Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information for:

Solvent-free organocatalytic preparation of cyclic organic carbonates under scalable continuous flow conditions

Zhiguo Wang,[a,†] Romaric Gérardy,[a] Guillaume Gauron,[b] Christian Damblon[c] and Jean-Christophe M. Monbaliu[a,]*

[a] Center for Integrated Technology and Organic Synthesis, Research Unit MolSys, University of Liège, B-4000 Liège (Sart Tilman), Belgium

[b] Corning Reactor Technologies, Corning SAS, 7 bis, Avenue de Valvins CS 70156 Samois sur Seine, 77215 Avon Cedex, France

[c] CREMAN NMR Center, Research Unit MolSys, University of Liège, B-4000 Liège (Sart Tilman), Belgium

[†]Current address: Hubei Key laboratory of Mine Environmental Pollution Control and Remediation, School of Chemistry and Chemical Engineering, Hubei Polytechnic University, Huangshi, 435003, Hubei, China

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1. Continuous flow setups

1.1 Description of reactor elements

All continuous flow reactors were assembled with commercially available parts.

1.1.1 Pumps

Chemicals were pumped with HPLC pumps or with Chemyx Fusion 6000® High Force syringe pumps equipped with stainless steel syringes with Dupont™ Kalrez® Spectrum™ AS-568 O-rings (0.549 x 0.103”). The pilot-scale glass mesofluidic reactor was fed with a Corning dosing line (FUJI Technologies™ pumps).

1.1.2 SS coil reactors and pre-heating loops

SS coil reactors and SS pre-heating loops were constructed with deburred-end, steam-cleaned and acid-passivated 316 SS tubing (1.58 mm outer diameter, 500 µm internal diameter) of fixed internal volumes.

1.1.3 SS packed-bed reactor

A SS column (5 cm × 10 mm o.d. × 7.5 mm i.d.) was utilized for the packed-bed reactor (heterogeneous carbonation).

1.1.4 PEEK tubing

The sections of the reactor that were not subjected to high temperatures were constructed from PEEK tubing (green striped, 1.58 mm outer diameter, 750 µm internal diameter).

1.1.5 PFA tubing and coils

The sections of the reactor not subjected to high pressure and temperature were constructed from PFA tubing (high purity PFA; 1.58 mm outer diameter, 750 µm internal diameter), including the section of tubing connecting the BPR to the collection flask, the in- and outlets of the on-line IR and NMR spectrometer and the reaction coil utilized for the homogeneous carbonation of glycerol.

1.1.6 Connectors, ferrules and mixers

Sections of the reactor that were not subjected to high temperature were equipped with coned PEEK fittings and micromixers. Sections of the reactor that were subjected to high temperature were equipped with Valco SS fittings, ferrules and unions. Connectors, ferrules and unions were purchased from IDEX/Upchurch (Table S1).

1.1.7 Check-valves

The check-valves inserted between the pumps and the reactors were purchased from IDEX/Upchurch Scientific, and were installed in a PEEK check-valve holder (IDEX/Upchurch Scientific).

1.1.8 Back-pressure regulators

Dome-type BPRs were purchased from Zaiput Flow Technologies. The dome-type BPR was connected to a compressed gas cylinder (nitrogen or argon) to set the working pressure (7-11 bar).

1.1.9 Thermoregulatory devices

Microscale reactors (PFA coils, SS coils, and SS columns) were operated in thermoregulated oil baths (Heidolph™ MR Hei-Tec® equipped with a Pt-1000 temperature sensors). Glass mesofluidic reactors were thermoregulated with LAUDA® Proline RP 845 thermostats.

1.1.10 On-line NMR spectrometer

On-line NMR (qualitative) analysis was carried out with a 43 MHz Spinsolve™ Carbon NMR spectrometer from Magritek® equipped with the flow-through module. NMR spectra were analyzed with the Mestrenova software.

1.1.11 On-line IR spectrometer

On-line reaction monitoring was carried out with a FlowIR™ (SN# 2964) from Mettler-Toledo equipped with a DTGS detector using HappGenzel apodization, a Silicon probe connected via a FlowIR™ sensor and a high pressure heated 10 µL cell. Sampling was performed from 4000 to 650 cm^{-1} at 8 wavenumber resolution with 128 scans.

1.2 Part numbers & vendors

The reactor coils were constructed from standard fluidic elements purchased from IDEX/Upchurch Scientific and Valco Instruments Co. Inc (Table S1).

Table S1. Connectors, ferules and unions

Item	Details	Vendor	Reference
Connectors	One-Piece Fingertight, PEEK, 10-32 Coned, for 1/16” OD	IDEX/ Upchurch Scientific	F-120X
	Super Flangeless Nuts, natural PEEK 1/4-28 thread for 1/16” OD tubing	IDEX/ Upchurch Scientific	P-255X
	Super Flangeless Ferrule Tefzel (ETFE) and SS ring 1/4-28 thread for 1/16” OD tubing	IDEX/ Upchurch Scientific	P-259X
	SS Nut, standard, for 1/16” OD tubing	VICI (Valco Ins. Co. Inc.)	ZN1-10
	SS ferrule, 303, for 1/16” OD tubing	VICI (Valco Ins. Co. Inc.)	ZF1-10
Unions	Natural polypropylene standard low pressure union 1/4-28	IDEX/ Upchurch Scientific	P-620
	SS ZDV union Valco type for 1/16” OD, tubing	IDEX/ Upchurch Scientific	U-322
Mixers	T-mixer, natural PEEK 1/4-28 thread for 1/16" o.d. tubing, 0.02" through hole	IDEX/ Upchurch Scientific	P-712
Check-valve	Check-valve inline cartridge 1.5 psi	IDEX/ Upchurch Scientific	CV-3001
Cartridge holder	check-valve cartridge holder, PEEK	IDEX/ Upchurch	P-465

		Scientific	
Dome-type BPR	Dome-type BPR, metal-free, with adjustable set point	Zaiput Flow Techn.	BPR-10
Tubing	316 SS tubing (1.58 mm outer diameter, 500 µm internal diameter)	VICI (Valco Ins. Co. Inc.)	TSS120
	PEEK tubing (green striped, 1.58 mm outer diameter, 750 µm internal diameter).	VICI (Valco Ins. Co. Inc.)	JR-T-6003-M3
	High-purity PFA tubing, 1.58 mm outer diameter, 750 µm internal diameter	VICI (Valco Ins. Co. Inc.)	JR-T-4002-M25

1.3 Detailed continuous flow setups

1.3.1 Continuous flow setup for the homogeneous carbonation of glycerol (microscale)

The reader is referred to the main manuscript for experimental details (Feed concentrations, flow rates, counter-pressures).

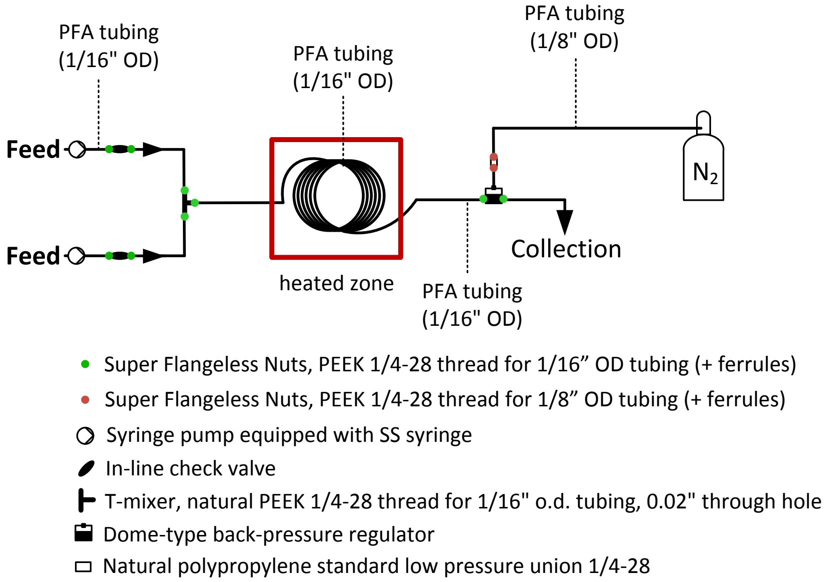


Figure S1. Continuous flow setup for the homogeneous carbonation of glycerol.

1.3.2 Continuous flow setup for the heterogeneous carbonation of glycerol (microscale)

The reader is referred to the main manuscript for experimental details (Feed concentrations, flow rates, counter-pressures).

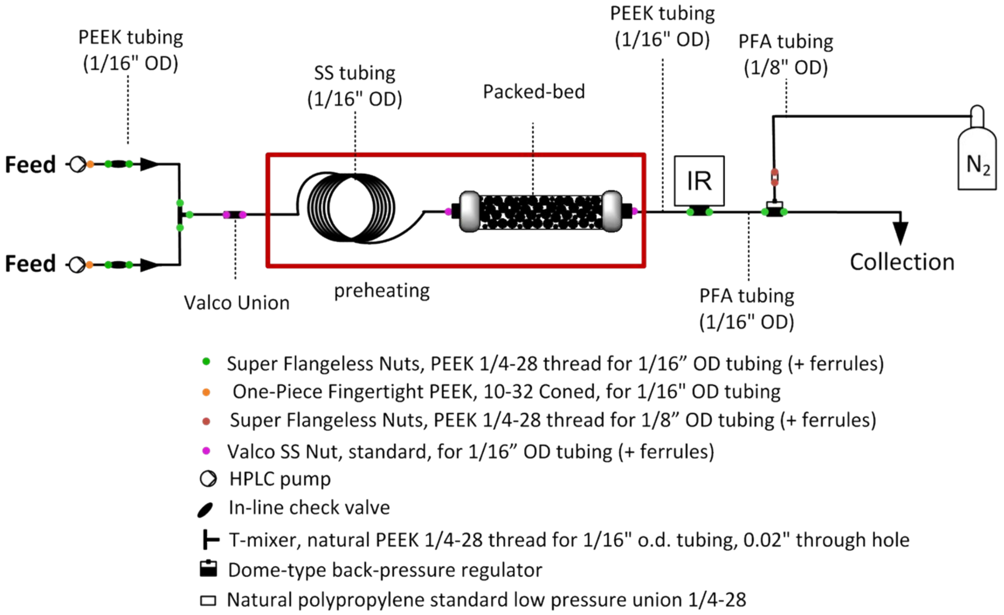


Figure S2. Continuous flow setup for the heterogeneous carbonation of glycerol.

1.3.3 Continuous flow setup for the homogeneous carbonation of diols (microscale)

The reader is referred to the main manuscript for experimental details (Feed concentrations, flow rates, counter-pressures).

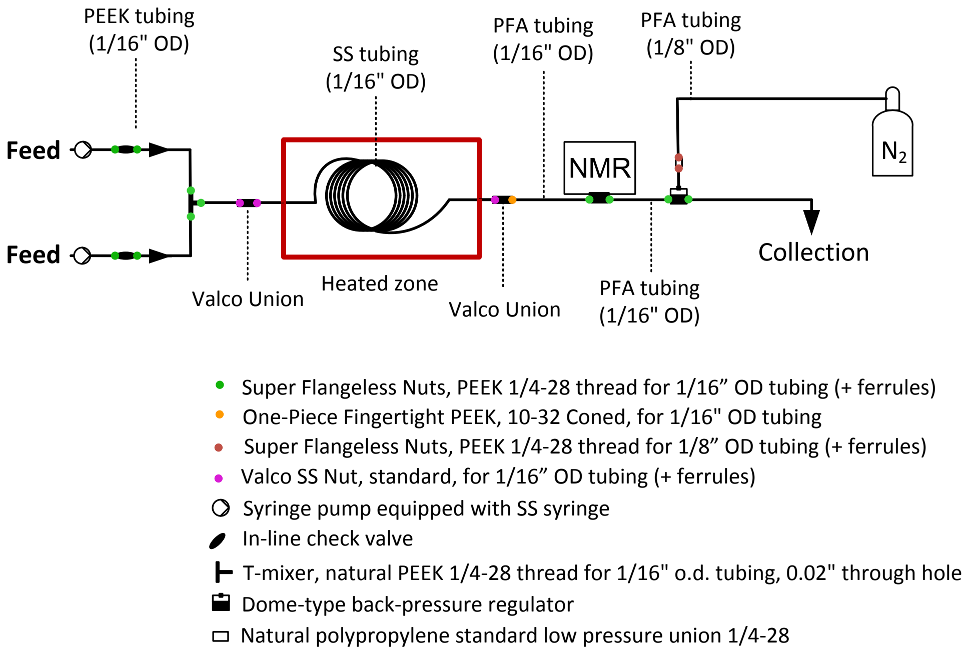


Figure S3. Continuous flow setup for the homogeneous carbonation of diols.

1.3.4 Continuous flow setup for the homogeneous carbonation of glycerol (mesoscale)

The reader is referred to the main manuscript for experimental details (Feed concentrations, flow rates, counter-pressures).

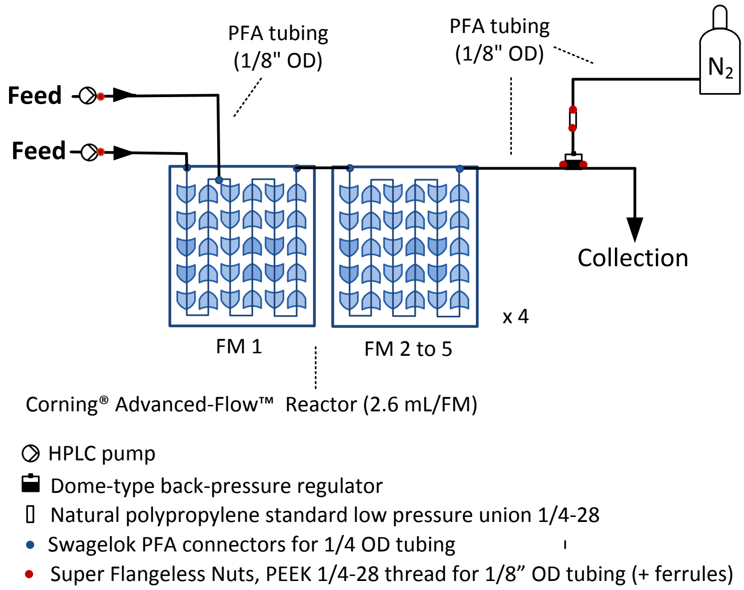


Figure S4. Continuous flow setup for the homogeneous carbonation of glycerol (13 mL internal volume reactor). Heat exchangers and thermostats are omitted for clarity.

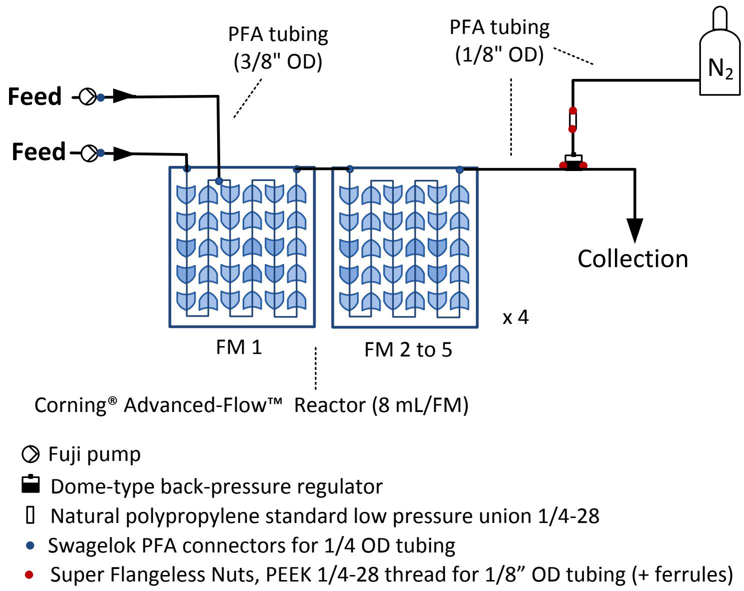


Figure S5. Continuous flow setup for the homogeneous carbonation of glycerol (40 mL internal volume reactor). Heat exchangers and thermostats are omitted for clarity.

1.4 Operation to steady state

Homogeneous carbonation reactors were stabilized for minimum 3 residence times before collection. Steady state was experimentally determined for heterogeneous carbonation reactors by collecting and analyzing successive fractions.

2. Additional experimental details

2.1 Calculations

$$Residence\ time\ (min) = \frac{reactor\ internal\ volume\ (mL)}{diol\ flow\ rate\ \left(\frac{mL}{min}\right) + DMC\ flow\ rate\ \left(\frac{mL}{min}\right)}$$

(eq. S1)

$$WHSV\ \left(h^{-1}\right) = \frac{glycerol\ flow\ rate\ (\frac{g}{h})}{mass\ of\ supported\ organocatalyst\ (g)}$$

(eq. S2)

$$Selectivity\ for\ carbonate\ xx\ (\%) = 100 \times \frac{yield\ of\ carbonate\ xx\ (\%)}{conversion\ of\ diol\ yy\ (\%)}$$

(eq. S3)

2.2 Chemicals

Chemicals, purity, CAS numbers and suppliers are listed in Table S2.

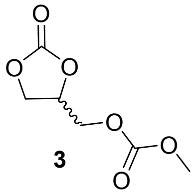
Table S2. Chemicals and suppliers

Products	Purity (%)	CAS Number	Supplier
Ethanediol (ethylene glycol)	99.8%	107-21-1	Acros Organics
1,2-Propanediol	>99%	57-55-6	TCI
1,2,3-Propanetriol (glycerol)	99%	56-81-5	ABCR
3-Methoxy-1,2-propanediol	>98%	623-39-2	TCI
3-*tert*-Butoxy-1,2-propanediol	≥ 97%	74338-98-0	Merck/Sigma-Aldrich
1,2-Butanediol	>98%	584-03-2	TCI
2,3-Butanediol	>97%	513-85-9	TCI
3-Butene-1,2-diol	≥ 99%	497-06-3	Merck/Sigma-Aldrich
1,4-Anhydro-erythritol	95%	4358-64-9	Merck/Sigma-Aldrich
Dimethyl carbonate (DMC)	99%	616-38-6	Acros Organics

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)	>99%	6674-22-2	Merck/Sigma-Aldrich
2,8,9-Trimethyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (Verkade's base)	/	120666-13-9	Merck/Sigma-Aldrich
1,8-bis-(Dimethylamino)naphthalene (DMAN)	≥ 99%	20734-58-1	Merck/Sigma-Aldrich
1,1,3,3-Tetramethylguanidine (TMG)	99%	80-70-6	Merck/Sigma-Aldrich
2-*tert*-Butyl-1,1,3,3-tetramethylguanidine (Barton's base)	≥ 97%	29166-72-1	Merck/Sigma-Aldrich
1,8-bis(Tetramethylguanidino)naphthalene (TMGN)	≥ 98%	442873-72-5	Merck/Sigma-Aldrich
Imino-tris(dimethylamino)phosphorane (P_1-H)	97%	49778-01-0	Merck/Sigma-Aldrich
tert-Butylimino-tris(dimethylamino)phosphorane (P_1-*t*-Bu)	≥ 97%	81675-81-2	Merck/Sigma-Aldrich
tert-Octylimino-tris(dimethylamino)phosphorane (P_1-*t*-Oct)	≥ 97%	161118-69-0	Merck/Sigma-Aldrich
tert-Butylimino-tris(pyrrolidino)phosphorane (BTPP)	≥ 97%	161118-67-8	Merck/Sigma-Aldrich
2-*tert*-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP)	≥ 98%	98015-45-3	Merck/Sigma-Aldrich
Tetramethyl-(tris(dimethylamino)phosphoranylidene)-phosphorictriamid-ethyl-imine (P_2-Et)	≥ 98%	165535-45-5	Merck/Sigma-Aldrich
DBU, polystyrene-bound, 100-200 mesh, 1 % cross-linked with DVB, 1.5-2.5 mmol g^{-1} loading	/	/	Merck/Sigma-Aldrich
Phosphazene base P_2-*t*-Bu on polystyrene, 100-200 mesh, 2% cross-linked with DVB, 1.6 mmol g^{-1} loading	/	/	Merck/Sigma-Aldrich
1,3-Dioxolan-2-one (ethylene carbonate)	98%	96-49-1	Merck/Sigma-Aldrich
4-Methyl-1,3-dioxolan-2-one (propylene carbonate)	99%	108-32-7	Merck/Sigma-Aldrich
4-Hydroxymethyl-1,3-dioxolan-2-one (glycerol carbonate)	>90%	931-40-8	TCI
(*R*)-4-Methoxymethyl-1,3-dioxolan-2-one	>98%	185836-34-4	TCI

4-Ethyl-1,3-dioxolan-2-one (1,2-butylene carbonate)	>98%	4437-85-8	TCI
4-Vinyl-1,3-dioxolan-2-one (vinyl ethylene carbonate)	99%	4427-96-7	Merck/Sigma-Aldrich

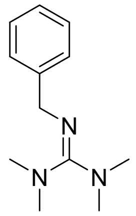
2.3 Procedures and characterization for compound **3**, **BnTMG** and **PS-TMG**



3

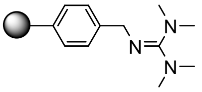
$C_6H_8O_6$
MW 176.12 g/mol

Methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (3).[S1] Methyl chloroformate (1.08 g, 11.43 mmol, 1.3 equiv.) was added dropwise over 1 h to a mixture of glycerol carbonate (1.02 g, 8.64 mmol, 1 equiv.) and pyridine (0.88 g, 11.13 mmol, 1.3 equiv.) under stirring at 0 °C. 5 mL of dichloromethane were added, and the reaction medium was stirred at rt for 16 h. The crude mixture was filtered to remove pyridine hydrochloride, and the solvent was removed under reduced pressure. An oil was obtained, and toluene was added to precipitate the product, which was isolated by filtration. 1.8 g of white solid were obtained and were washed with water to remove remaining pyridine hydrochloride. 1.0 g of methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (**3**, 66% yield) was obtained as a white solid. The NMR data matched those reported in the literature.[S2] **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 4.98 (1 H, td, *J* = 9.3 Hz, 4 Hz), 4.60 (1 H, t, *J* = 8.6 Hz), 4.45 (1 H, dd, *J* = 12.4 Hz, 3.2 Hz), 4.41-4.28 (2 H, m), 3.83 (3 H, s) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ = 155.2, 154.4, 73.7, 66.2, 65.9, 55.4 ppm.



$C_{12}H_{19}N_3$
MW 205.31 g/mol

2-Benzyl-1,1,3,3-tetramethylguanidine (BnTMG).[S3] Benzyl chloride (3.3 g, 26.1 mmol, 1 equiv.) was added dropwise to 1,1,3,3-tetramethylguanidine (30 mL, 239 mmol, 9 equiv.) under stirring at rt. The reaction medium was stirred at rt for 24 h. The crude mixture was filtered, and the filtrate was dissolved in 50 mL of diethyl ether. The organic phase was washed with water (4 × 50 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure, and a brown oil (4.12 g) was obtained. It was dissolved in toluene (200 mL), and the organic phase was washed with water (80 ml), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure, affording 2-benzyl-1,1,3,3-tetramethylguanidine (2.12 g, 40% yield) as a brown oil. The NMR data matched those reported in the literature.[S3] **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.40-7.12 (5 H, m), 4.39 (2 H, s), 2.78 (6 H, s), 2.74 (6 H, s) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ = 161.1, 143.8, 128.1, 127.2, 125.9, 53.2, 39.8, 39.1 ppm.



Polystyrene-supported 1,1,3,3-tetramethylguanidine (PS-TMG).[S4] A mixture of Merrifield resin (4 g, 2.0-3.0 mmol g^{-1} Cl loading, 100-200 mesh, cross-linked with 1% DVB) and dry 1,4-dioxane (50 mL) was stirred under nitrogen for 30 min at rt to swell the polymeric material. 1,1,3,3-Tetramethylguanidine (5.07 g, 44.0 mmol) was added and the reaction medium was stirred for 16 h at 70 °C under nitrogen. The heterogeneous mixture was filtered, and the beads were successively washed with MeOH (2 × 20 mL), CH_2Cl_2 (2 × 20 mL) and *n*-pentane (2 ×20 mL). The white beads were dried overnight under vacuum. The procedure (swelling, TMG addition, reaction, washing and drying) was repeated once. The beads were analyzed by solid-state NMR (see Section 2.8 and Figure S33), confirming the functionalization of Merrifield resin toward PS-TMG.

2.4 Process optimization for the homogeneous carbonation of glycerol (microscale)

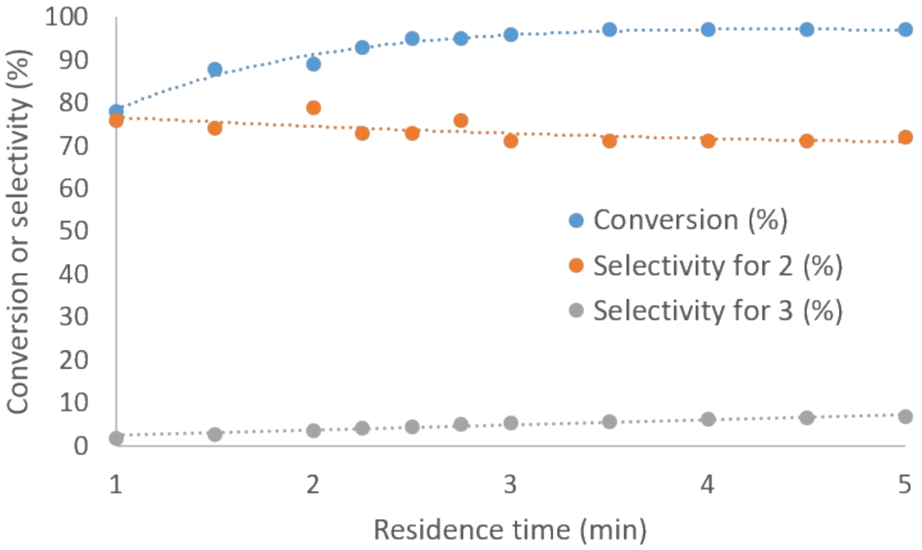


Figure S6. Evolution of the conversion of glycerol (blue dots), and of the selectivity for glycerol carbonate (orange dots) and methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (grey dots) as a function of the residence time. Conditions: 135 °C, 3 equiv. DMC, 1 mol% DBU.

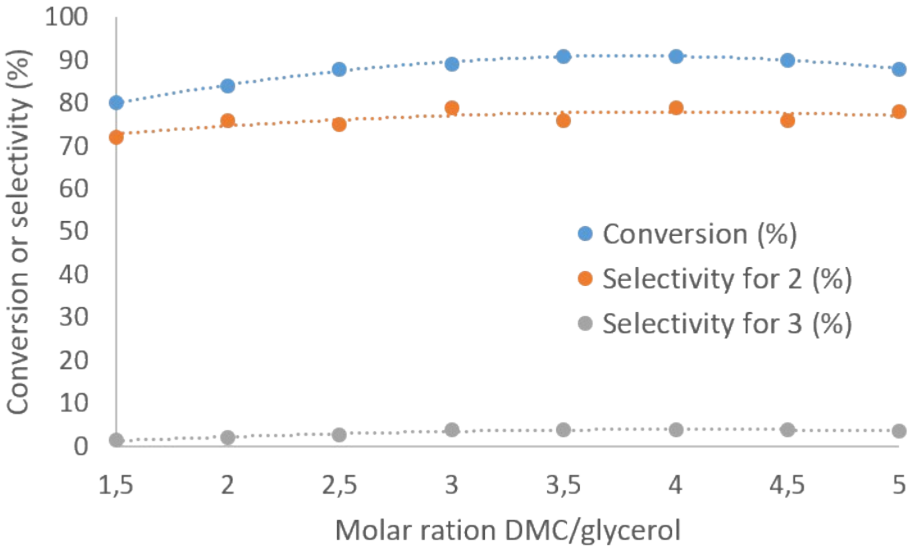


Figure S7. Evolution of the conversion of glycerol (blue dots), and of the selectivity for glycerol carbonate (orange dots) and methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (grey dots) as a function of the molar ratio between DMC and glycerol. Conditions: 135 °C, 2 min residence time, 1 mol% DBU.

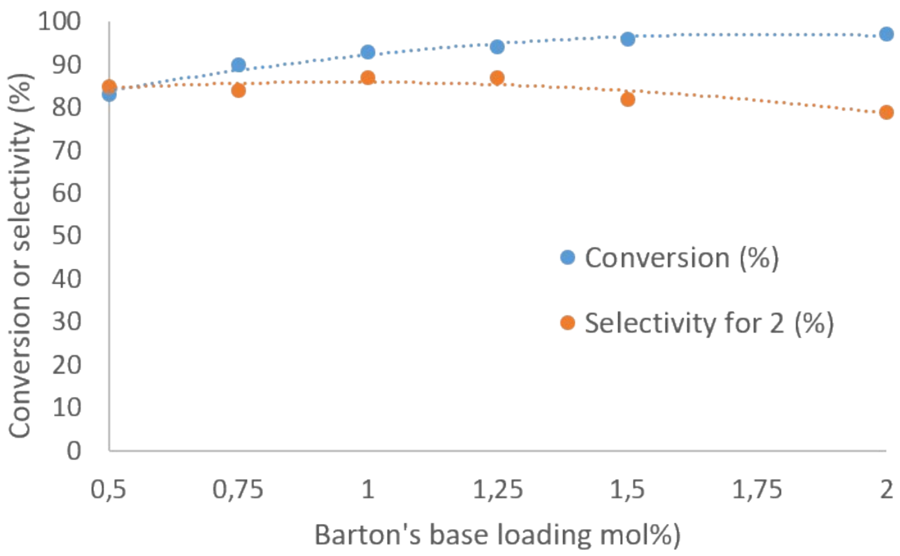


Figure. S8 Evolution of the conversion of glycerol (blue dots) and of the selectivity for glycerol carbonate (orange dots) as a function of the loading in Barton's base. Conditions: 135 °C, 2 min residence time, 3 equiv. DMC.

Table S3. Evaluation of organic superbases as organocatalysts using with 0.5, 1.5 and 2 mol% loadings

Catalyst	0.5 mol%		1.5 mol%		2 mol%	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
Verkade's base	-	-	93	80	97	80
DMAN	-	-	-	-	9	67
TMG	-	-	-	-	87	86
TMGN	77	83	-	-	95	82
P_1-H	76	86	93	80	96	84
P_1-*t*-Bu	84	88	96	78	97	78
P_1-*t*-Oct	85	86	96	80	97	81
BTPP	-	-	-	-	97	84
BEMP	83	86	96	79	97	80
P_2-Et	83	78	96	78	-	-

Conditions: 135 °C, 2 min residence time, 3 equiv. DMC. The amount of organocatalyst is relative to the number of moles of glycerol. Conversion and yield were determined by GC/FID.

2.5 Process optimization for the heterogeneous carbonation of glycerol (microscale)

2.5.1 IR spectral library

On-line reaction monitoring was recorded with the iC IR® software (version 4.3).

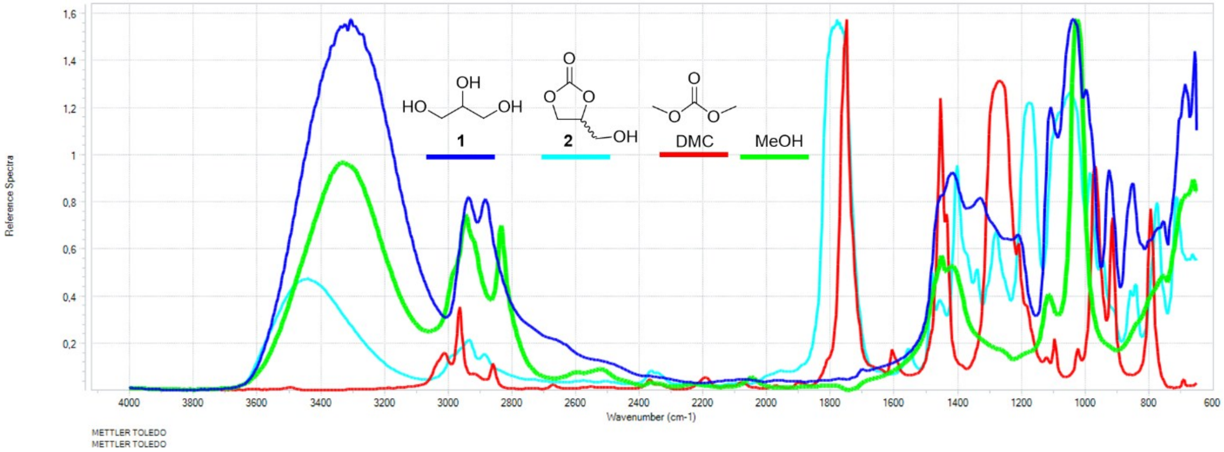


Figure S9. IR spectral library of DMC, glycerol (**1**), glycerol carbonate (**2**) and methanol.

2.5.2 Evaluation of PS-TMG stability over time at WHSV = 10.5 h^{-1}

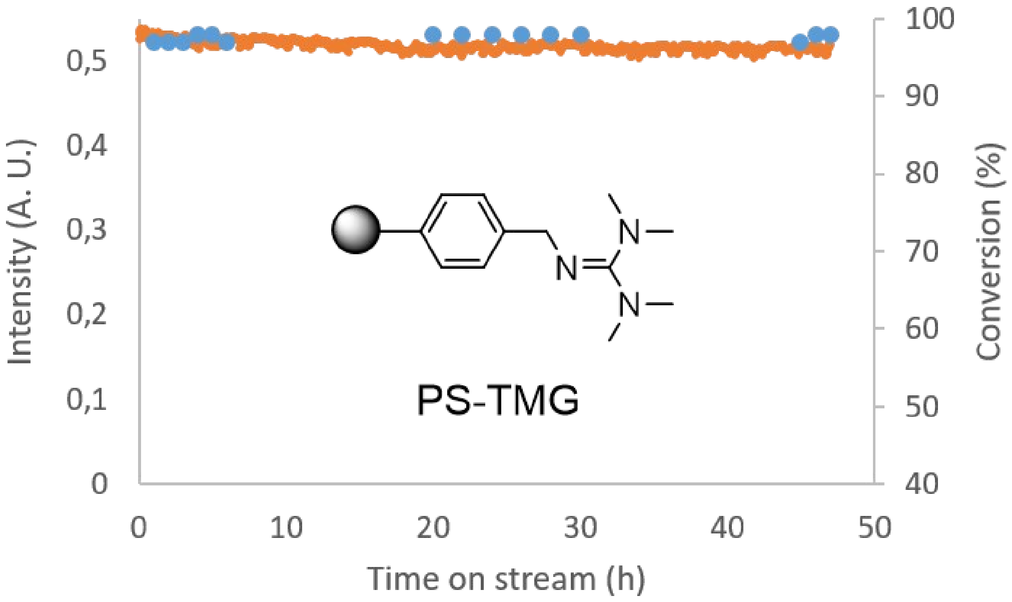


Figure S10. On-line reaction monitoring showing the evolution of the conversion toward glycerol carbonate by combining on-line IR qualitative monitoring (orange series, relative intensity of the 1403 cm^{-1} vibration band) and off-line quantitative GC/FID (blue dots, conversion of glycerol). Conditions: 135 °C, 3 equiv. DMC, WHSV = 10.5 h^{-1}, PS-TMG (0.5 g packed in the fixed-bed reactor).

2.6 Process (re)optimization for the homogeneous carbonation of diols

2.6.1 On-line qualitative NMR analysis

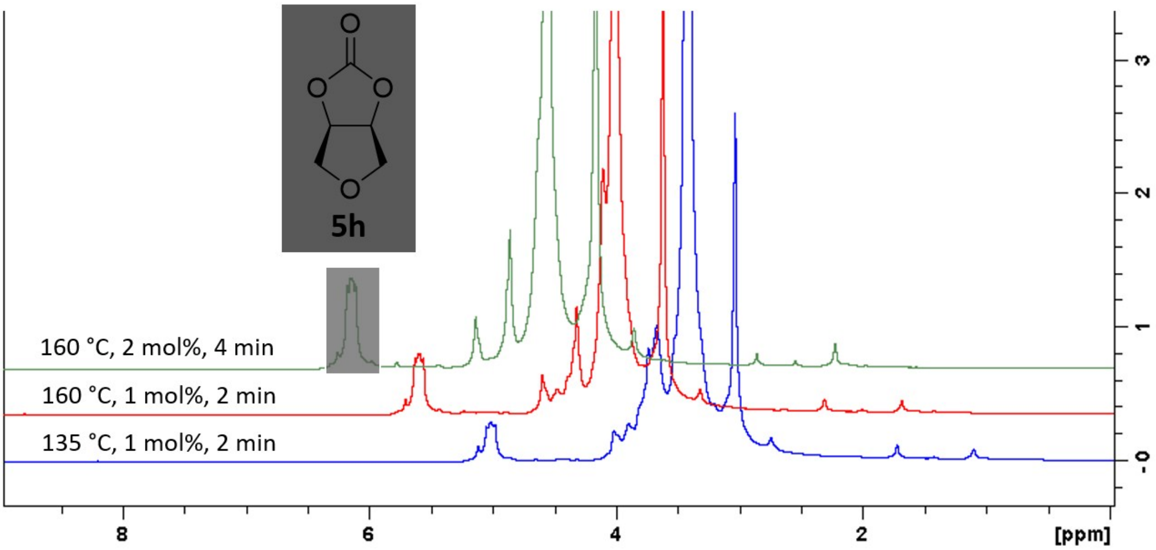


Figure S11. On-line NMR reaction monitoring showing the variation of the concentrations in anhydroerythritol carbonate (**5h**). The peak at 5 ppm (dark grey) was used to monitor the appearance of **5h**.

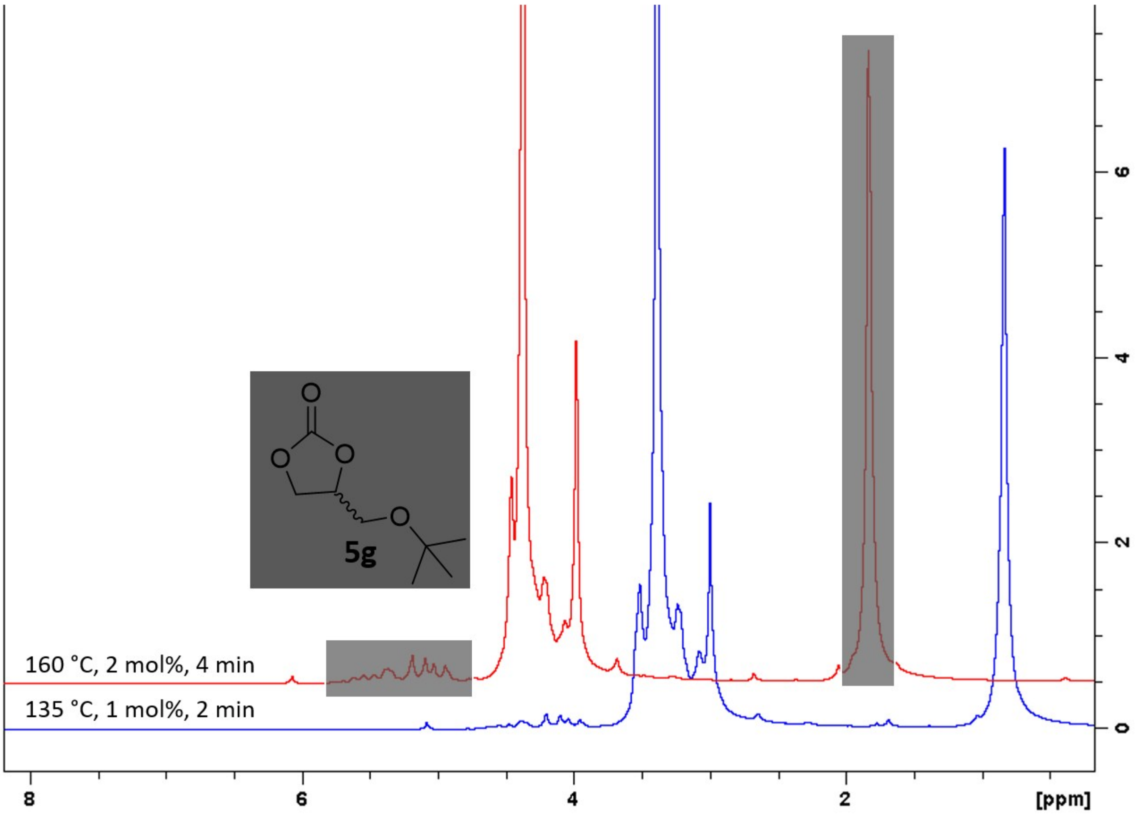


Figure S12. On-line NMR reaction monitoring showing the variation of the concentrations in 4-*tert*-butoxymethyl-1,3-dioxolan-2-one (**5g**). The singlet at 0.8 ppm and the multiplet at 3.75-4.75 ppm (dark grey) were used to monitor the appearance of **5h**.

2.6.2 Quantitative results

Table S4. Process optimization for the homogeneous carbonation of diols **4c**, **4e**, **4g** and **4h**.

Entry	Diol	Residence time	Catalyst loading	Temperature	Conv. (%)	Selec. (%)
1[a]	**4e**	2 min	1 mol%	135 °C	38	78
2[a]	**4e**	4 min	1 mol%	160 °C	52	78
3[a]	**4e**	4 min	2 mol%	160 °C	81	91
4[b]	**4g**	2 min	1 mol%	135 °C	52	86
5[b]	**4g**	4 min	2 mol%	160 °C	63	91
6[b]	**4h**	2 min	1 mol%	135 °C	41	80
7[b]	**4h**	2 min	1 mol%	160 °C	55	n.d.
8[b]	**4h**	4 min	2 mol%	160 °C	96	87
9[b]	**4c**	2 min	1 mol%	135 °C	<5%	n.d.
10[d]	**4c**	8 min	2 mol%	180 °C	72[e]	

Conditions: 3 equiv. of DMC, P = 7 bar, catalyst = Barton's base, the amount of organocatalyst is relative to the number of moles of diol. [a] Conversion and yield were determined by GC/FID. [b] Conversion was determined by GC/FID and yield was determined by high-field ^1H NMR in $CDCl_3$ with mesitylene as internal standard. [d] P = 11 bar. [e] Yield, determined by high-field ^1H NMR in $CDCl_3$ with mesitylene as internal standard.

2.7 Off-line (quantitative) NMR analysis

2.7.1 General Information

Analytical ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100.6 MHz, respectively, on a Bruker Avance III HD spectrometer (9.4 Tesla) equipped with a high-resolution multinuclear probe operated in the 40-400 MHz range.

2.7.2 Procedure for quantitative ^1H NMR analysis

Free induction decays were acquired at 298 K using a standard pulse sequence (Bruker, zg30). The spectral width was 20 ppm (8012.820 Hz). A 30 ° excitation pulse and a 4 s relaxation delay were used to collect 64 scans. Spectra were recorded in 5 mm NMR tube (Norell). The NMR samples were prepared by weighting known amounts of reactor effluents (typically 30-50 mg) and mesitylene (typically 5-10 mg), followed by dilution with 600 µL of $CDCl_3$. Three NMR samples were prepared for each data point to ensure reproducibility of the analysis.

2.7.3 Representative examples of quantitative NMR analysis

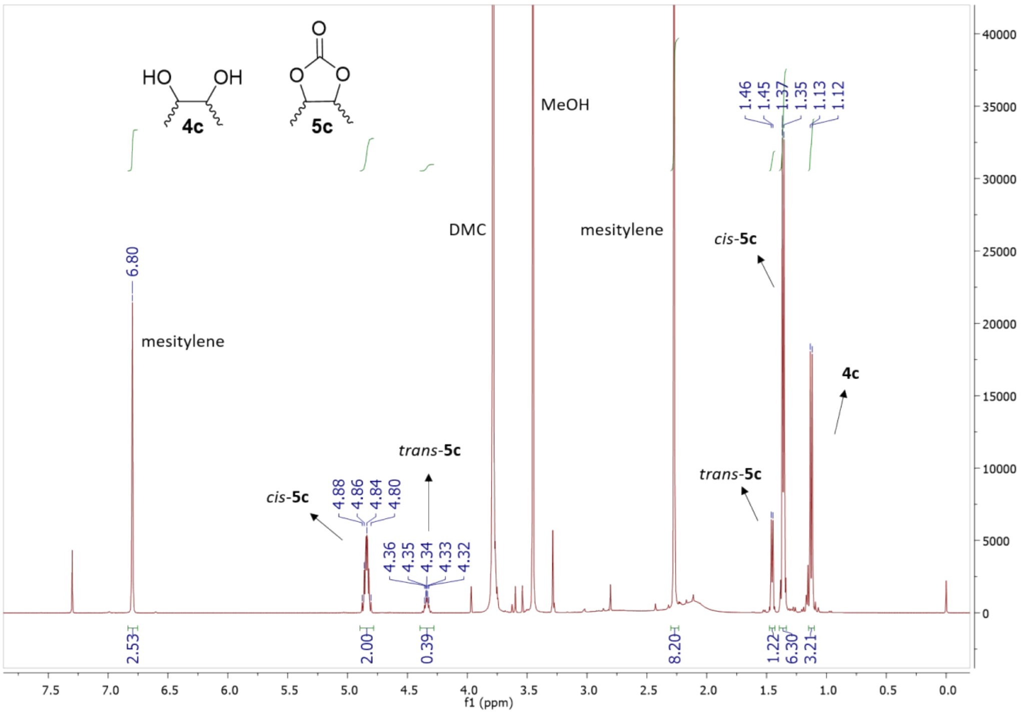


Figure S13.^{1}H NMR (400 MHz) spectrum of crude reactor effluent in $CDCl_3$ for the carbonation of **4c**. Conditions: 180 °C, 8 min residence time, 3 equiv. of DMC, 2 mol% Barton's base, 11 bar (72% yield for **5c**, *cis*/*trans* 5:1).

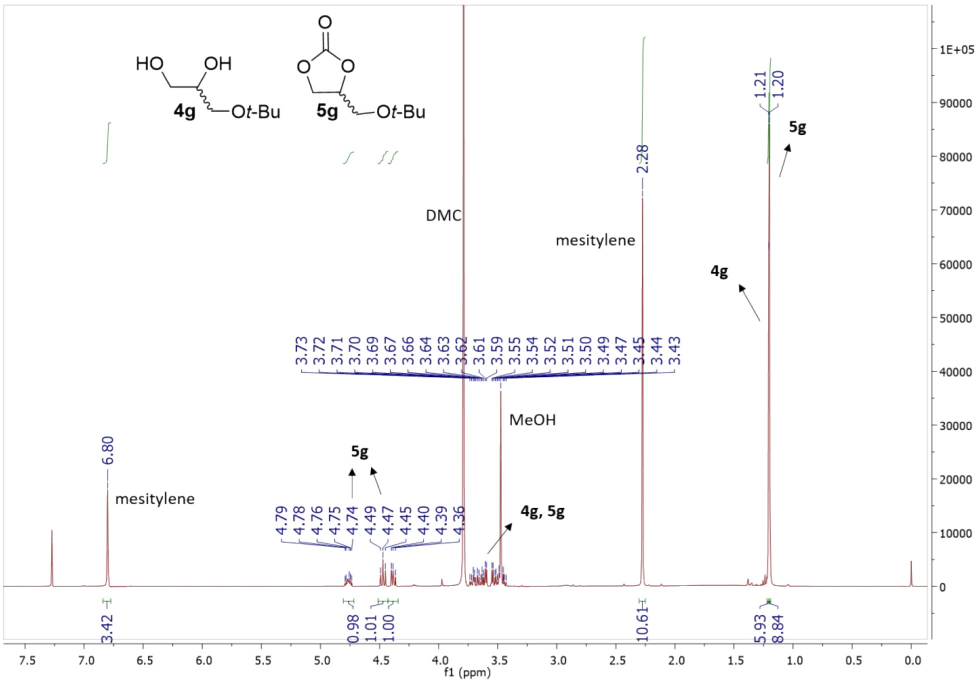


Figure S14.^{1}H NMR (400 MHz) spectrum of crude reactor effluent in $CDCl_3$ for the carbonation of **4g**. Conditions: 160 °C, 4 min residence time, 3 equiv. of DMC, 2 mol% Barton's base, 7 bar (57% yield for **5g**).

2.7.4 Copies of ^{1}H and ^{13}C NMR spectra

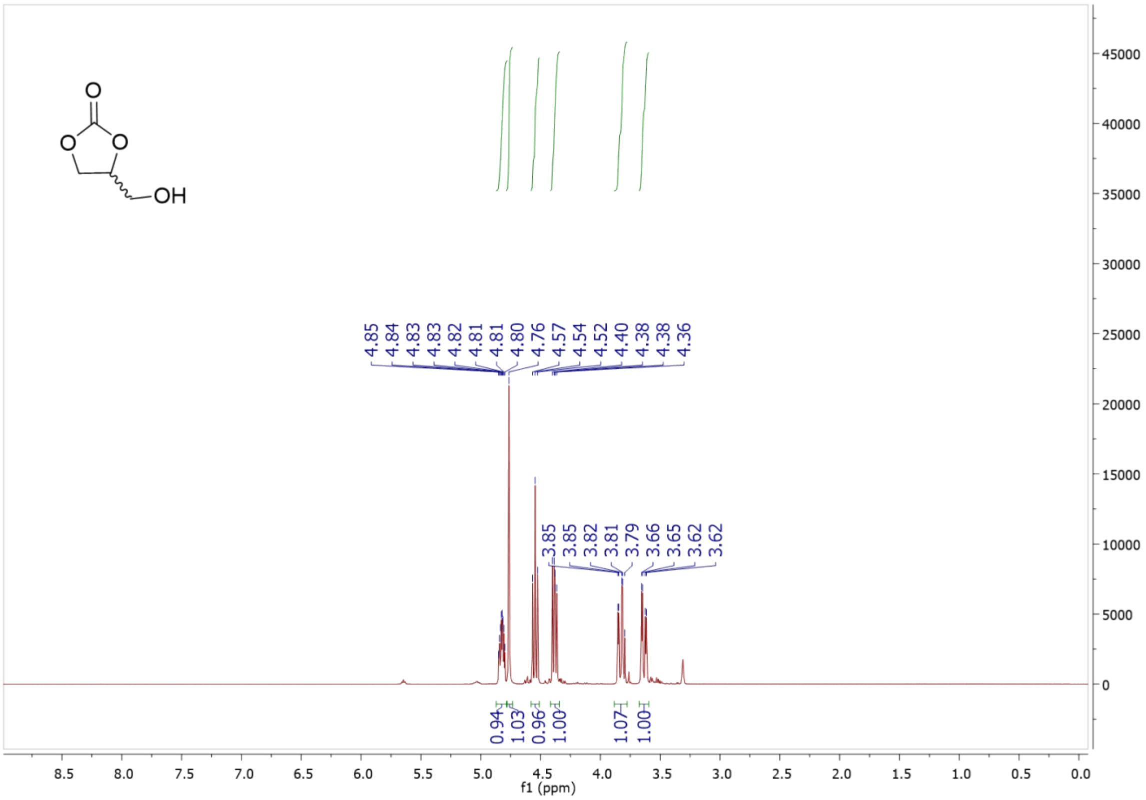


Figure S15. ^{1}H NMR spectrum (400 MHz) of glycerol carbonate (**2**) in CD_3OD.

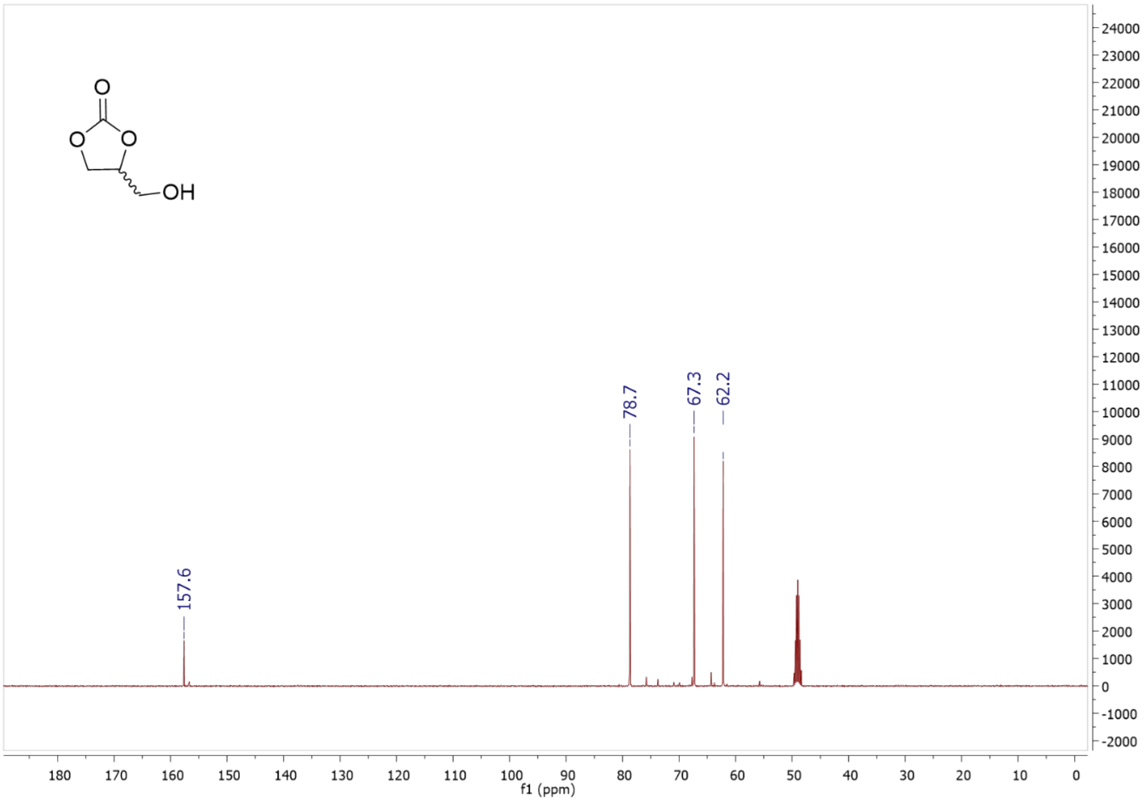


Figure S16. ^{13}C NMR spectrum (100.6 MHz) of glycerol carbonate (**2**) in CD_3OD.

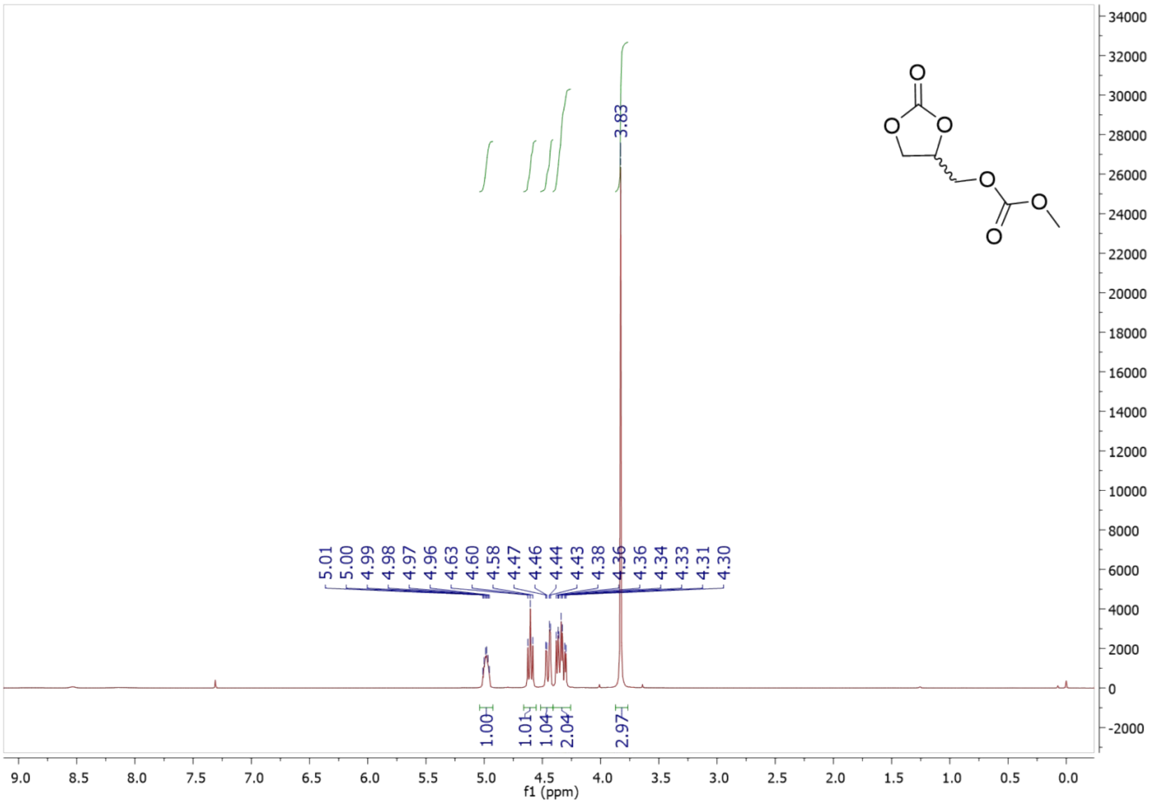


Figure S17. ^{1}H NMR spectrum (400 MHz) of methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (**3**) in $CDCl_3$.

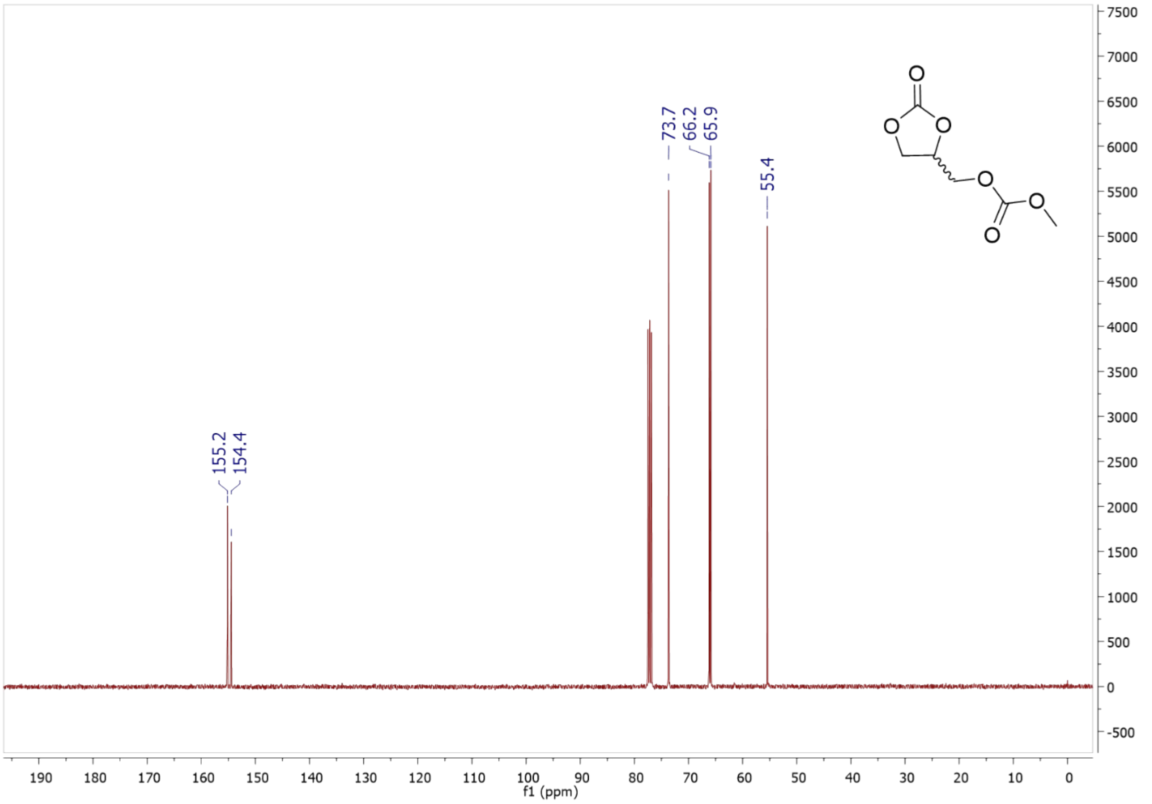


Figure S18. ^{13}C NMR spectrum (100.6 MHz) of methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (**3**) in $CDCl_3$.

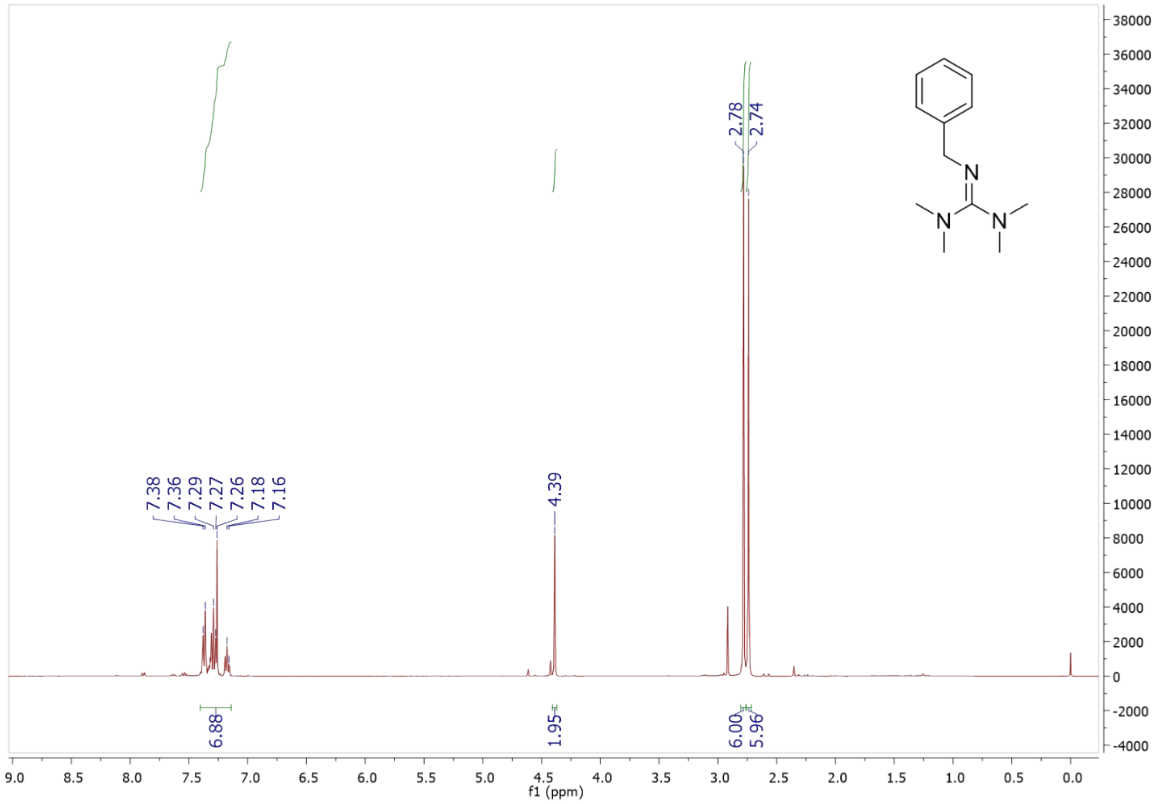


Figure S19. ^1H NMR spectrum (400 MHz) of 2-benzyl-1,1,3,3-tetramethylguanidine (BnTMG) in $CDCl_3$.

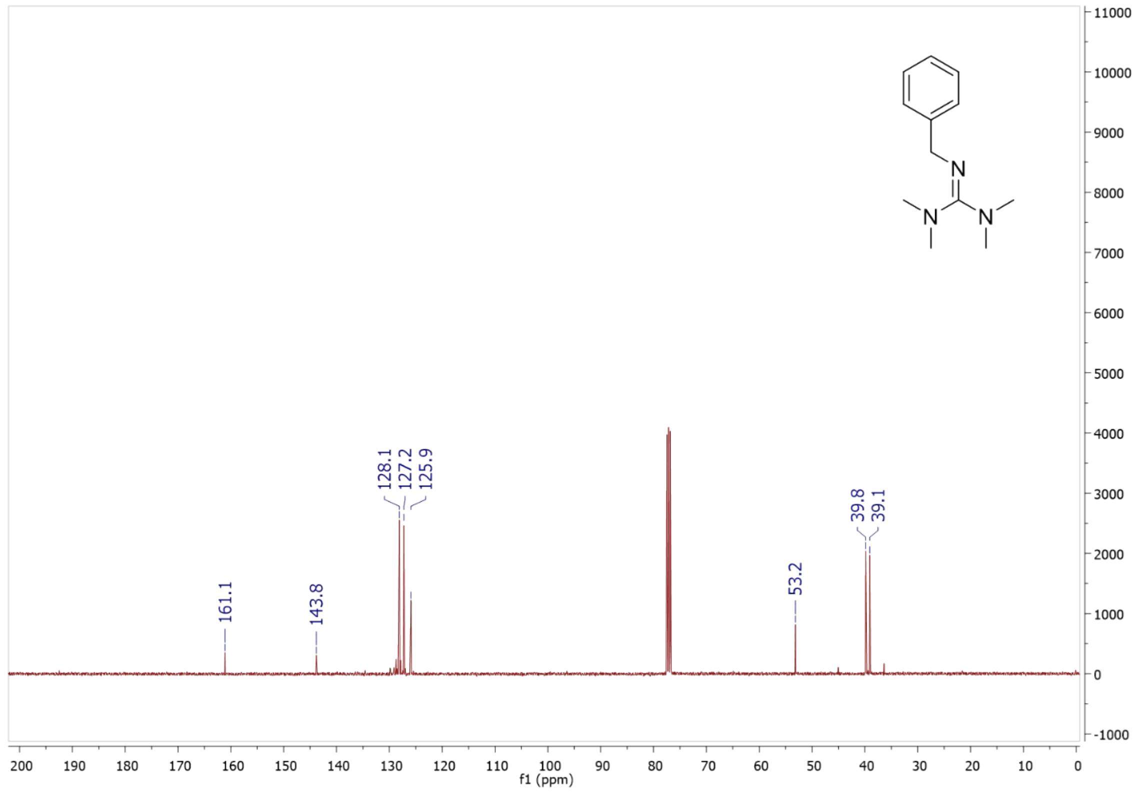


Figure S20. ^{13}C NMR spectrum (100.6 MHz) of 2-benzyl-1,1,3,3-tetramethylguanidine (BnTMG) in $CDCl_3$.

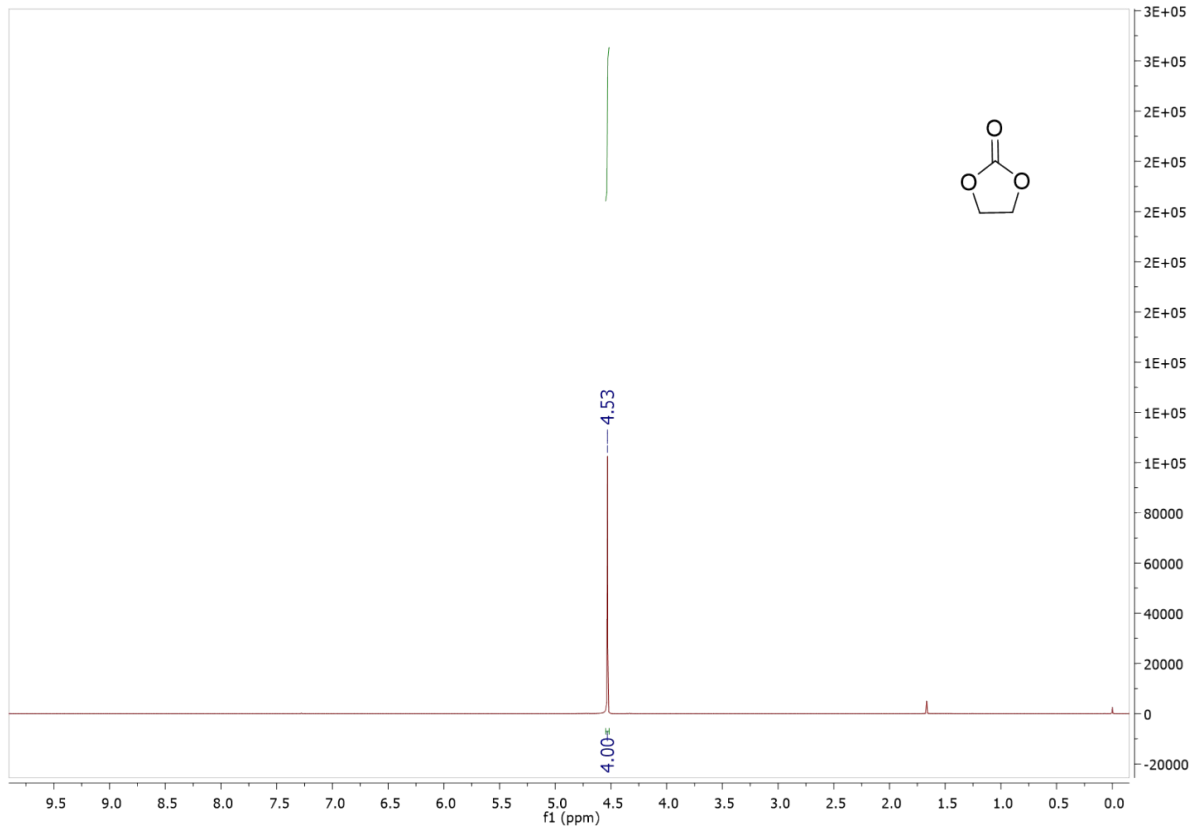


Figure S21. ^{1}H NMR spectrum (400 MHz) of ethylene carbonate (**5a**) in CDCl$_3$.

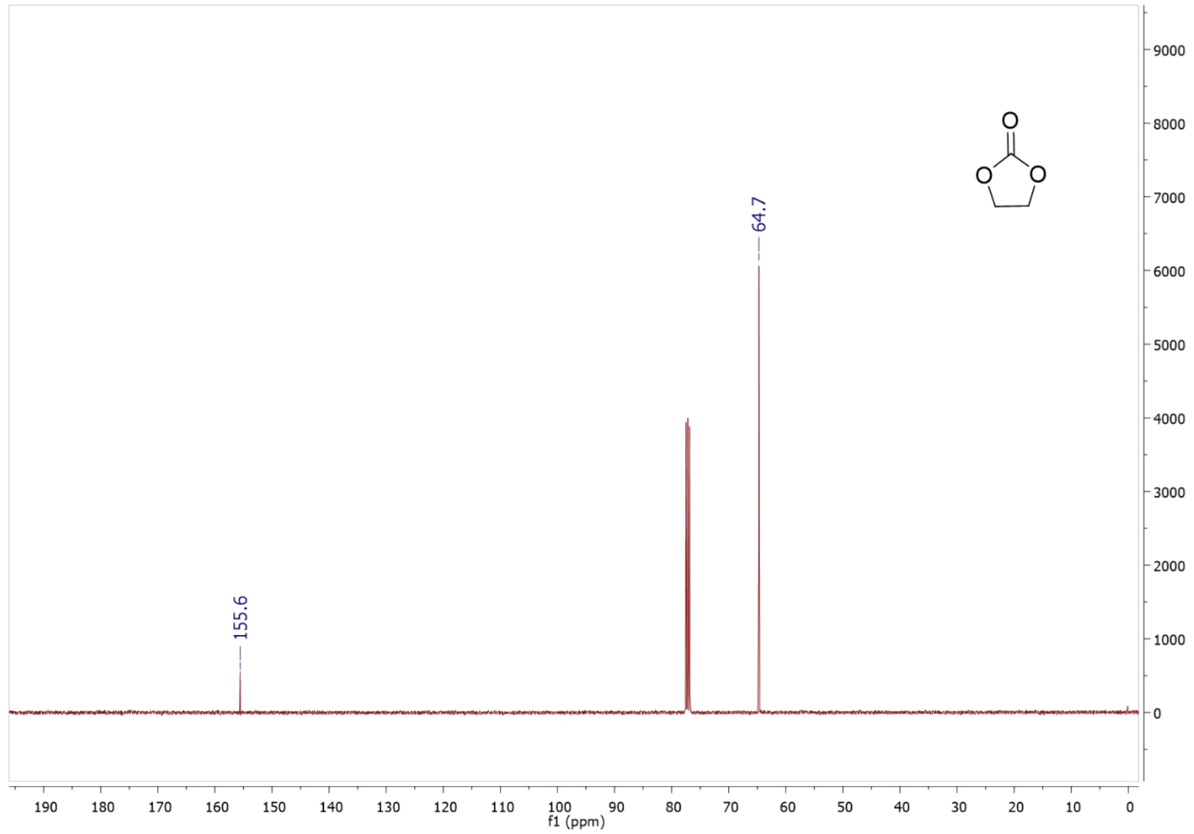


Figure S22. ^{13}C NMR spectrum (100.6 MHz) of ethylene carbonate (**5a**) in CDCl$_3$.

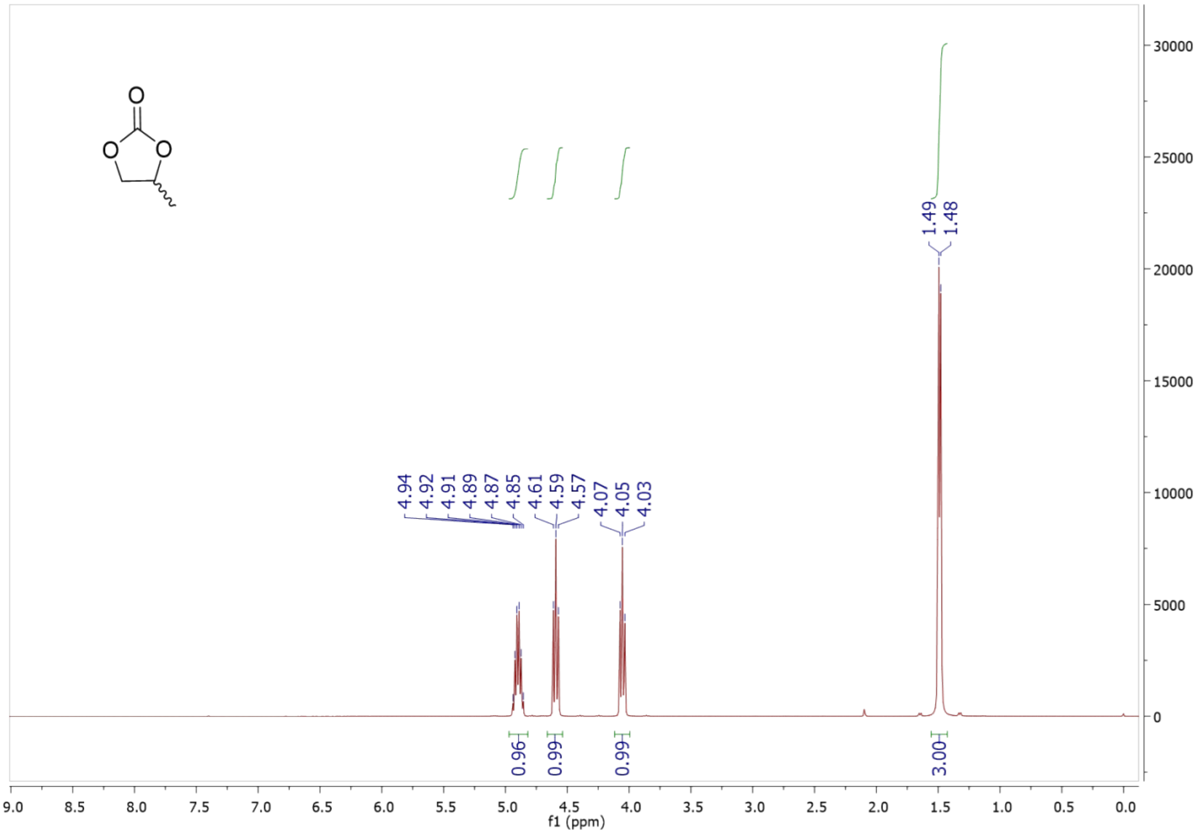


Figure S23. ^1H NMR spectrum (400 MHz) of propylene carbonate (**5b**) in $CDCl_3$.

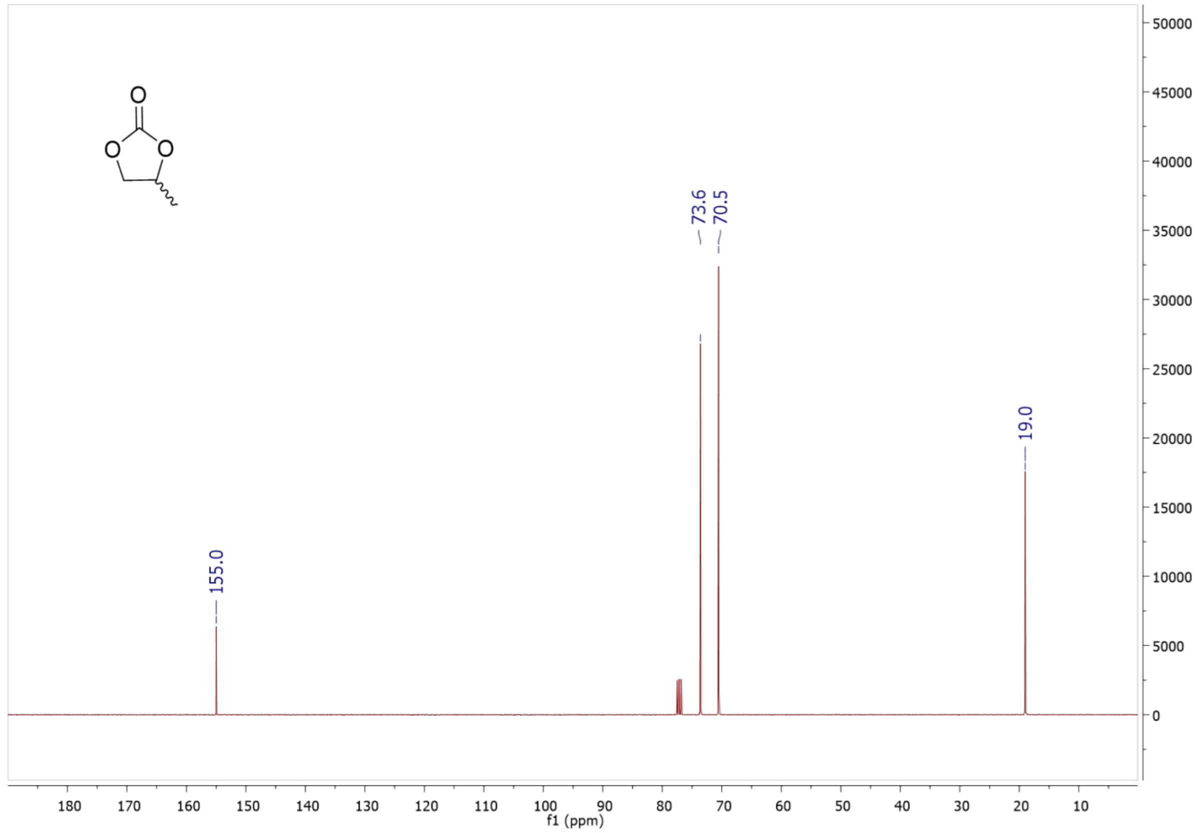


Figure S24. ^{13}C NMR spectrum (100.6 MHz) of propylene carbonate (**5b**) in $CDCl_3$.

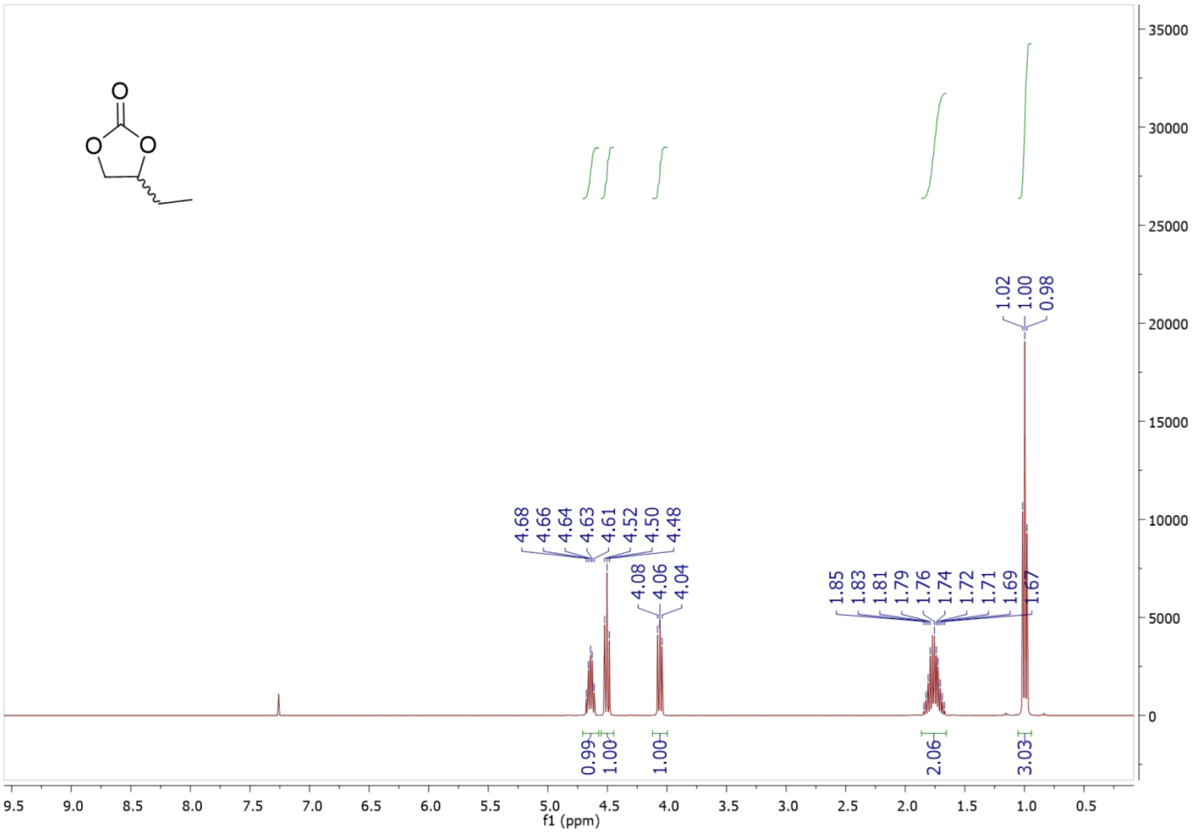


Figure S25. ^{1}H NMR spectrum (400 MHz) of 1,2-butylene carbonate (**5d**) in CDCl$_3$.

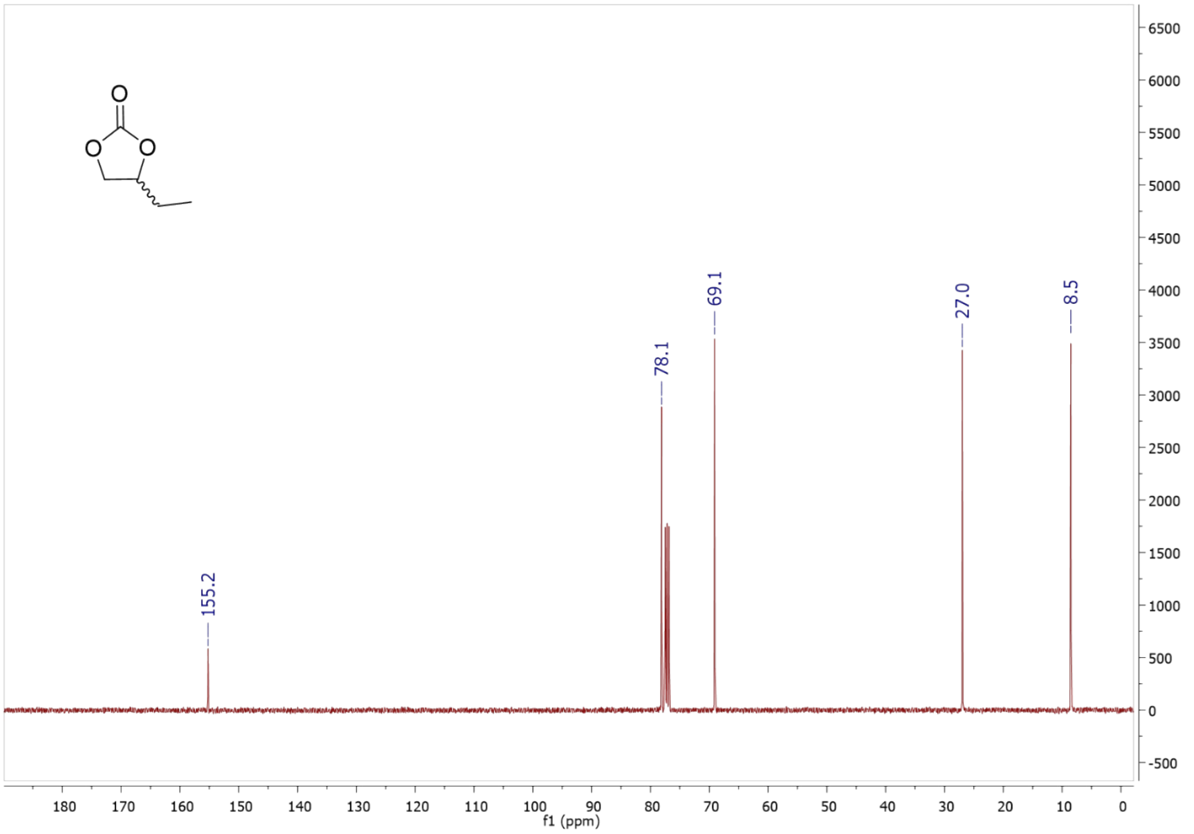


Figure S26. ^{13}C NMR spectrum (100.6 MHz) of 1,2-butylene carbonate (**5d**) in CDCl$_3$.

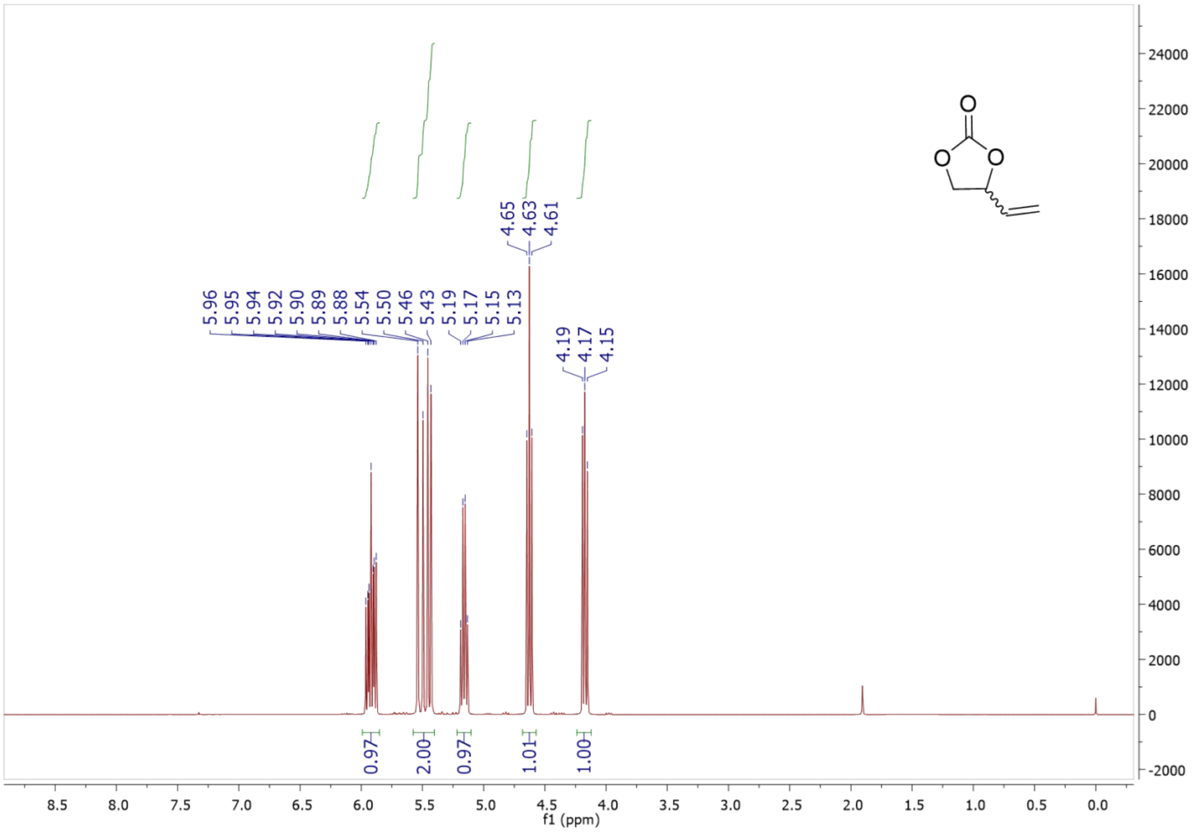


Figure S27. ^{1}H NMR spectrum (400 MHz) of vinyl ethylene carbonate (**5e**) in $CDCl_3$.

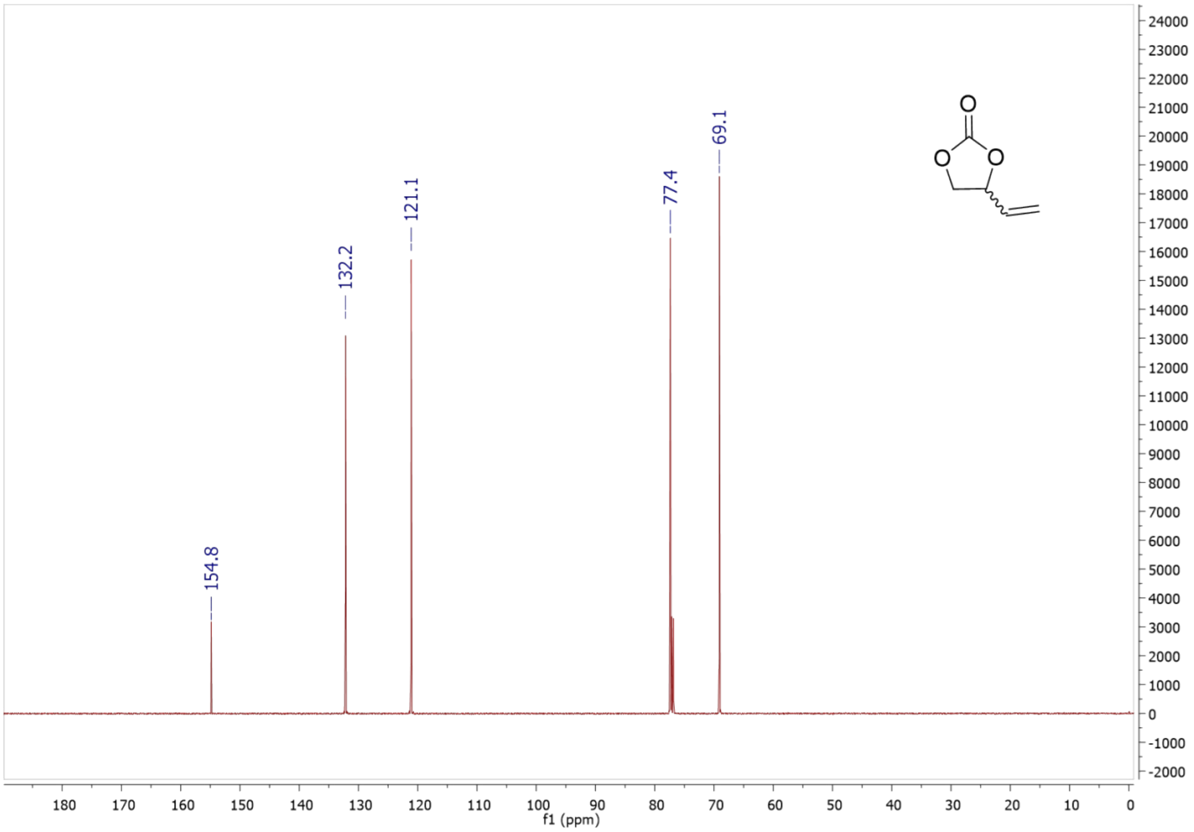


Figure S28. ^{13}C NMR spectrum (100.6 MHz) of vinyl ethylene carbonate (**5e**) in $CDCl_3$.

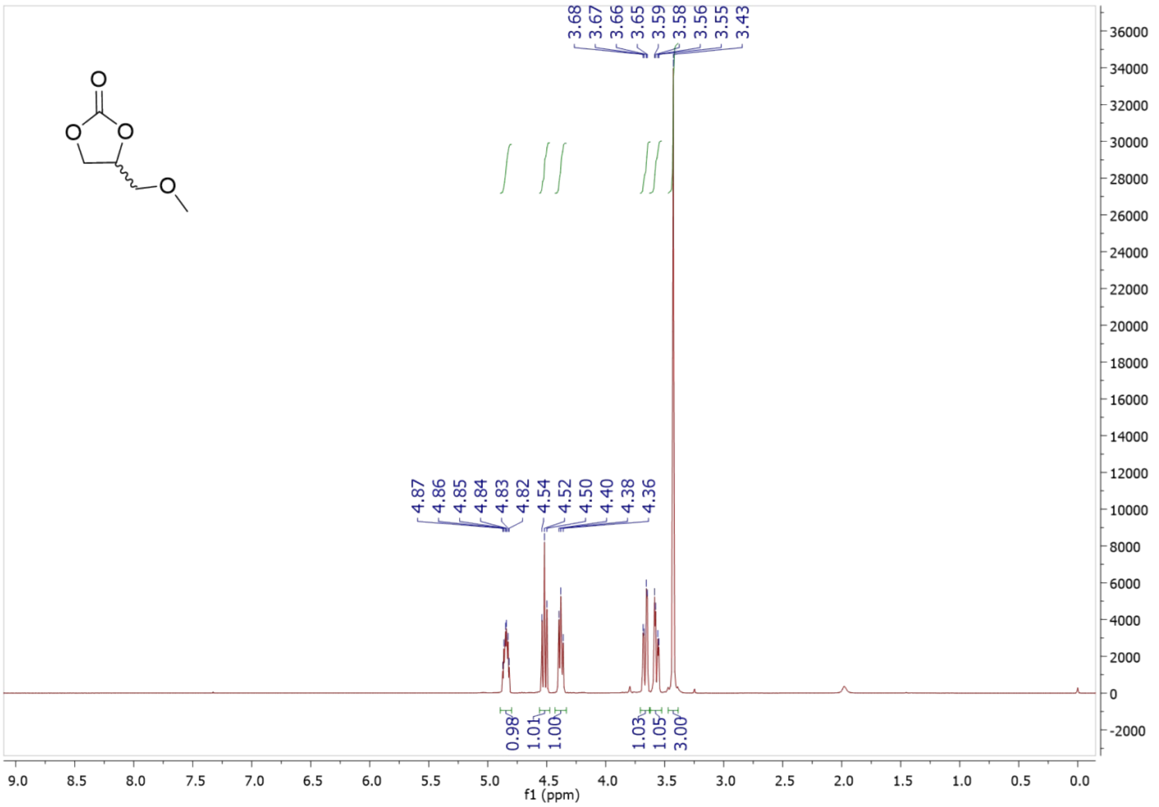


Figure S29. ^{1}H NMR spectrum (400 MHz) of 4-methoxymethyl-1,3-dioxolan-2-one (**5f**) in CDCl$_3$.

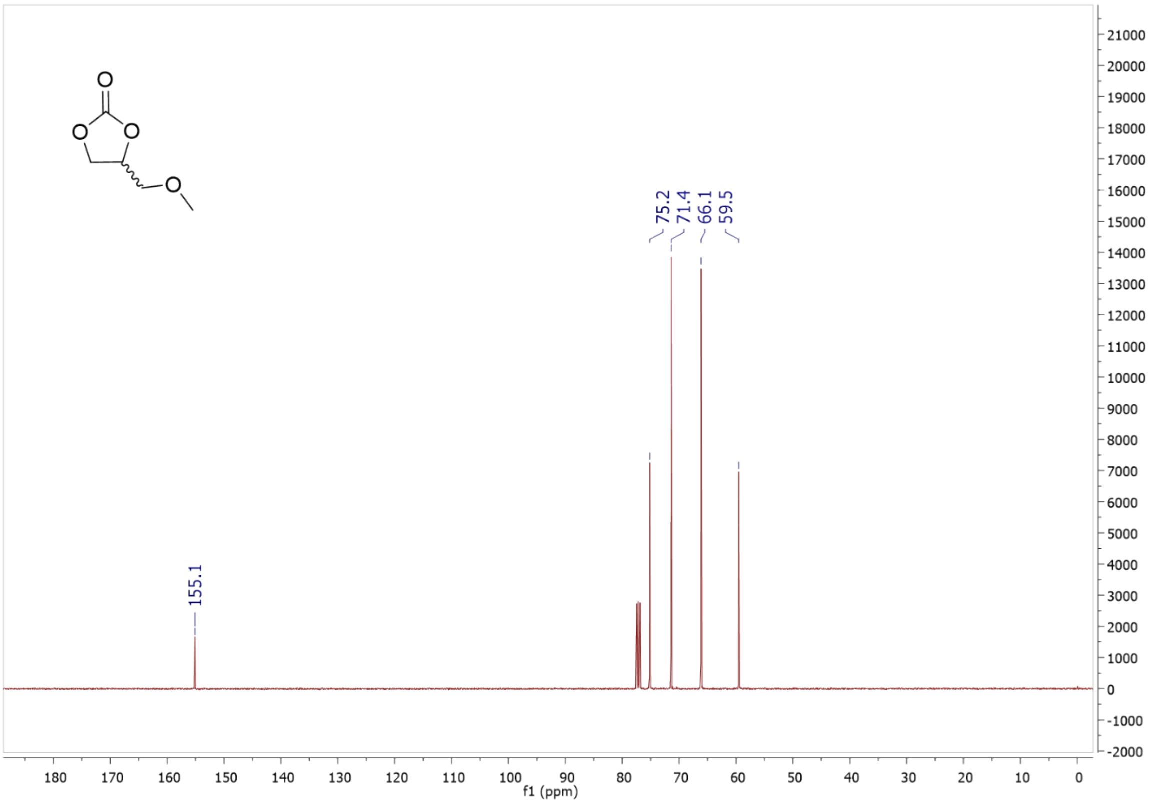


Figure S30. ^{13}C NMR spectrum (100.6 MHz) of 4-methoxymethyl-1,3-dioxolan-2-one (**5f**) in CDCl$_3$.

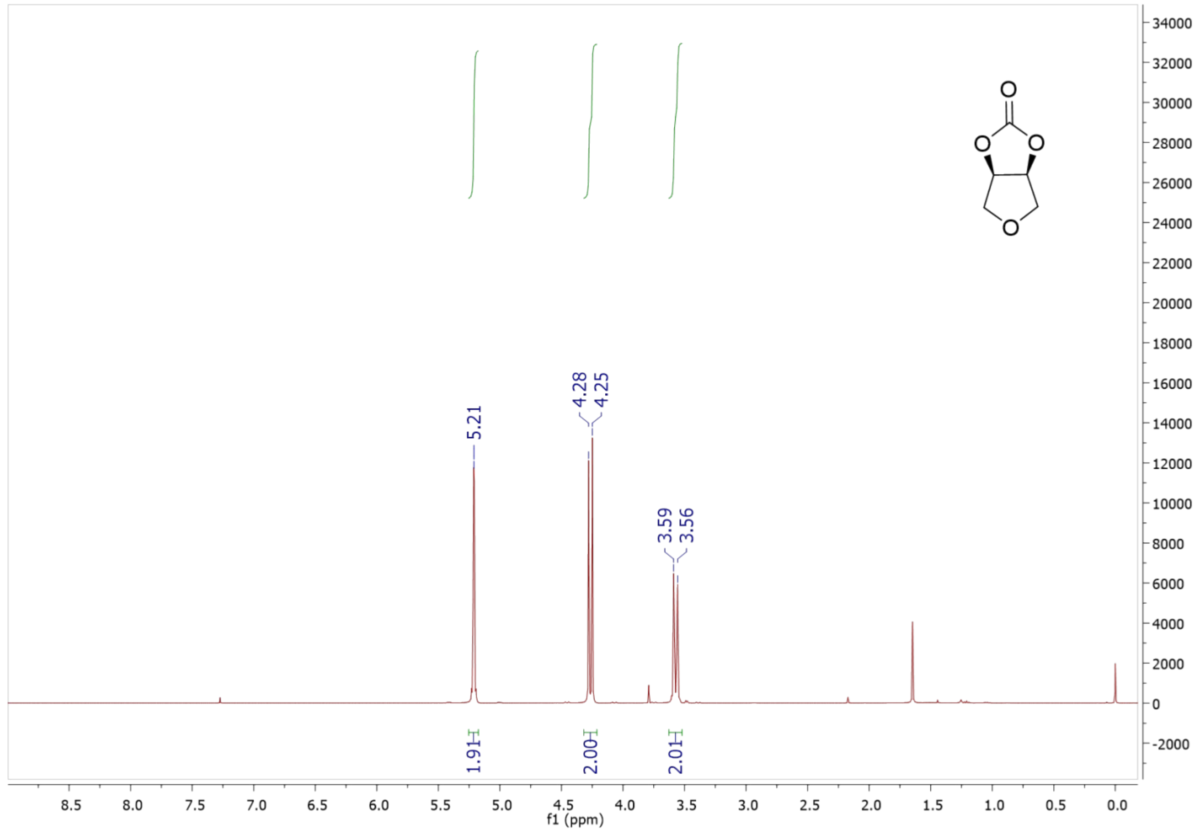


Figure S31. ^{1}H NMR spectrum (400 MHz) of anhydroerythritol carbonate (**5h**) in $CDCl_3$.

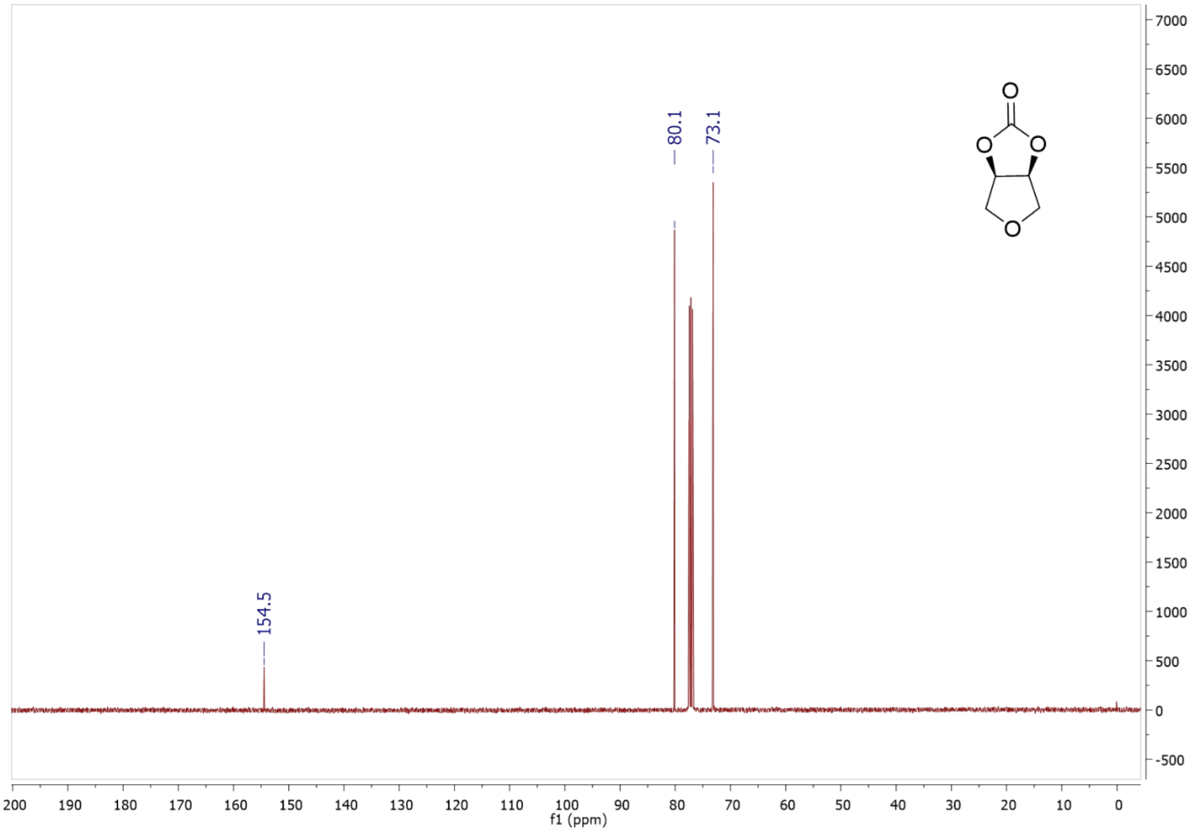


Figure S32. ^{13}C NMR spectrum (100.6 MHz) of anhydroerythritol carbonate (**5h**) in $CDCl_3$

2.8 Off-line solid state NMR

2.8.1 General Information

^{13}C CPMAS NMR spectra were recorded at 100.6 MHz, on a Bruker Avance III HD spectrometer (9.4 Tesla) equipped with a Standard bore MAS multinuclear probe operated in the 40-400 MHz range. Free induction decays were acquired at room temperature using a standard pulse sequence (Bruker, CP). The spectral width was 405 ppm (40761 Hz). A 90 ° proton excitation pulse of 2.5 µs, a spinlock time of 2 ms and a 2 s relaxation delay were used to collect 300 scans. Spectra were recorded in 4 mm rotor (Bruker) at spinning rate of 12 kHz.

2.8.2 Analysis of Polystyrene-supported 1,1,3,3-tetramethylguanidine (**PS-TMG**)

The rotor spinning rate was 12 kHz in order to avoid spinning side band interfering with the signal of interest. Characteristic signal of the Merrifield resin (CH_2Cl: 46.8 ppm) were decreasing in intensity after the reaction with tetramethylguanidine and characteristic signals of PS-TMG appeared at 40.8 ppm (-N-CH3); 53 ppm (-CH2-N=C) and 163.5 ppm (C=N-) (Figure S33).

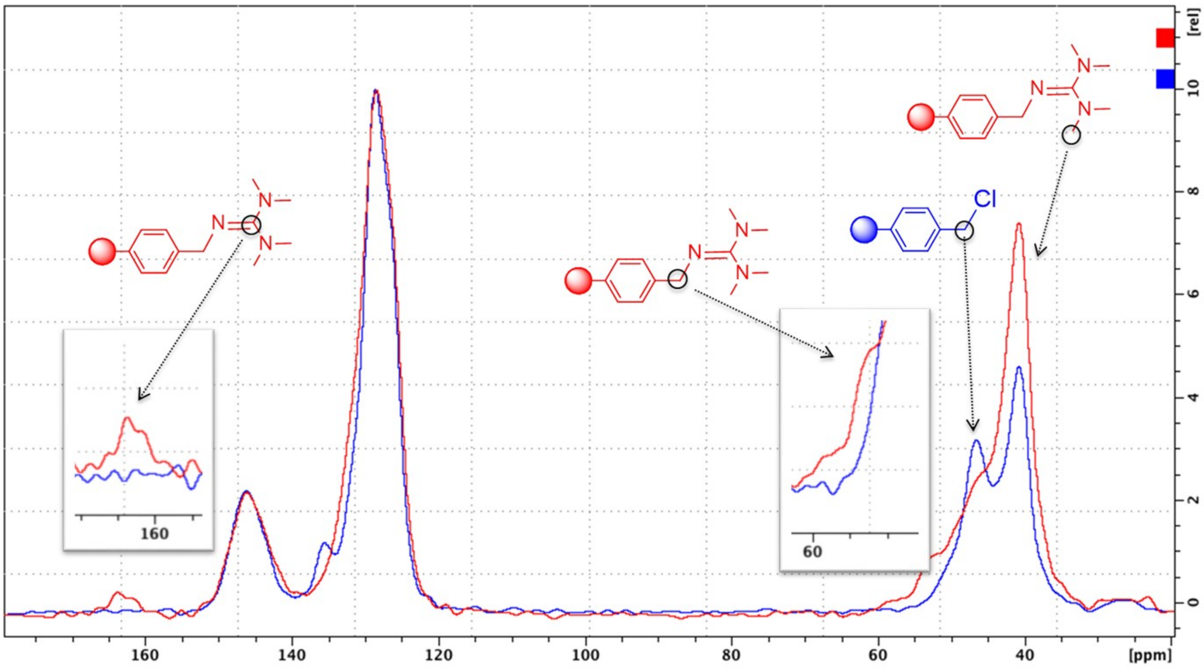


Figure S33. Solid State NMR spectra of polystyrene-supported TMG (PS-TMG) in red and unmodified Merrifield resin in blue.

3 References

S1. H.-J. Kim, S-Il Yoo and J.-S. Chung, *New electrolytes and lithium ion battery using the same*, WO Pat. 0152340A1.

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S4. N. E. Leadbeater and C. Van Der Pol, *J. Chem. Soc. Perkin Trans. 1*, 2001, 2831–2835.