Structure Effect of Imidazolium-Based Dicationic Ionic Liquids on Claisen Rearrangement

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SUPPLEMENTARY INFORMATION

Instruments

The melting points of DILs were determined by Stuart SMP3 apparatus. UV-VIS spectra were recorded on UV/VIS Spectrometer Lambda 25. High-resolution mass spectra were obtained with Agilent 6230 TOF LC/MS instrument. Negative-ion ESI-MS analysis was performed on Agilent 6230 TOF LC/MS mass spectrometer. ESI-MS spectra were obtained for the solutions (10^{-3} M) of DILs in acetonitrile-water (1:1, v:v). 5 μ L of the samples were injected directly into the spectrometer at a constant flow 5 μ L/min. Source was used with the following parameters: negative ionization mode, drying gas flow 10 mL/min and 200 °C temperature, fragmentor ionization was set in a range of 0 to 130 V. N₂ was used as the sheath gas at flow 8 ml/min and 200 °C temperature. The mass scan range was from m/z 50 to 3000. Peak detection and spectrum extraction were performed with MassHunter Software (Agilent). Thermogravimetric analysis was performed by SII Extar6000 TG-DTA6300 under nitrogen atmosphere (temperature gradient 50...500 °C, heating rate – 10 °C/min). The products of the Claisen rearrangement were identified by GC (Shimadzu GC-2010) using Restek Rtx®-1 Ms column (30 m x 0,25 mm x 0,25 μ m) equipped with mass spectrometer (Shimadzu GC/MS-QP2010). Quantitative analysis of the reaction mixture was performed by GC (YL6100 GC) using the same column equipped with a flame ionization detector (FID). Helium was exploited as the carrier gas (flow rate – 1 mL/min).

Pure 2-allylphenol (**4**) was isolated by flash chromatography using Isolera One (Biotage) instrument, equipped with a silica gel column SNAP 10 g (Biotage).

Characterization Data of Dicationic Ionic Liquids

Scheme S1

Scheme S2

1,3-Bis(3-butyylimidazolium-1-yl)propane dibromide (5a). Prepared from 1-butyylimidazole (**6a**) and 1,3-dibromopropane (**7a**), obtained as a white solid, 85% yield. M.p. 124-125 °C. ¹H NMR (DMSO-*d*₆) δ 0.91 (6H, t, *J* = 7.4 Hz, CH₃CH₂), 1.28 (4H, sext, *J* = 7.4 Hz, CH₃CH₂CH₂), 1.79 (4H, quint, *J* = 7.4 Hz, C₂H₅CH₂CH₂), 2.43 (2H, quint, *J* = 7.1 Hz, NCH₂CH₂CH₂N), 4.22 (8H, dt, *J* = 30.3, 7.1 Hz, C₃H₇CH₂N, NCH₂CH₂CH₂N), 7.85 (4H, d, *J* = 1.6 Hz, NCHCHN), 9.34 (2H, s, NCHN). HRMS (ESI): MH⁺, found 289.2401. [C₁₇H₂₉N₄]⁺ requires 289.2387.

1,4-Bis(3-butyylimidazolium-1-yl)butane dichloride (5b). Prepared from 1-butyylimidazole (**6a**) and 1,4-dichlorobutane (**7b**). The reaction mixture was heated in toluene (25 mL) at 95 °C for 24 h and the product was washed with boiling toluene (3 x 15 mL). Obtained as a viscous, slightly yellow substance, 72% yield. ¹H NMR (DMSO-*d*₆) δ 0.89 (6H, t, *J* = 7.4 Hz, CH₃CH₂), 1.25 (4H, sext, *J* = 7.5 Hz, CH₃CH₂CH₂), 1.87-1.72 (8H, m, C₂H₅CH₂CH₂, NCH₂CH₂CH₂CH₂N), 4.20 (4H, t, *J* = 7.2 Hz, C₃H₇CH₂N), 4.29 (4H, t, *J* = 6.0 Hz, NCH₂(CH₂)₂CH₂N), 7.89-7.83 (2H, m, NCHCHN), 7.95-7.89 (2H, m, NCHCHN), 9.70 (2H, s, NCHN). HRMS (ESI): MH⁺, found 303.2539. [C₁₈H₃₁N₄]⁺ requires 303.2543.

1,6-Bis(3-butyylimidazolium-1-yl)hexane dichloride (5c). Prepared from 1-butyylimidazole (**6a**) and 1,6-dichlorohexane (**7c**). The reaction mixture was heated under reflux in 2-propanol (25 mL) for 16 h and the product was washed with diethyl ether (3 x 15 mL). Obtained as a viscous, slightly yellow substance, 87% yield. ¹H NMR (DMSO-*d*₆) δ 0.90 (6H, t, *J* = 7.4 Hz, CH₃CH₂),

1.32-1.18 (8H, m, N(CH₂)₂CH₂CH₂(CH₂)₂N, CH₃CH₂CH₂), 1.87-1.71 (8H, m, NCH₂CH₂(CH₂)₂CH₂CH₂N, C₂H₅CH₂CH₂), 4.18 (8H, td, *J* = 7.2, 2.4 Hz, C₃H₇CH₂N, NCH₂(CH₂)₄CH₂N), 7.83-7.80 (2H, m, NCHCHN), 7.86-7.83 (2H, m, NCHCHN), 9.42 (2H, s, NCHN). HRMS (ESI): MH⁺, found 331.2854. [C₂₀H₃₅N₄]⁺ requires 331.2856.

1,3-Bis(3-methylimidazolium-1-yl)propane dibromide (5d). Prepared from 1-methylimidazole (**6b**) and 1,3-dibromopropane (**7a**), obtained as a white solid, 92% yield. M.p. 161-162 °C (lit. 161-162 °C).^[1] ¹H NMR (DMSO-*d*₆) δ 2.39 (2H, quint, *J* = 6.8 Hz, NCH₂CH₂CH₂N), 3.87 (6H, s, CH₃N), 4.31-4.17 (4H, m, NCH₂CH₂CH₂N), 7.75 (2H, s, NCHCHN), 7.81 (2H, s, NCHCHN), 9.24 (2H, s, NCHN). HRMS (ESI): MH⁺, found 205.1438. [C₁₁H₁₇N₄]⁺ requires 205.1448.

1,4-Bis(3-methylimidazolium-1-yl)butane dichloride (5e). Prepared from 1-methylimidazole (**6b**) and 1,4-dichlorobutane (**7b**), obtained as a white solid, 92% yield. M.p. 182-183 °C. ¹H NMR (DMSO-*d*₆) δ 1.86-1.73 (4H, m, NCH₂CH₂CH₂CH₂N), 3.88 (6H, s, CH₃N), 4.28 (4H, s, NCH₂(CH₂)₂CH₂N), 7.76 (2H, s, NCHCHN), 7.88 (2H, s, NCHCHN), 9.50 (2H, s, NCHN). HRMS (ESI): MH⁺, found 219.1594. [C₁₂H₁₉N₄]⁺ requires 219.1604.

1,6-Bis(3-methylimidazolium-1-yl)hexane dichloride (5f). Prepared from 1-methylimidazole (**6b**) and 1,6-dichlorohexane (**7c**), obtained as a white solid, 87% yield. M.p. 154-156 °C (lit. 154-156 °C).^[1] ¹H NMR (DMSO-*d*₆) δ 1.33-1.19 (4H, m, N(CH₂)₂CH₂CH₂(CH₂)₂N), 1.85-1.71 (4H, m, NCH₂CH₂(CH₂)₂CH₂CH₂N), 3.87 (6H, s, CH₃N), 4.19 (4H, t, *J* = 7.1 Hz, NCH₂(CH₂)₄CH₂N), 7.76 (2H, s, NCHCHN), 7.87 (2H, s, NCHCHN), 9.48 (2H, s, NCHN). HRMS (ESI): MH⁺, found 247.1929. [C₁₄H₂₃N₄]⁺ requires 247.1917.

1,3-Bis(3-butyl-2-methylimidazolium-1-yl)propane dibromide (9a). Prepared from 1-butyl-2-methylimidazole (**8a**) and 1,3-dibromopropane (**7a**). The reaction mixture was heated under reflux in 2-propanol (25 mL) for 24 h and the product was washed with boiling toluene (3 x 15 mL). Obtained as a viscous, slightly brown substance, 64% yield. ¹H NMR (DMSO-*d*₆) δ 0.95-

0.86 (6H, m, CH_3CH_2), 1.30 (4H, sext, $J = 7.5$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.77-1.63 (4H, m, $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2$), 2.34-2.20 (2H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.67 (6H, s, CH_3C), 4.12 (4H, t, $J = 7.4$ Hz, $\text{C}_3\text{H}_7\text{CH}_2\text{N}$), 4.24 (4H, t, $J = 7.5$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 7.75 (4H, dd, $J = 14.5, 2.1$ Hz, NCHCHN). HRMS (ESI): MH^+ , found 317.2681. $[\text{C}_{19}\text{H}_{33}\text{N}_4]^+$ requires 317.2700.

1,3-Bis(2,3-dimethylimidazolium-1-yl)propane dibromide (9b). Prepared from 1,2-dimethylimidazole (**8b**) and 1,3-dibromopropane (**7a**). The reaction mixture was heated under reflux in 2-propanol (25 mL) for 16 h and the product was washed with cold 2-propanol (2 x 10 mL). Obtained as a white solid, 92% yield. M.p. 293-294 °C (decomp.) (lit. 298 °C).^[1] ^1H NMR ($\text{DMSO-}d_6$) δ 2.21 (2H, quint, $J = 7.5$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.62 (6H, s, CH_3C), 3.76 (6H, s, CH_3N), 4.22 (4H, t, $J = 7.4$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 7.66 (2H, d, $J = 2.1$ Hz, NCHCHN), 7.71-7.67 (2H, m, NCHCHN). HRMS (ESI): MH^+ , found 233.1755. $[\text{C}_{13}\text{H}_{21}\text{N}_4]^+$ requires 233.1761.

1,4-Bis(2,3-dimethylimidazolium-1-yl)butane dichloride (9c). Prepared from 1,2-dimethylimidazole (**8b**) and 1,4-dichlorobutane (**7b**) in a similar way as **9b**, obtained as a white solid, 60% yield. M.p. 249-250 °C. ^1H NMR ($\text{DMSO-}d_6$) δ 1.79-1.66 (4H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.61 (6H, s, CH_3C), 3.76 (6H, s, CH_3N), 4.19 (4H, t, $J = 5.8$ Hz, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_2\text{N}$), 7.69 (4H, dd, $J = 24.0, 2.0$ Hz, NCHCHN). HRMS (ESI): MH^+ , found 247.1896. $[\text{C}_{14}\text{H}_{23}\text{N}_4]^+$ requires 247.1917.

1,6-Bis(2,3-dimethylimidazolium-1-yl)hexane dichloride (9d). Prepared from 1,2-dimethylimidazole (**8b**) and 1,6-dichlorohexane (**7c**) in a similar way as **9b**, obtained as a white solid, 81% yield. M.p. 149-150 °C. ^1H NMR ($\text{DMSO-}d_6$) δ 1.29 (4H, quint, $J = 3.7$ Hz, $\text{N}(\text{CH}_2)_2\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{N}$), 1.70 (4H, quint, $J = 7.0$ Hz, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{N}$), 2.59 (6H, s, CH_3C), 3.76 (6H, s, CH_3N), 4.11 (4H, t, $J = 7.3$ Hz, $\text{NCH}_2(\text{CH}_2)_4\text{CH}_2\text{N}$), 7.68 (4H, dd, $J = 17.4, 2.1$ Hz, NCHCHN). HRMS (ESI): MH^+ , found 311.1997. $[\text{C}_{16}\text{H}_{28}\text{N}_4\text{Cl}]^+$ requires 311.2010.

1,3-Bis(3-butyylimidazolium-1-yl)propane bis(trifluoromethylsulfonyl)imide (1a). Prepared from 1,3-bis(3-butyylimidazolium-1-yl)propane dibromide (**5a**) and lithium bis(trifluoromethylsulfonyl)imide, obtained as a viscous, slightly yellow liquid, 97% yield. ^1H NMR ($\text{DMSO-}d_6$) δ 0.92 (6H, t, $J = 7.4$ Hz, CH_3CH_2), 1.28 (4H, sext, $J = 7.5$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.79 (4H, quint, $J = 7.4$ Hz, $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2$), 2.40 (2H, quint, $J = 7.1$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 4.19 (8H, dt, $J = 21.5, 7.1$ Hz, $\text{C}_3\text{H}_7\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 7.77 (2H, s, NCHCHN), 7.82 (2H, s, NCHCHN), 9.16 (2H, s, NCHN). HRMS (ESI): MH^+ , found 289.2372. $[\text{C}_{17}\text{H}_{29}\text{N}_4]^+$ requires 289.2387.

1,3-Bis(3-butyylimidazolium-1-yl)propane hexafluorophosphate (1b). Prepared from 1,3-bis(3-butyylimidazolium-1-yl)propane dibromide (**5a**) and potassium hexafluorophosphate, obtained as a white solid, 79% yield. M.p. 96-97 °C (lit. 96-98 °C).^[3] ^1H NMR ($\text{DMSO-}d_6$) δ 0.92 (6H, t, $J = 7.4$ Hz, CH_3CH_2), 1.28 (4H, sext, $J = 7.6$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.86-1.68 (4H, m, $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2$), 2.39 (2H, quint, $J = 7.1$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 4.19 (8H, dt, $J = 19.3, 7.2$ Hz, $\text{C}_3\text{H}_7\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 7.80 (4H, dt, $J = 22.9, 1.7$ Hz, NCHCHN), 9.15 (2H, s, NCHN). HRMS (ESI): MH^+ , found 289.2368. $[\text{C}_{17}\text{H}_{29}\text{N}_4]^+$ requires 289.2387.

1,4-Bis(3-butyylimidazolium-1-yl)butane bis(trifluoromethylsulfonyl)imide (1c). Prepared from 1,4-bis(3-butyylimidazolium-1-yl)butane dichloride (**5b**) and lithium bis(trifluoromethylsulfonyl)imide, obtained as a viscous, slightly yellow liquid, 94% yield. ^1H NMR ($\text{DMSO-}d_6$) δ 0.91 (6H, t, $J = 7.4$ Hz, CH_3CH_2), 1.27 (4H, sext, $J = 7.5$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.87-1.73 (8H, m, $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 4.26-4.11 (8H, m, $\text{C}_3\text{H}_7\text{CH}_2\text{N}$, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_2\text{N}$), 7.76 (2H, s, NCHCHN), 7.79 (2H, s, NCHCHN), 9.16 (2H, s, NCHN). HRMS (ESI): MH^+ , found 303.2531. $[\text{C}_{18}\text{H}_{31}\text{N}_4]^+$ requires 303.2543.

1,6-Bis(3-butyylimidazolium-1-yl)hexane bis(trifluoromethylsulfonyl)imide (1d). Prepared from 1,6-bis(3-butyylimidazolium-1-yl)hexane dichloride (**5c**) and lithium

bis(trifluoromethylsulfonyl)imide, obtained as a viscous, slightly yellow liquid, 98% yield. ^1H NMR (DMSO- d_6) δ 0.90 (6H, t, J = 7.4 Hz, CH_3CH_2), 1.36-1.17 (8H, m, $\text{N}(\text{CH}_2)_2\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{N}$, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.84-1.74 (8H, m, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{N}$, $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2$), 4.23-4.09 (8H, m, $\text{C}_3\text{H}_7\text{CH}_2\text{N}$, $\text{NCH}_2(\text{CH}_2)_4\text{CH}_2\text{N}$), 7.77 (4H, dt, J = 6.9, 1.8 Hz, NCHCHN), 9.16 (2H, s, NCHN). HRMS (ESI): MH^+ , found 331.2859. $[\text{C}_{20}\text{H}_{35}\text{N}_4]^+$ requires 331.2856.

1,3-Bis(3-methylimidazolium-1-yl)propane bis(trifluoromethylsulfonyl)imide (1e). Prepared from 1,3-bis(3-methylimidazolium-1-yl)propane dibromide (**5d**) and lithium bis(trifluoromethylsulfonyl)imide, obtained as a white solid, 85% yield. M.p. 49-50 °C. ^1H NMR (DMSO- d_6) δ 2.36 (2H, quint, J = 7.0 Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.86 (6H, s, CH_3N), 4.20 (4H, t, J = 7.0 Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 7.73 (4H, s, NCHCHN), 9.07 (2H, s, NCHN). HRMS (ESI): MH^+ , found 205.1458. $[\text{C}_{11}\text{H}_{17}\text{N}_4]^+$ requires 205.1448.

1,3-Bis(3-methylimidazolium-1-yl)propane hexafluorophosphate (1f). Prepared from 1,3-bis(3-methylimidazolium-1-yl)propane dibromide (**5d**) and potassium hexafluorophosphate, obtained as a white solid, 83% yield. M.p. 135-136 °C (lit. 131 °C).^[1] ^1H NMR (DMSO- d_6) δ 2.36 (2H, quint, J = 7.0 Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.86 (6H, s, CH_3N), 4.20 (4H, t, J = 6.9 Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 7.74 (4H, s, NCHCHN), 9.08 (2H, s, NCHN). HRMS (ESI): MH^+ , found 205.1471. $[\text{C}_{11}\text{H}_{17}\text{N}_4]^+$ requires 205.1448.

1,4-Bis(3-methylimidazolium-1-yl)butane bis(trifluoromethylsulfonyl)imide (1g). Prepared from 1,4-bis(3-methylimidazolium-1-yl)butane dichloride (**5e**) and lithium bis(trifluoromethylsulfonyl)imide, obtained as a white solid, 93% yield. M.p. 57-58 °C (lit. 54-56 °C).^[2] ^1H NMR (DMSO- d_6) δ 1.85-1.67 (4H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.85 (6H, s, CH_3N), 4.19 (4H, t, J = 6.0 Hz, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_2\text{N}$), 7.72 (4H, dt, J = 9.0, 1.8 Hz, NCHCHN), 9.07 (2H, s, NCHN). HRMS (ESI): MH^+ , found 219.1588. $[\text{C}_{12}\text{H}_{19}\text{N}_4]^+$ requires 219.1604.

1,6-Bis(3-methylimidazolium-1-yl)hexane bis(trifluoromethylsulfonyl)imide (1h). Prepared from 1,6-bis(3-methylimidazolium-1-yl)hexane dichloride (**5f**) and lithium bis(trifluoromethylsulfonyl)imide, obtained as a viscous, colorless liquid, 92% yield. ^1H NMR ($\text{DMSO-}d_6$) δ 1.35-1.18 (4H, m, $\text{N}(\text{CH}_2)_2\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{N}$), 1.89-1.69 (4H, m, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{N}$), 3.85 (6H, s, CH_3N), 4.14 (4H, t, $J = 7.2$ Hz, $\text{NCH}_2(\text{CH}_2)_4\text{CH}_2\text{N}$), 7.71 (4H, dt, $J = 17.3, 1.8$ Hz, NCHCHN), 9.08 (2H, s, NCHN). HRMS (ESI): MH^+ , found 247.1901. $[\text{C}_{14}\text{H}_{23}\text{N}_4]^+$ requires 247.1917.

1,3-Bis(3-butyl-2-methylimidazolium-1-yl)propane bis(trifluoromethylsulfonyl)imide (4a). Prepared from 1,3-bis(3-butyl-2-methylimidazolium-1-yl)propane dibromide (**9a**) and lithium bis(trifluoromethylsulfonyl)imide, obtained as a viscous, slightly yellow liquid, 77% yield. ^1H NMR ($\text{DMSO-}d_6$) δ 0.92 (6H, t, $J = 7.4$ Hz, CH_3CH_2), 1.30 (4H, sext, $J = 7.5$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.75-1.65 (4H, m, $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2$), 2.23 (2H, quint, $J = 7.5$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.62 (6H, s, CH_3C), 4.11 (4H, t, $J = 7.4$ Hz, $\text{C}_3\text{H}_7\text{CH}_2\text{N}$), 4.17 (4H, t, $J = 7.6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 7.68 (4H, dd, $J = 20.5, 2.1$ Hz, NCHCHN). HRMS (ESI): MH^+ , found 317.2682. $[\text{C}_{19}\text{H}_{33}\text{N}_4]^+$ requires 317.2700.

1,3-Bis(2,3-dimethylimidazolium-1-yl)propane bis(trifluoromethylsulfonyl)imide (4b). Prepared from 1,3-bis(2,3-dimethylimidazolium-1-yl)propane dibromide (**9b**) and lithium bis(trifluoromethylsulfonyl)imide, obtained as a white solid, 93% yield. M.p. 90-91 °C (lit. 91 °C).^[1] ^1H NMR ($\text{DMSO-}d_6$) δ 2.20 (2H, quint, $J = 7.5$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.59 (6H, s, CH_3C), 3.75 (6H, s, CH_3N), 4.17 (4H, t, $J = 7.5$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 7.62 (4H, dd, $J = 12.7, 2.1$ Hz, NCHCHN). HRMS (ESI): MH^+ , found 233.1762. $[\text{C}_{13}\text{H}_{21}\text{N}_4]^+$ requires 233.1761.

1,4-Bis(2,3-dimethylimidazolium-1-yl)butane bis(trifluoromethylsulfonyl)imide (4c). Prepared from 1,4-bis(2,3-dimethylimidazolium-1-yl)butane dichloride (**9c**) and lithium bis(trifluoromethylsulfonyl)imide, obtained as a white solid, 94% yield. M.p. 126-127 °C. ^1H

NMR (DMSO-*d*₆) δ 1.81-1.63 (4H, m, NCH₂CH₂CH₂CH₂N), 2.57 (6H, s, CH₃C), 3.75 (6H, s, CH₃N), 4.13 (4H, s, NCH₂(CH₂)₂CH₂N), 7.61 (4H, dd, *J* = 7.5, 2.1 Hz, NCHCHN). HRMS (ESI): MH⁺, found 247.1924. [C₁₄H₂₃N₄]⁺ requires 247.1917.

1,6-Bis(2,3-dimethylimidazolium-1-yl)hexane bis(trifluoromethylsulfonyl)imide (4d).

Prepared from 1,6-bis(2,3-dimethylimidazolium-1-yl)hexane dichloride (**9d**) and lithium bis(trifluoromethylsulfonyl)imide, obtained as a viscous, colorless liquid, 88% yield. ¹H NMR (DMSO-*d*₆) δ 1.29 (4H, quint, *J* = 3.7 Hz, N(CH₂)₂CH₂CH₂(CH₂)₂N), 1.76-1.62 (4H, m, NCH₂CH₂(CH₂)₂CH₂CH₂N), 2.57 (6H, s, CH₃C), 3.74 (6H, s, CH₃N), 4.09 (4H, t, *J* = 7.3 Hz, NCH₂(CH₂)₄CH₂N), 7.63-7.60 (4H, m, NCHCHN). HRMS (ESI): MH⁺, found 275.2232. [C₁₆H₂₇N₄]⁺ requires 275.2230.

Table S1

Figure S1

Figure S2

Figure S3

Figure S4

Figure S5

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Table S1. Thermal stability of the investigated imidazolium-based DILs

Entry	DIL	Stability ^a (°C)	Entry	DIL	Stability ^a (°C)
1	5a	250	12	1g	410
2	1b	310	13	5f	250
3	1a	390	14	1h	400
4	5b	250	15	9a	260
5	1c	400	16	4a	380
6	5c	210	17	9b	290
7	1d	380	18	4b	410
8	5d	290	19	9c	290
9	1e	400	20	4c	410
10	1f	330	21	9d	270
11	5e	300	22	4d	400

^aTemperature at which the decomposition starts.

Scheme S1. Preparation of the investigated imidazolium-based DILs **1a-h** and **5a-f**.

Scheme S2. Preparation of the investigated imidazolium-based DILs **4a-d** and **9a-d**.

Figure S1. Peak distribution in negative-ion ESI mass spectra (fragmentor voltage – 40 V) of DILs **1e**, **1f**, **1h**, **5a**, and **5d**.

Figure S2. ^1H NMR spectrum of pure DIL **5a**.

Figure S3. ^1H NMR spectrum of DIL **5a** after heating at 250 °C temperature for 30 min.

Figure S4. ^1H NMR spectrum of pure DIL **1b**.

Figure S5. ^1H NMR spectrum of DIL **1b** after heating at 250 °C temperature for 60 min.