Niobium(V)chloride and imidazolium bromides as efficient dual catalyst system for the cycloaddition of carbon dioxide and propylene oxide

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Supporting Information

1. Experimental Details

All catalytic runs and the preparation of the 2-alkyl-1,3-bis-(2',3',4',5',6'-pentafluorobenzyl) and 2-alkyl-1,3-dibenzylimidazoliumbromides, were performed under protective atmosphere, whereas the synthesis of 1,2-dialkylimidazoliumbromides was performed under standard atmosphere. Benzyl bromide 1-bromobutane, 1-bromooctane, 2-ethylimidazole, 1-methylimidazole and 2-methylimidazole were purchased at ABCR. Chlorotrimethylsilane, 2-isopropylimidazole, iodomethane, 1,2-dimethylimidazole, niobium(V) chloride (99 %), 2,3,4,5,6-pentafluorobenzyl bromide, tetrabutylammonium bromide and iodide were purchased from Sigma Aldrich. 1,2,4,5-Tetramethylimidazole was purchased from TCI Chemicals, propylene oxide from Acros Organics (99.5 %, AcroSeal) and carbon dioxide (99.995 vol.-%) from Westfalen AG. The tetrabutylammonium salts were dried for 24 h at 70 °C in vacuum prior to use in catalysis. All other chemicals were used as received without any further purification.

1.1. Analytical Equipment

¹H, ¹³C, ¹⁹F NMR spectra were recorded in CDCl₃, MeOD-d₃ or DMSO-d₆ using a 400-MHz Bruker Avance DPX-400 spectrometer. The microanalyses of the synthesized products were determined in the Mikroanalytisches Labor of the Technische Universität München in Garching. For the determination of the melting points, a MPM-H2 melting point meter was used. The catalytic runs were monitored by GC on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett-Packard integration unit 3396 Series II. The melting points (m.p.) of compounds were determined on a MPM-H2 melting point meter.

1.2. Experimental procedure for the catalytic cycloaddition of PO with CO₂

Under protective atmosphere, a Fisher-Porter-bottle is charged with 27.0 mg niobium(V) chloride (0.10 mmol, 1 mol.-%) and a magnetic stirring bar. Subsequently 0.7 mL propylene oxide (10 mmol) are added through a syringe. Due to the exothermic reaction of PO and niobium(V) chloride (adduct formation), the mixture was stirred until it cooled down to room temperature. Afterwards, the nucleophile (0.20 mmol, 2 mol-%) is added to the reaction mixture under Ar and a constant pressure of 4 bar CO_2 is applied to the system for 1 min. The Fisher-Porter-bottle is closed and the reaction is conducted for the desired time. The system is

cooled to 0 °C and the overpressure of CO_2 is slowly released. To collect the reaction mixture, 5.0 mL of chloroform are added and an aliquot for the analysis through gas chromatography (GC) is taken.

1.3. Comparison of TBAB and TBAI as nucleophiles

The outcome of the reaction of PO and CO_2 using NbCl₅/TBAB and NbCl₅/TBAI as catalytic systems (NbCl₅/nucleophile/substrate ratio: 1/2/100, r.t., 4 bar CO_2) after the respective reaction time is shown in Figure S1.



Figure S1. Kinetic curve of the reaction of PO and CO₂ using NbCl₅/TBAB and NbCl₅/TBAI.

1.4. In-situ IR measurements

1.14 mmol of the nucleophile and 0.57 mmol (0.154 g) of NbCl₅ were weighed in the glove box. NbCl₅ was dissolved in 114 mmol (8 mL) of propylene oxide. After the solution cooled down to room temperature, it was added via syringe to the vial containing the ionic liquid.

The reaction mixture was then injected into the Multimax IR reactor. It was left to stir for 5 minutes before introducing CO_2 and the reaction was left to run for 6 h with IR measurements taken every minute. Upon completion of the reaction, the autoclave was opened and an aliquot for the determination of the yield and selectivity through NMR in $CDCl_3$ is taken.

1.5. Synthesis of the nucleophiles

1-Methyl-2-ethylimidazole,^[S1] 1-methyl-2-isopropylimidazole,^[S2] 1-butyl-2-isopropylimidazole^[S3] and the 2-alkyl-1-(trimethylsilyl)-imidazoles^[S4] were synthesized as described in literature. Furthermore, the 1-butylimidazolium bromides **1**, **2**,^[S5] **5**,^[S6] as well as the 1octylimidazolium compounds **6**,^[S7] 7,^[S8] the 1-benzylimidazolium bromides **14**,^[S9] **15**,^[S10] **26**, **27**^[S11] and 2,3,4,5,6-pentafluorobenzyl imidazolium salts **18**,^[S12] **24**^[S13] and **29**^[S14] were synthesized according to literature procedures. The purity of the compounds was determined with ¹H-, ¹³C-, ¹⁹F-NMR spectroscopy and elemental analysis.

1.5.1. Preparation of 1,2-dialkylimidazoliumbromides

To a stirred solution of the 1,2-dialkylimidazole (10 mmol, 1.0 equiv.) in THF (12 mL), the respective bromide (11 mmol, 1.1 equiv.) was added dropwise (see scheme 1). After stirring in a pressure tube for 24 h at 100 °C, the solvent was removed in vacuum and the resulting residue was washed with diethylether and hexane. The desired imidazolium bromides were obtained after drying in vacuum for 24 h at 70 °C as colourless powders or pale yellow solids in high to moderate yields.



 $R^{1} = Bu; R^{3} = Me; R^{4} = H; R^{2} = H (1), Me (2), Et (3),$ *i*-Pr (4), Bu (5) $R^{1} = Oc; R^{3} = Me; R^{4} = H; R^{2} = H (6), Me (7), Et (8),$ *i*-Pr (9), Bu (10) $R^{2} = Me; R^{3} = Me; R^{4} = Me; R^{1} = Bu (11), R^{1} = Oc(12)$ $S^{4} = S^{4} = S^{4$ Scheme S1. General synthesis of imidazolium bromides 1-30 (Me = methyl, Et = ethyl, i-Pr = isopropyl, Bu = n-butyl, Oc = n-octyl, Bz = benzyl, $Bz^{F5} = 1-(2,3,4,5,6-pentafluoro)benzyl)$.

1-Butyl-2-isopropyl-3-methylimidazolium bromide 4: colourless solid; yield: 82%, $C_{11}H_{21}BrN_2$ (261.21 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) δ = 7.89 (d, ³J = 2.00 Hz, 1H, NCH), 7.62 (d, ³J = 2.00 Hz, 1H, NCH), 4.26 (t, ³J = 7.60 Hz, 2H, NCH₂), 4.08 (s, 3H, NCH₃), 3.61 (st, ³J = 7.20 Hz, 1H, NCCH), 1.80 (m, 2H, CH₂), 1.50 (d, ³J = 7.20 Hz, 6H, CH₃), 1.40 (m, 2H, CH₂), 0.95 (t, ³J = 7.40 Hz, 3H, CH₂CH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) δ = 148.7, 124.6, 121.9, 49.1, 37.1, 32.8, 25.1, 19.7, 19.4, 13.7; m.p. 99 °C, elemental analysis (%): calcd: C 50.58, H 8.10, 10.72 N ; found: C 50.31, H 8.23, N 10.66.

2-Isopropyl-1-methyl-3-octylimidazolium bromide 9: colorless solid; yield: 60%, $C_{15}H_{29}BrN_2$ (317.31 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) δ = 7.91 (d, ³J = 2.00 Hz, 1H, NCH), 7.59 (d, ³J = 2.00 Hz, 1H, NCH), 4.23 (t, ³J = 7.60 Hz, 2H, NCH₂), 4.05 (s, 3H, NCH₃), 3.60 (st, ³J = 7.20 Hz, 1H, NCCH), 1.75 (m, 2H, CH₂), 1.44 (d, ³J = 7.20 Hz, 6H, CH₃), 1.15 (m, 10H, CH₂), 0.78 (t, ³J = 7.20 Hz, 3H, CH₂CH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) δ = 148.6, 124.4, 121.7, 49.2, 37.0, 31.6, 30.7, 29.0, 28.9, 26.3, 25.0, 22.5, 19.3, 14.0; m.p. 84 °C, elemental analysis (%): calcd: C 56.78, H 9.21, N 8.83; found: C 56.51, H 9.37, N 8.50.

2-Butyl-1-methyl-3-oktylimidazolium bromide 10: colourless solid; yield: 68 %; $C_{16}H_{31}BrIN_2$ (331.33 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) δ = 7.90 (d, ³J = 2.00 Hz, 1H, NCH), 7.57 (d, ³J = 2.00 Hz, 1H, NCH), 4.14 (t, ³J = 7.60 Hz, 2H, NCH₂), 4.02 (s, 3H, NCH₃), 3.07 (t, ³J = 7.60 Hz, 2H, NCCH₂), 1.81 (m, 2H, CH₂), 1.58 (m, 2H, CH₂), 1.44 (m, 2H, CH₂), 1.25 (m, 10H, CH₂), 0.94 (t, (t, ³J = 7.20 Hz, 3H, CH₂CH₃), 0.83 (t, ³J = 7.20

Hz, 3H, CH₂CH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) δ = 146.5, 123.7, 121.1, 48.7, 36.1, 31.7, 30.3, 29.4, 26.5, 23.8, 22.6, 22.5, 14.1, 13.7; m.p. 112 °C, elemental analysis (%): calcd: C 58.00, H 9.43, N 8.45; found: C 57.88, H 9.60, N 8.11.

3-Butyl-1,2,4,5-tetramethylimidazolium bromide 11: pale yellow solid; yield: 93 %; $C_{11}H_{21}BrN_2$ (261.21 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) $\delta = 4.07$ (t, ³J = 7.80 Hz, 2H, NCH₂), 3.83 (s, 3H, NCH₃), 2.87 (s, 3H, NC(CH₃)N), 2.25 (s, 3H, CH₃NCCH₃), 2.23 (s, 3H, CH₂NCCH₃), 1.68 (m, 2H, CH₂), 1.41 (m, 2H, CH₂), 0.97 (t, ³J = 7.40 Hz, 3H, CH₂CH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) $\delta = 142.4$, 126.1, 124.9, 45.8, 33.2, 31.7, 19.8, 13.6, 11.7, 9.1, 8.9; m.p. 95 °C, elemental analysis (%): calcd: C 50.58 , H 8.10 , N 10.72; found: C 49.91, H 8.17, N 10.84.

3-Octyl-1,2,4,5-tetramethyllimidazolium bromide 12: pale yellow solid; yield: 93 %; $C_{15}H_{29}BrN_2$ (317.31 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) $\delta = 4.03$ (t, ³J = 7.80 Hz, 2H, NCH₂), 3.81 (s, 3H, NCH₃), 2.82 (s, 3H, NC(CH₃)N), 2.23 (s, 3H, CH₃NCCH₃), 2.21 (s, 3H, CH₂NCCH₃), 1.66 (m, 2H, CH₂), 1.28 (m, 10H, CH₂), 0.84 (t, ³J = 7.10 Hz, 3H, CH₂CH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) $\delta = 142.6$, 126.2, 124.8, 46.1, 33.3, 31.7, 29.9, 29.1, 26.7, 22.6, 14.1, 11.9, 9.2, 9.0; m.p. 79 °C, elemental analysis (%): calcd: C 56.78, H 9.21, N 8.83; found: C 56.70, H 9.73, N 9.11.

1,3-Dibutyl-2-isopropylimidazolium bromide 13: colourless solid; yield: 79%, C₁₄H₂₇BrN₂ (303.29 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) δ = 7.80 (s, 2H, NCH), 4.33 (t, ³J = 7.70 Hz, 4H, NCH₂), 3.62 (st, ³J = 7.20 Hz, 1H, NCCH), 1.80 (m, 4H, CH₂), 1.52 (d, ³J = 7.20 Hz, 6H, CH₃), 1.45 (m, 4H, CH₂), 0.99 (t, ³J = 7.40 Hz, 6H, CH₂CH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) δ = 148.4, 122.8, 49.1, 32.8, 25.0, 20.0, 19.8, 13.7; m.p. 91 °C, elemental analysis (%): calcd: C 55.44, H 8.97, N 9.24; found: C 55.27, H 9.09, N 9.38.

1-Benzyl-2-ethyl-3-methylimidazolium bromide 16: colourless solid; yield: 95 %; $C_{13}H_{17}BrN_2$ (281.19 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) δ = 7.79 (d, ³J = 2.00 Hz, 1H, NCH), 7.64 (d, ³J = 2.00 Hz, 1H, NCH), 7.36 (m, 5H, CH_{ar}), 5.54 (s, 2H, NCH₂), 4.00 (s, 3H, NCH₃), 2.13 (q, ³J = 7.60 Hz, 2H, NCCH₂), 1.05 (t, ³J = 7.60 Hz, 3H, CH₂CH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) δ = 148.0, 133.4, 129.3, 129.0, 128.0, 123.1, 122.0, 52.2, 35.8, 17.8, 11.0; m.p. 175 °C, elemental analysis (%): calcd: C 55.53, H 6.09, N 9.96; found: C 55.37, H 6.09, N 9.92.

1-Benzyl-2-isopropyl-3-methylimidazolium bromide 17: colourless solid; yield: 86 %; $C_{14}H_{19}BrIN_2$ (295.22 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) δ = 7.95 (d, ³J = 2.00 Hz, 1H, NCH), 7.77 (d, ³J = 2.00 Hz, 1H, NCH), 7.34 (m, 5H, CH_{ar}), 5.65 (s, 2H, CH₂), 4.08 (s, 3H, NCH₃), 3.68 (st, ³J = 7.40 Hz, 1H, NCHN), 1.34 (d, ³J = 7.20 Hz, 6H, CHCH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) δ = 150.0, 133.7, 129.5, 129.2, 127.7, 124.4, 122.7, 52.9, 37.1, 25.5, 19.0; m.p. 152 °C, elemental analysis (%): calcd: C 56.96, H 6.49, N 9.49; found: C 56.93, H 6.60, N 9.52.

1,2-Dimethyl-3-(2', 3', 4', 5', 6'-pentafluorobenzyl)imidazolium bromide 19: colourless solid; yield: 97 %; C₁₂H₁₀BrF₅N₂ (357.12 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) δ = 7.79 (d, ³J = 2.40 Hz, 1H, NCH), 7.51 (d, ³J = 2.00 Hz, 1H, NCH), 5.71 (s, 2H, NCH₂), 3.99 (s, 3H, NCH₃), 2.90 (s, 3H NCCH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) δ = 145.2, 123.7, 121.6, 40.7, 36.5, 11.4; ¹⁹F-NMR (CDCl₃, 376.46 MHz, RT, ppm) δ = -140.3 (dd, ³J = 22.0, 7.0 Hz, 2F, CF_{ortho}), -149.6 (t, ³J = 21.0 Hz, 1F, CF_{para}), -159.1 (m, 2F, CF_{meta}); m.p. 184 °C, elemental analysis (%): calcd: C 40.36, H 2.82, N 7.84; found: C 40.17, H 2.77, N 7.87.

2-Ethy1-1-methyl-3-(2', 3', 4', 5', 6'-pentafluorobenzyl)imidazolium bromide 20: colourless solid; yield: 88 %; $C_{13}H_{12}BrF_5N_2$ (371.15 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) $\delta = 7.89$ (d, , ³J = 2.00 Hz, 1H, NCH), 7.59 (d, ³J = 2.00 Hz, 1H, NCH), 5.76 (s, 2H, NCH₂), 4.02 (s, 3H, NCH₃), 3.29 (q, ³J = 7.70 Hz, 2H, NCCH₂), 1.23 (t, ³J = 7.70 Hz, 3H, CH₂CH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) $\delta = 148.8$, 123.9, 121.8, 40.7, 36.2, 18.0, 11.2; ¹⁹F-NMR (CDCl₃, 376.46 MHz, RT, ppm) $\delta = -140.3$ (dd, ³J = 21.9, 6.8 Hz, 2F, CF_{ortho}), -149.6 (t, ³J = 21.1 Hz, 1F, CF_{para}), -159.2 (m, 2F, CF_{meta}); m.p. 182 °C, elemental analysis (%): calcd: C 42.07, H 3.26, N 7.55; found: C 41.76, H 3.28, N 7.68.

2-Isopropyl-1-methyl-3-(2', 3', 4', 5', 6'-pentafluorobenzyl)imidazolium bromide 21: colourless solid; yield: 79 %; $C_{13}H_{12}BrF_5N_2$ (371.15 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) $\delta = 8.00$ (d, ³J = 2.00 Hz, 1H, NCH), 7.60 (d, ³J = 2.00 Hz, 1H, NCH), 5.87 (s, 2H, NCH₂), 4.09 (s, 3H, NCH₃), 3.82 (st, ³J = 7.20 Hz, 2H, NCCH), 1.47 (d, ³J = 7.20 Hz, 6H, CHCH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) $\delta = 150.0$, 125.2, 122.0, 41.3, 37.4, 25.3, 19.0; ¹⁹F-NMR (CDCl₃, 376.46 MHz, RT, ppm) $\delta = -140.4$ (dd, ³J = 21.4, 6.4 Hz, 2F, CF_{ortho}),

-149.6 (t, ${}^{3}J = 21.0$ Hz, 1F, CF_{para}), -159.1 (m, 2F, CF_{meta}); m.p. 208 °C, elemental analysis (%): calcd: C 43.66, H 3.66, N 7.27; found: C 43.62, H 3.67, N 7.34.

1-Benzyl-2,3,4,5-tetramethylimidazolium bromide 22: pale yellow solid; yield: 96 %; $C_{14}H_{19}BrN_2$ (295.22 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) $\delta = 7.30$ (m, 3H, CH_{meta,para}), 7.05 (m, 2H, CH_{ortho}), 5.42 (s, 2H, CH₂), 3.81 (s, 3H, NCH₃), 2.76 (s, 3H, NC(CH₃)N), 2.25 (s, 3H, CH₃NCCH₃), 2.14 (s, 3H, CH₂NCCH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) $\delta = 143.4$, 133.1, 129.4, 128.6, 126.3, 126.2, 125,7, 49.3, 33.3, 12.0, 9.2, 9.1; m.p. 163 °C, elemental analysis (%): calcd: C 56.96, H 6.49, N 9.49; found: C 56.71, H 6.58, N 9.44.

3-(2', 3', 4', 5', 6'-pentafluorobenzyl)-1,2,4,5-tetramethylimidazolium bromide 23: colourless solid; yield: 97 %; C₁₄H₁₄BrF₅N₂ (371.15 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) δ = 5.62 (s, 2H, CH₂), 3.76 (s, 3H, NCH₃), 2.91 (s, 3H, NC(CH₃)N), 2.21 (s, 3H, CH₃NCCH₃), 2.17 (s, 3H, CH₂NCCH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) δ = 144.4, 126.5, 125.8, 39.2, 33.3, 12.2, 9.1, 8.9; ¹⁹F-NMR (CDCl₃, 376.46 MHz, RT, ppm) δ = -140.7 (dd, ³J = 21.9, 7.0 Hz, 2F, CF_{ortho}), -150.5 (t, ³J = 21.0 Hz, 1F, CF_{para}), -159.6 (m, 2F, CF_{meta}); m.p. 133 °C, elemental analysis (%): calcd: C 43.66, H 3.66, N 7.27; found: C 43.36, H 3.79, N 7.25.

1-Butyl-2-isopropyl-3-(2', 3', 4', 5', 6'-pentafluorobenzyl)imidazolium bromide 25: colourless solid; yield: 89 %; $C_{17}H_{20}BrF_5N_2$ (427.26 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) δ = 7.81 (d, ³J = 2.00 Hz, 1H, NCH), 7.69 (d, ³J = 2.00 Hz, 1H, NCH), 5.93 (s, 2H, NCH₂), 4.29 (t, ³J = 7.80 Hz, 2H, NCH₂), 3.84 (st, ³J = 7.20 Hz, 2H, NCCH), 1.89 (m, 2H, CH₂), 1.51 (d, ³J = 7.20 Hz, 6H, CHCH₃), 1.45 (m, 2H, CH₂), 0.98 (t, ³J = 7.40 Hz, 3H, CH₂CH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) δ = 149.6, 123.3, 122.4, 49.2, 41.4, 32.6, 25.1, 19.7, 19.6, 13.5; ¹⁹F-NMR (CDCl₃, 376.46 MHz, RT, ppm) δ = -140.5 (dd, ³J = 21.3, 6.5 Hz, 2F, CF_{ortho}), -149.7 (t, ³J = 21.0 Hz, 1F, CF_{para}), -159.2 (m, 2F, CF_{meta}); m.p. 126 °C, elemental analysis (%): calcd: C 47.79, H 4.72, N 6.56; found: C 47.95, H 4.72, N 6.25.

1.5.2. Preparation of 2-alkyl-1,3-bis-(2',3',4',5',6'-pentafluorobenzyl) and 2-alkyl-1,3dibenzylimidazoliumbromides

To a stirred solution of 2-alkyl-1-(trimethylsilyl)imidazole (10.0 mmol, 1.0 eq.) in THF_{abs} (12 mL), benzylbromide or pentafluorobenzylbromide (22.0 mmol, 2.2 eq.) were added dropwise. The reaction mixture is stirred under reflux for 24 h, during which time a colourless precipitate was formed, which was collected by filtration and washed with THF and diethylether. After drying in vacuum at 70 °C for 16 h the respective imidazolium bromides were obtained as colourless powders in high yields.

1,3-Dibenzyl-2-isopropyl-imidazolium bromide 27: colourless solid; yield: 94 %; $C_{20}H_{23}BrN_2$ (371.32 g/mol); ¹H-NMR (DMSO-d₆, 400 MHz, RT, ppm) δ = 7.84 (s, 2H, NCH), 7.40 (m, 6H, CH_{meta,para}), 7.28 (m, 4H, CH_{ortho}), 5.60 (s, 4 H, NCH₂), 3.73 (st, ³J = 7.20 Hz, 1H, NCCH), 1.14 (d, ³J = 7.20 Hz, 6H, CHCH₃); ¹³C-NMR (DMSO-d₆, 100.28 MHz, RT, ppm) δ = 149.8, 135.0, 129.0, 128.4, 127.2, 123.0, 51.2, 24.5, 18.5; m.p. 164 °C, elemental analysis (%): calcd: C 64.69, H 6.24, N 7.54; found: C 64.12, H 6.35, N 7.51.

1,3-Bis-(2', 3', 4', 5', 6'-pentafluorobenzyl)-2-methylimidazolium bromide 29: colourless solid; yield: 92 %; C₁₈H₉BrF₁₀N₂ (523.17 g/mol); ¹H-NMR (DMSO-d₆, 400 MHz, RT, ppm) δ = 7.75 (s, 2H, NCH), 5.65 (s, 4H, NCH₂), 2.73 (s, 3H CH₃); ¹³C-NMR (MeOD-d₃, 100.28 MHz, RT, ppm) δ = 147.6, 123.4, 108.8, 40.9, 10.3; ¹⁹F-NMR (DMSO-d₆, 376.46 MHz, RT, ppm) δ = -140.9 (dd, ³J = 23.3, 6.8 Hz, 4F, CF_{ortho}), -152.8 (t, ³J = 22.3 Hz, 2F, CF_{para}), -161.6 (m, 4F, CF_{meta}); m.p. 207 °C, elemental analysis (%): calcd: C 41.32, H 1.73, N 5.35; found: C 41.25, H 1.64, N 5.40.

1,3-Bis-(2', 3', 4', 5', 6'-pentafluorobenzyl)-2-isopropylimidazolium bromide 30: colourless solid; yield: 97 %; C₁₈H₉BrF₁₀N₂ (371.15 g/mol); ¹H-NMR (CDCl₃, 400 MHz, RT, ppm) δ = 7.62 (s, 2H, NCH), 5.84 (s, 4H, NCH₂), 3.96 (st, ³J = 7.20 Hz, 1H, NCCH), 1.58 (d, ³J = 7.20 Hz, 6H, CHCH₃); ¹³C-NMR (CDCl₃, 100.28 MHz, RT, ppm) δ = 151.0, 123.0, 41.7, 25.6, 19.5; ¹⁹F-NMR (CDCl₃, 376.46 MHz, RT, ppm) δ = -140.2 (dd, ³J = 22.3, 6.2 Hz, 4F, CF_{ortho}), -148.6 (t, ³J = 21.0 Hz, 2F, CF_{para}), -158.5 (m, 4F, CF_{meta}); m.p. 149 °C, elemental analysis (%): calcd: C 43.58, H 2.38, N 5.08; found: C 42.99, H 2.65, N 5.37.

2. References

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