

## Supporting Information

### Copolymerization of Epoxides with Carbon Dioxide Catalyzed by Iron–corrole Complexes: Synthesis of a Crystalline Copolymer

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## General Methods.

NMR spectra were recorded in on a JEOL JNM-ECP500 ( $^1\text{H}$  500 MHz;  $^{13}\text{C}$  126 MHz) spectrometers or a JEOL-ECS400 spectrometer ( $^1\text{H}$  400 MHz;  $^{13}\text{C}$  101 MHz). Chemical shifts are reported in ppm from an internal standard: tetramethylsilane (0 ppm) for  $^1\text{H}$  and  $\text{CDCl}_3$  (77.16 ppm) for  $^{13}\text{C}$  in  $\text{CDCl}_3$ , THF- $d_7$  (3.58 ppm) for  $^1\text{H}$  and THF- $d_8$  (67.21 ppm) for  $^{13}\text{C}$  in THF- $d_8$ , and DMSO- $d_5$  (2.49 ppm) for  $^1\text{H}$  and DMSO- $d_6$  (39.50 ppm) for  $^{13}\text{C}$  in DMSO- $d_6$ . Data are presented in the following space: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. Size-exclusion-chromatography (SEC) analyses were carried with two columns (Shodex KF-804L) using tetrahydrofuran as an eluent at 40 °C at 1 mL/min for PO/ $\text{CO}_2$  and CHO/ $\text{CO}_2$  copolymers and PO homopolymers, and with two columns [Tosoh TSKgel HR-H(S)HT] using 1,2-dichlorobenzene as an eluent at 140 °C at 1 mL/min for GPE/ $\text{CO}_2$  copolymers. The molecular weight was calibrated against standard polystyrene samples. Glass-transition ( $T_g$ ), melting ( $T_m$ ), and crystallization ( $T_c$ ) temperatures were measured by DSC apparatus. Heating and cooling rates were 10 °C and -20 °C per minute, respectively. These temperatures were determined from the second heating and cooling scans. Thermal decomposition was analyzed by TG-DTA apparatus. Heating rates were 20 °C per minute. Thermal decomposition temperatures  $T_{d5}$  were defined as the temperature of 5%-weight loss, respectively.

All manipulations involving air- and/or moisture-sensitive compounds were carried out using the standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11 or in a glove box under argon atmosphere. All the solvents used for reactions were distilled under argon after drying over an appropriate drying reagent or passed through solvent purification columns (Glass Contour solvent purification system). Most of reagents were purchased from Aldrich Chemical Co. or Kanto Kagaku Co., Ltd., and were used without further purification unless otherwise specified. Propylene oxide and cyclohexene oxide were distilled under argon after drying over calcium hydride. 5,10,15-Tris(pentafluorophenyl)corrole,<sup>1</sup> 5,10,15-triphenylcorrole,<sup>2</sup> and iron-corrole complexes (**1a**,<sup>3</sup> **2**,<sup>3</sup> **3**,<sup>3</sup> and **1b**<sup>4</sup>) were prepared according to the procedure described in the literature. Although the obtained complexes included some inseparable impurity such as hydrocarbon, they are used for the copolymerization without further purification.

## Synthetic Procedures

### Synthesis of Iron–corrole Complex 1a

A flame-dried 20-mL Schlenk tube containing a magnetic stirring bar was charged with 5,10,15-tris(pentafluorophenyl)corrole (80 mg, 0.10 mmol), FeCl<sub>2</sub> (254 mg, 2.0 mmol), and DMF (8 mL) under argon. After stirred at 140 °C for 3 h in the dark, the solvent was pumped off. The resulting residue was dissolved in diethyl ether, and passed through a short pad of silica gel. After, the solvent was evaporated, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and washed with 1 M aqueous NaOH (15 mL × 3). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the title compound a dark brown (124 mg). NMR data are identical to those in the literature.<sup>3</sup> Anal. Calcd for C<sub>74</sub>H<sub>16</sub>F<sub>30</sub>Fe<sub>2</sub>N<sub>8</sub>O (%): C, 51.84; H, 0.94; N, 6.54. Found (%): C, 51.01; H, 1.59; N, 6.27.

### Synthesis of Iron–corrole Complex 1b

The title compound was obtained as a green solid (21 mg) by using 5,10,15-triphenylcorrole (53 mg, 0.10 mmol), FeCl<sub>2</sub> (253 mg, 2.0 mmol) and DME (10 mL) according to the procedure for **1a**. NMR data are identical to those in the literature.<sup>4</sup> Anal. Calcd for C<sub>74</sub>H<sub>46</sub>Fe<sub>2</sub>N<sub>8</sub>O (%): C, 75.65; H, 3.95; N, 9.54. Found (%): C, 74.98; H, 4.50; N, 8.73.

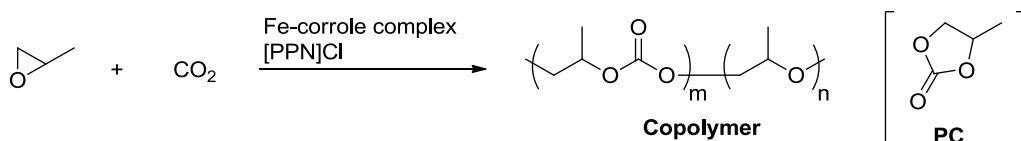
### Synthesis of Iron–corrole Complex 2

A flame-dried 20-mL Schlenk tube containing a magnetic stirring bar was charged with 5,10,15-tris(pentafluorophenyl)corrole (80 mg, 0.10 mmol), FeCl<sub>2</sub> (254 mg, 2.0 mmol), and DMF (8 mL) under argon. After stirred at 140 °C for 1.5 h in the dark, the solvent was pumped off. The resulting residue was dissolved in diethyl ether, and passed through a short pad of silica gel. After, the solvent was evaporated, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and washed with 7% aqueous HCl (15 mL × 3). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the title compound as a dark brown solid (72 mg). NMR data are identical to those in the literature.<sup>3</sup> Anal. Calcd for C<sub>37</sub>H<sub>8</sub>ClF<sub>15</sub>FeN<sub>4</sub> (%): C, 50.23; H, 0.91; N, 6.33. Found (%): C, 50.57; H, 1.56; N, 5.85.

### Synthesis of Iron–corrole Complex 3

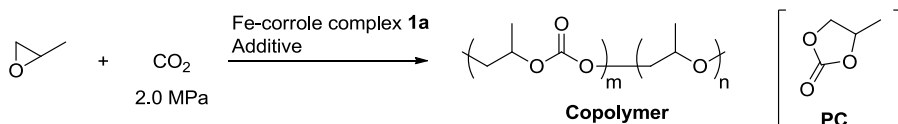
A 100-mL J Young tube containing a magnetic stirring bar was charged with 5,10,15-tris(pentafluorophenyl)corrole (120 mg, 0.15 mmol), FeCl<sub>2</sub> (380 mg, 3.0 mmol), and DMF (45 mL) under argon. After stirred at 130 °C for 1.5 h in the dark, the solvent was pumped off. The resulting residue was dissolved in diethyl ether, and passed through a short pad of silica gel in a glove box twice. The filtrate was filtered through DISMIC<sup>®</sup>-13HP syringe filter (0.2 μm) and concentrated under reduced pressure to give the title compound (67 mg). NMR data are identical to those in the literature.<sup>3</sup> Anal. Calcd for C<sub>45</sub>H<sub>28</sub>F<sub>15</sub>FeN<sub>4</sub>O<sub>2</sub> (%): C, 54.18; H, 2.83; N, 5.62. Found (%): C, 54.25; H, 2.55; N, 5.47.

## Representative Procedure for the Copolymerization of Propylene Oxide (PO) with Carbon Dioxide.



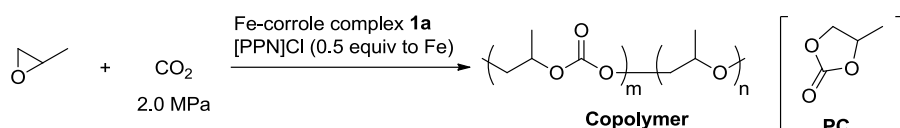
A 50-mL autoclave containing a magnetic stirring bar was charged with propylene oxide (1.0 mL, 14 mmol), complex **1a** [ $3.5\sim 3.6 \times 10^{-3}$  mmol ( $7.0\sim 7.2 \times 10^{-3}$  mmol of Fe)] and [PPN]Cl (desired amount) under argon. After CO<sub>2</sub> was introduced, the reaction mixture was stirred at a desired temperature for 1 h. The autoclave was cooled to 0 °C, and the CO<sub>2</sub> was released. The polymerization mixture was diluted with CDCl<sub>3</sub>, and phenanthrene was added as an internal standard. Analyses of the small aliquot of the mixture by <sup>1</sup>H NMR spectroscopy gave the yield of copolymer and propylene carbonate, and the carbonate linkage content. To the rest of the polymerization mixture was added CH<sub>2</sub>Cl<sub>2</sub>, and two drops of 1 M aqueous HCl/MeOH (1/1) solution. The resulting mixture was stirred and concentrated under reduced pressure. The resulting residue was analyzed by SEC to determine molecular weight and molecular-weight distribution.

**Table S1.** Effect of Additives in the PO/CO<sub>2</sub> Copolymerization Catalyzed by Complex **1a**<sup>[a]</sup>



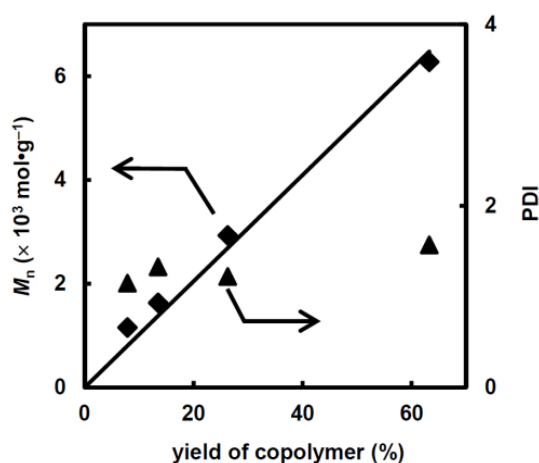
Additive (equiv. to Fe)	Y of copolymer + PC [%] <sup>[b]</sup>	copolymer/PC <sup>[b]</sup>	TOF for copolymer <sup>[c]</sup>	carbonate linkage [%] <sup>[b]</sup>	$M_n$ [g·mol <sup>-1</sup> ] <sup>[d]</sup>	$M_w/M_n$ <sup>[d]</sup>
[PPN]Cl (0.5) <sup>[e]</sup>	51	>99/<1	1004	17	29000	1.26
[PPN]N <sub>3</sub> (0.5)	27	>99/<1	542	19	15000	1.44
[PPN][OCOC <sub>6</sub> F <sub>5</sub> ] (0.5)	19	>99/<1	383	20	13000	1.17
[PPN]X (0.5) <sup>[f]</sup>	34	>99/<1	682	18	29000	1.22
[Bu <sub>4</sub> N][NO <sub>3</sub> ] (0.5)	8	>99/<1	167	22	9900	1.20
[Bu <sub>4</sub> N]Cl (0.5)	2	>99/<1	44	23	---	---
DMAP (0.6)	12	>99/<1	241	20	10000	1.32

[a] PO (1.0 mL, 14.3 mmol), CO<sub>2</sub> (2.0 MPa), complex **1a** [ $3.5\sim 3.6 \times 10^{-3}$  mmol ( $7.0\sim 7.2 \times 10^{-3}$  mmol of Fe)] in a 50-mL autoclave at 60 °C for 1 h (2 h when using DMAP). [b] Determined on the basis of <sup>1</sup>H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] TOF = [(mol of carbonate repeating unit) + (mol of ether repeating unit)]·(mol of Fe center)<sup>-1</sup>·h<sup>-1</sup>. [d] Determined by size-exclusion chromatography analysis using a polystyrene standard. [e] Entry 1 in Table 1. [f] X = 2,4-dinitrophenoxide

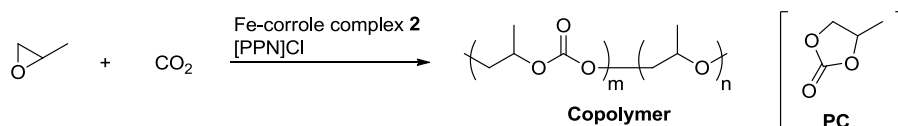
**Table S2.** Relationship between the Copolymer Yield and Molecular Weight<sup>[a]</sup>

Time [h]	Y of copolymer + PC [%] <sup>[b]</sup>	copolymer/PC <sup>[b]</sup>	TOF for copolymer <sup>[c]</sup>	carbonate linkage [%] <sup>[b]</sup>	$M_n$ [g·mol <sup>-1</sup> ] <sup>[d]</sup>	$M_w/M_n$ <sup>[d]</sup>
2	8	>99/<1	197	24	12000	1.15
4	14	>99/<1	169	28	16000	1.33
8	26	>99/<1	165	27	29000	1.22
16	63	>99/<1	195	22	63000	1.57

[a] PO (2.5 mL, 35.8 mmol), CO<sub>2</sub> (2.0 MPa), complex **1a** [ $3.5\sim 3.6 \times 10^{-3}$  mmol ( $7.0\sim 7.2 \times 10^{-3}$  mmol of Fe)], [PPN]Cl ( $3.5\sim 3.7 \times 10^{-3}$  mmol) in a 50-mL autoclave at 60 °C for 1 h. [b] Determined on the basis of <sup>1</sup>H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] TOF = [(mol of carbonate repeating unit) + (mol of ether repeating unit)]·(mol of Fe center)<sup>-1</sup>·h<sup>-1</sup>. [d] Determined by size-exclusion chromatography analysis using a polystyrene standard.

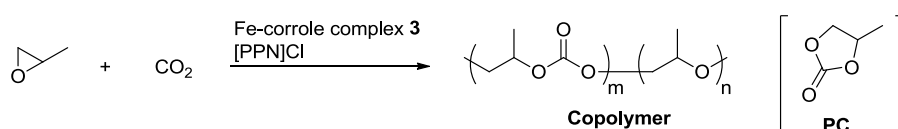
**Figure S1.** Relationship between the yield of copolymer and molecular weight (■: number-average molecular weight; ▲: PDI).

**Comment for the results in Table S2:** Copolymerization proceeded under the diluted condition (PO/**1a** = 10000), while the catalytic activity decreased (TOF  $\sim 200$  h<sup>-1</sup>) compared to the standard condition in this report (PO/**1a** = 4000). Living nature of the copolymerization was suggested by linearity of the plot of molecular weight against the polymer yield and by the constant PDI.

**Table S3.** Copolymerization of PO with CO<sub>2</sub> by Using Complex **2**<sup>[a]</sup>

[PPN]Cl (equiv. to Fe)	CO <sub>2</sub> [MPa]	temp. [°C]	Y of copolymer + PC [%] <sup>[b]</sup>	copolymer/PC <sup>[b]</sup>	TOF for copolymer <sup>[c]</sup>	carbonate linkage [%] <sup>[b]</sup>	M <sub>n</sub> [g·mol <sup>-1</sup> ] <sup>[d]</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>[d]</sup>
0.50 <sup>[e]</sup>	2.0	60	35	>99/<1	701	18	30,000	1.21
0.76	2.0	60	26	>99/<1	514	21	13,000	1.21
0.50	20	40	5	>99/<1	106	23	---	---
0.50	0.5	60	85	>99/<1	1676	4	48,000	1.29
0.50	4.9	60	17	>99/<1	346	28	10,000	1.31

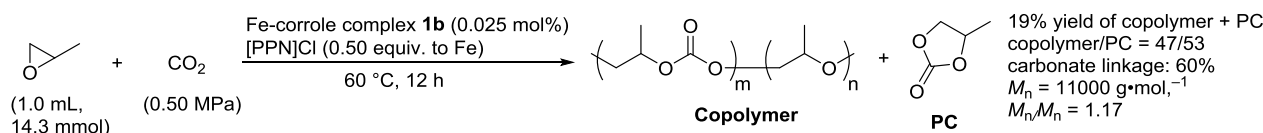
[a] PO (1.0 mL, 14.3 mmol), complex **2** (7.0~7.2 × 10<sup>-3</sup> mmol) in a 50-mL autoclave for 1 h. [b] Determined on the basis of <sup>1</sup>H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] TOF = [(mol of carbonate repeating unit) + (mol of ether repeating unit)]·(mol of Fe center)<sup>-1</sup>·h<sup>-1</sup>. [d] Determined by size-exclusion chromatography analysis using a polystyrene standard. [e] Entry 10 in Table 1.

**Table S4.** Copolymerization of PO with CO<sub>2</sub> by Using Complex **3**<sup>[a]</sup>

[PPN]Cl (equiv. to Fe)	CO <sub>2</sub> [MPa]	temp. [°C]	Y of copolymer + PC [%] <sup>[b]</sup>	copolymer/PC <sup>[b]</sup>	TOF for copolymer <sup>[c]</sup>	carbonate linkage [%] <sup>[b]</sup>	M <sub>n</sub> [g·mol <sup>-1</sup> ] <sup>[d]</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>[d]</sup>
0.50 <sup>[e]</sup>	2.0	60	60	>99/<1	1209	19	39000	1.18
0.50	5.0	60	45	>99/<1	891	27	19000	1.30

[a] PO (1.0 mL, 14.3 mmol), complex **3** (7.1~7.2 × 10<sup>-3</sup> mmol) in a 50-mL autoclave for 1 h. [b] Determined on the basis of <sup>1</sup>H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] TOF = [(mol of carbonate repeating unit) + (mol of ether repeating unit)]·(mol of Fe center)<sup>-1</sup>·h<sup>-1</sup>. [d] Determined by size-exclusion chromatography analysis using a polystyrene standard. [e] Entry 11 in Table 1.

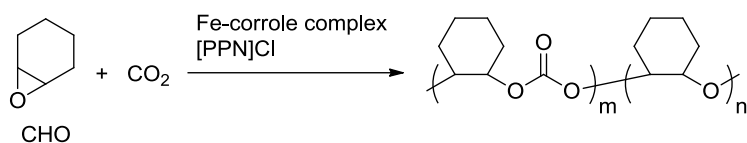
### Copolymerization of PO with CO<sub>2</sub> by Using Complex **1b**



19% yield of copolymer + PC  
 copolymer/PC = 47/53  
 carbonate linkage: 60%  
 M<sub>n</sub> = 11000 g·mol<sup>-1</sup>  
 M<sub>w</sub>/M<sub>n</sub> = 1.17

**Comment:** Iron complexes **1b** with a phenyl-substituted corrole ligand gave the copolymer with higher carbonate-linkage content than complex **1a** with a C<sub>6</sub>F<sub>5</sub>-substituted corrole ligand. The copolymerization under the standard CO<sub>2</sub> pressure (2.0 MPa) did not give any polymeric materials, while the decrease in CO<sub>2</sub> pressure (0.5 MPa) resulted in the copolymerization.

## Representative Procedure for the Copolymerization of Cyclohexene Oxide (CHO) with Carbon Dioxide.



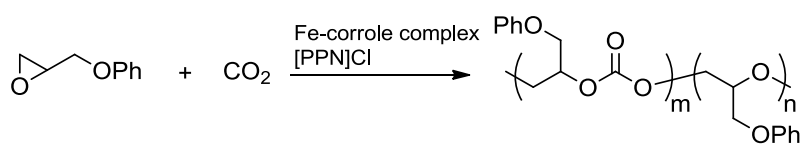
The same procedure as that for propylene oxide was applied. The meso-racemo ratio was estimated to be about 1:1 by <sup>13</sup>C NMR spectroscopy (Figure S4).

**Table S5.** Copolymerization of Cyclohexene Oxide with Carbon Dioxide by Using Fe–corrole Complexes<sup>[a]</sup>

entry	Fe complex	temp. [°C]	Time [h]	TOF for copolymer <sup>[c]</sup>	carbonate linkage [%] <sup>[b]</sup>	<i>M<sub>n</sub></i> [g·mol <sup>-1</sup> ] <sup>[d]</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>[d]</sup>
1	<b>1a</b>	60	12	30	95	6500	1.37
2	<b>1a</b>	80	3	99	92	7100	1.62
3	<b>2</b>	60	12	50	94	4500	1.33
4	<b>2</b>	80	3	99	94	6800	1.67
5	<b>3</b>	60	12	42	95	12000	1.37
6	<b>3</b>	80	3	109	84	7700	1.40
7	<b>1b</b>	60	12	23	96	8700	1.34

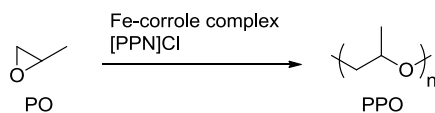
[a] CHO (2.0 mL, 20 mmol), complex **1**, **2**, or **3** ( $0.98\sim 1.0 \times 10^{-2}$  mmol of Fe) in a 50-mL autoclave for 12 h. [b] Determined on the basis of <sup>1</sup>H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] TOF = [(mol of carbonate repeating unit) + (mol of ether repeating unit)]•(mol of Fe center)<sup>-1</sup>•h<sup>-1</sup>. [d] Determined by size-exclusion chromatography analysis using a polystyrene standard.

## Representative Procedure for the Copolymerization of Glycidyl Phenyl Ether (GPE) with Carbon Dioxide.



A 50-mL autoclave containing a magnetic stirring bar was charged with GPE (1.1 g, 7.4 mmol), complex **1a** ( $1.8 \times 10^{-3}$  mmol) and [PPN]Cl ( $1.8 \times 10^{-3}$  mmol) under argon. After CO<sub>2</sub> was introduced, the reaction mixture was stirred at 60 °C. The autoclave was cooled to 25 °C, and the CO<sub>2</sub> was released. The polymer was purified as follows for entries 2–6 in Table 2: The polymerization mixture was dissolved in dimethyl sulfoxide at 180 °C and reprecipitated by addition of methanol. (In entry 1, the crude product was dispersed in CH<sub>2</sub>Cl<sub>2</sub> and reprecipitated by MeOH to give 36 mg of the product.) The copolymers were analyzed by SEC using 1,3-dichlorobenzene as an eluent at 140 °C to determine molecular weight and molecular-weight distribution. The carbonate linkage in % was analyzed by <sup>1</sup>H NMR spectroscopy (Figure S5). The *meso/racemo* of the polyether diad was determined by <sup>13</sup>C NMR spectroscopy (Figure S6). Judging from the polycarbonate <sup>13</sup>C NMR spectrum in Figure S6 the carbonyl carbon of the carbonate linkage was expected to appear around 154 ppm. However, the signal was beyond detection limit under the current signal/noise ratio. This indicates that the polycarbonate linkage exist in middle of a chain rather than exists as a block. TGA thermogram of poly(GPE-*co*-CO<sub>2</sub>) obtained in entry 3 of Table 2 is attached as Figure S7.

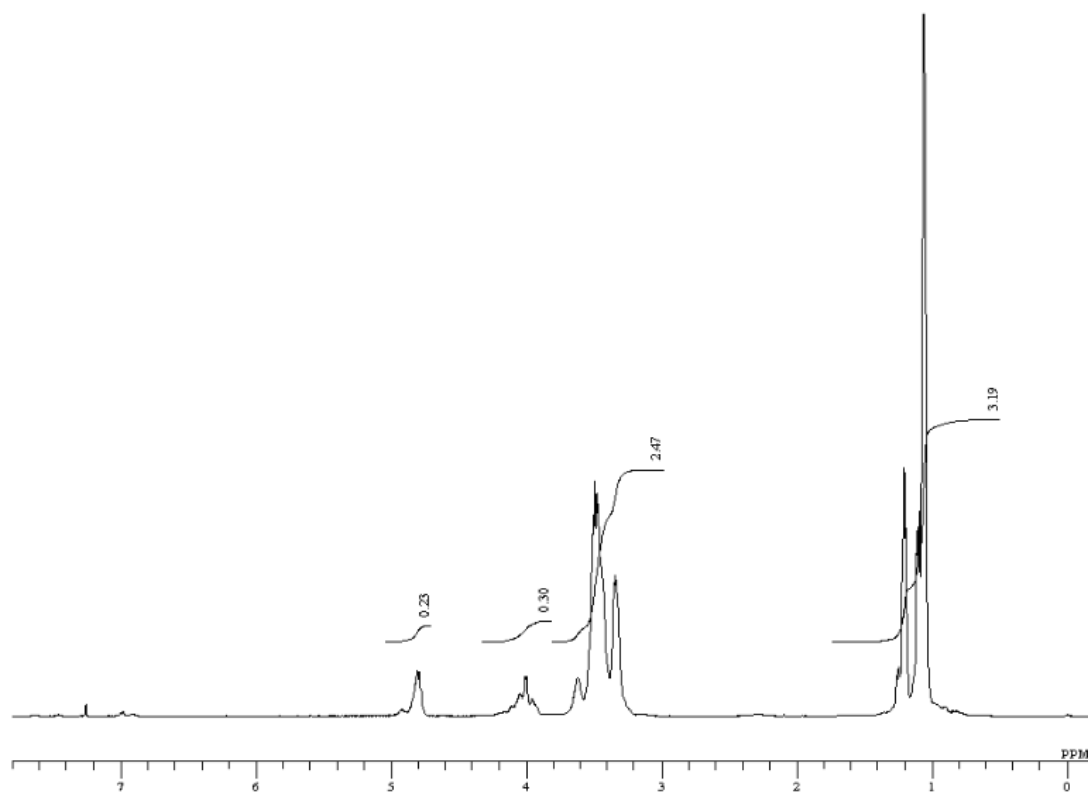
**Table S6.** Homopolymerization of Propylene Oxide by Using Fe–corrole Complexes<sup>[a]</sup>



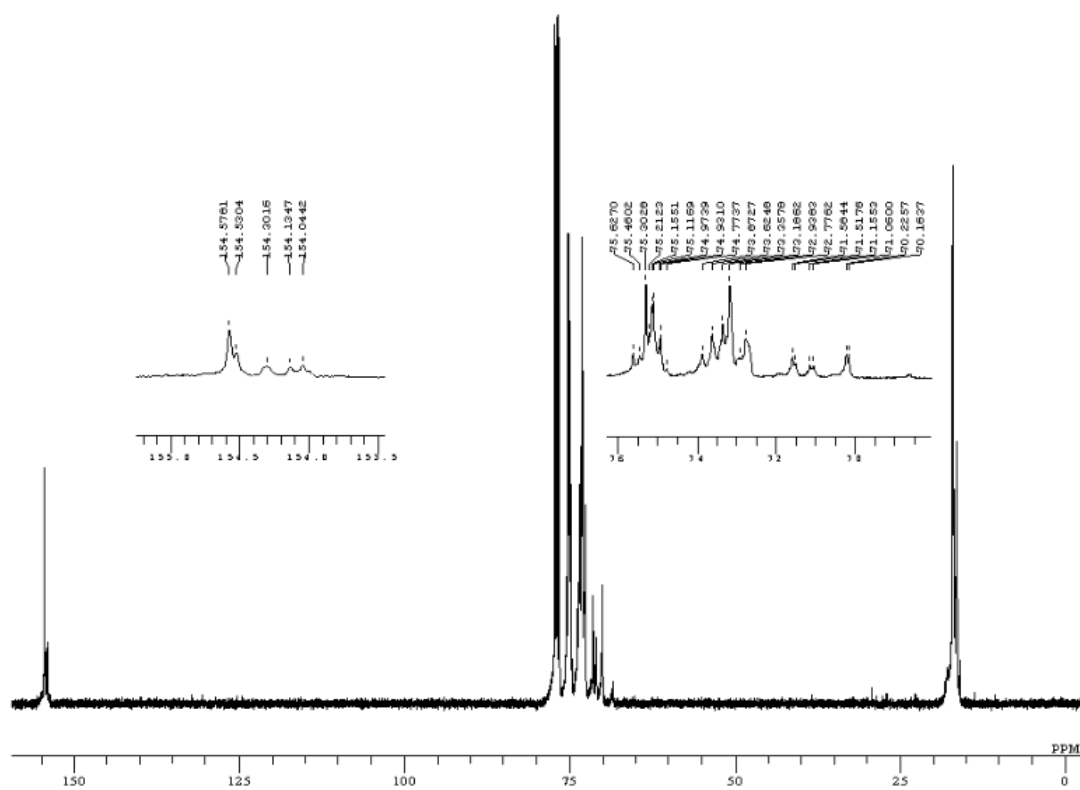
entry	Fe complex	temp. [°C]	time [h]	TOF for polymer <sup>[b,c]</sup>	$M_n$ [g·mol <sup>-1</sup> ] <sup>[d]</sup>	$M_w/M_n$ <sup>[d]</sup>
1	<b>1a</b>	25	12	88	19000	1.33
2	<b>2</b>	25	1.5	929	16000	1.30
3	<b>3</b>	25	2	685	95000	1.22

[a] PO (1.0 mL, 14.3 mmol), complex **1**, **2**, or **3** ( $7.1\sim 7.2 \times 10^{-3}$  mmol of Fe) in a 20-mL Schlenk tube. [b] Determined on the basis of <sup>1</sup>H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] TOF = (mol of repeating unit)·(mol of Fe center)<sup>-1</sup>·h<sup>-1</sup>. [d] Determined by size-exclusion chromatography analysis using a polystyrene standard.

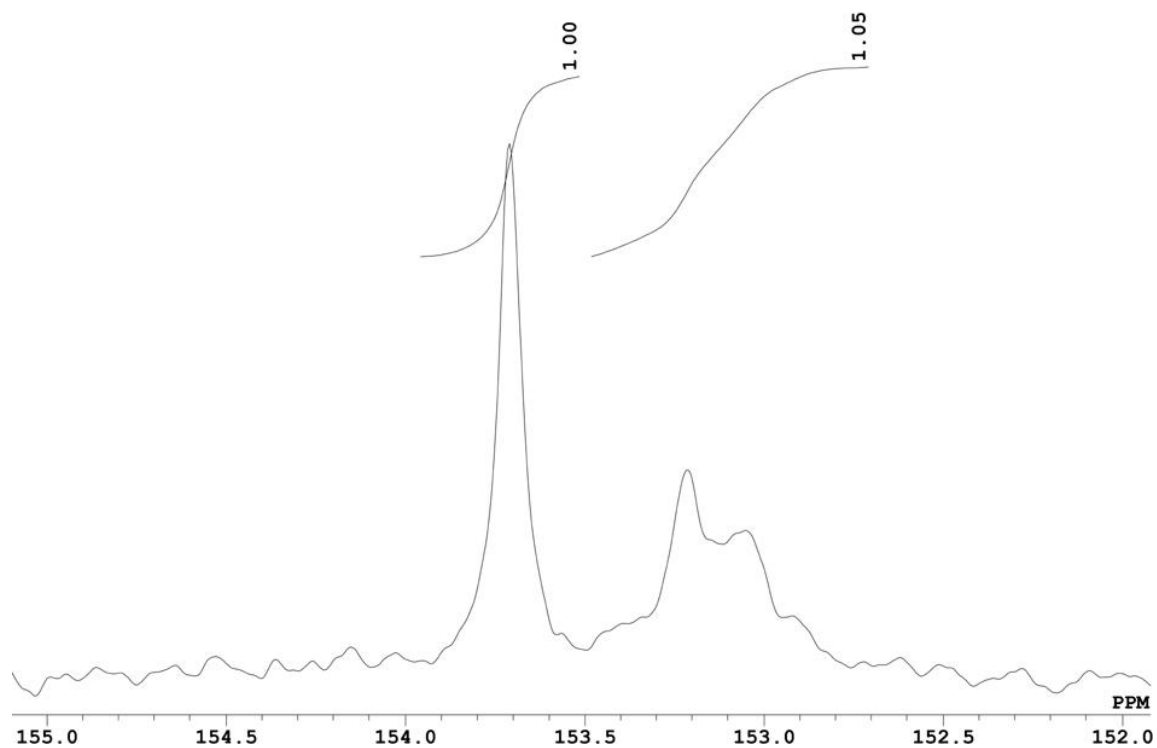




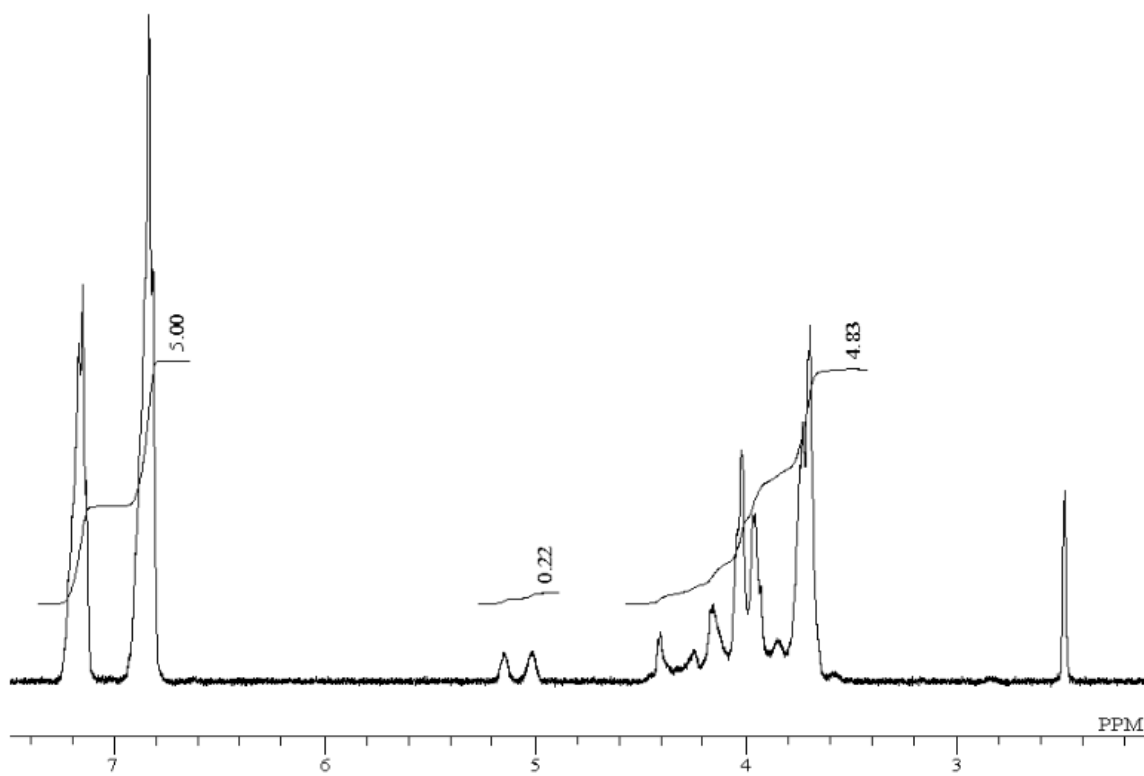
**Figure S2.**  $^1\text{H}$  NMR spectrum of the representative poly(propylene oxide-*co*- $\text{CO}_2$ ) (carbonate linkage: 17%) obtained by using complex **1a** under a similar condition to entry 1 in Table 1 ( $\text{CDCl}_3$ ).



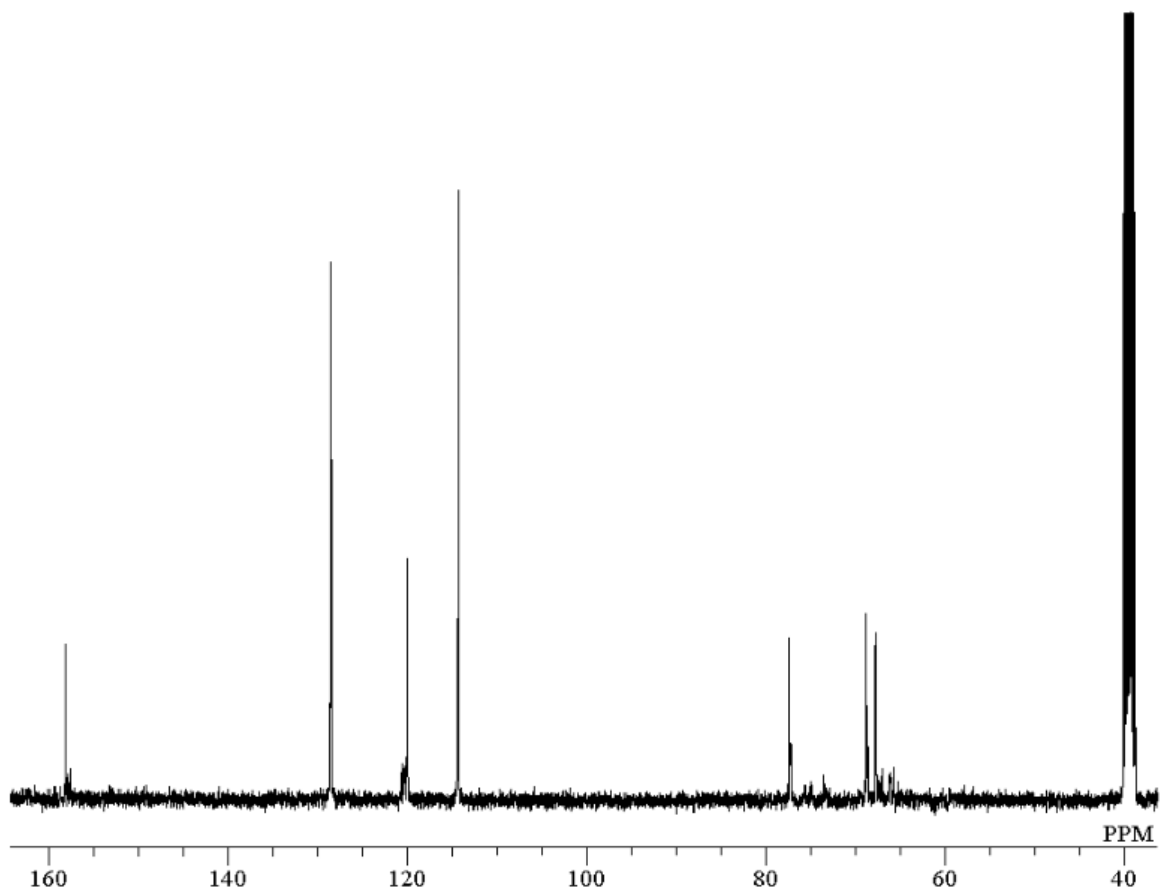
**Figure S3.**  $^{13}\text{C}$  NMR spectrum of the representative poly(propylene oxide-*co*- $\text{CO}_2$ ) (carbonate linkage: 17%) obtained by using complex **1a** under a similar condition to entry 1 in Table 1 ( $\text{CDCl}_3$ ).



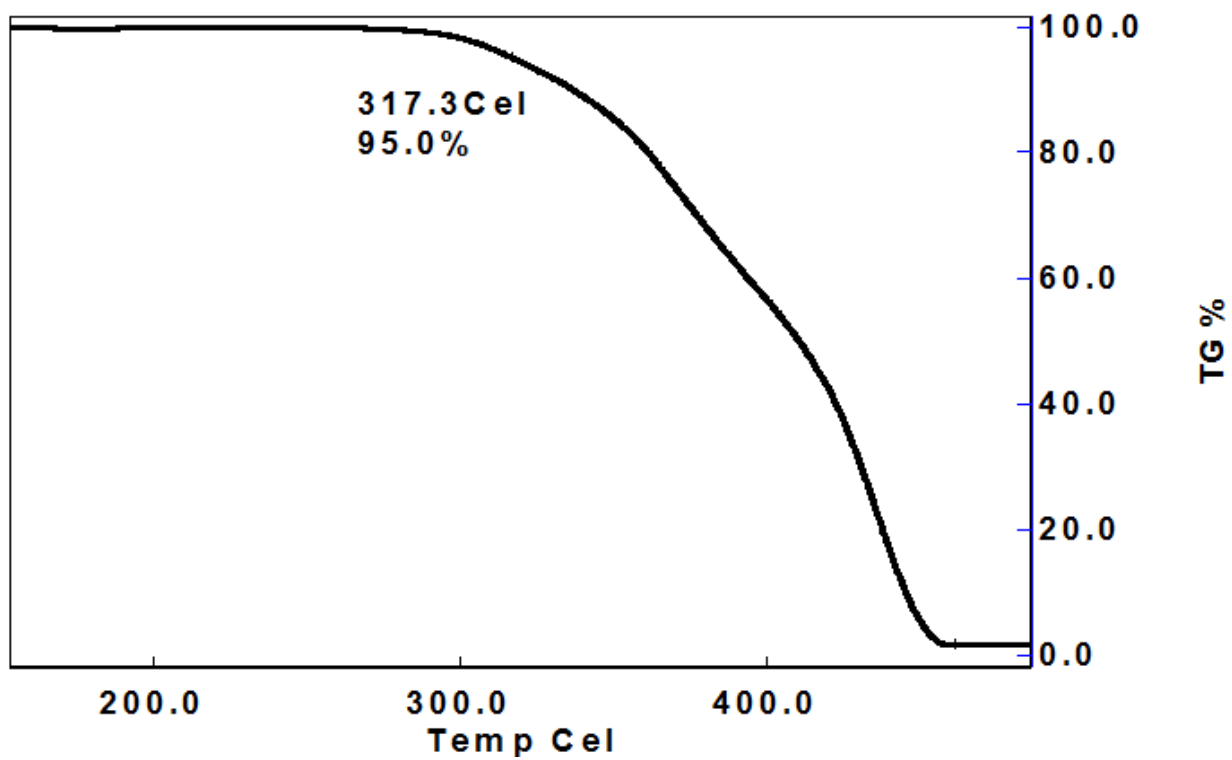
**Figure S4.** Carbonyl region of the  $^{13}\text{C}$  NMR spectrum of poly(cyclohexene carbonate) obtained by using complex **3** ( $\text{CDCl}_3$ ).



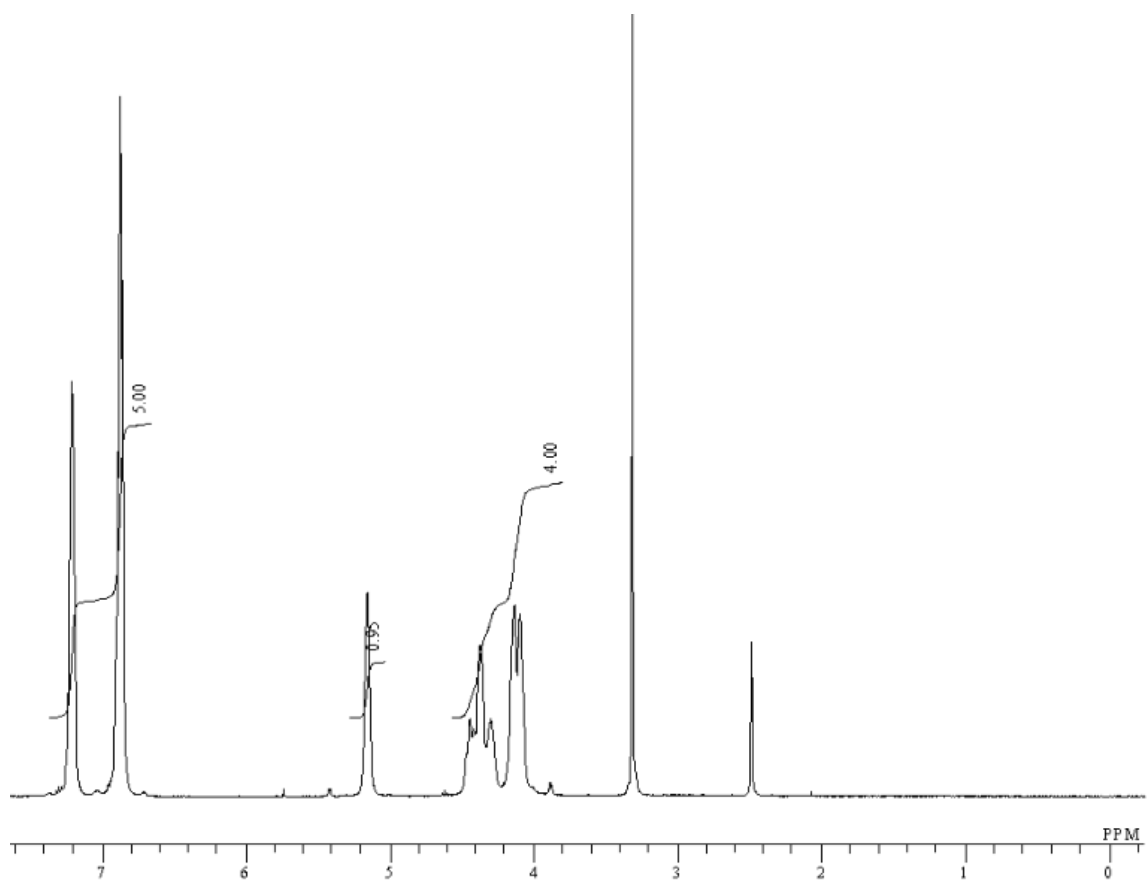
**Figure S5.**  $^1\text{H}$ NMR of poly(GPE-co- $\text{CO}_2$ ) obtained in entry 3 of Table 2 ( $\text{DMSO-}d_6$ ,  $150\text{ }^\circ\text{C}$ ).



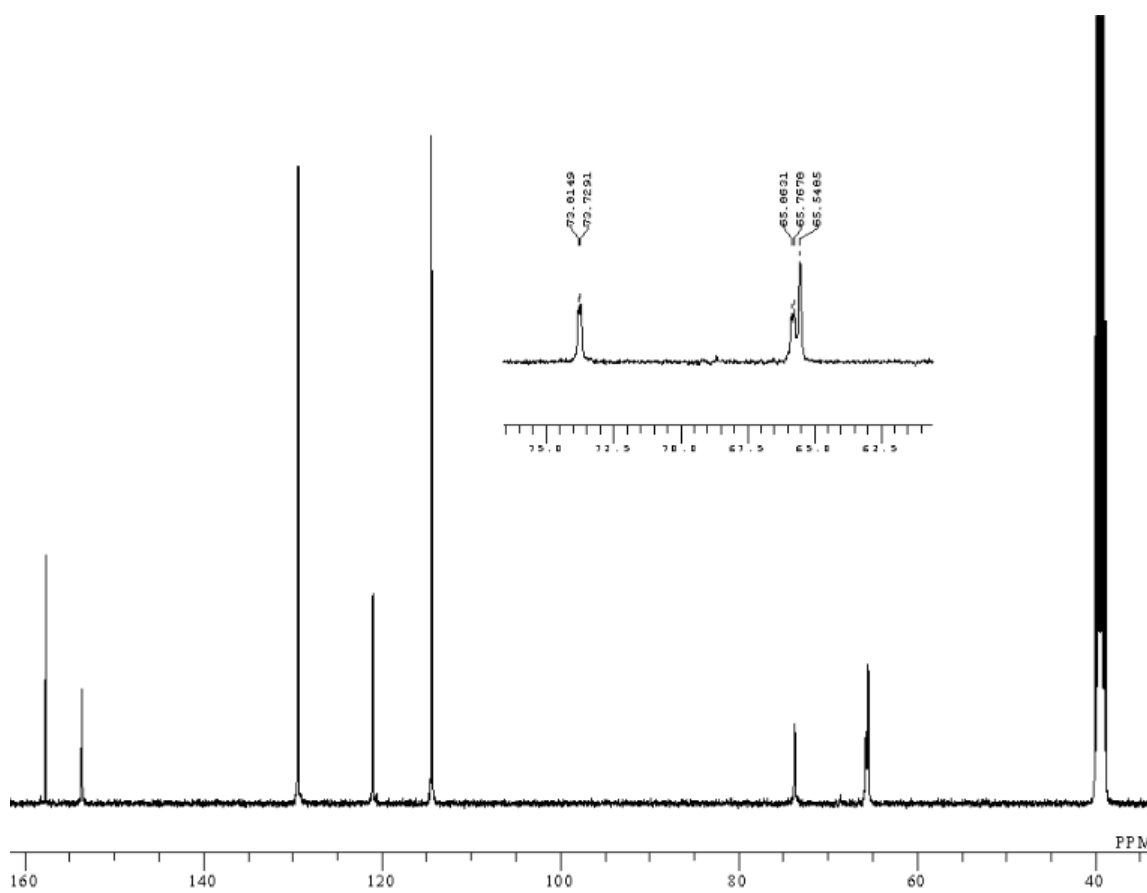
**Figure S6.**  $^{13}\text{C}$  NMR of poly(GPE-*co*-CO<sub>2</sub>) obtained in entry 3 of Table 2 (DMSO-*d*<sub>6</sub>, 150 °C).



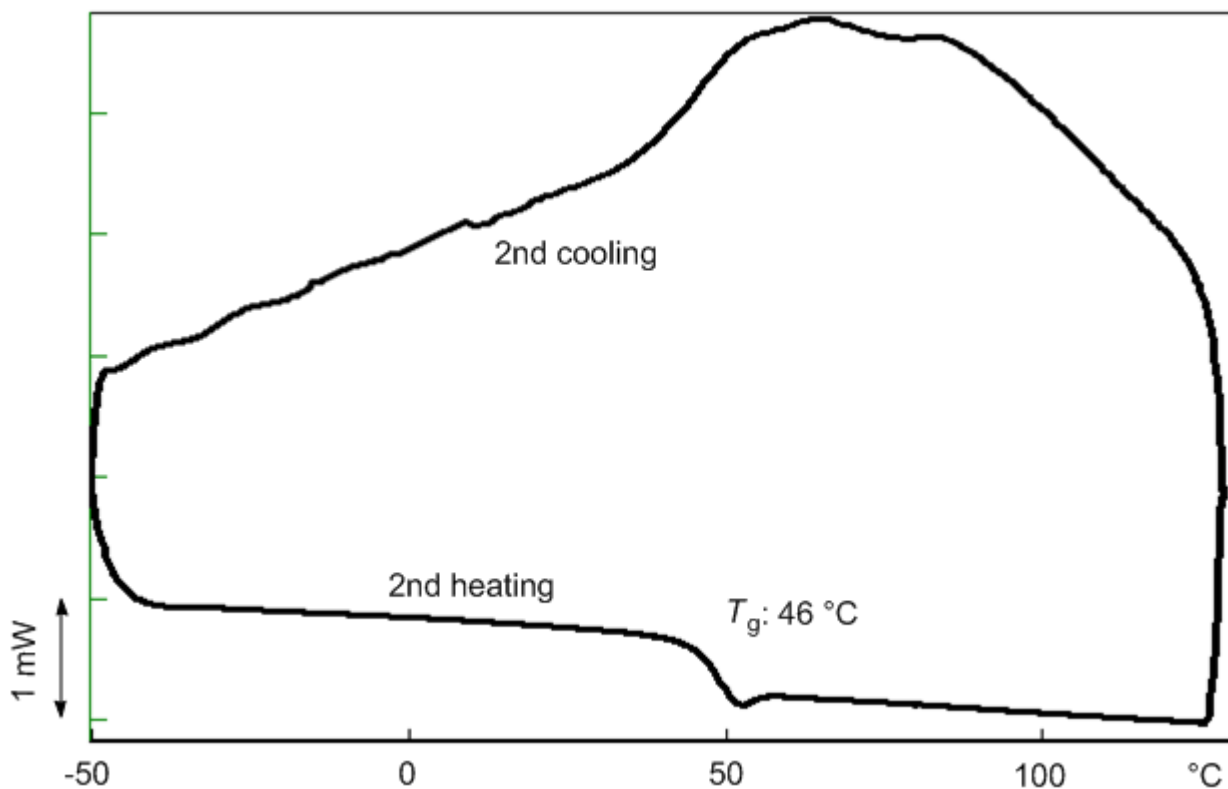
**Figure S7.** TGA thermogram of poly(GPE-*co*-CO<sub>2</sub>) obtained in entry 3 of Table 2.



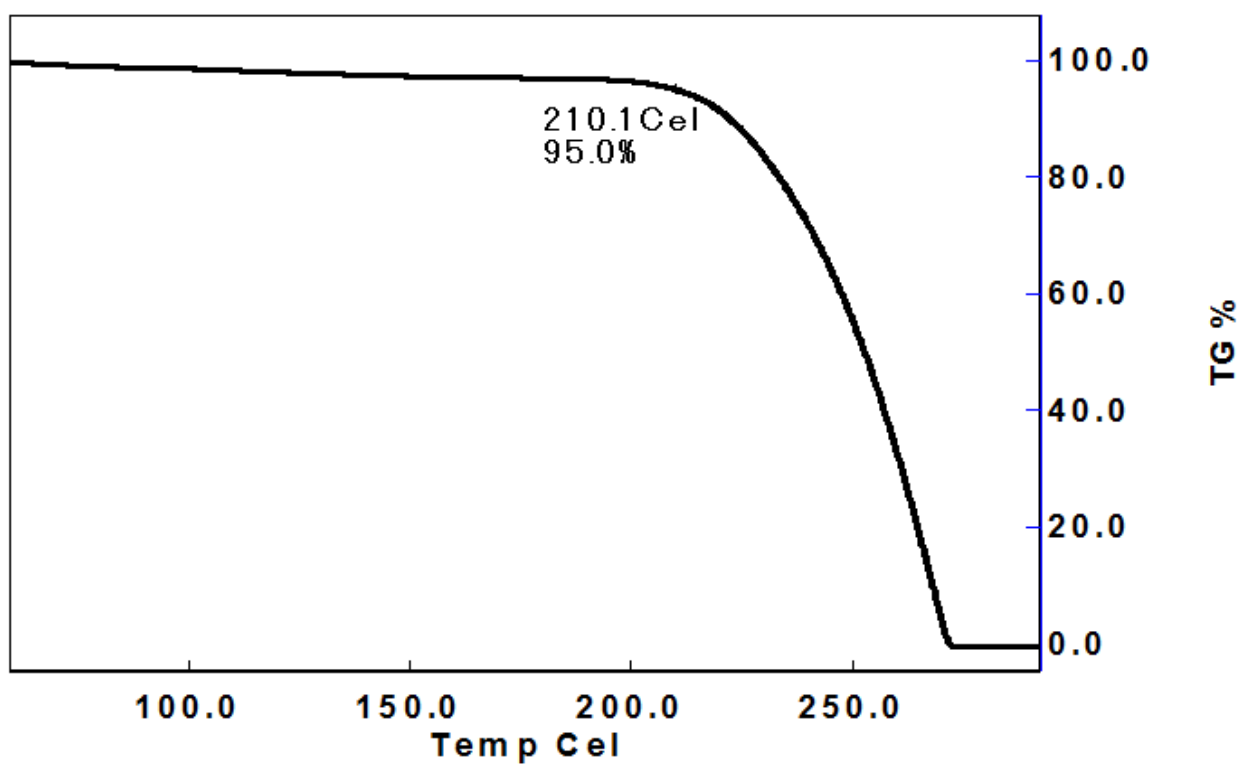
**Figure S8.**  $^1\text{H}$ NMR of poly(GPE-*co*-CO<sub>2</sub>) obtained in entry 5 of Table 2 (DMSO-*d*<sub>6</sub>, 25 °C).



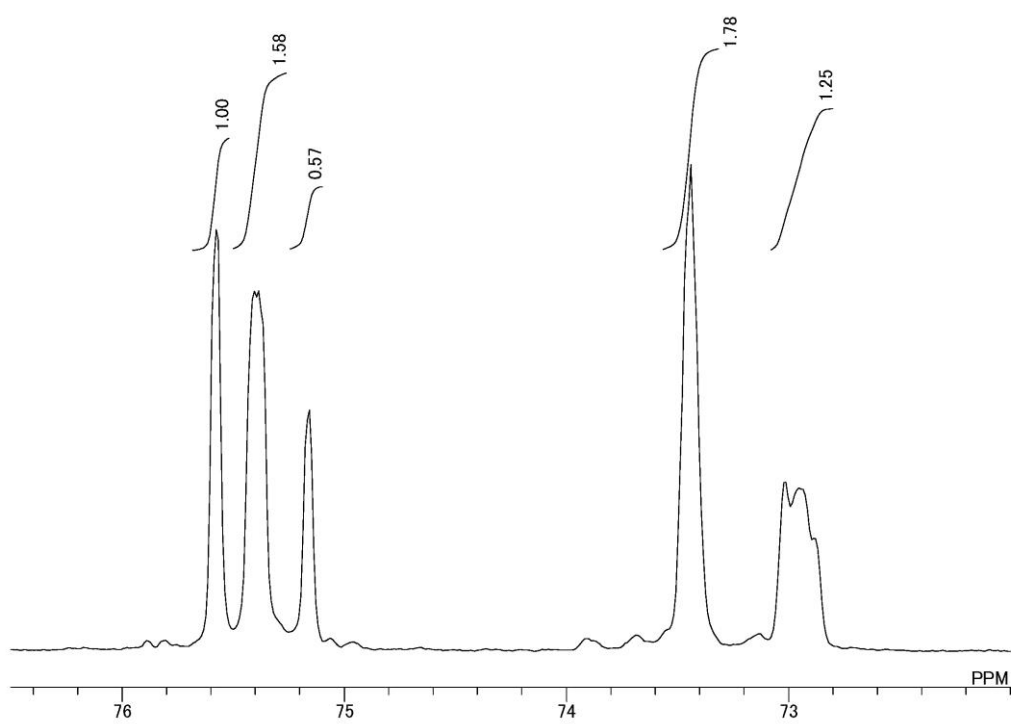
**Figure S9.**  $^{13}\text{C}$  NMR of poly(GPE-*co*-CO<sub>2</sub>) obtained in entry 5 of Table 2 (DMSO-*d*<sub>6</sub>, 25 °C).



**Figure S10.** DSC curve of poly(GPE-co-CO<sub>2</sub>) obtained in entry 5 of Table 2.



**Figure S11.** TGA thermogram of poly(GPE-co-CO<sub>2</sub>) obtained in entry 5 of Table 2.



**Figure S12.** Methine and methylene region of the  $^{13}\text{C}$  NMR spectrum of poly(propylene oxide) obtained by using complex **2** ( $\text{CDCl}_3$ ).

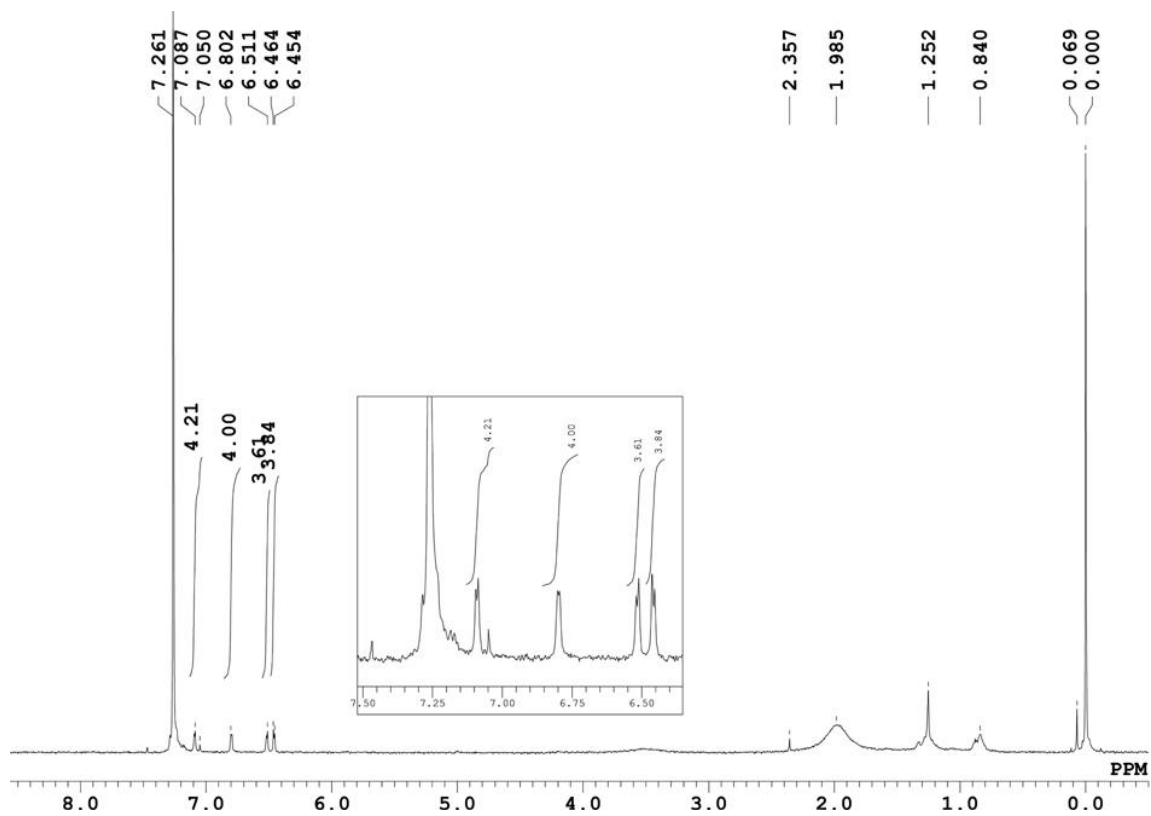


Figure S13.  $^1\text{H}$  NMR spectrum of iron-corrole complex **1a** ( $\text{CDCl}_3$ ).

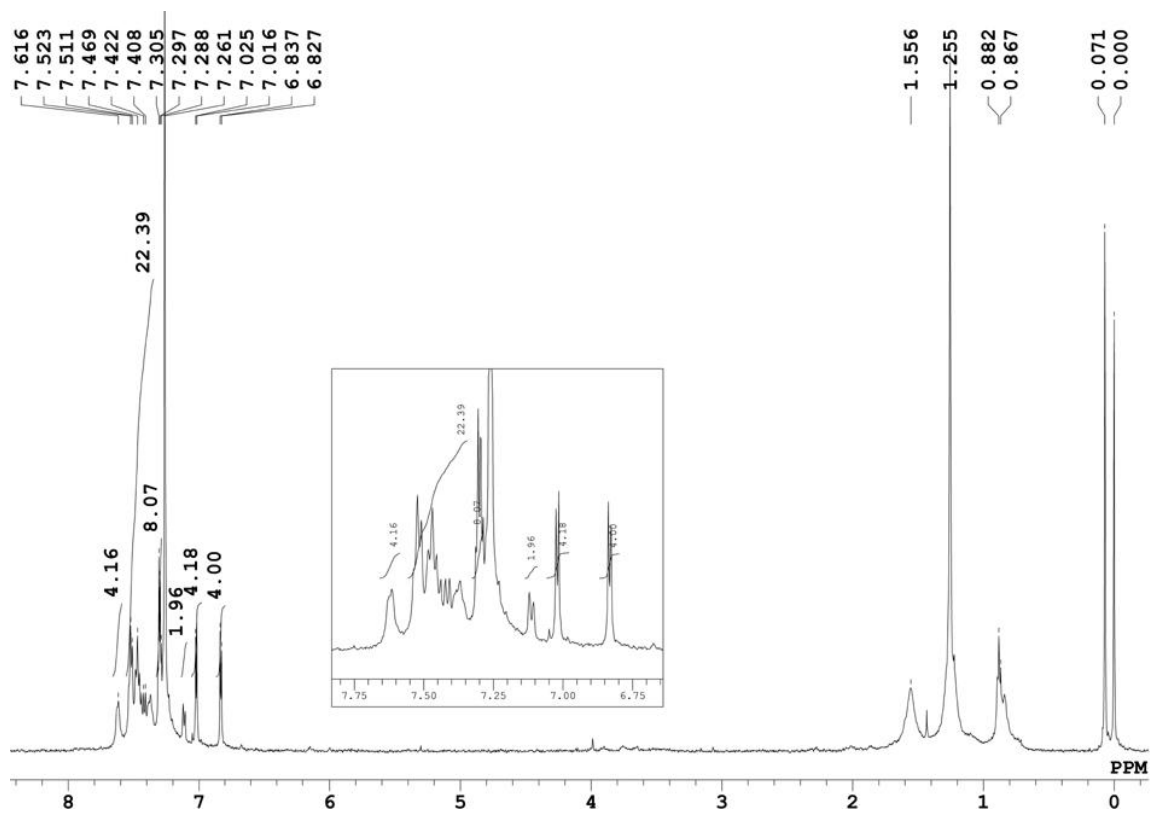


Figure S14.  $^1\text{H}$  NMR spectrum of iron-corrole complex **1b** ( $\text{CDCl}_3$ ).

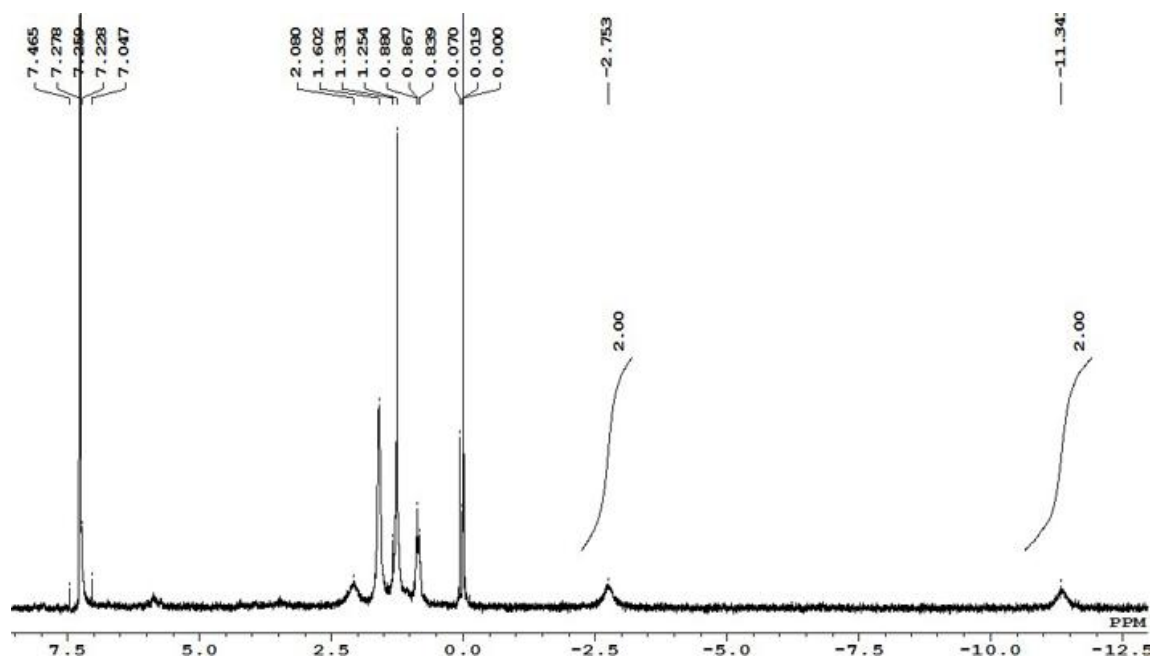


Figure S15.  $^1\text{H}$  NMR spectrum of iron-corrole complex **2** ( $\text{CDCl}_3$ ).

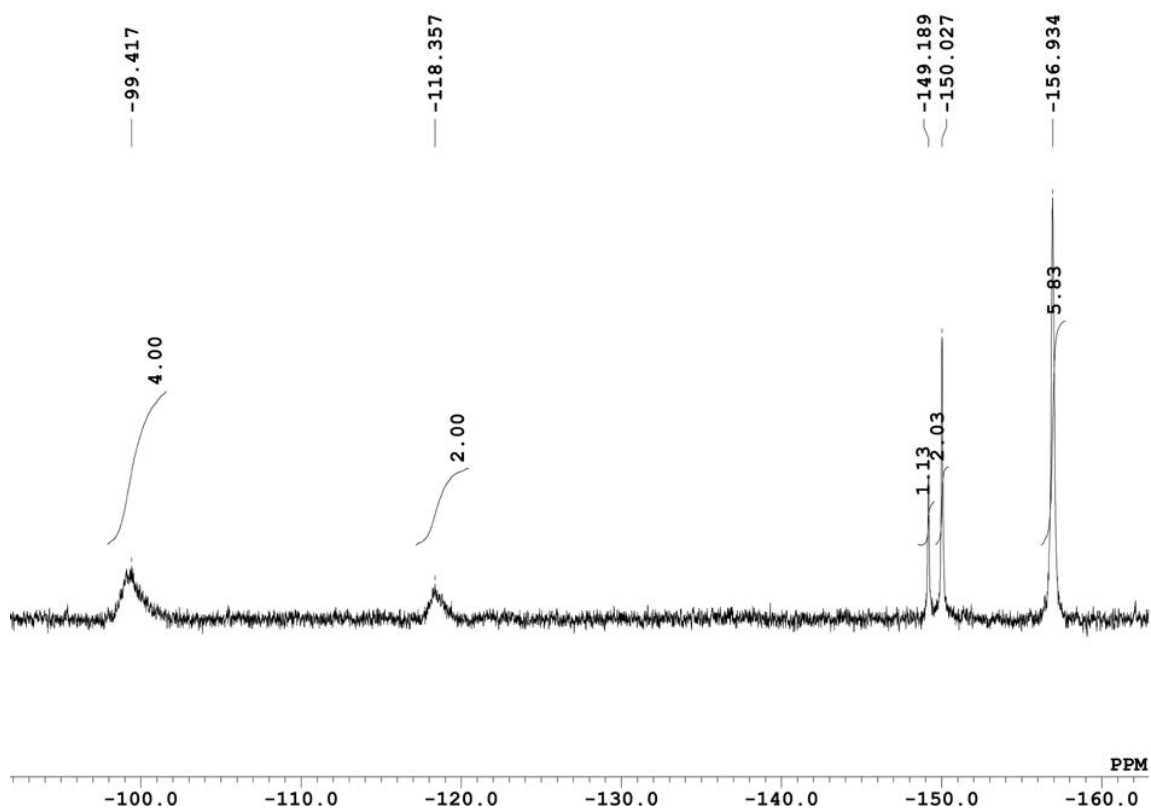


Figure S16.  $^{19}\text{F}$  NMR spectrum of iron-corrole complex **3** ( $\text{C}_6\text{D}_6$ ).



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