Supporting Information for:

Copolymerization of Ethylene and 3,3,3-Trifluoropropene Using (Phosphine-Sulfonate)Pd(Me)(dmso) as Catalyst

Dominik Lanzinger, Marco M. Giuman, Timo M. J. Anselment, Bernhard Rieger*
WACKER-Lehrstuhl für Makromolekulare Chemie , Technische Universität München,
Lichtenbergstraße 4, 85747 Garching
E-mail: rieger@tum.de

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I. Experimental procedures

Materials and general consideration:

All manipulations were performed using a *MBraun LABMASTER 130* glove box or Schlenk techniques under an argon atmosphere. Dimethylsulfoxide (≥ 99%, Aldrich) was distilled from CaH_2, tetrahydrofurane, toluene, and methylene chloride (Merck pro analysis) were dried in a Mbraun MB-SPS-800 solvent purification system and degassed prior to use. Ethylene (99.95%) was supplied by Westfahlen and used without further purification. Ethylene-d_4 (99.8 atom % D) was supplied by CDN ISOTOPES and compressed by condensation into a 25 mL gas cylinder prior to use.

Preparation of catalyst 1 {(κ^2-P,O)-2-[di(2-methoxyphenyl)-phosphine]benzenesulfonato}(dimethylsulfoxide)

{(κ^2-P,O)-2-[di(2-methoxyphenyl)-phosphine]benzenesulfonato}(dimethylsulfoxide) was prepared according to reported procedures.[1]

Polymerisation experiments:

Polymerisation experiments were performed in a 50 mL steel autoclave. 30 mL of toluene were transferred into the reactor and heated to 95 °C. 1.8 mg (3 µmol) of catalyst **1**, as well as 33 mg (150 µmol) of 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) were dissolved in 0.9 mL of methylene chloride. This solution was then transferred into a sample drum attached to the reactor under exclusion of light. For the copolymerisation experiments the required amount (determined by a *Bronkhorst HIGH-TECH B.V. E7000* flow meter) of TFP was condensed into a previously evacuated sample drum at -78 °C and slowly warmed to room temperature over a period of 30 minutes. Subsequently the catalyst/BHT-solution was transferred into the reactor via the TFP pressure. Ethylene was added via the same sample drum to reach the desired ethylene partial pressure. This pressure was kept constant during the reaction. After 30 minutes the reactor was cooled to room temperature and the pressure was released in order to stop the reaction. The formed polymer was isolated by precipitation from methanol and centrifugation. The polymer was dried under reduced pressure at 60 °C for 24 hours.

The copolymerization of etylene-d_4 and TFP was performed in a 50 mL steel autoclave which was filled with 30 mL of toluene and heated to 95 °C. Then ethylene-d_4 was added to the toluene solution until a constant ethylene-d_4 partial pressure of 3 bar was reached. A solution of 1.8 mg (3 µmol) of catalyst 1 in 0.9 mL of methylene chloride was added together with 8.7 g of TFP. The reaction was stopped after 30 min by depressurizing the reactor and adding the reaction solution to methanol. The formed polymer was isolated by precipitation from methanol and centrifugation. The polymer was dried under reduced pressure at 60 °C for 24 hours yielding 64 mg of copolymer.

Polymer characterization:

For all ethylene-TFP copolymers ^{1}H- and ^{13}C-NMR spectra were Recorded with a *BRUKER AVIII-300* spectrometer at 130 °C using bromobenzene-d_5 as solvent. The furthest upfield peak of the solvent signal was referenced to $\delta = 7.00$ ppm for ^{1}H-NMR and $\delta = 123.00$ ppm for ^{13}C-NMR. The spectral width, as well as the transmitter frequency offset was customized to enhance the quality of the spectra. Polymers with high fluorine contents (*e.g.* entry 8) are sufficiently soluble in bromobenzene d5 to allow room temperature NMR. For ^{13}C- and ^{1}H-NMR we could show for the polymer of entry 8 that the ratios of all integrals are the same for high temperature and room temperature measurements. Nevertheless the quality of the spectra was better for those measurements performed on the spectrometers with stronger magnetic fields (11.75 T; 500 MHz for ^{1}H). Therefore we chose to present the room temperature ^{13}C-NMR spectrum in the manuscript. ^{19}F-NMR spectra were recorded at 20 °C on a *Bruker AV500CRYO* spectrometer for the polymer of entry 8 and were referenced to a hexafluorobenzene standard (δ = -164.9 ppm). COSY-, HSQC- and HMBC-NMR spectra were recorded at 20 °C on a *Bruker AV500* spectrometer.

The ^{19}F-NMR spectrum of the ethylene-d_4-TFP copolymer was Recorded with a *Bruker Avance DRX 400* spectrometer at 80 °C. The spectral width, as well as the transmitter frequency offset was customized to enhance the quality of the spectrum.

Molecular weights were determined by size exclusion chromatography at 160°C in 1,2,4-trichlorobenzene using a *Polymer Laboratories* chromatograph *PL-GPC 220* equipped with two *Olexis 300-7.5 mm* columns, differential refraction index detector, differential viscosimeter and light scattering detector at 15° and 90° angles. Evaluation of the molecular weights was performed by triple detection method using Cyrrus Software package.

Elemental analyses were performed by using the *Vario EL analyzer (Elementar)* at the Department of Inorganic Chemistry, Technische Universität München.

II. Table of analytical data for all polymerization experiments

Table S 1. Copolymerization of ethylene and 3,3,3-trifluoropropene.[a]

entry	TFP (g)	p(C2H4)[c]	yield (g)	F/(E+G)[d]	CH_3-/10^3 C[e]	CF_3-/10^3 C[f]	% F (NMR)[g]	% F (EA)[h]	TFP (mol %)[i]	Mw [kg/mol][j]	Mn [Kg/mol][j]	PDI[j]
1[b]	0	5	0.85	1.3	6.0	0.0	0.0	0.0	0.0	12.6	7.5	1.7
2	0	5	0.78	0.75	6.5	0.0	0.0	0.0	0.0	15.4	9.9	1.6
3	4.35	2.5	0.18	1.8	9.4	21	7.7	6.6	3.5	8.4	5.2	1.6
4	4.35	5	0.79	0.79	5.1	9.6	3.6	3.9	2.0	8.3	5.2	1.6
5	4.35	15	1.61	0.59	2.3	4.6	1.7	1.2	0.6	17.4	10.4	1.7
6	4.35	30	3.02	0.20	< 5.0	< 5.0	n.d.	0.6	0.3	24.1	15.0	1.6
7	8.7	5	0.16	3.8	6.6	19	7.0	6.8	3.6	9.8	6.1	1.6
8	8.7	2.5	0.11	2.1	6.2	47	17	15	8.9	8.3	5.1	1.6
9[b]	4.35	5	0.60	1.1	4.6	13	5.0	4.6	2.4	12.5	8.0	1.6

[a] Conditions: 3 µmol of complex **1**, 30 mL of toluene, 0.9 mL of methylene chloride, 150 µmol BHT, 95 °C, 30 min, in a 50 mL autoclave. [b] Experiments were conducted without BHT. [c] Ethylene partial pressure in bar. [d] Ratio of internal to terminal olefinic groups determined from ^{1}H-NMR spectra. [e] Amount of CH_3-branches determined from ^{13}C-NMR spectra. [f] Amount of CF_3-branches determined from ^{13}C-NMR spectra. [g] Fluorine content in wt % calculated from CF_3 /10^3 C. [h] Fluorine content in wt% determined by elemental analysis. [i] mol% of TFP incorporated into the copolymer calculated from % F (EA). [j] Determined by size exclusion chromatography.

III. Representative NMR spectra of a TFP-rich ethylene/TFP copolymer

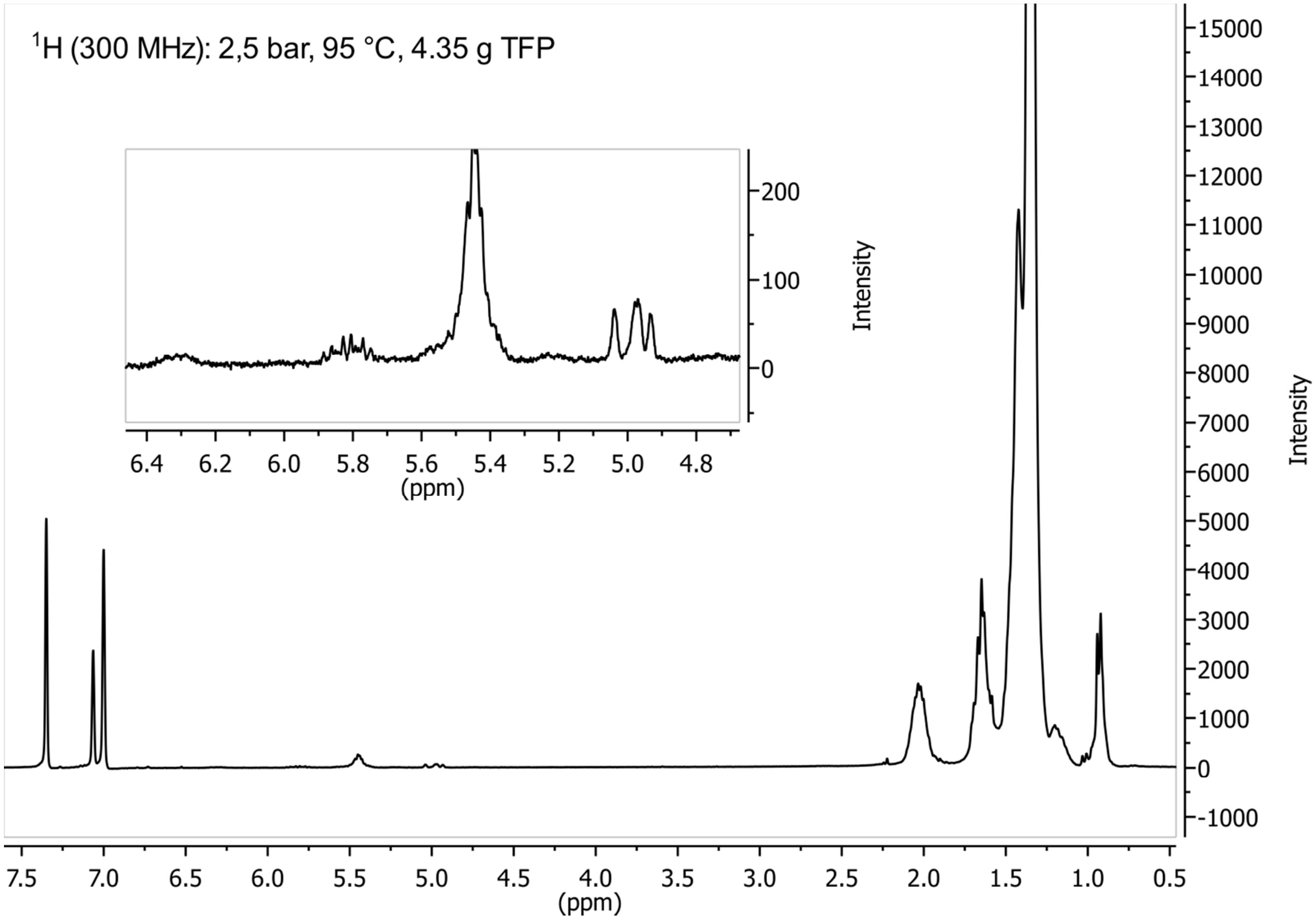


Figure S 1. ^{1}H-NMR spectrum (300 MHz, C_6D_5Br, 130 °C) of ethylene/TFP copolymer from entry 8. Recorded with a *Bruker AVIII-300* spectrometer with a spectral width of 8 ppm and a transmitter offset frequency of 4 ppm. Expansion of the δ 0.5 to 7.5 ppm and δ 4.7 to 6.4 ppm region.

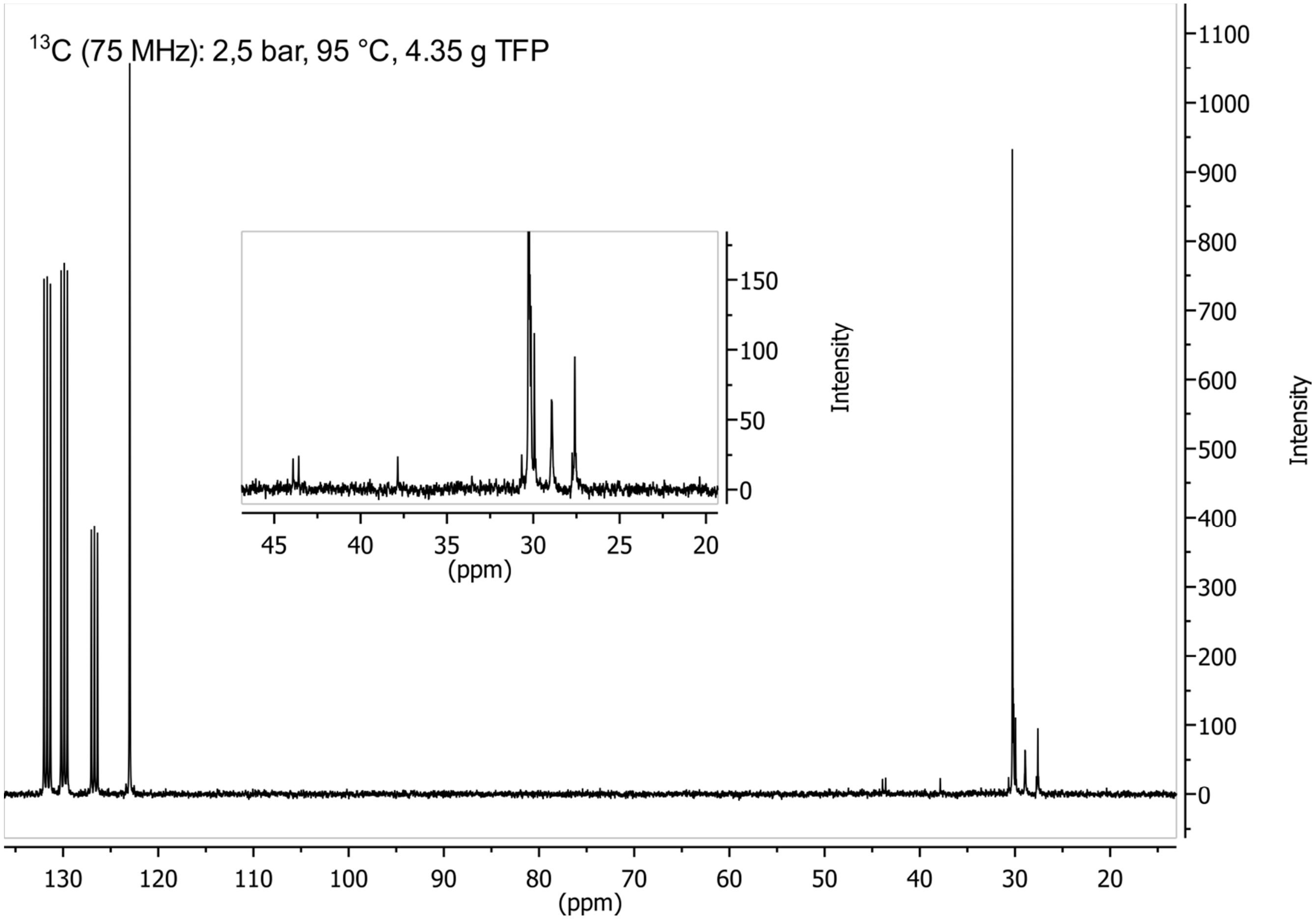


Figure S 2: ^{13}C-NMR spectrum (75 MHz, C_6D_5Br, 130 °C) of ethylene/TFP copolymer from entry 2. Recorded with a *Bruker AVIII-300* spectrometer with a spectral width of 130 ppm and a transmitter offset frequency of 75 ppm. Expansion of the δ 15 to 135 ppm and δ 20 to 46 ppm region.

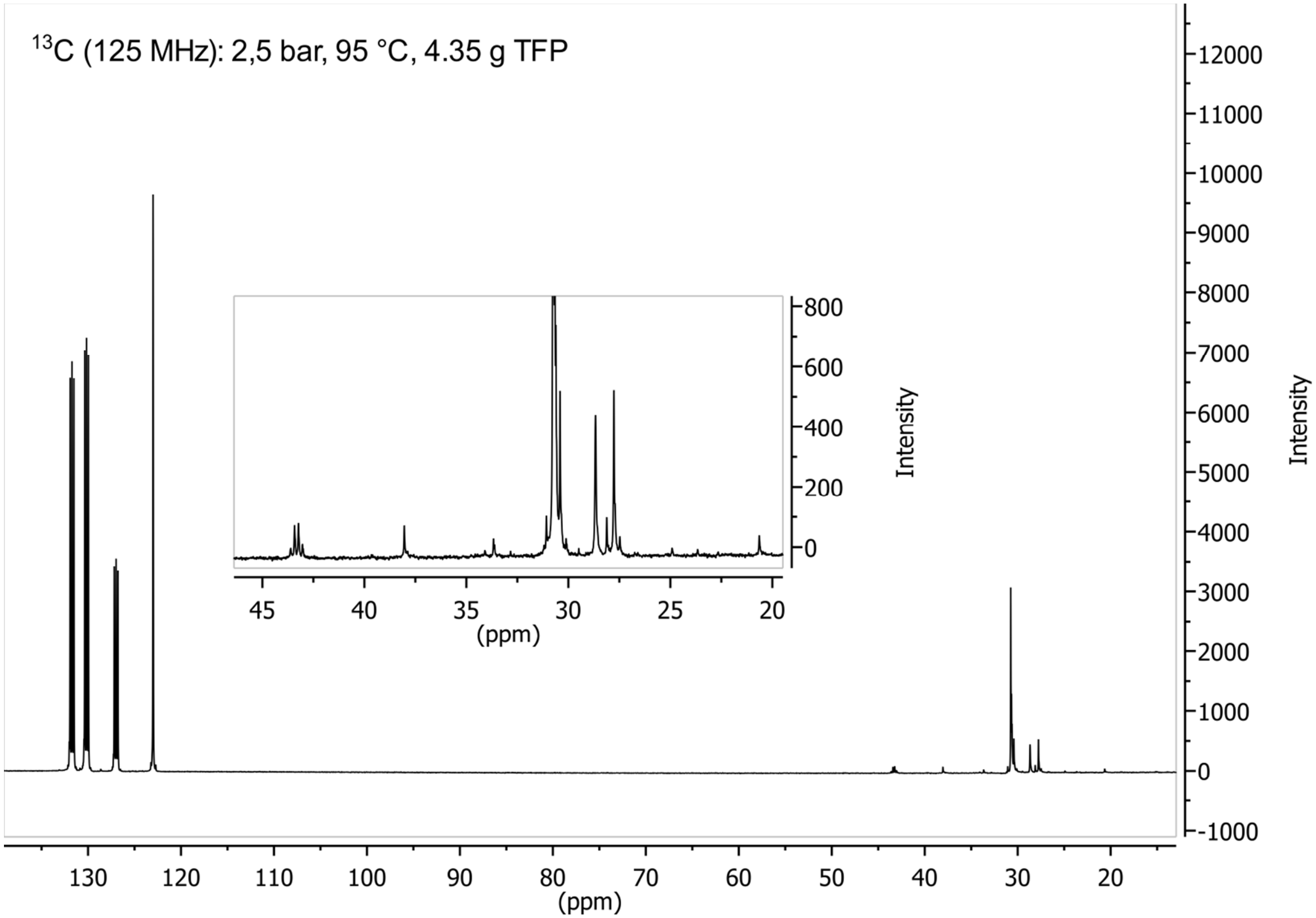


Figure S 3: ^{13}C-NMR spectrum (125 MHz, C_6D_5Br, 20 °C) of ethylene/TFP copolymer from entry 2. Recorded with a *Bruker AV500CRYO* spectrometer. Expansion of the δ 15 to 135 ppm and δ 20 to 46 ppm region.

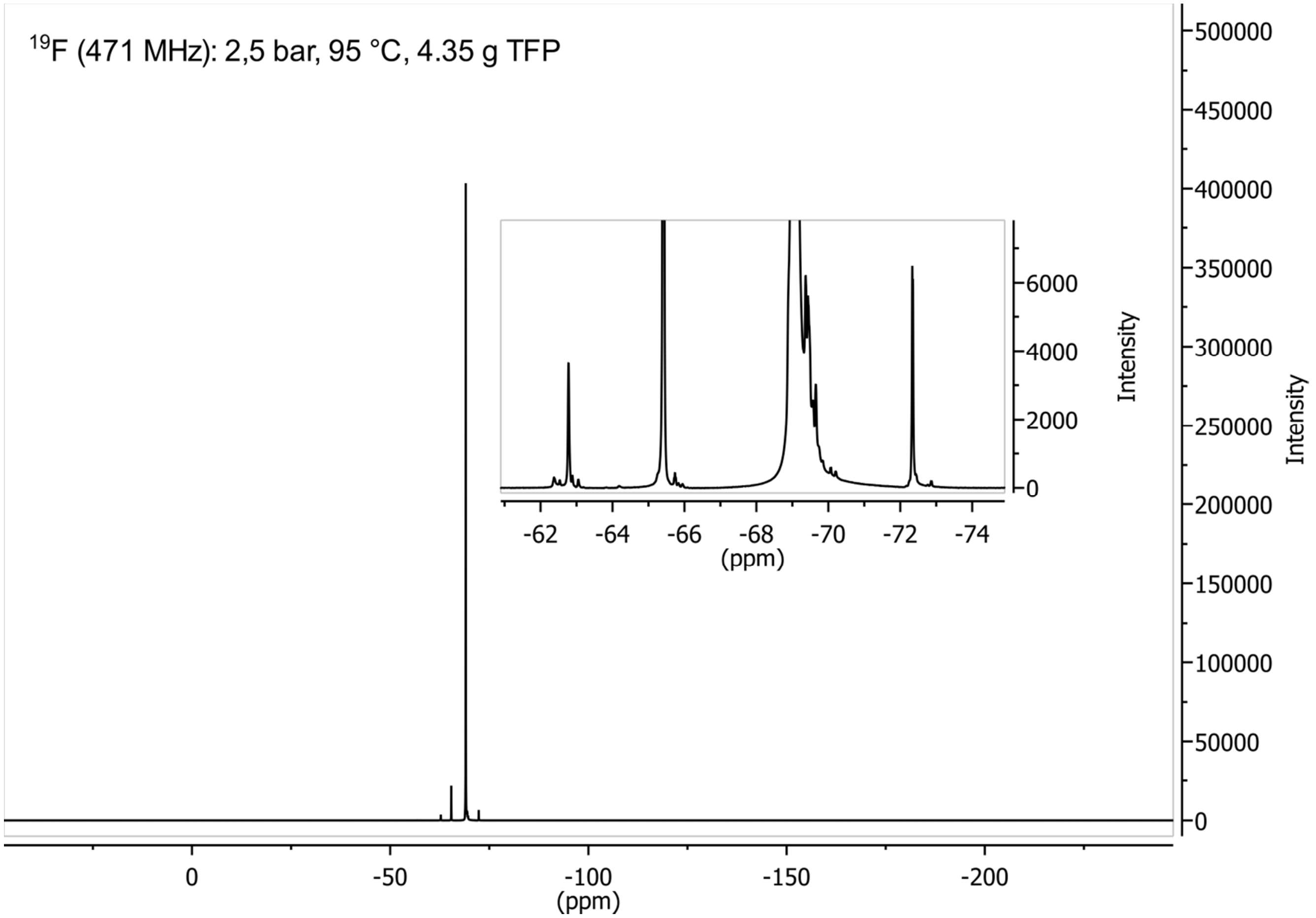


Figure S 4: **^{19}F-NMR spectrum (471 MHz, C_6D_5Br, 20 °C) of ethylene/TFP copolymer from entry 8. Recorded with a Bruker *AV500CRYO* spectrometer. Expansion of the δ -240 to 40 ppm and δ -74 to -61 ppm region.**

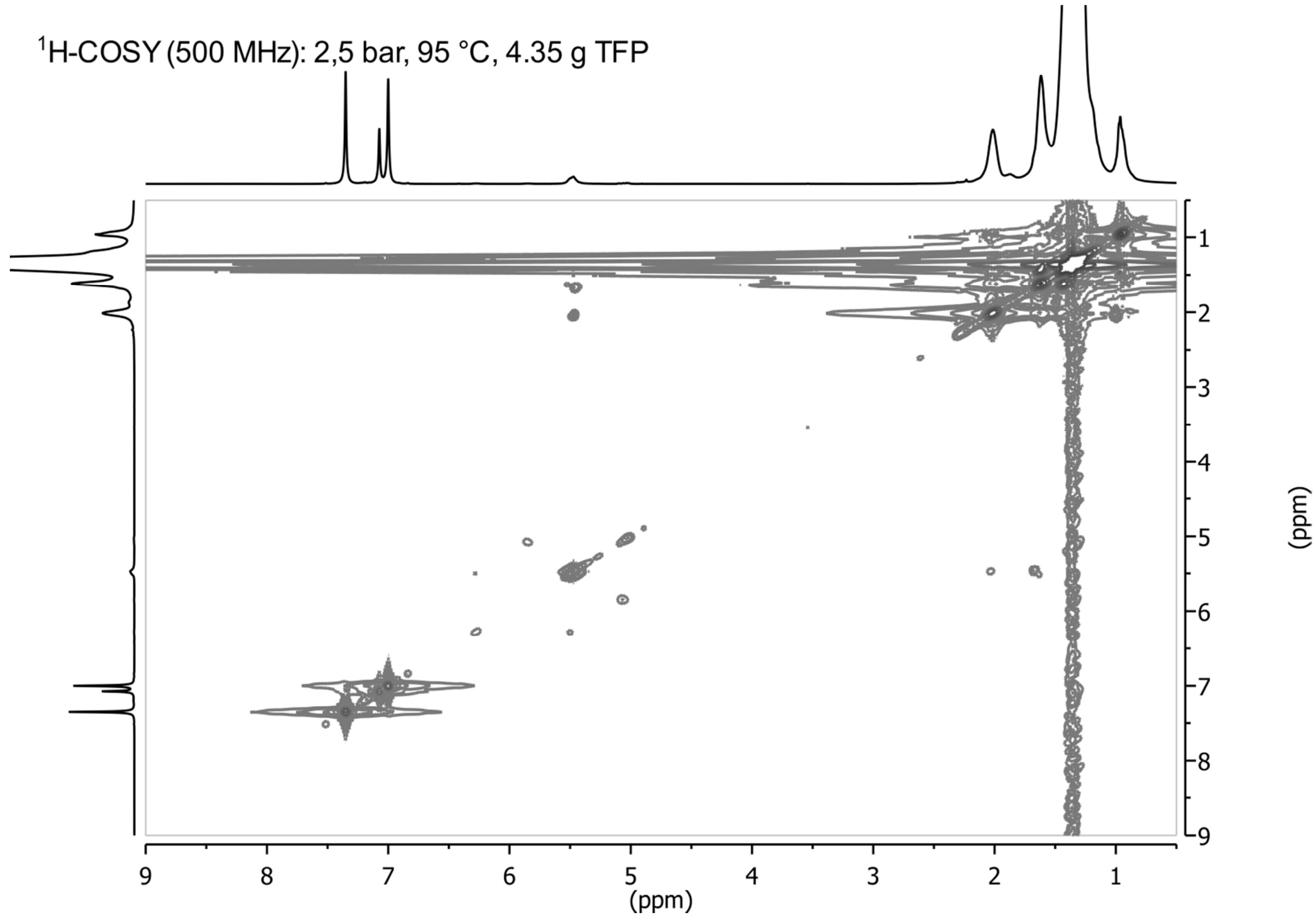


Figure S 5: ^{1}**H-COSY-NMR spectrum (500 MHz C_6D_5Br, 20 °C) of ethylene/TFP copolymer from entry 8. Recorded with a** ***Bruker AV500*** **spectrometer. Expansion of the δ 0.5 to 9 ppm region.**

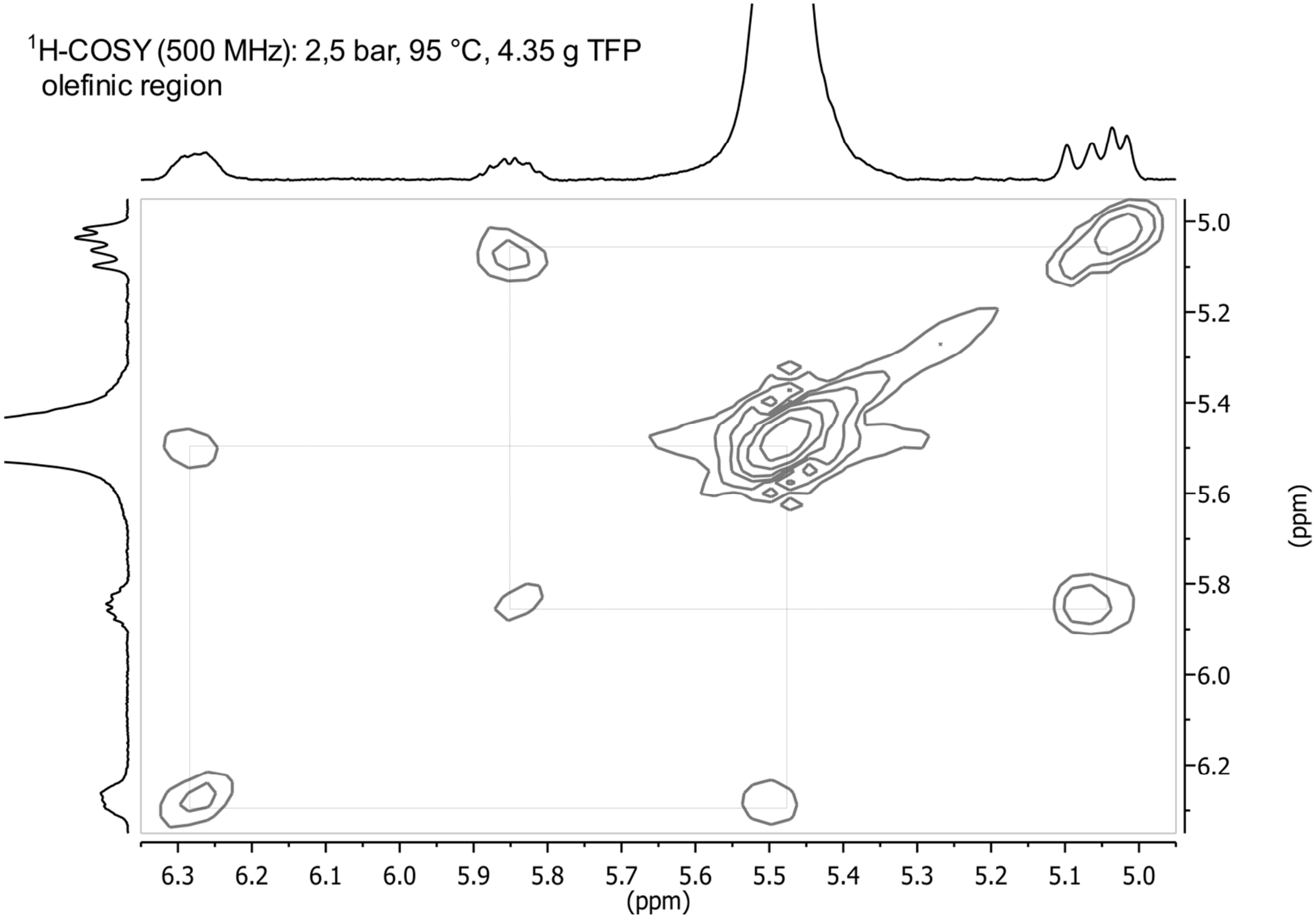


Figure S 6: ^{1}H-COSY-NMR spectrum (500 MHz C_6D_5Br, 20 °C) of ethylene/TFP copolymer from entry 8. Recorded with a *Bruker AV500* spectrometer. Expansion of the δ 5.0 to 6.3 ppm region.

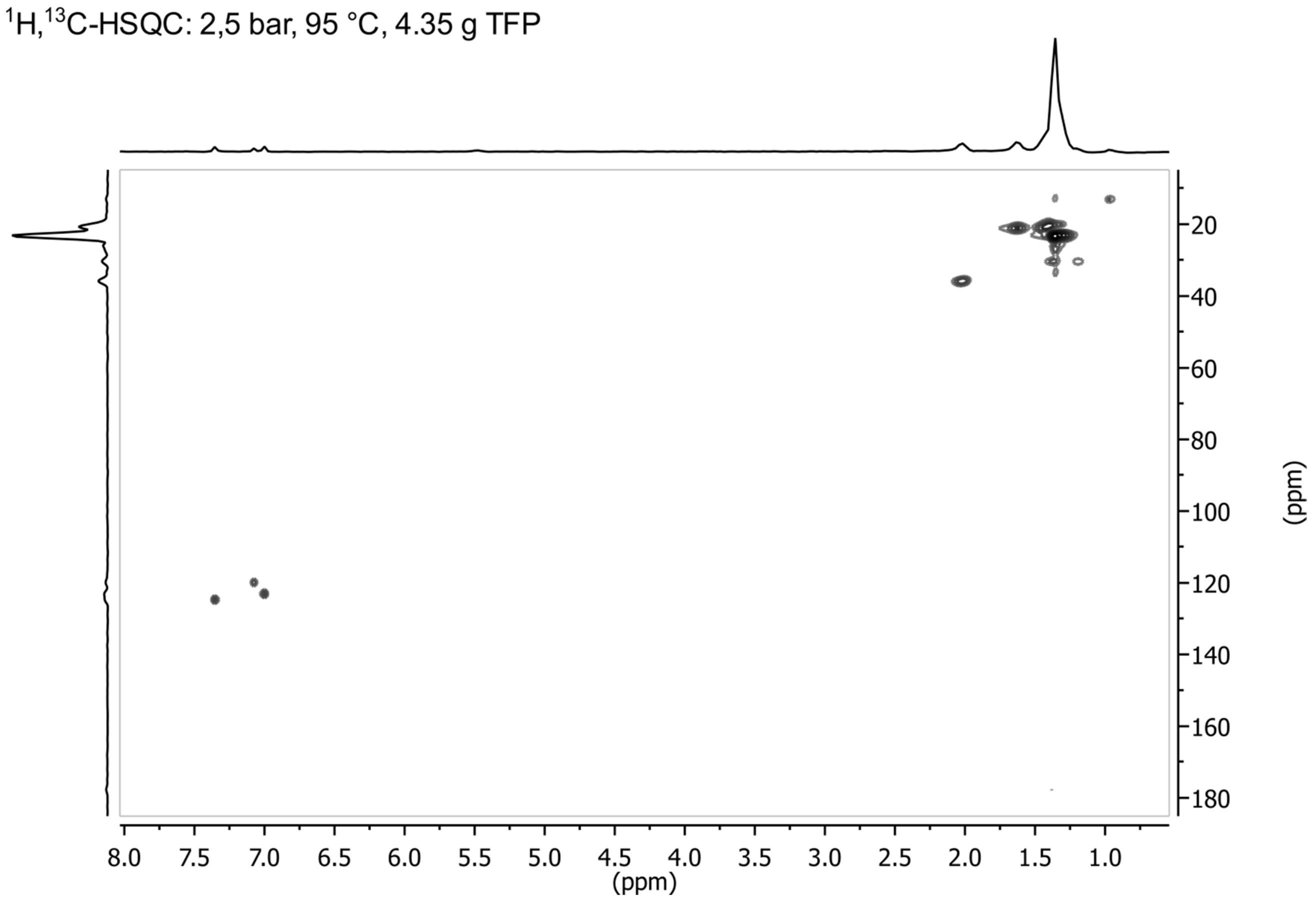


Figure S 7: HSQC-NMR spectrum (C_6D_5Br, 20 °C) of ethylene/TFP copolymer from entry 8. Recorded with a *Bruker AV500* spectrometer. Expansion of the δ 0.5 to 8 ppm region.

IV. Representative NMR spectra of a ethylene homopolymer sample

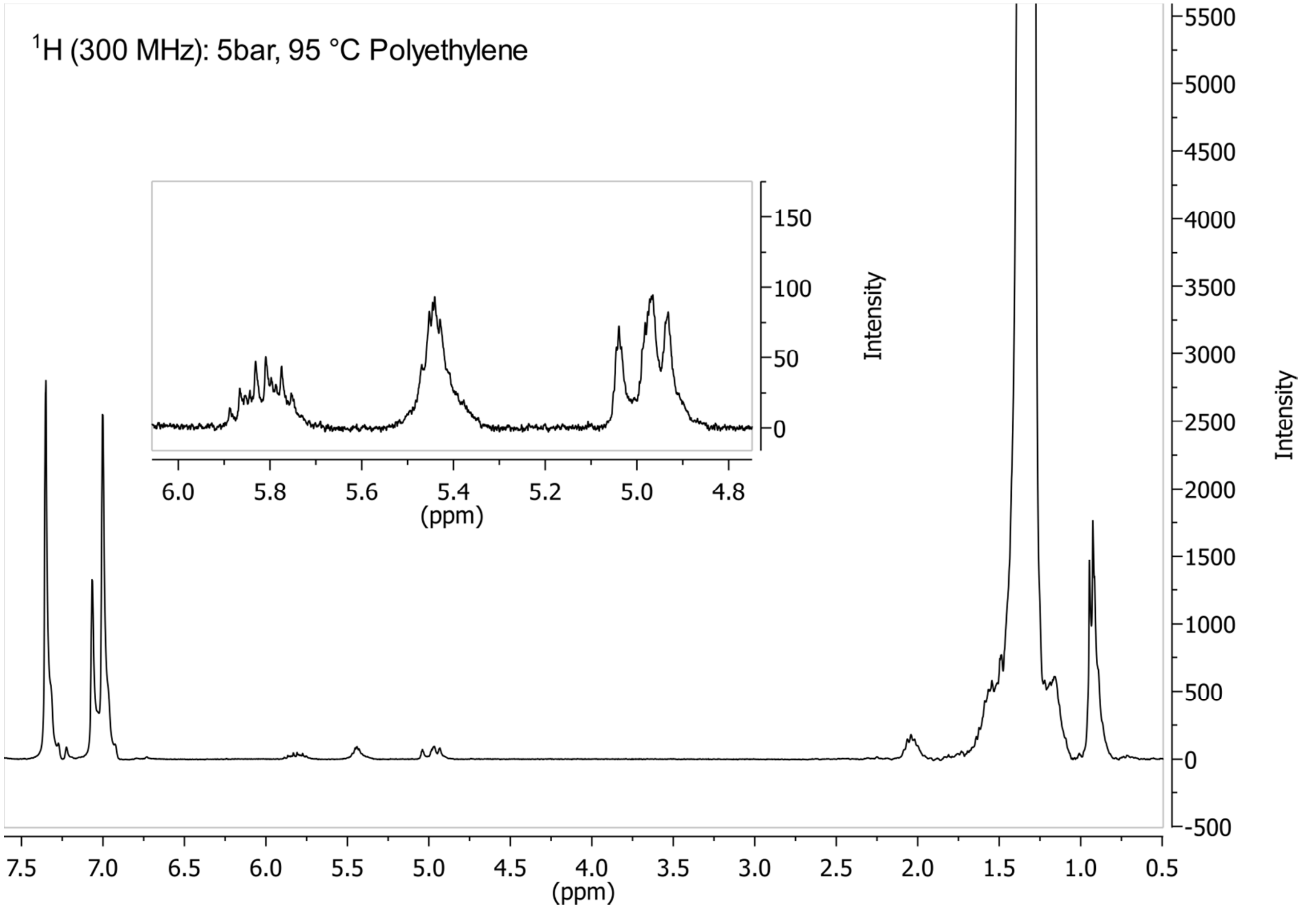


Figure S 8: ^{1}H-NMR spectrum (300 MHz, C_6D_5Br, 130 °C) of polyethylene from entry 2. Recorded with a *Bruker AVIII-300* spectrometer with a spectral width of 8 ppm and a transmitter offset frequency of 4 ppm. Expansion of the δ 0.5 to 7.5 ppm and δ 4.8 to 6.0 ppm region.

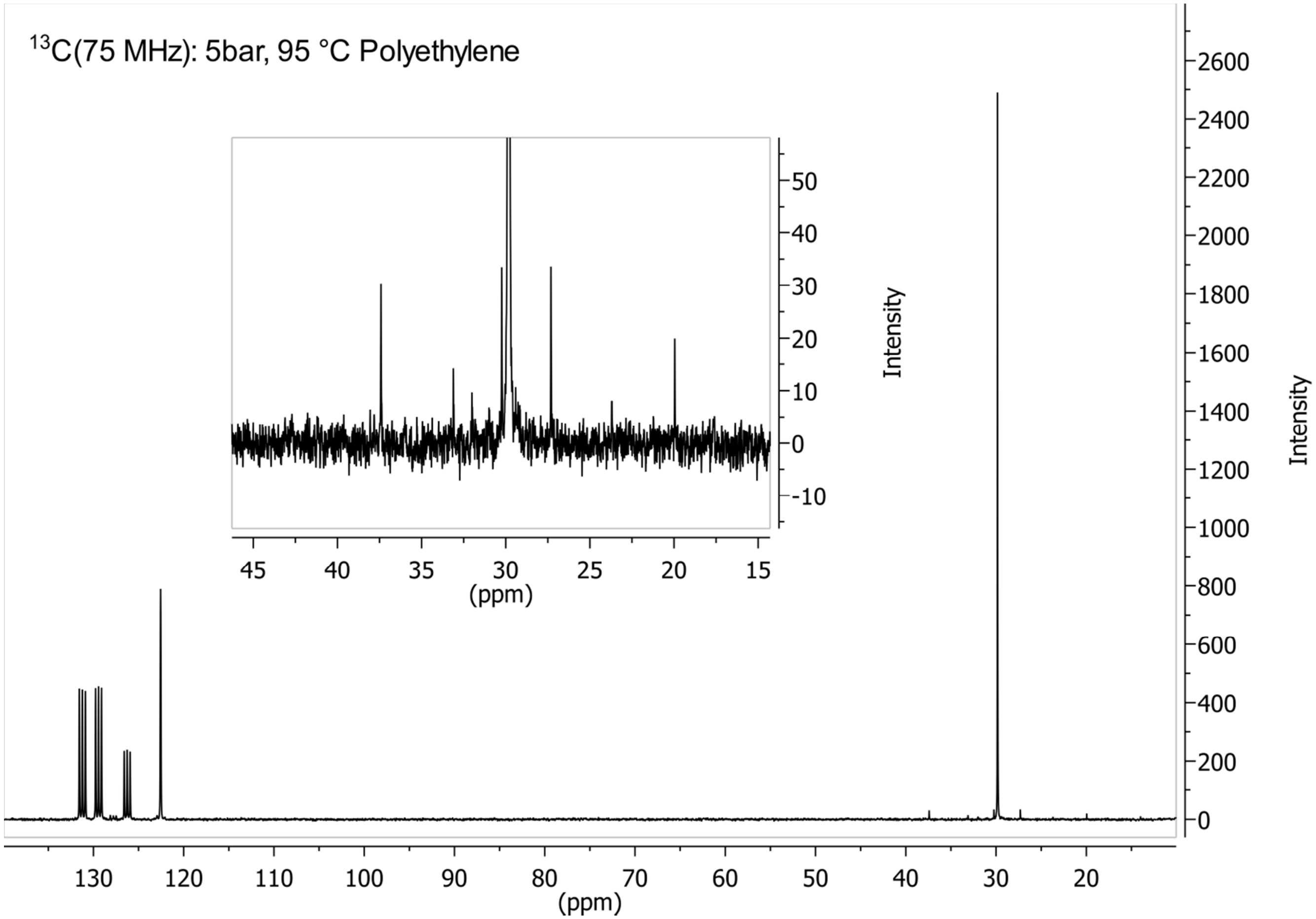


Figure S 9: **^{13}C-NMR spectrum (75 MHz, C_6D_5Br, 130 °C) of polyethylene from entry 2. Recorded with a *Bruker AVIII-300* spectrometer with a spectral width of 130 ppm and a transmitter offset frequency of 75 ppm. Expansion of the δ 15 to 135 ppm and δ 20 to 46 ppm region.**

V. ^{19}F-NMR spectrum of a C_2D_2/TFP copolymer

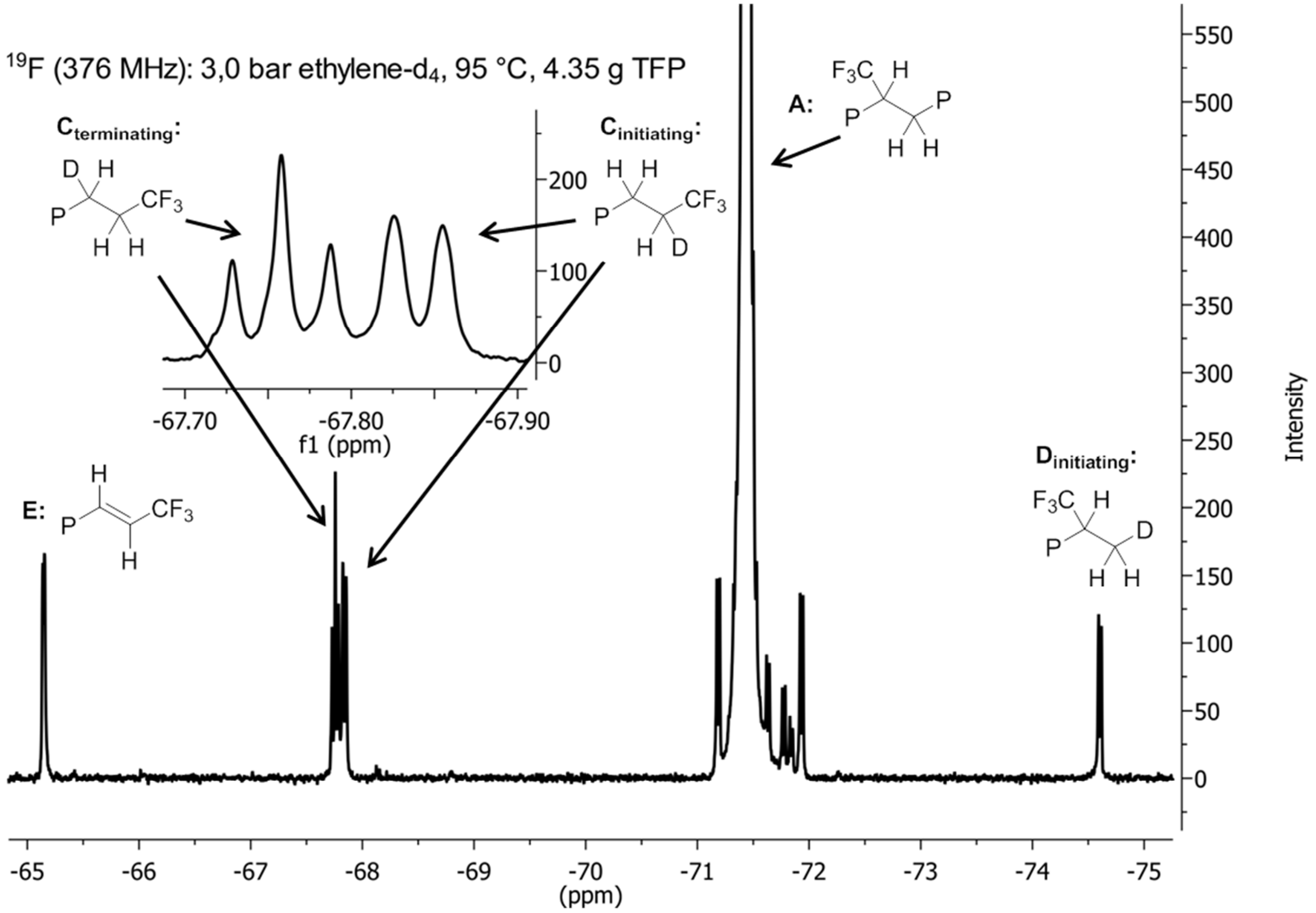
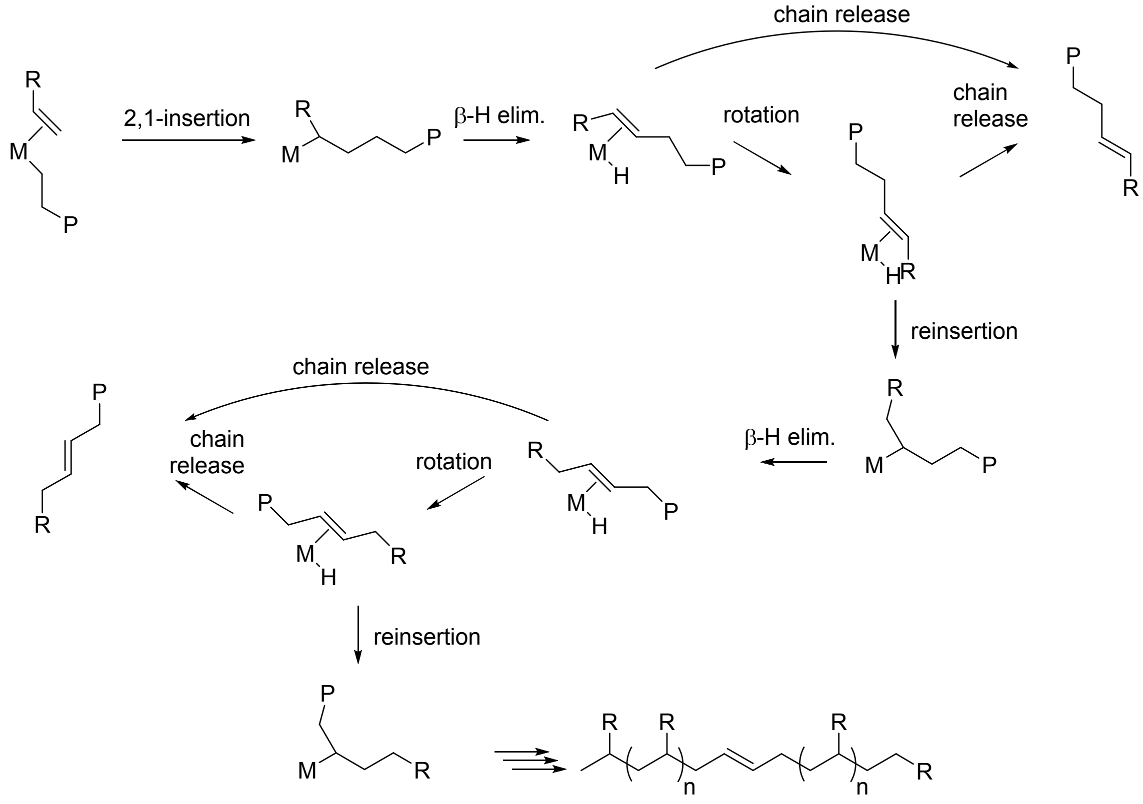
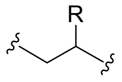


Figure S 10: ^{19}F-NMR (376 MHz, C_6D_5Br, 80 °C) spectrum of the ethylene-d_4-TFP copolymer. Recorded with a *Bruker Avance DRX 400* spectrometer at 80 °C with a spectral width of 30 ppm and a transmitter offset frequency of -68 ppm. The main signal was referenced to -71.44 ppm according to the chemical shift of signal A_F determined for the TFP-ethylene copolymer from entry 8. δ: -65.15 (d, *J* = 6.0 Hz, E), -67.76 (t, *J* = 11.1 Hz, $C_{terminating}$), -67.84 (d, *J* = 11.1 Hz, $C_{initiating}$), -71.44 (d, *J* = 9.7 Hz, A), -74.60 (d, *J* = 9.2 Hz, $D_{initiating}$).

VI. Chain walking mechanism

Scheme S 1: Insertion of TFP (R = CF_3) or C_2H_4 (R = H) into the Pd-C bond of a growing polymer chain, followed by chain walking.[2,3]

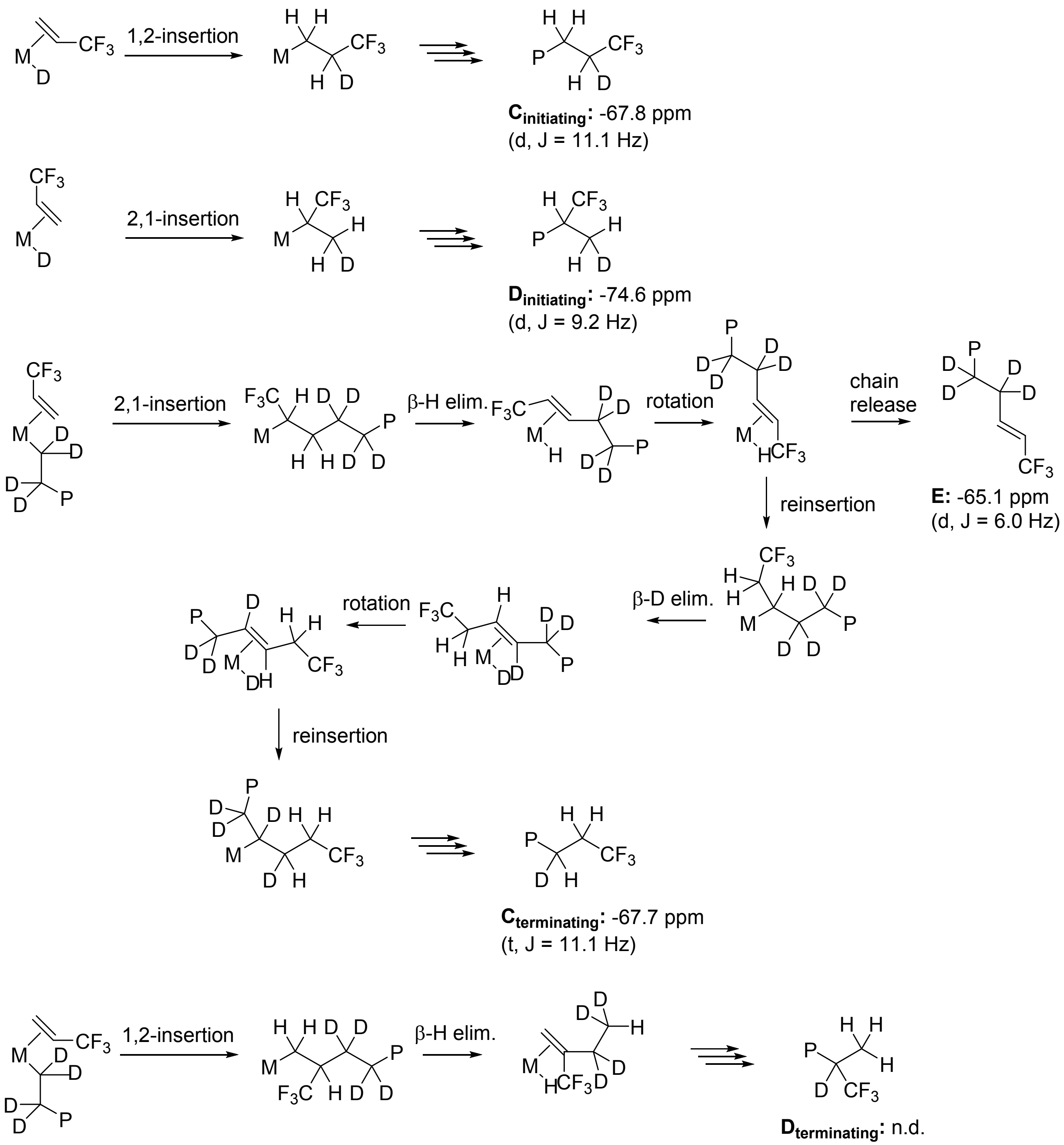




represents a repetition unit (*i.e.* either TFP or ethylene). For reasons of simplification only 2,1-insertion was depicted in this scheme, although both, 2,1- and 1,2- insertion can take place.

VII. Mechanisms towards end groups C, D and E in C_2D_2/TFP copolymer

Scheme S 2: Mechanism of the formation of groups $C_{initiating}$, $C_{terminating}$, $D_{initiating}$, $D_{terminating}$ and E.



VIII. References:

[1] Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2008**, *131*, 422-423

[2] Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999,** *283* (5410), 2059-2062

[3] Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2009,** *131* (39), 14088-14100.