SUPPLEMENTARY INFORMATION

A catalytic domino approach towards oxo-alkyl carbonates and polycarbonates from CO2, propargylic alcohols and (mono- and di-) alcohols

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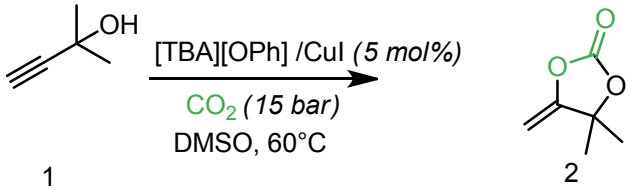
1. **Determination of the alkynol conversion for the carboxylative cyclization of 2-methyl-3-butyn-2-ol.**



Scheme S1: *Carboxylative cyclization of 2-methyl-3-butyn-2-ol*

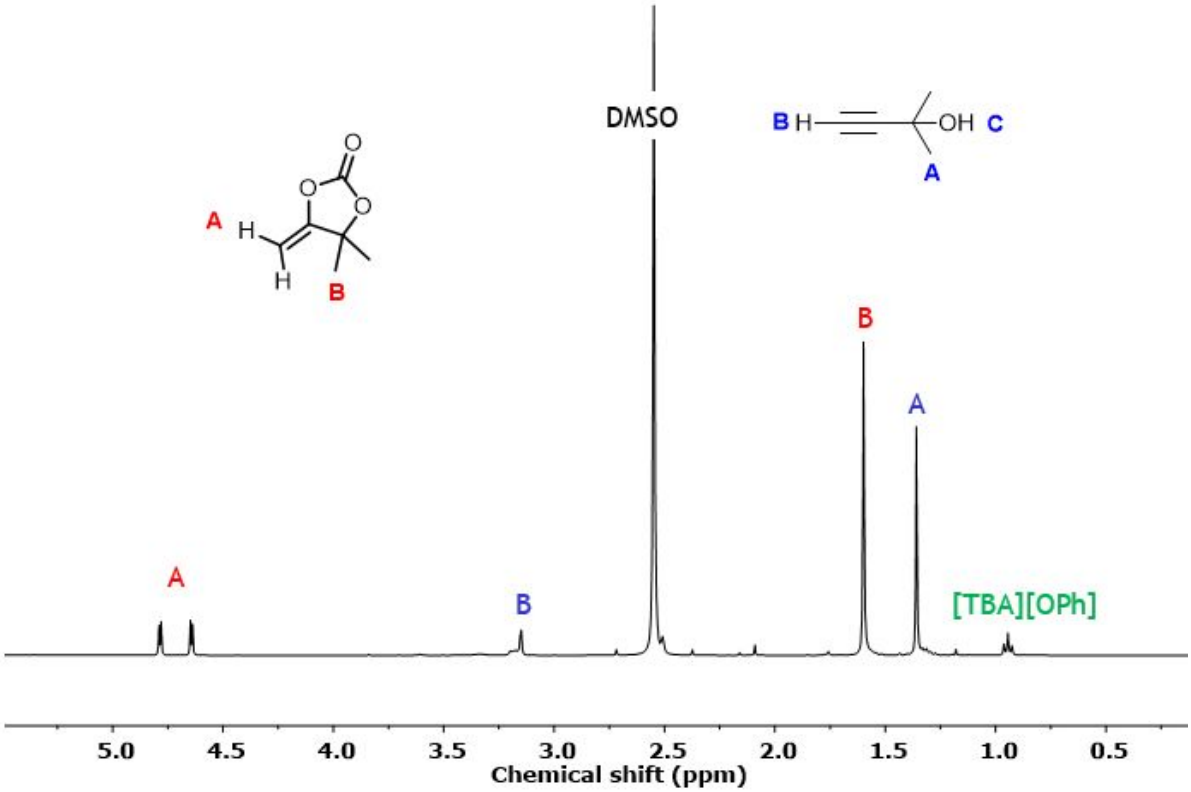


Figure S1. Representative ^{1}H-NMR spectrum (in DMSO-d_6) for the reaction of 2-methyl-3-butyn-2-ol with CO_2 (15 bar) in the presence of [TBA][OPh] (5 mol%) and CuI (2.8 mol%) in DMSO after 2 h at 60 °C.

The alkynol conversion was estimated by comparison of the relative intensities of the peaks associated to olefinic protons at 4.64 and 4.79 ppm of the cyclic carbonate, and the peak of the methyl groups of the alkynol at 1.35 ppm according to the equation:

$$Conversion\ \% = \left(\frac{I_{1.36}/6}{((I_{4.64} + I_{4.79})/2) + I_{1.36}/6)}\right) \times 100 \qquad \textbf{Equation S1}$$

2. ^{1}H NMR spectra of the reaction mixture catalysed by [TBA][OPh] and CuI/AgI

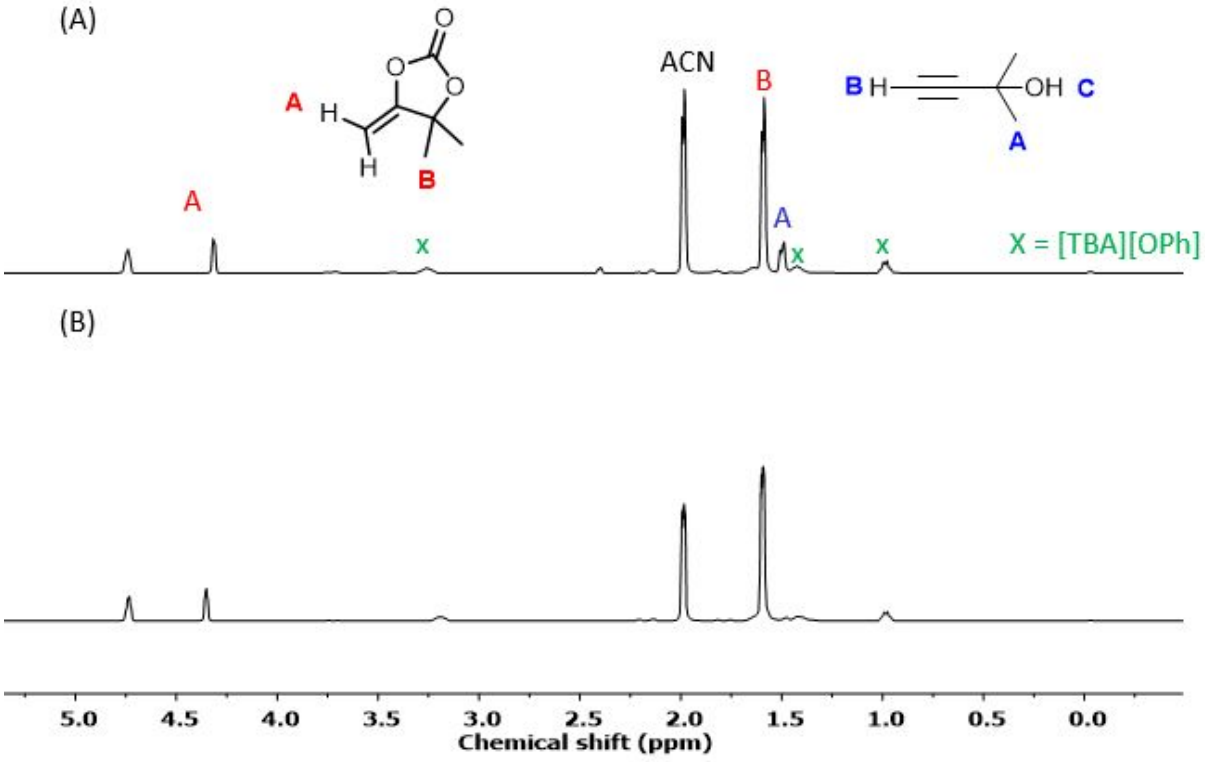


Figure S2. Synthesis of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one by organocatalyzed coupling of CO_2 to 2-methyl-3-butyn-2-ol. (a) [TBA][OPh]/CuI and (b) [TBA][OPh]/AgI. Conditions: 2-methyl-3-butyn-2-ol (2 mL, 0.0206 mmol), [TBA][OPh] (5 mol%), CuI/AgI (5 mol%), 40 °C, 15 bar, ACN (2 mL)

3. Carboxylative cyclization of 2-methyl-3-butyn-2-ol followed by FT-IR spectroscopy

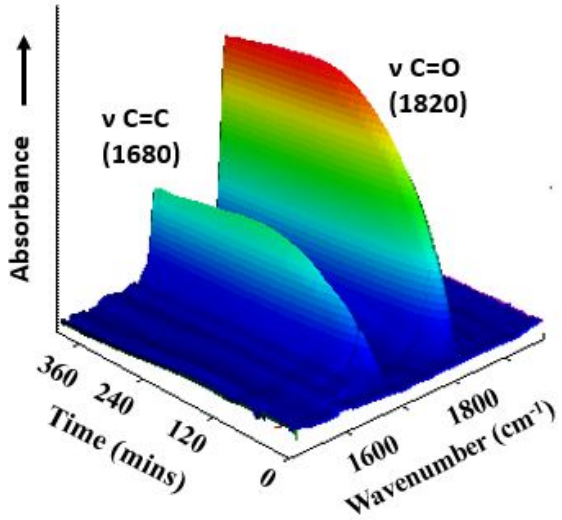


Figure S3. Synthesis of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one by organocatalyzed coupling of CO_2 to 2-methyl-3-butyn-2-ol. 3D profile showing the C=O absorption region obtained by on-line FT-IR spectroscopy for the reaction catalyzed by [TBA][OPh]/CuI. Conditions: 2-methyl-3-butyn-2-ol (16 mL, 0.165 mmol), [TBA][OPh] (5 mol%), CuI (5 mol%), 40 °C, 15 bar, DMSO (16 mL)

4. Determination of the yield in cyclic carbonate by FT-IR spectroscopy

For a reaction wherein complete conversion of 2-methyl-3-butyn-2-ol into 100% αCC is obtained, the concentration of αCC is given by equation S2

$$Concentration\left(\frac{mol}{l}\right) = \left(\frac{n_{alkynol}}{V_{solvent}}\right) = 10.30\ mol/l \qquad \textbf{Equation S2}$$

The molar extinction coefficient of the cyclic carbonate was determined based on Beer Lambert's. The absorbance of a solution of known concentration was measured, and the molar extinction coefficient determined based on equations S3 and S4

$$Absorbance = (\varepsilon l C) \qquad \textbf{Equation S3}$$

$$\varepsilon l = \left(\frac{Absorbance}{C_{\alpha CC}}\right) \qquad \textbf{Equation S4}$$

Using the values obtained from equation S4, we could then convert the absorbances measured after various times into a concentration using equation S5 and hence determine the yield in cyclic carbonate with equation S6.

$$C_{\alpha CC} = \left(\frac{Absorbance}{\varepsilon l}\right) \qquad \textbf{Equation S5}$$

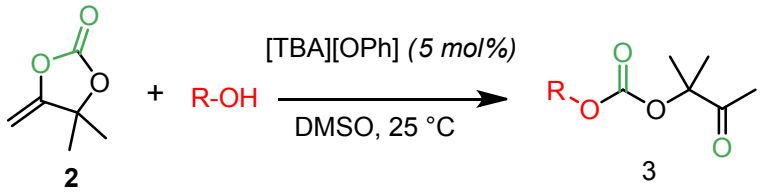
$$Yield_{\alpha CC}(\%) = \left(\frac{C_{DMACC\ determined}}{10.30} \times 100\right) \qquad \textbf{Equation S6}$$

A similar procedure was followed for the determination of the yield in oxoalkyl carbonate

5. Computational details

Preliminary calculations of equilibrium structures were performed using a semi-empirical model (PM6-D3H4) to determine the most stable conformations. These semi-empirical calculations were performed using the AMPAC software. The CHAIN algorithm was used for locating intermediates and transition states along the reaction path. The lowest energy structures obtained at the PM6-D3H4 level were further investigated using the Density Functional Theory method (DFT) implemented in the Gaussian 16 package. DFT calculations of geometries, energies, and vibrational frequencies reported in this article were carried out with the M06-2X functional using the 6-311 G(d,p) basis set except for Ag, Cu and I atoms which have been treated with the help of the LANL2DZ pseudo potential. All frequencies of each structure have also been calculated to verify the presence of a single imaginary frequency for transition states and the absence of imaginary frequency for ground states. The intrinsic reaction coordinate (IRC) method has been used to verify that the obtained transition states were effectively connected to the desired minima. For all activating systems, a wide range of possible configurations and interactions have been modelled and the more stable of them are reported in this work. To consider entropic effects, the energies mentioned in this study correspond to the Gibbs free energy (G).

6. Determination of the conversion for the alcoholysis of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (αCC)



Scheme S2: *Alcoholysis of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one*

The αCC conversion was estimated by comparison of the relative intensities of the peaks associated to olefinic protons at 4.64 and 4.79 ppm of αCC and the peak of the methyl group in α-position of the ketone at 2.11 ppm according to equation S7.

$$Conversion\ \% = \left(\frac{(I_{4.64} + I_{4.79})/2}{((I_{4.64} + I_{4.79})/2) + I_{2.11}/3)}\right) \times 100$$ **Equation S7**

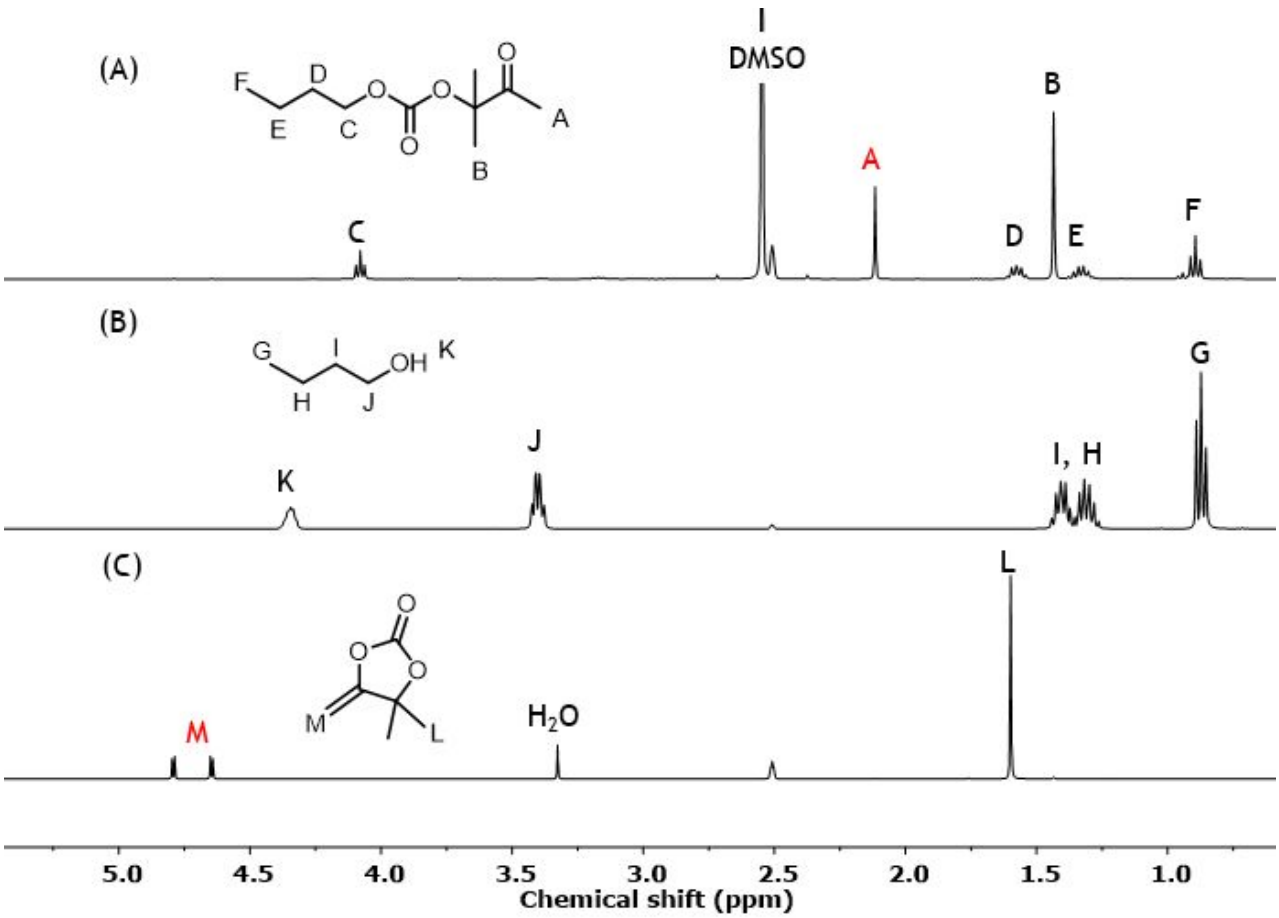
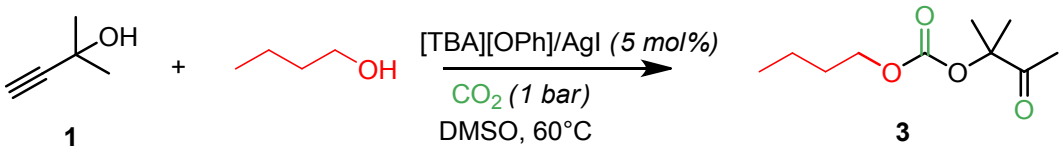


Figure S4. ^{1}H-NMR spectra in DMSO-d_6 of (A) the reaction mixture after 1 h at 25 °C, (B) 1-butanol and (C) αCC.

7. Determination of the conversion for the one-pot cascade reaction of 2-methyl-2-butyn-3-ol, CO2 and 1-butanol.



Scheme S3: *One-pot cascade reaction of 2-methyl-2-butyn-3-ol, CO2 and 1-butanol*

The alkynol conversion was estimated by comparison of the relative intensities of the peaks associated to the methyl group in alpha of the ketone at 2.11 ppm of the oxo-alkylcarbonate, and the peak of the methyl groups of the alkynol at 1.35 ppm according to equation S8.

$$Conversion\ \% = \left(\frac{I_{1.36}/6}{(I_{2.11})/3) + I_{1.36}/6)}\right) \times 100$$ **Equation S8**

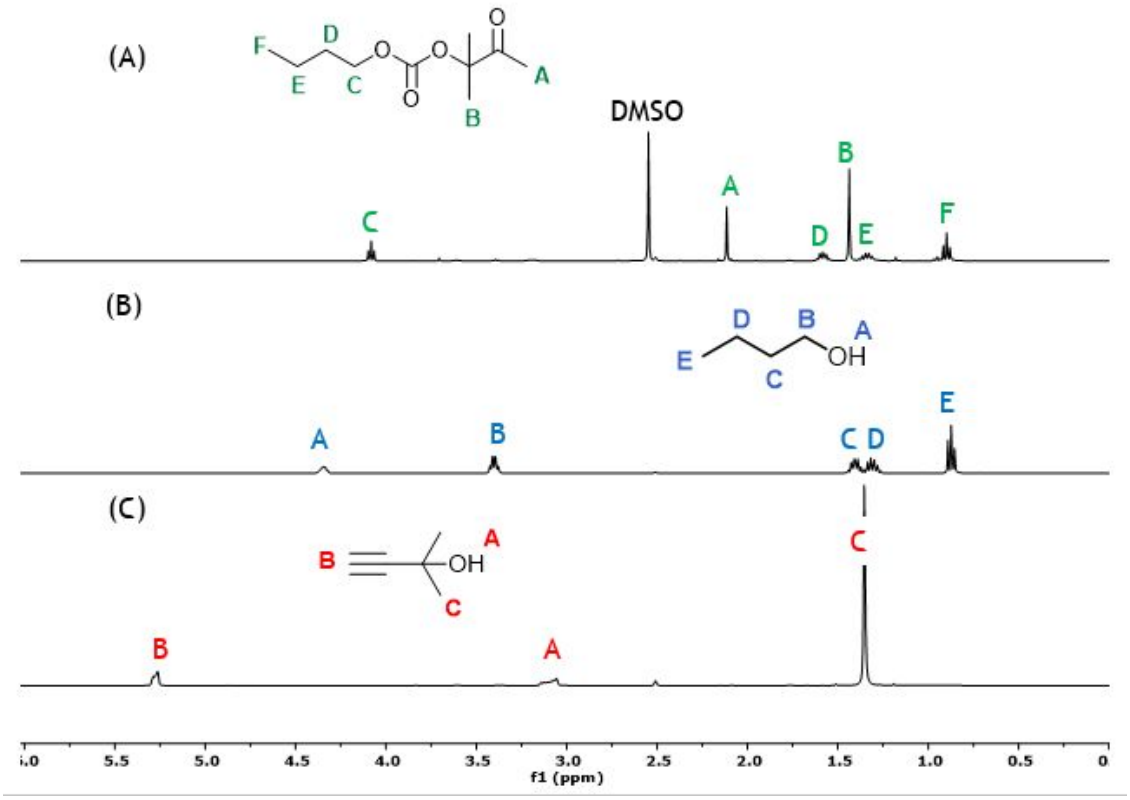
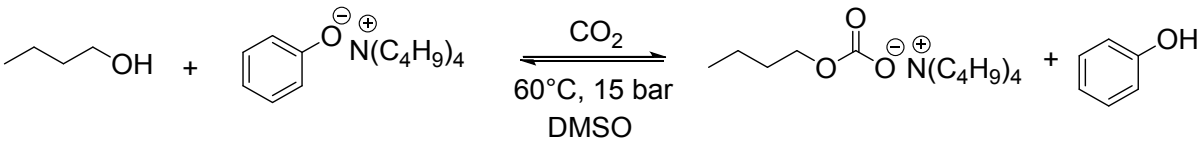


Figure S5. ^{1}H-NMR spectra in DMSO-d_6 of (A) the reaction mixture at 60 °C after 10 h, (B) 1-butanol and (C) 2-methyl-3-butyn-2-ol.

8. Carbonation of 1-butanol by in-situ FT-IR spectroscopy.



Scheme S4: *Reaction of butanol with CO_2 in the presence of [TBA][OPh]*

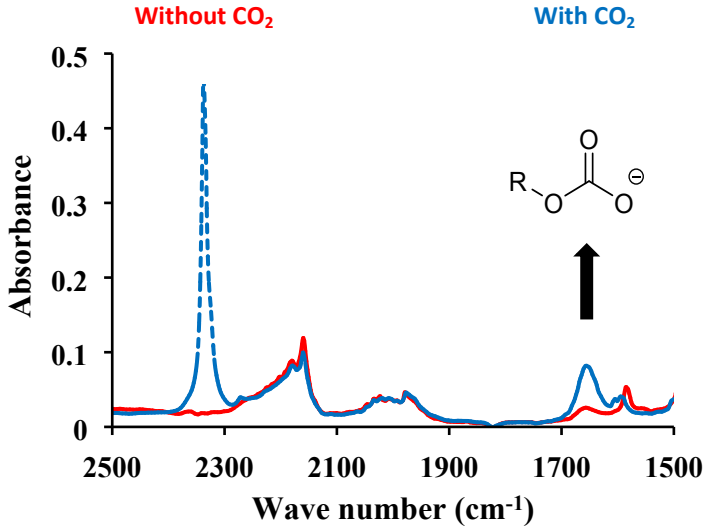


Figure S6. FT-IR spectra of a mixture of [TBA][OPh] (5 mol%), 1-butanol and DMSO exposed (blue) or not (red) to CO_2 (15 bar) for 5 min at 60 °C.

9. ^{1}H-, ^{13}C-NMR and IR spectra of oxo-alkylcarbonates

9.1. Butyl (2-methyl-3-oxobutan-2-yl) carbonate

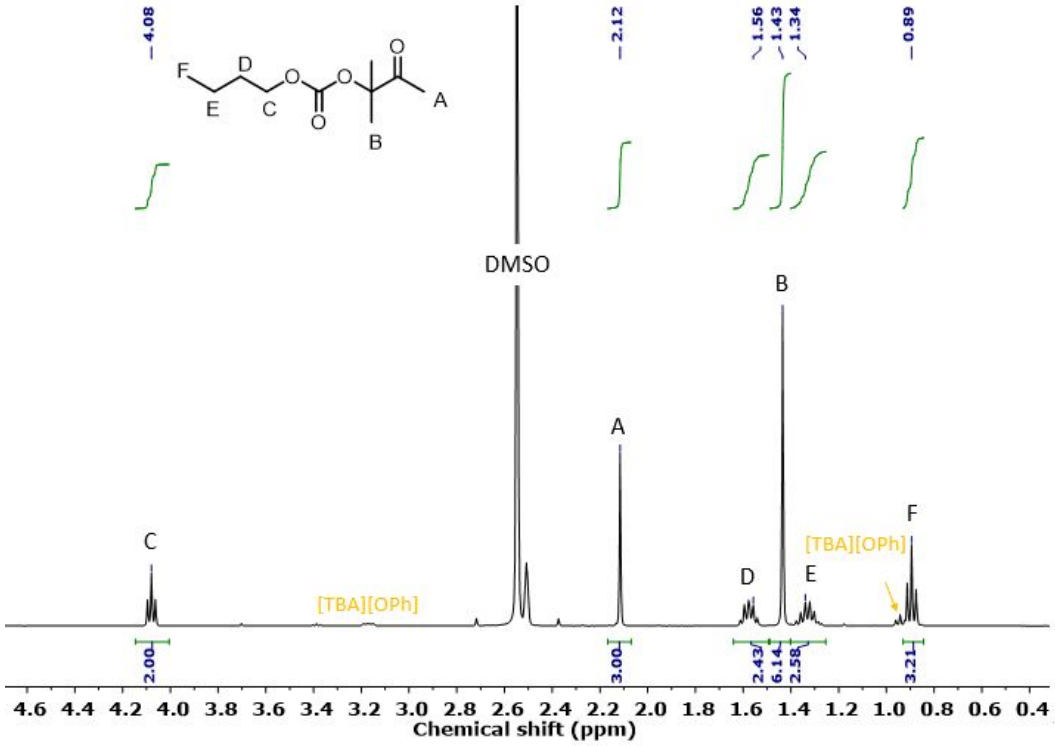


Figure S7. ^{1}H-NMR spectrum of butyl (2-methyl-3-oxobutan-2-yl) carbonate in DMSO-d_6.

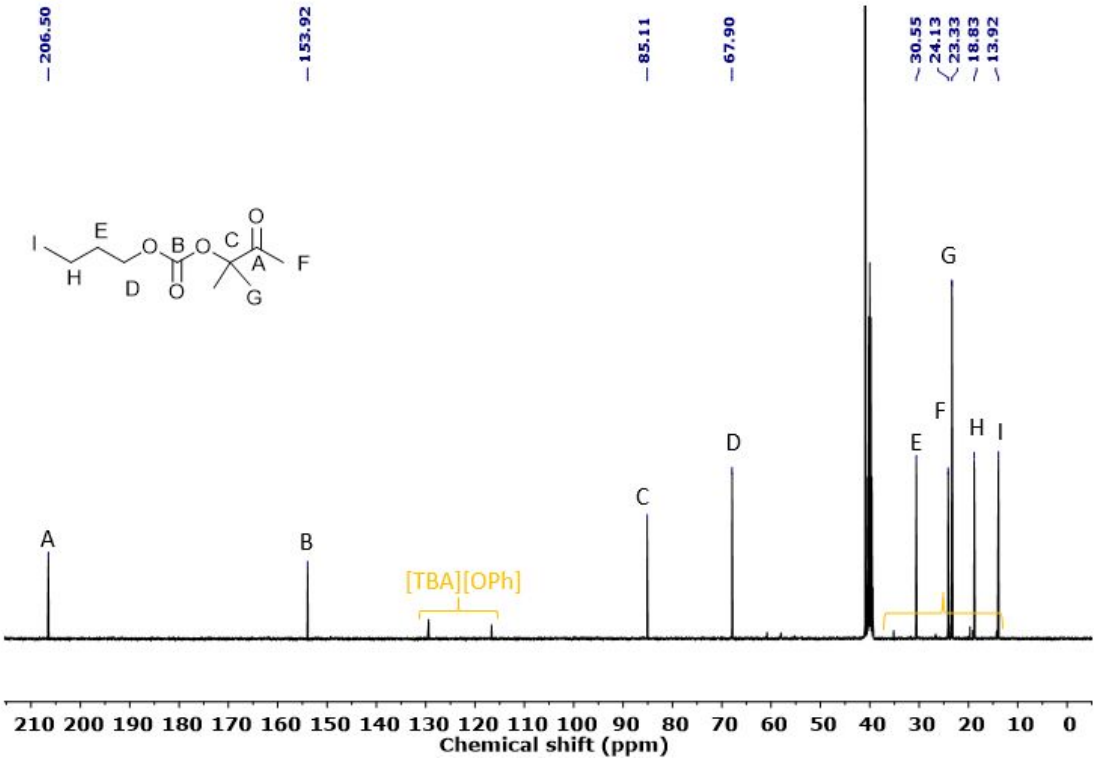


Figure S8. ^{13}C-NMR spectrum of butyl (2-methyl-3-oxobutan-2-yl) carbonate in DMSO-d_6. Characterization in accordance with the literature[1]

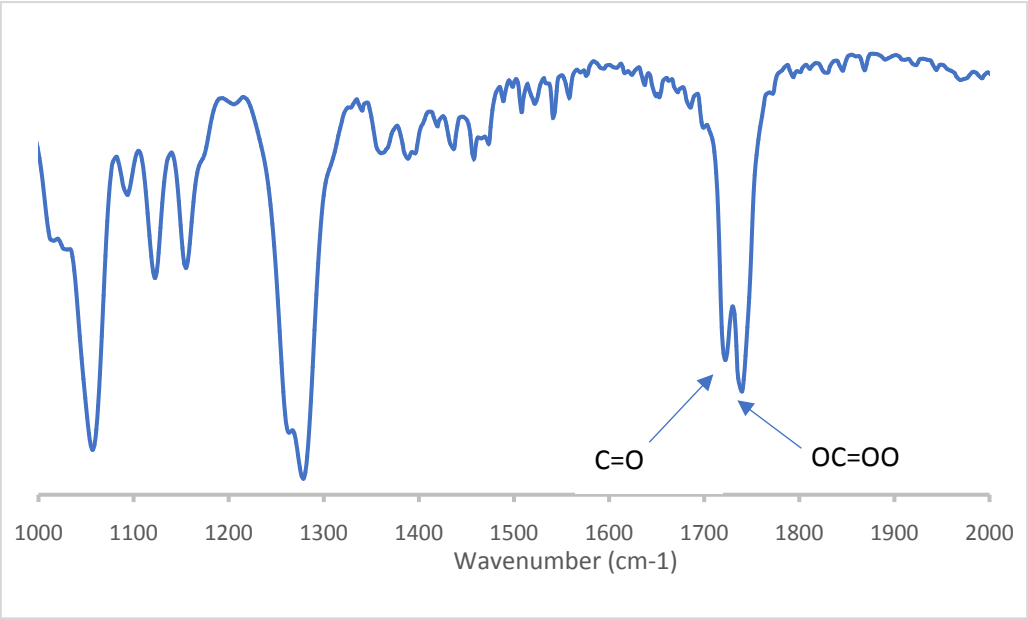


Figure S9. FT-IR spectrum of butyl (2-methyl-3-oxobutan-2-yl) carbonate

9.2. Benzyl (2-methyl-3-oxobutan-2-yl) carbonate

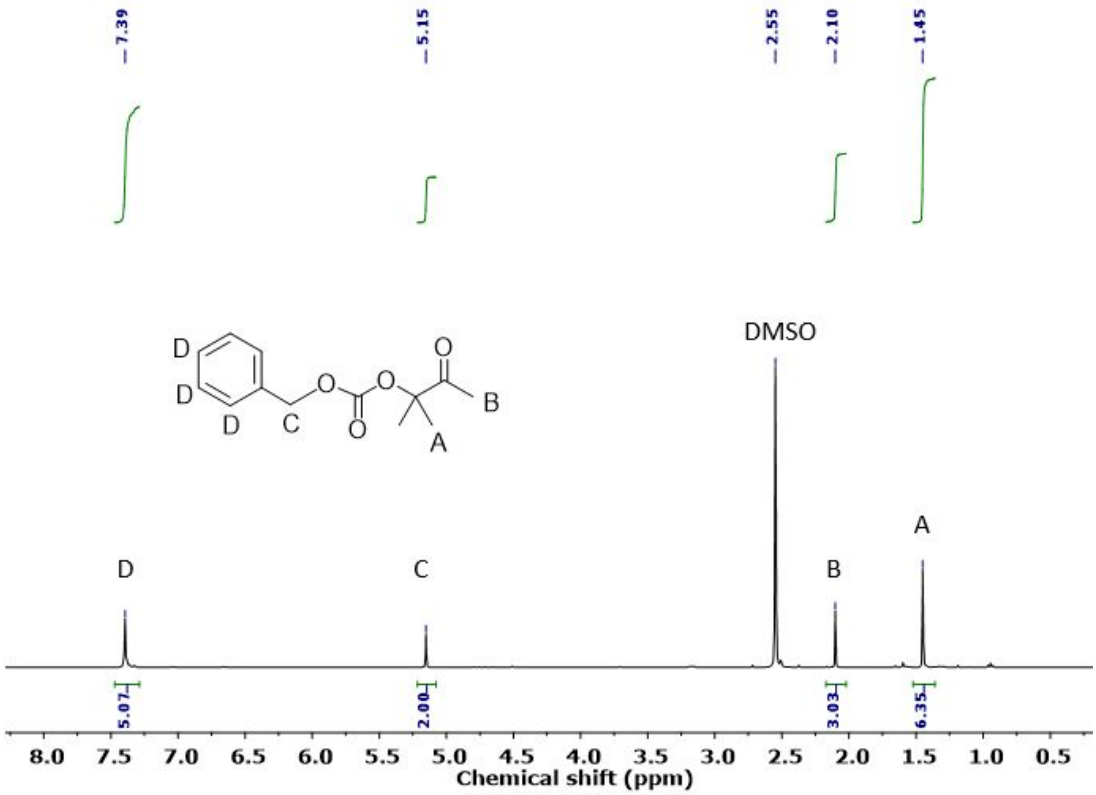


Figure S10. ^{1}H-NMR spectrum of benzyl (2-methyl-3-oxobutan-2-yl) carbonate in DMSO-d_6.

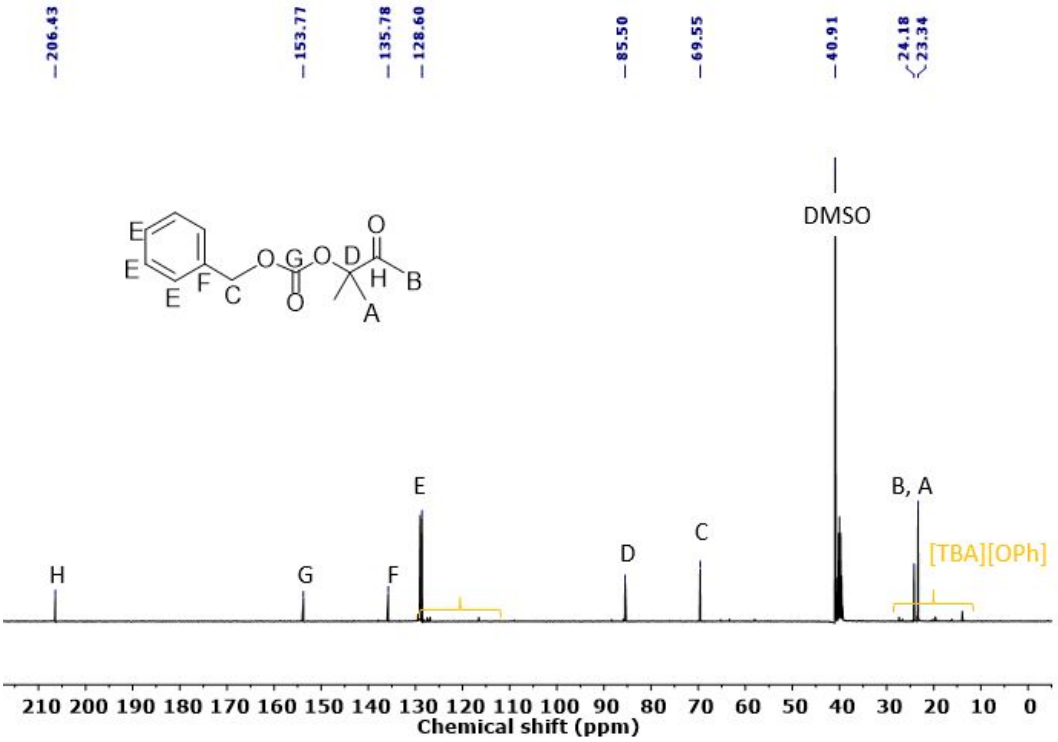


Figure S11. ^{13}C-NMR spectrum of benzyl (2-methyl-3-oxobutan-2-yl) carbonate in DMSO-d_6. Characterization in accordance with the literature[2]

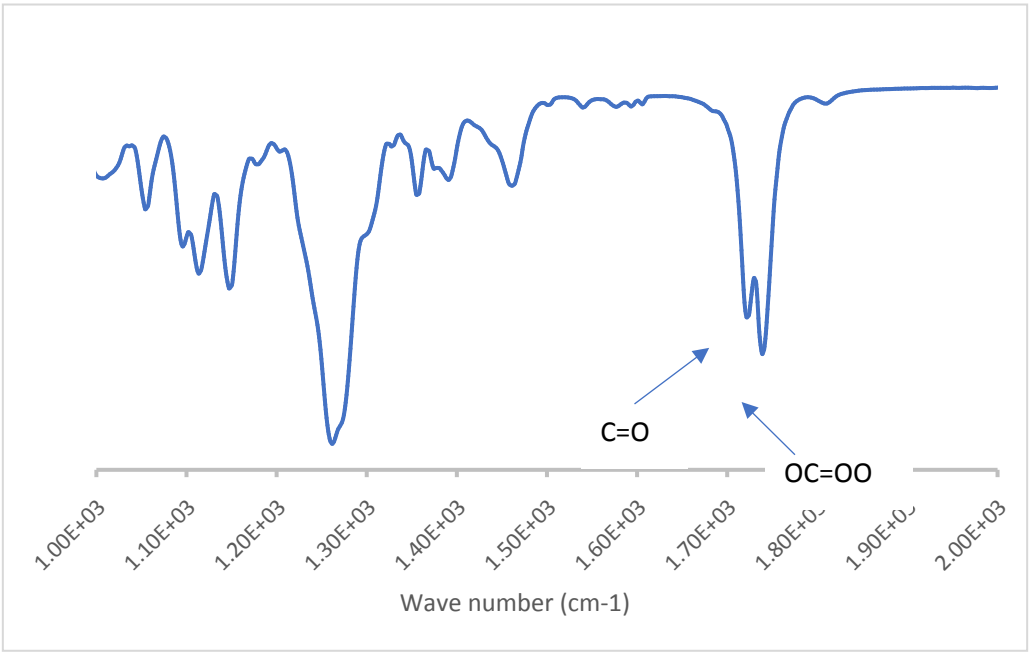


Figure S12. FT-IR spectrum of benzyl (2-methyl-3-oxobutan-2-yl) carbonate

9.3. Isopropyl (2-methyl-3-oxobutan-2-yl) carbonate

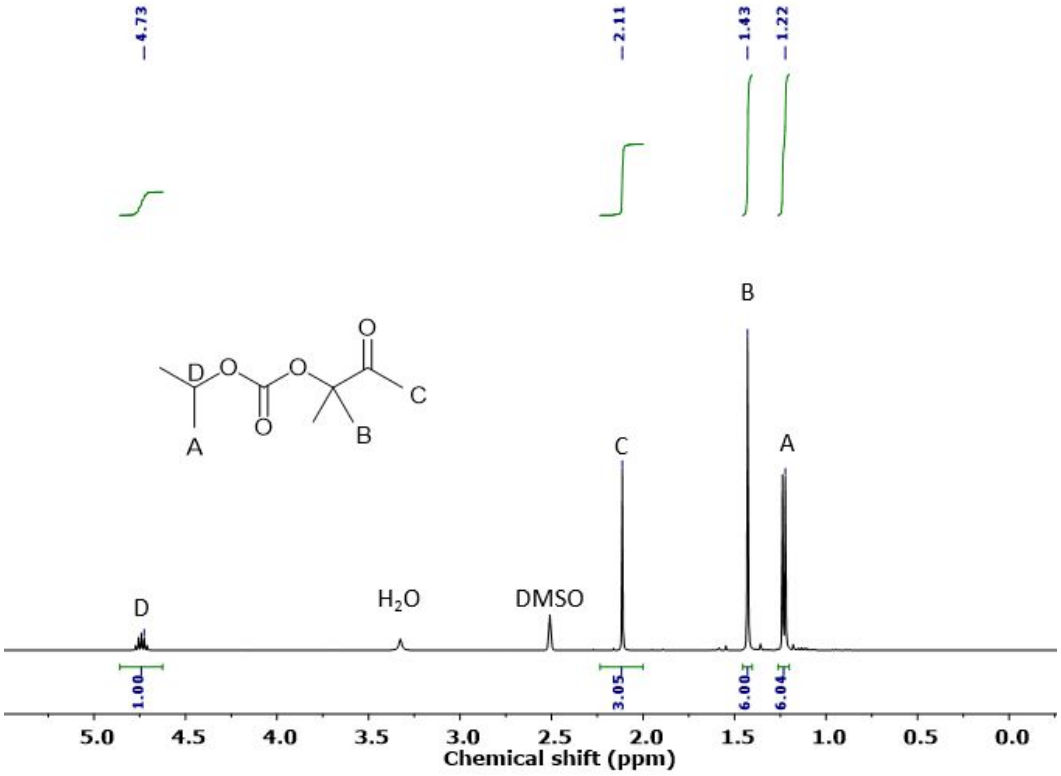


Figure S13. ^{1}H-NMR spectrum of isopropyl (2-methyl-3-oxobutan-2-yl) carbonate in DMSO-d_6.

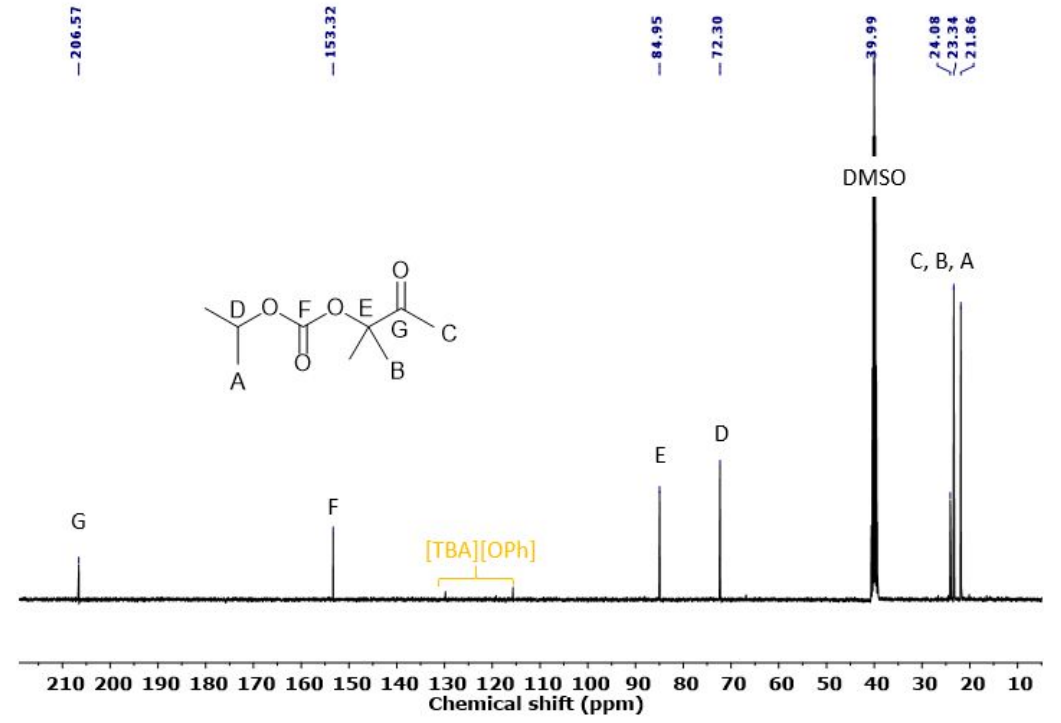


Figure S14. ^{13}C-NMR spectrum of isopropyl (2-methyl-3-oxobutan-2-yl) carbonate in DMSO-d_6. Characterization in accordance with the literature[1]

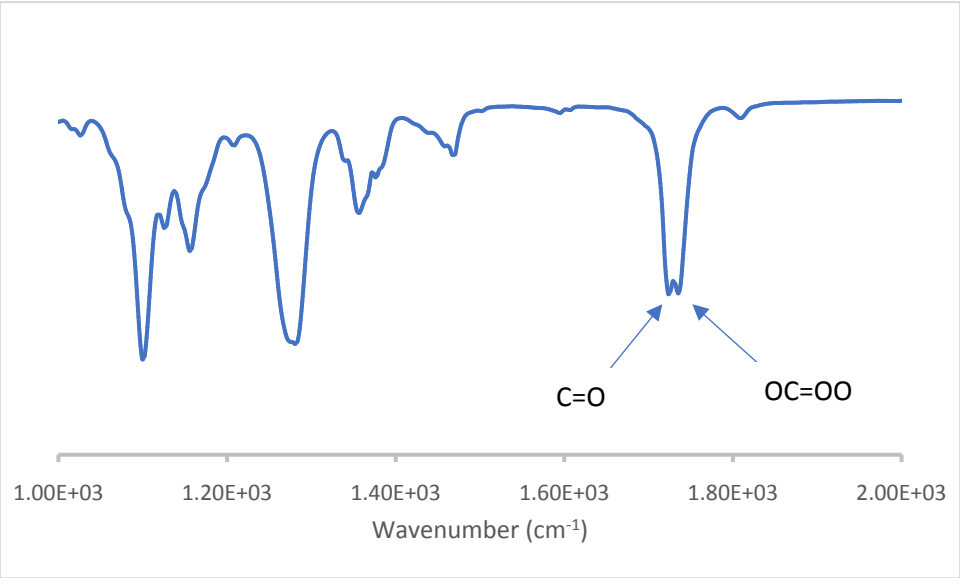


Figure S15. FT-IR spectrum of isopropyl (2-methyl-3-oxobutan-2-yl) carbonate

9.3. Butyl (3-methyl-2-oxopentan-3-yl) carbonate

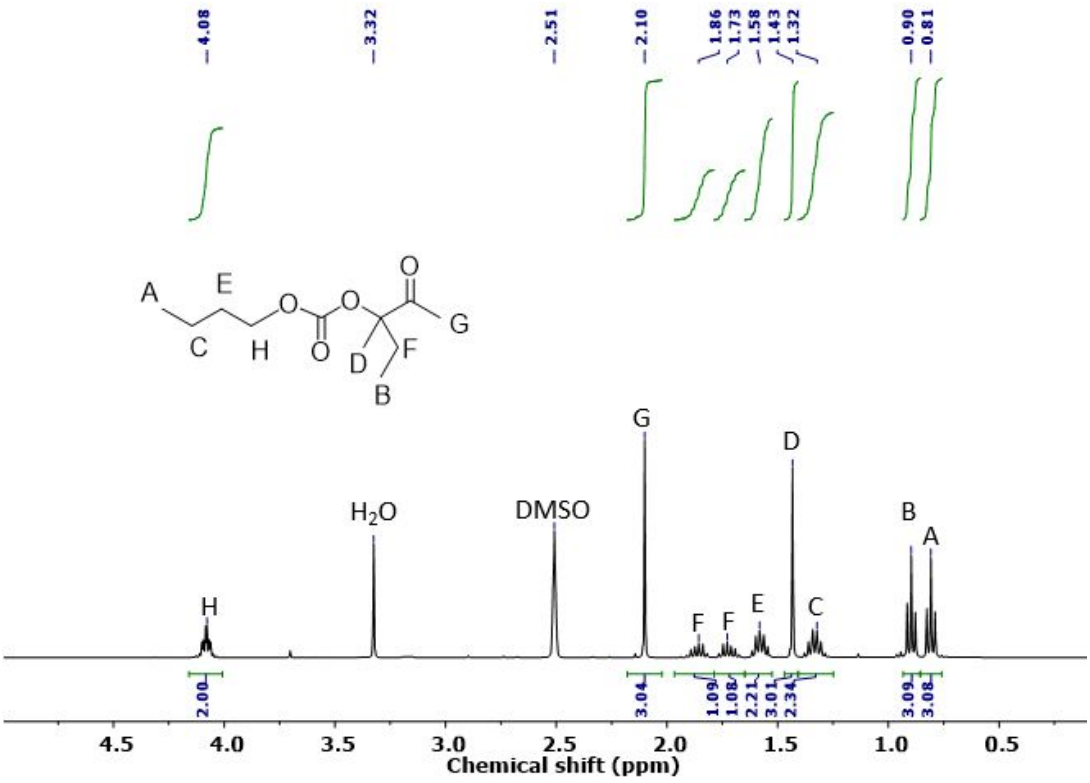


Figure S16. ^{1}H-NMR spectrum of butyl (3-methyl-2-oxopentan-3-yl) carbonate in DMSO-d_6.

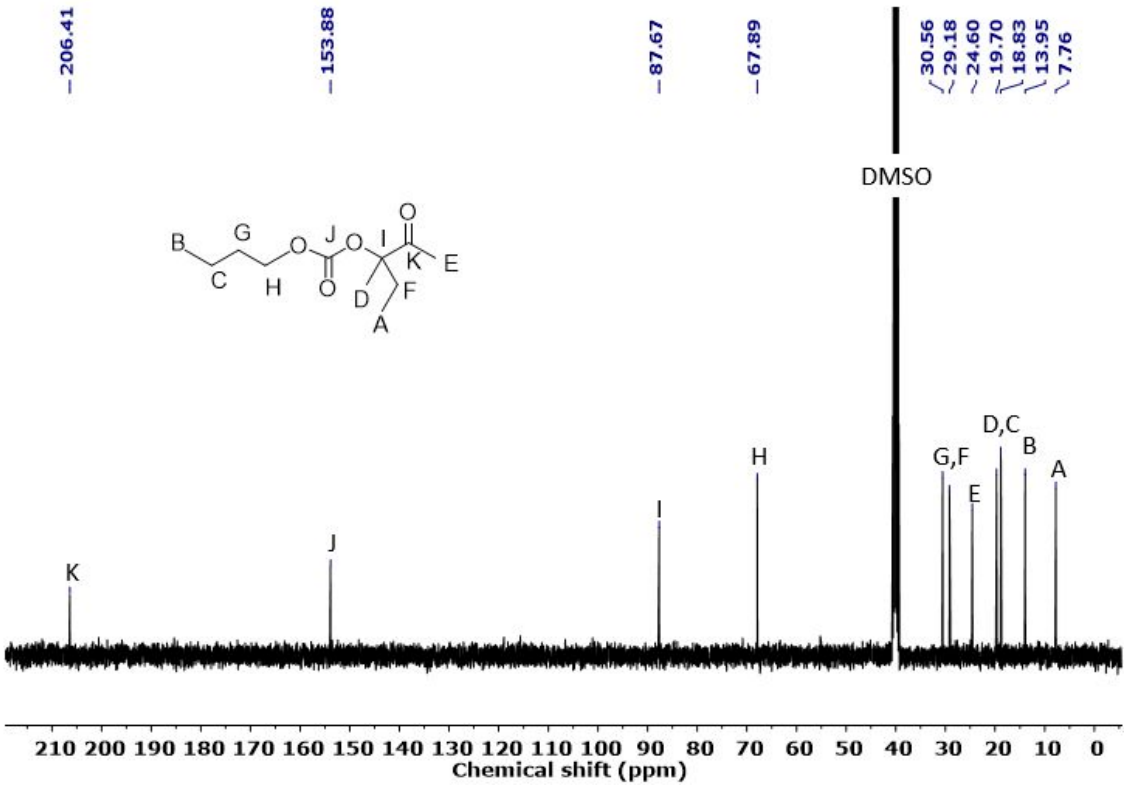


Figure S17. ^{13}C-NMR spectrum of butyl (3-methyl-2-oxopentan-3-yl) carbonate in DMSO-d_6.

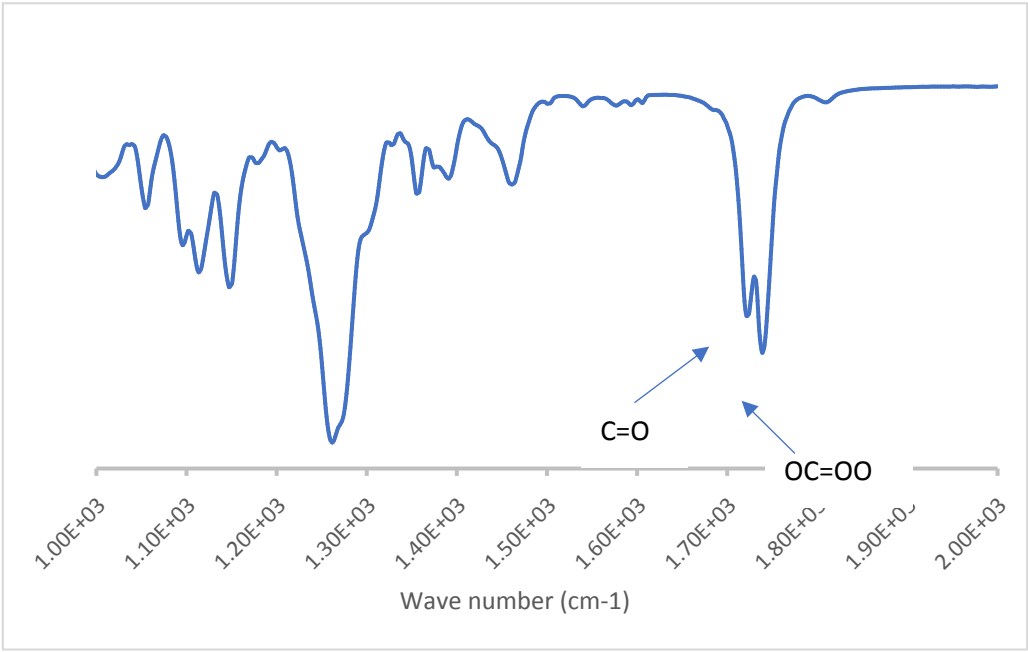


Figure S18. IR spectrum of butyl (3-methyl-2-oxopentan-3-yl) carbonate

9.4. Butyl (3,5-dimethyl-2-oxohexan-3-yl) carbonate

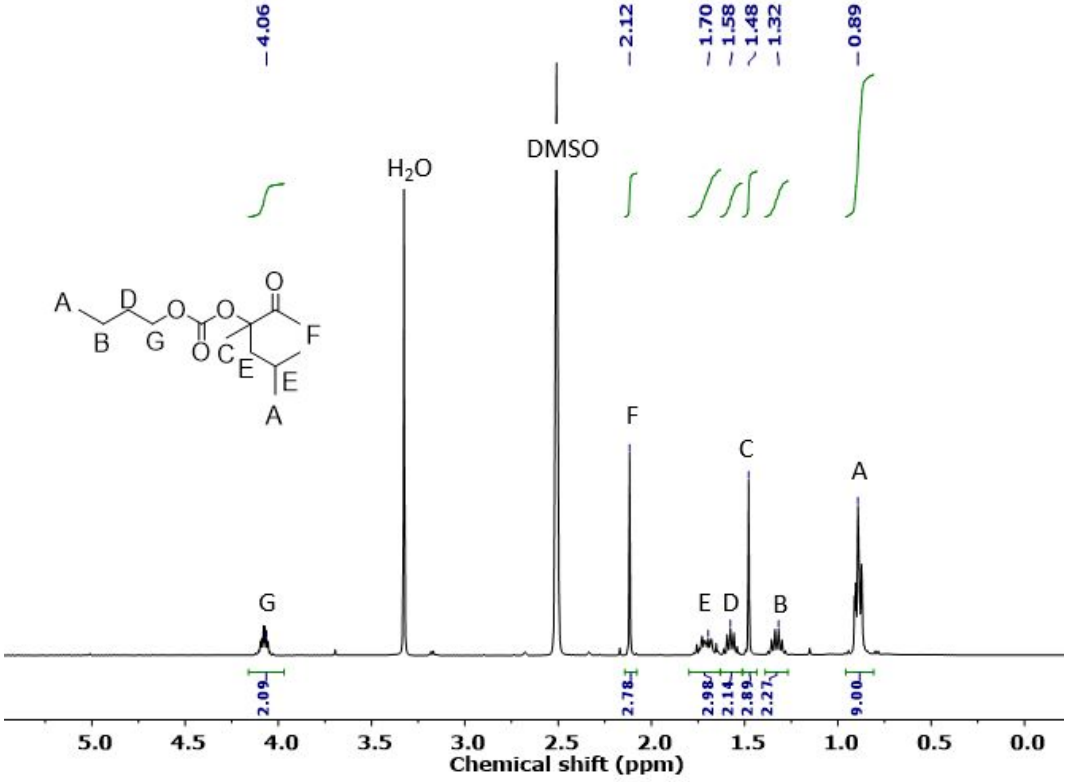


Figure S19. [1]H-NMR spectrum of butyl (3,5-dimethyl-2-oxohexan-3-yl) carbonate in DMSO-d_6

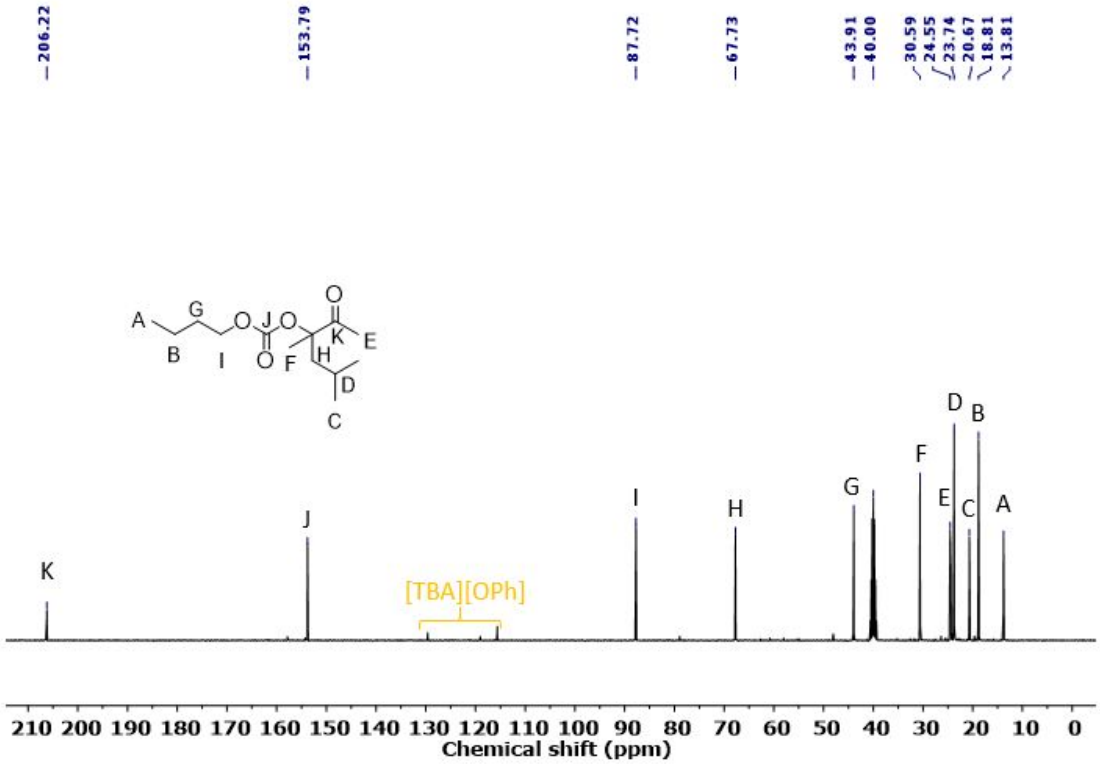


Figure S20. [13]C-NMR spectrum of butyl(3,5-dimethyl-2-oxohexan-3-yl)carbonate in DMSO-d_6

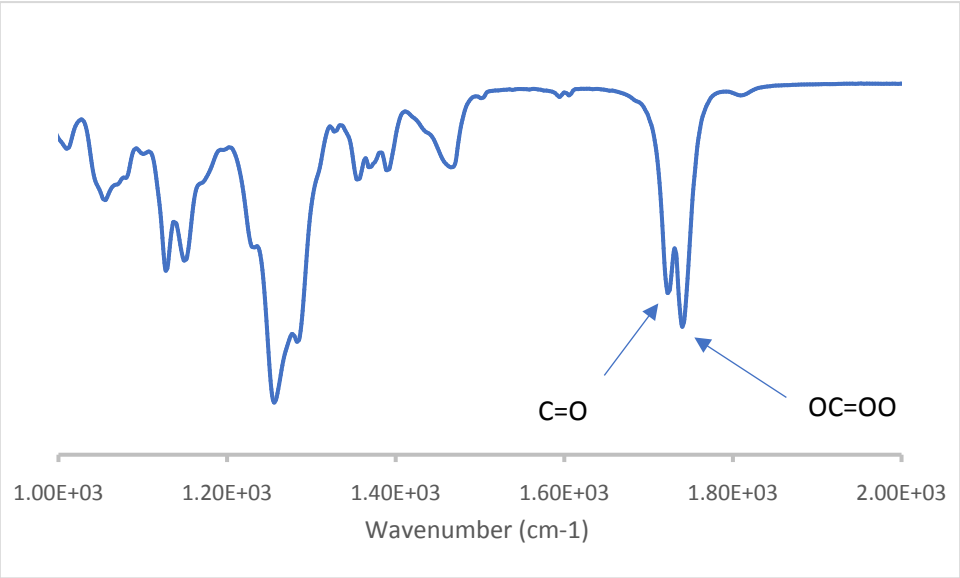
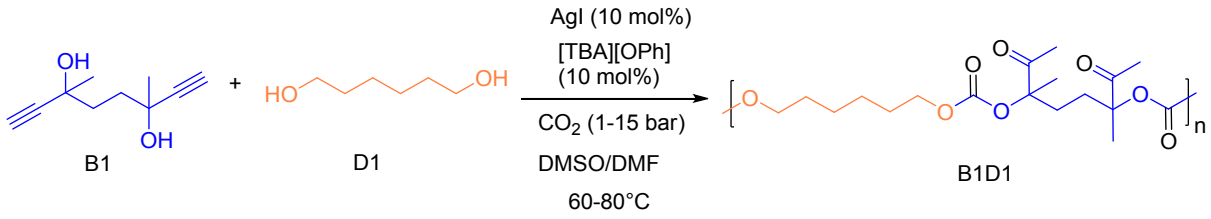


Figure S21. FT-IR spectrum of butyl(3,5-dimethyl-2-oxohexan-3-yl)carbonate

10. Characterizations of the poly(β-oxocarbonate) prepared by the one-pot cascade reaction.



Scheme S5: *Synthesis of poly(β-oxocarbonate) by one-pot cascade reaction*

10.1 SEC analyses of the crude samples reported in Table 4.

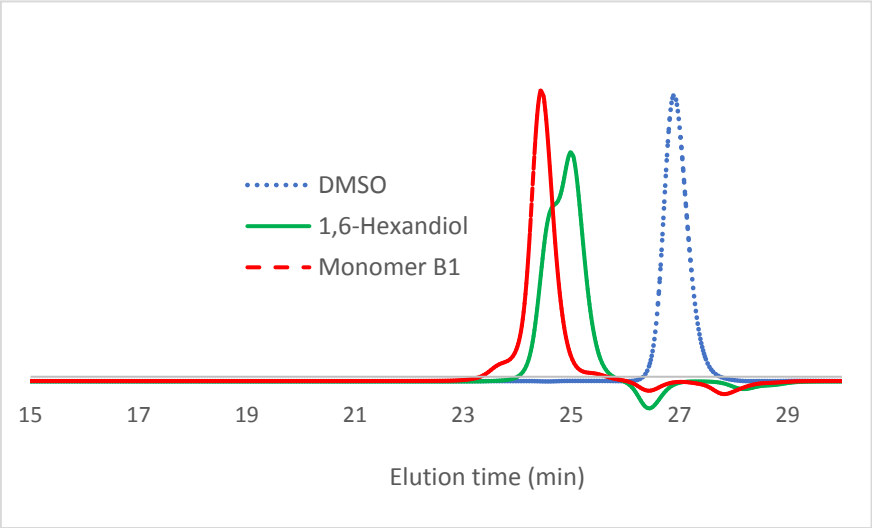


Figure S22. SEC chromatograms of monomer **B1** (- - -), 1,6-hexandiol (——) and DMSO (·····)

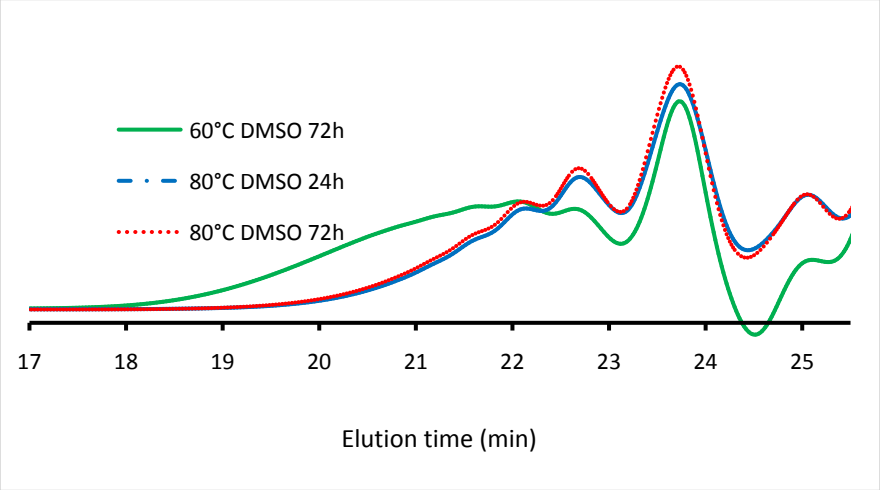


Figure S23. SEC chromatograms (before purification) of poly(ß-oxo-carbonate)s **B1D1** synthesized at 60 °C, 15 bar in DMSO, after 72 h (——), at 80 °C, 15 bar after 24 h (– . – . –) or 72 h (·····) of reaction (Table 4, entries 3, 4 and 5).

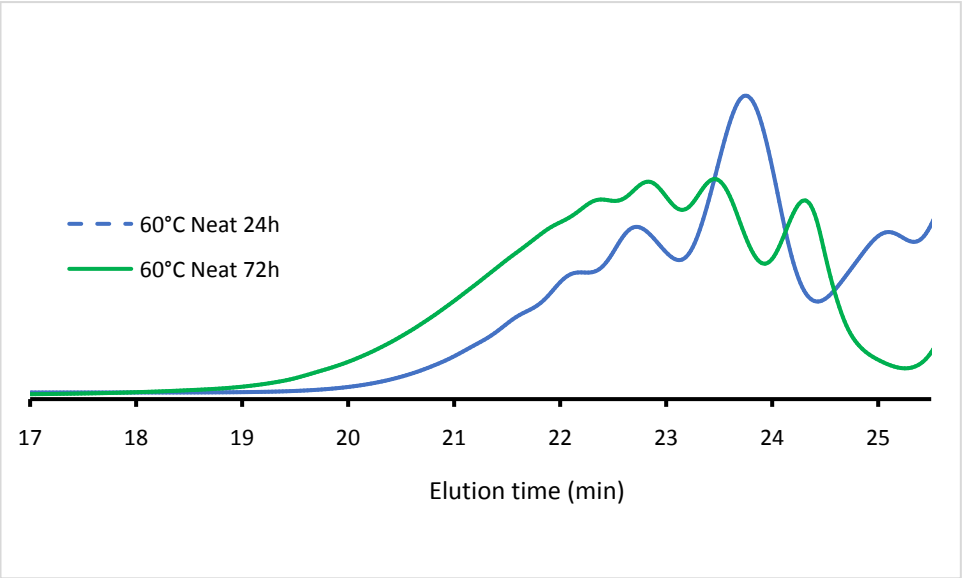


Figure S24. SEC chromatograms (before purification) of poly(ß-oxo-carbonate)s **B1D1** synthesized at 60 °C, 15 bar under neat conditions, after 24 h (- - -) or after 72 h (—) of reaction (Table 4, entries 6 and 7).

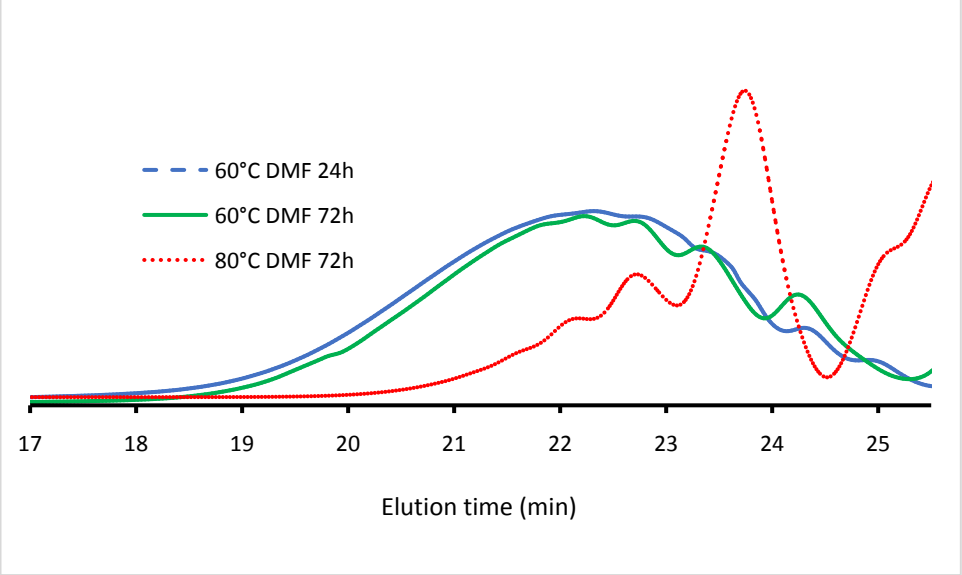


Figure S25. SEC chromatograms (before purification) of poly(ß-oxo-carbonate)s **B1D1** synthesized at 60 °C, 15 bar in DMF, after 24 h (- - -), after 72 h (—) or 80 °C, 15 bar after 72 h (.....) of reaction (Table 4, entries 8, 9 and 10).

10.2. Supplementary NMR characterizations.

The conversion of the 1,6-hexandiol was determined by using the following equation:

$$Conversion\ D1\ \% = \left(\frac{I_{3.38}}{(I_{4.06} + I_{3.38})}\right) \times 100 \qquad \textbf{Equation S9}$$

where $I_{3.38}$ corresponds to the intensity of the peak at 3.38 ppm (F) characteristic of the methylene linked to the OH function and group in α-position of the aromatic ring of the polymer and $I_{4.06}$ the intensity of peak at 4.06 ppm (G) characteristic of the methylene linked to the carbonate function of the poly(ß-oxo-carbonate).

Polymer B1D1

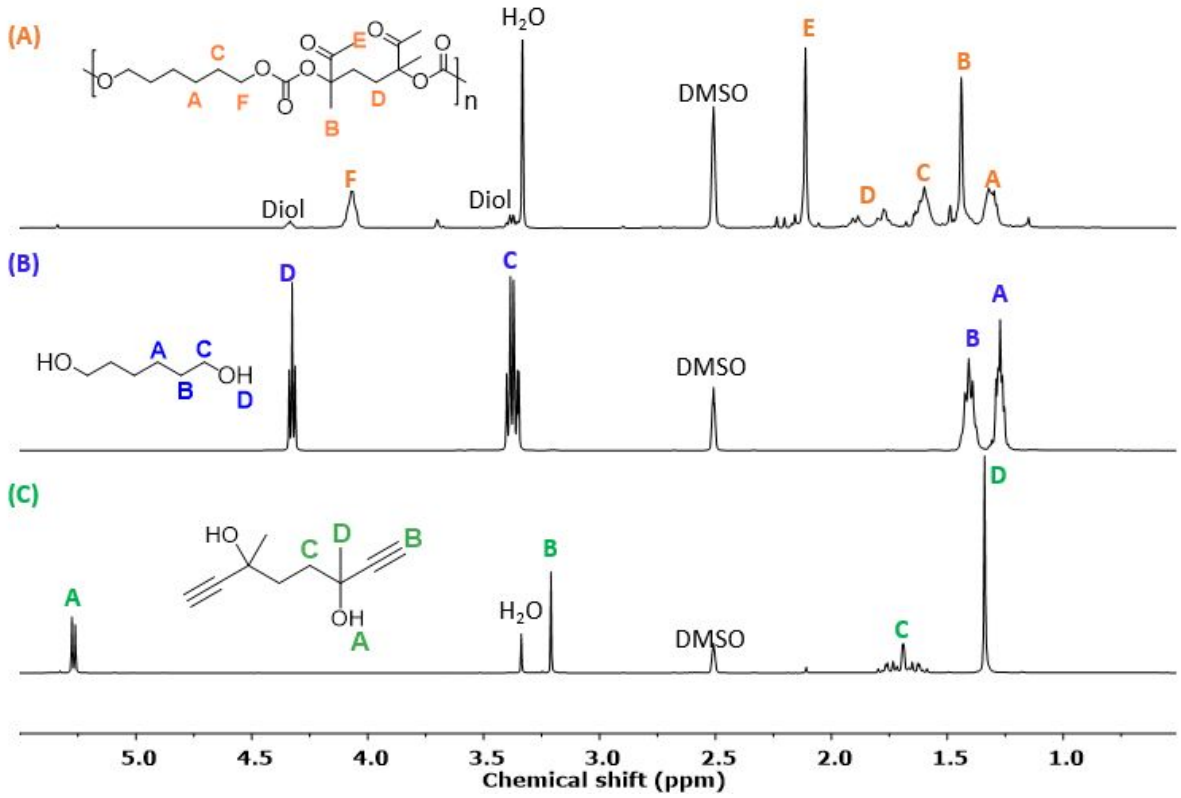


Figure S26. ^{1}H-NMR spectra (in DMSO-d_6) of (a) poly(ß-oxo-carbonate)s **B1D1**, (b) 1,6-hexandiol **D1** and (c) bis(propargylic alcohol) **B1**

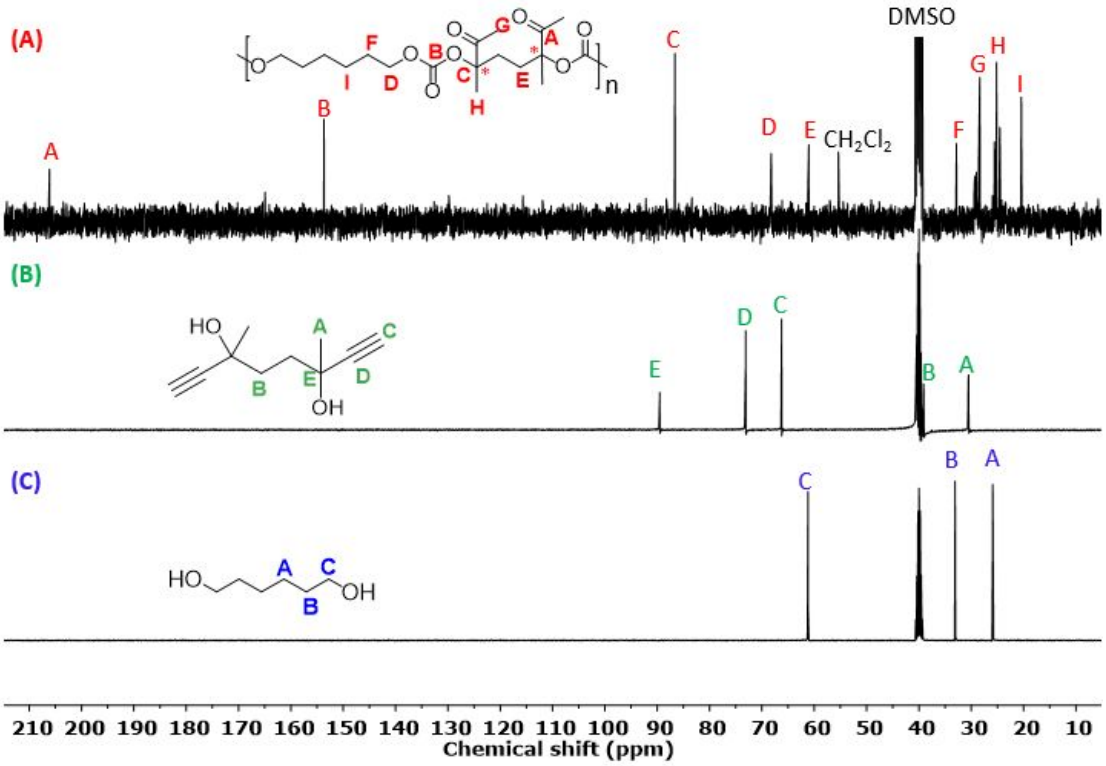


Figure S27. ^{13}C-NMR spectrum (in DMSO-d_6) of (a) poly(ß-oxo-carbonate)s **B1D1**,(b) bis(propargylic alcohol) **B1** and (c) 1,6-hexandiol **D1**

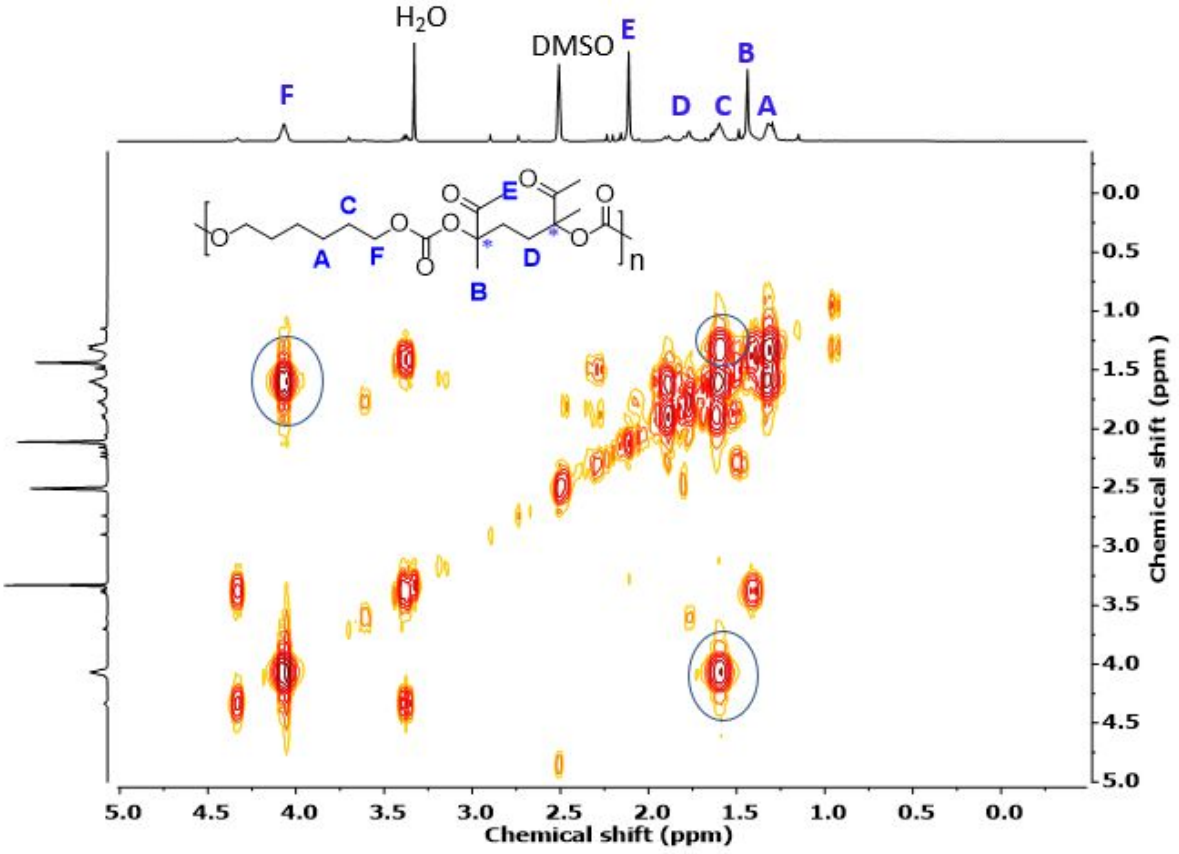


Figure S28. ^{1}H-^{1}H COSY spectrum in d_6-DMSO of poly(ß-oxo-carbonate)s **B1D1**

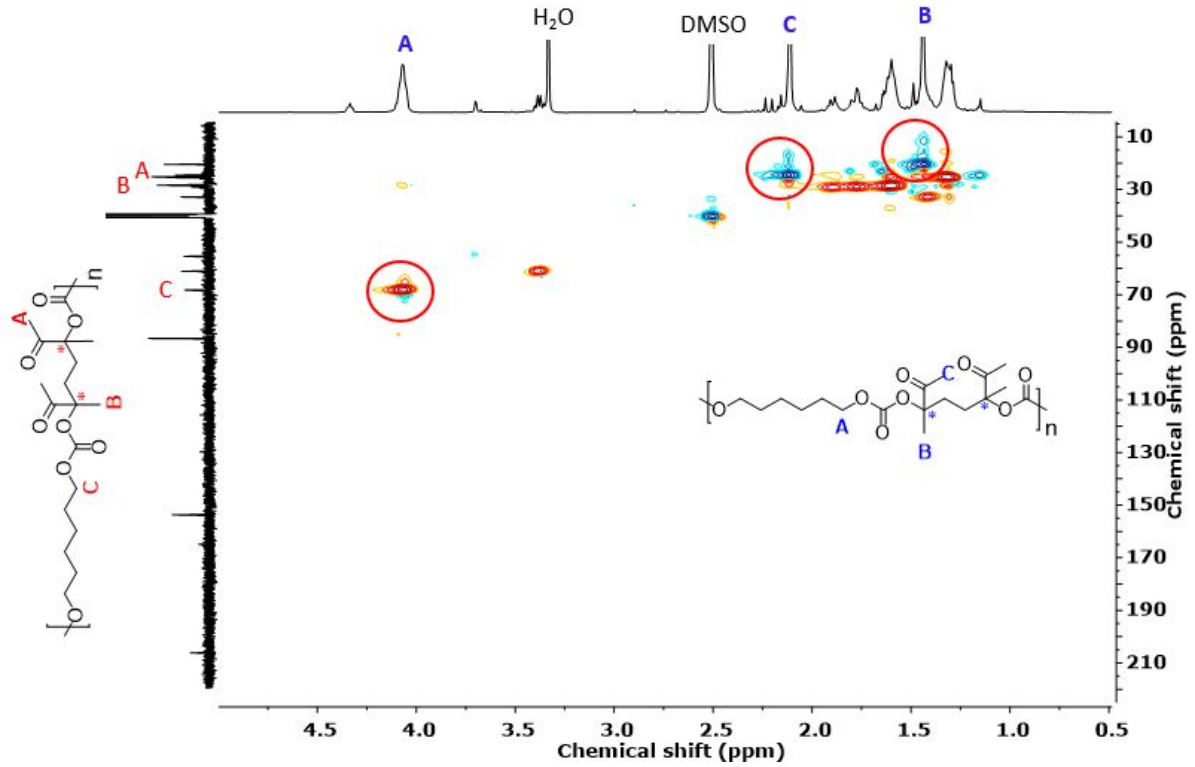


Figure S29. HSQC spectrum in d_6-DMSO of poly(ß-oxo-carbonate)s **B1D1**

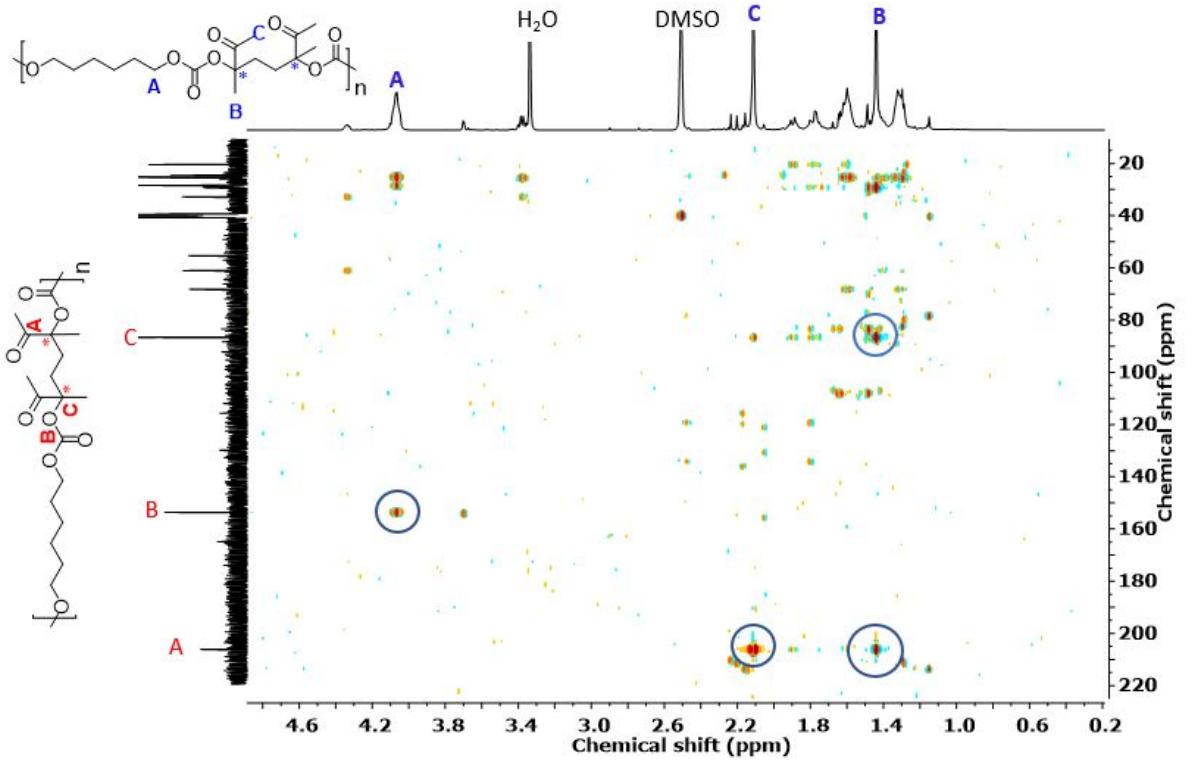


Figure S30. HMBC spectrum in d_6-DMSO of poly(ß-oxo-carbonate)s **B1D1**

Polymer B1D2

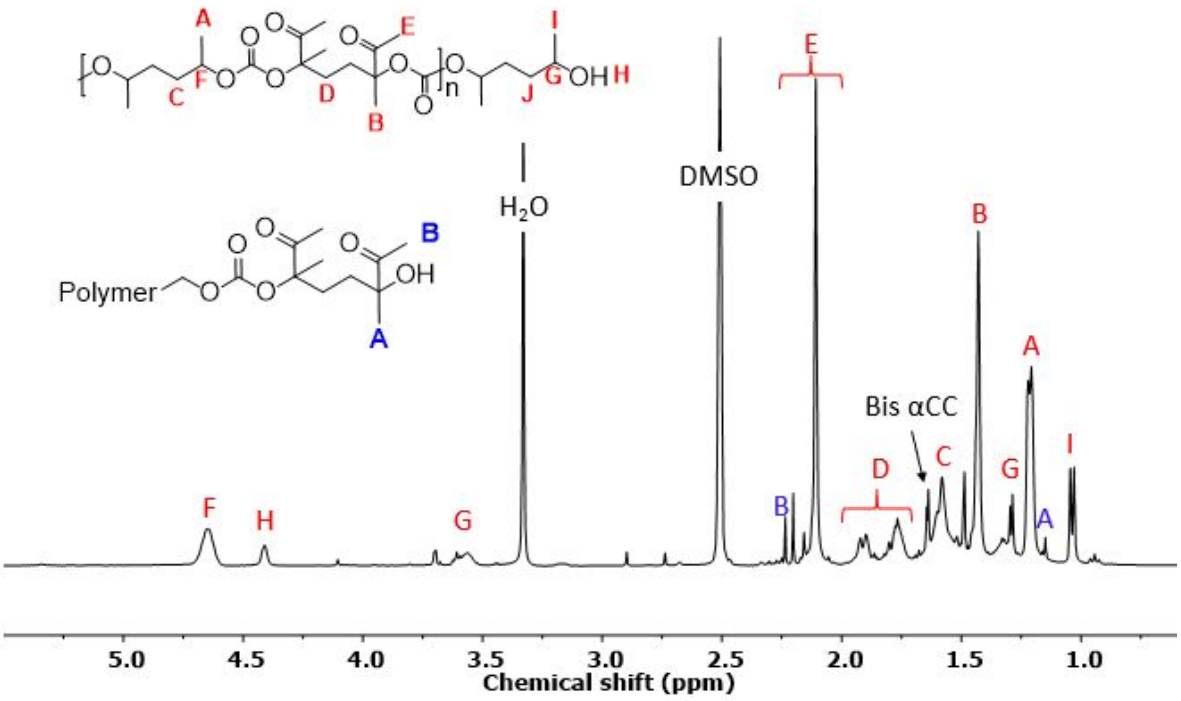


Figure S31. ^{1}H-NMR spectrum in d_6-DMSO of (a) poly(ß-oxo-carbonate)s **B1D2**, (b) bis(propargylic alcohol) **B1** and (c) 2,5-hexandiol **D2**.

Polymer B1D3

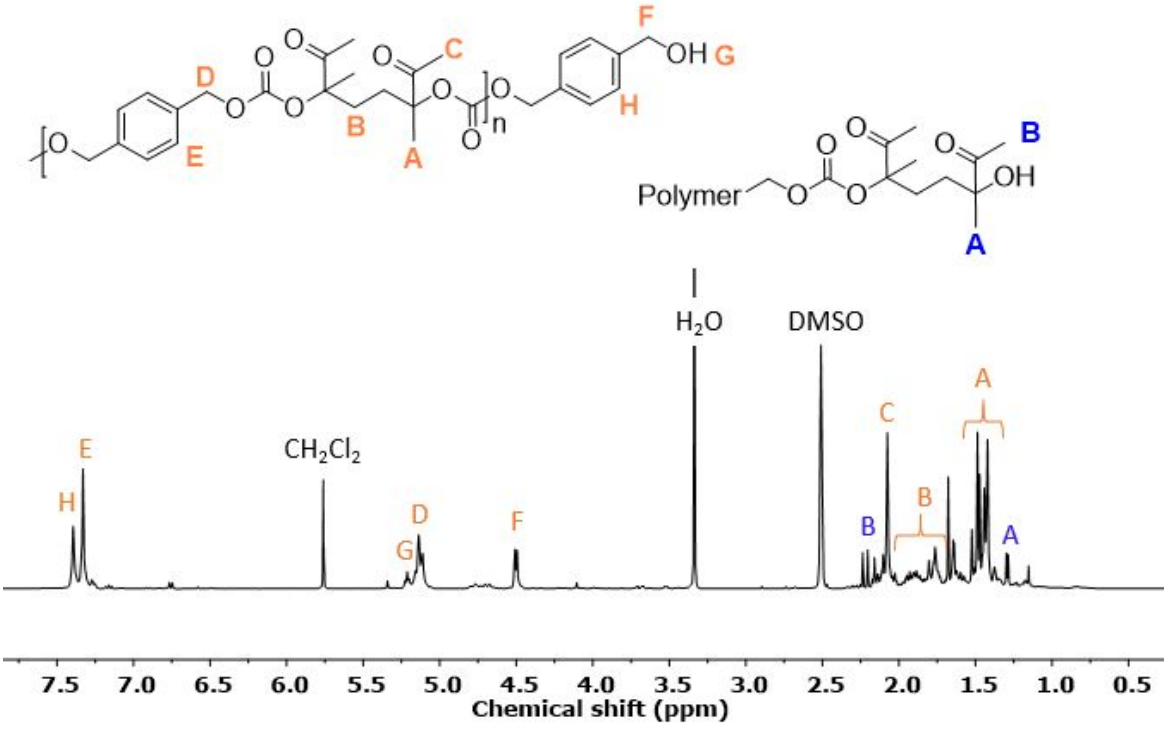


Figure S32. ^{1}H-NMR spectrum in d_6-DMSO of poly(ß-oxo-carbonate)s **B1D3**

Polymer B1D4

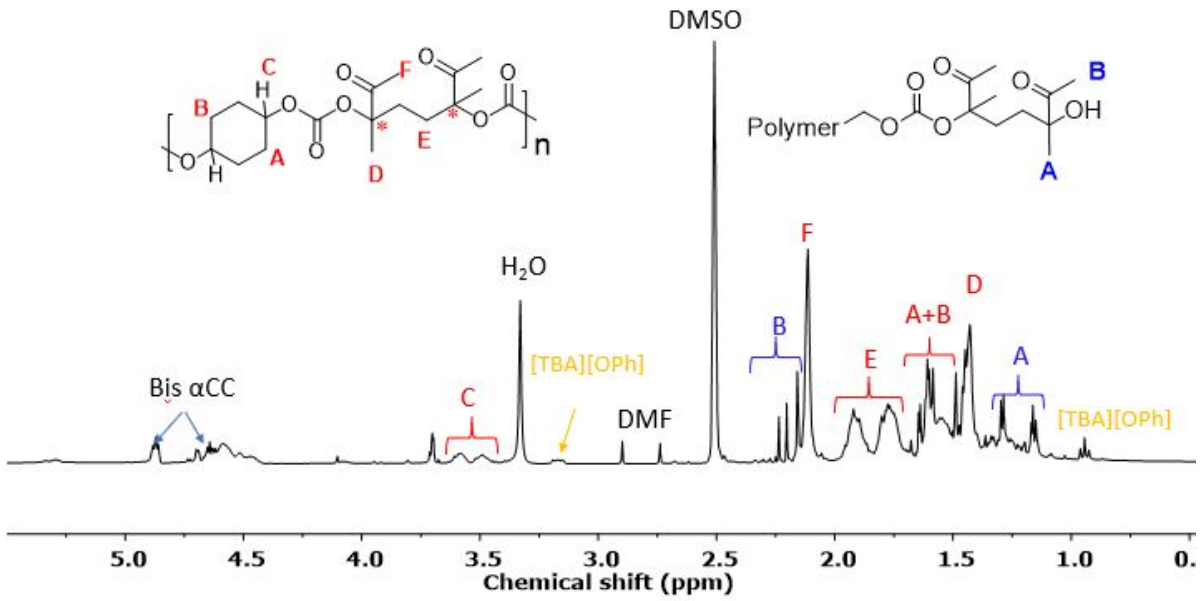


Figure S33. ^{1}H-NMR spectrum in d_6-DMSO of poly(ß-oxo-carbonate)s **B1D4**

Polymer B2D1

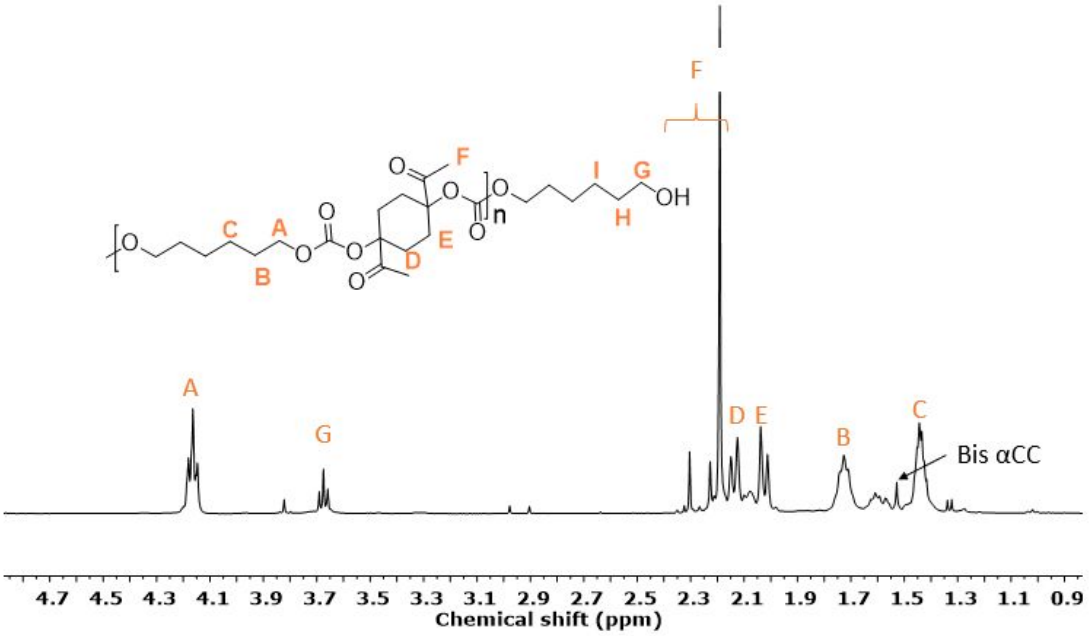


Figure S34. ^{1}H-NMR spectrum in in $CDCl_3$ of poly(ß-oxo-carbonate)s **B2D1**

Polymer B2D2

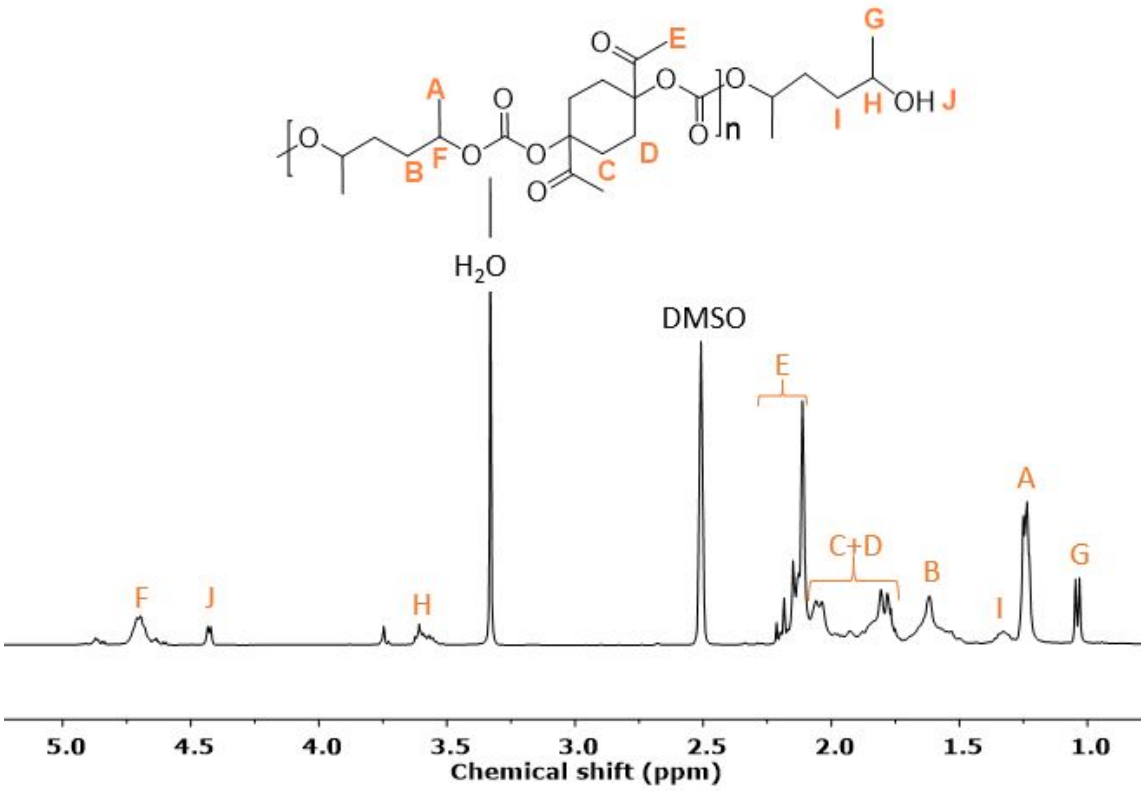


Figure S 25*:* ^{1}H-NMR spectrum in d_6-DMSO of poly(ß-oxo-carbonate)s B2D2 after removal of catalyst and DMF

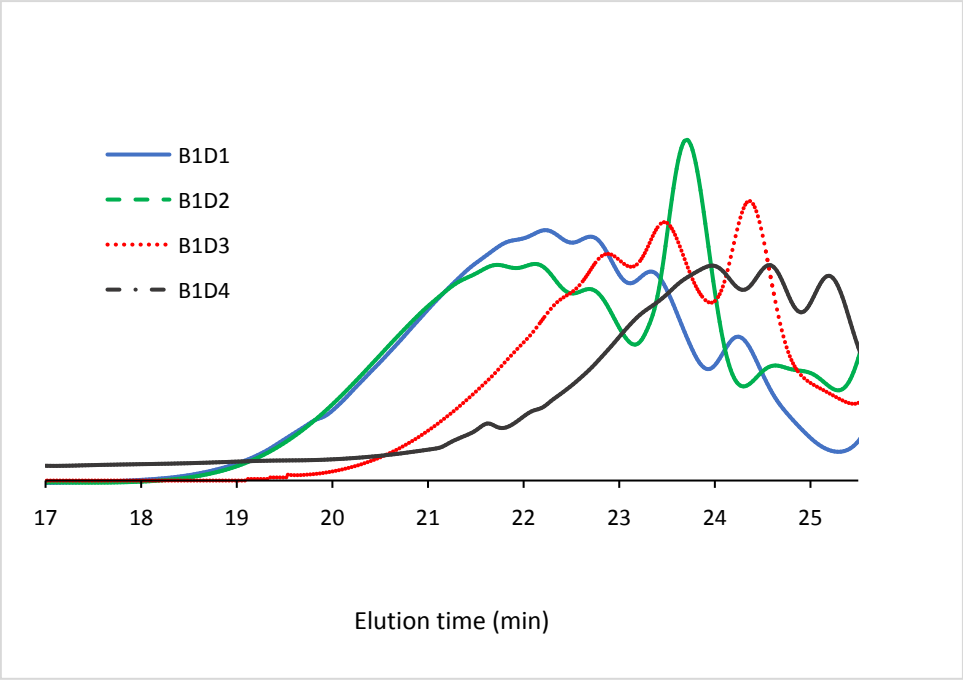


Figure S36. SEC chromatograms (before purification) of poly(ß-oxo-carbonate)s (a) B1D1, B1D2, B1D3 and B1D4, synthesized at 60 °C, 15 bar in DMF for 72 h.

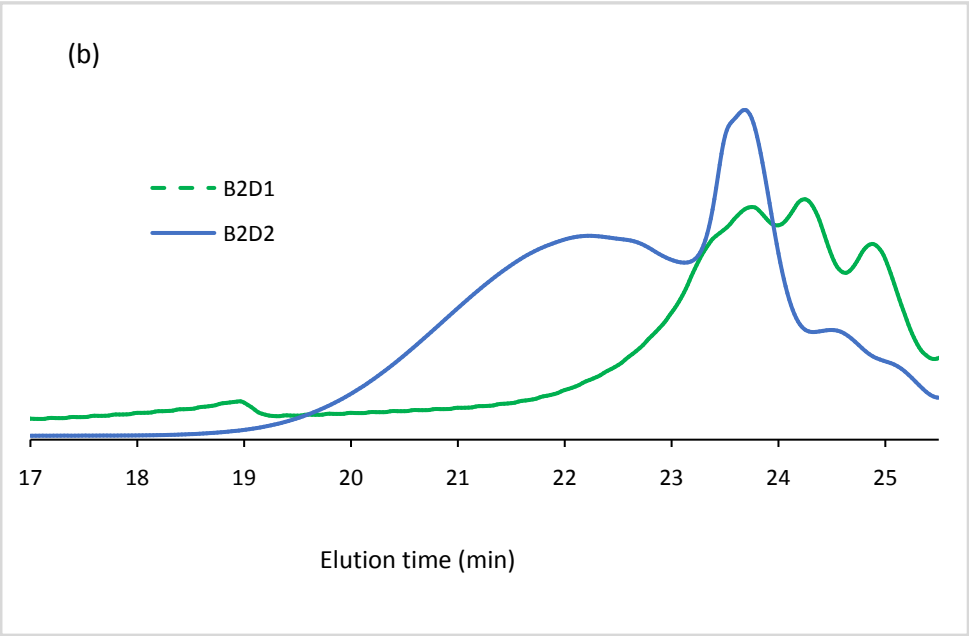


Figure S37. SEC chromatograms (before purification) of poly(ß-oxo-carbonate)s B2D1 and B2D2 synthesized at 60 °C, 15 bar in DMF for 72 h.

References:

[1] Hu, J.; Ma, J.; Lu, L.; Qian, Q.; Zhang, Z.; Xie, C.; Han, B. Synthesis of Asymmetrical Organic Carbonates Using CO2 as a Feedstock in AgCl/Ionic Liquid System at Ambient Conditions. *ChemSusChem* **2017**, *10* (6), 1292–1297. DOI 10.1002/cssc.201601773.

[2] Zhou, Z.-H.; Song, Q.-W.; Xie, J.-N.; Ma, R.; He, L.-N. Silver(I)-Catalyzed Three-Component Reaction of Propargylic Alcohols, CO2 and Monohydric Alcohols: Thermodynamically Feasible Access to Beta-Oxopropyl Carbonates. *Chem. Asian J.* **2016**, 11, 2067. DOI 10.1002/asia.201600600.