Electronic Supplementary Information

High activity and switchable selectivity in the synthesis of cyclic and polymeric cyclohexene carbonates with iron amino triphenolate catalysts

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Synthesis of Fe-complex **1c**

A tetrahydrofuran solution (30 mL) of the hexa-chlorinated amino-triphenol pre-ligand (612 mg, 1.13 mmol) was slowly added to a suspension of sodium hydride (81 mg, 3.39 mmol) in tetrahydrofuran (10 mL). The suspension was stirred overnight and then added to anhydrous iron (III) chloride (183 mg, 1.13 mmol), whereby the suspension immediately turned dark brown. The mixture was stirred for a further 5 h before being filtered through a pad of Celite® and the solvent was removed under reduced pressure to afford a brown powder; yield: 685 mg (91%). Crystals suitable for single crystal X-ray diffraction studies were obtained by slow evaporation of a concentrated tetrahydrofuran solution. HRMS (MALDI+, dctb): *m/z* = 593.8459, calcd. for $[M{-}THF]^+$: 593.8268; UV−vis (CH_2Cl_2): λ = 429 nm (6,355 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$), 338 nm (7,045 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$); IR (neat, cm^{-1}): ν = 1585 (vw), 1554 (vw), 1468 (m), 1451(s), 1435 (s), 1358 (m), 1302 (s), 1275 (w), 1241 (m), 1211 (m), 1178 (m), 1102 (vw), 1078 (w), 1034 (vw), 1013 (w), 970 (w), 929 (vw), 870 (m), 857 (s), 766 (s), 742 (m), 730 (m), 672 (m), 630 (vw), 582 (s), 520 (w), 483 (s), 407 (vw). X-ray quality crystals were grown from THF. Pertinent data is located in the crystallographic information file (cif), refer to CCDC 943926. A visual representation of the structure is provided in Fig. S1.

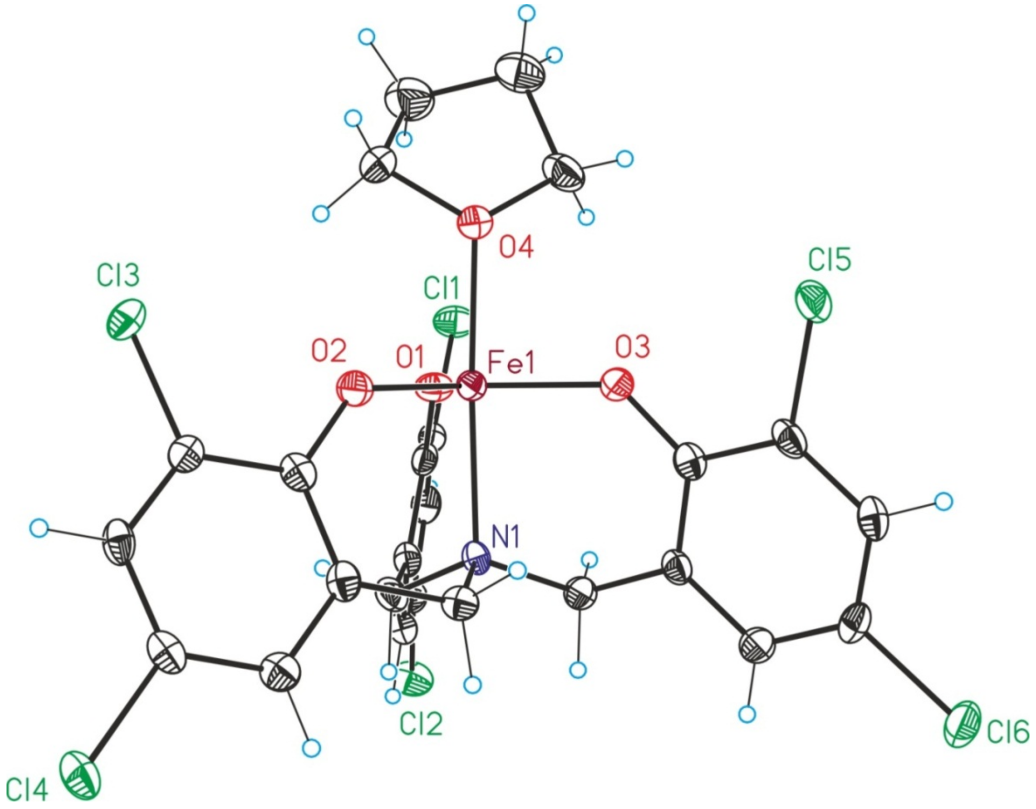


Figure S1. X-ray analysis of Fe-complex 1c. Further details are provided in the crystallographic information file (CIF), see CCDC 943926.

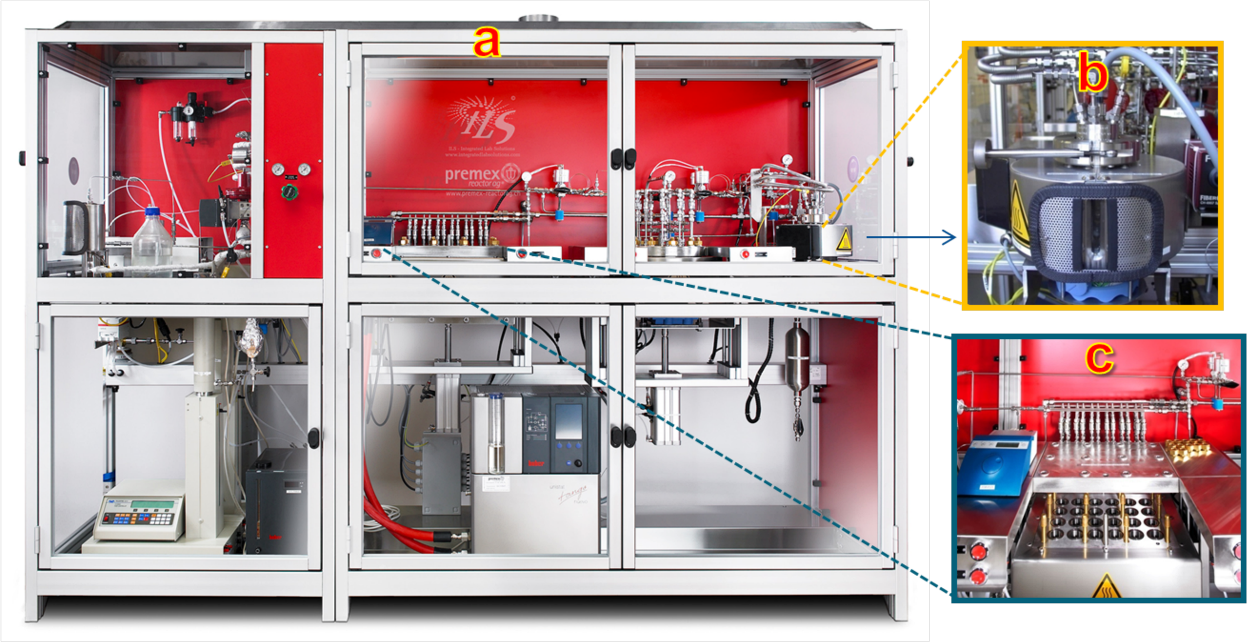


Figure S2. Supercritical CO_2 high-throughput platform used for the catalytic test (a): visualisation reactor (b) and 24 parallel batch reactors unit (c).

Characterisation of the reaction products:

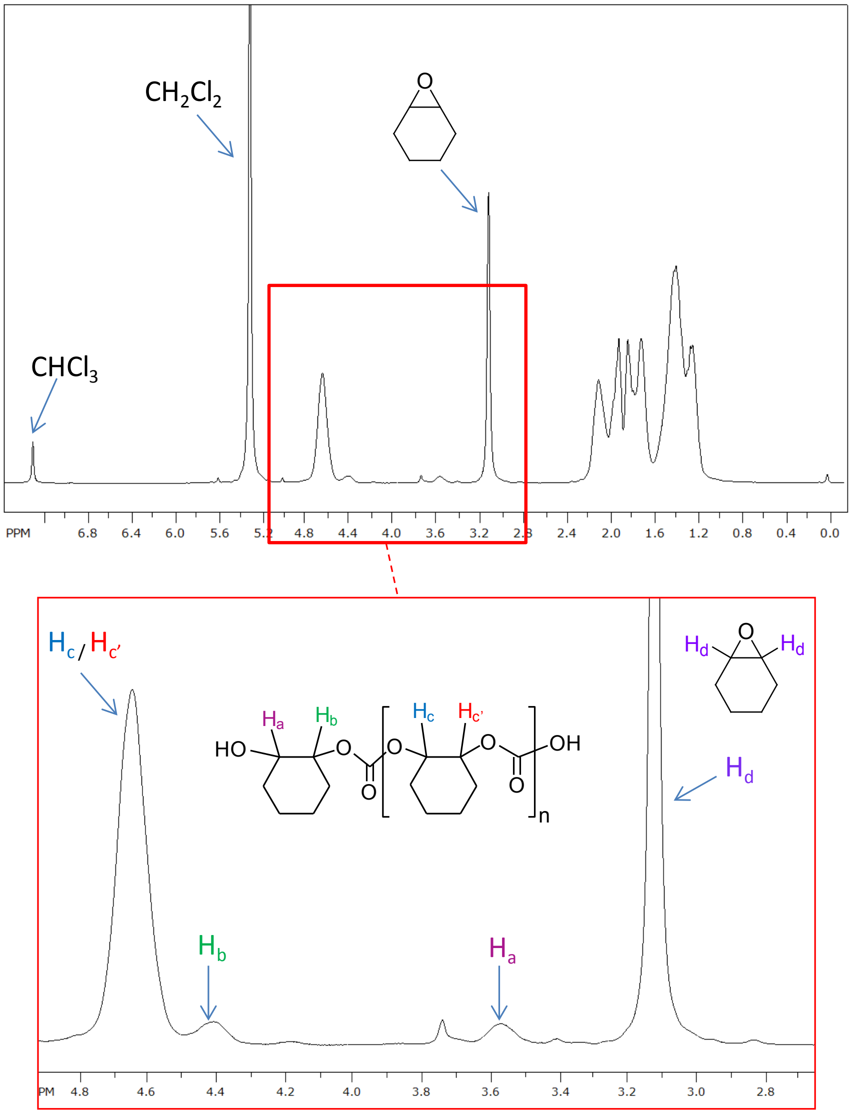


Figure S3. ^{1}H NMR spectrum of the reaction mixture using catalyst **1b** 0.1 mol% and co-catalyst **2e** 0.1 mol% (Table 2, entry 10) in CDCl$_3$. Two H atoms of cyclohexene oxide (H$_d$) appear at 3.12 ppm. The H atoms in the repeating unit of poly(cyclohexene carbonate) appear at 4.63 ppm (H$_c$ and H$_{c'}$). The H atoms of the end groups of poly(cyclohexene carbonate) appear at 3.56 and 4.40 ppm (H$_a$ and H$_b$). The assignment of a hydroxyl as end-capping group is based on a previously reported value of the chemical shift of H$_a$,[33] and is supported by the fact that the peak of H$_a$ is in the same position in the spectra of all polycarbonates, regardless of the nature of the halide in the co-catalyst (Cl, Br or I). This also indicates that halogen-terminated polymers, if any, are present only in low amounts.

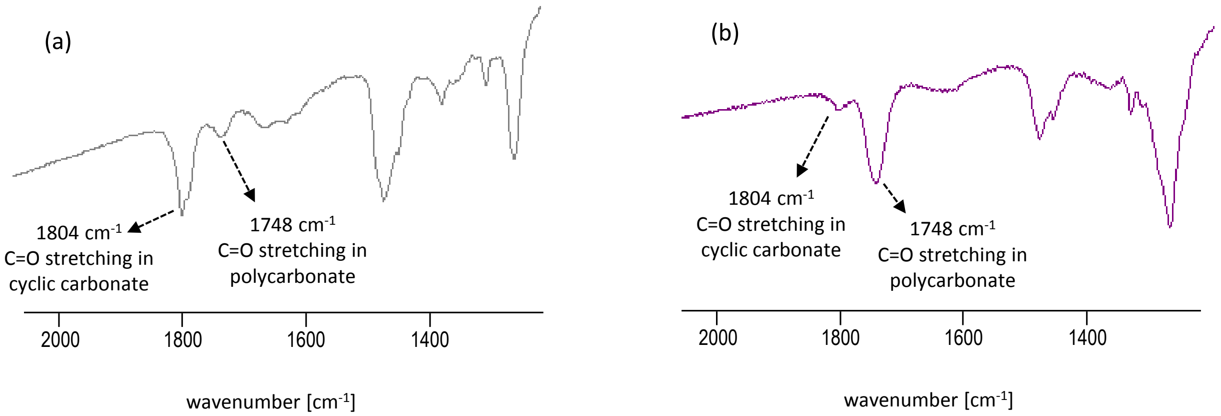


Figure S4. Examples of FT-IR spectra used for determining the ratio between cyclic cyclohexene carbonate (CHC) and poly(cyclohexene carbonate) (PCHC): (a) reaction catalysed by complex **1a** and NBu_4F in 1:5 ratio (Table 1, entry 2); (b) reaction catalysed by complex **1a** and NBu_4F in 1:1 ratio (Table 1, entry 3). The selectivity (%) towards the cyclic carbonate product was calculated as $100 \times A_{CHC}/(A_{CHC} + A_{PCHC})$, where A is the absorbance [$A = \log (T_0 / T_1)$] that can be calculated from the measured values of T_0 (transmittance of the baseline) and T_i (transmittance of the C=O band). The selectivity towards the polycarbonate product was calculated as $100 \times A_{PCHC} /(A_{CHC} + A_{PCHC})$.

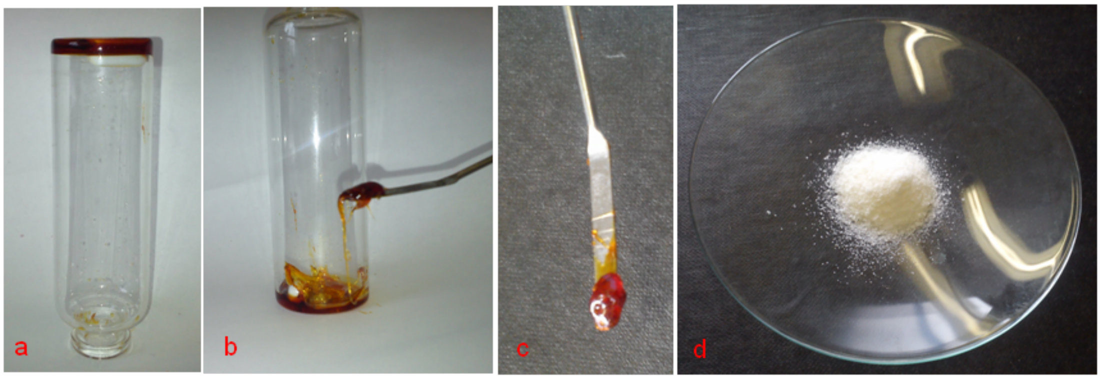


Figure S5. Purification of poly(cyclohexene carbonate): a typical reaction mixture at the end of the catalytic test (a-c); polymer powder after re-precipitation and drying in a Schlenk line (d).

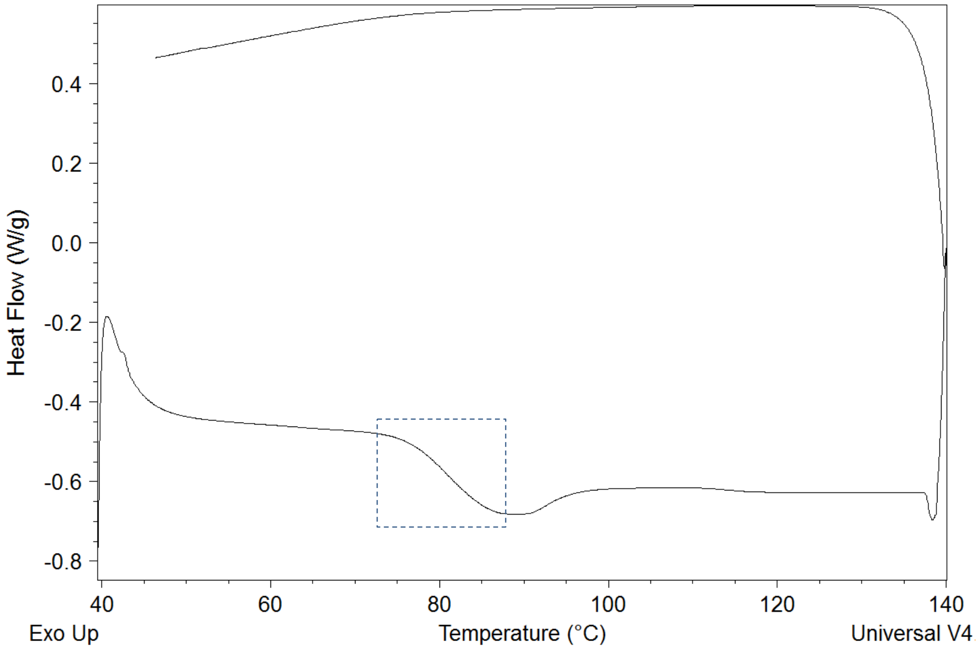


Figure S6. DSC thermogram of poly(cyclohexene carbonate) produced with catalyst **1a** 0.1 mol% and co-catalyst **2e** 0.025 mol% (Table 3, entry 2). The signal at around 80°C is identified as the glass transition temperature (T_g) of the polymeric material. This assignment is supported by the persistence of the signal in the second analysis cycle, thus ruling out the possibility that it originated from solvent or moisture evaporation.

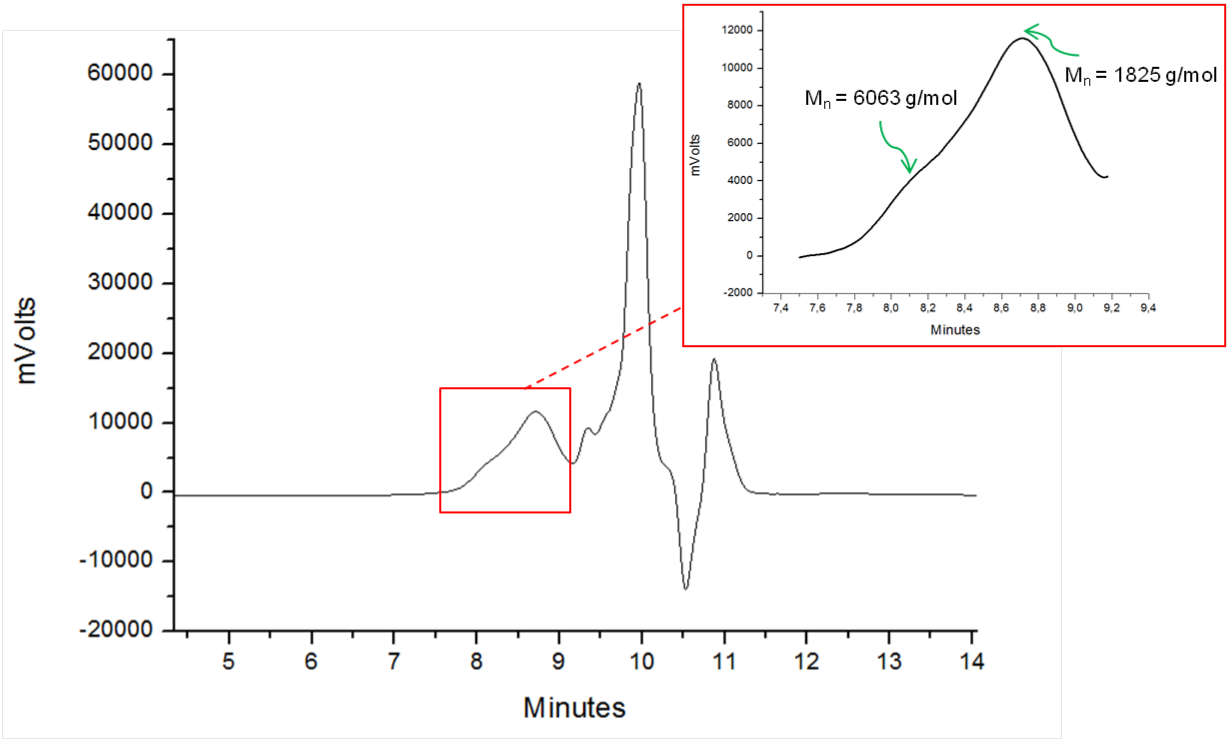


Figure S7. Bimodal GPC trace of poly(cyclohexene carbonate) produced using catalyst **1b** 0.1 mol% and co-catalyst **2e** 0.1 mol% (Table 2, entry 10).

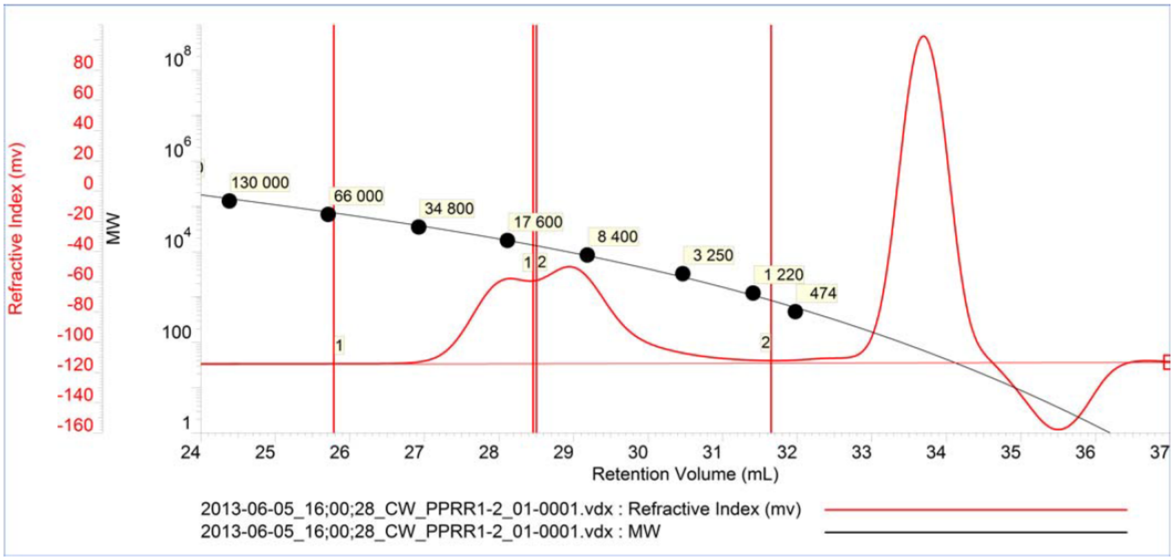


Figure S8. GPC analysis of poly(cyclohexene carbonate) formed under anhydrous conditions (Table 5, entry 1).

Figure S9. Schlenk reactor vessel.

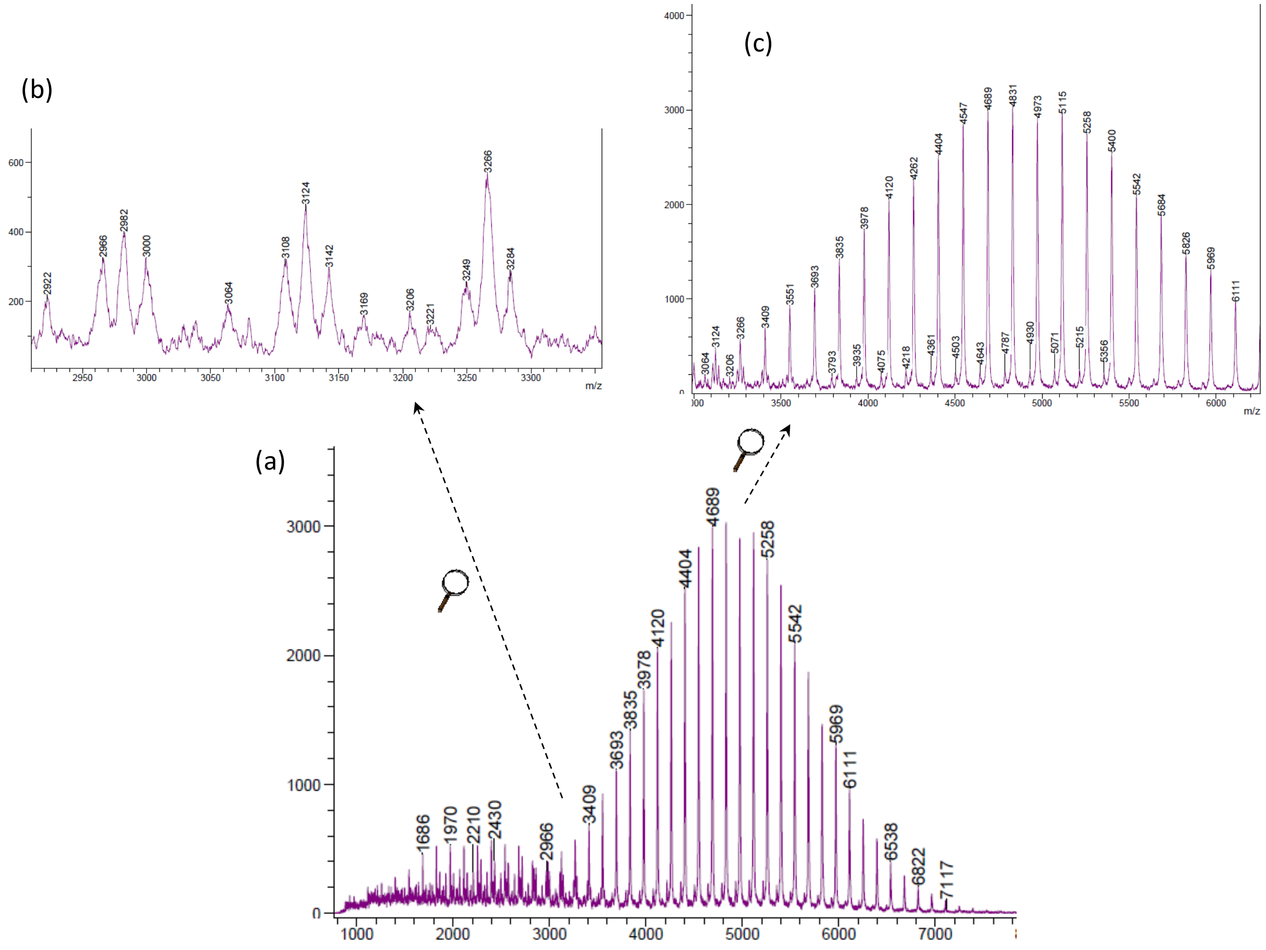
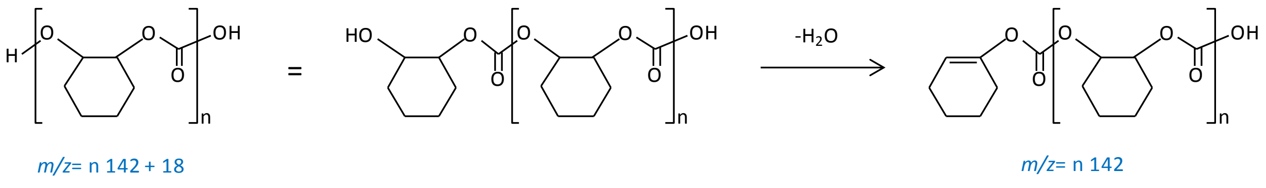


Figure S10. MALDI-TOF mass spectrum of the poly(cyclohexene)carbonate product of entry 2, Table 5: (a) full mass spectrum; (b) zoom of the region *m/z* = 2900-3350; (c) zoom of the region *m/z* = 3000-6200. The mass spectrum shows main peaks corresponding to [$(C_7H_{10}O_3)_n + H_2O$] and to the loss of H_2O, which most likely leads to cyclohexene end-capped polymers. See below for a visual representation of this loss of H_2O and for the proposed assignment of a representative group of peaks.



m/z:	***Assignment:***
3142	Polycarbonate based on 22 repeating units end-capped with a hydroxyl (calcd. 3142)
3124	Polycarbonate with *m/z* = 3142 having lost H_2O; i.e., most likely a cyclohexene end-group is present (calcd. 3124)
3108	Species obtained by fragmentation of the polycarbonate with *m/z* = 3124 by loss of an O atom from the terminal carbonate group (calcd. 3108)
3064	Species obtained by fragmentation of the polycarbonate with *m/z* = 3124 by loss of the terminal carbonate group, or by fragmentation of the polycarbonate with *m/z* = 3108 by

loss of CO_2 (calcd. 3064)

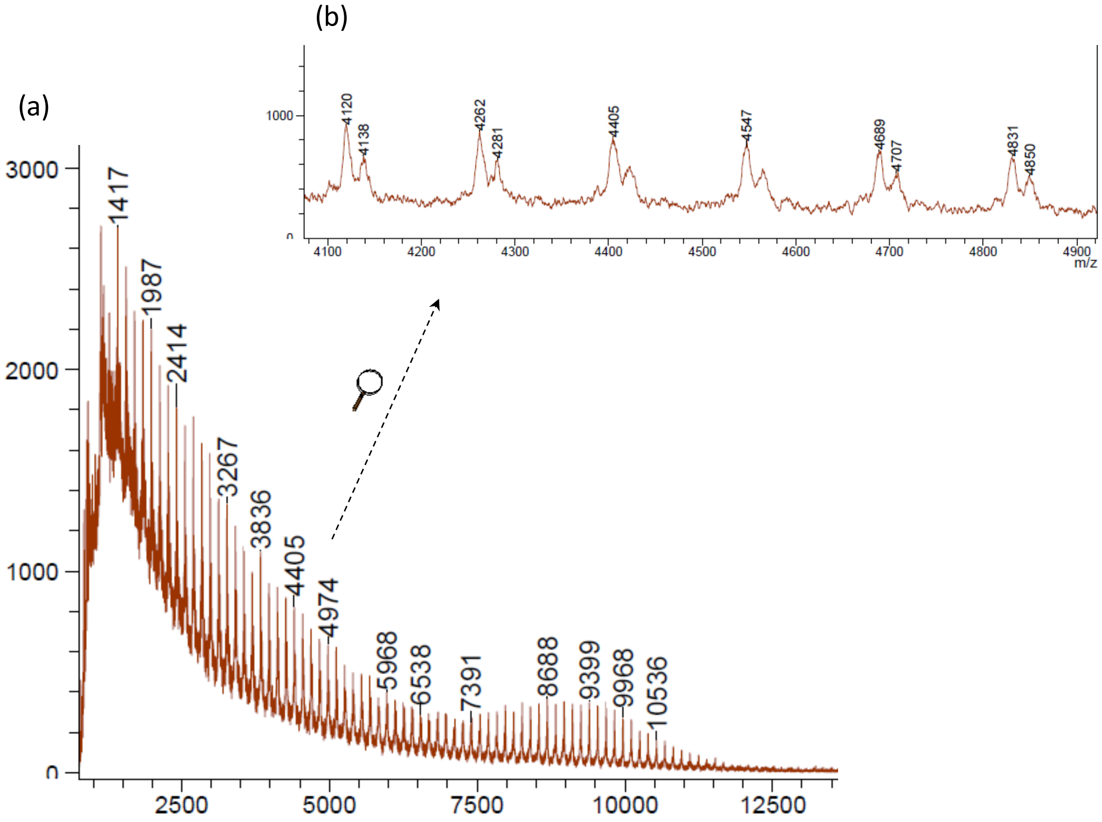


Figure S11. MALDI-TOF mass spectrum of the poly(cyclohexene)carbonate product of entry 1, Table 5: (a) full mass spectrum; (b) zoom of the region *m/z* = 4100-4900. The peak at *m/z* = 4281 relates to a hydroxyl-capped polycarbonate based on 30 repeating units (calcd. 4278). The peak at *m/z* = 4262 is assigned to the polymer with *m/z* = 4281 having lost H_2O (calcd. 4260). Similar assignments hold for the other peaks. Note that the higher molecular weight fraction is generally not observed with this technique.[26]

Employed chemicals

Tetrabutylammonium iodide (TBAI, ≥99%), tetrabutylammonium bromide (TBAB, ≥99%), tetrabutylammonium chloride (TBAC, ≥97%), bis(triphenylphosphine)iminium chloride (PPNCl, 97%), and *cis*-cyclohexene oxide (98%) and the employed solvents [tetrahydrofuran (THF), methanol (MeOH), dichloromethane (DCM)] were purchased from Sigma-Aldrich and used without extra purification. Deuterated chloroform (+99.6 atom%) as solvent for the samples measured by ^{1}H NMR and ^{13}C{^{1}H} NMR was purchased from Acros Organics.