Bifunctional Nanoparticle-SILP Catalysts (NPs@SILP) for the Selective Deoxygenation of Biomass Substrates

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1. Experimental

Safety Warning

High-pressure experiments with compressed $H_{2(g)}$ must be carried out only with appropriate equipment and under rigorous safety precautions.

1.1. General

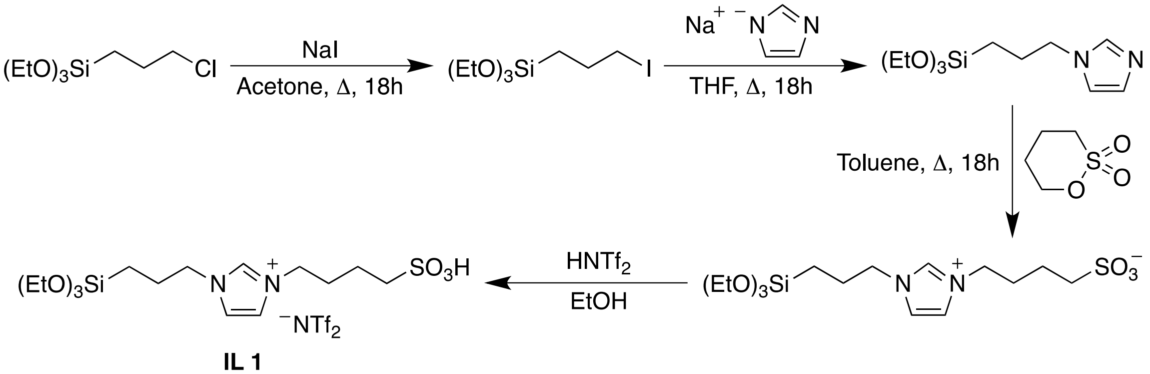
If not otherwise stated, the synthesis of ionic liquids (ILs), supported ionic liquid phases (SILPs) and ruthenium nanoparticles supported on SILPs (RuNPs@SILP) were carried out under an inert atmosphere using standard Schlenk techniques. After synthesis, ILs, SILPs and RuNPs@SILPs were stored under an inert atmosphere prior to use. The catalysis substrates 4-(2-tetrahydrofuryl)-2-butanol (**3**) and 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol (**10**) were stored under atmospheric conditions prior to use. Catalyst solutions and substrates were handled under air, but were flushed with $H_{2(g)}$ prior to catalysis. 4-(2-tetrahydrofuryl)-2-butanol (**3**),[1] 4-(5-hydroxymethylfuryl)-2-but-3-en-2-one,[2] [1-butyl-3-(3-(triethoxysilyl)propyl)imidazolium]Cl,[3] 3-iodopropyltriethoxysilane,[4] N-(3-triethoxysilyl)propyl imidazole,[4] 1-(4-sulfobutyl)-3-(3-triethoxysilylpropyl)imidazolium zwitterion,[5] [1-butyl-3-(4-sulfobutyl)imidazolium]NTf_2,[1] [1-butyl-3-methylimidazolium]$SO_3(OEt)$,[6] [1-butyl-3-methylimidazolium]NTf_2[7] were synthesized according to known literature methods. SiO_2 (Merck Grade 10184, pore size 100Å, 63-200 μm) was dehydroxylated *in vacuo* at 500°C for at least 16h prior to use. Anhydrous acetone was prepared by distillation of pre-dried acetone using 4Å molecular sieves. Toluene and THF were prepared by distillation and drying over activated alumina using a purification system. EtOH (extra dry, absolute) was purchased from Acros Organics. All other chemicals and solvents were purchased from commercial sources and used without purification.

1.2. Analytics

Solution-state nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV300, 400 or 600 MHz spectrometer. ^{1}H and ^{13}C NMR spectra were calibrated to TMS using the residual solvent signal. Water content of [EMIM]NTf$_2$ phases was determined using a Metrohm 756 Coulometric Karl-Fischer titrator. ^{29}Si solid-state NMR spectra were obtained using a Bruker AV700 spectrometer. FTIR spectra of the SILP were obtained using a Bruker Alpha spectrometer in the DRIFT mode. Mass spectra (MS) were recorded in positive electrospray mode with a Thermo Scientific LTQ Orbitrap ESI/APCI. Inductively coupled plasma (ICP) was performed at Mikroanalytisches Laboratorium Kolbe (Mülheim an der Ruhr, Germany) using a Perkin Elmer AAnalyst 200 Atomic Absorption Spectrometer. High-pressure experiments were performed using in-house engineered 10 and 20 mL stainless steel finger autoclaves. Catalysis reactions were performed in glass inlets using a magnetic stirbar (1000 rpm) and an aluminum heating block. Gas chromatography (GC) was performed on a Thermo Scientific Chromatograph Tace GC Ultra equipped with a CP-WAX-52CB column. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were collected using a Hitachi aberration-corrected scanning transmission electron microscope (HD-2700C) operated at 200kV. Extended X-ray absorption find structure (EXAFS) spectroscopy was performed on the X18A beamline at the National Synchrotron Light Source (NSLS) in the Brookhaven National Laboratory (NY, USA).

2. Synthesis and Characterization of Ionic Liquids and Catalytic Substrates

2.1. [1-(4-sulfobutyl)-3-(3-triethoxysilylpropyl)imidazolium]NTf$_2$ (IL 1)[4, 5]



IL 1

Scheme S1: Synthetic pathway for the preparation of IL **1**.

1-(4-sulfobutyl)-3-(3-triethoxysilylpropyl)imidazolium zwitterion[4, 5] (10.0 g, 24.4 mmol) and bis(trifluoromethane)sulfonimide (7.20 g, 25.6 mmol) were dissolved in anhydrous EtOH (10 mL) and stirred at rt for 1h. Upon solvent removal, the product was dried *in vacuo* overnight to yield a viscous amber oil (14.0 g, 83 %).

^{1}H NMR (400 MHz, D$_2$O): δ = 8.77 (s, 1H, NCHN), 7.48 (m, 2H, NCHCHN), 4.25-4.11 (m, 4H, NCH$_2$), 3.60 (q, *J* = 7.1 Hz, 6H, OCH$_2$), 2.89 (m, 2H, SCH$_2$), 2.04-1.88 (m, 4H, CH$_2$), 1.69 (m, 2H, CH$_2$), 1.15 (t, *J* = 7.1 Hz, 9H, OCH$_2$CH$_3$), 0.57 (m, 2H, SiCH$_2$). ^{13}C NMR (100 MHz, D$_2$O): δ = 135.2 (s, 1C, NCHN), 122.4 (s, 2C, NCHCHN), 119.9 (q, J_{CF} = 318 Hz, 2C, CF$_3$), 57.4 (s, 3C, OCH$_2$), 51.6 (s, 1C, NCH$_2$), 50.0 (s, 1C, NCH$_2$), 48.9 (s, 1C, SCH$_2$), 28.0 (s, 1C, CH$_2$), 23.2 (s, 1C, CH$_2$), 20.9 (s, 1C, CH$_2$), 16.7 (s, 3C, OCH$_2$CH$_3$), 8.6 (s, 1C, SiCH$_2$). HRMS/ESI(+) (MeOH) m/z = 395.16669 and 367.13562, calcd. for $[C_{15}H_{31}N_2O_6SSi]^+$ = 395. 16721 and $[C_{13}H_{27}N_2O_6SSi]^+$ = 367.13591.

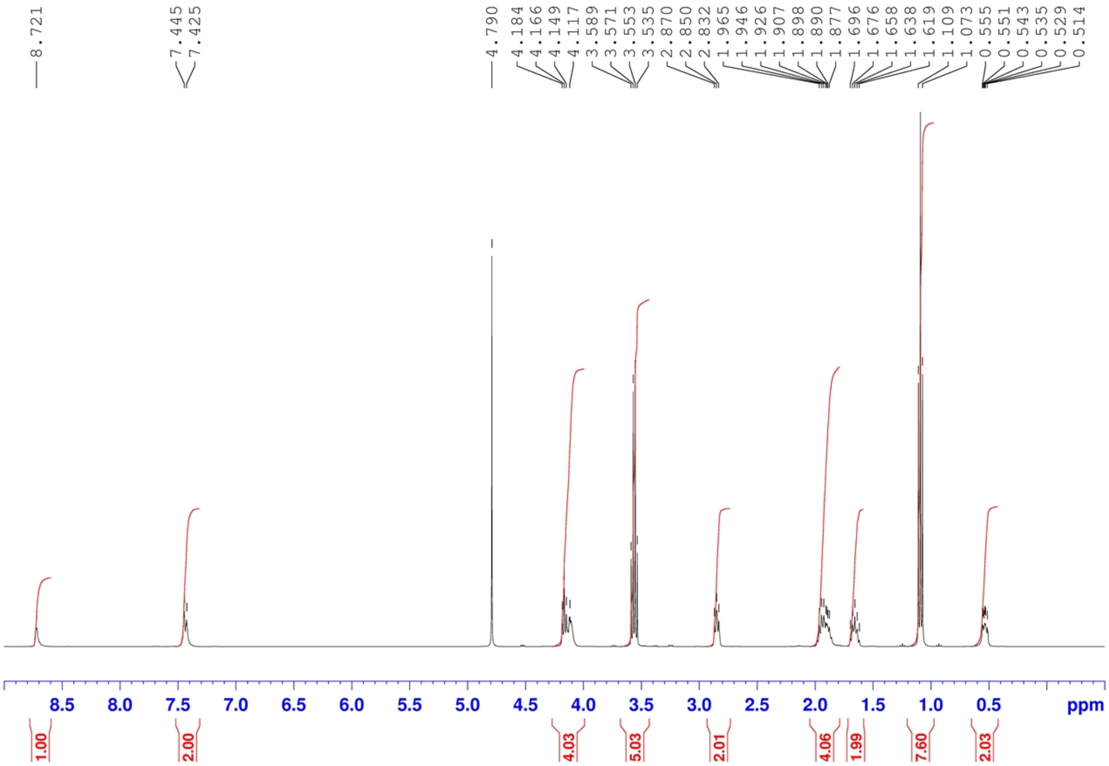


Figure S1: ^{1}H NMR spectrum of IL **1** in D_2O obtained using a 400 MHz spectrometer.

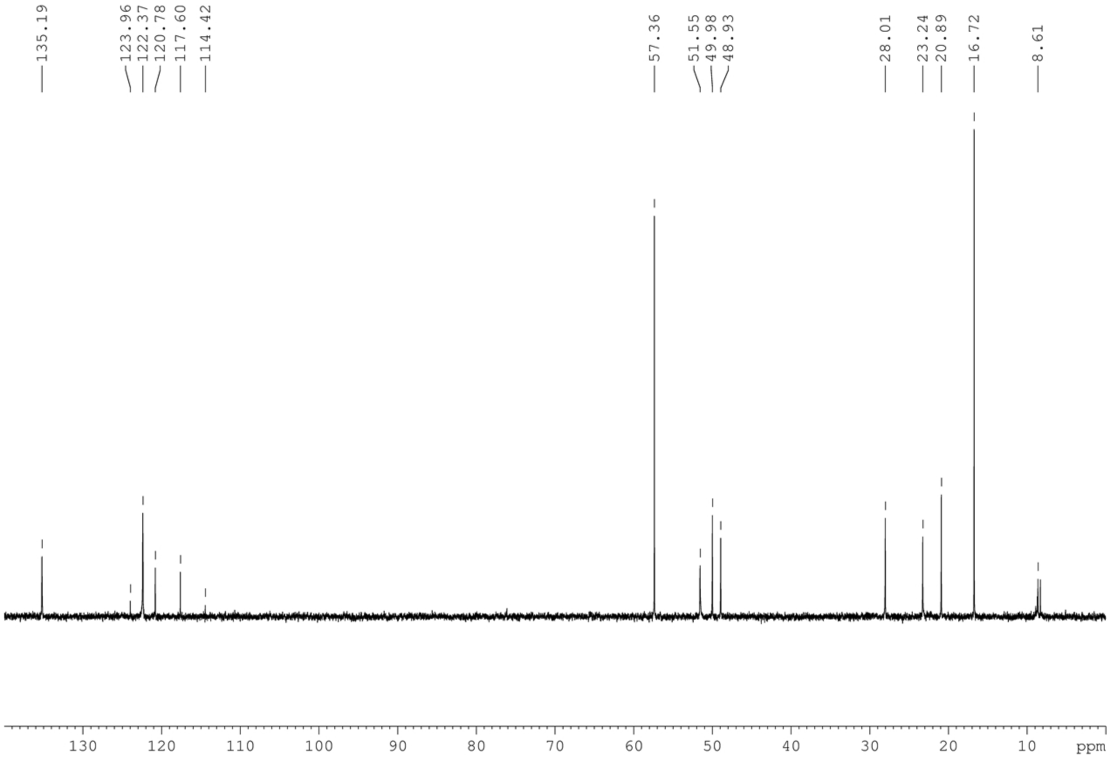


Figure S2: ^{13}C NMR spectrum of IL **1** in D_2O obtained using a 100 MHz spectrometer.

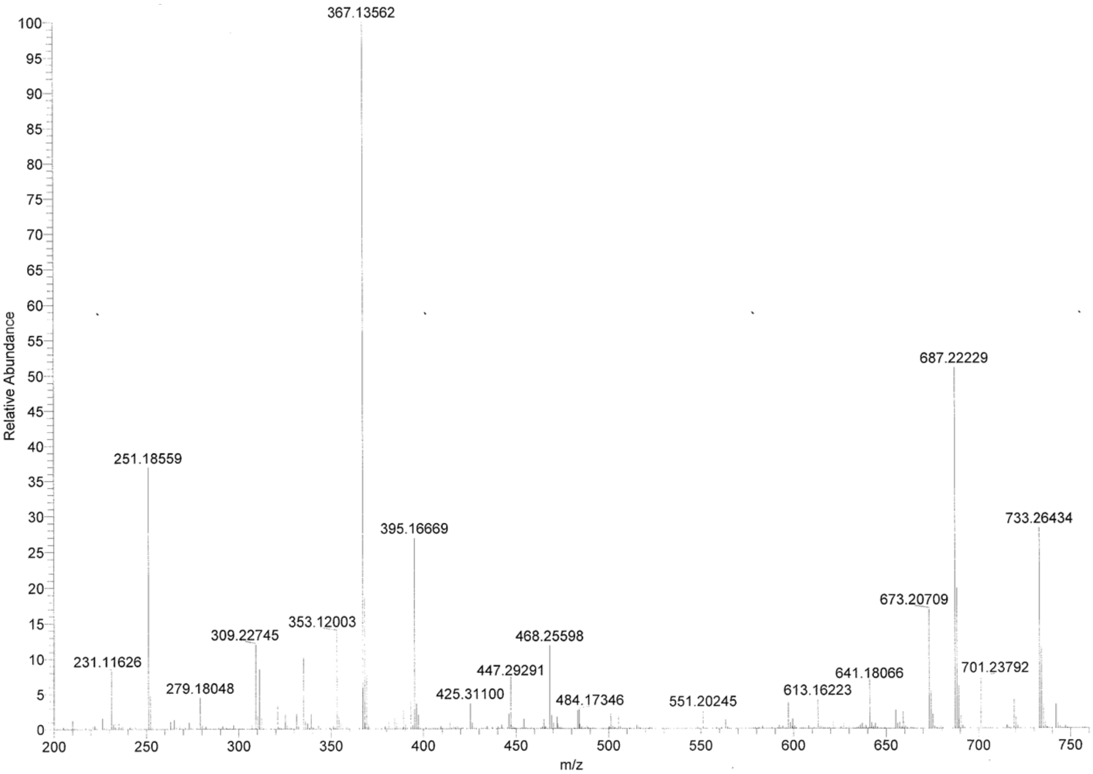
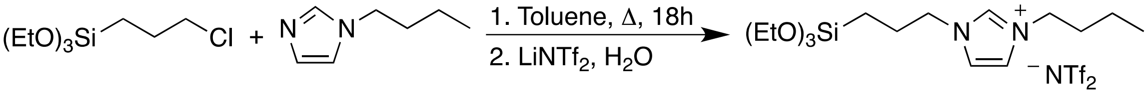


Figure S3: HRMS ESI(+) spectrum of IL **1** in MeOH.

2.2. [1-butyl-3-(3-triethoxysilylpropyl)imidazolium]NTf$_2$ (IL 2)



IL 2

Scheme S2: Synthetic pathway for the preparation of IL **2**.

1-butyl-3-(3-triethoxysilylpropyl)imidazolium chloride[8] (3.23 g, 8.85 mmol) and bis(trifluoromethane)sulfonimide lithium salt (2.65 g, 9.24 mmol) were dissolved in water (15 mL) and stirred at rt for 10h. The aqueous phase was extracted with DCM (5x20 mL) and the combined organic phase was washed with water (3x20 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was dried *in vacuo* to yield a viscous, colourless liquid (4.86 g, 90%).

^1H NMR (300 MHz, $CDCl_3$): δ = 8.78 (s, 1H, NCHN), 7.31 (m, 2H, NCHCHN), 4.18 (m, 4H, NCH_2), 3.78 (q, *J* = 7.0 Hz, 6H, OCH_2), 2.01-1.68 (m, 4H, CH_2), 1.34 (m, 2H, CH_2), 1.19 (t, *J* = 7.0 Hz, 9H, OCH_2CH_3), 0.93 (t, *J* = 7.3 Hz, 3H, CH_3), 0.55 (m, 2H, $SiCH_2$). ^{13}C NMR (150 MHz, CD_3Cl): δ = 135.4 (s, 1C, NCHN), 122.6 (s, 1C, NCHCHN), 122.5 (s, 1C, NCHCHN), 119.9 (q, J_{CF} = 327 Hz, 2C, CF_3), 58.7 (s, 3C, OCH_2), 52.0 (s, 1C, NCH_2), 50.0 (s, 1C, NCH_2), 32.0 (s, 1C, CH_2), 24.3 (s, 1C, CH_2), 19.4 (s, 1C, CH_2), 18.1 (s, 3C, OCH_2CH_3), 13.2 (s, 1C, CH_3), 7.0 (s, 1C, $SiCH_2$). HRMS/ESI(+) (MeOH): m/z = 343.24014 and 329.22501, calcd. for $[C_{17}H_{35}N_2O_3Si]^+$ = 343.24169 and $[C_{16}H_{33}N_2O_3Si]^+$ = 329.22605.

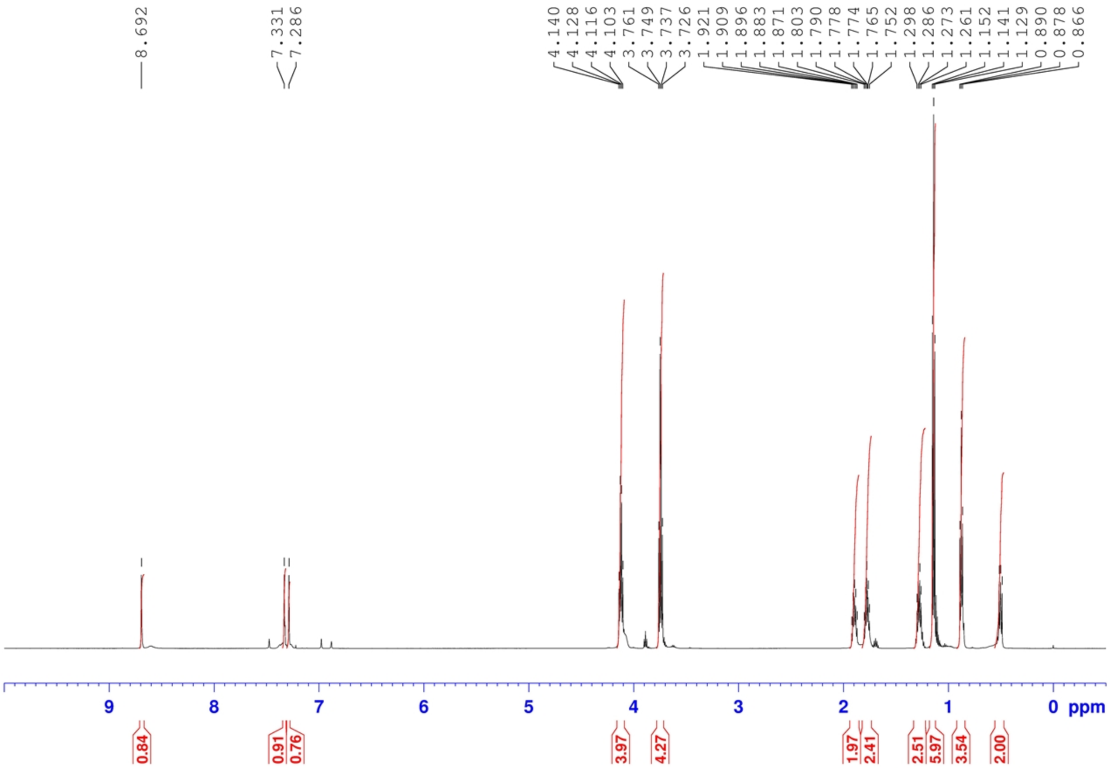


Figure S4: ^{1}H NMR spectrum of IL **2** in CD_3Cl obtained using a 300 MHz spectrometer.

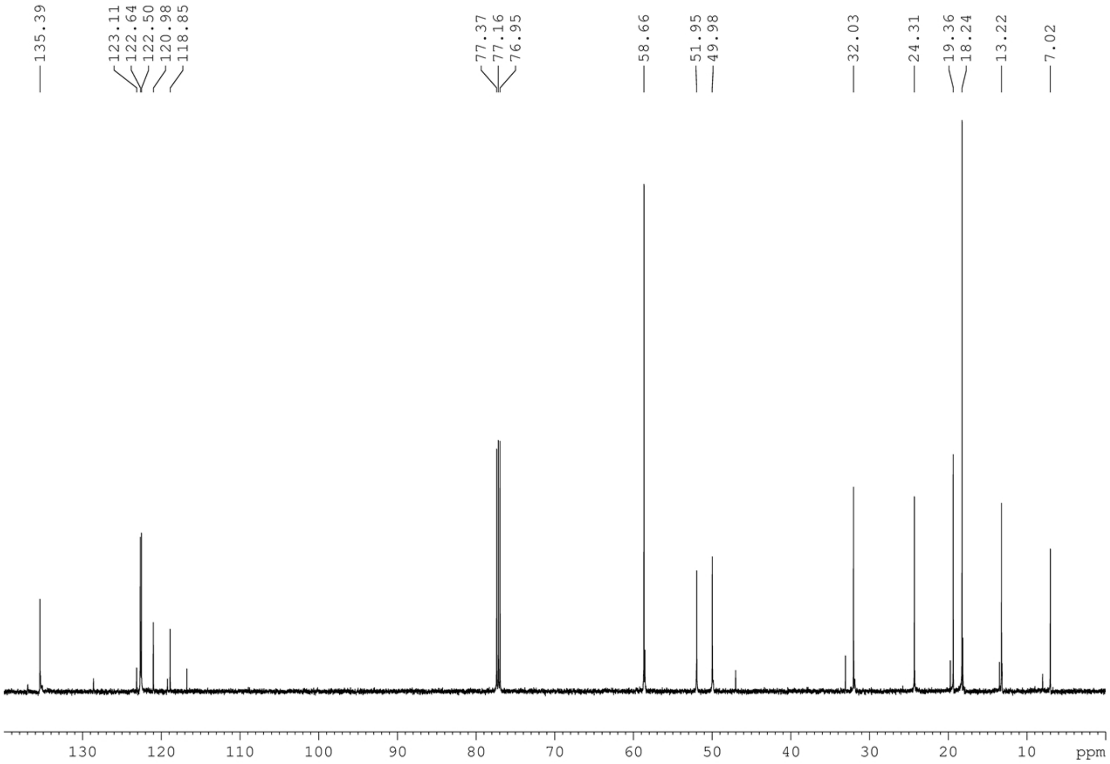


Figure S5: ^{13}C NMR spectrum of IL **2** in CD_3Cl obtained using a 150 MHz spectrometer.

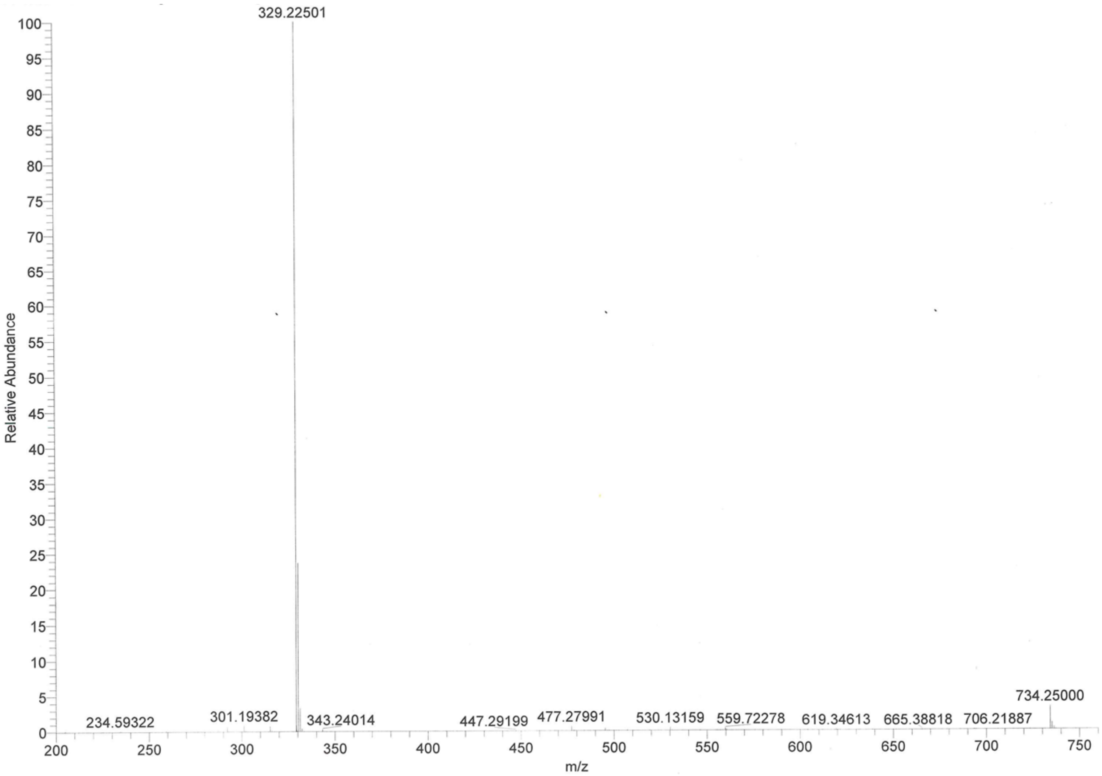
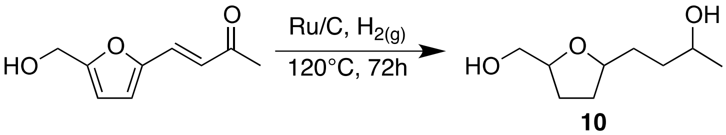


Figure S6: HRMS ESI(+) spectrum of IL **2** in MeOH.

2.3. 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol (10)



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Scheme S3: Synthetic pathway for the preparation of 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol.

5-hydromethylfurfuralacetone[2] (2.98 g, 17.9 mmol) and Ru/C (5 wt%, 125 mg) were combined in a high-pressure reactor. The reaction mixture was heated at 120°C under an atmosphere of $H_{2(g)}$ (120 bar) for 48 h. The reactor was periodically pressurized with $H_{2(g)}$ to maintain a constant pressure. The reaction mixture was purified over SiO_2 (EtOAc:MeOH, 99:1) to yield a colourless liquid (1.89 g, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.96 (m, 1H, CHOH), 3.89-3.66 (m, 2H, CH_2OH), 3.62 (ddd, *J* = 5.9, 5.6, 1.7 Hz, 1H, furyl-OCH), 3.43 (ddd, *J* = 5.9, 5.6, 1.7 Hz, 1H, furyl-OCH), 3.04 (s, 2H, OH), 1.97-1.78 (m, 2H, furyl-CH_2), 1.73-1.63 (m, 1H, furyl-CH_2), 1.63-1.54 (m, 2H, butyl-CH_2 and furyl-CH_2), 1.54-1.39 (m, 3H, butyl-CH_2), 1.12 (d, *J* = 6.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 80.1 (dd, furyl-OCH), 77.2 (t, furyl-OCH), 67.8 (d, CHOH), 65.0 (d, CH_2OH), 36.0 (d, butyl-CH_2), 32.1 (d, butyl-CH_2), 31.5 (d, furyl-CH_2), 27.0 (d, furyl-CH_2), 23.5 (d, CH_3). HRMS/ESI(+) (MeOH with $MeCO_2H$): m/z = 197.11478, calcd. for $[C_9H_{18}O_3Na]^+$ = 197.11482.

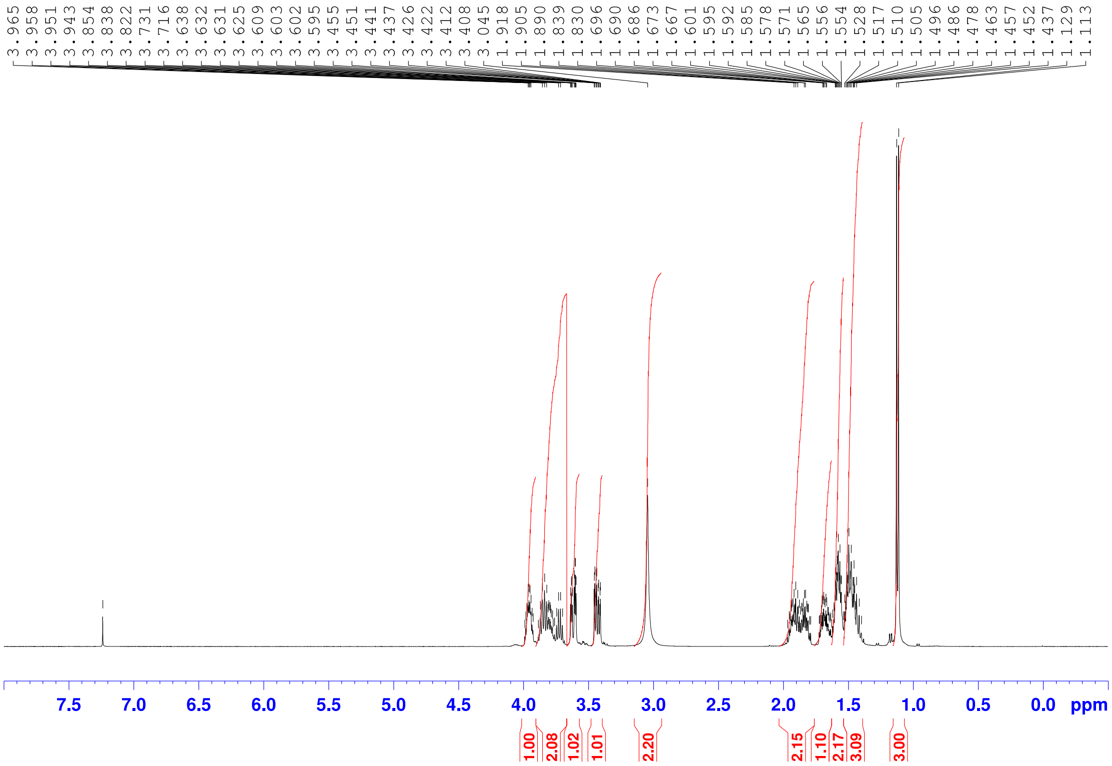

Figure S7: ^{1}H NMR spectrum of 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol in $CDCl_3$ obtained using a 400 MHz spectrometer.

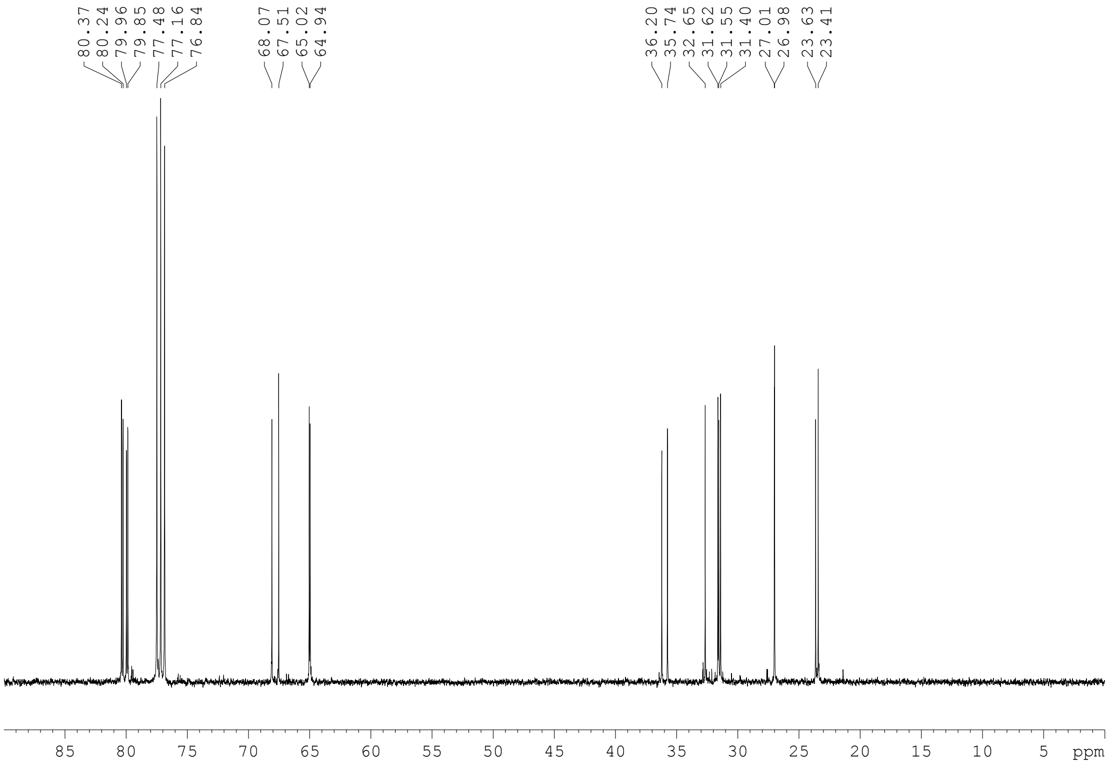

Figure S8: ^{13}C NMR spectrum of 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol in $CDCl_3$ obtained using a 100 MHz spectrometer.

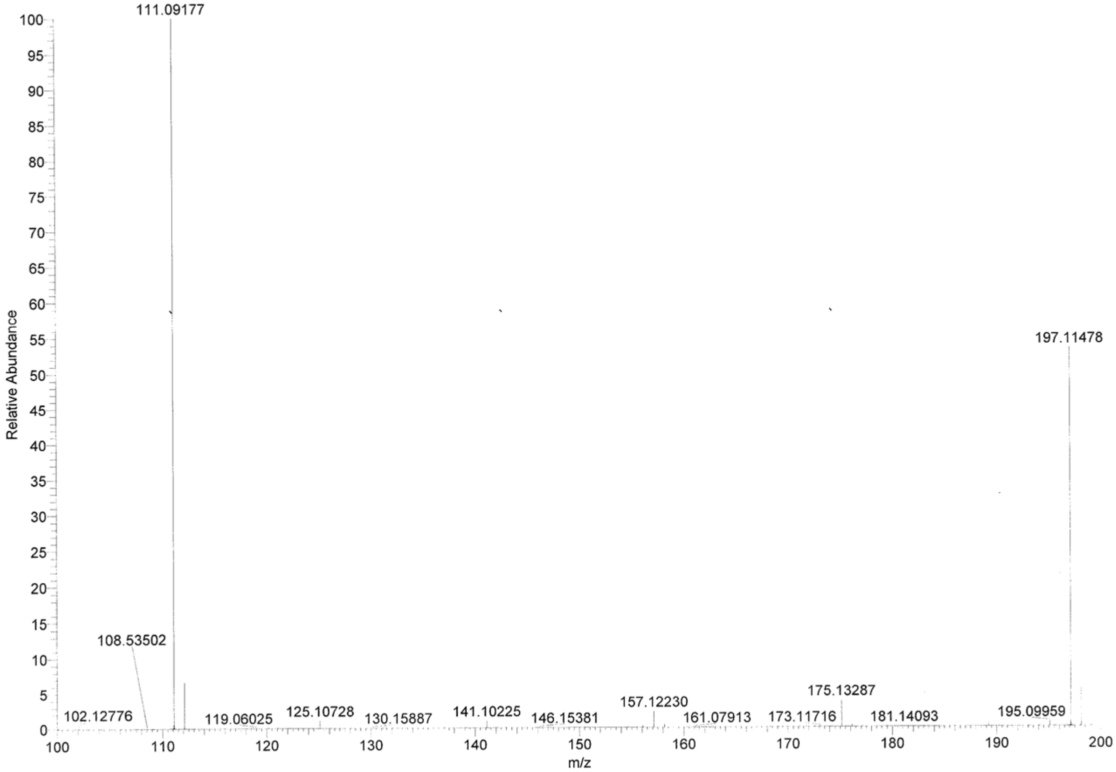

Figure S9: HRMS ESI(+) spectrum of 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol in MeOH with $MeCO_2H$.

3. Characterization of Supported Ionic Liquid Phases and Bifunctional Catalysts

3.1. Infrared Spectroscopy of SILPs

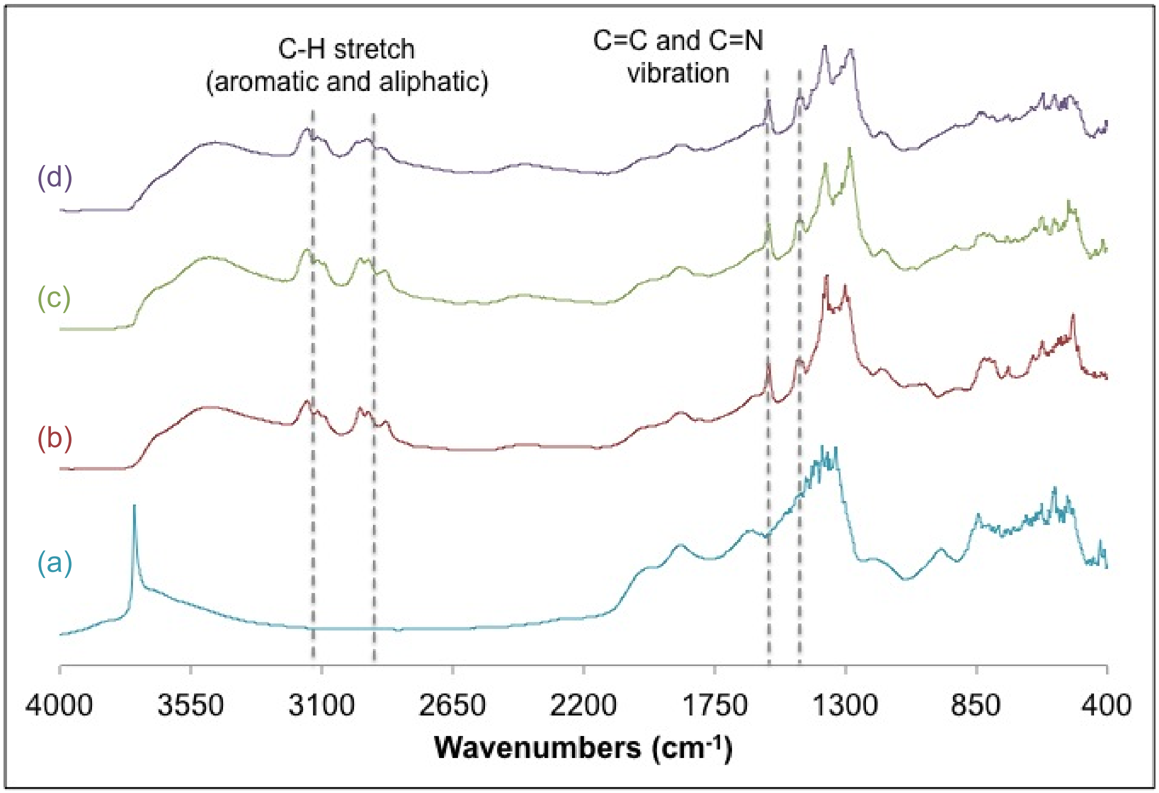

Figure S10: Infrared spectra of (a) dehydroxylated SiO_2; (b) SILP-0.33; (c) SILP-0.66; and (d) SILP-1.00

3.2. ^{29}Si Solid-State NMR of SILPs

The ^{29}Si solid-state NMR spectra were obtained using a Bruker AV700 spectrometer operating at a ^{1}H resonance frequency of 700.24 MHz and a ^{29}Si frequency of 139.10 MHz. For all samples, the ^{29}Si spectra were recorded at rt by employing a one-pulse sequence with ^{1}H decoupling during the acquisition. For the SiO_2 and SILP-1.00, a spinning speed of 5 kHz and a recycle delay of 300 s were used. Preliminary tests showed that this value was long enough for quantitative information. For comparison reasons, the spectrum of IL **1** was measured using a single pulse sequence with decoupling during acquisition under static conditions and using a recycle delay of 10 s. All spectra were calibrated to TMS.

The ^{29}Si data analysis was performed using the dmfit program[9] for which the experimental spectrum was deconvoluted with the help of several components to account for the various presented signals. The best fit was obtained by using Gauss line shapes to model each observed peak.

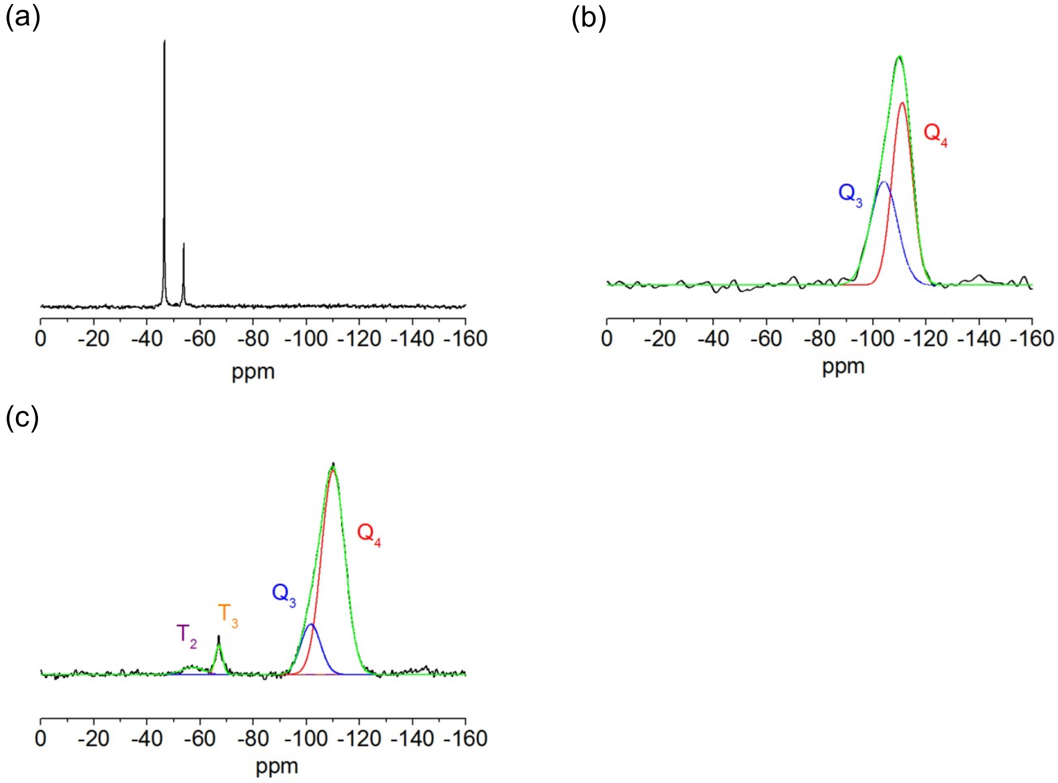

Figure S11: ^{29}Si MAS NMR spectra of (a) IL **1**; (b) SiO_2; and (c) SILP-1.00 (For experimental data = black, T_2 = purple, T_3 = yellow, Q_3 = blue, Q_4 = red, sum of fitted data (T_2+T_3+Q_3+Q_4) = green)

Table S1: ^{29}Si MAS NMR data of SiO_2 and SILP-1.00

Sample	**T_2**		**T_3**		**Q_3**		**Q_4**	
	δ (ppm)	**Area (%)**	**δ (ppm)**	**Area (%)**	**δ (ppm)**	**Area (%)**	**δ (ppm)**	**Area (%)**
SiO_2	—	—	—	—	-104.1	43.2	-111.0	56.8
SILP-1.00	-57.0	2.6	-67.1	3.4	-101.6	16.3	-110.1	77.7

3.3. STEM of Bifunctional Catalysts

Specimens for scanning transmission electron microscopy (STEM) were prepared by mechanical grinding of powder samples followed by ultrasound dispersion in acetone. A drop of obtained suspension was deposited on a copper transmission electron microscopy grid with lacey carbon support film. High angle annular dark field (HAADF) STEM images were collected using a Hitachi aberration-corrected scanning transmission electron microscope (HD-2700C) operated at 200kV.

3.4. EXAFS Analyses of Bifunctional Catalysts

XAS experiments were performed at the X18A beamline at the NSLS at Brookhaven National Laboratory (NY, USA). Beamline X18A is a bending magnet line, which uses a Si {1 1 1} channel-cut monochromator and a rhodium-coated toroidal focusing mirror that delivers a ≈ 1.0 mm (horizontal) ≈ 0.5 mm (vertical) spot size with a flux of $\approx 2.5 \times 10^{11}$ photons/s at 10 keV. Passivated Implanted Planar Silicon (PIPS) detector has been used to record Ru fluorescence signal. Five consecutive scans were averaged after alignment using the spectra obtained from the Ru foil in the reference ion chamber, recorded simultaneously with those of the sample. Samples were encapsulated between two Kapton foil sheets. Data reduction and analysis were performed using IFEFFIT package.[10] Calculated spectra were fitted to the experimental EXAFS data in *r* space. The parameters describing local structural environment (coordination numbers CN, bond length R, and their mean-squared relative derivation σ^2) around absorbing atoms were varied during fitting. The values of passive electron reduction factor, S_0^2, were obtained by fitting reference spectra of Ru metal and RuO_2.

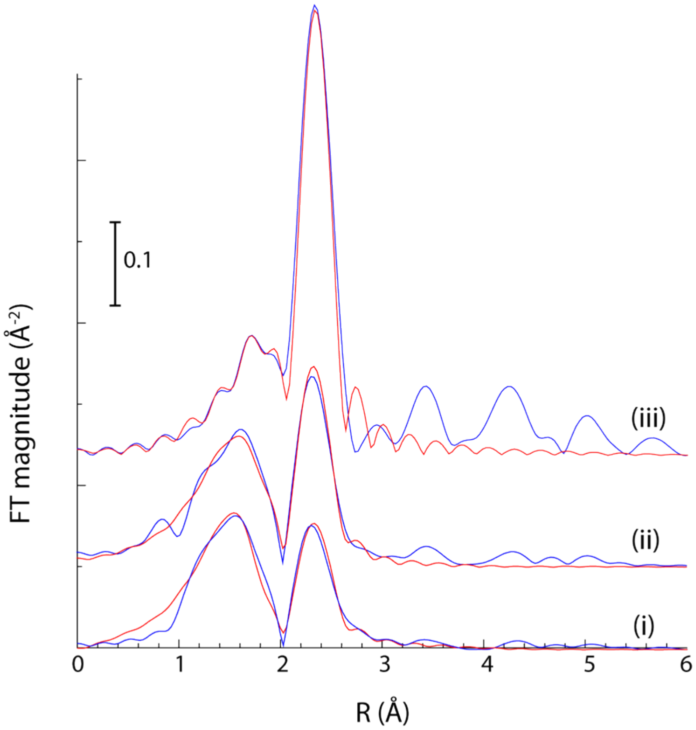

Figure S12. Fourier transformed magnitudes of the EXAFS experimental data (blue) and calculated data using FEFF theory (red) for (i) RuNPs@SILP-1.00 before catalysis, (ii) RuNPs@SILP-1.00 after the 3rd cycle of catalysis and (iii) Ru foil (reference).

Table S2. Structural parameters from the curve-fitting analysis of the EXAFS spectra for RuNPs@SILP-1.00 before and after catalysis with reference to Ru foil

Sample	**Ab-Sc**[a]	**Parameters**		
		Coordination Number[b]	**Atomic Distance (Å)**	**$\sigma^2 \times 10^3$**
RuNPs@SILP-1.00: Before	Ru-Ru	4.6(3)	2.67(1)	5(1)
	Ru-O	2.2(3)	2.04(2)	5(3)
RuNPs@SILP-1.00: After 3rd Cycle	Ru-Ru	6.9(6)	2.67(1)	5(1)
	Ru-O	2.1(9)	2.03(5)	8(4)
Ru Foil	Ru-Ru	12*	2.67(4)	2.3(6)

[a] X-ray absorbing (Ab) and X-ray-scattering atoms (Sc)
[b] Coordination number is fixed at a crystallographic value.

4. Catalytic Data from the Hydrogenolysis of 4-(2-tetrahydrofuryl)-2-butanol and 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol

4.1. Reaction Profiles for the Hydrogenolysis of 4-(2-tetrahydrofuryl)-2-butanol using RuNPs@SILP

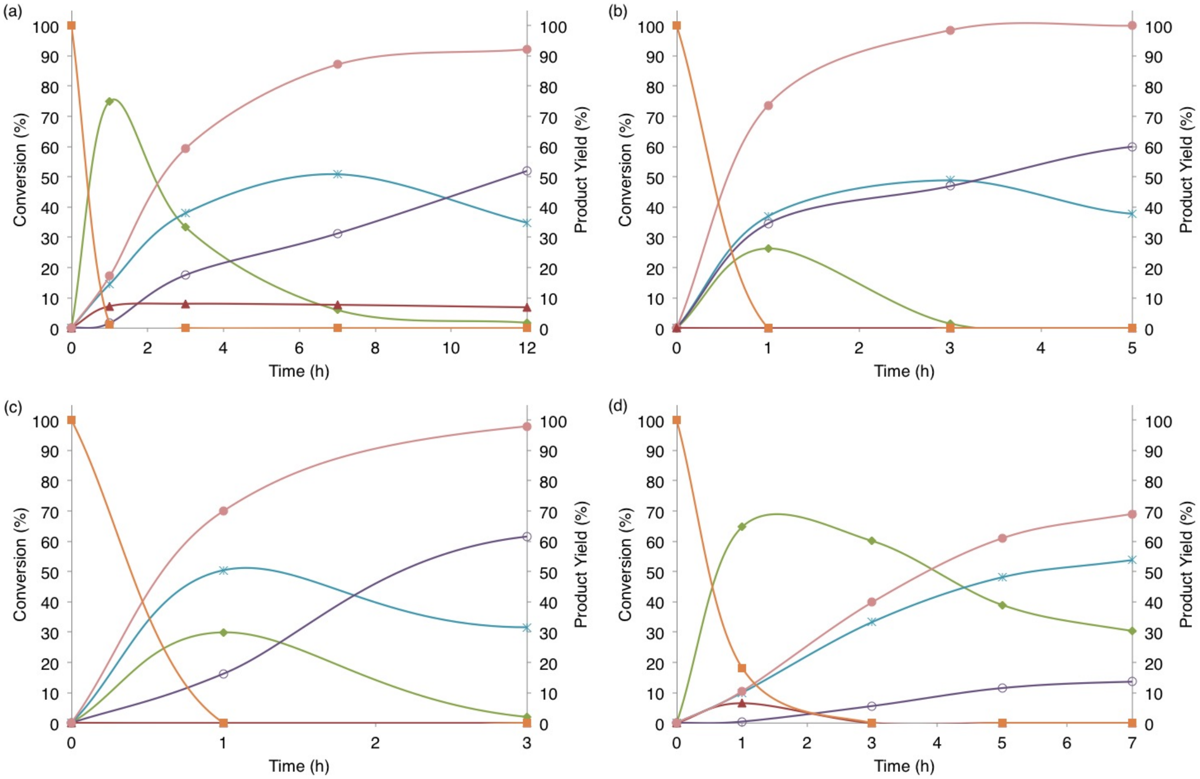

Figure S13. Reaction profile for the hydrogenolysis of 4-(2-tetrahydrofuryl)-2-butanol (**3**) using (a) RuNPs@SILP-0.33, (b) RuNPs@SILP-0.66, (c) RuNPs@SILP-1.00 and (d) RuNPs@SILP-1.00 with 0.10 mL of added water (For Substrate **3** = orange ■, Cyclic ethers (**4** + **5**) = green ◆, Alcohol **6** = blue ✳, Aliphatic ethers (**7** + **8**) = purple ❍, Others (Isomers and Condensation products of **3**) = red ▲, C_8-OL Yield (**6** + **7** + **8**) = pink ●)

Reaction conditions: [Ru] (0.016 mmol), SILP (0.5 g), [EMIM]NTf_2 (2.9 mL), Substrate (1.6 mmol), H_2 (120 bar), 150°C.

4.2. Catalytic Data for the Hydrogenolysis of 4-(2-tetrahydrofuryl)-2-butanol Toward 2-butyltetrahydrofuran Selectivity

Table S3. Catalytic data for the hydrogenolysis of 4-(2-tetrahydrofuryl)-2-butanol (**3**) towards the selective formation of 2-butyltetrahydrofuran (**4**) using RuNPs@SILP-0.33

T (°C)	**$p(H_2)$ (bar)**	**Product Yield (%)[a]**								
		Substrate	**Cyclic Ethers**		**Alcohol**	**Aliphatic Ethers**		**Alkane**	**Others**	**C_8-OL Yield (6+7+8)**
		3	**4**	**5**	**6**	**7**	**8**	**9**		
150	120	0	3	3	42	46	6	0	0	94
125	120	0	74	1	19	6	0	0	0	25
100[b]	120	28	13	0	0	0	0	0	59	0
125	100	0	78	1	16	5	0	0	0	21
125	80	0	83	1	13	4	0	0	0	17

Reaction conditions: [Ru] (0.016 mmol), SILP-0.33 (0.5 g), [EMIM]NTf_2 (2.9 mL), Substrate (1.6 mmol).

[a] Conversion >99%, C_8-OL Yield = 1-octanol (**6**) + 1,1-dioctylether (**7**) + ethyloctylether (**8**).

[b] THFA conversion = 72%, Others = Isomers and Condensation products of **3**.

4.3. Simplex Optimization Data

Table S4: Catalytic data for the simplex optimization of the hydrogenolysis of 4-(2-tetrahydrofuryl)-2-butanol (**3**) towards the selective formation of 1-octanol (**6**) using RuNPs@SILP-1.00

Entry	**Reaction Parameters**			**Product Yield (%)**						
	Time (h)	**Volume of H_2O (mL)**	**T (°C)**	**Cyclic Ethers**		**Alcohol**	**Aliphatic Ethers**		**Alkane**	**C_8-OL Yield (6+7+8)**
				4	**5**	**6**	**7**	**8**	**9**	
1	12	0.050	160	0	1	42	49	5	3	97
2	10	0.065	155	1	1	48	46	4	0	98
3	6	0.085	145	38	1	45	14	2	0	61
4	9	0.070	153	7	2	58	30	3	0	92
5	17	0.120	153	14	2	58	24	2	0	84
6	14	0.100	155	4	1	58	34	3	0	95
7	7	0.070	148	18	2	53	24	3	0	80
8	12	0.090	155	1	1	50	43	4	1	98
9	15	0.120	150	8	2	59	28	3	0	90
10	15	0.130	145	23	2	52	21	2	0	76
11	13	0.100	153	5	3	58	30	3	1	92
12	14	0.120	147	34	2	45	16	2	1	64
13	14	0.110	150	10	2	56	29	3	0	88
14	10	0.085	150	17	2	55	23	3	0	81
15	16	0.125	150	14	1	60	22	3	0	85
16	14	0.100	150	10	2	59	26	3	1	88

Reaction conditions: [Ru] (0.016 mmol), SILP (0.5 g), [EMIM]NTf_2 + H_2O (2.9 mL), Substrate (1.6 mmol).

Table S5: Catalytic data for the simplex optimization of the hydrogenolysis of 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol (**10**) towards the selective formation of 1-nonanol (**13**) using RuNPs@SILP-1.00

Entry	**Reaction Parameters**			**Product Yield (%)**						
	Time (h)	**Volume of H_2O (mL)**	**T (°C)**	**Cyclic Ethers**		**Alcohol**	**Aliphatic Ethers**		**Alkane**	**C_9-OL Yield (13+14+15)**
				11	**12**	**13**	**14**	**15**	**16**	
1	21	0.110	165	1	17	56	12	3	11	71
2	22	0.080	165	1	5	44	26	5	19	75
3	19	0.095	160	4	11	52	15	5	13	72
4	18	0.070	155	2	28	55	7	2	6	64
5	19	0.050	155	3	10	34	31	6	16	71
6	19	0.085	160	2	8	48	15	4	23	67
7	20	0.075	160	2	10	48	26	4	10	78
8	25	0.130	175	0	1	18	14	2	65	34
9	20	0.100	160	8	33	47	2	2	8	51
10	22	0.130	165	1	12	55	13	2	17	70
11	22	0.110	170	0	2	38	16	5	39	59
12	17	0.090	155	29	1	57	7	2	4	66
13	20	0.075	155	1	16	56	11	4	12	71
14	19	0.050	150	6	32	45	5	4	8	54
15	19	0.085	155	3	23	53	7	4	10	64
16	19	0.060	155	5	21	49	8	4	13	61

Reaction conditions: [Ru] (0.016 mmol), SILP (0.5 g), [EMIM]NTf_2 + H_2O (2.9 mL), Substrate (1.6 mmol).

4.4. Gas Chromatograms of Catalysis Reaction Mixtures and Products

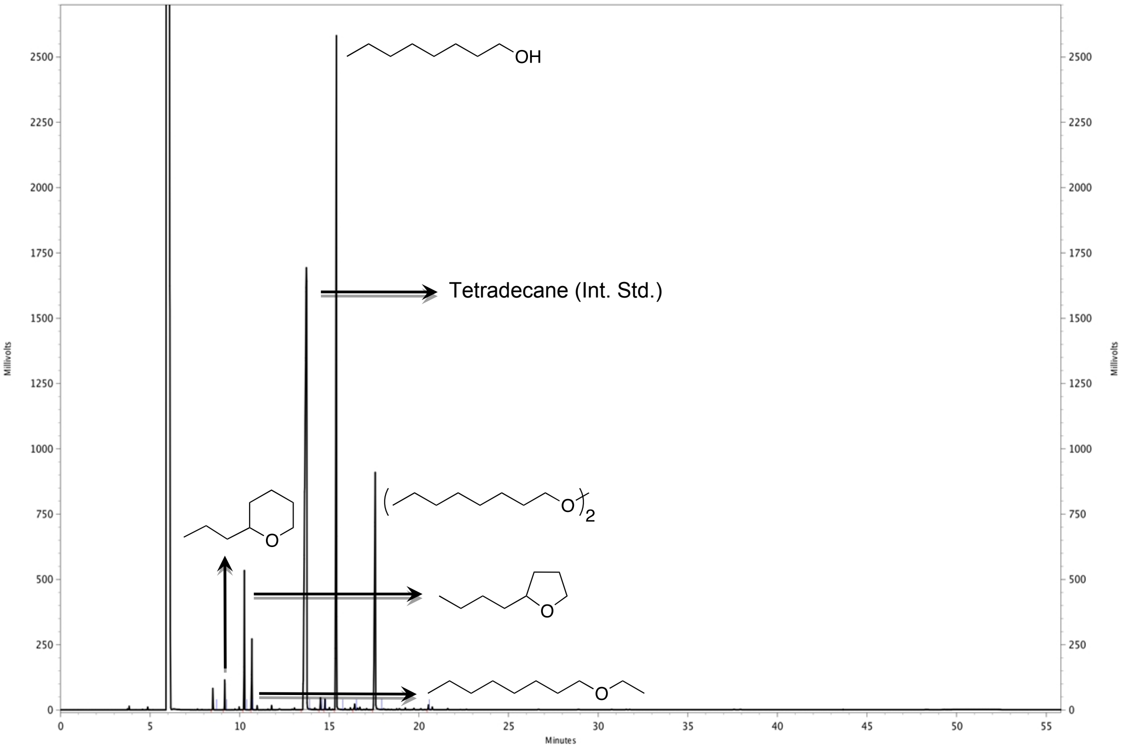

Figure S14: GC/MS of the reaction mixture from the hydrogenolysis 4-(2-tetrahydrofuryl)-2-butanol (**3**).

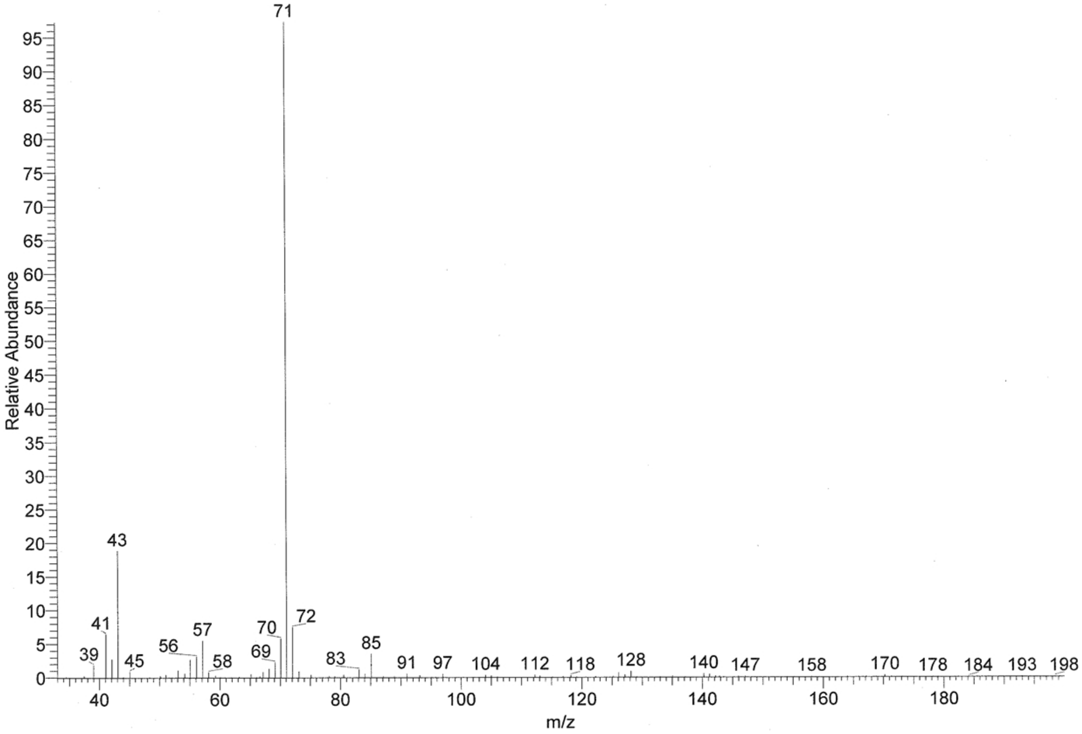

Figure S15: GC/MS of 2-butyltetrahydrofuran (**4**)[11]

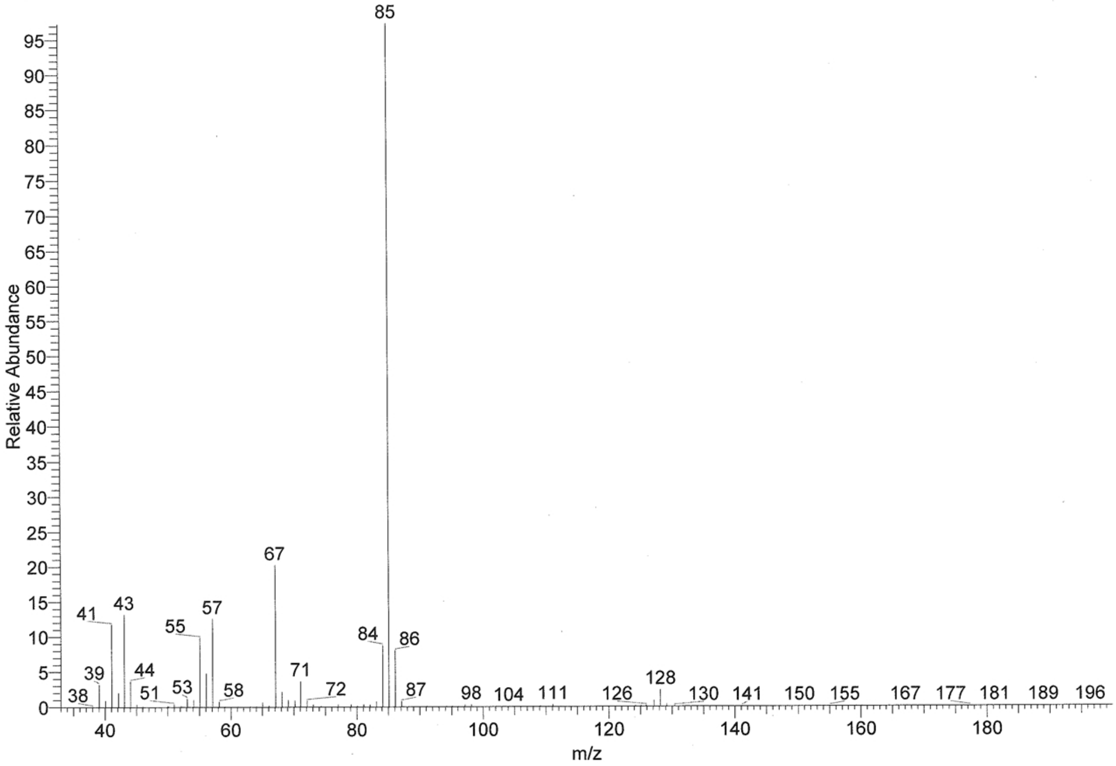

Figure S16: GC/MS of 2-propyltetrahydropyran (**5**)[11]

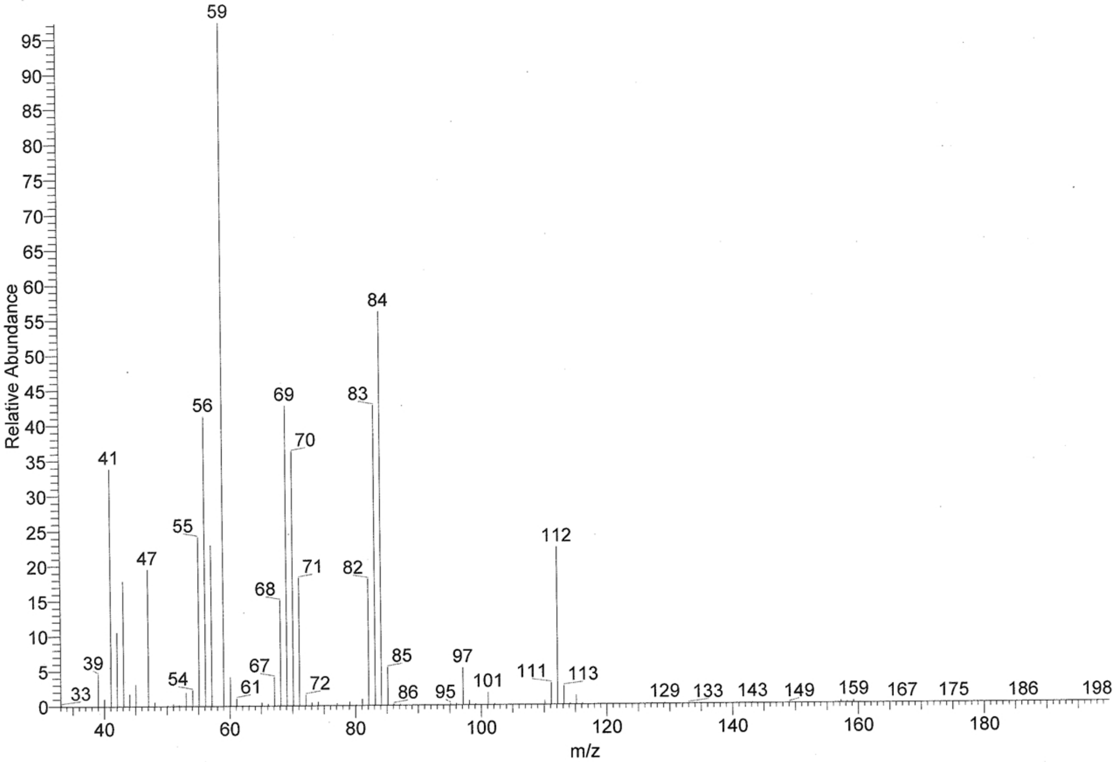

Figure S17: GC/MS of ethyloctylether (**8**)

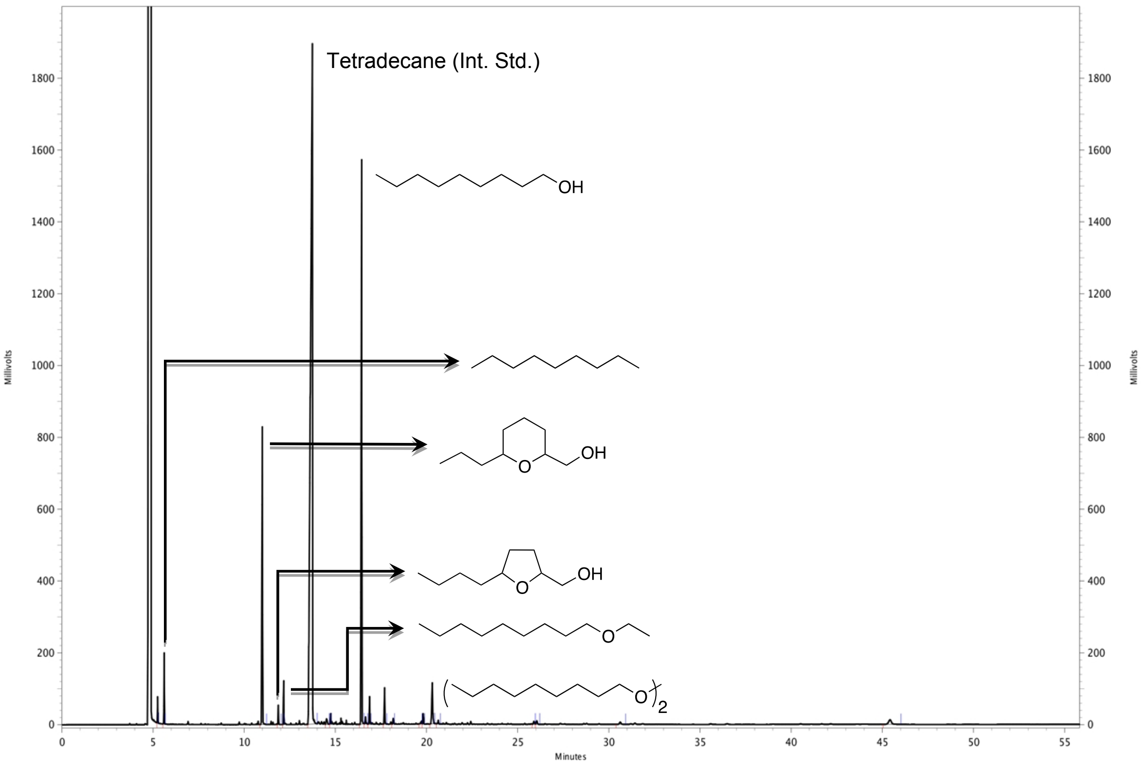

Figure S18: GC/MS of the reaction mixture from the hydrogenolysis of 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol (**10**).

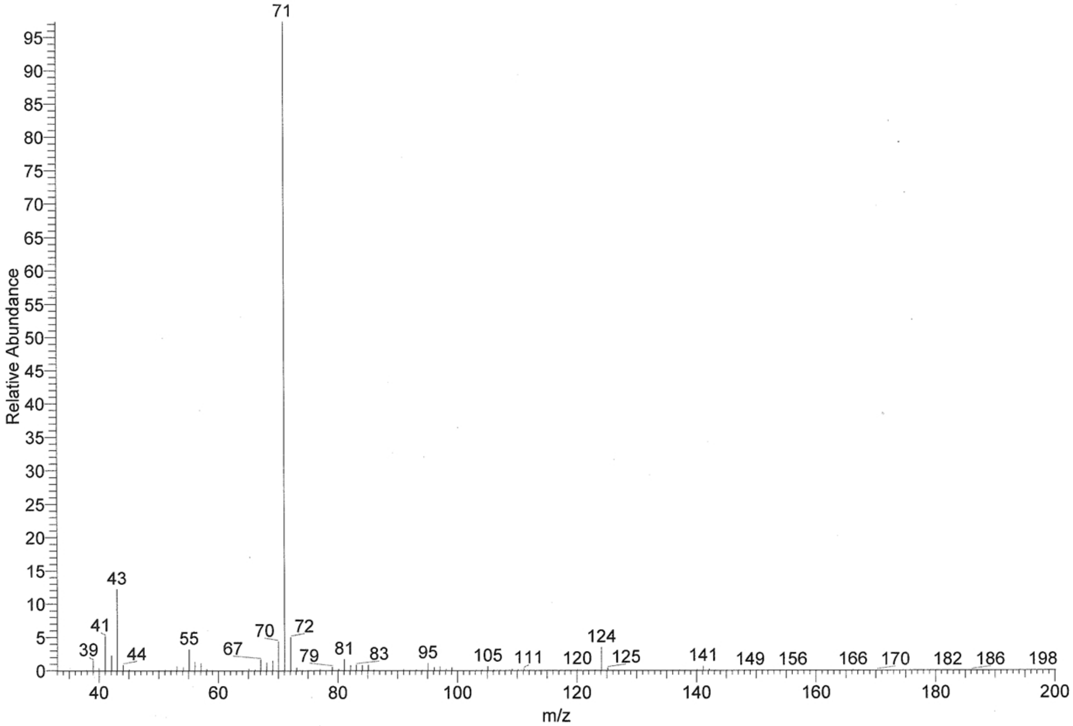

Figure S19: GC/MS of 5-hydroxymethyl-2-butyltetrahydrofuran (**11**)

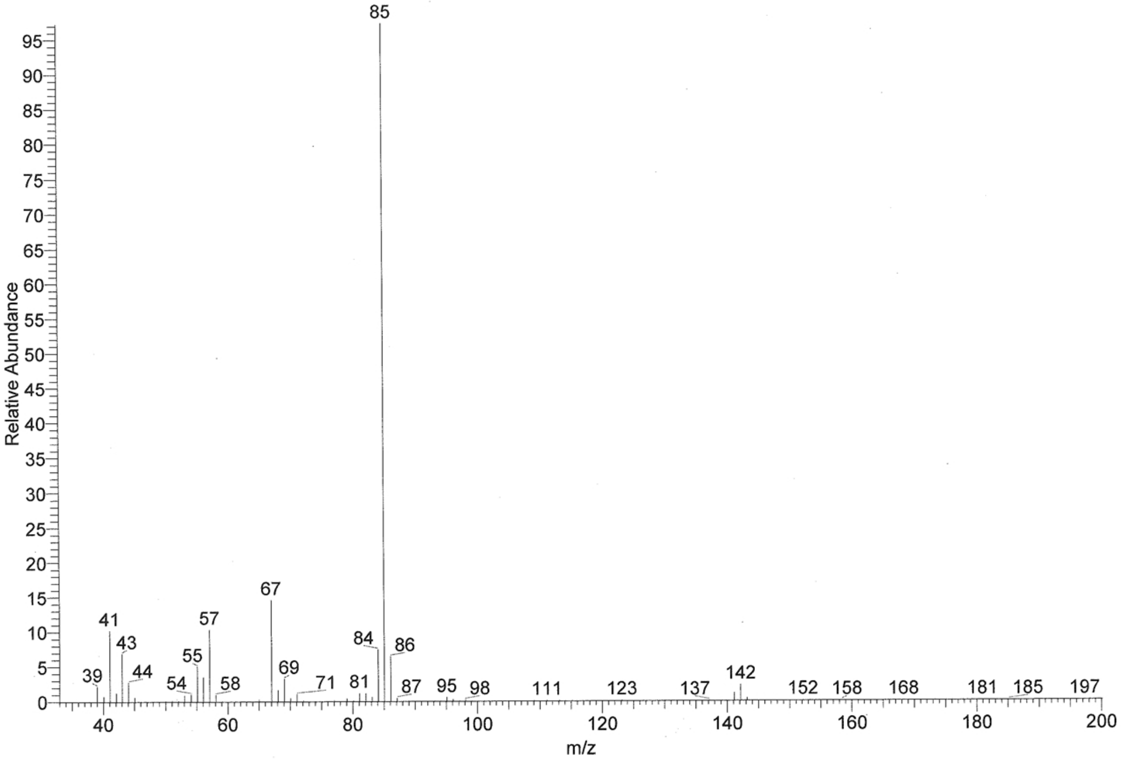

Figure S20: GC/MS of 6-hydroxymethyl-2-propyltetrahydropyran (**12**)

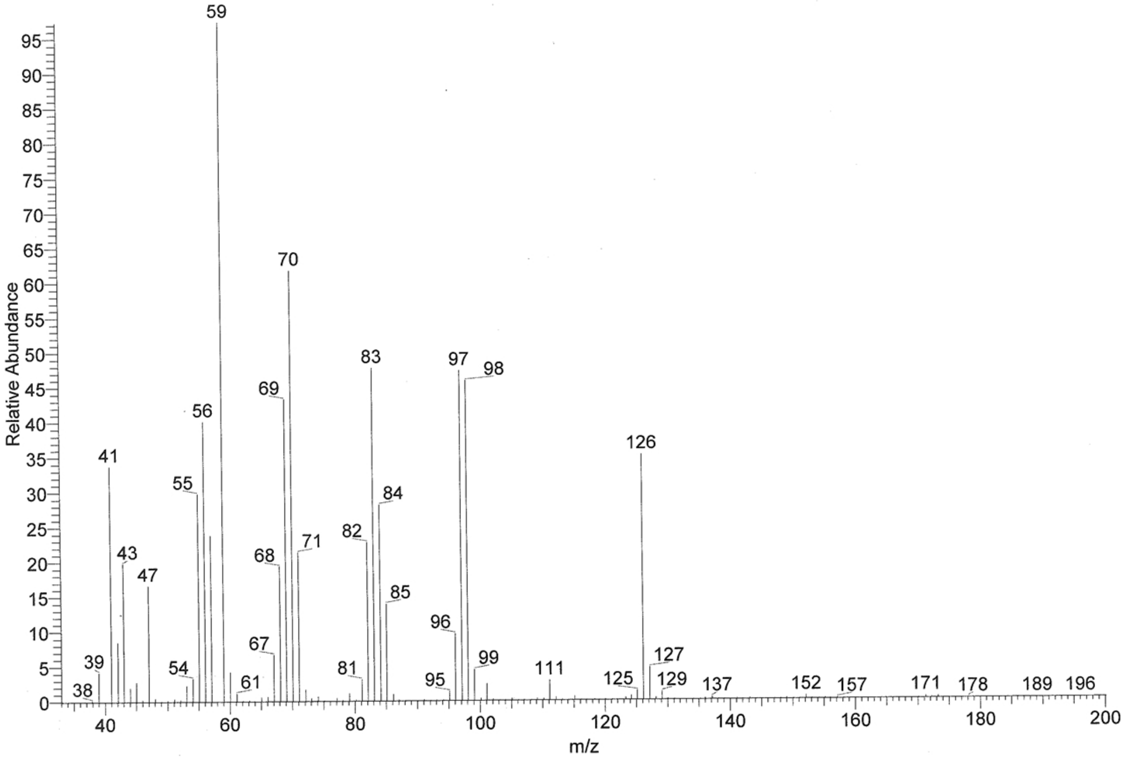

Figure S21: GC/MS of ethylnonylether (**15**)

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