Metal-free catalytic systems based on imidazolium chloride and strong bases for selective oxidative esterification of Furfural to Methyl Furoate

Beatriz Fuerte-Díez,[a] Elizabeth Rangel-Rangel,[a,] Marta Iglesias,[a] and Eva M. Maya,[a,*]*

[a] Instituto de Ciencia de Materiales de Madrid . CSIC. Sor Juana Inés de la Cruz, 3, 28049, Spain.

e-mail: eva.maya@csic.es, e.rangel.r.21@csic.es

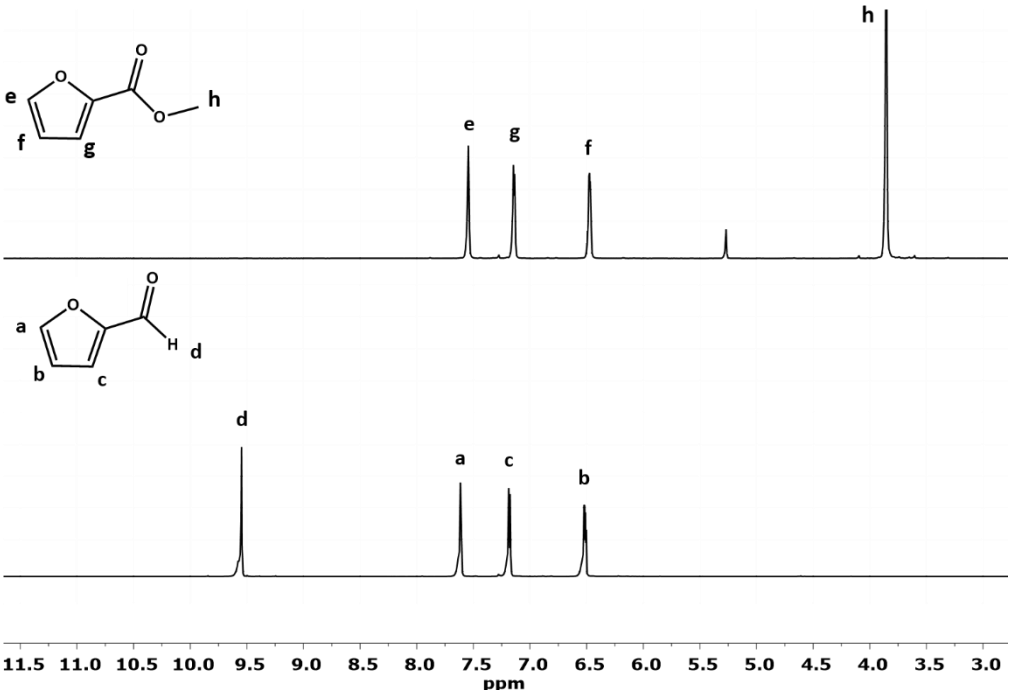

Figure S1. ^{1}H-NMR spectra of commercial furfural and 2-methyl Furoate.

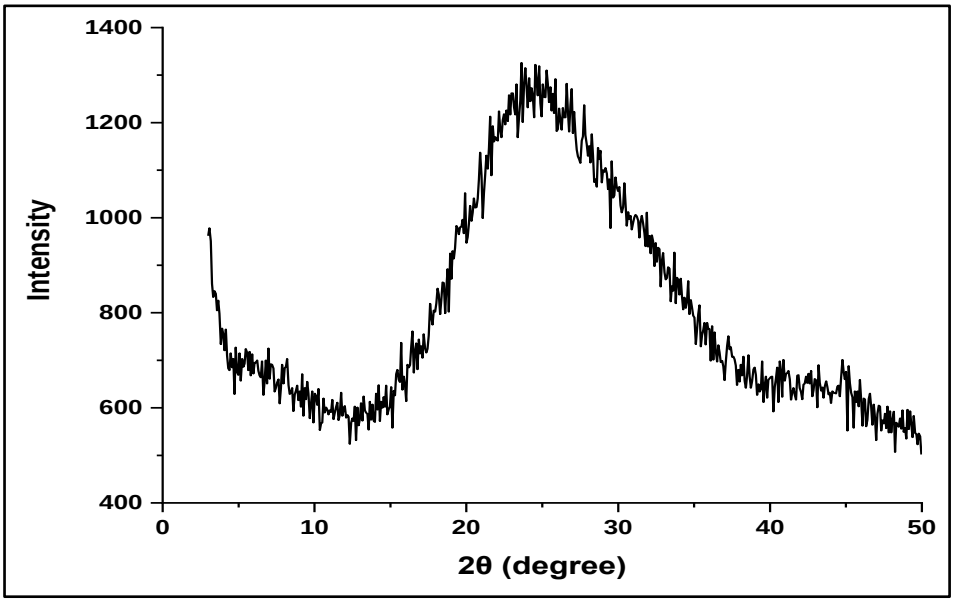

Figure S2. PXRD difractogram of HCP-BzmimCl.

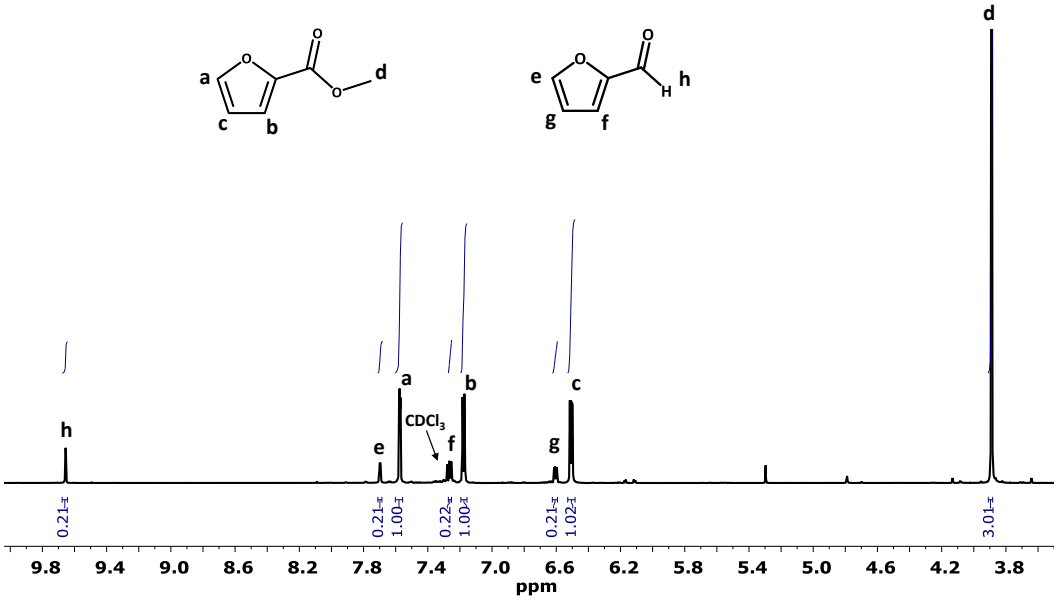

Figure S3. ^{1}H-NMR ($CDCl_3$) spectrum of run 8, Table 1. Reaction conditions: 1.0 mmol of furfural, 1.0 mmol of HCP-BzmimCl, 0.5 mmol of Cs_2CO_3, 2 mL MeOH, 24 h, P(O2) = 5 bar, T= 60 °C.

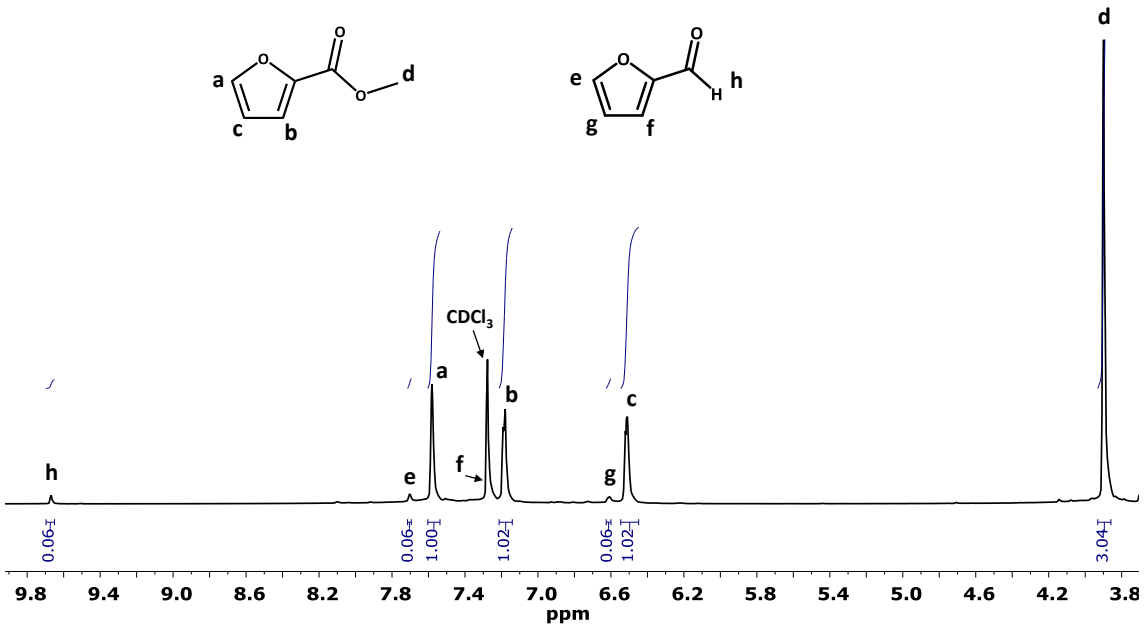

Figure S4. ^{1}H-NMR ($CDCl_3$) spectrum of run 10, Table 1. Reaction conditions: 1.0 mmol of furfural , 1.0 mmol of HCP-BzmimCl, 1.0 mmol of Cs_2CO_3, 2 mL MeOH, 24 h, P(O_2) = 5 bar, T= 60°C.

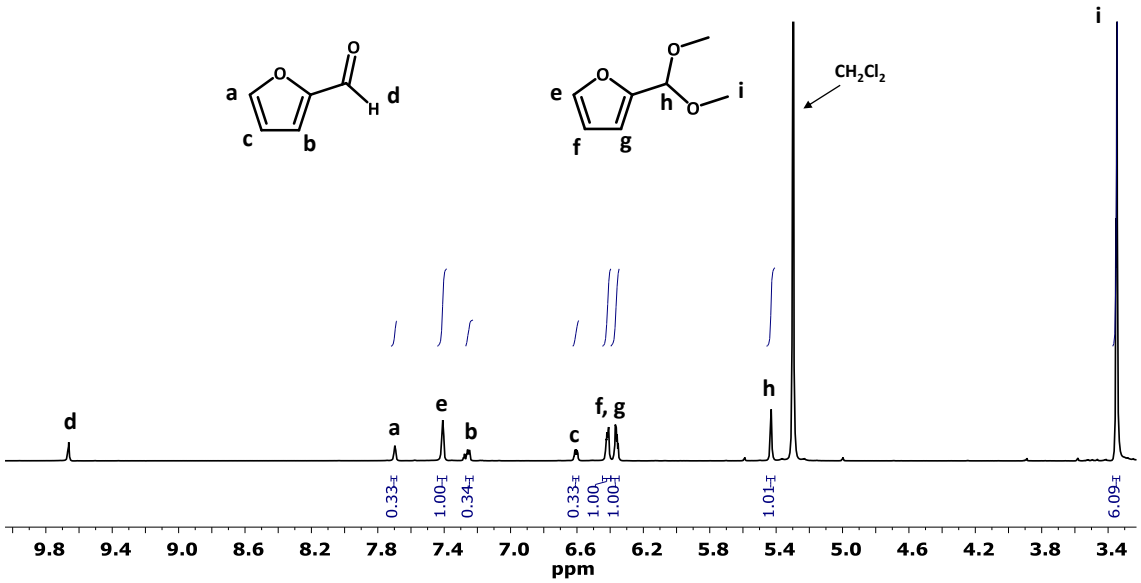

Figure S5. ^{1}H-NMR ($CDCl_3$) spectrum of run 11, Table 1. Reaction conditions: 1.0 mmol of furfural, 1.0 mmol of HCP-BzmimCl, without base, 2 mL MeOH, 24 h, $P(O_2)$ = 5 bar, T 60 °C. CH_2Cl_2: Dichloromethane.

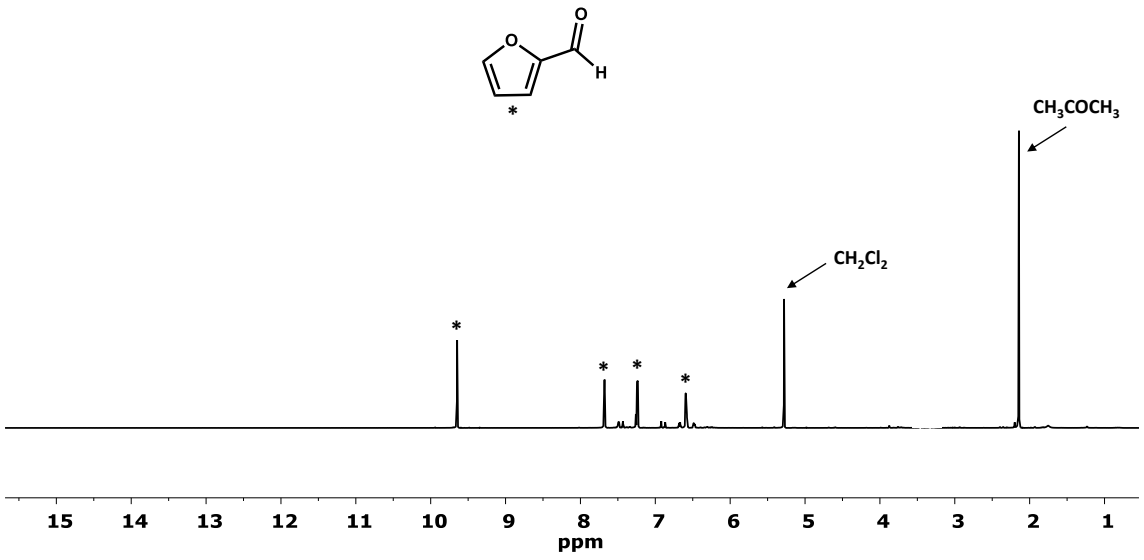

Figure S6. ^{1}H-NMR ($CDCl_3$) spectrum of run 12, Table 1. Reaction conditions: 1.0 mmol of furfural, 1.0 mmol of Cs_2CO_3, 2 mL MeOH, 24 h, $P(O_2)$ = 5 bar, T 60 °C. CH_2Cl_2. Dichloromethane, CH_3COCH_3: acetone

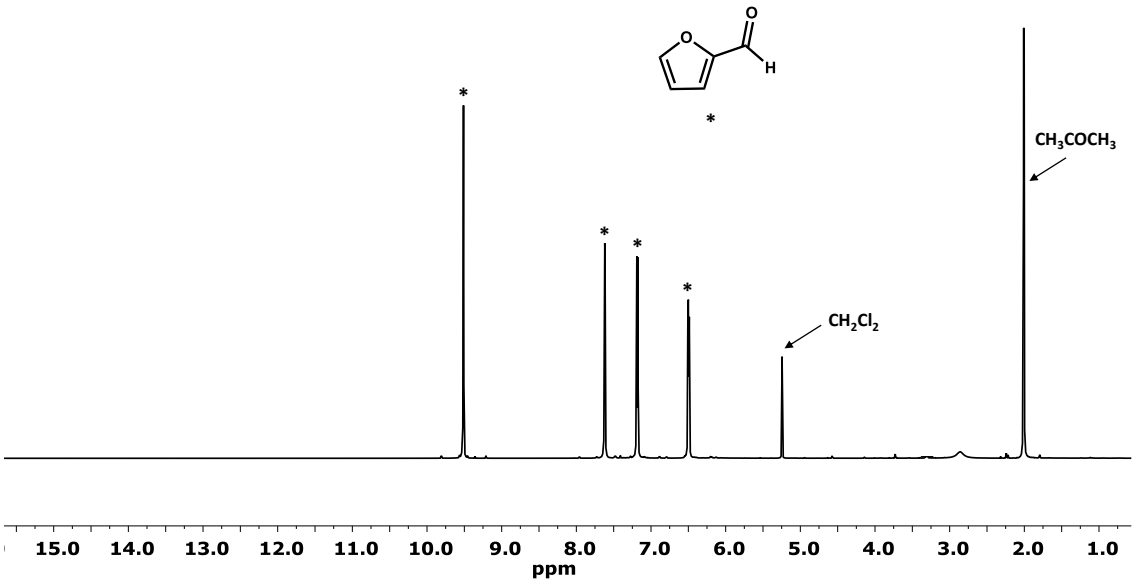

Figure S7. ^{1}H-NMR ($CDCl_3$) spectrum of run 13, Table 1. Reaction conditions: 1.0 mmol of furfural, 1.0 mmol of Cs_2CO_3, 1.0 mmol of HCP-BzmimCl, 2 mL MeOH, 24 h, P(N_2) = 2 bar, T 60 °C. CH_2Cl_2. Dichloromethane, CH_3COCH_3: acetone

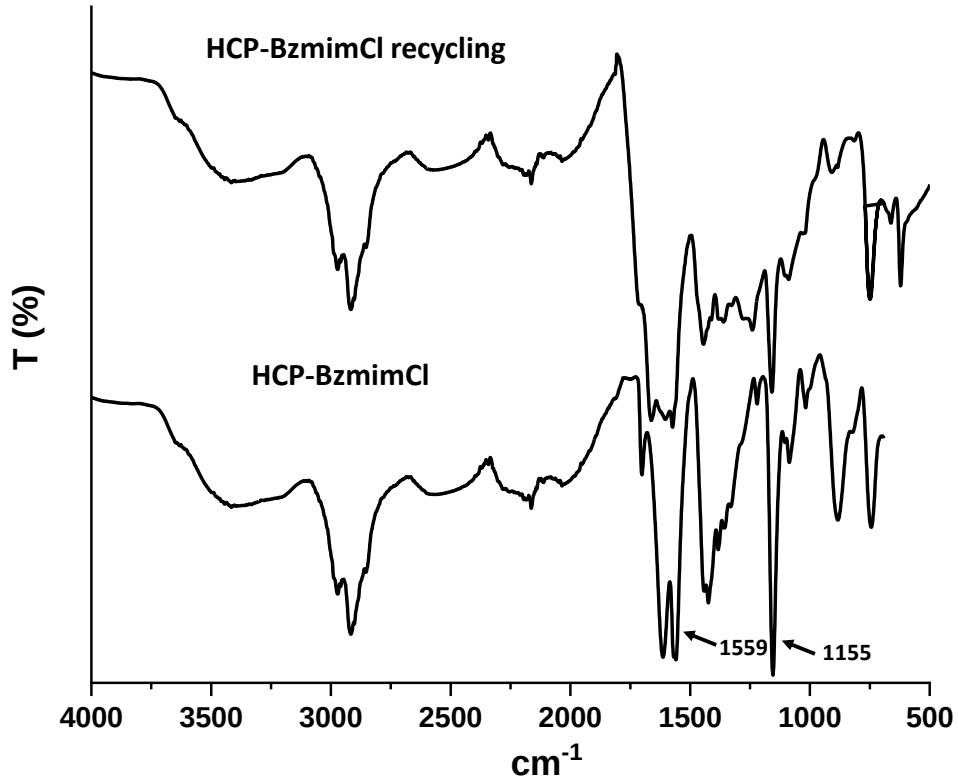

Figure S8. FT-IR of HCP-BzmimCl catalyst fresh and recovered after recycling experiments.

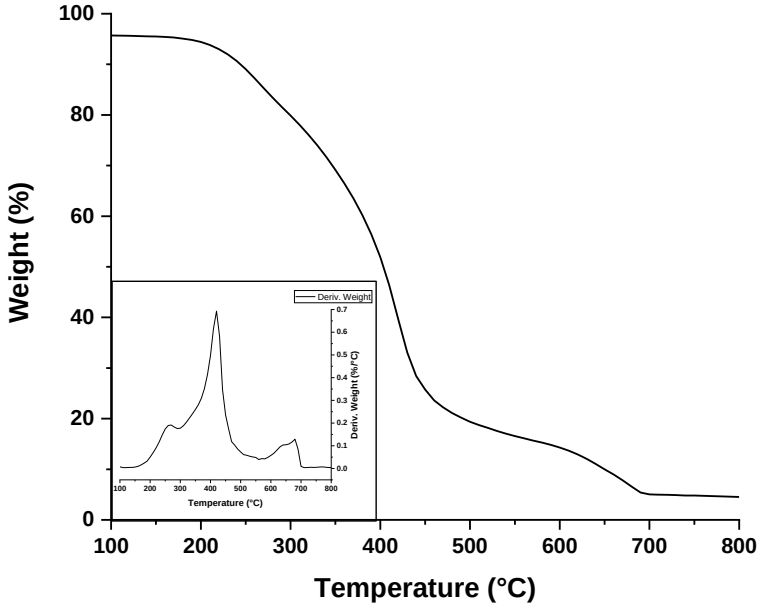

Figure S9. TGA of HCP-BzmimCl after recycling experiments.

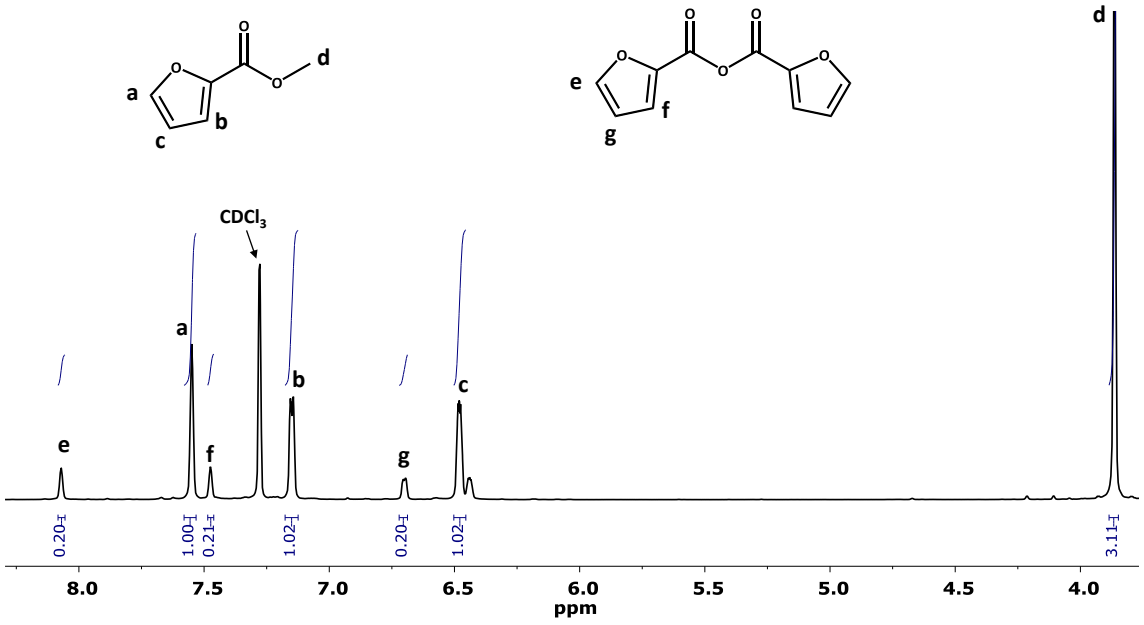

Figure S10. ^{1}H-NMR of run 5 of Table 2. Reaction conditions: 1.0 mmol FA, 0.5 mmol HCP-BzmimCl, 1.2 mmol of DBU, 2 mL MeOH, 24 h, P(O_2) = 5 bar, T= 60 °C.

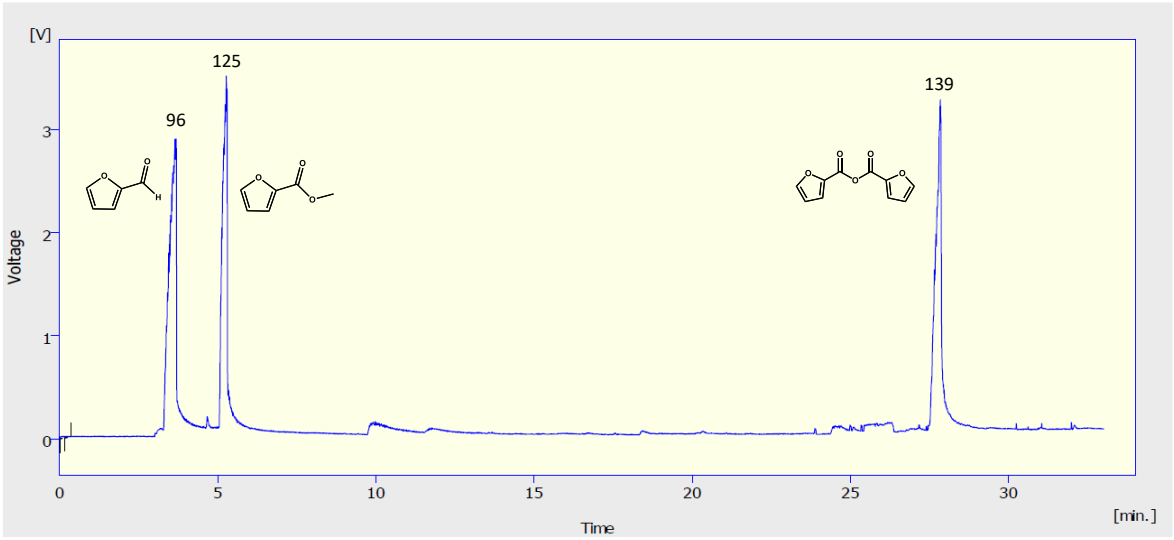

Figure S11. GC Chromatogram of run 5 of Table 2. Reaction conditions: 1.0 mmol FA, 0.5 mmol HCP-BzmimCl, 1.2 mmol of DBU, 2 mL MeOH, 24 h, $P(O_2)$ = 5 bar, T= 60 °C.

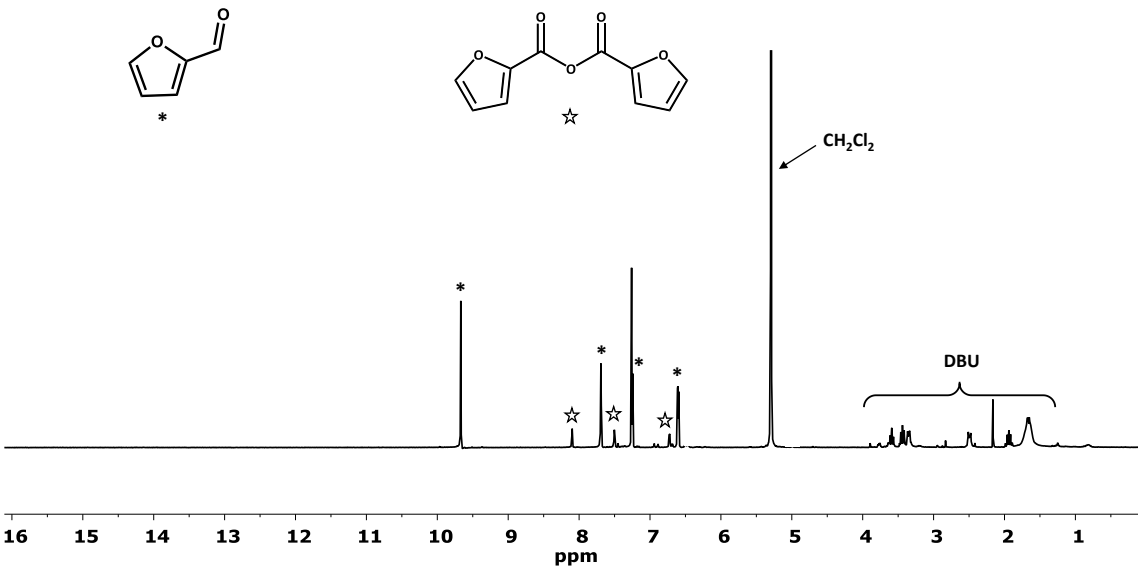

Figure S12. ^{1}H-NMR ($CDCl_3$) spectrum of run 10, Table 2. Reaction conditions: 1.0 mmol FA, 1.2 mmol of DBU, 2 mL MeOH, 24 h, $P(O_2)$ = 5 bar, T 60 °C. CH_2Cl_2: Dichloromethane.

Table S1. Elemental analysis of HCP-BzmimCl catalyst.

Catalyst		C(%)	H(%)	N(%)	C/H	N/H
HCP-BzmimCl	Calculated[a]	72.53	6.04	9.40	12.00	1.55
HCP-BzmimCl	Experimental	67.35	5.86	8.57	11.49	1.46

[a]Two units of BzmimCl per biphenyl.

Table S2. Selected literature data for oxidative esterification of furfural using O2 as an oxidizing agent

Catalyst	T (°C)	$P(O_2)$	time	Furfural Conv. (%)	MF Select. (%)	Ref.
Au/ZrO_2	100	1	90 min	90	98	9
AuZ400	120	6	6 h	99	95	10
AuZ	120	6	90 min	100	100	11
$Au25(SG)_{18}/ZrO_2$	100	6	24 h	100	100	12
Ce500Au500	120	6	90 min	74	100	13
$Au/TiO_2/NaOCH_3$	22	1	10-12 h	100	n.r.	14
Z-Au	120	5	90 min	82	92	16
Au/MgO	110	6	2 h	98	97	17
nano Au $/K_2CO_3$	140	3	4 h	91.8	98.7	18
Au/CMK-3	120	15	3 h	99.7	99.6	19
NCH/DBU	25	1	24 h	n.r	63	22
1)NCH/DBU 2)CAL-B	40	1	1)4h 2)24 h	81.4	83.7	23
$BzmimCl/Cs_2CO_3$	60	5	24	82	100	*This work*
BzmimCl/DBU	60	5	24	100	92	*This work*
$HCP\text{-}BzmimCl/Cs_2CO_3$	60	5	24	94	100	*This work*
HCP-BzmimCl/DBU	60	5	24	98	100	*This work*