

Supplementary data

Control of molecular weight in Ni(II)-catalyzed polymerization via the reaction medium

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Materials and General Considerations. Unless noted otherwise, all manipulations of nickel complexes were carried out under an inert atmosphere using standard glovebox or Schlenk techniques. All glassware was flame-dried under vacuum before use. Toluene and methyl cyclohexane were distilled from sodium, diethylether and THF from sodium / benzophenone under argon. Heptane and Pyridine were distilled from CaH₂. [(tmeda)NiMe₂] was supplied by MCAT (Konstanz, Germany), 4-(non-5-yl)pyridine was supplied by ABCR. Ethylene (3.5 grade) and carbon dioxide (5.5 grade) supplied by Praxair and Air Liquide, respectively, were used as received.

NMR spectra were recorded on a Varian Unity INOVA 400 or on a Bruker Avance DRX 600 spectrometer. ¹H and ¹³C NMR chemical shifts were referenced to the solvent signal. Multiplicities are given as follows: s: singlet, d: doublet, t: triplet, vt: virtual triplet, m: multiplet. High-temperature NMR spectroscopy of polyethylenes was performed in 1,1,2,2-tetrachloroethane-*d*₂ at 130 °C. Differential scanning calorimetry (DSC) was performed on a Netzsch Phoenix 204 F1 at a heating/cooling rate of 10 K min⁻¹. DSC data reported are from second heating cycles. Polymer crystallinities were calculated based on a melt enthalpy of 293 J g⁻¹ for 100% crystalline polyethylene. Gel permeation chromatography (GPC) was carried out in 1,2,4-trichlorobenzene at 160°C at a flow rate of 1 mL min⁻¹ on a Polymer Laboratories 220 instrument equipped with Olexis columns with differential refractive index, viscosity and light scattering (15° and 90°) detectors. Data reported were determined via triple detection employing the PL GPC220 software algorithm. As the instrument records light scattering at only two angles, data analysis involves an iteration for the calculation of molecular weights and form factors for each measured interval. The instrument was calibrated with narrow polystyrene and polyethylene standards. Data given is referenced to linear polyethylene.

The identity and purity of compounds **3**, **4** and **5** were established by ¹H, ¹³C and ³¹P NMR and elemental analysis. NMR assignments were confirmed by ¹H, ¹H gCOSY, ¹H, ¹³C gHSQC and ¹H, ¹³C gHMBC.

Polymerizations in organic solvents were carried out in a 250 mL stainless steel mechanically stirred (750 rpm) pressure reactor equipped with a heating/cooling jacket supplied by a thermostat controlled by a thermocouple dipping into the polymerization mixture. A valve controlled by a pressure transducer allowed for applying and keeping up a constant ethylene pressure. The required flow of ethylene, corresponding to ethylene consumed by polymerization was monitored by a mass flow meter and recorded digitally.

Prior to a polymerization experiment, the reactor was heated under vacuum to the desired reaction temperature for 30 – 60 min and then back-filled with argon. Solvent was introduced to the reactor. The catalyst precursor was weighed into a dry syringe in the drybox. Solvent was introduced to the reactor in an argon counter stream. The reactor was vented, and in a slight argon stream, solvent was soaked into the syringe several times, dissolving and transferring to the reactor the catalyst precursor. The reactor was closed and a constant ethylene pressure was applied. After the desired reaction time the reactor was rapidly vented and cooled to room temperature. The reaction mixture was stirred with an excess volume of methanol. The polymer was isolated by filtration, washed several times with methanol, and dried in vacuo at 50 °C.

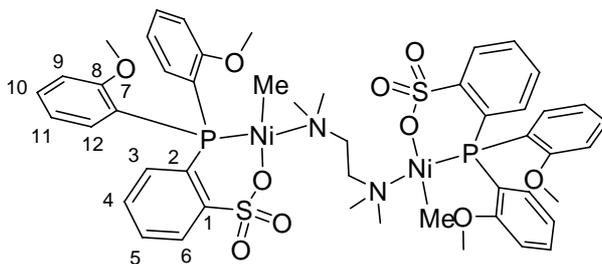
Polymerizations in supercritical carbon dioxide were carried out in a high-pressure view cell (NWA GmbH, Lörrach, Germany). The stainless steel cell has a variable internal volume between 30 and 60 cm³ tuneable by means of a piston operated by a hydraulic system. The piston material is a transparent sapphire which, together with a sapphire view window on the opposite side of the cell, allows for visually observing the contents of the cell. The cell contents can be agitated by means of a magnetically coupled stainless steel mechanical propeller stirrer. It can be heated by means of two stainless steel cartridge heaters lodged in cavities of the metallic body of the cell. The temperature inside the cell is measured by a thermocouple, and the pressure is monitored with a Bourdon type manometer.

The gases were introduced via high pressure pumps (up to 60 MPa for carbon dioxide and up to 40 MPa for ethylene) which employ the corresponding cold condensed liquids as a reservoir. The rate of the ethylene addition was controlled by a two way HPLC valve, with an internal loop volume of 1 mL. The quantities of gases introduced were estimated by the change in piston position and the pressure. Prior to a polymerization experiment, the reactor was heated under a low pressure of carbon dioxide (6 MPa) to the desired reaction temperature for 30 – 60 min, and then flushed 3 times with carbon dioxide. The catalyst precursor was added as a compressed pellet via a modified syringe. The reactor was closed and filled with carbon dioxide to the desired pressure (10 MPa). Under continuous stirring the

pressure was increased (to 30 MPa) by decreasing the cell volume via the piston, and the ethylene was added at constant pressure. After the addition of the desired amount of monomer, the polymerisations were carried out at a pressure of 65 MPa adjusted by moving the piston forward. The reaction was stopped by increasing the volume of the cell and the reactor was carefully vented.

***N,N'*-Bis[κ^2 -*P,O*-2-[di(2-methoxyphenyl)phosphino]benzenesulphonato]nickel(II)-methyl]-*N,N,N',N'*-tetramethylethylenediamine (3)**

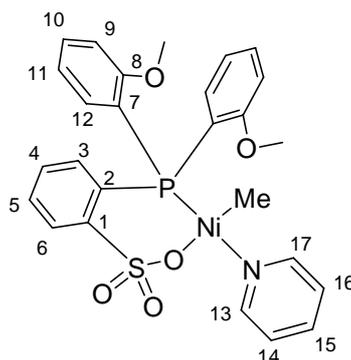
330 mg (0.82 mmol) of **2** and 168 mg (0.82 mmol) of [(tmeda)NiMe₂] were cooled to -30°C. 6 ml of cold THF (-30°C) were added to the solids. Gas evolution was observed followed by immediate precipitation of a yellow solid. The solution was stirred for 30 minutes at room temperature. The yellow precipitate was filtered off, washed with diethyl ether and dried under reduced pressure to yield 437 mg (0.80 mmol, 98%) of **3**.



¹H NMR (400 MHz, DMSO-*d*₆, 25 °C): δ 7.88 (m, 4H, 12-H), 7.70 (m, 2H, 3-H), 7.54 (vt, *J* = 8.31 Hz, 4H, 10-H), 7.46 (vt, *J* = 7.28 Hz, 2H, 4-H), 7.35 (vt, *J* = 8.03 Hz, 2H, 6-H), 7.18 (vt, *J* = 8.03, 2H, 5-H), 7.10 (m, 4H, 9-H), 7.06 (vt, *J* = 7.08, 4H, 11-H), 3.67 (s, 12H, OCH₃), 2.28 (s, 4H, NCH₂), 2.11 (s, 12H, NCH₃), -1.31 (d, ³*J*_{PH} = 5.7 Hz, 6H, NiCH₃). ³¹P NMR (400 MHz, dmsO-*d*₆, 25 °C): δ 14.87 Anal. Calcd. (%) for C₄₈H₅₈N₂Ni₂O₁₀P₂S₂: C, 54.06; H, 5.48; N, 2.63; Found: C, 54.90; H, 5.36; N, 2.27.

**{ κ^2 -*P,O*-2-[Di(2-methoxyphenyl)phosphino]benzenesulphonato}nickel(II)-methyl
pyridine (4)**

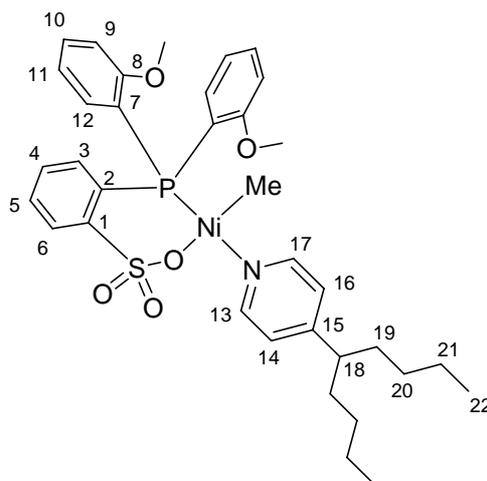
82.5 mg (0.20 mmol) of **2** and 42 mg (0.20 mmol) of [(tmeda)NiMe₂] were cooled to -30 °C. 4 ml of cold THF and 0.5 ml of pyridine were added to the solids under vigorous stirring. The solution was stirred for 30 minutes at room temperature. The yellow precipitate was filtered off, washed with diethyl ether and dried under reduced pressure to yield 98 mg (0.18 mmol, 86%) of **4**.



¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 8.85 (s, br, 2H, 13- and 17-H), 7.91 (m, 1H, 3-H), 7.83 (m, 2H, 12-H), 7.55 (vt, *J* = 8.0 Hz, 2H, 10-H), 7.44 (vt, *J* = 7.4 Hz, 1H, 4-H), 7.26 (m, 2H, 5- and 6-H), 7.04 (vt, *J* = 8.0 Hz, 2H, 11-H), 7.01 (m, 2H, 9-H), 14-, 15- and 16-H not detected, 3.81 (s, 6H, OCH₃), -0.98 (d, ³*J*_{PH} = 7.6 Hz, 3H, NiCH₃). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 25 °C): δ 161.2 (d, ²*J*_{PC} = 2.5 Hz, 2 × C8), 150.7 (br, C13 and C17), 148.3 (d, ²*J*_{PC} = 14.7 Hz, C1), 137.8 (d, ²*J*_{PC} = 11.4 Hz, C12), 134.5 (C5), 133.5 (d, ⁴*J*_{PC} = 1.6 Hz, C10), 130.5 (d, ³*J*_{PC} = 1.7 Hz, C4), 129.1 (d, ³*J*_{PC} = 6.3 Hz, C6), 127.6 (d, ¹*J*_{PC} = 40.7 Hz, C2), 125.3 (br, C14 and C16), 121.1 (d, ³*J*_{PC} = 10.4 Hz, C11), 117.1 (d, ¹*J*_{PC} = 52.5 Hz, C7), 111.9 (d, ³*J*_{PC} = 4.2 Hz, C9), 55.9 (OCH₃), -10.5 (d, ²*J*_{PC} = 34.8 Hz, Ni-CH₃), C3 and C15 not detected. ³¹P NMR (400 MHz, CD₂Cl₂, 25 °C): δ 16.22. Anal. Calcd. (%) for C₂₆H₂₆NNiO₅PS: C, 56.35; H, 4.73; N, 2.53; Found: C, 56.43; H, 4.95; N, 2.58.

{ κ^2 -*P,O*-[2-Di(2-methoxyphenyl)phosphino]benzenesulphonato}nickel(II)-methyl 4-(non-5-yl)pyridine (5)

100 mg (0.22 mmol) of **2** and 46 mg (0.22 mmol) of [(tmeda)NiMe₂] were cooled to -30 °C. 4 ml of cold THF and 0.1 ml of 4-(non-5-yl)pyridine were added to the solids under vigorous stirring. The orange solution was allowed to stir at room temperature for 1 hour. The solvent was removed under reduced pressure and the residue was washed with pentane and dissolved in benzene. The solvent was removed by sublimation at -10°C (crushed ice / sodium chloride) under high vacuum (10⁻³ mbar) to yield 113 mg (76%) of **5**.



¹H NMR (600 MHz, C₆D₆, 25 °C): δ 8.90 (2 H, s, 13- and 17-H), 8.48 (1 H, dd, ³J_{HH} = 7.5, ⁴J_{PH} = 4.6, 6-H), 8.14 (2 H, dd, ³J_{PH} = 12.7, ³J_{HH} = 6.5, 12-H), 7.30 (1 H, vt, J = 7.3, 3-H), 7.12 (2 H, vt, J = 7.8, 10-H), 6.97 (1 H, vt, J = 7.5, 5-H), 6.86 – 6.79 (3 H, m, 11-H and 4-H), 6.47 (2 H, d, J = 7.8, 9-H), 6.45 (2 H, d, J = 7.8, 14- and 16-H), 3.25 (6 H, s, OCH₃), 2.03 (1 H, m, 18-H), 1.33 – 0.80 (12 H, m, 19- to 21-H), 0.77 (6 H, t, ³J_{HH} = 7.3, 22-H), -0.55 (3 H, d, ³J_{PH} = 7.1, NiCH₃). ¹³C{¹H} NMR (151 MHz, C₆D₆, 25°C): δ 161.38 (s, C8), 150.80 (s, C13 and C17), 150.64 (d, ²J_{PC} = 14.9, C1), 138.26 (d, ²J_{PC} = 9.9, C12), 134.08 (s, C3), 133.12 (s, C10), 130.54 (s, C5), 128.10 (C4), 127.98 (C6), C2 obscured by solvent signal, 124.37 (br. s, C14 and C16), 121.26 (d, ³J_{PC} = 10.5, C11), 118.31 (d, ¹J_{PC} 51.6, C7), 111.90 (d, J = 4.2, C9), 55.49 (s, OCH₃), 45.98 (s, C18), 35.99 (s, C19), 30.10 (s, C20), 23.35 (s, C21), 14.43 (s, C22), -10.10 (d, ²J_{PC} = 36.5 Ni-CH₃). C15 not detected. ³¹P NMR (400 MHz, C₆D₆, 25°C): δ 13.32. Anal. Calcd. (%) for C₃₅H₄₄NNiO₅PS: C, 61.78; H, 6.52; N, 2.06; Found: C, 61.57; H, 6.51; N, 2.15.

X-Ray diffraction analysis of complex 4. Rhombohedral pale yellow crystals of **4** suitable for X-Ray diffraction analysis were grown by slow diffusion of pentane into a methylene chloride solution.

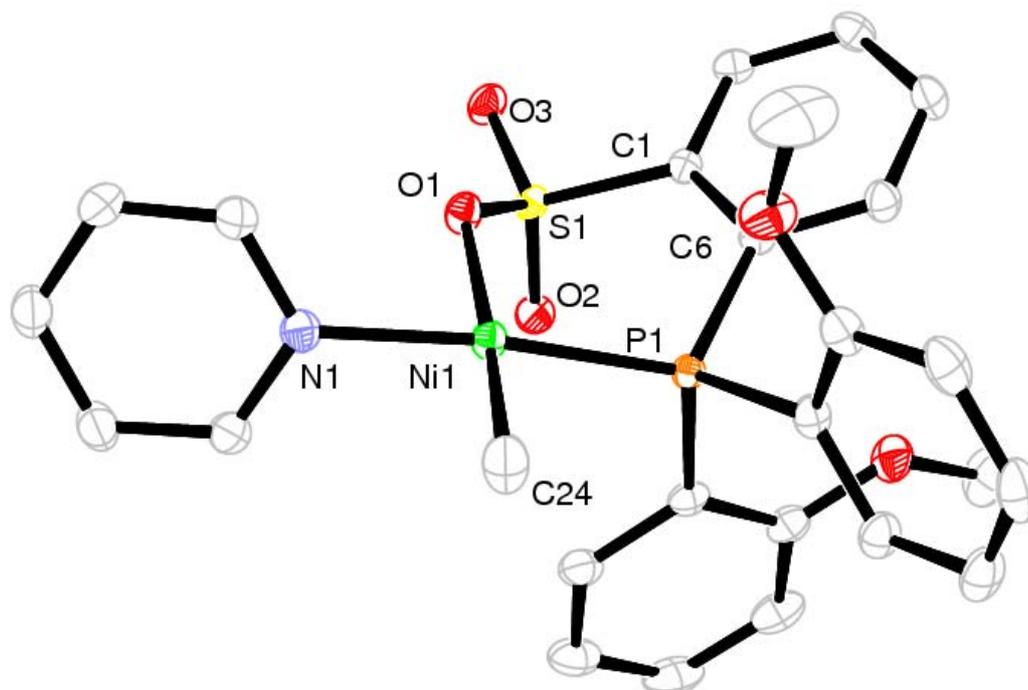


Figure S1. Molecular structure of complex **4** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S1. Selected bond distances [Å] and angles [°] for **4**.

Ni1-C24	1.930(2)	N1-Ni1-C24	91.57(9)	O1-Ni1-P1-C6	24.38(8)
Ni1-N1	1.9364(17)	O1-Ni1-C24	74.52(9)	Ni1-P1-C6-C1	64.76(12)
Ni1-O1	1.9696(14)	P1-Ni1-C24	89.17(7)	P1-C6-C1-S1	4.4(2)
Ni1-P1	2.1588(5)	N1-Ni1-P1	171.29(5)	C6-C1-S1-O1	24.38(8)
P1-C6	1.8335(19)	Ni1-P1-C6	112.54(6)	C24-Ni1-P1-C6	152.09(11)
S1-O1	1.4857(14)	Ni1-O1-S1	127.81(8)	C24-Ni1-O1-S1	166.4(9)
S1-O2	1.4456(14)	O1-S1-C1	104.96(8)	N1-Ni1-O1-S1	144.73(12)
S1-O3	1.4430(14)	S1-C1-C6	121.75(14)	Ni1-O1-S1-C1	64.76(12)
S1-C1	1.7780(19)	C1-C6-P1	121.39(14)		

Table S2. Crystallographic Data of Complex 4

CCDC deposit no	CCDC 693181
Crystal description	pale yellow rhombus
Formula	C ₂₆ H ₂₆ N Ni O ₅ P S
Crystal Size [mm ³]	0.4 × 0.3 × 0.15
Crystal System	monoclinic
Space group	P21/c (No 14)
<i>a</i> [Å]	11.4740(7)
<i>b</i> [Å]	13.8165(6)
<i>c</i> [Å]	16.0318(10)
α [°]	90
β [°]	98.617(5)
γ [°]	90
<i>V</i> [Å ³]	2512.8(2)
<i>Z</i>	4
<i>M_r</i> [g·mol ⁻¹]	554.22
ρ_{calc} [g·cm ⁻³]	1.465
μ (Mo-K α) [cm ⁻¹]	0.957
<i>F</i> (000) [e]	1152
<i>T</i> [K]	100(2)
Wavelength [Å]	0.71073 (Mo-K α)
Diffractometer	STOE IPDS 2T
Scan	ω -scan
$\theta_{\text{min-max}}$ [°]	1.8 - 28
($\sin\theta/\lambda$) _{max} [Å ⁻¹]	0.6605
Data total / unique	41727 / 6018
<i>R</i> _{int}	0.0921
<i>R</i> _{sigma}	0.0521
Data obs ($F^2 \geq 4\sigma(F^2)$)	5141
<i>hkl</i> -range	-15:15; -18:17; -21:21
Absorption correction	Numerical Integration ^[1]
Structure Solution	SHELXS-97 ^[2]
Structure Refinement	SHELXL-97 ^[3]
H atoms	geom, mixed
Number Parameters	316
<i>R</i> (<i>F</i>) obs. / all	0.035 / 0.0491
w <i>R</i> (<i>F</i> ²) all	0.0863
<i>w</i> (<i>a</i> , <i>b</i>) ^[a]	0.0394, 2
Go <i>F</i> (<i>F</i> ²)	1.089
<i>dU</i> _{max}	0.000
$\Delta\rho_{\text{fin}}$ (min./max.) [e·Å ⁻³]	-0.47 / 0.43

[a] weighting scheme: $w = 1/[\sigma^2(\text{Fo}^2) + (a \cdot \text{P})^2 + b \cdot \text{P}]$, $\text{P} = [\max(\text{Fo}^2, 0) + 2 \text{Fc}^2]/3$.

[1] X-RED version 1.31, Stoe Data Reduction Program, Darmstadt, Germany, 2005.

[2] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Analysis, Univ. Göttingen, Germany, 1997.

[3] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Univ. Göttingen, Germany, 1997.

[4] C. K. Johnson, M. N. Burnett, ORTEP-III, v. 1.0.2, Oak Ridge National Laboratory, Tennessee, USA, 1996.

Low molecular weight polyethylene obtained at 90°C, 40 bar ethylene with complex 4 in toluene (table 1 entry 8)

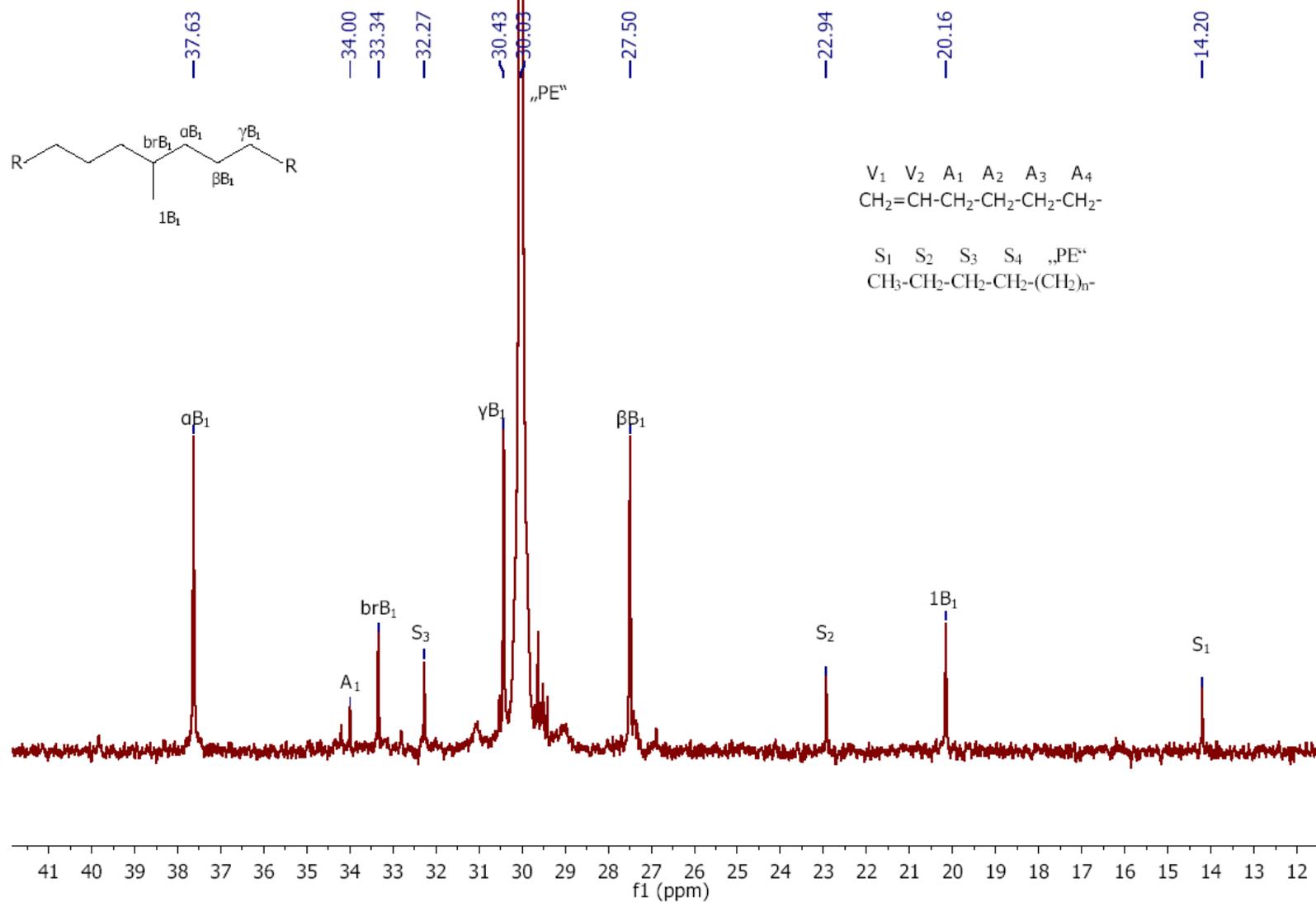


Figure S2. ^{13}C NMR spectrum of a low molecular weight branched polyethylene (Table 1, entry 8).

High molecular weight polyethylene obtained at 90°C, 40 bar ethylene with complex 4 in heptane (table 1 entry 10)

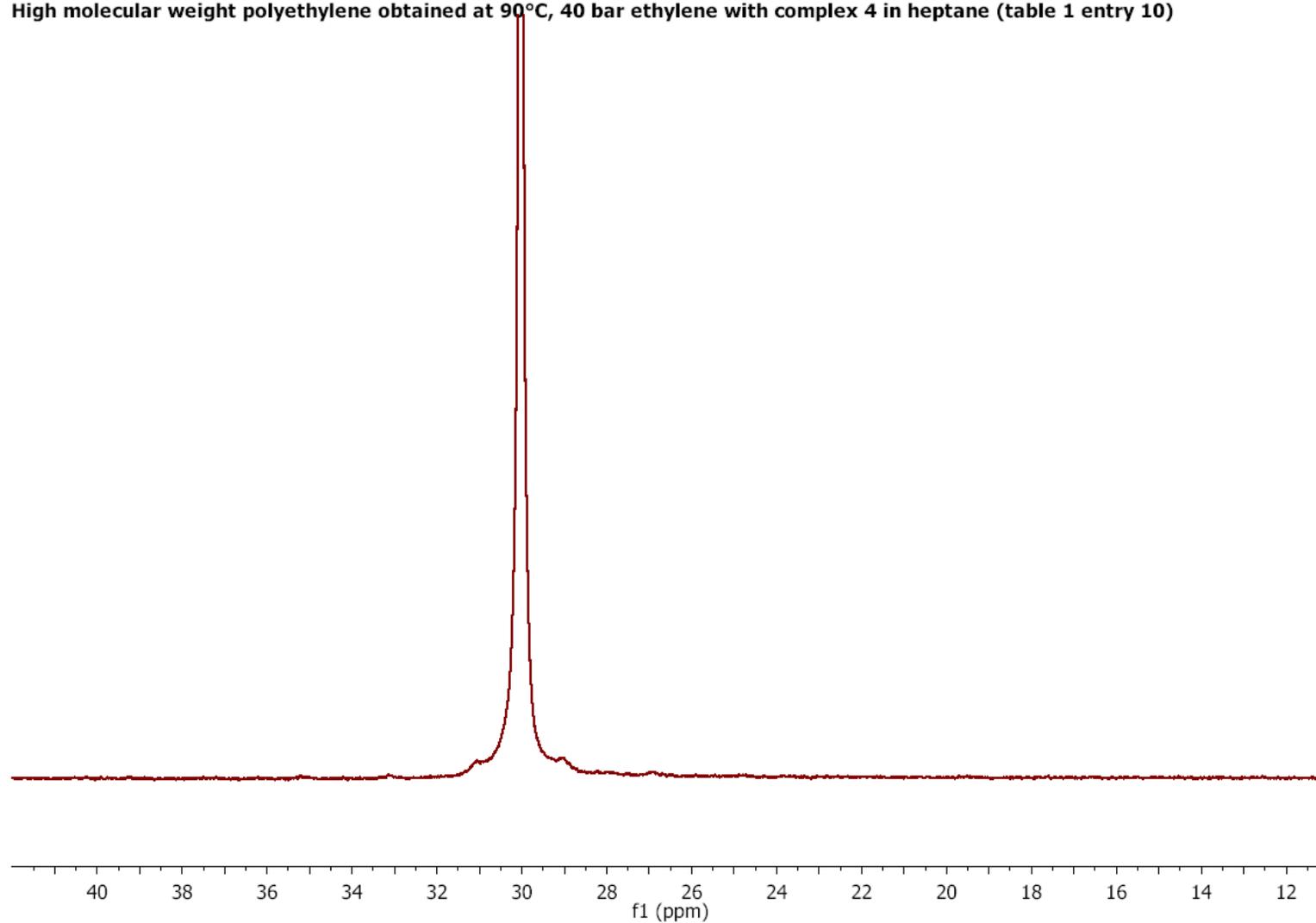


Figure S3. ^{13}C NMR spectrum of a high molecular weight linear polyethylene (Table 1, entry 10).

