Supporting Information

Phenylene-Bridged OSSO-type Titanium Complexes in the Polymerization of Ethylene and Propylene

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Materials and Methods

All air- and moisture-sensitive manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques and a MBraun glove box. All reagents and solvents were purchased from Sigma-Aldrich. Dry solvents were obtained by standard methods and distilled before use. Methylaluminoxane, modified with $Al(iBu)_3$ (MMAO), was obtained from Akzo Nobel Corp. (as a heptane solution with a total Al concentration of 1.7 M). Polymerization-grade ethylene and propylene were purchased from Rivoira. A Bruker Avance 400 spectrometer (^1H, 400.01 MHz; ^{13}C, 100.62 MHz) and a ASCEND 600 spectrometer were used for the acquisition of the NMR spectra. Deuterated solvents (Cambridge Isotope Laboratories, Inc.) were dried following standard procedures. The 2D EXchange SpectroscopY (EXSY) experiments were carried out at 233 K for **1** and 303 K for **2** with a mixing times of 500 ms. ^{13}C NMR spectra of the polyethylene samples were recorded at 110 °C using 1,1,2,2-tetrachloroethane-d_2 as solvent (0.5 mL, 20 wt%) with an acquisition time of 1.5 s and a delay time of 4.0 s. Analysis of the polymers by gel permeation chromatography (GPC) was carried out at 145 °C using ortodichlorobenzene as solvent and a narrow-MWD polystyrene standard sample as reference. GPC curves were recorded with a Freeslate Rapid GPC setup, equipped with a set of two mixed-bed Agilent PLgel 10 μm columns and a Polymer Char IR4 detector, at HTExplore, a spin-off of the Federico II University of Naples (Italy). Thermal analysis of the polymers was performed by differential scanning calorimetry (DSC) with a TA Instruments DSC 2920 using a heating rate of 10 °C min^{-1}.

Single-Crystal X-ray Crystallography

A suitable crystal of $(OSSO_{tBu})TiCl_2$ (**1**) was mounted on a goniometer head and kept at room temperature. The X-ray intensity data for the structure were measured on a Bruker SMART Apex II CCD area detector diffractometer. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.3° ω steps. The software SMART[1] was used for collecting frames of data, indexing reflections, and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program[1] and an empirical absorption correction was applied using SADABS.[2] The structures were solved by direct methods (SIR 2004)[3] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL),[4] using anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were added in calculated positions, included in the final stage of refinement with isotropic thermal parameters, $U(H) = 1.2\ U_{eq}(C)$ [$U(H) = 1.5\ U_{eq}$(C-Me)], and allowed to ride on their carrier carbons.

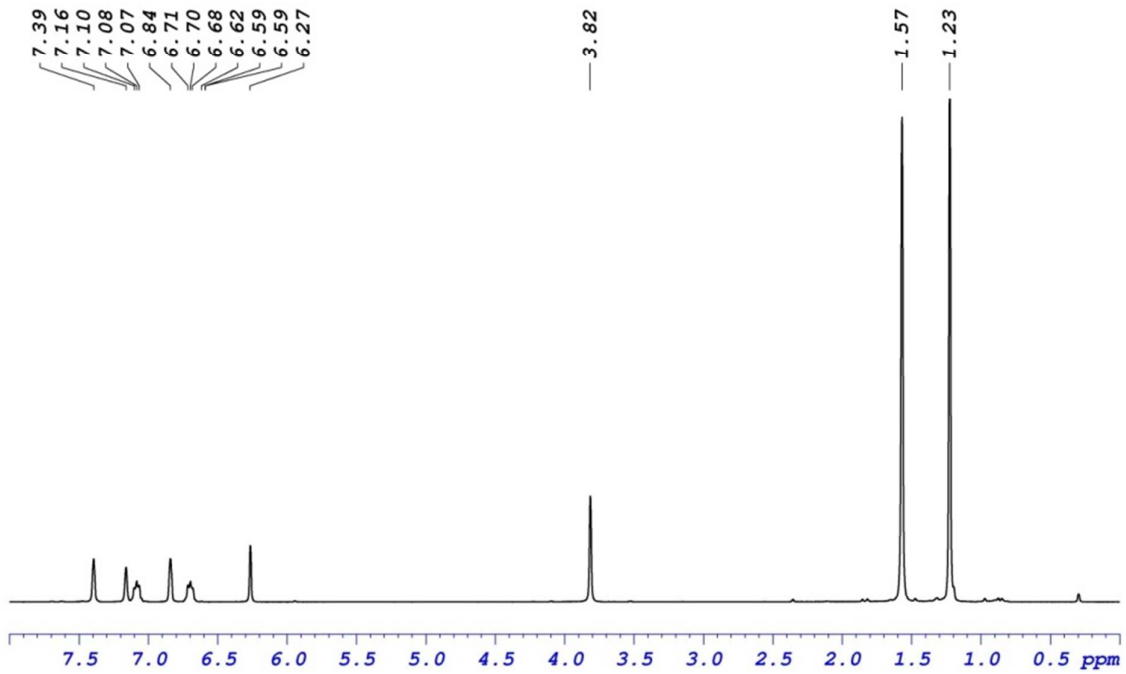

Figure S1. ^{1}H NMR of 6,6'-((1,2-phenylenebis(sulfanediyl)bis(methylene))bis(2,4-di-tert-butyl-2-yl)phenol) ($OSSO_{tBu}$-*H*) (250MHz, C_6D_6, 25°C).

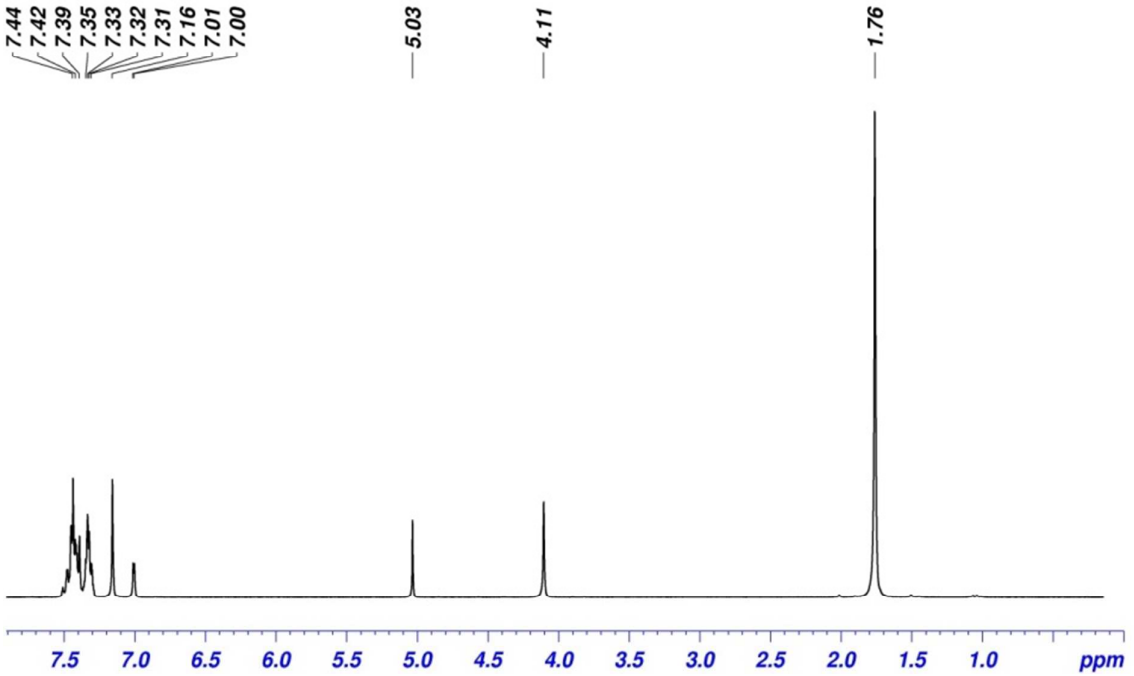

Figure S2. ^{1}H NMR of 6,6'-((1,2-phenylenebis(sulfanediyl)bis(methylene))bis(2,4-di-phenylpropan-2-yl)phenol ($OSSO_{Cum}$-*H*) (250MHz, C_6D_6, 25°C).

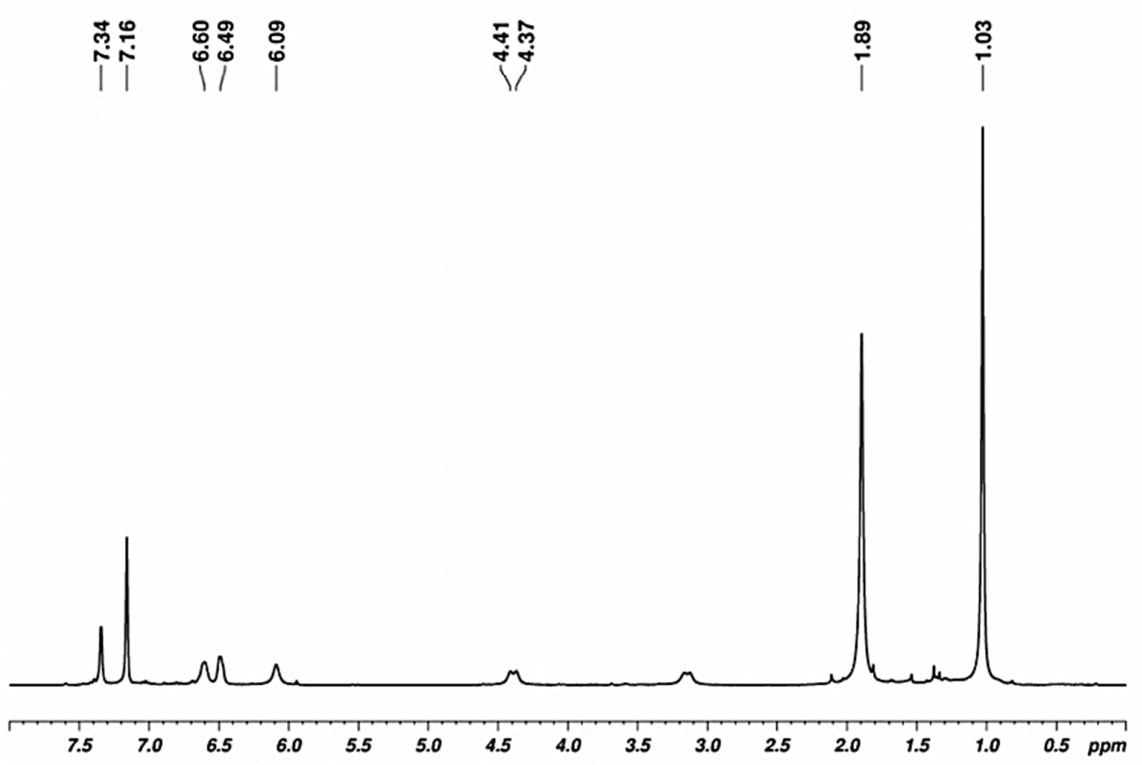

Figure S3. ^{1}H NMR of (OSSO$_{tBu}$)TiCl$_2$ (**1**) (300 MHz,C_6D_6, 25°C).

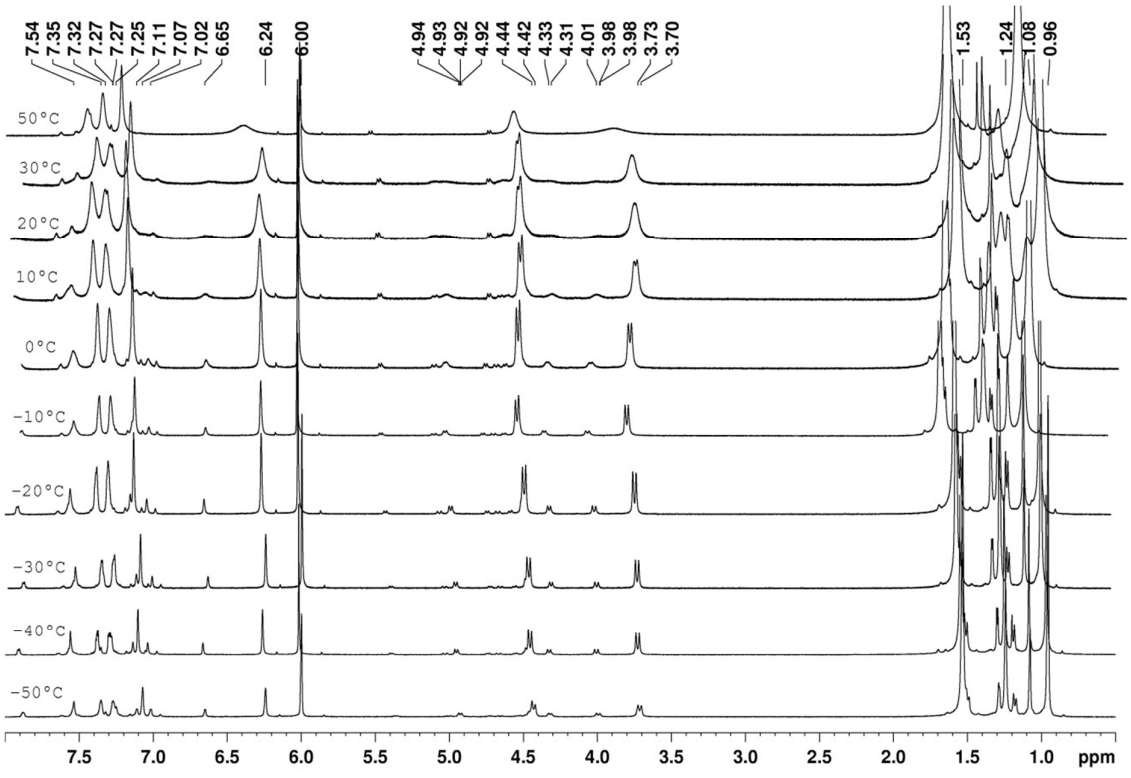

Figure S4. Variable temperature ^{1}H NMR of (OSSO$_{tBu}$)TiCl$_2$ (**1**) (600 MHz, TCDE).

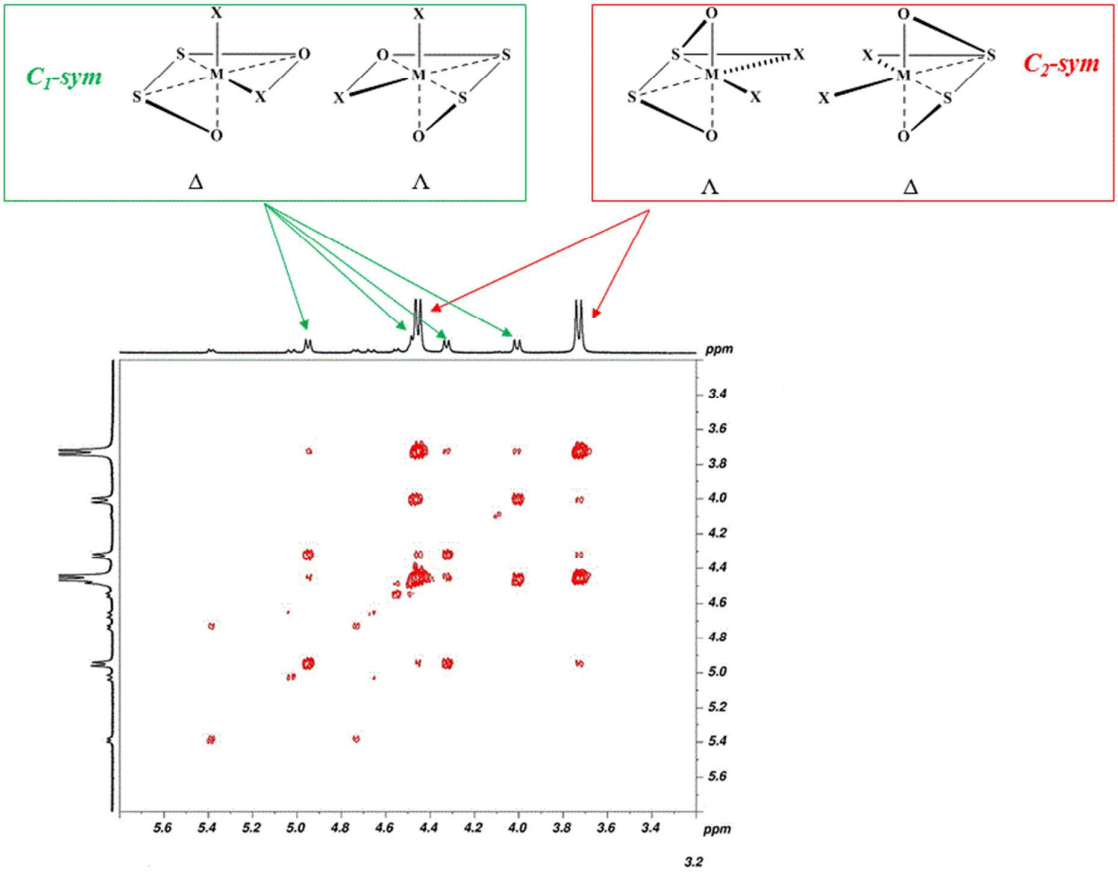

Figure S5. EXSY spectrum of ($OSSO_{tBu}$)$TiCl_2$ (**1**) (τ_m= 0.500s, TCDE, 600 MHz).

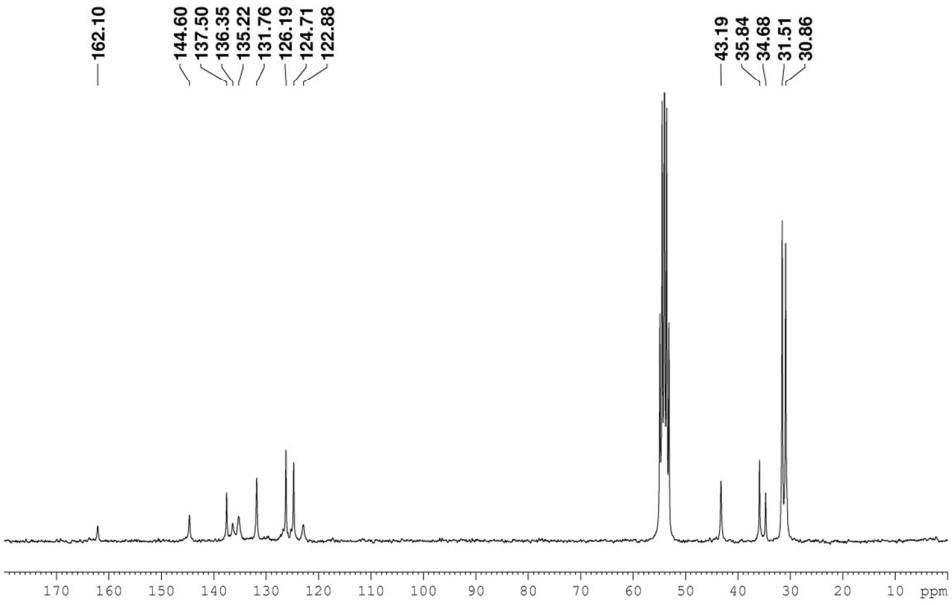

Figure S6. ^{13}C NMR of ($OSSO_{tBu}$)$TiCl_2$ (**1**) (75.5 MHz, CD_2Cl_2, 25 C°).

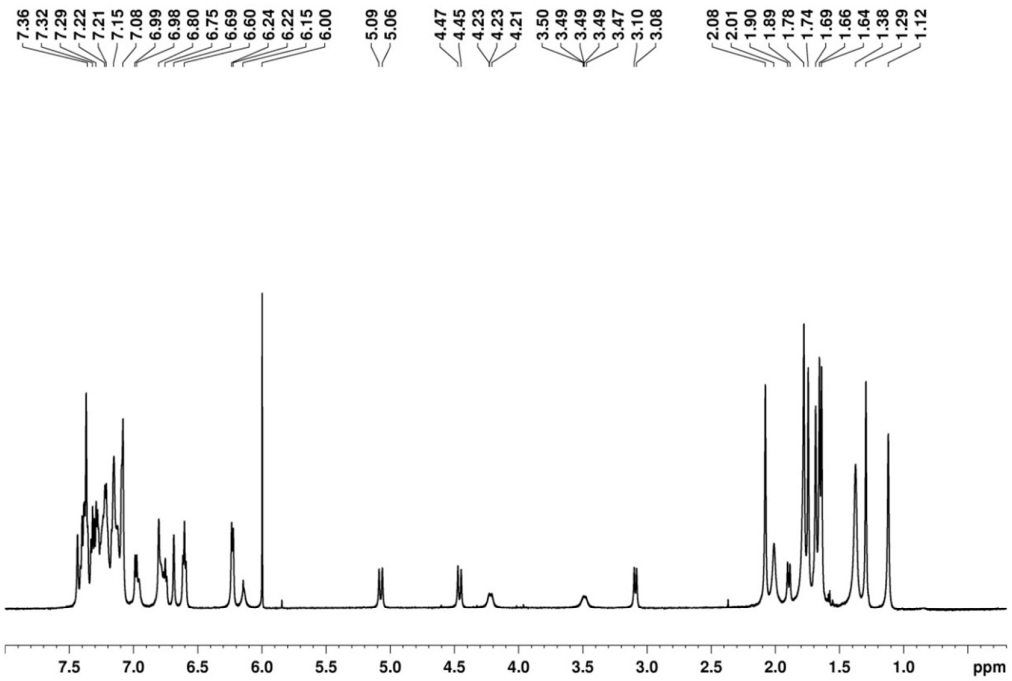

Figure S7. ^{1}H NMR of (OSSO$_{Cum}$)TiCl$_2$ (**2**) (TCDE, 30 °C, 600 MHz).

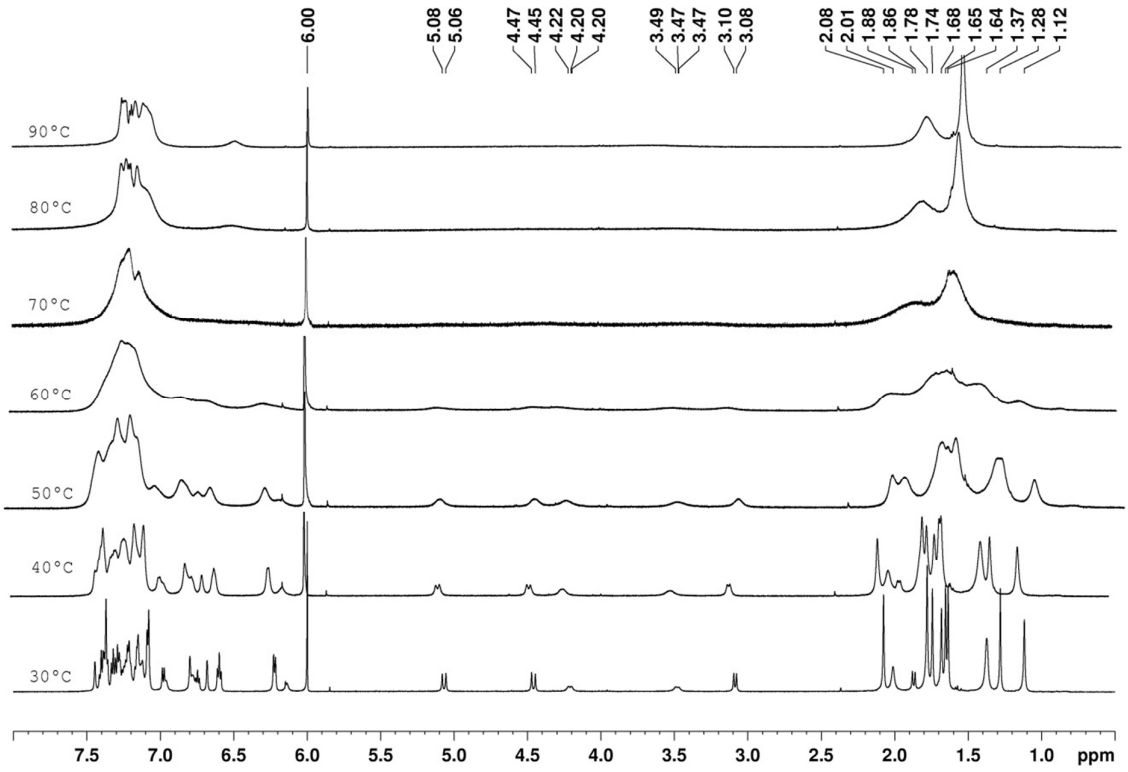

Figure S8. Variable temperature ^{1}H NMR of (OSSO$_{Cum}$)TiCl$_2$ (**2**) (600 MHz, TCDE)**.**

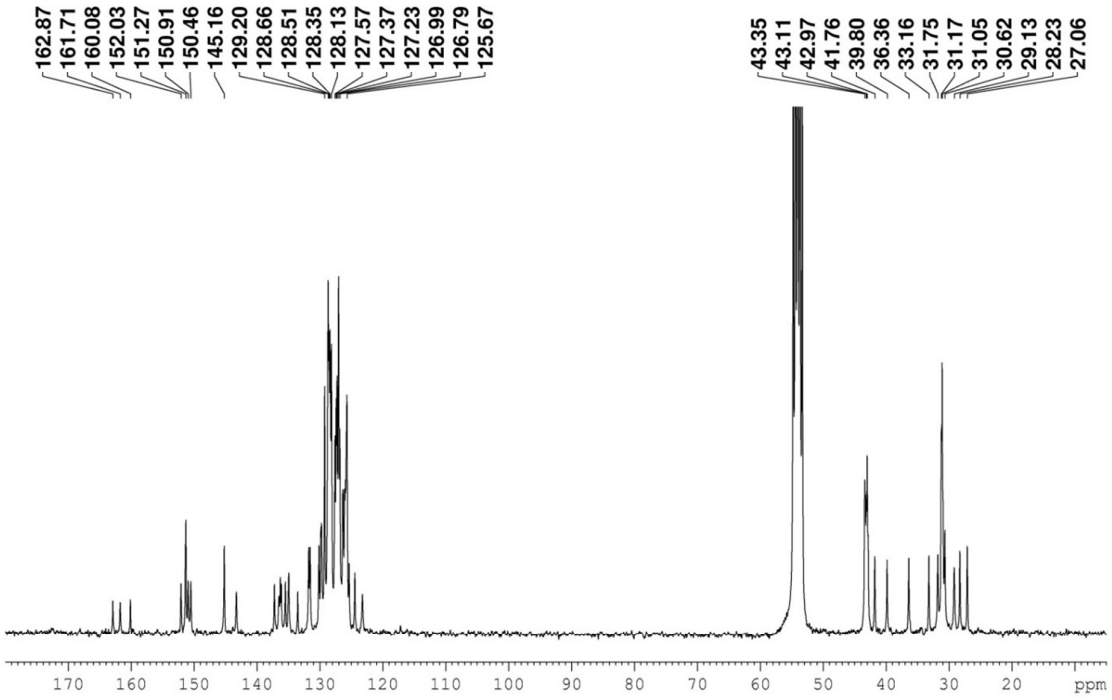

Figure S9. ^{13}C NMR of $(OSSO_{Cum})TiCl_2$ (**2**) (75.5 MHz, CD_2Cl_2, 25 C°).

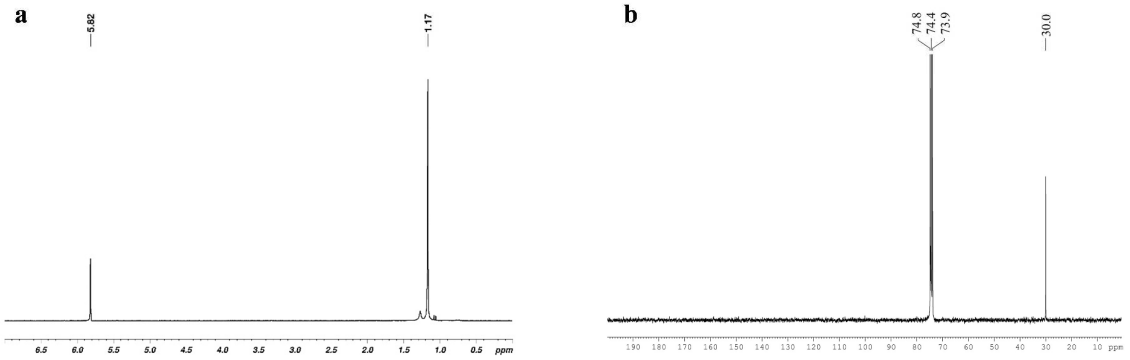

Figure S10. ^{1}H (a) and ^{13}C NMR (b) spectra of polyethylene from entry 2 of Table 1 (1,1,2,2-tetrachloroethane-d_2, 110 °C, TMS scale).

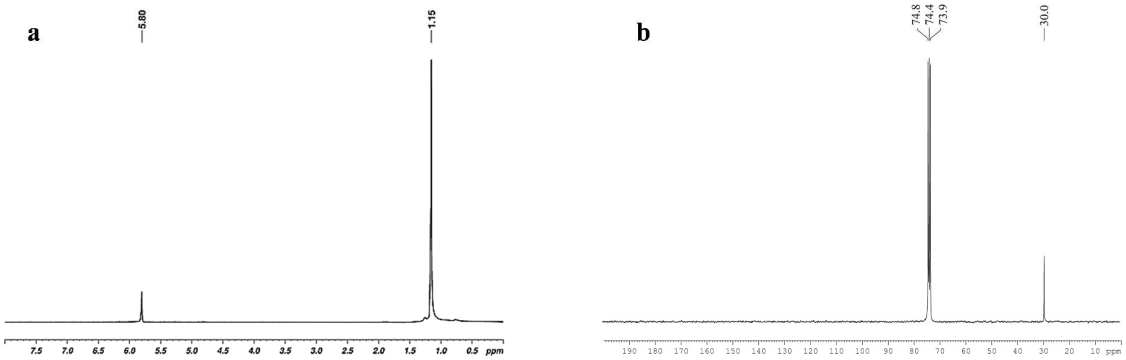

Figure S11. ^{1}H (a) and ^{13}C NMR (b) spectra of polyethylene from entry 6 of Table 1 (1,1,2,2-tetrachloroethane-d_2, 110 °C, TMS scale).

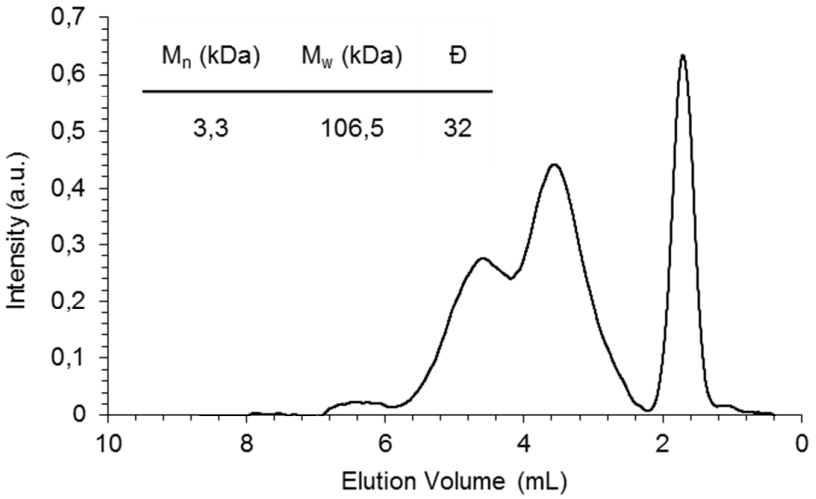

Figure S12. High temperature gel permeation chromatography trace of polyethylene sample reported in entry 6, Table1.

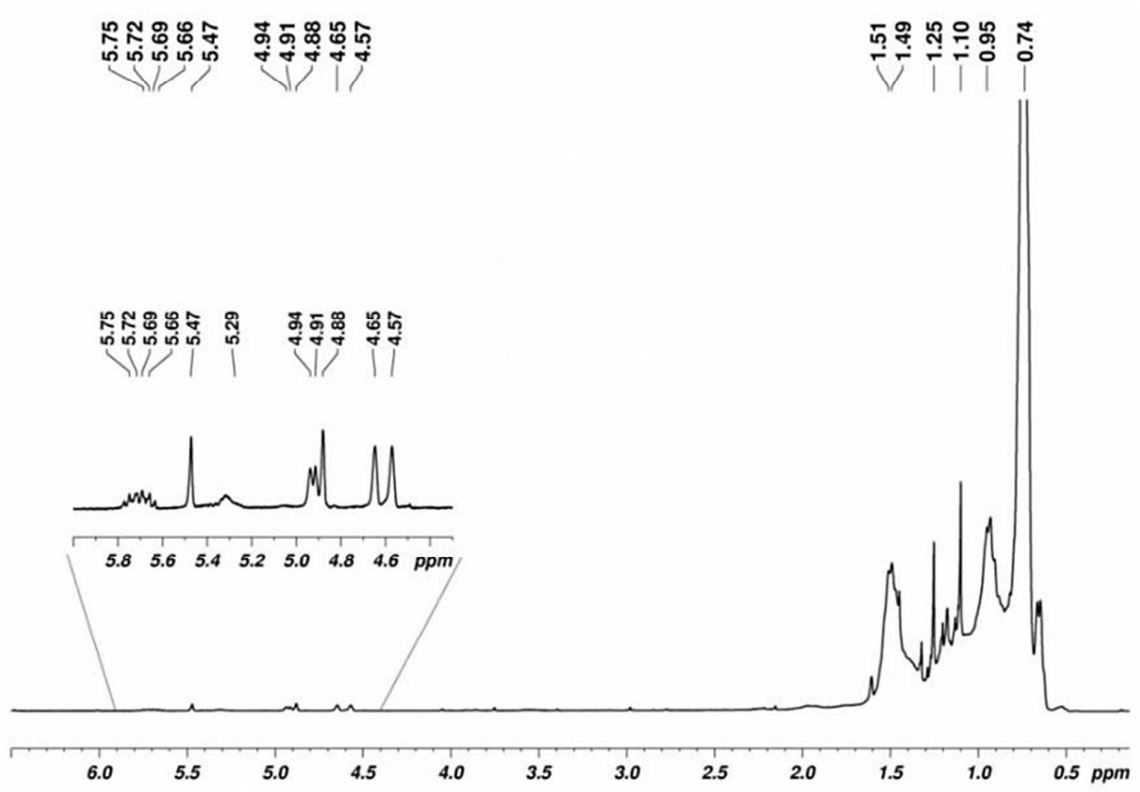

Figure S13 ^{1}H NMR spectrum of polypropylene oligomers sample from run 7 in Table 2 ($CDCl_3$, 25 °C, 300 MHz).

References

1) SMART & SAINT Software Reference Manuals, version 5.051 (Windows NT Version), Bruker Analytical X–ray Instruments Inc.: Madison, WI, **1998**.

2) Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, **1996**.

3) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. SIR2004: an Improved Tool for Crystal Structure Determination and Refinement. *J. Appl. Crystallogr*. **2005**, *38*, 381–388.

4) G. M. Sheldrick, SHELXTLplus (Windows NT Version) Structure Determination Package, Version 5.1. Bruker Analytical X–ray Instruments Inc.: Madison, WI, USA, **1998**.