Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Salen, Salan and Salalen Iron (III) Complexes as Catalysts for CO_2/Epoxides Reactions and ROP of Cyclic Esters

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1. Synthesis and Characterization of Complexes 1-4

*Synthesis of SalanFeCl complex **1***

SalanFeCl complex **1** was prepared according to a published procedure[1]. To a methanol solution (10 mL) of anhydrous iron chloride $FeCl_3$ (61.8 mg, $3.81 \cdot 10^{-4}$ mol) was added a methanol solution (15 mL) of the salan ligand (200 mg, $3.81 \cdot 10^{-4}$ mol). Triethylamine (0.100 mL, $7.62 \cdot 10^{-4}$) was added to give a dark red solution. The resulting mixture was stirred for 2 h. Next, the solvent was removed under vacuum. The solid product was dissolved in acetone and filtered through Celite three times. Removal of solvent under vacuum yielded a violet powder (73%). Characterization of salanFeCl complex **1** was done by means of IR and UV-vis spectroscopy, MALDI-ToF mass spectrometry and Evans NMR technique. The results were in agreement with those reported in the literature.[1] IR (KBr, cm^{-1}): 2949, 2739, 2677, 2492, 1474, 1442, 1413, 1398, 1384, 1361, 1307, 1272, 1246, 1203, 1170, 1129, 1036, 928, 877, 837, 808, 746, 543 (Fe-N), 476 (Fe-O). UV–vis (CH_3CN, 0.08 mM, 25 °C, ε = L·mol^{-1} ·cm^{-1}): 234 nm (ε = 9450), 281 nm (ε = 8525), 337 nm (ε = 5183), 552 nm (ε = 3463). MS (MALDI-ToF) m/z: 613.321 ($\mathrm{FeCl[Salan]}^{\cdot+}$), 578,353 ($\mathrm{Fe[Salan]}^{\cdot+}$). Magnetic moment (298 K) μ_{eff} = 5.32 μ_B.

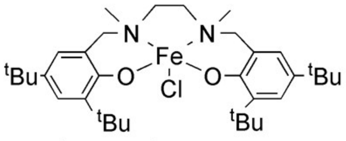
*Synthesis of SalenFeCl complex **2***

SalenFeCl complex **2** was prepared according to a published procedure[2]. To a methanol solution (10 mL) of anhydrous iron chloride $FeCl_3$ (74.1 mg, $4.57 \cdot 10^{-4}$ mol) was added a methanol solution (8 mL) of the salen ligand (150 mg, $3.044 \cdot 10^{-4}$ mol). Triethylamine (0.100 mL, $7.62 \cdot 10^{-4}$) was added to give a dark violet solution. The resulting mixture was stirred for five hours at reflux and then overnight at room temperature. Next, the solvent was removed under vacuum. The solid product was dissolved in acetone and filtered through Celite three times. Removal of solvent under vacuum yielded a dark red powder (89%). Characterization of salenFeCl complex **2** was done by means of IR and UV-vis spectroscopy, MALDI-ToF mass spectrometry and Evans NMR technique. The results were in agreement with those reported in the literature.[2] IR (KBr cm^{-1})): 2952, 2677, 1610 (C=N), 1535. 1438, 1385, 1362, 1330, 1301, 1270, 1252, 1198, 1172, 1044, 974, 837, 811, 779, 749, 547 (Fe-N), 480 (Fe-O). UV–vis (CH_3CN, 0.08 mM, 25 °C, ε = L·mol^{-1} ·cm^{-1}): 230 nm (ε = 31588), 265 nm (ε = 26950), 327 nm (ε = 12338), 504 nm (ε = 3936). MS (MALDI-ToF) m/z: 581,258 ($\mathrm{FeCl[Salen]}^{\cdot+}$), 546,289 ($\mathrm{Fe[Salen]}^{\cdot+}$). Magnetic moment (298 K) μ_{eff} = 5.99 μ_B.

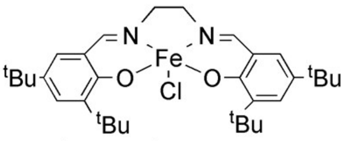
*Synthesis of SalenC3FeCl complex **4***

SalenC3FeCl complex **4** was prepared according to a published procedure[2]. To a methanol solution (12 mL) of anhydrous iron chloride $FeCl_3$ (96.0 mg, $5.92 \cdot 10^{-4}$ mol) was added a methanol solution (12 mL) of the salenC3 ligand (200 mg, $3.95 \cdot 10^{-4}$ mol). Triethylamine (0.110 mL, $7.90 \cdot 10^{-4}$) was added to give a dark violet solution. The resulting mixture was stirred for three hours at reflux and then overnight at room temperature. Next, the solvent was removed under vacuum. The solid product was dissolved in acetone and filtered through Celite three times. Removal of solvent under vacuum yielded a dark red powder (89%). Characterization of the salenC3FeCl complex **4** was done by means of IR and UV-vis spectroscopy, MALDI-ToF mass spectrometry and Evans NMR technique. The results were in agreement with those reported in the literature.[2] IR (KBr, cm^{-1})): 2948, 2677, 1713, 1609 (C=N), 1537, 1454, 1430, 1387, 1361, 1305, 1272, 1256, 1219, 1200, 1073, 1091, 970, 876, 838, 810, 780, 746, 540 (Fe-N), 482, 449(Fe-O). UV−vis (CH$_3$CN, 0.08 mM, 25 °C, ε = L·mol^{-1} ·cm^{-1}): 242 nm (ε = 7135), 273 nm (ε = 5186), 332 nm (ε = 2475), 524 nm (ε = 1022). MS (MALDI-ToF) m/z: 581,258 (FeClK[SalenC3]$^{\cdot+}$), 546,289 (Fe[SalenC3Cl]$^{\cdot+}$). Magnetic moment (298 K) μ_{eff} = 5.82 μ_B.

Iron (III) Complexes **1-4**



SalanFeCl complex **1**



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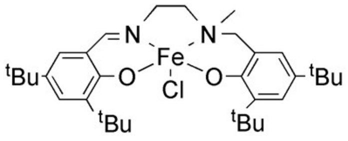
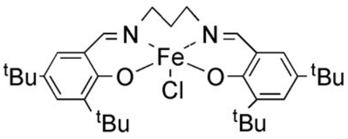


SalalenFeCl complex **3**



SalenC3FeCl complex **4**

1.1 MALDI-ToF mass spectrometry

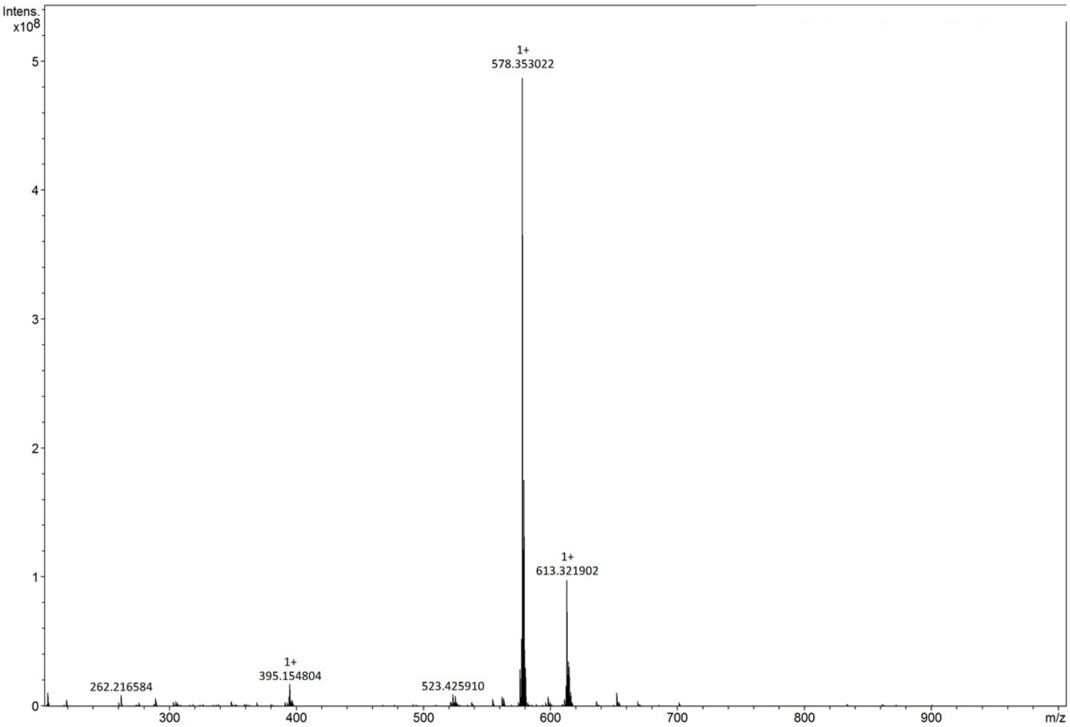


Figure S1. MALDI-ToF mass spectrum of **1**, peak at 613.3 m/z belongs to molecular ion of complex **1**, peak at 578.3 m/z belongs to the dechlorinated complex **1**

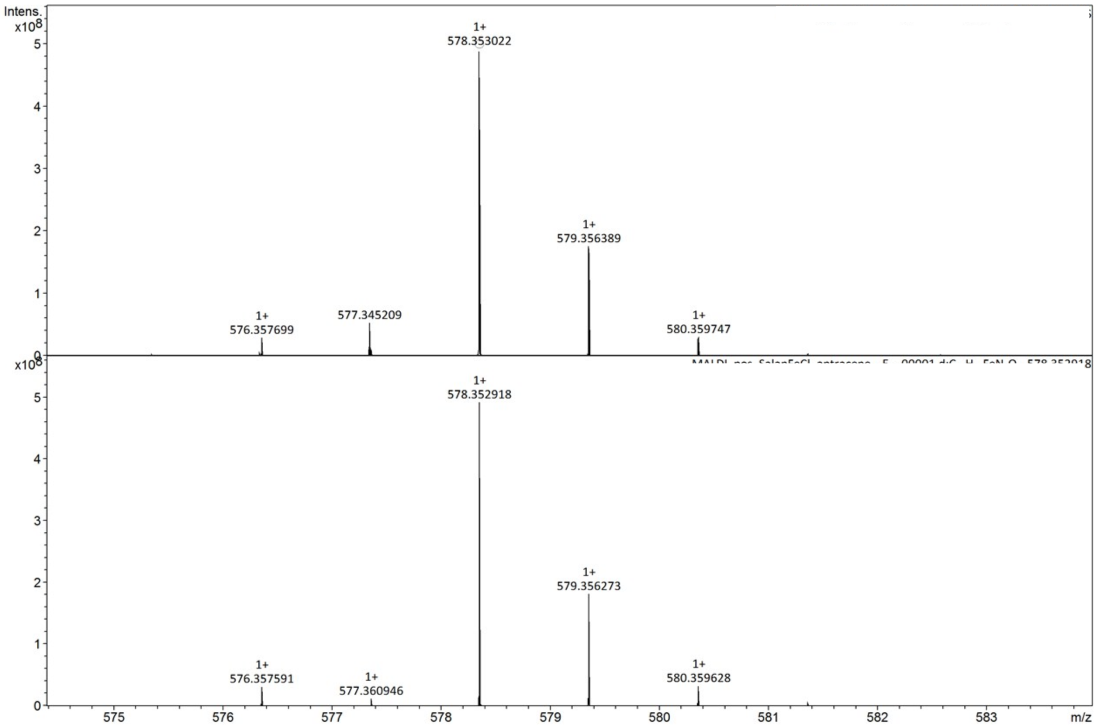


Figure S2. Experimental and Theoretical isotopic distribution pattern for **1**

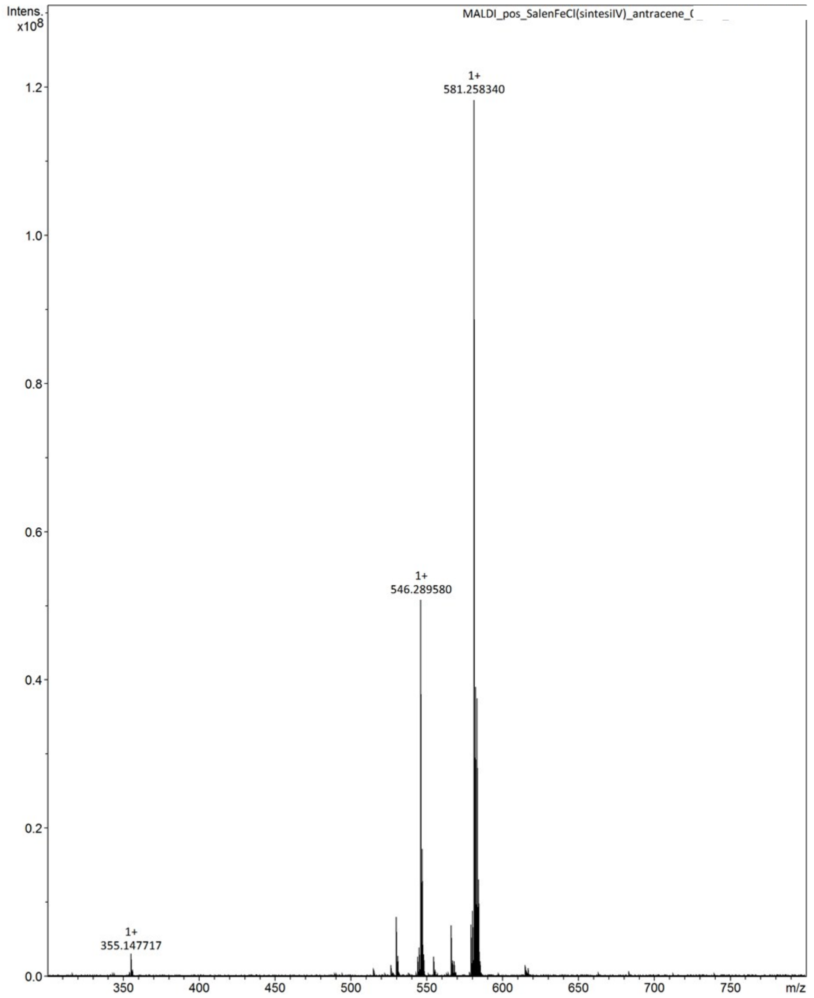


Figure S3. MALDI-ToF mass spectrum of **2**, peak at 581.2 m/z belongs to the molecular ion of complex **2**, peak at 546.3 m/z belongs to the dechlorinated complex **2**

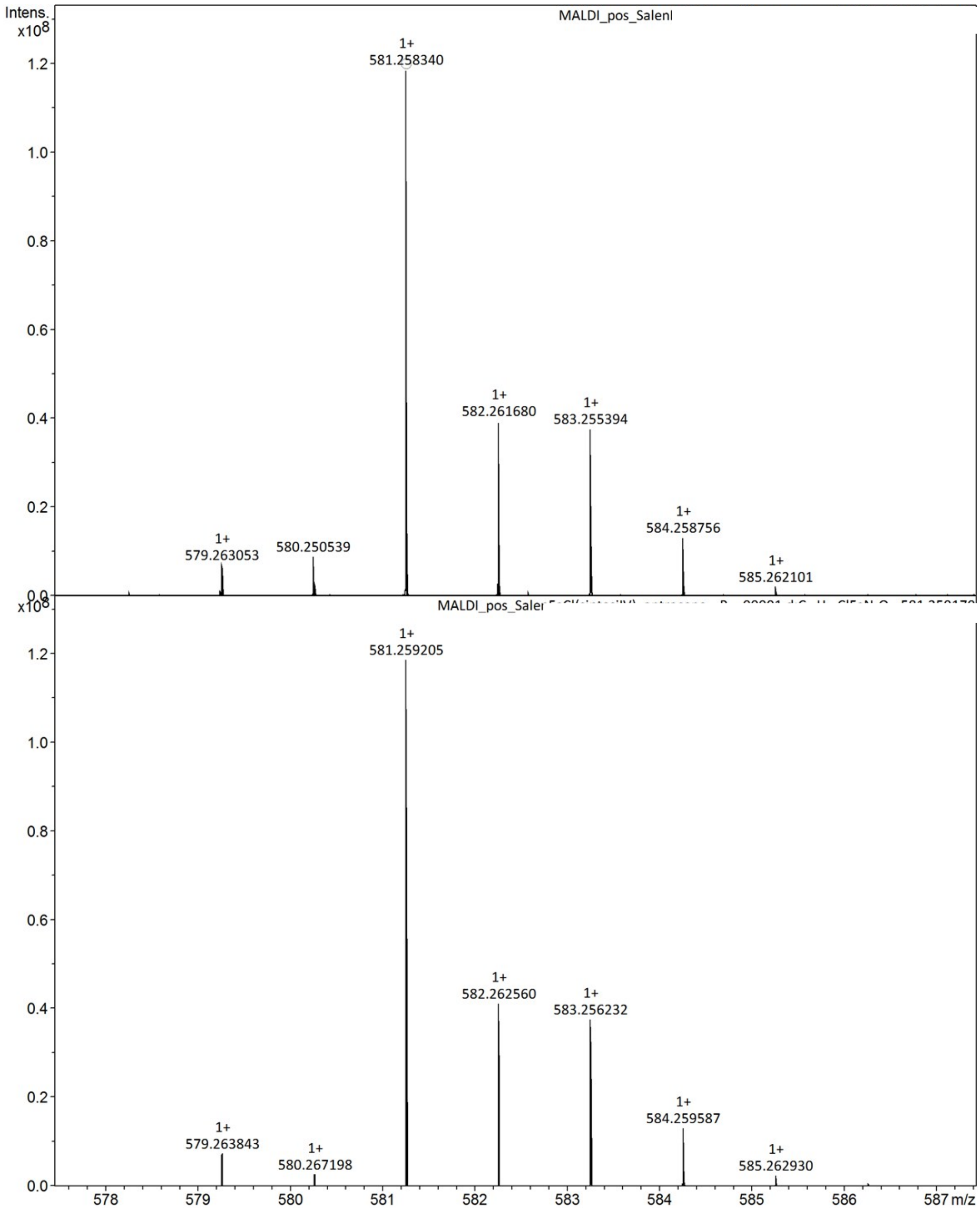


Figure S4. Experimental and Theoretical isotopic distribution pattern for complex **2**

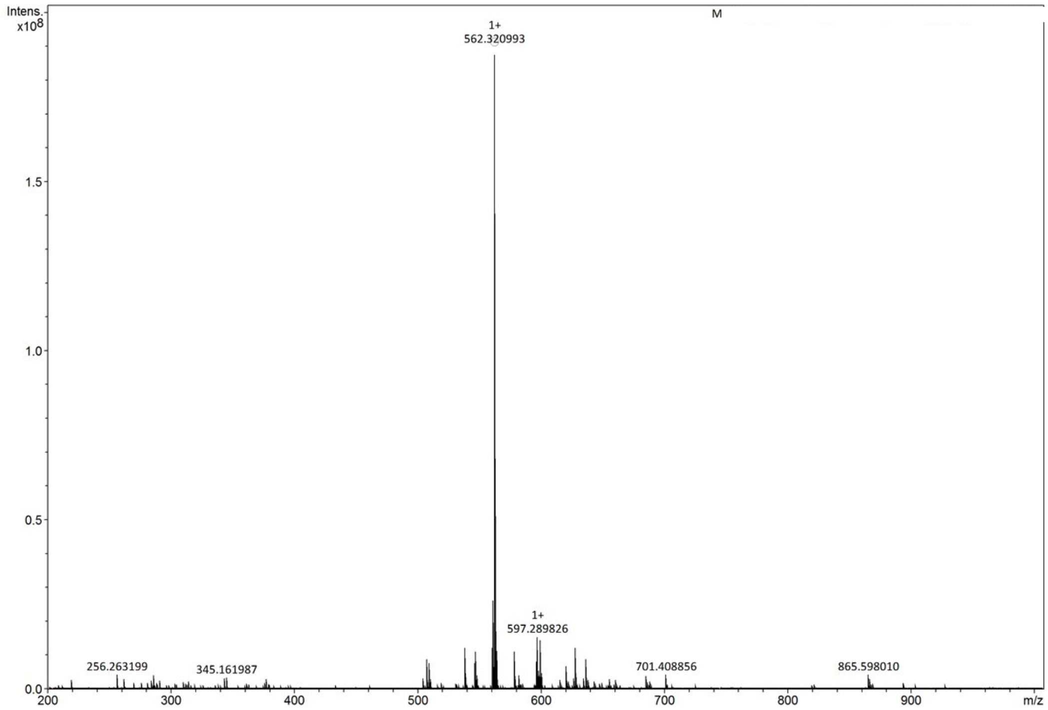


Figure S5. MALDI-ToF mass spectrum of **3**, peak at 597.3 m/z belongs to the molecular ion of complex **3**, 562.3 m/z belongs to the dechlorinated complex **3**

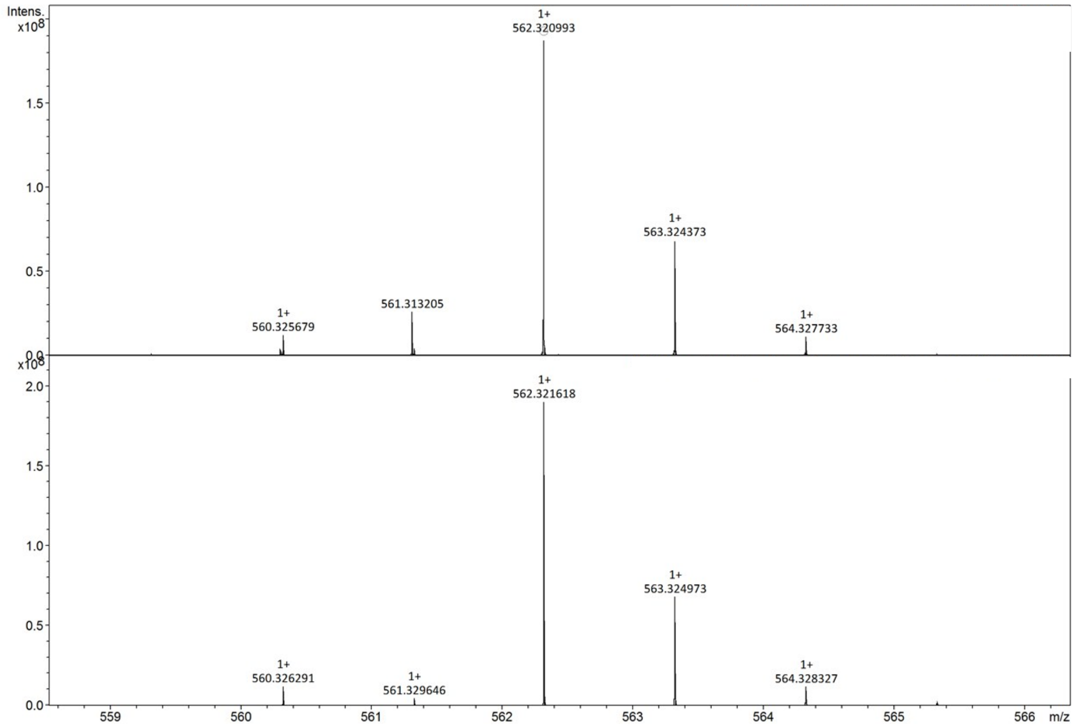


Figure S6. Experimental and Theoretical isotopic distribution pattern for complex **3**

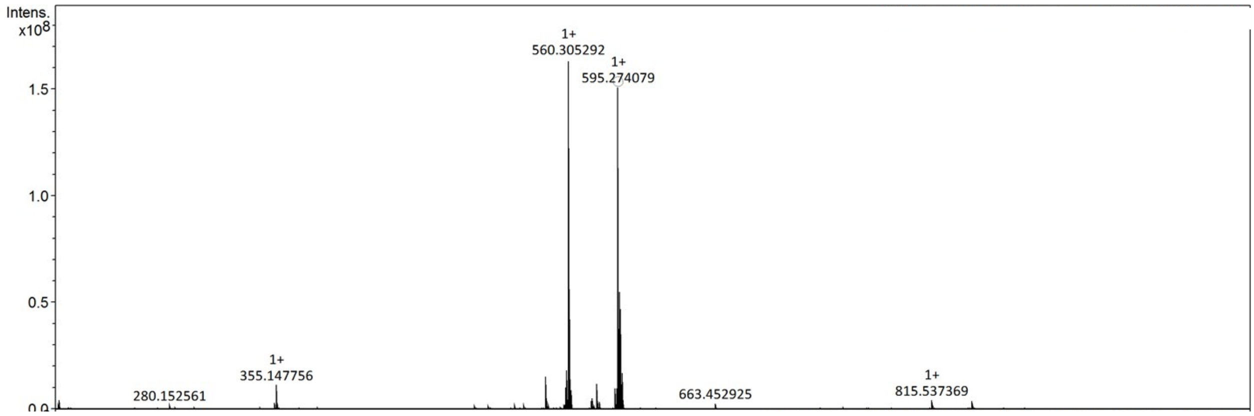


Figure S7. MALDI-ToF mass spectrum of **4**, peak at 595.3 m/z belongs to the molcualar ion of complex **4**, peak at 560.3 m/z belongs to the dechlorinated complex **4**

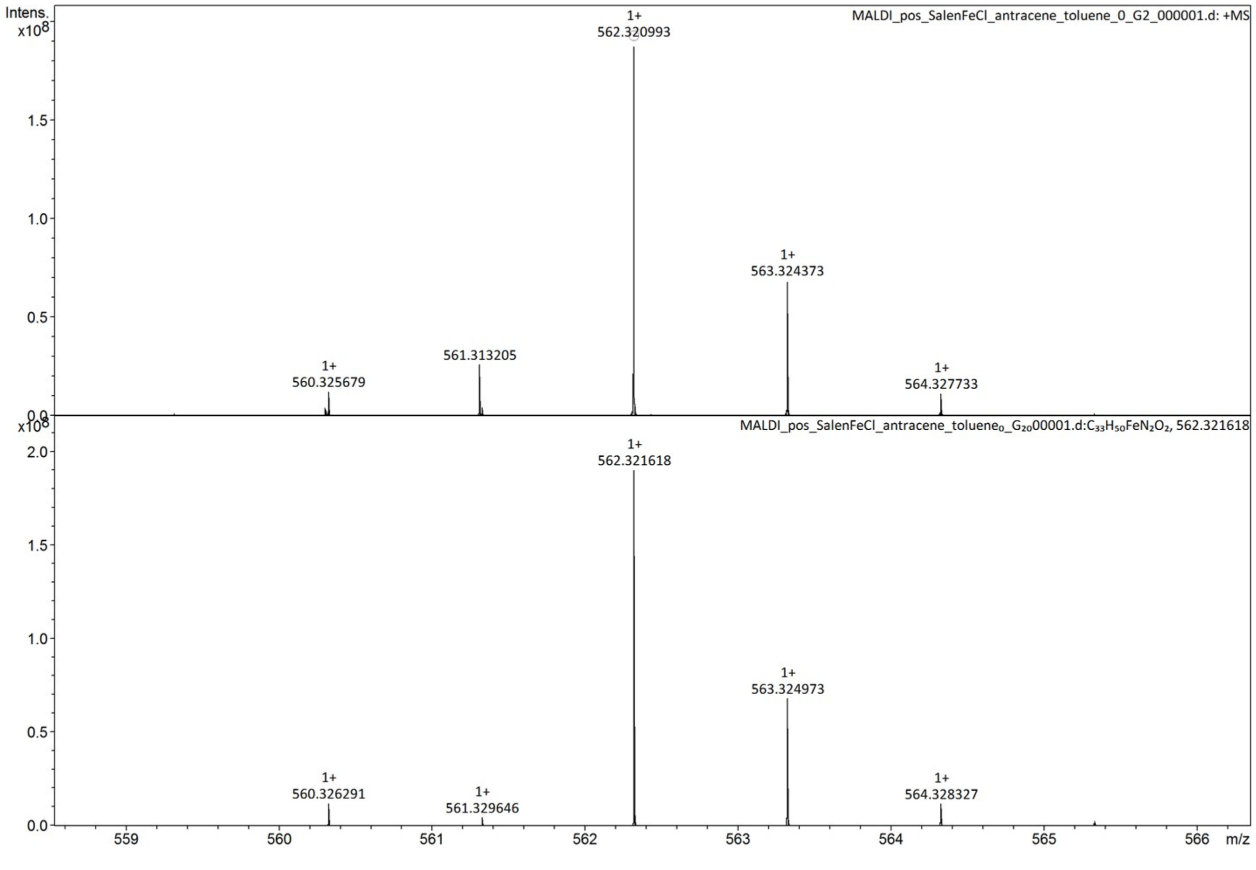


Figure S8 Experimental and Theoretical isotopic distribution pattern for complex **4**

1.2 UV-visible spectroscopy

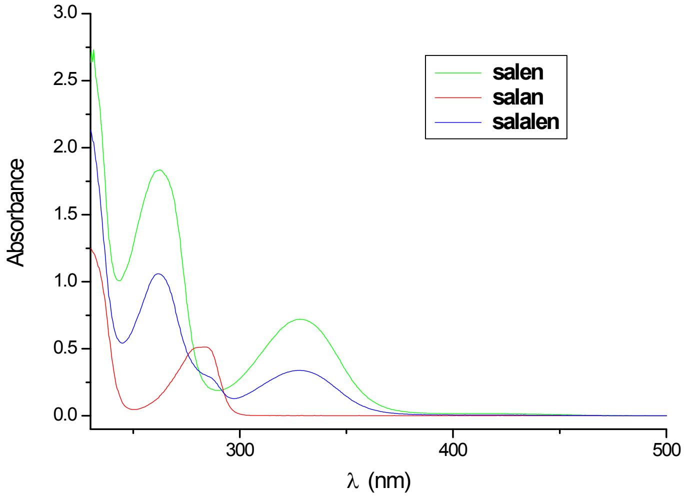


Figure S9. Electronic absorption spectra of salen, salan and salalen ligands in acetonitrile.

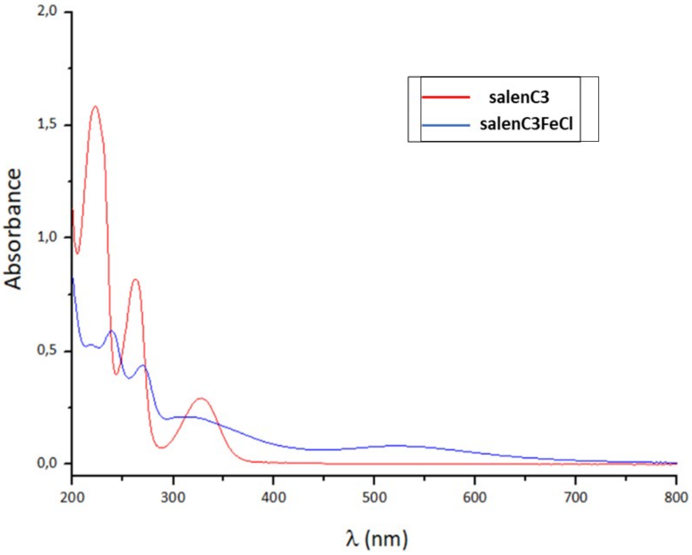


Figure S10. Electronic absorption spectra of salenC3 ligand and salenC3FeCl complex **4** in acetonitrile

1.3 FT-IR spectroscopy

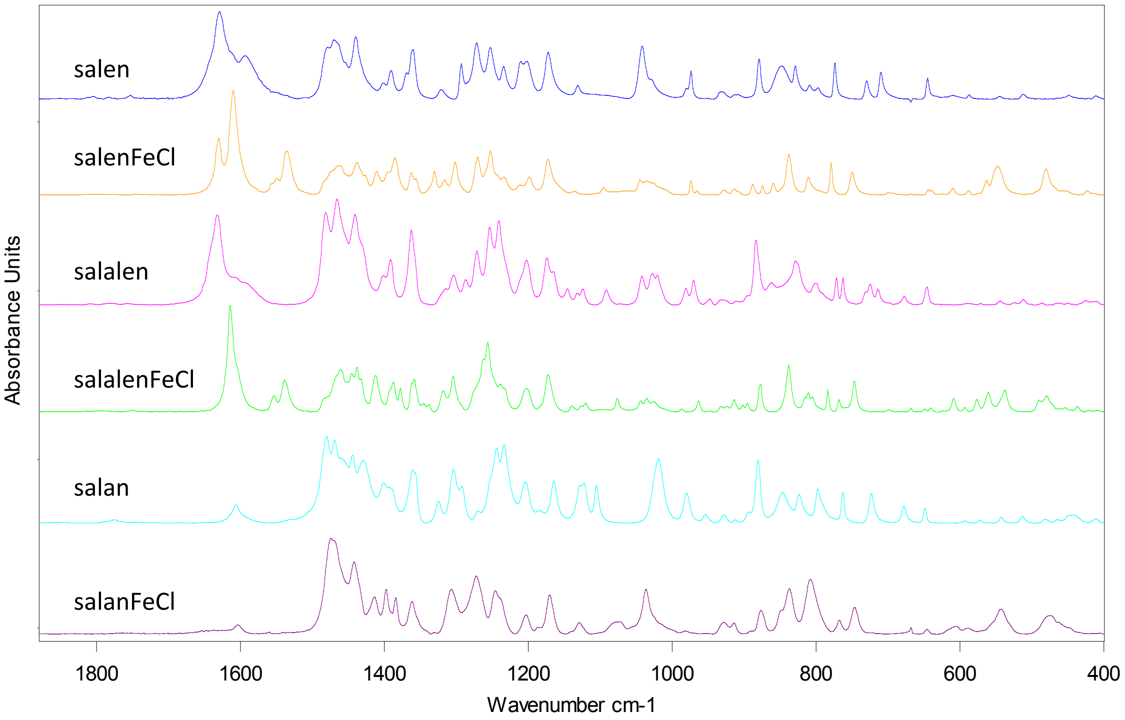
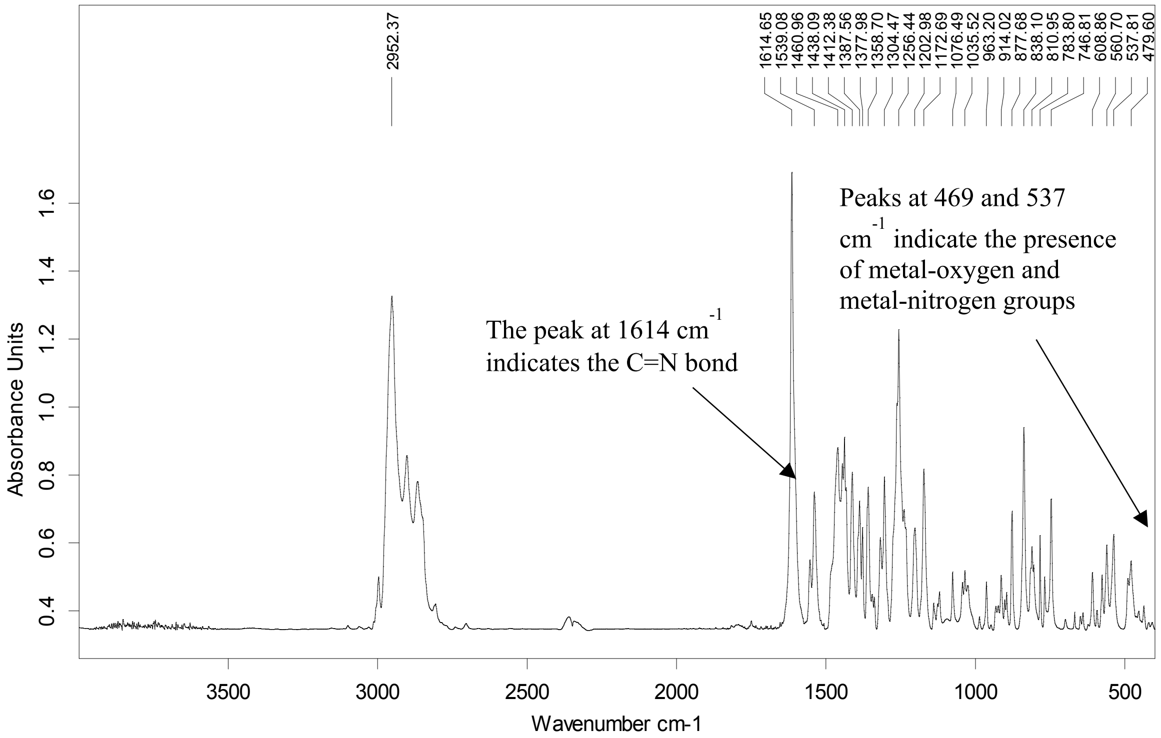


Figure S11. FT-IR spectra of salen, salalen, salan ligands and of the corresponding complexes **1-3**



The peak at 1614 cm^{-1} indicates the C=N bond

Peaks at 469 and 537 cm^{-1} indicate the presence of metal-oxygen and metal-nitrogen groups

Figure S12. FT-IR spectrum of SalalenFeCl complex **3**

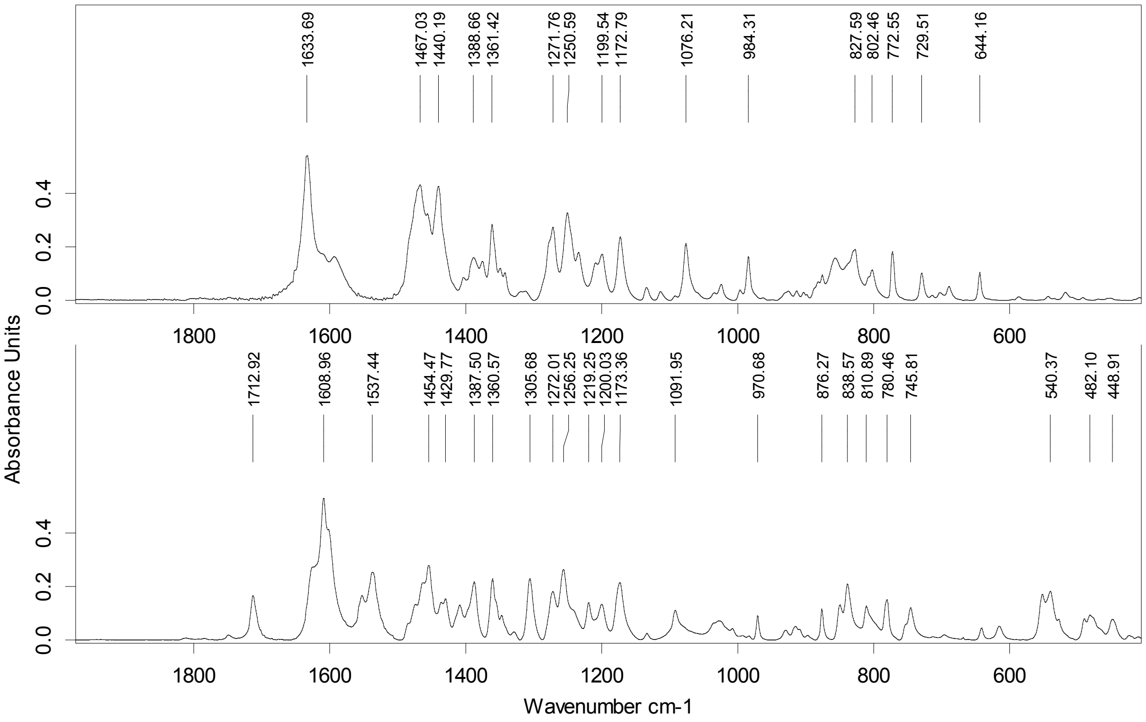


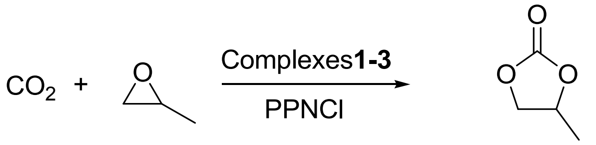
Figure S13. FT-IR spectra of salenC3 ligand (up) and of salenC3FeCl complex **4** (bottom)

2. X-ray data

Table S1. Selected bond lengths (Å) and angles (°) for complex **3** and analogous complexes **1** and **2.**

Complex	**1**	**2**	**3**
Fe—N_1	2.1623(18)	2.082(3)	2.0647(14)
Fe—N_2	2.2824(18)	2.086(3)	2.2980(14)
Fe—O_1	1.8636(16)	1.868(2)	1.9091(12)
Fe—O_2	1.8615(14)	1.882(2)	1.8517(13)
Fe—Cl	2.2481(6)	2.2351(12)	2.2325(19)
O_1—Fe—N_2	158.39(7)	132.78(12)	164.03(5)
O_1—Fe—N_1	85.15(7)	86.17(10)	85.47(5)
O_2—Fe—N_1	140.08(7)	161.23(11)	117.26(6)
O_2—Fe—N_2	88.06(6)	86.76(11)	88.55(5)
Cl—Fe—N_1	107.03(5)	92.64(9)	124.64(4)
Cl—Fe—O_2	112.00(5)	101.77(9)	117.27(5)
Cl—Fe—N_2	96.43(5)	108.00(9)	93.68(4)
Cl—Fe—O_1	102.59(6)	116.78(9)	97.70(5)
N_1—Fe—N_2	79.49(6)	77.30(11)	78.83(5)
O_1—Fe—O_2	94.17(7)	97.77(11)	96.09(6)
τ	0.31	0.47	0.78

3. Cycloaddition of carbon dioxide with PO



The reaction was carried out using a ratio epoxide/complex = 4400 and PPNCl/complex= 8. In a glove-box, catalyst (0.0163 mmol) and PPNCl (0.075 mmol) were dissolved in the epoxide (4400 equiv., 72 mmol) and then transferred into a autoclave. The autoclave was pressurized at 28 bar of pressure of CO_2, and the mixture was allowed to stir at 100°C for 16 hours. After the prescribed time, the reaction mixture was quenched by immersing the autoclave in an ice bath, opened at air and a small sample of the crude reaction mixture was used to calculate the conversion of epoxide into cyclic carbonate by ^1H NMR spectroscopy.

TableS2. CO_2/PO reaction promoted by complexes **1-3** and PPNCl

Entry	Cat	Cocat	Conversion (%)	TON	TOF (h^{-1})
1	**1**	**PPNCl**	85	3723	233
2	**2**	**PPNCl**	79	3463	216
3	**3**	**PPNCl**	55	2409	151
4	-	**PPNCl**	64		

General conditions: Complexes: **1**-**3** = 16.3 µmol (0.023mol%), PO = 5 mL (4400 equiv), PPNCl = 0.075 mmol (8 equiv), P_{CO_2} = 28 bar, Temperature = 100°C, time = 16 h.

4. Cycloaddition of carbon dioxide with CHO

The cycloaddition of carbon dioxide with cyclohexene oxide (CHO) promoted by complexes **1**-**4** gave *cis*-cyclohexenecarbonate (*cis*-CHC) as exclusive product in all cases.

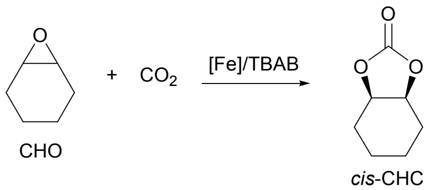
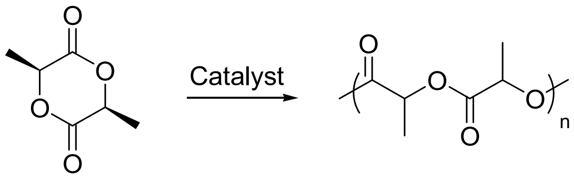


Figure S14. Coupling reaction of CHO with CO_2

5. Ring-Opening Polymerization of L-lactide



ROP of L-LA

TableS3. ROP of L-LA promoted by complexes **1**-**3**

Entry	Cat	Co-Cat (eq)	Conversion (%)
1	**2**	-	33
2	**2**	PPNCl (1eq)	63
3	**1**	PPNCl (1eq)	0
4	**3**	PPNCl (1eq)	0

General conditions: Complexes: **1**-**3** = 17.2 µmol, solvent: PO = 2 mL, L-LA= 1.7 mmol (100 equiv), temperature = 60°C, time = 4h.

5.1 NMR characterization of PLA

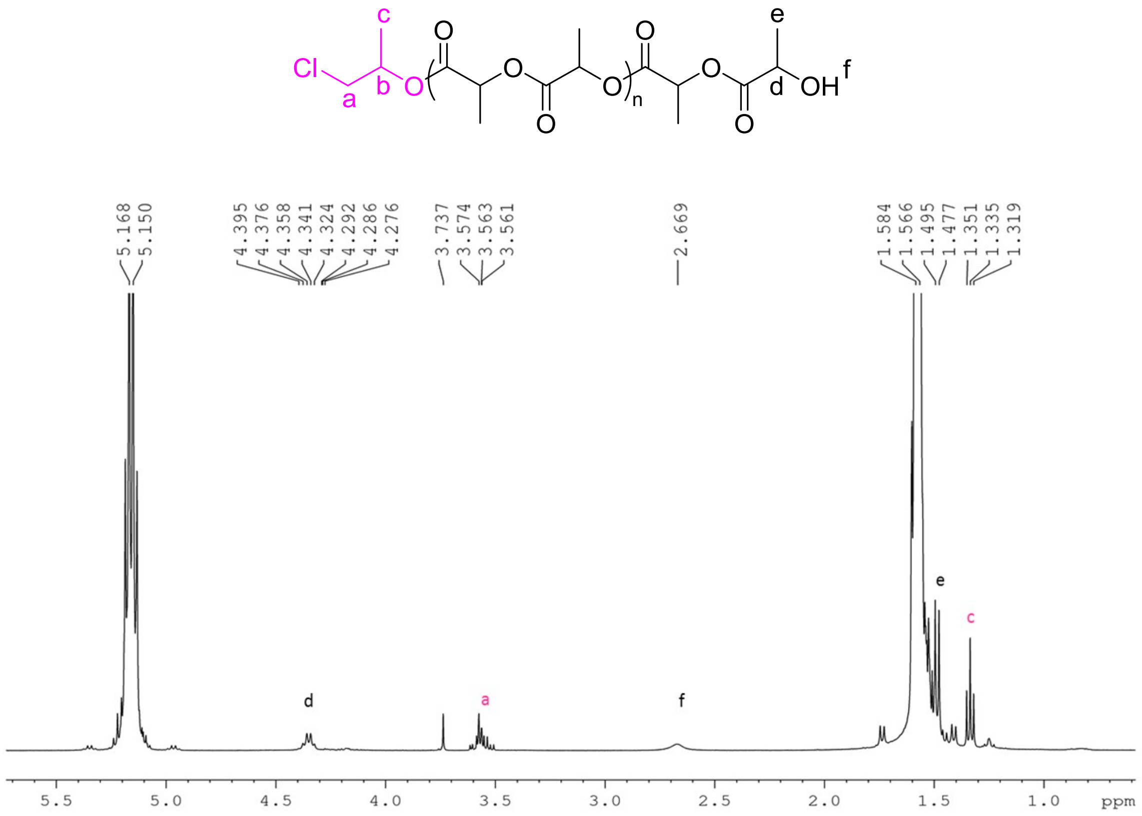


Figure S15.^{1}H NMR spectrum (400 MHz, CDCl$_3$, RT) of a PLA sample (entry 1 in Table S3).

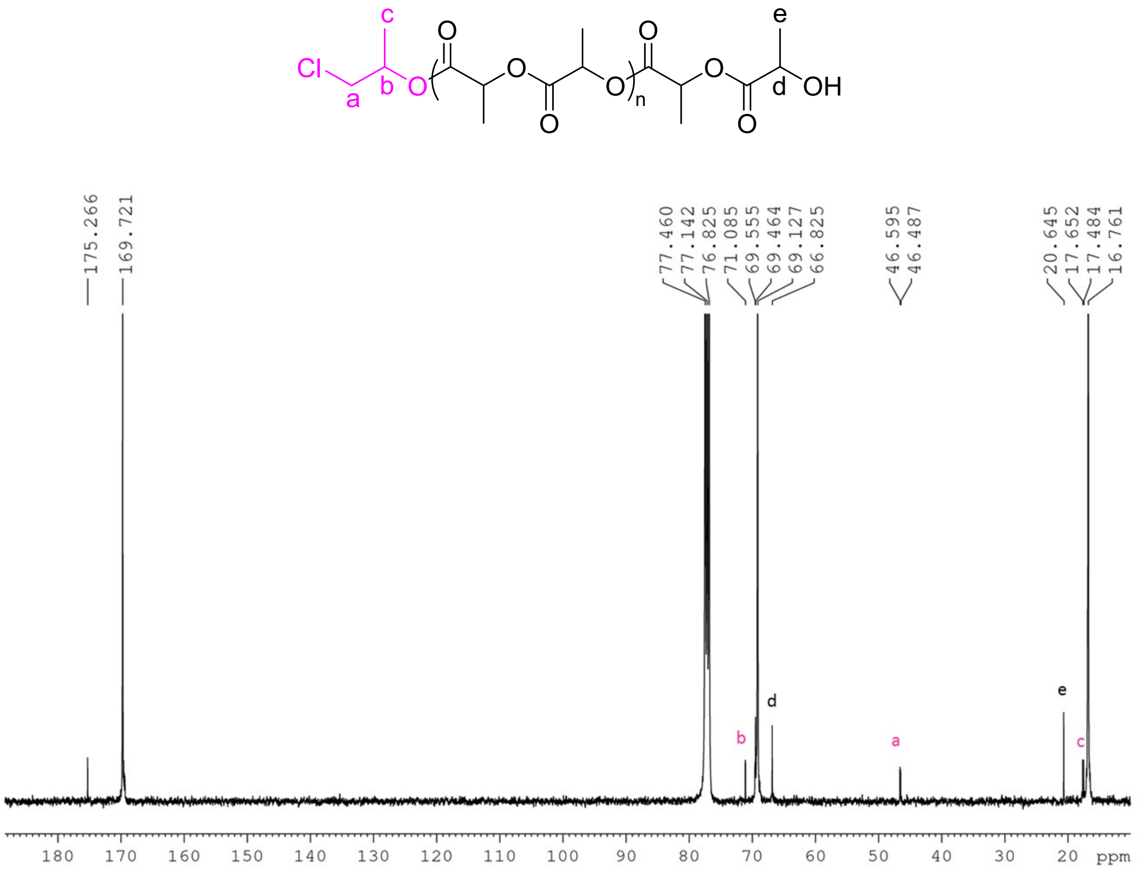
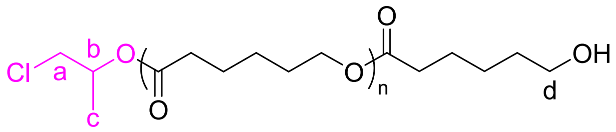


Figure S16. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$, RT) of a PLA sample (entry 1 in Table S3).

6. NMR characterization of PCL



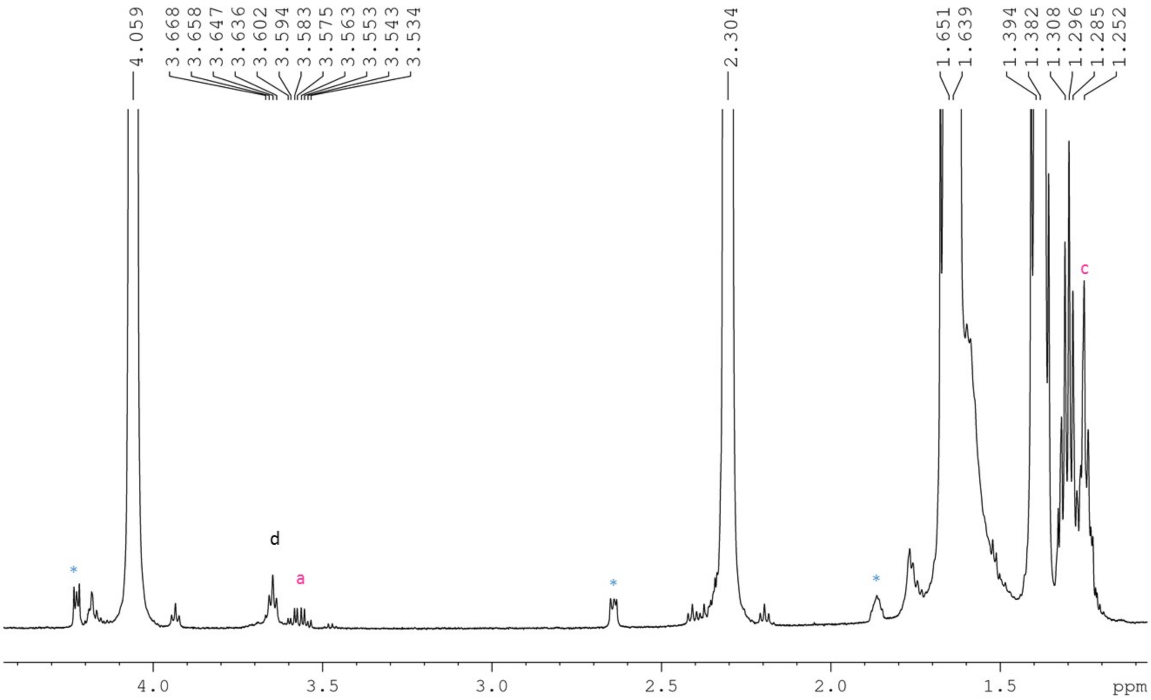


Figure S17. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, RT) of a PCL sample (entry 1 in Table 3). The peaks denoted with the blue star are related to residual ε-CL monomer.

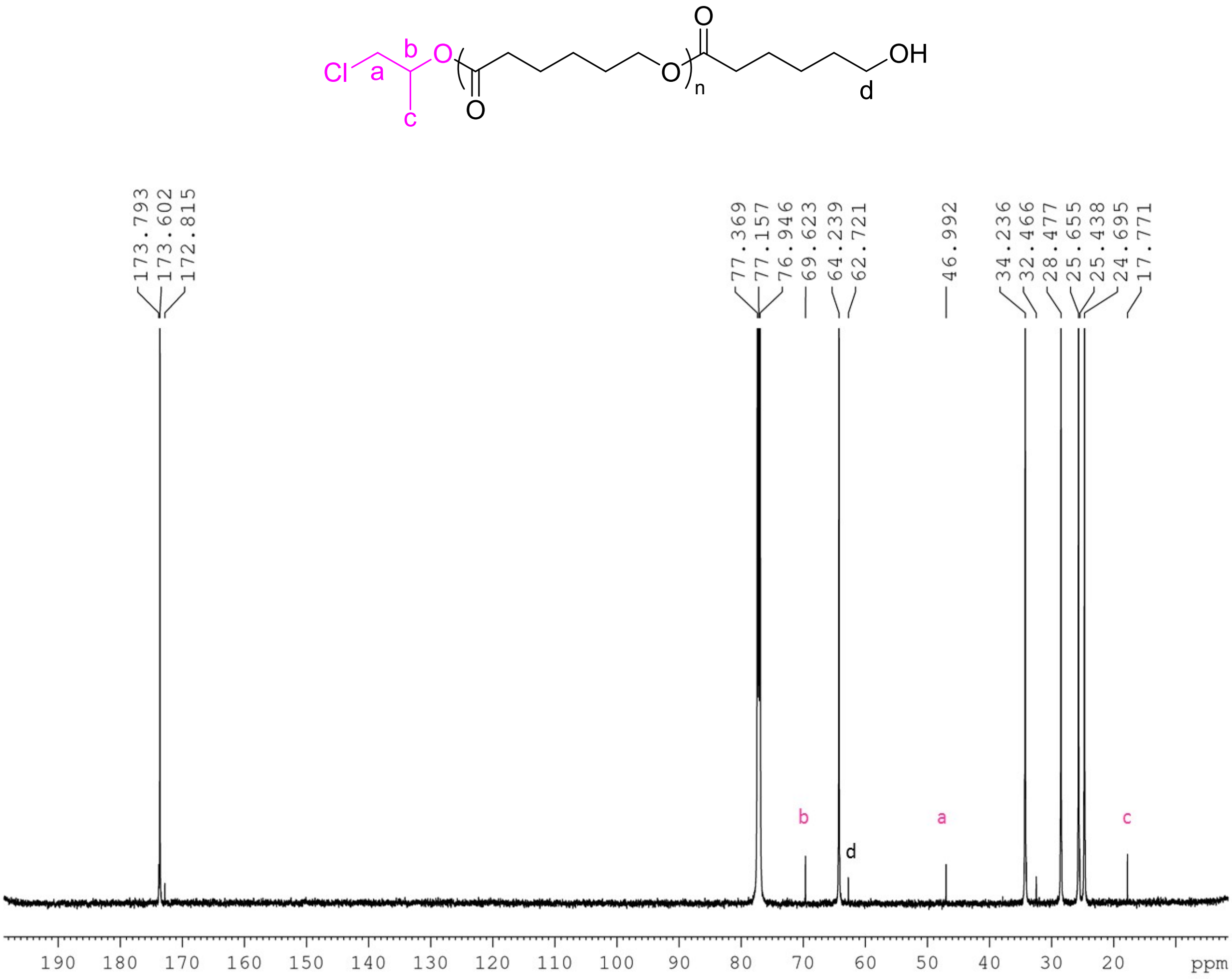


Figure S18.^{13}C NMR spectrum (100.6 MHz, $CDCl_3$, RT) of a PCL sample (entry 1 in Table 3)

7. References

1. K. Hasan, C. Fowler, P. Kwong, A. K. Crane, J. L. Collins and C. M. Kozak, *Dalton Trans.*, 2008, 2991–2998.

2. a) S. Liao and B. Lista, *Adv. Synth. Catal.*, 2012, **354**, 2363-2367. b) R. Duan, C. Hu, X. Li , X. Pang, Z. Sun, X. Chen and X. Wang, *Macromolecules*, 2017, **50**, 9188–9195.