Supporting Information
to
Cationic Tungsten Imido Alkylidene N-Heterocyclic Carbene Complexes for Stereospecific Ring-Opening Metathesis Polymerization of Norbornene Derivatives

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Experimental Section

General Information

All reactions were performed in the absence of moisture and air using standard Schlenk techniques unless indicated otherwise. Reactions with metal complexes were performed in a glove box filled with nitrogen (MBraun Labmaster 130). Glassware was stored overnight at 120 °C and cooled in an evacuated antechamber. 1H and 13C NMR spectra were recorded using a Bruker Avance III 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts are given in ppm of tetramethylsilane, with solvent resonance from the remaining solvent protons (CDCl3: 7.26 ppm, C6D6 7.16 ppm, CD2Cl2 5.13 ppm) for reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, br = broad, m = multiplet), coupling constant (Hz), and integral. Elemental analyses were performed at the Institute of Inorganic Chemistry, University of Stuttgart, Germany. IR spectra were measured on a Nicolet alpha spectrometer. A Bruker Autoflex III (337 nm, reflector mode) was used for MALDI-ToF MS measurements. Size exclusion chromatography (SEC) was performed in CHCl3. The system consisted of a 1260 Infinity system (Agilent Technologies Inc.) equipped with a precolumn (8 × 50 mm) and three columns and stored over 4 Å Linde type molecular sieves inside a nitrogen filled glove box. Deuterated solvents (Eurisotop) were used as purchased and diethyl ether, toluene, pentane and THF were dried using an MBraun SPS-800 solvent purification system with alumina drying columns and stored over 4 Å Linde-type molecular sieves. Anhydrous benzene and acetonitrile were purchased (Sigma) and stored under 4 Å Linde-type molecular sieves inside a nitrogen filled glove box. Deuterated solvents (Eurisotop) were used as purchased and stored under Lindes-type 4 Å molecular sieves in a glove box. The following reagents were prepared according to literature: LiOHMT (OHMT = O-2,6-(2,4,6-Me3C6H3)2C6H4),1 LiOHIP (OHPT = O-2,6-(2,4,6-Pr3C6H3)2C6H4),2 sodium tetrais(3,5-bis(trifluoromethyl)phenyl) borate ([Na(BArF)4]),3 LiPr4,4 ICy,5 W(N-2,6-Me2C6H4)(CHCMe3Ph)O2Cl(DME),6 W(N-2,6-Pr2C6H4)(CHCMe3Ph)O2Cl(DME),7 W(N-2,6-C6H4Cl)[(CHCMe3Ph)2Ph],8 W(O)(CHCMe3Ph)(OHMT)(Cl)[(PMe2Ph)],9 W(N-2,6-Pr2C6H4)(CHCMe3Ph)(Br)[(IMes)]2[B(ArF)4]],10 M1 – M2,11 M3,12 M4,11 I13,3 I14-I17,16 I8-19,17 I10-I15,10 and I17-I26.10

Preparation of Polymers

Stock solutions of the monomers (M1 – M4) (500 mM, 100 eq) and of the initiators (I1 – I31) (500 μM, 1 eq) in CDCl3 were prepared. Subsequently, both solutions, 500 μL each, were mixed in a scintillation vial (4 mL) under vigorous stirring (600 rpm). The reactions were stirred at rt until completion or for 24 h. Polymers were precipitated in MeOH in Falcon tubes (50 mL) and centrifuged (4500 rpm, 30 min). After drying in vacuo overnight, the samples were subjected to SEC.

For experiments involving the use of BCF, a stock solution of BCF in CDCl3 (250 mM) was added to the initiator solution 30 min prior to mixing with the monomer. All other details remain unchanged.

Kinetics measurements were conducted using stock solutions of the monomers (500 mM in CDCl3, 500 μL, 0.25 mmol, 100 eq, 0.5 M toluene as internal standard) and solutions of the initiators (500 μM in CDCl3, 1 eq). 500 μL of both solutions were mixed in a screw-cap NMR tube and the reaction was monitored by 1H NMR. Conversion was determined by change of the olefinic protons of the monomers with respect to the methyl group of the internal standard.

Quenching experiments were conducted by dissolving the initiator (0.0171 mmol, 15 eq) in CDCl3 (500 μL). 500 μL stock solution of the monomers (M2) (500 mM, 100 eq) were added under vigorous stirring (600 rpm) at rt. After 1 h, 2-methoxyxystyrene (50 μL, 25 eq) was added after which an immediate change in color was observed. The polymer was precipitated in pentane in Falcon tubes (50 mL) and centrifuged (4500 rpm, 30 min).

For MALDI-TOF sample preparation, solutions of the matrix (2,5-dihydroxybenzoic acid, 5 mg/mL in THF), the polymer (5 mg/mL THF) and NaOTf (0.1 M in 90% acetone, 10% water) were mixed in a 2:1:2 ratio.

The analytical data for cis-it poly([+]-DMNBME),11 cis-st, and trans-it poly([+]-DMNBME),16 cis-st, and trans-it cis-st poly([M3])16,17 as well as for cis-st poly([M4])16 were in accordance to literature.

cis-st poly([+]-DMNBME)1 NH MNR (400 MHz, CDCl3) δ = 5.31 (d, J = 7.6 Hz, 1H), 5.24 (d, J = 8.1 Hz, 1H), 3.38 – 3.26 (m, 7H), 3.24 (s, 3H), 3.04 – 2.92 (m, 1H), 2.71 – 2.53 (m, 1H), 2.15 – 2.02 (m, 1H), 1.92 – 1.82 (m, 1H), 1.77 – 1.66 (m, 1H), 1.32 – 1.25 (m, 1H).13C NMR (101 MHz, CDCl3) δ = 134.0, 131.2, 74.5, 73.9, 58.8, 58.7, 48.9, 45.5, 41.0, 40.2, 39.3. IR v[cm–1] = 2978, 2921, 2866, 2822, 2805, 2733, 1475, 1449, 1382, 1260, 1185, 950, 757, 705.

trans-it poly([+]-DMNBME).1 NH MNR (400 MHz, CDCl3) δ = 5.42 (dd, J = 15.2, 7.7 Hz, 1H), 5.32 (dd, J = 15.0, 7.6 Hz, 1H), 3.41 – 3.20 (m, 10H), 2.71 – 2.52 (m, 1H), 2.30 – 2.15 (m, 1H), 2.17 – 2.04 (m, 1H), 1.81 (dt, J = 12.7, 6.2 Hz, 1H), 1.74 – 1.65 (m, 1H), 1.39 (dd, J = 15.8, 6.8 Hz, 1H).13C NMR (101 MHz, CDCl3) δ = 133.7, 130.8, 74.8,
Preparation of Catalysts

\[ \text{Scheme S1. General procedure for the synthesis of cationic tungsten imido neophyldene complexes bearing bulky ligands starting from tungsten imido neophyldene dichloro DME complexes; intermediate complex after addition of lithium aryloxide in mostly oily solids and/or isolation resulted in poor yields.} \]

\[ \text{W(N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OHMT})(\text{Cl})(\text{IiPr}) \text{:} \]

\[ \text{W(N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{Cl})_2(\text{DME}) (520 \text{ mg, 0.88 mmol, 1 eq) was dissolved in toluene (20 mL) and the solution was cooled to -35 °C. LiOHMT (300 mg, 0.88 mmol, 1 eq) was also dissolved in toluene (10 mL) and the solution was cooled to -35 °C. Both solutions were mixed and stirred at room temperature for 2 h. The solvents were removed in vacuo, and the resulting residue was taken up in pentane (30 mL) and filtered through Celite. The filtered solution was coevaporated with pentane (3 x 10 mL), dissolved in pentane, LiPr (130 g; 0.88 mmol; 1 eq) was added and the mixture was stirred at room temperature for 2 h. The solution was dried in vacuo, coevaporated with pentane (3 x 10 mL) and dried in vacuo. Yield: 470 mg, 56%; the off-white product exists in a mixture of two isomers, shifts of both isomers are reported.} \]

\[ \text{[W(N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OHMT})(\text{IiPr})]^+\text{[BAr}^+\text{F}^-\text{]}_2 \text{ (I29):} \]

\[ \text{W(N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CHCMc}_2\text{Ph})(\text{OHMT})(\text{Cl})(\text{IiPr}) \text{(250 mg, 0.26 mmol, 1 eq) was dissolved in dichloromethane (10 mL), to which NaB[A}^+\text{F}^-\text{]}_2 (260 mg, 0.26 mmol, 1 eq) was added. The resulting mixture was stirred at room temperature for 1 h, filtered through Celite, dried in vacuo, and washed with pentane (3 x 5 mL) to afford a yellow compound. Yield: 440 mg, 94%.} \]

\[ \text{\textbf{Reference:} C, 64.32; H, 6.56; N, 4.41. Found: C, 64.32; H, 6.63; N, 4.39.} \]

\[ \text{W(N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OHMT})(\text{Cl})(\text{Icy}) \text{ (I29):} \]

\[ \text{W(N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{Cl})_2(\text{DME}) (300 mg, 0.50 mmol, 1 eq) was dissolved in toluene (10 mL) and the solution was cooled to -35 °C, and LiOHMT (170 mg, 0.50 mmol, 1 eq) was also dissolved in toluene (5 mL) and the solution was cooled to -35 °C. Both solutions were combined and stirred at room temperature for 2 h. The solvents were removed in vacuo, and the resulting residue was taken up in pentane (30 mL) and filtered over Celite. The filtered solution was coevaporated with pentane (3 x 10 mL), dissolved in pentane, Icy (120 mg, 0.50 mmol, 1 eq) was added and stirred at room temperature for 2 h. The solution was dried in vacuo, coevaporated with pentane (3 x 10 mL) and again dried in vacuo to yield an off-white solid. Yield: 370 mg, 71%.} \]

\[ \text{\textbf{Reference:} C, 56.00; H, 4.19; N, 2.36. Found: C, 55.94; H, 4.44; N, 2.40.} \]

\[ \text{S3} \]
the off

W(N[2,6-Me2C6H3])(CHCMe2Ph)(OHMT)(ICy)\[B(\text{Ar}^7)^{\text{III}}\] \[\text{I}(130)\]: W(N[2,6-Me2C6H3])(CHCMe2Ph)(OHMT)(Cl)(ICy) (200 mg, 0.19 mmol, 1 eq) was dissolved in dichloromethane (5 mL), to which NaB(\text{Ar}^7)^{\text{III}} (170 mg, 0.19 mmol, 1 eq) was added. The resulting mixture was stirred at room temperature for 1 h, filtered off, and the off-white solid was washed with pentane (3 x 5 mL), to afford a yellow compound. Yield: 310 mg, 83%. \[\text{H NMR} \ (\text{CDCl}_3, 400 \text{ MHz}) \delta = 10.72 \ (s, 1H), 7.75 \ (s, 8H), 7.58 \ (s, 4H), 7.33 \ (s, 2H), 7.24 \ (t, 1H), 7.13 – 7.03 \ (m, 6H), 6.99 – 6.92 \ (m, 4H), 6.91 \ (s, 2H), 6.88 \ (2H), 3.91 \ (tt, 2H), 2.25 \ (s, 6H), 2.11 \ (s, 6H), 2.05 \ (s, 6H), 1.83 – 1.56 \ (m, 16H), 1.50 – 1.38 \ (m, 10H), 1.13 – 0.84 \ (m, 6H). \[\text{C NMR} \ (\text{CDCl}_3, 101 \text{ MHz}) \delta = 282.3 \ (s), 179.2 \ (s), 162.2 \ (m), 158.6 \ (s), 153.8 \ (s), 149.0 \ (s), 138.2 \ (s), 136.7 \ (s), 136.6 \ (s), 136.2 \ (s), 134.9 \ (s), 132.0 \ (s), 131.8 \ (s), 129.4 \ (m), 128.5 \ (s), 128.1 \ (s), 126.9 \ (s), 126.5 \ (s), 126.4 \ (s), 125.4 \ (s), 123.7 \ (s), 121.8 \ (s), 117.9 \ (m), 62.9 \ (s), 34.7 \ (s), 34.6 \ (s), 33.9 \ (s), 33.6 \ (s), 32.8 \ (s), 25.5 \ (s), 25.2 \ (s), 24.8 \ (s), 21.5 \ (m), 21.2 \ (m), 19.4 \ (s). \[\text{F NMR} \ (\text{CDCl}_3, 376 \text{ MHz}) \delta = -62.81 \ (s). \[\text{Elemental analysis} \ (%) \text{ of C}_{36}H_{62}BCl_{34}N_{2}O_{3}W. \text{ Calculated}: C, 37.46; H, 6.04; N, 1.63. \text{ Found}: C, 37.35; H, 6.17; N, 1.55. S4
of both isomers are reported. \(^1\)H NMR (CD$_2$Cl$_2$, 400 MHz) \(\delta = 10.77\) (s, 0.04H), 10.26 (s, 0.96H), 7.35 (s, 1H), 7.29 – 7.04 (m, 9H), 7.01 – 6.68 (m, 7H), 3.85 – 3.52 (m, 3H), 3.28 – 2.80 (m, 5H), 1.54 (d, \(J = 6.7\) Hz, 3H), 1.36 (d, \(J = 6.8\) Hz, 3H), 1.14 (d, \(J = 6.8\) Hz, 3H), 1.08 (d, \(J = 6.8\) Hz, 3H), 1.05 – 0.97 (m, 12H), 0.93 – 0.85 (m, 3H), 0.74 – 0.52 (m, 6H). 13C NMR (CD$_2$Cl$_2$, 101 MHz) \(\delta = 272.0\), 188.8, 159.8, 151.4, 150.8, 149.1, 148.2, 148.0, 147.7, 147.5, 146.3, 138.9, 138.7, 135.2, 134.4, 132.0, 131.6, 128.7, 128.2, 126.8, 126.2, 125.4, 123.1, 121.1, 121.5, 120.3, 117.6, 117.3, 36.6, 34.8, 34.6, 31.1, 31.0, 30.9, 27.9, 26.9, 26.7, 26.1, 25.1, 25.0, 24.6, 24.5, 24.4, 24.3, 24.0, 23.5, 23.2, 22.9.  

**Elemental analysis** (\%) of Cs$_2$HgCl$_3$N$_2$O$_3$W. Calculated: C, 63.08; H, 6.94; N, 3.62. Found: C, 63.06; H, 7.08; N, 3.54.

\[
\text{[W(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(HOIPT)(IIPr)\text{][B(Ar$^\text{f}$)$_2$]] (I22)}: \text{W(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(HOIPT)(CI)(IIPr) \text{[200 mg, 0.17 mmol, 1 eq]}} \text{dissolved in dichloromethane (2 mL), the solution was cooled to \(-35^\circ\text{C}\), then NaB(Ar$^\text{f}$)$_2$ \text{[153 mg, 0.17 mmol, 1 eq]}} \text{was added, the resulting mixture was stirred at room temperature for 1 h, then filtered through Celite, dried in vacuo with pentane (4 x 2 mL) to afford a yellow solid. Yield: 303 mg, 88\%}.  
\]

13C NMR (CD$_2$Cl$_2$, 101 MHz) \(\delta = 290.7, 173.8, 162.5, 162.0, 161.5, 161.0, 159.3, 149.3, 147.3, 147.4, 146.8, 143.8, 133.4, 132.6, 130.8, 129.3, 129.0, 128.7, 128.4, 128.0, 126.9, 125.9, 125.6, 124.2, 123.2, 121.9, 121.6, 121.5, 120.5, 117.4, 55.8, 54.8, 34.6, 34.1, 31.2, 31.1, 29.9, 25.0, 24.9, 24.1, 24.0, 23.7, 23.5, 23.2, 22.3, 13.8.  

\[
\text{[W(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(2,5-Me$_2$Pyr)r)](I)} \text{[Me]: 1,3-Dimethylimidazolium iodide \text{[190 mg, 84 mmol, 1 eq]}} \text{dissolved in diethyl ether (3 mL), to which KHMDMS \text{[170 mg, 0.84 mmol, 1 eq]}} \text{was added and stirred at room temperature for 30 min. The solution was filtered through Celite and added to a \(-35^\circ\text{C}\) cold solution of W(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph) \text{[530 mg, 0.84 mmol, 1 eq]}} \text{in THF (6 mL). The mixture was stirred at room temperature for 3 h, the solvent was removed in vacuo and the remaining solid was washed with diethyl ether \text{[3 x 5 mL]} \text{and dried in vacuo. Yield: 240 mg, 40\%}.}  
\]

\[
\begin{align*}
\text{[W(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(2,5-Cl$_2$Pyr)r)](Cl)} \text{[I]: Dimethylimidazolium iodide \text{[190 mg, 84 mmol, 1 eq]}} \text{dissolved in diethyl ether (3 mL), the solution was cooled to \(-35^\circ\text{C}\) and the remaining solid was washed with diethyl ether \text{[3 x 5 mL]} \text{and dried in vacuo. Yield: 240 mg, 40\%}.}  
\end{align*}
\]

A yellow solid was obtained. Yield: 240 mg, 40\%.  

**Elemental analysis** (\%) of W(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(2,5-Cl$_2$Pyr)r)](I). Calculated: C, 58.42; H, 6.30; N, 9.73. Found: C, 58.02; H, 6.270; N, 9.33.

**Scheme S2.** Synthesis of I27 from W(N-2,6-Cl$_2$C$_6$H$_3$)(CHC(CH$_3$)$_2$Ph)(2,5-Me$_2$Pyr):  

\[\text{[W(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(2,5-Cl$_2$Pyr)r)](Cl)} \text{[I]: Dimethylimidazolium iodide \text{[190 mg, 84 mmol, 1 eq]}} \text{dissolved in diethyl ether (3 mL), the solution was cooled to \(-35^\circ\text{C}\) and the remaining solid was washed with diethyl ether \text{[3 x 5 mL]} \text{and dried in vacuo. Yield: 240 mg, 40\%}.}  
\]

Elemental analysis (\%) of W(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(2,5-Cl$_2$Pyr)r)](Cl). Calculated: C, 58.42; H, 6.30; N, 9.73. Found: C, 58.02; H, 6.270; N, 9.33.
Scheme S3. Reaction of the precursor complex with acetonitrile thereby avoiding the use of MeCN as solvent; possible side reactions can occur.

\[
W(\text{N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{NC(CH}_3\text{)}\text{CHC(CH}_3\text{)}\text{CPh})(\text{OHMT})(\text{Cl}) : W(\text{N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{NC(CH}_3\text{)}\text{CHC(CH}_3\text{)}\text{CPh})\text{Cl}_2(\text{DME}) (300 \text{ mg; 0.46 mmol; 1 eq}) was dissolved in toluene (10 mL) and the solution was cooled to -35 °C. LiOHMT (150 mg; 0.46 mmol; 1 eq) was dissolved in toluene (5 mL) and the solution was cooled to -35 °C. Both solutions were mixed and stirred at room temperature for 2 h. The solvents were removed in vacuo, and the resulting residue was taken up in pentane and filtered through Celite. The filtered solution was coevaporated with pentane (3 x 10 mL), dissolved in pentane, five drops of acetonitrile were added and stirred at room temperature for 2 h. The solution was again dried in vacuo, coevaporated with pentane (3 x 5 mL) and dried in vacuo. Yield: 0.12 g; 29%. \]

**1H NMR** (CDCl3, 400 MHz) \(\delta = 7.21 (m, 5H), 7.12 (m, 3H), 7.07 (d, 2H), 6.96 (s, 2H), 6.92 (t, 1H), 6.85 (s, 2H), 4.92 (m, 1H), 3.05 (sept, 2H), 2.26 (s, 6H), 2.14 (s, 6H), 2.01 (s, 6H), 1.36 (s, 3H), 1.33 (s, 3H), 1.10 (d, 6H), 1.03 (d, 6H), 0.95 (s, 3H).

**13C NMR** (CDCl3, 101 MHz) \(\delta = 158.2 (s), 151.6 (s), 150.60 (s), 150.5 (s), 143.8 (s), 137.7 (s), 137.5 (s), 136.9 (s), 134.2 (s), 132.1 (s), 130.5 (s), 128.9 (s), 128.5 (s), 128.4 (s), 126.6 (s), 126.0 (s), 125.9 (s), 124.0 (s), 122.1 (s), 38.4 (s), 31.8 (s), 31.6 (s), 28.3 (s), 24.0 (s), 23.5 (s), 21.3 (s), 21.0 (s), 20.8 (s), 19.7 (s).

**Elemental analysis (%) of C48H57ClN2O.** Calculated: C, 64.25; H, 6.40; N, 3.12. Found: C, 63.98; H, 6.616; N, 3.11.

Scheme S4. Preparation of the nitrile-free complex I16.

\[
[W(\text{N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{CHCMesPh})(\text{OC}_6\text{F}_5)(\text{IMes})^+][\text{B(ArF)}_4^-] \] (I16): A solution of \([W(\text{N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{CHCMesPh})(\text{Br})][\text{B(ArF)}_4^-] \) (300 mg, 0.172 mmol, 1.0 eq) in CH2Cl2 (4 mL) was added to a suspension of LiOC6F5 (32.8 mg, 0.172 mmol, 1.0 eq) in CH2Cl2 (4 mL). The suspension was stirred for 16 hours at room temperature followed by filtration through a pad of Celite. The solvent was removed in vacuo and the residue was triturated with pentane to give a yellow foam. Yield: 200 mg, 0.10 mmol, 60 %. \(1^H\text{ NMR} \) (CDCl3, 400 MHz): \(\delta = 10.35 \) (s, 1H), 7.69 (s, 8H), 7.50 (s, 4H), 7.45 (s, 2H), 7.36 – 7.12 (m, 6H), 7.05 (s, 2H), 7.01 (m, 2H), 6.95 (s, 2H), 6.81 (m, 2H), 3.02 (h, 2H), 2.34 (s, 6H), 2.00 (s, 12H), 1.52 (s, 3H), 1.17 (m, 12H), 0.93 (d, 6H), 0.65 (s, 3H) ppm. \(1^F\text{ NMR} \) (CDCl3, 376 MHz): \(\delta = -62.43 \) (24F), -158.15 (2F), 161.56 (3F) ppm. \(1^3C\text{ NMR} \) (CDCl3, 101 MHz): \(\delta = 283.13, 162.44, 161.94, 161.45, 160.95, 151.28, 148.13, 146.44, 143.07, 135.43, 134.80, 131.75, 130.38, 129.05, 128.72, 128.37, 127.67, 126.64, 125.90, 124.66, 123.63, 123.19, 120.48, 117.44, 54.10, 31.90, 28.89, 28.02, 23.59, 22.36, 21.05, 17.96, 17.65, 17.03, 14.39, 14.07 ppm. **Elemental analysis (%) of C81H57BF29N3OW.** Calculated: C, 52.82; H, 3.56; N, 2.28. Found: C, 52.70; H, 3.833; N, 2.19.
Scheme S5. Preparation of 128.

W(O)(CHCMe₂Ph)(5-MeCl₂)(OHMT)(Cl): W(O)(CHCMe₂Ph)(OHMT)(Cl)(PMe₂Ph) (140 mg, 0.156 mmol) was dissolved in 10 mL of benzene. Solid AgI-1,3-dimethyl-4,5-dichloroimidazol-2-ylidine (75 mg, 1.2 eq) was added under stirring (more equivalents of AgI-1,3-dimethyl-4,5-dichloroimidazol-2-ylidine and gentle heating to 50 °C might be necessary on larger scales to obtain full conversion). The reaction mixture was stirred for another 12 h at room temperature. All solids were filtered off over celite and the filtrate was reduced to dryness. The residue was taken up in a mixture of diethyl ether and pentane (4 mL, 1:1). The colorless insoluble solid that formed was filtered off. The filtrate was reduced to 1 mL and filtered once again. Then the solution was stored at -35 °C overnight. An off-white solid material precipitated. Yield 78 mg, 58%. ³¹H NMR (400 MHz, CDCl₃) δ 10.24 (s, J = 125.9 Hz, 1H, W=CH), 7.15 (m, 3H, Ar), 7.09 (m, 2H, Ar), 7.03 (br s, 2H, Ar), 6.95 (br m, 2H, Ar), 6.79 (br s, 2H, Ar), 6.56 (br s, 1H, Ar), 3.08 (br s, 6H, Me-NHC). Analysis of 128: C, 50.66; H, 3.38; N, 2.43. Found: C, 50.51; H, 3.33; N, 2.40.

[128]: W(O)(CHCMe₂Ph)(5-MeCl₂)(OHMT)(MeCN)³⁺[B(AlF₄)₄−] (128): W(O)(CHCMe₂Ph)(5-MeCl₂)(OHMT)(Cl) (67 mg, 0.0776 mmol) was dissolved in 4 mL CH₂Cl₂ and the solution was cooled to -35 °C. Solid Ag(MeCN)₂B(AlF₄)₄ (1 eq) was added under stirring. Immediately, the color changed to bright yellow. The reaction was stirred for 30 min at room temperature. The reaction mixture was cooled to 35 °C. All insoluble solids were filtered off over celite. The filtrate was reduced to dryness to obtain a yellow foam. The foam was triturated with pentane until a yellow solid formed. The pentane phase was decanted and the remaining solid was dried in vacuo. Yield: 119 mg, 89%. ³¹H NMR (400 MHz, CDCl₃) δ 11.66 (s, JCH = 125.6 Hz, 1H, W=CH), 7.71 (br m, 8H, o- Ar-B(AlF₄)₄), 7.23 – 7.1 (m, 6H, Ar), 7.04 (br s, 2H, Ar-Mes), 6.95 – 6.9 (m, 2H, Ar), 6.81 (br s, 2H, Ar-Mes), 3.07 (br s, 6H, Me-NHC), 2.34 (s, 6H, Me-Mes), 2.14 (s, 3H, MeCN), 2.04 (s, 6H, Me-Mes), 1.69 (s, 6H, Me-Mes), 1.56 (s, 3H, CMe₂Ph), 1.50 (s, 3H, CMe₂Ph). ¹³C NMR (101 MHz, CDCl₃) δ 306.6 (W=CH), 186.8 (NCN-NHC), 161.6 (Ar), 156.4 (Ar), 146.4 (Ar), 138.4 (Ar), 136.6 (Ar), 135.7 (Ar), 133.8 (Ar), 130.5 (Ar), 130.3 (Ar), 129.2 (Ar), 128.7 (Ar), 128.6 (Ar), 127.3 (Ar), 126.1 (Ar), 125.4 (Ar), 124.2 (Ar), 123.4 (Ar), 120.0 (Ar), 117.6 (Ar), 51.1 (CMe₂Ph), 36.4 (Me-NHC), 29.4 (CMe₂Ph), 29.1 (CMe₂Ph), 21.3 (Me-Mes), 21.2 (Me-Mes), 20.0 (Me-Mes), 119.6 (Me-Mes). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.38 (s, 24F, B(AlF₄)₄). Analysis of 128 (%): C, 50.66; H, 3.38; N, 2.43. Found: C, 50.51; H, 3.33; N, 2.40.
Solution NMR Spectra of Catalysts

Figure S1. $^1$H-NMR of W(N-2,6-Me$_2$C$_6$H$_3$)(CHC(CH$_3$)$_2$Ph)(OHMT)(Cl)(iPr) in C$_6$D$_6$.

Figure S2. $^{13}$C-NMR of W(N-2,6-Me$_2$C$_6$H$_3$)(CHC(CH$_3$)$_2$Ph)(OHMT)(Cl)(iPr) in C$_6$D$_6$. 
Figure S3. $^1$H-NMR of [W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHMT)(iPr)][B(ArF)$_4$] (I29) in CD$_2$Cl$_2$.

Figure S4. $^{13}$C-NMR of [W(N-2,6-Me$_2$C$_6$H$_3$)(CHC(CH$_3$)$_2$Ph)(OHMT)(iPr)][B(ArF)$_4$] (I29) in CD$_2$Cl$_2$. 
Figure S5. $^{19}$F-NMR of [W(2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHMT)(tIiPr)][B(ArF)$_4$]$^-$ (I29) in CD$_2$Cl$_2$.

Figure S6. $^1$H-NMR of W(2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHMT)(Cl)(tCy) in CD$_2$Cl$_2$. 
Figure S7. $^{13}$C-NMR of W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHMT)(Cl)(ICy) in CD$_2$Cl$_2$.

Figure S8. $^1$H-NMR of [W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHMT)(ICy)]$^+$[B(ArF)$_4$]$^-$ (I30) in CD$_2$Cl$_2$. 
Figure S9. $^{13}$C-NMR of $[W(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{CHCM}_{2}\text{Ph})(\text{OHMT})(\text{ICy})]^+[\text{B(ArF)}_4]^-$ (I30) in CD$_2$Cl$_2$.

Figure S10. $^{19}$F-NMR of $[W(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{CHCM}_{2}\text{Ph})(\text{OHMT})(\text{ICy})]^+[\text{B(ArF)}_4]^-$ (I30) in CD$_2$Cl$_2$. 
Figure S11. $^1$H-NMR of W(N-2,6-MeC$_6$H$_3$)(CHCMe$_2$Ph)(OHIPT)(Cl) in CD$_2$Cl$_2$.

Figure S12. $^{13}$C-NMR of W(N-2,6-MeC$_6$H$_3$)(CHCMe$_2$Ph)(OHIPT)(Cl) in CD$_2$Cl$_2$. 
Figure S13. $^1$H-NMR of W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHIPT)(Cl)(iPr) in CD$_2$Cl$_2$.

Figure S14. $^{13}$C-NMR of W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHIPT)(Cl)(iPr) in CD$_2$Cl$_2$. 
Figure S15. $^1$H-NMR of [W(2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHIPT)(Cl)(IIPr)$_2$][B(ArF)$_4$] (I31) in CD$_2$Cl$_2$.

Figure S16. $^{13}$C-NMR of [W(2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHIPT)(Cl)(IIPr)$_2$][B(ArF)$_4$] (I31) in CD$_2$Cl$_2$. 
Figure S17. $^{19}$F-NMR of $[\text{W}(\text{N}-2,6-\text{Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OHIPT})(\text{Cl})(\text{liPr})]^+\text{[B(ArF)]_4}^- (\text{I31})$ in CD$_2$Cl$_2$.

Figure S18. $^1$H-NMR of $\text{W}(\text{N}-2,6-\text{Cl}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OHIPT})(\text{Cl})(\text{liPr})$ in CD$_2$Cl$_2$. 
Figure S19. $^{13}$C-NMR of W(N-2,6-Cl$_2$C$_6$H$_3_2$)(CHCMe$_2$Ph)(OHIP)(Cl)(iiPr) in CD$_2$Cl$_2$.

Figure S20. $^1$H-NMR of [W(N-2,6-Cl$_2$C$_6$H$_3_2$)(CHCMe$_2$Ph)(OHIP)(iiPr)][B(ArF)$_4$]+ (I32) in CD$_2$Cl$_2$. 
Figure S21. $^{13}$C-NMR of [W(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHIPT)(liPr)][B(ArF)$_4$] (I32) in CD$_2$Cl$_2$.

Figure S22. $^{19}$F-NMR of [W(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHIPT)(liPr)][B(ArF)$_4$] (I32) in CD$_2$Cl$_2$. 
Figure S23. $^1$H-NMR von W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(2,5-Me$_2$Pyr)$_2$(IME) in CD$_2$Cl$_2$.

Figure S24. $^{13}$C-NMR von W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(2,5-Me$_2$Pyr)$_2$(IME) in CD$_2$Cl$_2$. 
Figure S25. $^1$H-NMR of $[W(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(2,5-\text{Me}_2\text{Pyr})(\text{IMe})]^+ [\text{B(ArF)}_4^-]$ (I27) in CD$_2$Cl$_2$.

Figure S26. $^{13}$C-NMR of $[W(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(2,5-\text{Me}_2\text{Pyr})(\text{IMe})]^+ [\text{B(ArF)}_4^-]$ (I27) in CD$_2$Cl$_2$. 
Figure S27. $^{19}$F-NMR of $[\text{W}(\text{N}-2,6-\text{Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(2,5-\text{Me}_2\text{Pyr})(\text{IMe})^+][\text{B(ArF})_4^-]$ (127) in CD$_2$Cl$_2$.

Figure S28. $^1$H-NMR of $\text{W}(\text{N}-2,6-\text{iPr}_2\text{C}_6\text{H}_3)(\text{NC(CH}_3\text{CHC(CH}_3\text{)_2Ph})(\text{OHMT})(\text{Cl})$ in CD$_2$Cl$_2$. 
Figure S29. $^{13}$C-NMR of W(N-2,6-(Pr$_2$C$_6$H$_3$))(NC(CH$_3$)CHC(CH$_3$)$_2$Ph)(OHMT)(Cl) in CD$_2$Cl$_2$.

Figure S30. $^1$H-NMR of [W(N-2,6-(Pr$_2$C$_6$H$_3$))(CHCMe$_2$Ph)(OC$_6$F$_5$)(IMes)$^+$][{(ArF)$_2$}$_4$]$^-$ (I16) in CDCl$_3$. 
Figure S31. $^{19}$F-NMR of [W(2,6-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OC$_6$F$_5$)(IMes)]$^+$/[(B(ArF)$_4$)$_{-}$] (I16) in CDCl$_3$.

Figure S32: $^{13}$C-NMR of [W(2,6-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OC$_6$F$_5$)(IMes)]$^+$/[(B(ArF)$_4$)$_{-}$] (I16) in CDCl$_3$. 

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Figure S33. $^1$H NMR spectrum of W(O)(CHCMe$_2$Ph)(5-MeCl$_2$)(OHMT)(Cl) in CDCl$_3$.

$^1$C NMR (101 MHz, CDCl$_3$) 5290.5, 189.6, 159.1, 150.3, 136.4, 131.0, 129.5, 128.0, 127.1, 126.1, 125.8, 125.8, 118.2, 49.2, 36.0, 30.5, 30.2, 21.7, 21.2, 19.6.

Figure S34. $^{13}$C NMR spectrum of W(O)(CHCMe$_2$Ph)(5-MeCl$_2$)(OHMT)(Cl) in CDCl$_3$.
Figure S35. $^1$H NMR spectrum of I28 in CDCl$_3$.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 11.66, 7.71, 7.52, 7.16, 7.04, 6.91, 6.81, 3.67, 2.34, 2.14, 2.04, 1.69, 1.56, 1.50.

Figure S36. $^{13}$C NMR spectrum of I28 in CDCl$_3$.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 306.6, 186.8, 161.6, 156.4, 146.4, 138.4, 136.6, 135.7, 135.0, 133.8, 130.5, 130.3, 129.2, 128.7, 128.6, 127.1, 126.1, 125.4, 124.2, 123.4, 120.0, 117.6, 51.1, 36.4, 29.4, 29.1, 21.3, 21.2, 20.0, 2.9.
Figure S37. $^{19}$F NMR spectrum of I28 in CDCl$_3$. 

^{19}F NMR (376 MHz, CDCl$_3$) $\delta$ -62.38.
Solution NMR Spectra of Polymers

**Figure S38.** $^1$H-NMR of cis-st poly[(+DMMNBE); polymerization of 100 eq. (+)-(2S,3S)-2,3-(dimethoxymethyl)norborn-5-ene (M1) by the action of I1 in CDCl₃.

**Figure S39.** Olefinic region of cis-st poly[(+DMMNBE); polymerization of 100 eq. (M1) by the action of I1 in CDCl₃.
Figure S40. $^{13}$C-NMR of cis-st poly[(+DMMNBE); polymerization of 100 eq. (M1) by the action of I1 in CDCl$_3$.

Figure S41. $^1$H-NMR of cis-it poly[(+DMMNBE); polymerization of 100 eq. (+)-(2S,3S)-2,3-(dimethoxymethyl)norborn-5-ene (M1) by the action of I2 in CDCl$_3$. 
Figure S42. Olefinic region of the $^1$H-NMR spectrum of cis-it poly[(+DMMNBE)]; polymerization of 100 eq. (M1) by the action of I2 in CDCl$_3$.

Figure S43. $^{13}$C-NMR of cis-it poly[(+DMMNBE)]; polymerization of 100 eq. (M1) by the action of I2 in CDCl$_3$. 
Figure S44. $^1$H-NMR of trans-it poly[(+)DMMNBE]; polymerization of 100 eq. (+)-(2S,3S)-2,3-(dimethoxymethyl)norbom-5-ene (M1) by the action of I3 in CDCl3.

Figure S45. Olefinic region of the $^1$H-NMR of trans-it poly[(+)DMMNBE]; polymerization of 100 eq. (M1) by the action of I3 in CDCl3.
Figure S46. $^{13}$C-NMR of trans-1t poly[(+)-DMMNBE]; polymerization of 100 eq. (M1) by the action of I3 in CDCl3.

Figure S47. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I14 in CDCl3.
Figure S48. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I14 with 5 eq. BCF in CDCl$_3$.

Figure S49. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I12 in CDCl$_3$. 
Figure S50. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I25 in CDCl₃.

Figure S51. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I25 with 5 eq. BCF in CDCl₃.
Figure S52. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I26 in CDCl$_3$.

Figure S53. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I13 in CDCl$_3$. 
Figure S54. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I8 in CDCl₃.

Figure S55. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I9 in CDCl₃.
Figure S56. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I7 in CDCl$_3$.

Figure S57. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I16 in CDCl$_3$. 

I7: R = R' = $i$Pr, X = 2,5-Me$_2$-pyr

I16: R = Mes, X = OC$_2$F$_5$, Y = H, L = none
Figure S58. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I15 in CDCl$_3$.

Figure S59. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I15 with 5 eq. BCF in CDCl$_3$. 

I15. R = Mes, X = OC$_6$F$_5$, Y = H, L = PivCN

+ 5 eq. BCF
Figure S60. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I17 in CDCl$_3$.

Figure S61. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I17 with 5 eq. BCF in CDCl$_3$. 
Figure S62. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I24 in CDCl$_3$.

Figure S63. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I24 with 5 eq. BCF in CDCl$_3$. 

I24: $R = R' = Cl, X = OCF_2F_5$
Figure S64. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I22 in CDCl₃.

Figure S65. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I22 with 5 eq. BCF in CDCl₃.
Figure S66. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I23 in CDCl$_3$.

Figure S67. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I4 in CDCl$_3$. 

I23: R = R' = Cl, X = OTf

I4: X = Cl
Figure S68. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I5 in CDCl$_3$.

Figure S69. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I6 in CDCl$_3$. 
Figure S70. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I10 in CDCl$_3$.

Figure S71. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I11 in CDCl$_3$. 

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Figure S72. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I18 in CDCl$_3$.

Figure S73. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I19 in CDCl$_3$. 
**Figure S74.** Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I20 in CDCl$_3$.

**Figure S75.** Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I21 in CDCl$_3$. 

I20: $R = tbu$, $R' = H$, $X = OTf$

I21: $R = tbu$, $R' = H$, $X = OC_6F_5$
Figure S76. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I28 in CDCl$_3$.

Figure S77. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I28 with 5 eq. BCF in CDCl$_3$. 
**Figure S78.** Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I29 in CDCl₃.

**Figure S79.** Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I30 in CDCl₃.
Figure S80. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I31 in CDCl$_3$.

Figure S81. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M1) by the action of I32 in CDCl$_3$. 
**Figure S82.** Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M2) by the action of I7 in CDCl$_3$.

**Figure S83.** Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M3) by the action of I7 in CDCl$_3$. 

I7: $R = R' = i$Pr, $X = 2.5$-Me$_2$-pyr
Figure S84. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M2) by the action of I16 in CDCl$_3$.

Figure S85. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M3) by the action of I16 in CDCl$_3$. 
Figure S86. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M2) by the action of I28 in CDCl$_3$.

Figure S87. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M3) by the action of I28 in CDCl$_3$. 
Figure S88. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M4) by the action of I28 in CDCl$_3$.

Figure S89. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M2) by the action of I29 in CDCl$_3$. 

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Figure S90. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M3) by the action of I29 in CDCl$_3$.

Figure S91. Olefinic region of the $^1$H-NMR spectrum of the polymerization of 100 eq. (M4) by the action of I29 in CDCl$_3$. 

I29: $R^1$ = $\beta$-Pr, $R^2$ = $R^3$ = Me
IR Spectra of Polymers

Figure S92. IR spectrum of cis-st poly[(+)-DMMNBE]; polymerization of 100 eq. (M1) by the action of I1 in CDCl₃.

Figure S93. IR spectrum of trans-it poly[(+)-DMMNBE]; polymerization of 100 eq. (M1) by the action of I3 in CDCl₃.
Influence of Tris(pentafluorophenyl)borane on Selectivity

Figure S94. Influence of tris(pentafluorophenyl)borane on selectivity in the polymerization of M1 by the action of I15; general reaction conditions applied.

Kinetics Measurements

Figure S95. Monomer consumption and polymer formation vs. time for initiator I16 and M1. CDCl₃, 0 °C, [M]₀ = 0.25 M.
Figure S96. 1st-order plot of monomer consumption for initiator I16 and M1. CDCl₃, 0 °C, [M]₀ = 0.25 M.

\[ y = -1.107 \times 10^{-3} x - 4.298 \times 10^{-1} \]
\[ R^2 = 9.998 \times 10^{-1} \]

Figure S97. Monomer consumption and polymer formation vs. time for initiator I28 and M2. CDCl₃, 0 °C, [M]₀ = 0.25 M.
Figure S98. 1st-order plot of monomer consumption for initiator I28 and M2. CDCl₃, 0 °C, [M]₀ = 0.25 M.

Figure S99. Monomer consumption and polymer formation vs. time for initiator I28 and M3. CDCl₃, 0 °C, [M]₀ = 0.25 M.
Figure S100. 1st-order plot of monomer consumption for initiator I28 and M3. CDCl₃, 0 °C, [M]₀ = 0.25 M.

Figure S101. Monomer consumption and polymer formation vs. time for initiator I28 and M4. CDCl₃, 0 °C, [M]₀ = 0.25 M.
Figure S102. 1st-order plot of monomer consumption for initiator I28 and M4. CDCl₃, 0 °C, [M]₀ = 0.25 M.
**Figure S103.** MALDI-ToF MS analysis of poly(M2) synthesized by the action of I28 using 15 equivalents of monomer. \( m/z = 7 \times 210.7 \) (repeat unit) + 14.02 (=CH2) + 132.09(=CHCMe2Ph) +22.99 (Na) = 1639.59, \( \Delta = 0.11 \).
References