

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.

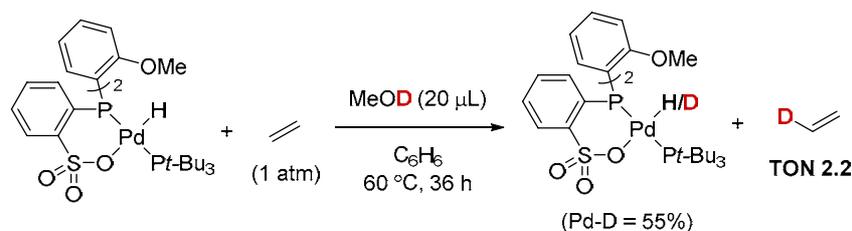
Instrumentation: Nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER Ascend500 (^1H : 500 MHz, ^2H : 77 MHz, ^{13}C : 126 MHz, ^{31}P : 202 MHz) NMR spectrometer. Chemical shift values for protons are referenced to the residual proton resonance of benzene- d_6 (δ : 7.16) or CDCl_3 (δ : 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)

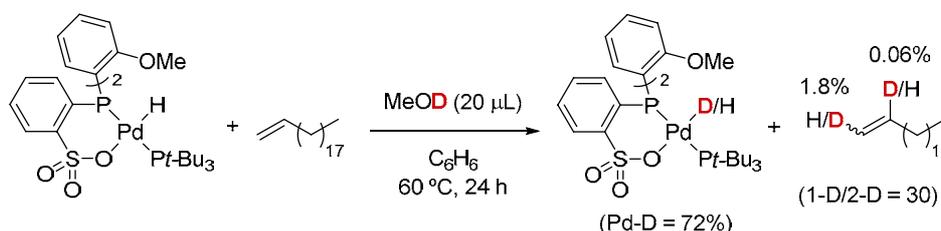
A 300-mL autoclave charged with catalyst (0.010 mmol) and toluene (100 mL) was stirred under ethylene pressure (3.0 MPa or 1.0 MPa) at 80 °C for 1 h. After cooling to room temperature, methanol (200 mL) was added into the autoclave. The polymer was isolated by filtration, washed with methanol, and dried 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

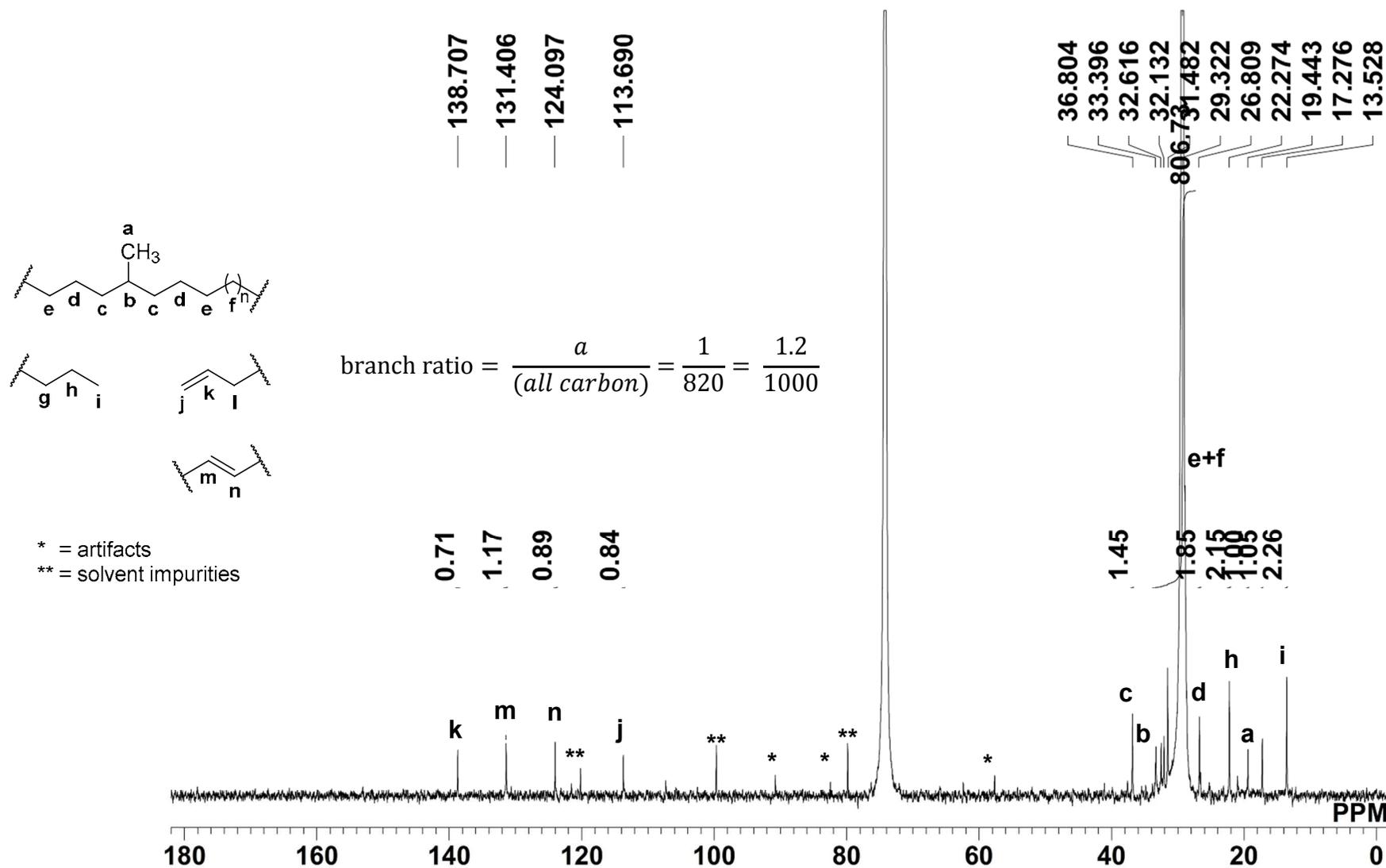
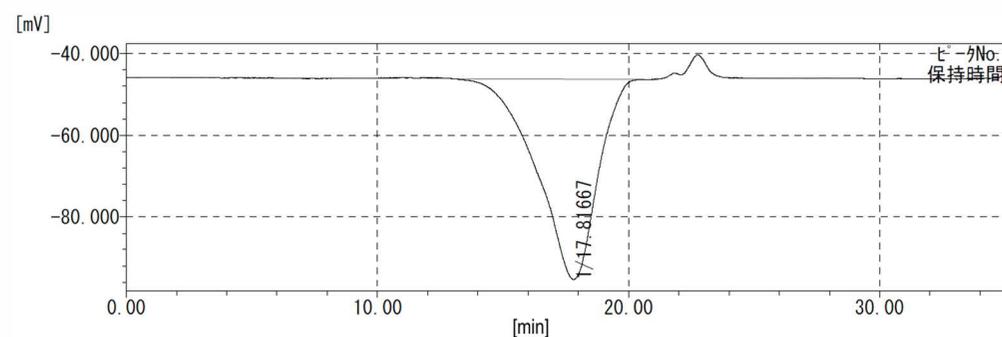


Figure S1. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M Cr(acac)₃, 120 °C) of polyethylene obtained by [2-(*t*-Bu₂P)C₆H₄SO₃]PdMe(2,6-lutidine) under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 2).

Sample name : 73-08-112 Measurement date : 2014/06/26 03:14:14
 Database name : mike.mdb Calculation date : 2014/06/26 14:16:08
 Saved file name : RSLT0293
 Method data : RSLT0291



	[min]	[mV]	[MOL]		
Peak start	13.18	-46.227	2.092.013	Mn	: 10.365
Peak top	17.82	-95.334	15.803	Mw	: 64.542
Peak end	20.63	-46.285	236	Mz	: 311.417
				Mz+1	: 690.353
Area [mV * sec]		7.441.343		Mv	: 64.542
Area [%]		100.000		Mp	: 17.418
Height [mV]		49.071		Mz/Mw	: 4.825
[η]		64.541.75991		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.

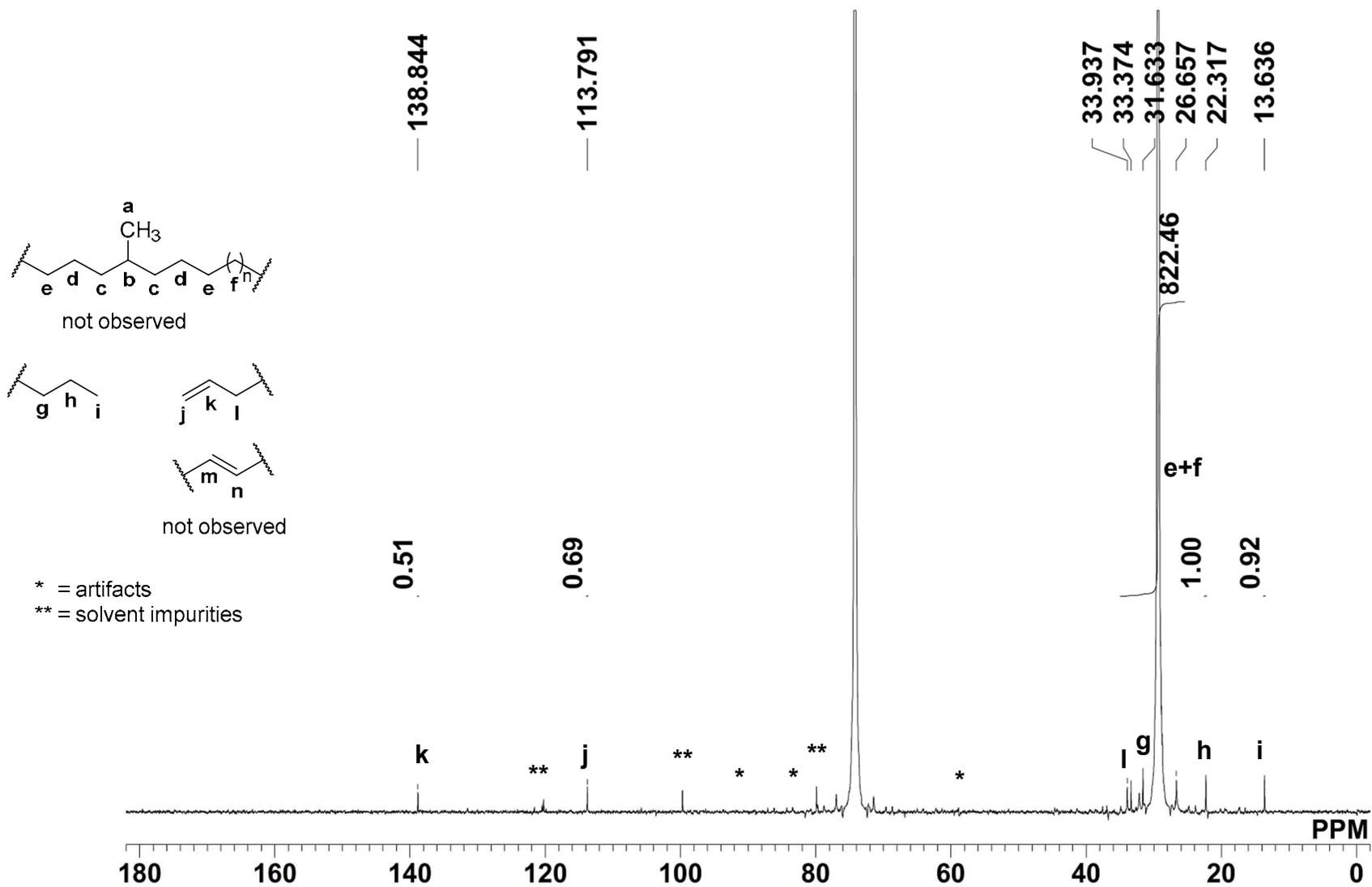
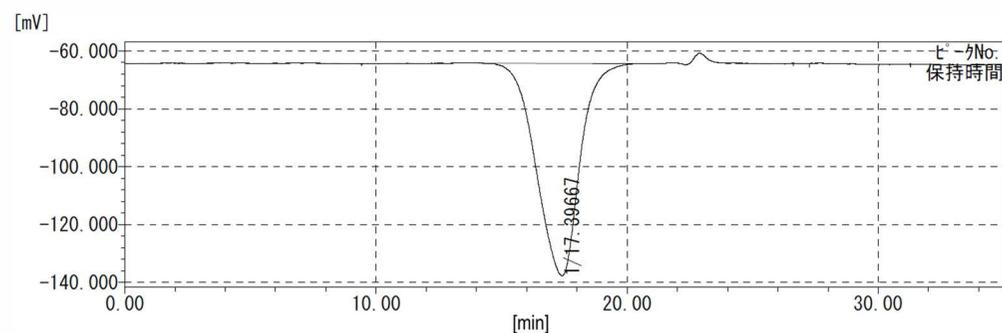


Figure S3. Quantitative ¹³C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M Cr(acac)₃, 120 °C) of polyethylene obtained by [2-(*i*-Pr₂P)C₆H₄SO₃]PdMe(2,6-lutidine) under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 5).

Sample name : 73-08-113 Measurement date : 2014/07/03 18:52:50
 Database name : mike.mdb Calculation date : 2014/07/03 20:55:07
 Saved file name : RSLT0299
 Method data : RSLT0291



	[min]	[mV]	[MOL]		
Peak start	14.01	-64.228	1.058,858	Mn	: 19,330
Peak top	17.40	-137.790	27,350	Mw	: 49,374
Peak end	20.63	-64.384	236	Mz	: 105,192
				Mz+1	: 196,612
Area [mV * sec]		8,039.466		Mv	: 49,374
Area [%]		100.000		Mp	: 28,909
Height [mV]		73.482		Mz/Mw	: 2.131
[η]		49,374.12828		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.

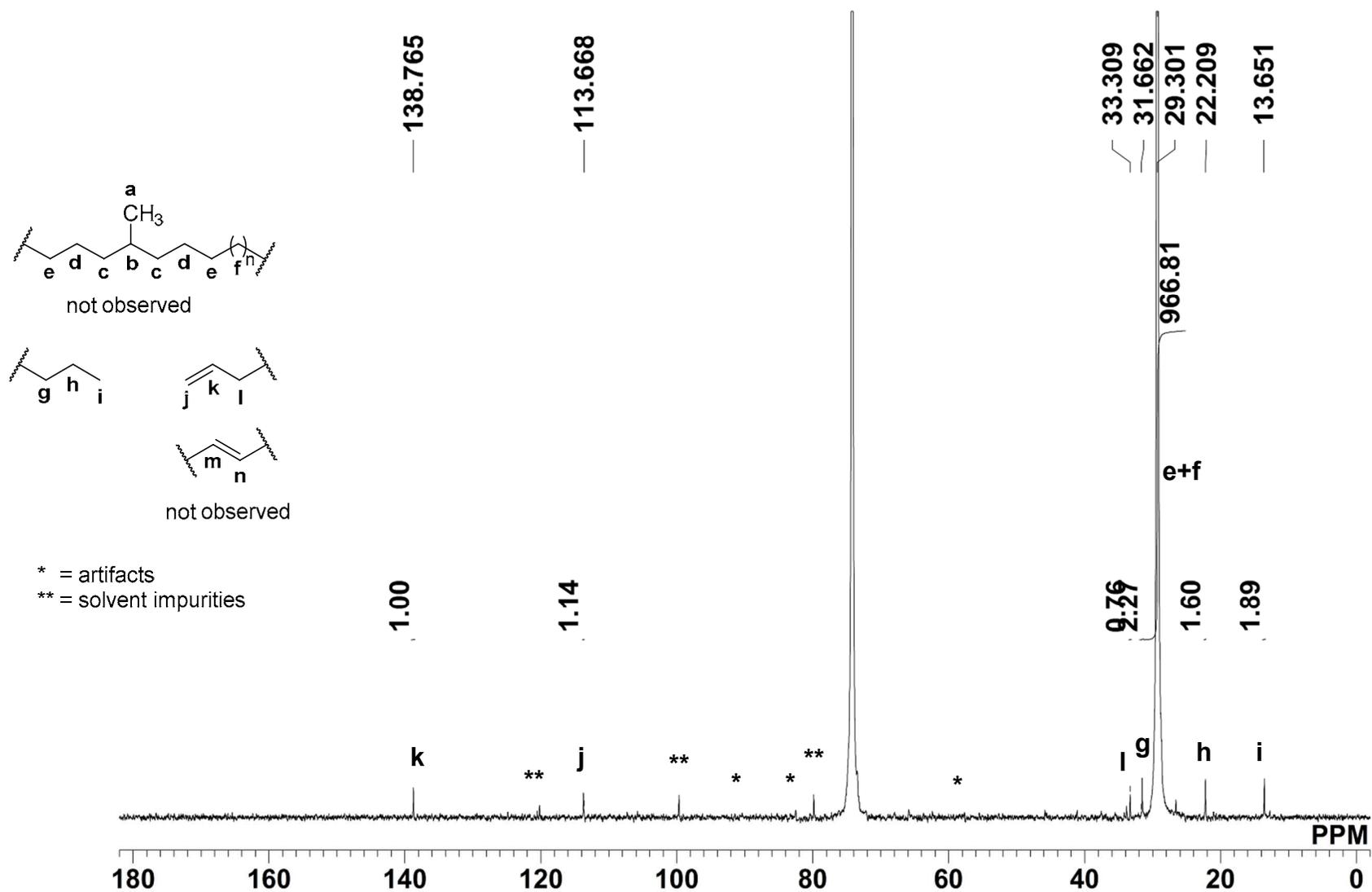
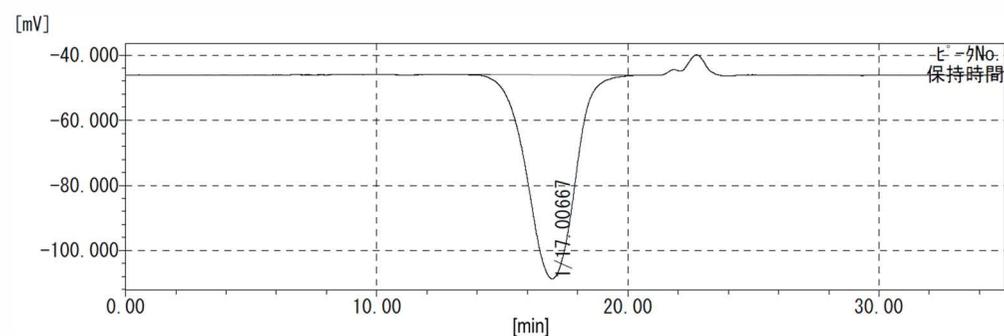


Figure S5. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M $\text{Cr}(\text{acac})_3$, 120 °C) of polyethylene obtained by [2-(Cy_2P) $\text{C}_6\text{H}_4\text{SO}_3$] PdMe (2,6-lutidine) under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 7).

Sample name : 73-08-114 Measurement date : 2014/06/26 03:59:18
 Database name : mike.mdb Calculation date : 2014/06/26 10:08:42
 Saved file name : RSLT0294
 Method data : RSLT0291



	[min]	[mV]	[MOL]		
Peak start	13.30	-45.936	1,910,090	Mn	: 27,183
Peak top	17.01	-108.692	44,680	Mw	: 76,910
Peak end	20.34	-46.158	383	Mz	: 183,563
				Mz+1	: 380,900
Area [mV * sec]		7,761.280		Mv	: 76,910
Area [%]		100.000		Mp	: 50,115
Height [mV]		62.639		Mz/Mw	: 2.387
[τ]		76,909.70165		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.

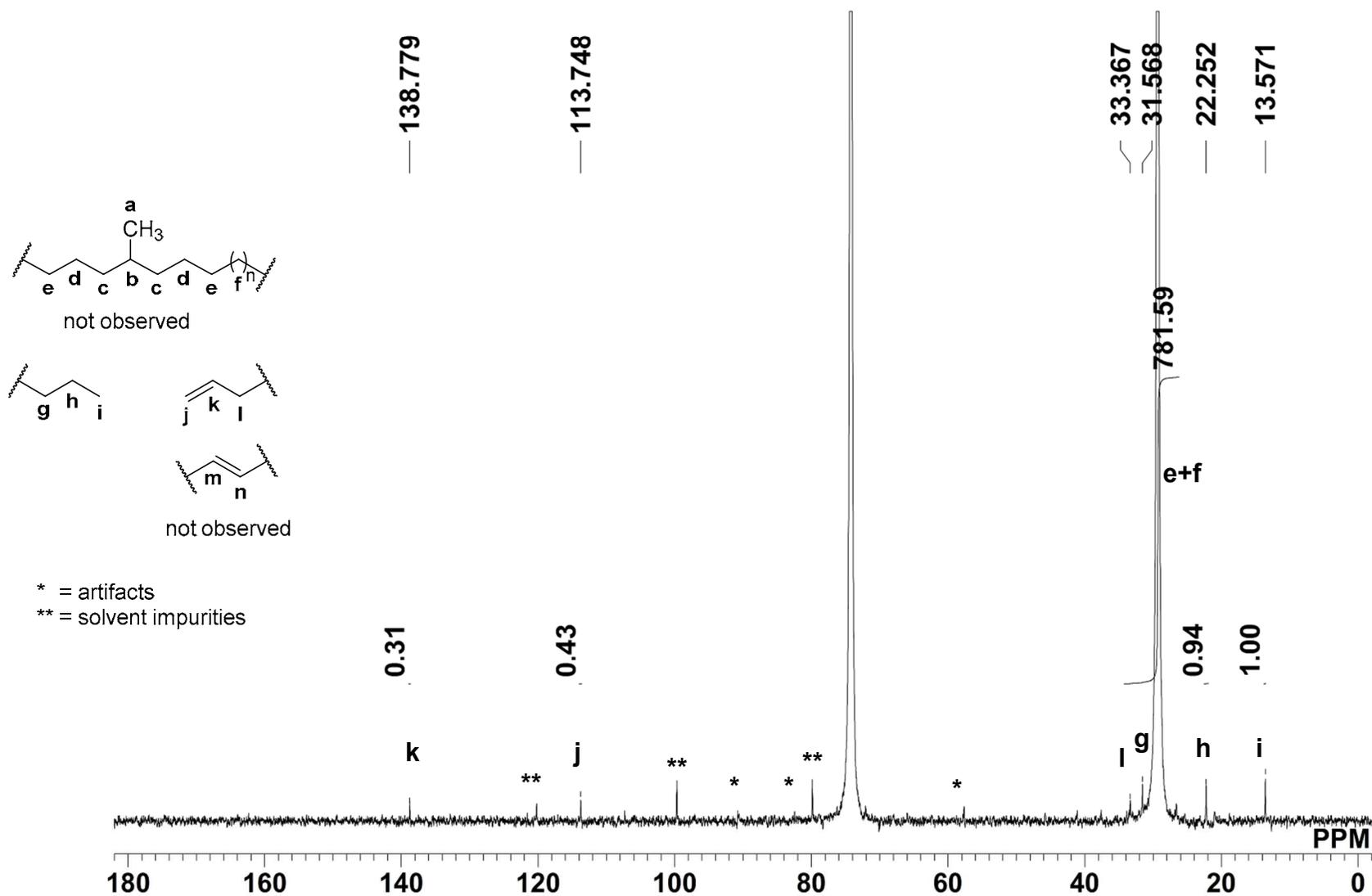
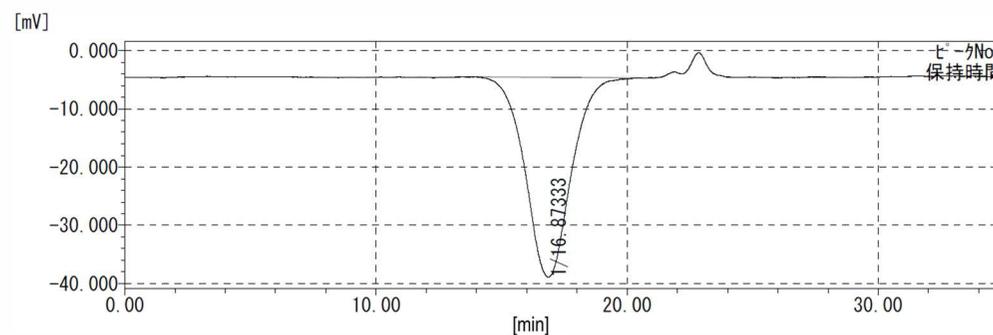


Figure S7. Quantitative ¹³C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M Cr(acac)₃, 120 °C) of polyethylene obtained by [2-(Cy₂P)C₆H₄SO₃]PdMe(2,6-lutidine) under 3.0 MPa of ethylene pressure at 80 °C in the presence of additional 9.0 equivalent of 2,6-lutidine (Table 1, entry 9).

Sample name : 73-09-074 Measurement date : 2014/08/06 16:51:49
 Database name : mike.mdb Calculation date : 2014/08/06 20:07:30
 Saved file name : RSLT0339
 Method data : RSLT0291



	[min]	[mV]	[MOL]		
Peak start	13.54	-4.490	1,579,985	Mn	: 27,146
Peak top	16.87	-38.930	52,626	Mw	: 77,845
Peak end	20.63	-4.679	236	Mz	: 165,946
				Mz+1	: 309,285
Area [mV * sec]		4,000.714		Mv	: 77,845
Area [%]		100.000		Mp	: 55,927
Height [mV]		34.351		Mz/Mw	: 2.132
[η]		77,845.38471		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.

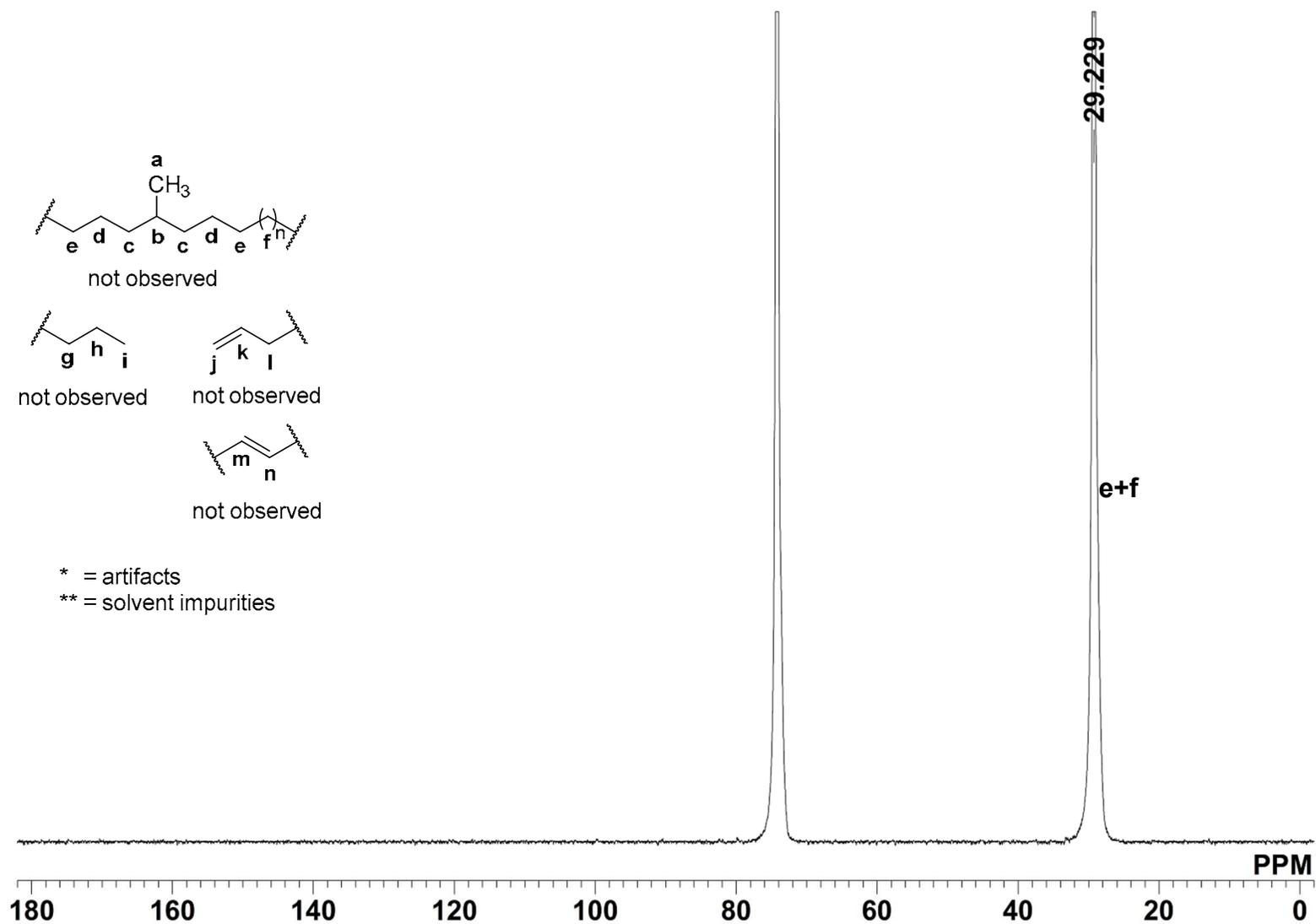
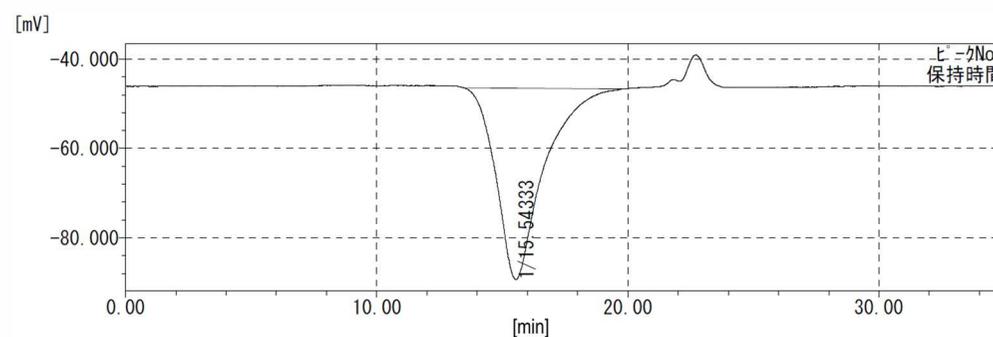


Figure S9. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M Cr(acac)₃, 120 °C) of polyethylene obtained by [2-(Men₂P)C₆H₄SO₃]PdMe(2,6-lutidine) under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 11).

Sample name : 73-08-115 Measurement date : 2014/06/26 04:44:23
 Database name : mike.mdb Calculation date : 2014/06/26 14:11:52
 Saved file name : RSLT0295
 Method data : RSLT0291



	[min]	[mV]	[MOL]		
Peak start	13.48	-46.451	1,658,931	Mn	: 67,827
Peak top	15.54	-89.344	239,924	Mw	: 248,852
Peak end	19.80	-46.665	894	Mz	: 428,648
				Mz+1	: 600,605
Area [mV * sec]		5,079.734		Mv	: 248,852
Area [%]		100.000		Mp	: 252,960
Height [mV]		42.823		Mz/Mw	: 1.723
[η]		248,852.00733		Mw/Mn	: 3.669
				Mz+1/Mw	: 2.414

Figure S10. SEC chart 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).

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

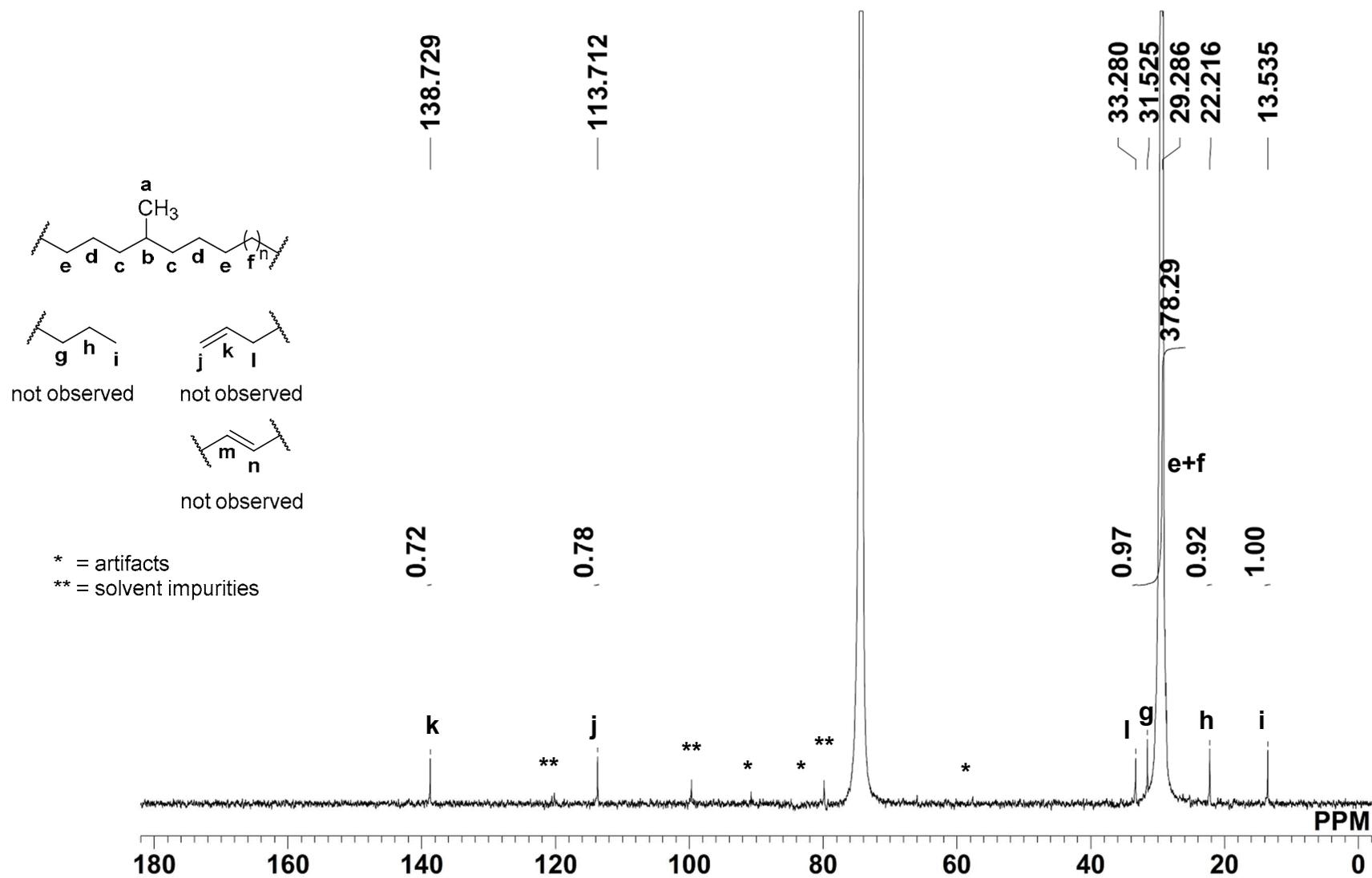
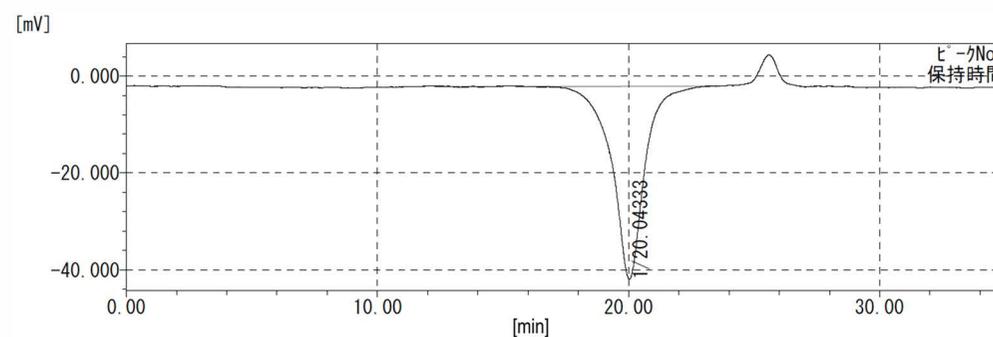


Figure S11. Quantitative ¹³C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M Cr(acac)₃, 120 °C) of polyethylene obtained by [2-(Ph₂P)C₆H₄SO₃]PdMe(2,6-lutidine) under 3.0 MPa of ethylene pressure at 80 °C (Table 1, entry 12).

Sample name : 73-09-070 Measurement date : 2015/06/18 20:32:07
 Database name : mike.mdb Calculation date : 2015/09/20 21:18:31
 Saved file name : RSLT0669
 Method data : 20150605



	[min]	[mV]	[MOL]		
Peak start	16.08	-2.175	551.385	Mn	: 11,542
Peak top	20.04	-41.933	16,103	Mw	: 22,960
Peak end	23.65	-2.089	122	Mz	: 47,523
				Mz+1	: 119,397
Area [mV * sec]		3,296.214		Mv	: 22,960
Area [%]		100.000		Mp	: 16,631
Height [mV]		39.803		Mz/Mw	: 2.070
[η]		22,959.75092		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.

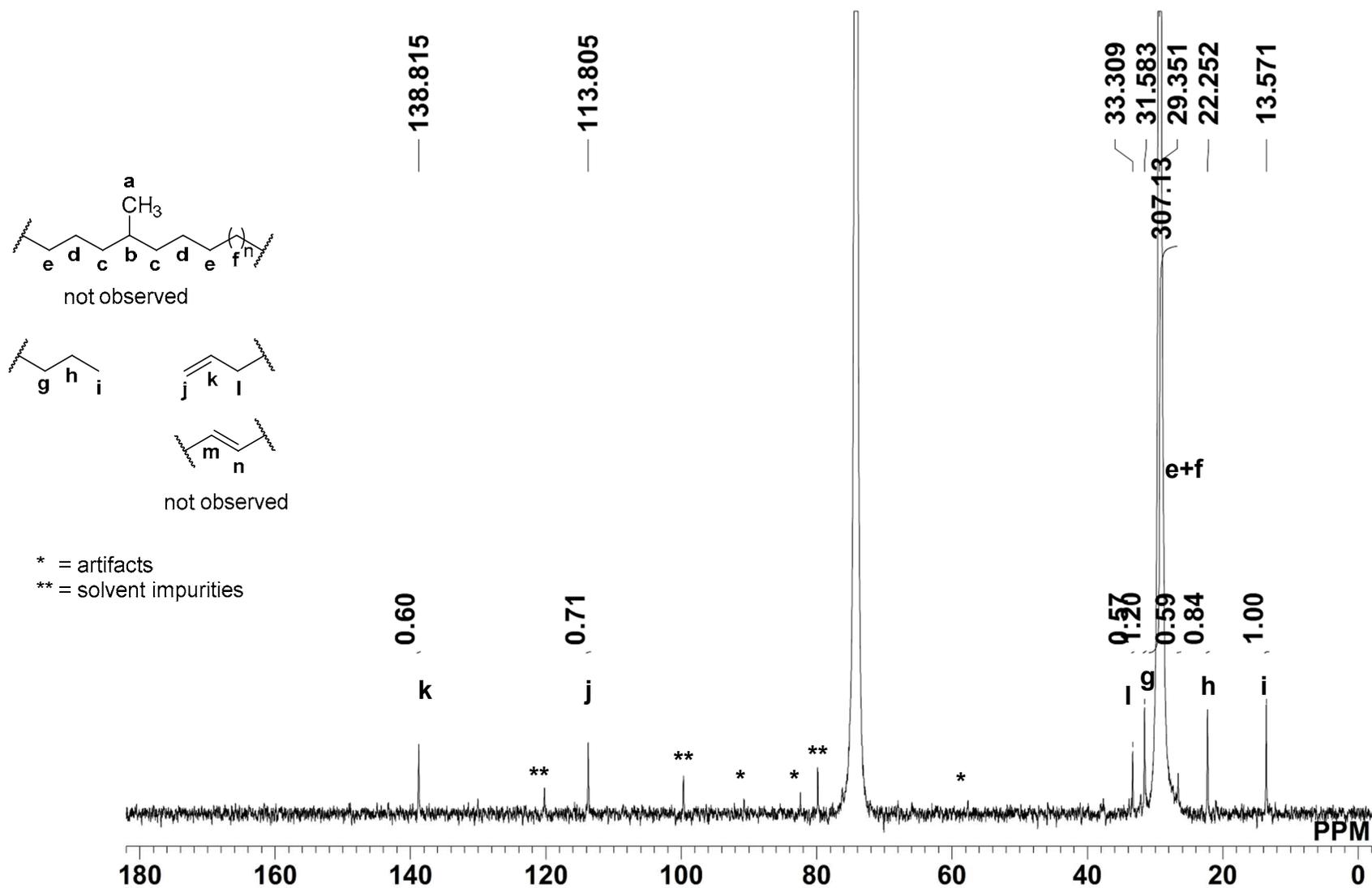
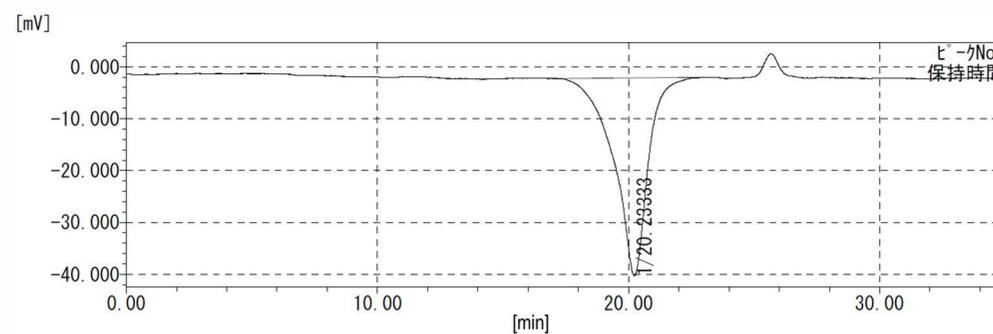


Figure S13. Quantitative ¹³C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M Cr(acac)₃, 120 °C) of polyethylene obtained by [2-(Ph₂P)C₆H₄SO₃]PdMe(2,6-lutidine) under 1.0 MPa of ethylene pressure at 80 °C (Table 1, entry 13).

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	Mn	: 11,742
Peak top	20.23	-40.297	13,098	Mw	: 21,790
Peak end	23.06	-1.993	319	Mz	: 41,310
				Mz+1	: 72,385
Area [mV * sec]		3,261.705		Mv	: 21,790
Area [%]		100.000		Mp	: 13,243
Height [mV]		38.194		Mz/Mw	: 1.896
[η]		21,790.41028		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.

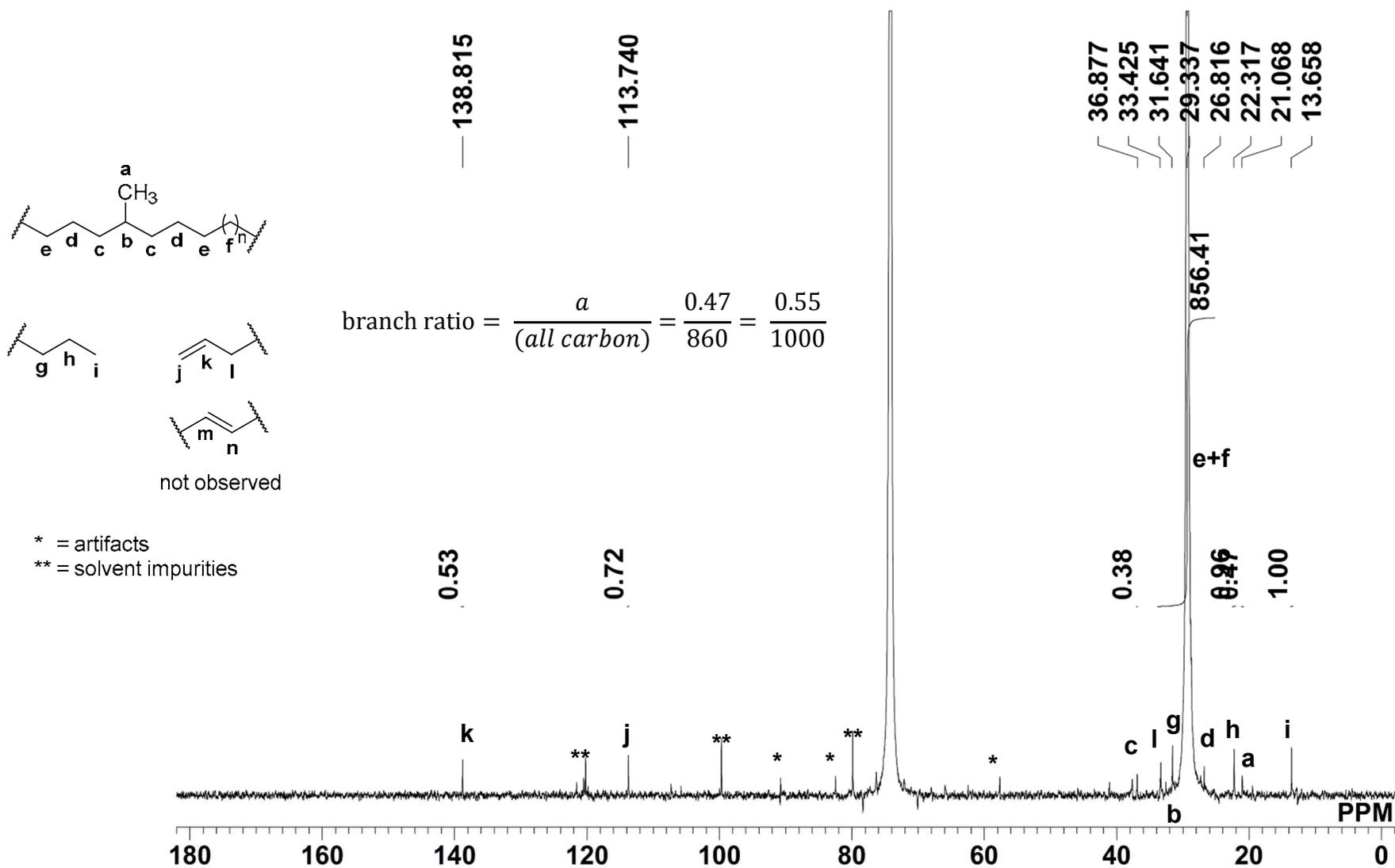
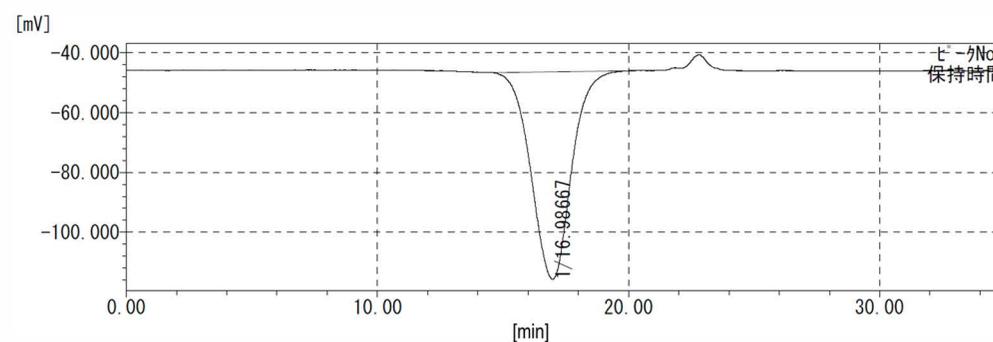


Figure S15. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M Cr(acac)₃, 120 °C) of polyethylene obtained by [2-(*o*-Ani₂P)C₆H₄SO₃]PdMe(2,6-lutidine) under 3.0 MPa of ethylene pressure at 80 °C (Table 1, entry 16).

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	Mn	: 31,561
Peak top	16.99	-115.740	45.796	Mw	: 66,074
Peak end	19.86	-46.054	814	Mz	: 116,336
				Mz+1	: 179,984
Area [mV * sec]		7,040.892		Mv	: 66,074
Area [%]		100.000		Mp	: 48,702
Height [mV]		69.327		Mz/Mw	: 1.761
[η]		66,073.89301		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.

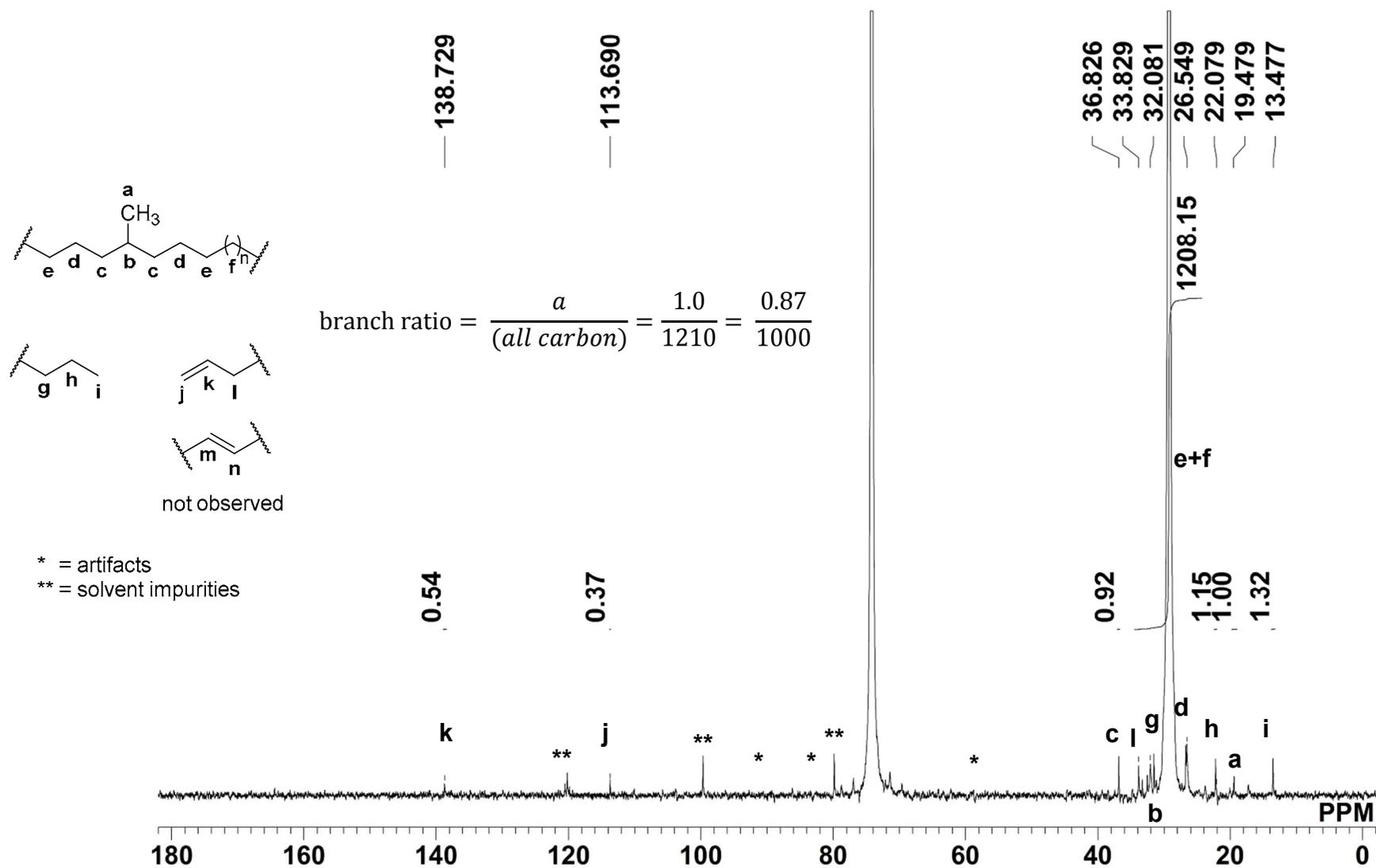
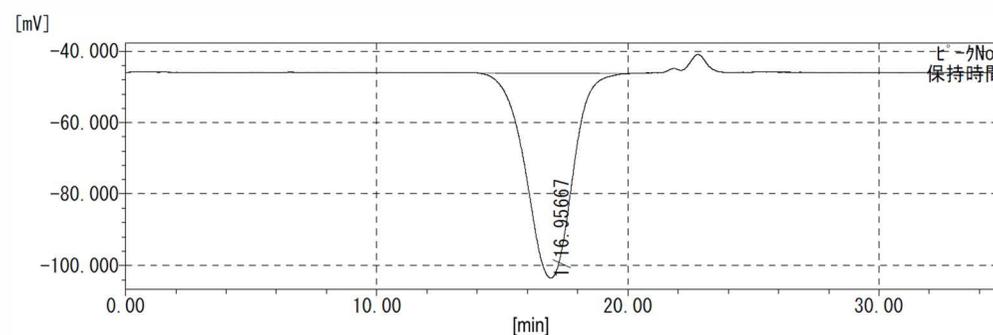


Figure S17. Quantitative ^{13}C NMR spectrum (inverse gated decoupling, 126 MHz, 1,1,2,2-tetrachloroethane, 0.05-M $\text{Cr}(\text{acac})_3$, 120 °C) of polyethylene obtained by $[2\text{-(}o\text{-Ani}_2\text{P)C}_6\text{H}_4\text{SO}_3\text{]PdMe(2,6\text{-lutidine})}$ under 1.0 MPa of ethylene pressure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

Sample name : 73-08-110 Measurement date : 2014/06/26 01:44:20
 Database name : mike.mdb Calculation date : 2014/06/26 10:05:34
 Saved file name : RSLT0291
 Method data : RSLT0291



	[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*-Ani₂P)C₆H₄SO₃]PdMe(2,6-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

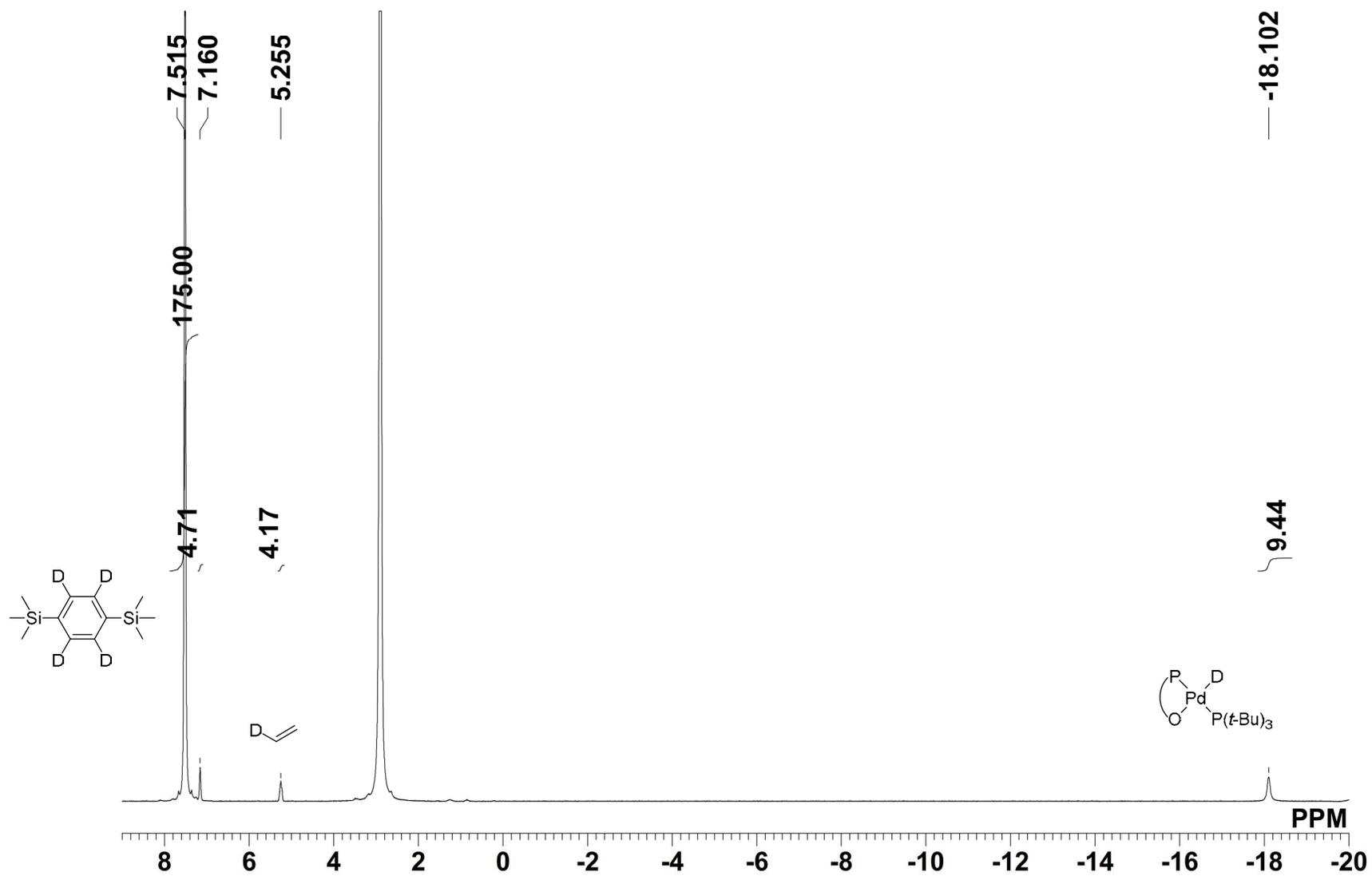


Figure S19. ^2H NMR spectrum (77 MHz, benzene, 25 °C) of the reaction mixture after deuteration of ethylene (Scheme 4).

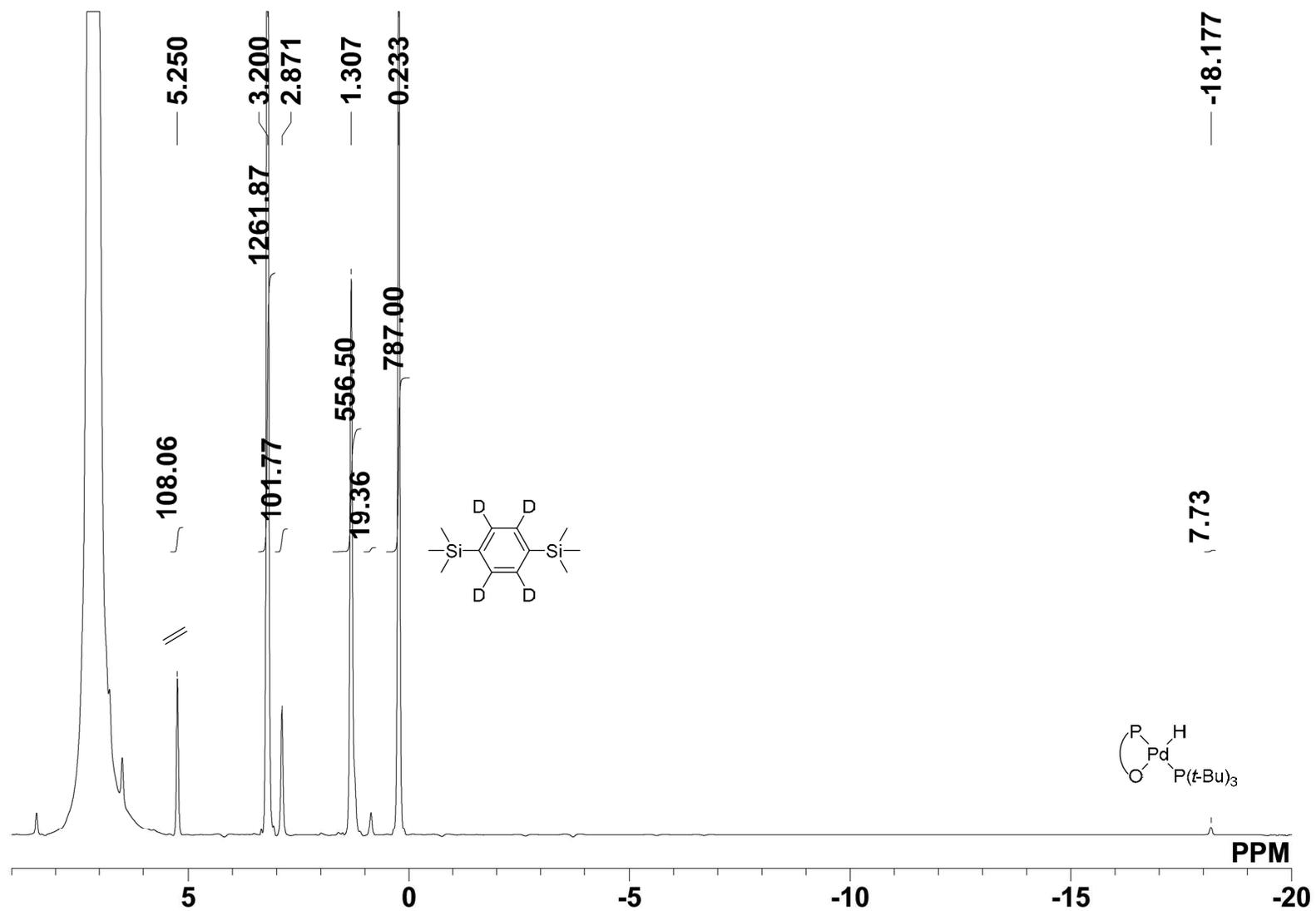


Figure S20. ^1H NMR spectrum (500 MHz, benzene, 25 °C) of the reaction mixture after deuteration of ethylene (Scheme 4).

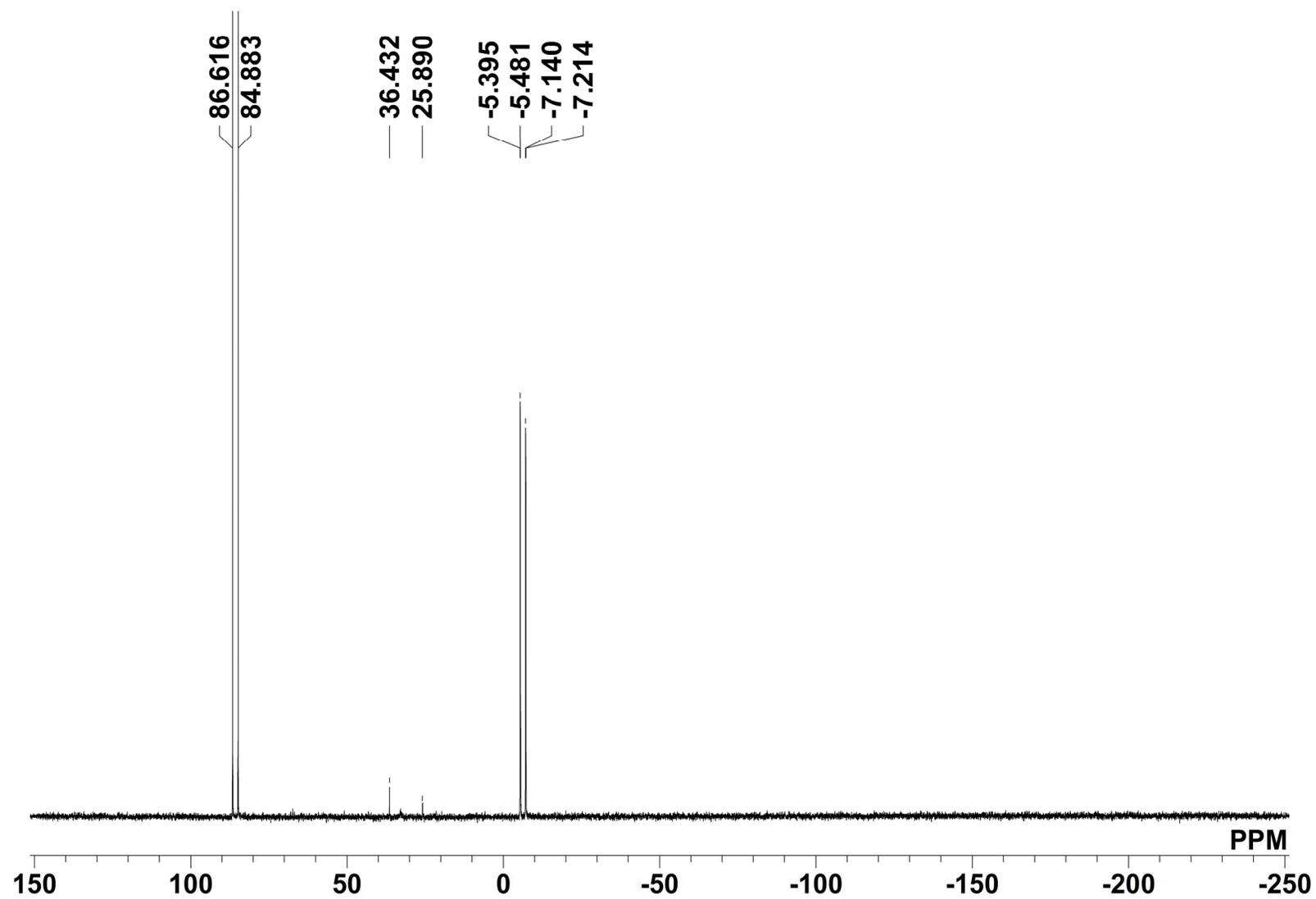


Figure S21. ^{31}P NMR spectrum (202 MHz, benzene, 25 °C) of the reaction mixture after deuteration of ethylene (Scheme 4).

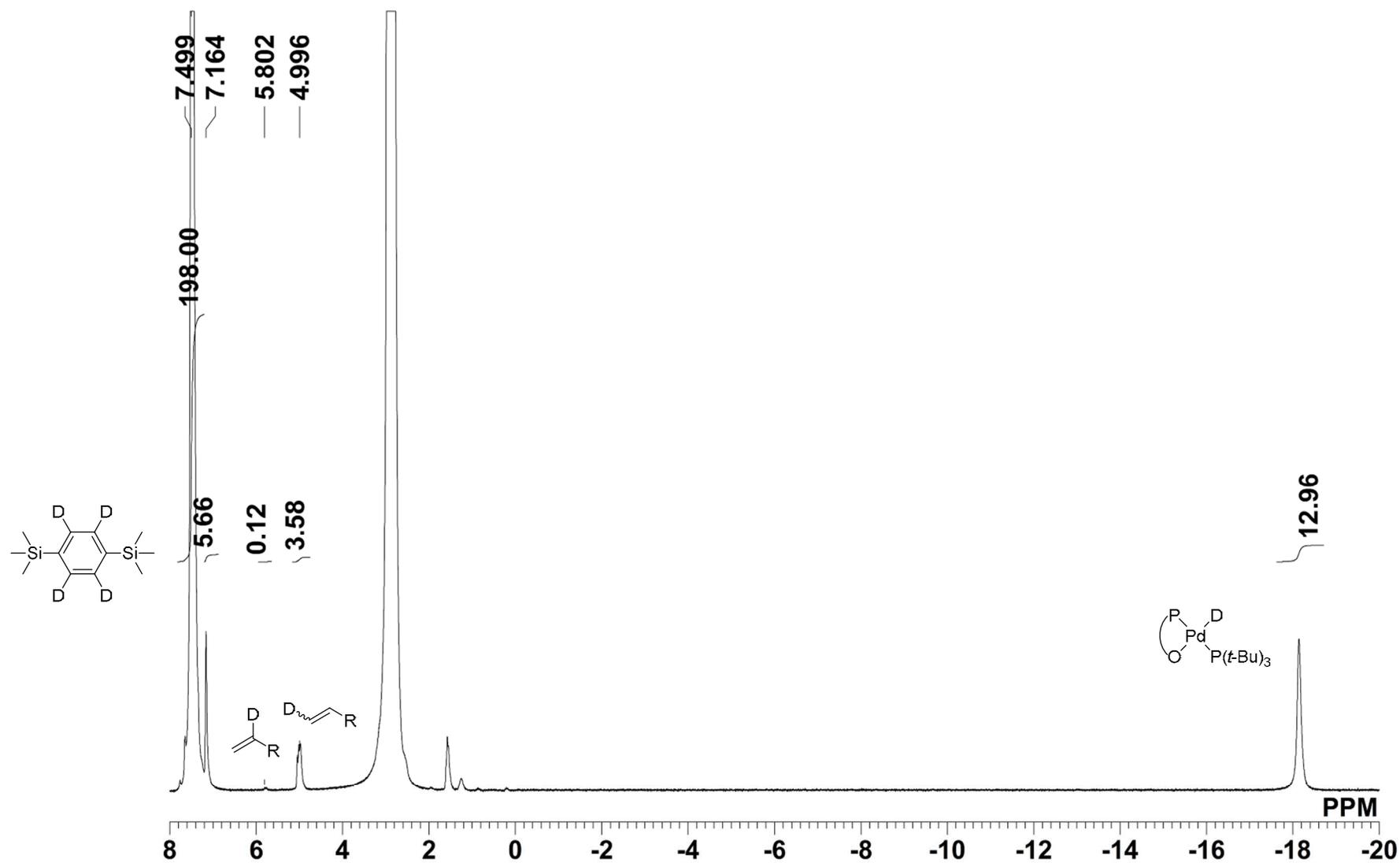


Figure S22. ^{31}P NMR spectrum (77 MHz, benzene, 25 °C) of the reaction mixture after deuteration of 1-eicocene (Scheme 6).

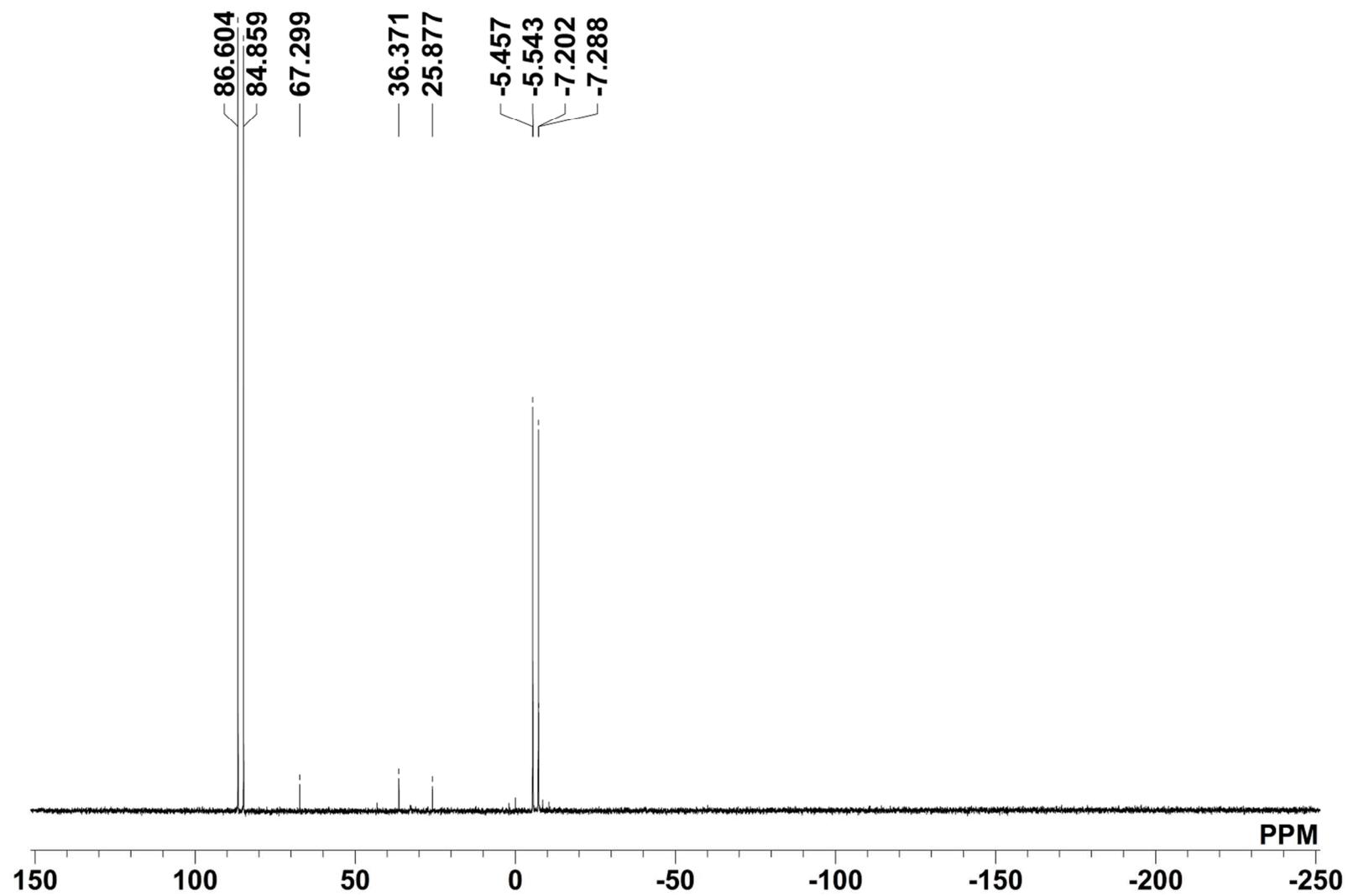


Figure S24. ^{31}P NMR spectrum (202 MHz, benzene, 25 °C) of the reaction mixture after deuteration of 1-eicocene (Scheme 6).

III. References

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