Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information For:

Copolymerisation of Ethylene with Polar Monomers by Palladium Catalysts Bearing an N-Heterocyclic Carbene–Phosphine Oxide Bidentate Ligand

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Contents

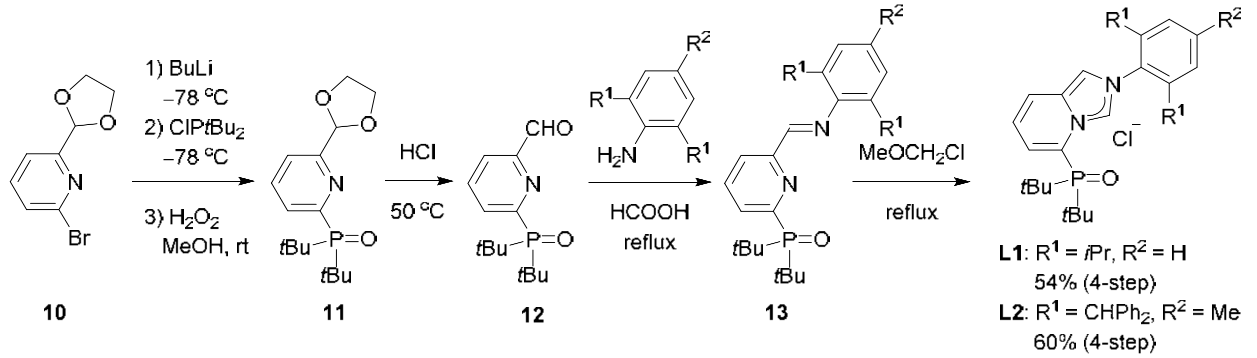
1. Materials and Methods

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 50-mL stainless steel autoclaves.

Instrumentation: Nuclear magnetic resonance (NMR) spectra were recorded on 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 at ambient temperature unless otherwise noted. Chemical shift values for protons were referenced to the residual proton resonance of chloroform-*d* (δ: 7.26) or 1,1,2,2-tetrachloroethane-d_2 (δ: 6.00). 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 Cr(acac)$_3$ as a relaxation agent in 1,1,2,2-tetrachloroethane 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 of 2 s, and inverse-gated decoupling (JEOL JNM-ECS400) or 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 chloroform-*d* (δ: 77.16) or 1,1,2,2-tetrachloroethane-d_2 (δ: 73.80). 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 by universal calibration using the Mark–Houwink parameters reported by Rudin *et al.*: $K = 1.75 \times 10^{-2}$ cm^3/g and $\alpha = 0.67$ for polystyrene, $K = 5.90 \times 10^{-2}$ cm^3/g and $\alpha = 0.69$ for LLDPE.[4] X-ray crystallographic analyses were performed on a Rigaku Varimax with a Saturn diffractometer. Elemental analysis was performed by the Microanalytical Laboratory, Department of Chemistry, Graduate School of Science, The University of Tokyo, or by One-stop Sharing Facility Center for Future Drug Discoveries, Graduate School of Pharmaceutical Sciences, The University of Tokyo. High resolution mass spectra were recorded on JEOL JMS-T100LP AccuTOF LC-plus.

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 dichloromethane, diethyl ether, tetrahydrofuran (THF), and toluene were purchased from Kanto Chemical Co. Inc. (Kanto) and purified by the method of Pangborn *et al.*[5] Dehydrated pentane was purchased from Kanto and used as received. The other solvents were purchased from Kanto, Tokyo Chemical Industry Co., Ltd. (TCI), Sigma-Aldrich Chemical Co. LLC (Aldrich) or Wako Pure Chemical Industries, Ltd. (Wako) and were used as received unless otherwise noted. The following reagents were purchased from TCI and distilled from calcium hydride before use: methyl acrylate, allyl acetate, allyl chloride, and vinyl acetate. The following reagents were purchased and used as received: 6-bromopicolinaldehyde (Kanto), butyllithium in hexane (Kanto), chloromethyl methyl ether (TCI), di-*tert*-butylchlorophosphine (TCI), 2,6-diisopropylaniline (TCI), *p*-toluidine (TCI), benzhydrol (TCI), silver hexafluoroantimonate (TCI), silver triflate (TCI), hydrogen peroxide (30−35%, Kanto), sodium sulfate (Kanto), sodium thiosulfate (Kanto), and sodium carbonate (Kanto). The following compounds and complexes were prepared according to literature procedures: 2,6-dibenzhydryl-4-methylaniline,[6] PdMeCl(cod),[7] and $NaB[3,5-(CF_3)_2C_6H_4]_4$ ($NaBAr^F_4$).[8]

Synthesis of Ligand Precursor L1



[Synthesis of **11**] A 100-mL Schlenk flask containing a solution of 2-bromo-6-(1,3-dioxolan-2-yl)pyridine[9] **10** (0.95 g, 4.15 mmol) in THF (20 mL) was cooled in dry ice/acetone cold bath. To the solution was added BuLi (1.55 M, 3.2 mL, 4.97 mmol) dropwise while the color of the solution became dark red. After stirring for another 1 h with cooling, $t\mathrm{Bu}_2\mathrm{PCl}$ (1.0 mL, 5.4 mmol) was added dropwise. Then the cooling bath was removed, and the mixture was stirred overnight at room temperature. The reaction was quenched by slow addition of water (2.0 mL). After the volatile matters were removed in vacuo, methanol (ca. 15 mL) was added to dissolve the crude product. An aqueous solution of hydrogen peroxide (ca. 10 M, 0.84 mL, ca. 8.4 mmol) was added slowly and the mixture was stirred for another 1 h at room temperature. After quenching the excess hydrogen peroxide by aqueous sodium thiosulfate (1.6 g, ca. 10 mmol), the mixture was extracted by dichloromethane twice. The combined organic phase was dried over sodium sulfate, and evaporated to dryness, to afford the crude solid containing **11**, which was used for next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.11 (m, 1H), 7.87–7.83 (m, 1H), 7.58–7.56 (m, 1H), 5.85 (s, 1H), 4.20–4.18 (m, 2H), 4.11–4.08 (m, 2H), 1.29 (d, J = 14Hz, 18H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.8.

[Synthesis of **12**] To the above crude mixture including **11** in THF (ca. 20 mL) was added aqueous hydrochloric acid (1.0 M, ca. 20 mL), and the mixture was stirred overnight at 50 °C. Then, the mixture was added water (ca. 20 mL) and sodium carbonate until bubbling of carbon dioxide ceased, and extracted with dichloromethane. The organic phase was dried over sodium sulfate, and evaporated to dryness, to afford the crude product including **12** (1.00 g), which was used for next step without further purification. ^{1}H NMR (500

MHz, $CDCl_3$) δ 10.09 (d, *J* = 0.5 Hz, 1H), 8.40–8.37 (m, 1H), 8.03–7.98 (m, 2H), 1.33 (d, *J* = 14 Hz, 18H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.5.

[Synthesis of **13a**] In a 50-mL round bottom flask equipped with a reflux condenser, the crude mixture including **12** (1.00 g), 2,6-diisopropylaniline (796 mg, 4.49 mmol) and formic acid (1 drop) was refluxed in methanol (20 mL) overnight. After removing the volatile matters in vacuo, the mixture was purified by silica-gel column chromatography (1st elution with ethyl acetate and hexane (1:2) to wash impurities, and then 2nd elution with ethyl acetate, hexane and methanol (2:6:1) to elute **13a**), to afford a crude product including **13a** (1.15 g), which was used for next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.31–8.29 (m, 1H), 8.24 (dd, *J* = 6.8, 4.8 Hz, 1H), 7.96 (td, *J* = 7.8, 3.0 Hz, 1H), 7.19–7.12 (m, 3H), 2.95 (sept, *J* = 6.9 Hz, 2H), 1.31 (d, *J* = 14 Hz, 18 H), 1.19 (d, *J* = 6.5 Hz, 12 H).

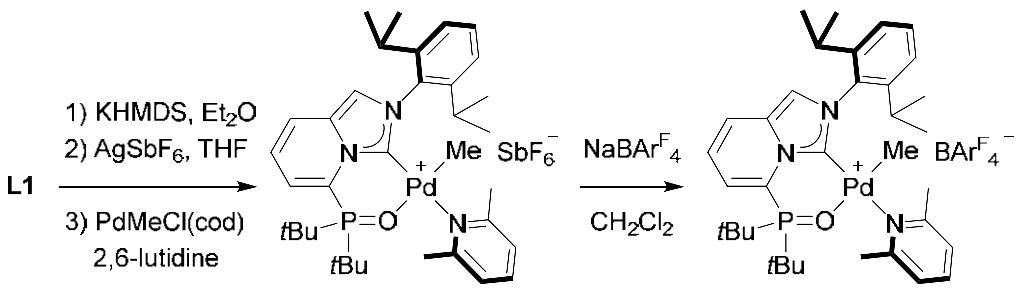
[Synthesis of **L1**] The crude compound **13a** (1.15 g) and chloromethyl methyl ether (4.1 mL, 53.9 mmol) were refluxed overnight in a 10-mL J-young Schlenk tube. After cooling to room temperature, the volatile matters were removed in vacuo. The crude product was dissolved in dichloromethane (ca. 10 mL), filtered through a pad of Celite, and the pad was washed with dichloromethane twice (ca. 5.0 mL × 2). The volatile matters were evaporated in vacuo again, and then the crude solid was stirred overnight in dichloromethane (ca. 0.5 mL) and diethyl ether (ca. 20 mL). The formed precipitate was filtered, washed with diethyl ether (ca. 5 mL), and dried under vacuo at 100 °C for 2.0 h, to afford pure **L1** (1.11 g, 2.34 mmol, 54% from **10**) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.79 (d, *J* = 1.5 Hz, 1H), 9.22 (d, *J* = 9.0 Hz, 1H), 9.15 (s, 1H), 7.60–7.50 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.07 (sept, *J* = 6.9 Hz, 2H), 1.38 (d, *J* = 15 Hz, 18 H), 1.22 (d, *J* = 7.0 Hz, 6H), 1.09 (d, *J* = 7.0 Hz, 6H); ^{31}P NMR (202 MHz, $CDCl_3$) δ 61.9; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 132.5 (d, *J* = 2.5 Hz, 1C), 132.3, 130.8, 127.4 (d, *J* = 3.5 Hz, 2C), 126.8 (d, *J* = 8.6 Hz, 1C), 126.0 (d, *J* = 1.8 Hz, 1C), 125.2, 124.7 (2C), 123.2 (d, *J* = 7.7 Hz, 1C), 119.0, 38.5 (d, *J* = 59 Hz, 2C), 28.9 (2C), 26.5 (6C), 24.7 (2C), 23.9 (2C). HRMS-ESI (*m*/*z*) calcd for $C_{27}H_{40}N_2OP$ ($[M+H]^+$) 439.2878, found 439.2900.

Synthesis of Ligand Precursor L2

[Synthesis of **13b**] In a 50-mL round bottom flask equipped with a reflux condenser, a crude compound **12** (0.66 g, synthesized from **10** (0.64 g, 2.76 mmol) as above mentioned), 2,6-dibenzhydryl-4-methylaniline (493 mg, 1.12 mmol), and formic acid (1 drop) was refluxed in methanol (20 mL) overnight. After removing the volatile matters in vacuo, the mixture was purified by silica-gel column chromatography (1st elution with ethyl acetate and hexane (1:1) to wash impurities, and then 2nd elution with ethyl acetate, hexane and ethanol (30:10:3) to elute **13b**), to afford a crude product including **13b** (1.02 g), which was used for next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dt, *J* = 8.0, 1.6 Hz, 1H), 8.11 (ddd, *J* = 7.6, 4.4, 1.2 Hz, 1H), 7.85 (td, *J* = 7.6, 2.8 Hz, 1H), 7.18–7.08 (m, 12H), 7.04 (s, 1H), 7.01–6.98 (m, 8H), 6.66 (s, 2H), 5.43 (s, 2H), 2.15 (s, 3H), 1.15 (d, *J* = 14 Hz, 18H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.5.

[Synthesis of **L2**] The crude compound **13b** (1.02 g) and chloromethyl methyl ether (2.2 mL, 29.6 mmol) were refluxed overnight in a 10-mL J-young Schlenk tube. After cooling to room temperature, the volatile matters were removed in vacuo. The crude product was dissolved in dichloromethane (ca. 10 mL), filtered through a pad of Celite, and the pad was washed with dichloromethane twice (ca. 5.0 mL × 2). The volatile matters were evaporated in vacuo again, and then the crude solid was stirred overnight in dichloromethane (ca. 0.5 mL) and diethyl ether (ca. 20 mL). The formed precipitate was filtered, washed with diethyl ether (ca. 5 mL), and dried under vacuo at 100 °C for 2.0 h, to afford pure **L2** (1.01 g, 1.37 mmol, 60% from **10**) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.43 (d, *J* = 5.5 Hz, 1H), 8.26 (s, 1H), 7.56–7.54 (m, 2H), 7.23–7.15 (m, 12H), 6.91–6.86 (m, 8H), 6.79 (s, 2H), 5.12 (s, 2H), 2.23 (s, 3H), 1.22 (d, *J* = 15 Hz, 18H); ^{31}P NMR (202 MHz, $CDCl_3$) δ 61.7; ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 141.4, 141.2, 140.4, 131.2 (d, *J* = 2.4 Hz, 1C), 130.9, 130.8 (2C), 129.3 (4C), 129.0 (8C), 128.8 (4C), 127.6, 127.4, 127.4 (2C), 127.0–126.9 (2C), 124.8 (d, *J* = 67 Hz, 1C), 124.1, 123.7–123.6 (2C), 118.1, 52.0 (2C), 38.3 (d, *J* = 59 Hz, 2C), 26.5 (6C), 22.0. HRMS-ESI (*m*/*z*) calcd for $C_{44}H_{35}N_2OP$ ([M+H]$^+$) 701.3661, found 701.3648.

Synthesis of Palladium Complexes 4a and 4b



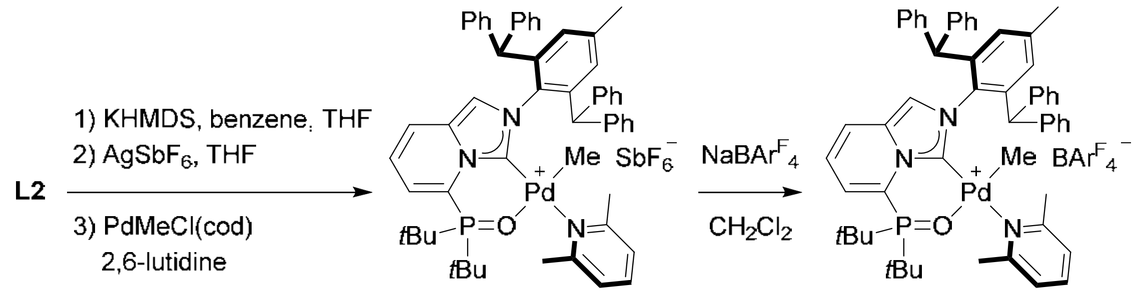
4a: 86% **4b**: 77%

[Synthesis of **4a**] In a glove box, **L1** (60 mg, 0.13 mmol) and potassium bis(trimethylsilyl)amide (KHMDS, 27 mg, 0.13 mmol) were dissolved in diethyl ether (ca. 5.0 mL) in a 15-mL scintillation vial, and the mixture was stirred for 15 min at room temperature. Then, the mixture was filtered through a pad of Celite and the pad was washed with diethyl ether (ca. 2.0 mL). To the filtrate were added $AgSbF_6$ (35 mg, 0.14 mmol) and

THF (ca. 3.0 mL), and the mixture was stirred for 1 h at ambient temperature under darkness. Then, PdMeCl(cod) (34 mg, 0.13 mmol) and 2,6-lutidine (14 mg, 0.13 mmol) were added, and the mixture was stirred for 3 h at ambient temperature under darkness. The mixture was filtered through a pad of Celite and the pad was washed with THF (ca. 3.0 mL). After the volatiles matters were removed under vacuum, the crude product was washed with diethyl ether (ca. 5.0 mL) and dried under vacuum for 1 h to afford complex **4a** as pale yellow solid (98 mg, 86%).The single crystal for X-ray crystallographic analysis was obtained by slow volatilization of saturated solution of complex **4a** with dichloromethane and hexane. ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 9.5 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.49–7.46 (m, 2H), 7.32–7.28 (m, 3H), 7.21 (t, J = 7.8 Hz, 1H), 7.13 (d, J = 7.5 Hz, 2H), 3.02 (s, 6H), 2.90 (sept, J = 7.0 Hz, 2H), 1.37 (d, J = 6.5 Hz, 6H), 1.27 (d, J = 15 Hz, 18H), 1.01 (d, J = 6.5 Hz, 6H), −0.30 (s, 3H). ^{31}P NMR (202 MHz, $CDCl_3$) δ 63.0. ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 158.8, 144.5, 138.3, 136.8, 131.2 (d, J = 2.8 Hz, 1C), 130.5, 127.2 (d, J = 77 Hz, 1C), 126.5 (d, J = 12 Hz, 2C), 124.3 (2C), 123.4 (d, J = 2.5 Hz, 1C), 122.8 (2C), 121.1 (d, J = 10 Hz, 2C), 118.5, 38.5 (d, J = 59 Hz, 2C), 28.8 (2C), 27.1 (2C), 27.0 (6C), 25.6 (2C), 22.9 (2C), −10.7. HRMS-ESI (*m*/*z*) calcd for $C_{35}H_{51}N_3OPPd$ ($[M+H]^+$) 666.2799, found 666.2824.

[Synthesis of **4b**] In a 20-mL Schlenk flask, complex **4a** (98 mg, 0.11 mmol) and $NaBAr^F_4$ (77 mg, 0.087 mmol) in dichloromethane (ca. 10 mL) were stirred overnight at ambient temperature. The volatile matters were removed under vacuum and then the Schlenk flask was transferred into the glove box. The mixture was extracted with diethyl ether (ca. 10 mL) twice, and the combined filtrate was evaporated to dryness. Finally the mixture was washed with pentane (ca. 5.0 mL) and dried under vacuum for 1 h at ambient temperature to afford complex **4b** as a pale yellow solid (128 mg, 77%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 8H), 7.58–7.55 (m, 2H), 7.514 (s, 4H), 7.50–7.48 (m, 1H), 7.45 (s, 1H), 7.30 (d, J = 7.5Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.05–7.01 (m, 1H), 6.89–6.86 (m, 1H), 3.00 (s, 6H), 2.86 (sept, J = 6.8 Hz, 2H), 1.37 (d, J = 7.0 Hz, 6H), 1.20 (d, J = 15 Hz, 18H), 0.99 (d, J = 7.0 Hz, 6H), −0.27 (s, 3H). ^{31}P NMR (202 MHz, $CDCl_3$) δ 62.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ −62.4; ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 162.4–161.3 (m, 4C), 158.7, 144.3, 138.4, 136.6, 134.9 (8C), 130.8 (d, J = 2.8 Hz, 1C), 130.8, 129.0 (qq, J = 31, 2.8 Hz, 8C), 128.1 (d, J = 77 Hz, 1C), 124.7 (q, J = 273 Hz, 8C), 125.1 (d, J = 12 Hz, 2C), 124.5 (2C), 123.3 (d, J = 2.6 Hz, 1C), 122.8 (2C), 119.7 (d, J = 10 Hz, 2C), 118.6, 117.6 (sept, J = 3.8 Hz, 4C), 38.5 (d, J = 58 Hz, 2C), 28.9 (2C), 27.0 (2C), 26.9 (6C), 25.5 (2C), 22.8 (2C), −10.2. Elemental analysis, Calcd for $C_{67}H_{63}BF_{24}N_3OPPd$ C, 52.58; H, 4.15; N, 2.75. found C, 52.03; H, 4.34; N, 2.69. HRMS-ESI (*m*/*z*) calcd for $C_{35}H_{51}N_3OPPd$ ($[M+H]^+$) 666.2799, found 666.2823.

Synthesis of Palladium Complex 4c



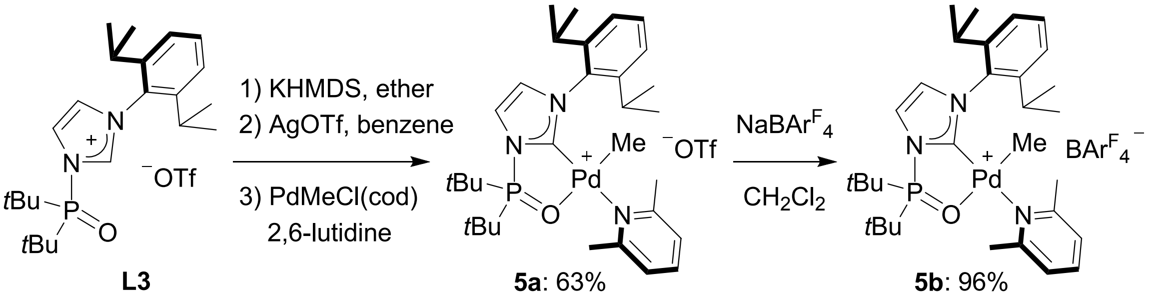
4c: 61% (2 steps)

[Synthesis of **4c**] In a glove box, **L2** (50 mg, 0.068 mmol) and KHMDS (15 mg, 0.071 mmol) were dissolved in benzene/THF (ca. 3.0 mL each) in a 15-mL scintillation vial, and the mixture was stirred for 15 min at room temperature. Then, the mixture was filtered through a pad of Celite and the pad was washed with THF (ca. 3.0 mL). To this filtrate was added $AgSbF_6$ (19 mg, 0.074 mmol). The mixture was stirred at ambient temperature under darkness for ca. 0.5 h and PdMeCl(cod) (18 mg, 0.068 mmol) and 2,6-lutidine (7.3 mg, 0.068 mmol) were added and the mixture was stirred for another 3 h at ambient temperature under darkness. The mixture was filtered through a pad of Celite and the pad was washed with THF (ca. 3.0 mL). After the volatiles were removed in vacuo, the crude product was washed with diethyl ether and dried under vacuum for 1 h, to afford the palladium hexafluoroantimonate complex (59 mg, 0.051 mmol), which was used for next step without further purification. ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (t, *J* = 7.8 Hz, 1H), 7.30–7.06 (m, 17H), 6.98–6.88 (m, 2H), 6.85 (s, 2H), 6.81–6.79 (m, 2H), 6.72–6.70 (m, 4H), 5.50 (s, 1H), 5.48 (s, 2H), 3.15 (s, 6H), 2.25 (s, 3H), 1.34 (d, *J* = 15 Hz, 18H), 0.05 (s, 3H); ^{31}P NMR (202 MHz, $CDCl_3$) δ 63.3.

In a 20-mL Schlenk flask, the above palladium hexafluoroantimonate complex and $NaBAr^F_4$ (36 mg, 0.041 mmol) in dichloromethane (ca. 10 mL) were stirred overnight at ambient temperature. The volatile matters were removed and then the Schlenk flask was transferred into the glove box. The mixture was extracted with diethyl ether (ca. 10 mL), and passed through a pad of Celite with the aid of additional ether (3.0 mL). The extraction was repeated twice, and the combined filtrate was evaporated to dryness. Finally the mixture was washed with pentane and dried under vacuum for 1 h to afford complex **4c** as a pale yellow solid (74 mg, 61% over two steps). ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 8H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.51 (s, 4H), 7.31–7.20 (m, 6H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.14–7.08 (m, 8H), 6.98–6.94 (m, 1H), 6.90–6.87 (m, 1H), 6.85 (s, 2H), 6.79–6.74 (m, 2H), 6.71–6.69 (m, 4H), 6.65–6.62 (m, 1H), 5.52 (d, *J* = 1.0 Hz, 1H), 5.46 (s, 2H), 3.13 (s, 6H), 2.26 (s, 3H), 1.30 (s, 9H), 1.27 (s, 9H), 0.08 (s, 3H); ^{31}P NMR (202 MHz, $CDCl_3$) δ 62.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ −62.4; ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4–161.3 (m, 4C) 158.7, 158.5, 142.4, 141.9, 141.2, 140.7, 140.6, 140.6 (d, *J* = 5.0 Hz, 1C), 140.0, 138.5, 136.5, 134.9 (8C), 130.2 (2C), 129.7 (4C), 129.1, 129.0 (qq, *J* = 31, 2.8 Hz, 8C), 129.5 (d, *J* = 2.9 Hz, 1C), 128.9 (4C), 128.7 (d, *J* = 4.7 Hz, 8C), 127.7 (d, *J* =

4.0 Hz, 1C), 127.1 (d, J = 5.0 Hz, 4C), 124.7 (q, J = 273 Hz, 8C), 124.5 (d, J = 12 Hz, 1C), 123.6 (d, J = 2.8 Hz, 1C), 123.0, 120.8, 118.5 (d, J = 10 Hz, 1C), 117.6 (sept, J = 3.8 Hz, 4C), 52.3 (2C), 38.8 (d, J = 58 Hz, 2C), 27.3 (2C), 26.9 (6C), 26.3, 22.0, −9.3. Elemental analysis, Calcd for $C_{88}H_{73}BF_{24}N_3OPPd$ C, 58.96; H, 4.10; N, 2.34. found C, 59.10; H, 4.51; N, 2.44. HRMS-ESI (*m*/*z*) calcd for $C_{56}H_{61}N_3OPPd$ ($[M+H]^+$) 928.3582, found 928.3626.

Synthesis of Palladium Complexes 5a and 5b



L3 **5a**: 63% **5b**: 96%

[Synthesis of **5a**] In a glove box, **L3**[10] (30 mg, 0.056 mmol) and KHMDS (12 mg, 0.056 mmol)) were dissolved in ether (ca. 5.0 mL) in a 15-mL scintillation vial, and the mixture was stirred for 1 h at room temperature under darkness. The mixture was filtered through a pad of Celite and the pad was washed with diethyl ether (ca. 3.0 mL). To the filtrate were added AgOTf (14 mg, 0.056 mmol) and THF (ca. 3.0 mL), and the mixture was stirred for 2 h at ambient temperature under darkness. To the resulting mixture were added PdMeCl(cod) (15 mg, 0.056 mmol) and 2,6-lutidine (6.0 mg, 0.056 mmol), and the mixture was stirred under darkness overnight at ambient temperature. The mixture was filtered through a pad of Celite and the pad was washed with THF (ca. 3.0 mL). After the volatile matters of the filtrate were removed in vacuo, benzene (ca. 5.0 mL) was added into the mixture. The mixture was filtered through a pad of Celite and washed with benzene (ca. 3.0 mL). The remaining white solid on the pad of Celite was extracted by THF. The volatile matters of the filtrate were removed under vacuum and the remaining solid was washed with diethyl ether and dried under vacuum for ca. 1 h at ambient temperature to afford complex **5a** as a colorless solid (27 mg, 63%). The single crystal for X-ray crystallographic analysis was obtained by slow volatilization of saturated solution of complex **5a** with dichloromethane and hexane. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.61 (t, J = 7.8 Hz , 1H), 7.45 (t, J = 8.0Hz, 1H), 7.24 (d, J = 7.5 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 2.95 (s, 6H), 2.54 (sept, J = 6.9 Hz, 2H), 1.47 (d, J = 16 Hz, 18H), 1.32 (d, J = 6.5 Hz, 6H), 1.17 (d, J = 6.5 Hz, 6H), −0.25 (s, 3H); ^{31}P NMR (202 MHz, $CDCl_3$) δ 85.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ −78.2; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2 (d, J = 11 Hz, 1C), 158.9, 144.8, 138.6, 134.8, 130.9, 128.3 (d, J = 4.2 Hz, 2C), 124.2 (2C), 122.9 (2C), 122.9 (2C), 121.0 (q, J = 321 Hz, 1C), 37.9 (d, J = 62 Hz, 2C), 28.8 (2C), 26.6 (2C), 26.2 (6C), 24.5 (2C), 23.2 (2C), −9.7. Elemental analysis, Calcd for $C_{32}H_{49}F_3N_3O_4PPdS$ C, 50.16;

H, 6.45; N, 5.48. found C, 49.71; H, 6.42; N, 5.32.

[Synthesis of **5b**] In the glove box, complex **5a** (30 mg, 0.039 mmol) and NaBAr$^F_4$ (31 mg, 0.035 mmol) were added into a 20 mL Schlenk flask and the flask was trasfeered outside of glove box. After dichloromethane (ca. 10 mL) was added under the argon atmosphere, the mixture was stirred for 3 h at ambient temperature. The volatile matters were removed under vacuum at ambient temperature and the Schlenk was then transferred into glove box. After diethyl ether (ca. 10 mL) was added, the mixture was filtered through a pad of Celite and the pad was washed with diethyl ether (ca. 3.0 mL). The extraction was repeated twice, and the combined filtrate was evaporated to dryness. The white solid product is washed with pentane (ca. 10 mL) and dried under vacuum for 1 h at ambient temperature, to afford **5b** as a colorless solid (50 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 8H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.52 (s, 4H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.28 (s, 2H), 7.11–7.10 (m, 3H), 2.92 (s, 6H), 2.49 (sept, *J* = 7.0 Hz, 2H), 1.36 (d, *J* = 16 Hz, 18H), 1.33 (d, *J* = 7.0 Hz, 6H), 1.14 (d, *J* = 7.0 Hz, 6H), −0.19 (s, 3H); ^{31}P NMR (202 MHz, $CDCl_3$) δ 84.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ −62.4; ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8 (d, *J* = 11 Hz, 1C), 162.4–161.3 (m, 4C), 158.7, 144.6, 138.8, 134.9 (8C), 134.3, 131.4, 129.0 (qq, *J* = 31, 2.8 Hz, 8C), 127.6 (d, *J* = 3.9 Hz, 2C), 124.5 (2C), 123.0 (2C), 119.9 (d, *J* = 4.3 Hz, 2C), 117.6 (sep, *J* = 3.8 Hz, 4C), 37.9 (d, *J* = 62 Hz, 2C), 29.0 (2C), 26.5 (2C), 25.8 (6C), 24.4 (2C), 23.0 (2C), −8.9. HRMS-ESI (*m*/*z*) calcd for $C_{31}H_{49}N_3OPPd$ ($[M+H]^+$) 616.2643, found 616.2614.

Procedure of Ethylene Homopolymerization (Table 1, Entries 1–7)

A 50-mL stainless steel autoclave was dried in an oven for 3 h at 120 °C, sealed, and evacuated under vacuum for 2 h at 140 °C. After cooling to room temperature, a freshly prepared solution of catalyst (2.5 μmol, 5.0 mL of 0.50 mmol/L solution in toluene) and dehydrated toluene (5.0 mL) were added under argon atmosphere. Then, the autoclave was pressurized with ethylene (3.0 MPa), sealed, and stirred in an isothermal heating block under given conditions. After cooling to room temperature and venting redundant ethylene, the reaction was quenched by addition of ethanol (ca. 20 mL). The formed precipitates were collected by filtration, washed with ethanol, and dried under high vacuum for at least 2 h at 100 °C to afford polyethylene. The molecular weight and molecular weight distribution were determined by size exclusion chromatography. The extent of branching in the polymer backbone was determined by quantitative ^{13}C NMR analysis.

Procedure of Ethylene Oligomerization (Table 1, Entry 8)

A 50-mL stainless steel autoclave was dried in an oven for 3 h at 120 °C, sealed, and evacuated under vacuum for 2 h at 140 °C. After cooling to room temperature, a freshly prepared solution of catalyst (2.5 μmol, 5.0 mL of 0.50 mmol/L solution in toluene) and dehydrated toluene (5.0 mL) were added under argon atmosphere. Then, the autoclave was pressurized with ethylene (3.0 MPa), sealed, and stirred in an isothermal heating block under given conditions. After cooling with ice-water bath and venting redundant ethylene, tridecane (32 mg) was added and the mixture was stirred for 2 min and the product was analyzed by gas chromatography.

Procedure of Ethylene/Polar Monomer Copolymerization (Table 2)

A 50-mL stainless steel autoclave was dried in an oven for 3 h at 120 °C, sealed, and evacuated under vacuum for 2 h at 140 °C. After cooling to room temperature, a solution of catalyst **4b** (5.0 μmol, 5.0 mL of 1.0 mmol/L solution in toluene) was added under argon atmosphere. To the mixture were added 2.0 mL of a polar monomer and 3.0 mL of toluene (entries 1, 3, and 5) or 5.0 mL of a polar monomer (entries 2, 4, 6, and 7). Then the autoclave was charged with ethylene (3.0 MPa), sealed, and stirred in an isothermal heating block for 3.0 h at 30 °C.

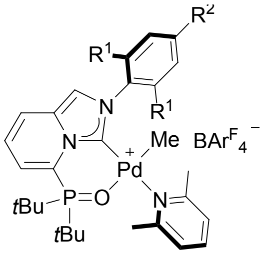
After cooling to room temperature and venting redundant ethylene, the reaction was quenched by addition of ethanol (ca. 20 mL), and the volatile matters were removed in vacuo. After THF (ca. 30 mL) was added, the formed precipitates were collected by filtration, washed with THF (ca. 10 mL), and dried under high vacuum for at least 3.0 h at 100 °C to afford ethylene/polar monomer copolymers. The molecular weight and molecular weight distribution were determined by size exclusion chromatography. The incorporation ratio of polar monomers was calculated based on ^{1}H NMR analysis.

2. Full Data of Polymerization

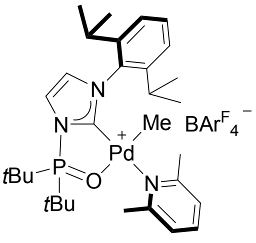
Table S1. Ethylene Polymerization by Various Palladium Complexes[a]

entry	catalyst	T (°C)	time (h)	polymer (g)	activity (kg/mol·h)	M_n[b] (kg/mol)	M_w/M_n[b]	branch[c]	T_m (°C)[d]
1	**4b** (2.5 µmol)	30	1.0	0.11	44	12	2.1	0	133.4
2	**4b** (2.5 µmol)	30	2.0	0.25	50	11	2.3	0	133.3
3	**4b** (2.5 µmol)	30	5.0	0.42	44	13	2.0	0	132.7
4	**4b** (2.5 µmol)	30	10	0.84	34	11	2.3	0	132.3
5	**4b** (2.5 µmol)	50	1.0	0.38	152	7.2	2.3	0	131.6
6	**4b** (2.5 µmol)	50	2.0	0.41	83	6.5	2.3	0	131.6
7	**4c** (2.5 µmol)	30	2.0	0.15	29	19	2.2	0	133.6
8	**5b** (2.5 µmol)	30	2.0	trace	---	oligomer		---	---
S1	**3a** (5.0 µmol)	30	2.0	0.011	1.1	2.9	1.6	---	---
S2[e]	**3a** (1.0 µmol)	80	1.0	0.033	33	26	2.1	4.5	---
S3[e]11	**3a** (1.0 µmol)	100	1.0	0.69	690	76	2.4	11.6	---
S4	**2a** (2.5 µmol)	30	2.0	0.017	3.4	17	1.5	---	---
S5[f]	**2a** (0.75 µmol)	100	1.0	2.0	2700	31	3.1	5	---
S6	**1a** (2.5 µmol)	30	2.0	2.1	427	15	4.8	---	---

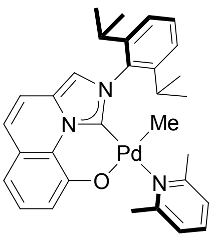
[a] A mixture of catalyst (2.5 µmol) and ethylene (3.0 MPa) in toluene (10 mL) was stirred under the indicated. [b] Number-average molecular weight determined by size-exclusion chromatography using polystyrene as an internal standard and corrected by universal calibration. [c] Methyl branches per 1000C determined by quantitative ^{13}C NMR analyses. [d] Melting temperature determined by DSC analysis. [e] Data from reference 11; Ethylene (4.0 MPa), toluene 20 mL. [f] Data from reference 12; toluene 15 mL.



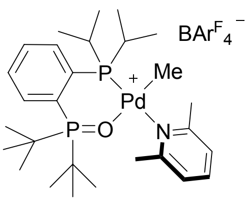
4b: R1= *i*Pr; R2 = H
4c: R1= CHPh2; R2 = Me



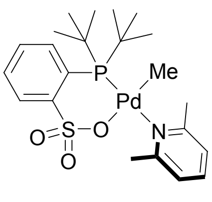
5b



3a



2a

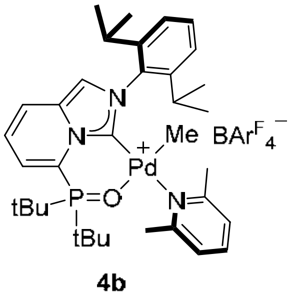


1a

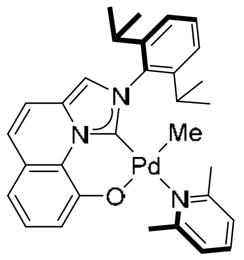
Table S2. Copolymerization of Ethylene with Polar Monomers by Complex **4b**[a]

entry	cat.	comonomer (mL)	polymer (mg)	activity (kg/mol·h)	M_n[b] (kg/mol)	M_w/M_n[b]	i.r.[c] (mol%)	yield based on comonomer[d] (%)	branch[e]	T_m (°C)[f]
1	**4b**	AAc (2.0)	198	13	9.4	2.3	0.15	0.057	nd	131.2
2	**4b**	AAc (5.0)	67	4.5	7.4	2.2	0.58	0.030	nd	126.3
3	**4b**	MA (2.0)	72	4.8	7.0	2.3	0.27	0.031	nd	131.2
4	**4b**	MA (5.0)	26	1.7	4.8	2.1	0.61	0.010	nd	128.6
5[g]	**4b**	MA (5.0)	127	2.1	4.1	2.7	0.50	0.041	0	129.2
6[h]	**4b**	MA (5.0)	0	---	---	---	---	---	---	---
7	**4b**	AC (2.0)	71	4.7	8.1	2.1	0.19	0.020	nd	130.1
8	**4b**	AC (5.0)	38	2.5	6.8	2.1	0.47	0.010	nd	128.1
9[i]	**4b**	VA (5.0)	25	2.5	6.9	2.3	0	---	nd	131.4
S1[j]	**3a**	AAc (1.0)	134	4.5	7.4	2.5	1.4	---	6.3	---
S2[j]	**3a**	MA (0.2)	319	11	17	2.0	0.8	---	8.1	---
S3[j]	**3a**	AC (0.4)	38	1.3	3.9	2.1	0.5	---	4.3	---
S4[j]	**3a**	VA (1.0)	188	6.3	11	2.5	<0.1	---	7.4	---

[a] A mixture of catalyst (5.0 μmol), polar monomer, and ethylene (3.0 MPa) in toluene (10 mL including polar monomer) was stirred at 30 °C for 3.0 h under the conditions mentioned in Table S2. Abbreviations, AAc: allyl acetate, MA: methyl acrylate, AC: allyl chloride, VA: vinyl acetate, nd: not determined. [b] Number-average molecular weight measured by size-exclusion chromatography using polystyrene as an internal standard and corrected by universal calibration. [c] Molar ratio of polar monomers incorporated in copolymers to ethylene polymerized, calculated based on ^{1}H NMR spectra of copolymers. [d] Molar ratio of the amount of polar monomers incorporated into copolymers to that used in the feed. [e] Methyl branches per 1000 C determined by quantitative ^{13}C NMR analyses. [f] Melting temperature determined by DSC analysis. [g] Catalyst (20 μmol). [h] Homopolymerization of methyl acrylate in the absence of ethylene. [i] Polymerization time: 2.0 h. [j] A mixture of catalyst **3a** (10 μmol), polar monomer, and ethylene (4.0 MPa) in toluene (20 mL including polar monomer) was stirred at 100 °C for 3.0 h under the conditions mentioned in Table S2.



4b



3a

3. NMR Spectra of Ligands and Catalysts

3.1 Ligand Precursors L1 and L2

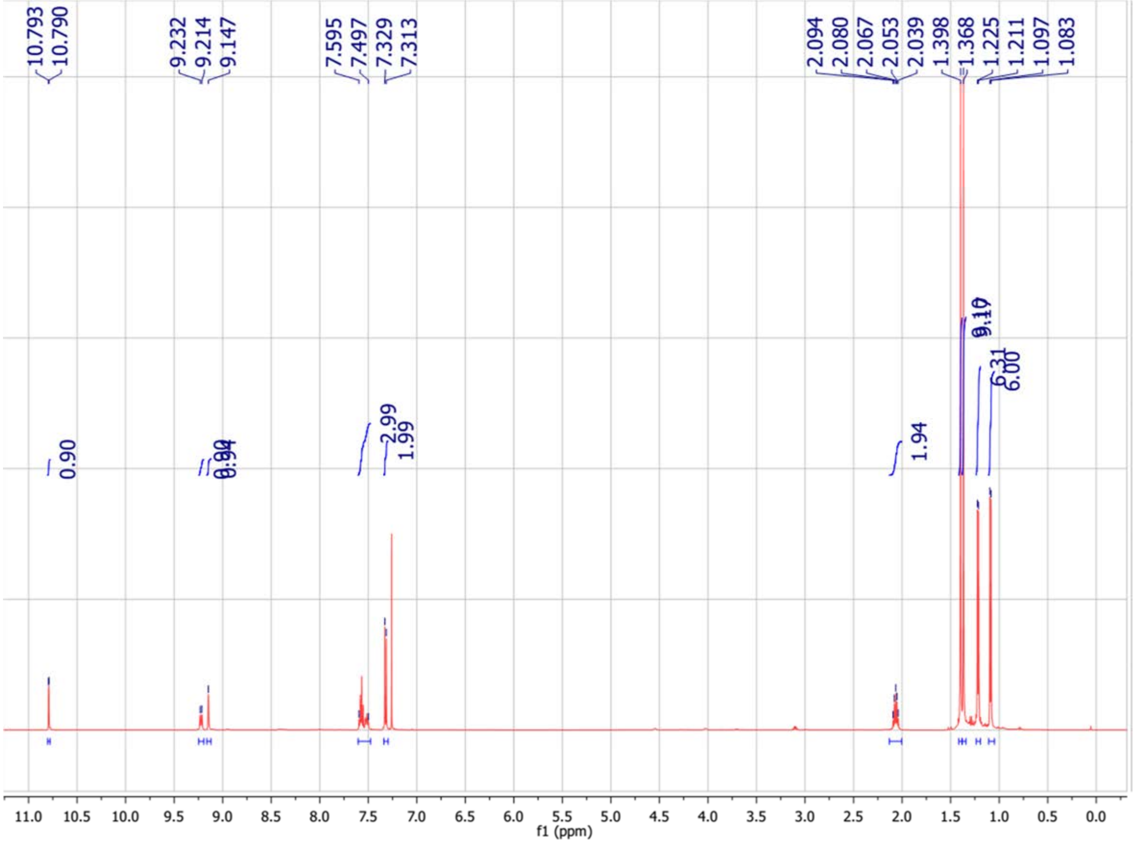


Figure S1: ^{1}H NMR (500 Hz, $CDCl_3$) spectrum of ligand precursor **L1**.

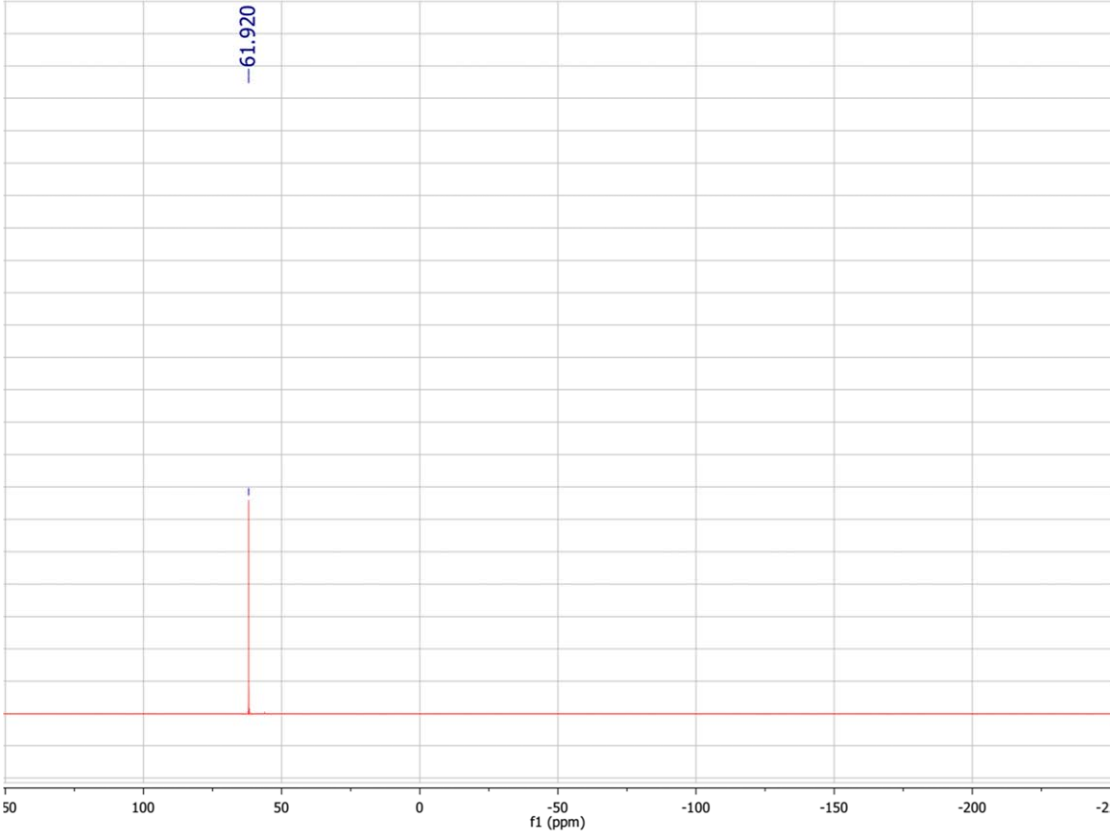


Figure S2: ^{31}P NMR (202 Hz, $CDCl_3$) spectrum of ligand precursor **L1**.

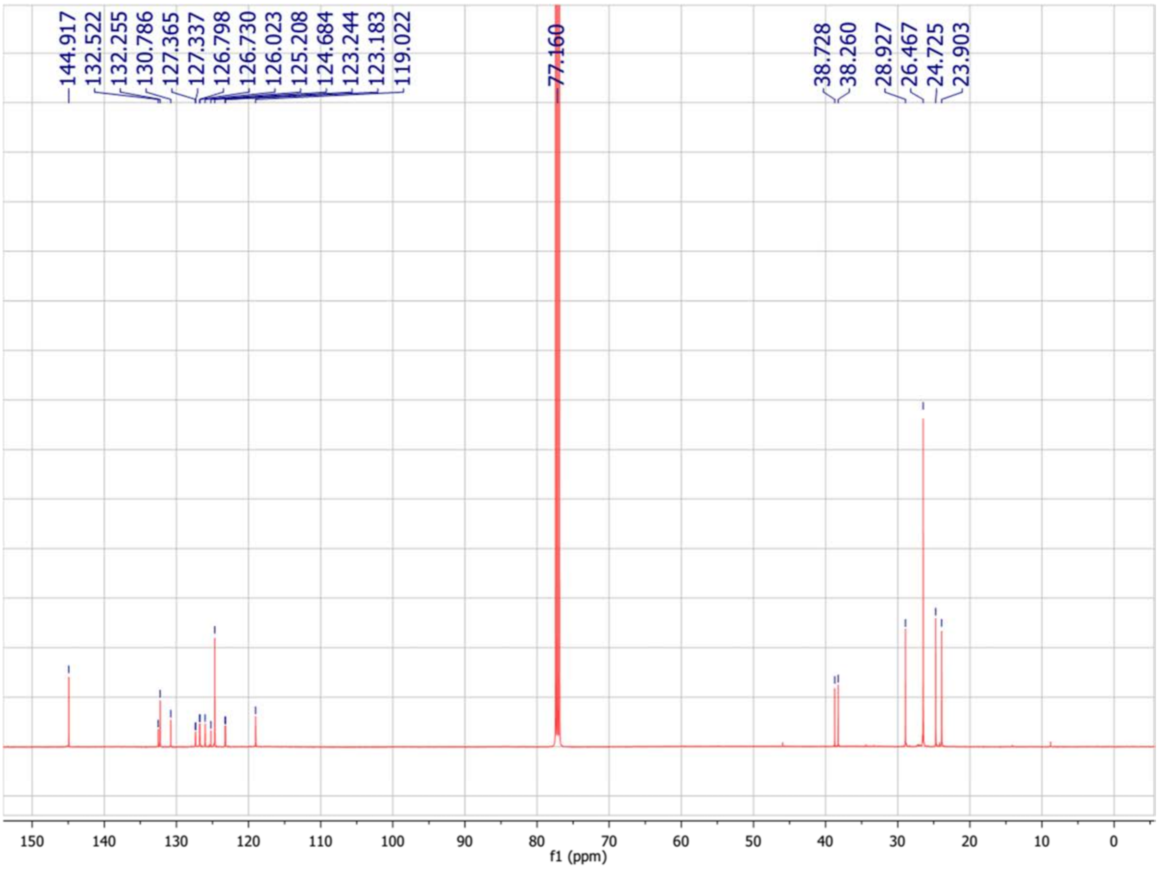


Figure S3: ^{13}C NMR (126 Hz, CDCl$_3$) spectrum of ligand precursor **L1**.

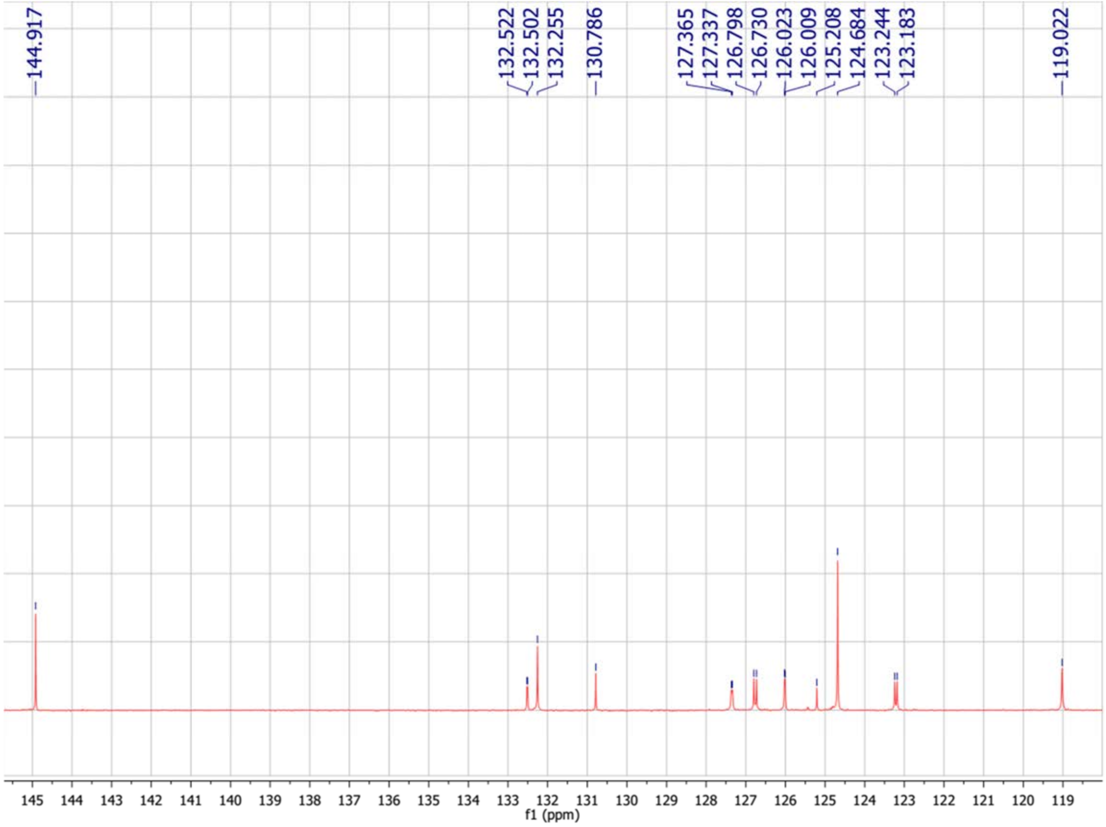


Figure S4: ^{13}C NMR (126 Hz, CDCl$_3$) spectrum (118–146 ppm) of ligand precursor **L1**.

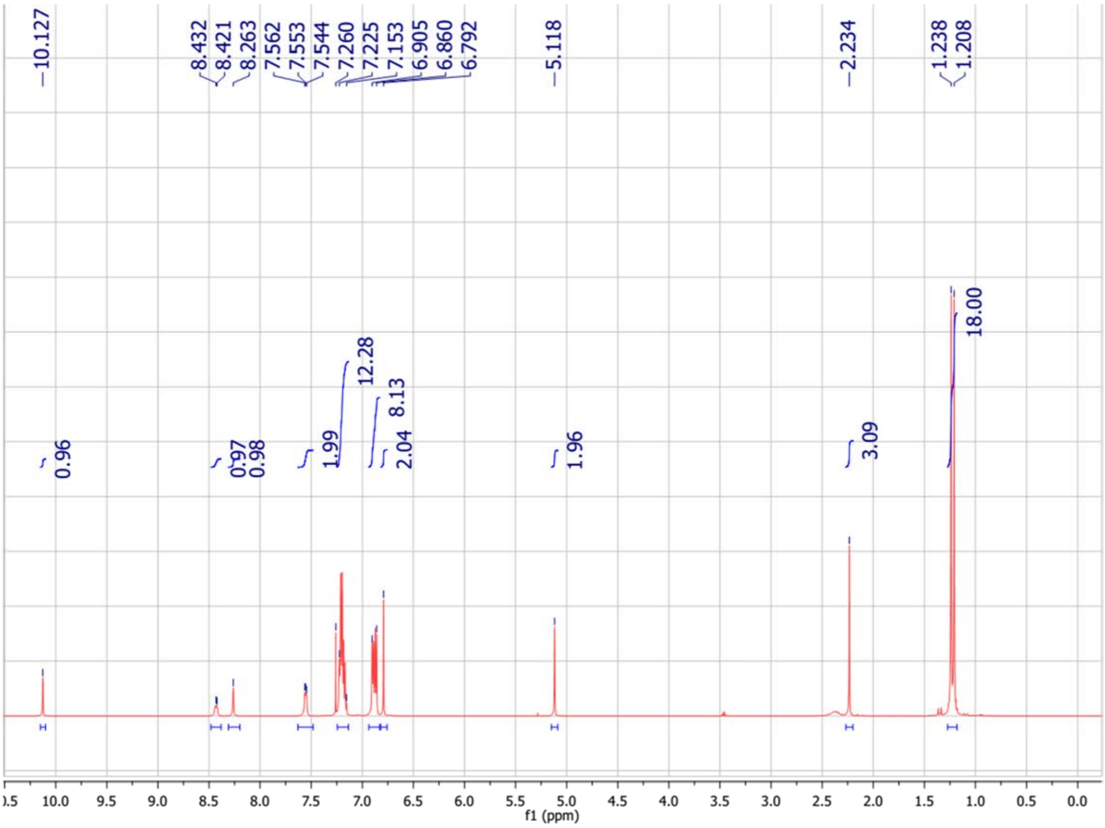


Figure S5: ^{1}H NMR (500 Hz, CDCl$_3$) spectrum of ligand precursor **L2**.

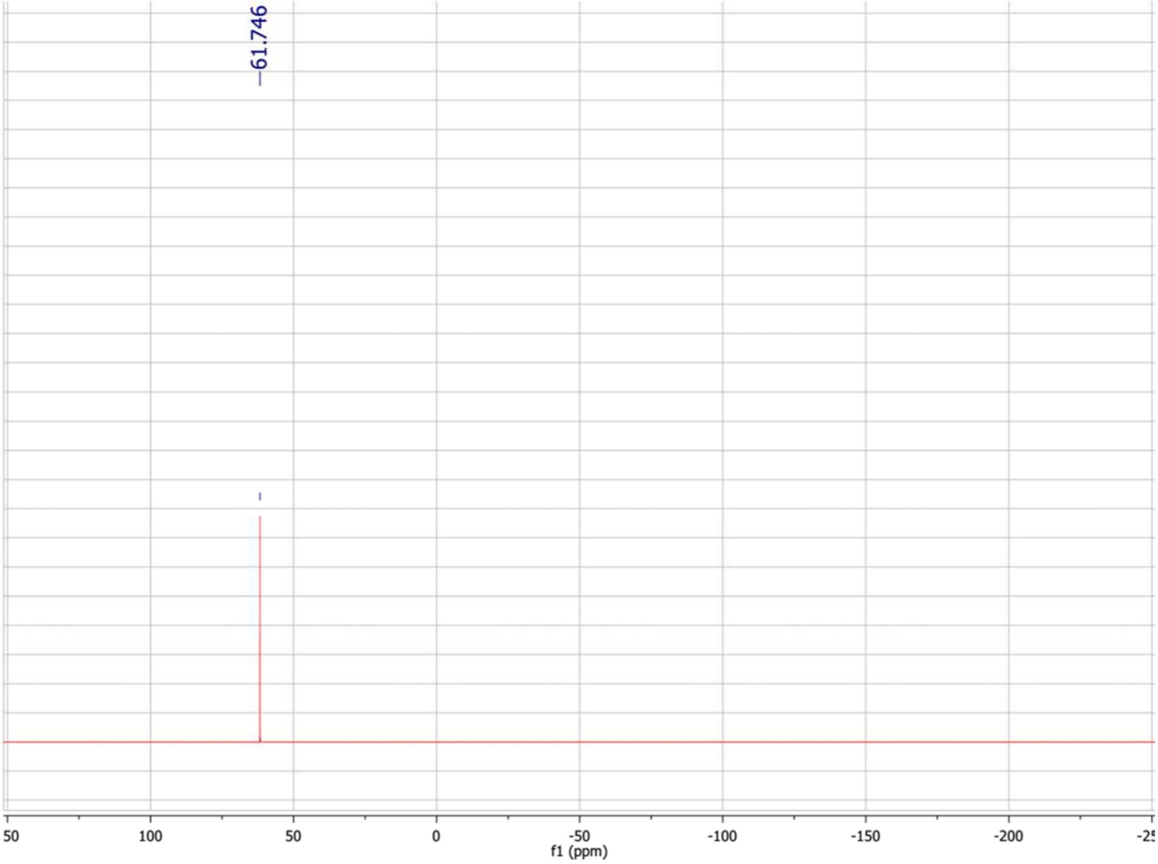


Figure S6: ^{31}P NMR (202 Hz, CDCl$_3$) spectrum of ligand precursor **L2**.

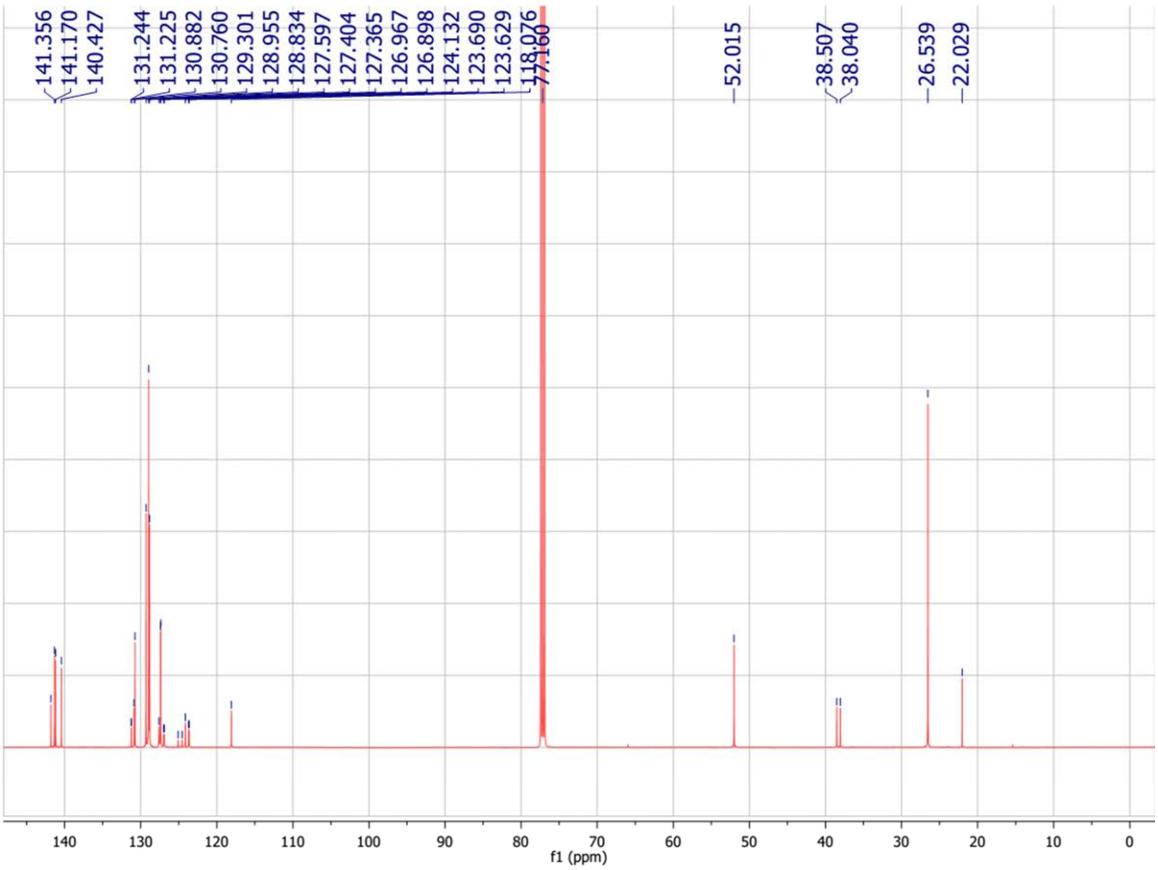


Figure S7: ^{13}C NMR (126 Hz, $CDCl_3$) spectrum of ligand precursor **L2**.

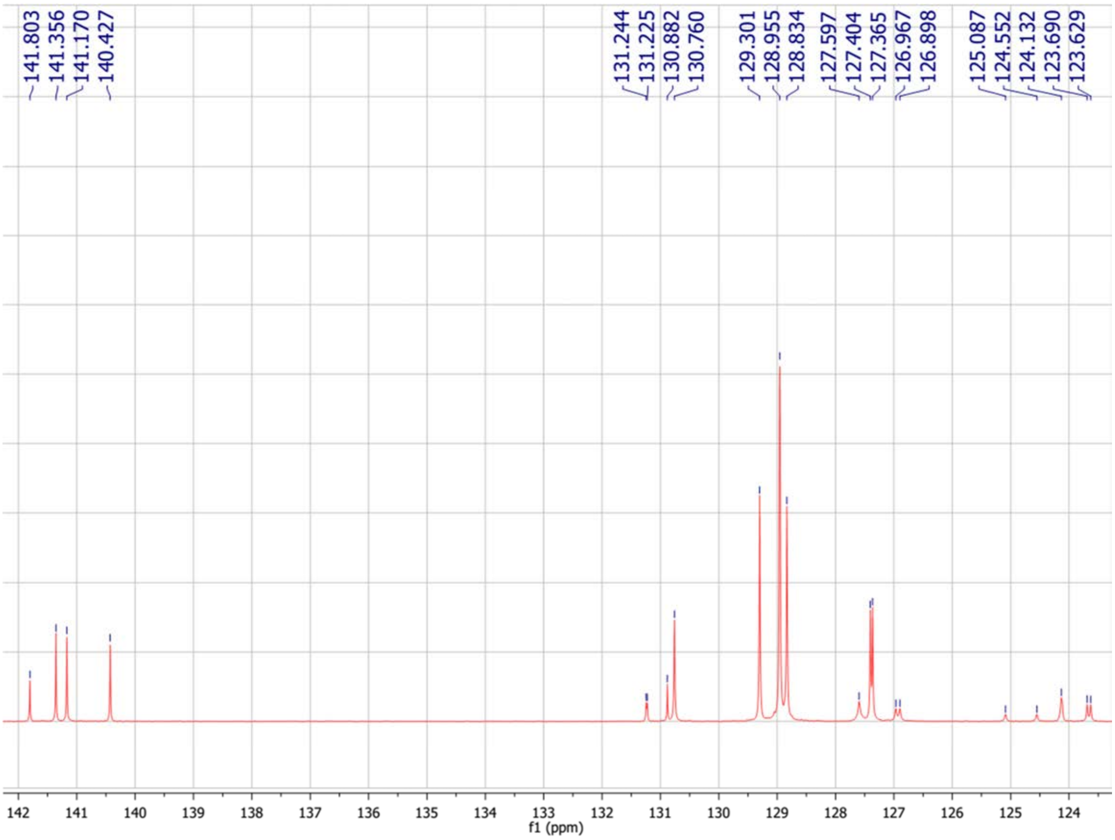


Figure S8: ^{13}C NMR (126 Hz, $CDCl_3$) spectrum (120–145 ppm) of ligand precursor **L2**.

3.2 Complexes 4a, 4b, 4c and 5a, 5b

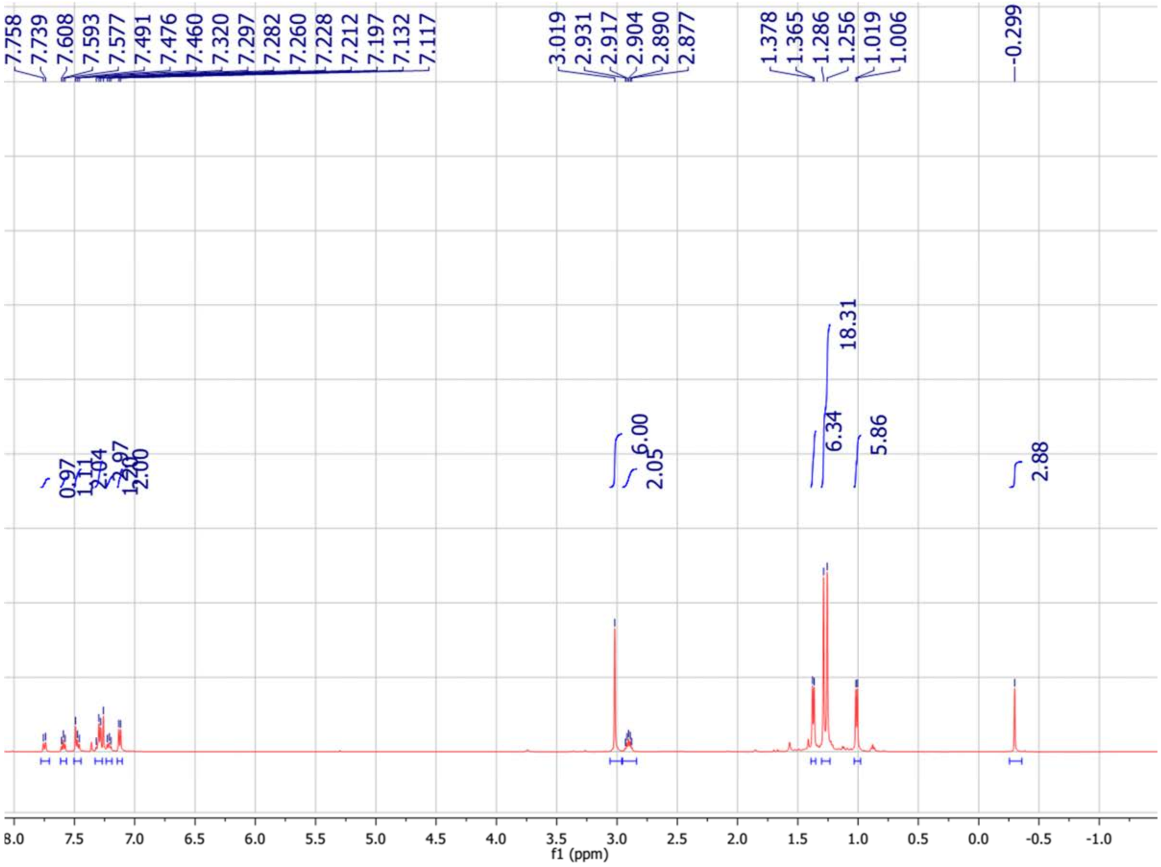


Figure S9: ^{1}H NMR (500 Hz, $CDCl_3$) spectrum of complex **4a**.

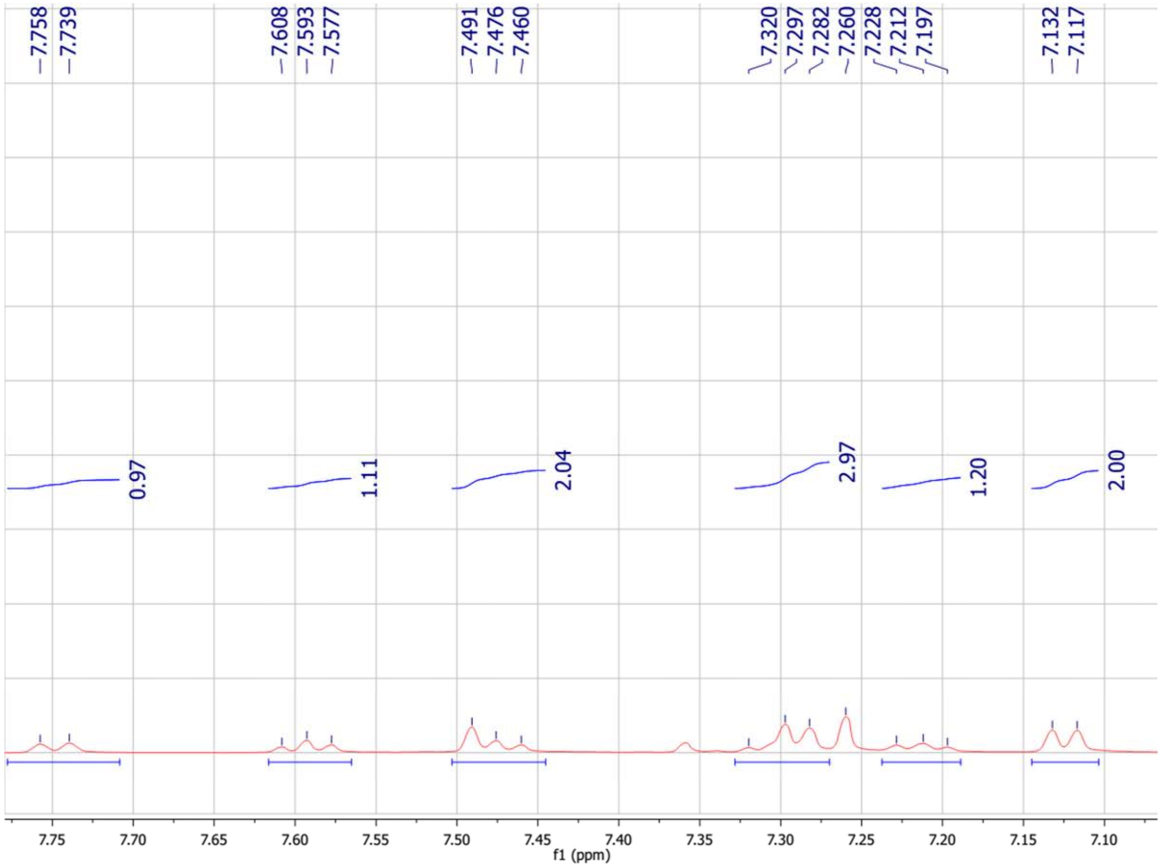


Figure S10: ^{1}H NMR (500 Hz, $CDCl_3$) spectrum (7.10–7.80 ppm) of complex **4a**.

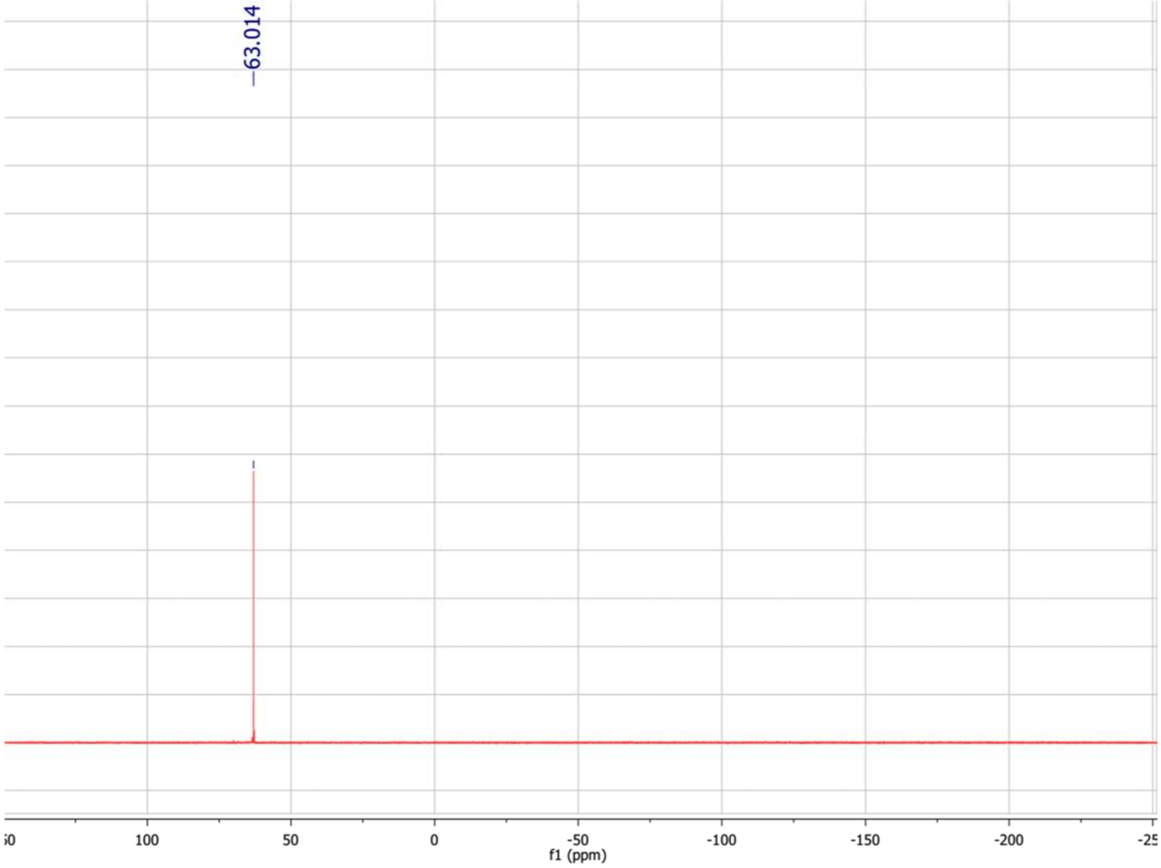


Figure S11: ^{31}P NMR (202 Hz, CDCl$_3$) spectrum of complex **4a**.

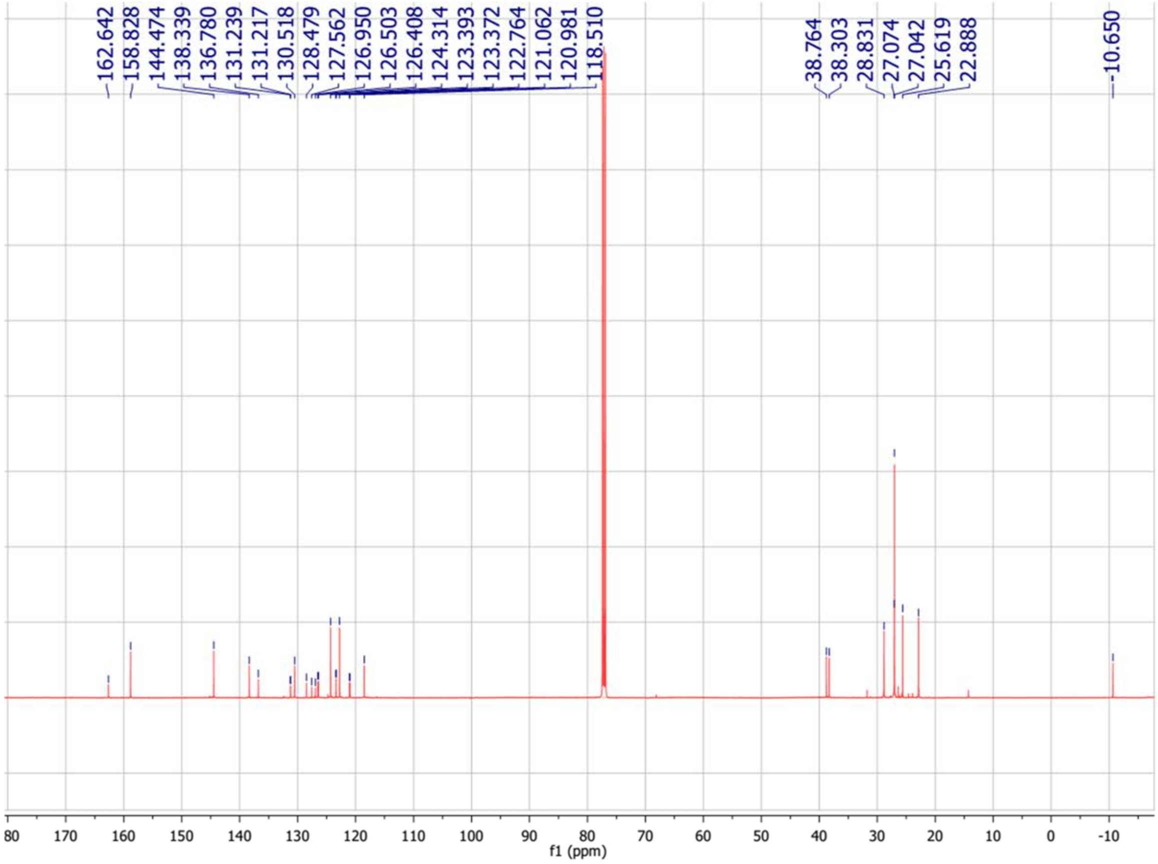


Figure S12: ^{13}C NMR (126 Hz, CDCl$_3$) spectrum of complex **4a**.

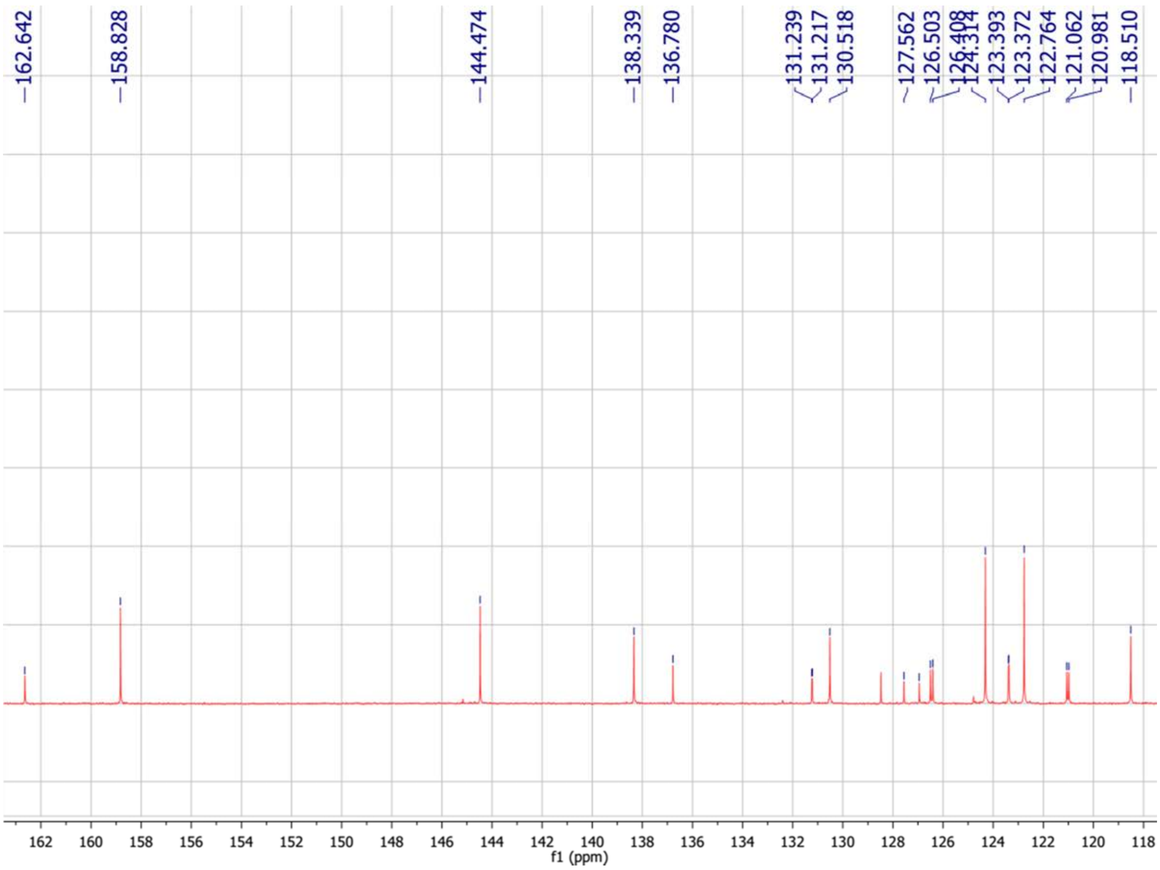


Figure S13: ^{13}C NMR (126 Hz, CDCl$_3$) spectrum (118–164 ppm) of complex **4a**.

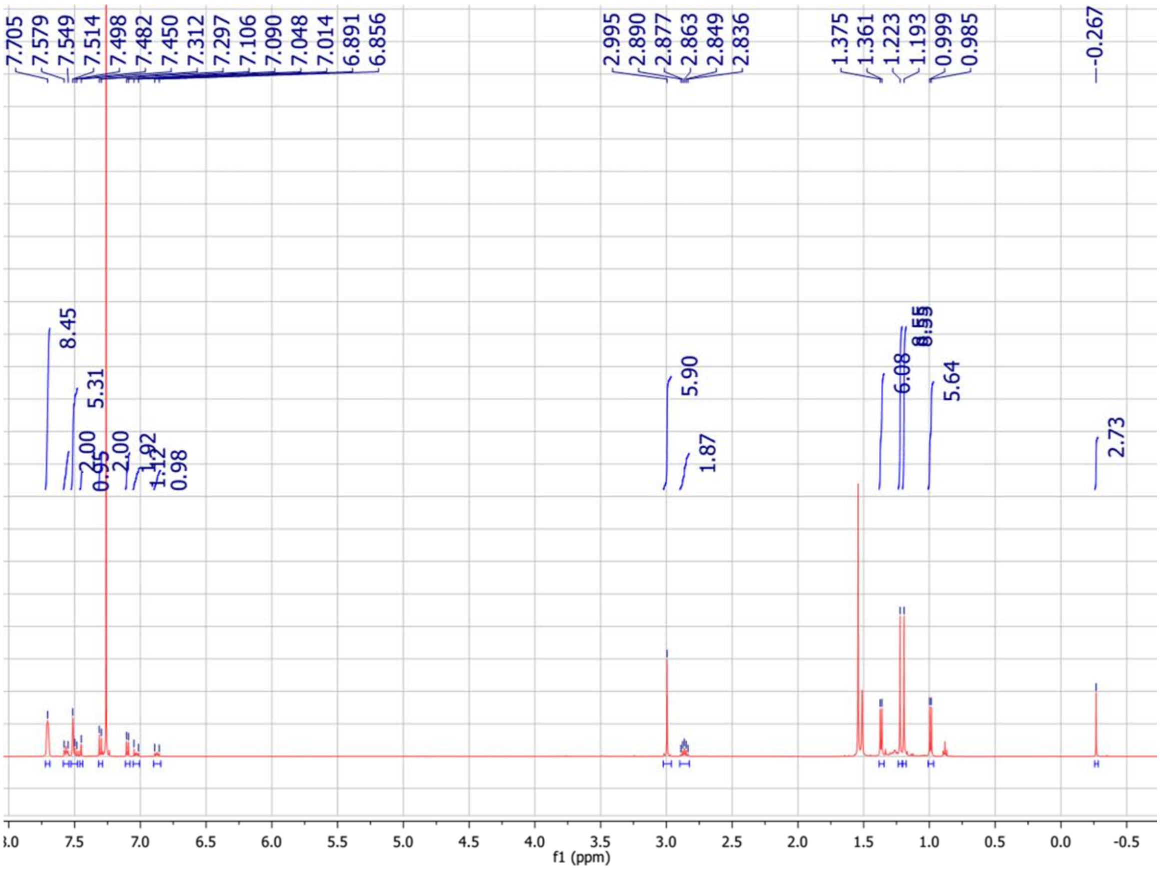


Figure S14: ^{1}H NMR (500 Hz, CDCl$_3$) spectrum of complex **4b**.

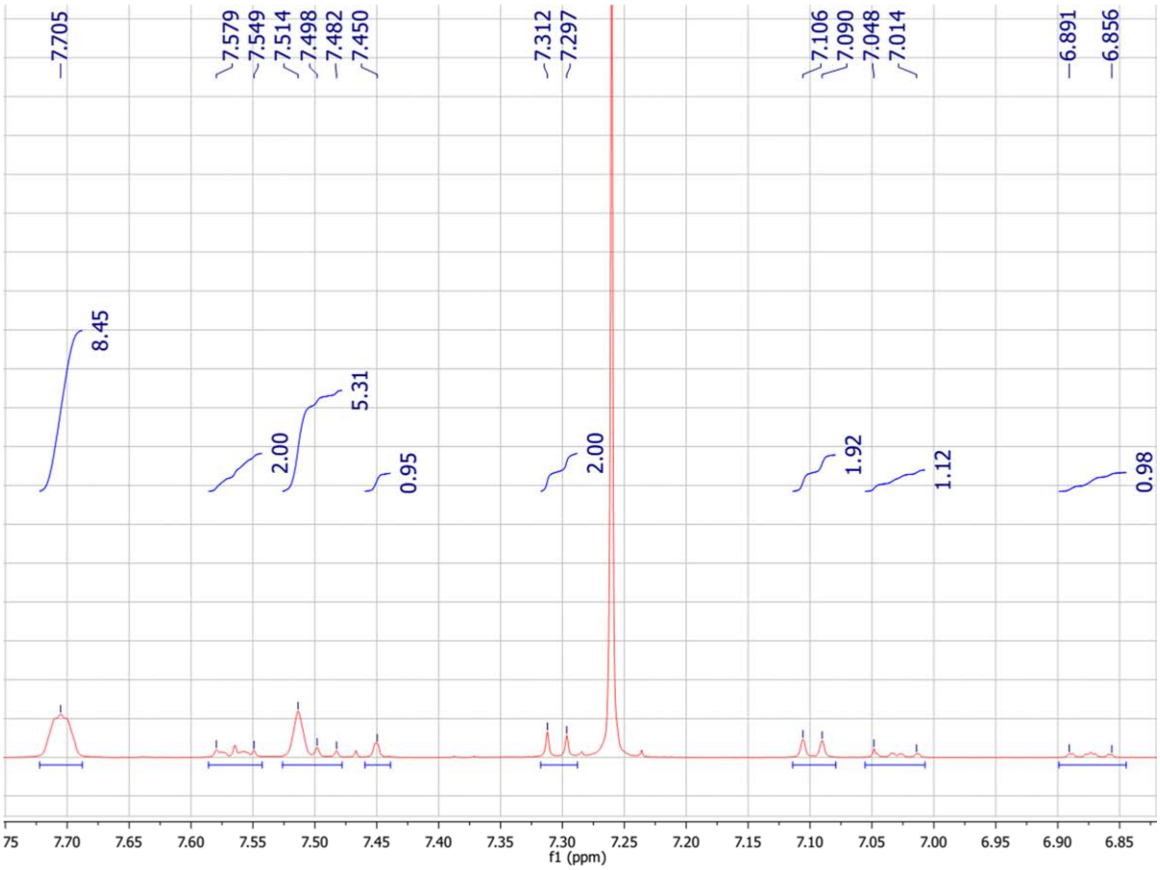


Figure S15: ^{1}H NMR (500 Hz, $CDCl_3$) spectrum (6.80–7.75 ppm) of complex **4b**.

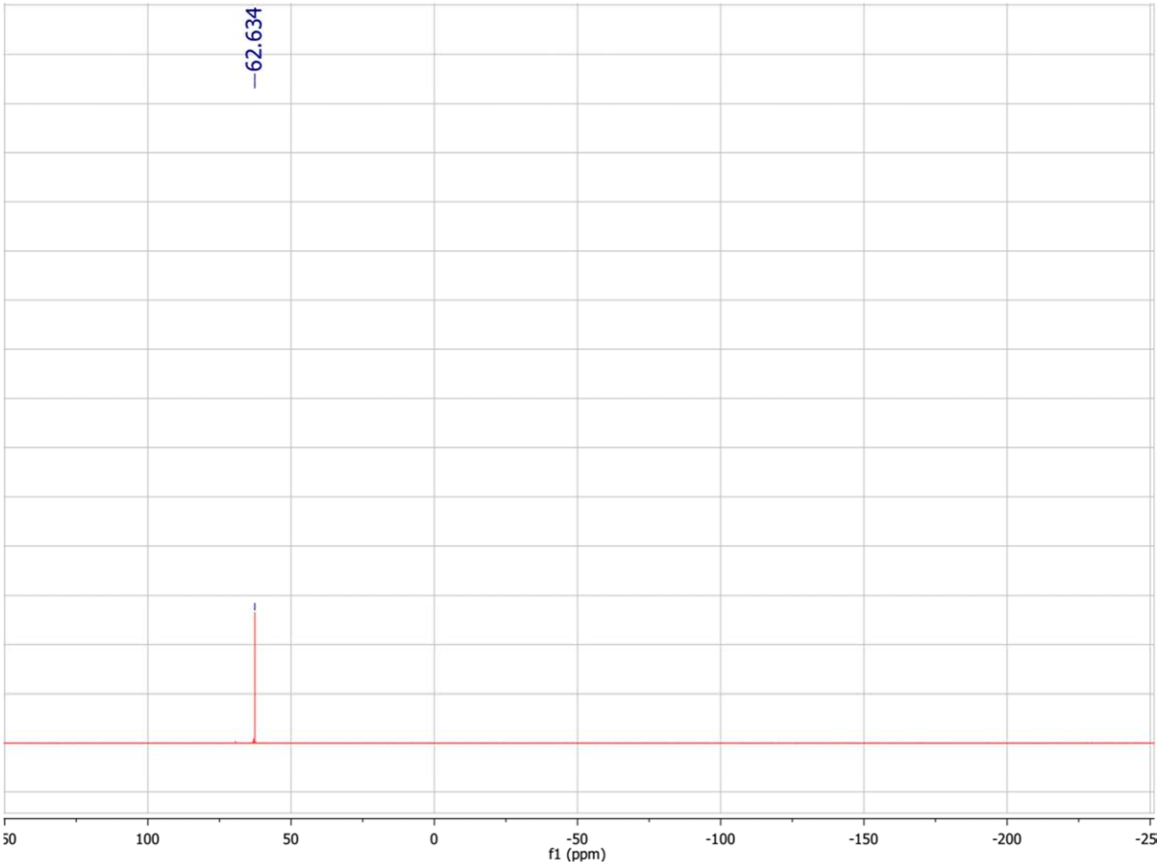


Figure S16: ^{31}P NMR (202 Hz, $CDCl_3$) spectrum of complex **4b**.

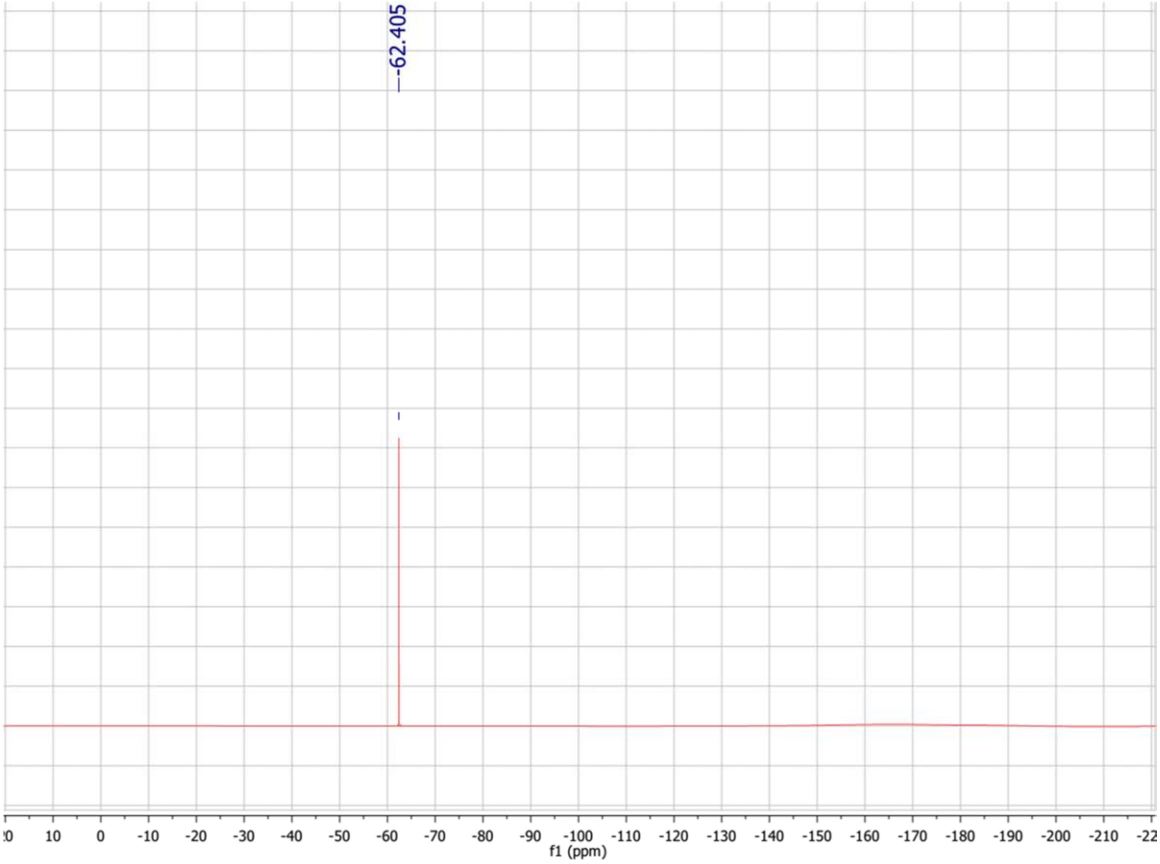


Figure S17: ^{19}F NMR (470 Hz, CDCl$_3$) spectrum of complex **4b**.

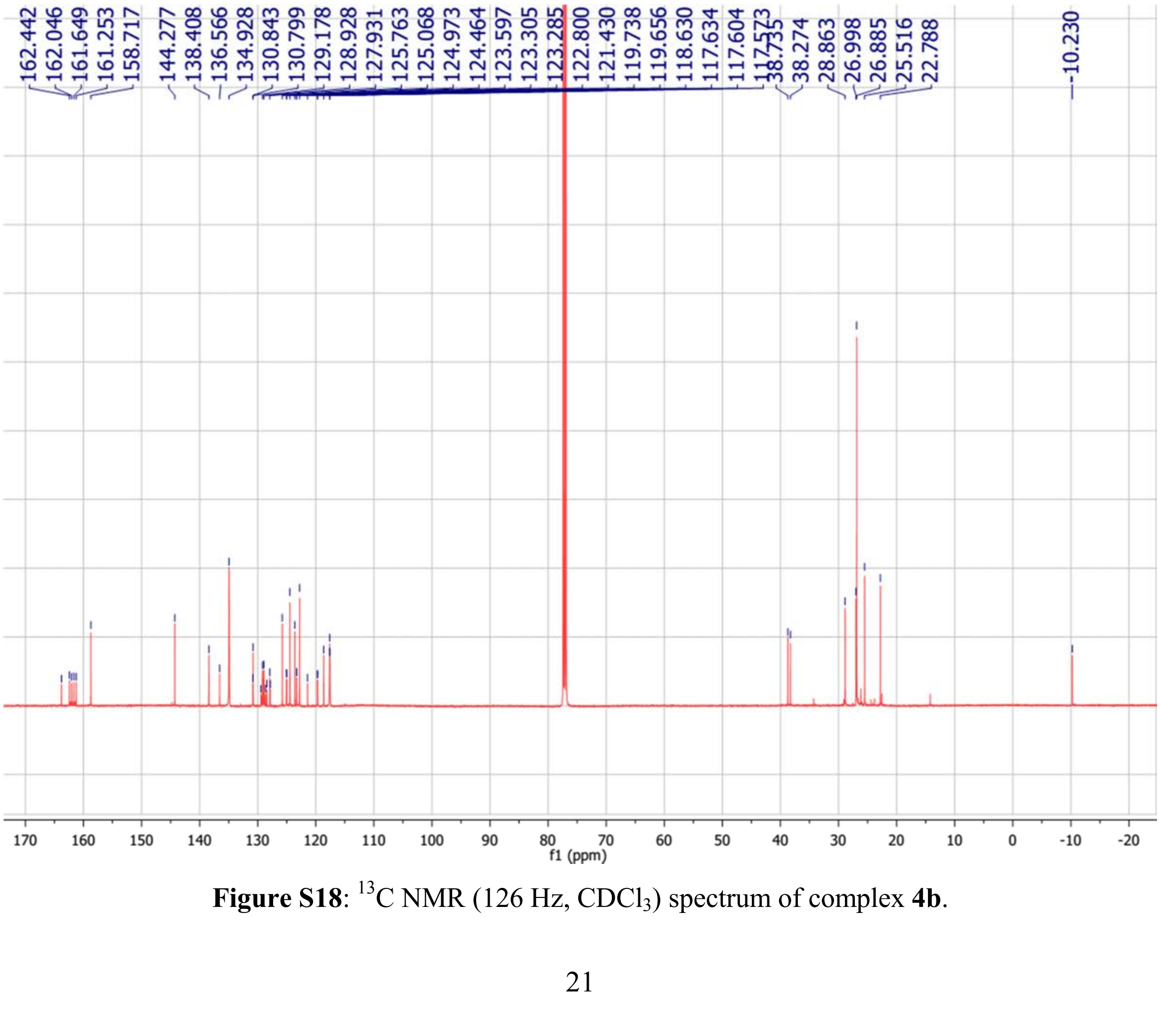


Figure S18: ^{13}C NMR (126 Hz, CDCl$_3$) spectrum of complex **4b**.

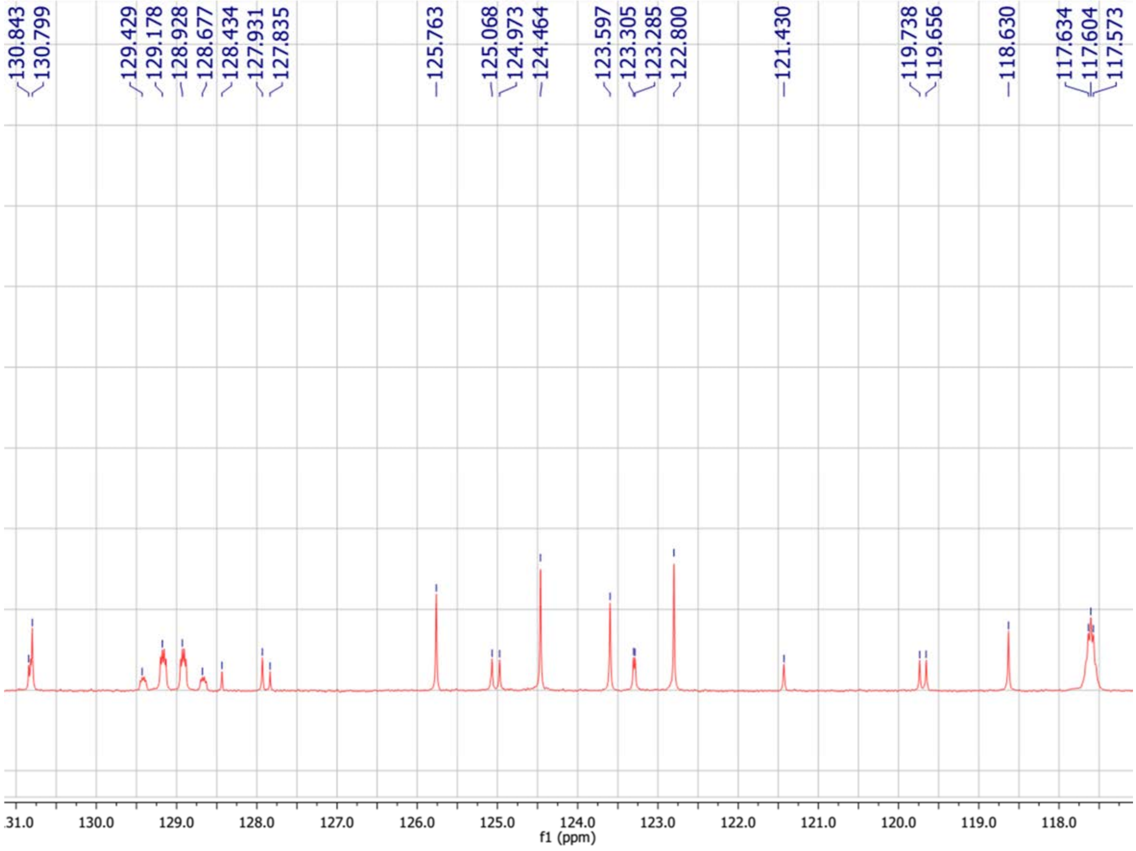


Figure S19: ^{13}C NMR (126 Hz, CDCl$_3$) spectrum (116–131 ppm) of complex **4b**.

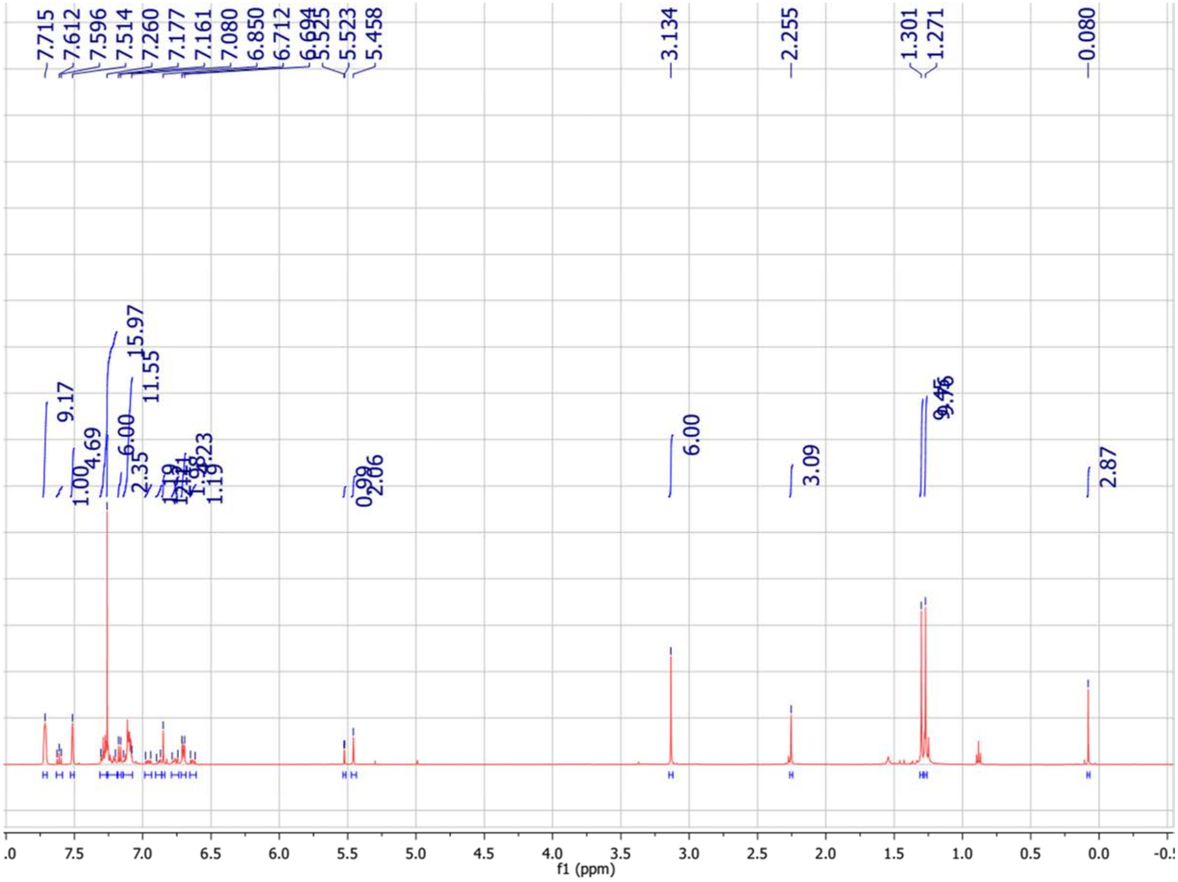


Figure S20: ^{1}H NMR (500 Hz, CDCl$_3$) spectrum of complex **4c**.

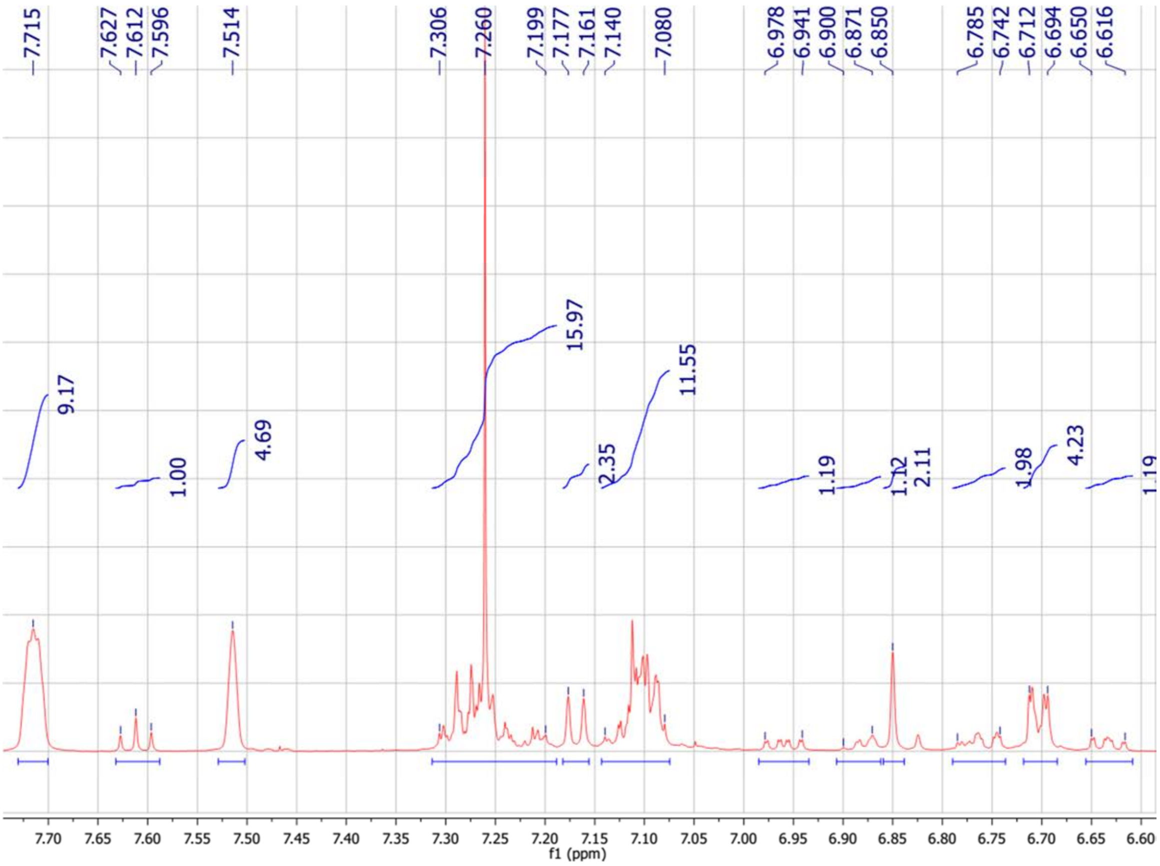


Figure S21: ^{1}H NMR (500 Hz, $CDCl_3$) spectrum (6.60–7.80 ppm) of complex **4c**.

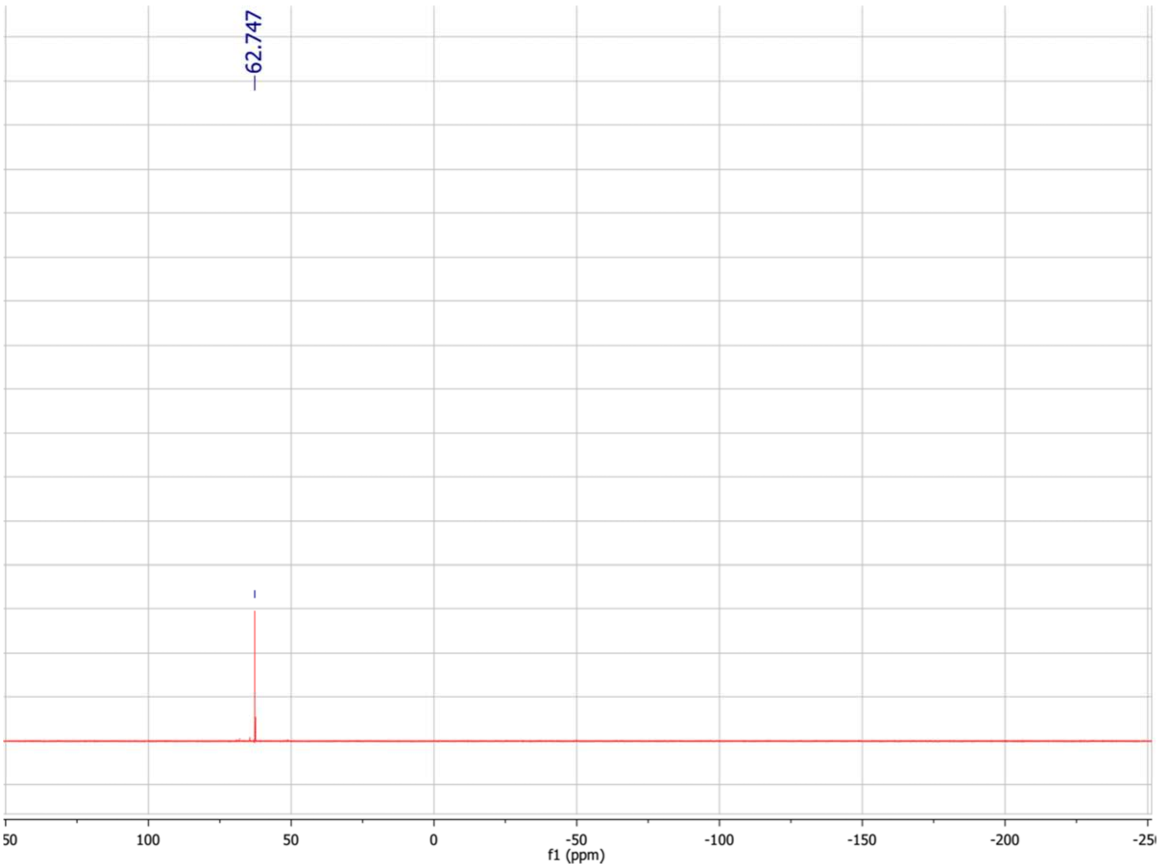


Figure S22: ^{31}P NMR (202 Hz, $CDCl_3$) spectrum of complex **4c**.

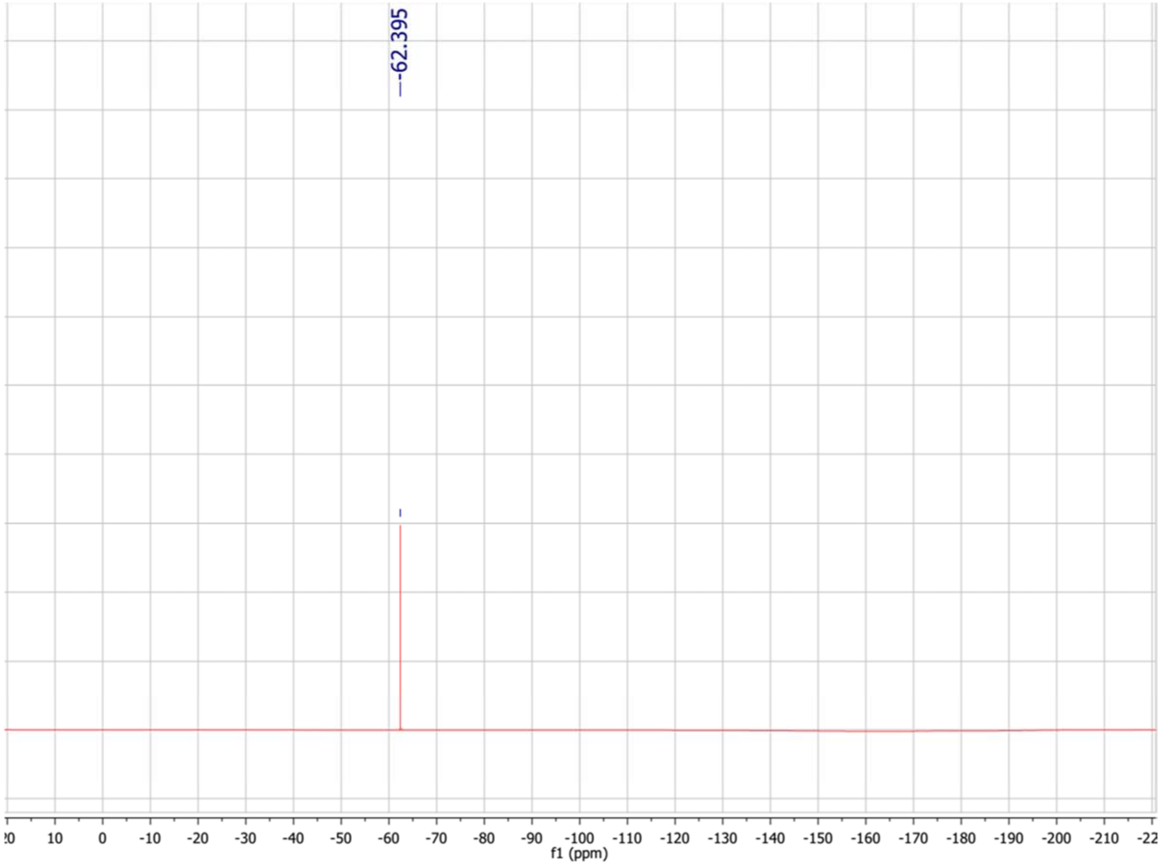


Figure S23: ^{19}F NMR (470 Hz, CDCl$_3$) spectrum of complex **4c**.

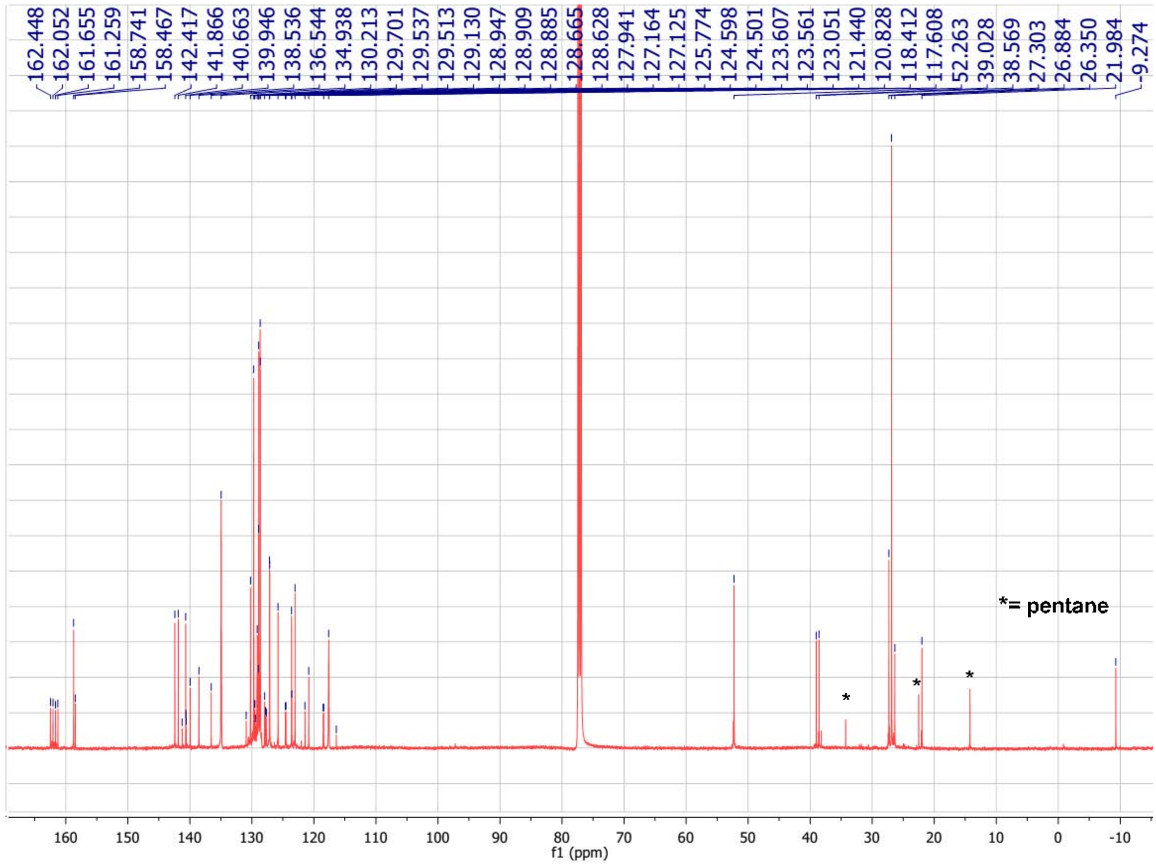


Figure S24: ^{13}C NMR (126 Hz, CDCl$_3$) spectrum of complex **4c**.

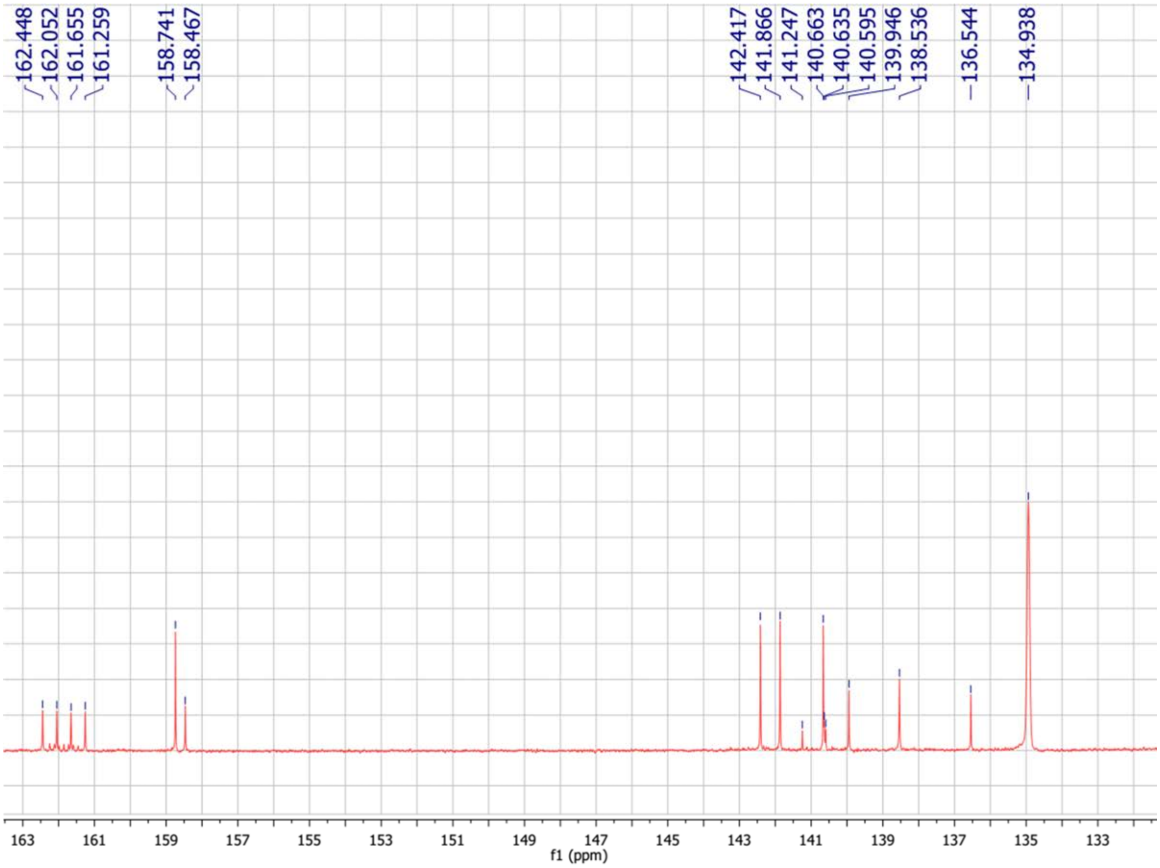


Figure S25: ^{13}C NMR (126 Hz, CDCl$_3$) spectrum (δ 133–163 ppm) of complex **4c**.

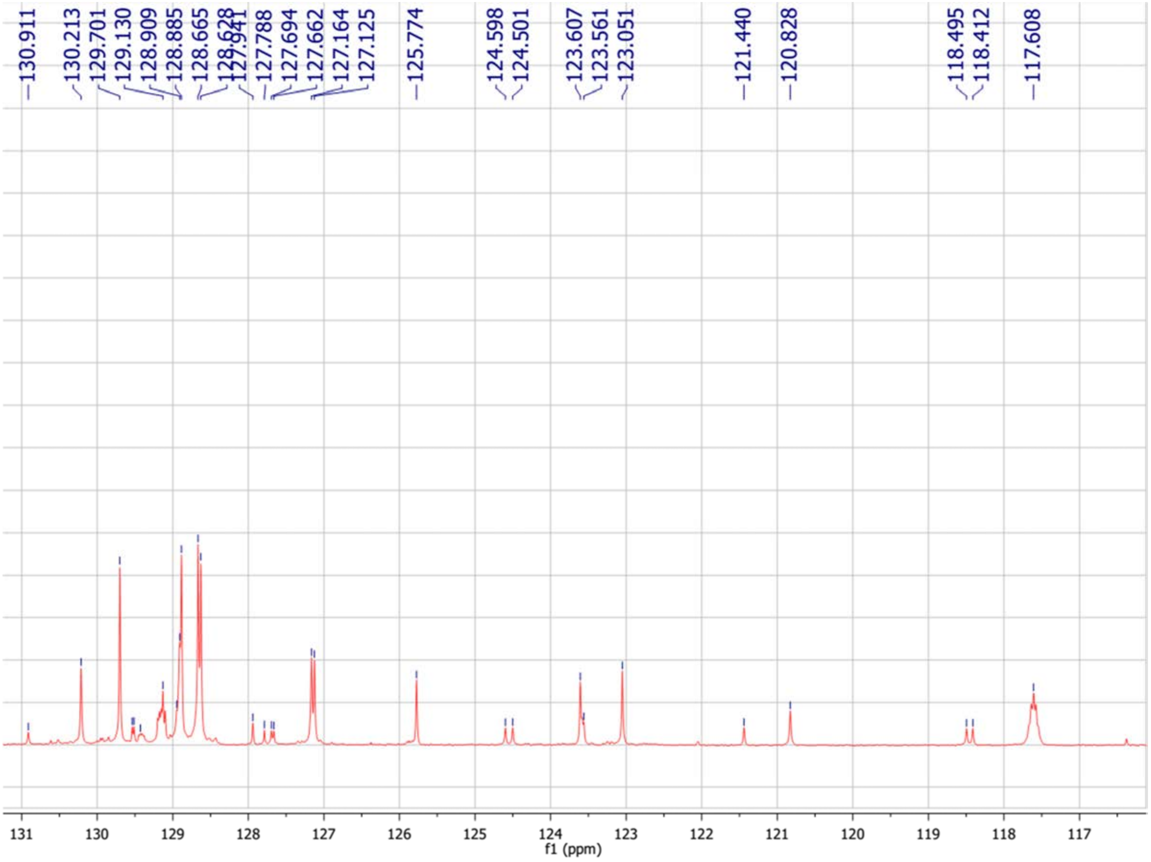


Figure S26: ^{13}C NMR (126 Hz, CDCl$_3$) spectrum (δ 117–131 ppm) of complex **4c**.

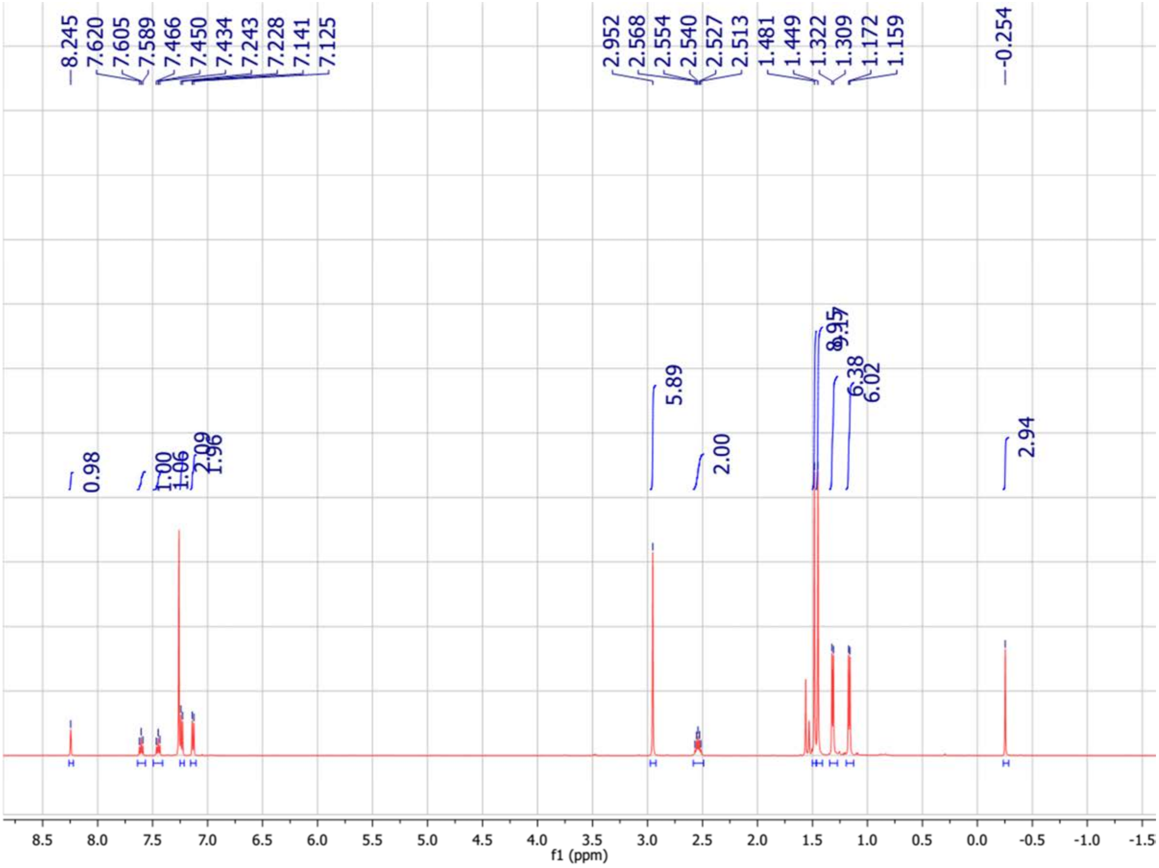


Figure S27: ^{1}H NMR (500 Hz, CDCl$_3$) spectrum of complex **5a**.

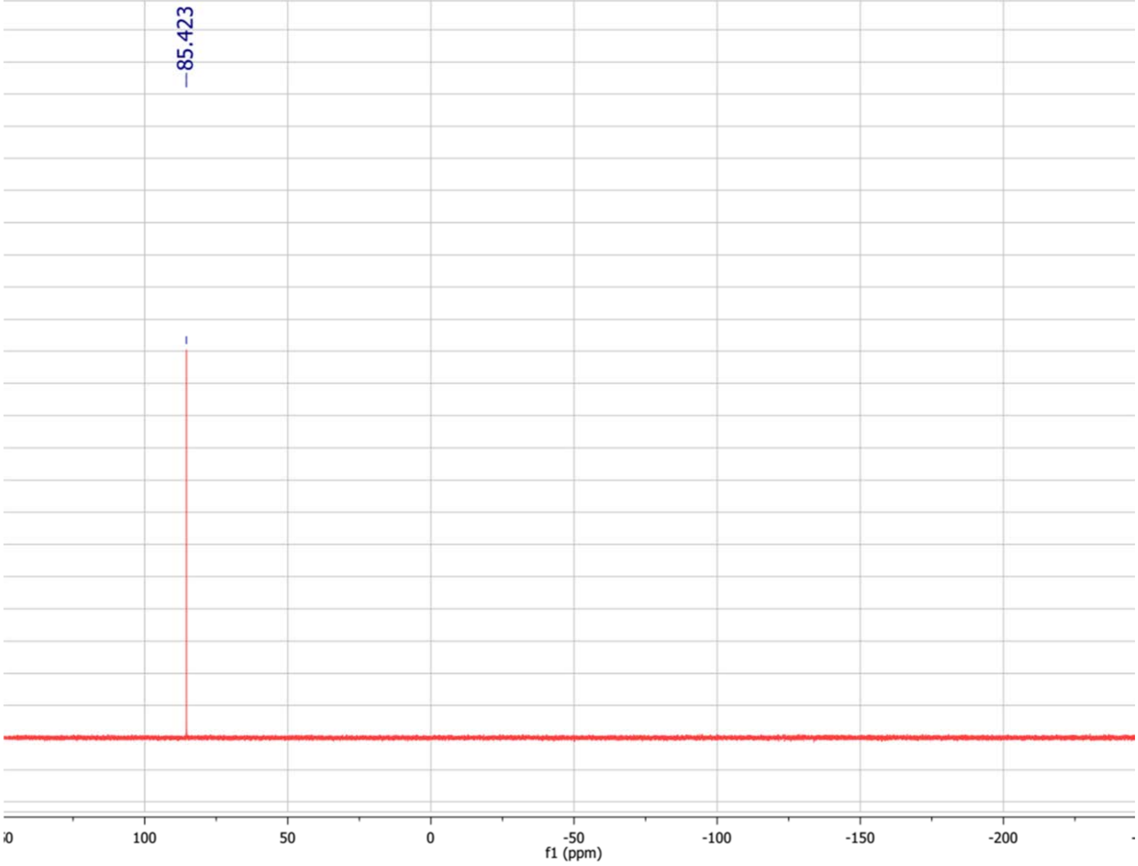


Figure S28: ^{31}P NMR (202 Hz, CDCl$_3$) spectrum of complex **5a**.

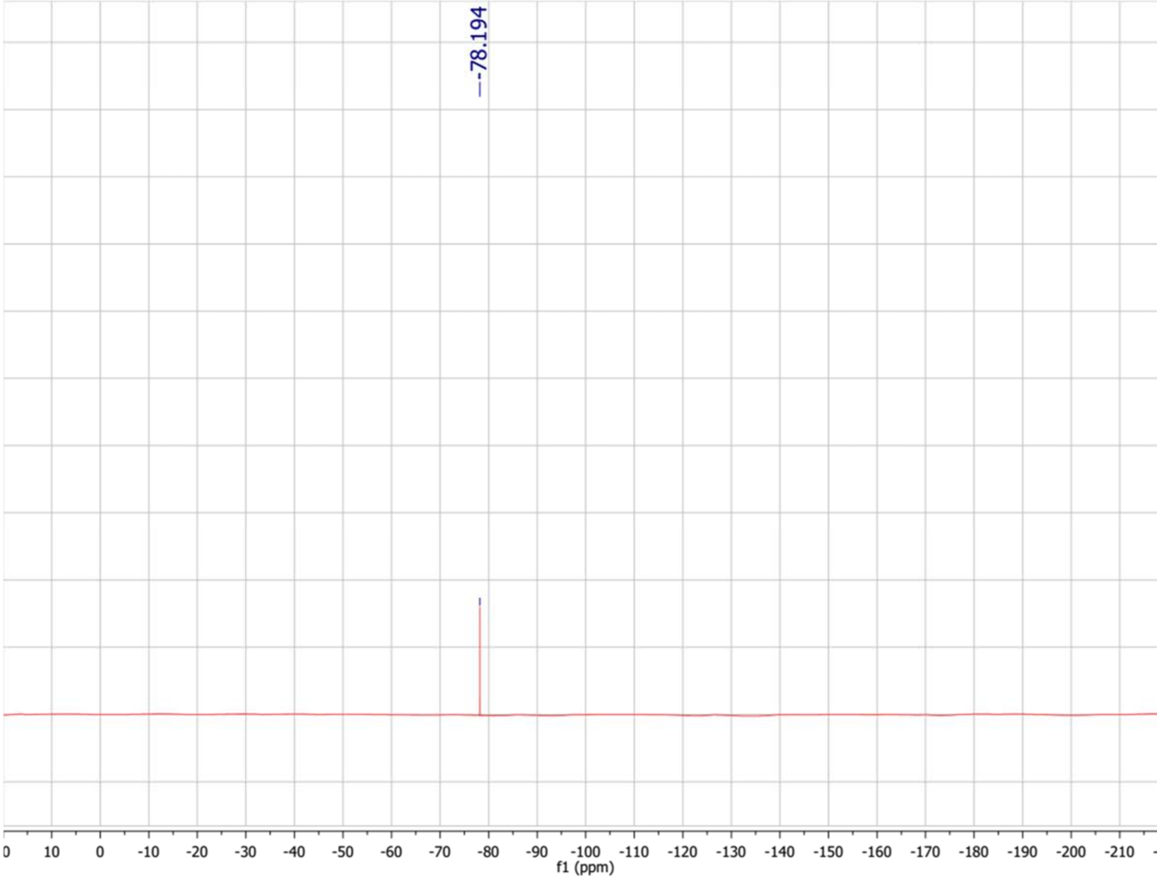


Figure S29: ^{19}F NMR (470 Hz, CDCl$_3$) spectrum of complex **5a**.

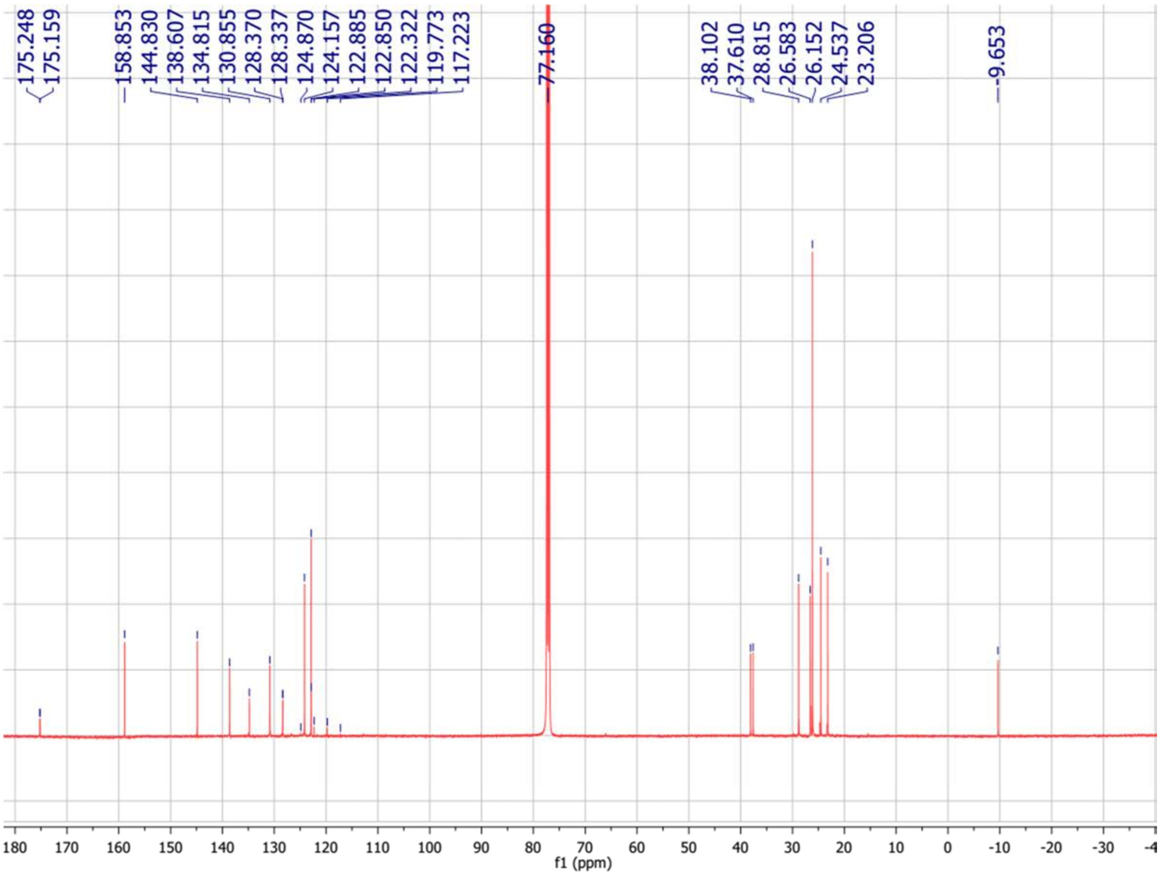


Figure S30: ^{13}C NMR (126 Hz, CDCl$_3$) spectrum of complex **5a**.

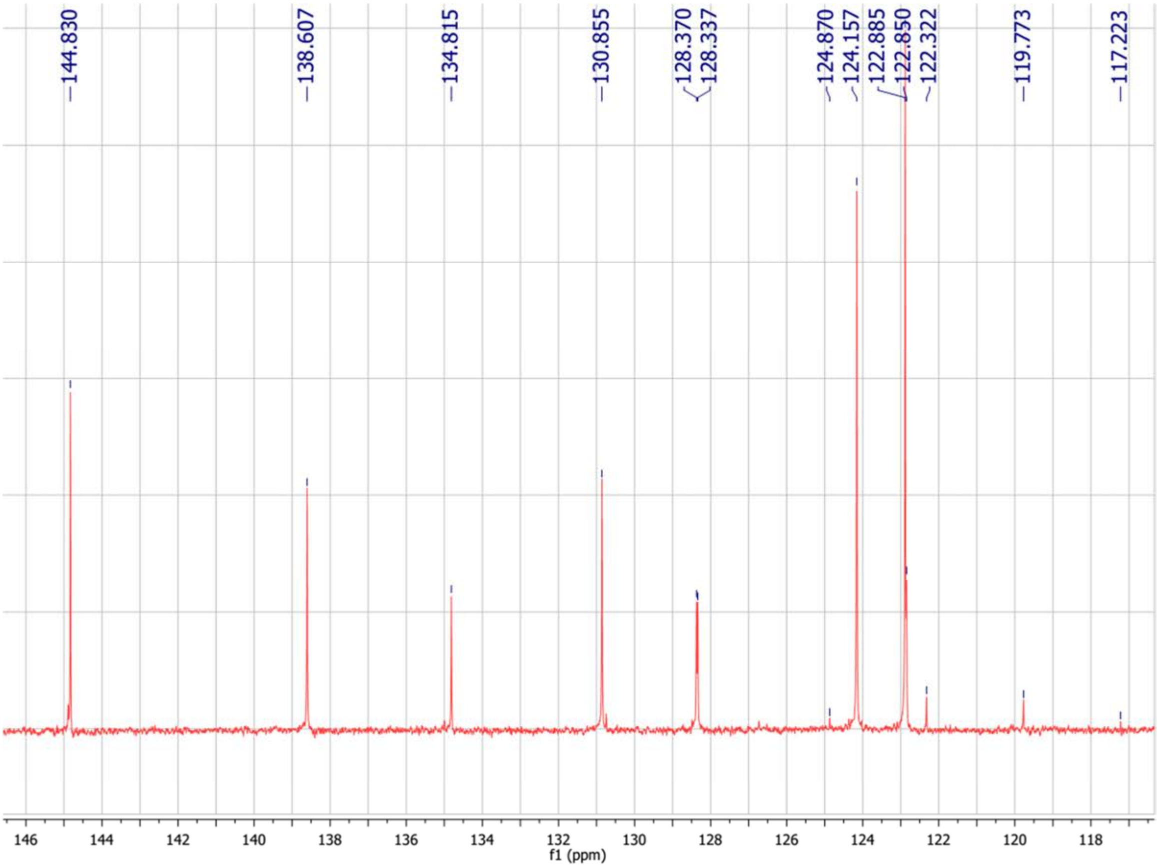


Figure S31: ^{13}C NMR (126 Hz, $CDCl_3$) spectrum (117–146 ppm) of complex **5a**.

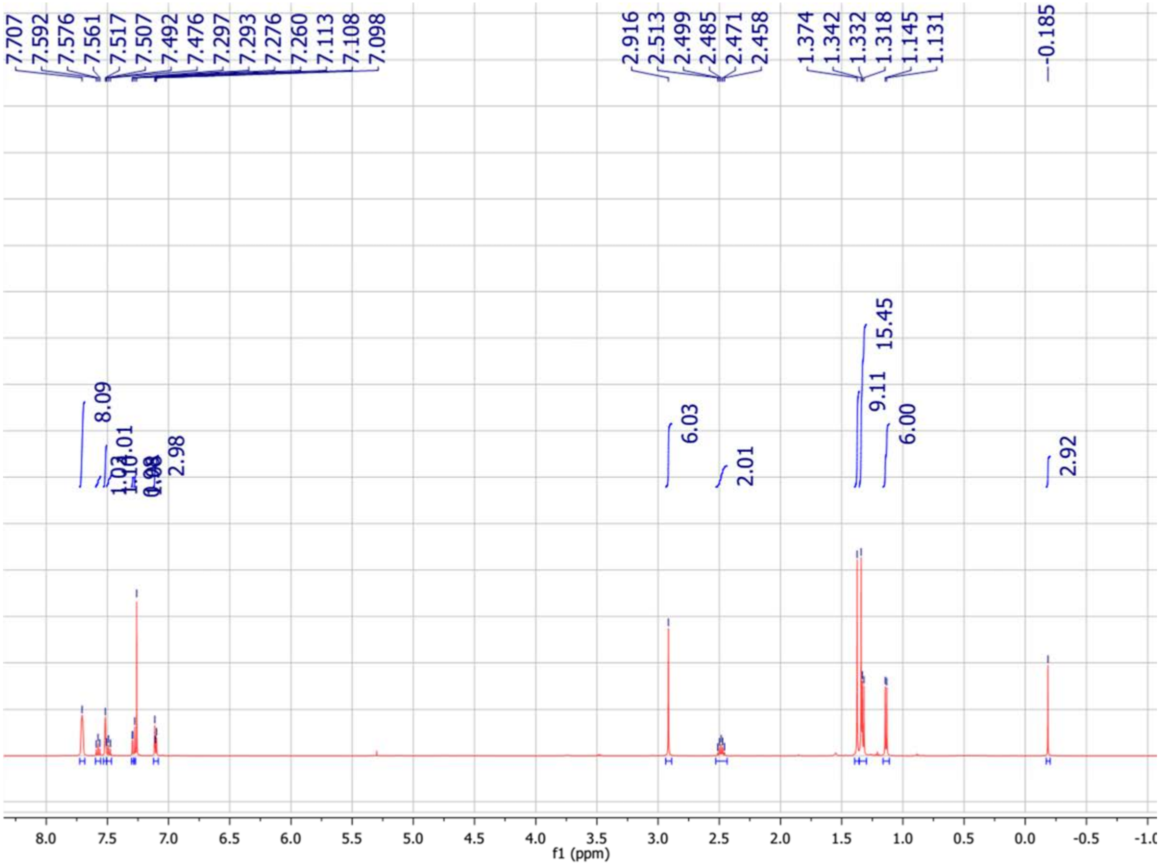


Figure S32: ^{1}H NMR (500 Hz, $CDCl_3$) spectrum of complex **5b**.

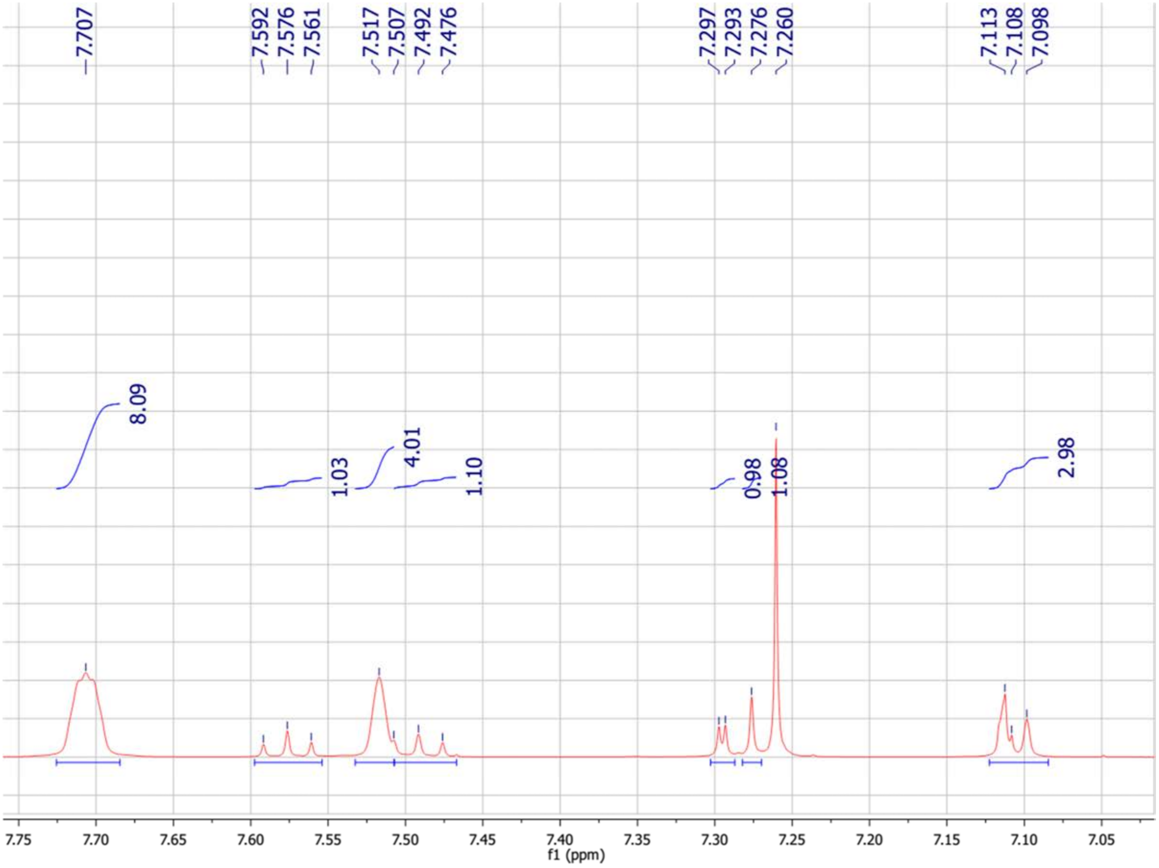


Figure S33: ^{1}H NMR (500 Hz, CDCl$_3$) spectrum (7.00–7.75 ppm) of complex **5b**.

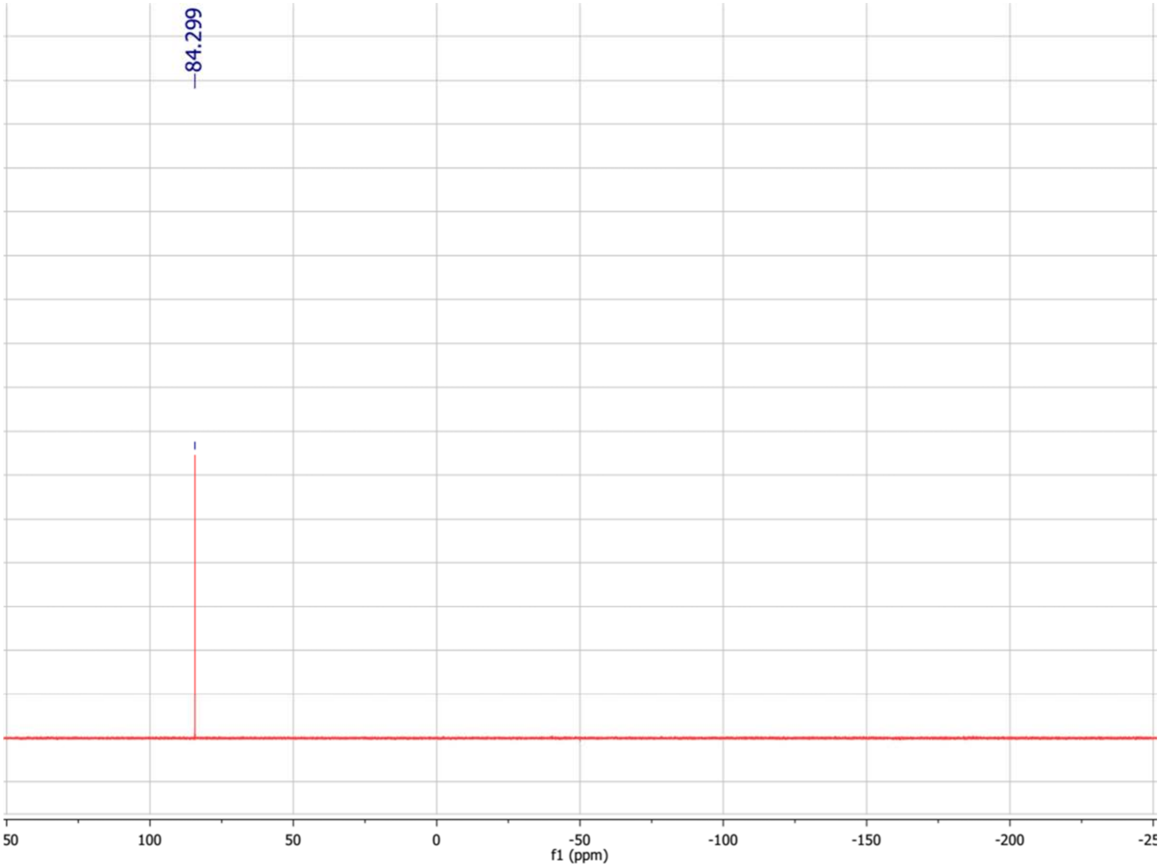


Figure S34: ^{31}P NMR (202 Hz, CDCl$_3$) spectrum of complex **5b**.

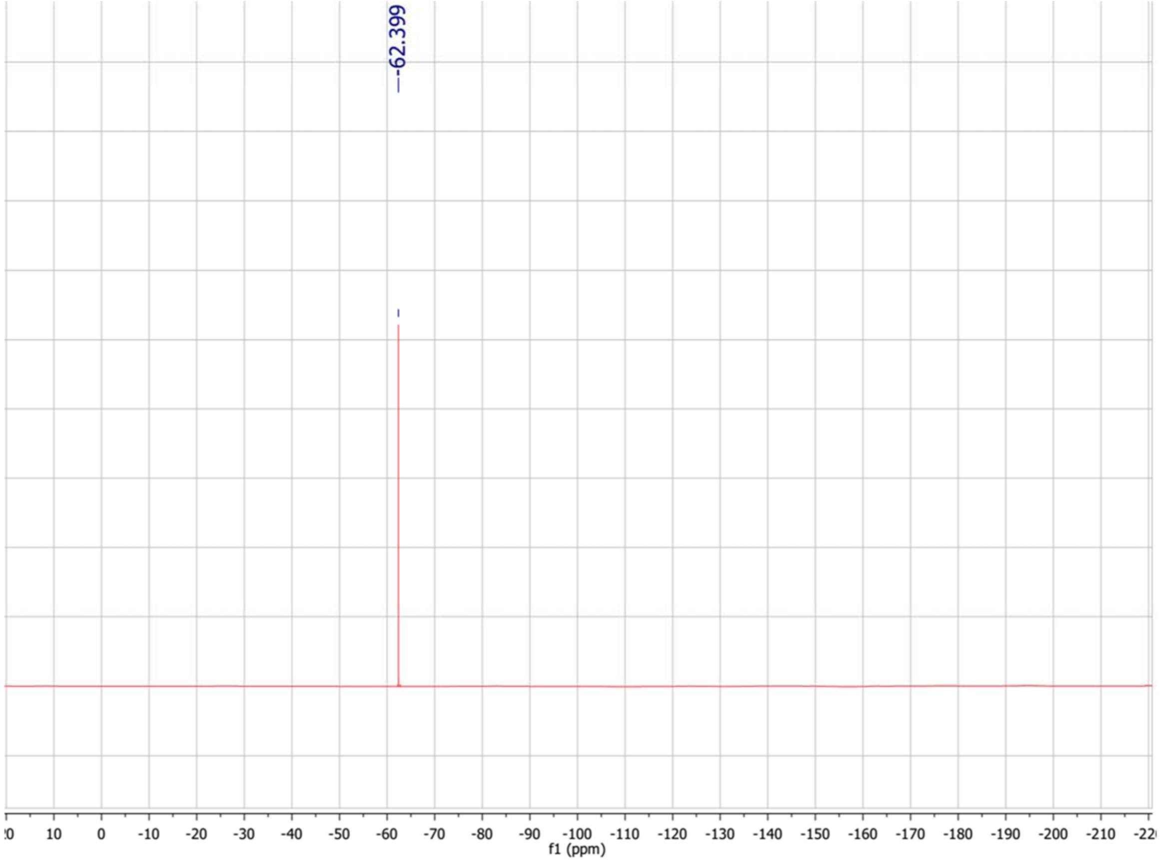


Figure S35: ^{19}F NMR (470 Hz, $CDCl_3$) spectrum of complex **5b**.

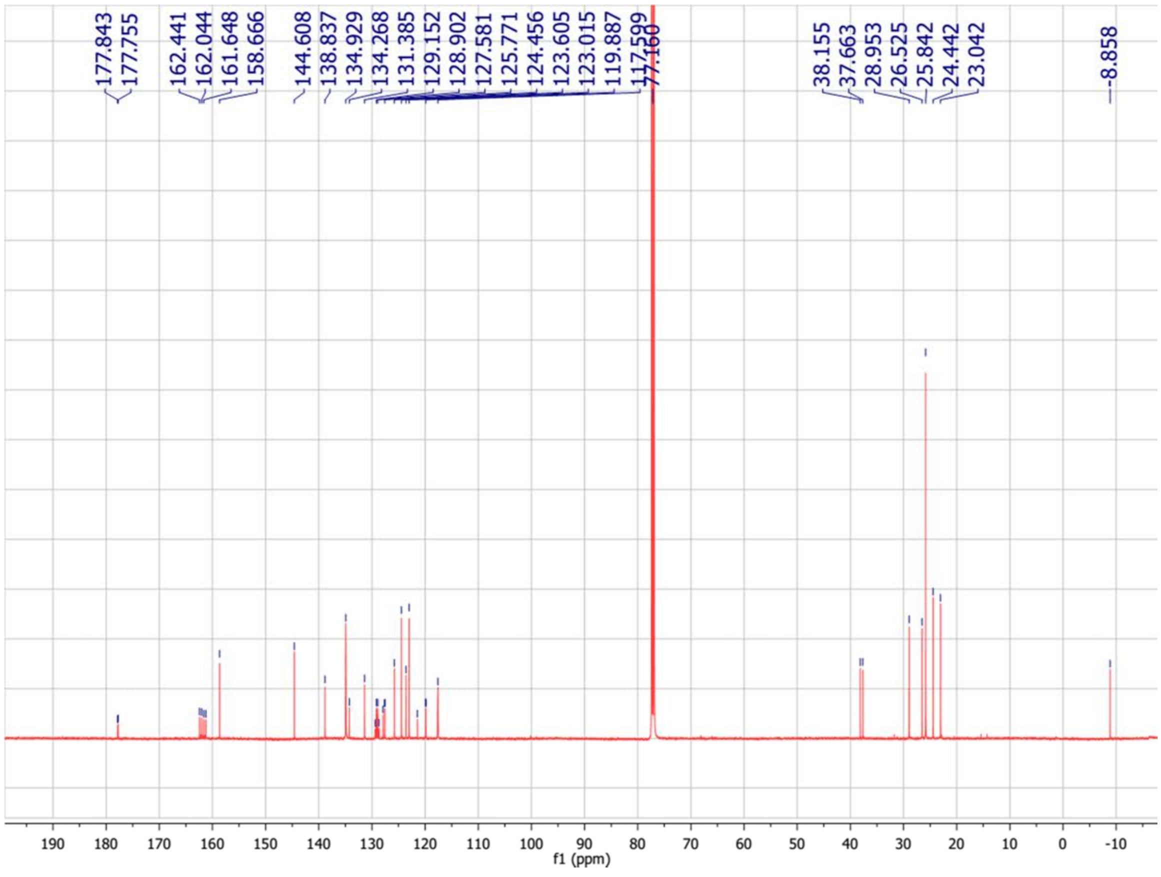


Figure S36: ^{13}C NMR (500 Hz, $CDCl_3$) spectrum of complex **5b**.

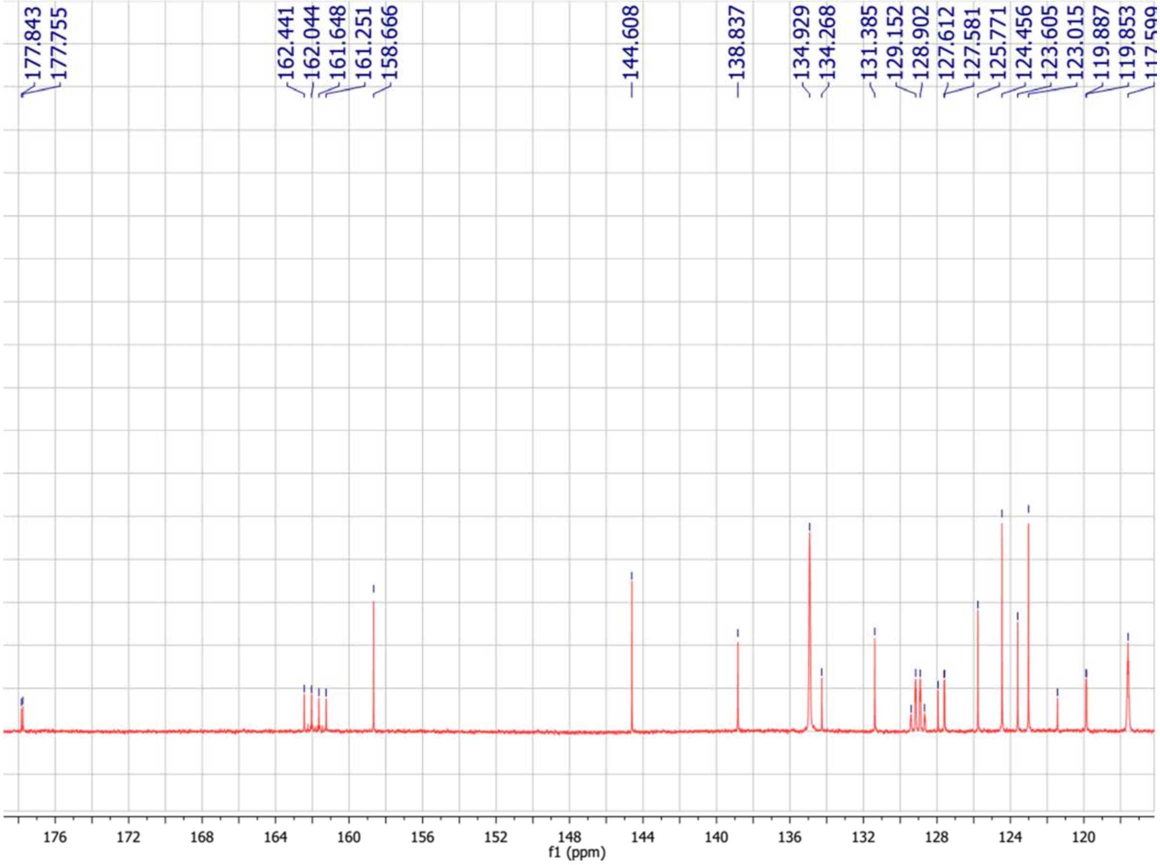


Figure S37: ^{13}C NMR (500 Hz, CDCl$_3$) spectrum (116–180 ppm) of complex **5b**.

4. X-ray Crystallographic Data of Complexes 4a and 5a

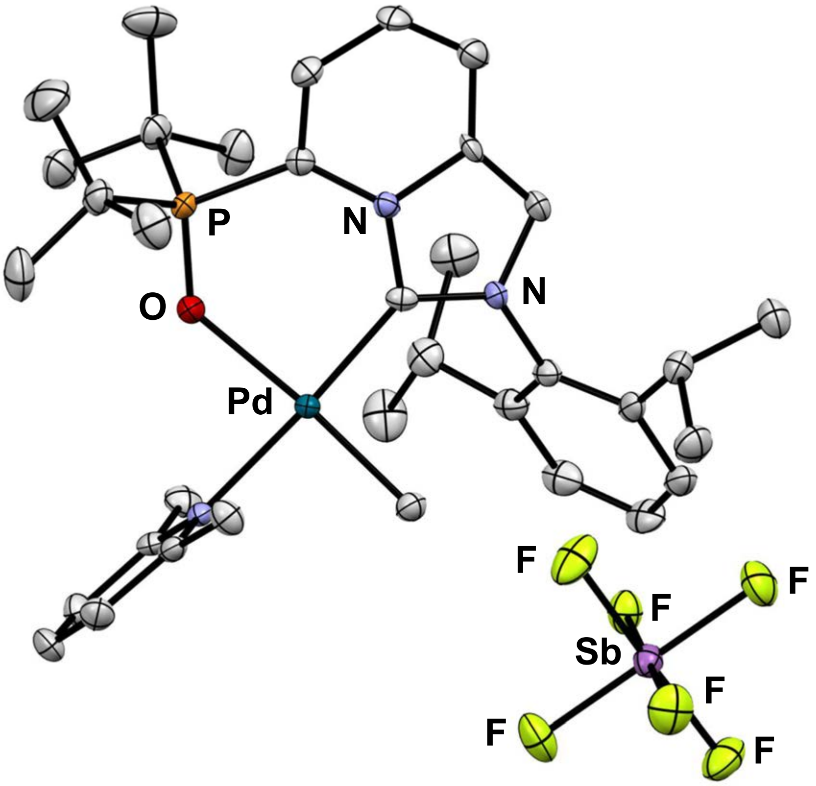


Figure S38. X-ray structure of **4a** with thermal ellipsoids of 50% probability. Hydrogen atoms are omitted for clarity.

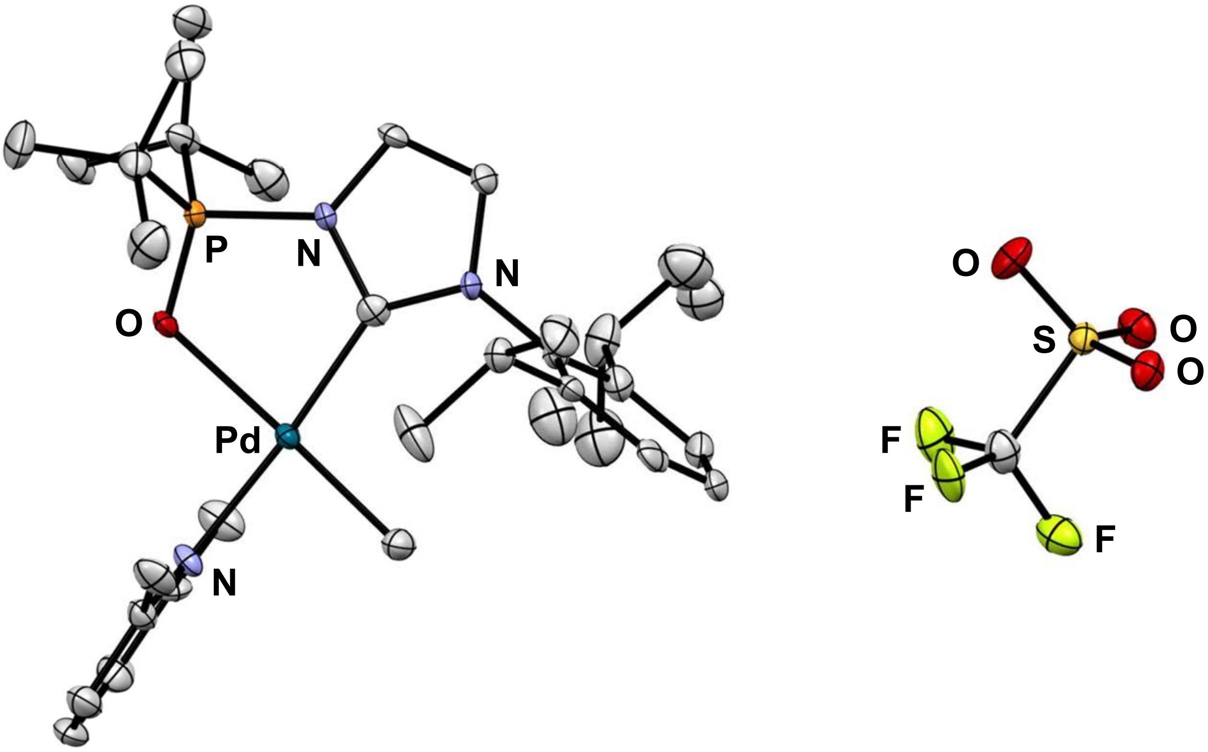


Figure S39. X-ray structure of **5a** with thermal ellipsoids of 50% probability. Hydrogen atoms are omitted for clarity.

Table S3. Crystal Data and Structure Refinement for Complexes **4a** and **5a**.

Complex		**4a**	**5a**
CCDC number		1525118	1525117
Empirical formula		$C_{35}H_{51}F_6N_3OPPdSb$	$C_{32}H_{49}F_3N_3O_4PPdS$
Formula weight		902.90	766.17
Temperature (K)		93	93
Wavelength (Å)		0.71075	0.71075
Crystal system		monoclinic	monoclinic
Space group		$P2_1/c$	$P2_1$/n
Unit cell dimensions	a (Å)	10.179(3)	10.844(3)
	b (Å)	22.751(8)	20.403(6)
	c (Å)	16.348(6)	17.005(5)
	α(°)	90	90
	β(°)	93.349(6)	94.838(5)
	γ(°)	90	90
Volume (Å^3)		3786(2)	3749.0(19)
Z		4	4
Density (calculated) (g/cm^3)		1.584	1.357
Absorption coefficient (mm^{-1})		1.292	0.645
F(000)		1824	1592
Crystal size (mm^3)		0.25 × 0.25 × 0.10	0.20 × 0.10 × 0.03
Theta (max)		25.999	25.999
Index ranges		−12<=h<=12	−12<=h<=13
		−27<=k<=28	−25<=k<=24
		−20<=l<=18	−20<=l<=19
Reflections collected		26298	26195
Independent reflections [R(int)]		7435 [R(int) = 0.0730]	7350 [R(int) = 0.0801]
Data completeness		99.9%	99.9%
Absorption correction		Multi-scan	Multi-scan
Max. and min. transmission		1.000 and 0.788	1.000 and 0.617
Refinement method		Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters		7435 / 0 / 446	7350 / 36 / 442
Goodness-of-fit on F^2		1.067	1.124
Final R indices [I>2σιναλ		$R_1 = 0.0447$, w$R_2 = 0.0819$	$R_1 = 0.0651$, w$R_2 = 0.1425$
R indices (all data)		$R_1 = 0.0573$, w$R_2 = 0.0869$	$R_1 = 0.0743$, w$R_2 = 0.1478$
Max/min diff. peaks (e.Å^{-3})		0.735 / −0.588	1.823 / −1.428

5. NMR Spectra, SEC Charts, and DSC Charts of Polymers

General Notes for the Characterization

In ^{13}C NMR analyses, artifact pairs derived from the solvent signal of 1,1,2,2-tetrachloroethane (typically at δ = 78.3 and 70.7 ppm, 82.5 and 65.9 ppm, 90.8 and 57.6 ppm, 99.1 and 49.3 ppm, 107.4 and 41.1 ppm, marked with *) and impurities in the solvent ($CHCl_2CCl_3$: δ = 79.8 and 99.7 ppm, CCl_2CCl_2: δ = 120.2 ppm, $CHClCCl_2$: δ = 116.6 and 121.6 ppm, marked with **) were excluded from the calculation of the extent of branches and the incorporation ratio of polar monomers.

Observed ^{13}C NMR signals of polyethylenes were assigned according to the following literatures; polyethylene and ethylene/allyl monomer copolymers[13], ethylene/acrylate copolymers.[14]

5.1 Data of polyethylene (Table 1)

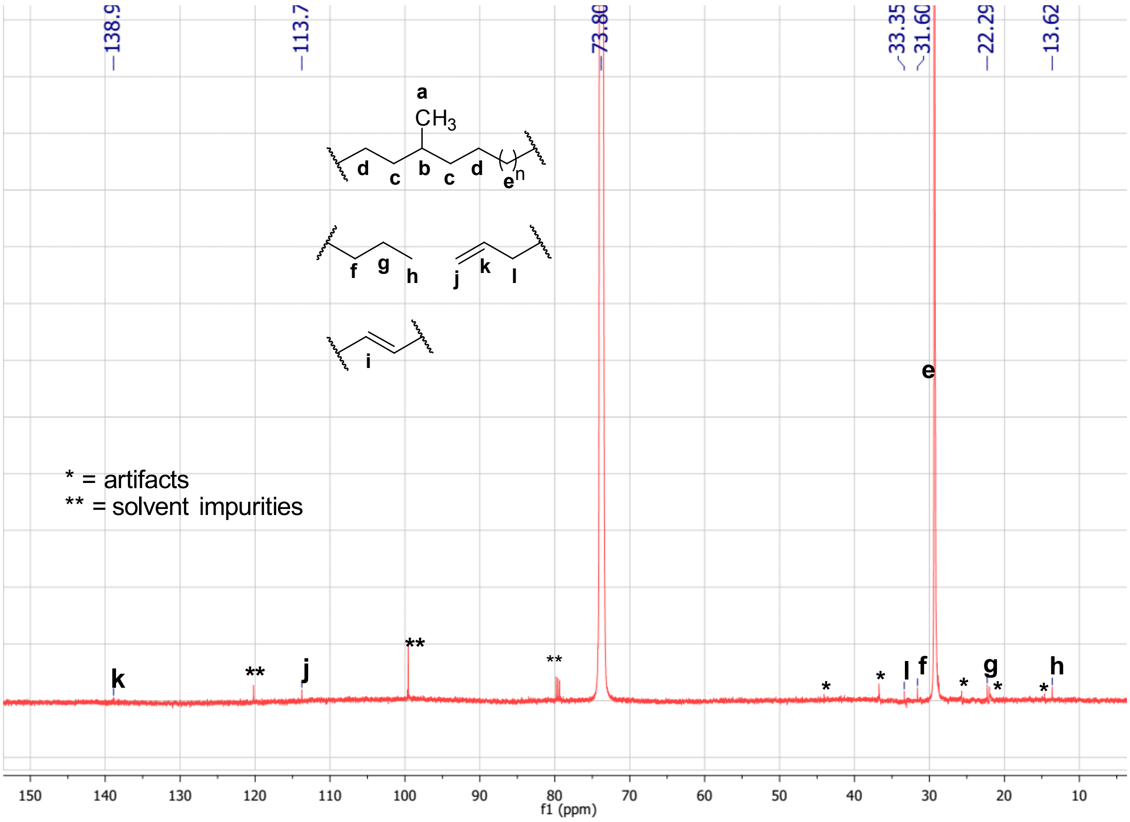
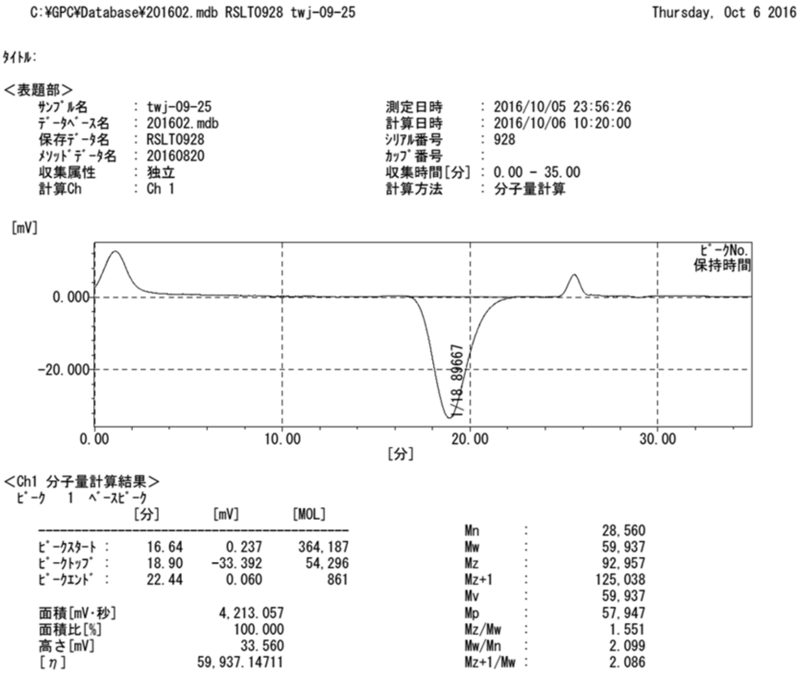


Figure S40. Quantitative ^{13}C NMR spectrum (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, inverse gated) of polyethylene obtained by **4b** at 30 °C (Table 1, entry 1).



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    ﾋﾟｰｸﾄｯﾌﾟ :       18.90    -33.392       54,296                Mz        :        92,957
    ﾋﾟｰｸｴﾝﾄﾞ :       22.44      0.060          861                Mz+1      :       125,038
                                                                  Mv        :        59,937
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    面積比[%]                   100.000                           Mz/Mw     :         1.551
    高さ[mV]                     33.560                           Mw/Mn     :         2.099
    [η]                    59,937.14711                           Mz+1/Mw   :         2.086
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Figure S41. SEC chart of polyethylene obtained by **4b** (Table 1, entry 1).

M_n (PS) = 29 kg/mol was corrected to M_n (PE) = 12 kg/mol by universal calibration.

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サンプル名:        twj-09-25                   2*     200  -50       10   30  0.5
サンプル質量:      3.342 mg                    3*     -50  200       10    5  0.5
リファレンス名:                                4*     200   30       10    5  0.5
リファレンス質量:  0.000 mg
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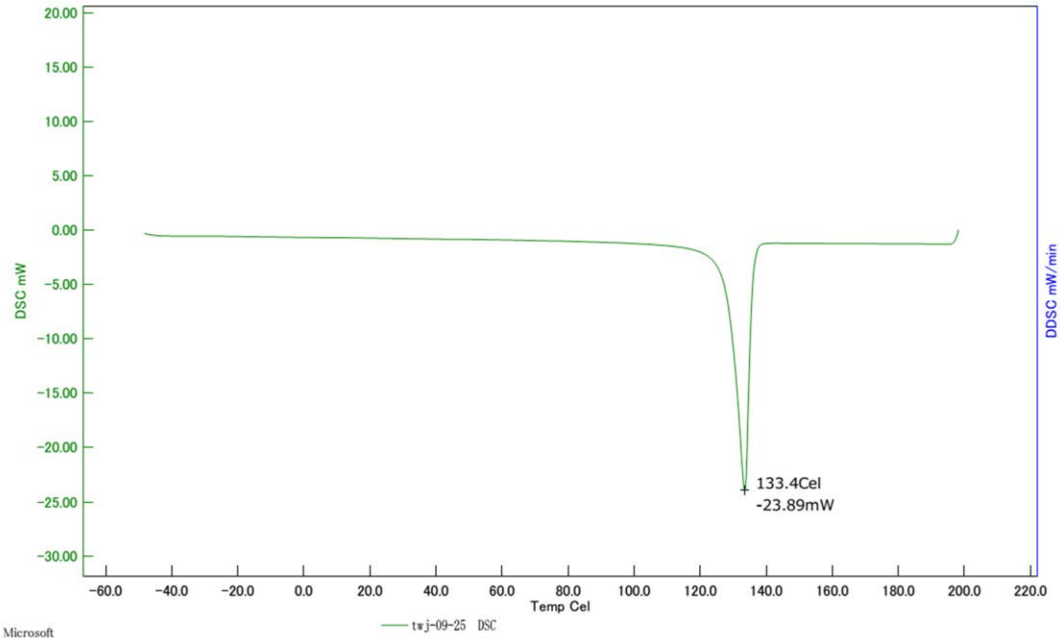


Figure S42. DSC traces of polyethylene obtained by **4b** (Table 1, entry 1).

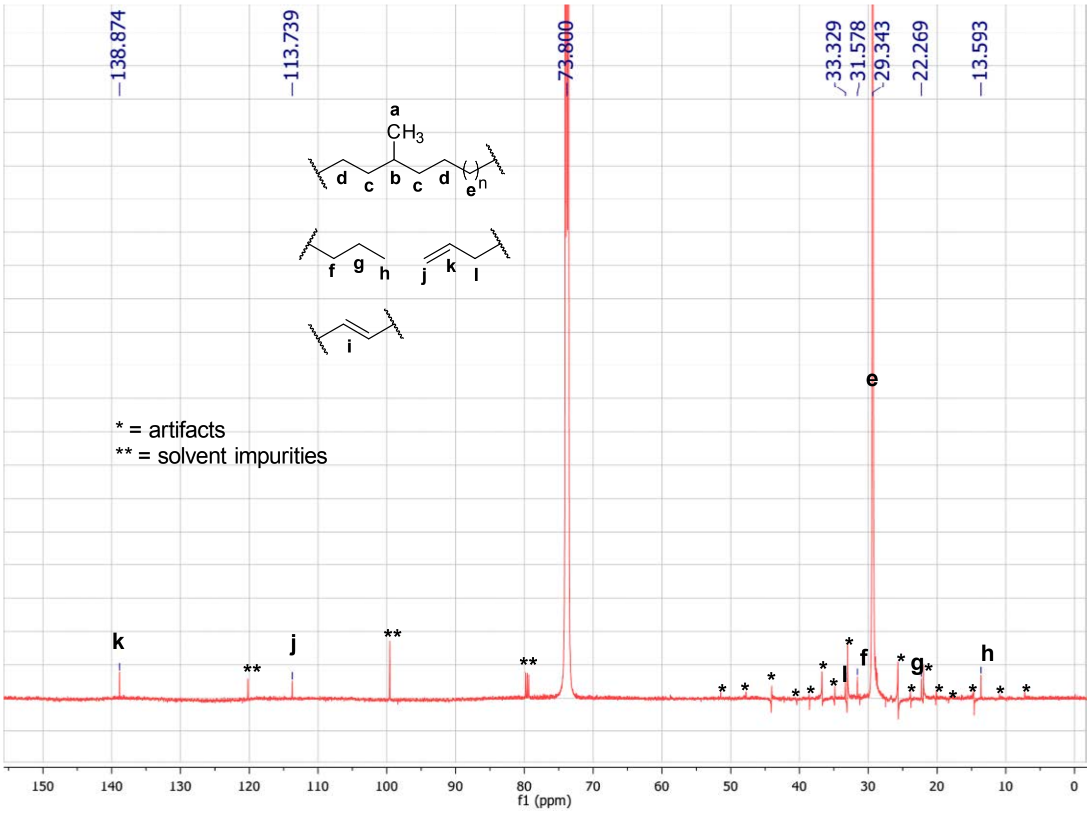
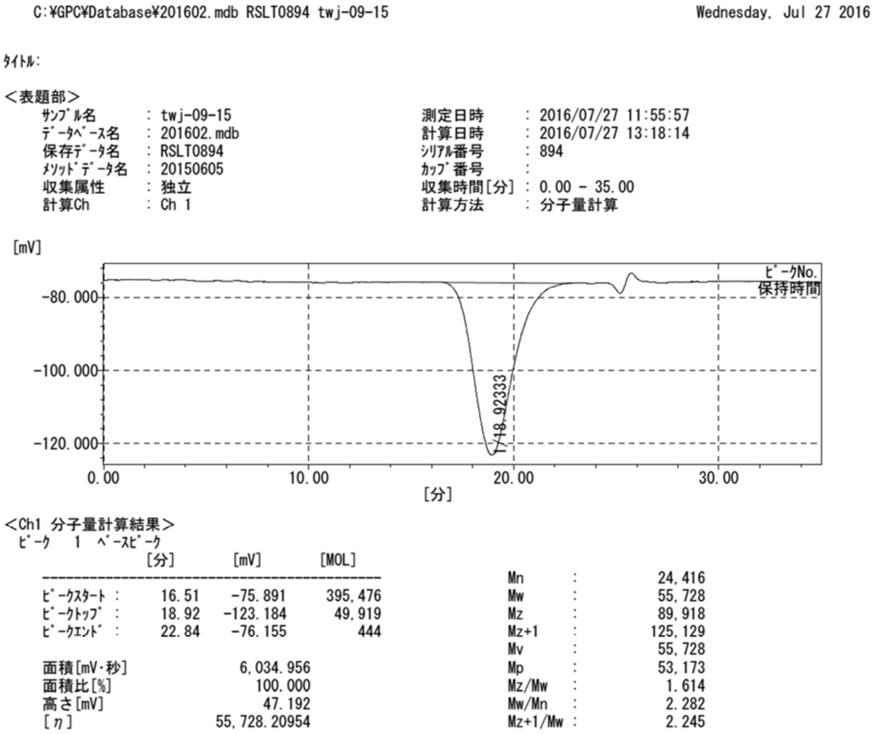


Figure S43. Quantitative ^{13}C NMR spectrum (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, inverse gated) of polyethylene obtained by **4b** at 30 °C (Table 1, entry 2).



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    ﾋﾟｰｸﾄｯﾌﾟ :      18.92    -123.184       49,919                Mz        :       89,918
    ﾋﾟｰｸｴﾝﾄﾞ :      22.84     -76.155          444                Mz+1      :      125,129
                                                                  Mv        :       55,728
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    面積比[%]                   100.000                           Mz/Mw     :        1.614
    高さ[mV]                     47.192                           Mw/Mn     :        2.282
    [η]                  55,728.20954                             Mz+1/Mw   :        2.245
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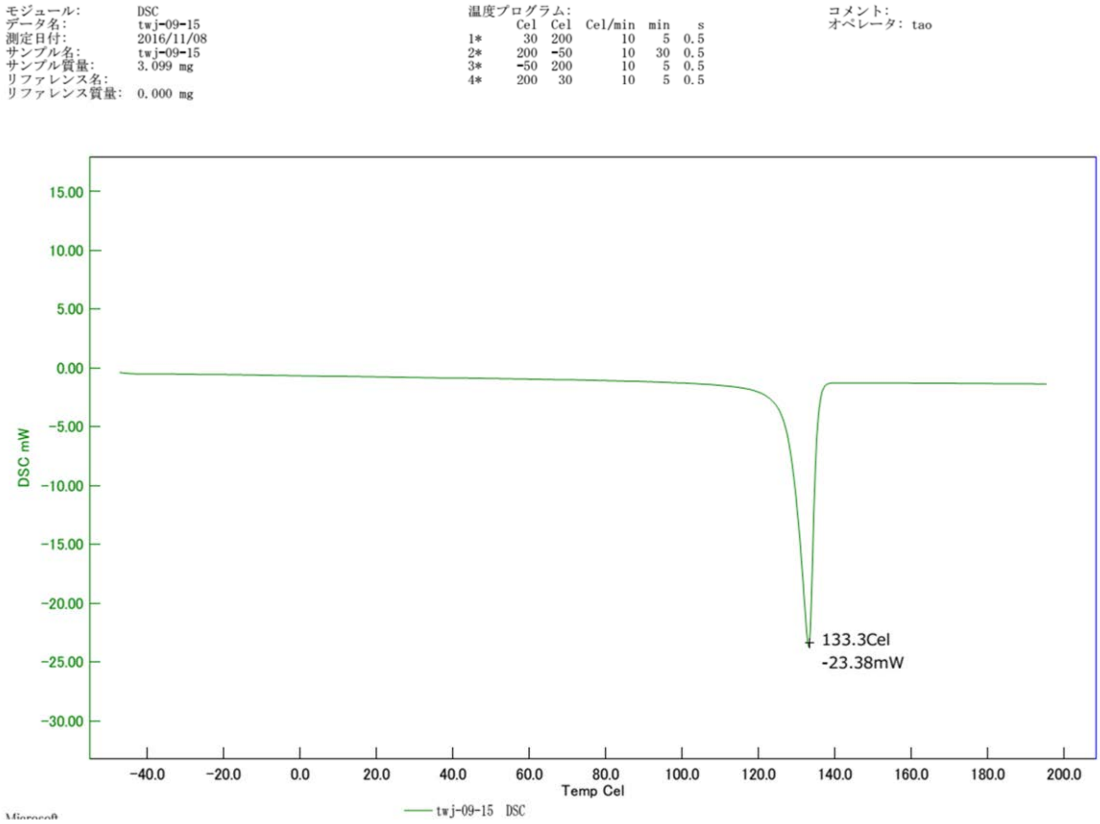
Figure S44. SEC chart of polyethylene obtained by **4b** (Table 1, entry 2).
M_n (PS) = 24 kg/mol was corrected to M_n (PE) = 11 kg/mol by universal calibration.



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測定日付:            2016/11/08                   1*     30   200       10    5   0.5
サンプル名:          twj-09-15                    2*    200   -50       10   30   0.5
サンプル質量:        3.099 mg                     3*    -50   200       10    5   0.5
リファレンス名:                                   4*    200    30       10    5   0.5
リファレンス質量:    0.000 mg
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Figure S45. DSC traces of polyethylene obtained by **4b** (Table 1, entry 2).

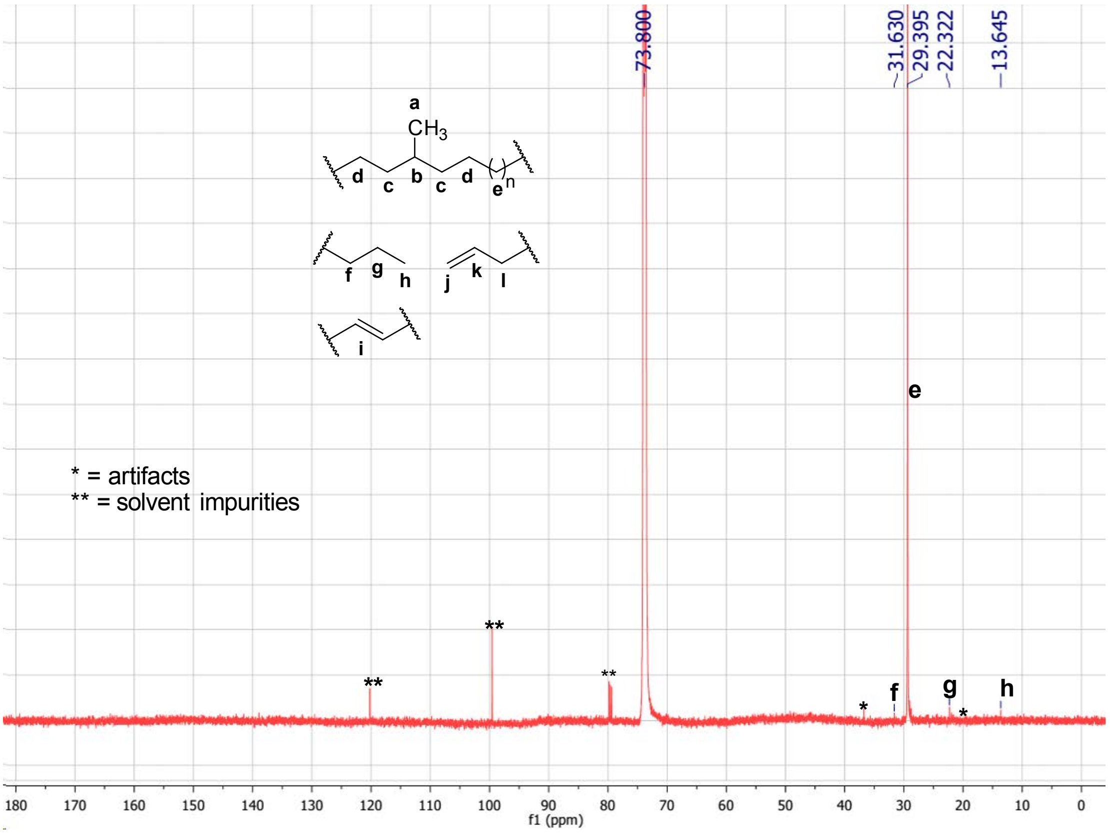
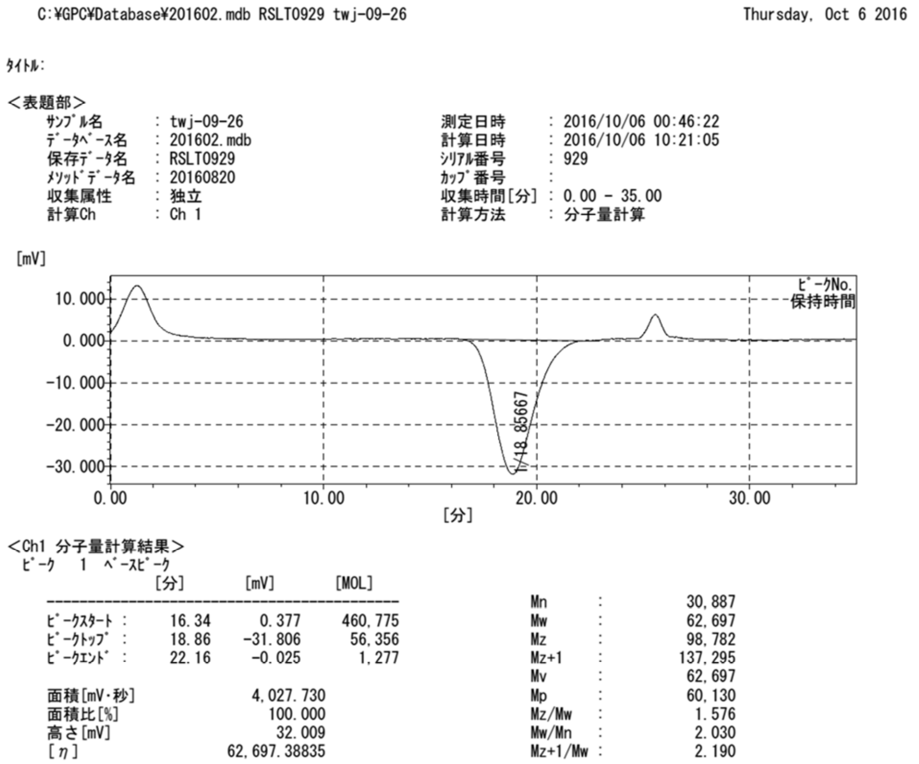


Figure S46. Quantitative ^{13}C NMR spectrum (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, inverse gated) of polyethylene obtained by **4b** at 30 °C (Table 1, entry 3).



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                                                              Mv        :        62,697
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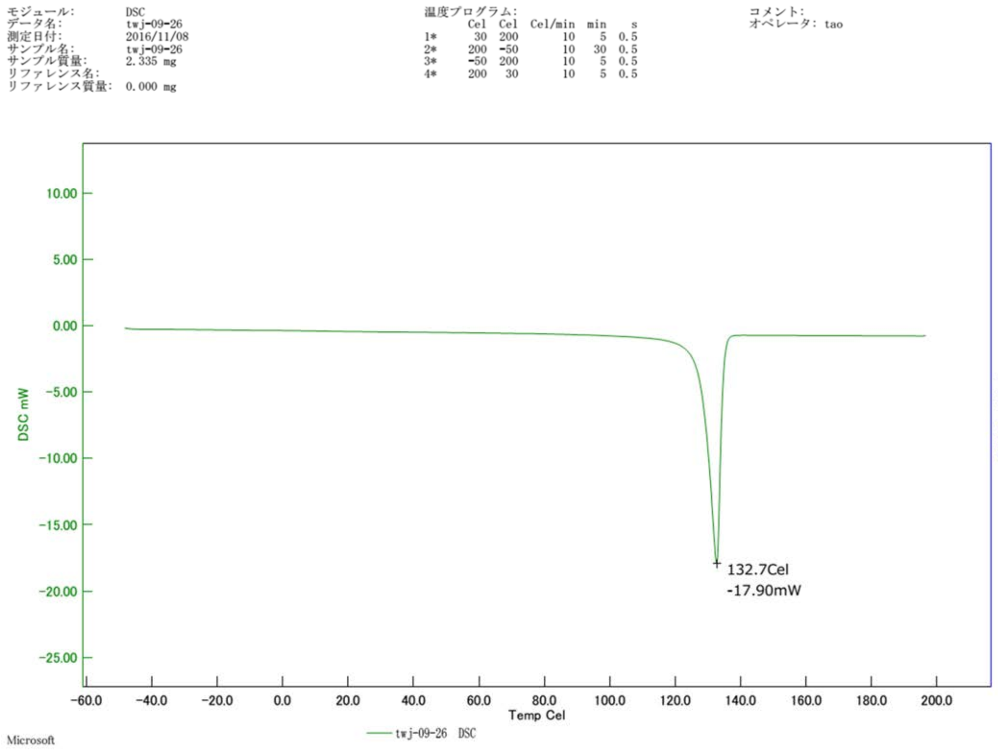
    面積比[%]                 100.000                         Mz/Mw     :         1.576
    高さ[mV]                   32.009                         Mw/Mn     :         2.030
    [η]                  62,697.38835                         Mz+1/Mw   :         2.190
```

Figure S47. SEC chart of polyethylene obtained by **4b** (Table 1, entry 3).

M_n (PS) = 31 kg/mol was corrected to M_n (PE) = 13 kg/mol by universal calibration.



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サンプル名:        twj-09-26              2*    200  -50       10   30  0.5
サンプル質量:      2.335 mg               3*    -50  200       10    5  0.5
リファレンス名:                           4*    200   30       10    5  0.5
リファレンス質量:  0.000 mg
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Figure S48. DSC traces of polyethylene obtained by **4b** (Table 1, entry 3).

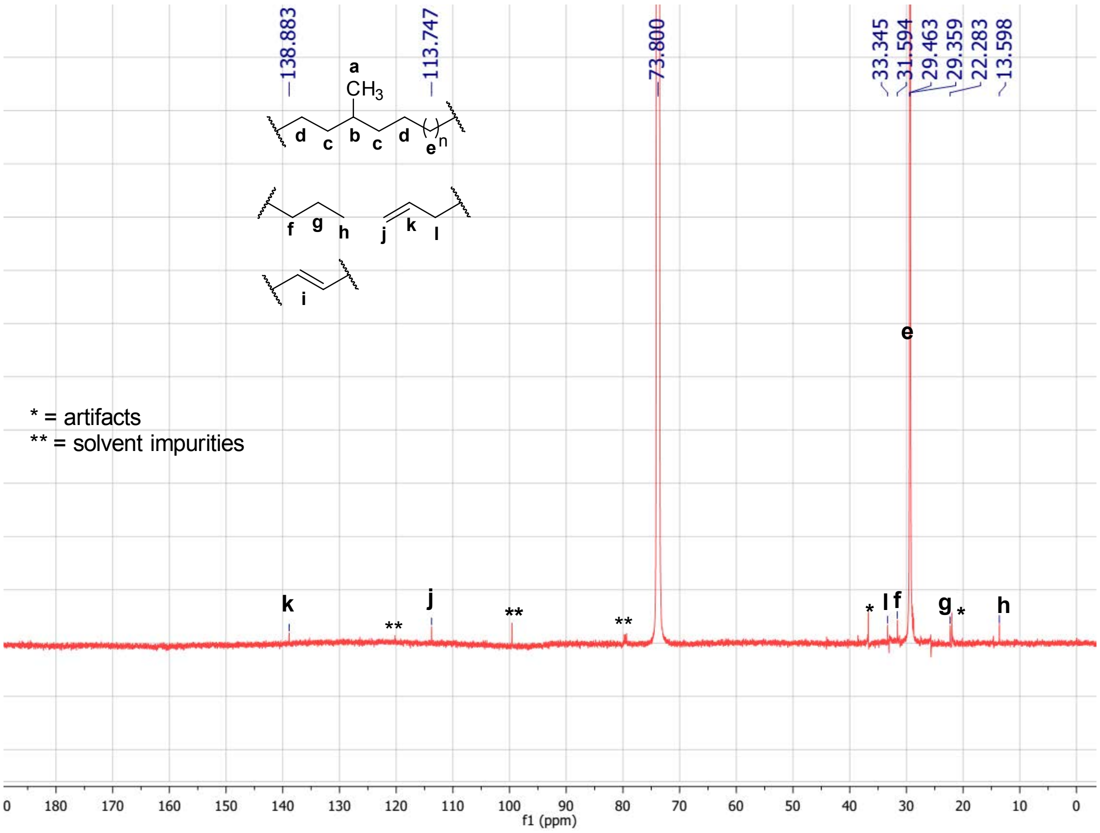
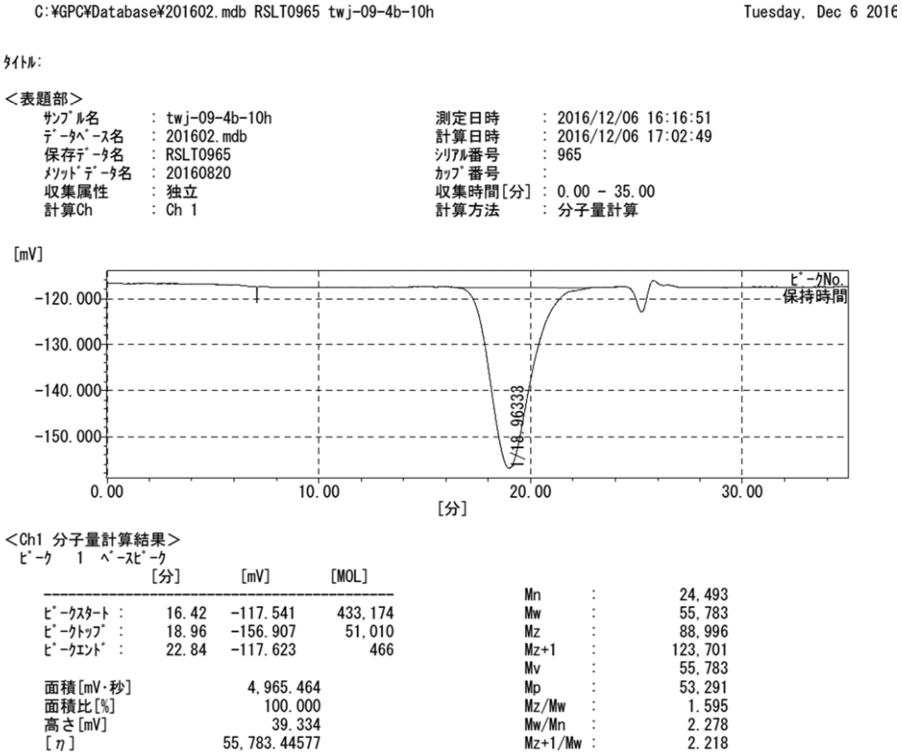


Figure S49. Quantitative ^{13}C NMR spectrum (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, inverse gated) of polyethylene obtained by **4b** at 30 °C (Table 1, entry 4).



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                                                               Mv        :        55,783
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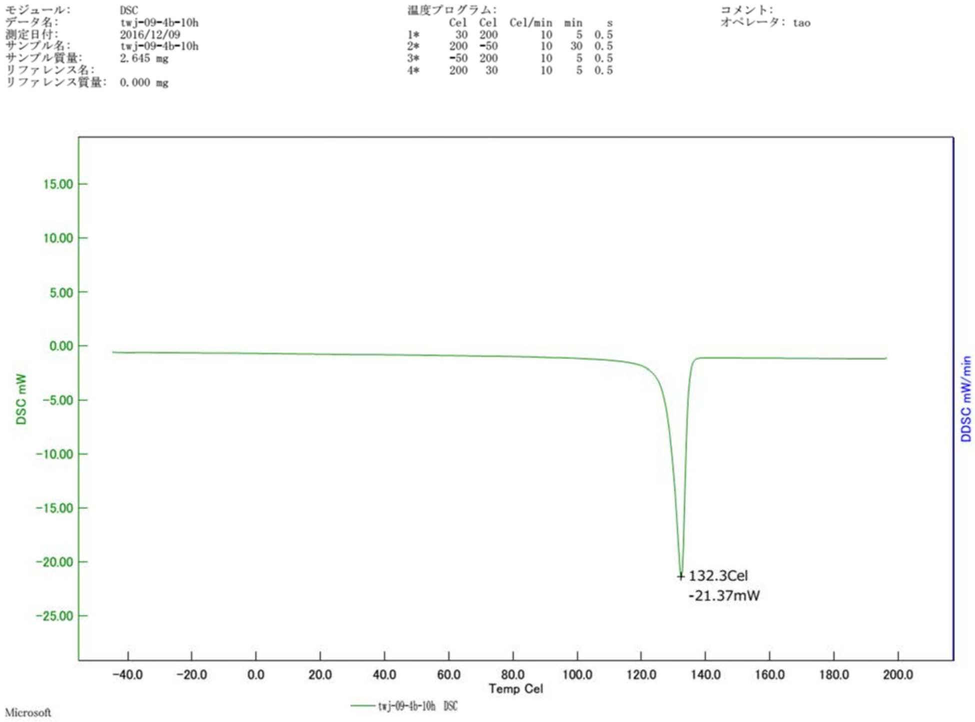
    面積比[%]                   100.000                        Mz/Mw     :         1.595
    高さ[mV]                     39.334                        Mw/Mn     :         2.278
    [η]                     55,783.44577                       Mz+1/Mw   :         2.218
```

Figure S50. SEC chart of polyethylene obtained by **4b** (Table 1, entry 4). M_n (PS) = 25 kg/mol was corrected to M_n (PE) = 11 kg/mol by universal calibration.



```
モジュール:         DSC                         温度プログラム:                           コメント:
データ名:           twj-09-4b-10h                     Cel  Cel  Cel/min  min    s       オペレータ: tao
測定日付:           2016/12/09                  1*     30  200       10    5  0.5
サンプル名:         twj-09-4b-10h               2*    200  -50       10   30  0.5
サンプル質量:       2.645 mg                    3*    -50  200       10    5  0.5
リファレンス名:                                 4*    200   30       10    5  0.5
リファレンス質量:   0.000 mg
```

Figure S51. DSC traces of polyethylene obtained by **4b** (Table 1, entry 4).

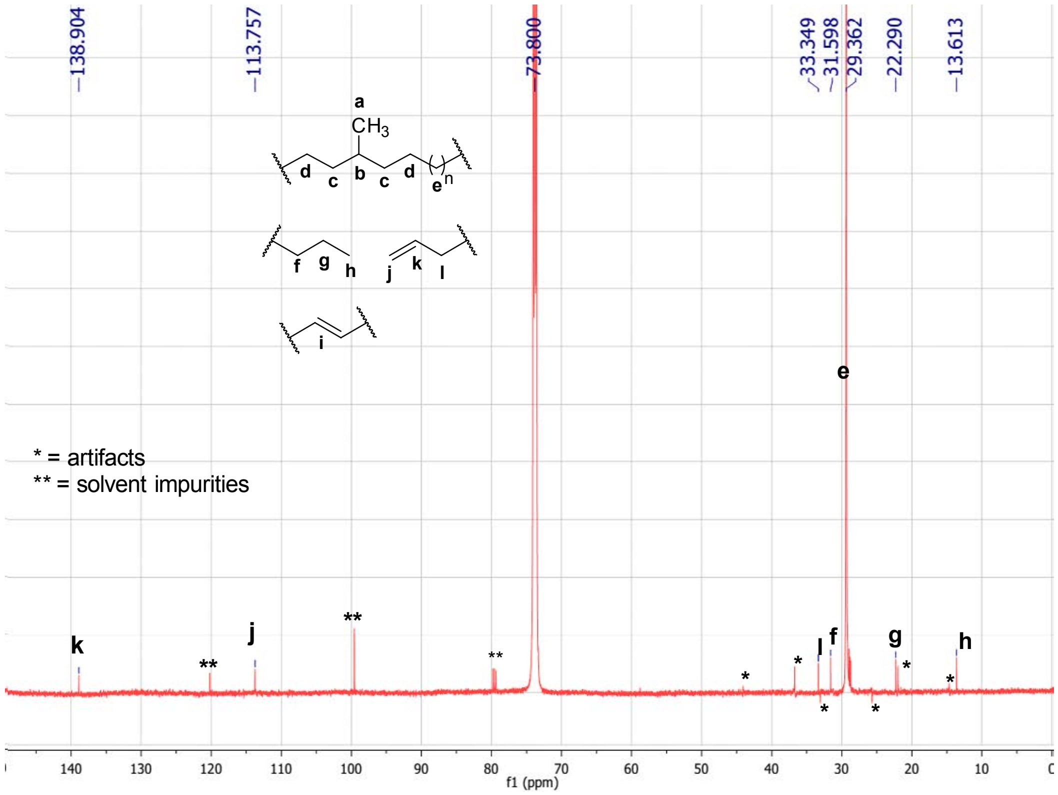
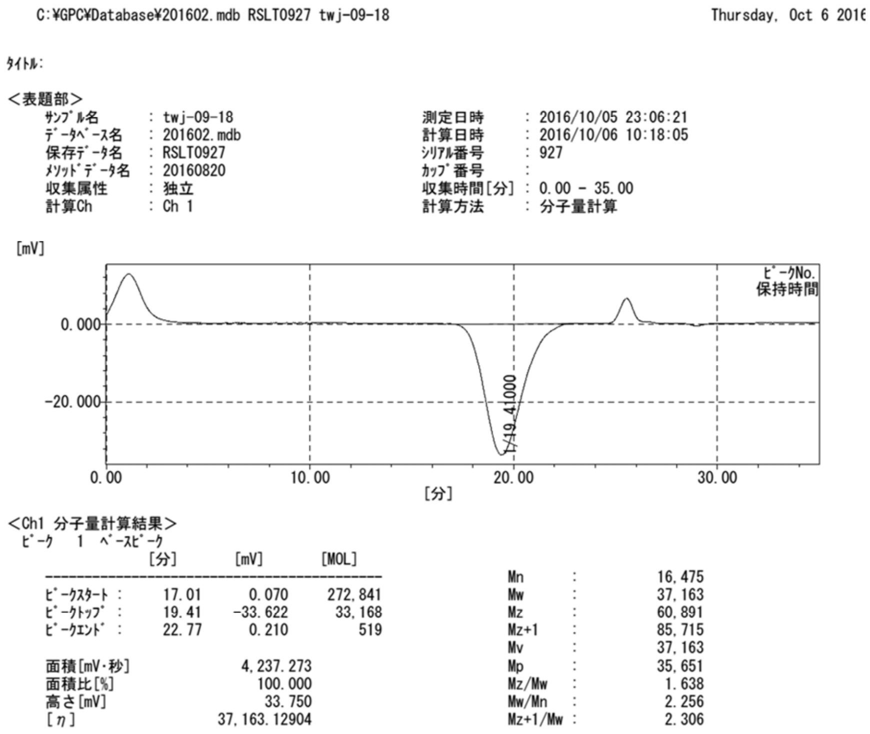


Figure S52. Quantitative ^{13}C NMR spectrum (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, inverse gated) of polyethylene obtained by **4b** at 50 °C (Table 1, entry 5). Note: No signal assigned as methyl branch (around 19.5 ppm) or other branches were observed.



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C:¥GPC¥Database¥201602.mdb RSLT0927 twj-09-18                    Thursday, Oct 6 2016

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    ﾒｿｯﾄﾞﾃﾞｰﾀ名     : 20160820                  ｶｯﾌﾟ番号       :
    収集属性        : 独立                      収集時間[分]   : 0.00 - 35.00
    計算Ch          : Ch 1                      計算方法       : 分子量計算
```

```
<Ch1 分子量計算結果>
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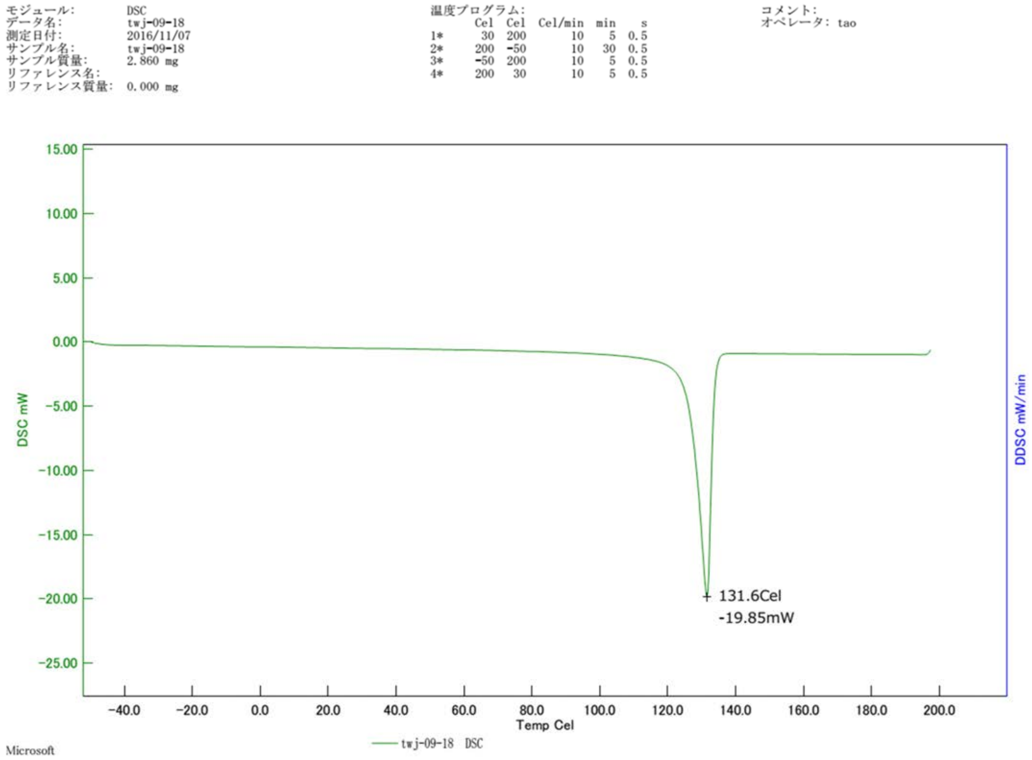
                 [分]        [mV]        [MOL]
    ------------------------------------------                  Mn        :        16,475
    ﾋﾟｰｸｽﾀｰﾄ :    17.01       0.070     272,841                 Mw        :        37,163
    ﾋﾟｰｸﾄｯﾌﾟ :    19.41     -33.622      33,168                 Mz        :        60,891
    ﾋﾟｰｸｴﾝﾄﾞ :    22.77       0.210         519                 Mz+1      :        85,715
                                                                Mv        :        37,163
    面積[mV・秒]           4,237.273                            Mp        :        35,651
    面積比[%]                100.000                            Mz/Mw     :         1.638
    高さ[mV]                  33.750                            Mw/Mn     :         2.256
    [η]               37,163.12904                            Mz+1/Mw   :         2.306
```

Figure S53. SEC chart of polyethylene obtained by **4b** (Table 1, entry 5).
M_n (PS) = 16 kg/mol was corrected to M_n (PE) = 7.2 kg/mol by universal calibration.



```
モジュール:          DSC                                      温度プログラム:                                      コメント:
データ名:            twj-09-18                                     Cel  Cel  Cel/min  min    s                  オペレータ: tao
測定日付:            2016/11/07                               1*     30  200       10    5  0.5
サンプル名:          twj-09-18                                2*    200  -50       10   30  0.5
サンプル質量:        2.860 mg                                 3*    -50  200       10    5  0.5
リファレンス名:                                                4*    200   30       10    5  0.5
リファレンス質量:    0.000 mg
```

Figure S54. DSC traces of polyethylene obtained by **4b** (Table 1, entry 5).

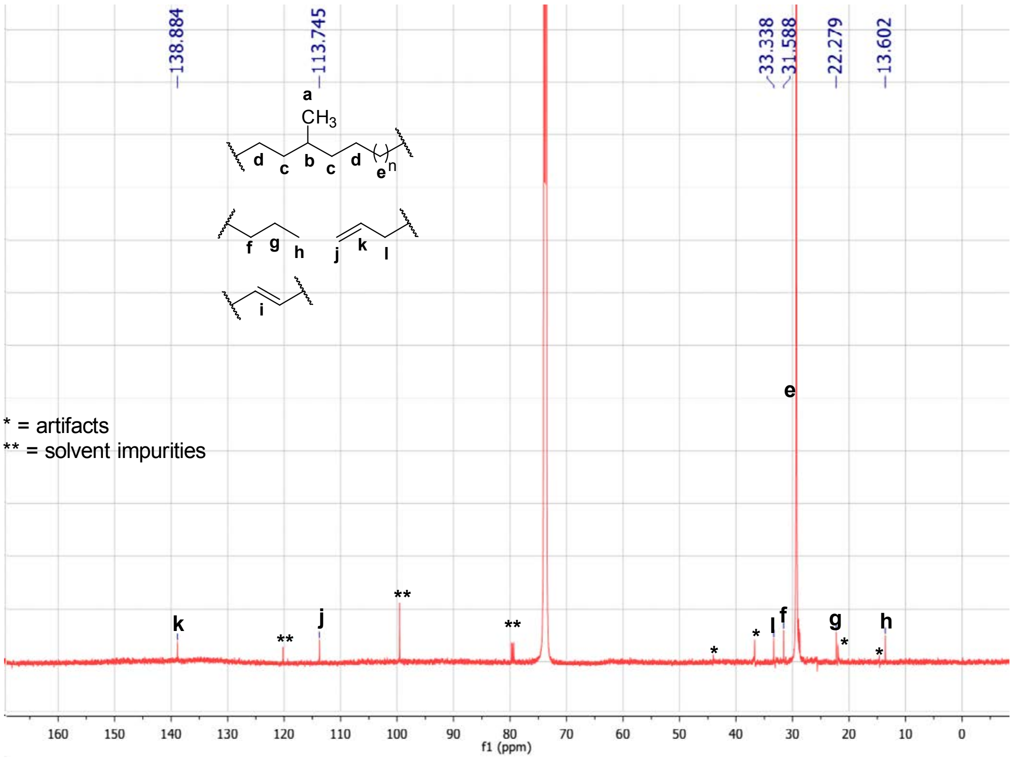
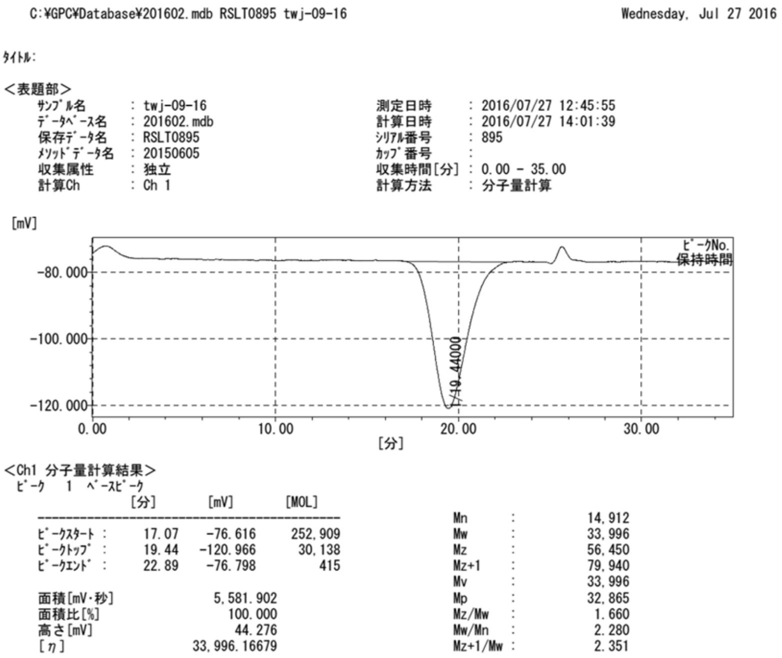


Figure S55. Quantitative ^{13}C NMR spectrum (126 MHz, 1,1,2,2-tetrachloroethane-*d*$_2$, 120 °C, inverse gated) of polyethylene obtained by **4b** at 50 °C (Table 1, entry 6).



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C:¥GPC¥Database¥201602.mdb RSLT0895 twj-09-16                    Wednesday, Jul 27 2016

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    収集属性       : 独立                      収集時間[分]   : 0.00 - 35.00
    計算Ch         : Ch 1                      計算方法       : 分子量計算
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<Ch1 分子量計算結果>
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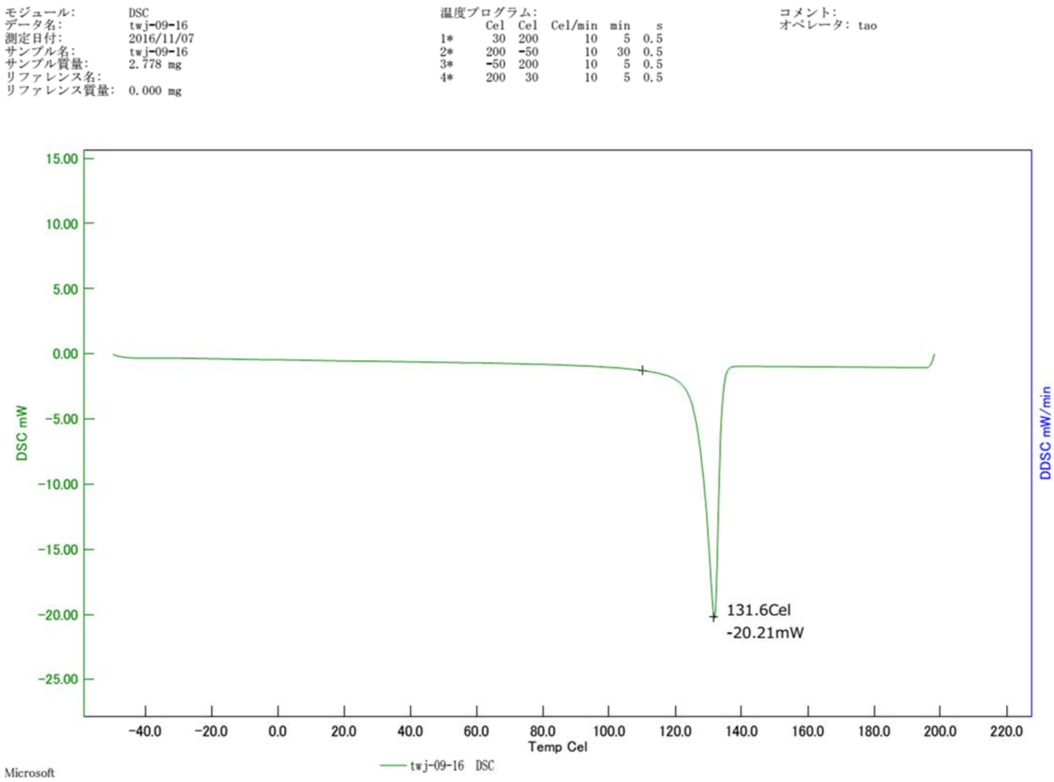
                    [分]       [mV]        [MOL]
    -----------------------------------------------          Mn        :        14,912
    ﾋﾟｰｸｽﾀｰﾄ :      17.07     -76.616      252,909           Mw        :        33,996
    ﾋﾟｰｸﾄｯﾌﾟ :      19.44    -120.966       30,138           Mz        :        56,450
    ﾋﾟｰｸｴﾝﾄﾞ :      22.89     -76.798          415           Mz+1      :        79,940
                                                             Mv        :        33,996
    面積[mV・秒]               5,581.902                      Mp        :        32,865
    面積比[%]                    100.000                      Mz/Mw     :         1.660
    高さ[mV]                      44.276                      Mw/Mn     :         2.280
    [η]                    33,996.16679                      Mz+1/Mw   :         2.351
```

Figure S56. SEC chart of polyethylene obtained by **4b** (Table 1, entry 6).
M_n (PS) = 15 kg/mol was corrected to M_n (PE) = 6.5 kg/mol by universal calibration.



```
モジュール:        DSC                        温度プログラム:                            コメント:
データ名:          twj-09-16                         Cel  Cel  Cel/min  min    s         オペレータ: tao
測定日付:          2016/11/07                 1*      30  200       10    5  0.5
サンプル名:        twj-09-16                  2*     200  -50       10   30  0.5
サンプル質量:      2.778 mg                   3*     -50  200       10    5  0.5
リファレンス名:                               4*     200   30       10    5  0.5
リファレンス質量:  0.000 mg
```

Figure S57. DSC traces of polyethylene obtained by **4b** (Table 1, entry 6).

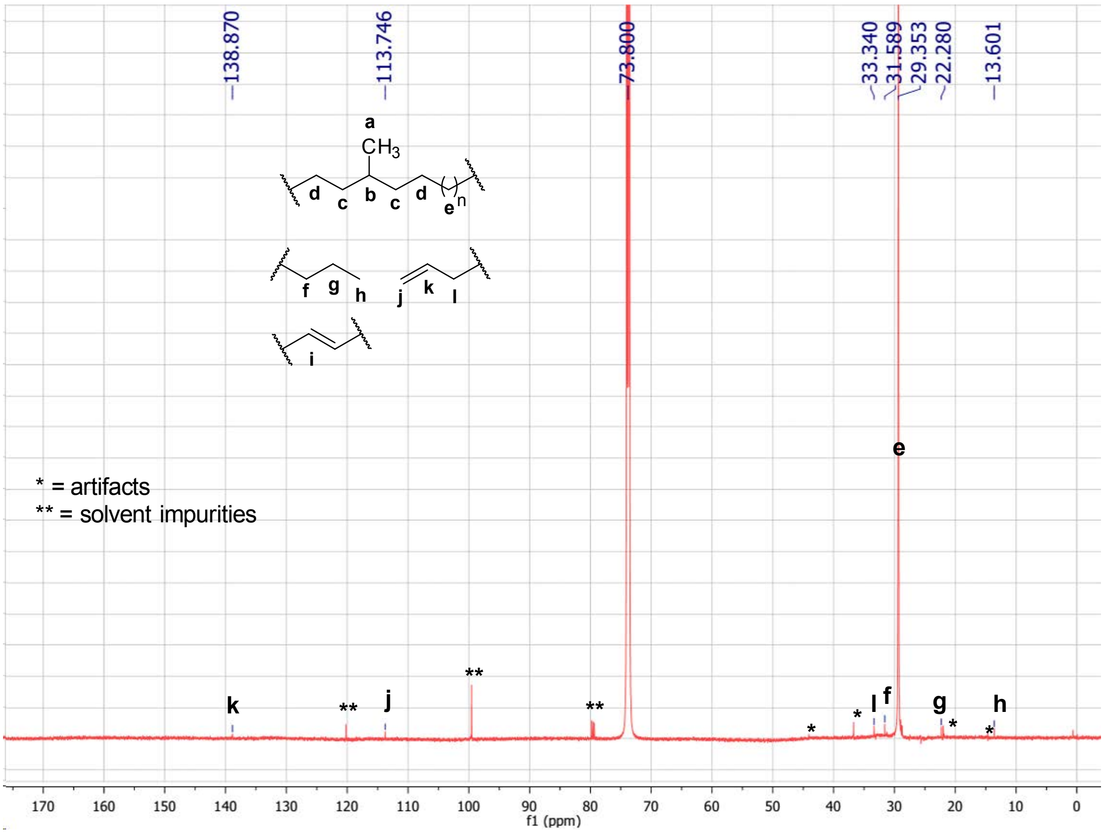
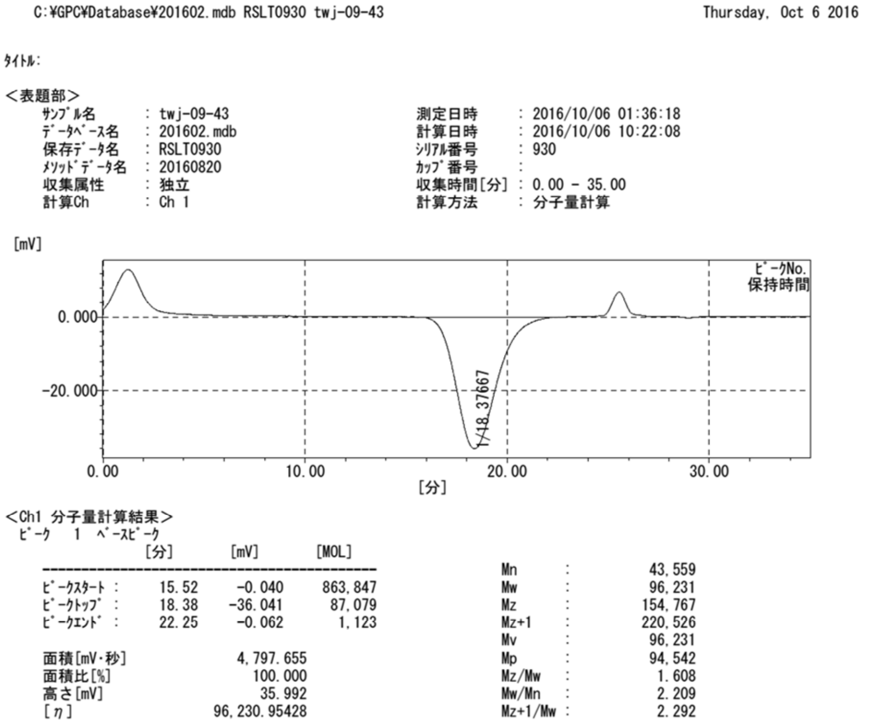


Figure S58. Quantitative ^{13}C NMR spectrum (126 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, inverse gated) of polyethylene obtained by **4c** at 30 °C (Table 1, entry 7).



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C:¥GPC¥Database¥201602.mdb RSLT0930 twj-09-43                        Thursday, Oct 6 2016

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    保存ﾃﾞｰﾀ名     : RSLT0930               ｼﾘｱﾙ番号         : 930
    ﾒｿｯﾄﾞﾃﾞｰﾀ名    : 20160820               ｶｯﾌﾟ番号         :
    収集属性       : 独立                   収集時間[分]     : 0.00 - 35.00
    計算Ch         : Ch 1                   計算方法         : 分子量計算
```

```
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                  [分]       [mV]        [MOL]
    ----------------------------------------              Mn        :          43,559
    ﾋﾟｰｸｽﾀｰﾄ :    15.52      -0.040      863,847              Mw        :          96,231
    ﾋﾟｰｸﾄｯﾌﾟ :    18.38     -36.041       87,079              Mz        :         154,767
    ﾋﾟｰｸｴﾝﾄﾞ :    22.25      -0.062        1,123              Mz+1      :         220,526
                                                              Mv        :          96,231
    面積[mV･秒]             4,797.655                         Mp        :          94,542
    面積比[%]                 100.000                         Mz/Mw     :           1.608
    高さ[mV]                   35.992                         Mw/Mn     :           2.209
    [η]                  96,230.95428                         Mz+1/Mw   :           2.292
```

Figure S59. SEC chart of polyethylene obtained by **4c** (Table 1, entry 7).

M_n (PS) = 44 kg/mol was corrected to M_n (PE) = 19 kg/mol by universal calibration.

```
モジュール:        DSC                              温度プログラム:                          コメント:
データ名:          twj-09-43                            Cel  Cel  Cel/min  min   s       オペレータ: tao
測定日付:          2016/11/09                       1*   30  200       10    5  0.5
サンプル名:        twj-09-43                        2*  200  -50       10   30  0.5
サンプル質量:      2.560 mg                         3*  -50  200       10    5  0.5
リファレンス名:                                     4*  200   30       10    5  0.5
リファレンス質量:  0.000 mg
```

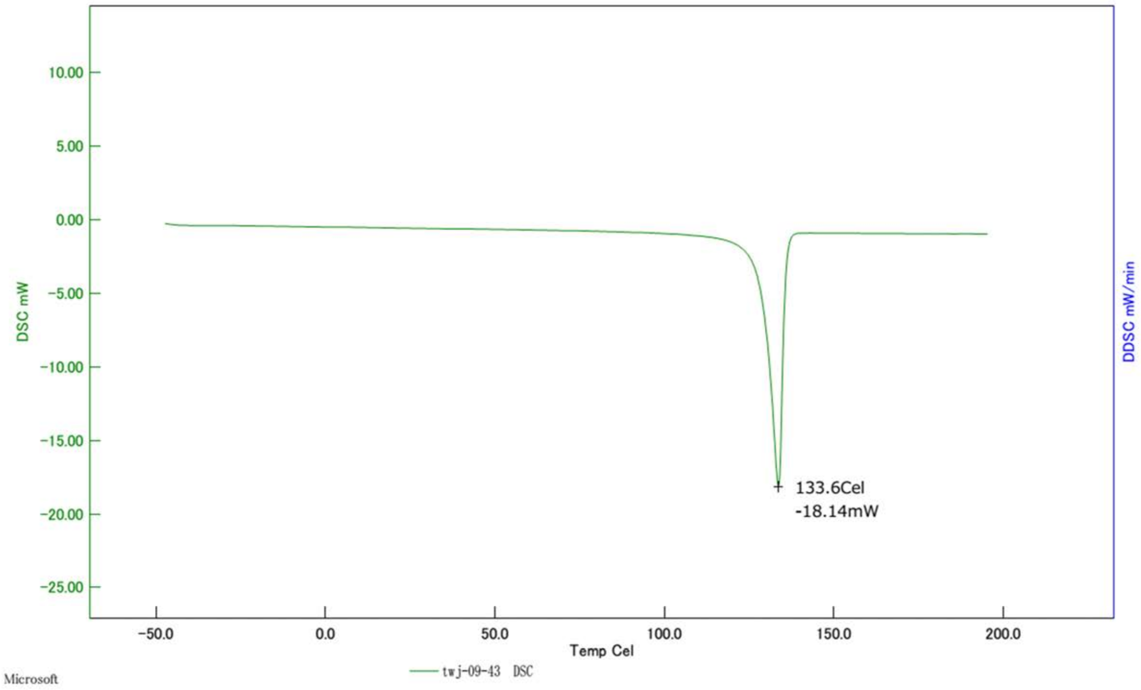


Figure S60. DSC traces of polyethylene obtained by **4c** (Table 1, entry 7).

2016/11/14 17:57:40 Page 1 /

==== Shimadzu LabSolutions クロマトグラム ====

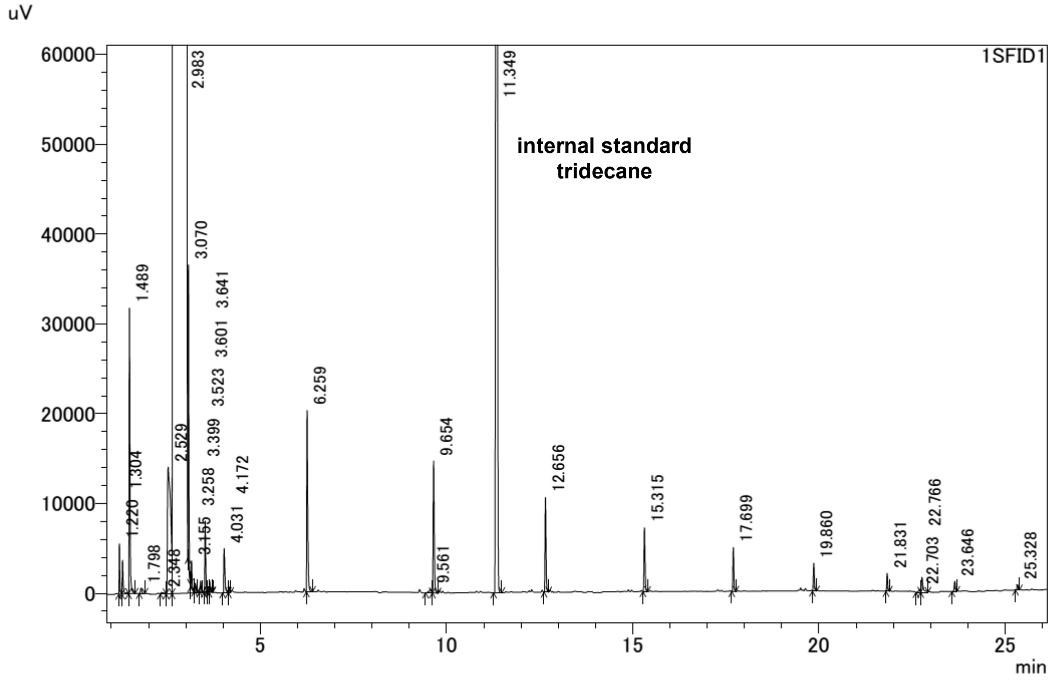


Figure S61. GC spectrum of ethylene oligomer obtained by **5b** at 30 °C with tridecane as internal standard (Table 1, entry 8).

5.2 Data of copolymers (Table 2)

5.2.1 Data of ethylene/allyl acetate copolymers

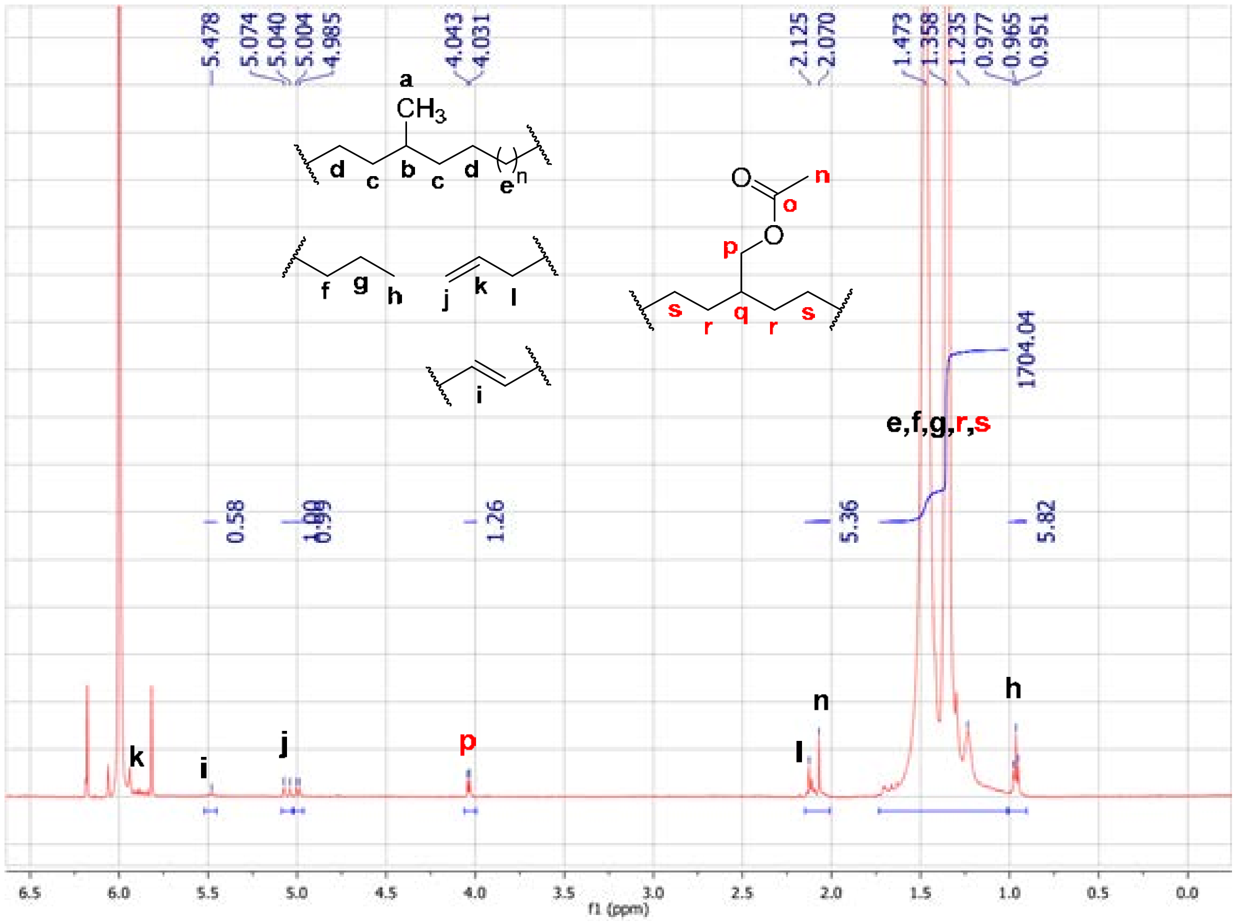


Figure S62. ^{1}H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, relaxation delay 10 s) of copolymer with allyl acetate obtained by **4b** at 30 °C (Table 2, entry 1).

Note: Calculation of incorporation ratio of allyl acetate:

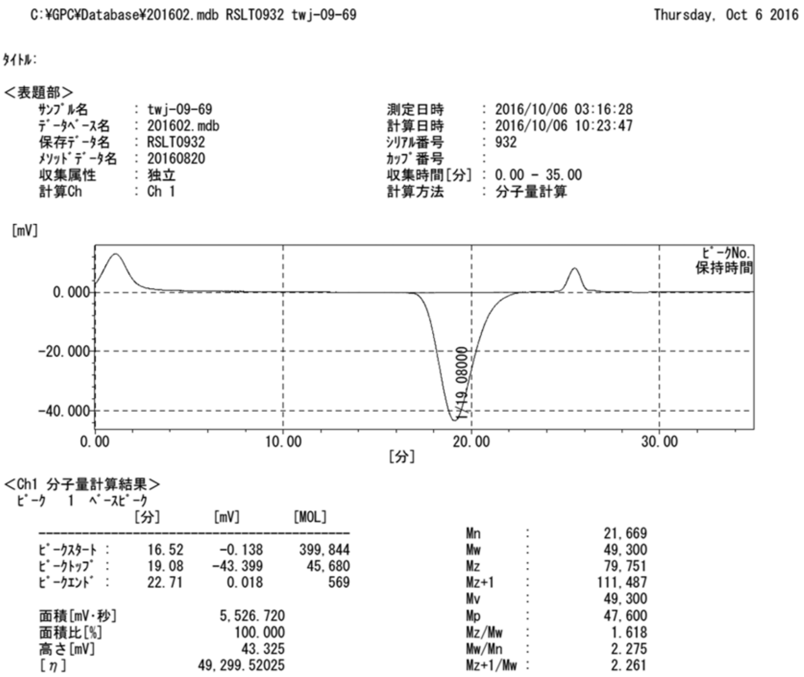
Assume (1−x) mol% ethylene and x mol% allyl acetate in the copolymer,

$$\frac{2x}{8x+4(1-x)} = \frac{p}{p+e+f+g+h+j+k+l+i+n+q+r+s}$$

$$x = \frac{2p}{e+f+g+h+j+k+l+i+n+q+r+s-p}$$

In entry 1 of Table 2, the incorporation ratio of allyl acetate is calculated as follows:

(2 × 1.26) / (1704.04 + 5.82 + 5.36 + 3.00 + 0.58 − 1.26) = 0.15 mol%



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C:¥GPC¥Database¥201602.mdb RSLT0932 twj-09-69                         Thursday, Oct 6 2016

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   計算Ch          : Ch 1                         計算方法       : 分子量計算
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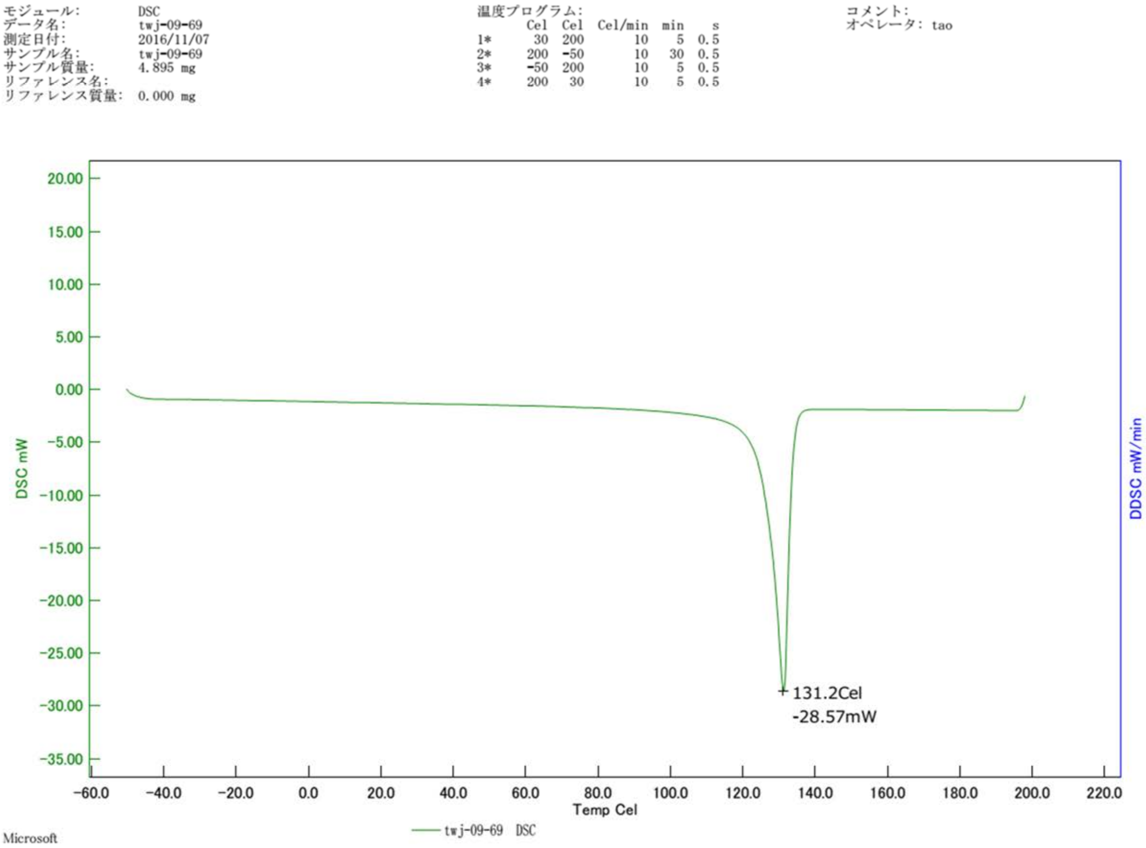
 ﾋﾟｰｸ   1  ﾍﾞｰｽﾋﾟｰｸ
                [分]       [mV]       [MOL]
   ------------------------------------------
   ﾋﾟｰｸｽﾀｰﾄ :    16.52     -0.138     399,844           Mn       :        21,669
   ﾋﾟｰｸﾄｯﾌﾟ :    19.08    -43.399      45,680           Mw       :        49,300
   ﾋﾟｰｸｴﾝﾄﾞ :    22.71      0.018         569           Mz       :        79,751
                                                        Mz+1     :       111,487
                                                        Mv       :        49,300
   面積[mV・秒]               5,526.720                 Mp       :        47,600
   面積比[%]                    100.000                 Mz/Mw    :         1.618
   高さ[mV]                      43.325                 Mw/Mn    :         2.275
   [η]                      49,299.52025                Mz+1/Mw  :         2.261
```

Figure S63. SEC chart of ethylene/allyl acetate copolymer obtained by **4b** (Table 2, entry 1). M_n (PS) = 22 kg/mol was corrected to M_n (PE) = 9.4 kg/mol by universal calibration.



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データ名:            twj-09-69                      Cel   Cel  Cel/min  min    s            オペレータ: tao
測定日付:            2016/11/07              1*      30   200       10    5  0.5
サンプル名:          twj-09-69               2*     200   -50       10   30  0.5
サンプル質量:        4.895 mg                3*     -50   200       10    5  0.5
リファレンス名:                              4*     200    30       10    5  0.5
リファレンス質量:    0.000 mg
```

Figure S64. DSC traces of ethylene/allyl acetate copolymer obtained by **4b** (Table 2, entry 1).

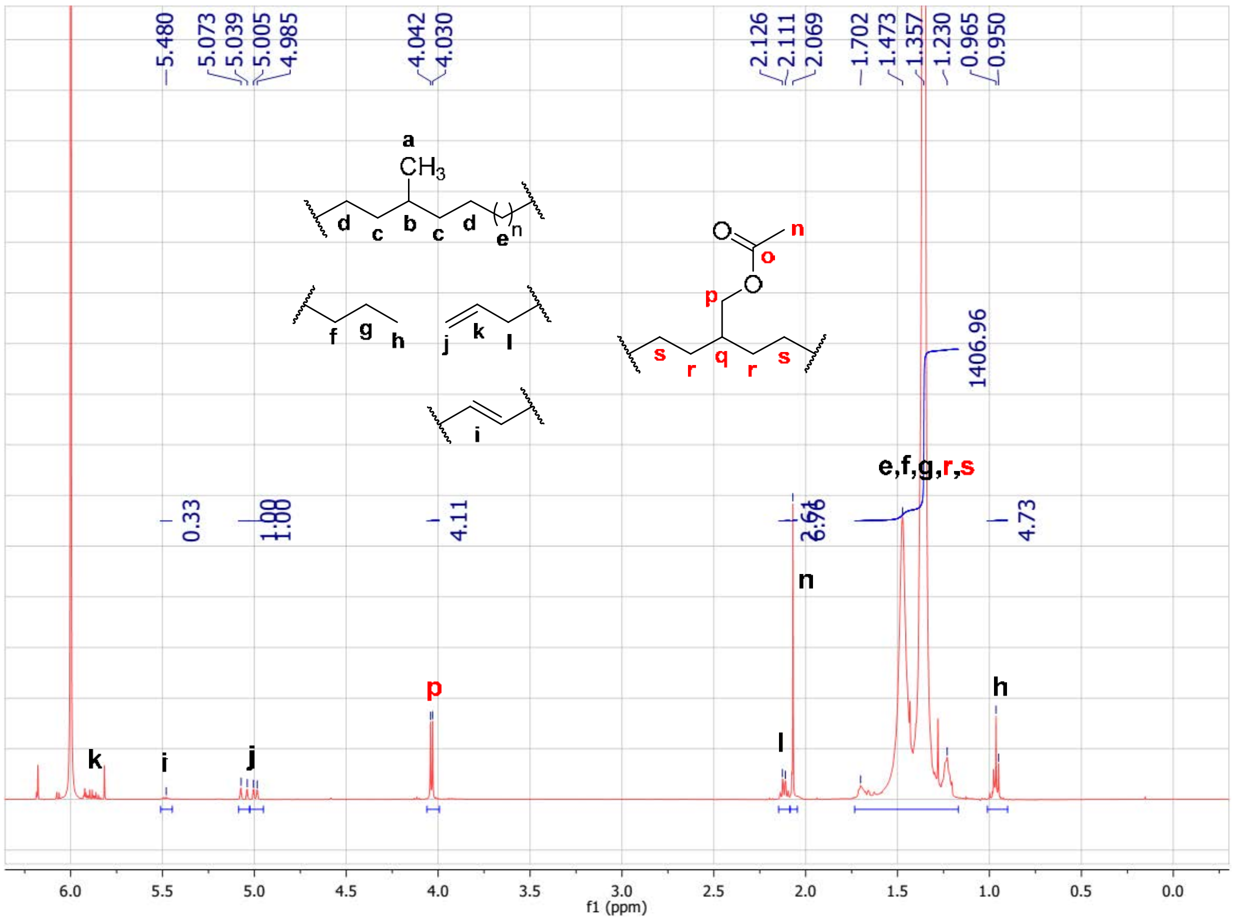
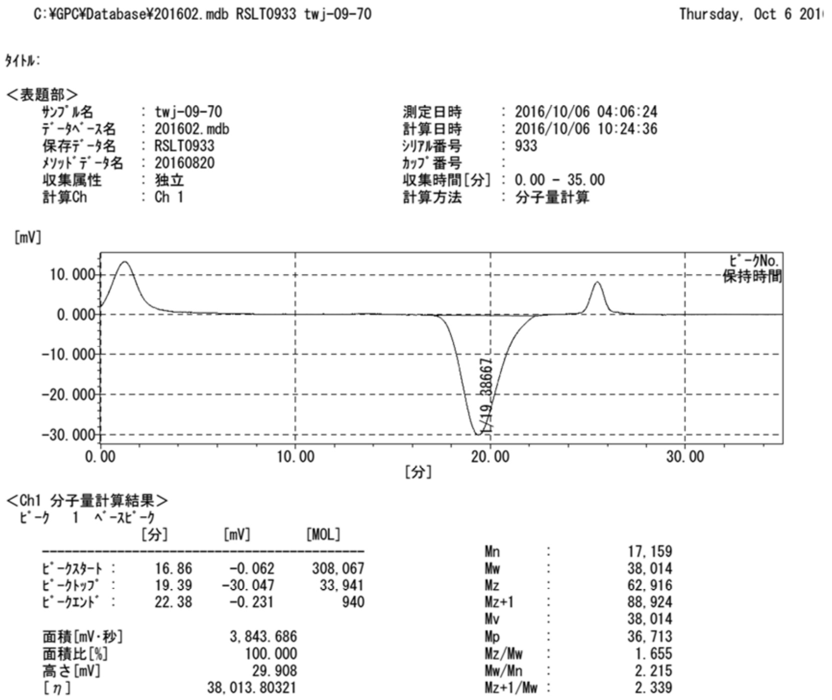


Figure S65. ^{1}H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, relaxation delay 10 s) of copolymer with allyl acetate obtained by **4b** at 30 °C (Table 2, entry 2).

Note: In entry 2 of Table 2, the incorporation ratio of allyl acetate is calculated as follows:

$(2 \times 4.11) / (4.73 + 1406.96 + 3.00 + 0.33 + 2.61 + 6.76 - 4.11) = 0.58$ mol%



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    ﾒｿｯﾄﾞﾃﾞｰﾀ名      : 20160820               ｶｯﾌﾟ番号        :
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    計算Ch           : Ch 1                   計算方法        : 分子量計算
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                  [分]        [mV]        [MOL]
    ----------------------------------------------
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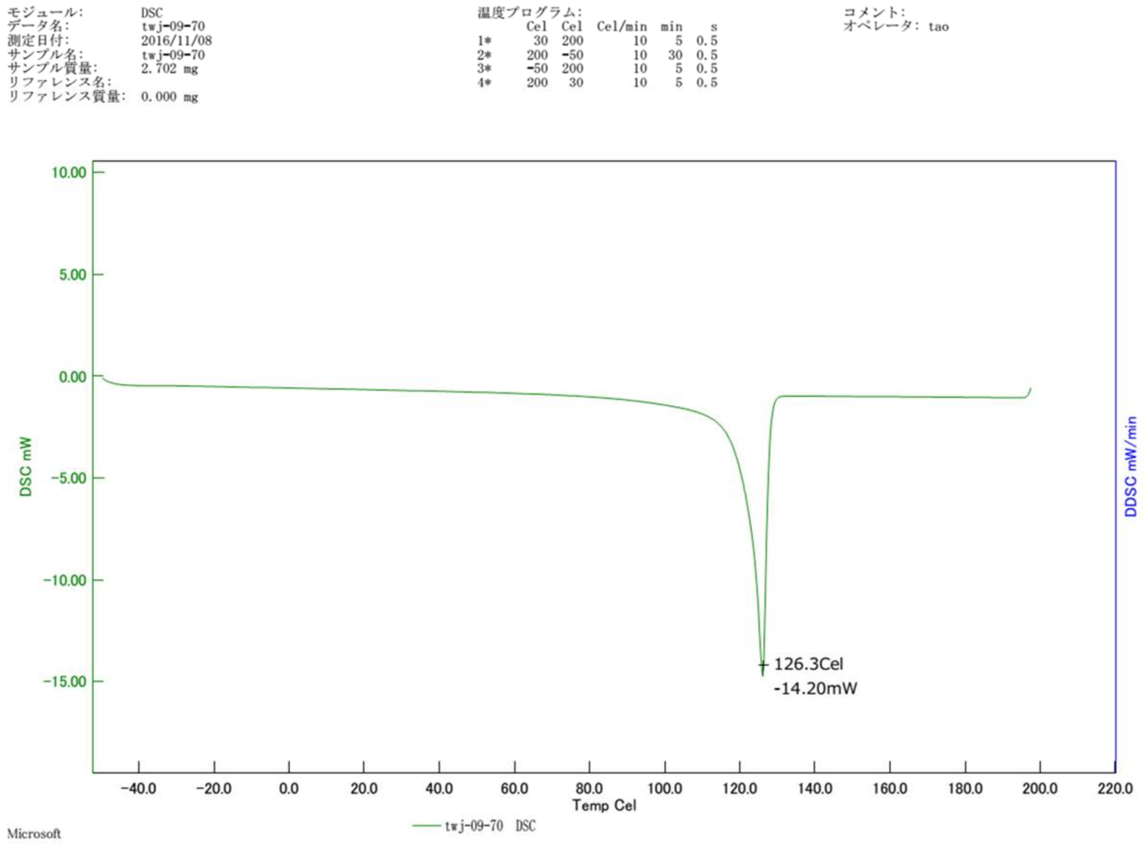
    ﾋﾟｰｸﾄｯﾌﾟ :    19.39     -30.047      33,941           Mw        :        38,014
    ﾋﾟｰｸｴﾝﾄﾞ :    22.38      -0.231         940           Mz        :        62,916
                                                          Mz+1      :        88,924
                                                          Mv        :        38,014
    面積[mV･秒]             3,843.686                     Mp        :        36,713
    面積比[%]                 100.000                     Mz/Mw     :         1.655
    高さ[mV]                   29.908                     Mw/Mn     :         2.215
    [η]                   38,013.80321                    Mz+1/Mw   :         2.339
```

Figure S66. SEC chart of ethylene/allyl acetate copolymer obtained by **4b** (Table 2, entry 2). M_n (PS) = 17 kg/mol was corrected to M_n (PE) = 7.4 kg/mol by universal calibration.



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データ名:            twj-09-70                          Cel   Cel  Cel/min  min    s            オペレータ: tao
測定日付:            2016/11/08                  1*      30   200       10    5  0.5
サンプル名:          twj-09-70                   2*     200   -50       10   30  0.5
サンプル質量:        2.702 mg                    3*     -50   200       10    5  0.5
リファレンス名:                                  4*     200    30       10    5  0.5
リファレンス質量:    0.000 mg
```

Figure S67. DSC traces of ethylene/allyl acetate copolymer obtained by **4b** (Table 2, entry 2).

5.2.2. Data of ethylene/methyl acrylate copolymers

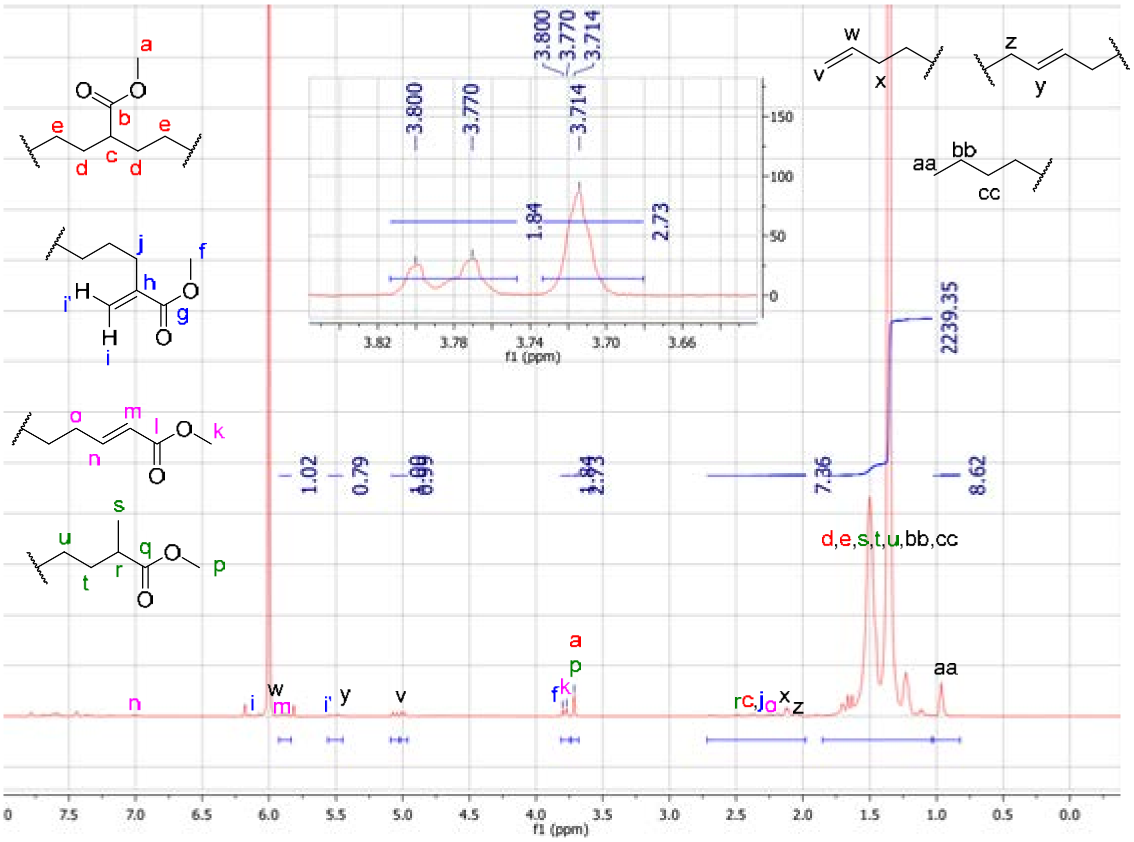


Figure S68. ^{1}H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, relaxation delay 10 s) of copolymer with methyl acrylate obtained by **4b** at 30 °C (Table 2, entry 3).

Note: Calculation of incorporation ratio of methyl acrylate:

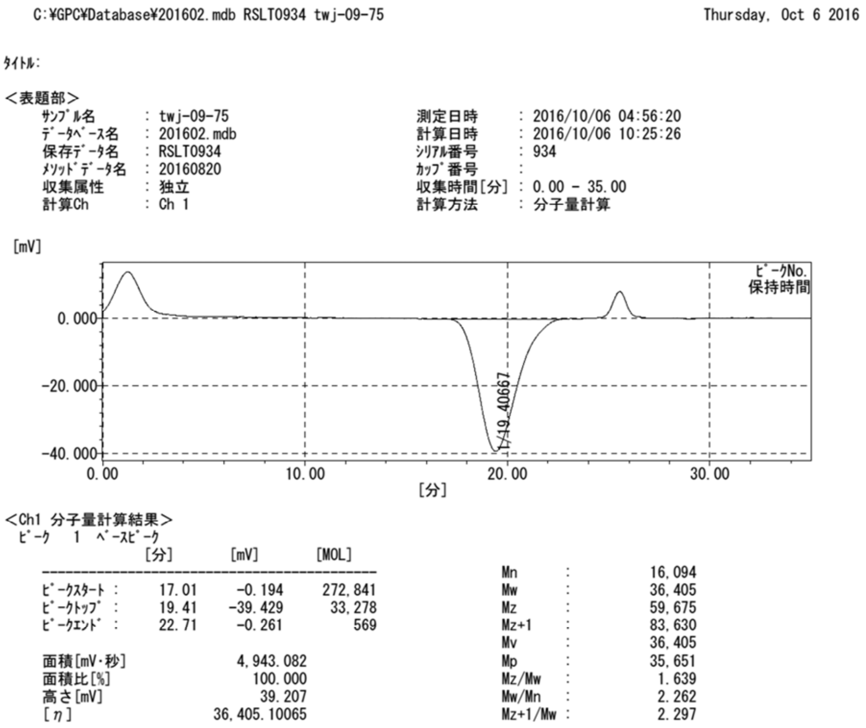
Assume (1-x) mol% ethylene and x mol% methyl acrylate in the copolymer,

$$\frac{3x}{3x+4(1-x)} = \frac{p+a+f+k}{\mathrm{n+i+i'+m+y+v+w+r+c+j+o+x+z+d+e+s+t+u+bb+cc+aa}}$$

$$\mathrm{x} = \frac{\mathrm{4(p+a+f+k)}}{3(n+i+i'+m+y+v+w+r+c+j+o+x+z+d+e+s+t+u+bb+cc+aa)+p+a+f+k}$$

In entry 3 of Table 2, the incorporation ratio of allyl acetate is calculated as follows:

(4 × (1.84 + 2.73)) / (3×(8.62 + 2239.35 + 7.36 + 3.02 + 0.79)+1.84 + 2.73) = 0.27 mol%.



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C:¥GPC¥Database¥201602.mdb RSLT0934 twj-09-75                                Thursday, Oct 6 2016

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                  [分]        [mV]        [MOL]
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    ﾋﾟｰｸｽﾀｰﾄ  :    17.01      -0.194      272,841          Mw        :        36,405
    ﾋﾟｰｸﾄｯﾌﾟ  :    19.41     -39.429       33,278          Mz        :        59,675
    ﾋﾟｰｸｴﾝﾄﾞ  :    22.71      -0.261          569          Mz+1      :        83,630
                                                           Mv        :        36,405
    面積[mV・秒]            4,943.082                      Mp        :        35,651
    面積比[%]                 100.000                      Mz/Mw     :         1.639
    高さ[mV]                   39.207                      Mw/Mn     :         2.262
    [η]                36,405.10065                        Mz+1/Mw   :         2.297
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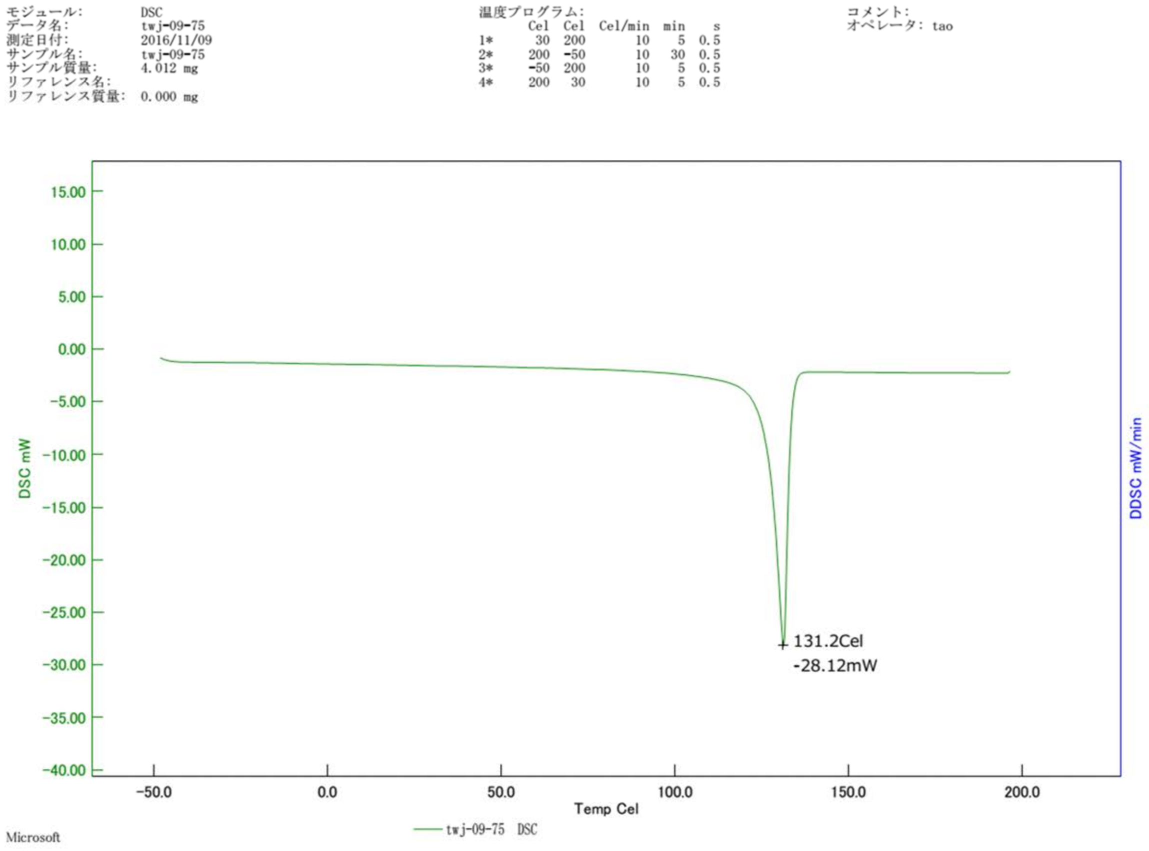
Figure S69. SEC chart of ethylene/methyl acrylate copolymer obtained by **4b** (Table 2, entry 3). M_n (PS) = 16 kg/mol was corrected to M_n (PE) = 7.0 kg/mol by universal calibration.



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サンプル名:         twj-09-75            2*    200   -50       10   30  0.5
サンプル質量:       4.012 mg             3*    -50   200       10    5  0.5
リファレンス名:                          4*    200    30       10    5  0.5
リファレンス質量:   0.000 mg
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Figure S70. DSC traces of ethylene/methyl acrylate copolymer obtained by **4b** (Table 2, entry 3).

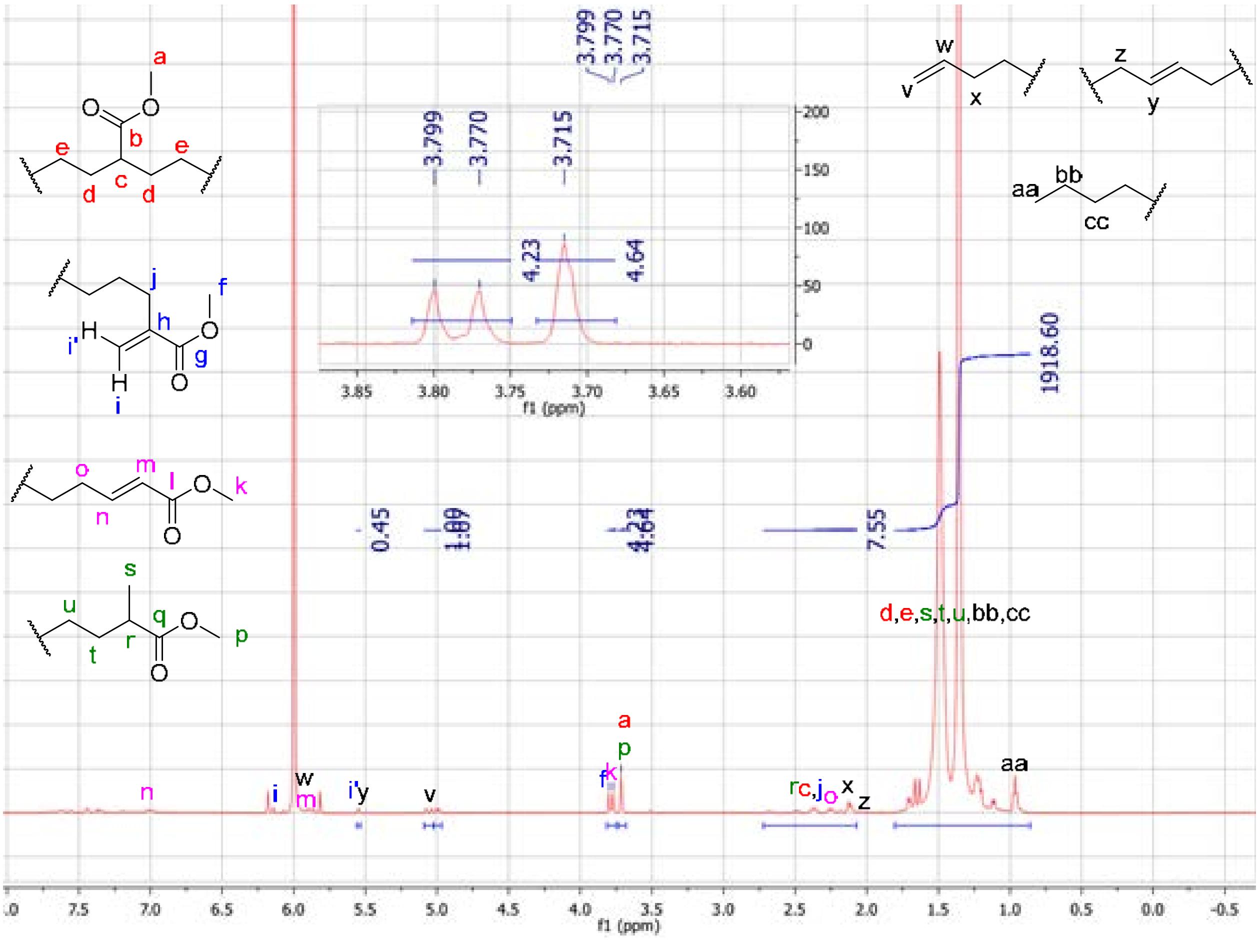
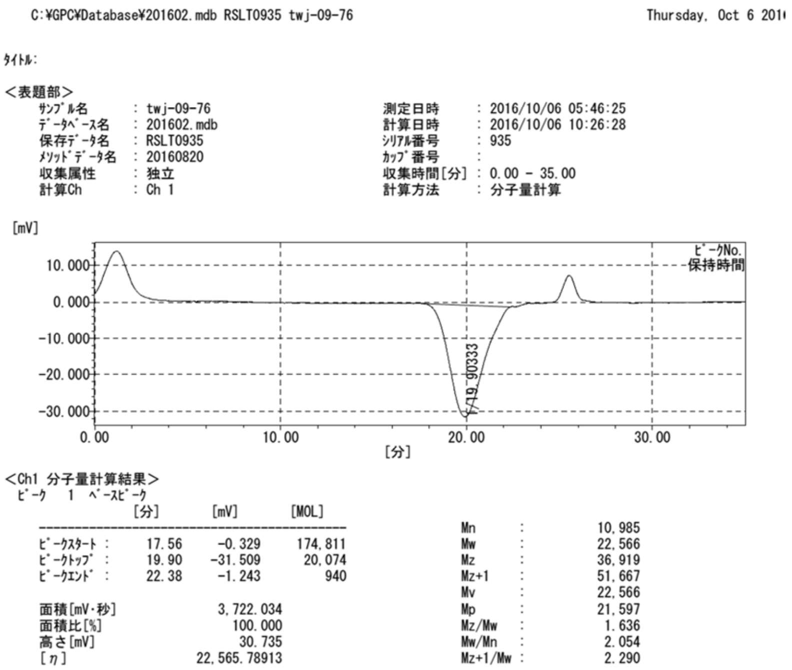


Figure S71. ^{1}H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, relaxation delay 10 s) of copolymer with methyl acrylate obtained by **4b** at 30 °C (Table 2, entry 4).

Note: In entry 3 of Table 2, the incorporation ratio of allyl acetate is calculated as follows:
(4 × (4.23 + 4.64)) / (3×(1918.60 + 7.55 + 3.00 + 0.45 + 0.45) + 4.23 + 4.64) = 0.61 mol%



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                [分]       [mV]        [MOL]
    ---------------------------------------                    Mn        :      10,985
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    ﾋﾟｰｸﾄｯﾌﾟ :   19.90    -31.509      20,074                  Mz        :      36,919
    ﾋﾟｰｸｴﾝﾄﾞ :   22.38     -1.243         940                  Mz+1      :      51,667
                                                               Mv        :      22,566
    面積[mV･秒]             3,722.034                          Mp        :      21,597
    面積比[%]                 100.000                          Mz/Mw     :       1.636
    高さ[mV]                   30.735                          Mw/Mn     :       2.054
    [η]                22,565.78913                            Mz+1/Mw   :       2.290
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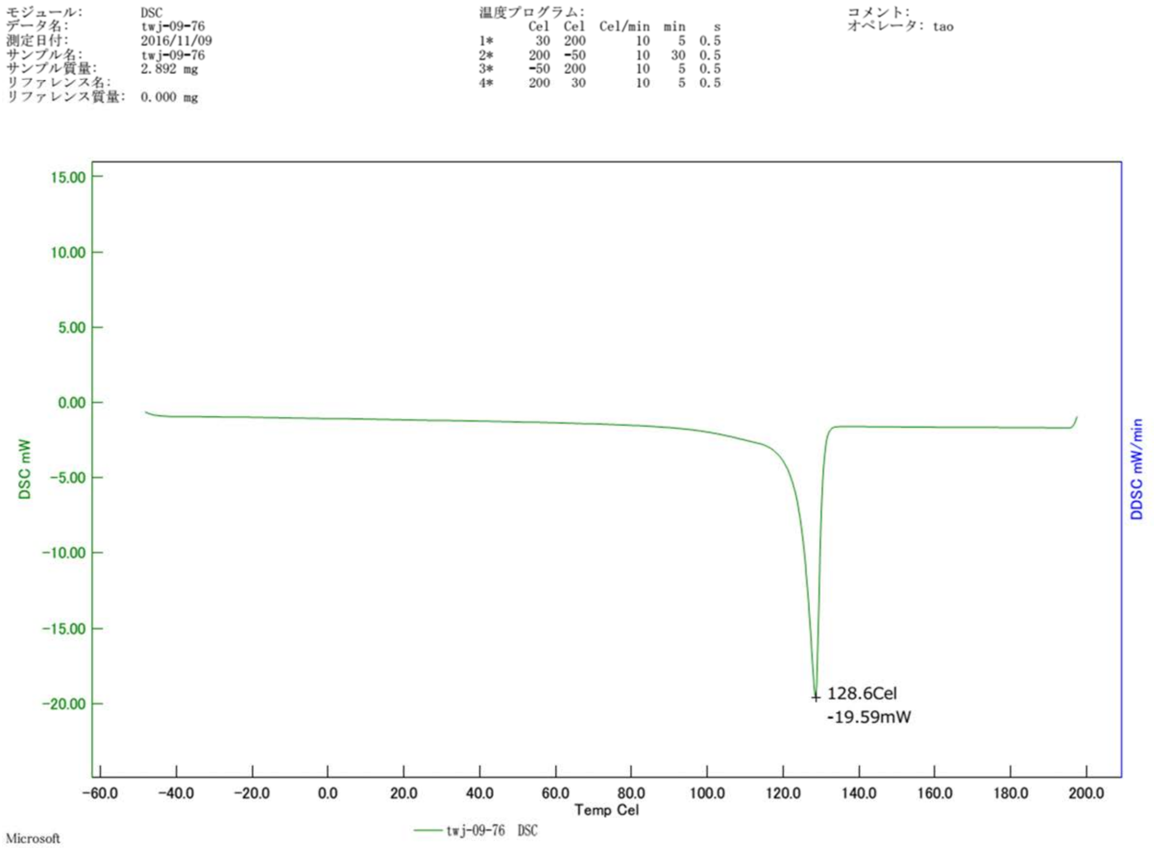
Figure S72. SEC chart of ethylene/methyl acrylate copolymer obtained by **4b** (Table 2, entry 4). M_n (PS) = 11 kg/mol was corrected to M_n (PE) = 4.8 kg/mol by universal calibration.



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サンプル名:          twj-09-76            2*     200  -50       10   30  0.5
サンプル質量:        2.892 mg             3*     -50  200       10    5  0.5
リファレンス名:                           4*     200   30       10    5  0.5
リファレンス質量:    0.000 mg
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Figure S73. DSC traces of ethylene/methyl acrylate copolymer obtained by **4b** (Table 2, entry 4).

Supplementary Information for the Assignment of Ethylene/Methyl Acrylate Copolymer

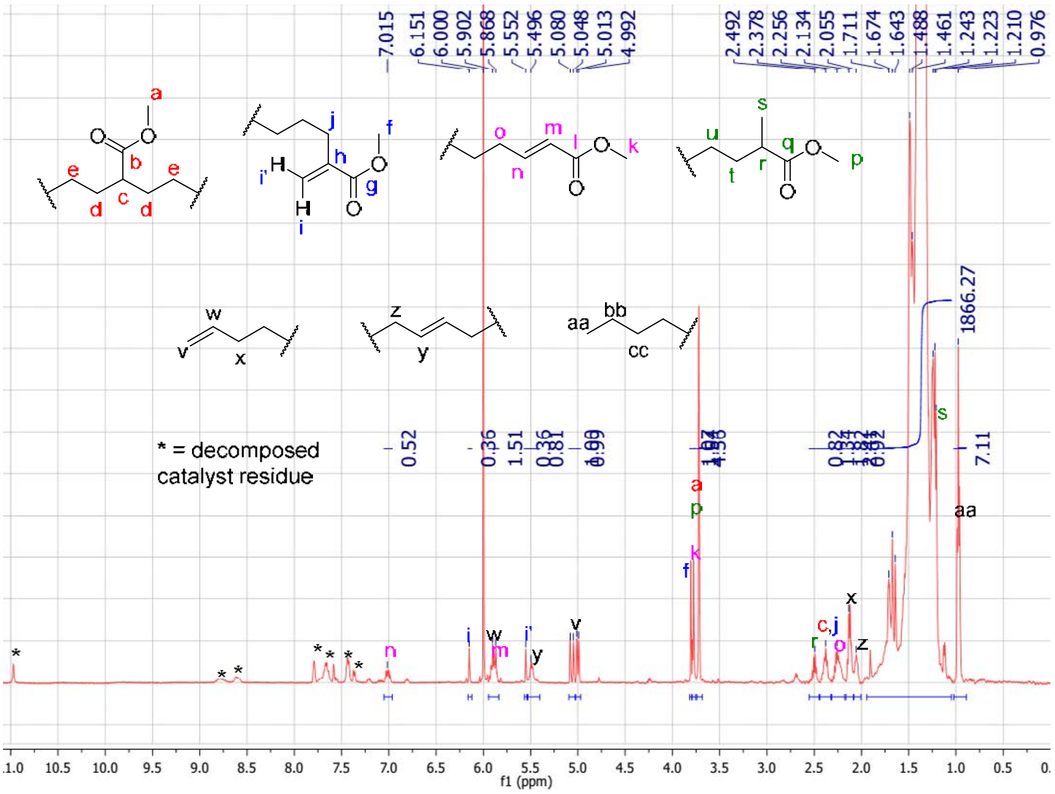


Figure S74. ^{1}H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, relaxation delay 10 s) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

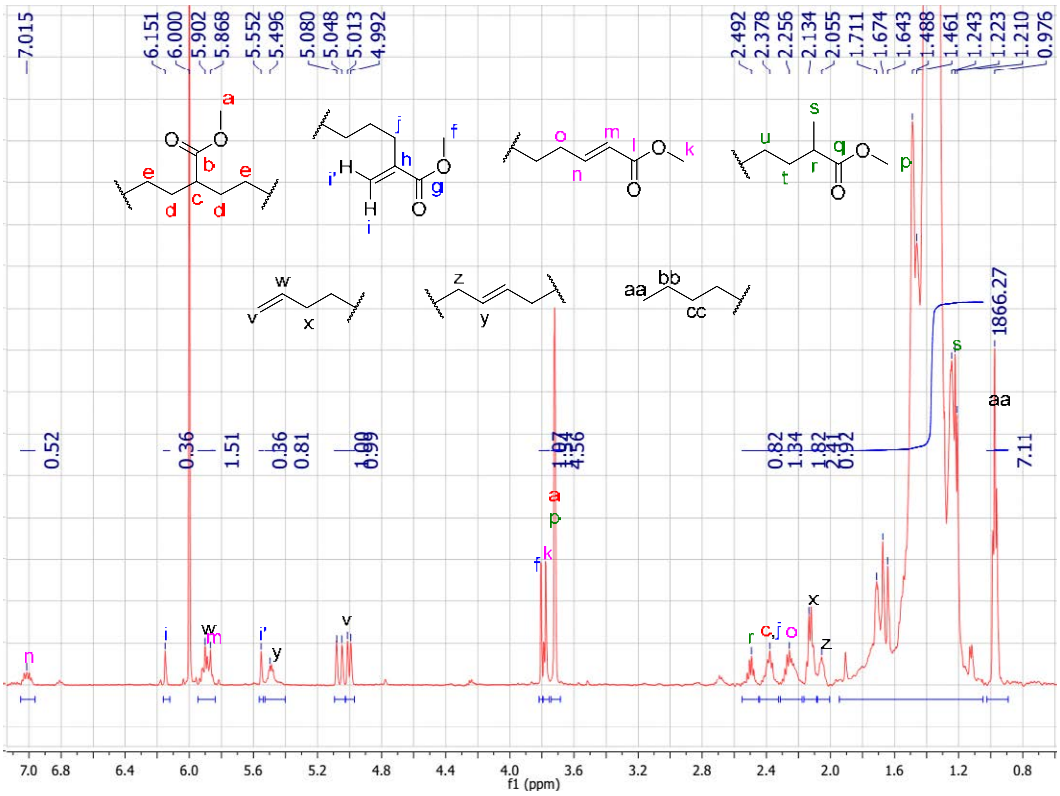


Figure S75. ^{1}H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, relaxation delay 10 s, δ = 0.5–7.1 ppm) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

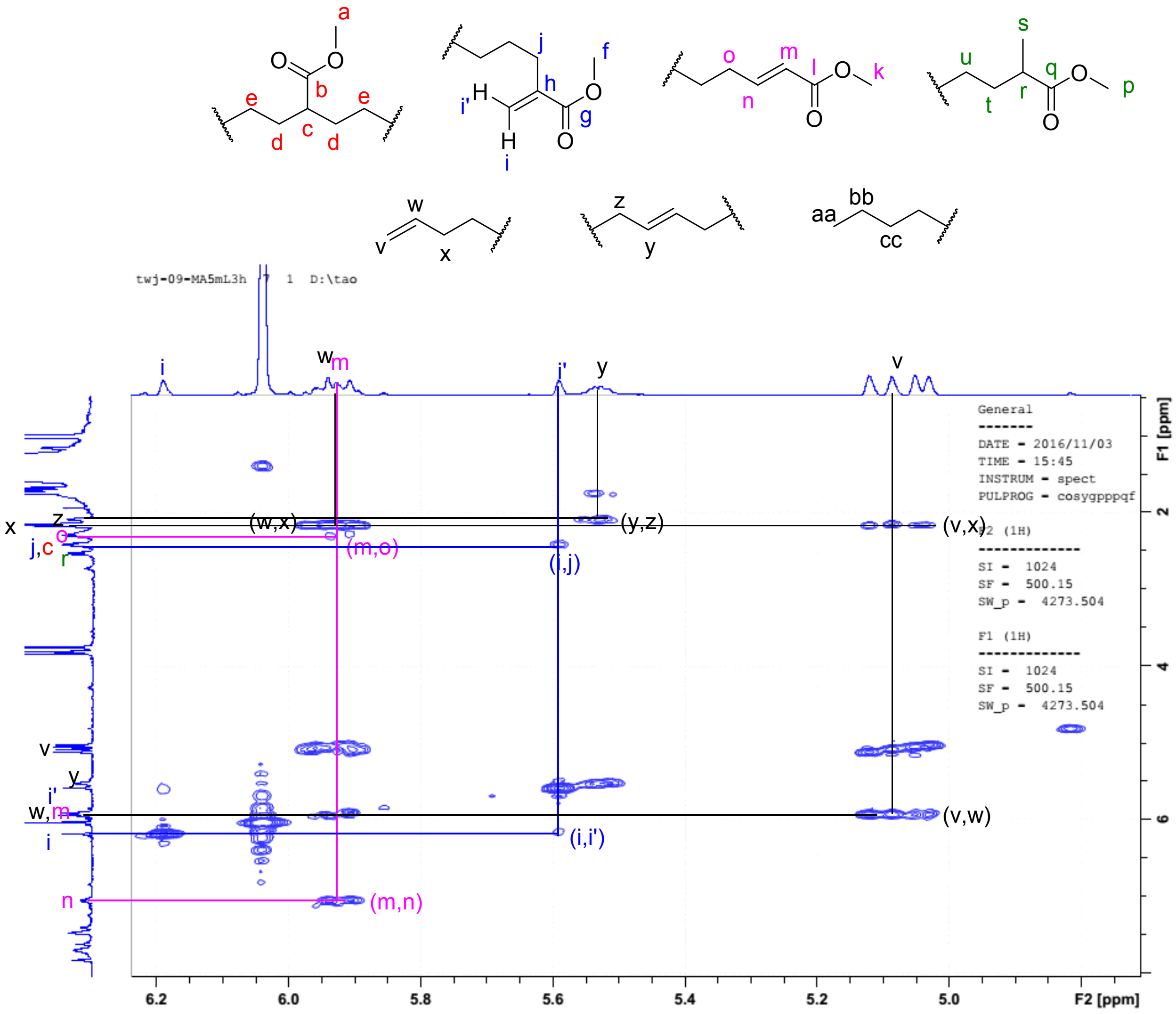


Figure S76. ^{1}H–^{1}H COSY spectrum (1,1,2,2-tetrachloroethane-d_2, 120 °C, δ 4.5-6.3 ppm) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

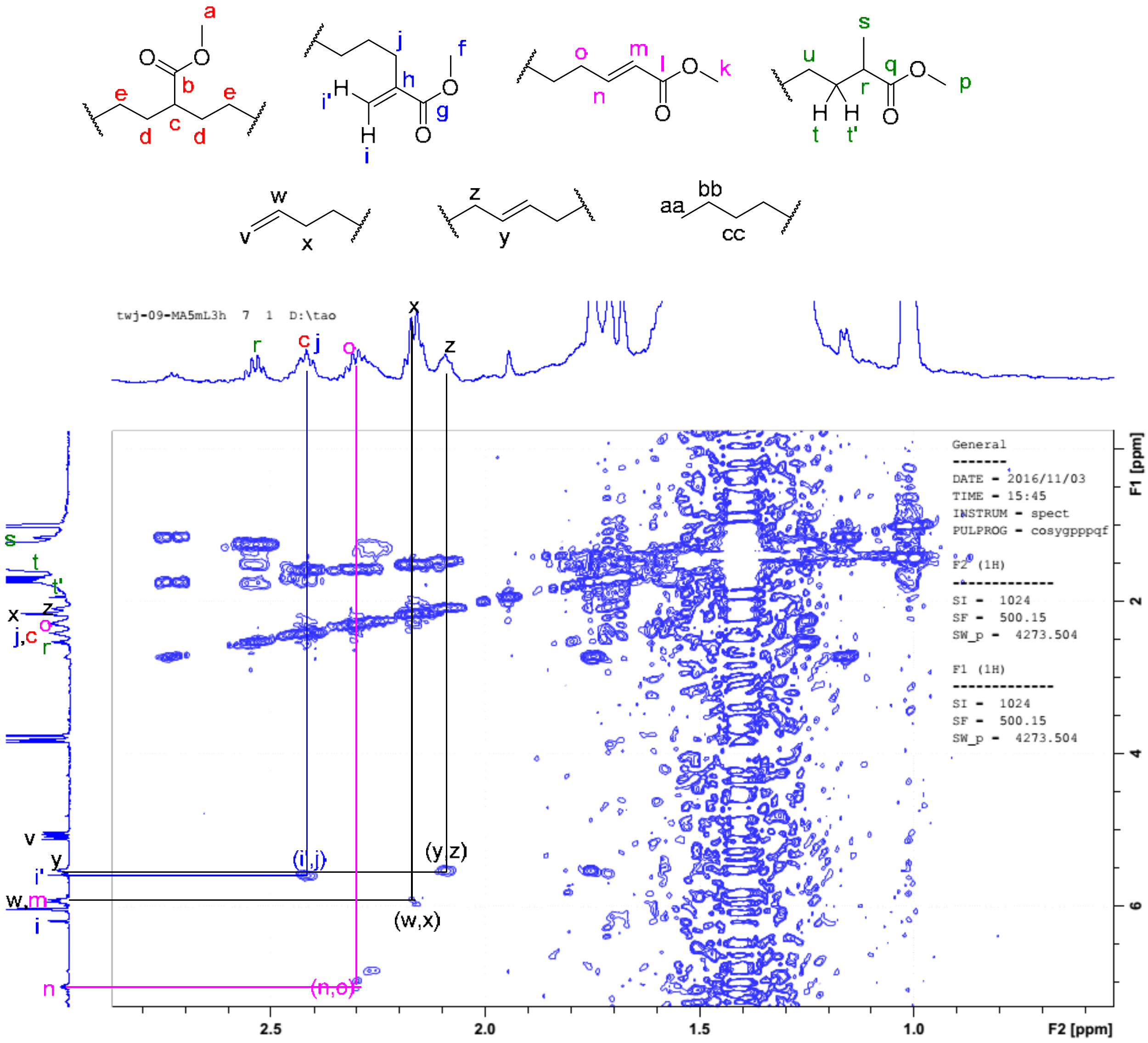


Figure S77. ^{1}H–^{1}H COSY spectrum (1,1,2,2-tetrachloroethane-*d*$_2$, 120 °C, δ 0.5–3.0 ppm) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

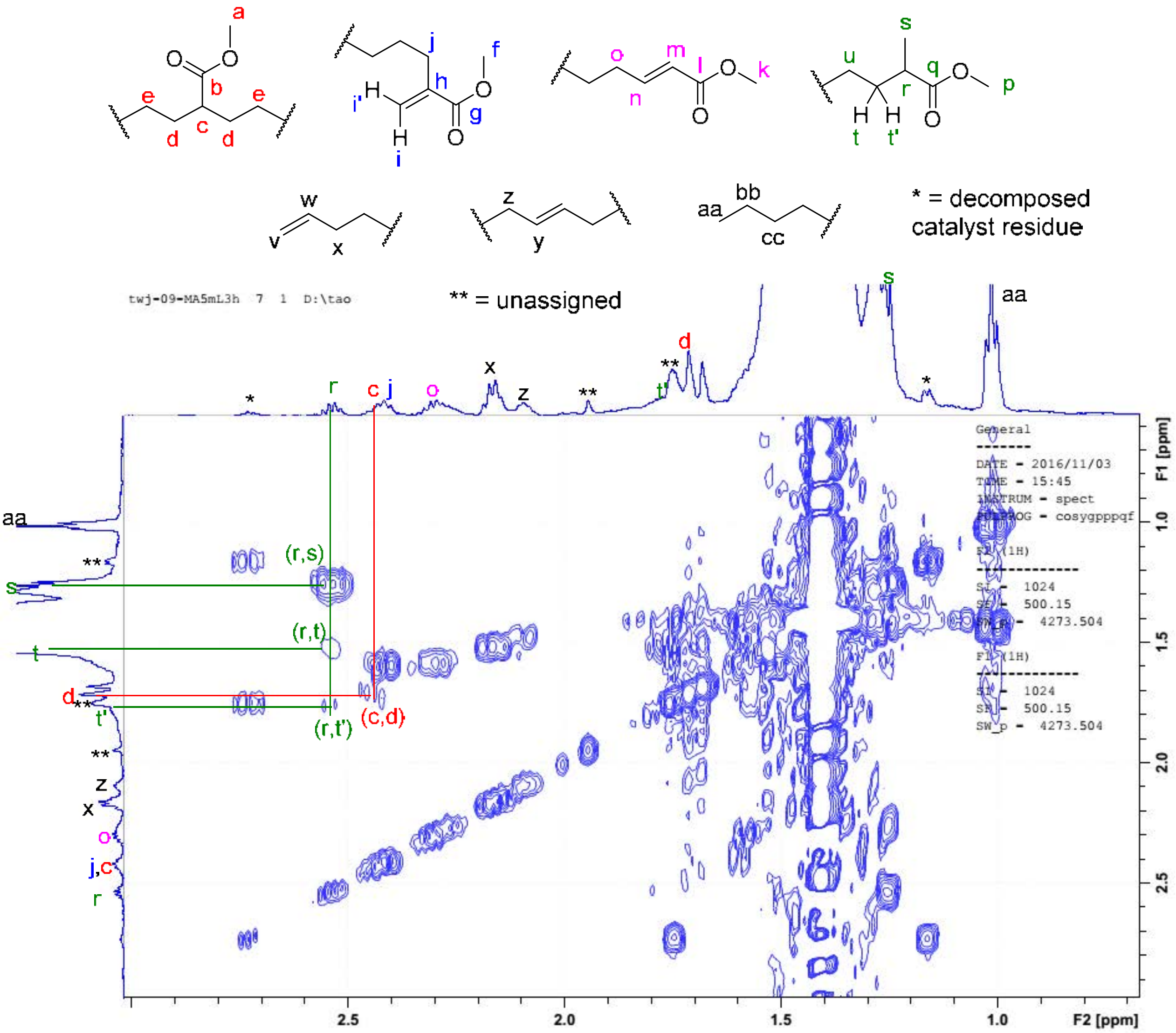


Figure S78. ^{1}H–^{1}H COSY spectrum (1,1,2,2-tetrachloroethane-d_2, 120 °C, δ 0.5-3.0 ppm) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

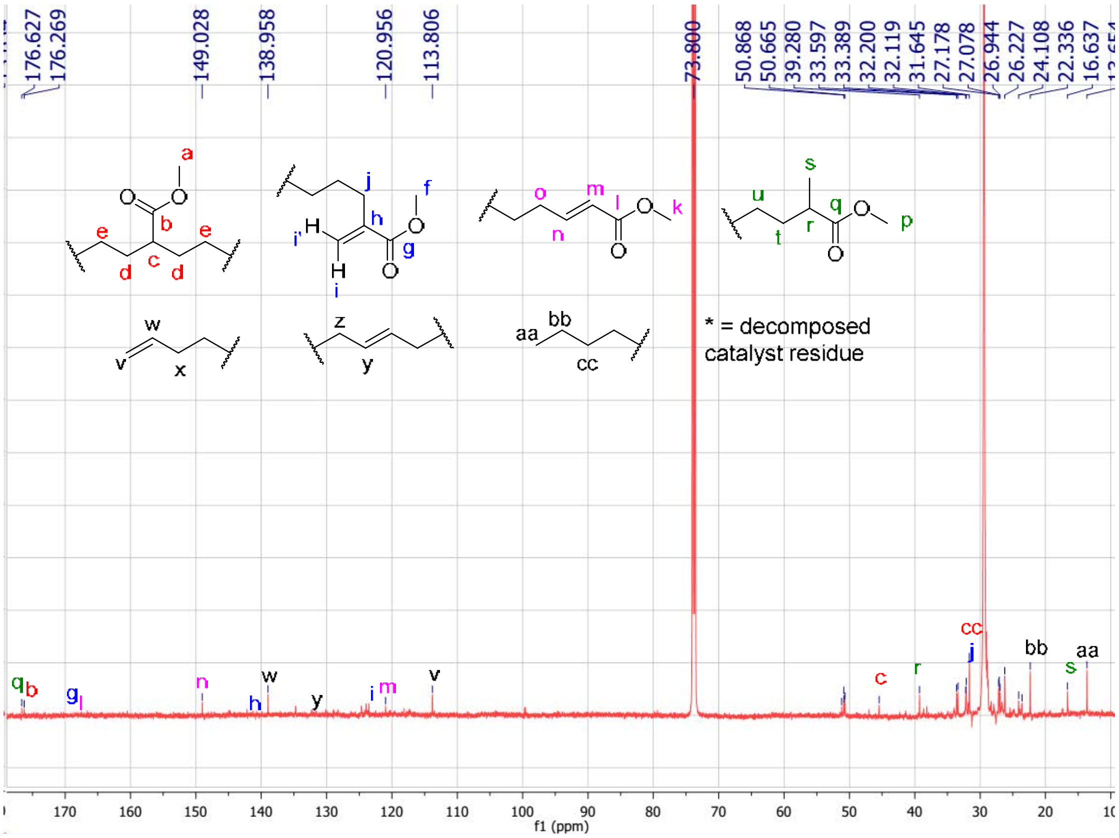


Figure S79. ^{13}C NMR spectrum (1,1,2,2-tetrachloroethane-d_2, 120 °C) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

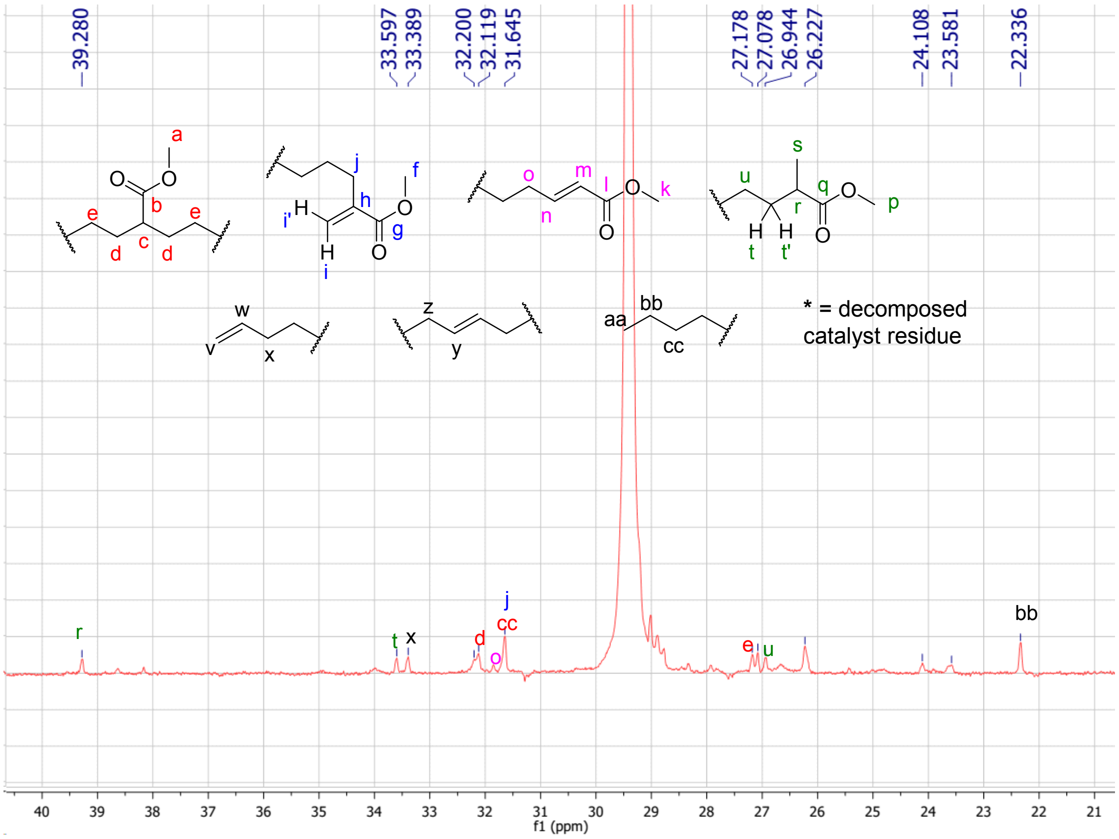


Figure S80. ^{13}C NMR spectrum (1,1,2,2-tetrachloroethane-d_2, 120 °C) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

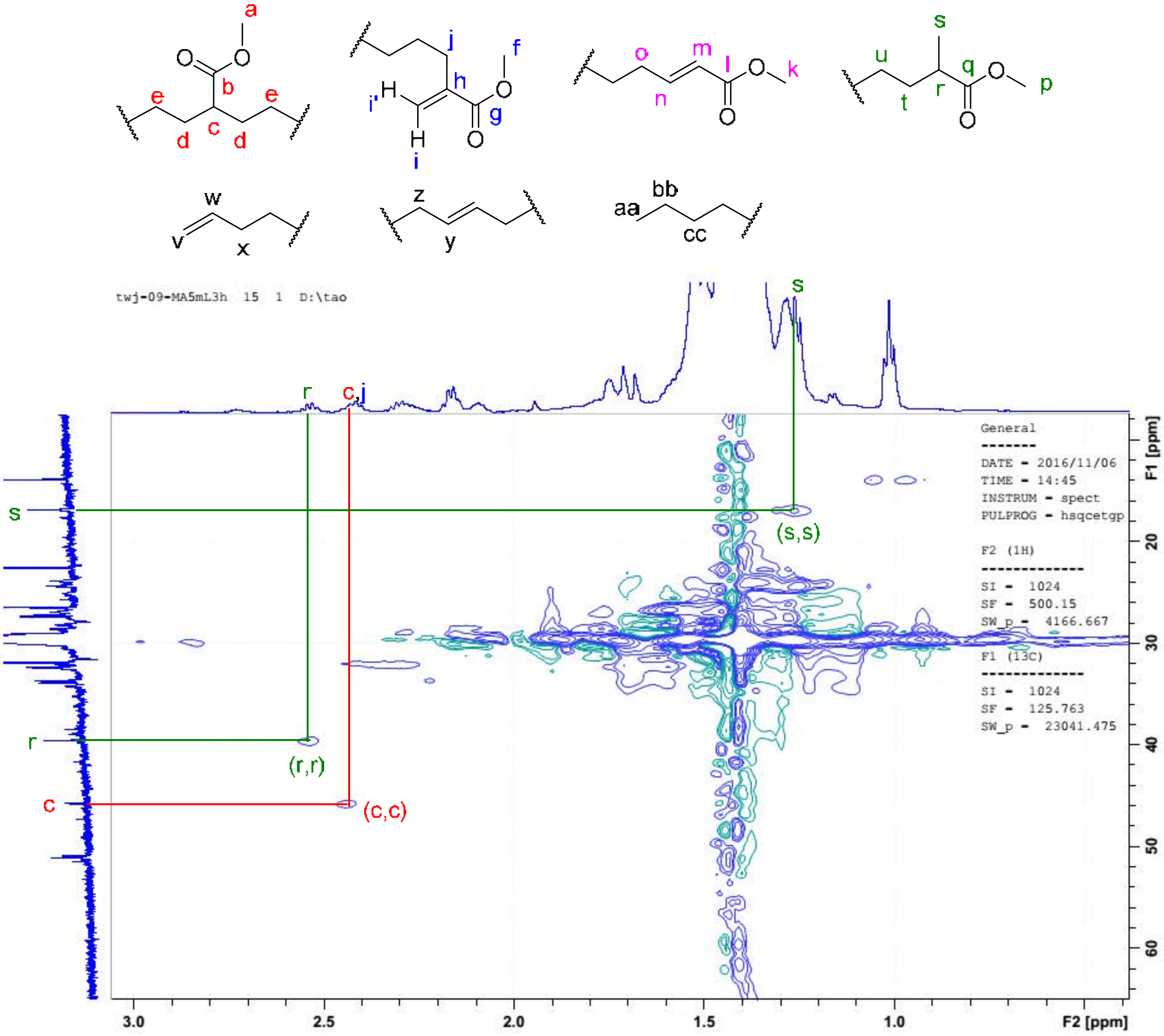


Figure S81. HSQC spectrum (1,1,2,2-tetrachloroethane-d_2, 120 °C, δ 0.5–3.0 ppm) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

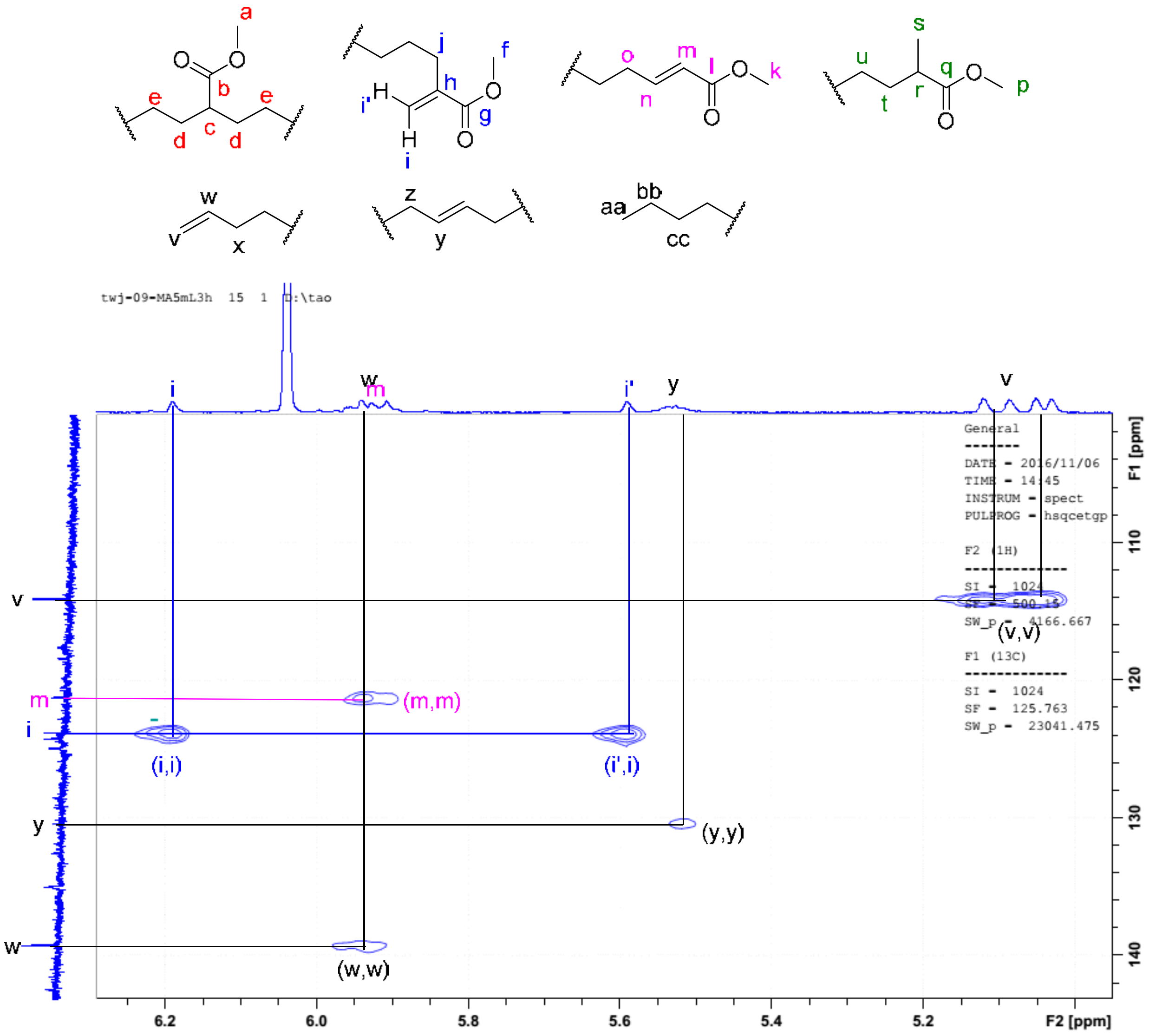


Figure S82. HSQC spectrum (1,1,2,2-tetrachloroethane-d_2, 120 °C, δ 5.0–6.3 ppm) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

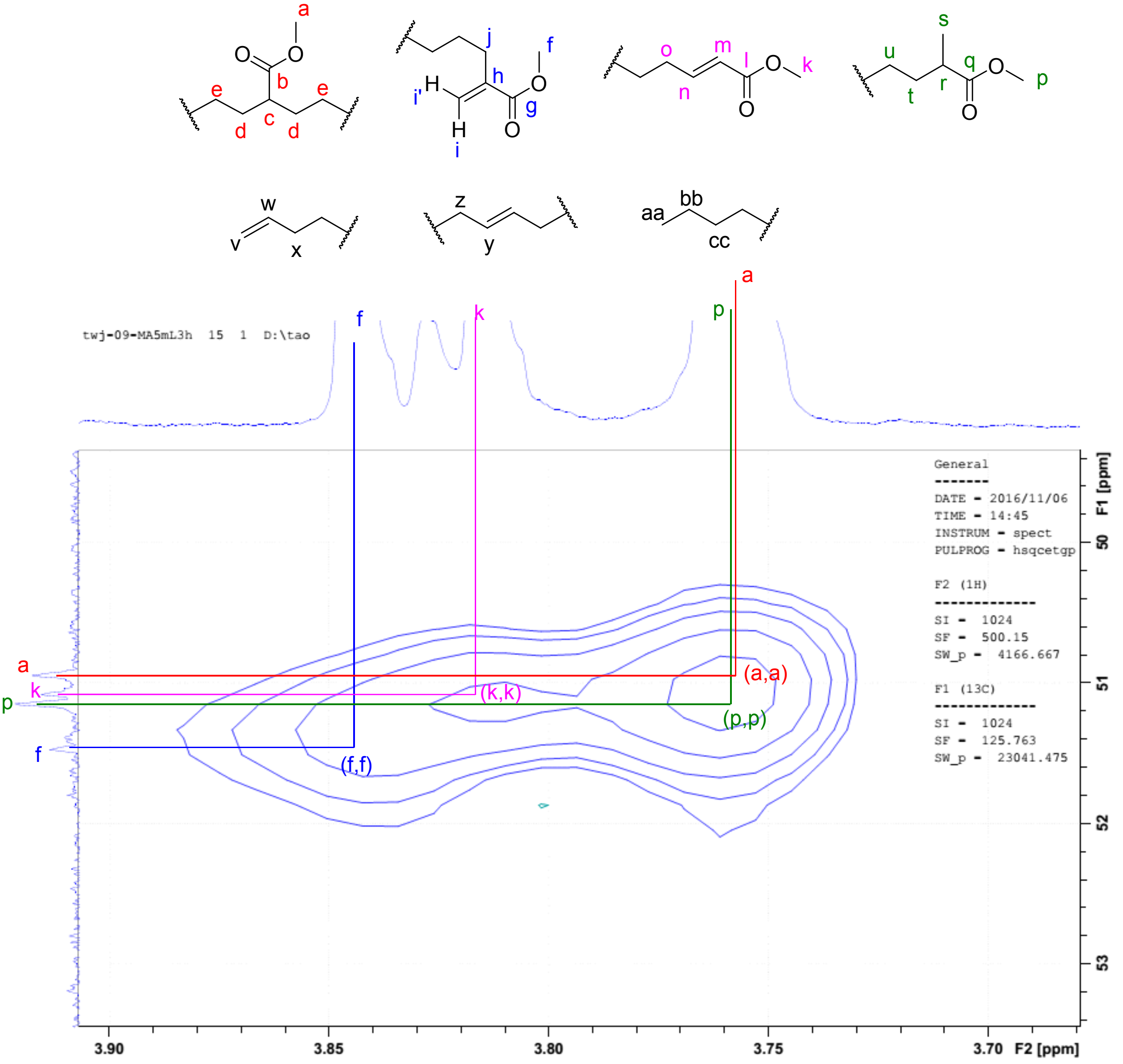


Figure S83. HSQC spectrum (1,1,2,2-tetrachloroethane-d_2, 120 °C, δ 3.70–3.90 ppm) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

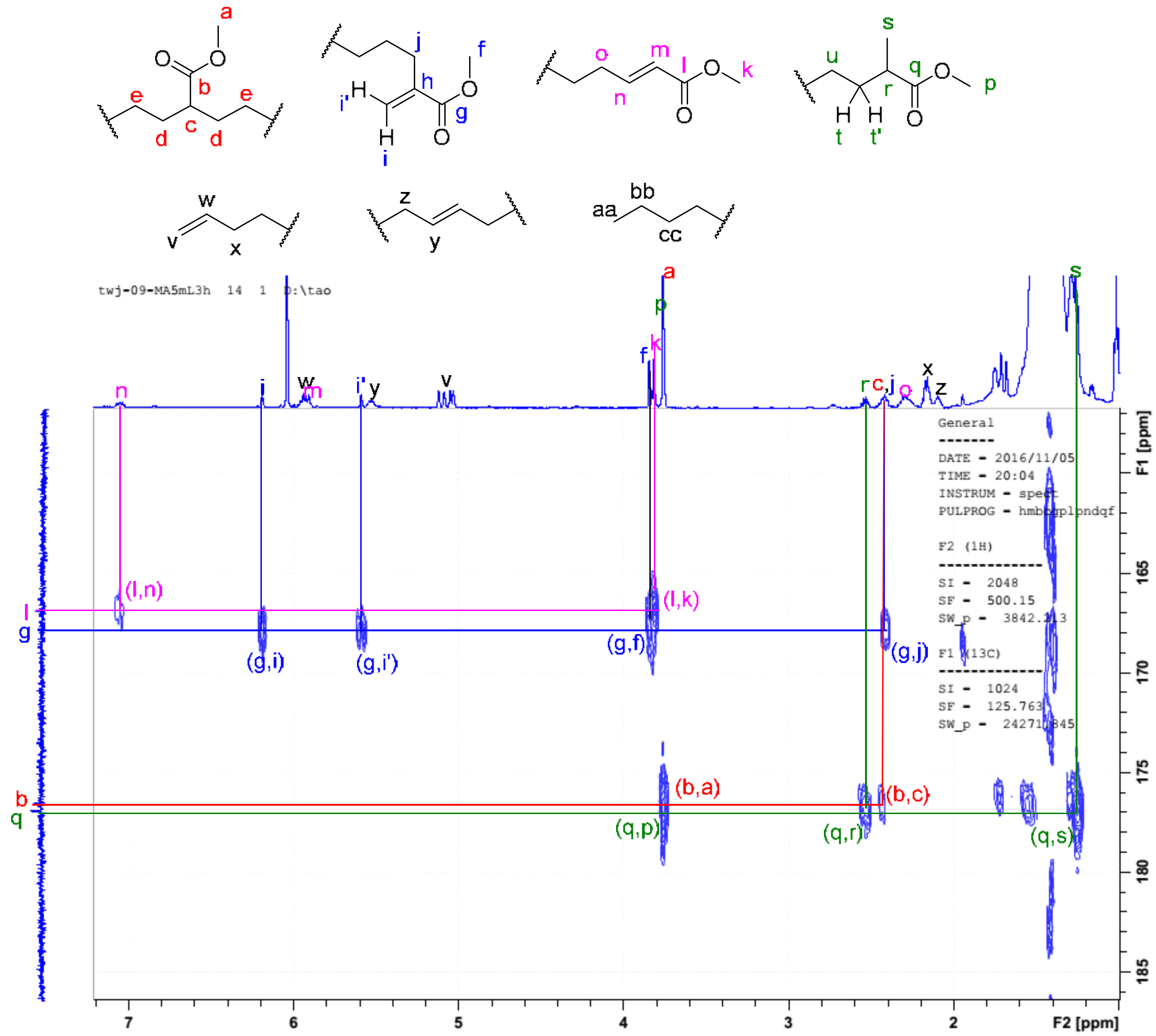


Figure S84. HMBC spectrum (1,1,2,2-tetrachloroethane-d_2, 120 °C, δ 160–185 ppm) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

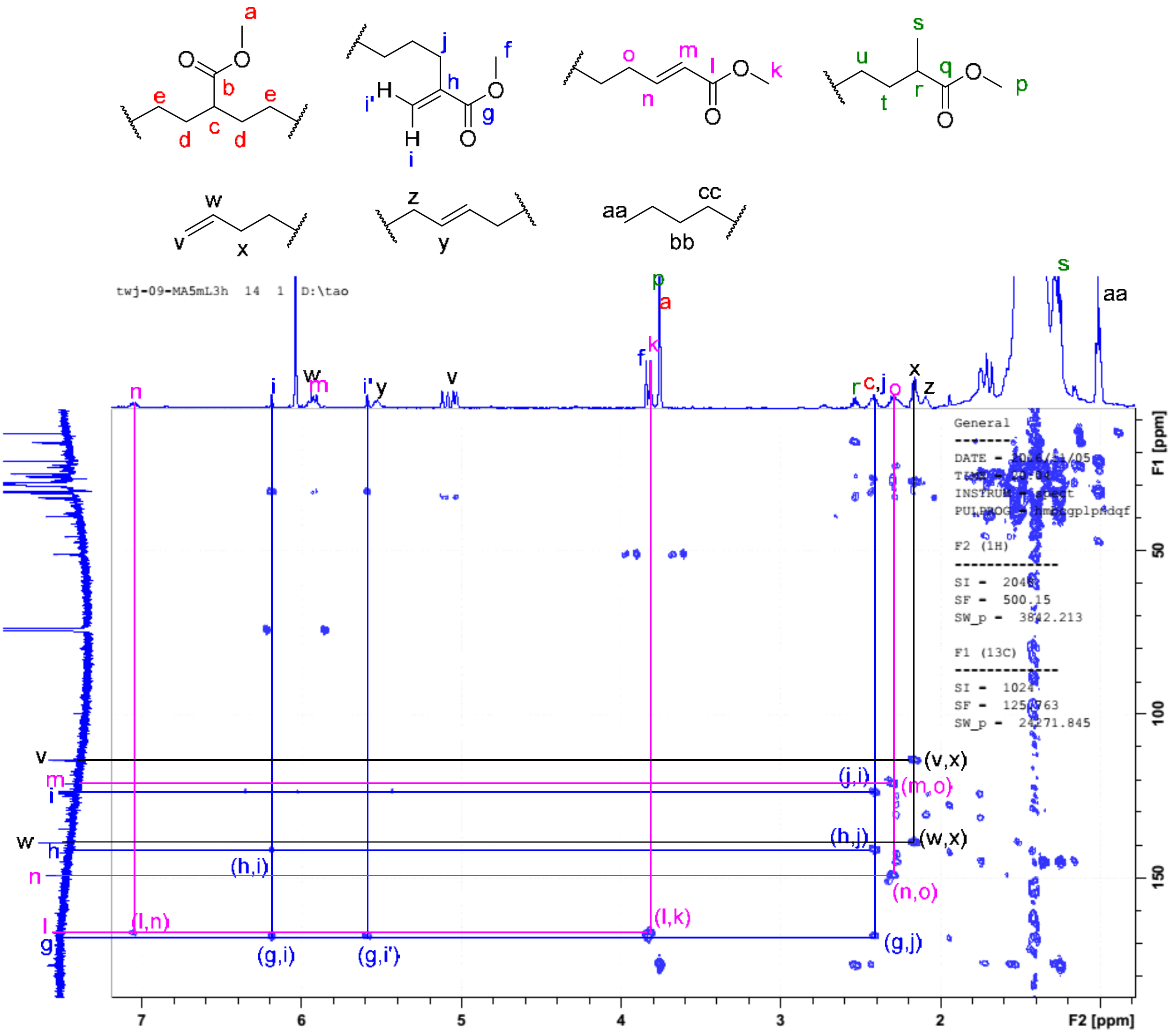
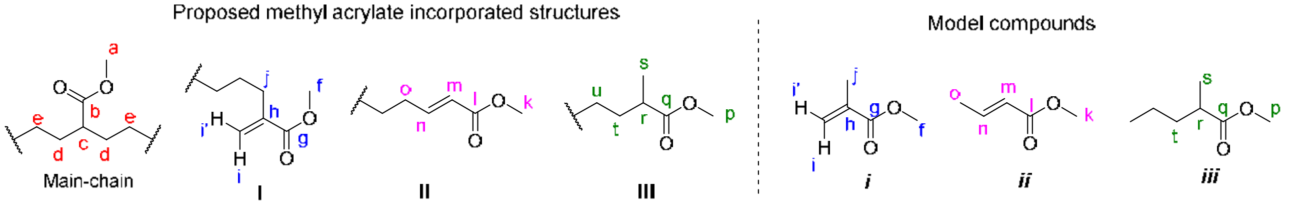


Figure S85. HMBC spectrum (1,1,2,2-tetrachloroethane-d_2, 120 °C, δ 100–180 ppm) of ethylene/methyl acrylate copolymer obtained by **4b** at 30 °C (Table S2, entry 5).

Table S4. ^{1}H and ^{13}C NMR chemical shifts of the proposed structures and related model compounds *i*, *ii*, and *iii*.



label	Reported structure[11]		Model compound *i*[15]		Model compound *ii*[16]		Model compound *iii*[17]		observed	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
a	---	50.6							3.72	50.7
b	---	176.0							---	176.3
c	---	45.3							2.38	45.5
d	---	32.0								32.1
e	---	27.1								27.2
f			3.75	51.8					3.81	51.2
g			---	167.9					---	167.9
h				136.5					---	140.7
i’			5.55	125.4					5.55	123.5
i			6.10						6.15	
k					3.67	51.3			3.78	50.8
l					---	167.0			---	166.9
m					5.76	122.6			5.87	121.0
n					6.90	144.7			7.02	149.0
p							3.67	51.3	3.72	50.9
q							---	177.2	---	176.6
r							2.46	39.4	2.69	39.3
s							1.14	17.1	1.13	16.6
t							1.39	36.2	1.53	33.6
t’							1.64		1.77	

Main-chain incorporation structure:

All the typical signals of methoxycarbonyl group in the main chain are consistent with those in literature.エラー! ブックマークが定義されていません。 The integral ratio of signal **c** at 2.38 ppm should be (1.34 – 0.36 × 2 = 0.62). The integral of corresponding signal **a** at 3.72 ppm should be ca. (0.62 × 3 = 1.86).

Structure I:

The existence of structure **I** with one remaining terminal 1,1-substituted double bond (signals **i**, **i'**, **f**, **g**, **h** and **j**, see Table S4 for the assignment) was confirmed by the correlations observed in ^{1}H–^{1}H COSY and HMBC spectra (Figures S76–78, 84–85) and their chemical shifts. The integral ratio (0.36) of signal **i** at 6.151 ppm matches with that of signal **f** at 3.807 ppm (integral ratio: 1.07) and that of signal **i'** at 5.552 ppm (integral ratio: 0.36) (Figure S75).

Structure II:

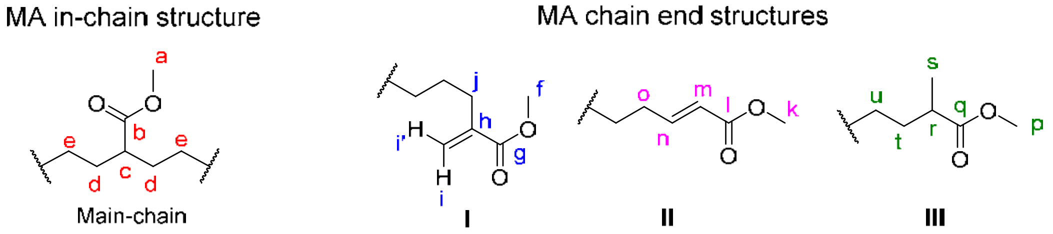
The existence of structure **II** with one remaining trans internal double bond (signals **m**, **n**, **k**, **l** and **o**, see Table S4 for the assignment) was confirmed by the correlations observed in ^{1}H–^{1}H COSY and HMBC spectra (Figures S76–78, 84–85) and their chemical shifts. The integral ratio of signal **m** at 5.89 ppm (0.51) matches with that of signal **n** at 7.015 ppm (integral ratio: 0.52) and that of the signal **k** at 3.78 ppm (integral ratio: 1.54) (Figure S75).

Structure III:

The existence of structure **III** (peaks **s**, **r**, **t**, **p** and **q**, see Table S4 for the assignment) was confirmed by the correlations observed in ^{1}H–^{1}H COSY and HMBC spectra (Figures S76–78, 84–85) and their chemical shifts. The integral ratio of signal **r** at 2.49 ppm (0.82) matches with that of signal **p** at 3.72 ppm (integral ratio: 4.56 – 1.86 = 2.70) (Figure S75).

The ratio of chain end/in-chain methyl acrylate

Table S5. Ratio of chain end methyl acrylate structures **I**, **II**, **III** and in-chain methyl acrylate structure in Table S2.



	MA chain end structure I	MA chain end structure II	MA chain end structure III	MA in-chain structure	MA chain ends / MA in-chain
Entry 3	0.21	0.43	0.49	0.38	(0.21+0.43+0.49)/0.38=3.0
Entry 4	0.47	0.53	0.49	0.60	(0.47+0.53+0.49)/0.60=2.5
Entry 5	0.36	0.51	0.82	0.62	(0.36+0.51+0.82)/0.62=2.7

5.2.3. Data of ethylene/allyl chloride copolymers

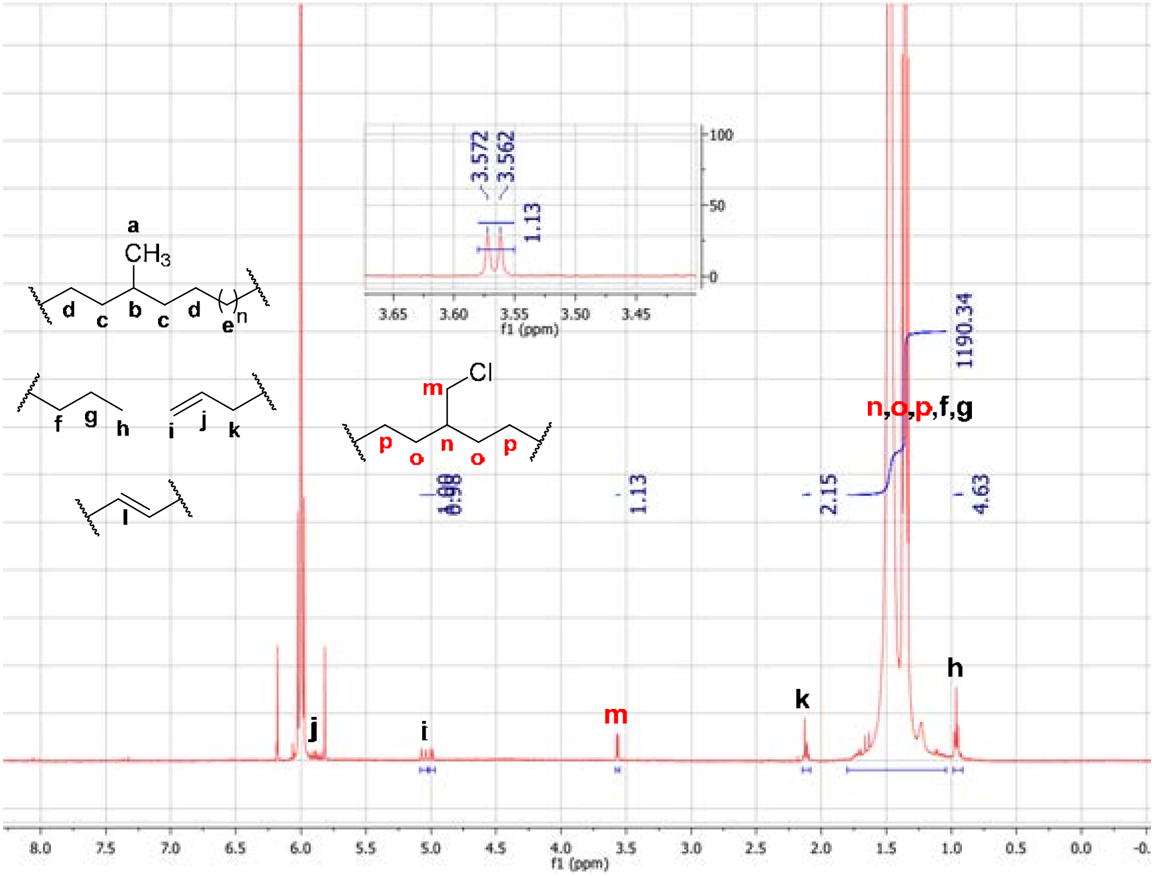


Figure S86. ^{1}H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, relaxation delay 10 s) of ethylene/allyl chloride copolymer obtained by **4b** at 30 °C (Table 2, entry 5).

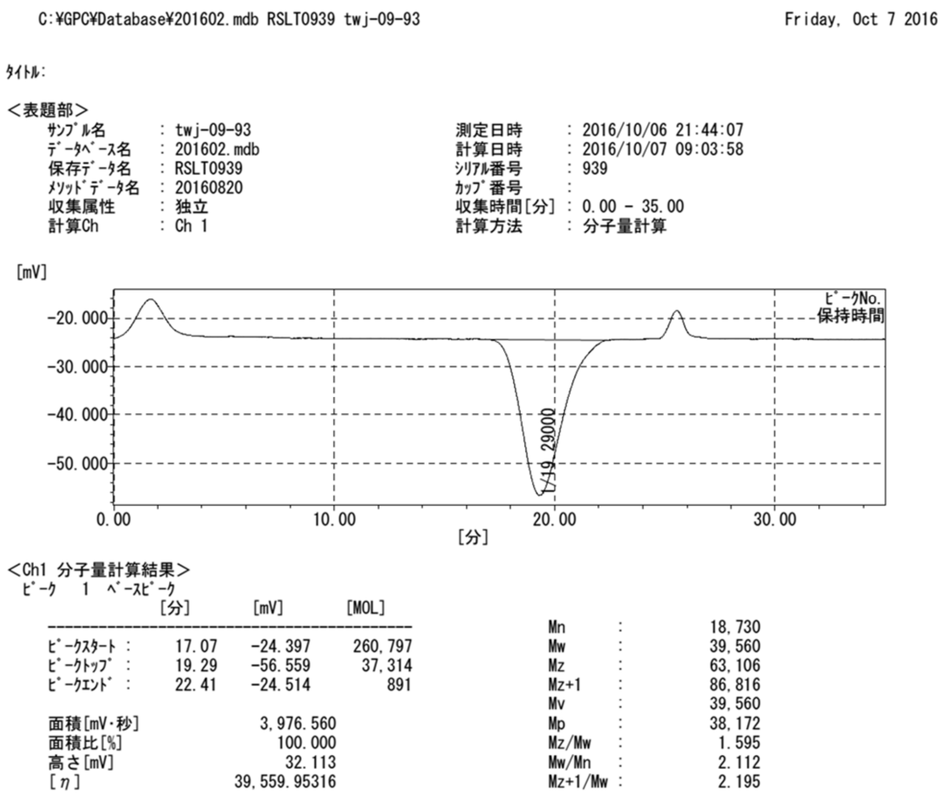
Note: Calculation of Incorporation ratio of allyl chloride:

Assume (1−x) mol% ethylene and x mol% allyl chloride in the copolymer,

$$\frac{2x}{3x + 4(1 - x)} = \frac{m}{\mathrm{e + f + g + h + i + j + k + n + o + p}}$$

$$\mathrm{x} = \frac{2\mathrm{m}}{e + f + g + h + j + k + n + o + p + 0.5m}$$

In entry 5 of Table 2, the incorporation ratio of allyl acetate is calculated as follows:
(2 x 1.13) / (1190.34 + 4.63 + 2.15 + 3.00 + 0.5 × 1.13) = 0.19 mol%



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                 [分]       [mV]        [MOL]
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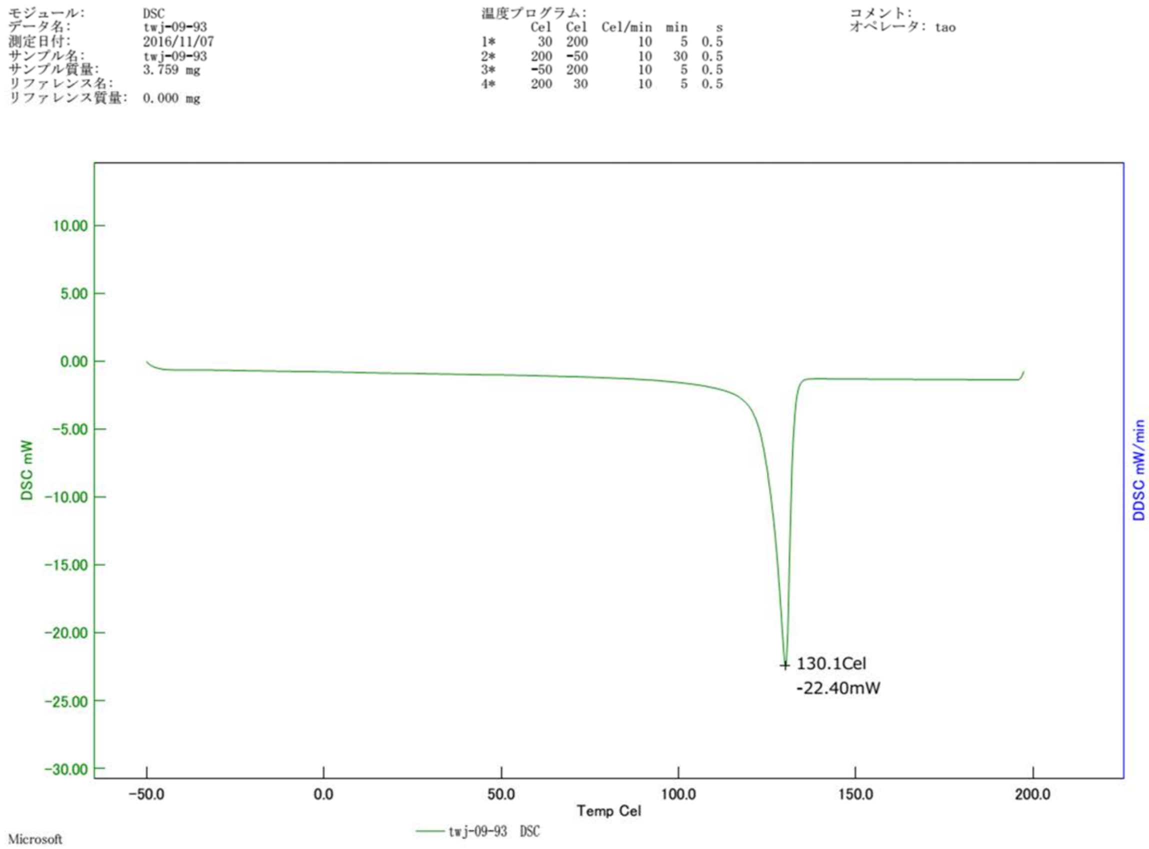
    ﾋﾟｰｸﾄｯﾌﾟ :    19.29     -56.559      37,314             Mz        :        63,106
    ﾋﾟｰｸｴﾝﾄﾞ :    22.41     -24.514         891             Mz+1      :        86,816
                                                            Mv        :        39,560
    面積[mV・秒]             3,976.560                      Mp        :        38,172
    面積比[%]                  100.000                      Mz/Mw     :         1.595
    高さ[mV]                    32.113                      Mw/Mn     :         2.112
    [η]                 39,559.95316                        Mz+1/Mw   :         2.195
```

Figure S87. SEC chart of ethylene/allyl chloride copolymer obtained by **4b** (Table 2, entry 5). M_n (PS) = 19 kg/mol was corrected to M_n (PE) = 8.1 kg/mol by universal calibration.



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リファレンス質量:    0.000 mg
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Figure S88: DSC traces of ethylene/allyl chloride copolymer obtained by **4b**. (Table 2, entry 5)

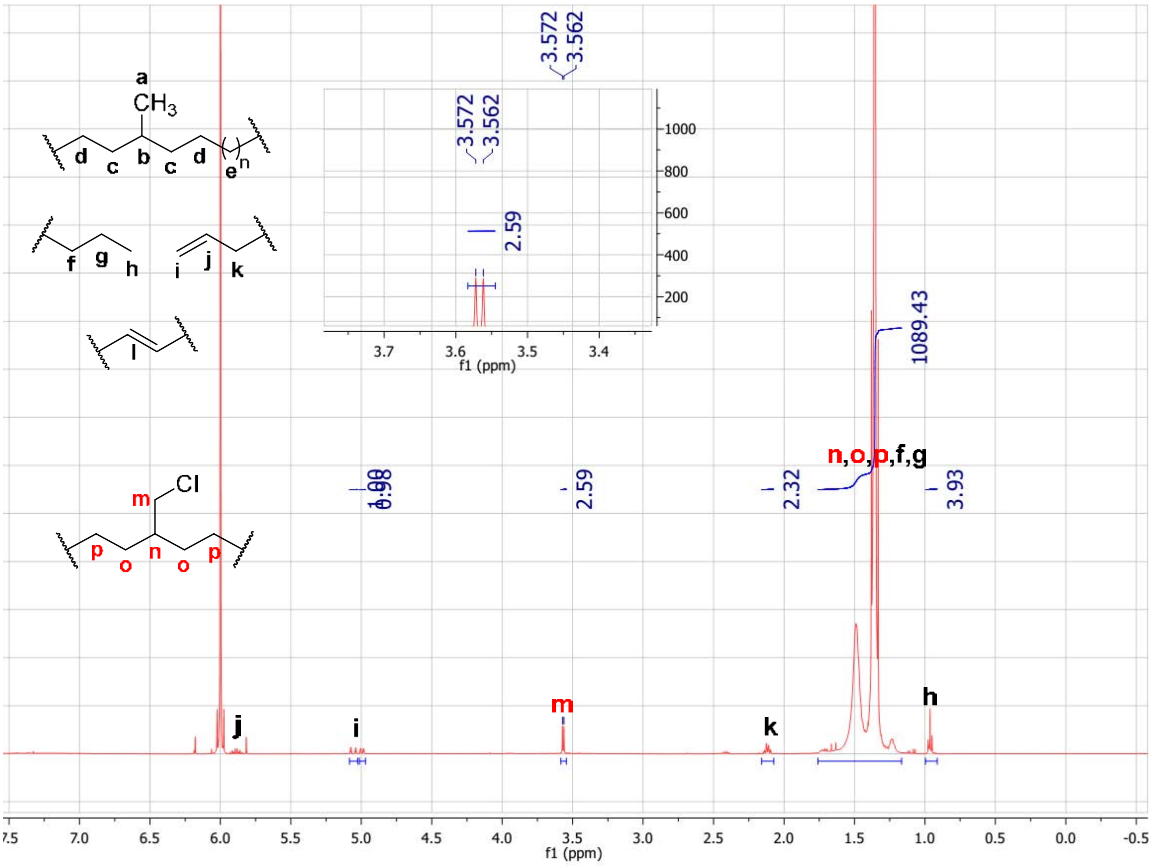
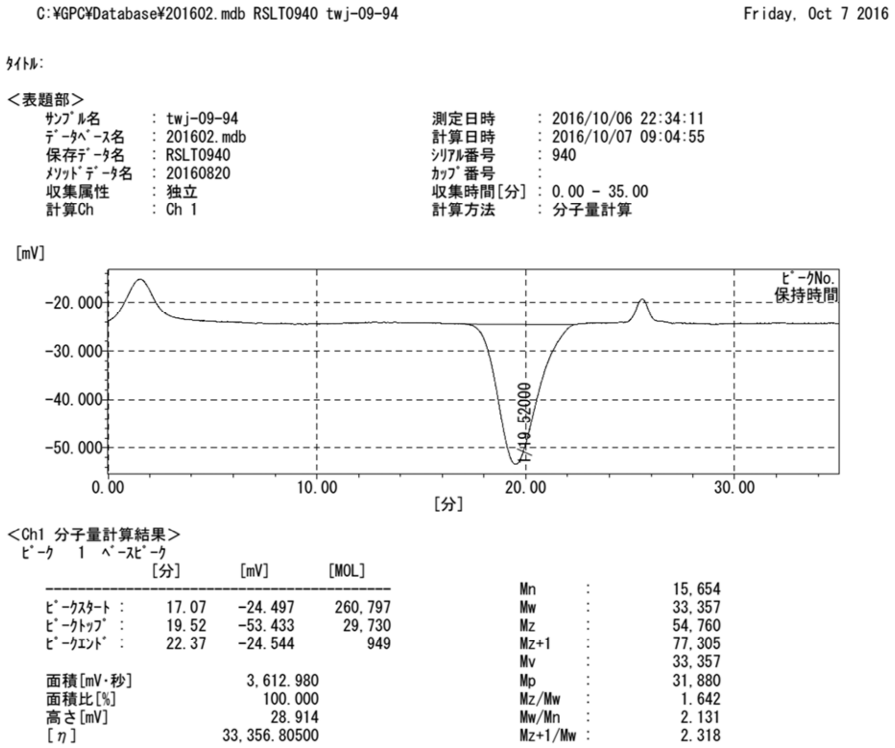


Figure S89. ^{1}H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, relaxation delay 10 s) of ethylene/allyl chloride copolymer obtained by **4b** at 30 °C (Table 2, entry 6).

Note: In entry 6, table 2, the incorporation ratio of allyl acetate is calculated as follows:
$(2 \times 2.59) / (1089.43+3.93+2.32+3.00+0.5\times2.59) = 0.47$ mol%



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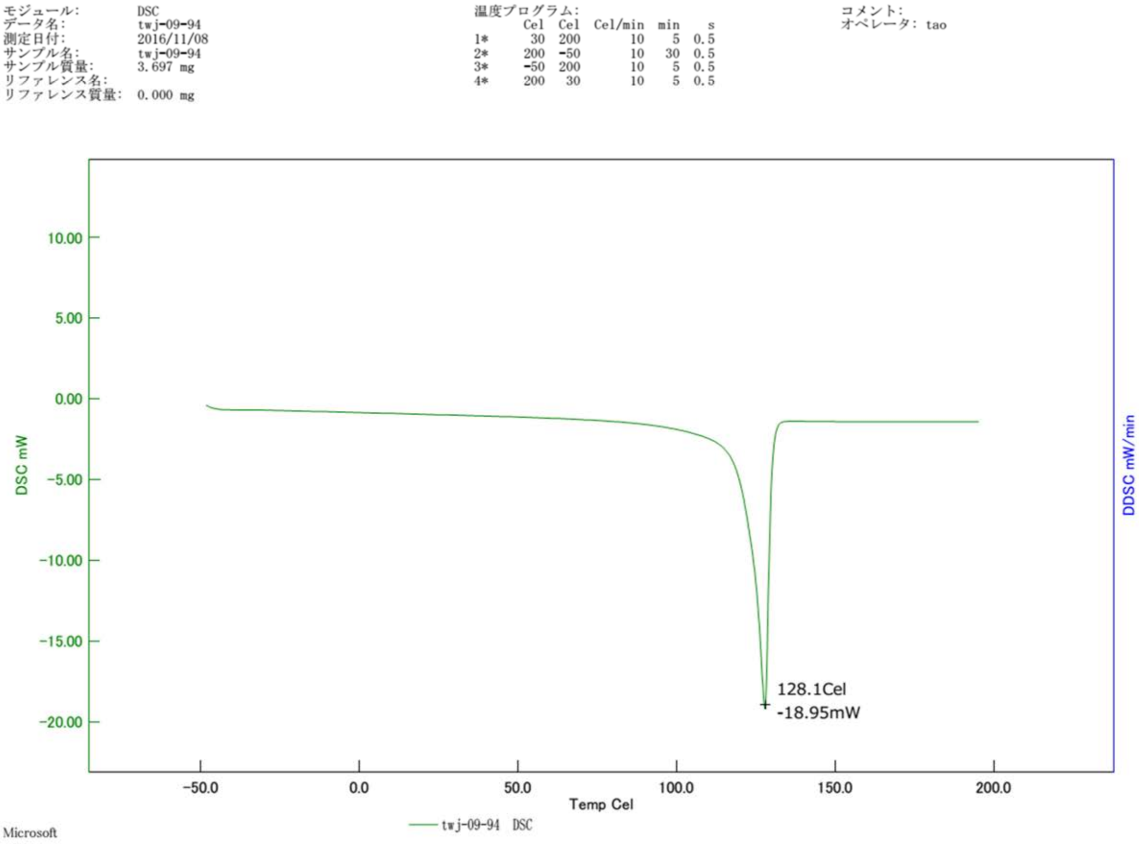
     ﾒｿｯﾄﾞﾃﾞｰﾀ名      : 20160820                      ｶｯﾌﾟ番号        :
     収集属性         : 独立                          収集時間[分]    : 0.00 - 35.00
     計算Ch           : Ch 1                          計算方法        : 分子量計算
```

```
<Ch1 分子量計算結果>
 ﾋﾟｰｸ   1  ﾍﾞｰｽﾋﾟｰｸ
                   [分]         [mV]         [MOL]
     ---------------------------------------------                    Mn         :          15,654
     ﾋﾟｰｸｽﾀｰﾄ :    17.07      -24.497      260,797                    Mw         :          33,357
     ﾋﾟｰｸﾄｯﾌﾟ :    19.52      -53.433       29,730                    Mz         :          54,760
     ﾋﾟｰｸｴﾝﾄﾞ :    22.37      -24.544          949                    Mz+1       :          77,305
                                                                      Mv         :          33,357
     面積[mV・秒]              3,612.980                              Mp         :          31,880
     面積比[%]                   100.000                              Mz/Mw      :           1.642
     高さ[mV]                     28.914                              Mw/Mn      :           2.131
     [η]                  33,356.80500                              Mz+1/Mw    :           2.318
```

Figure S90. SEC chart of ethylene/allyl chloride copolymer obtained by **4b** (Table 2, entry 6). M_n (PS) = 16 kg/mol was corrected to M_n (PE) = 6.8 kg/mol by universal calibration.



```
モジュール:       DSC                      温度プログラム:                              コメント:
データ名:         twj-09-94                      Cel  Cel  Cel/min  min    s           オペレータ: tao
測定日付:         2016/11/08               1*     30  200       10    5  0.5
サンプル名:       twj-09-94                2*    200  -50       10   30  0.5
サンプル質量:     3.697 mg                 3*    -50  200       10    5  0.5
リファレンス名:                            4*    200   30       10    5  0.5
リファレンス質量: 0.000 mg
```

Figure S91: DSC traces of ethylene/allyl chloride copolymer obtained by **4b** (Table 2, entry 6).

5.2.4. Data of polyethylene obtained in attempted ethylene/vinyl acetate copolymerization

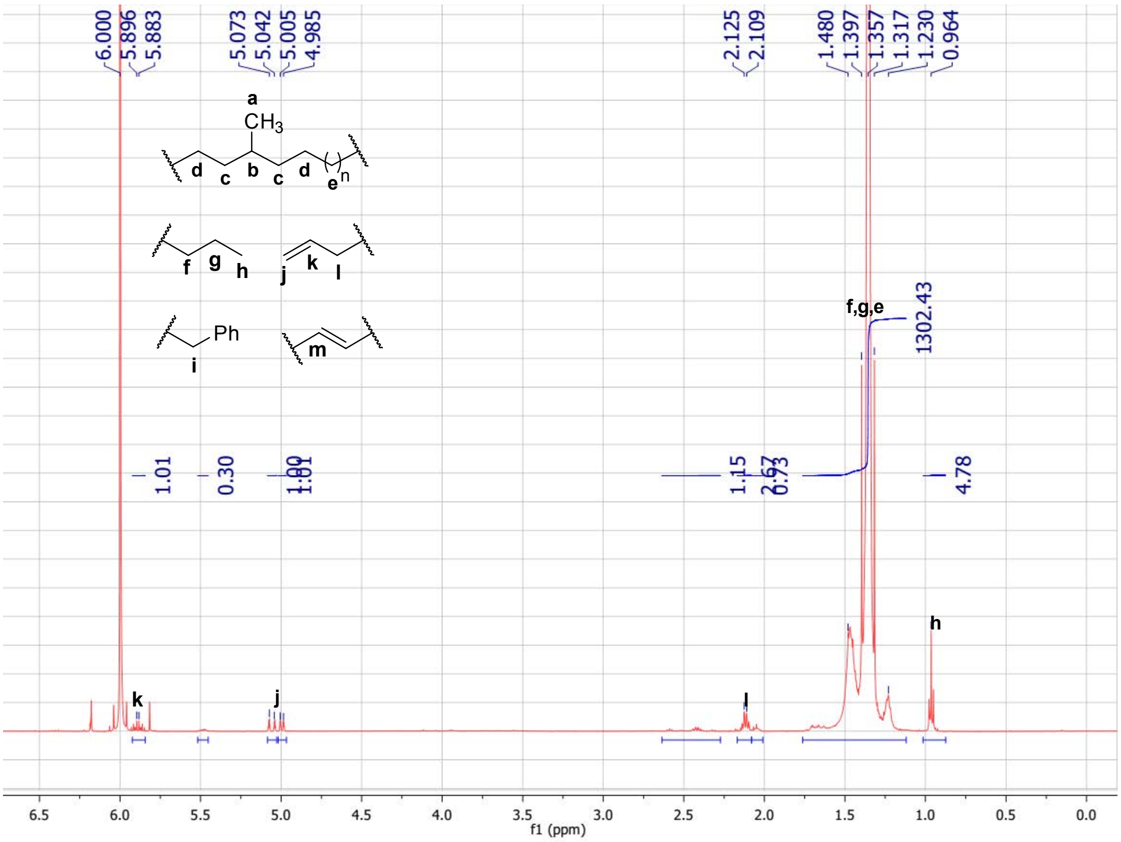
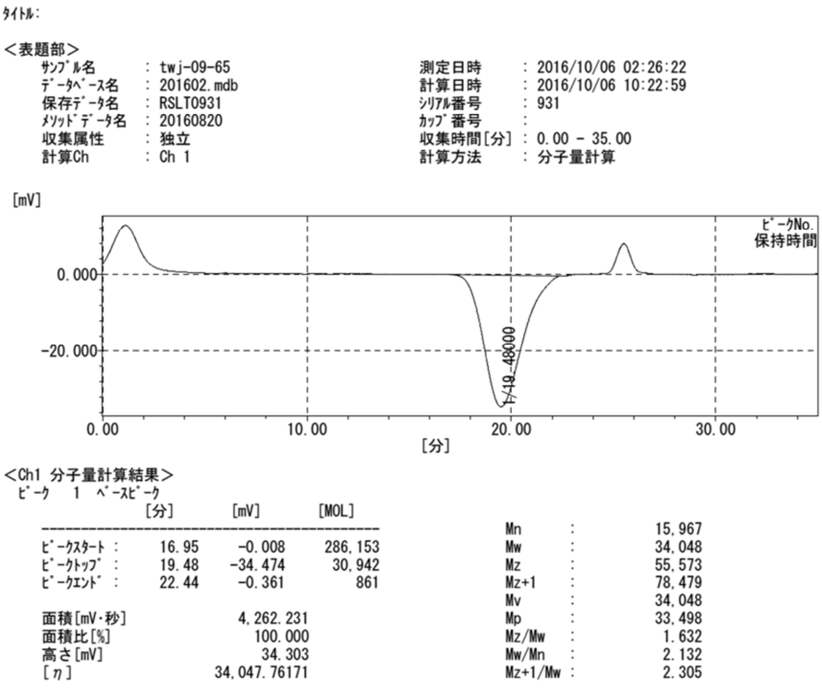


Figure S92. ^{1}H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C, relaxation delay 10 s) of polyethylene obtained by **4b** in the presence of vinyl acetate at 30 °C (Table 2, entry 7).



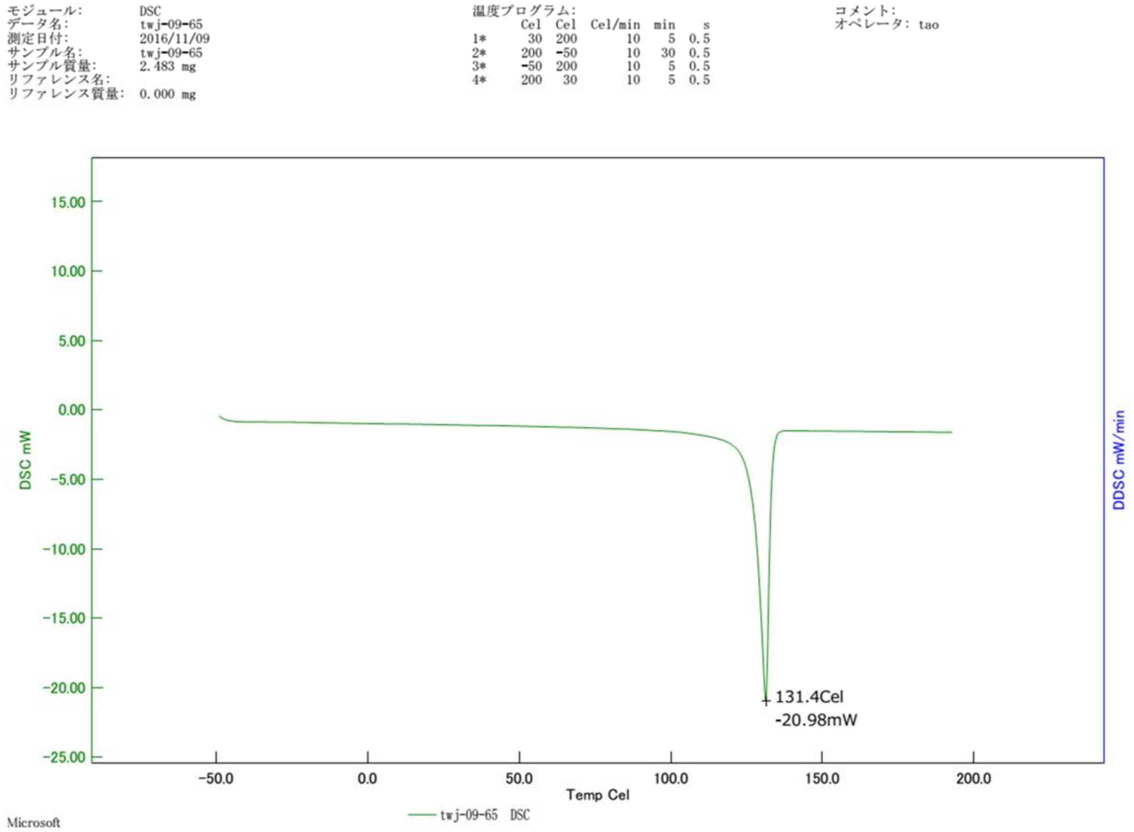
```
ﾀｲﾄﾙ:

<表題部>
    ｻﾝﾌﾟﾙ名          : twj-09-65                 測定日時        : 2016/10/06 02:26:22
    ﾃﾞｰﾀﾍﾞｰｽ名       : 201602.mdb                計算日時        : 2016/10/06 10:22:59
    保存ﾃﾞｰﾀ名       : RSLT0931                  ｼﾘｱﾙ番号        : 931
    ﾒｿｯﾄﾞﾃﾞｰﾀ名      : 20160820                  ｶｯﾌﾟ番号        :
    収集属性         : 独立                      収集時間[分]    : 0.00 - 35.00
    計算Ch           : Ch 1                      計算方法        : 分子量計算

<Ch1 分子量計算結果>
 ﾋﾟｰｸ   1  ﾍﾞｰｽﾋﾟｰｸ
                  [分]        [mV]        [MOL]
    ----------------------------------------------             Mn        :     15,967
    ﾋﾟｰｸｽﾀｰﾄ  :   16.95      -0.008     286,153             Mw        :     34,048
    ﾋﾟｰｸﾄｯﾌﾟ  :   19.48     -34.474      30,942             Mz        :     55,573
    ﾋﾟｰｸｴﾝﾄﾞ  :   22.44      -0.361         861             Mz+1      :     78,479
                                                            Mv        :     34,048
    面積[mV･秒]             4,262.231                       Mp        :     33,498
    面積比[%]                 100.000                       Mz/Mw     :      1.632
    高さ[mV]                   34.303                       Mw/Mn     :      2.132
    [η]                34,047.76171                       Mz+1/Mw   :      2.305
```

Figure S93. SEC chart of polyethylene obtained by **4b** (Table 2, entry 7).

M_n (PS) = 16 kg/mol was corrected to M_n (PE) = 6.9 kg/mol by universal calibration.



モジュール: DSC
データ名: twj-09-65
測定日付: 2016/11/09
サンプル名: twj-09-65
サンプル質量: 2.483 mg
リファレンス名:
リファレンス質量: 0.000 mg

温度プログラム:

	Cel	Cel	Cel/min	min	s
1*	30	200	10	5	0.5
2*	200	-50	10	30	0.5
3*	-50	200	10	5	0.5
4*	200	30	10	5	0.5

コメント:
オペレータ: tao

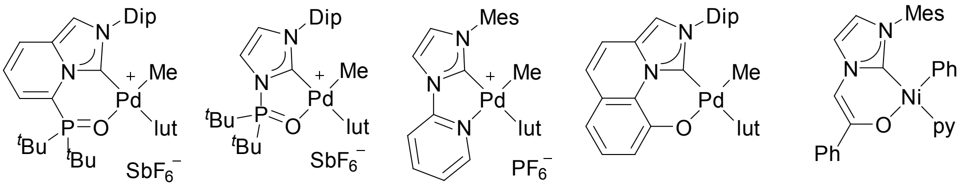
Figure S94. DSC traces of polyethylene obtained by **4b** (Table 2, entry 7).

6. Determination of The Mean Dihedral Angles

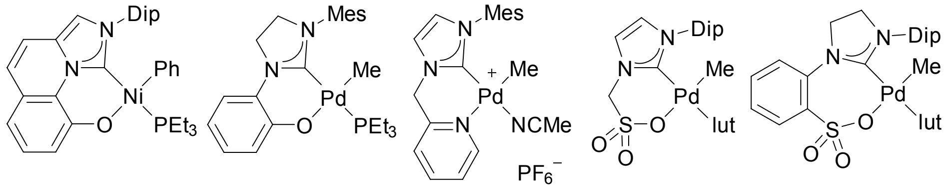
The mean dihedral angle was defined by the dihedral angle between the plane of NHC and the plane of metal's coordination square.[11] The plane of NHC was determined by principal component analysis (PCA) of the four atoms of the carbene atom, the two conjugating nitrogen atoms, and the metal center. The plane of metal's coordination square was determined by PCA of the five atoms of the metal center and the coordinating four atoms. The obtained 3rd eigenvectors were used as the normal vector of each plane. R (version 3.2.3) was used for the calculation.[18]

Plane of NHC　　Plane of metal's coordination square

Figure S95. Selected atoms for the definition of *plane of NHC* and *plane of metal's coordination square*.



	This work		Albrecht[19]	Nozaki[11]	Waymouth[20]
			2012	2015	2005
mean dihedral angle	32.5°	1.50°	5.24°	26.1°	22.3°
activity of ethylene polymerization	**linear PE** **(TON >10000)**	oligomer	oligomers (TON ~10)	**linear PE** **(TON >24600)**	**linear PE** **(TON ~1000)**



	Nozaki[21]	Grubbs[22]	Albrech[19]	Nozaki[23]	Jordan[24]
	2016	2004	2012	2009	2011
mean dihedral angle	33.1°	39.0°	44.2°	48.3°*	65.5°*
activity of ethylene polymerization	**linear PE** **(TON >4300)**	no activity	no activity	trace oligomer	no activity

*average of the two molecules

Figure S96. Calculated mean dihedral angles between the NHC plane and the plane of metal's coordination square of various NHC-ligated metal complexes.

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