Supporting Information

Synthesis of mono- and di-branched α-olefins via elongation and branching by ethylene

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1. Analysis

For **Gas chromatography** the soluble product fractions were diluted with cumene or benzene and analyzed using an Agilent 6890N gas chromatograph, equipped with a flame ionization detector and a (30 m x 0.32 mm x 0.25 µm) HP-5 column. Methylcyclohexane p.a. (Thermo Scientific) was used as an internal standard.

The values given for 1-butene and 1-hexene are calculated from 1-octene via α-value. The α-value was calculated by $n(C_{m+2})/n(C_m)$ with n being the amount of substance, C_m being the product fraction considered and C_{m+2} being the product fraction elongated by one ethylene unit. Then the n ratios were averaged from 1-octene to 1-dodecene if detectable to give the α-value.

NMR spectra were recorded on a Varian INOVA 300 (^{1}H: 299.9 MHz; ^{13}C: 75.4 MHz) or a Varian INOVA 400 (^{1}H: 399.8 MHz; ^{13}C: 100.5 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra, measured at 25 °C, were referenced internally using the residual solvent resonances; chemical shifts (δ) are reported in ppm.

For **Mass spectroscopy** with **Gas chromatography** an Agilent / Gerstel GC7890B MSD 5977A TDU 2 GC-MS (2004) with HP-5MS UI (L = 30m, ID = 0.25mm FT = 0.25µm)(Temp. limits: -60-350°C) or DB-5MS (L = 30m, ID = 0.25mm FT = 0.25µm)(Temp. limits: -60-350°C) column and Quadropol MS Detector with EI of 1000 eV was used. Samples were prepared in acetone with a concentration of 0.5 mg/mL.

2. General considerations

All manipulations were performed with the rigorous exclusion of oxygen and moisture by using standard Schlenk type glassware on a dual-manifold Schlenk line and glovebox techniques (mBraun 120-G) with a high-capacity circulation (< 0.1 ppm O_2) under an atmosphere of argon or nitrogen. Deuterated solvents were obtained from Euriso-top, degassed, distilled and stored over activated 3 Å molecular sieves prior to use. Solvents such as cumene (Acros, anhydrous, 99.0%), methylcyclohexane (Thermo Scientific, anhydrous, 99.0%) and α-olefins (Acros, TCI, 99.0%) were dried and purified by distillation from $LiAlH_4$, potassium, Na/K alloy or sodium benzophenone ketyl under argon atmosphere before use.

Ethylene (Linde AG, polymer grade) used for oligomerizations was passed over columns of Al_2O_3 (Fischer Scientific) and a BASF R3-11 supported Cu oxygen scavenger. d-MAO (depleted methylaluminoxane) was obtained by removing the volatile components from a methylaluminoxane solution in toluene (Chemtura Europe Limited). Triisobutylaluminium (TIBA, Aldrich) was used as received. All further reagents were purchased with a purity of at least 97% and used without further purification. [1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imido]-[N-(2,6-diisopropylphenyl)-6-(2,4,6-triisopropylphenyl)pyridin-2-amido]-di(phenylmethanido)titanium(IV) **1** was synthesized according to the literature.[1] [2]

2.1 Multigram synthesis of mono- or di-branched α-olefins

Stock solutions of the precatalyst **1** (0.001 M), the cocatalyst d-MAO (0.035 M) and the scavenger TIBA (0.400 M) were prepared in cumene. The multigramm synthesis of ethylene α-olefin co-oligomerizations was carried out in a 1000 mL steel autoclave (Büchi) with integrated temperature control, electrical heating and water cooling, in semi batch mode. Prior to every experiment the autoclave was evacuated. A mechanical stirrer (1000 rpm) was used, the ethylene gas flow was monitored by a Bronkhorst High-Tech El-Flow unit.

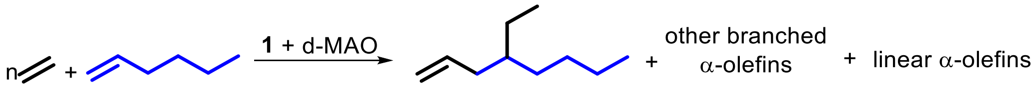
For branched α-olefin synthesis the evacuated autoclave was filled with 300 mL of the corresponding α-olefin via steel flask and pressurized with ethylene at 1.0 bar.

Subsequently, about 1.0 g of internal standard (methylcyclohexane), 1.0 mL scavenger-, 1.0 mL co-catalyst- and 1.0 mL precatalyst stock solution were injected. Then the respective ethylene pressure was adjusted and the ethylene consumption was recorded. In intervals of 5 L_n, 10 L_n, 20 L_n, 30 L_n, 50 L_n, 100 L_n, 150 L_n and 200 L_n ethylene consumed the stirring was terminated, a sample was taken from the reaction and stirring was reactivated.

The synthesis was terminated by stopping the ethylene flow and injecting demineralized H_2O (1.0 mL) into the autoclave. The product solutions were solvent extracted with demineralized H_2O, the organic phase was separated, filtered using silica and remaining water was removed using $MgSO_4$.

The liquid organic phase of the product mixture was analyzed by gas-chromatography (GC). The masses of the fractions produced during catalysis were calculated in reference to the mass of the internal standard. Mass balances of the product mixture were calculated from the sample of 200 L_n ethylene gas consumed.

2.1.1 Synthesis of 4-ethyl-1-octene (a)



Parameters of the synthesis of 4-ethyl-1-octene (**a**) are listed in table S1. Mass balances of the products observed are listed in table S2 for the linear α-olefins and in table S3 for the branched α-olefins. The ethylene consumption over time is plotted in figure S1.

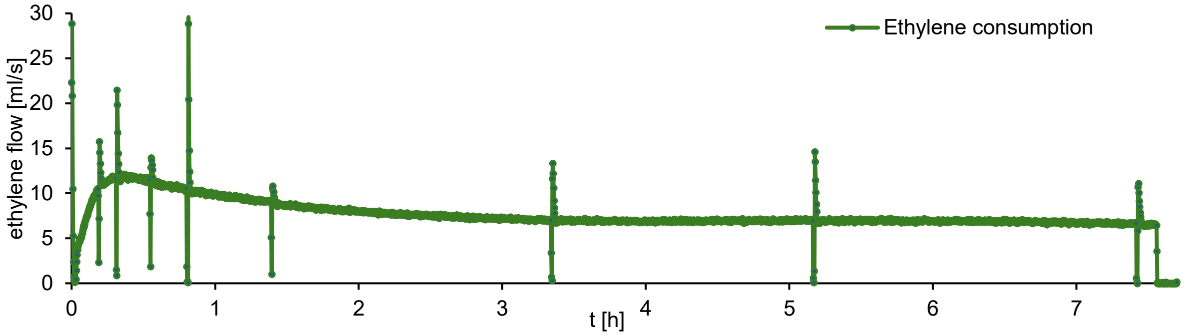


Fig. S1. Ethylene consumption plot over time für synthesis of **a**.

Tab. S1: Parameters of the 4-ethyl-1-octene synthesis.

n_1 [μmol]	$m_{\text{d-MAO}}$ [mg]	n_{TIBA} [μmol]	$V_{\text{1-hexene}}$ [mL]	T [°C]	p_{ethylene} [bar]	V_{ethylene} [L_n]	t [h]
1.0	2.0	400	300	30	2.5	200	7.5

Tab. S2: Mass balances of the linear α-olefin products from synthesis of **a**.

1-butene	1-hexene	1-octene	1-decene	1-dodecene
136.9 g	41.0 g	9.6 g	2.2 g	0.3 g

Tab. S3: Mass balances of the branched α-olefin products from synthesis of **a**.

2-ethyl-1-hexene	4-ethyl-1-hexene	2-ethyl-1-octene	4-ethyl-1-octene (**a**)	other br. olefins
1.2 g	24.5 g	2.7 g	53.5 g	10.3 g

4-ethyl-1-octene (**a**) ^{1}H NMR (300 MHz, C_6D_6, 296 K) δ = 5.82 – 5.68 (m, 1H, $\mathrm{CH_2{=}C}H\text{-}\mathrm{CH_2}\text{-}$), 5.08 – 5.01 (m, 2H, $\mathrm{C}H_2\mathrm{{=}CH}\text{-}$), 2.01 – 1.99 (m, 2H, $\mathrm{{=}CH\text{-}C}H_2\text{-}\mathrm{CH}\text{-}$), 1.31 – 1.24 (m, 9H, $\mathrm{CH_3\text{-}C}H_2\text{-}\mathrm{C}H\text{-}\mathrm{C}H_2\text{-}\mathrm{C}H_2\text{-}\mathrm{C}H_2\text{-}\mathrm{CH_3}$), 0.87 (dt, *J*=14.0 Hz, 6.6 Hz, 6H, $\text{-}\mathrm{CH_2\text{-}C}H_3$) ppm.

4-ethyl-1-octene (**a**) ^{13}C NMR (75 MHz, C_6D_6, 296 K) δ = 137.73 ($\text{=}C\mathrm{H}\text{-}$), 115.82 ($C\mathrm{H_2}\text{=}$), 39.30 ($\text{-}C\mathrm{H}\text{-}$), 38.09 ($\text{-}C\mathrm{H_2}\text{-}$), 33.04 ($\text{-}C\mathrm{H_2}\text{-}$), 29.40 ($\text{-}C\mathrm{H_2}\text{-}$), 26.13 ($\text{-}C\mathrm{H_2}\text{-}$), 23.50 ($\text{-}C\mathrm{H_2}\text{-}$), 14.42 ($C\mathrm{H_3}$), 11.18 ($C\mathrm{H_3}$) ppm.

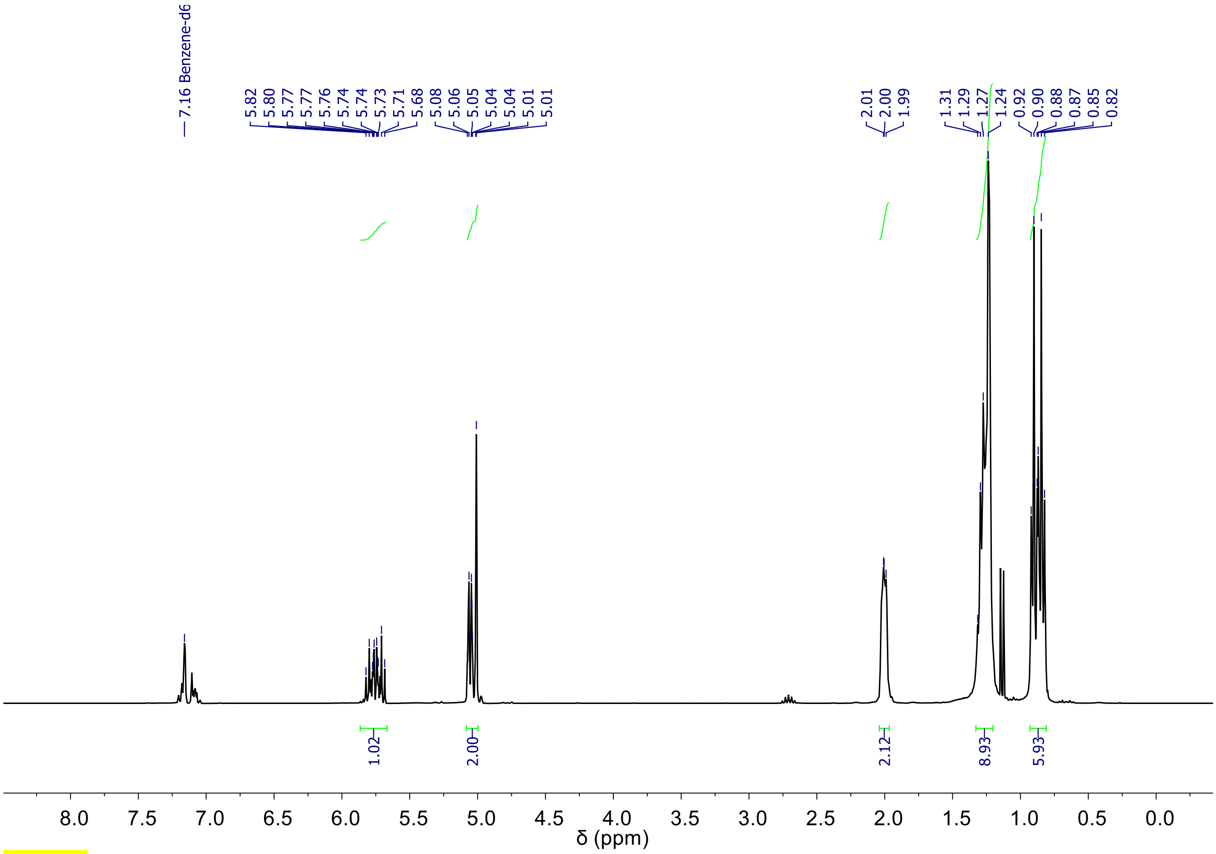


Fig. S2. ^{1}H NMR spectrum of 4-ethyl-1-octene (**a**) (300 MHz, C_6D_6, 296 K).

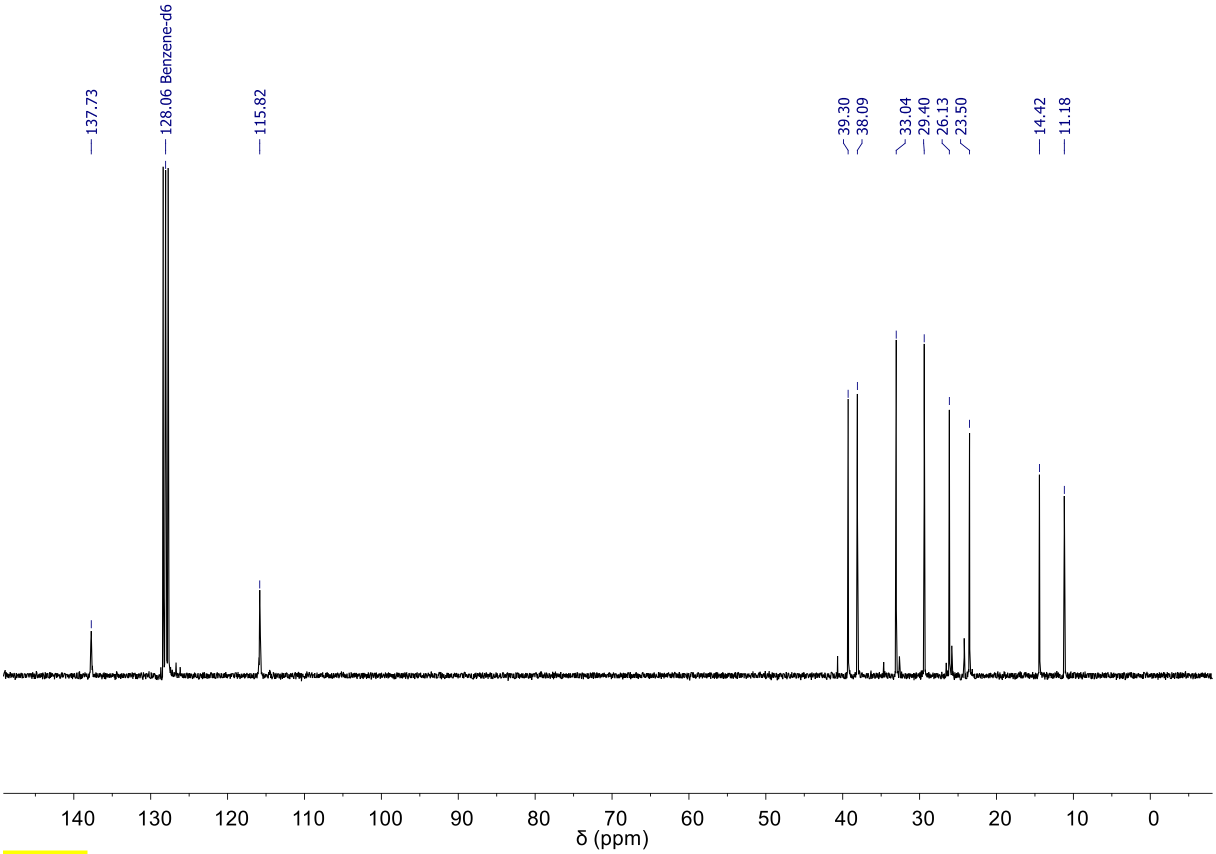


Fig. S3. ^{13}C NMR spectrum of 4-ethyl-1-octene (**a**) (75 MHz, C_6D_6, 296 K).

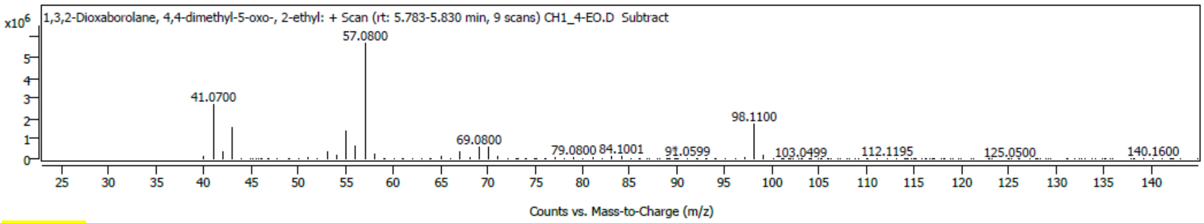
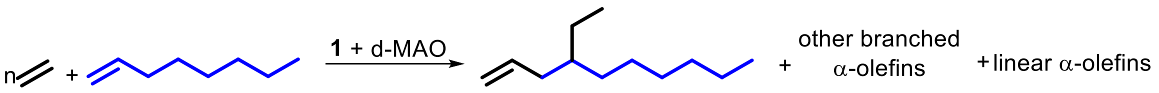


Fig. S4. Mass spectrum of 4-ethyl-1-octene (**a**).

m/z calculated for 4-ethyl-1-octene (**a**) = 140 (100 %), 141 (11.0 %)

m/z observed for 4-ethyl-1-octene (**a**) = 140 (100 %).

2.1.2 Synthesis of 4-ethyl-1-decene (b)



Parameters of the synthesis of 4-ethyl-1-decene (**b**) are listed in table S4. Mass balances of the linear α-olefin products are listed in table S5. The amount of 1-octen produced during catalysis was calculated via α-value. In table S6 the branched α-olefin product mass balances are listed. Here the signal for 2-ethyl-1-hexene cannot be used because it is overlapped by a broad 1-octene signal in GC. The ethylene consumption over time is plotted in figure S5.

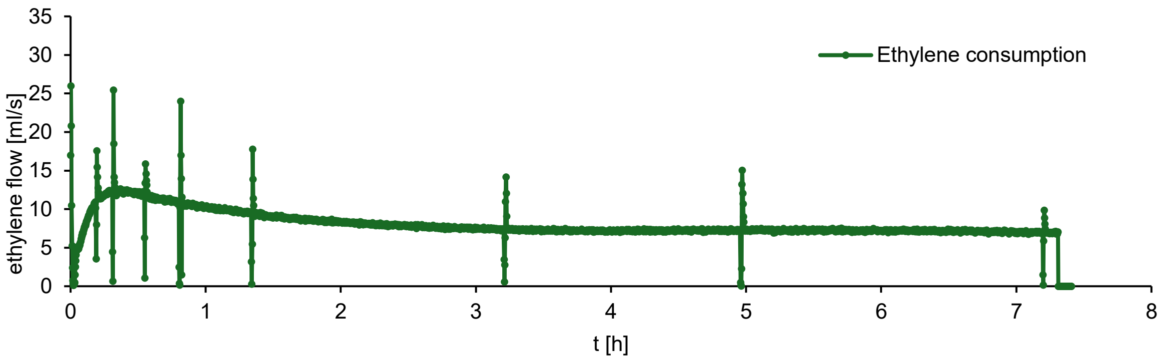


Fig. S5. Ethylene consumption plot over time für synthesis of **b**.

Tab. S4: Parameters of the synthesis of **b**.

n_1 [µmol]	$m_{d\text{-}MAO}$ [mg]	n_{TIBA} [µmol]	$V_{1\text{-}hexene}$ [mL]	T [°C]	$p_{ethylene}$ [bar]	$V_{ethylene}$ [L_n]	t [h]
1.0	2.0	400	300	30	2.5	200	7.2

Tab. S5: Mass balances of the linear α-olefin products from the synthesis of **b**.

1-butene	1-hexene	1-octene	1-decene	1-dodecene
126.9 g	43.7 g	13.4 g	3.9 g	1.1 g

Tab. S6: Mass balances of the branched α-olefin products from the synthesis of **b**.

2-ethyl-1-hexene	4-ethyl-1-hexene	2-ethyl-1-octene	4-ethyl-1-octene	2-ethyl-1-decene	4-ethyl-1-decene	other br. olefins
-	22.3 g	3.7 g	8.4 g	1.2 g	64.6 g	9.4 g

4-ethyl-1-decene (**b**) ^{1}H NMR (300 MHz, C_6D_6, 296 K) δ = 5.84 – 5.70 (m, 1H, CH_2=C*H*-CH_2-), 5.09 – 5.02 (m, 2H, C*H*$_2$=CH-), 2.04 – 2.01 (m, 2H, =CH-C*H*$_2$-CH-), 1.33 – 1.26 (m, 14H, CH_3-C*H*$_2$-C*H*-C*H*$_2$-C*H*$_2$-C*H*$_2$-CH_3), 0.88 (dt, *J*=14.1 Hz, 6.8 Hz, 6H, -CH_2-C*H*$_3$) ppm.

4-ethyl-1-decene (**b**) ^{13}C NMR (75 MHz, C_6D_6, 296 K) δ = 137.74 (=*C*H-), 115.84 (*C*H$_2$=), 39.35 (-*C*H-), 38.11 (-*C*H$_2$-), 33.39 (-*C*H$_2$-), 32.39 (-*C*H$_2$-), 30.22 (-*C*H$_2$-), 27.18 (-*C*H$_2$-), 26.16 (-*C*H$_2$-), 23.18 (-*C*H$_2$-), 14.41 (*C*H$_3$), 11.20 (*C*H$_3$) ppm.

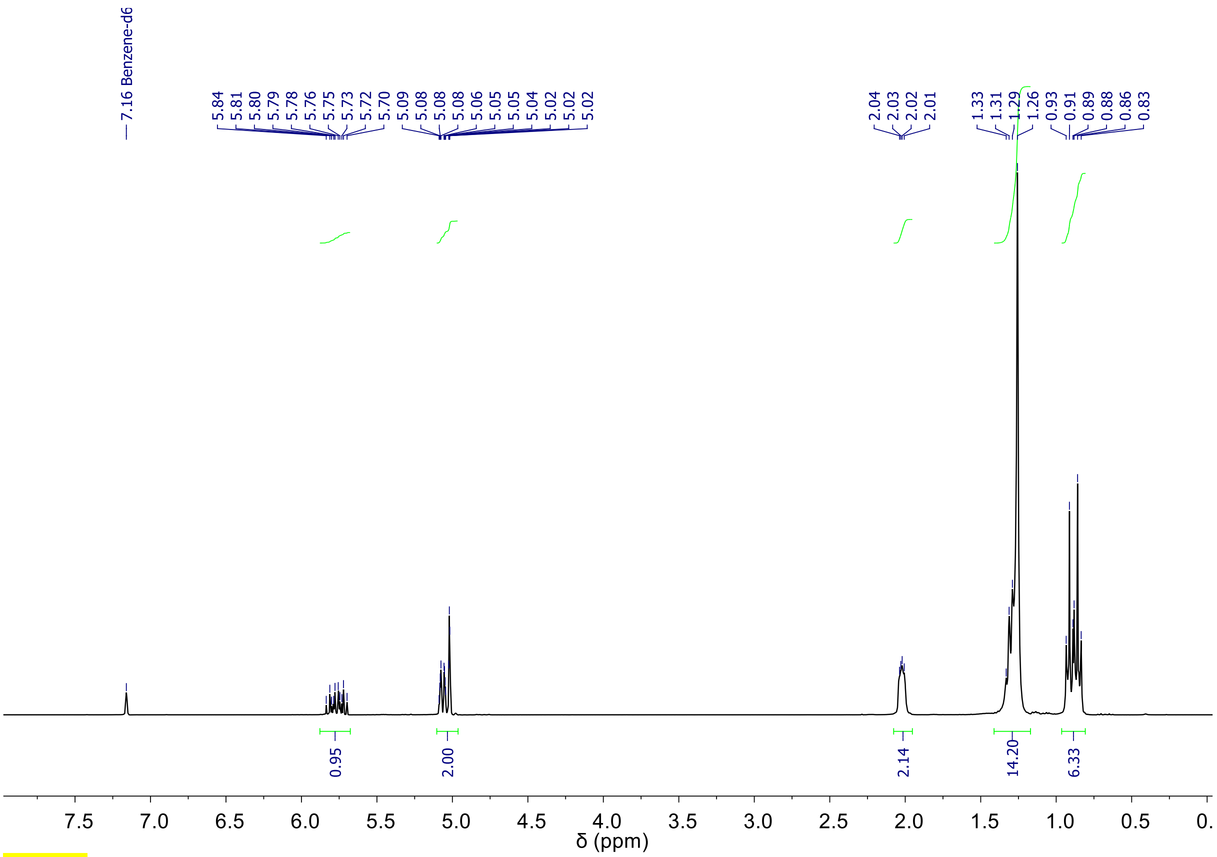


Fig. S6. ^{1}H NMR spectrum of 4-ethyl-1-decene (**b**) (300 MHz, C_6D_6, 296 K).

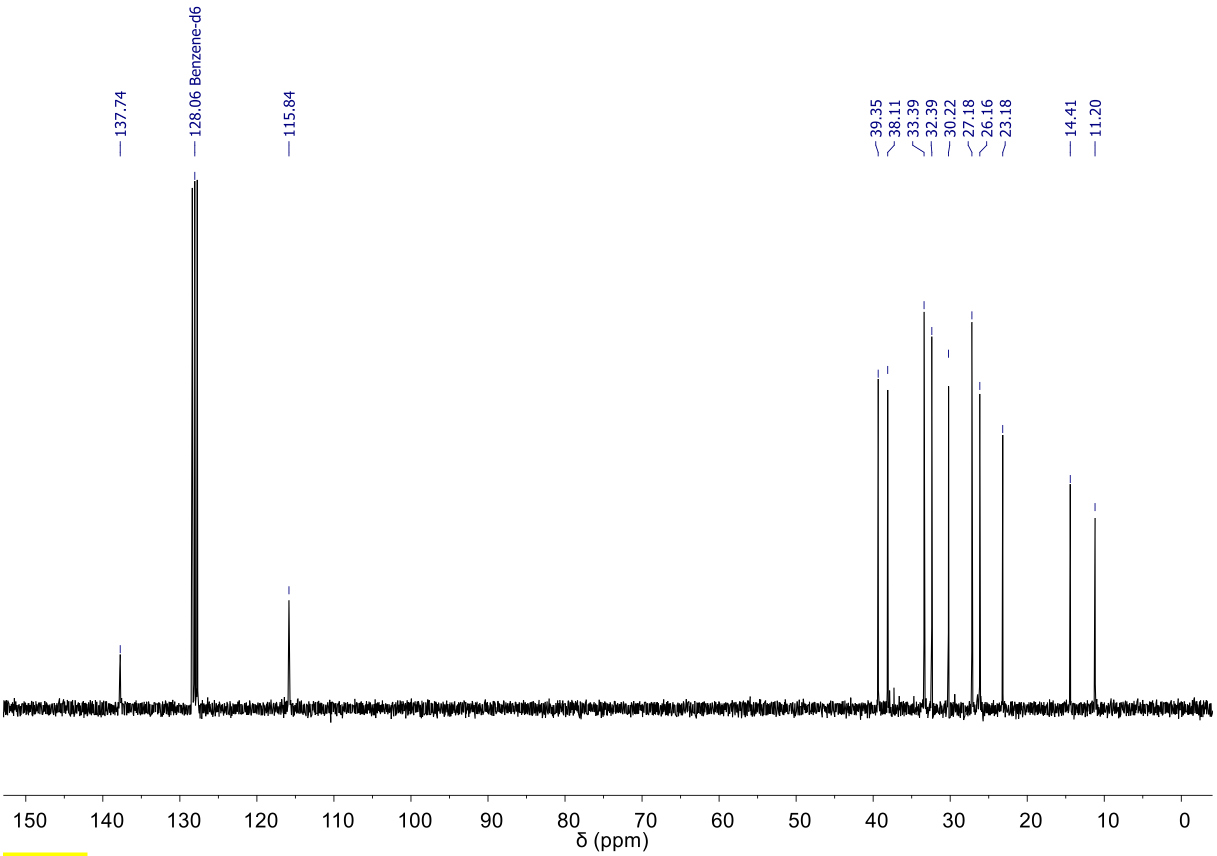


Fig. S7. ^{13}C NMR spectrum of 4-ethyl-1-decene (**b**) (75 MHz, C_6D_6, 296 K).

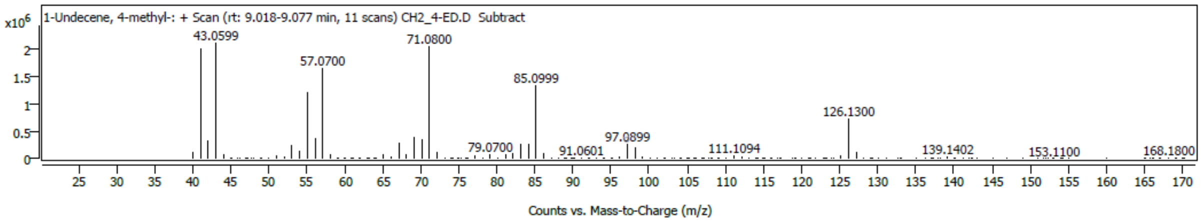
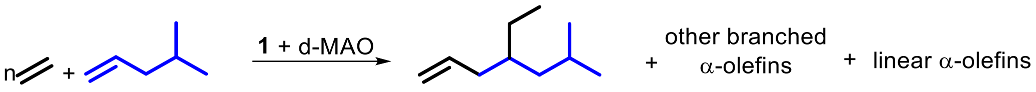


Fig. S8. Mass spectrum of 4-ethyl-1-decene (**b**).

m/z calculated for 4-ethyl-1-decene (**b**) = 168 (100 %), 169 (13.3 %).

m/z observed for 4-ethyl-1-decene (**b**) = 168 (100 %).

2.1.3 Synthesis of 4-ethyl-6-methyl-1-heptene (c)



Here precatalyst-, activator- and scavenger-stock solutions were prepared in benzene with concentrations as mentioned above.

Parameters of the synthesis of 4-ethyl-6-methyl-1-heptene (**c**) are listed in table S7. Mass balances of the products observed are listed in table S8 for the linear α-olefins and in table S9 for the branched α-olefins. The ethylene consumption over time is plotted in figure S9.

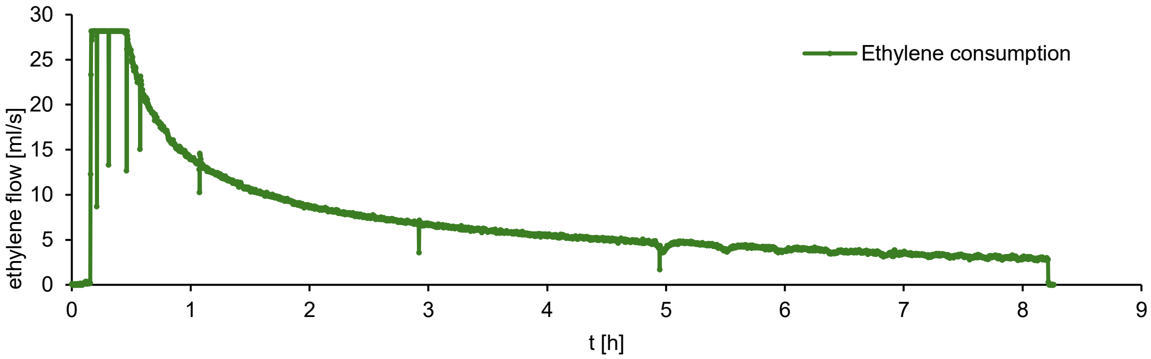


Fig. S9. Ethylene consumption plot over time für synthesis of **c**.

Tab. S7: Parameters of the synthesis of **c**.

n_1 [µmol]	$m_{\text{d-MAO}}$ [mg]	n_{TIBA} [µmol]	$V_{\text{1-hexene}}$ [mL]	T [°C]	p_{ethylene} [bar]	V_{ethylene} [L_n]	t [h]
3.0	6.0	400	300	30	2.5	200	8.0

Tab. S8: Mass balances of the linear α-olefin products from the synthesis of **c**.

1-butene	1-hexene	1-octene	1-decene	1-dodecene
136.7 g	32.8 g	7.0 g	1.5 g	0.3 g

Tab. S9: Mass balances of the branched α-olefin products from the synthesis of **c**.

2-ethyl-1-hexene	4-ethyl-1-hexene	2-ethyl-4-methyl-1-penten	4-ethyl-6-methyl-1-heptene	4-ethyl-1-octene	other br. olefins
0.2 g	24.4 g	0.5 g	17.2 g	7.1 g	18.7 g

4-ethyl-6-methyl-1-heptene (**c**) ^{1}H NMR (300 MHz, C_6D_6, 296 K) δ = 5.82 – 5.68 (m, 1H, $\mathrm{CH_2{=}C}\mathit{H}\mathrm{{-}CH_2{-}}$), 5.07 – 5.01 (m, 2H, $\mathrm{C}\mathit{H_2}\mathrm{{=}CH{-}}$), 1.99 (t, *J*=6.6 Hz, 2H, $\mathrm{{=}CH{-}C}\mathit{H_2}\mathrm{{-}CH{-}}$), 1.66 – 1.52 (m, 1H, $\mathrm{{-}CH_2{-}C}\mathit{H}\mathrm{{-}CH_2{-}}$), 1.43 – 1.32 (m, 1H, $\mathrm{{-}CH_2{-}C}\mathit{H}\mathrm{{-}CH_3}$), 1.29 – 1.22 (m, 2H, $\mathrm{{-}C}\mathit{H_2}\mathrm{{-}}$), 1.11 – 1.06 (m, 2H, $\mathrm{{-}C}\mathit{H_2}\mathrm{{-}}$), 0.87 – 0.81 (m, 9H, $\mathrm{{-}C}\mathit{H_3}$) ppm.

4-ethyl-6-methyl-1-heptene (**c**) ^{13}C NMR (75 MHz, C_6D_6, 296 K) δ = 137.56 ($\mathrm{{=}}\mathit{C}\mathrm{H{-}}$), 115.93 ($\mathit{C}\mathrm{H_2{=}}$), 43.19 ($\mathrm{{-}}\mathit{C}\mathrm{H{-}}$), 38.12 ($\mathrm{{-}}\mathit{C}\mathrm{H{-}}$), 36.71 ($\mathrm{{-}}\mathit{C}\mathrm{H_2{-}}$), 26.26 ($\mathrm{{-}}\mathit{C}\mathrm{H_2{-}}$), 25.52 ($\mathrm{{-}}\mathit{C}\mathrm{H_2{-}}$), 23.07 ($\mathrm{{-}}\mathit{C}\mathrm{H_3}$), 10.97 ($\mathrm{{-}}\mathit{C}\mathrm{H_3}$) ppm.

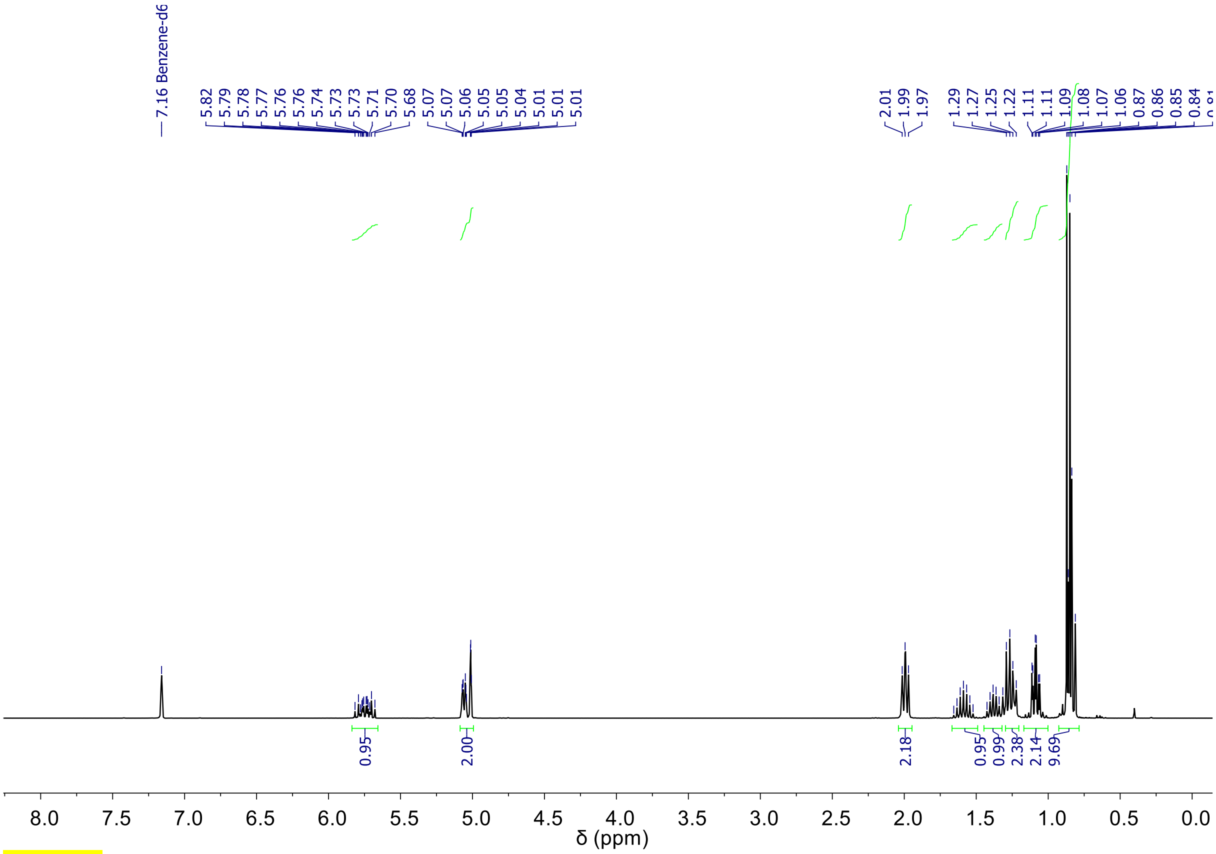


Fig. S10. ^{1}H NMR spectrum of 4-ethyl-6-methyl-1-heptene (**c**) (300 MHz, C_6D_6, 296 K).

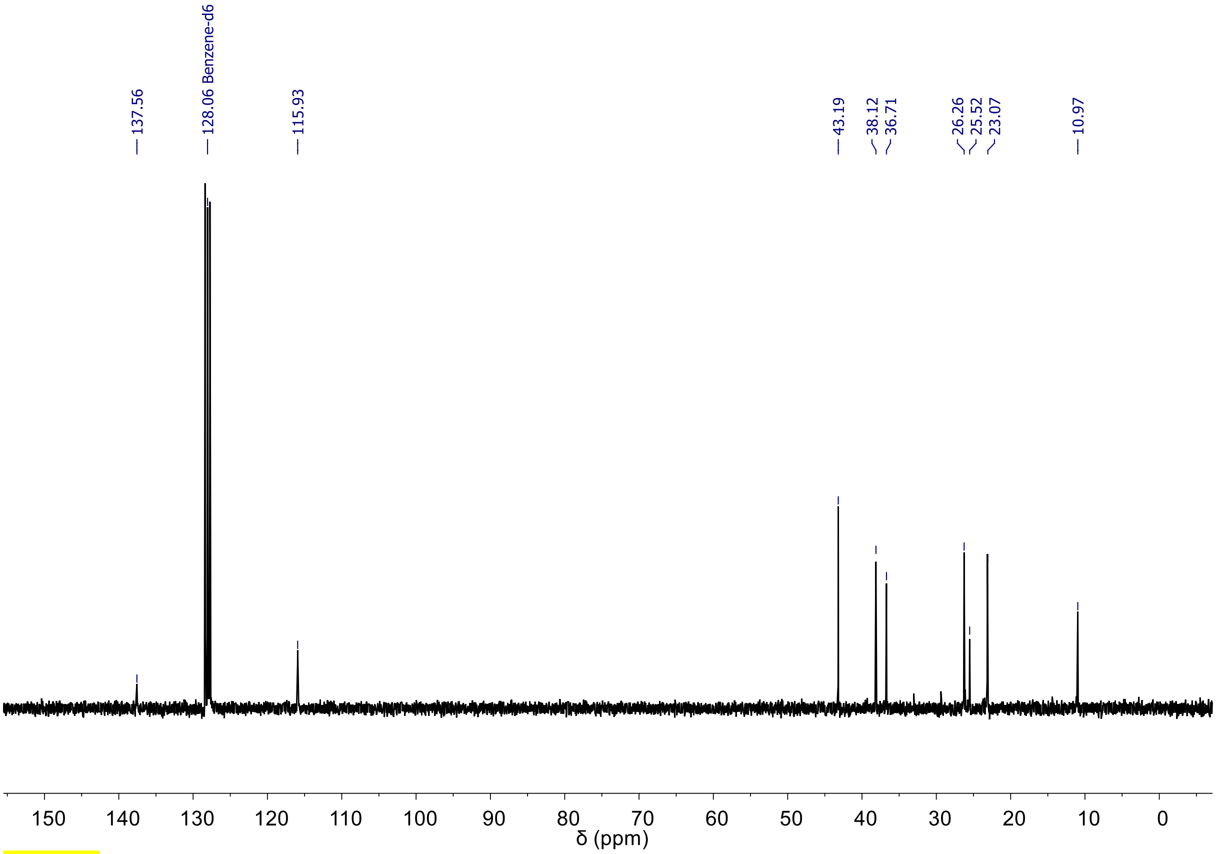


Fig. S11. ^{13}C NMR spectrum of 4-ethyl-6-methyl-1-heptene (**c**) (75 MHz, C_6D_6, 296 K).

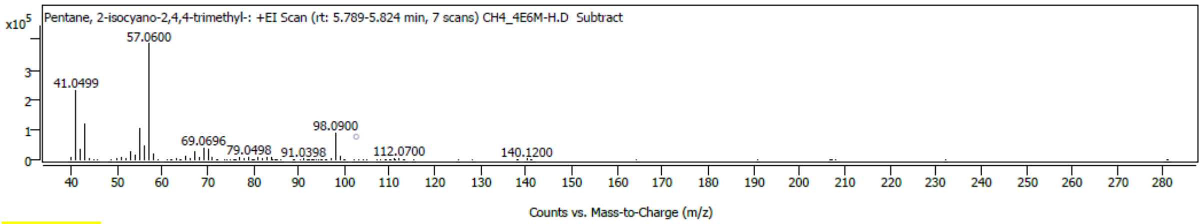


Fig. S12. Mass spectrum of 4-ethyl-6-methyl-1-heptene (**c**).

m/z calculated for 4-ethyl-6-methyl-1-heptene (**c**) = 140 (100 %), 141 (11.0 %).

m/z observed for 4-ethyl-6-methyl-1-heptene (**c**) = 140 (100 %).

3. Distillation of the branched and linear α-olefine product mixtures

For purification and separation of the branched and linear α-olefins synthesized the product mixture was distilled. In table S10 boiling points and atmospheric pressure of the referring fractions are given. The α-olefin fractions of 2-ethyl-1-hexene, 1-octene and the fractions of 2-ethyl-1-octene, 4-ethyl-1-octene, 6-ethyl-1-octene and the fractions of 2-ethy-1-decene, 4-ethyl-1-decene, 6-ethyl-1-decene, 8-ethyl-1-decene form azeotropic mixtures each. Here are the boiling points of these azeotropic mixtures listed.

Tab. S10: Boiling point and corresponding atmospheric pressure of the α-olefins produced by ethylene α-olefin co-oligomerization.

Fraction	T [°C]	p [mbar]
1-hexene	63	1000
2-ethyl-1-butene	65	1000
4-ethyl-1-hexene	112	1000
2-ethyl-1-hexene 1-octene	120	1000
4-ethyl-6-methyl-1-heptene	95	300
2-ethyl-1-octene 4-ethyl-1-octene 6-ethyl-1-octene	110	200
1-decene	172	1000
2-ethyl-1-decene 4-ethyl-1-decene 6-ethyl-1-decene 8-ethyl-1-decene	115	15
1-dodecene	213	1000

Literature

[1] Dietel T. *et al.*, Elongation and branching of α-olefins by two ethylene molecules, *Science*, **2022**, *375*, 1021-1024.

[2] Lukas F. *et al.*, Synthesis of Branched α-Olefins via Trimerization and Tetramerization of Ethylene, *Sci. Adv.*, **2024**, *38*, 2405653.