Electronic Supplementary Material (ESI) for Polymer Chemistry.

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. ^{1}H and ^{13}C 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 ($CDCl_3$: 7.26 ppm, C_6D_6 7.16 ppm, CD_2Cl_2 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 $CHCl_3$. The system consisted of a 1260 Infinity system (Agilent Technologies Inc.) equipped with a precolumn (8 × 50 mm) and three consecutive separation columns (8 × 300 mm, PSS, Mainz, Germany, porosities 1000, 100 000, and 1 000 000 Å, particle size 5µm) and an Agilent 1200 Series G1362A RI detector. The flow rate was set to 1.0 mL/min; the column oven temperature was set to 35°C. An injection volume of 100 µL was used. The system was calibrated with narrow polystyrene standards (800 ≤ M_n≤ 3 000 000 g/mol). CH_2Cl_2, 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 over 4 Å Linde-type molecular sieves inside a nitrogen filled glove box. Deuterated solvents (Eurisotop) were used as purchased and stored over Linde-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-$Me_3C_6H_2)_2C_6H_3$),[1] LiOHIPT (OHPT = O-2,6-(2,4,6-*i*$Pr_3C_6H_2)_2C_6H_3$),[2] sodium tetrakis(3,5-bis(trifluoromethyl)phenyl) borate ($NaB(Ar^F)_4$),[3] IiPr,[4] ICy,[5] W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)Cl_2(DME) (DME = 1,2-dimethoxyethane),[6] W(N-2,6-*i*$Pr_2C_6H_3$)(CHCMe_2Ph)Cl_2(DME),[7] W(N-2,6-$Cl_2C_6H_3$)(CHCMe_2Ph)Cl_2(DME),[8] W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(2,5-Me_2Pyr)$_2$,[8] W(O)(CHCMe_2Ph)(OHMT)(Cl)(PMe_2Ph),[9] [W(N-2,6-*i*$Pr_2C_6H_3$)(CHCMe_2Ph)Br(IMes)]$^+$[$B(Ar^F)_4$]$^-$,[10] **M1** – **M2**,[11] **M3**,[12] **M4**,[11] **I1**,[13] **I2**,[11] **I3**,[14] **I4**-**I7**,[10] **I8**-**I9**,[15] **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 $CDCl_3$ 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 $CDCl_3$ (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 $CDCl_3$, 500 µL, 0.25 mmol, 100 eq, 0.5 M toluene as internal standard) and solutions of the initiators (500 µM in $CDCl_3$, 1 eq). 500 µL of both solutions were mixed in a screw-cap NMR tube and the reaction was monitored by ^{1}H 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 (0.017 mmol, 15 eq) in $CDCl_3$ (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-methyoxystyrene (50 µL, 25 eq) was added upon 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-dihydroxybenzoeic 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.

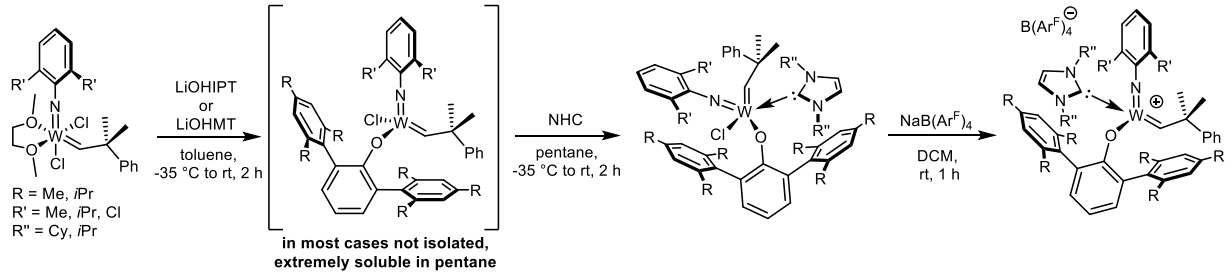
The analytical data for *cis*-it **poly[(+)-DMMNBE]**,[11] *cis*-st, and *trans*-it **poly[(+)-DCMNBE]**,[16] *cis*-st, and *trans*-it *cis*-st poly[**M3**][16, 17] as well as for *cis*-st poly[**M4**][18] were in accordance to literature.

cis-st poly[(+)-DMMNBE]. **^{1H} NMR** (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). **^{13}C 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, 1096, 950, 757, 705.

trans-it poly[(+)-DMMNBE]. **^{1}H NMR** (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). **^{13}C NMR** (101 MHz, CDCl3) δ = 133.7, 130.8, 74.8,

74.2, 58.9, 58.6, 48.4, 45.3, 44.1, 39.5. **IR v[cm^{-1}]** = 2975, 2918, 2863, 2822, 2804, 2732, 1475, 1449, 1380, 1187, 1097, 1039, 975, 936.

Preparation of Catalysts



Scheme S1. General procedure for the synthesis of cationic tungsten imido neophylidene complexes bearing bulky ligands starting from tungsten imido neophylidene dichloro DME complexes; intermediate complex after addition of lithium aryloxide in most cases not isolated – mostly oily solids and/or isolation resulted in poor yields.

W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHMT)(Cl)(IiPr): W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)Cl$_2$(DME) (520 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, IiPr (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. **^{1}H NMR** (C$_6$D$_6$, 400 MHz) δ 10.43 (s, 0.4H), 10.13 (s, 0.6H), 7.45 – 7.26 (m, 5H), 7.16 – 6.56 (m, 10H), 6.49 – 6.14 (m, 2H), 4.55 – 3.55 (m, 2H), 3.11 – 1.76 (m, 23H), 1.62 – 1.35 (m, 3H), 1.34 – 0.95 (m, 4H), 0.86 – 0.63 (m, 9H), 0.60 – 0.48 (m, 3H). **^{13}C NMR** (CD$_2$Cl$_2$, 101 MHz) δ = 286.9 (s), 266.6 (s), 188.66 (s), 162.5 (s), 160.2 (s), 154.1 (s), 153.3 (s), 151.4 (s), 150.4 (s), 138.7 (s), 138.3 – 134. 9 (m), 130.5 (s), 129.2.0 – 127.1 (m), 126.7 (s), 125.5 (s), 124.2 (s), 118.6 (s), 117.4 (s), 35.6 (s), 31.6 (s), 30.4 (s), 29.6 (s), 24.0 – 20.5 (m), 19.7 (s). **Elemental analysis** (%) of C$_{51}$H$_{62}$ClN$_3$OW. Calculated: C, 64.32; H, 6.56; N, 4.41. Found: C, 64.32; H, 6.637; N, 4.39.

[W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHMT)(IiPr)$^+$][B(Ar^F)$_4^-$] (I29): W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHMT)(Cl)(IiPr) (250 mg, 0.26 mmol, 1 eq) was dissolved in dichloromethane (10 mL), to which NaB(Ar^F)$_4$ (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%. **^{1}H NMR** (CD$_2$Cl$_2$, 400 MHz) δ = 9.94 (s, 1H), 7.76 (s, 8H), 7.59 (s, 4H), 7.37 (s, 2H), 7.32 – 7.17 (m, 6H), 7.09 (d, 2H), 7.05 (m, 5H), 6. 88 (s, 2H), 4.10 (sept, 2H), 2.29 (s, 6H), 2.00 (s, 6H), 1.91 (s, 6H), 1.68 (s, 6H), 1.45 (d, 6H), 1.30 (d, 6H), 1.08 (s, 3H), 1.06 (s, 3H). **^{13}C NMR** (CD$_2$Cl$_2$, 101 MHz) δ = 282.8 (s), 177.0 (s), 162.2 (m), 157.7 (s), 154.3 (s),148.1 (s), 138.5 (s), 137.2 (s), 136.2 (s), 135.3 (s), 134.9 (s), 134.2 (s), 132.2 (s), 131.5 (s), 129. 7 – 128.8 (m), 128.3 (s), 127.9 (s), 127.3 (s), 126.4 (s), 126.3 (s), 126.2 (s), 123.7 (s), 121.8 (s), 117.9 (m), 33.6 (s), 29.4 (s), 23.7 (s), 23.5 (s), 23.0 (s), 21.2 (s), 20.6 (s), 19.2 (s). **^{19}F NMR** (CD$_2$Cl$_2$, 376 MHz) δ = -62.78 (s). **Elemental analysis** (%) of C$_{83}$H$_{74}$BF$_{24}$N$_3$OW. Calculated: C, 56.00; H, 4.19; N, 2.36. Found: C, 55.94; H, 4.449; N, 2.40.

W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OHMT)(Cl)(ICy): W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)Cl$_2$(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%. **^{1}H NMR** (CD$_2$Cl$_2$, 400 MHz) δ = 10.15 (s, 1H), 7.42 (d, 2H), 7.22 (m, 3H), 7.13 – 6.97 (m, 2H), 6.98 – 6.77 (m, 5H), 6.75 – 6.61 (m, 3H). 6.49 (s, 1H), 6.27 (s, 1H), 4. 48 (m, 1H), 4.02 (m, 1H), 2.58 (s, 3H), 2.37 – 2.16 (m, 12H), 2.11 – 1.60 (m, 20H), 1.55 (s, 6H), 1.31 (s, 6H), 1.41 (s, 3H). **^{13}C NMR** (CD$_2$Cl$_2$, 101 MHz) δ = 277.1 (s), 190.7 (s), 162.6 (s), 154.3 (s), 151.9 (s), 149.9 (s), 140.2 (s), 139. 4 (s), 137.8 (m), 135.4 (s), 134.3 (s), 133.7 (s), 131.9 (s), 130.7 (s), 130.0 (m), 128.7 (s), 128.4 (s), 127. 7 (m), 127.4 (s), 125.3 (s), 124.4 (s), 121.0 (s), 118.4 (m), 117.4 (s),

60.2 (s), 58.9 (s), 36.4 (s), 35.1 (s), 34. 4 (s), 33.9 (s), 33.0 (s), 32.8 (s), 29.9 (s), 26.2 – 24.9 (m), 22.3 – 20.9 (m), 20.4 (s), 20.0 (s), 18.2 (s). **Elemental analysis** (%) of $C_{57}H_{70}ClN_3OW$. Calculated: C, 66.31; H, 6.83; N, 4.07. Found: C, 66.51; H, 6.933; N, 3.90.

[W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHMT)(ICy)$^+$][B(Ar^F)$_4^-$] (I30): W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHMT)(Cl)(ICy) (200 mg, 0.19 mmol, 1 eq) was dissolved in dichloromethane (5 mL), to which NaB(Ar^F)$_4$ (170 mg, 0.19 mmol, 1 eq) was added. The resulting mixture was stirred at room temperature for 1 h, filtered over Celite, dried *in vacuo* and washed with pentane (3 x 5 mL) to afford a yellow compound. Yield: 310 mg, 83%. **^{1}H NMR** (CD_2Cl_2, 400 MHz) δ = 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 (s, 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). **^{13}C NMR** (CD_2Cl_2, 101 MHz) δ = 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), 21.3 (m), 21.2 (m), 19.4 (s). **^{19}F NMR** (CD_2Cl_2, 376 MHz) δ = -62.81 (s). **Elemental analysis** (%) of $C_{89}H_{82}BF_{24}N_3OW$. Calculated: C, 57.46; H, 4.44; N, 2.26. Found: C, 57.39; H, 4.549; N, 2.35.

W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl): W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)Cl_2(DME) (300 mg, 0.46 mmol, 1 eq) was dissolved in toluene (10 mL) and the solution was cooled to -35 °C. LiOHIPT (250 mg, 0.46 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 and filtered through Celite. The solution was coevaporated several times with pentane and Novec 7100 until an off-white solid was obtained. Yield: 130 mg, 29%. **^{1}H NMR** (CD_2Cl_2, 400 MHz) δ = 8.83 (s, 1H), 7.21 (m, 3H), 7.11 (m, 2H), 7.07 (m, 4H), 7.02 (m, 3H), 6.93 (m, 2H), 6.67 (m, 1H), 2.83 (sept, 2H), 2. 74 (sept, 4H), 1.96 (s, 6H), 1.28 (s, 3H), 1.23 (s, 3H), 1.21 (s, 6H), 1.19 (s, 3H), 1.18 (s, 3H), 1.16 (s, 3H), 1.14 (s, 3H), 1.09 (s, 15H), 1.06 (s, 3H). **^{13}C NMR** (CD_2Cl_2, 101 MHz) δ = 262.1 (s), 158.3 (s), 153.9 (s), 151.9 (s), 148.5 (s), 146.9 (s), 146.8 (s), 134.7 (s), 132.6 (s), 133.5 (s), 133.4 (s), 127.8 (s), 127.2 (s), 126.0 (s), 125. 6 (s), 125.1 (s), 122.6 (s), 121.2 (s), 121.0 (s), 51.6 (s), 34.2 (s), 33.3 (s), 33.8 (s), 30.9 (m), 25.1 (m), 23.9 (s), 23.8 (s), 23.5 (s), 23.1 (s), 19.2. **Elemental analysis** (%) of $C_{54}H_{70}ClNOW$. Calculated: C, 66.97; H, 7.29; N, 1.45. Found: C, 66.94; H, 7.502; N, 1.48.

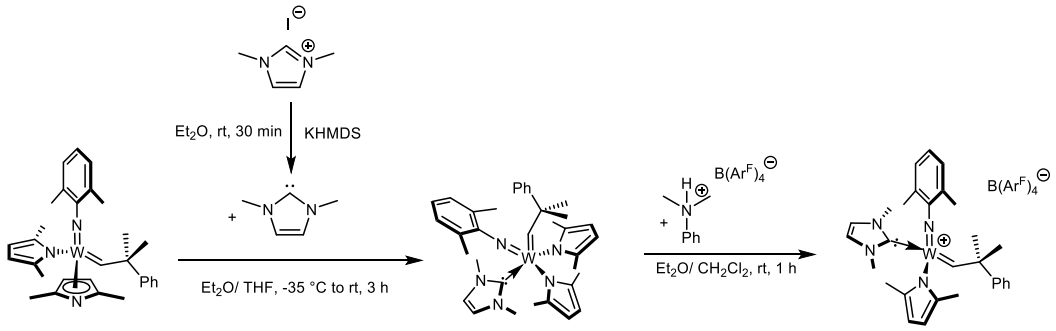
W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl)(IiPr): W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl) (311 mg, 0.32 mmol, 1 eq) was dissolved in pentane (7 mL). IiPr (49 mg, 0.32 mmol, 1 eq) was dissolved in pentane (3 mL). Both solutions were combined and stirred at room temperature for 45 min after which an off-white solid precipitated. The solid was washed with pentane (5 x 10 mL) and the off-white solid was dried *in vacuo*. Yield: 335 mg; 93%%; the product exists in a mixture of two isomers, shifts of both isomers are reported. **^{1}H NMR** (CD_2Cl_2, 400 MHz) δ = 10.92 (s, 0.15H), 10.52 (s, 0.85H), 7.48 – 6.50 (m, 17H), 4.60 – 2.37 (m, 8H), 2.38 – -0.01 (m, 60H).**^{13}C NMR** (CD_2Cl_2, 101 MHz) δ = 278.5, 270.6, 189.0, 163.2, 160.0, 154.7, 153.9, 151.6, 151.3, 149.4, 149.1, 148.5, 148.3, 147.9, 147.6, 147.5, 147.1, 146.9, 146.4, 140.3, 139.8, 139.5, 139.1, 138.7, 135.4, 134.8, 134.5, 133.8, 132.7, 132.6, 131.9, 131.7, 128.1, 127.1, 126.7, 126.2, 125.9, 125.1, 124.6, 124.3, 123.2, 122.8, 121.9, 121.7, 121.0, 120.1, 117.8, 117.3, 117.0, 54.0, 36.5, 34.8, 34.7, 34.6, 31.2, 31.0, 30.7, 30.5, 28.1, 27.5, 27.0, 26.8, 26.0, 25.7, 25.2, 25.0, 24.7, 24.4, 23.9, 23.5, 23.2, 22.9, 19.7, 14.4. **Elemental analysis** (%) of $C_{63}H_{86}ClN_3OW$. Calculated: C, 67.52; H, 7.74; N, 3.75. Found: C, 67.46; H, 7.951; N, 3.66.

[W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(IiPr)$^+$][B(Ar^F)$_4^-$] (I31): W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl)(IiPr) (180 mg, 0.16 mmol, 1 eq) was dissolved in dichloromethane (2 mL), to which NaB(Ar^F)$_4$ (142 mg, 0.16 mmol, 1 eq) was added. The resulting mixture was stirred at room temperature for 45 min, filtered through Celite, dried *in vacuo* and washed with pentane (4 x 2 mL) to afford a yellow compound. Yield: 290 mg; 93%. **^{1}H NMR** (CD_2Cl_2, 400 MHz) δ = 11.33 (s, 1H), 7.72 (s, 8H), 7.56 (s, 4H), 7.36 – 6.92 (m, 17H), 4.01 – 3.85 (m, 2H), 2.97 (hept, *J* = 7.7 Hz, 2H), 2.82 – 2.69 (m, 2H), 2.61 – 2.48 (m, 2H), 1.53 (s, 3H), 1.43 (s, 6H), 1.41 – 1.20 (m, 21H), 1.10 (d, *J* = 6.4 Hz, 6H), 1.08 – 1.00 (m, 9H), 0.93 – 0.70 (m, 15H). **^{13}C NMR** (CD_2Cl_2, 101 MHz) δ = δ 287.9, 174.4, 163.1, 162.6, 162.1, 161.6, 159.8, 153.9, 149.9, 148.0, 147.8, 147.4, 135.4, 134.2, 133.9, 133.4, 131.6, 130.0, 129.6, 129.4, 128.9, 128.4, 128.0, 127.5, 124.5, 123.8, 122.8, 122.4, 122.0, 121.1, 118.0, 56.5, 55.5, 35.2, 34.7, 31.9, 31.7, 30.6, 25.7, 25.5, 24.7, 24.4, 24.1, 24.1, 23.7, 22.9, 18.7, 14.4. **^{19}F NMR** (CD_2Cl_2, 376 MHz) δ = -61.03 (s). **Elemental analysis** (%) of $C_{95}H_{98}BF_{24}N_3OW$. Calculated: C, 58.56; H, 5.07; N, 2.16. Found: C, 58.81; H, 5.344; N, 2.18.

W(N-2,6-$Cl_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl)(IiPr): W(N-2,6-$Cl_2C_6H_3$)(CHCMe_2Ph)Cl_2(DME) (400 mg, 0.63 mmol, 1 eq) was dissolved in toluene (7 mL); LiOHMT (317 mg, 0.50 mmol, 1 eq) was dissolved in toluene (3 mL). 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 (100 mL) and filtered over Celite. The filtered solution was coevaporated with pentane (3 x 10 mL), dissolved in pentane, IiPr (95 mg, 0.63 mmol, 1 eq) was added and the mixture was stirred at room temperature for 1 h. All volatiles were removed *in vacuo*, the residue was washed with pentane (25 mL) and the off-white product again dried *in vacuo*. Yield: 451 mg; 62%. The product exists in a mixture of two isomers, shifts

of both isomers are reported. **^{1}H NMR** (CD_2Cl_2, 400 MHz) δ = 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), 1.34 – 1.27 (m, 9H), 1.27 – 1.18 (m, 12H), 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).**^{13}C NMR** (CD_2Cl_2, 101 MHz) δ = 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, 122.1, 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 $C_{61}H_{80}Cl_3N_3OW$. Calculated: C, 63.08; H, 6.94; N, 3.62. Found: C, 63.06; H, 7.078; N, 3.54.

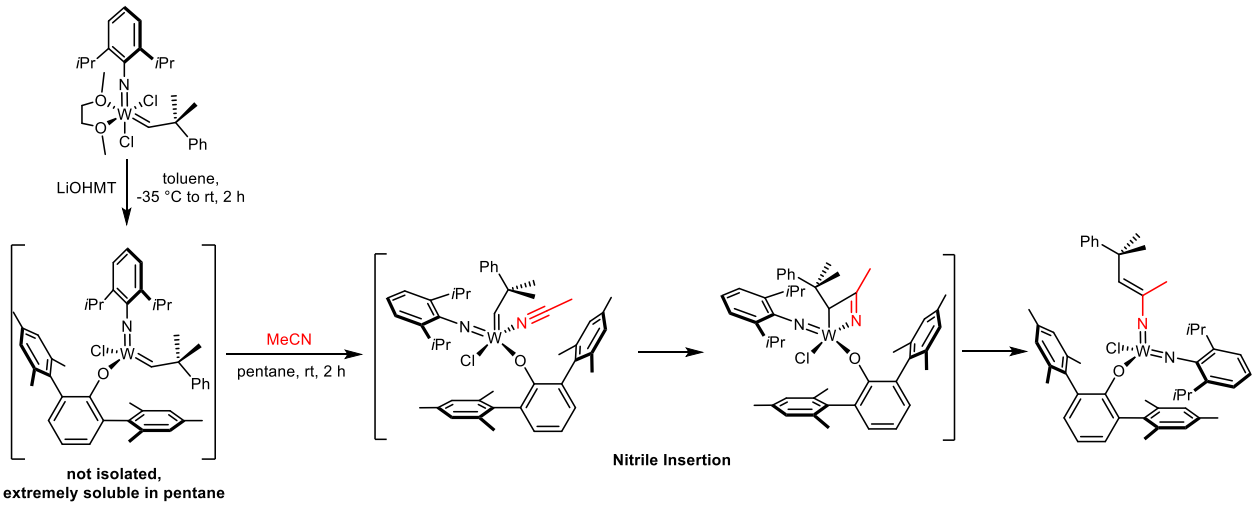
[W(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(OHIPT)(IiPr)$^+$][B(Ar^F)$_4^-$] (I32): W(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(OHIPT)(Cl)(IiPr) (200 mg, 0.17 mmol, 1 eq) was dissolved in dichloromethane (2 mL), the solution was cooled to -35 °C, then NaB(Ar^F)$_4$ (153 mg, 0.17 mmol, 1 eq) was added, the resulting mixture was stirred at room temperature for 1 h, then filtered through Celite, dried *in vacuo* and washed with pentane (4 x 2 mL) to afford a yellow solid. Yield: 303 mg; 88%. **^{1}H NMR** (CD_2Cl_2, 400 MHz) δ = δ 11.51 (s, 1H), 7.75 (s, 8H), 7.58 (s, 4H), 7.35 – 7.16 (m, 12H), 7.13 – 7.03 (m, 5H), 3.93 (hept, *J* = 6.5 Hz, 2H), 2.97 (hept, *J* = 6.9 Hz, 2H), 2.77 (hept, *J* = 6.8 Hz, 2H), 2.65 (hept, *J* = 6.6 Hz, 2H), 1.59 (s, 3H), 1.39 – 1.19 (m, 21H), 1.13 – 0.99 (m, 18H), 0.95 – 0.80 (m, 12H). **^{13}C NMR** (CD_2Cl_2, 101 MHz) δ = 290.7, 173.8, 162.5, 162.0, 161.5, 161.0, 159.3, 149.3, 147.4, 147.1, 146.8, 134.8, 133.4, 132.6, 131.2, 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. **^{19}F NMR** (CD_2Cl_2, 376 MHz) δ = - 62.81 (s). **Elemental analysis** (%) of $C_{93}H_{92}BCl_2F_{24}N_3OW$. Calculated: C, 56.15; H, 4.66; N, 2.11. Found: C, 55.76; H, 4.675; N, 1.98.



Scheme S2. Synthesis of **I27** from W(N-2,6-$Me_2C_6H_3$)(CHC(CH$_3$)$_2$Ph)(2,5-Me$_2$Pyr).

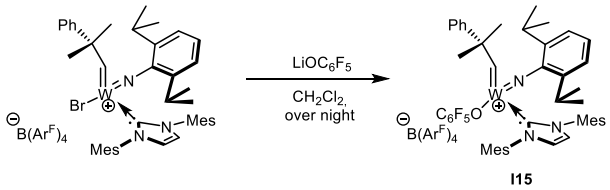
W(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(2,5-Me$_2$Pyr)$_2$(IMe): 1,3-Dimethylimidazolium iodide (190 mg, 84 mmol, 1 eq) was dissolved in diethyl ether (3 mL), to which KHMDS (170 mg, 0.84 mmol, 1 eq) was added and stirred at room temperature for 30 min. The solution was filtered through Celite and added to a -35 °C cold solution of W(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(2,5-Me$_2$Pyr)$_2$ (530 g, 0.84 mmol, 1 eq) 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 (3 x 5 mL) and dried *in vacuo*. Yield: 240 mg, 40%. **^{1}H NMR** (CD_2Cl_2, 400 MHz) δ = 9.50 (s, 1H), 7.37 (s, 1H), 7.24 – 7.01 (m, 6H), 6.91 (m, 1H), 6.75 (s, 2H), 5.62 (d, 4H), 3.09 (s, 6H), 2.38 (s, 6H), 1.96 (m, 9H), 1.74 (s, 6H), 1.64 (s, 3H). Broad signals were observed; likely due to a switching between an η^1 – and an η^5-coordination of the pyrrolide ligands on the NMR timescale. **^{13}C NMR** (CD_2Cl_2, 101 MHz) δ = 280.9 (s), 196.5 (s), 155.1 (s), 149.8 (s), 136.4 (m), 134.7 (s), 128. 7 (m), 128.3 (s), 126.5 (s), 125.5 (m), 123.7 (s), 108.4 (m), 106.6 (s), 32.1 (s), 30.5 (s), 19.9 (s), 17.9 (m). **Elemental analysis** (%) of $C_{35}H_{45}N_5W$. Calculated: C, 58.42; H, 6.30; N, 9.73. Found: C, 58.02; H, 6.270; N, 9.33.

[W(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(2,5-Me$_2$Pyr)(IMe)$^+$][B(Ar^F)$_4^-$] (I27): W(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(2,5-Me$_2$pyr)$_2$(IMe) (200 mg, 0.28 mmol, 1 eq) was dissolved in dichloromethane (8 mL), mixed with a solution of anilinium B(Ar^F)$_4$ (290 mg, 0.28 mmol, 1 eq) in diethyl ether (8 mL) and the mixture was stirred at room temperature for 1 h. All volatiles were removed *in vacuo*, the residue was washed with pentane (3 x 5 mL) and recrystallized from a mixture of dichloromethane and pentane. Yield: 210 mg, 51%. **^{1}H NMR** (CD_2Cl_2, 400 MHz) δ = 11.83 (s, 1H), 7.74 (s, 8H), 7.57 (s, 4H), 7.33 – 7.18 (m, 6H), 7.16 – 7.05 (m, 4H), 6. 30 (d, 1H), 6.06 (d, 1H), 3.68 – 3.26 (m, 6H), 2.64 (s, 3H), 2.15 (s, 6H), 1.79 (s, 3H), 1.59 (s, 3H), 1.54 (s, 3H). **^{13}C NMR** (CD_2Cl_2, 101 MHz) δ = 300.3 (s), 174.7 (s), 162.2 (m), 152.4 (s), 148.1 (s), 147.2 (s), 142.0 (s), 135.2 (s), 134.0 (s), 129.1 (m), 126. 8 (m), 123.6 (s), 120.9 (s), 117.9 (m), 112.9 (s), 103.8 (s), 101.7 (s), 57.8 (s), 40.7 (s), 31.0 (s), 30.4 (s), 19.4 (s), 18.3 (s), 14.5 (s). **^{19}F NMR** (CD_2Cl_2, 376 MHz) δ = - 62.80 (s). **Elemental analysis** (%) of $C_{61}H_{49}BF_{24}N_4W$. Calculated: C, 49.22; H, 3.32; N, 3.76. Found: C, 49.18; H, 3.515; N, 3.91.



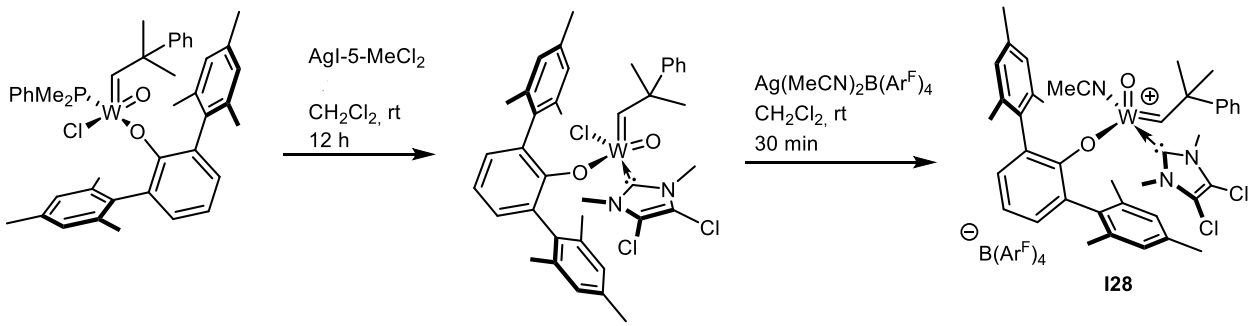
Scheme S3. Reaction of the precursor complex with acetonitrile thereby avoiding the use of MeCN as solvent; possible side reactions can occur.

W(N-2,6-*i*Pr$_2$C$_6$H$_3$)(NC(CH$_3$)CHC(CH$_3$)$_2$Ph)(OHMT)(Cl): W(N-2,6-*i*Pr$_2$C$_6$H$_3$)(CHC(CH$_3$)$_2$Ph)Cl$_2$(DME) (300 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%. **^{1}H NMR** (CD$_2$Cl$_2$, 400 MHz) δ = 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). **^{13}C NMR** (CD$_2$Cl$_2$, 101 MHz) δ = 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 C$_{48}$H$_{57}$ClN$_2$OW. 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(N-2,6-*i*Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OC$_6$F$_5$)(IMes)$^+$][B(Ar^F)$_4^-$] (I16): A solution of [W(N-2,6-*i*Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)Br(IMes)$^+$] [B(Ar^F)$_4^-$] (300 mg, 0.172 mmol, 1.0 eq) in CH$_2$Cl$_2$ (4 mL) was added to a suspension of LiOC$_6$F$_5$ (32.8 mg, 0.172 mmol, 1.0 eq) in CH$_2$Cl$_2$ (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 NMR** (CDCl$_3$, 400 MHz): δ 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, 3H), 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. **^{19}F NMR** (CDCl$_3$, 376 MHz): δ -62.43 (24F), -158.15 (2F), 161.56 (3F) ppm. **^{13}C NMR** (CDCl$_3$, 101 MHz): δ 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 pmm. **Elemental analysis** (%) of C$_{81}$H$_{65}$BF$_{29}$N$_3$OW. Calculated: C, 52.82; H, 3.56; N, 2.28. Found: C, 52.70; H, 3.833; N, 2.19.



Scheme S5. Preparation of **I28**.

W(O)(CHCMe$_2$Ph)(5-MeCl$_2$)(OHMT)(Cl): W(O)(CHCMe$_2$Ph)(OHMT)(Cl)(PMe$_2$Ph) (140 mg, 0.156 mmol) was dissolved in 10 mL of benzene. Solid AgI·1,3-dimethyl-4,5-dichloroimidazol-2-ylidene (75 mg, 1.2 eq) was added under stirring (more equivalents of AgI·1,3-dimethyl-4,5-dichloroimidazol-2-ylidene 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%. **^{1}H NMR** (400 MHz, $CDCl_3$) 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), 2.32 (br s, 12H, Me-Mes), 1.86 (br s, 3H, Me-Mes), 1.61 (s, 3H, C$\underline{Me}_2$Ph), 1.49 (s, 3H, C$\underline{Me}_2$Ph), 1.36 (br s, 3H, Me-Mes). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 290.5 (W=CH), 189.6 (NCN-NHC), 159.1 (Ar), 150.3 (Ar), 136.4 (Ar), 131.0 (Ar), 129.5 (Ar), 128.0 (Ar), 127.1 (Ar), 126.1 (Ar), 125.8 (Ar), 120.8 (Ar), 118.2 (Ar), 49.2 (C$\underline{Me}_2$Ph), 36.8 (Me-NHC), 30.5 (C$\underline{Me}_2$Ph), 30.2 (C$\underline{Me}_2$Ph), 21.7 (Me-Mes), 21.2 (Me-Mes), 19.6 (Me-Mes). **Elemental analysis** (%) of $C_{39}H_{43}Cl_3N_2O_2W$. Calculated: C, 54.34; H, 5.03; N, 3.25. Found: C, 54.37; H, 5.09; N, 3.23.

[W(O)(CHCMe$_2$Ph)(5-MeCl$_2$)(OHMT)(MeCN)$^+$][B(Ar^F)$_4^-$] (I28): W(O)(CHCMe$_2$Ph)(5-MeCl$_2$)(OHMT)(Cl) (67 mg, 0.0776 mmol) was dissolved in 4 mL CH_2Cl_2 and the solution was cooled to -35 °C. Solid Ag(MeCN)$_2$B(Ar^F)$_4$ (1 eq) was added under stirring. Immediately, the color changed to bright yellow. The reaction was stirred for 30 min at room temperature. Subsequently, the solvent was reduced to 50% and the 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%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.66 (s, $^1J_{CH}$ = 125.6 Hz, 1H, W=CH), 7.71 (br m, 8H, *o*-Ar-B(Ar^F)$_4$), 7.52 (br m, 4H, *p*-Ar-B(Ar^F)$_4$), 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, C$\underline{Me}_2$Ph), 1.50 (s, 3H, C$\underline{Me}_2$Ph). **^{13}C NMR** (101 MHz, $CDCl_3$) 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), 135.0 (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 (C$\underline{Me}_2$Ph), 36.4 (Me-NHC), 29.4 (C$\underline{Me}_2$Ph), 29.1 (C$\underline{Me}_2$Ph), 21.3 (Me-Mes), 21.2 (Me-Mes), 20.0 (Me-Mes), 2.9 (MeCN). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.38 (s, 24F, B(Ar^F)$_4$). **Elemental analysis** (%) calcd. of $C_{73}H_{58}BCl_2F_{24}N_3O_2W$. Calculated C, 50.66; H, 3.38; N, 2.43. Found: C, 50.51; H, 3.33; N, 2.40.

Solution NMR Spectra of Catalysts

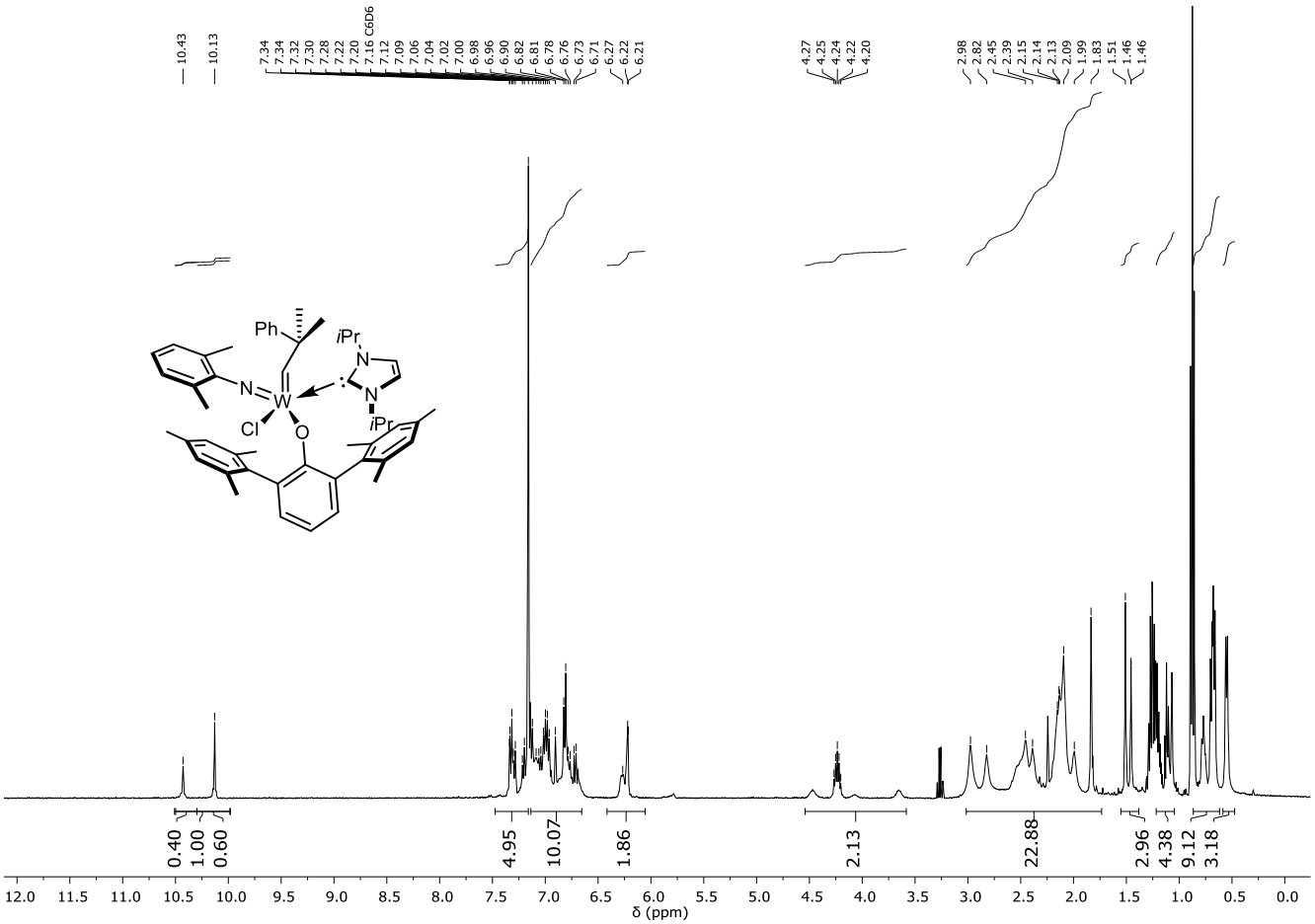


Figure S1. ^{1}H-NMR of W(N-2,6-$Me_2C_6H_3$)(CHC(CH_3)$_2$Ph)(OHMT)(Cl)(IiPr) in C_6D_6.

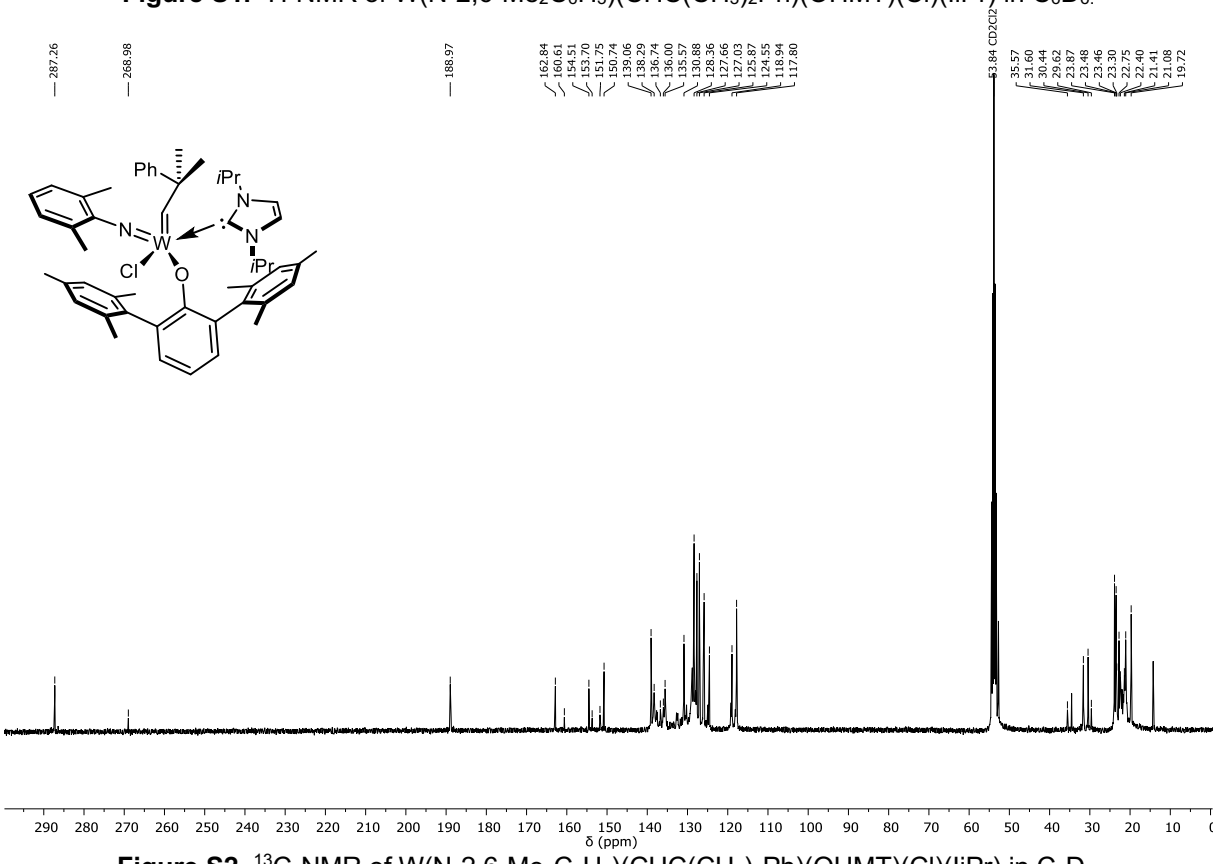


Figure S2. ^{13}C-NMR of W(N-2,6-$Me_2C_6H_3$)(CHC(CH_3)$_2$Ph)(OHMT)(Cl)(IiPr) in C_6D_6.

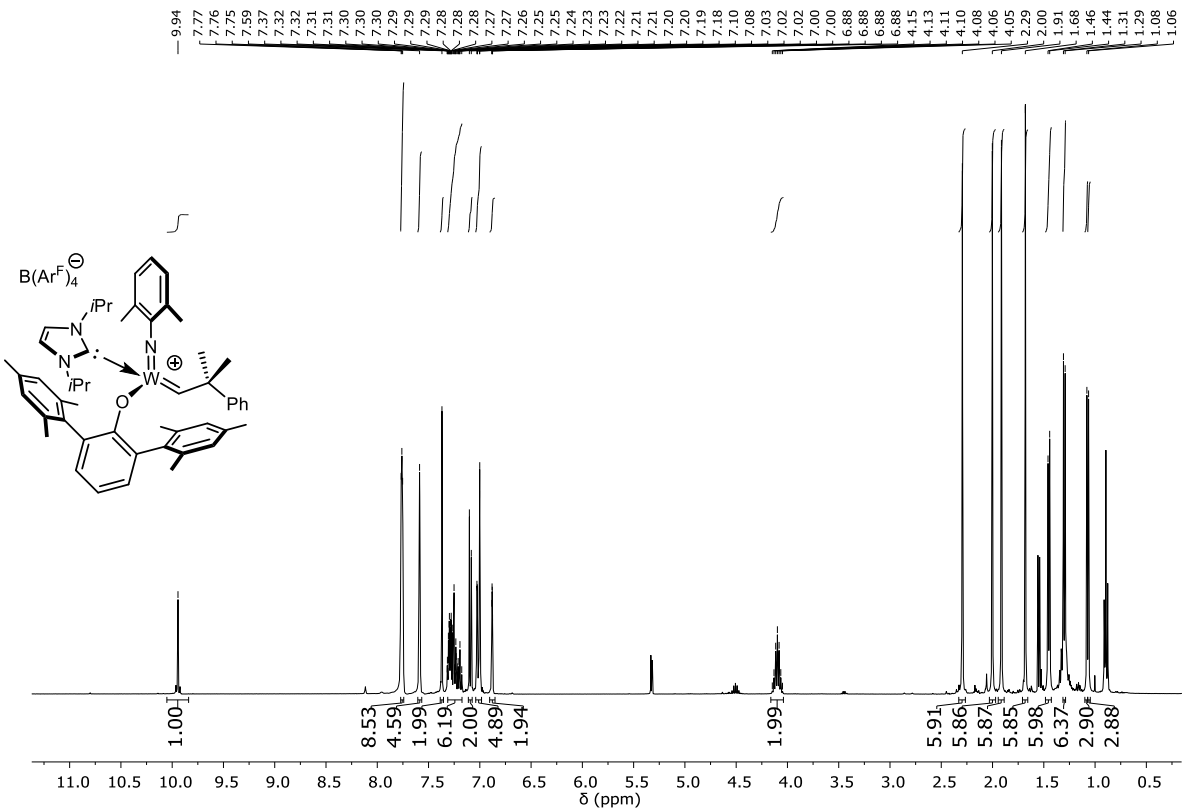


Figure S3. ^{1}H-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHMT)(IiPr)]$^{+}$[B(Ar^F)$_4$]$^{-}$ (**I29**) in CD_2Cl_2.

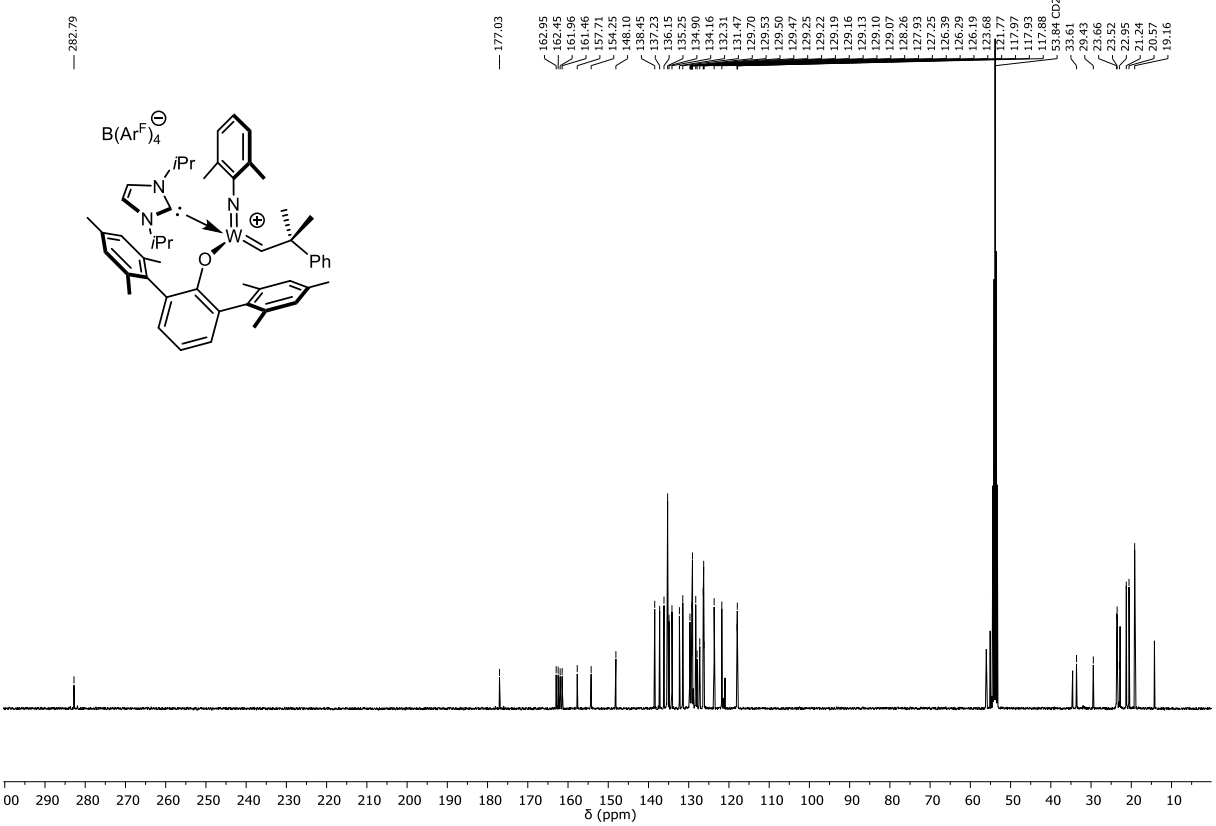


Figure S4. ^{13}C-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHC(CH_3)$_2$Ph)(OHMT)(IiPr)]$^{+}$[B(Ar^F)$_4$]$^{-}$ (**I29**) in CD_2Cl_2.

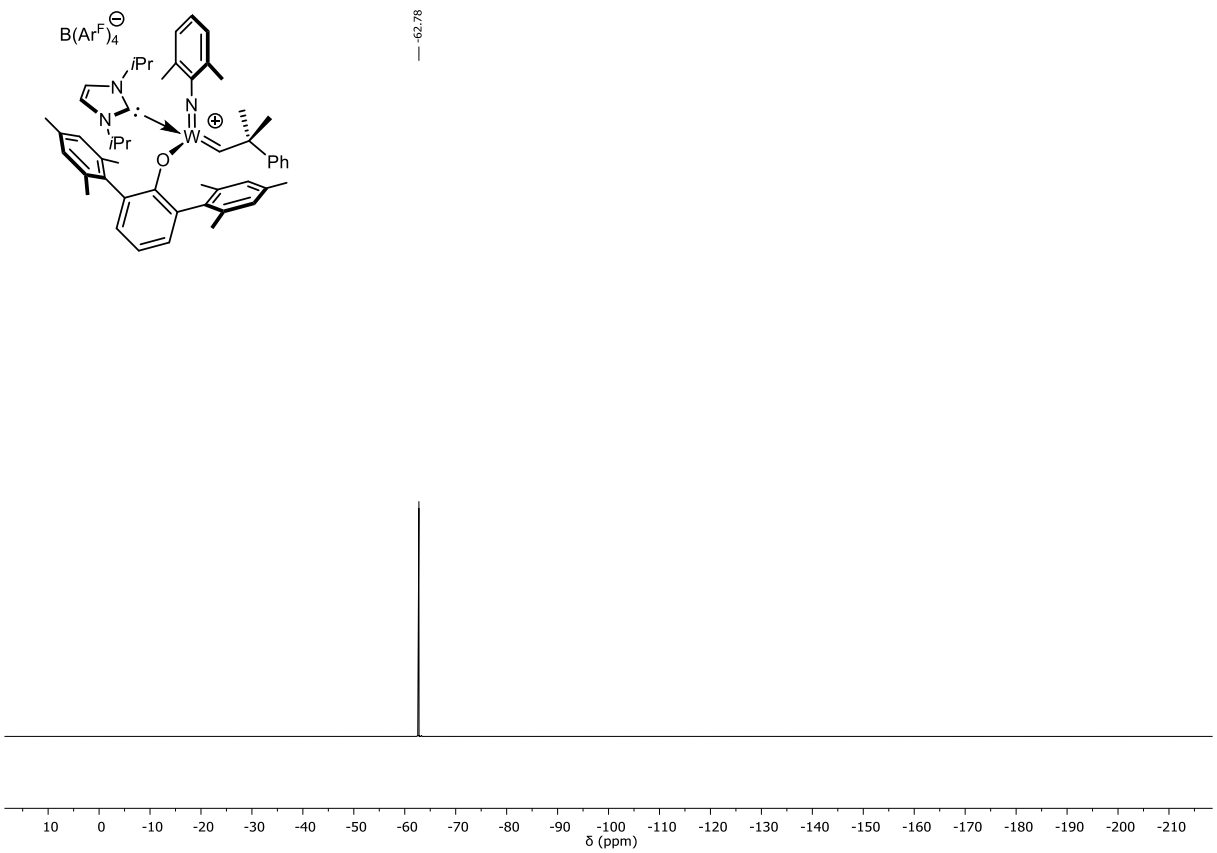


Figure S5. ^{19}F-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHMT)(IiPr)]$^+$[$B(Ar^F)_4$]$^-$ (**I29**) in CD_2Cl_2.

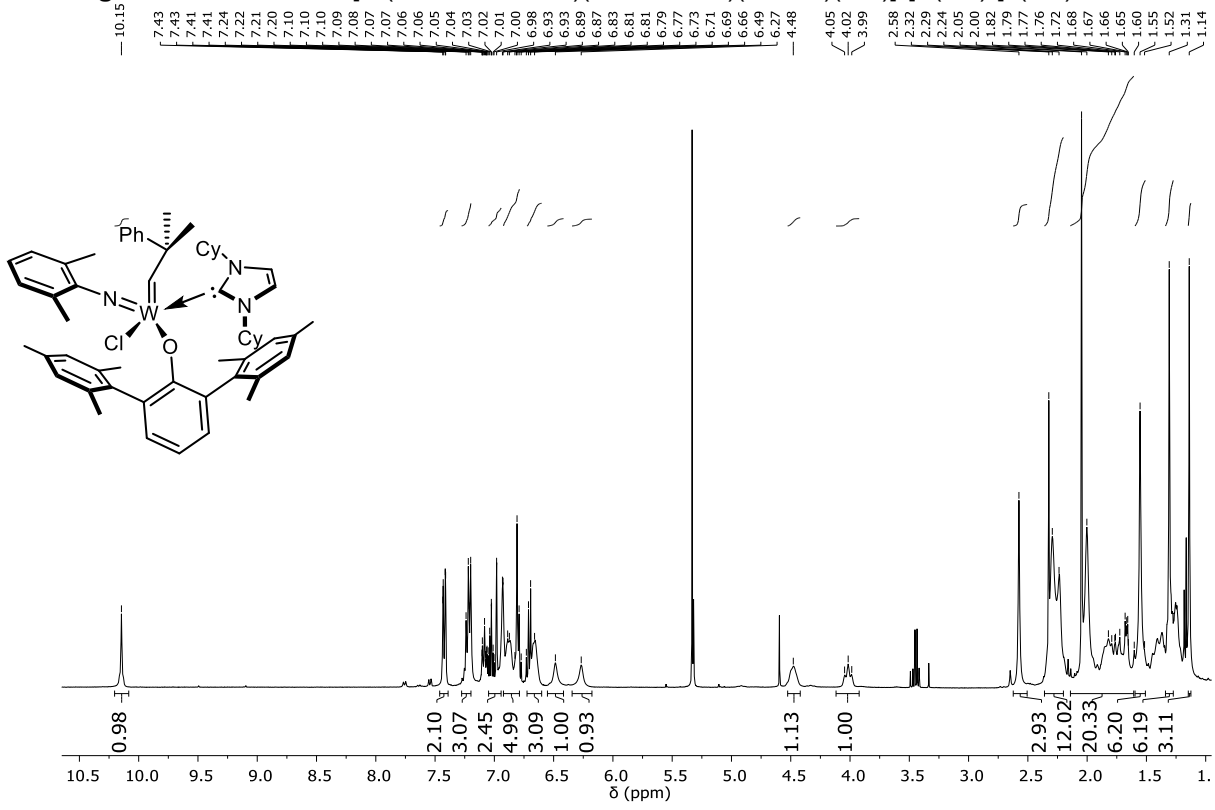


Figure S6. ^{1}H-NMR of W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHMT)(Cl)(ICy) in CD_2Cl_2.

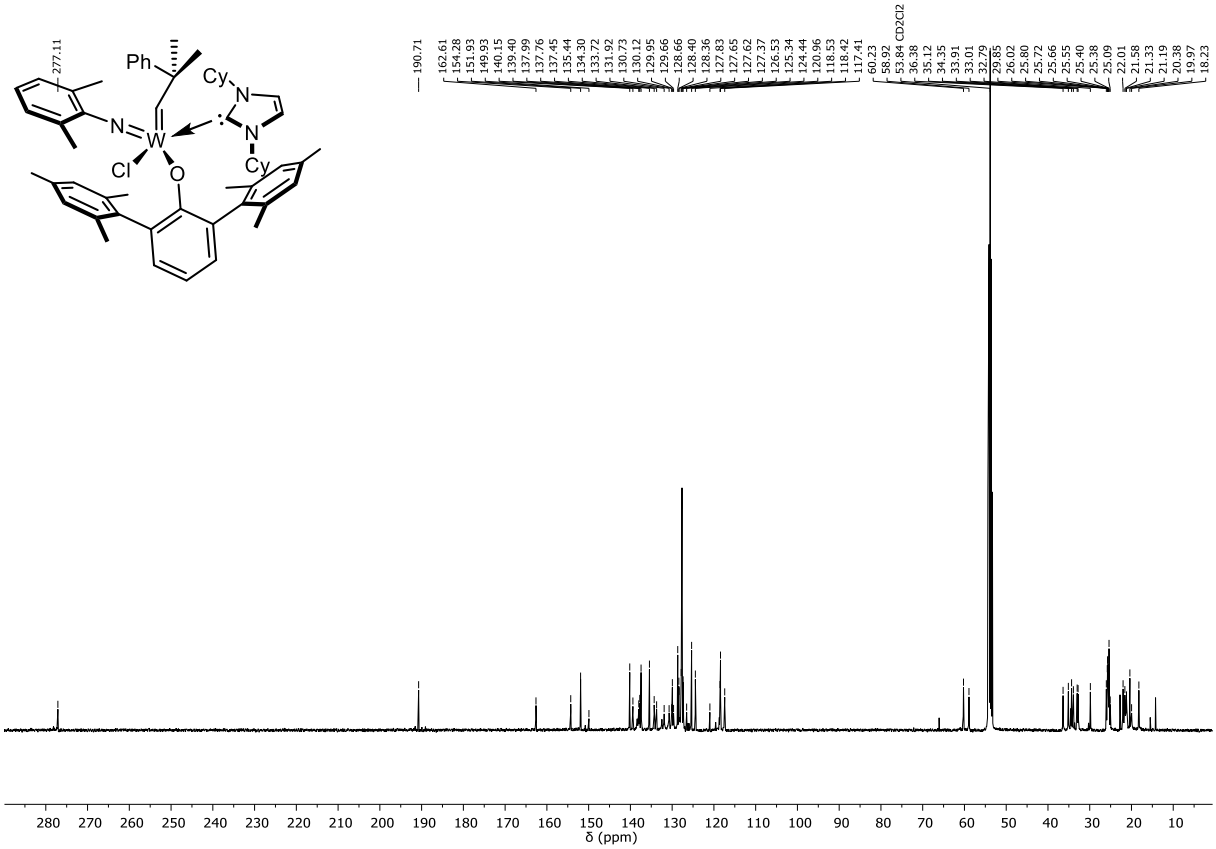


Figure S7. ^{13}C-NMR of W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHMT)(Cl)(ICy) in CD_2Cl_2.

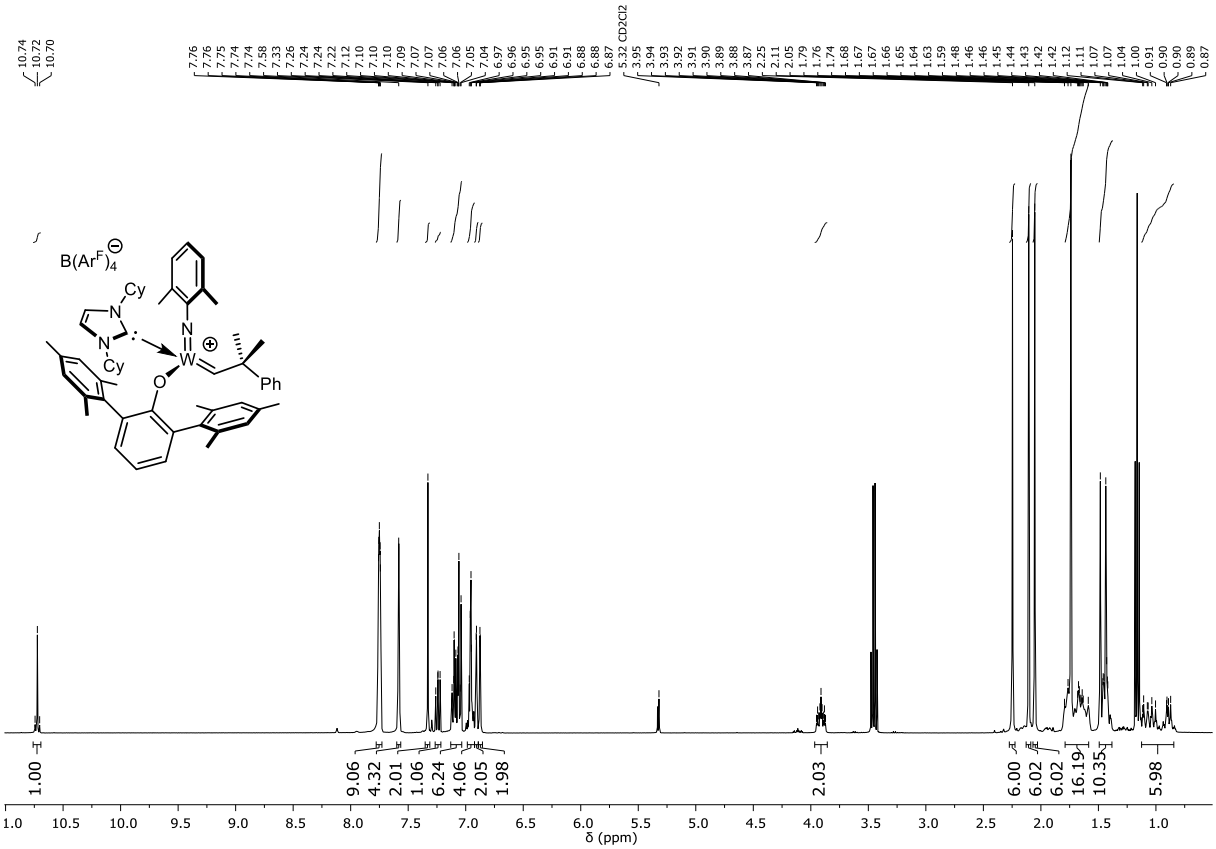


Figure S8. ^{1}H-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHMT)(ICy)]$^+$[B(Ar^F)$_4$]$^-$ (**I30**) in CD_2Cl_2.

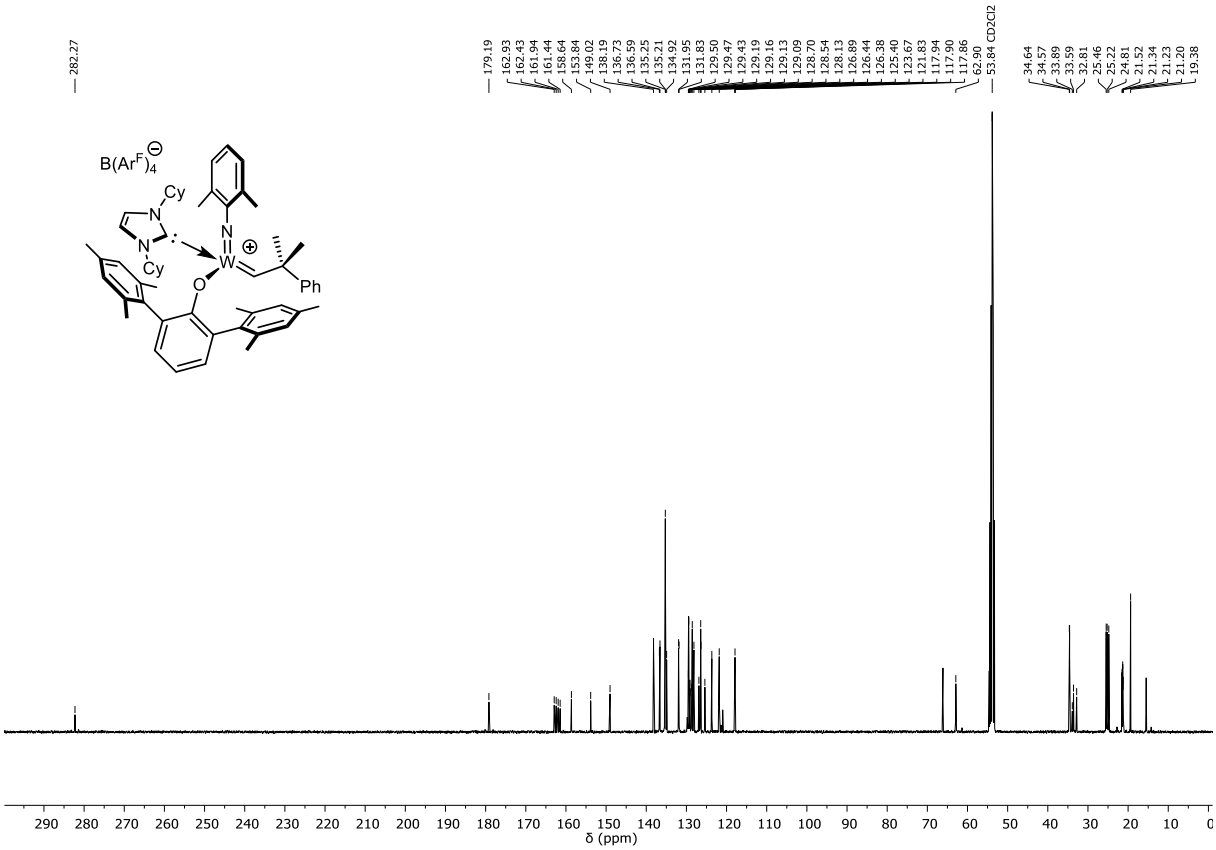


Figure S9. ^{13}C-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHMT)(ICy)]$^+$[B(Ar^F)$_4$]$^-$ (**I30**) in CD_2Cl_2.

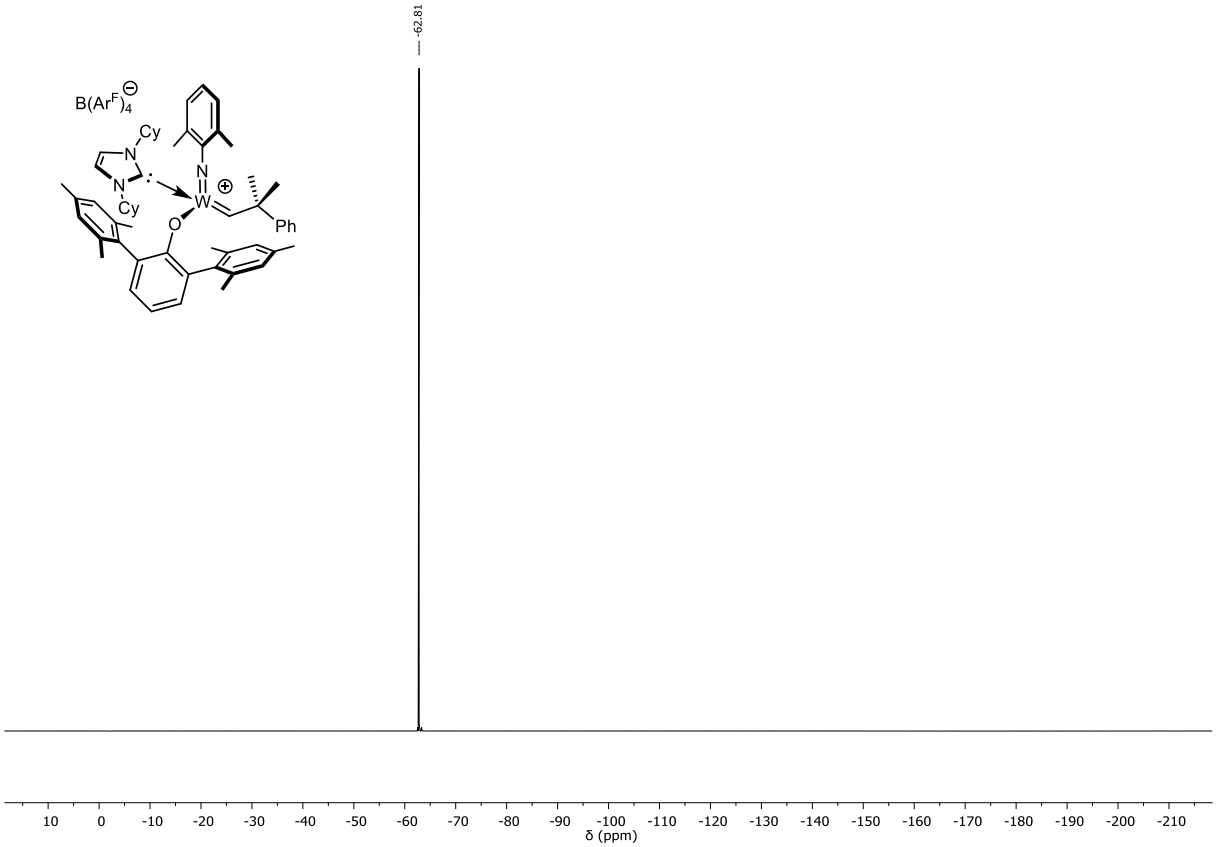


Figure S10. ^{19}F-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHMT)(ICy)]$^+$[B(Ar^F)$_4$]$^-$ (**I30**) in CD_2Cl_2.

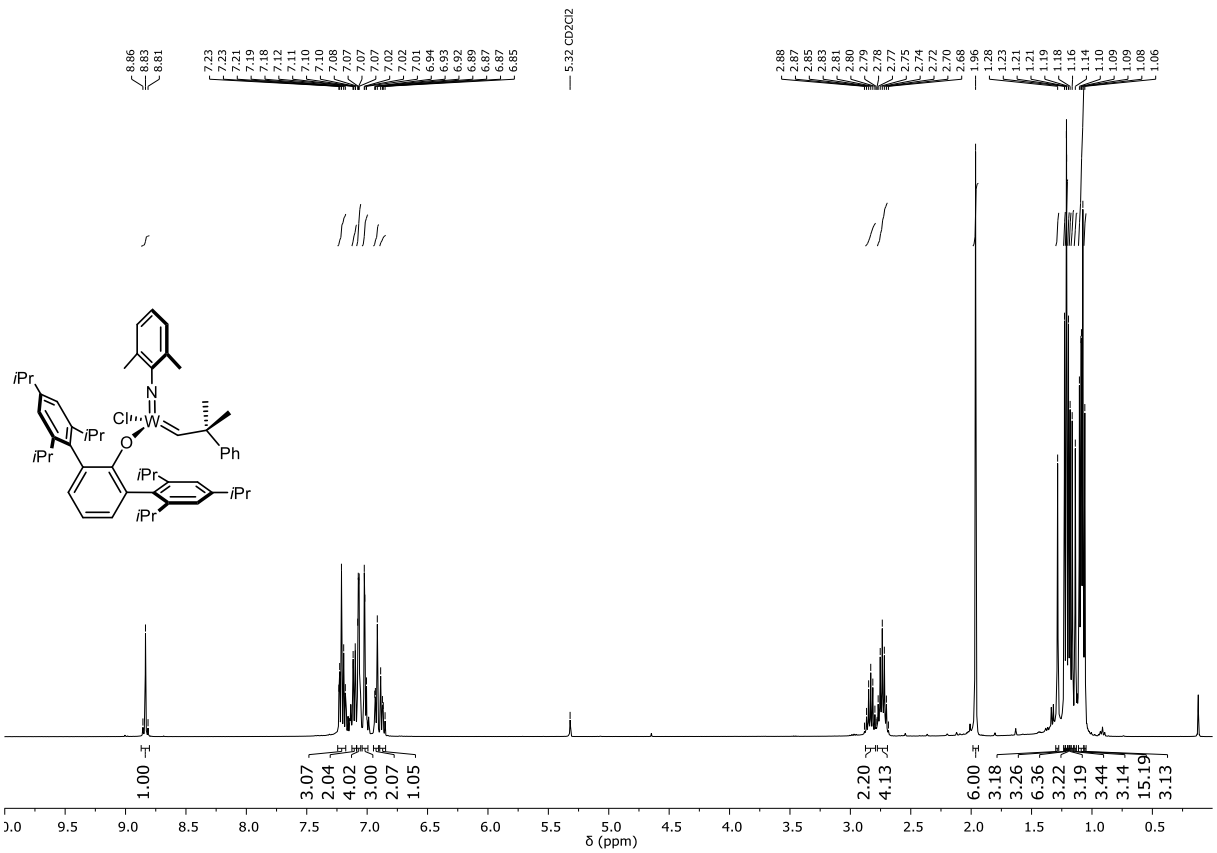


Figure S11. ^{1}H-NMR of W(N-2,6-MeC_6H_3)(CHCMe_2Ph)(OHIPT)(Cl) in CD_2Cl_2.

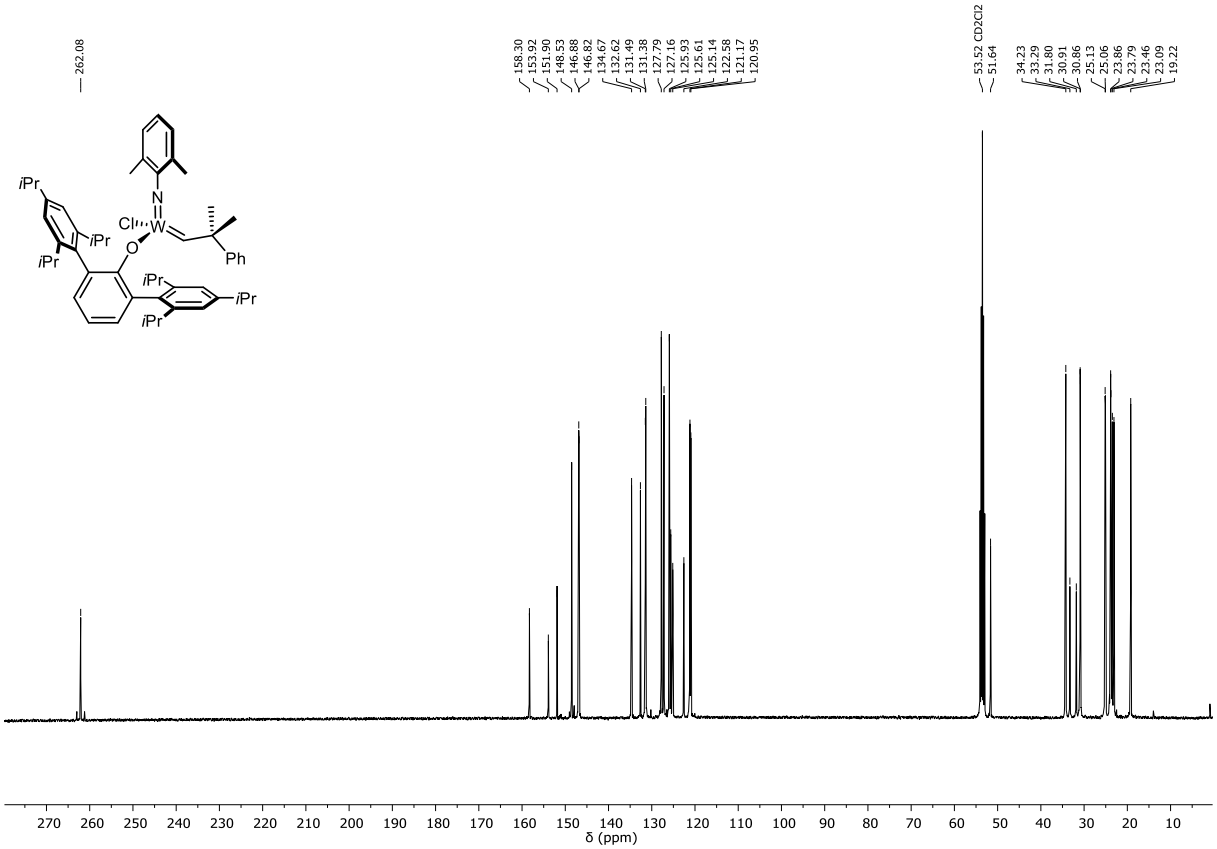


Figure S12. ^{13}C-NMR of W(N-2,6-MeC_6H_3)(CHCMe_2Ph)(OHIPT)(Cl) in CD_2Cl_2.

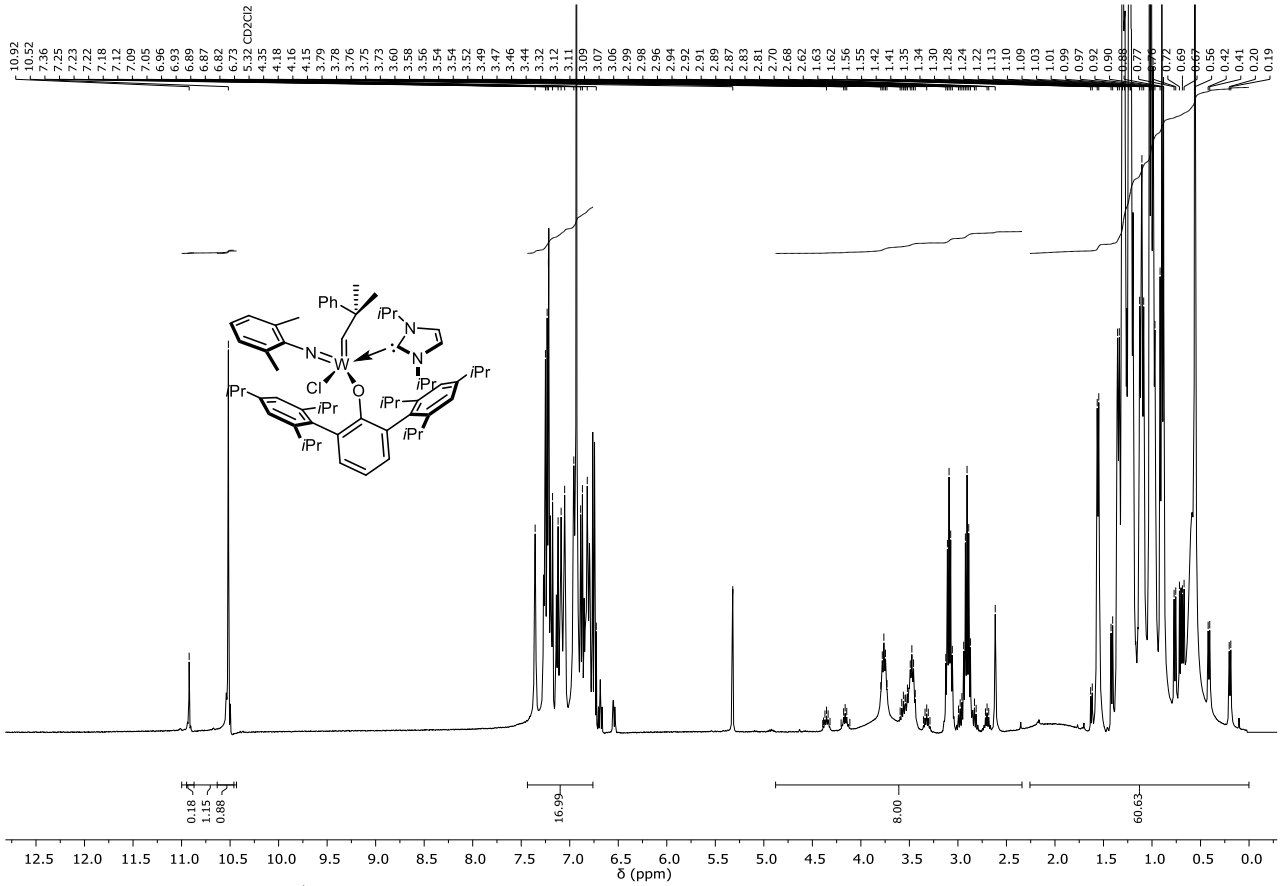


Figure S13. ^{1}H-NMR of W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl)(IiPr) in CD_2Cl_2.

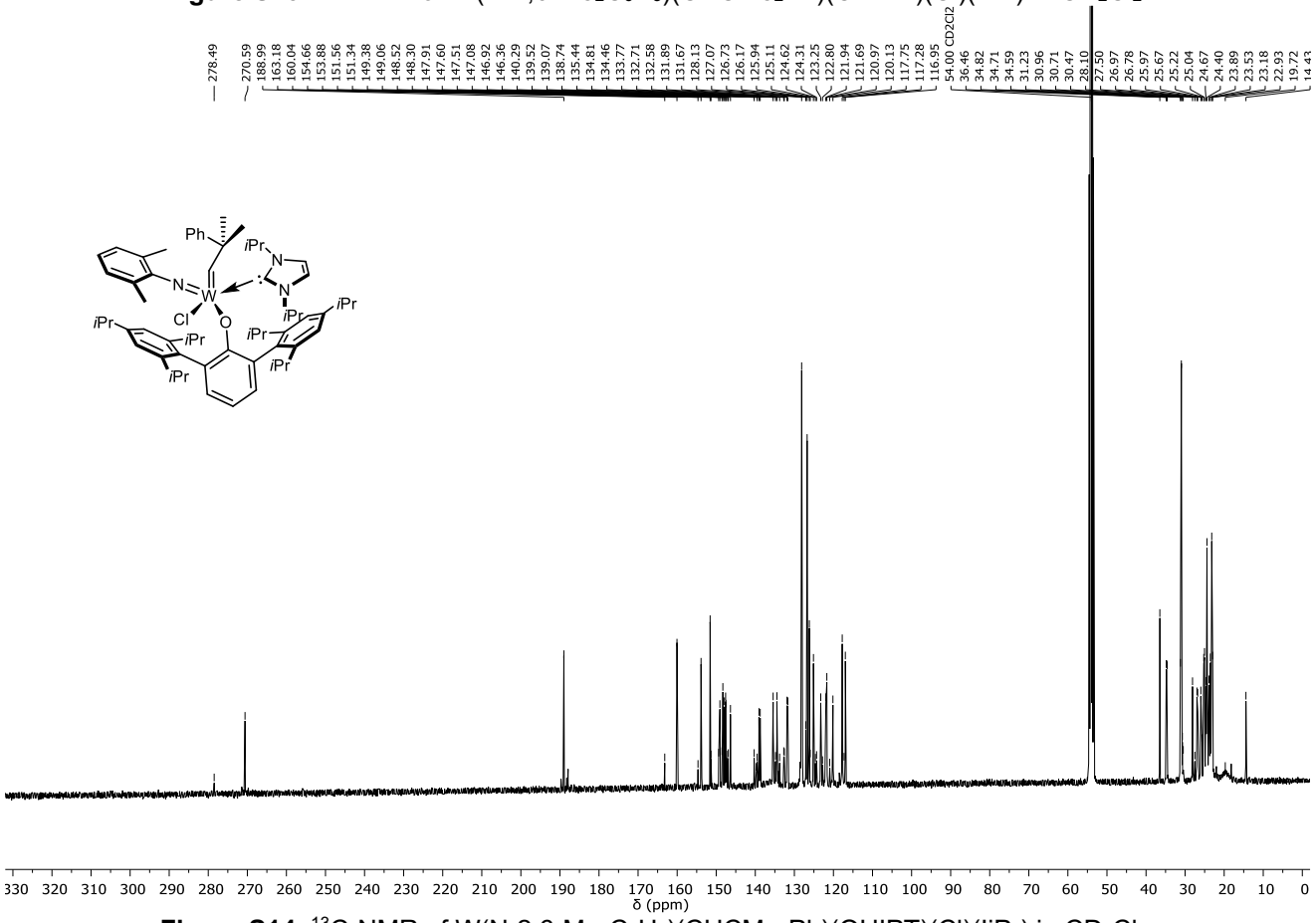


Figure S14. ^{13}C-NMR of W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl)(IiPr) in CD_2Cl_2.

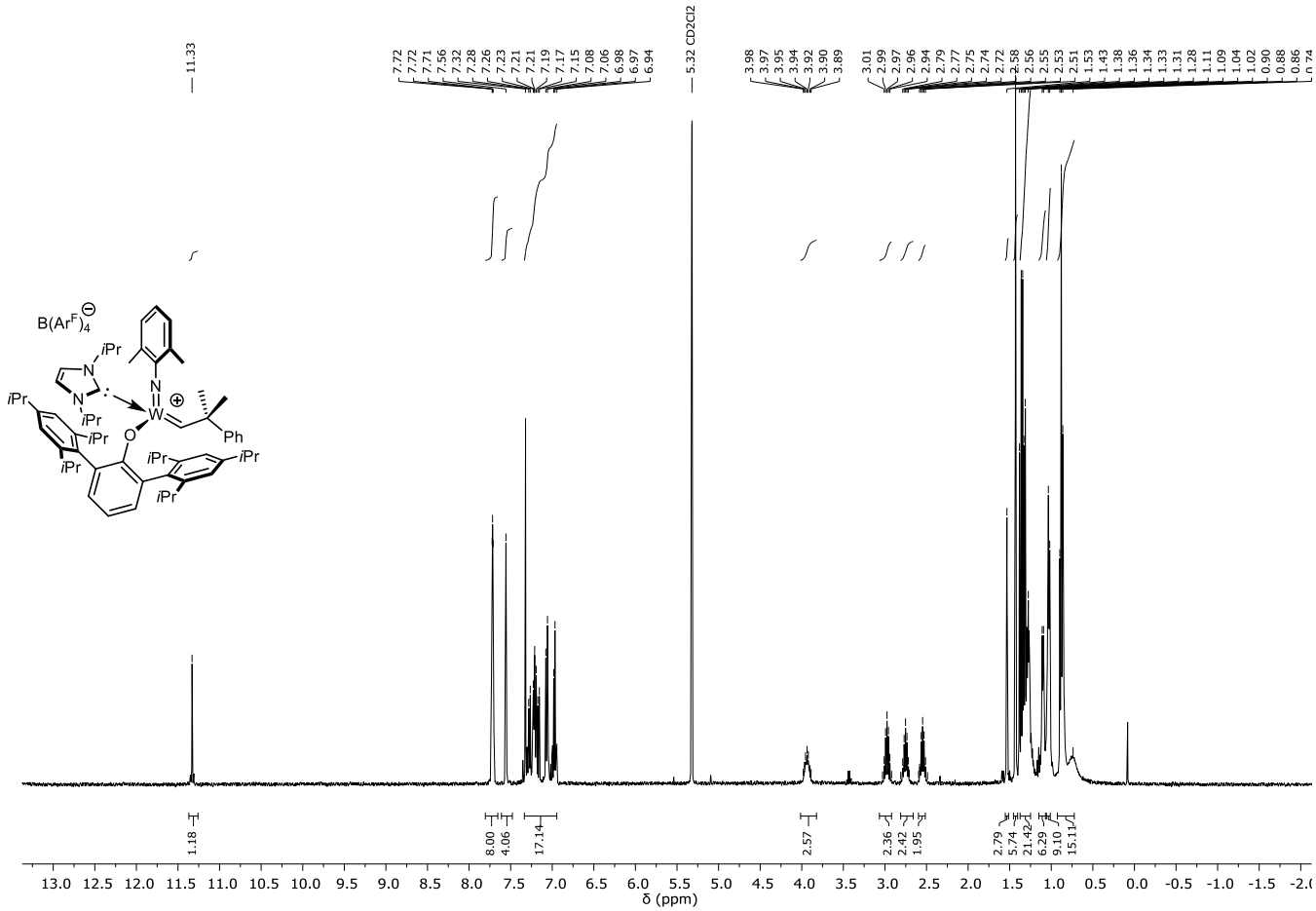


Figure S15. ^{1}H-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl)(IiPr)$^{+}$][$B(Ar^F)_4^-$] (**I31**) in CD_2Cl_2.

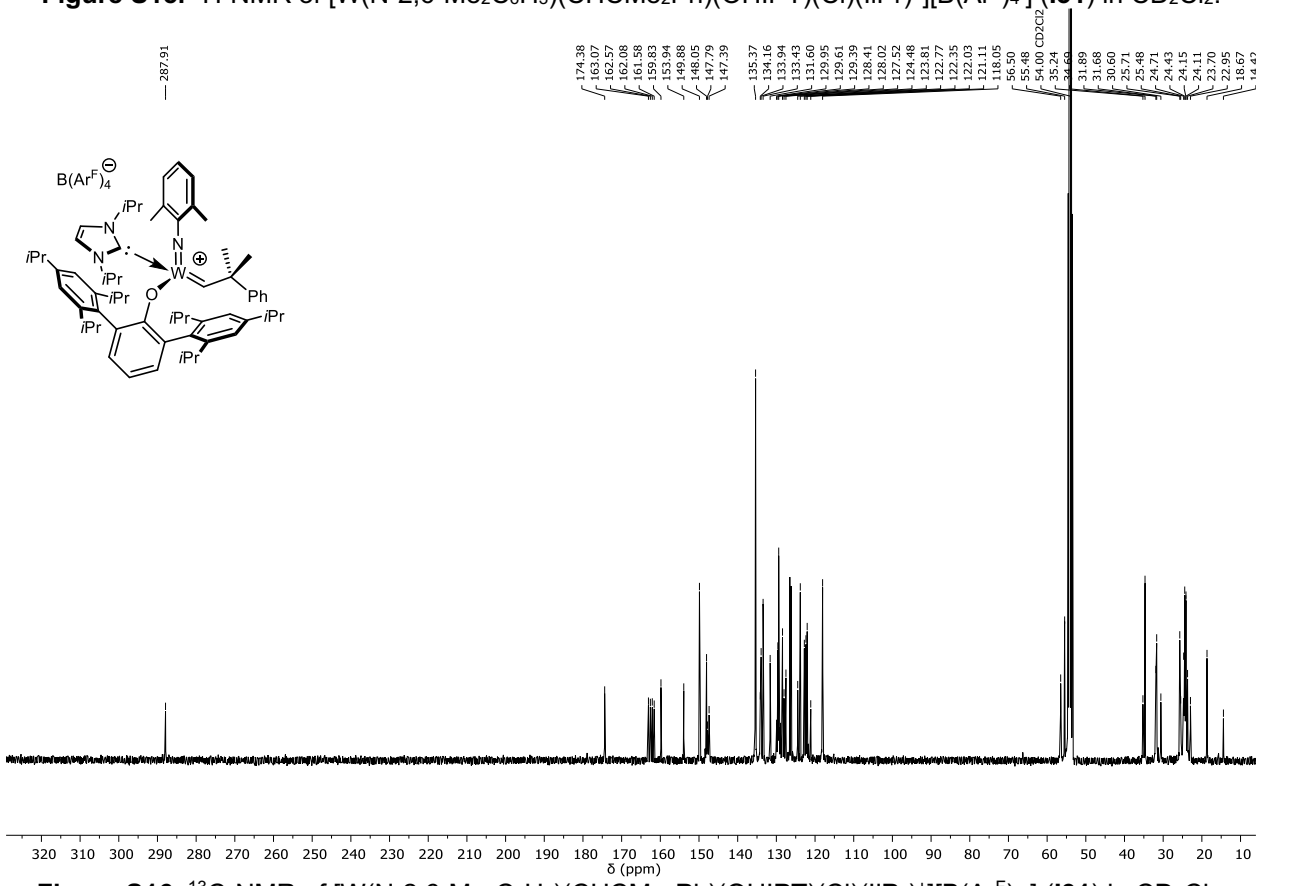


Figure S16. ^{13}C-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl)(IiPr)$^{+}$][$B(Ar^F)_4^-$] (**I31**) in CD_2Cl_2.

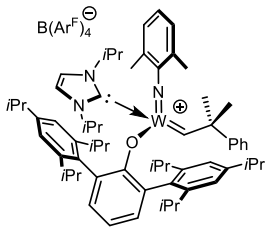


Figure S17. ^{19}F-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl)(IiPr)$^+$][B(Ar^F)$_4^-$] (**I31**) in CD_2Cl_2.

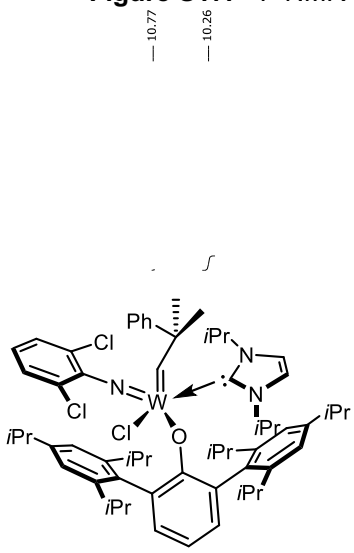


Figure S18. ^{1}H-NMR of W(N-2,6-$Cl_2C_6H_3$)(CHCMe_2Ph)(OHIPT)(Cl)(IiPr) in CD_2Cl_2.

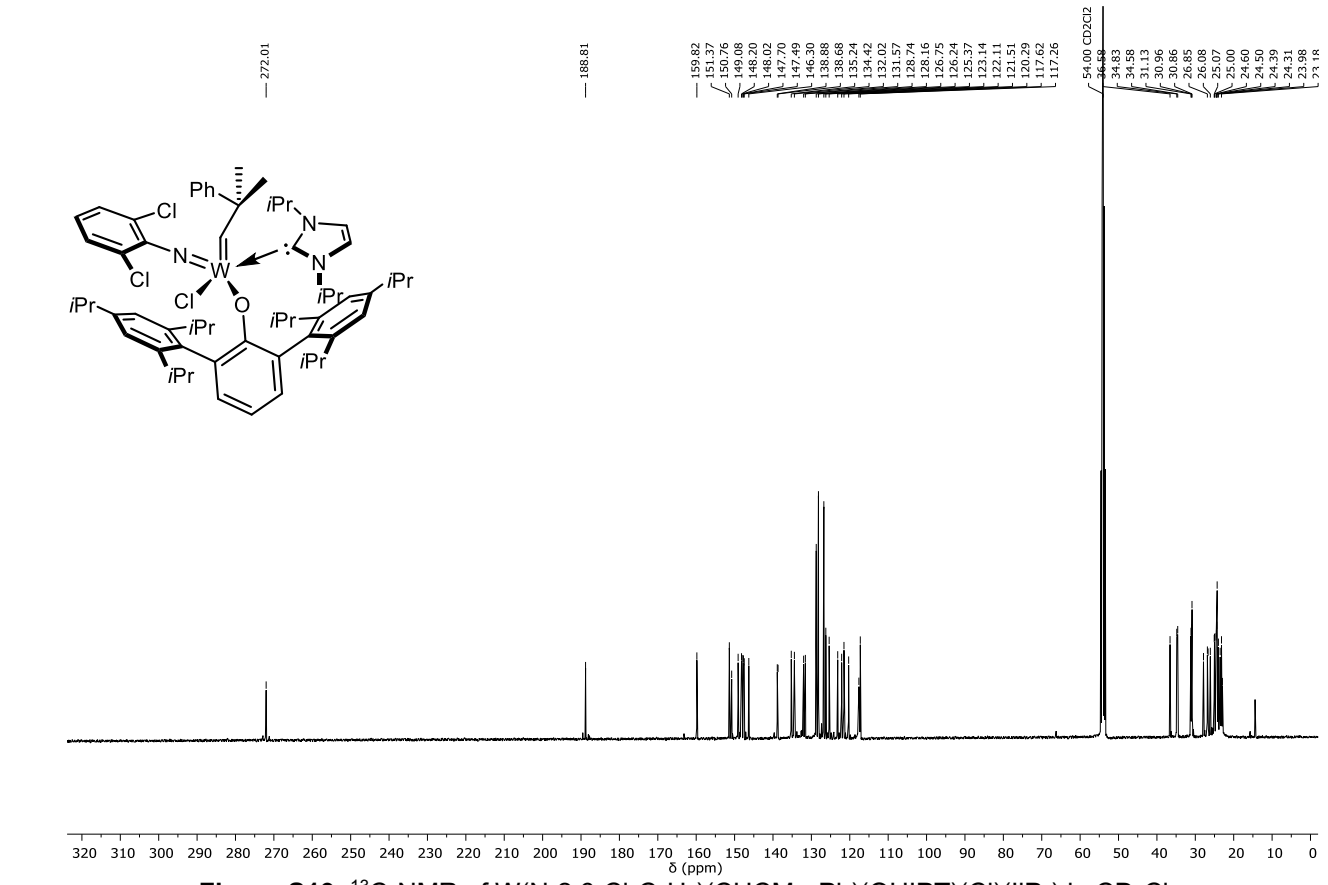


Figure S19. ^{13}C-NMR of W(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(OHIPT)(Cl)(IiPr) in CD_2Cl_2.

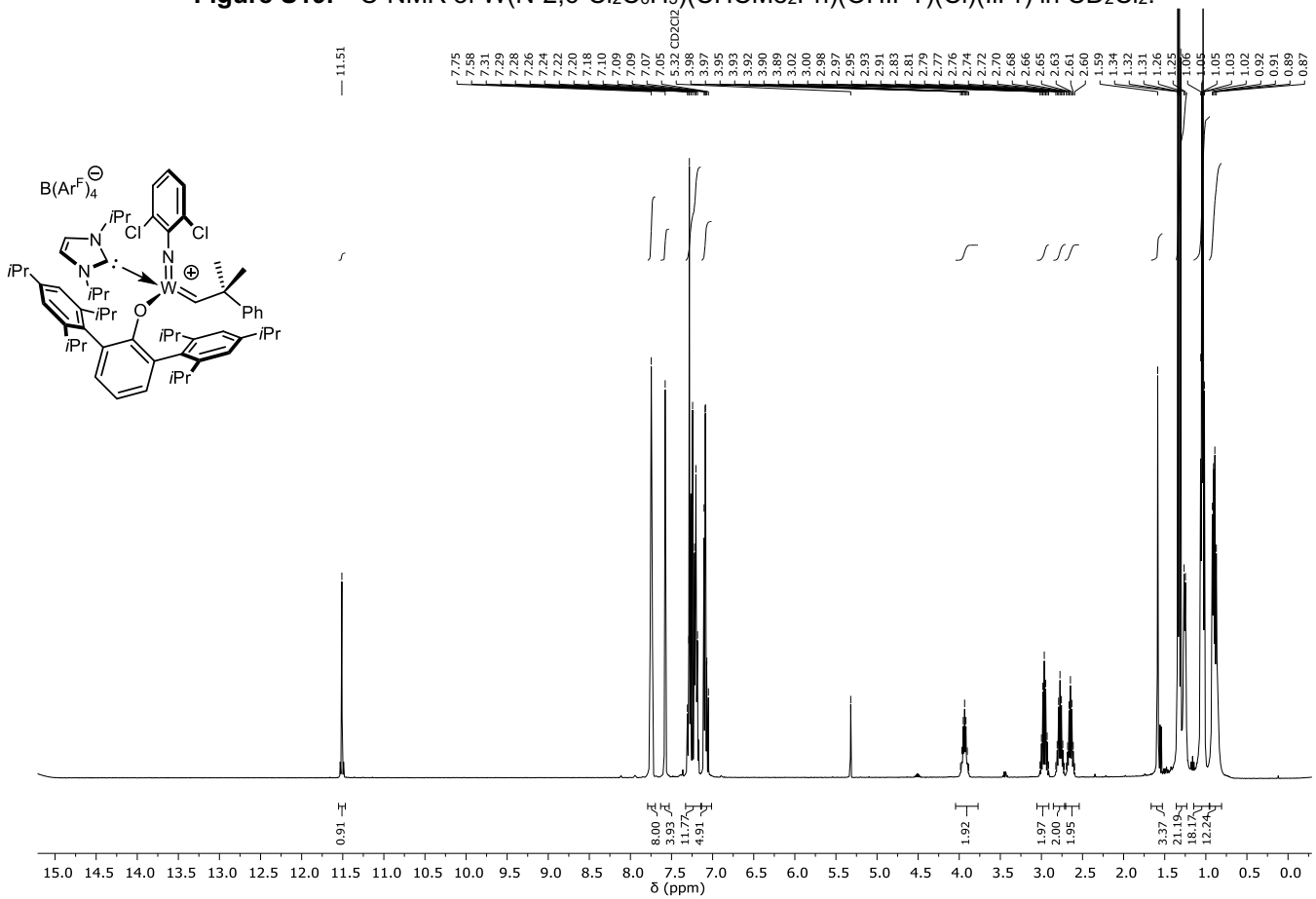


Figure S20. ^{1}H-NMR of [W(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(OHIPT)(IiPr)$^+$][B(Ar^F)$_4^-$] (**I32**) in CD_2Cl_2.

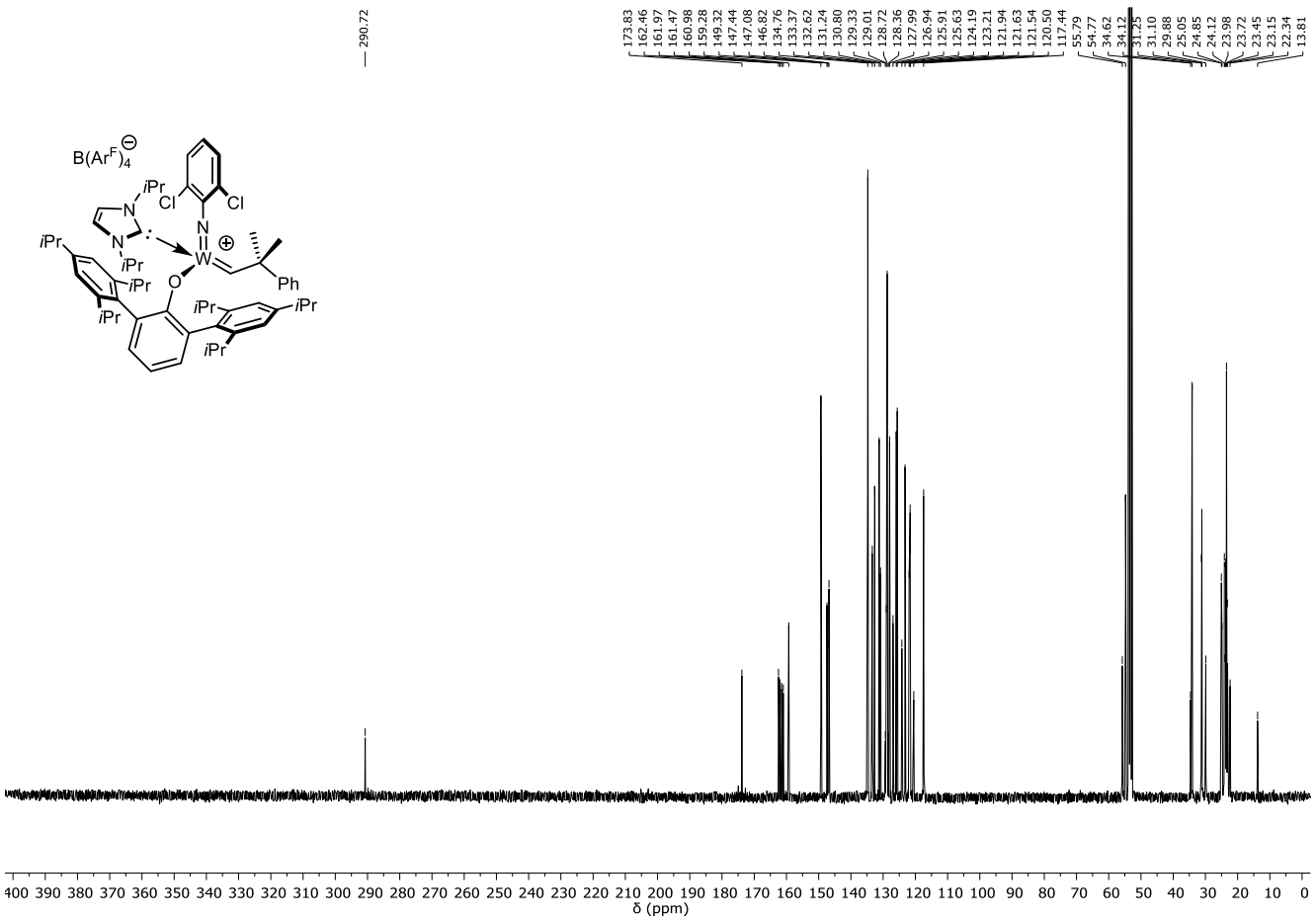


Figure S21. ^{13}C-NMR of [W(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(OHIPT)(IiPr)$^+$][B(Ar^F)$_4^-$] (**I32**) in CD_2Cl_2.

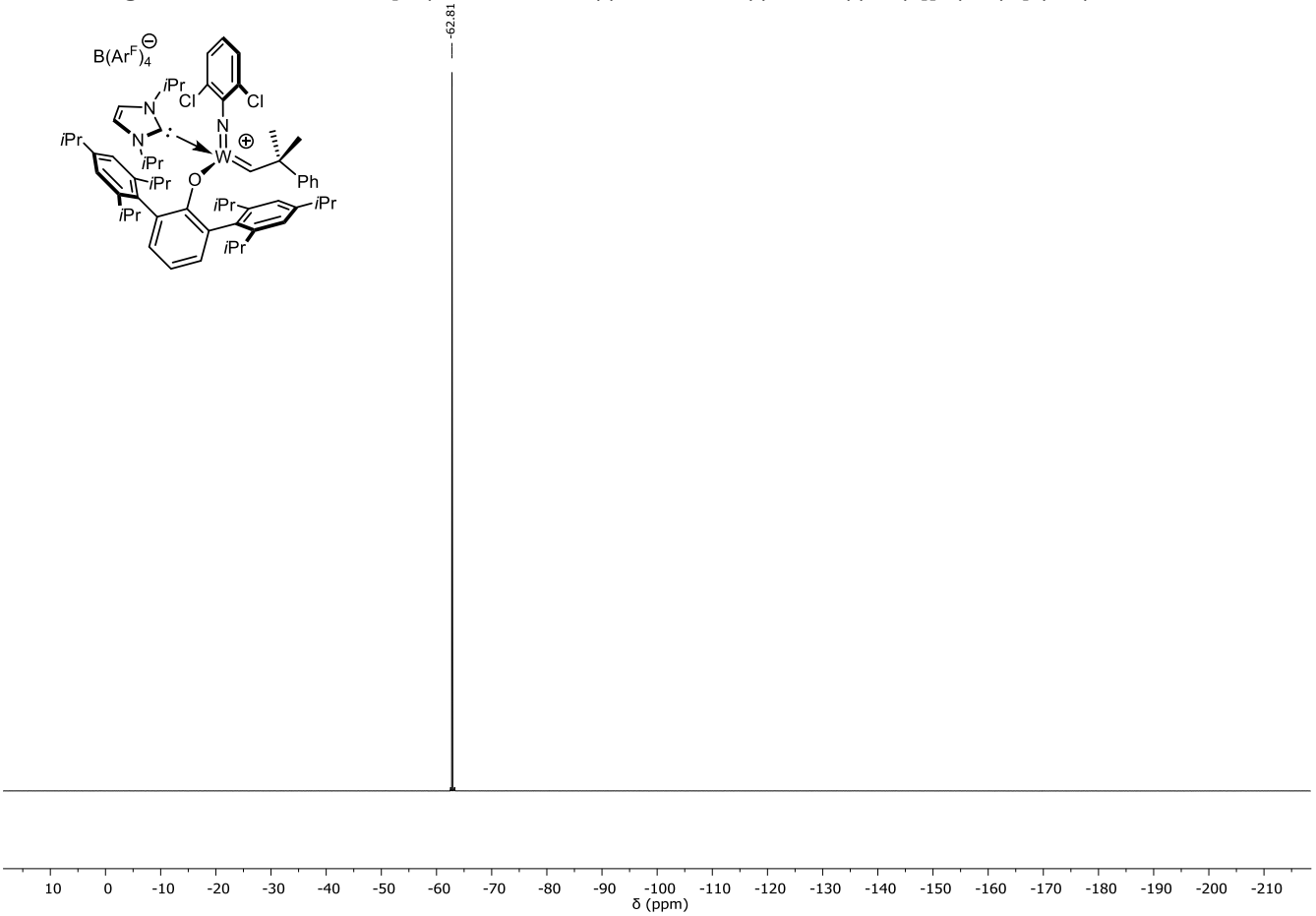


Figure S22. ^{19}F-NMR of [W(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(OHIPT)(IiPr)$^+$][B(Ar^F)$_4^-$] (**I32**) in CD_2Cl_2.

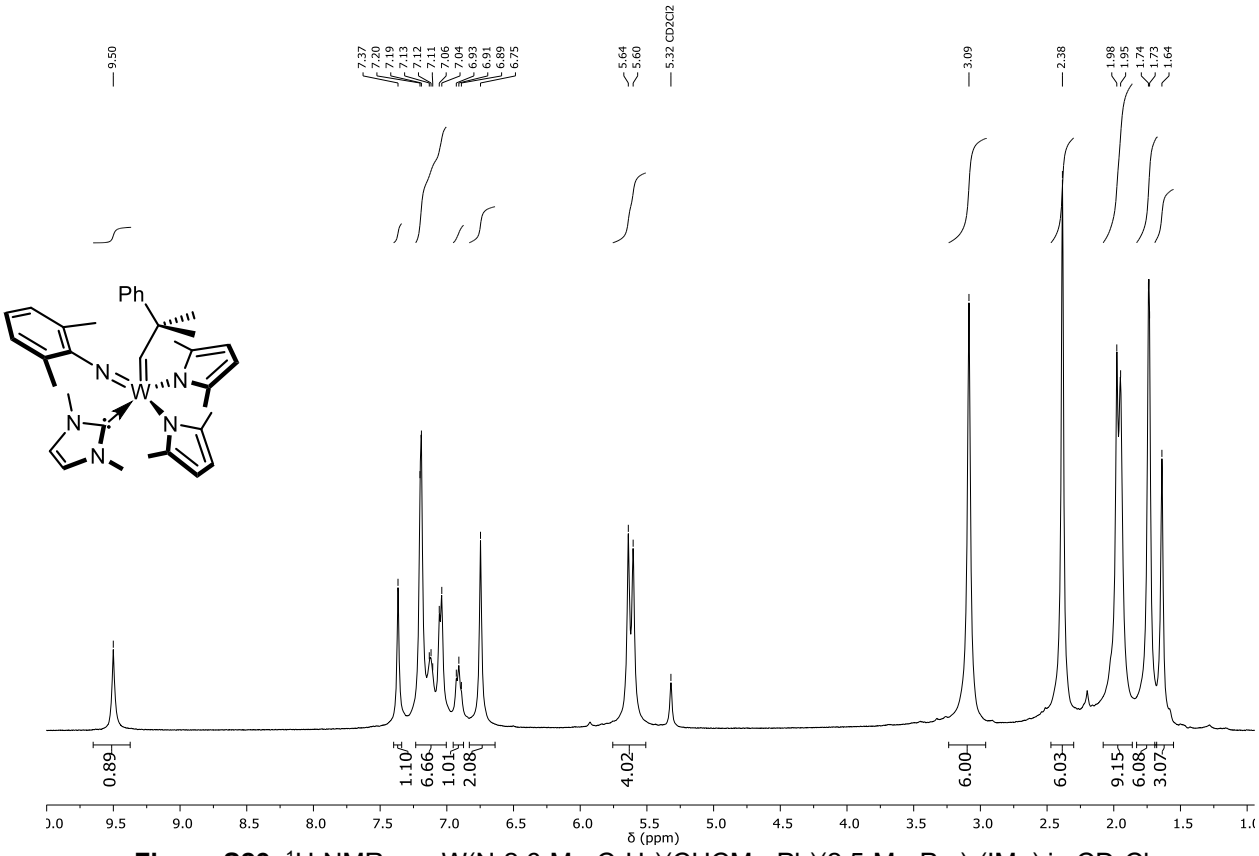


Figure S23. ^{1}H-NMR von W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(2,5-Me_2Pyr)$_2$(IMe) in CD_2Cl_2.

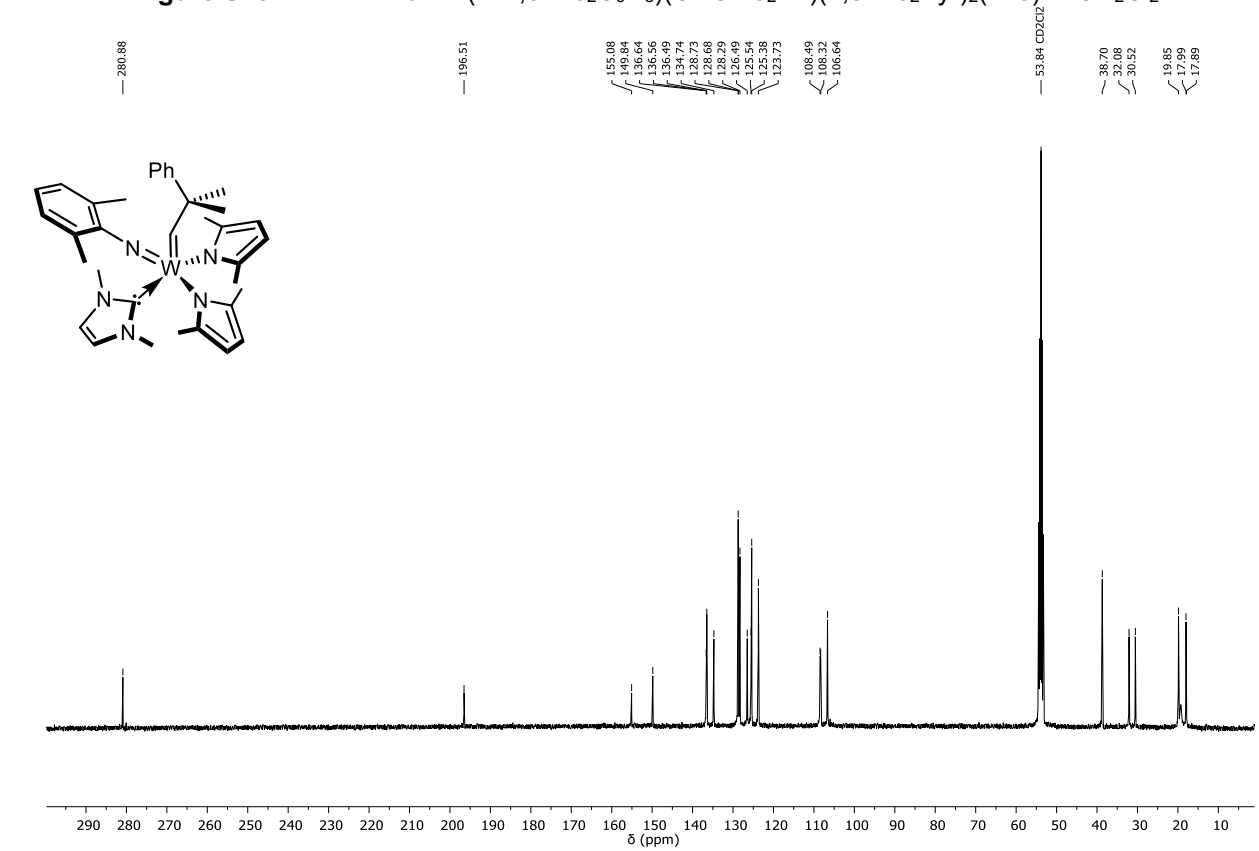


Figure S24. ^{13}C-NMR von W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(2,5-Me_2Pyr)$_2$(IMe) in CD_2Cl_2.

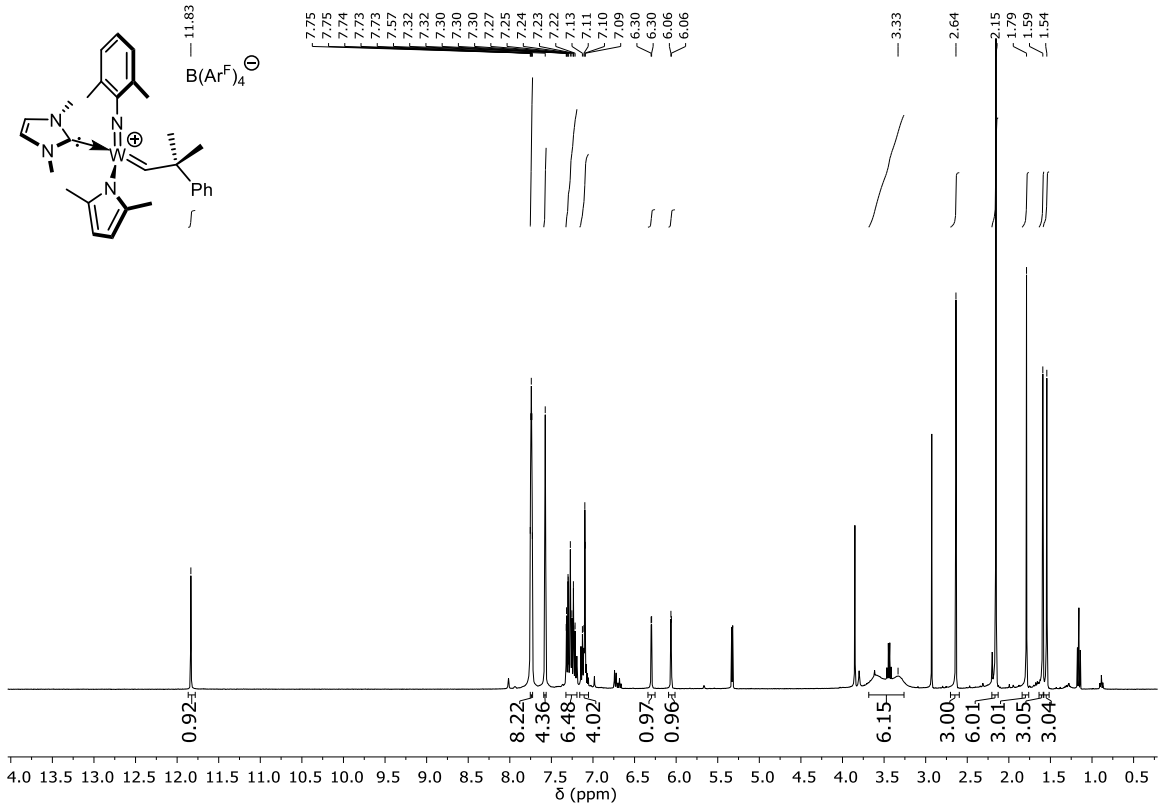


Figure S25. ^{1}H-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(2,5-Me_2Pyr)(IMe)$^{+}$] [B(Ar^F)$_4^-$] (**I27**) in CD_2Cl_2.

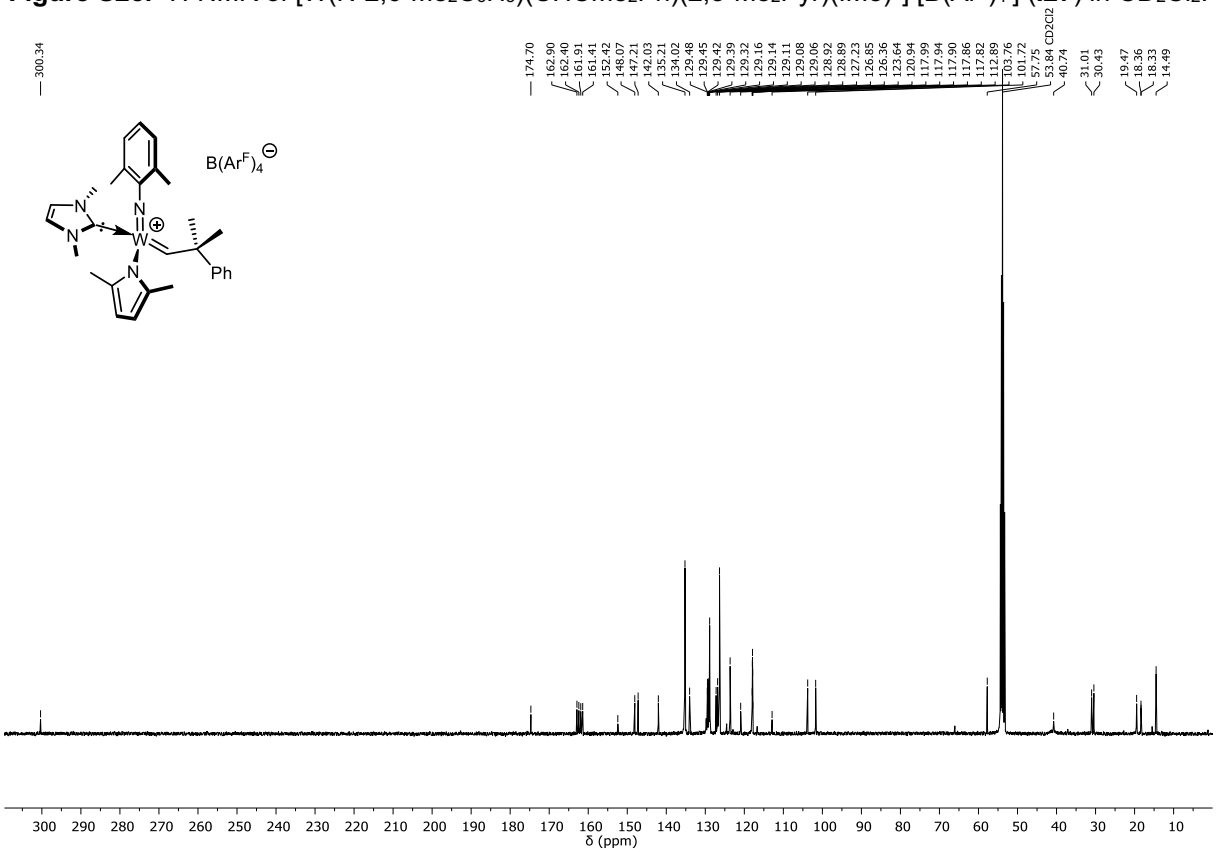


Figure S26. ^{13}C-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(2,5-Me_2Pyr)(IMe)$^{+}$] [B(Ar^F)$_4^-$] (**I27**) in CD_2Cl_2.

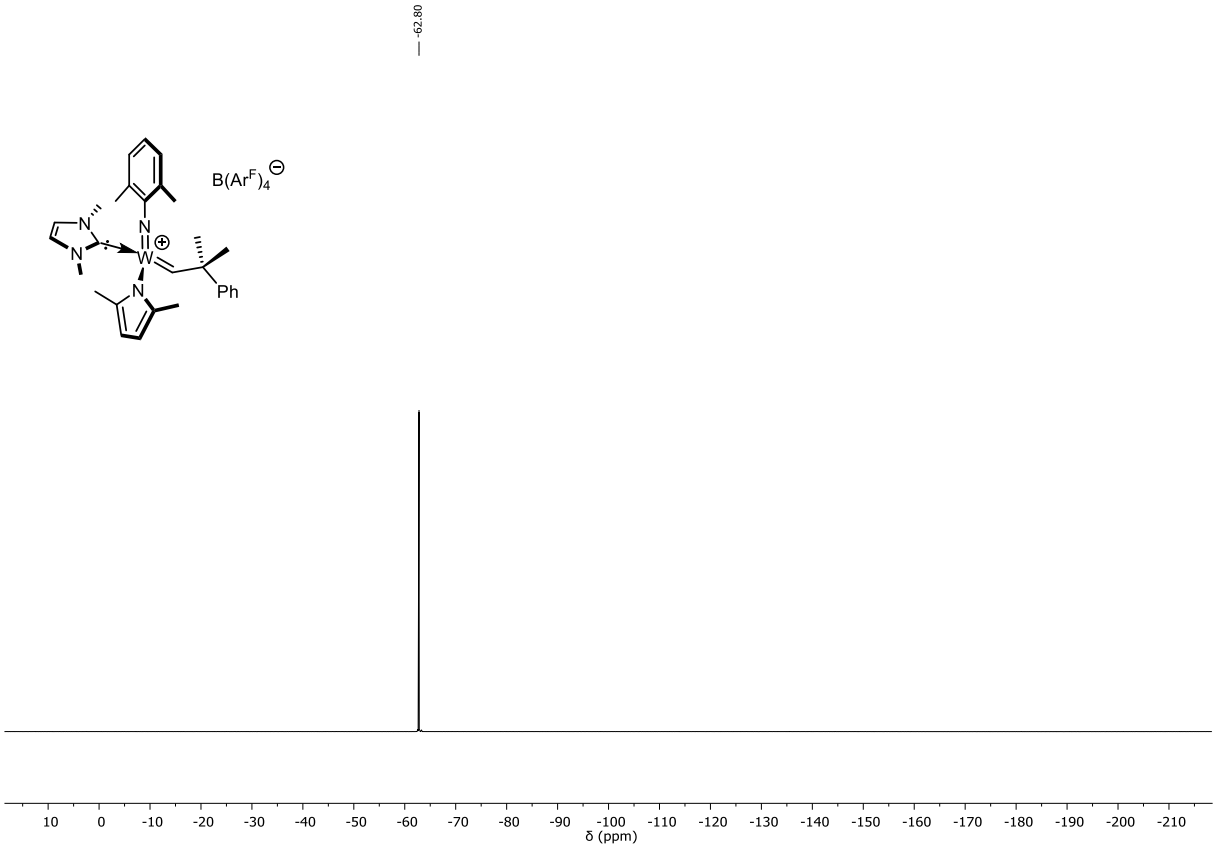


Figure S27. ^{19}F-NMR of [W(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(2,5-Me_2Pyr)(IMe)$^+$] [$B(Ar^F)_4^-$] (**I27**) in CD_2Cl_2.

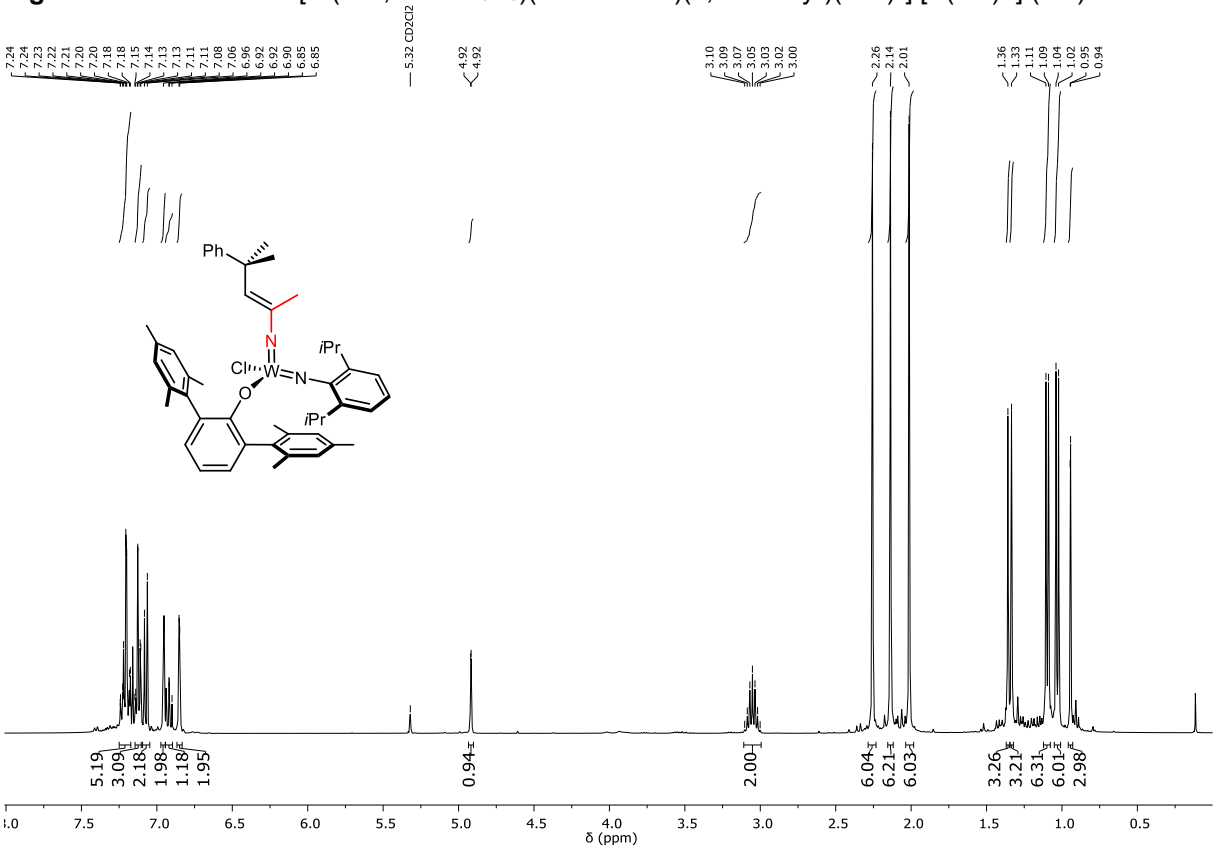


Figure S28. ^{1}H-NMR of W(N-2,6-*i*$Pr_2C_6H_3$)(NC(CH_3)CHC(CH_3)$_2$Ph)(OHMT)(Cl) in CD_2Cl_2.

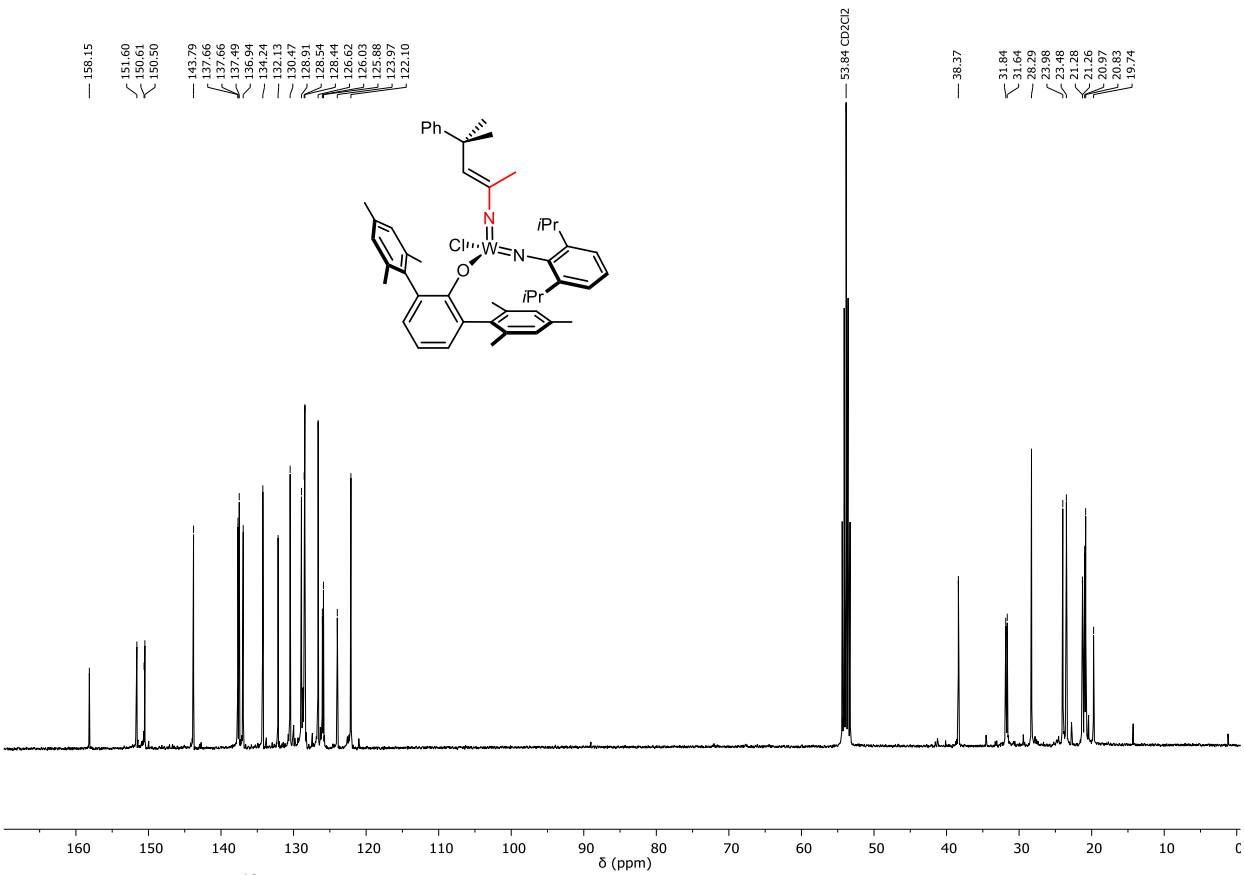


Figure S29. ^{13}C-NMR of W(N-2,6-*i*Pr$_2$C$_6$H$_3$)(NC(CH$_3$)CHC(CH$_3$)$_2$Ph)(OHMT)(Cl) in CD$_2$Cl$_2$.

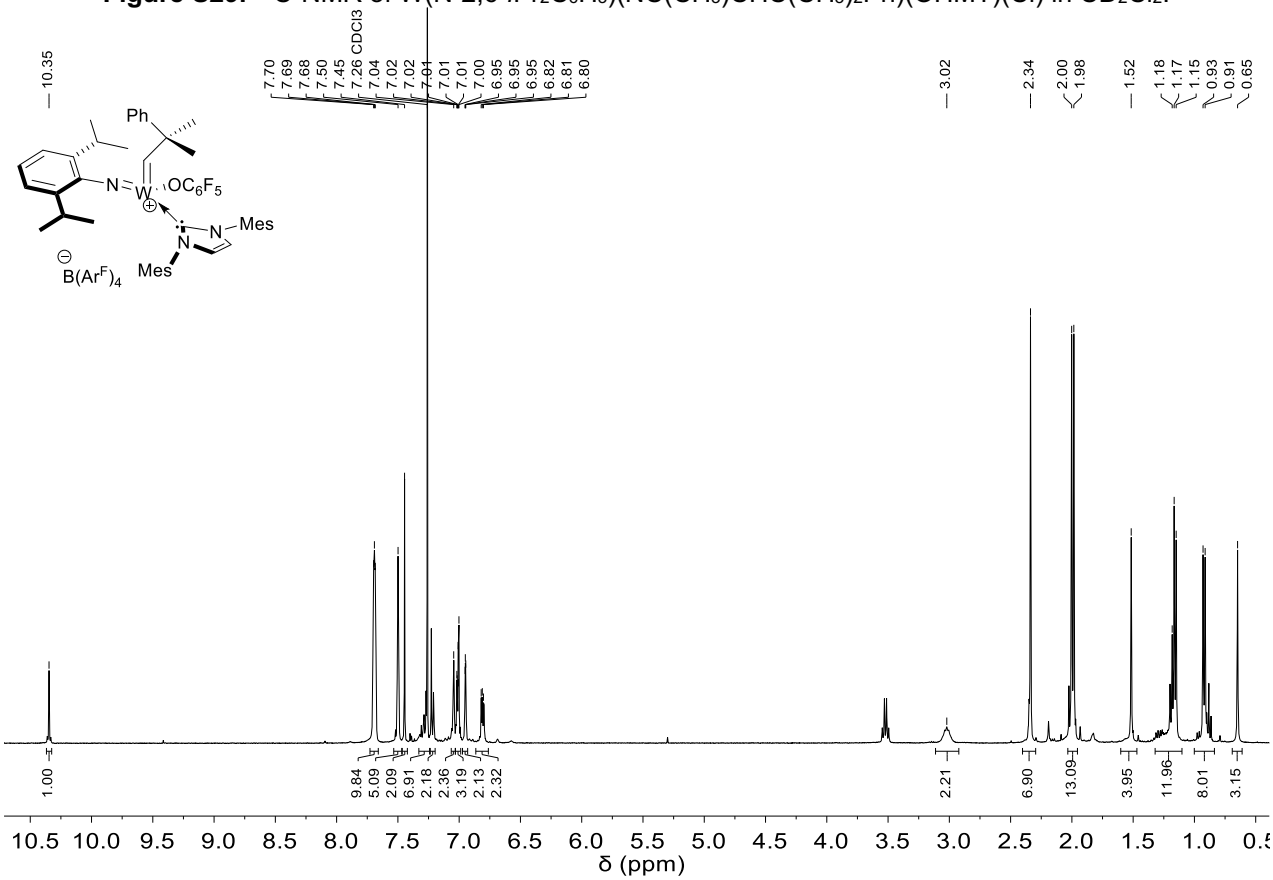


Figure S30. ^{1}H-NMR of [W(N-2,6-*i*Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OC$_6$F$_5$)(IMes)$^+$] [(B(Ar^F)$_4^-$] (**I16**) in CDCl$_3$.

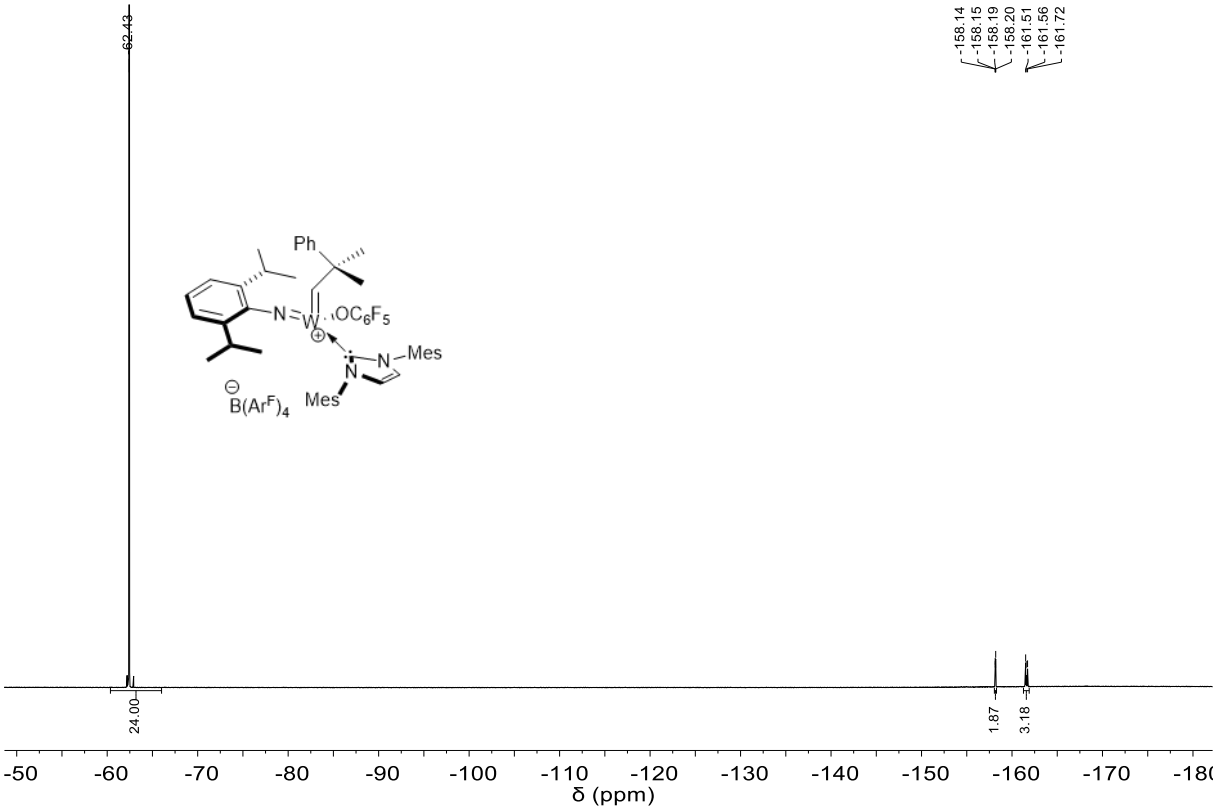


Figure S31. ^{19}F-NMR of [W(N-2,6-*i*Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OC$_6$F$_5$)(IMes)$^+$] [(B(Ar^F)$_4^-$] (**I16**) in CDCl$_3$.

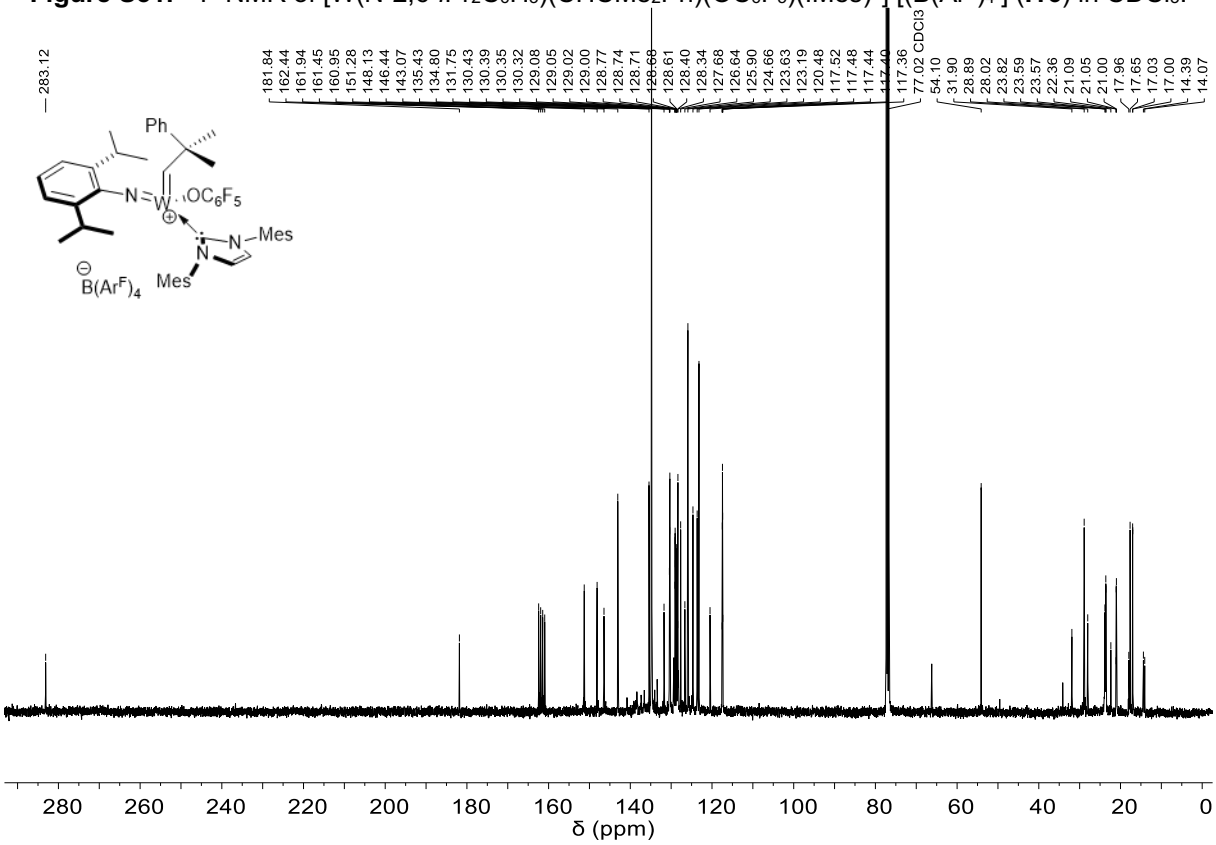


Figure S32:^{13}C-NMR of [W(N-2,6-*i*Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OC$_6$F$_5$)(IMes)$^+$] [(B(Ar^F)$_4^-$] (**I16**) in CDCl$_3$.

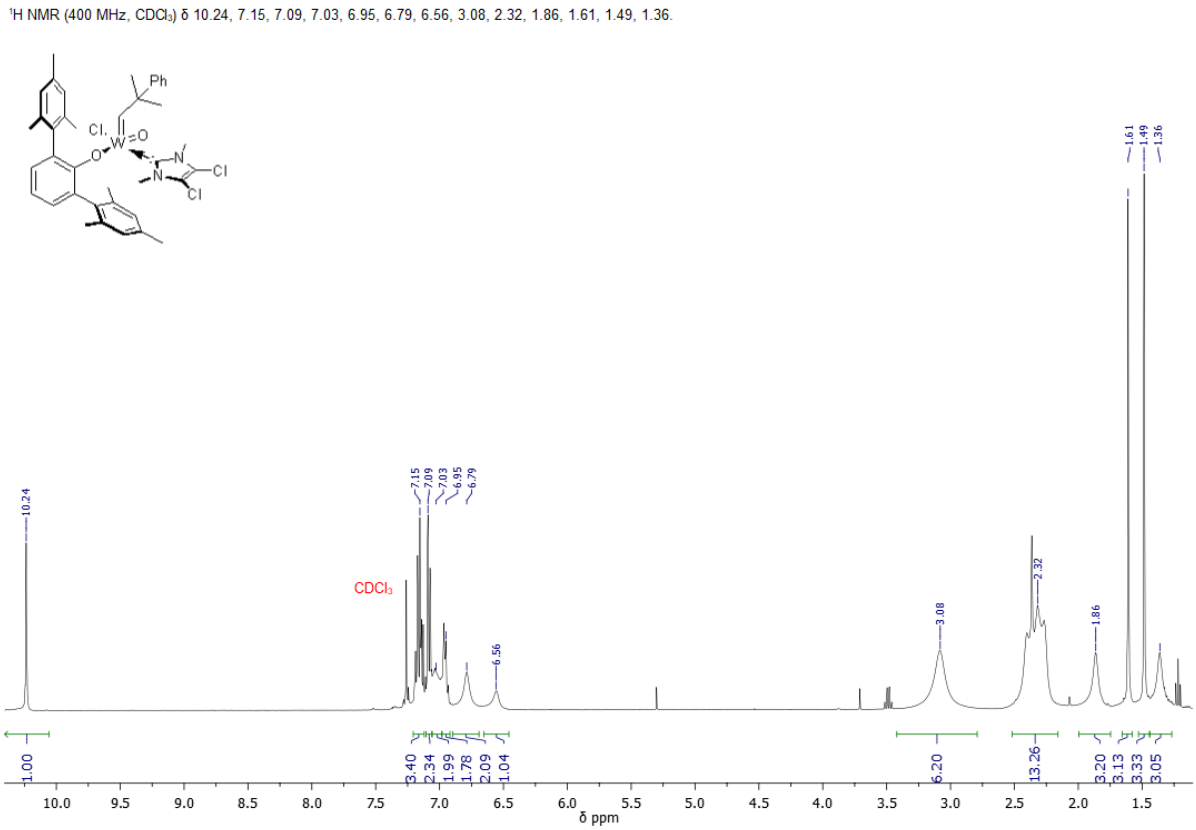


Figure S33. ^{1}H NMR spectrum of W(O)(CHCMe$_2$Ph)(5-MeCl$_2$)(OHMT)(Cl) in CDCl$_3$.

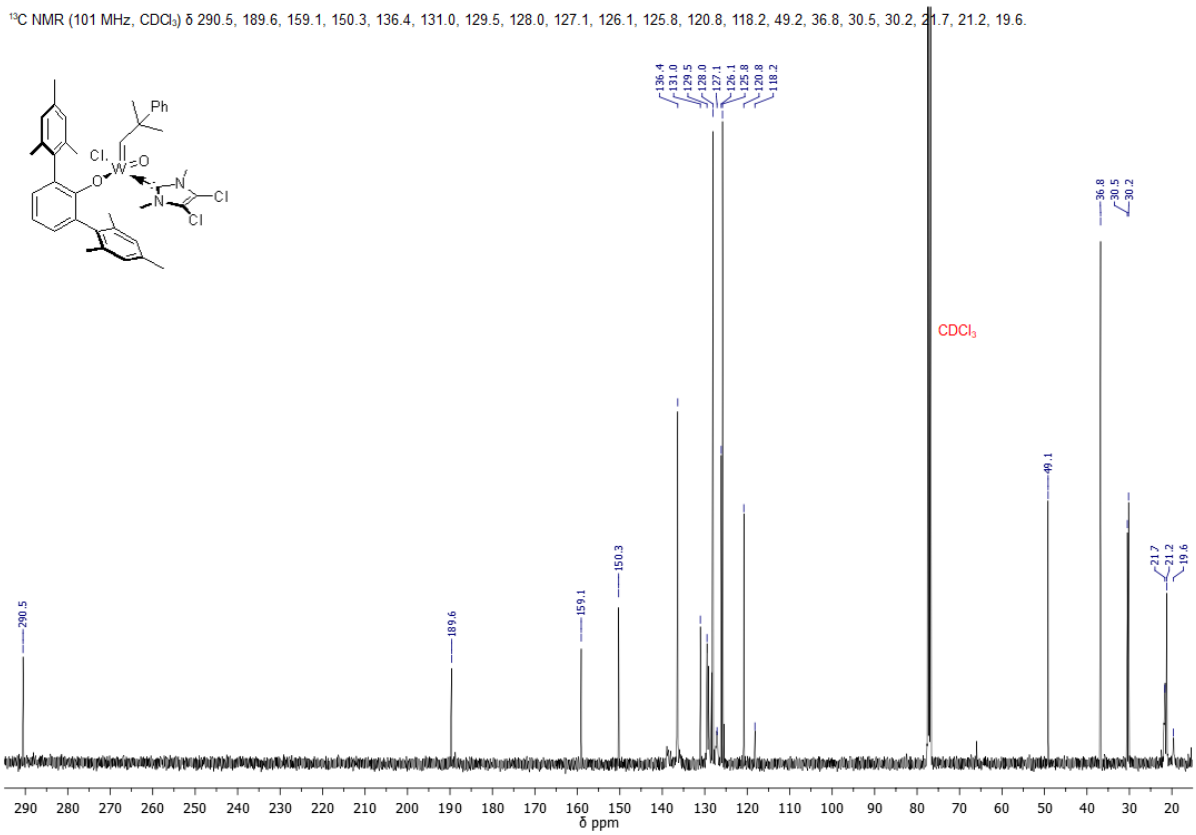


Figure S34. ^{13}C NMR spectrum of W(O)(CHCMe$_2$Ph)(5-MeCl$_2$)(OHMT)(Cl) in CDCl$_3$.

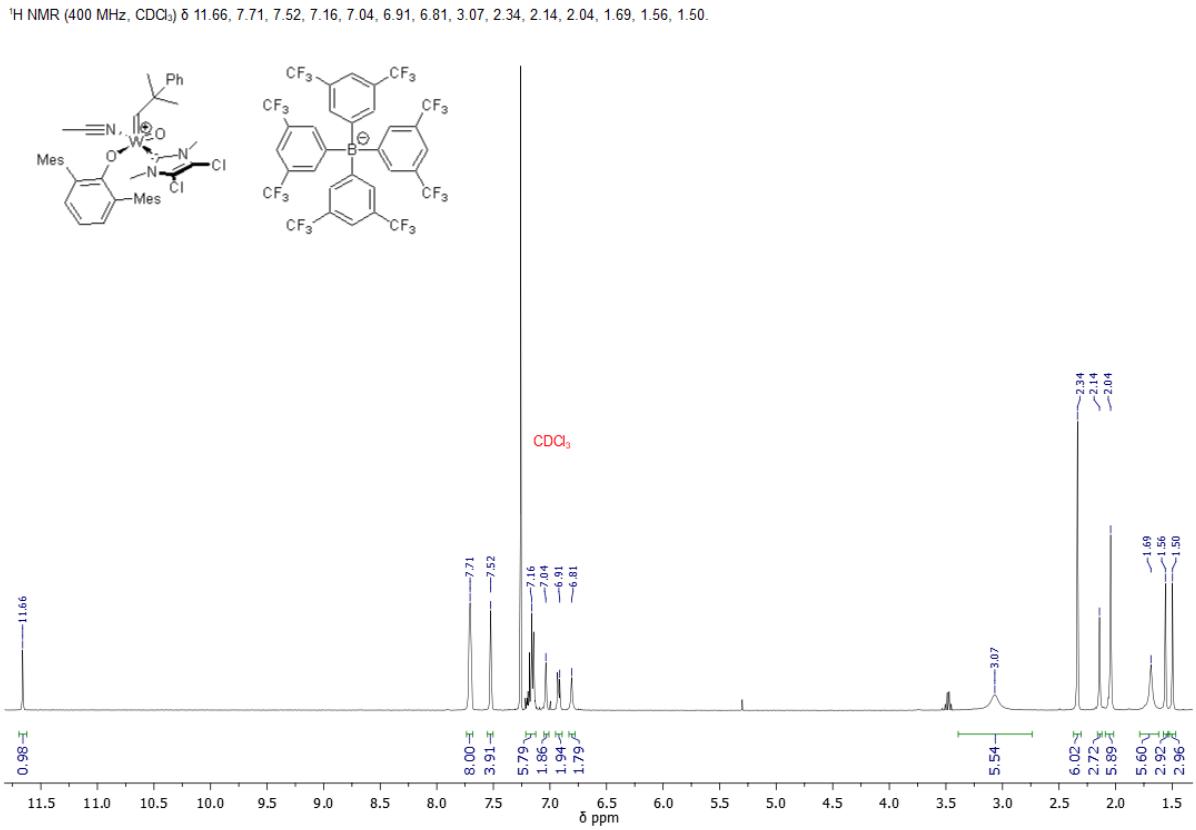


Figure S35. ^{1}H NMR spectrum of **I28** in $CDCl_3$.

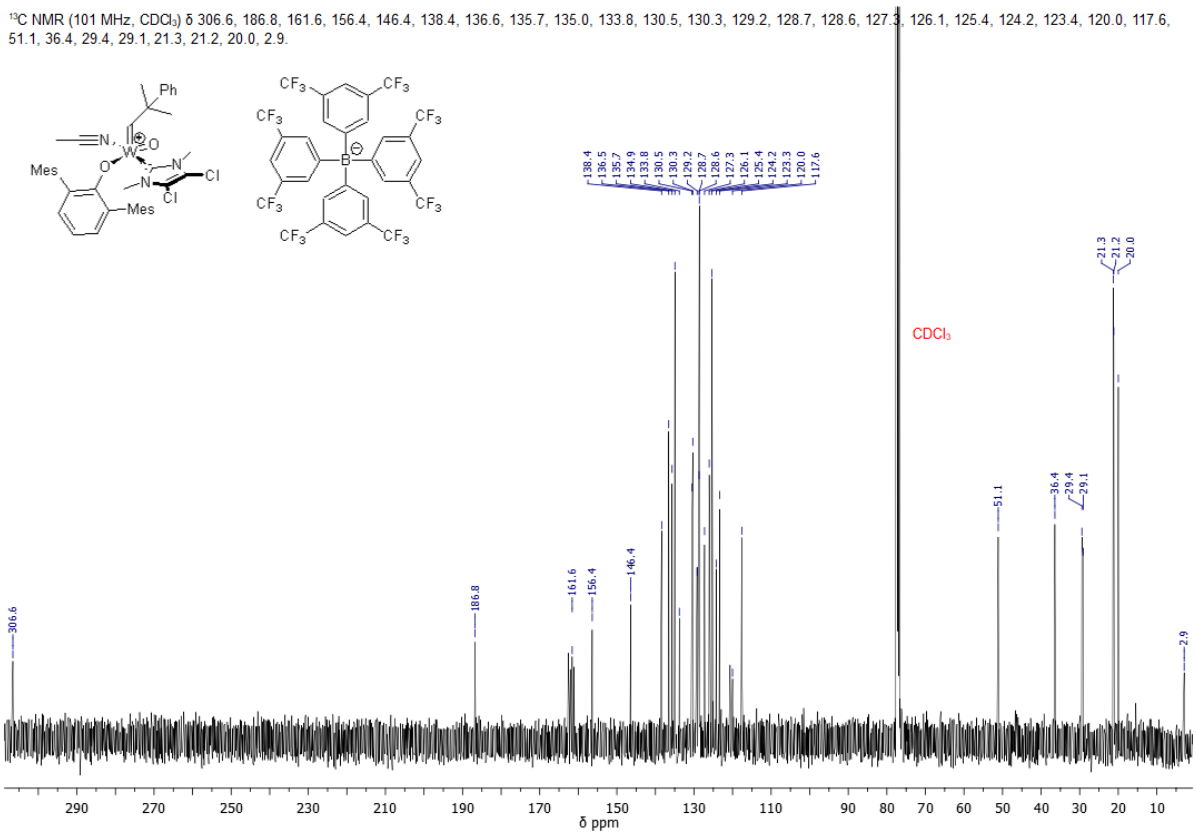


Figure S36. ^{13}C NMR spectrum of **I28** in $CDCl_3$.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.38.

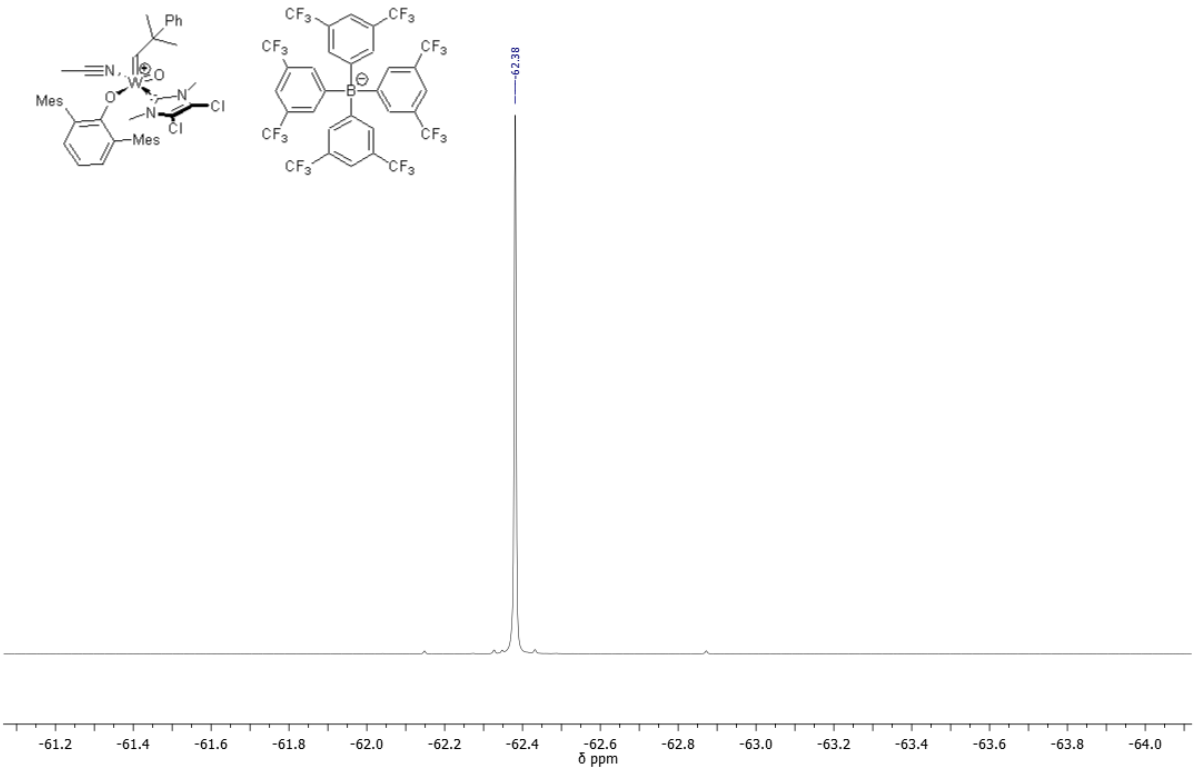


Figure S37. ^{19}F NMR spectrum of **I28** in $CDCl_3$.

Solution NMR Spectra of Polymers

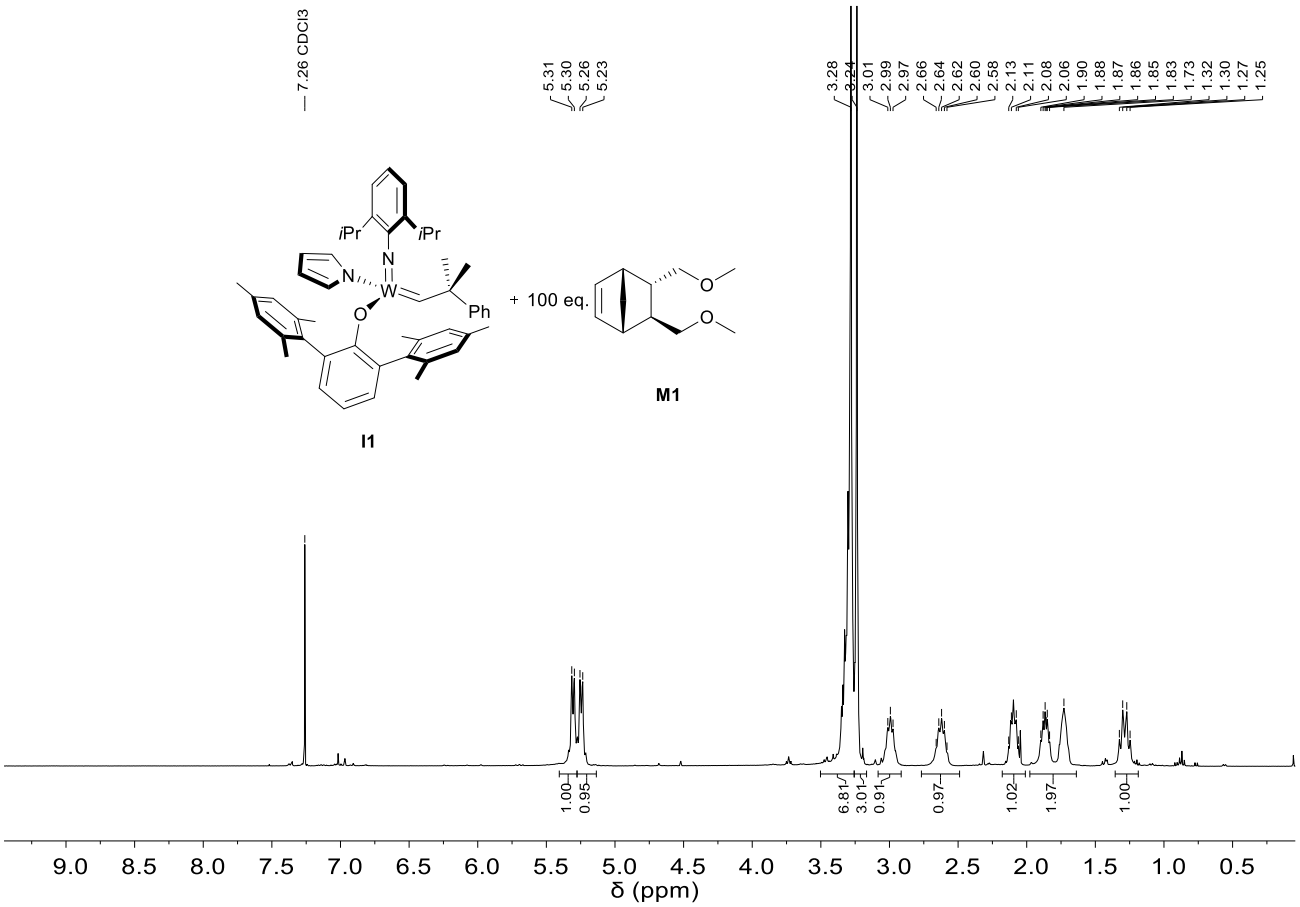


Figure S38. ^{1}H-NMR of *cis*-st poly[(+)DMMNBE]; polymerization of 100 eq. (+)-(2S,3S)-2,3-(dimethoxymethyl)norborn-5-ene (**M1**) by the action of **I1** in $CDCl_3$.

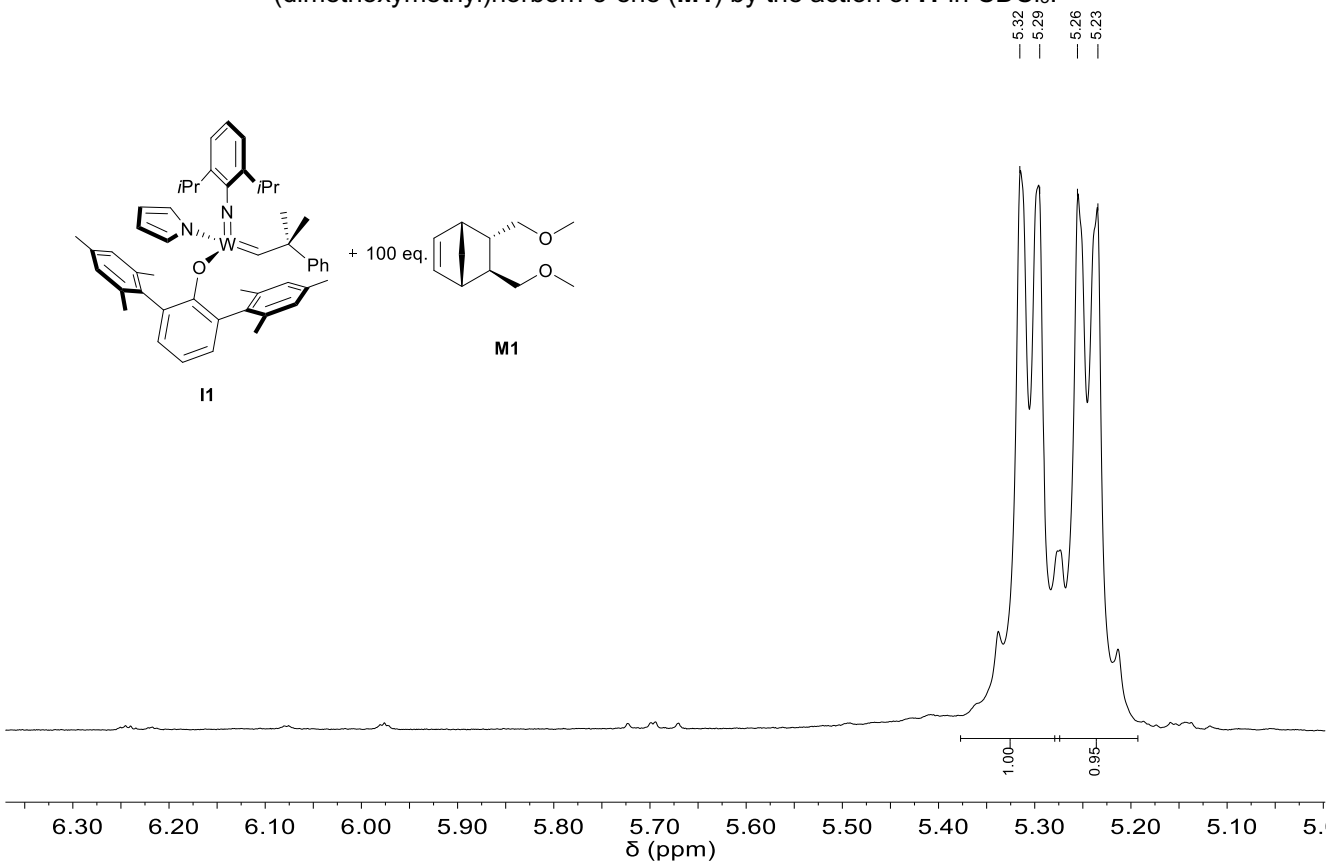


Figure S39. Olefinic region of *cis*-st poly[(+)DMMNBE]; polymerization of 100 eq. (**M1**) by the action of **I1** in $CDCl_3$.

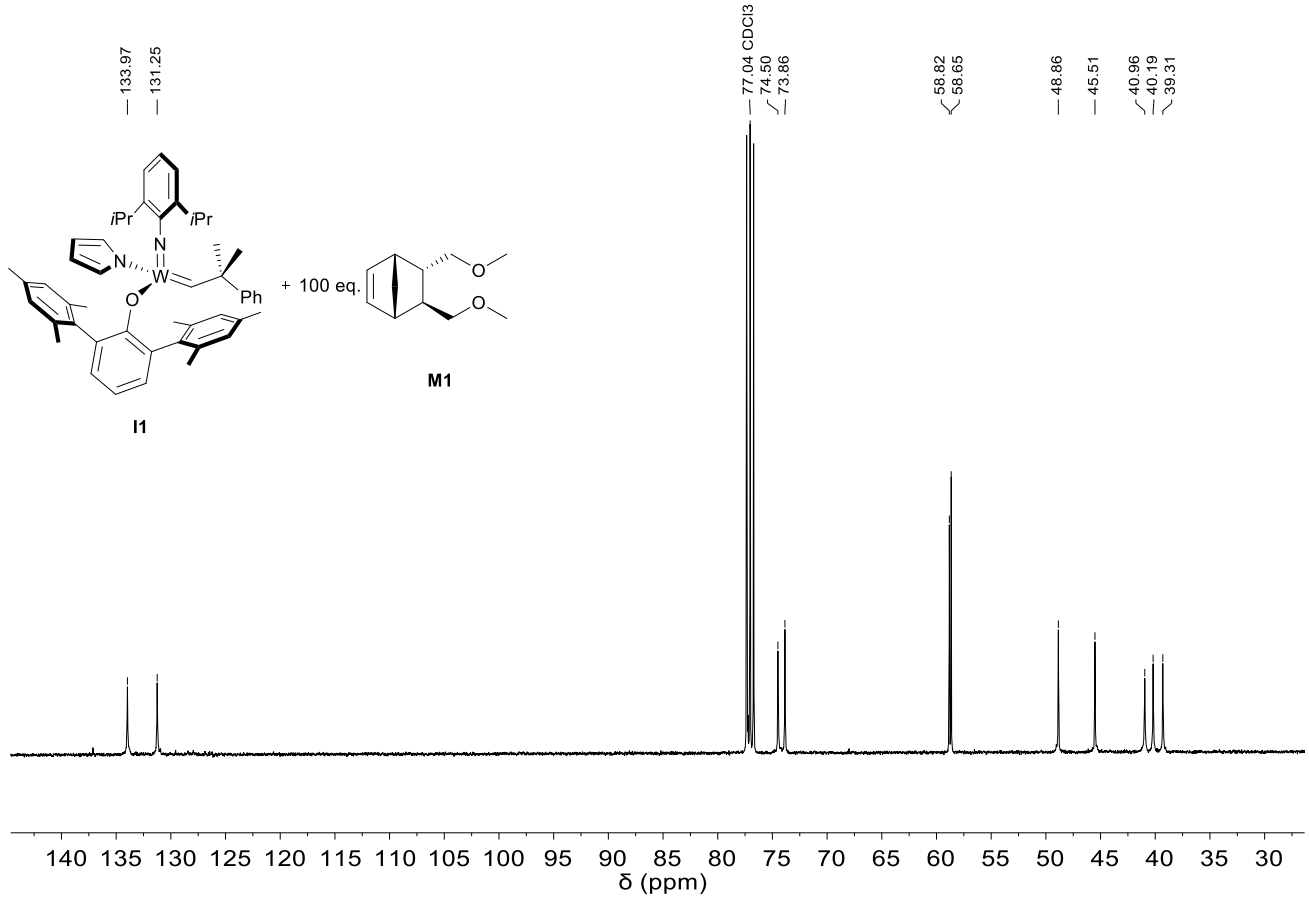


Figure S40. ^{13}C-NMR of *cis*-st poly[(+)DMMNBE]; polymerization of 100 eq. (**M1**) by the action of **I1** in $CDCl_3$.

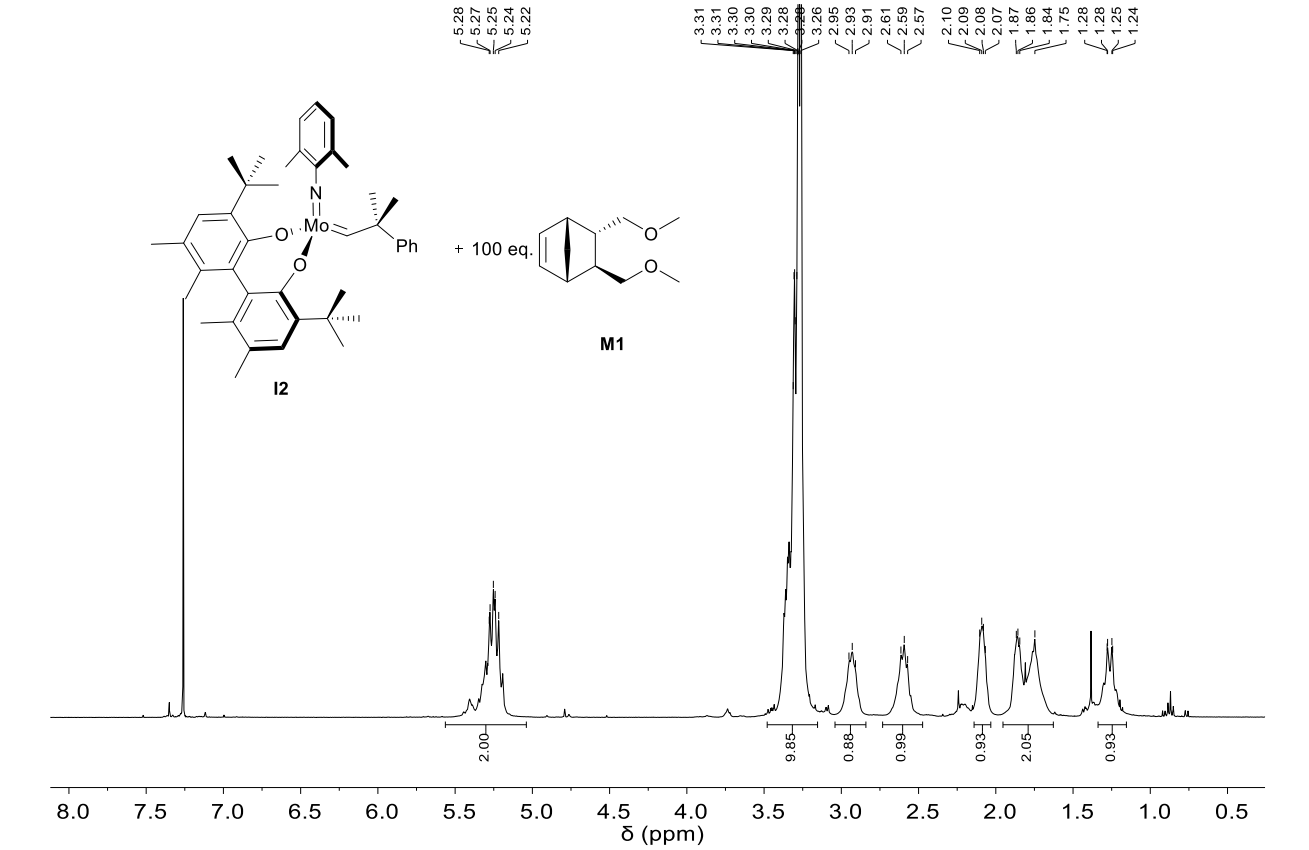


Figure S41. ^{1}H-NMR of *cis*-it poly[(+)DMMNBE]; polymerization of 100 eq. (+)-(2S,3S)-2,3-(dimethoxymethyl)norborn-5-ene (**M1**) by the action of **I2** in $CDCl_3$.

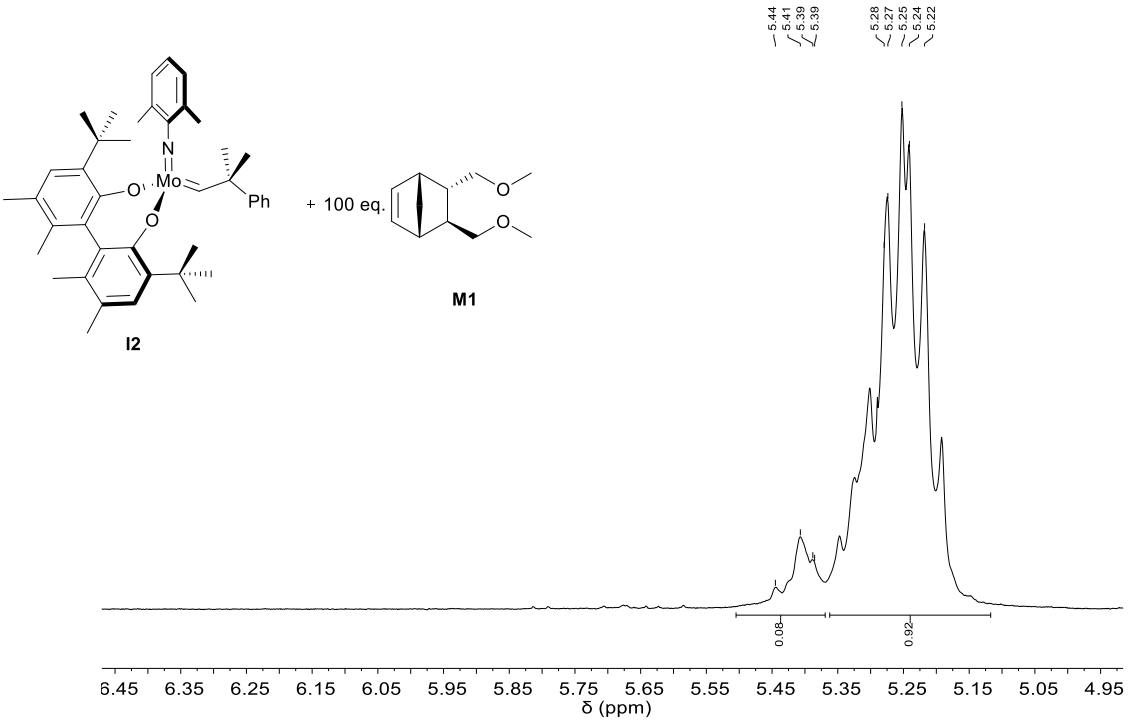


Figure S42. Olefinic region of the ^{1}H-NMR spectrum of *cis*-it poly[(+)DMMNBE]; polymerization of 100 eq. (**M1**) by the action of **I2** in $CDCl_3$.

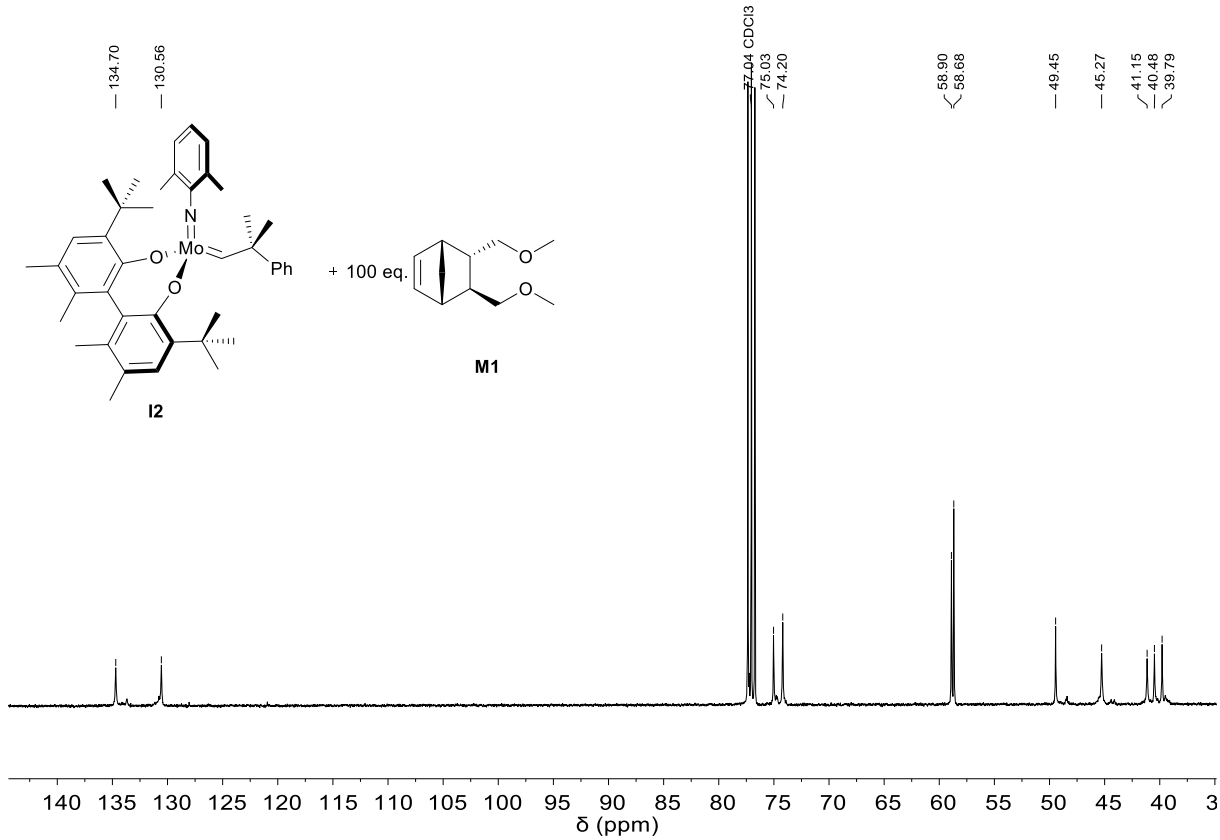


Figure S43. ^{13}C-NMR of *cis*-it poly[(+)DMMNBE]; polymerization of 100 eq. (**M1**) by the action of **I2** in $CDCl_3$.

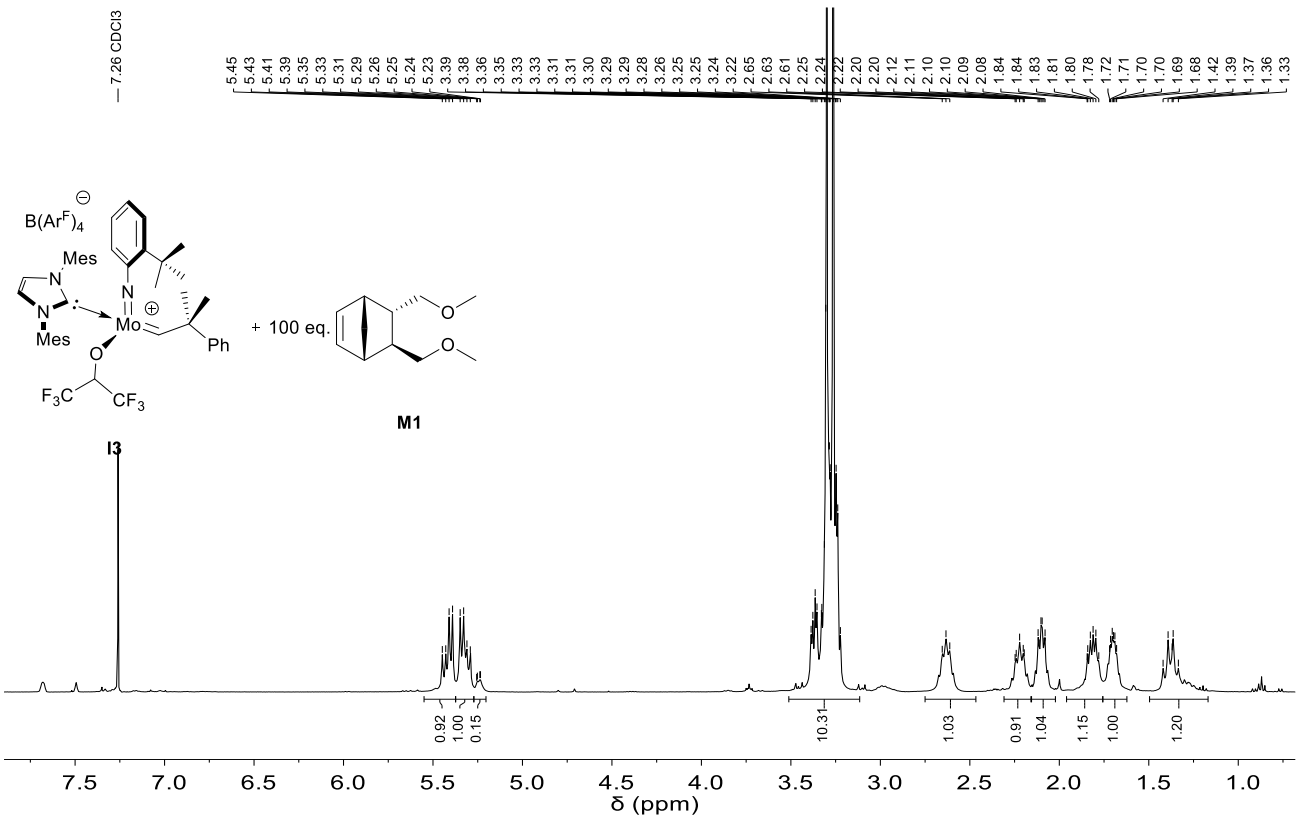


Figure S44. ^{1}H-NMR of *trans*-it poly[(+)DMMNBE]; polymerization of 100 eq. (+)-(2S,3S)-2,3-(dimethoxymethyl)norborn-5-ene (**M1**) by the action of **I3** in $CDCl_3$.

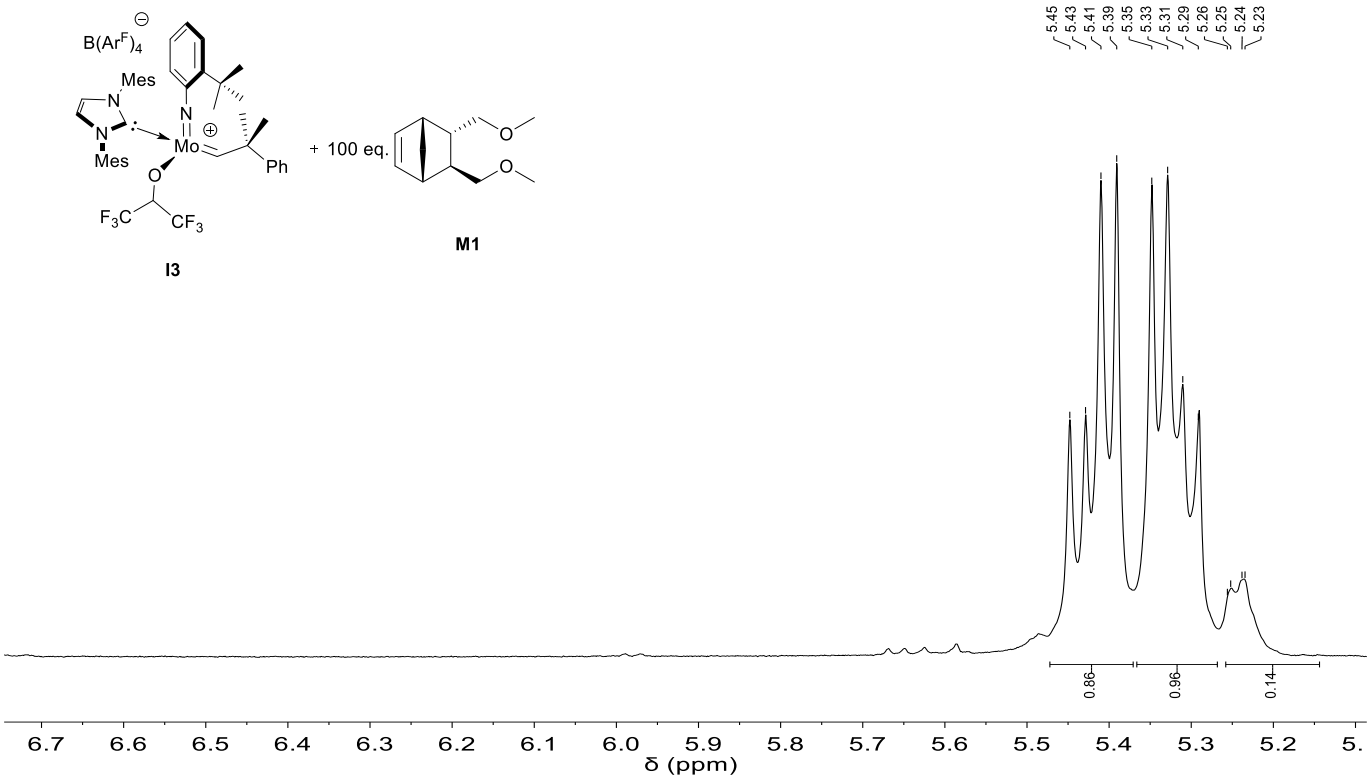


Figure S45. Olefinic region of the ^{1}H-NMR of *trans*-it poly[(+)DMMNBE]; polymerization of 100 eq. (**M1**) by the action of **I3** in $CDCl_3$.

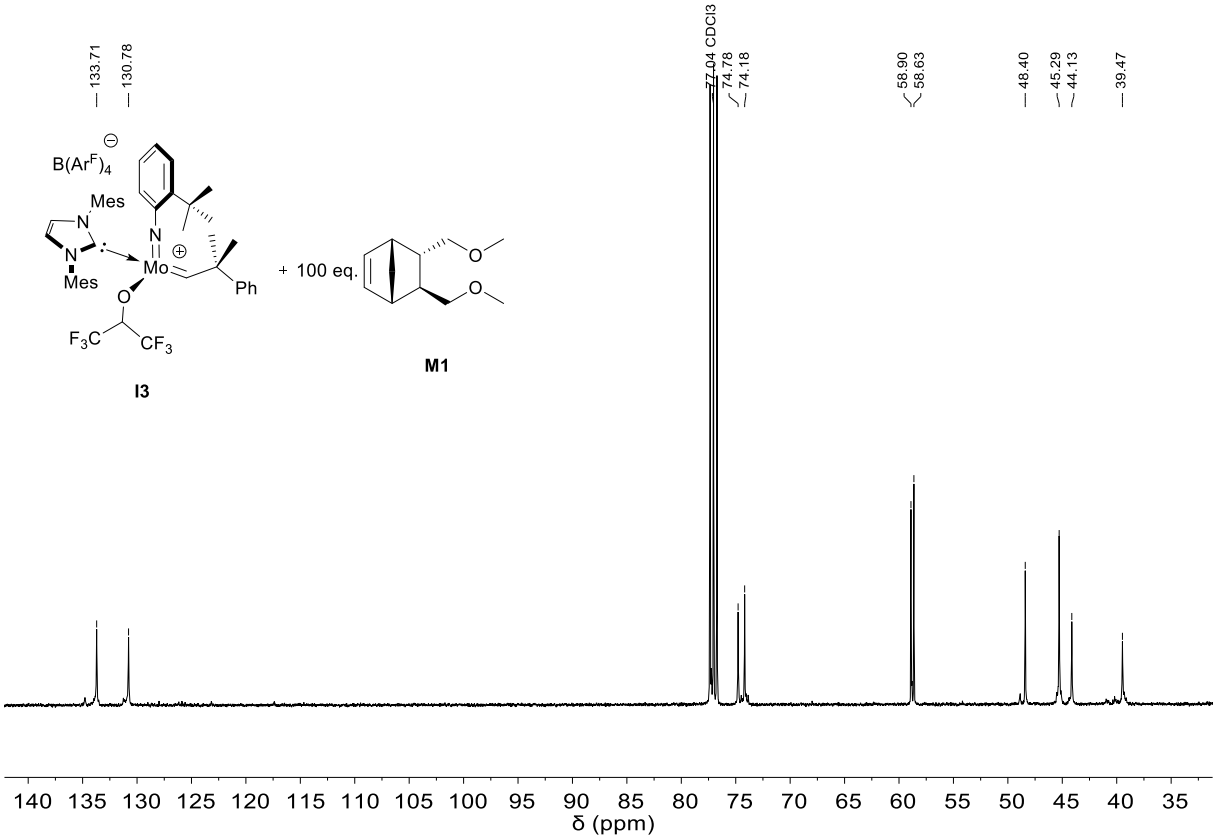


Figure S46. ^{13}C-NMR of *trans*-it poly[(+)DMMNBE]; polymerization of 100 eq. (**M1**) by the action of **I3** in $CDCl_3$.

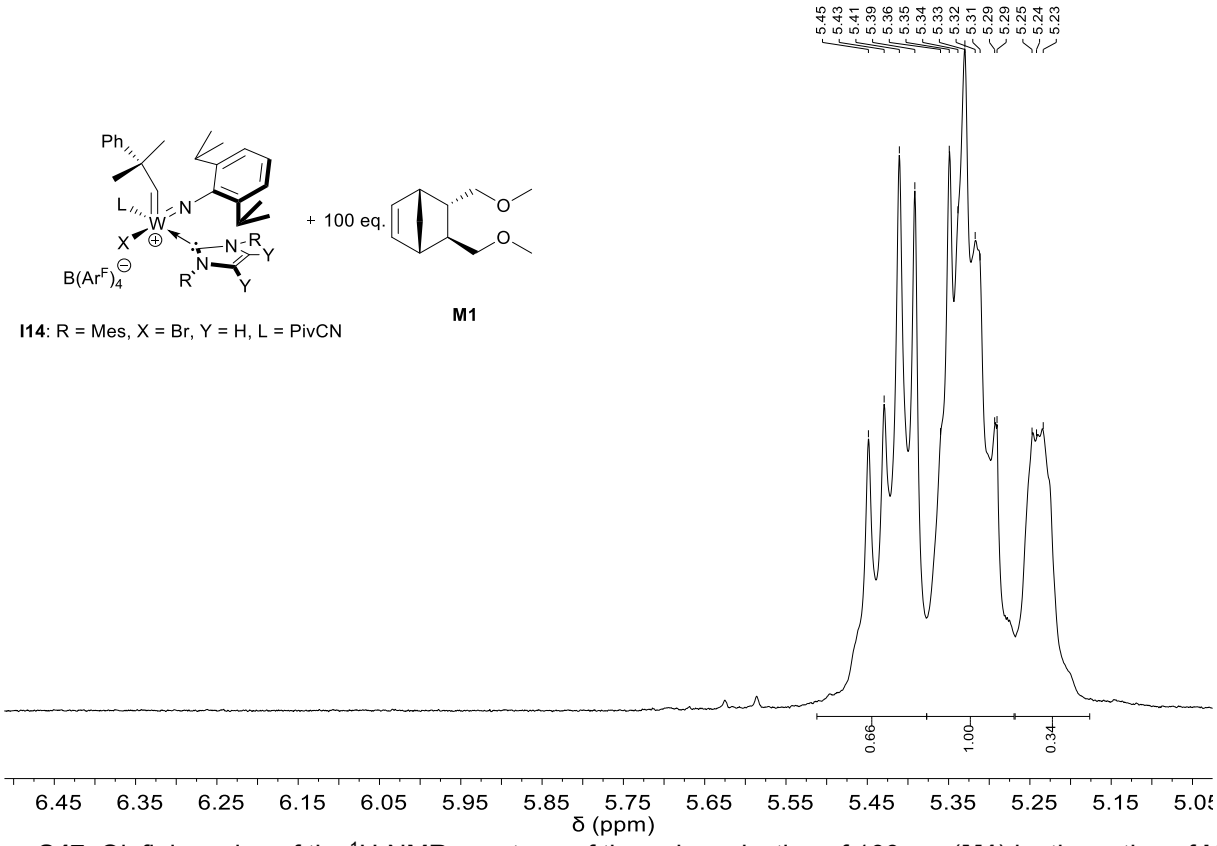


Figure S47. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I14** in $CDCl_3$.

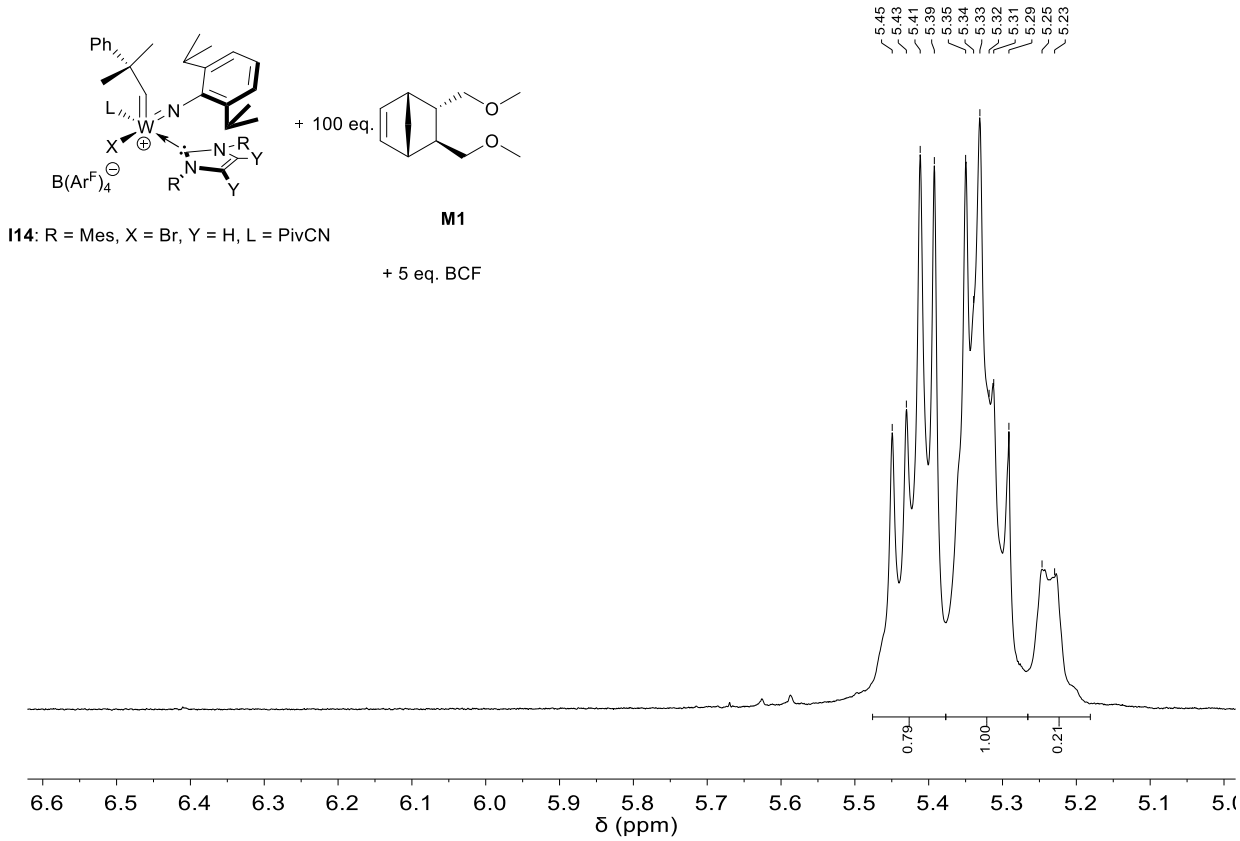


Figure S48. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I14** with 5 eq. BCF in $CDCl_3$.

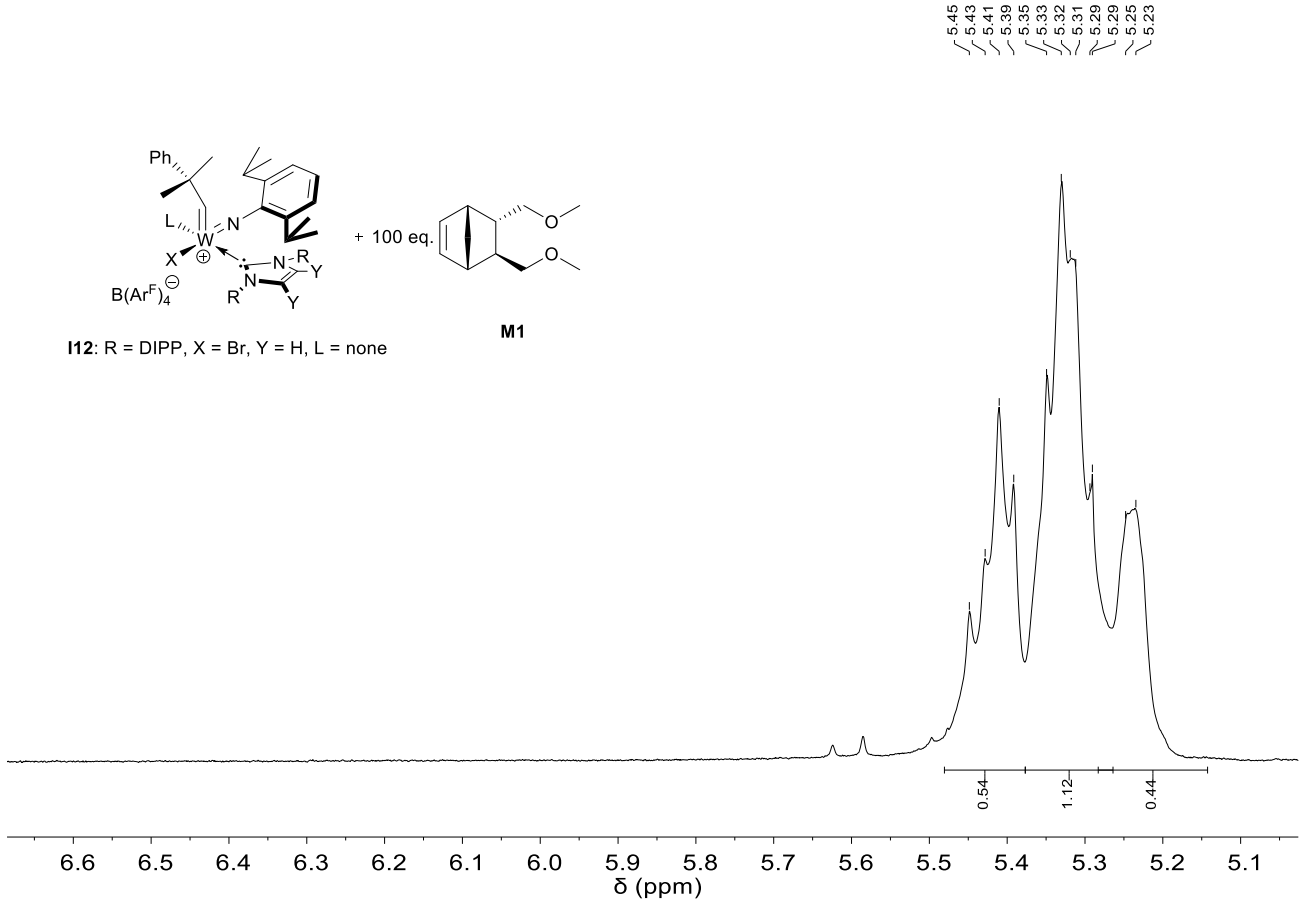


Figure S49. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I12** in $CDCl_3$.

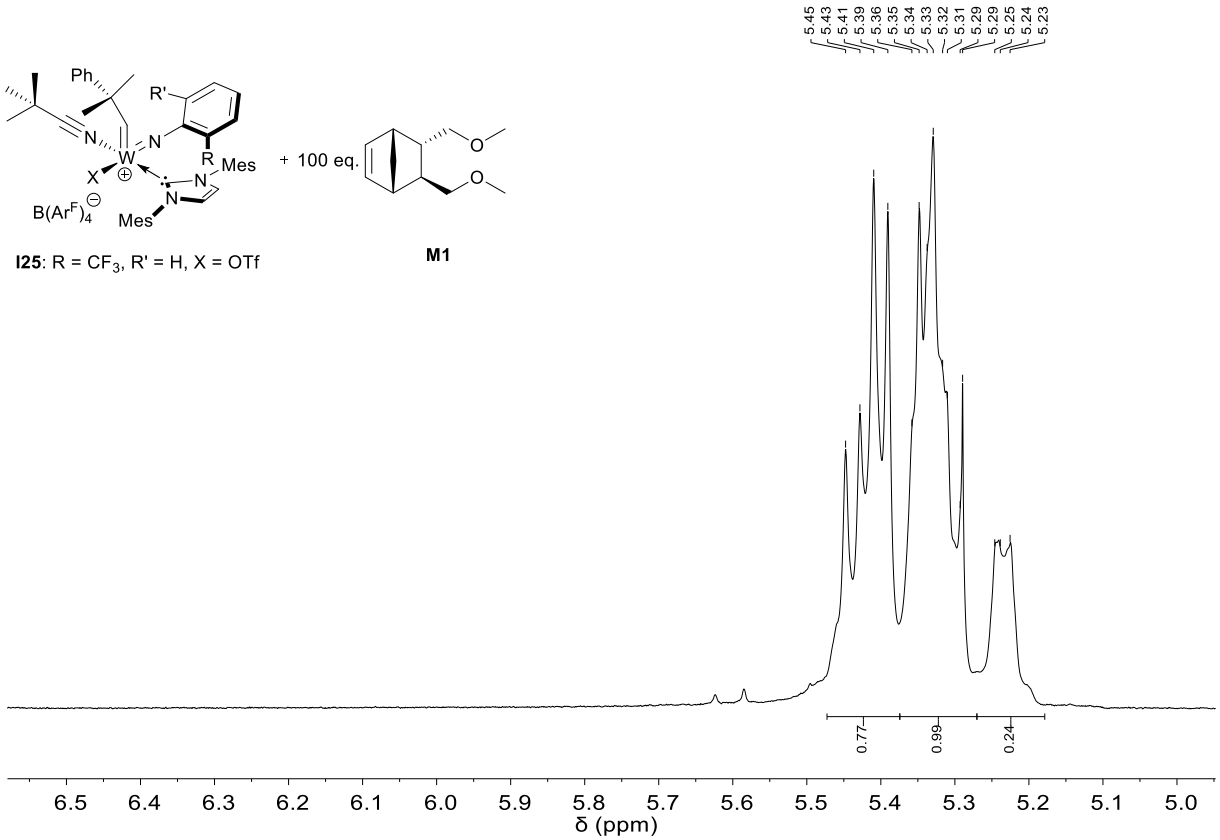


Figure S50. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I25** in $CDCl_3$.

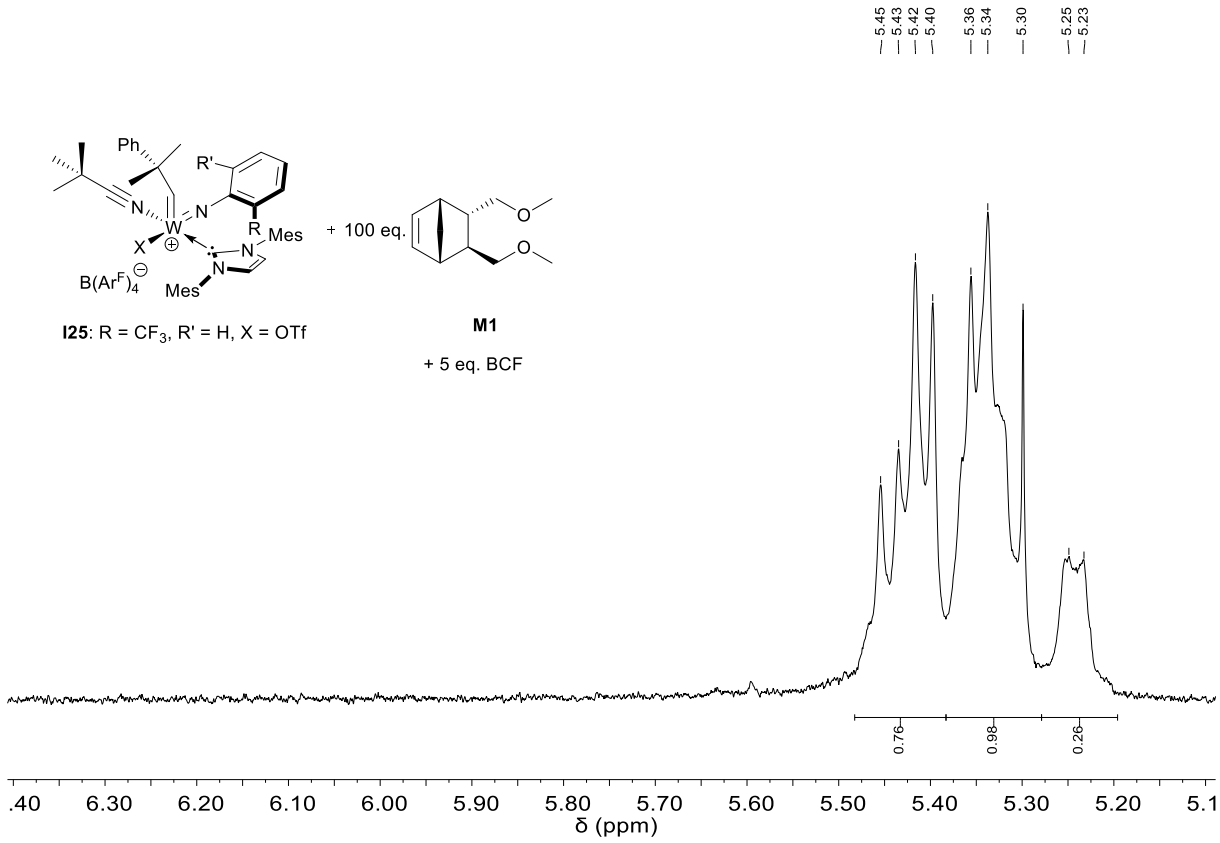


Figure S51. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I25** with 5 eq. BCF in $CDCl_3$.

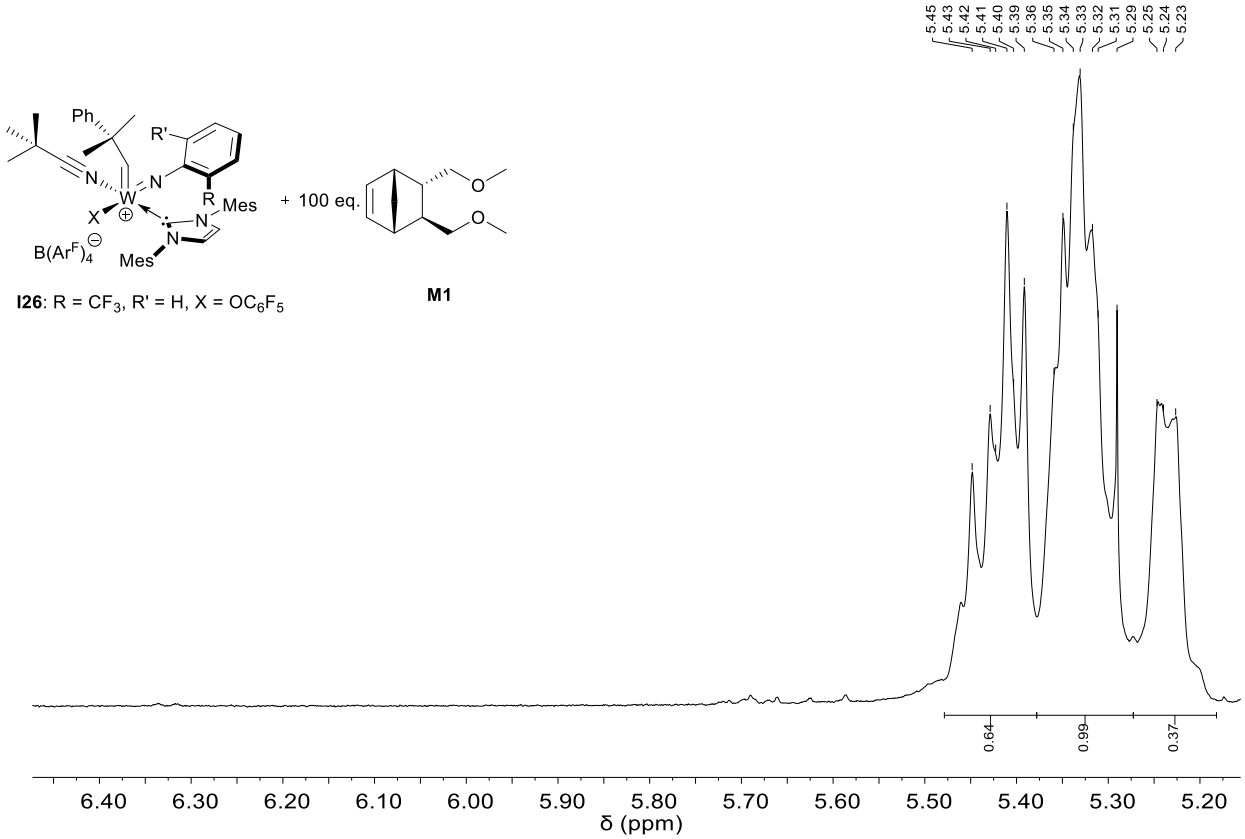


Figure S52. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I26** in $CDCl_3$.

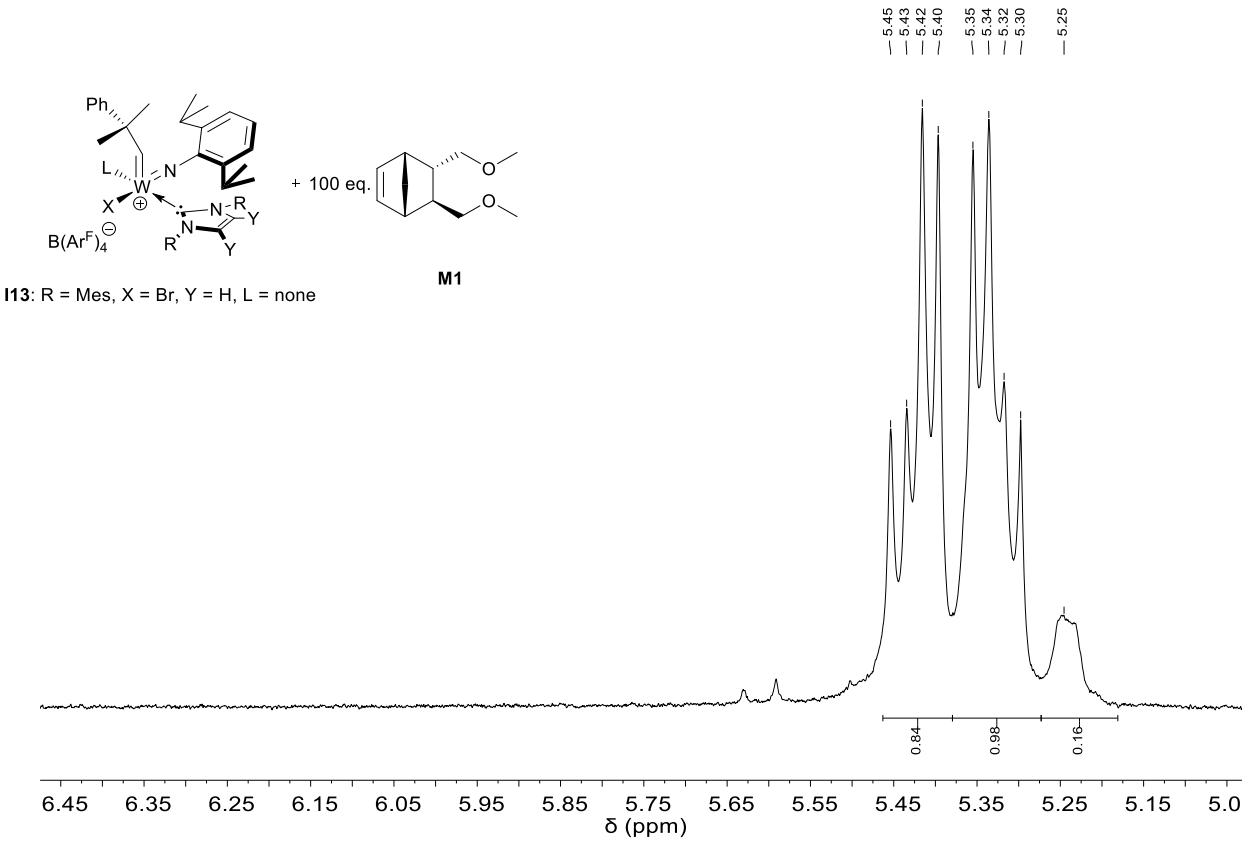


Figure S53. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I13** in $CDCl_3$.

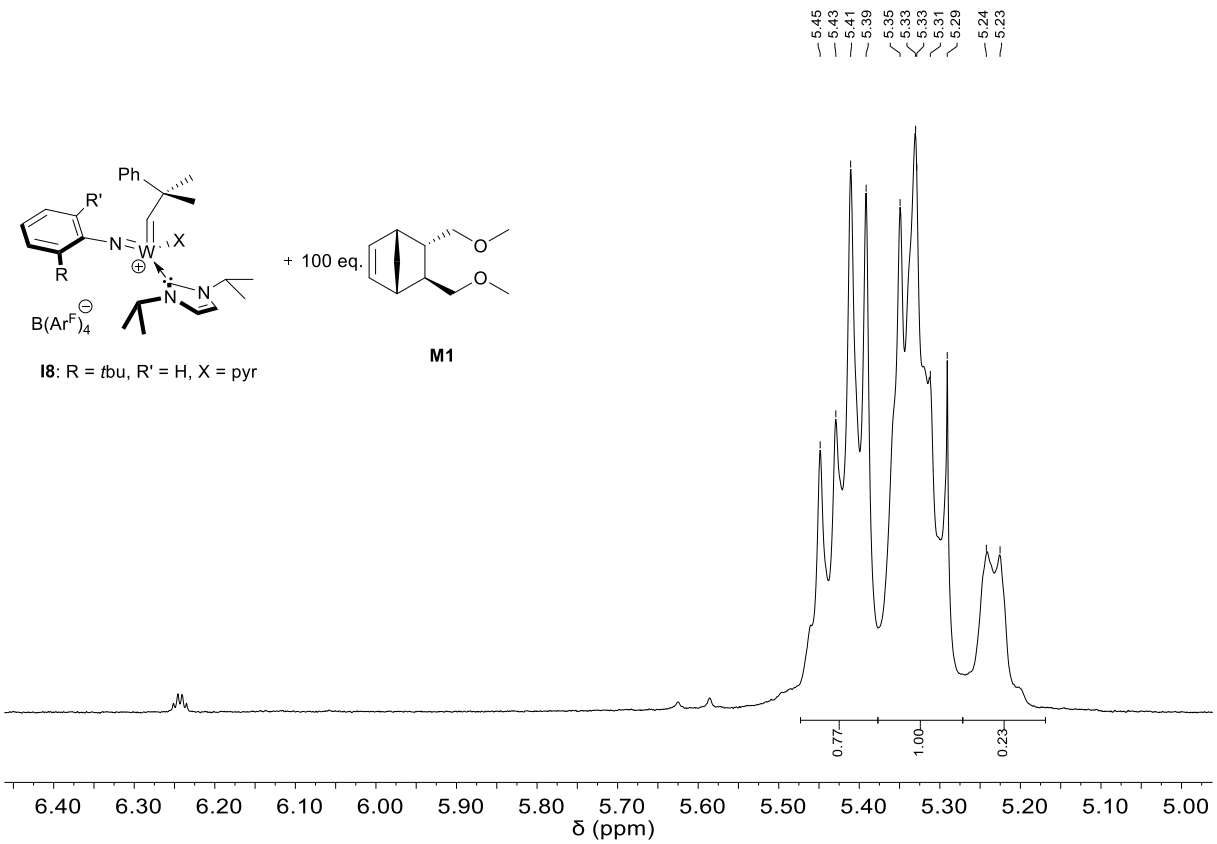


Figure S54. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I8** in $CDCl_3$.

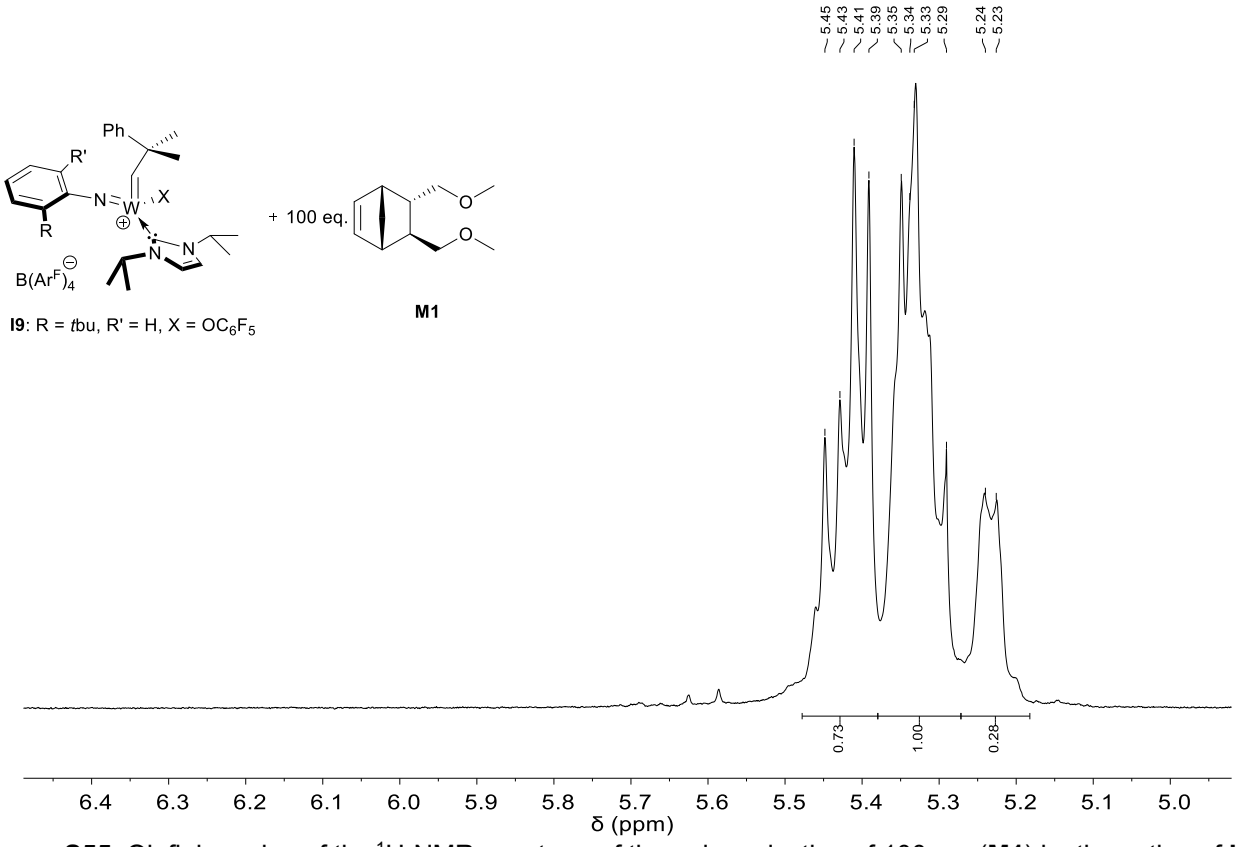


Figure S55. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I9** in $CDCl_3$.

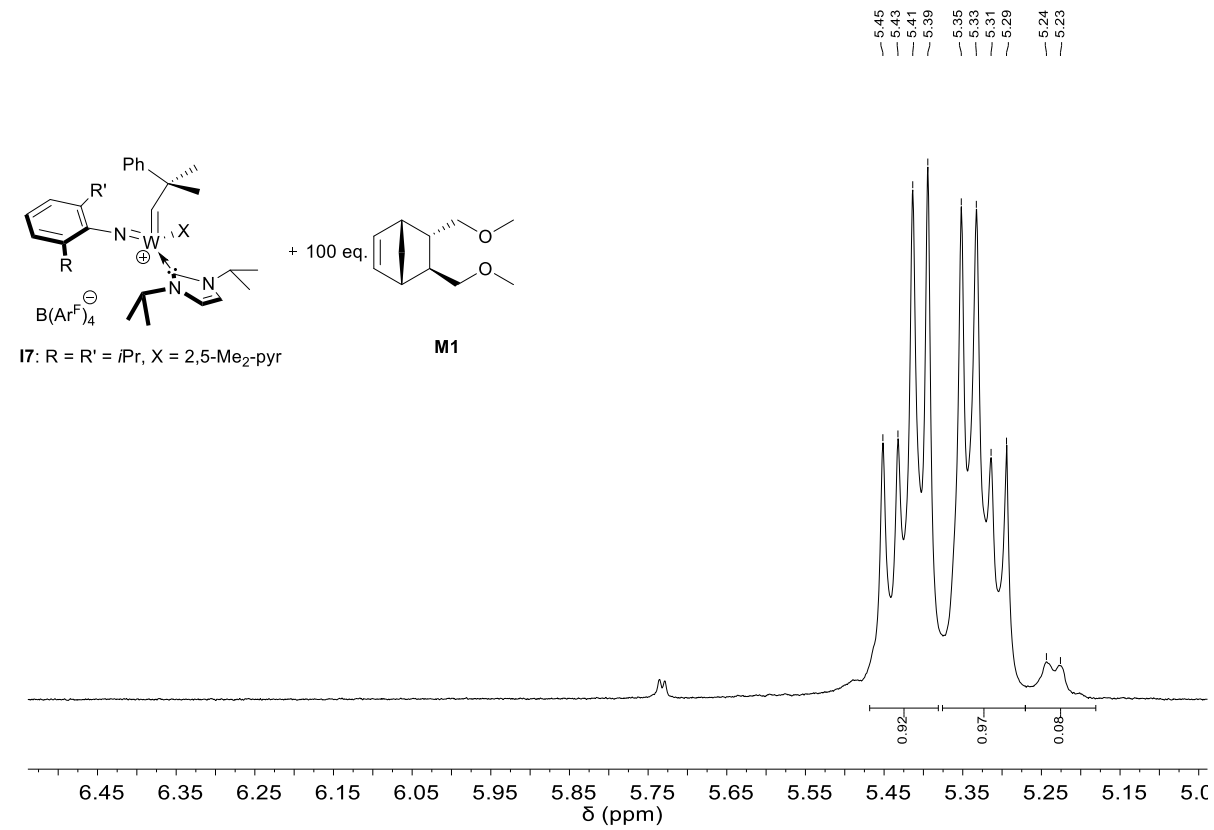


Figure S56. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I7** in $CDCl_3$.

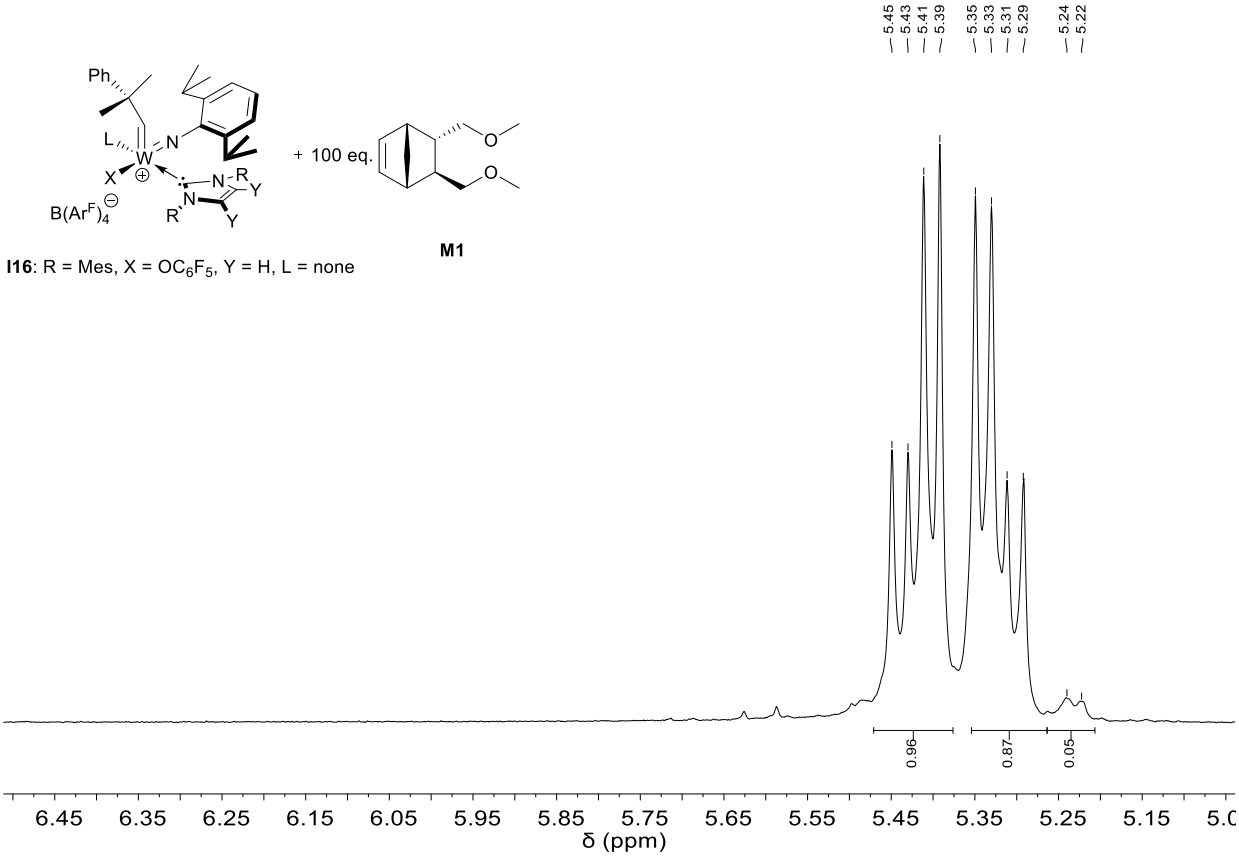


Figure S57. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I16** in $CDCl_3$.

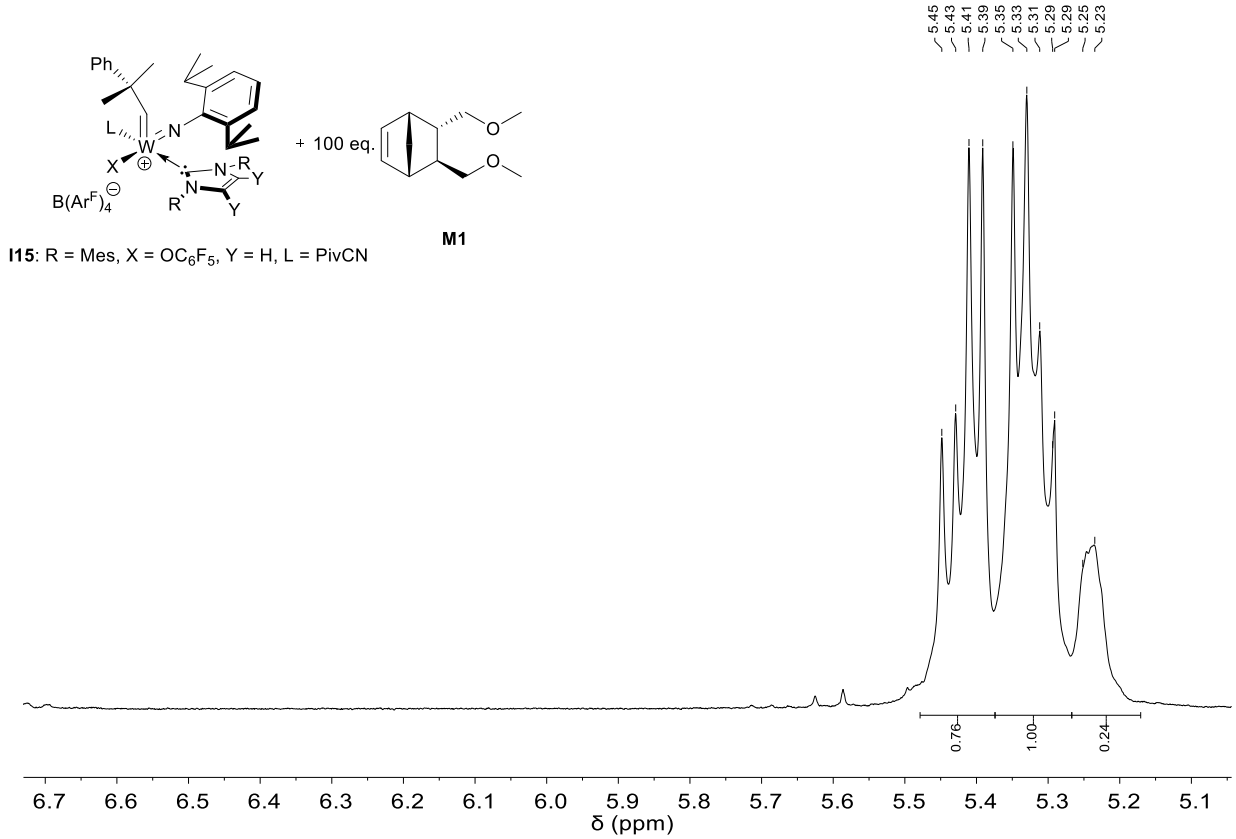


Figure S58. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I15** in $CDCl_3$.

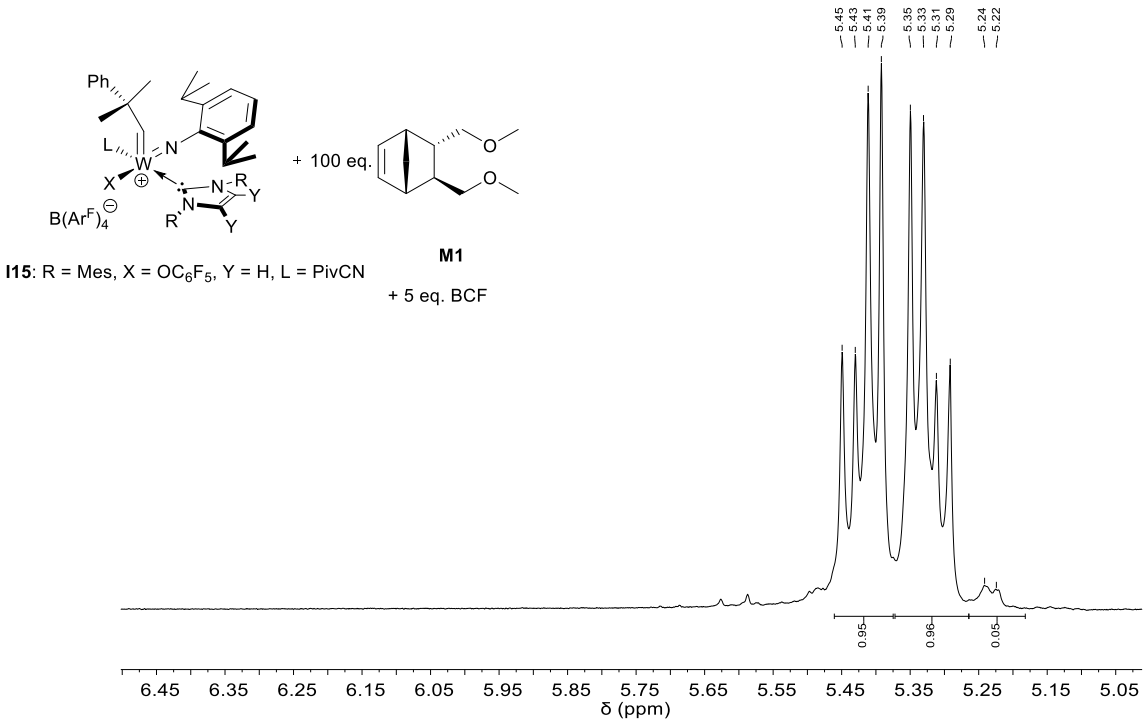


Figure S59. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I15** with 5 eq. BCF in $CDCl_3$.

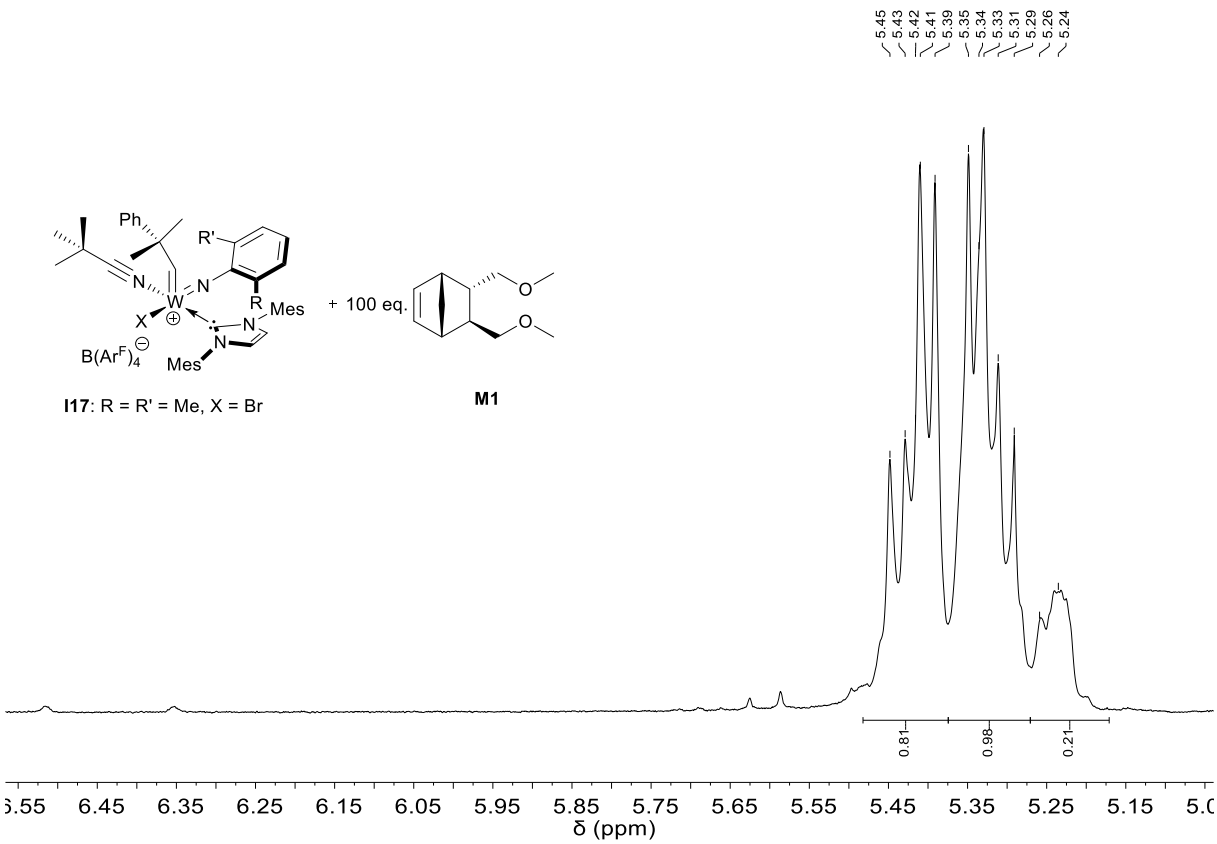


Figure S60. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I17** in $CDCl_3$.

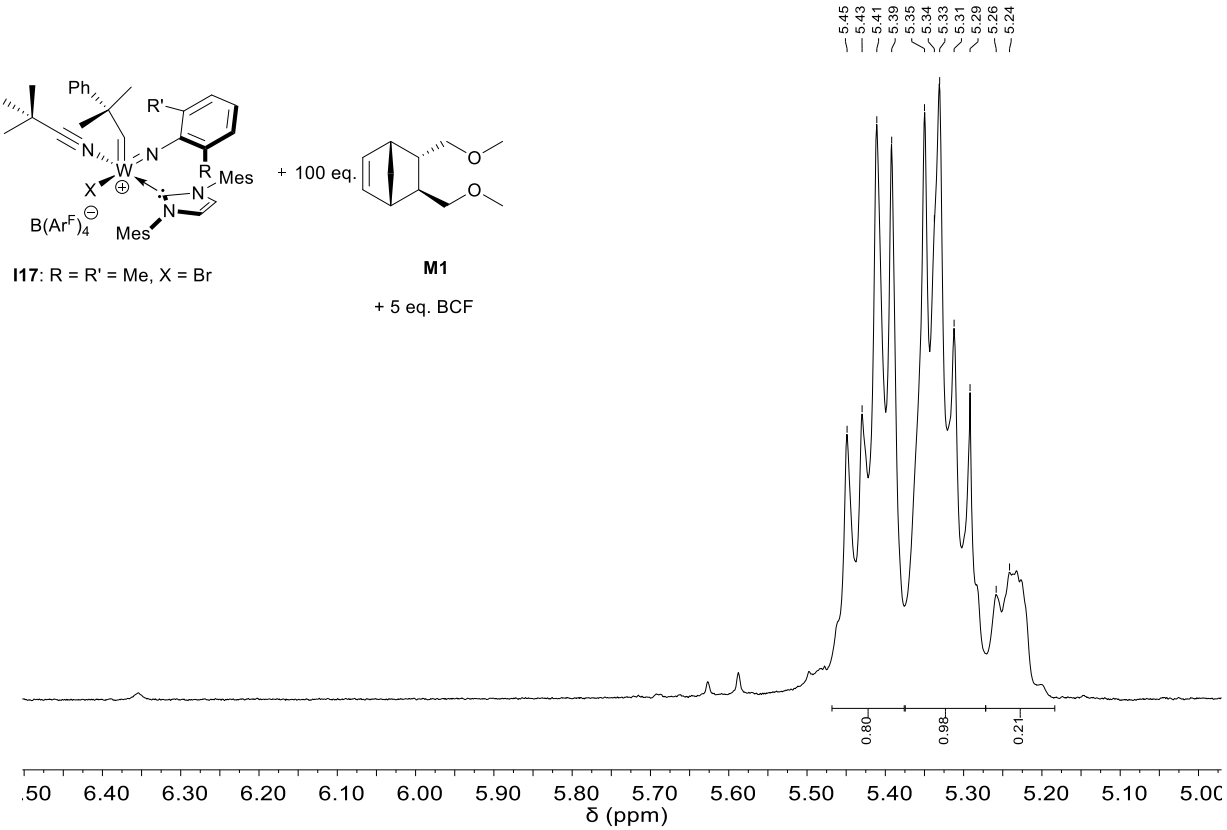


Figure S61. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I17** with 5 eq. BCF in $CDCl_3$.

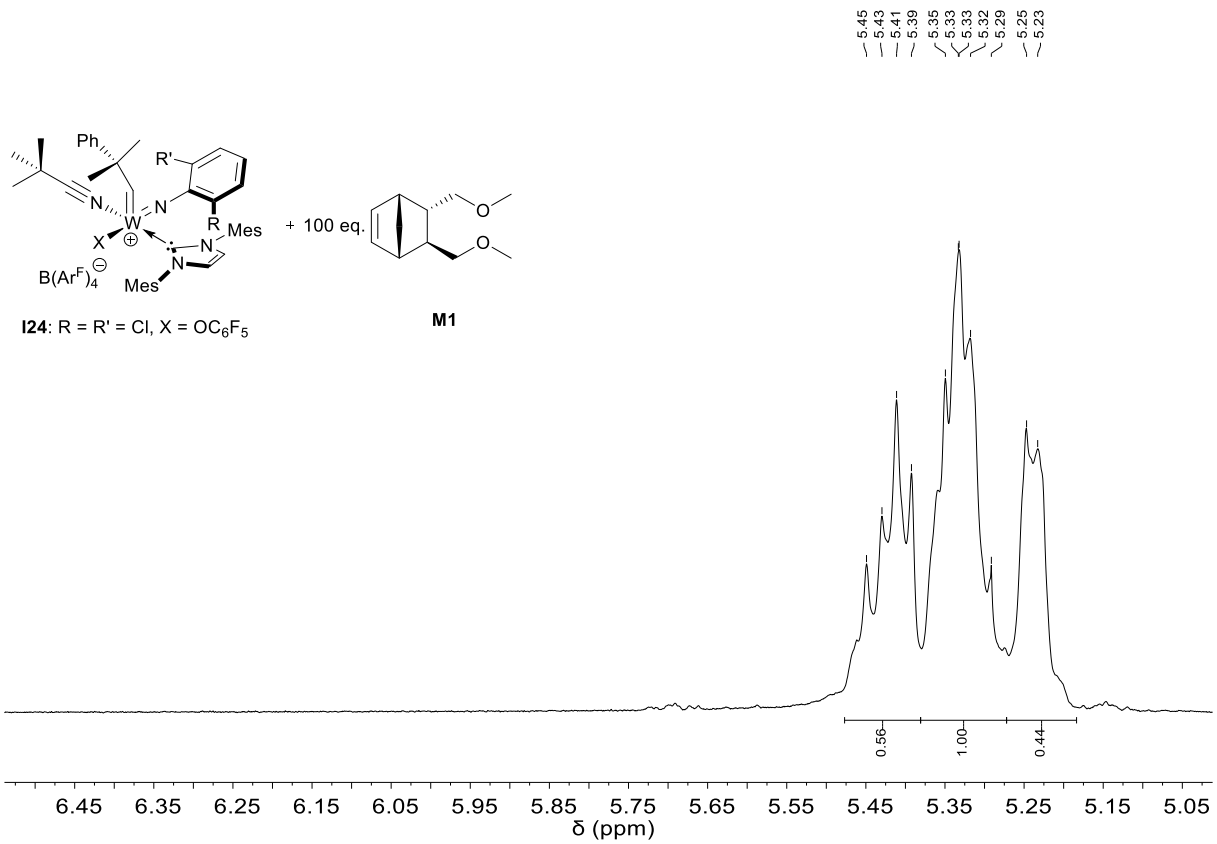


Figure S62. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I24** in $CDCl_3$.

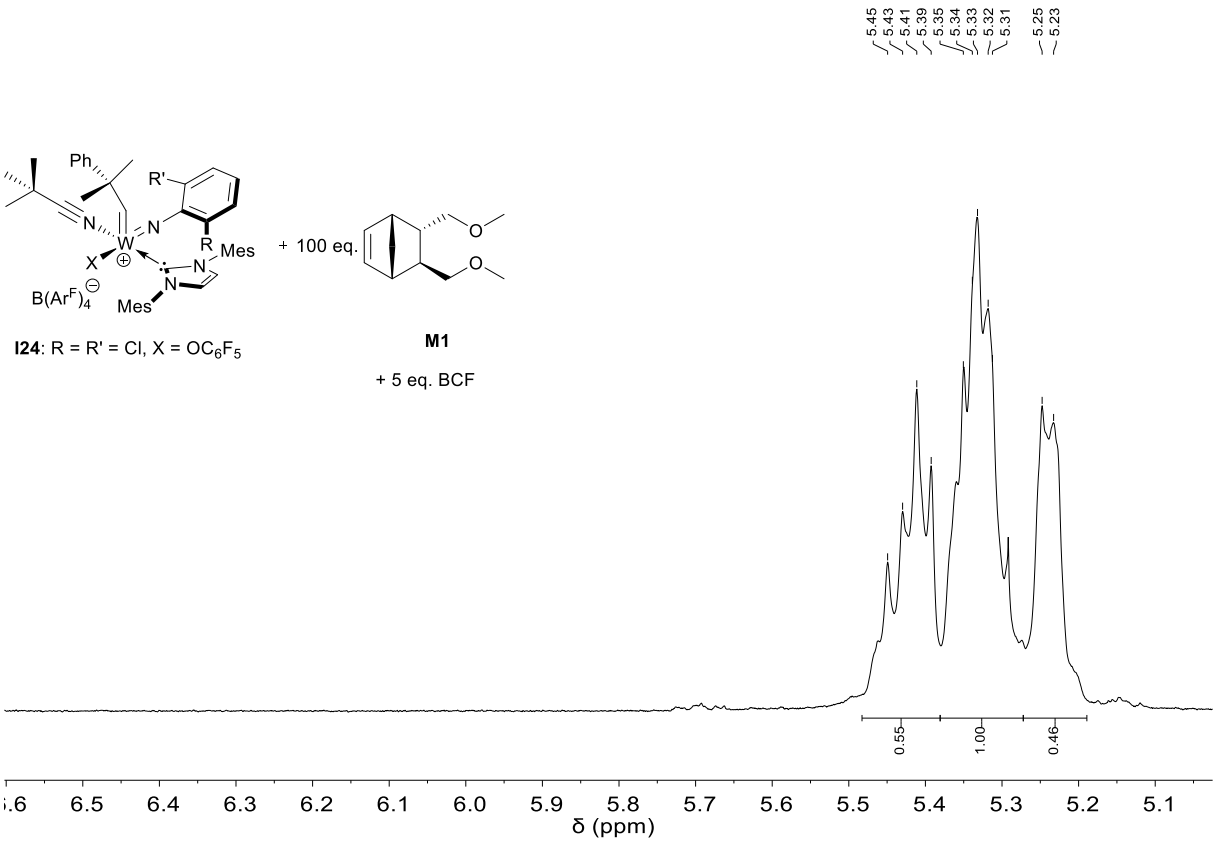


Figure S63. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I24** with 5 eq. BCF in $CDCl_3$.

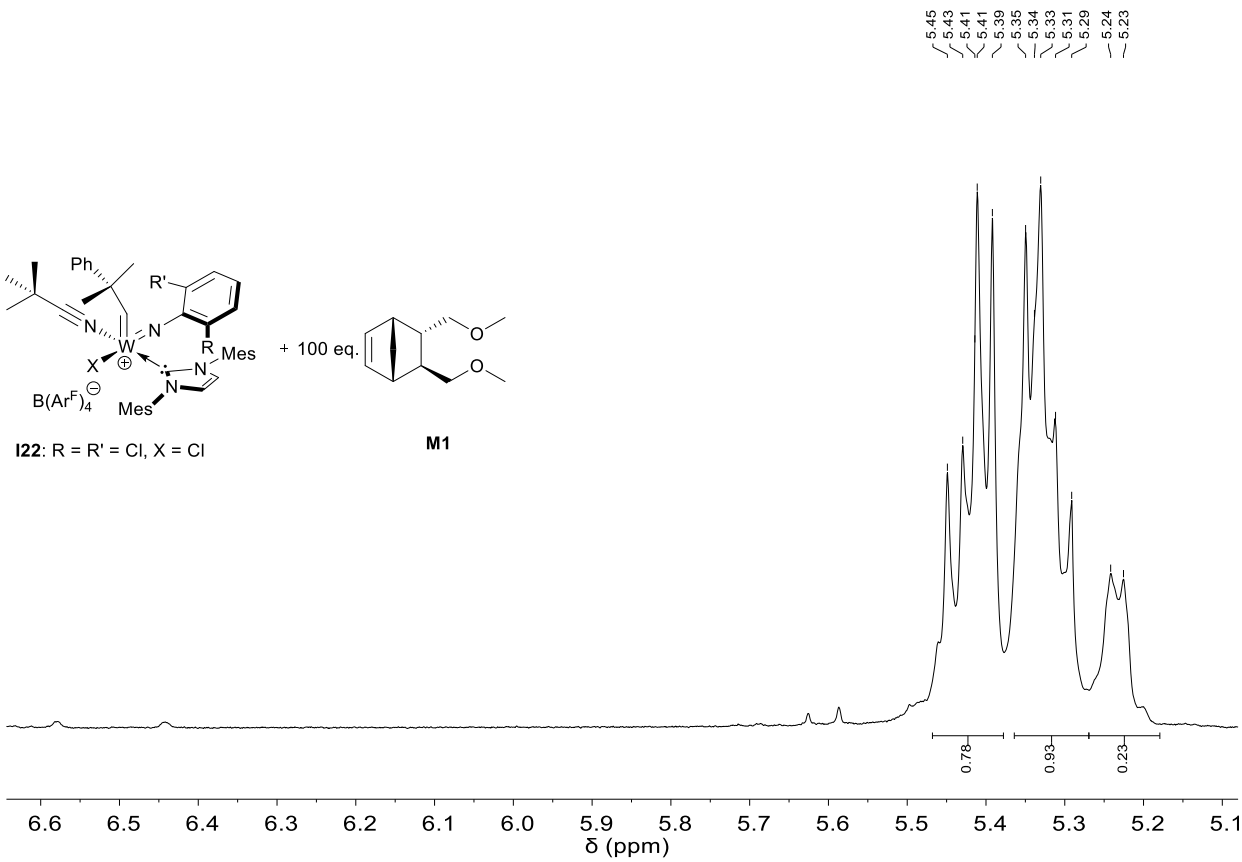


Figure S64. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I22** in $CDCl_3$.

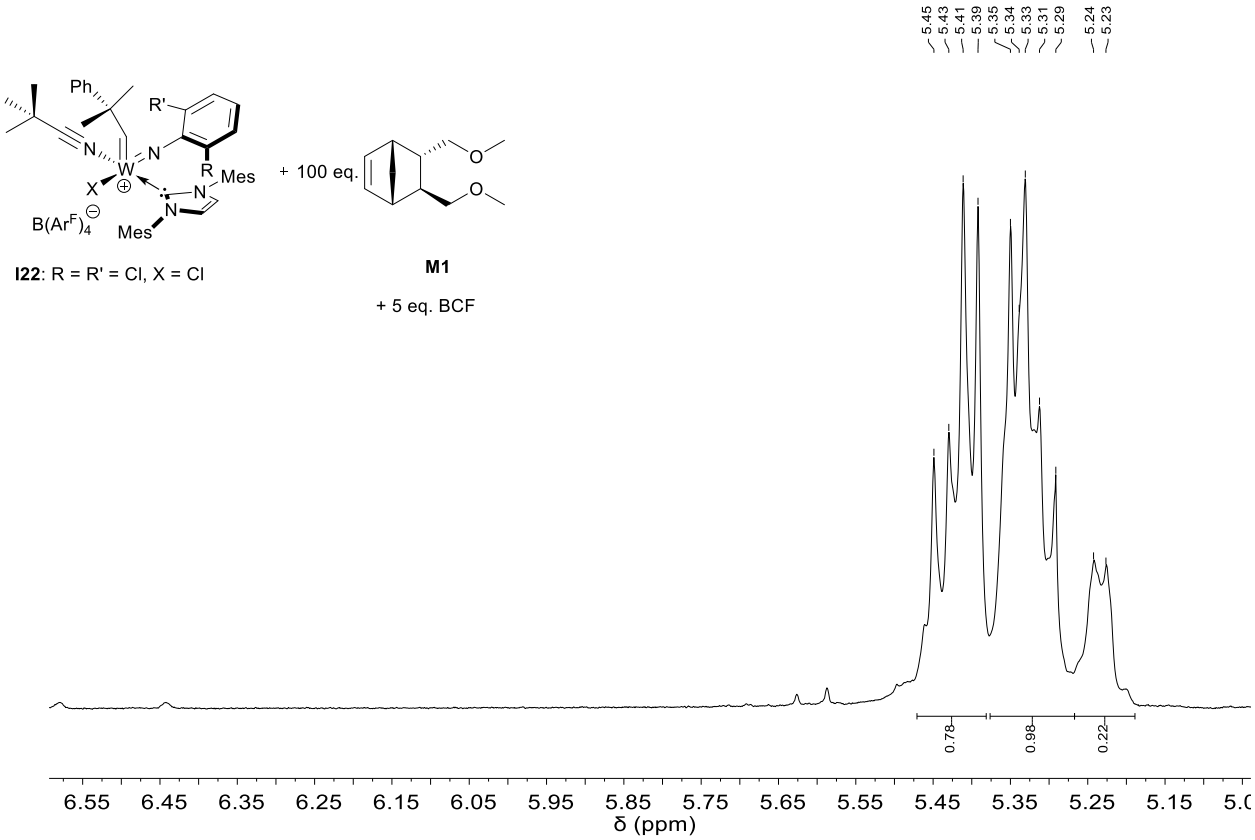


Figure S65. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I22** with 5 eq. BCF in $CDCl_3$.

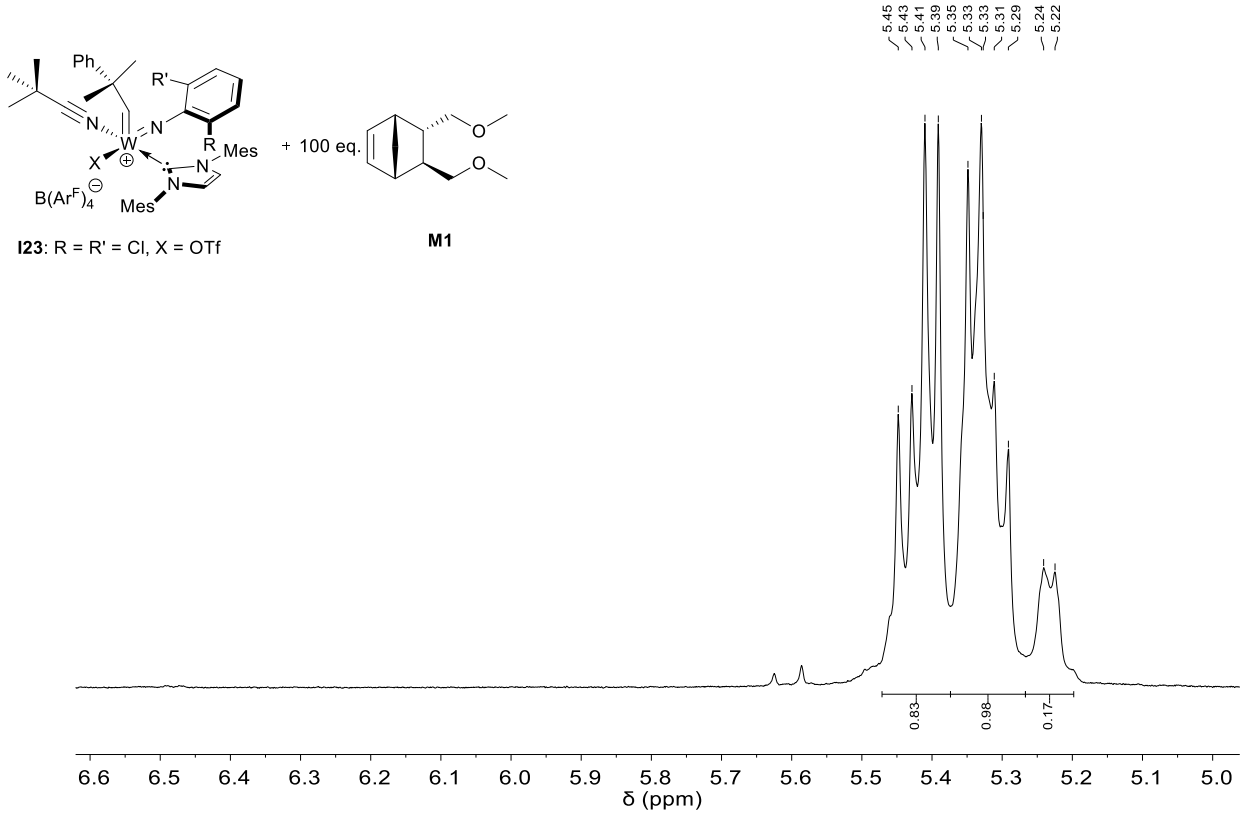


Figure S66. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I23** in $CDCl_3$.

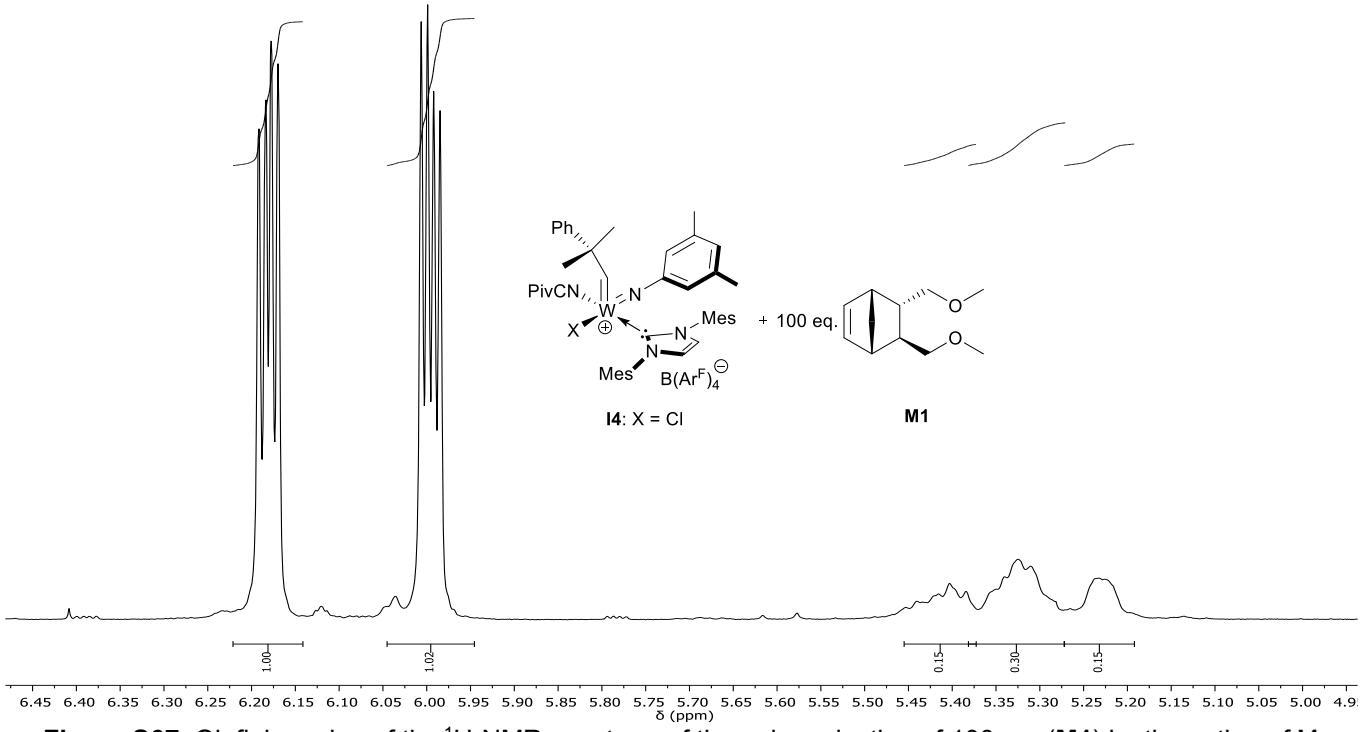


Figure S67. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I4** in $CDCl_3$

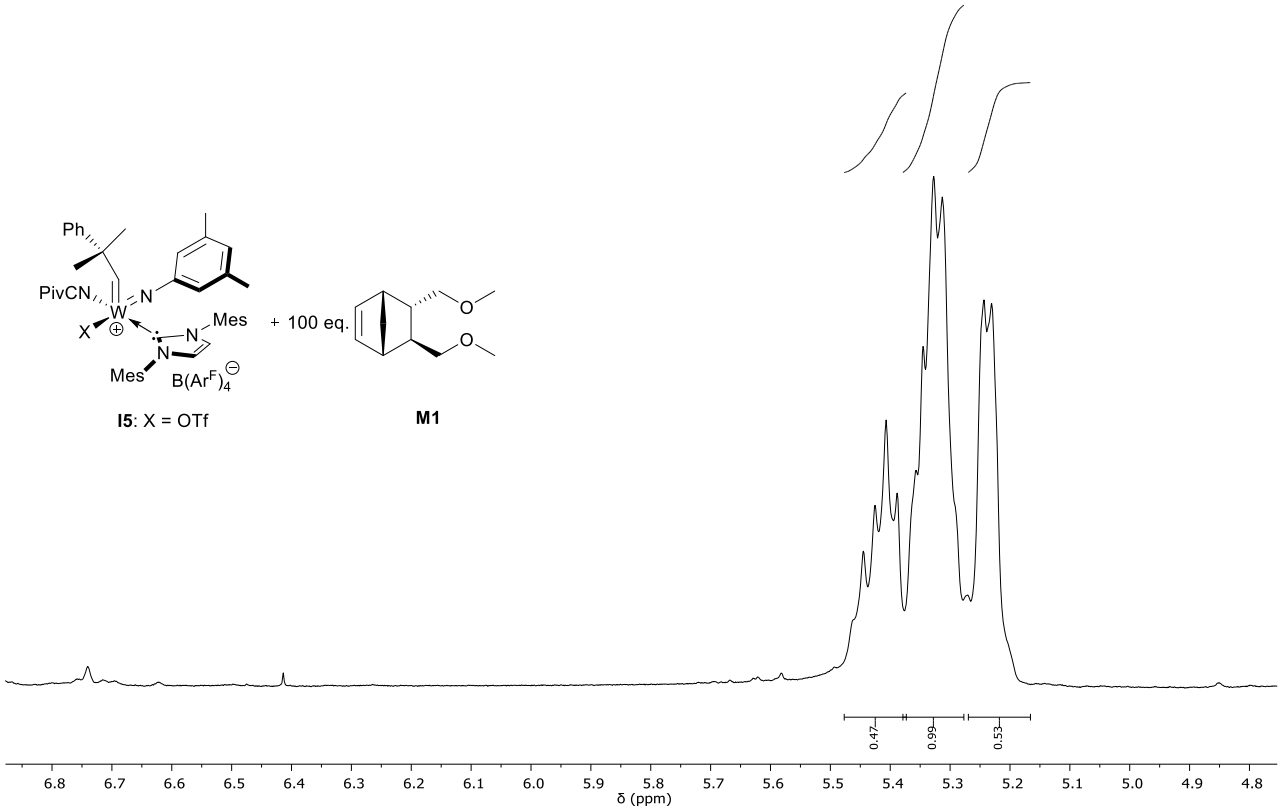


Figure S68. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I5** in $CDCl_3$.

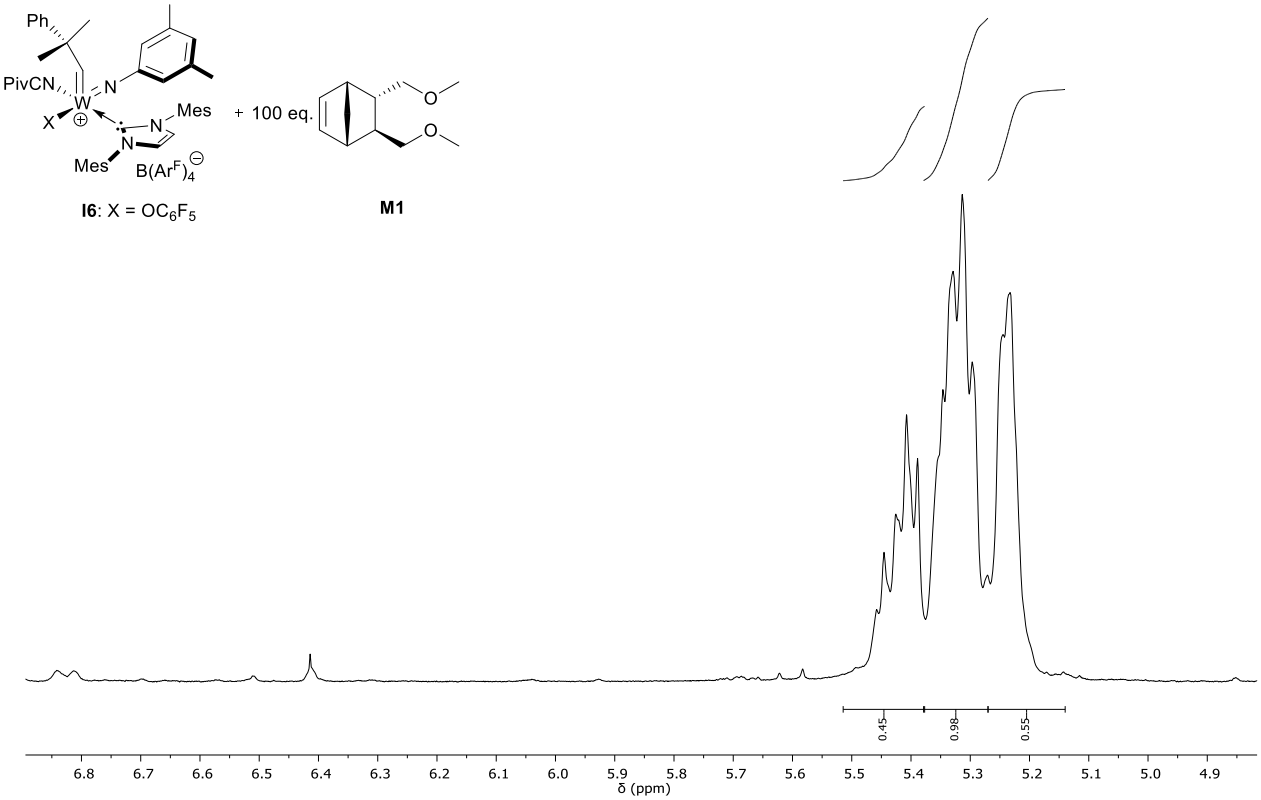


Figure S69. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I6** in $CDCl_3$.

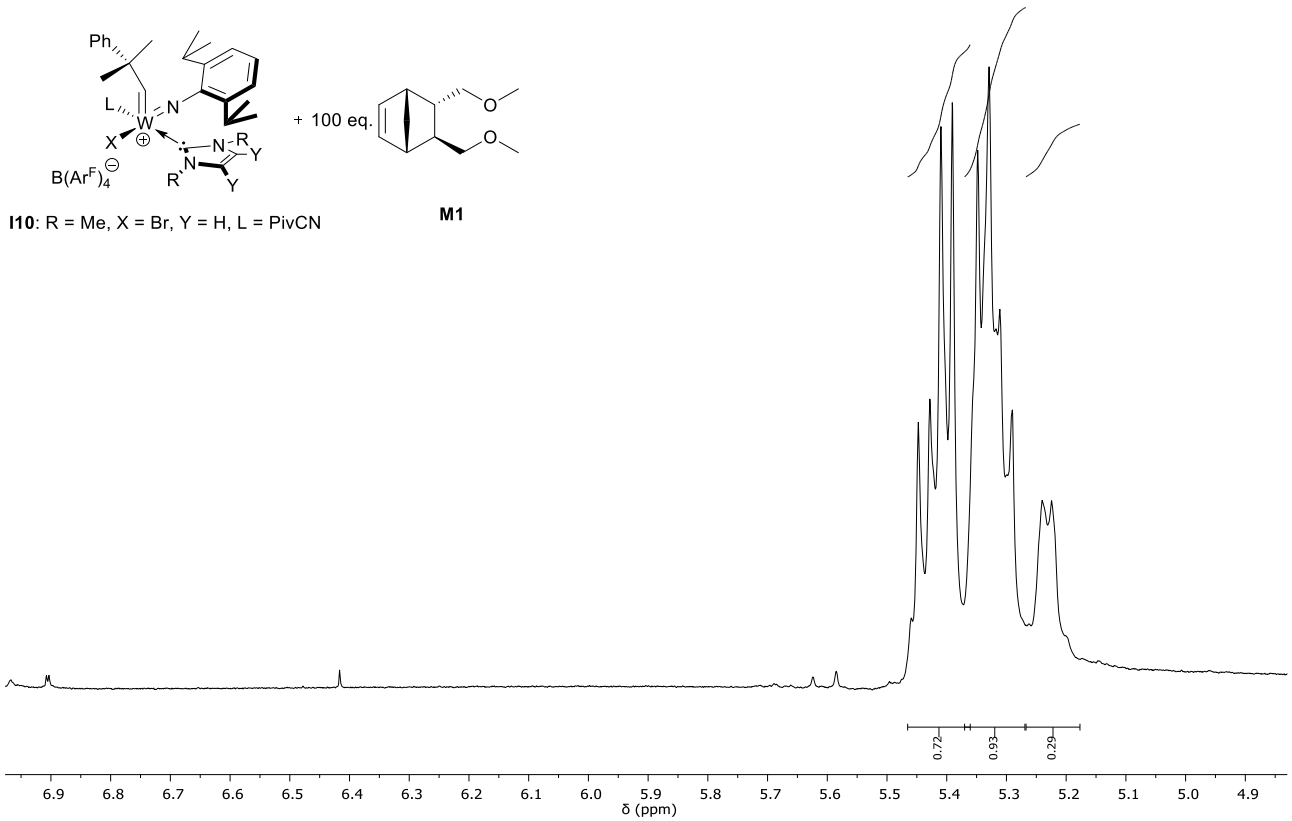


Figure S70. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I10** in $CDCl_3$.

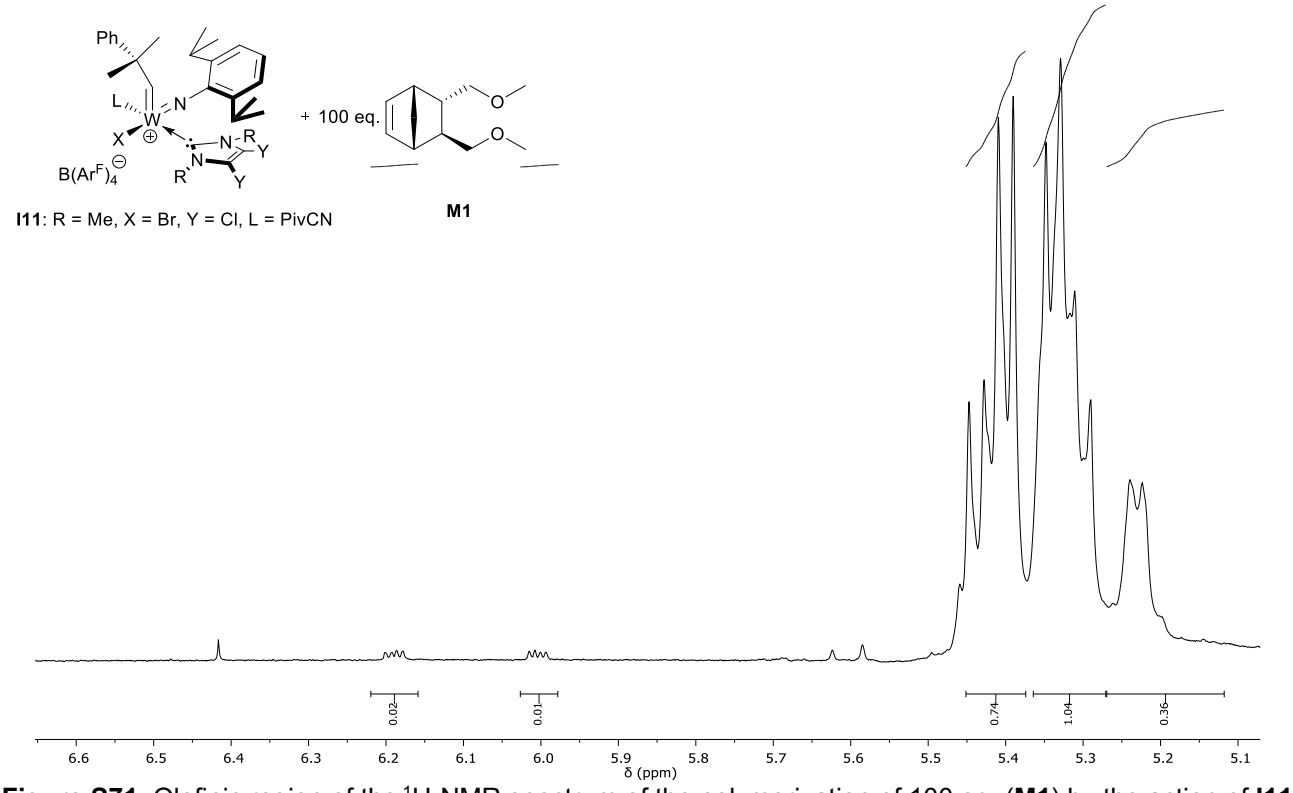


Figure S71. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I11** in $CDCl_3$.

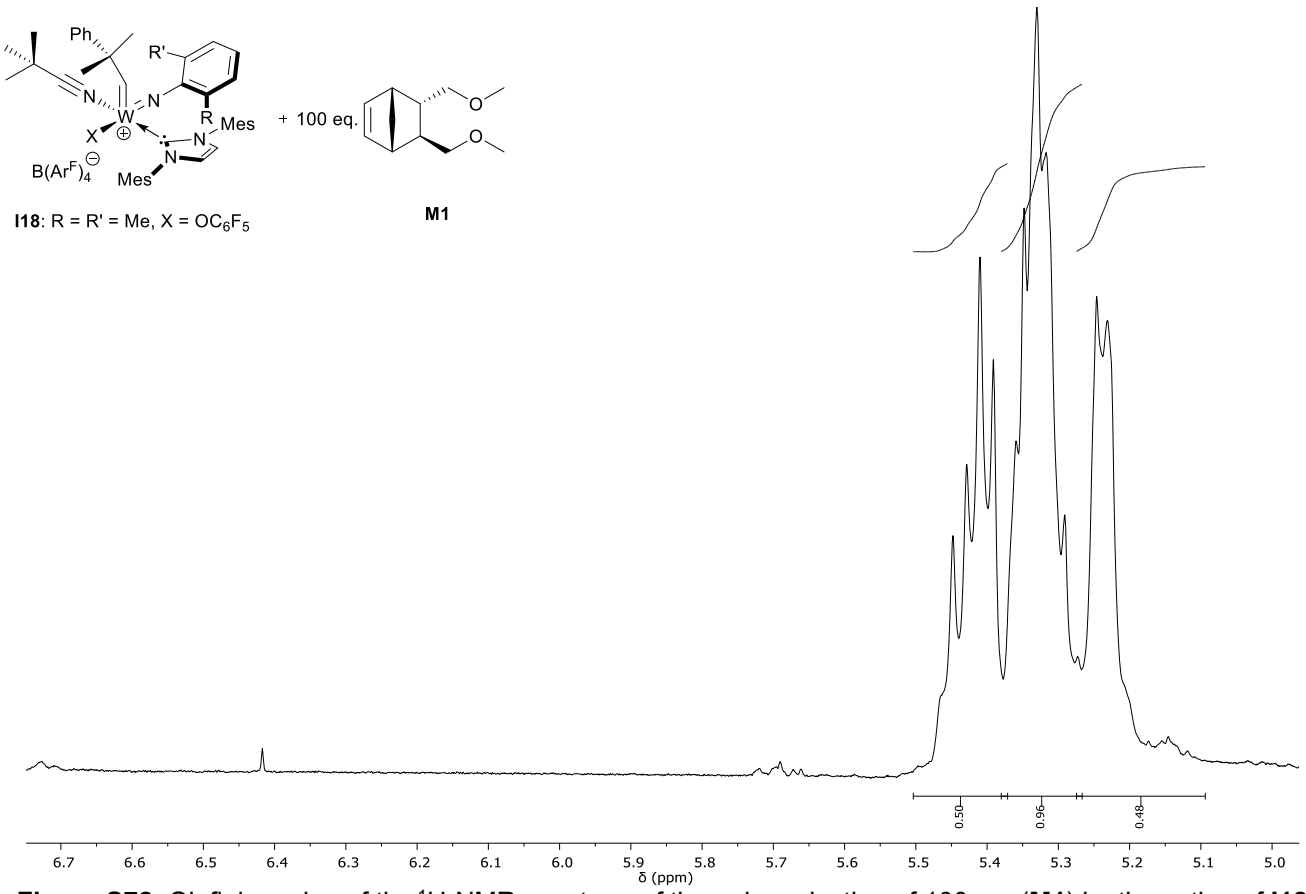


Figure S72. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I18** in $CDCl_3$.

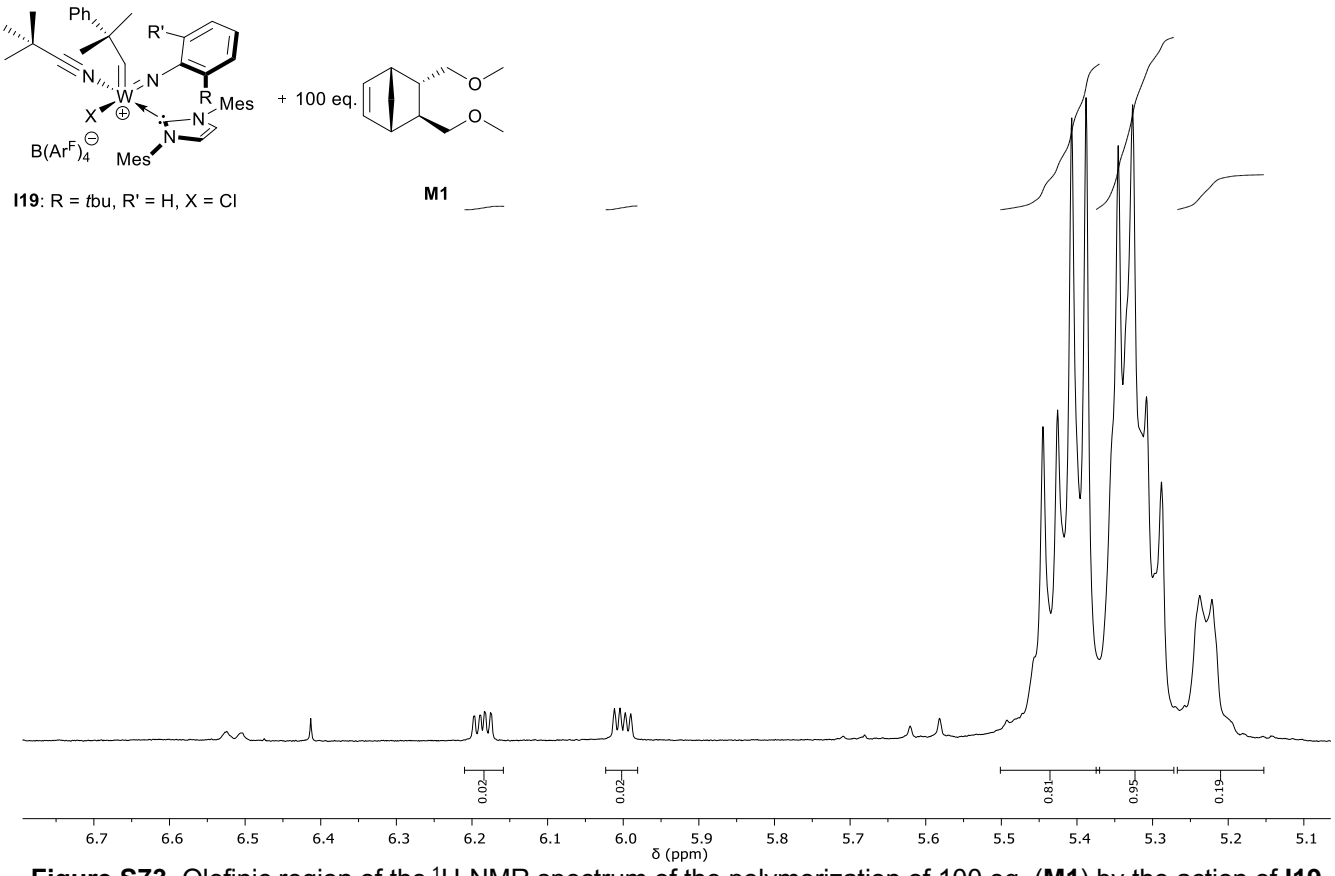


Figure S73. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I19** in $CDCl_3$.

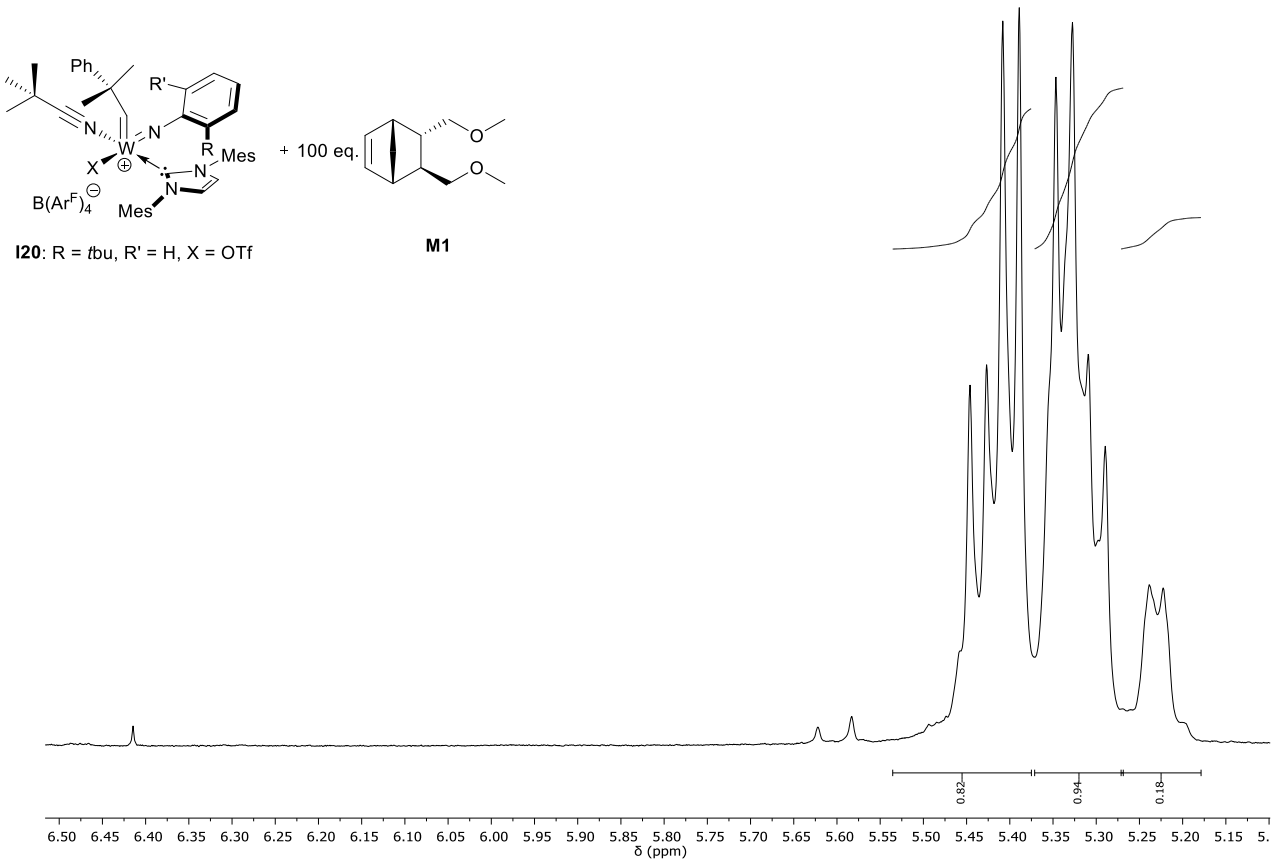


Figure S74. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I20** in $CDCl_3$.

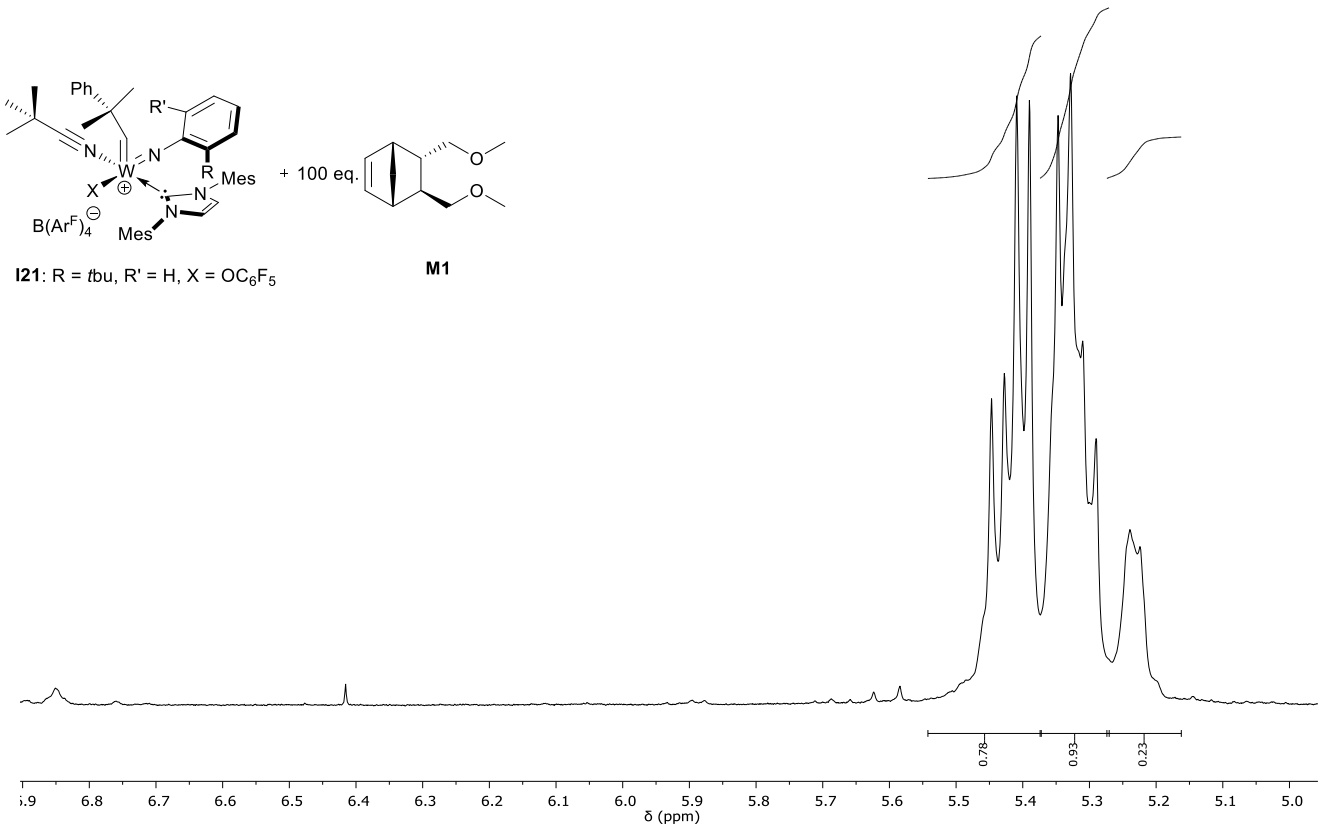


Figure S75. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I21** in $CDCl_3$.

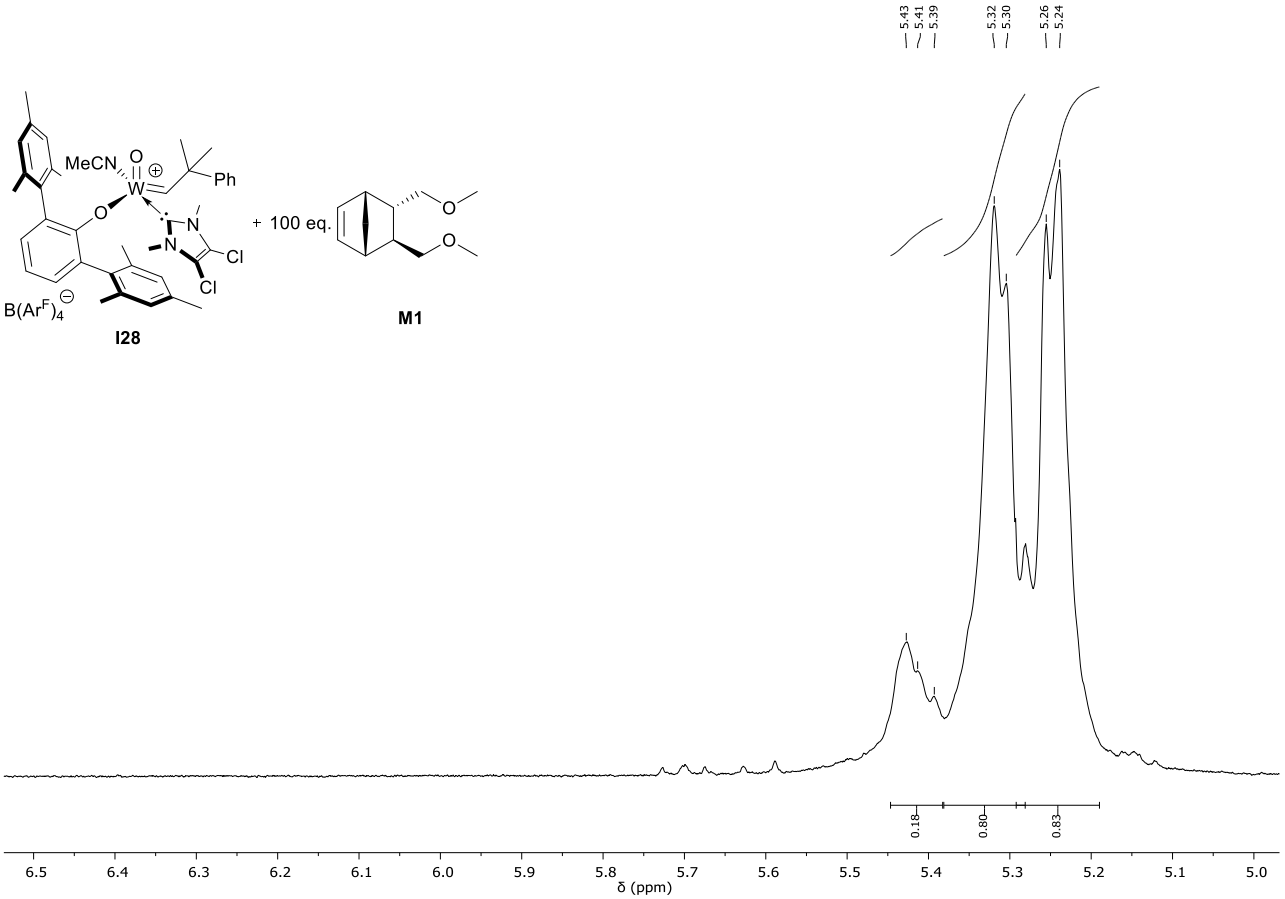


Figure S76. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I28** in $CDCl_3$.

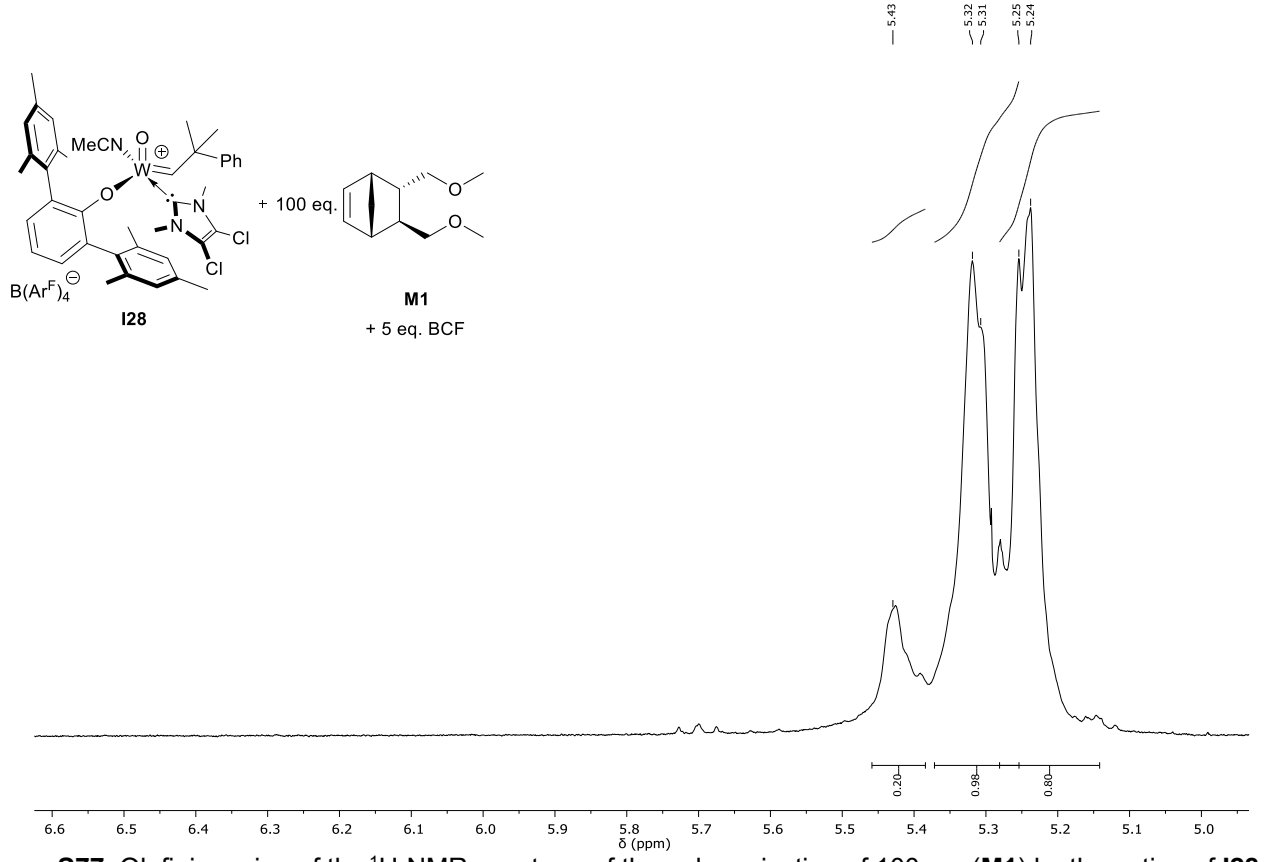


Figure S77. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I28** with 5 eq. BCF in $CDCl_3$.

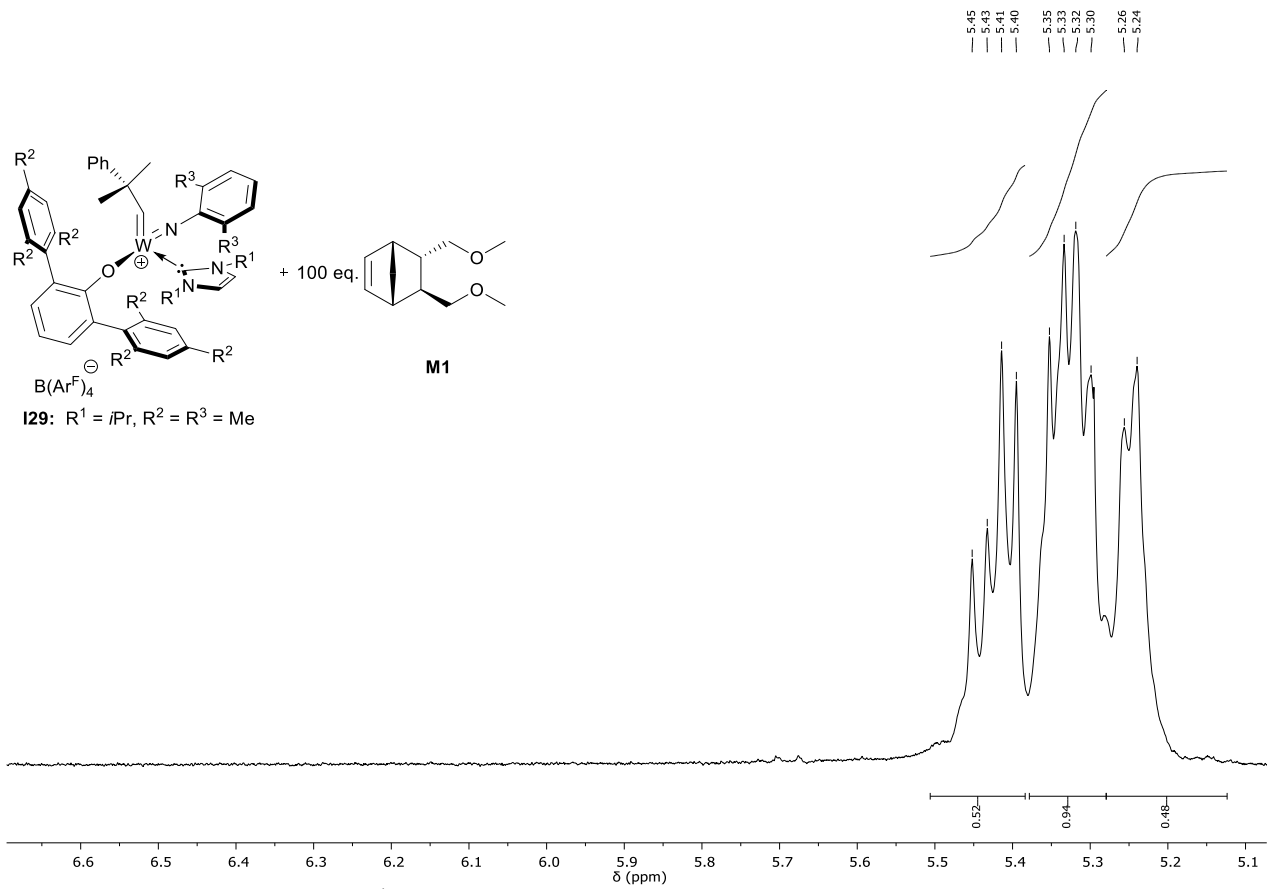


Figure S78. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I29** in $CDCl_3$.

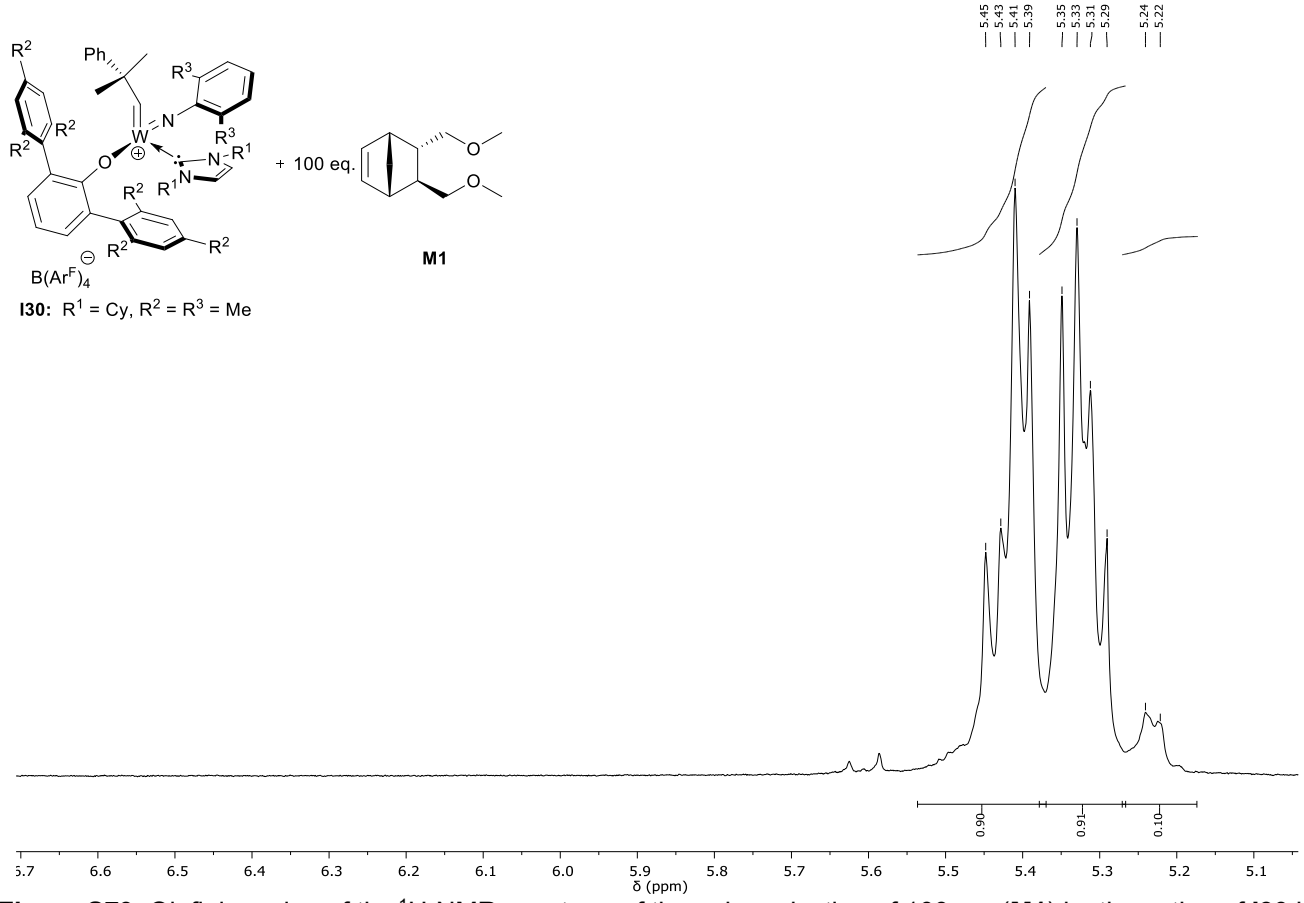


Figure S79. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I30** in $CDCl_3$.

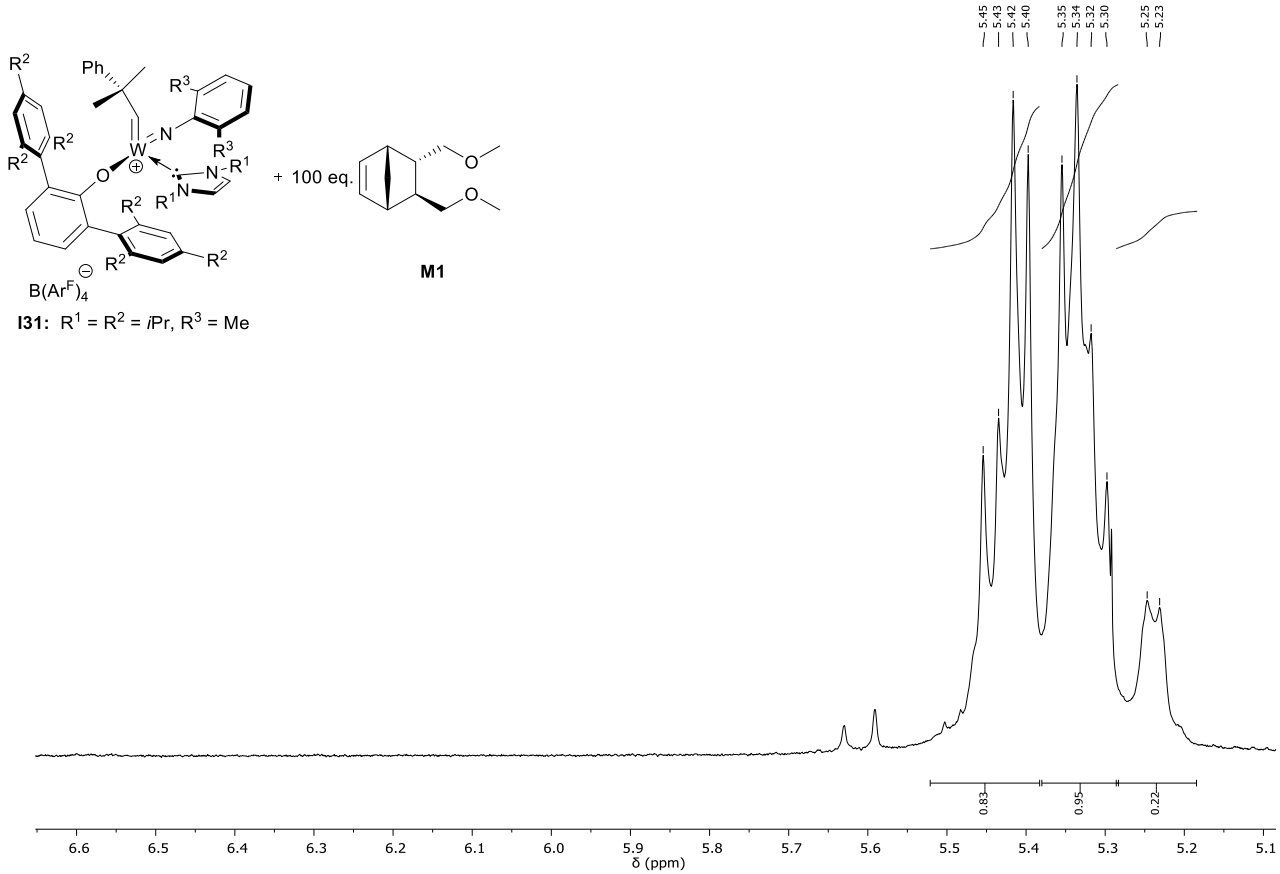


Figure S80. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I31** in $CDCl_3$.

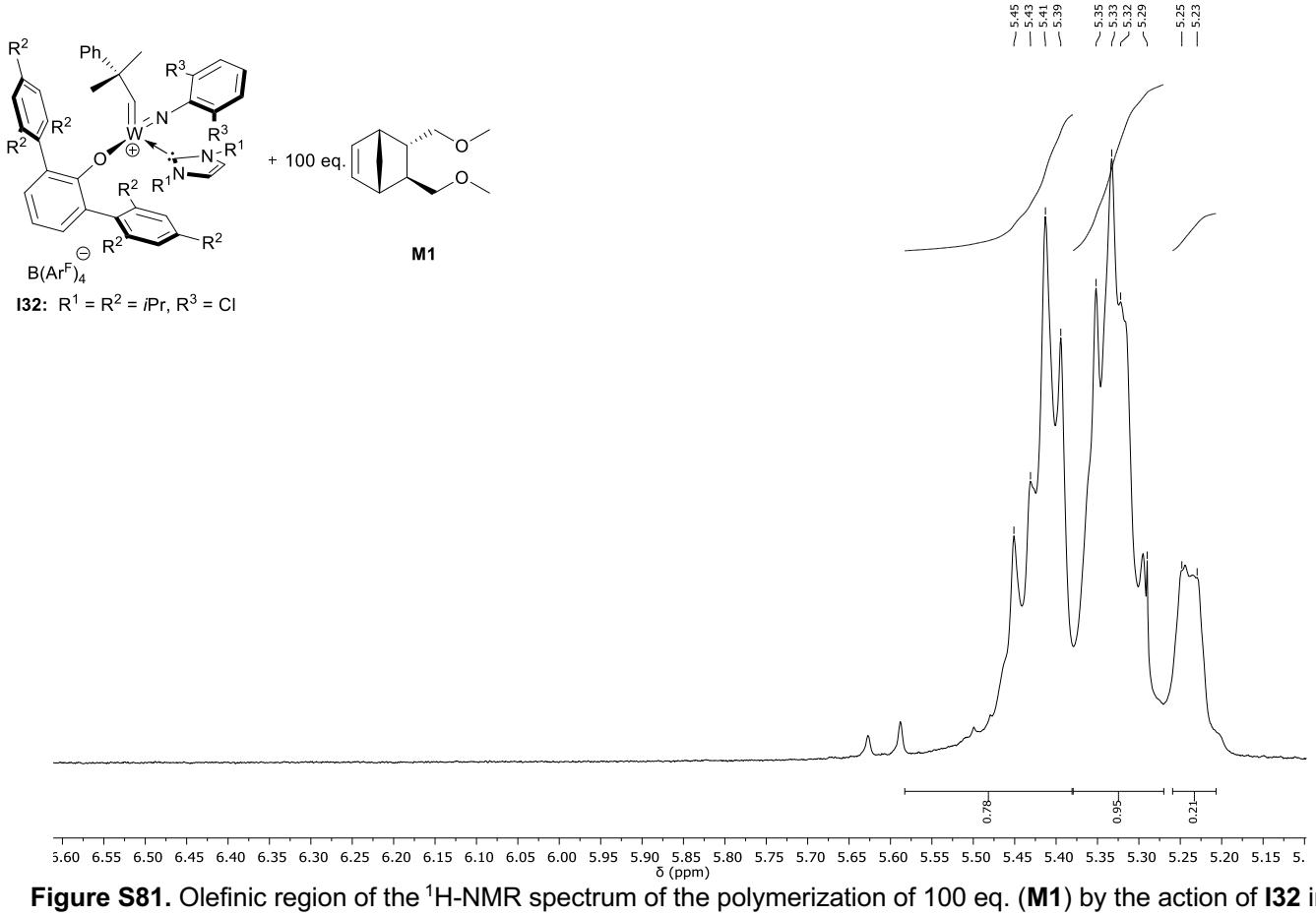


Figure S81. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M1**) by the action of **I32** in $CDCl_3$.

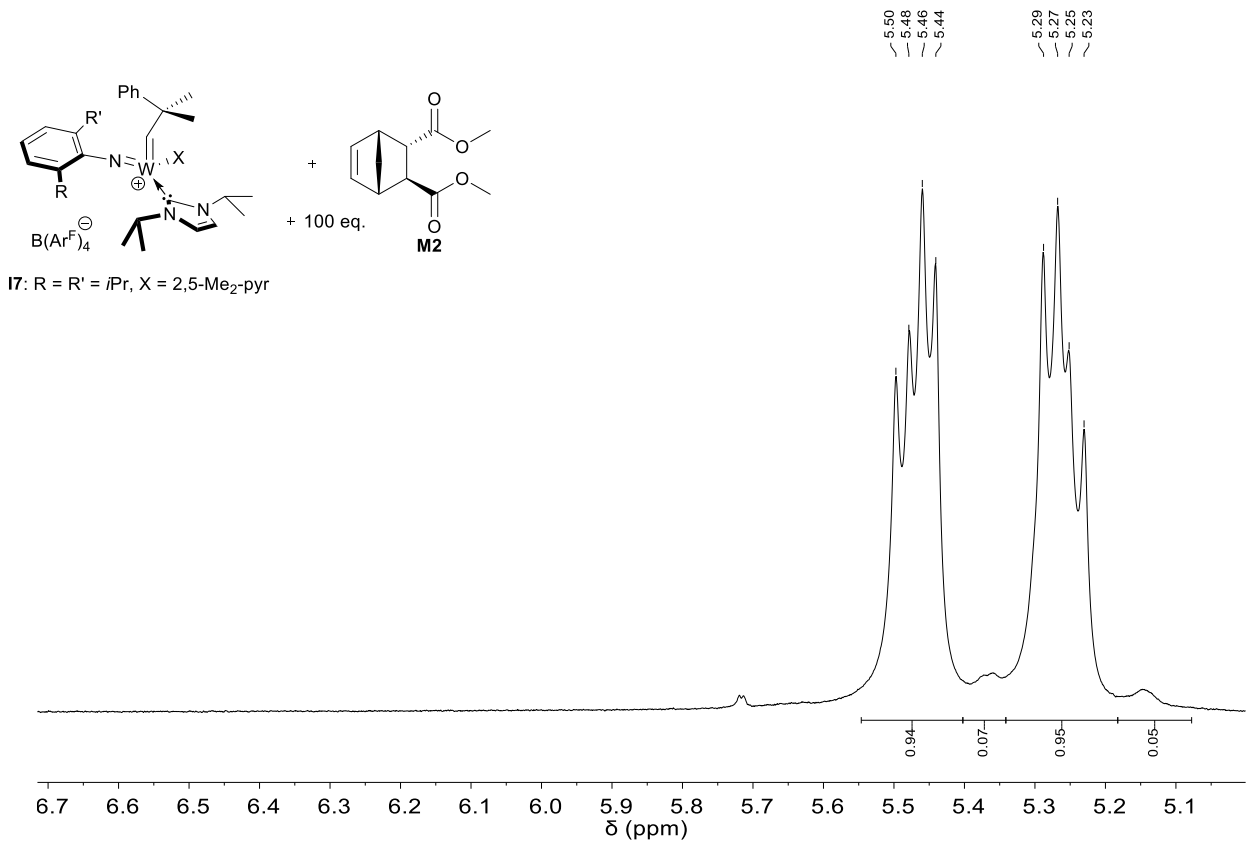


Figure S82. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M2**) by the action of **I7** in $CDCl_3$.

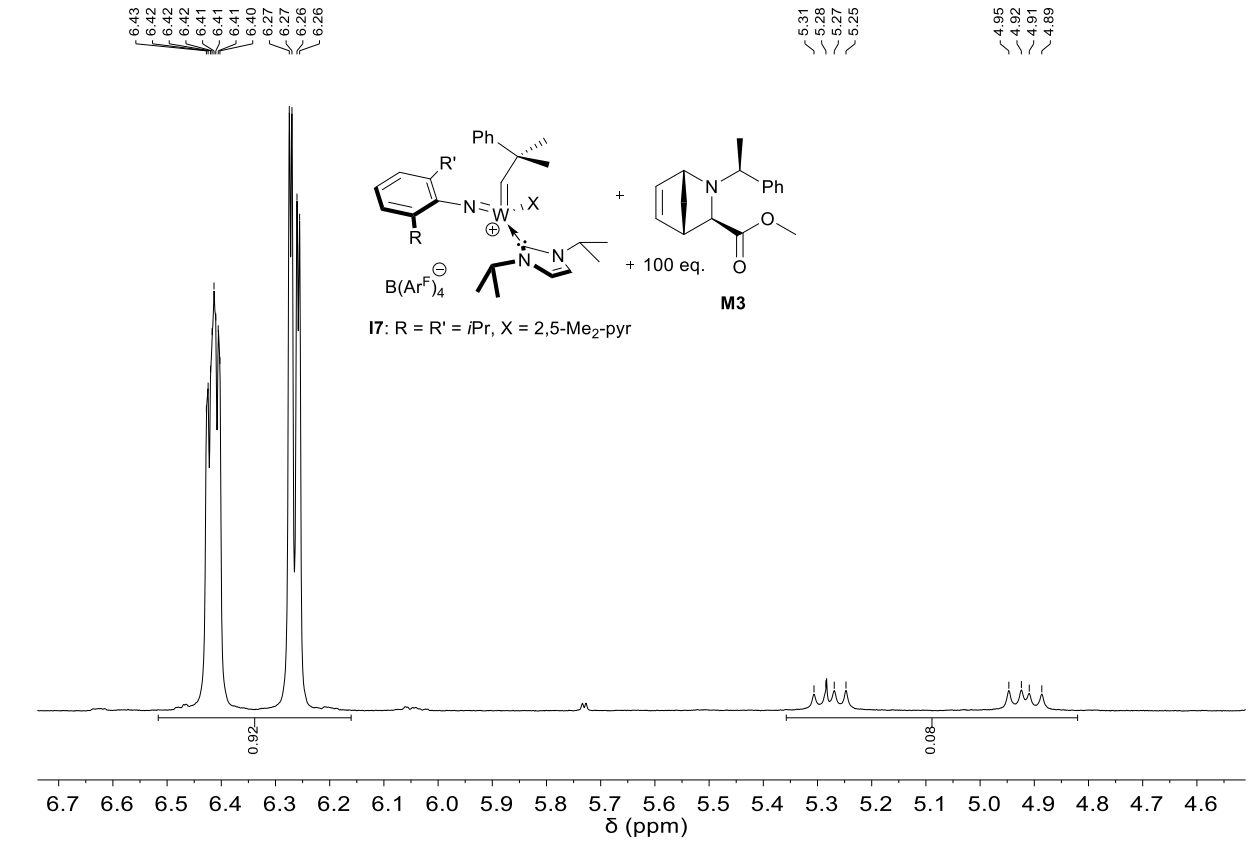


Figure S83. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M3**) by the action of **I7** in $CDCl_3$.

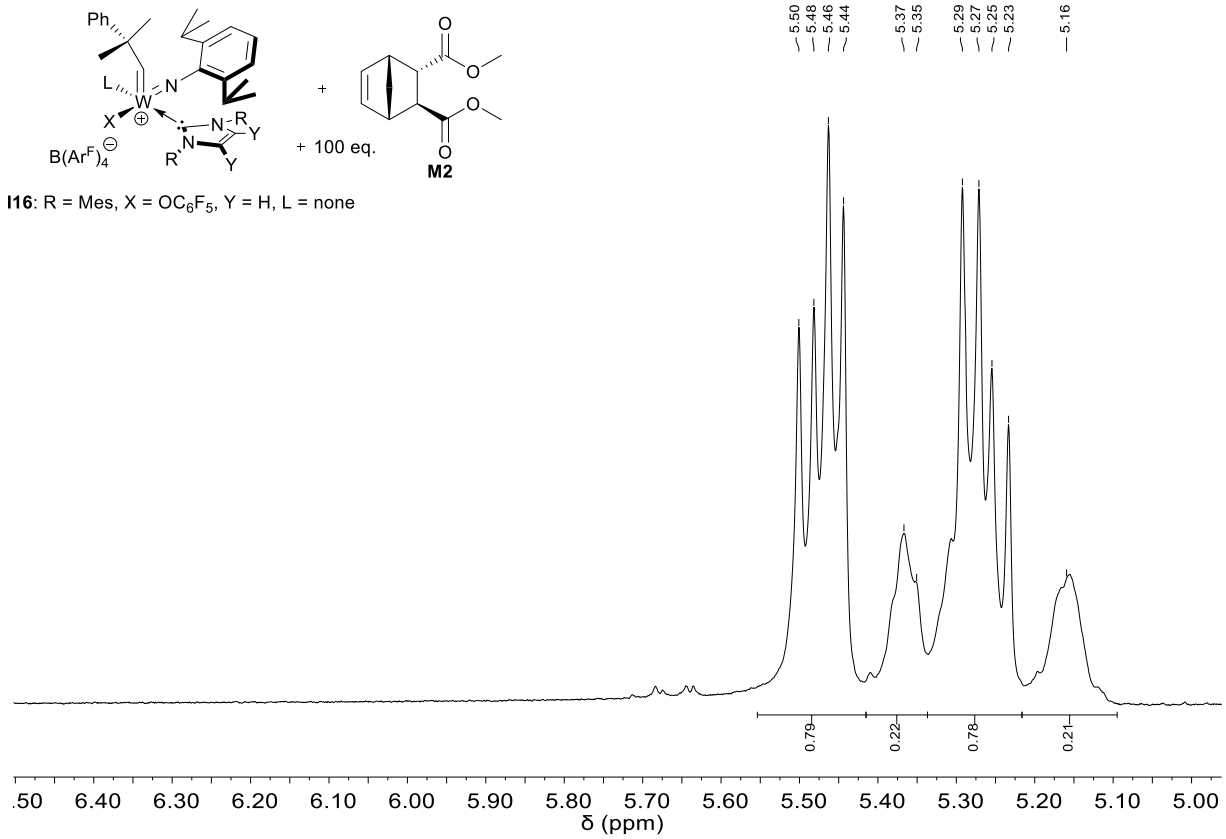


Figure S84. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M2**) by the action of **I16** in $CDCl_3$.

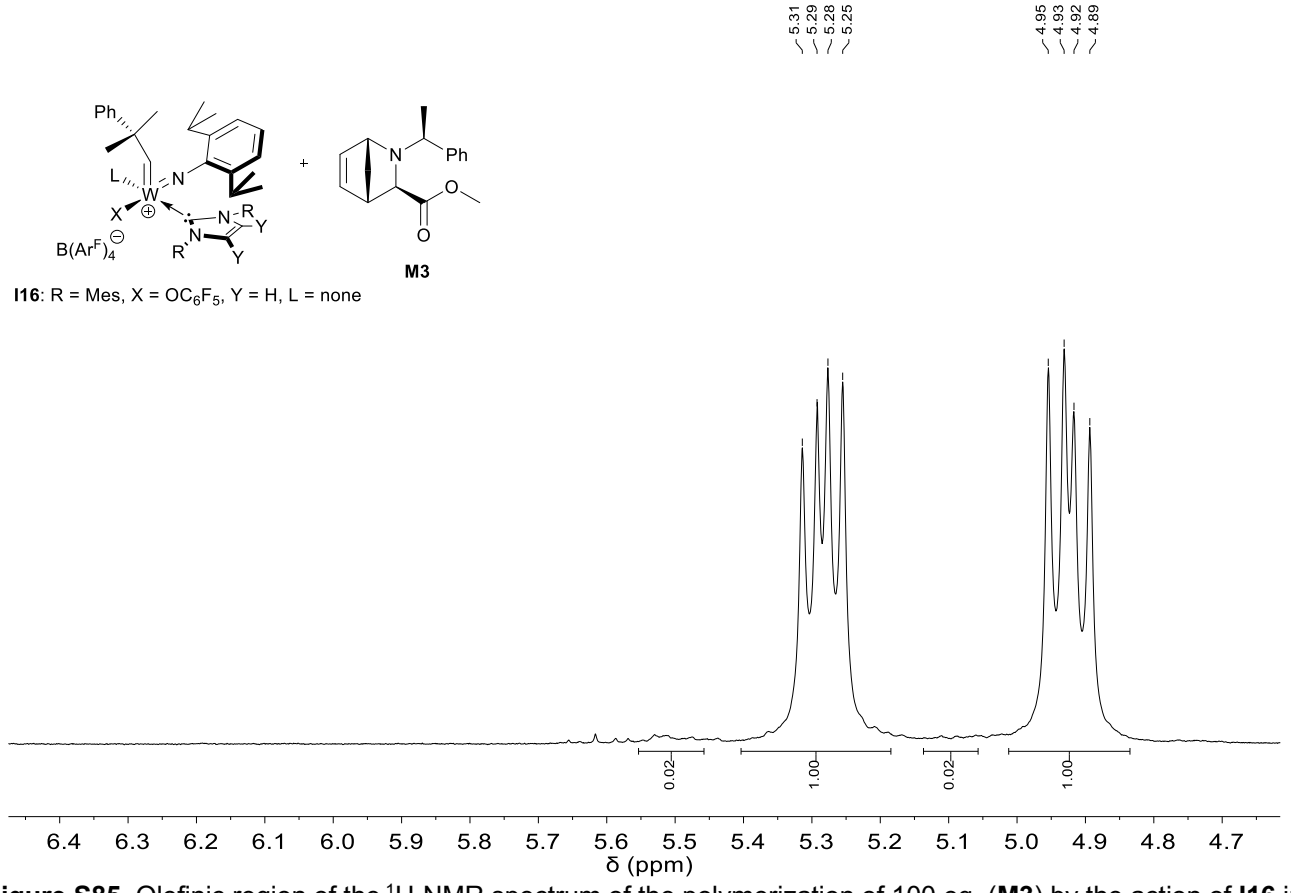


Figure S85. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M3**) by the action of **I16** in $CDCl_3$.

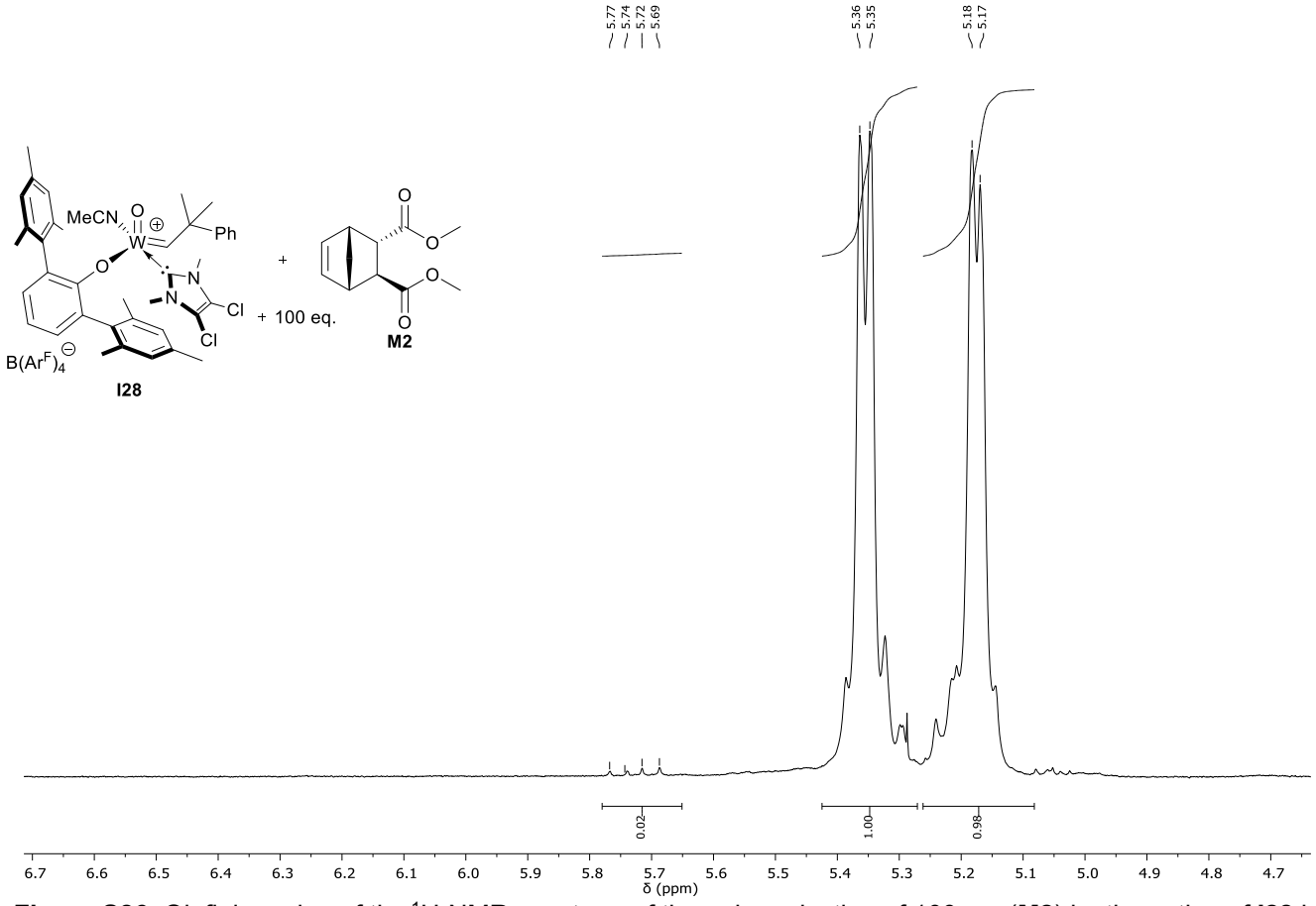


Figure S86. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M2**) by the action of **I28** in $CDCl_3$.

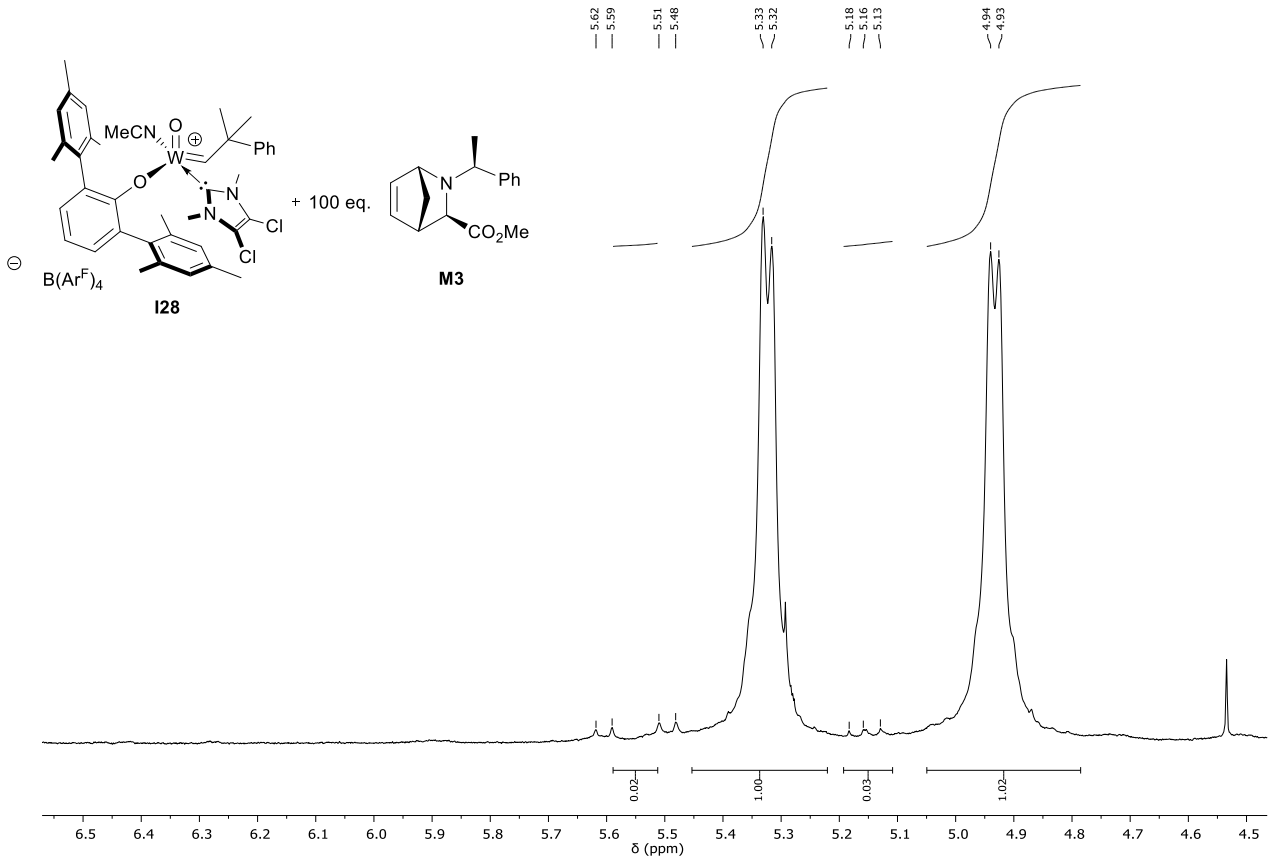


Figure S87. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M3**) by the action of **I28** in $CDCl_3$.

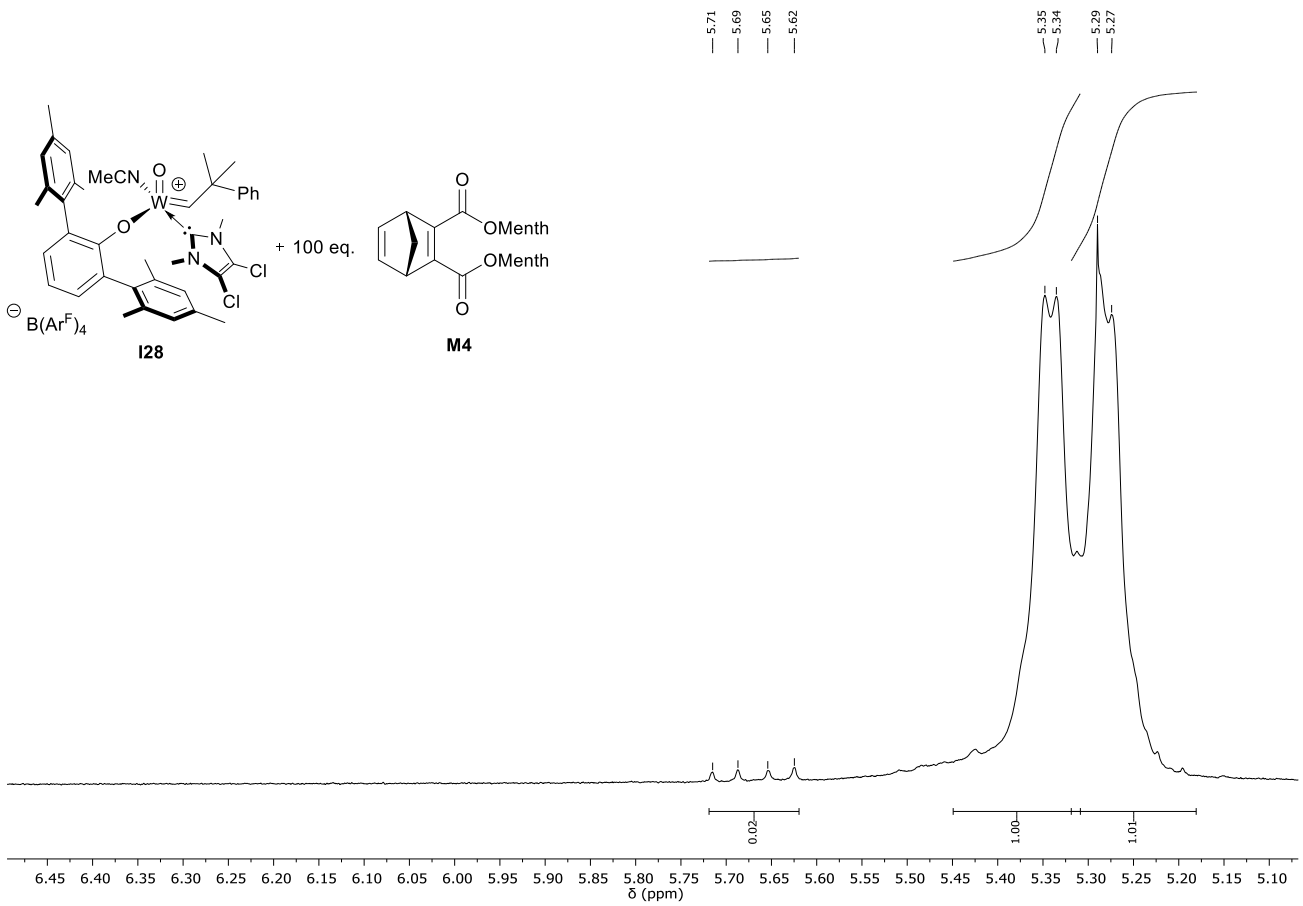


Figure S88. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M4**) by the action of **I28** in $CDCl_3$.

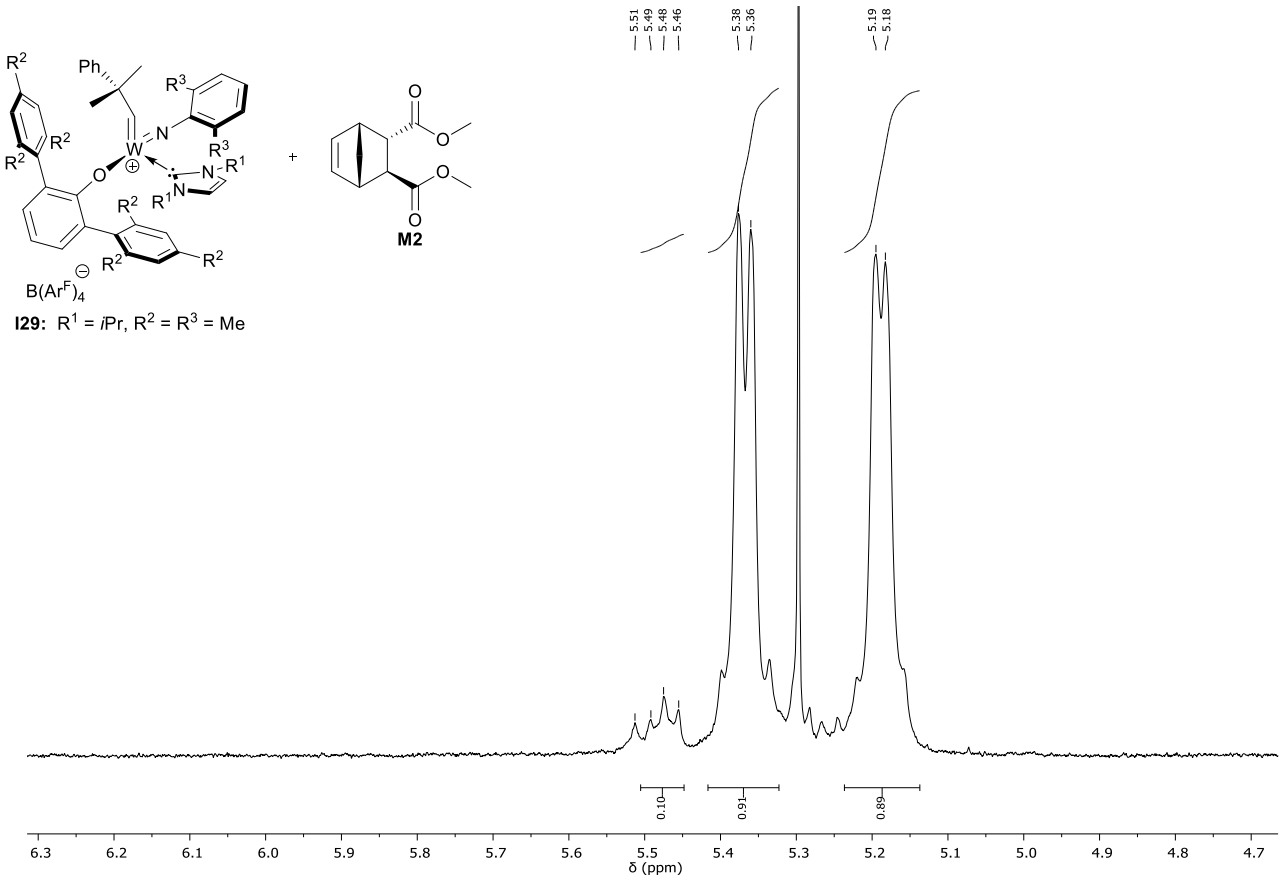


Figure S89. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M2**) by the action of **I29** in $CDCl_3$.

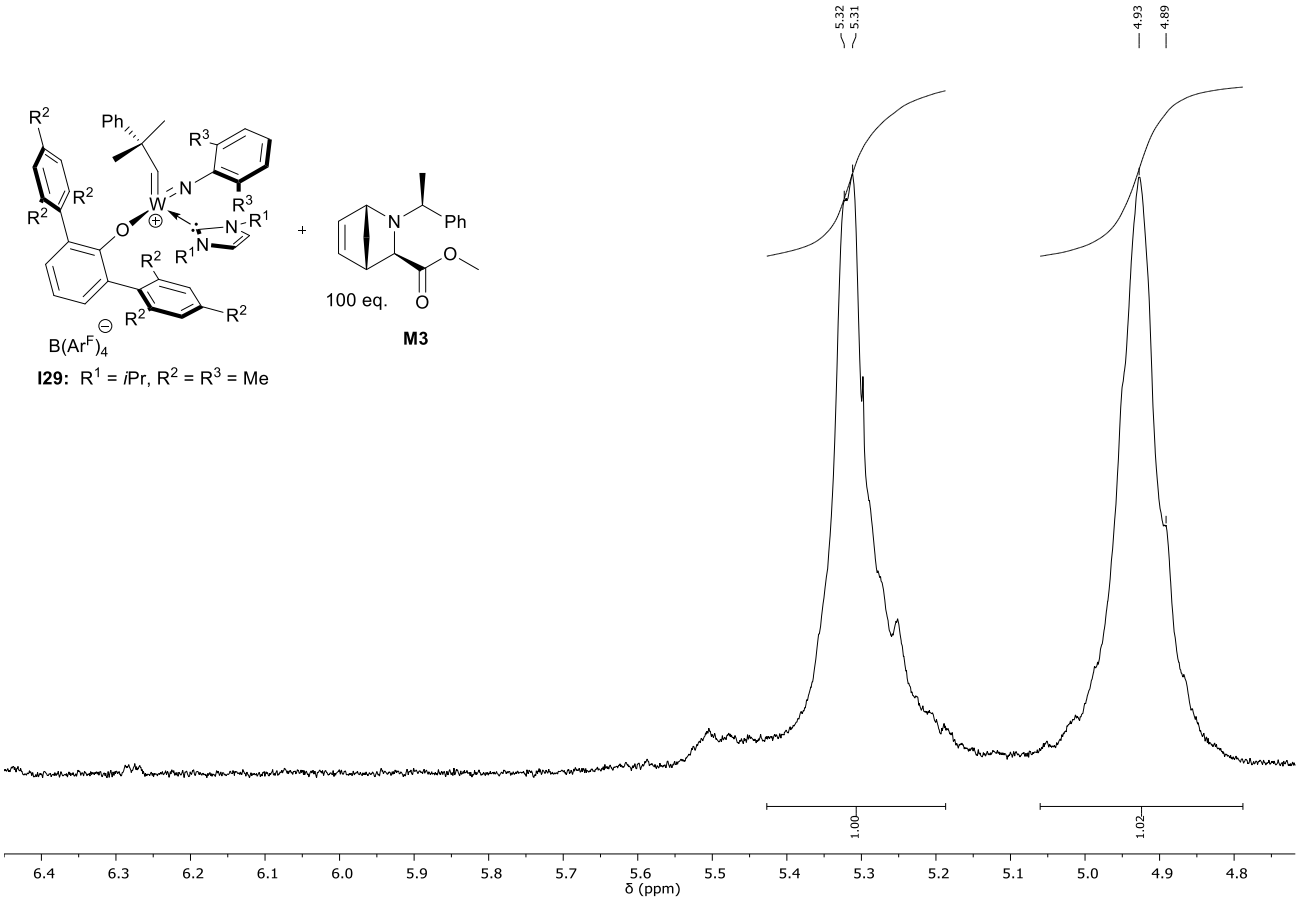


Figure S90. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M3**) by the action of **I29** in $CDCl_3$.

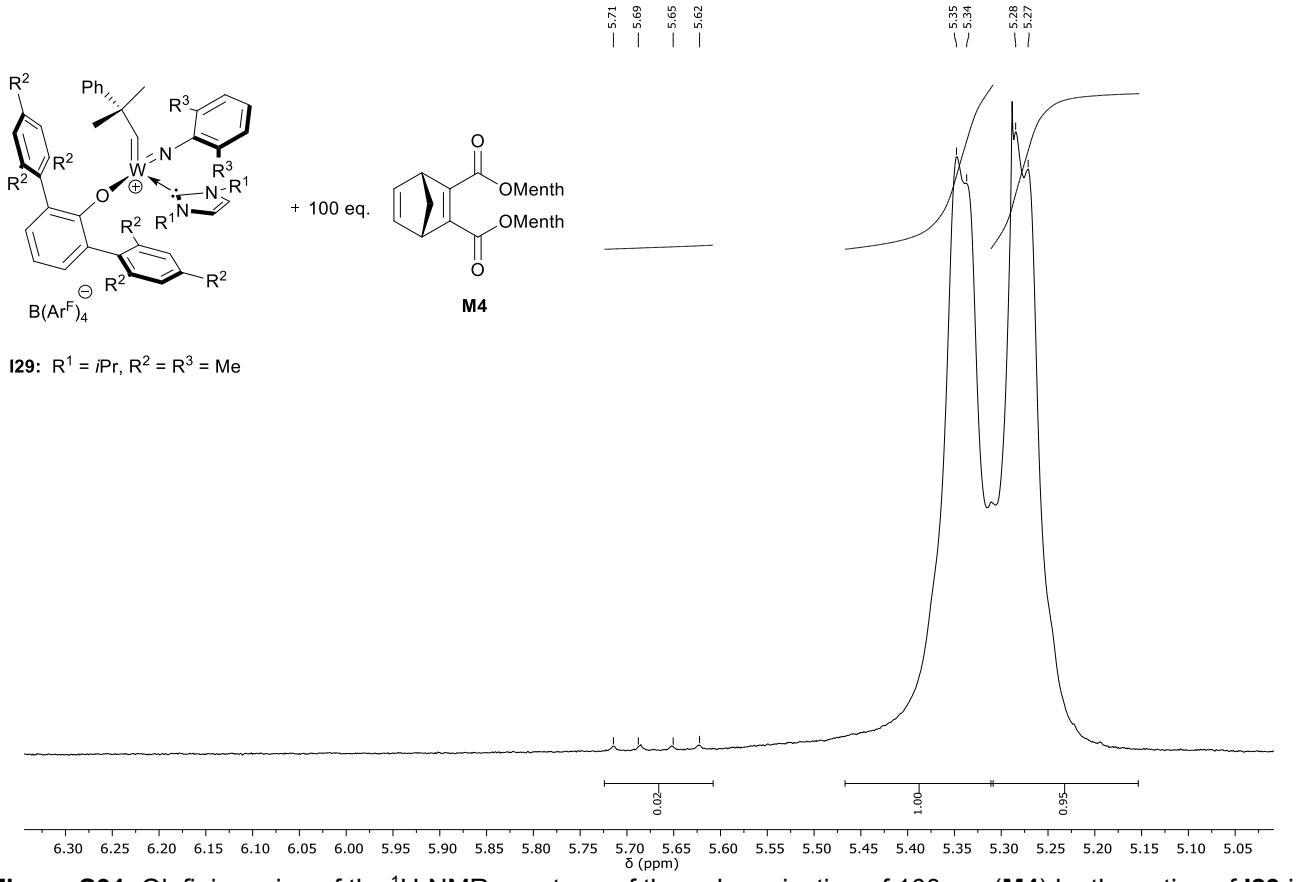


Figure S91. Olefinic region of the ^{1}H-NMR spectrum of the polymerization of 100 eq. (**M4**) by the action of **I29** in $CDCl_3$.

IR Spectra of Polymers

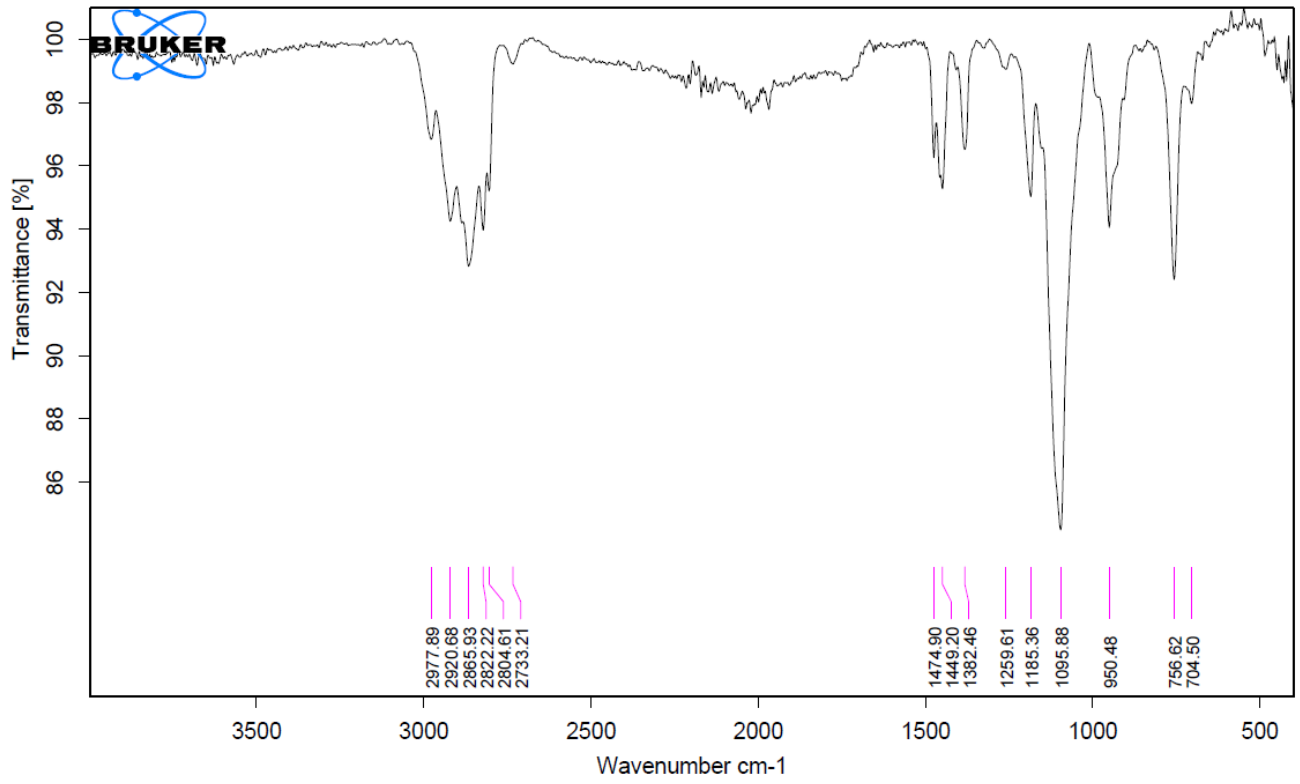


Figure S92. IR spectrum of *cis*-st poly[(+)DMMNBE]; polymerization of 100 eq. (**M1**) by the action of **I1** in $CDCl_3$.

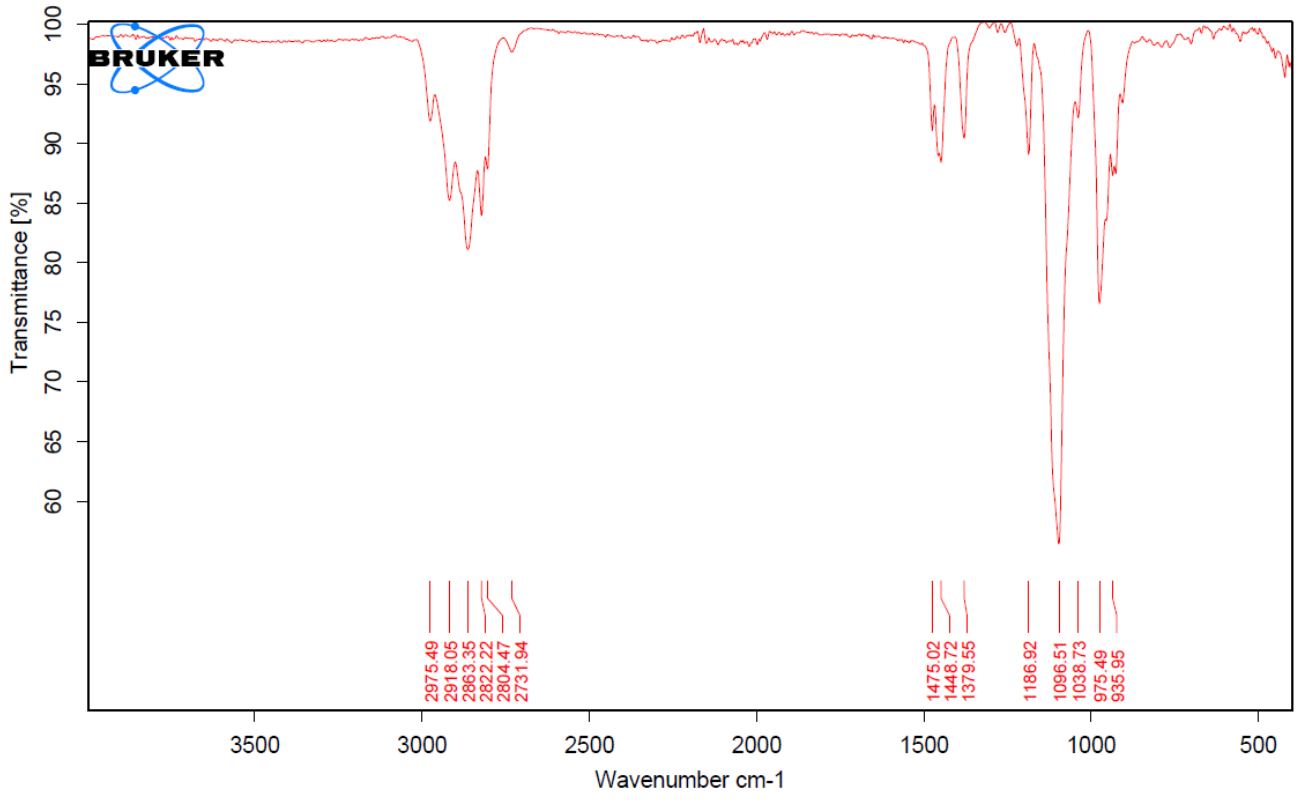


Figure S93. IR spectrum of *trans*-it poly[(+)DMMNBE]; polymerization of 100 eq. (**M1**) by the action of **I3** in $CDCl_3$.

Influence of Tris(pentafluorophenyl)borane on Selectivity

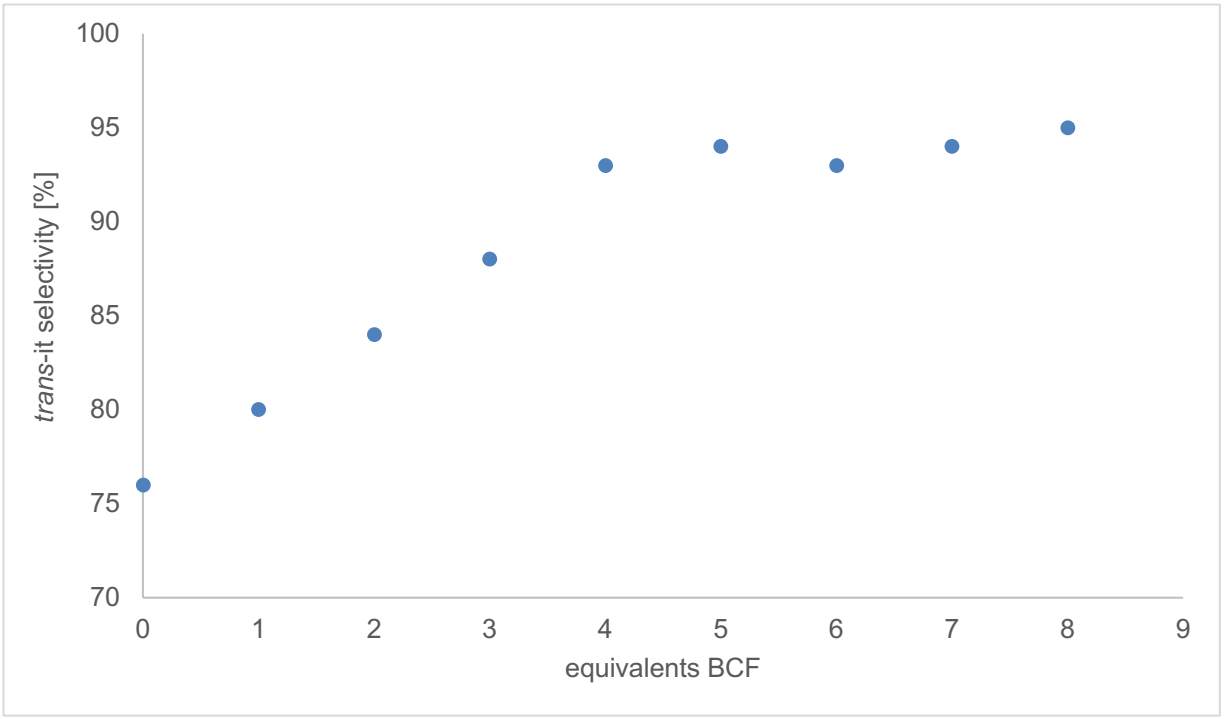


Figure S94. Influence of tris(pentafluorophenyl)borane on selectivity in the polymerization of **M1** by the action of **I15**; general reaction conditions applied.

Kinetics Measurements

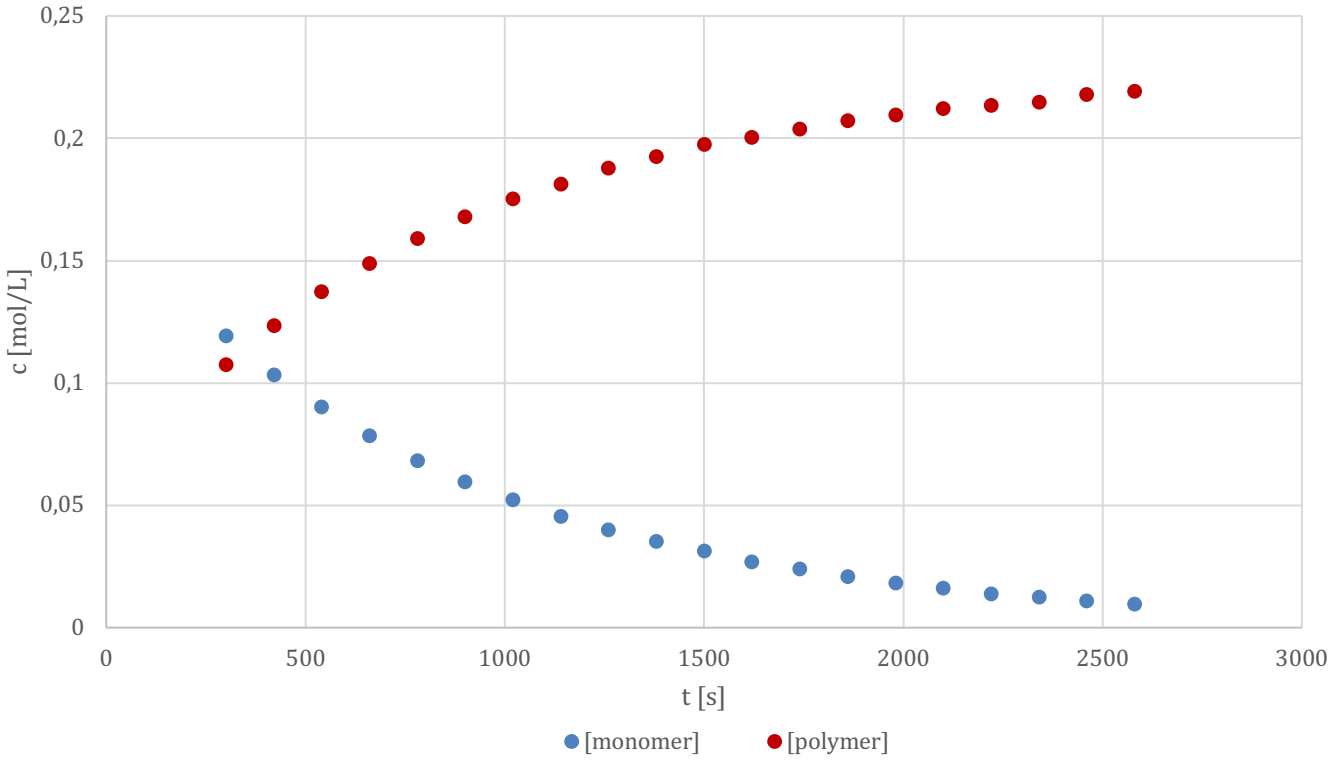


Figure S95. Monomer consumption and polymer formation vs. time for initiator **I16** and **M1**. $CDCl_3$, 0 °C, $[M]_0$ = 0.25 M.

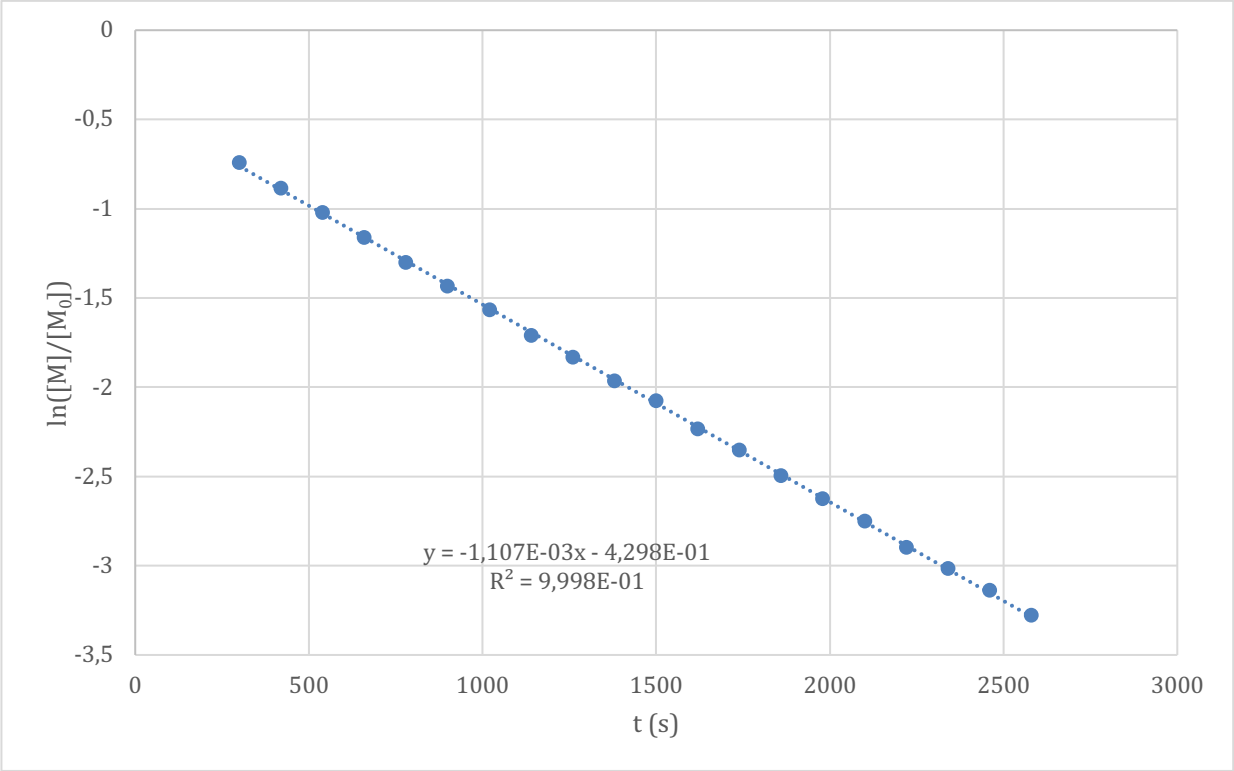


Figure S96. 1st-order plot of monomer consumption for initiator **I16** and **M1**. $CDCl_3$, 0 °C, $[M]_0$ = 0.25 M.

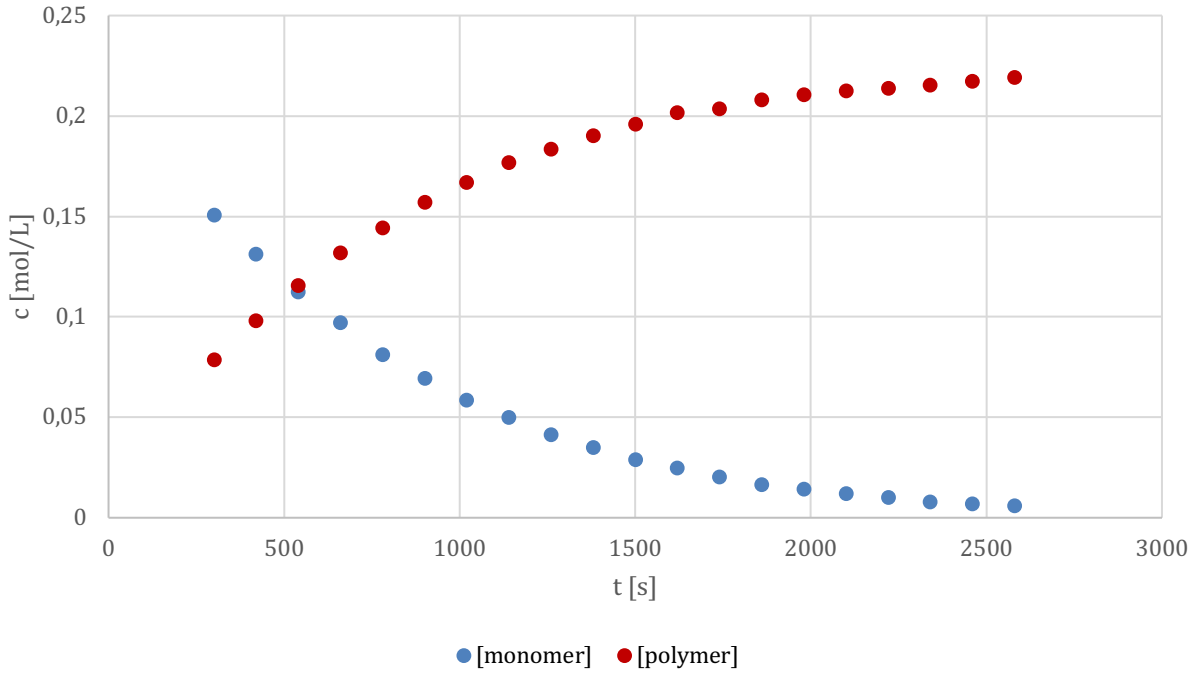


Figure S97. Monomer consumption and polymer formation vs. time for initiator **I28** and **M2**. $CDCl_3$, 0 °C, $[M]_0$ = 0.25 M.

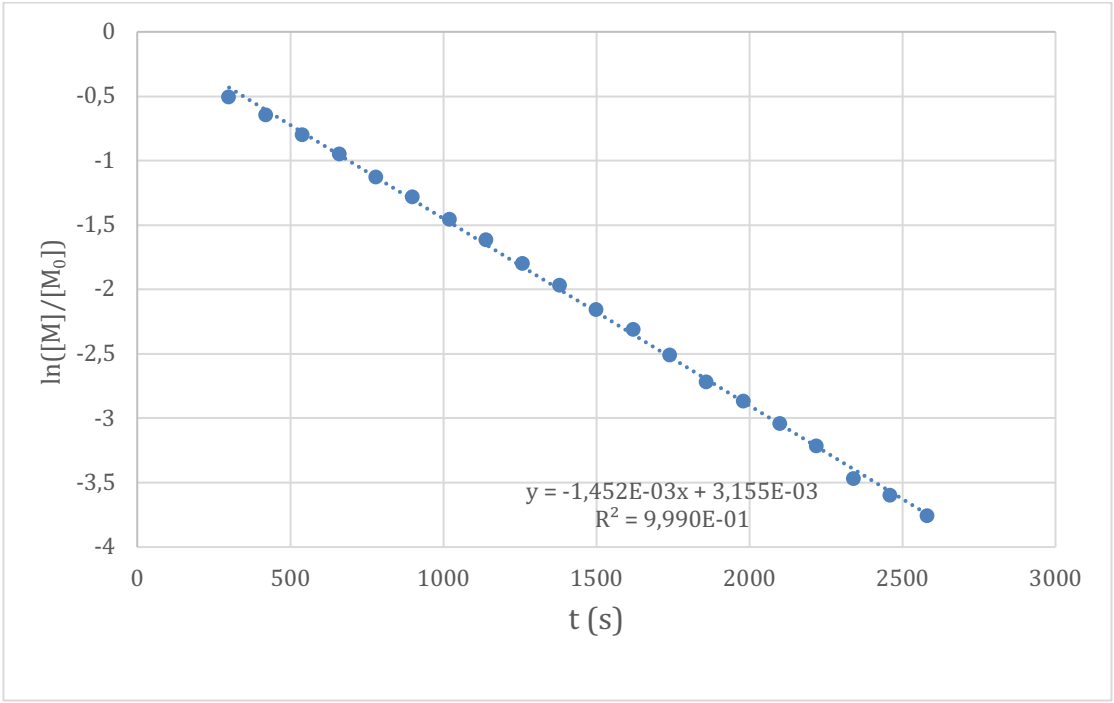


Figure S98. 1st-order plot of monomer consumption for initiator **I28** and **M2**. $CDCl_3$, 0 °C, $[M]_0$ = 0.25 M.

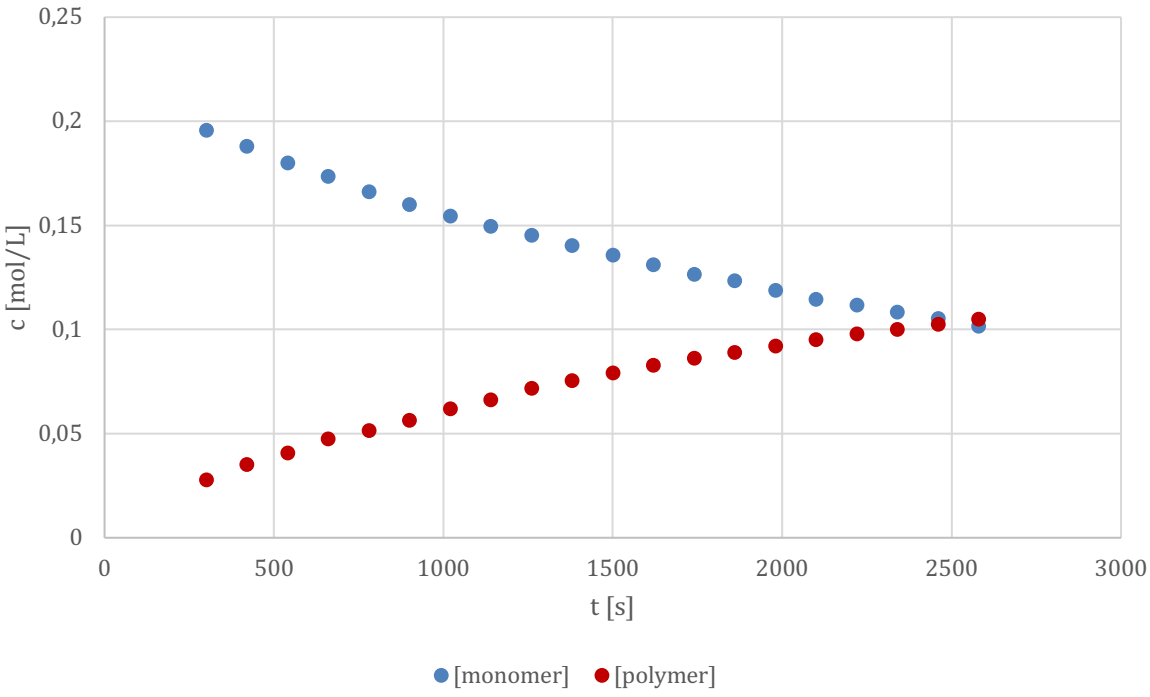


Figure S99. Monomer consumption and polymer formation vs. time for initiator **I28** and **M3**. $CDCl_3$, 0 °C, $[M]_0$ = 0.25 M.

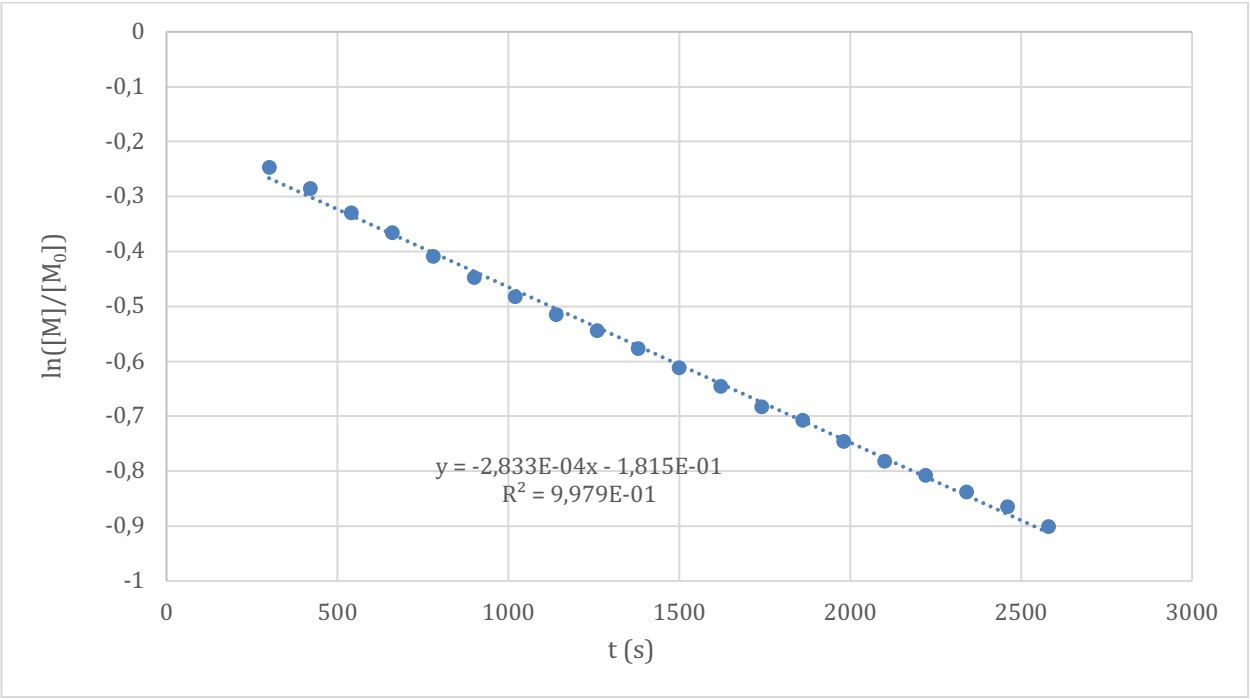


Figure S100. 1st-order plot of monomer consumption for initiator **I28** and **M3**. $CDCl_3$, 0 °C, $[M]_0$ = 0.25 M.

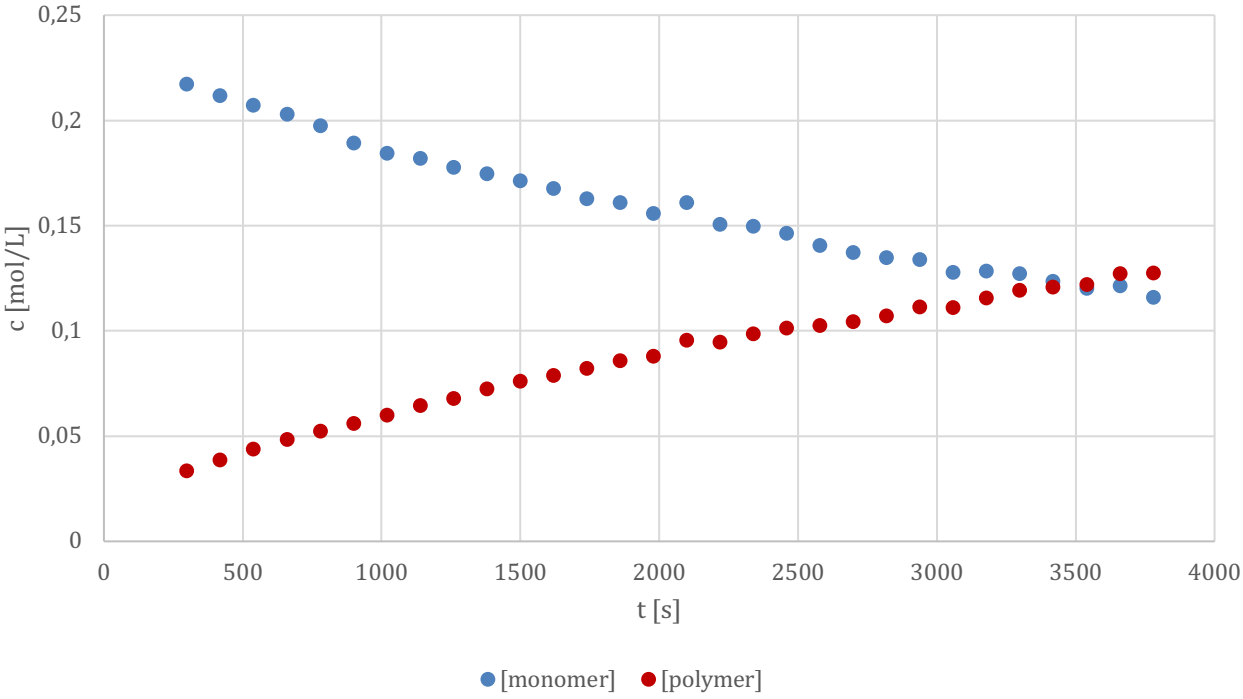


Figure S101. Monomer consumption and polymer formation vs. time for initiator **I28** and **M4**. $CDCl_3$, 0 °C, $[M]_0$ = 0.25 M.

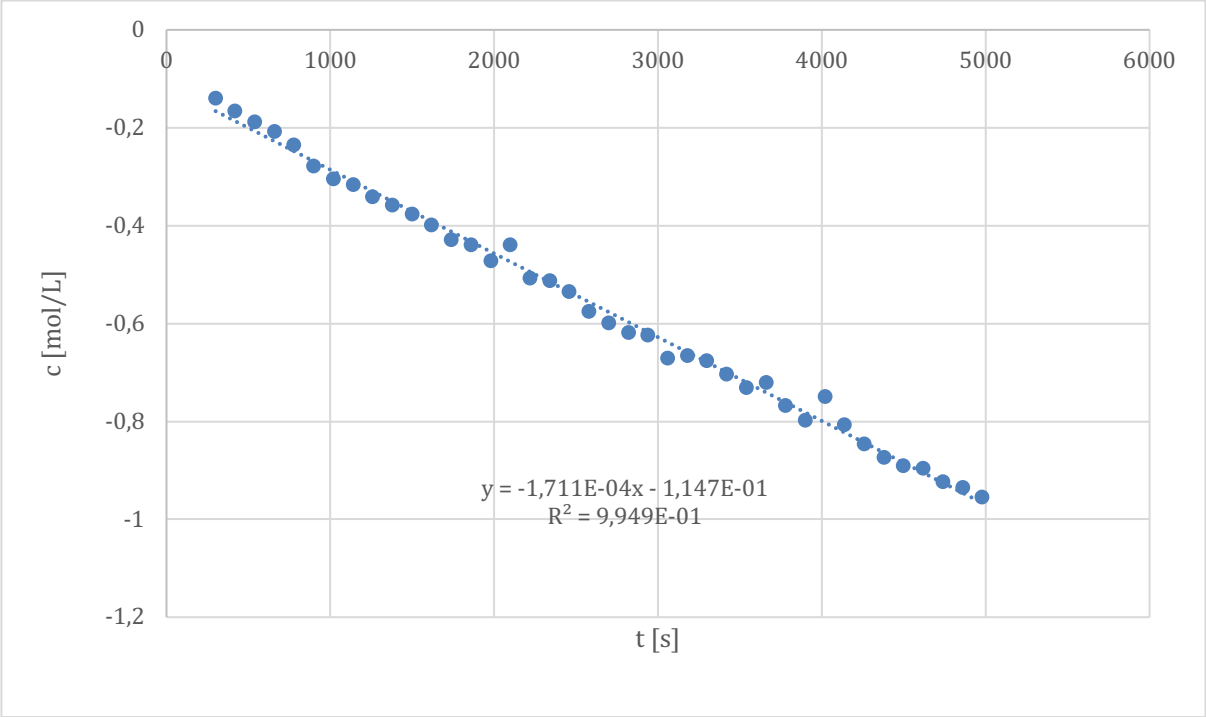


Figure S102. 1st-order plot of monomer consumption for initiator **I28** and **M4**. $CDCl_3$, 0 °C, $[M]_0$ = 0.25 M.

MALDI TOF Measurements

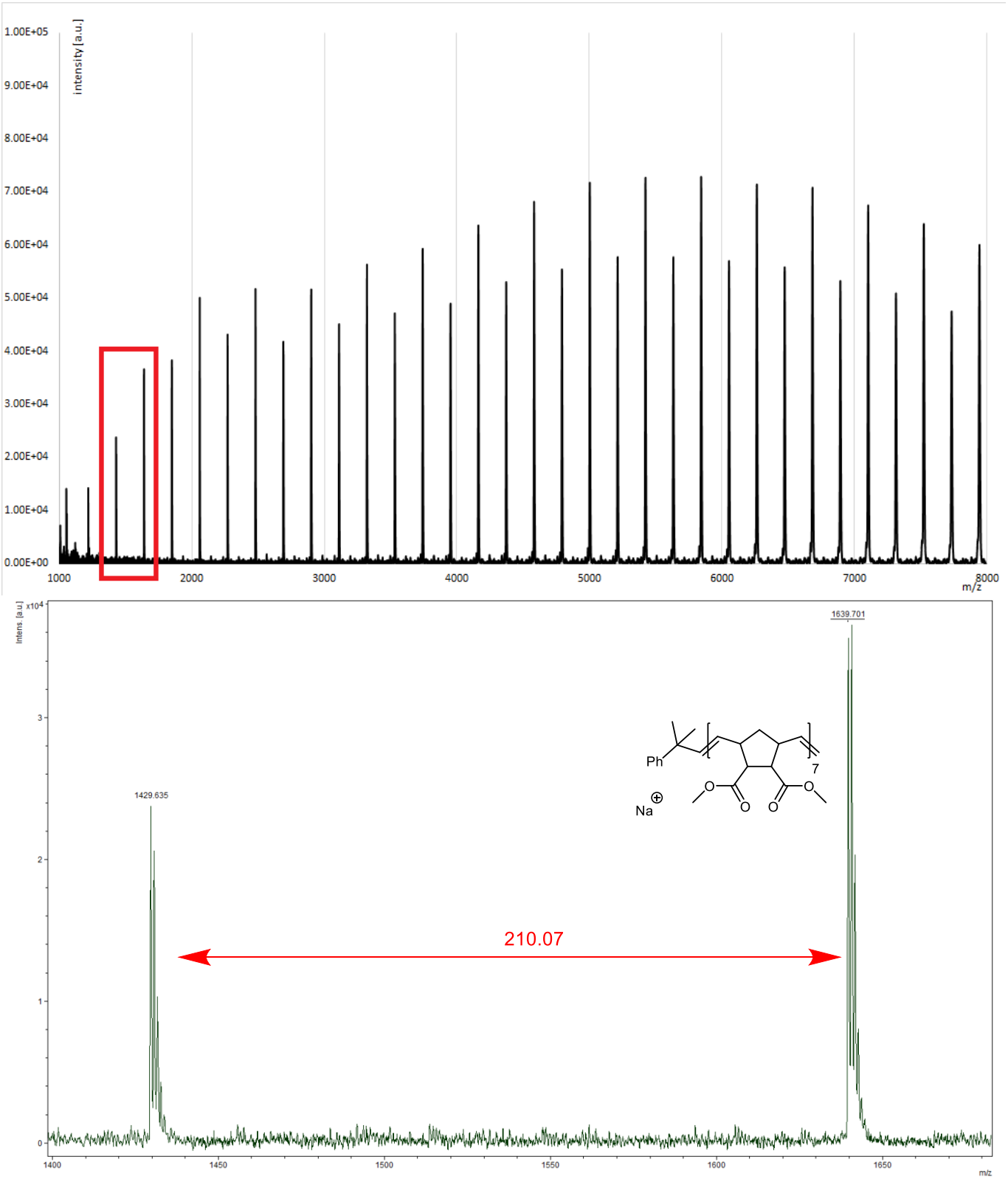


Figure S103. MALDI-ToF MS analysis of poly(**M2**) synthesized by the action of **I28** using 15 equivalents of monomer. *m/z* = 7 x 210.7 (repeat unit) + 14.02 (=CH_2) + 132.09(=$CHCMe_2Ph$) +22.99 (Na) = 1639.59, Δ = 0.11.

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