

Supporting Information:

Elucidating the Key Role of Phosphine–Sulfonate Ligands in Palladium-Catalyzed Ethylene Polymerization: Effect of Ligand Structure on the Molecular Weight and Linearity of Polyethylene

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I. Experimental Procedures

General: All reactions and polymerizations were carried out using a standard glovebox or Schlenk techniques under argon purified by passing through a hot column packed with BASF catalyst R3-11. All polymerization reactions were performed in a 300-mL stainless steel autoclave.

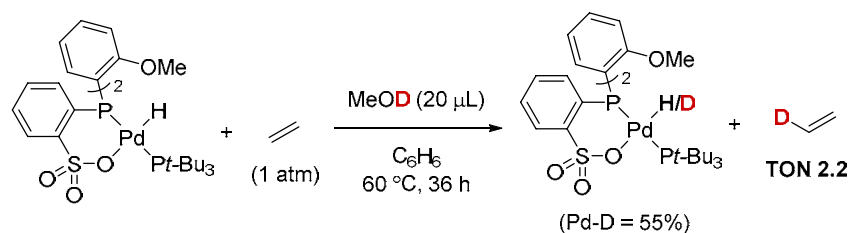
Instrumentation: Nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER Ascend500 (^1H : 500 MHz, ^2H : 77 MHz, ^{13}C : 126 MHz, ^{31}P : 202 MHz) NMR spectrometer. Chemical shift values for protons are referenced to the residual proton resonance of benzene- d_6 (δ : 7.16) or CDCl_3 (δ : 7.26). Chemical shift values for deuteriums are referenced to the deuterium resonance of benzene- d (δ : 7.16). Quantitative ^{13}C NMR analyses of polymers were performed in a 5-mm probe on ca. 5~15 weight% solutions of the polymers and 0.05-M $\text{Cr}(\text{acac})_3$ as a relaxation agent in 1,1,2,2-tetrachloroethane unlocked at 120 °C using a 30° pulse of 16.8 μs , a spectral width of 30 kHz, a relaxation time of 2 s, an acquisition time of 1.1 s, and inverse-gated decoupling (BRUKER Ascend500).^{1,2,3} Chemical shift values for carbons are referenced to the carbon resonance of 1,1,2,2-tetrachloroethane (δ : 74.20). Size exclusion chromatography (SEC) analyses were carried out with a Tosoh instrument (HLC-8121GPC/HT) equipped with two SEC columns (Tosoh TSKgel GMHHR-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 and were corrected for by universal calibration using the Mark–Houwink parameters reported by Rudin *et al.*: $K = 1.75 \times 10^{-2} \text{ cm}^3/\text{g}$ and $\alpha = 0.67$ for polystyrene, $K = 5.90 \times 10^{-2} \text{ cm}^3/\text{g}$ and $\alpha = 0.69$ for LLDPE.⁴

Materials: Ethylene (>99.9%) was purchased from Takachiho Chemical Industrial Co., Ltd. (Takachiho), and dried, deoxygenated by passing through a dry column DC-HDF300-A3 made by Nikka Seiko Co., Ltd. Anhydrous toluene were purchased from Kanto Chemical Co. Inc. (Kanto) and purified by the method of Pangborn *et al.*⁵ Dehydrated benzene were purchased from Kanto and used as received. 2,6-lutidine and 1-eicocene were purchased from Tokyo Chemical Industry, Co., Ltd. (TCI) and distilled from calcium hydride before use. The other reagents were purchased from TCI, Kanto, or Sigma-Aldrich Chemical Co. and used as received. The following compounds were prepared according to literature procedures: [2-(*t*-Bu₂P)C₆H₄SO₃]PdMe(2,6-lutidine),⁶ [2-(*i*-Pr₂P)C₆H₄SO₃]PdMe(2,6-lutidine),⁷ [2-(Cy₂P)C₆H₄SO₃]PdMe(2,6-lutidine),⁸ [2-(Men₂P)C₆H₄SO₃]PdMe(2,6-lutidine),⁶ [2-(Ph₂P)C₆H₄SO₃]PdMe(2,6-lutidine),⁹ [2-(bis(2-methoxyphenyl)P)C₆H₄SO₃]PdMe(2,6-lutidine),¹⁰ and [2-(*o*-Ani₂P)C₆H₄SO₃]PdH(*t*-Bu₃P).¹¹

General Procedure of the Homopolymerization of Ethylene (Table 1)

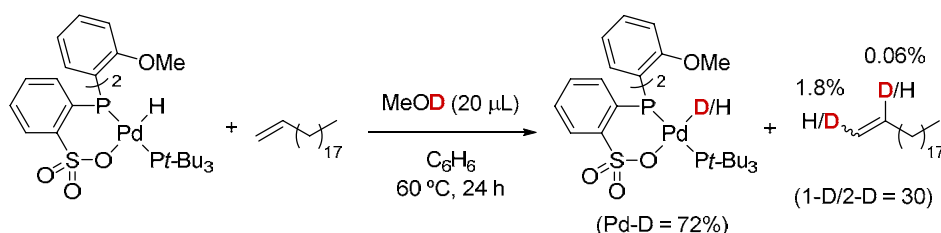
A 300-mL autoclave charged with catalyst (0.010 mmol) and toluene (100 mL) was stirred under ethylene pressure (3.0 MPa or 1.0 MPa) at 80 °C for 1 h. After cooling to room temperature, methanol (200 mL) was added into the autoclave. The polymer was isolated by filtration, washed with methanol, and dried under vacuum. The obtained polyethylene was analyzed without further purification. The number of branches per 1000 carbons was determined by quantitative ^{13}C NMR analysis using inverse-gated decoupling.

H/D Exchange Reaction of Ethylene and MeOD using [2-(*o*-Ani₂P)C₆H₄SO₃]PdH(*t*-Bu₃P)



In a 5-mm J-young NMR tube (internal volume 3.0 mL), [2-(*o*-Ani₂P)C₆H₄SO₃]PdH(*t*-Bu₃P) (14.2 mg, 20 μmol) and 1,4-bis(trimethylsilyl)benzene-*d*₄ (9.9 mg, 44 μmol, as an internal standard) in benzene (0.50 mL) and MeOD (20 μL) was cooled with liquid nitrogen bath and evacuated under high vacuum. After warming to ambient temperature, to the mixture was added atmospheric pressure of ethylene. Then, the mixture was sealed and heated at 60 °C for 36 h with using a shaking apparatus (Tosoh DF-8020). During the above experiment, not the formation of palladium black, but a slight formation of colorless precipitate was observed. After cooling to ambient temperature, the ratio of deuterium in ethylene and palladium–hydride was determined by quantitative ¹H and ²H NMR measurements; 3.7% in ethylene, and 72% in palladium–hydride. Given that the atmospheric ethylene was also deuterated in the same ratio, the total amount of deuterated ethylene was calculated as follows; {1.1 mmol (=atmospheric ethylene) + 0.1 mmol (ethylene in benzene)} × 0.037 = 44 μmol.

H/D Exchange Reaction of 1-Eicocene and MeOD using [2-(*o*-Ani₂P)C₆H₄SO₃]PdH(*t*-Bu₃P)



In a 5-mm J-young NMR tube, [2-(*o*-Ani₂P)C₆H₄SO₃]PdH(*t*-Bu₃P) (14.2 mg, 20 μmol), 1-eicocene (56.0 mg, 0.20 mmol), and 1,4-bis(trimethylsilyl)benzene-*d*₄ (11.2 mg, 49.4 μmol, as an internal standard) in benzene (0.50 mL) and MeOD (20 μL) was heated at 60 °C for 24 h with using a shaking apparatus (Tosoh DF-8020). During the above experiment, the formation of palladium black was not observed, but the formation of a slight amount of colorless precipitates was observed.

After cooling to ambient temperature, the ratio of deuterium in the resulting 1-eicocene and palladium–hydride complex was determined by quantitative ¹H and ²H NMR measurements; 1.8% in C1 position of 1-eicocene, 0.06% in C2 position of 1-eicocene, and 72% in the palladium–hydride complex. Even with ignoring natural occurrence of deuterium, the selectivity of the C1/C2 deuteration reached ca. 30.

After the reaction, most of the phosphine species observed by ³¹P NMR analysis remained as the initial palladium–hydride or the deuterated palladium–deuteride complexes. However, the quantitative ¹H and ²H NMR analyses suggested ca. 10% of the initial palladium–hydride complex was converted to something other than the two complexes. Judging from the formation of a slight amount of colorless precipitates observed after the reaction and the reactivity of [2-(*o*-Ani₂P)C₆H₄SO₃]PdH(*t*-Bu₃P) complex reported by Mecking and coworkers, the loss of palladium/phosphine–sulfonate species can be attributed to the formation of (P⁺O)₂Pd species which is not soluble in the reaction media.

II. NMR Spectra and SEC Charts of Polyethylene

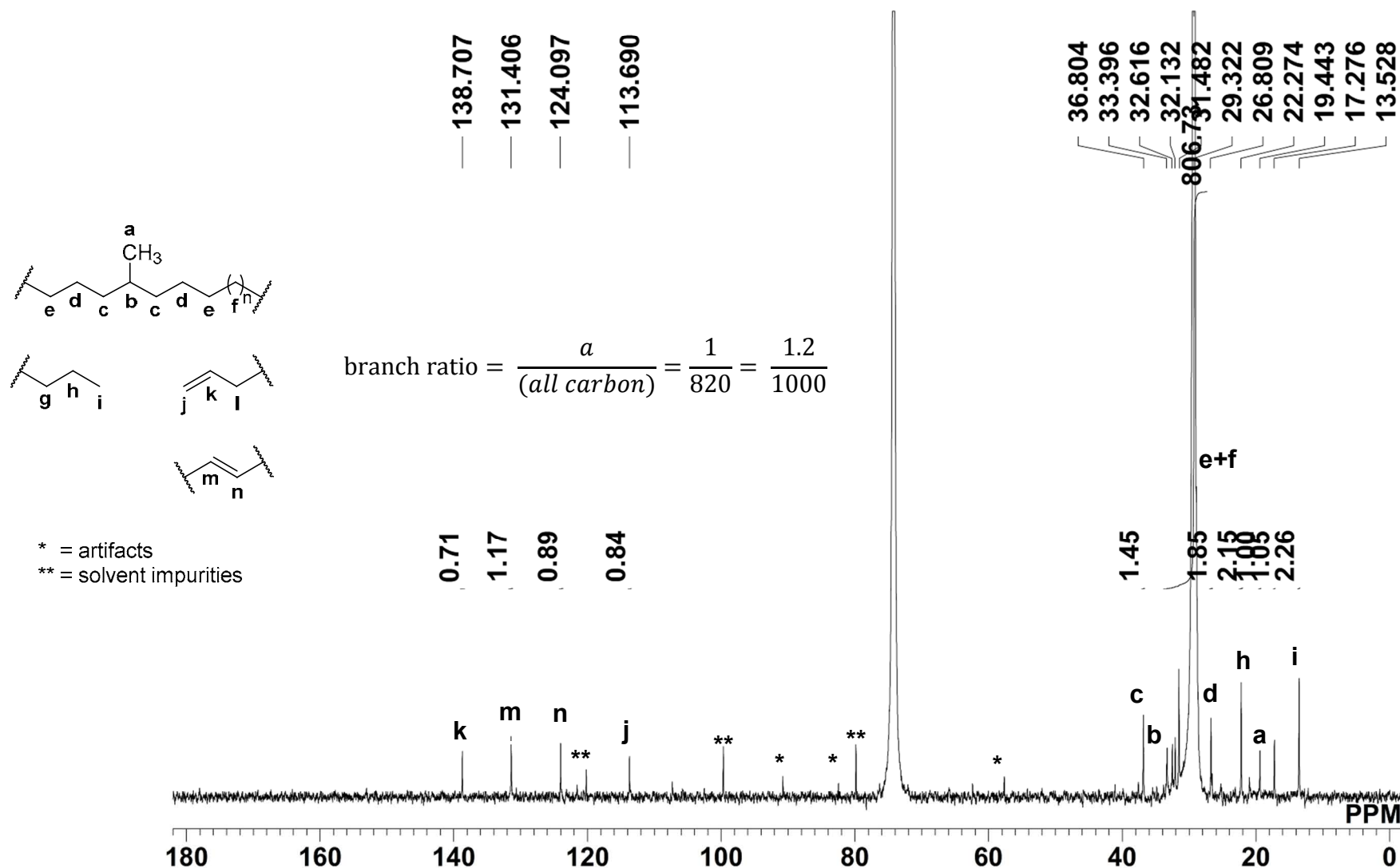
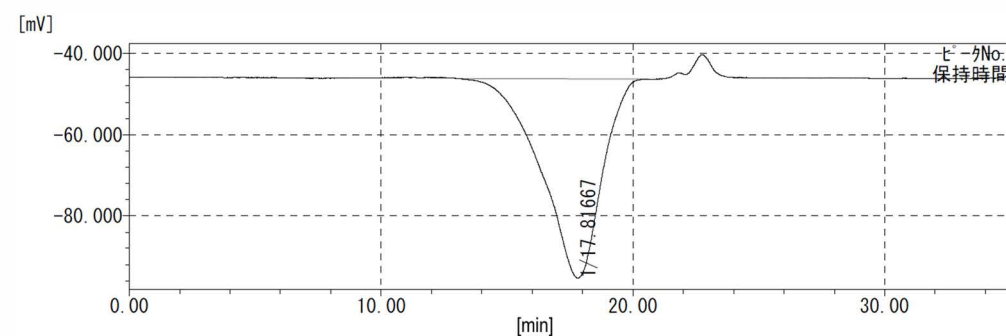


Figure S1. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M Cr(acac)₃, 120 °C) of polyethylene obtained by [2-(*t*-Bu₂P)C₆H₄SO₃]₂PdMe(2,6-lutidine) under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 2).

Sample name : 73-08-112
 Database name : mike.mdb
 Saved file name : RSLT0293
 Method data : RSLT0291

Measurement date : 2014/06/26 03:14:14
 Calculation date : 2014/06/26 14:16:08



	[min]	[mV]	[MOL]
Peak start	13.18	-46.227	2,092.013
Peak top	17.82	-95.334	15,803
Peak end	20.63	-46.285	236
Area [mV * sec]		7,441.343	
Area [%]		100.000	
Height [mV]		49.071	
[η]		64,541.75991	

Mn	:	10,365
Mw	:	64,542
Mz	:	311,417
Mz+1	:	690,353
Mv	:	64,542
Mp	:	17,418
Mz/Mw	:	4.825
Mw/Mn	:	6.227
Mz+1/Mw	:	10.696

Figure S2. SEC chart of polyethylene obtained by $[2-(t\text{-Bu}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 2).

M_n (PS) = 10,400 was corrected to M_n (PE) = 4,500 by universal calibration.

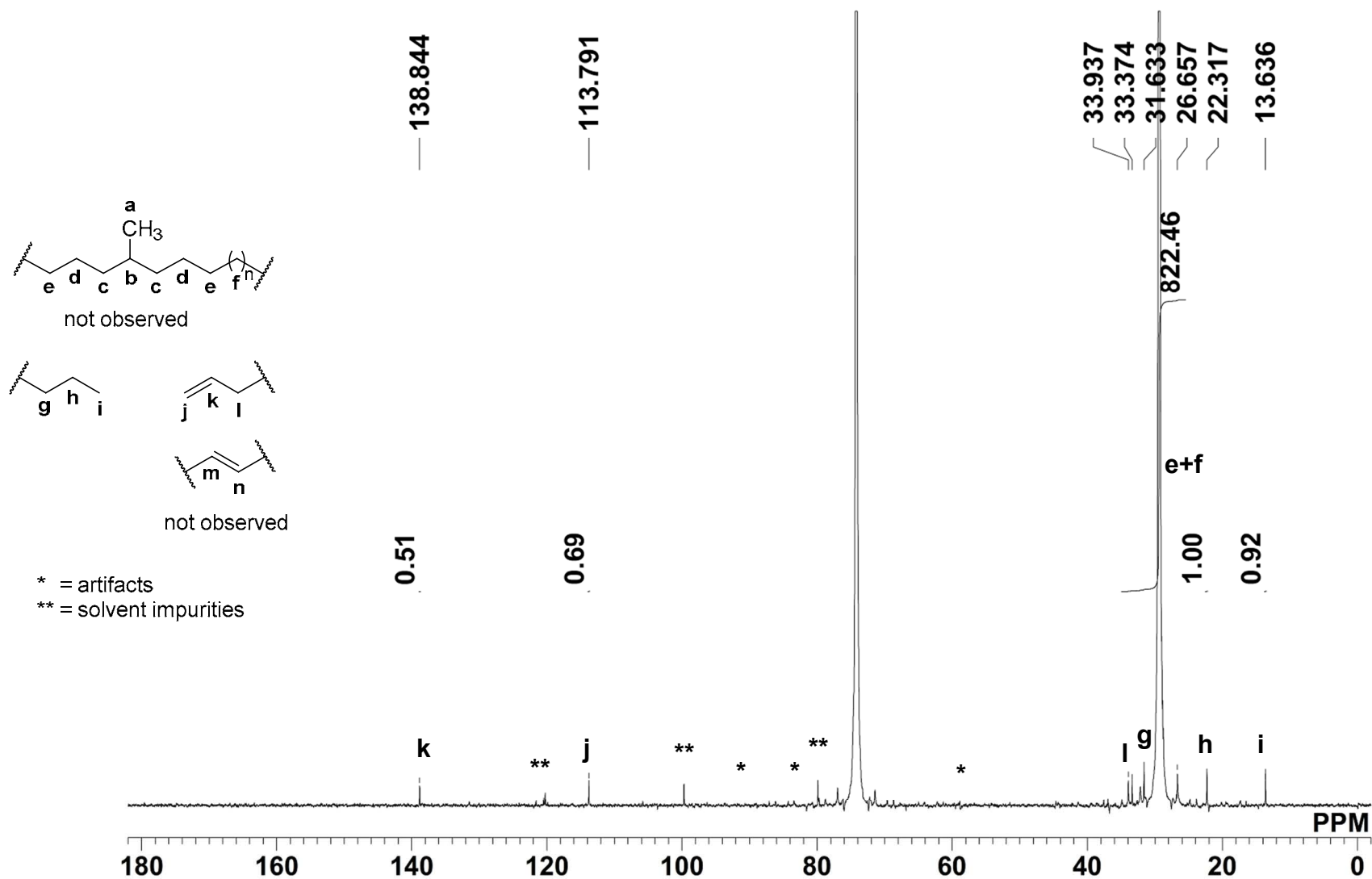
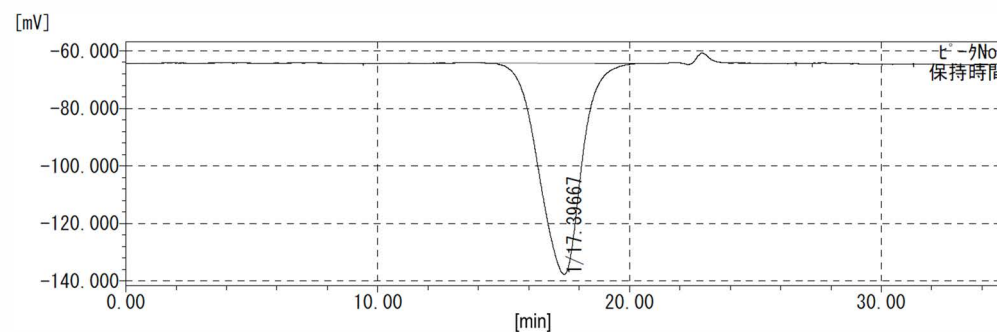


Figure S3. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of polyethylene obtained by $[2-(i\text{-Pr}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 1.0 MPa of ethylene pressure at 80 $^\circ\text{C}$ (Table 1, entry 5).

Sample name : 73-08-113
 Database name : mike.mdb
 Saved file name : RSLT0299
 Method data : RSLT0291

Measurement date : 2014/07/03 18:52:50
 Calculation date : 2014/07/03 20:55:07



	[min]	[mV]	[MOL]
Peak start	14.01	-64.228	1,058,858
Peak top	17.40	-137.790	27,350
Peak end	20.63	-64.384	236
Area [mV * sec]		8,039.466	
Area [%]		100.000	
Height [mV]		73.482	
[η]		49,374.12828	

Mn	:	19,330
Mw	:	49,374
Mz	:	105,192
Mz+1	:	196,612
Mv	:	49,374
Mp	:	28,909
Mz/Mw	:	2.131
Mw/Mn	:	2.554
Mz+1/Mw	:	3.982

Figure S4. SEC chart of polyethylene obtained by $[2-(i\text{-Pr}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 5).

M_n (PS) = 8,400 was corrected to M_n (PE) = 26,000 by universal calibration.

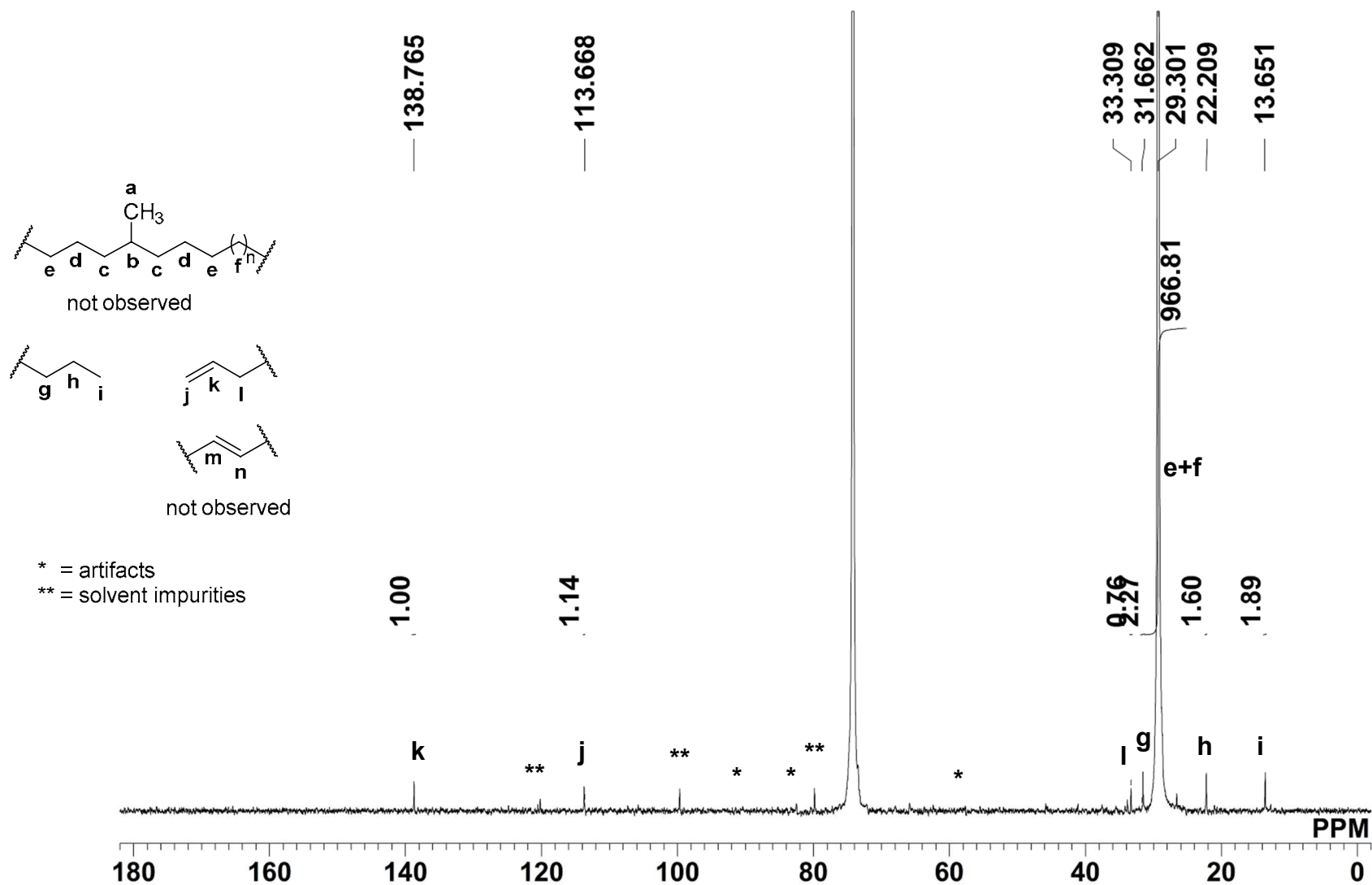
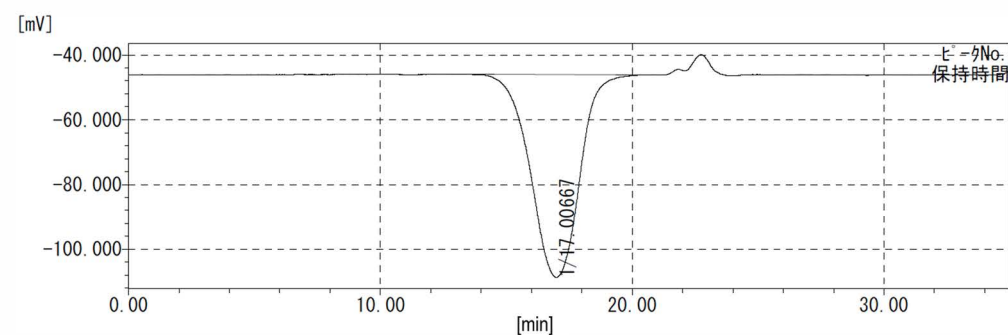


Figure S5. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of polyethylene obtained by $[\text{2-(Cy}_2\text{P)C}_6\text{H}_4\text{SO}_3]\text{PdMe(2,6-lutidine)}$ under 1.0 MPa of ethylene pressure at 80 $^\circ\text{C}$ (Table 1, entry 7).

Sample name : 73-08-114
 Database name : mike.mdb
 Saved file name : RSLT0294
 Method data : RSLT0291

Measurement date : 2014/06/26 03:59:18
 Calculation date : 2014/06/26 10:08:42



	[min]	[mV]	[MOL]
Peak start	13.30	-45.936	1,910,090
Peak top	17.01	-108.692	44,680
Peak end	20.34	-46.158	383
Area [mV * sec]		7,761.280	
Area [%]		100.000	
Height [mV]		62.639	
[η]		76,909.70165	

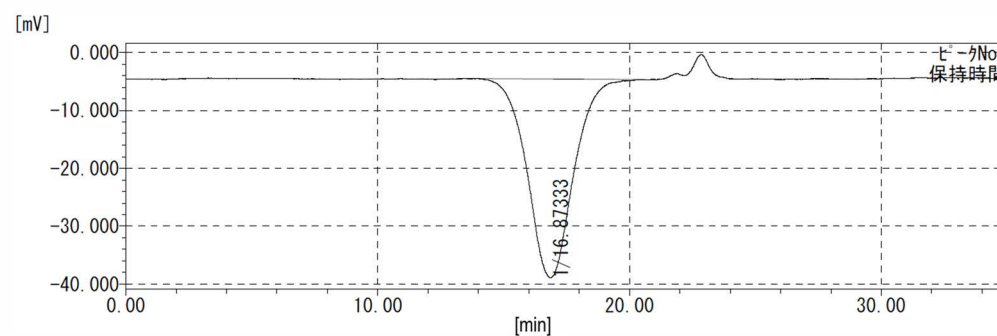
Mn	:	27,183
Mw	:	76,910
Mz	:	183,563
Mz+1	:	380,900
Mv	:	76,910
Mp	:	50,115
Mz/Mw	:	2.387
Mw/Mn	:	2.829
Mz+1/Mw	:	4.953

Figure S6. SEC chart of polyethylene obtained by $[2-(\text{Cy}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 7).

M_n (PS) = 27,200 was corrected to M_n (PE) = 12,000 by universal calibration.

Sample name : 73-09-074
 Database name : mike.mdb
 Saved file name : RSLT0339
 Method data : RSLT0291

Measurement date : 2014/08/06 16:51:49
 Calculation date : 2014/08/06 20:07:30



	[min]	[mV]	[MOL]
Peak start	13.54	-4.490	1,579,985
Peak top	16.87	-38.930	52,626
Peak end	20.63	-4.679	236
Area [mV * sec]		4,000.714	
Area [%]		100.000	
Height [mV]		34.351	
[η]		77,845.38471	

Mn	:	27,146
Mw	:	77,845
Mz	:	165,946
Mz+1	:	309,285
Mv	:	77,845
Mp	:	55,927
Mz/Mw	:	2.132
Mw/Mn	:	2.868
Mz+1/Mw	:	3.973

Figure S8. SEC chart of polyethylene obtained by $[2-(\text{Cy}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 3.0 MPa of ethylene pressure at 80 °C in the presence of additional 9.0 equivalent of 2,6-lutidine (Table 1, entry 9). $M_n(\text{PS}) = 27,100$ was corrected to $M_n(\text{PE}) = 12,000$ by universal calibration.

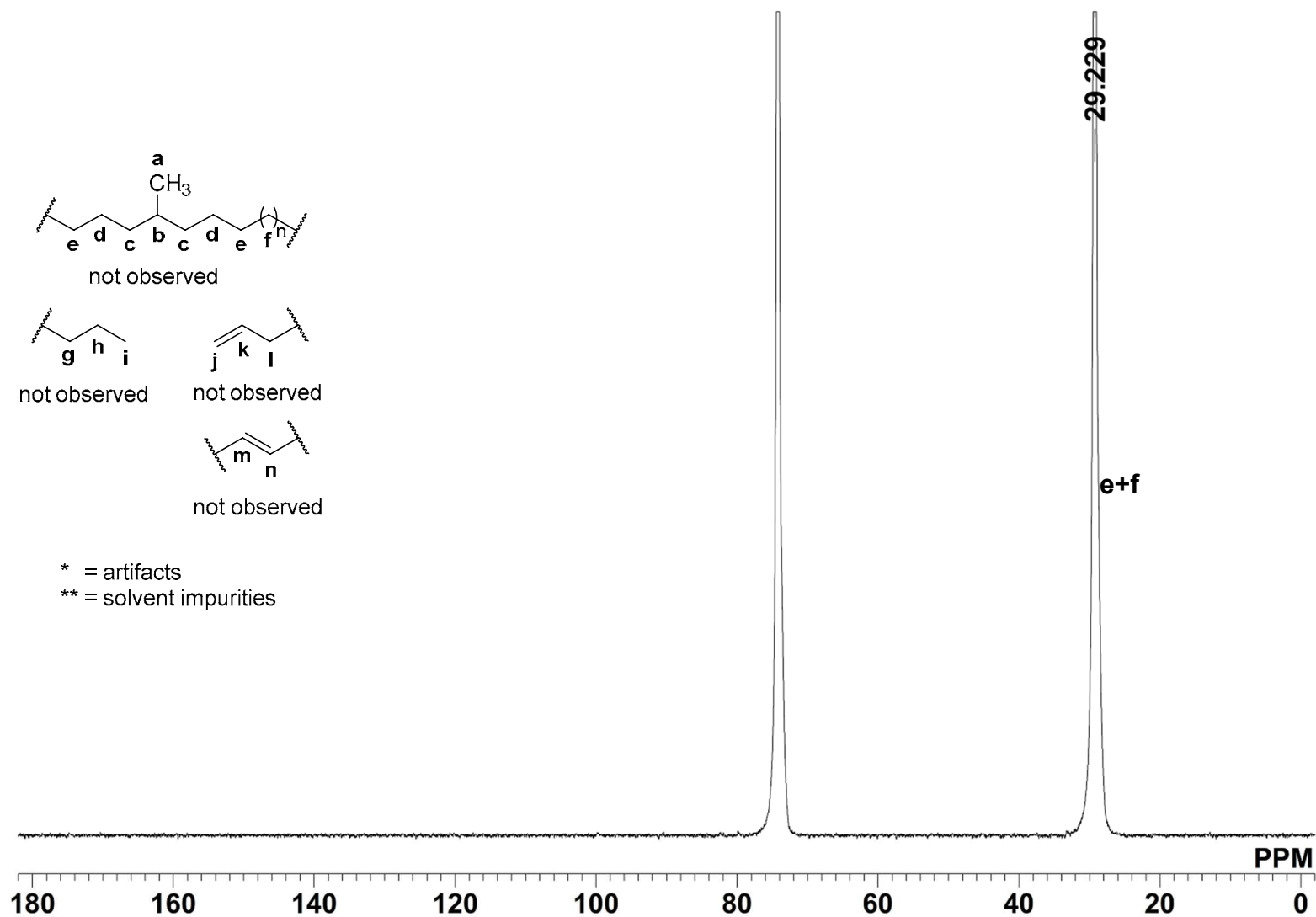
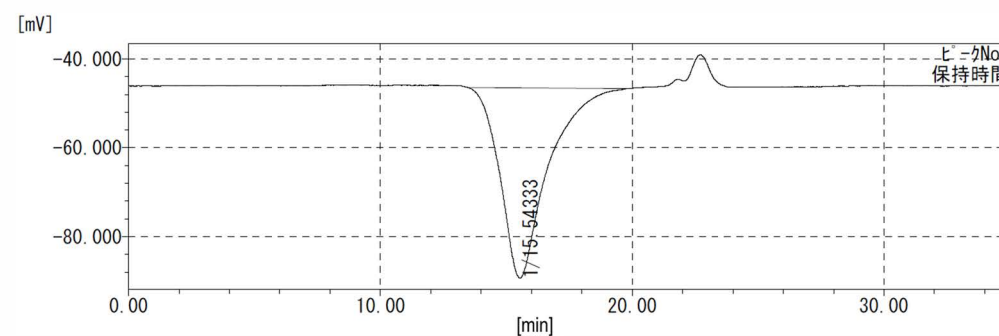


Figure S9. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M Cr(acac)₃, 120 °C) of polyethylene obtained by [2-(Men₂P)C₆H₄SO₃]PdMe(2,6-lutidine) under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 11).

Sample name : 73-08-115
 Database name : mike.mdb
 Saved file name : RSLT0295
 Method data : RSLT0291

Measurement date : 2014/06/26 04:44:23
 Calculation date : 2014/06/26 14:11:52



	[min]	[mV]	[MOL]
Peak start	13.48	-46.451	1,658,931
Peak top	15.54	-89.344	239,924
Peak end	19.80	-46.665	894
Area [mV * sec]		5,079.734	
Area [%]		100.000	
Height [mV]		42.823	
[η]		248,852.00733	

Mn	:	67,827
Mw	:	248,852
Mz	:	428,648
Mz+1	:	600,605
Mv	:	248,852
Mp	:	252,960
Mz/Mw	:	1.723
Mw/Mn	:	3.669
Mz+1/Mw	:	2.414

Figure S10. SEC chart of polyethylene obtained by $[2-(\text{Men}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 11).

M_n (PS) = 67,800 was corrected to M_n (PE) = 29,000 by universal calibration.

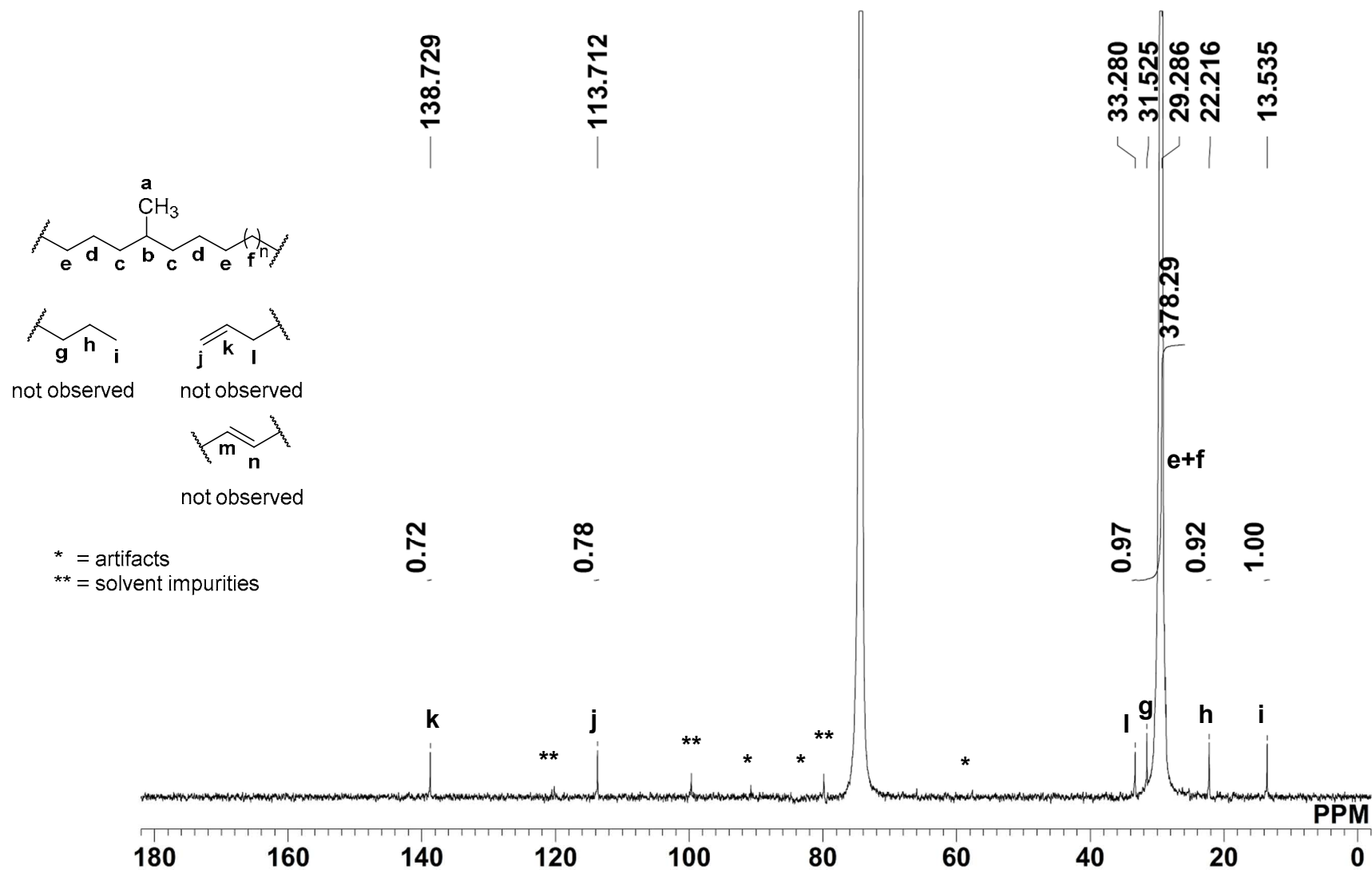
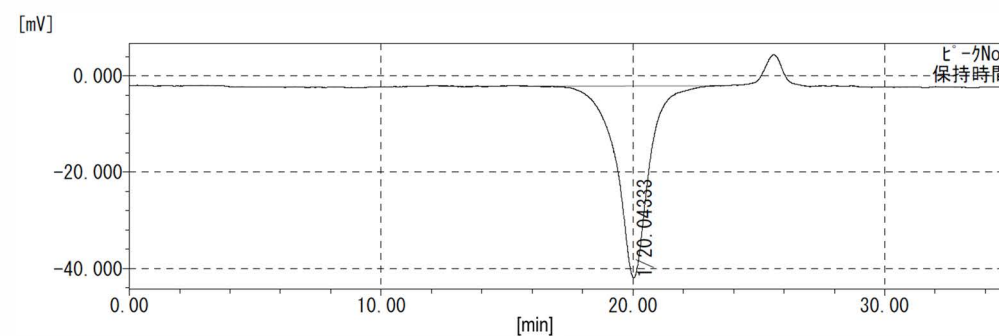


Figure S11. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, $1,1,2,2$ -tetrachloroethane, 0.05-M Cr(acac)_3 , 120°C) of polyethylene obtained by $[2\text{-(Ph}_2\text{P)C}_6\text{H}_4\text{SO}_3]\text{PdMe(2,6-lutidine)}$ under 3.0 MPa of ethylene pressure at 80°C (Table 1, entry 12).

Sample name : 73-09-070
 Database name : mike.mdb
 Saved file name : RSLT0669
 Method data : 20150605

Measurement date : 2015/06/18 20:32:07
 Calculation date : 2015/09/20 21:18:31



	[min]	[mV]	[MOL]
Peak start	16.08	-2.175	551.385
Peak top	20.04	-41.933	16.103
Peak end	23.65	-2.089	122
Area [mV * sec]		3,296.214	
Area [%]		100.000	
Height [mV]		39.803	
[η]		22,959.75092	

Mn	:	11,542
Mw	:	22,960
Mz	:	47,523
Mz+1	:	119,397
Mv	:	22,960
Mp	:	16,631
Mz/Mw	:	2.070
Mw/Mn	:	1.989
Mz+1/Mw	:	5.200

Figure S12. SEC chart of polyethylene obtained by $[2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 3.0 MPa of ethylene pressure at 80 °C (Table 1, entry 12).

M_n (PS) = 11,500 was corrected to M_n (PE) = 5,000 by universal calibration.

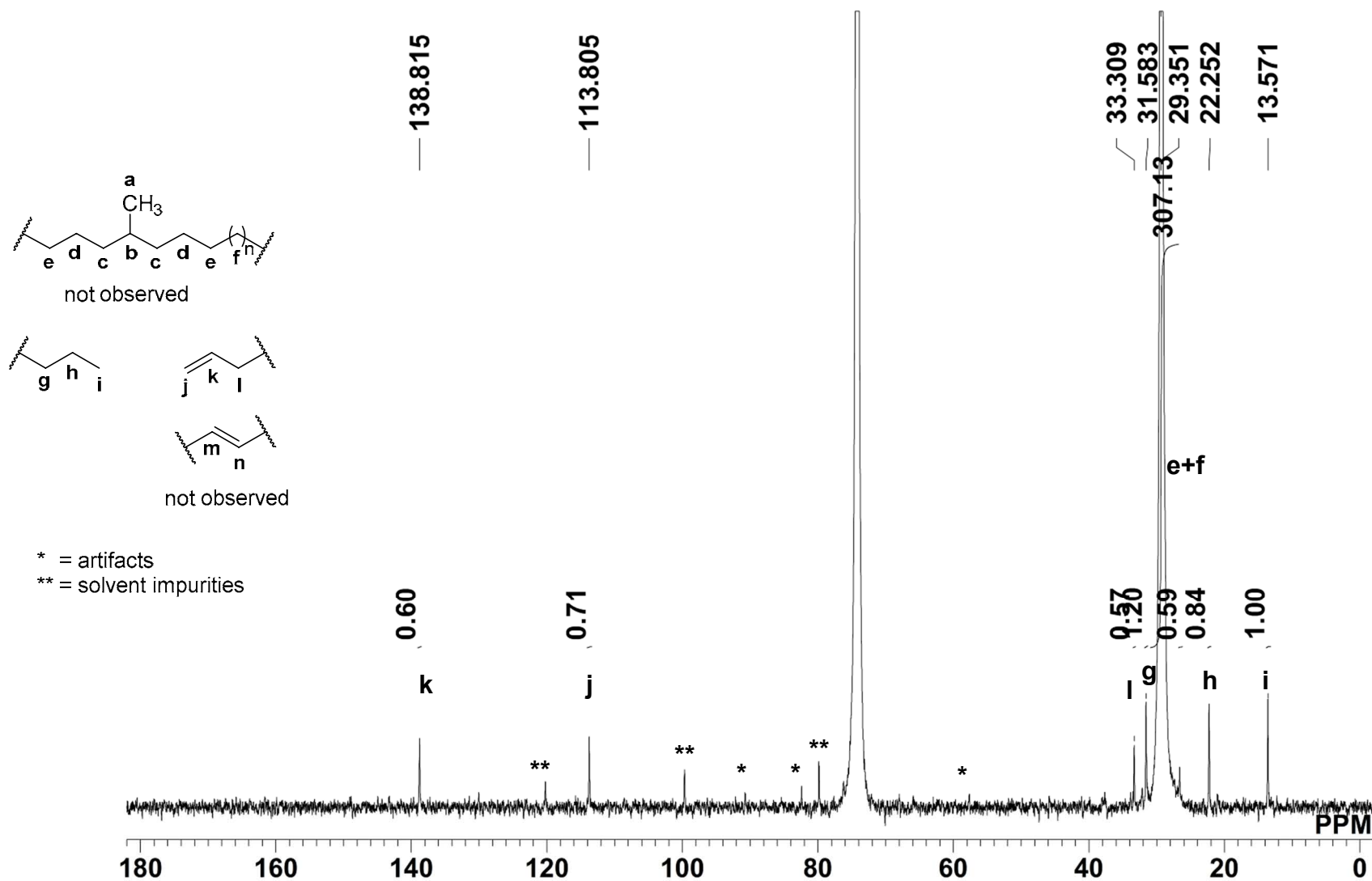
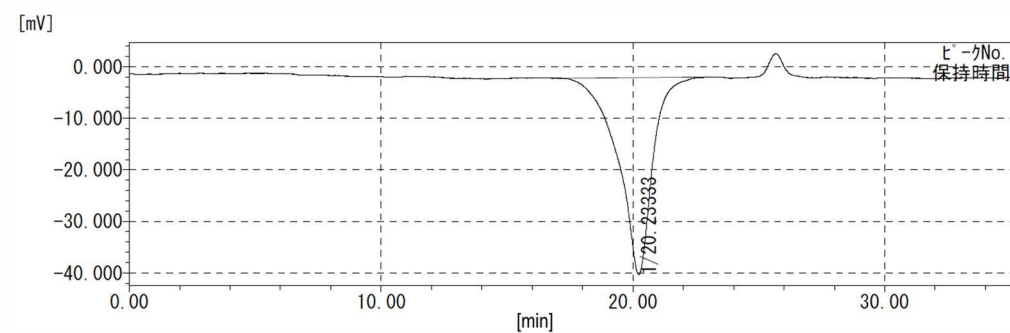


Figure S13. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, $1,1,2,2$ -tetrachloroethane, $0.05\text{-M Cr}(\text{acac})_3$, 120°C) of polyethylene obtained by $[2\text{-(Ph}_2\text{P)C}_6\text{H}_4\text{SO}_3]\text{PdMe(2,6-lutidine)}$ under 1.0 MPa of ethylene pressure at 80°C (Table 1, entry 13).

Sample name : 73-09-071
 Database name : mike.mdb
 Saved file name : RSLT0667
 Method data : 20150605

Measurement date : 2015/06/18 18:22:07
 Calculation date : 2015/06/18 20:29:19



	[min]	[mV]	[MOL]
Peak start	16.79	-2.238	315.977
Peak top	20.23	-40.297	13.098
Peak end	23.06	-1.993	319
Area [mV * sec]		3.261.705	
Area [%]		100.000	
Height [mV]		38.194	
[η]		21,790.41028	

Mn	:	11,742
Mw	:	21,790
Mz	:	41,310
Mz+1	:	72,385
Mv	:	21,790
Mp	:	13,243
Mz/Mw	:	1.896
Mw/Mn	:	1.856
Mz+1/Mw	:	3.322

Figure S14. SEC chart of polyethylene obtained by $[2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 13).

M_n (PS) = 11,700 was corrected to M_n (PE) = 5,100 by universal calibration.

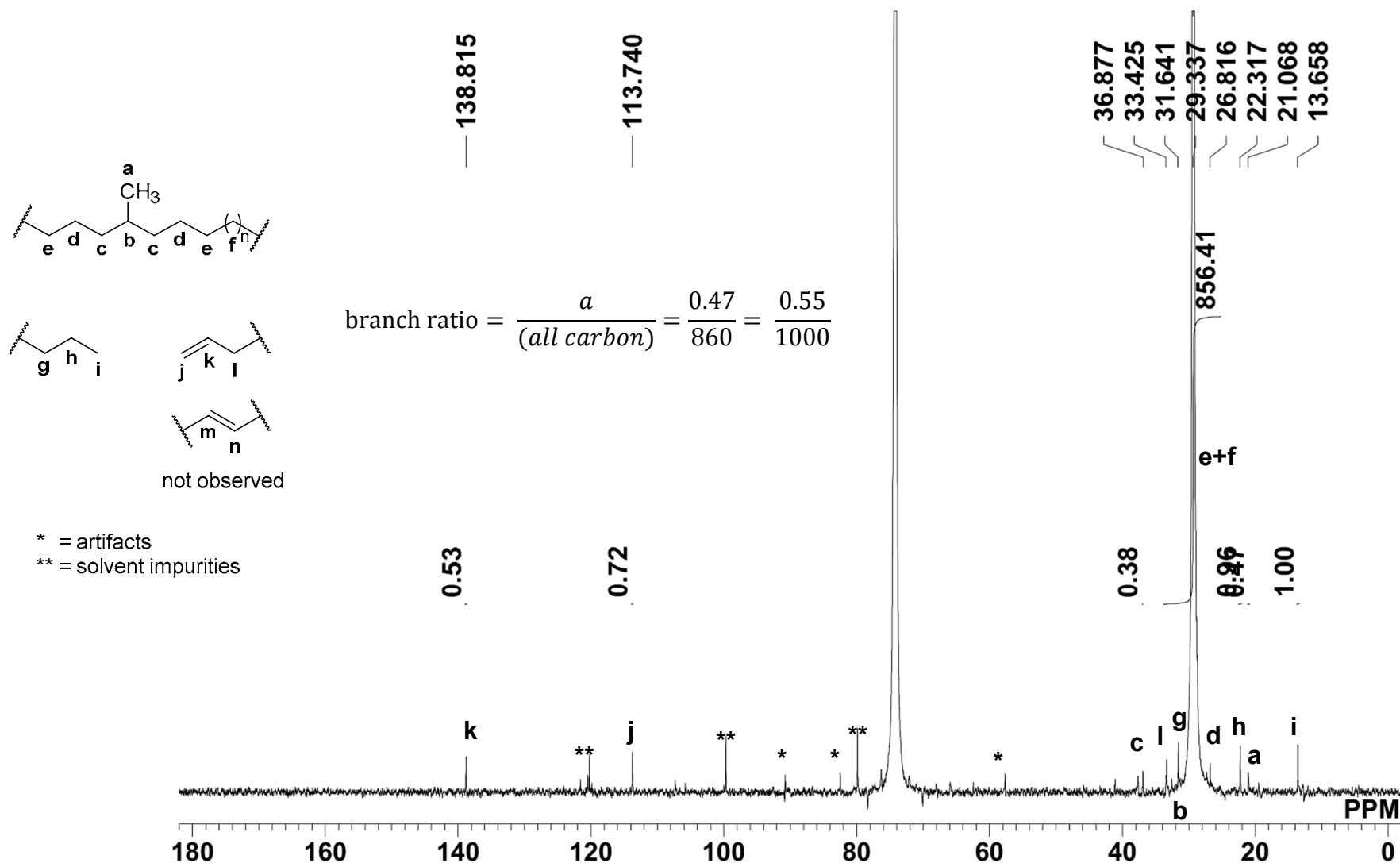
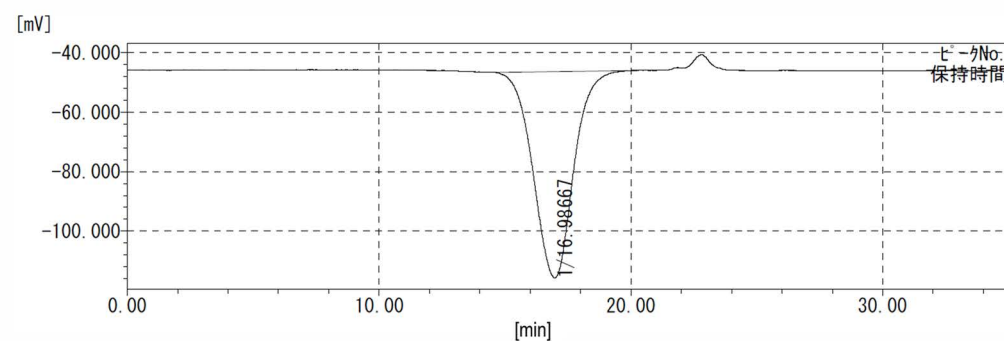


Figure S15. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of polyethylene obtained by $[2-(o\text{-Ani}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 3.0 MPa of ethylene pressure at 80 $^\circ\text{C}$ (Table 1, entry 16).

Sample name : 73-08-109
 Database name : mike.mdb
 Saved file name : RSLT0290
 Method data : RSLT0291

Measurement date : 2014/06/26 00:59:16
 Calculation date : 2014/06/26 10:04:33



	[min]	[mV]	[MOL]
Peak start	14.66	-46.703	584.364
Peak top	16.99	-115.740	45.796
Peak end	19.86	-46.054	814
Area [mV * sec]		7,040.892	
Area [%]		100.000	
Height [mV]		69.327	
[η]		66,073.89301	

Mn	:	31,561
Mw	:	66,074
Mz	:	116,336
Mz+1	:	179,984
Mv	:	66,074
Mp	:	48,702
Mz/Mw	:	1.761
Mw/Mn	:	2.094
Mz+1/Mw	:	2.724

Figure S16. SEC chart of polyethylene obtained by $[2-(o\text{-Ani}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 3.0 MPa of ethylene pressure at 80 °C (Table 1, entry 16).

M_n (PS) = 31,600 was corrected to M_n (PE) = 14,000 by universal calibration.

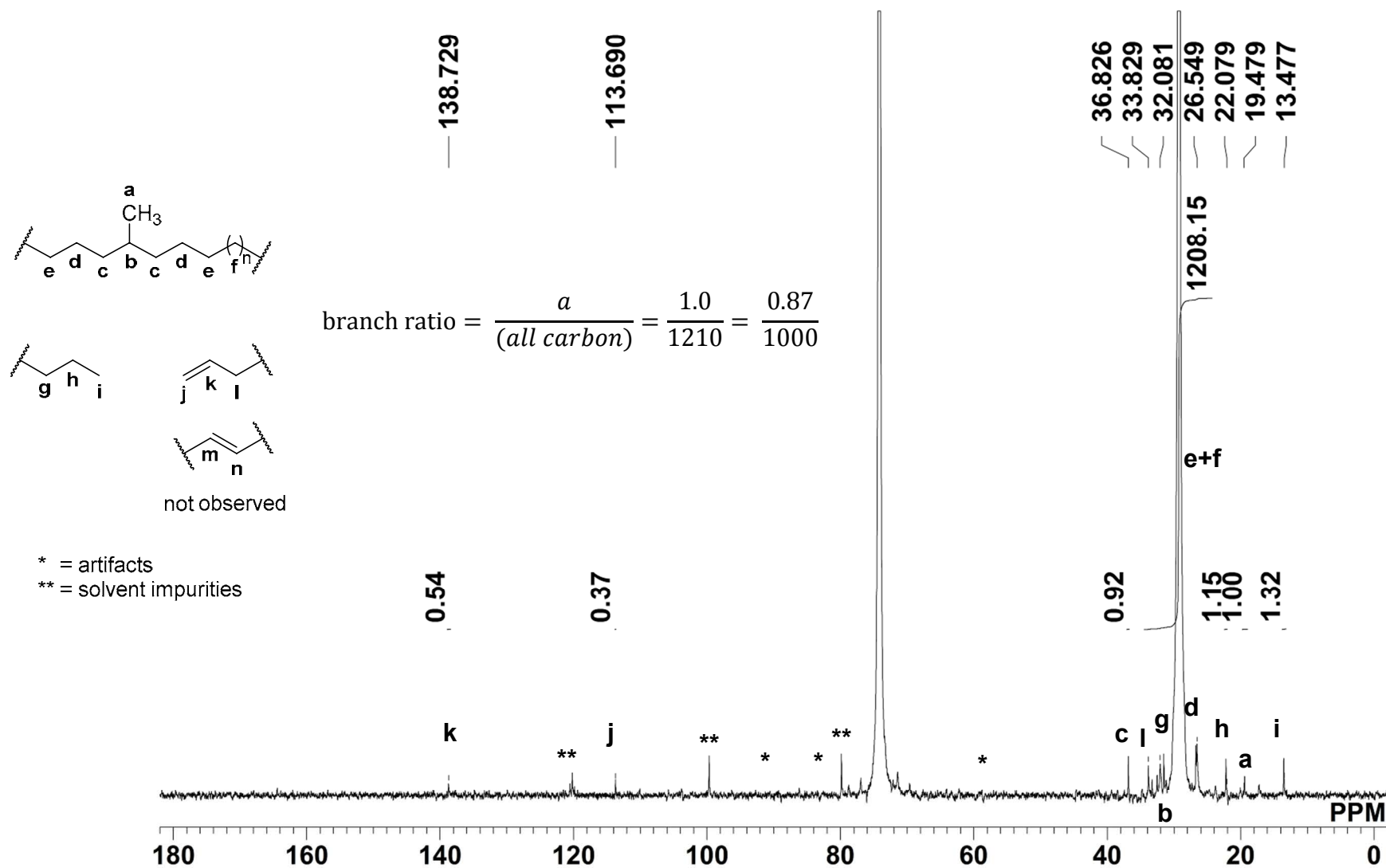
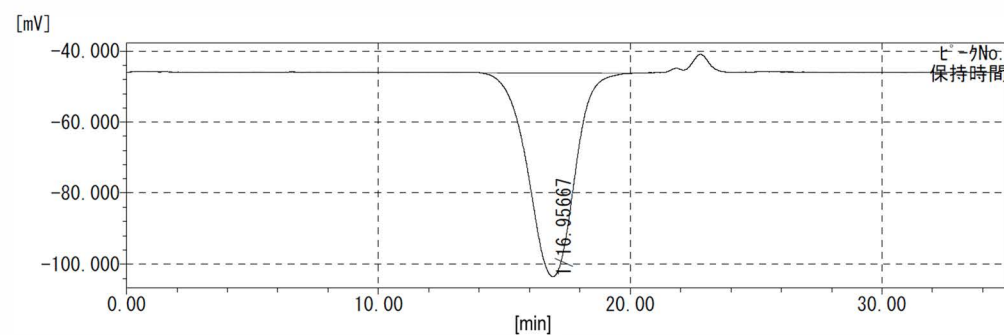


Figure S17. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of polyethylene obtained by $[2\text{-(}o\text{-Ani}_2\text{P)C}_6\text{H}_4\text{SO}_3]\text{PdMe(2,6-lutidine)}$ under 1.0 MPa of ethylene pressure at 80 $^\circ\text{C}$ (Table 1, entry 17).

Sample name : 73-08-110
 Database name : mike.mdb
 Saved file name : RSLT0291
 Method data : RSLT0291

Measurement date : 2014/06/26 01:44:20
 Calculation date : 2014/06/26 10:05:34



	[min]	[mV]	[MOL]		
Peak start	14.01	-46.135	1,058,858	Mn	: 30,965
Peak top	16.96	-103.530	47,520	Mw	: 80,162
Peak end	20.10	-46.218	560	Mz	: 171,679
				Mz+1	: 300,839
Area [mV * sec]		6,821.167		Mv	: 80,162
Area [%]		100.000		Mp	: 53,924
Height [mV]		57.355		Mz/Mw	: 2.142
[η]		80,162.49861		Mw/Mn	: 2.589
				Mz+1/Mw	: 3.753

Figure S18. SEC chart of polyethylene obtained by $[2-(o\text{-Ani}_2\text{P})\text{C}_6\text{H}_4\text{SO}_3]\text{PdMe}(2,6\text{-lutidine})$ under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 17).

M_n (PS) = 30,000 was corrected to M_n (PE) = 13,000 by universal calibration.

III. NMR Spectra from H/D Exchange Experiments

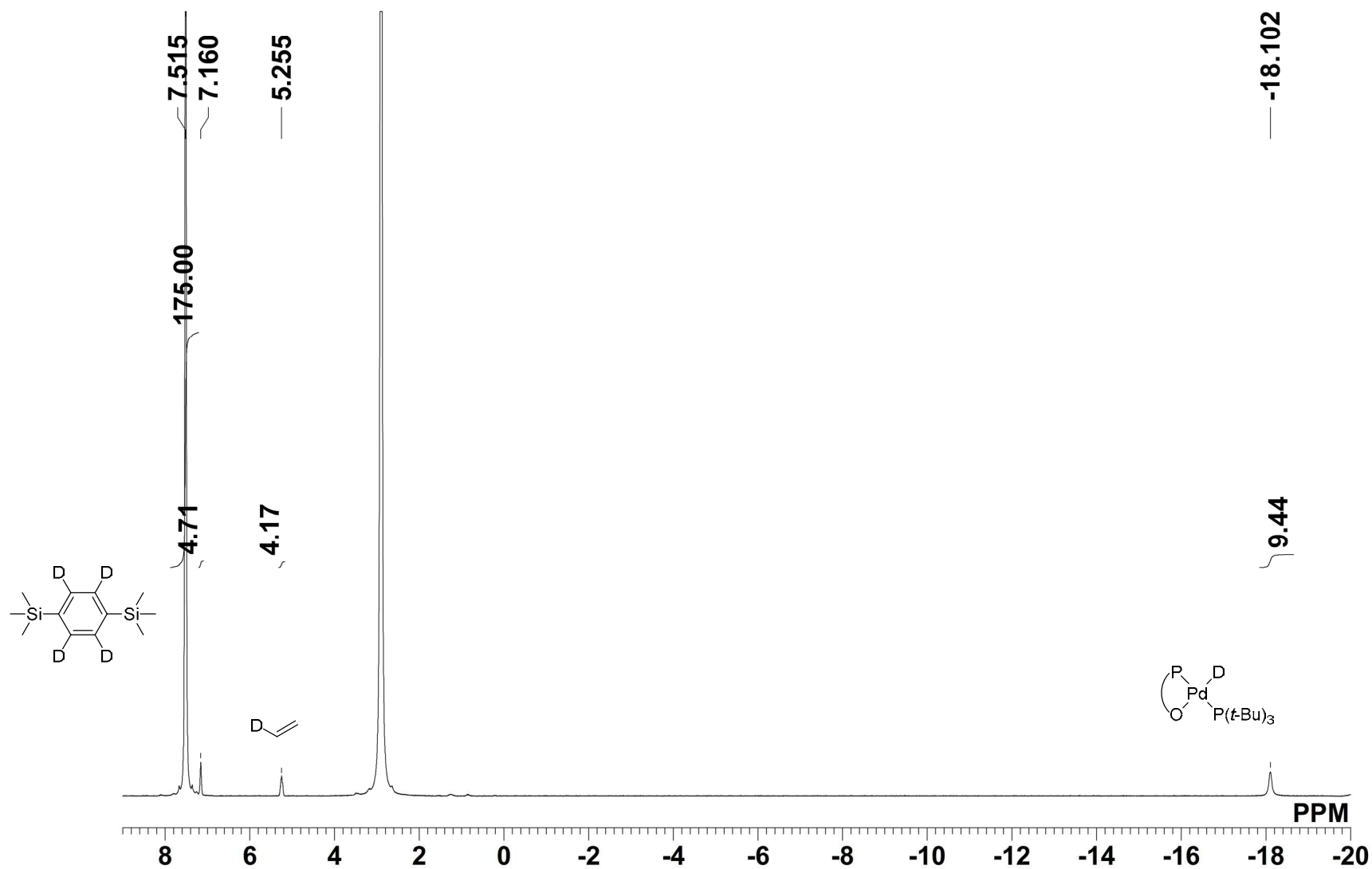


Figure S19. ^2H NMR spectrum (77 MHz, benzene, 25 °C) of the reaction mixture after deuteration of ethylene (Scheme 4).

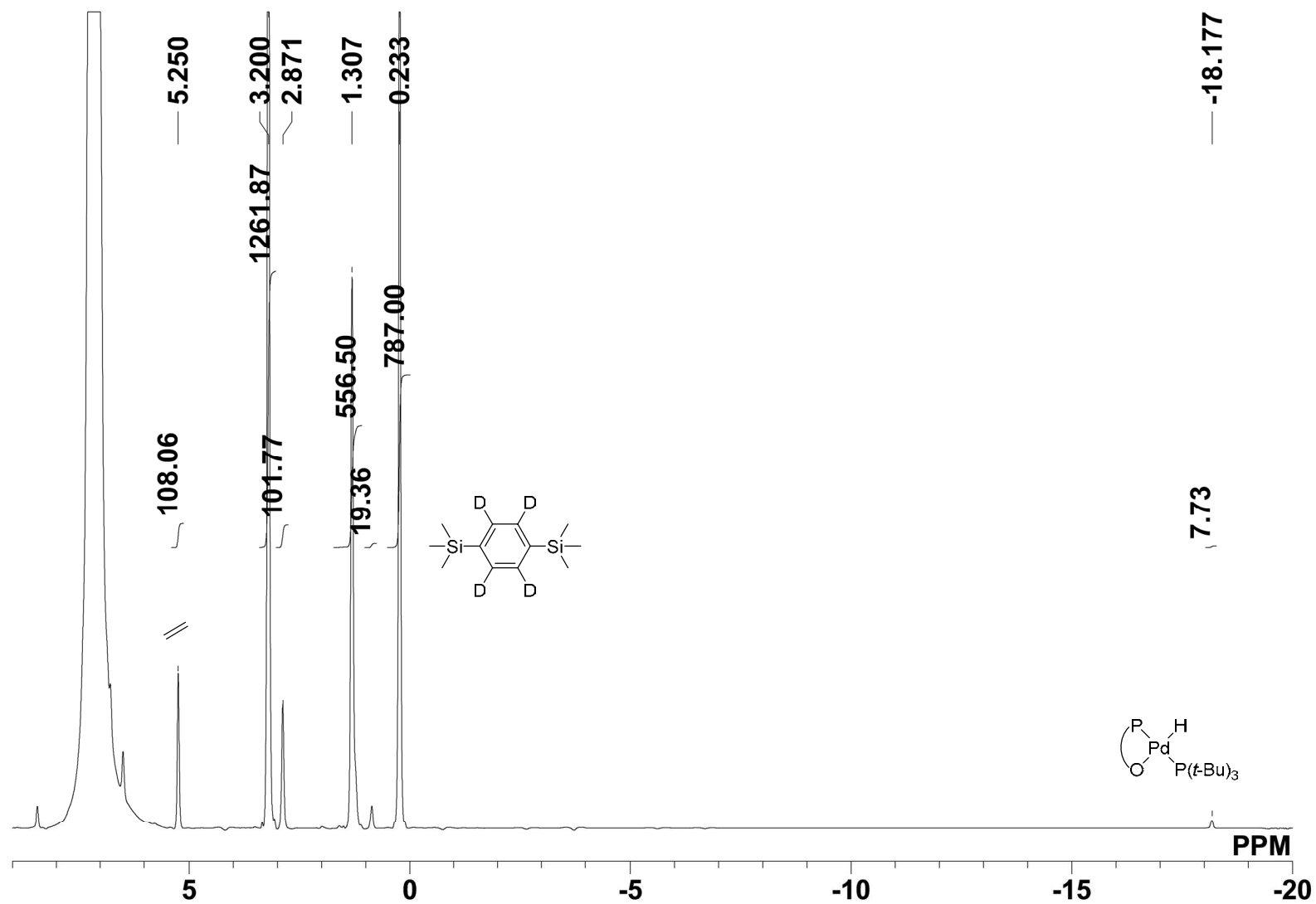


Figure S20. ^1H NMR spectrum (500 MHz, benzene, 25 °C) of the reaction mixture after deuteration of ethylene (Scheme 4).

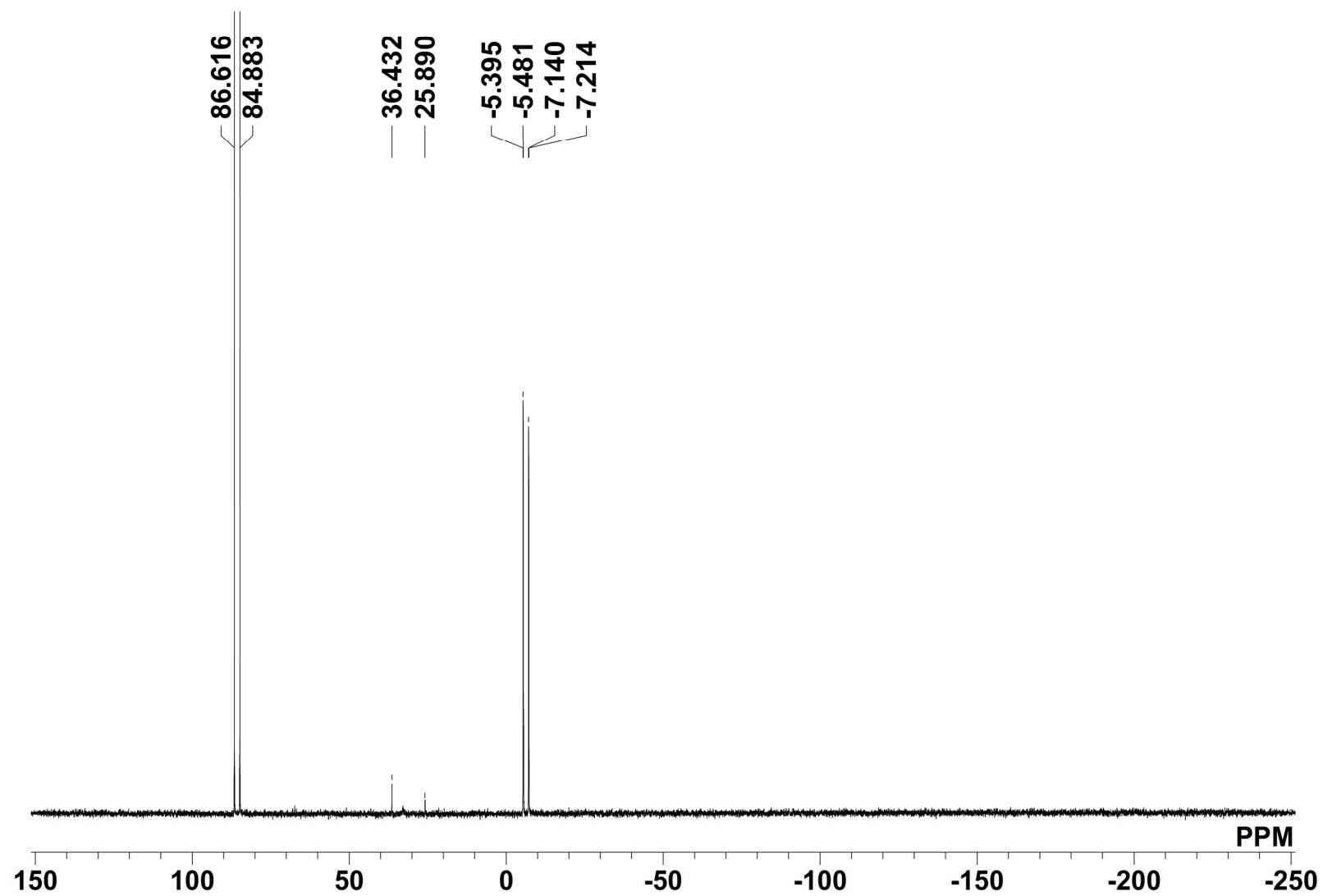


Figure S21. ^{31}P NMR spectrum (202 MHz, benzene, 25 °C) of the reaction mixture after deuteration of ethylene (Scheme 4).

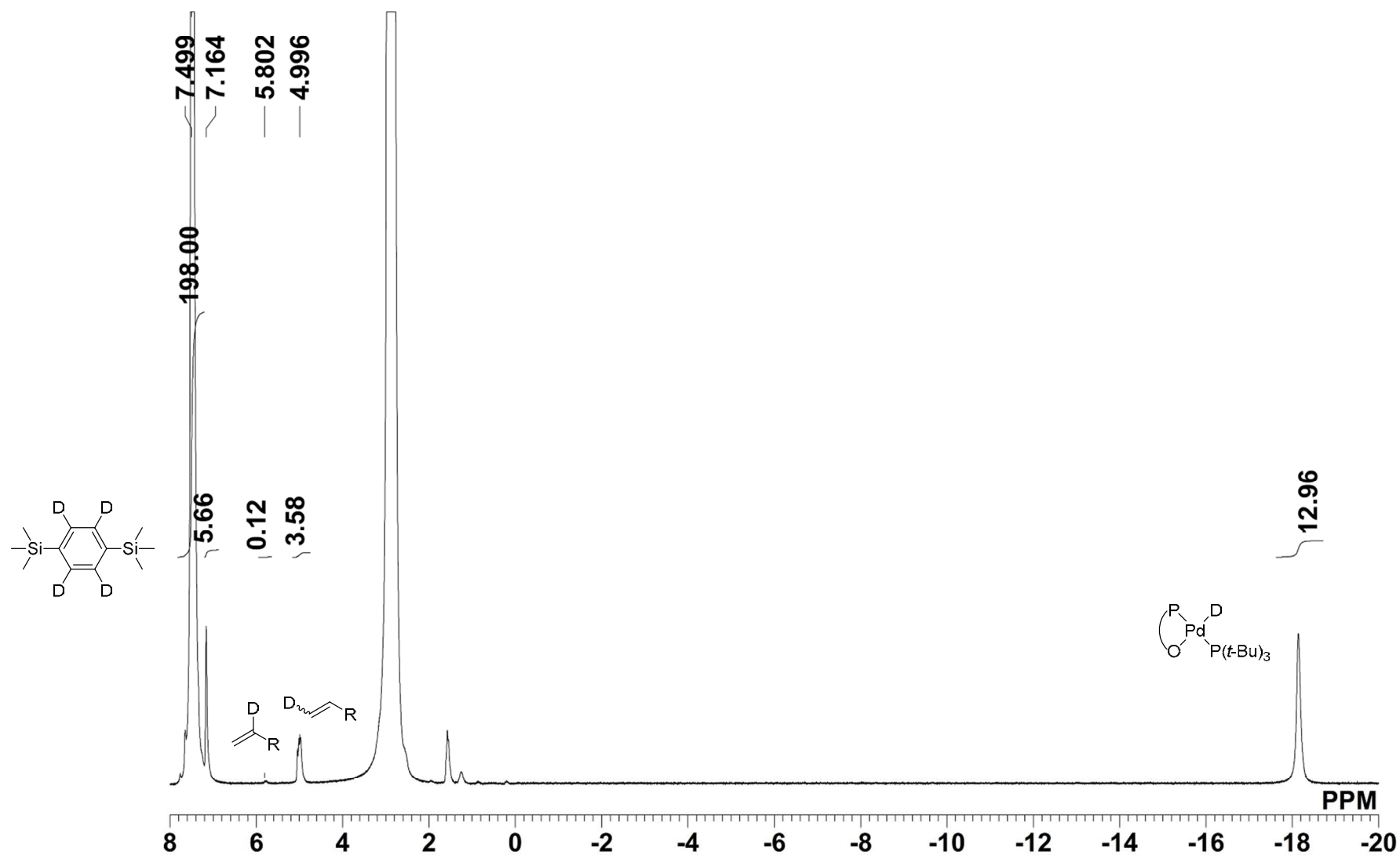


Figure S22. ^{31}P NMR spectrum (77 MHz, benzene, 25 °C) of the reaction mixture after deuteration of 1-eicocene (Scheme 6).

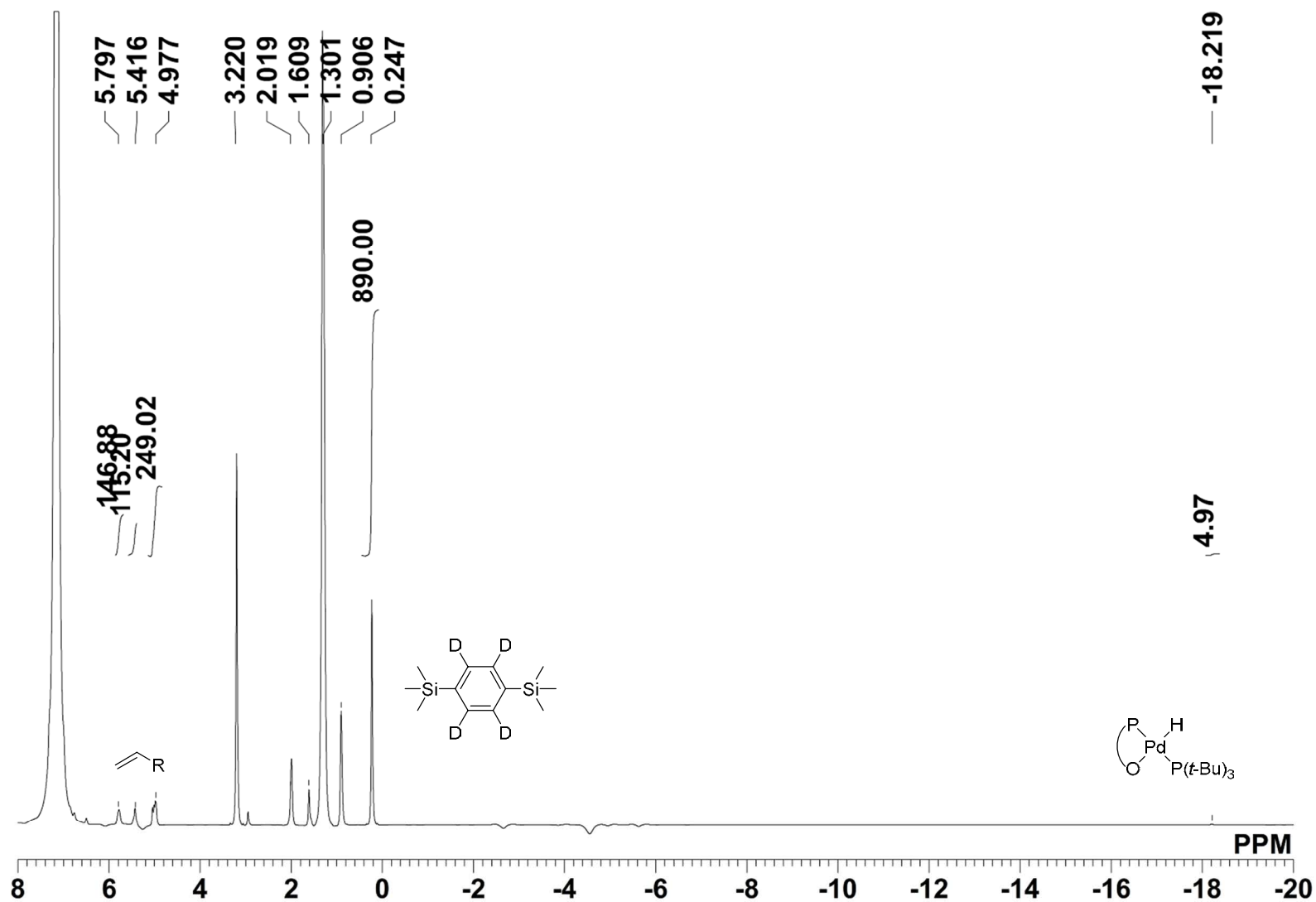


Figure S23. ^1H NMR spectrum (500 MHz, benzene, 25 °C) of the reaction mixture after deuteration of 1-eicocene (Scheme 6).

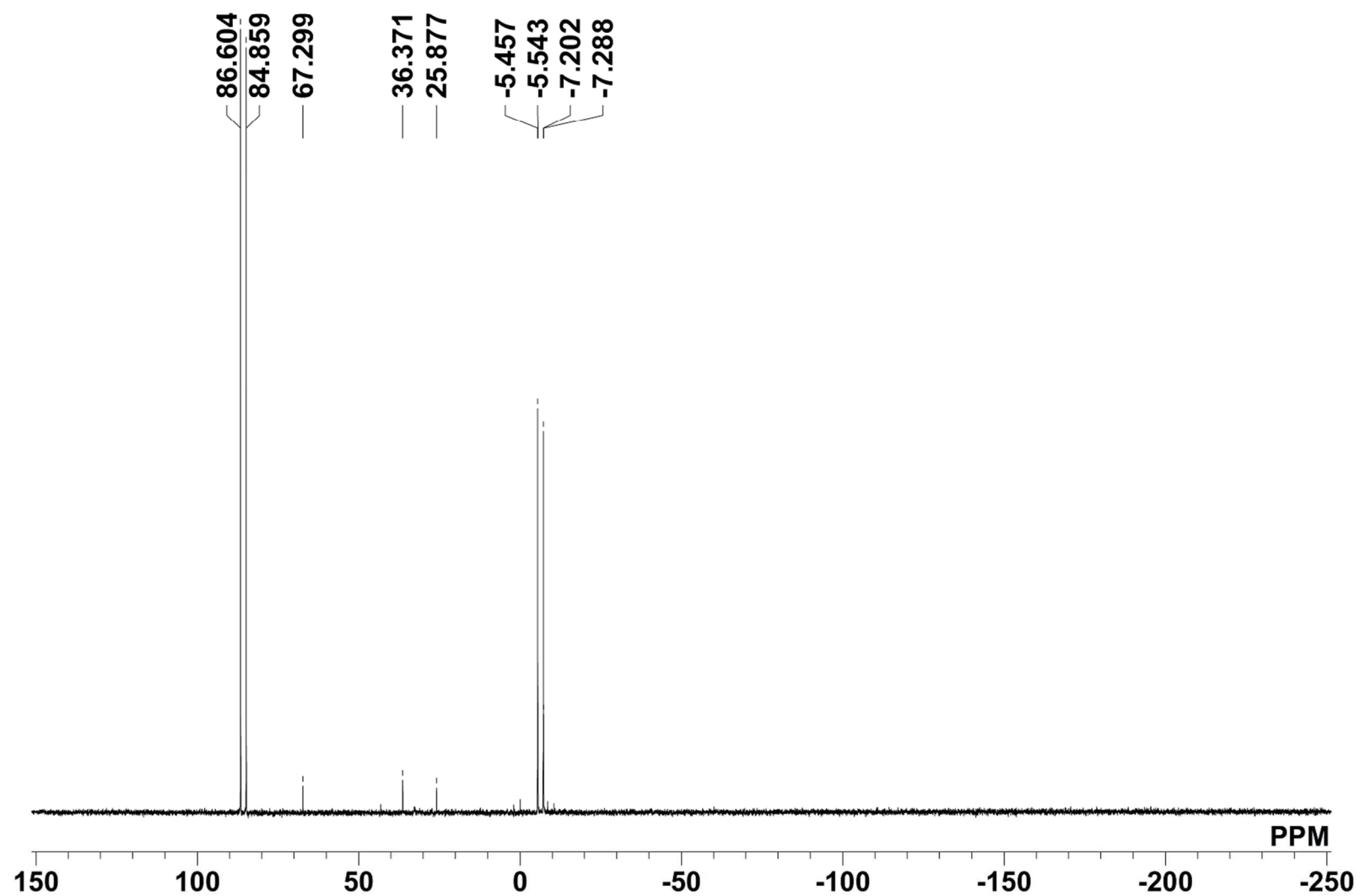


Figure S24. ^{31}P NMR spectrum (202 MHz, benzene, 25 °C) of the reaction mixture after deuteration of 1-eicocene (Scheme 6).

III. References

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