ELECTRONIC SUPPORTING INFORMATION

Very Efficient Organo-Zinc Scorpionates for the CO_2 Fixation into a Variety of Cyclic Carbonates: Synthesis, Coordination Ability and Catalytic Studies

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1) Materials and methods

General procedures. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or a glovebox. Solvents were predried over sodium wire and distilled under nitrogen from sodium (toluene and *n*-hexane) or sodium-benzophenone (THF and diethyl ether). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. The carbodiimides bis(*p*-tolyl)carbodiimide,[1] bis(*p*-trifluoromethylphenyl)carbodiimide,[1] the protioligand Hphbp^{t}amd,[2,3] and the sterically hindered scorpionate zinc-based complexes [ZnMe(κ^3-phbp^{t}amd)][4] (**4**) were prepared according to the literature procedures. All isocyanate and epoxide substrates were used as received unless specified otherwise (Aldrich, Across, Carbosynth). CO_2 (99.99%) was commercially obtained and used without further purification. All kinetics experiments were repeated at least twice and were mutually consistent.

Instruments and measurements

NMR spectra were recorded on a Varian Inova FT-500 spectrometer and were referenced to the residual deuterated solvent signal. ^{1}H NMR homodecoupled and NOESY-1D spectra were recorded on the same instrument with the following acquisition parameters: irradiation time 2 s and 256 scans, using standard VARIAN-FT software. 2D NMR spectra were acquired using the same software and processed using an IPC-Sun computer.

2) Preparation of Compounds 1−3 and Complexes 5−6

Synthesis of bis(3,5-ditrifluoromethylphenyl)carbodiimide (1). In a 100 mL Schlenk tube equipped with a magnetic stirring bar, 3,5-bis(trifluoromethyl)phenyl isocyanate (2.5 mL, 17.5 mmol) was placed and cooled to 0 ºC. Under nitrogen and vigorous agitation, 3-methyl-1-phenylphospholene 1-oxide (170 mg, 0.88 mmol) was then added and vigorous bubbling inside the flask was immediately observed. The Schlenk flask was connected to an oil bubbler to allow exiting the carbon dioxide formed. The mixture was kept stirring at the same temperature until no more gas formation was observed in the bubbler. The white solid formed was then washed with dry *n*-hexane (2 × 25 mL), and purified by flash chromatography using a solvent gradient of hexane-EtOAc (9:1), to give the pure carbodiimine identified as **1** (3.7 g, 8.0 mmol, 91%). Anal. Calcd. for $C_{17}H_6F_{12}N_2$: C, 43.80; H, 1.30; N, 6.01. Found: C, 43.90; H, 1.45; N, 6.05. ^{1}H-NMR (400 MHz, C_6D_6, 297 K), δ 7.74 (m, 2 H, $NC_6H_3(CF_3)_2$), 7.63 (m, 4 H, $NC_6H_3(CF_3)_2$). ^{13}C-{^{1}H}-NMR (100 MHz, C_6D_6, 297 K), δ 138.9 (C^b), 133.3 ($J^2_{C\text{-}F}$=34.0 Hz), 131.6, 124.7, ($NC_6H_3(CF_3)_2$), 122.7 ($J^1_{C\text{-}F}$=271 Hz, $C_6H_3(CF_3)_2$), 119.8 $NC_6H_3(CF_3)_2$ ($J^3_{C\text{-}F}$=3.8 Hz).

Synthesis of HFphbp^{t}amd (2). In a 250 mL Schlenk tube, a solution of Bu^{n}Li (1.6 M in hexane) (1.68 mL, 2.68 mmol) was added dropwise to a cooled (-70 °C) stirred solution of bdtbpzm (1.00 g, 2.68 mmol) in THF (70 mL), and the resulting suspension was maintained at this temperature over a period of 1 h. Then, a solution of bis(*p*-trifluoromethylphenyl)carbodiimide (0.89 g, 2.68 mmol) in THF (30 mL) was added dropwise to the suspension and stirred for 1 h at room temperature. The solvent was evaporated to dryness under reduced pressure, and the resulting sticky yellow pale product was washed with hexane (20 mL). The resulting powder was dissolved in diethyl ether (70 mL) and a saturated solution of NH_4Cl in water (40 mL) was added. The organic product was extracted with diethyl ether (3 × 30 mL), the organic layers were combined, dried over $MgSO_4$, filtered, and the volatiles removed from the filtrate under reduced pressure to yield the title compound as a yellow pale solid. After concentration and cooled at –26 ºC, compound **2** was obtained as

colourless crystals. Yield: 1.73 g, 92 %. Anal. Calcd. for $C_{38}H_{48}F_6N_6$: C, 64.94; H, 6.88; N, 11.96. Found: C, 65.03; H, 6.80; N, 12.04. ^{1}H-NMR (400 MHz, $CDCl_3$, 297 K), δ 7.55 (m, 4 H, $NC_6\underline{H}_4$-*p*-CF_3), δ 7.45 (d, $^3J_{H-H}$ = 8.2 Hz, 2 H, $NC_6\underline{H}_4$-*p*-CF_3), δ 7.17 (s, 1 H, *H*-NC_6H_4-*p*-CF_3), δ 6.96 (s, 1 H, CH), 6.64 (d, $^3J_{H-H}$ = 8.2 Hz, 2 H, $NC_6\underline{H}_4$-*p*-CF_3), 5.98 (s, 2 H, H^4), 1.24 (s, 18 H, $^tBu^5$), 1.09 (s, 18 H, $^tBu^3$). ^{13}C-{^{1}H}-NMR (100 MHz, $CDCl_3$, 297 K), δ 160.8 (C^b), 152.0, 151.0 ($C^{3,3'or5,5'}$), 151.5 ($N\underline{C}_6H_4CF_3$), 142.8 ($HN\underline{C}_6H_4CF_3$), 126.2 (J^3_{C-F} =3.7 Hz, $N\underline{C}_6H_4CF_3$), 126.0 (J^3_{C-F} =3.6 Hz, $HN\underline{C}_6H_4CF_3$), 125.0 (J^2_{C-F} =32.3 Hz, $N\underline{C}_6H_4CF_3$), 124.5 (J^2_{C-F} =32.4 Hz, $HN\underline{C}_6H_4CF_3$), 124.5 (J^1_{C-F} =271 Hz, $N\underline{C}_6H_4CF_3$), 124.4 (J^1_{C-F} =271 Hz, $HN\underline{C}_6H_4CF_3$), 121.3 ($N\underline{C}_6H_4CF_3$), 119.2 ($HN\underline{C}_6H_4CF_3$), 102.7 (C^4), 71.5 (C^a), 32.0, 31.5 (ipso $^tBu^3$ y $^tBu^5$), 30.2, 29.9 ($^tBu^3$ y $^tBu^5$).

Synthesis of HF_2phbp^{t}amd (3). The synthesis of **3** was carried out in an identical manner to **2** and was obtained as a white solid. Bu^nLi (1.6 M in hexane) (1.68 mL, 2.68 mmol), bdtbpzm (1.00 g, 2.68 mmol), bis(3,5-ditrifluoromethylphenyl)carbodiimide (**1**) (1.25 g, 2.68 mmol).Yield: 2.11 g, 94 %. Anal. Calcd. for $C_{40}H_{46}F_{12}N_6$: C, 57.27; H, 5.53; N, 10.02. Found: C, 57.41; H, 5.63; N, 9.93. ^{1}H-NMR (400 MHz, $CDCl_3$, 297 K), δ 7.90 (s, 2 H, $NC_6\underline{H}_3$-3,5-$(CF_3)_2$), δ 7.54 (s, 1 H, $NC_6\underline{H}_3$-3,5-$(CF_3)_2$), δ 7.48 (s, 1 H, $NC_6\underline{H}_3$-3,5-$(CF_3)_2$), δ 7.30 (s, 1 H, *H*-$NC_6\underline{H}_3$-3,5-$(CF_3)_2$), δ 6.95 (s, 2 H, $NC_6\underline{H}_3$-3,5-$(CF_3)_2$), δ 6.92 (s, 1 H, CH), 6.00 (s, 2 H, H^4), 1.23 (s, 18 H, $^tBu^5$), 1.07 (s, 18 H, $^tBu^3$). ^{13}C-{^{1}H}-NMR (100 MHz, $CDCl_3$, 297 K), δ 161.2 (C^b), 152.6, 149.6 ($C^{3,3'or5,5'}$), 152.2 ($N\underline{C}_6H_4CF_3$), 140.9 ($HN\underline{C}_6H_4CF_3$), 132.4 (J^2_{C-F} =33 Hz, $N\underline{C}_6H_4CF_3$), 132.2 (J^2_{C-F} =33 Hz, $HN\underline{C}_6H_4CF_3$), 123.2 (J^1_{C-F} =271 Hz, $N\underline{C}_6H_4CF_3$), 123.2 (J^1_{C-F} =271 Hz, $HN\underline{C}_6H_4CF_3$), 121.4($N\underline{C}_6H_4CF_3$), 119.7 ($HN\underline{C}_6H_4CF_3$), 116.6 (J^3_{C-F} =3.7 Hz, $N\underline{C}_6H_4CF_3$), 116.5 (J^3_{C-F} =3.8 Hz, $HN\underline{C}_6H_4CF_3$), 103.2 (C^4), 71.5 (C^a), 32.1, 31.5 (ipso $^tBu^3$ y $^tBu^5$), 30.1, 29.8 ($^tBu^3$ y $^tBu^5$).

Synthesis of [ZnMe(*κ*^{3}-Fphbp^{t}amd)] (5). In a 100 mL Schlenk tube, HFphbp^{t}amd (1.00 g, 1.42 mmol) was dissolved in dry *n*-hexane (25 mL) and cooled to −70 ºC. A solution of $ZnMe_2$ (1.2 M in toluene) (1.18 mL, 1.42 mmol) was added and the mixture was allowed to warm up to room temperature and stirred for 6 hours. After concentration and cooled at −26 ºC, compound **5** was

obtained as colourless crystals. Yield: 0.96 g, 86 %. Anal. Calcd. for $C_{39}H_{50}F_6N_6Zn$: C, 59.88; H, 6.44; N, 10.74 Found: C, 60.04; H, 6.61; N, 10.62. ^{1}H-NMR (400 MHz, C_6D_6, 297 K), δ 7.83 (s, 1 H, CH), 7.05 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2 H, $NC_6\underline{H}_4$-*p*-CF_3), 6.99 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2 H, $NC_6\underline{H}_4$-*p*-CF_3), 6.68 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2 H, $NC_6\underline{H}_4$-*p*-CF_3), 6.50 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2 H, $NC_6\underline{H}_4$-*p*-CF_3), 6.03 (s, 2 H, H^4), 1.35 (s, 18 H, ^{t}Bu^5), 1.34 (s, 18 H, ^{t}Bu^3), 0.15 (s, 3 H, ZnMe). ^{13}C-{^{1}H}-NMR (100 MHz, C_6D_6, 297 K), δ 163.6 (C^b), 156.4, 155.3 ($C^{3,3'or5,5'}$), 153.9, 152.0, 125.4 ($J^1_{C\text{-}F}$ =269 Hz), 125.1 ($J^3_{C\text{-}F}$ =3.9 Hz), 123.2, 122.9 ($J^2_{C\text{-}F}$ =32.3 Hz), 122.6 ($J^2_{C\text{-}F}$ =31.9 Hz), 121.5, 103.2 (C^4), 76.0 (C^a), 32.5 (ipso-^{t}Bu^3), 32.3 (ipso-^{t}Bu^5), 31.0 (^{t}Bu^3), 30.2 (^{t}Bu^5),-7.3 (ZnMe).

Synthesis of [ZnMe(*κ*^{3}-F_2phbp^{t}amd)] (6). The synthesis of **6** was carried out in an identical manner to **5** and was obtained as an orange solid. HF_2phbp^{t}amd (1.00 g, 1.19 mmol), $ZnMe_2$ (1.2 M in toluene) (1.00 mL, 1.19 mmol). Yield: 0.95 g, 87 %. Anal. Calcd. for $C_{41}H_{48}F_{12}N_6Zn$: C, 53.63; H, 5.27; N, 9.15. Found: C, 53.79; H, 5.39; N, 9.05. ^{1}H-NMR (400 MHz, C_6D_6, 297 K), δ 7.79 (s, 1 H, CH), 7.30 (s, 2 H, $NC_6\underline{H}_3$-3,5-$(CF_3)_2$), 7.11 (s, 2 H, $NC_6\underline{H}_3$-3,5-$(CF_3)_2$), 7.07 (s, 2 H, $NC_6\underline{H}_3$-3,5-$(CF_3)_2$), 5.97 (s, 2 H, H^4), 1.29 (s, 18 H, ^{t}Bu^5), 1.28 (s, 18 H, ^{t}Bu^3), 0.21 (s, 3 H, ZnMe). ^{13}C-{^{1}H}-NMR (100 MHz, C_6D_6, 297 K), δ 164.3 (C^b), 158.8, 155.7 ($C^{3,3'or5,5'}$), 151.6, 150.1, 131.9 ($J^2_{C\text{-}F}$ =32.5 Hz), 123.8 ($J^1_{C\text{-}F}$ =285 Hz), 122.4, 121.2, 114.2 ($J^3_{C\text{-}F}$ =3.6 Hz), 103.4 (C^4), 75.5 (C^a), 32.3 (ipso-^{t}Bu^3, ipso-^{t}Bu^5), 30.8 (^{t}Bu^3), 30.0 (^{t}Bu^5),-7.3 (ZnMe).

3) Spectroscopy Details of Compounds 1−3 and Complexes 5−6

Figures S1–S5. ^{1}H and ^{13}C-^{1}H NMR spectra of compounds **1**−**3** and complexes **5**−**6**

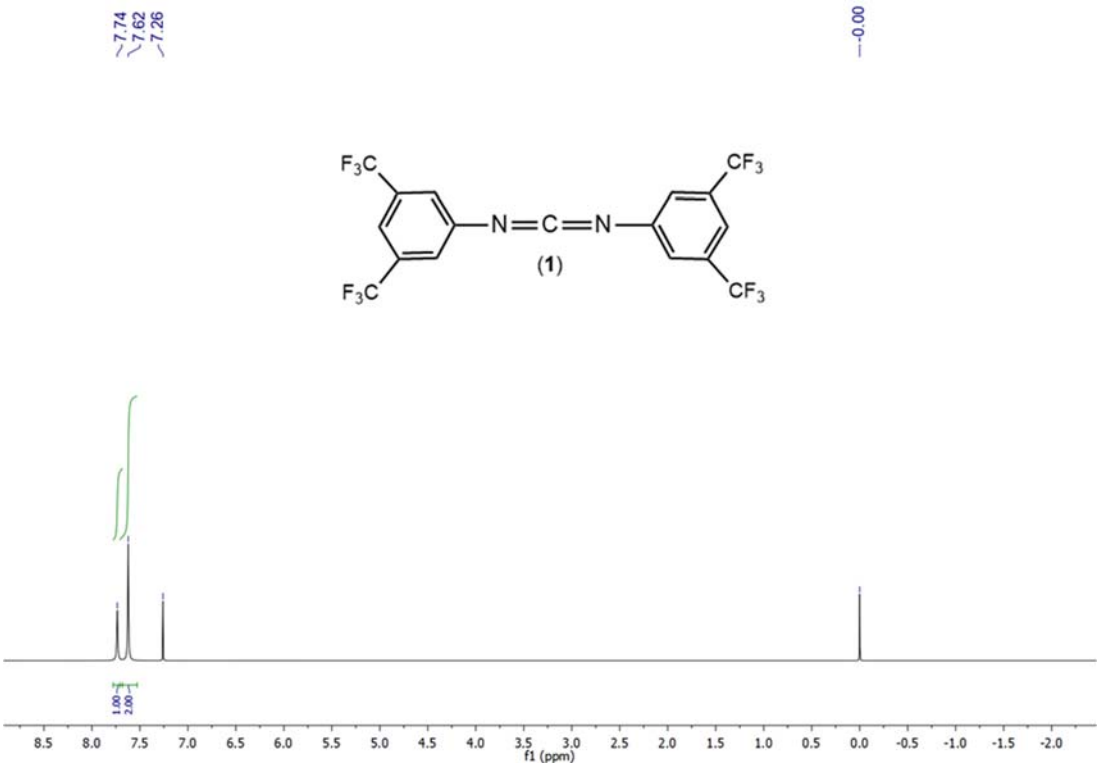

Figure S1a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for compound **1**.

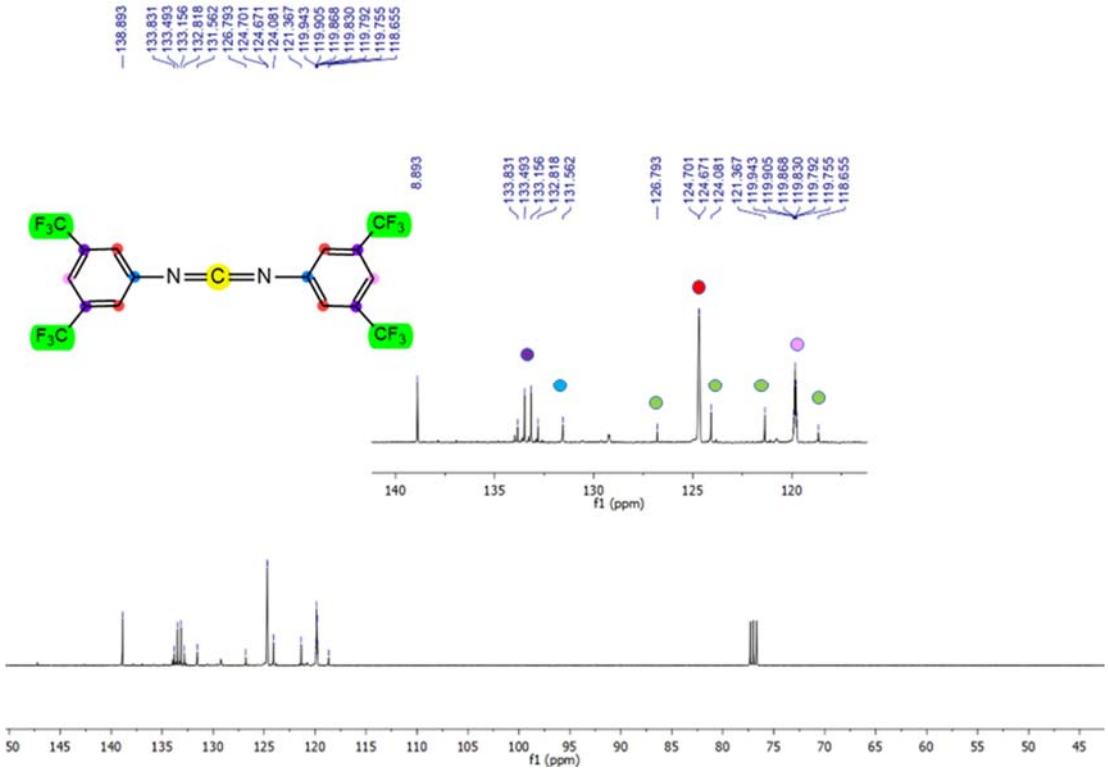

Figure S1b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for compound **1**.

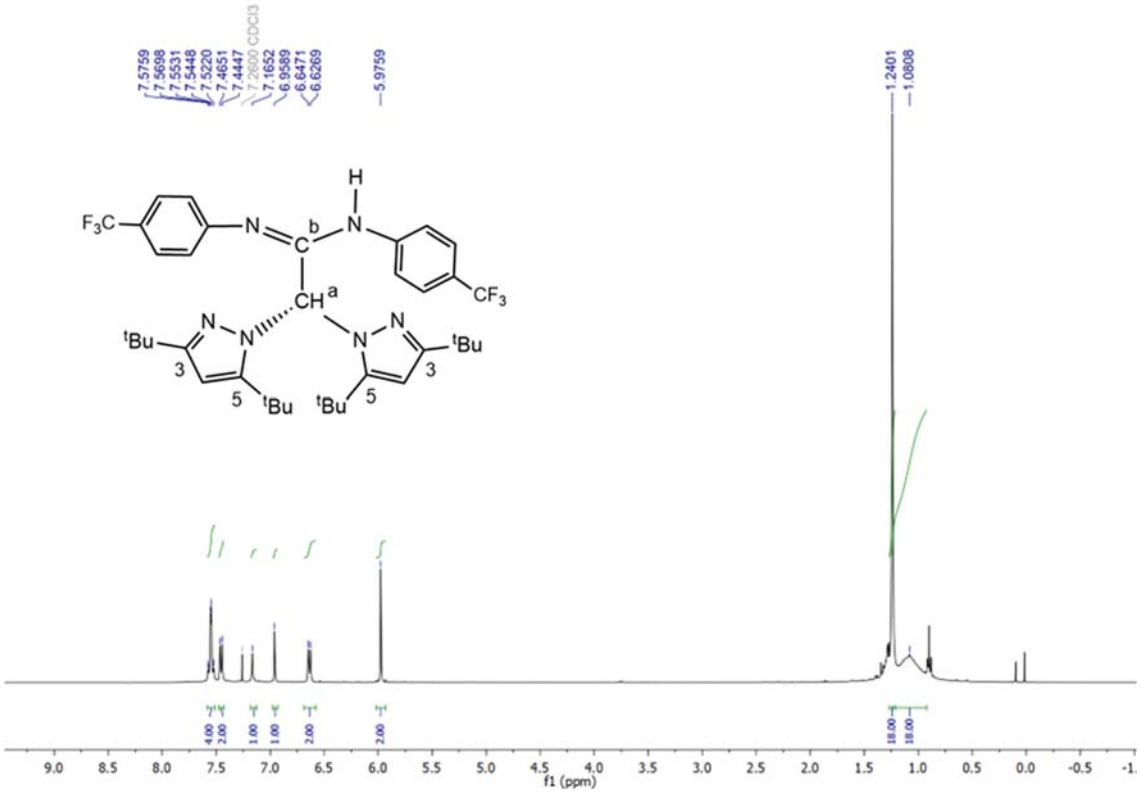

Figure S2a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for compound **2**.

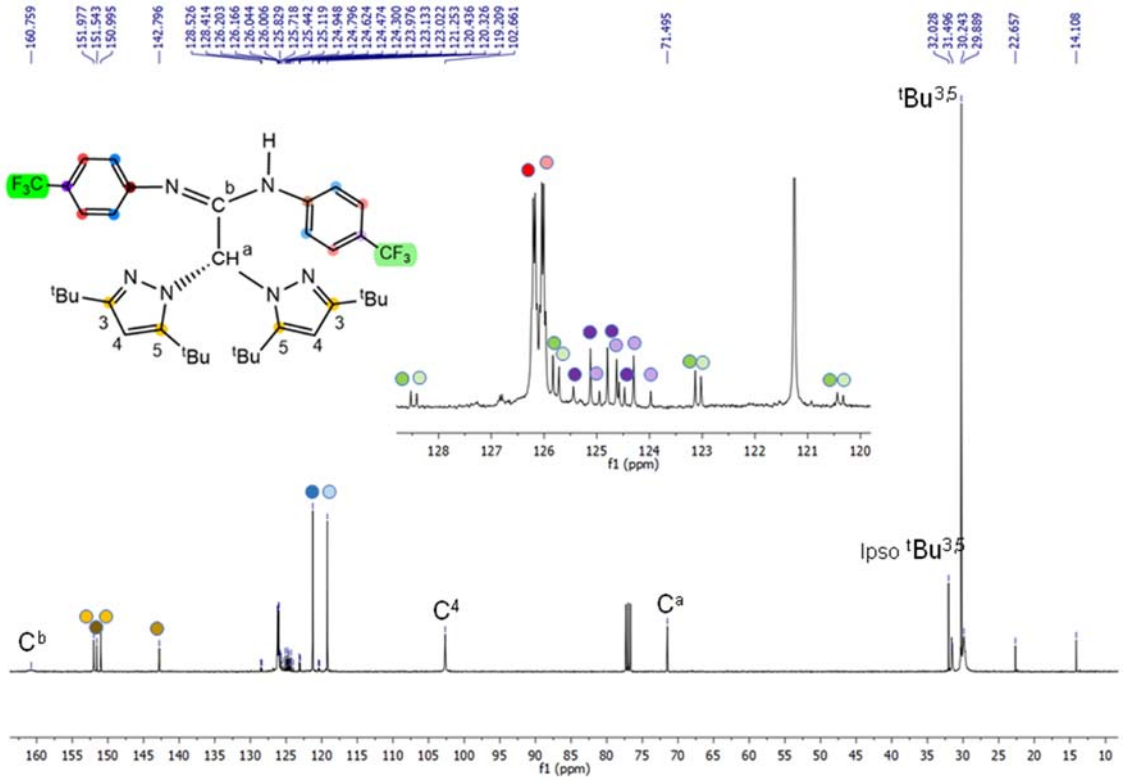

Figure S2b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for compound **2**.

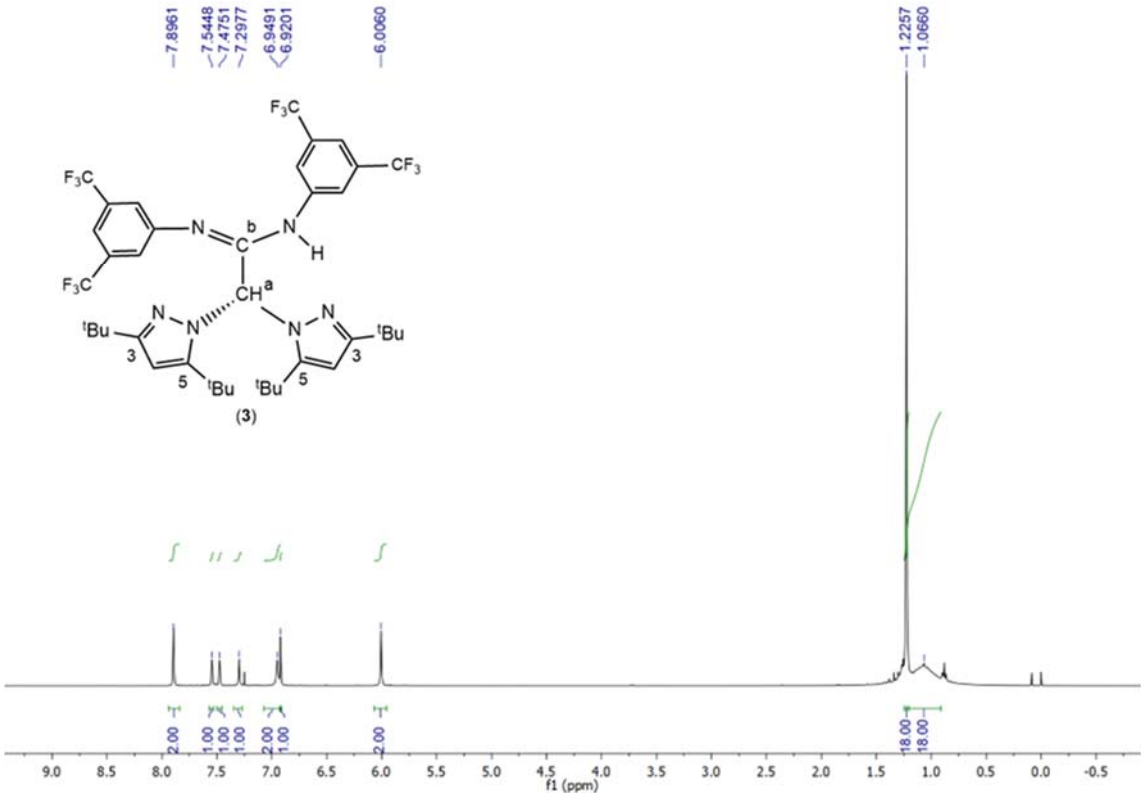

Figure S3a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for compound **3**.

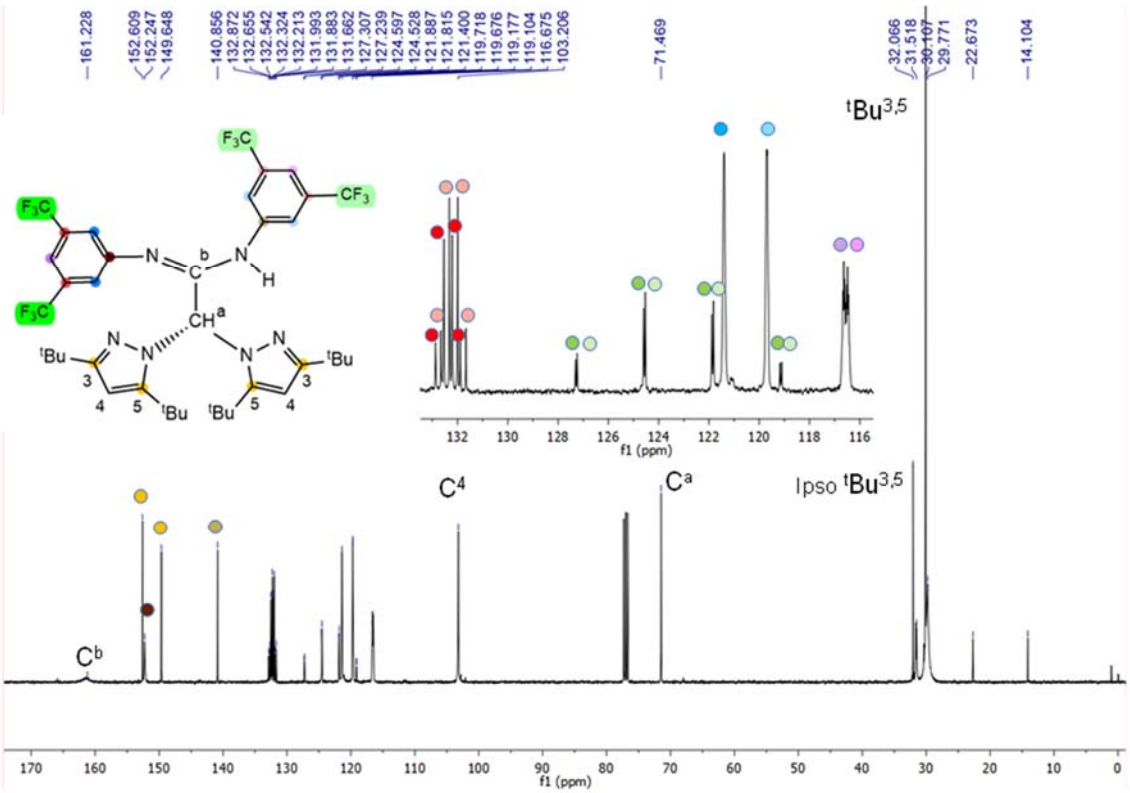

Figure S3b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for compound **3**.

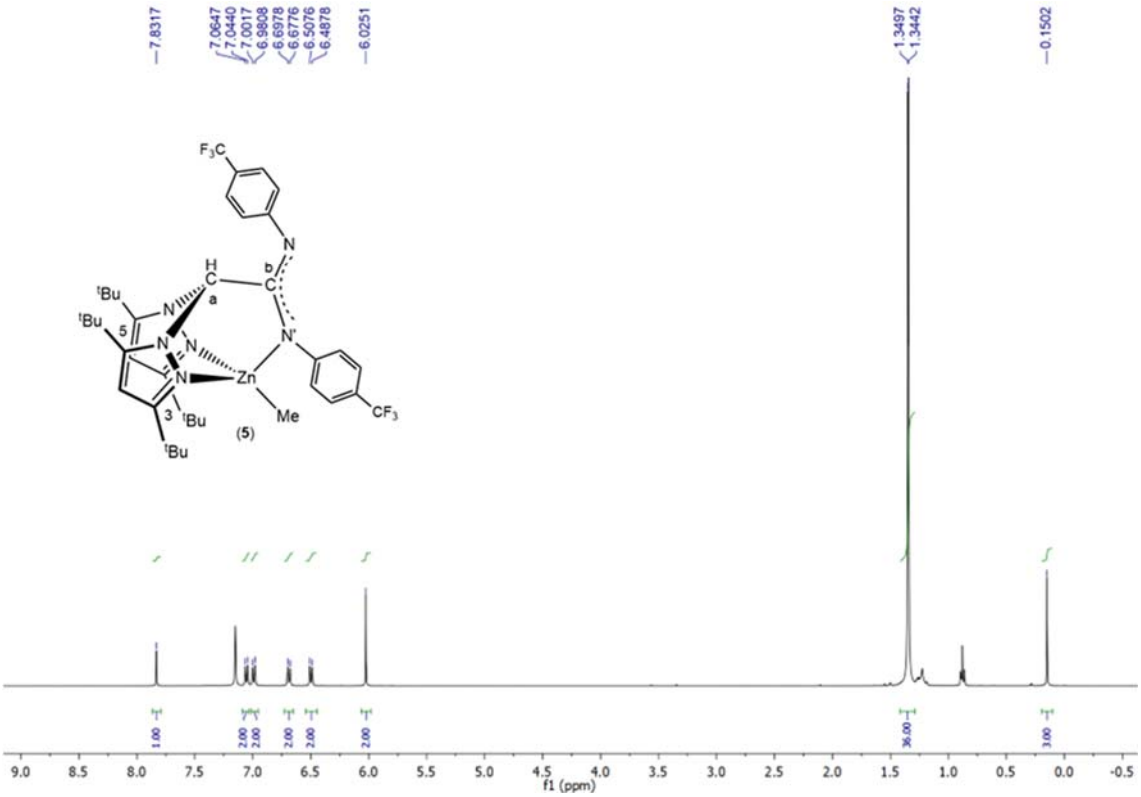

Figure S4a. ^{1}HNMR spectrum (400 MHz, 297 K, C_6D_6) for complex **5**.

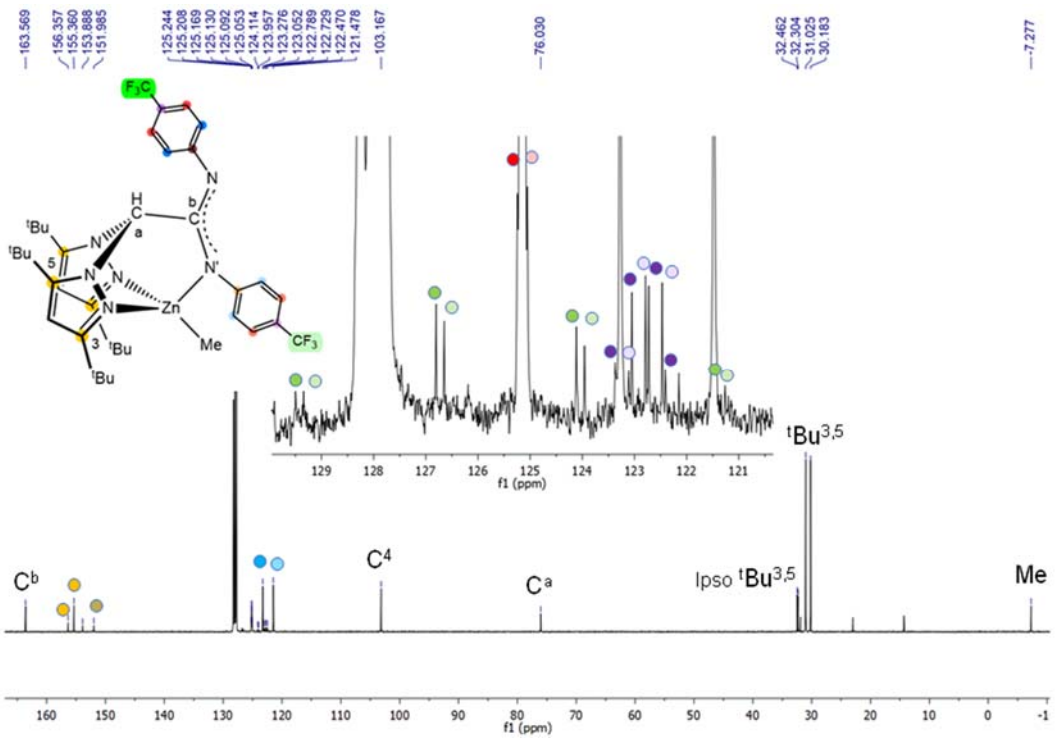

Figure S4b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, C_6D_6) for complex **5**.

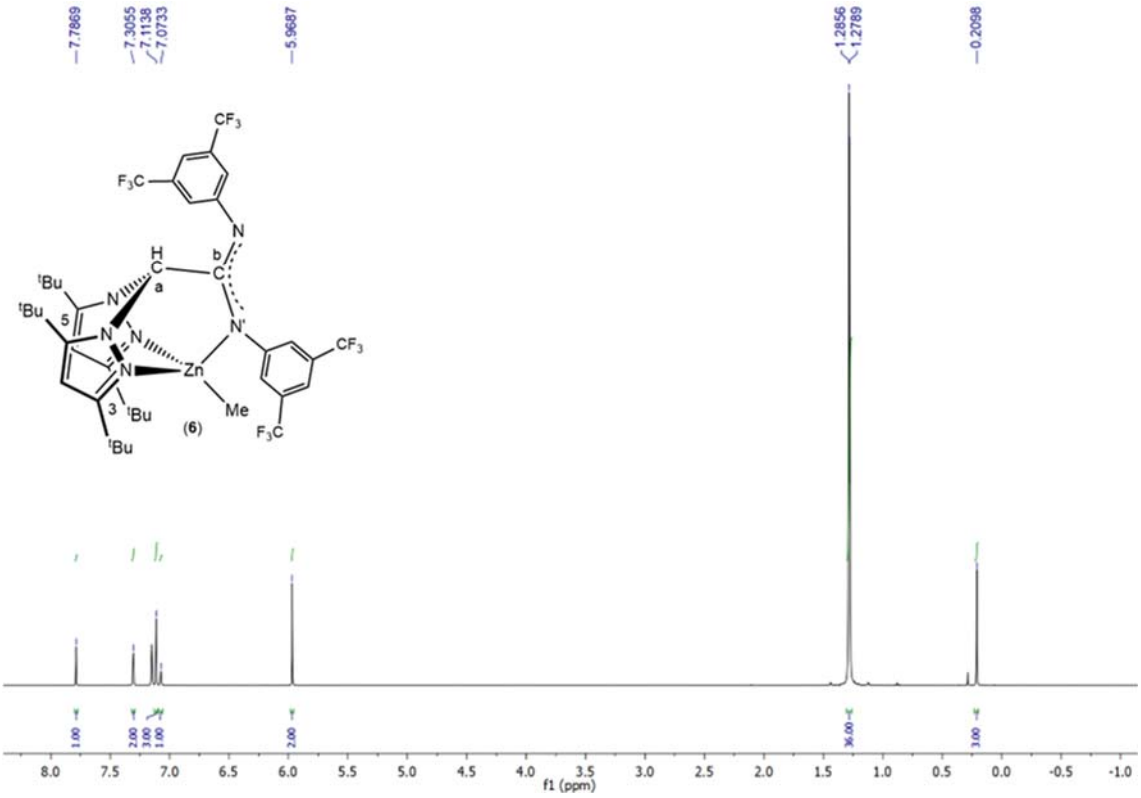

Figure S5a. ^{1}HNMR spectrum (400 MHz, 297 K, C_6D_6) for complex **6**.

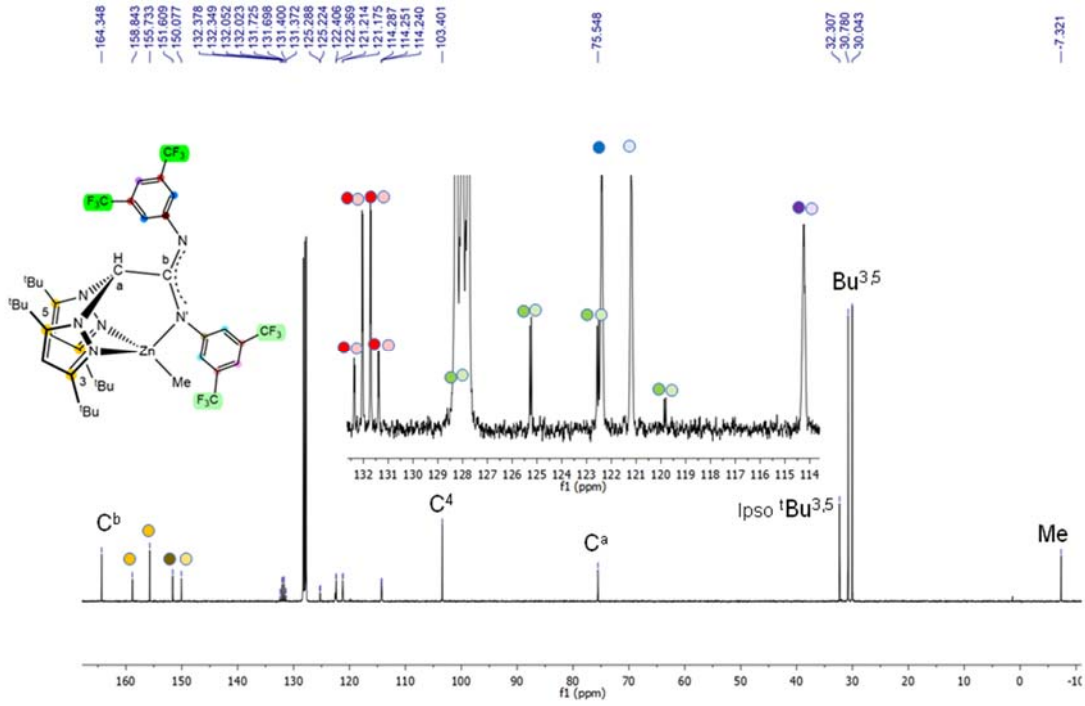

Figure S5b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, C_6D_6) for complex **6**.

4) X-Ray Diffraction Studies: Crystallographic Structure Determination for the Compound 2 and Complex 5.

Details for crystallographic studies and structural refinement.

Crystals suitable for X-ray diffraction were obtained for **2** and **5**. The crystals were selected under oil and attached to the tip of a MiTeGen mount. Single crystals of **2** and **5** were measured at 150 K with a Bruker Kappa Apex II system, with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) from a conventional sealed tube. The initial cell constants were obtained from 9122 reflections above 20 σ(I) with 5.250° < 2θ < 52.67° (for **2**) and 9908 reflections above 20 σ(I) with 5.717° < 2θ < 49.37° (for **5**). The reflections were successfully indexed by an automated indexing routine built in the SAINT program.[5]. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[6] A successful solution by the direct methods[7] provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients unless specified otherwise. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients.

In the molecular model of compound **2,** the disorder exhibited by three of the four trifluoromethyl groups in the two molecules present in the asymmetric unit was modelled with the aid of geometrical restraints. In **5,** the disorder in both CF_3 and one of the *t*-Bu groups (containing the atoms C31-C34) also needed the use of similar restraints to attain the convergence of the model.

Final R(F), *w*R(F^2) and goodness-of-fit agreement factors, details on the data collection and analysis for **2** and **5** can be found in Table S1 in this section (ESI).

Table S1. Crystal data and structure refinement for **2** and **5**

Empirical formula	**$C_{38}H_{48}F_6N_6$ (2)**	**$C_{42}H_{57}F_6N_6Zn$ (5)**
Formula weight	702.82 g/mol	825.30 g/mol
Temperature	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ 1	P -1
a(Å)	21.5588(6)	10.4556(5)
b(Å)	13.0726(4)	14.8272(8)
c(Å)	7.5796(8)	15.0122(8)
α(°)	90	73.194(3)
β(°)	96.1396(13)	76.162(3)
γ(°)	90	81.890(3)
Volume(Å^3)	7728.2(4)	2156.8(2)
Z	8	2
Density (calculated) (g/cm^3)	1.208	1.271
Absorption coefficient (mm^{-1})	0.092	0.631
F(000)	2976	870
Crystal size (mm^3)	0.192 x 0.387 x 0.394	0.034 x 0.206 x 0.216
Theta range for data collection	1.68 to 25.35°	3.07 to 25.35°
Index ranges	-25<=h<=19, -15<=k<=15, -33<=l<=33	-12<=h<=12, -17<=k<=17, -18<=l<=18
Reflections collected	98078	46443
Independent reflections	14133 [R(int) = 0.0248]	7884 [R(int) = 0.0489]
Completeness to theta = 25.242°	99.9%	99.7 %
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.9820 and 0.9640	0.9790 and 0.8760
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	14133 / 938 / 1015	7884 / 581 / 597
Goodness-of-fit on F^2	1.000	1.069

Final R indices [I>2sigma(I)]	R_1 = 0.0492, wR_2 = 0.1330	R_1 = 0.0397, wR_2 = 0.1022
R indices (all data)	R_1 = 0.0627, wR_2 = 0.1551	R_1 = 0.0513, wR_2 = 0.1084
Largest diff. peak and hole ($e.Å^{-3}$)	0.564 and -0.438	0.625 and -0.380

5) Experimental details for the synthesis of cyclic carbonates

General procedures for catalytic studies

General procedure for the synthesis of cyclic carbonates 8a−8j, 10a−10b, 12a−12d and 16 at 10-20 bar pressure

An epoxide **7a**−**7j**, **9a**−**9b**, **11a**−**11d** or **15** (12.0-2.4 mmol), catalyst **5** (51 mg, 62.0 μmol) and TBAB (20 mg, 62.0 μmol) were placed in stainless steel reactor with a magnetic stirrer bar. The reactor was pressurized to 10 bar of carbon dioxide and the reaction mixture was stirred at 25−50 ºC for 8−18h. After that, the reactor was cooled down to ambient temperature and depressurized, and the conversion of these epoxides into cyclic carbonates **8a**−**8j**, **10a**−**10b**, **12a**−**12d** or **16** was determined by analysis of a sample by ^{1}H-NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *under vacuum* to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography using a solvent gradient as follows: hexane, hexane-EtOAc (9:1), hexane-EtOAc (6:1), hexane-EtOAc (3:1) and finally EtOAc to give the pure cyclic carbonate. Cyclic carbonates **8a**−**8j**, **10a**−**10b**, **12a**−**12d** or **16** are all known compounds and the spectroscopic data for samples prepared using catalyst **5** were consistent with those reported in the literature.[8,9]

General procedure for the synthesis of cyclic carbonate 14

(*R*)-(+)-limonene oxide (*cis* and *trans* mixture) **13** was previously dried with calcium hydride overnight and distilled under vacuum and stored under nitrogen. Stainless-steel reactor was dried under vacuum at 80 ºC for 18 hours.

In a representative experiment, 0.93 g of (*R*)-(+)-limonene oxide (*cis/trans* mixture) (1 mL, 6.10 mmol), catalyst **4** (21 mg, 30.5 μmol) and TBAC (29.5 mg, 91.5 μmol) were placed in the dried stainless-steel reactor with a magnetic stirrer bar. The reactor was pressurized to 10−20 bar of carbon

dioxide and the reaction mixture was stirred at 70−100 ºC for 24−72 h. After that, the reactor was cooled down to ambient temperature and depressurized, and the conversion of epoxide into cyclic carbonate **14** was determined by analysis of a sample by ^{1}H-NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated under vacuum and later purified by flash chromatography using a solvent gradient as follows: hexane, hexane-EtOAc (9:1), hexane-EtOAc (6:1), hexane-EtOAc (3:1) and finally EtOAc to give the pure cyclic carbonate. Cyclic carbonate **14** is a known compound and the spectroscopic data for samples prepared using catalyst **4** were consistent with those reported in the literature.[2]

General procedure for the multi-feed studies of catalyst 5 with propylene oxide 15

Propylene oxide **15** (2.60 mL, 37.1 mmol) and catalyst **5** (49 mg, 57.4 μmol) and TBAB (20 mg, 57.4 μmol) were placed in stainless steel reactor with a magnetic stirrer bar. The reactor was pressurized to 10 bar of carbon dioxide and the reaction mixture was stirred at 100 ºC for 2 h. The conversion of epoxide to cyclic carbonate **16** was then determined by analysis of a sample by ^{1}H NMR spectroscopy. Then, the remaining epoxide was evaporated in vacuo and the cycloaddition was then restarted with 1 equiv of PO and this operation was repeated six more times, until reaching 6 equiv of PO. Finally, the remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated under vacuum and later purified by flash chromatography using a solvent gradient as follows: hexane, hexane-EtOAc (9:1), hexane-EtOAc (6:1), hexane-EtOAc (3:1) and finally EtOAc to give the pure propylene carbonate.

^{1}H and ^{13}C-{^{1}H} NMR spectroscopic data of compounds 8a−8j, 10a−10b, 12a−12d, 14 and 16

Styrene carbonate (8a). Isolated in 85% yield as a white solid (4.48 g, 88%). ^{1}H NMR ($CDCl_3$, 298 K) δ 7.47-7.33 (m, 5 H, Ar-H), 5.67 (m, 1 H, OC*H*), 4.80 (m, 1 H, OC*H*$_2$), 4.34 (m, 1 H, OC*H*$_2$). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.8 (*C*=O), 135.7 (*C*^{ipso}), 129.7, 129.2, 125.8 (Ph), 78.0 (Ph*C*HO), 71.1 (O*C*H$_2$).

1,2-Hexylene carbonate (8b). Isolated in 88 % yield as a colourless liquid (4.11 g, 92 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.70 (m, 1 H, OC*H*), 4.52 (m, 1 H, OC*H*$_2$), 4.06 (m, 1 H, OCH$_2$), 1.73 (m, 2 H, C*H*$_2$), 1.40 (m, 4 H, C*H*$_2$), 0.91 [t, 3 H, $^{3}J_{H-H}$ = 8 Hz, C*H*$_3$]. ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.1 (*C*=O), 77.0 (O*C*H), 69.4 (O*C*H$_2$), 33.6, 26.4, 22.2 (-*C*H$_2$-),13.8 (*C*H$_3$).

1,2-Decylene carbonate (8c). Isolated in 84% yield as a colourless liquid (5.59 g, 90 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4,68 (m, 1 H, OC*H*), 4.50 (m, 1 H, OC*H*$_2$), 4.04 (m, 1 H, OC*H*$_2$), 1.71 (m, 2 H, C*H*$_2$), 1.37 (m, 12 H, C*H*$_2$), 0.86 [t, 3 H, $^{3}J_{H-H}$ = 8 Hz, C*H*$_3$]. ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.1 (*C*=O), 77.0 (O*C*H), 69.4 (O*C*H$_2$), 33.9, 31.8, 29.3, 29.2 29.1, 24.3, 22.6 (-*C*H$_2$-),14.1 (*C*H$_3$).

1,2-Dodecylene carbonate (8d). Isolated in 87 % yield as a colourless liquid (6.58 g, 93 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.68 (m, 1 H, OC*H*), 4.50 (m, 1 H, OC*H*$_2$), 4.04 (m, 1 H, OC*H*$_2$), 1.72 (m, 2 H, -C*H*$_2$-), 1.23 (m, 16 H, -C*H*$_2$-), 0.85 [t, 3 H, $^{3}J_{H-H}$ = 8 Hz, C*H*$_3$]. ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.1 (*C*=O), 77.0 (O*C*H), 69.4 (O*C*H$_2$), 33.9, 31.9, 29.5, 29.4, 29.3, 29.2, 29.1, 24.3, 22.6 (-*C*H$_2$-),14.1 (*C*H$_3$).

3-Chloropropylene carbonate (8e). Isolated in 86 % yield as a colourless liquid (3.81 g, 90 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.94 (m, 1 H, OC*H*), 4.57 (m, 1 H, OC*H*$_2$), 4.40 (dd, 1 H, $^{3}J_{H-H}$ = 9 Hz, 8.7 Hz, OC*H*$_2$), 3.73 (m, 2 H, C*H*$_2$Cl). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.1 (C=O), 74.16 (O*C*H), 66.9 (O*C*H$_2$), 43.5 (*C*H$_2$Cl).

Glycerol carbonate (8f). Isolated in 94% yield as a colourless liquid (3.66 g, 100%).^{1}H NMR ($CDCl_3$, 298 K) δ 4.80 (m, 1 H, OC*H*), 4.49 (m, 2 H, OC*H*$_2$), 3.99 (m, 1 H, C*H*$_2$OH), 3.71 (m, 1 H, C*H*$_2$OH), 2.59 (m, 1 H, O*H*). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.0 (*C*=O), 76.7 (O*C*H), 65.7 (O*C*H$_2$), 61.7 (*C*H$_2$OH).

3-Phenoxypropylene carbonate (8g). Isolated in 83% yield as a white solid (5.24 g, 87%). ^{1}H NMR ($CDCl_3$, 298 K) δ 7.29 (m, 2 H, Ar-H), 7.00 (m, 1 H, Ar-H), 6.89 (m, 2 H, Ar-H), 5.01 (m, 1 H, OC*H*), 4.60 (m, 1 H, PhOC*H*$_2$), 4.52 (m, 1 H, PhOC*H*$_2$), 4.22 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 10.6 Hz, 4.2 Hz, OC*H*$_2$), 4.12 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 12 Hz, 4 Hz, OC*H*$_2$). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 157.7 (OPh^{ipso}), 154.7 (O*C*OO), 129.7, 121.9, 114.5 (Ph), 74.1 (*C*H$_2$OPh), 66.8 (O*C*H), 66.2 (-*C*H$_2$O).

3-Vinyloxypropylene carbonate (8h). Isolated in 89% as a white solid (4.61 g, 94%). ^{1}H NMR ($CDCl_3$, 298 K) δ 5.85 (m, 1 H, -C*H*=CH$_2$), 5.23 (m, 2 H, C*H*$_2$=CH-), 4.80 (m, 1 H, OC*H*), 4.48 (m, 1 H, OC*H*$_2$), 4.38 (m, 1 H, OC*H*$_2$), 4.03 (m, 2 H, =CH-C*H*$_2$O), 3.67 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 10.6 Hz, 4 Hz, C*H*$_2$O-allyl), 3.59 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 10.6 Hz, 4 Hz, C*H*$_2$O-allyl). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.9 (*C*=O), 133.6, 118.0 (*C*=*C*), 74.9 (O*C*H), 72.6 (=CH-*C*H$_2$O), 68.8 (O*C*H$_2$), 66.2 (*C*H$_2$O-allyl).

4-Chlorostyrene carbonate (8i). Isolated in 94 % yield as a white solid (6.14 g, 100 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 7.42 (dd, 2 H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, Ar-H), 7.30 (dd, 2 H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, Ar-H), 5.66 (m, 1 H, OC*H*), 4.80 (m, 1 H, OC*H*$_2$), 4.29 (m, 1 H, OC*H*$_2$). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.5 (*C*=O), 135.7 (C^{ipso}), 134.2, 129.5, 127.2 (Ph), 77.3 (O*C*H), 71.0 (O*C*H$_2$).

4,4'-((Butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (8j). Isolated in 92 % yield as a colourless liquid (9.00 g, 100 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.80 (m, 2 H, OC*H*), 4.49 (m, 2 H, OC*H*$_2$), 4.39 (m, 2 H, OC*H*$_2$), 3.68 (dd, 2 H, $^{3}J_{H\text{-}H}$ = 12 Hz, 4 Hz, C*H*$_2$O-R), 3.58 (dd, 2 H, $J_{H\text{-}H}$ = 12 Hz, 4 Hz, C*H*$_2$O-R), 3.52 (m, 4 H, - CH$_2$-O-C*H*$_2$-), 1.63 (m, 4 H, -C*H*$_2$-C*H*$_2$-). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.1 (*C*=O), 75.2 (O*C*H), 71.6 (O*C*H$_2$) 69. 6 (*C*H$_2$O-R) 66.2 (- CH$_2$-O-*C*H$_2$-), 26.0 (-CH$_2$-).

***cis*-1,2-Cyclohexene carbonate (10a).** Isolated in 93% yield as a white solid (1.71 g, 97%). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.65 (m, 2 H, OC*H*), 1.86 (m, 4 H, C*H*$_2$), 1.58 (m, 4 H, C*H*$_2$),1.39 (m, 4 H, C*H*$_2$). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.3 (*C*=O), 75.7 (O*C*H), 26.7 (*C*H$_2$), 19.1 (*C*H$_2$).

***cis*-1,2-Cyclopentene carbonate (10b).** Isolated in 95% yield as a white solid (0.79 g, 100%). ^{1}H NMR ($CDCl_3$, 298 K) δ 5.09 (m, 2 H, OC*H*), 2.13 (m, 2 H, C*H*$_2$), 1.72 (m, 4 H, C*H*$_2$). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.5 (*C*=O), 81.8 (O*C*H), 33.2 (*C*H$_2$), 21.5 (*C*H).

4-(Furan-2-ylmethoxy)-1,3-dioxolan-2-one (12a). Isolated in 94% yield as an orange liquid (6.02 g, 98%). ^{1}H NMR ($CDCl_3$, 298 K) δ 7.40 (m, 1 H, OC*H*=CH), 6.33 (m, 2 H, C*H*=C*H*), 4.76 (m, 1 H, OC*H*), 4.42 (m, 4 H, OC*H*$_2$), 3.64 (m, 2 H, C*H*$_2$). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.8 (C=O), 150.6 (O*C*(=CHR)CH_2), 143.7 (O*C*H=CHR), 110.4, 110.1 (RH*C*-*C*HR), 74.8 (O*C*H_2), 68.4 (OCH_2*C*HOR) 66.3 (C_4H_3O-*C*H_2) 65.3 (O*C*H_2).

Bis((2-oxo-1,3-dioxolan-4-yl)methyl) fumarate (12b). Isolated in 89 % yield as a white solid (8.74 g, 92 %). ^{1}H NMR (DMSO-*d*^{6}, 298 K) δ 6.81 (m, 2 H, -C*H*=C*H*-), 5.08 (m, 2 H, OC*H*), 4.57 (m, 4 H, OC*H*$_2$), 4.44 (m, 4 H, OC*H*$_2$), 4.34 (m, 4 H, -C*H*$_2$-). ^{13}C {^{1}H} (DMSO-*d*^{6}, 298 K) δ 163.2 (O=*C*O), 154.2 (O=*C*OO), 132.6 (-*C*H=*C*H-), 73.6 (O*C*H), 65.5 (O*C*H_2), 64.0 (-*C*H_2-).

Bis((2-oxo-1,3-dioxolan-4-yl)methyl) succinate (12c). Isolated in 91 % yield as a white solid (9.38 g, 95 %). ^{1}H NMR (DMSO-*d*^{6}, 298 K) δ 5.02 (m, 2 H, OC*H*), 4.56 (m, 4 H, OC*H*$_2$), 4.28 (m, 4 H, OC*H*$_2$), 4.27 (m, 8 H, OC*H*$_2$), 2.61 (m, 4 H, COC*H*$_2$-).^{13}C {^{1}H} (DMSO-*d*^{6}, 298 K) δ 171.1 (O=*C*O), 154.2 (O=*C*OO), 73.7 (O*C*H), 65.5 (O*C*H_2), 63.1 (CO*C*H_2-), 27.9 (-*C*H_2-).

Bis((2-oxo-1,3-dioxolan-4-yl)methyl) glutarate (12d). Isolated in 96 % yield as a white solid (10.30 g, 100 %). ^{1}H NMR (DMSO-*d*^{6}, 298 K) δ 5.03 (m, 2 H, OC*H*), 4.40 (m, 8 H, OC*H*$_2$), 2.40 (m, 4 H, COC*H*$_2$), 1.77 (m, 2 H, $COCH_2C$*H*$_2$). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 172.3 (O=*C*O), 154.9 (O=*C*OO), 74.5 (O*C*H), 66.2 (O*C*H_2), 63.6 (-*C*H_2OC(O)-), 32.5 (-O*C*(O)CH_2-), 19.9 (-*C*H_2-).

(*R*)-(+)-Limonene carbonate (14). Isolated in 36 % yield as a colourless oil in a 6:94 mixture of *cis*- and *trans*-isomers (0.44 g, 39 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.69 (m, 1 H, MeC=C*H*$_2$), 4.66 (m, 1 H, MeC=C*H*$_2$), 4.33 (dd, $^{3}J_{HH}$ = 9.6 Hz and 7.0 Hz, 1 H, OC*H*), 2.36-2.21 (m, 2 H, -C*H*$_2$-), 1.87 (tt, $^{3}J_{HH}$ = 12.0 Hz and 3.2 Hz, C*H*), 1.65 (s, 3 H, -C(*Me*)=CH_2), 1.64-1.55 (m, 2H, -C*H*$_2$-), 1.40 (s, 3H, -COC*H*$_3$), 1.38-1-31 (m, 2H, -C*H*$_2$-). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.9 (O=*C*OO), 147.4 (-*C*(CH_3)=CH_2), 110.3 (-C(CH_3)=*C*H_2), 82.2 (-*C*(O)Me), 80.7 (-*C*O), 40.1 (*C*-C(CH_3)(=CH_2)), 34.1, 33.2, 25.8 (-*C*H_2-), 26.3 (-CO(*C*H_3)), 20.7 (C-C(*C*H_3)(=CH_2).

Propylene carbonate (16). Isolated in 81 % yield as a white solid (3.29 g, 83 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.84 (m, 1 H, OC*H*), 4.54 (m, 1 H, OC*H*$_2$), 4.01 (m, 1 H, OC*H*$_2$), 1.48 (d, 3 H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, OCH_2CH_3). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.0 (O=*C*O), 73.5 (O*C*H), 70.6 (O*C*H$_2$), 19.3 (OCH_2CH_3).

Figures S6–S24. ^{1}H and ^{13}C-{^{1}H} NMR spectra of compounds **8a**–**8j**, **10a**–**10b**, **12a**–**12d**, **14** and **16**

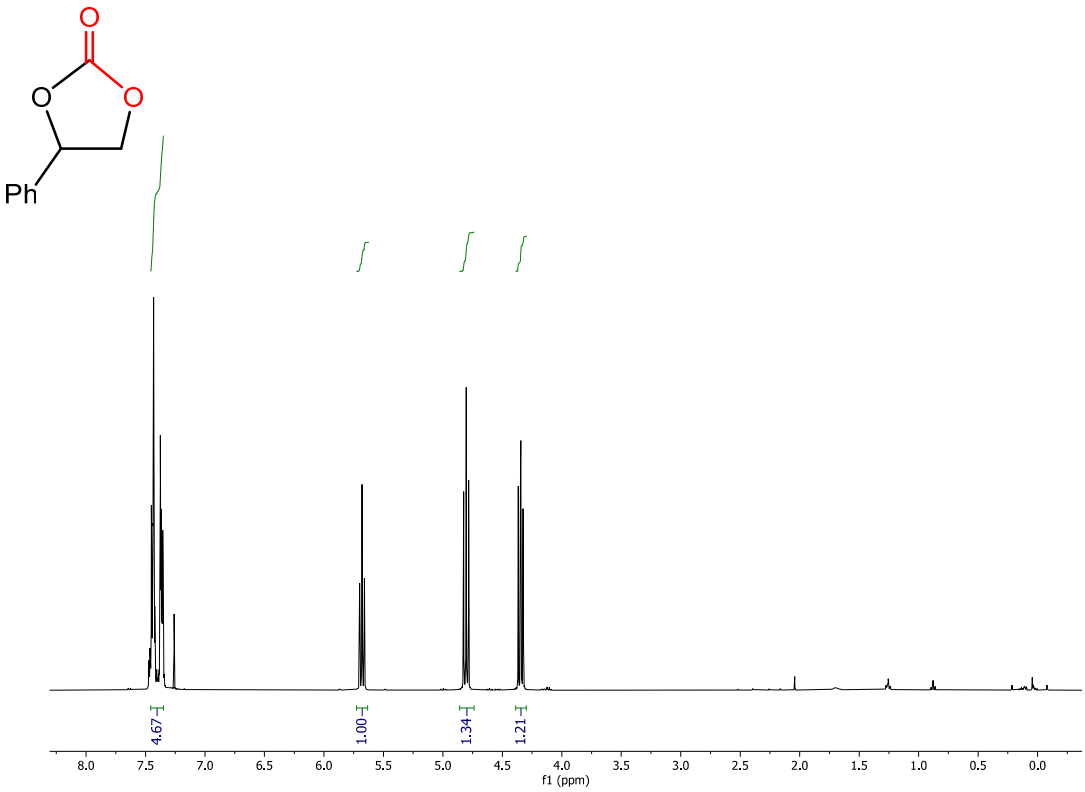

Figure S6a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for styrene carbonate **8a**.

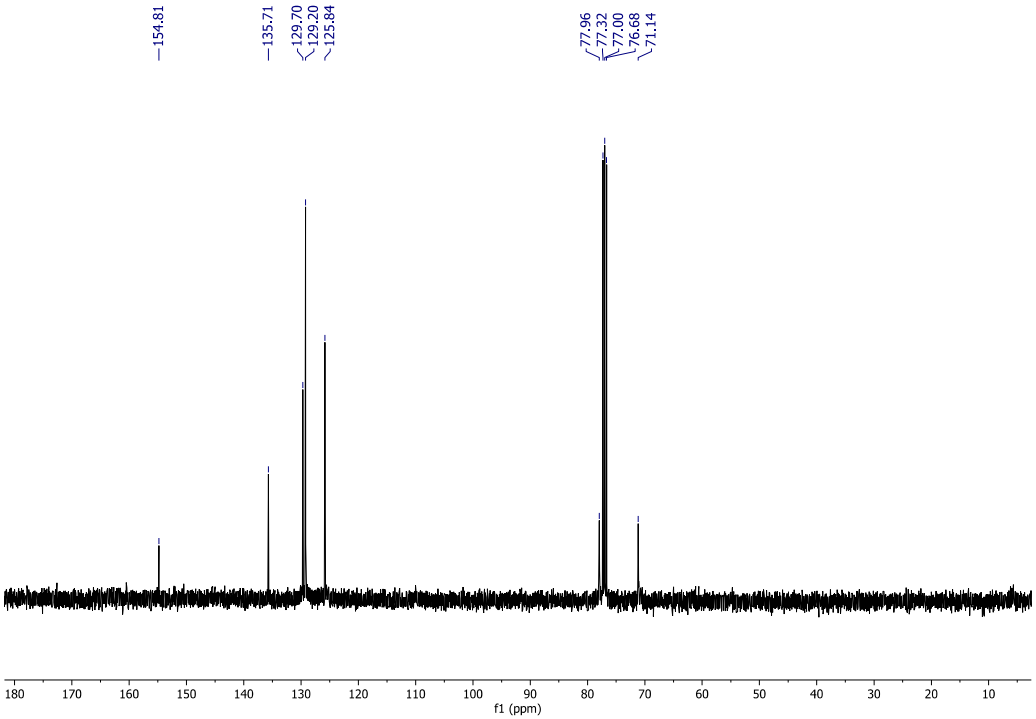

Figure S6b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for styrene carbonate **8a**.

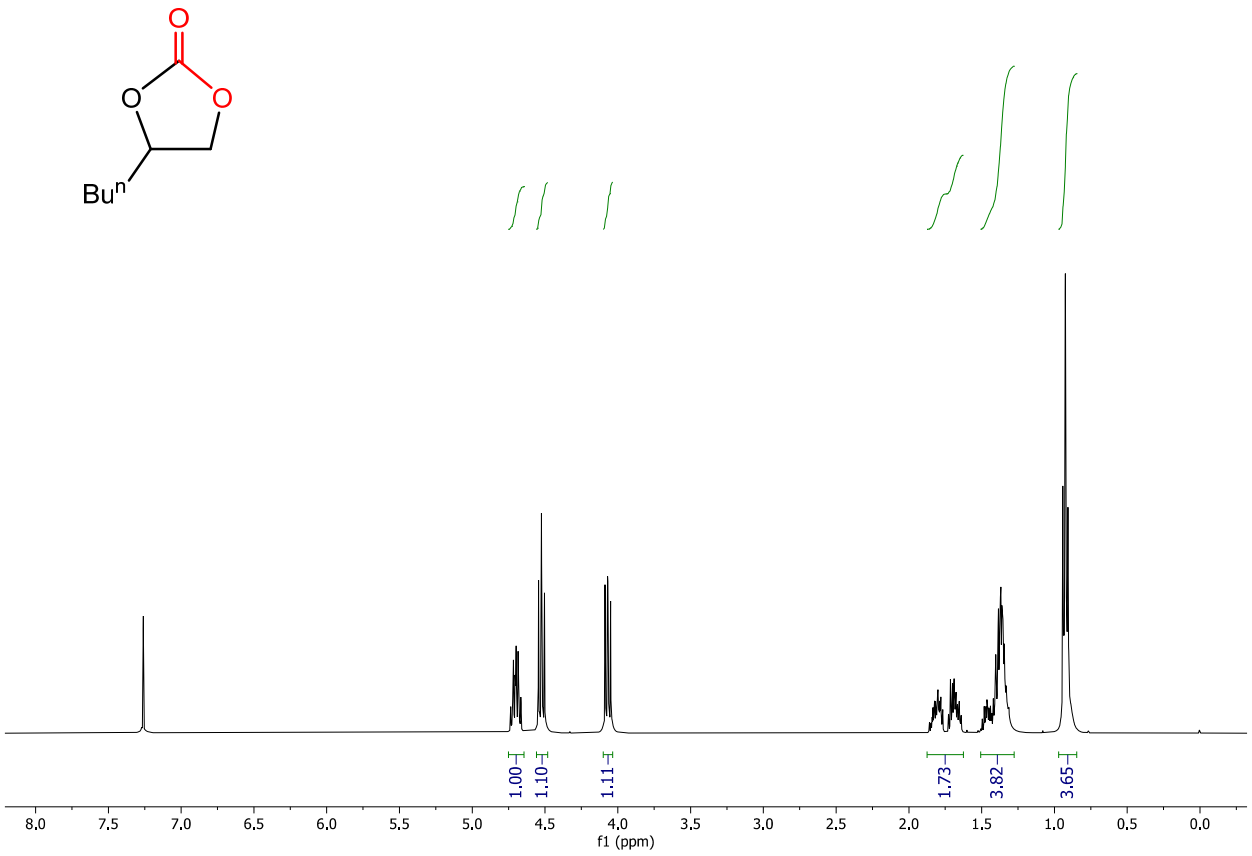

Figure S7a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 1,2-hexylene carbonate **8b**.

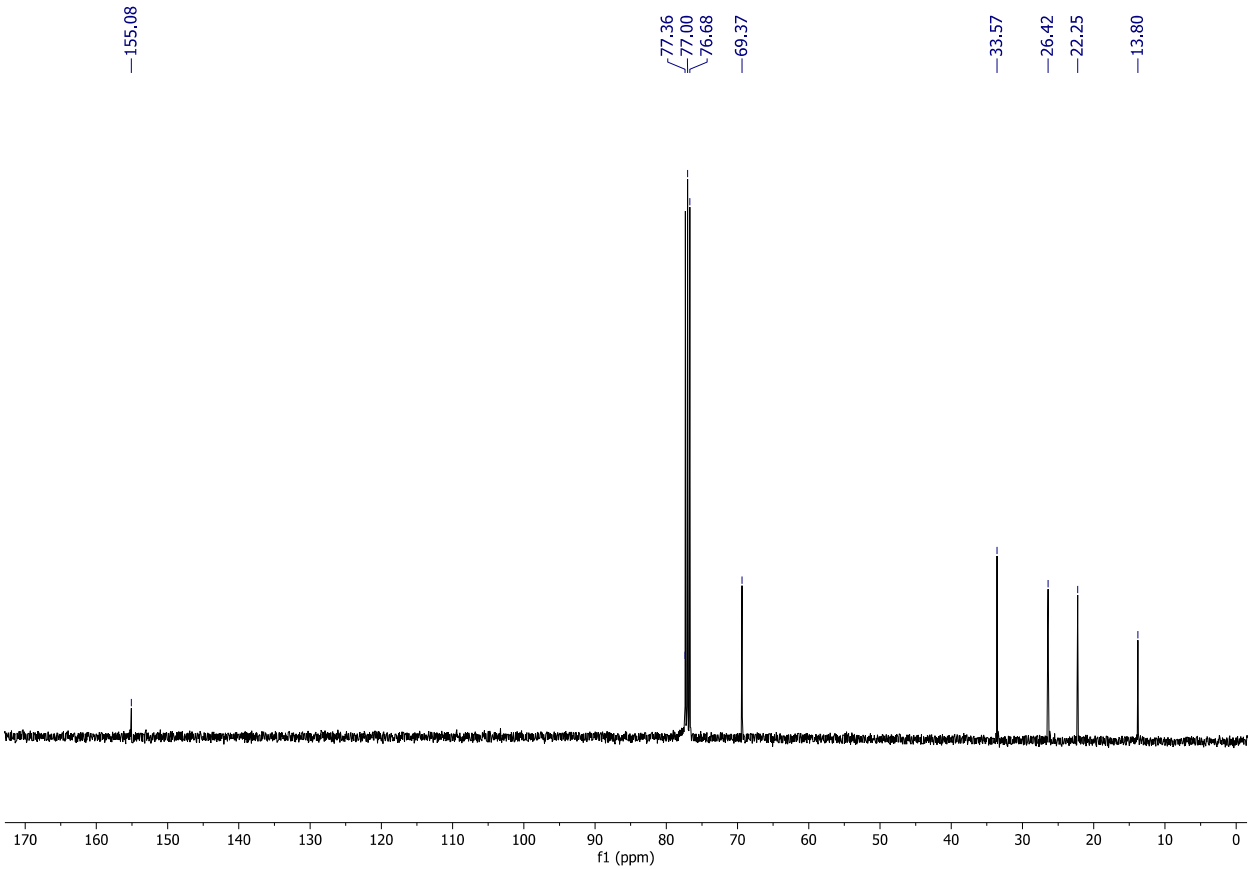

Figure S7b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 1,2-hexylene carbonate **8b**.

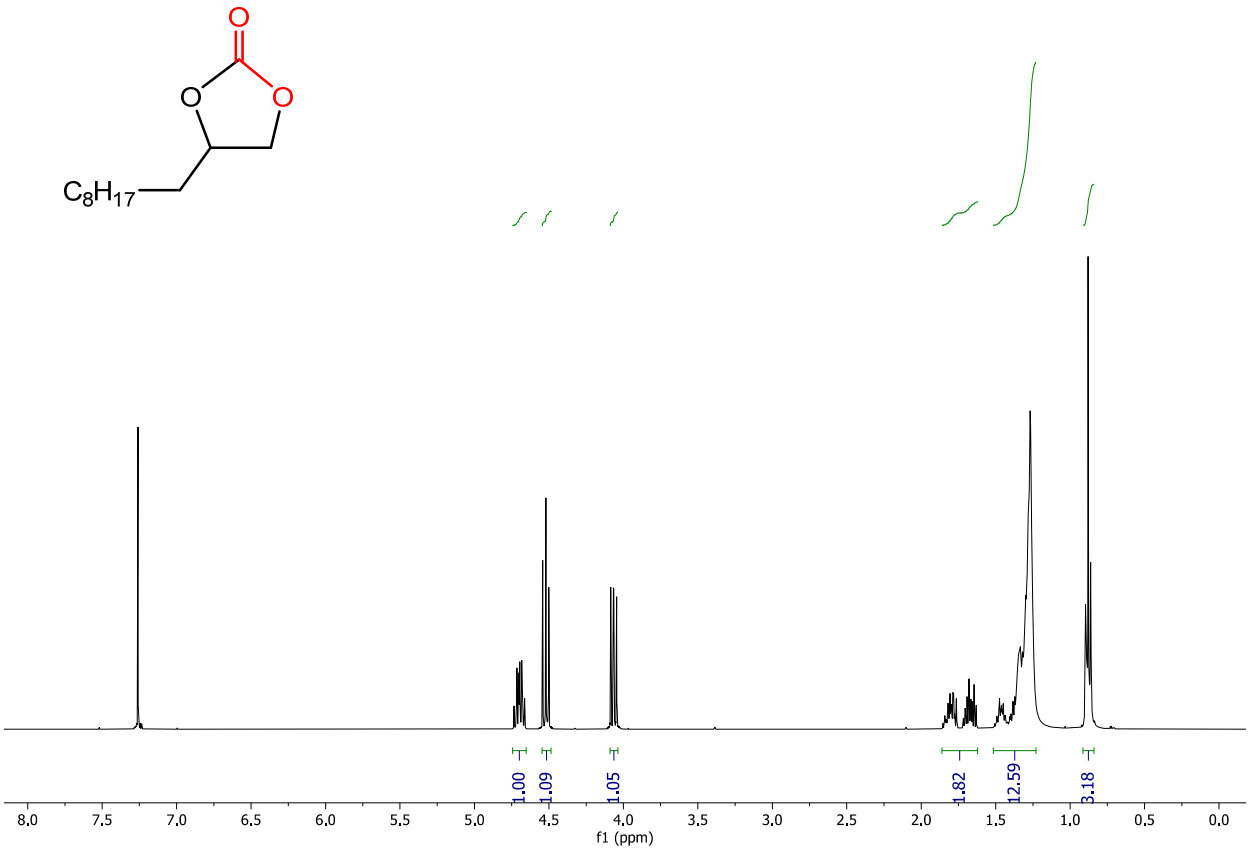

Figure S8a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 1,2-decylene carbonate **8c**.

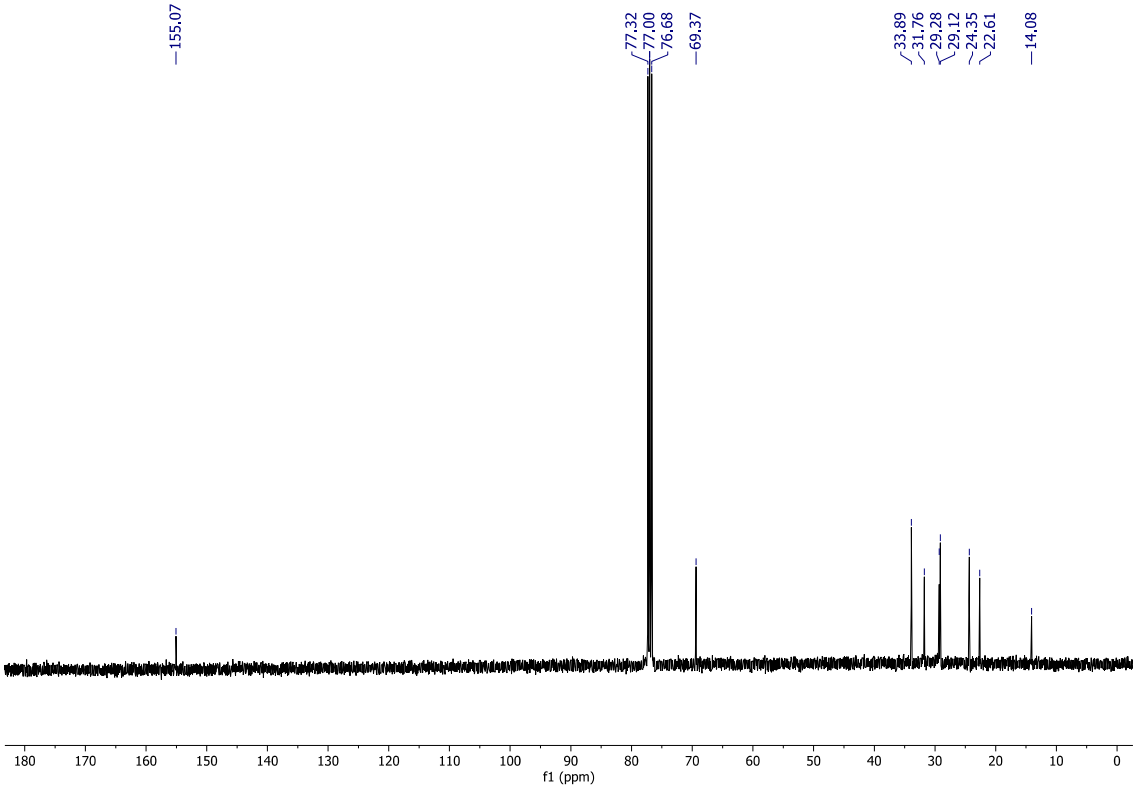

Figure S8b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 1,2-decylene carbonate **8c**.

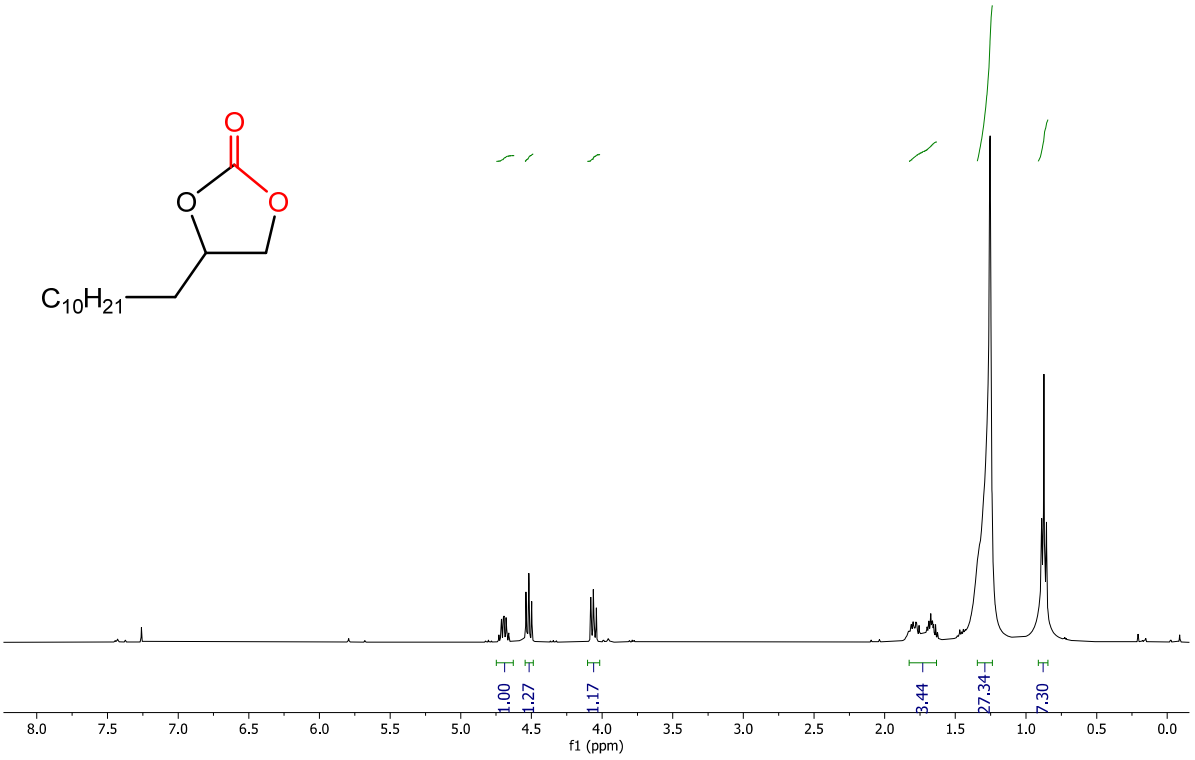

Figure S9a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 1,2-dodecylene carbonate **8d**.

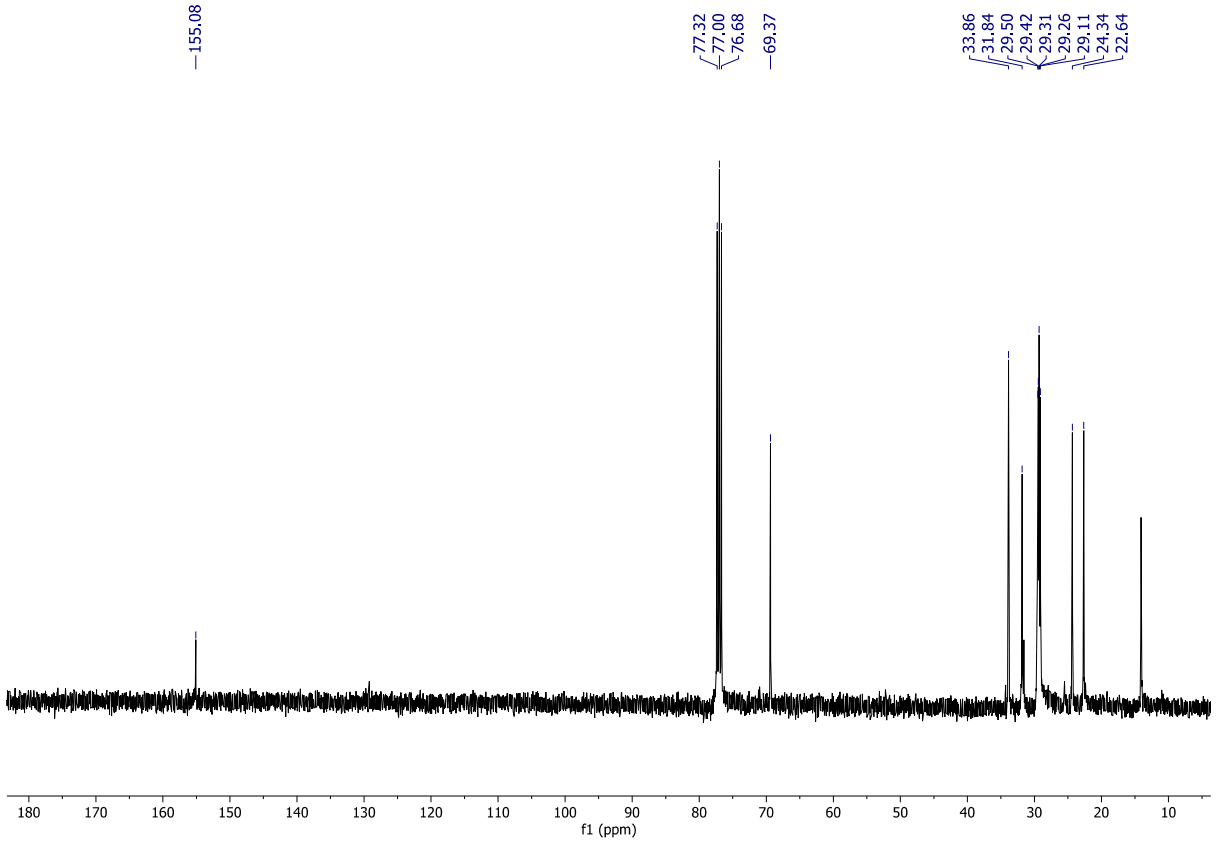

Figure S9b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 1,2-dodecylene carbonate **8d**.

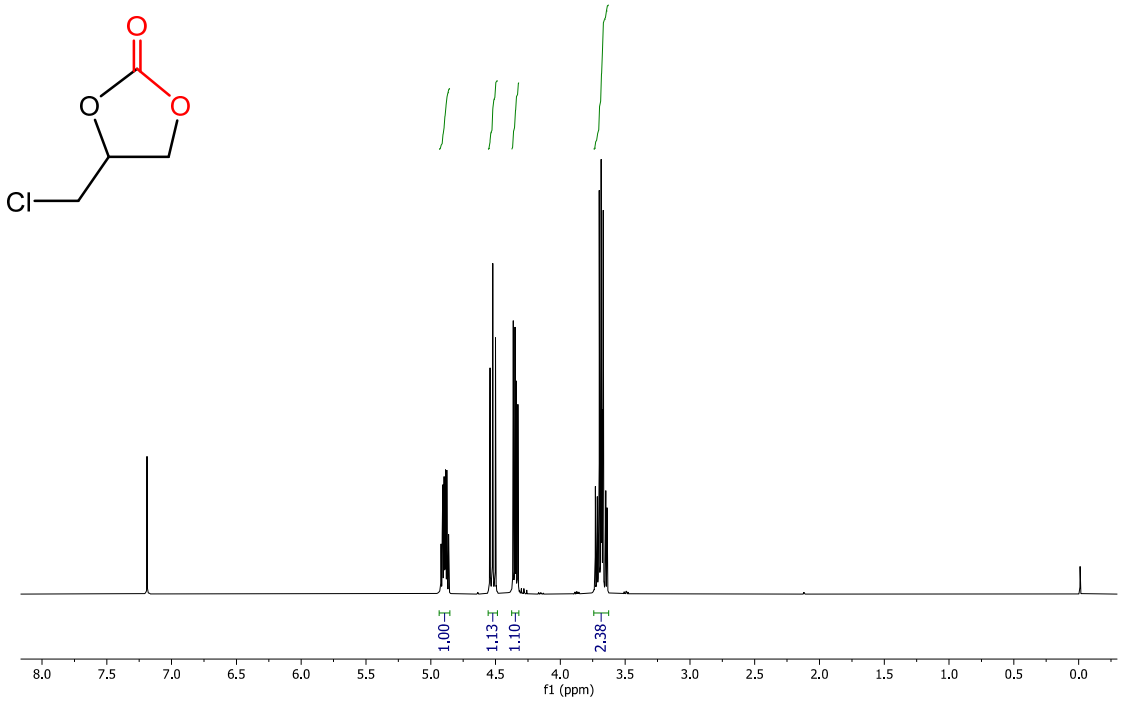

Figure S10a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 3-chloropropylene carbonate **8e**.

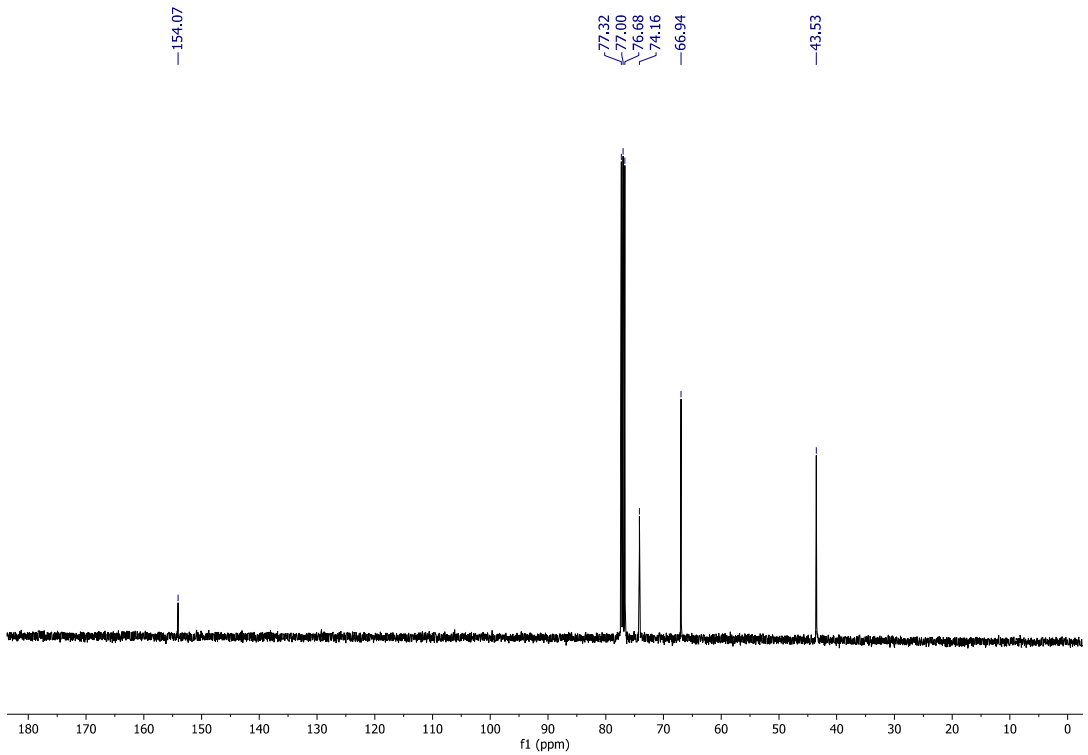

Figure S10b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 3-chloropropylene carbonate **8e**.

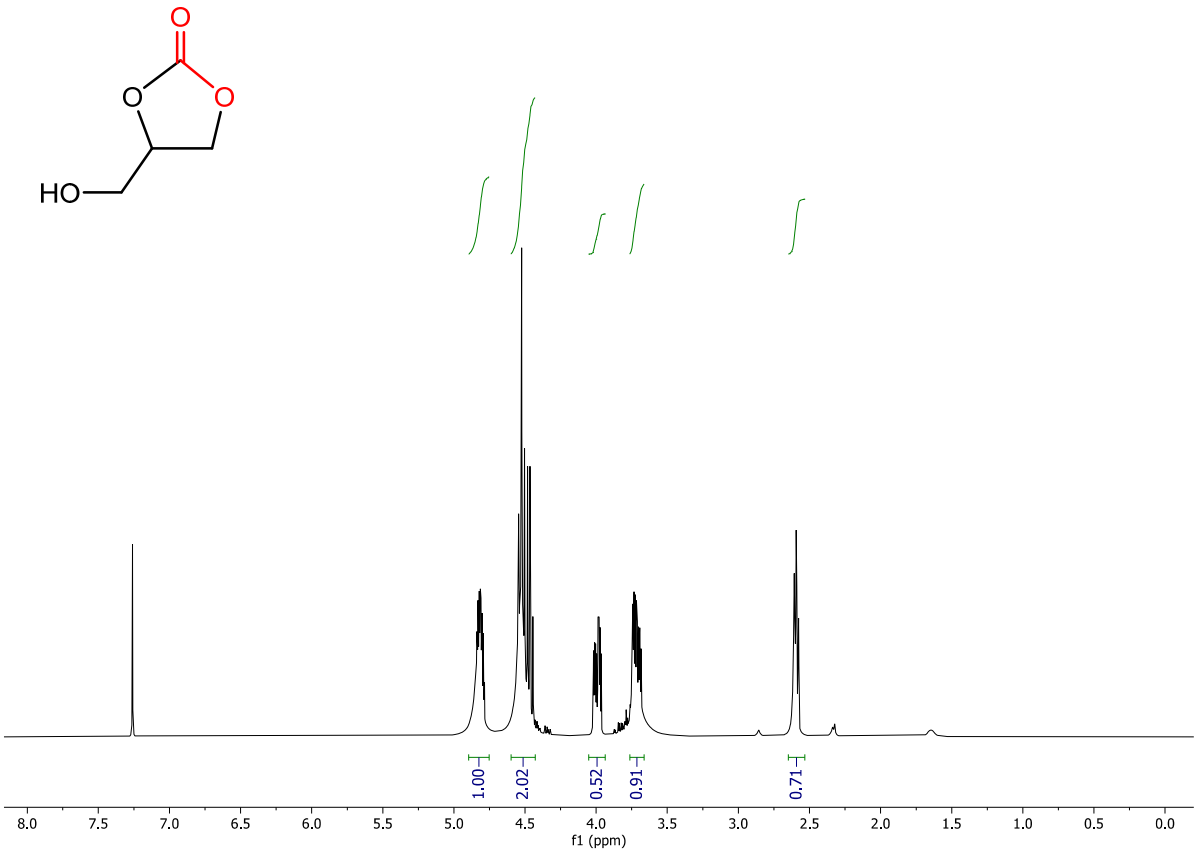

Figure S11a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for glycerol carbonate **8f**.

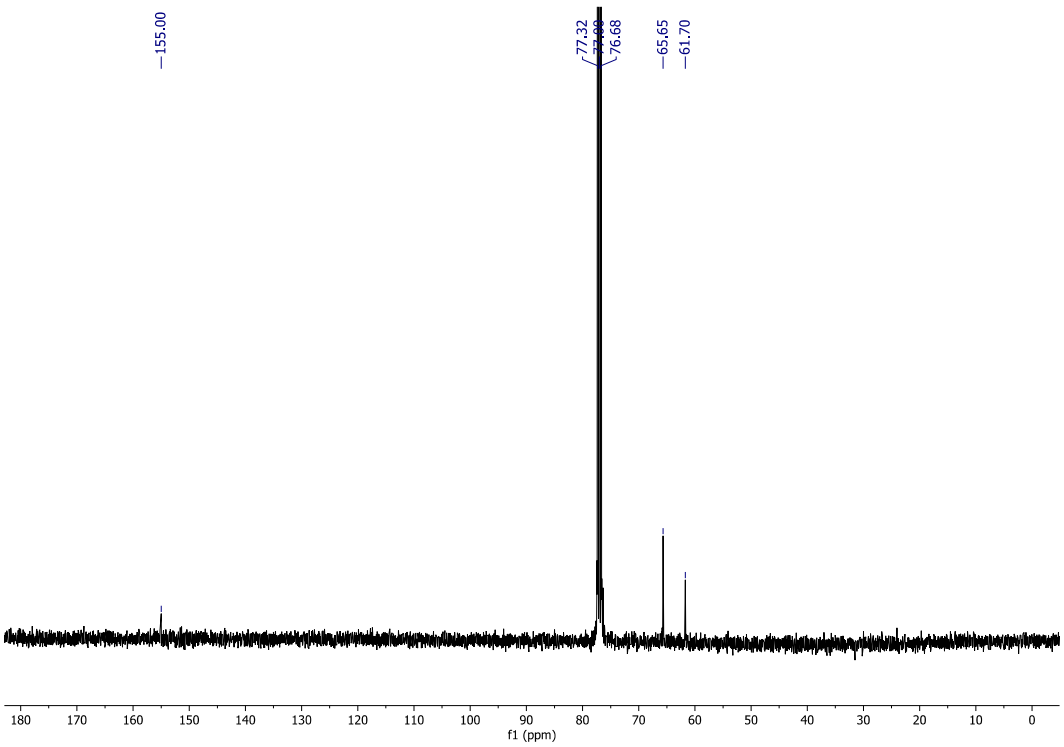

Figure S11b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for glycerol carbonate **8f**.

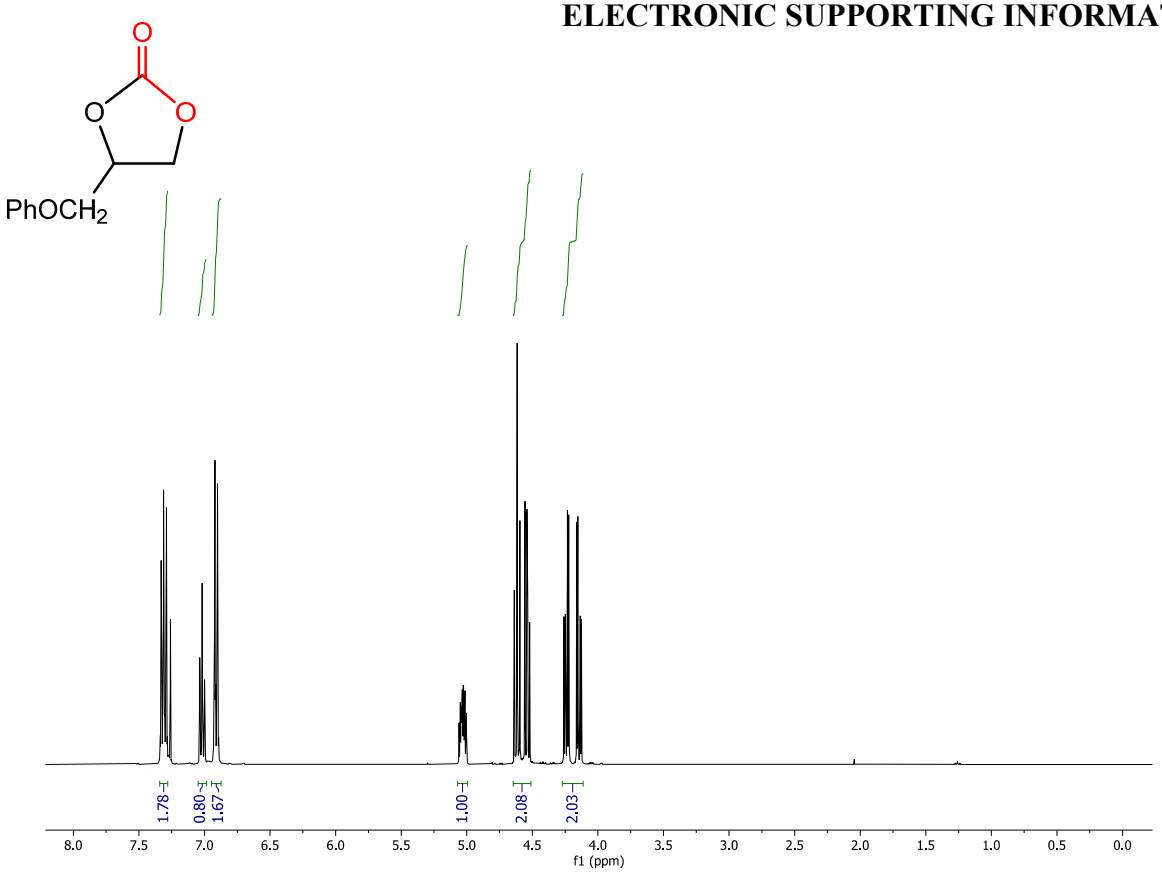

Figure S12a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 3-phenoxypropylene carbonate **8g**.

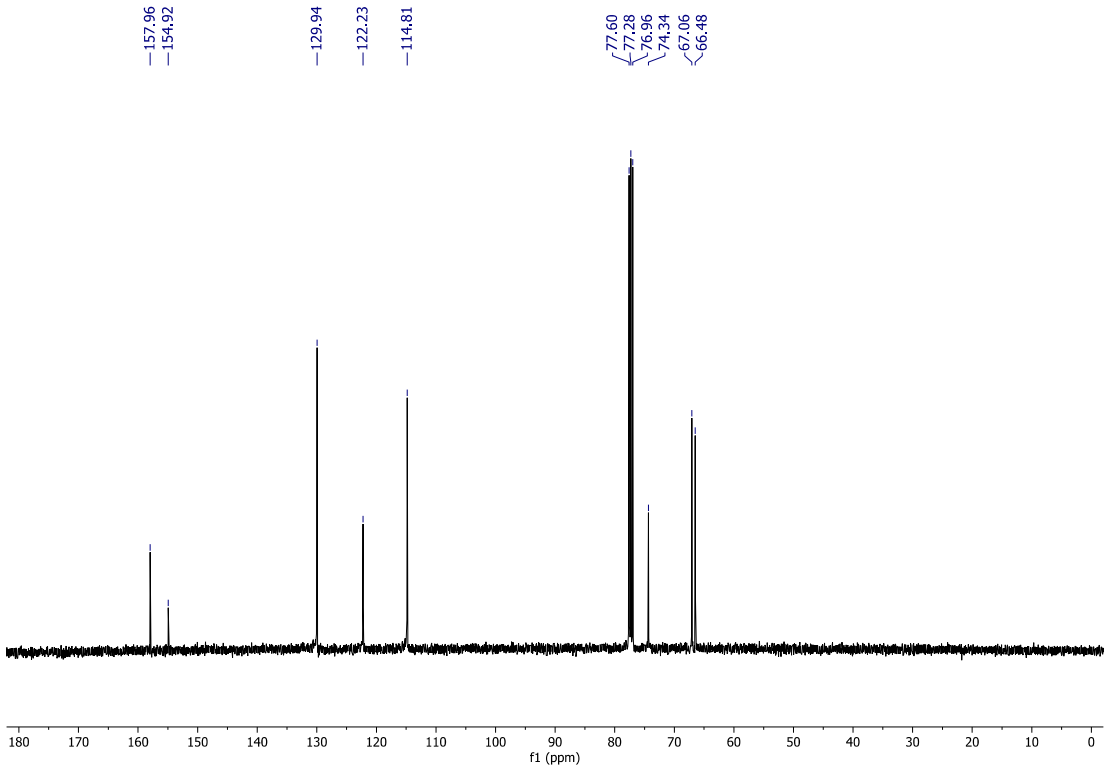

Figure S12b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 3-phenoxypropylene carbonate **8g**.

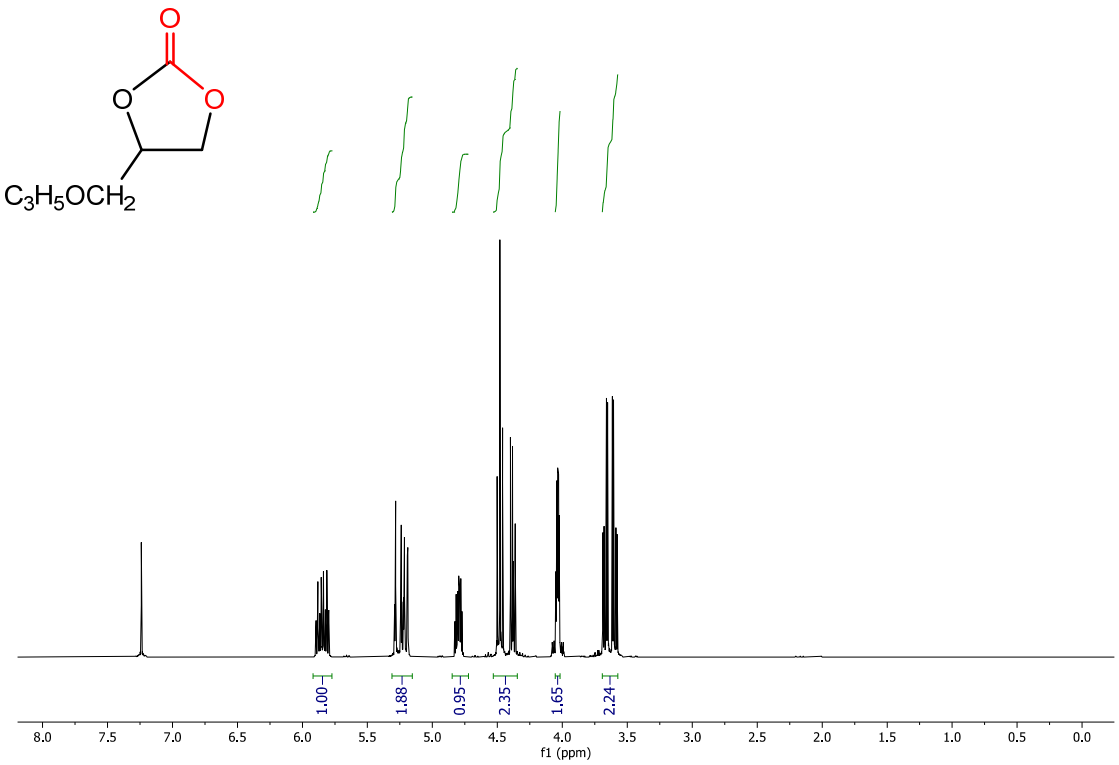

Figure S13a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 3-vinyloxypropylene carbonate **8h**.

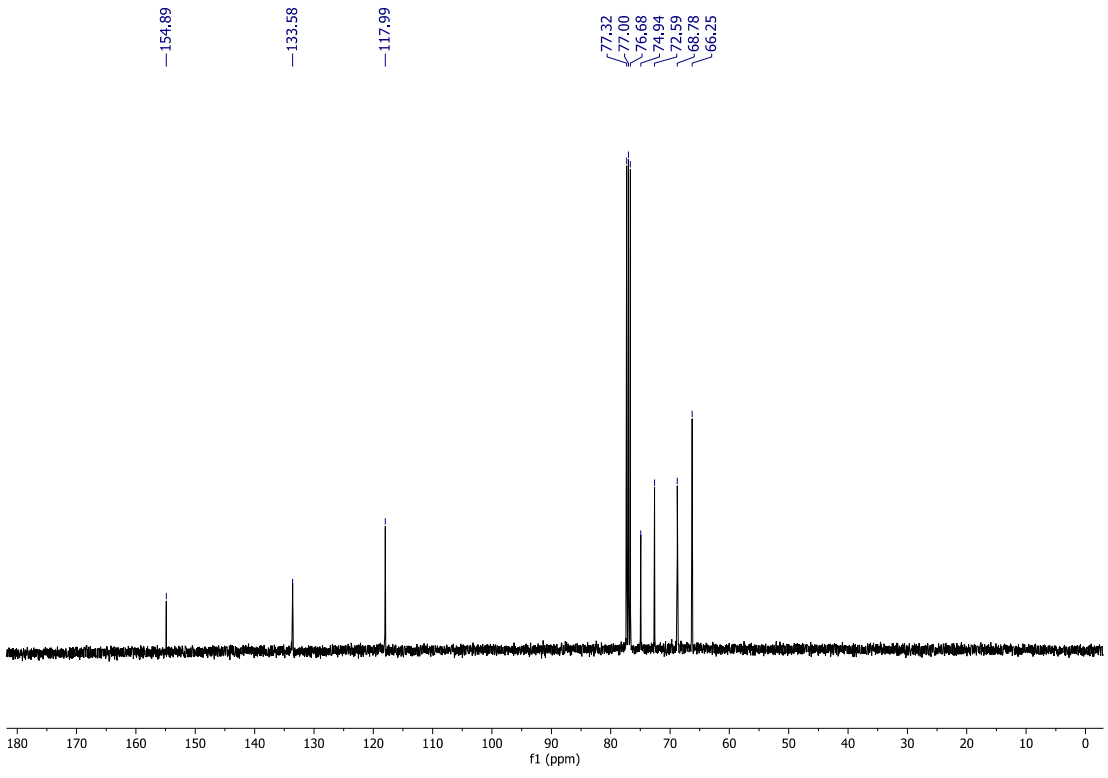

Figure S13b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 3-vinyloxypropylene carbonate **8h**.

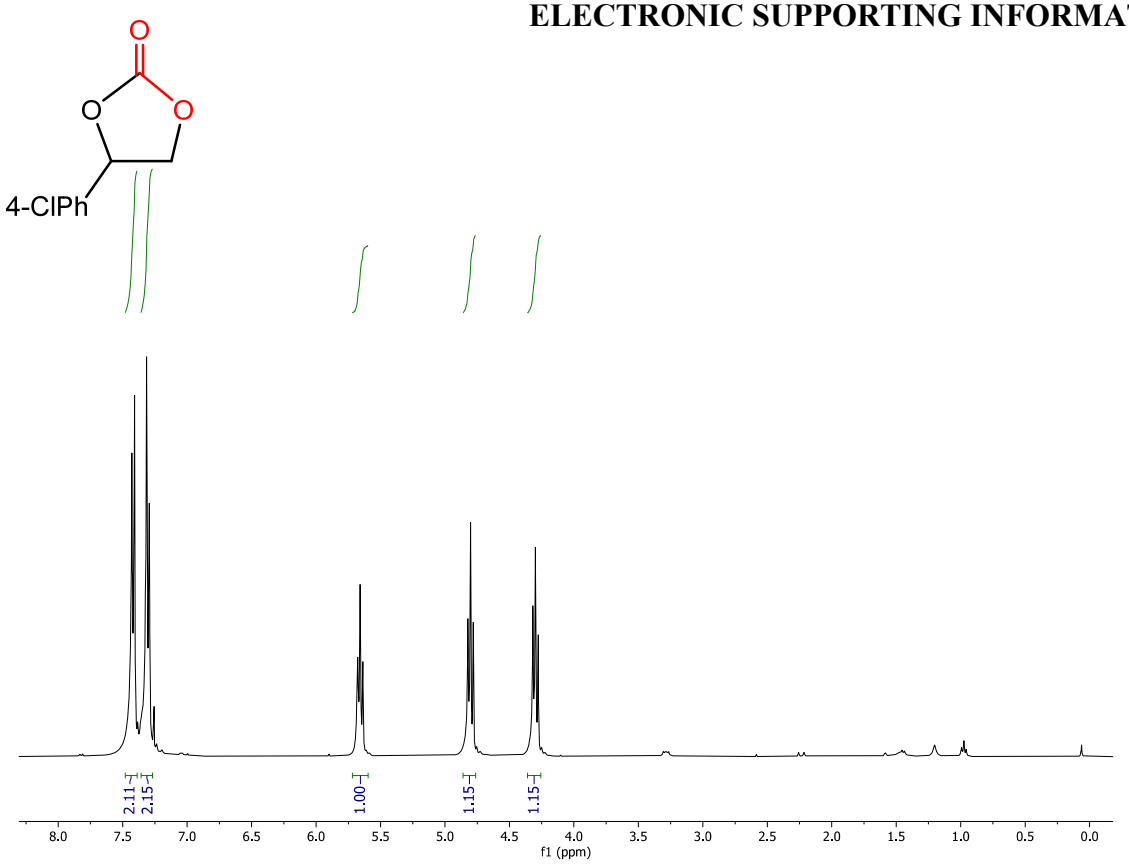

Figure S14a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 4-chlorostyrene carbonate **8i**.

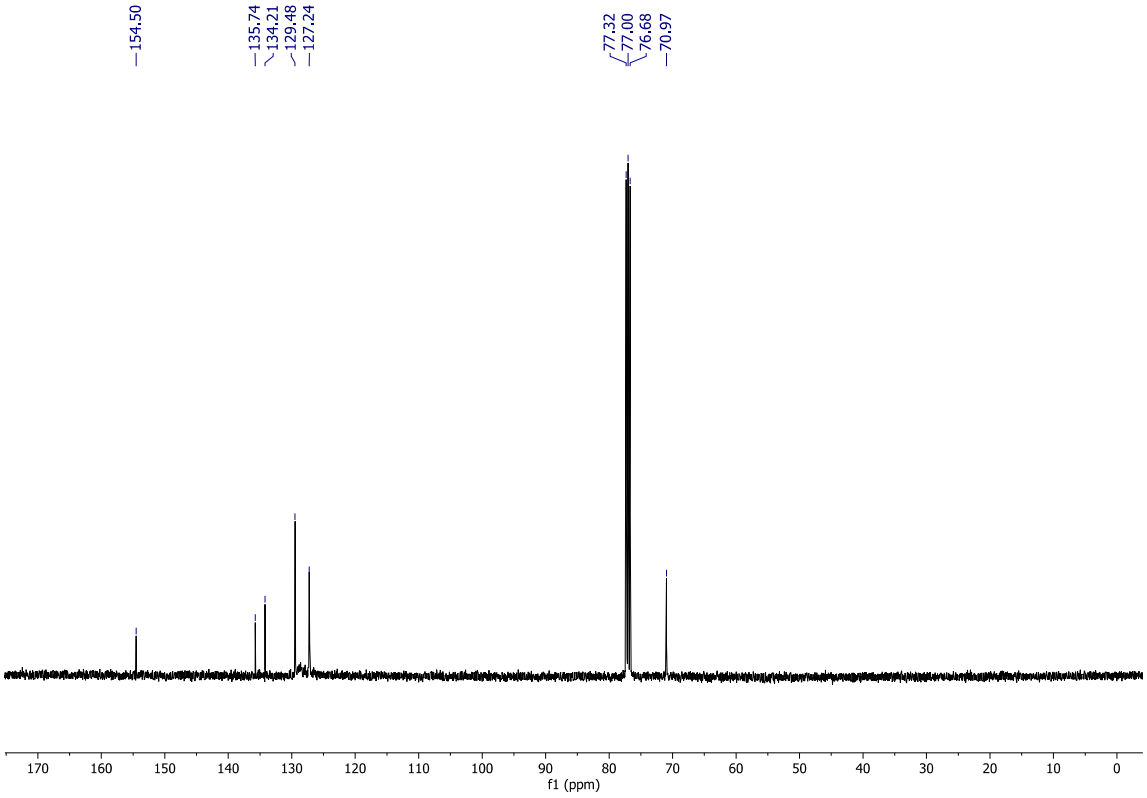

Figure S14b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 4-chlorostyrene carbonate **8i**.

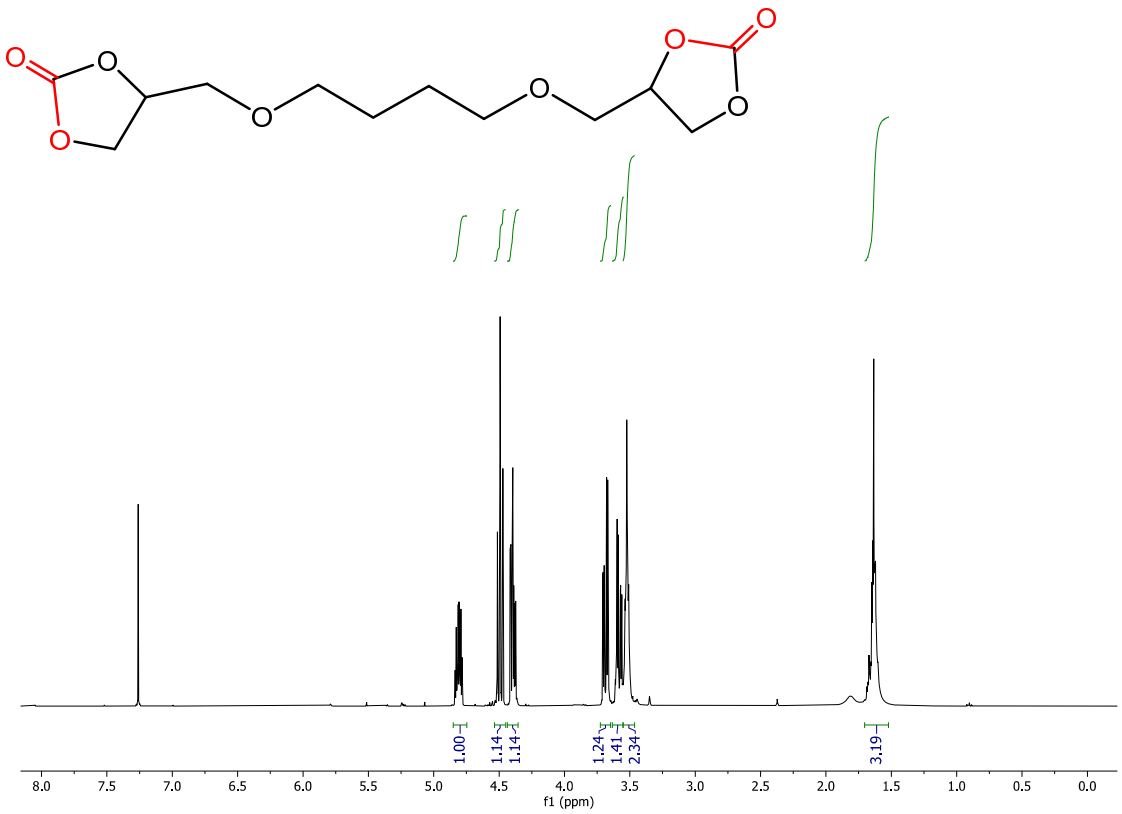

Figure S15a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) **8j**.

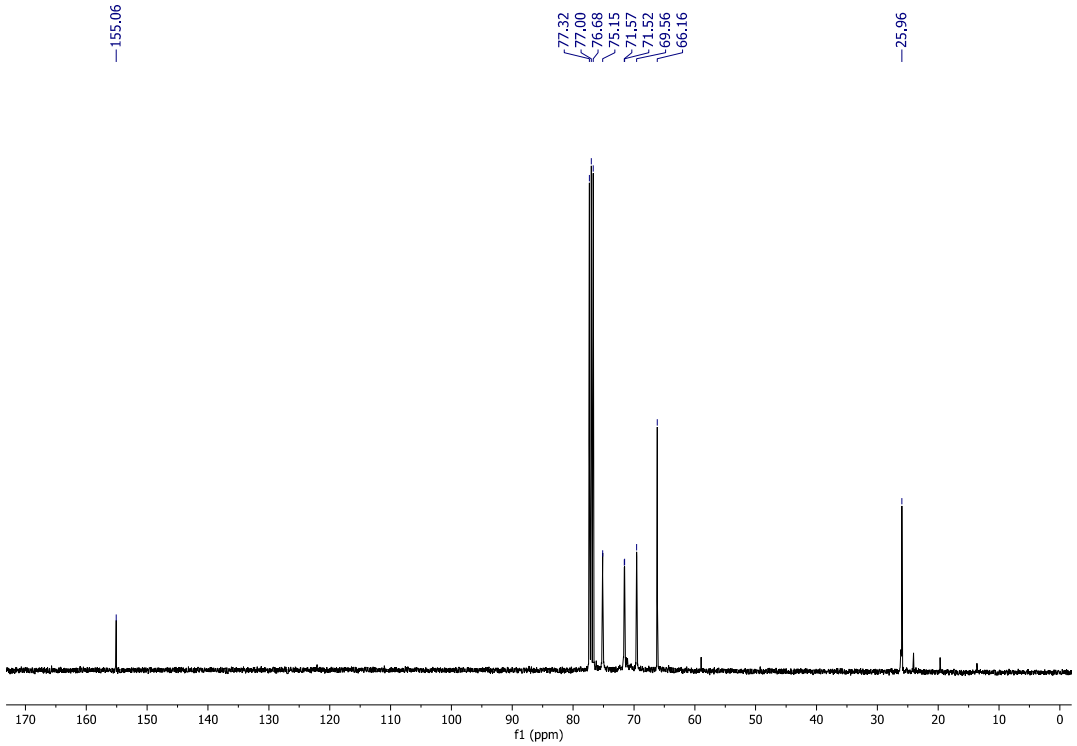

Figure S15b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) **8j**.

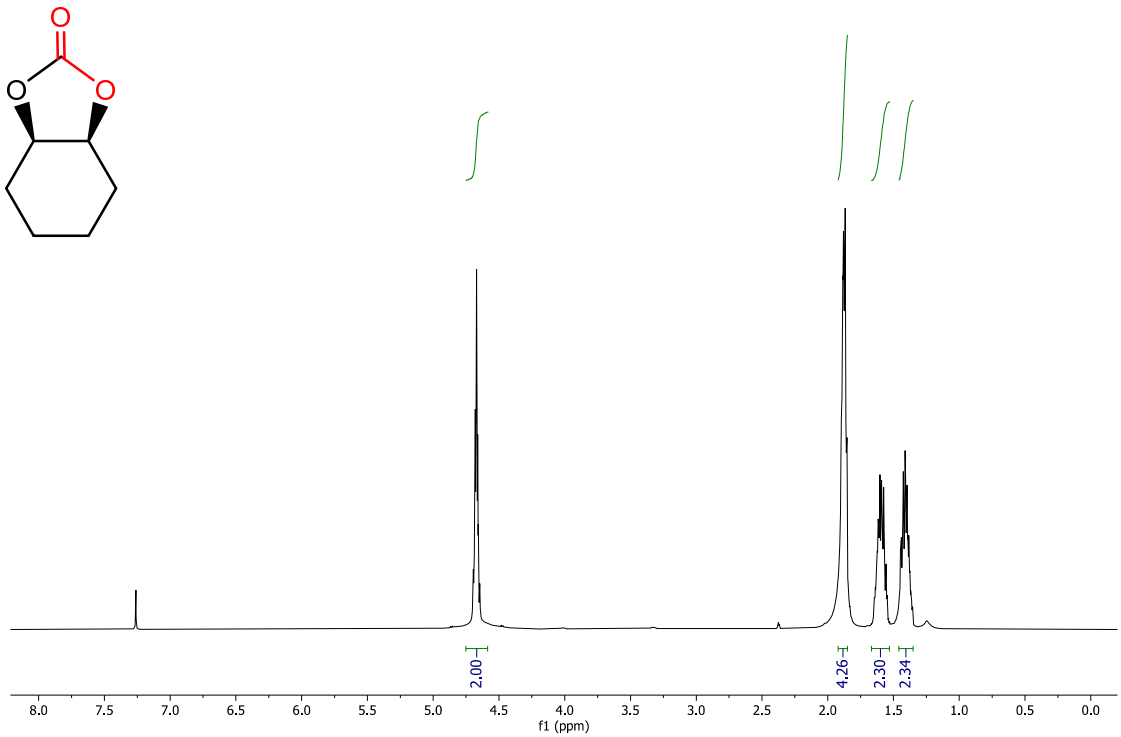

Figure S16a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for *cis*-1,2-cyclohexene carbonate **10a**.

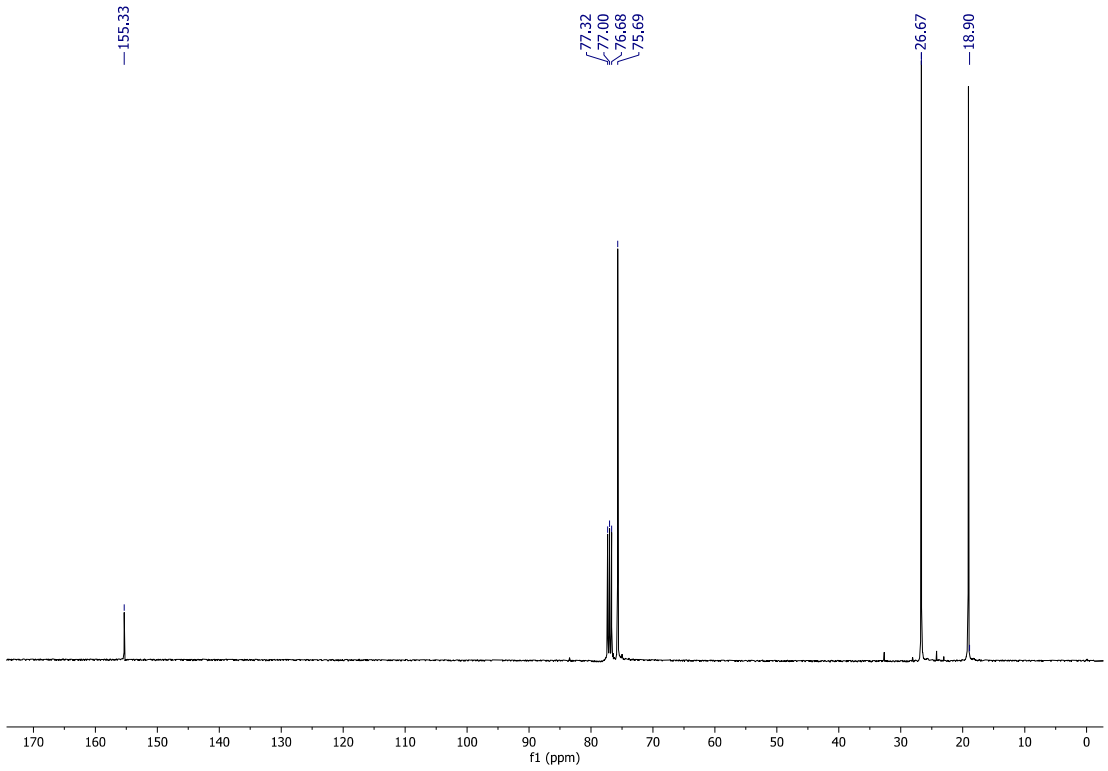

Figure S16b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for *cis*-1,2-cyclohexene carbonate **10a**.

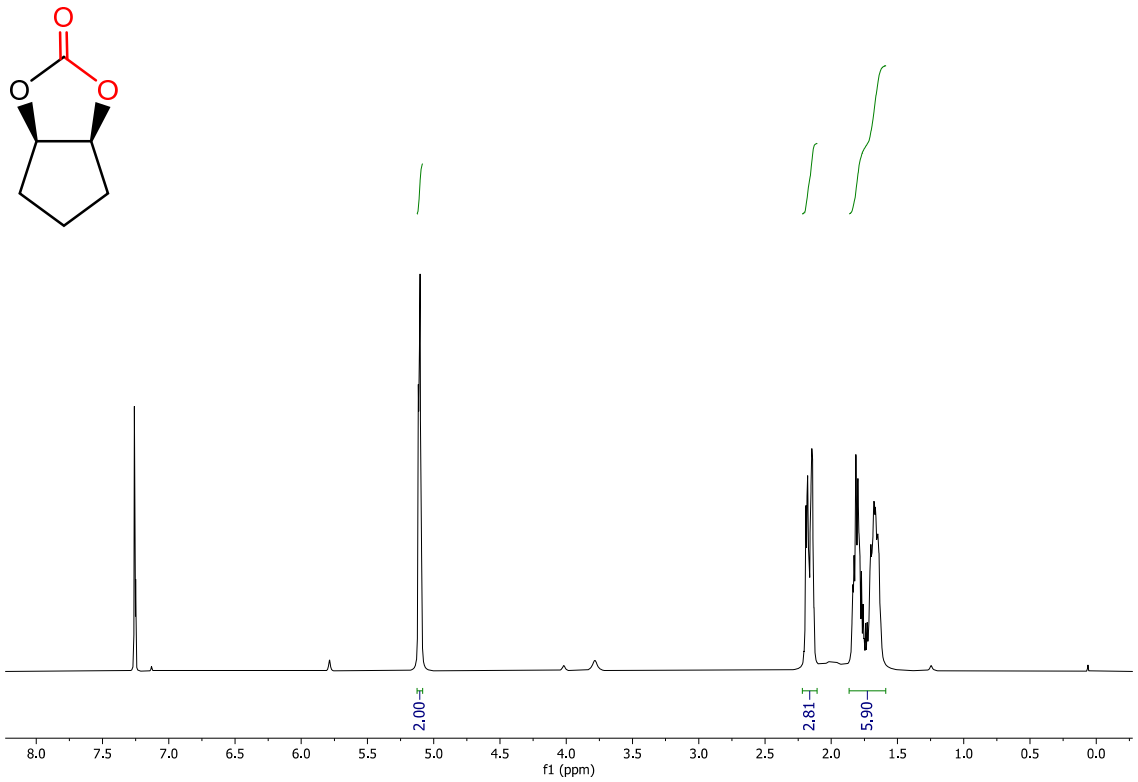

Figure S17a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for *cis*-1,2-cyclopentene carbonate **10b**.

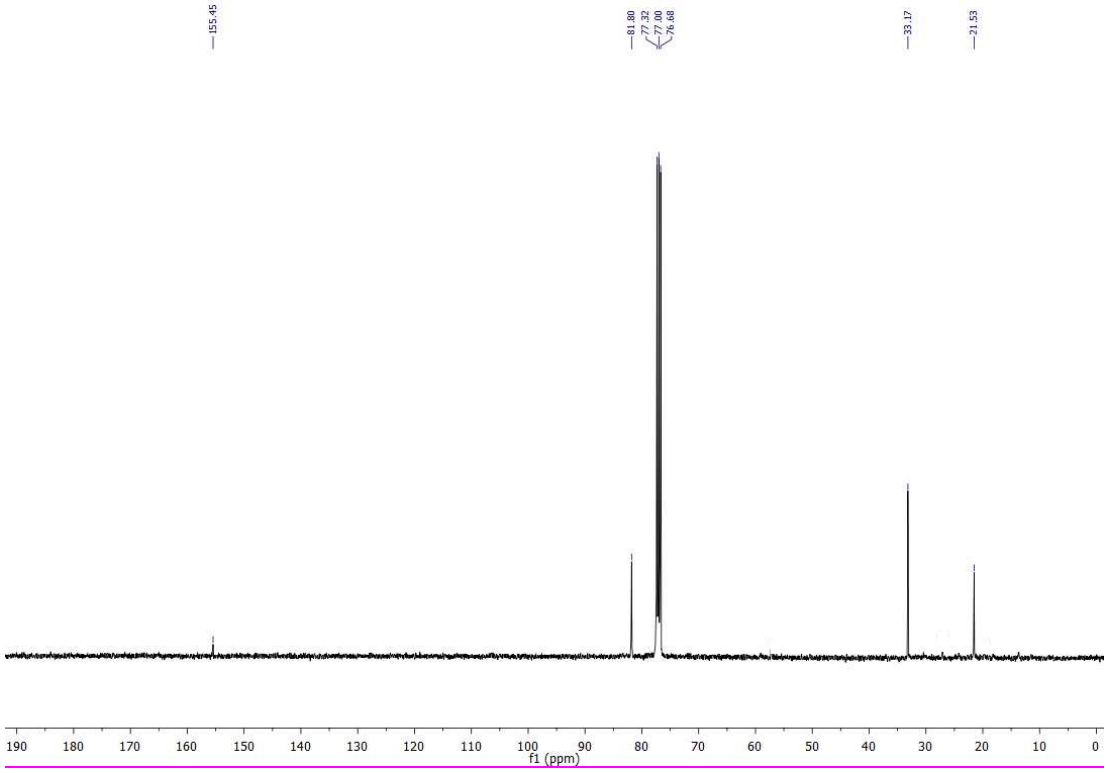

Figure S17b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for c*is*-1,2-cyclopentene carbonate **10b**.

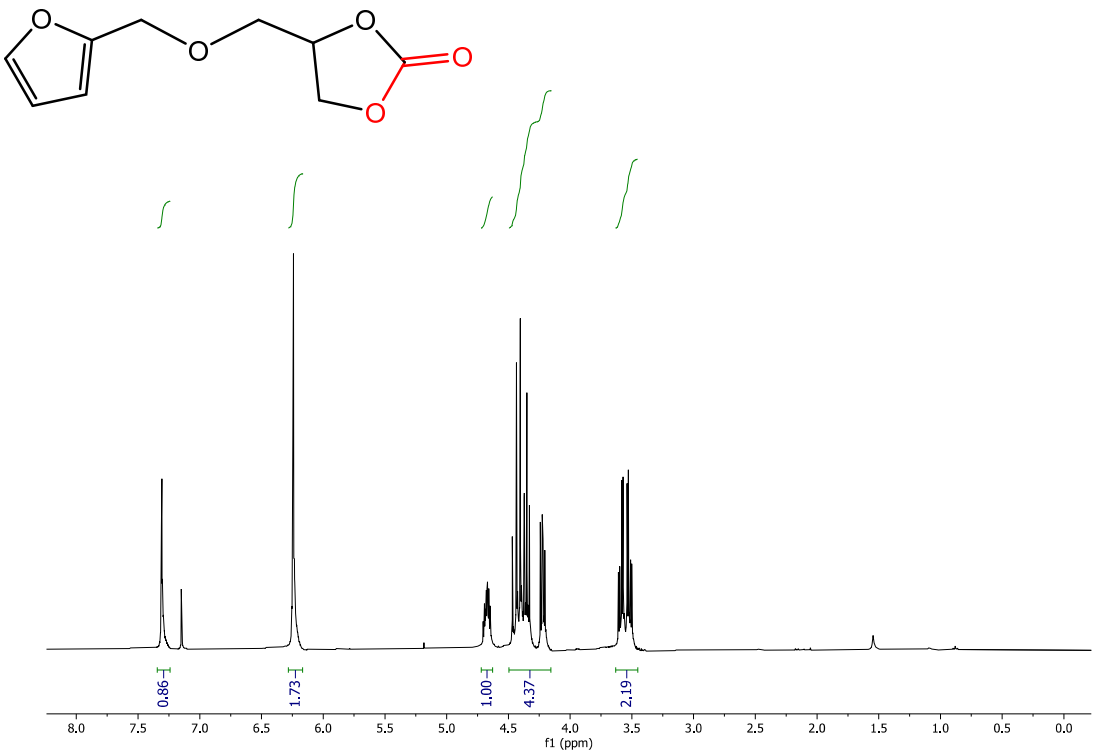

Figure S18a. ^{1}H-NMR spectrum (400 MHz, 297 K, $CDCl_3$) for 4-(furan-2-ylmethoxy)-1,3-dioxolan-2-one **12a**.

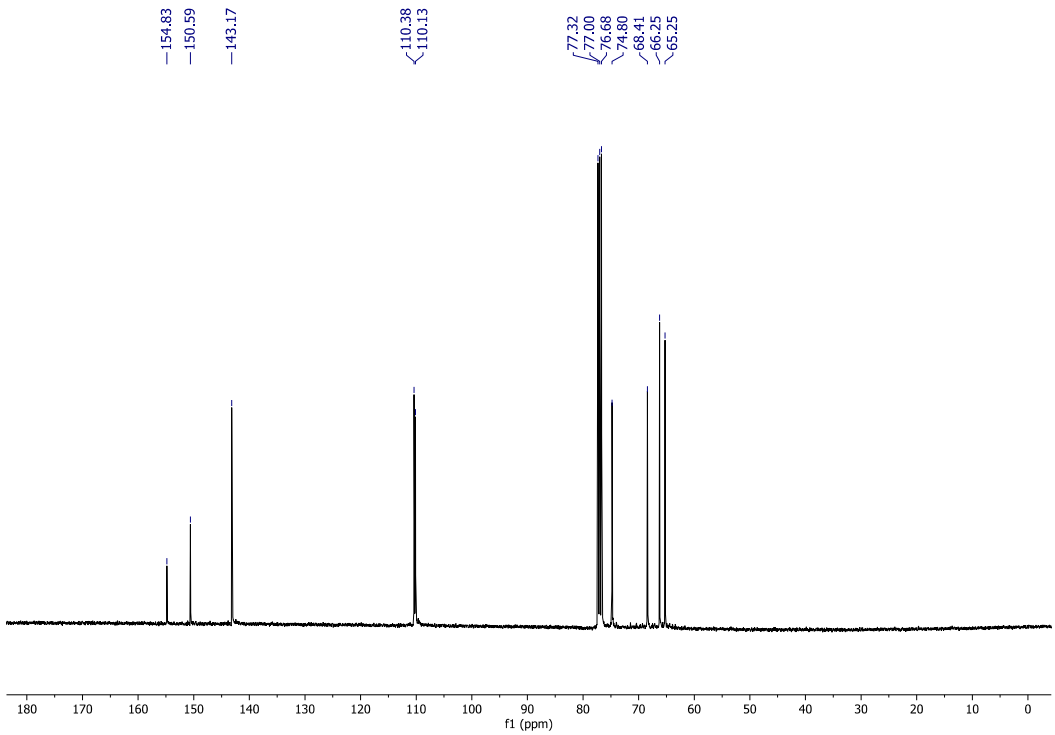

Figure S18b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 4-(furan-2-ylmethoxy)-1,3-dioxolan-2-one **12a**.

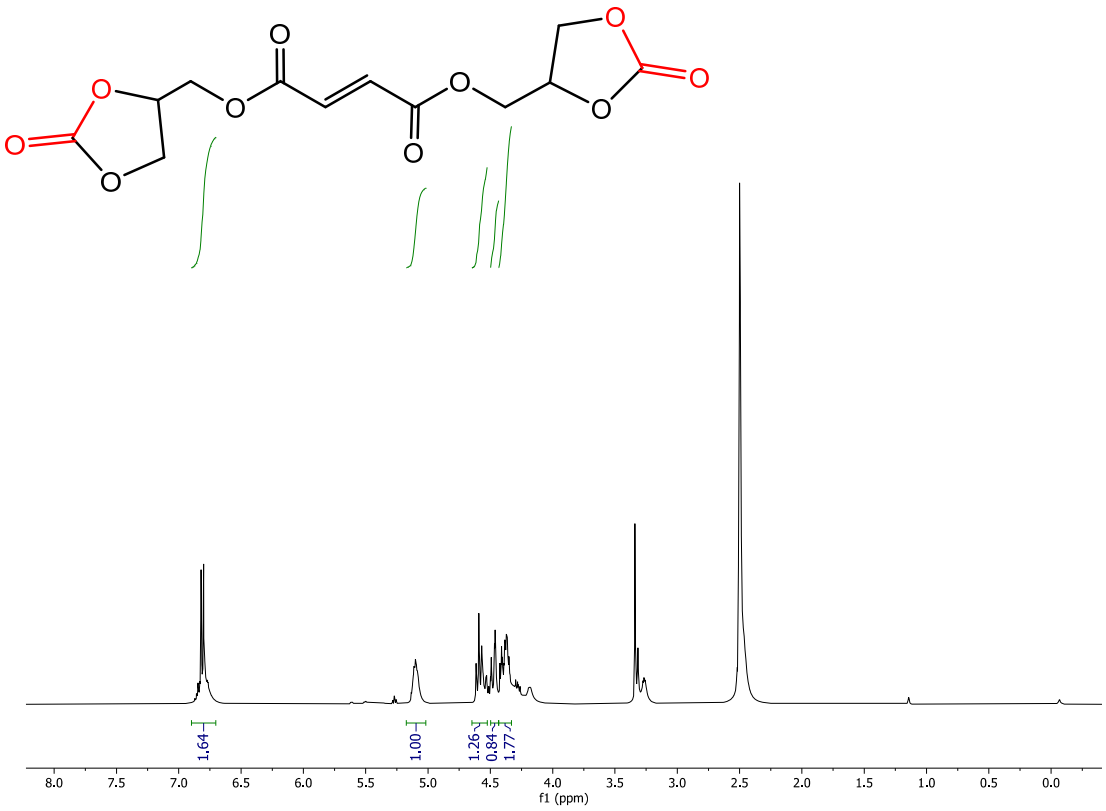

Figure S19a. ^{1}H-NMR spectrum (400 MHz, 297 K, DMSO-d_6) for bis((2-oxo-1,3-dioxolan-4-yl)methyl) fumarate **12b**.

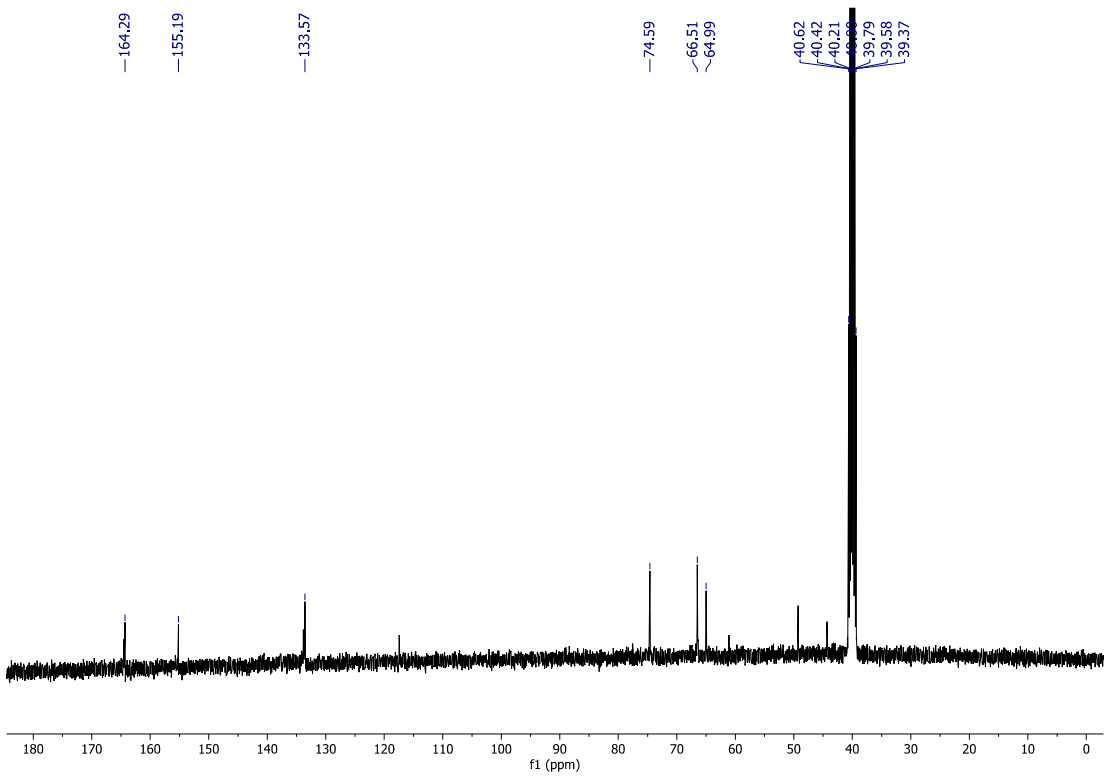

Figure S19b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, DMSO-d_6) for bis((2-oxo-1,3-dioxolan-4-yl)methyl) fumarate **12b**.

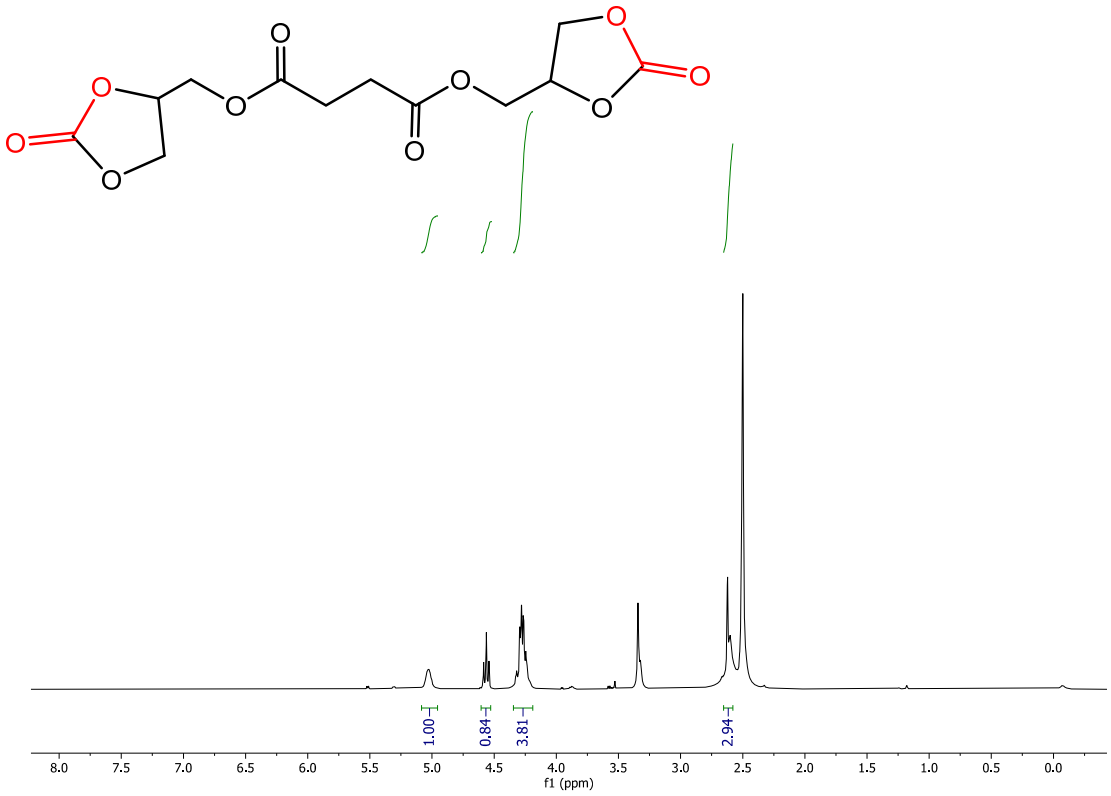

Figure S20a. ^{1}H-NMR spectrum (400 MHz, 297 K, DMSO-d_6) for bis((2-oxo-1,3-dioxolan-4-yl)methyl) succinate **12c**.

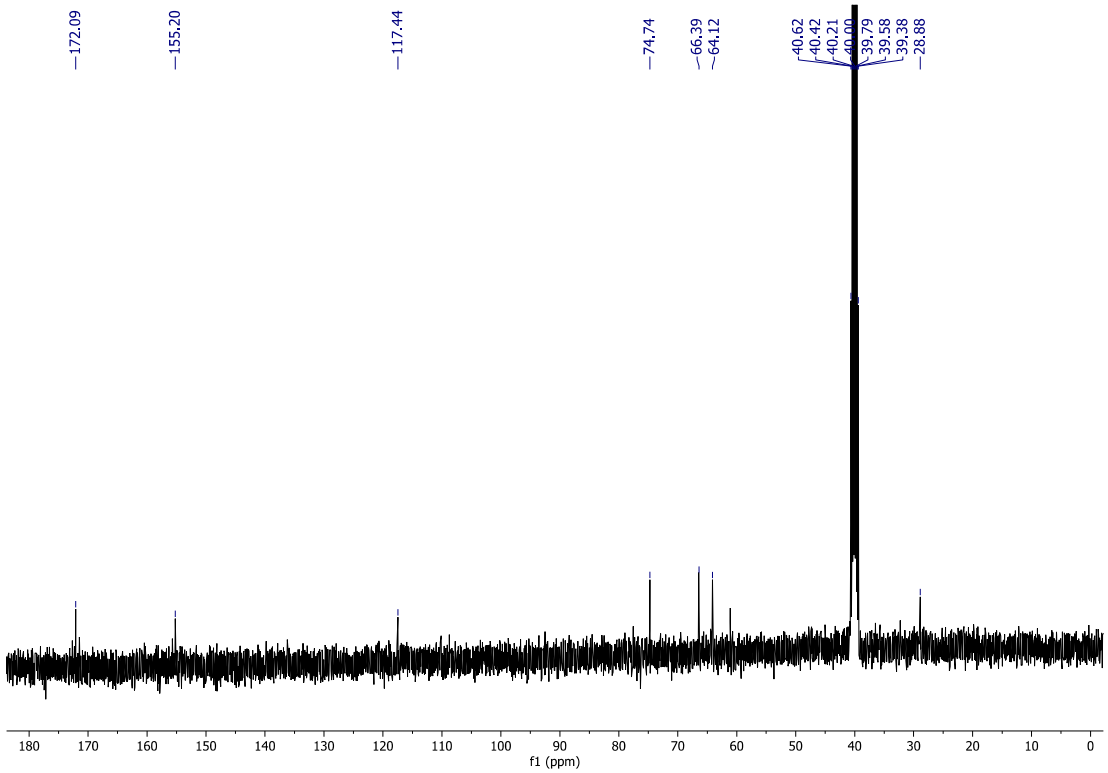

Figure S20b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, DMSO-d_6) for bis((2-oxo-1,3-dioxolan-4-yl)methyl) succinate **12c**.

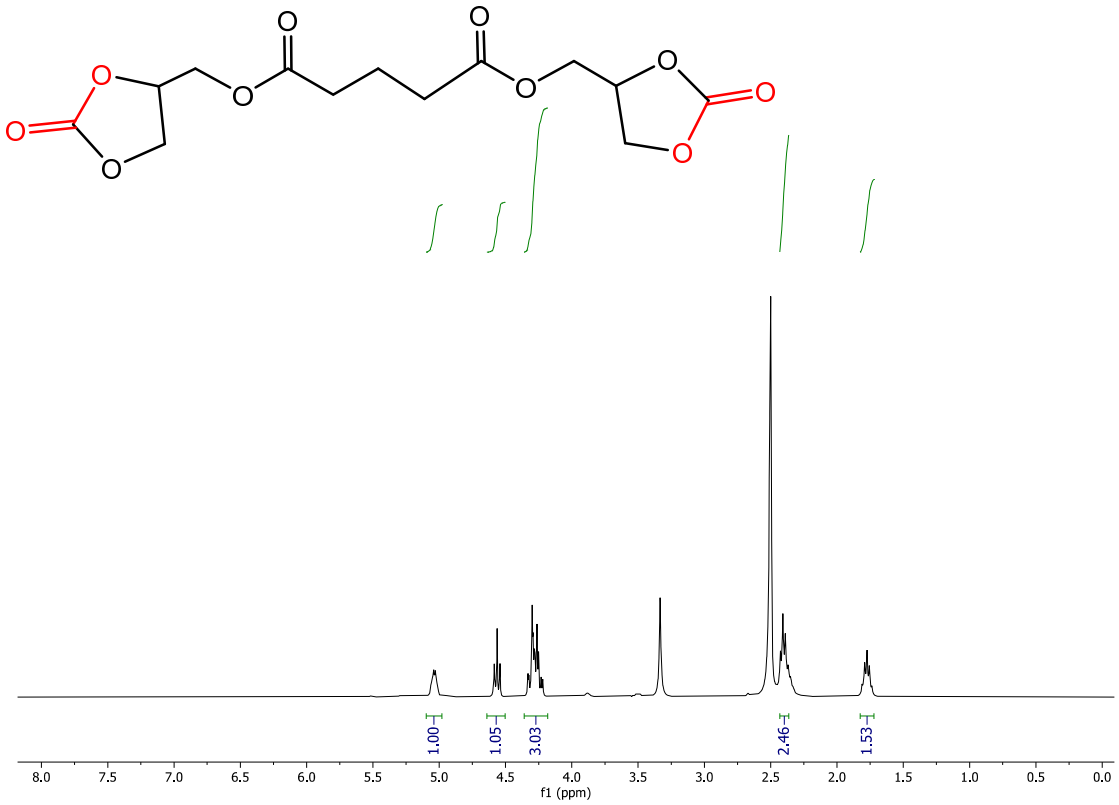

Figure S21a. ^{1}H-NMR spectrum (400 MHz, 297 K, DMSO-d_6) for bis((2-oxo-1,3-dioxolan-4-yl)methyl) glutarate **12d**.

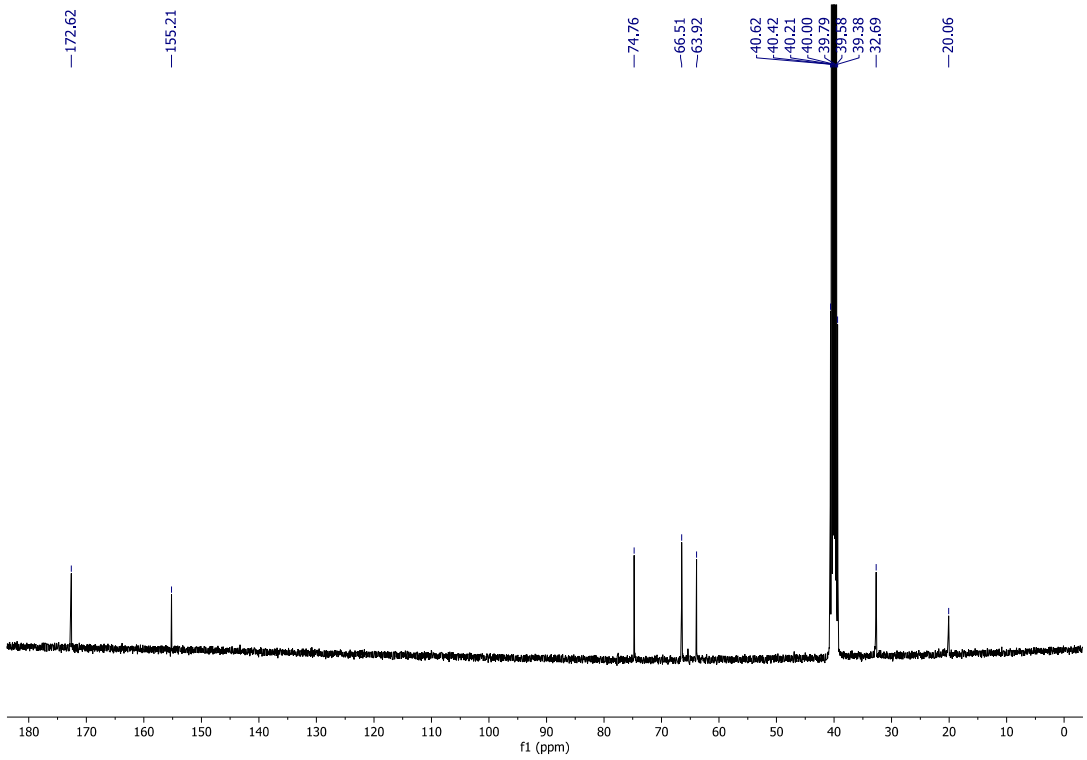

Figure S21b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, DMSO-d_6) for bis((2-oxo-1,3-dioxolan-4-yl)methyl) glutarate **12d**.

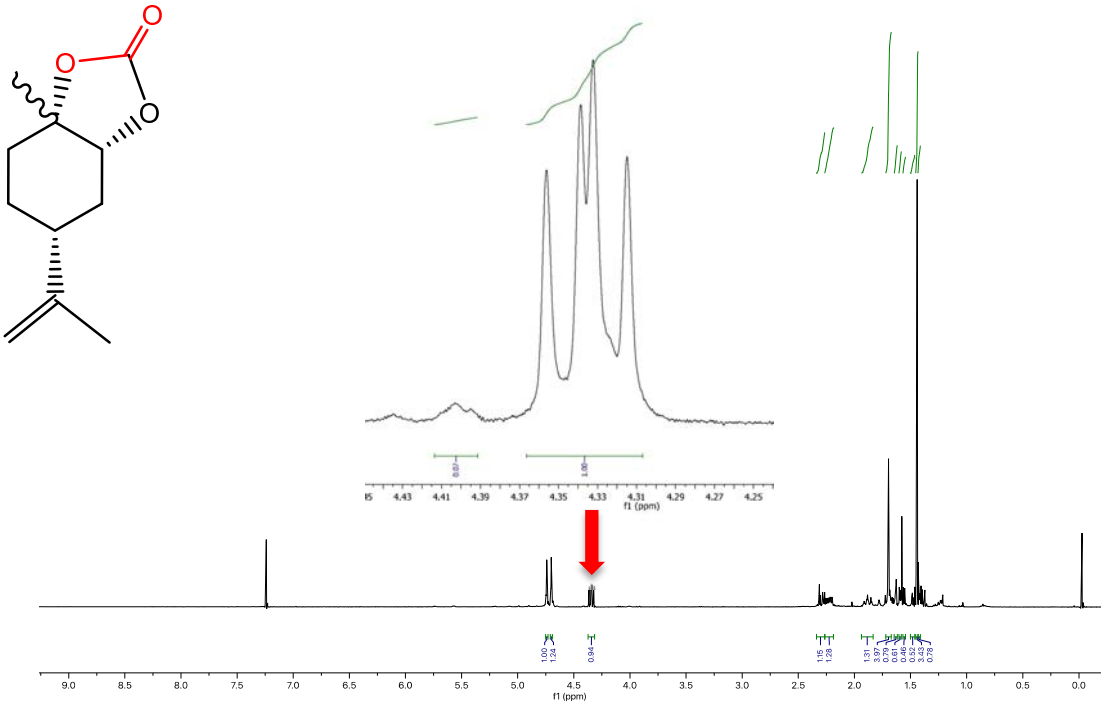

Figure S22a. ^{1}H-NMR spectrum (500 MHz, 297 K, $CDCl_3$) for 3a-methyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*][1,3]dioxol-2-one **14**. (mixture *cis*/*trans*: 6:94)

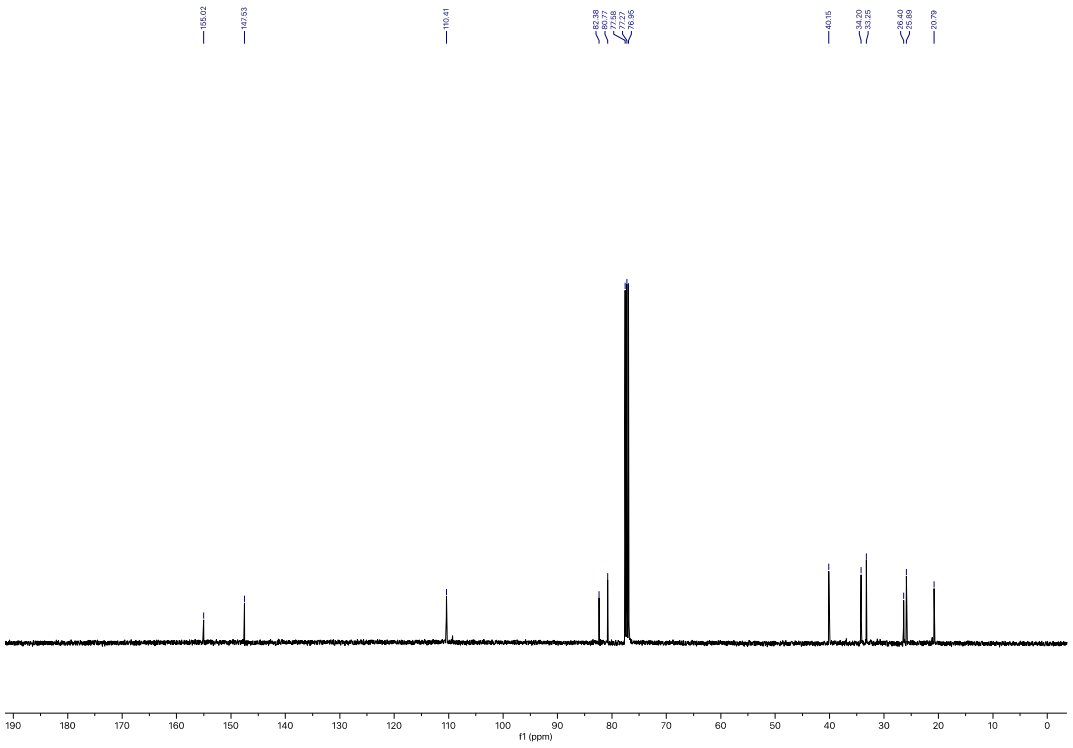

Figure S22b. ^{13}C-{^{1}H}-NMR spectrum (125 MHz, 297 K, $CDCl_3$) for 3a-methyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*][1,3]dioxol-2-one **14**. (mixture *cis*/*trans*: 6:94)

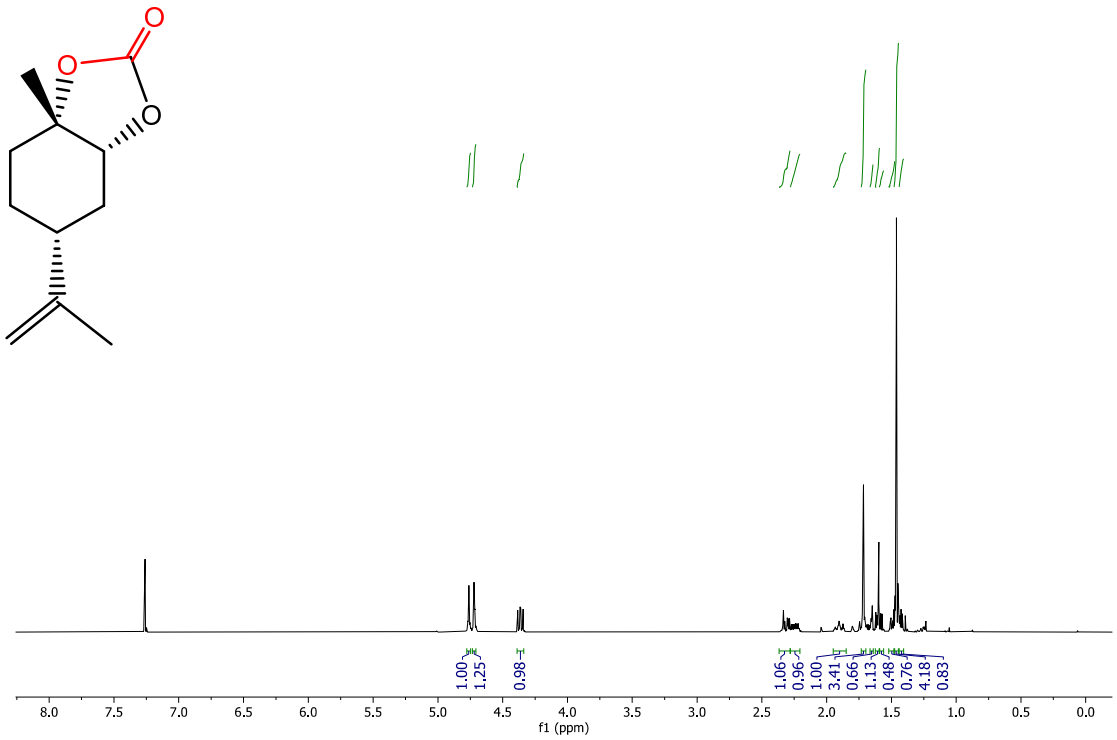

Figure S23a. ^{1}H-NMR spectrum (500 MHz, 297 K, $CDCl_3$) for 3a-methyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*][1,3]dioxol-2-one **14**. (*trans* > 99%)

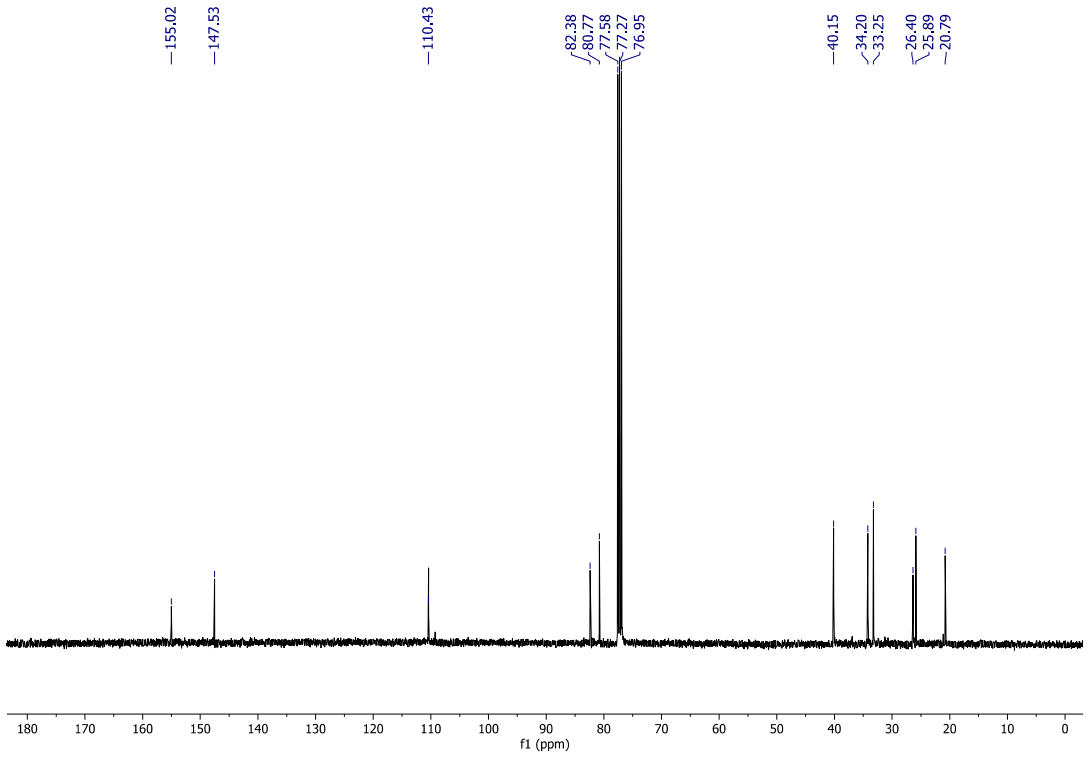

Figure S23b. ^{13}C-{^{1}H}-NMR spectrum (125 MHz, 297 K, $CDCl_3$) for 3a-methyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*][1,3]dioxol-2-one **14**. (*trans* > 99%)

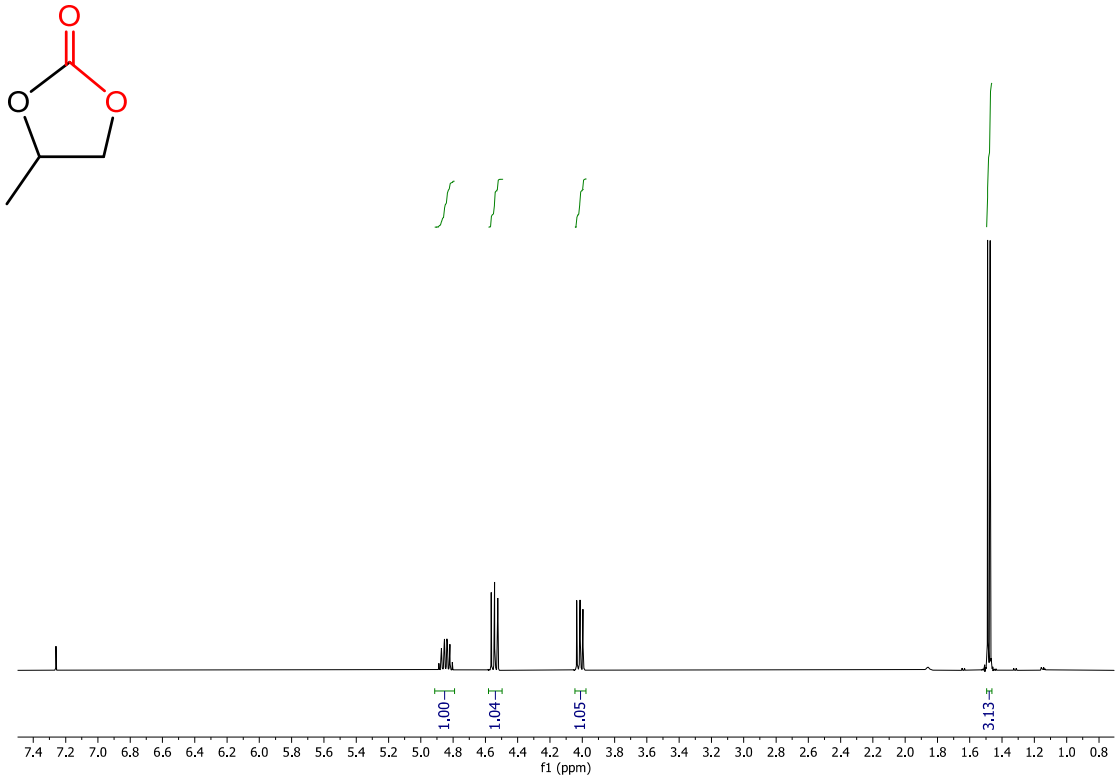

Figure S24a. ^{1}H-NMR spectrum (500 MHz, 297 K, $CDCl_3$) for propylene carbonate **16**.

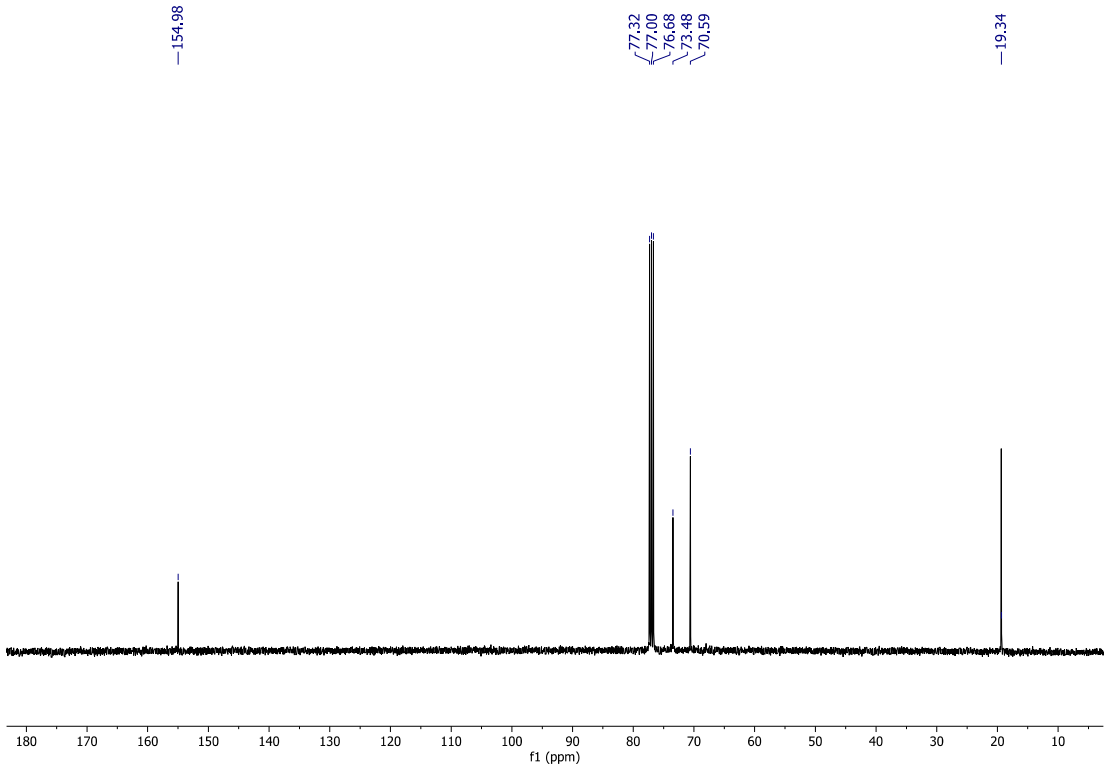

Figure S24b. ^{13}C-{^{1}H}-NMR spectrum (125 MHz, 297 K, $CDCl_3$) for propylene carbonate **16**.

6) Kinetic investigations to determine the order with respect the catalyst and the cocatalyst

Typical kinetic experiment procedure

Styrene oxide **7a** (0.54 g, 4.49 mmol, 8.77 M), complex **4** (121 mg, 0,179 mmol), and TBAB (59,8 mg, 0,179 mmol), were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask fitted with a rubber stopper pierced by a deflated balloon. The conical flask was placed in an oil bath thermostatted at 40 ºC. Cardice pellets were added to the conical flak and the reaction mixture was stirred at this temperature during the whole experiment. Samples of the mixture were withdrawn at different time intervals and the conversion of the epoxide to cyclic carbonate was determined by ^{1}H NMR analysis.

Similar experimental procedures were followed for additional runs but employing the corresponding amount of each substance according to the established loading for catalyst and/or co-catalyst (from 1 % to 4 %).

Kinetics analysis

Once evidenced that the plot of ln[**7a**] *vs.* time clearly exhibited a linear correlation that indicates a first-order dependence of the reaction rate with [**7a**] (see Figure 6 in the manuscript), the general rate equation for this reaction, shown in equation 1, can be rewritten in the form of equation 2 as follows:

$$\text{Rate} = k_1\,[\mathbf{7a}]^{a}[CO_2]^{b}[\mathbf{4}]^{c}[\text{TBAB}]^{d} \quad [1]$$

$$\text{Rate} = k_{1,\text{obs.}}\,[\mathbf{7a}], \text{ where } k_{1,\text{obs.}} = k_1[CO_2]^{b}[\mathbf{4}]^{c}[\text{TBAB}]^{d} \quad [2]$$

In addition, kinetic measurements were performed at early stages of the reaction in order to determine the reaction order with respect catalyst and co-catalyst concentrations. Under these conditions, the general rate law formulae, expressed by equation 1, can be simplified to:

$$\text{Rate}_0 = k_{0,\text{obs.}}[\mathbf{4}]^{c}[\text{TBAB}]^{d}, \quad \text{where } k_{0,\text{obs}} = [\mathbf{7a}]^{a}[CO_2]^{b} \quad [3]$$

That simplification is based on the fact that during the early stages of the reaction (between 5% and 20% conversion) both [CO_2] and [**7a**] may be considered pseudo-constant.

Thus, we performed kinetics experiments using equation 3 to estimate the initial rate of the reaction for different catalyst and co-catalyst concentrations. By keeping one of them constant, it is possible to determine the order with respect the other species.

Firstly, we determined the order with respect complex **4**. Consequently, [**7a**] and [TBAB] were fixed constant to 8.77 *M* and 0.351 *M*, respectively, whilst concentration of complex **4** was varied over the range 0.0877 *M* to 0.351 *M*. In all these runs, 1 bar CO_2 pressure and 40 ºC were employed as experimental conditions. Transformation of **7a** was evaluated at early stages (5%-20% conversion), and a linear dependence on the initial [**7a**] *vs*. time was observed for all the experiments (Figure S25a), as expected for a zero-order reaction.

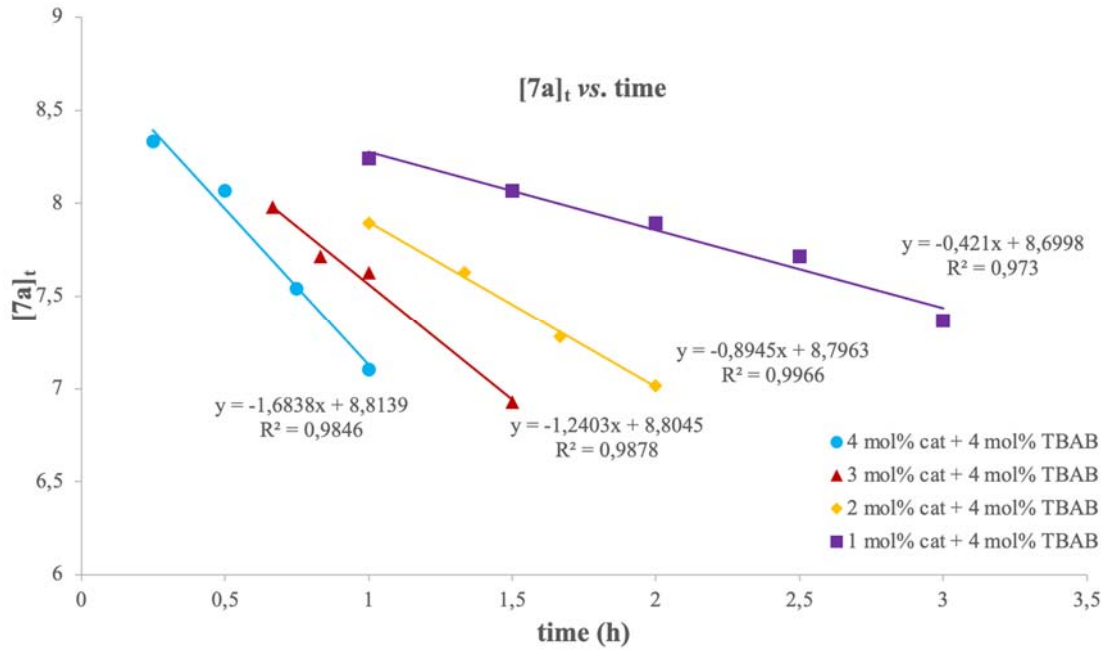

Figure S25a. *Plot of [**7a**] vs time (h) at early stages (5%-20% range) showing a linear fit. [**7a**]$_0$ = 8.77 M, [**4**] = 0.0877 M (violet); 0.175 M (yellow); 0.263 M (red); 0.351 M. (blue); [TBAB]= 0.351 M, at 40 ºC, 1 bar CO_2.*

Initial rates of the reaction can be obtained from the slope of these straight lines for each catalyst concentration studied. Under these conditions, the general equation 1 can be rewritten as:

$$\text{Rate}_0 = k_{0,\text{obs.}}[\mathbf{4}]^c, \text{ where } k_{0,\text{obs}} = [\mathbf{7a}]^a[CO_2]^b[\text{TBAB}]^d \qquad [4]$$

If we take the logarithm of both sides of the equation, we obtain:

$$\ln(\text{rate}_0). = \ln k_{0,\text{obs.}} + c \ln[\mathbf{4}] \quad [5]$$

Catalyst order can be determined from the slope of the plot between ln(rate$_o$) and ln[**4**]. As it is showed in Figure S25b, the order was found to be 1 with respect catalyst **4** concentration.

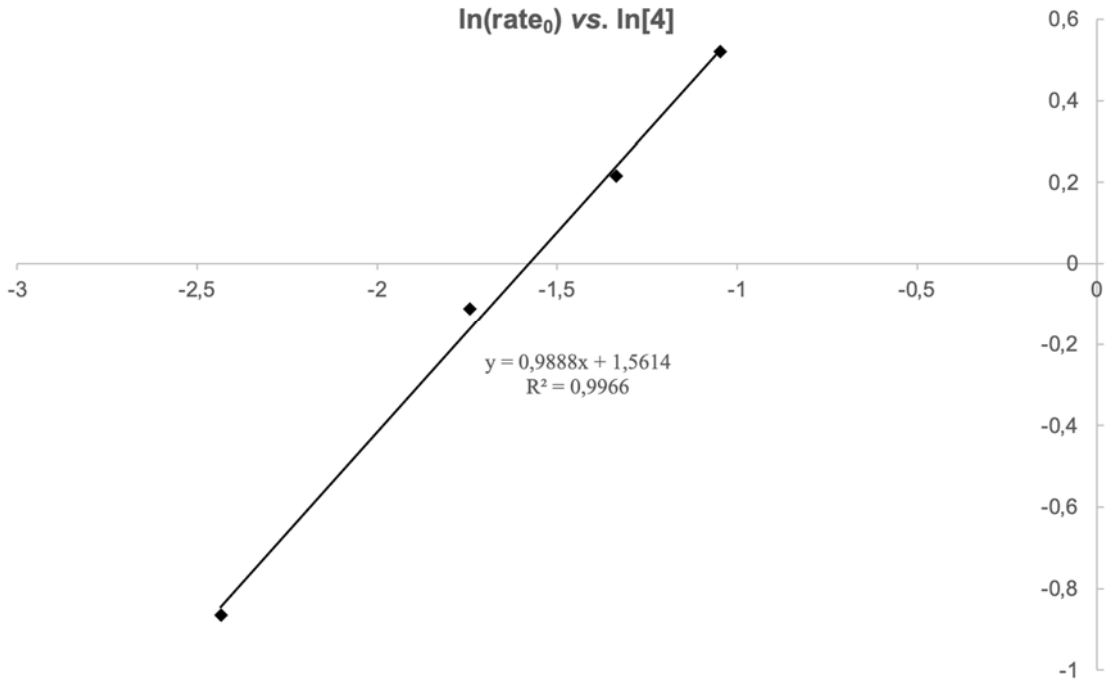

Figure S25b. *Plot of natural logarithm of initial rate vs. ln[4] with [4] = 0.0877 M to 0.351 M; [**7a**]$_0$ = 8.77 M, [TBAB] = 0.351 M, at 40 ^{o}C and 1 bar CO_2.*

The order with respect co-catalyst can be determined following a similar procedure under the same conditions, but keeping concentration of complex **4** constant, 4% (0.351 *M*) of initial epoxide concentration (8.77 *M*), and varying [TBAB] from 0.0877 M to 0.351 M. Again, a linear dependence

on the initial epoxide concentration *vs*. time was observed at early stages of the reaction, as it is shown in Figure S25c.

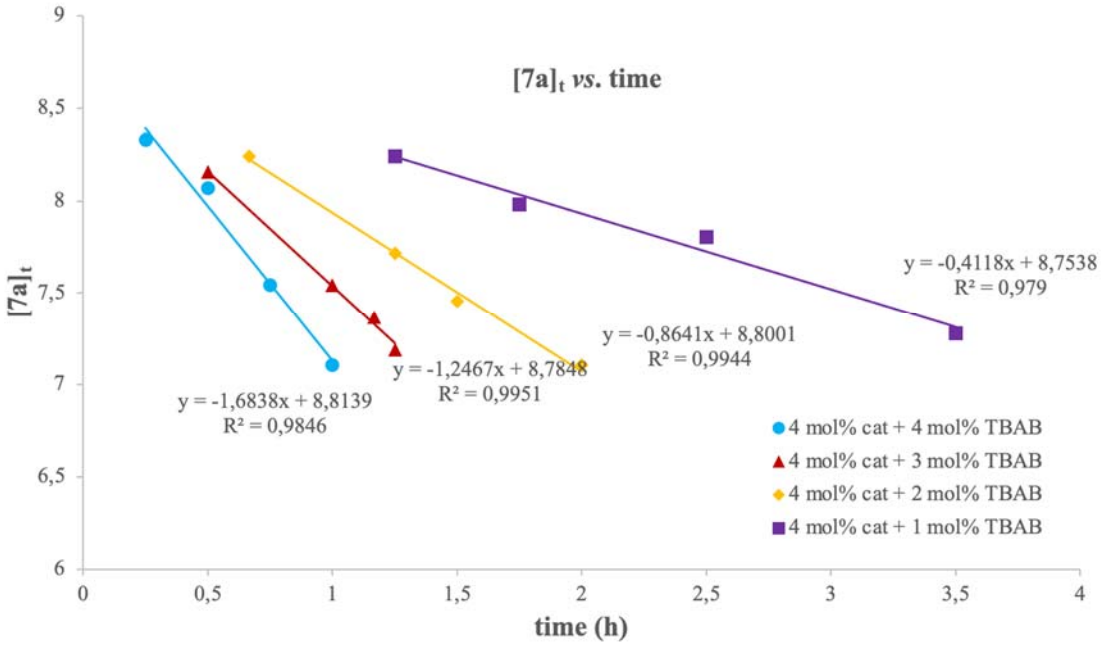

Figure S25c. *Plot of [**7a**] vs time (h) at early stages (5%-20% range) showing a linear fit. [**7a**]$_0$ = 8.77 M, [TBAB] = 0.0877 M (green); 0.175 M (red); 0.263 M (orange); 0.351 M. (blue); [**4**] = 0.351 M, at 40 ^{o}C, 1 bar CO_2.*

As shown previously, initial rates of the reaction of each experiment can be obtained from the slopes of the straight lines. The general rate law can be then expressed under these conditions as:

$$\text{Rate}_0 = k'_{0,\text{obs.}}[\text{TBAB}]^d, \text{ where } k'_{0,\text{obs}} = [\mathbf{7a}]^a[CO_2]^b[\mathbf{4}]^d \qquad (6)$$

By taking logarithm in both sides of equation 6, we obtain:

$$\ln(\text{rate}_0) = \ln k'_{0,\text{obs.}} + d \ln[\text{TBAB}] \qquad [7]$$

Co-catalyst order can be determined from the slope of the plot between ln(rate)$_0$ and ln[TBAB]. As it is showed in Figure S25d, the order was found to be 1 with respect co-catalyst concentration.

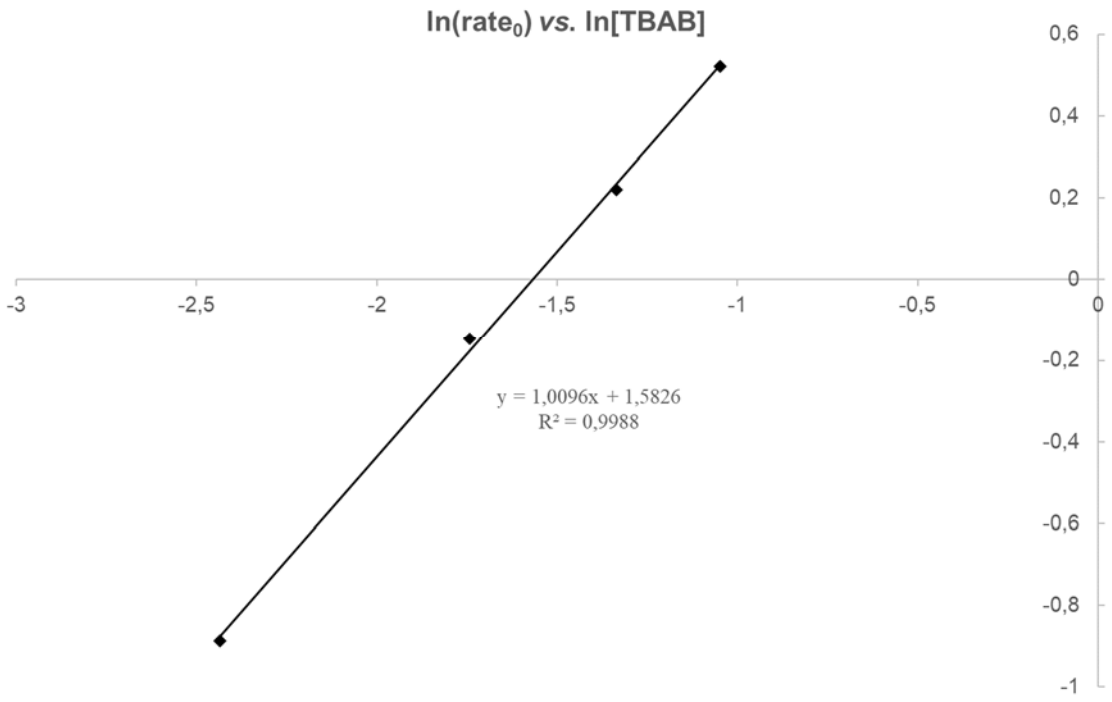

Figure S25d. *Plot of natural logarithm of initial rate vs. ln[TBAB] with [TBAB] = 0.0877 M to 0.351 M; [**7a**]$_0$ = 8.77 M, [**4**] = 0.351 M, at 40 °C and 1 bar CO_2.*

Complete set of kinetic data are summarized in Tables S2a and S2b with the corresponding associated error

Table S2a. Initial rate (r_0) for experiments conducted fixing the amount of TBAB

Conc. (mM)	r_0 **(h^{-1})**	**Error (h^{-1})**	r_0 **(s^{-1})**	**Error (s^{-1})**	r_0 **(s^{-1}) × 10^4**	**Error (s^{-1})× 10^4**	r_0 **± error (s^{-1}) × 10^4**
87.7	0.421	4.05E-02	1.169E-04	1.13E-05	1.2	0.1	1.2 ± 0,1
175	0.895	3.72E-02	2.485E-04	1.03E-05	2.5	0.1	2.5 ± 0,1
263	1.240	9.77E-02	3.445E-04	2.71E-05	3.4	0.3	3.4 ± 0,3
351	1.684	1.49E-01	4.677E-04	4.13E-05	4.7	0.4	4.7 ± 0,4

Reaction order with respect [4] = 0.988 ± 0.04

Table S2b. Initial rate (r_0) for experiments conducted fixing the amount of complex **4**

Conc. (mM)	r_0 **(h^{-1})**	**Error (h^{-1})**	r_0 **(s^{-1})**	**Error (s^{-1})**	r_0 **(s^{-1}) × 10^4**	**Error (s^{-1})× 10^4**	r_0 **± error (s^{-1}) × 10^4**
87.7	0.412	4.26E-02	1.144E-04	1.18E-05	1.1	0.1	1.1 ± 0,1
175	0.864	4.57E-02	2.400E-04	1.27E-05	2.4	0.1	2.4 ± 0,1
263	1.247	6.20E-02	3.463E-04	1.72E-05	3.5	0.2	3.5 ± 0,2
351	1.684	1.49E-01	4.677E-04	4.13E-05	4.7	0.4	4.7 ± 0,4

Reaction order with respect [TBAB] = 1.01 ± 0.02

7) Mechanistic studies

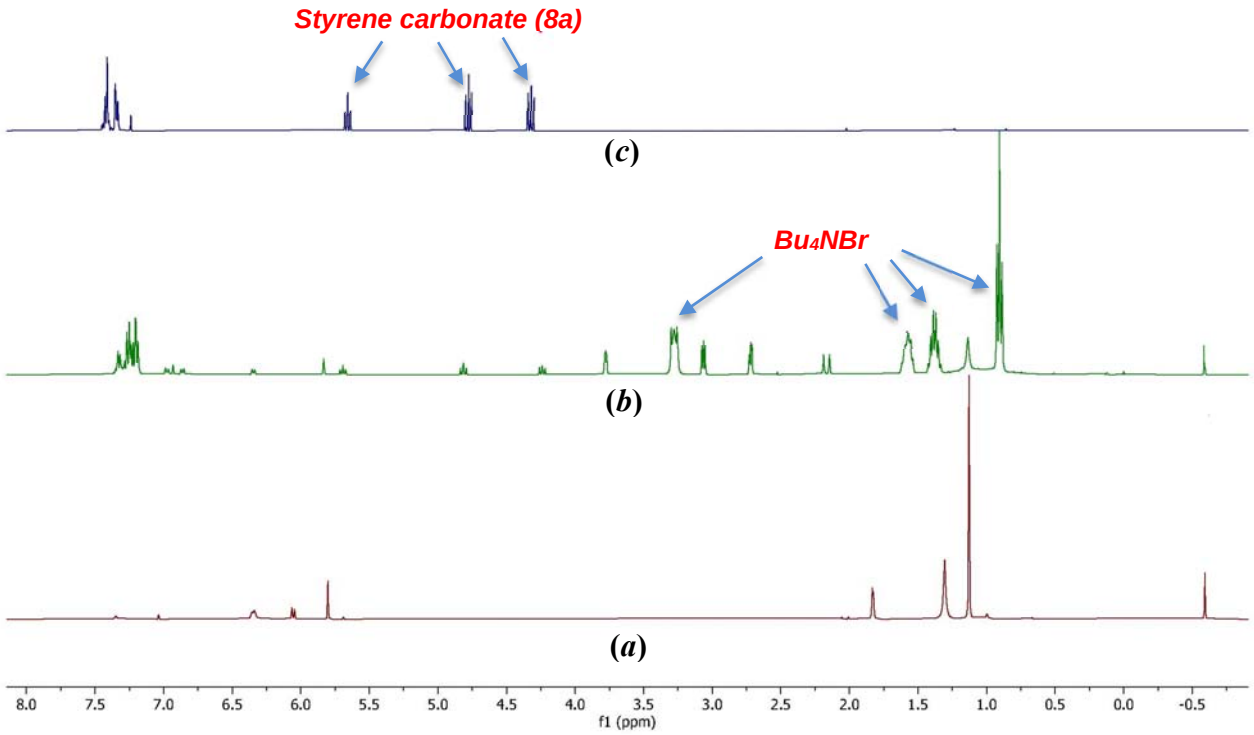

Figure S26. ^{1}H-NMR spectrum (500 MHz, 297 K, $CDCl_3$) of *(a)* [ZnMe(κ^3-phbp^{t}amd)] (**4**), *(b)* the reaction of complex **4** with styrene oxide **7a** and Bu_4NBr as co-catalyst in 1:1:8 proportion in the presence of 1 bar CO_2 pressure in a Young tube after 3 h at 50 ºC, *(c)* styrene carbonate **8a**.

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