Novel Iron(III) Catalyst for the Efficient and Selective Coupling of Carbon Dioxide and Epoxides to Cyclic Carbonates

Antonio Buonerba,[a,b] *Assunta De Nisi,*[a] *Alfonso Grassi,*[a,b] *Stefano Milione,*[a,b] *Carmine Capacchione,*[a,b,]* *Sergei Vagin*[c] *and Bernhard Rieger*[c]

[a] Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, via Giovanni Paolo II, 132-84084 Fisciano (SA), Italy.

[b] NANOMATES, Research Centre for NANOMAterials and nanoTEchnology at Salerno University, 84084 Fisciano (SA), Italy.

[c] WACKER Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenbergstrasse 4, 85748 Garching, Germany

* E-mail: ccapacchione@unisa.it

Table of Contents

1. Experimental Section.

1.1. General considerations, materials and characterizations.

All manipulation involving air- and/or moisture-sensitive compounds were performed under nitrogen atmosphere using standard Schlenk technique and a MBraun glovebox. Toluene (Carlo Erba, 99.5 %) and THF (99%; Sigma-Aldrich) were used as received or refluxed for 48 h over sodium and distilled before use for moisture- and oxygen-sensitive reactions. *p*-*tert*-Butylphenol (≥99%; Sigma-Aldrich), paraformaldehyde (reagent grade, crystalline; Sigma-Aldrich), hydrobromic acid solution in acetic acid (33 *wt*%; Sigma-Aldrich), 2,4-di-*tert*-butylphenol (98%, Sigma-Aldrich), sulfur monochloride (98%, Sigma-Aldrich), zinc (≥98; Sigma-Aldrich), carbon dioxide (4.8 purity grade, Rivoira) were used as received. (±)-Propylene oxide (≥99.5%; Sigma-Aldrich), (±)-epichlorohydrin (≥99%; Sigma-Aldrich), glycidol (99%; Sigma-Aldrich), allyl glycidyl ether (≥99%; Sigma-Aldrich), phenyl glycidyl ether (99%; Sigma-Aldrich), (*R*)-styrene oxide (97%; Sigma-Aldrich), cyclopentene oxide (98%; Sigma-Aldrich) and cyclohexene oxide (98%; Sigma-Aldrich) were distilled under reduced pressure over calcium hydride. 3,5-di-*tert*-butyl-2-hydroxythiophenol (**1**, Scheme 2), 2,6-di(bromomethyl)-4-(*tert*-butyl)phenol (**2**, Scheme 2) were synthesized according to the procedures of Pastor[1] and Williams[2] respectively. Deuterated solvents were purchased from Euriso-Top or Sigma-Aldrich and used as received.

NMR spectra were collected on AVANCE Bruker spectrometers (600, 400, 300 and 250 MHz for ^{1}H): the chemical shifts were referenced to tetramethylsilane (TMS) as external reference, using the residual protio signal of the deuterated solvents. ^{1}H NMR diagnostic signals (CD_2Cl_2; δ in ppm) for cyclic carbonate products: 4-methyl-1,3-dioxolan-2-one [4.77-4.75 (m, 1H, ring *CH*CH$_3$), 4.45 (t, 1H*,* J=8Hz, ring C*H*H*,),* 3.91(t, 1H*,* J = 8 Hz, ring CH*H),* 1.33-1.31 (d, 3H, J= 6 Hz, C*H*$_3$)]; 4-(chloromethyl)-1,3-dioxolan-2-one [4.97-4.95 (m, 1H, ring C*H*), 4.49 (t, 1H, J=8.6, ring C*H*$_2$ *),* 4.25 (dd, 1H, ring C*H*$_2$ *),* 3.80(dd, 1H, J = 3, 12 Hz, C*H*$_2$Cl), 3.67 (dd, 1H, C*H*$_2$Cl)]; 4-((allyloxy)methyl)-1,3-dioxolan-2-one [5.74-5.81 (m, 1H, C*H*), 5.08-5.22 (m, 2H, C*H*$_2$), 4.74(m, 1H, C*H*), 4.39 (t, 1H, C*H*), 4.22(t, 1H, C*H*), 3.9 (m, 2H, C*H*$_2$),3.2-3.6 (m, 2H, C*H*$_2$)]; 4-phenoxymethyl-1,3-dioxolan-2-one:[7.31 (m, 2 H, Ph) 7.02 (t, 1 H, J = 7.5 Hz, Ar*H*), 6.91 (d, 2 H, J = 8.7 Hz, Ar*H*), 5.03 (m, 1 H, OC*H*), 4.60 (t, 1 H, J = 8.5 Hz, PhOC*H*2), 4.50 (m, 1 H, PhOC*H*2), 4.24 (dd, 1 H, J = 3.8, 11 Hz, OC*H*2), 4.15 (dd, 1 H, J = 3.8, 10.8 Hz, OC*H*2)]; 4-phenyl-l,3-dioxolan-2one:[7.22(m, 4H, ring Ar*H*), 5.44 (t, 1H*,* J =8 Hz, PhC*H*O), 4.52 (t, 1H, *J* = 8 Hz, OC*H*2 *),* 4.0 (t, 1H, J = 8 Hz, OC*H*2)]; (3a*R*,7a*S*)-hexahydrobenzo[d][1,3]dioxol-2-one: [4.58 (m, 2H, OC*H*), 1.76 (m, 4H),1.27 (m, 2H), 1.14(m, 2H)]; 4-hydroxy-1,3-dioxolan-2-one:[5.16 (m, O*H*), 4.77 (m, 1H, C*H*), 4.46(m, 1H, C*H*2OCO), 4.30 (m, 1H, C*H*2OCO2), 3.71-3.67 (m, 1 H, C*H*2OH), 3.53-3.49 (m, 1H, C*H*2OH)]; (3a*R*,6a*S*)-tetrahydro-3aH-cyclopenta[d][1,3]dioxol-2-one: [4.91 (m, 2H), 2.2-1.8 (6H, m)]. Elemental analysis was performed on a

CHNS Thermo Scientific Flash EA 1112 equipped with a thermal conductivity detector. ESI-MS spectra were acquired on a Quattro *micro*™ API triple quadrupole mass spectrometer from Waters equipped with electrospray ion source, using CH_2Cl_2 or THF as solvent. FT-IR measurements were carried out on a Bruker Vertex 70 spectrometer equipped with DTGS detector and a Ge/KBr beam splitter. The samples were analysed as dichloromethane solutions or in the form of KBr disks. UV-Vis acquisitions were collected on a PerkinElmer Lambda EZ 201. HPLC analyses of the reaction course of the coupling CO_2/(*R*)-styrene oxide were performed with a Jasco PU-2089 Plus equipped with a Jasco MD-2010 Plus multiwavelength detector and a Chiralcel ODH (250×4.6 mm) column (elution condition: *n*-hexane/2-propanol v/v = 9:1; 1.0 mL/min; retention time for (*R*)-styrene carbonate = 21.4 min).[3]

1.2. Synthesis of the ligand precursor 6,6'-(((5-(*tert*-butyl)-2-hydroxy-1,3-phenylene)*bis*(methylene))*bis*(sulfanediyl))-*bis*(2,4-di-tert-butylphenol) (3, Scheme 2).

A 100 mL two-neck round-bottom flask equipped with condenser and magnetic stirring bar was charged, under nitrogen atmosphere, with 15 g of 3,5-di-*tert*-butyl-2-hydroxythiophenol (63 mmol, compound **1**, Scheme 2) dissolved in 25 mL of ethanol, 2.5 g of NaOH (63 mmol) and the mixture was refluxed about 1 hour until complete dissolution of the hydroxide. 10.4 g of 2,6-di(bromomethyl)-4-(*tert*-butyl)phenol, dissolved in 10 mL of ethanol (31 mmol, compound **2**, Scheme 2), were slowly added at 0 °C and the mixture heated to the reflux of the solvent that was kept for 1 h. The solvent was distilled off, water was added until dissolution of NaBr by-product and the aqueous phase extracted twice with diethyl ether. The combined organic phases were dried with $MgSO_4$ and, after evaporation of the solvent, the resulting crude white solid was purified by repeated dissolutions in hot acetone and crystallizations at -78 °C. Yield (6.0 g). EA for $C_{40}H_{58}O_3S_2$ calc.: C, 73.80; H, 8.98, O, 7.37; S 9.85; found: C, 73.69; H, 9.13; S, 9.20; O, 7.98. Mass spectrum: m/z 673.6 (MNa^+ 100%).

1.3. Synthesis of the iron(III) complex (4, Scheme 2).

A 500 mL two-neck round-bottom flask, equipped with a magnetic stirring bar was charged with 416 mg of sodium hydride (17.3 mmol) suspended in 100 mL of THF and a solution of 3,50 g of the ligand precursor **3** (5,38 mmol) dissolved in 150 mL of THF was slowly added at room temperature under protective nitrogen atmosphere, thus allowed to react overnight. The resulting suspension was filtered through celite and slowly added at room temperature to 863 mg of anhydrous iron(III) chloride (5.32 mmol) dissolved in 70 mL of THF. The rapid change of the colour to the dark blue was observed and the reaction kept overnight. The mixture was then filtered through celite and the solvent removed under reduced pressure affording a deep blue crystalline solid. Yield: 2,70 g, 72 %. EA for $C_{80}H_{110}Fe_2O_6S_4$ calc.: C, 68.26; H, 7.88; Fe, 7.93; O, 6.82; S, 9.11; found: C, 67.47; H, 7.87; S, 8.98; O+Fe, 15.68. Mass spectrum: m/z 1409.2 (MH^+ 100%). UV-Vis: ε_{620} = 6508 $Lmol^{-1}cm^{-1}$.

1.4. Typical procedure for CO_2/epoxide coupling to cyclic carbonates catalyzed by 4/TBAB (referred to entry 16, Table 1).

A 60 mL stainless steel pressure reactor equipped with a magnetic stirring bar was charged, under CO_2 atmosphere, with 24.6 mg of catalyst **4** (0.0175 mmol) and 22.6 mg of TBAB (0.070 mmol) dissolved in 4.9 mL of PO (70 mmol). The reaction mixture was pressurized with CO_2 at 20 bar and stirred at 100 °C for 6 h. The reactor was cooled with ice, the CO_2 released, mesitylene was added as an internal standard and the mixture was analysed by ^{1}H-NMR spectroscopy, using CD_2Cl_2 as solvent. Yield 87 %.

2. NMR Characterization.

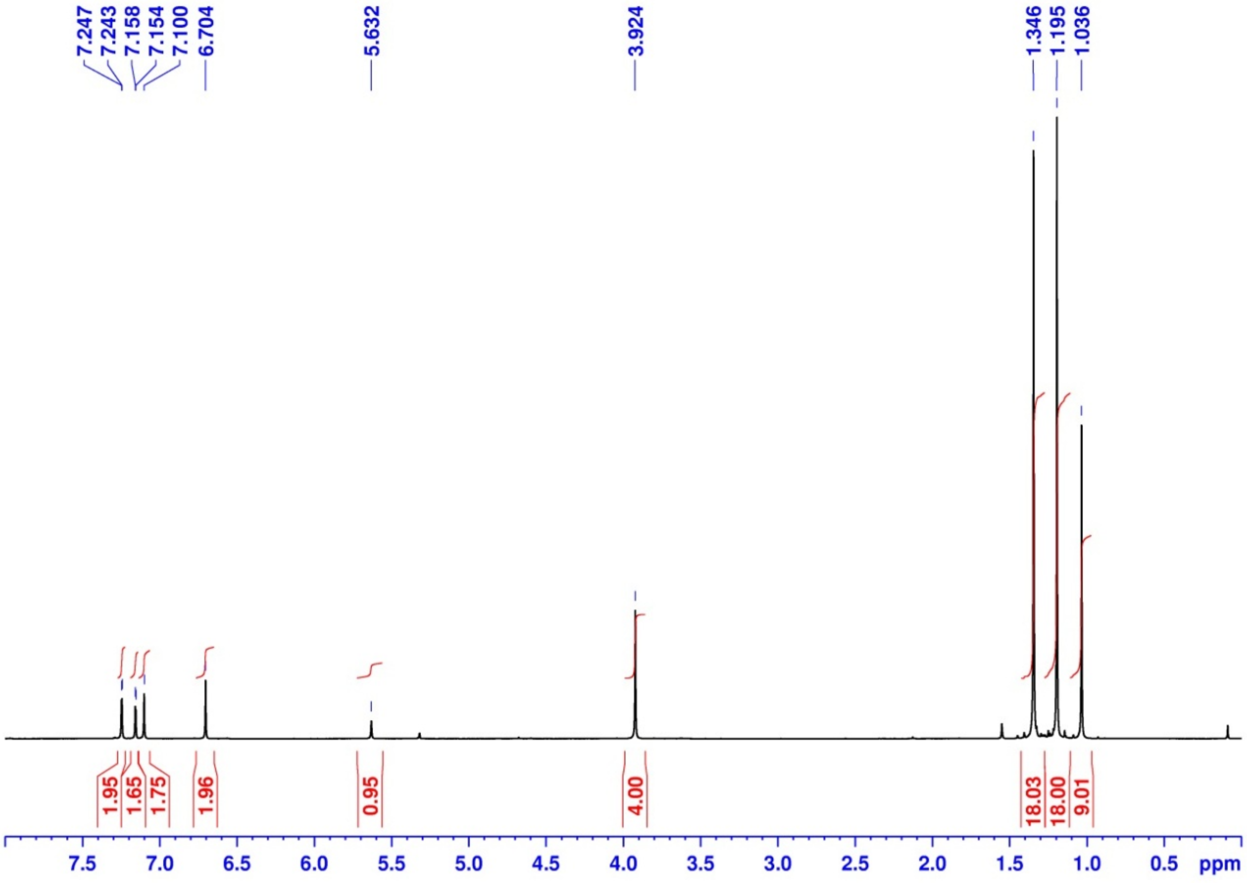

Figure S1. ^{1}H NMR spectrum of compound **3** (CD_2Cl_2, 600 MHz) .

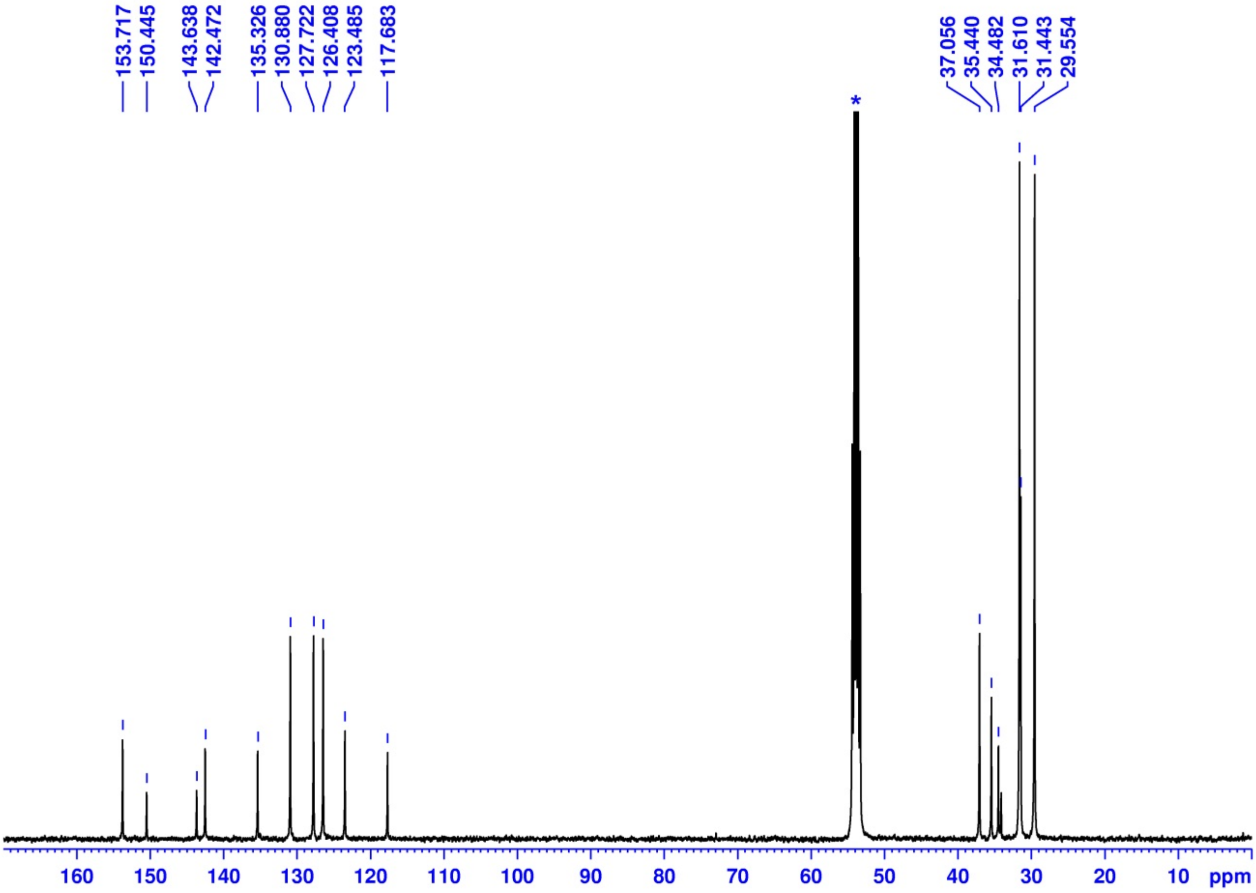

Figure S2. ^{13}C NMR spectrum of compound **3** (*CD_2Cl_2, 600 MHz).

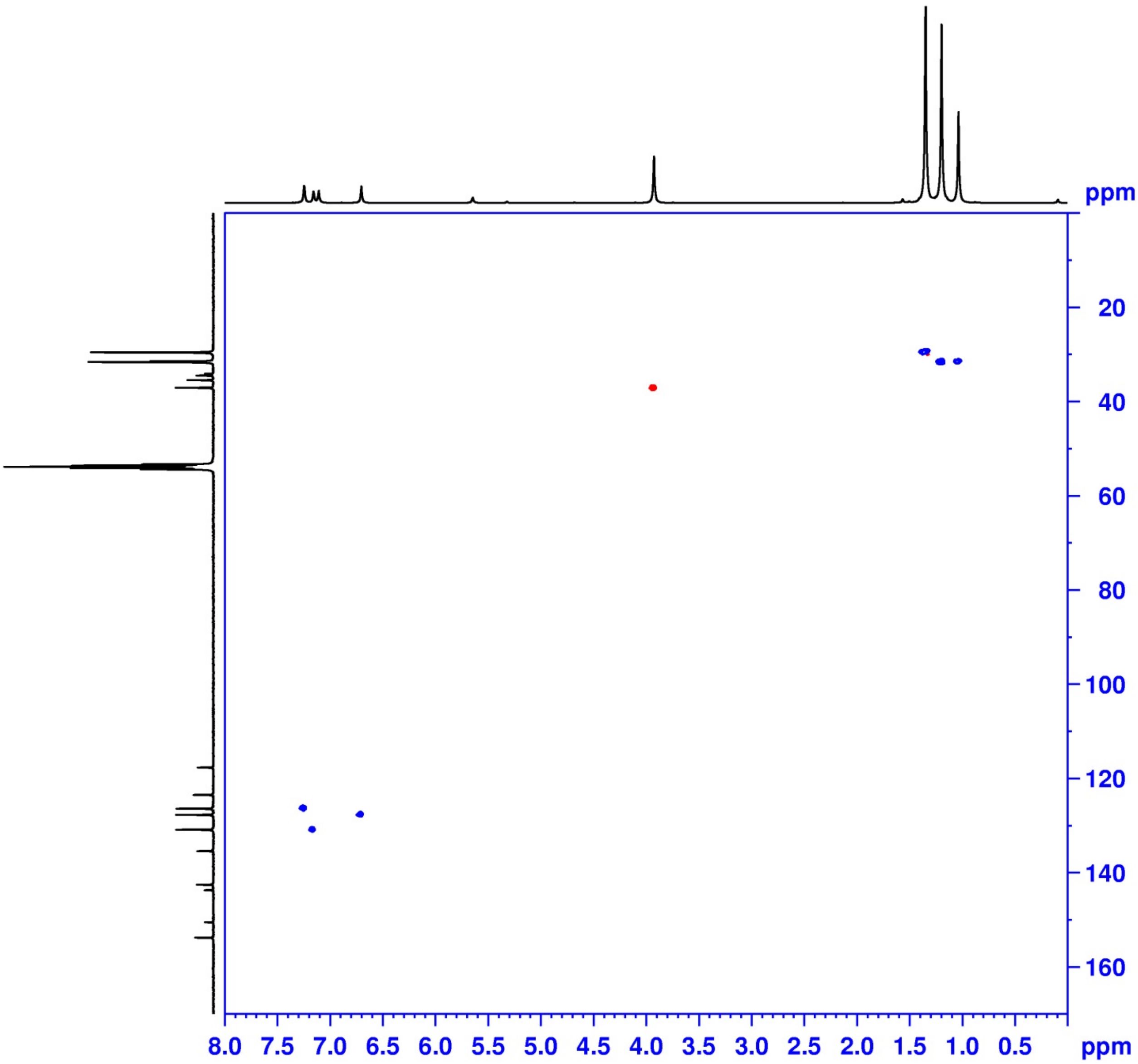

Figure S3.^{1}H-^{13}C HSQC spectrum of the compound **3** (CD_2Cl_2, 400 MHz) .

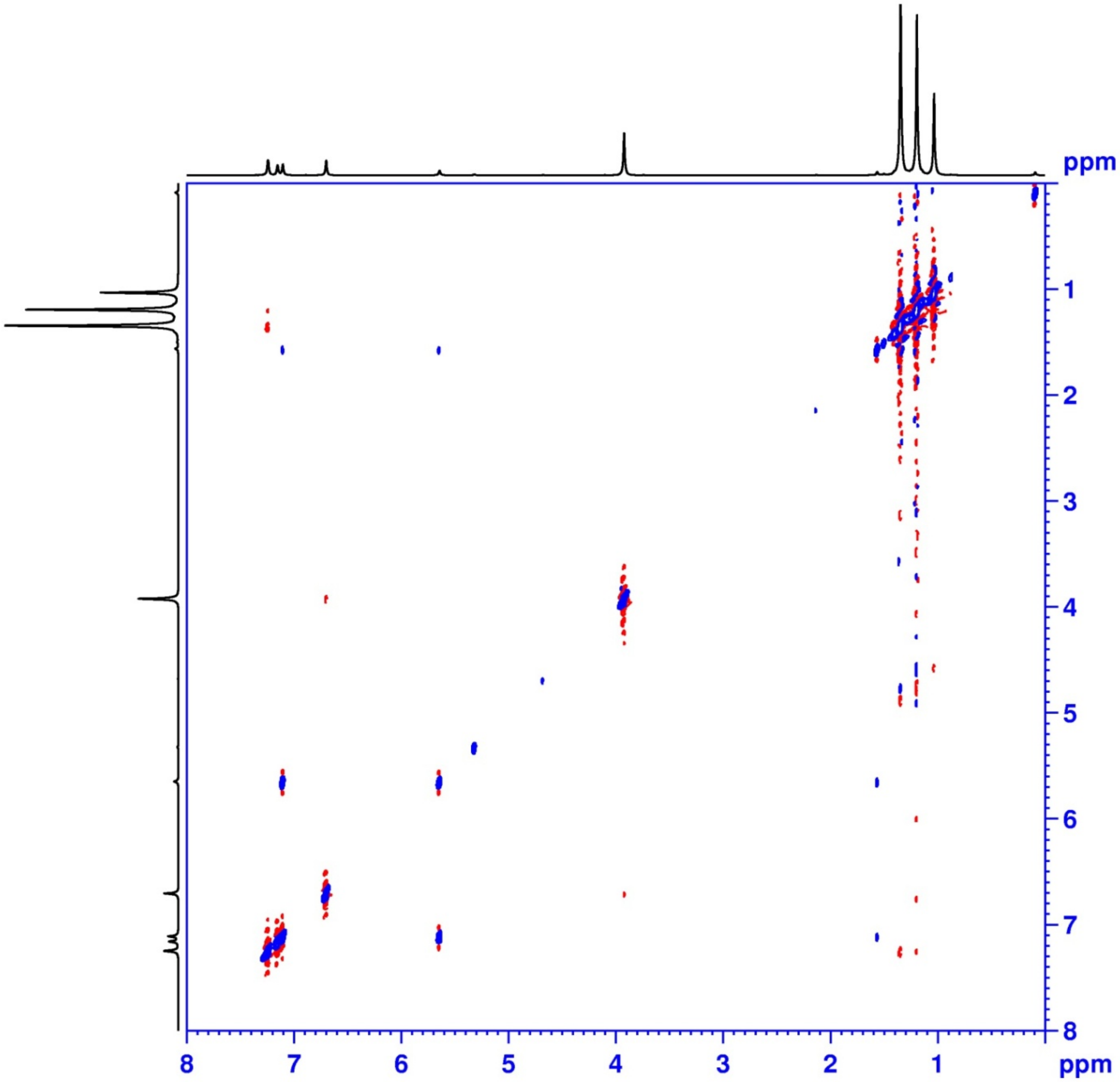

Figure S4. NOESY spectrum of the compound **3** (CD_2Cl_2, 400 MHz) .

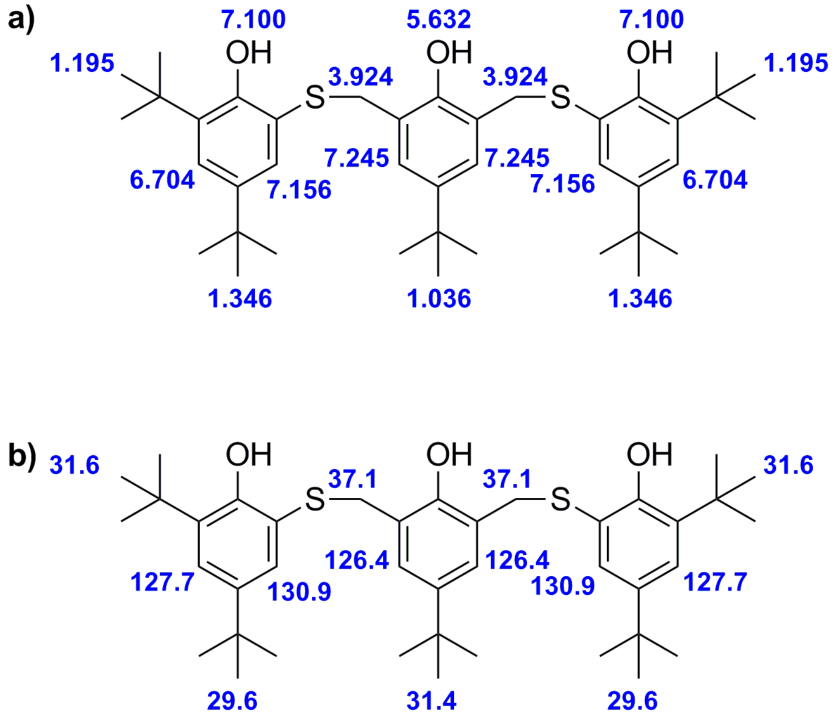

Figure S5.^{1}H (a) and ^{13}C (b) NMR signal assignments for the pro-ligand **3**.

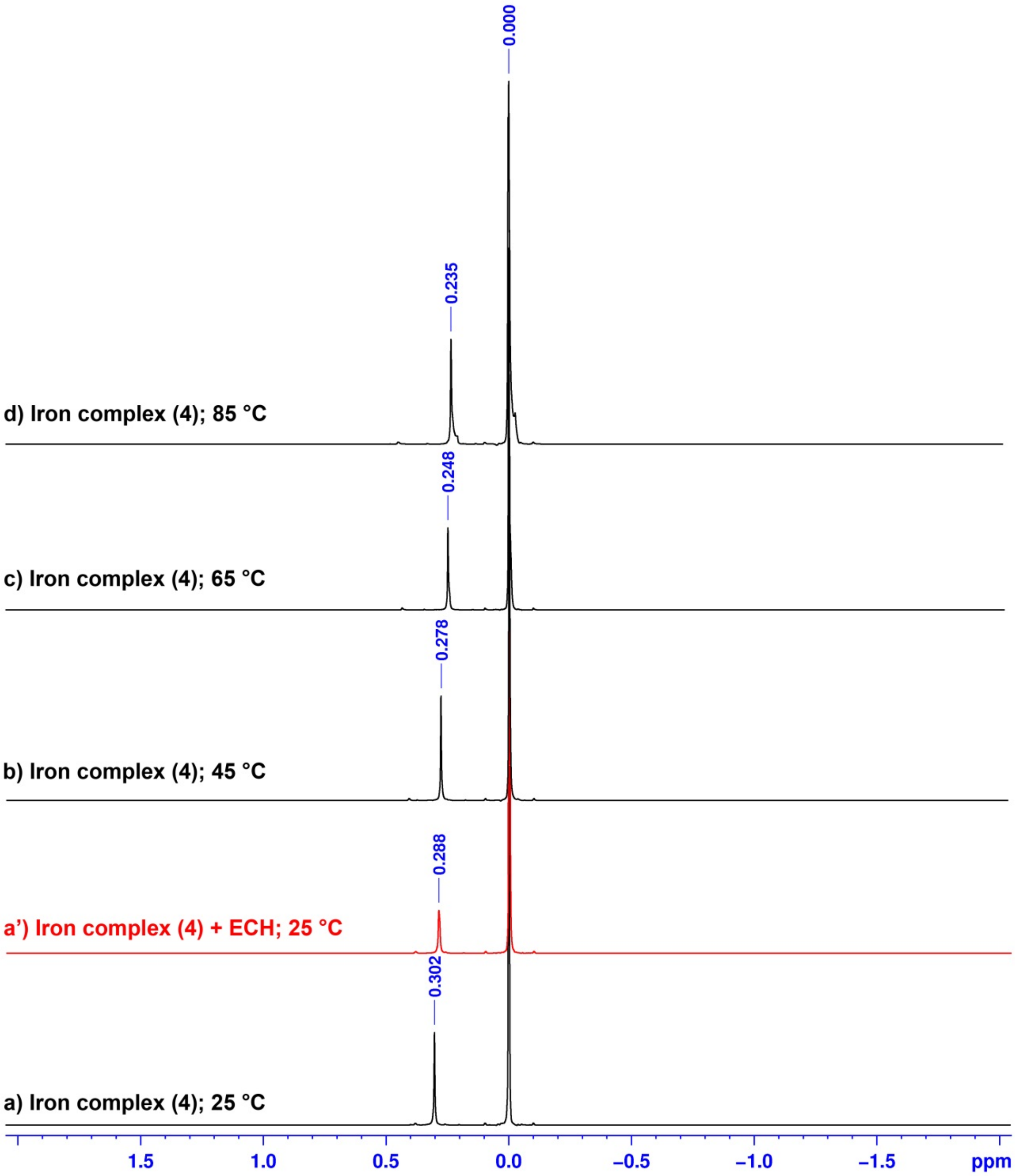

Figure S6. Plot of ^{1}H NMR spectra of the iron(III) catalyst (**4**) in toluene-d_8 (3.5×10^{-3} M) (curves **a-d**) and in presence of 50 *equiv*. of epichlorohydrin (curve **a’**) for the determination of the solution magnetic susceptibility by means of the method of Evans.

3. ESI-MS Characterization.

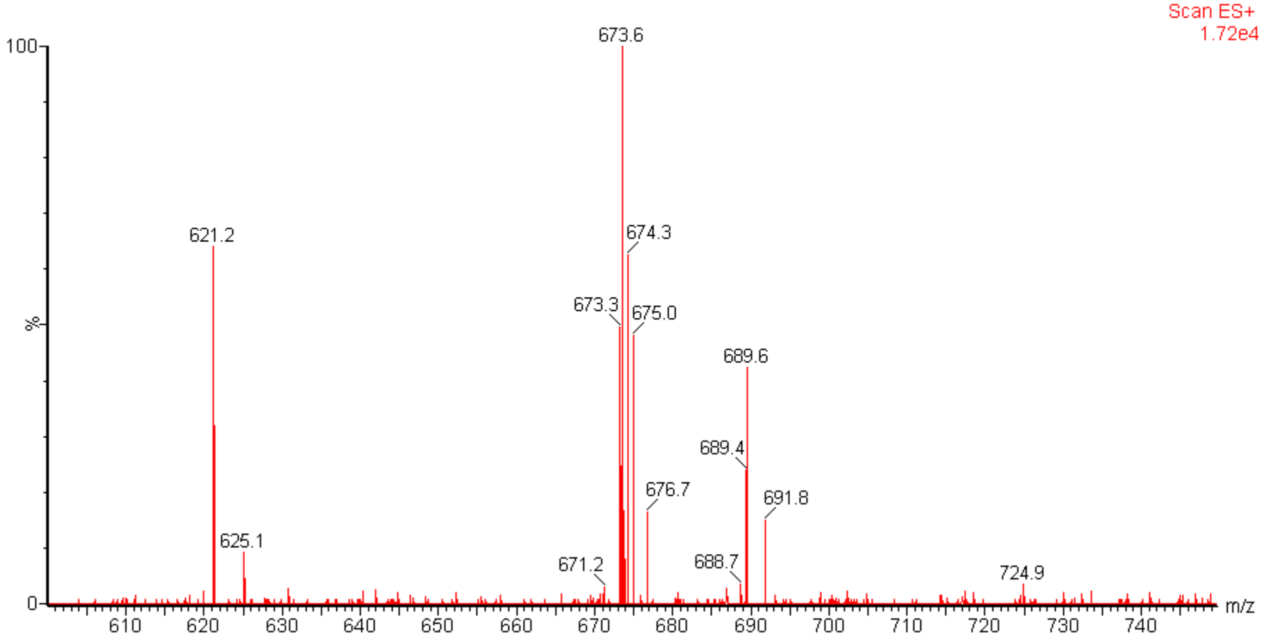

Figure S7. Mass spectrum of the compound **3** (CH_2Cl_2 as solvent).

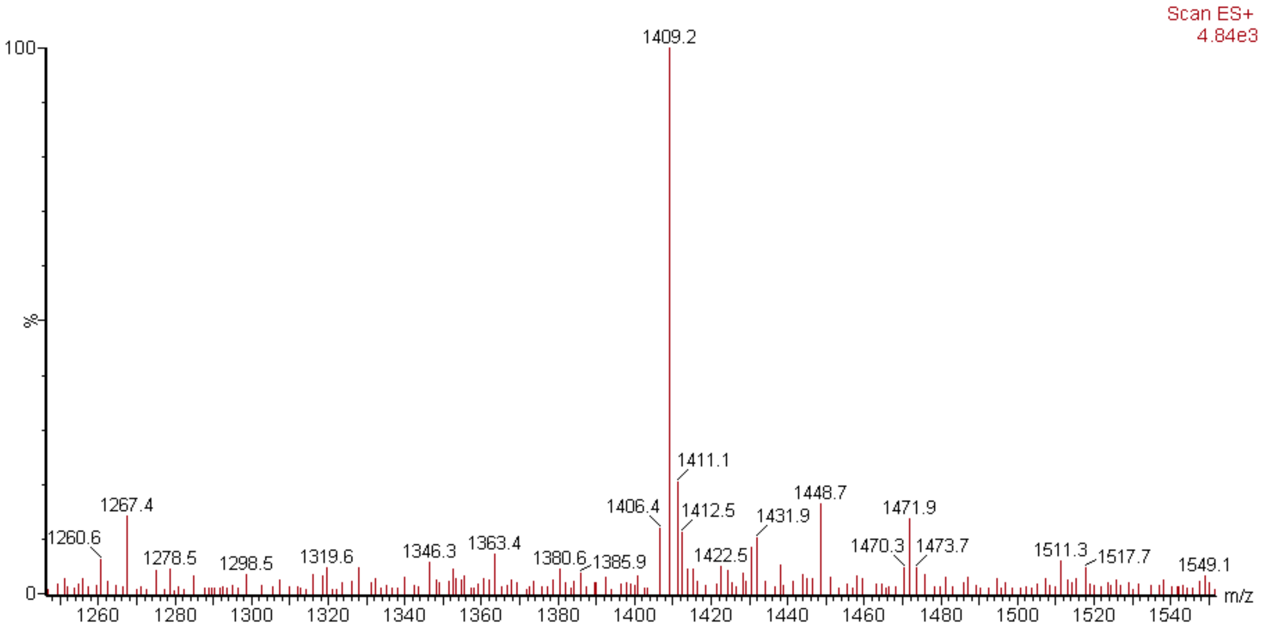

Figure S8. Mass spectrum of the iron(III) complex **4** (THF as solvent).

4. FT-IR Characterization.

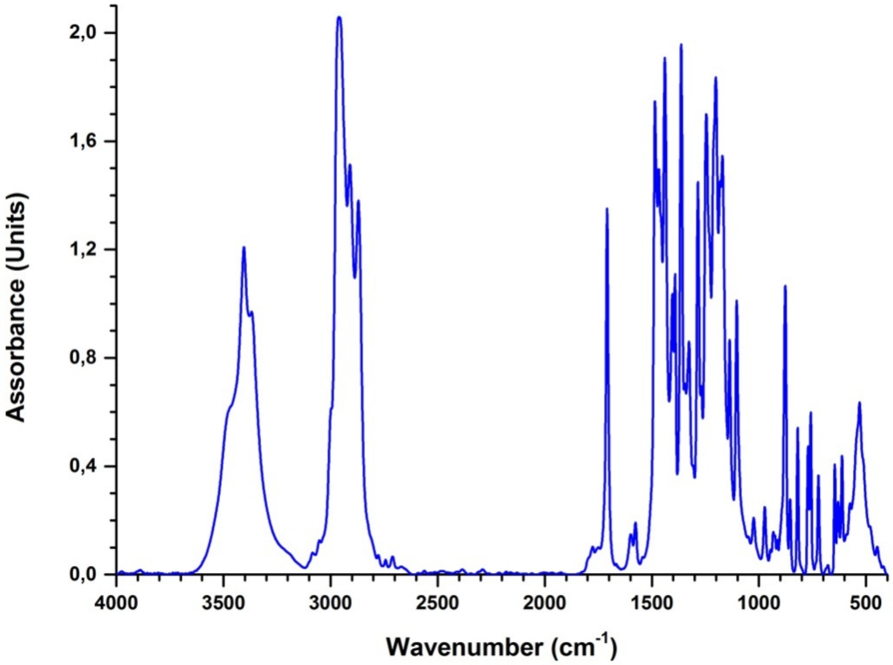

Figure S9. FT-IR spectrum of **3** (the vibration at 1709 cm^{-1} is due to acetone impurity).

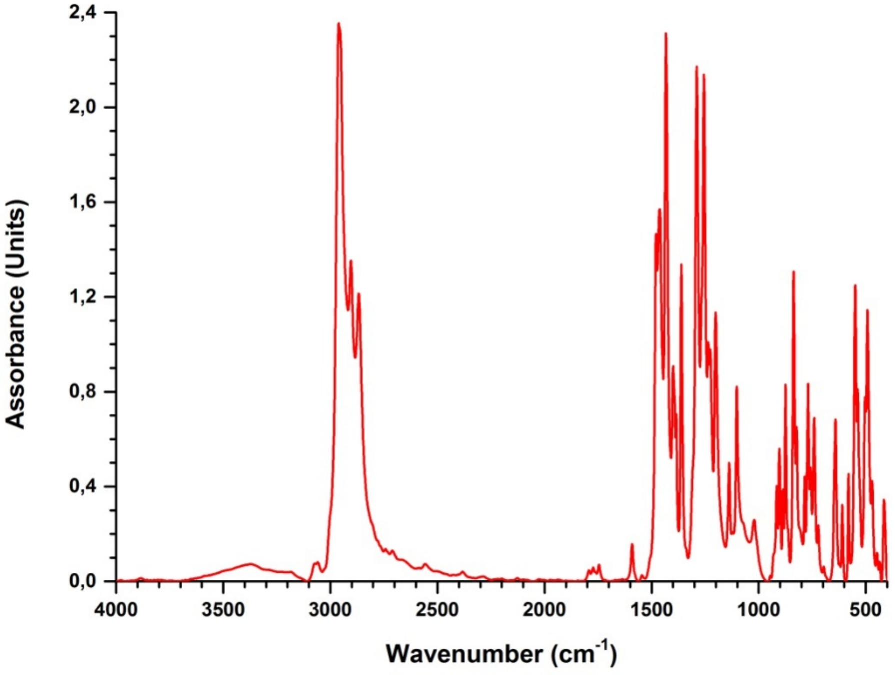

Figure S10. FT-IR spectrum of the iron(III) complex **4**.

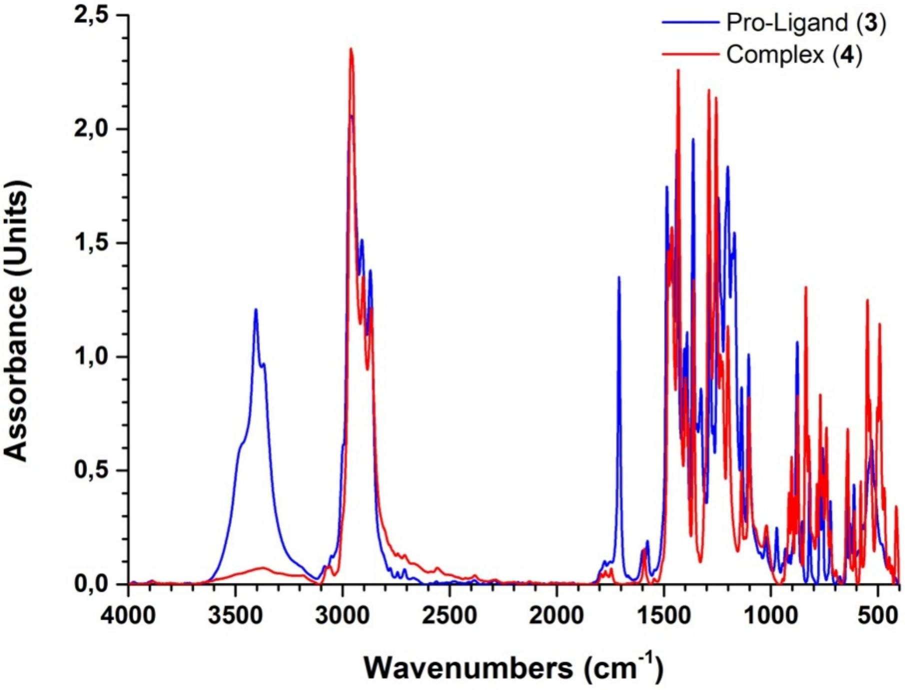

Figure S11. Comparison of the FT-IR spectra of the pro-ligand **3** (blue curve) and of the iron(III) complex **4** (red curve).

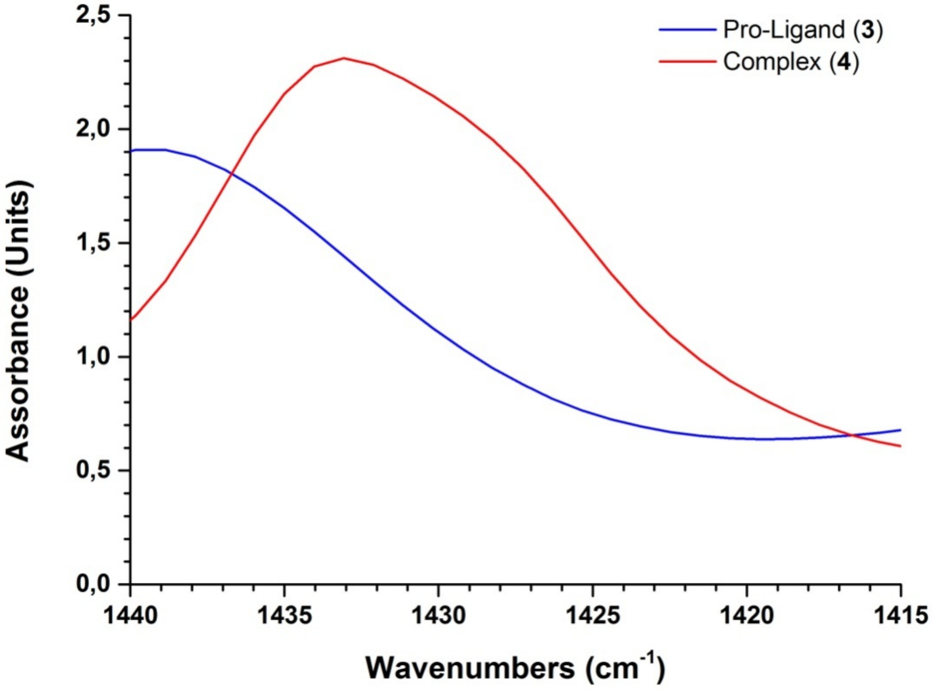

Figure S12. Magnification of the region 1440-1415 cm^{-1} (for the CH_2-S-C deformation)[4,5] of the FT-IR spectra in Figure S11.

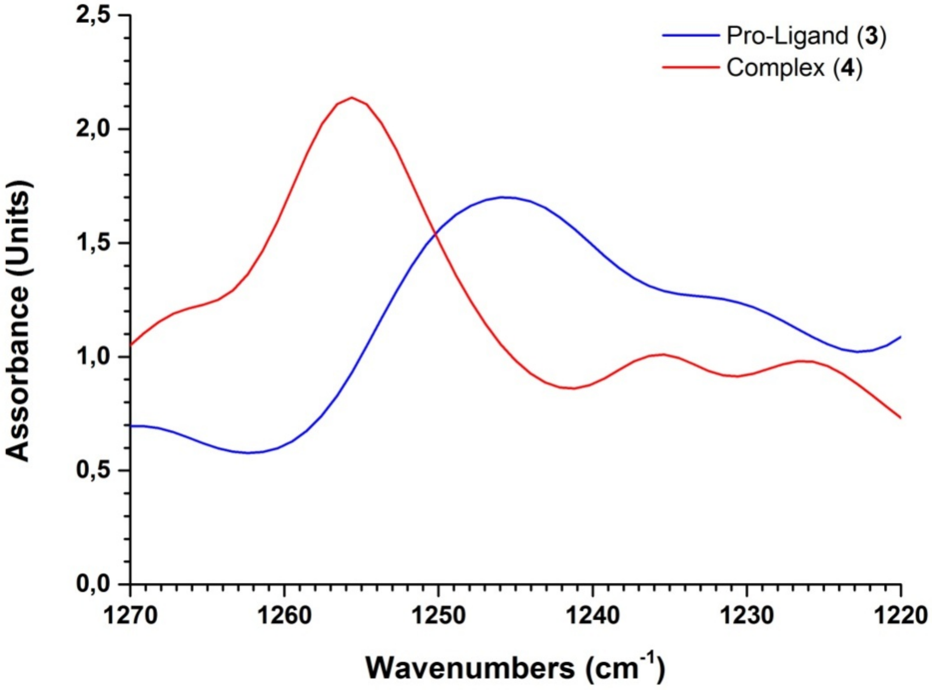

Figure S13. Magnification of the region 1270-1220 cm^{-1} (for the CH_2-S wagging)[4,5] of the FT-IR spectra in Figure S11.

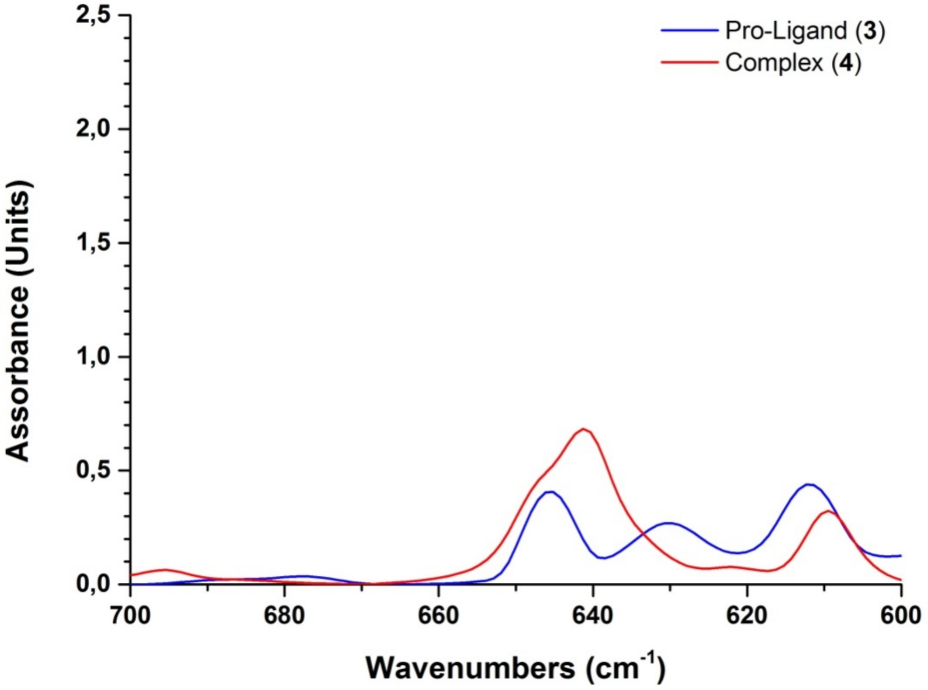

Figure S14. Magnification of the region 700-600 cm^{-1} (for the C-S stretching vibration)[4,5] of the FT-IR spectra in Figure S11.

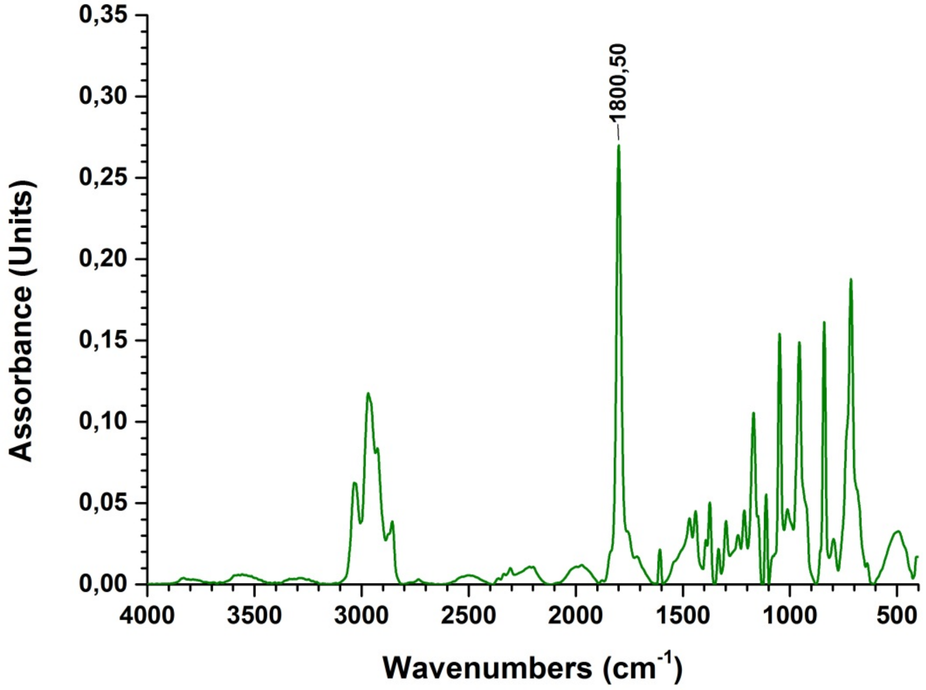

Figure S15. FT-IR spectrum of the reaction products of entry **25**, Table 2. The strong adsorption band at 1800 cm^{-1} indicates the formation of the *cis*-cyclopentene carbonate.[6]

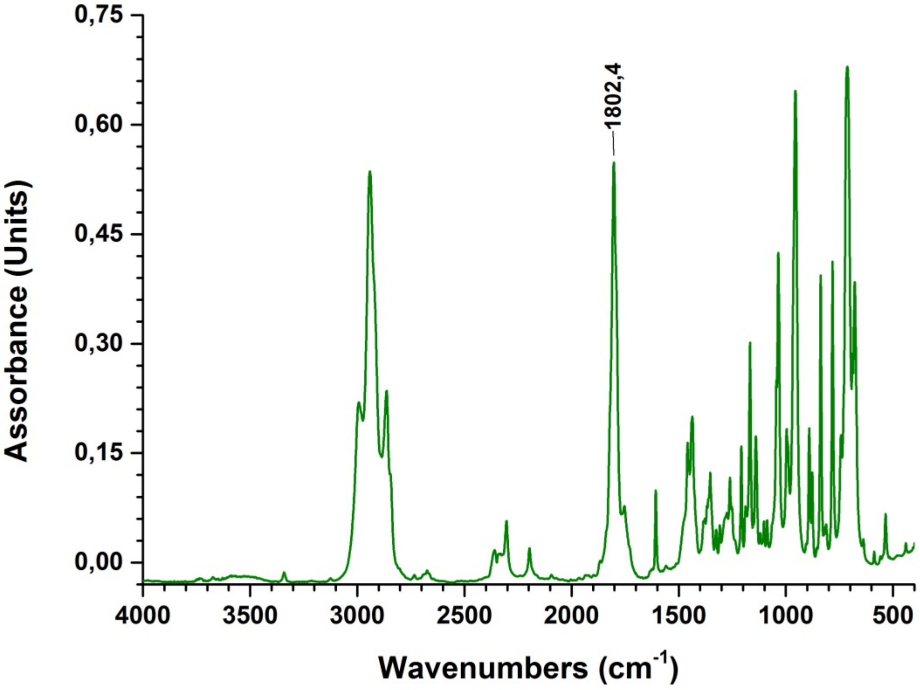

Figure S16. FT-IR spectrum of the reaction products of entry **26**, Table 2. The strong adsorption band at 1802 cm^{-1} indicates the formation of the *cis*-cyclohexene carbonate.[7]

5. UV-Vis Analysis.

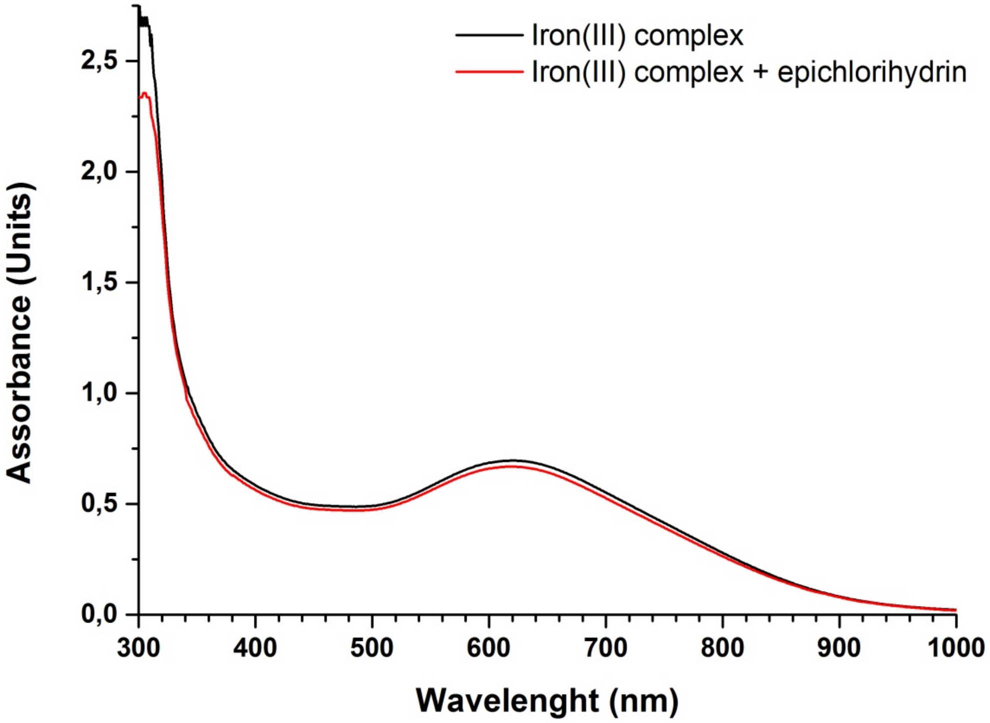

Figure S17. UV-Vis spectra of the iron(III) catalyst **4** in toluene (1.07×10^{-4} M; black curve) and in presence of 3738 equiv. of epichlorohydrin (red curve).

6. References.

1. S. D. Pastor and D. Z. Denney, *J. Heterocycl. Chem.*, 1988, **25**, 681-683.
2. M. V. Baker, M. J. Bosnich, D. H. Brown, L. T. Byrne, V. J. Hesler, B. W. Skelton, A. H. White and C. C. Williams, *J. Org. Chem.*, 2004, **69**, 7640-7652.
3. L. Jin, Y. Huang, H. Jing, T. Chang and P. Yan, *Tetrahedron: Asymmetry*, 2008, **19**, 1947-1953
4. *The Sadtler handbook of infrared spectra*. ed. W. W. Simons, Sadtler Research Laboratories, Philadelphia, 1978.
5. *Interpreting Infrared, Raman, and Nuclear Magnetic Resonance Spectra*, ed. R. A. Nyquist, Academic Press, San Diego, 2001, pp. 65-83.
6. D. J. Darensbourg, S. J. Lewis, J. L. Rodgers and J. C. Yarbrough, *Inorg. Chem.*, 2003, **42**, 581-589.
7. A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, *Chem. Commun.*, 2011, **47**, 212-214.