Electronic Supplementary Information (ESI)

Enzymatic synthesis of unsaturated polyesters: pre-polymerization functionalization, reversibility of the aza-Michael addition and discussion of the monomer's steric hindrance effect on the biocatalyst

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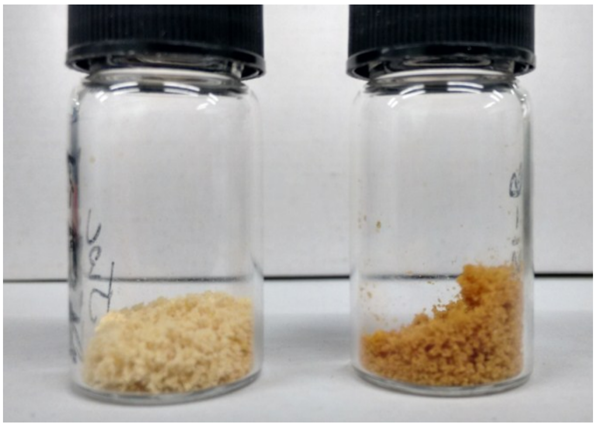

Figure S1. Products obtained from the chemocatalytic polycondensation of dimethyl itaconate with 1,4-butanediol (left) and glycerol (right). No radical inhibitor, T=24 h, 180 °C, Argon/high vacuum, Ti(OBu)$_4$ as catalyst.

Table S1. Solubility tests of A) poly(1,4-butylene itaconate) and B) poly(glycerol itaconate) synthesized via a traditional chemo-catalytic route.

Sample	Solvent									
	MeOH	**Toluene**	**CH_2Cl_2**	**$CHCl_3$**	**Hexane**	**DMSO**	**$CHCl_3$/TFA 50/50**	**$CHCl_3$/TFA 70/30**	**$CHCl_3$/TFA 80/20**	**TFA**
A	x	x	x	x	x	x	x	x	x	ps
B	x	x	x	x	x	x	x	x	x	ps

ps= partially soluble

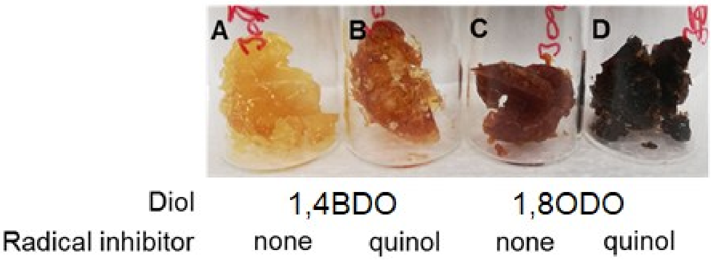

Figure S2. Products obtained from the chemocatalytic polycondensation of dimethyl itaconate with 1,4-butanediol (A & B) and 1,8-octanediol (C &D) without (A &C) and with (B & D) the use of 0.5 mol% of quinol as radical inhibitor. T=14 h, 180 °C, Argon/high vacuum, Ti(OBu)$_4$ as catalyst.

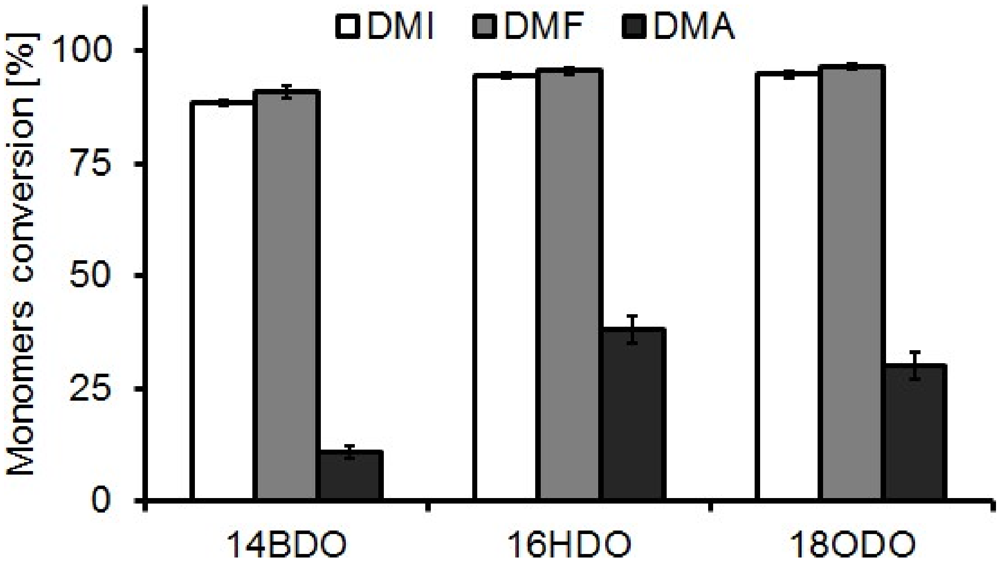

Figure S3. ^{1}H-NMR analysis of the polycondensation products of **1**, **2** and **3** with 14BDO, 16HDO and 18ODO respectively using immobilized CaLB as biocatalyst at 85 ºC for 24 h in a bulk reaction system.

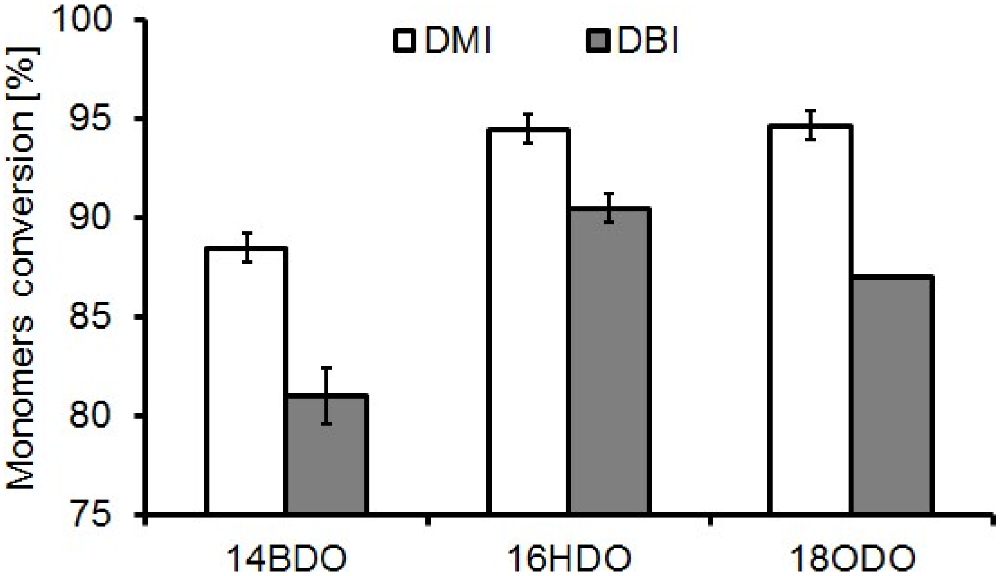

Figure S4. ^{1}H-NMR analysis of the polycondensation products of DMI (**1**) and DBI (**4**) with 14BDO, 16HDO and 18ODO respectively using immobilized CaLB as biocatalyst at 85 ºC for 24 h in a bulk reaction system.

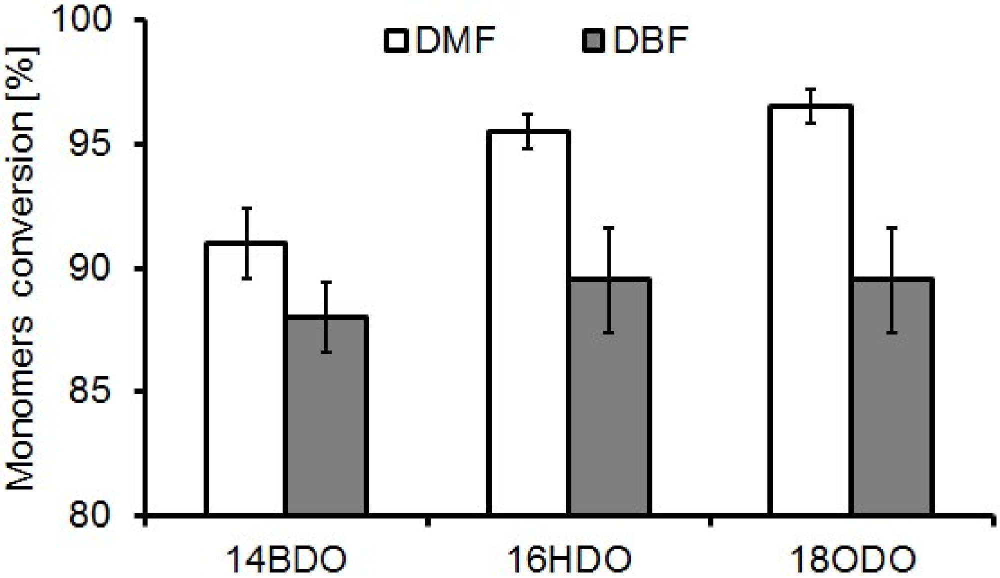

Figure S5. ^{1}H-NMR analysis of the polycondensation products of DMF (**2**) and DBF (**5**) with 14BDO, 16HDO and 18ODO respectively using immobilized CaLB as biocatalyst at 85 ºC for 24 h in a bulk reaction system.

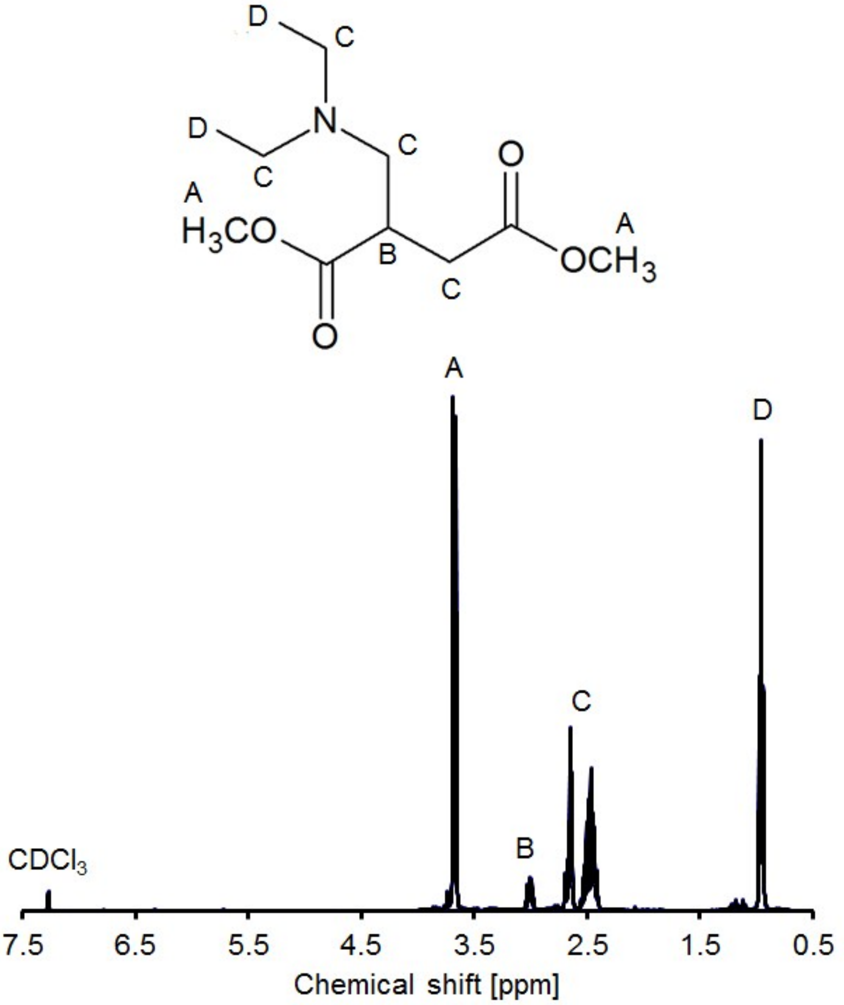

Figure S6. ^{1}H-NMR spectra for crude compound **1M** in $CDCl_3$. DMI:DEA=1:5, 25 °C, 400 rpm, 12 days. DEA excess was removed in vacuo producing a light brown slightly viscous liquid.

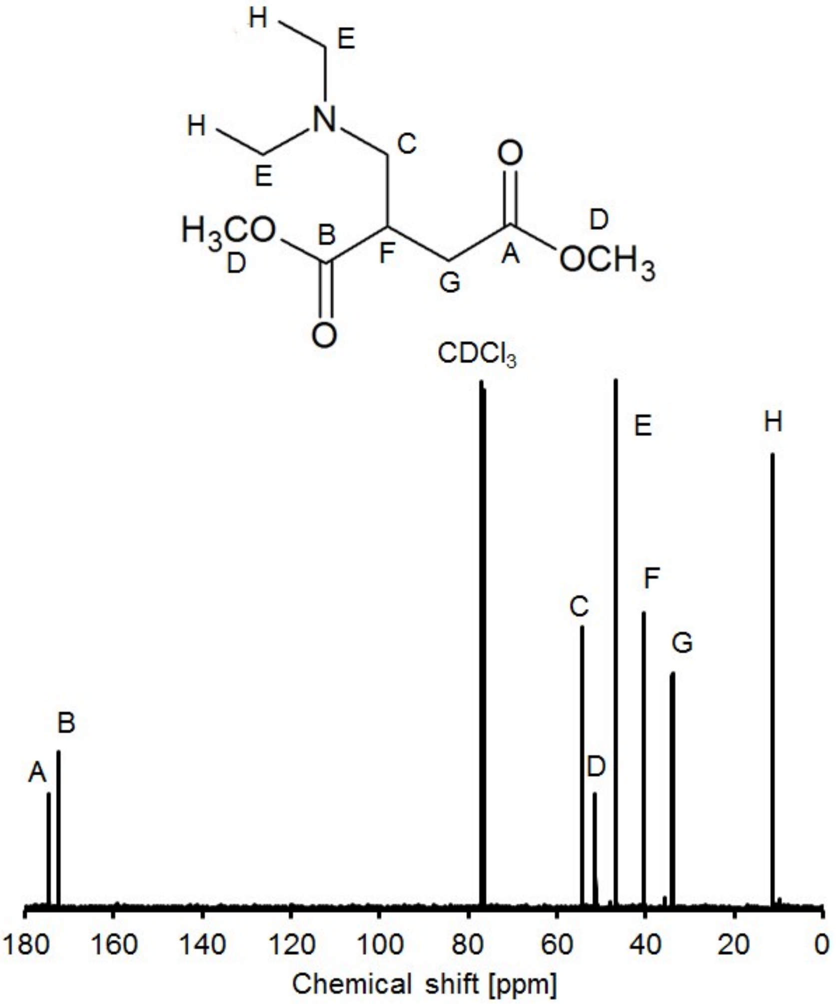

Figure S7. ^{13}C-NMR spectra for crude compound **1M** in $CDCl_3$. DMI:DEA=1:5, 25 °C, 400 rpm, 12 days. DEA excess was removed in vacuo producing a light brown slightly viscous liquid.

Table S2. ^{1}H-NMR conversions and GPC data of the enzymatic polymerization reactions of compounds **3M** and **4M** and the three selected diols.

Diester	**Diol**	**Conv. [%]***	**Mn [Da]$^{\gamma}$**	**Mw [Da]$^{\gamma}$**	**Đ$^{\gamma}$**
3M	14BDO	5	382	392	1.03
3M	16HDO	10	408	424	1.04
3M	18ODO	14	619	621	1.00
4M	14BDO	3	373	381	1.02
4M	16HDO	6	374	378	1.01
4M	18ODO	8	330	352	1.07

* Calculated via ^{1}H-NMR

$^{\gamma}$ Calculated via GPC using polystyrene standards 250-70000 Da

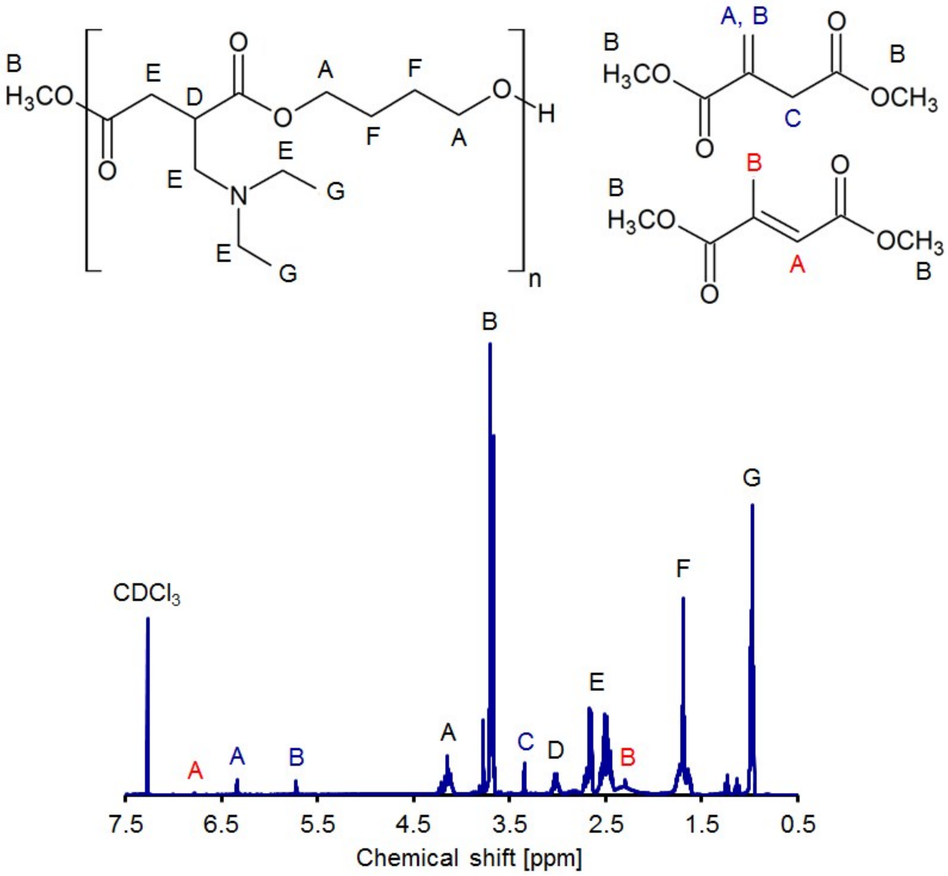

Figure S8. ^{1}H-NMR spectra for the DMIAP (**1M**) and 14BDO polymerization product after 24 h of reaction at 85 °C using 10% w w^{-1} of CaLB as biocatalyst.

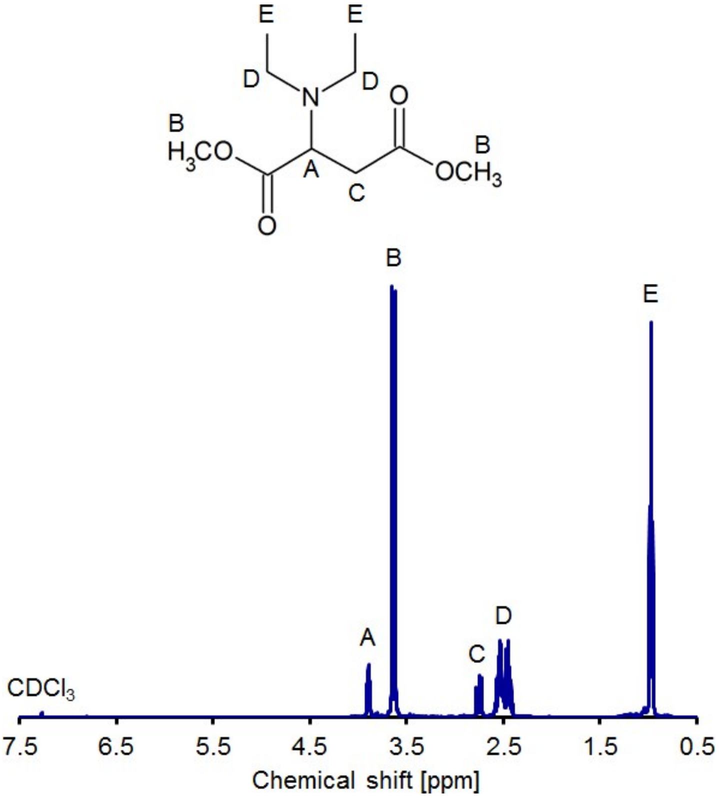

Figure S9. ^{1}H-NMR spectra of DMFAP (**2M**) after 1 month of storage at 21 °C in a dark environment.

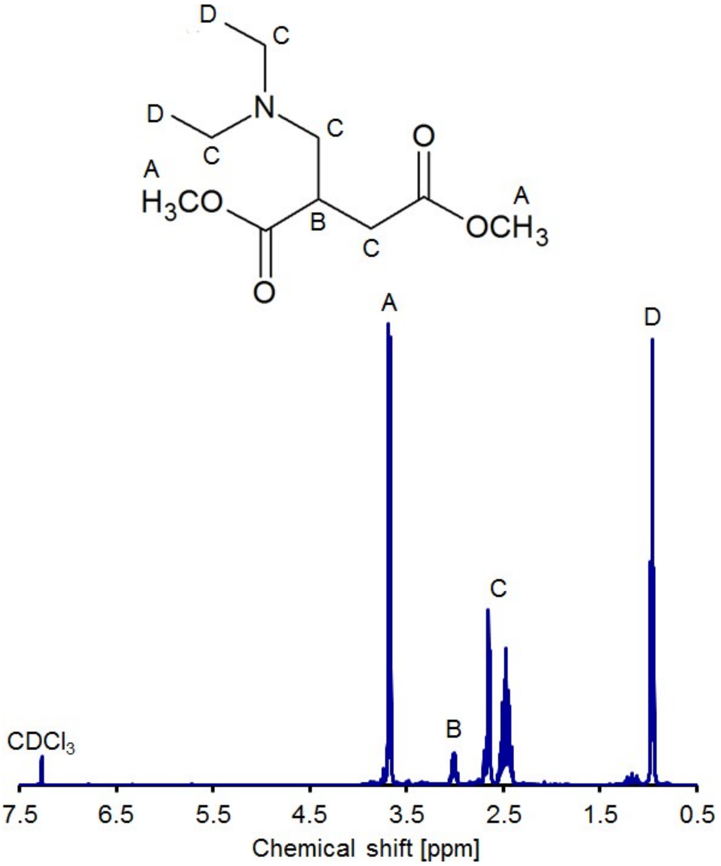

Figure S10. ^{1}H-NMR spectra of DMIAP (**1M**) after 1 month of storage at 21 °C in a dark environment.

Table S3. ^{1}H-NMR conversions and aza-Michael reversion data of compound **1M** reactions and blank runs (no enzyme added) and the three selected diols.

Reaction	Diol	Conv. [%]*	Michael rev. [%]*
CaLB catalyzed	1,4BDO	28	29
	1,6HDO	57	27
	1,8ODO	54	22
No Enzyme	1,4BDO	15	14
	1,6HDO	18	8
	1,8ODO	12	6

* Calculated via ^{1}H-NMR

Table S4. TG-IR analysis of the various unsaturated and amine pendant polymers synthesized in this study.

Diester	Diol	T_d 5% [ºC]	T_d 50% [ºC]	T_d 95% [ºC]
1	1,4BDO	262	387	693
	1,6HDO	240	407	693
	1,8ODO	318	415	658
1M	1,4BDO	147	242	693
	1,6HDO	164	350	693
	1,8ODO	141	366	682

For the COSMO software package if additional information is needed on the performed calculations we refer to the following publications:

(1) COSMOtherm, Version C3.0, Release 17.01; COSMOlogic GmbH & Co. KG, http://www.cosmologic.de

(2) Eckert, F. and A. Klamt, AIChE Journal, 48, 369 (2002).

Table S5. Monomer conversions and GPC data of the enzymatic polymerization reactions of compounds **1**-**5** and the three selected diols.

Diester	Diol	Conv. [%]*	Mn [Da]ɣ	Mw [Da]ɣ	Đɣ
1	1,4BDO	89	1375	2048	1.53
	1,6HDO	95	2161	4984	2.31
	1,8ODO	95	2599	5479	2.10
2	1,4BDO	91	1048	1330	1.27
	1,6HDO	96	2268	2681	1.18
	1,8ODO	97	2869	4271	1.49
3	1,4BDO	11	231	260	1.14
	1,6HDO	38	412	602	1.46
	1,8ODO	30	445	708	1.59
4	1,4BDO	81	1192	1942	1.63
	1,6HDO	91	1683	3694	2.19
	1,8ODO	87	2145	3726	1.74
5	1,4BDO	88	1494	1590	1.06
	1,6HDO	90	2673	3109	1.16
	1,8ODO	90	2473	3715	1.50

* Calculated via ^{1}H-NMR spectra

ɣ Calculated via GPC using polystyrene standards 250-70000 Da