Supplementary Information for:

Iron-Catalysed Homo- and Copolymerisation of Propylene: Steric Influence of Bis(imino)pyridine Ligands

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1. Experimental Section

1-1 General

Manipulations: All manipulations were carried out in a grove box or using standard Schlenk techniques under argon purified by passing through a hot column packed with BASF catalyst R3-11. Homo- and copolymerisation was performed in a 50-mL stainless autoclave.

Instrumentation. NMR spectra were recorded on JEOL JNM-ECP500 (^{1}H: 500 MHz, ^{13}C: 126 MHz), or JEOL JNM-ECS400 (^{1}H: 400 MHz, ^{13}C: 101 MHz), or Bruker Ascend 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz) NMR spectrometers. ^{1}H NMR analyses were performed in chloroform-*d* or 1,1,2,2-tetrachloroethane-d_2 with the number of FID's collected per sample of 64–256. Chemical shift values for protons are referenced to the residual proton resonance of chloroform-*d* (δ 7.26) or 1,1,2,2-tetrachloroethane-d_2 (δ 6.00). ^{13}C NMR analyses of polymers were performed in chloroform-*d* or 1,1,2,2-tetrachloroethane-d_2 with the number of FID's collected per sample of 1100–10000. Chemical shift values for carbons are referenced to the carbon resonance of chloroform-*d* (δ 77.2) or 1,1,2,2-tetrachloroethane-d_2 (δ 74.2). Infrared (IR) spectra were recorded on a Shimadzu FTIR 8400 spectrometer equipped with an attenuated total reflection (ATR) system. Melting point (m.p.) and decomposition point (d.p.) were recorded on an OptiMelt MPA-100 apparatus. Elemental analysis was performed by the Microanalytical Laboratory, Department of Chemistry, Graduated School of Science, The University of Tokyo. Size exclusion chromatography (SEC) analyses were carried out with a Tosoh instrument (HLC-8121GPC/HT) equipped with two SEC columns (Tosoh TSKgel GMH_{HR}-H(S)HT) and a refractive index (RI) detector by eluting the columns with 1,2-dichlorobenzene at 1.0 mL/min at 145 °C. Molecular weights were determined using narrow polystyrene standards.

Materials. Anhydrous dichloromethane, diethyl ether, hexane, tetrahydrofuran (THF), and toluene were purchased from Kanto Chemical Co., Inc. (Kanto) and purified by the method of Pangborn *et al*.[1] Propylene (>99.95%) was purchased from Takachiho Chemical Industrial Co., Ltd. and used as received. Allyl acetate and allyl methyl ether were purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and purified by distillation over CaH_2. The following reagents were purchased and used as received: acetone (Kanto), 2-propanol (Kanto), anhydrous pentane (Kanto), *p*-toluenesulfonic acid monohydrate (TCI), allyltrimethylsilane (TCI), allyltriethoxysilane (TCI), allylbenzene (TCI), 2,6-dimethylaniline (TCI), 2,6-diisopropylaniline (TCI), 2,6-diacetylpyridine (TCI), iron(II) chloride (Sigma-Aldrich), tri(isobutyl)aluminum (1.0 M solution in hexane, Sigma-Aldrich) and trityl tetrakis(pentafluorophenyl)borate) (Strem). The following compounds were prepared using literature

(1) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics*, 1996, **15**, 1518–1520.

procedures: allyl *t*-butyldimethylsilyl ether,[2,3] allyl triisopropylsilyl ether,[2] allyldimethyl(phenyl)silane,[4] 2,6-di(pentan-3-yl)aniline,[5] 2,6-di(heptan-4-yl)aniline,[5] 1-amino-2,7-diisopropylnaphthalene,[6] 1,1'-(pyridine-2,6-diyl)bis[*N*-(2,6-dimethylphenyl)ethan-1-imine] (**1a**),[7] dichlorido{1,1'-(pyridine-2,6-diyl)bis[*N*-(2,6-dimethylphenyl)ethan-1-1imine]}iron (**2a**),[7] 1,1'-(pyridine-2,6-diyl)bis[*N*-(2,6-diisopropylphenyl)ethan-1-imine] (**1b**),[7] dichlorido{1,1'-(pyridine-2,6-diyl)bis[*N*-(2,6-diisopropylphenyl)ethan-1-imine]}iron (**2b**),[7] *N*-(2,6-diisopropylphenyl)-1-(6-{1-[(2,6-dimethylphenyl)imino]ethyl}pyridine-2-yl)ethane-2-imine (**1f**),[7] dichlorido{*N*-(2,6-diisopropylphenyl)-1-(6-{1-[(2,6-dimethylphenyl)imino]ethyl}pyridine-2-yl)ethane-2-imine}iron (**2f**)[7]

(2) M. Iwasaki, S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.*, 2007, **129**, 4463–4469.
(3) M. E. Scheller, B. Frei, *Helv. Chim. Acta*, 1986, **69**, 44–52.
(4) E. Godineau, K. Schenk, Y. Landais, *J. Org. Chem.*, 2008, **73**, 6983–6993.
(5) S. Meiries, G. Le Duc, A. Chartoire, A. Collado, K. Speck, K. S. A. Arachchige, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J.*, 2013, **19**, 17358–17368.
(6) L. Vieille-Petit, H. Clavier, A. Linden, S. Blumentritt, S. P. Nolan, R. Dorta, *Organometallics*, 2010, **29**, 775–788.
(7) B. L. Small, M. Brookhart, *Macromolecules*, 1999, **32**, 2120–2130.

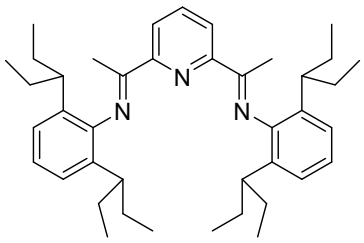
1-2. Preparation of Ligands and Catalysts

General Procedure of Preparation of Ligands 1

All ligands were prepared from the corresponding aniline and 2,6-diacetylpyridine in a similar procedure as reported.[5] The obtained ligands could be further purified by recrystallisation from acetone/2-propanol.

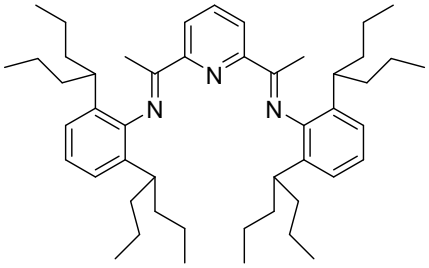
Compound data for 1

1,1'-(pyridine-2,6-diyl)bis{*N*-[2,6-di(pentan-3-yl)phenyl]ethan-1-imine} (1c)



89% yield from 2,6-diacetylpyridine (0.16 g, 1.0 mmol) and 2,6-di(pentan-3-yl)aniline (0.56 g, 2.4 mmol); m.p. 165.7–166.7 °C; IR (neat) cm^{-1} 3057, 3020, 2959, 2925, 2869, 1643, 1570, 1454, 1364, 824, 771; ^1H NMR (500 MHz, $CDCl_3$) δ 0.75 (12H, t, *J* = 7.3 Hz), 0.80 (12H, t, *J* = 7.3 Hz), 1.34–1.43 (4H, m), 1.52–1.68 (12H, m), 2.21 (6H, s), 2.32 (4H, tt, *J* = 8.1, 5.8 Hz), 7.04 (6H, m), 7.89 (1H, t, *J* = 7.8 Hz), 8.41 (2H, d, *J* = 7.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.8(4C, 1°), 12.8(4C, 1°), 17.7(2C, 1°), 27.2(4C, 2°), 29.8(4C, 2°), 42.6(4C, 3°), 121.9(2C, 3°), 123.0(2C, 3°), 123.7(4C, 3°), 132.8(4C, 4°), 136.7(1C, 3°), 149.6(2C, 4°), 155.2(2C, 4°), 165.8(2C, 4°); Anal. calcd for $C_{41}H_{59}N_3$ C, 82.91; H, 10.01; N, 7.07. found C, 82.72; H, 10.10; N, 6.68.

1,1'-(pyridine-2,6-diyl)bis{*N*-[2,6-di(heptan-4-yl)phenyl]ethane-1-imine} (1d)

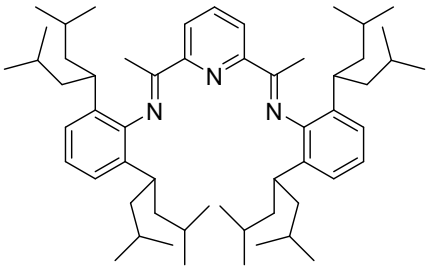


64% yield from 2,6-diacetylpyridine (0.46 g, 2.8 mmol) and 2,6-di(heptan-4-yl)aniline (1.7 g, 6.0 mmol); m.p. 116.3–116.9 °C; IR (neat) cm^{-1} 3057, 2953, 2928, 2870, 1643, 1568, 1450, 1366, 1231, 1119, 771, 739; ^1H NMR (500 MHz, $CDCl_3$) δ 0.78 (12H, t, *J* = 7.3 Hz), 0.80 (12H, t, *J* = 7.3 Hz), 1.10–1.25 (16H, m), 1.33–1.60 (12H, m), 2.19 (6H, s), 2.48 (4H, tt, *J* = 7.8, 6.4 Hz), 7.04 (6H, m), 7.89 (1H, t, *J* = 7.8 Hz), 8.37 (2H, d, *J* = 7.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1(4C, 1°), 14.2(4C, 1°), 17.5(2C, 1°), 20.0(4C, 2°), 20.9(4C, 2°), 37.4(4C, 2°), 38.4(4C, 3°), 39.3(4C, 2°), 121.5(2C, 3°), 122.8(2C, 3°), 123.3(4C, 3°), 133.4(4C, 4°), 136.4(1C, 3°), 148.7(2C, 4°), 154.9(2C, 4°), 165.8(2C, 4°); Anal. calcd for $C_{49}H_{75}N_3$ C, 83.34; H, 10.71; N, 5.95. found C, 83.19; H, 10.72; N, 5.92.

2,6-Di(2,6-dimethylheptan-4-yl)aniline

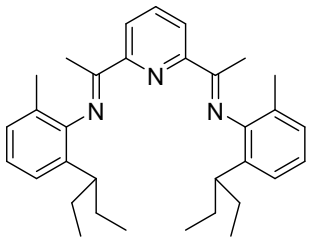
The title compound was prepared using literature procedure.[5] ^1H NMR yield: 64%. The crude material used for the next step without further purification.

1,1'-(Pyridine-2,6-diyl)bis{*N*-[2,6-bis(2,6-dimethylheptan-4-yl)phenyl]ethane-1-imine} (1e)



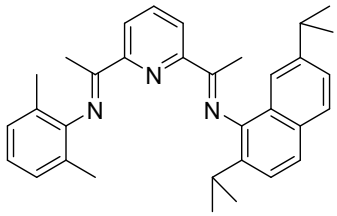
24% yield from 2,6-diacetylpyridine (0.98 g, 6.0 mmol) and 2,6-di(2,6-dimethylheptan-4-yl)aniline (crude: 19 mmol); m.p. 136.2–138.4 °C; IR (neat) cm^{-1} 3059, 2926, 2953, 2908, 2866, 2847, 1634, 1570, 1466, 1450, 1364, 1232, 1119, 775, 756; ^1H NMR (500 MHz, $CDCl_3$) δ 0.69 (12H, d, *J* = 6.4 Hz), 0.73 (12H, d, *J* = 6.1 Hz), 0.79 (12H, d, *J* = 6.4 Hz), 0.83 (12H, d, *J* = 6.1 Hz), 1.24–1.60 (24H, m), 2.21 (6H, s), 2.69 (4H, m), 7.06 (6H, s), 7.88 (1H, t, *J* = 7.7 Hz), 8.39 (2H, d, *J* = 7.7 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.0(2C, 1°), 22.2(4C, 1°), 22.3(4C, 1°), 23.7(4C, 1°), 23.9(4C, 1°), 25.6(4C, 3°), 25.6(4C, 3°), 34.2(4C, 2°), 45.8(4C, 2°), 46.2(4C, 3°), 121.7(2C, 3°), 123.4(2C, 3°), 123.9(4C, 3°), 134.5(4C, 4°), 136.7(1C, 3°), 148.4(2C, 4°), 155.1(2C, 4°), 166.7(2C, 4°); Anal. calcd for $C_{57}H_{91}N_3$ C, 83.66; H, 11.21; N, 5.13. found C, 83. 51; H, 11.18; N, 5.10.

1,1'-(Pyridine-2,6-diyl)bis{*N*-[2-methyl-6-(pentan-3-yl)phenyl]ethane-1-imine} (1g)



12% yield after recrystallisation from 2,6-diacetylpyridine (0.66 g, 4.0 mmol) and 2-methyl-6-(pentan-3-yl)aniline (1.7 g, 9.6 mmol); m.p. 135.1–136.1 °C; IR (neat) cm^{-1} 3063, 3020, 2957, 2924, 2870, 1634, 1566, 1454, 1362, 1236, 1192, 1121, 1105, 822, 766, 754, 739; ^1H NMR (500 MHz, $CDCl_3$) δ 0.75 (6H, t, *J* = 7.3 Hz), 0.82 (6H, td, *J* = 7.3, 0.6 Hz), 1.44–1.65 (8H, m), 2.02 (6H, s), 2.23 (6H, s), 2.39–2.46 (2H, m), 6.98–7.06 (6H, m), 7.90 (1H, t, *J* = 7.8 Hz), 8.42 (1H, d, *J* = 6.8 Hz), 8.44 (1H, d, *J* = 7.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 12.0(2C, 1°), 12.4(2C, 1°), 17.1(2C, 1°), 18.3(2C, 1°), 27.2(2C, 2°), 28.9(2C, 2°), 42.7(2C, 3°), 122.0(2C, 3°), 123.0(2C, 3°), 124.3(2C, 3°), 124.9(2C, 4°), 127.6(2C, 3°), 133.5(2C, 4°), 136.8(1C, 3°), 148.9(2C, 4°), 155.2(2C, 4°), 166.7(2C, 4°); Anal. calcd for $C_{33}H_{43}N_3$ C, 82.28; H, 9.00; N, 8.72. found C, 82.12; H, 9.15; N, 8.65.

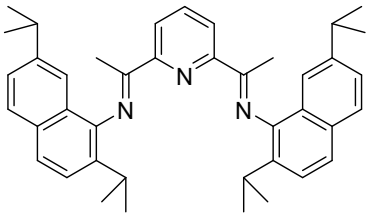
***N*-(2,7-Diisopropylnaphthalen-1-yl)-1-(6-{1-[(2,6-dimethylphenyl)imino]ethyl}pyridin-2-yl)ethan-1-imine (1h)**



To a solution of 2,6-diacetylpyridine (0.16 g, 1.0 mmol), 2,6-dimethylaniline (0.12 g, 1.0 mmol) and 1-amino-2,7-diisopropyl-naphthalene hydrochloride (0.26 g, 1.0 mmol) in toluene (20 mL) was added *p*-toluenesulfonic acid monohydrate (3.0 mg, 0.016 mmol), and the solution was refluxed for 35 hours. After the solvent was removed by evaporation, the residue was purified by HPLC and rescrystallisation from acetone/2-propanol to obtain **1h** in 25% yield (0.12 g); m.p. 177.1–178.2 °C; IR (neat) cm^{-1} 3053, 3013, 2957, 2922, 2866, 1636, 1560, 1458, 1362, 1317, 1302, 1248, 1202, 1122, 1068, 841, 824, 771, 762, 743; ^1H NMR (500 MHz, $CDCl_3$) δ

1.23 (3H, d, *J* = 7.0 Hz), 1.24 (3H, d, *J* = 7.0 Hz), 1.25 (3H, d, *J* = 7.0 Hz), 1.26 (3H, d, *J* = 7.0 Hz), 2.07 (3H, s), 2.08 (3H, s), 2.24 (3H, s), 2.26 (3H, s), 2.98 (1H, sept, *J* = 7.0 Hz), 3.06 (1H, sept, *J* = 7.0 Hz), 6.96 (1H, t, *J* = 7.4 Hz), 7.09 (2H, d, *J* = 7.4 Hz), 7.32 (1H, s), 7.35 (1H, dd, *J* = 8.5 Hz, 1.8 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 7.60 (1H, d, *J* = 8.5 Hz), 7.78 (1H, d, *J* = 8.5 Hz), 7.99 (1H, t, *J* = 7.8 Hz), 8.54 (1H, dd, *J* = 7.8 Hz, 1.1 Hz), 8.63 (1H, dd, *J* = 7.8 Hz, 1.1 Hz) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 16.6(1C, 1°), 17.4(1C, 1°), 18.1(1C, 1°), 18.1(1C, 1°), 23.1(1C, 1°), 23.1(1C, 1°), 24.2(2C, 1°), 28.5(1C, 3°), 34.7(1C, 3°), 119.8(1C, 3°), 122.6(1C, 3°), 122.6(1C, 3°), 123.2(1C, 3°), 123.4(1C, 3°), 123.4(1C, 3°), 124.5(1C, 4°), 124.8(1C, 3°), 125.6(2C, 4°), 128.1(2C, 3°), 128.1(1C, 3°), 131.2(1C, 4°), 131.4(1C, 4°), 137.2(1C, 3°), 143.4(1C, 4°), 146.3(1C, 4°), 148.9(1C, 4°), 155.3(1C, 4°), 155.4(1C, 4°), 167.4(1C, 4°), 168.9(1C, 4°); Anal. calcd for $C_{33}H_{37}N_3$ C, 83.33; H, 7.84; N, 8.83. found C, 83. 19; H, 7.95; N, 8.80.

1,1'-(Pyridine-2,6-diyl)bis[*N*-(2,7-diisopropylnaphthalen-1-yl)ethane-1-imine] (1i)



26% yield from 2,6-diacetylpyridine (81 mg, 0.50 mmol) and 1-amino-2,7-diisopropylnaphthalene hydrochloride (0.34 g, 1.3 mmol); m.p. 199.6–200.6 °C; IR (neat) cm^{-1} 3051, 2957, 2926, 2866, 1715, 1634, 1562, 1362, 1236, 1122, 1068, 839, 823, 741, 644, 609, 550; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24–1.29 (24H, m), 2.26 (6H, s), 2.95–3.15 (4H, m), 7.34–7.37 (4H, m), 7.45 (2H, dd, *J* = 8.5 Hz, 0.9 Hz), 7.61 (2H, d, *J* = 8.5 Hz), 7.78 (2H, d, *J* = 8.5 Hz), 8.06(1H, t, *J* = 7.8 Hz), 8.68 (1H, d, *J* = 7.8 Hz), 8.69 (1H, d, *J* = 7.8 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.4(1C, 1°), 17.4(1C, 1°), 23.1(1C, 1°), 23.1(1C, 1°), 23.2(1C, 1°), 23.2(1C, 1°), 24.2(4C, 1°), 28.6(2C, 3°), 34.7(2C, 3°), 119.9(2C, 3°), 122.8(2C, 3°), 123.4(2C, 3°), 123.5(2C, 3°), 124.5 (2C, 4°), 124.7(1C, 3°), 124.8(1C, 3°), 128.1(2C, 3°), 131.2(1C, 4°), 131.3(1C, 4°), 131.4(2C, 4°), 137.3(1C, 3°), 143.4(2C, 4°), 146.3(2C, 4°), 155.4(1C, 4°), 155.4(1C, 4°), 169.1(2C, 4°); Anal. calcd for $C_{41}H_{47}N_3$ C, 84.64; H, 8.14; N, 7.22. found C, 84.20; H, 8.21; N, 7.15.

General Procedure of Preparation of Complexes 2

A mixture of ligand (1.05 equiv) and $FeCl_2$ (1.0 equiv) in dry THF was stirred under inert atmosphere overnight, resulting in the formation of a deep blue suspension or solution. In the case that suspension was obtained, pentane was added and the formed solid was corrected by filtration and washed with ether and pentane. In the case that solution was obtained, the solvent was removed in vacuo, and the remaining solid was repeatedly washed with ether and/or pentane.

Compound data for 2

Dichlorido[1,1'-(pyridine-2,6-diyl)bis{*N*-[2,6-di(pentan-3-yl)phenyl]ethan-1-imine}]iron (2c)

d.p. ca. 160 °C; IR (neat) cm^{-1} 3069, 2959, 2930, 2872, 1578, 1462, 1439, 1369, 1274, 1209, 814, 789, 777, 721; Anal. calcd for $C_{41}H_{59}N_3FeCl_2$ C, 68.33; H, 8.25; N, 5.83. found C, 68.19; H, 8.33; N, 5.81; HRMS calcd. for $[M-Cl]^+$ 684.3747 found 684.3734.

Dichlorido[1,1'-(pyridine-2,6-diyl)bis{*N*-[2,6-di(heptan-4-yl)phenyl]ethane-1-imine}]iron(2d)

d.p. ca. 140 °C; IR (neat) cm^{-1} 3057, 2953, 2927, 2868, 1651, 1576, 1450, 1367, 1269, 1232, 1200, 1119, 1097, 1074, 811, 790, 779, 770, 739, 719, 540, 419; Anal. calcd for $C_{49}H_{75}N_3FeCl_2$ C, 70.66; H, 9.08; N, 5.05. found C, 70.17; H, 9.39; N, 4.98 (Although the values are not within the acceptable ranges, they are provided to illustrate the best values obtained to date. The difficulty is due to instability of **2d** during purification); HRMS calcd. for $[M-Cl]^+$ 796.4999 found 796.4982.

Dichlorido[1,1'-(pyridine-2,6-diyl)bis{*N*-[2-methyl-6-(pentan-3-yl)phenyl]ethane-1-imine}]iron (2g)

d.p. ca. 235 °C; IR (neat) cm^{-1} 3097, 3063, 3020, 2961, 2930, 2872, 1624, 1589, 1465, 1433, 1375, 1261, 1205, 1107, 1024, 810, 787, 775; Anal. calcd for $C_{49}H_{75}N_3FeCl_2$ C, 65.14; H, 7.12; N, 6.91. found C, 64.73; H, 7.22; N, 6.82; HRMS calcd. for $[M-Cl]^+$ 572.2495 found 572.2469.

Dichlorido[*N*-(2,7-diisopropylnaphthalen-1-yl)-1-(6-{1-[(2,6-dimethylphenyl)imino]ethyl}pyridin-2-yl)ethan-1-imine]iron (2h)

d.p. ca. 200 °C; IR (neat) cm^{-1} 2961, 2923, 2916, 2868, 1622, 1587, 1468, 1367, 1263, 1213, 1065, 839, 814, 773, 766, 733, 613, 419; HRMS calcd. for $[M-Cl]^+$ 566.2025 found 566.2019.

Dichlorido{1,1'-(pyridine-2,6-diyl)bis[*N*-(2,7-diisopropylnaphthalen-1-yl)ethane-1-imine]}iron (2i)

d.p. ca. 195 °C; IR (neat) cm^{-1} 3051, 2959, 2930, 2868, 1624, 1582, 1510, 1464, 1385, 1369, 1301, 1273, 1209, 1151, 1120, 1103, 1082, 1067, 1047, 837, 810, 754, 731, 611, 557, 419; HRMS calcd. for $[M-Cl]^+$ 672.2808 found 672.2831.

1-3. General Procedure for Polymerisations

General Procedure of Homopolymerisation of Propylene (Table 2)

A mixture of iron precatalyst **2** (1.0 equiv) and MMAO (800 equiv in hexane) in toluene (15−(the amount of *n*-hexane) mL) in a 50-mL autoclave was stirred under propylene pressure (0.20 MPa) at −20 °C for 1 h. The polymerisation was quenched with MeOH and a 1.0-M solution of HCl in H_2O and the mixture was stirred overnight. The polymer was isolated by filtration, washed with acetone, and dried under vacuum at 100 °C. The obtained polypropylene was analyzed without further purification. Molecular weights were determined by SEC analysis.

General Procedure of Copolymerisation of Propylene and Allyl Monomers (Table 3)

To a mixture of iron precatalyst **2** (1.0 equiv) and MMAO (800 equiv in hexane) in toluene ((15−(the volume of *n*-hexane)−(the volume of comonomer) mL) in a 50-mL autoclave was added allylic comonomer (0.20 or 0.40 mL) and then propylene (5.7–11 g) and the mixture was stirred at 30 °C for 16 h. The polymerisation was quenched with MeOH and a 1.0-M solution of HCl in H_2O and the mixture was stirred overnight. The polymer was isolated by filtration, washed with acetone, and dried under vacuum at 100 °C. The obtained polypropylene was analyzed without further purification. Molecular weights were determined by SEC analysis. The molar incorporation ratio of polar monomer was determined by ^{1}H NMR analysis.

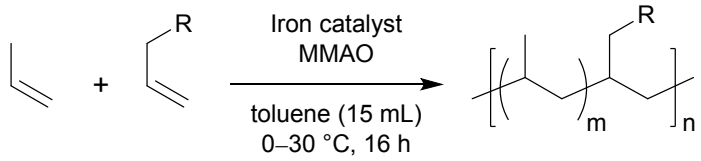
Control Experiment 1: Propylene polymerisation in the absence of iron catalyst

To a solution of MMAO (3.3 M in hexane, 2.5 mL, 8.0 mmol) in toluene (12.5 mL) in a 50-mL autoclave was added propylene (7.9 g), and the mixture was stirred at 30 °C for 4 h. The polymerisation was quenched with MeOH and a 1.0-M solution of HCl in H_2O and the mixture was stirred overnight. After filtration, no solid polymer was obtained.

Control Experiment 2: Propylene polymerisation in the presence of ethyl acetate

To a mixture of iron precatalyst **2b** (12 mg, 20 μmol) and MMAO (4.4 M in hexane, 3.6 mL, 800 equiv) in toluene (11 mL) in a 50-mL autoclave was added ethyl acetate (0.40 mL), and then propylene (3.5 g) and the mixture was stirred at 30 °C for 16 h. The polymerisation was quenched with MeOH and a 1.0-M solution of HCl in H_2O and the mixture was stirred overnight. After filtration, no solid polymer was obtained.

Table S1. Complete Data Set for the Copolymerisation of Propylene with Polar Monomers.



Entry	catalyst	R in comonomer	comonomer (mL)	propylene (g)	T (°C)	Yield (g)	activity (g·mmol^{-1}·h^{-1})	$M_n/10^3$ [c] (g/mol)	M_w/M_n [c]	incorp.[d] (%)
S1	**2a**	R = OAc	0.20	6.0	30	3.8	12	1.6	2.1	0
1	**2b**	R = OAc	0.20	9.4	30	2.7	8.5	3.3	6.9	0
S2	**2b**[e]	R = OAc	0.40	7.6	30	3.8	12	1.6	2.8	0
2	**2b**	R = OAc	0.80	9.5	30	0.0	---	---	---	---
3	**2b**	R = OMe	0.40	9.2	30	0.37	1.1	3.7	2.1	0
4	**2b**	R = OSi^{t}BuMe$_2$	0.40	6.9	30	1.9	5.9	3.4	2.0	0
5	**2b**	R = OSi^{i}Pr$_3$	0.40	9.2	30	2.7	8.4	2.4	2.0	0
S3	**2a**	R = Ph	0.40	12	30	3.3	10	1.4	1.8	0.71
6	**2b**	R = Ph	0.40	5.7	30	2.3	7.2	0.97	2.1	1.4
7	**2b**	R = SiMe$_3$	0.40	7.0	30	1.4	4.5	1.3	7.8	2.1
S4	**2a**	R = SiMe$_2$Ph	0.40	9.4	30	5.0	16	1.4	1.9	1.0
8	**2b**	R = SiMe$_2$Ph	0.40	7.3	30	0.67	2.1	2.0	1.9	1.7
9	**2b**	R = Si(OEt)$_3$	0.40	11	0	0.44[f]	1.3	3.2	2.4	0.30

[a] A mixture of catalyst **2a** or **2b**, propylene and a comonomer in toluene (15 mL) in a 50-mL autoclave was stirred for 16 hours at an indicated temperature. [b] Isolated yields after washing with MeOH/1-M HCl aq. mixture and acetone. [c] Molecular weights determined by SEC analysis using polystyrene standards. [d] Molar incorporation ratios of comonomers determined by ^{1}H NMR analysis. [e] Catalyst was activated by Al(*i*-Bu)$_3$ (5.0 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (20 μmol) instead of MMAO. [f] Isolated yield after Soxhlet extraction with toluene.

4. Data of (Co)Polymers

Polypropylene Obtained in Entry 1 of Table 2:

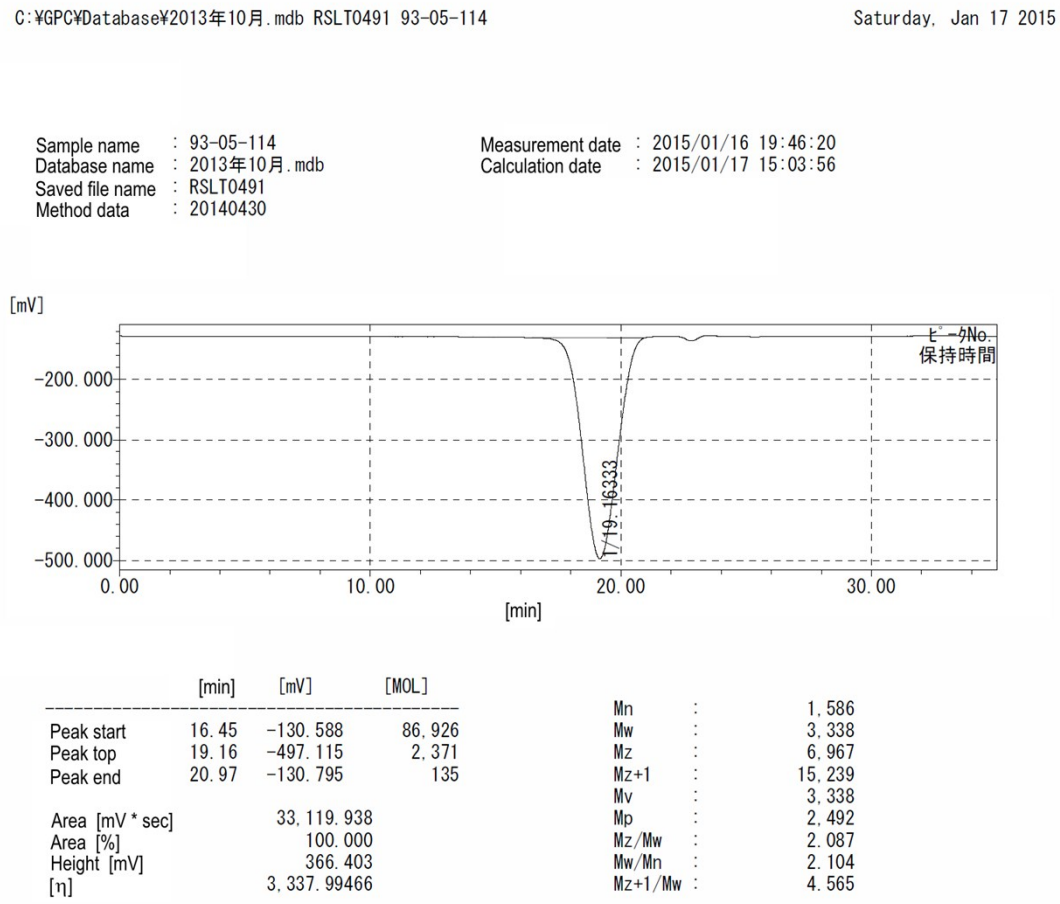


Figure S1. SEC trace of polypropylene obtained in entry 1 in Table 2.

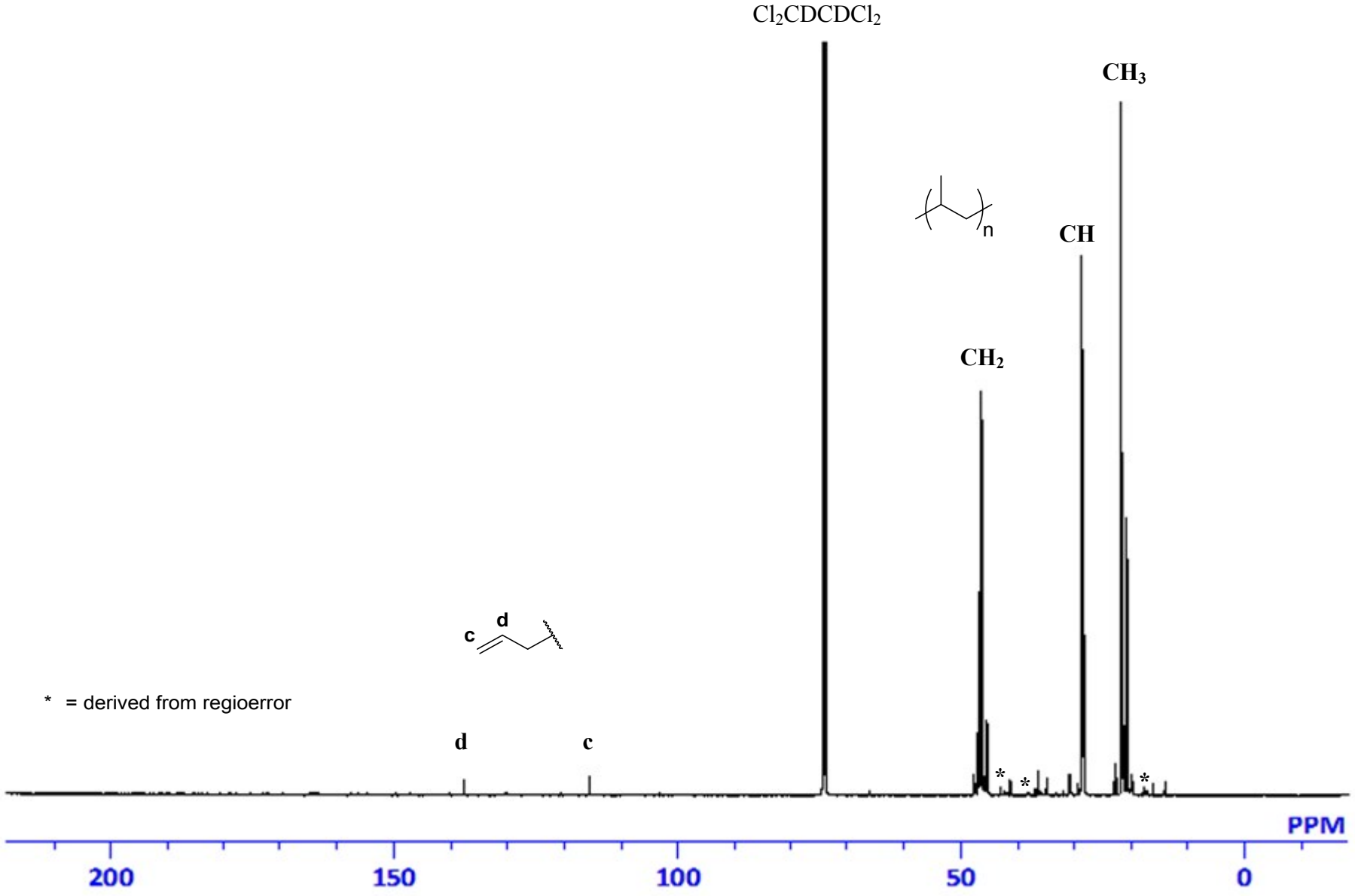
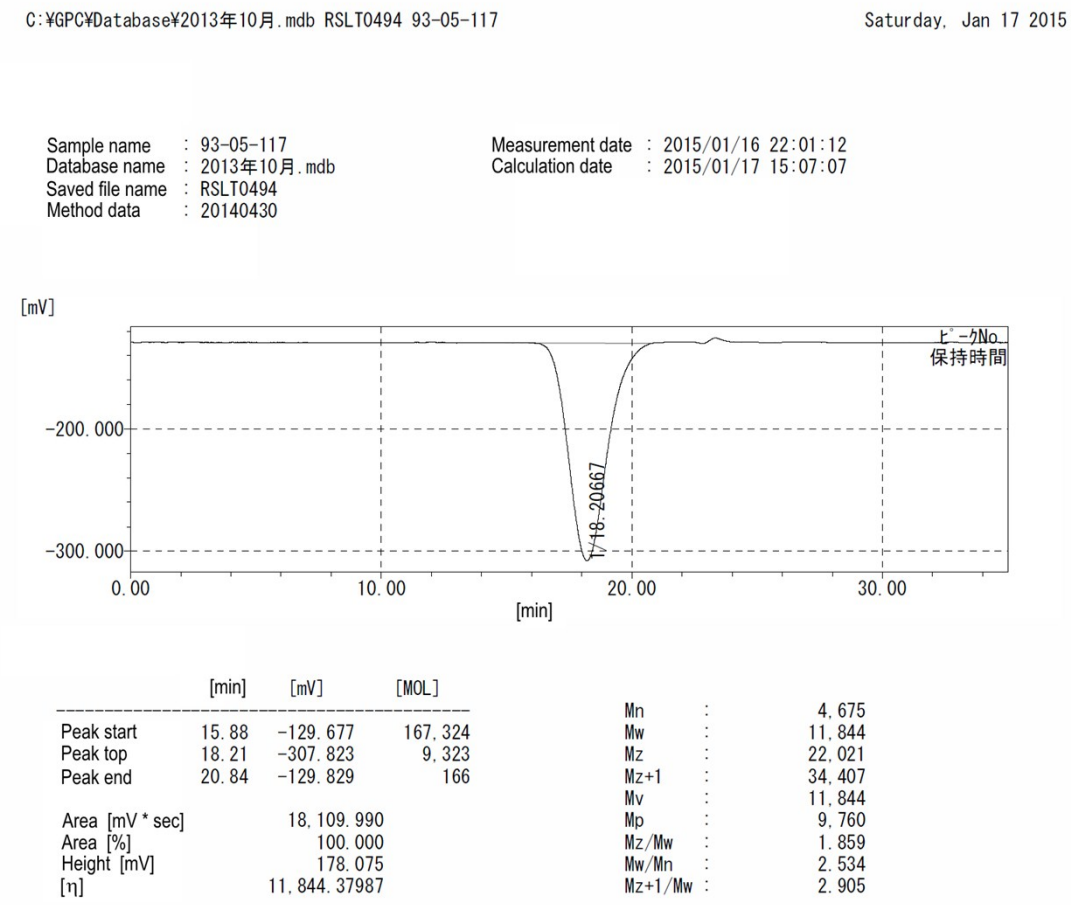


Figure S2. ^{13}C NMR spectrum of polypropylene obtained in entry 1 in Table 2 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Polypropylene Obtained in Entry 2 of Table 2:



	[min]	[mV]	[MOL]
Peak start	15.88	-129.677	167,324
Peak top	18.21	-307.823	9,323
Peak end	20.84	-129.829	166
Area [mV * sec]		18,109.990	
Area [%]		100.000	
Height [mV]		178.075	
[η]		11,844.37987	

Mn	:	4,675
Mw	:	11,844
Mz	:	22,021
Mz+1	:	34,407
Mv	:	11,844
Mp	:	9,760
Mz/Mw	:	1.859
Mw/Mn	:	2.534
Mz+1/Mw	:	2.905

Figure S3. SEC trace of polypropylene obtained in entry 2 in Table 2.

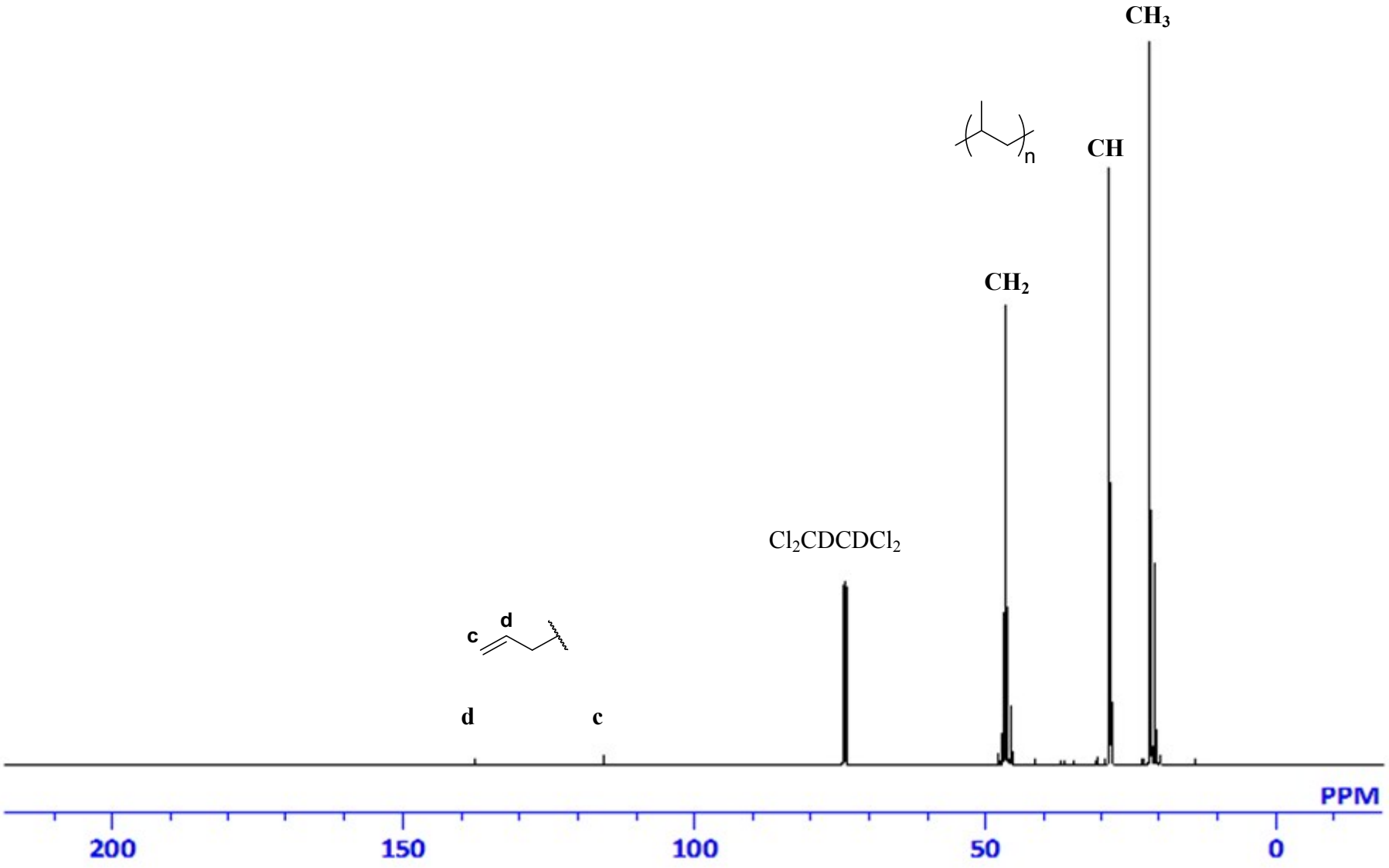


Figure S4. ^{13}C NMR spectrum of polypropylene obtained in entry 2 in Table 2 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

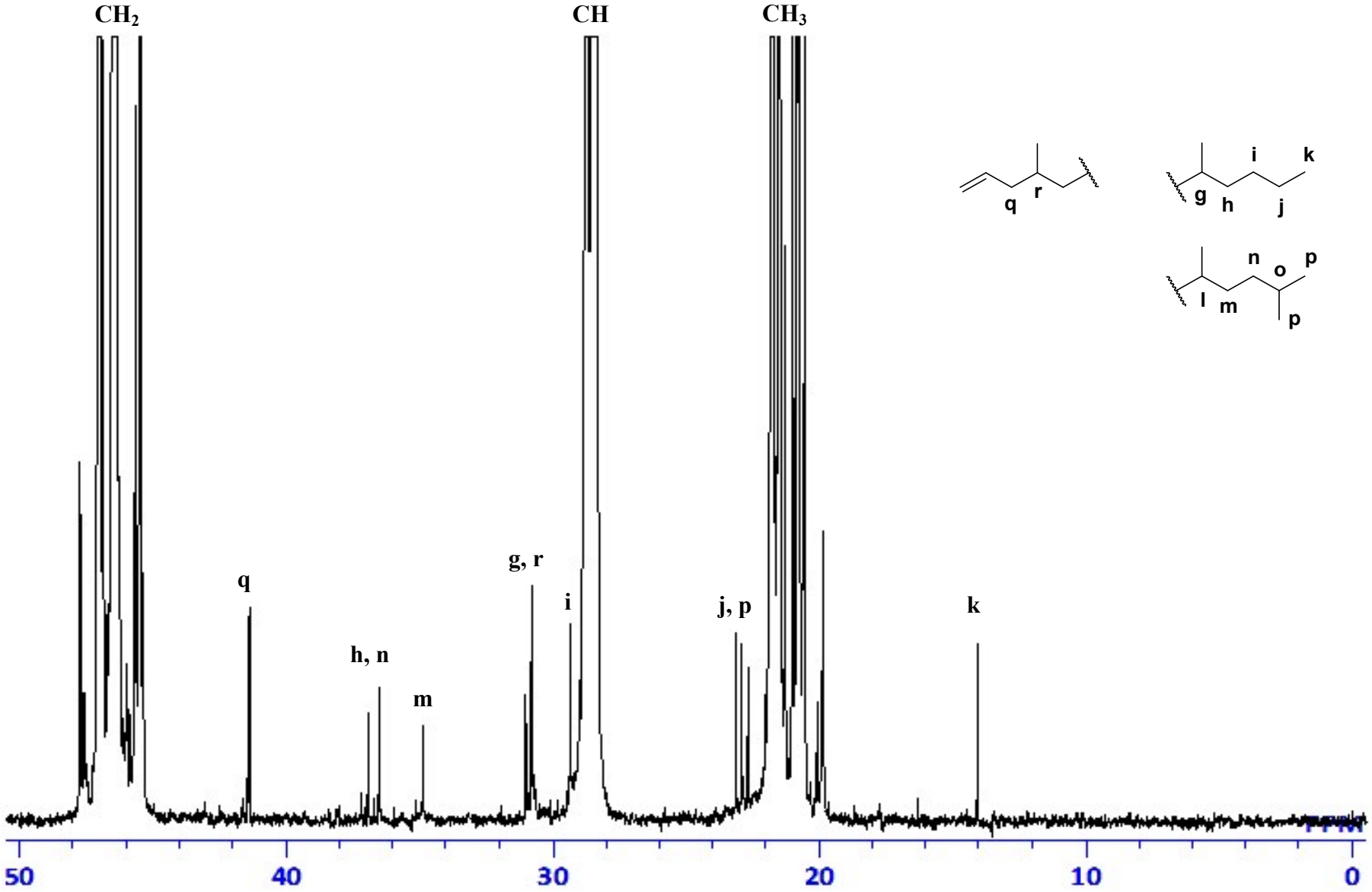


Figure S5. High-field region of ^{13}C NMR spectrum of polypropylene obtained in entry 2 in Table 2 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Polypropylene Obtained in Entry 3 of Table 2:

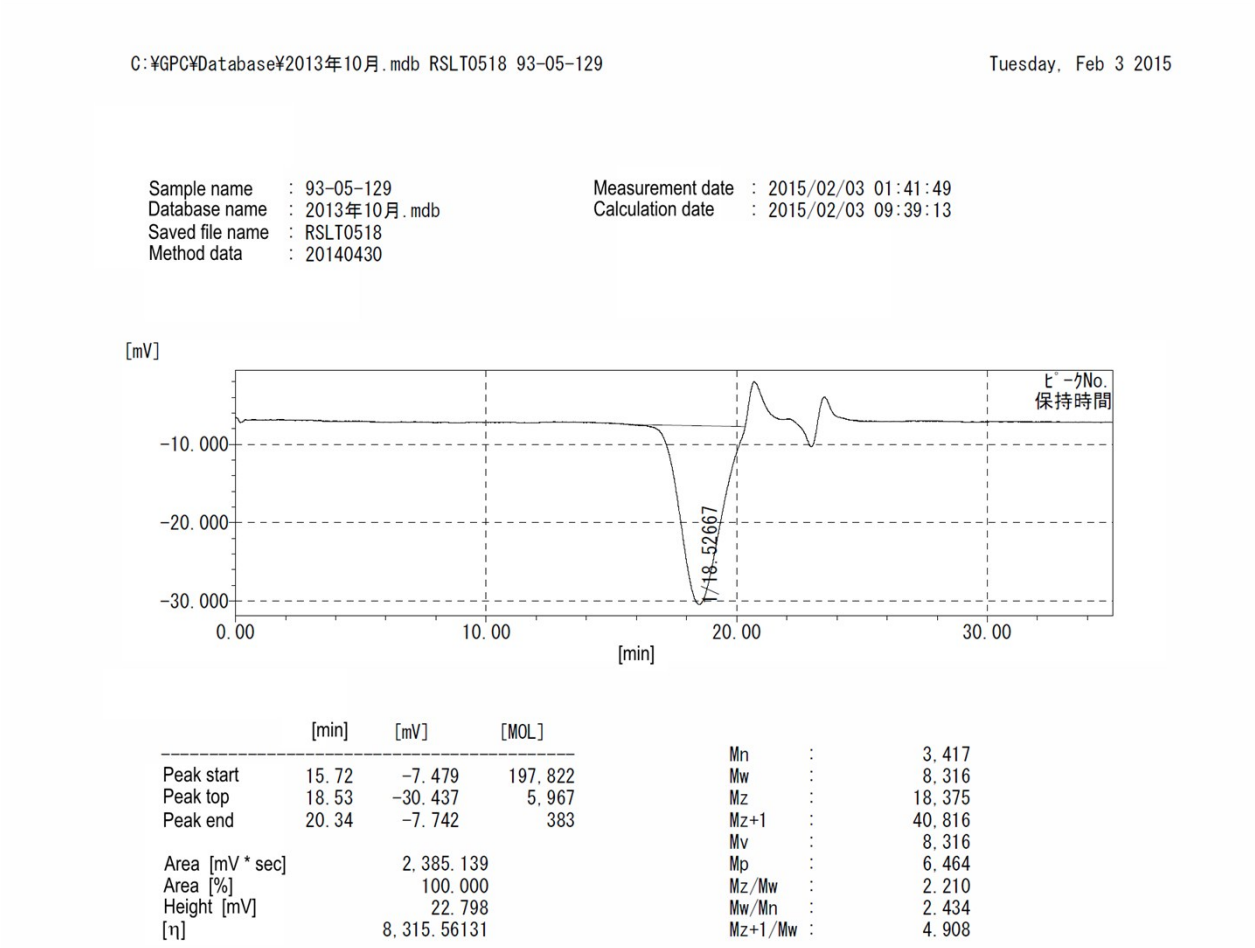


Figure S6. SEC trace of polypropylene obtained in entry 3 in Table 2.

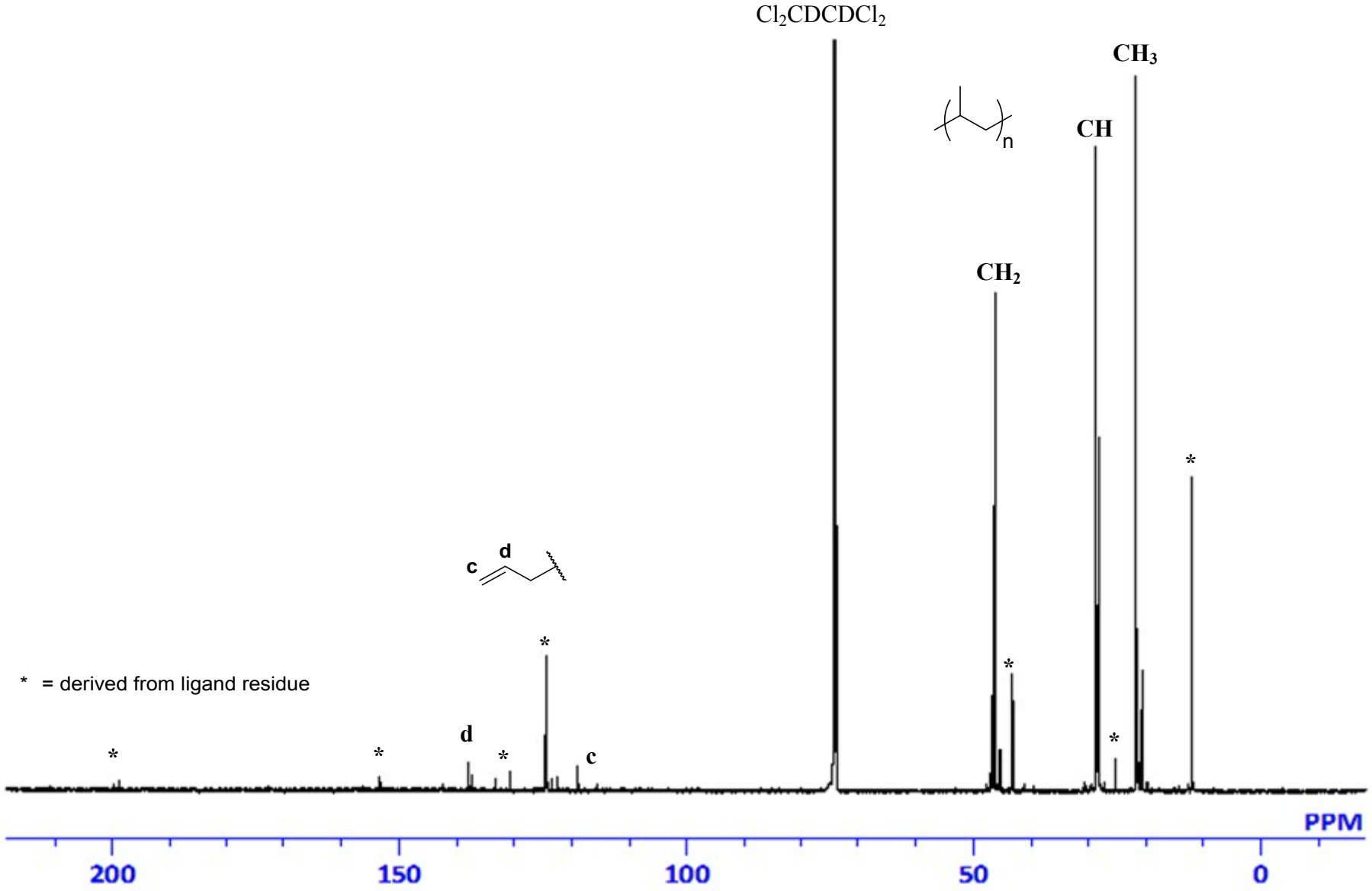


Figure S7. ^{13}C NMR spectrum of polypropylene obtained in entry 3 in Table 2 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Polypropylene Obtained in Entry 4 of Table 2:

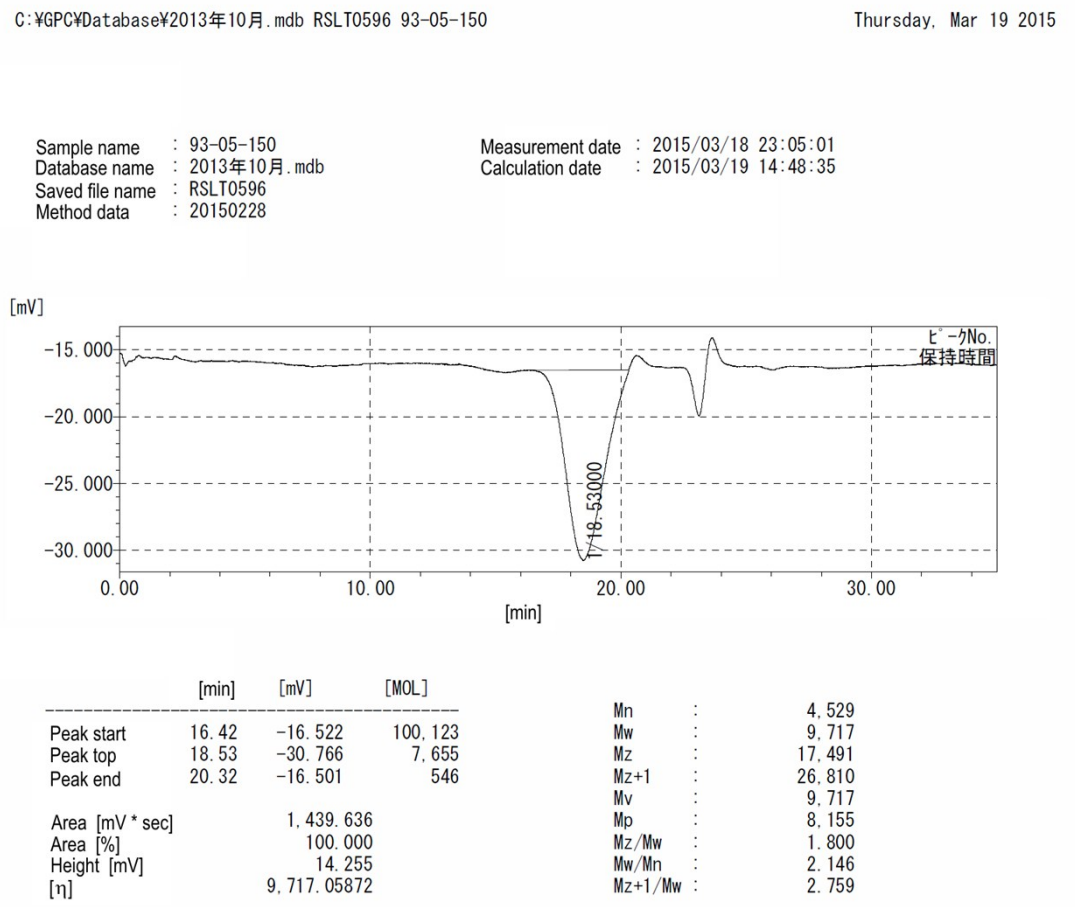


Figure S8. SEC trace of polypropylene obtained in entry 4 in Table 2.

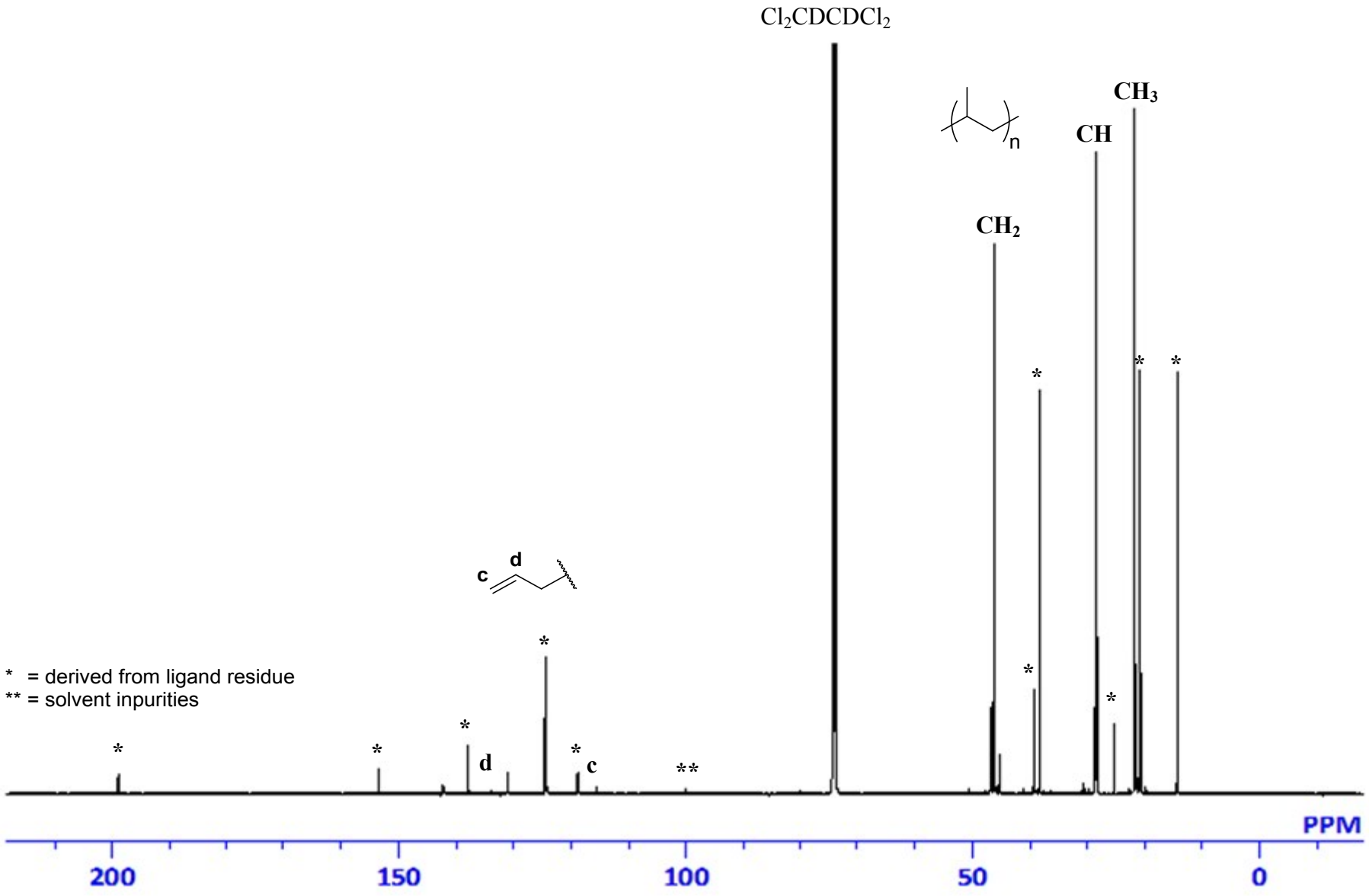


Figure S9. ^{13}C NMR spectrum of polypropylene obtained in entry 4 in Table 2 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Polypropylene Obtained in Entry 5 of Table 2:

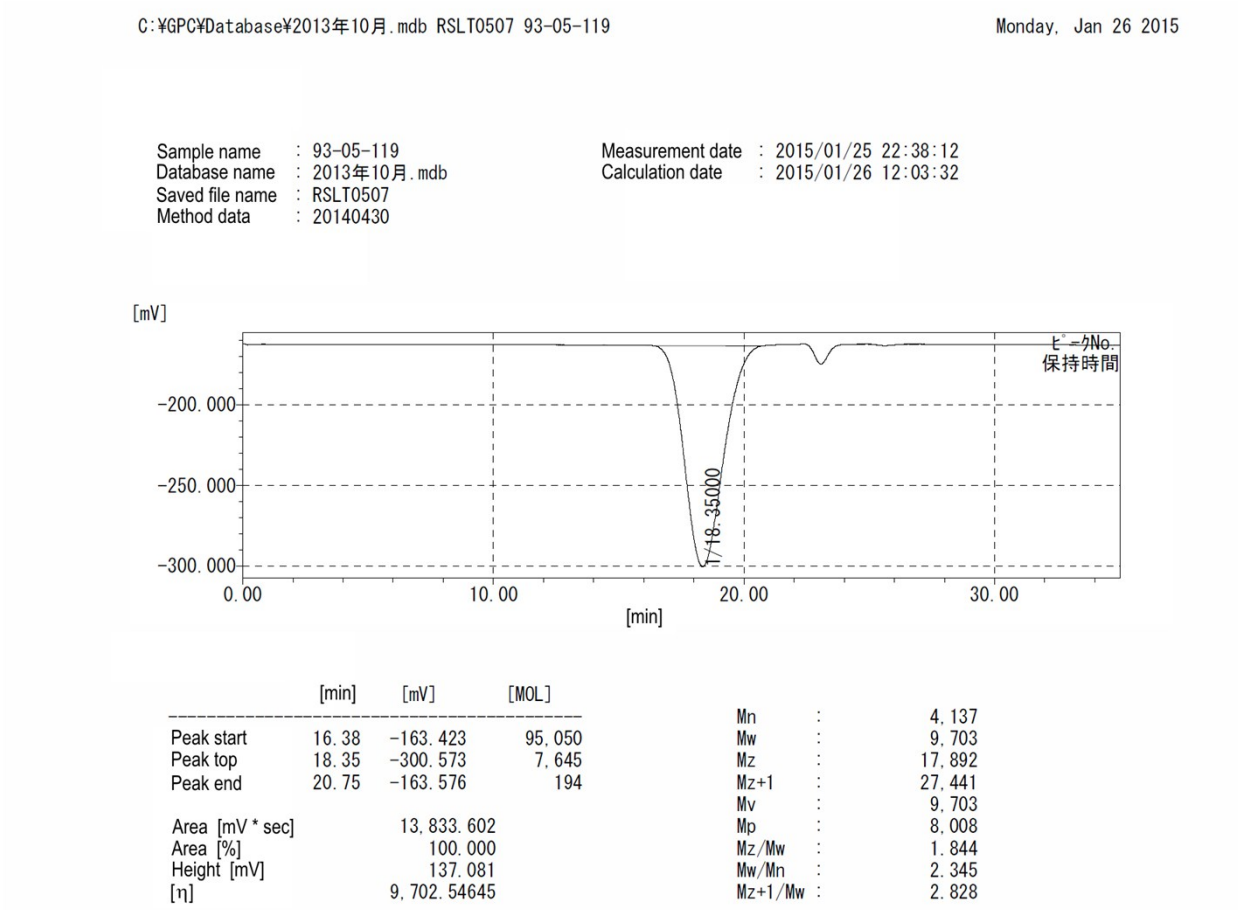


Figure S10. SEC trace of polypropylene obtained in entry 5 in Table 2.

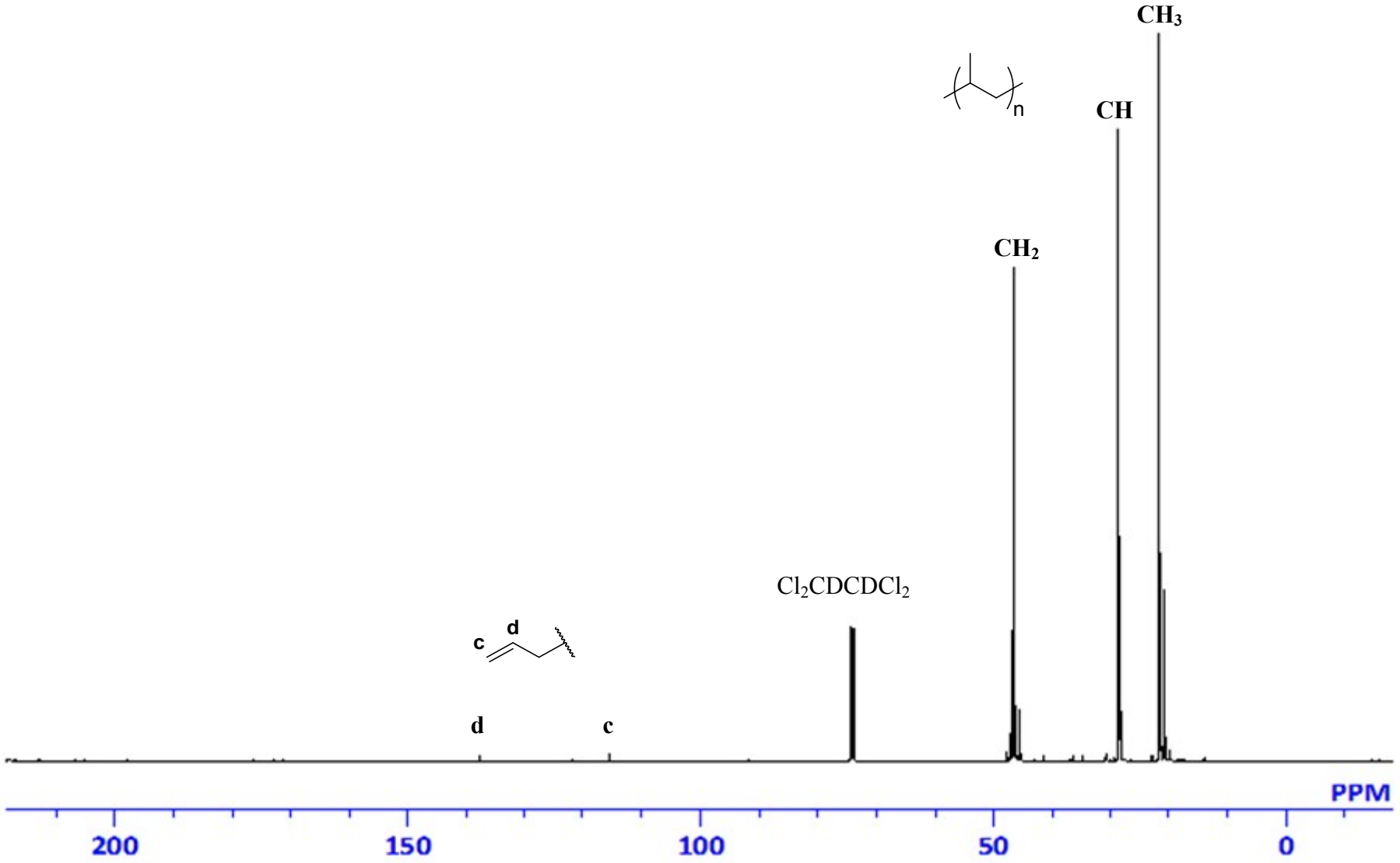


Figure S11. ^{13}C NMR spectrum of polypropylene obtained in entry 5 in Table 2 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Polypropylene Obtained in Entry 6 of Table 2:

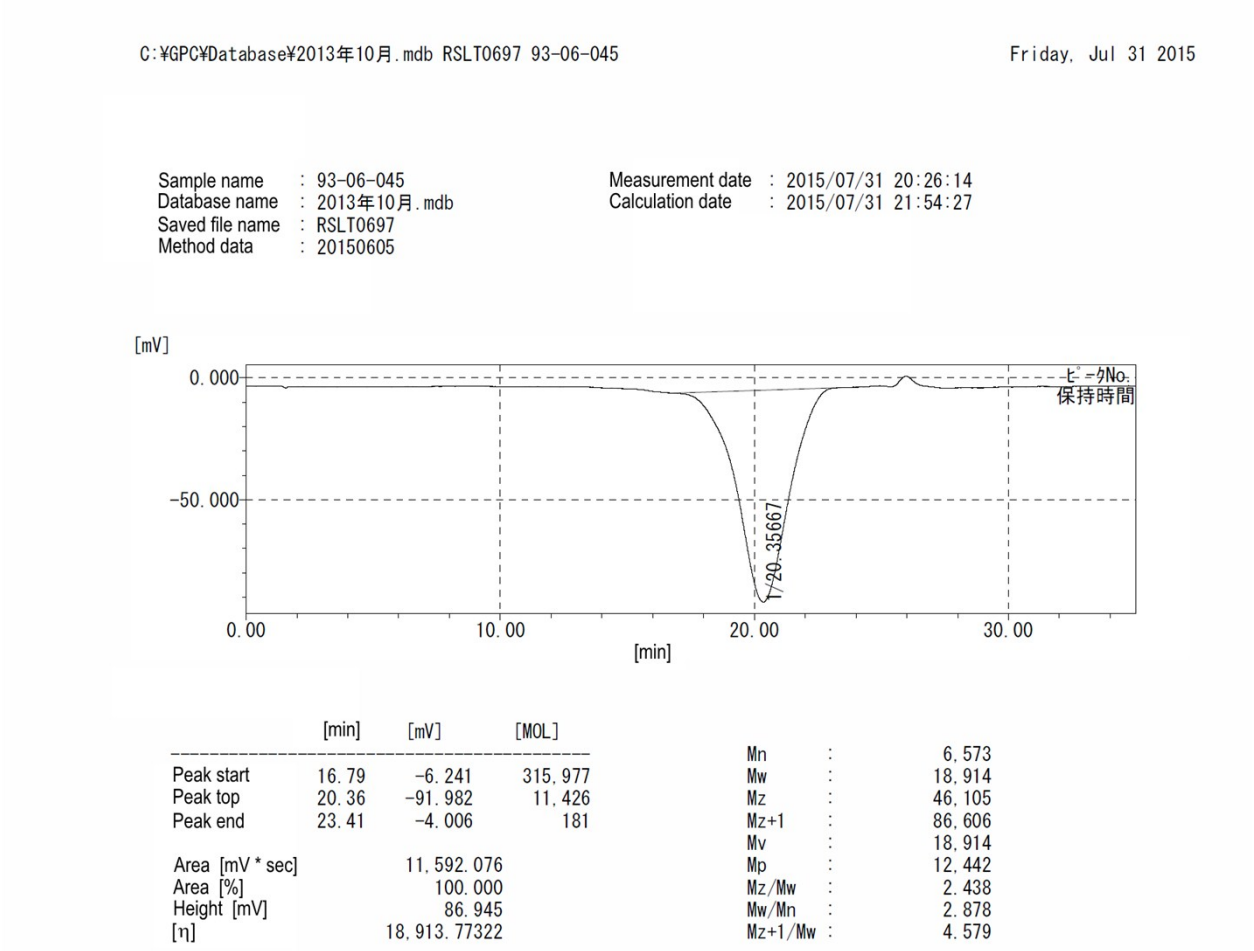


Figure S12. SEC trace of polypropylene obtained in entry 6 in Table 2.

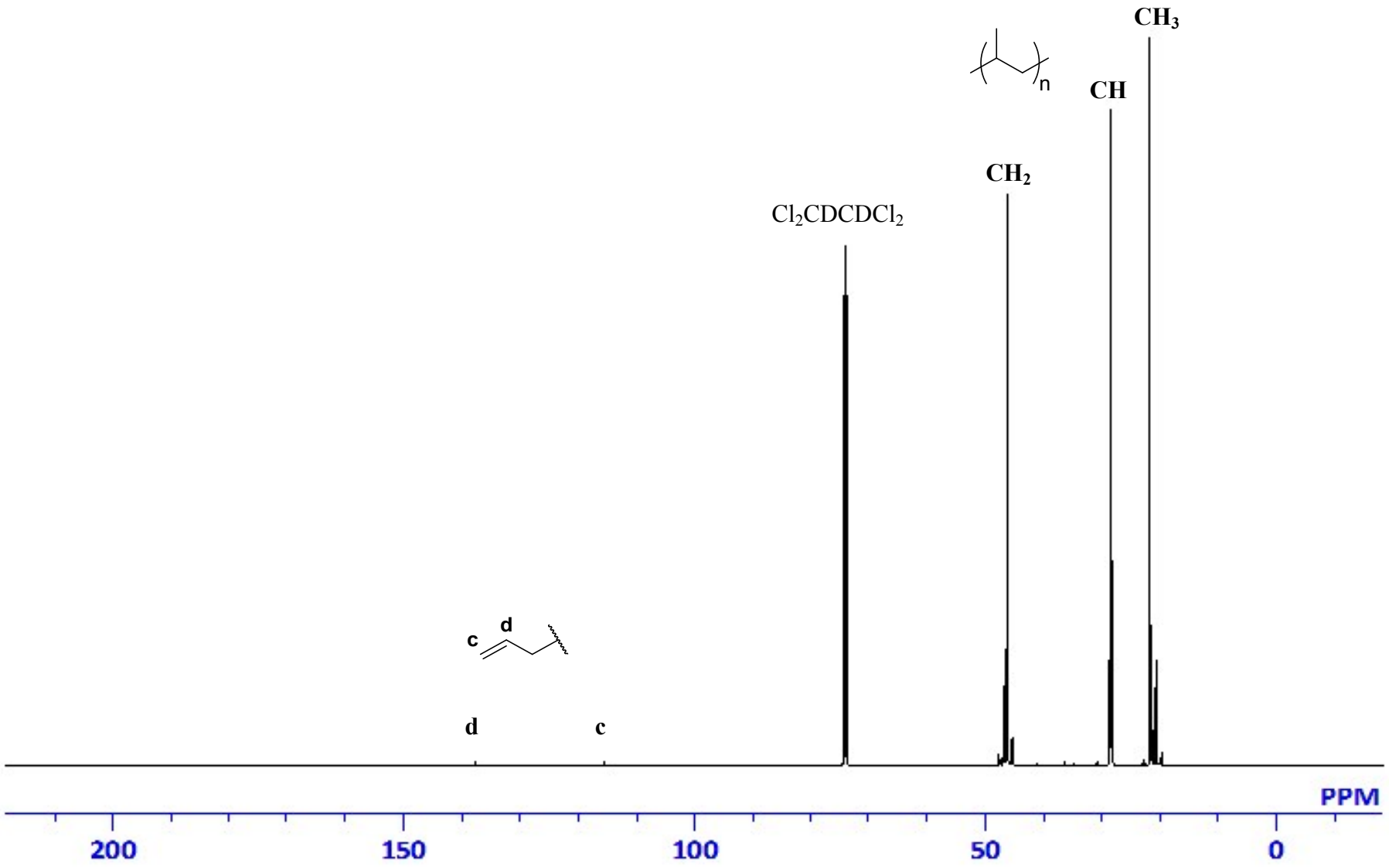


Figure S13. ^{13}C NMR spectrum of polypropylene obtained in entry 6 in Table 2 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Polypropylene Obtained in Entry 7 of Table 2:

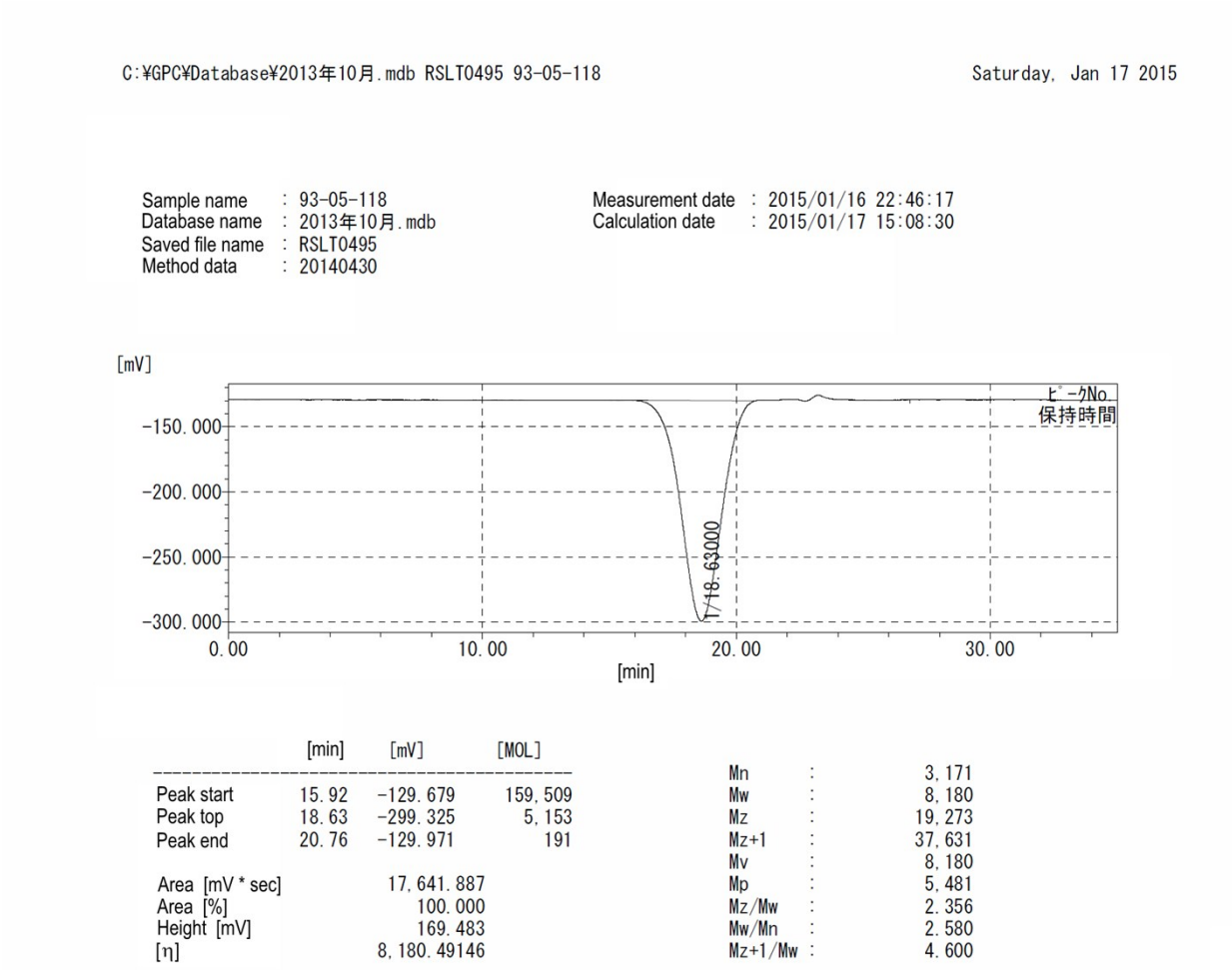


Figure S14. SEC trace of polypropylene obtained in entry 7 in Table 2.

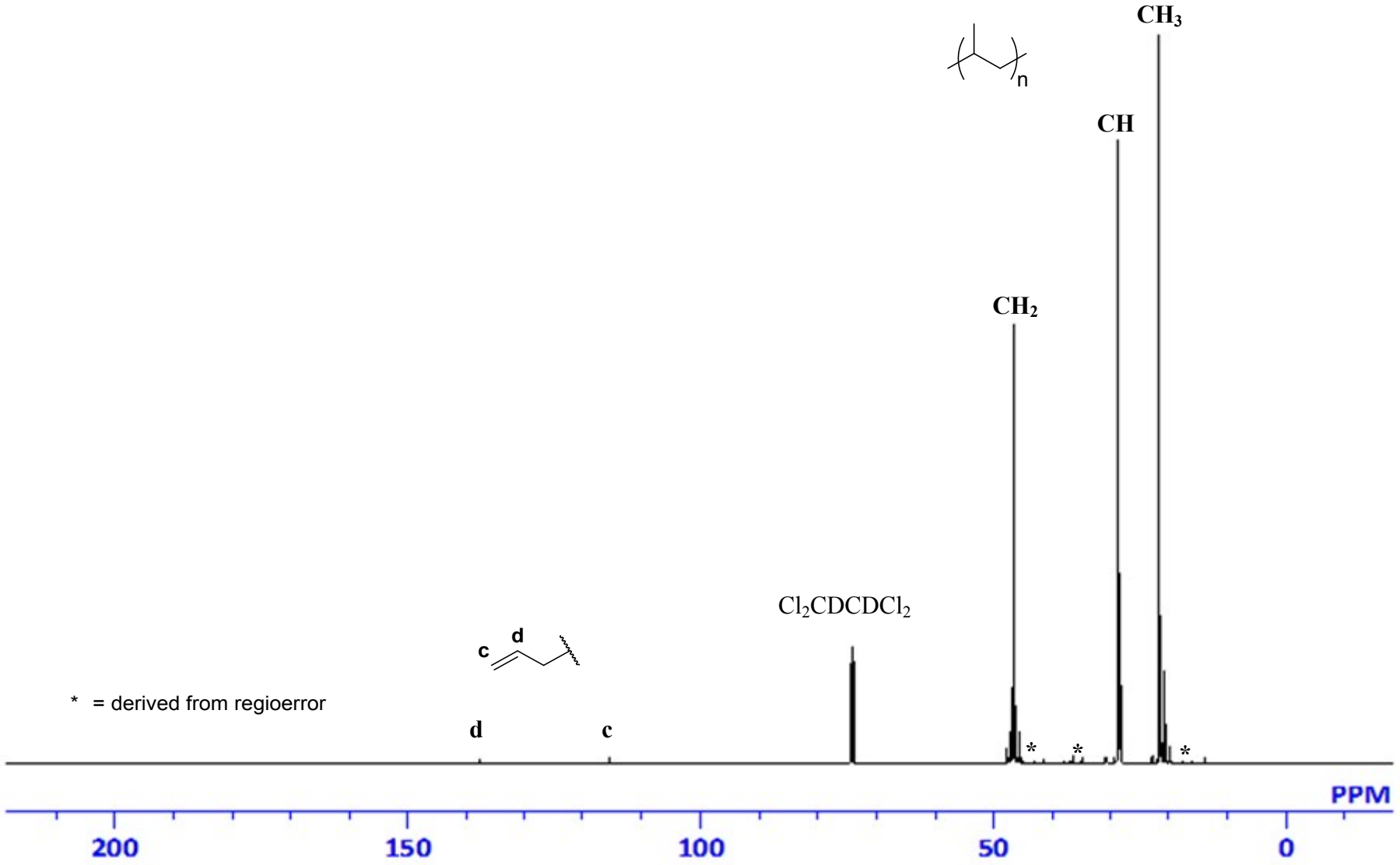


Figure S15. ^{13}C NMR spectrum of polypropylene obtained in entry 7 in Table 2 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Polypropylene Obtained in Entry 8 of Table 2:

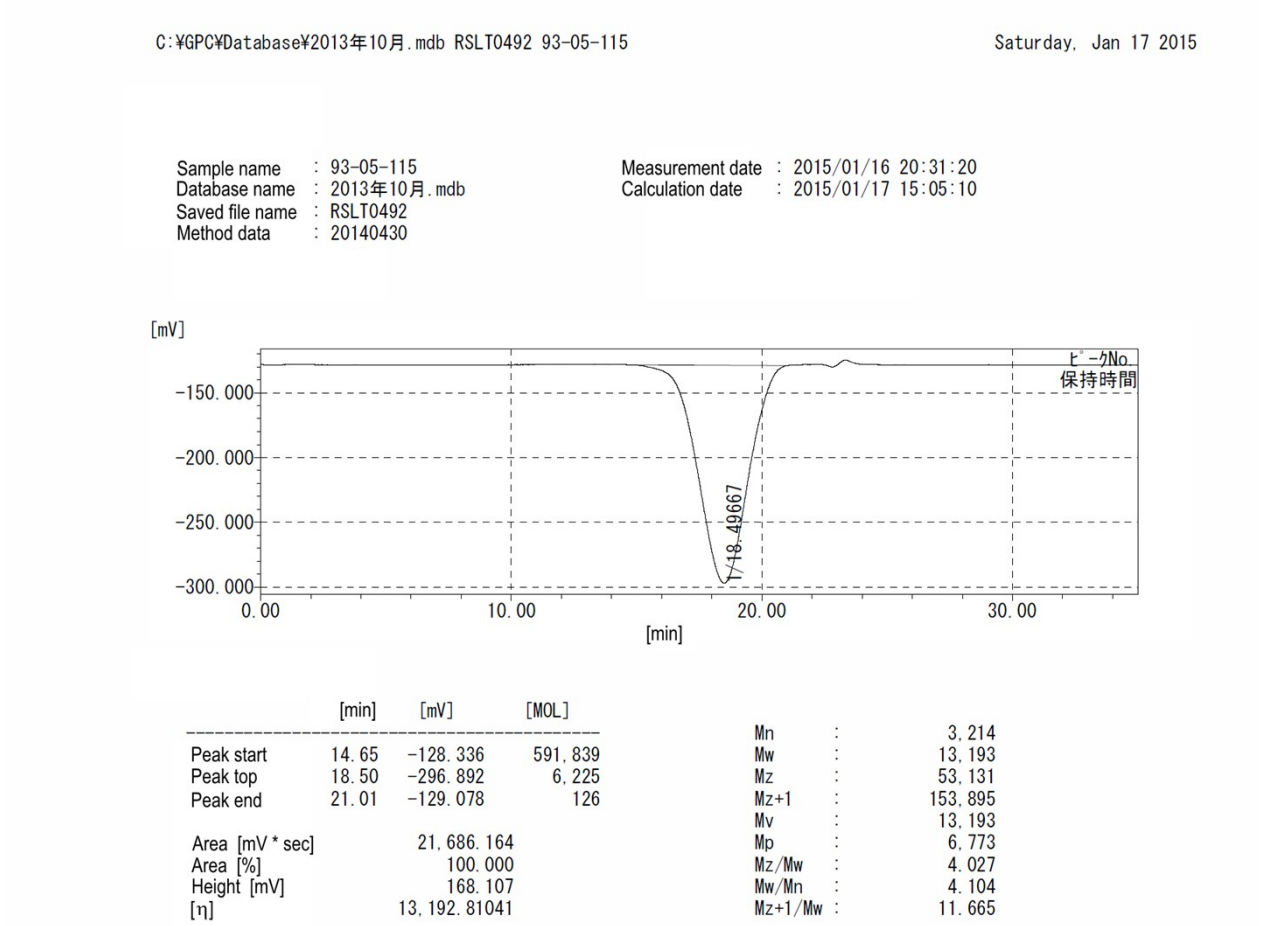


Figure S16. SEC trace of polypropylene obtained in entry 8 in Table 2.

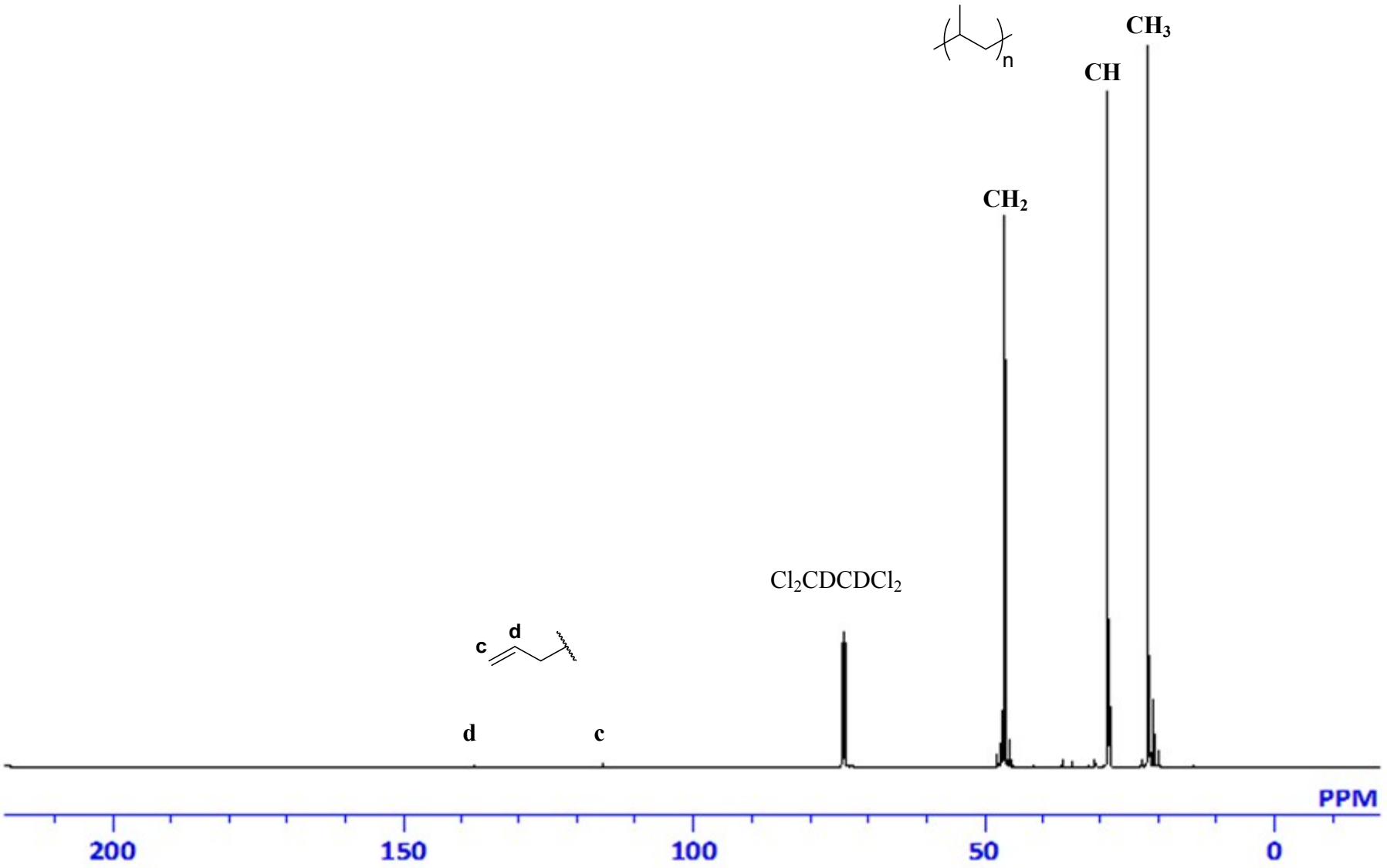


Figure S17. ^{13}C NMR spectrum of polypropylene obtained in entry 8 in Table 2 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Poly(propylene-*co*-allylbenzene) Obtained in Entry 6 of Table 3:

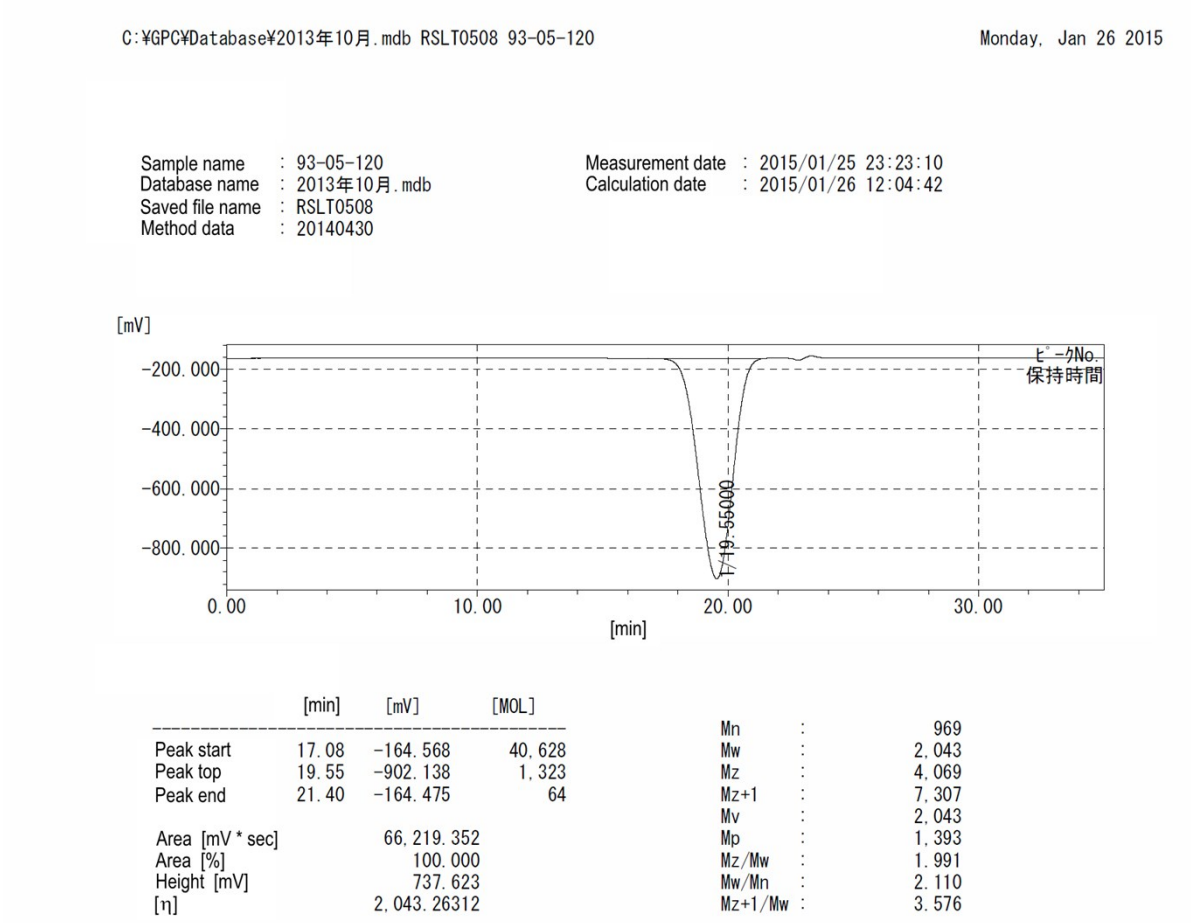


Figure S18. SEC trace of copolymer obtained in entry 6 in Table 3.

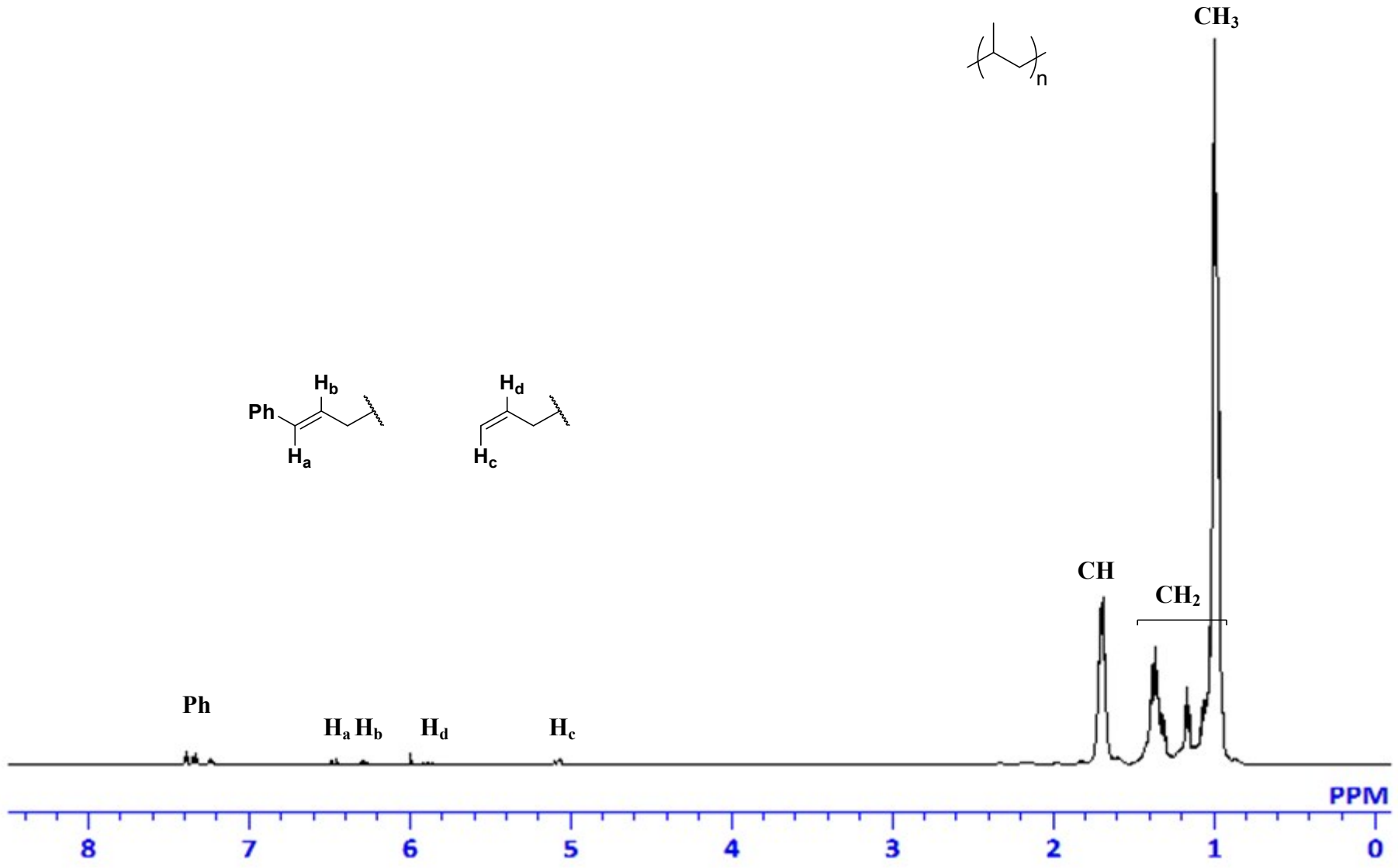


Figure S19. ^{1}H NMR spectrum of copolymer obtained in entry 6 in Table 3 (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

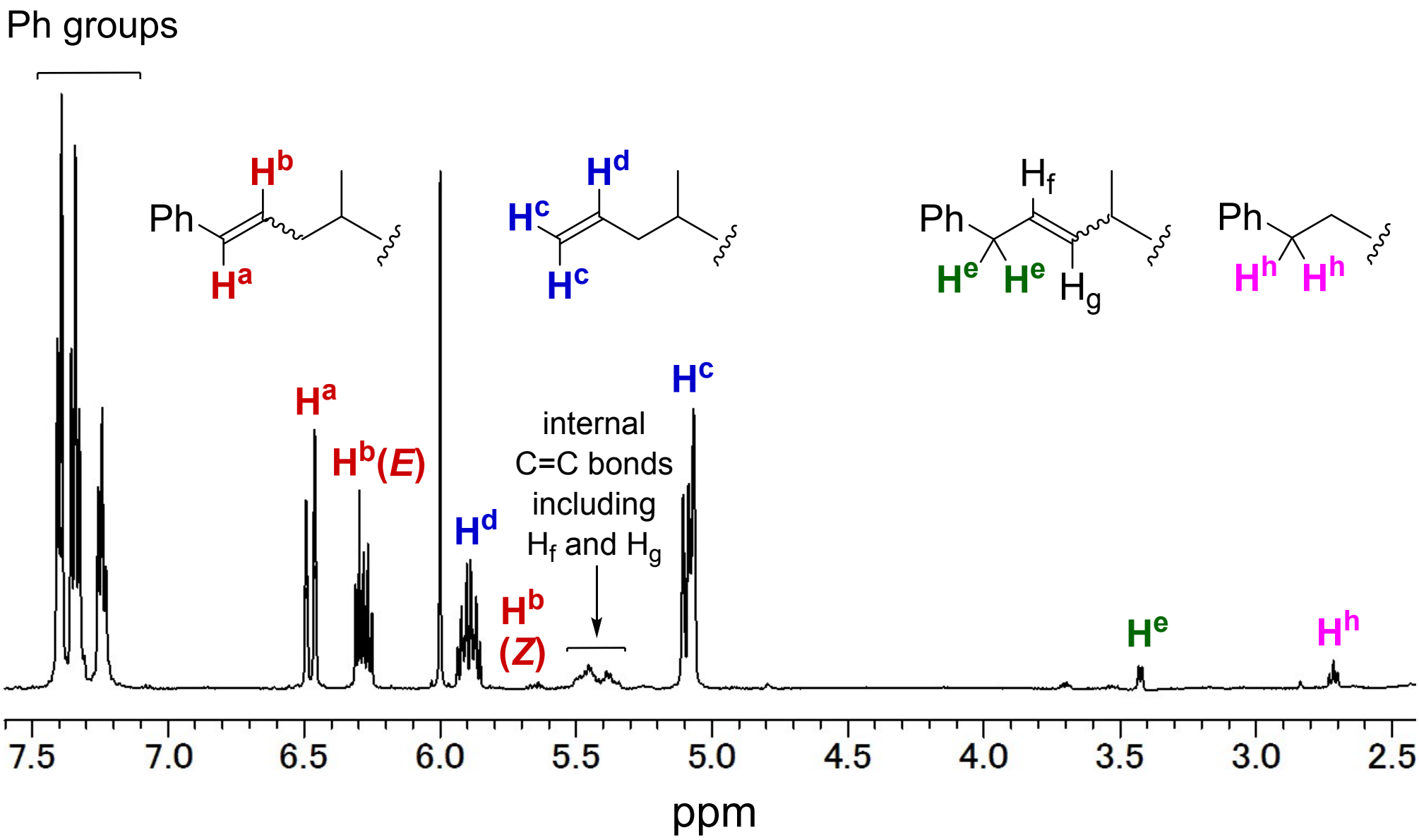


Figure S19-2. Enlarged ^{1}H NMR spectrum of Figure S19.

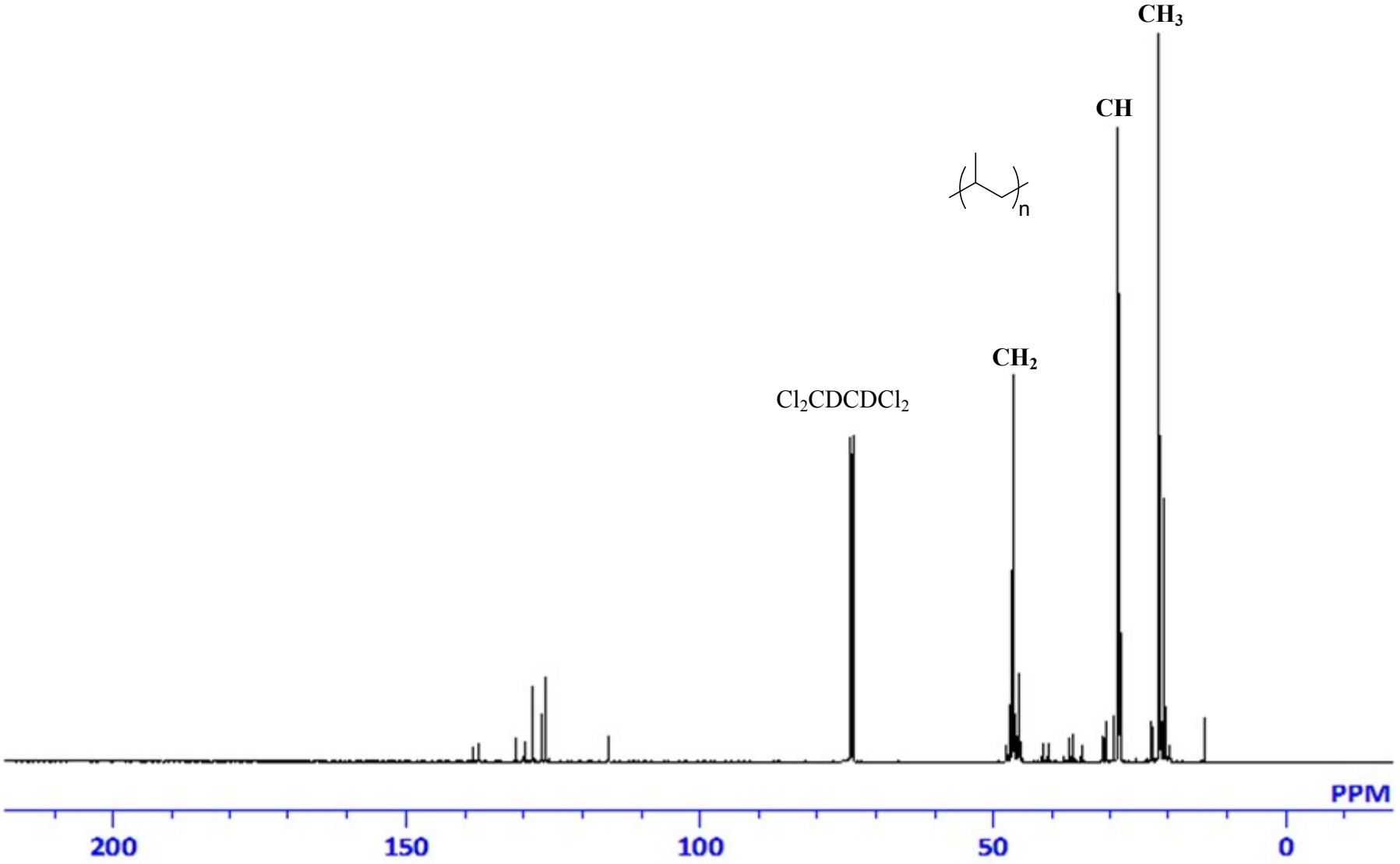


Figure S20. ^{13}C NMR spectrum of copolymer obtained in entry 6 in Table 3 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

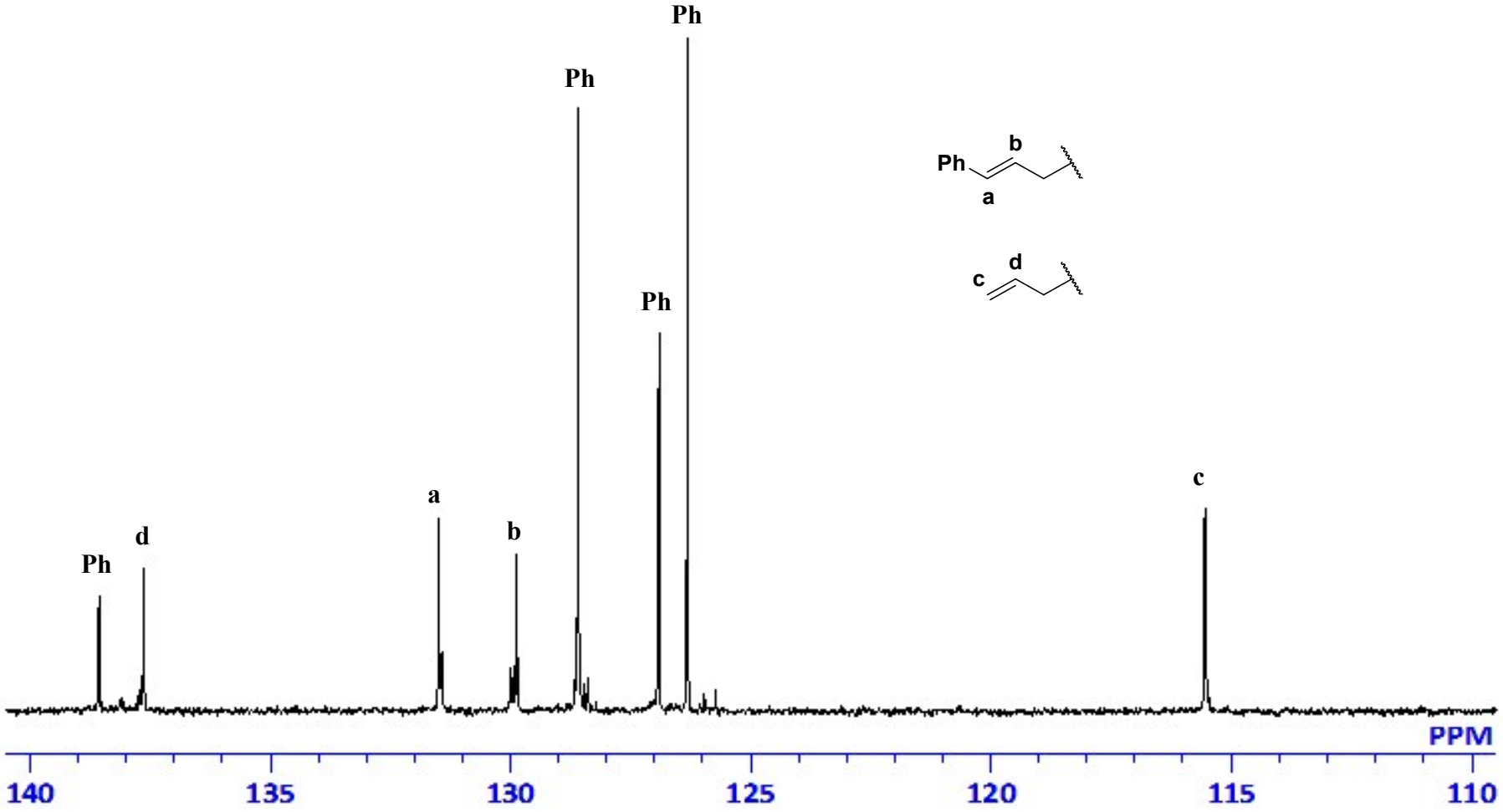


Figure S21. Low-field region of ^{13}C NMR spectrum of copolymer obtained in entry 6 in Table 3 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Poly(propylene-*co*-allyltrimethylsilane) Obtained in Entry 7 of Table 3:

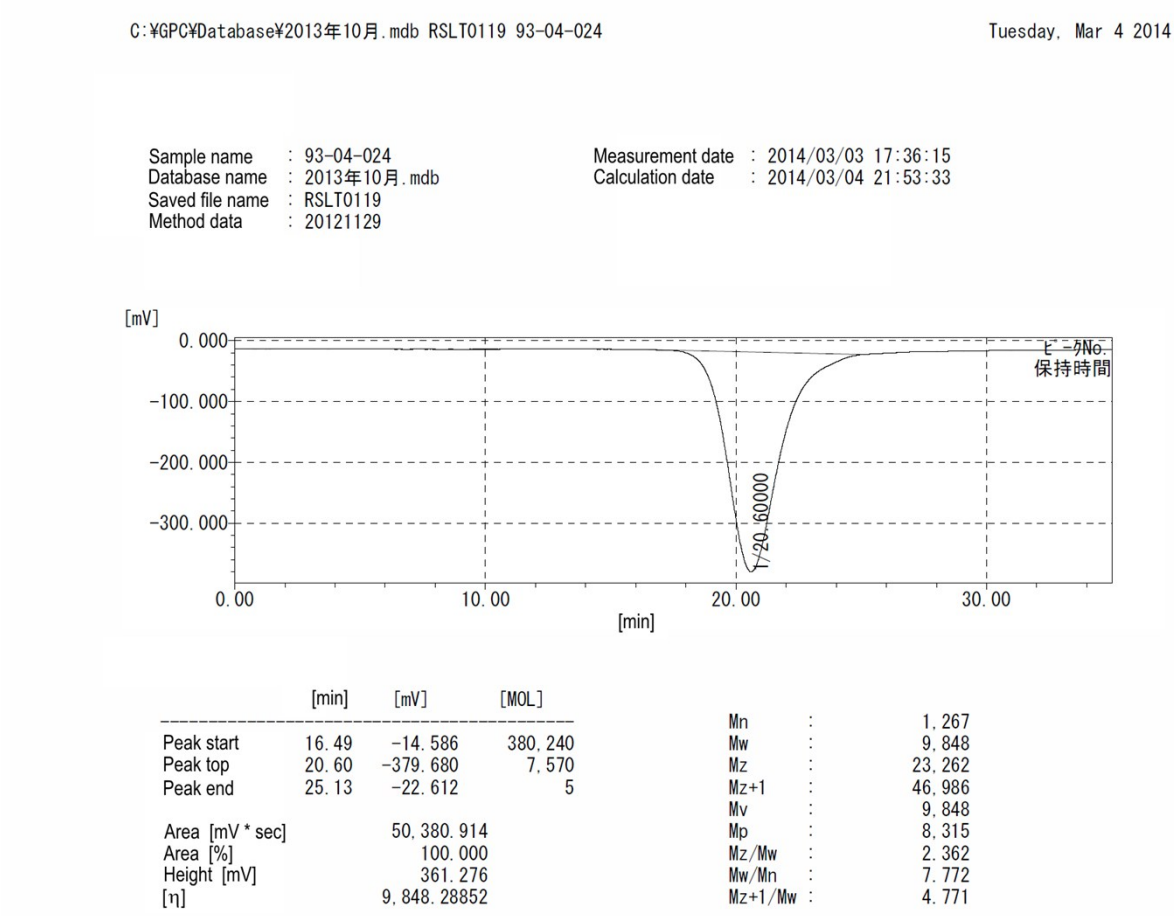


Figure S22. SEC trace of copolymer obtained in entry 7 in Table 3.

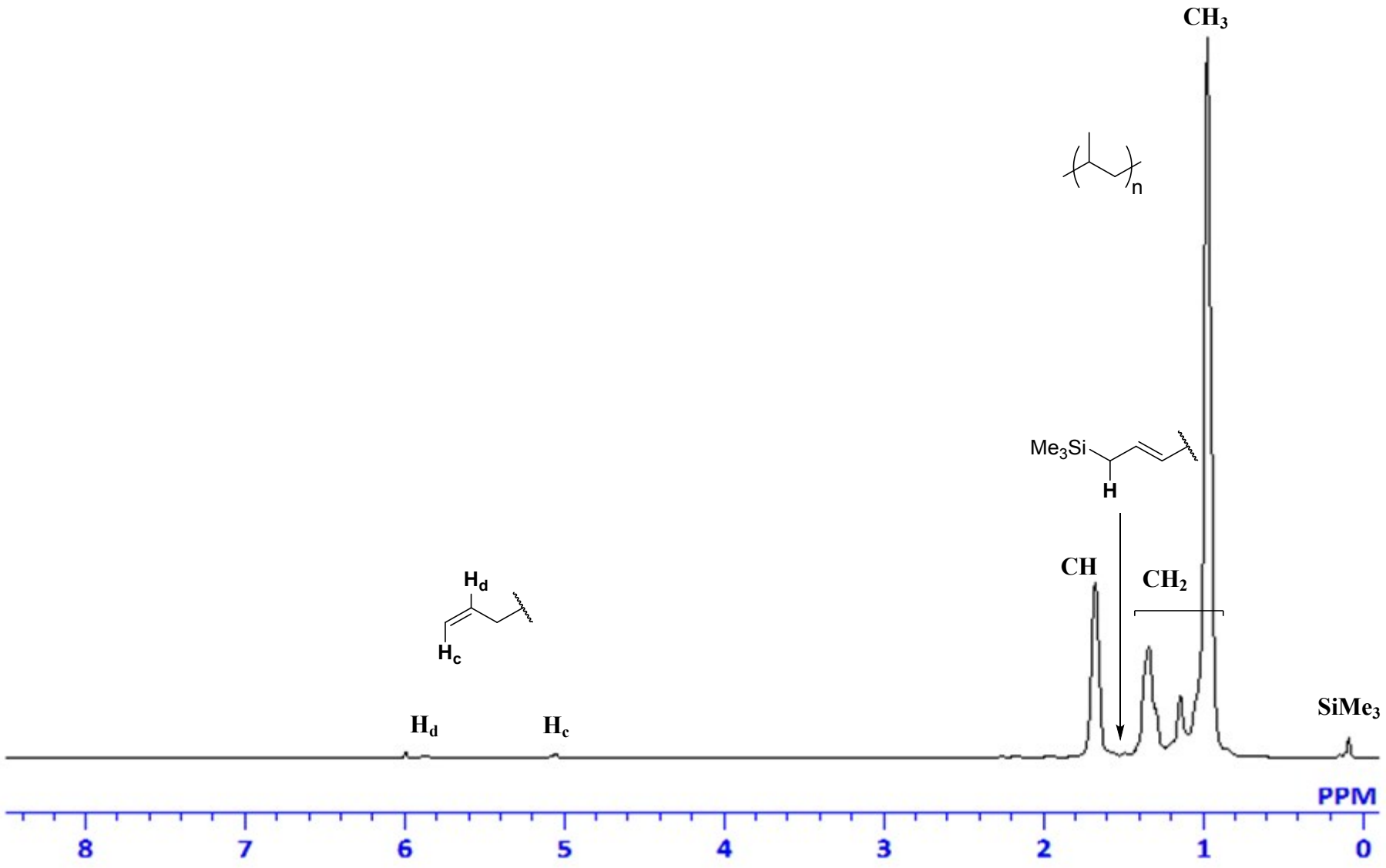


Figure S23 ^{1}H NMR spectrum of copolymer obtained in entry 7 in Table 3 (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

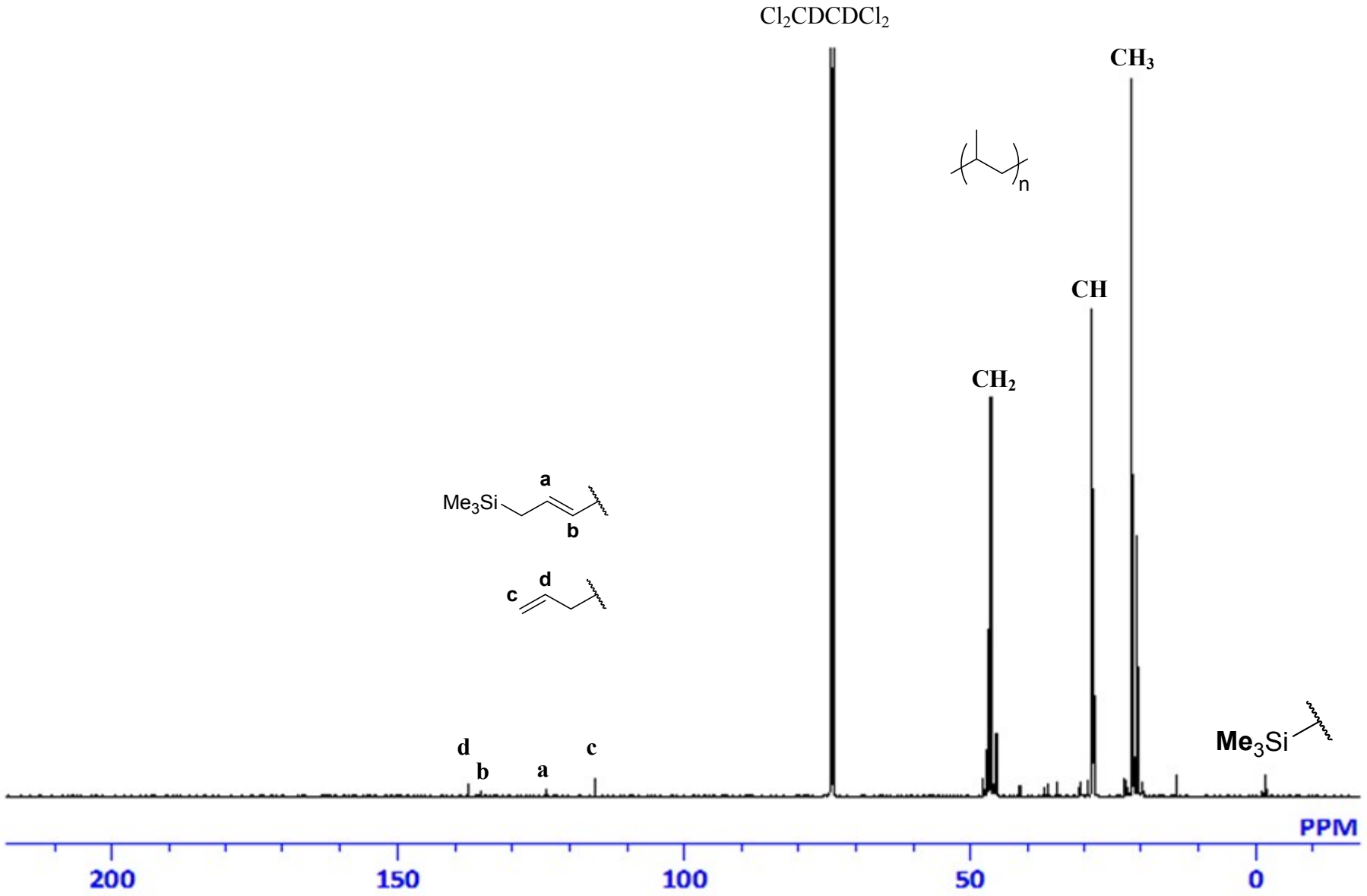


Figure S24. ^{13}C NMR spectrum of copolymer obtained in entry 7 in Table 3 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

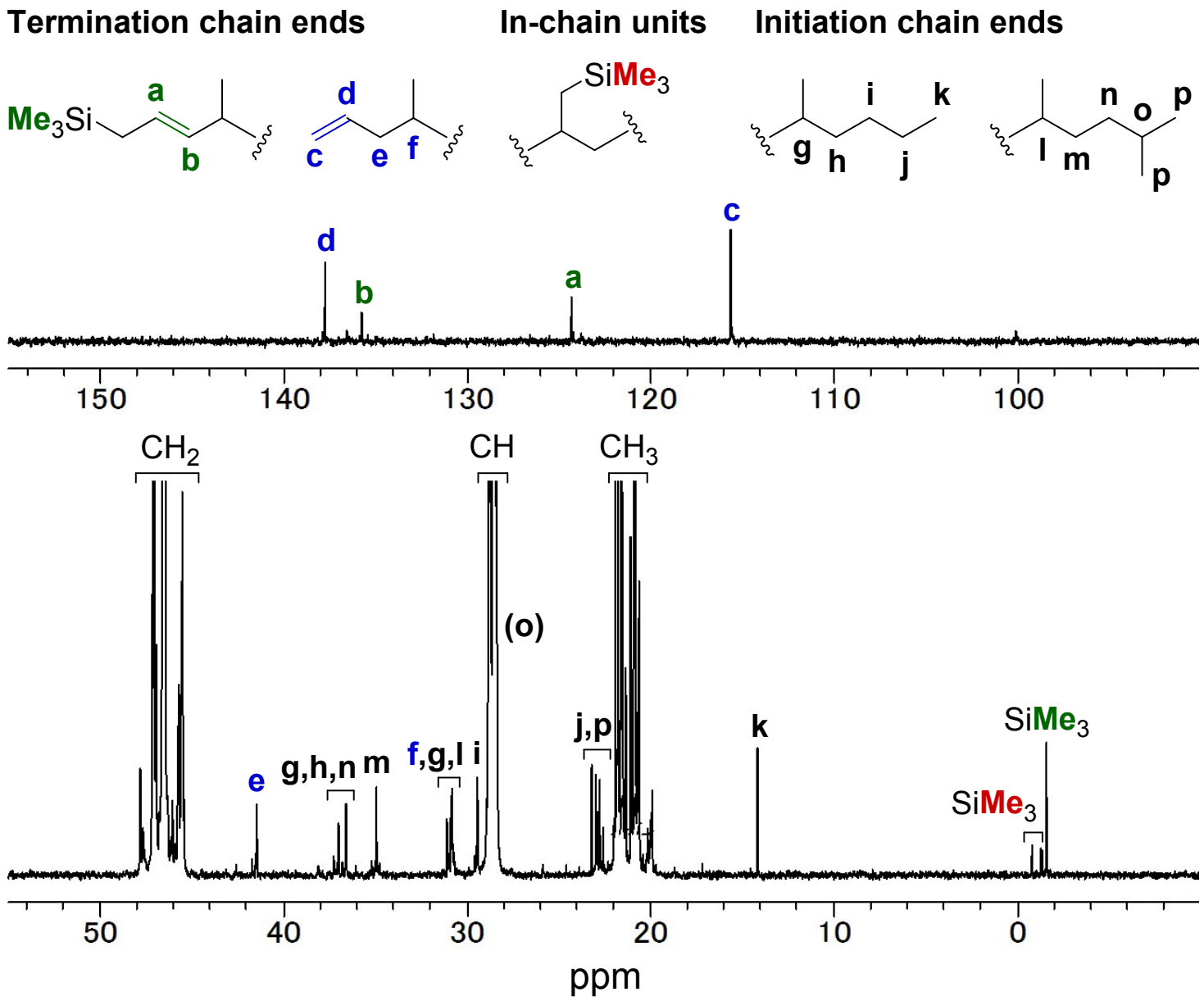


Figure S24-2. Enlarged ^{13}C NMR spectrum of Figure S24.

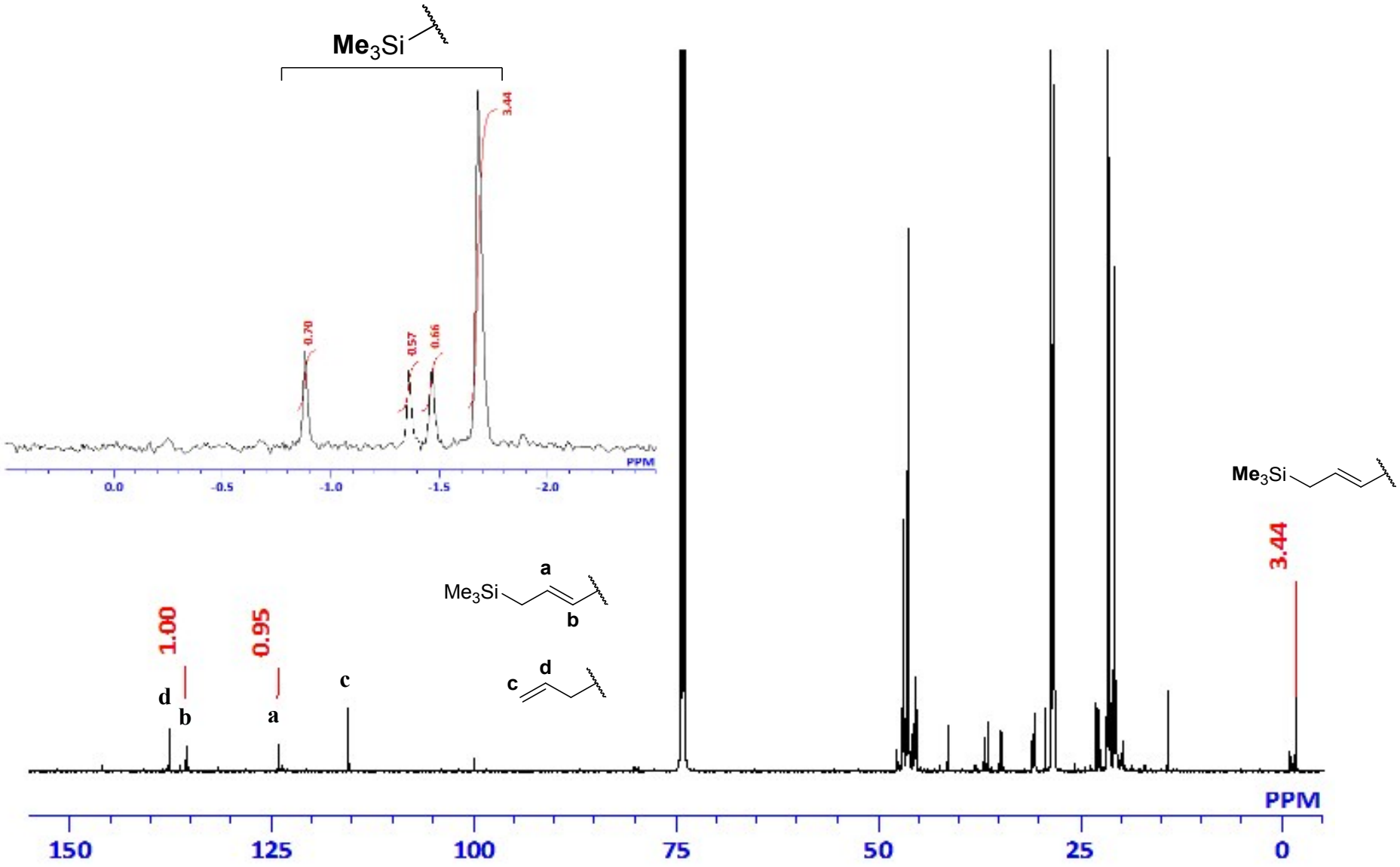


Figure S25. Quantitative ^{13}C NMR spectrum of copolymer obtained in entry 7 in Table 3 (with inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Poly(propylene-*co*-allyldimethylphenylsilane) Obtained in Entry 8 of Table 3:

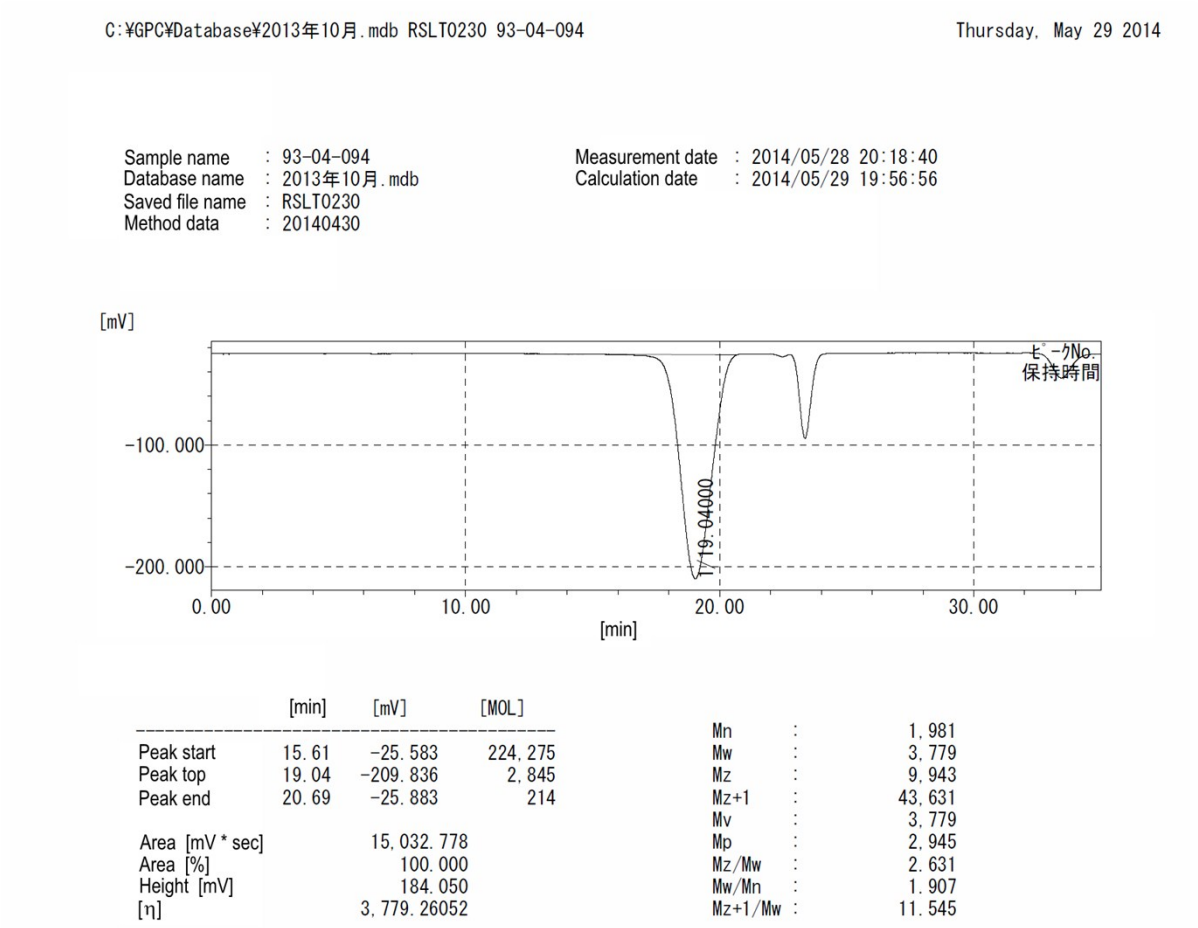


Figure S26. SEC trace of copolymer obtained in entry 8 in Table 3.

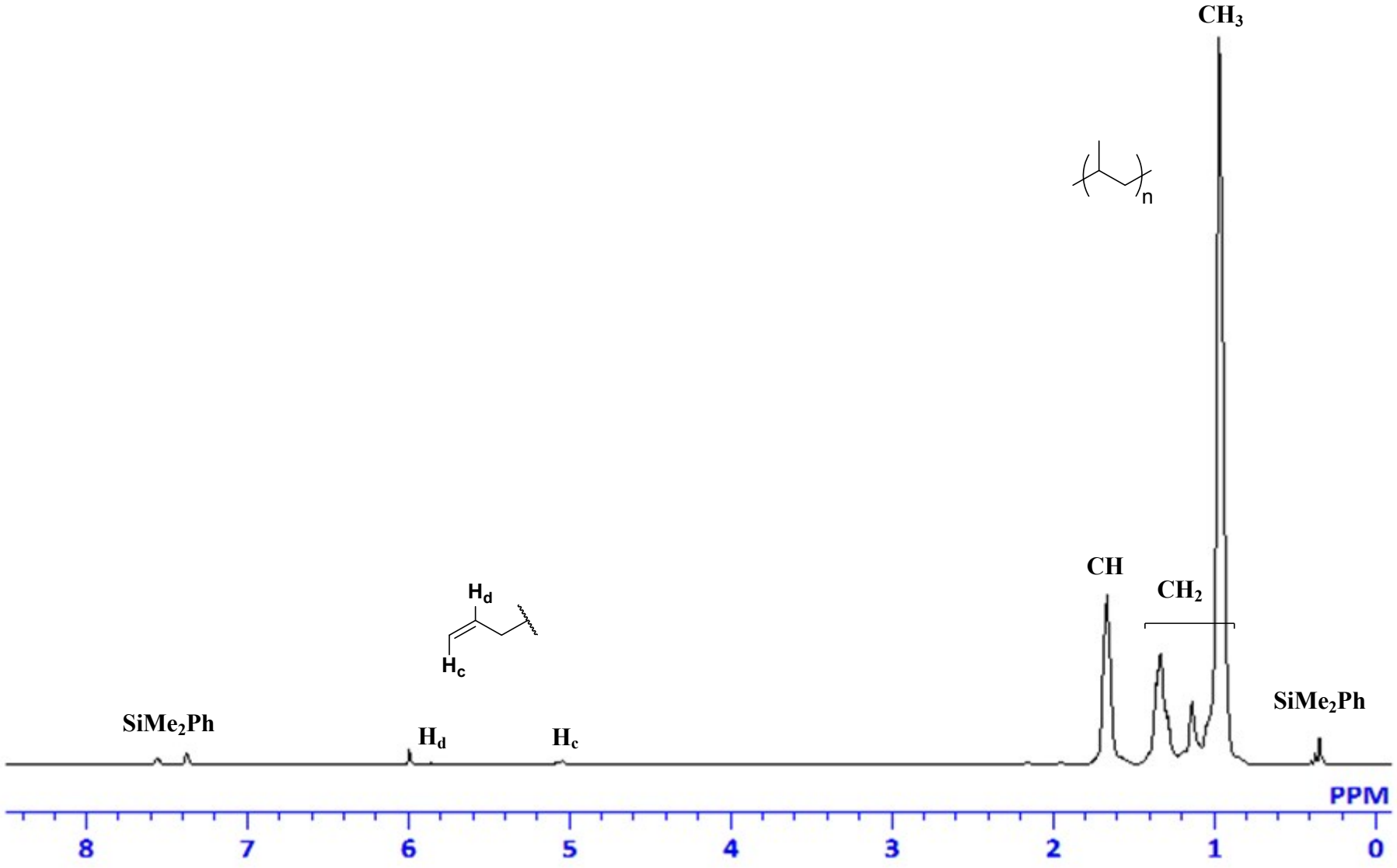


Figure S27 ^{1}H NMR spectrum of copolymer obtained in entry 8 in Table 3 (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

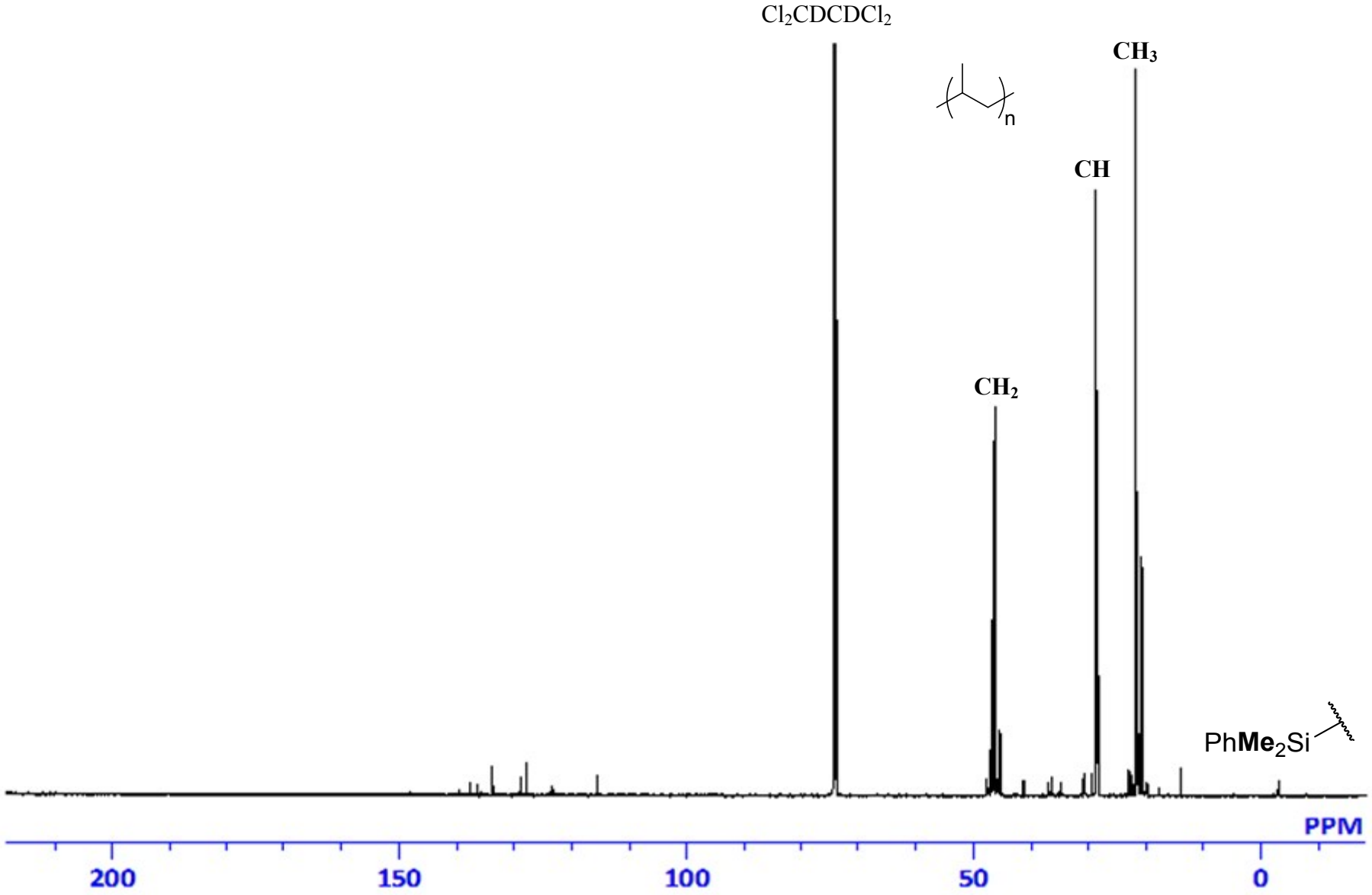


Figure S28. ^{13}C NMR spectrum of copolymer obtained in entry 8 in Table 3 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

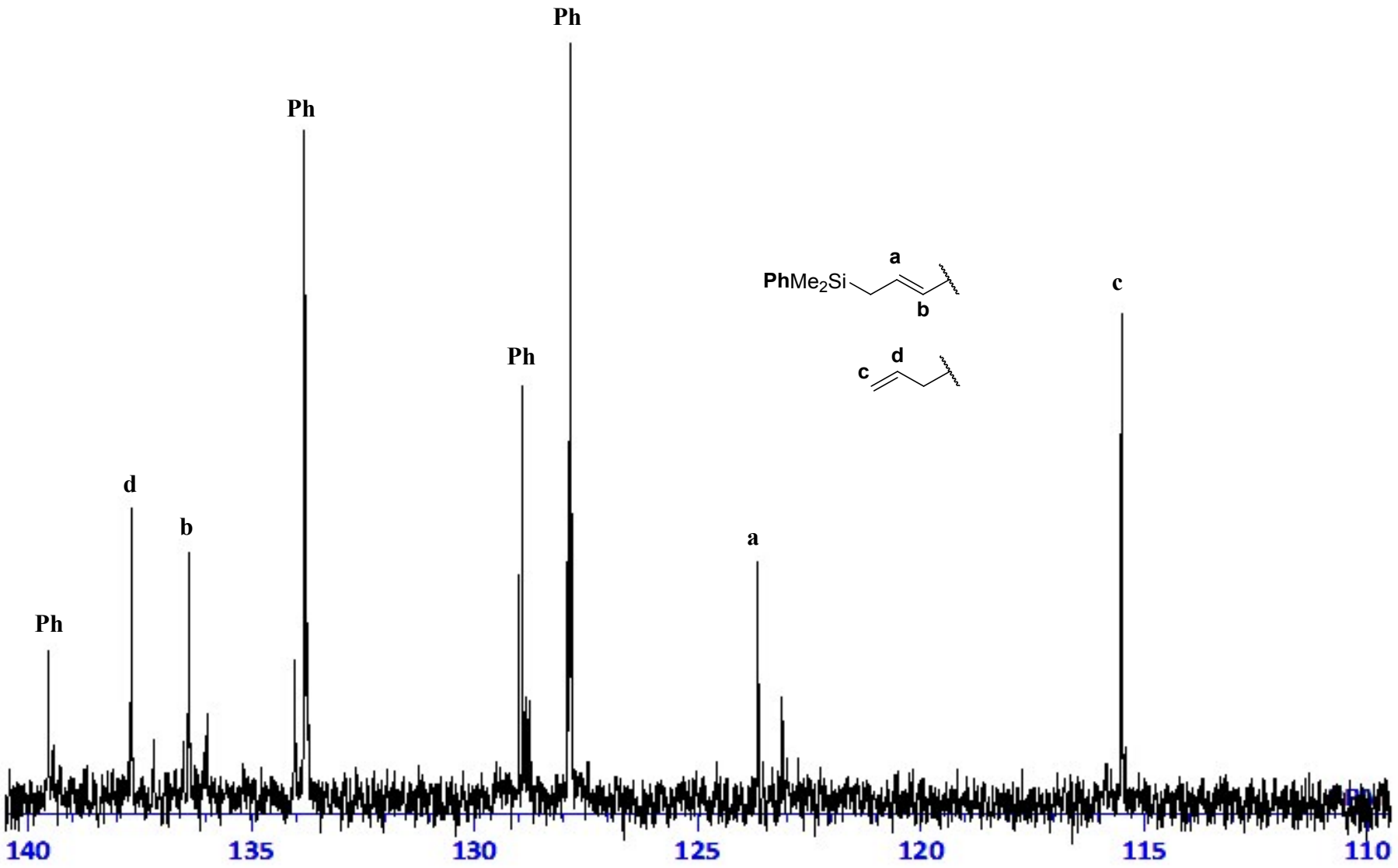


Figure S29. Low-field region of ^{13}C NMR spectrum of copolymer obtained in entry 8 in Table 3 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

Poly(propylene-co-allyltriethoxysilane) Obtained in Entry 9 of Table 3:

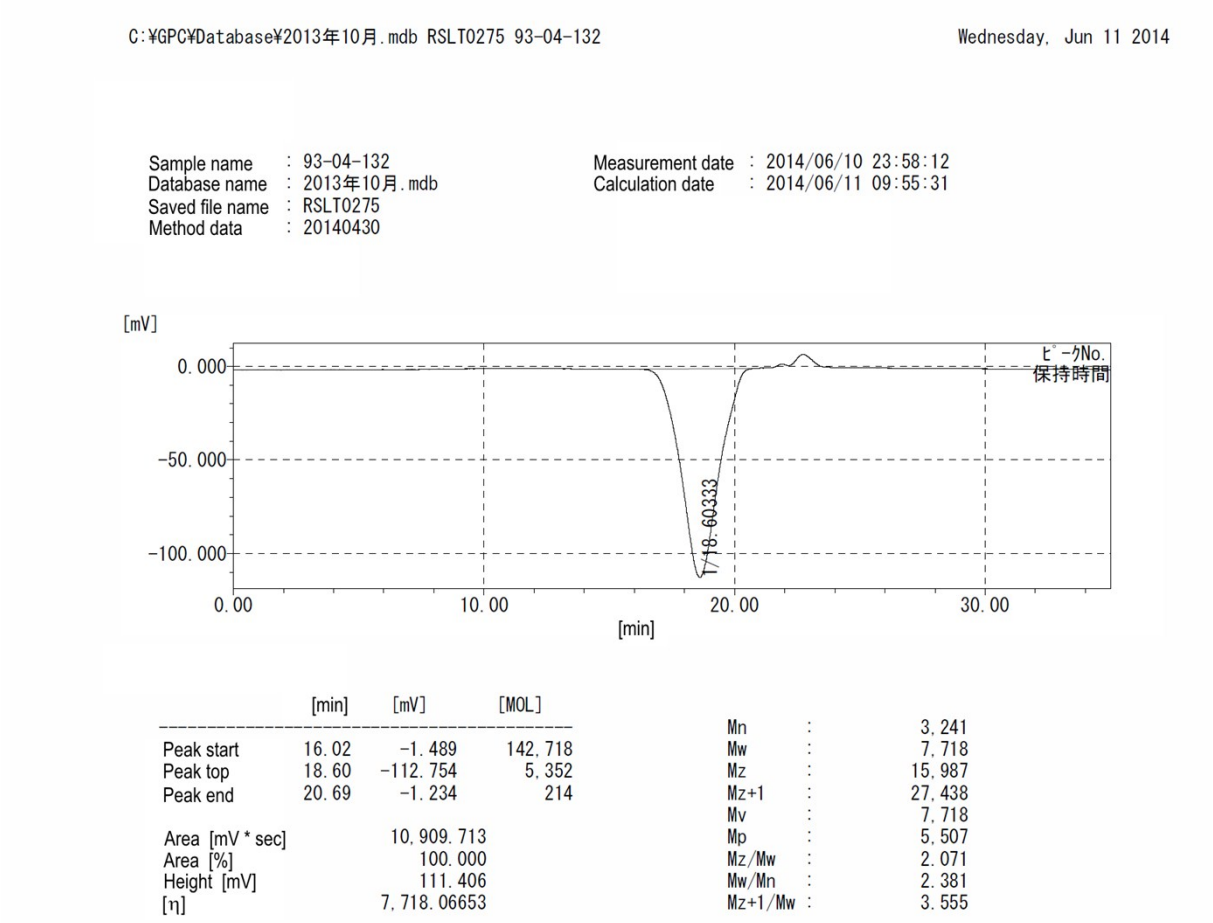


Figure S30. SEC trace of copolymer obtained in entry 9 in Table 3.

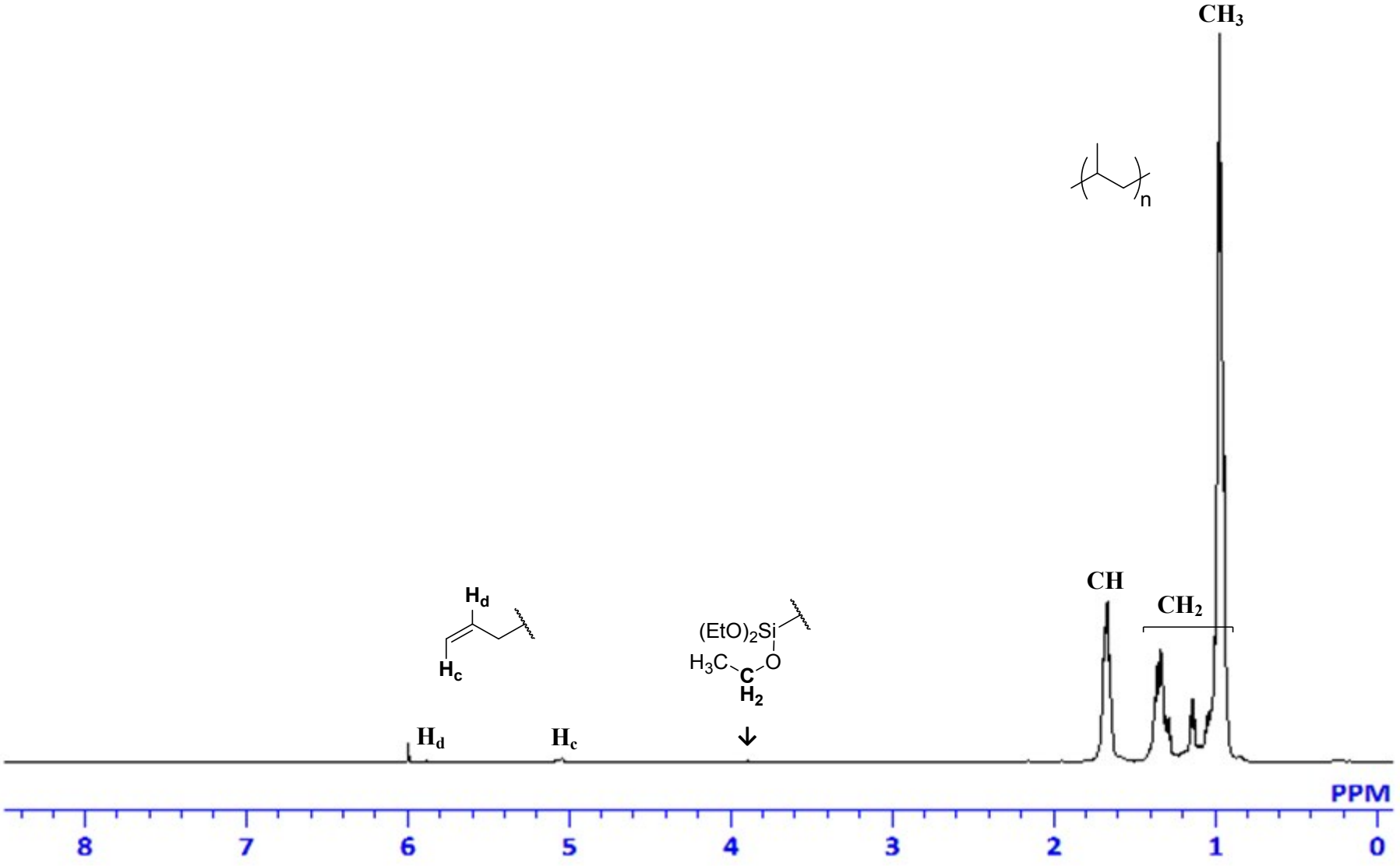


Figure S31. [1]H NMR spectrum of copolymer obtained in entry 9 in Table 3 (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

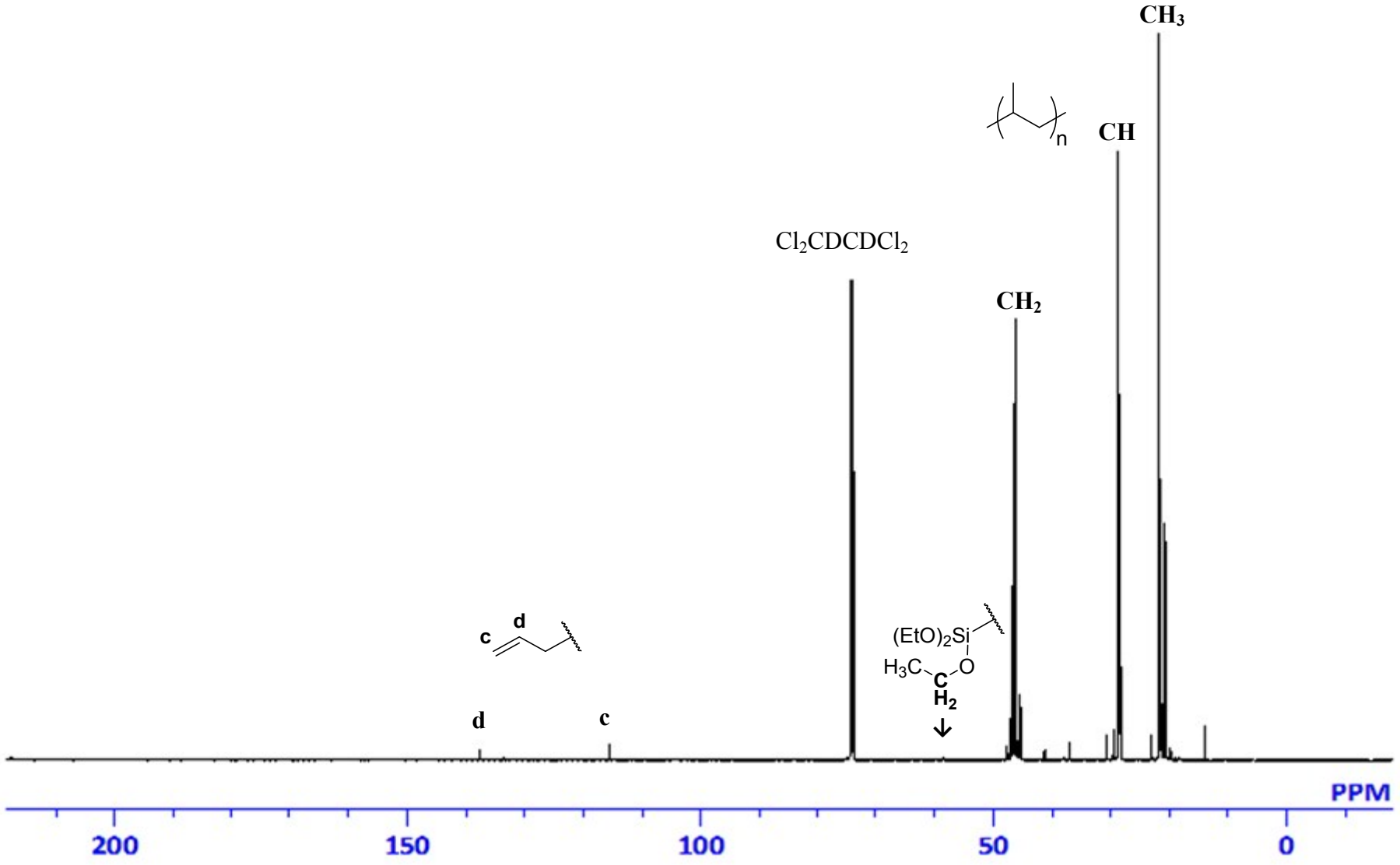


Figure S32. ^{13}C NMR spectrum of copolymer obtained in entry 9 in Table 3 (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C).

4. X-Ray Crystallographic Data

A single crystal was mounted with mineral oil on a loop-type mount and transferred to the goniometer of a Rigaku Saturn CCD diffractometer. The radiation was performed with graphite-monochromated Mo *K*α (λ = 0.71075 Å). The structures were solved by direct method with (SHELXT 2014)[8] and refined by full-matrix least-squares techniques against F^2 (SHELXL 2014).[9] The intensities were corrected for Lorentz and polarisation effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Table S2. Crystal data and structure refinement for **2c**, **2d'**, and **2g**.

Compound	**2c**	**2d'**	**2g**·2CH_2Cl_2
CCDC number	1416774	1416775	1416776
Molecular formula	$C_{41}H_{59}Cl_2FeN_3$	$C_{49}H7_5Cl_4FeN_3O$	$C_{35}H_{47}Cl_6FeN_3$
Formula weight	720.66	975.62	778.30
Temperature (K)	93(2)	93(2)	93(2)
Wavelength (Å)	0.71075	0.71075	0.71075
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$Pna2_1$	$P2_12_12_1$
Unit cell dimensions a (Å)	12.012(5)	16.951(4)	10.126(6)
b (Å)	18.204(8)	22.374(6)	15.208(9)
c (Å)	18.855(8)	13.224(3)	25.208(15)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
Volume (Å^3)	4123(3)	5015(2)	3882(4)
Z	4	4	4
Density (calculated) (Mg·m^{-3})	1.161	1.292	1.332
Absorption coefficient (mm^{-1})	0.525	0.829	0.829
F(000)	1544	2072	1624
Crystal size (mm^3)	0.35×0.20×0.05	0.20×0.15×0.15	0.45×0.018×0.010
Theta range (°)	2.75–26.00	2.86–26.00	2.10–26.00
Index ranges	−14<=h<=13	−20<=h<=20	−12<=h<=11
	−21<=k<=22	−27<=h<=27	−18<=k<=18
	−23<=l<=23	−15<=l<=15	−31<=l<=30
Reflections collected	29743	35235	18066
Independent reflections	8001	9714	6879
R(int)	0.1002	0.0888	0.0798
Max. and min. transmission	0.974, 0.838	0.886, 0.852	0.922, 0.707
Data / restraints / parameters	8101 / 0 / 434	9714 / 1 / 542	6879 / 96 / 414
Goodness-of-fit on F^2	1.113	1.122	1.116
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0713	R_1 = 0.0695	R_1 = 0.919
	wR_2 = 0.1190	wR_2 = 0.1094	wR_2 = 0.2268
R indices (all data) [$I > 2\sigma(I)$]	R_1 = 0.0795	R_1 = 0.0779	R_1 = 0.1078
	wR_2 = 0.1231	wR_2 = 0.1130	wR_2 = 0.2461
Absolute structure parameter	0.075(16)	0.080(12)	0.375(19)
Largest diff. peak and hole (e.Å^{-3})	0.458, −0.421	0.606, −0.500	0.979, −0.904

Note: The Flack parameter of crystal **2g**·2CH_2Cl_2 too large to allow the absolute structure to be determined. This is because the aryl groups on the nitrogen atoms are slightly disordered, but the disorder could not be fully solved.

(8) G. M. Sheldrick, University of Göttingen: Göttingen, Germany, 2014.
(9) G. M. Sheldrick, University of Göttingen: Göttingen, Germany, 2014.