Electronic Supplementary Material (ESI) for Polymer Chemistry.

Diblock Metallocopolymers Containing Various Iron Sandwich Complexes: Living ROMP Synthesis and Selective Reversible Oxidation

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Supplementary information

2. Synthesis and kinetic study of the ROMP of monomer **7**

3. Synthesis and kinetic study of the ROMP of monomer **8**

4. Synthesis and kinetic study of the ROMP of the monomer **9**

5. Diblock copolymer **11**

6. Diblock copolymer **13**

7. Diblock copolymer **15**

1. General data

Cis-5-norbornene-*exo*-2,3-dicarboxylic anhydride (95%, NDA), ethyl vinyl ether (99%, EVE) and Grubbs 2nd generation catalyst were purchased from Aldrich, and used directly. Grubbs 3rd generation catalyst **1**,[s1] chlorocarbonyl ferrocene (FcCOCl),[s2] *N*-[11'-amine-3',6',9'-trioxahendecyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide **5**,[s2] ferrocene-containing monomer **7**,[s2] chlorocarbonyl pentamethylferrocene (Fc*COCl),[s3] pentamethylferrocene-containing monomer **8**,[s3] chlorocarbonyl mixed-sandwich iron complex $[(\eta^6\text{-}C_6Me_6)Fe(\eta^5\text{-}C_5H_4COCl)][PF_6]$,[s4] *N*-(2-aminoethyl)-*cis*-5-norbornene-*exo*-2, 3-dicarboximide **6**,[s5] and the cationic organoiron monomer **9**[s6] were prepared by the method reported in the literatures. All the other chemicals were from commercial sources and used as received. All the solvents used were dried and freshly distilled.

^{1}H NMR (300, 400 or 600 MHz) and ^{13}C NMR (50, 75 or 150 MHz) spectra were recorded at 25 °C with a Bruker AC (200, 300, 400 or 600 MHz) spectrometers. All the chemical shifts are reported in parts per million (δ, ppm) with reference to tetramethylsilane (TMS). Mass spectra were recorded using an Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer. The infrared spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer in the range 400-4000 cm^{-1}. UV-visible absorption spectra were measured with a Perkin-Elmer Lambda 19 UV-vis. spectrometer.

Cyclic voltammetry (CV) measurements was recorded on a PAR 273 potentiostat under nitrogen atmosphere at 20 °C using dry dichloromethane (CH_2Cl_2) or dimethylformamide (DMF) as solvent and $[n\text{-}Bu_4N][PF_6]$ 0.1M as supporting electrolyte. The working and counter electrodes were Pt, and the reference electrode was Ag. The internal reference was $[FeCp^*_2]$ (Cp* = η^5-C_5Me_5), and the scan rate was 400 mV.s^{-1}. The Bard-Anson electrochemical method[s7] was used to calculate the number of electrons involved in the reduction wave of the copolymers. The experiments were conducted by preparing a known amount of copolymer in dry CH_2Cl_2 or DMF, then a known amount of $[FeCp^*_2]$ in CH_2Cl_2 or DMF was added to the solution. After recording the CV, the intensities of the oxidation waves of the copolymer and the internal reference $[FeCp^*_2]$ were measured. The values were introduced into the Bard-Anson equation[s7]: $n_p = (i_{dp}/C_p)/(i_{dm}/C_m)\,(M_p/M_m)^{0.275}$ to provide the final number of transferred electrons (n_p).

Size exclusion chromatography (SEC) measurements were carried out using the PL-GPC 50 plus Integrated GPC system from Polymer laboratories-Varian equipped with refractometric and UV detectors, column oven and integrated degasser. Columns from TOSOH: TSKgel TOSOH, HXL-L (guard column 6.0 mm ID × 4.0 cm L), G4000HXL (7.8 mm ID × 30.0 cm L), G3000HXL (7.8 mm ID × 30.0 cm L), G2000HXL (7.8 mm ID × 30.0 cm L). Flow Marker: TCB (trichlorobenzene, $C_6H_3Cl_3$), Flow: 1.0 ml/min, Solvent: tetrahydrofuran (THF) from Aldrich, loop: 100 μl.

Abbreviations: Cp = η^5-C_5H_4- (monosubstituted cyclopentadienyl) or η^5-C_5H_5; Fc = ferrocenyl, FcH = ferrocene, Fc* = 1,2,3,4,5-pentamethylferrocenyl; Fc*H = pentamethylferrocene; FbX = $[Fe(\eta^5\text{-}C_5H_4\text{-})(\eta^6\text{-}C_6Me_6)][PF_6]$; FbHX = $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)][PF_6]$.

2. Synthesis and kinetic study of the ROMP of monomer 7[s2]

Triethylamine (0.1 mL, 0.72 mmol) was added dropwise at room temperature (r. t.) under nitrogen (N_2) atmosphere to a suspension of ferrocene carboxylic acid (0.4 g, 1.74 mmol) in dry CH_2Cl_2 (35 mL). Then, oxalyl chloride (0.75 mL, 8.7 mmol) was added dropwise at 0 ^{o}C. The obtained mixture was stirred overnight at r. t. and dried *in vacuo*. The residual red solid of crude chlorocarbonyl ferrocene (FcCOCl) was dissolved in dry CH_2Cl_2 (15 mL) and added dropwise to a CH_2Cl_2 solution (20 mL) of **5** (0.2 g, 0.59 mmol) and triethylamine (1.5 mL, 10.7 mmol). The mixture was stirred overnight under N_2 atmosphere at r. t., then washed with saturated $NaHCO_3$ solution (1 × 100 mL) and distilled water (3 × 100 mL). The organic solution was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The product **7** was purified by column chromatography with CH_2Cl_2/methanol (1% → 20%) as eluent and obtained as a brown sticky oil. Yield: 0.258 g, 79.4%. ^{1}H NMR (300 MHz, $CDCl_3$), δ_{ppm}: 6.45 (t, J = 9.9 Hz, 1H, NHCO), 6.25 (t, J = 3.6 Hz, 2H, CH=CH), 4.69 (t, J = 3.6 Hz, 2H, sub. Cp), 4.30 (t, J = 3.6 Hz, 2H, sub. Cp), 4.17 (s, 5H, free Cp), 3.70-3.54 (m, 16H, $4\times CH_2CH_2$), 3.23 (t, J = 3.4 Hz, 2H, =CH-C***H***), 2.65 (d, J = 0.9 Hz, 2H, CO-CH), 1.45 (d, J = 9.9 Hz, 1H, CH_2-bridge), 1.32 (d, J = 10.0 Hz, 1H, CH_2-bridge). ^{13}C NMR (50 MHz, $CDCl_3$), δ_{ppm}: 177.8 (CON), 170.2 (CONH), 137.7 (CH=CH), 70.4, 70.2, 70.1, 70.0, 69.7, 69.6, 68.2 ($-OCH_2CH_2OCH_2CH_2OCH_2-$, sub. Cp and free Cp), 66.8 (-***C***H_2NH), 47.7 (CO-***C***H), 45.1 (=CH-***C***H), 42.6 (CH_2-bridge), 39.2 (***C***H_2-NCO), 37.7 (-***C***H_2CH_2-NCO). MS (ESI *m/z*), calcd. for $C_{28}H_{34}N_2O_6Fe$: 550.4; found: 573.2 (M+Na$^+$).

Kinetic study of the ROMP of monomer 7

A kinetic study was carried out in order to determine the ROMP rate of monomer **7**. First, monomer **7** (0.46 g, 0.84 mmol) in 5.0 mL dry CH_2Cl_2 was added into the solution of Grubbs 3rd generation catalyst **1** (0.030 g, 0.033 mmol) in 0.5 mL dry CH_2Cl_2. Then, the obtained reaction mixture was vigorously stirred at r. t. under N_2 atmosphere. At different intervals (5, 15, 30 and 60 minutes, respectively), a 0.5 mL sample of the reaction mixture was taken out, quenched with 0.2 mL of EVE, precipitated by adding 5.0 mL of methanol. The obtained precipitate was washed with methanol (3 × 5 mL), vacuumed and checked for the ^{1}H NMR spectrum in $CDCl_3$. All the washing liquors and filtrate were collected, the solvent was removed *in vacuo*, and the ^{1}H NMR spectrum of the residue was recorded in $CDCl_3$, too. The monomer conversion was deemed to be 100% when the signal of the olefin protons for monomer **7** at 6.25 ppm disappeared. It was found that the conversion of monomer **7** achieved 100% after 15 minutes stirring.

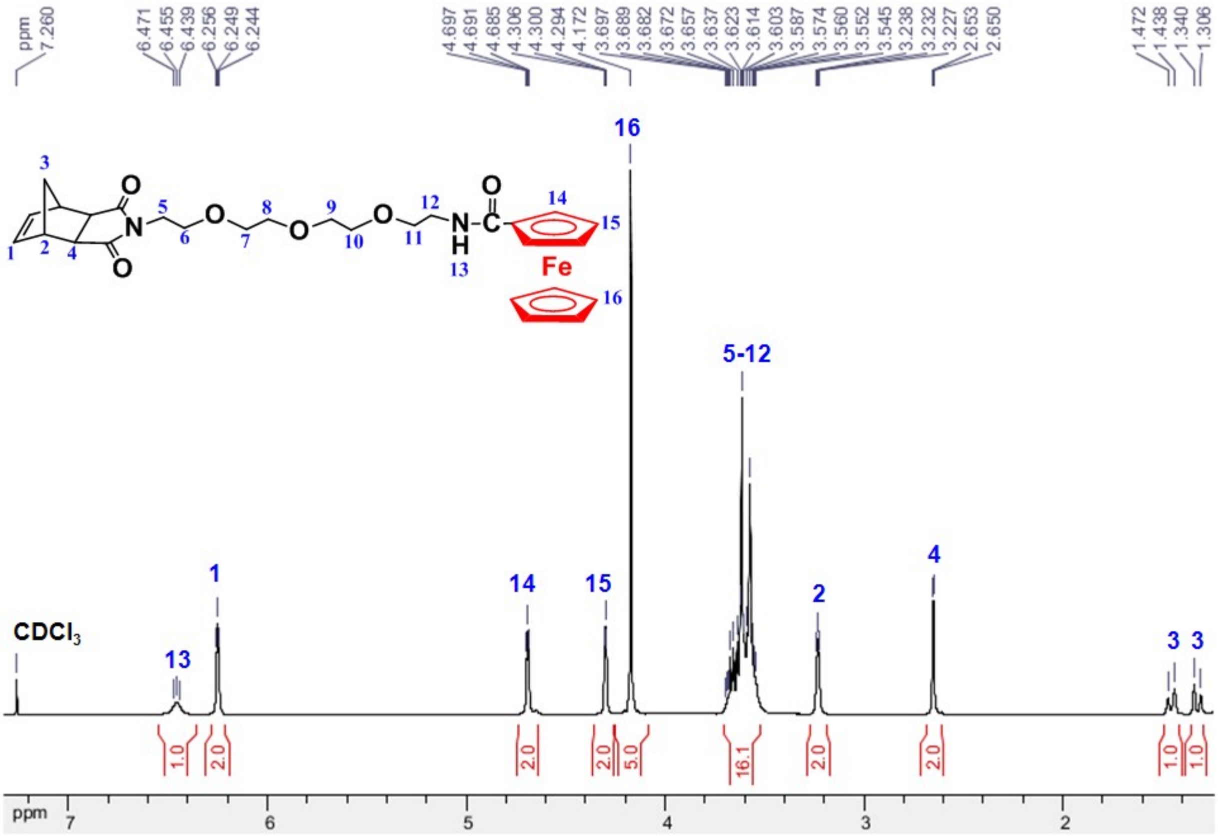


Figure S1 ^{1}H NMR spectrum of monomer **7** in $CDCl_3$.

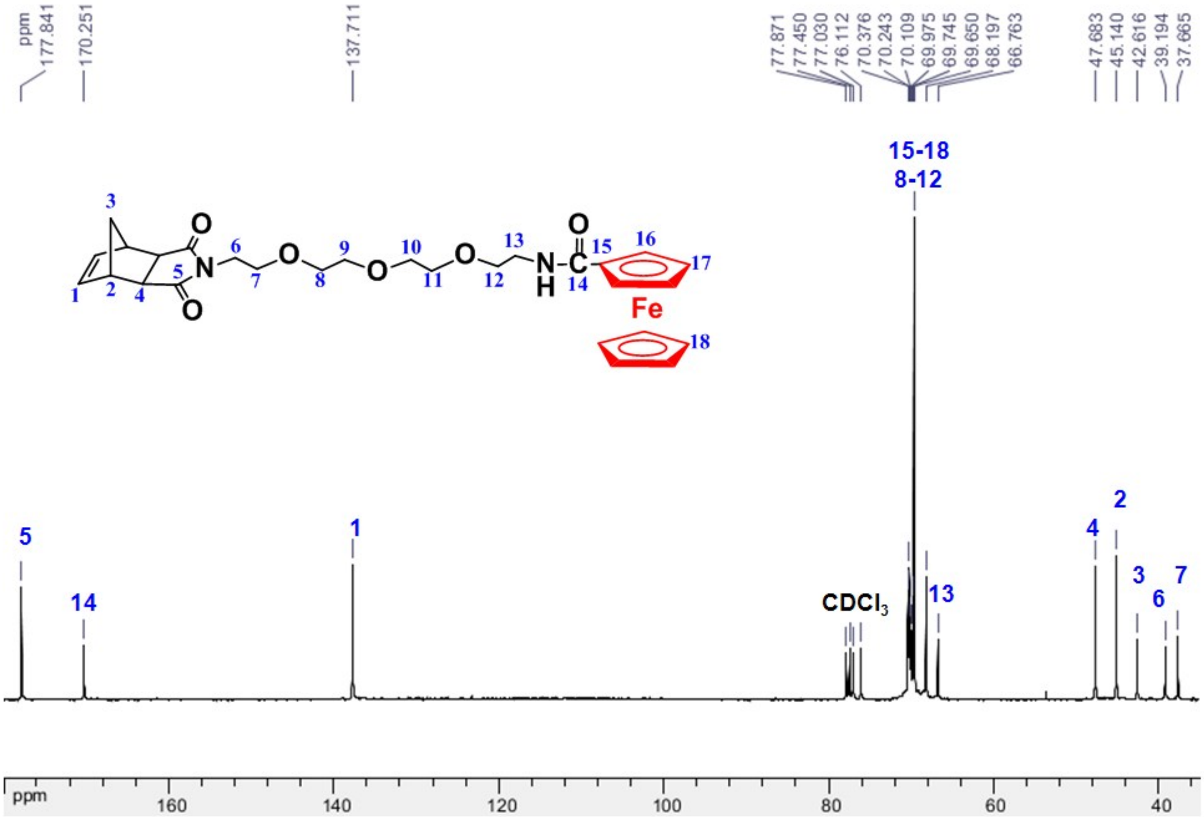


Figure S2 ^{13}C NMR spectrum of monomer **7** in $CDCl_3$.

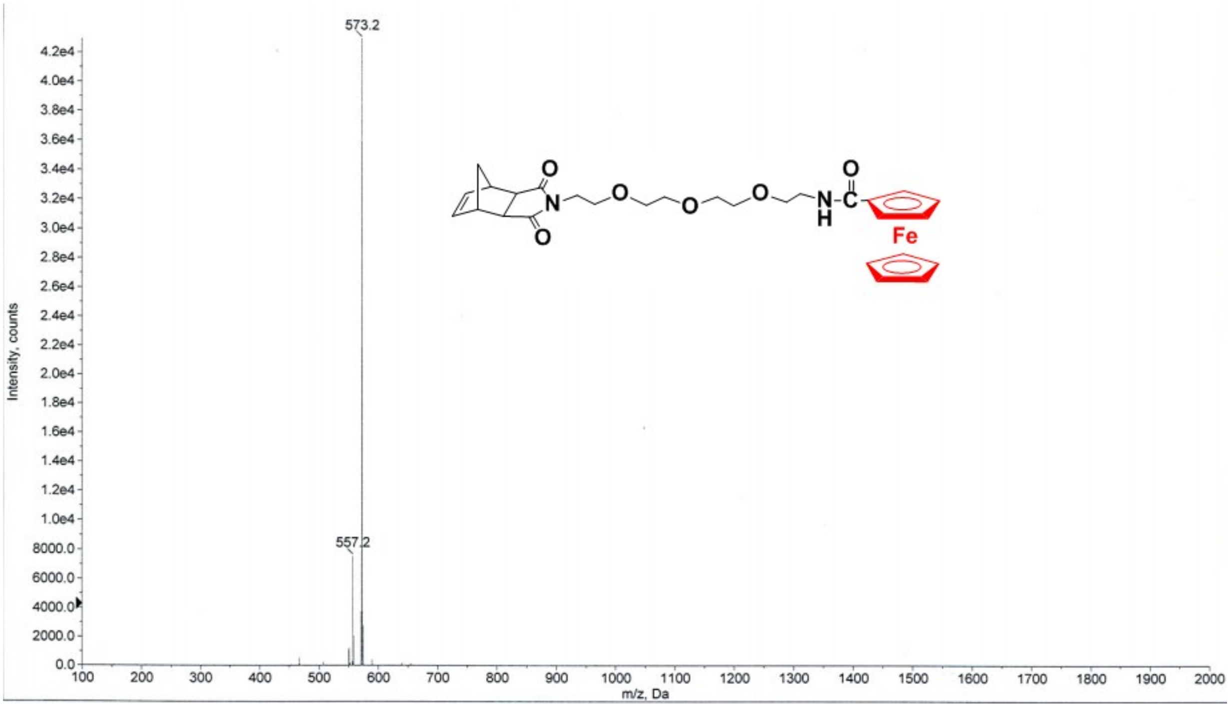


Figure S3 ESI mass spectrum of monomer **7**.

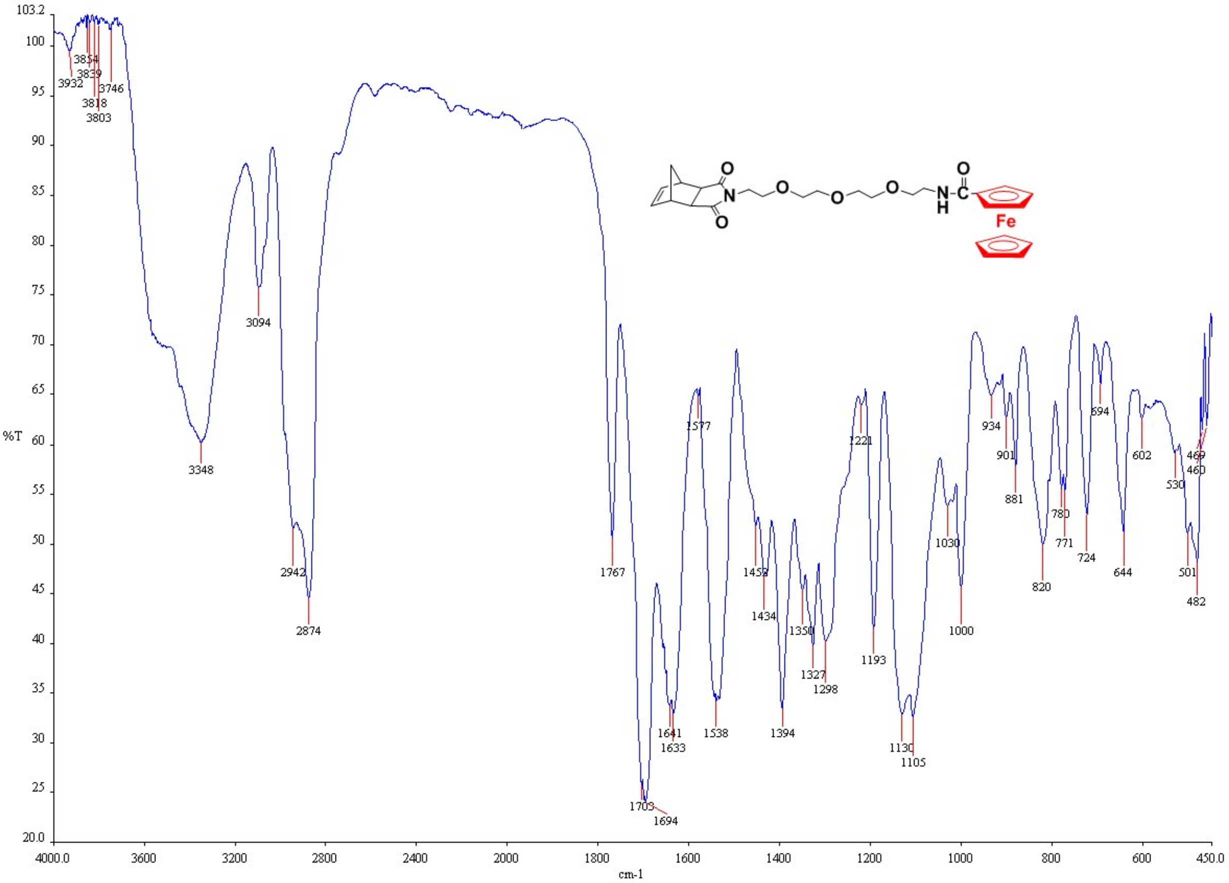


Figure S4 IR spectrum of monomer **7**.

3448 cm^{-1} (υ_{NH}), 2874 cm^{-1} (υ_{CH2}), 1767 cm^{-1} ($\upsilon_{C=C}$), 1694 cm^{-1} ($\upsilon_{NC=O}$), 1633 cm^{-1} ($\upsilon_{NHC=O}$), 820 cm^{-1}(υ_{FeII})

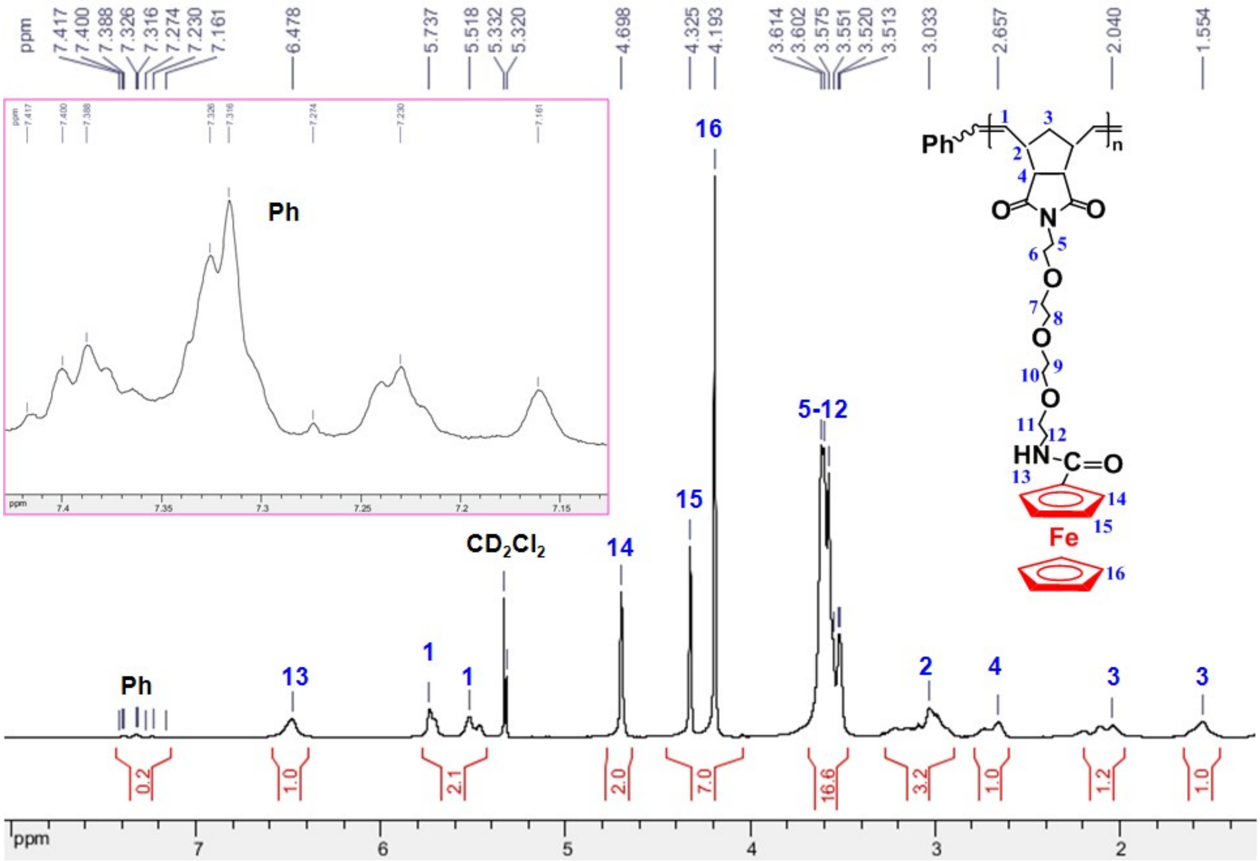


Figure S5 ^{1}H NMR spectrum (600 MHz) of homopolymer of **7** in CD_2Cl_2.

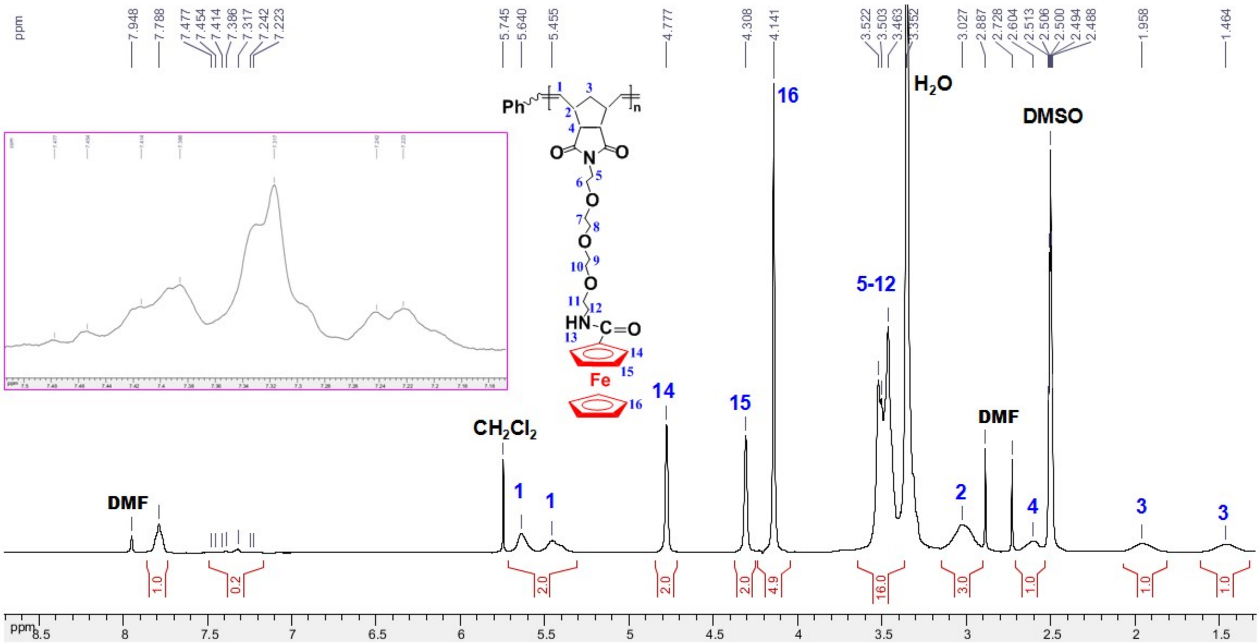


Figure S6 ^{1}H NMR spectrum (400 MHz) of homopolymer of **7** in DMSO-d_6.

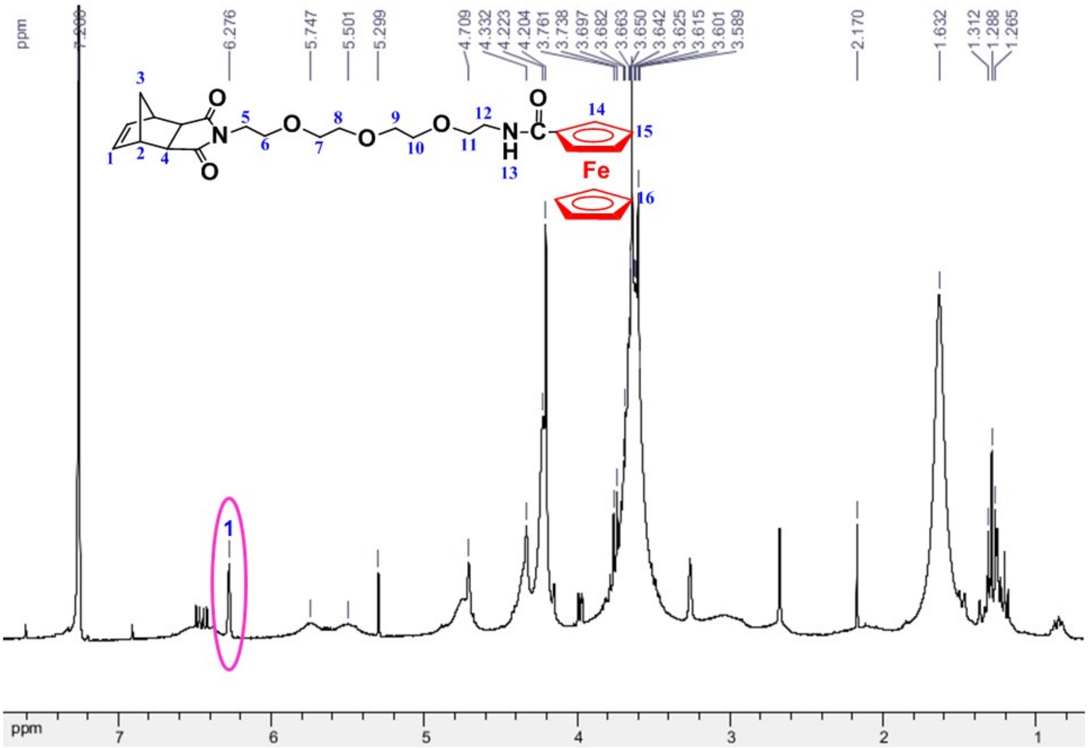


Figure S7 ^{1}H NMR spectrum (300 MHz) in $CDCl_3$ of the ROMP reaction mixture of monomer **7** after 5 minutes stirring. The ROMP of monomer **7** is not complete because the peak at 6.28 ppm for the olefinic protons of monomer **7** is still observed.

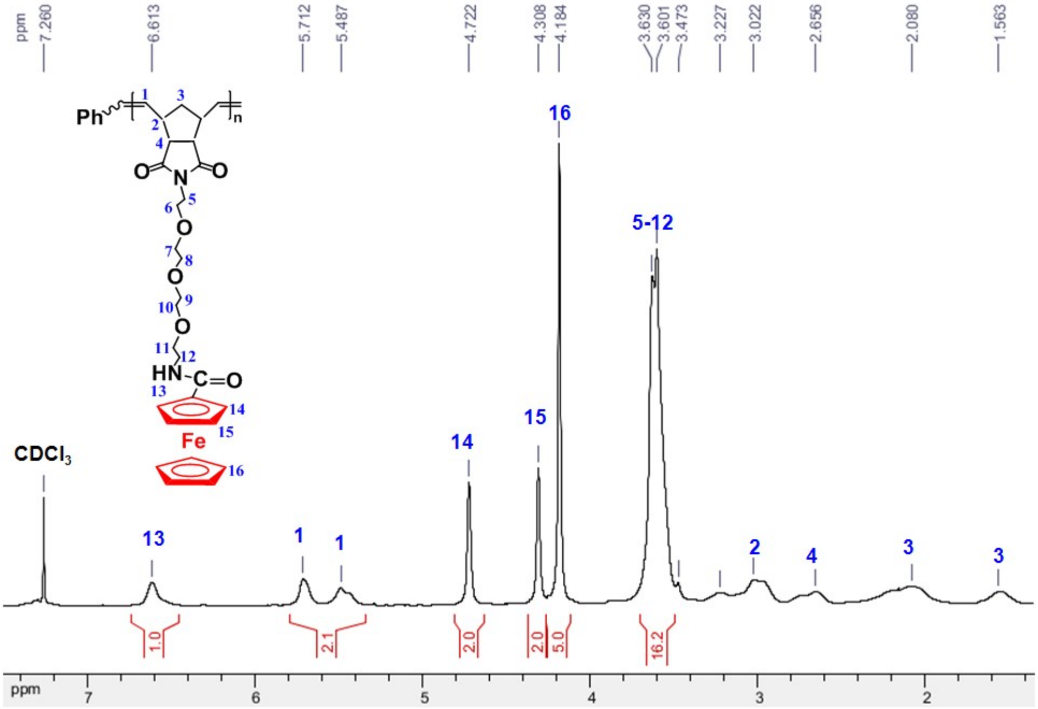


Figure S8 ^{1}H NMR spectrum (300 MHz) in $CDCl_3$ of the precipitate from the ROMP reaction mixture of monomer **7** after 5 minutes stirring. The precipitate is the purified homopolymer of **7**. There is no monomer **7** because no signal at 6.27 ppm or so was observed.

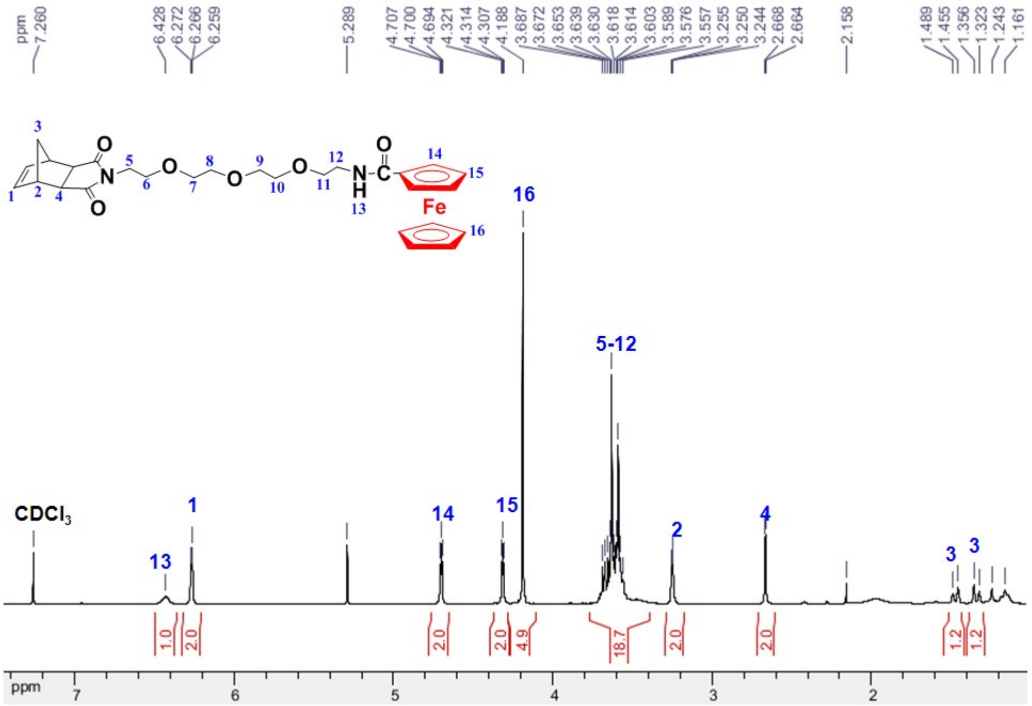


Figure S9 ^{1}H NMR spectrum (300 MHz) in $CDCl_3$ of products in filtrate and washing-liquors from the ROMP reaction mixture of monomer **7** after 5 minutes stirring. The ROMP of monomer **7** is not complete because the peaks for monomer **7** were observed.

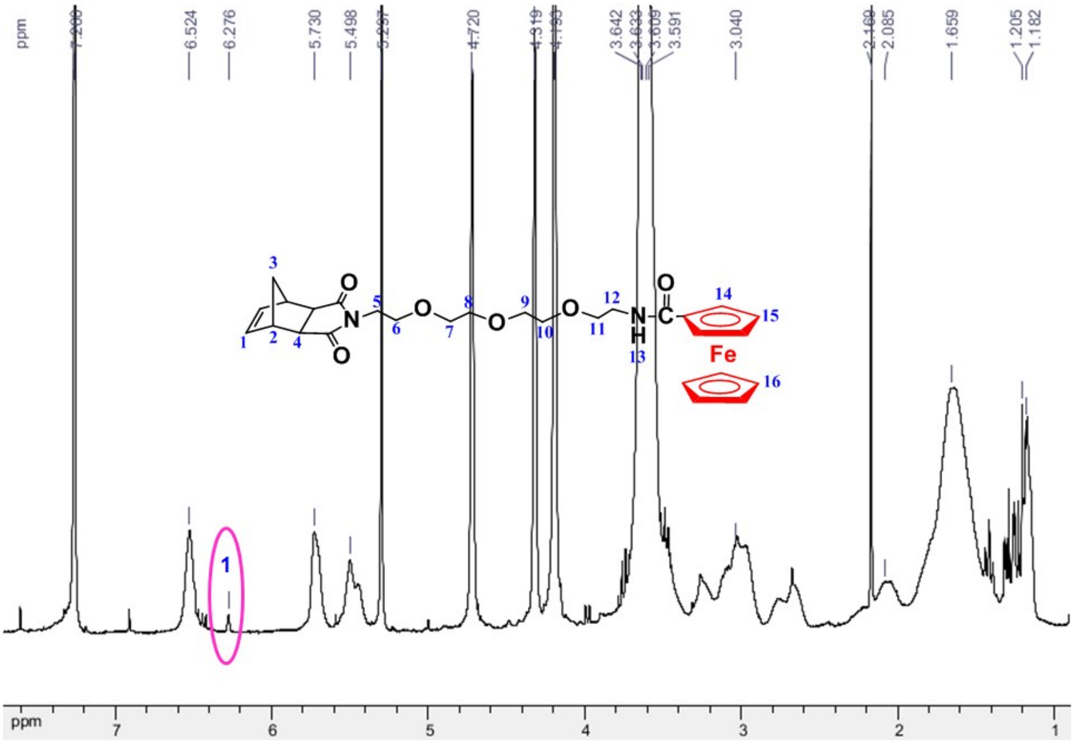


Figure S10 Enlarged ^{1}H NMR spectrum (300 MHz) in $CDCl_3$ of the ROMP reaction mixture of monomer **7** after 10 minutes stirring. The ROMP of monomer **7** is not complete because the small peak at 6.28 ppm for the olefinic protons of monomer **7** is still observed.

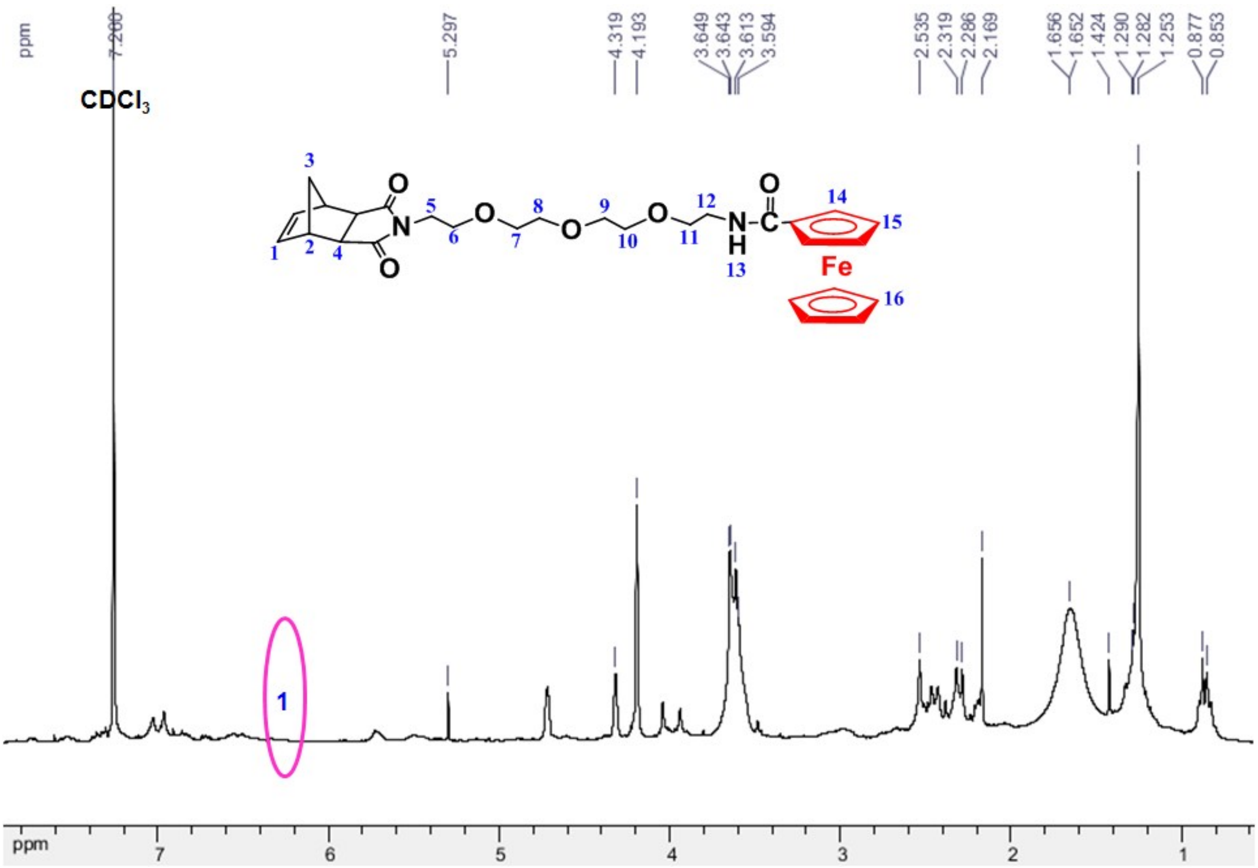


Figure S11 ^{1}H NMR spectrum (300 MHz) in $CDCl_3$ of products in filtrate and washing liquors from the ROMP reaction mixture of monomer **7** after 15 minutes stirring. The ROMP of monomer **7** is complete because no peak at 6.27 ppm or so for the olefinic protons of monomer **7** was found.

3. Synthesis and kinetic study of the ROMP of monomer 8[s3]

To a solution of pentamethylferrocene carboxylic acid (0.27 g, 0.90 mmol) in dry CH_2Cl_2 (40 mL), oxalyl chloride (0.40 mL, 4.5 mmol) was added dropwise at 0 °C under N_2 atmosphere. Then, the mixture was stirred overnight at 20 °C and dried *in vacuo*. The residual yellow-brown solid of crude chlorocarbonyl pentamethylferrocene was dissolved in dry CH_2Cl_2 (10 mL) and added dropwise to a CH_2Cl_2 solution (10 mL) of **5** (0.20 g, 0.59 mmol) and triethylamine (0.83 mL, 5.9 mmol). The obtained mixture was stirred overnight at 20 °C under N_2 atmosphere, then washed with 10% K_2CO_3 solution (50 mL) and distilled water (2 × 50 mL). The collected organic solution was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The product **8** was purified by using column chromatography with CH_2Cl_2/methanol (1 : 10 v/v) as eluent and obtained as a red-brown sticky oil (Yield: 0.32 g, 87.2%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS), δ_{ppm}: 6.23 (t, J = 3.7 Hz, 2H, CH=CH), 6.10 (t, J = 9.2 Hz, 1H, NHCO), 4.1 (t, J = 3.8 Hz, 2H, sub. Cp), 3.83 (t, J = 3.8 Hz, 2H, sub. Cp), 3.70-3.53 (m, 16H, 4×CH_2CH_2), 3.20 (t, J = 3.2 Hz, 2H, =CH-C***H***), 2.62 (d, J = 1.2 Hz, 2H, CO-CH), 1.78 (s, 15H, 5×CH_3), 1.43 (d, J = 9.8 Hz, 1H, CH_2-bridge), 1.31 (d, J = 9.8 Hz, 1H, CH_2-bridge). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS)), δ_{ppm}: 178.0 (CON), 169.2 (CONH), 137.8 (CH=CH), 81.1 (Cp*) (Cp* =η^5-C_5Me_5), 74.4 (sub. Cp), 70.6, 70.2, 70.0 (CH_2 and sub.Cp), 66.9 (-***C***H_2NH), 47.8 (CO-***C***H), 45.3 (=CH-***C***H), 42.7 (CH_2-bridge), 39.2 (***C***H_2-NCO), 37.7 (-***C***H_2CH_2-NCO), 10.5 (CH_3). MS (ESI *m/z*), calcd. for $C_{33}H_{44}N_2O_6Fe$: 620.6; found: 643.2 (M+Na$^+$).

Kinetic study of the ROMP of monomer 8

A kinetic study was carried out in order to determine the ROMP rate of monomer **8**. First, monomer **8** (0.52 g, 0.8384 mmol) in 5.0 mL dry CH_2Cl_2 was added into the solution of Grubbs 3rd generation catalyst **1** (0.0297 g, 0.0335 mmol) in 0.5 mL dry CH_2Cl_2. Then, the obtained reaction mixture was vigorously stirred at r. t. under N_2 atmosphere. At different intervals (10, 15, 30 and 60 minutes, respectively), a 0.5 mL sample of the reaction mixture was taken out, quenched with 0.2 mL of EVE, vacuumed and checked for the ^{1}H NMR spectrum in $CDCl_3$. The monomer conversion was deemed to be 100% when the signal of the olefin protons for monomer **8** at 6.23 ppm disappeared. It was found that the conversion of monomer **8** achieved 100% after 10 minutes stirring.

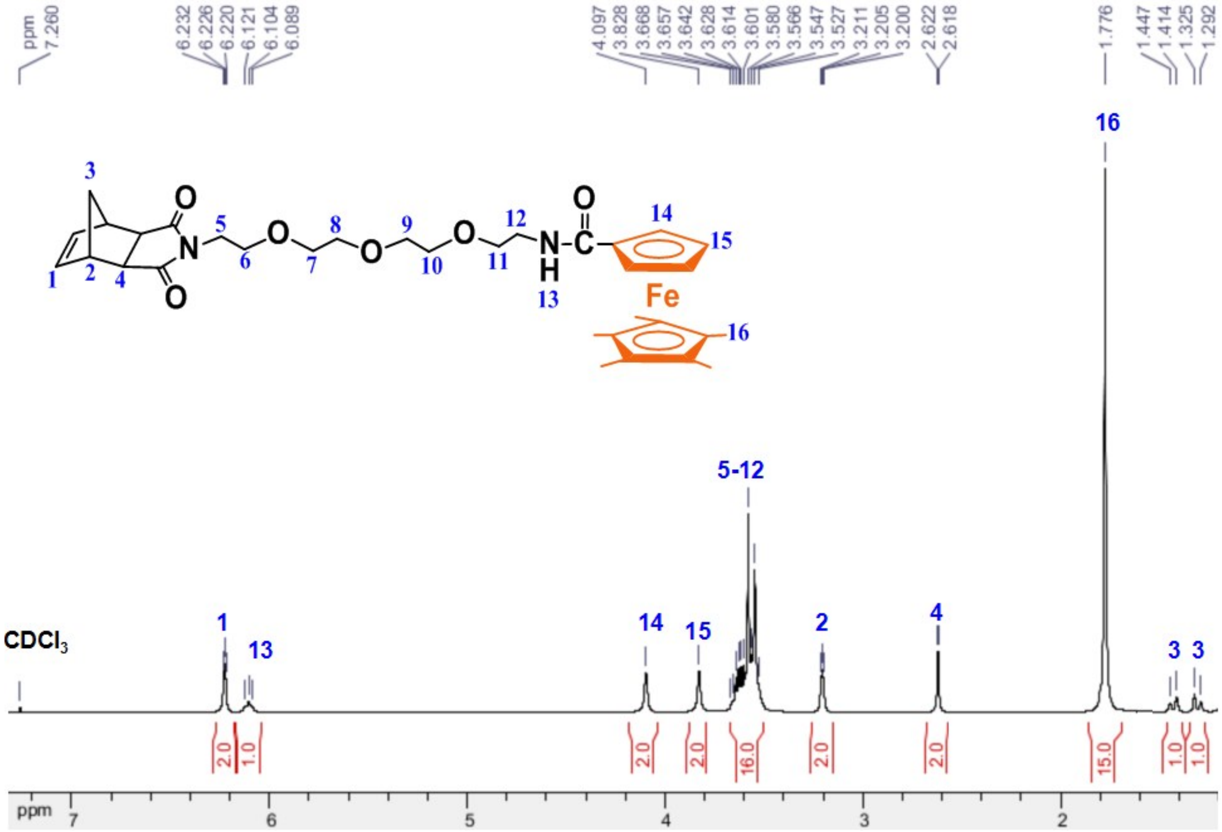


Figure S12 ^{1}H NMR spectrum of monomer **8** in CDCl$_3$.

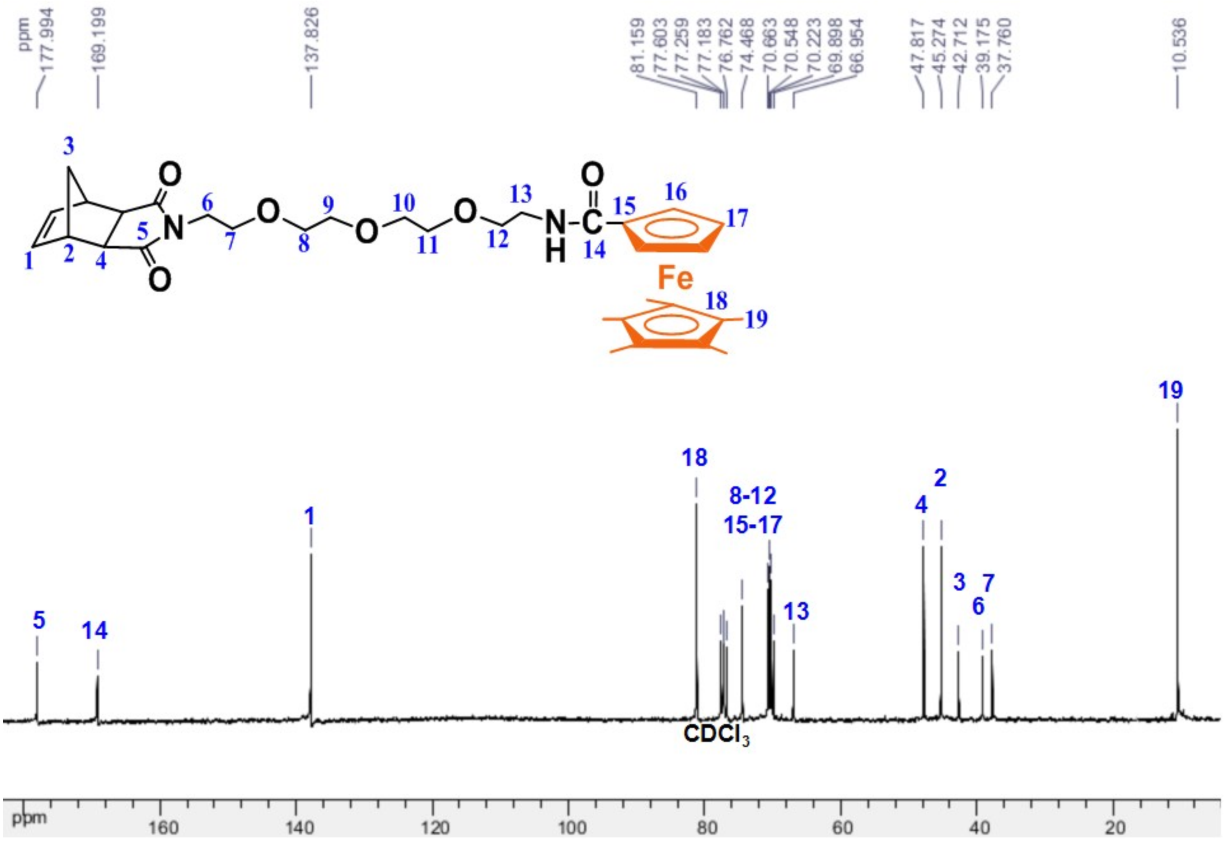


Figure S13 ^{13}C NMR spectrum of monomer **8** in CDCl$_3$.

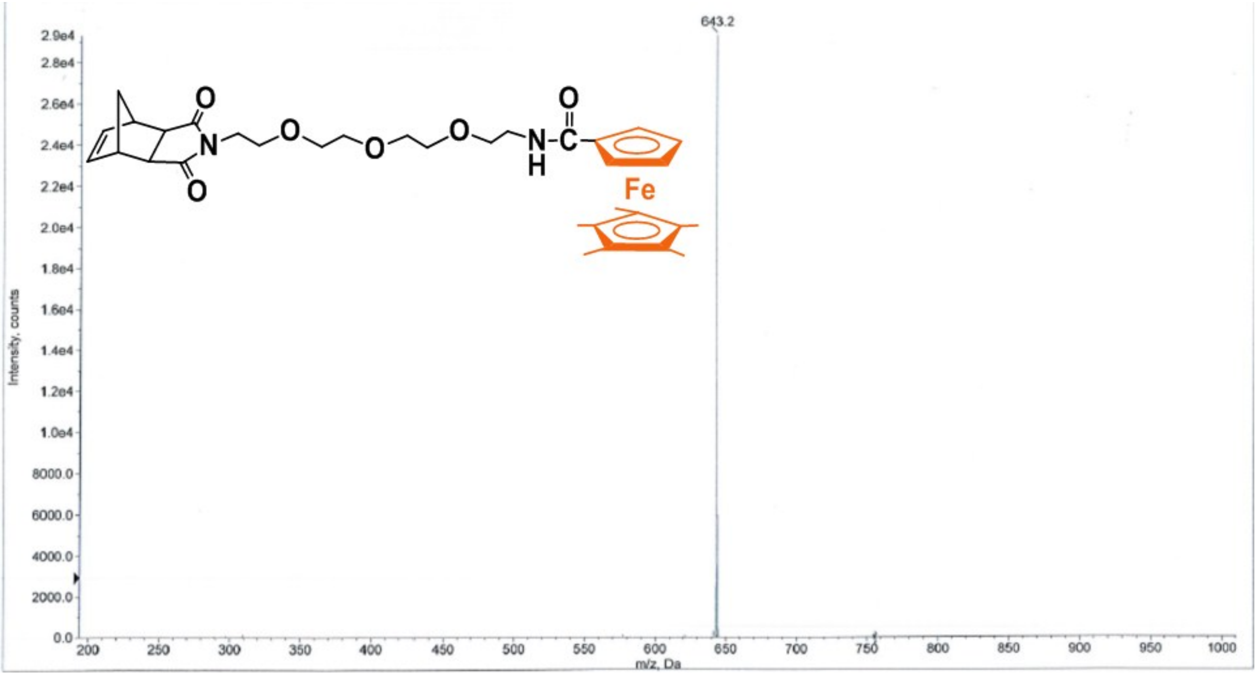


Figure S14 ESI mass spectrum of monomer **8**.

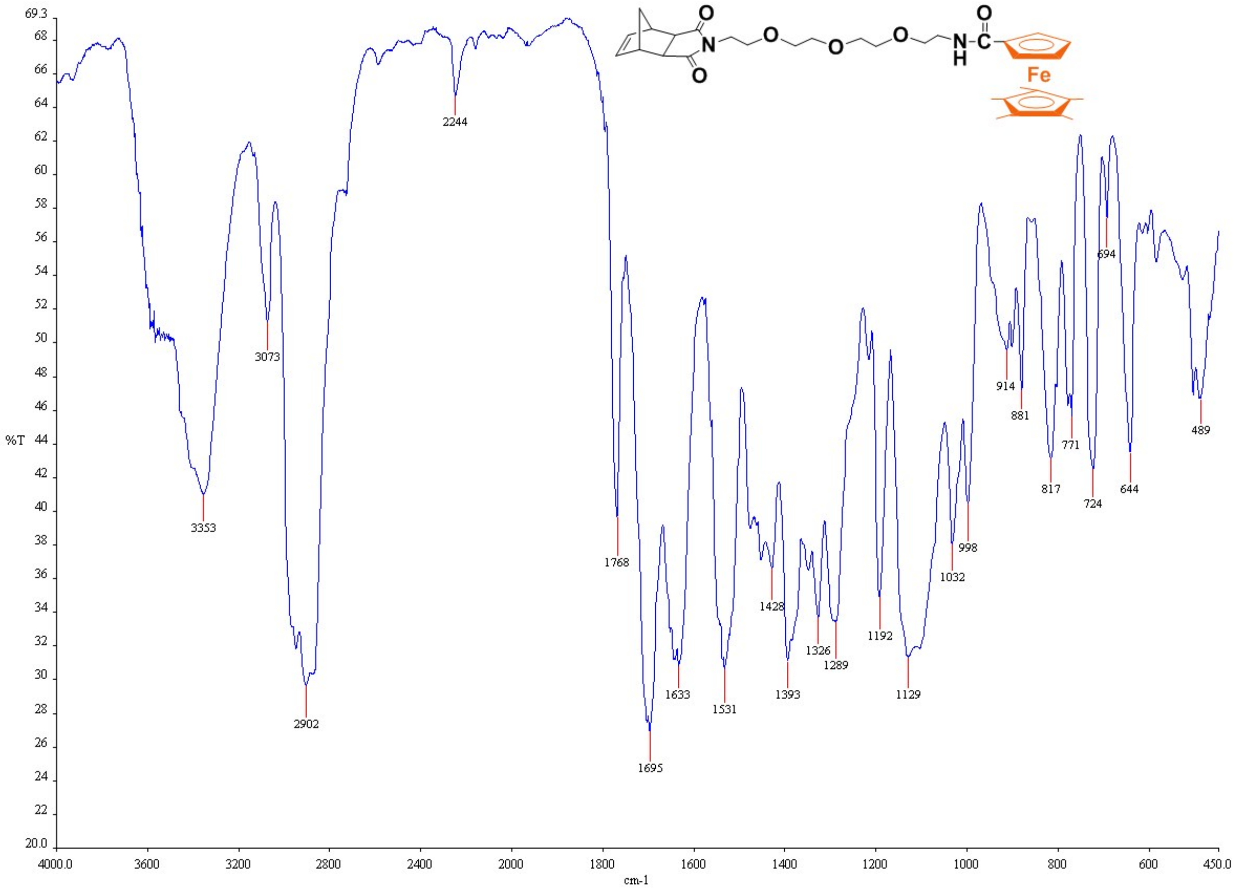


Figure S15 IR spectrum of monomer **8**.

3453 cm^{-1} (υ_{NH}), 2902 cm^{-1} (υ_{CH3}), 1768 cm^{-1} ($\upsilon_{C=C}$), 1695 cm^{-1} ($\upsilon_{NC=O}$), 1633 cm^{-1} ($\upsilon_{NHC=O}$), 817 cm^{-1}(υ_{FeII})

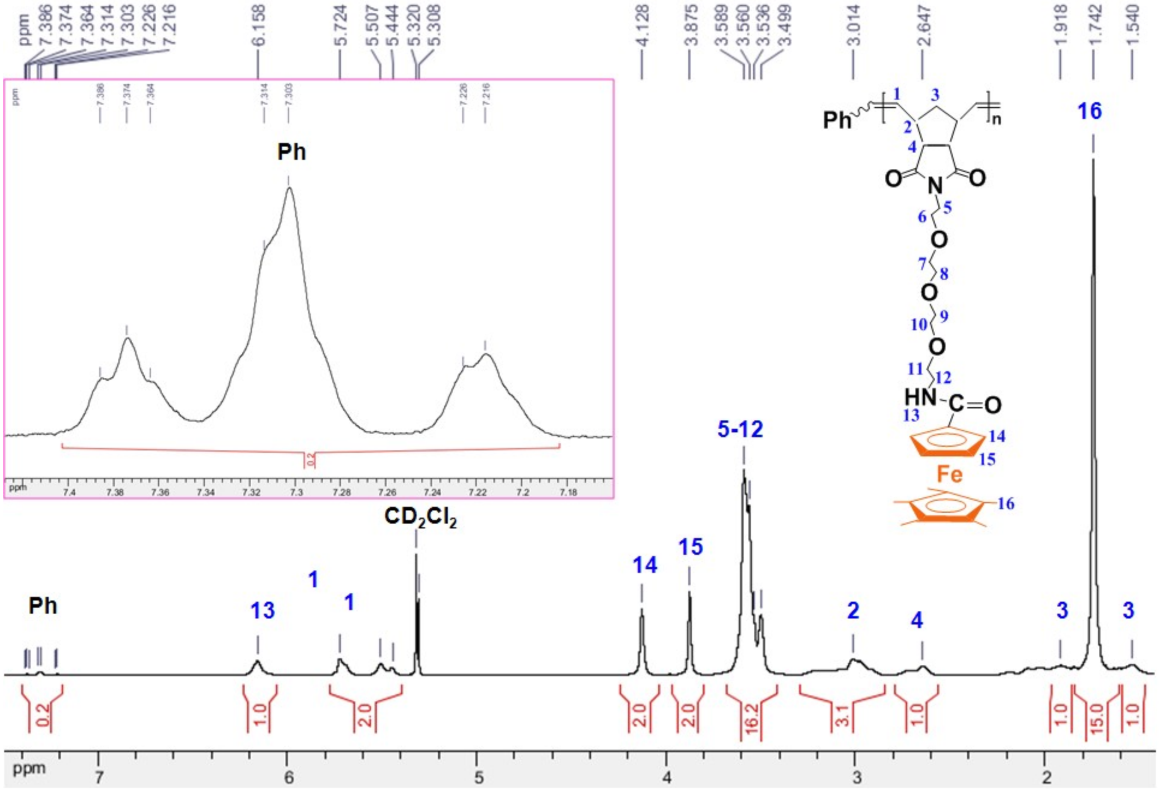


Figure S16 ^{1}H NMR spectrum of homopolymer of **8** in CD_2Cl_2.

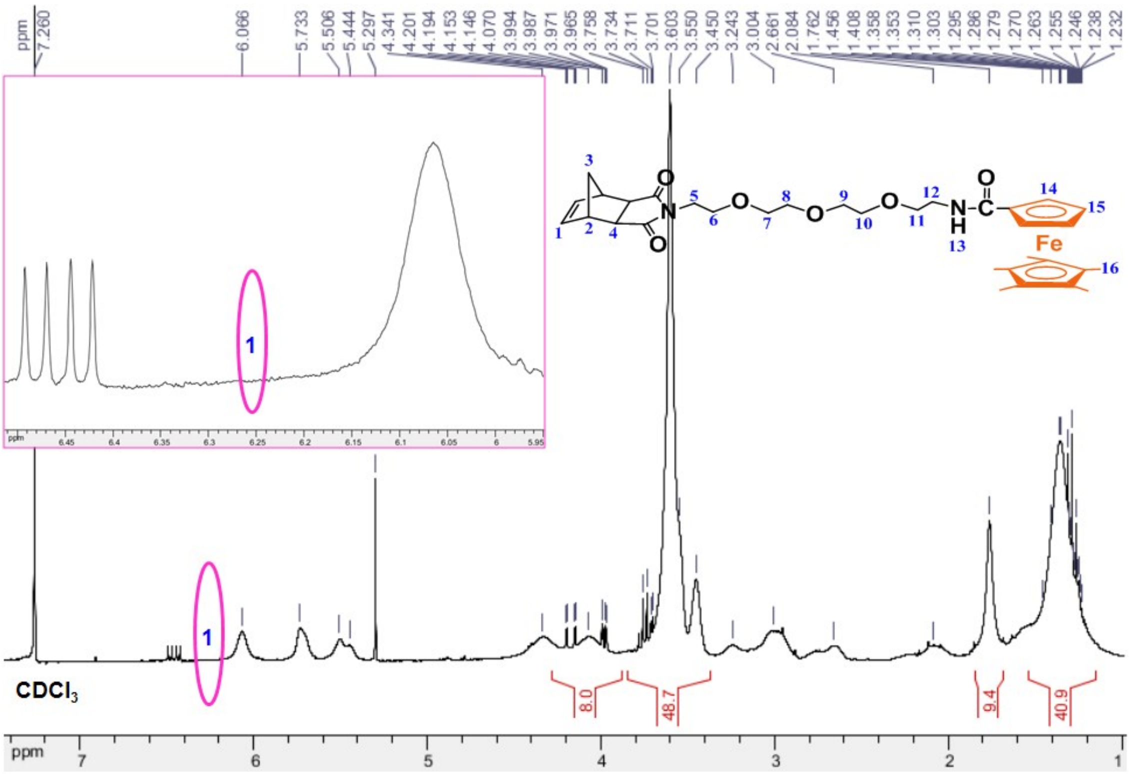


Figure S17 ^{1}H NMR spectrum (300 MHz) in $CDCl_3$ of the ROMP reaction mixture of monomer **8** after 10 minutes stirring. The ROMP of monomer **8** is complete because no peak at 6.23 ppm was observed.

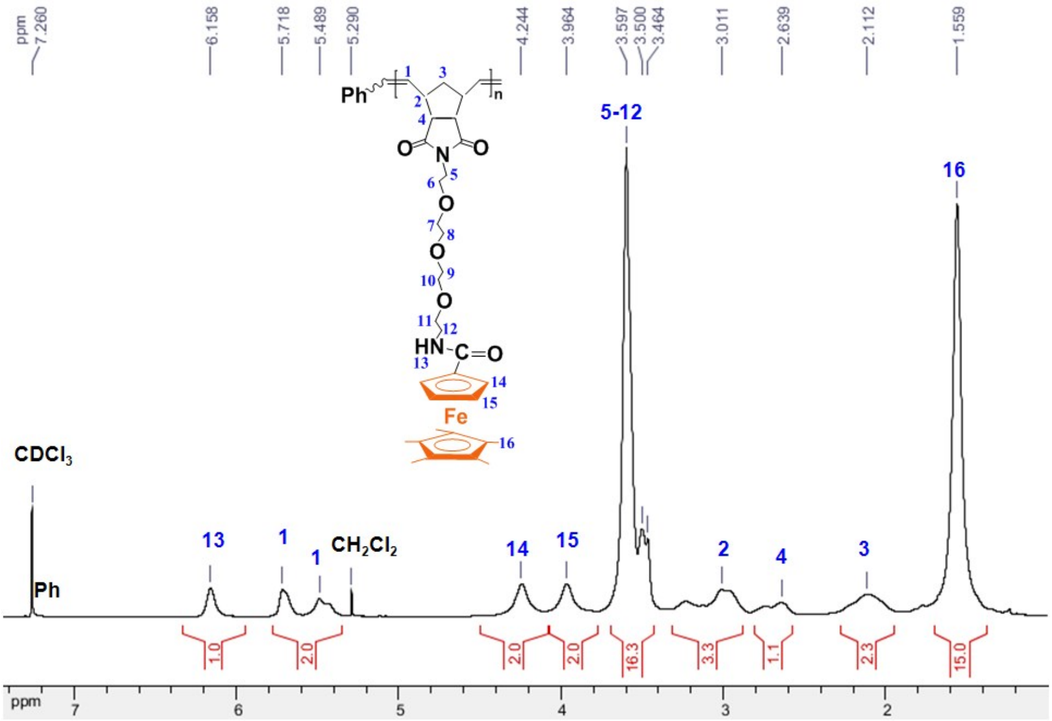


Figure S18 ^{1}H NMR spectrum (300 MHz) in CDCl$_3$ of methanol-washed products from the ROMP reaction mixture of monomer **8** after 10 minutes stirring. The product is the purified homopolymer of **8**. There is no monomer **8** because no signal at 6.23 ppm was observed.

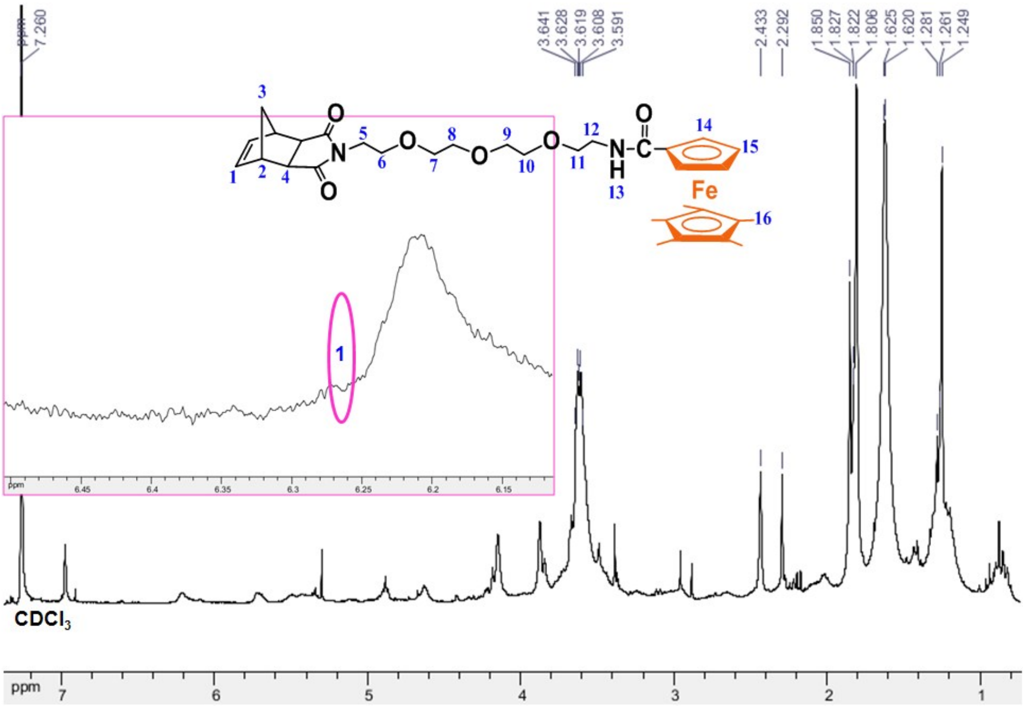


Figure S19 ^{1}H NMR spectrum (300 MHz) in CDCl$_3$ of products in the methanol washing-liquor from the ROMP reaction mixture of monomer **8** after 10 minutes stirring. The ROMP of monomer **8** is complete because no peak at 6.23 ppm for the olefinic protons of monomer **8** was found.

4. Synthesis and kinetic study of the ROMP of monomer 9[s6]

The carbonyl mixed-sandwich complex $[Fe(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_5H_4COOH)][PF_6]$ (0.687 g, 1.46 mmol) was refluxed in 50 mL of $SOCl_2$ under N_2 atmosphere for 48 h. Then, the excess $SOCl_2$ was removed using a trap-to-trap system under vacuum, and the resulting orange-red solid, which was the rude product of chlorocarbonyl complex $[Fe(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_5H_4COCl)][PF_6]$, was dissolved in 40 mL of dry CH_2Cl_2 under N_2 atmosphere. The mixture of *N*-(2-aminoethyl)-*cis*-5-norbornene-*exo*-2, 3-dicarboximide **6** (0.2 g, 0.97 mmol) and triethylamine (1.4 mL) in dry CH_2Cl_2 (10 mL) was added dropwise to the above solution, and the obtained mixture was stirred overnight at r. t. under N_2 atmosphere, then dried *in vacuo* to remove the solvent and excess triethylamine. The residual brown solid was dissolved in 80 mL CH_2Cl_2, washed with saturated $NaHCO_3$ solution (3 × 40 mL) and an aqueous solution of HPF_6 (5%, w/w, 1× 40 mL), respectively. The organic layer was separated, dried with anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum. The product was purified by precipitating from acetone with diethyl ether (Et_2O) to yield monomer **9** as a red-brown powder (0.545 g, 85% yield). ^1H NMR (300 MHz, acetone-d_6), δ_{ppm}: 1.24 (d, J = 9.7 Hz, 1H, CH_2-bridge), 1.40 (d, J = 9.6 Hz, 1H, CH_2-bridge), 2.51 (s, 18H, 6×CH_3), 2.68 (d, J = 1.3 Hz, 2H, CO-CH), 3.12 (t, J = 3.2 Hz, 2H, =CH-C***H***), 3.57-3.63 (m, 2H, CH_2), 3.66-3.71 (m, 2H, CH_2), 4.94 (s, 2H, sub. Cp), 5.10 (s, 2H, sub. Cp), 6.30 (t, J = 3.6 Hz, 2H, CH=CH), 7.77 (t, J = 9.6 Hz, 1H, NHCO). ^{13}C NMR (75 MHz, acetone-d_6), δ_{ppm}: 178.5 (CON), 164.2 (CONH), 138.5 (CH=CH), 100.3 (η^6-***C***$_6$Me$_6$), 85.0 (sub. Cp), 81.2 (sub. Cp), 77.2 (sub. Cp), 48.5 (CO-***C***H), 45.7 (=CH-***C***H), 43.4 (***C***H$_2$-bridge), 38.6 (***C***H$_2$-NCO), 38.5 (***C***H$_2$-NH-CO), 17.0 (-CH_3). MS (ESI *m/z*), calcd. For $C_{29}H_{35}N_2O_3Fe$: 515.1991; found: 515.1984 (M^+).

Kinetic study of the ROMP of monomer 9

A kinetic study was carried out in order to determine the ROMP rate of the cationic organoiron monomer **9**. Firstly, monomer **9** (0.454 g, 0.688 mmol) in 4.0 mL dry DMF was added into the solution of Grubbs 3rd generation catalyst **1** (0.0243 g, 0.0275 mmol) in 0.5 mL dry DMF. Then, the obtained reaction mixture was vigorously stirred at r. t. under N_2 atmosphere. At different intervals (0.5 h, 1 h and 2 h, and overnight (12h), respectively), 0.5 mL of the reaction mixture was taken out, quenched with 0.2 mL of EVE, precipitated by adding 2 mL of Et_2O. The obtained precipitate was washed with Et_2O (3 × 2 mL) and then CH_2Cl_2 (3 × 2 mL). All the washing liquors and filtrate were collected, the solvent was removed *in vacuo*, and the ^1H NMR spectrum of the residue was recorded in acetone-d_6. The monomer conversion was deemed to be 100% when the signal of the olefin protons of monomer **9** at 6.30 ppm disappeared. It was found that the conversion of monomer **9** reached 100% only after stirring overnight (i. e. 12 h).

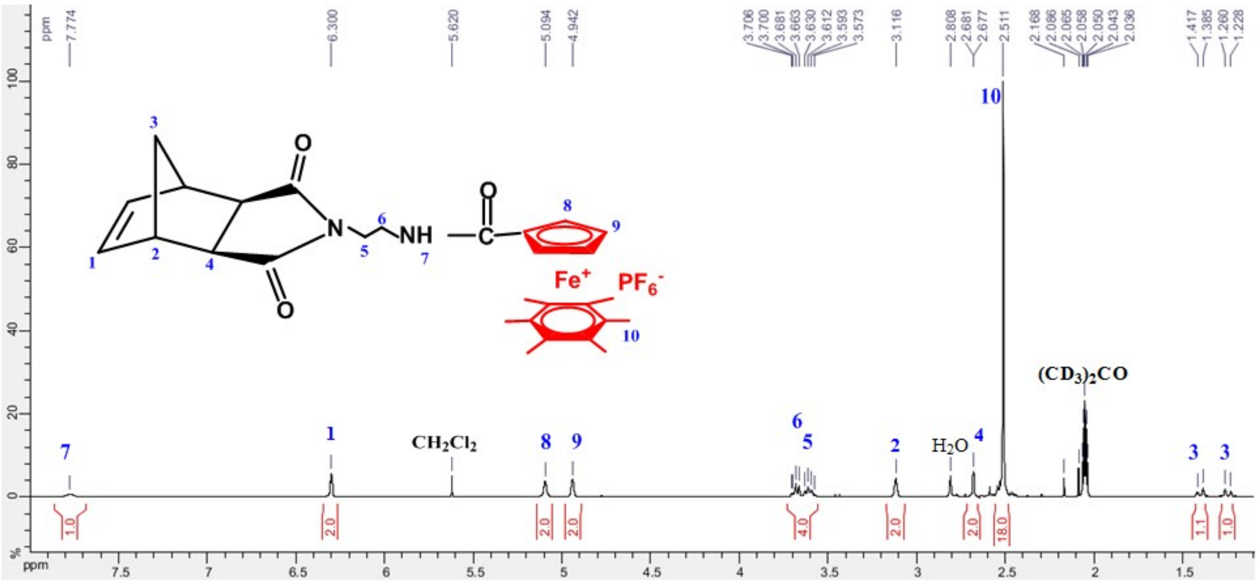


Figure S20 ^{1}H NMR spectrum of monomer **9** in acetone-d_6.

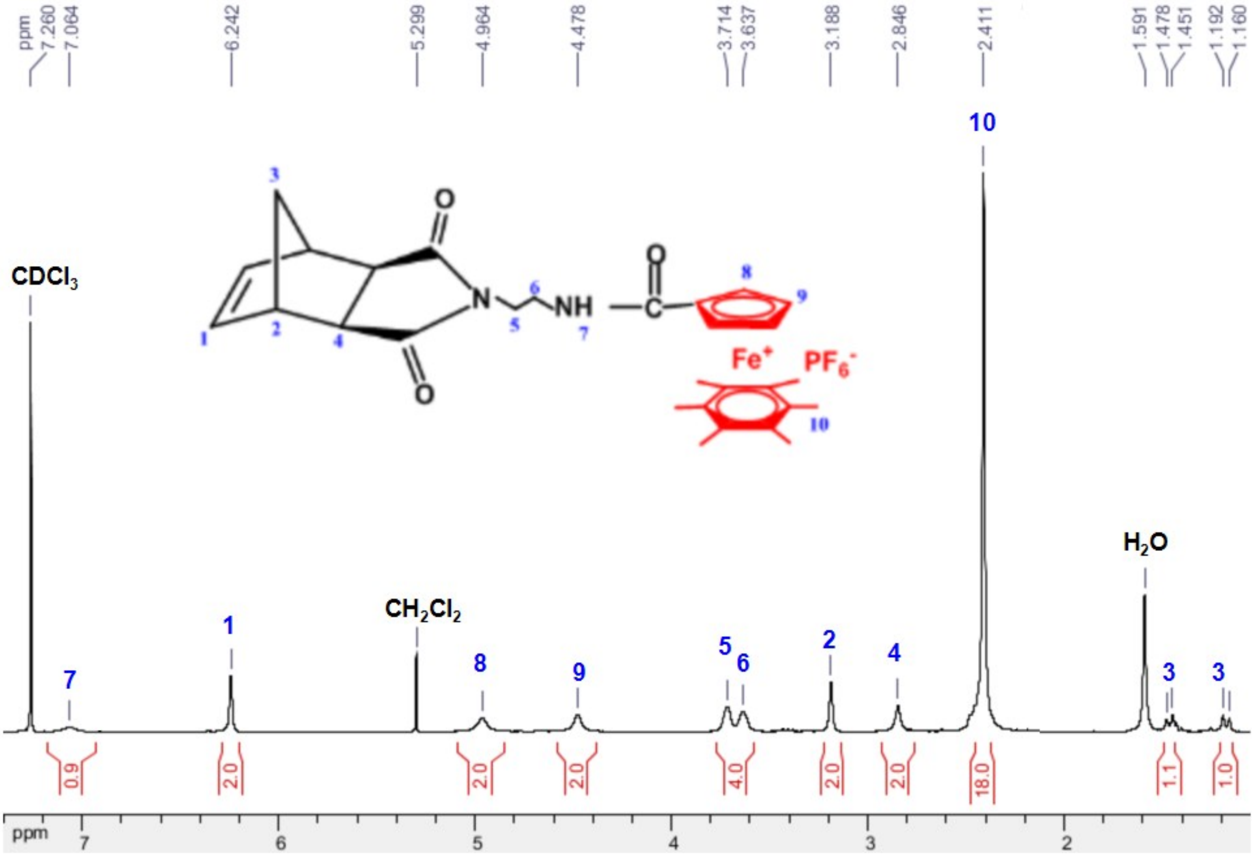


Figure S21 ^{1}H NMR spectrum of monomer **9** in $CDCl_3$.

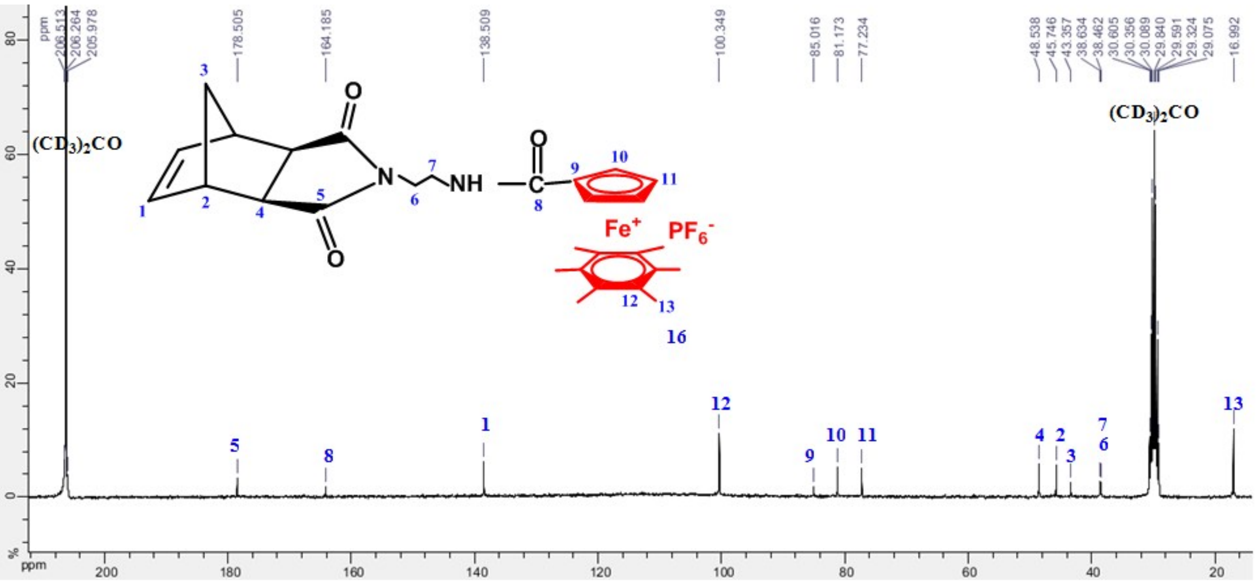
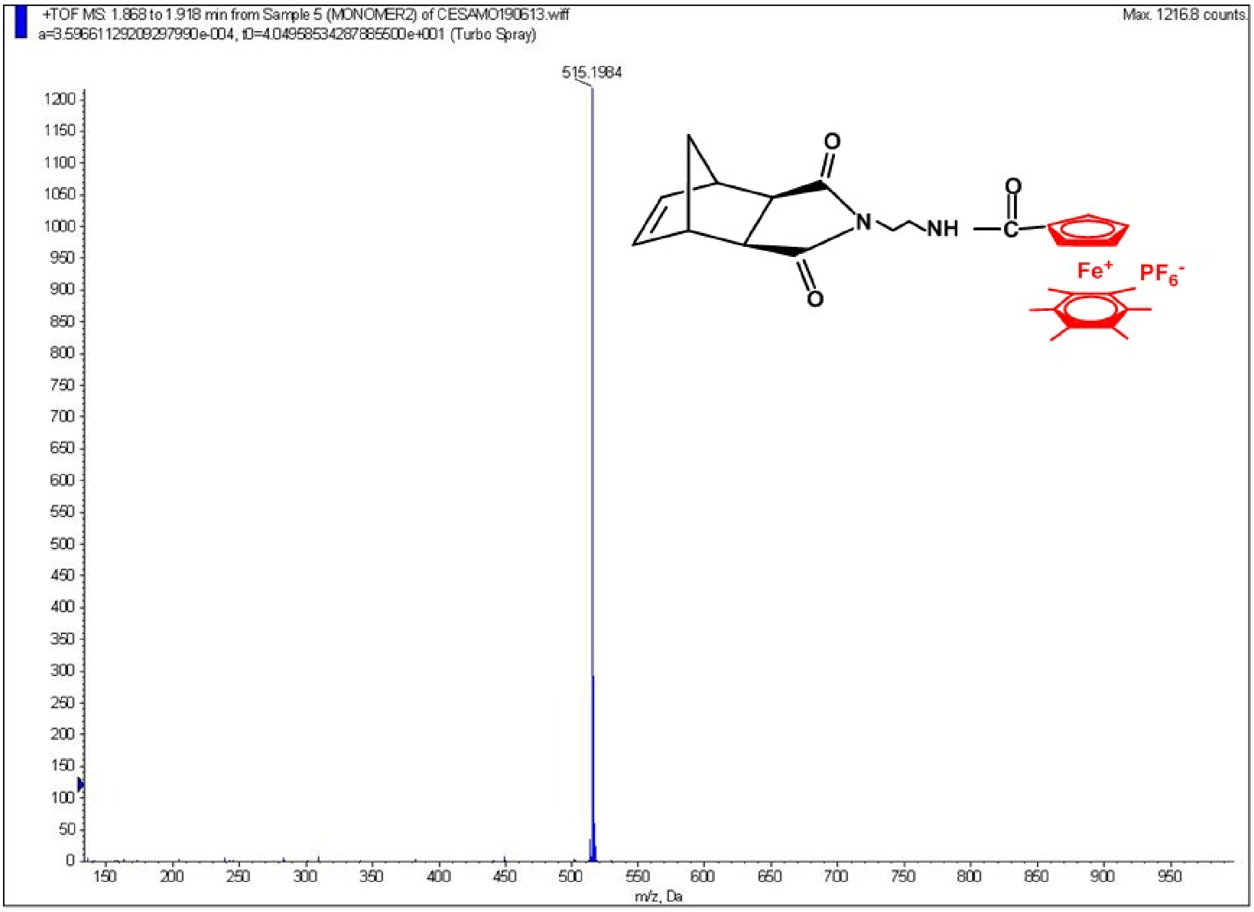


Figure S22 ^{13}C NMR spectrum of monomer **9** in acetone-d_6.



+TOF MS: 1.868 to 1.918 min from Sample 5 (MONOMER2) of CESAMO190613.wiff
a=3.59661129209297990e-004, t0=4.04958534287885500e+001 (Turbo Spray)

Max. 1216.8 counts.

Figure S23 ESI mass spectrum of monomer **9**.

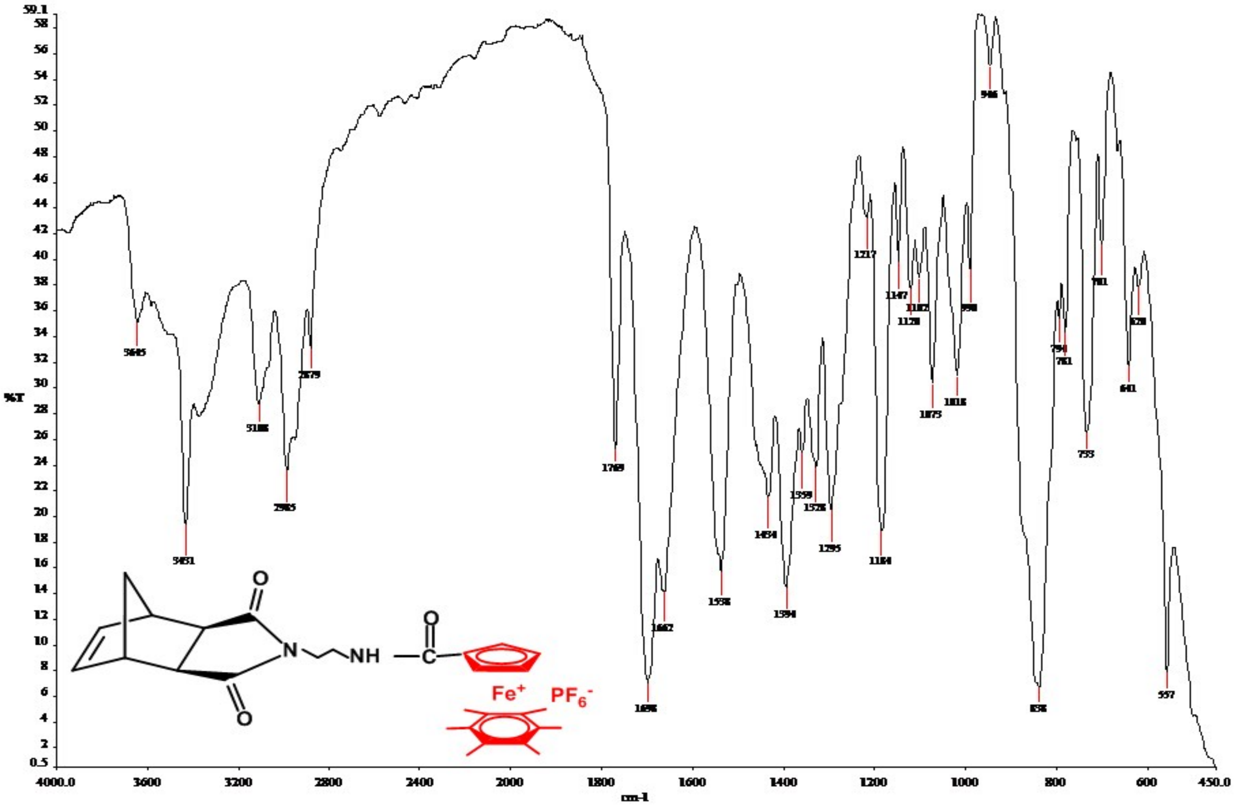


Figure S24 IR spectrum of monomer **9**.

3431 cm^{-1} (υ_{NH}), 2985 cm^{-1} (υ_{CH3}), 1769 cm^{-1} ($\upsilon_{C=C}$), 1698 cm^{-1} ($\upsilon_{NC=O}$), 1662 cm^{-1} ($\upsilon_{NHC=O}$), 838 cm^{-1} (υ_{PF6}).

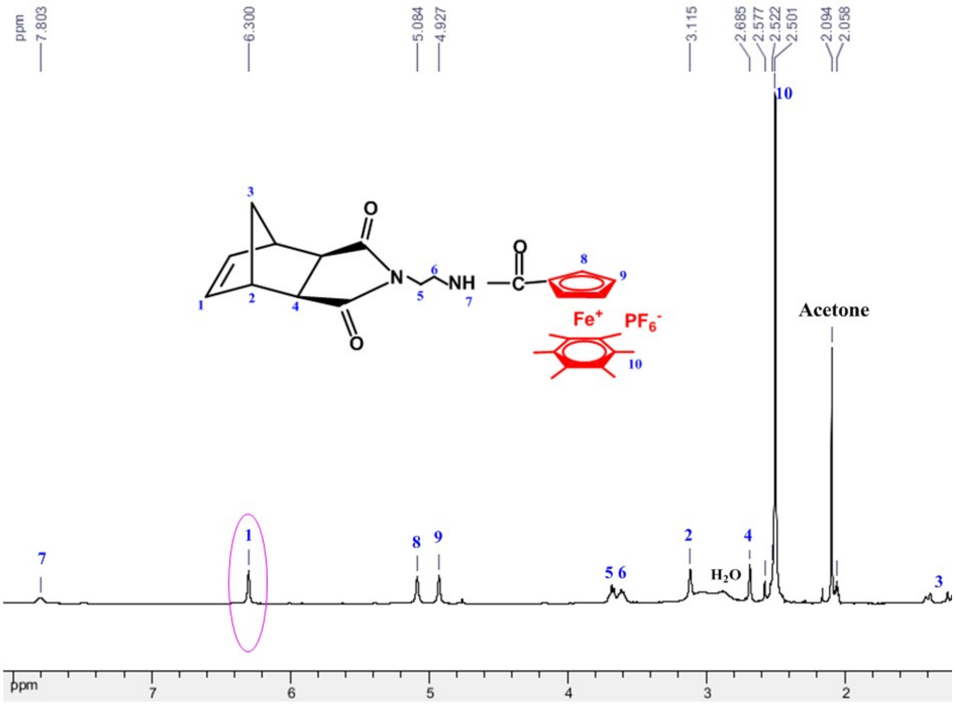


Figure S25 ^{1}H NMR spectrum (300 MHz) in acetone-d_6 of products in filtrate and washing-liquors from the ROMP reaction mixture of monomer **9** after 1 h stirring. The peak in pink circle corresponds to the olefin protons of monomer **9**.

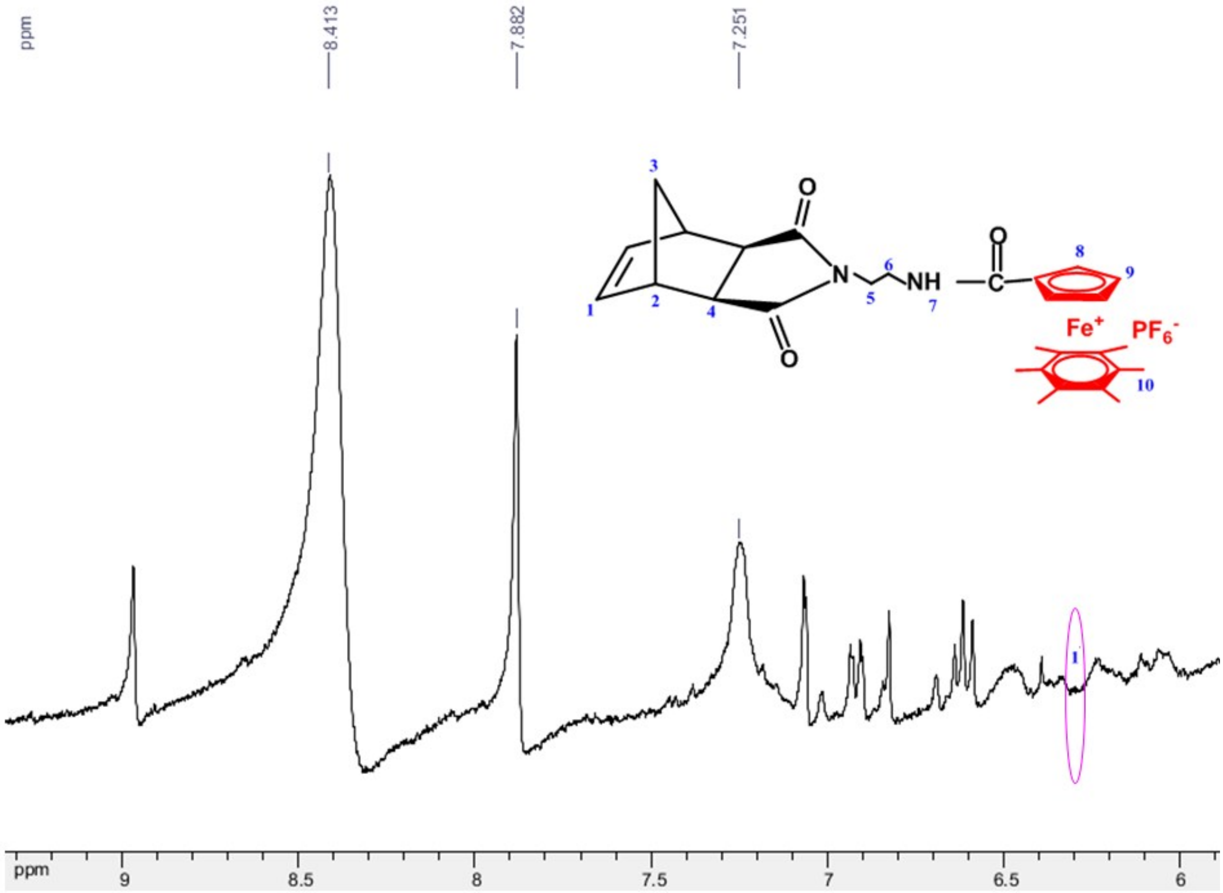


Figure S26 Enlarged ^1H NMR spectrum (300 MHz) in acetone-d_6 of products in filtrate and washing-liquors from the ROMP reaction mixture of monomer **9** after overnight stirring. No peak was observed at 6.30 ppm. Peaks at 8.41-6.61 probably arise from the protons of catalyst **1** and DMF or/ and noise.

5. Diblock copolymer 11

Synthesis

Monomers **7** (36.7 mg, 0.067 mmol) and **9** (44.0 mg, 0.067 mmol) were added into two separate small glass tubes, and dissolved in 0.4 mL and 0.6 mL of dry CH_2Cl_2, respectively. A desired amount of Grubbs catalyst 3rd **1** (2.36 mg, 0.0027 mmol) was added into a small Schlenk flask, flushed with nitrogen, and dissolved in 0.03 mL of dry CH_2Cl_2. First, monomer **7** was transferred to the flask containing the catalyst via a small syringe. The reaction mixture was stirred vigorously for 15 minutes at r. t., after which monomer **9** was added into the flask using a small syringe. The polymerization was allowed to continue for another 10 minutes, and then quenched with 0.2 mL of EVE. The yellow-brown solid polymer **11** was purified by precipitating from CH_2Cl_2 with Et_2O three times and dried *in vacuo* until constant weight. Yield: 95%. ^1H NMR (300 MHz, CD_2Cl_2), δ_{ppm}: 7.39-7.22 (m, N***H***CO-(η^5-C_5H_4)Fe(η^6-C_6Me_6) and phenyl), 6.51 (broad, 1H, N***H***CO-Fc), 5.72 and 5.51 (double broad, CH=CH), 4.70 (s, sub. Cp of Fc), 4.32 (s, sub. Cp of Fc), 4.19 (s, free Cp of Fc), 3.61-3.41 (m, $CH_2(CH_2OCH_2)_3CH_2$ and NCH_2CH_2N), 3.02 (broad, =CH-C***H***), 2.65 (broad, CO-C***H***), 2.38 (s, $C\boldsymbol{H_3}$ of (η^6-C_6Me_6)), 2.03 (broad, CH=CHCHC$\boldsymbol{H_2}$).

Kinetic Study

In order to know when the polymerization of the second FbX block finishes, the kinetic study was conducted as following: monomer **7** (0.482 g, 0.876 mmol) in 4 mL dry CH_2Cl_2 was added into the solution of Grubbs catalyst 3rd **1** (0.031 g, 0.035 mmol) in 0.3 mL dry CH_2Cl_2. The reaction mixture was stirred vigorously for 15 minutes at r. t. under N_2 atmosphere. Then, monomer **9** (0.578 g, 0.876 mmol) in 6 mL dry CH_2Cl_2 was added, and after 10, 15, 20, and 30 minutes, respectively, 0.5 mL of samples were taken out, quenched with 0.5 mL of EVE, and vacuumed. The *in situ* ^1H NMR analysis in $CDCl_3$ or acetone-d_6 was conducted, and the conversion of monomer **9** was deemed to be 100% when the peak at 6.24 or 6.30 ppm, the signal of olefinic protons for monomer **9**, disappeared. Actually, the polymerization of the second block finishes in 10 minutes with 100% monomer conversion.

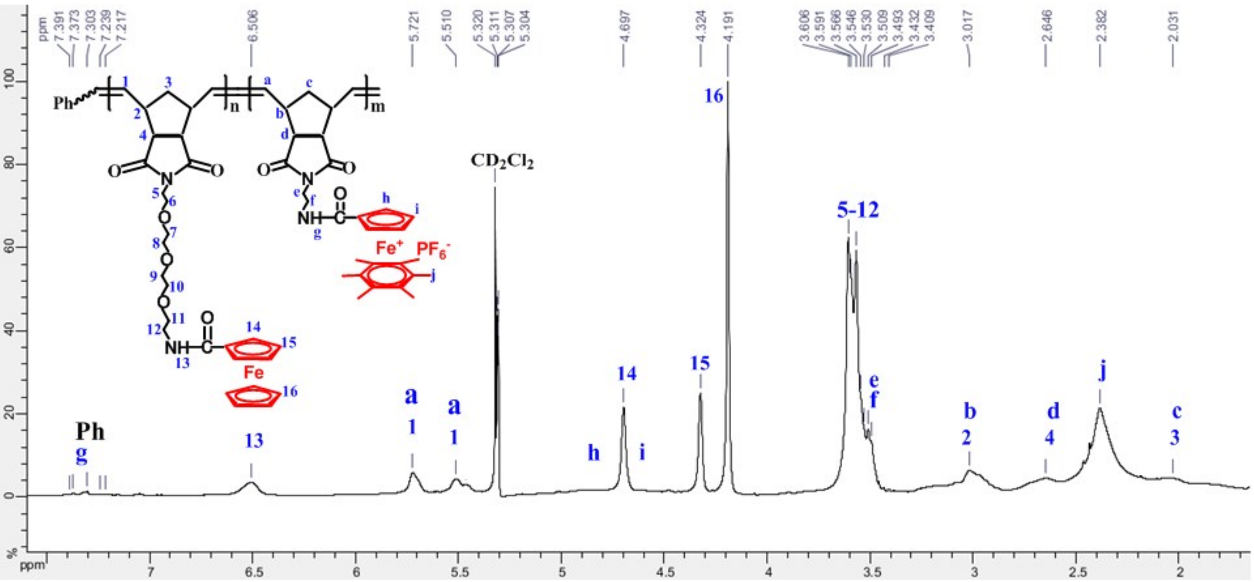


Figure S27 ¹H NMR spectrum of diblock copolymer **11** in CD_2Cl_2.

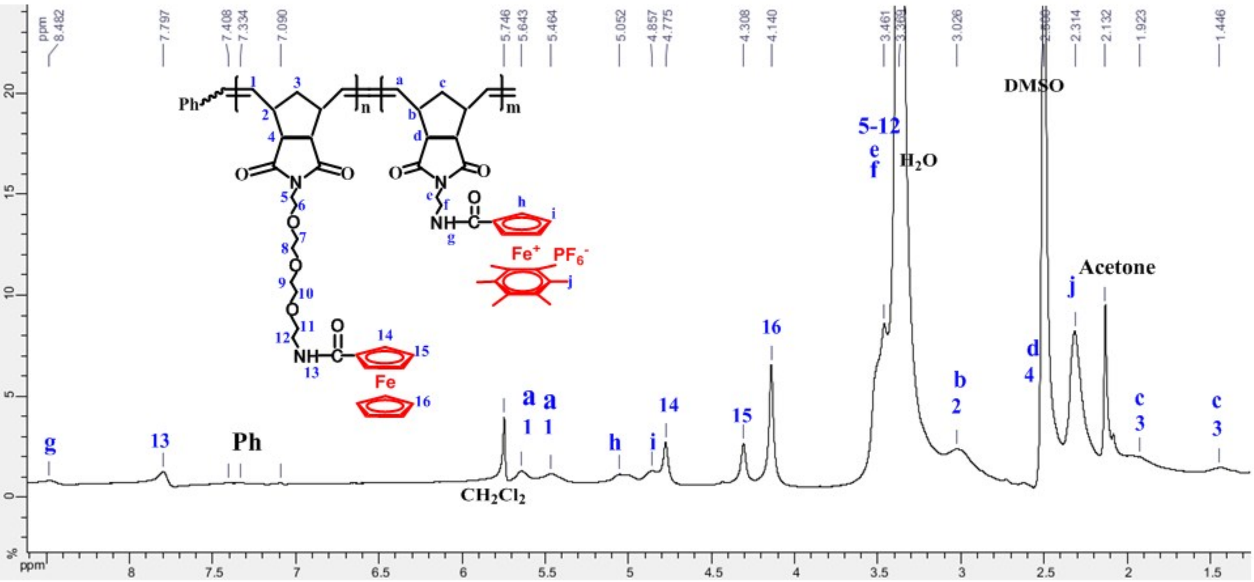


Figure S28 ¹H NMR spectrum of diblock copolymer **11** in DMSO-d_6.

¹H NMR (300 MHz, DMSO-d_6), δ_{ppm}: 8.48 (broad, N***H***CO-(η^5-C_5H_4)Fe(η^6-C_6Me_6)), 7.80 (s, N***H***CO-Fc), 7.41-7.09 (m, phenyl), 5.64 and 5.46 (double broad, CH=CH), 5.05 (broad, sub. Cp of (η^5-C_5H_4)Fe(η^6-C_6Me_6)), 4.86 (broad, sub. Cp of (η^5-C_5H_4)Fe(η^6-C_6Me_6)), 4.78 (s, sub. Cp of Fc), 4.31 (s, sub. Cp of Fc), 4.14 (s, free Cp of Fc), 3.46-3.37 (broad, $CH_2(CH_2OCH_2)_3CH_2$, H_2O and NCH_2CH_2N),3.03 (broad, =CH-C***H***), 2.50 (broad, DMSO and CO-C***H***), 2.31 (s, C$\boldsymbol{H_3}$ of η^6-C_6Me_6), 1.92 (broad, CH=CHCHC$\boldsymbol{H_2}$), 1.45 (broad, CH=CHCHC$\boldsymbol{H_2}$).

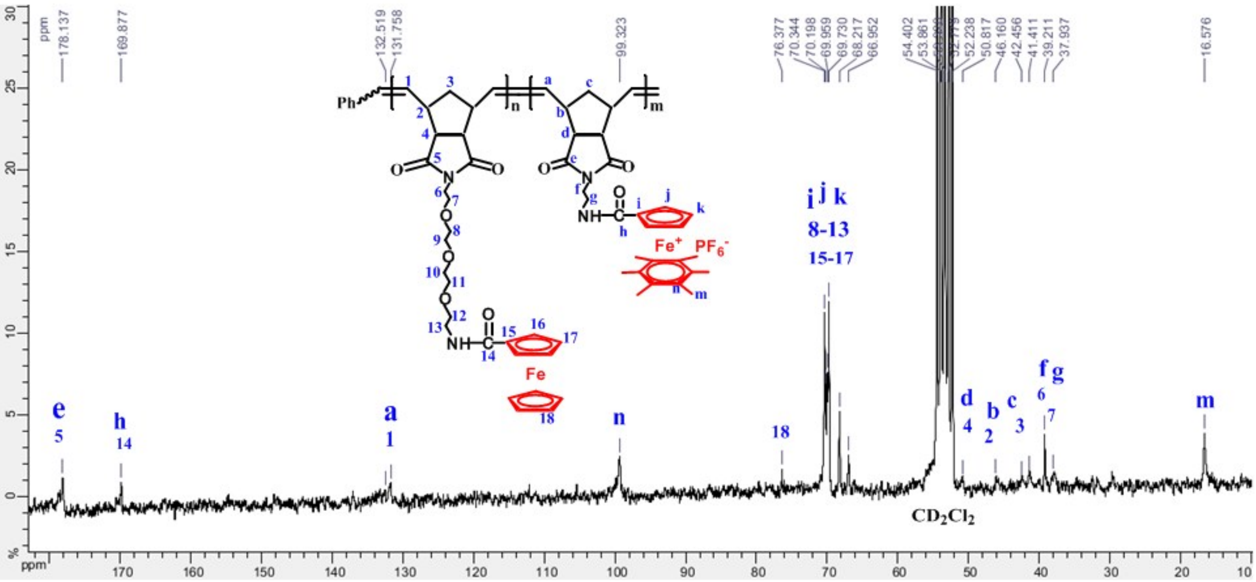


Figure S29 ^{13}C NMR spectrum of diblock copolymer **11** in CD_2Cl_2.

^{13}C NMR (50 MHz, CD_2Cl_2), δ_{ppm}: 178.1 (CON), 169.9 (CONH), 132.5, 131.758 (C=C), 99.3 (η^6-***C***$_6$Me$_6$), 76.4 (free Cp), 70.3, 70.2, 70.0, 69.7, 68.2, 68.9 (CH_2 and sub. Cp),50.9 (CO-***C***H and =CH-***C***H), 46.2 (CH_2 of cyclopentane), 42.5, 41.4 (***C***H_2-NCO), 39.2, 37.9 (-***C***H_2CH_2NCO), 16.6 (***C***H_3 of η^6-C_6Me_6).

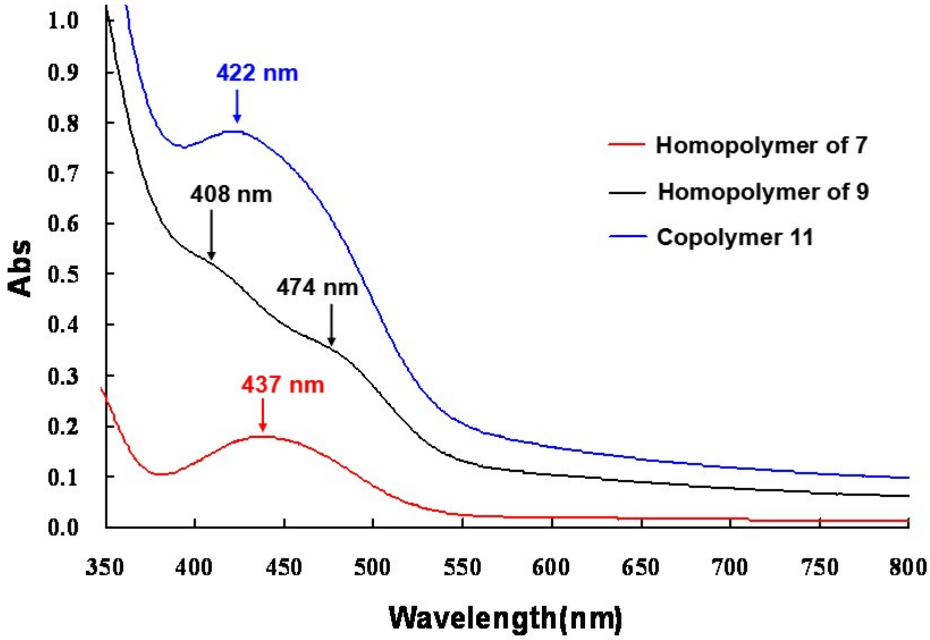


Figure S30 UV-vis. spectra of diblock copolymer **11**, Fc-containing homopolymer of **7** and FbX-containing homopolymer of **9** in CH_2Cl_2.

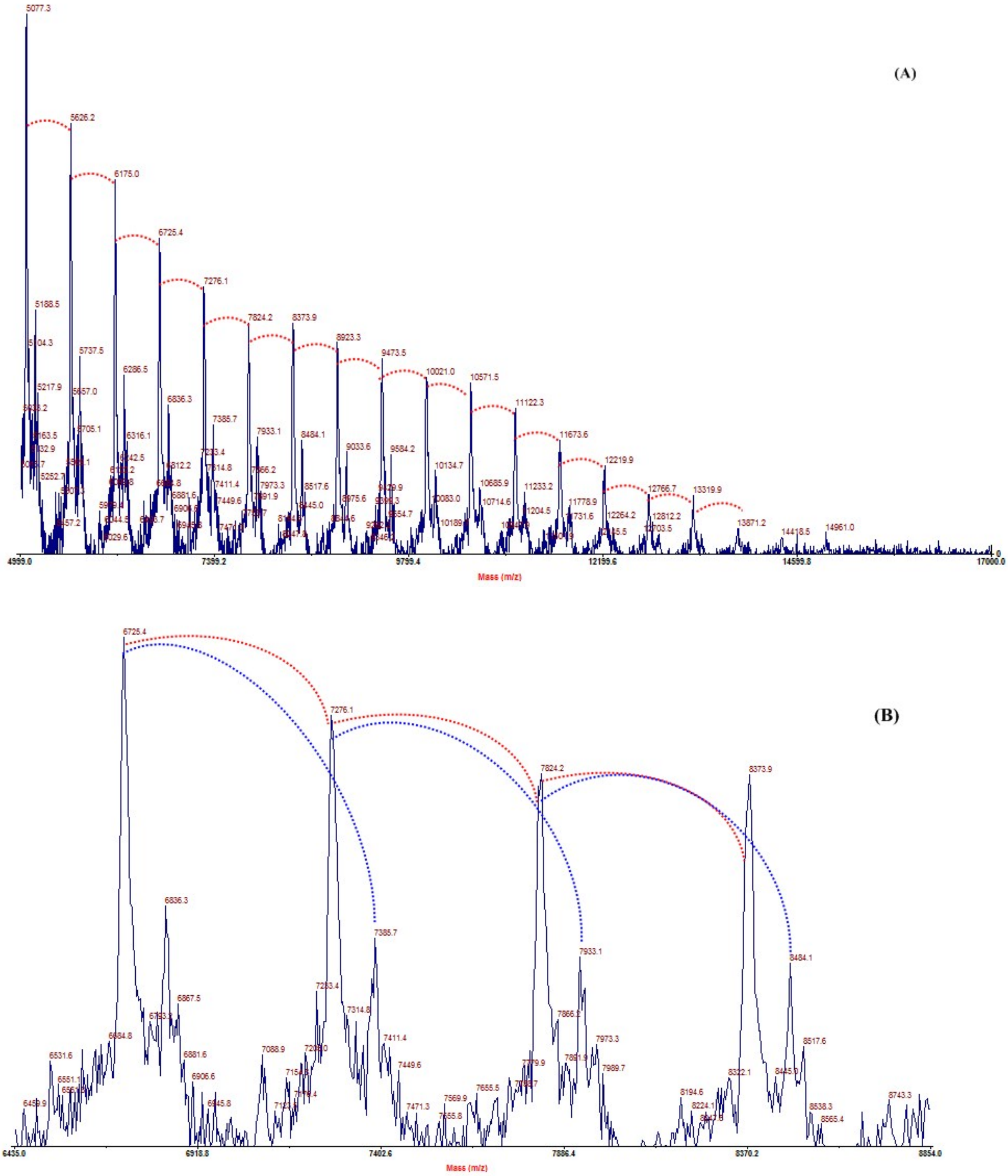


Figure S31 MALDI-TOF MS spectrum of diblock copolymer **11**. The feed molar ratio of monomers **7** and **9** to **1** is 25 : 25 : 1. (A) is the region of 5000-17000 in the spectrum; and (B) is the enlarged region of the spectrum from 6435 to 8854. The red dotted lines correspond to the difference between molecular peaks of a value of 550 ±1 Da (MW of monomer **7**). The blue dotted lines correspond to the difference between molecular peaks of a value of 660 ±1 Da (MW of monomer **9**).

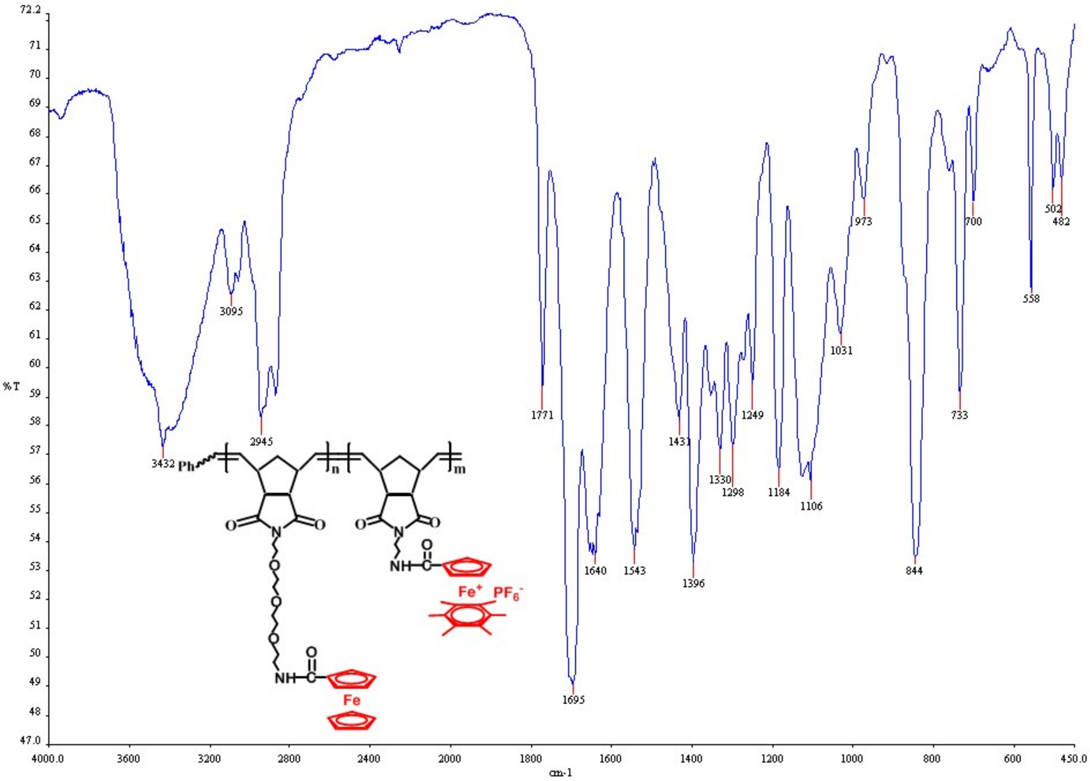


Figure S32 IR spectrum of diblock copolymer **11**.
3432 cm^{-1} (NH), 2945 cm^{-1} (CH_3), 1771 cm^{-1} (C=C), 1695 cm^{-1} (NC=O), 1640 cm^{-1} (NHC=O), 844 cm^{-1} (PF_6).

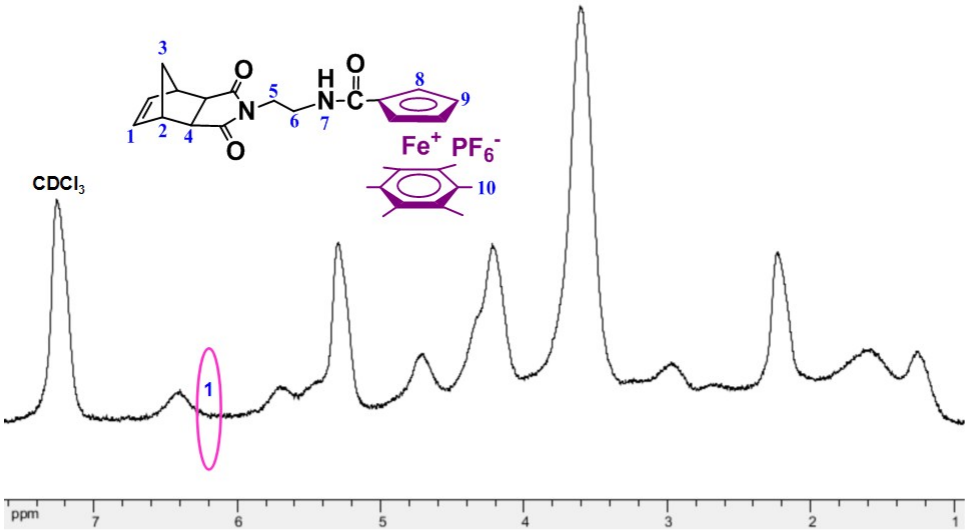


Figure S33 ^{1}H NMR spectrum (300 MHz) in $CDCl_3$ of the ROMP reaction mixture for the synthesis of diblock copolymer **11** after the addition of monomer **9** with 10 minutes stirring. No peak was observed at 6.24 ppm for the olefin protons of monomer **9**, namely no monomer **9** was left and the ROMP of **9** is complete.

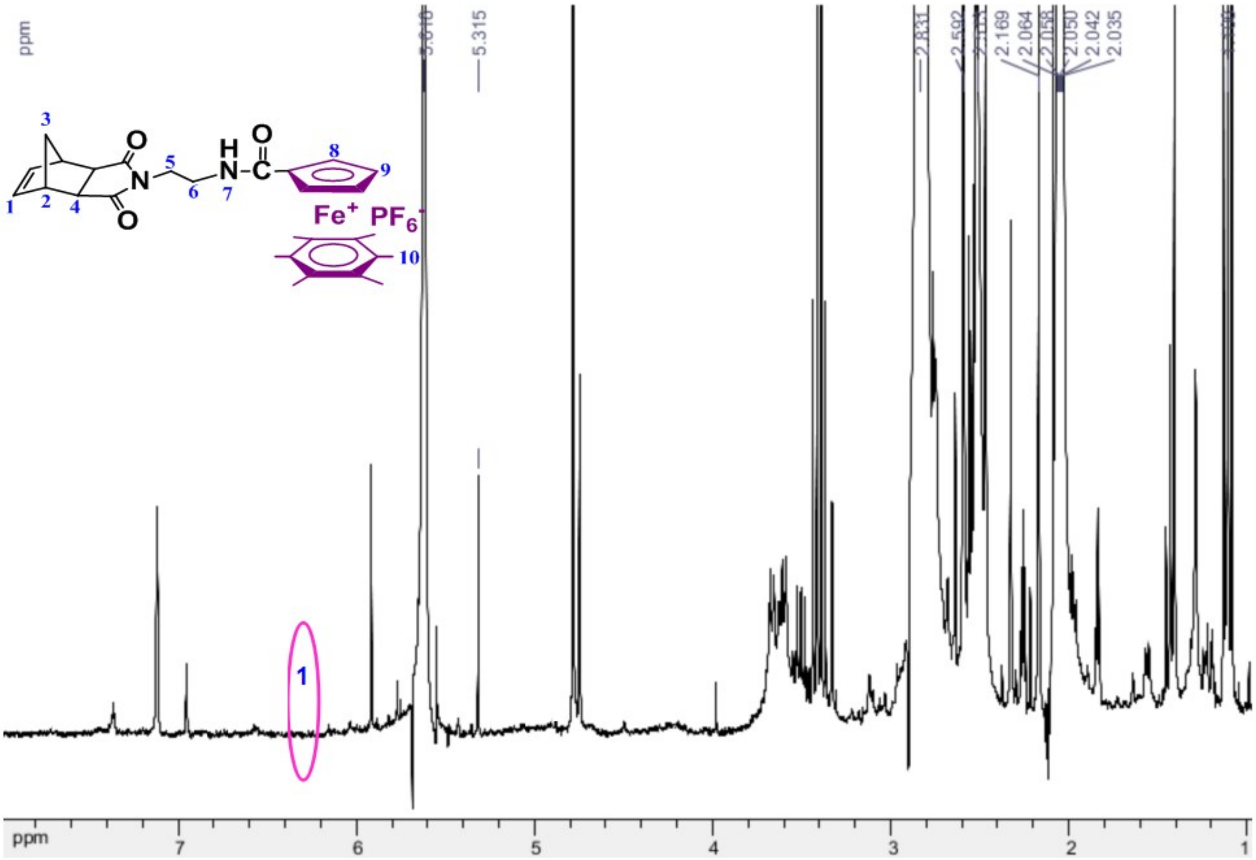


Figure S34 Enlarged ^1H NMR spectrum (300 MHz) in acetone-d_6 of the ROMP reaction mixture for the synthesis of diblock copolymer **11** after the addition of monomer **9** with 10 minutes stirring. No peak was observed at 6.30 ppm for the olefin protons of monomer **9**, namely no monomer **9** was left and the ROMP of **9** is complete.

Calculation of the polymer degrees of diblock copolymers 11 by ^1H NMR end-group analysis and errors

Table S1 Polymer degree of the first Fc block using the ^1H NMR spectrum in CD_2Cl_2 of homopolymer of **7**[a]

Proton peak	End-phenyl	Amido	olefinic	Sub. Cp	Sub. and free Cp	Methylene
δ_{ppm}	7.39-7.16	6.50	5.73 and 5.52	4.70	4.33 and 4.19	3.61-3.52
Integration	0.21	1.02-1.10	2.11-2.21	2.05-2.14	7.04-7.35	16.62-17.31
n_{p2a}[b]	-	24-26	25-26	24-25	24-25	24-25
n_{p2b}[c]	25 ± 1					

[a] Figure S5 was used for the calculation of the polymer degree of the first Fc block; [b] Calculated polymer degrees based on integral of each peak; [c] Average polymer degree according to n_{p2a} values.

Table S2 Polymer degree of the first Fc block using the ^{1}H NMR spectrum in DMSO-d_6 of homopolymer of **7**[a]

Proton peak	End-phenyl	Amido	olefinic	Sub. Cp	Sub. Cp	Free Cp
Δppm	7.48-7.23	7.79	5.64 and 5.45	4.78	4.31	4.14
Integration	0.21	1.01-1.04	2.01-2.15	2.01-2.04	2.04-2.06	4.91-5.02
n_{p2a}[b]	-	24-25	24-26	24-25	24-25	24-24
n_{p2b}[c]	25 ± 1					

[a] Figure S6 was used for the calculation of the polymer degree of the first Fc block. [b] Calculated polymer degrees based on integral of each peak. [c] Average polymer degree according to n_{p2a} values.

As shown in Table S1 and S2, both the ^{1}H NMR end-group analysis in CD_2Cl_2 and DMSO-d_6 provide the value of 25 ± 1 for the polymer degree of the first Fc block. These calculations were conducted by comparing the intensities of the signals of the five protons of the end-phenyl group with those of the characteristic protons in the Fc block. For example, in the ^{1}H NMR end-group analysis in CD_2Cl_2, proton integration for the end-phenyl group (7.39-7.16 ppm) was compared with those of the amide proton (6.50 ppm), olefin protons (5.74 and 5.52 ppm), Cp protons (4.70, 4.33 and 4.19 ppm) and methylene protons (3.61-3.52 ppm), respectively. The obtained values are 24-26, 25-26, 24-25, 24-25 and 24-25, respectively. Thus, the overage value of the polymer degree for the first block is 25 ± 1. The error is due to the integration error on each signal.

Table S3 Polymer degree of the second FbX block of copolymer **11**[a,b].

Proton peak	Amido in the first block	Substituted and free Cp in the first block	Amido in the second block	Substituted Cp in the second block	Methyl of C_6Me_6 in the second block
δ_{ppm}	7.80	4.31 and 4.14	8.48	5.05	2.31
Integration	0.93-1.03	7.04-7.11	0.74-0.81	1.80-1.82	13.1-13.6
n_{p2a}	-	-	17-23[c]	21-25[d]	17-20[e]
n_{p2b}[f]	21 ± 4				

[a] Figure 1C is used for the calculation of the polymer degree of the second FbX block. [b] The average polymer degree of 25 ± 1 for the first Fc block is used for the calculation of polymer degree of the second FbX block. [c] Calculated by comparing the amido proton integrations in the first and second blocks. [d] Calculated by comparing the amido proton integration in the first block and the substituted Cp proton integration in the second block. [e] Calculated by comparing the substituted and free Cp proton integration in the first block with the methyl proton integration in the second block. [f] Average polymer degree for the second block according to n_{p2a} values.

For the second FbX block, the polymer degree is 21 ± 4, as shown in Table S3. The error results from the following two sides. (1) This analysis is carried out by comparing the integration of characteristic peaks from the first Fc block and the second FbX block. The former is the amido peak at 7.80 ppm with integration of 0.93-1.03 and the substituted and free Cp peaks at 4.31 and 4.14 ppm with the total integration of 7.04-7.11; the latter is the amido peak at 8.48 ppm with the integration of 0.74-0.81, substituted Cp peak at 5.05 ppm with the integration of 1.80-1.82, and the methyl peak of C_6Me_6 at 2.31 ppm with the integration of 13.1-13.6. Obviously, integrations for each peak have errors that result in the corresponding error for the calculated polymer degree of the second block. (2) The above obtained polymer degree of 25 ± 1 for the first Fc block is used for the calculation of the polymer degree for the second FbX block, which also results in a larger error than for the first block. The obtained values are 17-23, 21-25 and 17-20, respectively, and then the average is 21 ± 4.

Table S4 Redox potentials, chemical (i_c/i_a) and electrochemical (E_{pa}-E_{pc} = ΔE) reversibility data for diblock copolymer **11**.

Fc redox center		FbX redox center	
$E_{1/2}$ (ΔE) (V)	i_c/i_a	$E_{1/2}$ (ΔE) (V)	i_c/i_a
0.630 (0.010)	1.06	-1.250 (0.050)	1.08

Calculation of polymerization degrees (n_{p3}) for diblock copolymer 11 by Bard-Anson's method

Bard-Anson's electrochemical equation:[S6]

$$n_p = \frac{(i_{dp}/C_p)}{(i_{dm}/C_m)}(\frac{M_p}{M_m})^{0.275}$$

(i_{dp}: intensity of polymer; C_p: concentration of polymer; i_{dm}: intensity of monomer; C_m: concentration of monomer; M_p: molecular weight of polymer; M_m: molecular weight of monomer).

In this part, the symbol of n_{p3} is used to stand for the polymerization degree. So,

$$n_{p3} = \frac{(i_{dp}/C_p)}{(i_{dm}/C_m)}(\frac{M_p}{M_m})^{0.275}$$

$$= (\frac{i_{dp}C_m}{i_{dm}C_p})(\frac{M_p}{M_m})^{0.275}$$

$$= (\frac{i_{dp}(n_m/v)}{i_{dm}(n_p/v)})(\frac{M_p}{M_m})^{0.275}$$ (n_m: mole of monomer; n_p: mole of polymer; v: volume of solution)

$$= \left(\frac{i_{dp} n_m}{i_{dm} n_p}\right)\left(\frac{M_p}{M_m}\right)^{0.275}$$

Here, we use decamethyferrocene ([FeCp*$_2$]) as the monomer reference, because (i) it has the same number of electron transferred between its reduced and oxidized forms as that of the monomers **7** and **9**, (ii) its redox potential is sufficiently far from that of Fc and FbX redox center in the polymers, which allows a clear distinction of the CV wave of the reference and that of the polymers **11**. This leads to calculate the polymerization degrees (n_{p3}) of Fc block and the mixed-sandwich FbX block for diblock copolymer **11** by the above equation, and the results are listed in Table S5.

Table S5 Polymerization degree (n_{p3}) for each metalloblock in copolymer **11** calculated using the Bard-Anson electrochemical method.

$[M_7] : [M_9] : [C]^a$	25 : 25 : 1	
$M_m{}^b$	326.3	
$M_p{}^c$	30354	
$n_m{}^d$ (mmol)	3.1×10^{-3}	
$n_p{}^e$ (mmol)	2.1×10^{-4}	
i_{dm} (cm)	2.8	
Redox centers	Fc	FbX
i_{dp} (cm)	1.6	1.3
$n_{p3}{}^f$	28 ± 3	24 ± 2

[a] $[M_7] : [M_9] : [C]$: feed molar ratio of monomers **7** and **9** to catalyst **1**. [b] Molecular weight of [FeCp*$_2$]. [c] Molecular weight of polymer calculated by monomer conversion determined by ^{1}H NMR. [d] n_m: mole of [FeCp*$_2$] added in the DMF solution of copolymer **11**. [e] n_p: mole of polymer **11** added in DMF. [f] n_{p3}: polymerization degree calculated by the above modified Bard-Anson's equation.

6. Diblock copolymer 13

Synthesis

Monomers **8** (44.4 mg, 0.0716 mmol) and **7** (39.4 mg, 0.0716 mmol) were added into two separate small glass tubes and dissolved in 0.4 mL and 0.3 mL of dry CH_2Cl_2, respectively. A desired amount of Grubbs catalyst **1** (2.53 mg, 0.00286 mmol) was added into a small Schlenk flask, flushed with nitrogen, and dissolved in 0.03 mL of dry CH_2Cl_2. First, monomer **8** was transferred to the flask containing the catalyst via a small syringe. The reaction mixture was stirred vigorously for 10 minutes at r. t., after which monomer **7** was added into the flask using a small syringe. The polymerization was allowed to continue for another 15 minutes, and then quenched with 0.2 mL of EVE. The yellow-brown solid polymer **13** was purified by precipitation from CH_2Cl_2 with methanol five times and dried *in vacuo* until constant weight. Yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$), δ_{ppm}: 7.34-7.14 (m, phenyl and $CDCl_3$), 6.48 (broad, 1H, N***H***CO-Fc), 6.09 (broad, 1H, N***H***CO-Fc*), 5.68 and 5.46 (double broad, 4H, 2×CH=CH), 4.68 (s, 2H, sub. Cp of Fc), 4.28 (s, 2H, sub. Cp of Fc), 4.15 (s, 7H, free Cp of Fc and sub. Cp of Fc*), 3.90 (s, 2H, sub. Cp of Fc*), 3.56 (broad, 32H, $2\times CH_2(CH_2OCH_2)_3CH_2$), 3.21 (broad, =CH-C***H***), 2.98 (broad, CO-CH), 2.63 (broad, CH=CHCHC$\boldsymbol{H_2}$), 2.03 (broad, CH=CHCHC$\boldsymbol{H_2}$), 1.59 (s, 15H, $5\times CH_3$).

Kinetic Study

In order to know when the polymerization of the second block finishes, the kinetic study was conducted as following: monomer **8** (0.405 g, 0.653 mmol) in 4 mL dry CH_2Cl_2 was added into the solution of Grubbs catalyst **1** (23.1 mg, 0.026 mmol) in 0.3 mL dry CH_2Cl_2. The reaction mixture was stirred vigorously for 10 minutes at r. t. under N_2 atmosphere. Then, monomer **7** (0.359 g, 0.653 mmol) in 3 mL dry CH_2Cl_2 was added, and after 5, 10, 15, 20, 30, 45 and 60 minutes, respectively, 0.5 mL of samples were taken out and quenched with 0.5 mL of EVE. The *In situ* ^{1}H NMR analysis in $CDCl_3$ was conducted, and the conversion of monomer **7** was deemed to be 100% when the peak at 6.26 ppm, the signal of olefinic protons for monomer **7**, disappeared. Actually, the polymerization of the second block finishes in 15 minutes with 100% monomer conversion.

Oxidation of copolymer 13 by ferricinium hexafluorophosphate

A freshly prepared solution of ferricinium hexafluorophosphate (3.11 mg, 9.40×10^{-3} mmol) in dry CH_2Cl_2 (2.5 mL) was added dropwise to a solution of polymer **13** (10.0 mg, 8.55×10^{-3} mmol of Fc*) in dry CH_2Cl_2 (1.5 mL) under nitrogen at 25 ^oC. The mixture was stirred for 5 min at 25 ^oC, and then the solvent was removed *in vacuo*. The blue-green residual solid of crude $[Fc^*]^+$-containing copolymer **14** was washed with pentane (5 × 5 mL), then dissolved in acetone, precipitated by addition of pentane, and dried *in vacuo* until constant weight (Yield: 10.8 mg, 96%). IR: ν bar = 3430 (N-H), 2923 (CH_3), 1771 (C=C), 1698 (C=O), 843 (PF_6^-) cm^{-1}; δ bar = 1655 (N-H) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} = 625, 754 nm. The structure was confirmed by reduction to the $[Fc^*]^+$-containing copolymer.

Reduction by decamethylferrocene of the [Fc*]$^+$-containing copolymer 14

A freshly prepared solution of decamethylferrocene (3.2 mg, 9.8×10^{-3} mmol) in dry CH_2Cl_2 (2.0 mL) was added dropwise to a solution of copolymer **14** (10.0 mg, 7.605×10^{-3} mmol of [Fc*]$^+$ hexafluorophosphate) in dry CH_2Cl_2 (5.0 mL) under nitrogen at 25 °C. The mixture was stirred for 5 min at 25 °C, and then the solvent was removed *in vacuo*. The residual solid was washed five times with methanol (5.0 mL), and the purified Fc*-containing polymer **13** was obtained as a yellow solid (Yield: 8.1 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$), δ_{ppm}: 7.36-7.17 (m, phenyl and $CDCl_3$), 6.49 (broad, 1H, N***H***CO-Fc), 6.03 (broad, 1H, N***H***CO-Fc*), 5.72 and 5.49 (double broad, 4H, 2×CH=CH), 4.71 (s, 2H, sub. Cp of Fc), 4.31 (s, 2H, sub. Cp of Fc), 4.18 (s, 7H, free Cp of Fc and sub. Cp of Fc*), 4.05 (s, 2H, sub. Cp of Fc*), 3.60 (broad, 32H, $2\times CH_2(CH_2OCH_2)_3CH_2$), 3.23 (broad, =CH-C***H***), 3.01 (broad, CO-CH), 2.66 (broad, CH=CHCHC$\boldsymbol{H_2}$), 2.09 (broad, CH=CHCHC$\boldsymbol{H_2}$), 1.34 (s, 15H, $5\times CH_3$). IR: *v* bar = 3394 (N-H), 2902 (CH_3), 1771 (C=C), 1701 (C=O), 824 (Fe^{II}) cm^{-1}; *δ* bar = 1637 (N-H) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} = 435 nm.

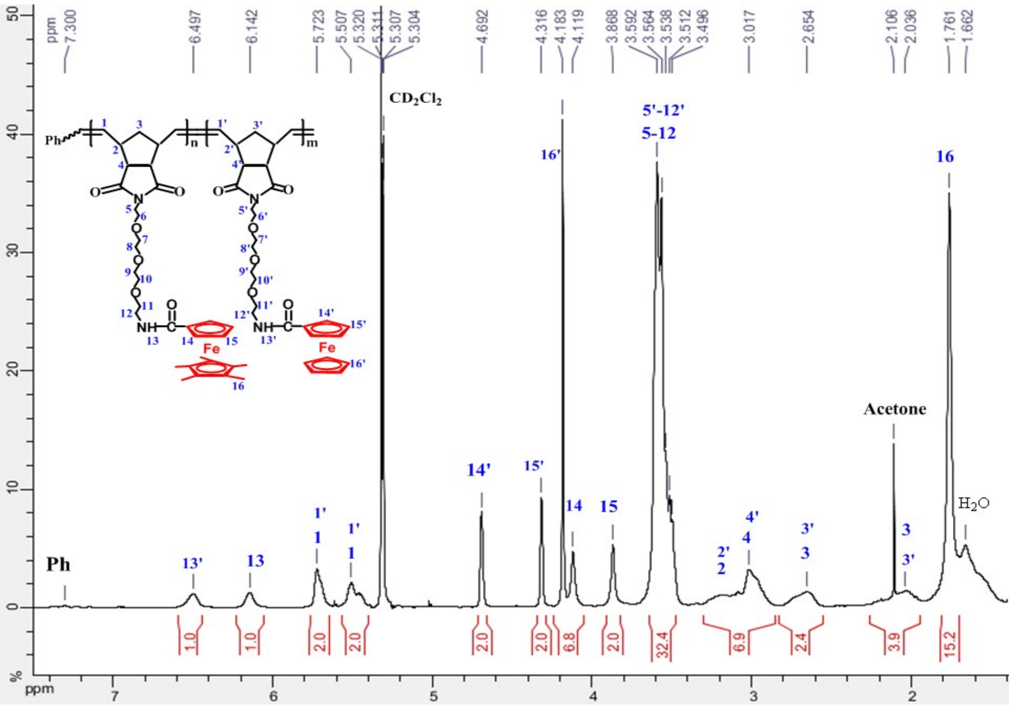


Figure S35 ^{1}H NMR spectrum of diblock copolymer **13** in CD_2Cl_2.

^{1}H NMR (300 MHz, CD_2Cl_2), δ_{ppm}: 7.41-7.27 (m, phenyl), 6.50 (broad, 1H, N***H***CO-Fc), 6.14 (broad, 1H, N***H***CO-Fc*), 5.72 and 5.51 (double broad, 4H, 2×CH=CH), 4.69 (s, 2H, sub. Cp of Fc), 4.32 (s, 2H, sub. Cp of Fc), 4.18 (s, 7H, free Cp of Fc), 4.12 (s, 2H, sub. Cp of Fc*), 3.87 (s, 2H, sub. Cp of Fc*), 3.59-3.50 (m and broad, 32H, $2\times CH_2(CH_2OCH_2)_3CH_2$), 3.19 (broad, =CH-C***H***), 3.02 (broad, CO-CH), 2.65 (broad, CH=CHCHC$\boldsymbol{H_2}$), 2.04 (broad, CH=CHCHC$\boldsymbol{H_2}$), 1.76 (s, 15H, $5\times CH_3$).

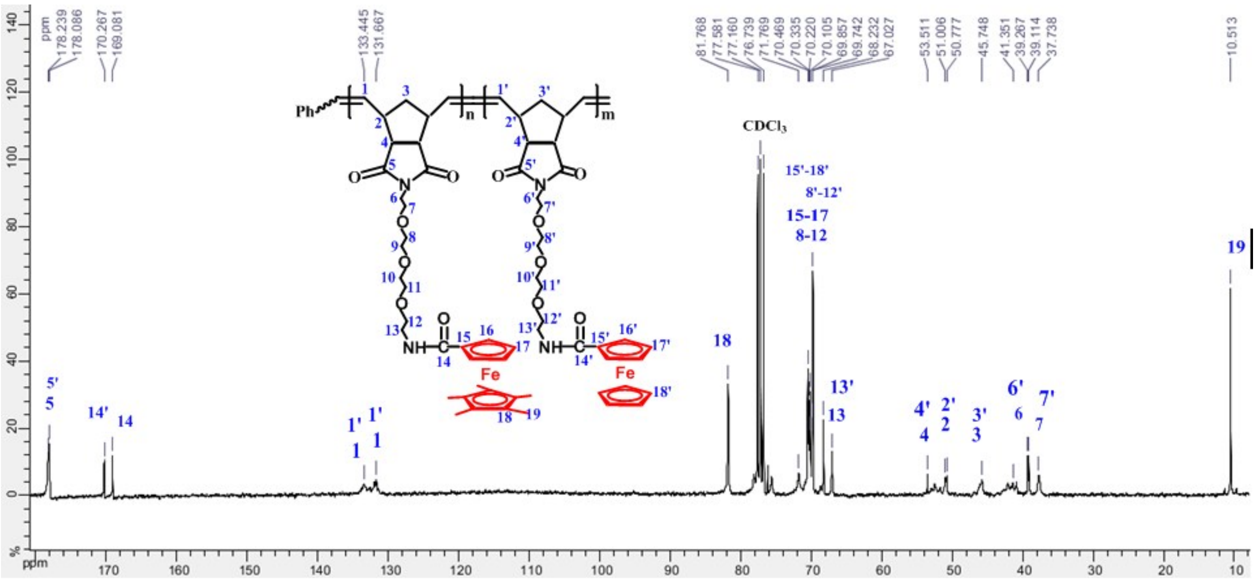


Figure S36 ^{13}C NMR spectrum of diblock copolymer **13** in $CDCl_3$.

^{13}C NMR (50 MHz, $CDCl_3$), δ_{ppm}: 178.2, 178.1 (CON), 170.2, 169.1 (CONH), 133.4, 131.7 (C=C), 81.8 (Cp*), 71.8, 70.5, 70.3, 70.2, 70.1, 69.8, 69.7, 68.2, (CH_2 and sub. Cp), 67.0(-***C***H_2NH), 53.5 (CO***C***H), 51.0, 50.8 (=CH***C***H), 45.7 (***C***H_2 of cyclopentane), 41.3, 39.3, 39.1 (***C***H_2NCO), 37.7 (***C***H_2CH_2NCO), 10.5 (CH_3).

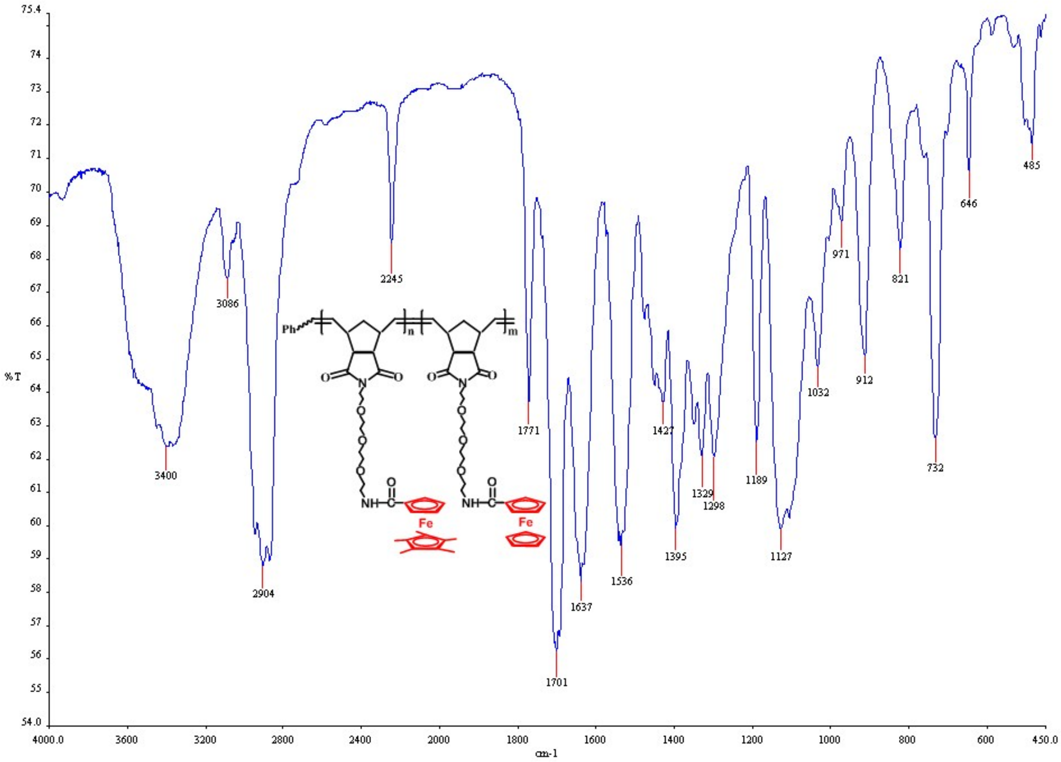


Figure S37 IR spectrum of diblock copolymer **13**.

3400 cm^{-1} ($\nu_{N\text{-}H}$), 2904 cm^{-1} (ν_{CH3}), 1771 cm^{-1} ($\nu_{C=C}$), 1701 cm^{-1} ($\nu_{C=O}$), 1637 cm^{-1} ($\delta_{N\text{-}H}$), 821 cm^{-1} (ν_{FeII}).

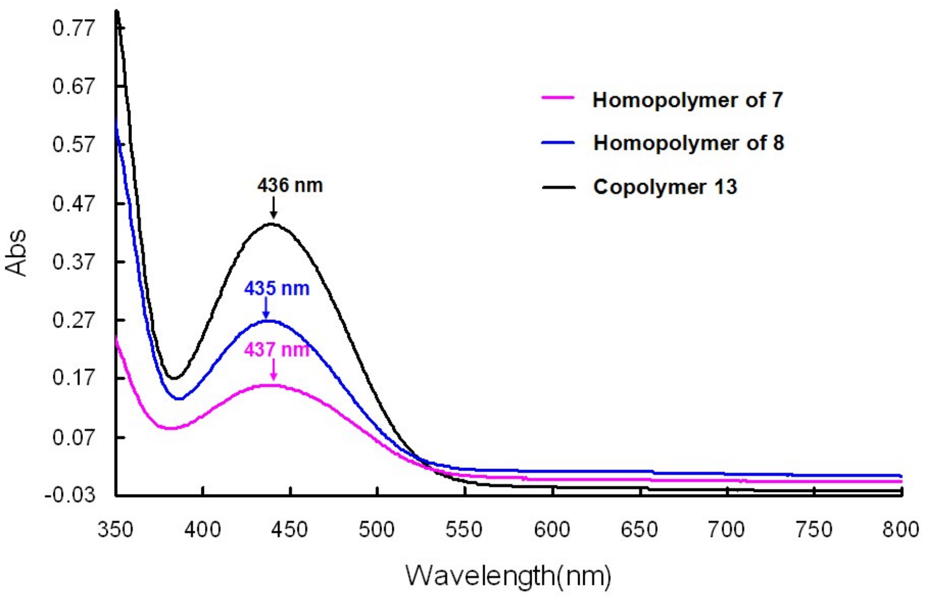
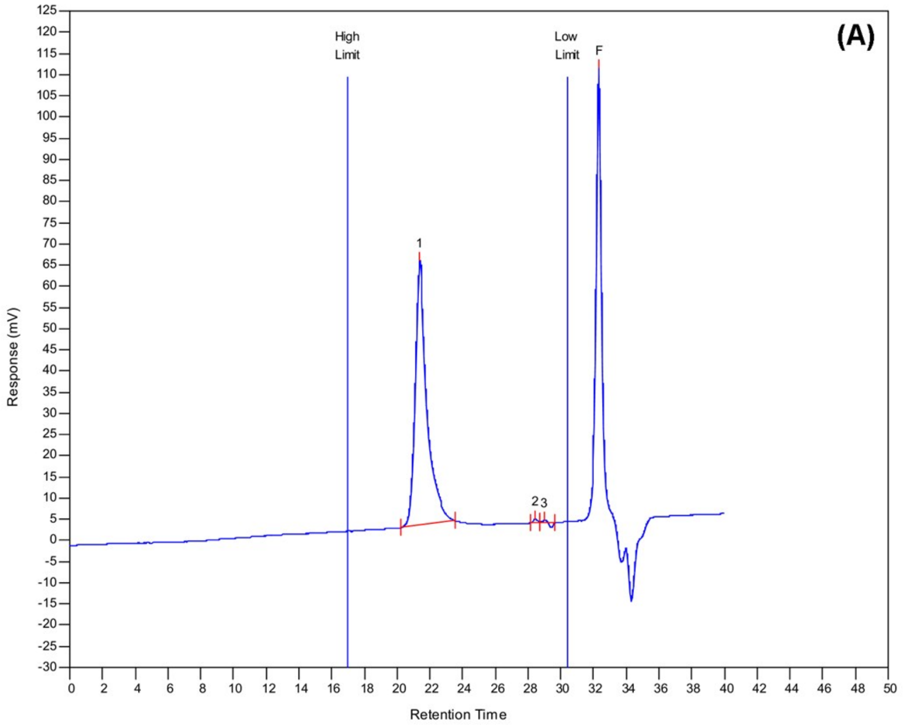
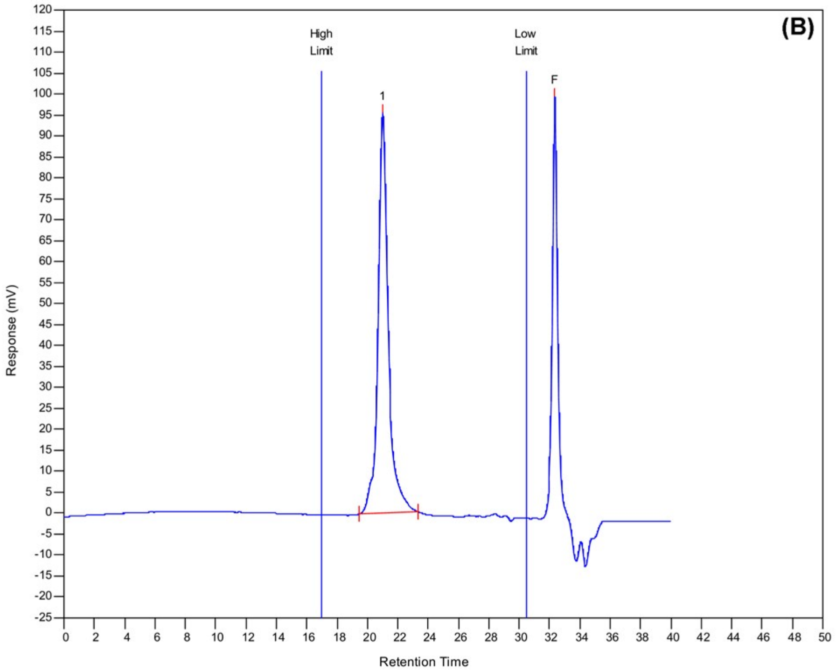


Figure S38 UV-vis. spectra of diblock copolymer **13**, Fc-containing homopolymer of **7** and Fc*-containing homopolymer of **8** in CH_2Cl_2.



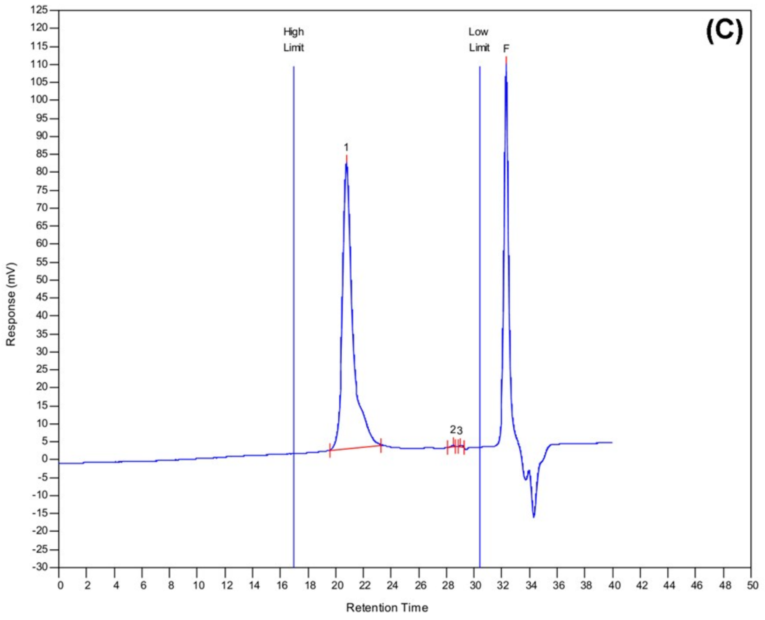
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9616	8415	9005	9526	9996	8923	1.07011
2	416	419	401	412	413	397	0.957041
3	322	338	315	327	328	310	0.931953
4	0	0	0	0	0	0	0



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12536	11449	12468	13516	14732	12318	1.089
2	0	0	0	0	0	0	0



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14101	11819	13123	14226	15212	12949	1.11033
2	416	419	417	419	420	417	0.995227
3	307	315	311	314	314	310	0.987302
4	0	0	0	0	0	0	0

Figure S39 SEC curves of the diblock copolymers **13** (A and C) and homopolymer of **8** (B). (A): The feed molar ratio [monomer **8**] : [monomer **7**] : [catalyst **1**] was 25 : 25 : 1; (B): The feed molar ratio [monomer **8**] : [catalyst **1**] was 50 : 1; (C): The feed molar ratio [monomer **8**] : [monomer **7**] : [catalyst **1**] was 50 : 50 : 1.

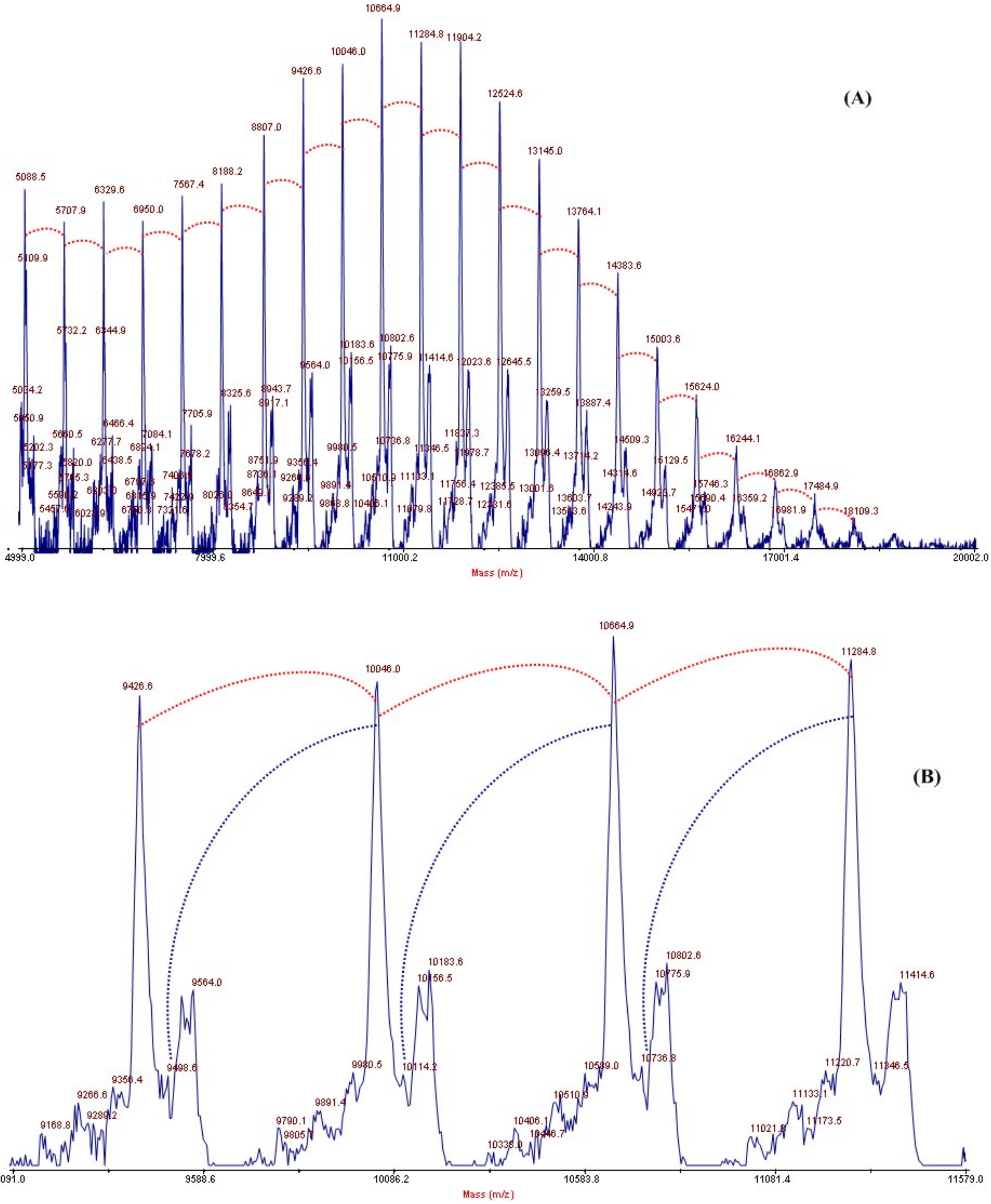


Figure S40 MALDI-TOF MS spectrum of diblock copolymer **13**.

The feed molar ratio of monomers **8** and **7** to **1** is 25 : 25 : 1. (A) is the region of 5000-20000 in the spectrum; and (B) is the enlarge region of the spectrum from 913 to 11560. The red dotted lines are corresponding to the difference between molecular peaks of a value of 620 ±1 Da (MW of monomer **8**). The blue dotted lines are corresponding to the difference between molecular peaks of a value of 550 ±1 Da (MW of monomer **7**).

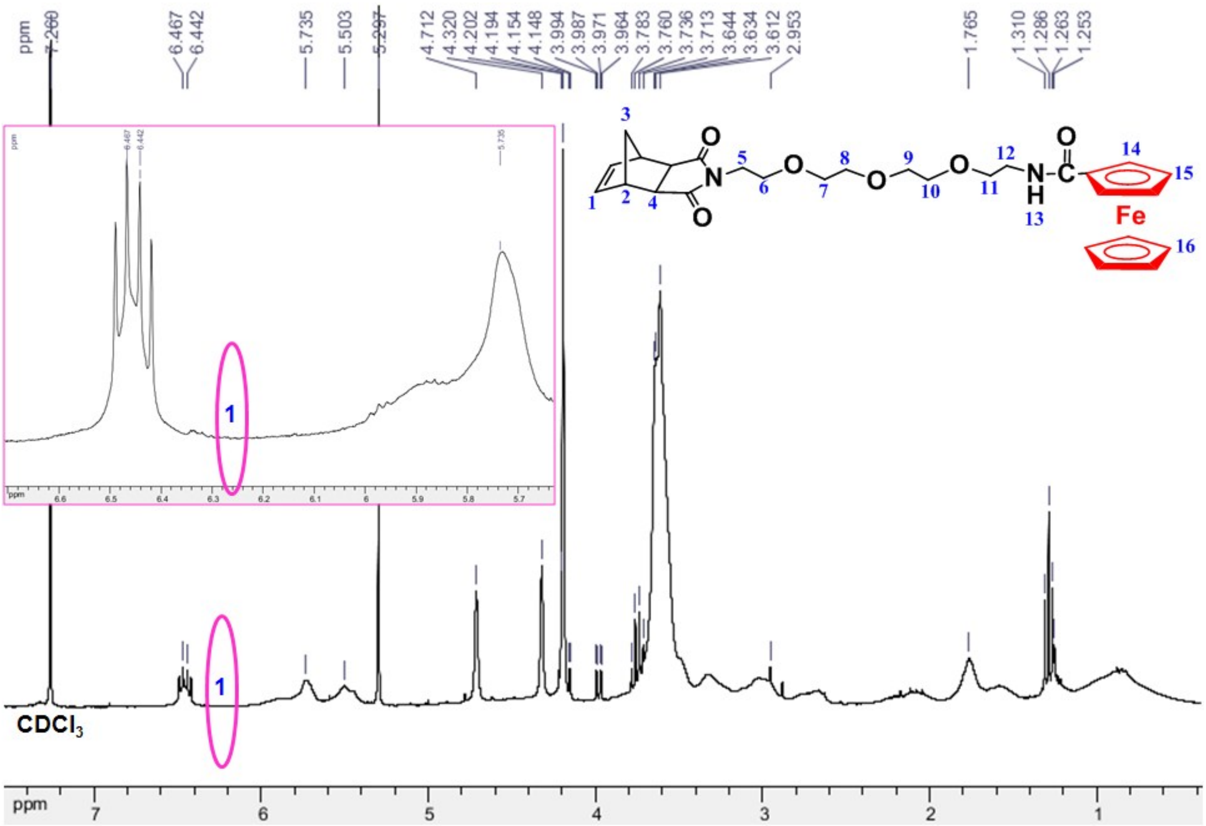


Figure S41 ^{1}H NMR spectrum in $CDCl_3$ of the ROMP reaction mixture for the synthesis of diblock copolymer **13** after the addition of monomer **7** with 15 minutes stirring. No peak is observed at 6.26 ppm or so for the olefin protons of monomer **7**, namely no monomer **7** is left and the ROMP of **7** is complete.

Calculation of the polymer degrees of diblock copolymers 13 by ^{1}H NMR end-group analysis and errors

Table S6 Polymer degree of the first Fc* block using the ^{1}H NMR spectrum in CD_2Cl_2 of homopolymer of **8**[a]

Proton peak	End-phenyl	Amido	olefinic	Sub. Cp	Substituted Cp	methylene	Methyl of C_5Me_5
δppm	7.38-7.22	6.16	5.72-5.50	4.13	3.87	3.59-3.50	1.74
Integr.	0.197	0.96-1.0	2.00-2.04	1.93-2.00	1.86-1.95	15.7-16.3	14.3-14.7
n_{p2a}[b]	-	24-25	25-26	25-25	24-25	25-26	24-25
n_{p2b}[c]	25 ± 1						

[a] Figure S16 is used for the calculation of polymer degree of the first Fc* block. [b] Calculated polymer degrees based on integral of each peak. [c] Average polymer degree according to n_{p2a} values.

As shown in Table S6, the ^{1}H NMR end-group analysis in CD_2Cl_2 provides the value of 25 ± 1 for the polymer degree of the first Fc* block. These calculations were conducted by comparing the intensities of the signals of the five protons of the end-phenyl group with those of characteristic protons in the Fc* block. Namely, the proton integration for end-phenyl group (7.39-7.22 ppm) was compared with those of the amide proton (6.16 ppm), olefin protons (5.72-5.50 ppm), Cp protons (4.13 and 3.87 ppm), methylene protons (3.5-3.50 ppm) and methyl protons of C_5Me_5 (1.74 ppm), respectively. The obtained values are 24-25, 25-26, 25-25, 24-25, 25-26 and 24-25, respectively. Thus, the overage value of the polymer degree for the first block is 25 ± 1. The error is due to the integration error on each signal.

Table S7 Polymer degree of the second Fc block using the ^{1}H NMR spectrum in CD_2Cl_2 of copolymer **13**. [a,b]

Proton peak	Amido in the first block	Sub. Cp in the first block	Amido in the second block	Sub. Cp in the second block	Sub. Cp in the second block
δ_{ppm}	6.139	3.868	6.498	4.692	4.316
Integration	0.99-1.01	1.99-2.01	1.00-1.01	1.99-2.00	1.98-2.00
n_{p2a}	-	-	24-26[c]	24-26[d]	24-26[d]
n_{p2b}[e]	25 ± 1				

[a] Figure S35 is used for the calculation of the polymer degree of the second block. [b] The average polymer degree of 25 ± 1 for the first Fc* block is used for the calculation of polymer degree of the second Fc block. [c] Calculated by comparing the amido proton integrations in the first and second blocks. [d] Calculated by comparing the substituted Cp proton integrations in the first and second blocks. [e] Average polymer degree for the second block according to the n_{p2a} values.

As shown in Table S7, the polymer degree for the second Fc blcok is 25 ± 1, too, which is equal to that of the first Fc* block. The analysis was carried out by using the above obtained polymer degree of 25 ± 1 for the first Fc* block. The integrations of amido peaks in the first and second blocks, 6.14 ppm with 0.99-1.01 and 6.50 ppm with 1.00-1.01, respectively, were compared, and the value of 24-26 was obtained. Similarly, the integrations of substituted Cp peaks in the first and second blocks were also compared. The former is 1.99-2.01 at 3.87 ppm, and the latter is 1.99-2.00 at 4.69 ppm and 1.98-2.0 at 4.32 ppm, respectively. The obtained corresponding polymer degrees for the second block are 24-26, too. So, the average value is 25 ± 1. Obviously, the used analysis method resulted in a small error.

Table S8 Redox potentials, chemical (i_c/i_a) and electrochemical (E_{pa}-E_{pc} = ΔE) reversibility data for the diblock copolymer **13**.

Fc center			Fc* center		
$E_{1/2}$ (mV)	ΔE (mV)	i_c/i_a	$E_{1/2}$ (mV)	ΔE (mV)	i_c/i_a
0.640	0.020	1.10	0.380	0.020	1.08

Calculation of the polymerization degrees (n_{p3}) for the diblock copolymer 13 by Bard-Anson's method

The following modified Bard-Anson's empirical electrochemical equation[S7] is used:

$$n_{p3} = (\frac{i_{dp} n_m}{i_{dm} n_p})(\frac{M_p}{M_m})^{0.275}$$

(i_{dp}: intensity of polymer; n_p: mole of polymer; i_{dm}: intensity of monomer; n_m: mole of monomer; M_p: molecular weight of polymer; M_m: molecular weight of monomer).

[FeCp*$_2$] was used as the monomer reference. The results of calculated polymerization degrees (n_{p3}) of Fc* and Fc blocks for diblock copolymer **13** are listed in Table S9.

Table S9 Polymerization degree (n_{p3}) for each metalloblock in copolymer **13** calculated using the Bard-Anson electrochemical method.[S7]

$[M_8] : [M_7] : [C]^a$	25 : 25 : 1	
$M_m{}^b$	326.3	
$M_p{}^c$	29354	
$n_m{}^d$ (mmol)	9.2×10^{-4}	
$n_p{}^e$ (mmol)	1.7×10^{-4}	
i_{dm} (cm)	2.6	
Redox centers	Fc*	Fc
i_{dp} (cm)	2.6	2.7
$n_{p3}{}^f$	19 ± 2	21 ± 2

[a] $[M_8] : [M_7] : [C]$: feed molar ratio of monomers **8** and **7** to **1**. [b] Molecular weight of [FeCp*$_2$]. [c] Molecular weight of copolymer **13** calculated by monomer conversion determined by ^{1}H NMR. [d] n_m: mole of [FeCp*$_2$] added in the CH_2Cl_2 solution of copolymer **13**. [e] n_p: mole of copolymer **13** in CH_2Cl_2. [f] n_{p3}: polymerization degree determined by the Bard-Anson's method.

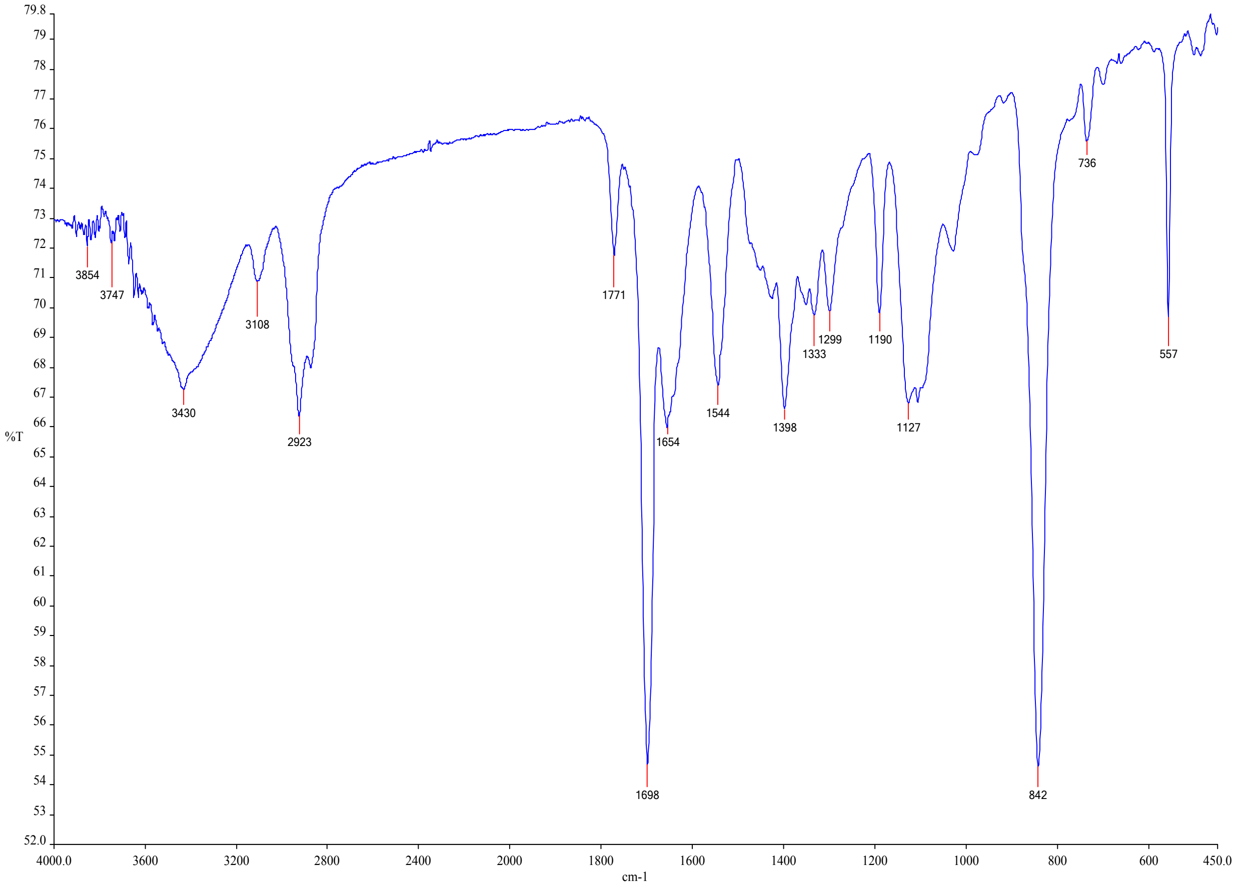


Figure S42 IR spectrum of $[Fc^{*}]^{+}$-containing diblock copolymer **14**.

3430 cm^{-1} (ν_{N-H}), 2923 cm^{-1} (ν_{CH3}), 2873 cm^{-1}, 1771 cm^{-1} ($\nu_{C=C}$), 1698 cm^{-1} ($\nu_{C=O}$), 1655 cm^{-1} (δ_{N-H}), 1544 cm^{-1}, 843 cm^{-1} (ν_{PF6-}), 558 cm^{-1}.

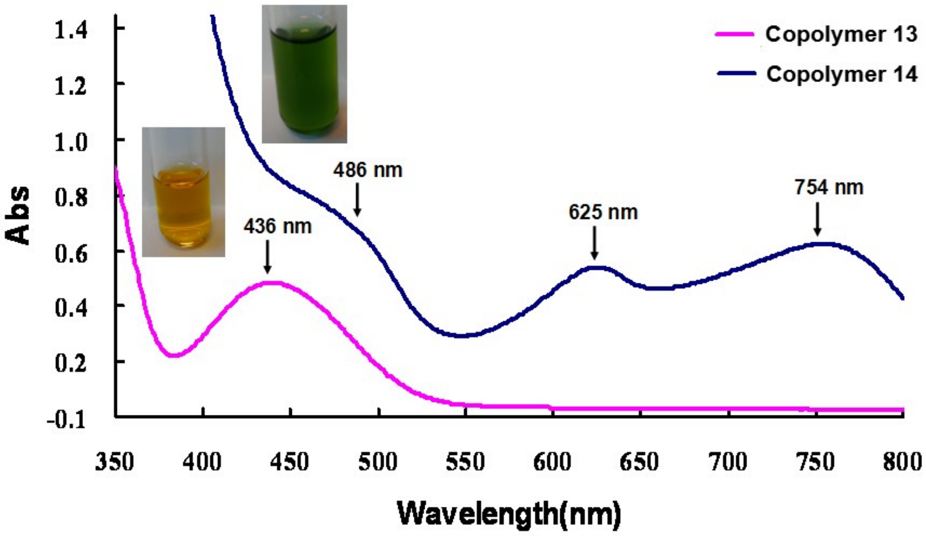


Figure S43 UV-vis. spectra and pictures of $[Fc^{*}]^{+}$-containing copolymer **14** and Fc*-containing copolymer **13** in CH_2Cl_2.

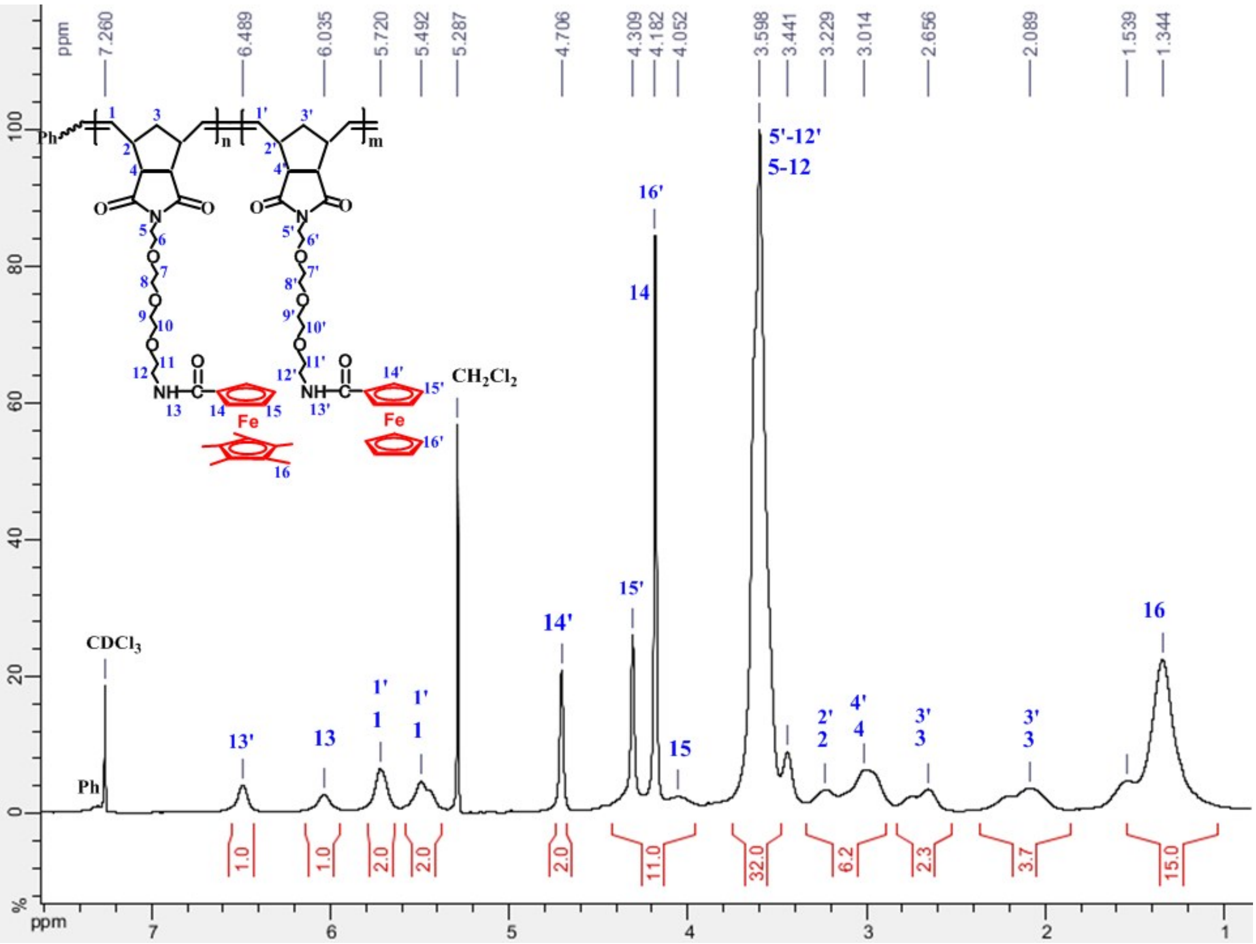


Figure S44 ^{1}H NMR spectrum in $CDCl_3$ of Fc*-containing diblock copolymer **13** prepared by the reduction of $[Fc^*]^+$-containing copolymer **14**.

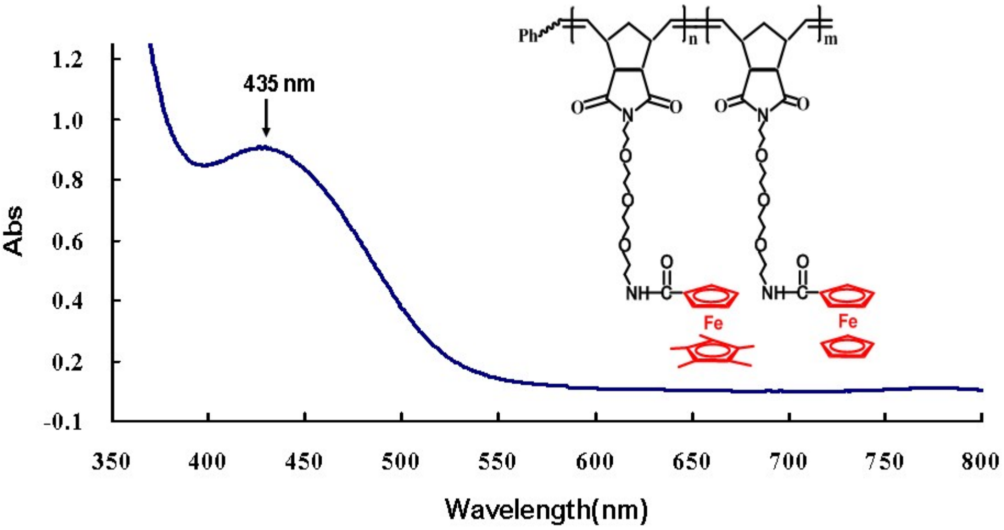


Figure S45 UV-vis. spectra of Fc*-containing copolymer **13** prepared by the reduction of $[Fc^*]^+$-containing copolymer **14**.

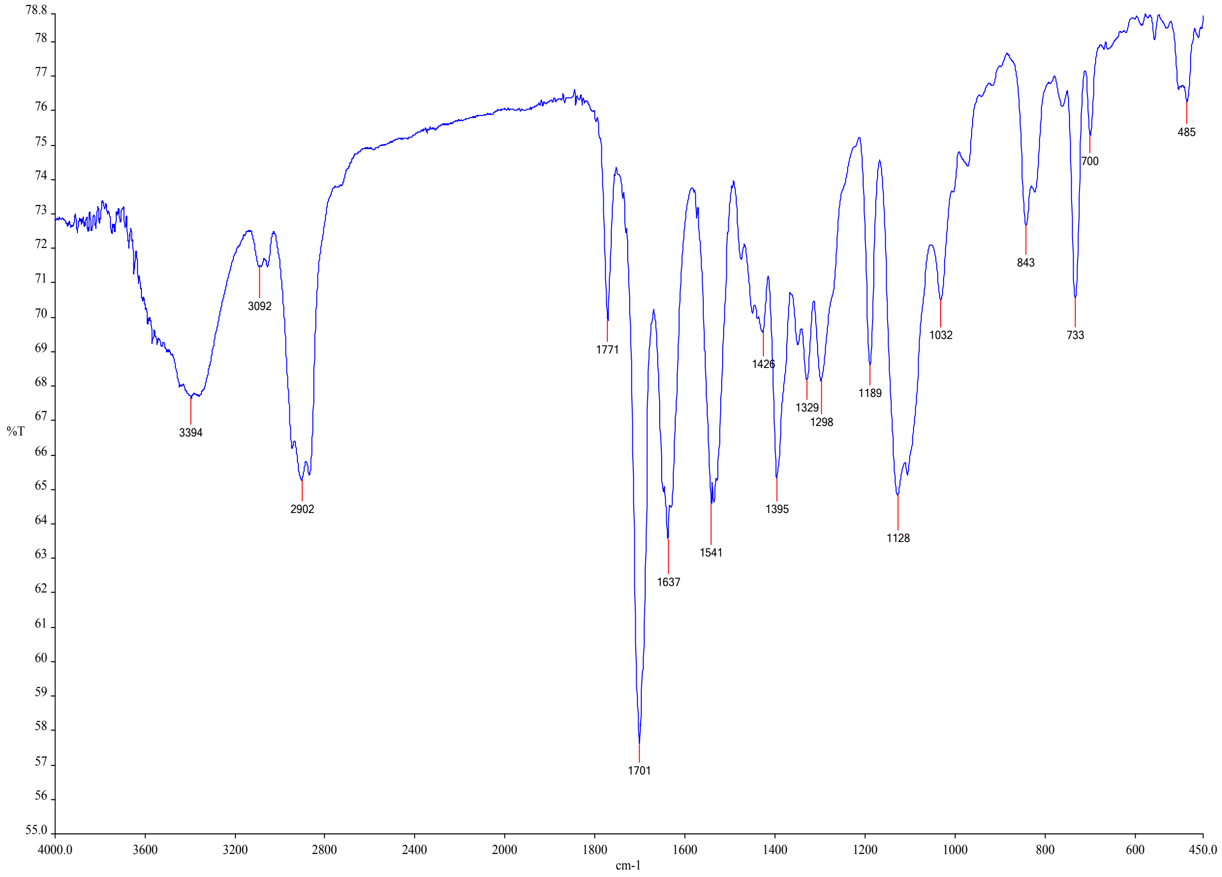


Figure S46 IR spectrum of Fc*-containing copolymer **13** prepared by the reduction of [Fc*]$^+$-containing copolymer **14**.

3394 cm^{-1} ($\nu_{\mathrm{N\text{-}H}}$), 2902 cm^{-1} ($\nu_{\mathrm{CH3}}$), 1771 cm^{-1} ($\nu_{\mathrm{C=C}}$), 1701 cm^{-1} ($\nu_{\mathrm{C=O}}$), 1637 cm^{-1} ($\delta_{\mathrm{N\text{-}H}}$), 824 cm^{-1} ($\nu_{\mathrm{FeII}}$).

7. Diblock copolymer 15

Synthesis

Monomers **8** (27.8 mg, 0.0448 mmol) and **9** (29.6 mg, 0.0448 mmol) were added into two separate small glass tubes, and dissolved in 0.25 mL and 0.4 mL of dry CH_2Cl_2, respectively. A desired amount of Grubbs catalyst 3rd **1** (1.59 mg, 0.0018 mmol) was added into a small Schlenk flask, flushed with nitrogen, and dissolved in 0.03 mL of dry CH_2Cl_2. First, monomer **8** was transferred to the flask containing the catalyst via a small syringe. The reaction mixture was stirred vigorously for 10 minutes at r. t., after which monomer **9** was added into the flask using a small syringe. The polymerization was allowed to continue for another 10 minutes, and then quenched with 0.2 mL of EVE. The yellow-brown solid polymer **15** was purified by precipitating from CH_2Cl_2 with Et_2O three times and dried *in vacuo* until constant weight. Yield: 92%. ^1H NMR (300 MHz, CD_2Cl_2), δ_{ppm}: 7.42-7.23 (m, N***H***CO-FbX and phenyl), 6.04 (broad, 1H, N***H***CO-Fc*), 5.74 and 5.52 (double broad, CH=CH), 4.88 (broad, sub. Cp of FbX), 4.61 (broad, sub. Cp of FbX), 4.41 (broad, sub. Cp of Fc*), 4.17 (broad, sub. Cp of Fc*), 3.59-3.47 (m, $CH_2(CH_2OCH_2)_3CH_2$), 3.32 (broad, NCH_2CH_2N), 3.01 (broad, =CH-C***H***), 2.67 (broad, CO-C***H***), 2.38 (s, $C\boldsymbol{H_3}$ of (η^6-C_6Me_6)), 2.03 (broad, $CH{=}CHCHC\boldsymbol{H_2}$), 1.66 (broad, $C\boldsymbol{H_3}$ of Fc*).

Kinetic Study

In order to know when the polymerization of the second block can finish, the kinetic study was conducted as following: Monomer **8** (0.364 g, 0.587 mmol) in 3 mL dry CH_2Cl_2 was added into the solution of Grubbs catalyst 3rd **1** (20.8 mg, 0.0235 mmol) in 0.2 mL dry CH_2Cl_2. The reaction mixture was stirred vigorously for 10 minutes at r. t. under N_2 atmosphere. Then, monomer **9** (0.387 g, 0.587 mmol) in 4 mL dry CH_2Cl_2 was added, and after 10, 15, 20 and 30 minutes, respectively, 0.5 mL of samples were taken out and quenched with 0.5 mL of EVE. The *In situ* ^1H NMR analysis in acetone-d_6 was conducted, and the conversion of monomer **9** was deemed to be 100% when the peak at 6.30 ppm, the signal of olefinic protons for monomer **9**, disappeared. Actually, the polymerization of the second block can finish in 10 minutes with 100% monomer conversion.

Oxidation of copolymer 15 by ferricinium hexafluorophosphate

A freshly prepared solution of ferricinium hexafluorophosphate (2.4 mg, 7.3×10^{-3} mmol) in dry CH_2Cl_2 (2.5 mL) was added dropwise to a solution of polymer **15** (8.46 mg, 6.61×10^{-3} mmol of PMF) in dry CH_2Cl_2 (2.5 mL) under nitrogen at 25 ^oC. The mixture was stirred for 5 min at 25 ^oC, and then the solvent was removed *in vacuo*. The blue-green residual solid of crude $[Fc^*]^+$-containing copolymer **16** was washed with pentane (5 × 5 mL), then dissolved in acetone, precipitated by addition of pentane, and dried *in vacuo* until constant weight (Yield: 8.66 mg, 92%). IR: ν bar = 3432 (N-H), 2922 (CH_3), 1771 (C=C), 1696 (C=O), 844 (PF_6^-) cm^{-1}; δ bar = 1659 (N-H) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} = 435, 626, 751 nm. The structure was confirmed by reduction to the Fc*-containing copolymer **15**.

Reduction of the [Fc*]$^+$**-containing copolymer 16 by decamethylferrocene**

A freshly prepared solution of decamethylferrocene (2.34 mg, 7.17 × 10^{-3} mmol) in acetone (2.0 mL) was added dropwise to a solution of copolymer **16** (8.5 mg, 5.97 × 10^{-3} mmol of [Fc*][PF_6] in acetone (5.0 mL) under nitrogen at 25 °C. The mixture was stirred for 5 min at 25 °C, and then the solvent was removed *in vacuo*. The residual solid was washed five times with methanol (5.0 mL), and the purified Fc*-containing copolymer **15** was obtained as a yellow solid (Yield: 7.1 mg, 93%). ^{1}H NMR (300 MHz, CD_2Cl_2), δ_{ppm}: 7.44-7.24 (m, N***H***CO-FbX and phenyl), 6.02 (broad, 1H, N***H***CO-Fc*), 5.76 and 5.54 (double broad, CH=CH), 4.90 (broad, sub. Cp of FbX), 4.62 (broad, sub. Cp of FbX), 4.48 (broad, sub. Cp of Fc*), 4.23 (broad, sub. Cp of Fc*), 3.60-3.46 (m, $CH_2(CH_2OCH_2)_3CH_2$), 3.30 (broad, NCH_2CH_2N), 3.03 (broad, =CH-C***H***), 2.70 (broad, CO-C***H***), 2.40 (s, C$\boldsymbol{H_3}$ of (η^6-C_6Me_6)), 2.05 (broad, CH=CHCHC$\boldsymbol{H_2}$), 1.68 (broad, C$\boldsymbol{H_3}$ of Fc*). IR: ν bar = 3434 (N-H), 2918 (CH_3), 1771 (C=C), 1699 (C=O), 846 cm^{-1} (ν_{PF6}) cm^{-1}; δ bar = 1642 (N-H) cm^{-1}; UV/Vis (DCM): λ_{max} = 423 nm.

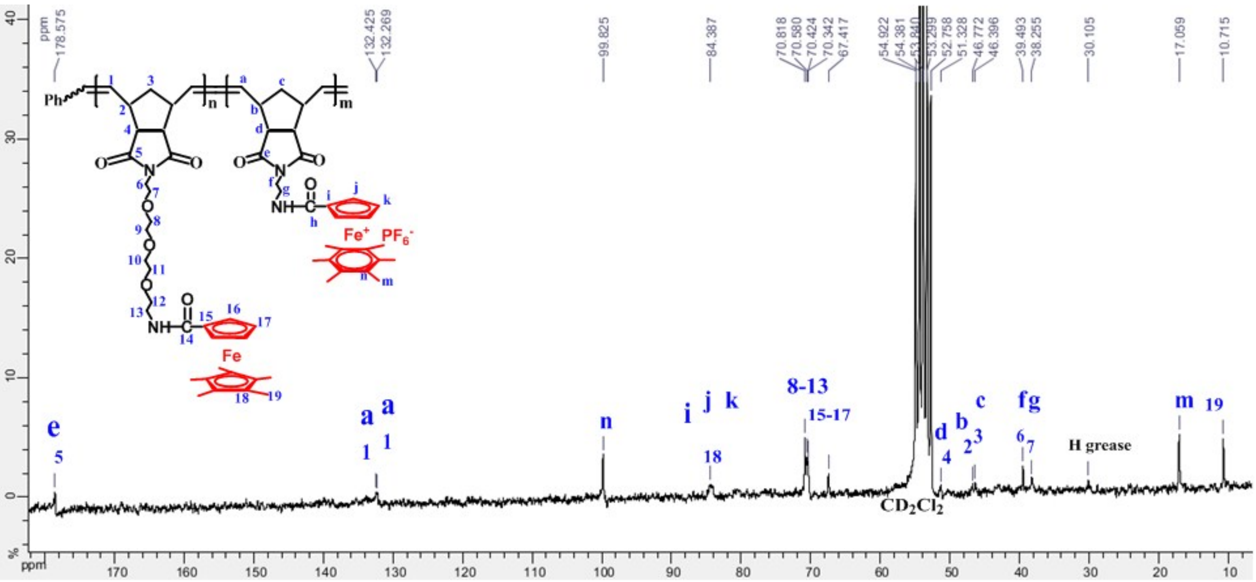


Figure S47 ^{13}C NMR spectrum of diblock copolymer **15** in CD_2Cl_2.

^{13}C NMR (50 MHz, CD_2Cl_2), δ_{ppm}: 178.6 (CON), 132.4, 132.3 (C=C), 99.8 (η^6-$\boldsymbol{C_6}Me_6$), 84.4 (η^5-$\boldsymbol{C_5}Me_5$ and sub. Cp), 70.8, 70.6, 70.4, 70.3, 67.4 (CH_2 and sub. Cp), 51.3 (CO-***C***H), 46.8 (=CH-***C***H), 46.4 (CH_2 of cyclopentane), 39.5, 38.2 (-***C***H_2CH_2-NCO), 17.1 (CH_3 of η^6-C_6Me_6), 10.7 (CH_3 of η^5-C_5Me_5).

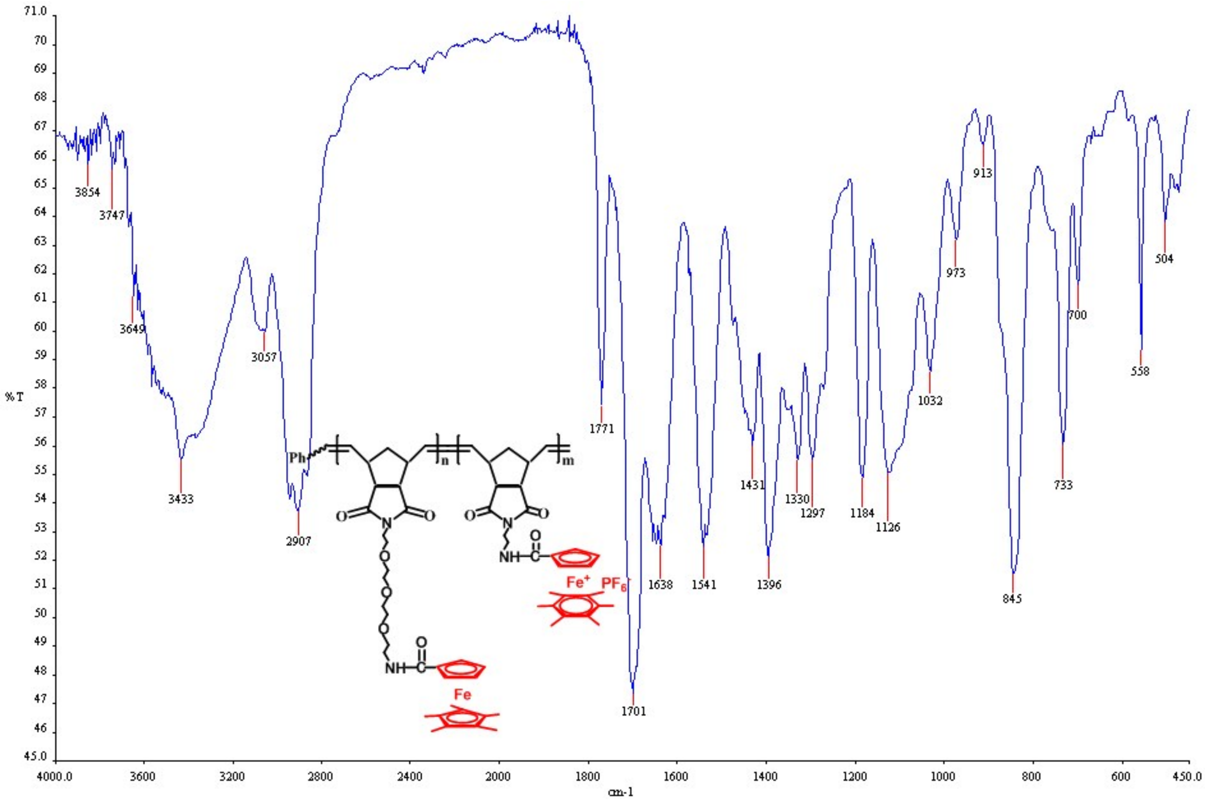


Figure S48 IR spectrum of diblock copolymer **15**.

3433 cm^{-1} ($\nu_{\text{N-H}}$), 2907 cm^{-1} (ν_{CH3}), 1771 cm^{-1} ($\nu_{\text{C=C}}$), 1701 cm^{-1} ($\nu_{\text{C=O}}$), 1638 cm^{-1} ($\delta_{\text{N-H}}$), 1541 cm^{-1}, 1396 cm^{-1}, 845 cm^{-1} (ν_{PF6}), 733 cm^{-1}.

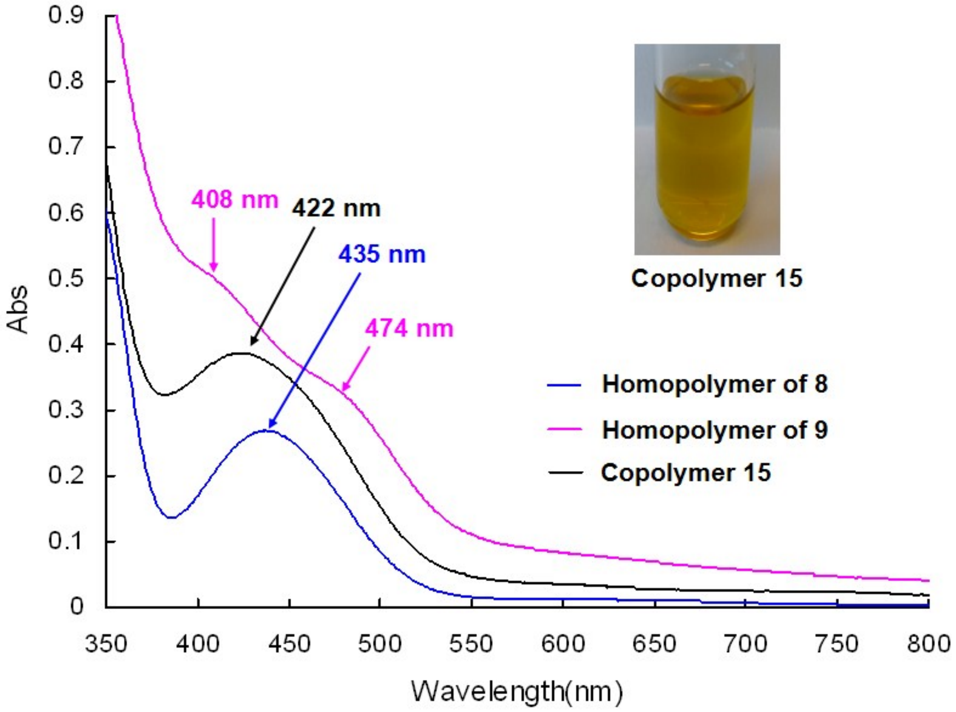


Figure S49 UV-Vis spectra of diblock copolymer **15**, Fc*-containing homopolymer of **8**, FbX-containing homopolymer of **9** in CH_2Cl_2.

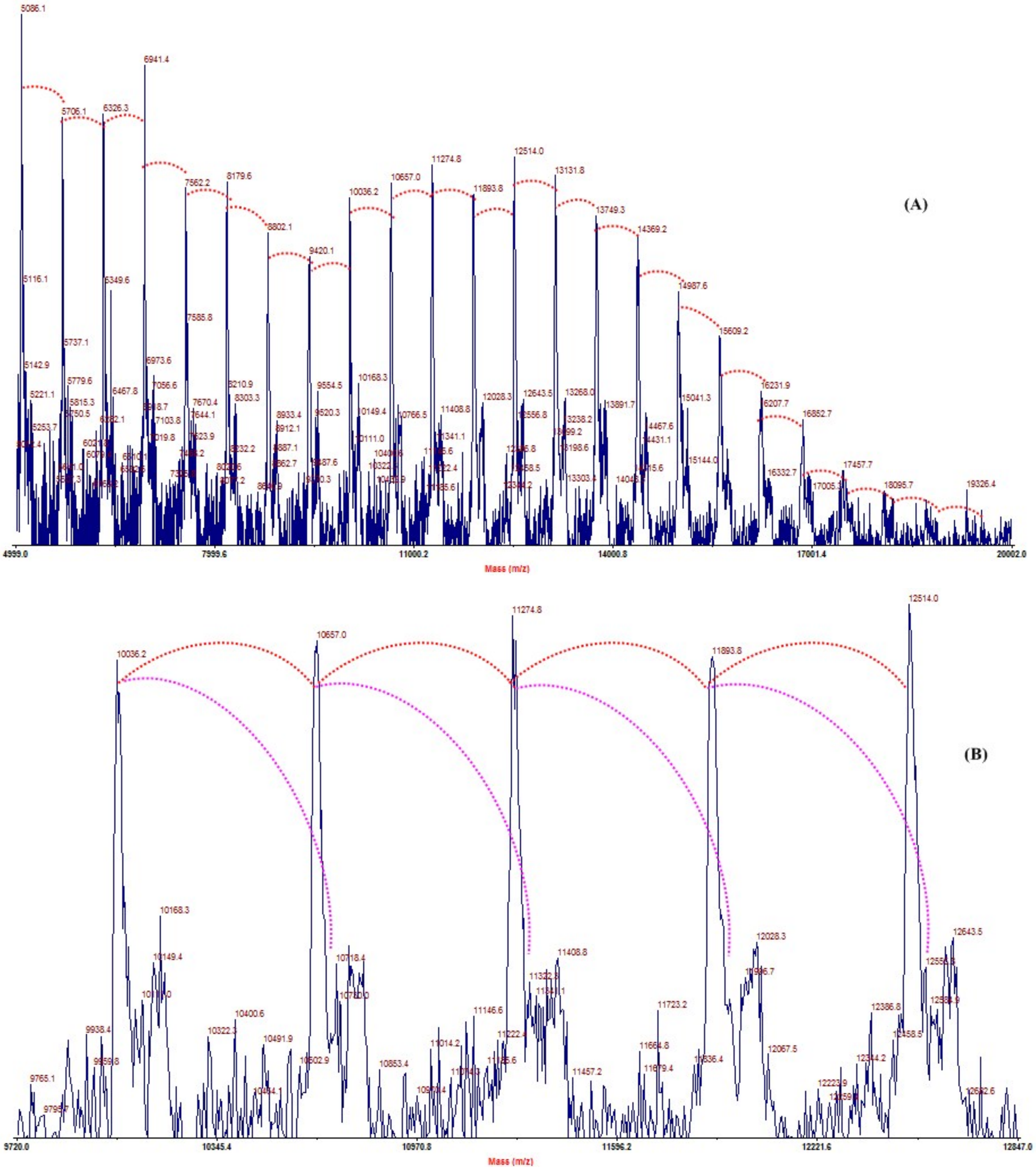


Figure S50 MALDI-TOF MS spectrum of diblock copolymer **15**. The feed molar ratio of monomers **8** and **9** to **1** is 25 : 25 : 1. (A) is the region of 5000-20000 in the spectrum; and (B) is the enlarged region of the spectrum from 9720 to 12847. The red dotted lines correspond to the difference between molecular peaks of a value of 620 ±1 Da (MW of monomer **8**). The pink dotted lines correspond to the difference between molecular peaks of a value of 660 ±1 Da (MW of monomer **9**).

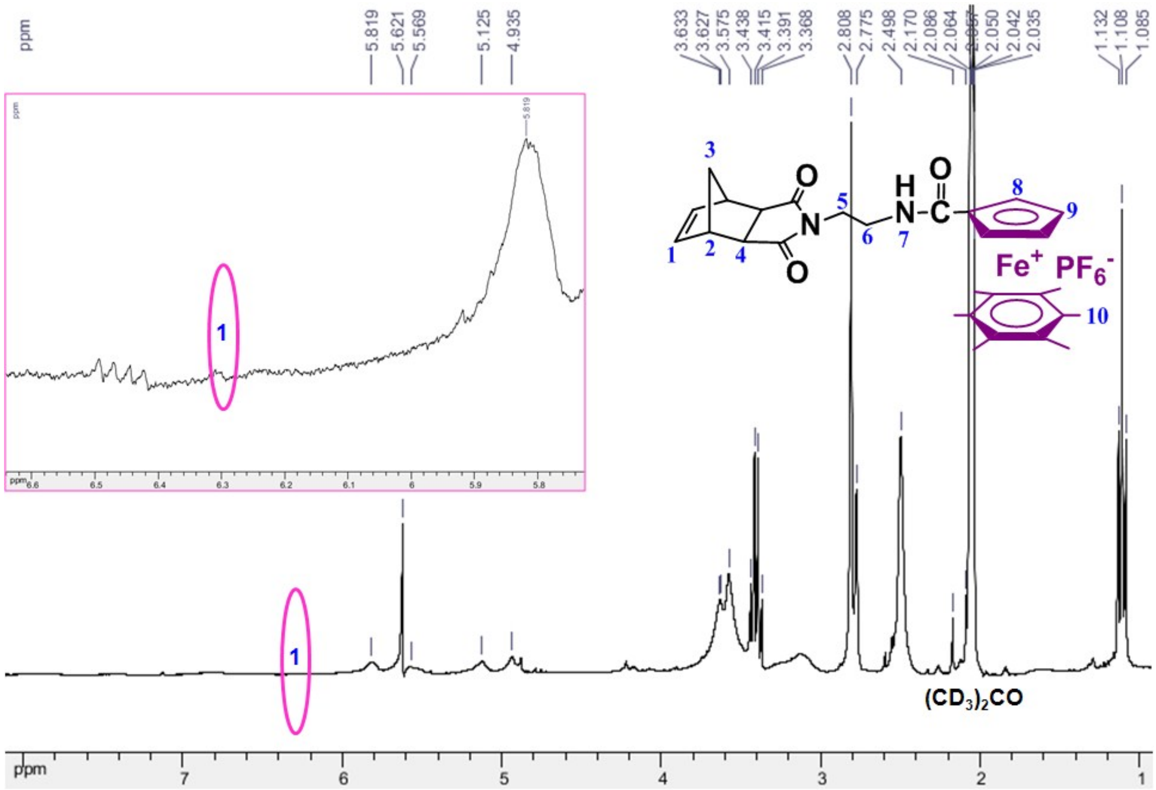


Figure S51 ^{1}H NMR spectrum in acetone-d_6 of the ROMP reaction mixture for the synthesis of diblock copolymer **15** after the addition of monomer **9** with 10 minutes stirring. No peak was observed at 6.30 ppm or so for the olefin protons of monomer **9**, namely no monomer **9** was left and the ROMP of **9** is complete.

Table S10 Polymer degree of the second FbX block using the ^{1}H NMR spectrum in CD_2Cl_2 of copolymer **15**. [a,b]

Proton peak	Amido in the first block	Sub. Cp in the second block	Sub. Cp in the second block	Methyl of C_6Me_6 in the second block
δ_{ppm}	6.04	4.88	4.61	2.38
Integration	1.15-1.19	2.07-2.15	2.03-2.20	17.2-17.6
n_{p2a}	-	21-24[c]	21-25[c]	19-22[d]
n_{p2b}[e]	22 ± 3			

[a] Figure 3 in the main text was used for the calculation of the polymer degree of the second block. [b] The average polymer degree of 25 ± 1 for the first Fc* block, as shown in Table S6, was used for the calculation of polymer degree of the second FbX block. [c] Calculated by comparing the amido proton integration in the first block and the substituted Cp proton integration in the second block. [d] Calculated by comparing the amido proton integration in the first block and the methyl proton integration of C_6Me_6 in the second block. [e] Average polymer degree for the second block according to the n_{p2a} values.

For the second FbX block, the polymer degree is 22 ± 3, as shown in Table S10. The largest error results from the following two sides. (1) This analysis was carried out by comparing the integration of the characteristic peaks of the first Fc* block and the second FbX block. The former is the amido peak at 6.04 ppm with integration of 1.15-1.19; the latter is the substituted Cp peaks at 4.88 ppm with the integration of 2.07-2.15 and 4.61 ppm with the integration of 2.03-2.20, and the methyl peak of C_6Me_6 at 2.38 ppm with the integration of 17.21-17.62. Obviously, integrations for each peak have error that results in the corresponding error for the calculated polymer degree of the second block. (2) The above obtained polymer degree of 25 ± 1 for the first Fc* block is used for the calculation of the polymer degree for the second FbX block, which also results in a larger error than for the first block. The obtained values are 21-24, 21-25 and 19-22, respectively, and then the average is 22 ± 3.

Table S11 Redox potentials, chemical (i_c/i_a) and electrochemical (E_{pa}-E_{pc} = ΔE) reversibility data for the diblock copolymer **15**

Fc* center		FbX center	
$E_{1/2}$ (ΔE) (V)	i_c/i_a	$E_{1/2}$ (ΔE) (V)	i_c/i_a
0.390 (0.02)	1.13	-1.290 (0.07)	1.50

Calculation of the polymerization degrees (n_{p3}) for diblock copolymer 15 by Bard-Anson's method

The following modified Bard-Anson's electrochemical equation is used:

$$n_{p3} = \left(\frac{i_{dp} n_m}{i_{dm} n_p}\right)\left(\frac{M_p}{M_m}\right)^{0.275}$$

(i_{dp}: intensity of polymer; n_p: mole of polymer; i_{dm}: intensity of monomer; n_m: mole of monomer; M_p: molecular weight of polymer; M_m: molecular weight of monomer).

[FeCp*$_2$] was used as the monomer reference. The results of calculated polymerization degrees (n_{p3}) of the Fc* and FbX blocks for diblock copolymer **15** are listed in Table S12.

Table S12 Polymerization degree (n_{p3}) for each metalloblock in polymer **15** calculated using the Bard-Anson electrochemical method.

$[M_8] : [M_9] : [C]$[a]	25 : 25 : 1	
M_m[b]	326.3	
M_p[c]	32104	
n_m[d] (mmol)	9.2×10^{-4}	
n_p[e] (mmol)	1.49×10^{-3}	
i_{dm} (cm)	2.5	
Redox center	Fc*	FbX
i_{dp} (cm)	1.7	1.8
n_{p1}[f]	20 ± 2	21 ± 2

[a] $[M_8] : [M_9] : [C]$: feed molar ratio of monomers **8** and **9** to **1**. [b] Molecular weight of decamethyferrocene. [c] Molecular weight of the copolymer **15** calculated by monomer conversion determined by ^{1}H NMR. [d] n_m: mole of $[FeCp^*_2]$ added in the DMF solution of the copolymer **15**. [e] n_p: mole of the copolymer **15** in DMF. [f] n_{p1}: polymerization degree determined by the Bard-Anson method.

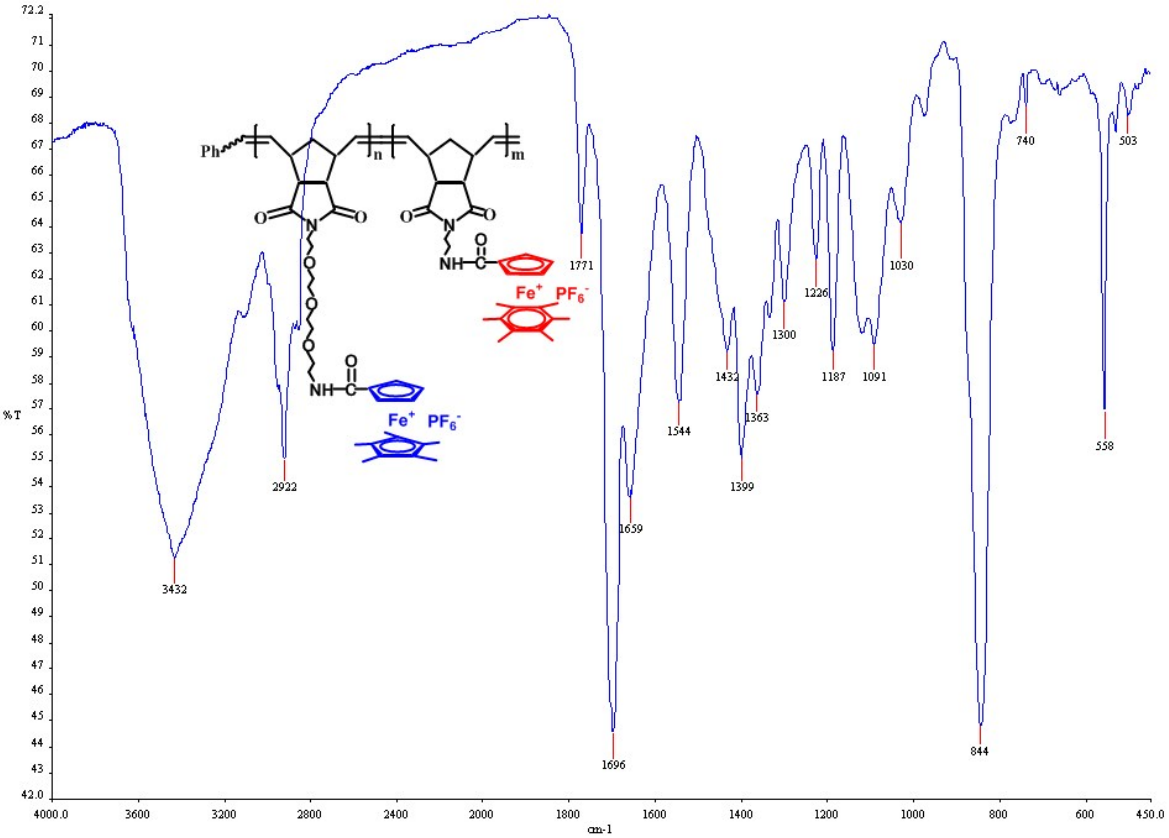


Figure S52 IR spectrum of $[Fc^*]^+$-containing diblock copolymer **16**.

3432 cm^{-1} ($\nu_{N\text{-}H}$), 2922 cm^{-1} (ν_{CH3}), 1771 cm^{-1} ($\nu_{C=C}$), 1696 cm^{-1} ($\nu_{C=O}$), 1659 cm^{-1} ($\delta_{N\text{-}H}$), 1544 cm^{-1}, 1399 cm^{-1}, 844 cm^{-1} ($\nu_{PF6\text{-}}$), 558 cm^{-1}.

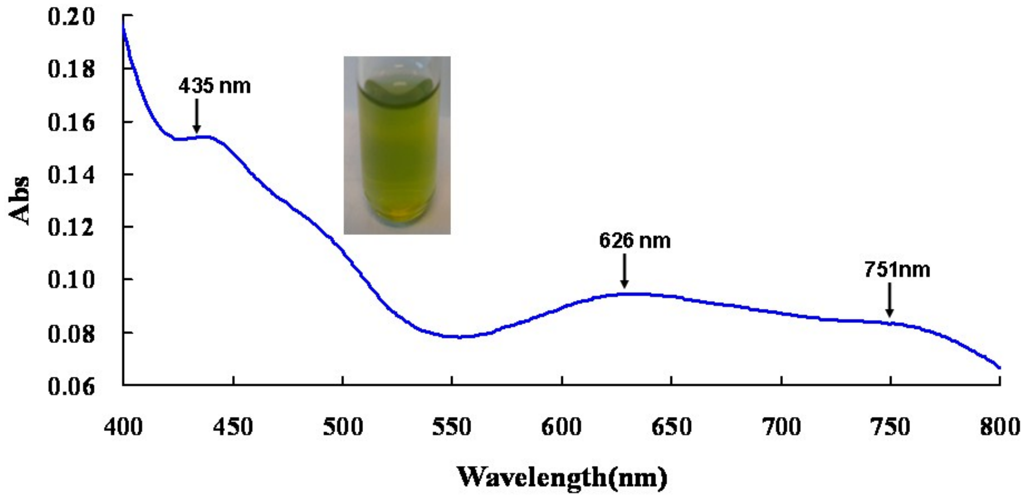


Figure S53 UV-vis. spectrum and picture of $[Fc^{*}]^{+}$-containing copolymer **16** in CH_2Cl_2.

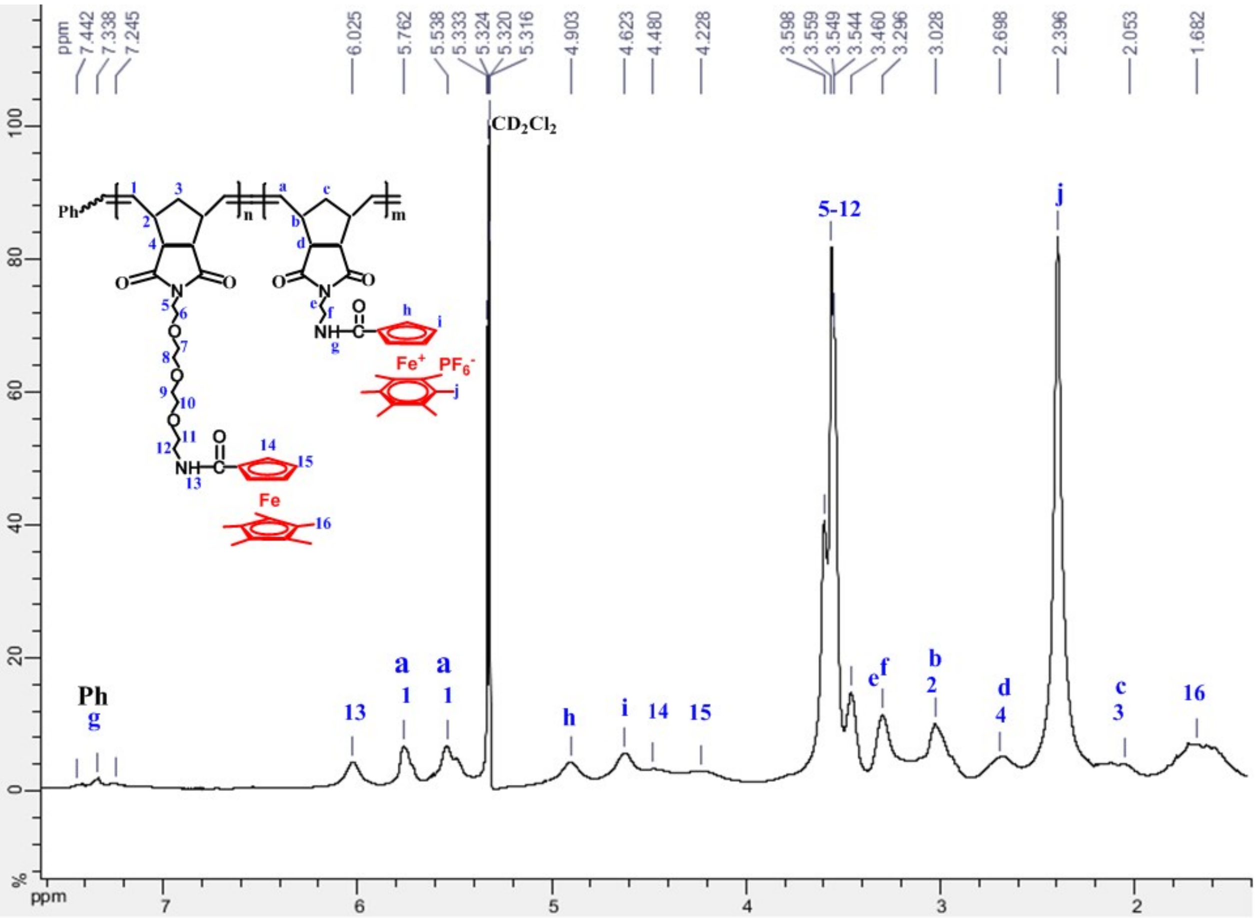


Figure S54 ^{1}H NMR spectrum in CD_2Cl_2 of Fc*-containing diblock copolymer **15** prepared by the reduction of $[Fc^{*}]^{+}$-containing copolymer **16**.

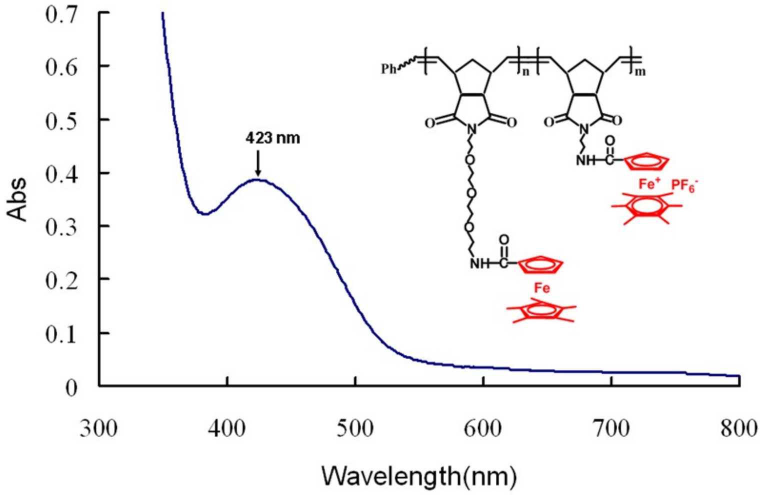


Figure S55 UV-vis. spectrum of Fc*-containing diblock copolymer **15** prepared by the reduction of $[Fc^*]^+$-containing copolymer **16**.

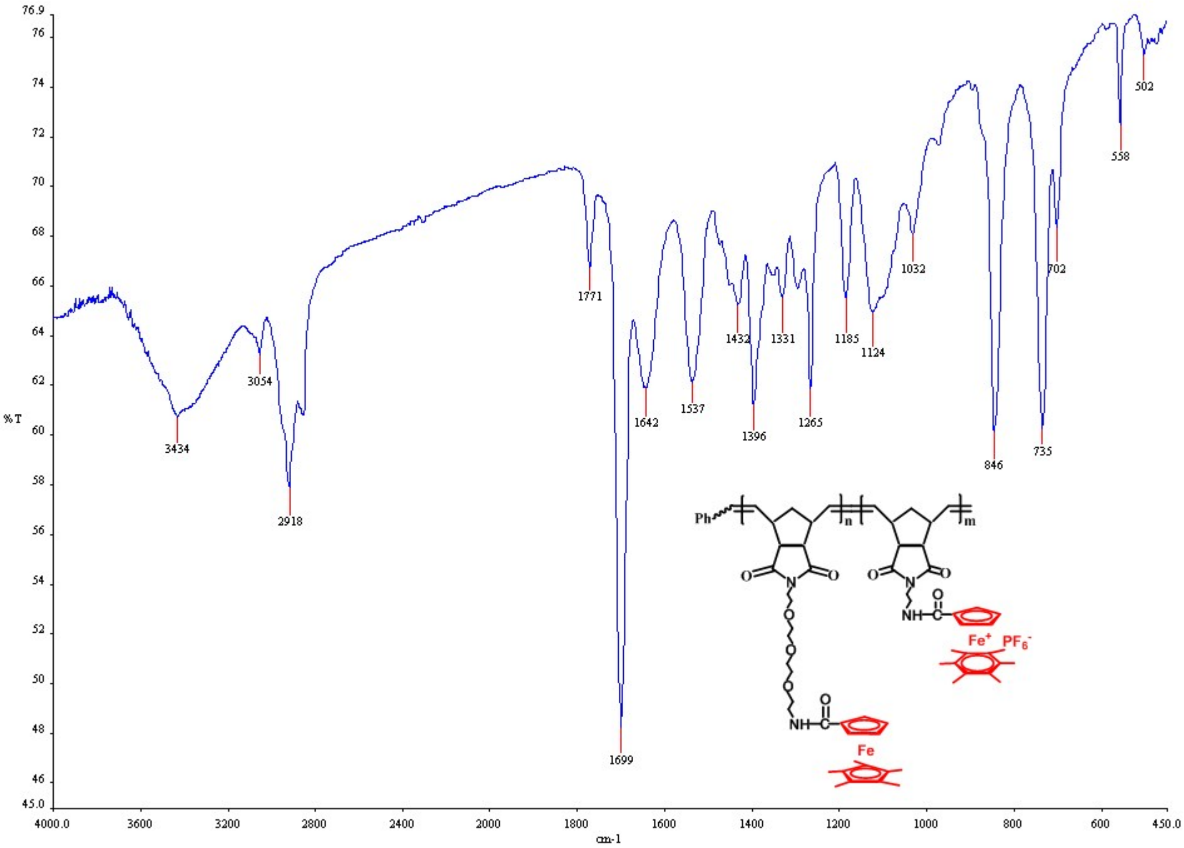


Figure S56 IR spectrum of Fc*-containing diblock copolymer **15** prepared by the reduction of $[Fc^*]^+$-containing copolymer **16**.

3434 cm^{-1} ($\nu_{N\text{-}H}$), 2918 cm^{-1} (ν_{CH3}), 1771 cm^{-1} ($\nu_{C=C}$), 1699 cm^{-1} ($\nu_{C=O}$), 1642 cm^{-1} ($\delta_{N\text{-}H}$), 1537 cm^{-1}, 1396 cm^{-1}, 846 cm^{-1} (ν_{PF6}), 735 cm^{-1}.

8. References

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