Supporting Information

Breaking the equilibrium limit: Synthesis of diethyl carbonate from CO_2 using regenerable bis-/tris- triethoxysilane substrates

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General Information

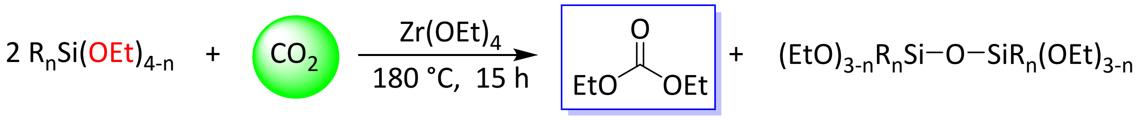
1. Materials & Characterization

All compounds purchased from Sigma-Aldrich, Alfa Aesar, TCI, Wako, Gelest, Inc. were used without further purification. According to the European Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) Legislation, some training and authorization are mandatory for protective and effective use of isocyanate compounds. However, Safety Data Sheet (SDS) of substrate isocyanate **1a** stated that "the substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605". ^{1}H NMR spectra were recorded by Bruker ADVANCE III HD (^{1}H NMR at 400 MHz and 600 MHz), (^{13}C{^{1}H} NMR at 100.7 MHz) and (^{29}Si NMR at 75.9 MHz). Gas chromatography (GC) analysis was performed by Shimadzu GC-2014 instrument equipped with a flame ionization detector using column TC-1. Gas chromatography-mass spectrometric (GC-MS) analysis was performed by Shimadzu QP-2010 spectrometer using column TC-1. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI–TOF MS) of the obtained oligomers was performed using a Bruker autoflex speed. Samples for the MALDI–TOF MS were prepared by mixing the oligomer (20 mg·mL^{-1}, 10 µL), a matrix (DCTB, 50 mg·mL^{-1}, 50 µL), and a cationic agent (sodium trifluoroacetate or silver trifluoroacetate, 25 mg·mL^{-1}, 20 µL) in THF. Gel permeable chromatography (GPC) analysis was performed by Shimadzu instrument in THF (1.0 mL·min^{-1}) at 40 °C using column Shodex GPC KF-803 (range of molecular weight 1,000 - 50,000, exclusion limit, 7×10^4). IR spectra were recorded by JASCO ATRS-100-CIR spectrophotometer. Elemental analysis was performed by WDXRF Bruker AXS T8 Tiger spectrophotometer.

2. DEC synthesis

DEC synthesis was carried out in an autoclave with an inner volume of 10 mL by similar manner with the previous method when TEOS was used as a substrate. About 0.3 g of $Zr(OEt)_4$ catalyst, 15.7 mmol of substrate **1a** were put into the autoclave together with stirring bar. The reactor was subsequently pressurized and purged with CO_2 up to 5 MPa at ambient condition. After CO_2 insertion, the reactor was heated to 100 - 180 °C. The mixture was constantly stirred during the reaction. After the specific reaction time, the reactor was cooled to room temperature and 0.1 g of mesitylene was added to the liquid phase as an internal standard for a quantitative analysis. The synthesis using other organosilicon substrates was conducted in a similar manner.

Conversion, yield, material balance, and TON number are calculated by following the previous manner,[1] when TEOS or other previous alkoxysilanes were used as substrate:



$$\textbf{Conv.(\%)} = \left(1 - \frac{mole\ of\ remaining\ substrate}{initial\ mole\ of\ substrate}\right) \times 100\%$$

$$\textbf{Yield (\%)} = \left(\frac{mole\ of\ detected\ DEC\ \times 2}{initial\ mole\ of\ substrate}\right) \times 100\%$$

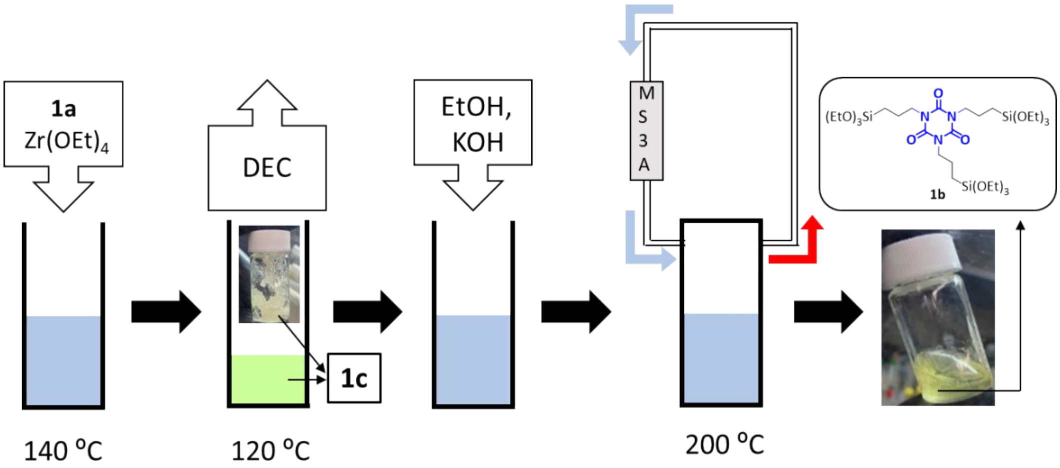
$$\textbf{TON} = \frac{mole\ of\ DEC}{mole\ of\ added\ catalyst}$$

3. Synthesis of intermediate **1b** from substrate **1a**

Synthesis of intermediate **1b** was performed in an Erlenmeyer flask under N_2 atmosphere. The isocyanate **1a** (10 mL) was stirred at 200 °C for 96-h reaction without addition of catalyst or additives. The product isocyanurate **1b** was subsequently used for DEC synthesis after the addition of $Zr(OEt)_4$ catalysts.

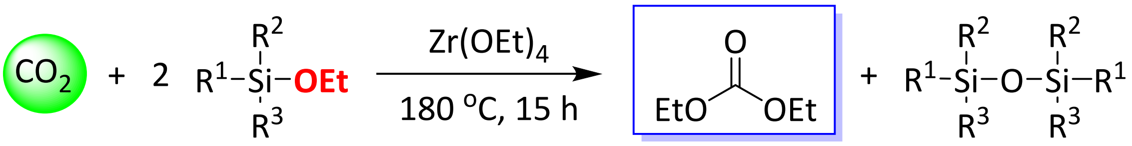
4. Reconversion of **1b** from **1c**

Procedure for regeneration of **1b** was performed in one pot system as a consecutive process of DEC synthesis under nitrogen atmosphere using 200-mL stainless steel autoclave. The autoclave is connected with a steel joint, heater and condenser to circulate the reaction mixture. The DEC was firstly synthesized by reacting substrate **1a** (100 g) with 5 MPa of CO_2 at room temperature using 6 gram of $Zr(OEt)_4$ catalyst. The mixture was reacted at 140 °C for 6 h to give 61% of DEC product. The DEC was subsequently removed under vacuum at 120 °C to obtain solid **1c**. The polyisocyanurate **1c** was then reconverted to isocyanurate **1b** by adding 100 g of super dehydrated EtOH with KOH catalyst to the autoclave. The autoclave was installed in the circulation system equipped with dehydrating agent MS3A. The reaction was conducted at 200 °C for 16 h to obtain viscous liquid isocyanurate **1b**.



Scheme S1. Schematic illustration of one pot DEC synthesis and regeneration of intermediate **1b** from **1c**.

Effect of ethoxy number on DEC synthesis



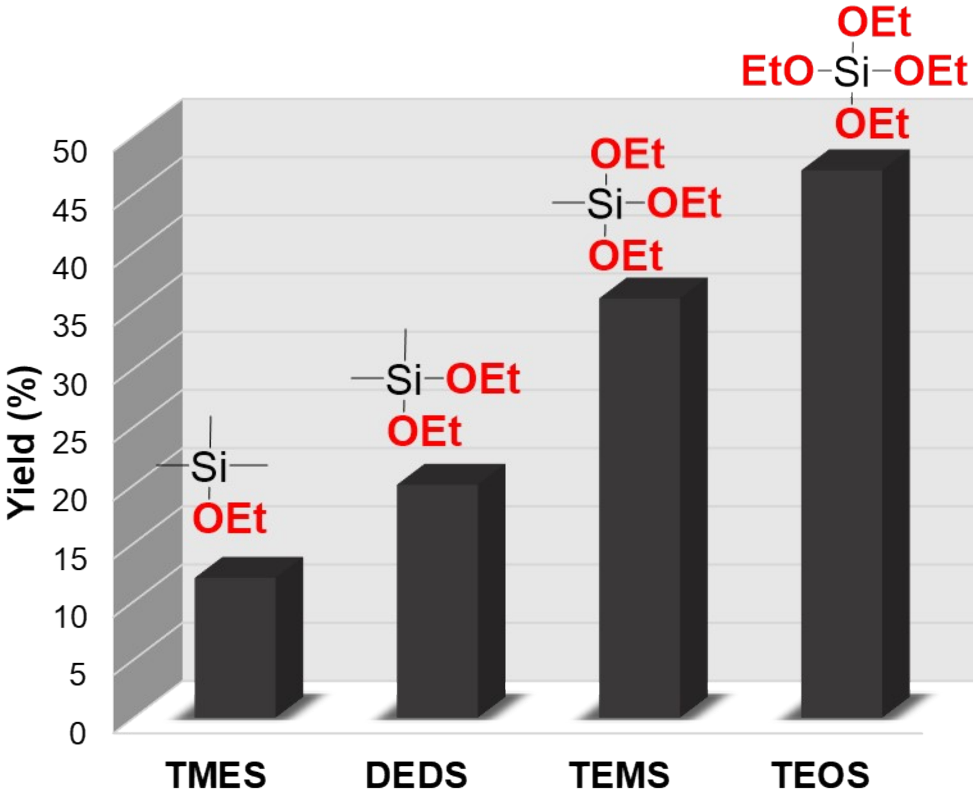
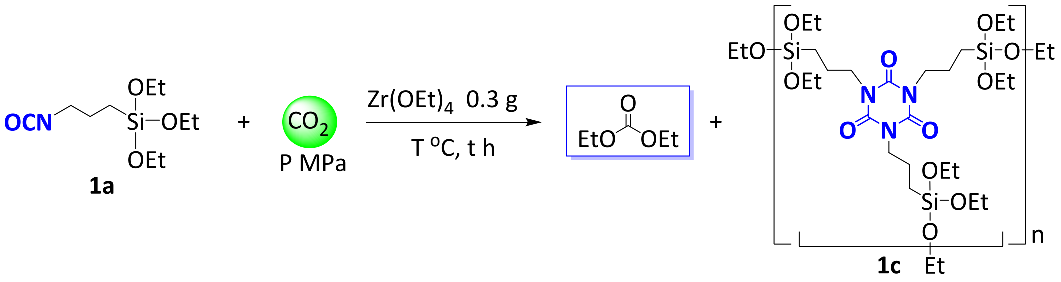


Figure S1. The effect of ethoxy group number on the alkoxysilane substrates for DEC formation.

Reaction optimization

Table S1. Reaction optimization for DEC synthesis using **1a**.

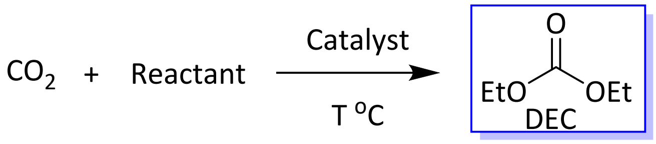


Entry	T (°C)	P (MPa)	t (h)	DEC (mmol)	Yield (%)
1	180	5	15	4.9	62
2	160	5	15	5.1	64
3	140	5	15	6.0	75
4	120	5	15	3.8	49
5	100	5	15	1.7	22
6	140	5	96	7.4	94
7	140	4	15	5.8	73
8	140	3	15	5.2	65

Reaction conditions: Substrate **1a**, 15.7 mmol; CO_2 pressure at room temperature; $Zr(OEt)_4$, 0.3 g (Si/Zr = 14)). Yield was determined by GC analysis using mesitylene as an internal standard.

Table S2. Comparative activity of DEC synthesis using CO_2

No	Reactant	Catalyst	Dehydrant	P (MPa)	T (°C)	t (h)	TON	Ref
1	EtOH	CeO_2	–	8	150	0.5	0.42	1
2	EtOH	ZrO_2	MS	7	150	4	0.38	2
3	EtOH	CeO_2	Butylene oxide	4.5	180	22	0.43	3
4	EtOH	CeO_2	2,2-diethoxypropane	5	120	24	4.51	4
5	EtOH	Bu_2SnO	2,2-diethoxypropane	5	160	20	1.42	5
6	EtOH	CeO_2	2-Cyanopyridine	5	120	4	4.61	6
7	EtOH	CeO_2	Triethyl orthoacetate	5	160	24	2.93	7
8	TEOS	$Zr(OEt)_4$	–	5	180	24	3.73	9
9	Isocyanate **1a**	$Zr(OEt)_4$	–	5	140	15	5.45	This Work



References

1. Y. Yoshida, Y. Arai, S. Kado, K. Kunimori and K. Tomishige, *Catal. Today*, 2006, **115**, 95–101.
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7. W. S. Putro, Y. Munakata, S. Ijima, S. Shigeyasu, S. Hamura, S. Matsumoto, T. Mishima, K. Tomishige, J.-C. Choi and N. Fukaya, *J. CO_2 Util.*, 2022, **55**, 101818.

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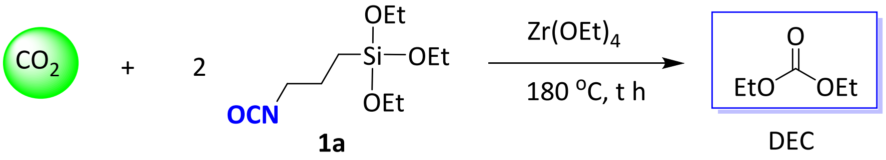
Time profile

Table S3. Time progress of DEC synthesis from CO_2 and substrate **1a** using $Zr(OEt)_4$ catalysts.



Entry	t (h)	DEC (mmol)	Yield (%)	Conv (%)	TON
1	6	3.6	46	100	3.3
2	15	4.9	62	100	4.4
3	24	5.1	65	100	4.6
4	40	5.3	67	100	4.8

Reaction conditions: Substrate **1a**, 15.7 mmol; CO_2, 5 MPa at room temperature; $Zr(OEt)_4$, 0.3 g (Si/Zr = 14); 180 °C. Yield was determined by GC analysis using mesitylene as an internal standard.

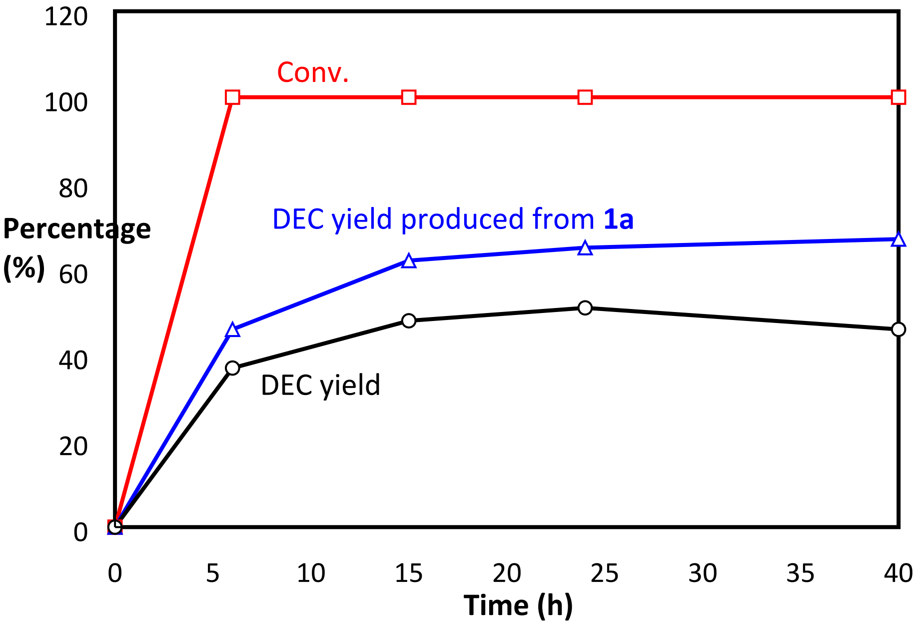
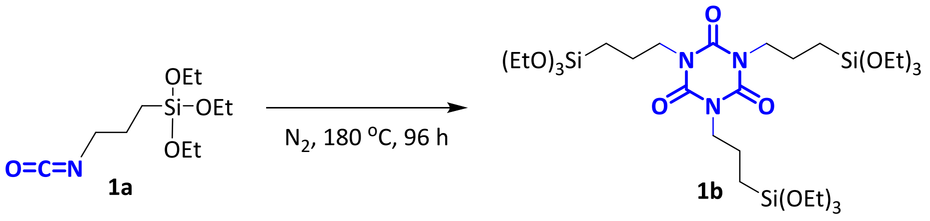


Figure S2. Profile of DEC yield produced from **1a** and from TEOS; and the conversion of **1a** from reaction of CO_2 with **1a**. *Reaction conditions*: substrate, 15.7 mmol; CO_2, 5 MPa at room temperature; $Zr(OEt)_4$, 0.3 g (Si/Zr = 14); reaction temperature using TEOS, 180 °C; reaction temperature using **1a**, 140 °C. DEC yield and **1a** conversion were determined by GC using mesitylene as an internal standard.

Characterization of intermediate 1b



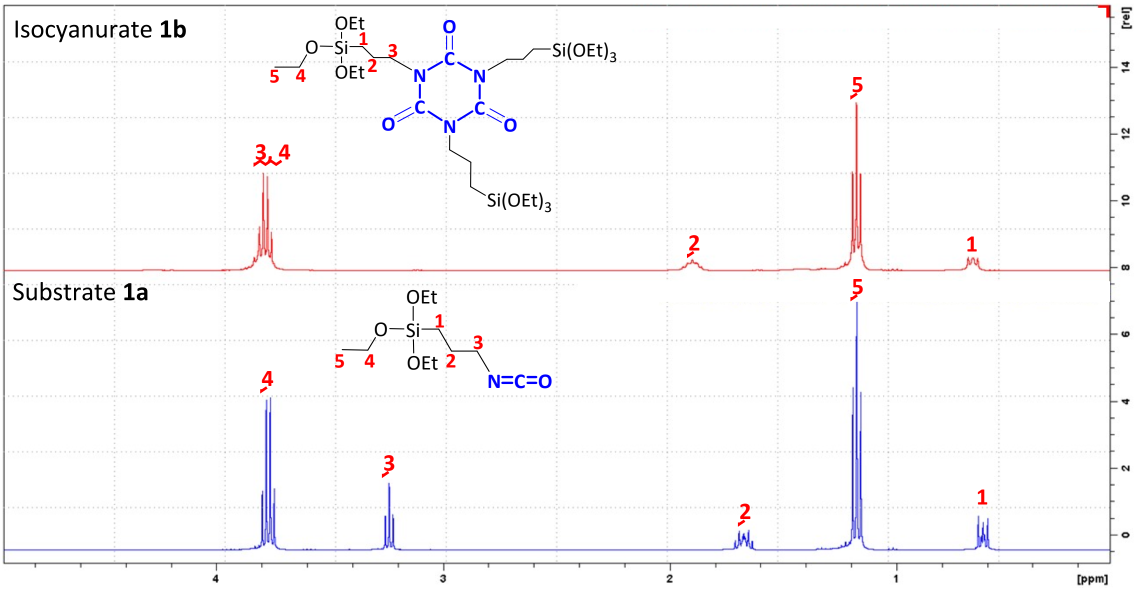


Figure S3. ^{1}H NMR of substrate **1a** and product isocyanurate **1b** from reaction without catalyst.

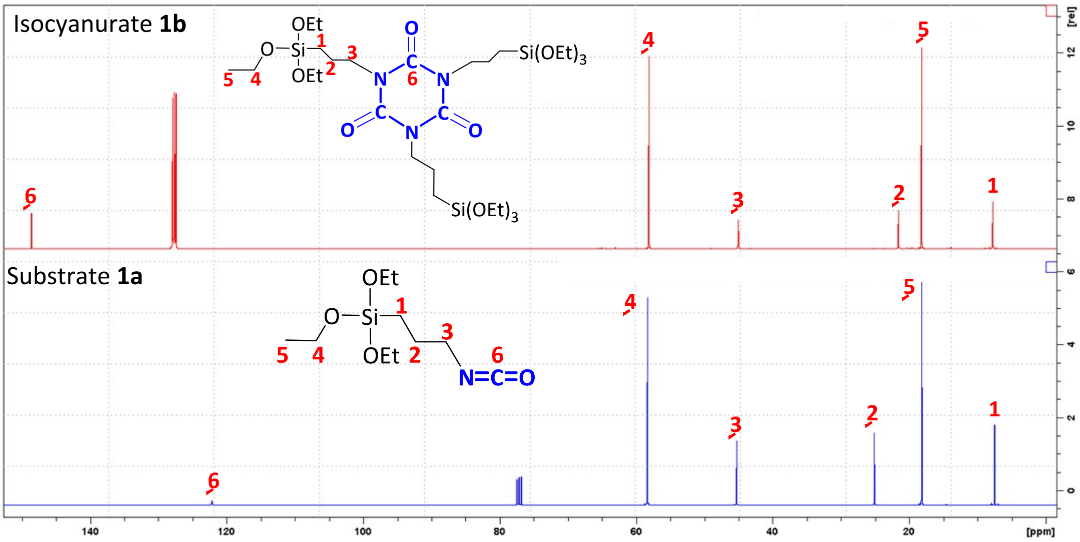


Figure S4. ^{13}C NMR of substrate **1a** and product isocyanurate **1b** from reaction without catalyst.

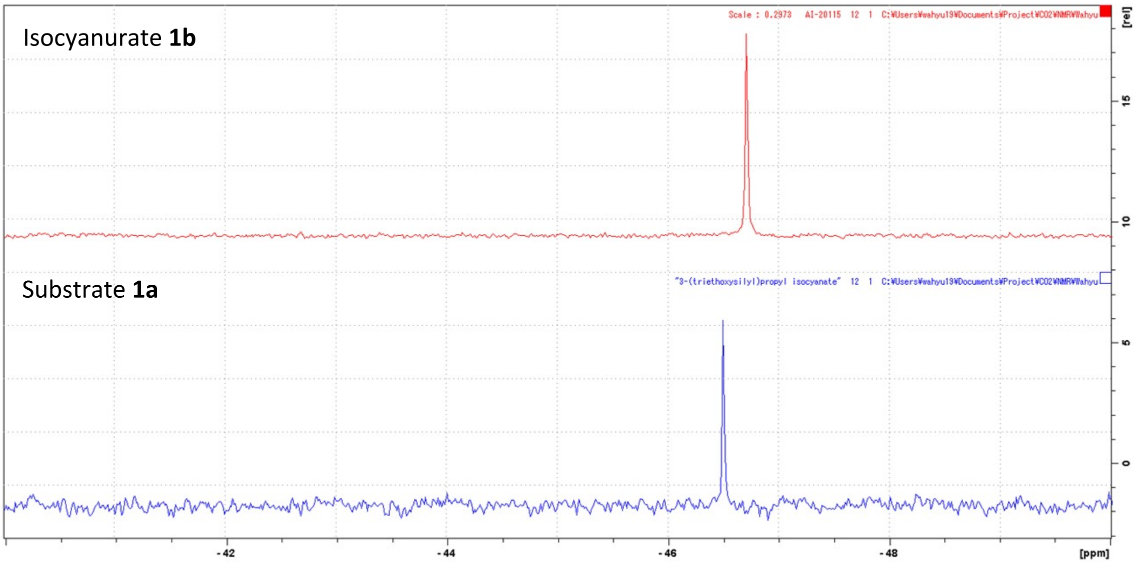


Figure S5. ^{27}Si NMR of substrate **1a** and product isocyanurate **1b** from reaction without catalyst.

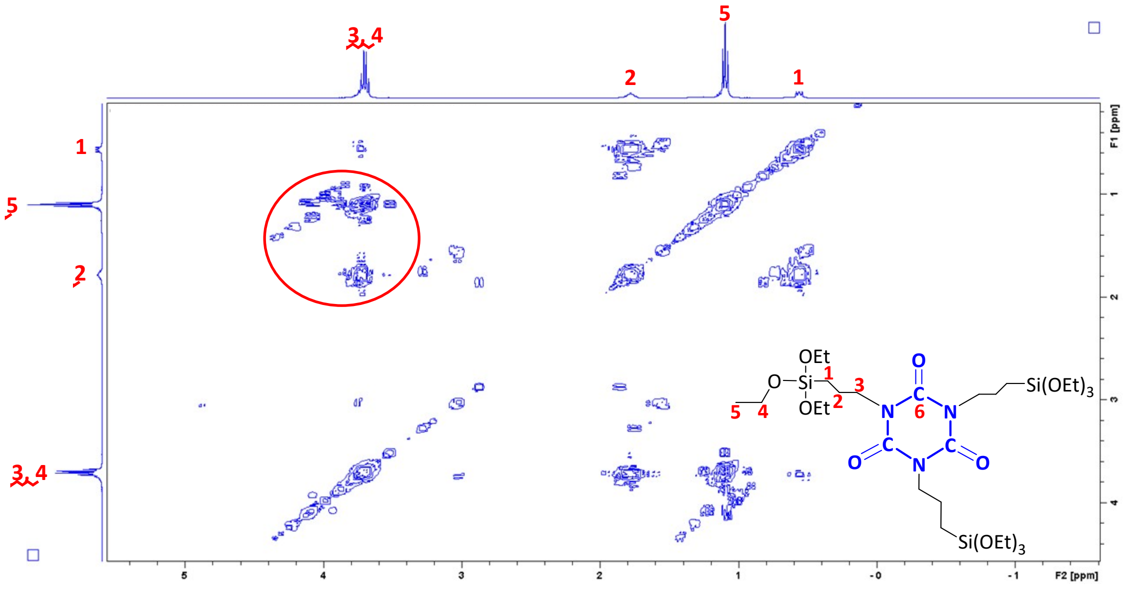


Figure S6. 2D (COSY) NMR result of isocyanurate **1b**.

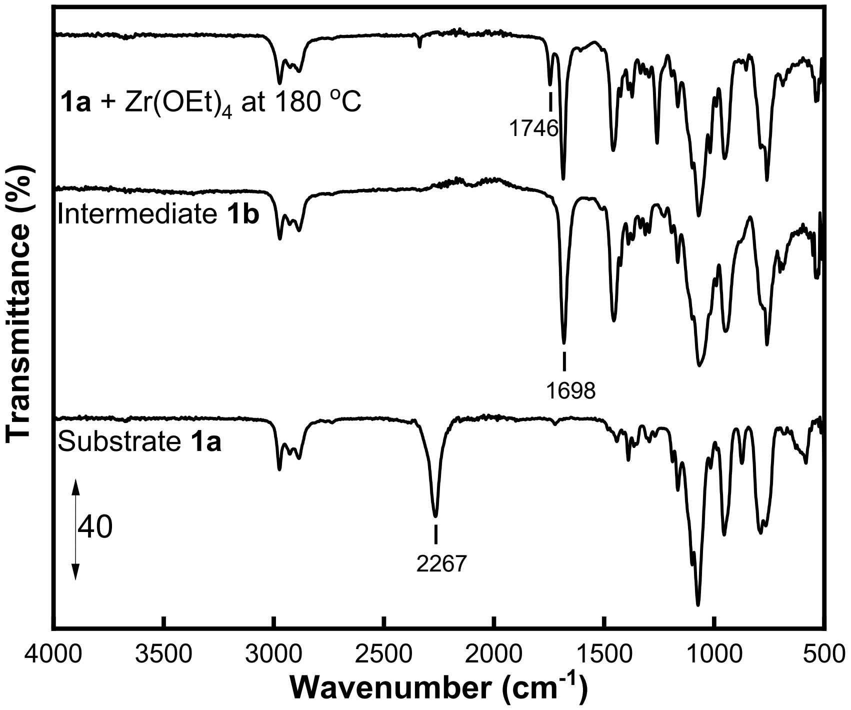


Figure S7. ATR-IR results of substrate **1a**, intermediate **1b** and liquid solution after DEC synthesis.

Table S4. The assignment of the ATR-IR results.

Wavenumber (cm^{-1})	Assignment	Ref
2267	–NCO of isocyanate	2
1746	C=O of DEC	3
1698	C=O of cyanurate	4

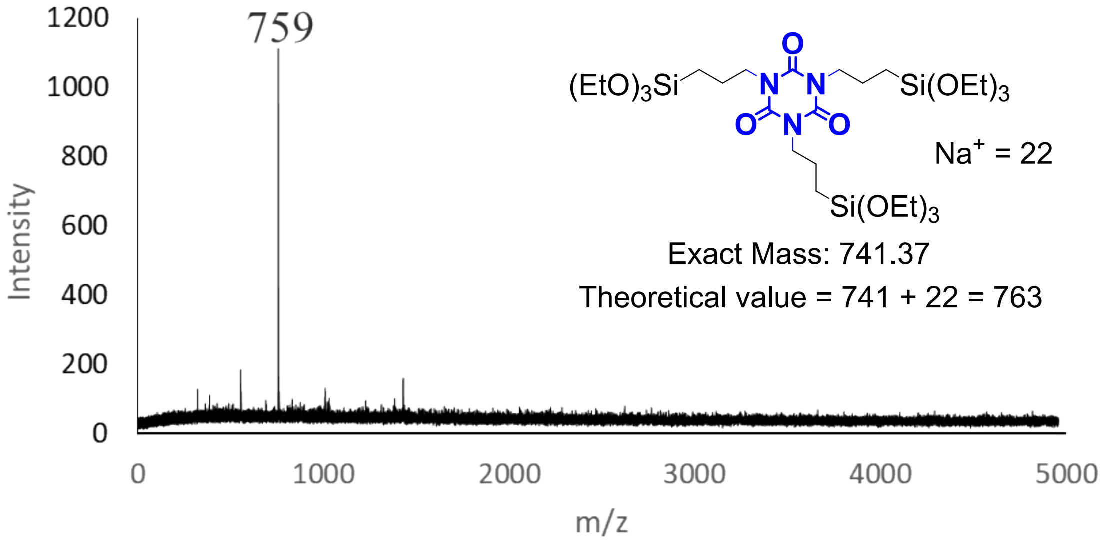


Figure S8. Molecular weight analysis of intermediate **1b** by MALDI-TOF.

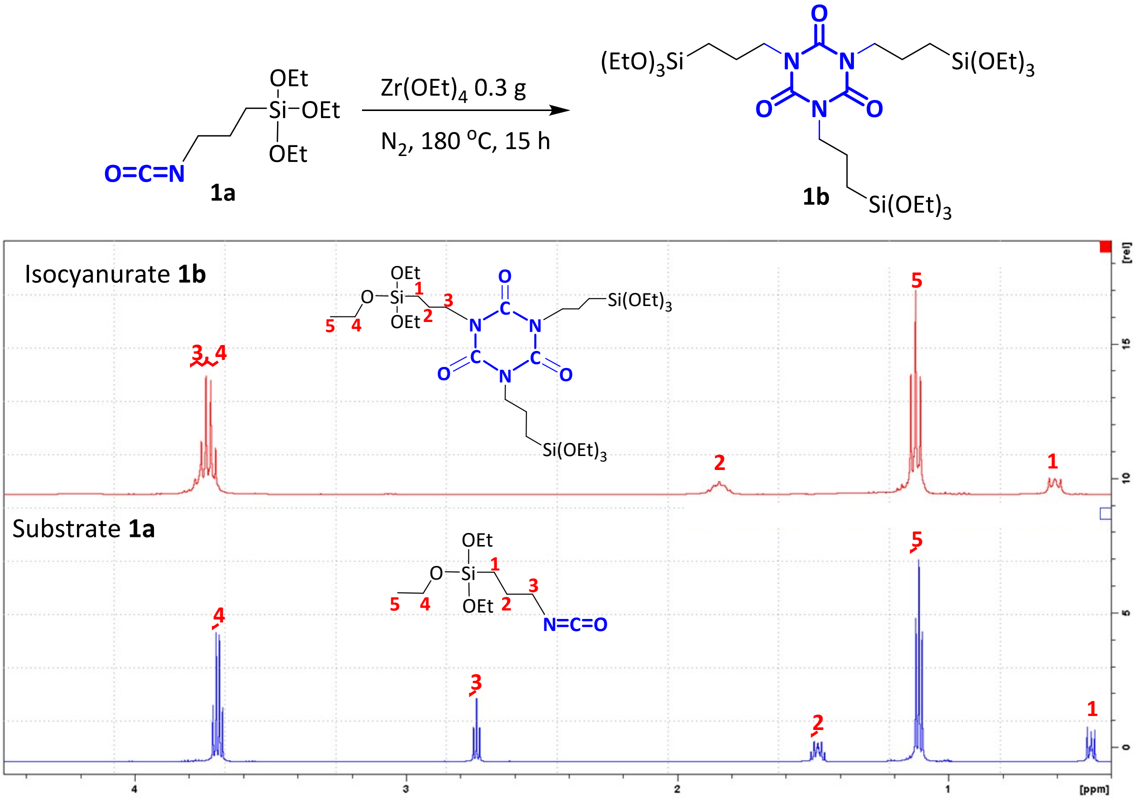


Figure S9. ^{1}H NMR of substrate **1a** and isocyanurate **1b** from reaction with $Zr(OEt)_4$ catalyst.

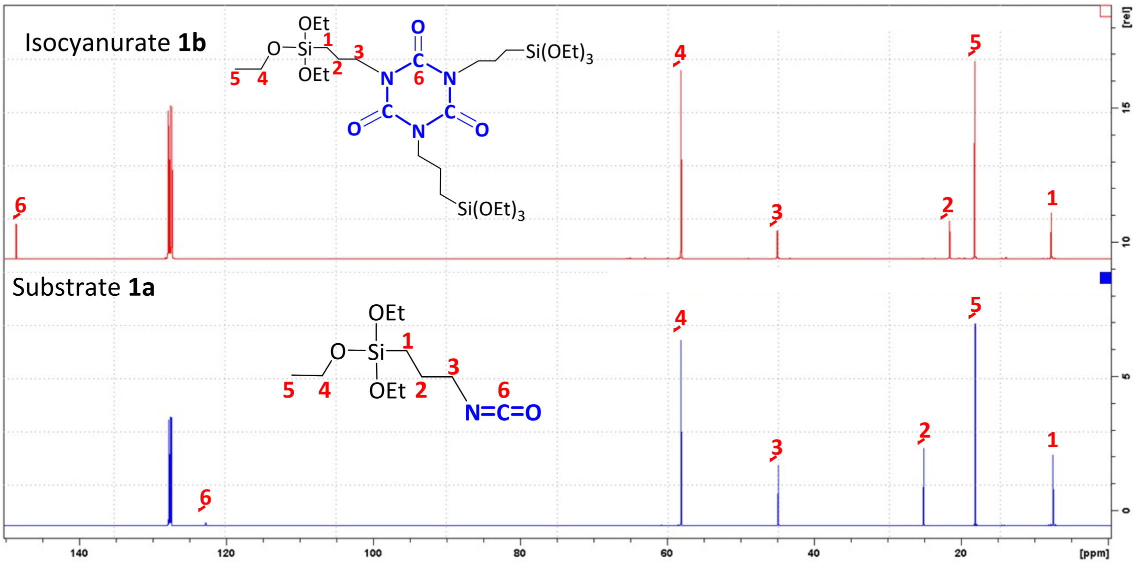


Figure S10. ^{13}C NMR of substrate **1a** and isocyanurate **1b** from reaction with Zr(OEt)$_4$ catalyst.

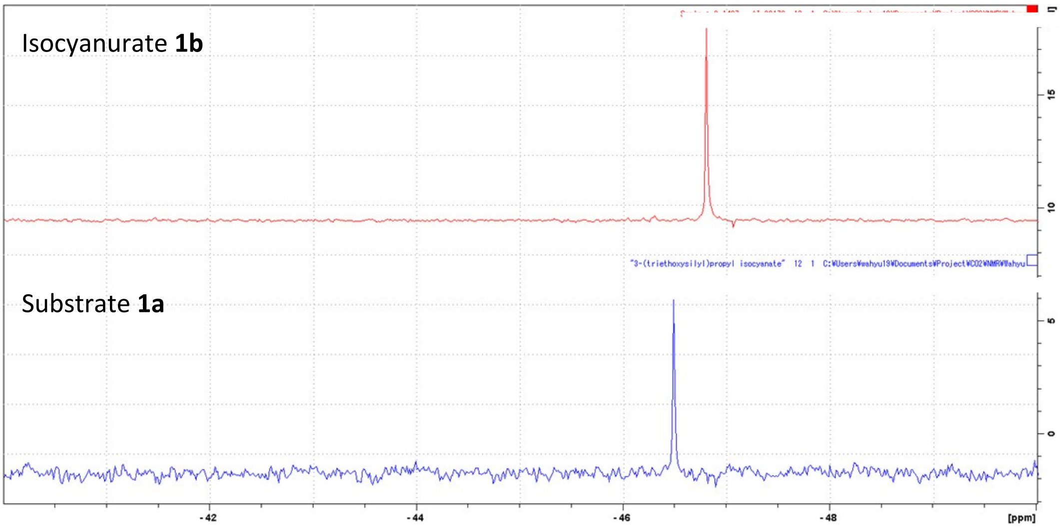
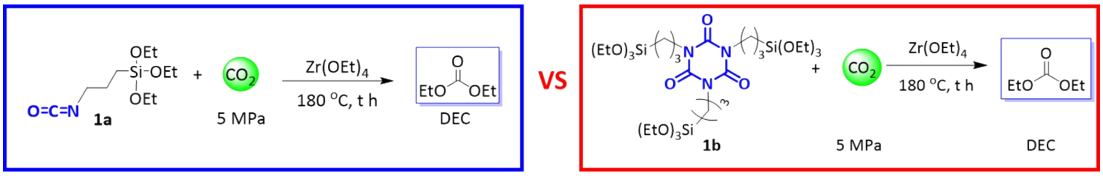


Figure S11. ^{27}Si NMR of substrate **1a** and isocyanurate **1b** from reaction with Zr(OEt)$_4$ catalyst.

DEC synthesis from substrate 1a vs intermediate 1b



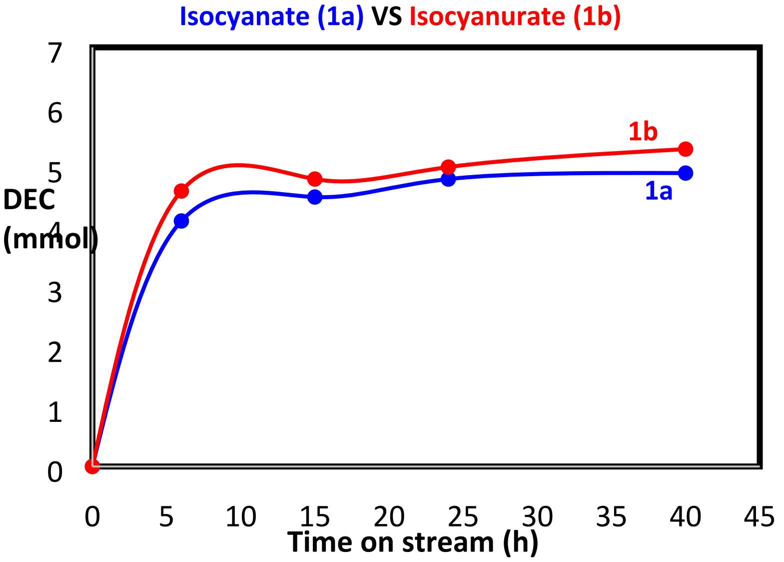


Figure S12. Profile of DEC formation from **1a** vs **1b** as substrate and CO_2 and $Zr(OEt)_4$ catalyst. *Reaction conditions*: substrate **1a**, 15.7 mmol; substrate **1b**, 5.2 mmol; CO_2, 5 MPa at room temperature; $Zr(OEt)_4$, 0.3 g (Si/Zr = 14)); 180 °C. DEC amount is determined by GC analysis using mesitylene as an internal standard.

Characterization of byproduct 1c

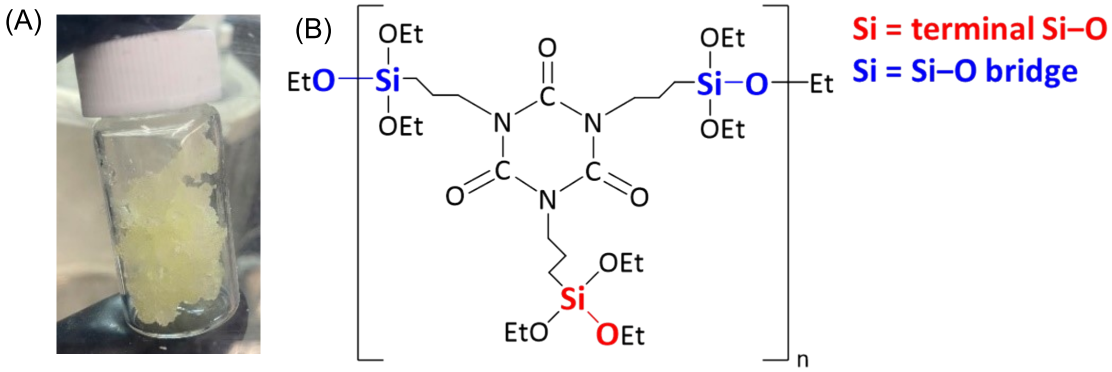
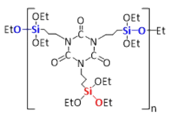
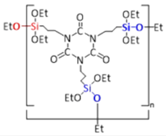
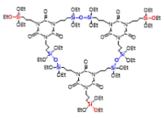
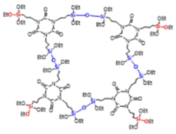
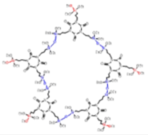
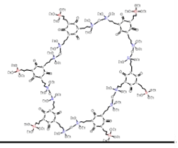
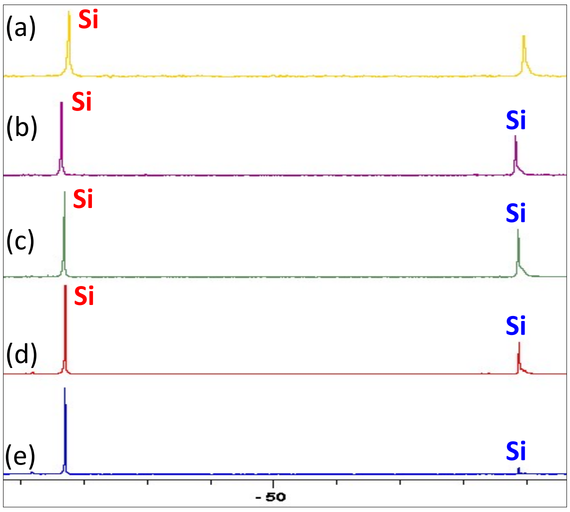


Figure S13. (A) photograph of product after DEC synthesis at 140 °C 96 h from **1a** and CO_2, (B) the chemical structure of oligomer byproduct **1c** which indicates the Si-terminal and Si-bridge.

Table S5. The terminal-bridge ratio of Si–O bond for possible structure of oligomer **1c** to predict the dominant structure detected by ^{29}Si NMR.

n	Linear  	Bridge  	Tri Cyclic 	Tetra Cyclic 	Penta Cyclic 	Hexa Cyclic 
2	4:2	(4:2)	–	–	–	–
3	5:4	(5:4)	3:6	–	–	–
4	6:6	6:6	4:8	4:8	–	–
5	7:8	7:8	5:10	5:10	5:10	–
6	8:10	8:10	4:14	4:14	6:12	6:12



Temp. (°C)	Si : Si	$\bar{n}$	DEC (mmol)
180	5 : 4	3	4.1
160	5 : 4.3	3	4.3
140	5 : 4.8	4	5.1
120	5 : 2.8	2	4.5
100	5 : 0.16	~1	3.4

Figure S14. Si NMR spectra of oligomer **1c** after DEC synthesis at (a) 180 °C, (b) 160 °C, (c) 140 °C, (d) 120 °C, (e) 100 °C.

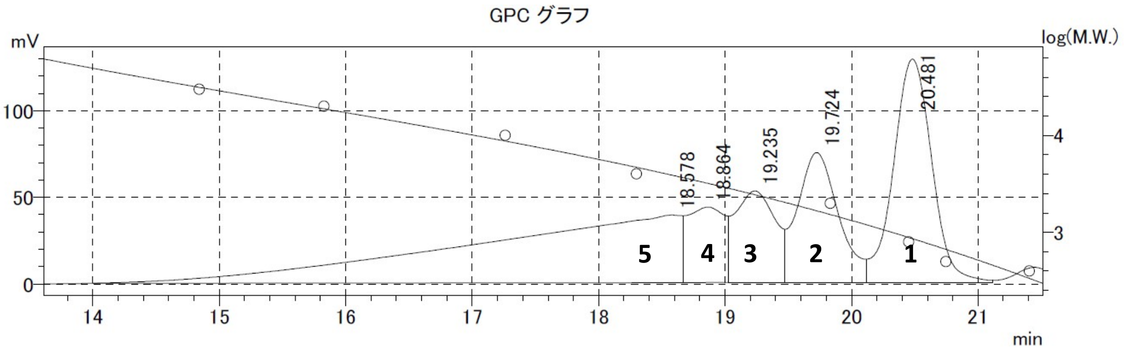
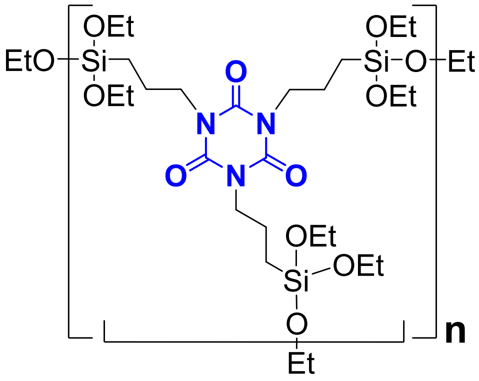


Figure S15. GPC result of oligomer **1c** after reaction for DEC formation.

Table S6. Estimated molecular weight of oligomer byproduct **1c** after reaction by GPC analysis.



n	Theoretical MW
1	742
2	1410
3	2078
4	2746
5	3414
6	4082
7	4750

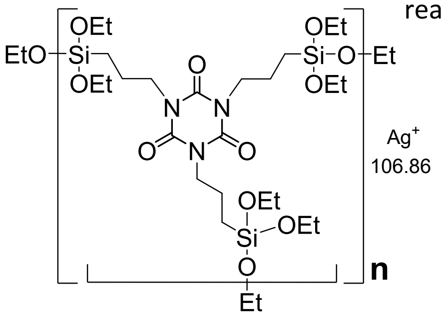
Entry	M_w	M_n	M_w/M_n	Estimated n	Percentage (%)
1	866	849	1.02	1	24.43
2	1650	1626	1.01	2	15.16
3	2446	2426	1.01	3	10.58
4	3256	3239	1.01	4	7.95
5	9705	7184	1.35	> 5	41.88

M_w = the weight average of molecular weight

M_n = the number average of molecular weight

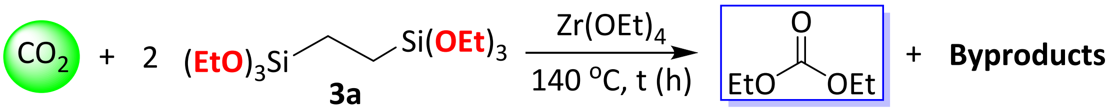
M_w/M_n = polydispersity index.

Table S7. The MALDI-TOF result and the theoretical value of oligomer byproduct **1c** after reaction.

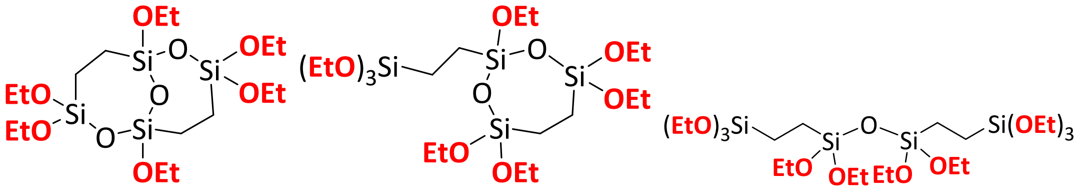


n	Result of MALDI -TOF (m/z)		Theoretical value (m/z)	
	Cyclic / branch	Linear	Cyclic	Linear
1	–	855.9	–	848.2
2	–	1519.5	–	1516.9
3	2111.2	2185.6	2110.8	2184.9
4	2779.5	2853.5	2778.8	2852.8
5	3448.3	3522.1	3446.8	3521.1
6	4117.4	4191.2	4114.8	4189.8
7	4784.4	4859.1	4782.7	4857.8

Byproduct produced from DEC synthesis using CO_2 and 3a



Byproducts



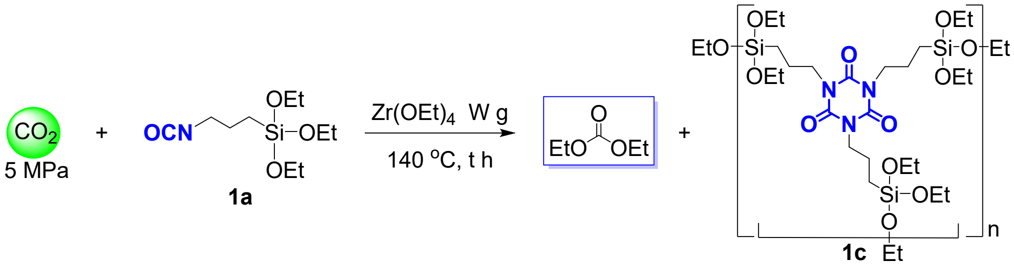
3b, [MW: 486] **3c**, [MW: 560] **3d**, [MW: 635]

Figure S16. Oligomeric byproducts of substrate **3a** after DEC synthesis detected by GC-MS and NMR results.

Scaling up experiment

Table S8. The comparison results of small (using 10 mL reactor) and large scale (200 mL reactor) experiment.

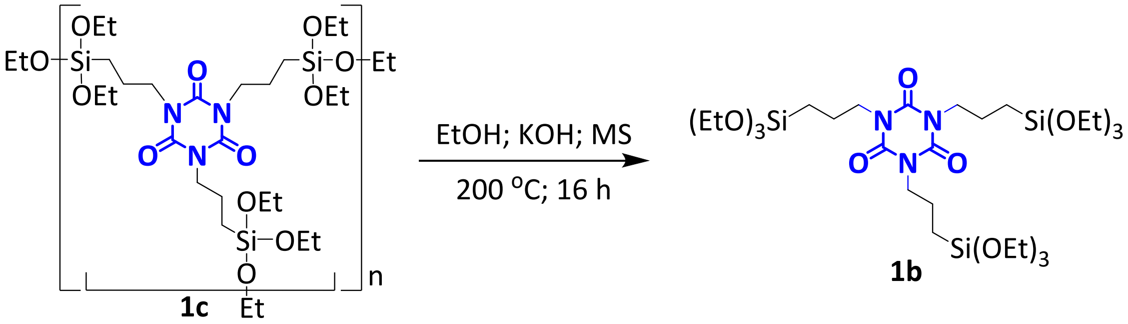
Entry	Reactor (mL)	$Zr(OEt)_4$ (g)	Substrate 1a (g)	Time (h)	DEC (mmol)	Yield (%)	TON
1	10	0.3	3.9	6	5.0	64[a]	4.5
2	200	6	78	6	96	61[a]	4.3
3	200	2	25	6	33	64[b]	4.5
4	200	0.2	25	18	20.7	40[b]	28
5	200	0.2	25	69	30.2	58[b]	41



[a] Yield determined by GC analysis. [b] Isolated Yield

Figure S17. Photograph of (a) 10 mL reactor, and (b) 200 mL reactor used in this experiment.

Reconversion of 1c to 1b



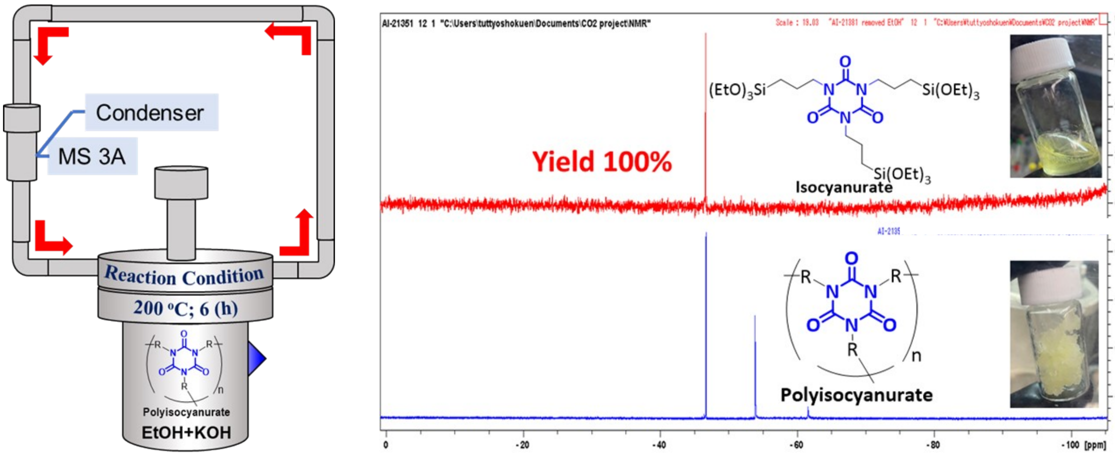


Figure S18. Reconversion of oligomer **1c** to intermediate **1b** using a circular reaction system; and

Si NMR results of **1c** after DEC synthesis and **1b** after regeneration from **1c**.