), 4.13–4.26 (m, 5H), 6.79 (s, 1H), 6.90 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 11.2, 14.0, 24.3, 25.7, 47.4, 50.0, 61.6, 119.2, 127.2, 144.2, 168.8; MS (ESI-HRMS) calcd for $C_{14}H_{22}N_2O_4$ $[M]^+$: 282.1580, found: 282.1570.

4.3.3. Diethyl 2-(1-ethyl-1*H*-imidazol-2-ylmethyl)-2-(1-methyl-1*H*-imidazol-2-ylmethyl)malonate (8ac). To a stirred solution of **7a** (1.00 g, 3.9 mmol) in dry THF (20 mL) was added NaH (60% dispersed in mineral oil) (468 mg, 11.7 mmol) at 0 °C under argon atmosphere. This mixture was allowed to stir at rt for 30 min. The reaction mixture was then cooled to 0 °C and **3c** (854 mg, 4.7 mmol) was added in portions over 10 min, followed by addition of NaI (705 mg, 4.7 mmol). The resulting mixture was allowed to stir at rt for 24 h. The reaction mixture was then poured into ice-cold water (100 mL) followed by extraction with dichloromethane (50 mL×3). The combined organic layer was washed with water, brine and dried over sodium sulfate. The residue obtained on evaporation of solvent was purified by silica gel column chromatography ($MeOH/CH_2Cl_2$=5:95) to produce **8ac** (406 mg, 30%) as a pale yellow oil. IR (neat): ν_{max} 1714, 1421, 1363, 1335, 1093, 919, 734 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.14 (t, J=7.0 Hz, 6H), 1.24 (t, J=7.3 Hz, 3H), 3.44 (s, 2H), 3.46 (s, 3H), 3.50 (s, 2H), 3.82 (q, J=7.3 Hz, 2H), 4.16 (q, J=7.0 Hz, 4H), 6.82 (s, 1H), 6.87 (s, 1H), 6.92–6.95 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 13.8, 15.9, 27.7, 27.8, 33.0, 40.7, 56.5, 62.0, 118.7, 120.9, 125.7, 125.9, 142.5, 143.3, 169.3. MS (FAB-HRMS) calcd for $C_{18}H_{26}N_4O_4$ $[M]^+$: 362.1954, found: 362.1932.

4.3.4. Diethyl 2-[1-(1-propyl)-1*H*-imidazol-2-ylmethyl]-2-[1-(2-propyl)-1*H*-imidazol-2-ylmethyl]malonate (8bd). The ester **8bd** was obtained in 52% yield (819 mg) as an oil from compounds **7b** (1.10 g, 3.9 mmol) and **3b** (916 mg, 4.7 mmol) in a similar fashion.

IR (neat): ν_{max} 1733, 1716, 1420, 1335, 1010, 918 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.81 (t, J=7.4 Hz, 3H), 1.14–1.25 (m, 12H), 1.52–1.60 (m, 2H), 3.58–3.65 (m, 4H), 4.10–4.34 (m, 7H), 6.70 (s, 1H), 6.80 (s, 1H), 6.90–6.95 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 11.1, 14.0, 23.4, 24.2, 28.4, 46.6, 47.1, 56.2, 61.8, 114.1, 114.2, 118.7, 127.2, 127.2, 143.1, 143.7, 170.1; MS (ESI-HRMS) calcd for $C_{21}H_{32}N_4O_4$ $[M]^+$: 404.2424, found: 404.2390.

4.3.5. 2-(1-Ethyl-1*H*-imidazol-2-ylmethyl)-2-(1-methyl-1*H*-imidazol-2-ylmethyl)propane-1,3-diol (9ac). Lithium aluminum hydride (167 mg, 4.4 mmol) was added portion wise to a stirred solution of ester **8ac** (362 mg, 1 mmol) in dry THF (15 mL) at 0 °C under argon atmosphere. The resulting reaction mixture was stirred at 0 °C for 30 min and then at rt for 1.5 h. Excess lithium aluminum hydride was quenched by slow addition of saturated aqueous sodium sulfate solution (5 mL) followed by filtration through Celite. Evaporation of the solvent afforded diol **9ac** (200 mg, 71%) as a colorless gummy oil. IR (neat): ν_{max} 3400, 2929, 1467, 1381, 1281, 1088, 908, 733 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.29 (t, J=7.3 Hz, 3H), 2.88 (s, 2H), 2.89 (s, 2H), 3.24 (s, 4H), 3.49 (s, 3H), 3.85 (q, J=7.3 Hz, 2H), 6.74 (d, J=1.1 Hz, 1H), 6.81 (d, J=1.1 Hz, 1H), 6.91 (d, J=1.1 Hz, 1H), 6.93 (d, J=1.1 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 16.3, 29.6, 30.1, 33.0, 40.9, 45.6, 65.8, 118.3, 120.4, 126.2, 126.3, 145.3, 146.1; MS (FAB-HRMS) calcd for $C_{14}H_{23}N_4O_2$ $[M+H]^+$: 279.1816, found: 279.1824.

4.3.6. 2-[1-(1-Propyl)-1*H*-imidazol-2-ylmethyl]-2-[1-(2-propyl)-1*H*-imidazol-2-ylmethyl]propane-1,3-diol (9bd). Compound **8bd** (404 mg, 1 mmol) was reduced under similar conditions to give diol **9bd** in 85% yield (272 mg).

IR (neat): ν_{max} 3450, 2968, 2361, 2342, 1270, 1080, 730 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.85 (t, J=7.3 Hz, 3H), 1.28–1.31 (m, 6H), 1.61 (q, J=7.3 Hz, 2H), 2.93 (s, 4H), 3.20 (s, 4H), 3.73 (t, J=7.2 Hz, 2H), 4.36–4.41 (m, 1H), 6.78 (s, 1H), 6.90 (s, 1H), 6.92–6.95 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 10.8, 23.2, 23.9, 29.6, 29.6, 44.9, 46.8, 47.1, 65.7, 114.3, 118.7, 125.8, 126.1, 144.3, 145.1; MS (FAB-HRMS) calcd for $C_{17}H_{29}N_4O_2$ $[M+H]^+$: 321.2285, found: 321.2278.

4.3.7. (1-Ethyl-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium)-6-spiro-6′-(1′-methyl-1′,5′,6′,7′-tetrahydropyrrolo-[1′,2′-*a*]imidazolium)dibromide (1c). A solution of diol **9ac** (150 mg, 0.53 mmol) and PBr_3 (1.5 mL) in toluene (10 mL) was stirred at reflux for 48 h under argon atmosphere. The reaction mixture was then allowed to cool and the toluene layer was decanted. The residue was washed three times with toluene and then neutralized with saturated aqueous sodium bicarbonate solution followed by extraction with dichloromethane (50 mL×3). The combined organic layer was washed with water, brine and dried over sodium sulfate. Evaporation of solvent afforded the corresponding dibromide, which was directly subjected to cyclization without further purification. A solution of crude dibromide in toluene (10 mL) was refluxed for 48 h under argon atmosphere. Evaporation of toluene and precipitation by adding dichloromethane produced spiro bis(imidazolium) dibromide (**1c**) (95 mg, 44%) as a white solid: mp >300 °C (CH_2Cl_2/MeOH); IR (neat): ν_{max} 3368, 2945, 2521, 2225, 2044, 1451, 1114, 1032 cm^{-1}; ^1H NMR (270 MHz, CD_3OD): δ 1.44 (t, J=7.3 Hz, 3H), 3.60–3.68 (m, 4H), 3.78 (s, 3H), 4.13 (q, J=7.3 Hz, 2H), 4.55–4.56 (m, 4H), 7.46–7.56 (m, 4H); ^{13}C NMR (68 MHz, CD_3OD): δ 15.1, 36.0, 36.9, 36.9, 45.6, 57.8, 59.4, 59.4, 119.5, 119.5, 126.6, 128.3, 150.7, 151.5; MS (FAB-HRMS) calcd for $C_{14}H_{20}BrN_4$ $[M-Br]^+$: 323.0866, found: 323.0857.

4.3.8. {1-(1-Propyl)-1,5,6,7-tetrahydropyrrolo[1,2-*a*]-imidazolium}-6-spiro-6′-{1′-(2-propyl)-1′,5′,6′,7′-tetrahydropyrrolo[1′,2′-*a*]imidazolium}dibromide (1d). Compound **9bd** (169 mg, 0.53 mmol) was treated with PBr_3 under similar reaction conditions to yield spiro bis(imidazolium) dibromide (**1d**) (78 mg, 33%).

Mp 118–120 °C (CH_2Cl_2/MeOH); IR (neat): ν_{max} 3391, 2948, 2836, 1024 cm^{-1}; ^1H NMR (270 MHz, CD_3OD): δ 1.01 (t, J=3.4 Hz, 3H), 1.56–1.59 (m, 6H), 1.91–1.97 (m, 2H), 3.58–3.61 (m, 2H), 3.76–3.80 (m, 2H), 4.12–4.17 (m, 2H), 4.29–4.34 (m, 2H), 4.64–4.66 (m, 3H), 7.54–7.65 (m, 4H); ^{13}C NMR (68 MHz, CD_3OD): δ 11.2, 18.4, 22.6, 24.0, 37.2, 37.5, 51.9, 54.1, 57.5, 59.2, 59.5, 119.5, 119.7, 124.5, 127.2, 149.9, 150.9; MS (FAB-HRMS) calcd for $C_{17}H_{26}BrN_4$ $[M-Br]^+$: 365.1335, found: 365.1327.

4.4. Representative procedure for counteranion exchange (Table 1)

4.4.1. 6,6′-Spirobi(1-methyl-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium) bis[bis(trifluoromethanesulfonyl)imide] (1e). To a stirred solution of bis(imidazolium)

salt (**1a**) (31 mg, 0.08 mmol) in water (3 mL) was added lithium bis(trifluoromethanesulfonyl)imide (49 mg, 0.17 mmol) at rt. The mixture was allowed to stir for 16 h. Precipitated solid was filtered and washed with water (5 mL) three times. Drying under reduced pressure at 100 °C gave **1e** (60 mg, 95%) as a white solid: mp 112 °C (CH_2Cl_2/MeOH); IR (neat): ν_{max} 1350, 1331, 1188, 1137, 1055 cm^{-1}; ^1H NMR (270 MHz, CD_3OD): δ 3.54 (s, 4H), 3.75 (s, 6H), 4.50 (s, 4H), 7.44–7.46 (m, 4H); ^{13}C NMR (68 MHz, CD_3OD): δ 35.7, 36.5, 57.8, 59.6, 119.2, 123.4, 128.4, 151.4; ^{19}F NMR (376 MHz, CD_3OD): δ −80.14; MS (ESI-HRMS) calcd for $C_{15}H_{18}F_6N_5O_4S_2$ $[M-Tf_2N]^+$: 510.0699, found: 510.0680.

4.4.2. 6,6′-Spirobi{1-(2-propyl)-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium} bis[bis(trifluoromethanesulfonyl)imide] (1f). Similarly, compound **1f** was obtained in 92% yield (62 mg) as a white solid from **1b** (35.6 mg, 0.08 mmol).

Mp 68 °C (CH_2Cl_2/MeOH); IR (neat): ν_{max} 1352, 1191, 1138, 1057 cm^{-1}; ^1H NMR (270 MHz, CD_3OD): δ 1.56 (dd, J=1.1, 6.8 Hz, 12H), 3.62–3.68 (m, 4H), 4.56–4.58 (m, 6H), 7.55–7.56 (m, 2H), 7.73–7.74 (m, 2H); ^{13}C NMR (68 MHz, CD_3OD): δ 22.5, 22.5, 37.4, 54.6, 57.2, 59.3, 119.6, 124.6, 142.0, 149.8; ^{19}F NMR (376 MHz, CD_3OD): δ −81.38; MS (ESI-HRMS) calcd for $C_{19}H_{26}F_6N_5O_4S_2$ $[M-Tf_2N]^+$: 566.1330, found: 566.1325. Anal. Calcd for $C_{21}H_{26}F_{12}N_6O_8S_4$: C, 29.79; H, 3.10; N, 9.93. Found: C, 29.92; H, 3.06; N, 9.80.

4.4.3. (1-Ethyl-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium)-6-spiro-6′-(1′-methyl-1′,5′,6′,7′-tetrahydropyrrolo-[1′,2′-*a*]imidazolium) bis[bis(trifluoromethanesulfonyl)-imide] (1h). The spiro bis(imidazolium)dibromide (**1c**) (32 mg, 0.08 mmol) yielded compound **1h** in 80% yield (51 mg) as a white solid.

Mp 116 °C (CH_2Cl_2/MeOH); IR (neat): ν_{max} 2072, 1655, 1449, 1350, 1119, 1031 cm^{-1}; ^1H NMR (270 MHz, CD_3OD): δ 1.51 (t, J=7.3 Hz, 3H), 3.63 (d, J=8.1 Hz, 4H), 3.84 (s, 3H), 4.18 (q, J=7.3 Hz, 2H), 4.58 (s, 4H), 7.53 (d, J=1.9 Hz, 1H), 7.56 (s, 2H), 7.56 (d, J=1.9 Hz, 1H); ^{13}C NMR (68 MHz, CD_3OD): δ 15.0, 35.7, 36.6, 36.7, 45.5, 57.7, 59.4, 59.7, 118.7, 119.3, 119.5, 126.7, 128.4, 151.2, 156.9; ^{19}F NMR (376 MHz, CD_3OD): δ −81.46. MS (ESI-HRMS) calcd for $C_{16}H_{20}F_6N_5O_4S_2$ $[M-Tf_2N]^+$: 524.0855, found: 524.0849.

4.4.4. {1-(1-Propyl)-1,5,6,7-tetrahydropyrrolo[1,2-*a*]-imidazolium}-6-spiro-6′-{1′-(2-propyl)-1′,5′,6′,7′-tetrahydropyrrolo[1′,2′-*a*]imidazolium} bis[bis(trifluoromethanesulfonyl)imide] (1i). Under identical conditions, spiro bis(imidazolium) salt (**1d**) (35.6 mg, 0.08 mmol) gave **1i** in 90% yield (61 mg) as a colorless oil.

T_g=−20 °C (determined by DSC); IR (neat): ν_{max} 1349, 1188, 1055 cm^{-1}; ^1H NMR (270 MHz, CD_3OD): δ 0.99 (t, J=7.4 Hz, 3H), 1.53–1.56 (m, 6H), 1.85–1.96 (m, 2H), 3.63 (d, J=8.2 Hz, 4H), 4.08 (t, J=7.2 Hz, 2H), 4.52–4.60 (m, 5H), 7.45 (dd, J=1.9, 2.1 Hz, 2H), 7.59 (d, J=1.9 Hz, 1H), 7.68 (d, J=2.1 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 11.0, 22.4, 22.5, 23.9, 37.1, 37.3, 51.8, 54.1, 57.4, 59.1, 59.5, 118.6, 119.3, 119.6, 123.3, 124.5, 127.2, 149.7, 150.7; ^{19}F NMR (376 MHz, CD_3OD): δ −81.28; MS (FAB-HRMS) calcd for $C_{19}H_{26}F_6N_5O_4S_2$ $[M-Tf_2N]^+$: 566.1330, found: 566.1301.

4.4.5. 6,6′-Spirobi{1-(2-propyl)-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium} bis[bis(heptafluoropropanesulfonyl)imide] (1g). Similarly **1g** was obtained in 85% yield (84 mg) as a colorless oil from **1b** (35.6 mg, 0.08 mmol) using lithium bis(heptafluoropropanesulfonyl)imide (83 mg, 0.17 mmol).

T_g=−10 °C (determined by DSC); IR (neat): ν_{max} 1355, 1171, 1067, 865 cm^{-1}; ^1H NMR (270 MHz, CD_3OD): δ 1.56 (dd, J=1.0, 6.8 Hz, 12H), 3.65–3.69 (m, 4H), 4.53–4.63 (m, 6H), 7.53–7.54 (m, 2H), 7.72–7.73 (m, 2H); ^{19}F NMR (376 MHz, CD_3OD): δ −83.17, −115.68, −126.41; MS (FAB-HRMS) calcd for $C_{23}H_{26}F_{14}N_5O_4S_2$ $[M-(CF_3CF_2CF_2SO_2)_2N)]^+$: 766.1197, found: 766.1206. Anal. Calcd for $C_{29}H_{26}F_{28}N_6O_8S_4$: C, 27.94; H, 2.10; N, 6.74. Found: C, 27.85; H, 2.14; N, 6.78.

4.5. NMR experiment for the distereomeric interaction of spiro bis(imidazolium) salt 1b with a chiral counteranion

To a solution of potassium (*S*)-2-methoxy-2-(trifluoromethyl)phenylacetate (potassium salt of Mosher's acid) (10 mg, 0.036 mmol) and 18-crown-6 (15 mg, 0.054 mmol) in 20% DMSO-d_6–$CDCl_3$, was added spiro bis(imidazolium) salt **1b** (8 mg, 0.018 mmol). The mixture was sonicated for 10 min in a NMR tube and the spectrum was recorded. ^1H NMR (400 MHz, 20% DMSO-d_6 in $CDCl_3$): δ 1.50–1.54 (m, 12H), 3.54 (s, 6H), 3.83 (d, J=8.0 Hz, 1H), 3.88 (d, J=8.0 Hz, 1H), 4.02 (d, J=5.9 Hz, 1H), 4.09 (d, J=5.9 Hz, 1H), 4.58–4.64 (m, 2H), 4.65 (d, J=5.1 Hz, 1H), 4.67 (d, J=4.9 Hz, 1H), 4.76 (d, J=2.7 Hz, 1H), 4.78 (d, J=2.6 Hz, 1H), 7.22–7.29 (m, 6H), 7.55 (d, J=6.3 Hz, 4H), 7.68–7.70 (m, 4H). The resonance for 18-crown-6 appeared at δ 3.28 as a singlet.

For comparison purposes, the ^1H NMR spectrum of **1b** was also recorded in 20% DMSO-d_6–$CDCl_3$: ^1H NMR (400 MHz, 20% DMSO-d_6 in $CDCl_3$): 1.60 (dd, J=6.5, 11.9 Hz, 12H), 4.09 (d, J=17.0 Hz, 2H), 4.41 (d, J=17.0 Hz, 2H), 4.70–4.77 (m, 2H), 4.89 (d, J=11.8 Hz, 2H), 5.02 (d, J=11.8 Hz, 2H), 7.43–7.46 (m, 2H), 7.49–7.55 (m, 2H).

4.6. Optical resolution of spiro bis(imidazolium) salt 1b

Spiro bis(imidazolium) salt **1b** was resolved by chiral HPLC. *Conditions*: Chiral stationary phase column SUMICHIRAL OA-4500 (4.6 mm ø×250 mm); hexane/2-propanol/methanol/trifluoroacetic acid (70:20:10:0.2), flow rate of 0.5 mL/min, UV detector (211 nm), temperature 40 °C, retention time 82 min and 84 min. *Preparative HPLC conditions*: Chiral stationary phase column SUMICHIRAL OA-4500 (20 mm ø×250 mm); hexane/2-propanol/methanol/trifluoroacetic acid (70:20:10:0.2), flow rate of 9.9 mL/min, UV detector (211 nm), temperature 25 °C, retention time 151.98 min and 168.38 min (recycled three times). First peak in HPLC $[\alpha]_D^{19}$ −1.86 (*c* 0.27, MeOH); second peak in HPLC $[\alpha]_D^{19}$ +1.79 (*c* 0.28, MeOH).

Counteranion exchange was carried out as described for *rac* **1g** to obtain enantiomerically pure ionic liquid **1g**. (−)-**1g**: $[\alpha]_D^{29}$ −1.74 (*c* 0.24, MeOH), T_g=−11 °C (determined by DSC). (+)-**1g**: $[\alpha]_D^{29}$ +1.75 (*c* 0.27, MeOH), T_g=−10 °C (determined by DSC).

4.6.1. Diethyl 2,2-bis(1-trityl-1*H*-imidazol-4-ylmethyl)-malonate (11). To a stirred solution of diethyl malonate (2.8 mL, 18.7 mmol) in dry THF (80 mL) was added NaH (60% dispersed in mineral oil) (4.5 g, 112.4 mmol) at 0 °C under argon atmosphere. After stirring at rt for 1 h, the reaction mixture was cooled to 0 °C and imidazolium salt **10**[19] (17 g, 43 mmol) was added in portions over 10 min, followed by addition of NaI (8.37 g, 56.2 mmol). The resulting mixture was allowed to stir at rt for 50 h. The reaction mixture was then poured into ice-cold water (100 mL) and extracted with dichloromethane (50 mL×3). The combined organic layer was washed with water, brine and dried over sodium sulfate. The residue obtained upon evaporation of solvent was purified by silica gel column chromatography (EtOAc/hexane=6:4) to give **11** (4.5 g, 30%) as a pale yellow solid: mp 191 °C (EtOAc); IR (KBr): ν_{max} 3684, 3621, 3014, 2400, 1522, 1423, 1207, 1046, 928 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.08 (t, *J*=7.1 Hz, 6H), 2.99 (s, 4H), 3.97 (q, *J*=7.1 Hz, 4H), 6.18 (s, 2H), 6.95–7.14 (m, 12H), 7.15–7.21 (m, 18H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 14.1, 30.4, 58.0, 60.9, 74.8, 120.4, 127.7, 127.7, 129.6, 136.7, 138.2, 142.3, 170.8; MS (ESI-HRMS) calcd for $C_{53}H_{48}N_4O_4$ $[M]^+$: 804.3676, found: 804.3699.

4.6.2. 2,2-Bis(1-trityl-1*H*-imidazol-4-ylmethyl)propane-1,3-diol (12). Lithium aluminum hydride (932 mg, 24.6 mmol) was added portion wise to a stirred solution of ester **11** (4.5 g, 5.6 mmol) in dry THF (100 mL) at 0 °C under argon atmosphere. The resulting reaction mixture was stirred at 0 °C for 30 min and then at rt for 16 h. Excess lithium aluminum hydride was quenched by addition of $MgSO_4 \cdot 10H_2O$. The resulting white solid was filtered and washed thoroughly with CH_2Cl_2. Evaporation of the solvent afforded diol **12** (3.8 g, 94%) as a white solid: mp 196 °C (EtOAc); IR (neat): ν_{max} 3320, 3014, 2434, 2400, 1522, 1476, 1423, 1215, 1046, 928 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 2.40 (s, 4H), 3.22 (s, 4H), 6.28 (s, 2H), 7.05–7.09 (m, 12H), 7.25–7.39 (m, 18H); ^{13}C NMR (68 MHz, CD_3OD): δ 31.2, 44.9, 65.5, 75.1, 120.0, 127.8, 127.9, 129.4, 137.8, 137.9, 142.1; MS (EI) *m/z* 721 $[M+H]^+$.

4.6.3. 5,5′-Bis(3-bromo-2-bromomethylpropyl)-1*H*-imidazole (13). A solution of diol **12** (5 g, 6.9 mmol) and PBr_3 (50 mL) in toluene (100 mL) was stirred at reflux for 48 h under argon atmosphere. The reaction mixture was then allowed to cool and the toluene layer was decanted. The residue was washed three times with toluene and then neutralized with saturated aqueous sodium bicarbonate solution followed by extraction with dichloromethane (50 mL×3). The combined organic layer was washed with water, brine and dried over sodium sulfate. The residue obtained after evaporation of solvent was purified by silica gel column chromatography (MeOH/CH_2Cl_2=2:8 as eluent) and afforded **13** (1.35 g, 56%) as a pale yellow solid: mp 121.9 °C (CH_2Cl_2); IR (neat): ν_{max} 3080, 2914, 2853, 1703, 1470, 1377, 1324, 1215, 1159, 722 cm^{-1}; ^1H NMR (270 MHz, CD_3OD): δ 2.69 (s, 4H), 3.39 (s, 4H), 7.01 (s, 2H), 7.66 (s, 2H); ^{13}C NMR (68 MHz, CD_3OD): δ 30.7, 40.1, 43.4, 120.5, 132.5, 135.8. Compound **13** was directly subjected to cyclization without further purification and characterization.

4.6.4. 6,6′-Spiro bis(6,7-dihydro-5*H*-pyrrolo[1,2-*c*])imidazole (14). To a stirred solution of dibromide **13** (0.2 g, 0.55 mmol) in dry THF (50 mL) was added 60% NaH (48 mg, 1.2 mmol) at 0 °C. The reaction mixture was then heated under argon atmosphere at 65 °C for 36 h. After cooling to 0 °C, the reaction mixture was quenched with water (1 mL) and extracted with CH_2Cl_2 (25 mL×3). The combined organic layer was washed with brine and dried over sodium sulfate. The residue obtained after evaporation of solvent was purified by silica gel column chromatography (MeOH/CH_2Cl_2=2:8 as eluent) to produce spiro imidazole **14** (70 mg, 63%) as a pale yellow solid: mp 176 °C (MeOH/CH_2Cl_2); IR (Nujol): ν_{max} 3085, 2924, 2853, 1703, 1457, 1377, 1324, 1215, 1159, 722 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.90–3.00 (m, 4H), 4.00–4.18 (m, 4H), 6.69 (s, 2H), 7.53 (s, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ 34.6, 55.4, 62.7, 120.5, 132.5, 136.4; MS (FAB-HRMS) calcd for $C_{11}H_{12}N_4$ $[M+H]^+$: 201.1140, found: 201.1162.

4.6.5. 6,6′-Spirobi{2-(2-propyl)-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazolium}diiodide (2a). To the stirred mixture of spiro imidazole **14** (26 mg, 0.13 mmol) in dry toluene (2 mL) was added 2-iodopropane (1 mL) and the reaction mixture was heated under argon atmosphere at 110 °C for 36 h. The residue obtained after evaporation of solvent was washed with CH_2Cl_2 and dried under vacuum to afford spiro imidazolium salt **2a** (66 mg, 89%) as a white solid: mp 302 °C (MeOH/CH_2Cl_2); IR (Nujol): ν_{max} 3384, 2924, 2853, 2361, 1462, 1376, 722 cm^{-1}; ^1H NMR (270 MHz, DMSO-d_6): δ 1.59 (d, *J*=6.7 Hz, 12H), 3.25–3.40 (m, 4H), 4.48–4.63 (m, 6H), 7.53 (s, 2H), 8.97 (s, 2H); ^{13}C NMR (68 MHz, CD_3OD): δ 22.5, 33.9, 52.5, 55.9, 58.8, 113.1, 130.2, 136.3; MS (FAB-HRMS) calcd for $C_{17}H_{26}I_2N_4$ $[M-I]^+$: 413.1202, found: 413.1231.

4.6.6. 6,6′-Spirobi{2-butyl-6,7-dihydro-5*H*-pyrrolo-[1,2-*c*]imidazolium}diiodide (2b). To the stirred mixture of spiro imidazole **14** (26 mg, 0.13 mmol) in dry toluene (2 mL) was added *n*-iodobutane (1 mL) and the reaction mixture was heated under argon atmosphere at 110 °C for 36 h. The residue obtained after evaporation of solvent was washed with CH_2Cl_2 and dried under vacuum to afford spiro imidazolium salt **2b** (66 mg, 89%) as a white solid; mp 122 °C (MeOH/CH_2Cl_2); IR (Nujol): ν_{max} 2924, 2853, 2361, 1462, 1376, 722 cm^{-1}; ^1H NMR (270 MHz, CD_3OD): δ 0.99 (t, *J*=7.2 Hz, 6H), 1.36–1.49 (m, 4H), 1.83–1.91 (m, 4H), 3.30–3.42 (m, 4H), 4.23 (t, *J*=7.2 Hz, 4H), 4.58 (q, *J*=12.2 Hz, 4H), 7.44 (s, 2H), 8.93 (s, 2H); MS (ESI-HRMS) calcd for $C_{19}H_{30}I_2N_4$ $[M-I]^+$: 441.0692, found: 441.0696.

4.6.7. 6,6′-Spirobi{2-(2-propyl)-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazolium} bis[bis(heptafluoropropanesulfonyl)imide] (2c). To the stirred mixture of imidazolium salt **2a** (43 mg, 0.08 mmol) in water (2 mL) was added lithium bis(heptafluoropropanesulfonyl)imide (83 mg, 0.17 mmol) and the reaction mixture was stirred at rt for about 16 h. The precipitated solid was filtered and washed

with water (5 mL) three times. Drying under reduced pressure at 100 °C gave expected product **2c** (70 mg, 70%); mp 95 °C (MeOH/CH_2Cl_2); ^{1}H NMR (270 MHz, CD_3OD): δ 1.59 (d, J=6.7 Hz, 12H), 3.25–3.40 (m, 4H), 4.48–4.63 (m, 6H), 7.53 (s, 2H), 8.97 (s, 2H); ^{13}C NMR (68 MHz, CD_3OD): δ 23.0, 35.2, 55.0, 57.4, 60.4, 111.8, 114.8, 130.1, 131.3, 138.3; ^{19}F NMR (376 MHz, CD_3OD): δ −83.17, −115.68, −126.41. Anal. Calcd for $C_{29}H_{26}F_{28}N_6O_8S_4$: C, 27.94; H, 2.10; N, 6.74. Found: C, 28.10; H, 1.85; N, 6.73.

4.6.8. 6,6′-Spirobi(2-butyl-6,7-dihydro-5*H*-pyrrolo-[1,2-*c*]imidazolium) bis[bis(trifluoromethanesulfonyl)-imide] (2d). Lithium bis(trifluoromethanesulfonyl)imide (47 mg, 0.16 mmol) was added to a stirred solution of bis(imidazolium) salt **2b** (26 mg, 0.05 mmol) in water (2 mL) at rt and allowed to stir for 16 h. The precipitated oily material was separated by decanting the water and then washing thoroughly with water (5 mL) three times. The obtained oil was dried under vacuum at 100 °C to produce ionic liquid **2d** (14 mg, 53%) as a pale yellow oil: T_g=−35 °C; ^{1}H NMR (270 MHz, CD_3OD): δ 0.98 (t, J=2.7 Hz, 6H), 1.33–1.48 (m, 4H), 1.84–1.91 (m, 4H), 3.28–3.33 (m, 4H), 4.2 (t, J=7.3 Hz, 4H), 4.45–4.62 (m, 4H), 7.41(s, 2H), 8.80 (s, 2H); ^{13}C NMR (68 MHz, CD_3OD): δ 13.7, 20.4, 33.2, 35.1, 51.1, 57.4, 60.4, 116.6, 118.6, 123.4, 138.2; ^{19}F NMR (376 MHz, CD_3OD): δ −77.75; MS (ESI-HRMS) calcd for $C_{23}H_{30}F_{12}N_6O_8S_4$ [M^+−NTf_2]: 594.0816, found: 594.0805.

4.7. Optical resolution of spiro bis(imidazole) 14

Spiro bisimidazole **14** was resolved by HPLC using chiral column. *Conditions*: Chiral stationary phase column Chiralpak IB (0.46 cm ø×25 cm); hexane/2-propanol/ethylenediamine (EDA) (80:20:0.1), flow rate of 1 mL/min, UV detector (230 nm), retention time 68 min and 89 min. *Preparative HPLC conditions*: Chiral stationary phase column Chiralpak IB (2 cm ø×25 cm); hexane/2-propanol/ethylenediamine (EDA) (80:20:1), flow rate of 6 mL/min, UV detector (230 nm), retention time 360 min and 420 min (recycled once).

The separated enantiomers were directly subjected for quaternization as described previously to obtain each enantiomer of **2b**, which upon counteranion exchange produced both enantiomers of chiral ionic liquid **2d**. (+)-**2d**: $[\alpha]_D^{19}$ +1.25 (*c* 0.32, MeOH), T_g=−30 °C. (−)-**2d**: $[\alpha]_D^{19}$ −1.35 (*c* 0.28, MeOH), T_g=−33 °C.

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