

Dinuclear [OSSO]-Fe complexes for the reaction of CO₂ with epoxides

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SUPPORTING INFORMATION

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General Considerations

Reagents and solvents were purchased from Sigma Aldrich Company or TCI chemicals. Solvents were dried and distilled before use. Deuterated solvents were degassed under a nitrogen flow and stored over activated 4 Å molecular sieves. Epoxides were stored on CaH₂ under inert atmosphere and freshly distilled before use. NMR spectra were recorded on Bruker AM 300 spectrometer (300 MHz for ¹H; 75 MHz for ¹³C), Bruker AVANCE 400 spectrometer (400 MHz for ¹H; 100 MHz for ¹³C) and Bruker ASCEND 600 spectrometer (600 MHz for ¹H; 150 MHz for ¹³C). NMR samples were prepared by dissolving about 10 mg of compound in 0.5 mL of deuterated solvent. Measurements of the effective magnetic moments (μ_{eff}) were performed on a Bruker ASCEND 600 spectrometer in deuterated methylene chloride using a 5 mm Wilmad coaxial NMR tube. The μ_{eff} values were calculated from the equation $\mu_{\text{eff}} = 8\chi_{\text{g}}MwT$, where χ_{g} (cm³/g) is the corrected molar susceptibility calculated with the equation $\chi_{\text{g}} = 3\Delta f/4\pi f_0 C Mw + c_0$ in which Δf is the frequency shift (Hz) of the residual ¹H signal of the solvent in the complex solution from the value of the pure solvent, C and Mw are the concentration (mol/cm³) and the molecular weight of the complex (g/mol), respectively, f_0 is the operating frequency of the spectrometer (Hz) and c_0 is the mass susceptibility of the pure solvent ($-0.6179 \cdot 10^{-6}$ cm³/g). $4\pi/3$ is the shape factor for a cylindrical sample in a superconducting magnet. ¹H and ¹³C chemical shifts are listed in parts per million (ppm) downfield from TMS and are referenced from the solvent peaks or TMS. Spectra are reported as follows: chemical shift (δ ppm), multiplicity and integration. Multiplicity is abbreviated as follows: singlet (s), doublet (d), triplet (t), multiplet (m), broad (br), overlapped (o). ESI-MS and MALDI-TOF analysis were performed on a Waters Quattro Micro triple quadrupole mass spectrometer equipped with an electrospray ion source. Infrared spectra were recorded with a Bruker Vertex70 spectrometer. SEC measurements were performed on PolymerLaboratoriesGPC50 equipped with a refractive index detector THF served as the solvent against polystyrene standards. Measurements were performed at 40 °C with a continuous solvent flow of 1 mL/min. Overlapping peaks were analyzed through deconvolution of the chromatogram.

Synthesis and characterization of **b**

A round-bottom flask equipped with a condenser and a magnetic stirrer was charged with 32.0 mmol of 2,4-di-tert-butyl-6-mercaptophenol, 32.0 mmol of NaOH and 70 mL of methanol. The mixture was refluxed at 70°C until complete dissolution of the reagents. Then, the system was left at 25 °C for about 20 minutes. At this point, 1,2,7,8-diepoxyoctane (16.0 mmol) was added. The reaction mixture was refluxed overnight. The solid produced was dissolved in 300 mL of diethyl ether and extracted with 300 mL of water. The organic phase was dried with Na₂SO₄, filtered and concentrated. The product precipitated from petroleum ether as a white solid. Yield 84%.

¹H NMR (CDCl₃, 600 MHz): δ 7.35 (d, 2H, Ar-H); 7.31 (d, 2H, Ar-H); 7.18 (b s, 2H, Ar-OH); 3.63 (m, 2H, CH₂-CH(OH)-CH₂); 2.72 (ddd, 4H, S-CH₂); 2.13 (br s, 2H, CH₂-CH(OH)-CH₂), 1.49 (o m, 2H, CH₂-CH(OH)-CH₂); 1.40 (s, 20H, CH₃ and CH₂-CH₂-CH(OH)); 1.28 (s, 20H, CH₃ and CH₂-CH₂-CH(OH)).

¹³C {¹H}NMR (CDCl₃, 125 MHz): δ 153.3 (Ar-C-OH); 142.5 (Ar-C-S); 135.7 (Ar-C-tBu); 130.4 (Ar-C-H); 126.1 ((Ar-C-H); 118.5 (Ar-C-tBu); 70.1 (CH₂-CH(OH)-CH₂); 44.5 (S-CH₂); 36.1 (C(CH₃)₃); 35.4 (C(CH₃)₃); 34.5 (C(CH₃)₃); 31.7 (C(CH₃)₃); 29.7 (C(CH₃)₃); 25.6 (CH₂).

Elemental analysis (%): Found (calcd) C 69.56; H 9.55; O 10.41; S 10.48 (C 69.86; H 9.45; O 10.34; S 10.36)

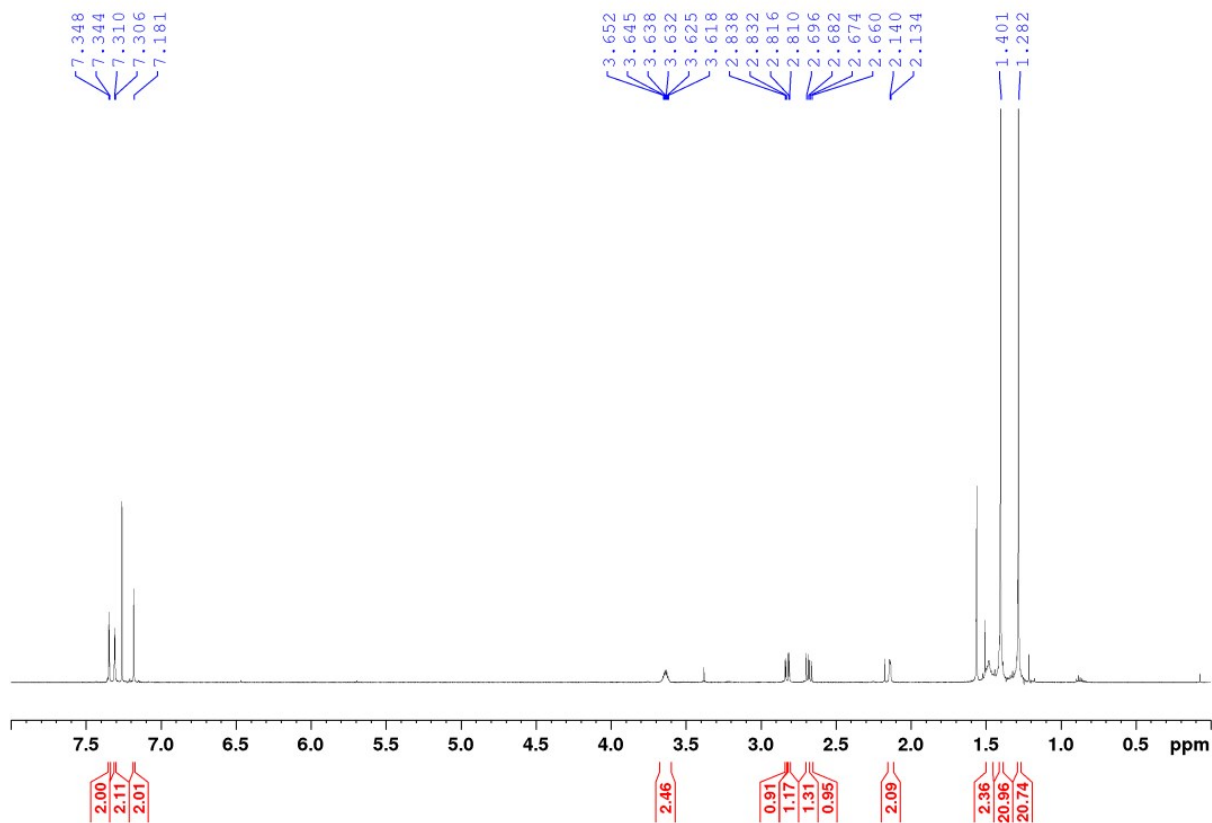


Figure S1. ^1H NMR of **b** (CDCl_3 , 600 MHz).

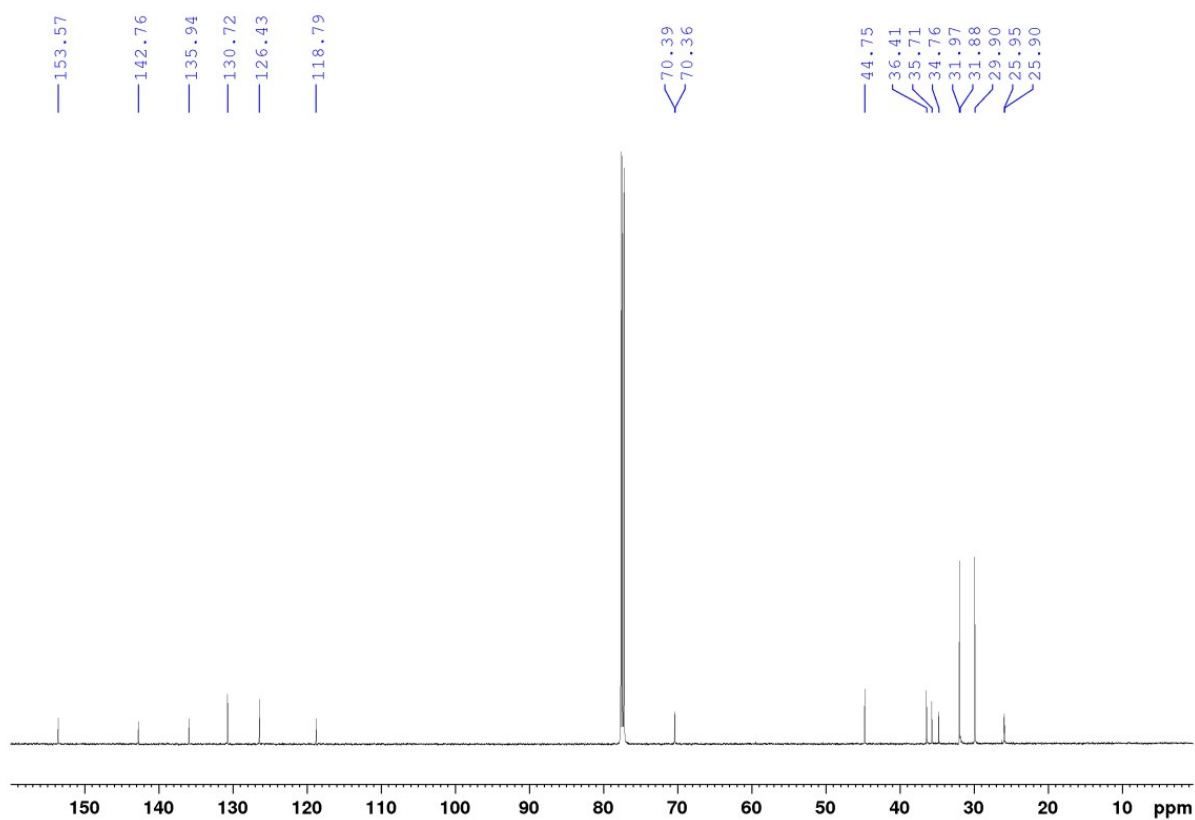


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR of **b** (CDCl_3 , 125 MHz).

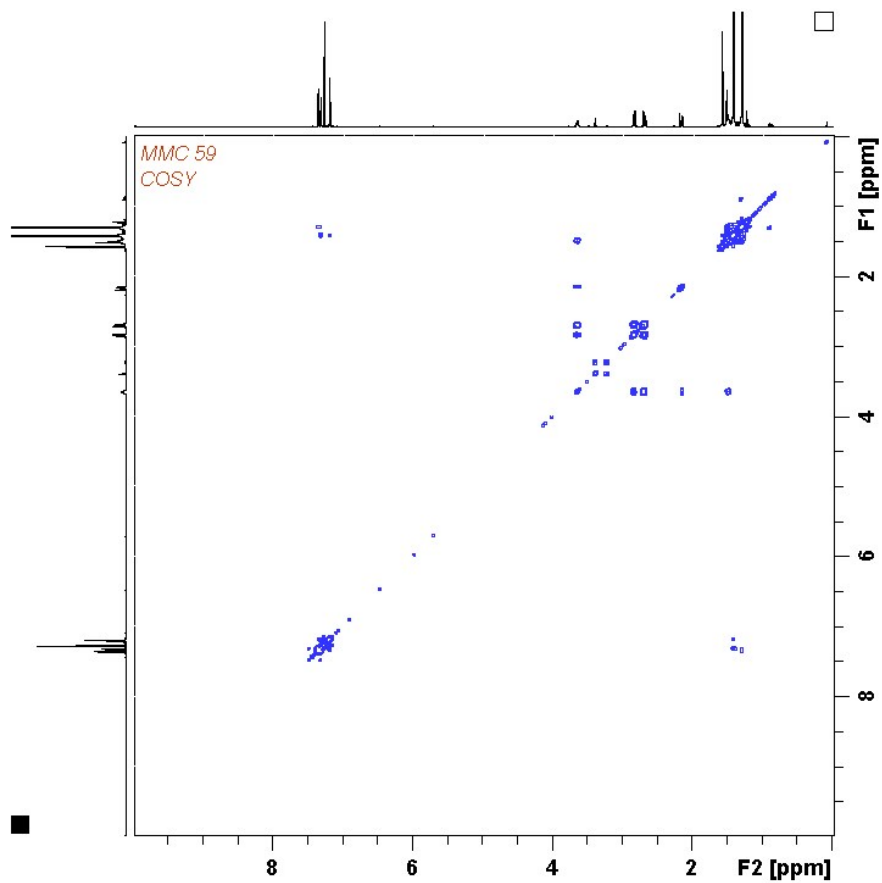


Figure S3. COSY NMR of **b** (CDCl_3 , 600 MHz).

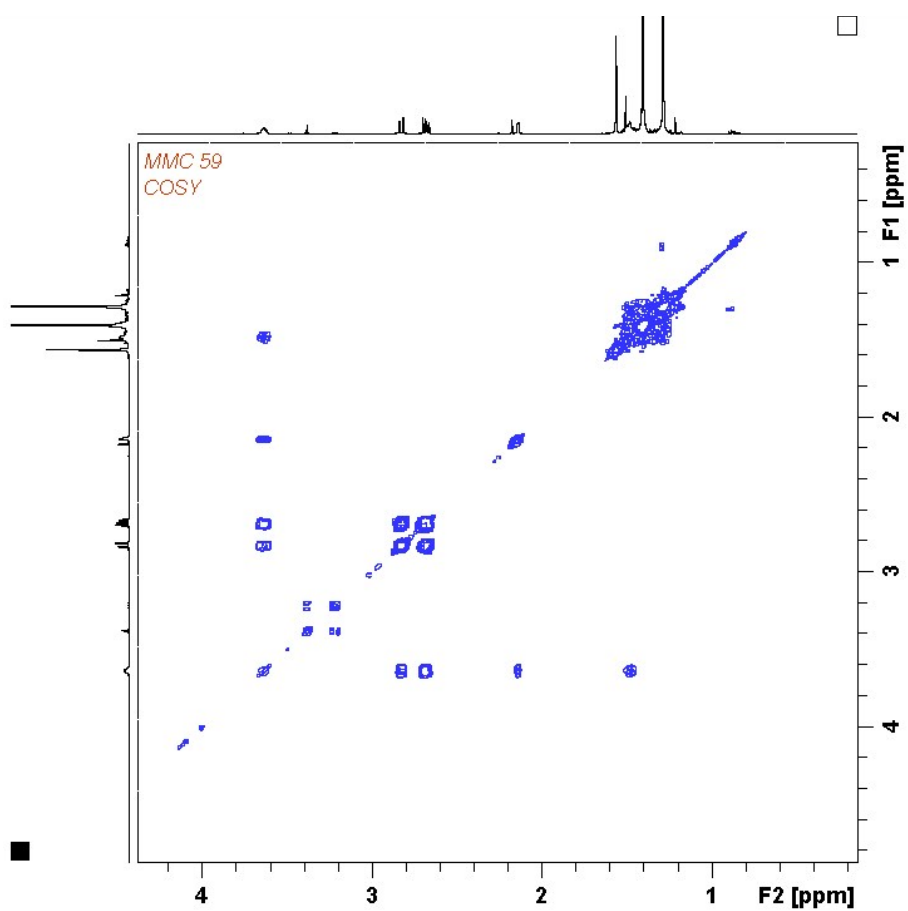


Figure S4 Enlargement of COSY NMR of **b** (CDCl_3 , 600 MHz).

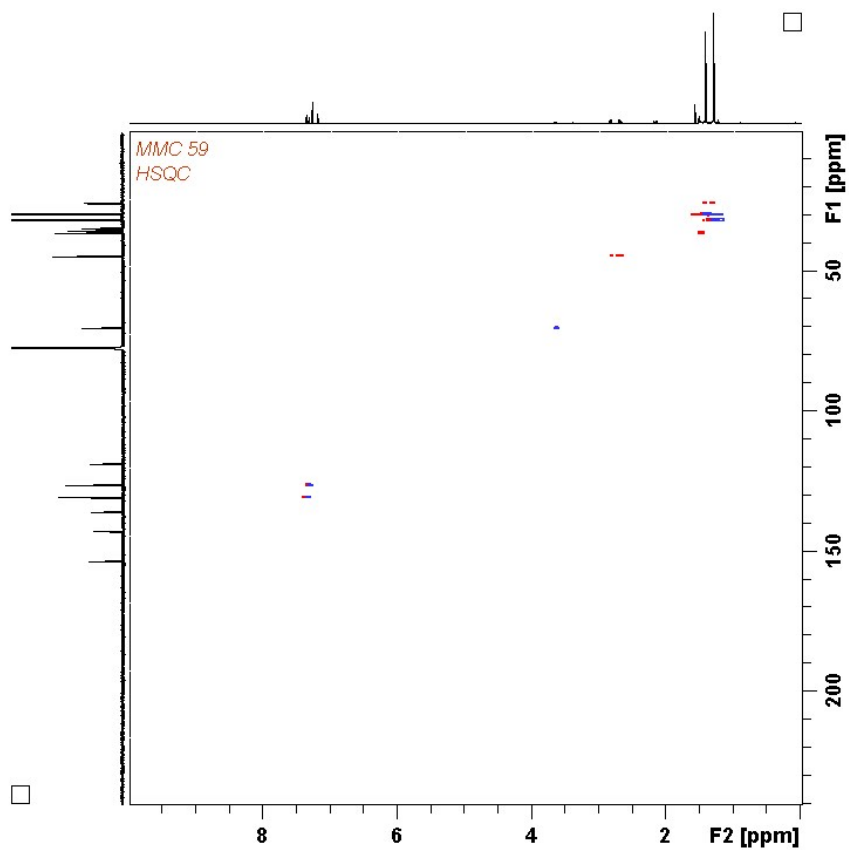


Figure S5. HSQC NMR of **b** (CDCl_3 , 600 MHz).

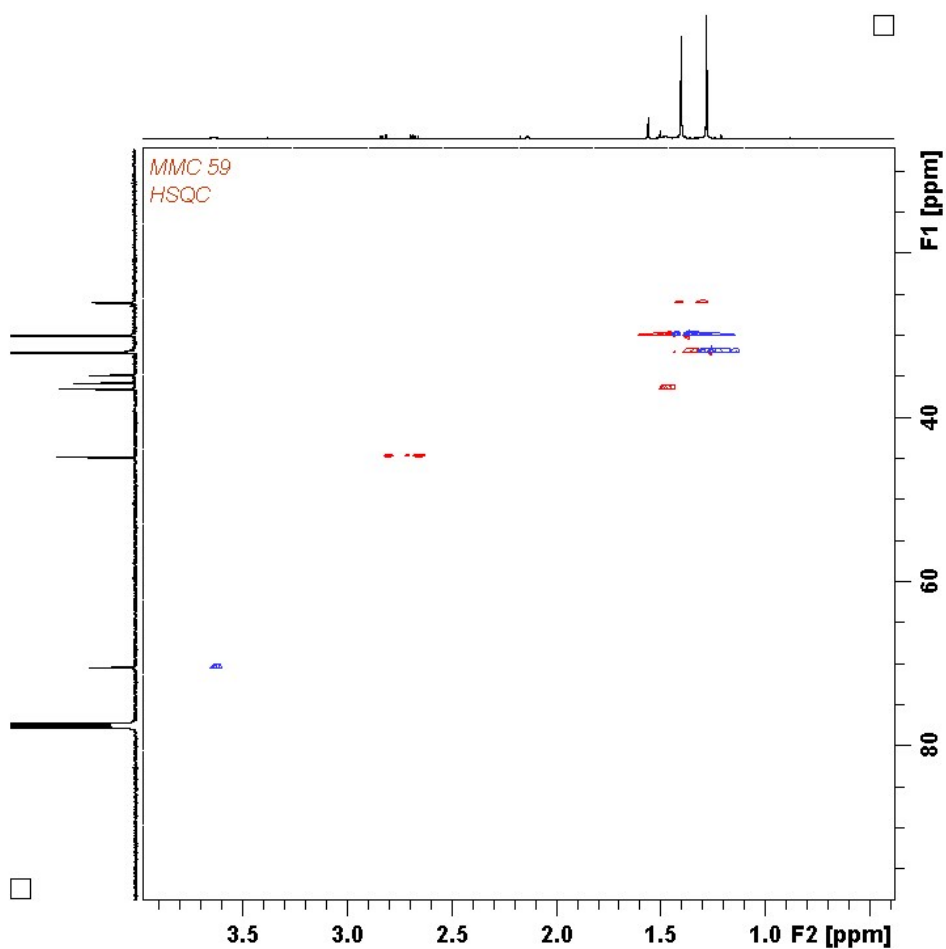


Figure S6. Enlargement of HSQC NMR of **b** (CDCl_3 , 600 MHz).

Synthesis and characterization of **c**

Compound **b** (8.1 mmol) was dissolved in 30 mL of dichloromethane and left in a cooling bath (-30 °C) for 20 minutes. Then, 16.1 mmol of thionyl chloride were added. After 10 min, the reaction mixture was refluxed overnight. The obtained mixture was concentrated, dissolved in 100 mL of diethyl ether and extracted with a solution of NaHCO₃ (w/w). The organic phase was dried with Na₂SO₄, filtered and concentrated. The product was obtained as a transparent oil after purification via column chromatography (eluent petroleum ether : diethyl acetate 9:1). Yield 53%.

¹H NMR (CD₂Cl₂, 400 MHz): δ 7.37 (o m, 4H); 7.08 (o m, 2H); 3.88 (br s, 1H), 3.61 (o m, 1H); 3.51 (o m, 1H); 2.98 (o m, 3H); 1.93 (o m, 2H); 1.72 (o m, 2H); 1.41 (s, 20H); 1.28 (s, 20H).

¹³C {¹H} NMR (CDCl₃, 100 MHz): δ 153.8; 153.2; 142.6; 142.5; 135.6; 131.1; 130.3; 126.7; 126.4; 117.9; 116.1; 61.3; 51.7; 47.2; 44.7; 36.7; 35.4; 34.5; 31.7; 31.3; 29.6; 26.2; 25.8.

Elemental analysis (%): Found (calcd) C 66.10; H 8.45; Cl 10.99; O 4.65; S 9.81 (C 65.93; H 8.61; Cl 10.81; O 4.88; S 9.78)

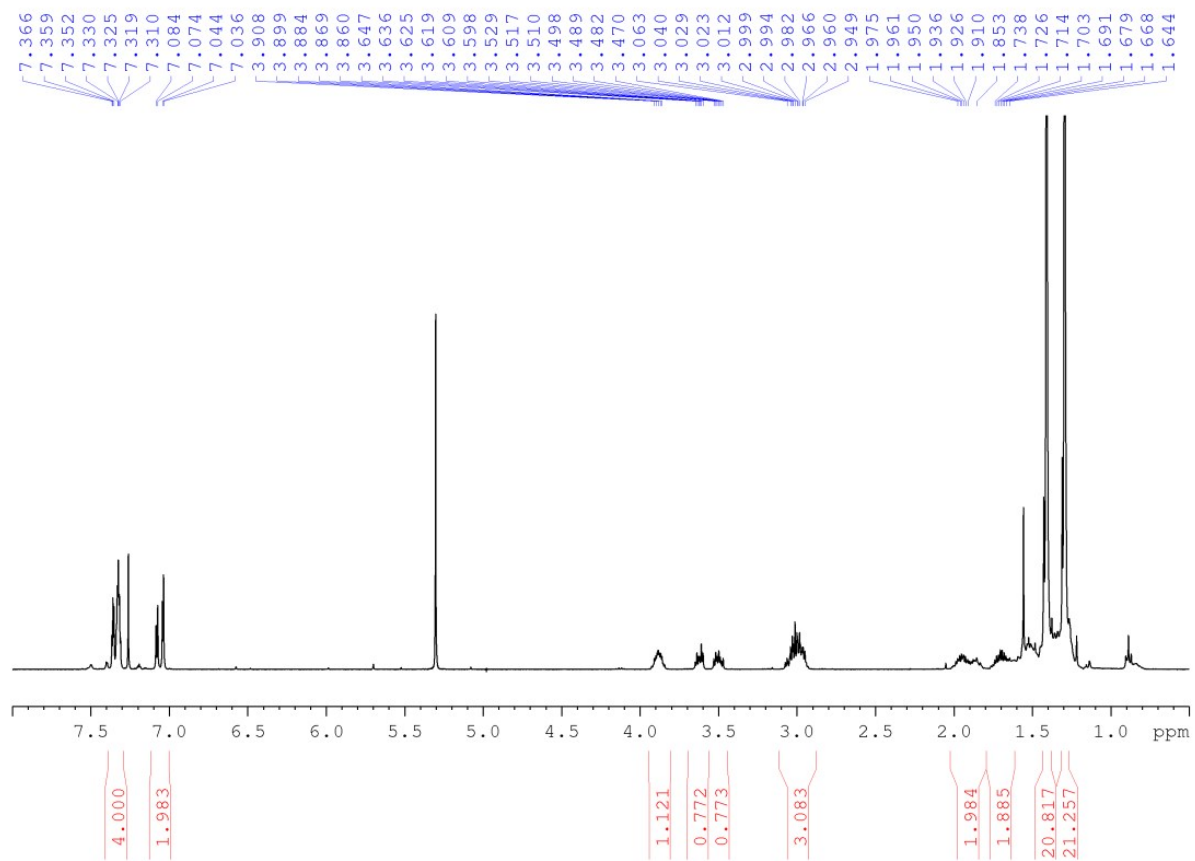


Figure S7. ^1H NMR of **c** (CD_2Cl_2 , 400 MHz).

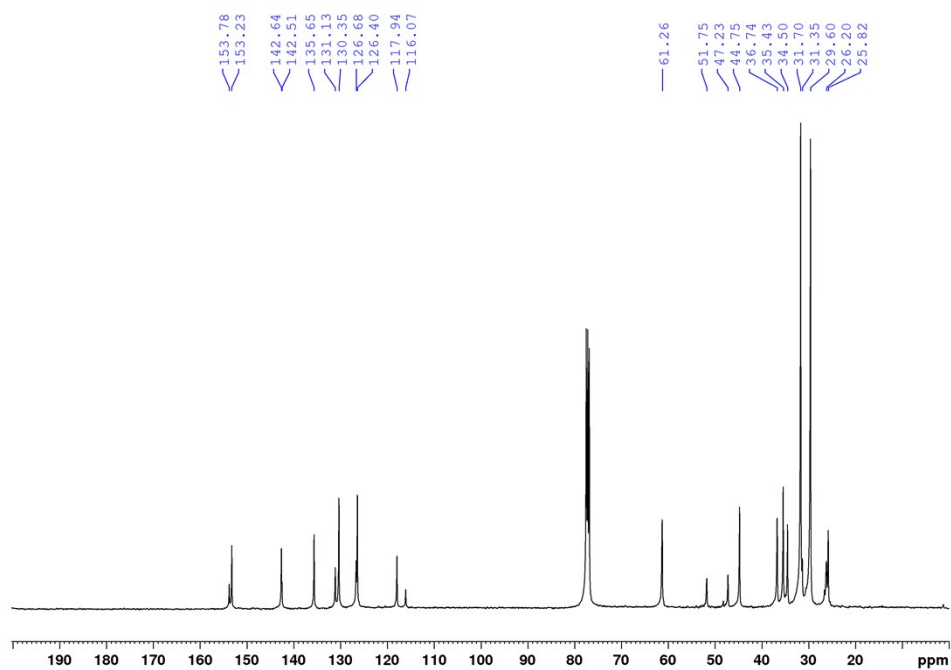


Figure S8. ^{13}C NMR of **c** (CD_2Cl_2 , 400 MHz).

Synthesis and characterization of **pro-L**

A flask equipped with a condenser and magnetic stirrer was charged with 5.13 mmol of 2,4-di-tert-butyl-6-mercaptophenol **a**, 5.13 mmol of NaOH and 10 mL of methanol. The mixture was refluxed at 70°C until complete dissolution of the reagents. After 20 min at 25 °C, 2.56 mmol of **c** were added and the mixture was refluxed overnight. The solid produced was dissolved in 50 mL of diethyl ether and extracted with 50 mL of water. The organic phase was dried with Na₂SO₄, filtered and concentrated. The product was precipitated as a white solid from methanol. Yield 66%.

¹H NMR (CD₂Cl₂, 400 MHz): δ 7.30 (o m, 8H); 7.21 (br s, 2H); 7.01 (br s, 2H); 2.78 (br s, 6H), 1.57 (o m, 1H); 1.58 (o m, 2H); 1.39 (s, 41H); 1.24 (s, 36H).

¹³C {¹H} NMR (CDCl₃, 100 MHz): δ 154.1; 153.3; 142.7; 142.5; 135.5; 131.1; 130.4; 126.6; 126.3; 118.7; 116.4; 50.7; 42.3; 35.5; 34.6; 33.2; 31.5; 30.1; 29.6.

m/z = 1097.613 (MK⁺)

Elemental analysis (%): Found (calcd) C 72.22; H 9.44; O 6.10; S 12.24 (C 72.54; H 9.32; O 6.04; S 12.10)

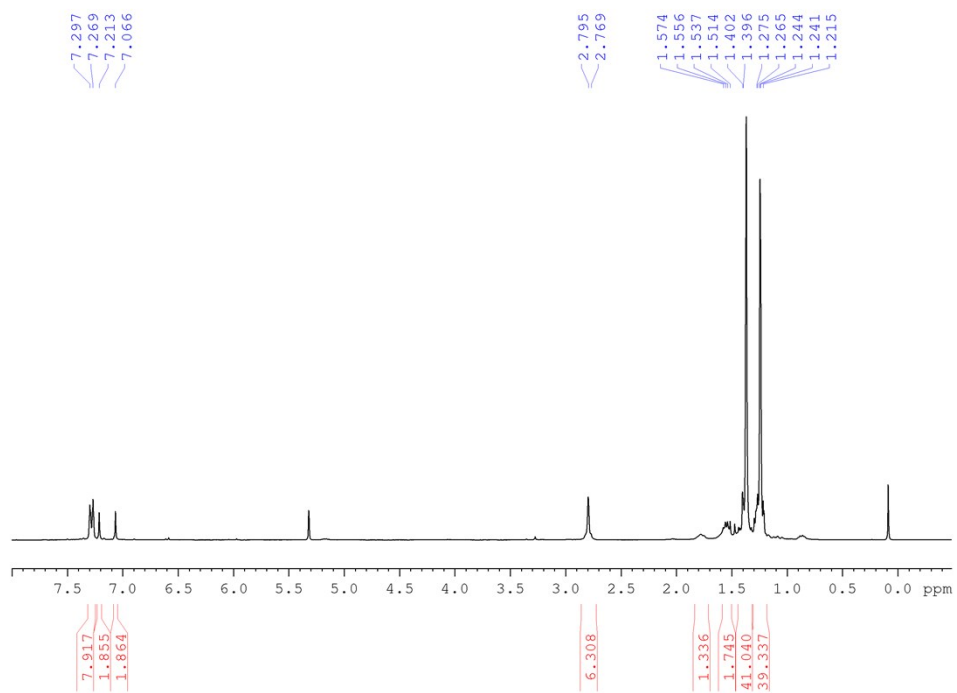


Figure S9. ^1H NMR of pro-L (CDCl_3 , 600 MHz).

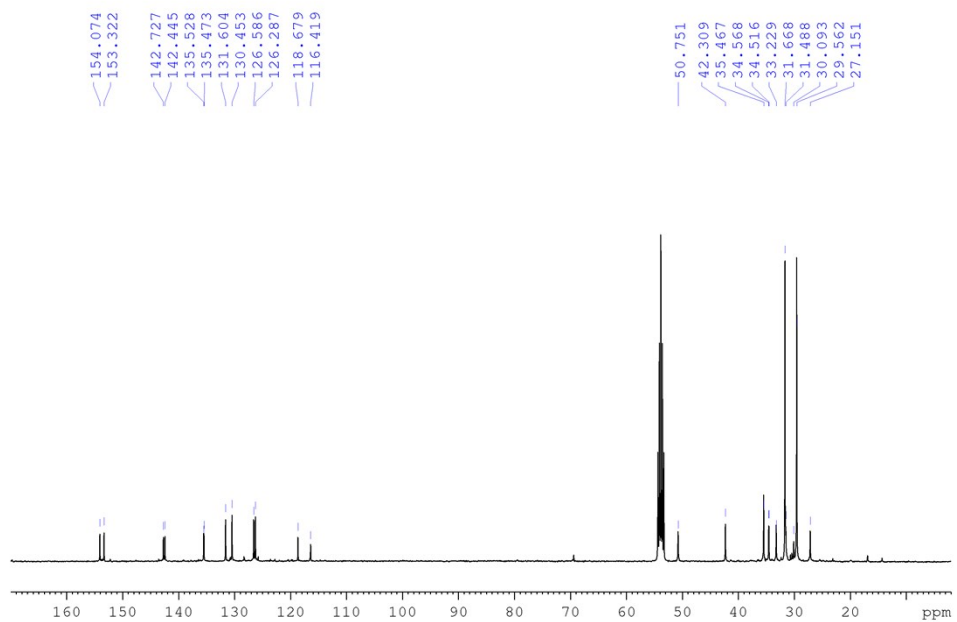
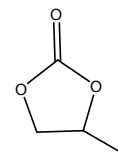


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR of pro-L (CD_2Cl_2 , 125 MHz).

List of ^1H MNR data for the Cyclic Organic Carbonate products

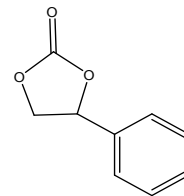
4-methyl-1,3-dioxolan-2-one (CDCl₃, 300 MHz)

4.99-4.82 (m, 1H, ring CHCH₃), 4.53 (t, 1H, J = 8.3 Hz, ring CHH), 4.00 (t, 1H, J = 8.3 Hz, ring CHH), 1.46 (d, 3H, J = 6.3 Hz, CH₃).



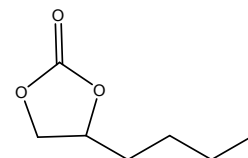
4-phenyl-1,3-dioxolan-2-one (CDCl₃, 400 MHz)

7.45-7.41 (m, 2H, Ar-H), 7.38-7.32 (m, 2H, Ar-H), 5.52 (t, 1H, J = 8.0 Hz, ring CHPh), 4.64 (t, 1H, J = 8.36 Hz, CHH), 4.19 (t, 1H, J = 8.37 Hz, CHH)



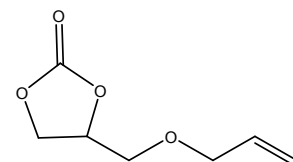
4-butyl-1,3-dioxolan-2-one (CDCl₃, 300MHz)

4.73-4.64 (m, 1H, ring CHCH₃), 4.51 (t, 1H, J = 8.1 Hz, ring CHH), 4.06 (t, J = 8.2 Hz, ring CHH), 1.85-1.77 (m, 1H, CHCH₂CH₂), 1.74-1.67 (m, 1H, CHCH₂CH₂), 1.53-1.33 (m, 4H, CH₂CH₂CH₂ and CH₂CH₂CH₃), 0.91 (t, 3H, ^3J = 6.9 Hz, CH₃)



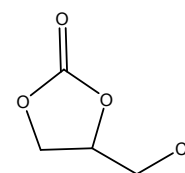
Allyloxymethyl-1,3-dioxolan-2-one (CDCl₃, 400MHz)

5.84-5.74 (m, 1H, CH=CH₂), 5.23 (dd, 1H, (E)-CH=CHH, J = 17.33 Hz, J = 1.4 Hz), 5.17 (dd, 1H, (Z)-CH=CHH, J = 10.4 Hz, J = 1.4 Hz), 4.82-4.75 (m, 1H, ring CHCH₂), 4.47 (t, 1H, ring CHCH₂, 8.3 Hz), 4.35 (dd, 1H, ring CHCH₂, J = 8.3 Hz, J = 6.1 Hz), 4.02 (d, 1H, ring CHCH₂, J = 5.3 Hz), 3.65-3.59 (m, 2H, CH₂-CH=CH₂).



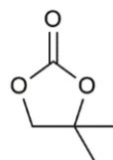
4-chloromethyl-1,3-dioxolan-2-one (CDCl₃, 300 MHz)

5.02-4.96 (m, 1H, ring CHCH₂Cl), 4.57 (dd, 1H, J = 8.8 Hz, J = 8.1 Hz, ring CHH), 4.40 (dd, 1H, J = 8.8 Hz, J = 5.8 Hz, ring CHH), 3.76 (m, 2H, CH₂Cl)



4,4'-dimethyl-1,3-dioxolan-2-one (CDCl₃, 300MHz)

4.15 (s, 2H, ring CH₂C(CH₃)₂), 1.53 (s, 6H, CH₃)



Synthesis and characterization of dinuclear complexes **2-Br** and **2-Cl**

Pro-L (0.52 mmol) was dissolved in 20 mL of THF. The solution was added to a suspension of sodium hydride (2.62 mmol) in 10 mL of THF and the mixture was stirred at 25 °C overnight. The resulting suspension was filtered through celite and slowly added to 1.02 mmol of the iron precursor (anhydrous iron(III) bromide or chloride) dissolved in 50 mL of THF. The reaction was kept overnight at room temperature. The resulting mixture was filtered through celite and concentrated affording the product as a dark blue crystalline solid. Quantitative yield.

2-Br = (C₆₄H₉₄Br₂Fe₂O₄S₄) (M-THF₂+Na)⁺ = 1347.2998 calcd, 1347.001 found; (C₆₄H₉₄Br₂Fe₂O₄S₄) (M-THF₂+K)⁺ 1363.2732 calcd. 1363.2741 found.

Elemental analysis (%): Found (calcd) C, 58.44; H, 7.67; Br, 11.01; Fe, 7.38; O, 6.71; S, 8.79 (C, 58.77; H, 7.54; Br, 10.86; Fe, 7.59; O, 6.52; S, 8.72)

2-Cl = (C₆₄H₉₄Cl₂Fe₂O₄S₄) (M-THF₂+Na)⁺ = 1259.4008 calcd, 1259.4054 found; (C₆₄H₉₄Cl₂Fe₂O₄S₄) (M-THF₂+K)⁺ 1275.3748 calcd. 1275.3803 found.

Elemental analysis (%): Found (calcd) C, 62.41; H, 8.23; Cl, 5.27; Fe, 8.22; O, 6.75; S, 9.12 (C, 62.55; H, 8.02; Cl, 5.13; Fe, 8.08; O, 6.94; S, 9.28)

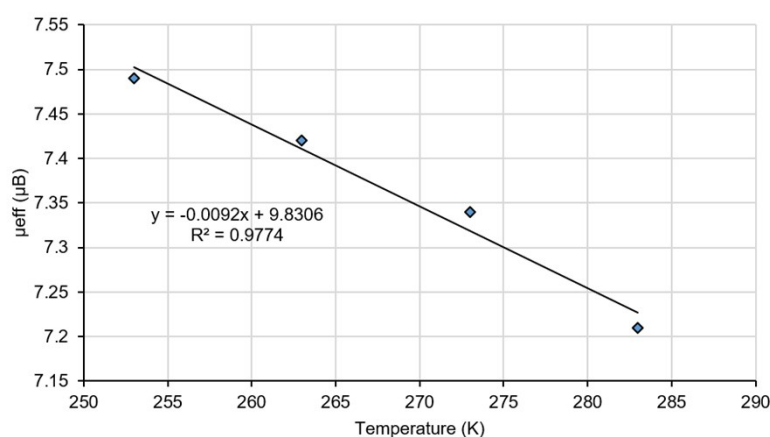


Figure S11. Effective magnetic moment μ_{eff} of complex **2-Br** versus temperature.

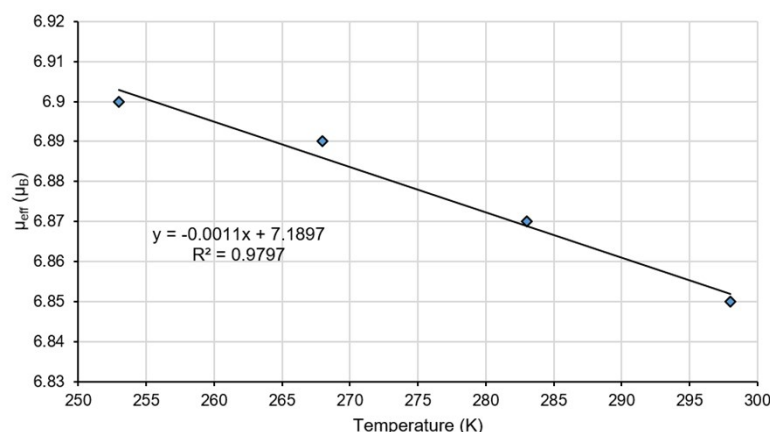


Figure S12. Effective magnetic moment μ_{eff} of complex **2-Cl** versus temperature.

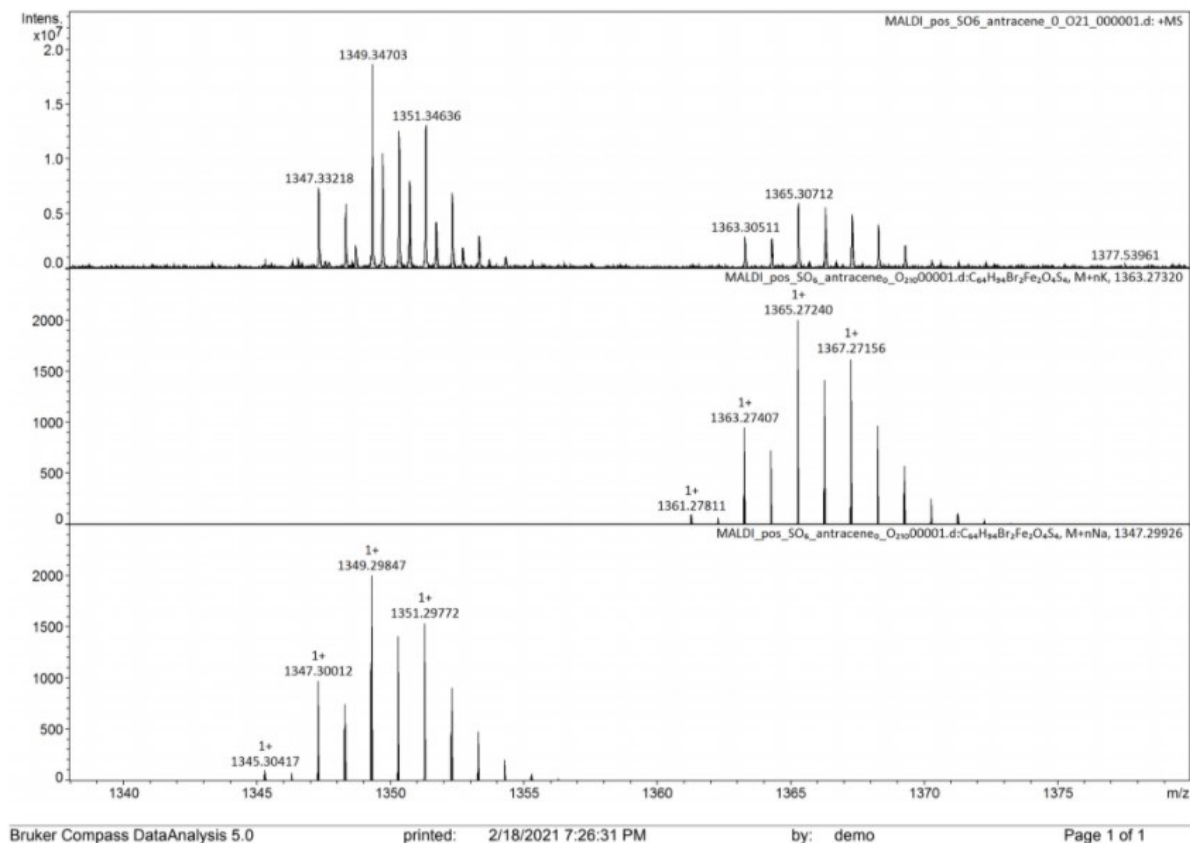


Figure S13. Mass Spectrum of complex **2-Br**: experimental (up), M-THF₂+K⁺calctd (middle), M-THF₂+Na⁺calctd (bottom).

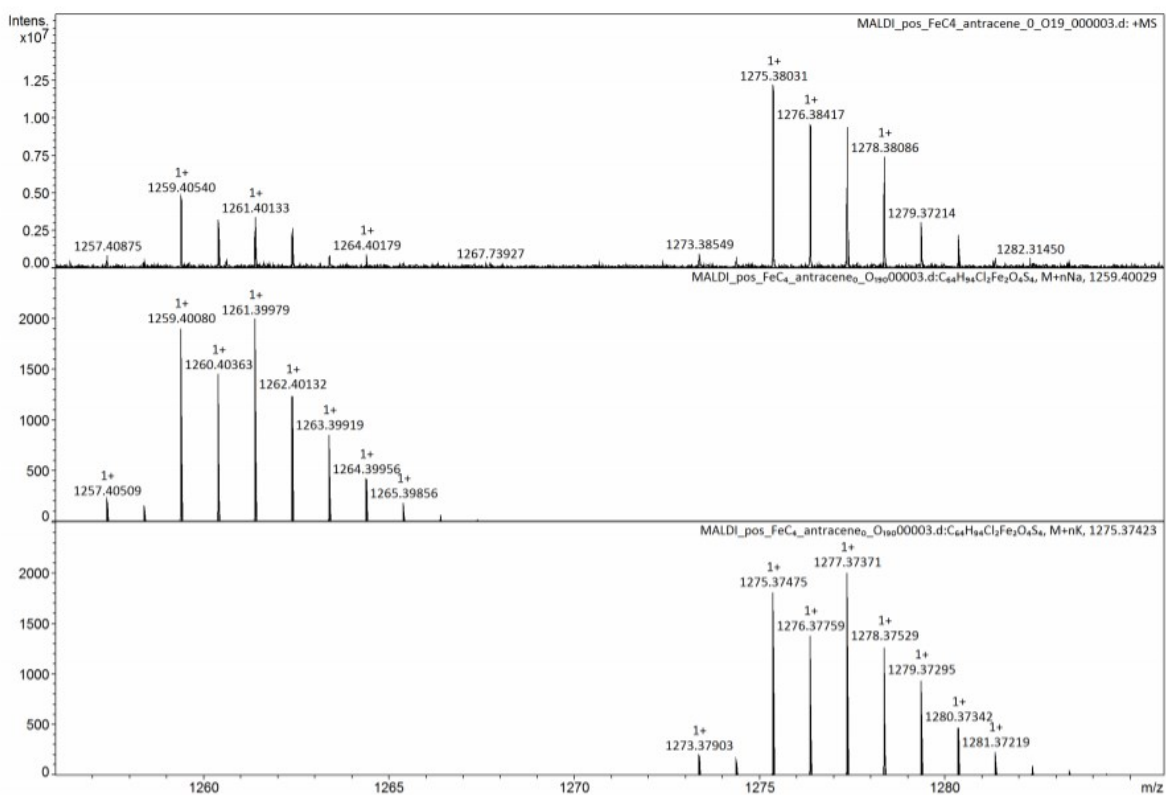


Figure S14. Mass Spectrum of complex **2-Cl**: experimental (up), M-THF₂+Na⁺calctd (middle), M-THF₂+K⁺calctd (bottom).

Typical Procedure for the coupling of CO₂ with epoxides

A 60 mL stainless steel autoclave, equipped with a magnetic stirrer, was purged with CO₂. After that, the catalyst and the cocatalyst, dissolved in the epoxide, were added. The reactor was charged with an appropriate pressure of CO₂, heated at the appropriate temperature and stirred. After that, the reactor was cooled with ice, depressurised and mesitylene (10%mol with respect to the epoxide) was added as the internal standard. The crude reaction mixture was analyzed by ¹H NMR spectroscopy using CDCl₃ as solvent.

Additional experimental data

Table S1. Effect of the nature of the nucleophile source in the presence of complex **2-Br**.

Entry ^[a]	cocat. ^[b]	Conversion (%) ^[c]	TOF (h ⁻¹) ^[d]
1	TBAC	-	-
2	TBAI	25	500
3	TBAN ₃	-	-

[a] Reaction conditions: PO (0.028 mol, 2 mL), PCO₂ (10 bar), temperature (35°C), [cocat]/[Fe] (2), loading cat. (0.05 %mol), time (1h), neat. [b] Nucleophile sources abbreviated as follows: TBAC (tetrabutylammonium chloride), TBAI (tetrabutylammonium iodide), TBAN₃ (tetrabutylammonium azide). [c] Determined by ¹H NMR using mesitylene as the internal standard. Selectivity towards the **COC** was always > 99%. For selected experiments, consistency of these results was proven by comparing with the PC isolated yields. [d] TOF = mol PO conv. • (mol **2-Br** • time)⁻¹.

Table S2. Couplings promoted by **TBAB/ 2-Br**

Entry ^[a]	Epoxide ^[b]	time (h)	Conversion (%) ^[c]	TOF (h ⁻¹) ^[d]
1	HO	6	51	170
2	HO	24	80	66
3	SO	6	38	126
4	SO	24	80	66
5	CHO	1	0	0
6	CHO	6	16	54
7	CHO	24	32	26
8 ^[e]	EPC	1	13	65
9 ^[e]	EPC	24	100	21
10	EPC	6	50	83
11 ^[e]	AGE	6	92	144
12	AGE	6	80	266
13	AGE	24	82	68
14 ^[e]	IBO	1	40	66
15 ^[e]	IBO	24	66	28
16	1,2-EPD	24	20	66

[a] Reaction conditions: epoxide (0.028 mol, 2 mL), PCO₂ (10 bar), temperature (70°C), [cocat]/[Fe] (2), loading cat. (0.05 %mol), neat. [b] Epoxides abbreviated as follows: HO (hexene oxide), SO (styrene oxide), CHO (cyclohexene oxide), EPC (epichlorohydrine), AGE (allyl glycidyl ether), IBO (isobutylene oxide), 1,2-EPD (1,2-epoxidodecane). [c] Determined by ¹H NMR using mesitylene as the internal standard. [d] TOF = mol epoxide conv. • (mol 2-Br • time)⁻¹. [e] loading cat. (0.1 %mol).

Kinetic experiments for PC formation promoted by **TBAB/2-Br**

General procedure for PO/CO₂ coupling with in situ ATR-IR

TBAB/**2-Br** were dissolved in a solution of propylene oxide in methylene chloride. The reaction mixture was put in the preheated autoclave and immediately pressurized with CO₂. The experiment was stopped when a constant intensity for the signal of the carbonyl oxygen (1802 cm⁻¹) was observed (Figure 29-32). Value of initial velocities v_0 were obtained from the slope of the initial straight line at low conversion of the epoxide.

Determination of the reaction order respect to **2-Br**

Table S3. Determination of the reaction order respect to **2-Br**

Entry	PO/TBAB/ 2-Br	[2-Br] (mM)	v_0 (L/s) · 10 ⁻⁴
1	250/1/1	14.3	8.1
2	500/2/1	7.2	5.1
3	1000/4/1	3.6	3.2
4	1500/6/1	2.4	1.7

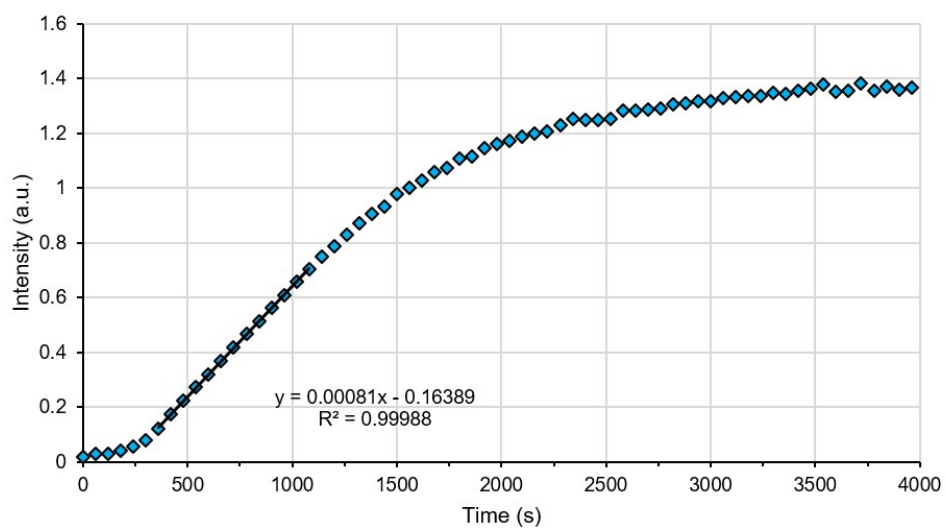
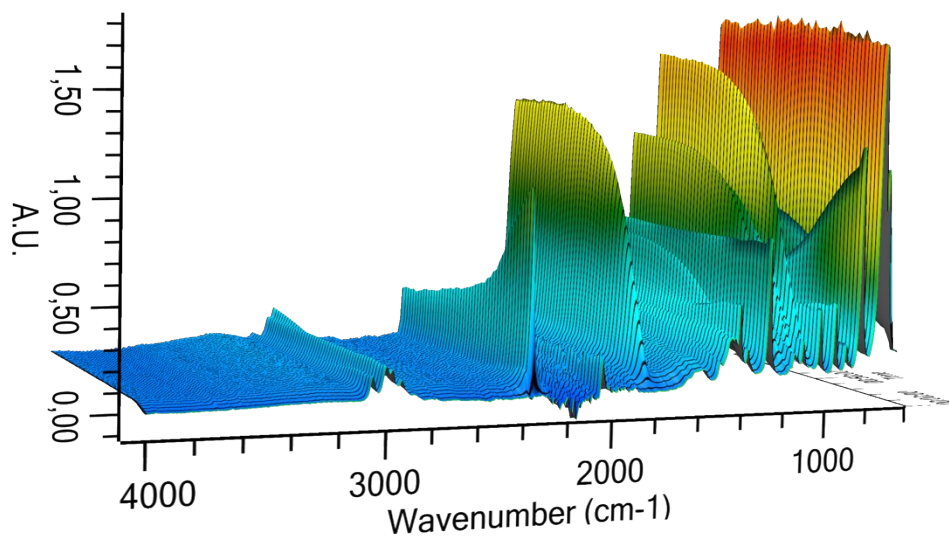


Figure S15. Coupling of Table S3 entry 1: Variation of the intensity of the PC C=O stretching band vs time (top), growth trace (bottom). Reaction conditions: [PO] (7.14 M in methylene chloride), PCO₂ (10 bar), loading **2-Br** (0.2 mol%); TBAB (0.2 mol%); T = 50°C.

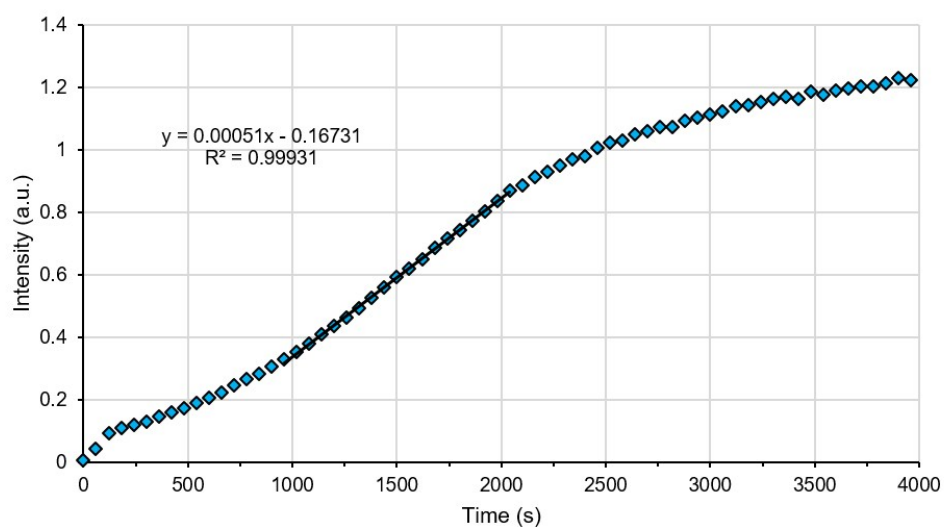
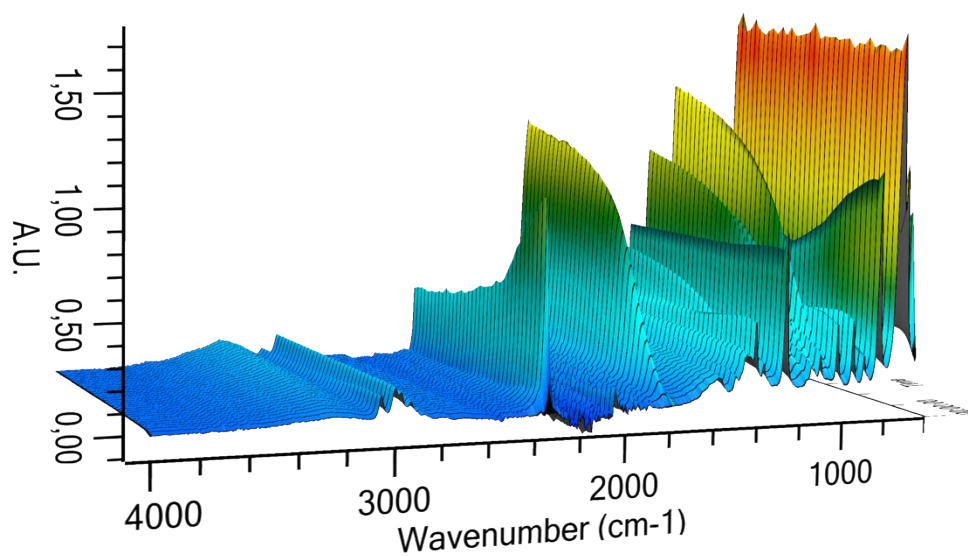


Figure S16. Coupling of Table S3 entry 2: Variation of the intensity of the PC C=O stretching band vs time (top), growth trace (bottom). Reaction conditions: [PO] (7.14 M in methylene chloride), PCO₂ (10 bar), loading **2-Br** (0.1 mol%); TBAB (0.2 mol%); T = 50°C.

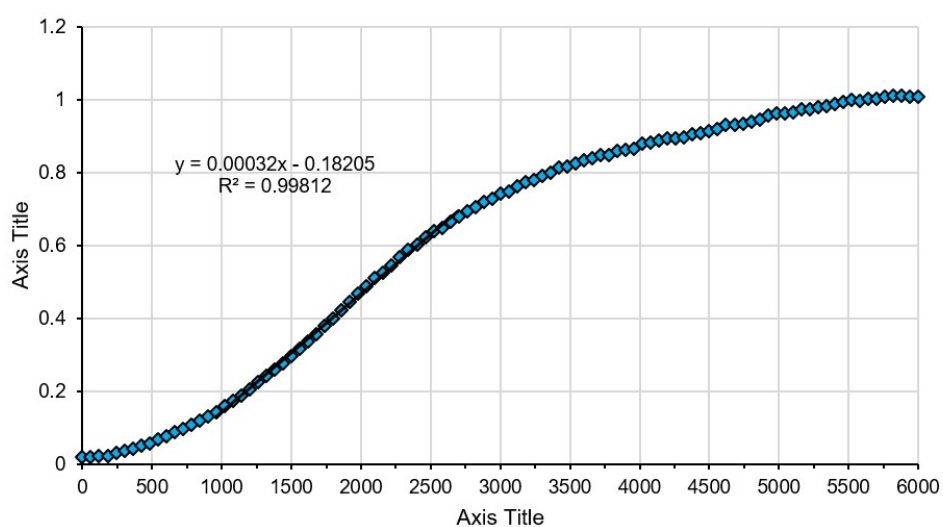
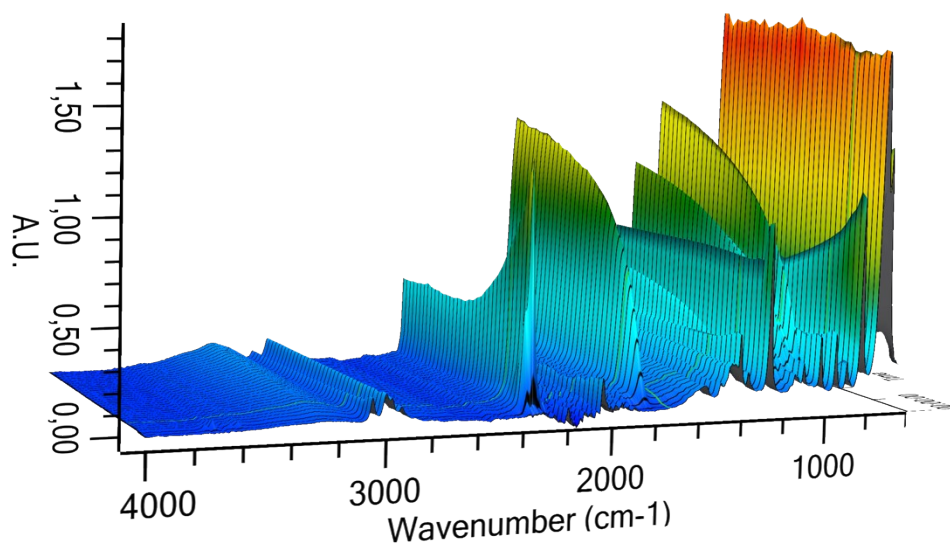


Figure S17. Coupling of Table S3 entry 3: Variation of the intensity of the PC C=O stretching band vs time (top), growth trace (bottom). Reaction conditions: [PO] (7.14 M in methylene chloride), PCO₂ (10 bar), loading **2-Br** (0.05 mol%); TBAB (0.2 mol%); T = 50°C.

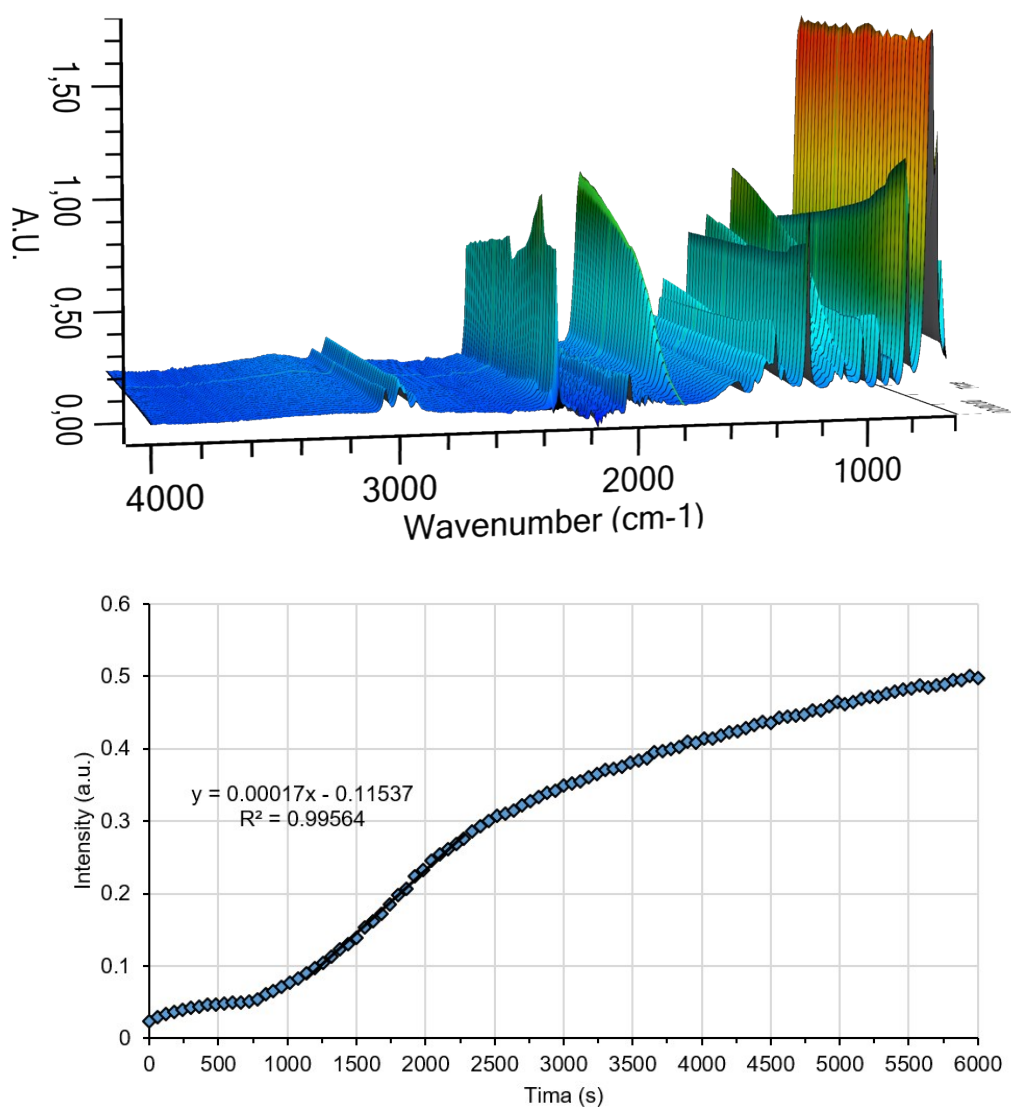


Figure S18. Coupling of Table S3 entry 3: Variation of the intensity of the PC C=O stretching band vs time (top), growth trace (bottom). Reaction conditions: [PO] (7.14 M in methylene chloride), PCO₂ (10 bar), loading **2-Br** (0.033 mol%); TBAB (0.2 mol%); T = 50°C.

GPC Analysis

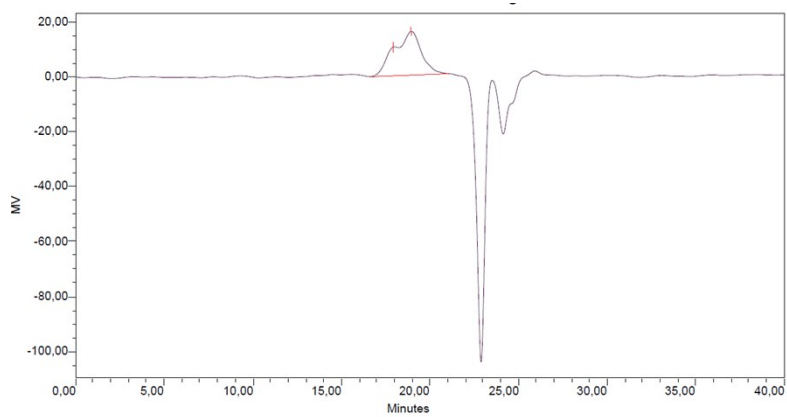


Figure S19. GPC curve from entry 6 of Table 2.

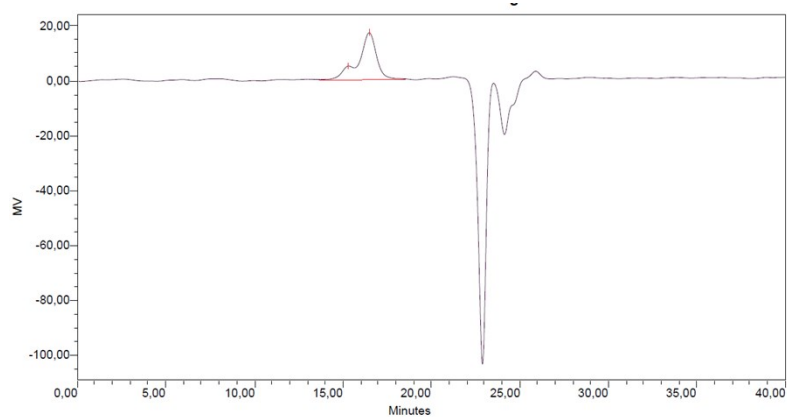


Figure S20. GPC curve from entry 7 of Table 2.

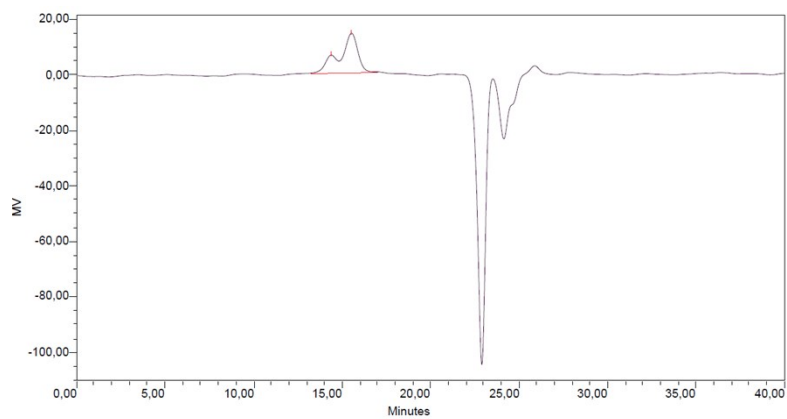


Figure S21. GPC curve from entry 8 of Table 2.