Supporting Information For:

Coordination−Insertion Copolymerization of Allyl Monomers with Ethylene

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Experimental Section

General: All manipulations were carried out using standard Schlenk techniques under argon purified by passing through a hot column packed with BASF catalyst R3-11. Copolymerization was performed in a 50 mL autoclave under ethylene pressure.

Instrumentation. NMR spectra were recorded on JEOL JNM-ECP500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{31}P: 202 MHz with digital resolution of 0.239, 0.960, 4.33 Hz, respectively) or JEOL JNM-ECS400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz with digital resolution of 0.09125, 0.767, 3.46 Hz, respectively) NMR spectrometers. ^{13}C NMR analyses of polymers were performed in 1,1,2,2-tetrachloroethane-d_4 or 1,2,4-trichlorobenzene at 120 °C using a 30° pulse of 3.0 μs, a spectral width of 31 kHz, a relaxation time of 2 s, and an acquisition time = 1 s. Quantitative ^{13}C NMR analyses of polymers were performed in a 5-mm probe on *ca.* 15 weight% solutions of the polymers and 0.05-M $Cr(acac)_3$ as a relaxation agent in 1,2,4-trichlorobenzene unlocked at 120 °C using a 90° pulse of 9.0 μs, a spectral width of 31 kHz, a relaxation time of 5–10 s, an acquisition time = 2 s, and inverse-gated decoupling[1,2] with the number of FID's collected per sample of 5000–10000. Chemical shift values for carbons are referenced to the carbon resonance of 1,2,4-trichlorobenzene (δ 127.9). Size exclusion chromatography (SEC) analyses were carried out with a Tosoh instrument (HLC-8121GPC/HT) equipped with two SEC columns (Shodex GPC AT-806MS or Tosoh TSKgel GMH_{HR}-H(S)HT) by eluting the columns with 1,2-dichlorobenzene at 1 mL/min at 145 °C. Molecular weights were determined using narrow polystyrene standards and were corrected for polyethylene by universal calibration using the Mark–Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ cm^3/g and $\alpha = 0.67$ for polystyrene and $K = 5.90 \times 10^{-2}$ cm^3/g and $\alpha = 0.69$ for LLDPE.[3]

Differential scanning calorimetry (DSC) measurements of polymers were performed on a Seiko DSC 7020 analyzer at a heating and cooling rate of 10 °C/min. The reported T_m values were determined from the second heating scan. Thermogravimetric (TG) analyses were performed on a Seiko EXSTAR 6000 TG/DTA 6200 analyzer.at a heating rate of 10 °C/min.

Materials. Anhydrous dichloromethane, diethyl ether, hexane, tetrahydrofuran (THF), and toluene were purchased from Kanto Chemical Co. Inc. and purified by the method of Pangborn *et al*.[3] Ethylene (>99.9%) was purchased from Takachiho Chemical Industrial Co., Ltd., dried, and deoxygenated by passing through columns. Allyl acetate (**2a**) was purchased from Tokyo Kasei Co. and purified by distillation over CaH_2. Allyl alcohol (**2b**) was purchased from Tokyo Kasei Co. and dried over molecular sieve 4A. Allylamine (**2c**) was purchased from Tokyo Kasei Co. and used as received. Allyl chloride (**2e**) was purchased from Tokyo Kasei Co. and used as received. Allyl bromide (**2f**) was purchased from Kanto Chemical Co. Inc. and used as received. The following compounds were prepared according to literature procedures: (*o*-$Cy_2PC_6H_4SO_3$)PdMe(2,6-$Me_2C_5H_3N$) (**1**)[4] and *N*-tert-butoxycarbonyl allylamine (**2d**).[5]

A Representative Procedure for the Copolymerization of Allyl Monomers with Ethylene (entry 3, Table 1)

To a 50-mL autoclave containing catalyst **1** (58.2 mg, 0.10 mmol) were transferred toluene (12.0 mL) and allyl acetate (**2a**) (3.0 mL) under argon atmosphere. After being charged with ethylene (3.0 MPa), the autoclave was stirred at 80 °C for 3 h. After cooling to room temperature, methanol (30 mL) was added into the autoclave. The polymer (1.38 g; **2a** incorporation ratio = 3.4%) was isolated by filtration, washed with methanol, and dried under vacuum at 80 °C. The copolymer was further purified by reprecipitation from hot 1,2-dichlorobenzene/CH_2Cl_2. Molecular weights was determined to be M_n = 5,300 and M_n/M_w = 2.6 by SEC analysis. The molar incorporation ratio of **2a** was determined to be 3.2% by quantitative ^{13}C NMR analysis.

Control Experiment for the Copolymerization of 2a with Ethylene in the Presence of Galvinoxyl.

To a 50-mL autoclave containing catalyst **1** (58.2 mg, 0.10 mmol) and galvinoxyl (42.2 mg, 0.10 mmol) were transferred toluene (12.0 mL) and allyl acetate (**2a**) (3.0 mL) under argon atmosphere. After being charged with ethylene (3.0 MPa), the autoclave was stirred at 80 °C for 3 h. After cooling to room temperature, methanol (30 mL) was added into the autoclave. The polymer (0.98 g) was isolated by filtration, washed with methanol, and dried under vacuum at 80 °C. The copolymer was further purified by reprecipitation from hot 1,2-dichlorobenzene/CH_2Cl_2. NMR and SEC analyses showed that the obtained copolymer has essentially the same structures as that obtained in

the absence of galvinoxyl (entry 3, Table 1). Molecular weights was determined to be M_n = 4,500 and M_n/M_w = 2.2. The molar incorporation ratio of **2a** was determined to be 3.8% by quantitative ^{13}C NMR analysis.

Comparison of Molecular Weights Determined by SEC and NMR analyses

In entry 3 in Table 1 (ethylene/**2a** copolymer with 3.2% incorporation), molecular weight by SEC using polystyrene standard was M_n = 12,100 and corrected by universal calibration to be M_n = 5,300. Molecular weights by ^1H NMR and ^{13}C NMR were M_n = 7,300 and 10,800, respectively.

In entry 10 in Table 1 (ethylene/**2e** copolymer with 0.9% incorporation), molecular weight by SEC using polystyrene standard was M_n = 9,700 and corrected by universal calibration to be M_n = 4,200. Molecular weights by ^1H NMR and ^{13}C NMR were M_n = 5,900 and 5,000, respectively.

Hydrolysis of Acetoxy Groups in the Ethylene/2a Copolymer (obtained in entry 3 in Table 1)

A mixture of ethylene/**2a** copolymer (obtained in entry 3 in Table 1; M_n = 5,300, M_w/M_n = 2.6, **2a** incorporation ratio = 3.2%, 300 mg) and KOH (24 mg) in toluene (40 mL) and EtOH (12 mL) was stirred at 80 °C for 6 h. After cooling to room temperature, the solvents were removed under reduced pressure. After adding Et_2O (50 mL), the resulting residue was washed with water (50 x 4 mL). The organic solvent was removed under reduced pressure to give ethylene/**2b** copolymer (272 mg). The molecular weights were estimated to be M_n = 4,700 and M_w/M_n = 2.4 by SEC. The molar incorporation ratio of allyl monomers was determined to be 3.3% by quantitative ^{13}C NMR analysis.

Deprotection of *N*-tert-butoxycarbonyl (Boc) Groups in the Ethylene/2d Copolymer (obtained in entry 8 in Table 1)

Ethylene/**2d** copolymer (obtained in entry 8 in Table 1; M_n = 4,500, M_w/M_n = 2.4, **2d** incorporation ratio = 1.8%, 300 mg) was treated with conc. HCl (20 mL) in toluene (30 mL) and EtOH (18 mL) at 78 °C for 3 h. After cooling to room temperature, the solvents were removed under reduced pressure to give ethylene/CH_2=$CHCH_2NH_3Cl$ copolymer (285 mg). Although the molecular weights (M_n and M_w) could not be determined by SEC due to the broadening traces (Figure S57), comparison of main-chain signals (carbon *e*) and chain-end signals (carbons *f*, *g*, and *h*) in ^{13}C NMR spectrum revealed that the backbone structure of the copolymer was not changed via the deprotection (Figure S32 and S58). The exact incorporation ratio of NH_3Cl group could not be determined by quantitative ^{13}C NMR analysis due to the broadening signals of α and β carbons to the NH_3Cl group (Figure S58).

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(1) (a) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059–2062. (b) Cotts, P. M.; Guan, Z.; McCord. E.; McLain, S. *Macromolecules* **2000**, *33*, 6945–6952.
(2) Randall, J. C.; Ruff, C. J.; Kelchtermans, M.; Gregory, B. H. *Macromolecules* **1992**, *25*, 2624–

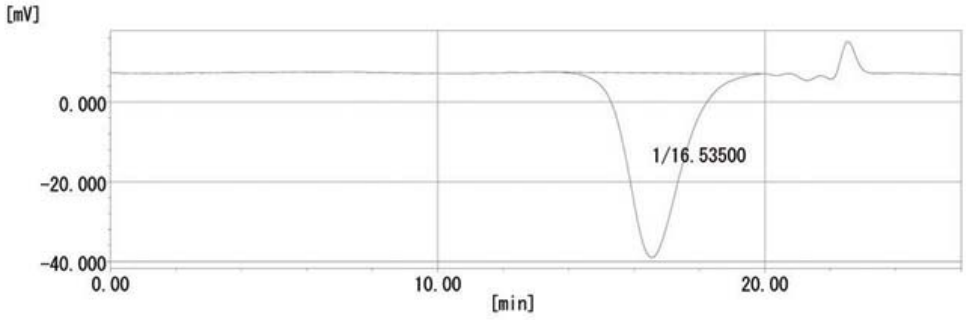
2633.
(3) Grinshpun, V.; Rudin, A. *Makrom. Chem., Rapid Commun.* **1985**, *6*, 219.
(4) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14606–14607.
(5) Kawamoto, A. M.; Wills, M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1916–1928.

Ethylene/2a Copolymer Obtained in Entry 1 in Table 1:

55-04-060-3

Sample name : 55-04-060-3
Database name : Yagyu.mdb
Saved file name : RSLT0203
Method data : 20100413std

Measurement date : 2010/09/24 15:20:20
Calculation date : 2010/09/27 09:41:24



	[min]	[mV]	[MOL]
Peak start	13.22	7.501	1,026,206
Peak top	16.53	-39.035	29,956
Peak end	19.91	7.108	506
Area [mV·sec]		5,199.163	
Area [%]		100.000	
Height [mV]		46.341	
[η]		35,226.35262	

Mn	:	15,320
Mw	:	35,226
Mz	:	69,648
Mz+1	:	144,059
Mv	:	35,226
Mp	:	30,448
Mz/Mw	:	1.977
Mw/Mn	:	2.299
Mz+1/Mw	:	4.090

Figure S1. SEC trace of ethylene/**2a** copolymer obtained in entry 1 in Table 1. M_n (PS) = 15,300 was corrected to M_n (PE) = 6,700 by universal calibration.

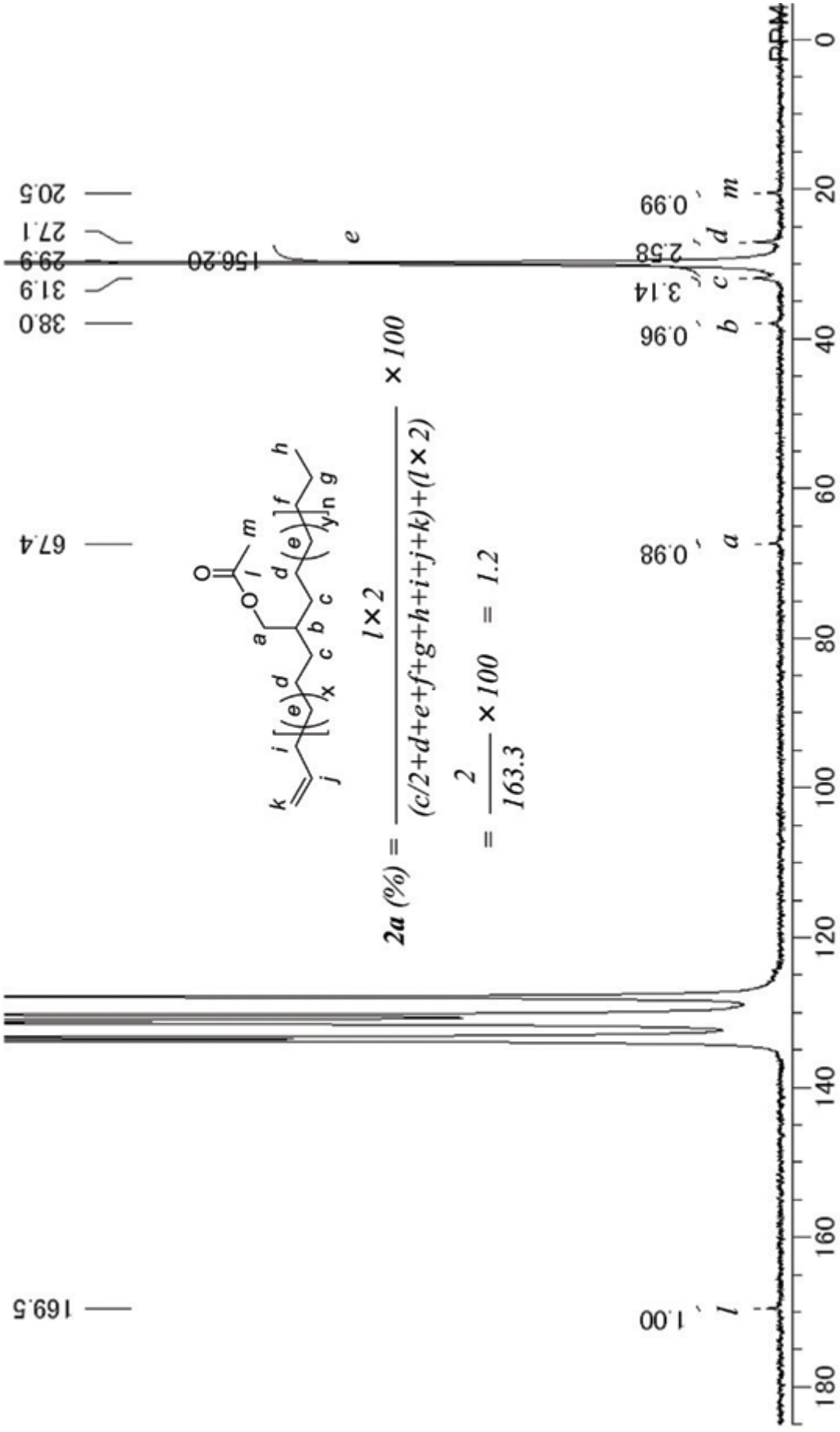


Figure S2. Quantitative ^{13}C NMR spectrum of ethylene/**2a** copolymer obtained in entry 1 in Table 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

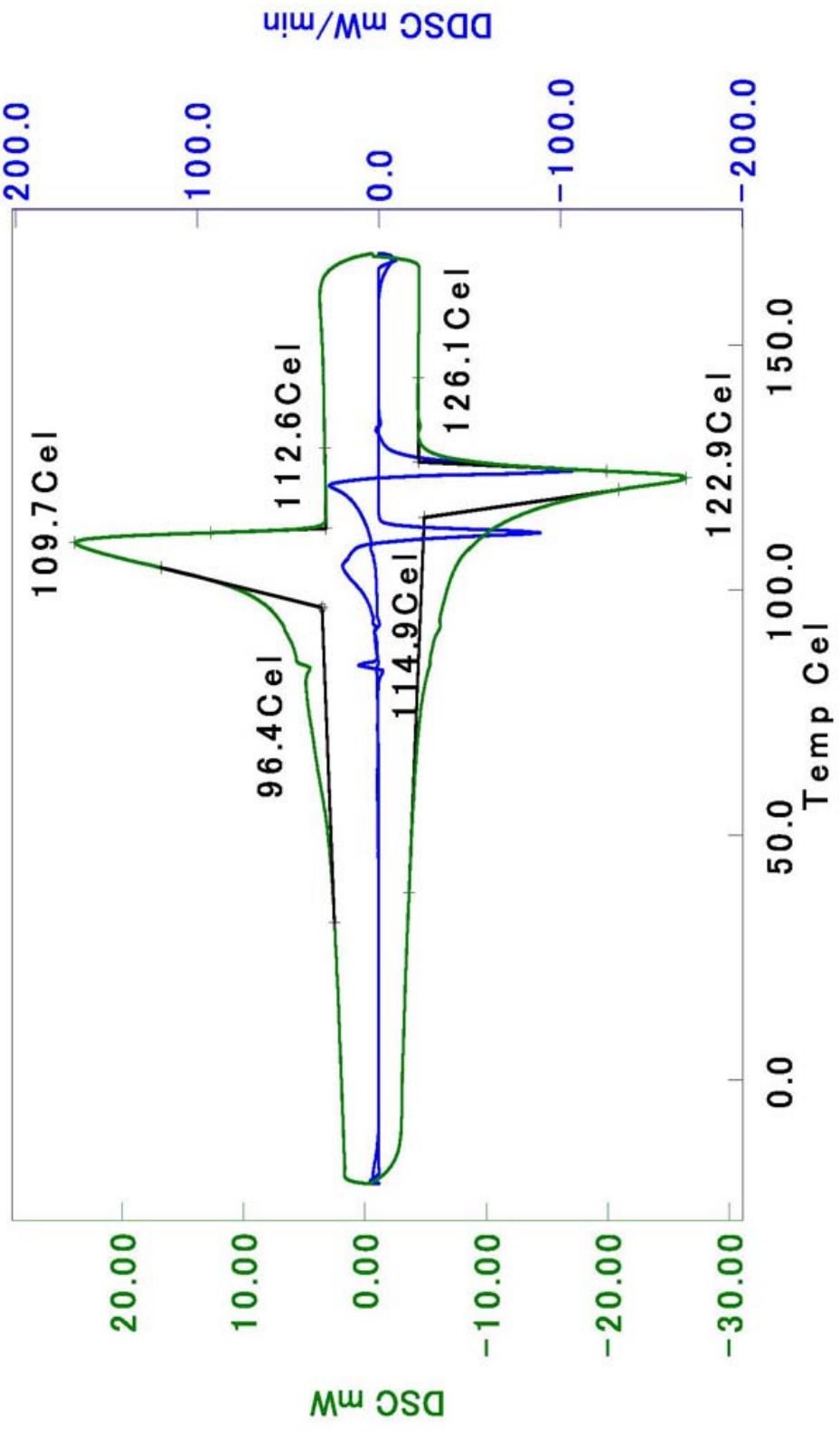


Figure S3. DSC chart of ethylene/**2a** copolymer obtained in entry 1 in Table 1.

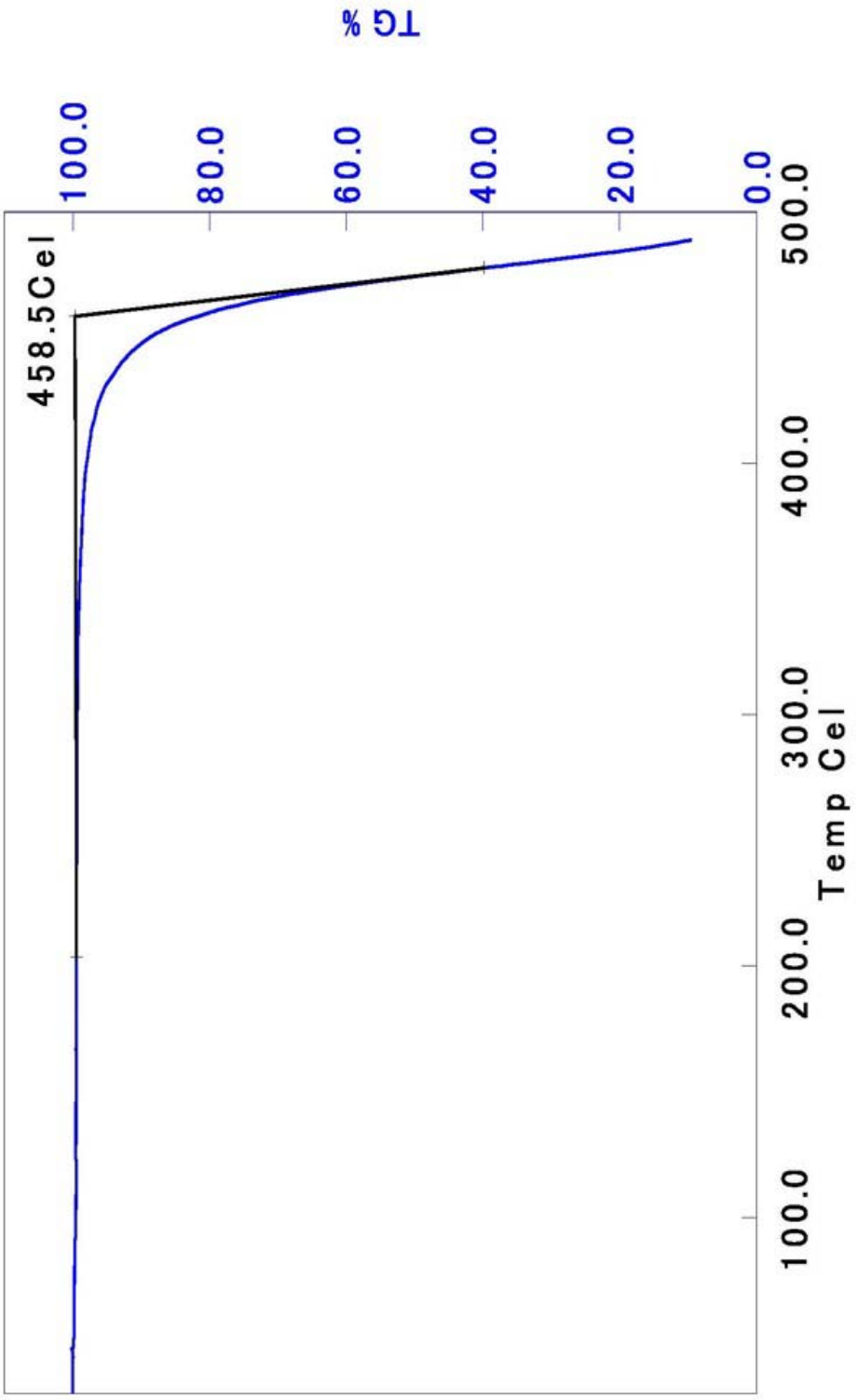


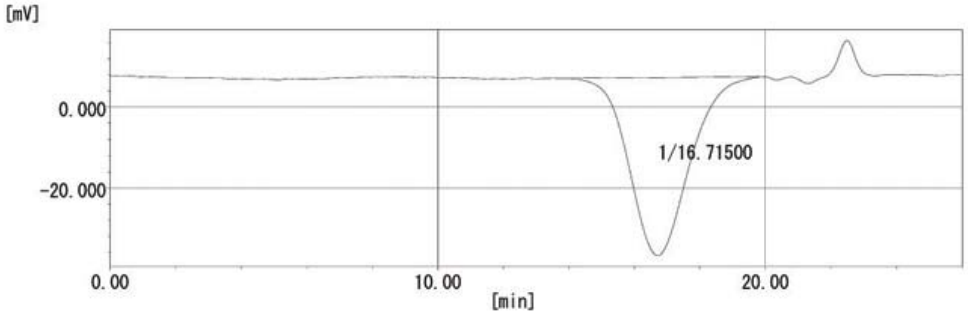
Figure S4. TG chart of ethylene/**2a** copolymer obtained in entry 1 in Table 1.

Ethylene/2a Copolymer Obtained in Entry 2 in Table 1:

55-04-062-3

Sample name : 55-04-062-3
Database name : Yagyu.mdb
Saved file name : RSLT0204
Method data : 20100413std

Measurement date : 2010/09/24 15:50:17
Calculation date : 2010/09/24 16:46:52



	[min]	[mV]	[MOL]
Peak start	13.91	7.076	483,243
Peak top	16.72	-36.685	24,627
Peak end	19.84	7.473	554
Area [mV·sec]		5,208.493	
Area [%]		100.000	
Height [mV]		43.948	
[η]		31,696.21387	

Mn	:	13,984
Mw	:	31,696
Mz	:	61,109
Mz+1	:	107,707
Mv	:	31,696
Mp	:	25,586
Mz/Mw	:	1.928
Mw/Mn	:	2.267
Mz+1/Mw	:	3.398

Figure S5. SEC trace of ethylene/**2a** copolymer obtained in entry 2 in Table 1. M_n (PS) = 14,000 was corrected to M_n (PE) = 6,100 by universal calibration.

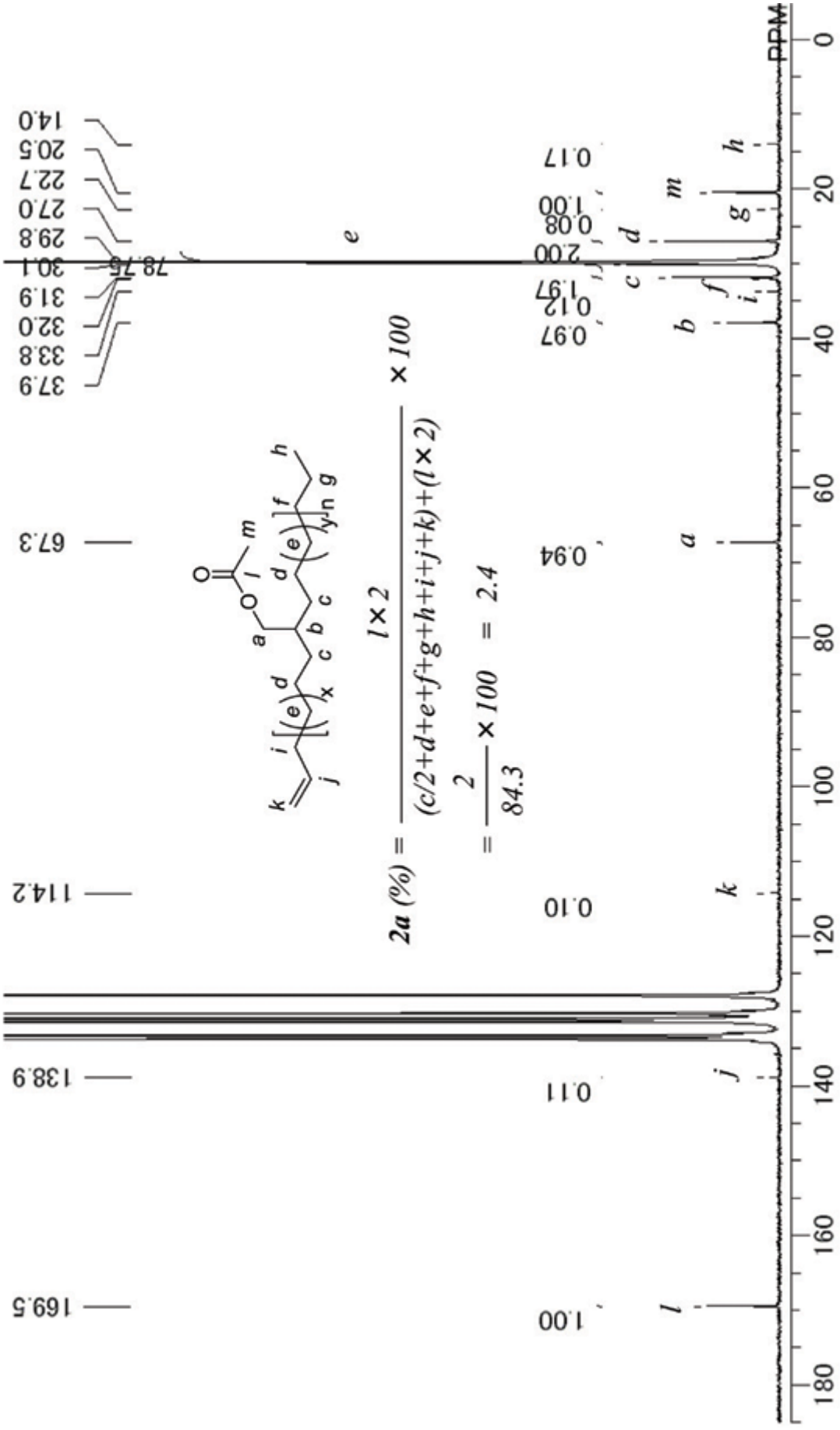


Figure S6. Quantitative ^{13}C NMR spectrum of ethylene/**2a** copolymer obtained in entry 2 in Table 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

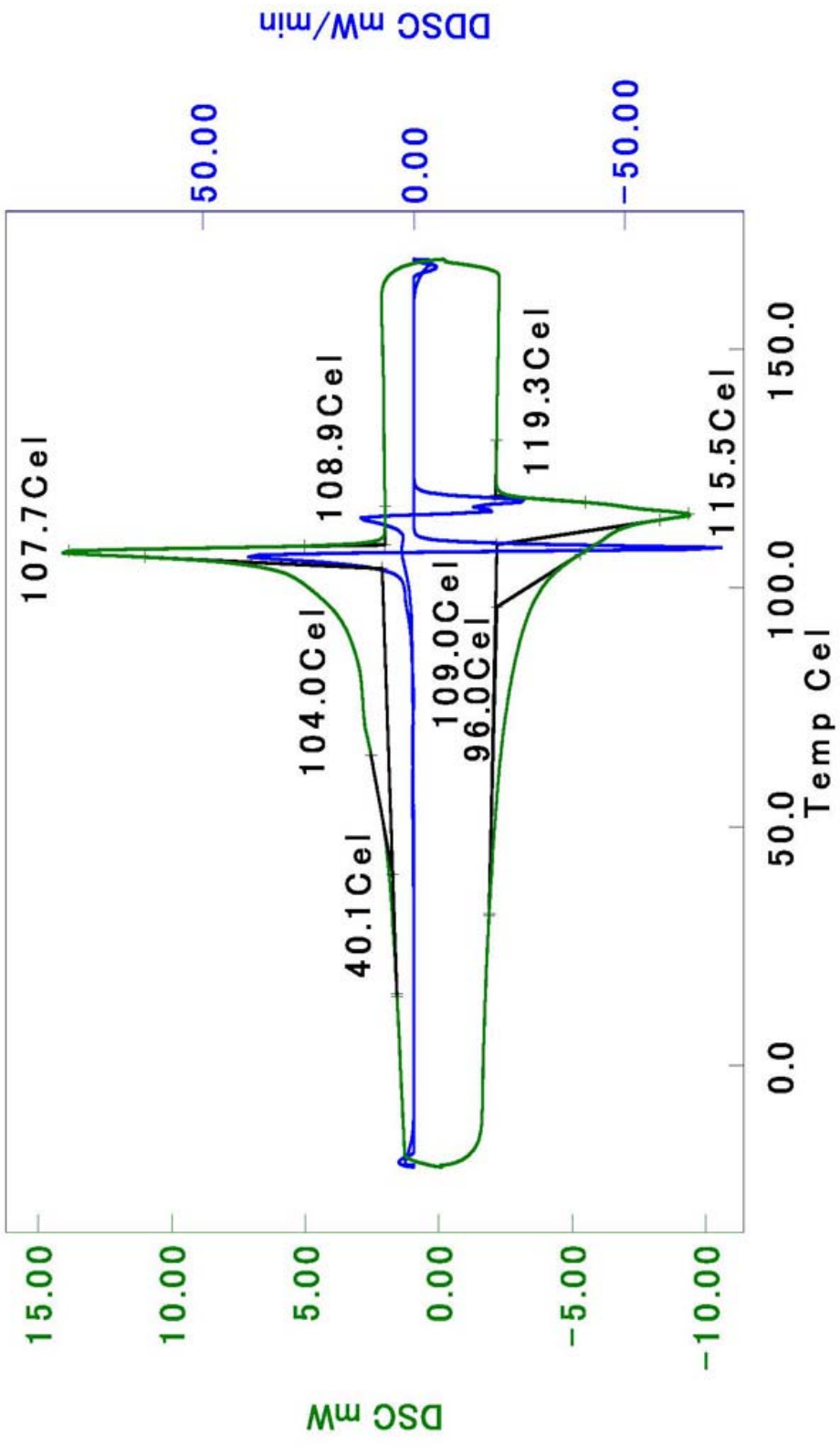


Figure S7. DSC chart of ethylene/**2a** copolymer obtained in entry 2 in Table 1.

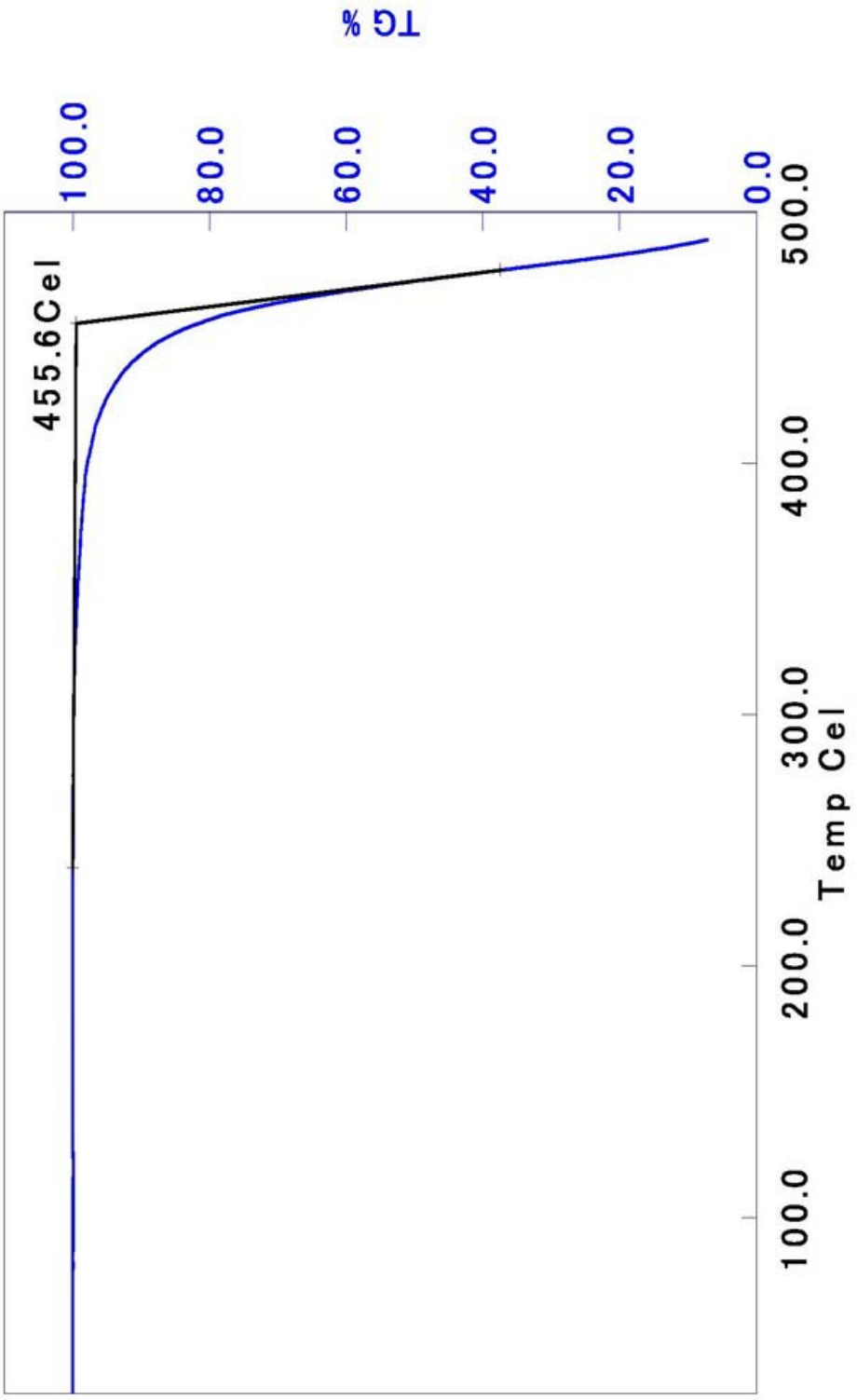


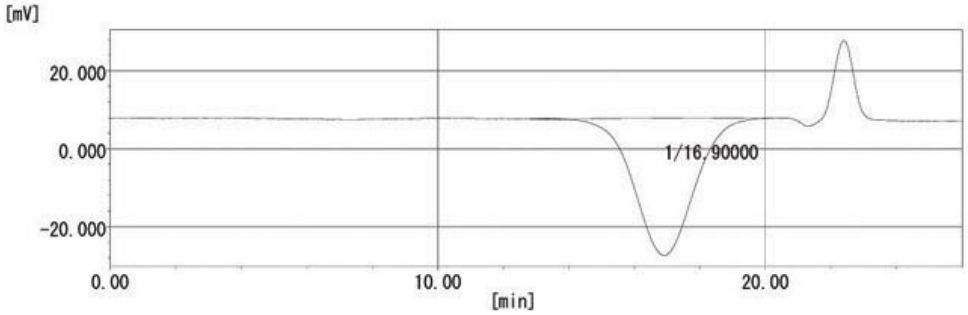
Figure S8. TG chart of ethylene/**2a** copolymer obtained in entry 2 in Table 1.

Ethylene/2a Copolymer Obtained in Entry 3 in Table 1:

55-04-064-3

Sample name : 55-04-064-3
Database name : Yagyu.mdb
Saved file name : RSLT0205
Method data : 20100413std

Measurement date : 2010/09/24 16:20:14
Calculation date : 2010/09/24 16:47:57



	[min]	[mV]	[MOL]
Peak start	12.71	7.691	1,810,551
Peak top	16.90	-27.371	20,103
Peak end	20.17	7.946	354
Area [mV·sec]		4,278.219	
Area [%]		100.000	
Height [mV]		35.205	
[η]		30,854.20982	

Mn	:	12,076
Mw	:	30,854
Mz	:	106,900
Mz+1	:	461,551
Mv	:	30,854
Mp	:	20,665
Mz/Mw	:	3.465
Mw/Mn	:	2.555
Mz+1/Mw	:	14.959

Figure S9. SEC trace of ethylene/**2a** copolymer obtained in entry 3 in Table 1. M_n (PS) = 12,100 was corrected to M_n (PE) = 5,300 by universal calibration.

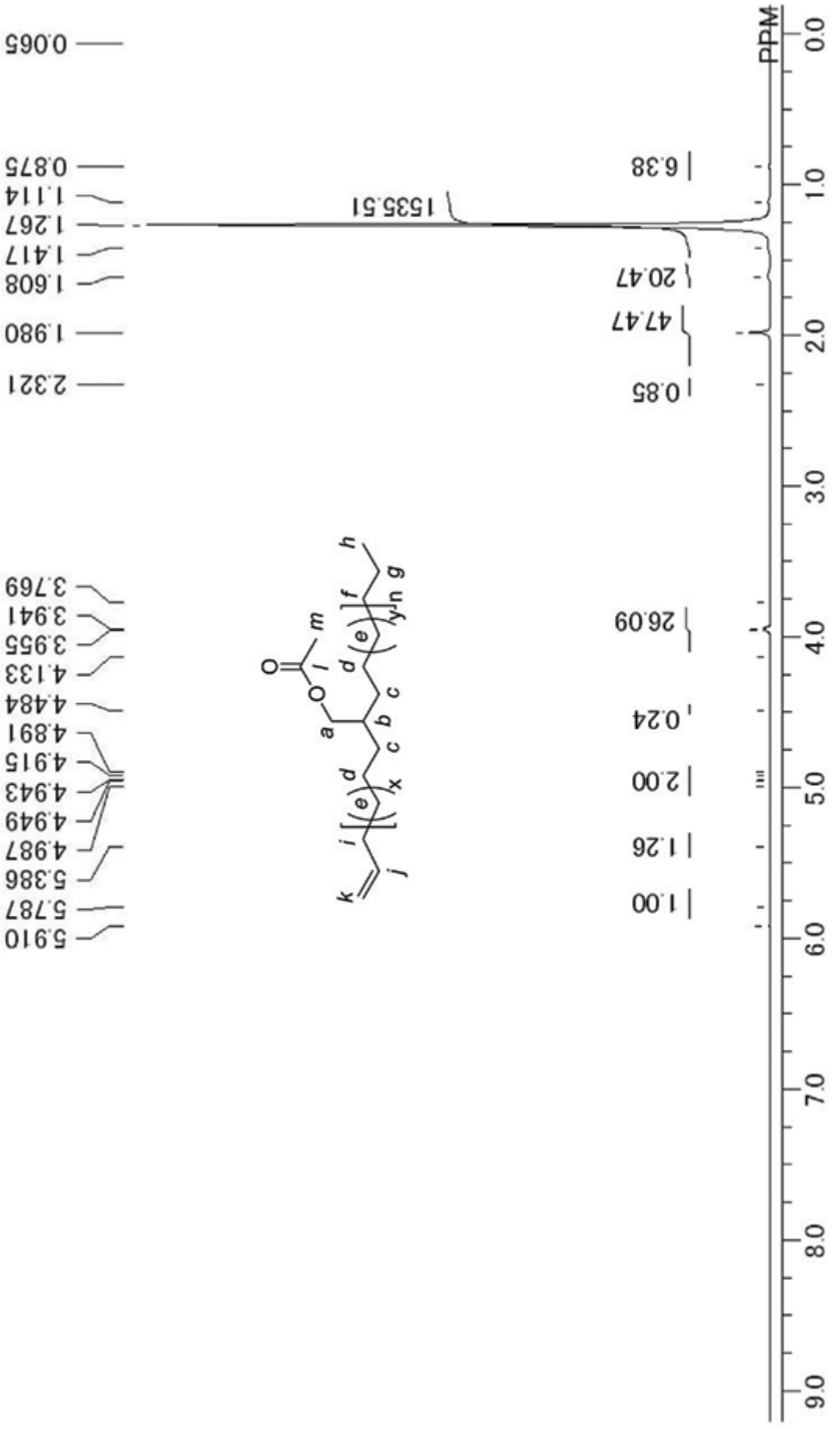


Figure S10. ^{1}H NMR spectrum of ethylene/**2a** copolymer obtained in entry 3 in Table 1 (400 MHz, $Cl_2CDCDCl_2$, 120 ˚C).

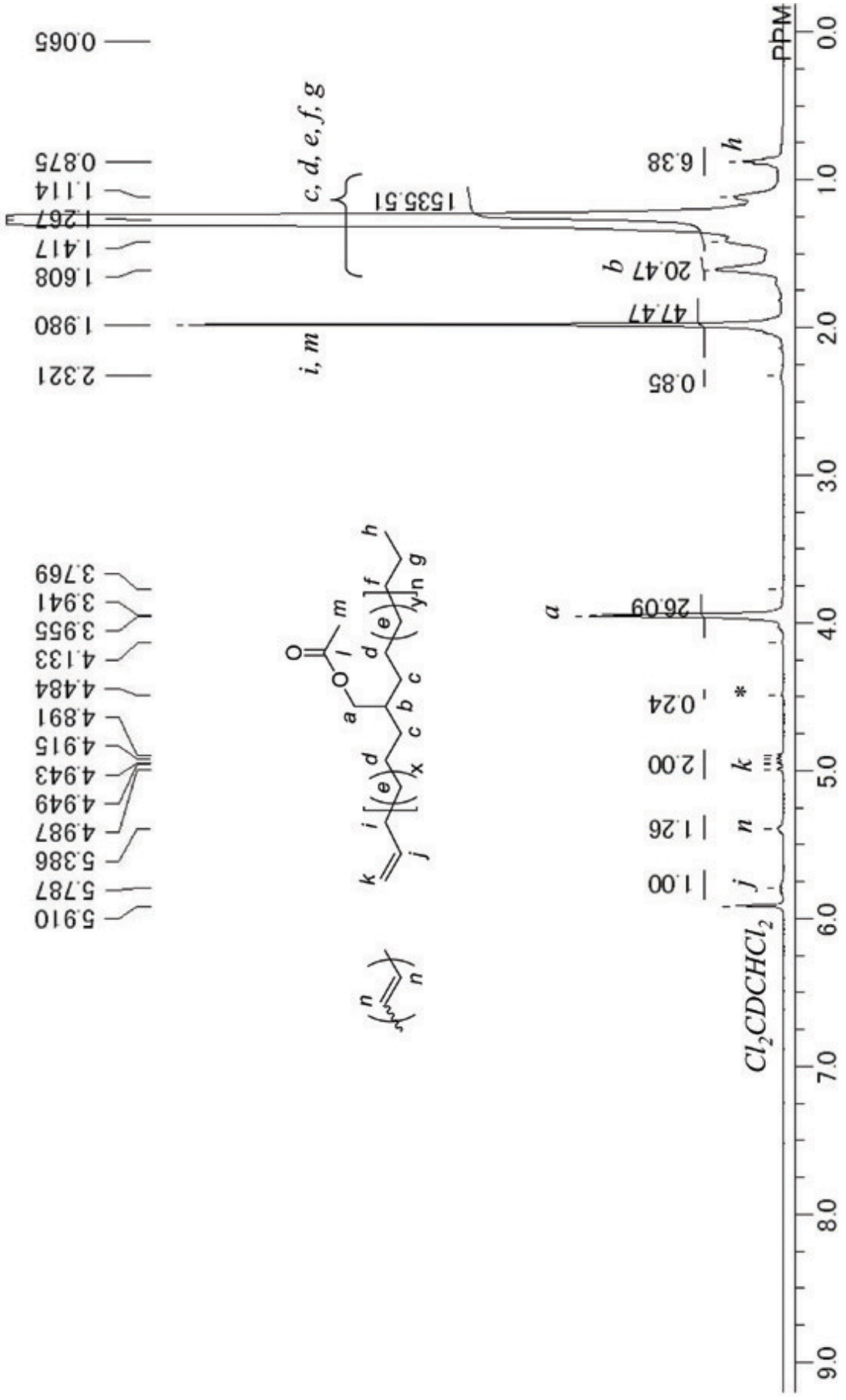


Figure S11. ^{1}H NMR spectrum of ethylene/**2a** copolymer obtained in entry 3 in Table 1 (400 MHz, $Cl_2CDCDCl_2$, 120 ˚C). * The signal could not be fully assigned. A possible structure is $–CH_2=CH–CH_2OAc$.

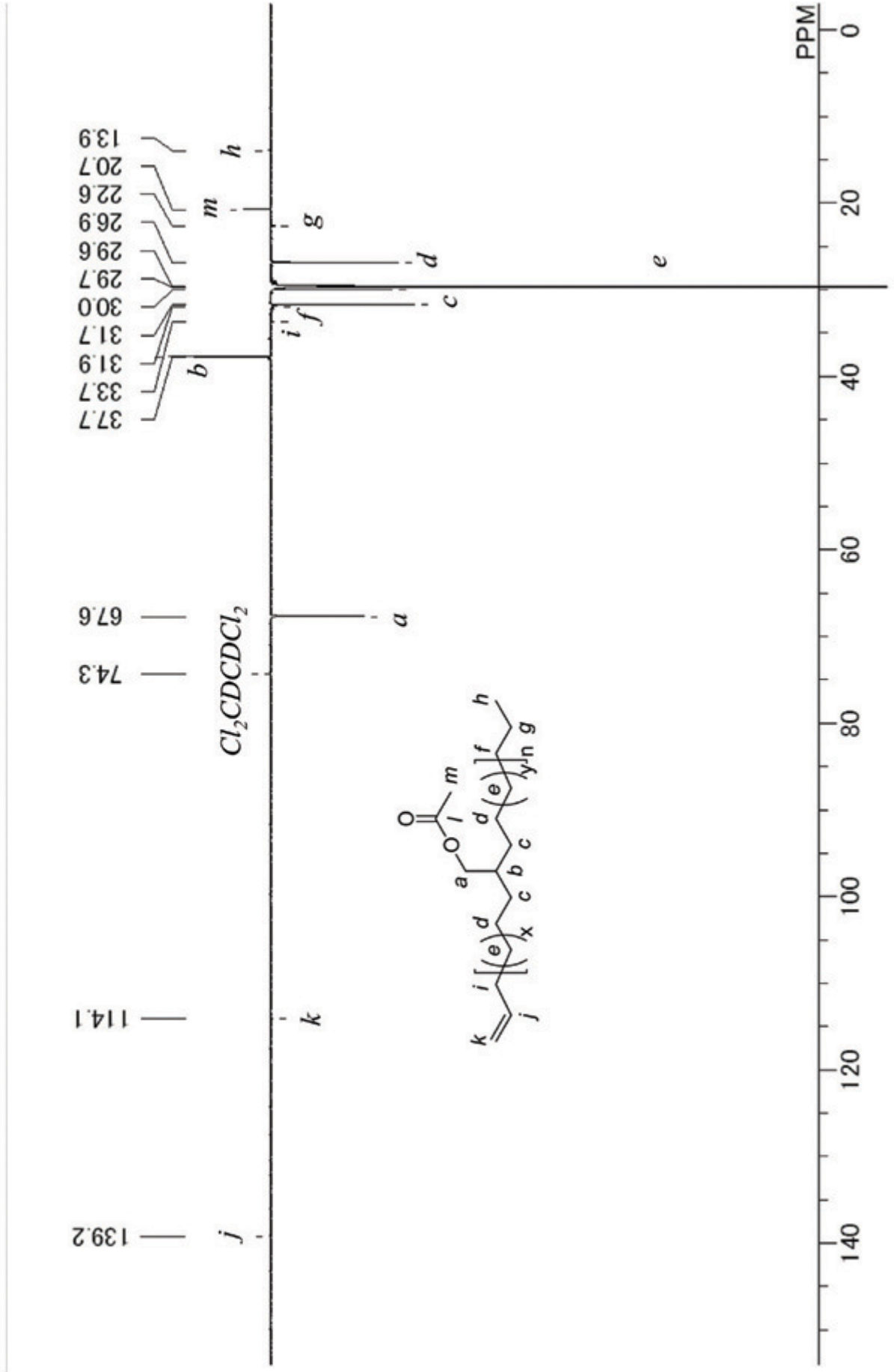


Figure S12. DEPT 135 NMR spectrum of ethylene/**2a** copolymer obtained in entry 3 in Table 1 (101 MHz, $Cl_2CDCDCl_2$, 120 ˚C).

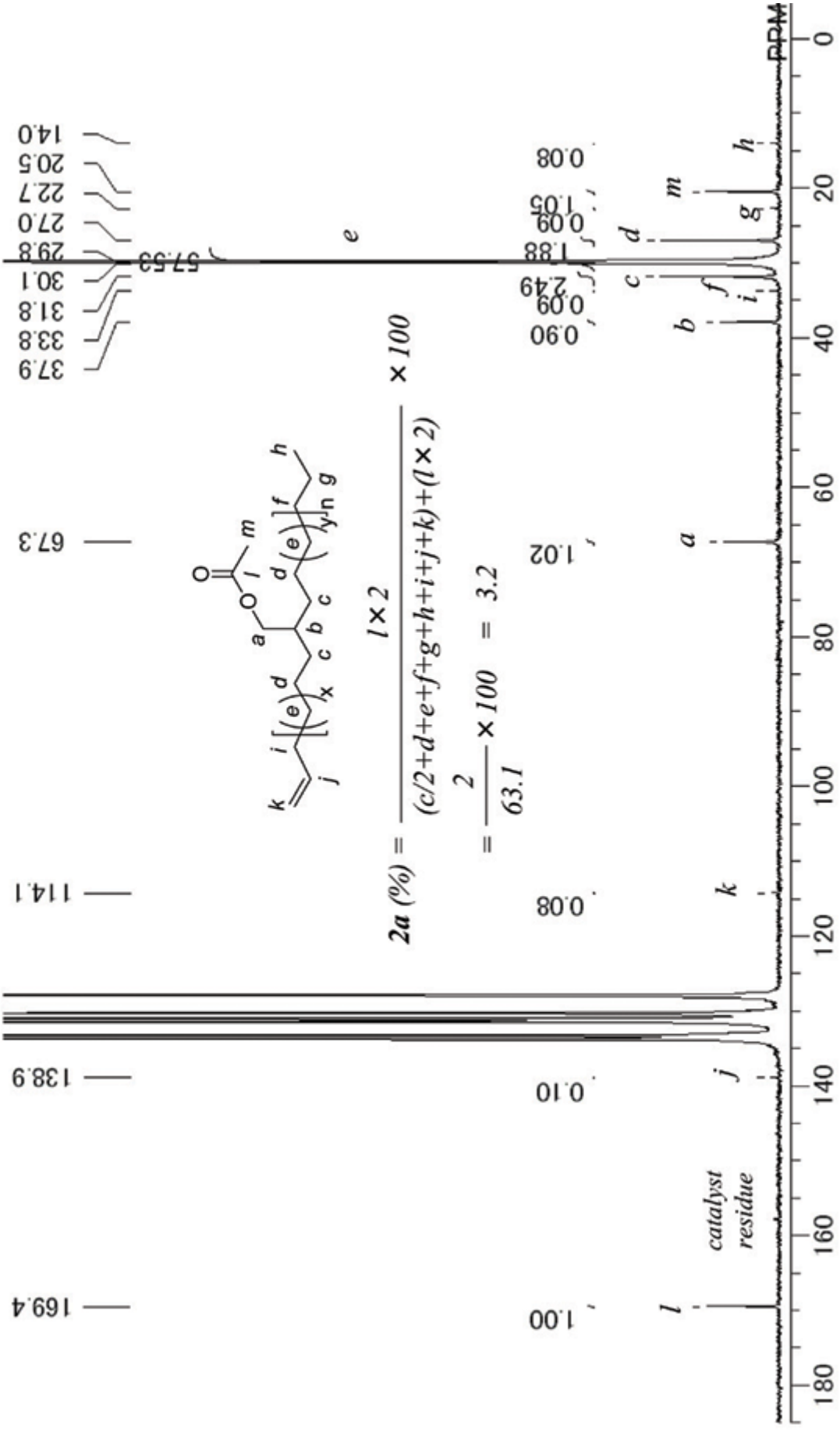


Figure S13. Quantitative ^{13}C NMR spectrum of ethylene/**2a** copolymer obtained in entry 3 in Table 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

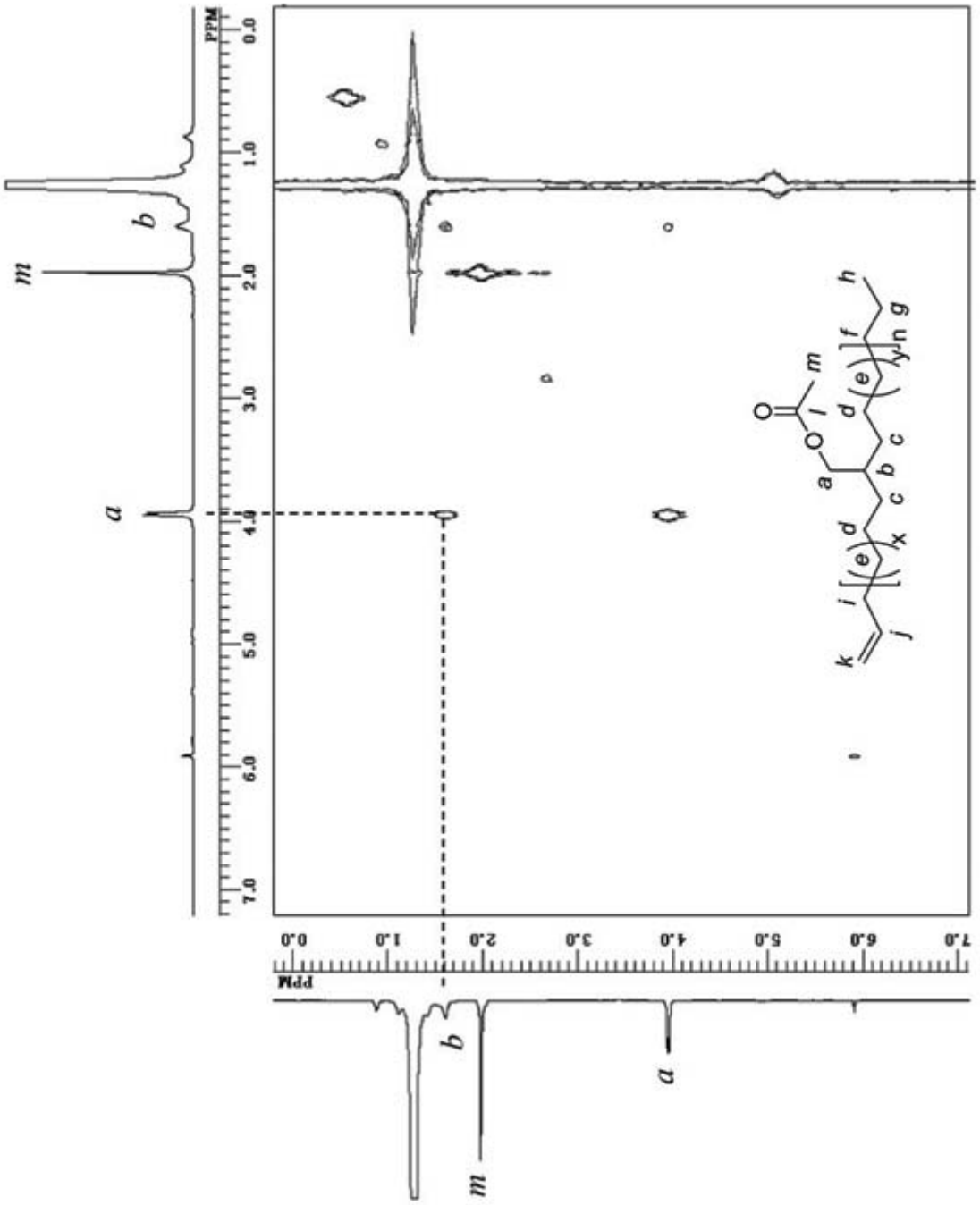


Figure S14. H–H COSY spectrum of ethylene/**2a** copolymer obtained in entry 3 in Table 1 ($Cl_2CDCDCl_2$, 120 ˚C).

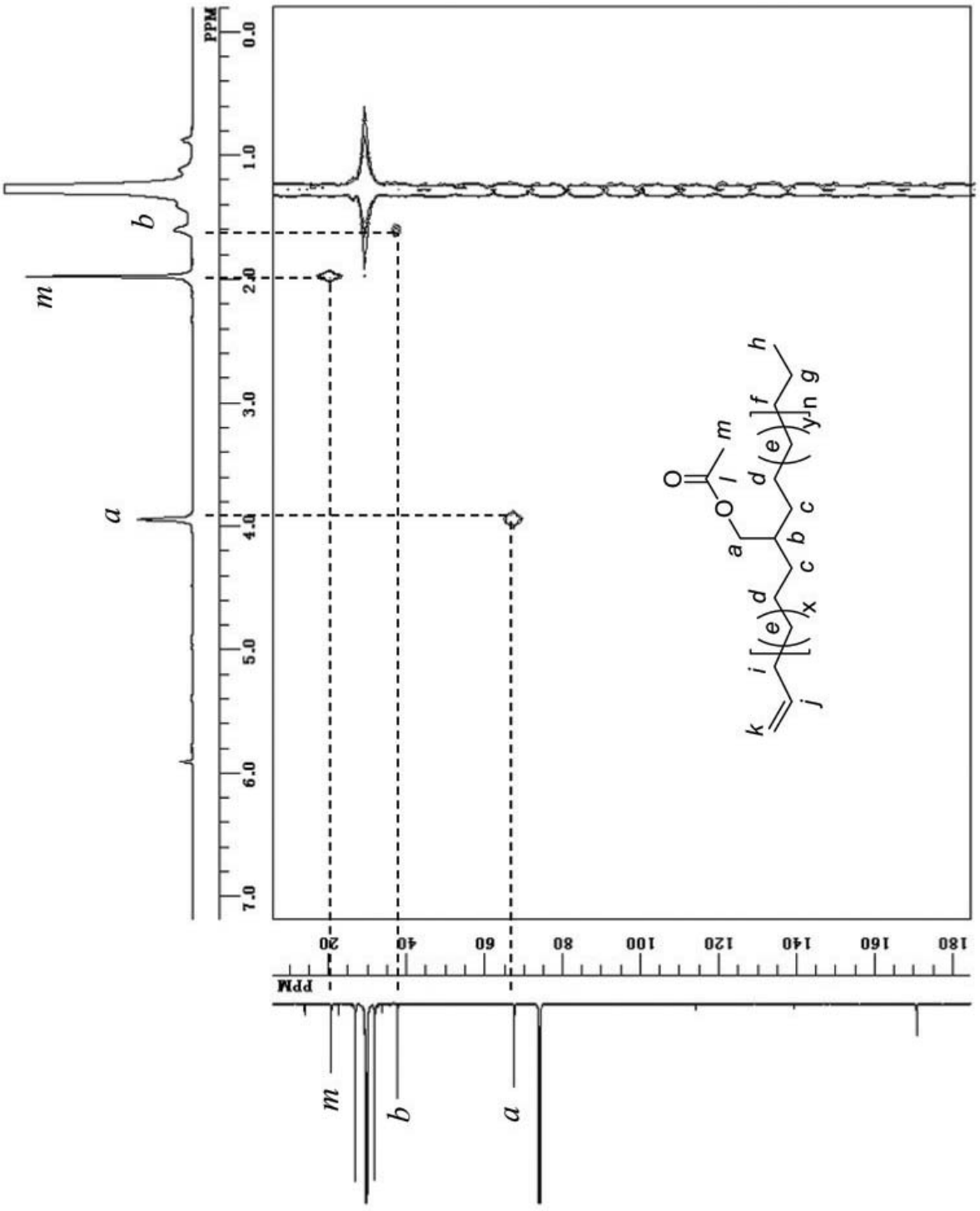


Figure S15. HMQC spectrum of ethylene/**2a** copolymer obtained in entry 3 in Table 1 ($Cl_2CDCDCl_2$, 120 ˚C).

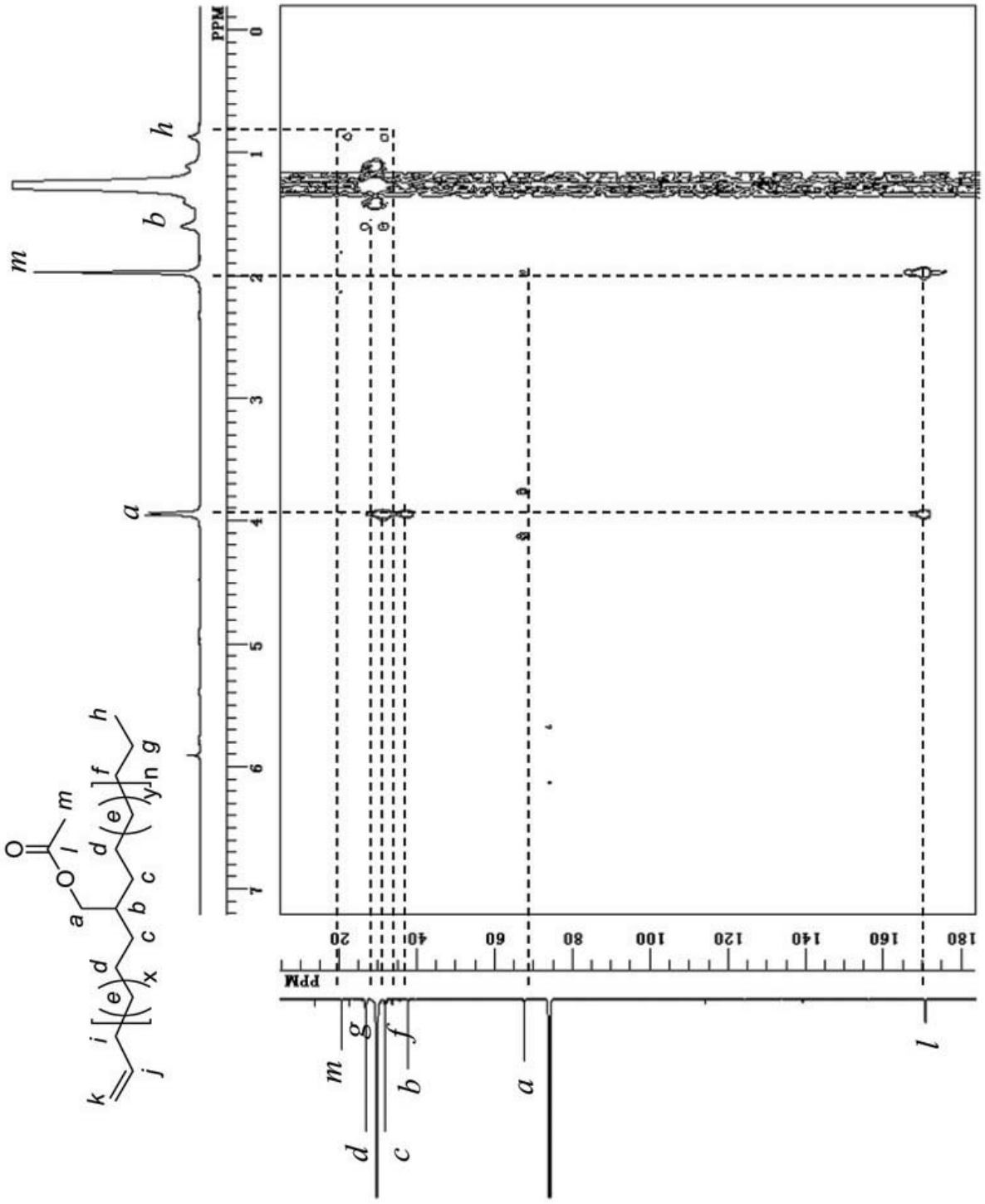


Figure S16. HMBC ^{13}C NMR spectrum of ethylene/**2a** copolymer obtained in entry 3 in Table 1 ($Cl_2CDCDCl_2$, 120 ˚C).

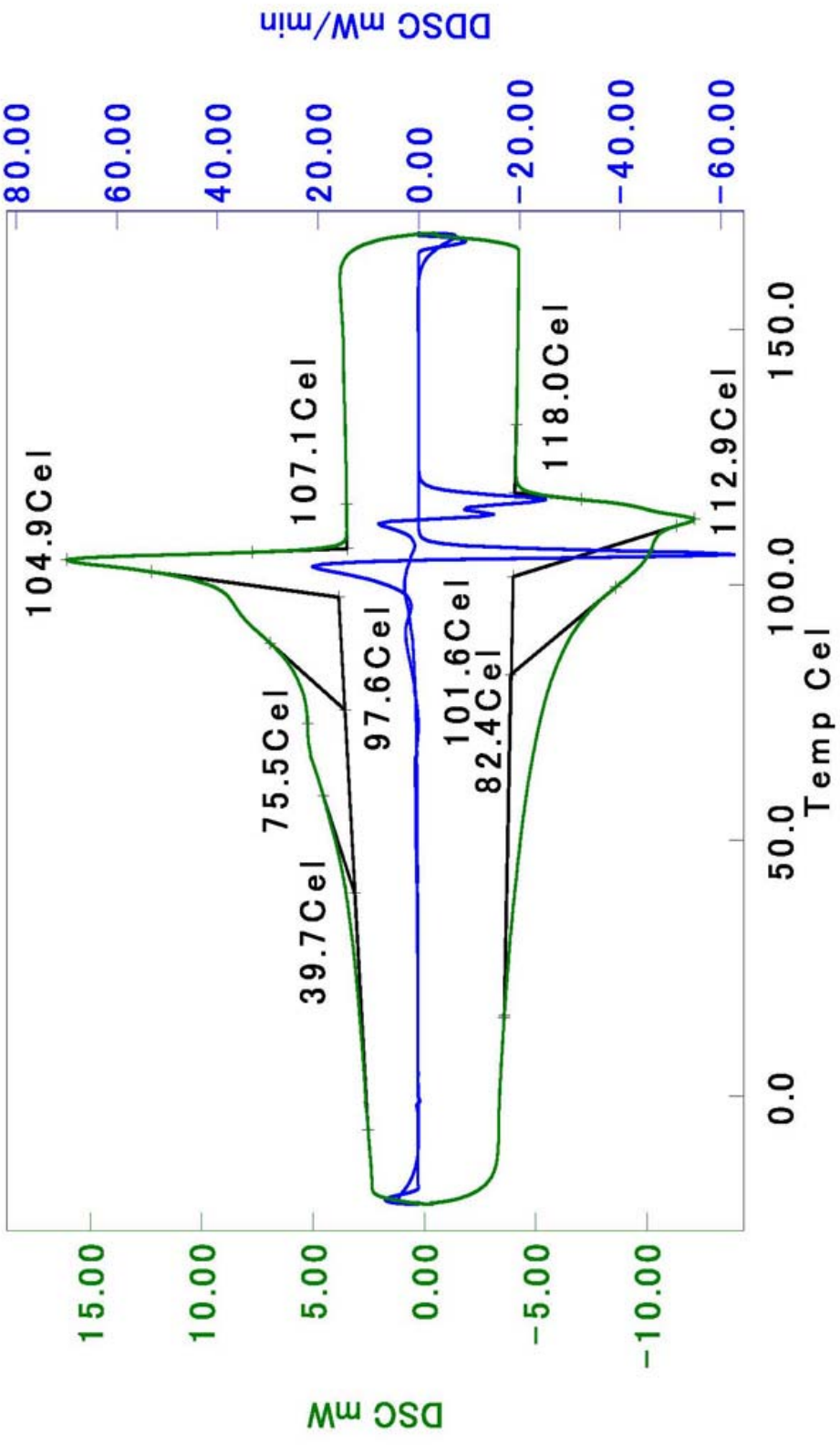


Figure S17. DSC chart of ethylene/**2a** copolymer obtained in entry 3 in Table 1.

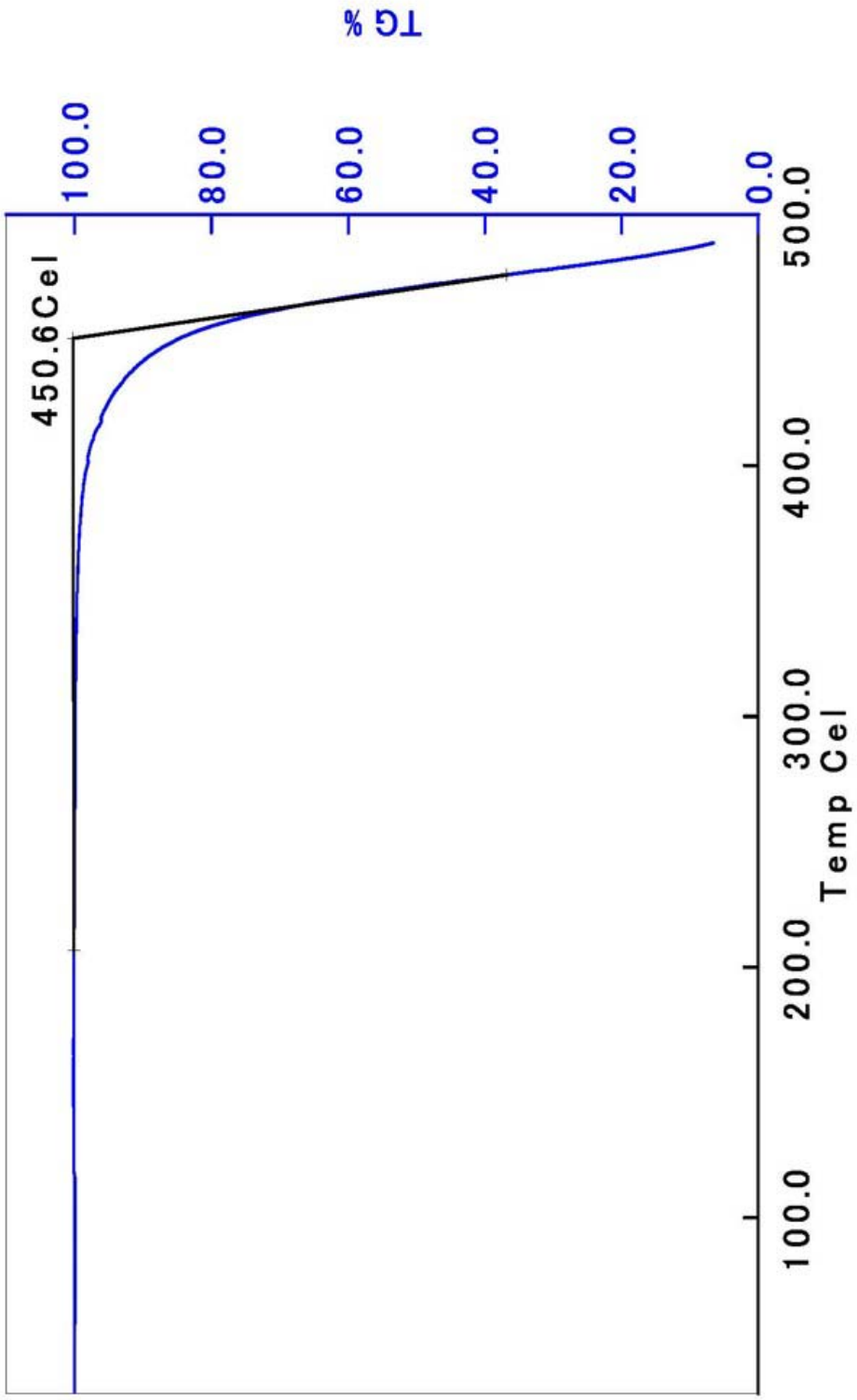


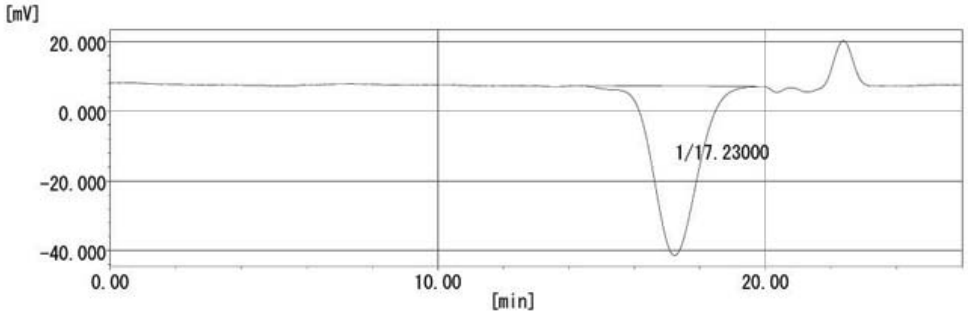
Figure S18. TG chart of ethylene/**2a** copolymer obtained in entry 3 in Table 1.

Ethylene/2a Copolymer Obtained in Entry 4 in Table 1:

55-04-070-3

Sample name : 55-04-070-3
Database name : Yagyu.mdb
Saved file name : RSLT0206
Method data : 20100413std

Measurement date : 2010/09/24 16:50:10
Calculation date : 2010/09/24 18:09:52



	[min]	[mV]	[MOL]
Peak start	14.14	7.274	380,094
Peak top	17.23	-41.444	13,933
Peak end	19.88	7.151	528
Area [mV·sec]		4,406.346	
Area [%]		100.000	
Height [mV]		48.652	
[η]		17,210.55502	

Mn	:	10,107
Mw	:	17,211
Mz	:	32,920
Mz+1	:	74,067
Mv	:	17,211
Mp	:	14,250
Mz/Mw	:	1.913
Mw/Mn	:	1.703
Mz+1/Mw	:	4.304

Figure S19. SEC trace of ethylene/**2a** copolymer obtained in entry 4 in Table 1. M_n (PS) = 10,100 was corrected to M_n (PE) = 4,400 by universal calibration.

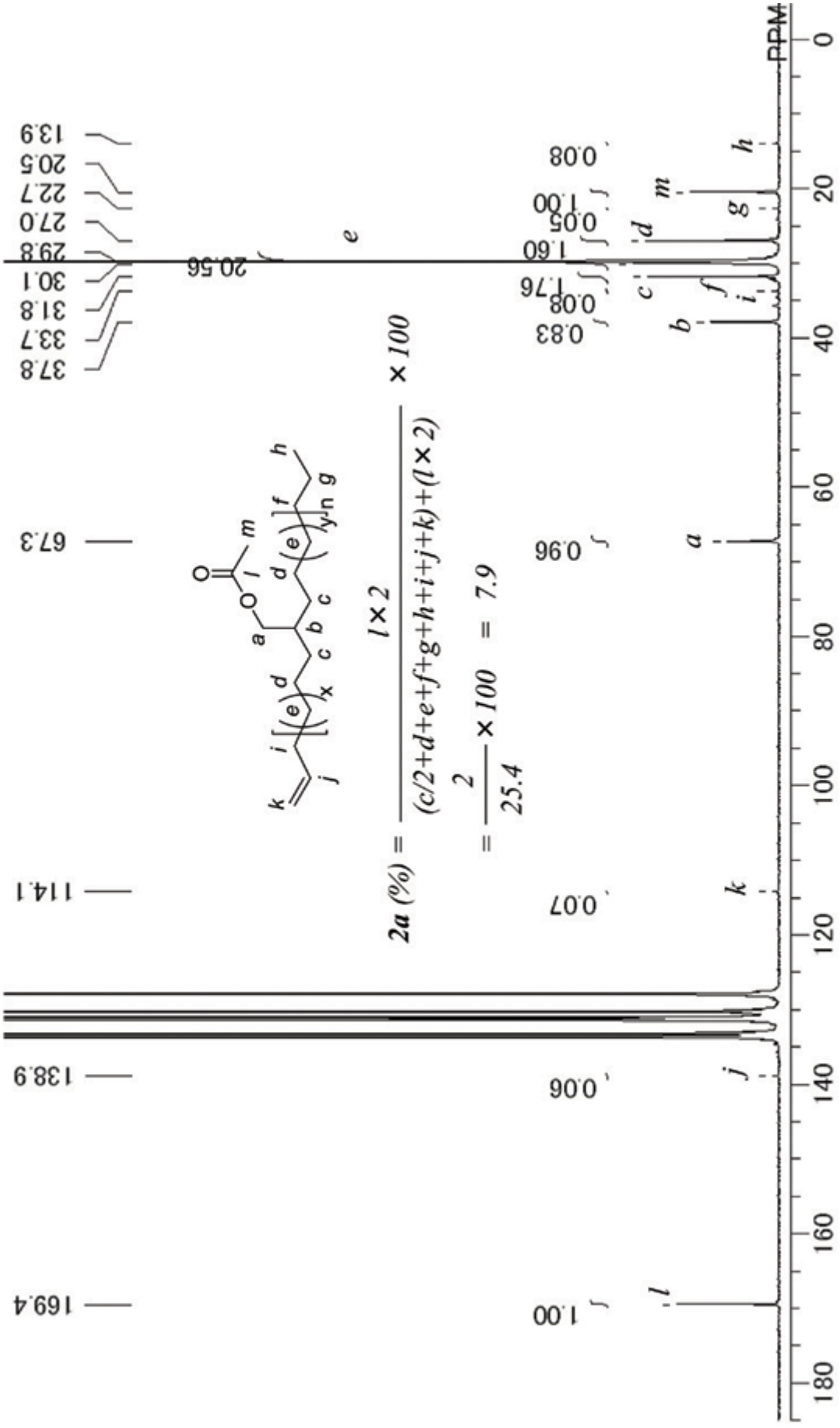


Figure S20. Quantitative ^{13}C NMR spectrum of ethylene/**2a** copolymer obtained in entry 4 in Table 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

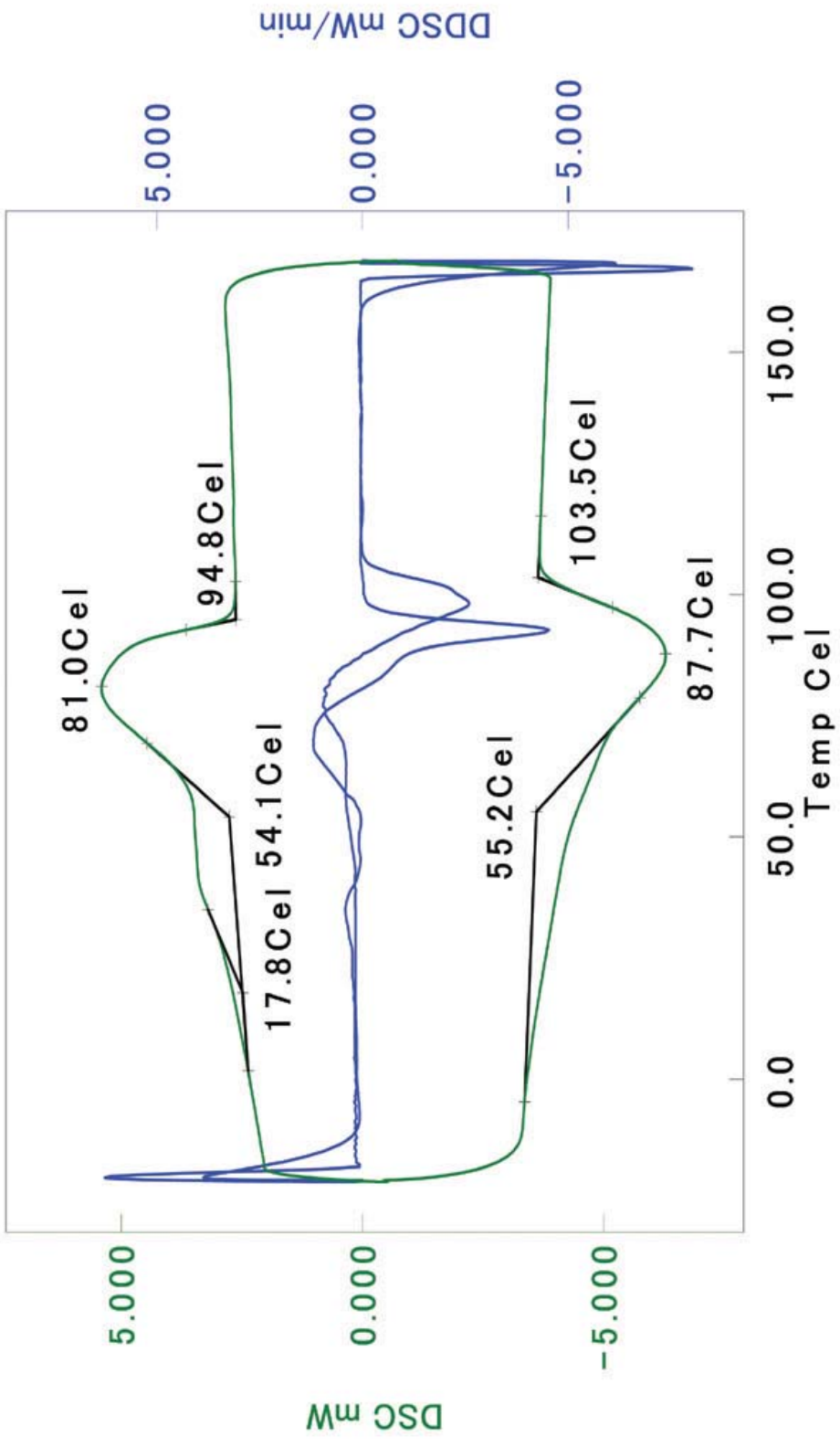


Figure S21. DSC chart of ethylene/**2a** copolymer obtained in entry 4 in Table 1.

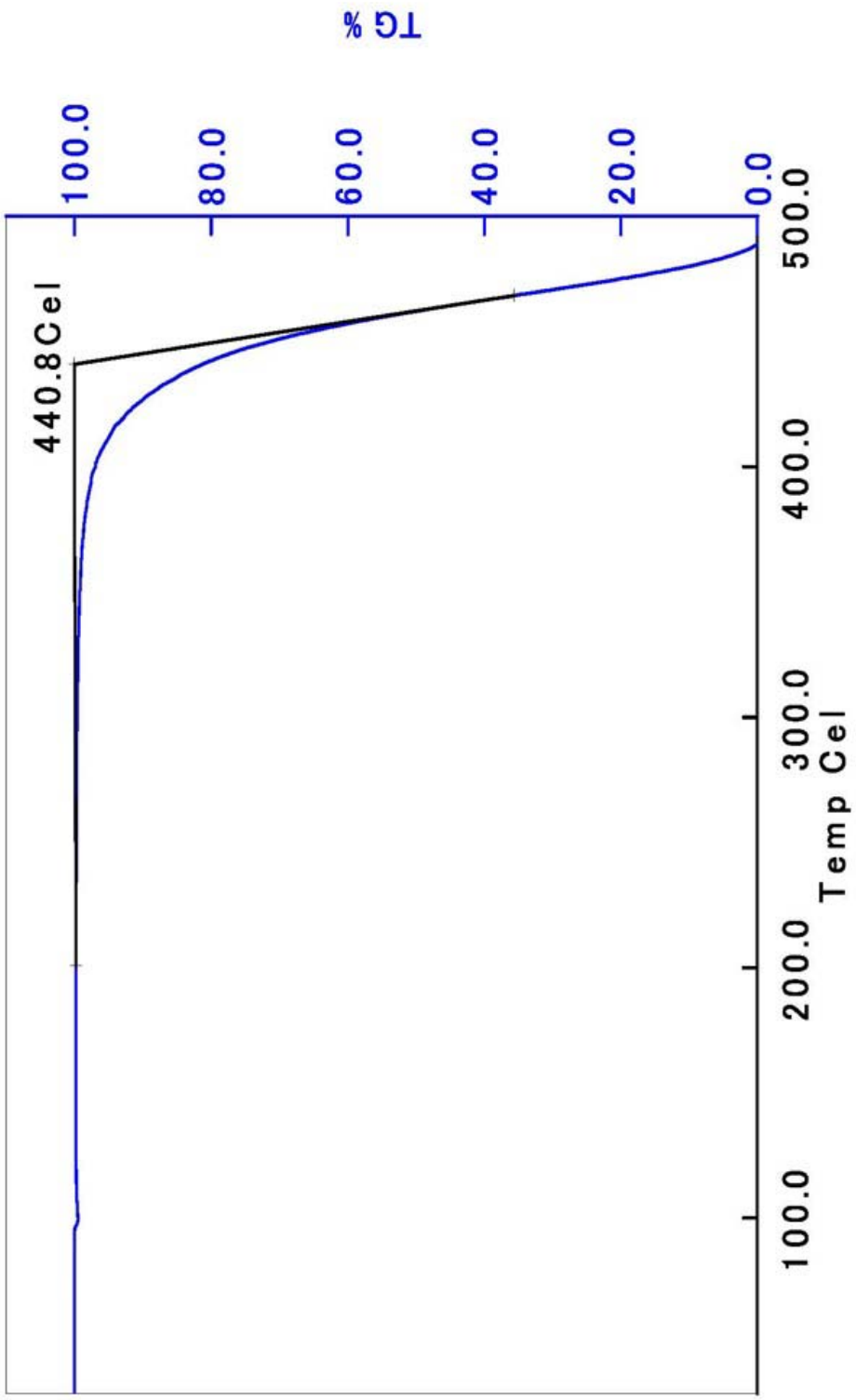


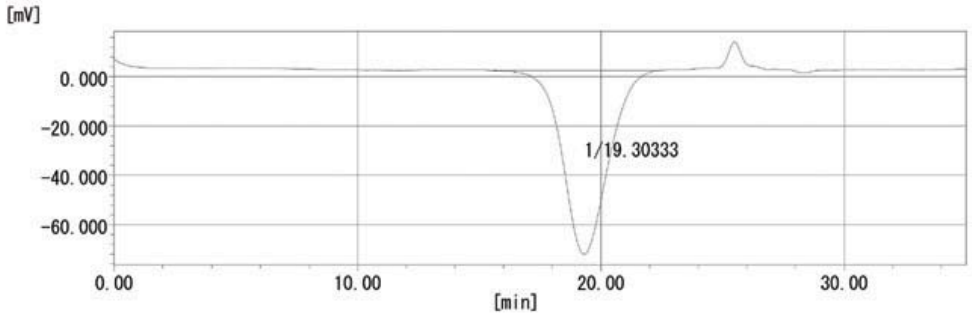
Figure S22. TG chart of ethylene/**2a** copolymer obtained in entry 4 in Table 1.

Ethylene/2a Copolymer Obtained in Entry 5 in Table 1:

55-05-002-3

Sample name : 55-05-002-3
Database name : GpcDataBase.mdb
Saved file name : RSLT0349
Method data : 20100614

Measurement date : 2010/11/24 23:01:14
Calculation date : 2010/11/25 17:18:04



	[min]	[mV]	[MOL]
Peak start	15.45	2.559	966,239
Peak top	19.30	-72.010	24,918
Peak end	22.45	2.509	455
Area [mV·sec]		9,118.845	
Area [%]		100.000	
Height [mV]		74.541	
[η]		32,279.56044	

Mn	:	14,273
Mw	:	32,280
Mz	:	74,266
Mz+1	:	198,142
Mv	:	32,280
Mp	:	26,732
Mz/Mw	:	2.301
Mw/Mn	:	2.262
Mz+1/Mw	:	6.138

Figure S23. SEC trace of ethylene/**2a** copolymer obtained in entry 5 in Table 1. M_n (PS) = 14,300 was corrected to M_n (PE) = 6,200 by universal calibration.

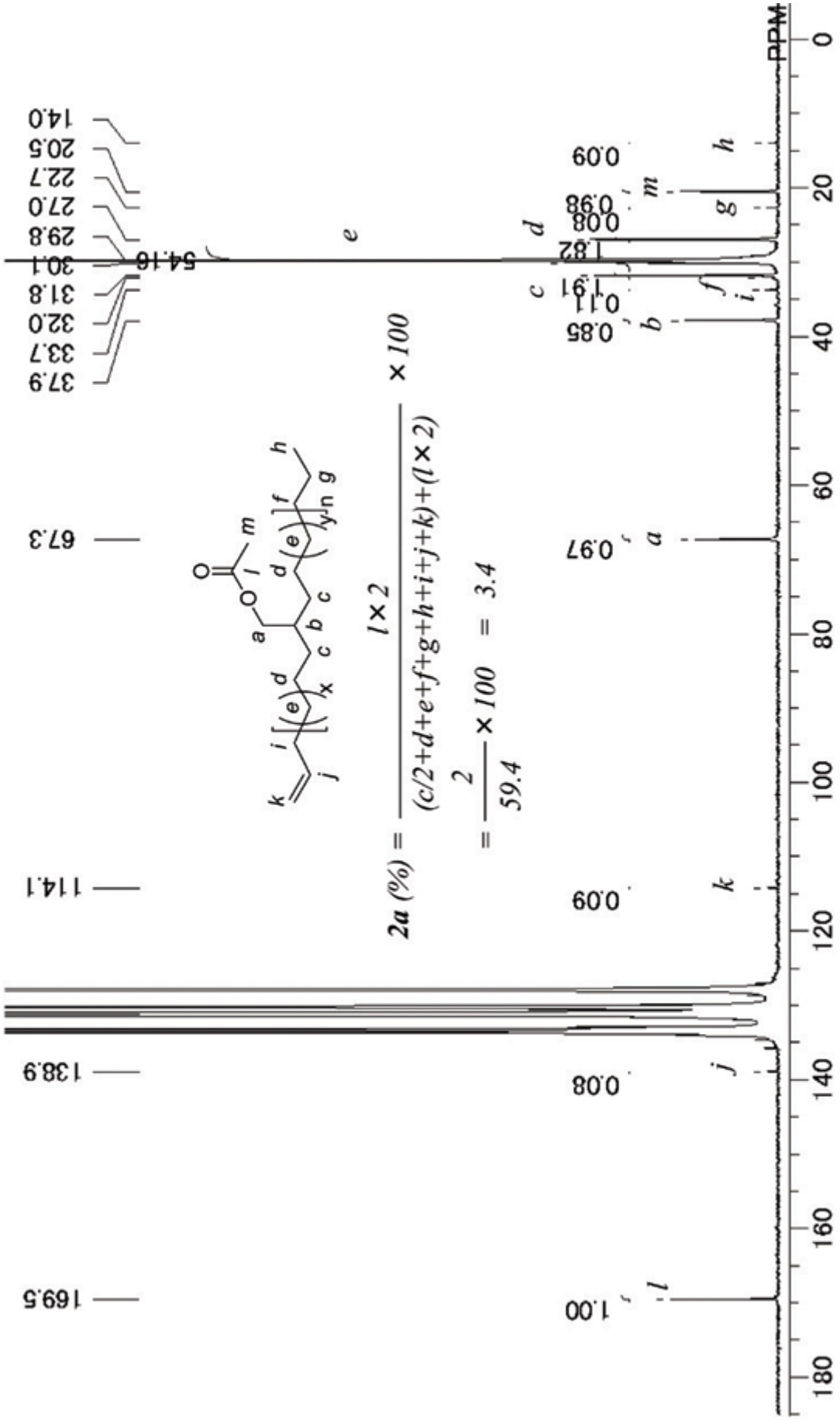


Figure S24. Quantitative ^{13}C NMR spectrum of ethylene/**2a** copolymer obtained in entry 5 in Table 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

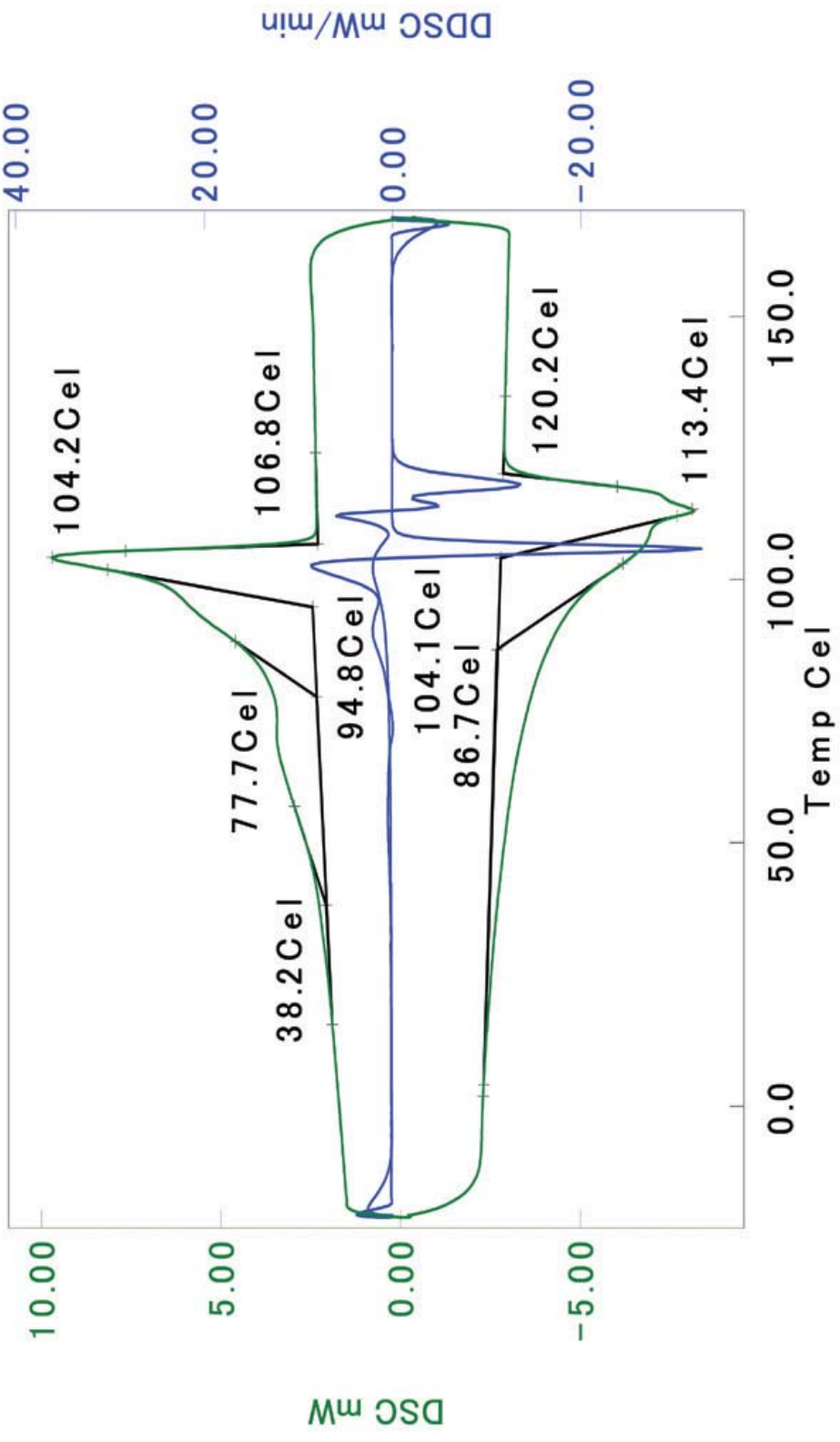


Figure S25. DSC chart of ethylene/**2b** copolymer obtained in entry 5 in Table 1.

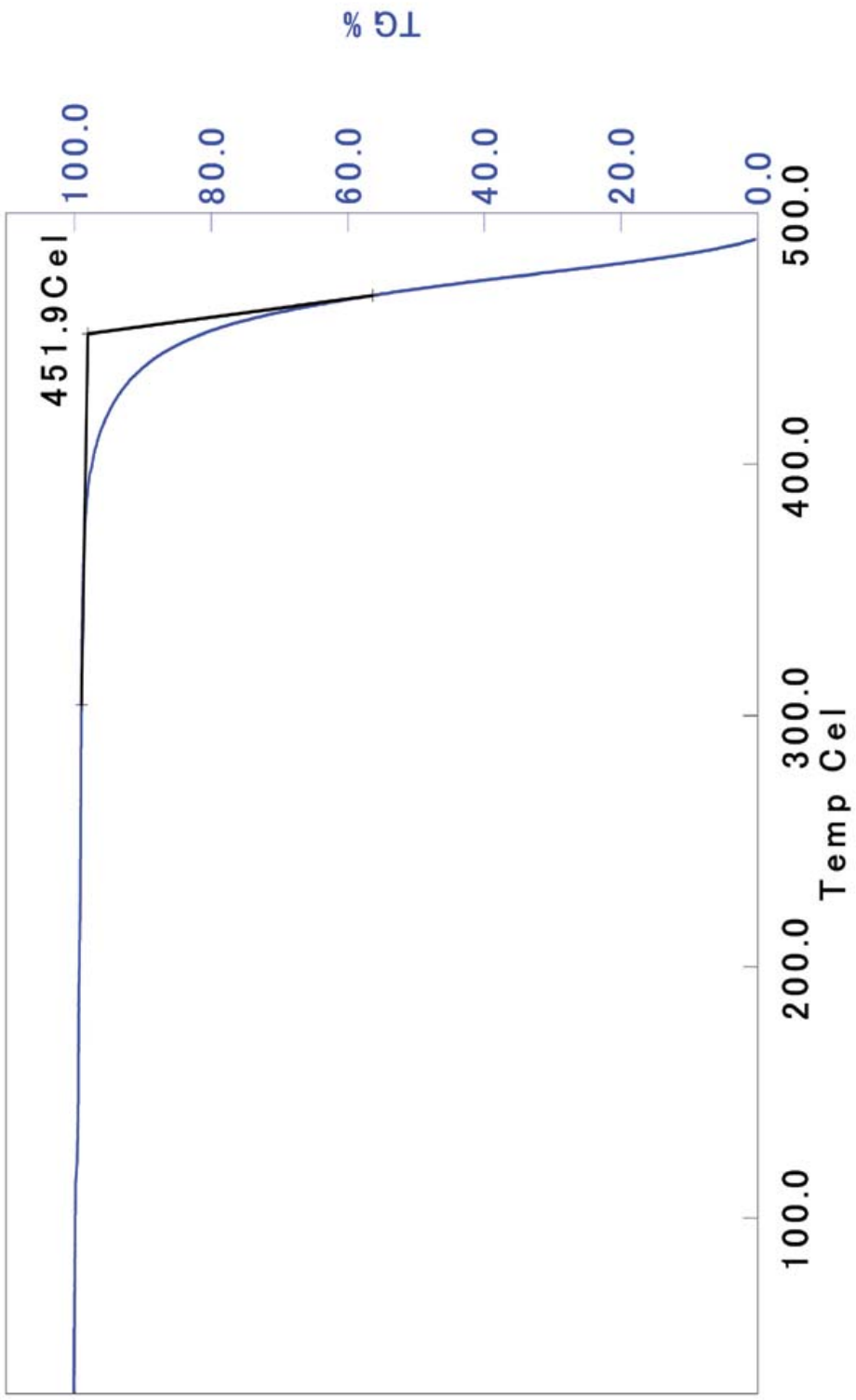


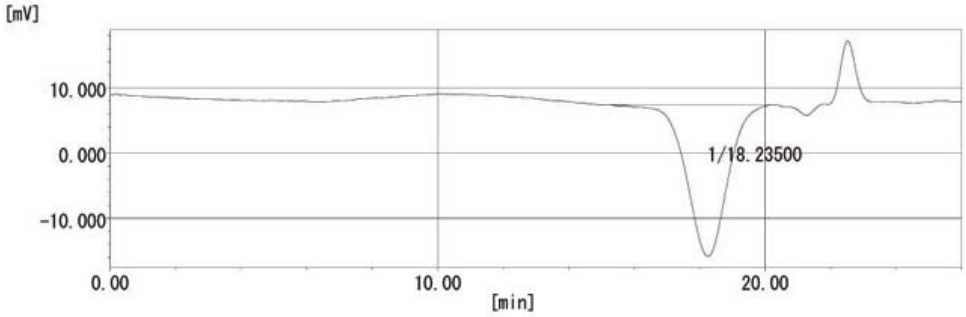
Figure S26. TG chart of ethylene/**2a** copolymer obtained in entry 5 in Table 1.

Ethylene/2b Copolymer Obtained in Entry 6 in Table 1:

55-04-008-3

Sample name : 55-04-008-3
Database name : Yagyu.mdb
Saved file name : RSLT0211
Method data : 20100413std

Measurement date : 2010/09/24 19:41:31
Calculation date : 2010/09/27 08:59:36



	[min]	[mV]	[MOL]
Peak start	15.25	7.380	117,730
Peak top	18.24	-15.817	4,359
Peak end	20.23	7.392	325
Area [mV·sec]		1,886.312	
Area [%]		100.000	
Height [mV]		23.204	
[η]		5,803.01397	

Mn	:	3,463
Mw	:	5,803
Mz	:	12,666
Mz+1	:	34,985
Mv	:	5,803
Mp	:	4,359
Mz/Mw	:	2.183
Mw/Mn	:	1.676
Mz+1/Mw	:	6.029

Figure S27. SEC trace of ethylene/**2b** copolymer obtained in entry 6 in Table 1. M_n (PS) = 3,500 was corrected to M_n (PE) = 1,500 by universal calibration.

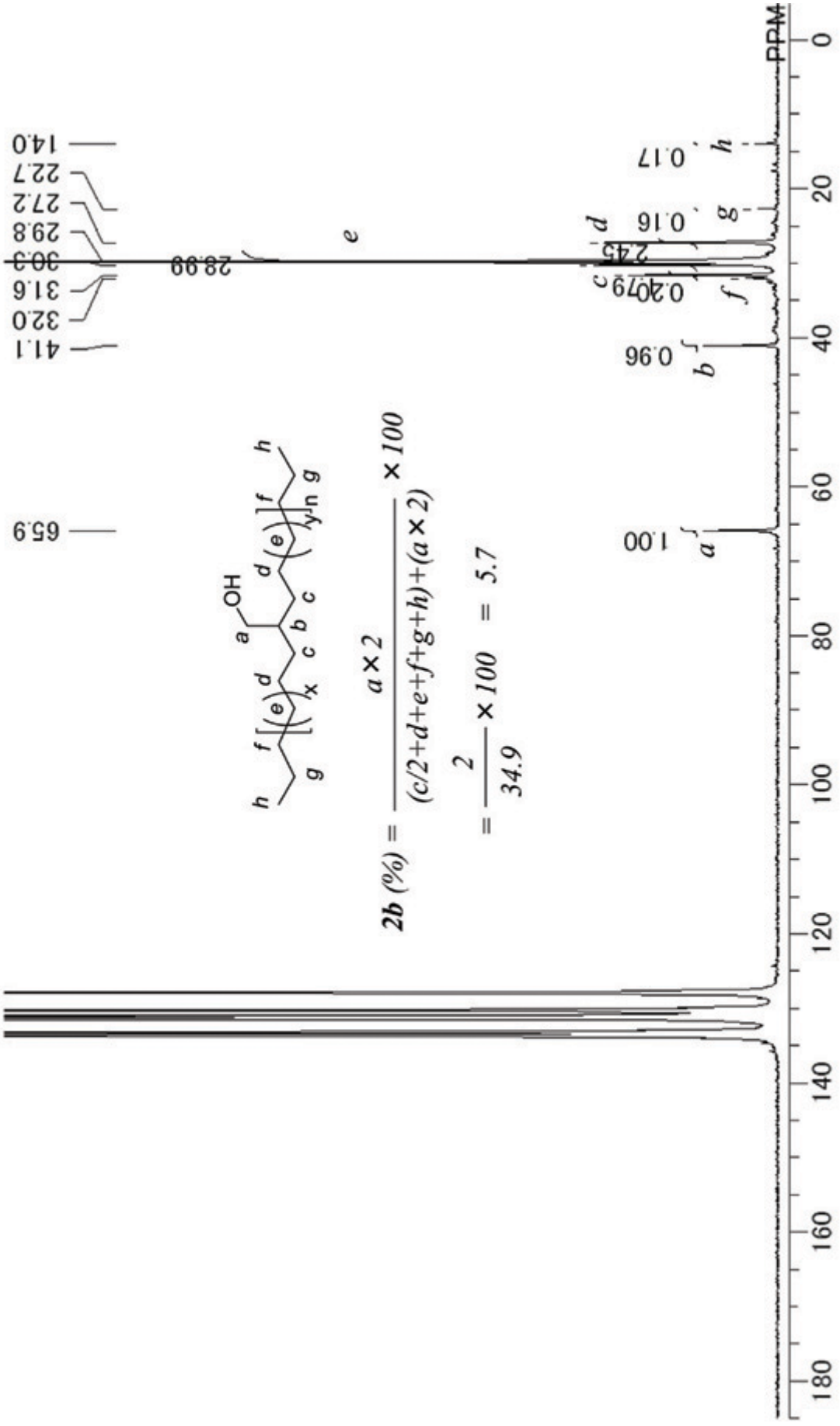


Figure S28. Quantitative ^{13}C NMR spectrum of ethylene/**2b** copolymer obtained in entry 6 in Table 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

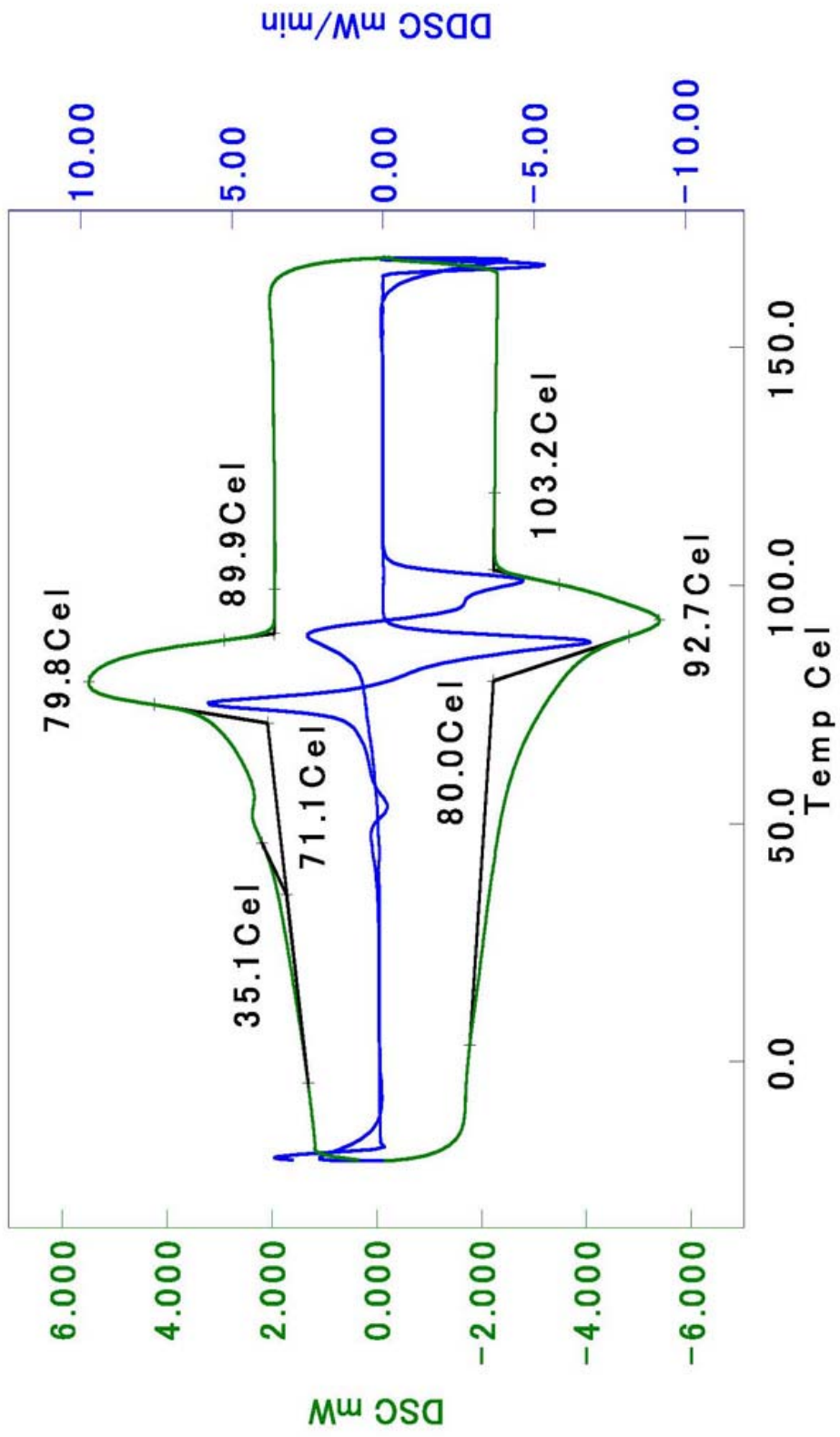


Figure S29. DSC chart of ethylene/**2b** copolymer obtained in entry 6 in Table 1.

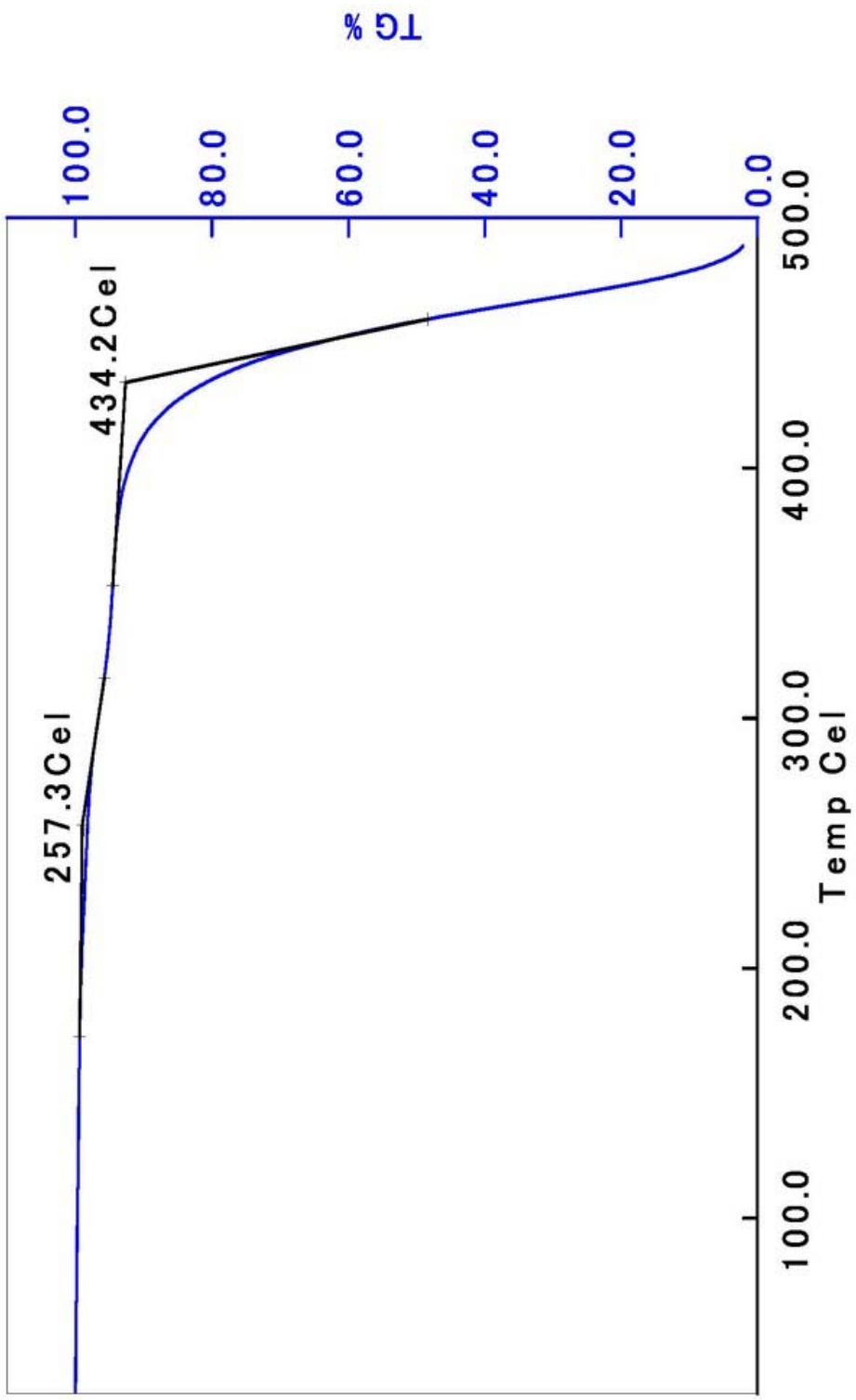


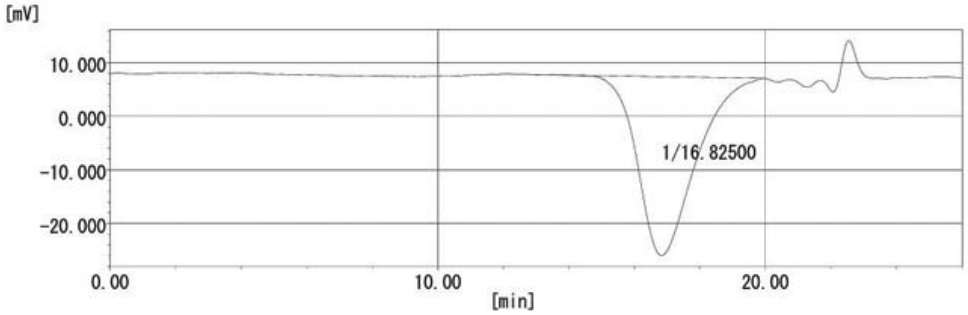
Figure S30. TG chart of ethylene/**2b** copolymer obtained in entry 6 in Table 1.

Ethylene/2d Copolymer Obtained in Entry 8 in Table 1:

55-04-094-3

Sample name : 55-04-094-3
Database name : Yagyu.mdb
Saved file name : RSLT0207
Method data : 20100413std

Measurement date : 2010/09/24 17:20:14
Calculation date : 2010/09/24 18:10:56



	[min]	[mV]	[MOL]
Peak start	12.65	7.824	1,937,640
Peak top	16.83	-25.991	21,832
Peak end	20.01	7.083	443
Area [mV·sec]		3,802.023	
Area [%]		100.000	
Height [mV]		33.394	
[η]		24,322.22386	

Mn	:	10,222
Mw	:	24,322
Mz	:	74,713
Mz+1	:	528,957
Mv	:	24,322
Mp	:	22,317
Mz/Mw	:	3.072
Mw/Mn	:	2.379
Mz+1/Mw	:	21.748

Figure S31. SEC trace of ethylene/**2d** copolymer obtained in entry 8 in Table 1. M_n (PS) = 10,200 was corrected to M_n (PE) = 4,500 by universal calibration.

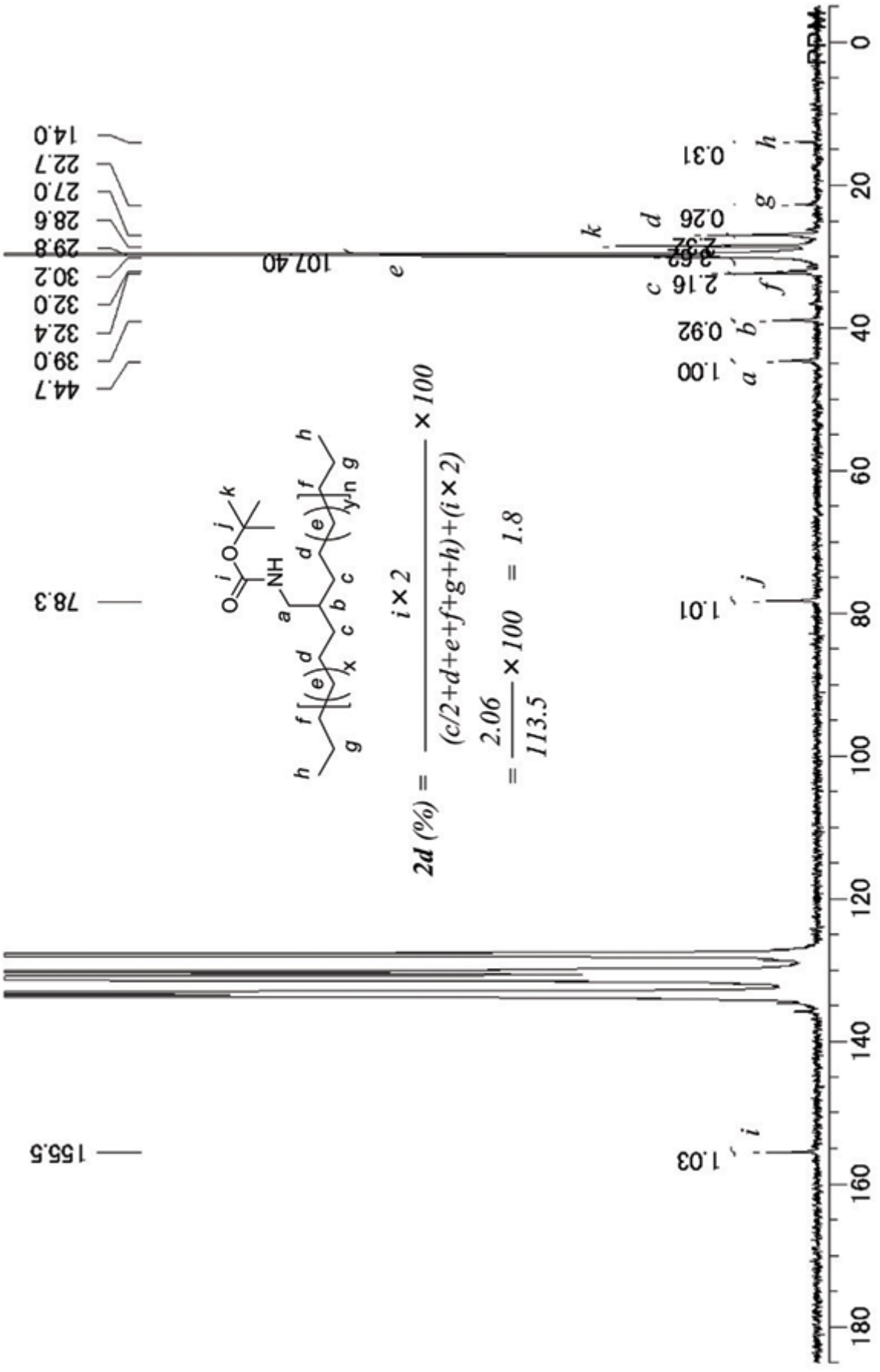


Figure S32. Quantitative ^{13}C NMR spectrum of ethylene/**2d** copolymer obtained in entry 8 in Table 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

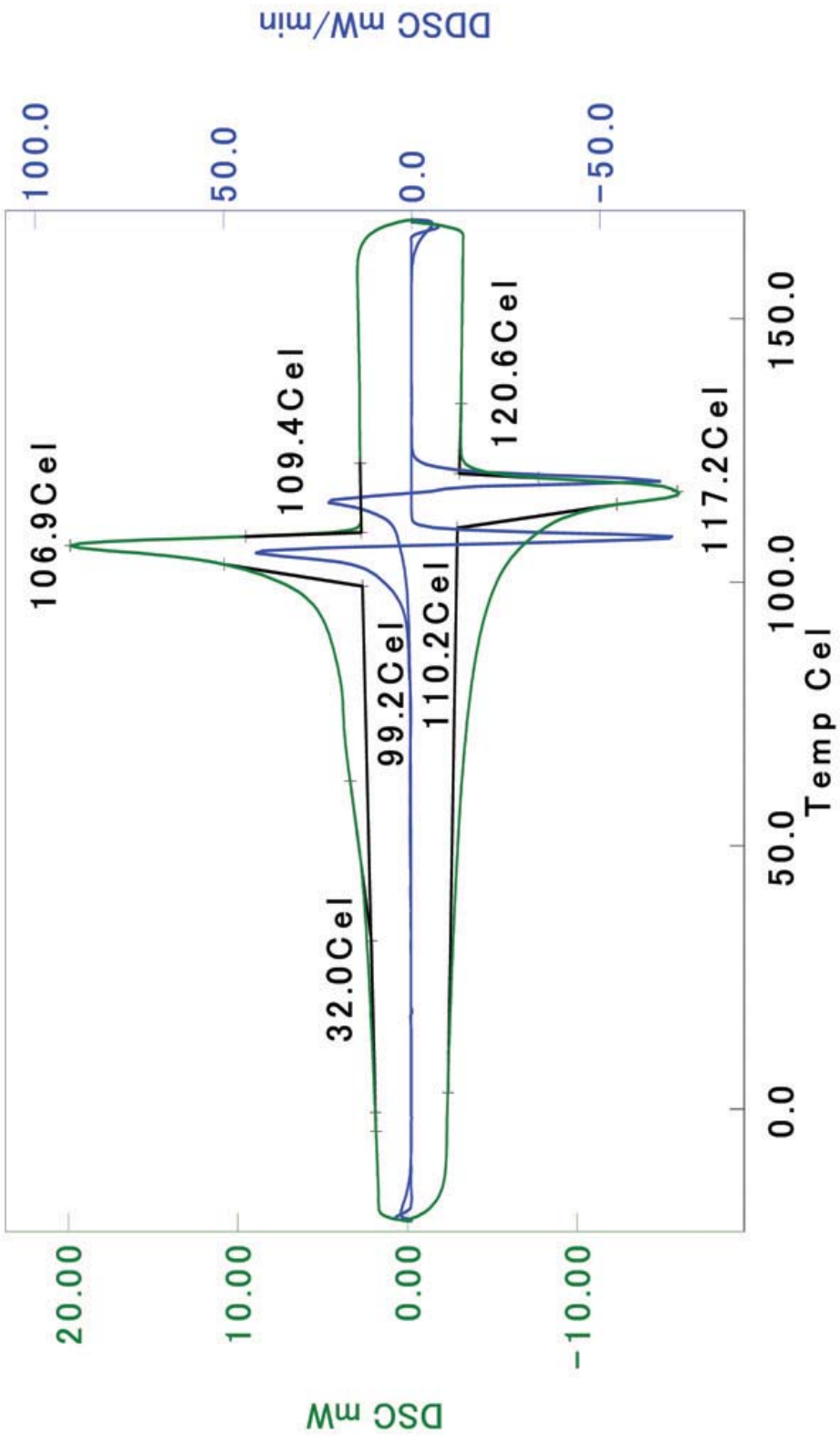


Figure S33. DSC chart of ethylene/**2d** copolymer obtained in entry 8 in Table 1.

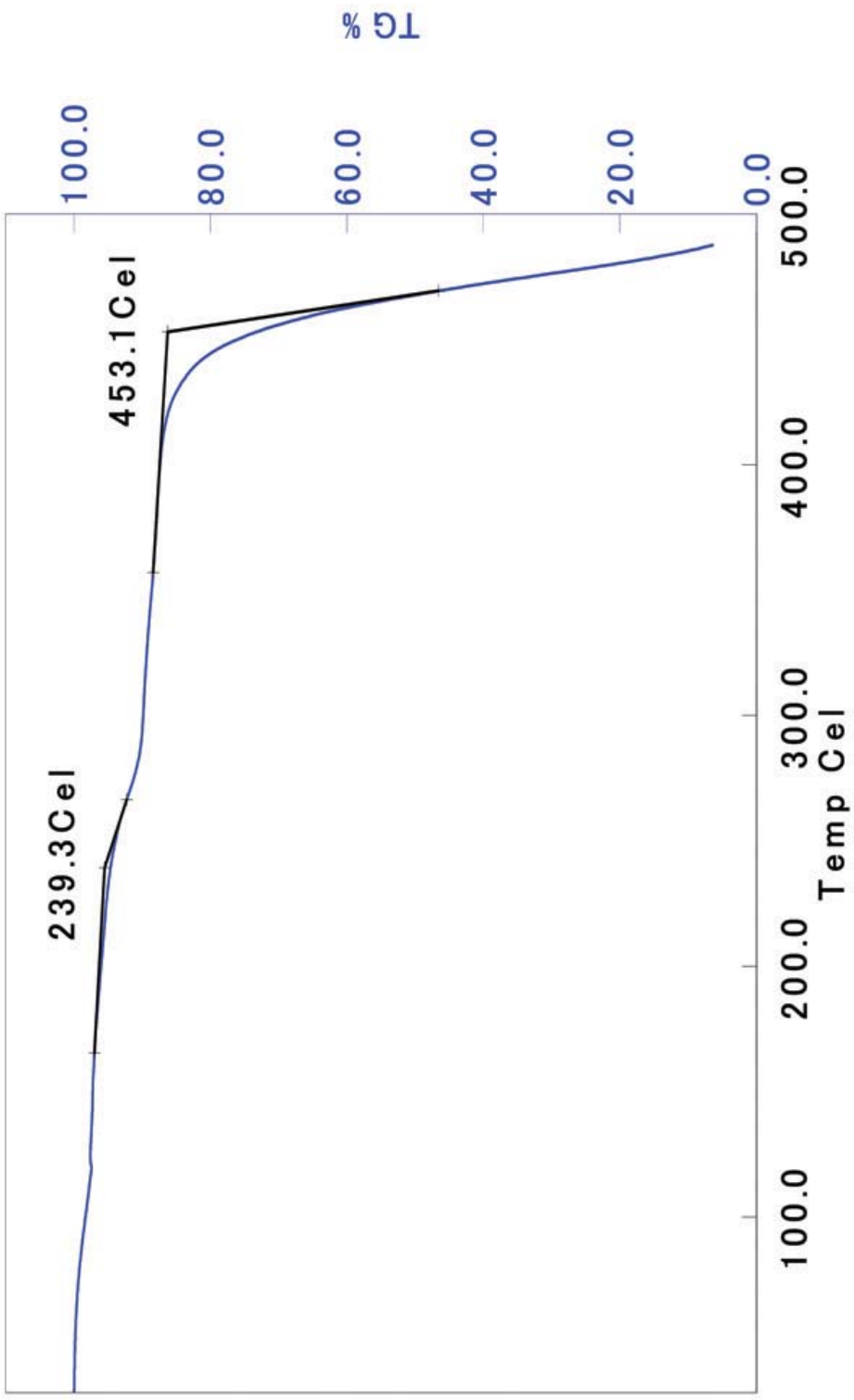


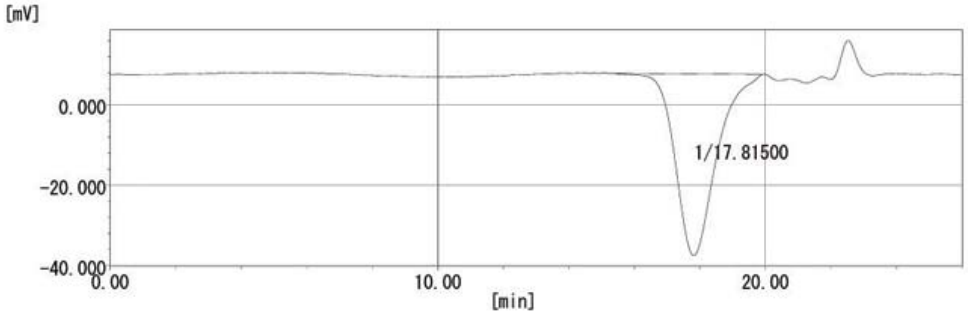
Figure S34. TG chart of ethylene/**2d** copolymer obtained in entry 8 in Table 1.

Ethylene/2d Copolymer Obtained in Entry 9 in Table 1:

55-04-104-3

Sample name : 55-04-104-3
Database name : Yagyu.mdb
Saved file name : RSLT0208
Method data : 20100413std

Measurement date : 2010/09/24 18:11:39
Calculation date : 2010/09/27 08:52:49



	[min]	[mV]	[MOL]
Peak start	15.03	7.875	149,205
Peak top	17.82	-37.483	7,151
Peak end	19.94	7.592	485
Area [mV·sec]		3,617.516	
Area [%]		100.000	
Height [mV]		45.197	
[η]		7,771.41566	

Mn	:	4,783
Mw	:	7,771
Mz	:	12,482
Mz+1	:	24,510
Mv	:	7,771
Mp	:	7,277
Mz/Mw	:	1.606
Mw/Mn	:	1.625
Mz+1/Mw	:	3.154

Figure S35. SEC trace of ethylene/**2d** copolymer obtained in entry 9 in Table 1. M_n (PS) = 4,800 was corrected to M_n (PE) = 2,100 by universal calibration.

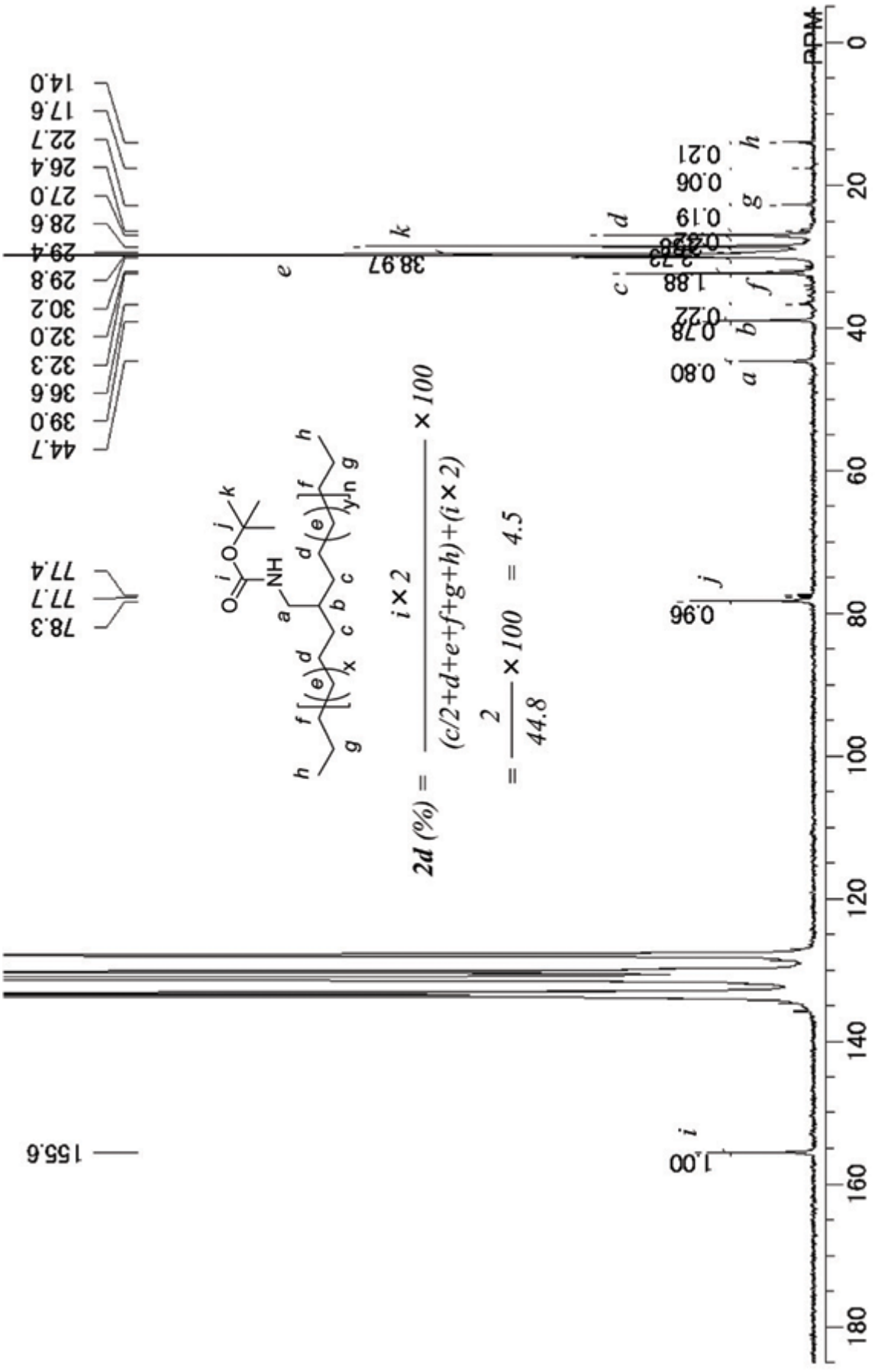


Figure S36. Quantitative ^{13}C NMR spectrum of ethylene/**2d** copolymer obtained in entry 9 in Table 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

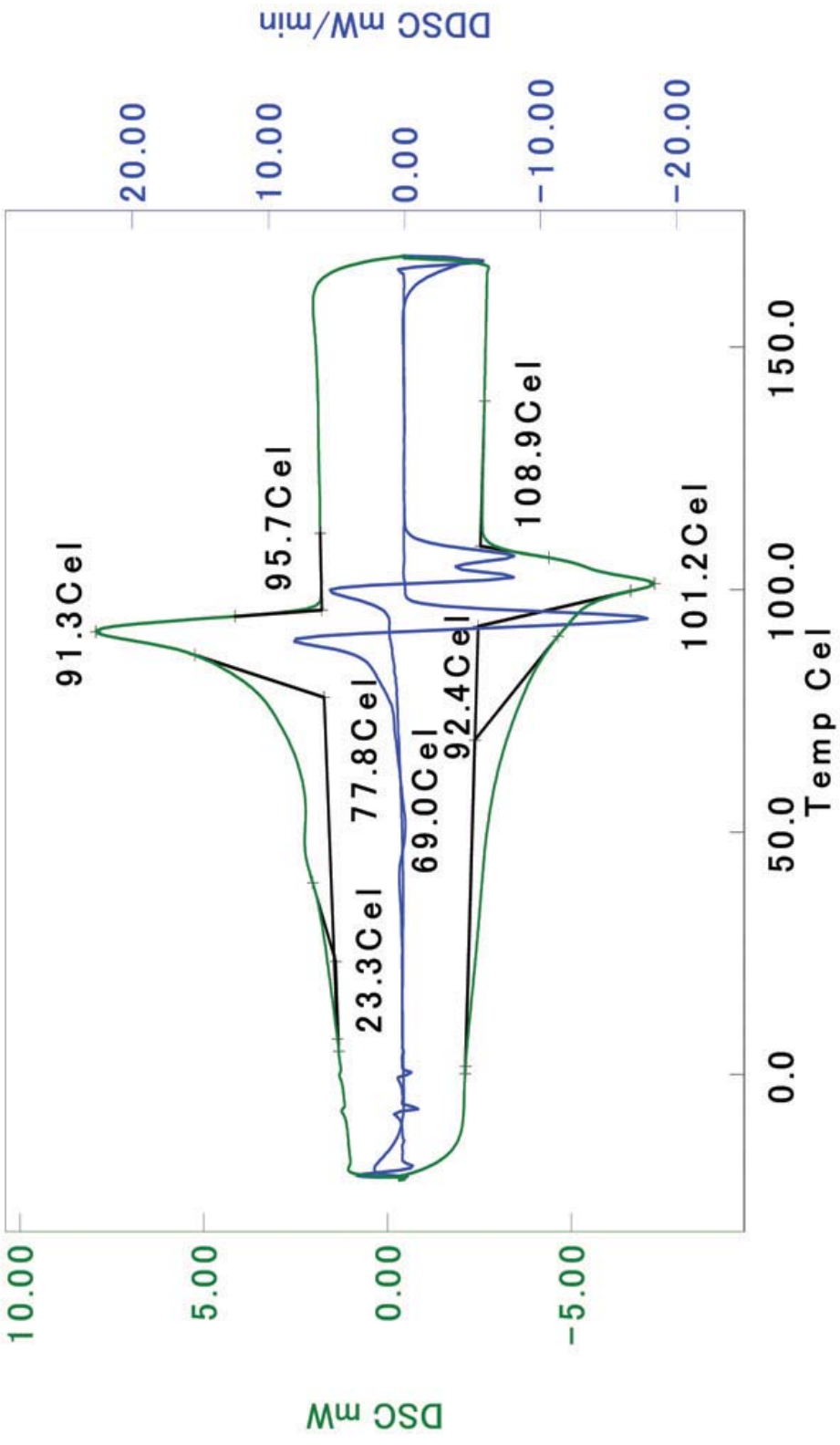


Figure S37. DSC chart of ethylene/**2d** copolymer obtained in entry 9 in Table 1.

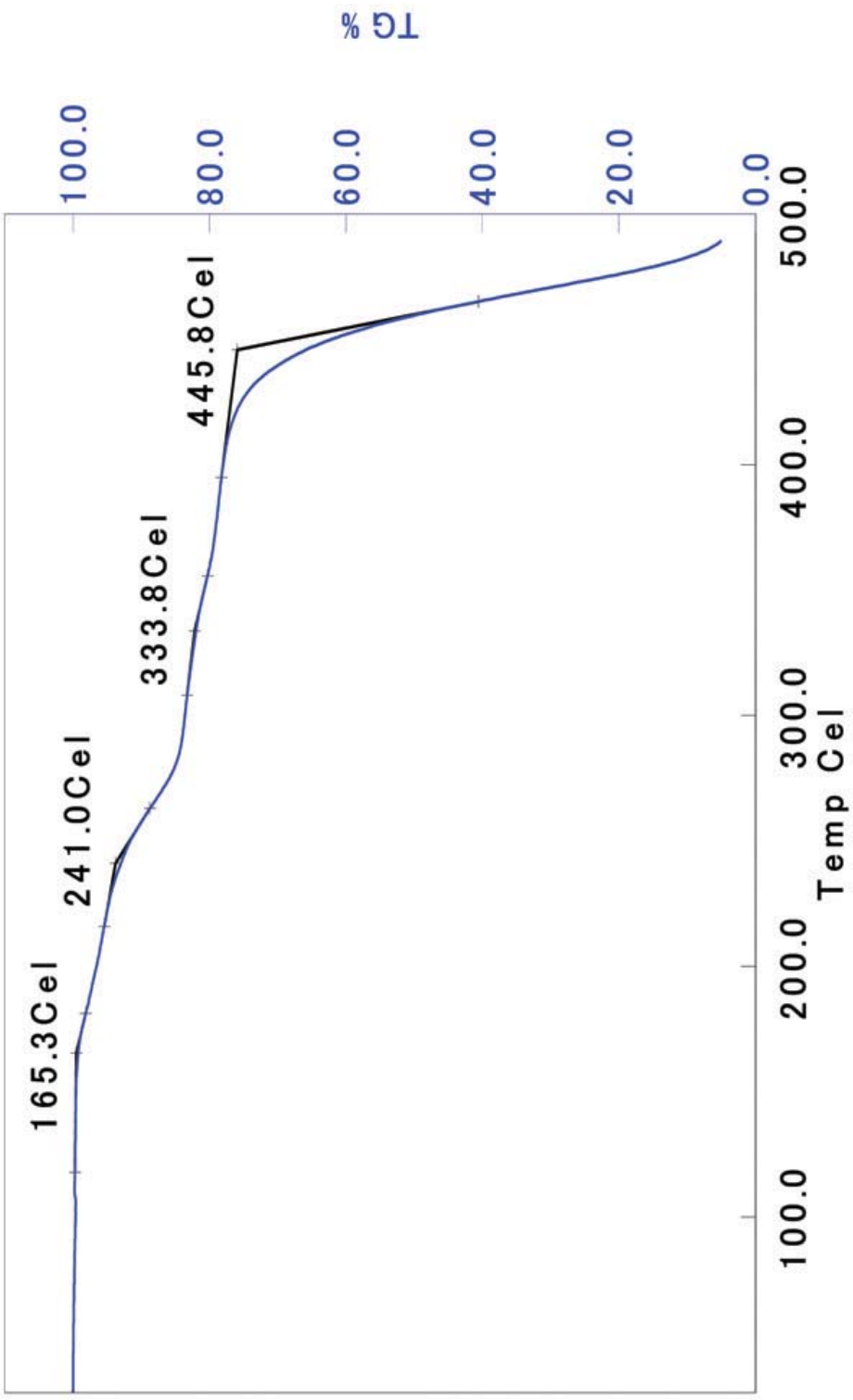


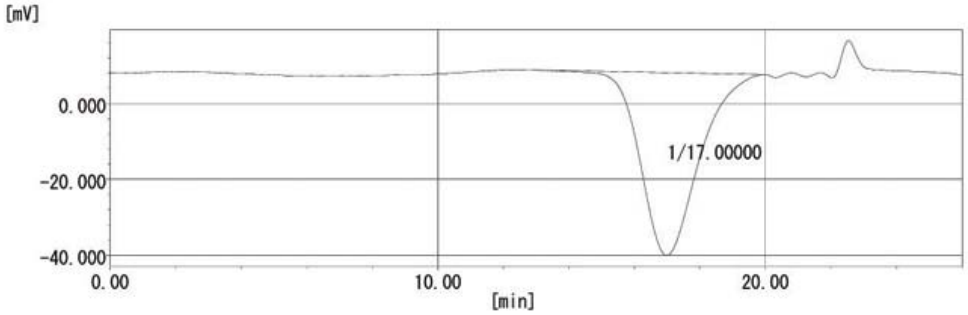
Figure S38. TG chart of ethylene/**2d** copolymer obtained in entry 9 in Table 1.

Ethylene/2e Copolymer Obtained in Entry 10 in Table 1:

55-04-014-3

Sample name : 55-04-014-3
Database name : Yagyu.mdb
Saved file name : RSLT0209
Method data : 20100413std

Measurement date : 2010/09/24 18:41:39
Calculation date : 2010/09/27 09:31:50



	[min]	[mV]	[MOL]
Peak start	12.97	8.832	1,360,511
Peak top	17.00	-40.098	18,001
Peak end	19.98	7.661	462
Area [mV·sec]		5,525.384	
Area [%]		100.000	
Height [mV]		48.256	
[η]		22,413.56994	

Mn	:	9,657
Mw	:	22,414
Mz	:	58,350
Mz+1	:	257,507
Mv	:	22,414
Mp	:	18,920
Mz/Mw	:	2.603
Mw/Mn	:	2.321
Mz+1/Mw	:	11.489

Figure S39. SEC trace of ethylene/**2e** copolymer obtained in entry 10 in Table 1. M_n (PS) = 9,700 was corrected to M_n (PE) = 4,200 by universal calibration.

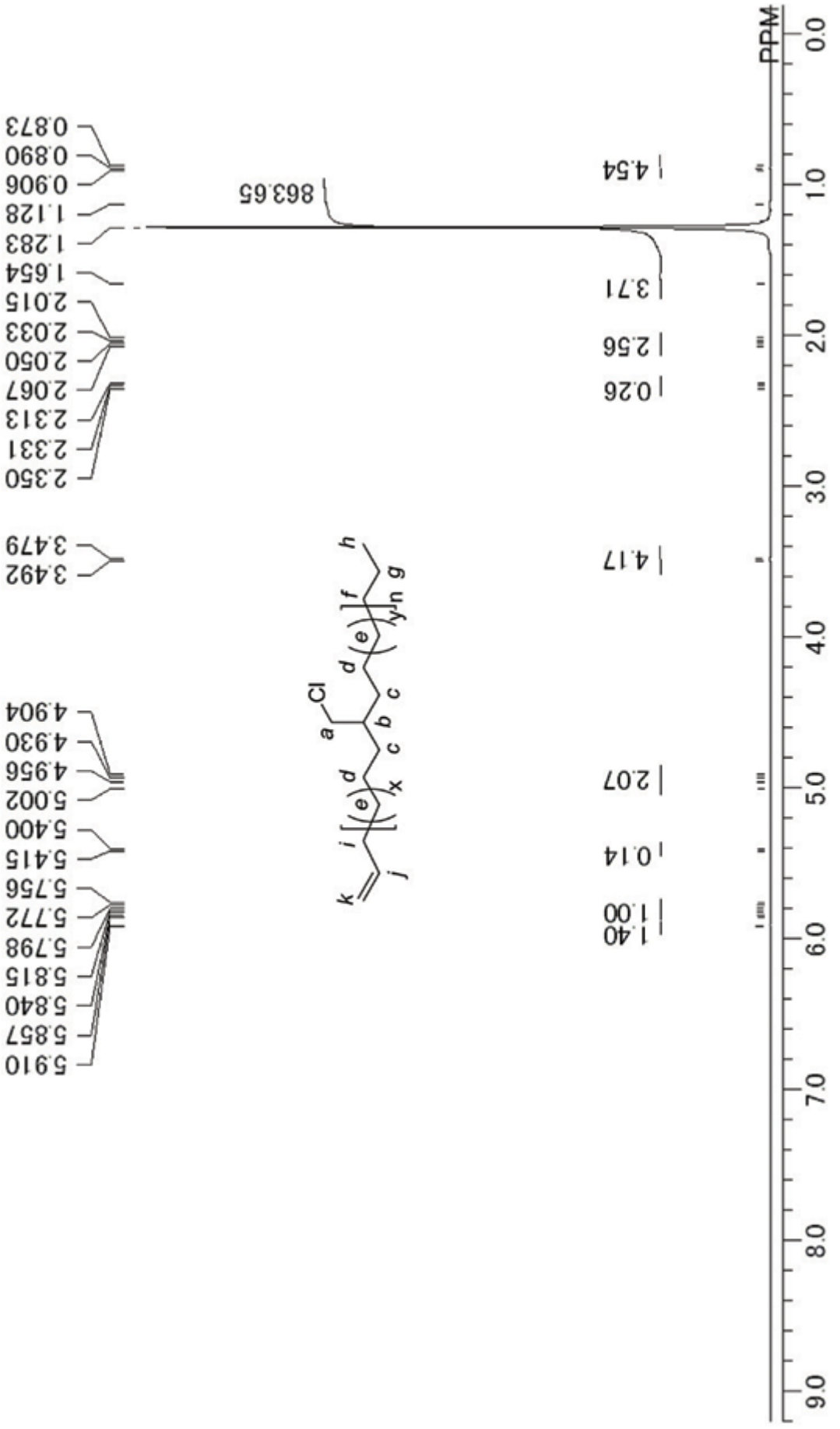


Figure S40. ^{1}H NMR spectrum of ethylene/**2e** copolymer obtained in entry 10 in Table 1 (400 MHz, $Cl_2CDCDCl_2$, 120 ˚C).

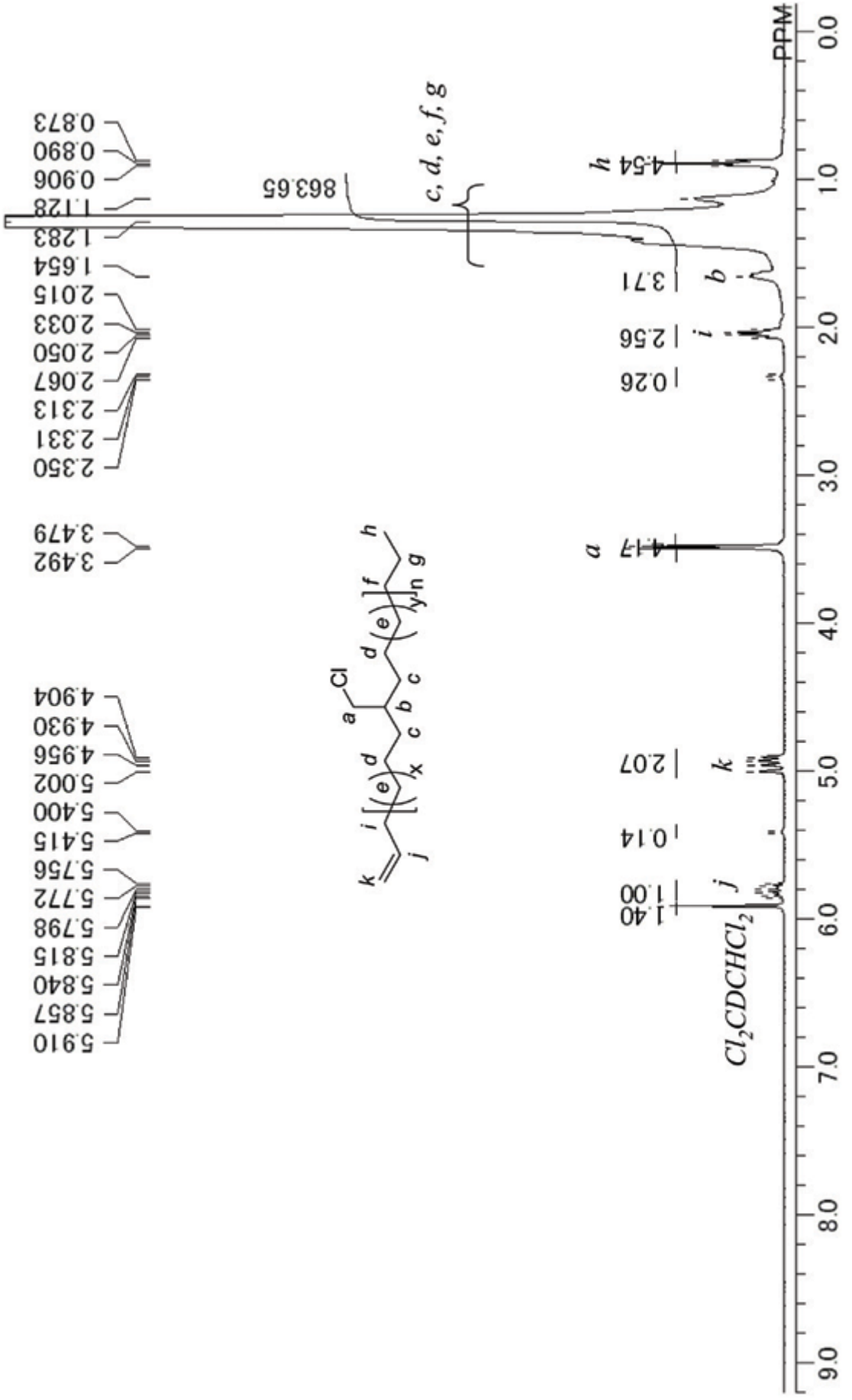


Figure S41. ^{1}H NMR spectrum of ethylene/**2e** copolymer obtained in entry 10 in Table 1 (400 MHz, $Cl_2CDCDCl_2$, 120 ˚C).

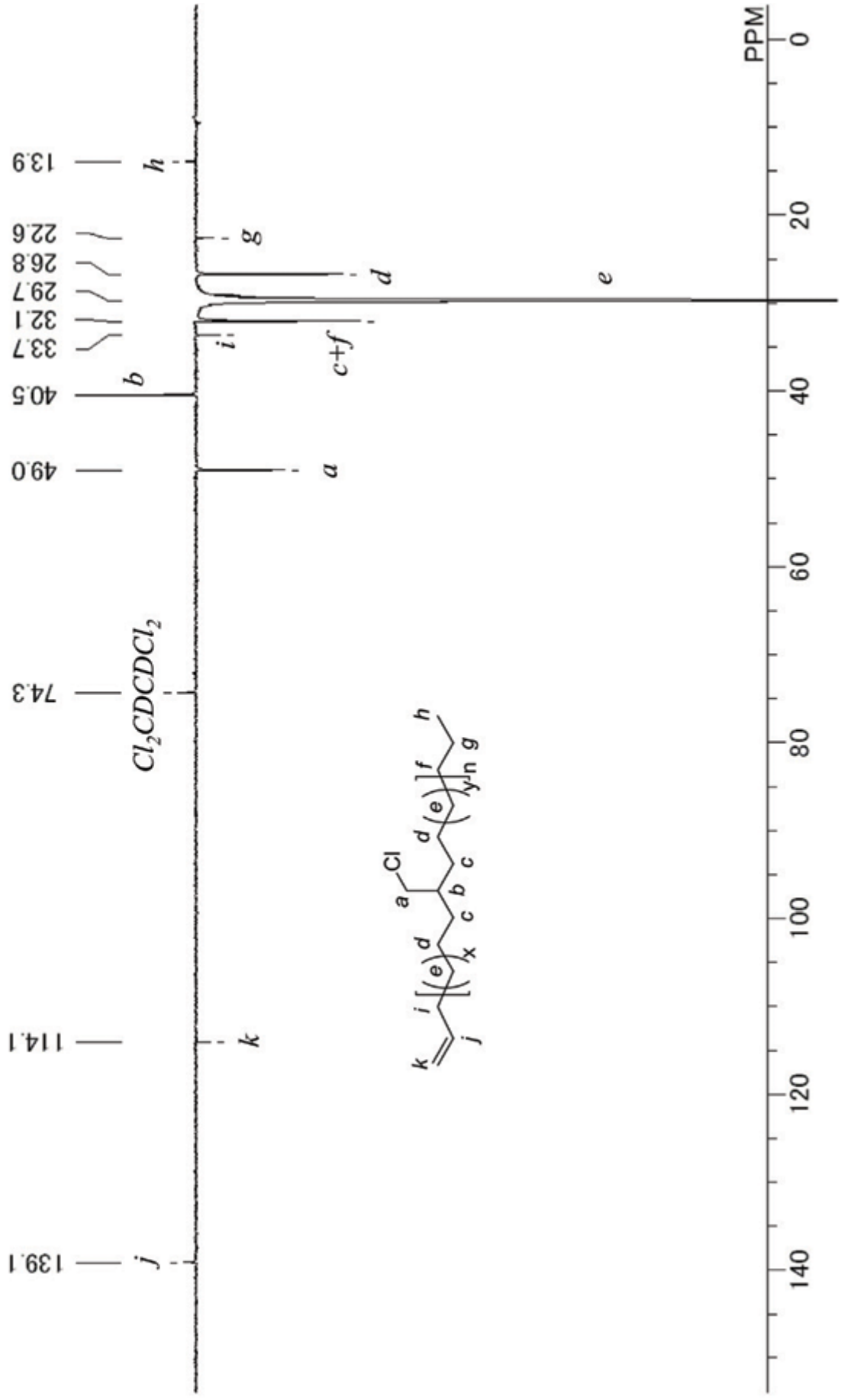


Figure S42. DEPT 135 NMR spectrum of ethylene/**2e** copolymer obtained in entry 10 in Table 1 (101 MHz, $Cl_2CDCDCl_2$, 120 ˚C).

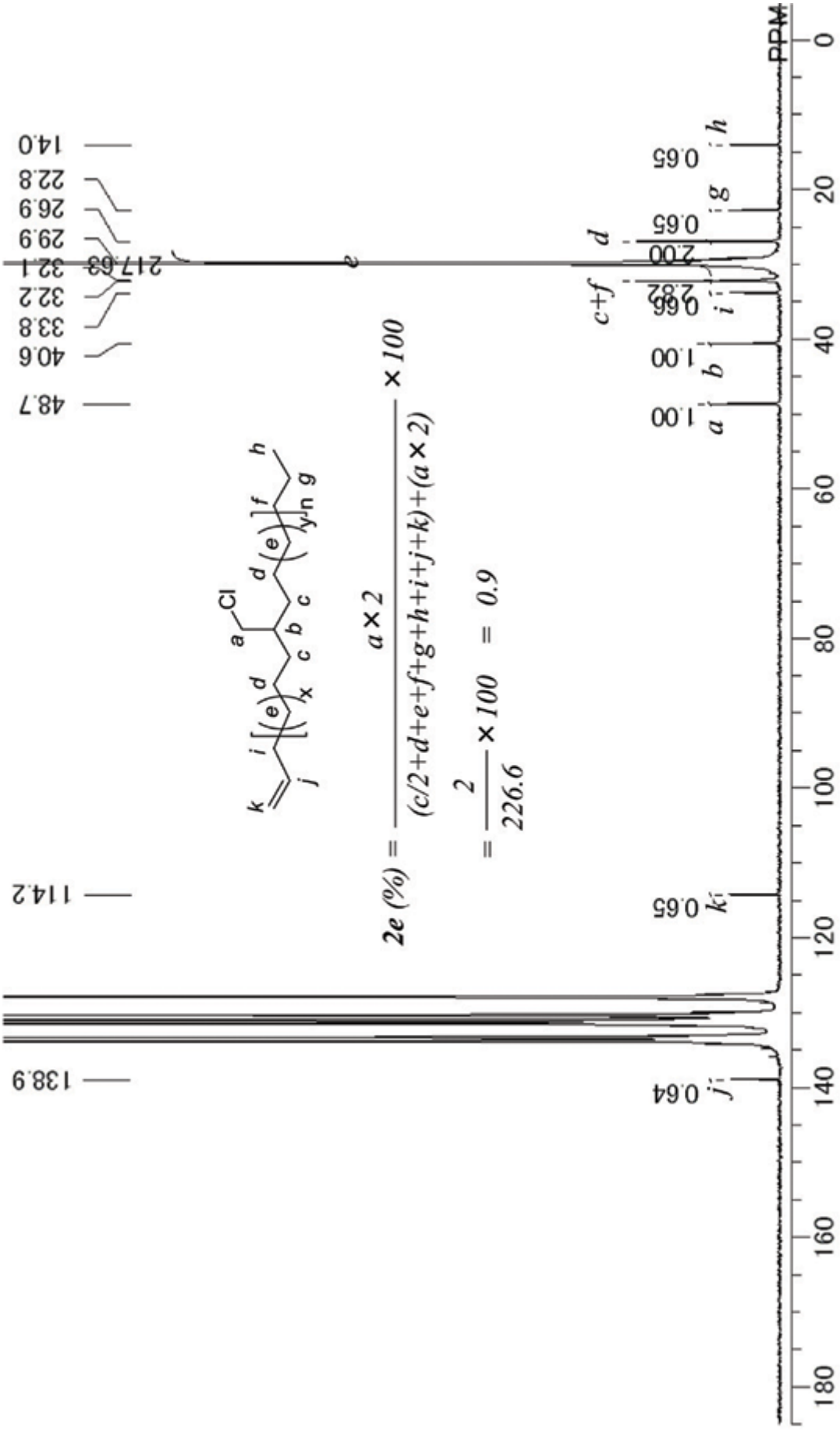


Figure S43. Quantitative ^{13}C NMR spectrum of ethylene/**2e** copolymer obtained in entry 10 in Table 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

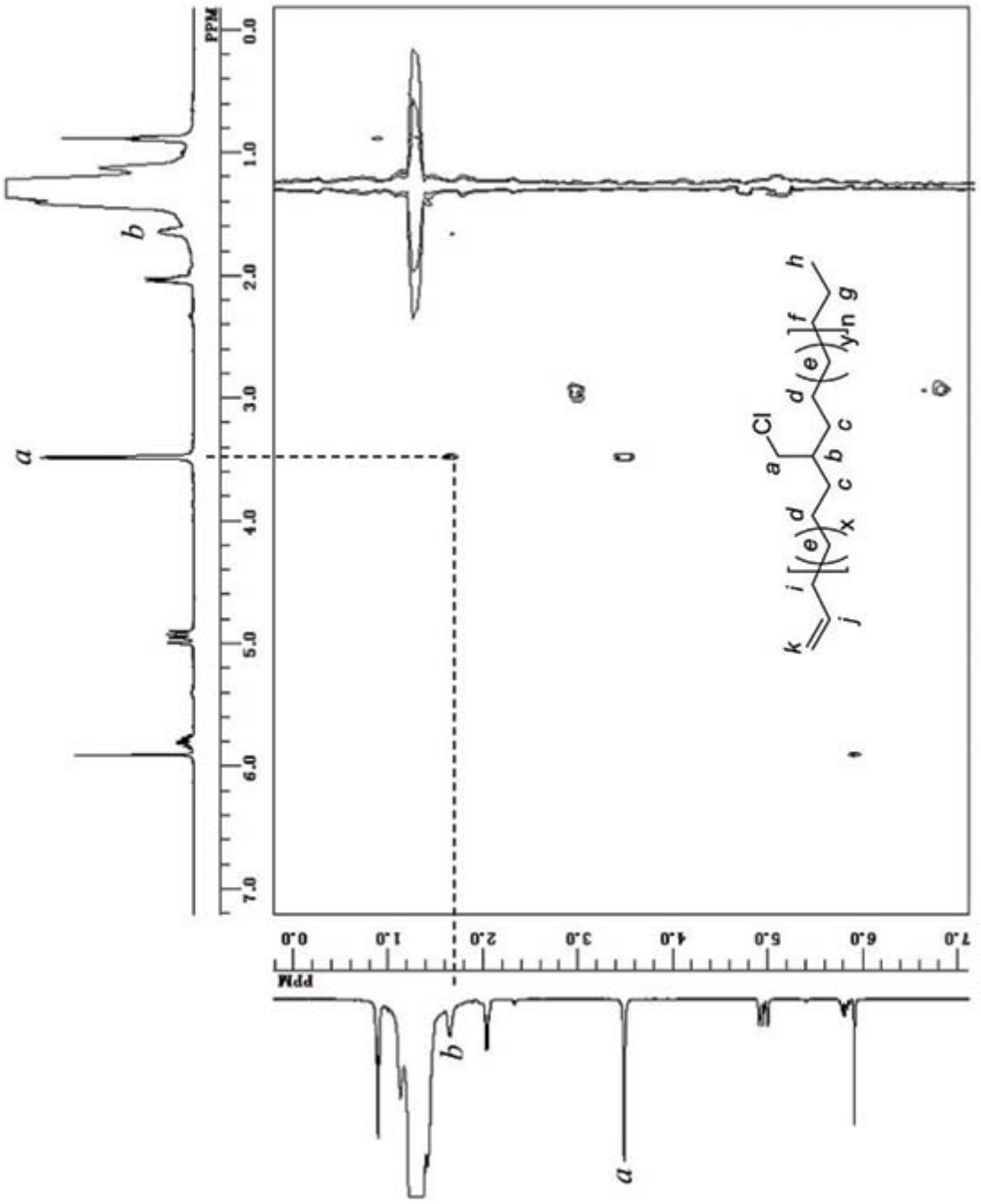


Figure S44. H–H COSY spectrum of ethylene/**2e** copolymer obtained in entry 10 in Table 1 ($Cl_2CDCDCl_2$, 120 ˚C).

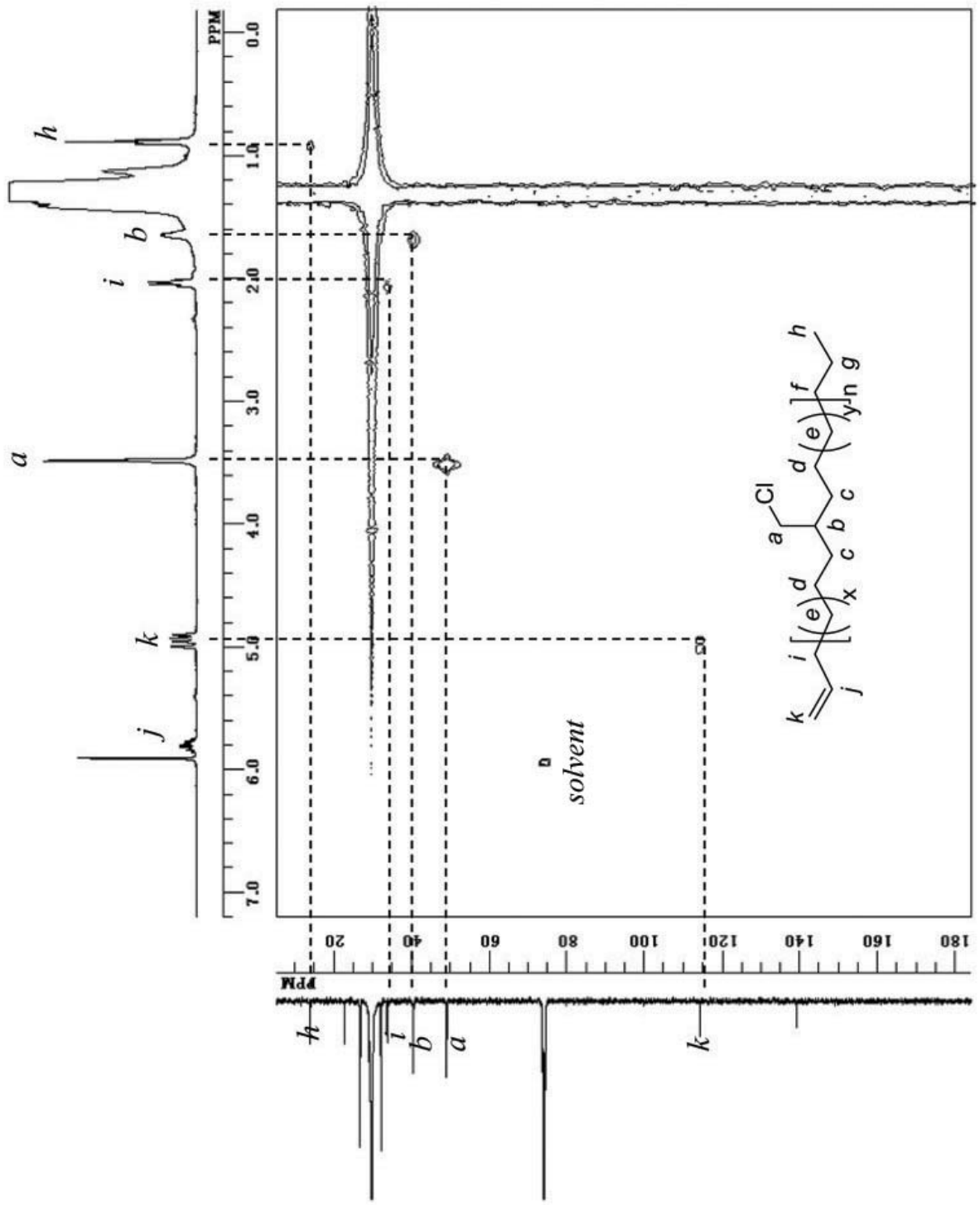


Figure S45. HMQC spectrum of ethylene/**2e** copolymer obtained in entry 10 in Table 1 ($Cl_2CDCDCl_2$, 120 ˚C).

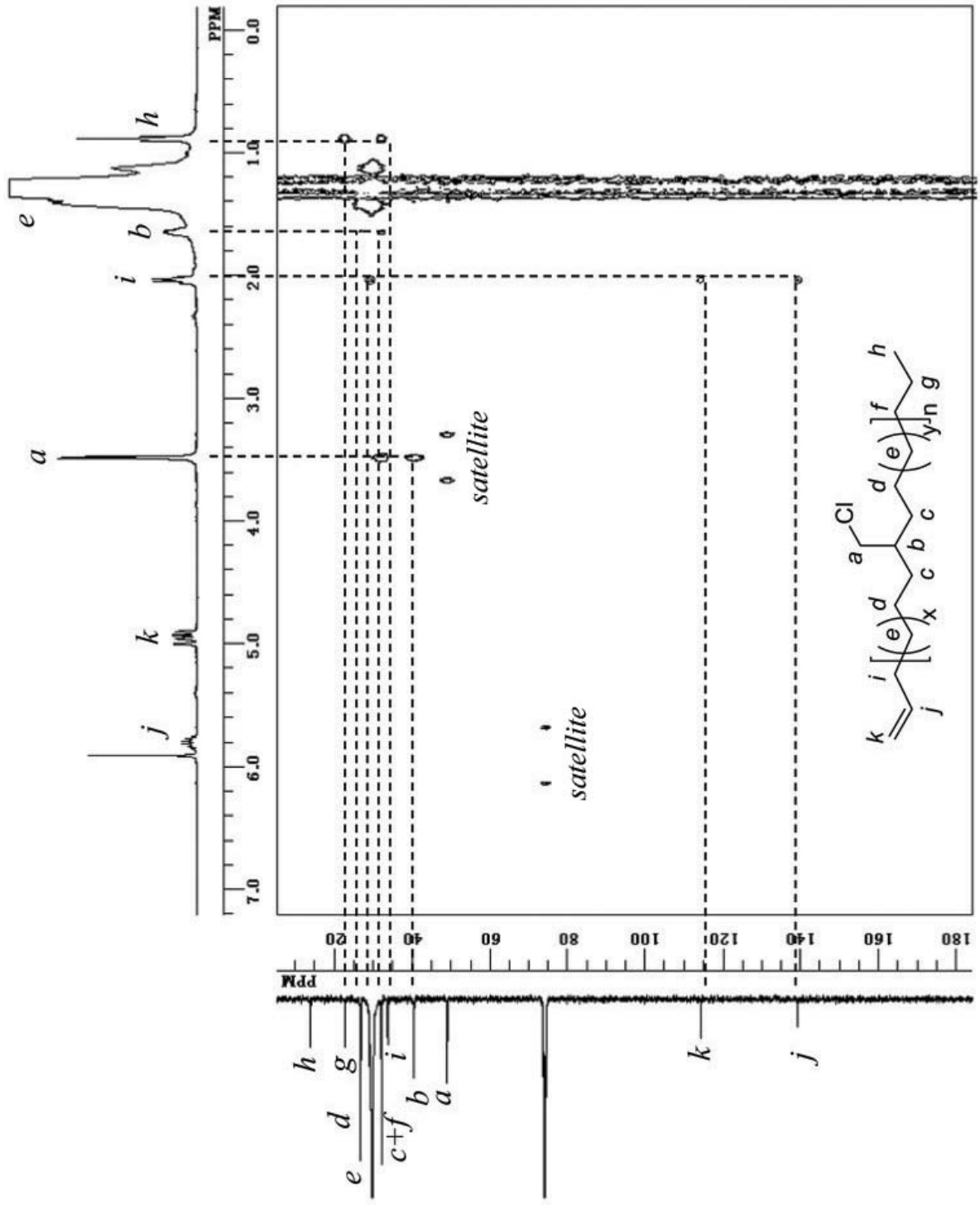


Figure S46. HMBC ^{13}C NMR spectrum of ethylene/**2e** copolymer obtained in entry 10 in Table 1 ($Cl_2CDCDCl_2$, 120 ˚C).

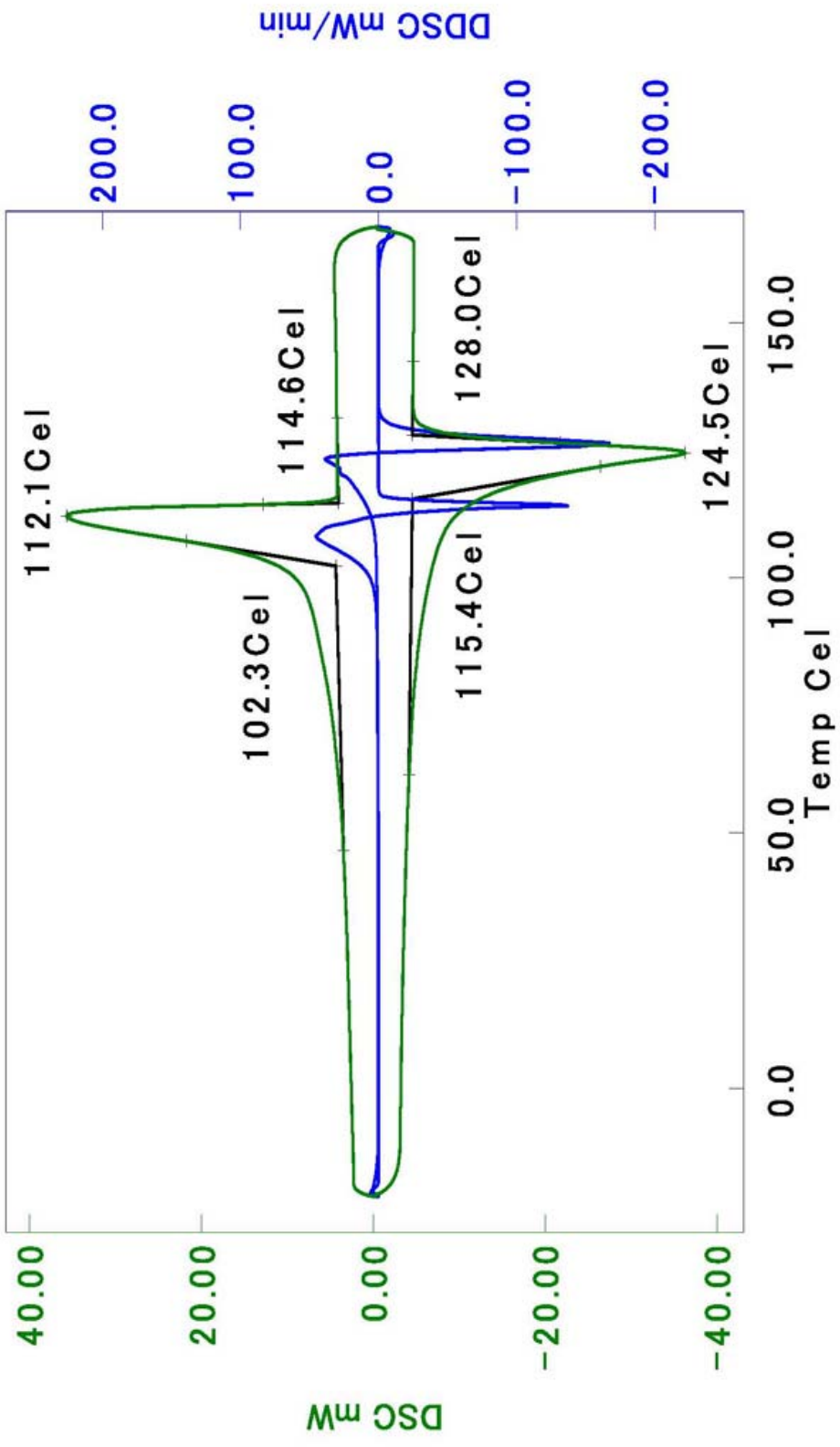


Figure S47. DSC chart of ethylene/**2e** copolymer obtained in entry 10 in Table 1.

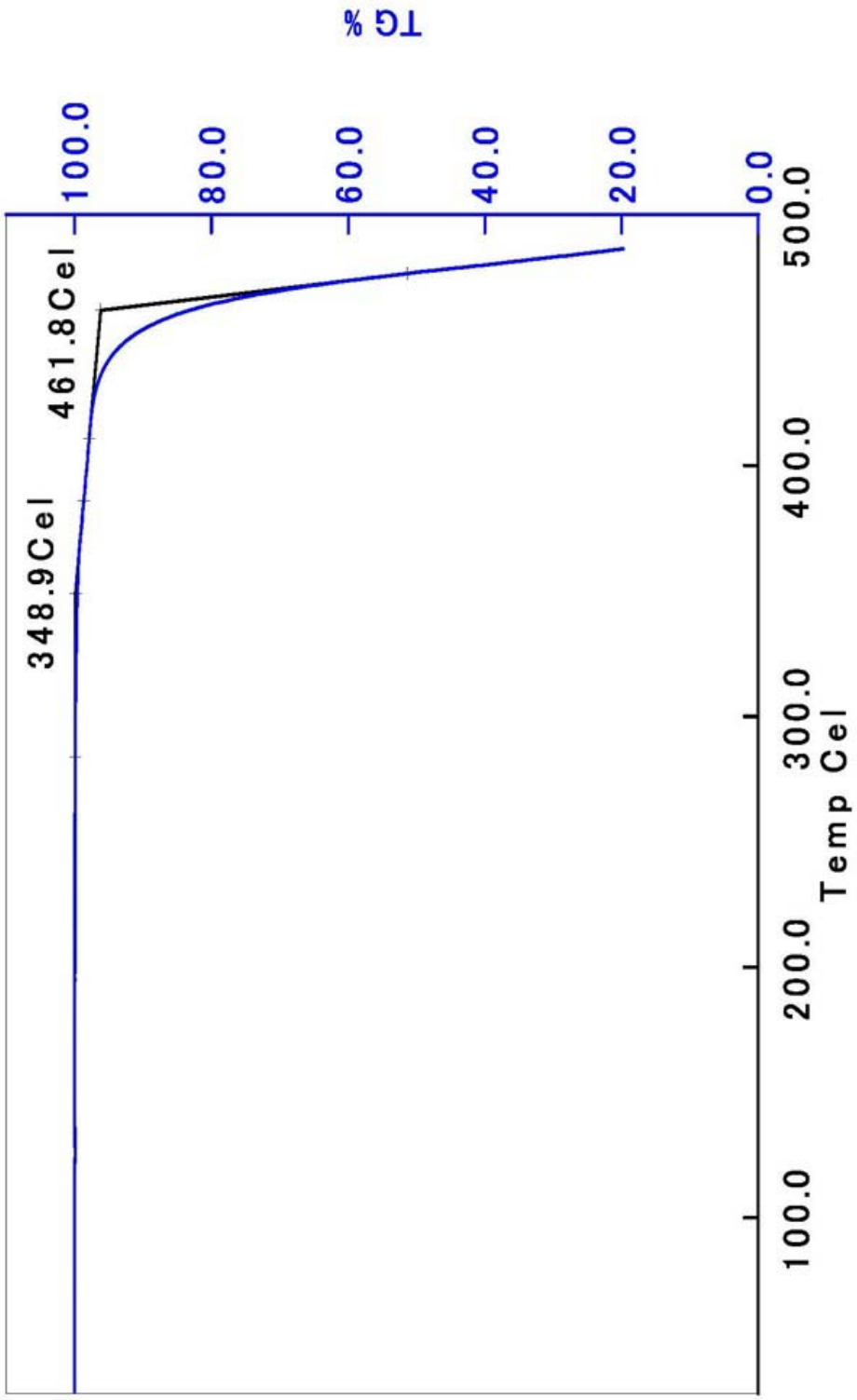


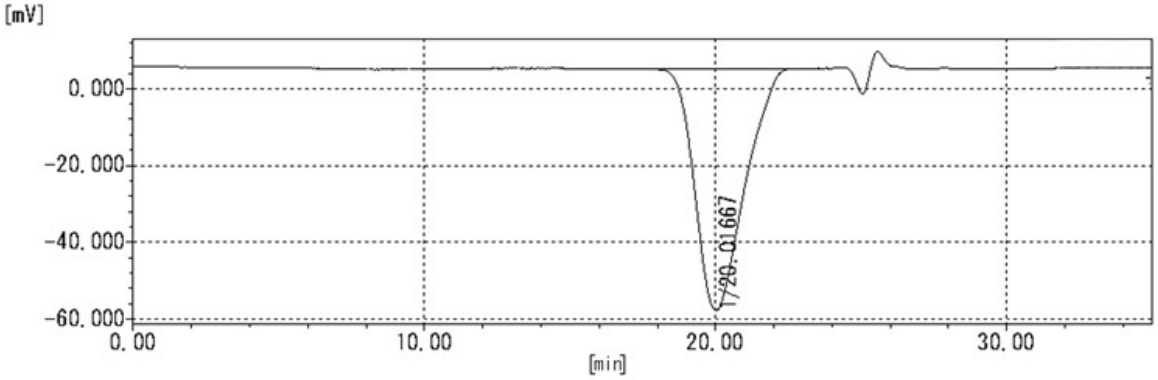
Figure S48. TG chart of ethylene/**2e** copolymer obtained in entry 10 in Table 1.

Ethylene/2f Copolymer Obtained in Entry 11 in Table 1:

C:¥GPC¥Database¥GpcDataBase.mdb RSLT0271 55-04-012-3Br

Sample name : 55-04-012-3Br
Database name : GpcDataBase.mdb
Saved file name : RSLT0271
Method data : 20100614

Measurement date : 2010/05/16 03:11:15
Calculation date : 2010/06/18 10:21:29



	[min]	[mV]	[MOL]
Peak start	18.00	4.979	86,775
Peak top	20.02	-57.830	11,780
Peak end	22.69	5.204	303
Area [mV・sec]		6,779.163	
Area [%]		100.000	
Height [mV]		62.906	
[η]		12,240.10714	

Mn	:	6,253
Mw	:	12,240
Mz	:	18,935
Mz+1	:	25,505
Mv	:	12,240
Mp	:	12,717
Mz/Mw	:	1.547
Mw/Mn	:	1.958
Mz+1/Mw	:	2.084

Figure S49. SEC trace of ethylene/**2e** copolymer obtained in entry 11 in Table 1. M_n (PS) = 6,300 was corrected to M_n (PE) = 2,800 by universal calibration.

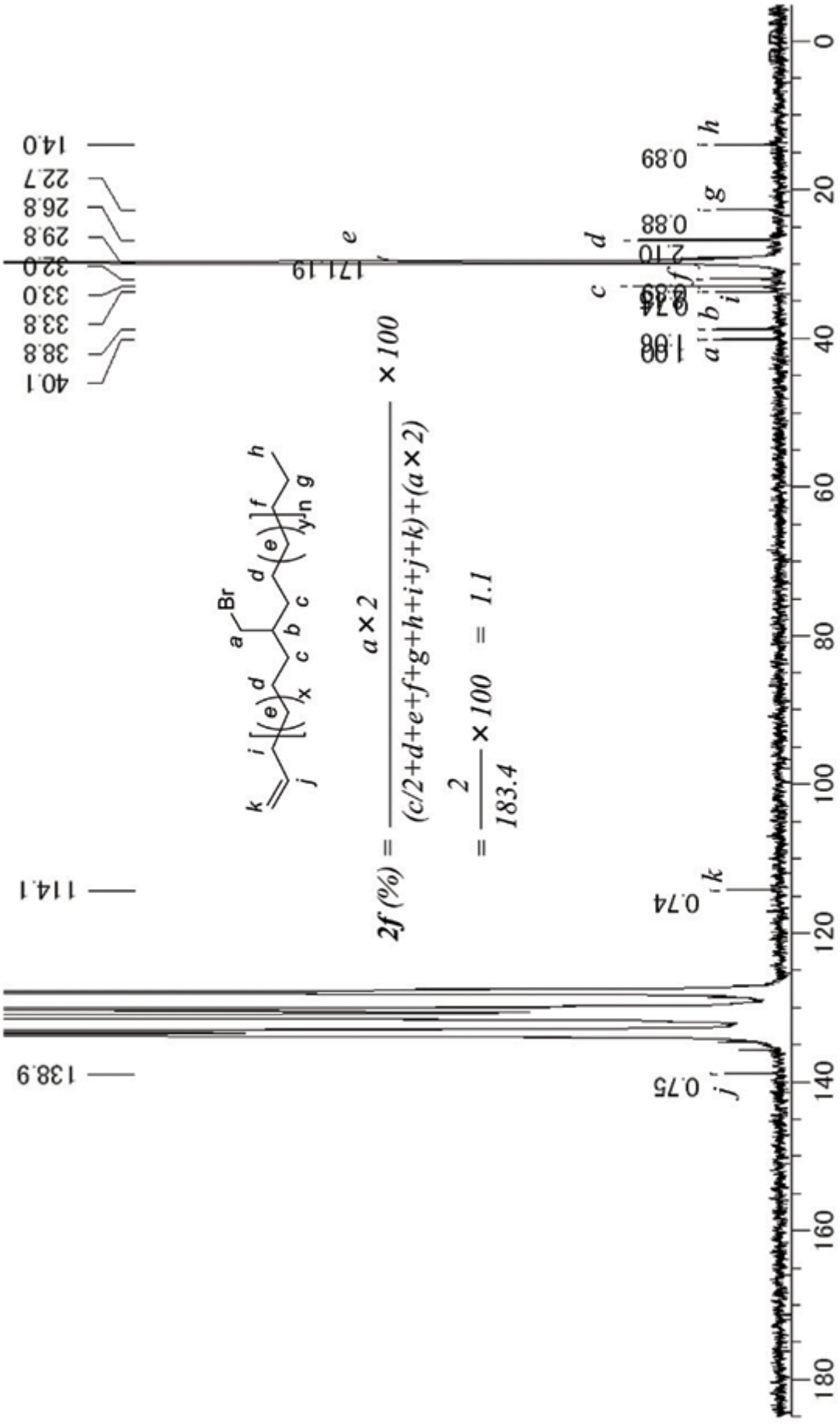


Figure S50. Quantitative ^{13}C NMR spectrum of ethylene/**2e** copolymer obtained in entry 11 in Table 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

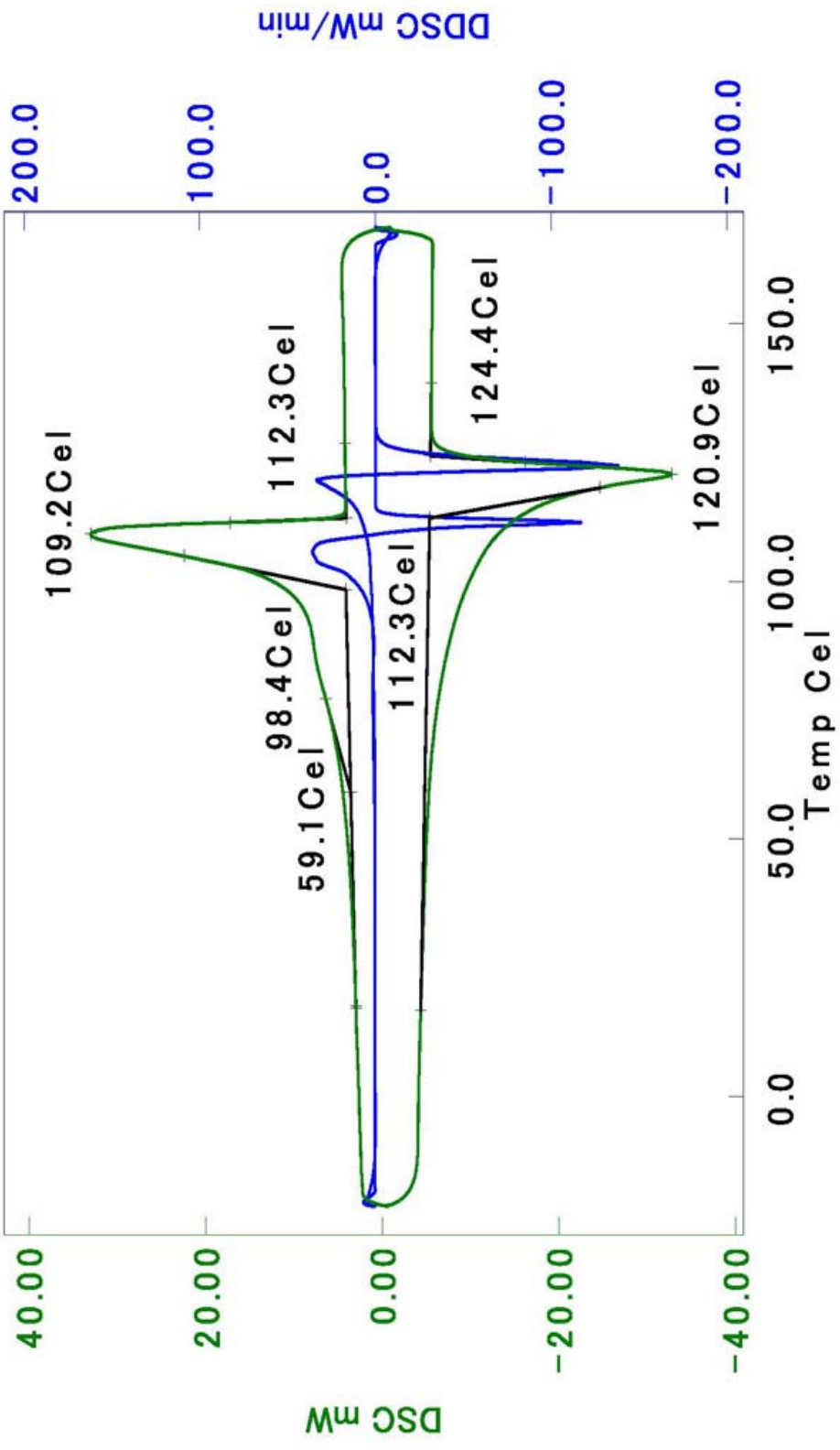


Figure S51. DSC chart of ethylene/**2f** copolymer obtained in entry 11 in Table 1.

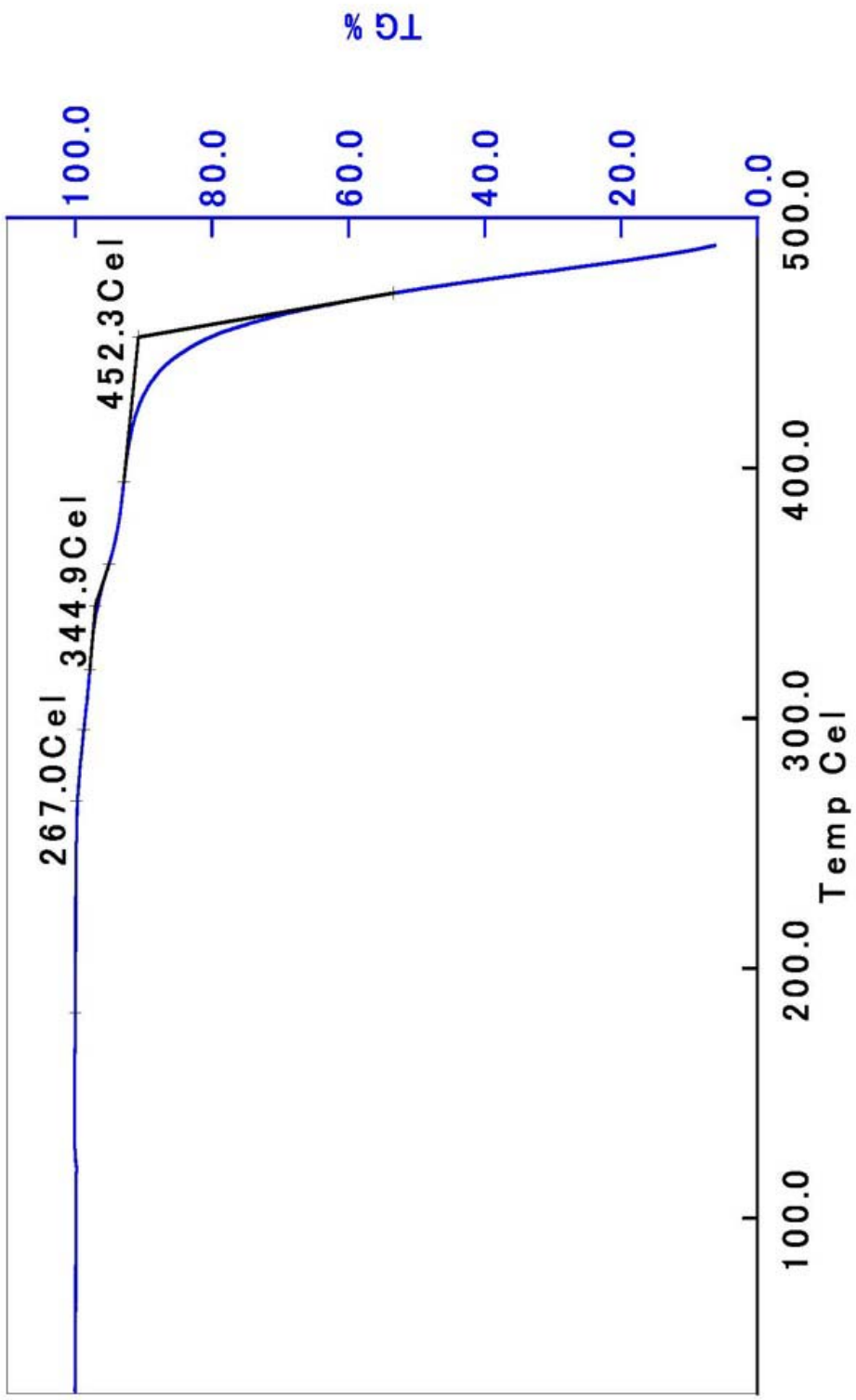


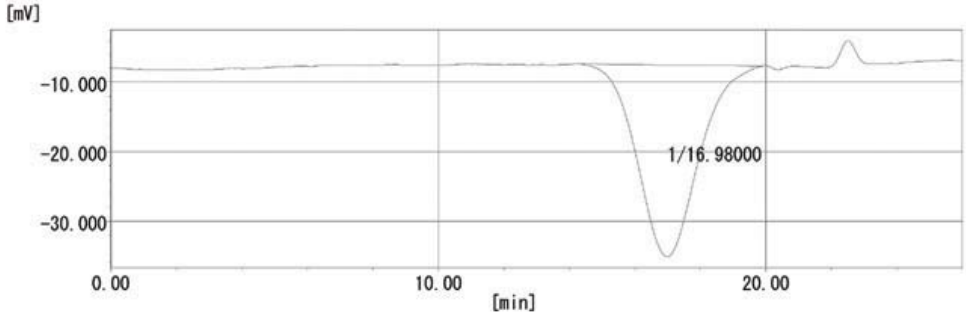
Figure S52. TG chart of ethylene/**2f** copolymer obtained in entry 11 in Table 1.

Ethylene/2b Copolymer Obtained by Hydrolysis of Ethylene/2a Copolymer:

55-04-066-1

Sample name : 55-04-066-1
Database name : Yagyu.mdb
Saved file name : RSLT0202
Method data : RSLT0197

Measurement date : 2010/10/06 16:32:11
Calculation date : 2010/10/06 17:04:30



	[min]	[mV]	[MOL]
Peak start	14.15	-7.366	374,077
Peak top	16.98	-35.143	18,404
Peak end	19.89	-7.671	524
Area [mV·sec]		3,348.573	
Area [%]		100.000	
Height [mV]		27.627	
[η]		24,940.91016	

Mn	:	10,462
Mw	:	24,941
Mz	:	49,326
Mz+1	:	84,780
Mv	:	24,941
Mp	:	18,920
Mz/Mw	:	1.978
Mw/Mn	:	2.384
Mz+1/Mw	:	3.399

Figure S53. SEC trace of ethylene/**2b** copolymer obtained in equation 1. M_n (PS) = 10,500 was corrected to M_n (PE) = 4,600 by universal calibration.

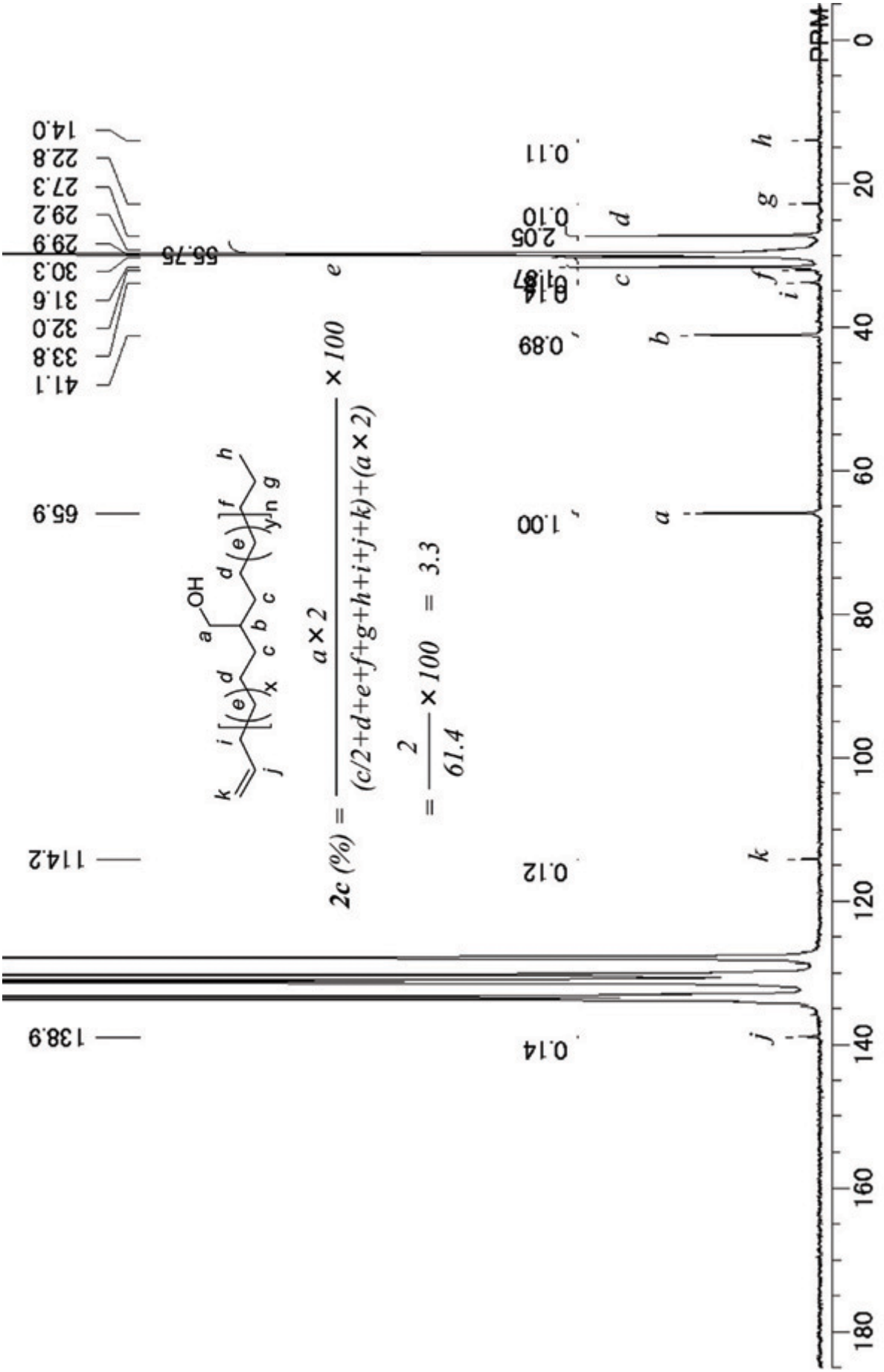


Figure S54. Quantitative ^{13}C NMR spectrum of ethylene/**2b** copolymer obtained in equation 1 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

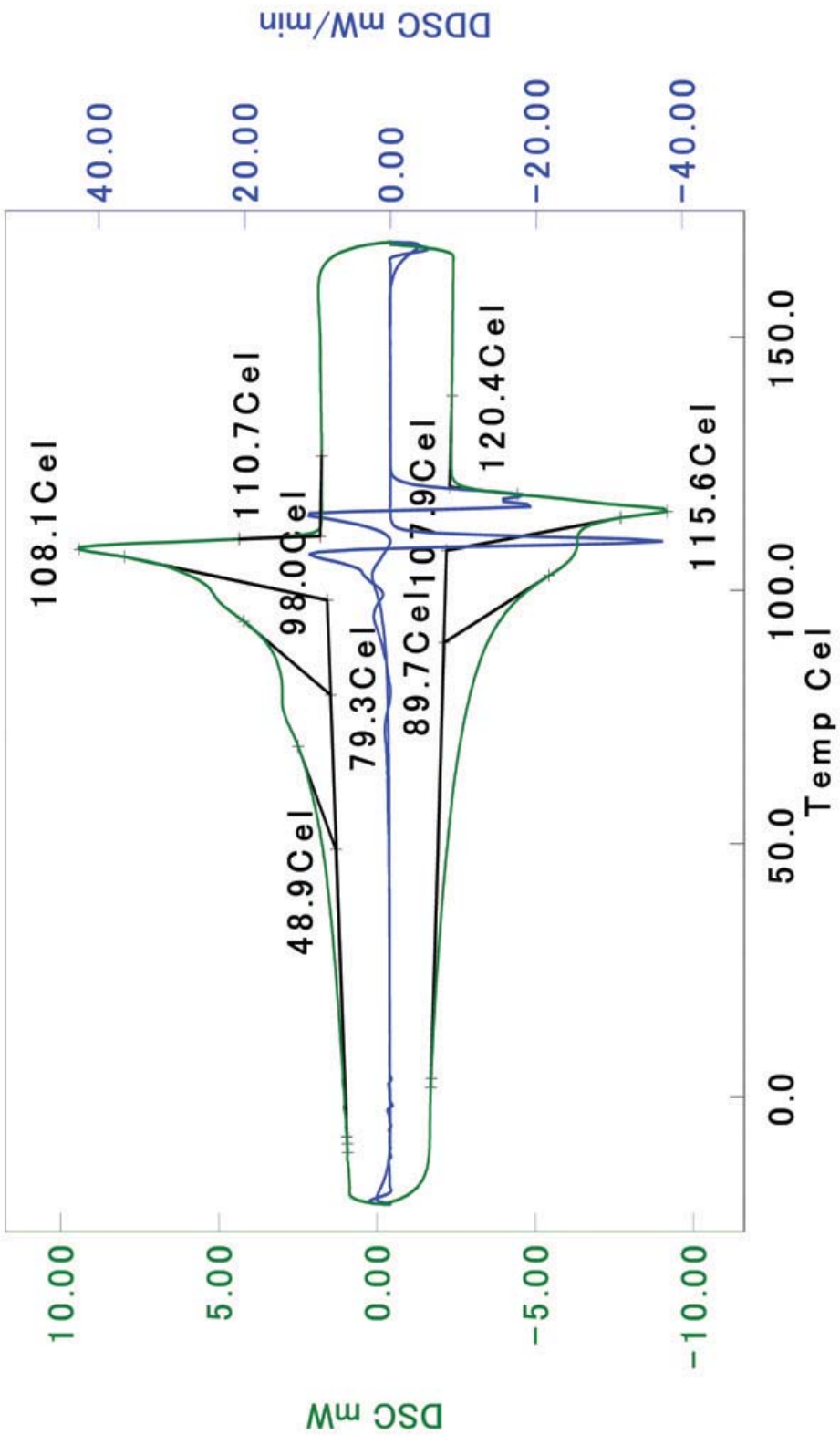


Figure S55. DSC chart of ethylene/**2b** copolymer obtained in equation 1.

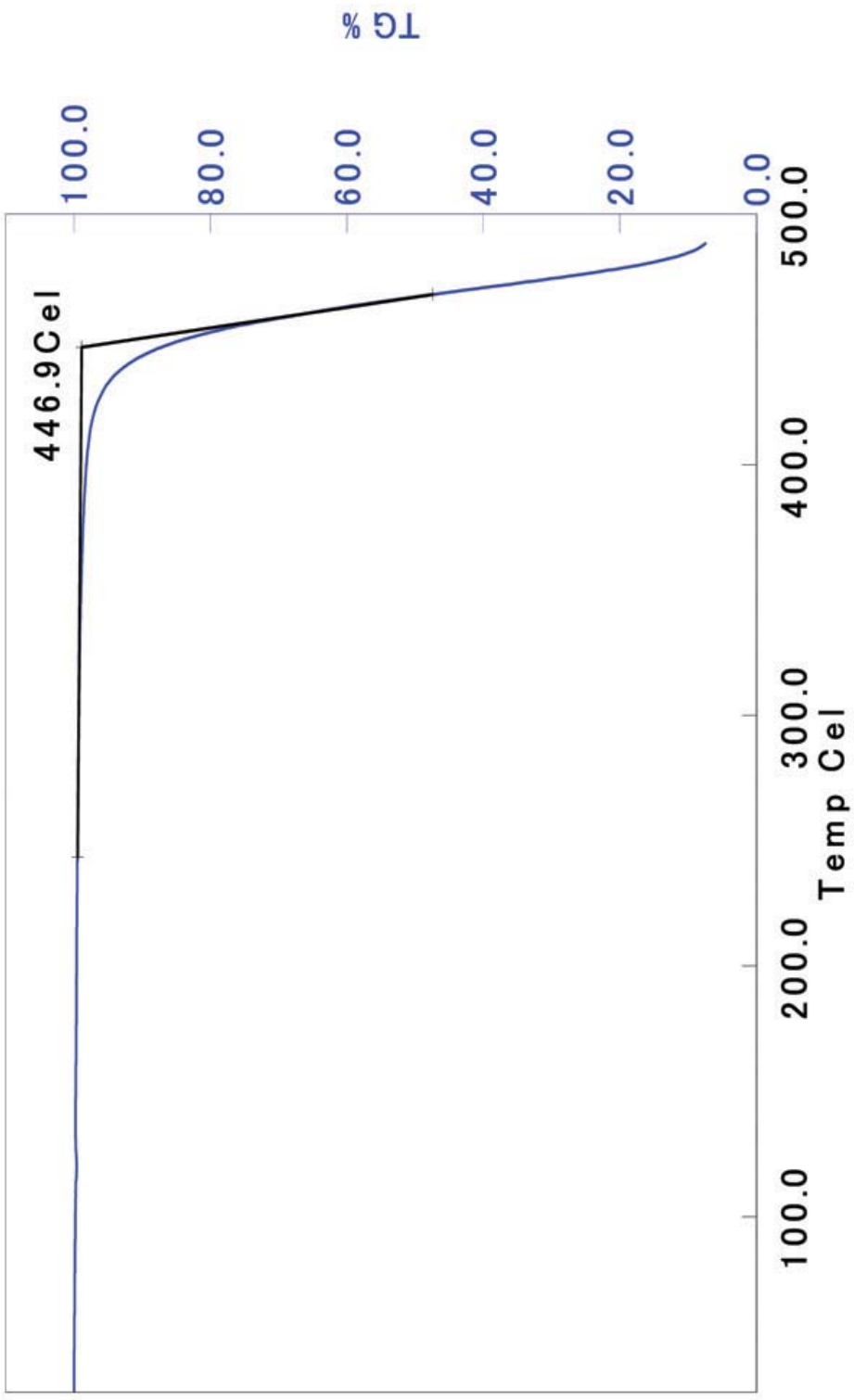


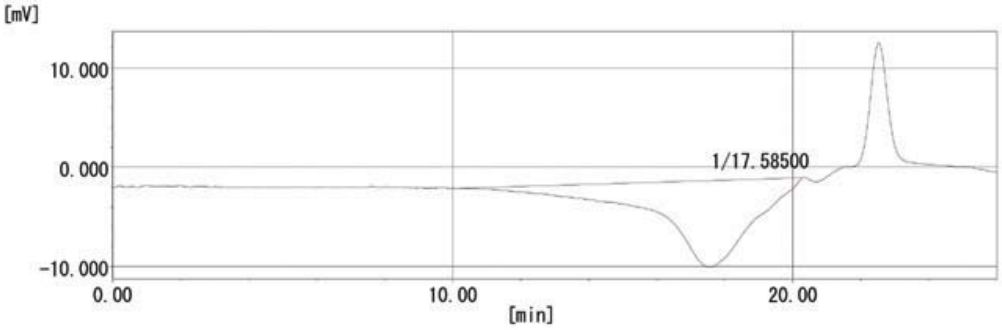
Figure S56. TG chart of ethylene/**2b** copolymer obtained in equation 1.

Ethylene/CH_2=$CHCH_2NH_3Cl$ Copolymer Obtained by Deprotection of Ethylene/2d Copolymer:

55-04-106-1

Sample name : 55-04-106-1
Database name : Yagyu.mdb
Saved file name : RSLT0206
Method data : RSLT0197

Measurement date : 2010/10/07 11:29:55
Calculation date : 2010/10/07 15:03:57



	[min]	[mV]	[MOL]
Peak start	10.12	-2.126	45,476,462
Peak top	17.59	-10.098	9,322
Peak end	20.34	-1.057	277

Area [mV·sec]		1,660.460
Area [%]		100.000
Height [mV]		8.753
[η]		266,377.14537

Mn	:	4,793
Mw	:	266,377
Mz	:	6,783,110
Mz+1	:	15,466,760
Mv	:	266,377
Mp	:	9,648
Mz/Mw	:	25.464
Mw/Mn	:	55.575
Mz+1/Mw	:	58.063

Figure S57. SEC trace of ethylene/**2c** copolymer obtained in equation 2.

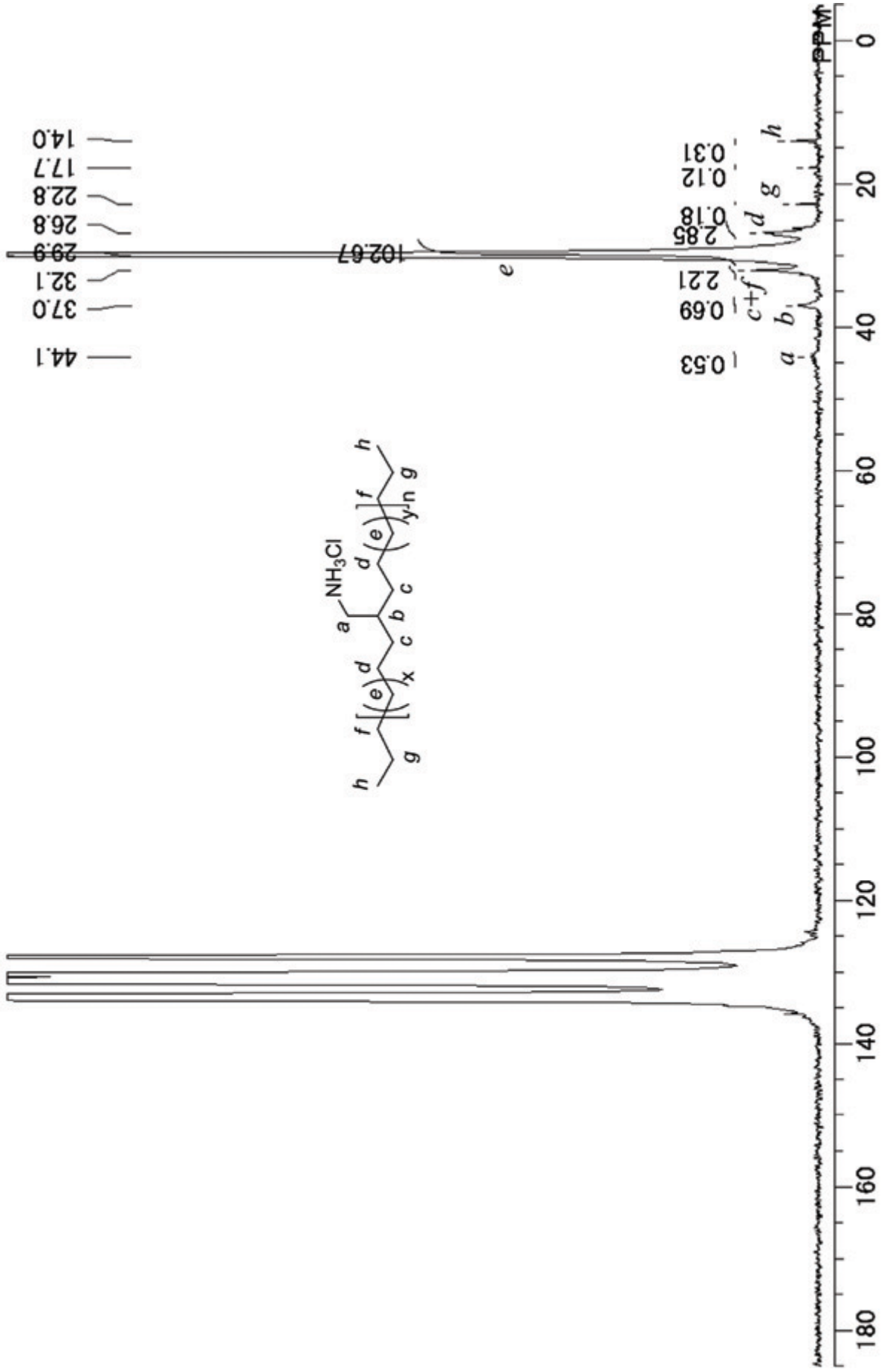


Figure S58. Quantitative ^{13}C NMR spectrum of ethylene/**2c** copolymer obtained in equation 2 (101 MHz, 1,2,4-$Cl_3C_6H_3$, 120 ˚C).

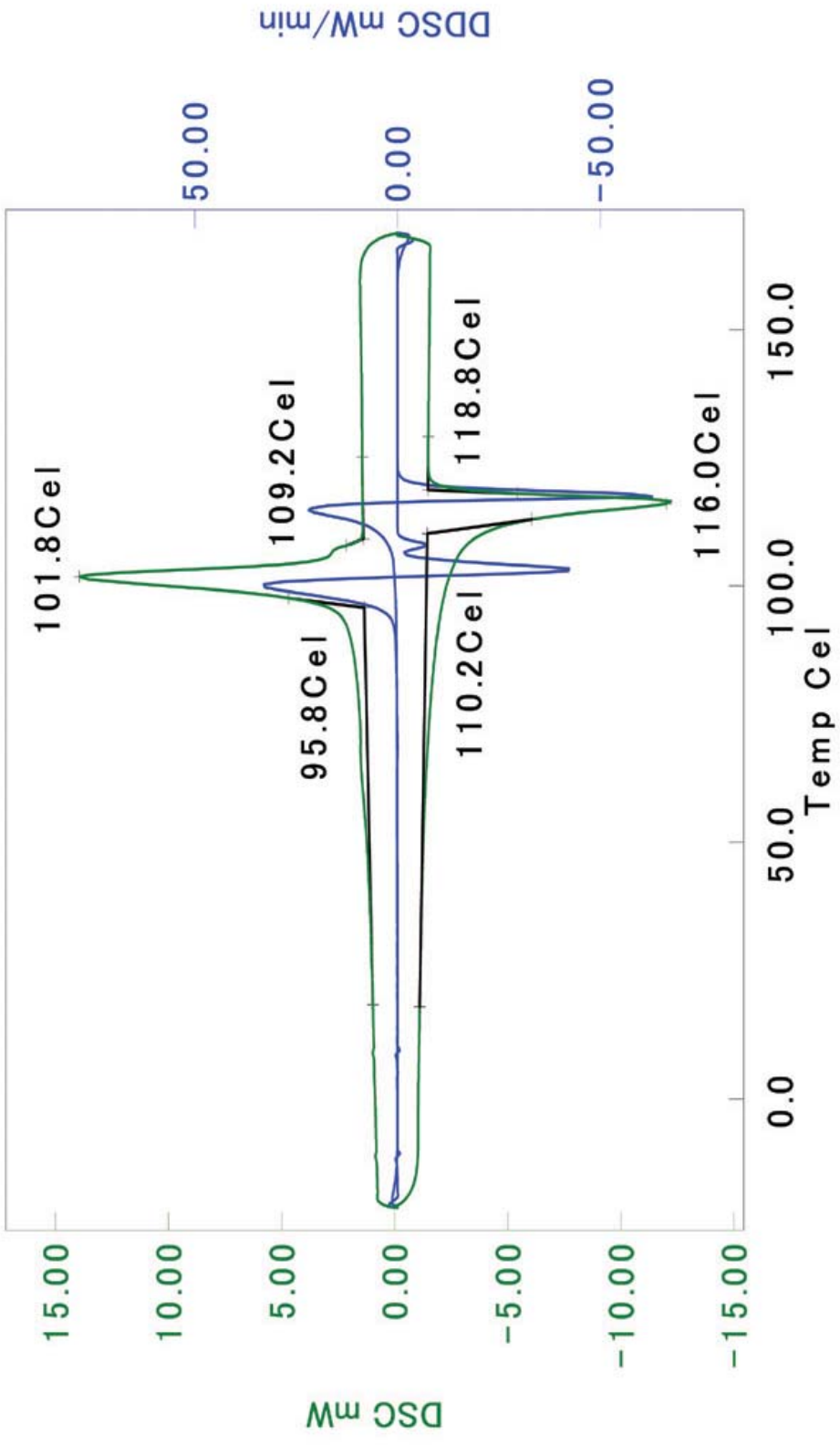


Figure S59. DSC chart of ethylene/**2c** copolymer obtained in equation 2.

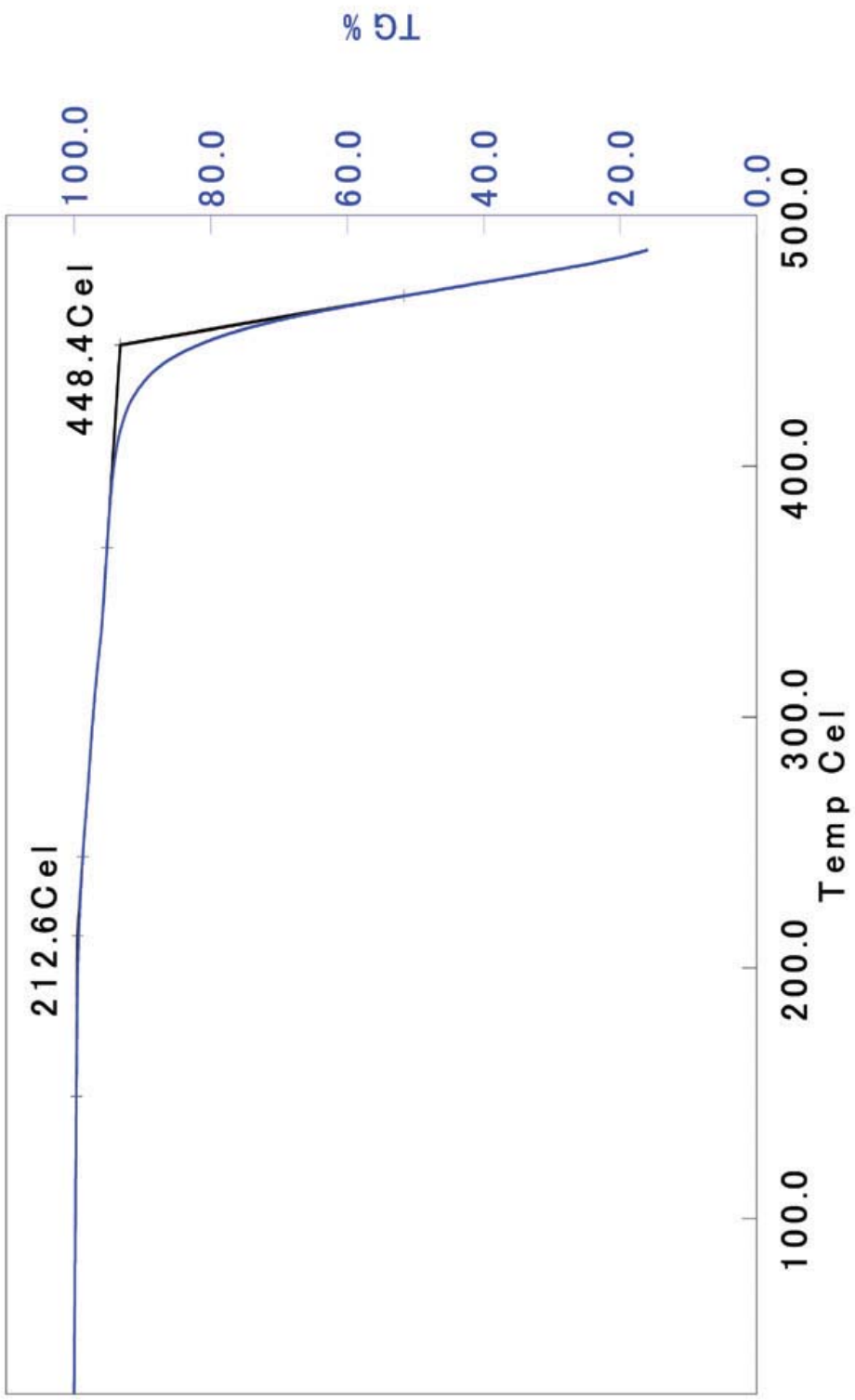


Figure S60. TG chart of ethylene/**2c** copolymer obtained in equation 2.

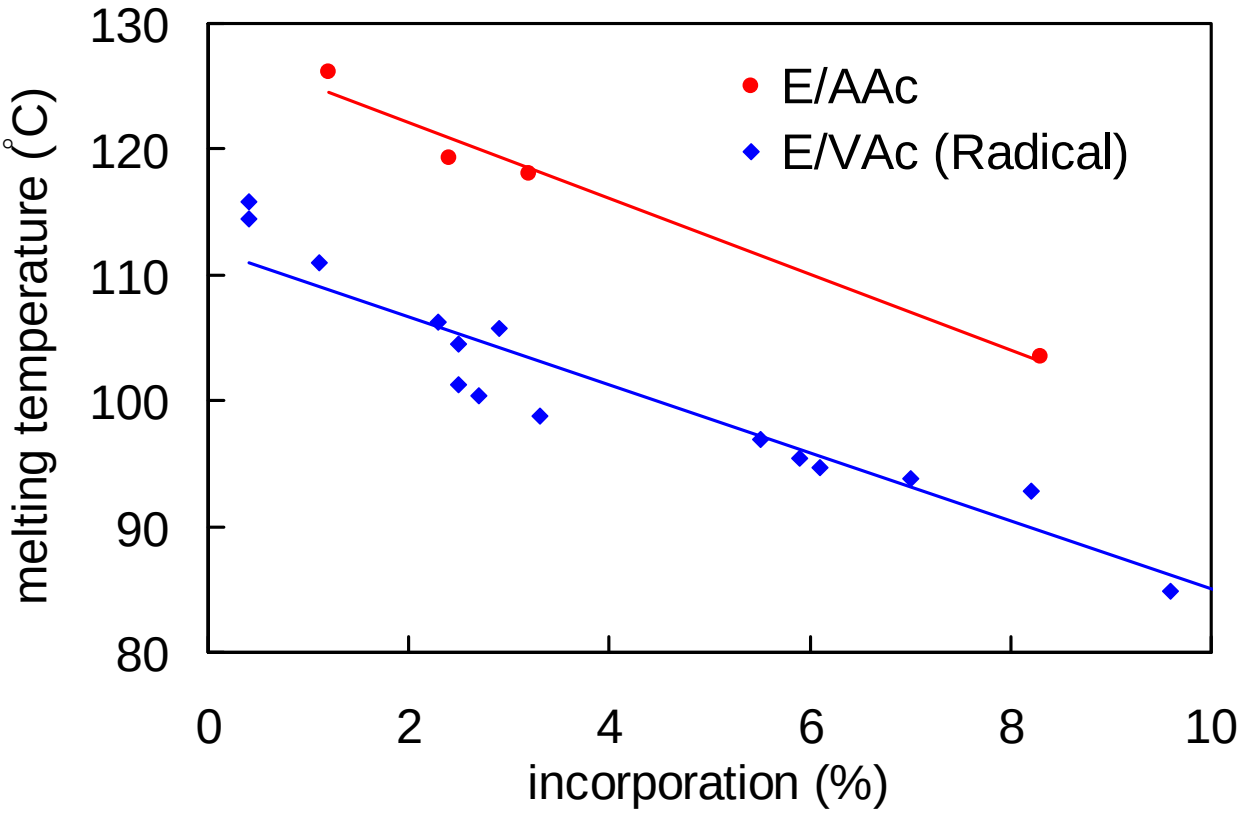


Figure S61. Comparison of extrapolated end melting temperatures (T_{mef}) measured by DSC analyses between the present ethylene/**2** copolymers and ethylene/vinyl acetate copolymers produced by radical methods.