Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Synthesis of 1-Octanol and 1,1-Dioctyl Ether from Biomass-Derived Platform Chemicals**

*Jennifer Julis and Walter Leitner**

ange_201203669_sm_miscellaneous_information.pdf

Safety Warning

High-pressure experiments with compressed hydrogen must be carried out only with appropriate equipment and under rigorous safety precautions.

General

If not stated otherwise, the syntheses of ionic liquids and nanoparticle solutions were carried out under argon inert gas atmosphere using standard Schlenk technique. Catalyst solutions and substrates were handled under air, but were flushed with hydrogen prior starting catalysis.

Analytics

Conversion and selectivity of catalytic reactions were determined *via* GC using a Thermo Scientific Chromatograph Tace GC Ultra equipped with a FID detector and a CP-WAX-52CB column (60 m, 50 °C-180 °C, 5 min iso, 12 °C/min, He). GCs were measured in dichlormethan wit tetradecan as internal standard. Signals were assigned *via* NMR, GC-MS and pure substance calibration. NMR spectra were recorded on a Bruker AV 400 or a Bruker DPX 300 spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C, respectively at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Chemical shifts are reported relative to Tetramethylsilan and solvent residual protons or carbon signals as internal reference.

1. Hydrogenation/Dehydration reaction

A. Hydrogenation/dehydration of 4-(2-tetrahydrofuryl)-2-butanol (THFA)

Ru/C and Ru/Alox were activated by hydrotreatment at 80 °C and 100 bar H_2-pressure for 10 h prior use. In a typical experiment Ru/C, Ru/alox or IL-stabilisied nanoparticles (0.016 mmol Ru) were placed in a 10 mL stainless-steel high-pressure reactor with a glass inlet. THFA (225.7 mg, 1.565 mmol), 2.9 mL [EMIM][NTf_2] and, in case of Ru/C and Ru/alox, the acidic additive (0.114 mmol) were added to the catalyst and the reactor was pressurized to 120 bar with hydrogen. The reaction mixture was stirred for 15 h at 150 °C. The reactor was cooled to ambient temperature and was carefully vented by using a cooling trap to retain any volatile organic products. For GC and NMR analysis the reaction mixture was extracted with pentane (3x 20 mL) and the pentane phase and the products in the cooling trap were combined. After drying with $MgSO_4$ and evaporation of pentane the products were obtained as a colorless solution. For some selected experiments mass balance was calculated *via* GC with tetradecan as

internal standard and the weight of the isolated product mixture. The values of the mass balance were 85-95 %.

B. Hydrogenation/dehydration of furfuralacetone (FFA)

Ru/C wasactivated by hydrotreatment at 80 °C and 100 bar H_2-pressure for 10 h prior use. In a typical experiment Ru/C (0.016 mmol Ru) was placed in a 10 mL stainless-steel high-pressure reactor with a glass inlet. After addition of FFA (213.1 g, 1.565 mmol) the reaction mixture was stirred at 120°C and 120 bar hydrogen pressure for 2h. The reactor was cooled to ambient temperature and was carefully vented. After addition of 2.9 mL [EMIM][NTf_2] and the acidic additive (0.114 mmol) the reactor was pressurized again and the reaction mixture was stirred at 150 °C and 120 bar H_2 pressure for 60 h. The reactor was cooled to ambient temperature and carefully vented by using a cooling trap to retain any volatile organic products. For GC and NMR analysis the reaction mixture was extracted with pentane (3x 20 mL) and the pentane phase and the products in the cooling trap were combined. After drying with $MgSO_4$ and evaporation of pentane the products were obtained as a colorless solution. For some selected experiments mass balance was calculated *via* GC with tetradecan as internal standard and the weight of the isolated product mixture. The values of the mass balance were 85-95 %.

C. Hydrogenation/dehydration of furfural (FF)

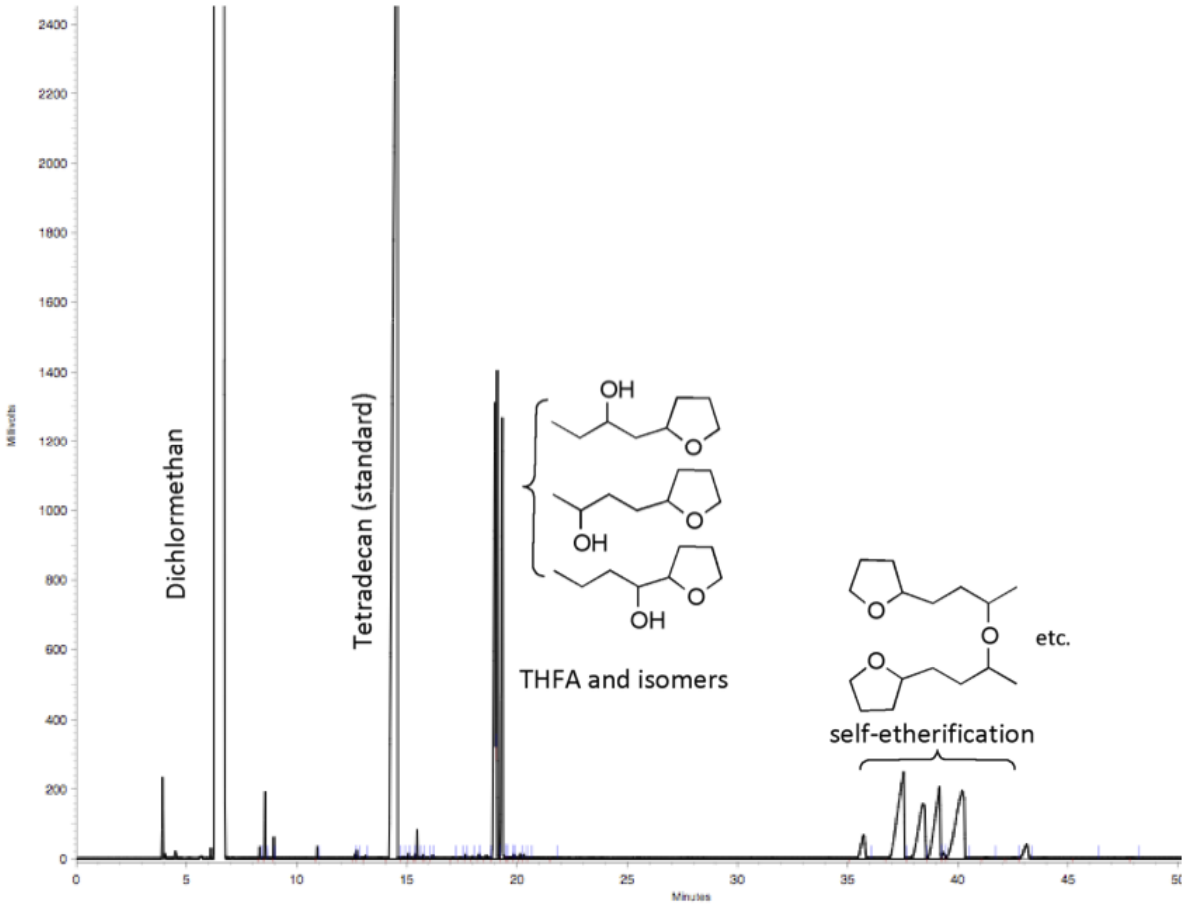
Furfural was distilled and stored under argon at -20 °C. Ru/C was activated by hydrotreatment at 80 °C and 100 bar H_2-pressure for 10 h prior use.

Furfural (150.4 g, 1.565 mmol) and acetone (1.15 mL, 15.652 mmol, 10 eq) were placed in a glas inlet. To start the reaction 50 □L of 0.1 M NaOH were slowly added to the solution, which immediately turned yellow. After stirring the reaction mixture for 16 h at room temperature 50 □L of 0.1 M HCl were added and the excess of acetone was evaporated. The glas inlet was transferred to a high-pressure reactor and after addition of Ru/C (0.016 mmol) the hydrogenation reaction was started by pressurizing the reactor with 120 bar H_2. For the following reaction and work-up procedure see **B**.

2. GC chromatograms

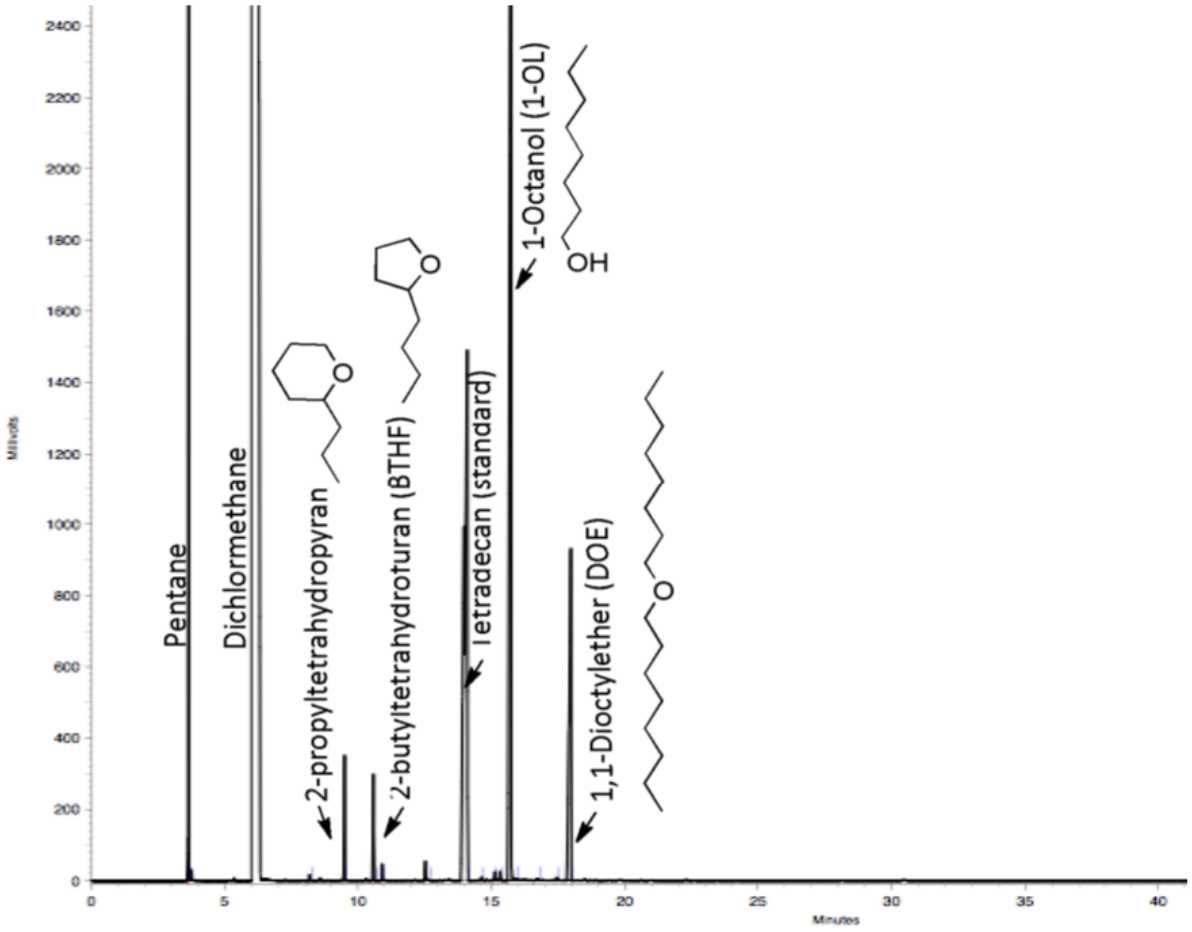
THFA, isomers of THFA and self-etherification products

(Ru@[BSO_3BIM][NTf_2]+THFA, 120 °C, 120 bar H_2, 15 h)



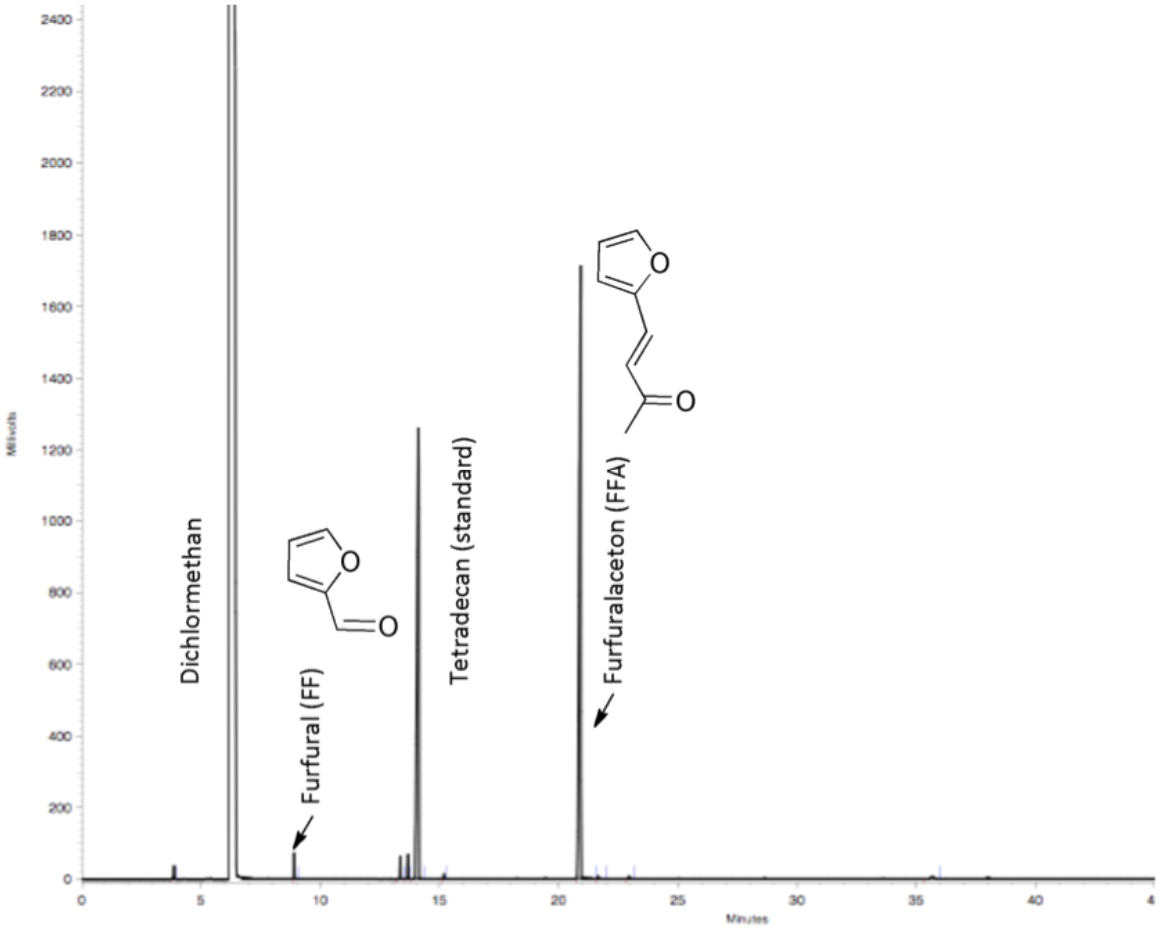
2-Butyltetrahydrofuran (BTHF), 1-octanol (1-OL) and dioctylether (DOE)

(Ru@[BSO_3BIM][NTf_2]+THFA+[EMIM][NTf_2], 120 °C, 150 bar H_2, 15 h)



Furfural and Furfuralaceton

(Furfural+Aceton+NaOH, 20 °C, 18 h)



2. Screening of selected commercially available Ru/C[a]

No.	Catalyst	Conv.[%]	Selectivity [%]					
			BTHF	1-OL	DOE	Self-etherification	Others[b]	C_8-OL
1	Abcr (5 wt% Ru, dry)	81.4	52.5	-	-	37.7	9.8	-
2	Abcr (5 wt%, reduced)	84.0	79.5	3.5	-	10.8	6.2	3.5
3	Abcr (5 wt%, 12-25 Å)	≥99	56.6	27.1	9.1	-	7.2	36.2
4	Strem (Escat™)[c]	≥99	46.6	31.9	16.2	-	5.3	48.1

[a]: 150 °C, 120 bar H_2, 15 h, 0.016 mmol Ru, 1.565 mmol THFA, 0.114 mmol acidic additive, 2.9 mL [EMIM][NTf_2] [b]: others are mainly 2-propyltetrahydropyran; [c]: dried at 80 °C under reduced pressure prior use.

3. Comparison of catalytic activity between two different batches of Ru/C (abcr, 5 wt%, 12-25 Å, batch A and B)

No.	substrate	steps	Selectivity [%]				
			BTHF	1-OL	DOE	Others[b]	C_8-OL
1**A**	THFA	1[a]	56.6	27.1	9.1	7.2	36.2
1**B**	THFA	1[a]	47.8	20.5	19.4	12.3	39.4
2**A**	FFA	2[b]	2.6	48.8	44.2	4.4	93.0
2**B**	FFA	2[b]	14.6	42.8	35.4	7.2	78.2

[a]: 0.016 mmol Ru, 1.565 mmol THFA, 0.114 mmol [BSO_3BIM][NTf_2], 2.9 mL [EMIM][NTf_2], 150 °C, 120 bar H_2, 15 h [b]: 1st step: 0.016 mmol Ru, 1.565 mmol FFA, 120 °C, 120 bar H_2, 2 h; 2nd step: 0.114 mmol [BSO_3BIM][NTf_2], 2.9 mL [EMIM][NTf_2], 150 °C, 120 bar H_2, 60 h; [c]: others are mainly 2-propyltetrahydropyran.

4. Reproducibility of the dehydration/hydrogenation step of THFA with Ru@[BSO_3BIM][NTf_2][a]

Batch No.	conv. [%]	Selectivity [%]				
		BTHF	1-OL	DOE	Others[b]	C_8-OL
1	≥99	26.9	35.9	30.2	7.0	66.1
2	≥99	21.8	44.9	26.1	7.2	71.0
3	≥99	19.1	42.5	28.6	9.8	71.1

[a]: 0.016 mmol Ru, 1.565 mmol THFA, 0.114 mmol [BSO_3BIM][NTf_2], 2.9 mL [EMIM][NTf_2], 150 °C, 120 bar H_2, 15 h [c]: others are mainly 2-propyltetrahydropyran

5. Synthesis of Ru@IL[1]

Ruthenium nanoparticles were prepared by chemical reduction of bis(methylallyl)(1,5-cyclooctadiene)ruthenium(II) with hydrogen in presence of an ionic liquid. In a typical experiment the precursor (5.0 mg, 0.016 mmol) was dispersed in the ionic liquid (0.114 mmol) and the suspension was placed in a 10 mL stainless-steel high-pressure reactor with a glass inlet. After pressurising with hydrogen to 60 bar, the reaction mixture was stirred for 2 h at 60 °C. The reactor was cooled to ambient temperature and was carefully vented. A dark brown solution was obtained, which was used directly in the hydrogenation/dehydration reaction.Size and size distribution of the nanoparticles were analysed via Transmission Electron Microscopy using a Hitachi-HF-200. The samples were prepared by dilution of Ru@IL with acetone and deposition on a carbon coated copper grid.

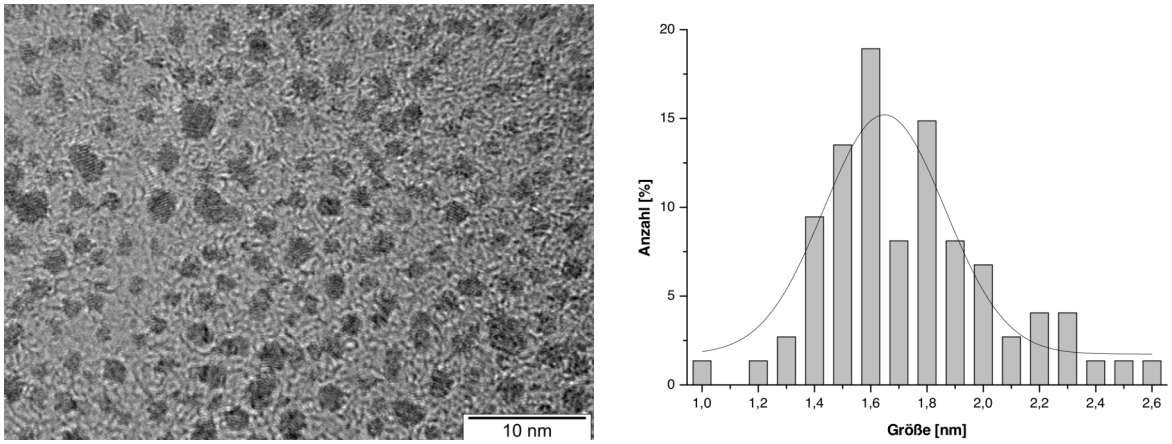


Figure 1. Ru@[BSO_3BIM][NTf_2]: TEM image (left side) and size distribution (right side).

6. Synthesis of ionic liquids

1-Butyl-3-(3-carboxypropyl)-imidazolium bis(trifluoromethylsulfonyl)imid [BCO_2BIM][NTf_2][2]

4-chlorobutanoic acid (2.52 g, 0.02 mol) was slowly added to 1-butylimidazol (2.55 g, 0.02 mol) and the reaction mixture was stirred for 6 h at 120 °C. A viscous solution was formed, which was diluted with 10 mL MilliQ H_2O. After addition of Lithiumbis(trifluoromethylsulfonyl)imid (5.86 g, 0.02 mmol) in 10 mL MilliQ H_2O the mixture was stirred for another 10 h at room temperature. Two layers were formed, which were separated and the aqueous layer was extracted with dichlormethan (3x15 mL). The combined organic layers were washed with MilliQ H_2O. Dichlormethan was evaporated and the resulting ionic liquid was dried for 10 hours at 50 °C under reduced pressure.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.27 (t, 3H, J_3=7.4 Hz, CH_3), 1.68 (tq, 2H, J_3=7.4 Hz, CH_2CH$_3$), 2.19 (tt, J_3=7.4 Hz, CH_2), 2.61 (tt, 2H, J_3=7.4 Hz, CH_2), 2.84 (t, 2H, J_3=8.1 Hz, CH_2COOH), 4.53 (t, 2H, J_3=7.4 Hz, NCH_2), 4.70 (t, 2H, J_3=7.4 Hz, NCH_2), 7.67 (s, 1H, NCHC*H*N), 7.71 (s, 1H, NC*H*CHN), 8.86 (s, 1H, NC*H*N), 11.21 (s, 1H, COO*H*) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ 13.3 (s, *C*H_3), 19.4 (s, *C*H_2), 22.2 (s, *C*H_2), 28.0 (s, *C*H_2), 32.0 (s, *C*H_2COOH), 49.8 (s, N*C*H_2), 69.0 (s, N*C*H_2), 119.8 (q, 2C, *C*F_3), 120. 6 (s, NCH*C*HN), 121.8(s, *NCHCHN*), 134.2 (s, N*C*HN), 178.8 (s, *C*OOH) ppm.

1-Butyl-3-(4-sulfobutyl)-imidazolium bis(trifluoromethylsulfonyl)imid [BSO_3BIM][NTf_2][3]

In a Schlenk roundflask *n*-butylimidazol (10.0 g, 0.08 mol) was diluted with 10 mL dry and degassed toluene. 1,4-butansulton (1.47 g, 0.08 mol) and 15 mL toluene were added and the mixture was stirred at 50 °C for 24 h. The colourless solution turned yellow and a white precipitate was formed. The precipitate was filtrated of the solution. After washing with toluene and acetone, the white solid 4-(*N*-butylimidazolium)butane-1-sulfonat was dried under reduced pressure. The filtrate was stirred for another 24 h and the formed precipitate was separated by filtration as before. This procedure was repeated until the conversion of n-butylimidazol was complete. 4-(*N*-butylimidazolium)butane-1-sulfonat (3.81 g, 0.01 mol) was dissolved in 6 mL MilliQ H_2O. An aqueous solution of bis(trifluoromethane)sulfonimide (80 %, 3.79 mL, 0.01 mmol) was added and the solution was stirred for 2 h at room temperature. After evaporation of water the viscous ionic liquid was dried under reduced pressure.

^{1}H-NMR (400 MHz, D_2O): δ0.77 (t, 3H, J_3=7.5 Hz, C*H*$_3$), 1.17 (tq, 2H, J_3=7.5 Hz, C*H*$_2$), 1.64 (tt, 2H, J_3=7.5 Hz, C*H*$_2$), 1.70 (tt, 2H, J_3=7.5 Hz, C*H*$_2$), 1.90 (tt, 2H, J_3=7.5 Hz, C*H*$_2$), 2.81 (t, J_3=7.5 Hz, C*H*$_2$$SO_3$H), 4.04 (t, 2H, J_3=7.3 Hz, C*H*$_2$N), 4.11 (t, 2H, J_3=7.3 Hz, C*H*$_2$N), 7.34 (s, 1H, NC*H*CHN), 7.38 (s, 1H, NCHC*H*N), 8.62 (s, 1H, NC*H*N) ppm.

^{13}C-NMR (100 MHz, D_2O): δ12.5 (s, *C*H_3), 18.7 (s, *C*H_2), 21.0 (s, *C*H_2), 28.2 (s, *C*H_2), 31.2 (s, *C*H_2), 48.9 (s, *C*H_2N), 49.3 (s, *C*$H_2$$SO_3$H), 50.1 (s, *C*$H_2$N), 119.3 (q, J_1=325 Hz), 122.3 (s, N*C*HCHN), 122.4 (s, NCH*C*HN),135.0 (N*C*HN) ppm.

1-Butyl-3-(4-sulfobutyl)-imidazolium trifluoromethanesulfonate [BSO_3BIM][OTf]

In a Schlenk roundflask *n*-butylimidazol (10.0 g, 0.08 mol) was diluted with 10 mL dry and degassed toluene. 1,4-butansulton (1.47 g, 0.08 mol) and 15 mL toluene were added and the mixture was stirred at 50 °C for 24 h. The colourless solution turned yellow and a white precipitate was formed. The precipitate was filtrated of the solution. After washing with toluene and acetone, the white solid 4-(*N*-butylimidazolium)butane-1-sulfonat was dried under reduced pressure. The filtrate was stirred for another 24 h and the formed precipitate was separated by filtration as before. This procedure was repeated until the conversion of n-butylimidazol was complete. 4-(*N*-butylimidazolium)butane-1-sulfonat (3.81 g, 0.01 mol) was dissolved in 6 mL MilliQ H_2O. Trifluoromethanesulfonic acid (0.01 mmol) was added and the solution was stirred for 2 h at room temperature. After evaporation of water the viscous ionic liquid was dried under reduced pressure.

^{1}H-NMR (400 MHz, D_2O): δ 0.76 (t, 3H, J_3=7.5 Hz, C*H*$_3$), 1.16 (tq, 2H, J_3=7.5 Hz, C*H*$_2$), 1.60 (m, 2H, C*H*$_2$), 1.70 (tt, 2H, J_3=7.5 Hz, C*H*$_2$), 1.88 (tt, 2H, J_3=7.5 Hz, C*H*$_2$), 2.79 (t, J_3=7.5 Hz, C*H*$_2$$SO_3$H), 4.04 (t, 2H, J_3=7.1 Hz, C*H*$_2$N), 4.10 (t, 2H, J_3=7.1 Hz, C*H*$_2$N), 7.36 (m, 2H, NC*H*C*H*N), 8.65 (s, 1H, NC*H*N) ppm.

^{13}C-NMR (100 MHz, D_2O): δ12.5 (s, *C*H_3), 18.7 (s, *C*H_2), 20.9 (s, *C*H_2), 28.0 (s, *C*H_2), 31.1 (s, *C*H_2), 48.9 (s, *C*H_2N), 49.3 (s, *C*H_2SO_3H), 50.0 (s, *C*H_2N), 119.6 (q, J_1=319 Hz), 122.4 (s, NCHCHN), 122.4 (s, NCHCHN), 135.1 (NCHN) ppm.

***N,N,N*-tributly-*N*-(4-sulfobutyl)ammonium bis(trifluoromethylsulfonyl)imide [$N_{444}BSO_3$][NTf_2]**[4]

Tributlyamine (3.57 g, 0.02 mol) and 1,4-Butansulton (2.66 g, 0.02 mol) were stirred for 24 h at 130 °C forming a pale yellow viscous liquid. After addition of 20 mL dry and degassed ethyl acetate the solution was stirred for another 2h at 90 °C. The reaction was cooled down to 0 °C and a white solid precipitated. Filtration of the precipitate, washing with ethyl acetate and drying under reduced pressure gave access to 4-(*N,N,N*-tributylammonium)butane-1-sulfonat as a white powder.

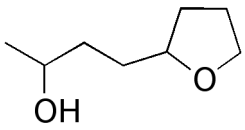
In a Schlenk roundflask 4-(*N,N,N*-tributylammonium)butane-1-sulfonat (2.88 g, 0.01 mol) was dissolved in 10 mL MilliQ H_2O. An aqueous solution of bis(trifluoromethan)sulfonimid (80 %, 2.30 mL, 0.01 mol)) was added and the solution was stirred for 2 h at room temperature. After evaporation of water the viscous ionic liquid was dried under reduced pressure.

^{1}H-NMR (400 MHz, DMSO): δ0.93 (t, 9H, J_3=7.2 Hz, C*H*$_3$), 1.30 (tq, 6H, J_3=7.2 Hz, C*H*$_2$), 1.58 (m, 8H, C*H*$_2$), 1.72 (m, 2H, C*H*$_2$), 2.57 (m, 2H, C*H*$_2$SO$_3$H), 3.02 (m, 2H, C*H*$_2$N), 4.10 (m, 6H, C*H*$_2$N) ppm.

^{13}C-NMR (100 MHz, D_2O): δ 13.4 (s, 3C, *C*H_3), 19.2 (s,3C, *C*H_2), 19.3 (s, 1C, *C*H_2), 23.0 (s, 3C, *C*H_2), 25.0 (s, 1C, *C*H_2), 50.1 (s, 3C, *C*H_2N), 51.7 (s, 1C, *C*H_2N), 57.5 (s, *C*H_2SO_3H) ppm.

7. Analytic Data

4-(2-tetrahydrofuryl)-2-butanol (THFA)



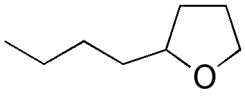
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.08 (dd, 3H, J_3= x Hz, C*H*$_3$), 1.32-1.58 (m, 5H, 2 x C*H*$_2$, tetrahydrofurylring: C*H*(4)), 1.71-1.92 (m, 3H, tetrahydrofruylring: C*H*$_2$(3),C*H*(4)), 3.60-3.65 (m, 1H, C*H*OH), 3.65-3.79 (m, 3H, tetrahydrofurylring: C*H*(2) CH$_2$(5)) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ 23.3 (d, *C*H_3), 25.6 (d, tetrahydrofurylring: *C*H_2), 31.4 (d, *C*H_2), 31.9 (d, tetrahydrofurylring: *C*H_2), 36.0 (d, *C*H_2), 67.5 (d, *C*HOH), 67.6 (s, tetrahydrofurylring: *C*H_2), 79.5 (d, tetrahydrofurylring: *C*H) ppm.

MS (CI): m/z 145 ([M^++H],44), 143 (11), 127 (81), 109 (46), 71 (100), 67 (10).

Correction factor GC: 1.81

2-butyltetrahydrofuran (BTHF)

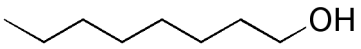


^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.80 (t, 3H, J_3= 6.8 Hz, CH_3), 1.28 (m, 7H, 3 x CH_2, tetrahydrofurylring: CH(4)), 1.80 (m, 3H, tetradhydrofurylring: CH_2(3), CH(4)), 3.66 (m, 3H, tetrahydrofurylring: CH(2), CH_2(5)) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ 13.9 (s, CH$_3$) , 22.8 (s, CH_2), 25.7 (s, CH_2), 28.5 (s, CH_2), 31.3 (s, CH_2), 35.4 (s, CH_2), 67.5 (s, tetrahydrofurylring: CH$_2$), 79.4 (s, tetrahydrofurylring: CH) ppm.

MS (EI): m/z 71 (100), 70 (10), 43 (25), 42 (17), 41 (37), 39 (17).

Correction factor GC: 1.28

1-octanol (1-OL)

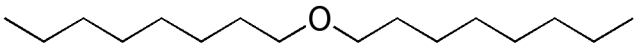


^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 3H, J_3= 6.7 Hz, CH_3), 1.26 (m, 10H, CH_2), 1.55 (tt, 2H, J_3= 6.9 Hz, CH_2CH$_2$OH), 3.39 (t, 2H, J_3= 6.7 Hz, CH_2OH) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.1 (s, CH$_3$), 22.6 (s, CH_2), 25.7 (s, CH$_2$), 29.3 (s, CH$_2$), 29.4 (s, CH$_2$), 31.8 (s, CH$_2$), 32.8 (s, CH$_2$), 63.0 (s, CH$_2$OH) ppm.

MS (EI): m/Z 84 (10), 83 (10), 70 (30), 69 (25), 56 (45), 55 (50), 43 (70), 43 (55), 41 (100), 39 (62).

Correction factor GC: 1.22

1,1-dioctylether (DOE)



^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.88 (m, 6H, CH_3), 1.27 (m, 20H, CH_2), 1.56 (tt, 4H, J_3= 6.8 Hz, CH_2CH$_2$OH), 3.39 (t, 4H, J_3= 6.8 Hz, CH_2OH) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ14.2 (s, CH$_3$), 22.8 (s, CH_2), 26.4 (s, CH$_2$), 29.4 (s, CH$_2$), 29.6 (s, CH$_2$), 29.9 (s, CH$_2$), 32.0 (s, CH$_2$), 71.1 (s, CH$_2$OH) ppm.

MS (EI): m/Z 84 (10), 83 (10), 71 (37), 69 (25), 57 (73), 55 (35), 43 (100), 41 (85).

Correction factor GC: 1.19

[1] J. Julis, M. Hölscher, W. Leitner, *Green Chemistry* 2010, *12*, 1634-1639.

[2] R. Abu-Reziq, D. Wang, M. Post, H. Alper, *Advanced Synthesis & Catalysis* 2007, *349*, 2145-2150.

[3] M. A. Liauw, S. Winterle, *Chemie Ingenieur Technik* 2010, *82*, 1211-1214.

[4] Y. Gu, C. Ogawa, S. Kobayashi, *Chemistry Letters* 2006, *35*, 1176-1177.