Electronic Supplementary Information (ESI)

Rhodium-catalyzed hydrogenation of olefins in γ-valerolactone-based ionic liquids

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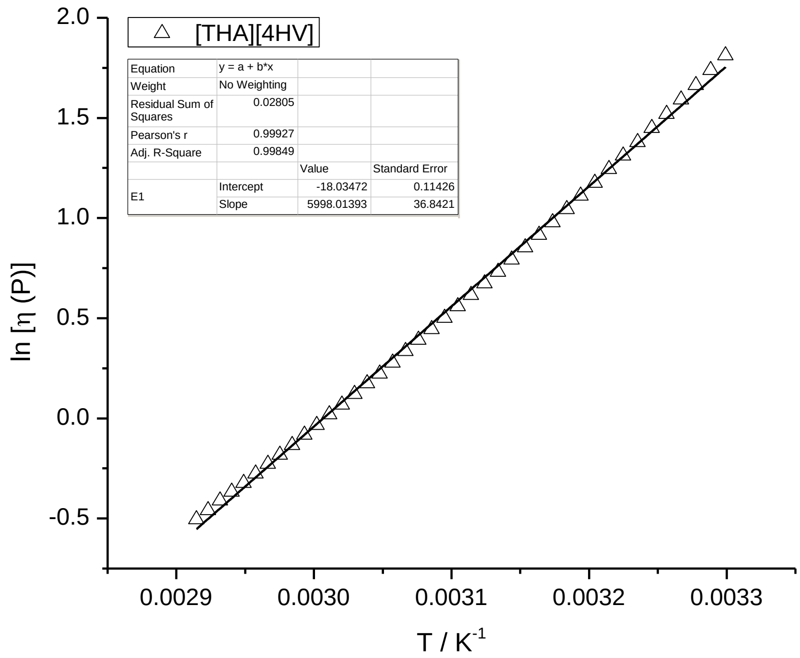
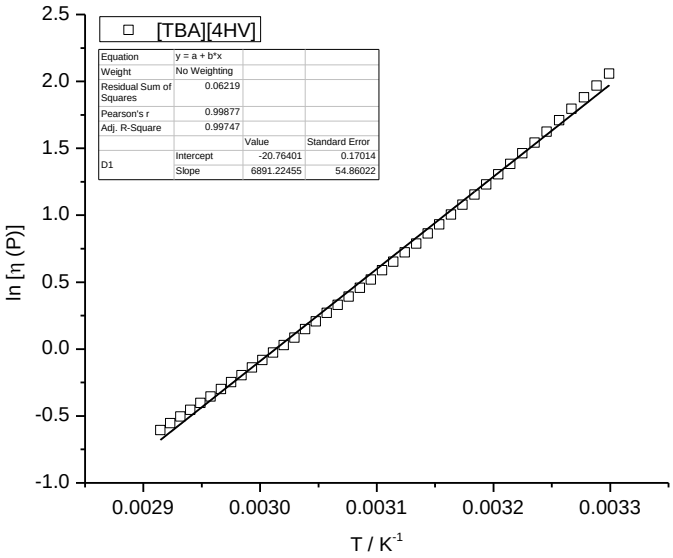
ESI – Table S1. Viscosity values of ionic liquids

T (°C)	□□□□□□□□□□□	□□B□□□□□□□□	□□B□□□□MeO□□	□□B□□□□EtO□□
	η (mPa· s)	η (mPa· s)	η (mPa· s)	η (mPa· s)
20	1380	2060	1170	1310
22	1170	1690	982	1100
25.1	911	1250	748	835
30.1	612	783	490	544
35.1	426	508	332	367
40.1	304	342	232	255
45.1	221	237	166	182
50.1	165	168	122	133
55.1	125	123	91.3	99.2
60.1	96.7	92	69.8	75.4
65.1	75.9	70.2	54.5	58.6
70.1	60.4	54.6	43.3	46.4

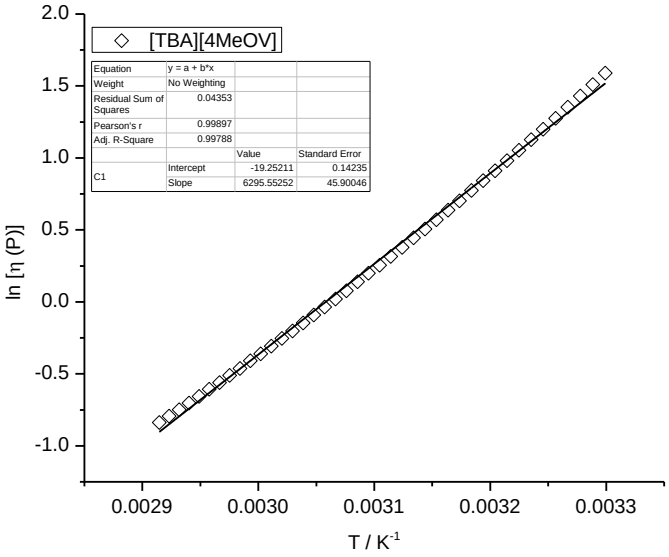
The activation energies (E_a) for viscous flow of the ionic liquids



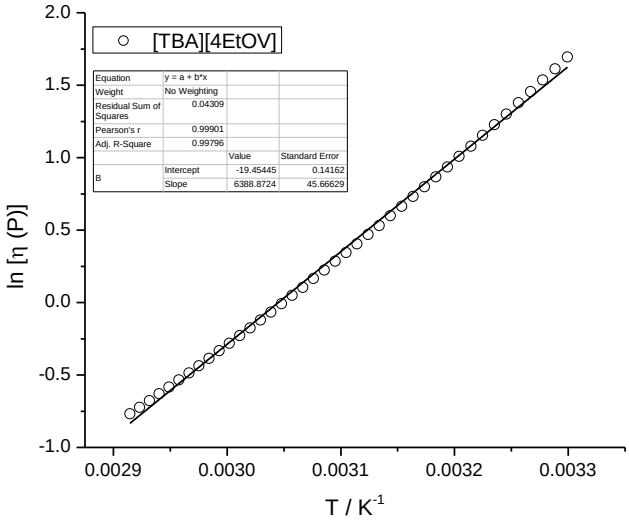
ESI-FIG S1. Activation energy (E_a) of [THA][4HV]



ESI-FIG S2. Activation energy (E_a) of [TBA][4HV]



ESI-FIG S3. Activation energy (E_a) of [TBA][4MeOV]



ESI-FIG S4. Activation energy (E_a) of [TBA][4EtOV]

ESI - Table S2. Hydrogenation of olefins in different ionic liquids

Entry	Substrate	$n_{substrate}$ (mmol)	Solvent	Reaction time (h)	Reaction time (min)	Yield of alkane (%)	$m_{catalyst}$ (mg)	$n_{catalyst} \times 10^3$ (mmol)	TOF (h^{-1})
1	hex-1-ene	9.70	[BMIM][Cl]	2.00	120	0	1.62	3.99	0
2	hex-1-ene	10.30	[TBA][4HV]	2.00	120	>99.9	1.56	3.84	1339
3	hex-1-ene	10.21	[THA][4HV]	0.50	30	>99.9	1.65	4.06	5022
4	hex-1-ene	10.41	[TMA][4MV]	2.00	120	17	1.80	4.43	200
5	hex-1-ene	10.14	[TMA][4EV]	2.00	120	70	1.70	4.19	847
6	hex-1-ene	9.71	[TBA][4MV]	0.34	20	>99.9	2.16	5.32	5360
7	hex-1-ene	9.26	[TBA][4EV]	0.25	15	>99.9	1.98	4.88	7588
8	oct-1-ene	8.44	[BMIM][Cl]	2.00	120	0	1.82	4.48	0
9	oct-1-ene	8.34	[TBA][4HV]	2.00	120	>99.9	1.69	4.16	1001
10	oct-1-ene	9.29	[THA][4HV]	1.50	90	>99.9	1.50	3.68	1679
11	oct-1-ene	8.08	[TMA][4MV]	2.00	120	20	1.70	4.19	193
12	oct-1-ene	7.49	[TMA][4EV]	2.00	120	35	1.70	4.19	313
13	oct-1-ene	9.30	[TBA][4MV]	0.34	20	>99.9	1.60	3.94	6933
14	oct-1-ene	7.97	[TBA][4EV]	0.25	15	>99.9	1.70	4.19	7605
15	dec-1-ene	6.73	[BMIM][Cl]	4.00	240	0	1.44	3.55	0
16	dec-1-ene	6.85	[TBA][4HV]	4.00	240	>99.9	1.50	3.69	463
17	dec-1-ene	6.03	[THA][4HV]	0.75	45	97	1.80	4.43	1759
18	dec-1-ene	5.74	[TMA][4MV]	2.00	120	52	1.60	3.94	379
19	dec-1-ene	6.30	[TMA][4EV]	2.00	120	50.2	1.60	3.94	401
20	dec-1-ene	6.04	[TBA][4MV]	2.00	120	>99.9	1.70	4.19	721
21	dec-1-ene	6.63	[TBA][4EV]	1.00	60	97	1.70	4.19	1536
22	cyclohexene	9.16	[BMIM][Cl]	3.00	180	0	1.80	4.43	0
23	cyclohexene	12.06	[TBA][4HV]	3.00	180	56	1.80	4.43	508

Entry	Substrate	$n_{substrate}$ (mmol)	Solvent	Reaction time (h)	Reaction time (min)	Yield of alkane (%)	$m_{catalyst}$ (mg)	$n_{catalyst} \times 10^3$ (mmol)	TOF (h^{-1})
24	cyclohexene	12.37	[THA][4HV]	3.00	180	70	1.90	4.68	617
25	cyclohexene	11.61	[TMA][4MV]	3.00	180	4.9	1.80	4.43	44
26	cyclohexene	11.16	[TMA][4EV]	3.00	180	4.8	1.90	4.68	39
27	cyclohexene	11.29	[TBA][4MV]	3.00	180	>99.9	1.60	3.94	941
28	cyclohexene	10.54	[TBA][4EV]	3.00	180	>99.9	1.70	4.19	898

Results and conditions of catalyst recycling

ESI – Table S3. Catalyst recycling in the hydrogenation of hexe-1-ene in [TBA][4HV]

Cycle	$m_{substrate}$ (g)	$n_{substrate}$ (mol)	t (h)	Conversion (%)	Rh leaching (ppb)
1	1.3485	0.0161	3*	99.9	267
2	1.3372	0.0159	1.5	99.9	271
3	1.3321	0.0159	1	99.9	278
4	1.3487	0.0161	1	99.9	188
5	1.3266	0.0158	1	99.9	170
6	1.3181	0.0157	1	99.9	68
7	1.3669	0.0163	1	99.9	114
8	1.355	0.0161	1	99.9	101
9	1.371	0.0163	1	99.9	189
10	1.351	0.0161	1	99.9	101

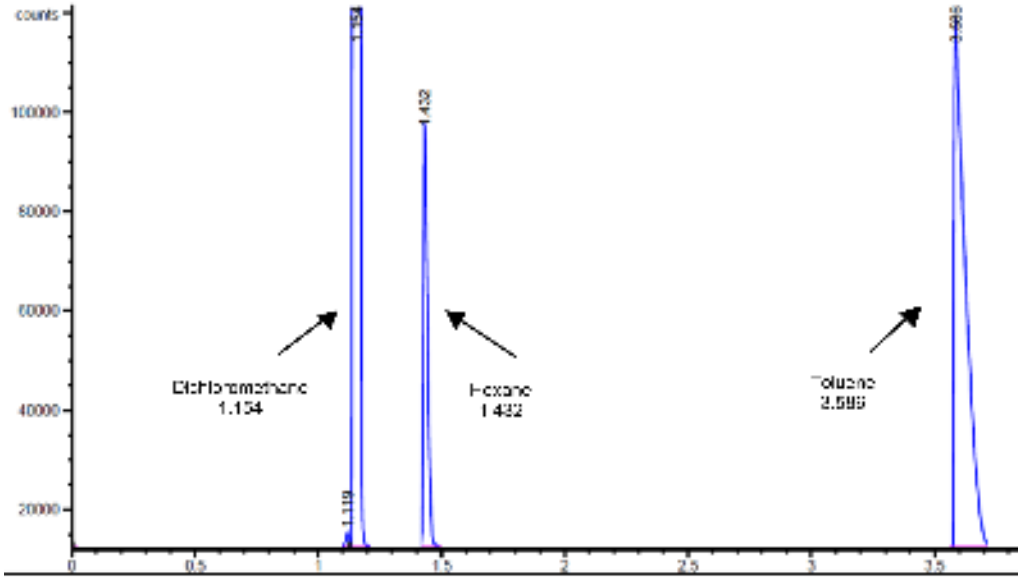
Conditions: 1.837 g (2 mL) [TBA][4HV]. 2.7 mg $[Rh(cod)_2][BF_4]$. 29.2 mg Bu-DPPDS (**L3**). 30 bar H_2. 60 °C in biphasic system.
*At the start of the experiment no pre-hydrogenation was applied.

ESI – Table S4. Catalyst recycling in the hydrogenation of cyclohex-2-en-1-one in [THA][4HV]

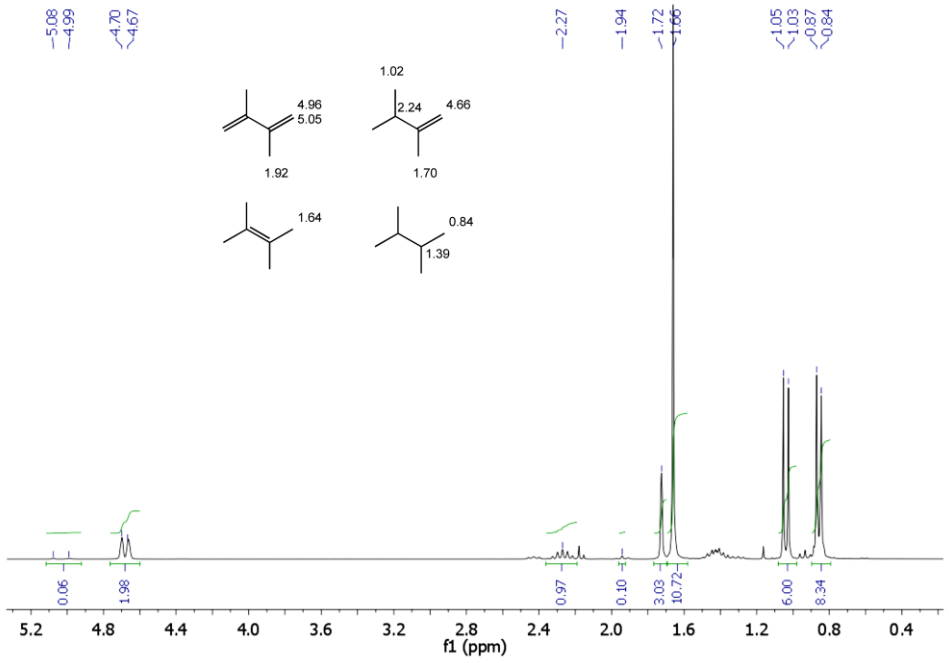
Cycle	$m_{substrate}$ (g)	$n_{substrate}$ (mol)	t (h)	Conversion (%)	Rh leaching (ppm)
1	1.3194	0.0137	6	13.3*	1.10
2	0.9978	0.0104	2	87.6	1.21
3	0.9951	0.0104	1.5	81.4	1.56
4	0.9818	0.0102	1.5	90.3	1.60
5	0.9461	0.0098	1.5	89.7	0.91
6	0.7928	0.0082	2	89.3	0.74
7	0.8969	0.0093	2	86.0	0.83
8	0.8355	0.0087	2	89.5	1.18
9	1.1562	0.0120	1.5	89.2	2.09
10	1.0268	0.0107	2	89.6	1.40

Conditions: 1.05 g (1 mL) [THA][4HV]. 1.80 mg $[Rh(cod)_2][BF_4]$. 12.70 mg Bu-DPPDS (**L3**). 30 bar H_2. 60 °C. in single phase system. The product was separated by extraction with 3x4 mL pentane.
*At the start of the experiment no pre-hydrogenation was applied.

Analytical data of the hydrogenation products

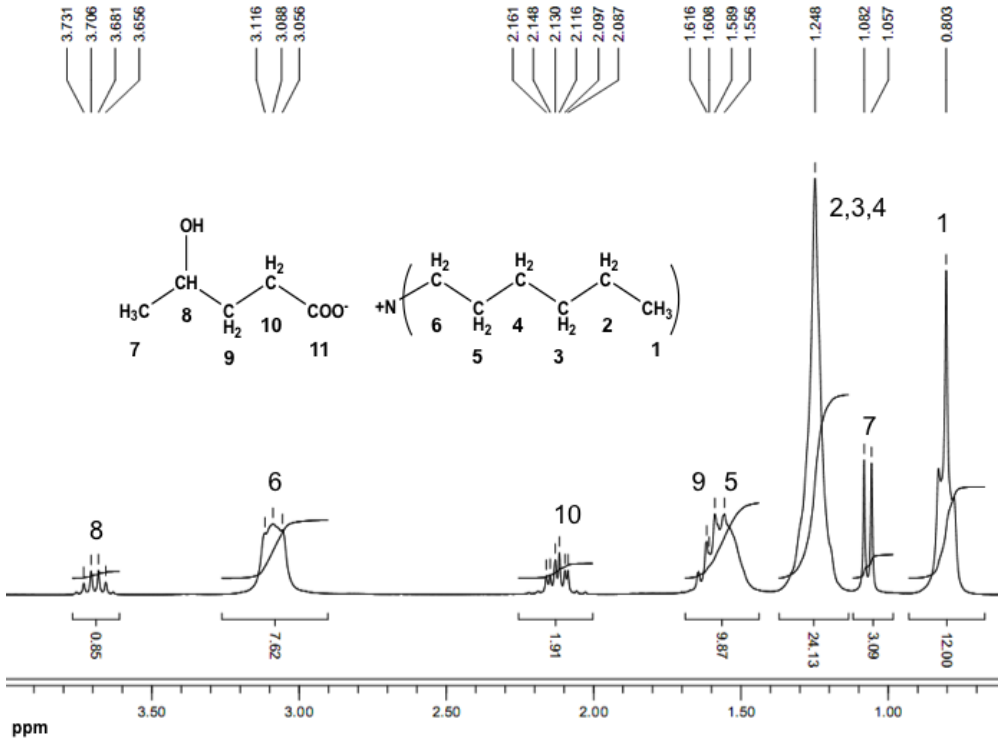


ESI-FIG S5. GC-FID of the reaction mixture of hex-1-ene hydrogenation in [TBA][4HV] after 2 h

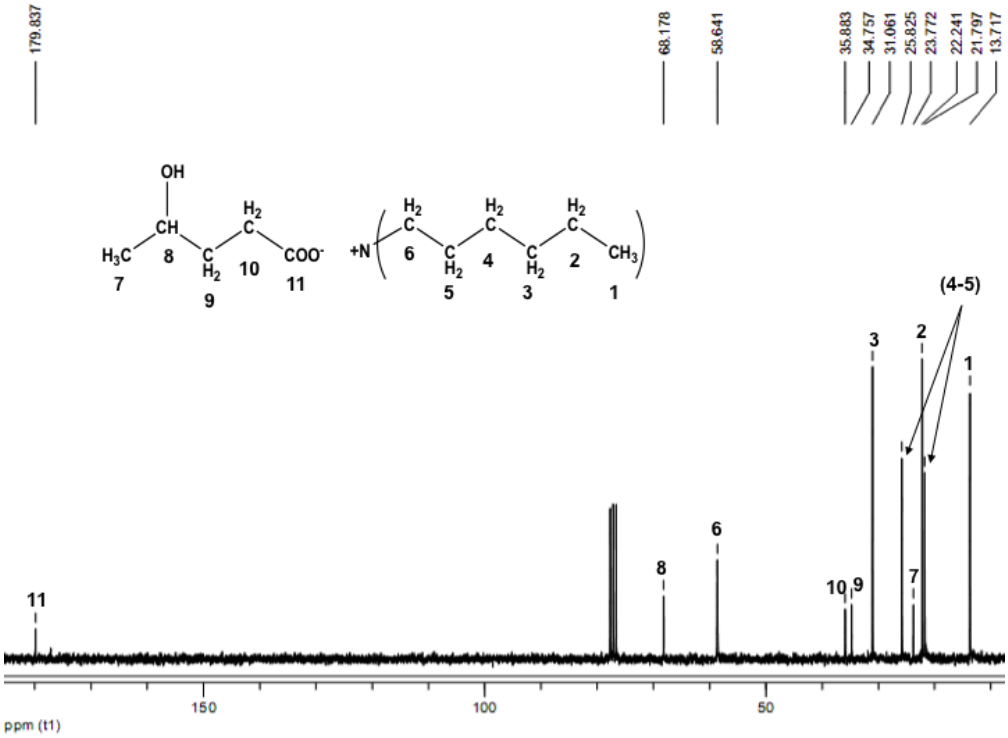


ESI-FIG S6. ^{1}H-NMR spectrum of the product mixture of the reduction of 2,3-dimethyl-1,3-butadiene in [TBA][4HV]

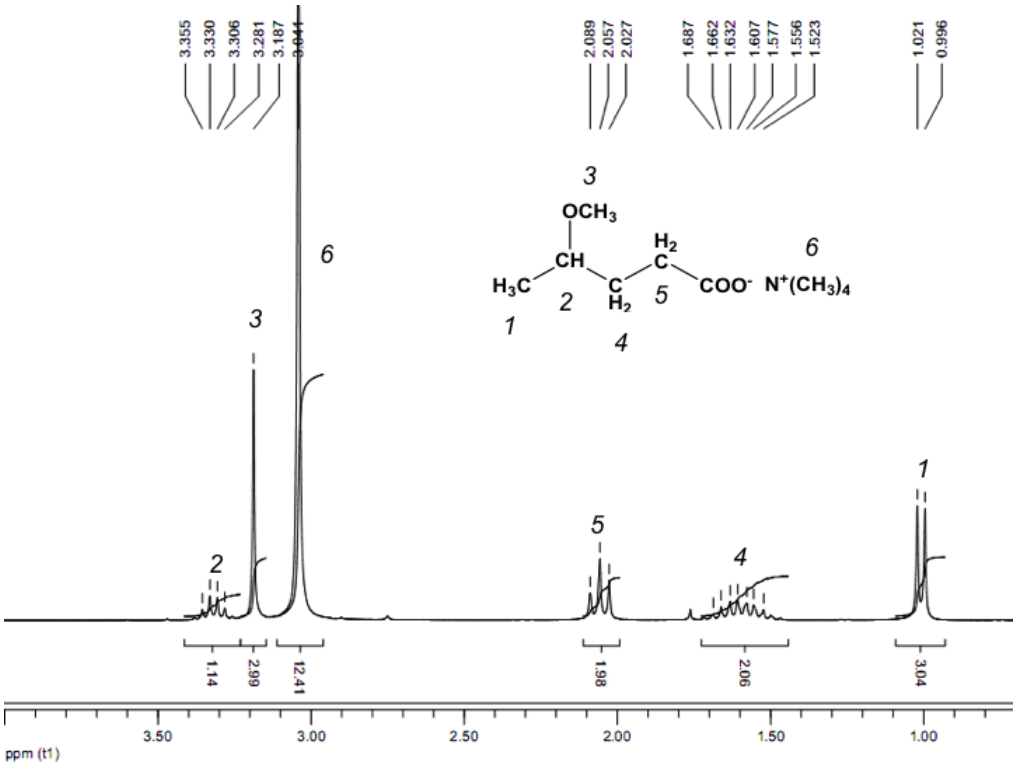
^{1}H-NMR and ^{13}C-NMR spectra of the ionic liquids



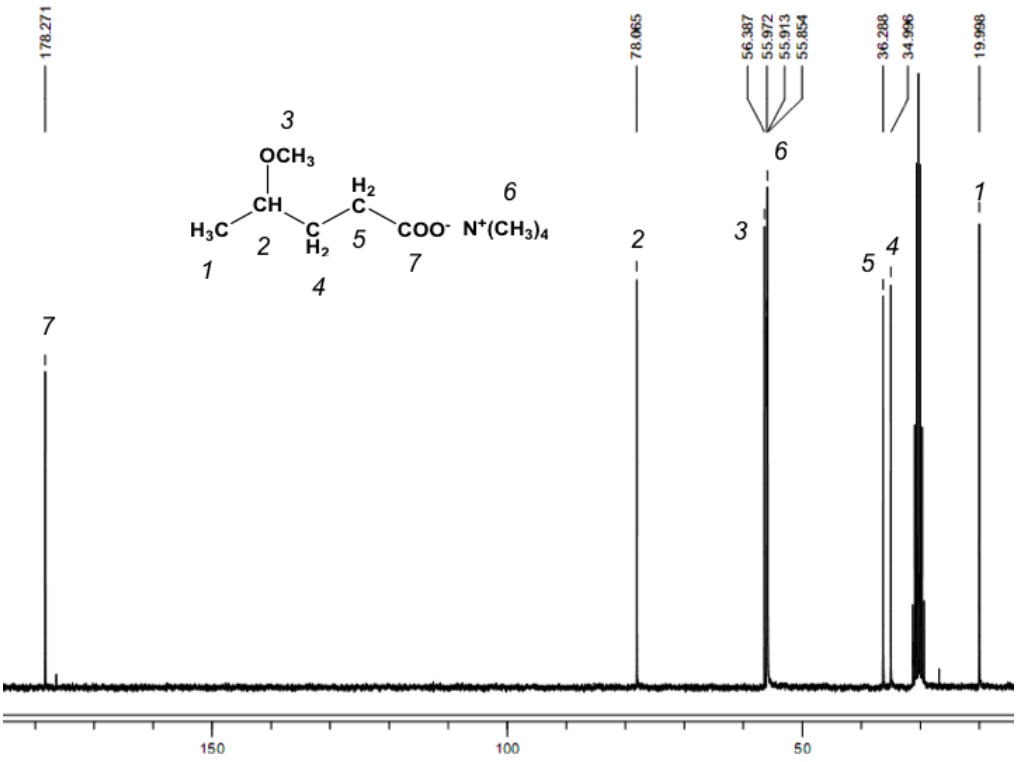
ESI-FIG S7. ^{1}H-NMR spectrum of [THA][4HV]



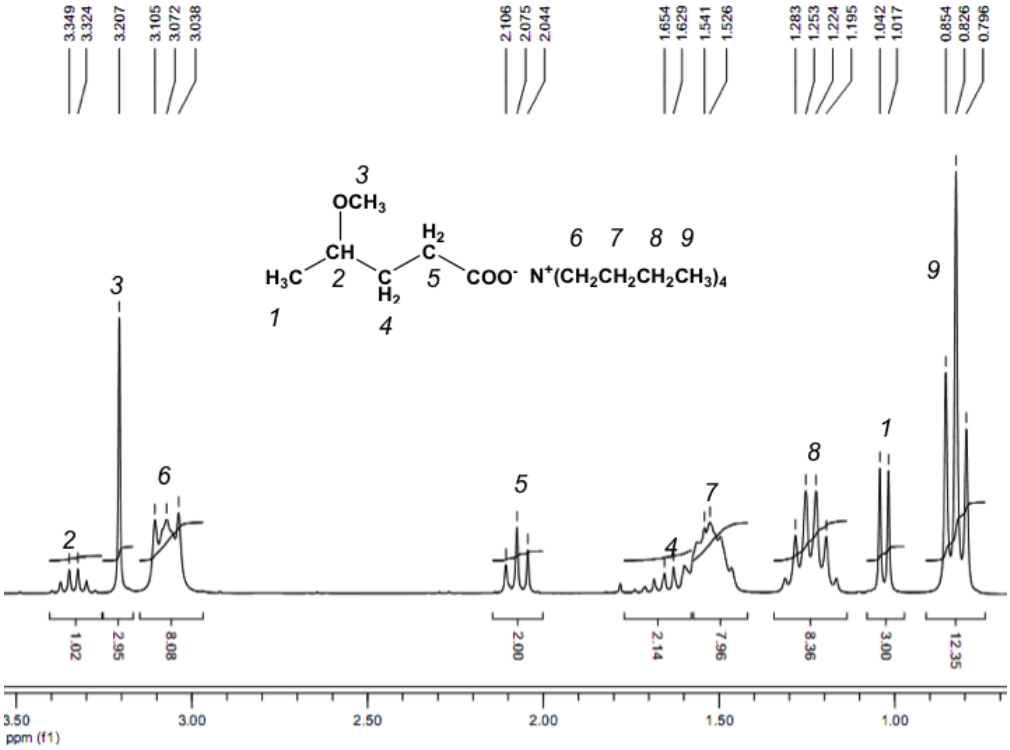
ESI-FIG S8. ^{13}C-NMR spectrum of [THA][4HV]



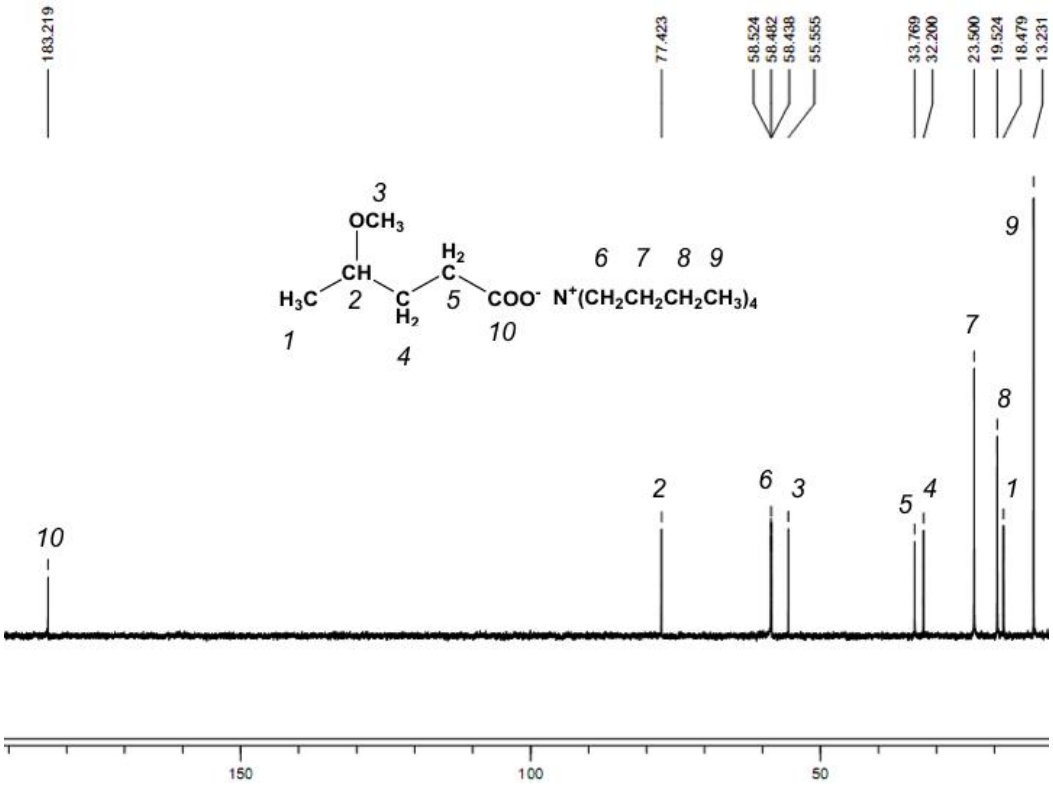
ESI-FIG S9. ^{1}H-NMR spectrum of [TMA][4MeOV]



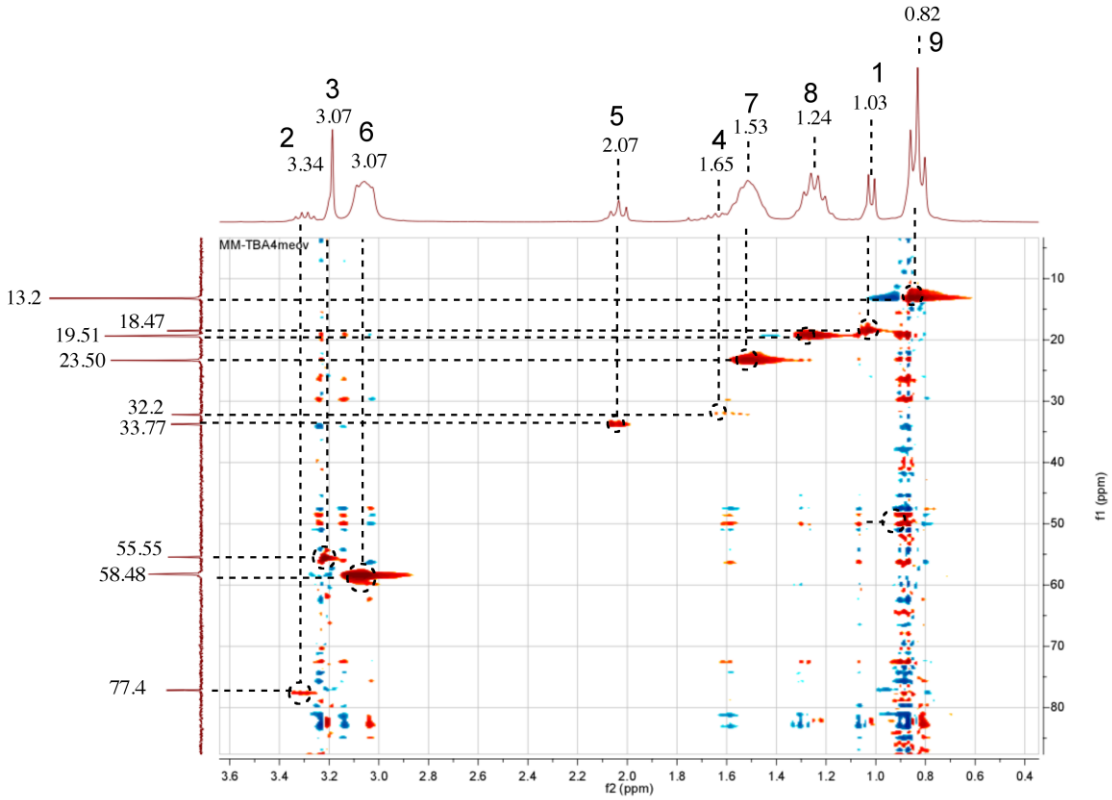
ESI-FIG S10. ^{13}C-NMR spectrum of [TMA][4MeOV]



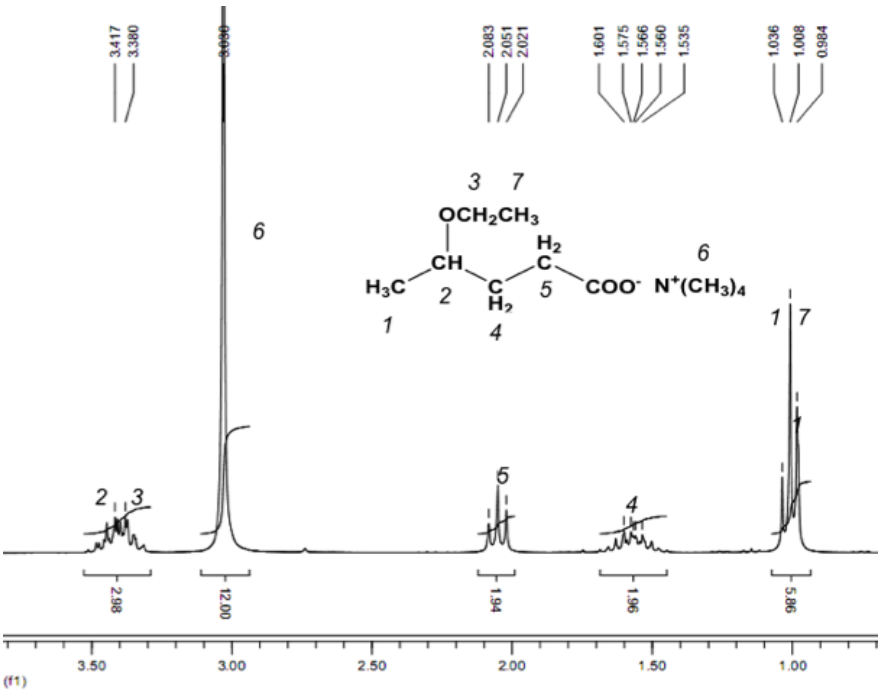
ESI-FIG S10. ^{1}H-NMR spectrum of [TBA][4MeOV]



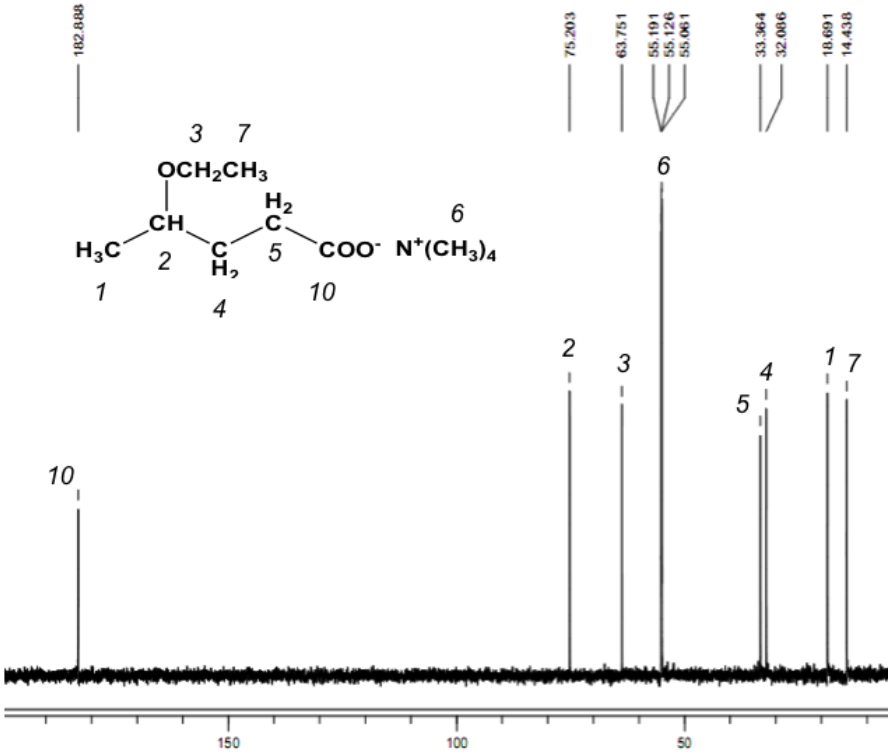
ESI-FIG S12. ^{13}C-NMR spectrum of [TBA][4MeOV]



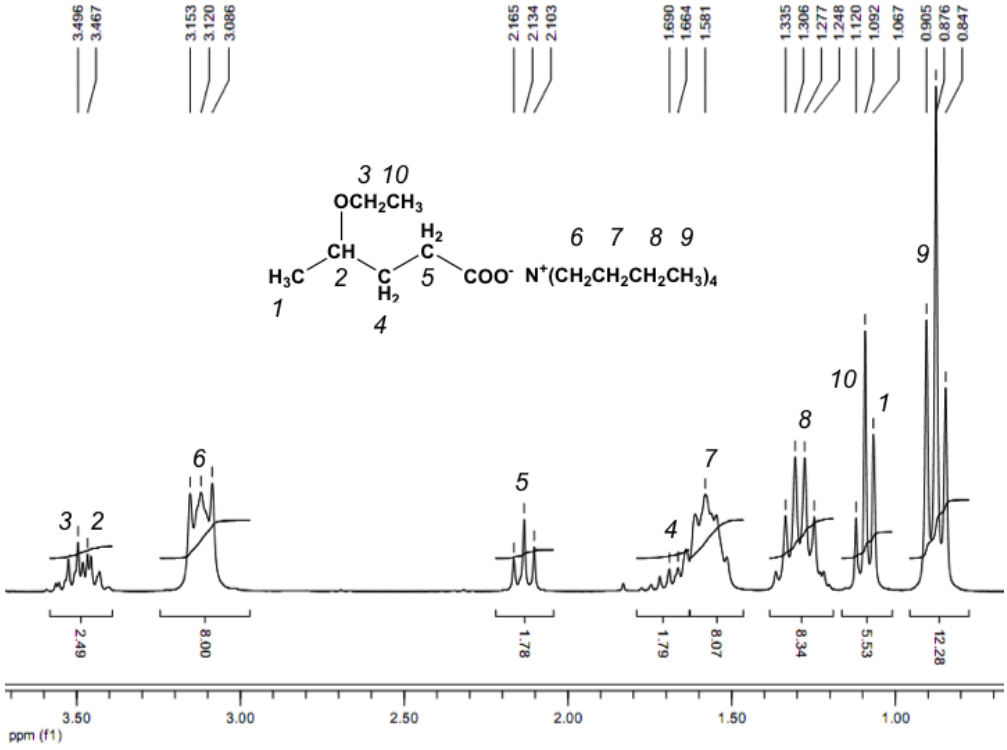
ESI-FIG S13. HMBC NMR spectrum of [TBA][4MeOV]



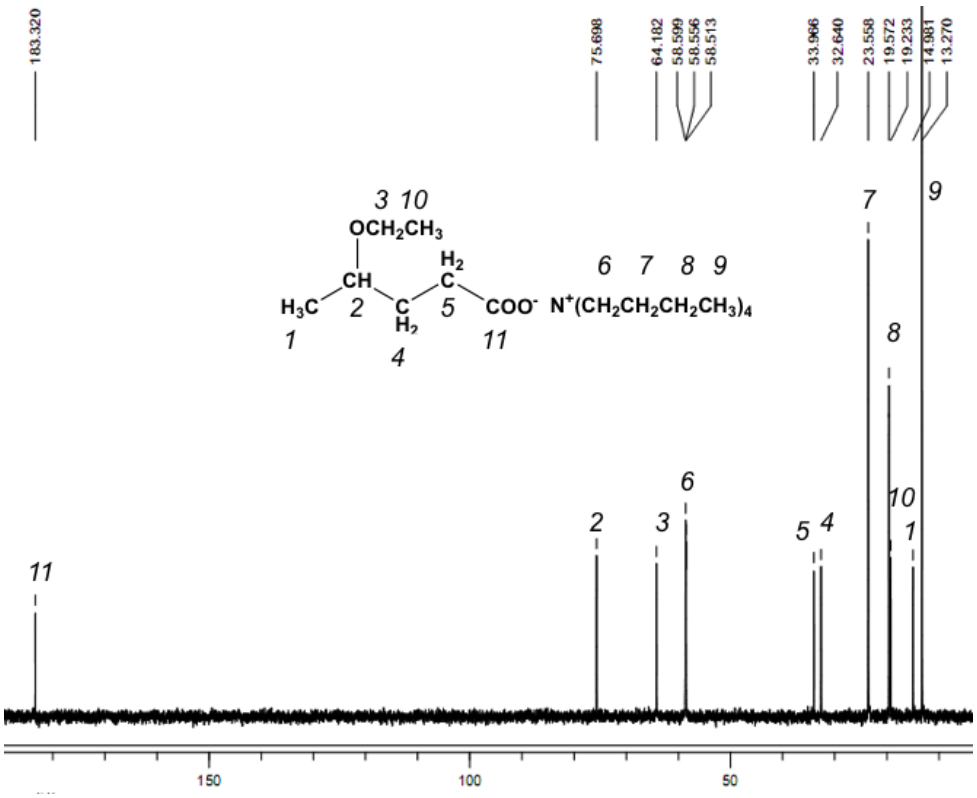
ESI-FIG S14. ^{1}H-NMR spectrum of [TMA][4EtOV]



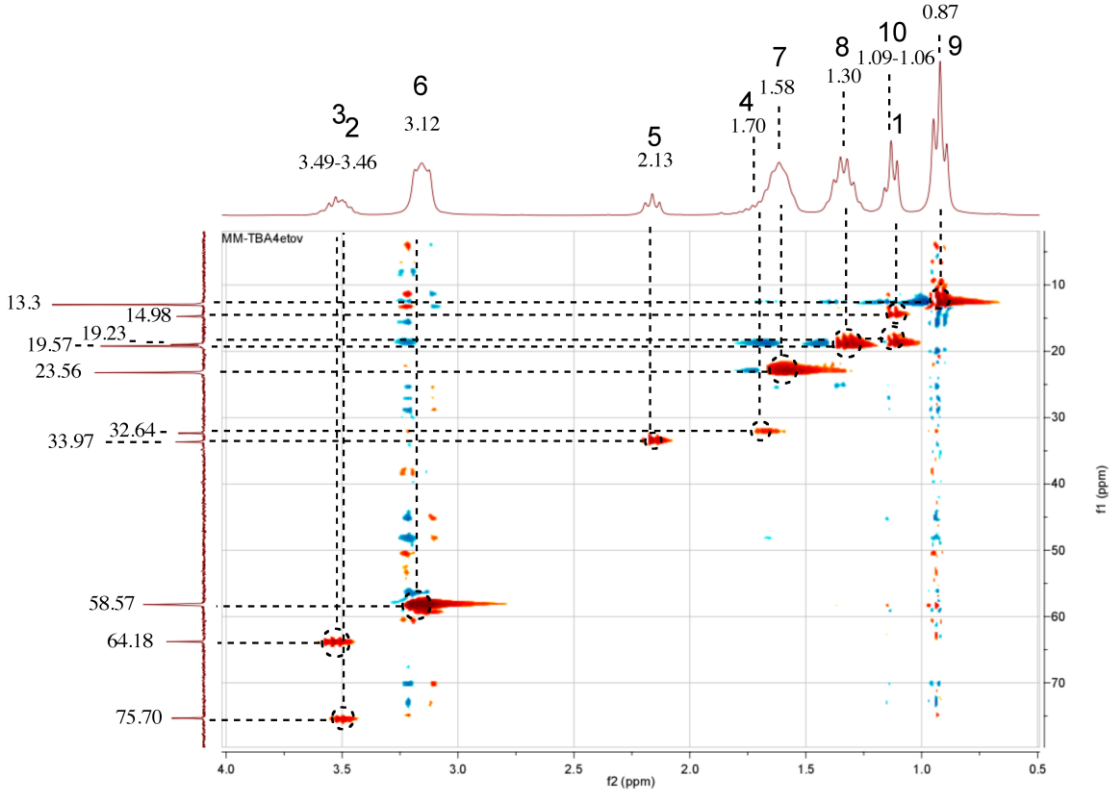
ESI-FIG S15. ^{13}C-NMR spectrum of [TMA][4EtOV]



ESI-FIG S16. ^{1}H-NMR spectrum of [TBA][4EtOV]

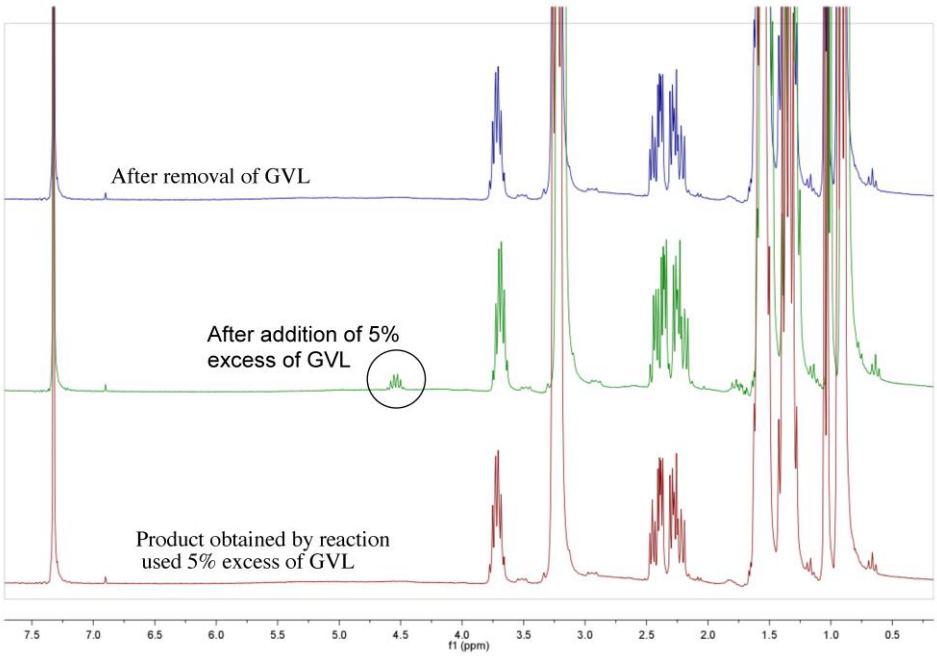


ESI-FIG S17. ^{13}C-NMR spectrum of [TBA][4EtOV]



ESI-FIG S18. HMBC NMR spectrum of [TBA][4EtOV]

Removal of GVL content from [TBA][4HV]



ESI-FIG S19. GVL removal from [TBA][4HV]