Combining Bio- and Chemo-Catalysis for the Conversion of Bio-Renewable Alcohols: Homogeneous Iridium Catalysed Hydrogen Transfer Initiated Dehydration of 1,3-Propanediol to Aldehydes

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Supplementary material

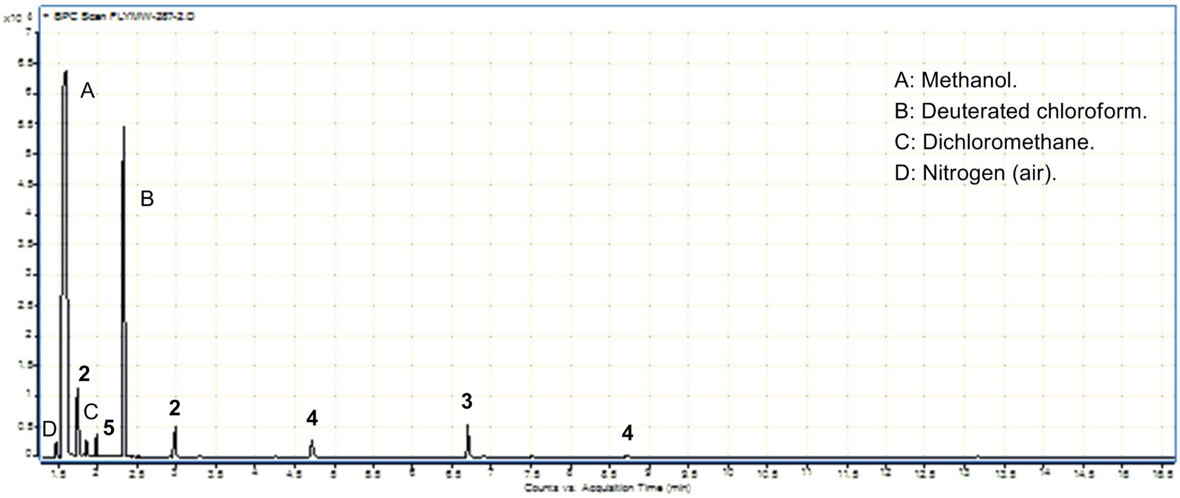


Figure S1. Example of a GC/MS spectrum of the isolated, crude product of HTID of 1,3-PDO in the presence of **1** and a base, in EmmimNTf$_2$ or N$_{1,8,8,8}$NTf$_2$, at temperature varying in the range 100 – 180 °C, and at a dynamic vacuum of *ca.* 0.35 bar. (**2**, **3**, and **4** generate, in the presence of CH$_3$OH, at the GC/MS experimental conditions, their hemiacetalic forms - the hemiacetalic form of **3** is not displayed in this particular GC/MS spectrum.)

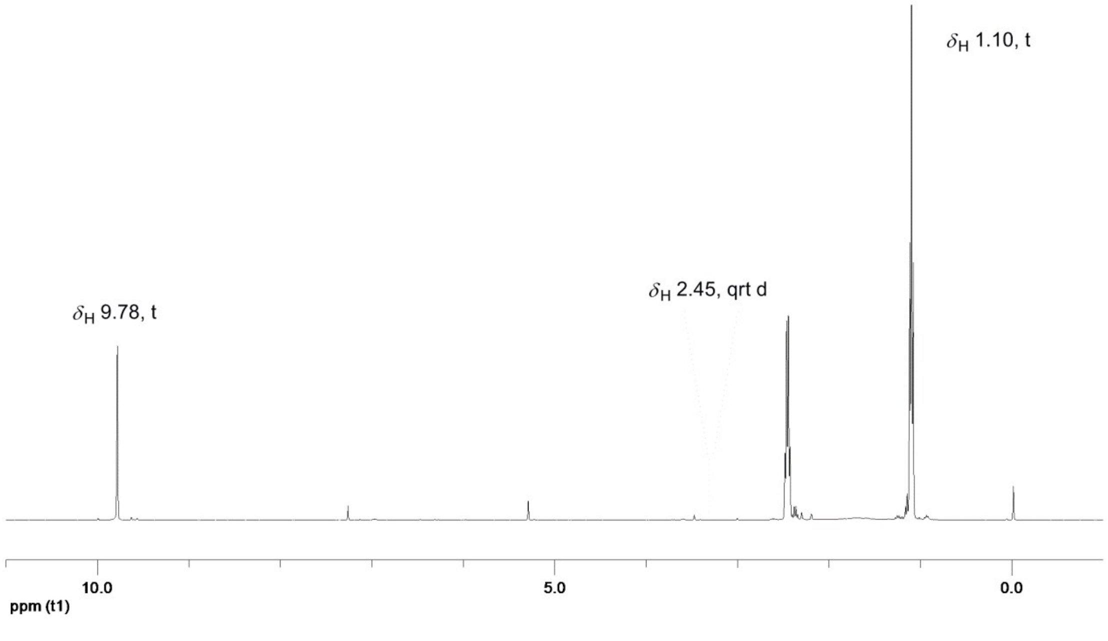
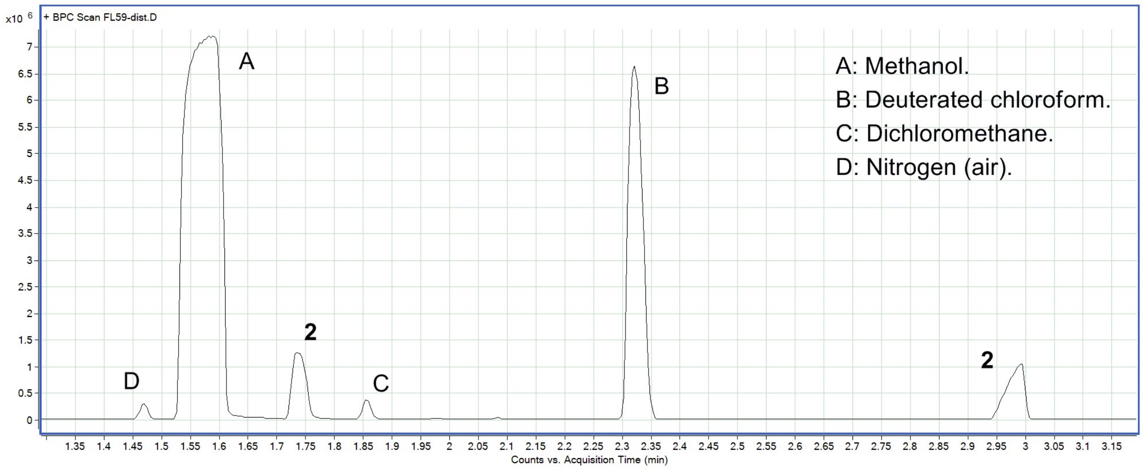


Figure S2. ^{1}H NMR spectrum of isolated, distilled **2**, synthesised *via* HTID of 1,3-PDO in the presence of **1** and a base, in EmmimNTf$_2$ or N$_{1,8,8,8}$NTf$_2$, at temperature varying in the range 100 – 180 °C, and at a dynamic vacuum of *ca.* 0.35 bar.

(b)



(a)

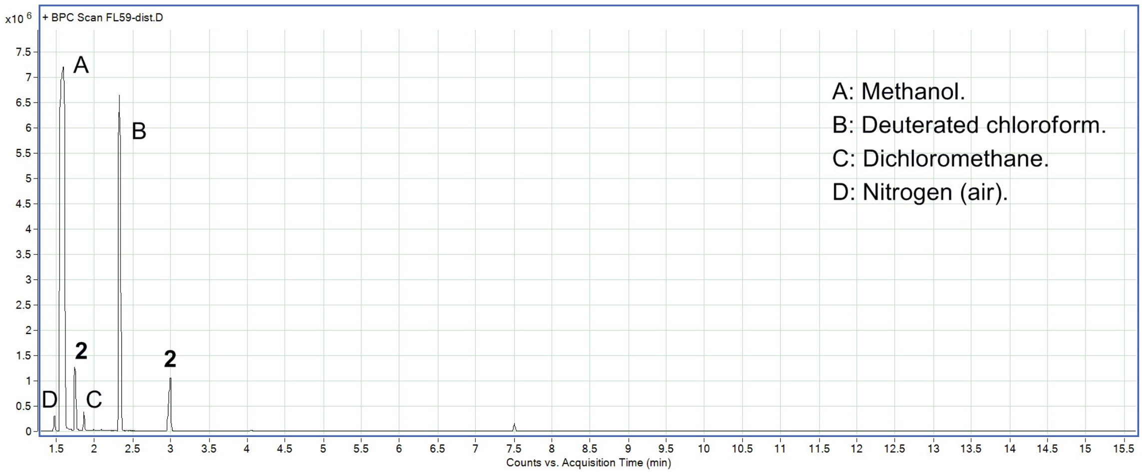


Figure S3. GCMS spectrum of isolated, distilled **2**, synthesised *via* HTID of 1,3-PDO in the presence of **1** and a base, in $EmmimNTf_2$ or $N_{1,8,8,8}NTf_2$, at temperature varying in the range 100 – 180 °C, and at a dynamic vacuum of *ca.* 0.35 bar: (a) full spectrum; (b) enlargement of the region 1.30 - 3.20 min. (**2** generates, in the presence of CH_3OH, at the GC/MS experimental conditions, its hemiacetalic form.)

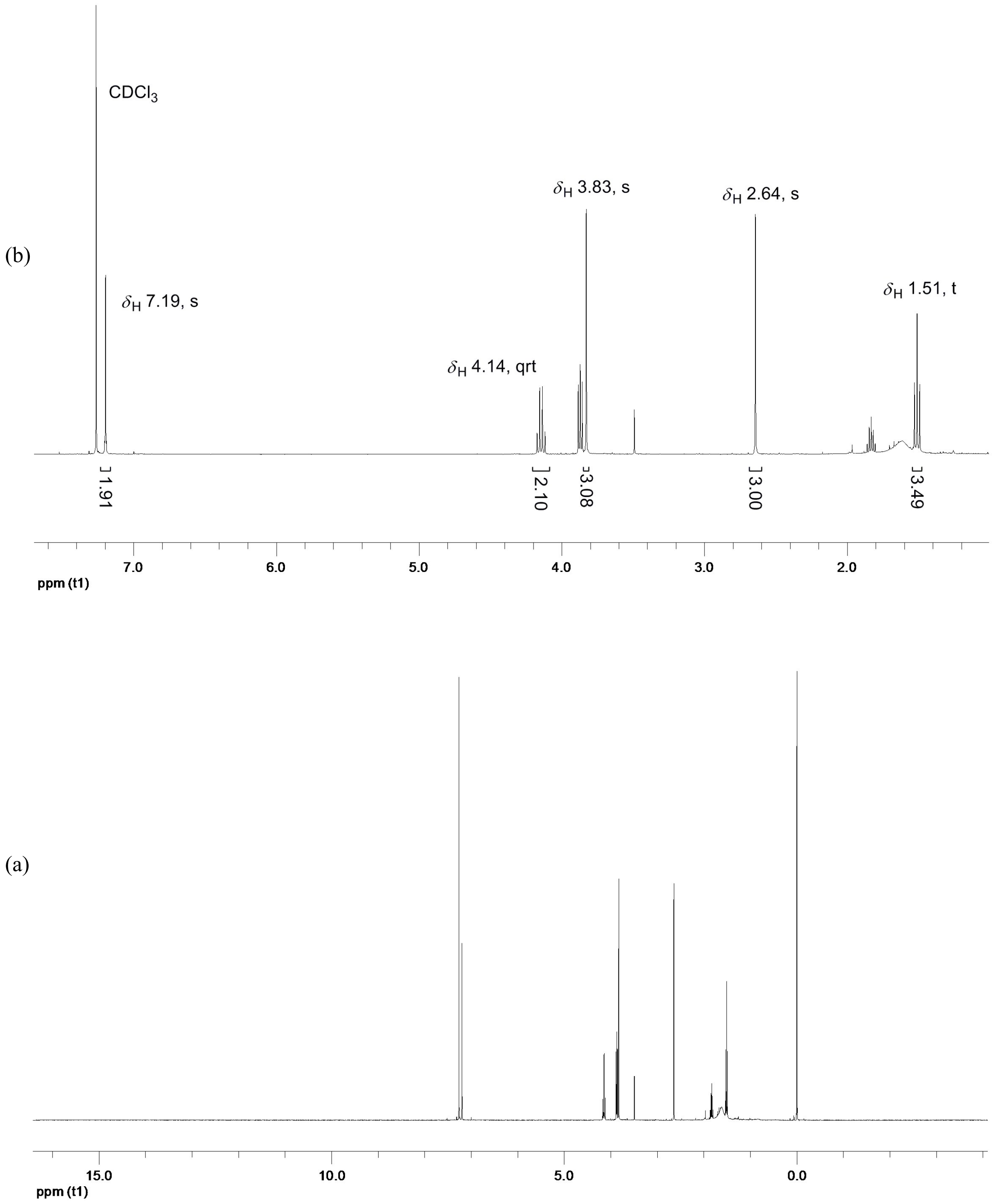
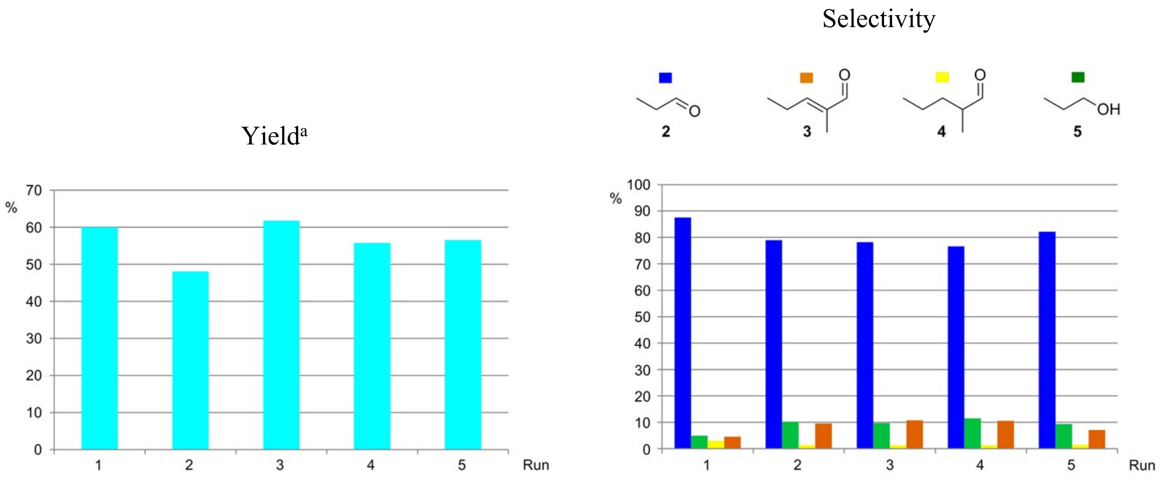
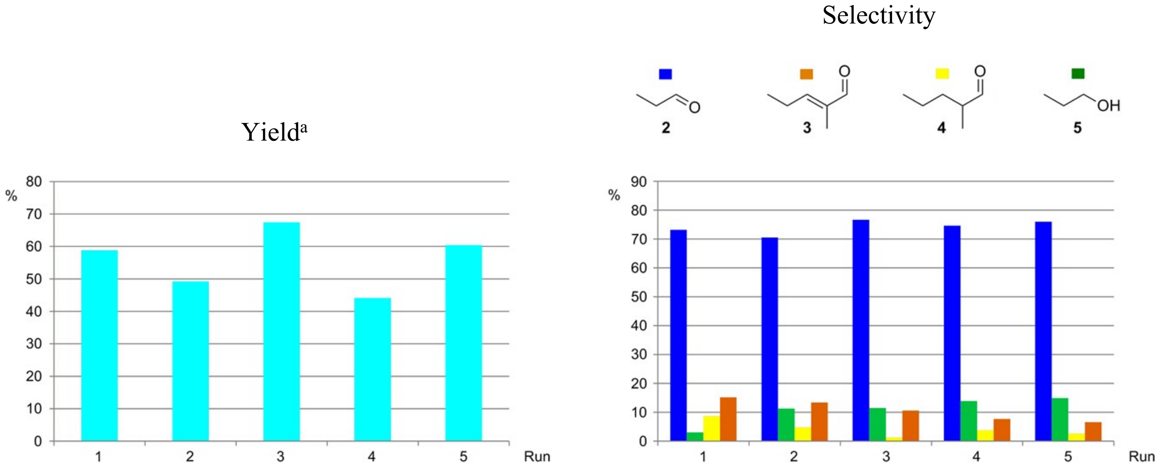


Figure S4. Recycling **1** as catalyst precursor towards HTID of 1,3-PDO in EmmimNTf$_2$: example of a ^{1}H NMR spectrum of the CDCl$_3$ solutions of the reacting mixture after the six hours reaction for any of the recycling runs (a: full spectrum; b: enlargement of the region δ_H 1.00 – 7.70 displaying the unchanged peaks due to EmmimNTf$_2$.).



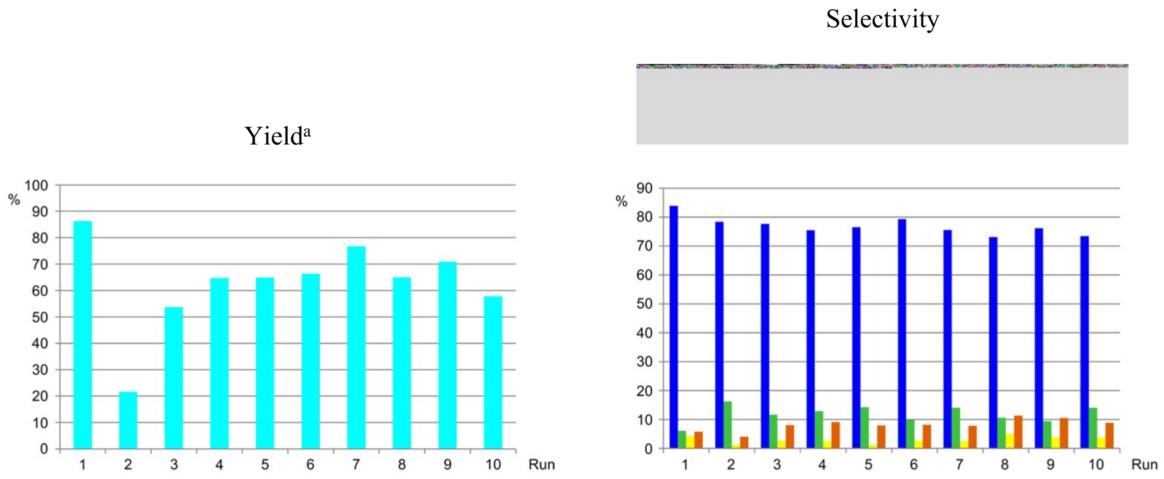
(a) (b)

Figure S5. Recycling **1** as catalyst precursor towards HTID of 1,3-PDO ([1,3-PDO]:[Ir] ≅ 220.0) in $N_{1,8,8,8}NTf_2$, in the presence of K_2CO_3, at 150 °C and 0.35 bar: (a) yield of crude **2**; (b) selectivity towards **2**, **3**, **4**, and **5**. [a] Crude, isolated product.



(a) (b)

Figure S6. Recycling **1** as catalyst precursor towards HTID of 1,3-PDO ([1,3-PDO]:[Ir] ≅ 75.0) in $N_{1,8,8,8}NTf_2$, in the presence of K_2CO_3, at 120 °C and 0.35 bar: (a) yield of crude **2**; (b) selectivity towards **2**, **3**, **4**, and **5**. [a] Crude, isolated product.



(a) (b)

Figure S7. Recycling **1** as catalyst precursor towards HTID of 1,3-PDO ([1,3-PDO]:[Ir] ≅ 75.0) in $N_{1,8,8,8}NTf_2$, in the presence of K_2CO_3, at 150 °C and 0.35 bar: (a) yield of crude **2**; (b) selectivity towards **2**, **3**, **4**, and **5**. [a] Crude, isolated product.

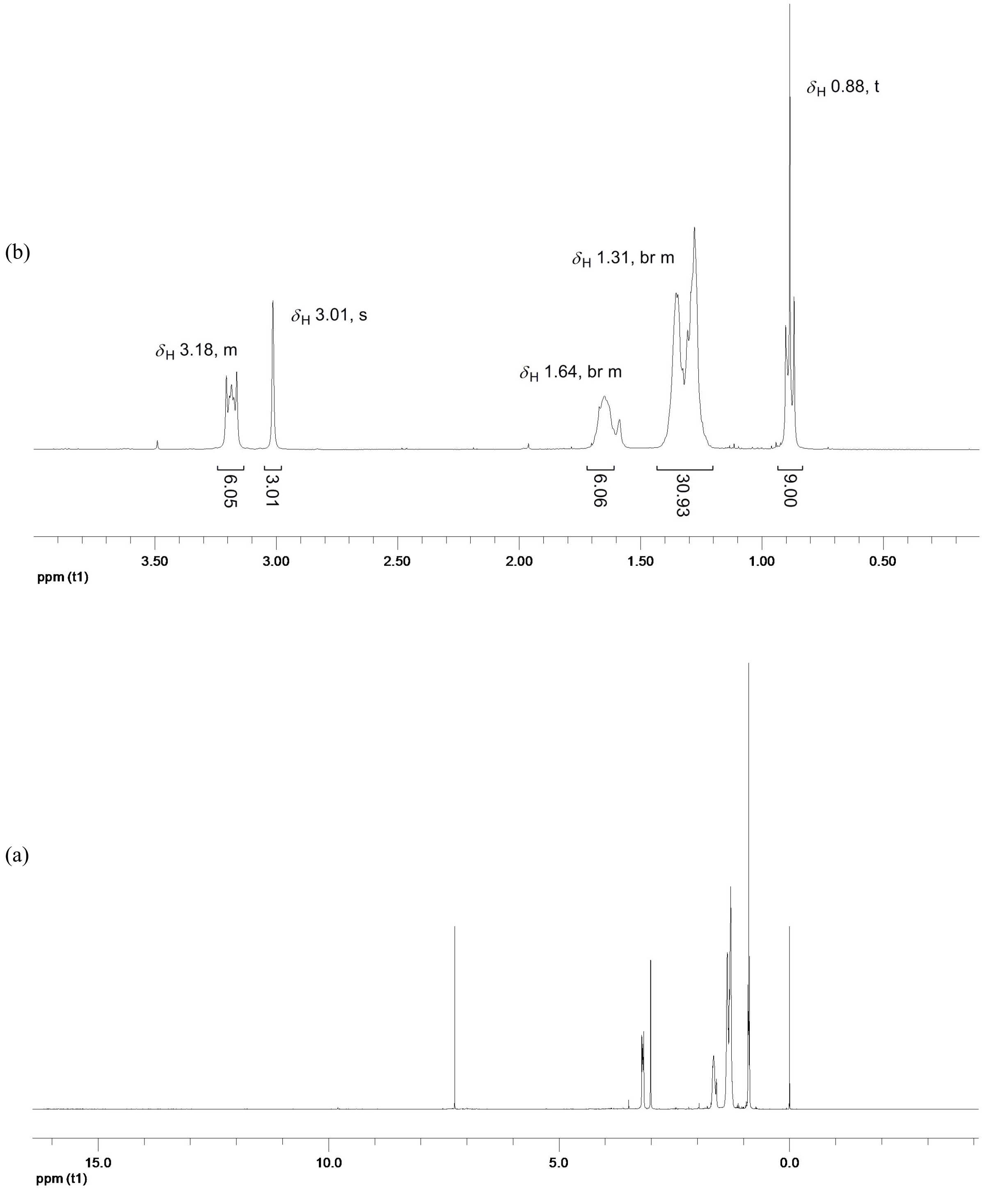


Figure S8. Recycling **1** as catalyst precursor towards HTID of 1,3-PDO in $N_{1,8,8,8}NTf_2$: example of a ^1H NMR spectrum of the $CDCl_3$ solutions of the reacting mixture after the six hours reaction for any of the recycling runs (a: full spectrum; b: enlargement of the region δ_H 0.10 – 4.00 displaying the unchanged peaks due to $N_{1,8,8,8}NTf_2$.).

Table S1. Recycling **1** as catalyst precursor for HTID of 1,3-PDO in the presence of K_2CO_3, in EmmimNTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: yields[a] of **2**, selectivity towards **2**, **3**, **4**, and **5**, and TOF.

Entry	[1,3-PDO]:[Ir]	[Base]:[1,3-PDO]	% Yield[a] (**2**)	**2**	**3**	**4**	**5**	TOF[b] [s^{-1}] ($\times 10^3$)
1	77.5	0.0303	82	71.7	11.1	6.1	11.1	2.94
2	76.5	0.0311	94	68.6	5.9	0.0	25.5	3.33
3	76.9	0.0310	77	71.4	4.9	0.0	23.7	2.75
4	76.4	0.0306	99	66.9	5.8	0.0	27.3	3.77
5	76.7	0.0304	99	66.5	4.6	0.0	28.9	3.55
6	76.4	0.0307	97	65.5	5.7	0.0	28.8	3.45
7	76.9	0.0306	89	67.9	4.7	0.0	27.4	3.15
8	75.9	0.0306	79	65.3	5.6	0.0	29.1	2.79
9	76.1	0.0308	80	66.0	5.7	0.0	28.3	2.80
10	77.0	0.0309	75	66.9	5.8	0.0	27.3	2.66

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a]Crude, isolated product. [b] TOF = n(product formed) / [n(catalyst) × time].

Table S2. Recycling **1** as catalyst precursor for HTID of 1,3-PDO in the presence of K_2CO_3, in EmmimNTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0: yields[a] of **2**, selectivity towards **2**, **3**, **4**, and **5**, and TOF.

Entry	[1,3-PDO]:[Ir]	[Base]:[1,3-PDO]	% Yield[a] (**2**)	**2**	**3**	**4**	**5**	TOF[b] [s^{-1}] ($\times 10^3$)
1	219.6	0.0310	73	77.6	9.4	6.6	6.4	7.41
2	219.9	0.0314	72	75.6	9.1	0.0	15.3	7.30
3	219.7	0.0314	71	70.4	14.6	1.2	13.8	7.21
4	221.1	0.0313	68	78.8	8.2	0.0	13.0	6.94
5	220.1	0.0304	74	76.2	9.2	0.0	14.6	7.54

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a]Crude, isolated product. [b] TOF = n(product formed) / [n(catalyst) × time].

Table S3. Recycling **1** as catalyst precursor for HTID of 1,3-PDO in the presence of K_2CO_3, in EmmimNTf$_2$, at T 120 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: yields[a] of **2**, selectivity towards **2**, **3**, **4**, and **5**, and TOF.

Entry	[1,3-PDO]:[Ir]	[Base]:[1,3-PDO]	% Yield[a] (**2**)	**2**	**3**	**4**	**5**	TOF[b] [s^{-1}] ($\times 10^3$)
1	74.0	0.0308	72	71.2	13.5	10.8	4.4	2.48
2	73.6	0.0309	72	75.6	11.7	6.4	6.3	2.47
3	73.7	0.0311	79	74.1	15.3	2.5	8.1	2.68
4	73.8	0.0311	79	75.2	13.0	2.5	9.3	2.70
5	74.3	0.0311	78	76.2	11.8	1.3	10.6	2.68

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a]Crude, isolated product. [b] TOF = n(product formed) / [n(catalyst) × time].

Table S4. Recycling **1** as catalyst precursor for HTID of 1,3-PDO in the presence of K_2CO_3, in $N_{1,8,8,8}$NTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0: yields[a] of **2**, selectivity towards **2**, **3**, **4**, and **5**, and TOF.

Entry	[1,3-PDO]:[Ir]	[Base]:[1,3-PDO]	% Yield[a] (**2**)	**2**	**3**	**4**	**5**	TOF[b] [s^{-1}] ($\times 10^3$)
1	221.4	0.0308	60	87.5	4.5	3.0	5.0	6.15
2	222.5	0.0305	48	78.9	9.5	1.3	10.2	4.95
3	222.8	0.0304	62	78.2	10.8	1.3	9.7	6.37
4	222.0	0.0305	56	76.6	10.6	1.3	11.5	5.73
5	222.1	0.0302	57	82.2	7.1	1.4	9.4	5.81

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a]Crude, isolated product. [b] TOF = n(product formed) / [n(catalyst) × time].

Table S5. Recycling **1** as catalyst precursor for HTID of 1,3-PDO in the presence of K_2CO_3, in $N_{1,8,8,8}NTf_2$, at T 120 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: yields[a] of **2**, selectivity towards **2**, **3**, **4**, and **5**, and TOF.

Entry	[1,3-PDO]:[Ir]	[Base]:[1,3-PDO]	% Yield[a] (**2**)	**2**	**3**	**4**	**5**	TOF[b] $[s^{-1}]$ ($\times 10^3$)
1	75.0	0.0308	59	73.2	15.1	8.7	3.0	2.04
2	74.8	0.0311	49	70.5	13.4	4.8	11.3	1.70
3	75.4	0.0307	67	76.6	10.6	1.3	11.5	2.35
4	75.0	0.0309	44	74.6	7.7	3.8	13.9	1.53
5	75.0	0.0305	60	76.0	6.5	2.6	14.9	2.10

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a]Crude, isolated product. [b] TOF = n(product formed) / [n(catalyst) × time].

Table S6. Recycling **1** as catalyst precursor for HTID of 1,3-PDO in the presence of K_2CO_3, in $N_{1,8,8,8}NTf_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: yields[a] of **2**, selectivity towards **2**, **3**, **4**, and **5**, and TOF.

Entry	[1,3-PDO]:[Ir]	[Base]:[1,3-PDO]	% Yield[a] (**2**)	**2**	**3**	**4**	**5**	TOF[b] $[s^{-1}]$ ($\times 10^3$)
1	77.0	0.0303	86	83.9	5.8	4.3	6.1	3.08
2	76.8	0.0311	22	78.4	4.1	1.3	16.2	0.77
3	76.9	0.0305	54	77.7	8.0	2.6	11.7	1.91
4	76.7	0.0312	65	75.5	9.1	2.6	12.9	2.30
5	76.3	0.0313	65	76.5	7.9	1.3	14.3	2.29
6	76.2	0.0307	66	79.3	8.2	2.7	9.8	2.34
7	76.0	0.0309	77	75.6	7.8	2.6	14.1	2.70
8	76.2	0.0311	65	73.1	11.3	4.9	10.6	2.29
9	75.3	0.0313	71	76.2	10.5	3.9	9.5	2.47
10	76.7	0.0309	58	73.4	8.9	3.7	14.0	2.05

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a]Crude, isolated product. [b] TOF = n(product formed) / [n(catalyst) × time].

Table S7. HTID of 1,3-PDO in the presence of **1** and K_2CO_3, at 120 °C, in EmmimNTf$_2$ and N$_{1,8,8,8}$NTf$_2$, and water, at [1,3-PDO]:[Ir] ≅ 75.0: selectivity towards **2**, **3**, **4**, and **5**.

Entry	Solvent	[1,3-PDO]:[Ir]	[Base]:[1,3-PDO]	**2**	**3**	**4**	**5**
1	EmmimNTf$_2$	75.0	0.0303	83.4	5.8	0.0	10.8
2[a]	N$_{1,8,8,8}$NTf$_2$	74.0	0.0312	44.2	31.3	14.2	10.3
2[b]	N$_{1,8,8,8}$NTf$_2$	74.0	0.0312	73.2	6.3	1.2	19.3

All operations were carried out (a) at P = 1.00 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a] Organic layer. [b] Water layer.

Experimental

Recycling Experiments

The recyclability of the catalyst precursor **1** was first tested on the addition of further aliquots of 1,3-PDO: the activity of the catalyst precursor quickly decreased and almost collapsed by the 2nd recycling run in $N_{1,8,8,8}NTf_2$, and the 4th recycling run in $EmmimNTf_2$. The recycling experiments were then repeated upon the addition of further aliquots of substrate and base.

HTID of 1,3-PDO in the presence of 1 and K_2CO_3, at 150 °C, in $EmmimNTf_2$ and $N_{1,8,8,8}NTf_2$, and at [1,3-PDO]:[Ir] ≅ 75.0: recycling experiments.

1,3-PDO (in Table S9 (for $EmmimNTf_2$) and Table S10 (for $N_{1,8,8,8}NTf_2$), see 1,3-PDO in entry 1), **1** (in Table S9 (for $EmmimNTf_2$) and Table S10 (for $N_{1,8,8,8}NTf_2$), see **1** in entry 1), K_2CO_3 (in Table S9 (for $EmmimNTf_2$) and Table S10 (for $N_{1,8,8,8}NTf_2$), see K_2CO_3 in entry 1), and $EmmimNTf_2$ (in Table S9, see $EmmimNTf_2$ in entry 1) or $N_{1,8,8,8}NTf_2$ (in Table S10, see $N_{1,8,8,8}NTf_2$ in entry 1), were mixed in a 50 mL round bottom flask connected, through a distillation condenser, to a 50 mL glass tube. The mixture was reacted at 150 °C, at a controlled pressure of *ca.* 0.35 bar, for six hours, stirring at 1000 rpm. The reaction product, a colourless liquid, was isolated by distillation, being collected, for the duration of the six hours reaction, in the collecting glass tube kept at *ca.* −196 °C (N_2 (l) bath). After separation from the minor water layer, the crude product (% yield (based on **2**): in Table S9 for $EmmimNTf_2$, and Table S10 for $N_{1,8,8,8}NTf_2$, see % Yield) was analysed by GC/MS (See Table S19 for $EmmimNTf_2$, and Table S20 for $N_{1,8,8,8}NTf_2$) and ^1H NMR (See Table S28 for $EmmimNTf_2$, and Table S29 for $N_{1,8,8,8}NTf_2$) spectroscopies. The reacted mixture, left in the 50 mL round bottom flask, was analysed by ^1H NMR spectroscopy. The following nine recycling experiments were carried out as follows: 1,3-PDO (in Table S9 (for $EmmimNTf_2$) and Table S10 (for $N_{1,8,8,8}NTf_2$), see 1,3-PDO in entries 2-10) and K_2CO_3 (in Table S9 (for $EmmimNTf_2$) and Table S10 (for $N_{1,8,8,8}NTf_2$), see K_2CO_3 in entries 2-10) were added to the reacted mixture resulting from the previous recycling experiment, in the 50 mL round bottom flask. The resulting mixture was reacted, and then analysed, as in the first cycle.

HTID of 1,3-PDO in the presence of 1 and K_2CO_3, at 150 °C, in EmmimNTf$_2$ and N$_{1,8,8,8}$NTf$_2$, and at [1,3-PDO]:[Ir] ≅ 220.0: recycling experiments.

1,3-PDO (in Table S11 (for EmmimNTf$_2$) and Table S12 (for N$_{1,8,8,8}$NTf$_2$), see 1,3-PDO in entry 1), **1** (in Table S11 (for EmmimNTf$_2$) and Table S12 (for N$_{1,8,8,8}$NTf$_2$), see **1** in entry 1), K_2CO_3 (in Table S11 (for EmmimNTf$_2$) and Table S12 (for N$_{1,8,8,8}$NTf$_2$), see K_2CO_3 in entry 1), and EmmimNTf$_2$ (in Table S11, see EmmimNTf$_2$ in entry 1) or N$_{1,8,8,8}$NTf$_2$ (in Table S12, see N$_{1,8,8,8}$NTf$_2$ in entry 1), were mixed in a 50 mL round bottom flask and reacted at 150 °C, using the same glassware apparatus, procedure and conditions as those described above. The crude product (% yield (based on **2**): in Table S11 for EmmimNTf$_2$, and Table S12 for N$_{1,8,8,8}$NTf$_2$, see % Yield) was analysed by GC/MS (See Table S21 for EmmimNTf$_2$, and Table S22 for N$_{1,8,8,8}$NTf$_2$) and ^{1}H NMR (See Table S30 for EmmimNTf$_2$, and Table S31 for N$_{1,8,8,8}$NTf$_2$) spectroscopies. The reacted mixture, left in the 50 mL round bottom flask, was analysed by ^{1}H NMR spectroscopy. The next four recycling experiments were carried out as follows: 1,3-PDO (in Table S11 (for EmmimNTf$_2$) and Table S12 (for N$_{1,8,8,8}$NTf$_2$), see 1,3-PDO in entries 2-5) and K_2CO_3 (in Table S11 (for EmmimNTf$_2$) and Table S12 (for N$_{1,8,8,8}$NTf$_2$), see K_2CO_3 in entries 2-5) were added to the reacted mixture resulting from the previous recycling experiment, in the 50 mL round bottom flask. The resulting mixture was reacted, and then analysed, as in the first cycle.

HTID of 1,3-PDO in the presence of 1 and K_2CO_3, at 120 °C, in EmmimNTf$_2$ and N$_{1,8,8,8}$NTf$_2$, and at [1,3-PDO]:[Ir] ≅ 75.0: recycling experiments.

1,3-PDO (in Table S13 (for EmmimNTf$_2$) and Table S14 (for N$_{1,8,8,8}$NTf$_2$), see 1,3-PDO in entry 1), **1** (in Table S13 (for EmmimNTf$_2$) and Table S14 (for N$_{1,8,8,8}$NTf$_2$), see **1** in entry 1), K_2CO_3 (in Table S13 (for EmmimNTf$_2$) and Table S14 (for N$_{1,8,8,8}$NTf$_2$), see K_2CO_3 in entry 1), and EmmimNTf$_2$ (in Table S13, see EmmimNTf$_2$ in entry 1) or N$_{1,8,8,8}$NTf$_2$ (in Table S14, see N$_{1,8,8,8}$NTf$_2$ in entry 1), were mixed in a 50 mL round bottom flask and reacted at 120 °C, using the same glassware apparatus, procedure and conditions as those described above. The crude product (% yield (based on **2**): in Table S13 for EmmimNTf$_2$, and Table S14 for N$_{1,8,8,8}$NTf$_2$, see % Yield) was analysed by GC/MS (See Table S23 for EmmimNTf$_2$, and Table S24 for N$_{1,8,8,8}$NTf$_2$) and ^{1}H NMR (See Table S32 for EmmimNTf$_2$, and Table S33 for N$_{1,8,8,8}$NTf$_2$) spectroscopies. The reacted mixture, left in the 50 mL round bottom flask, was analysed by ^{1}H NMR spectroscopy. The next four recycling experiments were carried out as follows: 1,3-PDO (in Table S13 (for EmmimNTf$_2$) and Table S14 (for N$_{1,8,8,8}$NTf$_2$), see 1,3-PDO in entries 2-5) and K_2CO_3 (in Table S13 (for EmmimNTf$_2$) and Table S14 (for

$N_{1,8,8,8}NTf_2$), see K_2CO_3 in entries 2-5) were added to the reacted mixture resulting from the previous recycling experiment, in the 50 mL round bottom flask. The resulting mixture was reacted, and then analysed, as in the first cycle.

HTID of 1,3-PDO in the presence of 1 and K_2CO_3, in $EmmimNTf_2$: mercury poisoning test of the iridium precatalyst 1.

1,3-PDO (1.2471 g, 0.0161 mol), **1** (0.0445 g, 0.078 mmol), K_2CO_3 (0.0695 g, 0.500 mmol), $EmmimNTf_2$ (2.8138 g, 0.0069 mol), and mercury (0.4870 g) were mixed in a 50 mL round bottom flask and reacted at 150 °C (Table S15), using the same glassware apparatus, procedure and conditions as those described above. The crude product (0.7146 g, % yield (based on **2**): 77 %) (Table S15) was analysed by GC/MS (Table S25) and ^1H NMR (Table S34) spectroscopies.

HTID of 1,3-PDO in the presence of 1 and K_2CO_3, at 120 °C, in $EmmimNTf_2$ and $N_{1,8,8,8}NTf_2$, and water, at $[1,3\text{-PDO}]:[Ir] \cong 75.0$.

1,3-PDO (in Table S16, see 1,3-PDO in entry 1 for $EmmimNTf_2$ and entry 2 for $N_{1,8,8,8}NTf_2$), **1** (in Table S16, see **1** in entry 1 for $EmmimNTf_2$ and entry 2 for $N_{1,8,8,8}NTf_2$), K_2CO_3 (in Table S16, see K_2CO_3 in entry 1 for $EmmimNTf_2$ and entry 2 for $N_{1,8,8,8}NTf_2$), $EmmimNTf_2$ (in Table S16, see Solvent in entry 1) or $N_{1,8,8,8}NTf_2$ (in Table S16, see Solvent in entry 2), and water (in Table S16, see H_2O in entry 1 for $EmmimNTf_2$ and entry 2 for $N_{1,8,8,8}NTf_2$) were mixed in a 50 mL round bottom flask. The mixture was reacted at 120 °C, at atmospheric pressure, for six hours, stirring at 1000 rpm. The reaction product, a colourless liquid, was isolated by distillation, being collected, for the duration of the six hours reaction, in the collecting glass tube kept at *ca.* -196 °C (N_2 (l) bath). The crude product organic and water layers were separated. Significant amounts of water were collected when using both $EmmimNTf_2$ and $N_{1,8,8,8}NTf_2$, preventing any evaluation of the % yield of the crude product; mass balance was evaluated *via* GC and NMR spectroscopy (Table S35). The organic and water layers were then analysed by GC/MS (See entry 1 for $EmmimNTf_2$, and entry 2 for $N_{1,8,8,8}NTf_2$, in Table S26) and ^1H NMR (See entry 1 for $EmmimNTf_2$, and entry 2 for $N_{1,8,8,8}NTf_2$, in Table S35) spectroscopies.

Table S8. HTID of 1,3-PDO in the presence of **1** and a base, in ionic liquids: experimental data for screening conditions experiments. (Entries 1-32 correspond to those in Table 1.).

Entry	1,3-PDO [g]	n(1,3-PDO) [mol]	**1** [g]	n(**1**) [mmol]	Base	Base [g]	n(Base) [mmol]	Solvent	Solvent [g]	n(Solvent) [mol]	T [°C]	% Yield[a] (**2**)
1	1.2301	0.0158	0.1210	0.212	K_2CO_3	0.0683	0.492	$N_{1,8,8,8}NTf_2$	4.6173	0.0071	150	84
2	1.2205	0.0157	0.1227	0.215	K_2CO_3	0.0678	0.488	$N_{1,8,8,8}NTf_2$	4.6085	0.0071	120	60
3	1.2451	0.0160	0.1205	0.211	K_2CO_3	0.0672	0.484	$N_{1,8,8,8}NTf_2$	4.6145	0.0071	100	27
4	1.2352	0.0159	0.1203	0.210	K_2CO_3	0.0688	0.495	$N_{1,8,8,8}NTf_2$	4.6166	0.0071	80	1
5	1.2152	0.0157	0.1221	0.214	K_2CO_3	0.0670	0.482	$N_{1,8,8,8}NTf_2$	4.6747	0.0072	150	84
6	1.2190	0.0157	0.0907	0.159	K_2CO_3	0.0673	0.485	$N_{1,8,8,8}NTf_2$	4.6828	0.0072	150	69
7	1.2216	0.0157	0.0409	0.072	K_2CO_3	0.0662	0.477	$N_{1,8,8,8}NTf_2$	4.6651	0.0072	150	51
8	1.2145	0.0156	0.0180	0.031	K_2CO_3	0.0674	0.485	$N_{1,8,8,8}NTf_2$	4.6729	0.0072	150	6
9	1.2114	0.0156	0.0411	0.072	K_2CO_3	0.0684	0.492	$N_{1,8,8,8}NTf_2$	4.6120	0.0071	180	49
10	1.2112	0.0156	0.1212	0.212	KOH	0.0561	0.850	$N_{1,8,8,8}NTf_2$	4.6065	0.0071	150	78
11	1.2280	0.0158	0.1209	0.212	KOH	0.0560	0.848	$N_{1,8,8,8}NTf_2$	4.6050	0.0071	100	11
12	1.2178	0.0157	0.0410	0.072	KOH	0.0560	0.848	$N_{1,8,8,8}NTf_2$	4.6099	0.0071	150	62
13	1.2247	0.0158	0.0413	0.072	KOH	0.0516	0.782	$N_{1,8,8,8}NTf_2$	4.6228	0.0071	100	2
14	1.2333	0.0159	0.0413	0.072	K_2CO_3	0.3011	2.168	$N_{1,8,8,8}NTf_2$	4.6053	0.0071	150	29
15	1.2326	0.0159	0.0416	0.073	K_2CO_3	0.6094	4.387	$N_{1,8,8,8}NTf_2$	4.6032	0.0071	150	20
16	1.2249	0.0158	0.0435	0.076	$CsCO_3$	0.1652	0.507	$N_{1,8,8,8}NTf_2$	4.6050	0.0071	150	17
17	1.2134	0.0156	No catalyst	/	K_2CO_3	0.0678	0.488	$N_{1,8,8,8}NTf_2$	4.6130	0.0071	150	/
18	1.2212	0.0157	0.0407	0.071	No base	/	/	$N_{1,8,8,8}NTf_2$	4.6037	0.0071	150	/
19	1.2374	0.0159	0.0402	0.070	K_2CO_3	0.0689	0.496	No IL	/	/	150	69
20	1.2331	0.0159	0.1207	0.211	K_2CO_3	0.0682	0.491	$EmmimNTf_2$	2.8107	0.0069	180	85
21	1.2255	0.0158	0.1202	0.210	K_2CO_3	0.0690	0.497	$EmmimNTf_2$	2.8906	0.0071	150	78
22	1.2418	0.0160	0.1209	0.212	K_2CO_3	0.0683	0.492	$EmmimNTf_2$	2.8879	0.0071	120	74
23	1.2314	0.0159	0.1213	0.212	K_2CO_3	0.0685	0.493	$EmmimNTf_2$	2.9095	0.0072	100	60
24	1.2218	0.0157	0.1202	0.210	K_2CO_3	0.0682	0.491	$EmmimNTf_2$	2.8713	0.0071	80	1
25	1.2330	0.0159	0.0409	0.072	K_2CO_3	0.0692	0.498	$EmmimNTf_2$	2.889	0.0071	180	62
26	1.2176	0.0157	0.0408	0.071	K_2CO_3	0.0686	0.494	$EmmimNTf_2$	2.8985	0.0072	150	70
27	1.2485	0.0161	0.0407	0.071	K_2CO_3	0.0680	0.490	$EmmimNTf_2$	2.9036	0.0072	120	51
28	1.2344	0.0159	0.0402	0.070	KOH	0.0582	0.882	$EmmimNTf_2$	2.8618	0.0071	150	54
29	1.2199	0.0157	0.1205	0.211	KOH	0.0560	0.848	$EmmimNTf_2$	2.8818	0.0071	80	1
30	1.2356	0.0159	0.0413	0.072	$CsCO_3$	0.1621	0.497	$EmmimNTf_2$	2.8904	0.0071	150	67
31	1.2565	0.0162	0.1209	0.212	K_2CO_3	0.0706	0.508	1,3-PDO	4.4294	0.0582	150	290[b]
32	1.2543	0.0162	0.1197	0.209	K_2CO_3	0.0695	0.500	1,3-PDO	2.0030	0.0263	150	197[b]

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a] Crude, isolated product. [b] In entries 31 and 32, 1,3-PDO was used as both the substrate and the solvent.

Table S9. HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $EmmimNTf_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: experimental data for recycling experiments. (Entries 1-10 correspond to those in Table S1.).

Entry	1,3-PDO [g]	n(1,3-PDO) [mol]	**1** [g]	n(**1**) [mmol]	K_2CO_3 [g]	n(K_2CO_3) [mmol]	$EmmimNTf_2$ [g]	n($EmmimNTf_2$) [mol]	% Yield[a] (**2**)
1	1.2654	0.0163	0.1202	0.210	0.0686	0.494	2.8794	0.0071	82
2	1.2496	0.0161	-	-	0.0695	0.500	-	-	94
3	1.2563	0.0162	-	-	0.0696	0.501	-	-	77
4	1.2467	0.0161	-	-	0.0682	0.491	-	-	99
5	1.2528	0.0162	-	-	0.0682	0.491	-	-	99
6	1.2471	0.0161	-	-	0.0685	0.493	-	-	97
7	1.2556	0.0162	-	-	0.0688	0.495	-	-	89
8	1.2395	0.0157	-	-	0.0679	0.489	-	-	79
9	1.2424	0.0160	-	-	0.0685	0.493	-	-	80
10	1.2574	0.0162	-	-	0.0694	0.500	-	-	75

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a] Crude, isolated product.

Table S10. HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}NTf_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: experimental data for recycling experiments. (Entries 1-10 correspond to those in Table S6.).

Entry	1,3-PDO [g]	n(1,3-PDO) [mol]	**1** [g]	n(**1**) [mmol]	K_2CO_3 [g]	n(K_2CO_3) [mmol]	$N_{1,8,8,8}NTf_2$ [g]	n($N_{1,8,8,8}NTf_2$) [mol]	% Yield[a] (**2**)
1	1.2604	0.0162	0.1205	0.211	0.0683	0.492	4.6080	0.0071	86
2	1.2572	0.0162	-	-	0.0700	0.504	-	-	22
3	1.2585	0.0162	-	-	0.0686	0.494	-	-	54
4	1.2547	0.0162	-	-	0.0701	0.505	-	-	65
5	1.2492	0.0161	-	-	0.0700	0.504	-	-	65
6	1.2471	0.0161	-	-	0.0686	0.494	-	-	66
7	1.2444	0.0160	-	-	0.0687	0.495	-	-	77
8	1.2467	0.0161	-	-	0.0693	0.499	-	-	65
9	1.2329	0.0159	-	-	0.0691	0.497	-	-	71
10	1.2557	0.0162	-	-	0.0694	0.500	-	-	58

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a] Crude, isolated product.

Table S11. HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0: experimental data for recycling experiments. (Entries 1-5 correspond to those in Table S2.).

Entry	1,3-PDO [g]	n(1,3-PDO) [mol]	**1** [g]	n(**1**) [mmol]	K_2CO_3 [g]	n(K_2CO_3) [mmol]	EmmimNTf$_2$ [g]	n(EmmimNTf$_2$) [mol]	% Yield[a] (**2**)
1	1.2408	0.0160	0.0416	0.073	0.0688	0.495	2.8074	0.0069	73
2	1.2425	0.0160	-	-	0.0698	0.503	-	-	72
3	1.2414	0.0160	-	-	0.0698	0.503	-	-	71
4	1.2493	0.0161	-	-	0.0700	0.504	-	-	68
5	1.2440	0.0160	-	-	0.0677	0.487	-	-	74

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a] Crude, isolated product.

Table S12. HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}$NTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0: experimental data for recycling experiments. (Entries 1-5 correspond to those in Table S4.).

Entry	1,3-PDO [g]	n(1,3-PDO) [mol]	**1** [g]	n(**1**) [mmol]	K_2CO_3 [g]	n(K_2CO_3) [mmol]	$N_{1,8,8,8}$NTf$_2$ [g]	n($N_{1,8,8,8}$NTf$_2$) [mol]	% Yield[a] (**2**)
1	1.2449	0.0160	0.0414	0.072	0.0685	0.493	4.6054	0.0071	60
2	1.2512	0.0161	-	-	0.0682	0.491	-	-	48
3	1.2530	0.0161	-	-	0.0682	0.491	-	-	62
4	1.2486	0.0161	-	-	0.0681	0.490	-	-	56
5	1.2492	0.0161	-	-	0.0676	0.487	-	-	57

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a] Crude, isolated product.

Table S13. HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$, at T 120 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: experimental data for recycling experiments. (Entries 1-5 correspond to those in Table S3.).

Entry	1,3-PDO [g]	n(1,3-PDO) [mol]	**1** [g]	n(**1**) [mmol]	K_2CO_3 [g]	n(K_2CO_3) [mmol]	EmmimNTf$_2$ [g]	n(EmmimNTf$_2$) [mol]	% Yield[a] (**2**)
1	1.2420	0.0160	0.1235	0.216	0.0685	0.493	2.8048	0.0069	72
2	1.2349	0.0159	-	-	0.0682	0.491	-	-	72
3	1.2368	0.0159	-	-	0.0689	0.496	-	-	79
4	1.2389	0.0160	-	-	0.0689	0.496	-	-	79
5	1.2473	0.0161	-	-	0.0694	0.500	-	-	78

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a] Crude, isolated product.

Table S14. HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}$NTf$_2$, at T 120 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: experimental data for recycling experiments. (Entries 1-5 correspond to those in Table S5.).

Entry	1,3-PDO [g]	n(1,3-PDO) [mol]	**1** [g]	n(**1**) [mmol]	K_2CO_3 [g]	n(K_2CO_3) [mmol]	$N_{1,8,8,8}$NTf$_2$ [g]	n($N_{1,8,8,8}$NTf$_2$) [mol]	% Yield[a] (**2**)
1	1.2437	0.0160	0.1221	0.214	0.0686	0.494	4.6033	0.0071	59
2	1.2401	0.0160	-	-	0.0690	0.497	-	-	49
3	1.2499	0.0161	-	-	0.0686	0.494	-	-	67
4	1.2446	0.0160	-	-	0.0689	0.496	-	-	44
5	1.2438	0.0160	-	-	0.0679	0.498	-	-	60

All operations were carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a] Crude, isolated product.

Table S15. Mercury poisoning test of the iridium precatalyst in HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $EmmimNTf_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0: experimental data.

1,3-PDO [g]	n(1,3-PDO) [mol]	**1** [g]	n(**1**) [mmol]	K_2CO_3 [g]	n(K_2CO_3) [mmol]	$EmmimNTf_2$ [g]	n($EmmimNTf_2$) [mol]	Hg [g]	% Yield[a] (**2**)
1.2471	0.0161	0.0445	0.078	0.0695	0.500	2.8138	0.0069	0.4870	77

The reaction was carried out (a) at P = 0.35 bar; (b) with reaction time: 6 h; (c) at RPM: 1000. [a] Crude, isolated product.

Table S16. HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $EmmimNTf_2$ and $N_{1,8,8,8}NTf_2$, and water, at T 120 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: experimental data.

Entry	1,3-PDO [g]	n(1,3-PDO) [mol]	**1** [g]	n(**1**) [mmol]	K_2CO_3 [g]	n(K_2CO_3) [mmol]	Solvent	Solvent [g]	n(Solvent) [mol]	H_2O [g]
1	1.2655	0.0163	0.1242	0.217	0.0686	0.494	$EmmimNTf_2$	2.8809	0.0071	3.0338
2	1.2505	0.0161	0.1244	0.218	0.0699	0.503	$N_{1,8,8,8}NTf_2$	4.6113	0.0071	3.0124

All operations were carried out (a) at P = 1.00 bar; (b) with reaction time: 6 h; (c) at RPM: 1000.

GC/MS analysis of reaction product solutions.

GC/MS analysis of reaction product solutions: $CH_3CH_2CH_2OH$ (5) / $CDCl_3$ / CH_3OH calibration.

Six solutions of **5** and $CDCl_3$ (internal standard) in CH_3OH were prepared (Table S17): **5** was first dissolved in 1.0 mL of CH_3OH; $CDCl_3$ (**6**) was then added. The resulting solutions were analysed by GC/MS spectroscopy. GC/MS spectroscopic data (A_5 and A_6) for each solution are reported in Table S17. The following calibration curve was attained (Figure S9):

$$y = 0.4449x - 0.0345 \ (R^2 = 0.9938) \ (x = C_5/C_6, \ y = A_5/A_6). \qquad \text{(Eq. S1)}$$

Table S17. GC/MS **5** / $CDCl_3$ / CH_3OH calibration: experimental and GC/MS data for the **5** / $CDCl_3$ solutions in CH_3OH.

Solution	**5** [g]	**6** [g]	CH_3OH [mL]	C_5 [M]	C_6 [M]	C_5/C_6	A_5	A_6	A_5/A_6
1	0.0008	0.0042	1.0	0.0129	0.0344	0.3738	1013034.22	7673580.57	0.1320
2	0.0019	0.0042	1.0	0.0305	0.0344	0.8878	2759672.87	7271535.13	0.3795
3	0.0017	0.0052	1.0	0.0273	0.0425	0.6416	2054314.61	8411117.17	0.2442
4	0.0025	0.0045	1.0	0.0401	0.0368	1.0903	3350151.93	7596100.42	0.4410
5	0.0031	0.0045	1.0	0.0497	0.0368	1.3520	3873803.95	6690433.20	0.5790
6	0.0029	0.0046	1.0	0.0465	0.0376	1.2372	3757553.96	7497487.91	0.5012

6 (Assay: 99.0 %): d, 1.500 g/mL; FW, 120.38 g/mol. **5** (Assay: 97.0 %): d, 0.804 g/mL; FW, 60.10 g/mol.

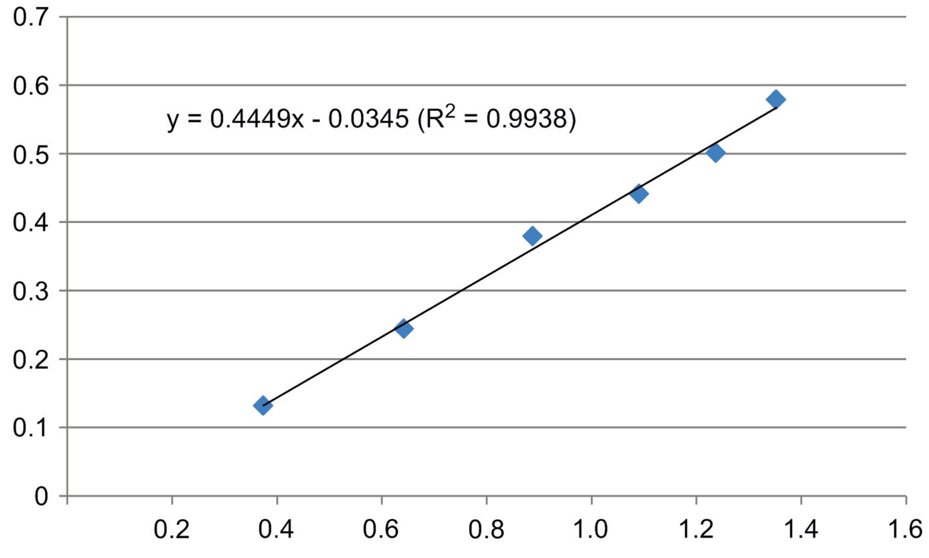


Figure S9. GC/MS **5** / $CDCl_3$ / CH_3OH calibration curve (where $x = C_5/C_6$, $y = A_5/A_6$).

GC/MS analysis of reaction product solutions: general methodology for screening conditions experiments, and catalyst recycling experiments.

A known amount of the reaction product solutions (**PS** in tables S18, S19, S20, S21, S22, S23, S24, S25, S26) was first dissolved in 1.0 mL of CH_3OH; $CDCl_3$ (**6** in tables S18, S19, S20, S21, S22, S23, S24, S25, S26) was then added. The resulting solutions were analysed by GC/MS spectroscopy. GC/MS spectroscopic data ($A_{\mathbf{5}}$ and $A_{\mathbf{6}}$) for each solution are reported in tables S18, S19, S20, S21, S22, S23, S24, S25, S26. [**5**] ($C_{\mathbf{5}}$) was then calculated using equation Eq. S1. Entries 1-32 in Table S18 correspond to entries 1-32 in Table 1, entries 1-10 in Table S19 correspond to entries 1-10 in Table S1, entries 1-10 in Table S20 correspond to entries 1-10 in Table S6, entries 1-5 in Table S21 correspond to entries 1-5 in Table S2, entries 1-5 in Table S22 correspond to entries 1-5 in Table S4, entries 1-5 in Table S23 correspond to entries 1-5 in Table S3, entries 1-5 in Table S24 correspond to entries 1-5 in Table S5, entries 1 and 2 in Table S26 correspond to entries 1 and 2 in Table S7.

Table S18. GC/MS analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and a base, in ionic liquids: experimental and GC/MS data for screening conditions experiments.

Entry	**PS** [g]	**6** [g]	CH_3OH [mL]	C_6 [M]	A_5	A_6	A_5/A_6	C_5 [M]
1	0.0084	0.0081	1.0	0.0663	102324.62	2985700.37	0.0343	0.0102
2	0.0061	0.0073	1.0	0.0597	272351.22	9837361.45	0.0277	0.0083
3	0.0073	0.0075	1.0	0.0614	155214.08	10751355.50	0.0144	0.0067
4	0.0076	0.0073	1.0	0.0597	517000.97	9632947.61	0.0537	0.0118
5	0.0126	0.0055	1.0	0.0451	1233902.77	7884826.09	0.1565	0.0193
6	0.0069	0.0031	1.0	0.0254	325930.45	5320797.82	0.0613	0.0055
7	0.0107	0.0058	1.0	0.0475	761932.58	7709523.86	0.0988	0.0142
8	0.0046	0.0038	1.0	0.0312	319835.37	11740461,92	0.0272	0.0043
9	0.0078	0.0077	1.0	0.0630	340378.24	10824496.75	0.0314	0.0093
10	0.0132	0.0076	1.0	0.0622	1358672.55	10444426.44	0.1301	0.0230
11	0.0079	0.0079	1.0	0.0646	497190.53	10635989.57	0.0467	0.0118
12	0.0135	0.0073	1.0	0.0597	988651.28	12438588.77	0.0795	0.0153
13	0.0047	0.0084	1.0	0.0687	283091.78	8224857.12	0.0344	0.0106
14	0.0124	0.0075	1.0	0.0614	1763943.87	10441529.91	0.1689	0.0281
15	0.0126	0.0072	1.0	0.0589	1704760.52	10188912.33	0.1673	0.0267
16	0.0092	0.0081	1.0	0.0663	146135.99	3388220.27	0.0431	0.0115
17	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-
19	0.0072	0.0082	1.0	0.0671	66107.31	3219458.48	0.0205	0.0082
20	0.0079	0.0073	1.0	0.0597	380637.06	7422572.89	0.0513	0.0115
21	0.0141	0.0074	1.0	0.0606	1154804.05	10112015.19	0.1142	0.0202
22	0.0069	0.0082	1.0	0.0671	56773.97	3107328.44	0.0183	0.0079
23	0.0128	0.0079	1.0	0.0646	584091.88	10134934.91	0.0576	0.0133
24	0.0059	0.0069	1.0	0.0565	196051.85	10050407.50	0.0195	0.0068
25	0.0075	0.0075	1.0	0.0614	491145.68	10575376.42	0.0464	0.0111
26	0.0072	0.0083	1.0	0.0679	477423.54	11598509.99	0.0412	0.0115
27	0.0063	0.0078	1.0	0.0638	[a]	7891567.82	[a]	[a]
28	0.0088	0.0088	1.0	0.0719	131971.90	3079263.98	0.0429	0.0125
29	0.0061	0.0083	1.0	0.0679	877749.49	10619803.41	0.0827	0.0178
30	0.0077	0.0075	1.0	0.0614	531112.79	7067782.58	0.0751	0.0151
31	0.0070	0.0079	1.0	0.0646	172080.59	8907511.33	0.0193	0.0078
32	0.0078	0.0072	1.0	0.0589	371426.13	9147734.29	0.0406	0.0099

6 (Assay: 99.0 %): d, 1.500 g/mL; FW, 120.38 g/mol. [a] The intensity of the GC peak due to **5** was so little that no reliable integration could be obtained.

Table S19. GC/MS analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: experimental and GC/MS data for recycling experiments.

Entry	**PS** [g]	**6** [g]	CH_3OH [mL]	C_6 [M]	A_5	A_6	A_5/A_6	C_5 [M]
1	0.0075	0.0072	1.0	0.0589	499200.96	6862519.11	0.0727	0.0142
2	0.0041	0.0071	1.0	0.0581	609014.43	6144735.96	0.0991	0.0174
3	0.0085	0.0069	1.0	0.0565	1081598.64	5667770.54	0.1908	0.0286
4	0.0044	0.0076	1.0	0.0622	573213.53	5929776.77	0.0967	0.0183
5	0.0044	0.0079	1.0	0.0646	588508.24	6243740.77	0.0943	0.0187
6	0.0037	0.0065	1.0	0.0532	534301.84	5927639.67	0.0901	0.0149
7	0.0034	0.0074	1.0	0.0606	454281.16	5780631.10	0.0786	0.0154
8	0.0042	0.0064	1.0	0.0524	546125.4	5351376.99	0.1021	0.0161
9	0.0041	0.0077	1.0	0.0630	497472.57	5820209.99	0.0855	0.0170
10	0.0037	0.0071	1.0	0.0581	438920.97	5699379.73	0.0770	0.0145

6 (Assay: 99.0 %): d, 1.500 g/mL; FW, 120.38 g/mol.

Table S20. GC/MS analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}$NTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: experimental and GC/MS data for recycling experiments.

Entry	**PS** [g]	**6** [g]	CH_3OH [mL]	C_6 [M]	A_5	A_6	A_5/A_6	C_5 [M]
1	0.0069	0.0066	1.0	0.0540	55277.21	6945973.55	0.0080	0.0051
2	0.0083	0.0074	1.0	0.0606	801444.24	6168126.25	0.1299	0.0224
3	0.0079	0.0067	1.0	0.0549	537506.57	5115698.34	0.1051	0.0172
4	0.0082	0.0066	1.0	0.0540	696444.39	4478957.85	0.1555	0.0231
5	0.0083	0.0073	1.0	0.0597	621060.09	5512967.13	0.1127	0.0197
6	0.0085	0.0069	1.0	0.0565	614588.57	5989198.85	0.1026	0.0174
7	0.0072	0.0065	1.0	0.0532	531945.86	5468938.47	0.0973	0.0157
8	0.0070	0.0066	1.0	0.0540	535487.16	5252853.60	0.1019	0.0165
9	0.0087	0.0083	1.0	0.0679	586837.64	5981514.96	0.0981	0.0202
10	0.0082	0.0070	1.0	0.0573	581773.19	5440390.86	0.1069	0.0182

6 (Assay: 99.0 %): d, 1.500 g/mL; FW, 120.38 g/mol.

Table S21. GC/MS analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0: experimental and GC/MS data for recycling experiments.

Entry	**PS** [g]	**6** [g]	CH_3OH [mL]	C_6 [M]	A_5	A_6	A_5/A_6	C_5 [M]
1	0.0089	0.0089	1.0	0.0728	256627.04	5177945.44	0.0496	0.0137
2	0.0103	0.0080	1.0	0.0654	619235.11	4961043.67	0.1248	0.0234
3	0.0096	0.0072	1.0	0.0589	542152.46	5032852.02	0.1077	0.0188
4	0.0095	0.0092	1.0	0.0752	514523.63	5198450.26	0.0990	0.0225
5	0.0091	0.0075	1.0	0.0614	511619.73	4911556.16	0.1042	0.0191

6 (Assay: 99.0 %): d, 1.500 g/mL; FW, 120.38 g/mol.

Table S22. GC/MS analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}$NTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0: experimental and GC/MS data for recycling experiments.

Entry	**PS** [g]	**6** [g]	CH_3OH [mL]	C_6 [M]	A_5	A_6	A_5/A_6	C_5 [M]
1	0.0095	0.0078	1.0	0.0638	156254.34	5055833.22	0.0309	0.0093
2	0.0090	0.0083	1.0	0.0679	343229.67	4614569.99	0.0744	0.0166
3	0.0088	0.0085	1.0	0.0695	370953.58	4976594.47	0.0745	0.0170
4	0.0090	0.0087	1.0	0.0711	472525.88	5035978.23	0.0938	0.0205
5	0.0088	0.0080	1.0	0.0654	346394.90	5192949.88	0.0667	0.0148

6 (Assay: 99.0 %): d, 1.500 g/mL; FW, 120.38 g/mol.

Table S23. GC/MS analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$, at T 120 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: experimental and GC/MS data for recycling experiments.

Entry	**PS** [g]	**6** [g]	CH_3OH [mL]	C_6 [M]	A_5	A_6	A_5/A_6	C_5 [M]
1	0.0090	0.0086	1.0	0.0703	83236.32	3498817.23	0.0238	0.0092
2	0.0086	0.0079	1.0	0.0646	117556.99	3074175.20	0.0382	0.0105
3	0.0079	0.0090	1.0	0.0736	125514.35	3144128.39	0.0399	0.0122
4	0.0081	0.0084	1.0	0.0687	154807.01	3218303.41	0.0481	0.0127
5	0.0080	0.0080	1.0	0.0654	194239.29	2883570.49	0.0674	0.0149

6 (Assay: 99.0 %): d, 1.500 g/mL; FW, 120.38 g/mol.

Table S24. GC/MS analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}$NTf$_2$, at T 120 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: experimental and GC/MS data for recycling experiments.

Entry	**PS** [g]	**6** [g]	CH_3OH [mL]	C_6 [M]	A_5	A_6	A_5/A_6	C_5 [M]
1	0.0086	0.0071	1.0	0.0581	101789.13	4800306.01	0.0212	0.0072
2	0.0081	0.0070	1.0	0.0573	466601.36	4898414.03	0.0953	0.0167
3	0.0070	0.0071	1.0	0.0581	425913.09	5024981.20	0.0848	0.0155
4	0.0049	0.0076	1.0	0.0622	310619.81	4970078.85	0.0625	0.0135
5	0.0074	0.0076	1.0	0.0622	511044.48	4660797.72	0.1096	0.0201

6 (Assay: 99.0 %): d, 1.500 g/mL; FW, 120.38 g/mol.

Table S25. Mercury poisoning test of the iridium precatalyst in HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$: experimental and GC/MS data.

PS [g]	**6** [g]	CH_3OH [mL]	C_6 [M]	A_5	A_6	A_5/A_6	C_5 [M]
0.0066	0.0091	1.0	0.0744	24321.41	3183422.67	0.0076	0.0070

6 (Assay: 99.0 %): d, 1.500 g/mL; FW, 120.38 g/mol.

Table S26. GC/MS analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, at 120 °C, in EmmimNTf$_2$ and $N_{1,8,8,8}$NTf$_2$, and water, at [1,3-PDO]:[Ir] ≅ 75.0: experimental and GC/MS data.

Entry	**PS** [g]	**6** [g]	CH_3OH [mL]	C_6 [M]	A_5	A_6	A_5/A_6	C_5 [M]
1	0.0116	0.0087	1.0	0.0711	19457.83	2860426.88	0.0068	0.0065
2[a]	0.0046	0.0088	1.0	0.0719	71335.84	2925316.90	0.0244	0.0095
2[b]	0.0051	0.0084	1.0	0.0687	25245.62	2932714.78	0.0086	0.0066

6 (Assay: 99.0 %): d, 1.500 g/mL; FW, 120.38 g/mol. [a] Organic layer. [b] Water layer.

GC/MS analysis of reaction product solutions: GC reference spectra of CH_3OH solutions of 2, 3, 4, and 5.

CH_3OH (1.0 mL) solutions of commercially available **2**, **3**, **4**, and **5** (*ca.* 0.005 g) were prepared and then analysed by GC/MS spectroscopy (Figures S10, S11, S12, S13, respectively).

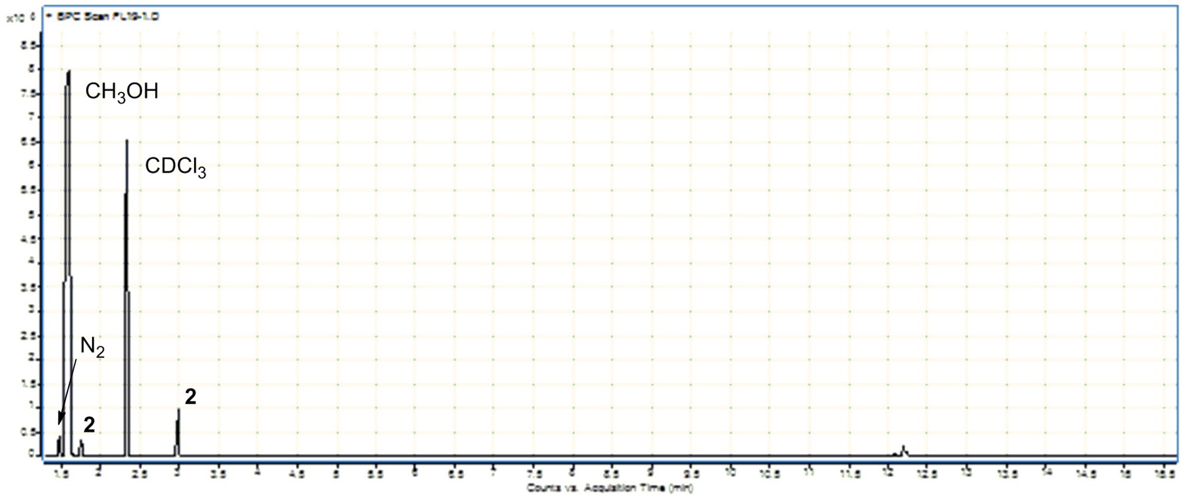


Figure S10. GC/MS spectrum of a CH_3OH solution of **2** (**2** generates, in the presence of CH_3OH, at the GC/MS experimental conditions, its hemiacetalic form.)

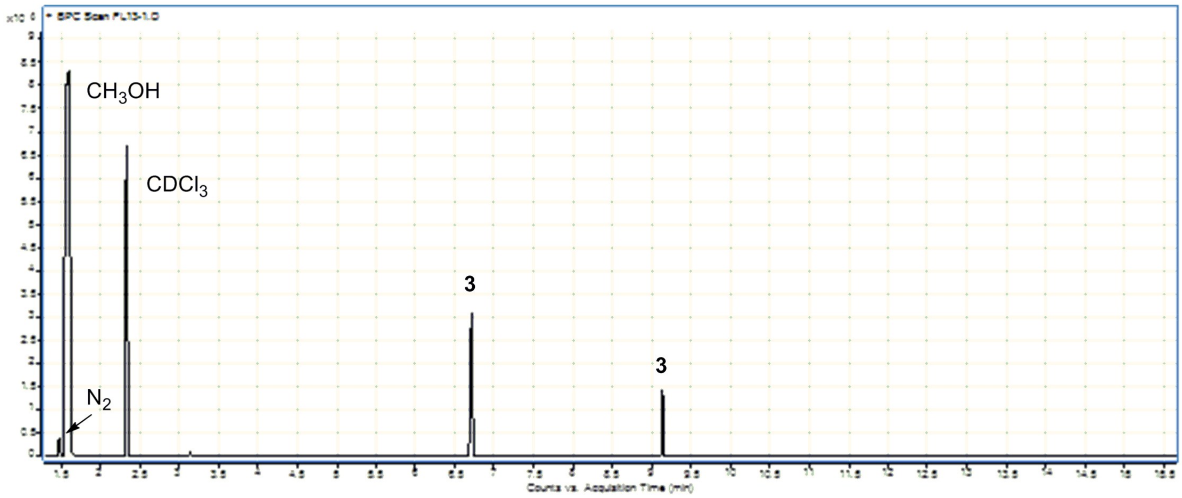


Figure S11. GC/MS spectrum of a CH_3OH solution of **3** (**3** generates, in the presence of CH_3OH, at the GC/MS experimental conditions, its hemiacetalic form.)

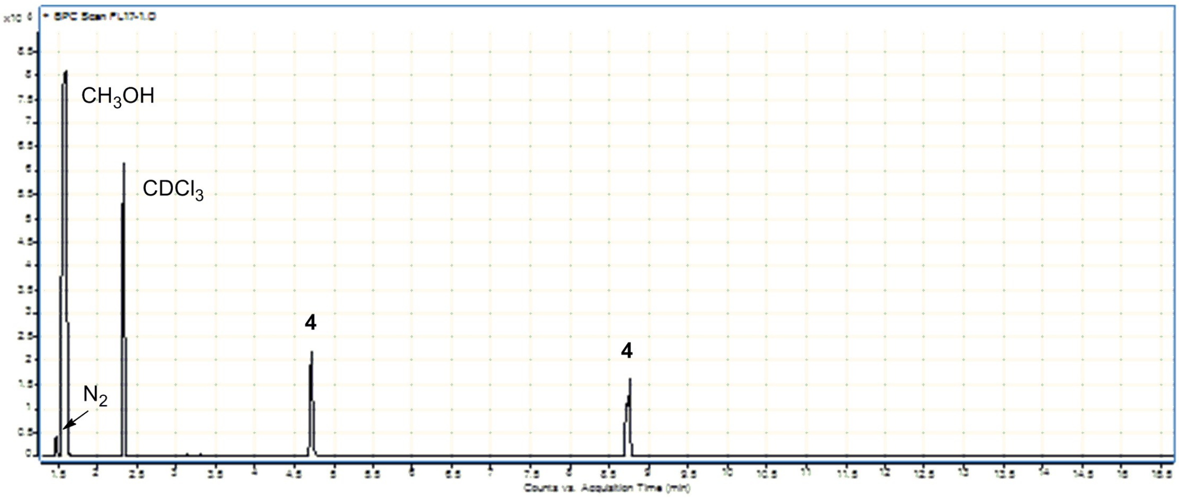


Figure S12. GC/MS spectrum of a CH$_3$OH solution of **4** (**4** generates, in the presence of CH$_3$OH, at the GC/MS experimental conditions, its hemiacetalic form.)

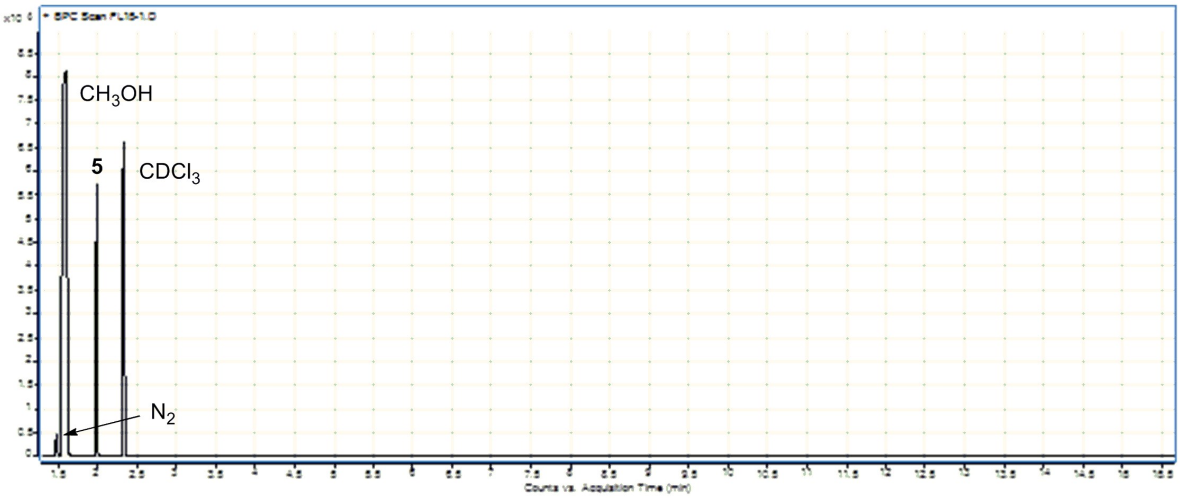


Figure S13. GC/MS spectrum of a CH$_3$OH solution of **5**.

^{1}H NMR analysis of reaction product solutions.

^{1}H NMR analysis of reaction product solutions. General procedure.

The collected reaction product solutions (*ca.* 0.010 g) were dissolved in $CDCl_3$ (*ca.* 0.7 mL). The following resonances of the four main components were investigated in the ^{1}H NMR spectrum of the resulting solutions: **5**, δ_H 3.60 (CH_2OH, t, J_{HH} = 6.64 Hz); **3**, δ_H 9.38 (C(O)*H*, s); **4**, δ_H 9.60 (C(O)*H*, d, J_{HH} = 2.02 Hz); **2**, δ_H 9.78 (C(O)*H*, m). The normalised ratio of the corresponding integrals ($I_{\mathbf{2}}$, $I_{\mathbf{3}}$, $I_{\mathbf{4}}$, $I_{\mathbf{5}}$ in tables S27, S28, S29, S30, S31, S32, S33, S34, S35) allowed calculating the molar ratio of **2**, **3**, **4**, and **5**.

Table S27. ^{1}H NMR analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and a base, in ionic liquids, and subsequent mass balance calculation: screening conditions experiments.

Entry	I_5	n_5[a] [mol]	I_2	n_2 [mol]	I_3	n_3 [mol]	I_4	n_4 [mol]	MB[b] [%]
1	0.15	0.0009	1.00	0.0125	0.04	0.0005	0.01	0.0001	89
2	0.33	0.0007	1.00	0.0045	0.31	0.0014	0.11	0.0005	45
3	0.12	0.0002	1.00	0.0039	0.10	0.0004	0.11	0.0004	31
4	1.00	0.00002	1.00	0.00003	1.39	0.00005	0.00	0.0000	1
5	0.24	0.0012	1.00	0.0097	0.08	0.0008	0.04	0.0004	77
6	0.15	0.0005	1.00	0.0067	0.12	0.0008	0.06	0.0004	53
7	0.14	0.0006	1.00	0.0089	0.09	0.0008	0.05	0.0004	69
8	0.11	0.0001	1.00	0.0010	0.08	0.00008	0.05	0.00005	7
9	0.16	0.0005	1.00	0.0067	0.05	0.0003	0.03	0.0002	50
10	0.20	0.0012	1.00	0.0123	0.07	0.0009	0.03	0.0004	95
11	0.22	0.0002	1.00	0.0014	0.07	0.0001	0.08	0.0001	11
12	0.13	0.0006	1.00	0.0099	0.05	0.0005	0.02	0.0002	71
13	2.79	0.00004	1.00	0.00003	0.06	0.000002	0.00	0.0000	0.4
14	0.45	0.0006	1.00	0.0027	0.27	0.0007	0.13	0.0004	28
15	0.38	0.0004	1.00	0.0021	0.24	0.0005	0.14	0.0003	21
16	0.21	0.0002	1.00	0.0018	0.08	0.0001	0.02	0.00004	14
17	-	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-	-
19	0.15	0.0007	1.00	0.0097	0.29	0.0028	0.13	0.0013	91
20	0.30	0.0011	1.00	0.0076	0.10	0.0008	0.03	0.0002	62
21	0.22	0.0010	1.00	0.0094	0.08	0.0008	0.07	0.0007	75
22	0.14	0.0008	1.00	0.0113	0.11	0.0012	0.06	0.0007	88
23	0.17	0.0006	1.00	0.0069	0.06	0.0004	0.15	0.0010	56
24	0.12	0.00001	1.00	0.0002	0.03	0.000006	0.22	0.00005	2
25	0.21	0.0009	1.00	0.0081	0.08	0.0006	0.03	0.0002	62
26	0.23	0.0010	1.00	0.0088	0.10	0.0009	0.05	0.0004	71
27	0.05	c	1.00	c	0.10	c	0.12	c	c
28	0.17	0.0007	1.00	0.0084	0.04	0.0003	0.01	0.0001	60
29	0.80	0.00003	1.00	0.00008	0.09	0.00001	0.66	0.0001	1
30	0.20	0.0012	1.00	0.0122	0.04	0.0005	0.02	0.0002	89
31	0.13	0.0030	1.00	0.0468	0.23	0.0108	0.10	0.0047	403[d]
32	0.19	0.0024	1.00	0.0248	0.16	0.0040	0.08	0.0020	205[d]

[a] n_5 was calculated *via* GC/MS analysis of the product solutions. [b] MB = Mass balance. [c] The intensity of the GC peak due to **5** was so little that no reliable integration could be obtained and so no reliable mass balance calculations could be achieved. [d] In entries 31 and 32, 1,3-PDO was used as both the substrate and the solvent.

Table S28. ^1H NMR analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 75.0, and subsequent mass balance calculations: recycling experiments.

Entry	I_5	n_5[a] [mol]	I_2	n_2 [mol]	I_3	n_3 [mol]	I_4	n_4 [mol]	MB[b] [%]
1	0.30	0.0015	1.00	0.0098	0.09	0.0009	0.05	0.0005	78
2	0.72	0.0037	1.00	0.0104	0.05	0.0005	0.00	0.0000	91
3	0.64	0.0025	1.00	0.0077	0.04	0.0003	0.00	0.0000	64
4	0.79	0.0042	1.00	0.0105	0.05	0.0005	0.00	0.0000	95
5	0.84	0.0040	1.00	0.0095	0.04	0.0004	0.00	0.0000	86
6	0.85	0.0037	1.00	0.0086	0.05	0.0004	0.00	0.0000	79
7	0.78	0.0038	1.00	0.0097	0.04	0.0004	0.00	0.0000	86
8	0.86	0.0028	1.00	0.0066	0.05	0.0003	0.00	0.0000	61
9	0.83	0.0031	1.00	0.0074	0.05	0.0004	0.00	0.0000	68
10	0.79	0.0028	1.00	0.0070	0.05	0.0004	0.00	0.0000	62

[a] n_5 was calculated *via* GC/MS analysis of the product solutions. [b] MB = Mass balance.

Table S29. ^1H NMR analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}$NTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 75.0, and subsequent mass balance calculations: recycling experiments.

Entry	I_5	n_5[a] [mol]	I_2	n_2 [mol]	I_3	n_3 [mol]	I_4	n_4 [mol]	MB[b] [%]
1	0.14	0.0006	1.00	0.0086	0.04	0.0003	0.03	0.0003	61
2	0.40	0.0006	1.00	0.0028	0.03	0.0001	0.01	0.00003	21
3	0.29	0.0011	1.00	0.0076	0.06	0.0005	0.02	0.0002	58
4	0.33	0.0017	1.00	0.0104	0.07	0.0007	0.02	0.0002	81
5	0.36	0.0014	1.00	0.0081	0.06	0.0005	0.01	0.0001	63
6	0.24	0.0013	1.00	0.0106	0.06	0.0006	0.02	0.0002	79
7	0.36	0.0016	1.00	0.0087	0.06	0.0005	0.02	0.0002	68
8	0.28	0.0014	1.00	0.0103	0.09	0.0009	0.04	0.0004	81
9	0.24	0.0015	1.00	0.0127	0.08	0.0010	0.03	0.0004	98
10	0.37	0.0012	1.00	0.0065	0.07	0.0005	0.03	0.0002	52

[a] n_5 was calculated *via* GC/MS analysis of the product solutions. [b] MB = Mass balance.

Table S30. ^{1}H NMR analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0, and subsequent mass balance calculations: recycling experiments.

Entry	I_5	n_5[a] [mol]	I_2	n_2 [mol]	I_3	n_3 [mol]	I_4	n_4 [mol]	MB[b] [%]
1	0.16	0.0010	1.00	0.0131	0.07	0.0009	0.05	0.0007	98
2	0.39	0.0015	1.00	0.0078	0.07	0.0005	0.00	0.0000	62
3	0.38	0.0013	1.00	0.0068	0.12	0.0008	0.01	0.0001	56
4	0.32	0.0015	1.00	0.0094	0.06	0.0006	0.00	0.0000	72
5	0.37	0.0015	1.00	0.0078	0.07	0.0005	0.00	0.0000	61

[a] n_5 was calculated *via* GC/MS analysis of the product solutions. [b] MB = Mass balance.

Table S31. ^{1}H NMR analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}$NTf$_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0, and subsequent mass balance calculations: recycling experiments.

Entry	I_5	n_5[a] [mol]	I_2	n_2 [mol]	I_3	n_3 [mol]	I_4	n_4 [mol]	MB[b] [%]
1	0.11	0.0006	1.00	0.0100	0.03	0.0003	0.02	0.0002	69
2	0.25	0.0008	1.00	0.0067	0.07	0.0005	0.01	0.0001	50
3	0.24	0.0011	1.00	0.0094	0.08	0.0007	0.01	0.0001	70
4	0.29	0.0012	1.00	0.0082	0.08	0.0007	0.01	0.0001	63
5	0.22	0.0009	1.00	0.0081	0.05	0.0004	0.01	0.0001	59

[a] n_5 was calculated *via* GC/MS analysis of the product solutions. [b] MB = Mass balance.

Table S32. ^{1}H NMR analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$, at T 120 °C, and at [1,3-PDO]:[Ir] ≅ 75.0, and subsequent mass balance calculations: recycling experiments.

Entry	I_5	n_5[a] [mol]	I_2	n_2 [mol]	I_3	n_3 [mol]	I_4	n_4 [mol]	MB[b] [%]
1	0.12	0.0007	1.00	0.0115	0.11	0.0013	0.09	0.0010	90
2	0.16	0.0008	1.00	0.0103	0.09	0.0009	0.05	0.0005	79
3	0.21	0.0011	1.00	0.0108	0.12	0.0013	0.02	0.0002	84
4	0.24	0.0012	1.00	0.0096	0.10	0.0010	0.02	0.0002	75
5	0.27	0.0014	1.00	0.0101	0.09	0.0009	0.01	0.0001	78

[a] n_5 was calculated *via* GC/MS analysis of the product solutions. [b] MB = Mass balance.

Table S33. ^{1}H NMR analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}$NTf$_2$, at T 120 °C, and at [1,3-PDO]:[Ir] ≅ 75.0, and subsequent mass balance calculations: recycling experiments.

Entry	I_5	n_5[a] [mol]	I_2	n_2 [mol]	I_3	n_3 [mol]	I_4	n_4 [mol]	MB[b] [%]
1	0.08	0.0005	1.00	0.0116	0.12	0.0014	0.07	0.0008	89
2	0.31	0.0009	1.00	0.0061	0.11	0.0007	0.04	0.0002	50
3	0.29	0.0014	1.00	0.0097	0.08	0.0008	0.01	0.0001	74
4	0.36	0.0011	1.00	0.0063	0.06	0.0004	0.03	0.0002	50
5	0.38	0.0015	1.00	0.0081	0.05	0.0004	0.02	0.0002	64

[a] n_5 was calculated *via* GC/MS analysis of the product solutions. [b] MB = Mass balance.

Table S34. ^{1}H NMR analysis of the product solutions of mercury poisoning test of the iridium precatalyst in HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$, and subsequent mass balance calculations.

I_5	n_5[a] [mol]	I_2	n_2 [mol]	I_3	n_3 [mol]	I_4	n_4 [mol]	MB[b] [%]
0.15	0.0008	1.00	0.0101	0.07	0.0007	0.05	0.0005	75

[a] n_5 was calculated *via* GC/MS analysis of the product solutions. [b] MB = Mass balance.

Table S35. ^{1}H NMR analysis of the product solutions of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, at 120 °C, in EmmimNTf$_2$ and $N_{1,8,8,8}$NTf$_2$, and water, at [1,3-PDO]:[Ir] ≅ 75.0, and subsequent mass balance calculations.

Entry	I_5	n_5[a] [mol]	I_2	n_2 [mol]	I_3	n_3 [mol]	I_4	n_4 [mol]	MB[b] [%]
1	0.25	0.0015	1.00	0.0123	0.04	0.0005	0.00	0.0000	88
2[c]	0.45	0.0005	1.00	0.0021	0.41	0.0008	0.19	0.0004	23
2[d]	0.51	0.0002	1.00	0.0007	0.05	0.00004	0.01	0.00001	6

[a] n_5 was calculated *via* GC/MS analysis of the product solutions. [b] MB = Mass balance. [c] Organic layer. [d] Water layer.

HTID of 1,3-PDO in the presence of 1 and K_2CO_3, in $N_{1,8,8,8}NTf_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0: monitoring potential decomposition of ionic liquids and 1.

1,3-PDO (in Table S36, see 1,3-PDO in entry 1), **1** (in Table S36, see **1** in entry 1), K_2CO_3 (in Table S36, see K_2CO_3 in entry 1), and $N_{1,8,8,8}NTf_2$ (in Table S36, see $N_{1,8,8,8}NTf_2$) were mixed in a 50 mL round bottom flask connected, through a distillation condenser, to a 50 mL glass tube. The mixture was reacted at 150 °C, at a controlled pressure of *ca.* 0.35 bar, for 1 hour, stirring at 1000 rpm. The reaction product, a colourless liquid, was isolated by distillation, being collected, for the duration of the 1 hour reaction, in the collecting glass tube kept at *ca.* -196 °C (N_2 (l) bath). The reacted mixture, left in the 50 mL round bottom flask, was analysed by ^1H NMR spectroscopy. The reaction was repeated reacting 1,3-PDO, **1**, K_2CO_3, and $N_{1,8,8,8}NTf_2$ for 2 (Table S36, entry 2), 3 (Table S36, entry 3), 4 (Table S36, entry 4), 5 (Table S36, entry 5), and 6 (Table S36, entry 6) hours. The reacted mixture, left in the 50 mL round bottom flask in each of such reactions, was analysed by ^1H NMR spectroscopy.

HTID of 1,3-PDO in the presence of 1 and K_2CO_3, in $EmmimNTf_2$ and $N_{1,8,8,8}NTf_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 75.0: monitoring iridium hydride complexes formation.

1,3-PDO (in $EmmimNTf_2$: 0.1245 g, 0.0016 mol; in $N_{1,8,8,8}NTf_2$: 0.1257 g, 0.0016 mol), **1** (in $EmmimNTf_2$: 0.0120 g, 0.021 mmol; in $N_{1,8,8,8}NTf_2$: 0.0112 g, 0.020 mmol), K_2CO_3 (in $EmmimNTf_2$: 0.0068 g, 0.049 mmol; in $N_{1,8,8,8}NTf_2$: 0.0069 g, 0.050 mmol), and $EmmimNTf_2$ (0.2789 g, 0.688 mmol) or $N_{1,8,8,8}NTf_2$ (0.4510 g, 0.695 mmol) were mixed in a 50 mL round bottom flask connected, through a distillation condenser, to a 50 mL glass tube. The mixture was reacted at 150 °C, at a controlled pressure of *ca.* 0.35 bar, for 3 hours, stirring at 1000 rpm. The reaction product, a colourless liquid, was isolated by distillation, being collected, for the duration of the 3 hours reaction, in the collecting glass tube kept at *ca.* -196 °C (N_2 (l) bath). The reacted mixture, left in the 50 mL round bottom flask, was analysed by ^1H NMR spectroscopy.

Table S36. HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}NTf_2$, at T 150 °C, and at [1,3-PDO]:[Ir] ≅ 220.0: experimental data for experiments on monitoring potential decomposition of ionic liquids and **1**.

Entry	1,3-PDO [g]	n(1,3-PDO) [mol]	**1** [g]	n(**1**) [mmol]	K_2CO_3 [g]	n(K_2CO_3) [mmol]	$N_{1,8,8,8}NTf_2$ [g]	n($N_{1,8,8,8}NTf_2$) [mol]
1	0.1244	0.0016	0.0115	0.020	0.0064	0.046	0.4615	0.0007
2	0.1245	0.0016	0.0124	0.022	0.0062	0.045	0.4750	0.0007
3	0.1209	0.0016	0.0119	0.021	0.0063	0.045	0.4650	0.0007
4	0.1223	0.0016	0.0112	0.020	0.0068	0.049	0.4623	0.0007
5	0.1152	0.0015	0.0112	0.020	0.0069	0.050	0.4781	0.0007
6	0.1205	0.0016	0.0121	0.021	0.0066	0.048	0.4633	0.0007

All operations were carried out (a) at P = 0.35 bar; (b) at RPM: 1000.

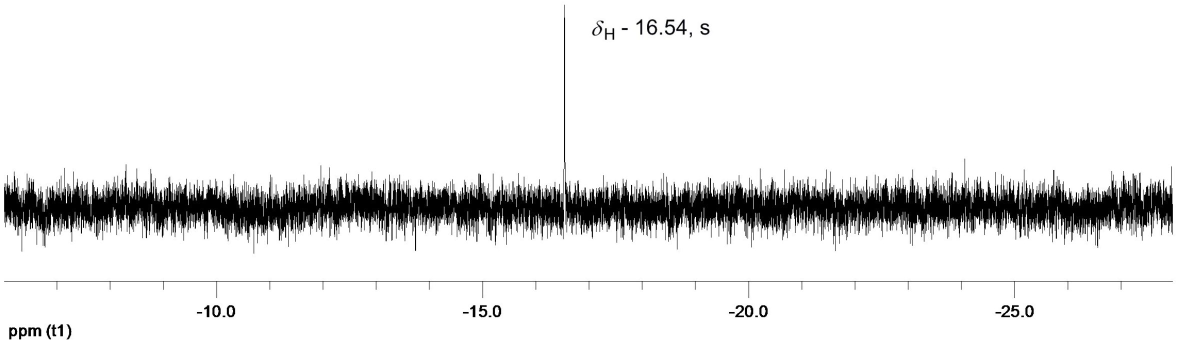


Figure S14. ^{1}H NMR spectrum of the reacting mixture of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in $N_{1,8,8,8}NTf_2$, at 150 °C, and at a dynamic vacuum of *ca.* 0.35 bar: enlargement of the hydride region (δ_H - 6.00 - δ_H - 28.00).

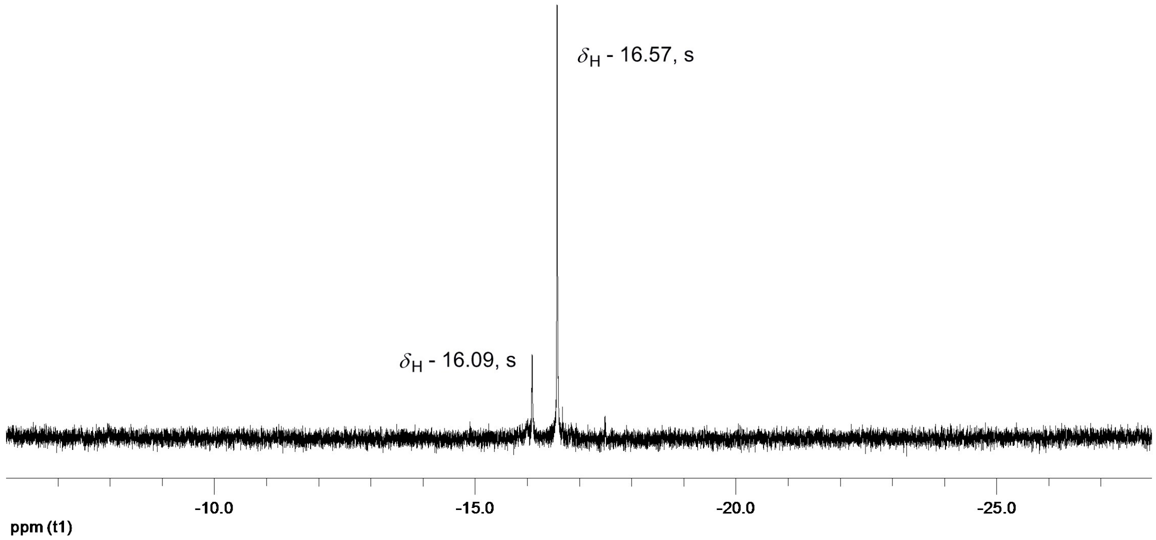


Figure S15. ^{1}H NMR spectrum of the reacting mixture of HTID of 1,3-PDO in the presence of **1** and K_2CO_3, in EmmimNTf$_2$, at 150 °C, and at a dynamic vacuum of *ca.* 0.35 bar: enlargement of the hydride region (δ_H - 6.00 - δ_H -28.00).

Figure S16. Experimental apparatus for the HTID of 1,3-PDO in the presence of **1** and a base, in ionic liquids, towards selective production of propionaldehyde.