Supporting Information for:

Versatile and scalable synthesis of cyclic organic carbonates under organocatalytic continuous flow conditions

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1. General Information

1.1 Chemicals

Chemicals, purity, CAS numbers and suppliers are listed in Table S1. Information on biobased glycerol is detailed in section 2.4.

Table S1. Chemicals and suppliers

Products	Purity (%)	CAS Number	Supplier
Ethanediol (ethylene glycol)	99.8%	107-21-1	Acros Organics
1,2-Propanediol (propylene glycol)	>99%	57-55-6	TCI
1,2,3-Propanetriol (glycerol)	≥99%	56-81-5	Honeywell Chemicals
3-Methoxy-1,2-propanediol	>98%	623-39-2	TCI
3-*tert*-Butoxy-1,2-propanediol	≥97%	74338-98-0	Merck/Sigma-Aldrich
3-Allyloxy-1,2-propanediol	>99%	123-24-2	TCI
3-(*o*-Tolyloxy)-1,2-propanediol (mephesin)	>98%	59-47-2	TCI
3-(Dimethylamino)-1,2-propanediol	>98%	623-57-4	TCI
3-Morpholino-1,2-propanediol	>98%	6425-32-7	TCI
1,2-Butanediol (1,2-butylene glycol)	>98%	584-03-2	TCI
2,3-Butanediol (2,3-butylene glycol)	>97%	513-85-9	TCI
3-Butene-1,2-diol	≥99%	497-06-3	Merck/Sigma-Aldrich
1,4-Anhydroerythritol	95%	4358-64-9	Merck/Sigma-Aldrich
cis-1,2-Cyclohexanediol	99%	1792-81-0	Acros Organics
trans-1,2-Cyclohexanediol	>99%	1460-57-7	TCI
1,2-Octanediol	>96%	1117-86-8	TCI
Dimethyl carbonate (DMC)	99%	616-38-6	Acros Organics
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-Epoxy-1-propanol (glycidol)	96%	556-52-5	Acros Organics
Dimethyl sulfoxide (DMSO)	>99%	67-68-5	VWR Chemicals
Tetramethylammonium bromide (NMe_4Br)	>97%	64-20-0	TCI
Tetraethylammonium bromide (NEt_4Br)	>98%	71-91-0	TCI
Tetrabutylammonium bromide (NBu_4Br)	>99%	1643-19-2	Acros Organics

Tetra-*n*-octylammonium bromide	98%	14866-33-2	Acros Organics
Tetramethylphosphonium bromide (PMe_4Br)	98%	4519-28-2	Merck/Sigma-Aldrich
Tetrabutylphosphonium bromide (PBu_4Br)	>99%	3115-68-2	TCI
Tetraphenylphosphonium bromide (PPh_4Br)	99%	2751-90-8	Janssen Chimica
Tetrabutylammonium chloride (NBu_4Cl)	>98%	1112-67-0	TCI
Tetrabutylammonium iodide	98%	311-28-4	Merck/Sigma-Aldrich
Tetrabutylammonium acetate [$NBu_4(OAc)$]	97%	10534-59-5	Merck/Sigma-Aldrich
Tetrabutylammonium 2-hydroxybenzoate (tetrabutylammonium salicylate)	>98%	22307-72-8	TCI
Tetrabutylammonium trifluoromethanesulfonate [tetrabutylammonium triflate, $NBu_4(OTf)$]	>99%	35895-70-6	Merck/Sigma-Aldrich
Tetrabutylammonium tetrafluoroborate (NBu_4BF_4)	>98%	429-42-5	TCI
Tetrabutylammonium hexafluorophosphate (NBu_4PF_6)	>98%	3109-63-5	TCI

1.2 Column chromatography

Column chromatography was performed using Davisil® LC60A 70-200 µm silica gel or Alumina Fluka, type 507 C (neutral), activity stage I. Thin layer chromatography (TLC) was conducted on POLYGRAM® SIL G/UV_{254} silica gel or Merck Aluminium oxide 60 F_{254} neutral precoated plates. Potassium permanganate was used as TLC stain.

1.3 Microfluidic setup and parts

Further details can be found in Table S2.

1.3.1 Pumps

Feed solutions were handled with Chemyx Fusion 6000 high force syringe pumps equipped with stainless steel (SS) syringes (6 or 20 mL) and Dupont™ Kalrez® Spectrum™ O-rings (0.549 x 0.103”); or with Knauer Azura P 4.1S HPLC pumps.

1.3.2 Connectors, ferrules and mixers

Sections of the reactor that were not subjected to high temperatures were equipped with Super Flangeless PEEK nuts, ETFE ferrules and SS rings; or coned PEEK fittings. Sections of the reactor that were subjected to high temperatures were equipped with Valco SS nuts, ferrules and (reducing) unions. Feed solutions were mixed in PEEK T-mixers (0.02” through hole). Connectors, ferrules and unions were purchased from IDEX/Upchurch.

1.3.3 Check-valves

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

1.3.4 Feed and collection lines

Feed and collection lines were constructed from PEEK tubing (green striped, 1.58 mm outer diameter, 750 µm internal diameter) or PFA tubing (high purity PFA; 1.58 mm outer diameter, 750 µm internal diameter).

1.3.5 SS coil reactors

SS coil reactors were constructed with deburred-end, steam-cleaned and acid-passivated 316 SS tubing (1.58 mm outer diameter, 500 µm internal diameter) of defined internal volumes (0.67 mL or 1.17 mL); or with type 304 SS tubing (3 mm outer diameter, 2.1 mm internal diameter) of defined internal volume (1.87 mL).

1.3.6 Thermoregulatory device

The reactors were thermoregulated with a Heidolph™ MR Hei-Tec® oil bath equipped with a Pt-1000 temperature sensor.

1.3.7 Back-pressure regulator

Downstream pressure was regulated with a dome-type back pressure regulator (Zaiput Flow Technologies BPR-10) connected to a nitrogen cylinder to set the working pressure.

1.3.8 In-line NMR spectrometer

Qualitative in-line NMR analyses were conducted on a 43 MHz Spinsolve™ Carbon NMR spectrometer from Magritek® equipped with the flow-through module.

1.4 Mesofluidic setup

1.4.1 Pumps

Feed solutions were handled with Corning dosing lines (HMP gear pumps).

1.4.2 Feed and collection lines

Feed and collection lines consisted of PFA tubing (1/4” o.d., 0.047 inch wall thickness) equipped with PFA or SS Swagelok connectors and ferrules.

1.4.3 Mesofluidic reactor

The silicon carbide mesofluidic reactor was manufactured by Corning SAS (Corning® Advanced-Flow™ G1 SiC reactor). It featured 6 fluidic modules connected in series (10 mL/FM) and integrated with heat exchangers.

1.4.4 Thermoregulatory device

The reactor was thermoregulated with a LAUDA Integral XT 280 thermostat using LAUDA Therm 180 silicone oil.

1.4.5 Back-pressure regulator

Downstream pressure was regulated with a dome-type back pressure regulator (Zaiput Flow Technologies BPR-1000) connected to a nitrogen cylinder to set the working pressure.

1.5 Part numbers & vendors

Fluidic components were purchased from commercial sources and are listed in Table S2.

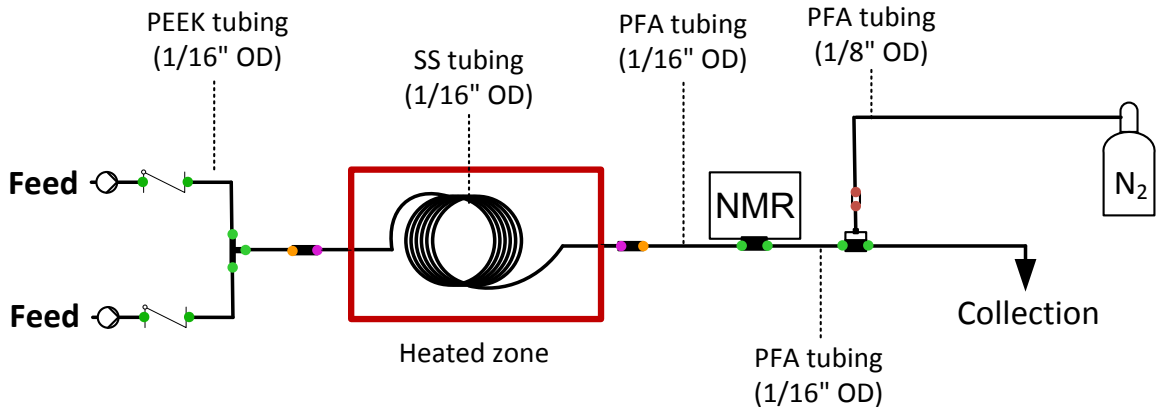
Table S2. Details of the microfluidic elements, vendors and references.

Item	Details	Vendor	Reference
Connectors	One-Piece Fingertight, 10-32 Coned, for 1/16" OD Natural	IDEX/Upchurch Scientific	F-120X
	Super Flangeless™ Nut PEEK, 1/4-28 Flat-Bottom, for 1/16" & 1/32" OD	IDEX/Upchurch Scientific	P-255X
	Super Flangeless™ Ferrule w/SST Ring, Tefzel™ (ETFE), 1/4-28 Flat-Bottom, for 1/16" OD Yellow	IDEX/Upchurch Scientific	P-259X
	SS Nut, for 1/16” OD	VICI (Valco Ins. Co. Inc.)	ZN1-10
	Ferrule, Stainless, type 303, for 1/16” OD	VICI (Valco Ins. Co. Inc.)	ZF1-10
	Super Flangeless™ Nut PEEK, 1/4-28 Flat-Bottom, for 1/8"	IDEX/Upchurch Scientific	P-331
	Super Flangeless™ Ferrule Tefzel™ (ETFE), 1/4-28 Flat-Bottom, for 1/8" OD	IDEX/Upchurch Scientific	P-359X
Unions	Standard Union Polypropylene 1/4-28	IDEX/Upchurch Scientific	P-620
	Union Assembly ZDV Valco Type, 10-32 Coned, for 1/16" OD	IDEX/Upchurch Scientific	U-322
	SS Reducing Union, 1/8” x 1/16” Tube OD	Swagelok	SS-200-6-1
Mixers	PEEK Low Pressure Tee Assembly 1/16" PEEK .020 thru hole	IDEX/Upchurch Scientific	P-712
Check-valves & holders	Check Valve Inline Assembly	IDEX/Upchurch Scientific	CV-3000
Back pressure regulators	Back Pressure Regulator, metal-free wetted parts, adjustable set point, 0.05-20 mL min^{-1} flow rates	Zaiput Flow Technologies	BPR-10
	Back Pressure Regulator, metal-free wetted parts, adjustable set point, 20-1000 mL min^{-1} flow rates	Zaiput Flow Technologies	BPR-1000
Tubing	PFA Tubing High Purity 1/16" OD x .030" ID	IDEX/Upchurch Scientific	1632L
	Green striped PEEK tubing, 1/16" OD, .030" ID	VICI (Valco Ins. Co. Inc.)	JR-T-6003
	316 Stainless steel tubing, 1/16” OD, .020" ID	VICI (Valco Ins. Co. Inc.)	TSS120
	Empty SS tubing (type 304) 1/8” OD x 2.1 mm ID	Supelco Analytical	20526-U

2 Additional experimental details

2.1 Detailed continuous flow setups

2.1.1 Microfluidic setup for the carbonation of diols **4a,2b-t** and for the assessment of the stability of **1a**



- Super Flangeless Nut PEEK, 1/4-28 Flat-Bottom, for 1/16" OD tubing (+ferrule)
- One-Piece Fingertight, 10-32 Coned, for 1/16" OD tubing
- Super Flangeless Nut PEEK, 1/4-28 Flat-Bottom, for 1/8" OD tubing (+ ferrule)
- SS Nut, for 1/16” OD tubing (+ ferrule)
- HPLC pump or syringe pump equipped with SS syringe
- Check Valve Inline Assembly
- Union Assembly ZDV Valco Type, 10-32 Coned, for 1/16" OD tubing
- PEEK Low Pressure Tee Assembly 1/16" PEEK .020 thru hole
- Dome-type back pressure regulator
- Standard Union Polypropylene 1/4-28

Figure S1. Microfluidic setup for the carbonation of diols **4a,2b-t** and for the assessment of the stability of **1a**. The in-line NMR spectrometer is optional.

2.1.2 Microfluidic setup for the carbonation of crude biobased glycerol (**4a**)

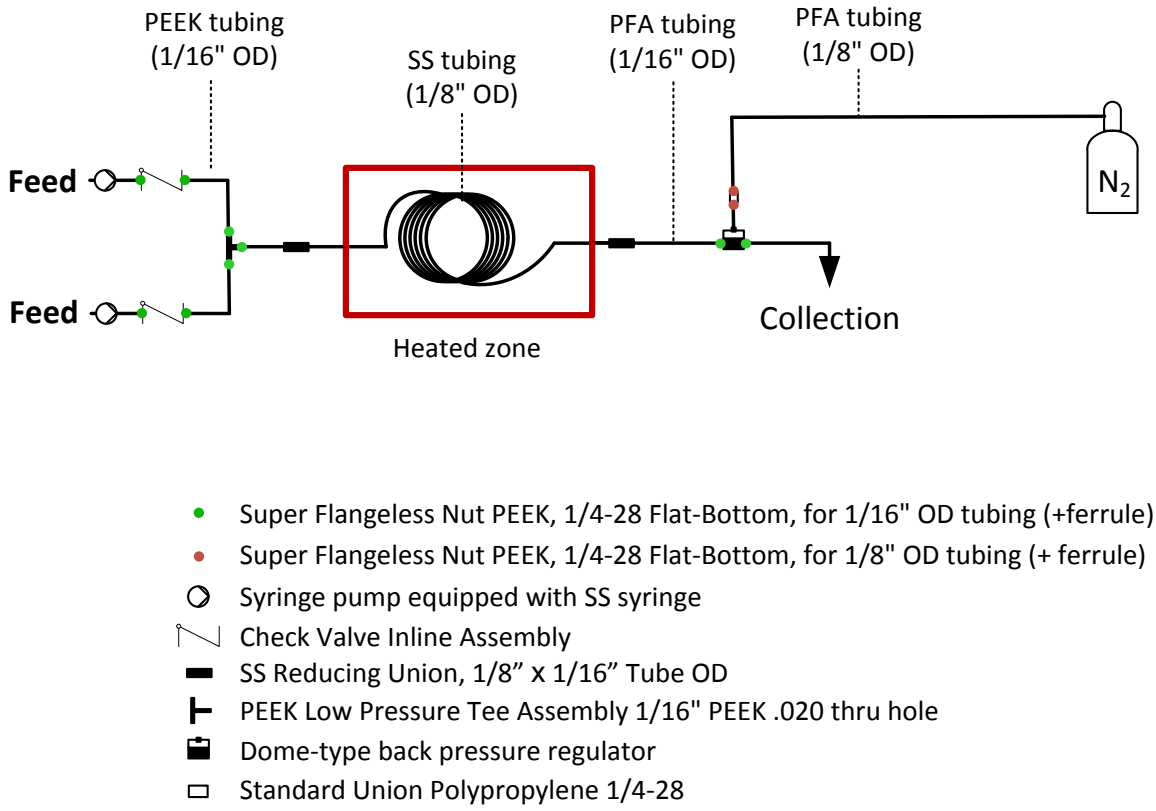


Figure S2. Microfluidic setup for the carbonation of crude biobased glycerol (**4a**).

2.1.3 Mesofluidic setup

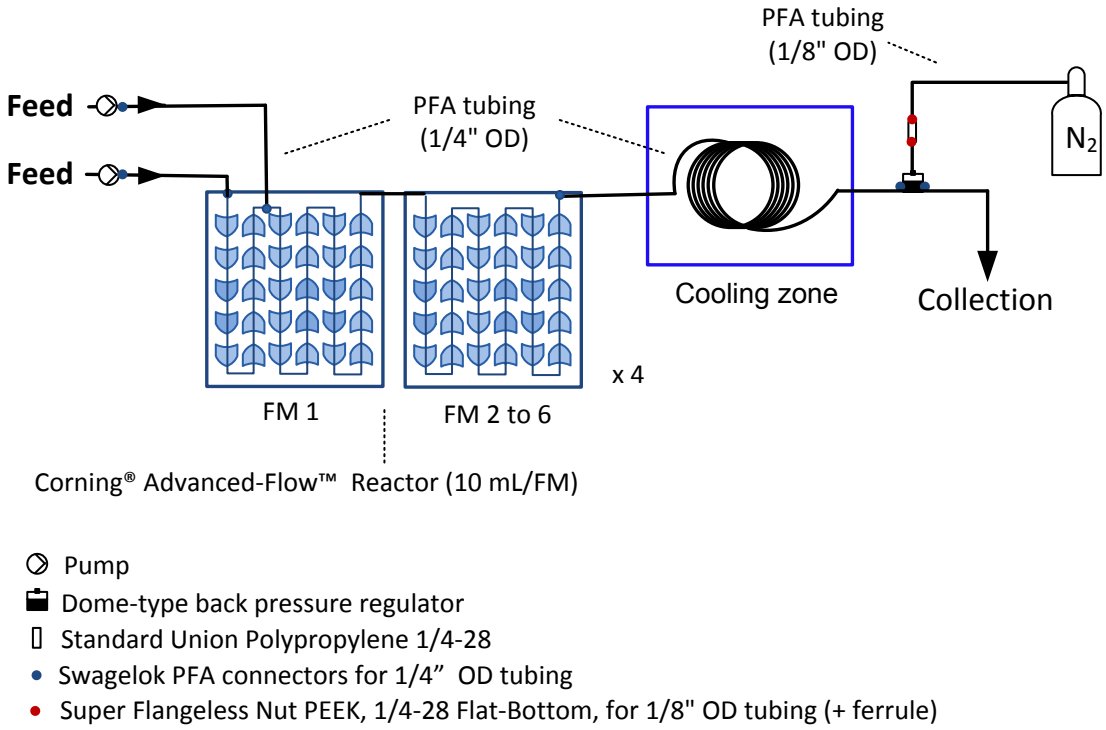


Figure S3. Mesofluidic (pilot-scale) setup for the carbonation of glycerol (**4a**).

2.2 GC/FID Analysis

2.2.1 Analytical method

Gas Chromatograph: Shimadzu GC-2014

Carrier gas: Helium (total flow = 42.9 mL min^{-1})

Column: 14% cyanopropylphenyl / 86% dimethyl polysiloxane (0.25 mm ID x 0.25 µm x 27 m)

Injection volume: 1 µL

Mode: Split (ratio = 20)

Oven temperature program:

Time (min)	T (°C)
0	50
3	50
8.2	153
19.2	164
23.5	250
26.5	250

2.2.2 Representative chromatogram

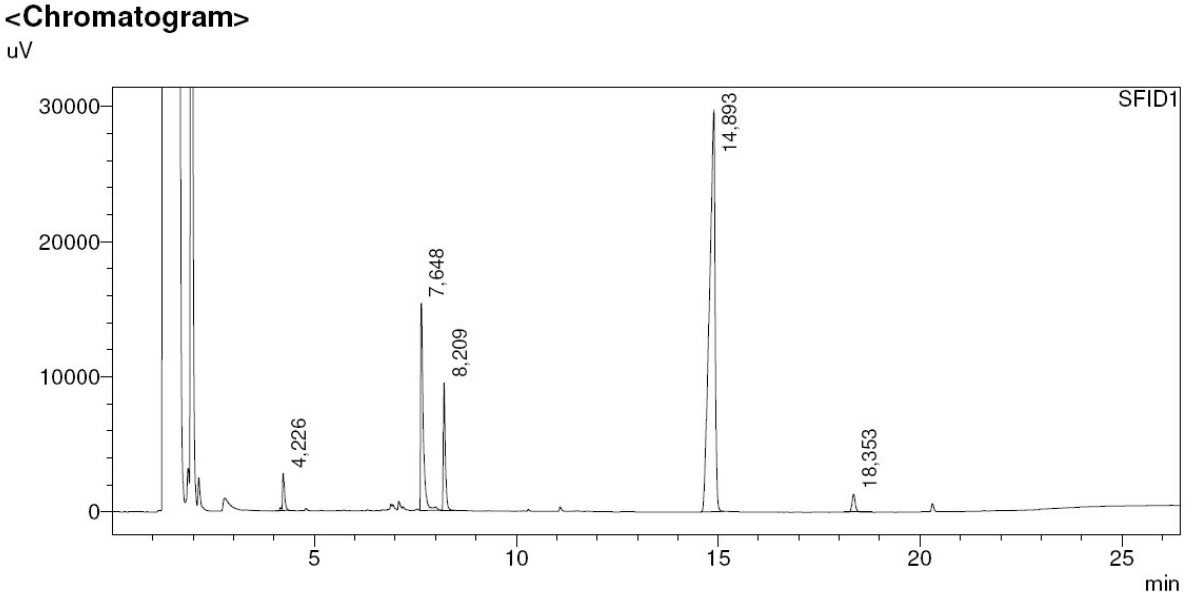


Figure S4. Representative GC/FID chromatogram of a crude reactor effluent from the carbonation of glycerol. Conditions: T = 160 °C, residence time = 5 min, P = 11 bar, 2.25 equiv. of DMC, 3.5 mol% of NBu4Br. **4a** conv. = 92%, selec. for **1a** = 80%. Peak #1 (4.23 min) = glycidol (**3a**), peak #2 (7.65 min) = NBu_4Br, peak #3 (8.21 min) = glycerol (**4a**), peak #4 (14.89 min) = glycerol carbonate (**1a**), peak #5 (18.35 min) = methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (**5a**).

2.3 Process optimization for the carbonation of glycerol (**4a**) toward **1a**

2.3.1 Influence of the residence time

The influence of the residence time on the reaction is depicted on Figure S5. An increase from 3 to 5 min slightly improved the conversion from 64 to 74% (with 1.4 equiv. of DMC), from 72% to 83% (with 1.7 equiv. of DMC), and from 84 to 92% (with 2.25 equiv. of DMC). The selectivity for glycerol carbonate (**1a**) was not affected by the residence time or the excess of DMC, and varied randomly in the 78-84% range. The selectivity for glycidol (**3a**) decreased with the increase in residence time from 6.1 to 2.4% (with 1.4 equiv. of DMC), from 5.4 to 3.3% (with 1.7 equiv. of DMC) and from 6.3 to 2.8% (with 2.25 equiv. of DMC). The selectivity for methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (**5a**) followed an opposite trend, slightly increasing from 0.2 to 0.3% (with 1.4 equiv. of DMC), from 0.1 to 0.8% (with 1.7 equiv. of DMC), and from 0.2 to 1.6% (with 2.25 equiv. of DMC).

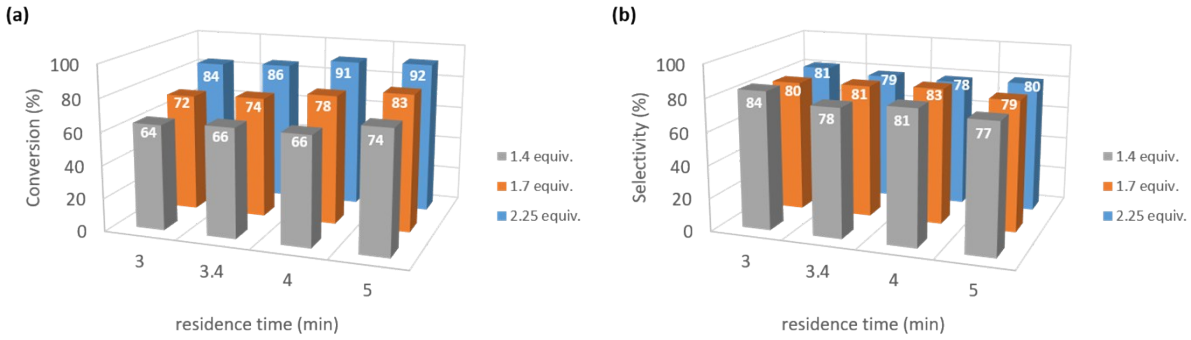


Figure S5. Evolution of **(a)** glycerol conversion and **(b)** glycerol carbonate selectivity as a function of the residence time and of the excess of dimethyl carbonate. Conditions: T = 160 °C, P = 11 bar, 3.5 mol% of NBu_4Br.

2.3.2 Influence of the temperature

The influence of the temperature on the reaction is depicted on Figure S6. Heating up the reactor from 150 °C to 180 °C increased the conversion of glycerol from 50 to 84% (with 1.4 equiv. of DMC), from 62 to 90% (with 1.7 equiv. of DMC), and from 71 to 95% (with 2.25 equiv. of DMC). The selectivity for **1a** varied randomly in the 78-84% range with the modification of the DMC/**4a** molar ratio or of the temperature. Similarly, the selectivity for glycidol (**3a**) varied randomly in the 0.4-6.1% range, regardless of the conditions utilized. By contrast, the selectivity for methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (**5a**) slightly increased with the temperature from 0.2 to 1.7% (with 1.4 equiv. of DMC), from 0.1 to 1.7% (with 1.7 equiv. of DMC), and from 0.2 to 3.6% (with 2.25 equiv. of DMC).

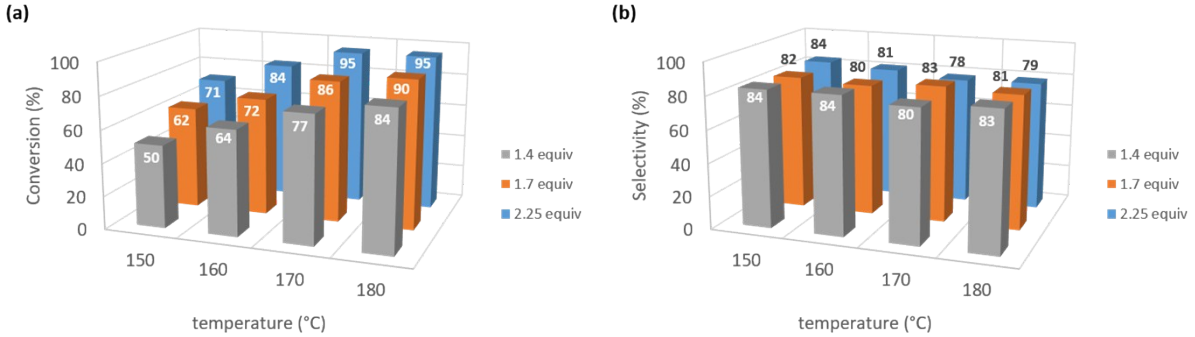


Figure S6. Evolution of **(a)** glycerol conversion and **(b)** glycerol carbonate selectivity as a function of the temperature and of the excess of dimethyl carbonate. Conditions: residence time = 3 min, P = 11 bar, 3.5 mol% of NBu_4Br.

2.4 Optimization of the purification of glycerol carbonate (**1a**) by liquid-liquid extraction

General procedure: A model crude solution was prepared by mixing 1.4 g of glycerol carbonate (**1a**, 11.9 mmol), 200 mg of glycidol (**3a**, 2.7 mmol), 75 mg of glycerol (**4a**, 0.81 mmol), 64 mg of methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (**5a**, 0.36 mmol) and 175 mg of tetrabutylammonium bromide (NBu_4Br, 0.54 mmol). The solution was diluted with 1 mL of an aqueous phase, and extracted with an organic solvent (see Table S3 for details). The organic phases were combined, dried over $MgSO_4$ and filtered. The aqueous and combined organic phases were diluted with EtOH, and analyzed by GC-FID.

Table S3. Optimization of the purification of glycerol carbonate (**1a**) by liquid-liquid extraction

Entry[a]	Organic Solvent	Aqueous phase	Volume of organic solvent	Amount of compound extracted in the organic solvent (%)				
				1a	**3a**	**4a**	**5a**	NBu_4Br
1	MIBK	H_2O	-[b]	-[b]				
2	MIBK	NaCl 1 wt%	3 x 5 mL	90	85	11	>99.9	98
3	AcOEt	H_2O	-[b]	-[b]				
4	AcOPr	H_2O	3 x 5 mL	79	76	0	95	59
5	AcOPr	NaCl 1 wt%	3 x 5 mL	81	81	0	>99.9	69
6	AcOBu	H_2O	3 x 5 mL	47	-[c]	0	>99.9	16
7	AcOBu	NaCl 1 wt%	3 x 5 mL	60	-[c]	0	>99.9	28
8	AcOBu	NaCl 5 wt%	3 x 5 mL	61	-[c]	0	>99.9	32
9	AcOBu	NaCl 10 wt%	3 x 5 mL	62	-[c]	0	>99.9	49
10	CH_2Cl_2	H_2O	3 x 5 mL	53	71	0	>99.9	98.7
11	CH_2Cl_2	H_2O	1 x 5 mL	39	56	0	95	90
12	$CHCl_3$	H_2O	3 x 5 mL	34	42	0	>99.9	94
13	$CHCl_3$	H_2O	1 x 5 mL	27	53	0	90	91
14	$CHCl_3$	H_2O	1 x 3 mL	20	43	0	81	83
15	DCE	H_2O	3 x 5 mL	50	67	0	>99.9	99.5
16	Et_2O	H_2O	3 x 5 mL	15	37	0	40	8
17	MTBE	H_2O	3 x 5 mL	29	51	0	68	5
18	MeTHF	H_2O	-[b]	-[b]				
19	toluene	H_2O	3 x 5 mL	8	11	0	50	1.6

AcOBu = *n*-butyl acetate, AcOEt = ethyl acetate, AcOPr = *n*-propyl acetate, DCE = 1,2-dichloroethane, Et_2O = diethyl ether, MeTHF = 2-methyltetrahydrofuran, MIBK = methyl isobutyl ketone, MTBE = methyl *tert*-butyl ether. [a] See the general procedure for details. [b] No phase separation. [c] Not determined, overlapping with the peak of the solvent (GC-FID).

2.5 Purification of glycerol carbonate (**1a**) and NBu_4Br from a crude reactor effluent

The following procedure was applied to 28 g of a crude reactor effluent produced following "typical run 1: microscale synthesis of glycerol carbonate (**1a**) from commercial glycerol" described in the experimental section of the manuscript.

Glycerol carbonate (1a): Methanol and the excess of dimethyl carbonate were removed under reduced pressure from the crude reactor effluent. The resulting transparent oil was diluted with 9 mL of H_2O, and washed with 1 x 27 mL of chloroform. The chloroform phase could be further processed following the procedure described below to recycle tetrabutylammonium bromide. 100 mg of NaCl were added to the aqueous phase, and it was extracted with 3 x 45 mL of methyl isobutyl ketone (MIBK). The MIBK phases were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield glycerol carbonate (**1a**, 60%) as a transparent oil, which was contaminated with glycidol (**3a**, 3.1 mol% with respect to **1a**), glycerol (**4a**, 2.7 mol% with respect to **1a**), methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (**5a**, 0.6 mol% with respect to **1a**) and tetrabutylammonium bromide (1.9 mol% with respect to **1a**).

Tetrabutylammonium bromide: The chloroform phase obtained following the procedure described above was concentrated under reduced pressure. The resulting yellow oil was diluted with 7 mL of H_2O, and extracted with 21 mL of chloroform. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude yellow oil was purified by recrystallization in 30 mL of ethyl acetate/methyl *tert*-butyl ether 2:1, affording tetrabutylammonium bromide as white crystals (18% isolated yield).

2.6 Specifications of refined and crude biobased glycerol

The purity of Cargill's refined biobased glycerol was 99.5%. The specifications of Cargill's and Valtris Champlor's crude biobased glycerol samples are detailed in Table S4 and S5, respectively.

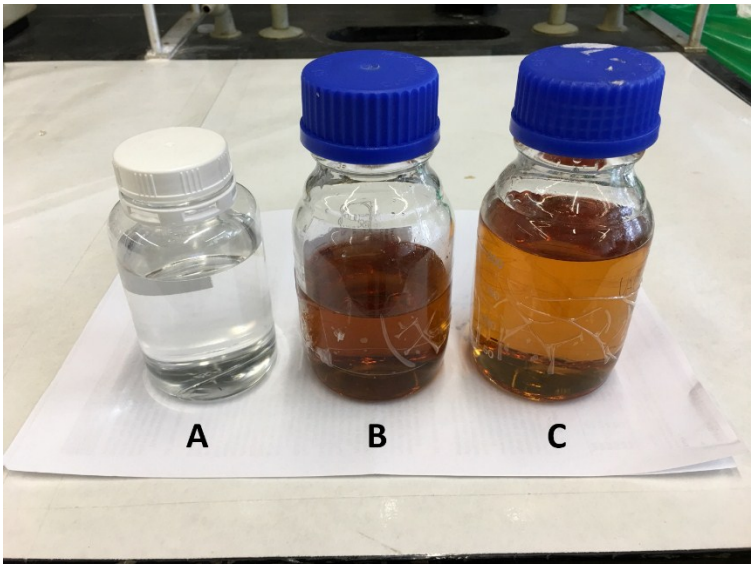


Figure S7. Photograph of biobased glycerol samples. **A** = Cargill's refined biobased glycerol; **B** = Cargill's crude biobased glycerol; **C** = Valtris Champlor's crude biobased glycerol.

Table S4. Specifications of Cargill's crude biobased glycerol.

Specification	Range
Glycerol content[a]	min 80.0%
Water content	max 15%
Matter Organic Non Glycerin (MONG)	max 2.5%
Salts (NaCl, as ash)	max 7.0%
Methanol content	max 0.2%

[a] The sample was analyzed by GC/FID, and contained 85% of glycerol.

Table S5. Specifications of Valtris Champlor's crude biobased glycerol.

Specification	Result
Glycerol content	84%
Water content	9%
Matter Organic Non Glycerin (MONG)	0.9%
Salts content	6%
K content	0.0%
Na content	1.9%

2.7 Off-line high field (quantitative) NMR

Analytical ^{1}H 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. Compounds were solubilized in $CDCl_3$ or MeOD-d_4, and chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as internal standard.

For quantitative ^{1}H NMR analyses (yields determination), 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. The NMR samples were prepared by weighting known amounts of reactor effluents (typically 40-60 mg) and mesitylene (typically 10-15 mg), which were diluted with 600 µL of $CDCl_3$. Three NMR samples were prepared for each data point to ensure reproducibility of the analysis.

2.8 Substrate scope

Table S6. Process (re)optimization for the carbonation of diols **2b-d**, **2f**, **2g**, **2s**

Entry[a]	Diol	Temperature (°C)	Residence time (min)	DMC (equiv.)	NBu_4Br (mol%)	Conv. (%)[b]	Selec. (%)[b]
1	**2b**	100	3	3	3.5	1	-
2	**2b**	120	3	3	3.5	17	82
3	**2b**	140	3	3	3.5	52	89
4	**2b**	160	3	3	3.5	81	87
5	**2b**	180	3	3	3.5	89	99
6	**2c**	180	3	2.25	1	69	91
7	**2c**	180	3	2.25	2	73	87
8	**2c**	180	3	2.25	3.5	77	89
9	**2c**	140	3	3	3.5	74	81
10	**2c**	160	3	3	3.5	93	82
11	**2c**	180	3	3	3.5	95	98
12	**2d**	180	3	2.25	2	75	87
13	**2d**	180	3	2.25	3.5	79	90
14	**2d**	180	3	3	3.5	98	92
15	**2f**	180	3	3	3.5	71	96
16	**2f**	180	6	3	3.5	80	88
17	**2g**	180	3	2.25	1	69	98
18	**2g**	180	3	2.25	3.5	79	>99
19	**2g**	180	3	3	3.5	97	93
20	**2s**	180	3	6	7	42[c]	
21	**2s**	180	6	6	7	65[c]	
22	**2s**	180	9	6	7	73[c]	

[a] Conditions: the diol + catalyst feedstock solution was pumped neat, P = 11 bar. [b] Conversion and yield were determined by GC/FID. [c] Yield, determined by high-field ^1H NMR in $CDCl_3$ with mesitylene as the internal standard.

2.9 Copies of in-line NMR spectra

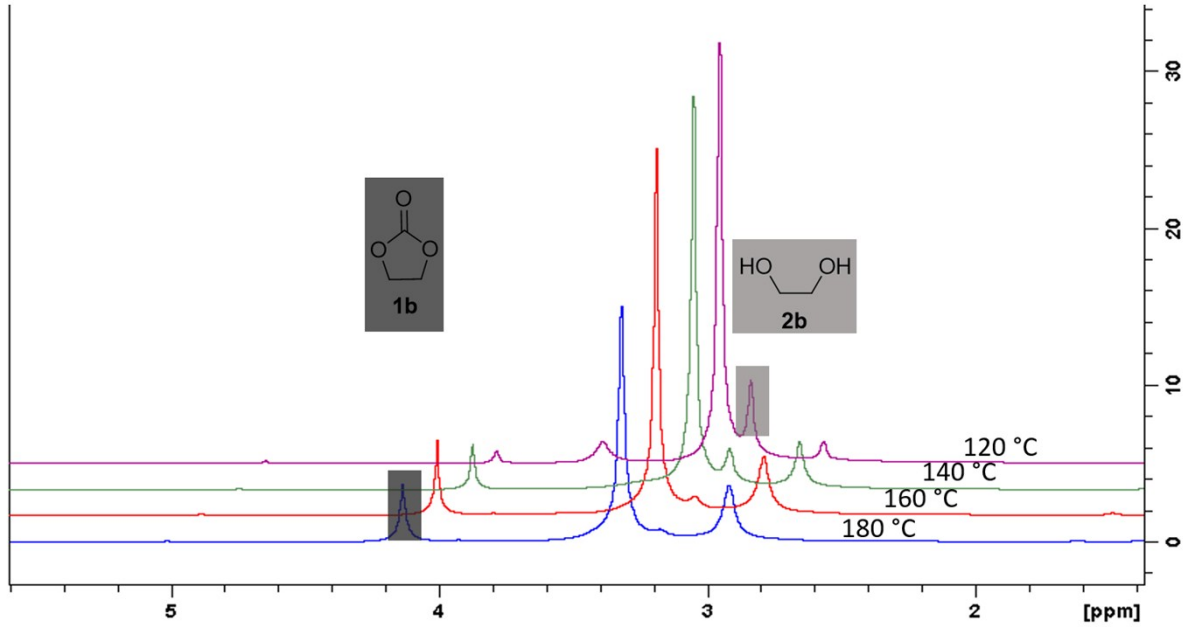


Figure S8. Representative low-field in-line NMR spectra obtained during the carbonation of **2b** into **1b** in the 120-180 °C range. The singlet at 3.2 ppm was used to monitor the variation of **2b** concentration (light grey). The singlet at 4.15 ppm was used to monitor the variation of **1b** concentration (dark grey). Conditions: residence time = 3 min, P = 11 bar, 3.5 mol% of NBu_4Br, 3 equiv. of DMC.

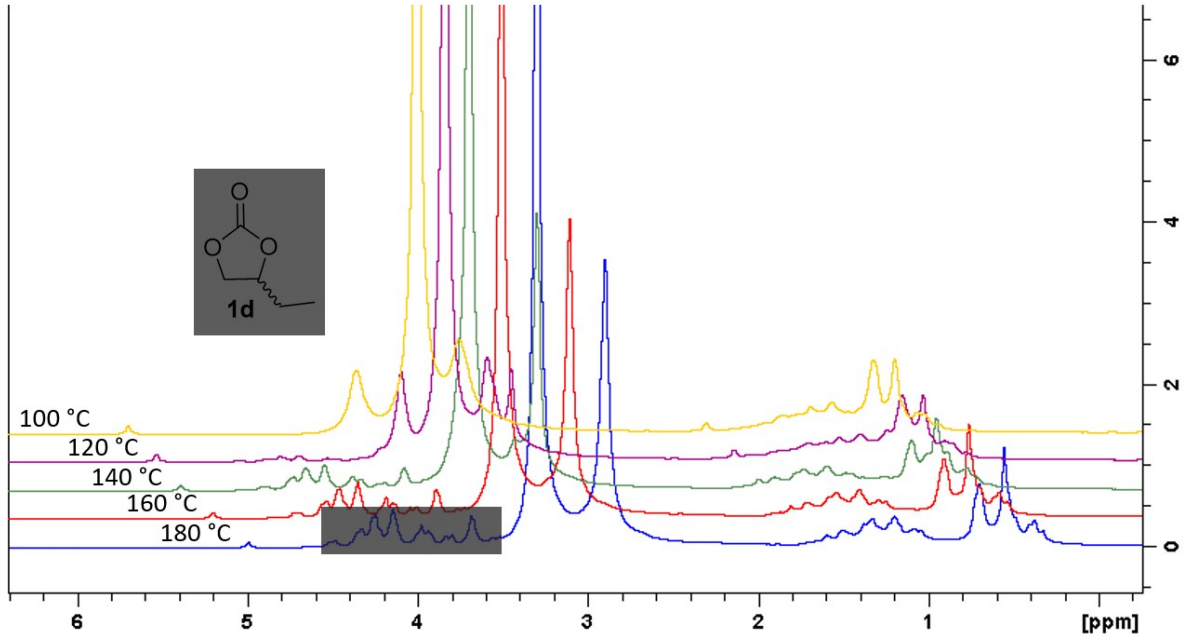
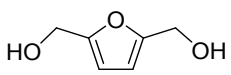


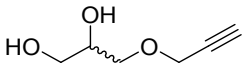
Figure S9. Representative low-field in-line NMR spectra obtained during the carbonation of **2d** into **1d** in the 100-180 °C range. The multiplet at 3.6-4.6 ppm was used to monitor the variation of **1d** concentration (dark grey). Conditions: residence time = 3 min, P = 11 bar, 3.5 mol% of NBu_4Br, 3 equiv. of DMC.

2.10 Synthesis and characterization of 2,5-bis(hydroxymethyl)furan and **2j**, **2k**, **2s**, **2t, 5a**



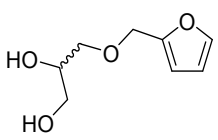
$C_6H_8O_3$
MW 128.13

2,5-Bis(hydroxymethyl)furan. The title compound was prepared following a literature procedure[S1] starting from furfuryl alcohol (11.3 g, 0.115 mol). It was obtained as a yellow solid (6.1 g, 0.048 mol, 41% yield) after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR (MeOD-d_4, 400 MHz):** δ = 6.24 (s, 2H), 4.49 (s, 4H) ppm. **^{13}C NMR (MeOD-d_4, 100.6 MHz):** δ = 155.7, 109.1, 57.5 ppm. The NMR data matched those reported in the literature.[S1] **ESI HRMS** m/z C6H8O3Na$^+$ $[M+Na]^+$: calcd 151.0366; found 151.0367.



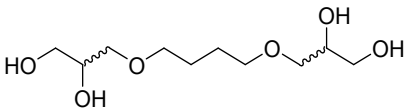
$C_6H_{10}O_3$
130.14

3-(Prop-2-yn-1-yloxy)propane-1,2-diol (2j). The title compound was prepared following a literature procedure starting from glycidyl propargyl ether (10.4 g, 0.093 mol).[S2] It was obtained as a yellow oil (11.1 g, 0.085 mol, 91% yield) after concentration of the reaction medium under reduced pressure. **^{1}H NMR ($CDCl_3$, 400 MHz):** *δ* = 4.20 (d, *J* = 2.4 Hz, 2H), 3.95-3.88 (m, 1H), 3.74-3.68 (m, 1H), 3.66-3.54 (m, 3H), 2.49 (t, *J* = 2.3 Hz, 1H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** *δ* = 79.4, 75.1, 71.4, 70.8, 63.9, 58.7 ppm. The NMR data matched those reported in the literature.[S2] **ESI HRMS** *m/z* $C_9H_{10}O_3Na^+$ $[M+Na]^+$: calcd 153.0522; found 153.0522.



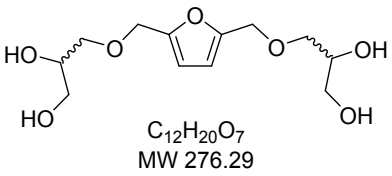
$C_8H_{12}O_4$
MW 172.18

3-(Furan-2-ylmethoxy)propane-1,2-diol (2k). The title compound was prepared following a literature procedure starting from furfuryl alcohol.[S2] It was obtained as an orange oil (4.8 g, 0.028 mol, 44% yield over 2 steps) after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** *δ* = 7.40 (s, 1H), 6.35-6.31 (m, 2H), 4.48 (s, 2H), 3.85 (s, 1H), 3.71-3.46 (m, 4H), 3.38 (s, 1H), 3.01 (s, 1H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** *δ* = 151.3, 143.0, 110.3, 109.7, 71.4, 70.7, 65.2, 63.9 ppm. **ESI HRMS** *m/z* $C_8H_{12}O_4Na^+$ $[M+Na]^+$: calcd 195.0627; found 195.0615.



$C_{10}H_{22}O_6$
MW 238.28

3,3'-(Butane-1,4-diylbis(oxy))bis(propane-1,2-diol) (2s). The title compound was prepared following a literature procedure starting from 1,4-butanediol diglycidyl ether (10 g, 0.049 mol).[S2] It was obtained as a transparent oil (10.5 g, 0.044 mol, 90% yield) after concentration of the reaction medium under reduced pressure. **^{1}H NMR (MeOD-d_4, 400 MHz):** *δ* = 3.80-3.70 (m, 2H), 3.62-3.38 (m, 12H), 1.65 (s, 4H) ppm. **^{13}C NMR (MeOD-d_4, 100.6 MHz):** *δ* = 73.2, 72.3, 72.2, 64.6, 27.4 ppm. **ESI HRMS** *m/z* $C_{10}H_{23}O_6^+$ $[M+H]^+$: calcd 239.1489; found 239.1489.

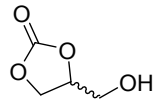


3,3'-((Furan-2,5-diylbis(methylene))bis(oxy))bis(propane-1,2-diol) (2t). The title compound was prepared following a literature procedure starting from 2,5-bis(hydroxymethyl)furan.[S2] It was obtained as a yellow solid (2.7 g, 9.8 mmol, 25% yield over 2 steps) after purification by column chromatography on silica gel (methanol/ethyl acetate gradient). **^{1}H NMR (MeOD-d_4, 400 MHz):** δ = 6.34 (s, 2H), 4.47 (s, 4H), 3.74 (p, *J* = 5.5 Hz, 2H), 3.67-3.42 (m, 10H), 3.35 (s, 2H) ppm. **^{13}C NMR (MeOD-d_4, 100.6 MHz):** δ = 153.5, 111.2, 73.8, 72.4, 72.2, 66.1, 64.5, 64.4 ppm. **ESI HRMS** *m/z* $C_{12}H_{20}O_7Na^+$ $[M+Na]^+$: calcd 299.1101; found 299.1101.

The synthesis and NMR data of methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (**5a**) are reported elsewhere.[S3]

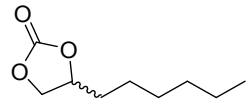
2.11 Characterization of cyclic carbonates **1a-t**

The NMR data of carbonates **1b-d**, **1f**, **1g** and **1r** are reported elsewhere.[S3]



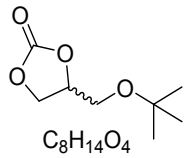
$C_4H_6O_4$
MW 118.09

4-Hydroxymethyl-1,3-dioxolan-2-one (1a). Obtained as a transparent oil after purification following the procedure described in section 2.5. **^{1}H NMR (MeOD-d$_4$, 400 MHz):** δ = 4.86-4.76 (m, 2H), 4.54 (t, *J* = 8.4 Hz, 1H), 4.42-4.35 (m, 1H), 3.86-3.79 (m, 1H), 3.67-3.59 (m, 1H) ppm. **^{13}C NMR (MeOD-d$_4$, 100.6 MHz):** δ = 157.6, 78.7, 67.3, 62.2 ppm. The NMR data matched those reported in the literature.[S3] **ESI HRMS** *m/z* $C_4H_6O_4Na^+$ $[M+Na]^+$: calcd 141.0158; found 141.0143.



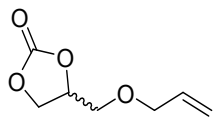
$C_9H_{16}O_3$
MW 172.22

4-Hexyl-1,3-dioxolan-2-one (1e). Obtained as a transparent oil after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 4.75-4.65 (m, 1H), 4.53 (t, *J* = 8.1 Hz, 1H), 4.11-4.03 (m, 1H), 1.88-1.75 (m, 1H), 1.74-1.61 (m, 1H), 1.55-1.22 (m, 8H), 0.89 (t, *J* = 6.7 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 155.2, 77.2, 69.5, 34.0, 31.6, 28.9, 24.4, 22.6, 14.1 ppm. The NMR data matched those reported in the literature.[S4] **ESI HRMS** *m/z* $C_9H_{16}O_3Na^+$ $[M+Na]^+$: calcd 195.0992; found 195.0993.



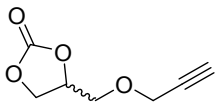
$C_8H_{14}O_4$
MW 174.20

4-(*tert*-Butoxymethyl)-1,3-dioxolan-2-one (1h). Obtained as a transparent oil after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 4.82-4.74 (m, 1H), 4.49 (t, *J* = 8.2 Hz, 1H), 4.43-4.37 (m, 1H), 3.66-3.60 (m, 1H) 3.58-3.52 (m, 1H), 1.22 (s, 9H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 155.3, 75.3, 74.0, 66.7, 61.4, 27.4 ppm. The NMR data matched those reported in the literature.[S4] **ESI HRMS** *m/z* $C_8H_{14}O_4Na^+$ $[M+Na]^+$: calcd 197.0784; found 197.0784.



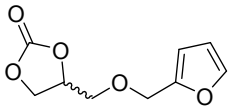
$C_7H_{10}O_4$
MW 158.15

4-((Allyloxy)methyl)-1,3-dioxolan-2-one (1i). Obtained as a transparent oil after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 5.93-5.79 (m, 1H), 5.33-5.17 (m, 2H), 4.86-4.76 (m, 1H), 4.49 (t, *J* = 8.4 Hz, 1H), 4.43-4.35 (m, 1H), 4.10-3.99 (m, 2H), 3.72-3.65 (m, 1H), 3.64-3.57 (m, 1H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 155.0, 133.8, 118.0, 75.1, 72.7, 68.9, 66.4 ppm. The NMR data matched those reported in the literature.[S4] **ESI HRMS** *m/z* $C_7H_{10}O_4Na^+$ $[M+Na]^+$: calcd 181.0471; found 181.0471.



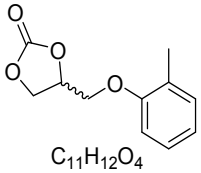
$C_7H_8O_4$
MW 156.14

4-((Prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one (1j). Obtained as a transparent oil after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 4.91- 4.82 (m, 1H), 4.52 (t, *J* = 8.4 Hz, 1H), 4.45-4.37 (m, 1H), 4.32-4.17 (m, 2H), 3.84-3.70 (m, 2H), 2.51 (t, *J* = 2.4 Hz, 1H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 154.9, 78.6, 75.7, 74.8, 68.5, 66.3, 58.9 ppm. The NMR data matched those reported in the literature.[S4] **ESI HRMS** *m/z* $C_7H_8O_4Na^+$ $[M+Na]^+$: calcd 179.0315; found 179.0315.



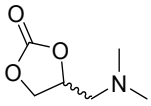
$C_9H_{10}O_5$
MW 198.17

4-((Furan-2-ylmethoxy)methyl)-1,3-dioxolan-2-one (1k). Obtained as an orange oil after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.40-7.43 (m, 1H), 6.37-6.33 (m, 2H), 4.82-4.74 (m, 1H), 4.59-4.42 (m, 3 H), 4.35-4.30 (m, 1H), 3.73-3.67 (m, 1H), 3.66-3.60 (m, 1H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 155.0, 150.8, 143.3, 110.5, 110.3, 75.0, 68.6, 66.4, 65.4 ppm. The NMR data matched those reported in the literature.[S4] **ESI HRMS** *m/z* $C_9H_{10}O_5Na^+$ $[M+Na]^+$: calcd 221.0420; found 221.0421.



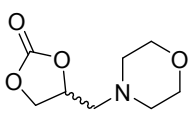
$C_{11}H_{12}O_4$
MW 208.21

4-((*o*-Tolyloxy)methyl)-1,3-dioxolan-2-one (1l). Transparent crystals were collected upon cooling of the reactor effluent to 5 °C, filtration and drying. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.19-7.12 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.80-6.75 (m, 1H), 5.08-5.00 (m, 1H), 4.65-4.53 (m, 2H), 4.29-4.22 (m, 1H), 4.16-4.09 (m, 1H), 2.22 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 155.9, 154.9, 131.2, 127.2, 127.0, 121.8, 111.0, 74.4, 67.1, 66.4, 16.1 ppm. The NMR data matched those reported in the literature.[S5] **ESI HRMS** *m/z* $C_{11}H_{12}O_4Na^+$ $[M+Na]^+$: calcd 231.0627; found 231.0623.



$C_6H_{11}NO_3$
MW 145.16

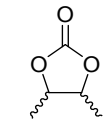
4-((Dimethylamino)methyl)-1,3-dioxolan-2-one (1m). Obtained as an orange oil after purification by column chromatography on alumina (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 4.79 (p, *J* = 6.2 Hz, 1H), 4.53 (t, *J* = 8.3 Hz, 1H), 4.23 (t, *J* = 7.8 Hz, 1H), 2.69-2.57 (m, 2H), 2.32 (s, 6H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 155.0, 75.2, 68.2, 61.4, 46.5 ppm. The NMR data matched those reported in the literature.[S6] **ESI HRMS** *m/z* $C_6H_{12}NO_3^+$ $[M+H]^+$: calcd 146.0812; found 146.0812.



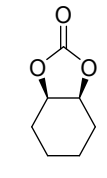
$C_8H_{13}NO_4$
MW 187.20

4-(Morpholinomethyl)-1,3-dioxolan-2-one (1n). Obtained as a yellow solid after purification by column chromatography on alumina (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 4.88-4.79 (m, 1H), 4.54 (t, *J* = 8.3 Hz, 1H), 4.29-4.21 (m, 1H), 3.70 (t, *J* = 4.6 Hz, 4H), 2.75-2.63 (m, 2H) 2.62-2.51 (m, 4H) ppm. **^{13}C NMR ($CDCl_3$,**

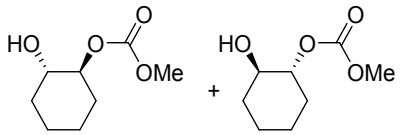
100.6 MHz): δ = 154.9, 75.1, 67.9, 66.9, 60.4, 54.5 ppm. The NMR data matched those reported in the literature.[S4] **ESI HRMS** *m/z* $C_8H_{14}NO_4^+$ $[M+H]^+$: calcd 188.0917; found 188.0917.


$C_5H_8O_3$
MW 116.12

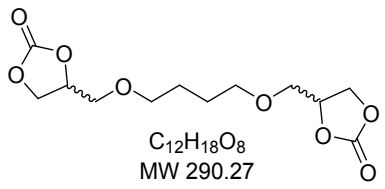
4,5-Dimethyl-1,3-dioxolan-2-one (1o, *cis/trans* 4:3). Obtained as a transparent oil after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 4.90-4.79 (m, 2H), 4.40-4.29 (m, 1.5H), 1.50-1.42 (m, 4.5H), 1.41-1.33 (m, 6H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 154.7, 154.6, 80.0, 76.1, 18.4, 14.4 ppm. The NMR data matched those reported in the literature.[S4] **ESI HRMS** *m/z* $C_5H_8O_3Na^+$ $[M+Na]^+$: calcd 139.0366; found 139.0366.


$C_7H_{10}O_3$
MW 142.15

***cis*-Hexahydro-1,3-benzodioxol-2-one (1p).** Obtained as a yellow oil after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 4.70 (q, *J* = 4.9, 3.6 Hz, 2H), 1.95-1.86 (m, 4H), 1.69-1.57 (m, 2H), 1.49-1.37 (m, 2H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 155.5, 75.8, 26.9, 19.3 ppm. The NMR data matched those reported in the literature.[S4] **ESI HRMS** *m/z* $C_7H_{10}O_3Na^+$ $[M+Na]^+$: calcd 165.0522; found 165.0516.

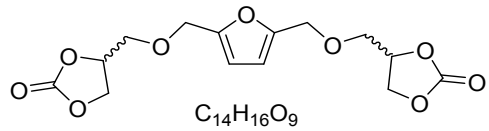

$C_8H_{14}O_4$
MW 174.20

(1*S*,2*S*)- and (1*R*,2*R*)-2-Hydroxycyclohexyl methyl carbonate (1q). Obtained as a white solid after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 4.48-4.38 (m, 1H), 3.80 (s, 3H), 3.65-3.55 (m, 1H), 2.37 (s, 1H), 2.17-2.00 (m, 2H), 1.80-1.64 (m, 2H), 1.43-1.20 (m, 4H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 155.8, 82.2, 72.6, 54.9, 32.9, 30.0, 23.9, 23.8 ppm. **ESI HRMS** *m/z* $C_8H_{14}O_4Na^+$ $[M+Na]^+$: calcd 197.0784; found 197.0785.


$C_{12}H_{18}O_8$
MW 290.27

4,4'-((Butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (1s). Obtained as a white solid after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 4.84-4.76 (m, 2H), 4.48 (t, *J* = 8.4 Hz, 2H), 4.38 (ddd, *J* = 8.2, 5.9, 2.0 Hz, 2H), 3.71-3.64 (m, 2H) 3.61-3.45 (m, 6H), 1.63 (p, *J* = 3.0 Hz, 4H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 155.19, 75.32, 71.72, 71.67, 69.74, 69.71, 66.31, 26.14, 26.12 ppm. The NMR data matched those reported in the literature.[S7] **ESI HRMS** *m/z* $C_{12}H_{18}O_8Na^+$ $[M+Na]^+$: calcd 313.0894; found 313.0893.

4,4'-(((Furan-2,5-diylbis(methylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (1t).



Obtained as a white solid after purification by column chromatography on silica gel (ethyl acetate/petroleum spirit 40-60 gradient). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 6.33 (s, 2H), 4.88-4.78 (m, 2H), 4.57-4.44 (m, 6H), 4.37 (dd, J = 8.4, 6.0 Hz, 2H), 3.80-3.72 (m, 2H), 3.69-3.62 (m, 2H) ppm. **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ = 155.07, 151.58, 110.92, 75.14, 75.12, 68.75, 66.26, 65.41, 65.37 ppm. The NMR data matched those reported in the literature.[S7] **ESI HRMS** *m/z* $C_{14}H_{16}O_9Na^+$ $[M+Na]^+$: calcd 351.0686; found 351.0686.

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

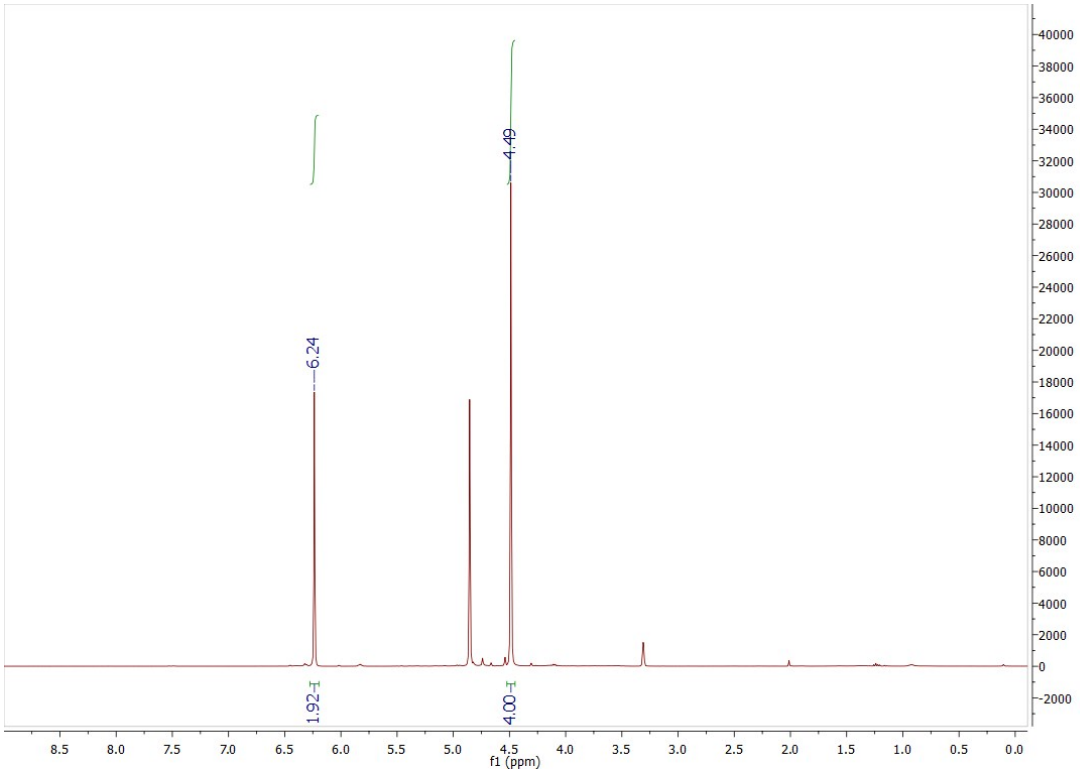


Figure S10. ^{1}H NMR spectrum (400 MHz) of 2,5-bis(hydroxymethyl)furan in MeOD-d_4.

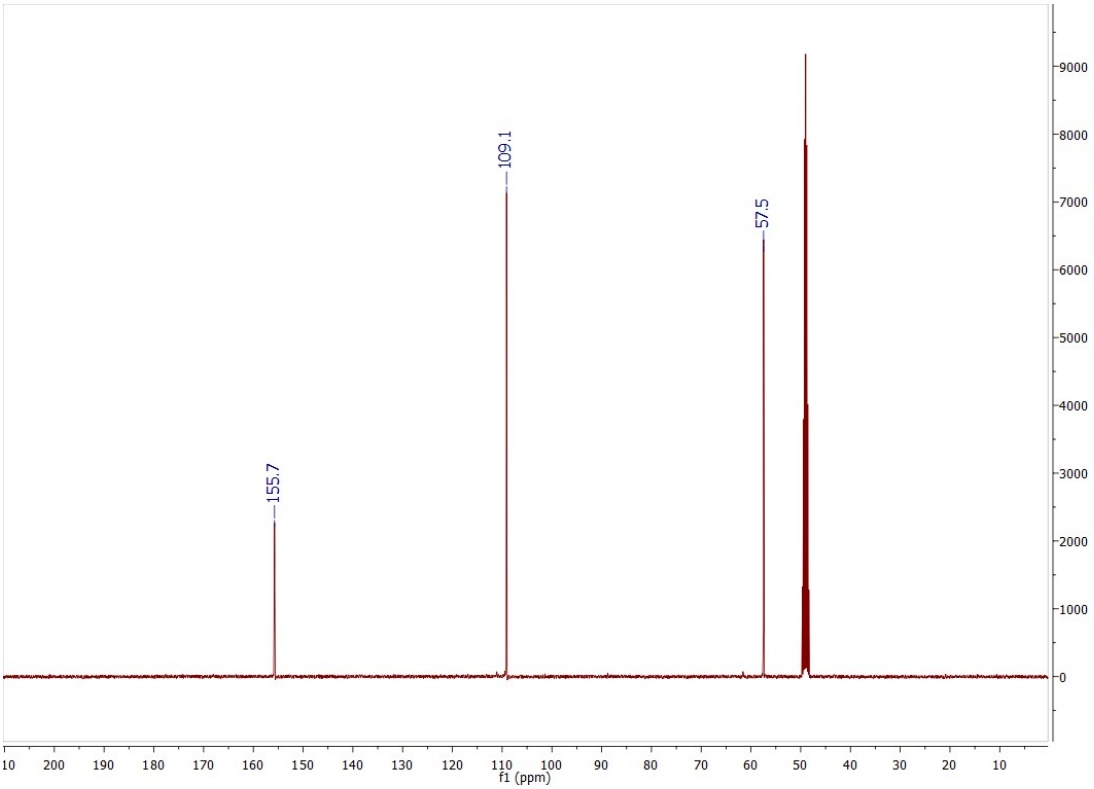


Figure S11. ^{13}C NMR spectrum (100.6 MHz) of 2,5-bis(hydroxymethyl)furan in MeOD-d_4.

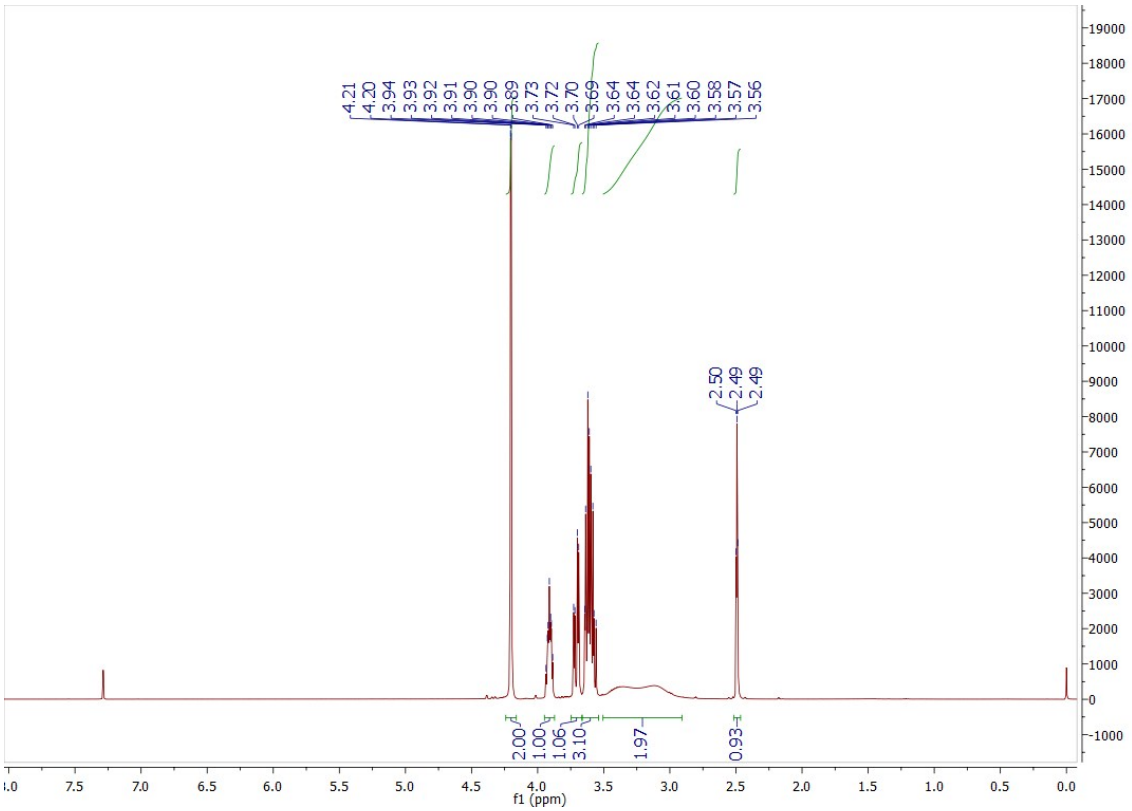


Figure S12. ^{1}H NMR spectrum (400 MHz) of 3-(prop-2-yn-1-yloxy)propane-1,2-diol (**2j**) in $CDCl_3$.

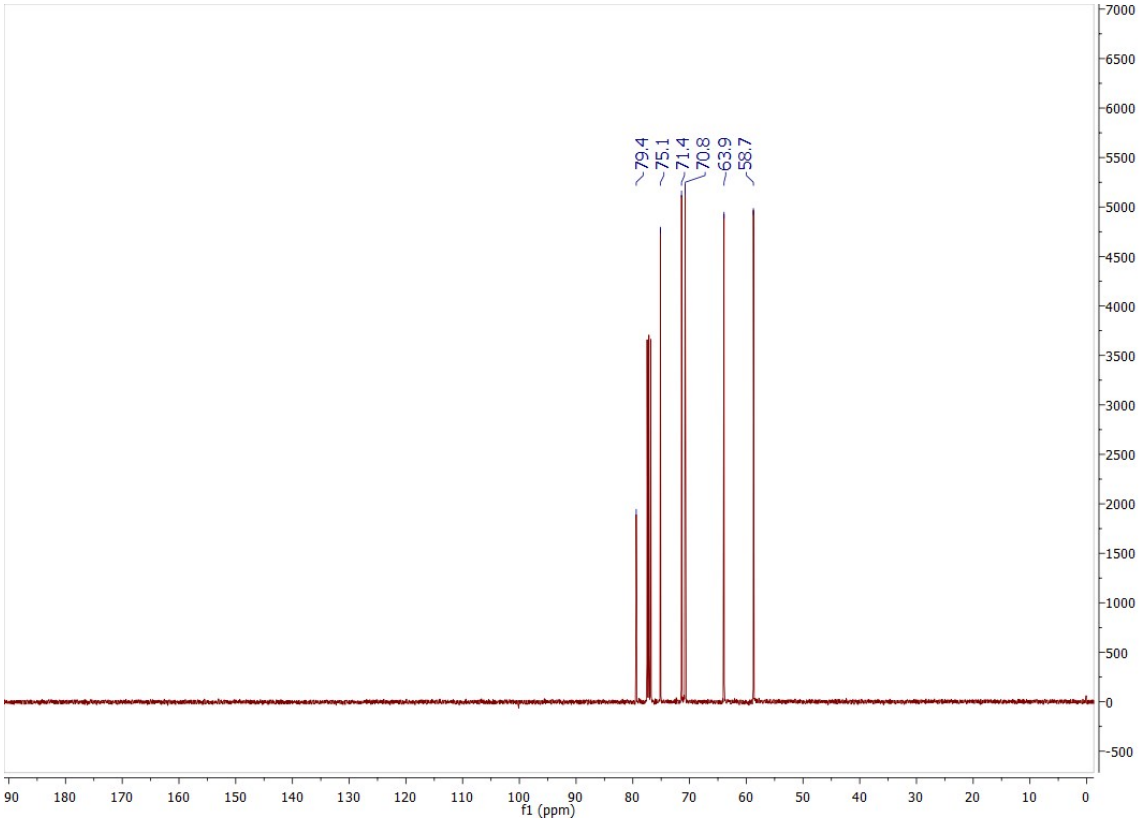


Figure S13. ^{13}C NMR spectrum (100.6 MHz) of 3-(prop-2-yn-1-yloxy)propane-1,2-diol (**2j**) in $CDCl_3$.

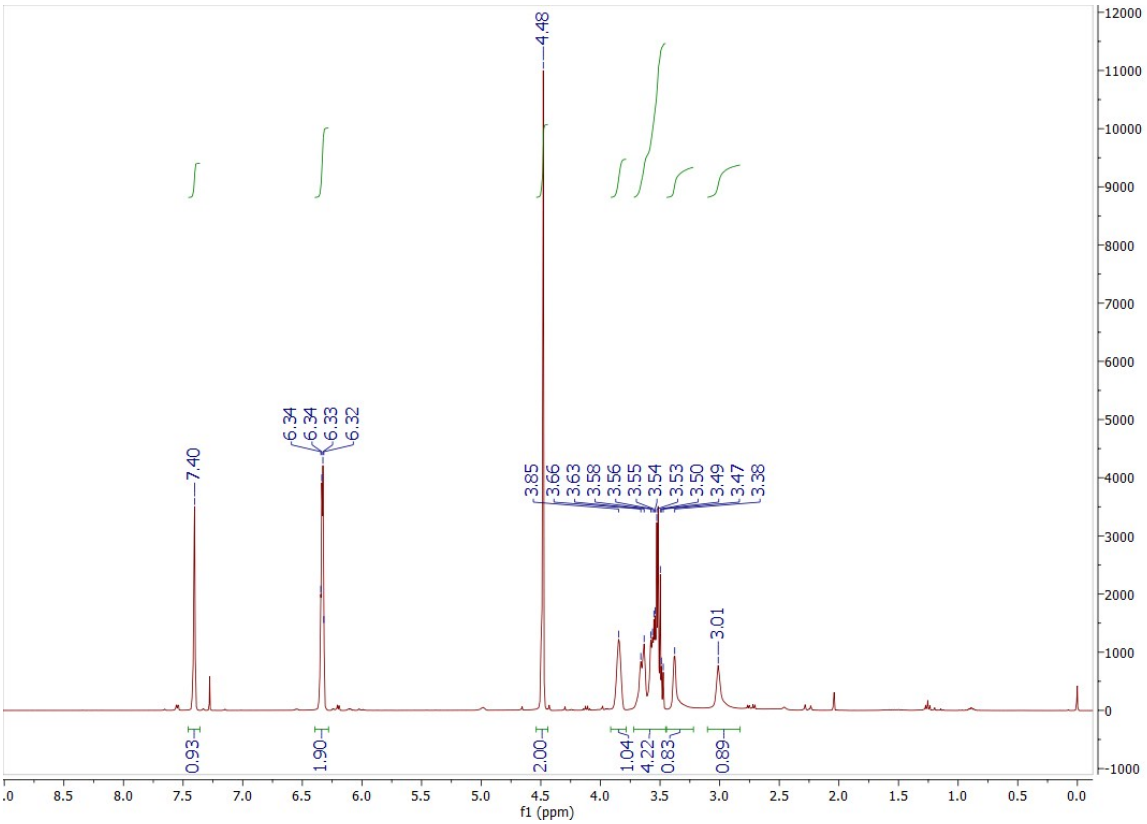


Figure S14. ^{1}H NMR spectrum (400 MHz) of 3-(furan-2-ylmethoxy)propane-1,2-diol (**2k**) in $CDCl_3$.

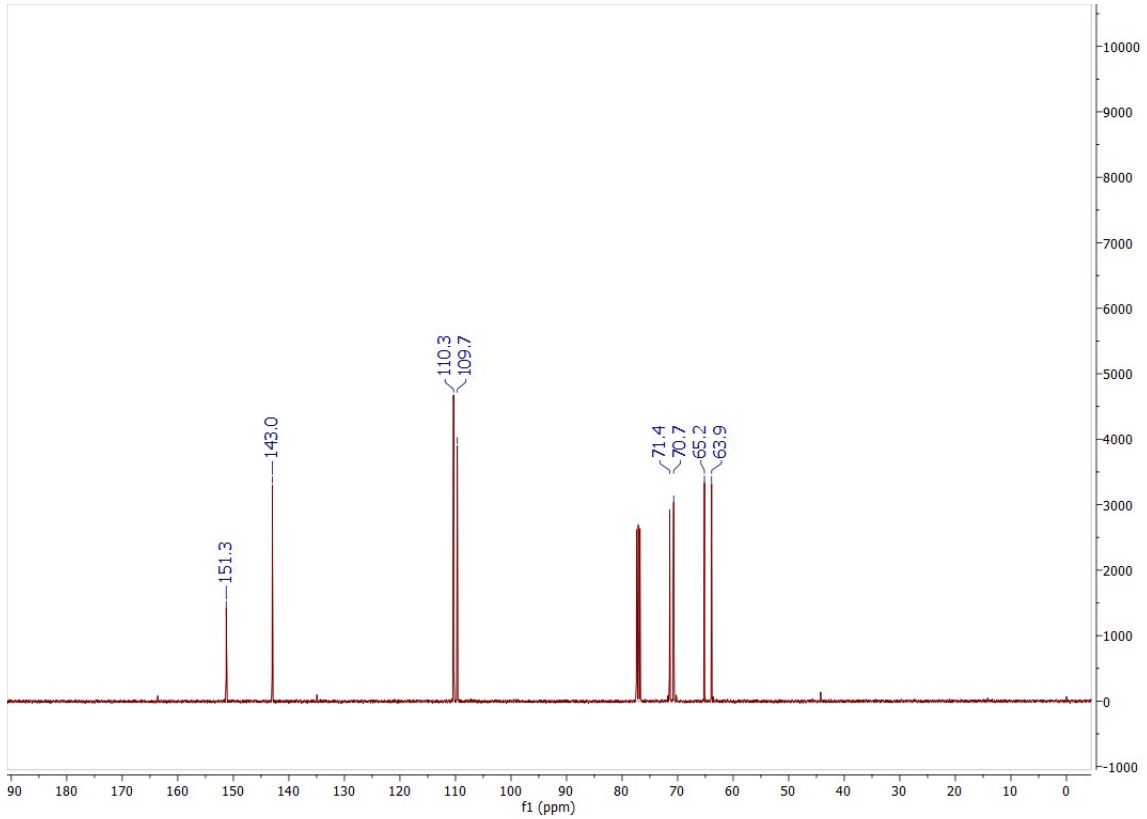


Figure S15. ^{13}C NMR spectrum (100.6 MHz) of 3-(furan-2-ylmethoxy)propane-1,2-diol (**2k**) in $CDCl_3$.

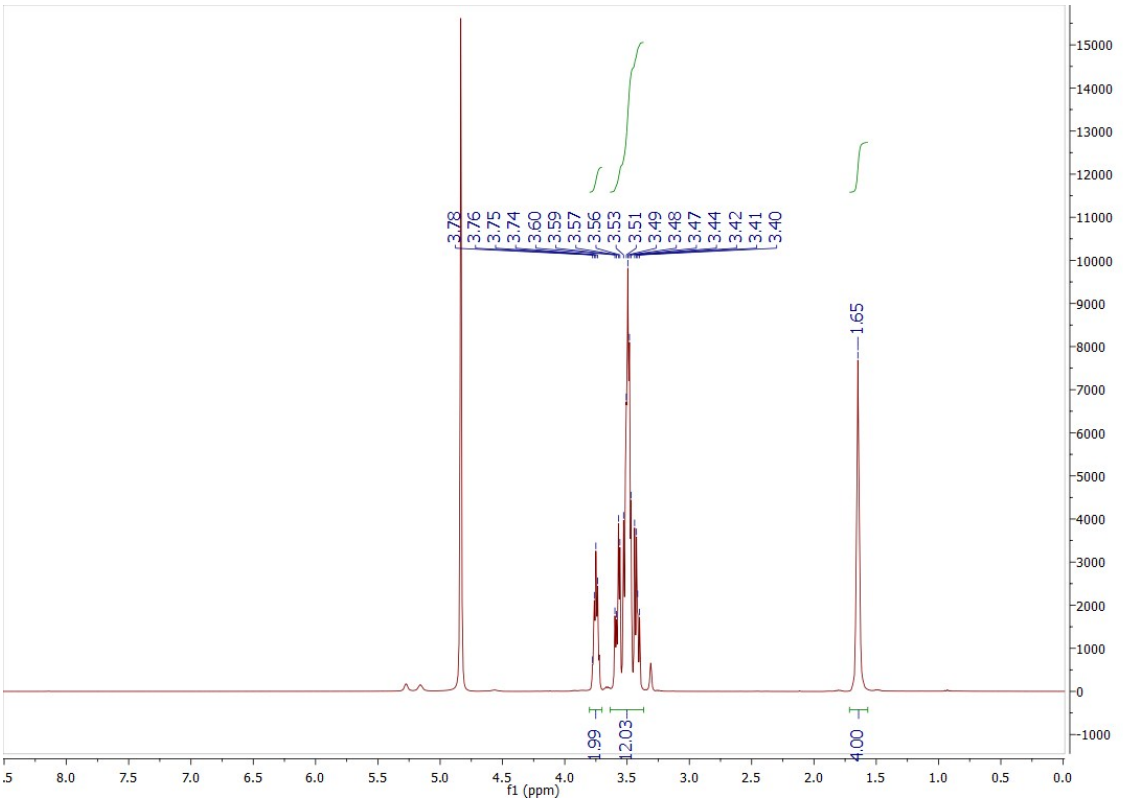


Figure S16. ^{1}H NMR spectrum (400 MHz) of 3,3'-(butane-1,4-diylbis(oxy))bis(propane-1,2-diol) (**2s**) in MeOD-d_4.

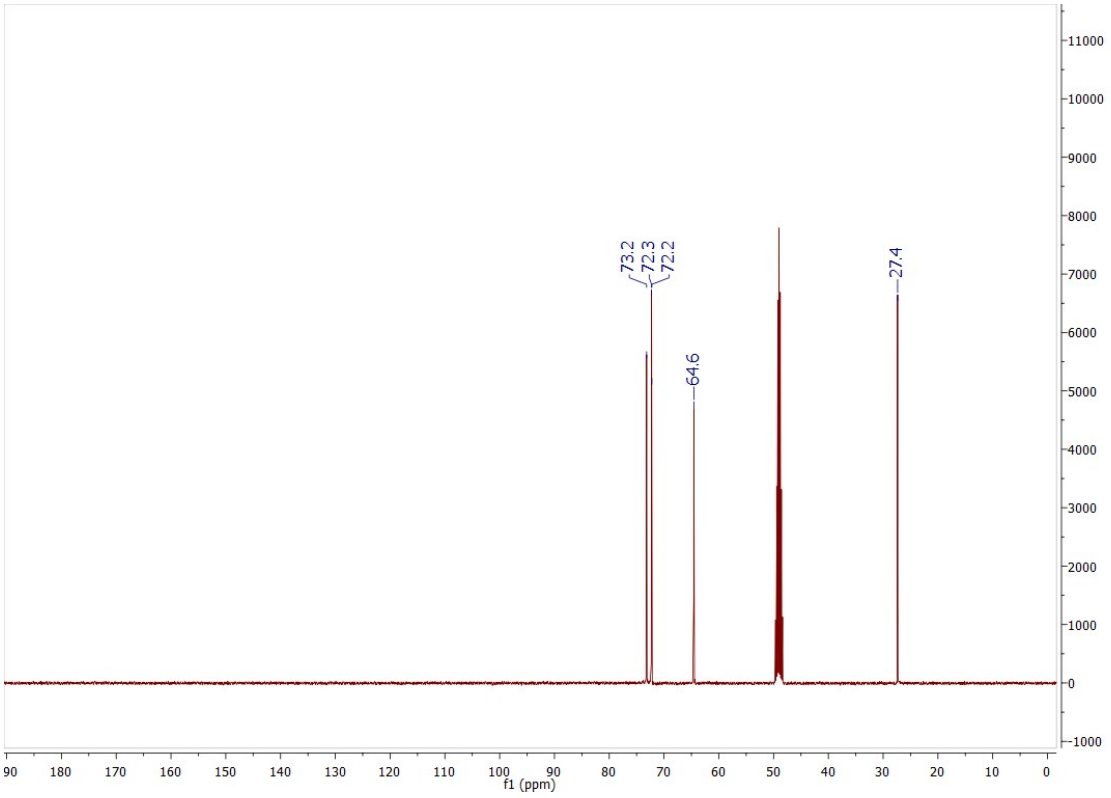


Figure S17. ^{13}C NMR spectrum (100.6 MHz) of 3,3'-(butane-1,4-diylbis(oxy))bis(propane-1,2-diol) (**2s**) in MeOD-d_4.

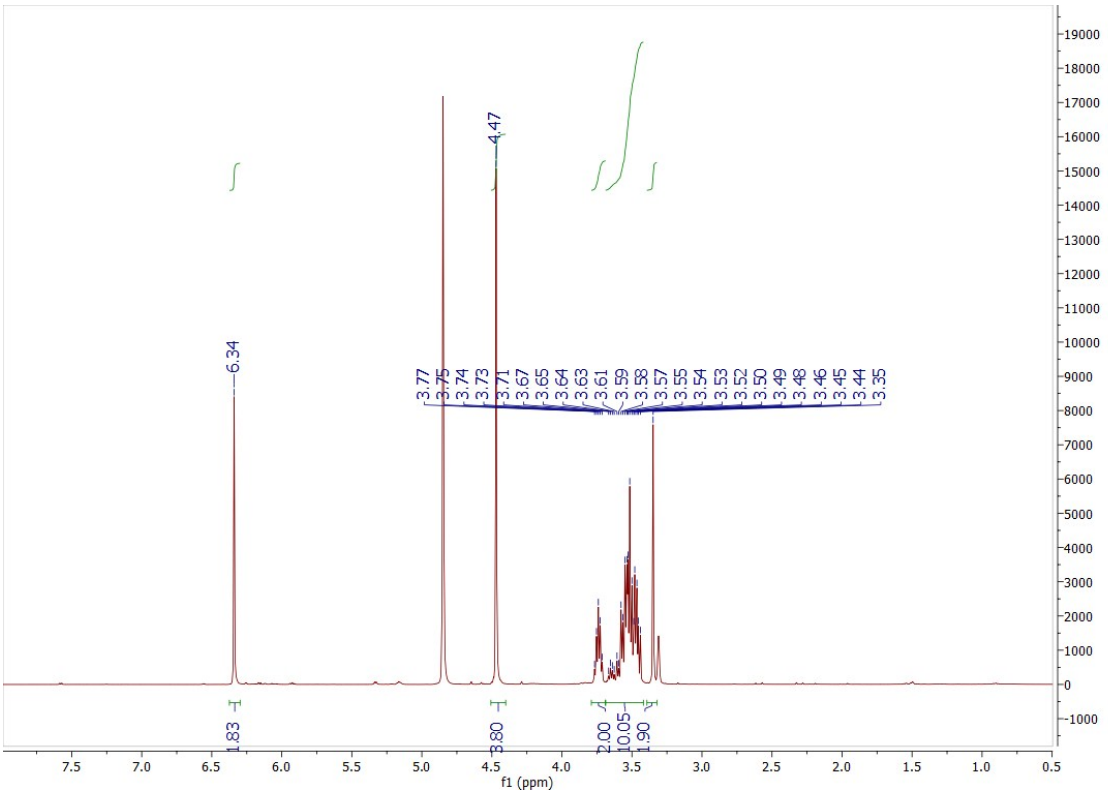


Figure S18. ^{1}H NMR spectrum (400 MHz) of 3,3'-((furan-2,5-diylbis(methylene))bis(oxy))bis(propane-1,2-diol) (**2t**) in MeOD-d_4.

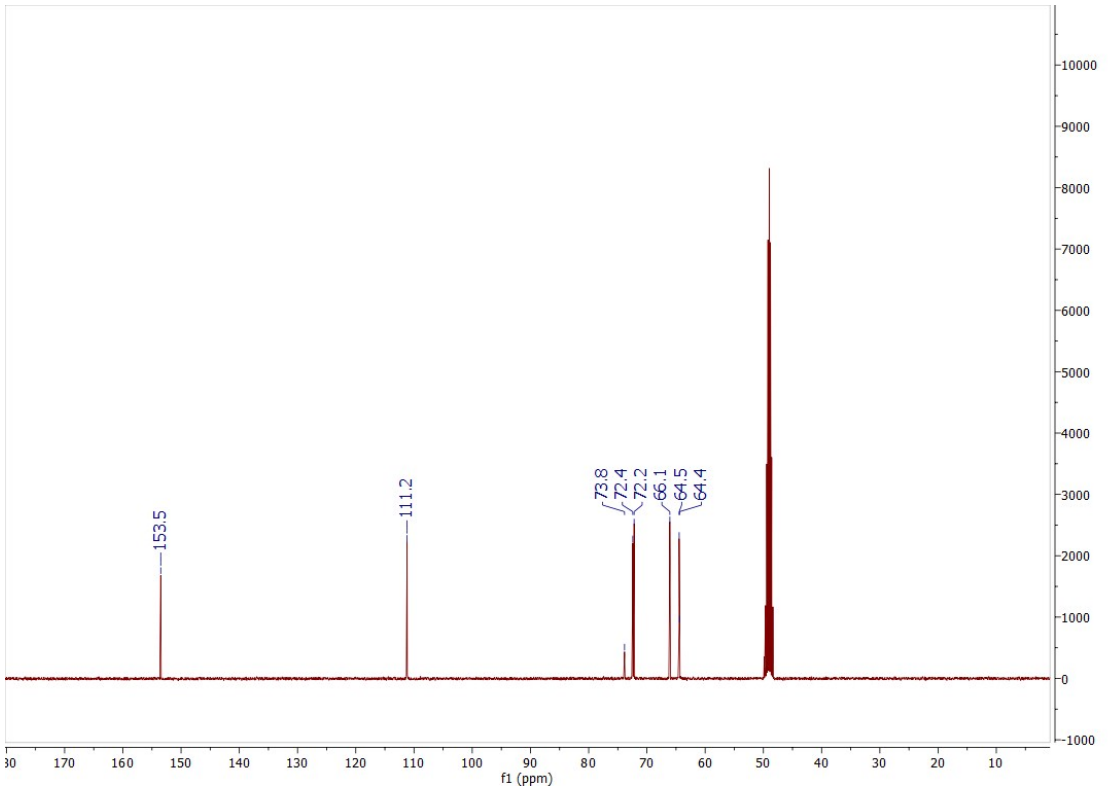


Figure S19. ^{13}C NMR spectrum (100.6 MHz) of 3,3'-((furan-2,5-diylbis(methylene))bis(oxy))bis(propane-1,2-diol) (**2t**) in MeOD-d_4.

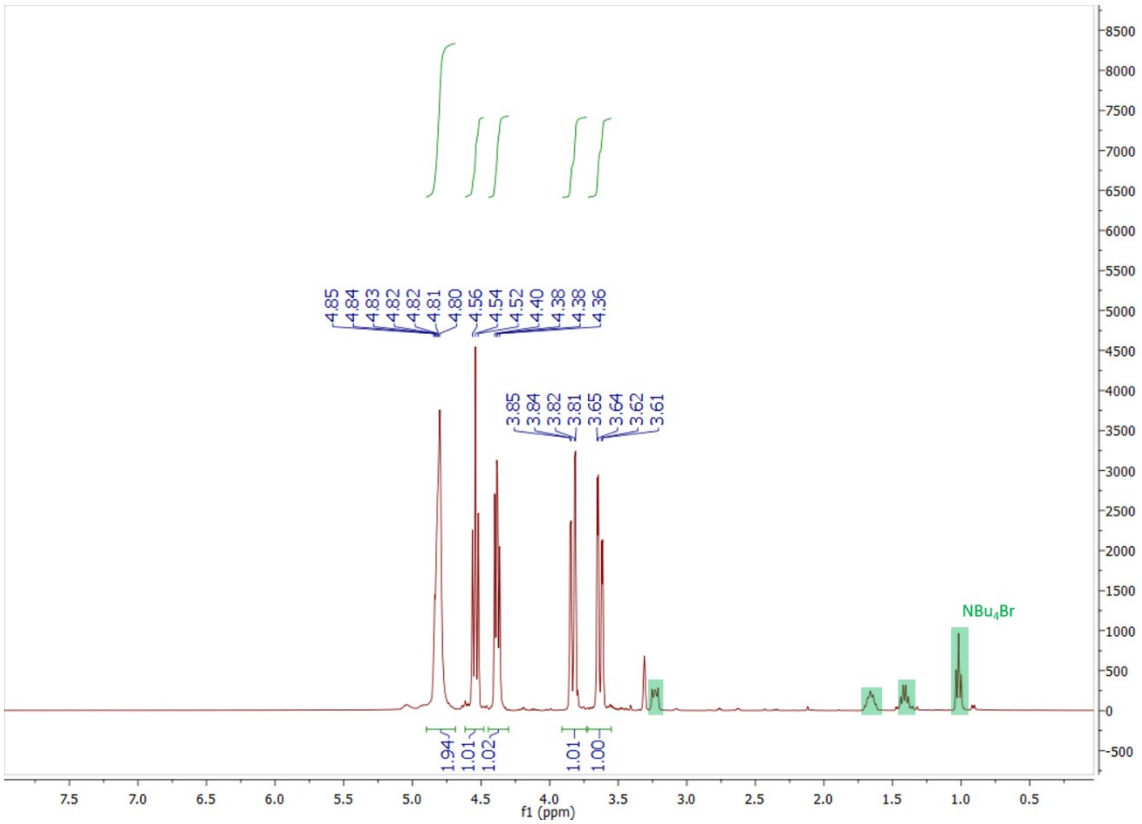


Figure S20. ^{1}H NMR spectrum (400 MHz) of 4-hydroxymethyl-1,3-dioxolan-2-one (**1a**) in MeOD-d_4.

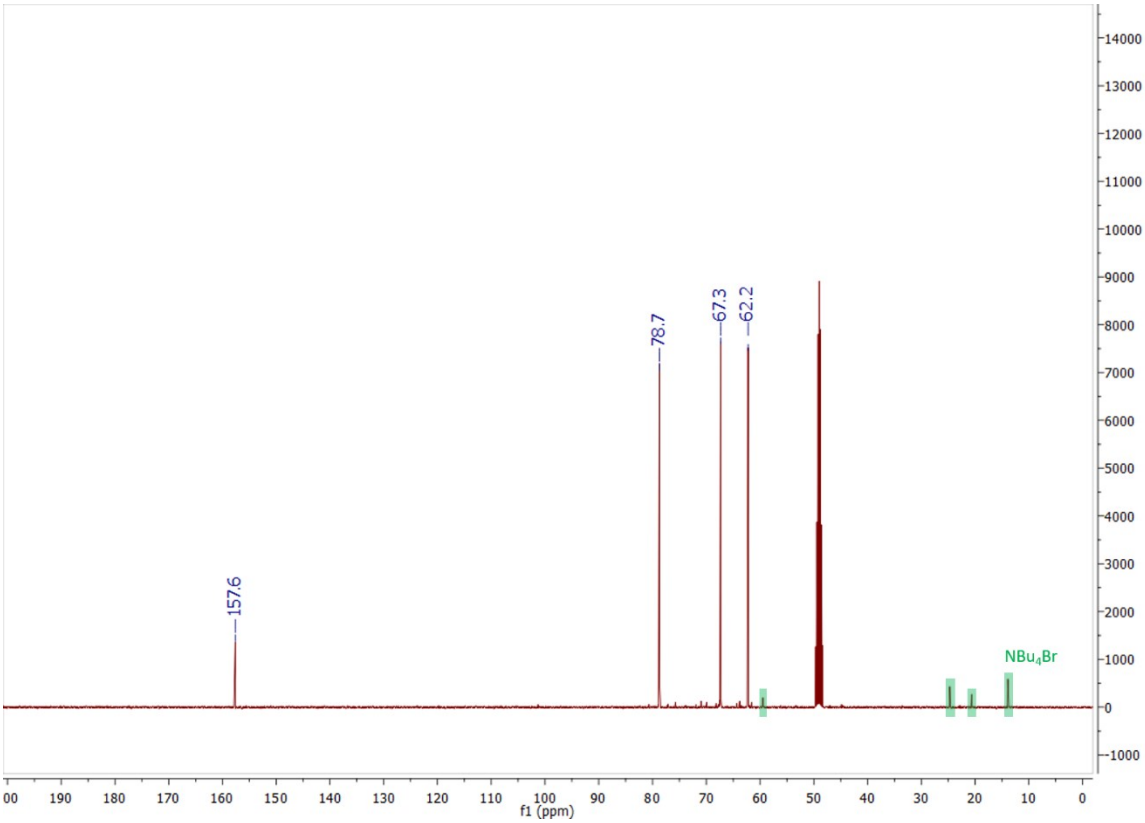


Figure S21. ^{13}C NMR spectrum (100.6 MHz) of 4-hydroxymethyl-1,3-dioxolan-2-one (**1a**) in MeOD-d_4.

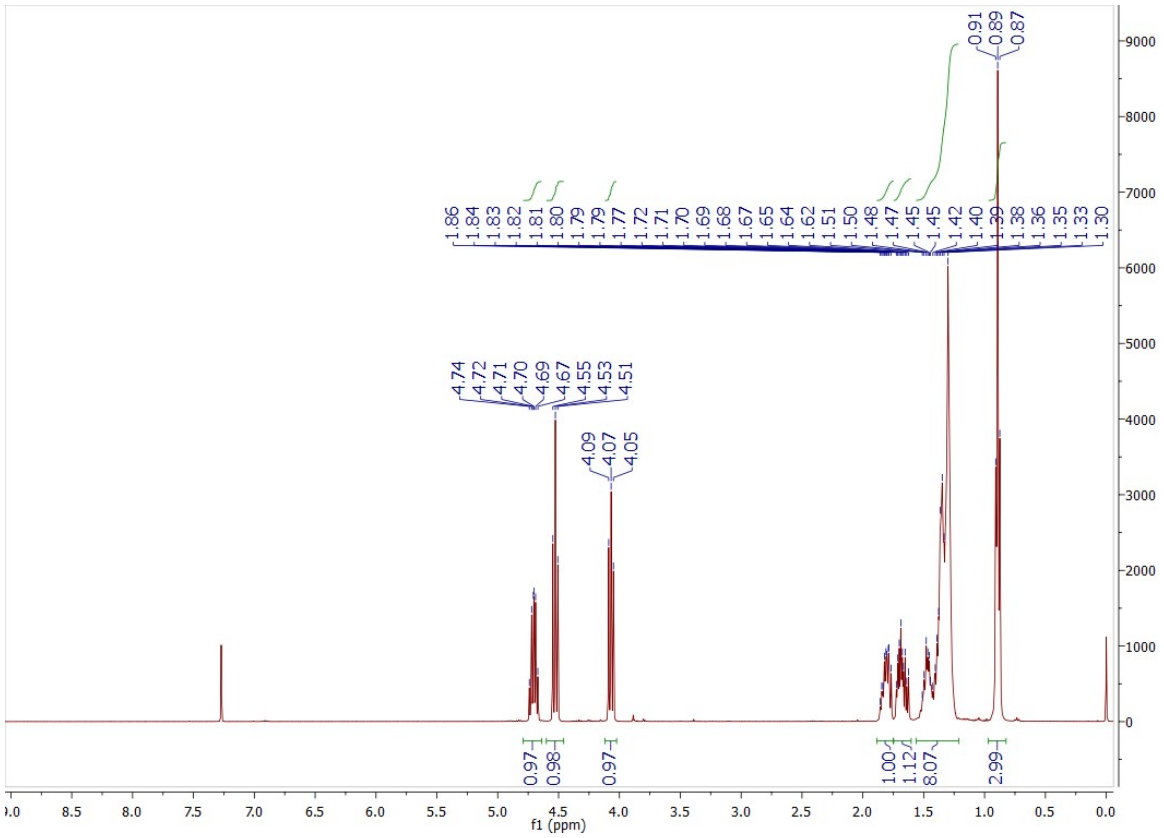


Figure S22. ^{1}H NMR spectrum (400 MHz) of 4-hexyl-1,3-dioxolan-2-one (**1e**) in $CDCl_3$.

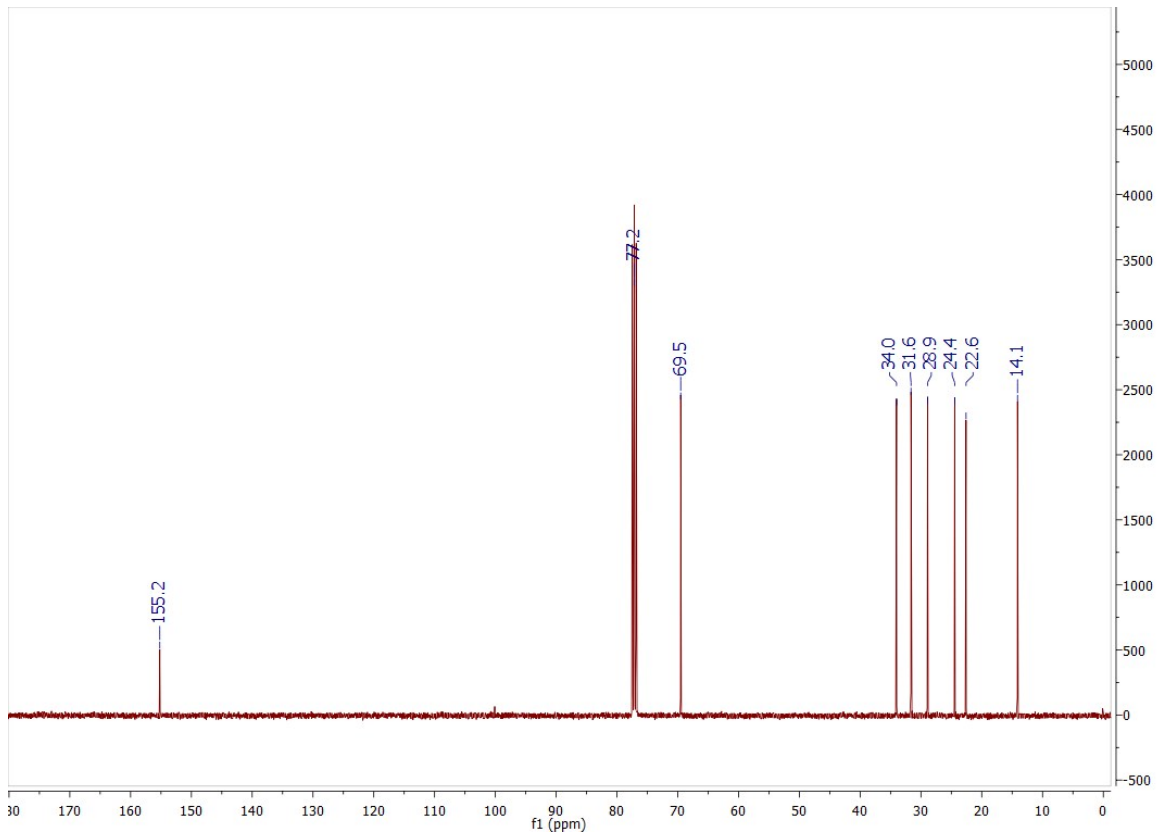


Figure S23. ^{1}H NMR spectrum (400 MHz) of 4-hexyl-1,3-dioxolan-2-one (**1e**) in $CDCl_3$.

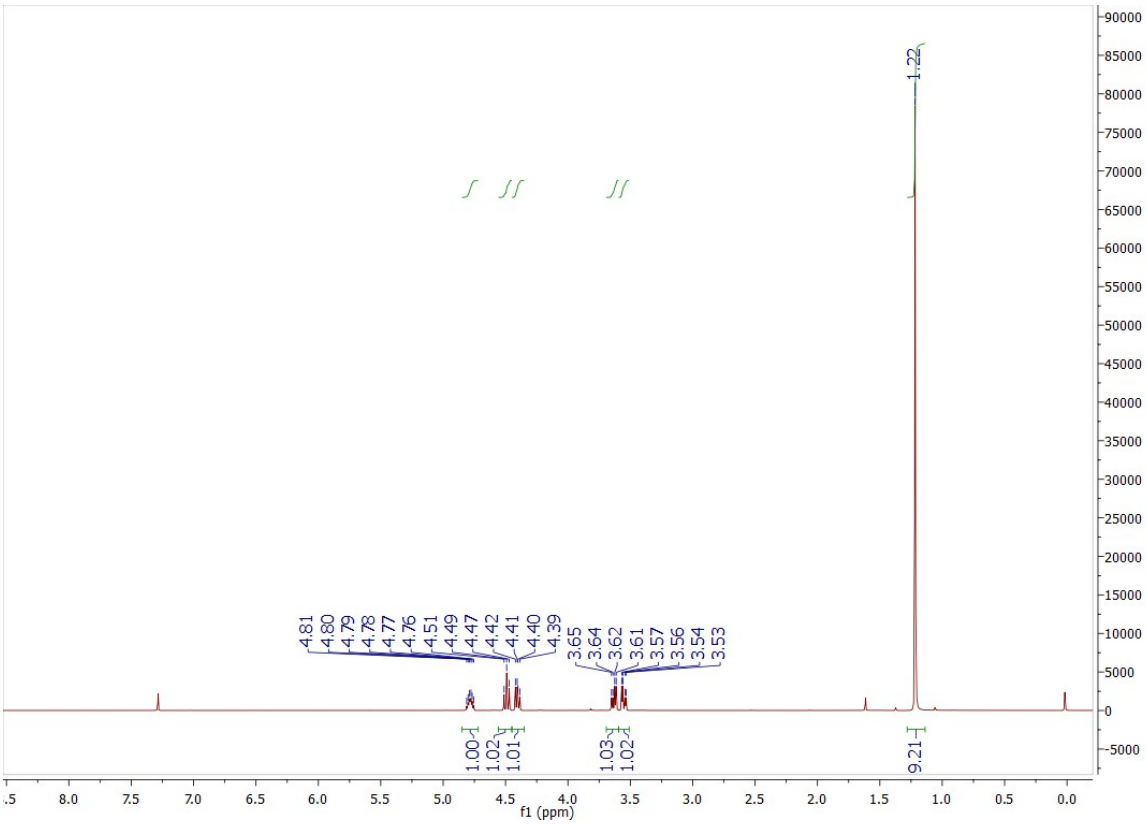


Figure S24. ^{1}H NMR spectrum (400 MHz) of 4-(*tert*-butoxymethyl)-1,3-dioxolan-2-one (**1h**) in $CDCl_3$.

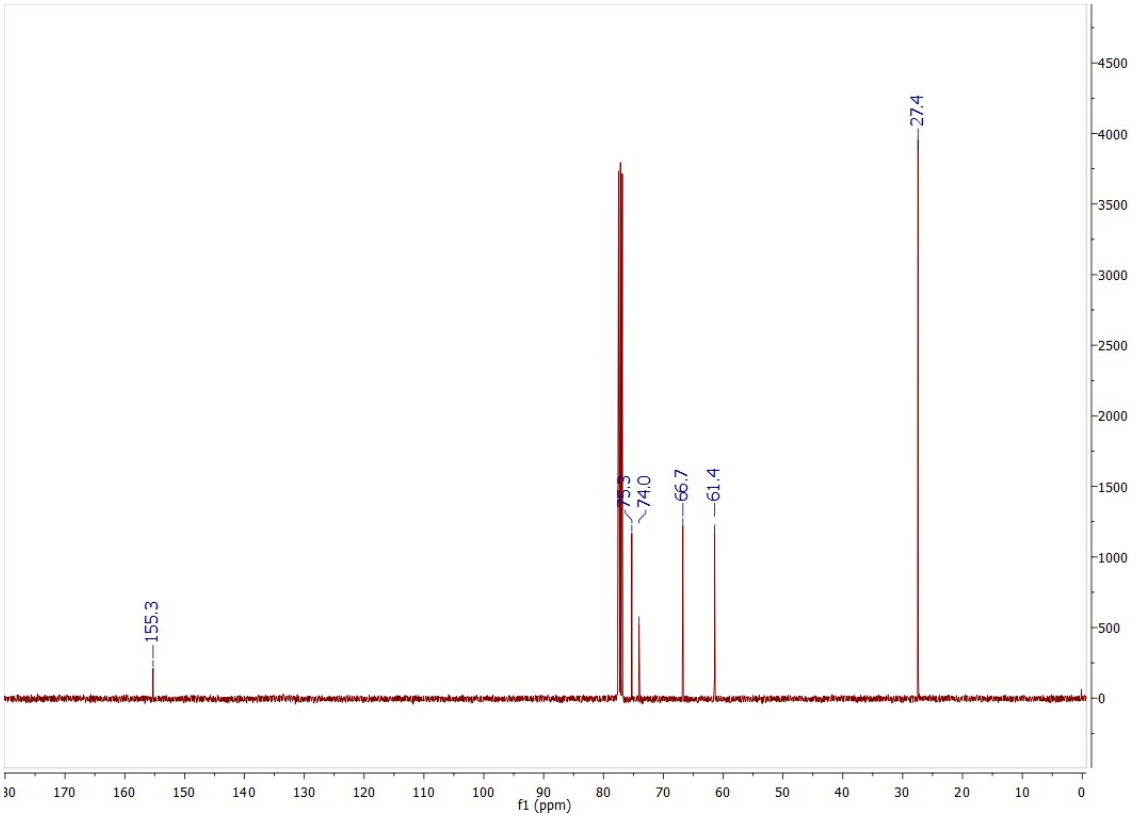


Figure S25. ^{13}C NMR spectrum (100.6 MHz) of 4-(*tert*-butoxymethyl)-1,3-dioxolan-2-one (**1h**) in $CDCl_3$.

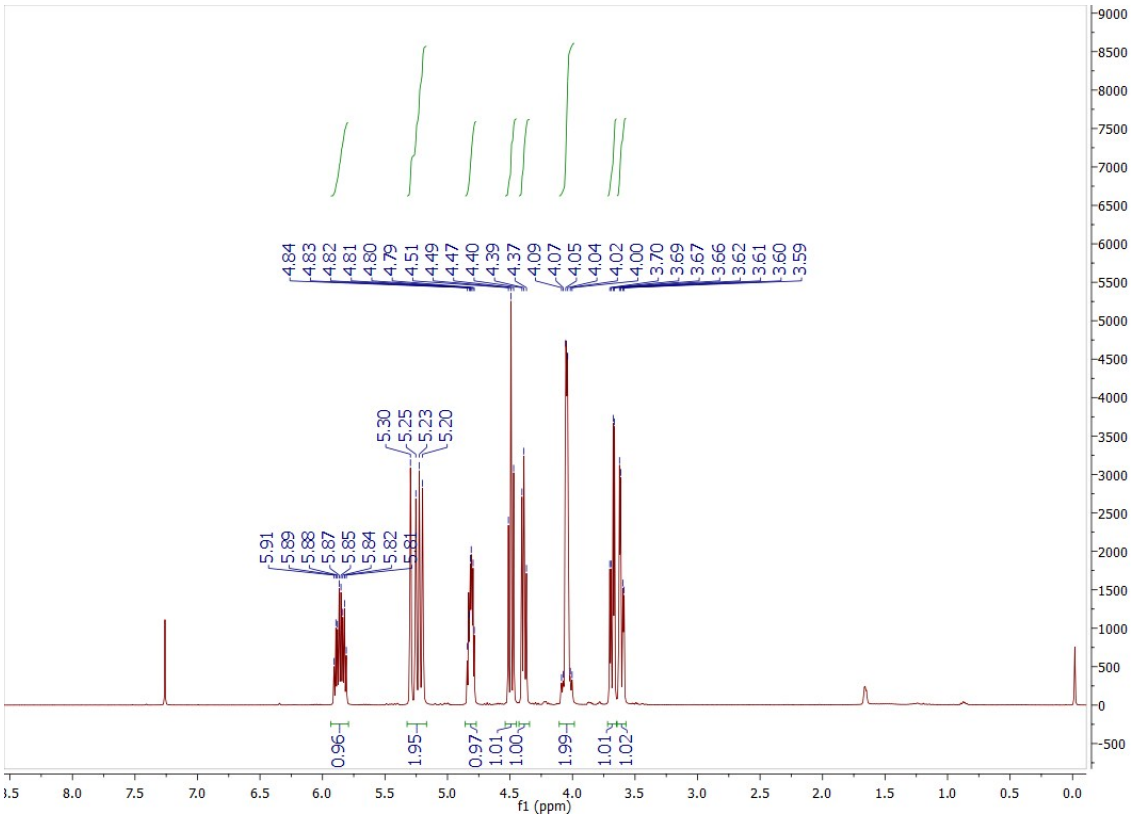


Figure S26. ^{1}H NMR spectrum (400 MHz) of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (**1i**) in $CDCl_3$.

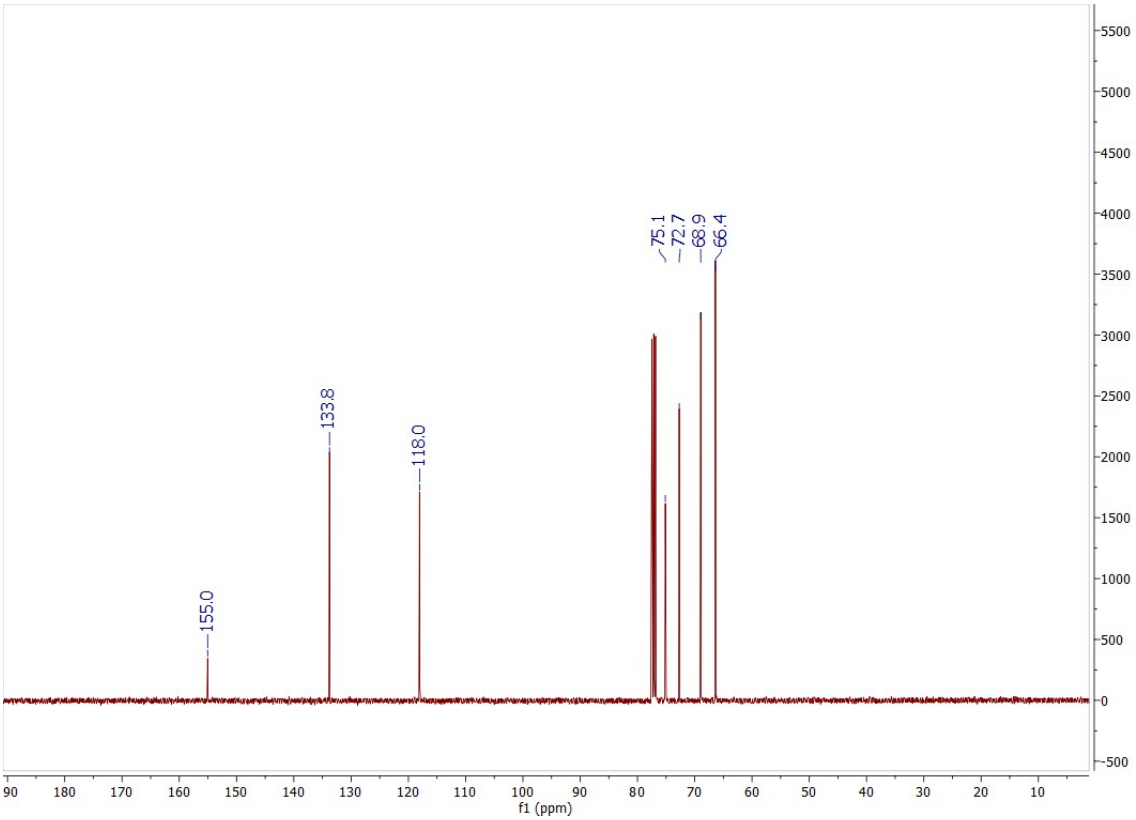


Figure S27. ^{13}C NMR spectrum (100.6 MHz) of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (**1i**) in $CDCl_3$.

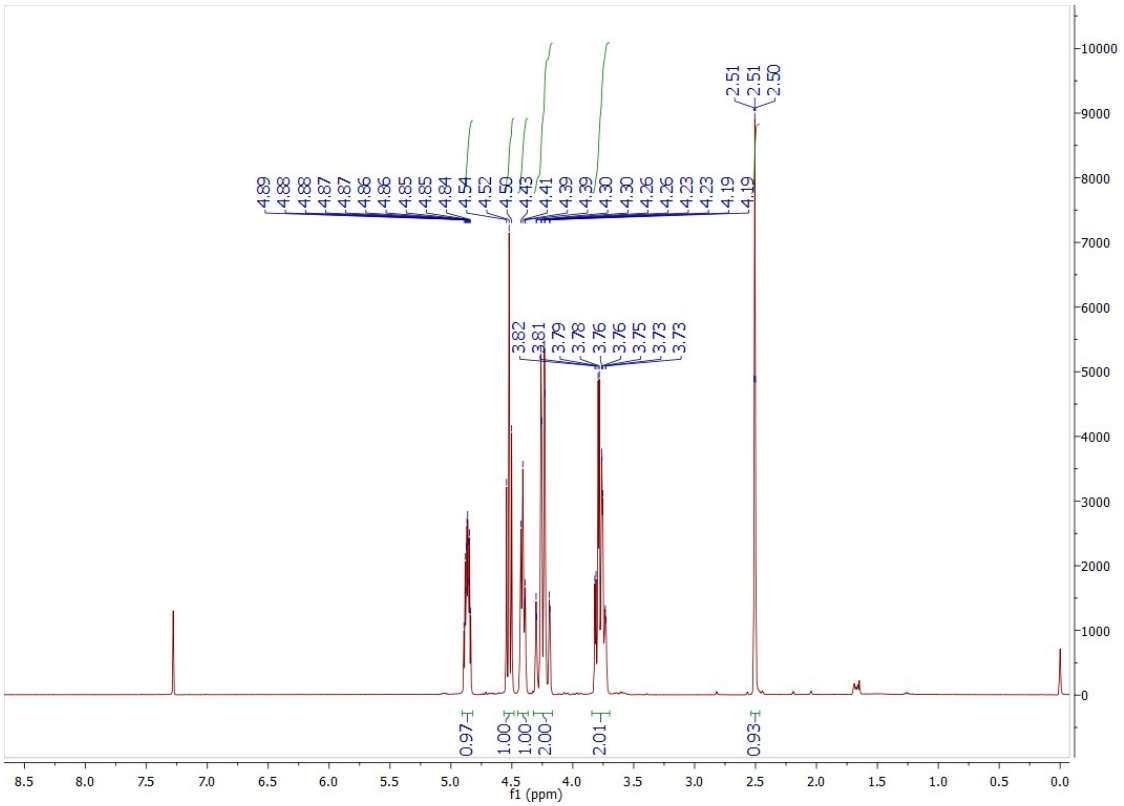


Figure S28. ^{1}H NMR spectrum (400 MHz) of 4-((prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one (**1j**) in $CDCl_3$.

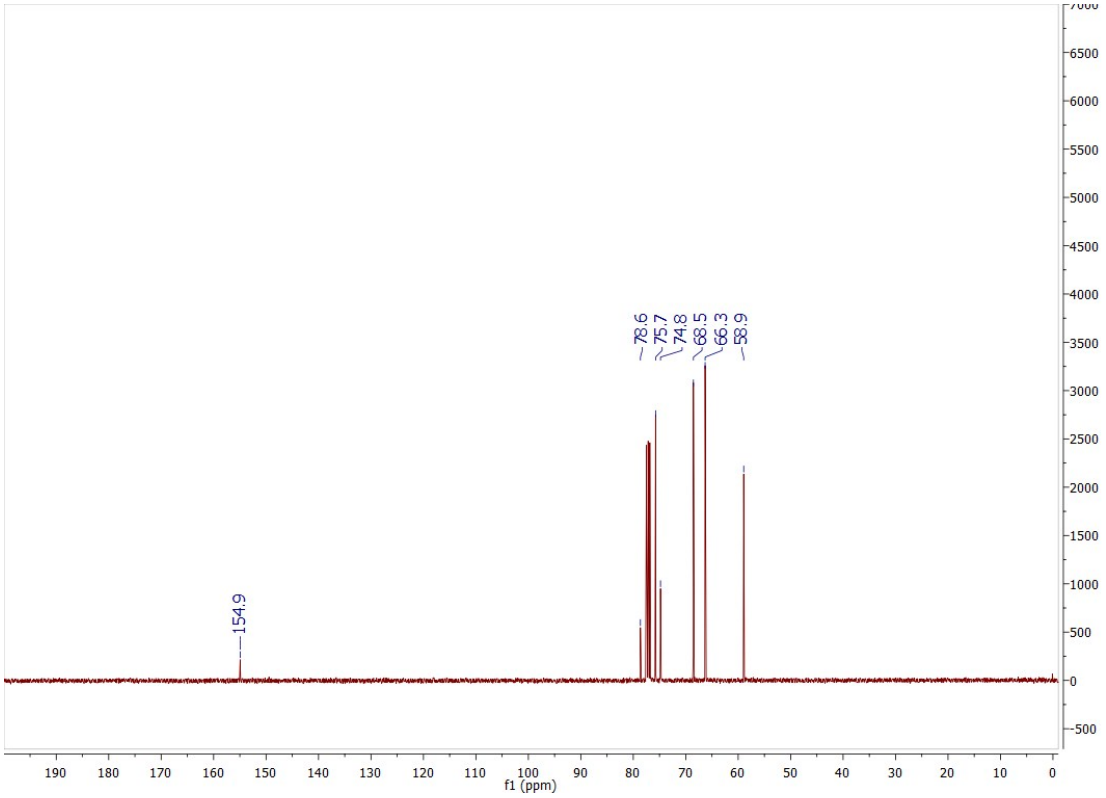


Figure S29. ^{13}C NMR spectrum (100.6 MHz) of 4-((prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one (**1j**) in $CDCl_3$.

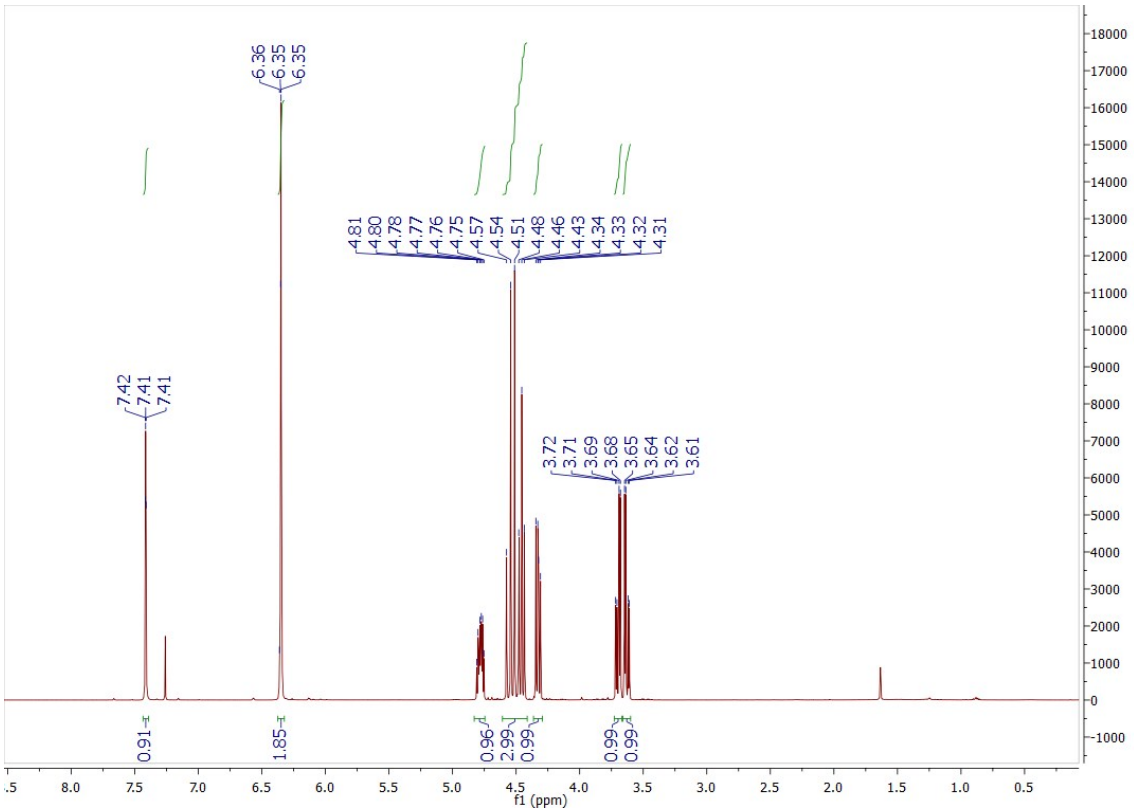


Figure S30. ^{1}H NMR spectrum (400 MHz) of 4-((furan-2-ylmethoxy)methyl)-1,3-dioxolan-2-one (**1k**) in $CDCl_3$.

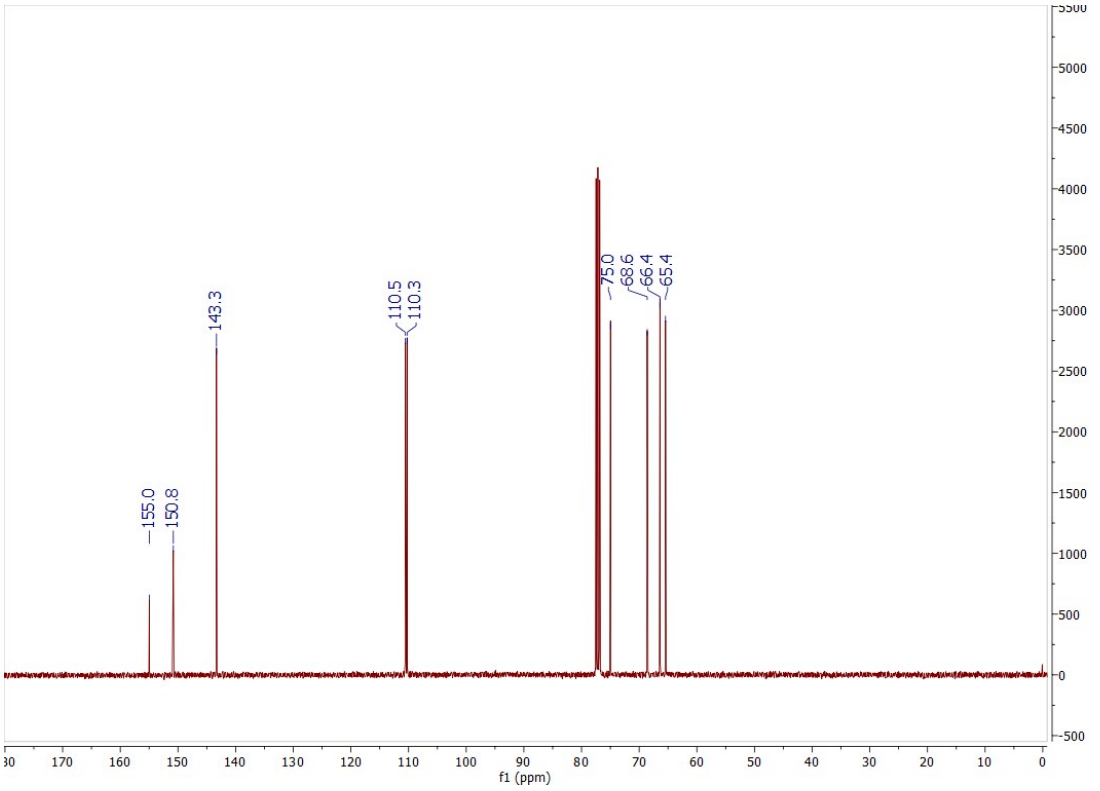


Figure S31. ^{13}C NMR spectrum (100.6 MHz) of 4-((furan-2-ylmethoxy)methyl)-1,3-dioxolan-2-one (**1k**) in $CDCl_3$.

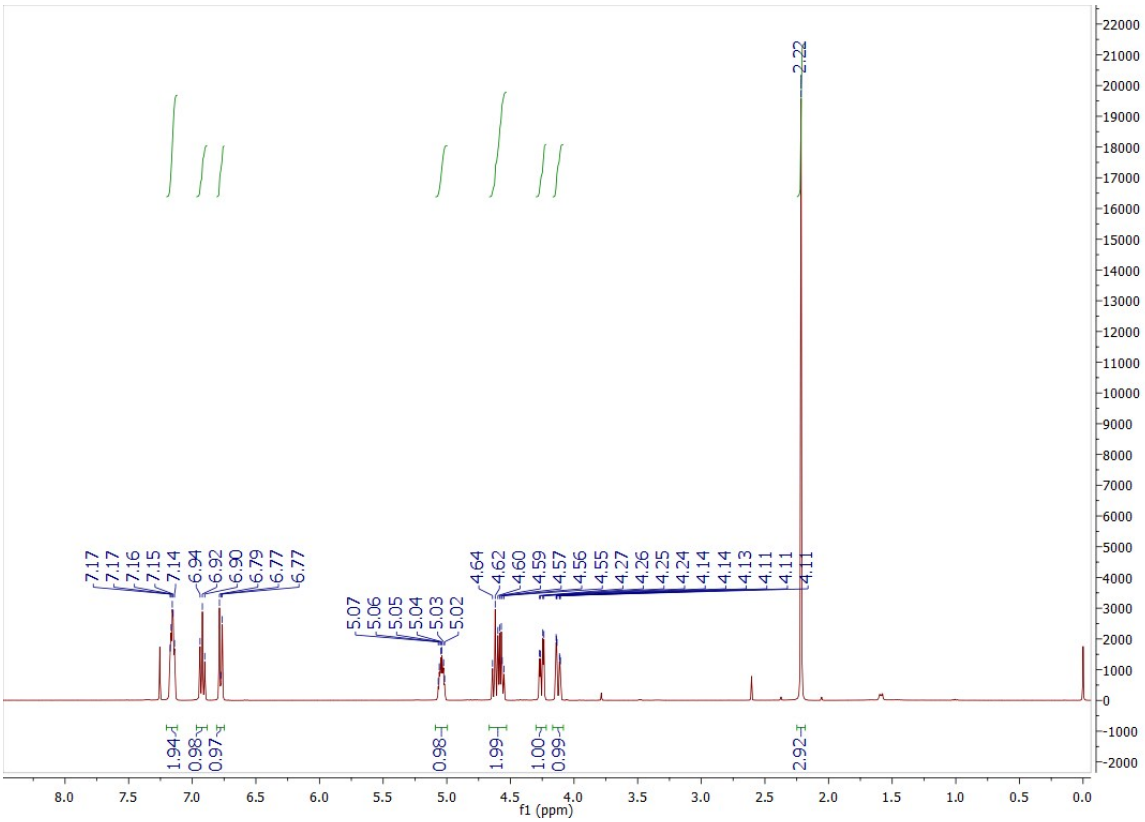


Figure S32. ^{1}H NMR spectrum (400 MHz) of 4-((*o*-tolyloxy)methyl)-1,3-dioxolan-2-one (**1l**) in $CDCl_3$.

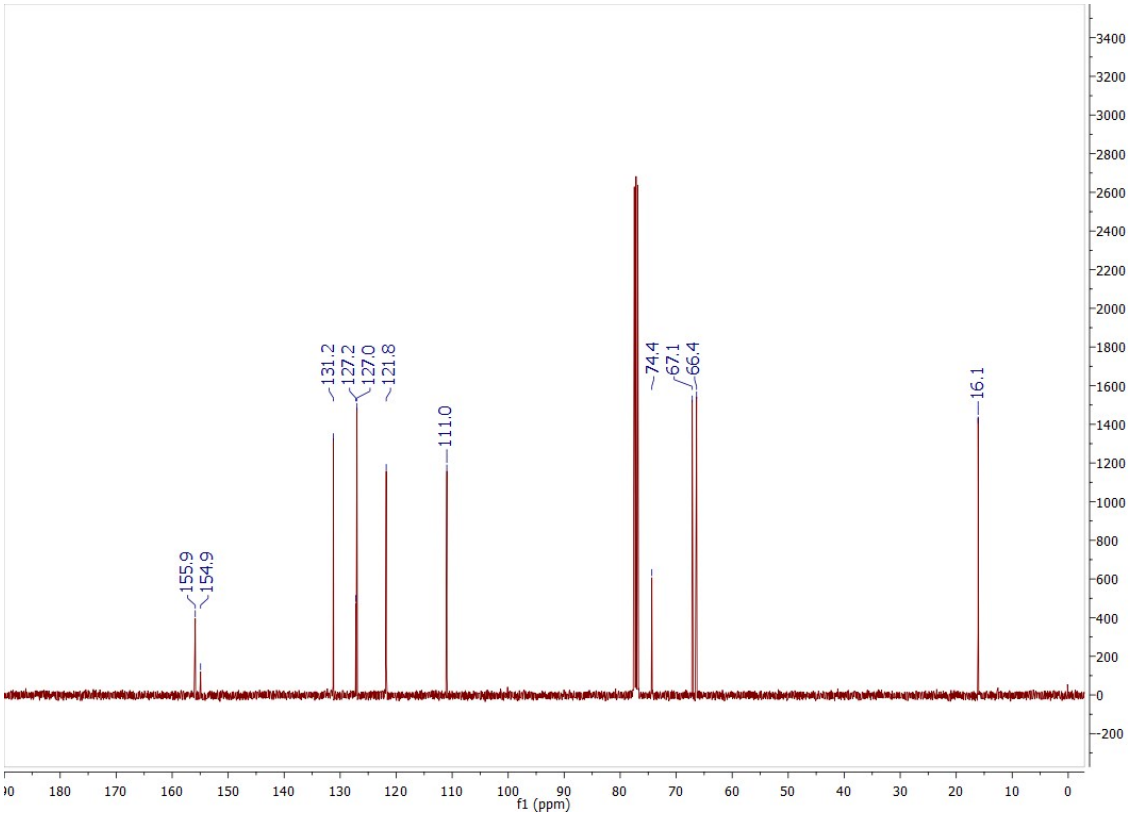


Figure S33. ^{13}C NMR spectrum (100.6 MHz) of 4-((*o*-tolyloxy)methyl)-1,3-dioxolan-2-one (**1l**) in $CDCl_3$.

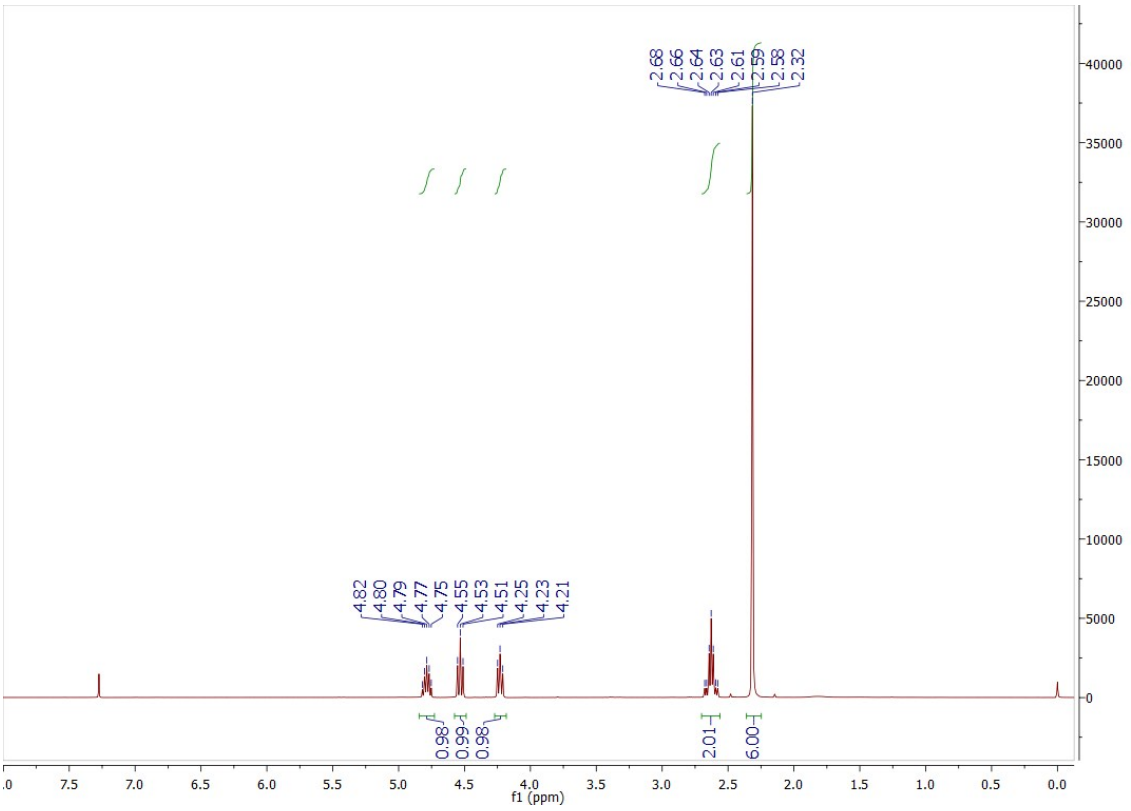


Figure S34. ^{1}H NMR spectrum (400 MHz) of 4-((dimethylamino)methyl)-1,3-dioxolan-2-one (**1m**) in $CDCl_3$.

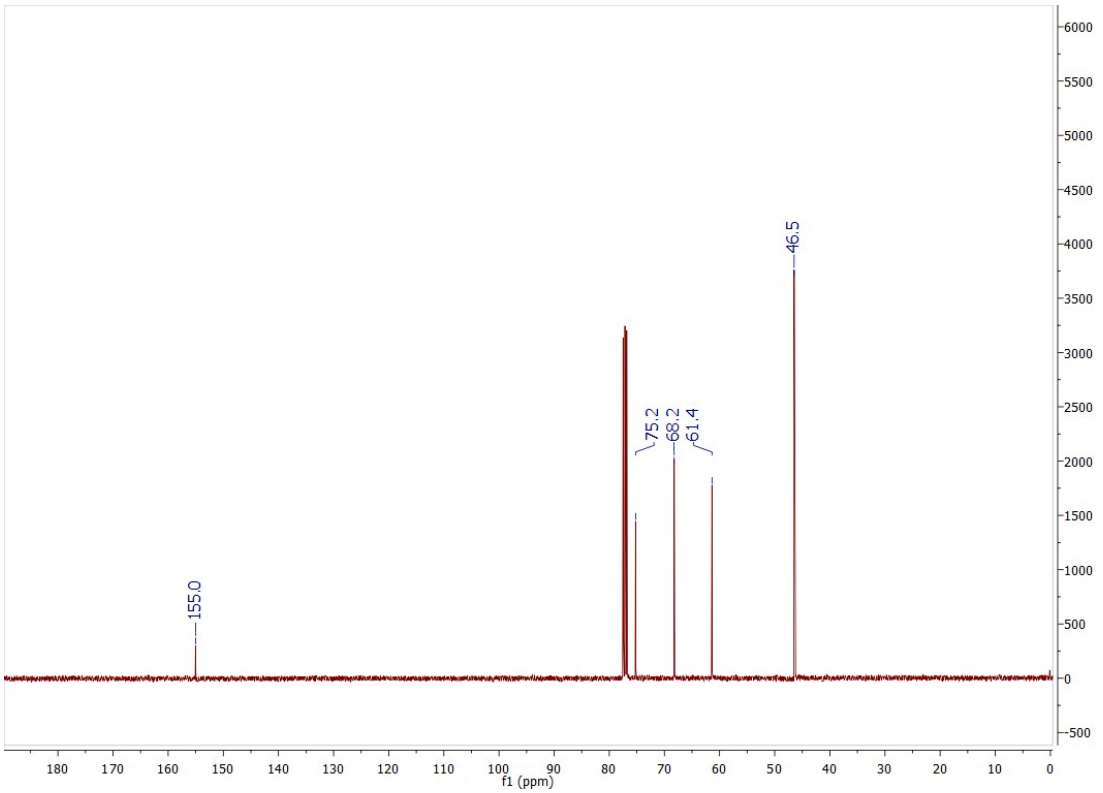


Figure S35. ^{13}C NMR spectrum (100.6 MHz) of 4-((dimethylamino)methyl)-1,3-dioxolan-2-one (**1m**) in $CDCl_3$.

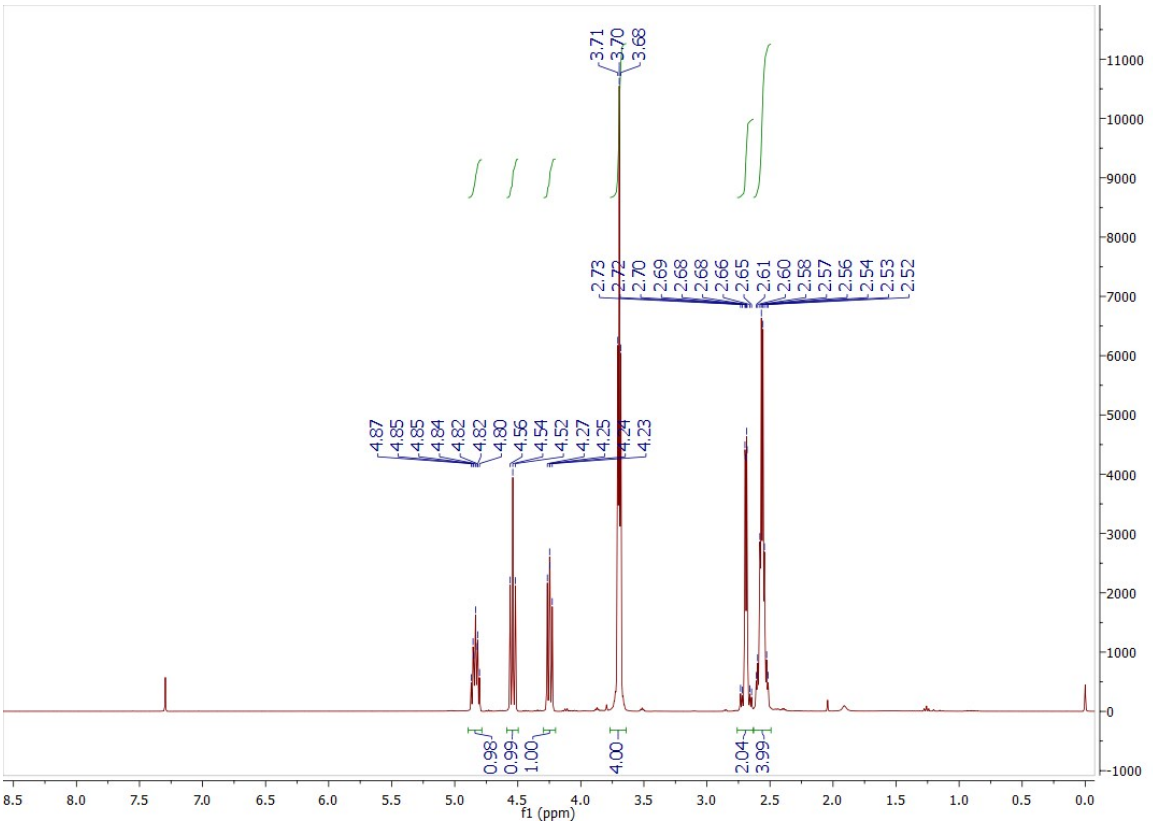


Figure S36. ^{1}H NMR spectrum (400 MHz) of 4-(morpholinomethyl)-1,3-dioxolan-2-one (**1n**) in $CDCl_3$.

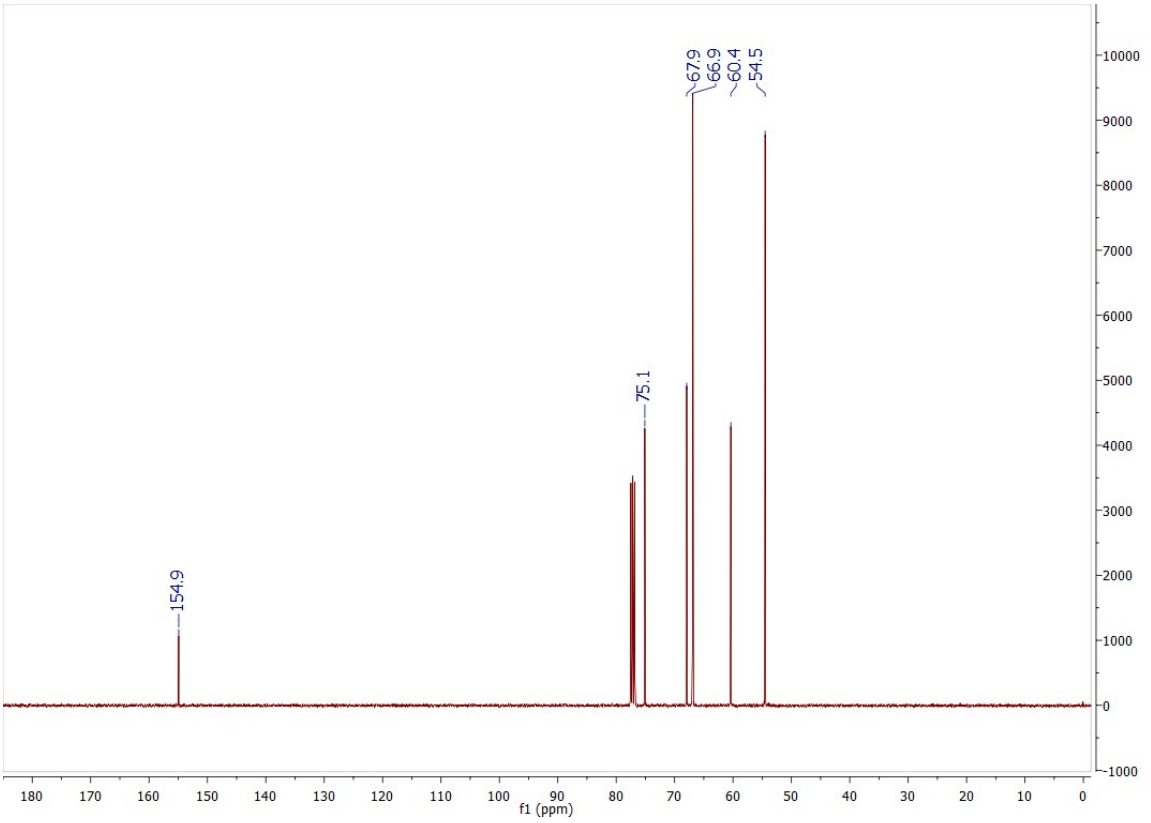


Figure S37. ^{13}C NMR spectrum (100.6 MHz) of 4-(morpholinomethyl)-1,3-dioxolan-2-one (**1n**) in $CDCl_3$.

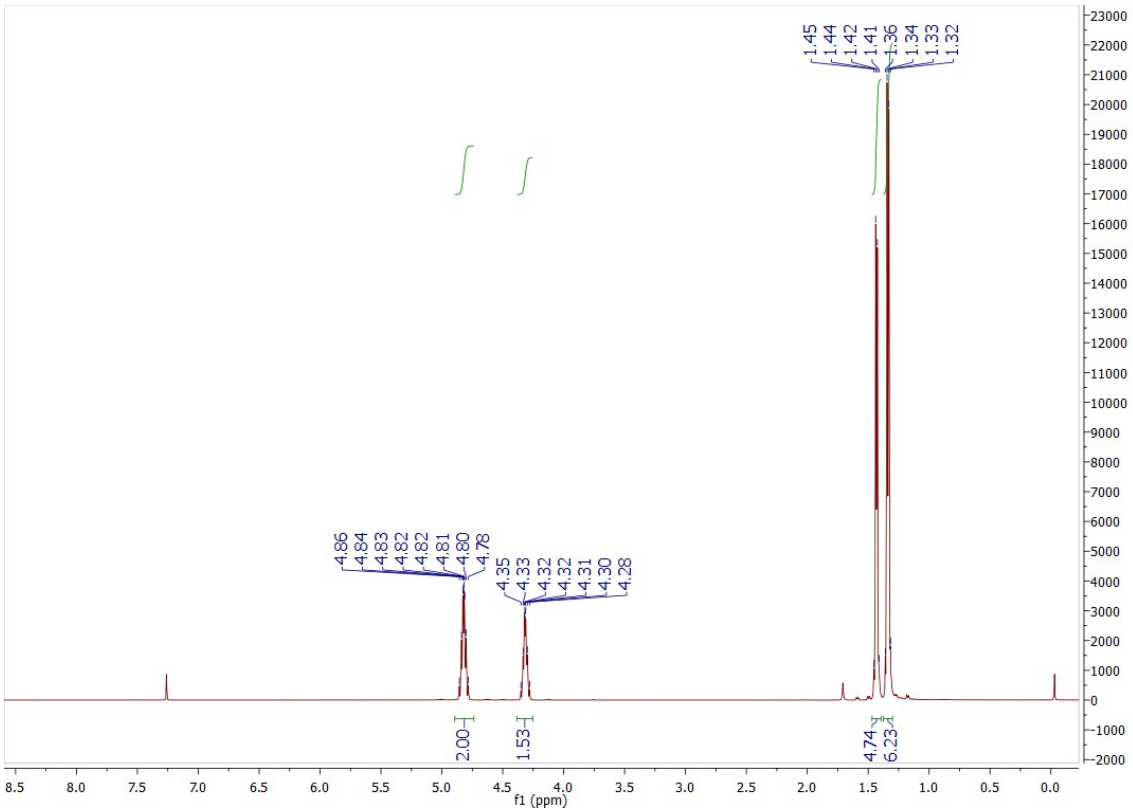


Figure S38. ^{1}H NMR spectrum (400 MHz) of 4,5-dimethyl-1,3-dioxolan-2-one (**1o**, *cis/trans* 4:3) in $CDCl_3$.

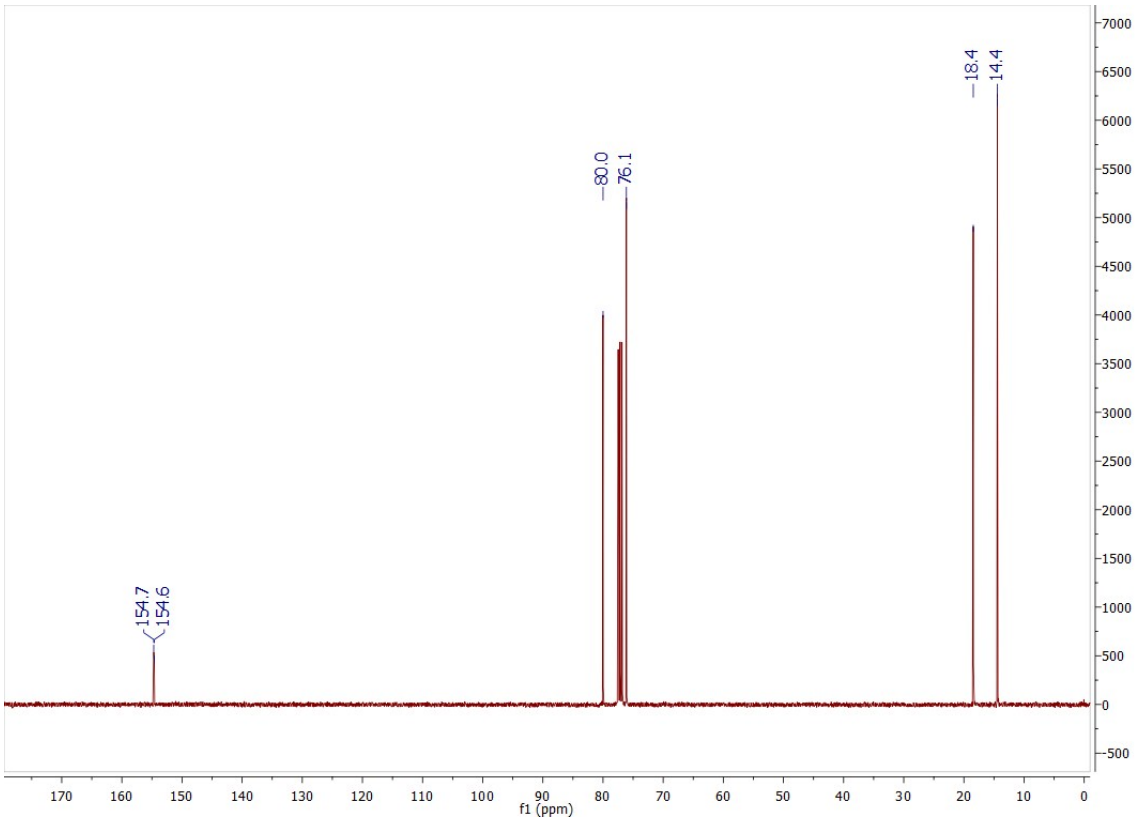


Figure S39. ^{13}C NMR spectrum (100.6 MHz) of 4,5-dimethyl-1,3-dioxolan-2-one (**1o**, *cis/trans* 4:3) in $CDCl_3$.

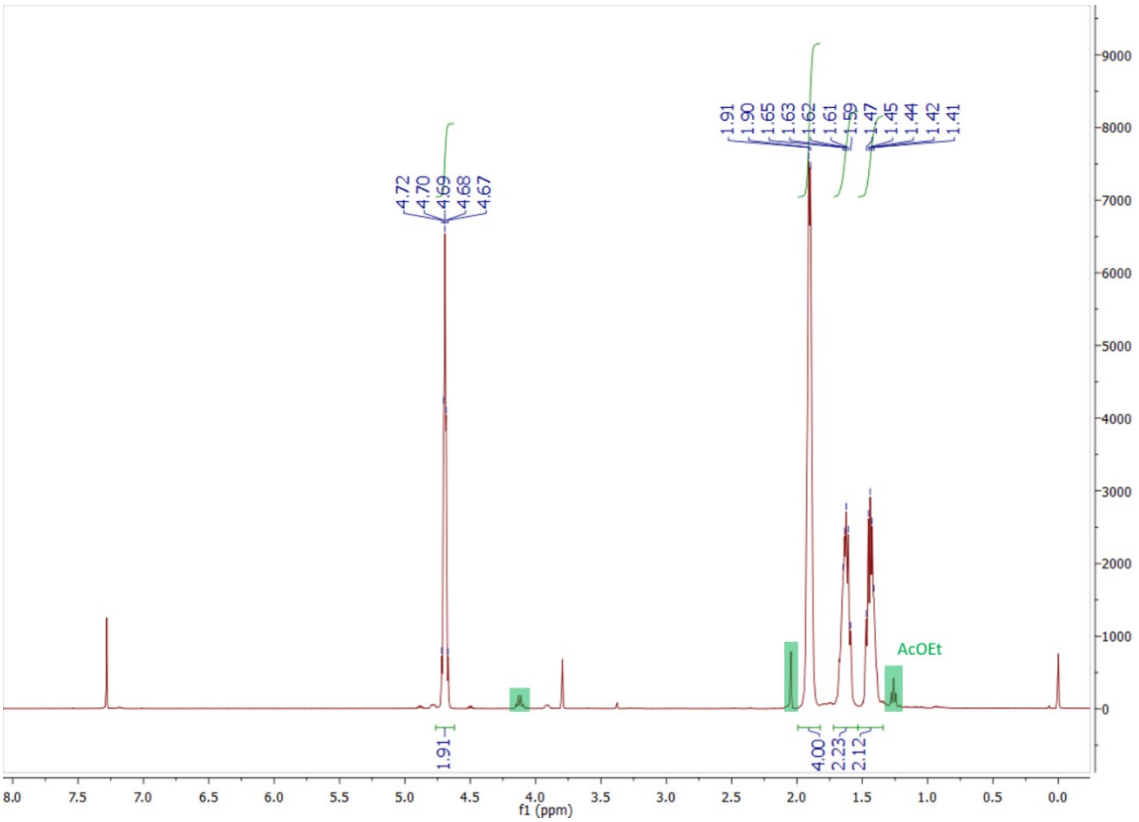


Figure S40. ^{1}H NMR spectrum (400 MHz) of *cis*-hexahydro-1,3-benzodioxol-2-one (**1p**) in $CDCl_3$.

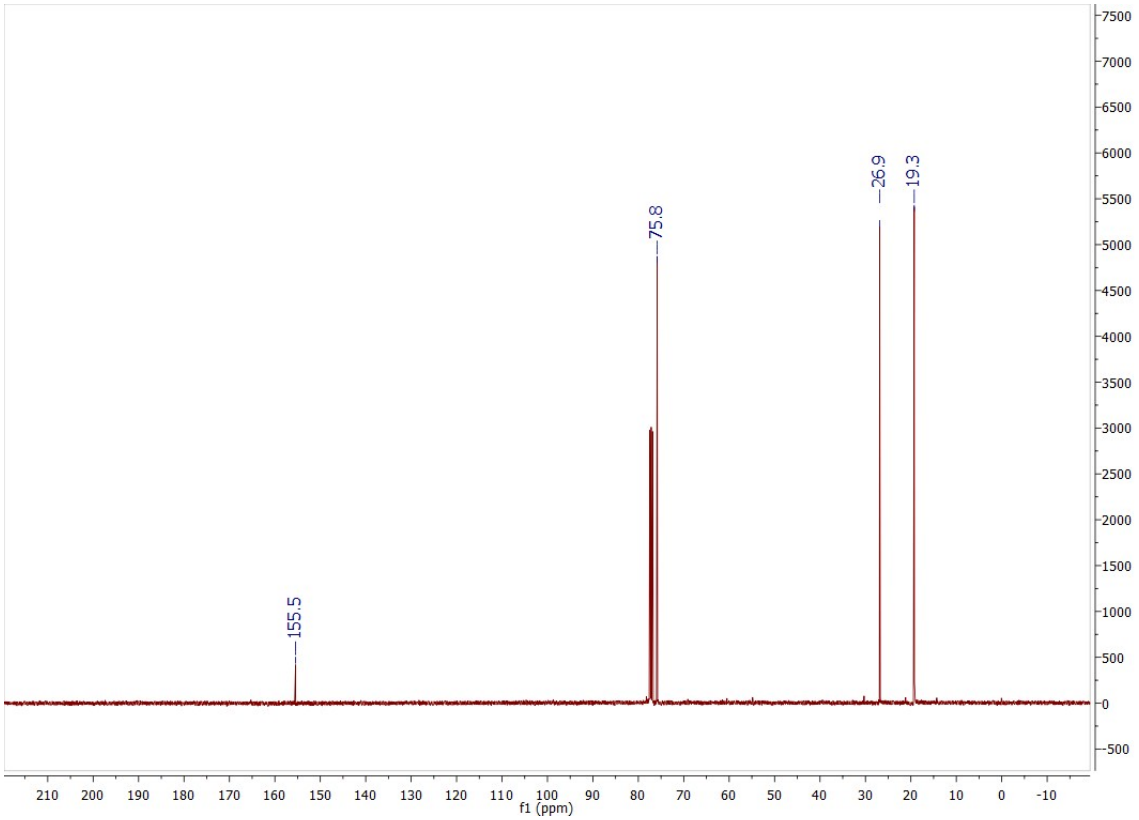


Figure S41. ^{13}C NMR spectrum (100.6 MHz) of *cis*-hexahydro-1,3-benzodioxol-2-one (**1p**) in $CDCl_3$.

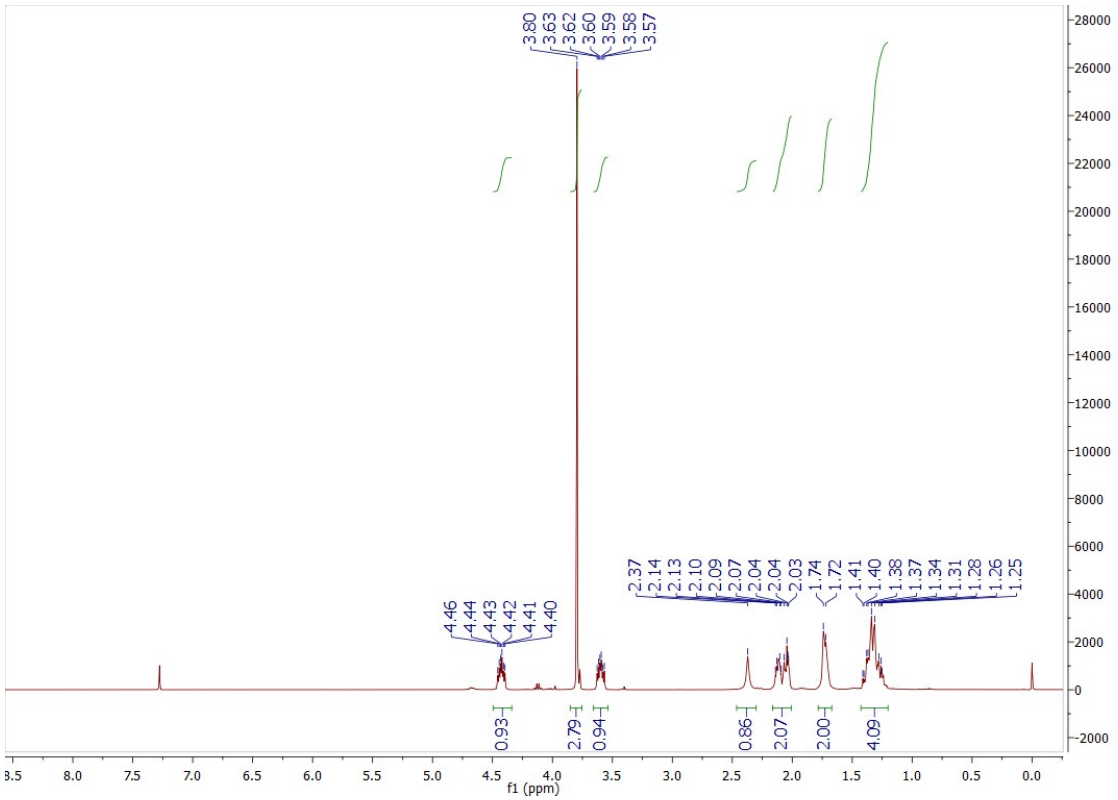


Figure S42. ^{1}H NMR spectrum (400 MHz) of (1*S*,2*S*)- and (1*R*,2*R*)-2-hydroxycyclohexyl methyl carbonate (**1q**) in $CDCl_3$.

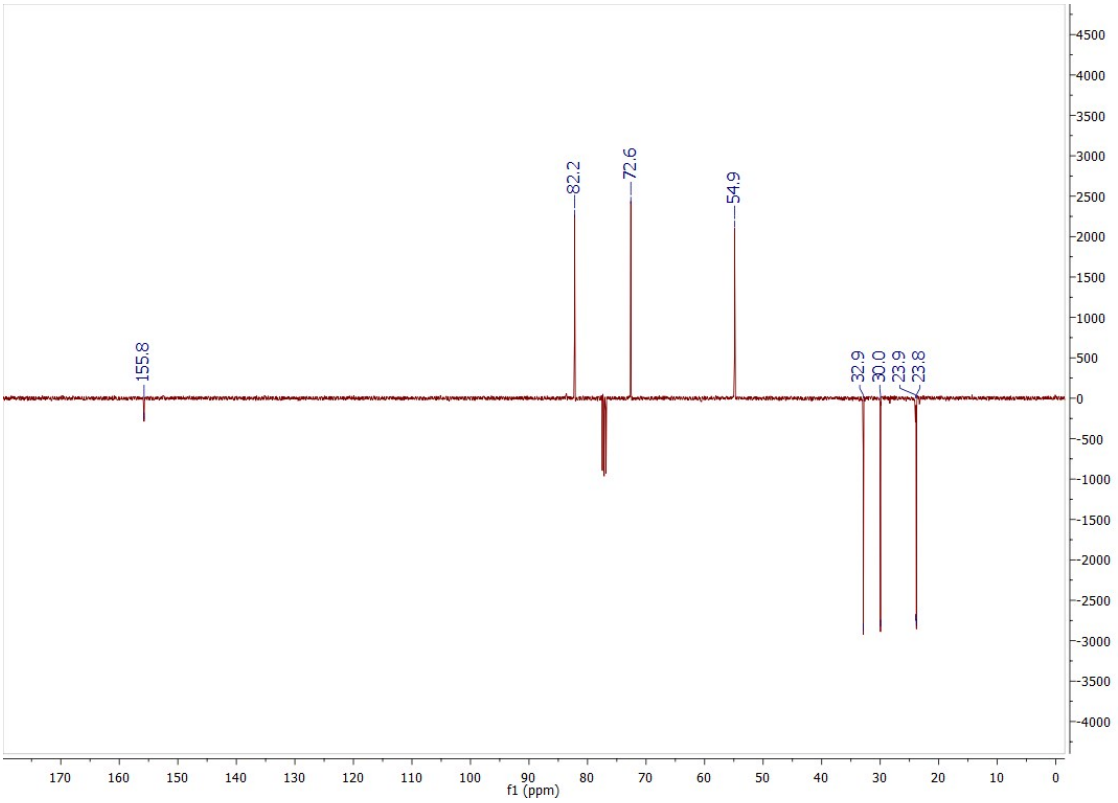


Figure S43. ^{13}C APT NMR spectrum (100.6 MHz) of (1*S*,2*S*)- and (1*R*,2*R*)-2-hydroxycyclohexyl methyl carbonate (**1q**) in $CDCl_3$.

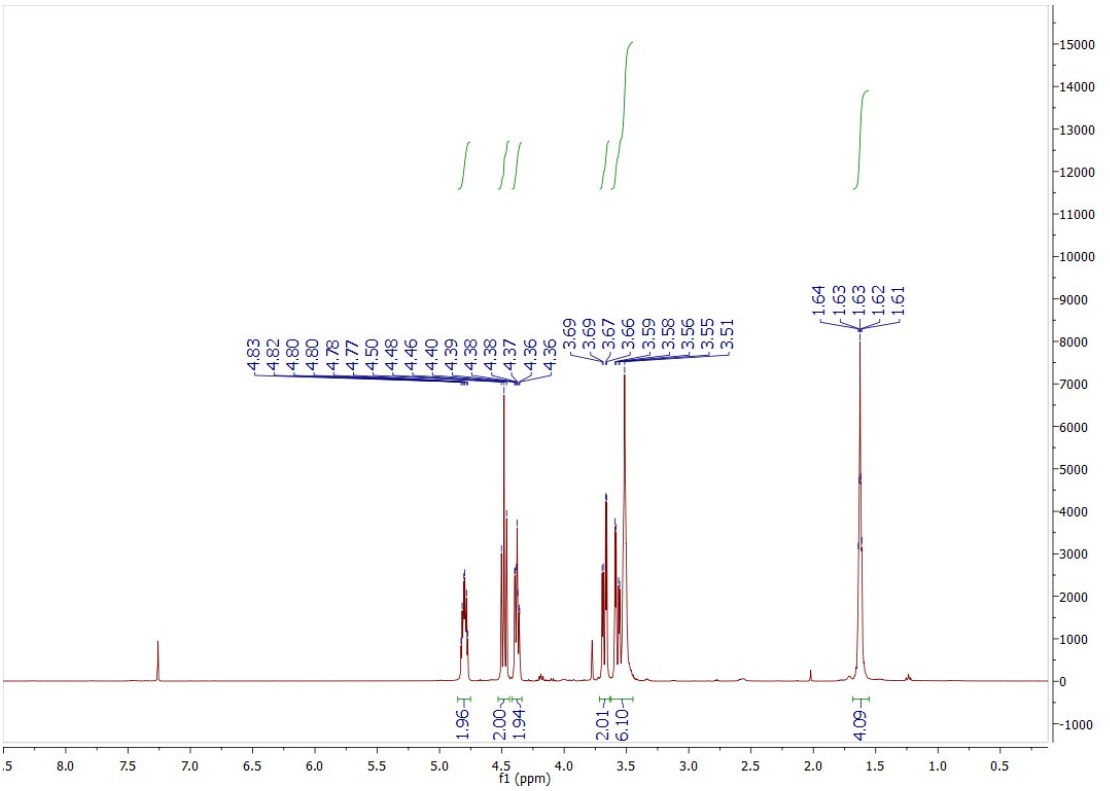


Figure S44. ^{1}H NMR spectrum (400 MHz) of 4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (**1s**) in $CDCl_3$.

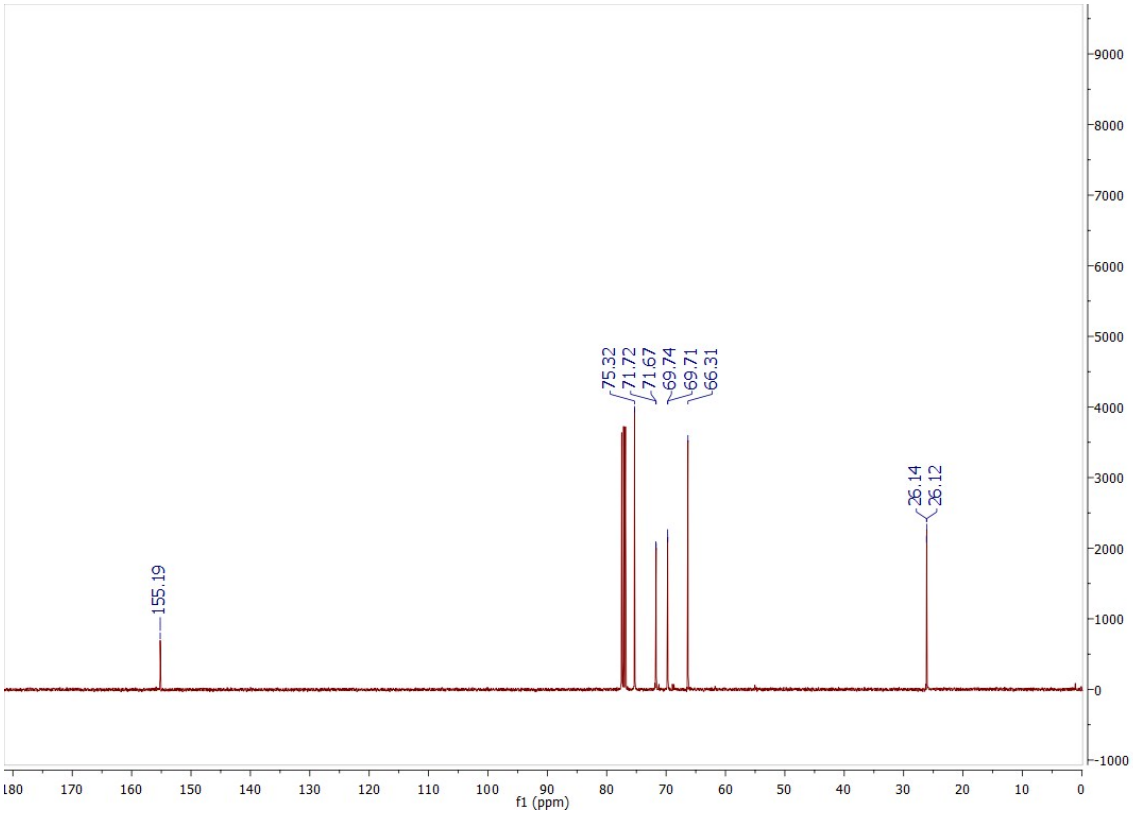


Figure S45. ^{13}C NMR spectrum (100.6 MHz) of 4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (**1s**) in $CDCl_3$.

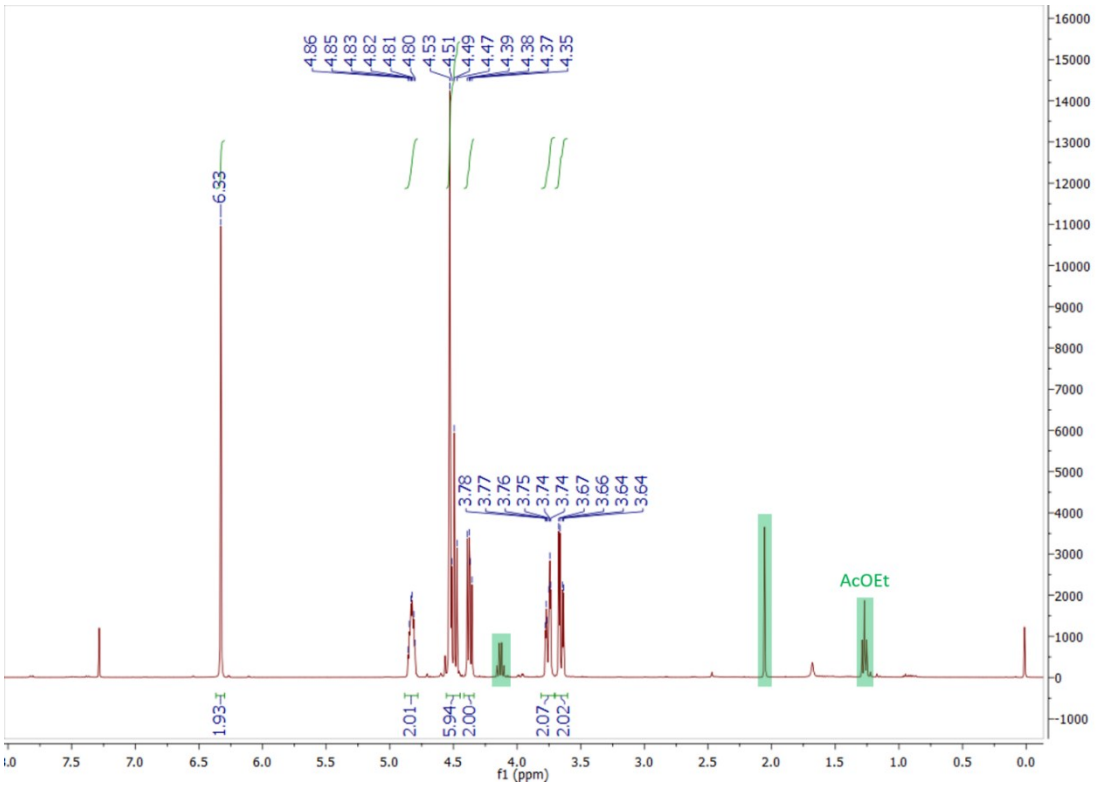


Figure S46. ^{1}H NMR spectrum (400 MHz) of 4,4'-(((furan-2,5-diylbis(methylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (**1t**) in $CDCl_3$.

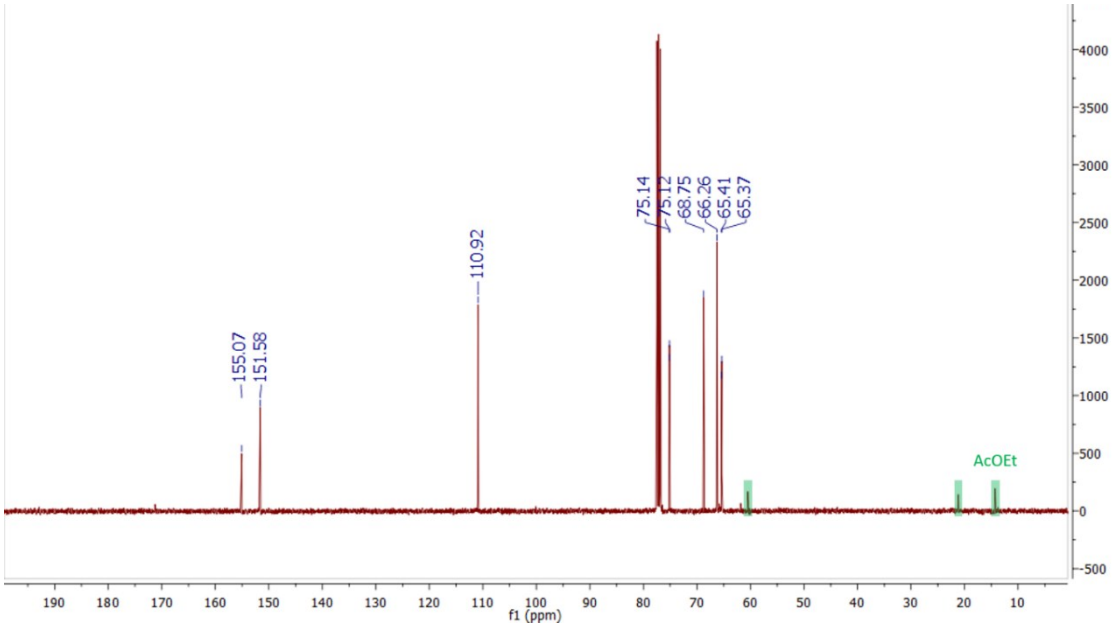


Figure S47. ^{13}C NMR spectrum (100.6 MHz) of 4,4'-(((furan-2,5-diylbis(methylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (**1t**) in $CDCl_3$.

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