Supported Ionic Liquid-Like Phases (SILLPs) for enzymatic processes: Continuous KR and DKR in SILLP–scCO$_2$ systems

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Supporting information

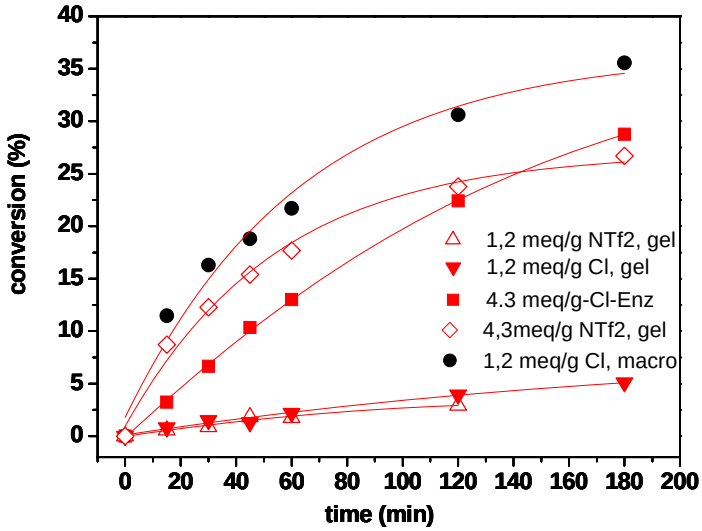

Figure S1. Conversion vs. time for the synthesis of (R)- 1-phenyl propionate catalysed by different CALB-SILLPs. **7** (1.1 meq Cl/g, R=C_4H_9, X=Cl, gel-typel); **8** (1.1 meq Cl/g, R=C_4H_9, X=NTf_2, gel-typel); **9** (4.3 meq Cl/g, R=C_4H_9, X=Cl, gel-typel); **10** (4.3 meq Cl/g, R=C_4H_9, X=NTf_2, gel-typel); **11** (1.2 meqCl/g, R=C_4H_9, X=Cl, macroporous).

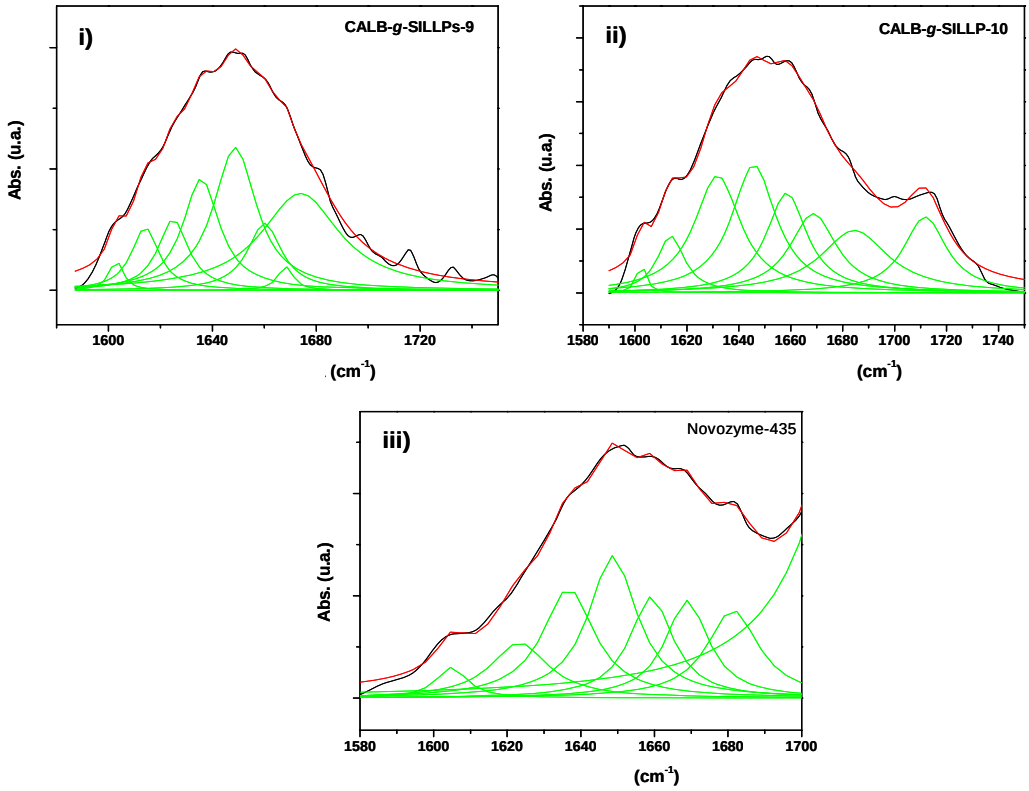

Figure S2. ATR-FT-IR for different CALB-SILLPs. i) CALB-g-SILLP-**9** (gel-type and high loading, X = Cl^-), ii) CALB-g-SILLP-**10** ((gel-type and high loading, X = NTf_2^-), iii) Novozyme 435.

Table S1. Peaks and ares corresponding to deconvolution of the amide I for different as CALB-g-SILLPs and Novozyme 435.

	CALB-*g*-SILLP-**9**		CALB-*g*-SILLP-**10**		**Novozyme 435**	
Entrada	**Peak (cm^{-1})**	**Area (%)**	**Peak (cm^{-1})**	**Area (%)**	**Peak (cm^{-1})**	**Area (%)**
1	1603	1.7	1602	1.0	1605	3.1
2	1614	7.0	1614	5.5	1623	10.6
3	1625	8.7	1632	19.3	1637	19.1
4	1636	16.5	1646	20.3	1649	23.1
5	1649	24.7	1658	14.3	1658	14.6
6	1660	9.2	1669	13.1	1669	14.1
7	1668	1.5	1684	15.0	1681	15.3

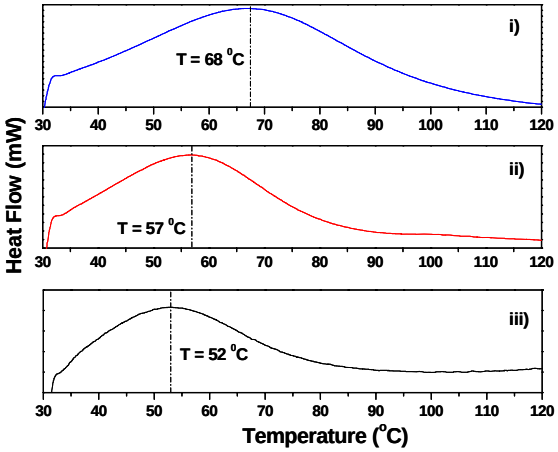

Figure S3. DSC for the corresponding supported enzyme. **i**) CALB-g-SILLP-**9** (4.3 meq Cl/g, R=C_4H_9, X=Cl), **ii**) CALB-g-SILLP-**10** (4.3 meq Cl/g, R=C_4H_9, X=NTf_2), **iii**) Novozyme 435.

Table S2 DKR of phenyletahnol with supported chemo and biocatalysts.

Reference	**DKR catalytic systemt**	**Acylating agent**	**System**	**Re-used**	**T (^{o}C)**	**Yield**	**ee**
Chem. Commun. **2003**, 1928 Chem Eur J. **2005**, 11, 386	CP814-E22 (zeolite) Novozyme 435	Vinyl octanoate (VO) Vinyl acetate (VO)	Biphasic (octane:water 50:50 mL), physically isolate, batch	2 reused	60	90% 18%	>99% >99%
Chem Eur J **2007**, 13, 541	Zr-beta-zeolite, Novozyme 435 Al-150 CALB	VO VO Vinyl butyrate (VB) VA	Monophasic (toluene) “one-pot”, batch	No data	60 (48h) 60	93 85-88%	83% 98% 92% 65%
Green Chem. **2007**, 9, 1104	$VOSO_4$, Novozyme 435	VO, (octane) VO (toluene)	Monophasic, isolated, batch		80 (3.5h)	93% 93%	99% 76%
Org. Lett.**2005**, 7,4523	PS-DVB-Ru-complex Novozyme 435	isopropenyl acetate and K3PO4	Monophasic Toluene “onepot”, batch	4 cycles 4th 99% ee 36% yield	25 (20h)	99%	99%
Green Chem **2009**, 11, 617	$[Ru(p\text{-}cymene)Cl_2]_2$ PSCI NafionSAC13 PSCI	Phenyl acetate, acetpphenone, tetrametlyl propane diamine Vinyl acetate	$scCO_2$ Batch, one-pot		40 (^{o}C) 10MPa	69% 81%	91-95% 85%
Biotechnol Lett **2006** 28 1559–1565	SCX (Silica gel modified with benzenesul Phonic acid groups) coated with IL (7.5 ul/mg SCX) Novozyme 435 coated with IL (1.8 ml/g of Novo435)	Vinyl propionate	Continuous Solid-IL-sscCO_2-IL-solid Physically isolated	Continuous used	40 (^{o}C) 10MPa	78%	97%
Green chem. **2009**, 11, 538	CP811E coated with [BMIN][PF6] Novozyme 435 coated with [BMIN][PF6]	Vinyl propionate	Continuous one-pot Solid-IL-sscCO_2-IL-solid	Continuous used	40 (^{o}C) 10MPa	73%	99%
This work	CALB-SILLP-**11** CP811E-150 coated with $[BtmA][NTf_2]$	Vinyl propionate	Continuous one-pot Solid-$scCO_2$-IL-solid	Continuous use 6 days	50 (^{o}C) 10MPa	**92%**	**>99%**