Supporting Information

Bimetallic Iron(III) Catalysts For CO_2/Epoxide Coupling to Produce Either Cyclic Carbonates or Polycarbonates

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Table of contents

1) Experimental Section

1.1) Materials and Methods

All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glove box. THF and hexane were freshly distilled under nitrogen from Na/benzophenone, then thoroughly degassed, before being stored under nitrogen... Cyclohexene oxide (CHO), propylene oxide (PO) and styrene oxide (SO) were distilled from CaH_2 under nitrogen, and stored under nitrogen. [$FeCl_3$DME] (DME = 1,2-dimethoxyethane) and the pro-ligand H_2L were prepared according to literature procedures.[1,2] Other reagents and chemicals were obtained from commercial sources (VWR for solvents, Strem Chemicals for anhydrous $FeCl_3$, Sigma-Aldrich for the rest) and used without further purification. Research grade carbon dioxide from BOC was used for the copolymerisation studies. ^{1}H and ^{13}C{^{1}H} NMR spectra were performed on a Bruker AV-400 instrument, operating at 400 MHz for ^{1}H, 75.5 MHz for ^{13}C. ESI mass spectrometry and LSI MS were performed using a Fisons Analytical (VG) Autospec spectrometer. Infra-red (IR) spectra were recorded in solution (CH_2Cl_2) using a Mettler Toledo ReactIR 4000 instrument and analysed using the ICIR 4.0 software. Elemental analyses were determined by Mr Stephen Boyer at London Metropolitan University, North Campus, Holloway Road, London, N7 8DB. GPC data were collected using a Polymer labs PL GPC-50 instrument with THF as the eluent, at a flow rate of 1mL min^{-1}. Two Polymer labs Mixed D columns, maintained at 30 °C, were used in series. Narrow M_w polystyrene standards were used to calibrate the instrument. MALDI-ToF mass spectroscopy was carried out at the EPSRC National mass spectrometry service centre (NMSSC), Swansea, UK. MALDI-ToF spectra were determined using a dithranol matrix, in THF, at a loading of 1:5 with NaOAc as the cationizing agent. Magnetisation measurements, at temperatures between 4 K and 300 K, were carried out using an Oxford Instruments vibrating sample magnetometer capable of operating at fields of up to 8 Tesla.

1.2) Synthesis of iron complex 1

In a vial in the glovebox, KH (44 mg, 1.09 mmol) was added by small portions to a solution of ligand H_2L (300 mg, 0.54 mmol) in cold THF (10 mL). After 4 h of stirring, the reaction mixture was centrifuged then [$FeCl_3$(DME)] (275 mg, 1.09 mmol) was added to the colourless solution, instantly producing a dark blue mixture, which was left to stir at room temperature ofor 20 h. KCl salts were eliminated by centrifugation, and the THF was removed *in vacuo*. The dark blue solid residue was finally washed with hexane (3 × 5 mL), then dried under vacuum for 20 h.

1 (370 mg, 0.46 mmol, 85% unoptimized). *m/z* (LSIMS): 767 ($[M - Cl]^+$, 20%), 732 ($[M - 2Cl]^+$, 100%), 697 ($[M - 3Cl]^+$, 100%). *m/z* (ESI): 750.2798 ($[M - 2Cl + H_2O]^+$, 100%, calc. 750.2428). Anal. Calcd for $C_{34}H_{54}Cl_4Fe_2N_4O_2$: C, 50.77; H, 6.77; N, 6.97. Found : C, 50.63; H, 6.67; N, 6.86. λ_{max}/nm (ε/M^{-1} cm^{-1} per dimer) [CH_2Cl_2] 237 (33,500), 274 (15,900), 321 (10,300), 353 (sh), and 580 (4400). μ_{eff} (Evans' NMR method):[3] 8.2 μ_B.

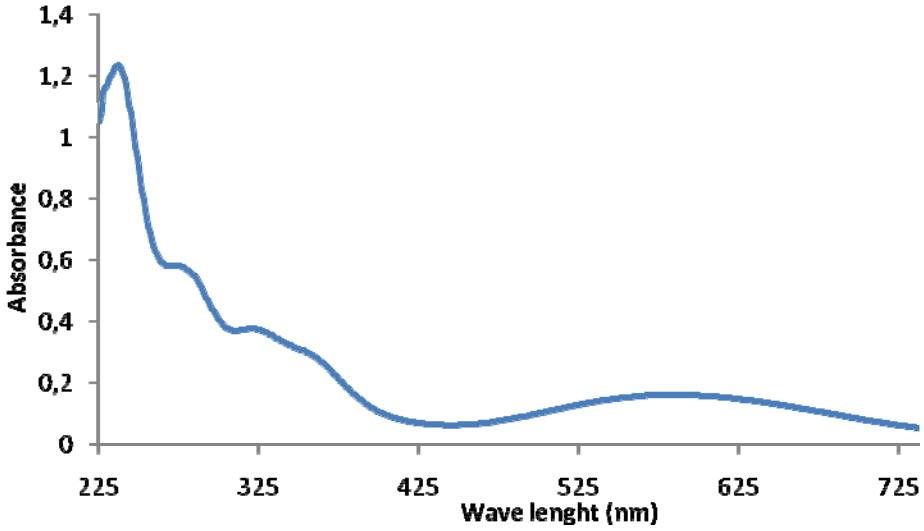


Figure S1. UV-Vis absorption spectrum of **1** ($1.53\ 10^{-5}$ M in CH_2Cl_2).

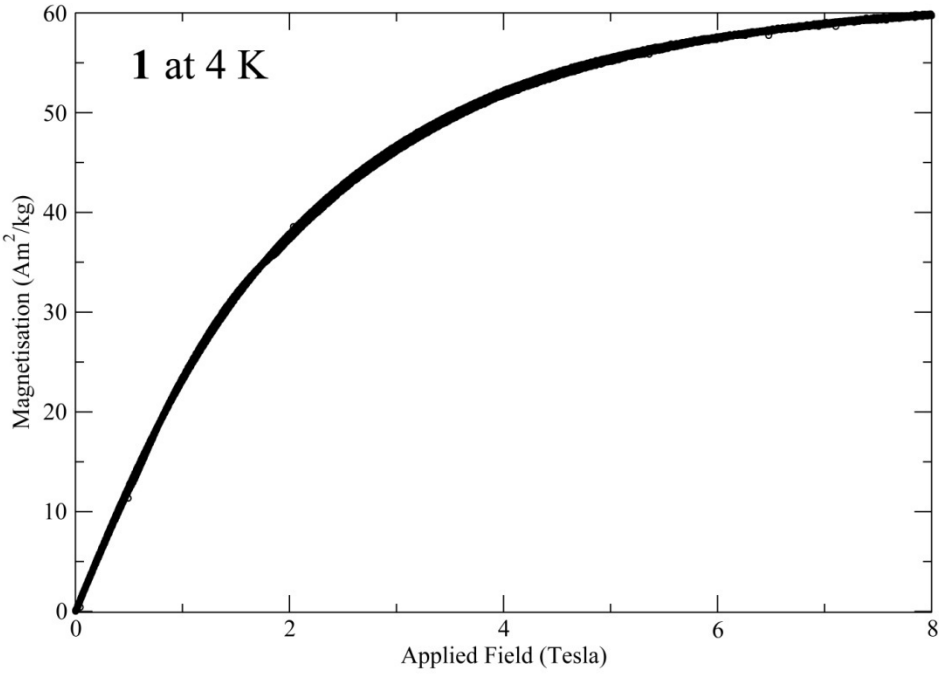


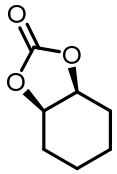
Figure S2. Magnetisation of **1** measured in an applied field of up to 8 Tesla at 4.2 K.

1.3) Catalysis

Typical Low Pressure (1 atm) Experiments

All low pressure catalytic reactions were carried out in magnetically stirred Schlenk tubes, using standard Schlenk techniques. The Schlenk tubes were dried, in an oven at 140 ºC, for 20 h before any use. In a typical reaction (*e.g.* entry 4 of table 1), cyclohexene oxide (2.5 mL, 24.7 mmol), [LFe_2Cl_4] **1** (19.9 mg, 0.0247 mmol) and [PPN]Cl (28.5 mg, 0.0494 mmol) were added to a Schlenk tube. The cyclohexene oxide was rapidly de-gassed, before being left stirring under 1 atm CO_2 (continuously fed using a reserve cylinder), at 80 °C, for 24 h. At the end of the reaction, the crude reaction mixture was dried *in vacuo* overnight. No further purification of the product was undertaken as the vacuum was sufficient to remove unreacted cyclohexene oxide. Selectivity was determined by normalisation of the integrals of the methylene protons resonances in the ^{1}H NMR spectra, including the copolymer carbonate linkages (broad signal δ=4.65 ppm), copolymer ether linkages (broad signal δ=3.45 ppm), and cyclic carbonate (multiplets : δ = 3.9 ppm (*trans*-CHC) or 4.63 ppm (*cis*-CHC)). Conversion was calculated as [(mass of the isolated product – weight of the catalyst)/142.1]/moles of starting CHO. Turn-over-number (TON) was calculated as conversion/moles catalyst. Turn-ove-frequency (TOF) was calculated as TON/time of reaction (in h).

Characterisation of *cis*-cyclohexene carbonate:



^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.37 (m, 2H, $OCHCH_2CH_2$), 1.54 (m, 2H, $OCHCH_2CH_2$), 1.81 (m, 4H, $OCHCH_2CH_2$), 4.63 (m, 2H, $OCHCH_2CH_2$) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 20 °C): δ = 19.1 (s, $OCHCH_2CH_2$), 26.7 (s, $OCHCH_2CH_2$), 75.8 (s, $OCHCH_2CH_2$), 155.4 (s, $OC^{IV}O_2$) ppm. m/z (CI): 160 ([M + NH_4]$^+$, 100%). IR ($\nu_{C=O}$, cm^{-1}, in CH_2Cl_2): 1801.

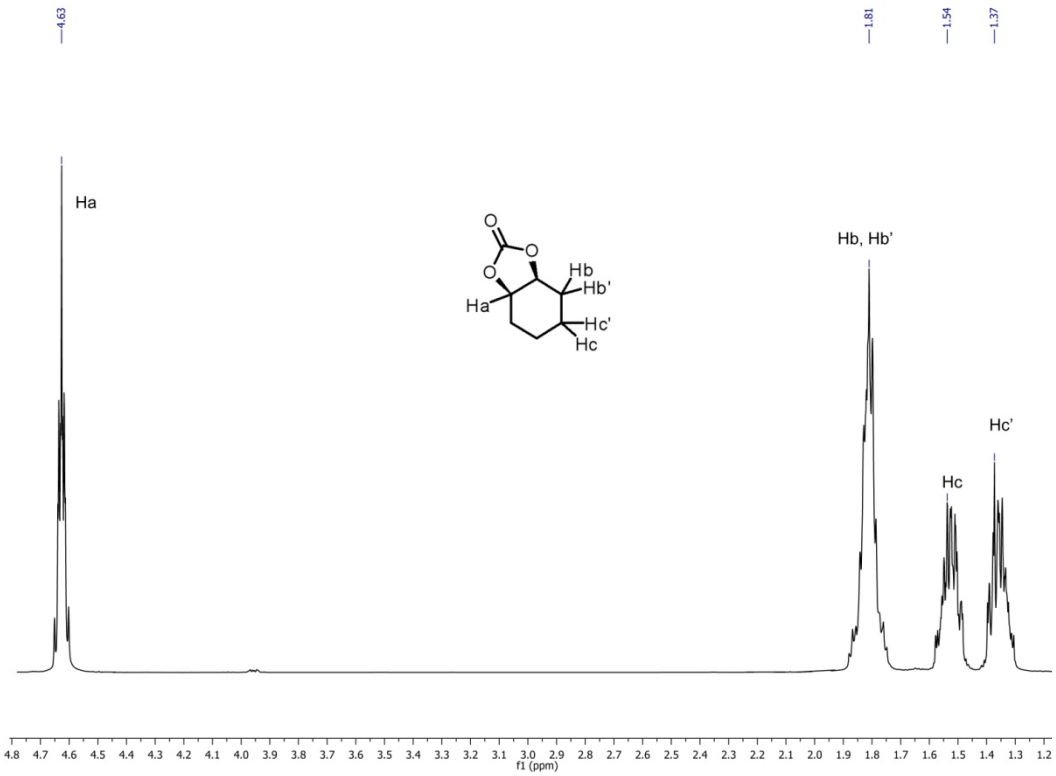


Figure S3. ^{1}H NMR spectrum in $CDCl_3$ of *cis*-cyclic cyclohexene carbonate (CHC) produced using **1** and [PPN]Cl (entry 5 of table 1).
Residual signal at 4.0 ppm corresponds to the 1% of the *trans* CHC obtained.

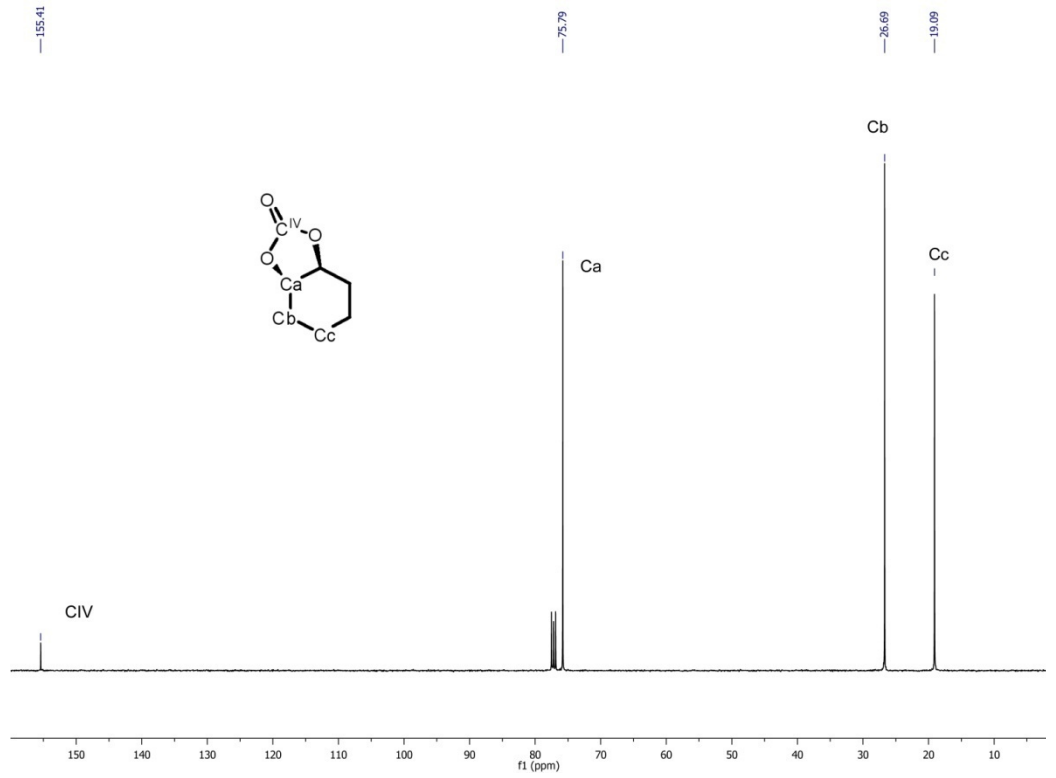


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of *cis*-cyclic cyclohexene carbonate (CHC) produced using **1** and [PPN]Cl (entry 3 of table 1).
Residual signal at 77.2 ppm corresponds to *C*DCl_3.

Typical CO_2/CHO copolymerisation procedure (10 atm):

All catalytic reactions were carried out in a, mechanically stirred, 70 mL stainless steel Parr reactor, equipped with a pressure gauge and needle valves for injections. The reaction vessel was dried, in an oven at 140 ºC for 20 h, before use. A typical reaction was performed by introducing, under nitrogen, **1** (15.9 mg, 19.8 μmol) and cyclohexene oxide (20 mL, 198 mmol) into the autoclave. The reactor was immediately de-gassed, then brought to 80 °C and 10 atm pressure of CO_2, and continuously heated, stirred and fed with CO_2 using a reserve cylinder, for 24 h. At the end of the reaction, the crude mixture was taken up in CH_2Cl_2 (15 mL), then dried *in vacuo* for 20 h. No further purification of the copolymer was undertaken as the vacuum was sufficient to remove unreacted cyclohexene oxide. Typically, the copolymer was then analyzed by NMR spectroscopy, GPC and MALDI-ToF mass spectrometry.

The reaction selectivity of was determined by normalisation of the integrals of the methylene protons resonances in the ^{1}H NMR spectra, including the copolymer carbonate linkages (broad signal δ=4.65 ppm), copolymer ether linkages (broad signal δ=3.45 ppm), and cyclic carbonate (mutiplets : δ = 3.9 ppm (*trans*-CHC) or 4.63 ppm (*cis*-CHC). Due to the similarity in chemical shifts of the *cis*-CHC and copolymer resonances, the absence of *cis*-CHC was also confirmed using FTIR spectroscopy (there was no C=O vibration at 1804 cm^{-1}). The copolymer tacticity was determined by ^{13}C NMR spectroscopy and analyzed as described by Nozaki *et al*.[4] The copolymers were atactic (see Figure S6). Conversion was calculated as [(mass of the isolated product – weight of the catalyst)/142.1]/moles of starting CHO. Turn-over-number (TON) was calculated as Conversion/moles catalyst. Turn-over-frequency (TOF) was calculated as TON/time of reaction (in h).

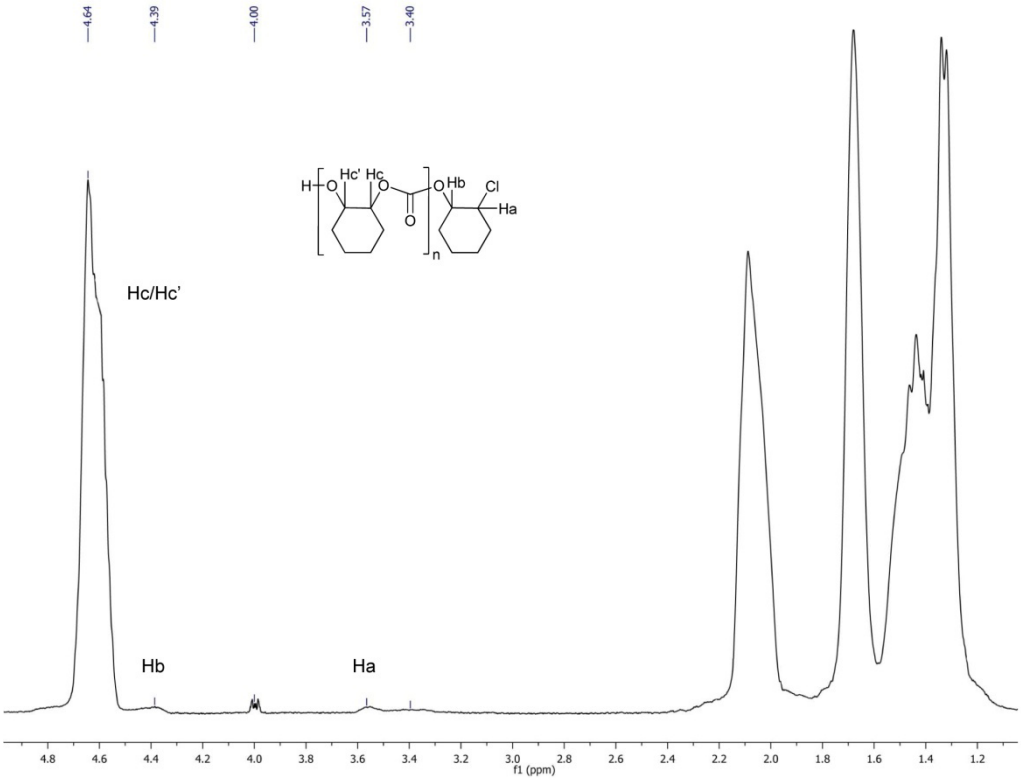


Figure S5. ^{1}H NMR spectrum of copolymer produced using **1** (table 1, entry 3) in $CDCl_3$. Peak Hc/Hc' (δ = 4.64 ppm) is assigned to the methyne groups in PCHC, peaks Hb (4.39 ppm) and Ha (3.55 ppm) are assigned to the PCHC end-group methylene resonances ($OCHC_4H_8CHCl$ and $OCHC_4H_8CHCl$, respectively). The residual signal at 4.0 ppm is assigned to the 1% of *trans*-CHC. The residual broad signal at 3.4-3.5 ppm corresponds to the 1% of ether linkages in PCHC.

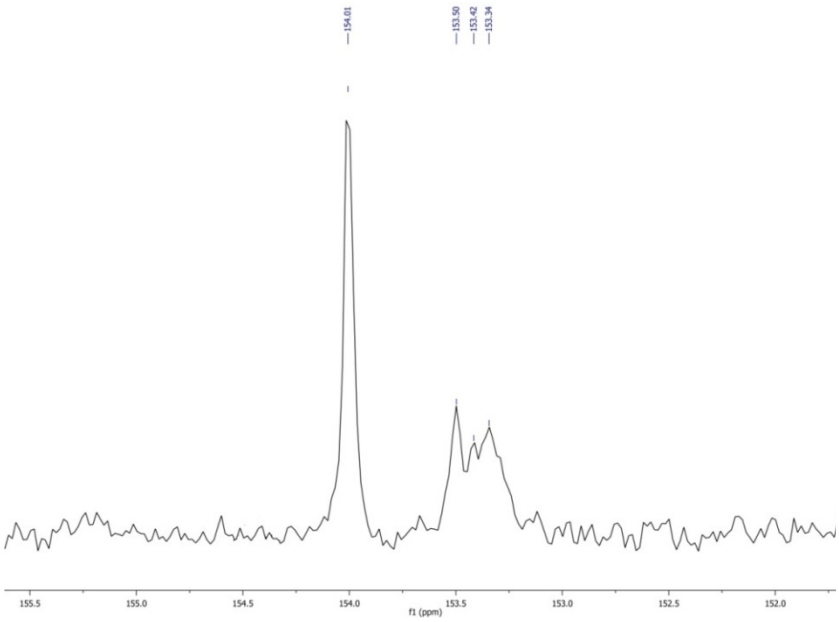


Figure S6. The carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum of PCHC produced using **1** (Table 1, entry 3) in $CDCl_3$. The reported assignment for δ 154 and 153.3 ppm are syndiotactic and isotactic diads, respectively.[4] The polymer is therefore atatctic.

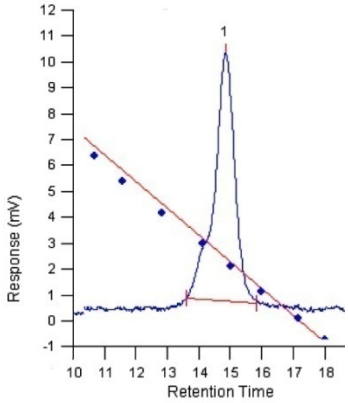


Figure S7. GPC traces for PCHC produced using **1**
(Table 1, entry 3, M_n : 11,300, M_w/M_n = 1.13) (THF eluent).

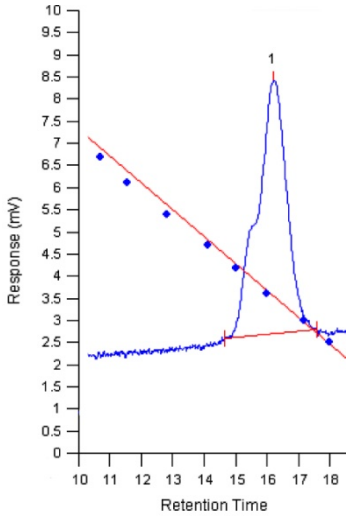


Figure S8. GPC traces for PCHC produced using **1**
(Table 1, entry 2, M_n : 3,100, M_w/M_n = 1.18) (THF eluent).

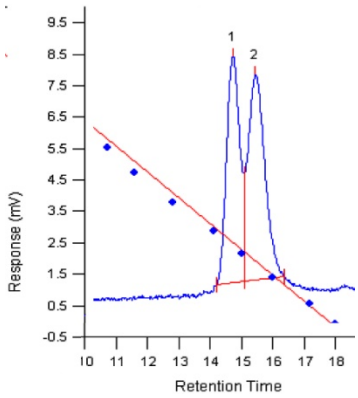


Figure S9. GPC traces for PCHC produced using **1**
(Table 1 entry 4, , M_n : 17,200 and 8,100, M_w/M_n = 1.03 and 1.06) (THF eluent).

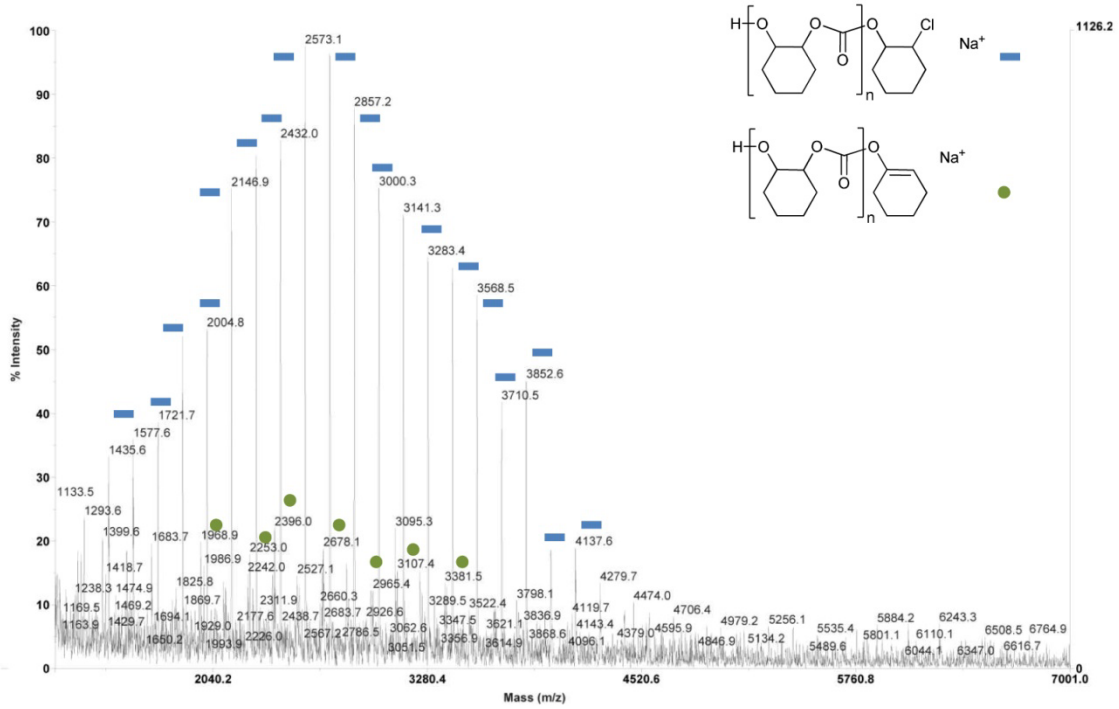


Figure S10. The MALDI-ToF spectrum of PCHC produced by **1** (Table 1, entry 2, M_n : 3,100, M_w/M_n = 1.18).

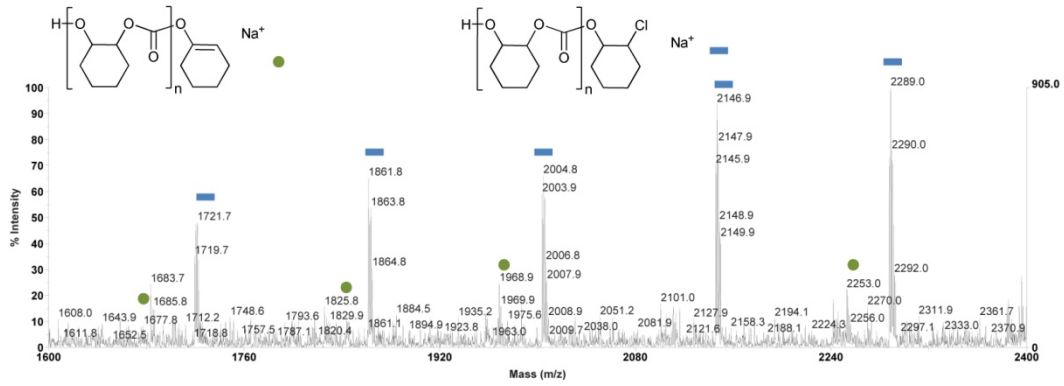


Figure S11. Selected area of nominal MALDI-ToF spectra of PCHC produced by **1** (entry 2 of table 1, M_n : 3,100, M_w/M_n = 1.18).

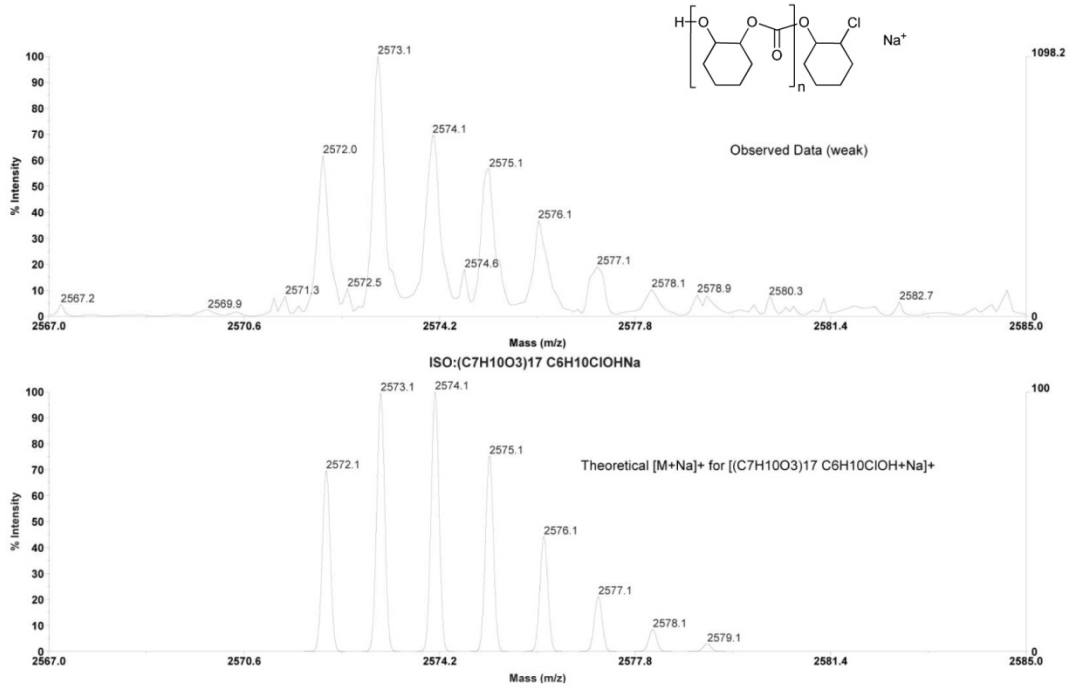


Figure S12. Comparison of theoretical and observed MALDI-ToF mass spectra for PCHC produced by **1** (Table 1, entry 2, M_n : 3,100, M_w/M_n = 1.18)

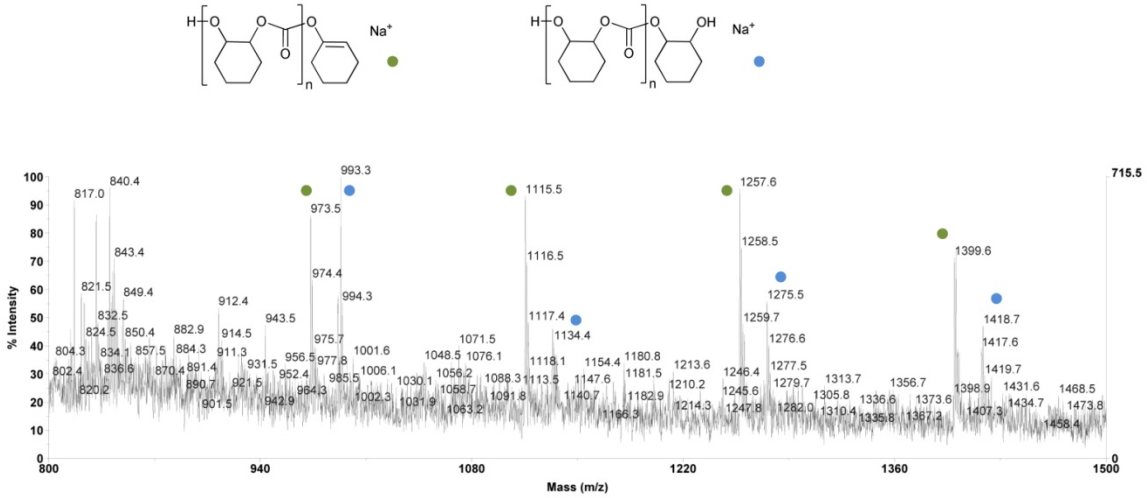


Figure S13. Selected area of the MALDI-ToF spectrum of PCHC produced by **1** (Table 1, entry 4, M_n : 17,200 and 8,100, M_w/M_n = 1.03 and 1.06).
N.B. A bimodal GPC is obtained but the higher M_n series was not observed by MALDI-ToF (M_n too high). Series with extra water molecule comes from water contamination.

2) References

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2. Michael R. Kember, Paul D. Knight, Palarp T. R. Reung and Charlotte K. Williams, *Angew. Chem. Int. Ed.*, 2009, **48**, 931-933.
3. D. F. Evans, *J. Chem. Soc., Chem. Commun.*, 1959, 2003-2005.
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