

Supporting Information

for

Comparing kinetic profiles between bifunctional and binary type of Zn(salen)-based catalysts for organic carbonate formation

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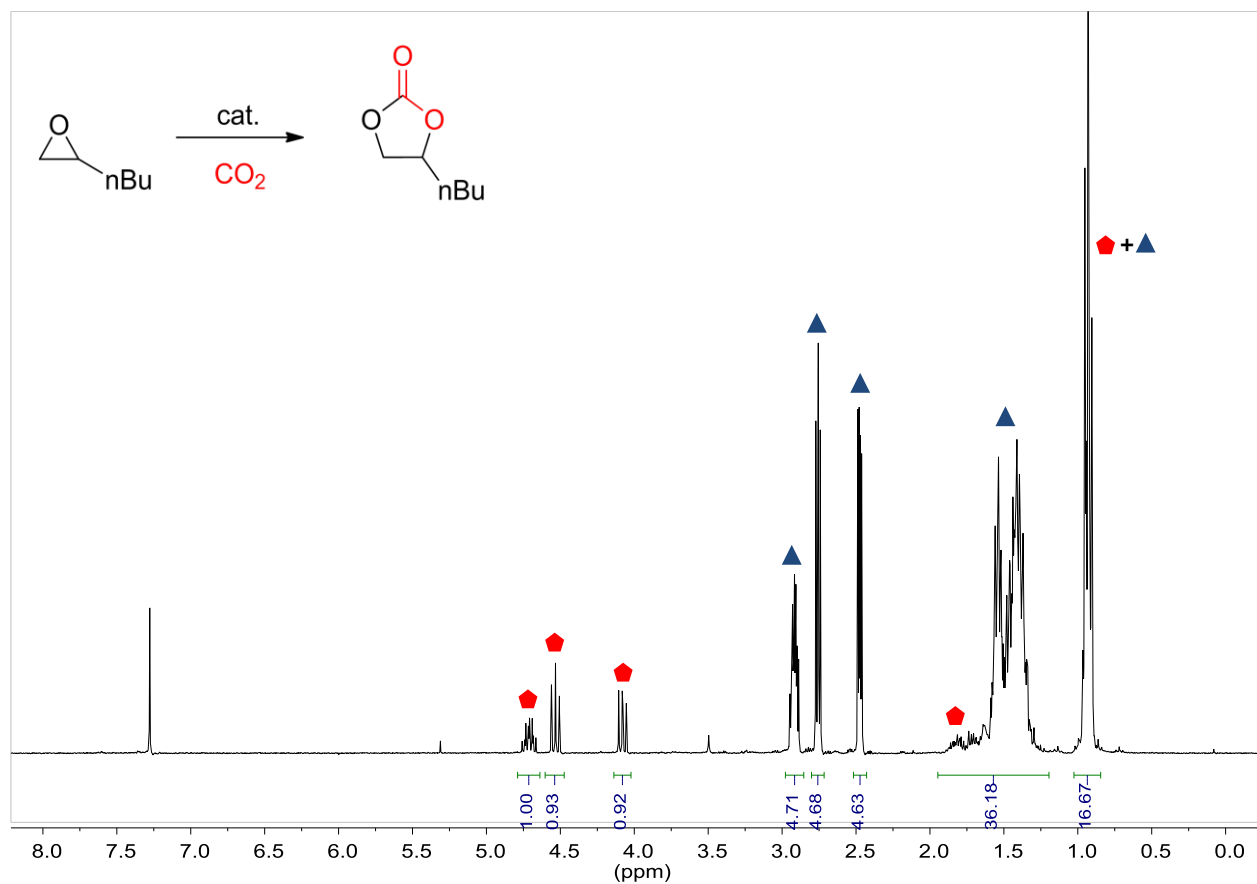
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Typical ^1H NMR spectrum of a product of the kinetic experiments:

Figure S1. ^1H NMR spectrum of a crude mixture in CDCl_3 (300 MHz) at RT.



The red pentagons represent the cyclic carbonate product whereas the blue triangles are related to the starting epoxide (1,2-epoxyhexane).

Spectroscopic data of epoxide and cyclic carbonate product:

1,2-Epoxybutane¹ (blue trace in Figure S1)

¹H NMR (300 MHz, CDCl₃): δ 2.95 – 2.88 (m, 1H), 2.76 (dd, $^2J_{HH} = 5.1$, $^3J_{HH} = 4.0$ Hz, 1H), 2.47 (dd, $^2J_{HH} = 5.1$, $^3J_{HH} = 2.7$ Hz, 1H), 1.60 – 1.30 (m, 6H), 0.93 (t, $^3J_{HH} = 7.0$ Hz, 3H).

4-butyl-1,3-dioxolan-2-one² (red trace in Figure S1)

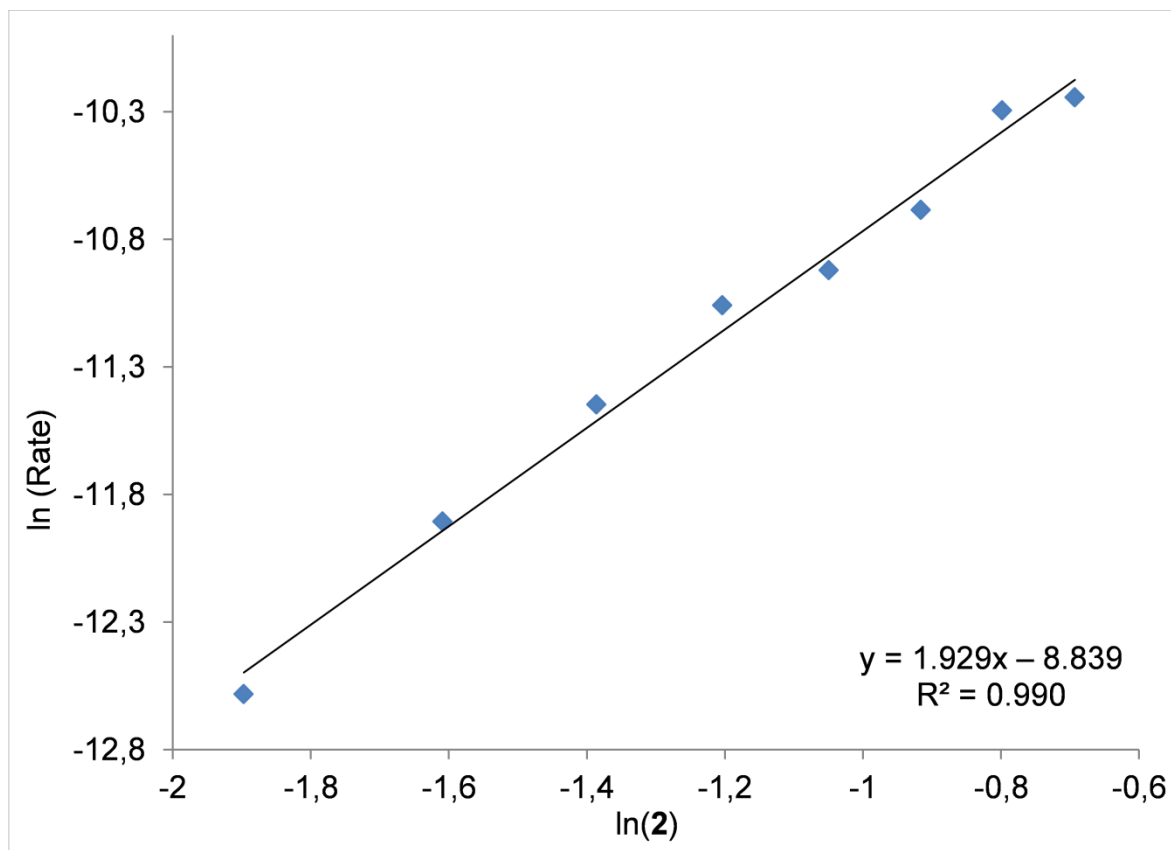
¹H NMR (300 MHz, CDCl₃): δ 4.76 – 4.66 (m, 1H), 4.53 (dd, $^2J_{HH} = 8.2$, $^3J_{HH} = 8.0$ Hz, 1H), 4.08 (dd, $^2J_{HH} = 8.3$, $^3J_{HH} = 7.3$ Hz, 1H), 1.90 – 1.61 (m, 2H), 1.53 – 1.30 (m, 4H), 0.94 (t, $^3J_{HH} = 7.1$ Hz, 3H).

¹ Substrate purchased from Sigma Aldrich.

² Jiang, J.-L.; Gao, F.; Hua, R.; Qiu, X.; *J. Org. Chem.*, 2005, **70**, 381 – 383. doi: 10.1021/jo0485785

Additional kinetic data:

Figure S2: Double logarithmic plot to determinate the order with respect to the bifunctional Zn-complex **2** at 50°C, 1 MPa CO₂ pressure, 18 h and using 1,2-epoxyhexane as substrate.



Tables containing conversions and rates of kinetic experiments:

Table S1. Effect of NBu₄I loading on the rate.^a

[cat]	conv % ^b	Conv mol·L ⁻¹	Rate mol·L ⁻¹ S ⁻¹	Ln(Rate)	Ln [cat]
0.12	19.7	1.6351	2.5233E-05	-10.5874	-2.12026
0.105	16.4	1.3612	2.10062E-05	-10.7707	-2.25379
0.09	14.5	1.2035	1.85725E-05	-10.8938	-2.40795
0.075	12.9	1.0707	1.65231E-05	-11.0107	-2.59027
0.06	11.5	0.9545	1.47299E-05	-11.1256	-2.81341
0.05	8.14	0.67562	1.04262E-05	-11.4712	-2.99573
0.04	8.57	0.71131	1.0977E-05	-11.4197	-3.21888
0.03	6.28	0.52124	8.04383E-06	-11.7306	-3.50656
0.02	4.64	0.38512	5.94321E-06	-12.0333	-3.91202
0.01	3.17	0.26311	4.06034E-06	-12.4142	-4.60517

^a General conditions: 1,2-epoxyhexane (10 mmol), catalyst (0.12 – 0.01 mol%), 18 h, $p(\text{CO}_2) = 1.0 \text{ MPa}$, 50°C, neat. ^b Conversion determined by ¹H NMR (CDCl₃); selectivity for the cyclic carbonate, >99%.

Table S2. Effect of the loading of **1** on the rate in the presence of an excess of NBu₄I.^a

[cat]	conv % ^b	Conv mol·L ⁻¹	Rate mol·L ⁻¹ ·S ⁻¹	Ln(Rate)	Ln [cat]
0.225	15.79	1.31057	0.000182024	-8.61137	-1.49165
0.2	14.83	1.23089	0.000170957	-8.6741	-1.60944
0.175	12.52	1.03916	0.000144328	-8.84342	-1.74297
0.15	11.56	0.95948	0.000133261	-8.9232	-1.89712
0.125	9.06	0.75198	0.000104442	-9.16688	-2.07944
0.1	7.53	0.62499	8.68042E-05	-9.35186	-2.30259
0.075	5.03	0.41749	5.79847E-05	-9.75533	-2.59027
0.05	3.96	0.32868	0.00004565	-9.99451	-2.99573
0.035	2.85	0.23655	3.28542E-05	-10.3234	-3.35241
0.025	2.52	0.20916	0.00002905	-10.4465	-3.68888

^a General conditions: 1,2-epoxyhexane (10 mmol), catalyst **1** (0.225 – 0.025 mol%), co-catalyst (0.4 mol%), 2 h, $p(\text{CO}_2)$ = 1.0 MPa, 30°C, neat. ^b Conversion determined by ¹H NMR (CDCl₃); selectivity for the cyclic carbonate, >99%.

Table S3. Effect of the loading of NBu₄I on the rate in the presence of an excess of **1**.^a

[cat]	conv % ^b	Conv mol·L ⁻¹	Rate mol L ⁻¹ ·S ⁻¹	Ln (Rate)	Ln [cat]
0.4	14.83	1.23089	0.000170957	-8.6741	-0.91629
0.2	9.4	0.7802	0.000108361	-9.13004	-1.60944
0.16	6.6	0.5478	7.60833E-05	-9.48368	-1.83258
0.12	5.98	0.49634	6.89361E-05	-9.58233	-2.12026
0.08	3.48	0.28884	4.01167E-05	-10.1237	-2.52573
0.04	1.89	0.15687	2.17875E-05	-10.7342	-3.21888

^a General conditions: 1,2-epoxyhexane (10 mmol), catalyst Zn **1** (0.20 mol%), co-catalyst (0.40 – 0.04 mol%), 2 h, *p*(CO₂) = 1.0 MPa, 30°C, neat. ^b Conversion determined by ¹H NMR (CDCl₃); selectivity for the cyclic carbonate, >99%.

Table S4. Effect of the loading of **1** and NBu₄I on the rate.^a

[cat]	conv % ^b	Conv mol·L ⁻¹	Rate mol·L ⁻¹ ·S ⁻¹	Ln(Rate)	Ln [cat]
0.35	13.74	1.14042	0.000158392	-8.75044	-1.04982
0.3	12.3	1.0209	0.000141792	-8.86115	-1.20397
0.25	10.6	0.8798	0.000122194	-9.0099	-1.38629
0.205	7.51	0.62333	8.65736E-05	-9.35452	-1.58475
0.172	5.78	0.47974	6.66306E-05	-9.61635	-1.76026
0.15	5.57	0.46231	6.42097E-05	-9.65336	-1.89712
0.125	4.96	0.41168	5.71778E-05	-9.76935	-2.07944
0.1	3.39	0.28137	3.90792E-05	-10.1499	-2.30259

^a General conditions: 1,2-epoxyhexane (10 mmol), catalyst **1**/NBu₄I (0.35 – 0.10 mol%), 2 h, *p*(CO₂) = 1.0 MPa, 30°C, neat. ^b Conversion determined by ¹H NMR (CDCl₃); selectivity for the cyclic carbonate, >99%.

Table S5. Effect of the loading of **2** on the rate at 80° C.^a

[cat]	conv % ^b	Conv mol·L ⁻¹	Rate mol·L ⁻¹ ·S ⁻¹	Ln(Rate)	Ln [cat]
0.69	27.65	2.29495	0.000318743	-8.05113	-0.37106
0.59	24.72	2.05176	0.000284967	-8.16314	-0.52763
0.5	13.38	1.11054	0.000154242	-8.77699	-0.69315
0.45	11.48	0.95284	0.000132339	-8.93014	-0.79851
0.4	11.04	0.91632	0.000127267	-8.96923	-0.91629
0.29	6.44	0.53452	7.42389E-05	-9.50822	-1.23787
0.205	3.12	0.25896	3.59667E-05	-10.2329	-1.58475

^a General conditions: 1,2-epoxyhexane (10 mmol), catalyst **2** (0.69 – 0.205 mol%), 2 h, $p(\text{CO}_2) = 1.0 \text{ MPa}$, 80°C, neat. ^b Conversion determined by ¹H NMR (CDCl₃); selectivity for the cyclic carbonate, >99%.

Table S6. Effects of the loading of **2** on the rate at 50° C.^a

[cat]	conv % ^b	Conv mol·L ⁻¹	Rate mol·L ⁻¹ ·S ⁻¹	Ln(Rate)	Ln [cat]
0.5	27.8	2.3074	3.5608E-05	-10.2429	-0.69315
0.45	26.4	2.1912	3.38148E-05	-10.2946	-0.79851
0.4	17.88	1.48404	2.29019E-05	-10.6843	-0.91629
0.35	14.11	1.17113	1.8073E-05	-10.9211	-1.04982
0.3	12.3	1.0209	1.57546E-05	-11.0584	-1.20397
0.25	8.34	0.69222	1.06824E-05	-11.4469	-1.38629
0.2	5.27	0.43741	6.75015E-06	-11.9059	-1.60944
0.15	2.68	0.22244	3.43272E-06	-12.5822	-1.89712

^a General conditions: 1,2-epoxyhexane (10 mmol), catalyst **2** (0.50 – 0.15 mol%), 18 h, $p(\text{CO}_2) = 1.0 \text{ MPa}$, 50°C, neat. ^b Conversion determined by ¹H NMR (CDCl₃); selectivity for the cyclic carbonate, >99%.

Table S7. Effect of the loading of **2** on the rate in the presence of an excess of NBu₄I.^a

[cat]	conv % ^b	Conv mol·L ⁻¹	Rate mol·L ⁻¹ ·S ⁻¹	Ln(Rate)	Ln [cat]
0.4	16.48	1.36784	0.000189978	-8.5686	-0.91629
0.3	14.13	1.17279	0.000162888	-8.72245	-1.20397
0.25	10.94	0.90802	0.000126114	-8.97833	-1.38629
0.235	11.45	0.95035	0.000131993	-8.93276	-1.44817
0.195	7.05	0.58515	8.12708E-05	-9.41772	-1.63476
0.18	8.88	0.73704	0.000102367	-9.18695	-1.7148
0.16	6.51	0.54033	7.50458E-05	-9.49741	-1.83258
0.15	5.63	0.46729	6.49014E-05	-9.64264	-1.89712
0.133	6.49	0.53867	7.48153E-05	-9.50049	-2.01741
0.1	5.39	0.44737	6.21347E-05	-9.68621	-2.30259

^a General conditions: 1,2-epoxyhexane (10 mmol), catalyst **2** (0.40 – 0.10 mol%), co-catalyst (0.6 mol%), 2 h, $p(\text{CO}_2) = 1.0 \text{ MPa}$, 40°C, neat. ^b Conversion determined by ¹H NMR (CDCl₃); selectivity for the cyclic carbonate, >99%.

Photographs of the reactors used for the catalytic studies:

Figure S3. Standard autoclaves used for the kinetic experiments mentioned in the table S4 and S5.



Figure S4. AMTEC SPR-16 system used for the kinetic studies.



Comparison of reactions carried out in the absence/presence of an internal standard:

- To quantify the amount of carbonate formed, mesitylene was used as internal standard (IS) in several cases. The deviation found was minimal when the amount of carbonate was calculated in the presence or absence of the internal standard. The benchmark substrate (1,2-epoxyhexane) was chosen for this comparative study complete selectivity towards the cyclic carbonate was noted in all studied cases. Thus it is possible to obtain the conversion by integration of the peaks related to the presence of cyclic carbonate formed and the unreacted epoxide with minimal error (see table below).

Table S8:

Catalyst	% cyclic carbonate in absence of IS	% cyclic carbonate in presence of IS
0.69 mol % cat. 2	27.65	27.66
0.45 mol % cat. 2	11.48	11.61
0.29 mol % cat. 2	6.44	6.23
0.25 mol % cat. 2	7.51	4.92
0.60 mol % cat. 1	25.90	22.62

Conditions: 1,2-epoxyhexane (10 mmol) as substrate, 1 MPa of CO₂, 2 h, 80 °C with catalyst **2** and 30°C with catalyst **1**.

Determination of steady-state domains:

Figure S5:

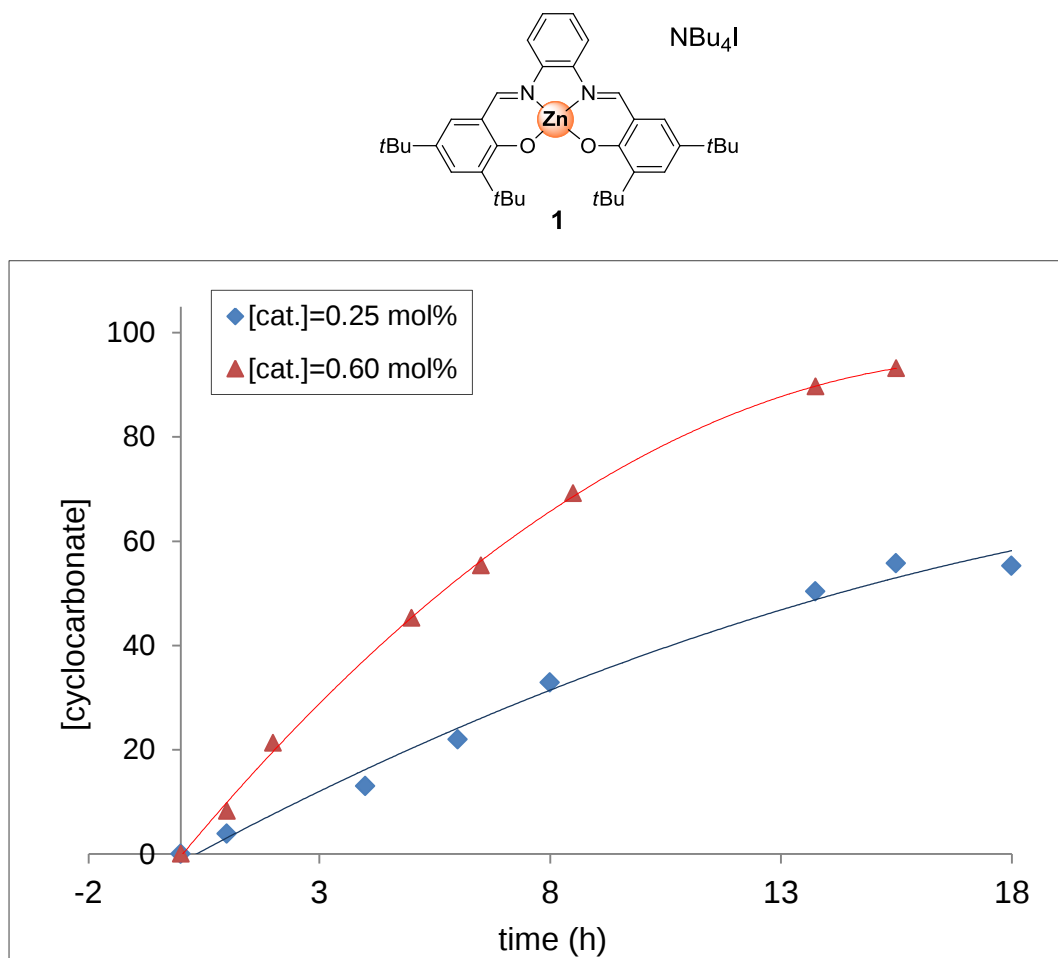


Figure S5: Cyclic carbonate formation in time at various concentrations of catalyst **1**. Conditions: 1,2-epoxyhexane (10 mmol) as substrate, 30°C, 1 MPa of CO₂, [Zn] = [NBu₄I] = 0.25 and 0.60 mol%.

It can be reasonably assumed that at both concentrations of catalyst a steady-state domain is apparent in the first two hours.

Figure S6:

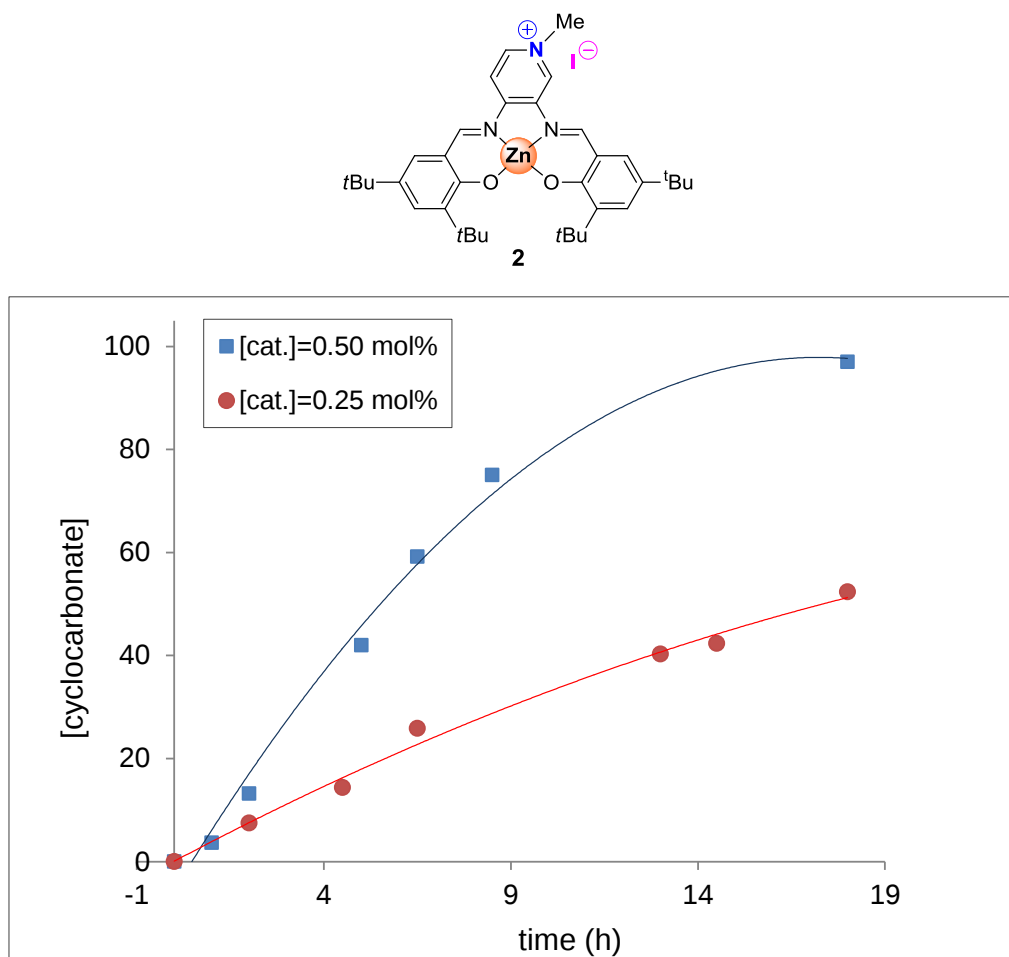


Figure S6: Cyclic carbonate formation in time at various concentration of catalyst **2**. Conditions: 1,2-epoxyhexane (10 mmol) as substrate, 80°C, 1 MPa of CO₂, [ZnI] = 0.25 and 0.50 mol%.

It can be reasonably assumed that at both concentrations of catalyst a steady-state domain is apparent in the first two hours.