Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Regio-Controlled Ring-Opening Polymerization of Perfluoroalkyl-Substituted Epoxides

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Contents

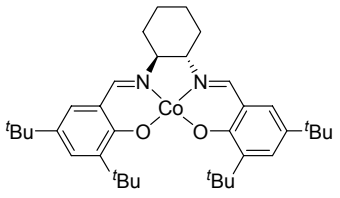
General Procedure. All manipulations involving air-sentitve and/or moisture-sentitive compounds were carried out using the standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11.

All NMR spectra of obtained polymers except for poly(3,3,3-trifluoro-1,2-epoxypropane) were recorded in hexafluorobenzene (C_6F_6) on JEOL JNM-ECP500 (^{1}H: 500 MHz; ^{13}C: 125 MHz; ^{19}F: 471 MHz) spectrometer. Exceptionally poly(3,3,3-trifluoro-1,2-epoxypropane) was recorded in acetone-d_6. Chemical shifts are reported in ppm from following internal standards: tetramethylsilane (0 ppm) for ^{1}H and ^{13}C, C_6F_6 (-162 ppm) for ^{19}F. Gas chromatography analyses were performed on a SHIMADZU GC-2010 equipped with Chrompack CHIRASIL-DEX CB column, and helium was used as the carrier gas. Gel permeation chromatography (GPC) analyses were carried out using two columns (Polymer Laboratories Ltd. gel mixed-C). The GPC columns were eluted with ASAHICLEAN® (CF_2ClCF_2CFHCl : $(CF_3)_2CHOH$ = 99 : 1, v/v) at 37 °C at 1 mL/min. Detailed information was described in previous report.[1] Exceptionally, in measuring poly(3,3,3-trifluoro-1,2-epoxypropane), GPC analysis was carried out using Gel permeation chromatography (GPC) analyses which were carried out using two columns (Shodex KF-804L) and tetrahydrofuran as an eluent at 40 °C at 1 mL/min Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 30. Heating rates were 5 °C/min. The reported T_g values were determined from the second heating scan. Optical rotations were measured on a JASCO DIP-360 spectrometer using a 10-cm cell.

All solvents and fluorinated epoxides used for reactions were distilled under argon after drying over an appropriate drying reagent. Most of the reagents were purchased from Aldrich Chemical Co., Tokyo Kasei Kogyo Co., LTD., Kanto Kagaku Co., Ltd., or Daikin Industries, LTD., and were used without further purification unless otherwise specified. For silica gel column chromatography, Silica gel 60N (spherical neutral, particle size 63-210 μm, Kanto Kagaku Co., Ltd.) was used. ^{i}PrONa was prepared according to literature method.[2]

Preparation of enantiopure epoxides through kinetic resolution of racemic epoxides. Enantiopure epoxides were prepared from slightly modified literature method for kinetic resolution.[3]

Preparation of (+)-3-(nonafluorobutyl)-1,2-epoxypropane. A 100 mL flask equipped with a magnetic stirring bar was charged with Co−salen complex (604 mg, 1.0 mmol). The catalyst was dissolved in toluene (12 mL) and treated with acetic acid (2 mL, 4.2 mmol). The solution was allowed to stir at room temperature open to air for 45 min over which time the color changed from orange-red to a dark brown. The solution was concentrated in vacuo to leave a crude dark brown solid. The resulting catalyst residue was dissolved in (±)-3-(nonafluorobutyl)-1,2-epoxypropane (16 mL, 91 mmol) at room temperature. The reaction flask was cooled to 0 °C, and H_2O (0.86 mL, 48 mmol) was added in one portion. The biphasic reaction mixture was stirred at 0 °C for 7 h when (+)-epoxide was exclusively seen. The termination of (−)-epoxide consumption was confirmed by chiral GC analysis (30 °C, CHIRASIL-DEX CB, isothermal, t_R (+) = 11 min, t_R (−) = 12 min). The mixture was added to 3Å molecular sieve to remove water. After removal of the molecular sieves, unreacted epoxide in the mixture was transferred to a 20 mL Schlenk tube, which was cooled with liquid nitrogen, under reduced pressure. The trapped crude epoxide was left at –27 °C for 3 h and the supernatant epoxide was transferred into another 20 mL Schlenk tube through syringe rapidly under Ar, leaving unidentified solid byproducts. Obtained epoxide (1.2 g, 4.5 mmol, 4.9% yield) was preserved under Ar at –27 ºC. $[\alpha]^{18}_{D}$ +3.6º (*c* 5.3 in AK-225®) (AK-225® = CF_2ClCF_2CFHCl : $CF_3CF_2CFHCl_2$ = 11 : 9, v/v).



Co-salen complex
for kinetic resolution

Preparation of (+)-3-[2-(tridecafluorohexyl)ethoxy]-1,2-epoxypropane. A 100 mL flask equipped with a magnetic stirring bar was charged with Co−salen complex (670 mg, 1.1 mmol). The catalyst was dissolved in toluene (30 mL) and treated with acetic acid (10 mL, 21 mmol). The solution was allowed to stir at room temperature open to air for 45 min over which time the color changed from orange-red to a dark brown as above. The solution was concentrated in vacuo to leave a crude dark brown solid. The resulting catalyst residue was dissolved in (±)-3-[2-(tridecafluorohexyl)ethoxy]-1,2-epoxypropane (30 mL, 110 mmol) and THF (15 mL) at room temperature. The reaction flask was cooled to 0 °C, and H_2O (1.1 mL, 61 mmol) was added in one portion. The biphasic reaction mixture was stirred for 12 h under 0 °C and another 3 h under room temperature when (+)-epoxide was exclusively seen as above. The termination of (−)-epoxide was confirmed by chiral GC analysis (100 °C, CHIRASIL-DEX CB, isothermal, t_R (+) = 8.3 min, t_R (−) = 8.6 min). The mixture was purified by silica-gel column chromatography

(hexane : AcOEt = 5 : 1, v/v). The resulting liquid was distilled (6 mmHg, 120 °C), and the obtained epoxide (5.7 g, 14 mmol, 12% yield) was preserved in a Schlenk tube under Ar at –27 °C. $[\alpha]^{16}_{D}$ +3.6º (*c* 2.0 in AK-225®)

Polymerization Conditions. A 20 mL Schlenk flask equipped with a magnetic stirring bar was charged with an initiator (0.025 mmol), C_6F_6 (2 mL), and an epoxide (2.8 mmol) under Ar at room temperature. The mixture was cooled to 0 ºC and trialkylaluminium (0.25 mmol, 0.25 mL of 1M toluene solution) was added in dropwise. After stirring at described temperature for desired period, the reaction was stopped by adding methanol/water (5mL, MeOH : H_2O = 4 : 1, v/v) and the mixture was dried off under reduced pressure. Fluorous solvent AK-225® (15 mL) was added to this mixture and the resulting suspension was filtered through Celite®. The filtrate was dried off to give polymer.

NMR data of polymers

Atactic poly[3-(nonafluorobutyl)-1,2-epoxypropane] (Table 1, runs 4-6). ^{1}H NMR (C_6F_6) δ 2.50-2.90 (br, 2H), 3.89-4.48 (br, 3H); ^{13}C NMR (C_6F_6) δ 36.2 (br, $CF_2\boldsymbol{C}H_2$), 73.6, 73.8, 74.3, 74.6 (br, $\boldsymbol{C}H_2O$), 76.1 (br, $\boldsymbol{C}H$), 109-124 (m, $\boldsymbol{C}F_3$ and $\boldsymbol{C}F_2$); ^{19}F NMR (C_6F_6) δ 79.5 (br, C$\boldsymbol{F}_3$), 109-112 (m, C$\boldsymbol{F}_2$CH$_2$), 122 (br, C$\boldsymbol{F}_2$), 124 (br, C$\boldsymbol{F}_2$CF$_3$).

Isotactic poly[3-(nonafluorobutyl)-1,2-epoxypropane] (Table 2, run 1). ^{1}H NMR (C_6F_6) δ 2.45-2.90 (br, 2H), 3.80-4.47 (br, 3H); ^{13}C NMR (C_6F_6) δ 36.2 (t, $^2J_{CF}$ = 27 Hz, $CF_2\boldsymbol{C}H_2$), 74.6 (s, $\boldsymbol{C}H_2O$), 76.1 (s, $\boldsymbol{C}H$), 109-124 (m, $\boldsymbol{C}F_3$ and $\boldsymbol{C}F_2$); ^{19}F NMR (C_6F_6) δ 79.5 (br, C$\boldsymbol{F}_3$), 110 (q, J = 346 Hz, C$\boldsymbol{F}_2$CH$_2$), 122 (br, C$\boldsymbol{F}_2$), 124 (br, C$\boldsymbol{F}_2$CF$_3$).

Atactic poly[3-(hepadecafluorooctyl)-1,2-epoxypropane] (Table 2, run 2). ^{1}H NMR (C_6F_6) δ 2.50-2.90 (br, 2H), 3.89-4.48 (br, 3H); ^{13}C NMR (C_6F_6) δ 36.3 (br, $CF_2\boldsymbol{C}H_2$), 73.7, 73.8, 74.5, 74.8 (br, $\boldsymbol{C}H_2O$), 76.1 (br, $\boldsymbol{C}H$), 109-124 (m, $\boldsymbol{C}F_3$ and $\boldsymbol{C}F_2$); ^{19}F NMR (C_6F_6) δ 79.2 (br, C$\boldsymbol{F}_3$), 109-112 (m, C$\boldsymbol{F}_2$CH$_2$), 118, 119, 120, 121 (br, C$\boldsymbol{F}_2$), 124 (br, C$\boldsymbol{F}_2$CF$_3$).

Atactic poly{3-[2-(tridecafluorohexyl)ethoxy]-1,2-epoxypropane} (Table 2, run 3). ^{1}H NMR (C_6F_6) δ 2.51-2.78 (br, 2H), 3.69-4.17 (br, 7H); ^{13}C NMR (C_6F_6) δ 34.2 (t, $^2J_{CF}$ = 21 Hz, $CF_2\boldsymbol{C}H_2$), 65.9 (br, $CF_2CH_2\boldsymbol{C}H_2O$), 72.8 (m, $\boldsymbol{C}H_2O$), 74.2, 74.3 (br, $\boldsymbol{C}H_2O$), 82.0 (s, $\boldsymbol{C}H$), 111-123 (m, $\boldsymbol{C}F_3$ and $\boldsymbol{C}F_2$); ^{19}F NMR (C_6F_6) δ 79.2 (br, C$\boldsymbol{F}_3$), 111, 119, 120, 121, 124 (br, C$\boldsymbol{F}_2$).

Isotactic poly{3-[2-(tridecafluorohexyl)ethoxy]-1,2-epoxypropane} (Table 2, run 4). ^{1}H NMR (C_6F_6) δ 2.43-2.83 (br, 2H), 3.60-4.20 (br, 7H); ^{13}C NMR (C_6F_6) δ 34.2 (t, $^2J_{CF}$ = 21 Hz,

$CF_2\boldsymbol{C}H_2$), 65.9 (s, $CF_2CH_2\boldsymbol{C}H_2O$), 72.8 (br, $\boldsymbol{C}H_2O$), 74.3 (br, $\boldsymbol{C}H_2O$), 82.0 (br, $\boldsymbol{C}H$), 111-123 (m, $\boldsymbol{C}F_3$ and $\boldsymbol{C}F_2$), ^{19}F NMR (C_6F_6) δ 79.2 (br, C$\boldsymbol{F}_3$), 111, 119, 120, 121, 124 (br, C$\boldsymbol{F}_2$).

Regioirregular poly(3,3,3-trifluoro-1,2-epoxypropane) (Table 2, run 5). ^{1}H NMR (Acetone-d_6) δ 2.82 (br), 2.85 (br), 3.96-4.22 (m, 2H), 4.27-4.38 (br, 1H); ^{13}C NMR (Acetone-d_6) δ 70.6-72.1 (m, $\boldsymbol{C}H_2$), 78.1-79.2 (m, $\boldsymbol{C}H$), 120.7-128.3 (m, C$\boldsymbol{F}_3$), ^{19}F NMR (C_6F_6) δ 75.0-75.5 (br, C$\boldsymbol{F}_3$)

Glass transition temperature of polymers.

Polymer	T_g (°C)	Polymer	T_g (°C)
Table 1 , run 4	−31	Table 2 , run 3	−47
Table 1 , run 5	−32	Table 2 , run 4	−48
Table 1 , run 6	−32	Table 2 , run 5	−47
Table 2 , run 1	−31		

Optical rotation of polymers.

Table 2, run 1: $[\alpha]^{18}_D$ +13º (*c* 1.1 in AK-225®)

Table 2, run 4: $[\alpha]^{16}_D$ +7.4º (*c* 2.0 in AK-225®).

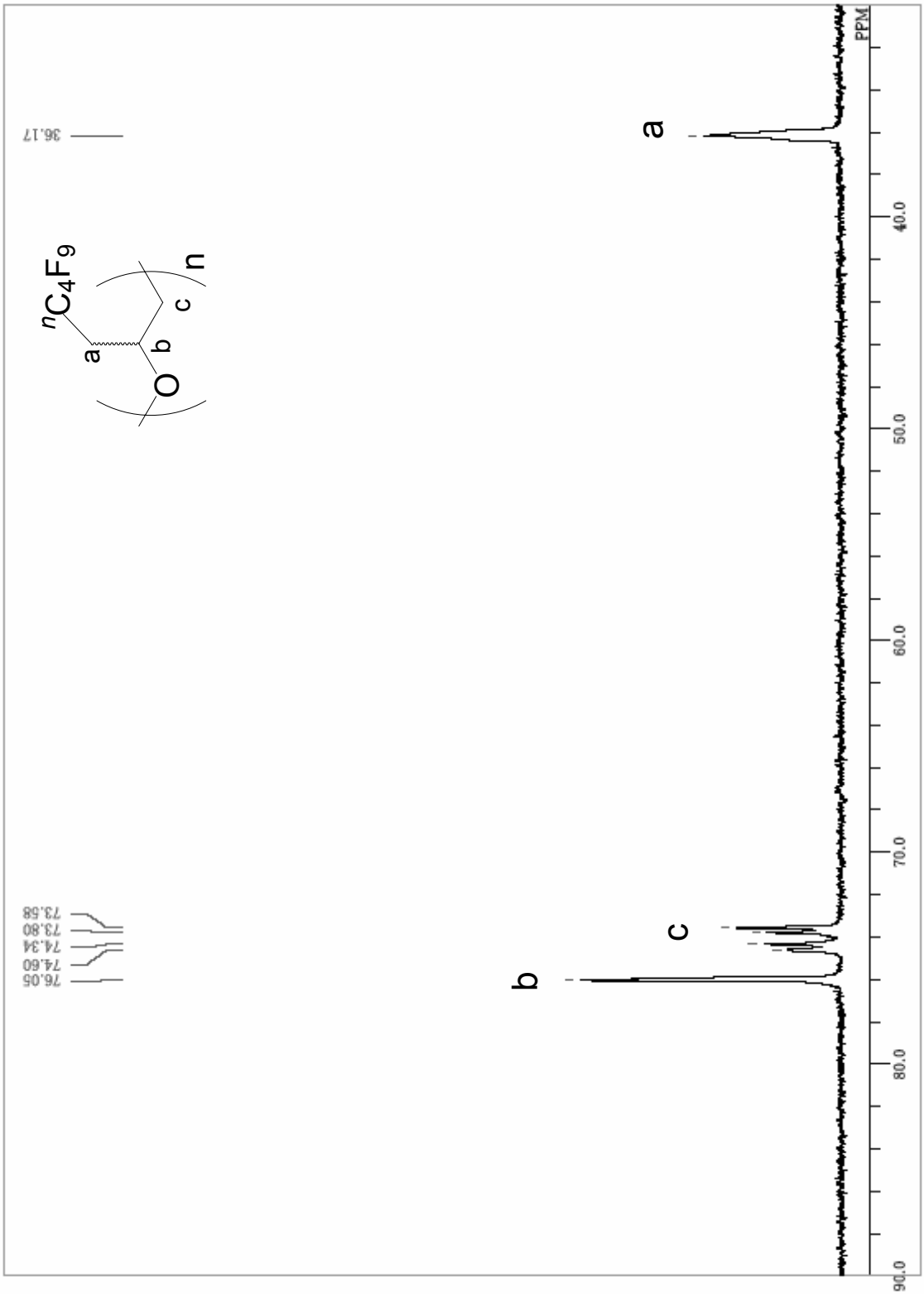


Fig. S1 ^{13}C NMR spectrum of the polymer from (±)-**1** (Table 1, run 6).

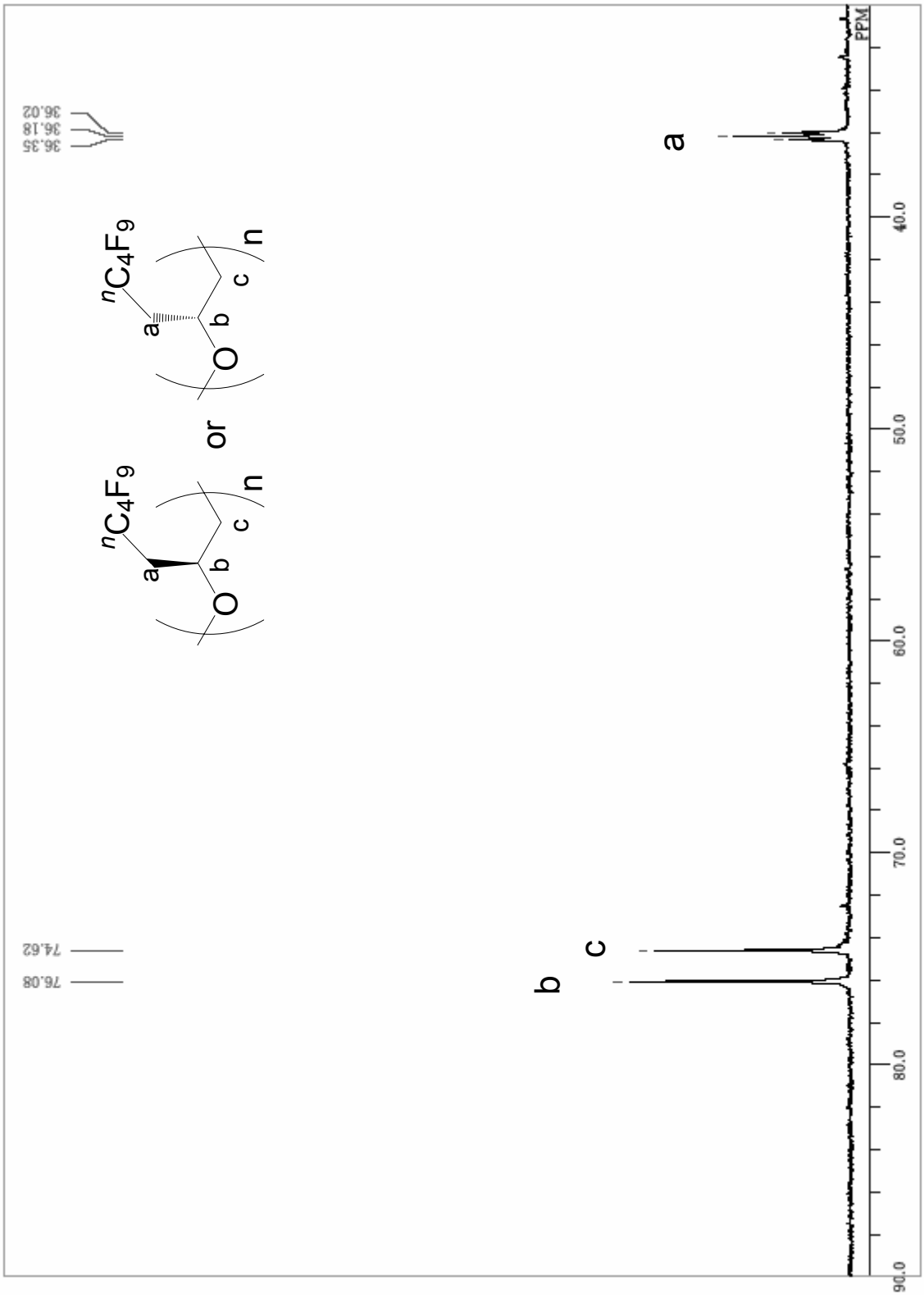


Fig. S2 ^{13}C NMR spectrum of the polymer from (+)-**1** (Table 2, run 1).

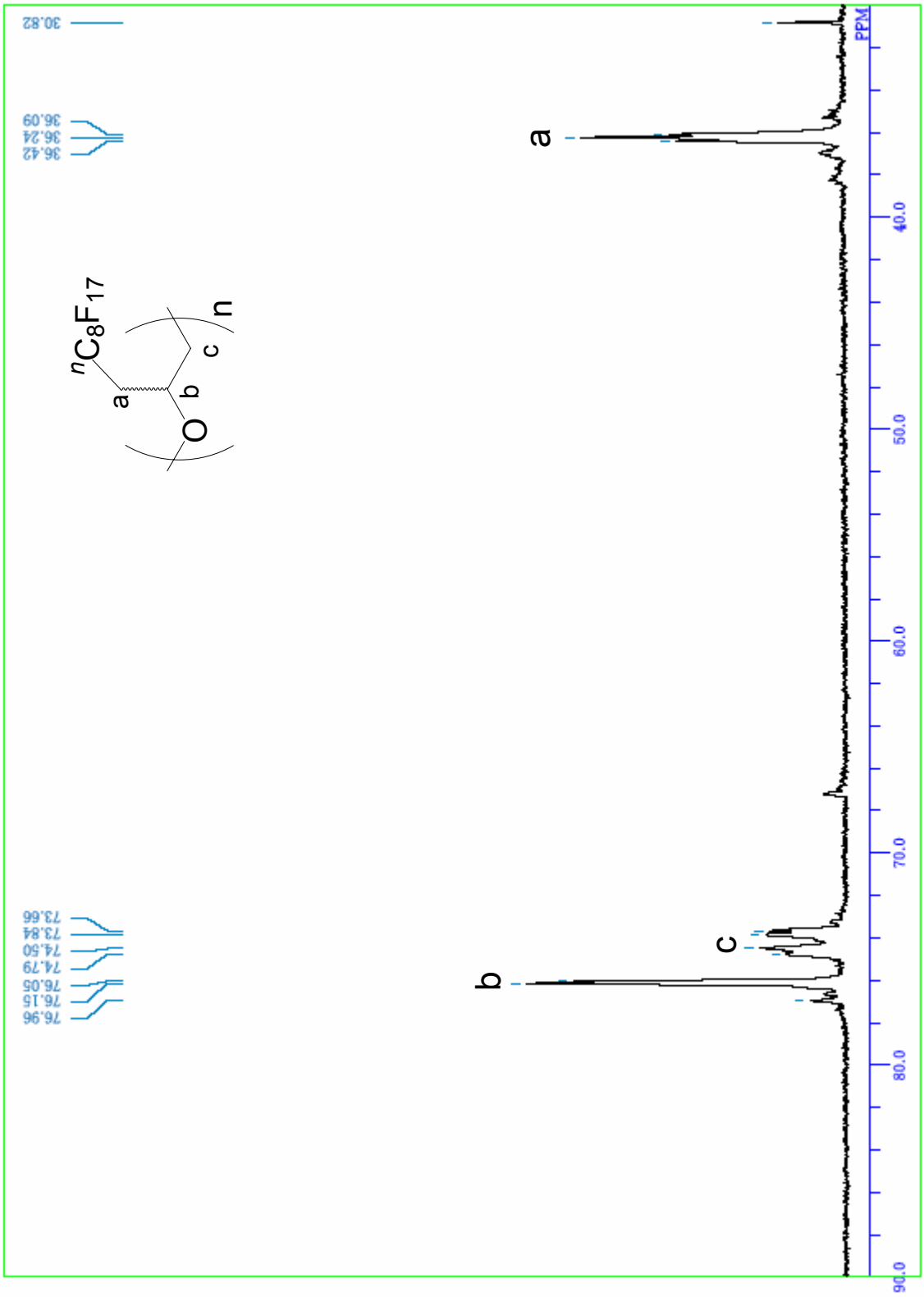


Fig. S3 ^{13}C NMR spectrum of the polymer from (±)-**2** (Table 2, run 2).

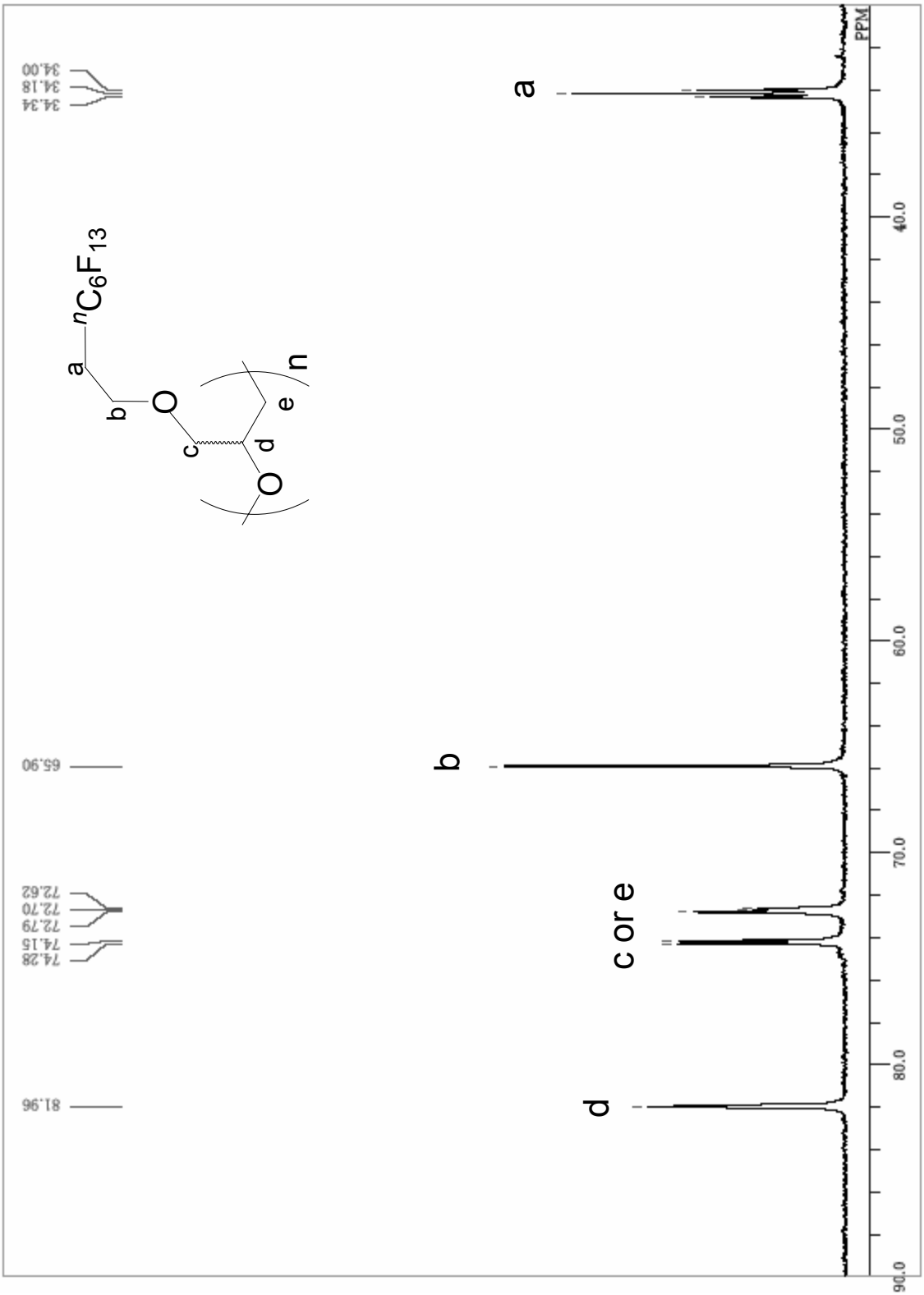


Fig. S4 ^{13}C NMR spectrum of the polymer from (±)-**3** (Table 2, run 3).

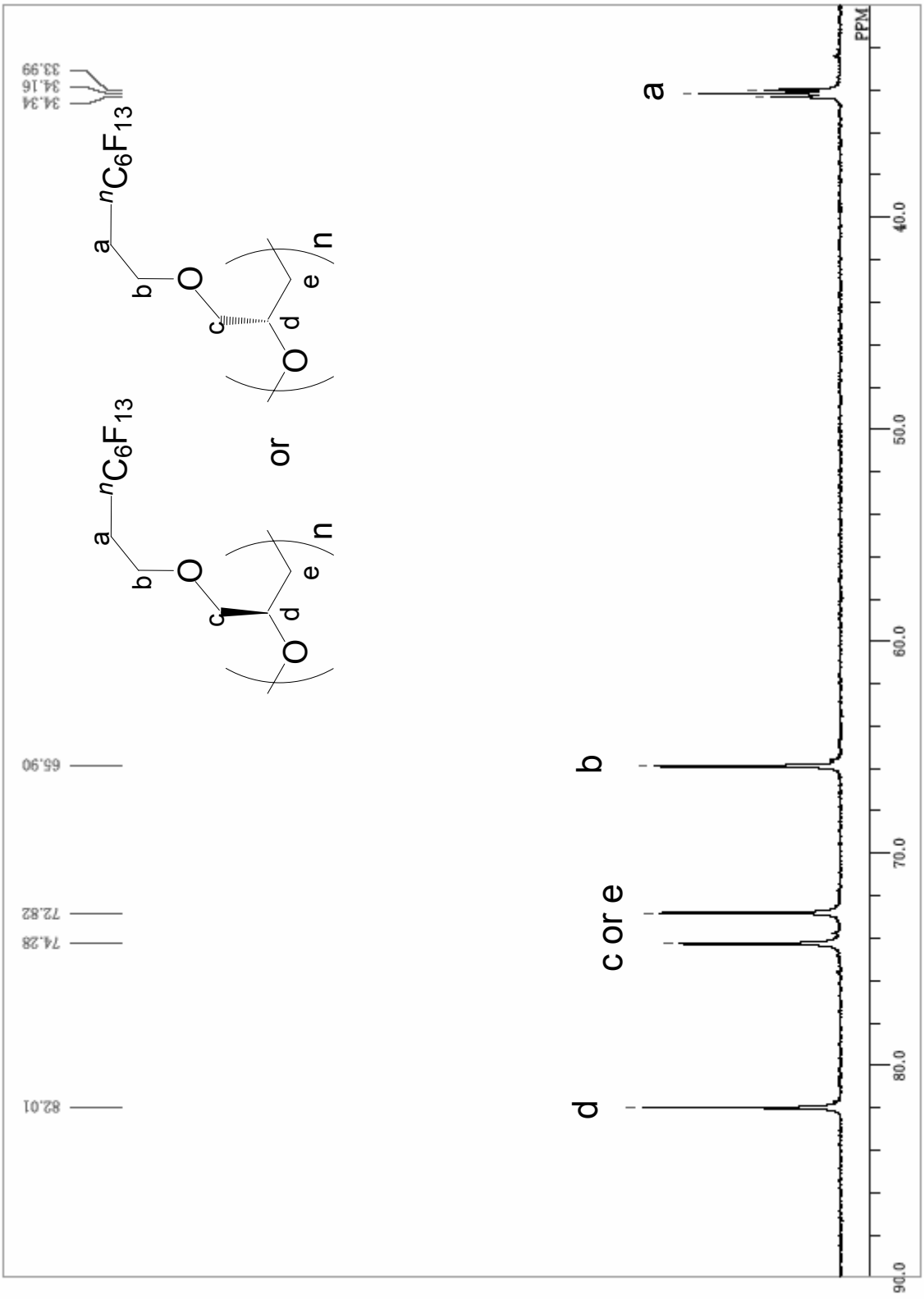


Fig. S5 ^{13}C NMR spectrum of the polymer from (+)-**3** (Table 2, run 4).

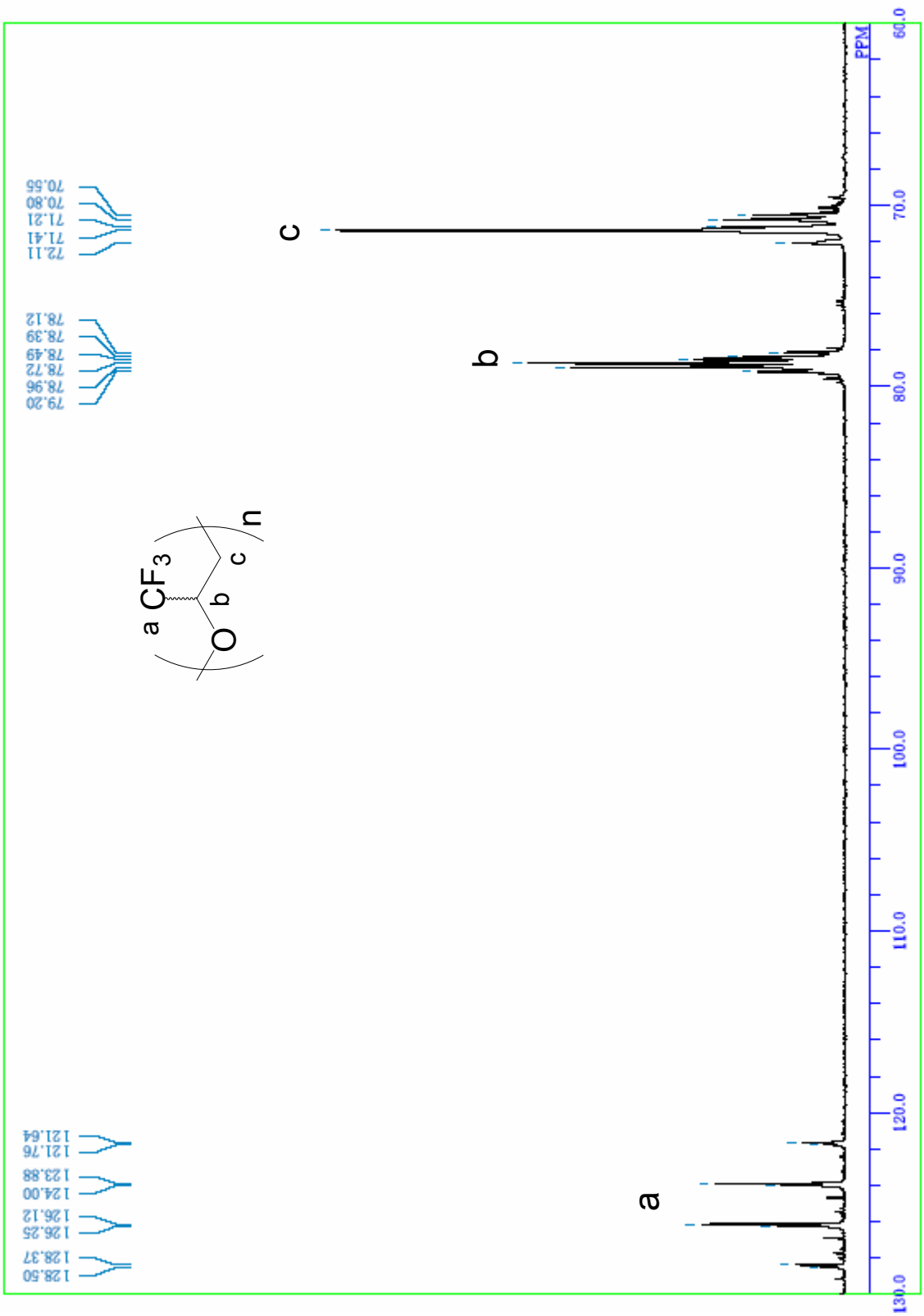


Fig. S6 ^{13}C NMR spectrum of the polymer from (+)-**4** (Table 2, run 5).

MALDI-TOF Mass Measurement. Low molecular-weight oligomers from **1** and **3** (monomer / initiator = 11.2) were prepared as above. Each of the obtained oligomers from **1** and **3** and the polymer from **4** was used for MALDI-TOF mass spectroscopy. MALDI-TOF mass spectrometric measurements were performed on an Applied Biosystems Voyager-DE STR spectrometer equipped with a 337-nm nitrogen laser (pulse width, 3 ns), along with a delayed extraction capability. An accelerating voltage of 20 kV was used, and all mass spectra were recorded in the linear mode. In general, mass spectra from 10000 laser shots were accumulated to produce a final spectrum. Insulin (bovine pancreas 28.3; MW = 5733.50) (Nacalai) were used as an internal standard to calibrate the mass scale. Samples for analysis were prepared by mixing oligomers (1.7 wt % in C_6F_6), a matrix (1,8-dihydroxy-9(10H)-anthracenone, 5.0 wt % in THF), and a cationizing agent (CF_3CO_2Na) in the weight ratio 1/40/1. Then, 1.0 μL portions of the mixture were placed onto gold-coated plate and dried under ambient conditions.

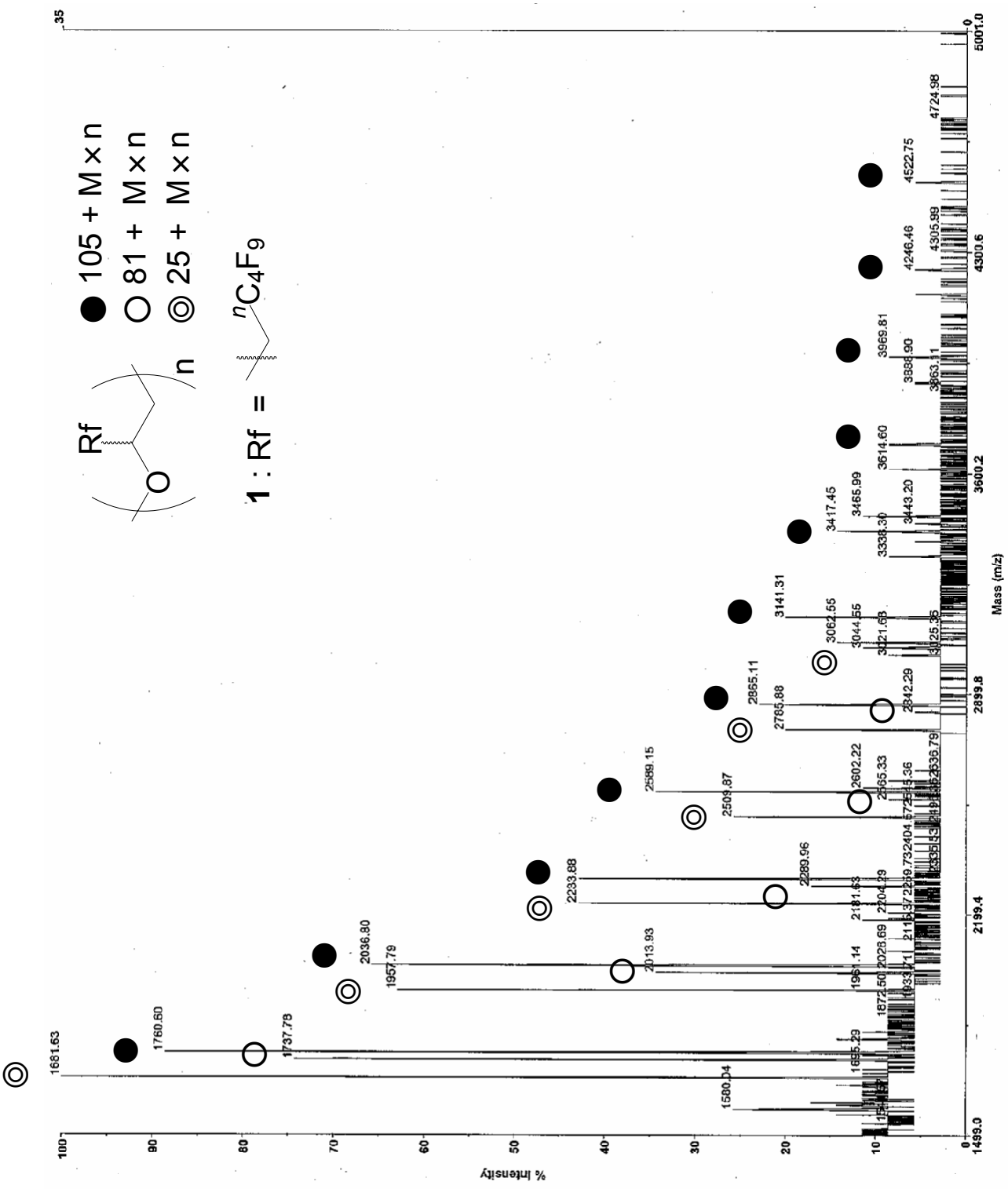


Fig. S7 MALDI-TOF mass spectrum of oligomer from **1**.

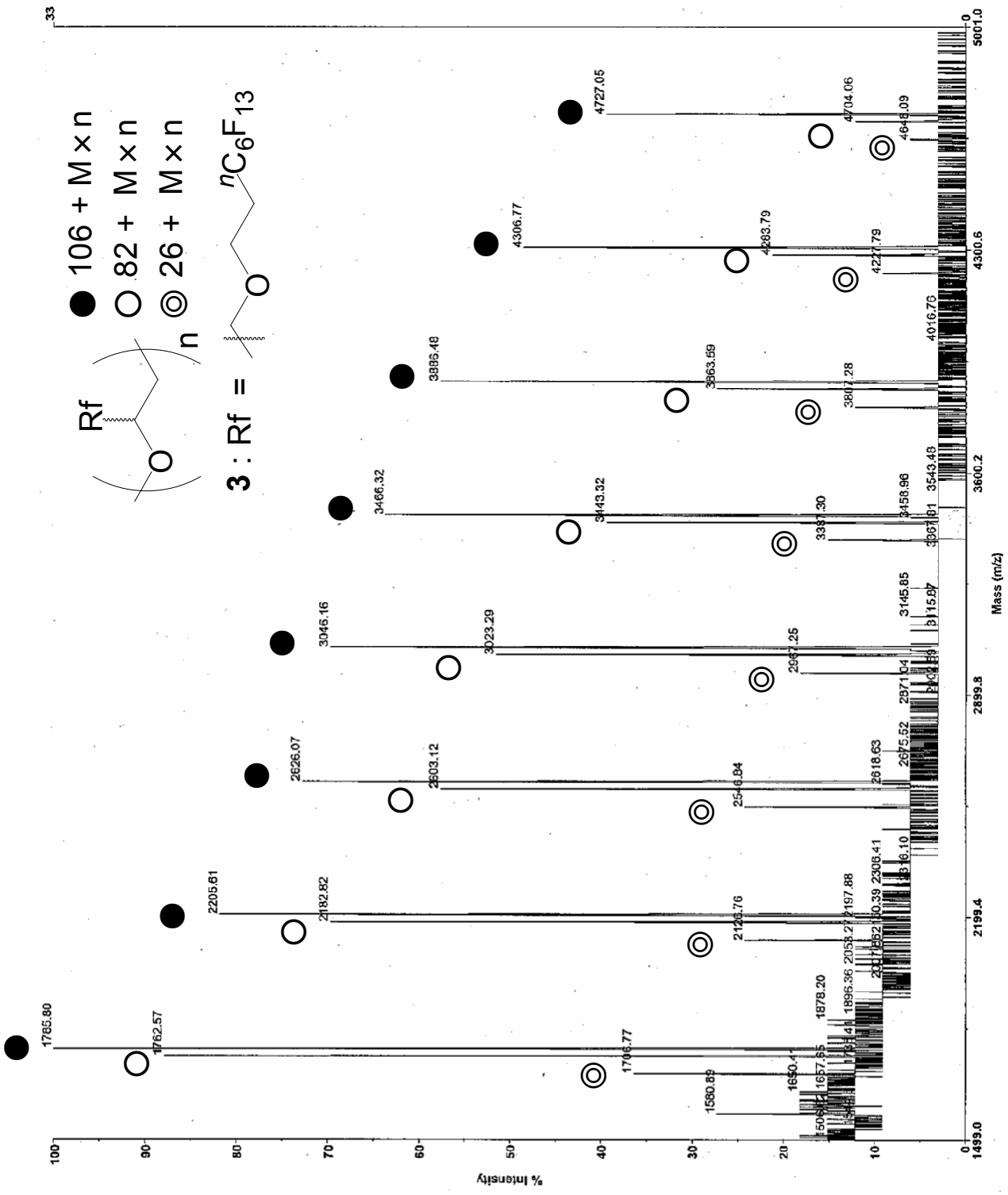


Fig. S8 MALDI-TOF mass spectrum of oligomer from **3**.

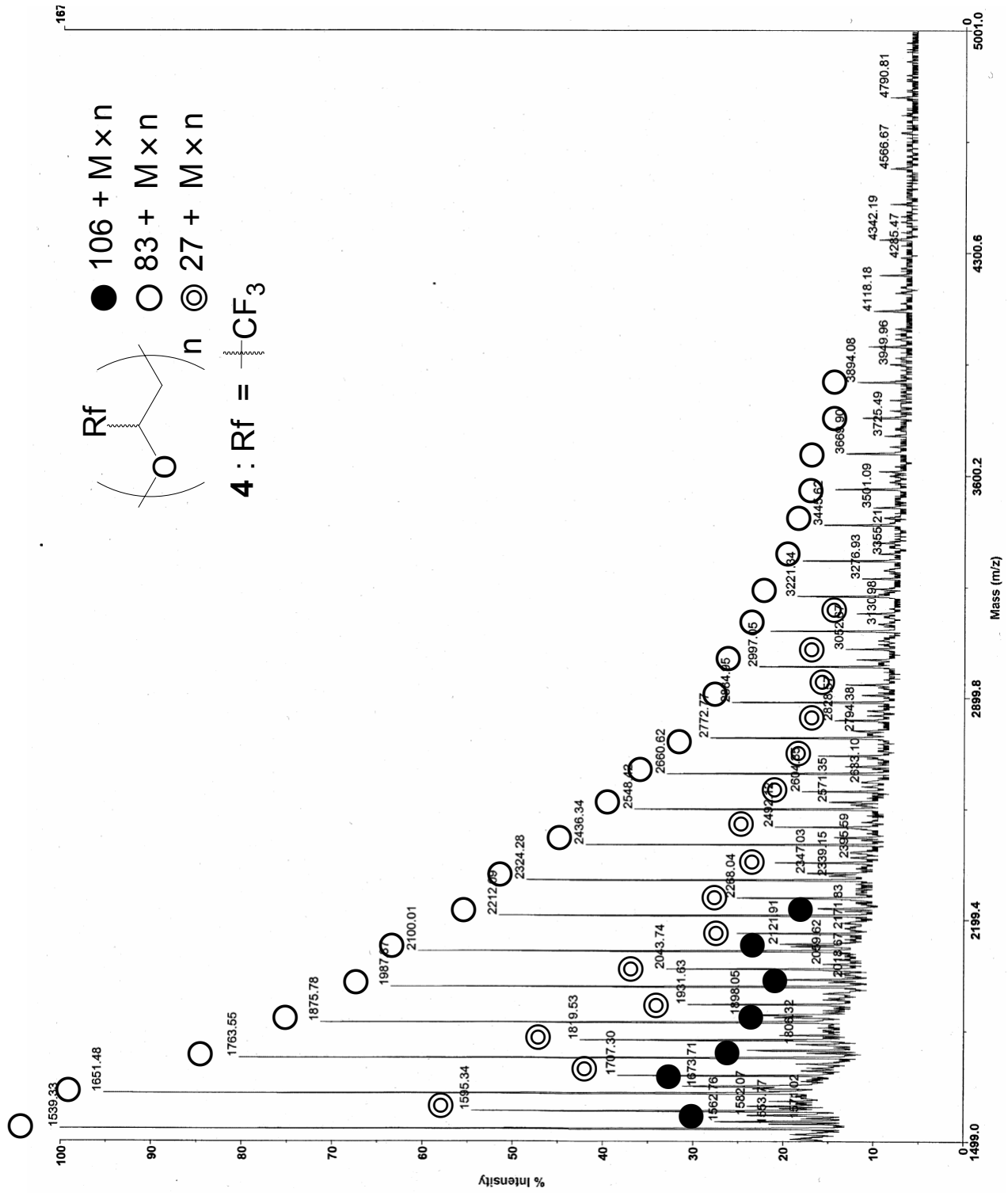


Fig. S9 MALDI-TOF mass spectrum of oligomer from **4**.

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