Supporting Information for:

Hydrogen Storage Materials Based on Imidazolium Ionic Liquids

Marcelo Paulo Stracke, Günter Ebeling, Renato Cataluña, Jairton Dupont *

Laboratory of Molecular Catalysis,

Av. Bento Gonçalves, 9500 Porto Alegre, Brasil

e-mail: dupont@iq.ufrgs.br

Experimental

General conditions

All preparative procedures were carried out under argon using standard Schlenk tube techniques. The hydrogenation experiments were performed by simple placing the salts (20 mmol) with the desired catalyst (1 mass % in relation to the salt) in a 100 mL stainless steel Parr reactor at 70 °C for **2e** and **2f** and 90 °C for **2g,** under 35 atm for **2e** and 50 atm for **2f** and **2g**. A deliberated stirring of 800 rpm was used and the fall in the hydrogen pressure in the reactor was monitored with a pressure transducer interfaced through a Novus converter to a PC and the data workup via Microcal Origin 5.0. The dehydrogenation reactions were performed by melting the salts (20 mg) in the presence of Pd/C (5%) (salt / catalyst = 100/1 in mass) and placing the obtained melts in a borosilicate glass U-type tube reactor (height, 25 cm; tube internal diameter, 2 mm; bottom bulb volume, 0.5 mL) connected to a TCD detector, maintaining a constant flux of argon (25 mL/min). The heating of the reactor was performed from room temperature to 300 °C (1 °C/min) and the system was kept at this last temperature for more 20 min. The IR spectra were recorded on a Bomem MB spectrophotometer as neat liquid films. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian

Gemini 300 MHz spectrometer. The chemical shifts were measured in ppm relative to TMS or acetone-d_6 as external standard. The ESI-HRMS spectra were recorded in a Waters Micromass Q-Tof micro Mass Spectrometer YB 320. DSC measurements were carried out on a Thermal Analyst 2100 (TA instruments), calibrated using an indium primary standard. Ionic liquid samples were sealed in Al pans (in the nitrogen-filled glove box) with an empty Al pan was used as reference. DSC measurements were carried out in a nitrogen atmosphere on samples of different sizes and the samples initially examined using different rates of heating and cooling. All of the DSC data discussed in the manuscript were measured on 7-12mg samples. TGA measurements were carried out on a Thermogravimetric Analyser 2950 (Du Pont instruments) calibrated using a nickel standard. TGA measurements were carried out in a nitrogen atmosphere on samples of different sizes and the samples initially examined using rate 20°C/min of heating. All of the TGA data discussed in the manuscript were measured on 8-12mg samples.

Synthesis of the compounds used in the manuscript

Benzyl methanesulfonate. To a solution of benzyl alcohol (2.16 g, 20.0 mmol) and triethylamine (3.03 g, 30.0 mmol) in dichloromethane (60 mL), kept between -10 and 0 ºC, was added methanesulfonyl chloride (2.52 g, 22.0 mmol) over a period of 5-10 min. Stirring for an additional 10-15 min completed the reaction. The reaction mixture was transferred to a separatory funnel and was successively washed with ice water (3 x 20 mL), cold 10% hydrochloric acid (10 mL), saturated sodium bicarbonate solution (3 X 30 mL) and saturated brine solution (3 x 20 mL). Evaporation of the solvent under reduced pressure yielded the desired product (3.40 g, 92%). IR (film, cm^{-1}): 3129-3081, 2985-2876, 1592, 1497, 1446, 1355, 1171, 778. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.40 (m, 5H), 5.24 (s, 2H), 2.90 (s, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 133.4, 129.1, 128.1, 78.3, 38.2.

3-(Phenyl)-propyl methanesulfonate. To a solution of the 3-phenyl-propan-1-ol (13.62 g, 100.0 mmol) in dichloromethane (60 mL), containing triethylamine (21 mL) and kept between -10 and 0ºC, was added methanesulfonyl chloride (11.45 g, 100.0 mmol) over a period of 5-10 minutes. Stirring was continued for additional 2 h. at room temperature. The reaction mixture was transferred to a separatory funnel and was

successively washed with ice water (3 x 50 mL), cold 10% hydrochloric acid (30 mL), saturated sodium bicarbonate solution (3 X 30 mL) and saturated sodium chloride solution (3 x 20 mL). Evaporation of the solvent under reduced pressure yielded the desired product (19.47 g, 91% yield). IR (film, cm^{-1}): 3030, 2940, 1605, 1498, 1455, 1357, 1174, 976, 803, 701. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.29-7.16 (m, 5H), 4.25 (t, *J* = 6.3 Hz, 2H), 2.98 (s, 3H), 2.74 (apparent t , *J* = 7.4 Hz, 2H), 2.10-2.00 (m, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 144.2, 133.1, 129.2, 128.8, 127.9, 122.7, 121.5, 51.9, 39.4, 35.3, 10.1.

2-(Phenyl)-ethyl methanesulfonate. To a solution of 2-phenyl-ethanol (12.20g, 100.0 mmol) in dichloromethane (60 mL) containing of triethylamine (21 mL) and kept between -10and 0ºC, was added methanesulfonyl chloride (11.45g, 100.0 mmol) over a period of 5-10 minutes. Stirring for more 50 min. completed the reaction. The reaction mixture was transferred to a separatory funnel and was successively washed with ice water (3 x 50 mL), cold 10% hydrochloric acid (30 mL), saturated sodium bicarbonate solution (3 X 30 mL) and saturated sodium chloride solution (3 x 20 mL). Evaporation of the solvent under reduced pressure yielded the desired product (19.10 g, 95% yield). IR (film, cm^{-1}): 3028, 2939, 1496, 1454, 1172, 973, 802, 700, 528. ^{1}H NMR (acetone d_6) δ (ppm): 7.29-7.19 (m, 5H), 4.23 (t, *J* = 7.1 Hz, 2H), 3.11 (s, 3H), 2.74 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (acetone d_6) δ (ppm): 138.5, 130.5, 130.4, 129.9, 129.6, 128.1, 72.0, 37.6, 36.6.

2,2-(Diphenyl)-ethyl methanesulfonate. To a solution of 2,2-diphenyl-ethanol (6.92 g, 32.6 mmol) and triethylamine (7 mL) in dichloromethane (60 mL), was added methanesulfonyl chloride (3.73 g, 32.6 mmol) at -10 to 0ºC over a period of 5-10 minutes. Stirring for an additional 50 min. completed the reaction. The reaction mixture was transferred to a separatory funnel and was successively washed with ice water (3 x 20 mL), cold 10% hydrochloric acid (10 mL), saturated sodium bicarbonate solution (2 X 10 mL) and saturated sodium chloride solution (2 x 10 mL). Evaporation of the solvent under reduced pressure yielded the desired product (8.69 g, 91% yield). Mp = 56-57 ºC. IR (film, cm^{-1}): 3004, 2964, 2939, 1508, 1419, 1174, 956, 816, 802, 761. ^{1}H NMR (acetone d_6) δ (ppm): 7.41-7.21 (m, 10H), 4.80 (d, *J* = 7.7 Hz, 2H), 4.51 (t, *J* = 7.7 Hz, 1H), 3.00 (s, 3H). ^{13}C NMR (acetone d_6) δ (ppm): 142.2, 130.1, 129.7, 128.5, 73.3, 51.8, 37.7.

1-Benzyl-3-methyl-imidazolium methanesulfonate 1a. Imidazolium salt **1a** was prepared by mixing benzyl methanesulfonate (5.60 g, 30.0 mmol) and 1-methyl-imidazole (2.60 g, 32.0 mmol) at 0°C and keeping the mixture at room temperature for 24 h. The obtained solid was crushed, washed with small portions of ethyl acetate (3x 2 mL) and filtered. The resulting colorless solid was dried under vacuum. (7.70 g, 96% yield). ESI-HRMS positive ion, calculated for $[C_{11}H_{13}N_2]^+$, *m*/*z* 173.1079; found. *m*/*z* 173.1079. ESI-HRMS negative ion, calculated for $[CH_3SO_3]^-$, *m*/*z* 94.9803; found, *m*/*z* 94.9803. IR (film, cm^{-1}): 3169, 3081, 2985, 2936, 1588, 1497, 1456, 1192, 1041, 778. ^1H NMR ($CDCl_3$) δ (ppm): 9.82 (s, 1H), 7.49-7.32 (m, 7H), 5.43 (s, 2H), 3.95 (s, 3H), 2.74 (s, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 137.5, 133.3, 129.1, 128.6, 128.1, 126.7, 123.6, 121.8, 52.8, 39.6, 36.1.

1-Methyl-3-[2-(phenyl)-ethyl]-imidazolium methanesulfonate 1b. Compound **1b** was prepared by reaction of 2-(phenyl)-ethyl methanesulfonate (19.10 g, 95.0 mmol) and 1-methyl-imidazole (7.80 g, 95.0 mmol) at room temperature for 24 h. The viscous liquid obtained was washed with ethyl acetate (2x 10 mL) and dried under reduced pressure (24.30 g, 90% yield). ESI-HRMS positive ion, calculated for $[C_{12}H_{15}N_2]^+$, *m*/*z* 187.1235; found, *m*/*z* 187.1132. ESI-HRMS negative ion, calculated for $[CH_3SO_3]^-$, *m*/*z* 94.9803; found, *m*/*z* 94.9809. IR (film, cm^{-1}): 3130, 2950, 2884, 1610, 1593, 1437, 1353, 1198, 1073, 805. ^1H NMR ($CDCl_3$) δ (ppm): 9.71 (s, 1H), 7.32-7.10 (m, 7H), 4.53 (t, J = 7.1 Hz, 2H), 3.95 (s, 3H), 3.19 (t, J = 7.1 Hz, 2H), 2.77 (s, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 137.9, 136.9, 129.0, 128.9, 127.3, 122.9, 122.1, 50.9, 39.6, 36.4, 36.3.

1-Methyl-3-[3-(phenyl)-propyl]-imidazolium methanesulfonate 1c. The imidazolium salt **1c** was prepared by reaction of 3-(phenyl)-propyl methanesulfonate (19.50 g, 91.0 mmol) with 1-methyl-imidazole (7.50 g, 91.0 mmol) at room temperature for 24 h. The viscous liquid obtained was washed with ethyl acetate (2x 10 mL) and dried under reduced pressure (26.90g, 99% yield). ESI-HRMS positive ion, calculated for $[C_{13}H_{17}N_2]^+$, *m*/*z* 201.1392; found, *m*/*z* 201.1372. ESI-HRMS negative ion, calculated for $[CH_3SO_3]^-$, *m*/*z* 94.9803; found, *m*/*z* 94.9834. IR (film, cm^{-1}): 3130, 3038, 2890, 1611, 1592, 1483, 1437, 1123, 992, 804. ^1H NMR ($CDCl_3$) δ (ppm): 9.77 (s, 1H), 7.49 (s, 1H), 7.48 (s, 1H), 7.40-7.14 (m, 5H), 4.28

(t, J = 7.4 Hz, 2H), 3.96 (s, 3H), 2.96 (s, 3H), 2.69 (t, J = 7.4 Hz, 2H), 2.22 (quintet, J = 7.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 139.6, 137.6, 128.4, 128.0, 126.1, 123.5, 121.9, 49.1, 39.5, 32.0, 31.2

1-Methyl-3-[2,2-(diphenyl)-ethyl]-imidazolium methanesulfonate 1d. Compound **1d** was prepared by reaction of 2,2-(diphenyl)-ethyl methanesulfonate (8.70 g, 29.6 mmol) and 1-methyl-imidazole (2.40 g, 29.6 mmol) at 70 °C for 72 h. The viscous liquid obtained was washed with ethyl acetate (2x 4 mL) and the resulting product **1d** was dried under reduced pressure (9.60g, 90% yield). ESI-HRMS positive ion, calculated for $[C_{18}H_{19}N_2]^+$, *m*/*z* 263.1548; found, *m*/*z* 263.1540. ESI-HRMS negative ion, calculated for $[CH_3SO_3]^-$, *m*/*z* 94.9803; found, *m*/*z* 94.9803. IR (film, cm^{-1}): 3142, 3061, 3006, 2964, 2933, 1363, 1192, 1057, 784, 561. ^{1}H NMR ($CDCl_3$) δ (ppm): 9.57 (s, 1H), 7.40-7.10 (m, 12H), 4.89 (d, J = 8.5 Hz, 2H), 4.60 (t, J = 8.5 Hz, 1H), 3.78 (s, 3H), 2.75 (s, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 139.4, 137.8, 128.8, 128.3, 123.3, 122.3, 53.2, 51.4, 39.6, 36.0, 34.9.

1-Benzyl-3-methyl-imidazolium tetrafluoroborate 2a. To a solution of 1-benzyl-3-methyl-imidazolium methanesulfonate **1a** (22.0 g. 82.1 mmol) in water (11 mL) was added a solution of sodium tetrafluoroborate (9.00 g, 82.1 mmol) in water (11 mL) and the reaction mixture was stirred for 0.5 h. The product was isolated by simple extraction with CH_2Cl_2 (3 x 50 mL), followed by solvent evaporation under reduced pressure (19.80 g, 93% yield). ESI-HRMS positive ion, calculated for $[C_{11}H_{13}N_2]^+$, *m*/*z* 173.1079; found, *m*/*z* 173.1084. ESI-HRMS negative ion, calculated for $[BF_4]^-$, *m*/*z* 87.0029); found, *m*/*z* 87.0022. IR (film, cm^{-1}): 3157, 3117, 3005, 2967, 1576, 1565, 1457, 1164, 1061. ^{1}H NMR (acetone-d_6) δ (ppm): 9.08 (s, 1H), 7.74 (s, 1H), 7.73 (s, 1H), 7.70-7.39 (m, 5H), 5.58 (s, 2H), 4.04 (s, 3H). ^{13}C NMR (acetone-d_6) δ (ppm): 138.3, 135.9, 130.6, 130.5, 130.2, 125.7, 123.9, 54.2, 37.3.

1-Benzyl-3-methyl-imidazolium hexafluorophosphate 2b. A solution of 1-benzyl-3-methyl-imidazolium methanesulfonate **1a** (4.00 g, 15.0 mmol) in water (2 mL) was mixed at 0°C with a solution of sodium hydroxyde (0.60 g, 15.0 mmol) in water (2 mL). After 5 min., hexafluorophosphoric acid (60 wt. % in water, 2.5 mL, 17 mmol) was added to the solution and the reaction mixture was stired for 0.5 h at 0°C. The product was extracted with dichloromethane (2x 30 mL) and the combined organic extract was washed

with saturated sodium carbonate solution (2x 20 mL). Solvent evaporation under reduced pressure gave a pale yellow solid (4.40 g, 93% yield). ESI-HRMS positive ion, calculated for $[C_{11}H_{13}N_2]^+$, *m*/*z* 173.1079; found, *m*/*z* 173.1079. ESI-HRMS negative ion, calculated for $[F_6P]^-$, *m*/*z* 144.9642; found, *m*/*z* 144.9631. IR (film, cm^{-1}): 3154, 3113, 2966, 2924, 1576, 1560, 1498, 845, 557. ^1H NMR (acetone-d_6) δ (ppm): 9.10 (br s, 1H), 7.76 (t, *J* = 1.8 Hz, 1H), 7.73 (t, *J* = 1.8 Hz, 1H), 7.50-7.43 (m, 5H), 5.58 (s, 2H), 4.07 (s, 3H). ^{13}C NMR (acetone-d_6) δ (ppm): 138.1, 135.79, 130.6, 130.5, 130.0, 125.6, 123.9, 54.2, 37.2.

1-Methyl-3-[3-(phenyl)-propyl]-imidazolium hexafluorophosphate 2c. To a solution of 1-methyl-3-[3-(phenyl)-propyl]-imidazolium methanesulfonate **1c** (9.30 g. 31.4 mmol) in water (10 mL) was added a solution of potassium hexafluorophosphate (5.80 g, 31.4 mmol) in water (50 mL). The mixture was stirred for 0.5 h to ensure complete anion methatesis. The biphasic reaction mixture was extracted with dichloromethane (3 x 50 mL) and the product **2c** was obtained by solvent evaporation under reduced pressure (15.90 g, 95% yield). ESI-HRMS positive ion, calculated for $[C_{13}H_{17}N_2]^+$, *m*/*z* 201.1392; found, *m*/*z* 201.1358. ESI-HRMS negative ion, calculated for $[F_6P]^-$, *m*/*z* 144.9642); found, *m*/*z* 144.9645. IR (film, cm^{-1}): 3164, 3121, 3005, 2962, 2865, 1604, 1575, 1483, 1456, 1173, 841, 558. ^1H NMR (acetone d_6) δ (ppm): 8.61 (br s, 1H), 7.52 (t, *J* = 1.7 Hz, 1H), 7.45 (t, *J* = 1.7 Hz, 1H), 7.38-7.03 (m, 5H), 4.18 (t, *J* = 7.4 Hz, 2H), 4.02 (s, 3H), 2.63 (t, *J* = 7.4 Hz, 2H), 2.18 (quintet, *J* = 7.4 Hz, 2H). ^{13}C NMR (acetone d_6) δ (ppm): 141.9, 137.5, 129.8, 129.7, 127.5, 124.9, 123.5, 50.5, 36.8, 33.2, 32.6.

1-Benzyl-3-methyl-imidazolium bis-(trifluoromethanelsulfonyl) imidate 2d. To a solution of 1-benzyl-3-methyl-imidazolium methanesulfonate **1a** (2.70 g, 10.0 mmol) in water (15 mL) was added lithium bis-(trifluoromethanesulfonyl) imidate (2.90 g, 10.0 mmol) and the mixture was stirred for 1 h. Extraction with dichloromethane (2x 30 mL), washing of the combined extract with water (3 x 20 mL) and solvent evaporation under reduced pressure gave the desired product **2d** (4.10 g, 90 % yield). ESI-HRMS positive ion, calculated for $[C_{11}H_{13}N_2]^+$, *m*/*z* 173.1073; found, *m*/*z* 173.1044. ESI-HRMS negative ion, calculated for $[C_2F_6NO_4S_2]^-$, *m*/*z* 279.9173; found, *m*/*z* 279.9163. IR (film, cm^{-1}): 3154, 3117, 2964, 1562, 1457, 1350, 1190, 1055. ^1H NMR (acetone-d_6) δ (ppm): 9.10 (s, 1H), 7.77 (s, 1H), 7.73 (s, 1H), 7.70-7.42 (m, 5H), 5.58

(s, 2H), 4.08 (s, 3H). ^{13}C NMR (acetone-d_6) δ (ppm): 138.2, 135.7, 130.6, 130.7, 130.6, 130.1, 125.8, 124.13, 123.8, 119.5, 54.3, 37.4.

1-Methyl-3-[2-(phenyl)-ethyl]-imidazolium bis-(trifluoromethanesulfonyl) imidate 2e. To a solution of 1-methyl-3-[2-(phenyl) ethyl]-imidazolium methanesulfonate **1b** (24.30 g, 85.5 mmol) in water (80 mL) was added lithium bi(trifluoromethanesulfonyl) imidate (24.90 g, 87.0 mmol) and the mixture was stirred for 1 h. at room temperature. The resulting crude solid compound **2e**, insoluble in water, was filtered off and dissolved in dichloromethane (150 mL). The dichloromethane solution was washed with water (2 x 50 mL), the solvent was evaporated and the solid product **2e** was dried under reduced pressure (39.40 g, 98% yield). ESI-HRMS positive ion, calculated for $[C_{12}H_{15}N_2]^+$, *m*/*z* 187.1235; found, *m*/*z* 187.122. ESI-HRMS negative ion, calculated for $[C_2F_6NO_4S_2]^-$, *m*/*z* 279.9173; found, *m*/*z* 279.9106. IR (film, cm^{-1}): 3137-3106, 3050, 2995, 1597, 1438, 1154, 1335, 1154, 1098. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.47 (s, 1H), 7.31-7.08 (m, 7H), 4.36 (t, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 3.08 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 135.9, 135.6, 129.0, 128.6, 127.5, 123.6, 123.4, 122.2, 51.2, 36.2.

1-Methyl-3-[3-(phenyl)-propyl]-imidazolium bis-(trifluoromethanelsulfonyl) imidate 2f. To a solution of 1-methyl-3-[3-(phenyl)-propyl]-imidazolium methanesulfonate **1c** (26.90 g, 90.0 mmol) in water (80 mL) was added lithium bis-(trifluoromethylsulfonyl) imidate (26.10 g, 91.0 mmol) and the mixture was stirred for 1 h at room temperature. The resulting crude solid compound **2f**, insoluble in water, was filtered off and dissolved in dichloromethane (200 mL). The dichloromethane solution was washed with water (2 x 50 mL), the solvent was evaporated and the solid product **2f** was dried under reduced pressure (42.80 g, 97% yield). ESI-HRMS positive ion, calculated for $[C_{13}H_{17}N_2]^+$, *m*/*z* 201.1392; found, *m*/*z* 201.1379. ESI-HRMS negative ion, calculated for $[C_2F_6NO_4S_2]^-$, *m*/*z* 279.9173; found, *m*/*z* 279.9160. IR (film, cm^{-1}): 3137, 3015, 2948, 2865, 1609, 1588, 1461, 1339, 1222, 1103, 857, 779, 722, 581. ^{1}H NMR (acetone d_6) δ (ppm): 8.98 (s, 1H), 7.76 (s, 1H), 7.66 (s, 1H), 7.32-7.16 (m, 5H), 4.39 (t, *J* = 7.4 Hz, 2H), 4.02 (s, 3H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.31 (quintet, *J* = 7.4 Hz, 2H). ^{13}C NMR (acetone d_6) δ (ppm): 141.5, 137.6, 129.5, 127.2, 124.9, 123.5, 123.3, 119.0, 50.3, 36.8, 33.0, 32.4.

1-Methyl-3-[2,2-(diphenyl)-ethyl]-imidazolium bis-(trifluoromethanelsulfonyl) imidate 2g. To a solution of imidazolium methanesulfonate **1d** (9.56 g, 26.6 mmol) in water (20 mL), was added lithium bis-(trifluoromethanesulfonyl) imidate (7.64 g, 26.6 mmol) and the mixture was stirred for 1 h at room temperature. The resulting water insoluble solid compound was filtered off and dissolved in dichloromethane (100 mL). The dichloromethane solution was washed with water (2 x 30 mL), the solvent was evaporated and the solid product **2g** was dried under reduced pressure (14.60 g, 98% yield). ESI-HRMS positive ion, calculated for $[C_{18}H_{19}N_2]^+$, *m*/*z* 263.1548; found, *m*/*z* 263.1537. ESI-HRMS negative ion, calculated for $[C_2F_6NO_4S_2]^-$, *m*/*z* 279.9173; found, *m*/*z* 279.9167. IR (film, cm^{-1}): 3150, 3120, 3096, 3031, 2963, 1566, 1494, 1454, 1360, 1193, 1138, 1052, 708, 613. ^1H NMR ($CDCl_3$) δ (ppm): 8.44 (br s, 1H), 7.32-7.03 (m, 10H), 7.06 (d, *J* = 1.9 Hz, 1H), 7.04 (d, *J* = 1.9 Hz, 1H), 4.76 (d, *J* = 8.2 Hz, 2H), 4.42 (t, *J* = 8.2 Hz, 1H) 3.72 (s, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 139.1, 136.3, 129.2, 127.8, 127.6, 123.1, 122.5, 121.9, 117.6, 113.4, 53.9, 51.7, 36.1.

1-Methyl-3-[2-(cyclohexyl)-ethyl]-imidazolium bis-(trifluoromethanelsulfonyl) imidate 3a. Palladium catalyst (5 wt. % on carbon, 0.40 g, 0.20 mmol, 1/100 molar) was mixed under vigorous stirring with imidazolium salt **2e** (9.50 g, 20.3 mmol) placed in a Schlenk tube. The resulting black mixture was transferred under argon to a stainless steel reactor provided with magnetic stirring and the system was pressurized with 35 atm of H_2. The reactor was heated to 70°C with constant stirring (800rpm) for 104 h. After this time, the crude hydrogenation product was dissolved in dichloromethane (150 mL) and the solution was filtered through a short column packed with alumina / celite. Solvent evaporation under reduced pressure gave the product **3a** as a solid (9.12 g, 95% yield). ESI-HRMS positive ion, calculated for $[C_{12}H_{21}N_2]^+$, *m*/*z* 193.1705; found, *m*/*z* 193.1707. ESI-HRMS negative ion, calculated for $[C_2F_6NO_4S_2]^-$, *m*/*z* 279.9173; found, *m*/*z* 279.9158. IR (film, cm^{-1}): 3137, 2878-2877, 1547, 1460, 1408, 1222, 1154, 1099. ^1H NMR (acetone d_6) δ (ppm): 9.01 (s, 1H), 7.76 (s, 1H), 7.68 (s, 1H), 4.36 (t, *J* = 7.7 Hz, 2H), 4.06 (s, 3H), 1.92-1.60 (m, 6H), 1.42-0.92 (m, 7H). ^{13}C NMR (acetone d_6) δ (ppm): 137.9, 125.4, 124.0, 50.9, 49.1, 38.8, 36.2, 35.9, 34.0, 33.3, 20.5, 14.2.

1-Methyl-3-[3-(cyclohexyl)-propyl]-imidazolium bis-(trifluoromethanesulfonyl) imidate 3b. Palladium catalyst (5 wt. % on carbon, 0.40 g, 0.20 mmol, 1/100 molar) was mixed under vigorous stirring with imidazolium salt **2f** (9.60 g, 20 mmol) placed in a Schlenk tube. The resulting black mixture was transferred under argon to a stainless steel reactor provided with magnetic stirring and the system was pressurized with 50 atm of H_2. The reactor was heated to 70°C with constant stirring (800rpm) for 104 h. After this time, the crude hydrogenation product was dissolved in dichloromethane (250 mL) and the solution was filtered through a short column packed with alumina / celite. Solvent evaporation under reduced pressure gave the product **3b** as a viscous liquid (9.50 g, 97 % yield). ESI-HRMS positive ion, calculated for $[C_{13}H_{23}N_2]^+$, *m*/*z* 207.1861; found, *m*/*z* 207.1857. ESI-HRMS negative ion, calculated for $[C_2F_6NO_4S_2]^-$, *m*/*z* 279.9173; found, *m*/*z* 279.9169. IR (film, cm^{-1}): 3136, 2877, 1536, 1460, 1406, 1221, 1154, 1098, 757. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.72 (br s, 1H), 7.34 (t, *J* = 1.8 Hz, 1H), 7.32 (t, *J* = 1.8 Hz, 1H), 4.14 (t, *J* = 7.4 Hz, 2H), 3.93 (s, 3H), 1.91-1.66 (m, 6H), 1.27-1.04 (m, 4H), 0.92-0.81 (m, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 135.9, 123.7, 122.2, 50.4, 36.9, 36.2, 33.5, 33.5, 32.9, 27.4, 26.4, 26.1.

1-Methyl-3-[2,2-(dicyclohexyl)-ethyl]-imidazolium bis-(trifluoromethanelsulfonyl) imidate 3c. Palladium catalyst (5 wt. % on carbon, 0.40 g, 0.20 mmol, 1/100 molar) was mixed under vigorous stirring with imidazolium salt **2g** (10.30 g, 19.0 mmol) placed in a Schlenk tube. The resulting black mixture was transferred under argon to a stainless steel reactor provided with magnetic stirring and the system was pressurized with 50 atm of H_2. The reactor was heated to 90°C with constant stirring (800rpm) for 106 h. After this time, the crude hydrogenation product was dissolved in dichloromethane (200 mL) and the solution was filtered through a short column packed with alumina. Solvent evaporation under reduced pressure gave the product **3c** as a solid (9.90 g, 94% yield). ESI-HRMS positive ion, calculated for $[C_{18}H_{31}N_2]^+$, *m*/*z* 275.2487; found, *m*/*z* 275.2480. ESI-HRMS negative ion, calculated for $[C_2F_6NO_4S_2]^-$, *m*/*z* 279.9173; found, *m*/*z* 279.9158. IR (film, cm^{-1}): 3153, 3119, 2927, 2853, 1349, 1191, 1136, 1057, 616. ^{1}H NMR (acetone d_6) δ (ppm): 9.14 (br s, 1H), 7.82 (t, *J* = 1.9 Hz, 1H), 7.75 (t, *J* = 1.9 Hz 1H), 4.39 (d, *J* = 7.1 Hz, 2H), 4.07 (s, 3H), 1.80-1.11 (m, 23H). ^{13}C NMR (acetone d_6) δ (ppm): 138.3, 130.1, 129.9, 128.7, 125.5, 124.5, 123.7, 119.4, 51.4, 50.6, 39.6, 37.4, 32.6, 31.4, 28.1, 27.9, 27.7, 27.6.