

Supporting Information

1,3-Double Siloxo-Bridged Zirconium Metallocene for Propene and 1-Hexene Regioselective Oligomerization

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Alcalá de Henares. Spain. [§]X-ray diffraction studies.

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Experimental Details

General. All air- and moisture-sensitive manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques and an MBraun dry-box. Solvents were refluxed and distilled from sodium-benzophenone (toluene, hexane) before use. All organic preparations were carried out under aerobic atmospheric conditions. Ethylene and propene (S.O.N., polymerization grade) were dried by passing over activated 4Å molecular sieves. 1-Hexene (Aldrich) was purified by distillation over calcium hydride and stored in a refrigerator at -20 °C. Methylalumoxane (MAO) (Aldrich, 10 wt % solution in toluene) was dried under vacuum at 50 °C to remove the uncoordinated AlMe₃ and used as a solid after washing with hexane (d-MAO). Modified methylalumoxane (MMAO-3A) (Akzo Nobel, 7 wt % solution in heptane) was used as received.

Synthesis of [Zr{(η⁵-C₅H₅)₂-μ,μ-1,3-(Me₂SiOSiMe₂)₂}Cl₂] (2): 80 μl of H₂O (80 mg, 4.46 mmol) and 1.2 mL of NEt₃ (0.9 g, 8.92 mmol) were added to a solution of [Zr{η⁵-C₅H₅-1,3-[SiMe₂Cl]₂}Cl₃] (2 g, 4.46 mmol) in toluene cooled to -78 °C. The reaction mixture was warmed to room temperature and stirred for 4 days. The solvent was removed under reduced pressure to give a white powder which was recrystallized from toluene (5 x 30 mL), affording **2** in 75% yield (0.92 g). ¹H NMR (CDCl₃, 295 K, 400.13 MHz, J Hz): δ 7.16 (t, 2H, J = 1.8 Hz, C₃H₅), 7.05 (d, 4H, J = 1.8 Hz, C₃H₅), 0.41 (s, 12H, SiCH₃), 0.34 (s, 12H, SiCH₃). ¹³C NMR (CDCl₃, 295 K, 100.55 MHz): δ 133.6 (C₃H₅), 126.1 (C₃H₅), 123.6 (C_{ipso}, C₃H₅), 2.0 (CH₃), -0.6 (CH₃). Anal. Calcd for C₁₈H₃₀Cl₂O₂Si₄Zr: C, 39.10, H, 5.47. Found: C, 38.86, H, 5.27. Appropriate single crystals were obtained when **2** was recrystallized from acetone.

General Procedure for the polymerization:

Ethylene polymerization. The polymerization runs were carried out following a standard procedure. A 100-mL flask, equipped with a magnetic stirrer, was charged with a toluene solution (45 mL) containing an appropriate amount of MAO. The gas phase was pumped off and the solution was left to equilibrate at the prescribed temperature with ethylene supplied at atmospheric pressure. The polymerization run was started by injection of toluene solutions of the zirconium pre-catalyst (4.0×10⁻⁵ mol, 5 mL). The polymerization run was stopped after the prescribed time by adding a few milliliters of acidic ethanol. The polymer was precipitated with an excess of ethanol, recovered by filtration, washed with fresh ethanol and dried under vacuum at 80 °C.

Propene polymerization. The polymerization runs were carried out following a standard procedure. The polymerization runs were performed in a 250 mL Buchi glass autoclave equipped with a mechanical stirrer. The autoclave was charged under nitrogen with the toluene solution of MAO, the solution was stirred and the temperature regulated using a thermostat then the monomer gas feed was started. The polymerization run was started upon injection of a toluene solution containing 4×10^{-5} mol of the zirconium pre-catalyst. After the specified reaction time, the polymerization was stopped by venting the reactor and pouring the polymerization mixture into ethanol acidified with aqueous HCl. The absence of polymers and the formation of two well defined layers indicated the presence of oligomers. The oligomers were extracted from the reaction mixture with CHCl_3 and the organic phase was dried with anhydrous MgSO_4 . Finally, the excess solvent was removed by distillation.

1-hexene polymerization. Polymerizations were carried out in a sealed glass vial equipped with a magnetic stirrer without the addition of further solvent. 1×10^{-5} mol of precatalyst, the appropriate amount of MAO or MMAO, and 5 mL of 1-hexene were added to the reactor in that sequence. The reaction mixture was stirred vigorously at the desirable temperature. The polymerization run was stopped after the prescribed time by adding a few milliliters of acidic methanol. The oligomers were extracted from the reaction mixture with CHCl_3 and the organic phase was dried with anhydrous MgSO_4 . Finally, the excess solvent was removed by distillation.

Characterization of the oligomers and polymers. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AVANCE 400 spectrometer at 25 °C. The chemical shifts were referred to TMS as an external standard using the residual protio impurities of the deuterated solvent as reference. The ^{13}C NMR spectra of the polyethylene samples were recorded with an AM 250 Bruker spectrometer (63 MHz for ^{13}C) or a Bruker AVANCE 300 (75MHz for ^{13}C) at 110 °C using 1,1,2,2-tetrachloroethane- d_2 as solvent (0.5 mL, 20wt.-%). Spectra were recorded with an acquisition time of 1.5s and a delay of 4.0s. The ^{13}C NMR chemical shifts were calibrated using the methylene signal $S_{\delta\delta}$ of the polymethylene sequences at 30.0 ppm as the internal reference.

Gel Permeation Chromatography (GPC) analysis of the polymers was carried out by high temperature GPC at 140 °C using 1,2,4-trichlorobenzene as solvent and narrow MWD polystyrene standard sample as reference. The measurements were performed on a PL-

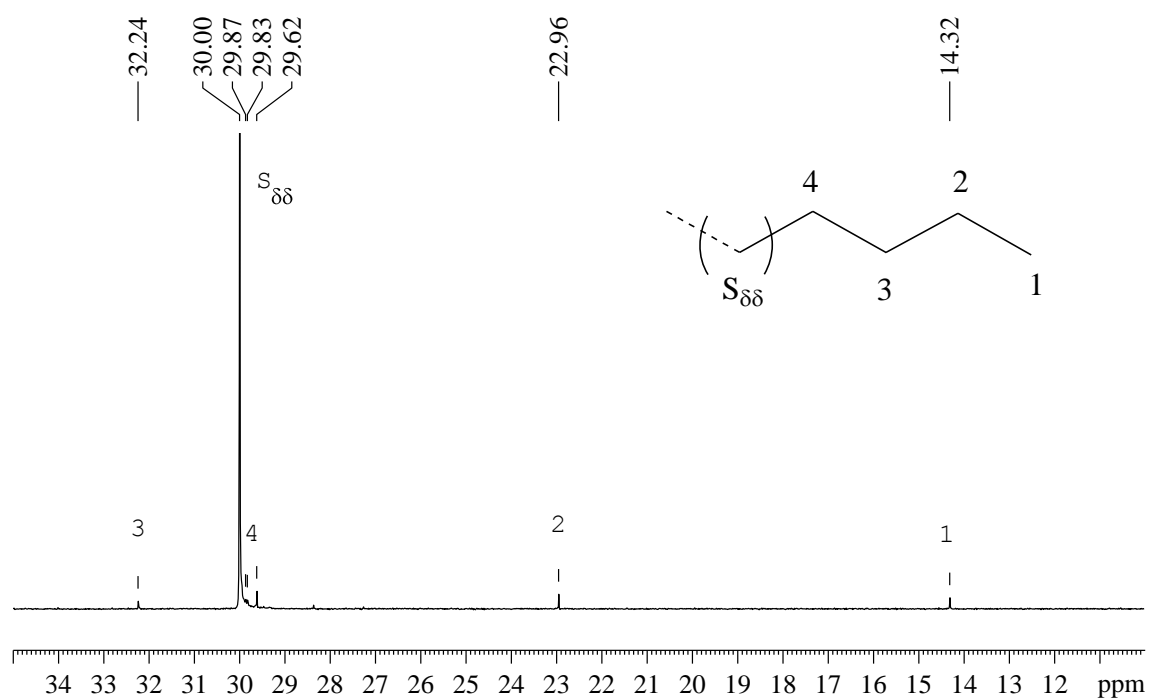
GPC210 with four PL-Gel Mixed A columns, RALLS (light scattering) detector (PD2040), H502 viscometer (Viscotek), refractive detector, and DM400 data manager (Viscotek).

The thermal analysis of the polymers was performed by Differential Scanning Calorimetry (DSC) with a TA Instrument DSC 2920 using a heating rate of 10 °C/min.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) analysis of the oligomers were performed using a MALDI-micro MX, (Waters Co.). The spectra were recorded in reflectron and positive mode. The matrix was dithranol (20 mg/mL), the cationizing agent silver trifluoroacetate (10 mg/mL). The polymer concentration was 10 mg/mL and the ratio polymer: matrix : cation = 1: 2: 1.

Gas chromatography data were obtained using an HP-5 capillary column (5% diphenyl-95%dimethylpolysiloxane, 50m, 0.20 mm i.d.) and a flame ionization detector. Temperature profile: isothermal at 40 °C (10 mins), 10 °C/minute, isothermal at 280 °C. The solutions of oligopropene were obtained from the quenching of the polymerization mixture with methanol. Benzene or heptene were used as internal standards.

Figure S1. ^{13}C NMR spectrum (1,1,2,2-tetrachloroethane- d_2 , 110 °C, TMS scale) of the polyethylene sample from run 6 of Table 2. (PE 90 °C)



Scheme S1. Mechanism accounting the formation of the four diastereoisomers for the oligomer with three repeating units.

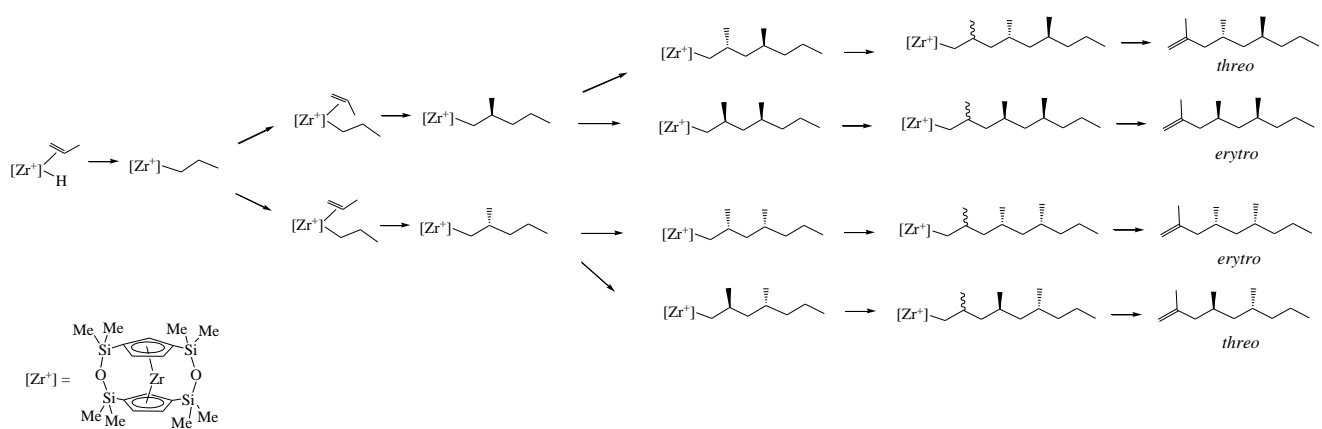


Figure S2. ^1H NMR spectrum (CDCl_3 , rt, 300 MHz) of the oligopropene sample from run 9 of Table 2

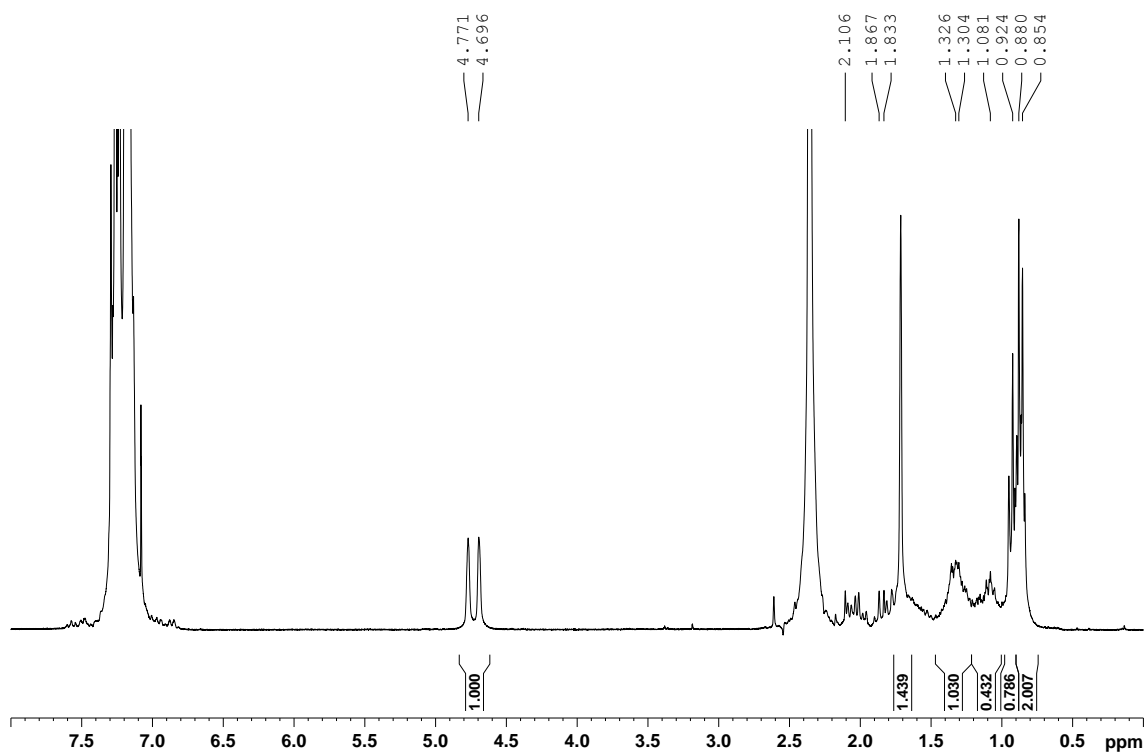


Figure S3. Aliphatic regions of the ^{13}C NMR spectra (CDCl_3 , rt, $d1=2\text{s}$, 75 MHz) of the oligopropene samples obtained at 25 °C (a), 50 °C (b) and 70 °C (c), runs 7-9 of Table 2.

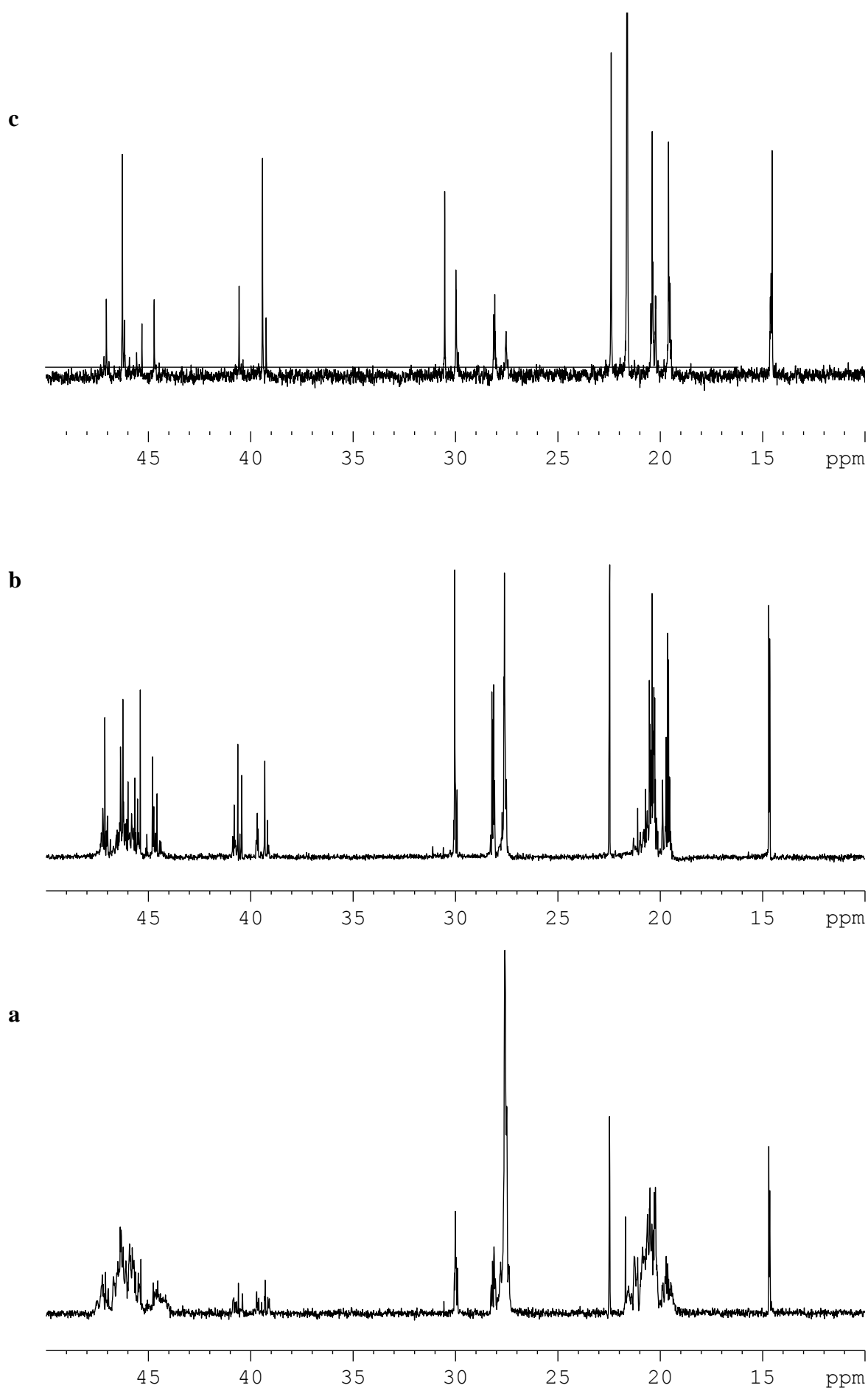


Figure S4. Aliphatic region of the ^{13}C NMR spectrum (CDCl_3 , rt, $d1=2\text{s}$, 75 MHz) of the oligopropene sample from run 7 of Table 2. For comparison, the DEPT135 experiment is reported.

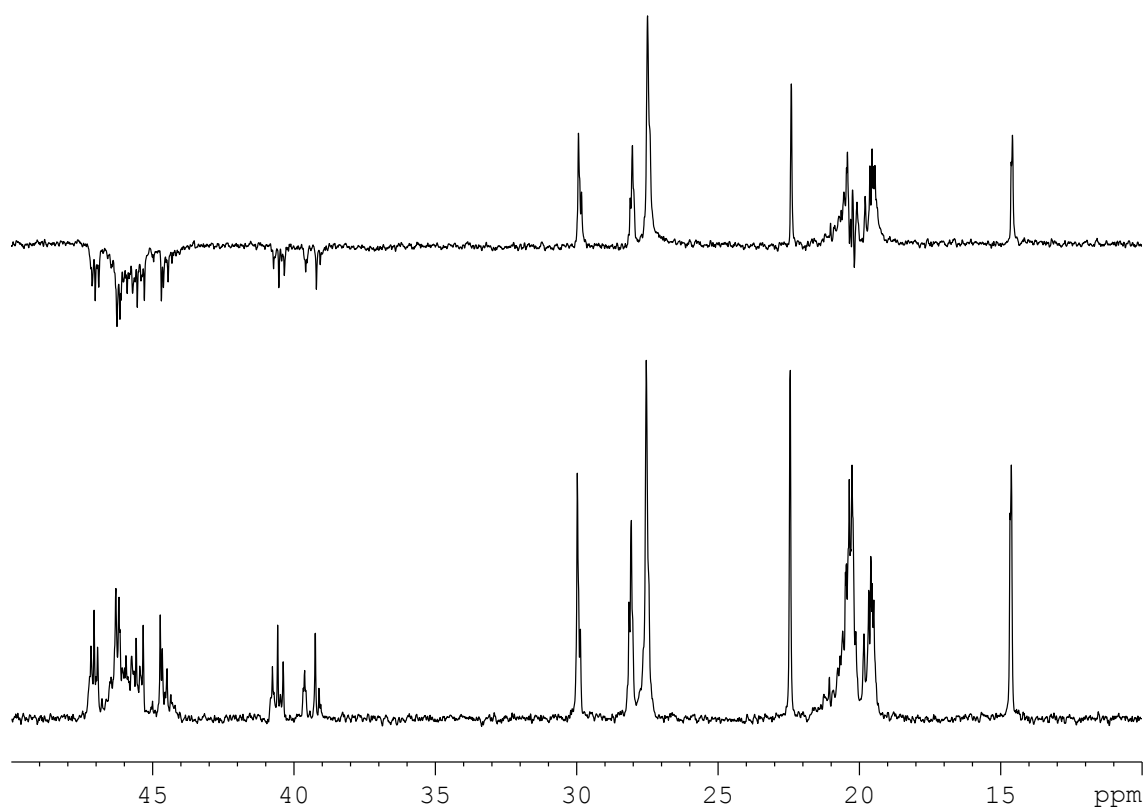


Figure S5. MALDI-TOF mass spectrum for run 7, Table 2. Peaks correspond to the silver adduct of *M_i* (*i* = degree of oligomerization, number of monomer units) (a.i. = arbitrary intensity).

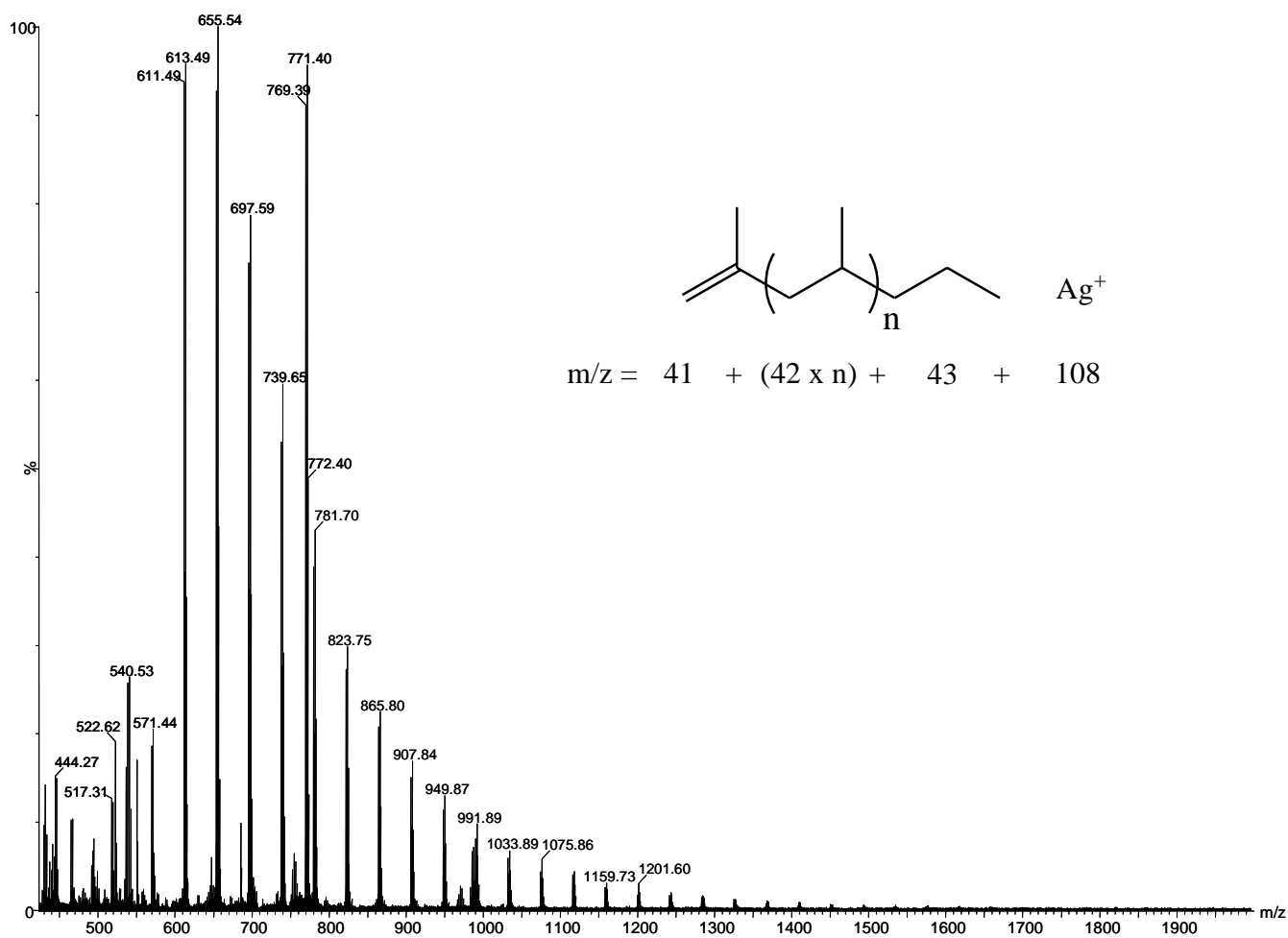


Figure S6. GC trace of the oligopropene sample from run 8 of Table 2.

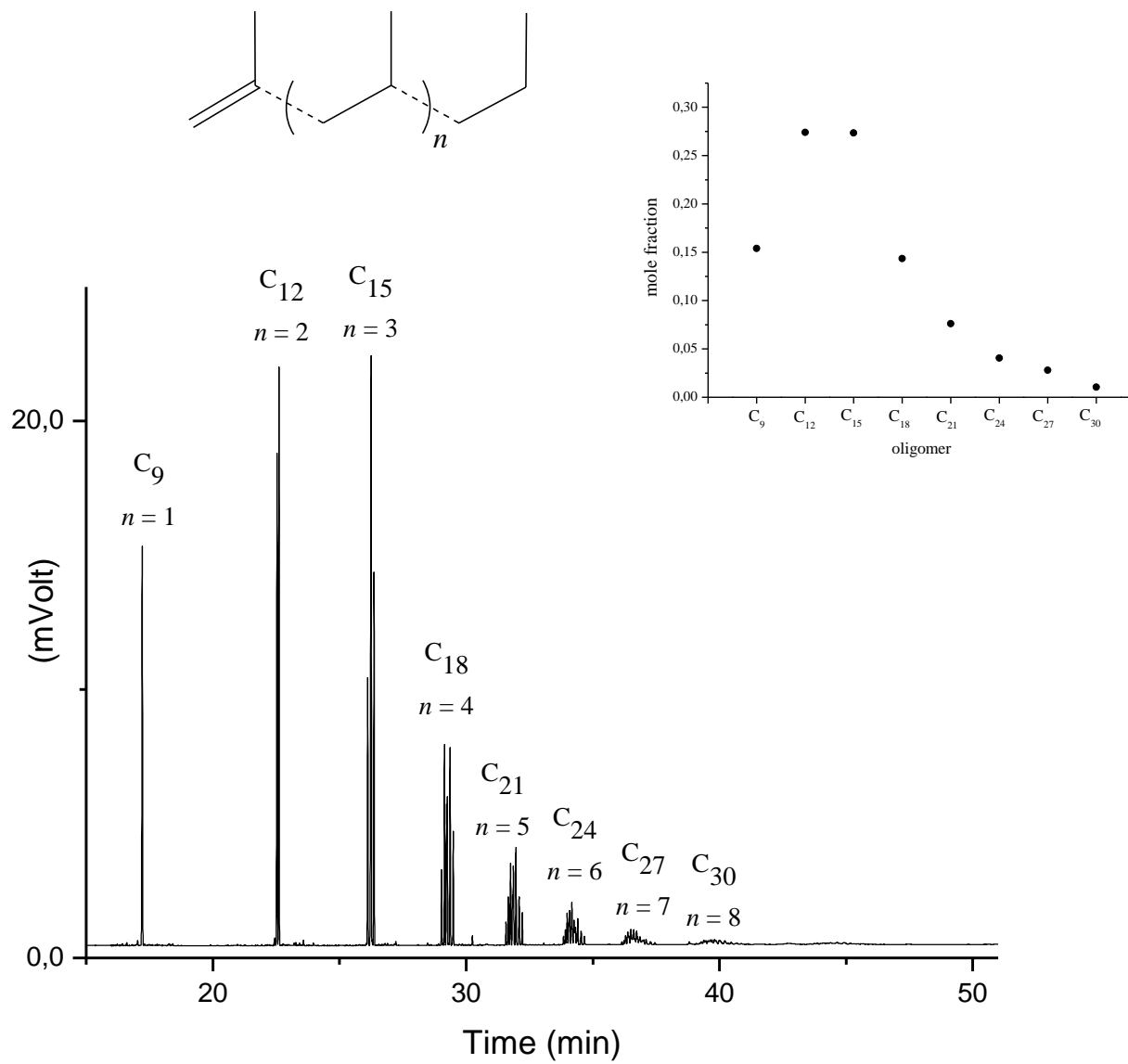
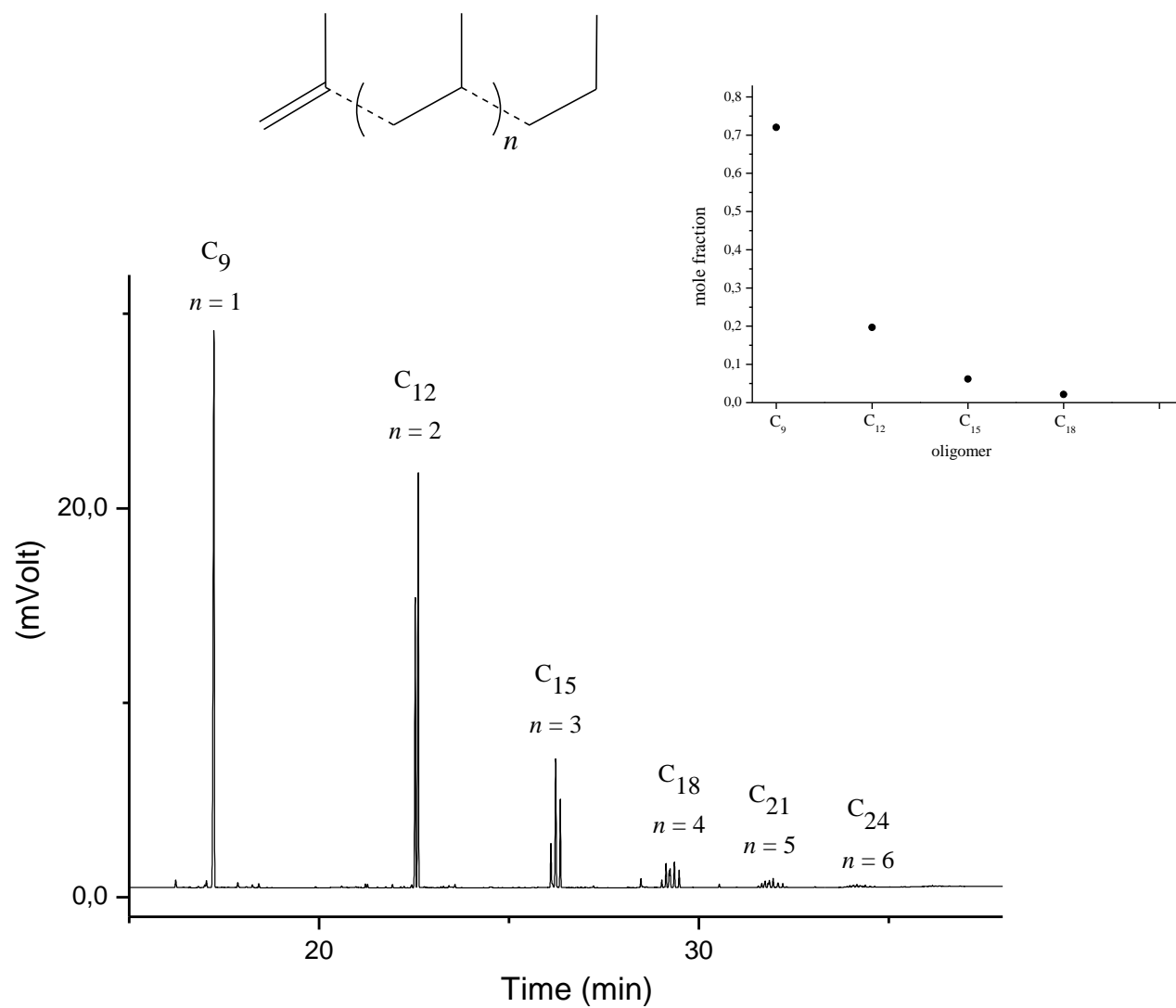


Figure S7. GC trace of the oligopropene sample from run 9 of Table 2.



Schulz-Flory Distribution

For a step-growth polymerization, the probability of chain propagation (α) can be defined as follows:

$$\begin{aligned}\alpha &= \text{rate of propagation} / (\text{rate of propagation} + \text{rate of chain transfer}) = \\ &= \text{moles of } C_{n+2} / \text{moles of } C_n\end{aligned}$$

The probability of chain propagation (α) is related to the ratio of the rate of chain transfer and chain propagation:

$$\alpha = 1 / (1 + \beta) \quad \text{where} \quad \beta = \text{rate of chain transfer/rate of propagation}$$

For the step-growth polymerization originally described mathematically by Schulz^[1] and also by Flory^[2], the product distribution can be described by the probability of chain propagation α according to the following equation:

$$W_n = (\ln^2 \alpha) n \alpha^n$$

where W_n is the weight fraction of the products with n the carbon number. The logarithmic form of this kinetic expression is shown below:

$$\log C_n = \log(\ln^2 \alpha) + n \log \alpha$$

where $C_n = W_n/n$ = mole fraction. According to the equation, a plot of $\log C_n$ versus n should give a straight line (ASF plot).

The mole fractions of the oligopropene products were obtained from MALDI-TOF data for the sample of run 7, Table 2 and from the GC data for the samples of runs 8 and 9, Table 2. The plots of the $\log(W_n/n)$ versus the oligomer chain length (n) showed the expected linear decrease in $\log(W_n/n)$ with increasing chain length. The Schulz-Flory chain length distributions of propene oligomers were observed in all catalytic runs.

Figure S8. Schulz-Flory distribution of oligomers obtained in the propene oligomerization of run 7, Table 2. ($R = 0.99606$)

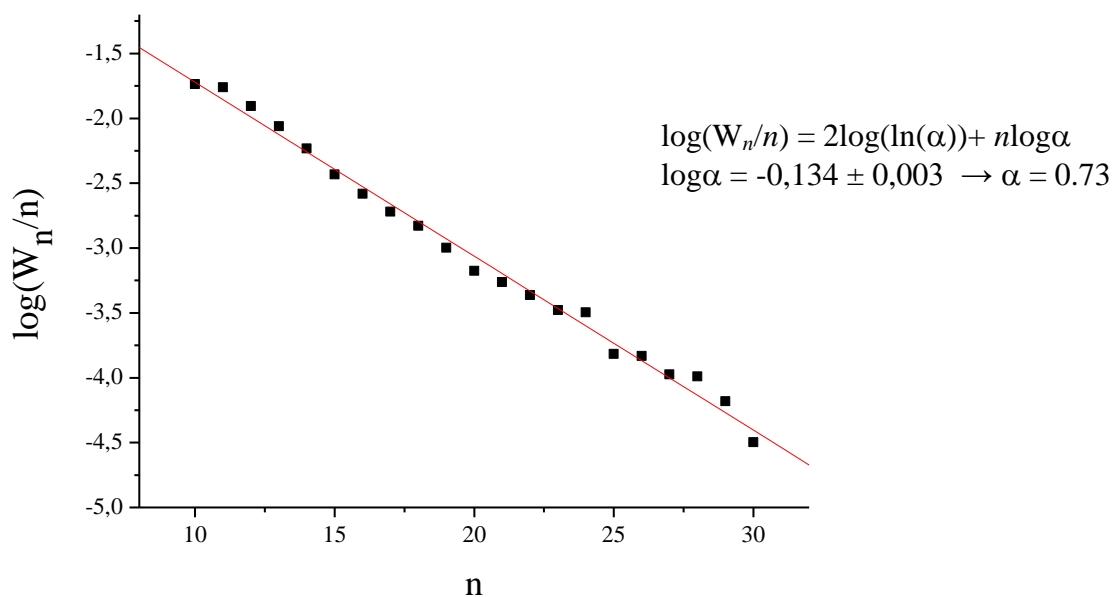


Figure S9. Schulz-Flory distribution of oligomers obtained in the propene oligomerization of run 8, Table 2. ($R = 0.98464$)

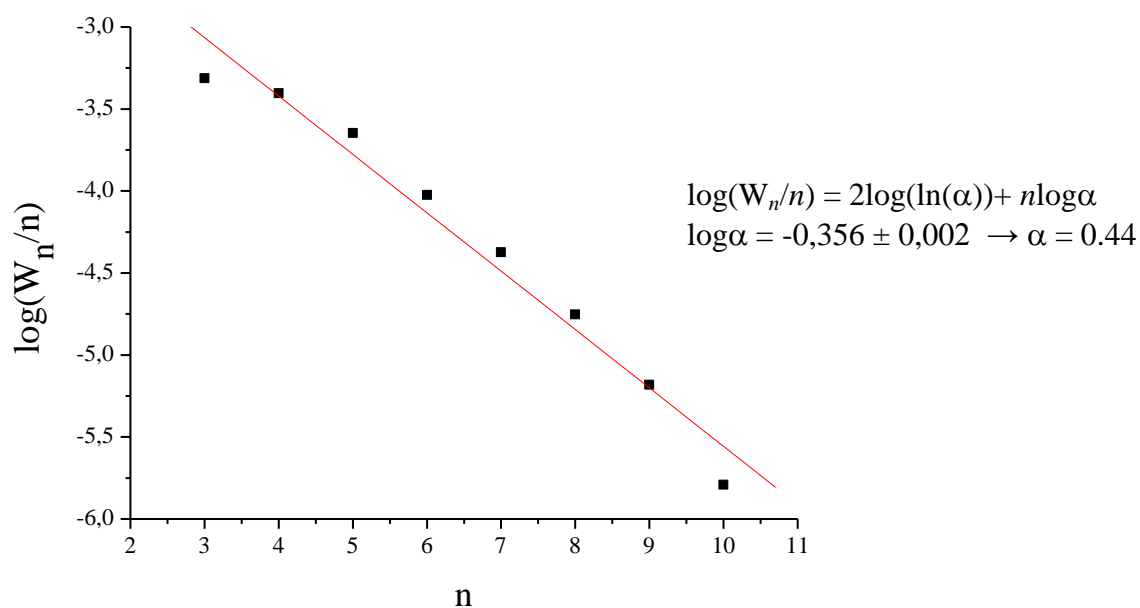
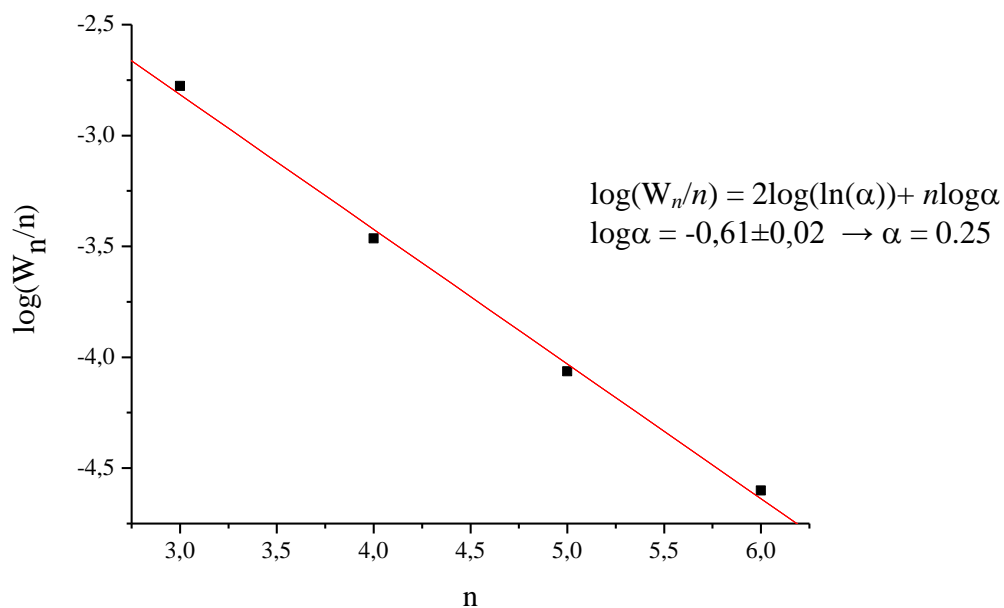


Figure S10. Schulz-Flory distribution of oligomers obtained in the propene oligomerization of run 9, Table 2. ($R = 0.99845$)



References

- [1] G.V. Schulz, Z. Phys. Chem. 32 (1936) 27.
- [2] P.J. Flory, J. Am. Chem. Soc. 58 (1936) 1877.

Figure S11. ^1H NMR spectrum (C_6D_6 , rt, 400 MHz) of the oligohexene sample from run 13 of Table 3

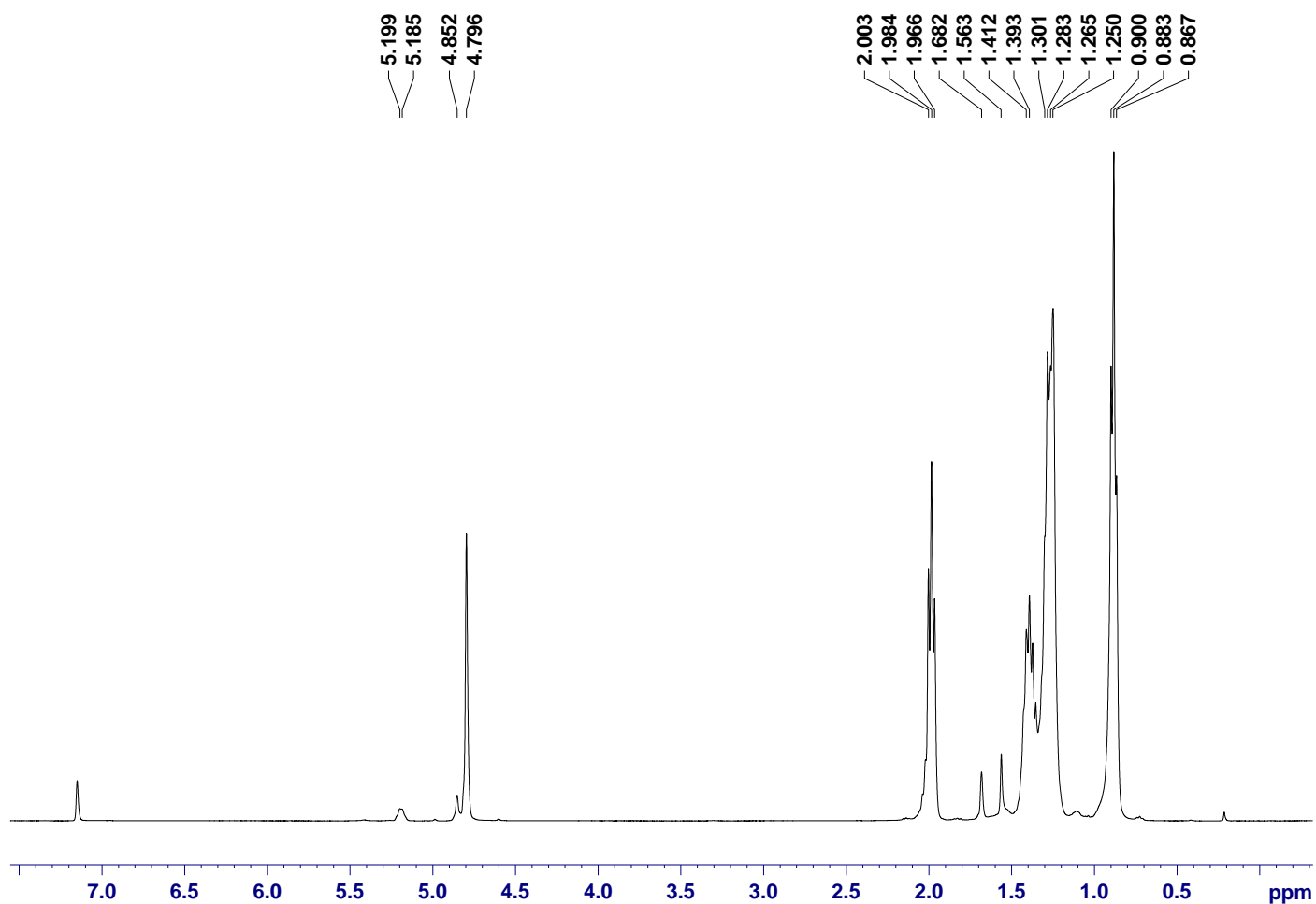
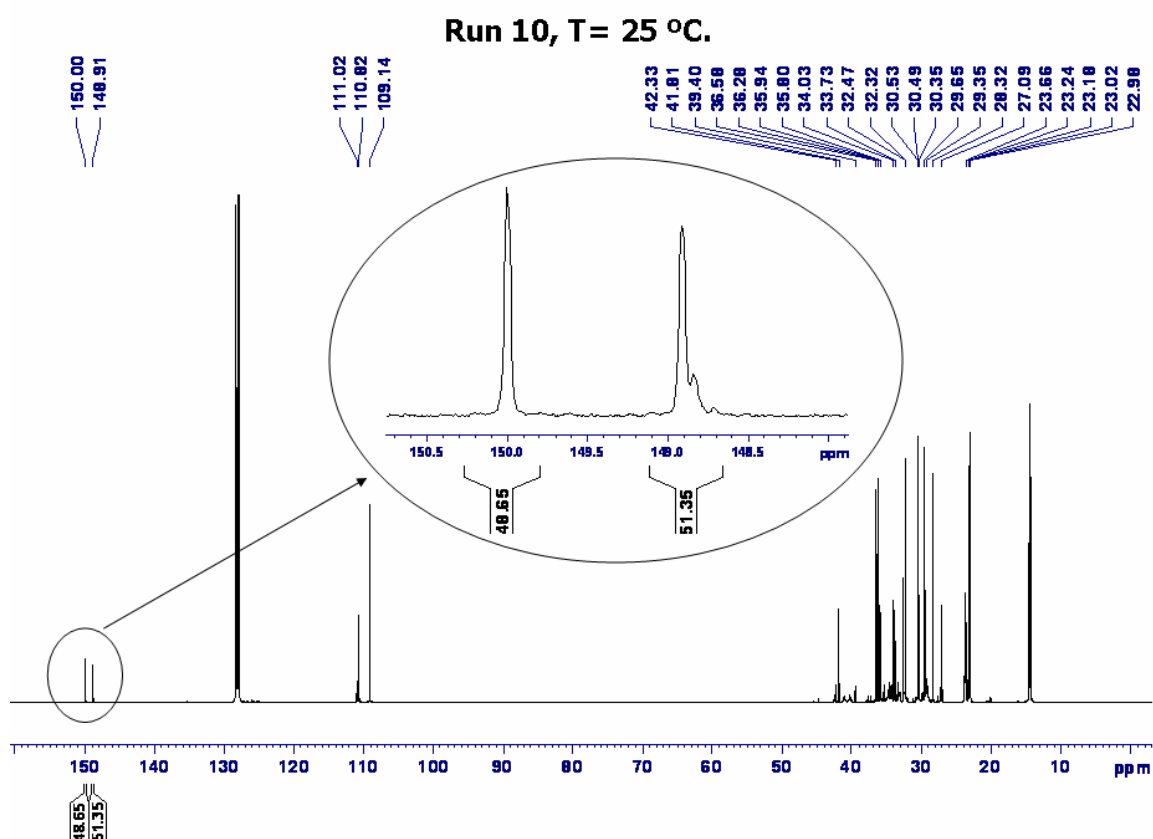
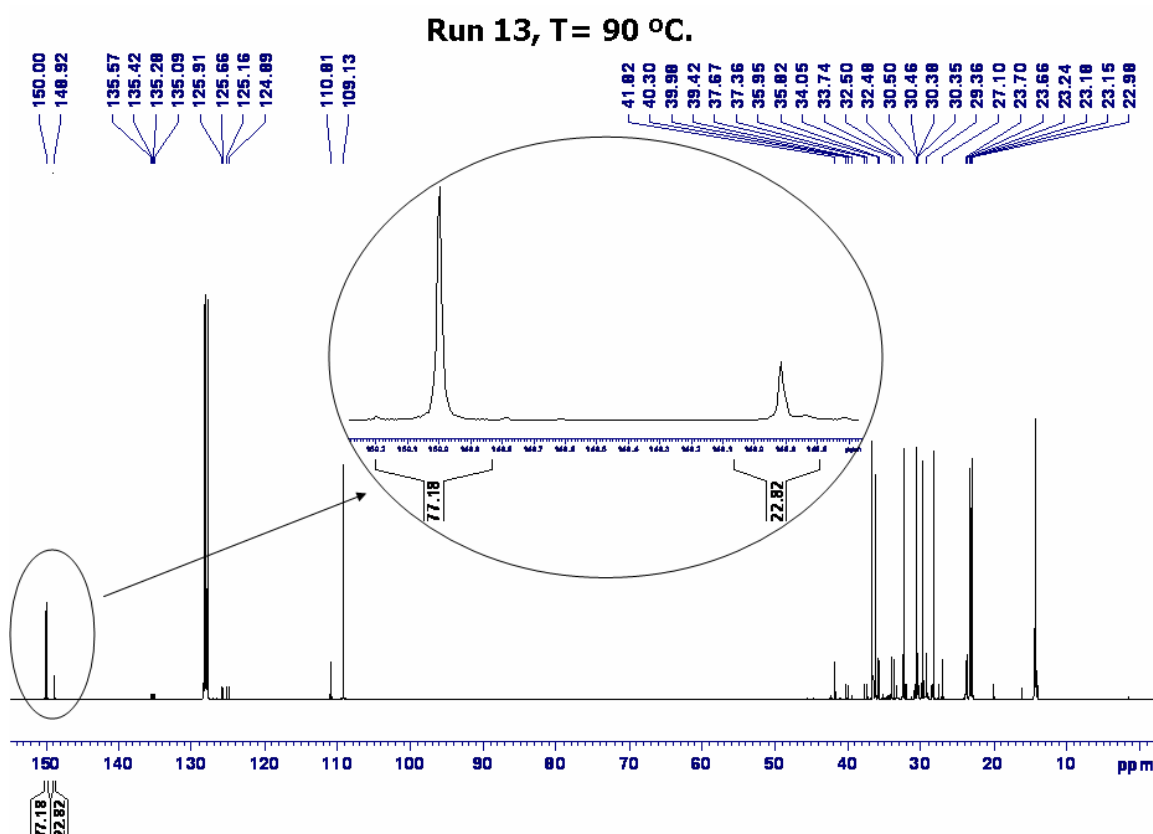


Figure S12. ^{13}C NMR spectrums (C_6D_6 , rt, d1=2s, 100 MHz) of the oligohexene sample from runs 10 and 13.



Run	% of the dimer ^a
10	48.65
11	54.07
12	61.50
13	77.18
a) Determined by ^{13}C -NMR analysis.	



Single-Crystal X-ray Structure Determination of Compound **2**·0.5C₃H₆O.

Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table 2. A suitable single crystal of **2** for the X-ray diffraction study was selected. Data collection was performed at 200(2) K, with the crystal covered with perfluorinated ether oil. The crystal was mounted on a Bruker-Nonius Kappa CCD single crystal diffractometer equipped with a graphite-monochromated Mo-K α radiation (λ = 0.71069 Å). Multiscan¹ absorption correction procedures were applied to the data. The structure was solved, using the WINGX package,² by direct methods (SHELXS-97) and refined using full-matrix least-squares against F^2 (SHELXL-97).³ All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms. A disordered acetone molecule per two molecules of **2** is present in the unit cell, this solvent molecule was found in the difference Fourier map but was very disordered and it was not possible to get a chemically sensible model for it, so the Squeeze procedure⁴ was used to remove its contribution to the structure factors. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-850723. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

1. R. H. Blessing, *SORTAV*, *Acta Cryst.*, 1995, **A51**, 33.
2. L. J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837.
3. G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **A64**, 112.
4. P. Van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* 1990, **A46**, 194.

Table S1. Crystallographic Data for 2·0.5C₃H₆O.

2·0.5C₃H₆O	
Formula	C ₁₈ H ₃₀ Cl ₂ O ₂ Si ₄ Zr·0.5 C ₃ H ₆ O
FW	581.94
Color/habit	White/prism
Cryst dimensions (mm ³)	0.30 x 0.27 x 0.15
Cryst syst	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	13.400(3)
<i>b</i> , Å	15.493(2)
<i>c</i> , Å	14.738(2)
β , (deg)	110.416(12)
<i>V</i> , Å ³	2867.5(8)
<i>Z</i>	4
<i>T</i> , K	200
ρ_{calcd} , g cm ⁻³	1.348
μ , mm ⁻¹	0.752
F(000)	1200
θ range, deg	3.54 – 27.51
no. of rflns collected	23936
no. of indep rflns / <i>R</i> _{int}	6570/0.1179
no. of data/restraints/params	6570 / 0 / 244
<i>R</i> 1/ <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0608 / 0.1415
<i>R</i> 1/ <i>wR</i> 2 (all data) ^a	0.1293 / 0.1613
GOF (on <i>F</i> ²) ^a	0.990
Largest diff peak / hole (e Å ⁻³)	0.595 and -0.426

$$^a R1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|; wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}; GOF = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$$

Supramolecular arrangement:

In the crystal the molecules are organized in chains along the *c*-axis connected through a hydrogen bond between Cl2 and one hydrogen atom from a Cp ring in the neighbouring molecule (C5-H5...Cl2, distance (C5...Cl2) = 3.819(5) Å and angle (C5-H5...Cl2) = 171.23(30)°). To achieve this arrangement, in the chain the molecules are rotated 90° in relation to each other.