Supporting Information

Design and Synthesis of Novel Chiral Spiro Ionic Liquids

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General methods

¹H- and ¹³C-NMR spectra were recorded on JEOL JNM-EX 270 (¹H-NMR 270 MHz, ¹³C-NMR 68 MHz), JEOL JNM-LA 400 (¹H-NMR 400 MHz). ¹⁹F-NMR was recorded on Bruker ARX 400 (¹⁹F-NMR 376 MHz). All signals were expressed as ppm down field from tetramethylsilane, used as internal standard (for ¹H- and ¹³C-NMR) and trifluoroacetic acid, used as external standard (for ¹⁹F-NMR). IR spectra were obtained with SHIMADZU FTIR-8300 instrument. Elemental analysis was performed on PERKIN-ELMER 2400. ESI-HRMS spectra were obtained on JMS-T100LC. FAB-HRMS spectra were obtained on JEOL JMS-700. X-Ray crystallographic analysis was carried out with RIGAKU AFC-7R, and all calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Melting points were measured with Yanaco micro melting point apparatus model MP-S9 and by Differential Scanning Calorimetry (DSC) on SHIMADZU DSC-60 (software of processing data ; TA-60WS).

Column chromatography was performed using Kanto Silica Gel 60 (40-100 μm). Anhydrous THF and toluene were purchased from Kanto Chemicals, Tokyo.

Preparation of imidazolium hydrochlorides (2a-d):

2a: R= Me; **2b:** R= *i*-Pr

2c: R= Et; **2d:** R= Pr

2-Chloromethyl-3-methyl-1*H*-imidazolium hydrochloride (**2a**) was prepared by known method¹ in three steps. Similar synthetic protocol was used for the synthesis of **2b-d** imidazolium hydrochlorides. **2a-d** were known compounds.

2-Chloromethyl-3-(2-propyl)-1*H*-imidazolium hydrochloride (**2b**)²: yield: 90%; mp 152-153 °C (CH₂Cl₂); ¹H-NMR (270 MHz, CD₃OD) : δ 1.57 (d, *J* = 6.7 Hz, 6H), 4.83-4.91 (m, 1H), 5.1 (s, 2H), 7.6 (d, *J* = 2.1 Hz, 1H), 7.8 (d, *J* = 2.1 Hz, 1H); ¹³C-NMR (68 MHz, CD₃OD): δ 22.9, 32.4, 52.4, 121.1, 121.2, 142.5.

2-Chloromethyl-3-ethyl-1*H*-imidazolium hydrochloride (**2c**)³: yield: 95%; ¹H NMR (270 MHz, CDCl₃) δ 1.62 (t, *J* = 7.1 Hz, 3H), 4.29 (q, *J* = 7.1 Hz, 2H), 5.18 (s, 2H), 7.25 (d, *J* = 1.4 Hz, 1H), 7.39 (d, *J* = 1.4 Hz, 1H); ¹³C-NMR (68 MHz, CDCl₃): δ 15.3, 31.0, 43.4, 119.6, 121.2, 153.4.

2-Chloromethyl-3-(1-propyl)-1*H*-imidazolium hydrochloride (**2d**)⁴: yield: 95%; mp 165-167 °C (CH₂Cl₂); ¹H-NMR (270 MHz, DMSO-*d*₆): δ 1.01 (t, *J* = 7.4 Hz, 3H), 1.91-1.99 (m, 2H), 4.25 (t, *J* = 7.4 Hz, 2H), 5.09 (s, 2H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.70 (d, *J* = 2.1 Hz, 1H); ¹³C-NMR (68 MHz, CD₃OD): δ 11.0, 24.3, 32.2, 50.6, 120.8, 124.5, 142.5.

Representative procedure for the synthesis of symmetrical spiro bis(imidazolium) salts (1a-b):

3a: R= Me; **3b:** R= *i*-Pr

Diethyl 2,2-bis(1-methyl-1*H*-imidazol-2-ylmethyl)malonate (**3a**): 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 **2a** (1.8 g, 11 mmol) was added in portions (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 x 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/CH₂Cl₂ = 3/97 as eluent) to give **3a** (1.2 g, 80 %) as pale yellow oil.

¹ Alcalde, E.; Alemany, M.; Gisbert, M. *Tetrahedron* **1996**, 52, 15171.

² Tasaka, A.; Teranishi, K.; Matsushita, Y.; Tamura, N.; Hayashi, R.; Okonogi, K.; Itoh, K. *Chem. Pharm. Bull.* **1994**, 42, 85.

³ Rondelez, Y.; Seneque, O.; Rager, M.-N.; Duprat, A. F.; Reinaud, O. *Chem. Eur. J.* **2000**, 6, 4218.

⁴ Shiraishi, M.; Baba, M.; Aikawa, K.; Kanzaki, N.; Seto, M.; Iizawa, Y. *PCT Int. Appl.* **2003**, 318.

IR (neat) ν_{mas} : 1734, 1558, 1541, 1507, 1204, 864, 746 cm^{-1} ; $^1\text{H-NMR}$ (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), 6.89 (d, J = 1.4 Hz, 2H); $^{13}\text{C-NMR}$ (68 MHz, CDCl_3): δ 14.0, 28.3, 32.7, 57.0, 61.9, 120.2, 127.1, 144.1, 169.9.

Similarly, compound **3b** was obtained in 89% yield (1.6 g) from **2b** (2.14 g, 11 mmol).

Diethyl 2,2-bis(1-(2-propyl)-1*H*-imidazol-2-ylmethyl)malonate (**3b**): IR (neat) ν_{mas} : 1731, 1424, 1212, 870, 740 cm^{-1} ; $^1\text{H-NMR}$ (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), 4.32-4.38 (m, 2H), 6.85-6.86 (m, 2H), 6.98-6.99 (m, 2H); $^{13}\text{C-NMR}$ (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 $\text{C}_{21}\text{H}_{32}\text{N}_4\text{O}_4$ $[\text{M}]^+$: 404.2424, Found: 404.2457.

Symmetrical diol (**4a-b**):

4a: R = Me; **4b**: R = *i*-Pr

2,2-Bis(1-methyl-1*H*-imidazol-2-ylmethyl)propane-1,3-diol (**4a**): Lithium aluminum hydride (645 mg, 17 mmol) was added portion wise to a stirred solution of ester **3a** (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 slow addition of saturated aqueous sodium sulfate solution (5 mL). After removal of resulting white solid by filtration through celite, evaporation of the solvent afforded diol **4a** (0.9 g, 90 %) as a white gummy material.

IR (neat) ν_{mas} : 3367, 2937, 1653, 1527, 1490, 1412, 1282, 1154, 1079, 1044, 935, 741 cm^{-1} ; $^1\text{H-NMR}$ (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); $^{13}\text{C-NMR}$ (68 MHz, CDCl_3): δ 29.8, 33.1, 45.8, 65.7, 120.5, 126.2, 146.1; MS (FAB-HRMS) calcd for $\text{C}_{13}\text{H}_{21}\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+$: 265.1659, Found: 265.1677.

Compound **4b** was obtained in 92% yield (1.15 g) from ester **3b** (1.58 g, 3.9 mmol) by the similar procedure for **4a**.

2,2-Bis(1-(2-propyl)-1*H*-imidazol-2-ylmethyl)propane-1,3-diol (**4b**): mp 119-122 °C (hexane/ethyl acetate); IR (neat) ν_{mas} : 3114, 2971, 1455, 1268 cm^{-1} ; $^1\text{H-NMR}$ (270 MHz, CDCl_3): δ 1.28 (d, J = 6.7 Hz, 12H), 2.94 (s, 4H), 3.24 (s, 4H), 4.38-4.46 (m, 2H), 6.85-6.86 (m, 2H), 6.93-6.94 (m, 2H); $^{13}\text{C-NMR}$ (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 $\text{C}_{17}\text{H}_{28}\text{N}_4\text{O}_2$ $[\text{M}]^+$: 320.2212, Found: 320.2253.

Spiro bis(imidazolium) salt (**1a-b**):

6,6'-Spirobi(1-methyl-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium) dibromide (**1a**): A solution of diol **4a** (714 mg, 2.7 mmol) and PBr_3 (8 mL) in toluene (20 mL) was stirred at reflux temperature 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 x 3). The combined organic layer was washed with water, brine and dried over sodium sulfate. Evaporation of solvent afforded **5a** as brown oil, which was directly subjected to cyclization without further purification. A solution of **5a** 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 (CH₂Cl₂/MeOH); IR (neat) ν_{mas} : 3371, 2947, 2835, 2520, 2039, 1659, 1555, 1449, 1113, 1026 cm⁻¹; ¹H-NMR (270 MHz, CD₃OD): δ 3.68 (s, 4H), 3.87 (s, 6H), 4.62 (s, 4H), 7.56 (s, 2H), 7.57 (s, 2H); ¹³C-NMR (68 MHz, CD₃OD): δ 35.9, 36.8, 57.9, 59.7, 119.3, 128.3, 151.6; MS (ESI-HRMS) calcd for C₁₃H₁₈BrN₄ [M-Br]⁺: 309.0709, Found: 309.0699.

Spiro bis(imidazolium) dibromide (**1b**) was obtained in 54% yield (650 mg) from diol **4b** (864 mg, 2.7 mmol) under reaction conditions identical to **1a**.

6,6'-Spirobi(1-(2-propyl)-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium) dibromide (**1b**): mp > 300 °C (CH₂Cl₂/MeOH); IR (neat) ν_{mas} : 3391, 2948, 2836, 2518, 2033, 1650, 1024 cm⁻¹; ¹H-NMR (270 MHz, CD₃OD): 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); ¹³C-NMR (68 MHz, CD₃OD): δ 22.6, 22.7, 37.6, 54.1, 57.3, 59.3, 119.7, 141.9, 145.0; MS (ESI-HRMS) calcd for C₁₇H₂₆BrN₄ [M-Br]⁺: 510.0699, Found: 510.0680.

Representative procedure for the synthesis of unsymmetrical spiro bis(imidazolium) salts (1c-d):

6a: R¹ = Me; **6b:** R¹ = Pr

Diethyl 2-(1-methyl-1*H*-imidazol-2-ylmethyl)malonate (**6a**): To a stirred solution of diethyl malonate (1.41 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 **2a** (1.00 g, 5.9 mmol) was added in portions (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 x 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/CH₂Cl₂ = 5/95 as eluent) to give **6a** (1.00 g, 67 %) as pale yellow oil.

IR (neat) ν_{mas} : 2984, 1732, 1525, 1497, 1466, 1417, 1371, 1340, 1281, 1239, 1173, 1096, 1033, 859, 754 cm⁻¹; ¹H-NMR (270 MHz, CDCl₃): 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); ¹³C-NMR (68 MHz, CDCl₃): δ 14.0, 25.5, 32.6, 50.1, 61.6, 120.5, 127.1, 144.7, 168.7.

Similarly, **2d** (1.15 g, 5.9 mmol) produced ester **6b** in 51% yield (848 mg).

Diethyl 2-(1-(1-propyl)-1*H*-imidazol-2-ylmethyl)malonate (**6b**): IR (neat) ν_{mas} : 2969, 1735, 1272, 1159 cm⁻¹; ¹H-NMR (270 MHz, CDCl₃): 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), 6.79-6.91 (m, 2H); ¹³C-NMR

(68 MHz, CDCl₃): 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 C₁₄H₂₂N₂O₄ [M]⁺: 282.1580, Found: 282.1570.

Unsymmetrical ester (3c-d):

3c: R¹ = Me, R² = Et

3d: R¹ = Pr, R² = *i*-Pr

Diethyl 2-(1-ethyl-1*H*-imidazol-2-ylmethyl)-2-(1-methyl-1*H*-imidazol-2-ylmethyl)malonate (**3c**): To a stirred solution of **6a** (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 **2c** (854 mg, 4.7 mmol) was added in portions (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 x 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/CH₂Cl₂ = 5/95 as eluent) to produce **3c** (406 mg, 30 %) as pale yellow oil.

IR (neat) ν_{max} : 2253, 1714, 1421, 1363, 1335, 1093, 919, 734 cm⁻¹; ¹H-NMR (270 MHz, CDCl₃): 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 (d, *J* = 1.1 Hz, 1H), 6.95 (d, *J* = 1.1 Hz, 1H); ¹³C-NMR (68 MHz, CDCl₃): 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.

The ester **3d** was obtained in 52% yield (819 mg) from compound **6b** (1.10 g, 3.9 mmol) and **2b** (916 mg, 4.7 mmol).

Diethyl 2-(1-(1-propyl)-1*H*-imidazol-2-ylmethyl)-2-(1-(2-propyl)-1*H*-imidazol-2-ylmethyl)malonate (**3d**): IR (neat) ν_{max} : 2359, 2342, 1733, 1716, 1420, 1335, 1010, 918 cm⁻¹; ¹H-NMR (270 MHz, CDCl₃): δ 0.81 (t, *J* = 7.4 Hz, 3H), 1.14-1.25 (m, 12H), 1.52-1.60 (q, *J* = 7.4 Hz, 2H), 3.58-3.65 (m, 4H), 4.10-4.34 (m, 7H), 6.70-6.81 (m, 2H), 6.90-6.90 (m, 2H); ¹³C-NMR (68 MHz, CDCl₃): 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, 127.5, 143.1, 143.7, 170.1; MS (ESI-HRMS) calcd for C₂₁H₃₂N₄O₄ [M]⁺: 404.2424, Found: 404.2390.

Unsymmetrical diol (4c-d):

4c: R¹ = Me, R² = Et

4d: R¹ = Pr, R² = *i*-Pr

2-(1-Ethyl-1*H*-imidazol-2-ylmethyl)-2-(1-methyl-1*H*-imidazol-2-ylmethyl)propane-1,3-diol (**4c**): Lithium aluminum hydride (167 mg, 4.4 mmol) was added portion wise to a stirred solution of ester **3c** (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 and evaporation of the solvent afforded diol **4c** (200 mg, 71 %) as colorless gummy oil.

IR (neat) ν_{mas} : 3400, 2929, 2253, 1467, 1381, 1281, 1088, 908, 733 cm^{-1} ; $^1\text{H-NMR}$ (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); $^{13}\text{C-NMR}$ (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 $\text{C}_{14}\text{H}_{23}\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+$: 279.1816, Found: 279.1824.

Compound **3d** (404 mg, 1 mmol) was reduced under the similar conditions to give diol **4d** in 85% yield (272 mg).

2-(1-(1-Propyl)-1*H*-imidazol-2-ylmethyl)-2-(1-(2-propyl)-1*H*-imidazol-2-ylmethyl)prop-ane-1,3-diol (**4d**): IR (neat) ν_{mas} : 3450, 2968, 2361, 2342, 1270, 1080, 730 cm^{-1} ; $^1\text{H-NMR}$ (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), 2.90 (d, $J = 3.1$ Hz, 4H), 3.20 (s, 4H), 3.73 (t, $J = 7.2$ Hz, 2H), 4.36-4.41 (m, 1H), 6.78-6.92 (m, 4H); $^{13}\text{C-NMR}$ (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 $\text{C}_{17}\text{H}_{29}\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+$: 321.2285, Found: 321.2278.

Spiro bis(imidazolium) salt (1c-d):

(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 **4c** (150 mg, 0.53 mmol) and PBr_3 (1.5 mL) in toluene (10 mL) was stirred at reflux temperature 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 x 3). The combined organic layer was washed with water, brine and dried over sodium sulfate. Evaporation of solvent afforded 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 ($\text{CH}_2\text{Cl}_2/\text{MeOH}$); IR (neat) ν_{mas} : 3368, 2945, 2521, 2225, 2044, 1451, 1114, 1032 cm^{-1} ; $^1\text{H-NMR}$ (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 (s, 2H), 4.56 (s, 2H), 7.47 (s, 2H), 7.49 (d, $J = 2.2$ Hz, 1H), 7.56 (d, $J = 2.2$ Hz, 1H); $^{13}\text{C-NMR}$ (68 MHz, CD_3OD): δ 15.1, 36.0, 36.9, 37.1, 45.6, 57.8, 59.4, 59.7, 119.3, 119.5, 126.6, 128.3, 150.7, 151.5; MS (FAB-HRMS) calcd for $\text{C}_{14}\text{H}_{20}\text{BrN}_4$ $[\text{M}-\text{Br}]^+$: 323.0866, Found: 323.0857.

Compound **4d** (169 mg, 0.53 mmol) was treated with PBr_3 under the similar reaction conditions to yield spiro bis(imidazolium) dibromide (**1d**) (78 mg, 33%).

(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**): mp 118-120 °C (CH₂Cl₂/MeOH); IR (neat) ν_{max} : 3391, 2948, 2836, 1024 cm⁻¹; ¹H-NMR (270 MHz, CD₃OD): 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); ¹³C-NMR (68 MHz, CDCl₃): 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 C₁₇H₂₆BrN₄ [M-Br]⁺: 365.1335, Found: 365.1327.

Representative procedure for the counter anion exchange.

Method A: (Table 1, entries 2, 3, **1e-f**)

1e: X = BF₄; **1f:** X = CF₃SO₃

Silver tetrafluoroborate (38 mg, 0.19 mmol) was added to a stirred solution of bis(imidazolium) salt (**1a**) (38 mg, 0.096 mmol) in dry methanol (2 mL) at room temperature under argon atmosphere. After stirring the reaction mixture for 16 h, the precipitated silver bromide was filtered off through celite. Evaporation of methanol produced bis(imidazolium) tetrafluoroborate (**1e**) (35 mg, 90 %) as a white solid.

6,6'-Spirobi(1-methyl-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium) bis(tetrafluoroborate) (**1e**): mp 272 °C (CH₂Cl₂/MeOH); ¹H-NMR (270 MHz, CD₃OD): δ 3.59 (s, 4H), 3.84 (s, 6H), 4.56 (s, 4H), 7.53-7.56 (m, 4H).

Similarly **1f** was obtained in 95% yield (48 mg) from bis(imidazolium) bromide (**1a**) (38 mg, 0.096 mmol) using silver triflate (49 mg, 0.19 mmol).

6,6'-Spirobi(1-methyl-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium) bis(trifluoromethanesulfonate) (**1f**): mp 166 °C (CH₂Cl₂/MeOH); ¹H-NMR (270 MHz, CD₃OD): δ 3.60 (s, 4H), 3.82 (s, 6H), 4.59 (s, 4H), 7.50-7.56 (m, 4H).

Method B: (Table 1, entries 4, 6, 7 and Scheme 2, **1j-k**)

1g: R¹ = Me, R² = Me; **1h:** R¹ = *i*-Pr, R² = *i*-Pr

1j: R¹ = Me, R² = Et; **1k:** R¹ = Pr, R² = *i*-Pr

6,6'-Spirobi(1-methyl-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium) bis(bis(trifluoromethanesulfonyl)imide) (**1g**): To a stirred solution of bis(imidazolium) salt (**1a**) (31.2 mg, 0.08 mmol) in water (3 mL) was added lithium bis(trifluoromethanesulfonyl)imide (49 mg, 0.17 mmol) at room temperature. The mixture was allowed to stir for 16 h at the same temperature. Precipitated solid was filtered and washed with water (5 mL) three times. Drying under reduced pressure at 100 °C gave **1g** (60 mg, 95 %) as a white solid.

mp 112 °C (CH₂Cl₂/MeOH); IR (neat) ν_{mas} : 1350, 1331, 1188, 1137, 1055 cm⁻¹; ¹H-NMR (270 MHz, CD₃OD): δ 3.54 (s, 4H), 3.75 (s, 6H), 4.50 (s, 4H), 7.44 (d, J = 2.2 Hz, 2H), 7.46 (d, J = 2.2 Hz, 2H); ¹³C-NMR (68 MHz, CD₃OD): δ 35.7, 36.5, 57.8, 59.6, 119.2, 123.4, 128.4, 151.4; ¹⁹F-NMR (376 MHz, CD₃OD): δ -80.14; MS (ESI-HRMS) calcd for C₁₅H₁₈F₆N₅O₄S₂ [M-Tf₂N]⁺: 510.0699, Found: 510.0680.

Similarly, compound **1h** was obtained in 92% yield (62 mg) as a white solid from **1b** (35.6 mg, 0.08 mmol) by method B.

6,6'-Spirobi(1-(2-propyl)-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium) bis(bis(trifluoromethanesulfonyl)imide) (**1h**): mp 68 °C (CH₂Cl₂/MeOH); IR (neat) ν_{mas} : 1352, 1191, 1138, 1057 cm⁻¹; ¹H-NMR (270 MHz, CD₃OD): δ 1.56 (dd, J = 1.1, 6.8 Hz, 12H), 3.68 (s, 4H), 4.56-4.58 (m, 6H), 7.55-7.56 (m, 2H), 7.73-7.74 (m, 2H); ¹³C-NMR (68 MHz, CD₃OD): δ 22.5, 22.5, 37.4, 54.6, 57.2, 59.3, 119.6, 124.6, 142.0, 149.8; ¹⁹F-NMR (376 MHz, CD₃OD): δ -81.38; MS (ESI-HRMS) calcd for C₁₉H₂₆F₆N₅O₄S₂ [M-Tf₂N]⁺: 566.1330, Found: 566.1325; *Anal.* Calcd for C₂₁H₂₆F₁₂N₆O₈S₄: C, 29.79, H, 3.10, N, 9.93, Found: C, 29.92, H, 3.06; N, 9.80.

The spiro bis(imidazolium) dibromide (**1c**) (32 mg, 0.08 mmol) yielded compound **1j** in 80% yield (51 mg) as a white solid by method B.

(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) (**1j**): mp 116 °C (CH₂Cl₂/MeOH); IR (neat) ν_{mas} : 2072, 1655, 1449, 1350, 1119, 1031 cm⁻¹; ¹H-NMR (270 MHz, CD₃OD): 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); ¹³C-NMR (68 MHz, CD₃OD): 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; ¹⁹F-NMR (376 MHz, CD₃OD): δ -81.46. MS (ESI-HRMS) calcd for C₁₆H₂₀F₆N₅O₄S₂ [M-Tf₂N]⁺: 524.0855, Found: 524.0849.

Under identical conditions using method B, spiro bis(imidazolium) salt (**1d**) (35.6 mg, 0.08 mmol) gave **1k** in 90% yield (61 mg) as a colorless oil.

(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) (**1k**): Tg -20 °C (determined by DSC); IR (neat) ν_{mas} : 1349, 1188, 1055 cm⁻¹; ¹H-NMR (270 MHz, CD₃OD): 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); ¹³C-NMR (68 MHz, CDCl₃): 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; ¹⁹F-NMR (376 MHz, CD₃OD): δ -81.28; MS (FAB-HRMS) calcd for C₁₉H₂₆F₆N₅O₄S₂ [M-Tf₂N]⁺: 566.1330, Found: 566.1296.

Similarly **1i** 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).

6,6'-Spirobi(1-(2-propyl)-1,5,6,7-tetrahydropyrrolo[1,2-*a*]imidazolium) bis(bis(heptafluoropropanesul-

fonyl)imidate) (**1i**): Tg $-10\text{ }^{\circ}\text{C}$ (determined by DSC); IR (neat) ν_{mas} : 1355, 1171, 1067, 865 cm^{-1} ; ^1H -NMR (270 MHz, CD_3OD): δ 1.56 (dd, $J = 1.0, 6.8\text{ Hz}$, 12H), 3.69 (s, 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 $\text{C}_{23}\text{H}_{26}\text{F}_{14}\text{N}_5\text{O}_4\text{S}_2$ [$\text{M}-(\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2)_2\text{N}$] $^+$: 766.1197, Found: 766.1206; Anal. Calcd for $\text{C}_{29}\text{H}_{26}\text{F}_{28}\text{N}_6\text{O}_8\text{S}_4$: C, 27.94, H, 2.10, N, 6.74, Found: C, 27.85, H, 2.14; N, 6.78.

NMR experiment for the distereomeric interaction of spiro bis(imidazolium) salt (1b**) with chiral counter anion:**

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% $\text{DMSO-}d_6\text{-CDCl}_3$, 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 % $\text{DMSO-}d_6$ in CDCl_3): δ 1.50-1.54 (m, 12H), 3.54 (s, 6H), 3.83 (d, $J = 8.0\text{ Hz}$, 1H), 3.88 (d, $J = 8.0\text{ Hz}$, 1H), 4.02 (d, $J = 5.9\text{ Hz}$, 1H), 4.09 (d, $J = 5.9\text{ Hz}$, 1H), 4.58-4.64 (m, 2H), 4.65 (d, $J = 5.1\text{ Hz}$, 1H), 4.67 (d, $J = 4.9\text{ Hz}$, 1H), 4.76 (d, $J = 2.7\text{ Hz}$, 1H), 4.78 (d, $J = 2.6\text{ Hz}$, 1H), 7.22-7.29 (m, 6H), 7.55 (d, $J = 6.3\text{ Hz}$, 4H), 7.68-7.70 (m, 4H). 18-crown-6 signal appeared at δ 3.28 as a singlet.

For comparison study ^1H -NMR spectrum of **1b** was recorded in 20% $\text{DMSO-}d_6\text{-CDCl}_3$.

1b: ^1H NMR (400 MHz, 20 % $\text{DMSO-}d_6$ in CDCl_3): 1.60 (dd, $J = 6.5\text{ Hz}, 11.9\text{ Hz}$, 12H), 4.08 (d, $J = 17.0\text{ Hz}$, 2H), 4.40 (d, $J = 17.0\text{ Hz}$, 2H), 4.70-4.77 (m, 2H), 4.88 (d, $J = 11.8\text{ Hz}$, 2H), 5.02 (d, $J = 11.8\text{ Hz}$, 2H), 7.43-7.46 (m, 2H), 7.49-7.55 (m, 2H).

Chart A

Chart B

The ¹H NMR **Chart A** shows the diastereomeric interaction of salt (**1b**) with potassium salt of (*S*)-Mosher's acid in 20% DMSO-*d*₆-CDCl₃ and **Chart B** shows the expanded region from 3.8 – 4.9 ppm value of **Chart A**.

Chart C

Chart D

The ^1H -NMR **Chart C** shows peak pattern of **1b** in 20% $\text{DMSO-}d_6\text{-CDCl}_3$ and **Chart D** is the expanded region from 4.0-5.1 ppm value of **Chart C**.

Optical Resolution of spiro bis(imidazolium) salt *1b*:

Spiro bis(imidazolium) salt **1b** was resolved by using chiral HPLC.

Conditions: Chiral stationary phase column SUMICHIRAL OA-4500 (4.6 mm ϕ x 250 mm); hexane/2-propanol/methanol/trifluoroacetic acid (70:20:10:0.2), flow rate (0.5 mL/min), UV detector (211 nm), temperature 40 °C, retention time 82 min, 84 min.

Preparative HPLC conditions: Chiral stationary phase column SUMICHIRAL OA-4500 (20 mm ϕ x 250 mm); hexane/2-propanol/methanol/trifluoroacetic acid (70:20:10:0.2), flow rate (9.9 mL/min), UV detector (211 nm), temperature 25 °C, retention time 151.98 min, 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)

Counter anion exchange was carried out as described in Table 1 to obtain chiral ionic liquid **1i**.

1i: $[\alpha]_D^{29} -1.74$ (c 0.24, MeOH), Tg : -11 °C (Determined by DSC)

$[\alpha]_D^{29} +1.75$ (c 0.27, MeOH), Tg : -10 °C (Determined by DSC)