Supporting Information

Candida antarctica Lipase B-catalyzed synthesis of polyesters: starting from ketone via tandem BVO/ROP process

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Content:

1 Optimization of the conditions for Baeyer–Villiger oxidation

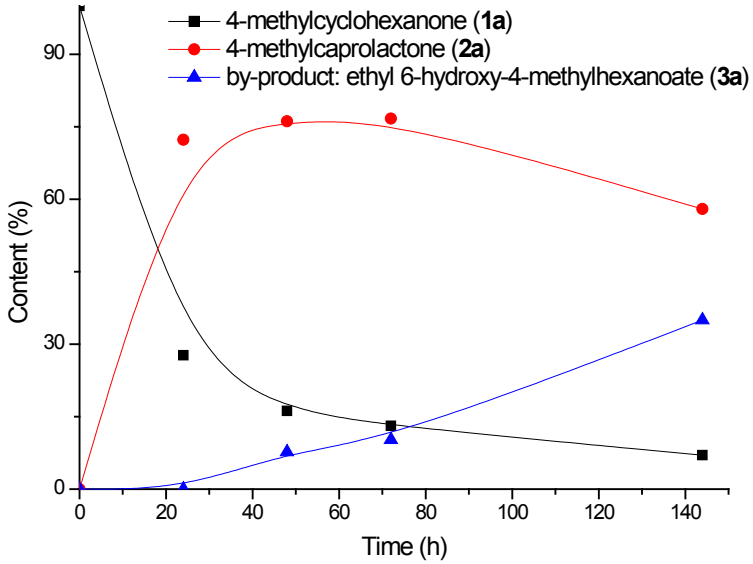


Fig. S1 Reaction time curves of the Baeyer–Villiger oxidation of 4-methylcyclohexanone (**1a**) at 50°C monitored by GC.

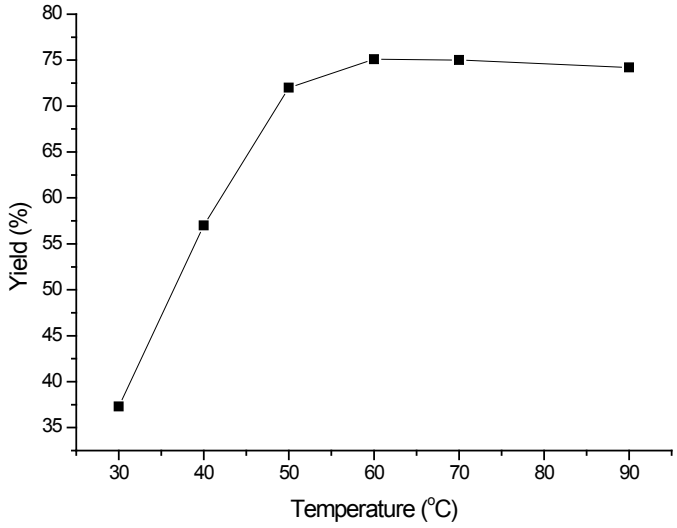


Fig. S2 Effect of temperature on the oxidation of 4-methylcyclohexanone (24h)

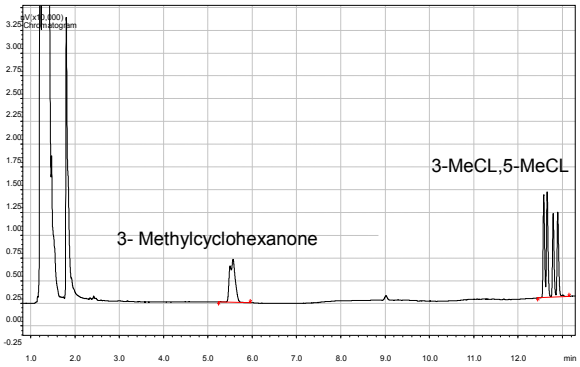


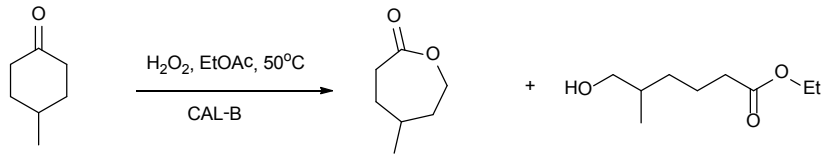
Fig. S3 GC chromatogram of the oxidation of 3-methylcyclohexanone at 50°C after 24h showing 3-MeCL and 5-MeCL in the crude reaction mixture.

Table S1 Different solvents used for the oxidation of 4-methylcyclohexanone[a].

Solvent	EA/ substrate	Yield%[b]
Toluene	2:1	-
Tert-amyl alcohol	2:1	-
Methyl Tertiary Butyl Ether	2:1	-
CH_2Cl_2	2:1	-
Ethyl acetate	-	72.3

[a] Reactions were carried out at 50 °C for 24h. [b] Determined by GC.

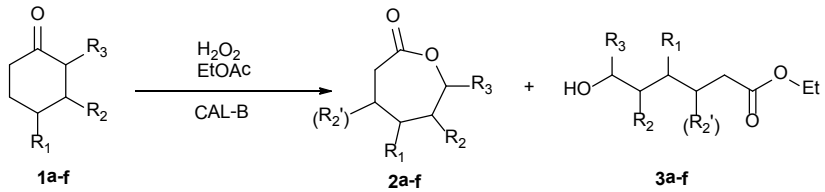
Table S2 Effect of molar ratio of H_2O_2/ substrate on the oxidation of 4-methylcyclohexanone.



1a **2a** **3a**

H_2O_2/ substrate	Time/H	Substrate%	Product%	By-product%
1/1	24	42.6	50.2	7.2
	48	27.9	53.9	18.2
	72	29.7	51.3	18.9
1.5/1	24	26.0	70.8	3.2
	48	12.5	76.2	11.3
	72	9.3	71.5	19.2
2/1	24	22.2	75.1	2.7
	48	9.1	77.7	13.2
	72	4.4	71.5	24.1
3/1	24	24.3	74.0	1.7
	48	15.7	80.3	4.0
	72	11.1	80.1	8.8

Table S3 Detailed data about the influence of reaction time and temperature on the oxidation of substituted cyclohexanones.



1a-f **2a-f** **3a-f**

Substrate	Entry	T/°C	Time/h	Substrate%	Product%	By-product%
4-Methylcyclohexanone	S1-1	30	24	62.7	37.3	-
(1a)	S1-2	30	48	39.3	58.7	2.0
	S1-3	30	72	35.3	60.5	4.2
	S1-4	**50**	**24**	**27.7**	**72.3**	**-**
	S1-5	50	48	16.2	76.1	7.7
	S1-6	50	72	13.1	76.7	10.2
	S1-7	70	24	19.7	75.0	5.3
	S1-8	70	48	17.0	69.4	13.6
	S1-9	70	72	17.0	56.9	26.1
	S1-10	90	24	23.6	74.3	2.1
	S1-11	90	48	15.0	76.3	8.7
	S1-12	90	72	13.8	74.0	12.2
4-Ethylcyclohexanone	S2-1	30	24	65.5	34.5	-
(1b)	S2-2	30	48	44.6	55.4	-
	S2-3	30	72	28.0	72.0	-
	S2-4	**50**	**24**	**23.2**	**76.8**	**-**
	S2-5	50	48	14.2	76.5	9.3
	S2-6	50	72	13.5	72.0	14.5
	S2-7	70	24	26.4	70.1	3.5
	S2-8	70	48	20.5	68.2	11.2
	S2-9	70	72	21.8	59.2	19.0
4-phenylcyclohexanone	S3-1	30	24	99	-	-
(1c)	S3-2	30	72	100	-	-
	S3-3	**50**	**24**	**57.6**	**42.4**	**-**
	S3-4	50	72	34.4	28.3	37.3
	S3-5	70	48	53.1	46.9	-
	S3-6	70	72	20.1	39.3	40.5
4-tert-Butylcyclohexanone	S4-1	30	24	62.4	37.6	-
(1d)	S4-2	30	48	38.3	61.7	-
	S4-3	30	72	27.3	53.3	19.4
	S4-4	50	24	27.1	72.3	0.6
	S4-5	50	48	21.2	77.8	1.0
	S4-6	50	72	18.4	77.7	3.9
	S4-7	**70**	**24**	**16.0**	**82.6**	**1.4**
	S4-8	70	48	8.7	86.5	4.8

	S4-9	70	72	5.2	84.8	10.0
2-Methylcyclohexanone	S5-1	30	24	29.0	67.6	3.5
(1e)	S5-2	30	48	8.3	83.2	8.5
	S5-3	30	72	3.0	82.2	14.8
	S5-4	**50**	**24**	**10.0**	**80.7**	**9.3**
	S5-5	50	48	3.1	73.7	23.2
	S5-6	50	72	3.3	73.4	23.3
	S5-7	70	24	16.2	76.2	7.6
	S5-8	70	48	7.9	69.2	22.9
	S5-9	70	72	1.7	52.7	45.6
3-Methylcyclohexanone	S6-1	30	24	77.5	22.5	-
(1f)	S6-2	30	48	55.0	45.0	-
	S6-3	30	72	48.5	48.9	2.6
	S6-4	50	24	37.7	62.3	-
	S6-5	50	48	30.4	65.1	4.5
	S6-6	50	72	24.3	69.3	6.4
	S6-7	**70**	**24**	**28.8**	**71.2**	**-**
	S6-8	70	48	17.5	70.0	12.5
	S6-9	70	72	14.4	65.8	19.8

2 Data of substituted lactones

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm) for 4-methylcaprolactone (4-MeCL, **2a**): 4.240-4.087 (m, 2 H), 2.628-2.518 (m, 2 H), 1.888-1.792 (m, 2 H), 1.702 (m, 1 H), 1.478-1.387 (dd, 1 H), 1.311-1.220 (dd, 1 H), 0.941 (d, 3 H). IR (cm^{-1}): 2955, 2927, 2872, 1732, 1449, 1391, 1338, 1282, 1179, 1164, 1079, 1007, 935.

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm) for 4-ethylcaprolactone (4-EtCL, **2b**): 4.293-4.073 (m, 2 H), 2.675-2.534 (m, 2 H), 1.931 (m, 2 H), 1.448 (m, 2 H), 1.313-1.222 (m, 3 H), 0.880 (t, 3 H). IR (cm^{-1}): 2961, 2928, 2875, 1733, 1460, 1381, 1350, 1248, 1169, 1100, 1059, 997.

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm) for 4-phenylcaprolactone (4-PhCL, **2c**): 7.340-7.186 (m, 5 H), 4.358 (m, 2 H), 2.788 (m, 3 H), 2.068 (m, 3 H), 1.868 (m, 1 H). IR (cm^{-1}): 2960, 2871, 1732, 1602, 1474, 1394, 1366, 1337, 1250, 1161, 1088, 1039, 995, 762, 702.

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm) for 4-tert-butylcaprolactone (4-tBuCL, **2d**): 4.277 (dd, 1 H), 4.086 (t, 1 H), 2.628 (dd, 1 H), 2.508 (t, 1 H), 1.978 (m, 2 H), 1.464 (dd, 1 H), 1.273 (t, 2 H), 0.824 (s, 9H). IR (cm^{-1}): 2963, 2870, 1736, 1477, 1437, 1396, 1367, 1339, 1294, 1253, 1194, 1177, 1078, 1021.

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm) for 6-methylcaprolactone (6-MeCL, **2e**): 4.421 (m, 1 H), 2.604 (m, 2 H), 1.879 (m, 3 H), 1.568 (m, 3 H), 1.304 (d, 3 H). IR (cm^{-1}): 2967, 2936, 2865, 1730, 1711, 1458, 1408, 1377, 1238, 1176, 1129, 1091.

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm) for 3-methylcaprolactone (3-MeCL, **2f-a**) and 5-methylcaprolactone (5-MeCL, **2f-b**): 4.237-4.125 (m, 2 H), 4.086-3.926 (m, 2 H), 2.606-2.515 (m, 4 H), 1.914-1.765 (m, 6 H), 1.655 (m, 1 H), 1.577 (m, 1 H), 1.366 (m, 2 H), 1.021 (d, 2 H), 0.915 (d, 2 H). IR (cm^{-1}): 2957, 2928, 2869, 1732, 1460, 1381, 1352, 1283, 1248, 1209, 1171, 1099, 995.

3. NMR spectra of 3-MeCL and 5-MeCL, and the corresponding polyester

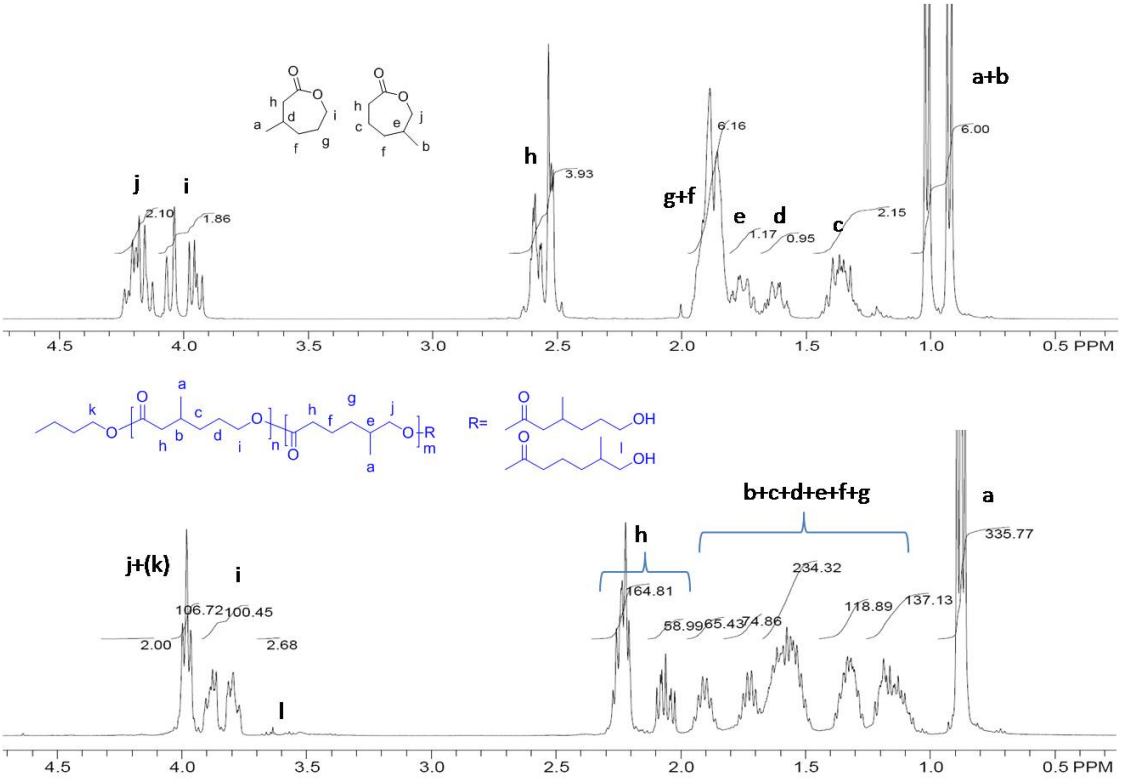


Fig. S4 ^{1}H-NMR of the mixture of 3-MeCL and 5-MeCL, and the corresponding polyester prepared via one-pot process.

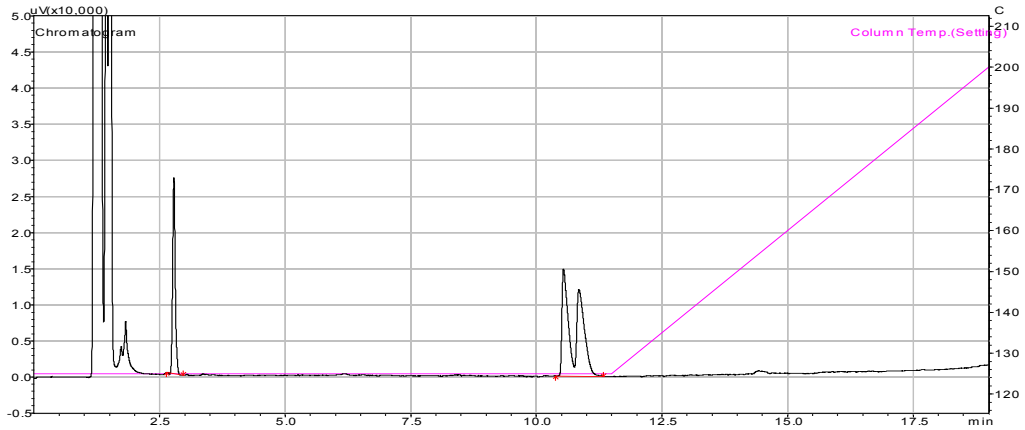
4. Representative Gas Chromatographic (GC) data

(1) Oxidation of 4-methylcyclohexanone

Column: CP-chirasil-DEX CB 25*0.25(Agilent), Column temperature: 125°C hold 11.5min, 125°C to 200°C, 10°C per min.

Table S3 Entry S1-4: Temperature=50 °C Time=24h Molar ratio of H_2O_2/ Substrate=2:1 CAL-B=10 wt%

4-Methylcyclohexanone: R_t=2.8 min 4-Methylcaprolactone: R_t=10.5-11.3 min

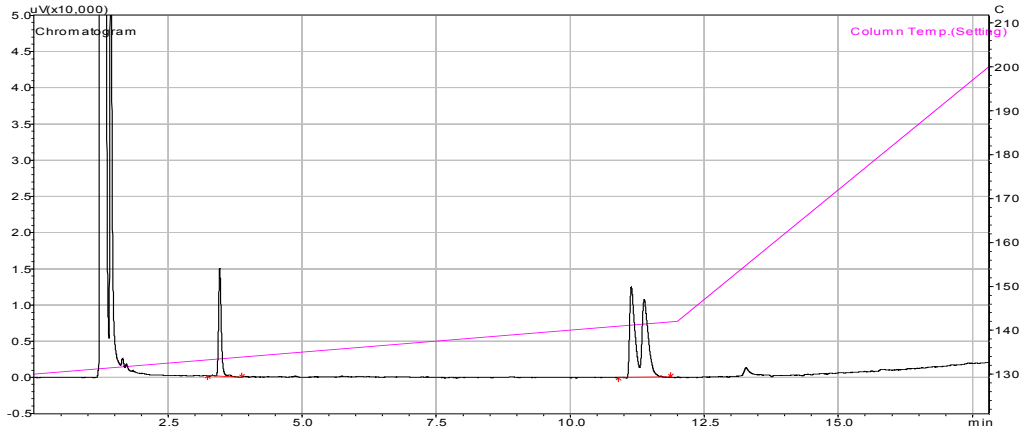


(2) Oxidation of 4-ethylcyclohexanone

Column: CP-chirasil-DEX CB 25*0.25(Agilent), Column temperature: 130°C to 142°C, 1°C per min, 125°C to 200°C, 10°C per min.

Table S3 Entry S2-4: Temperature=50 °C Time=24h Molar ratio of H_2O_2/ Substrate=2:1 CAL-B=10 wt%

4-Ethylcyclohexanone: R_t=3.2 min 4-Ethylcaprolactone: Rt=11.0-11.7 min

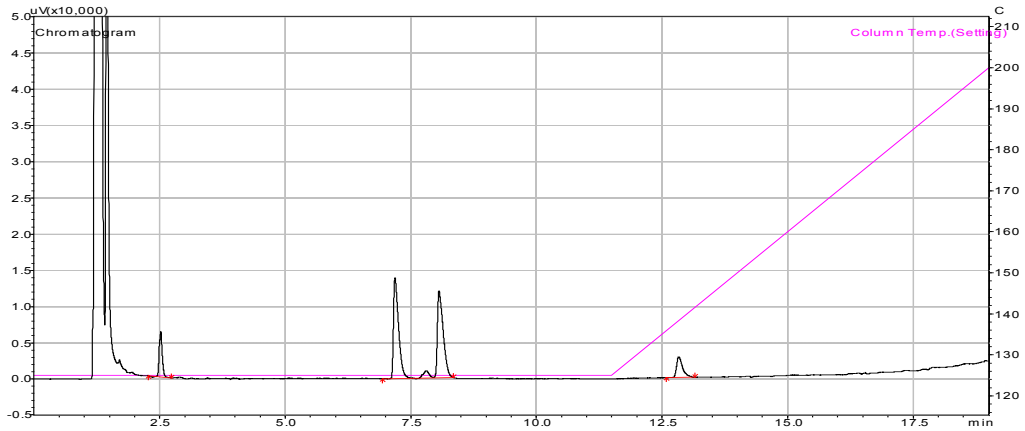


(3) Oxidation of 2-methylcyclohexanone

Column: CP-chirasil-DEX CB 25*0.25(Agilent), Column temperature: 125°C hold 11.5min, 125°C to 200°C, 10°C per min.

Table S3 Entry S5-4: Temperature=50 °C Time=24h Molar ratio of H_2O_2/ Substrate=2:1 CAL-B=10 wt%

2-Methylcyclohexanone: R_t=2.5 min 6-Methylcaprolactone: R_t=7.2, 8.0 min

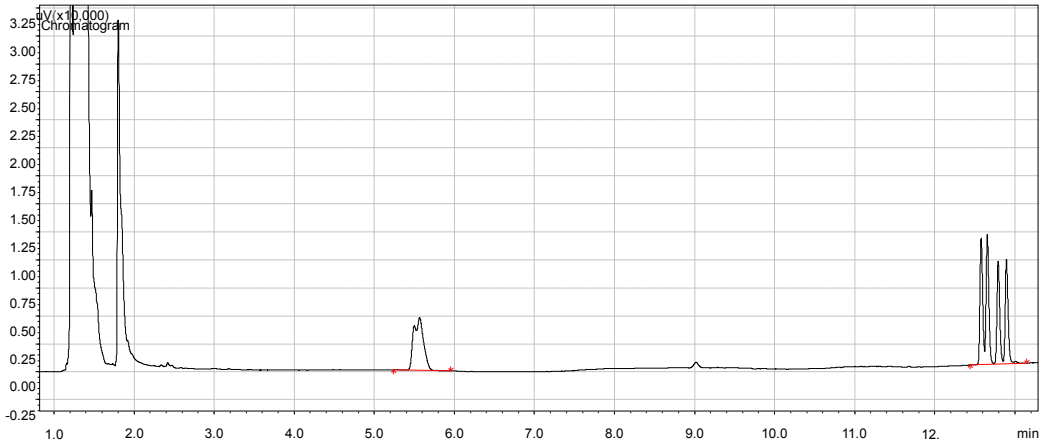


(4) Oxidation of 3-methylcyclohexanone

Column: CP-chirasil-DEX CB 25*0.25(Agilent), Column temperature: 100°C hold 7.0min, 100°C to 200°C, 10°C per min.

Table S3 Entry S6-4: Temperature=50 °C Time=24h Molar ratio of H_2O_2/ Substrate=2:1 CAL-B=10 wt%

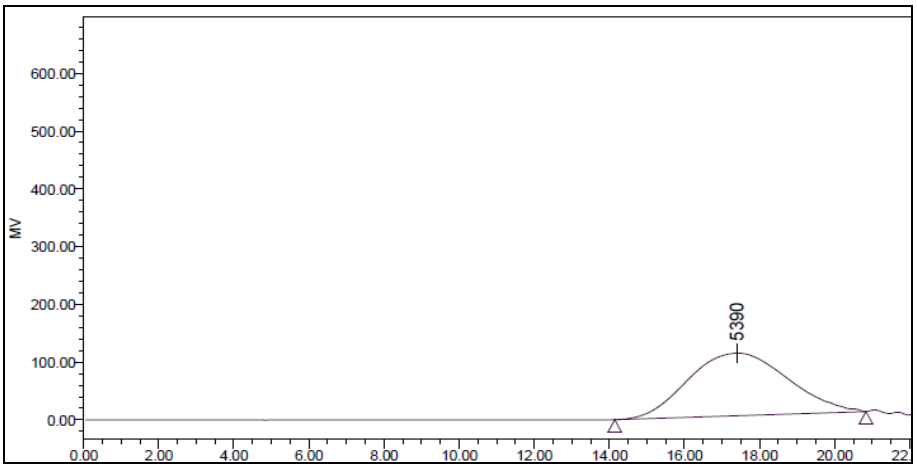
3-Methylcyclohexanone: R_t=5.5 min 3-Methylcaprolactone and 5-Methylcaprolactone: Rt=12.5-13.0 min



5. Representative gel permeation chromatography (GPC) data

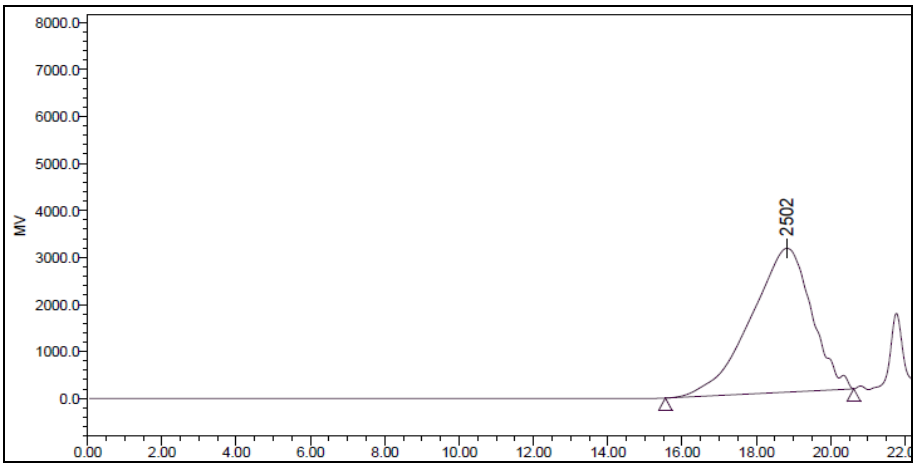
5.1 GPC chromatograms of reactions listed in Table 2

(1) P(4-methylcaprolactone) catalyzed by CAL-B listed in Table 2



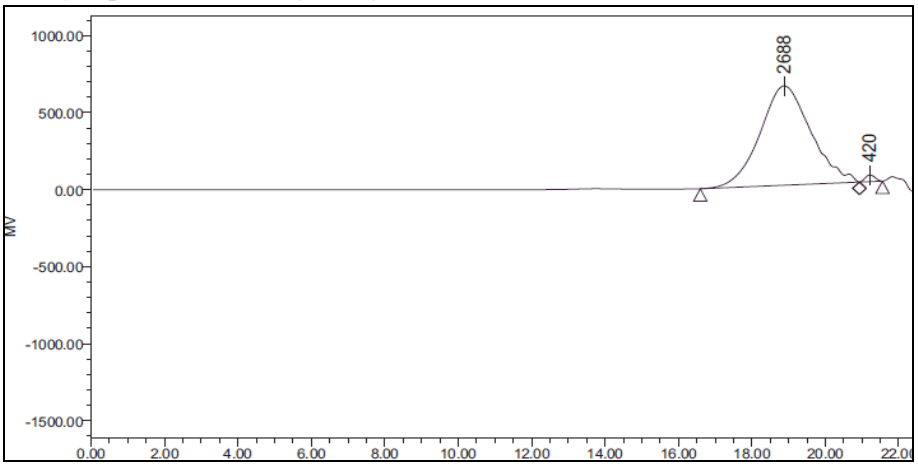
M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
4000	6102	5390	8543	10975	1.53	1.40	1.80

(2) P(4-methylcaprolactone) catalyzed by AK listed in Table 2



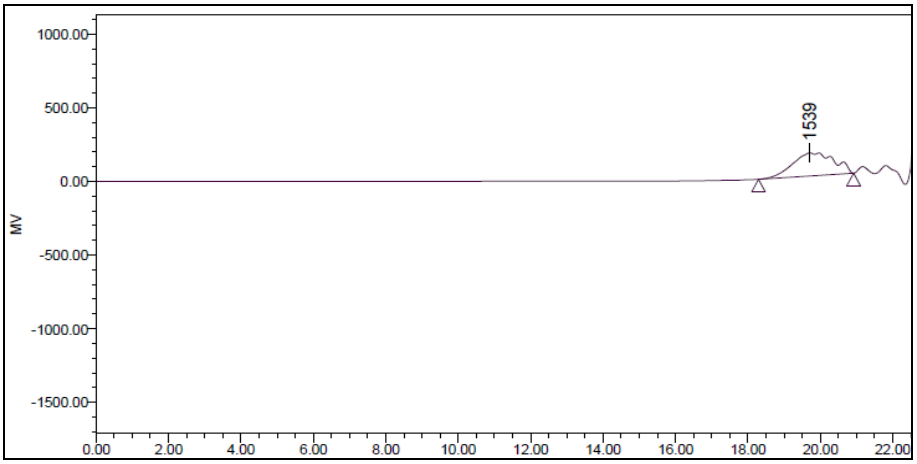
M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
2474	3165	2502	4021	5012	1.28	1.27	1.58

(3) Poly(4-ethylcaprolactone) catalyzed by CAL-B listed in Table 2



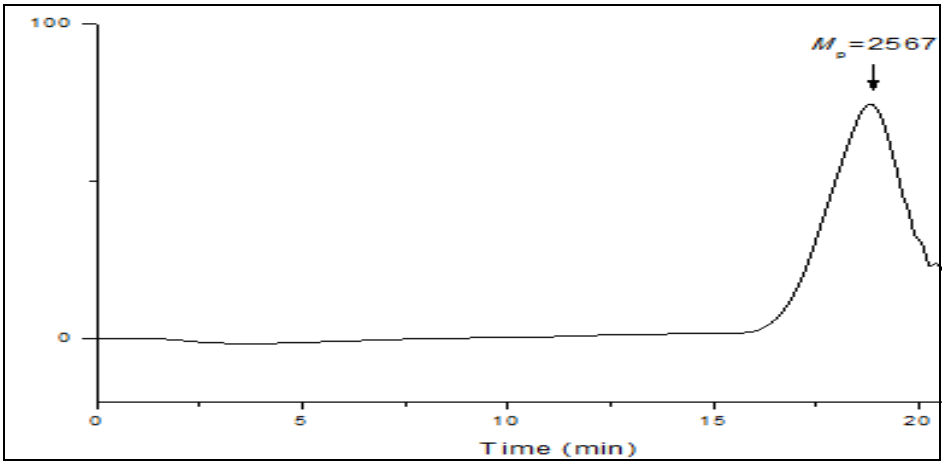
M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
2278	2745	2688	3198	3641	1.20	1.16	1.33

(4) Poly(4-ethylcaprolactone) catalyzed by PPL listed in Table 2



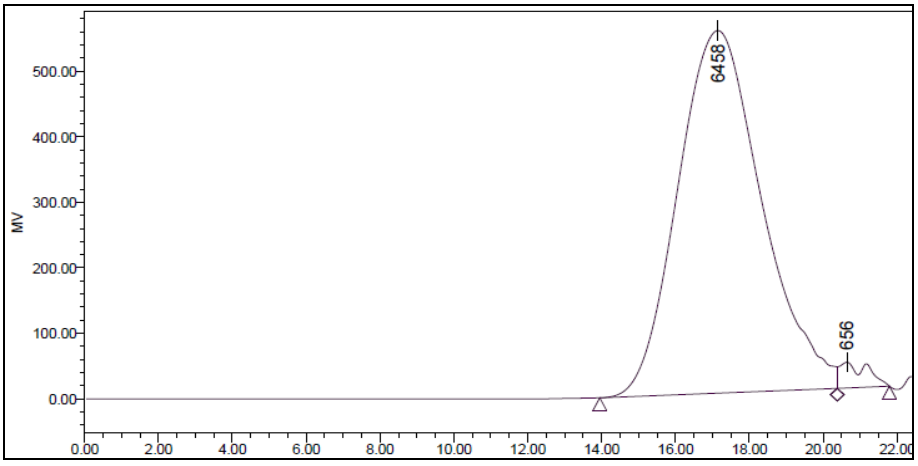
M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
1302	1490	1539	1685	1875	1.14	1.13	1.26

(5) Poly(4-phenylcaprolactone) catalyzed by CAL-B listed in Table 2



M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
2453	3100	2567	3827	4574	1.26	1.23	1.47

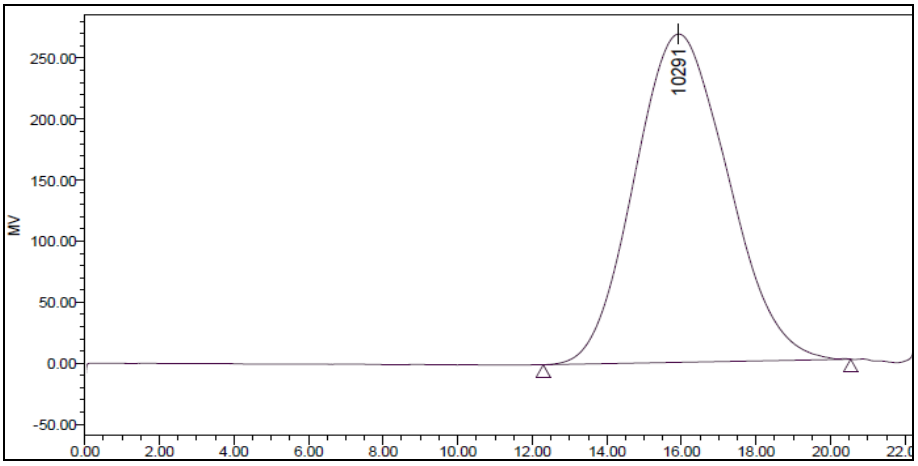
(6) Poly(3-methylcaprolactone)-co-poly(5-Methylcaprolactone) catalyzed by CAL-B listed in Table 2



M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
4804	6888	6458	9046	11255	1.43	1.31	1.63

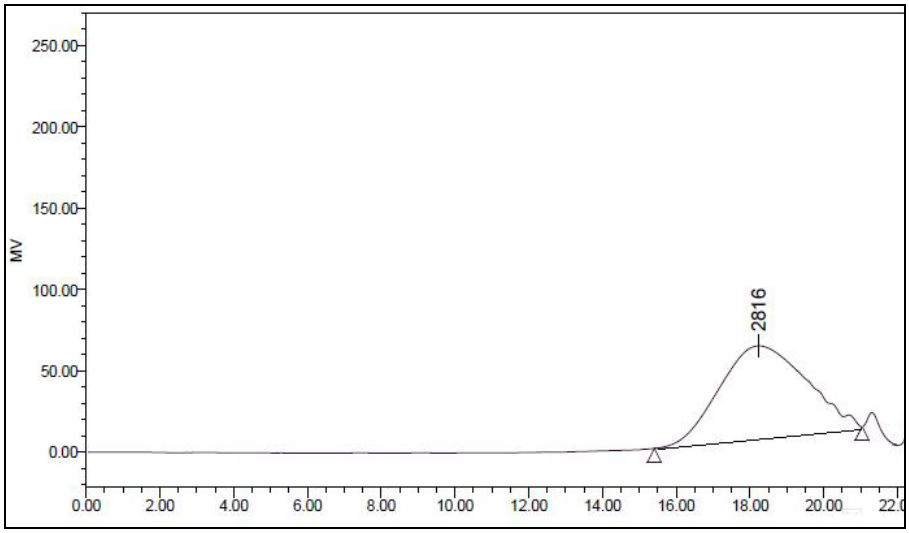
5.2 GPC chromatograms of reactions listed in Table 3

(1) P(4-methylcaprolactone) catalyzed by CAL-B listed in Table 3



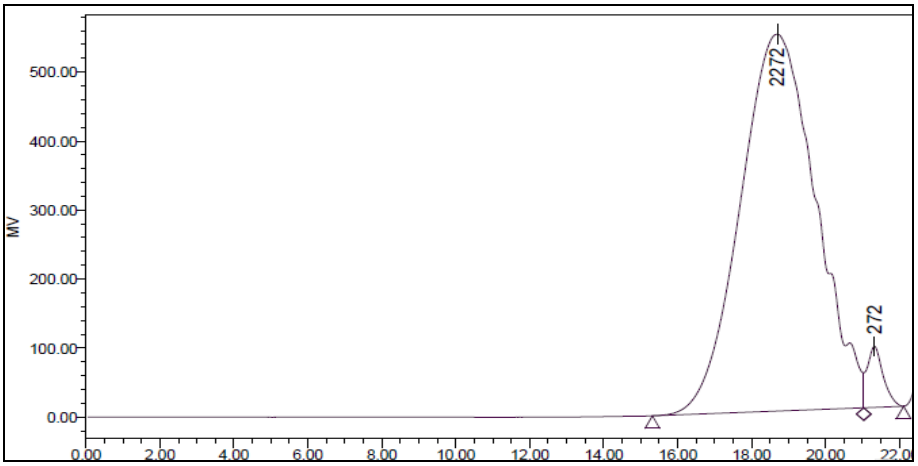
M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
7647	11640	10291	16862	23604	1.52	1.45	2.03

(2) Poly(4-ethylcaprolactone) catalyzed by CAL-B listed in Table 3



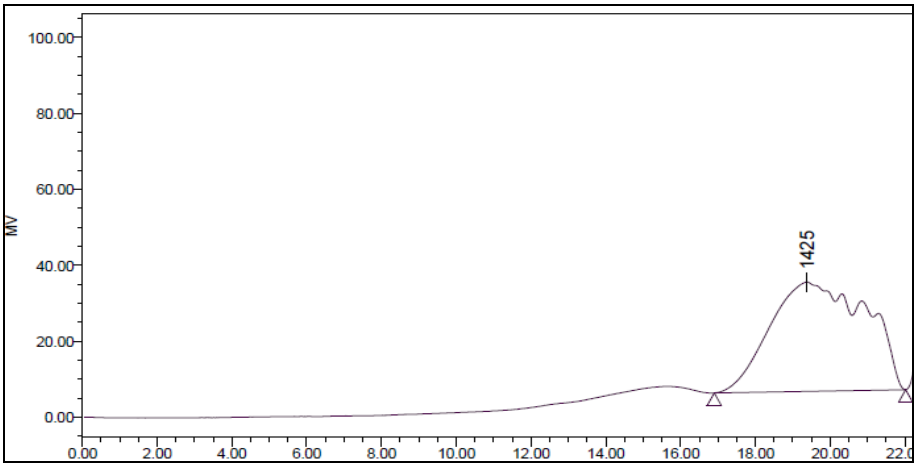
M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
2014	2740	2816	4122	5314	1.36	1.51	1.94

(3) Poly(4-phenylcaprolactone) catalyzed by CAL-B listed in Table 3



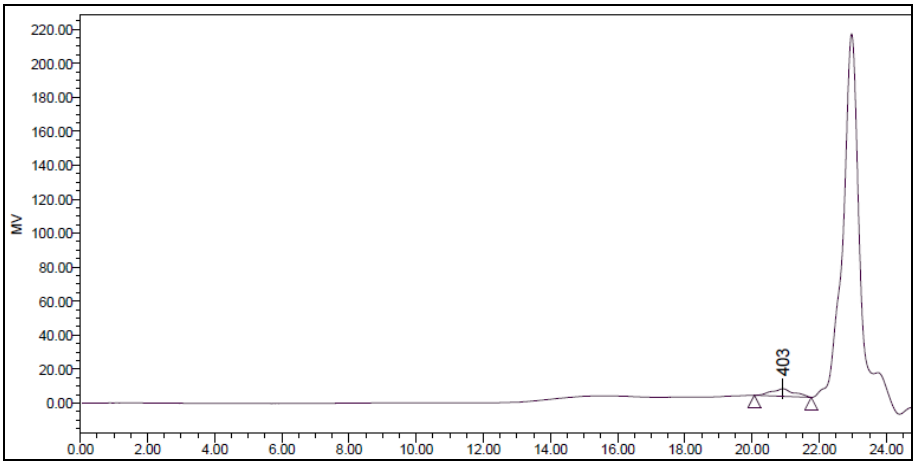
M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
1730	2521	2272	3408	4340	1.46	1.35	1.72

(4) Poly(4-tert-butylcaprolactone) catalyzed by CAL-B listed in Table 3



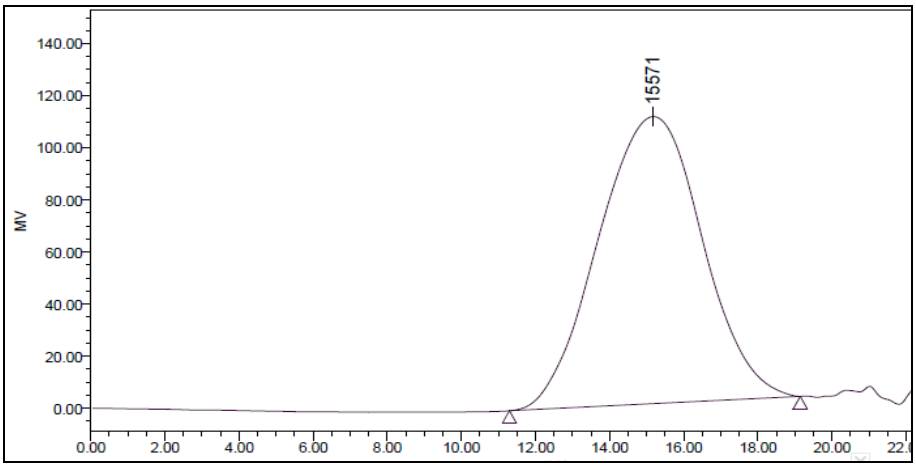
M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
721	1356	1425	2104	2728	1.88	1.55	2.01

(5) Poly(6-methylcaprolactone) catalyzed by CAL-B listed in Table 3



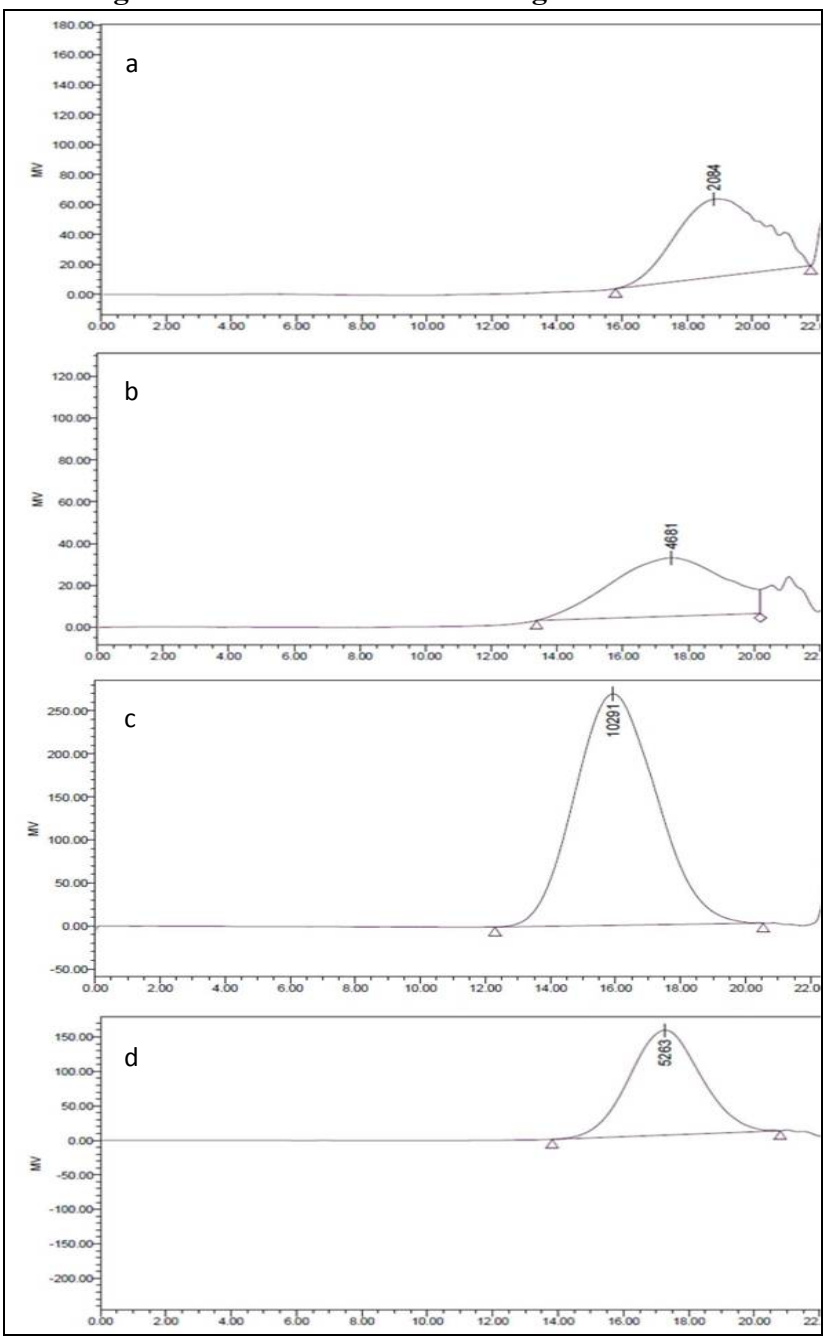
M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
373	412	403	450	486	1.10	1.09	1.18

(6) Poly(3-methylcaprolactone)-co-poly(5-Methylcaprolactone) catalyzed by CAL-B listed in Table 3



M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
12829	21639	15571	37504	61465	1.69	1.73	2.84

5.3 GPC chromatograms of reactions shown in Fig. 2



T/°C	M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
60	1139	2217	2084	3458	4569	1.95	1.56	2.06
70	3399	6931	4681	12574	18865	2.04	1.81	2.72
80	7647	11640	10291	16862	23604	1.52	1.45	2.03
90	4228	5963	5263	7991	10347	1.41	1.34	1.74

Figure S4. The GPC chromatograms of reactions shown in Fig. 2.
Temperature (a) 60°C; (b) 70°C; (c) 80°C; (d) 90°C.

5.4 GPC chromatograms of reactions shown in Fig. 3

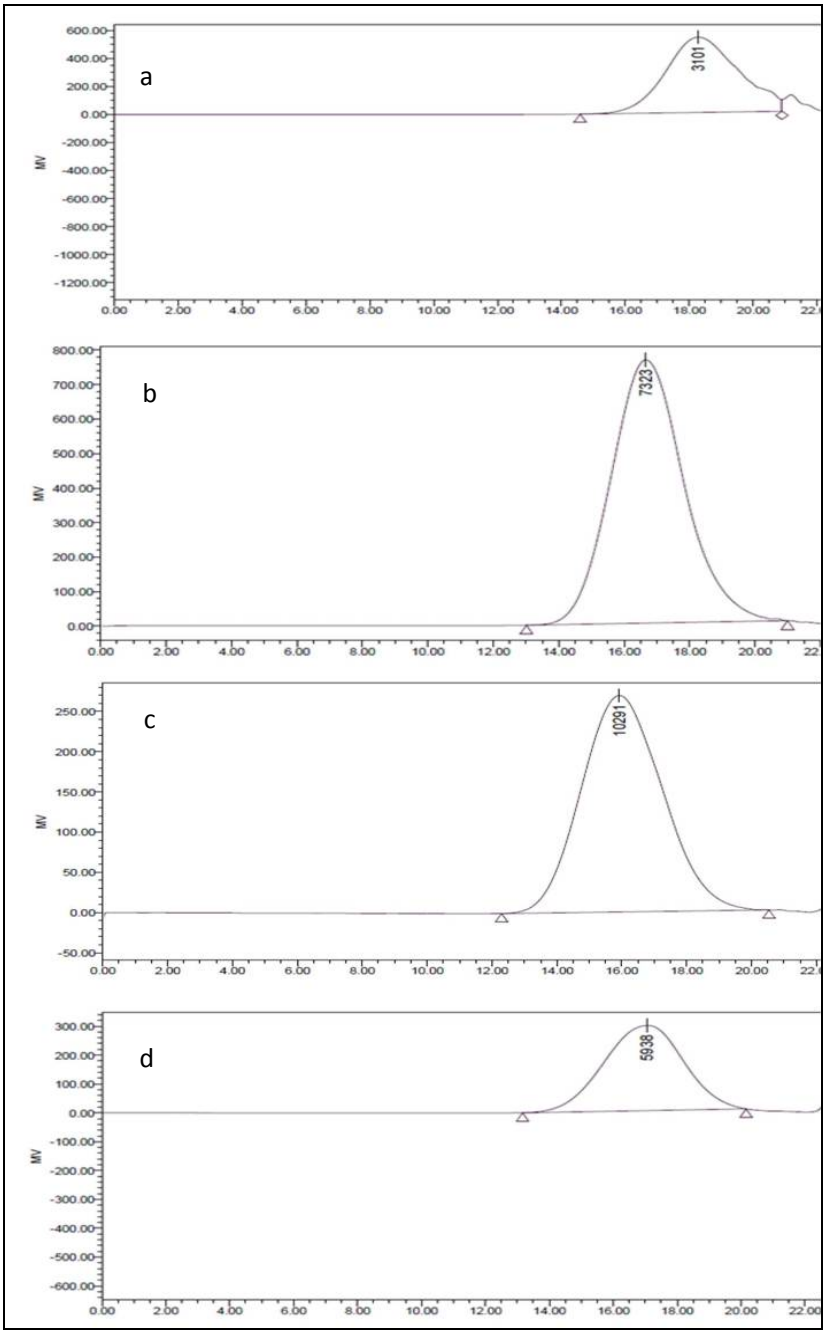
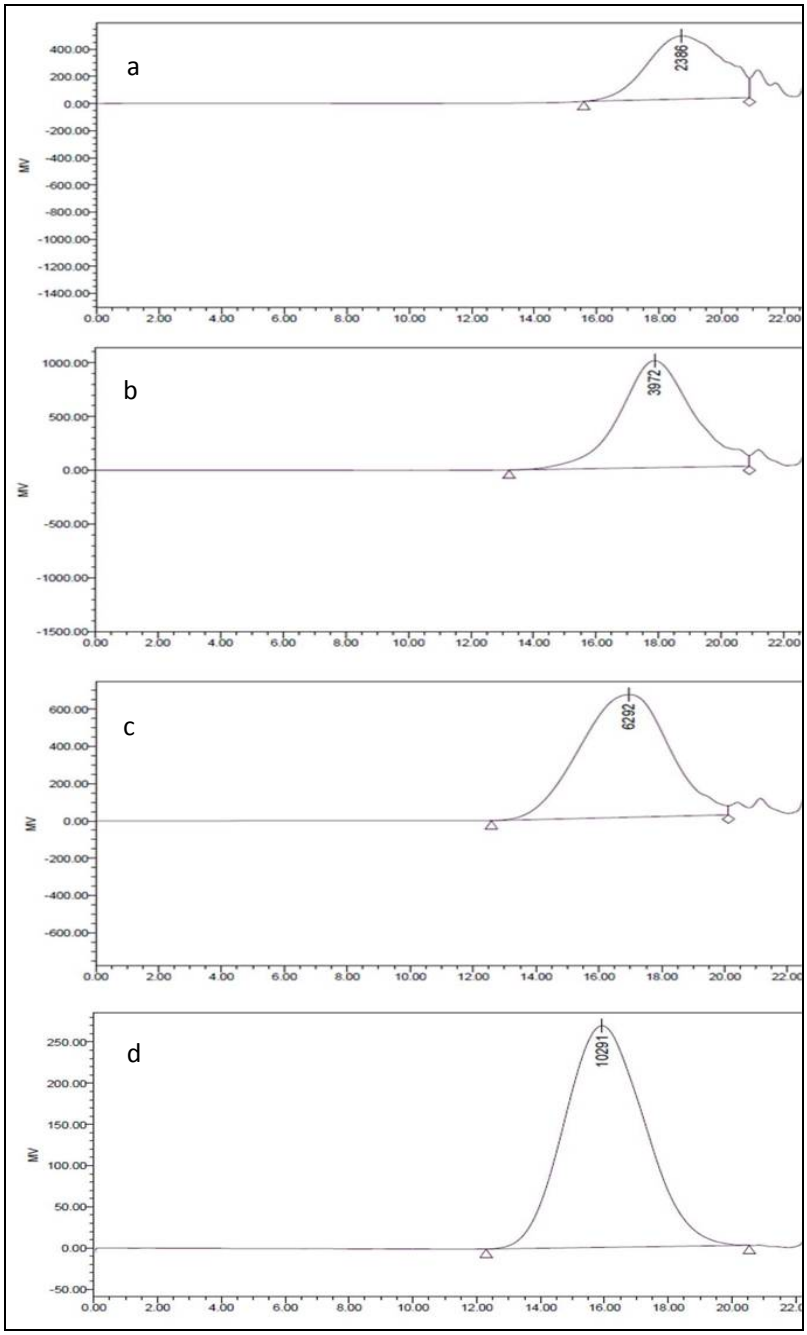


Figure S5. The GPC chromatograms of reactions shown in Fig. 3 Enzyme amount (a) 0.5 wt%; (b) 5 wt%; (c) 10 wt%; (d) 25 wt%.

Number	M_n	M_w	MP	M_z	M_{z+1}	DPi	M_z/M_w	M_{z+1}/M_w
a	2081	3258	3101	4610	6081	1.57	1.41	1.87
b	5520	8000	7323	10743	13923	1.45	1.34	1.74
c	7647	11640	10291	16862	23604	1.52	1.45	2.03
d	5102	7514	5938	10800	14967	1.47	1.44	1.99

5.5 GPC chromatograms of reactions shown in Fig. 4



Number	M_n	M_w	MP	M_z	M_{z+1}	DPI	M_z/M_w	M_{z+1}/M_w
a	1652	2592	2386	3752	4946	1.57	1.45	1.91
b	2746	4617	3972	7412	11930	1.68	1.60	2.58
c	5085	8539	6292	13588	20243	1.68	1.59	2.37
d	7647	11640	10291	16862	23604	1.52	1.45	2.03

Figure S6. The GPC chromatograms of reactions shown in Fig. 4.
Initiator/substrate (a) 1:10; (b) 1:20; (c) 1:30; (d) 1:50.