

## Supplemental Material

### **Aqueous biphasic systems using chiral ionic liquids for the enantioseparation of mandelic acid enantiomers**

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**Table S1.** Brief characterization of the CILs used: melting temperature ( $T_m$ ), decomposition temperature and specific rotation (values retrieved from Sintra, T. E. Synthesis of more benign ionic liquids for specific applications. PhD Thesis, University of Aveiro, 2017).

CILs	$T_m / (^{\circ}\text{C})$	$T_d / (^{\circ}\text{C})$	$[\alpha]_D^{25} (\pm 0.1)$
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ]	191.10	240.93	-124.0
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Val]I	222.10	230.84	8.9
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Val][C <sub>1</sub> SO <sub>4</sub> ]	48.61	212.50	15.1
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Pro]I	103.85	217.94	-18.7
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br	102.85	177.92	-28.6
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Pro][C <sub>1</sub> SO <sub>4</sub> ]	-42.77	275.04	-9.5

**Table S2.** Overall set of conditions evaluated and approximate mixture compositions used in the enantioseparation of mandelic acid studies with CIL-based ABS.

CIL	Salt	[[CIL] <sub>M</sub> , [Salt] <sub>M</sub> ] / (wt%, wt%)	[[R-MA] <sub>M</sub> , [S-MA] <sub>M</sub> ] / (wt%, wt%)	T (± 1) / °C
<b><i>CIL structure</i></b>				
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ]	K <sub>3</sub> PO <sub>4</sub>	(2.5, 18)	(0.8, 0.8)	25
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Pro]I	K <sub>3</sub> PO <sub>4</sub>	(14, 32)	(0.8, 0.8)	25
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br	K <sub>3</sub> PO <sub>4</sub>	(10, 35)	(0.8, 0.8)	25
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Val]I	K <sub>3</sub> PO <sub>4</sub>	(10, 35)	(0.8, 0.8)	25
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Val] [C <sub>1</sub> SO <sub>4</sub> ]	K <sub>3</sub> PO <sub>4</sub>	(10, 25)	(0.8, 0.8)	25
<b><i>TLL</i></b>				
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ]	K <sub>3</sub> PO <sub>4</sub>	(3, 15); (2.5, 18); (4, 20)	(0.8, 0.8)	25
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br	K <sub>3</sub> PO <sub>4</sub>	(10, 30); (10, 35); (10, 40)	(0.8, 0.8)	25
<b><i>Mixture points along the same TL - Phases weight ratio</i></b>				
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br	K <sub>3</sub> PO <sub>4</sub>	(30, 16); (20, 25); (10, 35); (5, 40)	(0.8, 0.8)	25
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br	K <sub>2</sub> HPO <sub>4</sub>	(20, 25); (15, 30); (10; 35); (5, 40)	(0.8, 0.8)	25
<b><i>Temperature</i></b>				
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ]	K <sub>3</sub> PO <sub>4</sub>	(2.5, 18)	(0.8, 0.8)	15, 25, 35, 45
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br	K <sub>3</sub> PO <sub>4</sub>	(10, 35)	(0.8, 0.8)	15, 25, 35, 45
<b><i>MA content</i></b>				
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ]	K <sub>3</sub> PO <sub>4</sub>	(2.5, 18)	(0.17, 0.17); (0.8, 0.8); (1.7; 1.7)	25
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br	K <sub>3</sub> PO <sub>4</sub>	(10, 35)	(0.17, 0.17); (0.8, 0.8); (1.7; 1.7)	25
<b><i>Salt</i></b>				
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br	K <sub>3</sub> PO <sub>4</sub>	(10; 35)	(0.8, 0.8)	25

[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br	K <sub>2</sub> HPO <sub>4</sub>	(10; 35)	(0.8, 0.8)	25
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br	K <sub>2</sub> CO <sub>3</sub>	(10; 35)	(0.8, 0.8)	25

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**Table S3.** Weight fraction data experimentally obtained for the ternary system composed of  $[C_1Qui][C_1SO_4] + K_3PO_4 + \text{water}$  at  $25 (\pm 1) ^\circ C$ .

$100w_{K_3PO_4}$	$100w_{CIL}$	$100w_{K_3PO_4}$	$100w_{CIL}$	$100w_{K_3PO_4}$	$100w_{CIL}$	$100w_{K_3PO_4}$	$100w_{CIL}$
13.48	3.48	15.65	1.81	17.31	1.04	18.24	0.70
12.99	3.35	15.49	1.79	17.10	1.03	18.06	0.69
13.63	3.27	15.67	1.78	17.34	1.02	18.35	0.68
13.18	3.17	15.43	1.75	17.17	1.01	18.11	0.67
13.81	3.09	15.82	1.73	17.43	0.99	18.36	0.67
13.44	3.01	15.66	1.71	17.26	0.98	18.21	0.66
13.97	2.95	15.91	1.69	17.43	0.98	18.44	0.66
13.78	2.91	15.60	1.66	17.26	0.97	18.26	0.65
14.00	2.89	16.06	1.63	17.51	0.96	18.51	0.64
13.91	2.87	15.85	1.61	17.35	0.95	18.28	0.63
14.21	2.83	16.08	1.59	17.58	0.94	18.61	0.62
13.88	2.77	15.92	1.58	17.39	0.93	18.24	0.61
14.25	2.73	16.14	1.56	17.59	0.92	18.70	0.60
14.14	2.71	15.94	1.55	17.40	0.91	18.26	0.59
14.31	2.69	16.24	1.53	17.65	0.90	18.95	0.57
14.13	2.65	16.00	1.51	17.45	0.89	18.45	0.55
14.41	2.63	16.30	1.49	17.68	0.88		
14.20	2.59	16.03	1.46	17.53	0.88		
14.65	2.54	16.41	1.44	17.76	0.87		
14.38	2.50	16.21	1.42	17.58	0.86		
14.59	2.48	16.46	1.41	17.78	0.85		
14.41	2.44	16.31	1.40	17.62	0.84		
14.78	2.41	16.55	1.38	17.82	0.84		
14.50	2.37	16.25	1.36	17.68	0.83		
14.82	2.34	16.60	1.34	17.88	0.82		
14.64	2.31	16.27	1.31	17.74	0.81		
14.85	2.29	16.62	1.29	17.94	0.81		
14.65	2.26	16.41	1.28	17.80	0.80		
15.06	2.23	16.80	1.26	17.95	0.80		
14.76	2.18	16.47	1.23	17.80	0.79		
15.15	2.15	16.80	1.21	18.05	0.78		
14.77	2.09	16.60	1.20	17.90	0.77		
15.23	2.06	16.84	1.19	18.08	0.77		
15.04	2.03	16.57	1.17	17.90	0.76		
15.32	2.01	16.92	1.15	18.20	0.75		
15.14	1.99	16.77	1.14	17.97	0.74		
15.41	1.97	17.00	1.13	18.18	0.74		
15.14	1.93	16.82	1.12	17.99	0.73		
15.51	1.91	17.16	1.10	18.11	0.72		
15.26	1.87	16.82	1.08	17.98	0.72		
15.61	1.85	17.24	1.06	18.13	0.71		
15.44	1.83	17.04	1.05	17.99	0.71		

**Table S4.** Weight fraction data experimentally obtained for the ternary system composed of [C<sub>1</sub>C<sub>1</sub>C<sub>1</sub>Val][C<sub>1</sub>SO<sub>4</sub>] + K<sub>3</sub>PO<sub>4</sub> + water at 25 (± 1) °C.

<b>100w<sub>K<sub>3</sub>PO<sub>4</sub></sub></b>	<b>100w<sub>ClL</sub></b>	<b>100w<sub>K<sub>3</sub>PO<sub>4</sub></sub></b>	<b>100w<sub>ClL</sub></b>
10.26	38.11	21.14	11.52
9.33	34.64	20.68	11.27
11.55	32.15	21.33	10.90
11.05	30.74	21.08	10.77
13.09	28.58	21.52	10.53
12.70	27.72	21.02	10.29
13.37	27.04	21.89	9.82
13.15	26.59	21.57	9.67
13.91	25.83	22.16	9.37
13.66	25.37	21.83	9.22
14.55	24.52	22.67	8.80
14.24	24.00	22.31	8.66
15.46	22.87	22.87	8.39
15.30	22.62	22.59	8.28
15.83	22.13	23.10	8.04
15.63	21.84	22.77	7.93
16.33	21.21	23.52	7.59
16.06	20.86	22.64	7.30
16.58	20.42	24.26	6.63
16.11	19.85	23.87	6.52
17.25	18.91	24.42	6.30
16.90	18.52	22.36	5.76
17.72	17.87	26.18	4.52
17.54	17.68	23.19	4.01
17.91	17.39		
17.71	17.20		
18.19	16.83		
17.95	16.62		
18.51	16.20		
18.12	15.86		
18.98	15.24		
18.60	14.93		
19.28	14.45		
18.91	14.17		
19.73	13.62		
19.44	13.42		
20.20	12.93		
19.92	12.75		
20.66	12.28		
20.27	12.05		

**Table S5.** Weight fraction data experimentally obtained for the ternary system composed of [C<sub>1</sub>C<sub>1</sub>C<sub>1</sub>Val]I + K<sub>3</sub>PO<sub>4</sub> + water at 25 (± 1) °C.

<b>100w<sub>K<sub>3</sub>PO<sub>4</sub></sub></b>	<b>100w<sub>Cl</sub></b>	<b>100w<sub>K<sub>3</sub>PO<sub>4</sub></sub></b>	<b>100w<sub>Cl</sub></b>
4.39	45.35	16.28	14.24
4.28	44.15	16.09	14.08
5.03	43.22	16.39	13.91
4.88	41.99	16.07	13.64
6.08	40.56	16.87	13.18
5.80	38.69	16.57	12.95
6.69	37.68	17.18	12.61
6.42	36.15	17.05	12.52
7.70	34.78	17.42	12.32
7.45	33.67	17.11	12.10
8.74	32.34	17.82	11.72
8.40	31.09	17.58	11.56
9.16	30.34	18.13	11.28
8.97	29.70	17.91	11.14
10.16	28.57	18.44	10.88
9.79	27.55	18.36	10.84
10.57	26.84	19.44	10.30
10.24	25.99	19.06	10.10
11.19	25.17	19.88	9.71
10.86	24.43	19.55	9.54
11.97	23.51	20.37	9.16
11.65	22.88	19.80	8.90
12.35	22.33	20.89	8.43
11.98	21.66	20.51	8.27
12.95	20.91		
12.59	20.34		
13.63	19.57		
13.23	18.99		
14.14	18.34		
13.83	17.94		
14.63	17.39		
14.47	17.20		
14.89	16.92		
14.50	16.48		
15.41	15.90		
15.20	15.68		
15.69	15.37		
15.39	15.07		
16.05	14.67		
15.85	14.50		

**Table S6.** Weight fraction data experimentally obtained for the ternary system composed of [C<sub>1</sub>C<sub>1</sub>C<sub>1</sub>Pro]I + K<sub>3</sub>PO<sub>4</sub> + water at 25 (± 1) °C.

<b>100w<sub>K<sub>3</sub>PO<sub>4</sub></sub></b>	<b>100w<sub>CIL</sub></b>
1.38	67.36
1.16	56.68
4.68	51.59
4.78	52.68
5.84	51.11
5.54	48.49
6.56	47.08
6.35	45.61
7.03	44.70
6.83	43.44
7.47	42.62
7.29	41.63
8.84	39.69
8.58	38.51
10.77	35.85
10.53	35.04
32.98	8.74
32.79	8.69
33.39	8.01
33.21	7.96
34.06	7.03
33.79	6.97
35.50	5.18
35.05	5.11



**Table S7.** Weight fraction data experimentally obtained for the ternary system composed of [C<sub>2</sub>C<sub>2</sub>C<sub>2</sub>Pro]Br + K<sub>3</sub>PO<sub>4</sub> + water at 25 (± 1) °C.

<b>100w<sub>K<sub>3</sub>PO<sub>4</sub></sub></b>	<b>100w<sub>Cl</sub></b>	<b>100w<sub>K<sub>3</sub>PO<sub>4</sub></sub></b>	<b>100w<sub>Cl</sub></b>	<b>100w<sub>K<sub>3</sub>PO<sub>4</sub></sub></b>	<b>100w<sub>Cl</sub></b>
1.69	45.76	22.24	14.27	25.99	8.49
3.28	43.84	22.70	13.89	26.42	8.22
3.16	42.18	22.59	13.82	26.17	8.15
3.85	41.38	22.90	13.56	26.73	7.80
3.73	40.04	22.79	13.49	26.48	7.73
4.60	39.07	23.12	13.22	27.00	7.42
4.54	38.56	23.00	13.16	26.76	7.35
5.08	37.96	23.31	12.91	27.36	7.01
4.93	36.88	23.19	12.84	27.06	6.93
6.03	35.71	23.48	12.61	27.69	6.58
5.87	34.76	23.37	12.55	27.39	6.51
6.83	33.78	23.67	12.32	28.12	6.12
6.66	32.95	23.55	12.26	27.79	6.05
7.68	31.92	23.81	12.06	28.82	5.52
7.60	31.59	23.70	12.01	28.43	5.44
8.03	31.17	23.98	11.80		
7.94	30.82	23.87	11.74		
8.78	30.00	24.11	11.56		
8.67	29.60	24.01	11.51		
9.47	28.83	24.34	11.27		
9.35	28.50	24.23	11.22		
10.12	27.77	24.45	11.06		
10.01	27.45	24.35	11.02		
11.07	26.47	24.57	10.86		
10.95	26.19	24.48	10.81		
11.94	25.29	24.71	10.65		
11.82	25.04	24.61	10.61		
15.99	21.27	24.83	10.45		
15.84	21.08	24.75	10.41		
16.71	20.30	25.03	10.21		
16.58	20.14	24.84	10.13		
19.82	17.30	25.25	9.85		
19.70	17.20	25.06	9.78		
21.01	16.07	25.51	9.48		
20.87	15.97	25.34	9.41		
21.62	15.33	25.72	9.16		
21.50	15.24	25.55	9.09		
22.12	14.71	25.92	8.85		
22.01	14.63	25.75	8.79		
22.36	14.34	26.15	8.54		

**Table S8.** Weight fraction data experimentally obtained for the ternary system composed of [C<sub>2</sub>C<sub>2</sub>C<sub>2</sub>Pro]Br + K<sub>2</sub>HPO<sub>4</sub> + water at 25 (± 1) °C.

<b>100w<sub>K<sub>2</sub>HPO<sub>4</sub></sub></b>	<b>100w<sub>CIL</sub></b>	<b>100w<sub>K<sub>2</sub>HPO<sub>4</sub></sub></b>	<b>100w<sub>CIL</sub></b>	<b>100w<sub>K<sub>2</sub>HPO<sub>4</sub></sub></b>	<b>100w<sub>CIL</sub></b>	<b>100w<sub>K<sub>2</sub>HPO<sub>4</sub></sub></b>	<b>100w<sub>CIL</sub></b>
3.40	44.79	14.10	20.62	20.08	12.28	24.22	7.93
3.25	42.85	13.98	20.44	19.98	12.22	24.05	7.87
3.70	42.33	14.62	19.93	20.22	12.08	24.53	7.63
3.59	41.11	14.50	19.77	20.13	12.03	24.37	7.58
5.13	39.36	14.94	19.43	20.40	11.87	24.76	7.39
4.82	36.96	14.82	19.27	20.35	11.84	24.60	7.34
6.34	35.36	15.42	18.82	20.46	11.77	25.08	7.11
6.22	34.69	15.30	18.67	20.37	11.72	24.84	7.04
6.93	33.96	15.81	18.28	20.73	11.50	25.42	6.77
6.82	33.40	15.69	18.15	20.63	11.45	25.25	6.73
7.45	32.76	15.94	17.96	20.86	11.31	25.82	6.46
7.22	31.76	15.81	17.81	20.78	11.26	25.58	6.40
8.19	30.81	16.36	17.40	21.03	11.12	26.32	6.06
8.11	30.53	16.11	17.14	20.92	11.06	26.05	6.00
8.43	30.22	16.85	16.60	21.22	10.89		
8.33	29.86	16.72	16.48	21.12	10.84		
8.87	29.35	17.18	16.15	21.42	10.67		
8.76	28.98	17.05	16.03	21.33	10.63		
9.33	28.45	17.50	15.72	21.59	10.48		
9.23	28.17	17.37	15.60	21.50	10.43		
9.91	27.55	17.91	15.23	21.82	10.25		
9.81	27.27	17.79	15.13	21.73	10.21		
10.27	26.85	18.11	14.91	21.87	10.13		
10.15	26.55	18.00	14.82	21.78	10.09		
10.77	25.99	18.33	14.60	22.06	9.93		
10.66	25.72	18.20	14.50	21.98	9.89		
11.20	25.25	18.51	14.29	22.20	9.77		
11.09	24.99	18.41	14.22	22.11	9.73		
11.76	24.41	18.75	14.00	22.40	9.58		
11.64	24.16	18.56	13.85	22.32	9.54		
12.04	23.82	19.07	13.52	22.54	9.42		
11.92	23.58	18.98	13.46	22.46	9.39		
12.55	23.04	19.25	13.29	22.70	9.26		
12.45	22.84	19.16	13.23	22.61	9.22		
13.04	22.35	19.52	13.00	22.84	9.11		
12.93	22.15	19.41	12.93	22.75	9.07		
13.48	21.70	19.64	12.79	23.51	8.67		
13.35	21.49	19.55	12.73	23.25	8.57		
13.75	21.17	19.86	12.54	23.88	8.24		
13.64	20.99	19.77	12.48	23.71	8.18		

**Table S9.** Weight fraction data experimentally obtained for the ternary system composed of [C<sub>2</sub>C<sub>2</sub>C<sub>2</sub>Pro]Br + K<sub>2</sub>CO<sub>3</sub> + water at 25 (± 1) °C.

<b>100w<sub>K<sub>2</sub>CO<sub>3</sub></sub></b>	<b>100w<sub>CIL</sub></b>	<b>100w<sub>K<sub>2</sub>CO<sub>3</sub></sub></b>	<b>100w<sub>CIL</sub></b>	<b>100w<sub>K<sub>2</sub>CO<sub>3</sub></sub></b>	<b>100w<sub>CIL</sub></b>	<b>100w<sub>K<sub>2</sub>CO<sub>3</sub></sub></b>	<b>100w<sub>CIL</sub></b>
2.71	52.51	21.03	20.81	29.06	10.34	31.89	5.25
2.65	51.39	21.92	20.18	28.82	10.25	32.81	4.99
5.70	48.10	21.71	19.99	29.18	10.08	31.76	4.83
5.42	45.70	22.30	19.58	28.90	9.98		
6.26	44.85	22.08	19.39	29.30	9.80		
6.15	44.06	22.65	19.00	29.04	9.71		
8.69	41.52	22.45	18.83	29.41	9.54		
8.16	38.95	23.06	18.42	29.17	9.46		
9.46	37.75	22.82	18.22	29.61	9.26		
9.34	37.26	23.53	17.76	29.24	9.15		
10.33	36.35	23.33	17.61	29.81	8.90		
10.19	35.83	24.55	16.81	29.51	8.81		
11.47	34.68	24.16	16.54	29.91	8.64		
11.30	34.16	24.92	16.06	29.58	8.55		
12.56	33.06	24.73	15.94	30.06	8.35		
12.37	32.54	25.36	15.54	29.69	8.25		
13.35	31.70	25.17	15.42	30.32	8.00		
13.17	31.29	27.58	13.94	29.91	7.89		
13.73	30.82	27.38	13.84	30.58	7.63		
13.54	30.40	27.83	13.57	30.16	7.52		
14.57	29.54	27.36	13.34	30.80	7.28		
14.37	29.13	28.03	12.95	30.32	7.17		
15.37	28.32	27.73	12.81	30.97	6.94		
15.15	27.92	28.40	12.43	30.56	6.85		
16.12	27.14	28.01	12.26	31.28	6.60		
15.95	26.85	28.38	12.05	30.88	6.51		
18.78	24.64	28.10	11.93	31.48	6.31		
18.43	24.18	28.62	11.65	31.13	6.24		
19.16	23.62	28.25	11.50	31.73	6.04		
18.97	23.38	28.63	11.30	31.34	5.97		
19.69	22.85	28.28	11.16	31.92	5.79		
19.48	22.60	28.71	10.95	31.58	5.73		
20.78	21.65	28.46	10.85	32.12	5.56		
20.56	21.42	28.96	10.61	31.75	5.50		
21.19	20.97	28.70	10.51	32.34	5.32		

**Table S10.** Merchuk equation parameters (*A*, *B* and *C*) with the respective standard deviations ( $\sigma$ ) for the ternary systems composed of CILs + salt + water at 25 ( $\pm 1$ ) °C.

<b>ABS</b>	<b><i>A</i> <math>\pm</math> <math>\sigma</math></b>	<b><i>B</i> <math>\pm</math> <math>\sigma</math></b>	<b><i>C</i> <math>\pm</math> <math>\sigma</math></b>
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub>	100.00 $\pm$ 0.17	-0.74 $\pm$ 0.01	2.99 $\times 10^{-4}$ $\pm$ 1.06 $\times 10^{-5}$
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Val][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub>	76.10 $\pm$ 23.54	-0.21 $\pm$ 0.10	1.04 $\times 10^{-4}$ $\pm$ 1.53 $\times 10^{-5}$
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Val]I + K <sub>3</sub> PO <sub>4</sub>	103.38 $\pm$ 7.64	-0.39 $\pm$ 0.03	9.36 $\times 10^{-5}$ $\pm$ 1.17 $\times 10^{-5}$
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Pro]I + K <sub>3</sub> PO <sub>4</sub>	82.01 $\pm$ 8.27	-0.23 $\pm$ 0.04	2.86 $\times 10^{-5}$ $\pm$ 8.25 $\times 10^{-6}$
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	63.96 $\pm$ 2.71	-0.24 $\pm$ 0.02	4.02 $\times 10^{-5}$ $\pm$ 3.47 $\times 10^{-6}$
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>2</sub> HPO <sub>4</sub>	77.05 $\pm$ 1.46	-0.31 $\pm$ 0.01	5.40 $\times 10^{-5}$ $\pm$ 1.84 $\times 10^{-6}$
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>2</sub> CO <sub>3</sub>	72.40 $\pm$ 3.34	-0.20 $\pm$ 0.02	3.75 $\times 10^{-5}$ $\pm$ 2.25 $\times 10^{-6}$

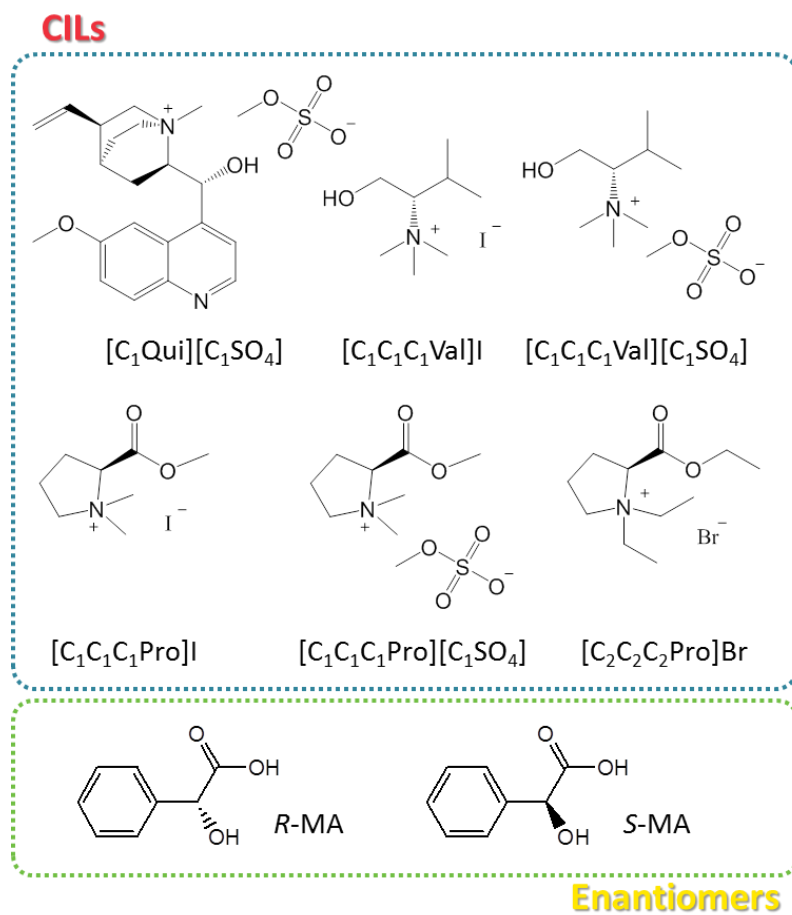
**Table S11.** Weight fraction composition (wt%) of both CIL-rich and salt-rich phases of biphasic ternary systems composed of CILs and salts at 25 ( $\pm 1$ ) °C, along with the respective values of tie-line length (TLL).

ABS	100 × weight fraction composition / (wt%)						TLL	
	[CIL] <sub>CIL</sub> / (wt%)	[Salt] <sub>CIL</sub> / (wt%)	[CIL] <sub>M</sub> / (wt%)	[Salt] <sub>M</sub> / (wt%)	[CIL] <sub>Salt</sub> / (wt%)	[Salt] <sub>Salt</sub> (wt%)		
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub>	29.39	2.75	3.09	14.73	1.96	15.25	30.14	
	40.22	1.53	2.37	17.71	0.65	18.45	43.04	
	63.12	0.39	3.75	20.77	0.13	22.01	66.60	
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Val][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub>	49.12	4.04	10.02	24.92	1.72	29.35	53.73	
	[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Val]I + K <sub>3</sub> PO <sub>4</sub>	50.98	3.23	9.98	34.49	0.01	42.09	64.10
	[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Pro]I + K <sub>3</sub> PO <sub>4</sub>	48.11	5.30	13.97	31.82	2.86	40.46	57.31
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	43.13	2.68	10.21	29.86	2.10	36.56	53.21	
	49.25	1.18	9.92	34.37	0.66	42.19	63.59	
	58.44	0.14	9.69	39.85	0.16	47.60	75.16	
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>2</sub> HPO <sub>4</sub>	55.38	1.11	9.89	34.97	0.17	42.20	68.81	
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>2</sub> CO <sub>3</sub>	44.95	5.60	9.87	34.43	1.42	41.37	56.34	

**Table S12.** Extraction efficiencies of mandelic acid enantiomers ( $EE_{R-MA}$  and  $EE_{S-MA}$ , %) and enantiomeric excesses ( $e.e.$ , %) plus the corresponding standard deviations ( $\sigma$ ) obtained using ABS composed of CIL and salts.

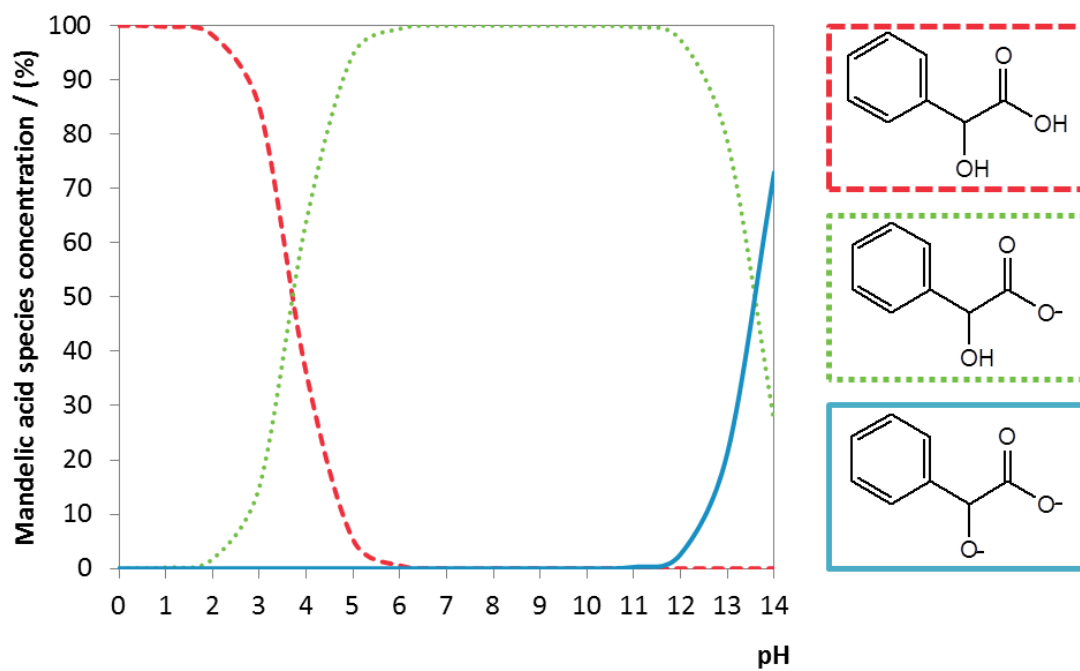
<b>ABS</b>	<b>[CIL]<sub>M</sub> ± σ</b>	<b>[Salt]<sub>M</sub> ± σ</b>	<b><math>EE_{R-MA}</math> ± σ</b>	<b><math>EE_{S-MA}</math> ± σ</b>	<b><math>e.e.</math> / (%)</b>
<b><i>CIL structure</i></b>					
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub>	2.43 ± 0.04	17.91 ± 0.16	23.32 ± 3.73	23.91 ± 4.30	1.61 ± 0.92
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Val][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub>	10.06 ± 0.34	24.89 ± 0.05	25.12 ± 1.37	34.86 ± 0.22	15.53 ± 1.11
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Val]I + K <sub>3</sub> PO <sub>4</sub>	9.83 ± 0.11	33.84 ± 0.92	61.87 ± 7.77	68.77 ± 9.23	9.29 ± 1.15
[C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> Pro]I + K <sub>3</sub> PO <sub>4</sub>	13.66 ± 0.44	31.46 ± 0.52	49.81 ± 2.99	65.90 ± 1.47	14.03 ± 0.93
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	9.94 ± 0.07	34.67 ± 0.20	44.62 ± 2.50	61.58 ± 3.96	17.37 ± 1.92
<b><i>TLL</i></b>					
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub>	2.96 ± 0.11	15.17 ± 0.47	24.93 ± 4.53	25.90 ± 5.36	2.06 ± 1.49
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub>	2.43 ± 0.04	17.91 ± 0.16	23.32 ± 3.73	23.91 ± 4.30	1.61 ± 0.92
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub>	3.95 ± 0.28	20.76 ± 0.00	33.21 ± 0.70	34.48 ± 0.45	1.87 ± 1.14
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	10.14 ± 0.14	29.56 ± 0.26	25.01 ± 1.50	31.13 ± 2.80	9.67 ± 2.79
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	9.94 ± 0.07	34.67 ± 0.20	44.62 ± 2.50	61.58 ± 3.96	17.37 ± 1.92
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	9.81 ± 0.18	39.73 ± 0.22	53.71 ± 5.56	55.46 ± 5.09	1.10 ± 3.41
<b><i>Mixture points along the same TL - Phases weight ratio</i></b>					
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	30.18 ± 0.13	15.94 ± 0.15	87.17 ± 7.70	86.63 ± 8.15	-0.55 ± 0.19
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	19.78 ± 0.22	24.84 ± 0.35	94.51 ± 5.94	92.81 ± 5.79	-1.98 ± 1.34
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	9.94 ± 0.07	34.67 ± 0.20	44.62 ± 2.50	61.58 ± 3.96	17.37 ± 1.92
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	5.08 ± 0.13	40.18 ± 0.21	37.32 ± 2.74	48.10 ± 2.62	12.33 ± 0.51
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>2</sub> HPO <sub>4</sub>	19.69 ± 0.13	25.27 ± 0.26	81.43 ± 1.25	81.55 ± 0.19	-1.48 ± 0.10
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>2</sub> HPO <sub>4</sub>	14.93 ± 0.15	29.99 ± 0.22	90.05 ± 5.13	85.76 ± 4.14	-2.37 ± 0.84
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>2</sub> HPO <sub>4</sub>	9.82 ± 0.14	35.02 ± 0.06	81.90 ± 5.59	81.63 ± 5.08	0.82 ± 0.18

[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>2</sub> HPO <sub>4</sub>	5.12 ± 0.04	39.77 ± 0.35	85.66 ± 2.71	84.04 ± 4.34	-1.00 ± 0.57
<b>Temperature</b>					
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub> (15 °C)	2.52 ± 0.10	17.82 ± 0.01	13.44 ± 0.39	15.54 ± 0.39	7.88 ± 0.70
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub> (25 °C)	2.43 ± 0.04	17.91 ± 0.16	23.32 ± 3.73	23.91 ± 4.30	1.61 ± 0.92
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub> (35 °C)	2.52 ± 0.01	18.08 ± 0.62	28.46 ± 4.81	28.65 ± 5.14	0.70 ± 0.22
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub> (45 °C)	2.40 ± 0.02	17.74 ± 0.06	59.03 ± 2.12	59.13 ± 3.96	-1.81 ± 1.44
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub> (15 °C)	9.82 ± 0.36	34.19 ± 0.42	45.48 ± 2.34	59.05 ± 5.19	12.48 ± 1.70
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub> (25 °C)	9.94 ± 0.07	34.67 ± 0.20	44.62 ± 2.50	61.58 ± 3.96	17.37 ± 1.92
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub> (35 °C)	9.99 ± 0.18	34.48 ± 0.16	46.45 ± 0.63	59.44 ± 0.89	11.54 ± 2.19
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub> (45 °C)	9.94 ± 0.20	34.71 ± 0.20	39.21 ± 4.48	50.03 ± 5.42	12.26 ± 3.73
<b>MA content</b>					
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub> (0.17 wt%)	2.49 ± 0.02	18.09 ± 0.27	31.30 ± 2.96	31.10 ± 1.84	-1.61 ± 1.95
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub> (0.8 wt%)	2.43 ± 0.04	17.91 ± 0.16	23.32 ± 3.73	23.91 ± 4.30	1.61 ± 0.92
[C <sub>1</sub> Qui][C <sub>1</sub> SO <sub>4</sub> ] + K <sub>3</sub> PO <sub>4</sub> (1.7 wt%)	2.51 ± 0.02	17.78 ± 0.19	13.48 ± 3.78	15.25 ± 4.41	6.04 ± 1.35
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub> (0.17 wt%)	9.88 ± 0.15	34.51 ± 0.23	79.16 ± 1.94	76.29 ± 2.66	-4.91 ± 1.34
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub> (0.8 wt%)	9.94 ± 0.07	34.67 ± 0.20	44.62 ± 2.50	61.58 ± 3.96	17.37 ± 1.92
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub> (1.7 wt%)	9.83 ± 0.15	34.60 ± 0.41	42.66 ± 3.33	38.19 ± 3.27	-6.40 ± 2.92
<b>Salt</b>					
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>3</sub> PO <sub>4</sub>	9.94 ± 0.07	34.67 ± 0.20	44.62 ± 2.50	61.58 ± 3.96	17.37 ± 1.92
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>2</sub> HPO <sub>4</sub>	9.82 ± 0.14	35.02 ± 0.06	81.90 ± 5.59	81.63 ± 5.08	0.82 ± 0.18
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> Pro]Br + K <sub>2</sub> CO <sub>3</sub>	10.06 ± 0.14	35.16 ± 0.10	55.13 ± 0.03	62.61 ± 2.31	5.79 ± 0.12



**Figure S1.** Chemical structures and abbreviations of the CILs and mandelic acid enantiomers investigated.





**Figure S2.** Speciation profile of mandelic acid as a function of the pH (content adapted from the chemical free database Chempider – [www.chemspider.com](http://www.chemspider.com), accessed February 10, 2018).