Solvent-Free Lipase-Mediated Synthesis of Six-Membered Cyclic Carbonates from Trimethylolpropane and Dialkyl carbonates

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Supplementary Data

Table S1. GC-MS and ^{1}H-NMR data for structure elucidation of products obtained from the reaction between TMP and dialkyl carbonates at 60 °C catalysed by Novozym®435

Run	Product	Formula	Molecular weight		^{1}H-NMR ($CDCl_3$)
			Calc.	Anal.	
1	**3**(DMC)	$C_8H_{16}O_5$	192.21	160.9 (-32, -$HOCH_3$)	0.879(3H, t), 1.323(2H, q), 3.614(4H, s), 4.239(3H, s)
2	**4**(DMC)	$C_7H_{12}O_4$	160.17	160.9	0.956(3H, t), 1.533(2H, q), 3.715(2H, s), 4.172(4H, dd)
3	**5**(DMC)	$C_{10}H_{18}O_7$	250.25	219.0 (-32, -$HOCH_3$)	0.889(3H, t), 1.444(2H, q), 3.485(2H, s), 3.777(6H, s), 4.098(2H, s), 4.105(2H, s)
4	**6**(DMC)	$C_9H_{14}O_6$	218.20	219.0	0.963(3H, t), 1.565(2H, q), 3.824(3H, s), 4.192(2H, s), 4.195(4H, dd)
5	**7**(DMC)	$C_{12}H_{20}O_9$	308.28	233.0 (-76, -$HOCOOCH_3$)	0.931(3H, t), 1.551(2H, q), 3.804(9H, s), 4.139(6H, s)
6	**3´**(DEC)	$C_9H_{18}O_5$	206.24	160.9 (-46, -$HOCH_2CH_3$)	0.889(3H, t), 1.335(5H, m), 3.624(4H, s), 4.218(2H, q), 4.252(2H, s)
7	**5´**(DEC)	$C_{12}H_{22}O_7$	278.30	233.0 (-46, -$HOCH_2CH_3$)	0.912(3H, t), 1.321(6H, t), 1.451(2H, q), 3.496(2H, s), 4.112(2H, s), 4.125(2H, s), 4.218(4H, q)
8	**6´**(DEC)	$C_{10}H_{16}O_6$	232.23	233.0	(not determined)

Table S2. Summary of the reactions between TMP and DMC using various amounts of Novozym®435 at 60 °C.

Run	Novozym®435 (% w/w)	Reaction Time (h)	Conversion (%)	Carbonate Products				
				Cyclic (%)		Linear (%)		
				4	**6**	**3**	**5**	**7**
1	2.5	48	58.3	26.0	4.0	62.0	8.0	0
2	2.5	120	83.3	39.8	12.9	34.5	12.8	0
3	5	48	87.2	24.6	11.7	43.1	20.6	0
4	5	120	98.1	26.8	24.3	17.6	28.4	2.9
5	10	48	98.5	14.5	16.4	28.6	36.7	3.8
6	10	120	100	13.0	25.3	9.8	42.1	9.8
7	20	48	98.5	7.6	13.2	26.0	45.6	7.6
8	20	120	100	5.0	18.8	10.9	50.9	14.3
9	40	48	99.9	2.6	16.5	6.6	48.7	25.6
10	40	120	100	1.5	15.8	1.7	43.1	37.8

Table S3. Summary for the reactions of TMP and DMC using 10 % Novozym®435 at 50, 60, and 70 °C, respectively

Run	Reaction Temp. (^{o}C)	Reaction Time (h)	Conversion (%)	Carbonate Products				
				Cyclic (%)		Linear (%)		
				4	**6**	**3**	**5**	**7**
1	50	48	90.2	14.4	7.8	50.2	26.5	1.1
2	50	96	97.7	17.9	18.7	29.1	29.8	4.5
3	60	48	98.5	14.5	16.4	28.6	36.7	3.8
4	60	96	99.7	10.0	21.3	14.9	45.8	8.0
5	70	48	88.7	50.4	24.7	14.0	9.0	1.9
6	70	96	96.4	39.4	31.5	11.4	14.6	3.1

Table S4. Summary for the reactions of TMP and DEC using various concentrations of Novozym®435 at 60 and 70 °C

Run	Lipase amount (% w/w TMP)	Reaction Time (h)	Reaction Temp. (°C)	Conversion (%)	Carbonate Products				
					Cyclic (%)		Linear (%)		
					4	**6**	**3**	**5**	**7**
1	2.5	48	60	19.6	0.6	0.0	99.4	0.0	0.0
2	2.5	120	60	52.8	71.5	3.5	23.7	1.2	0.0
3	5	48	60	34.3	2.2	0.0	97.8	0.0	0.0
4	5	120	60	71.3	58.0	10.1	28.5	3.4	0.0
5	10	48	60	65.4	4.7	0.0	87.5	7.8	0.0
6	10	120	60	89.4	44.2	19.8	28.2	7.8	0.0
7	20	48	60	88.4	3.9	0.0	74.9	21.3	0.0
8	20	120	60	98.7	26.1	39.5	15.8	16.2	2.4
9	10	48	70	44.1	47.2	0.0	52.8	0.0	0.0
10	10	120	70	90.9	31.9	18.7	36.3	13.0	0.0

Fig. S1. Effect of reaction temperature, 50 °C (●), 60 °C (▲), and 70 °C (◆), on the conversion of TMP during the reaction with DMC catalysed by 10 % (w/w of TMP) Novozym®435.