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Supplementary Information's

Isolation of Silica Supported Niobiumtetramethyl Complex by the SOMC Strategy: Synthesis, Characterization and Structure-Activity Relation in Ethylene Oligomerization Reaction

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General experimental procedure:

All experiments were carried out by using standard Schlenk and glovebox techniques under an inert argon atmosphere. The syntheses and the treatments of the surface species were carried out using high vacuum lines ($< 10^{-5}$ mbar) and glove-box techniques. Pentane was distilled from a Na/K alloy under argon and dichloromethane from CaH_2. All the solvents were degassed through freeze-pump-thaw cycles. SiO_{2-700} prepared from Aerosil silica from Degussa (specific area of 200 m^2/g), which were partly dehydroxylated at 700°C under high vacuum ($< 10^{-5}$ mbar) for 16 h to give a white solid having a specific surface area of 183 m^2/g and containing 0.5-0.7 OH/nm^2. The elemental analyses were performed at Mikroanalytisches Labor Pascher (Germany) and ACL KAUST.

Solid-State Nuclear Magnetic Resonance Spectroscopy:

One-dimensional ^1H MAS and ^{13}C CP/MAS solid-state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 400 or 600 MHz resonance frequencies for ^1H. The 400 MHz experiments employed a conventional double-resonance 4 mm CP/MAS probe, whereas experiments at 600 MHz utilized a 3.2 mm HCN triple resonance probe. In all cases the samples were packed into rotors under inert atmosphere inside gloveboxes. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references TMS and adamantane. ^{13}C CP/MAS NMR experiments used the following sequence: 90° pulse on the proton (pulse length = 2.4 s), then a cross-polarization step with a contact time of typically 2 ms, and finally acquisition of the ^{13}C signal under high-power proton decoupling. The delay between the scans was set to 5 s to allow the complete relaxation of the ^1H nuclei, and the number of scans ranged between 5 000 and 10 000 for ^{13}C and was 32 for ^1H. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to the Fourier transformations.

The 2D ^{1}H−^{13}C heteronuclear correlation (HETCOR) solid-state NMR spectroscopy experiments were conducted on a Bruker AVANCE III spectrometer operating at 600 MHz using a 3.2 mm MAS probe. These experiments were performed according to the following scheme: 90° proton pulse, t_1 evolution period, CP to ^{13}C, and detection of the ^{13}C magnetization under TPPM decoupling. During the cross-polarization step, a ramped radio frequency (RF) field centered at 75 kHz was applied to the protons, whereas the ^{13}C channel RF field was matched to obtain an optimal signal. A total of 32 t_1 increments with 4000 scans each were collected; sample spinning frequency was 8.5 kHz. Using a short contact time (0.2 ms) for the CP step, the polarization transfer in the dipolar correlation experiment was verified to be selective for the first coordination sphere around tungsten, such that correlations occurred only between pairs of attached ^{1}H−^{13}C spins (C−H directly bonded).

^{1}H−^{1}H Multiple-Quantum Spectroscopy. Two-dimensional double-quantum (DQ) and triple-quantum (TQ) experiments were recorded on a Bruker AVANCE III spectrometer operating at 600 MHz with a conventional double-resonance 3.2 mm CP/MAS probe, according to the following general scheme: excitation of DQ coherences, t_1 evolution, z-filter, and detection. The spectra were recorded in a rotor-synchronized fashion in t_1 such that the t_1 increment was set equal to one rotor period (45.45 μs). One cycle of the standard back-to-back (BABA) recoupling sequences was used for the excitation and reconversion period. Quadrature detection in w_1 was achieved using the States-TPPI method. A spinning frequency of 22 kHz was used. The 90° proton pulse length was 2.5 μs, whereas a recycle delay of 5 s was used. A total of 128 t_1 increments with 32 scans per increment were recorded. The DQ frequency in the w_1 dimension corresponds to the sum of two single-quantum (SQ) frequencies of the two coupled protons and correlates in the w_2 dimension with the two corresponding proton resonances. The TQ frequency in the w_1 dimension corresponds to the sum of the three SQ frequencies of the three-coupled protons and correlates in the w_2 dimension with the three individual proton resonances. Conversely, groups of fewer than three equivalent spins will not give rise to diagonal signals in the spectrum.

Infra-red spectroscopy:

IR spectra were recorded on pellets made out of ~30 mg of the sample. The pellet was then placed in a sample holder which can be loaded into an IR Cell made of pyrex glass fitted with CaF_2 windows. IR cell is designed in such a way that the measurements can be carried out either in vacuum or in controlled atmospheres. Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer typically accumulating 16 scans for each spectrum with a resolution of 4 cm^{-1}.

Synthesis of $Nb(CH_3)_2Cl_3$. $Nb(CH_3)_2Cl_3$ was prepared according to the reported procedure. Inside a glovebox, and to a double schlenk containing a yellow suspension of $NbCl_5$ (4.564 g, 16.87 mmol) in hexane (30 mL) was added $Zn(CH_3)_2$ (2.217 g, 21.84 mmol) at room temperature. After stirring for 14 hours at room temperature in the absent of light, the reaction mixture changed to a yellowish orange suspension. The reaction mixture was filtered through a celite plug supported by a medium porosity glass frit of the double schlenck, then transferred into another schlenk. The yellowish orange filtrate was evaporated to dryness to give $Nb(CH_3)_2Cl_3$ as yellowish orange solid. Yield = 64% (2.493 g, 10.85 mmol). $Nb(CH_3)_2Cl_3$ was used without further purification. ^1H NMR (25°C, 76.8 MHz, CD_2Cl_2) 2.95 ppm

Preparation of $Zn(^{13}CH_3)_2$

In a 200 mL Schlenk, 15 mL of 1.6 M BuLi was taken under argon, and to that was added dropwise 3.4 g (24 mmol) of ^{13}MeI diluted in 25 mL of pentane at −20°C with stirring. A white precipitate formed immediately, and the solution was stirred for another 3 hours. The precipitate was then filtered and dried under a vacuum to produce a white solid (^{13}MeLi). A small amount of ^{13}MeLi was taken and titrated with deoxygenated water to quantify the amount of methyl lithium present by quantifying the release of methane (around 55% ^{13}MeLi was found). In another double Schlenk, ^{13}MeLi (22 mmol, 484 mg) was added with 20 mL of pentane, and to that a solution of anhydrous $ZnCl_2$ (10 mmol in 10 mL) was added at -20°C. The reaction was allowed to reach at room temperature slowly and remained at that temperature for another 2 days. The volatiles were then trapped into a schlenk, and the dimethylzinc was collected as pentane solution.

Preparation of [(≡SiO-)NbCl$_3$CH$_3$] . 230 mg $NbMe_2Cl_3$ in slight excess (1.1 equivalent) with respect to the amount of surface accessible silanols (0.3 mmol silanol groups per gram) was reacted with 3.0 g of SiO_{2-700} at room temperature in pentane for 2 h. After filtration and three washing cycles, all volatile compounds were condensed to quantify methane evolved during the grafting. And the solid was dried under dynamic vacuum (< 10^{-5} Torr, 2 h). The volatile components were analysed by GC and 0.28 ±0.1 mmol of CH_4 per gram of SiO_{2-700} was determined. The reaction was monitored by FT-IR showing that 95% of isolated silanol disappeared with a concomitant appearance of weak bands at 2988-2875 cm^{-1} and 1500-1300 cm^{-1} region. Elemental analysis gave 2.69% Nb, 0.38% C, 2.87% Cl consistent with [(≡SiO-)NbCl$_3$Me] **1**. This was further confirmed by the hydrolysis of **1** at 298 K which produces 1.1 ± 0.1 mol of methane per mol Nb (expd: 1.0), and further analyses gave the ratio of Nb/C/Cl=1/1.1/2.8 (Theoretical: Nb/C/Cl=1/1/3).

Hydrolysis of solid [(≡SiO-)NbCl$_3$Me] 1. 100 mg of **1** (29 μmol of metal) was transferred in a Schlenk tube and H_2O vapor (2 mL was added and reacted with **1** at room temperature for 4 h to give methane exclusively (34 µmol of methane was quantified by GC to 1.1 ±0.1 per niobium atom).

Preparation of [(≡SiO-)Nb(CH_3)$_4$]. To a suspension of 1.0 g of [(≡SiO-)NbCl_3Me] in dichloromethane or pentane 0.45 mL of dimethyl zinc solution in hexane (1 M) was added slowly to it in side an argon atmosphere. Reaction was kept for 2 hours at room temperature. After filtration and three washing cycles the solid was dried under dynamic vacuum (<10^{-5} Torr, 2 h). The reaction was monitored by FT-IR shows an increase in the signals at 2988-2875 cm^{-1} and 1500-1300 cm^{-1} region. Elemental analysis of complex **2** gave 2.59% Nb, 1.28% C, 1.32% Cl, 1.11% Zn with a ratio of Nb/C =1/3.8 (Theoretical: Nb/C =1/4). This was further confirmed by the hydrolysis of **2** at 298°K which produces 4.2 ±0.1 mol of methane per mol Nb (expected: 4.0)

Oligomerization of ethylene with [(≡SiO-)NbCl_3Me] 1 & [(≡SiO-)Nb(CH_3)$_4$] 2 in semi-batch reactor. 100 mg of each catalyst in dry toluene (7 mL) were added into a glass vial equipped with a magnetic stirrer, and the glass vial was sealed in the glovebox. The vial was put into the autoclave of the ILS Premex parallel reactor system under pressure of 50 bar of ethylene at 100°C. The reaction was carried out for 60 min with vigorously stirring, and cooled to -10°C to condense all the products generated. An aliquot of the mixture was analyzed by GC to quantify the oligomers.

Solid state spectra of complex 1 after alkylating with excess $ZnMe_2$

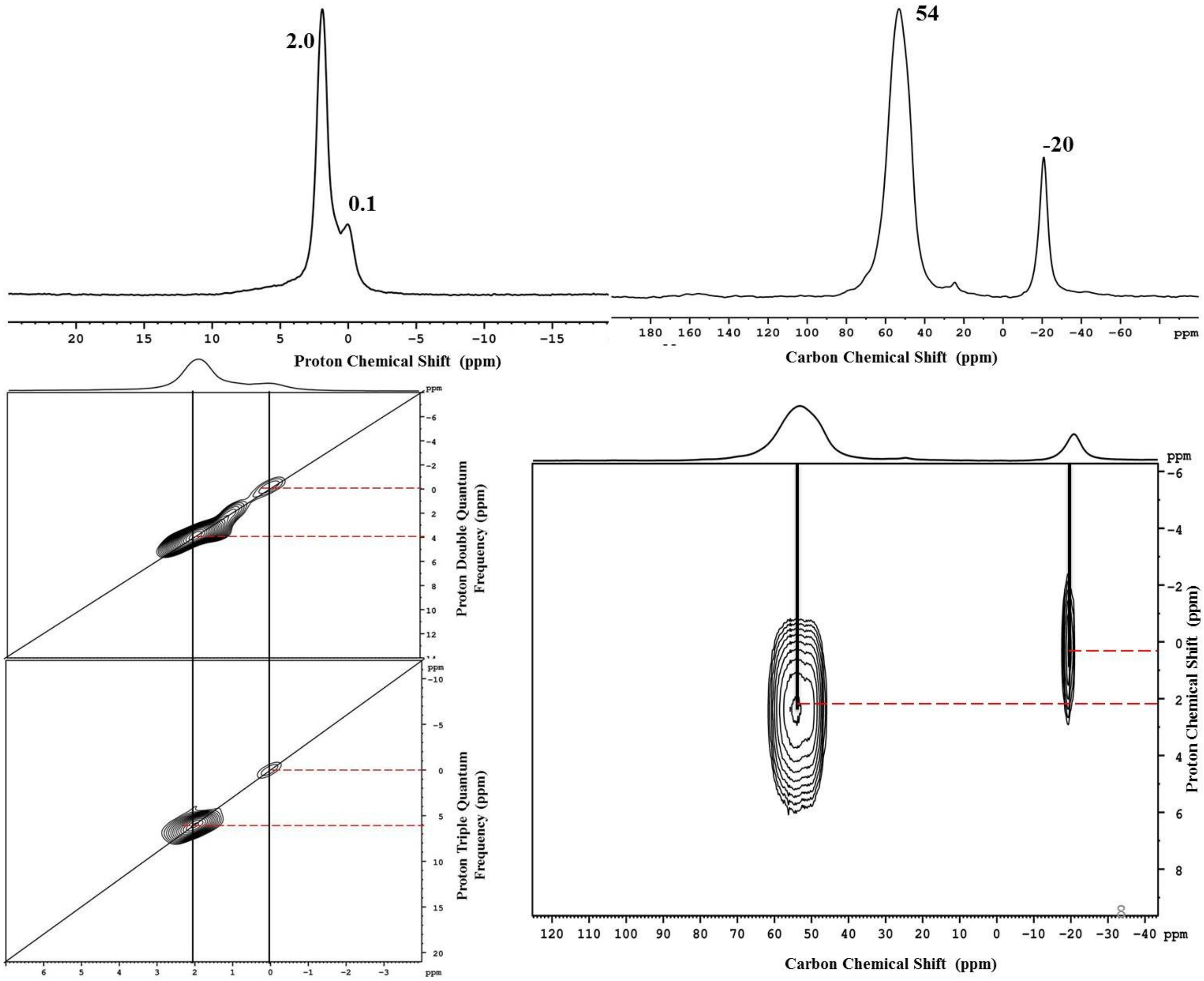

Figure S1: a) ^{1}H MAS NMR spectra of complex **2’** b) 2D $^{1}H-^{1}H$ DQ/SQ and (c) $^{1}H-^{1}H$ TQ/SQ NMR spectra of complex **2’** c) One-dimensional ^{13}C CP/MAS NMR spectra of complex **2’** d) 2D CP/MAS HETCOR NMR spectra of complex **2’**.

GC-Spectra after ethylene oligomerization using complex (1) & (2)

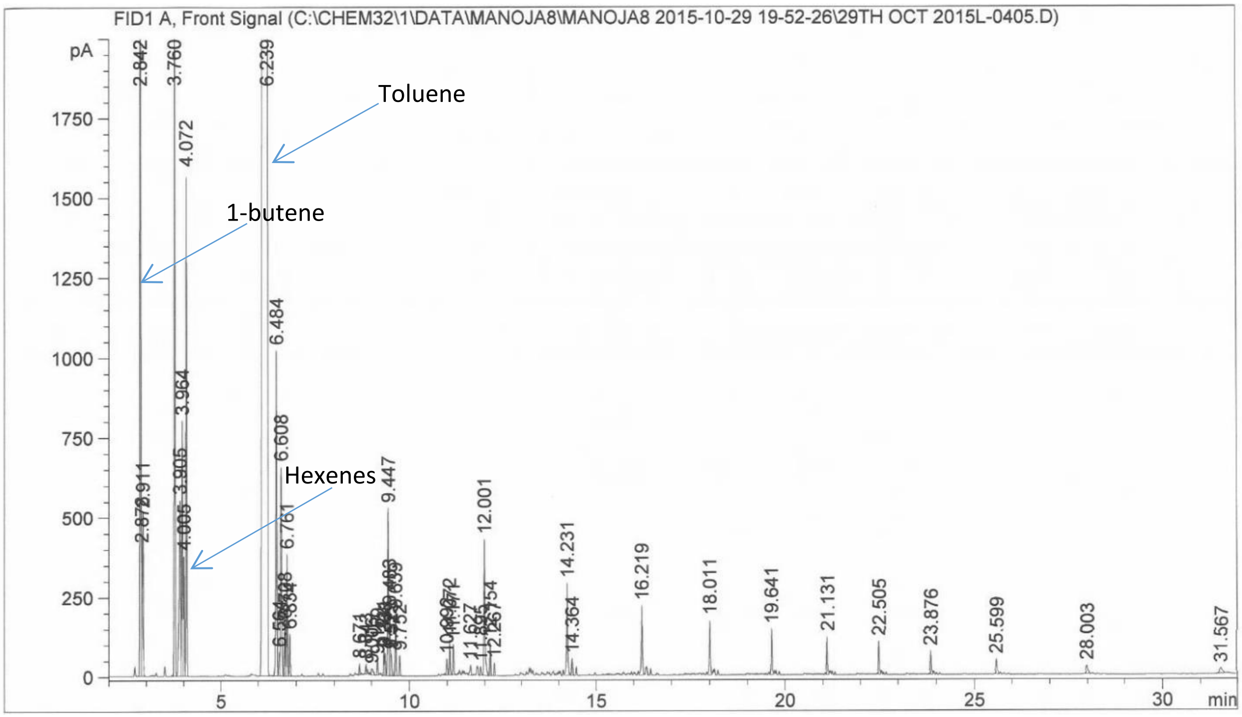

Figure S2: GC spectrum of the liquid phase products after a catalytic oligomerization reaction using 100 mg from batch #1 of [(≡SiO-)Nb^{V}Cl$_3$Me] after addition to a semi-batch reactor, solubilized in 7 ml of toluene and feed by ethylene pressure of 50 bar at 100^{o}C**.**

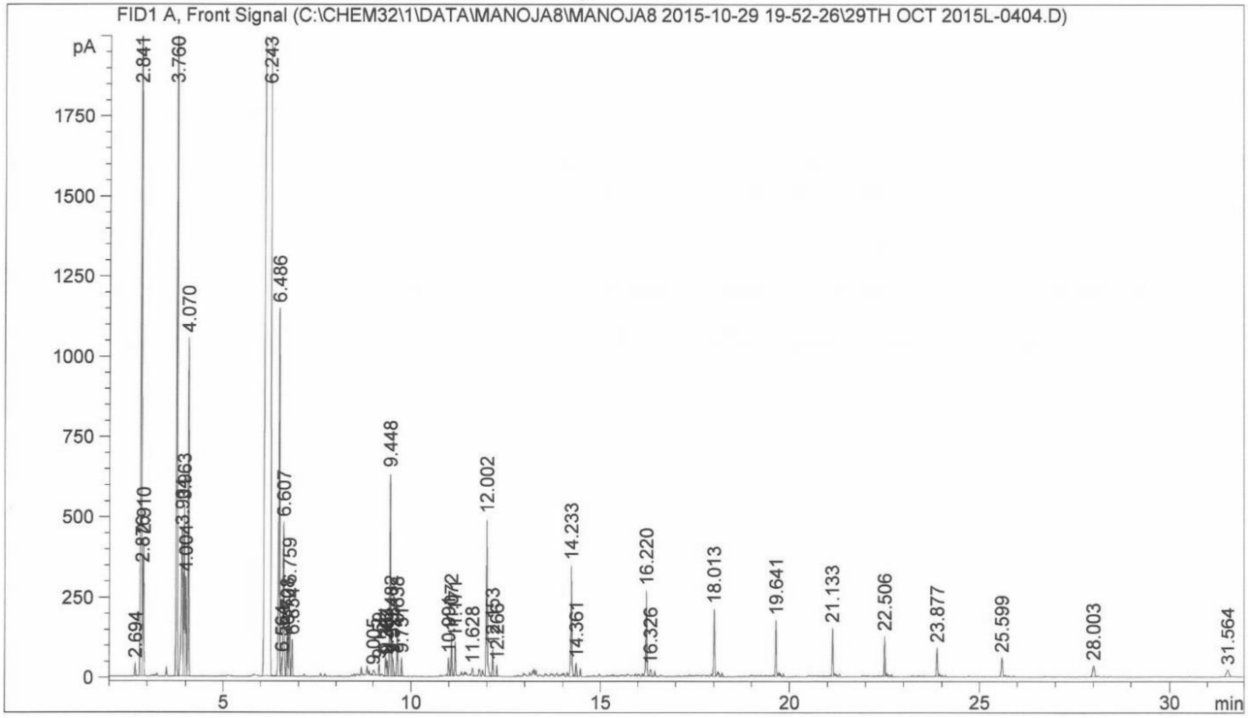

Figure S3: GC spectrum of the liquid phase products after a catalytic oligomerization reaction using 100 mg from batch #2 of [(≡SiO-)Nb^{V}Cl$_3$Me] after addition to a semi-batch reactor, solubilized in 7 ml of toluene and feed by ethylene pressure of 50 bar at 100^{o}C.

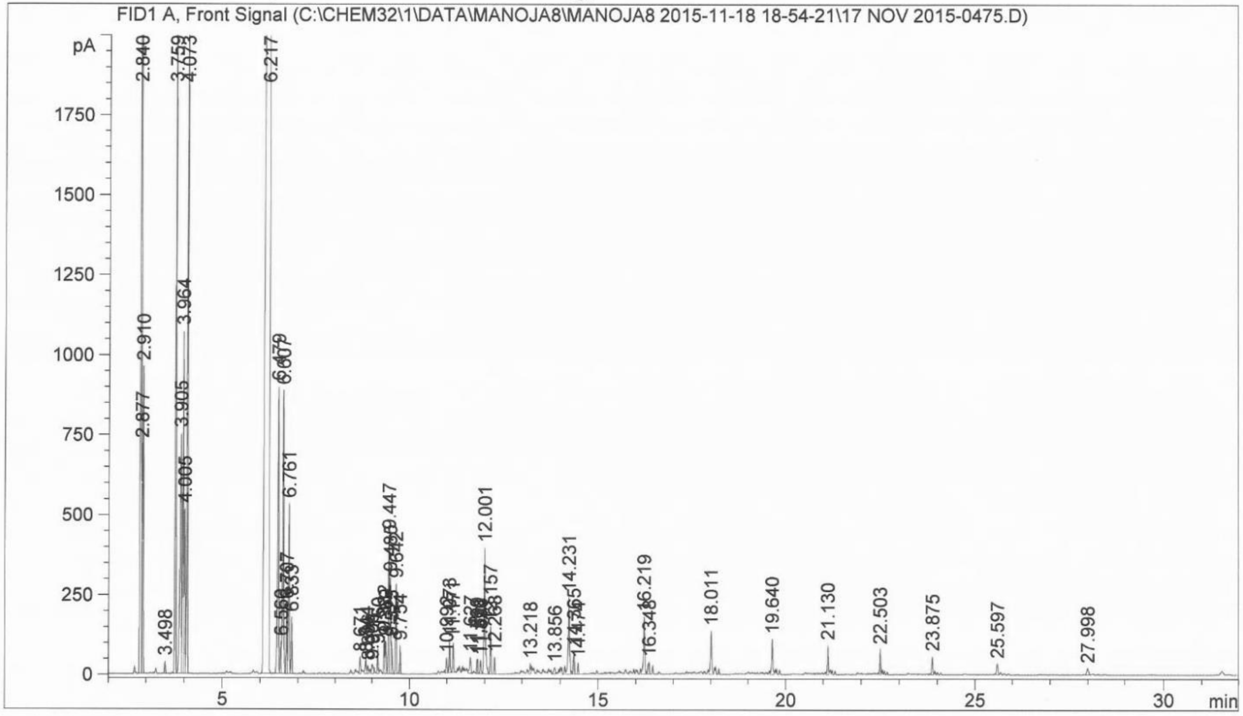

Figure S4: GC spectrum of the liquid phase products after a catalytic oligomerization reaction using 100 mg from batch #3 of [(≡SiO-)Nb^{V}Cl$_3$Me] after addition to a semi-batch reactor, solubilized in 7 ml of toluene and feed by ethylene pressure of 50 bar at 100^{o}C.

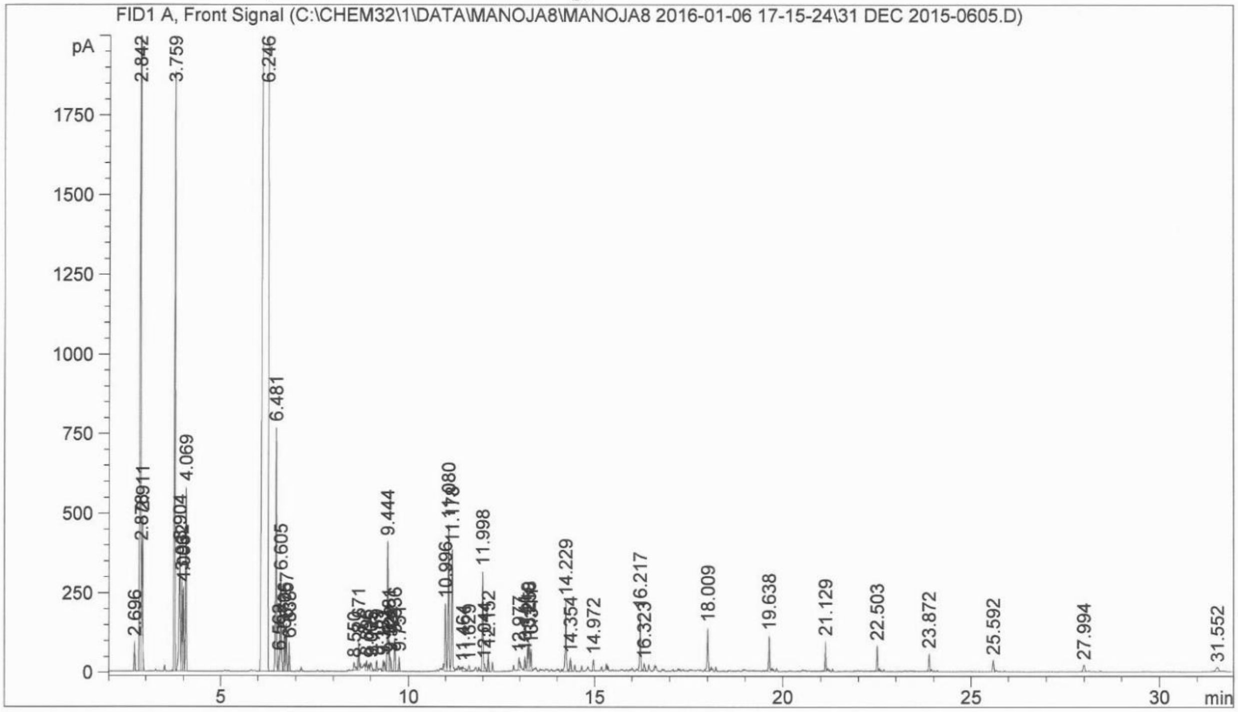

Figure S5:GC spectrum of the liquid phase products after a catalytic oligomerization reaction using 100 mg from batch #4 of [(≡SiO-)Nb^{V}Cl$_3$Me] after adding to a semi-batch reactor, solubilized in 7 ml of toluene and feed by ethylene pressure of 50 bar at 100^{o}C.

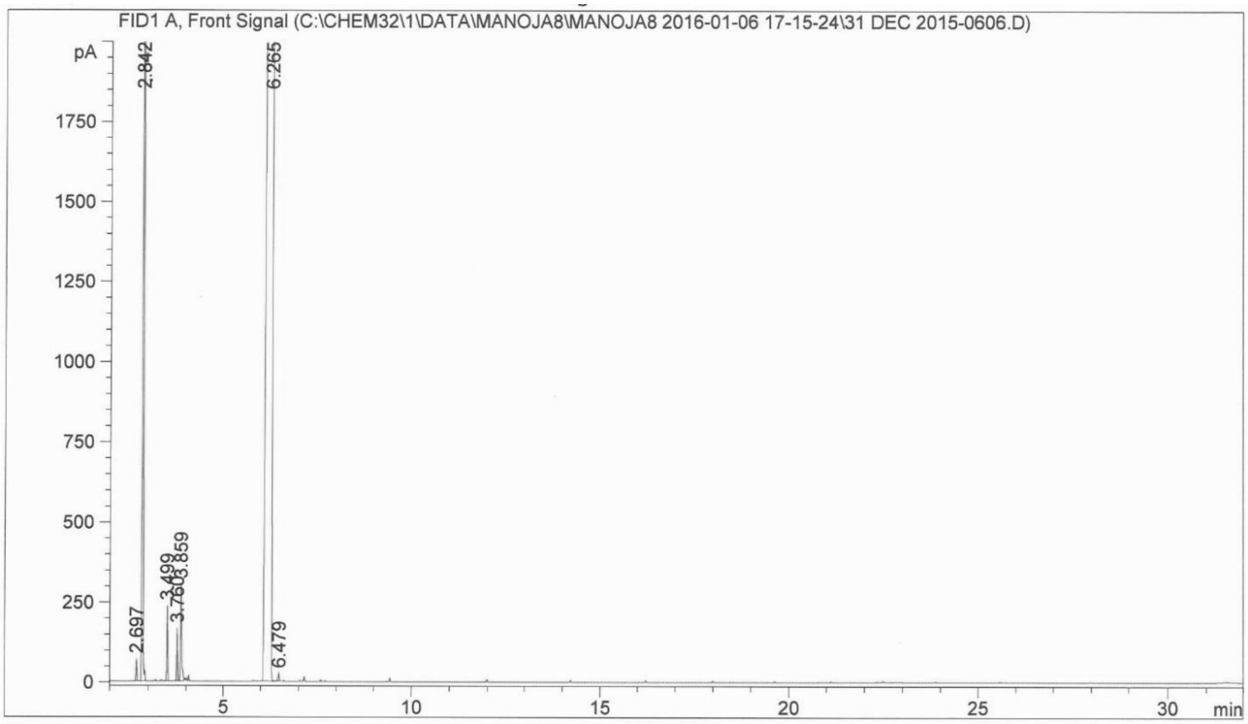

Figure S6: GC spectrum of the liquid phase products after a catalytic oligomerization reaction using 100 mg from batch #1 of [(≡SiO-)Nb^{v}Me$_4$] after adding to a semi-batch reactor, solubilized in 7 ml of toluene and feed by ethylene pressure of 50 bar at 100^{o}C.

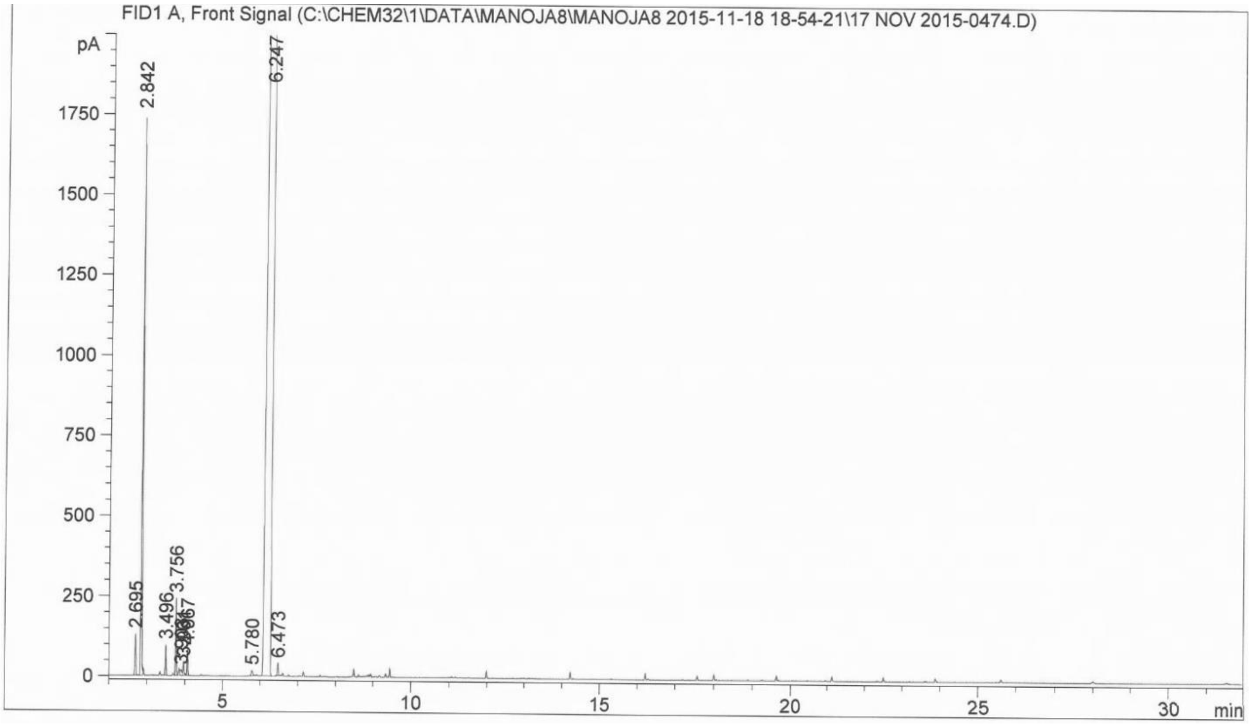

Figure S7: GC spectrum of the liquid phase products after a catalytic oligomerization reaction using 100 mg from batch #2 of [(≡SiO-)Nb^{v}Me$_4$] after adding to a semi-batch reactor, solubilized in 7 ml of toluene and feed by ethylene pressure of 50 bar at 100^{o}C.

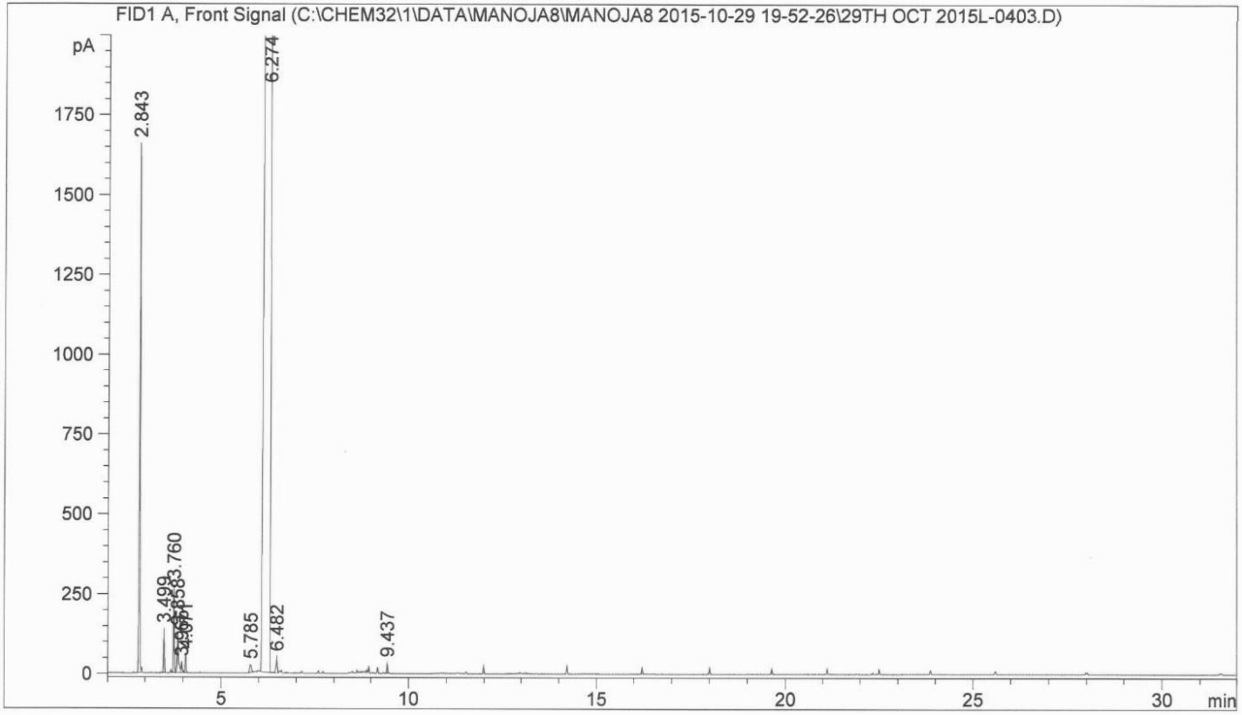

Figure S8: GC spectrum of the liquid phase products after a catalytic oligomerization reaction using 100 mg from batch #3 of [(≡SiO-)Nb^{v}Me$_4$] after adding to a semi-batch reactor, solubilized in 7 ml of toluene and feed by ethylene pressure of 50 bar at 100^{o}C.

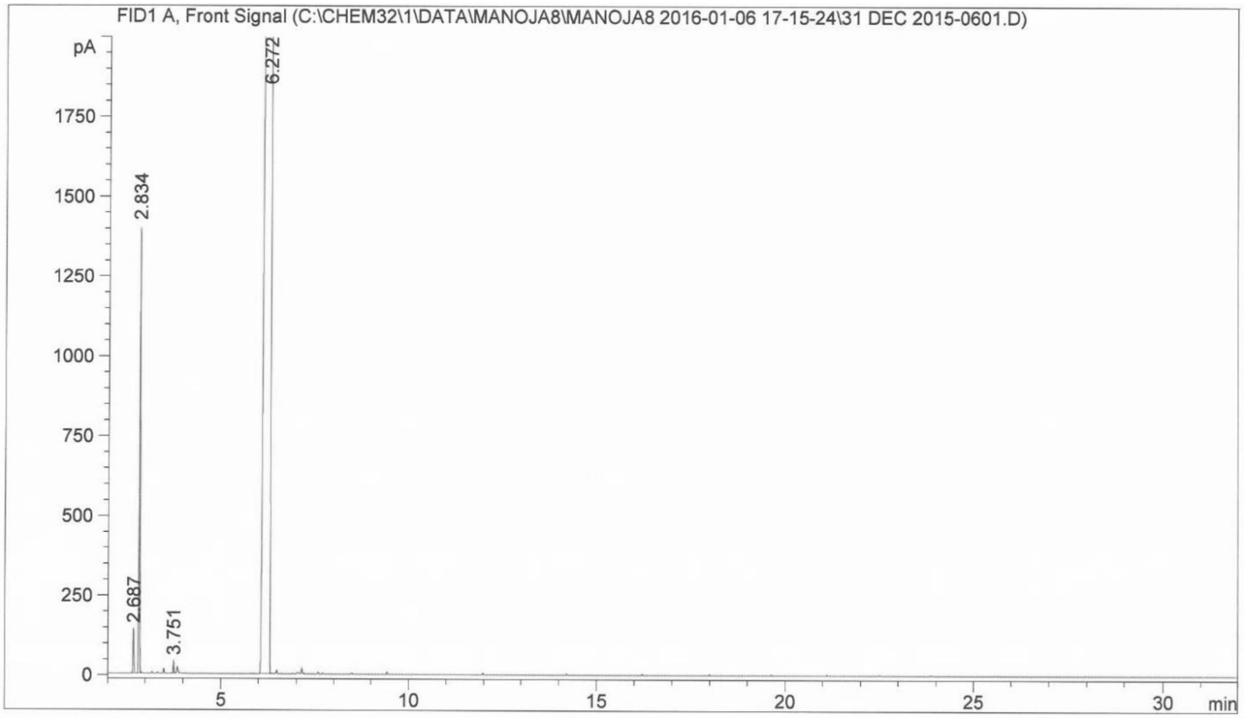

Figure S9: GC spectrum of the liquid phase products after a catalytic oligomerization reaction using 100 mg from batch #4 of [(≡SiO-)Nb^{v}Me$_4$] after adding to a semi-batch reactor, solubilized in 7 ml of toluene and feed by ethylene pressure of 50 bar at 100^{o}C.