Supporting Information

Synthesis, Structure, and 1-Hexene Polymerization Catalytic Ability of Group 5 Metal Complexes Incorporating an [OSSO]-Type Ligand

Tomoyuki Toda[†], Norio Nakata[†], Tsukasa Matsuo[‡§], and Akihiko Ishii*[†]

*E-mail: ishiiaki@chem.saitama-u.ac.jp

[†]Department of Chemistry, Graduate School of Science and Engineering,
Saitama University, 255 Shimo-okubo, Sakura-ku, Saitama 338-8570, Japan
[‡]Functional Elemento-Organic Chemistry Unit, RIKEN Advanced Science Institute,
2-1 Hirosawa, Wako, Saitama 351-0198, Japan
[§]Department of Chemistry, Faculty of Science and Engineering,
Kinki University, Higashi-osaka, Osaka 577-8502, Japan

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1. General Procedures. All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line-techniques or in an MBRAUM LABmaster Glovebox under an inert atmosphere of argon. Anhydrous hexane, toluene, dichloromethane, and diethyl ether were further dried by passage through columns of activated alumina and supported copper catalyst supplied by Hansen & Co., Ltd. Deuterated benzene (benzene-d_6) and 1-hexene were dried and degassed over a potassium mirror by the freeze-thaw cycle prior to use. Deuterated dichloromethane (CD_2Cl_2) and ethyl trichloroacetate (ETA) was dried and degassed over a calcium hydride by the freeze-thaw cycle prior to use. Other chemicals and gases were used as received. Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H (400 MHz) and $^{13}C\{^1H\}$ (100.5 or 125.8 MHz) spectra were obtained with Bruker DRX400, AVANCE500-T or JEOL JNM-ECS400 spectrometers. X-Ray crystallography was performed with a Rigaku Saturn724 diffractometer. Elemental analyses were performed by the Chemical Analysis Team of RIKEN Advanced Science Institute or Comprehensive Analysis Center for Science, Saitama University. The $^{13}C\{^1H\}$ NMR data of poly(1-hexene) were obtained in $CDCl_3$ at room temperature. The molecular weights and molecular weight distributions of poly(1-hexene) were determined against polystyrene standard by gel permeation chromatography measured by a GPC KF-804L (Shodex Corporation) using THF as an eluent (rate 1.0 mL/min). *trans*-Cyclooctane-1,2-dithiol,[1] [OSSO]H_2 ligand **3**[2] and dMAO[3] were prepared by the literature procedures.

2. Synthesis of Vanadium Oxo-Propoxy Complex 5. To a solution of **3** (675 mg, 1.10 mmol) in hexane (20 mL) was added VO(OPr)$_3$ (270 mg, 0.25 mL, 1.10 mmol) at −78 °C. The mixture was stirred for 18 h at room temperature, and the solvent was removed under reduced pressure. The residue was added hexane (2 mL) and recrystallized −30 °C to give **5** (616.3 mg, 76%) as dark purple crystals. **5**: Mp 145−147 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 0.77−1.98 (m, 48 H), 2.43 (br s, 1 H), 2.52 (br s, 1 H), 3.27 (d, ^2J = 13 Hz, 1 H), 3.45 (d, ^2J = 15 Hz, 1 H), 4.09 (d, ^2J = 13 Hz, 1 H), 4.50 (d, ^2J = 15 Hz, 1 H), 5.58−5.62 (m, 2 H), 6.70 (s, 1 H), 6.73 (s, 1 H), 7.54 (s, 2 H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6) δ 11.1, 25.3, 25.4, 26.3, 26.7, 26.8, 28.1, 29.9, 30.6, 30.7, 31.8, 31.9, 34.4, 34.5 (2C), 35.7, 35.9, 36.1, 45.7, 49.7, 87.6, 117.4, 123.4, 123.6, 125.6, 126.1, 129.3, 137.3, 139.3, 141.2, 142.3, 162.2, 164.5. Anal. Calcd. for $C_{41}H_{65}O_4S_2V$: C, 66.81; H, 8.89. Found: C, 66.57; H, 8.82.

3. Synthesis of Niobium Trichloro Complex 7. A solution of **1** (150 mg, 0.245 mmol) in toluene (5 mL) was added to a solution of $NbCl_5$ (66.4 mg, 0.245 mmol) in toluene (5 mL) at −40 °C. The mixture was stirred for 19 h at room temperature, and the solvent was removed under reduced pressure. The residue was washed with toluene (2 mL) and dried in vacuo to give **7** (176.5 mg, 89%) as orange crystals. **7**: Mp 158−160 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6, 79 °C) δ 1.04−1.84 (m, 48 H), 2.76 (br s, 2 H), 3.43 (d, ^2J = 16 Hz, 2 H), 5.59 (d, ^2J = 16 Hz, 2 H), 6.56 (s, 2 H), 7.47 (s, 2 H). (400 MHz, CD_2Cl_2, 27 °C) δ 1.12−2.13 (m, 48 H), 2.99 (br s, 2 H), 4.12 (d, ^2J = 15 Hz, 2 H), 5.59 (d, ^2J = 15 Hz, 2 H), 6.93 (d, ^2J = 2 Hz, 2 H), 7.40 (d, ^2J = 2 Hz, 2 H). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2) δ 25.7, 25.8, 29.3, 31.1, 31.4, 34.9, 35.9, 41.0, 51.5, 124.7, 125.7, 126.3, 141.2, 147.5, 156.6. Since **7** is extremely sensitive to air and moisture, satisfactory elemental analysis data for **7** were not obtained.

4. Synthesis of Tantalum Trichloro Complex 8. To a solution of **3** (1.01 g, 1.65 mmol) in hexane (40 mL) was added BuLi (1.57 M in hexane, 2.1 mL, 3.56 mmol) at 0 °C. The mixture was warmed to room temperature and then stirred for 1 h. The solvent was evaporated to dryness, and the resulting solids were collected by filtration and washed with hexane (2 mL) and dried in vacuo to give the dilithium salt as a colorless powder (692 mg). To a toluene (10 mL) slurry of $TaCl_5$ (220.0 mg, 0.614 mmol) at −78 °C was added a toluene solution of the dilithium salts **6** (383.0 mg, 0.614 mmol). The mixture was warmed to room temperature and then stirred for 17 h. Dichloromethane (10 mL) was added to the residue, and the insoluble inorganic materials were removed by decantation. The solvent of the filtration was removed in vacuo, and the residual solid was washed with toluene (2 mL) and dried in vacuo to give **8** (284 mg, 51%) as pale yellow crystals. **8**: Mp 171−172 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6, 79 °C) δ 1.05−1.75 (m, 48 H), 2.74 (br s, 2 H), 3.55 (d, ^2J = 16 Hz, 2 H), 5.53 (d, ^2J = 16 Hz, 2 H), 6.58 (s, 2 H), 7.54 (s, 2 H). (400 MHz, CD_2Cl_2, 27 °C) δ 1.10−2.12 (m, 48 H), 2.95 (br s, 2 H), 4.23 (d, ^2J = 16 Hz, 2 H), 5.55 (d, ^2J = 16 Hz, 2 H), 6.94 (d, ^2J = 2 Hz, 2 H), 7.47 (d, ^2J = 2 Hz, 2 H). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2) δ 25.7 (2C), 29.2, 31.1, 31.5, 34.8, 35.7, 40.3, 50.5, 123.7, 125.7, 126.1, 141.4, 146.8, 155.2. Since **8** is extremely sensitive to air and moisture, satisfactory elemental analysis data for **8** were not obtained.

5. General Procedure for 1-Hexene Polymerization. A 50 mL Schlenk flask was loaded sequentially with catalyst precursor **8** (0.020 mmol), cocatalyst (dried MAO

(DMAO) or ${}^{i}Bu_3Al/(Ph_3C)[B(C_6F_5)_4]$), and toluene at room temperature. After stirring for 1 min at room temperature, 1-hexene (3.0 g, 35.6 mmol) was added to the reaction mixture. The mixture was stirred at the desired temperature. After polymerization, the reaction was quenched by addition of methanol and concentrated hydrochloric acid. The mixture was extracted with toluene, and the organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated, and the residue was washed with acetone (2 mL). The solvent was removed in vacuo and at 70 °C overnight to leave poly(1-hexene).

A 50 mL Schlenk flask was charged sequentially with catalyst precursor **5** (0.020 mmol), toluene, 1-hexene, ETA, and DEAC. After polymerization, the reaction mixture was quenched by addition of methanol and concentrated hydrochloric acid. The mixture was extracted with toluene and the organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo at 70 °C overnight to leave polymer.

6. X-Ray Crystallographic Analyses. Dark purple single crystals of **5** were obtained from its saturated hexane solution at −30 °C, orange single crystals of **7** were obtained from its saturated benzene solution at room temperature, and pale yellow single crystals of **8** were grown by a mixture of hexane and CH_2Cl_2 solution at room temperature. The intensity data were collected at 100 K on a Rigaku AFC10 diffractometer equipped with a Saturn724 + CCD detector using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[4] Hydrogen atoms of **5**, **7**, and **8** were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. Crystallographic data and details of refinement for **5**: $C_{41}H_{65}O_4S_2V_1$•0.5(C_6H_{14}), MW = 780.08, monoclinic, space group $P2_1/c$, a = 14.843(3) Å, b = 16.907(4) Å, c = 17.478(4) Å, β = 93.767(4)°, V = 4376.6(17) Å^3, Z = 4, D_{calc} = 1.184 g cm^{-3}, R_1 ($I > 2\sigma I$) = 0.0627, wR_2 (all data) = 0.1604 for 8135 reflections, 492 parameters, and 64 restraints, GOF = 1.055. Crystallographic data and details of refinement for **7**: $C_{38}H_{58}Cl_3Nb_1O_2S_2$•0.5(C12)•2($C_6H_6$), MW = 1038.50, monoclinic, space group $P2_1/c$, a = 17.747(5) Å, b = 15.722(4) Å, c = 19.957(6) Å, β = 103.391(4)°, V = 5417(3) Å^3, Z = 4, D_{calc} = 1.273 g cm^{-3}, R_1 ($I > 2\sigma I$) = 0.0634, wR_2 (all data) = 0.1659 for 10048 reflections, 660 parameters, and 217 restraints, GOF = 1.077. Crystallographic data and details of refinement for **8**: $C_{38}H_{58}Cl_3Ta_1O_2S_2$•$C_6H_6$, MW = 976.37, monoclinic, space group $P2_1$, a = 14.0634(12) Å, b = 11.4960(10) Å, c = 14.0371(12) Å, β = 101.6606(14)°, V = 2222.6(3) Å^3, Z = 2, D_{calc} = 1.459 g cm^{-3}, R_1 ($I > 2\sigma I$) = 0.0232, wR_2 (all data) = 0.0587 for 6613 reflections, 481 parameters, and 1 restraints, GOF = 1.059.

7. References

(1) Ishii, A.; Ono, A.; Nakata, N. *J. Sulf. Chem.* **2009**, *30*, 236–244.

(2) Ishii, A.; Toda, T.; Nakata, N.; Matsuo, T. *J. Am. Chem. Soc.* **2009**, *131*, 13566–13567.

(3) Hasan, T.; Ioku, A.; Nishii, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2001**, *34*, 3142–3145.

(4) Sheldrick, G. M. SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

Figure S1. ^{1}H NMR spectrum of complex **5**.

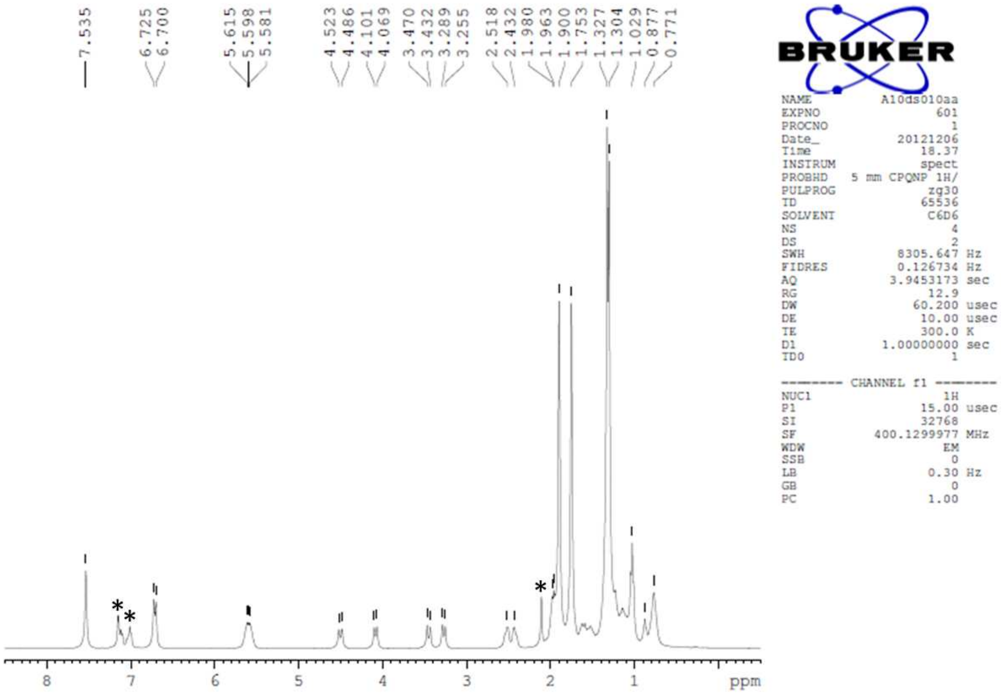

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Figure S2. ^{13}C{^{1}H} NMR spectrum of complex **5**.

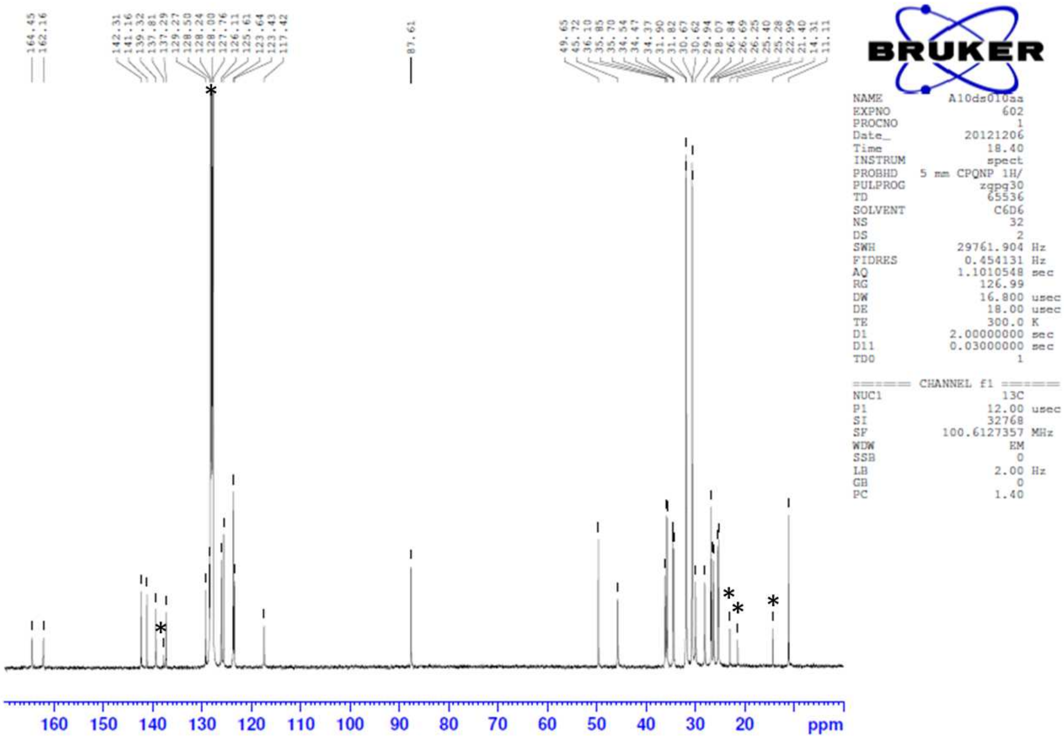

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Figure S3. ^{1}H NMR spectrum of complex **7**.

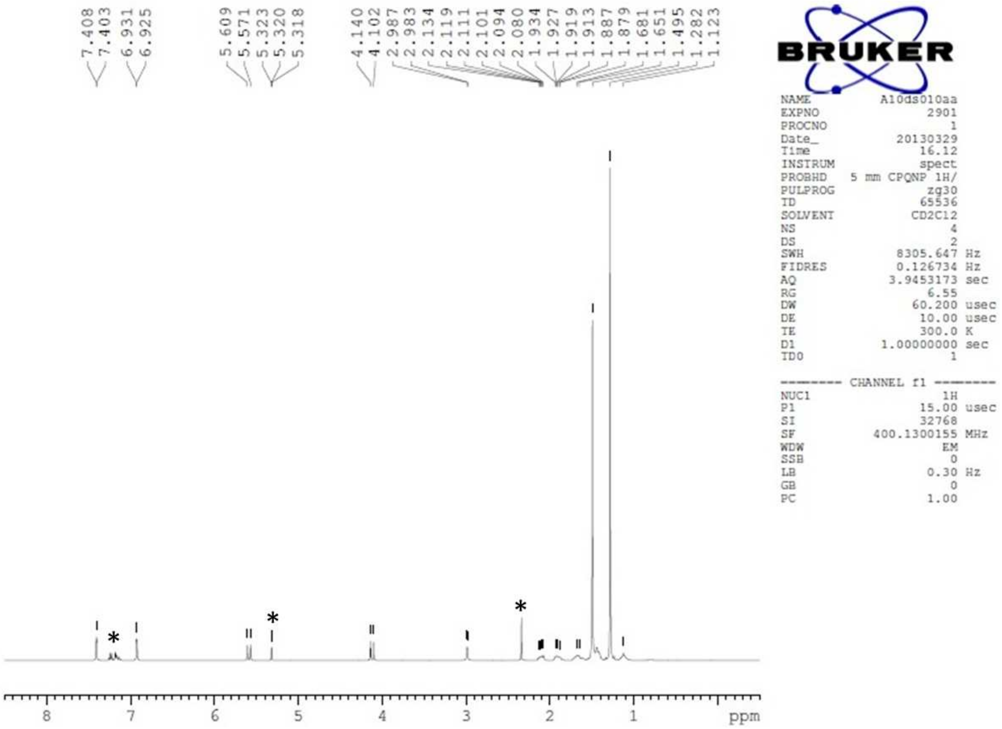

Figure S4. ^{13}C{^{1}H} NMR spectrum of complex **7**.

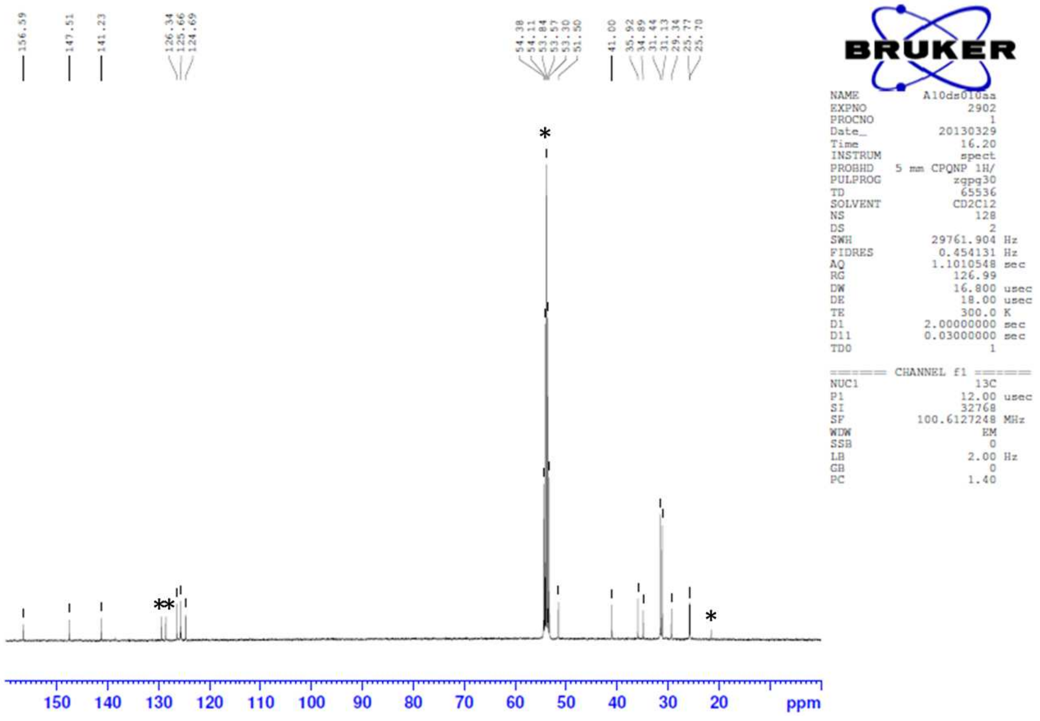

Figure S5. ^{1}H NMR spectrum of complex **8**.

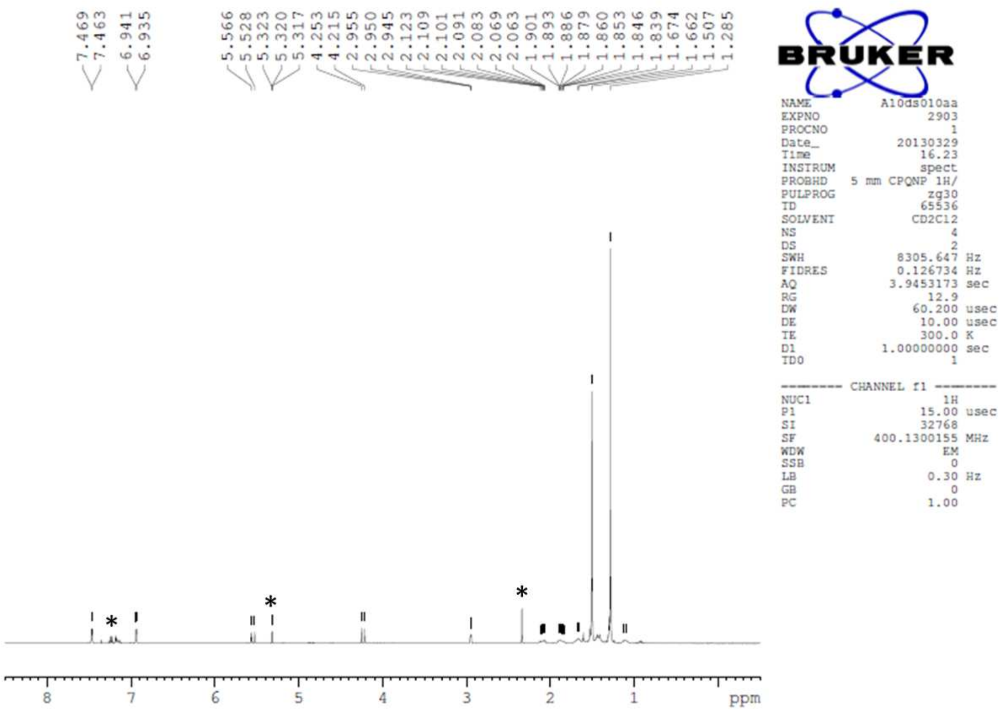

Figure S6. ^{13}C{^{1}H} NMR spectrum of complex **8**.

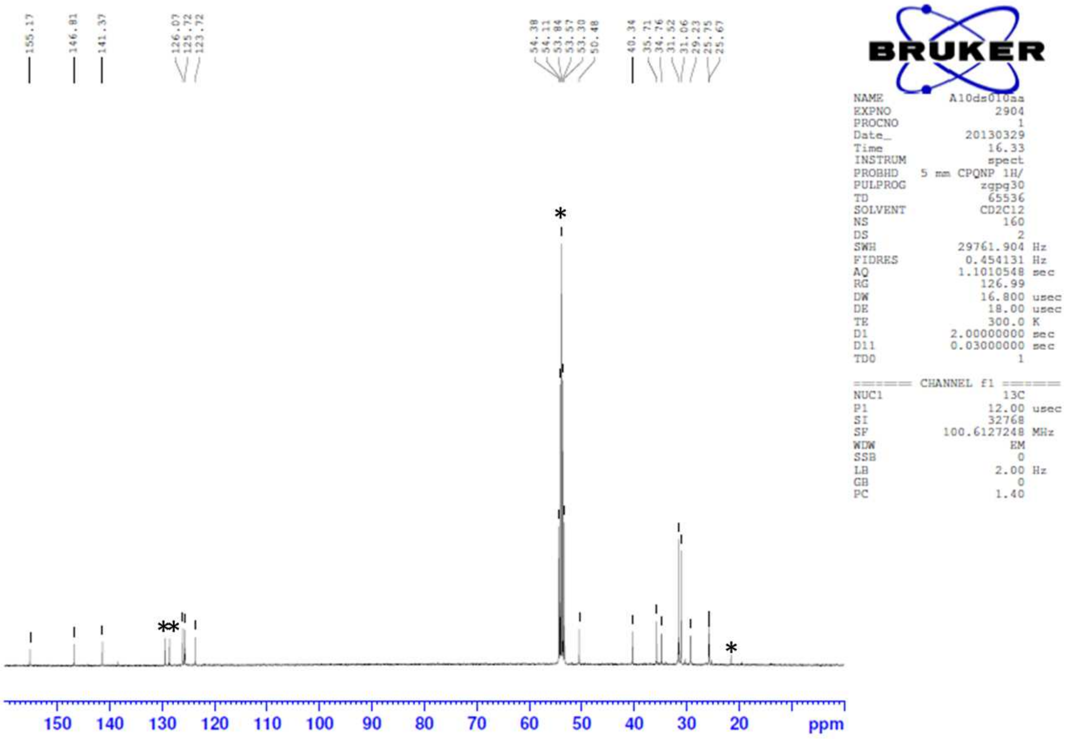

Figure S7. $^{13}C\{^1H\}$ NMR spectrum of poly(1-hexene) obtained by the **8** and $^iBu_3Al/(Ph_3C)[B(C_6F_5)_4]$ system (Table 1, Run 1).

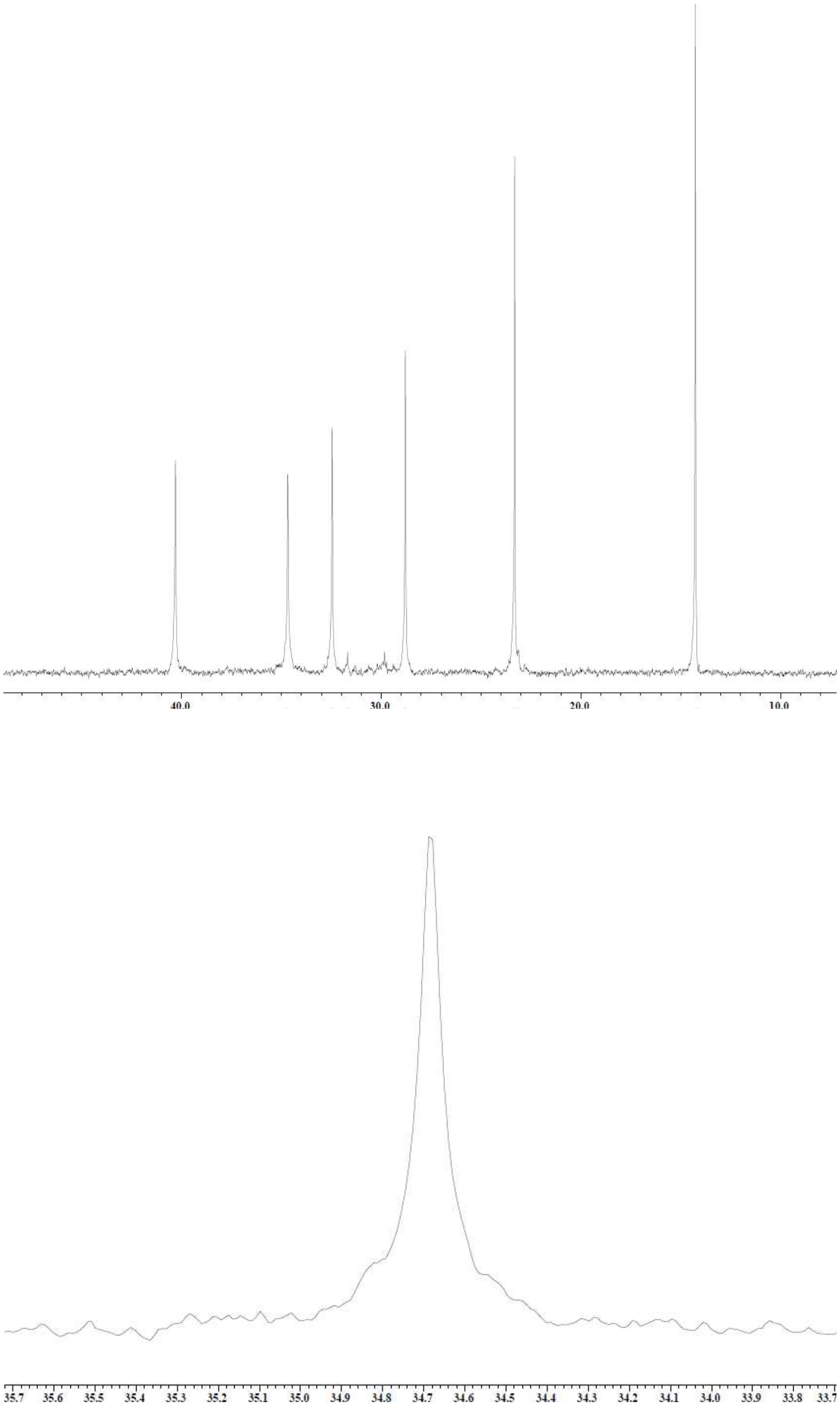

Figure S8. ^{1}H NMR spectrum of oligo(1-hexene) obtained by the **5**/Et$_2$AlCl/ETA system (Table 1, Run 2).

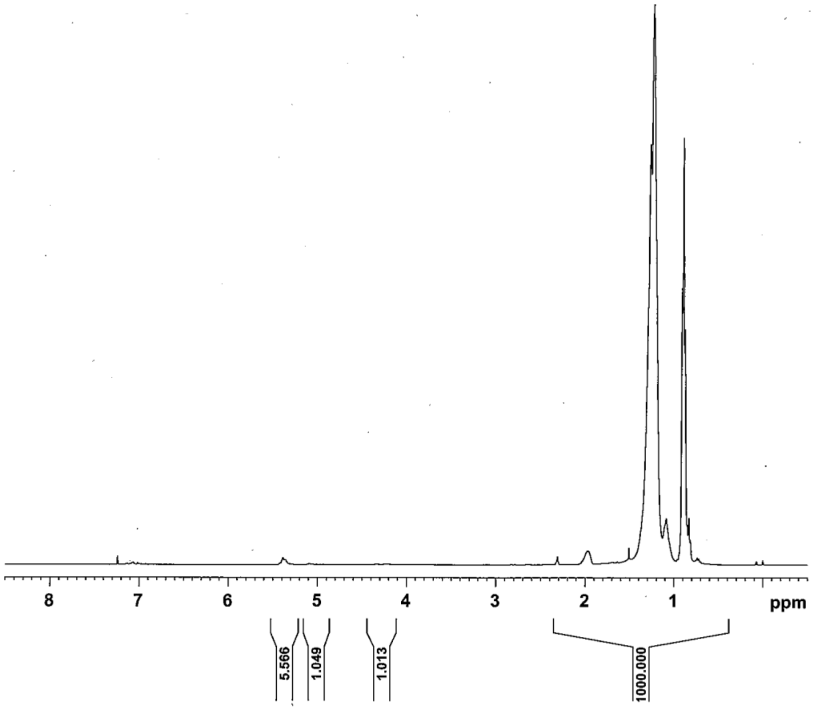

Figure S9. ^{13}C{^{1}H} NMR spectrum of oligo(1-hexene) obtained by the **5**/Et$_2$AlCl/ETA system (Table 1, Run 2).

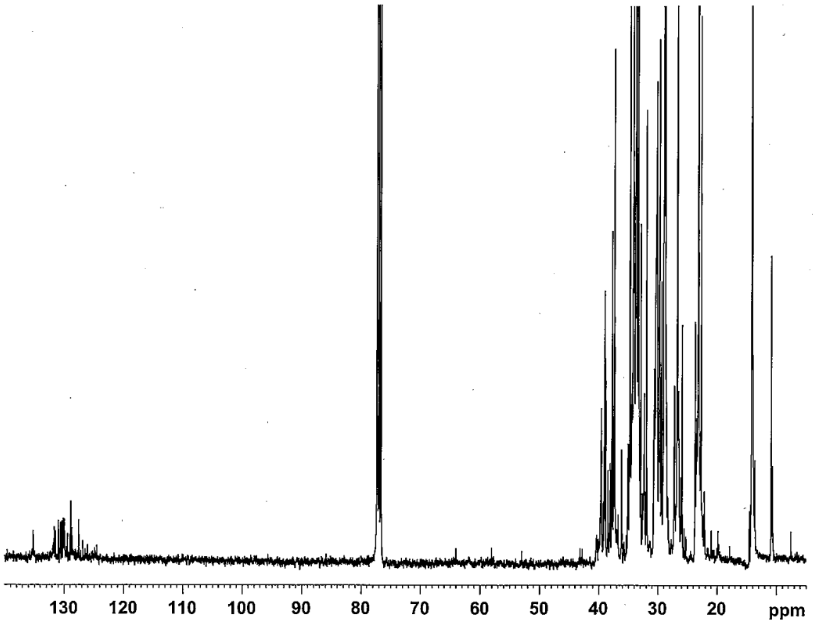

Figure S10. HMQC experiment of oligo(1-hexene) obtained by the **5**/Et_2AlCl/ETA system (Table 1, Run 2).

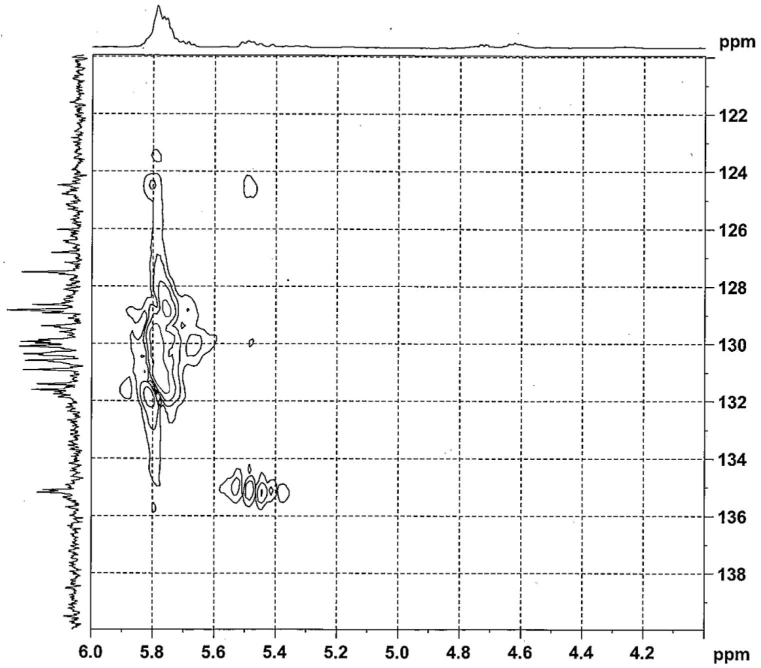

Figure S11. ^1H NMR spectrum of oligo(1-hexene) obtained by the **5**/Et_2AlCl/ETA system (Table 1, Run 3).