Safer bio-based solvents to replace toluene and tetrahydrofuran for the biocatalyzed synthesis of polyesters

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Table S1. CaLB-catalyzed synthesis of poly(1,4-butylene adipate) in solventless- and organic media-based reaction systems.

					^{1}H-NMR	GPC			
Monomers Amount [mol]	**Enzyme Amount [g]**	**Media**	**Amount**	**T [°C]**	**Monom. Conv. [%]**	**M_n**	**M_w**	**Đ**	
0.012	0.1586	Solventless		85	89	2227	2843	1.31	[1]
0.0016	0.02	TOL	4mL	85	81	1990	2361	1.19	This work
		TMO			77	1771	2449	1.33	
		PIN			77	2368	2721	1.15	
		TOL		50	45	744	974	1.25	
		TMO			83	2022	2339	1.16	
		PIN			90	2500	3046	1.20	
		THF			87	1674	2015	1.20	
		MeTHF			86	2051	2648	1.29	
		2MeTHF			57	841	1222	1.45	

[1] Pellis A. et al. **2018**, *Eur. Polym. J.*, 106, 79-84

Table S2. CaLB-catalyzed synthesis of poly(1,8-octylene adipate) in organic media-based reaction systems.

					^{1}H-NMR	GPC		
Monomers Amount [mol]	**Enzyme Amount [g]**	**Media**	**Amount**	**T [°C]**	**Monom. Conv. [%]**	**M_n**	**M_w**	**Đ**
0.0016	0.02	TOL	4mL	85	81	1990	2361	1.19
		TMO			77	1771	2449	1.33
		PIN			77	2368	2721	1.15
		TOL		50	45	744	974	1.25
		TMO			83	2022	2339	1.33
		PIN			90	2500	3046	1.20
		THF			87	1674	2015	1.20
		MeTHF			86	2051	2648	1.29
		2MeTHF			69	841	1222	1.45

Table S3. CaLB-catalyzed synthesis of poly(1,4-butylene 2,5-furandicarboxylate) in organic media-based reaction systems.

					^{1}H-NMR
Monomers Amount [mol]	**Enzyme Amount [g]**	**Media**	**Amount**	**T [°C]**	**Monom. Conv. [%]**
0.0016	0.02	TOL	4mL	85	30
		TMO			40
		PIN			51
		TOL		50	23
		TMO			43
		PIN			55
		THF			39
		MeTHF			59
		2MeTHF			53

Table S4. CaLB-catalyzed synthesis of poly(1,8-octylene 2,5-furandicarboxylate) in organic media-based reaction systems.

					^{1}H-NMR
Monomers Amount [mol]	**Enzyme Amount [g]**	**Media**	**Amount**	**T [°C]**	**Monom. Conv. [%]**
0.0016	0.02	TOL	4mL	85	44
		TMO			35
		PIN			41
		TOL		50	40
		TMO			24
		PIN			29
		THF			20
		MeTHF			41
		2MeTHF			39

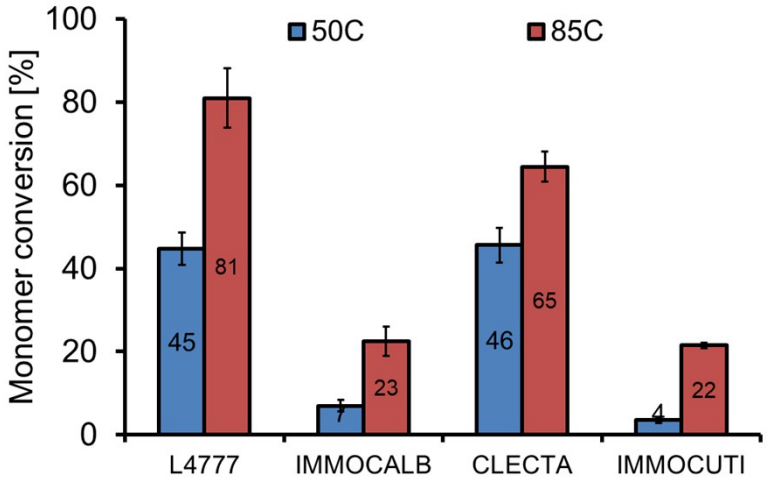

Figure S1. Monomer conversion values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in TOL.

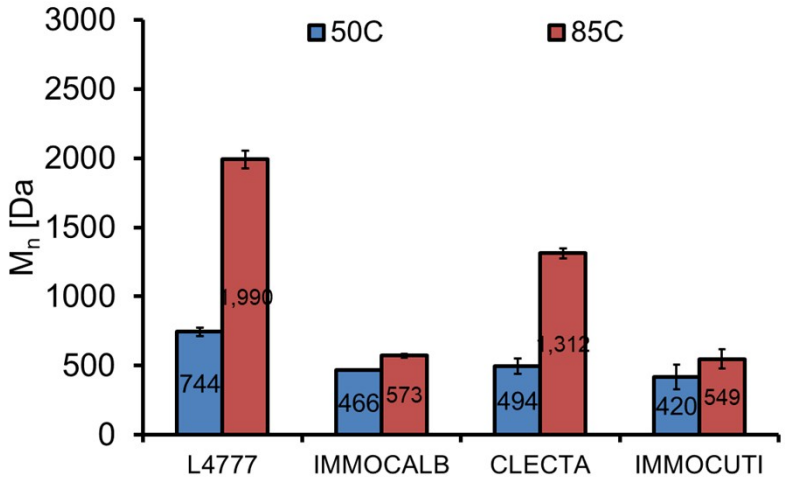

Figure S2. Molecular masses values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in TOL.

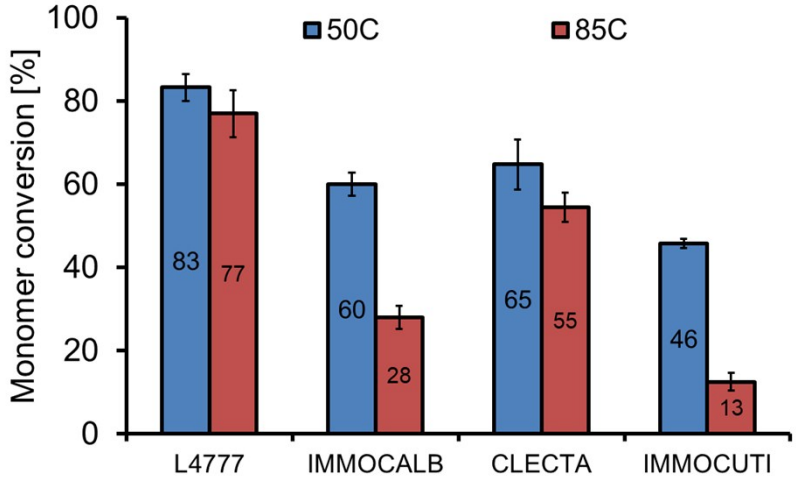

Figure S3. Monomer conversion values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in TMO.

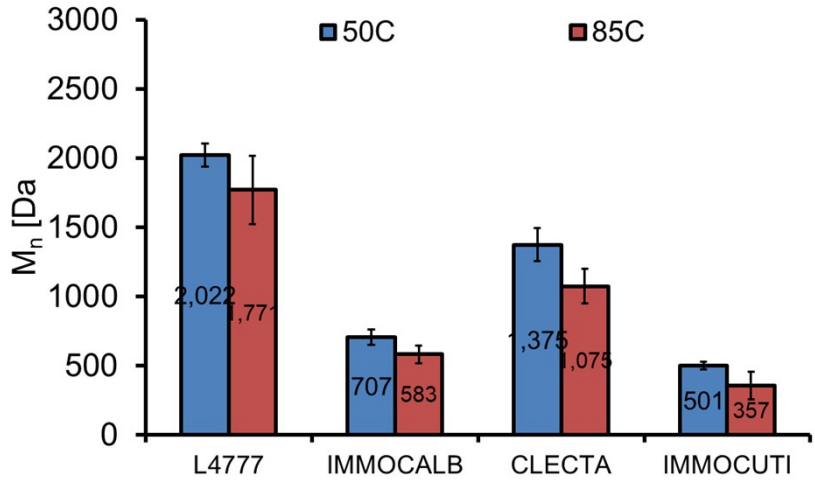

Figure S4. Molecular masses values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in TMO.

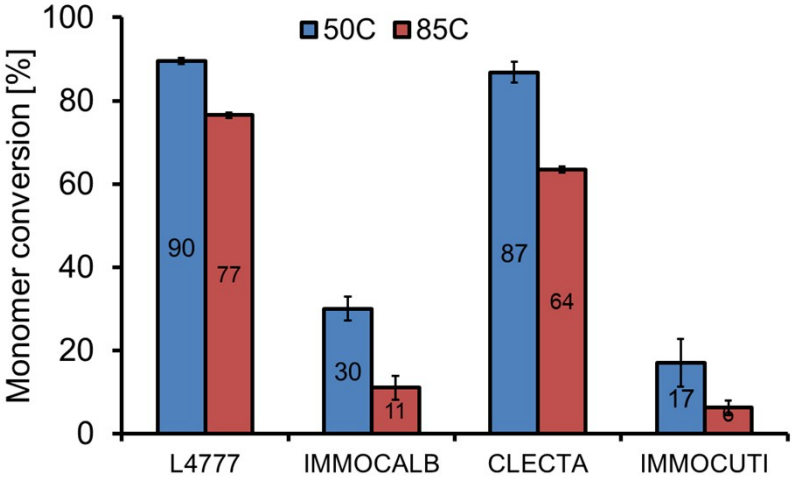

Figure S5. Monomer conversion values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in PIN.

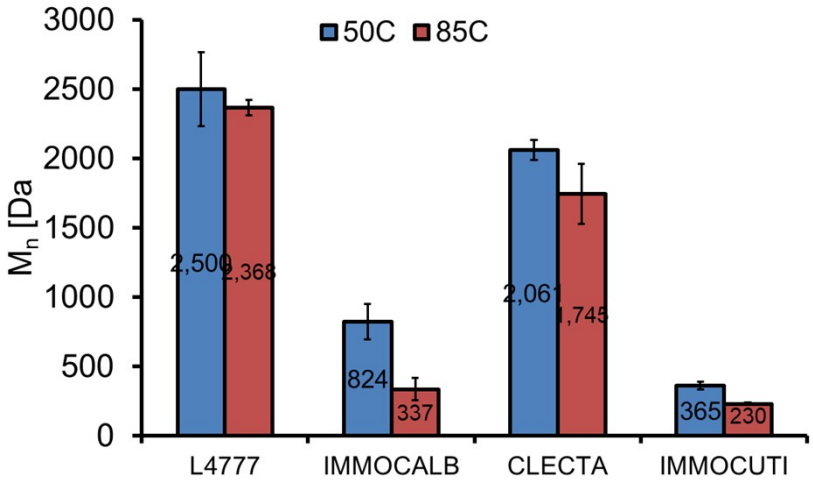

Figure S6. Molecular masses values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in PIN.

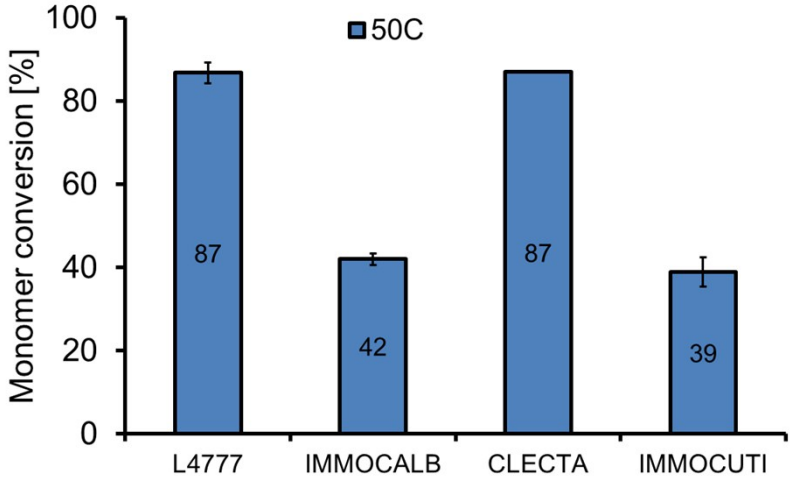

Figure S7. Monomer conversion values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in THF.

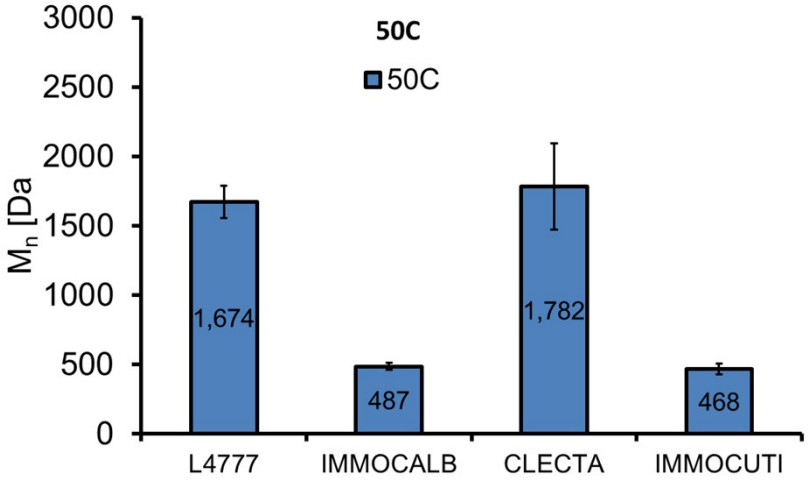

Figure S8. Molecular masses values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in THF.

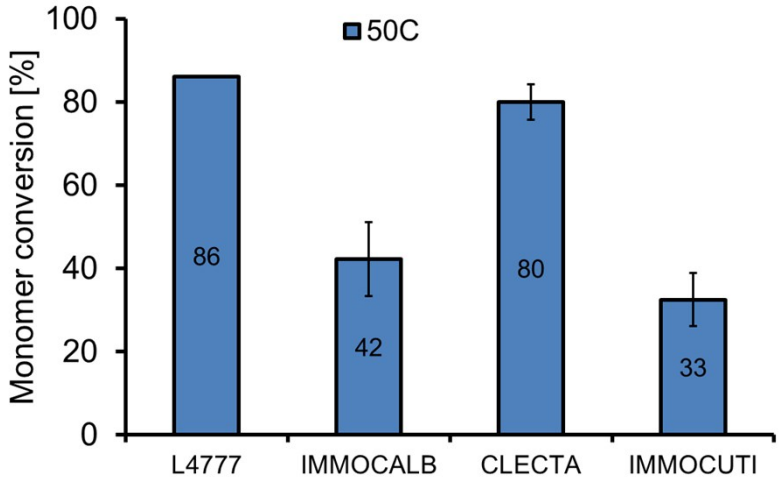

Figure S9. Monomer conversion values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in MeTHF.

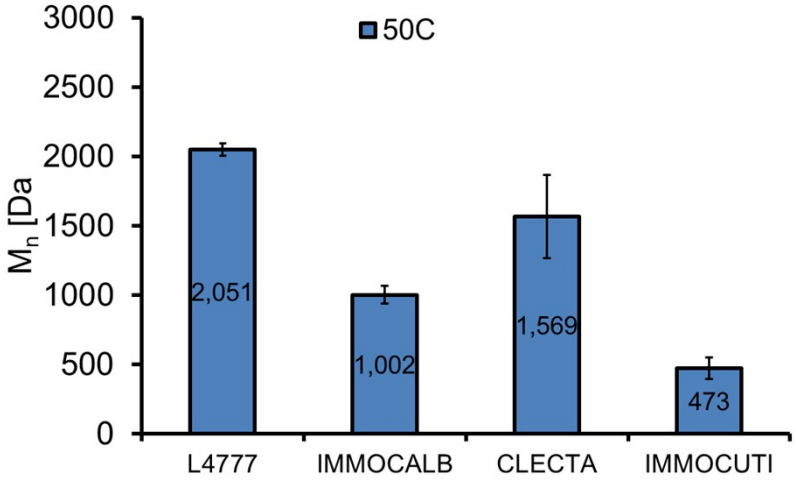

Figure S10. Molecular masses values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in MeTHF.

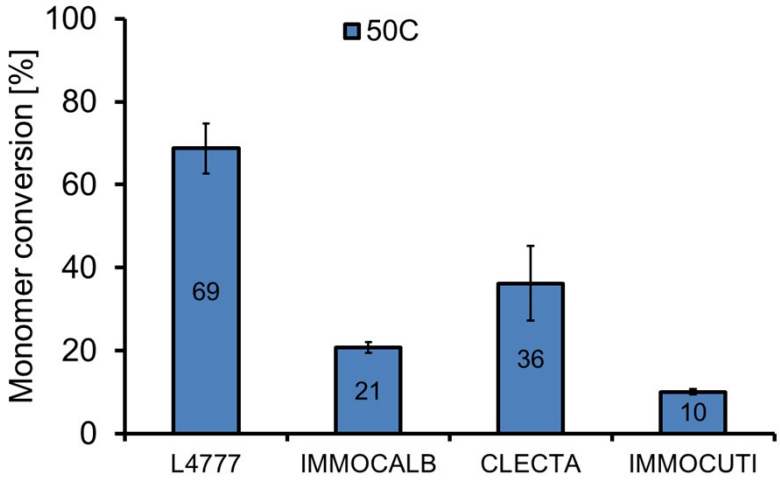

Figure S11. Monomer conversion values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in DMeTHF.

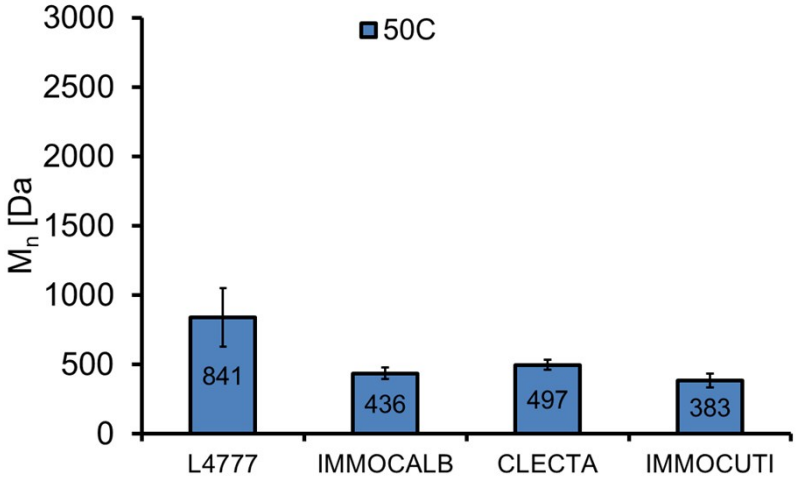

Figure S12. Molecular masses values of the biocatalyzed synthesis of poly(1,4-butylene adipate) in DMeTHF.

Table S5. COSMO-RS calculations of the c0 conformers energies of interactions in 1) standard conditions; 2) interactions without considering hydrogen bonding; 3) interactions without considering Van der Waals forces and 4) interactions without considering hydrogen bonding and Van der Waals forces.

Toluene	Standard			No H bonding			No VdW bonding			No H and VdW		
	30	50	85	30	50	85	30	50	85	30	50	85
DMA	-2.01265	-1.79338	-1.43983	-2.01265	-1.79338	-1.43983	4.24619	4.21078	4.13345	4.24619	4.21078	4.13345
BDO	0.01698	0.12944	0.30538	0.01698	0.12944	0.30538	3.51409	3.48599	3.42374	3.51409	3.48599	3.42374
ODO	-2.02648	-1.82002	-1.48688	-2.02648	-1.82002	-1.48688	4.01796	3.97871	3.89639	4.01796	3.97871	3.89639
DMA_BDO	-2.8115	-2.55075	-2.12839	-2.8115	-2.55075	-2.12839	4.60155	4.55991	4.47092	4.60155	4.55991	4.47092
DMA_ODO	-4.05186	-3.4484	-2.8086	-4.05186	-3.4484	-2.8086	6.57062	6.53749	6.45952	6.57062	6.53749	6.45952

THF	Standard			No H bonding			No VdW bonding			No H and VdW		
	30	50	85	30	50	85	30	50	85	30	50	85
DMA	-2.2325	-2.01917	-1.67373	-2.23191	-2.01868	-1.67337	4.03772	3.99696	3.91135	4.03831	3.99746	3.91172
BDO	-2.78382	-2.30302	-1.57225	-0.64569	-0.49564	-0.26009	0.83493	1.17035	1.65417	2.97013	2.97513	2.96434
ODO	-5.77272	-5.04265	-3.94575	-2.94184	-2.68556	-2.27593	0.52544	1.00166	1.66799	3.35208	3.35524	3.33545
DMA_BDO	-3.1178	-2.86431	-2.45245	-3.11556	-2.86243	-2.45107	4.35155	4.30204	4.20002	4.35379	4.30392	4.2014
DMA_ODO	-6.40607	-5.71576	-4.63571	-4.69939	-4.28791	-3.6165	4.24595	4.50566	4.85527	5.95026	5.93151	5.87306

2MeTHF	Standard			No H bonding			No VdW bonding			No H and VdW		
	30	50	85	30	50	85	30	50	85	30	50	85
DMA	-2.01929	-1.80643	-1.46214	-2.01876	-1.80598	-1.46181	4.23647	4.19619	4.11106	4.23701	4.19664	4.11139
BDO	-2.66423	-2.16766	-1.41547	-0.48115	-0.33135	-0.09793	0.96049	1.31182	1.81728	3.14187	3.14676	3.13399
ODO	-5.61054	-4.85751	-3.73216	-2.74715	-2.49054	-2.08131	0.70175	1.20123	1.89638	3.56359	3.5672	3.54696
DMA_BDO	-2.87906	-2.62387	-2.20923	-2.87701	-2.62216	-2.20799	4.5807	4.53386	4.43623	4.58275	4.53558	4.43747
DMA_ODO	-6.11721	-5.40913	-4.30412	-4.38512	-3.96926	-3.29088	4.53978	4.81809	5.19392	6.27089	6.25727	6.20686

25DMeTHF	Standard			No H bonding			No VdW bonding			No H and VdW		
	30	50	85	30	50	85	30	50	85	30	50	85
DMA	-1.81501	-1.60573	-1.26726	-1.81457	-1.60536	-1.26699	4.43844	4.3949	4.30449	4.43888	4.39527	4.30476
BDO	-2.20611	-1.73494	-1.03177	-0.25572	-0.11338	0.10674	1.41873	1.74484	2.20157	3.36759	3.36522	3.33944
ODO	-4.98986	-4.28065	-3.23502	-2.48219	-2.23423	-1.83936	1.32133	1.77737	2.39338	3.8279	3.82321	3.78906
DMA_BDO	-2.64896	-2.39606	-1.98496	-2.64728	-2.39467	-1.98395	4.80824	4.75952	4.65902	4.80992	4.76092	4.66003
DMA_ODO	-5.56042	-4.87562	-3.81355	-4.03368	-3.62225	-2.95105	5.09372	5.3493	5.68305	6.6197	6.60219	6.54542

TMO	Standard			No H bonding			No VdW bonding			No H and VdW		
	30	50	85	30	50	85	30	50	85	30	50	85
DMA	-1.64427	-1.43882	-1.10653	-1.64388	-1.43849	-1.1063	4.61295	4.56607	4.4703	4.61334	4.5664	4.47054
BDO	-2.41732	-1.87813	-1.07559	-0.1323	0.00769	0.22177	1.21247	1.60654	2.16257	3.49476	3.49028	3.45882
ODO	-5.20929	-4.40154	-3.22261	-2.31038	-2.06432	-1.67421	1.10842	1.6628	2.4119	4.00496	3.99863	3.96011
DMA_BDO	-2.44687	-2.19589	-1.78761	-2.44536	-2.19465	-1.78672	5.018	4.96785	4.86532	5.01952	4.96911	4.86622
DMA_ODO	-5.52213	-4.77708	-3.62995	-3.74703	-3.33469	-2.66265	5.14319	5.45926	5.8785	6.91672	6.90061	6.84547

Pinacolone	Standard			No H bonding			No VdW bonding			No H and VdW		
	30	50	85	30	50	85	30	50	85	30	50	85
DMA	-2.10077	-1.88505	-1.53407	-2.1004	-1.88473	-1.53382	4.15865	4.12021	4.04007	4.15902	4.12054	4.04033
BDO	-1.94595	-1.57187	-1.01511	-0.55691	-0.41382	-0.18875	1.66624	1.89524	2.20559	3.05411	3.05228	3.03119
ODO	-4.54024	-3.97383	-3.12931	-2.74207	-2.49169	-2.08933	1.74803	2.06164	2.47716	3.54489	3.54273	3.51645
DMA_BDO	-2.91254	-2.6534	-2.23012	-2.91103	-2.65212	-2.22916	4.54196	4.49816	4.40773	4.54346	4.49945	4.40869
DMA_ODO	-5.43835	-4.83358	-3.8851	-4.3473	-3.9313	-3.24909	5.19486	5.36982	5.58909	6.28514	6.27145	6.22465

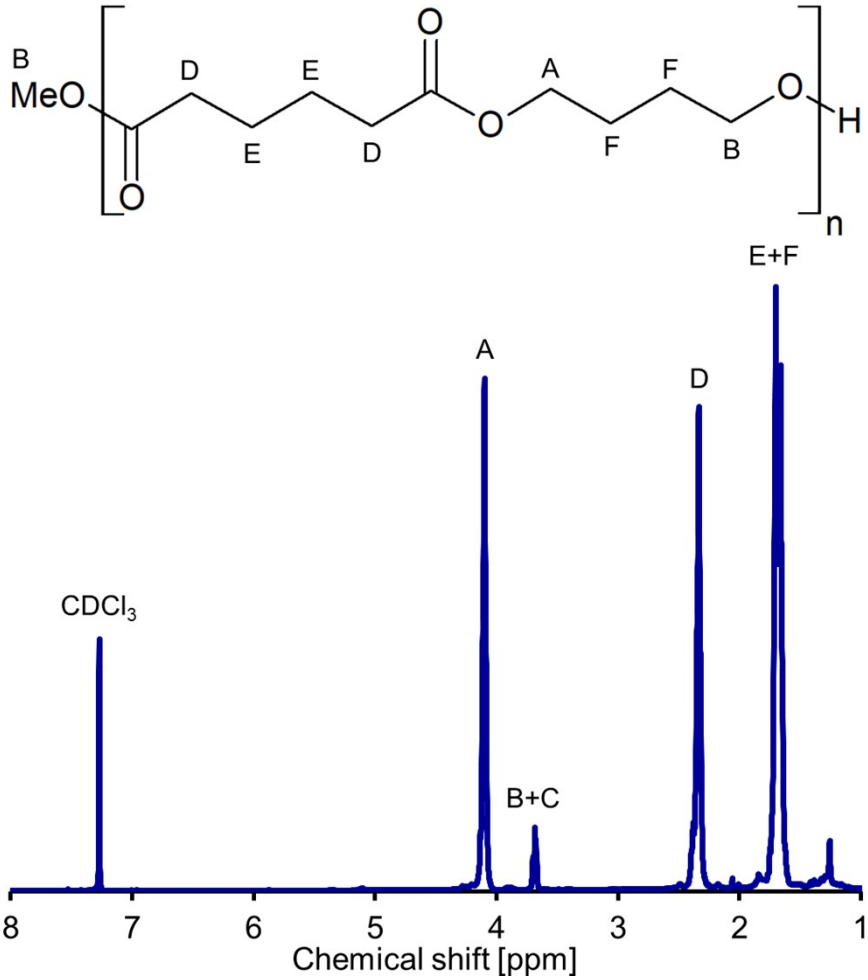

Figure S13. Fully assigned ^{1}H-NMR for the reaction between DMA and BDO catalyzed by CaLB L4777 in PIN at 50 °C.

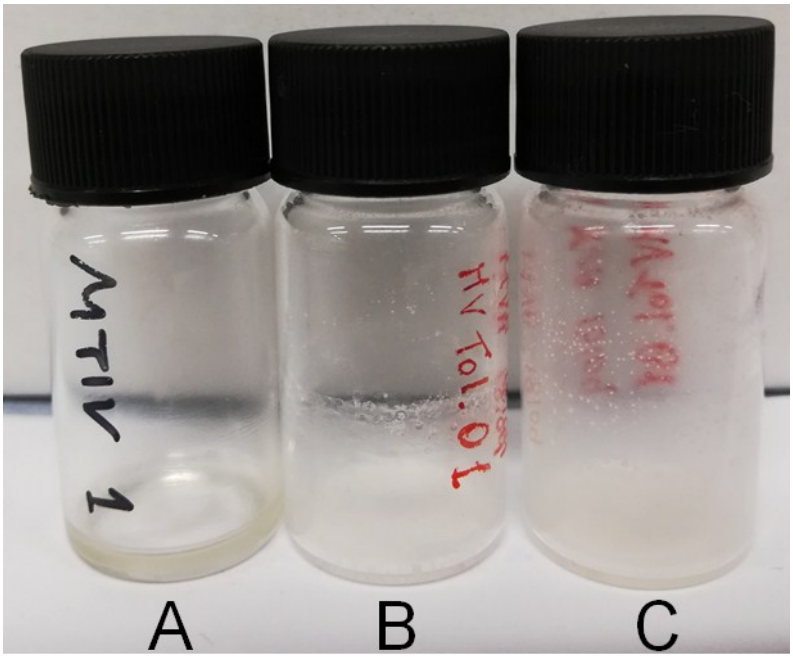

Figure S14. Photographs of the reaction products synthesized using CaLB L4777 in TOL at 50: DMA+BDO (A) DMA+ODO (B) and 85 °C: DMA+BDO (C).

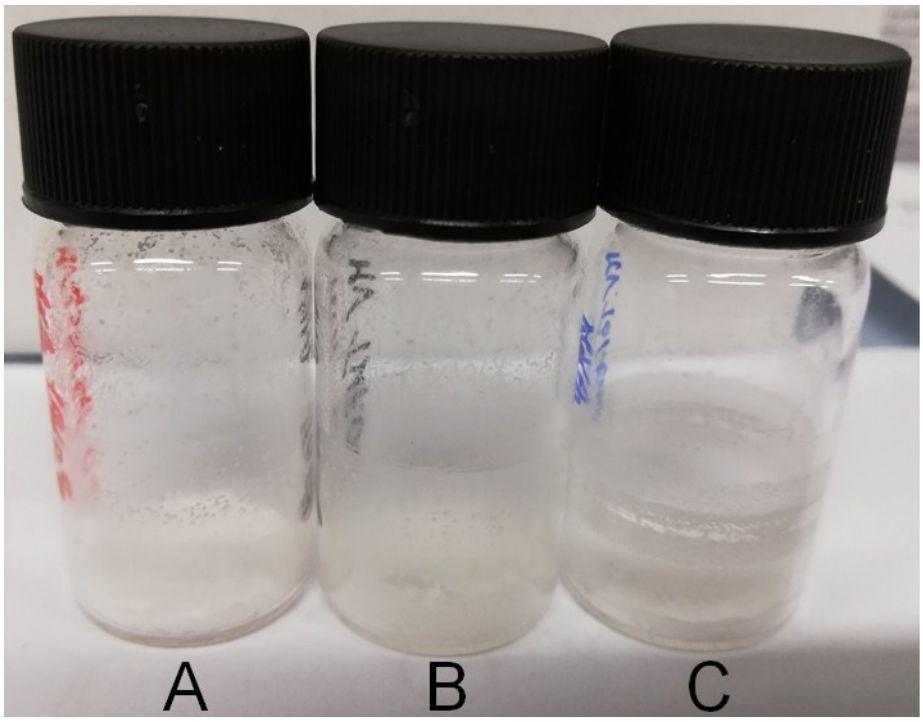

Figure S15. Photographs of the reaction products synthesized using CaLB L4777 in PIN at 30 (A), 50 (B) and 85 °C (C) starting from DMA and ODO.

Table S6. Hazard statements for solvents used in this work.

Toluene	TMO	PIN	THF	MeTHF	Me_2THF
CAS: 108-88-3	CAS: 15045-43-9	CAS: 75-97-8	CAS: 109-99-9	CAS: 96-47-9	CAS: 1003-38-9
 H315 H336	 H302	 H302 H332	 H302 H319 H335	 H302 H315 H318	Unknown acute toxicity
 H225	 H225	 H225	 H225	 H225	 H226
 H304 H361D H373	No known chronic toxicity hazards	No known chronic toxicity hazards	 H351	No known chronic toxicity hazards	No known chronic toxicity hazards
Source: ECHA	Source: SDS	Source: ECHA	Source: ECHA	Source: ECHA	Source: SDS
H225: Highly flammable liquid and vapour; H226: Flammable liquid and vapour; H302: Harmful if swallowed; H304: May be fatal if swallowed and enters airways;					

H315: Causes skin irritation; H318: Causes serious eye damage; H319: Causes serious eye irritation; H332: Harmful if inhaled; H335: May cause respiratory irritation; H336: May cause drowsiness or dizziness; H351: Suspected of causing cancer; H361D: Suspected of damaging the unborn child; H373: May cause damage to organs through prolonged or repeated exposure.