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Supporting Information

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Regioselective 1-Hexene Oligomerization Using Cationic Bis(phenolato) Group 4 Metal Catalysts: Switch from 1,2 to 2,1 Insertion

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List of Content

Experimental Section

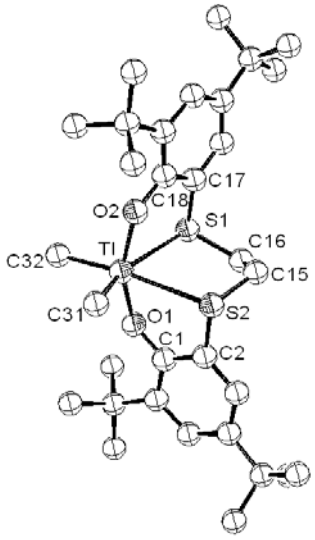


Figure S1. Molecular structure of (edtbp)$TiMe_2$ (**1a**) (hydrogen atoms were omitted for clarity). Selected bond lengths (Å) and angles (deg): Ti-C(31), 2.077(2); Ti-C(32), 2.084(2); Ti-O(1), 1.8617(14), Ti-O(2), 1.8616(14); Ti-S(1), 2.8056(7); Ti-S(2), 2.8417(7); O(1)-C(1), 1.345(2); S(2)-C(2), 1.776(2); C(31)-Ti-C(32), 98.70(12); C(31)-Ti-O(1), 98.39(9); C(31)-Ti-S(2), 83.75(9); C(31)-Ti-S(1), 155.43(9); C(31)-Ti-O(2), 97.44(9); S(1)-Ti-S(2), 74.04(2); S(1)-Ti-O(1), 85.45(5); S(1)-Ti-O(2), 72.52(5); O(1)-Ti-O(2), 155.42(7).

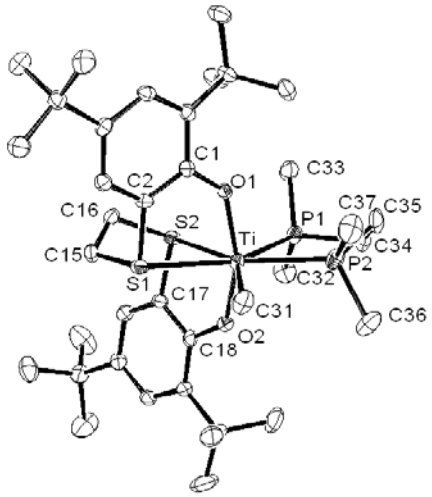


Figure S2. Molecular structure of $[(edtbp)TiMe(DMPE)]^+[MeB(C_6F_5)_3]^-$ (**5**·DMPE) (hydrogen atoms and anion were omitted for clarity). Selected bond lengths (Å) and angles (deg): Ti-O(1), 1.884(2); Ti-O(2), 1.875(2); Ti-S(1), 2.6645(10), Ti-S(2), 2.7024(10); Ti-C(31), 2.237(4); Ti-P(1), 2.6676(11); Ti-P(2), 2.5716(11); O(1)-Ti-O(2), 157.82(10); O(1)-Ti-C(31), 99.29(13); O(2)-Ti-C(31), 93.81(13); S(1)-Ti-S(2), 75.31(3); S(1)-Ti-C(31), 70.31(10); C(31)-Ti-P(2), 70.71(10); P(2)-Ti-P(1), 72.43(3); P(1)-Ti-S(2), 73.88(3).

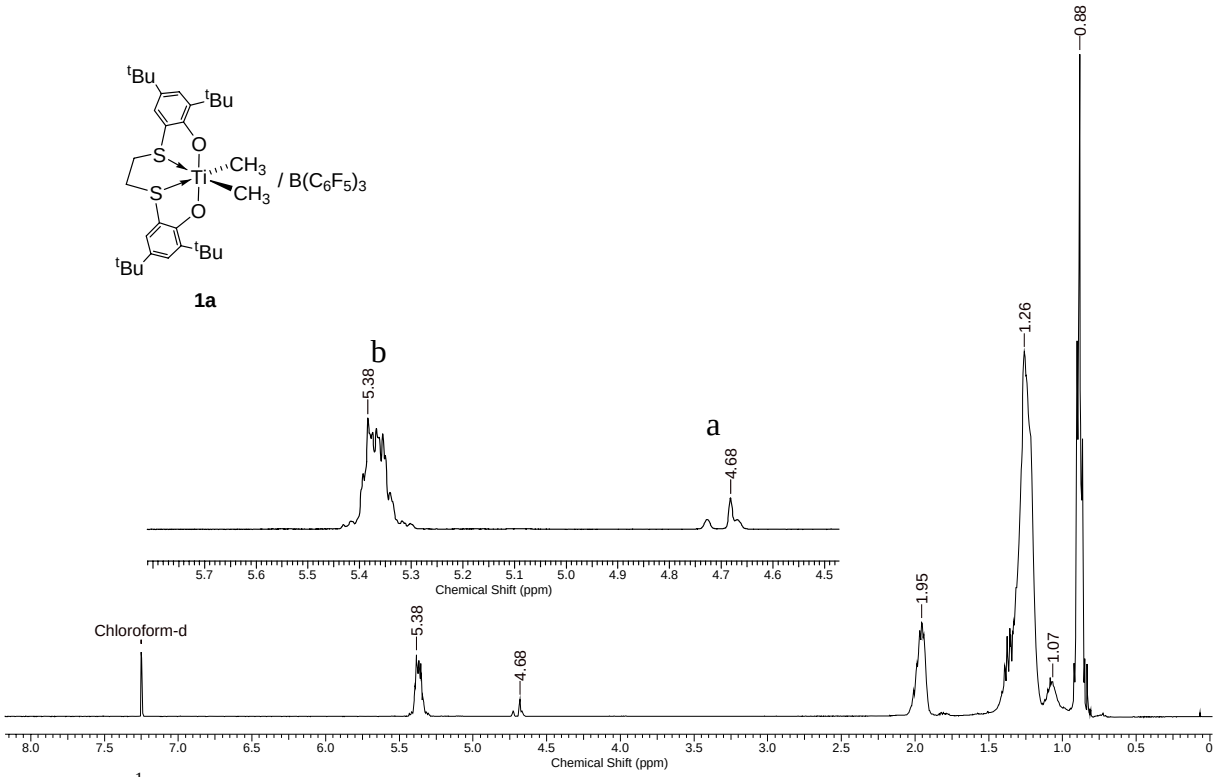


Figure S3a ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of oligo(1-hexene)s prepared by (edtbp)$TiMe_2$ (**1a**) / $B(C_6F_5)_3$. Label a and b refer to $(R^1)(R^2)C{=}CH_2$ and $(R^3)CH{=}CH(R^4)$, respectively.

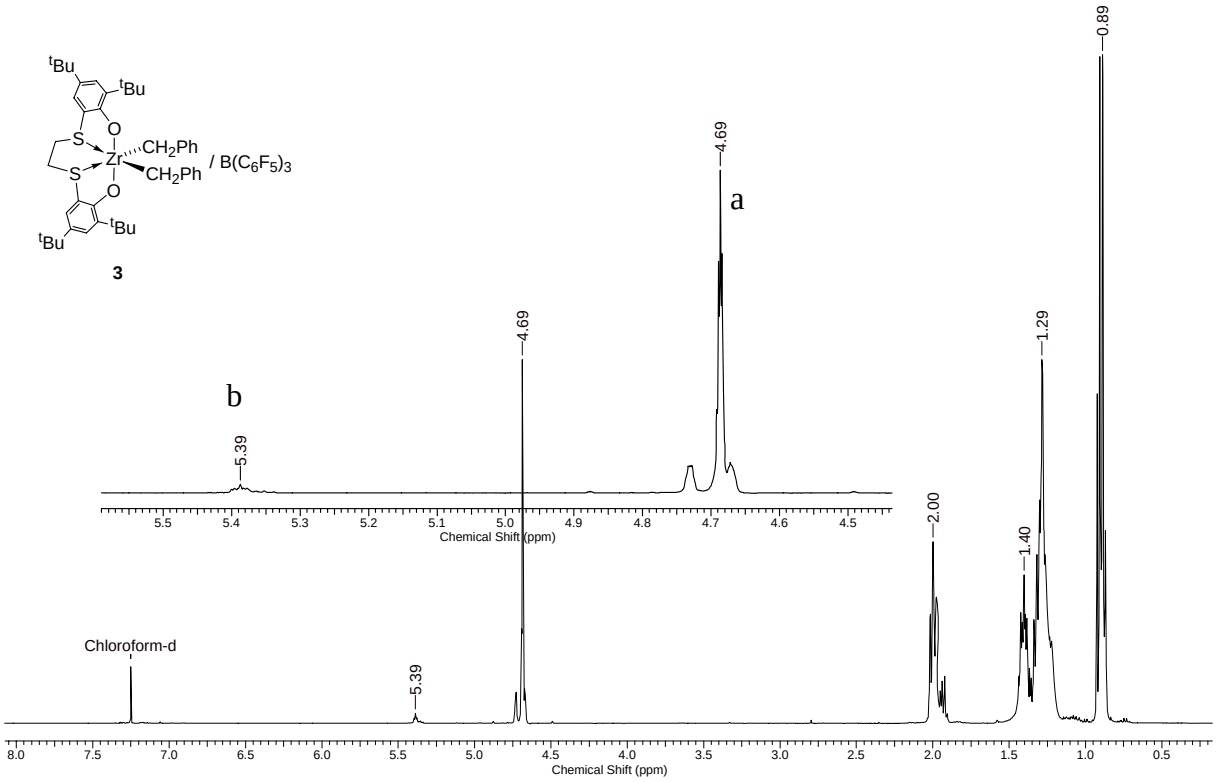


Figure S3b. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of oligo(1-hexene)s prepared by (edtbp)$Zr(CH_2Ph)_2$ (**3**)/ $B(C_6F_5)_3$. Label a and b refer to $(R^1)(R^2)C{=}CH_2$ and $(R^3)CH{=}CH(R^4)$, respectively.

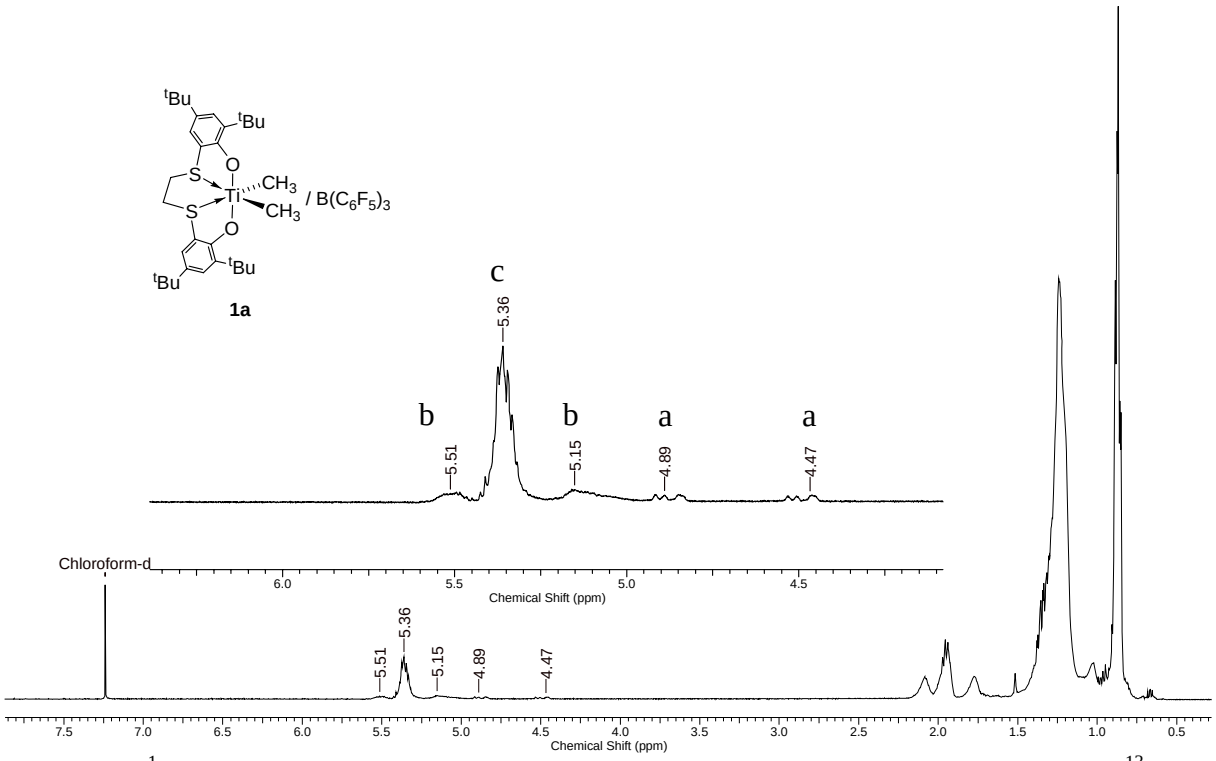


Figure S4a ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of oligo(1-hexene)s prepared from 1-^{13}C labeled 1-hexene and (edtbp)$TiMe_2$ (**1a**) / $B(C_6F_5)_3$. ((edtbp)$TiMe_2$: $B(C_6F_5)_3$: monomer = 1 : 1 : 30). Label a, b, and c refer to $(R^1)(R^2)C=^{13}CH_2$, $(R^3)CH=^{13}CH(R^4)$, and $(R^5)CH=CH(R^6)$ respectively.

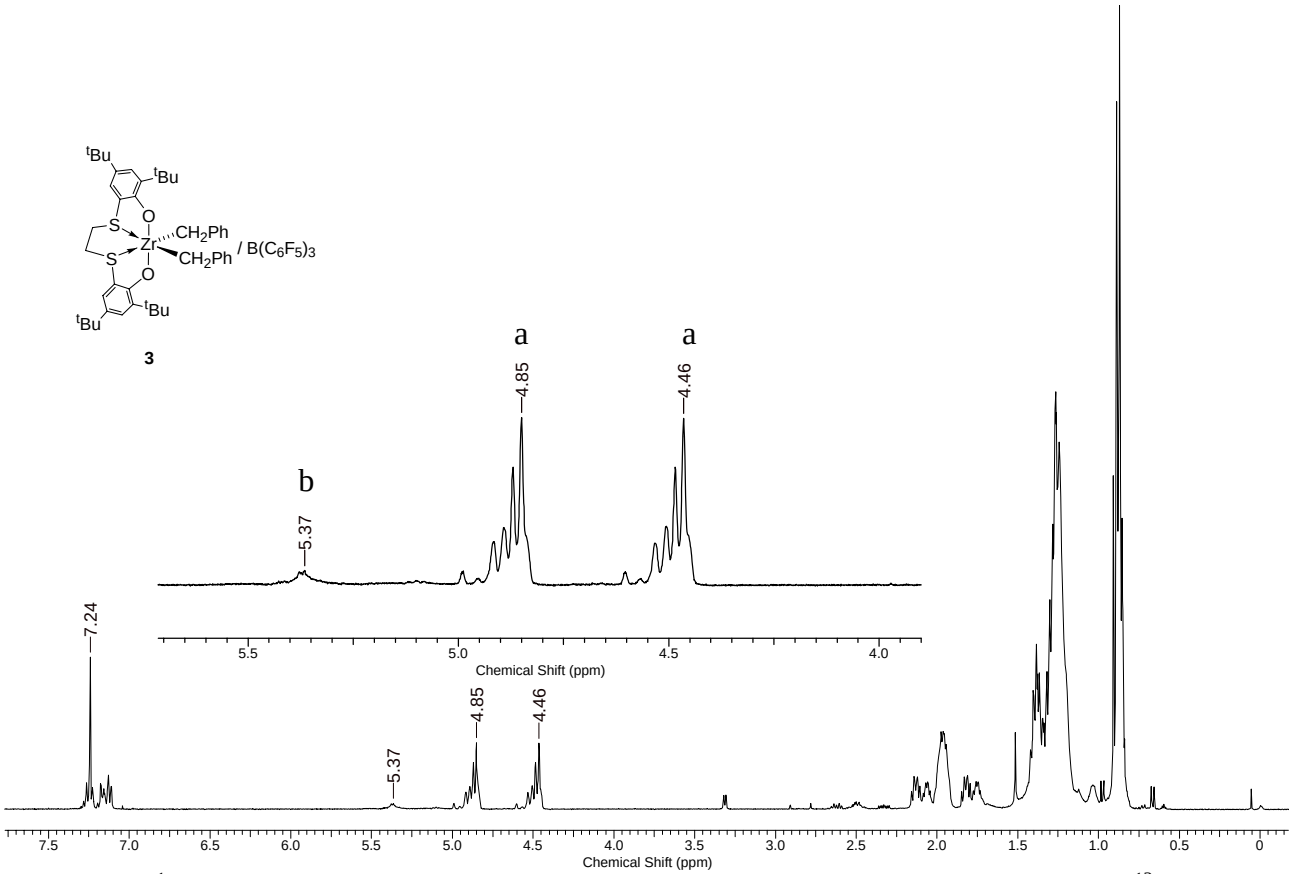


Figure S4b. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of oligo(1-hexene)s prepared from 1-^{13}C labeled 1-hexene and (edtbp)$Zr(CH_2Ph)_2$ (**3**)/ $B(C_6F_5)_3$. Label a and b refer to $(R^1)(R^2)C=^{13}CH_2$ and $(R^3)CH=CH(R^4)$, respectively.

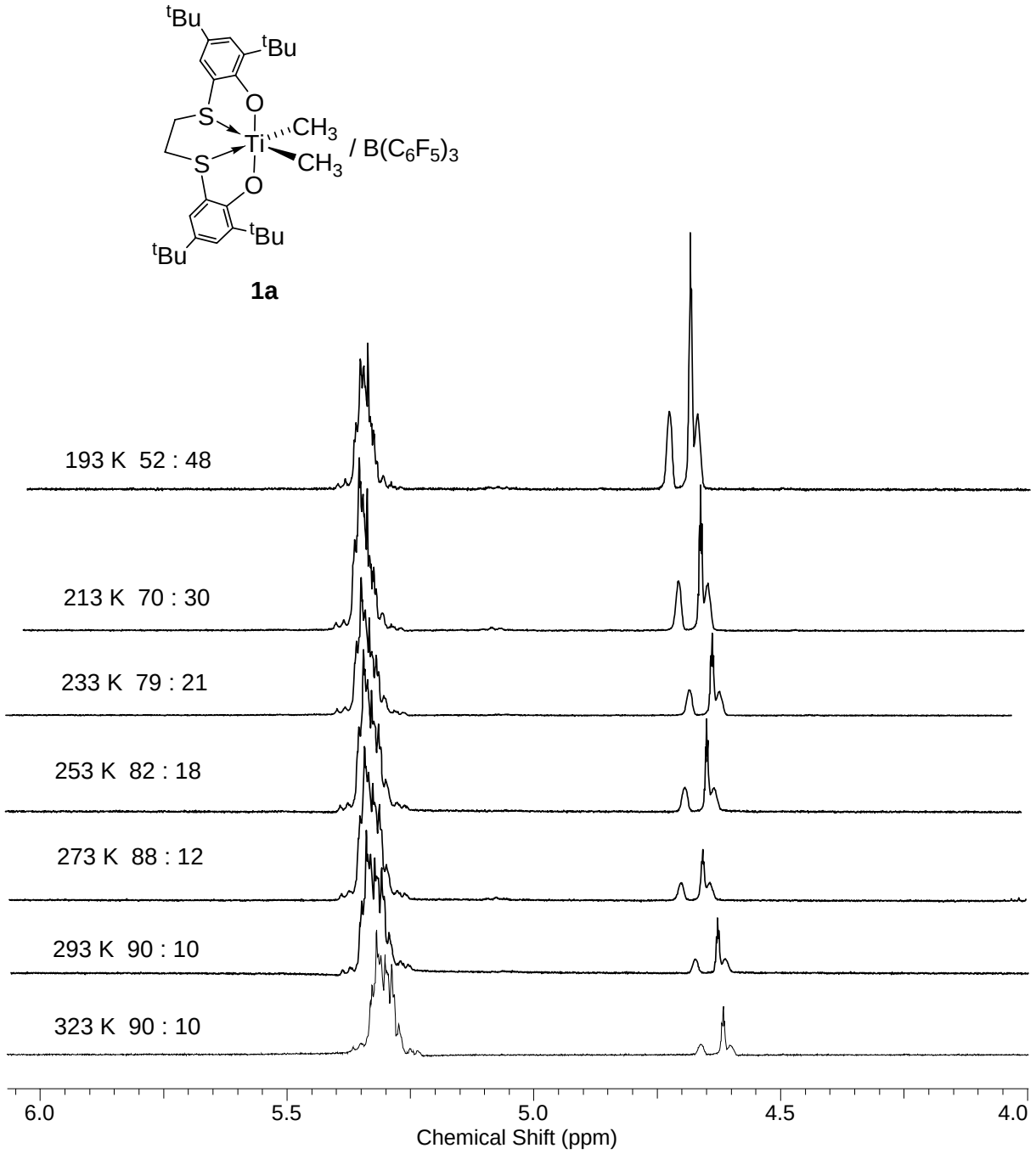


Figure S5. Oligomerization of 1-hexene using $B(C_6F_5)_3$-activated precursor (edtbp)$TiMe_2$ (**1a**) at different temperatures. ^1H NMR spectra (400 MHz, $CDCl_3$, 25 °C) of resonances in the C=C region, conditions see Table S3.

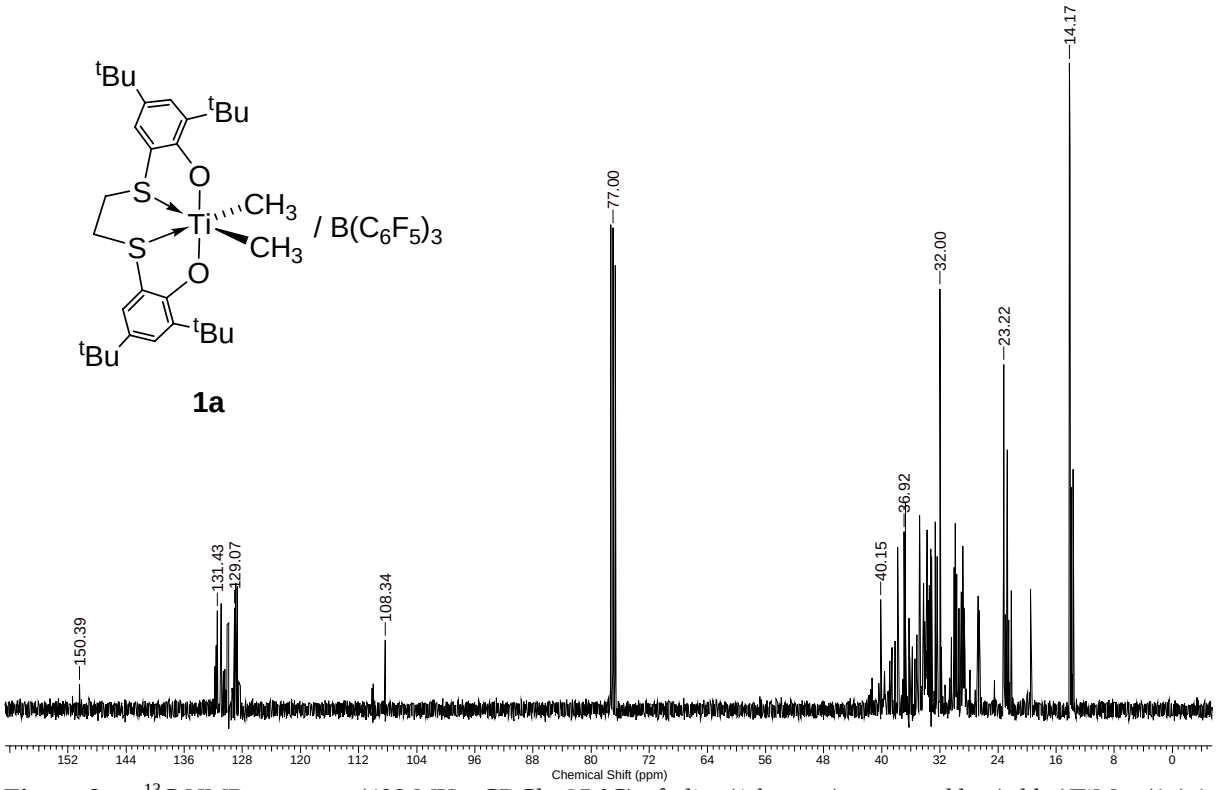


Figure 6a. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of oligo(1-hexene)s prepared by (edtbp)$TiMe_2$ (**1a**) / $B(C_6F_5)_3$.

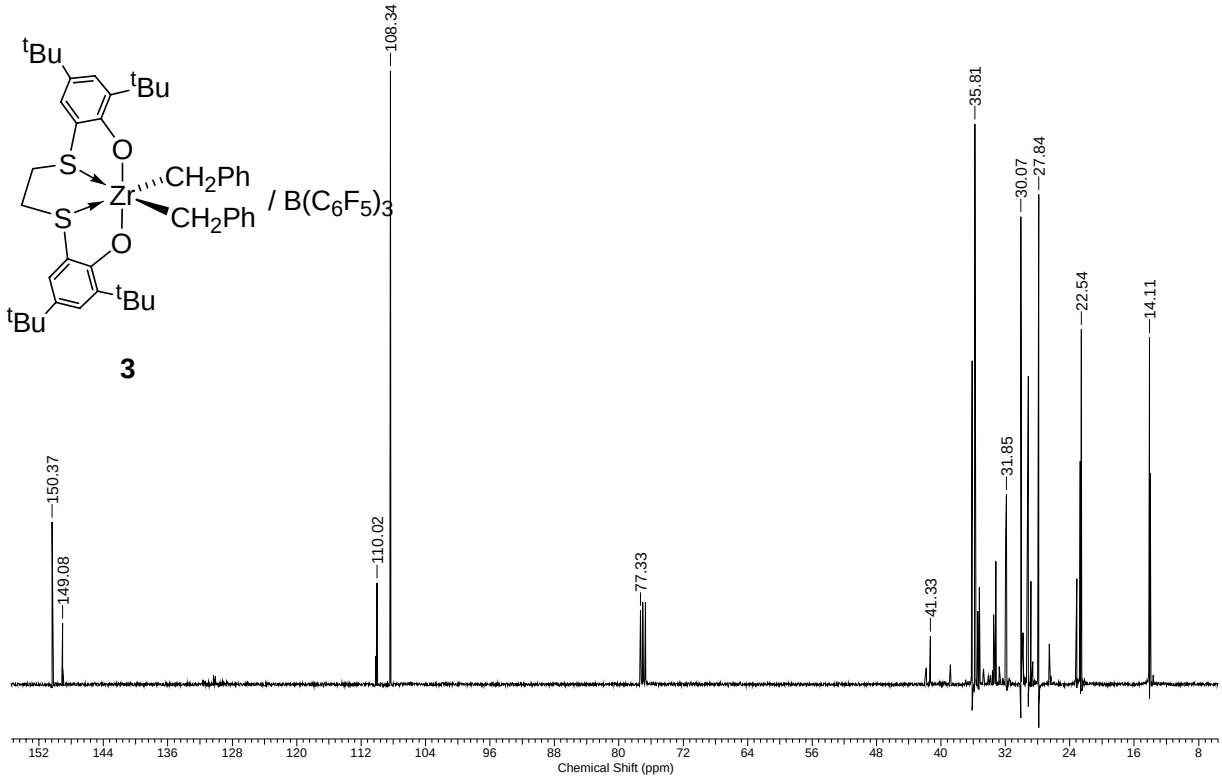


Figure 6b. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of oligo(1-hexene)s prepared by (edtbp)$Zr(CH_2Ph)_2$ (**3**)/ $B(C_6F_5)_3$.

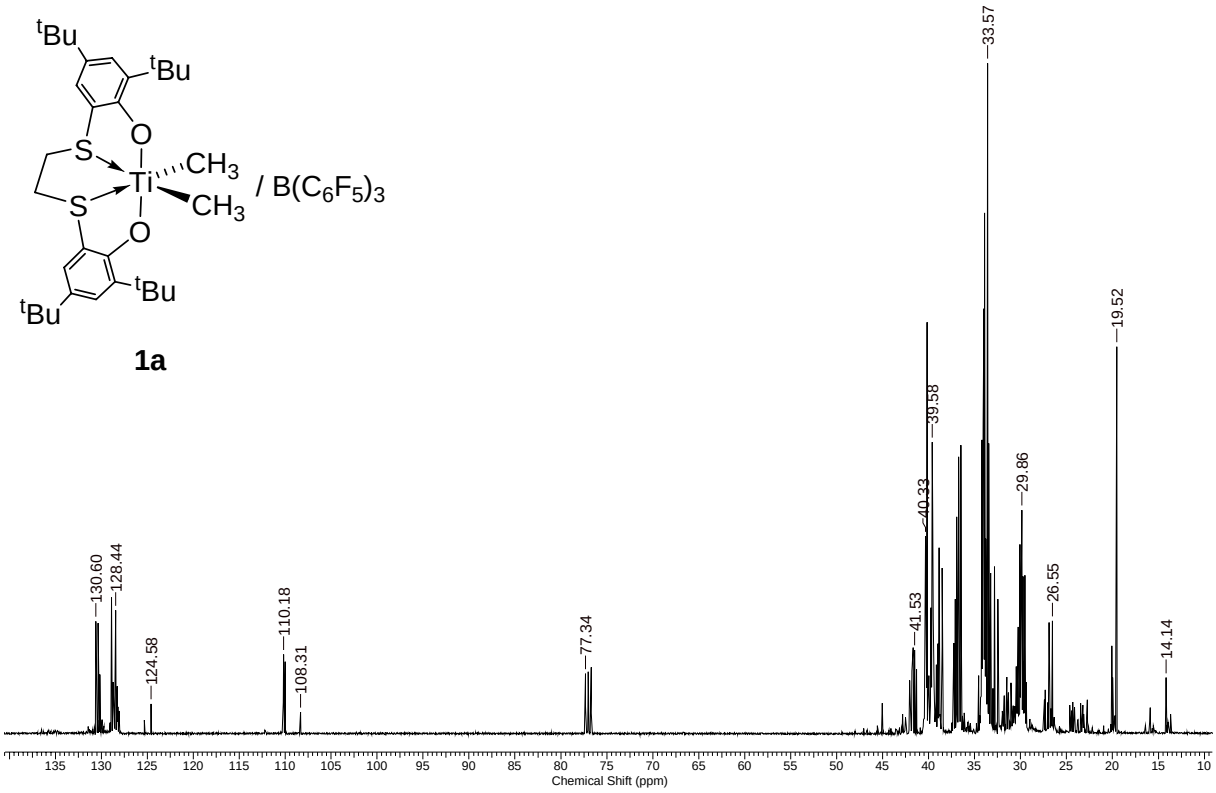


Figure 7a. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of oligo(1-hexene)s prepared from 1-^{13}C labeled 1-hexene and (edtbp)$TiMe_2$ (**1a**) / $B(C_6F_5)_3$. ((edtbp)$TiMe_2$: $B(C_6F_5)_3$: monomer = 1 : 1 : 30).

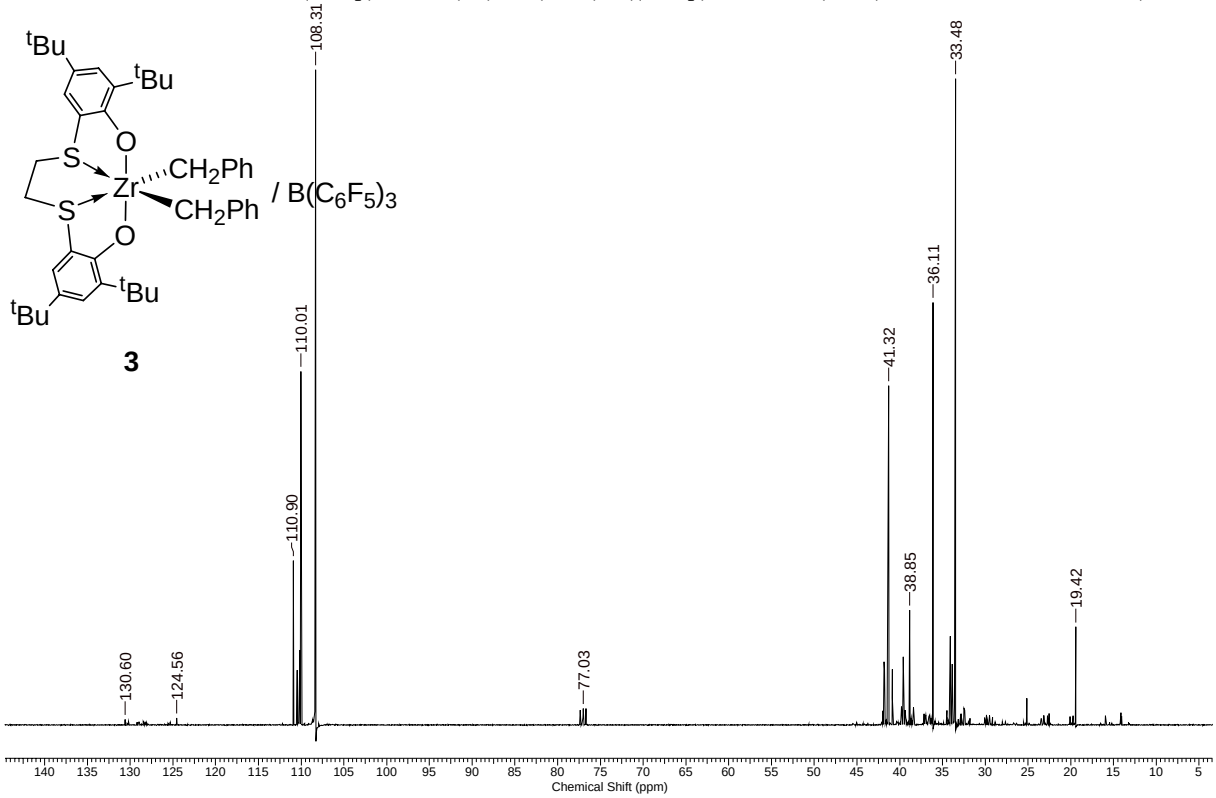


Figure 7b. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of oligo(1-hexene)s prepared from 1-^{13}C labeled 1-hexene and (edtbp)$Zr(CH_2Ph)_2$ (**3**)/ $B(C_6F_5)_3$.

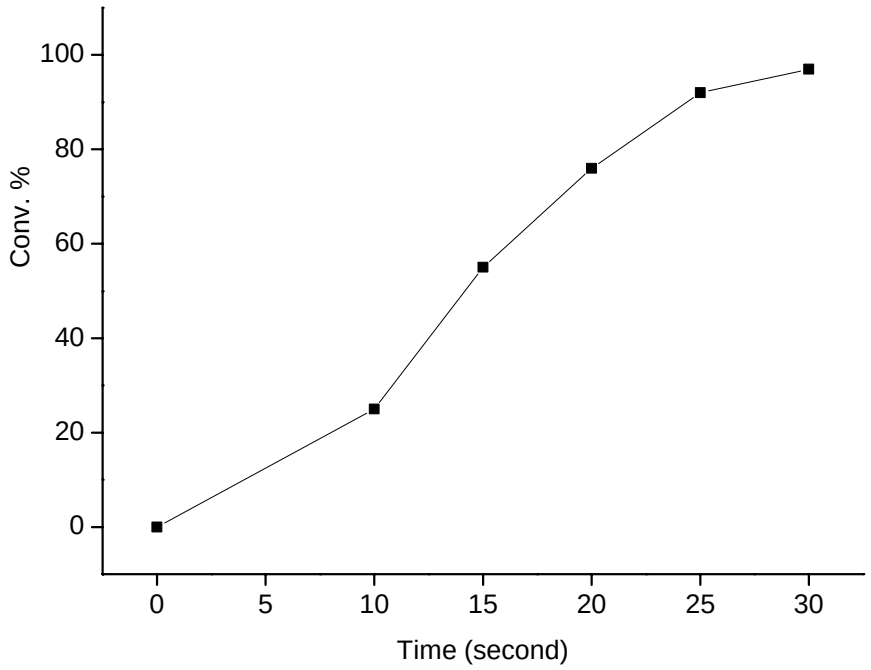
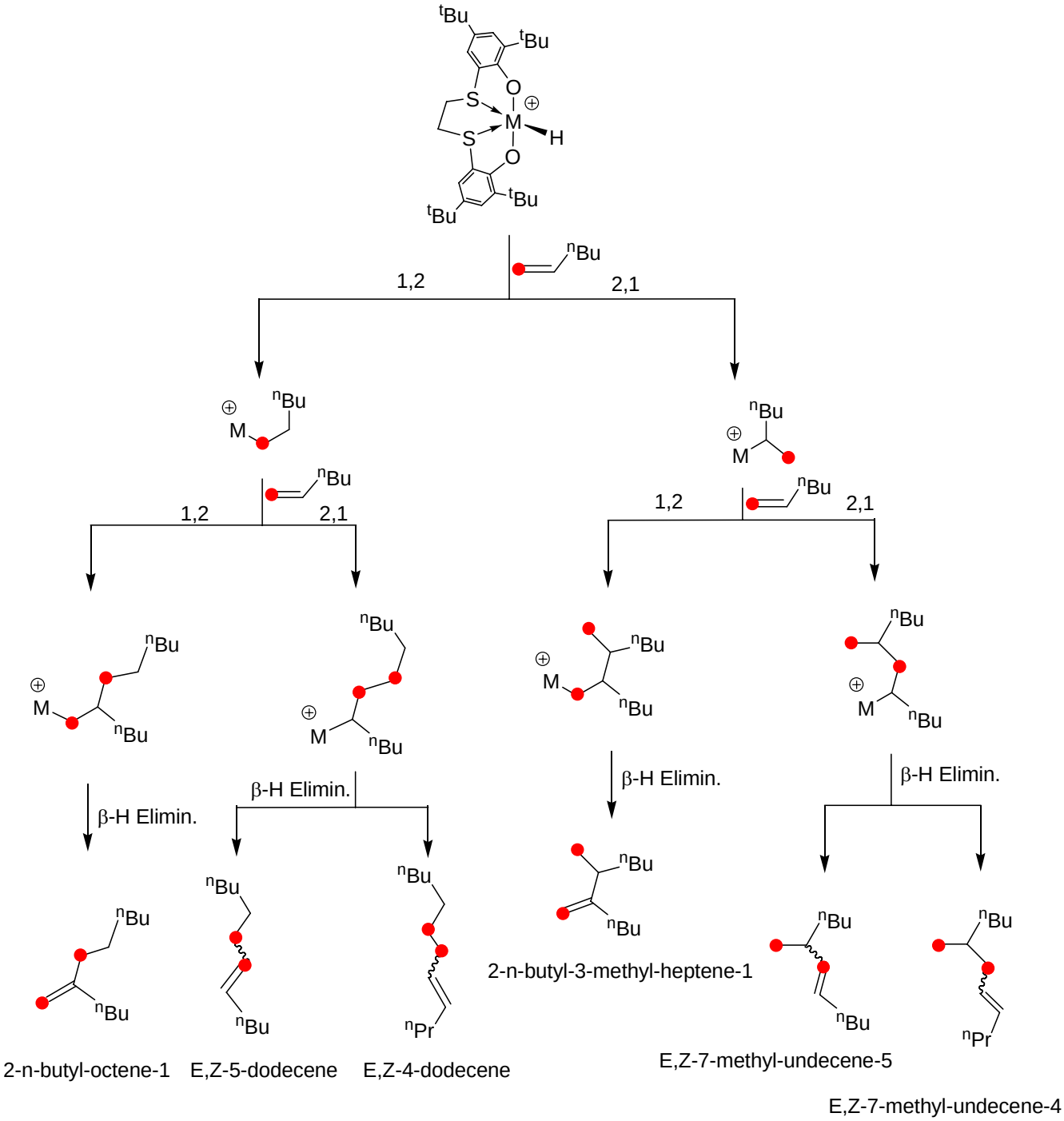


Figure S8. Plot of monomer conversion against time for 1-hexene oligomerization using **1a** / $B(C_6F_5)_3$ –60 °C**.** Conditions: [**1a**] = [$B(C_6F_5)_3$] = 0.02 mmol, [1-hexene]/[Ti] = 600:1, toluene = 10 mL.



Scheme S1. Isomers of 1-Hexene Dimers.

Table S1. Crystal and Structure Refinement Data for **1a** and **5**·DMPE.

Compound	**1a**	**5**·DMPE·C_5H_{12}
Empirical formula	$C_{32}H_{50}O_2S_2Ti$	$C_{61}H_{78}BF_{15}O_2P_2S_2Ti$
M_r	578.74	1313.00
Crystal system	triclinic	triclinic
Space group	*P* -1	*P* -1
a (Å)	9.5362(9)	13.4401(19)
b (Å)	11.6558(11)	13.9016(19)
c (Å)	15.7135(14)	18.146(3)
α (°)	82.772(3)	96.959(3)
β (°)	72.552(5)	105.595(3)
γ (°)	86.592(2)	91.718(3)
V (Å^3)	1652.6(3)	3232.9(8)
Z	2	2
D_{calc} (g·cm^{-3})	1.163	1.349
T (K)	120	130
μ(Mo Kα) (mm^{-1})	0.410	0.330
F(000)	624	1368
Crystal size	0.12 × 0.20 × 0.13	0.12 × 0.20 × 0.30
θ Range (°)	1.37-27.10	1.18-28.35
Number of reflections collected	14835	45037
Number of reflections observed [*I*> 2σ(*I*)]	5841	12102
Number of independent reflections (R_{int})	7184 (0.0264)	16053 (0.0586)
Data/restraints/parameters	7184/0/348	15053/1/775
Absorption correction	empirical	empirical
Goodness-of-fit on F^2	1.099	1.082
R_1, wR_2 [*I*> 2 σ(*I*)]	0.0441, 0.1203	0.0766, 0.1727
R_1, wR_2 (all data)	0.0577, 0.1310	0.1033, 0.1882
Largest difference in peak and hole (e Å^{-3})	0.572 and –0.367	1.703 and –0.786

Table S2. Oligomerization of 1-Hexene Using $B(C_6F_5)_3$-Activated Precursors (edtbp)$TiMe_2$ (**1a**), (edcp)$TiMe_2$ (**1b**), (edtbp)$Ti(CH_2Ph)_2$ (**2**), (edtbp)$Zr(CH_2Ph)_2$(**3**) and (edtbp)$Hf(CH_2Ph)_2$ (**4**).[a]

run	pre cat	*T* (°C)	*t* (min)	oligom. (g)	yield (%)	A[b]	TOF [c]	M_n[d]	M_w/M_n[d]	Selecti-vity [e]	Oligomer Distribution[f] (wt %)							
											C_{12}	C_{18}	C_{24}	C_{30}	C_{36}	C_{42}	C_{48}	C_{54}
1	**1a**	20	5	2.9	97	1740	20700	352	1.30	92 : 8	15.5	22.9	22.6	16.3	11.4	6.8	3.3	1.2
2	**1b**	20	5	2.9	97	1740	20700	256	1.22	99 : 1	33.6	29.5	20.0	9.6	5.4	1.6	0.3	-
3	**2**	20	5	2.8	94	1680	19960	352	1.33	93 : 7	18.9	23.7	22.2	15.5	10.0	5.9	2.9	0.9
4	**3**	20	120	0.66	22	16.5	196	224	1.23	5 : 95	38.5	40.3	14.1	4.8	1.7	0.6	-	-
5	**3**	–40	120	trace	< 1	-	-	-	-	-	-	-	-	-	-	-	-	-
6	**4**	20	960	0.102	3.4	0.32	3.8	338	1.38	7 : 93	30.7	25.2	16.1	11.7	8.8	5.3	2.2	-

[a] Oligomerization conditions: [precat] = [$B(C_6F_5)_3$] = 0.02 mmol; 1-hexane = 3 g; oligomerization time (unoptimized); Protocol = (cat.+ 1.5 g 1-hexene), ($B(C_6F_5)_3$ +1.5 g 1-hexene), then mix them. [b] g oligomer/mmol cat·h) [c] Mol of 1-hexene converted (mol of M)$^{-1}$·h^{-1}. [d] Determined by GPC in THF vs PS standards. [e] Ratio of the signals intensity (R^1)C*H*=C*H*(R^2):(R^3)(R^4)C=CH_2 in oligomer, determined by ^{1}H NMR spectroscopy in $CDCl_3$. [f] Determined by GC.

Table S3. Oligomerization of 1-Hexene Using $B(C_6F_5)_3$-Activated Precursor (edtbp)$TiMe_2$ (**1a**) at Different Temperatures.[a]

run	*T* (°C)	oligom. (g)	yield (%)	A[b]	TOF[c]	M_n[d]	M_w/M_n[d]	Selecti-vity [e]	Oligomer Distribution[f] (wt %)							
									C_{12}	C_{18}	C_{24}	C_{30}	C_{36}	C_{42}	C_{48}	C_{54}
7	+50	0.51	50	300	3564	360	1.33	90:10	16.3	23.3	22.1	16.0	11.8	6.6	2.8	1.1
8	+20	>0.99	>99	>600	>7128	354	1.34	90:10	19.1	22.4	20.8	15.6	11.3	6.4	3.0	1.4
9	±0	>0.99	>99	>600	>7128	358	1.33	88:12	18.6	21.0	20.6	15.3	10.9	7.1	4.2	2.3
10	–20	>0.99	>99	>600	>7128	376	1.40	82:18	21.3	19.5	19.7	14.7	10.7	7.3	4.4	2.4
11	–40	>0.99	>99	>600	>7128	370	1.43	79:21	20.6	18.1	19.8	15.1	11.5	7.7	4.7	2.5
12	–60	>0.99	>99	>600	>7128	348	1.41	70:30	26.2	16.3	19.0	14.1	10.6	7.2	4.3	2.3
13	–80	>0.99	>99	>600	>7128	317	1.46	52:48	35.7	15.6	17.5	12.2	8.9	5.6	3.0	1.5

[a] Oligomerization conditions: [**1a**] = [$B(C_6F_5)_3$] = 0.02 mmol; 1-hexane = 1.01 g, 1-hexene/Ti = 600:1; oligomerization time = 5 min (unoptimized); toluene = 10 mL, Protocol = (precat.+ 8 mL toluene + 1-hexene), ($B(C_6F_5)_3$ + 2 mL toluene), then mix them. [b] g oligomer/mol cat·h) [c] Mol of 1-hexene converted (mmol of M)$^{-1}$·h^{-1}. [d] Determined by GPC in THF vs PS standards. [e] Ratio of the signals intensity (R^1)C*H*=C*H*(R^2):(R^3)(R^4)C=CH_2 in oligomer, determined by ^{1}H NMR spectroscopy in $CDCl_3$. [f] Determined by GC.

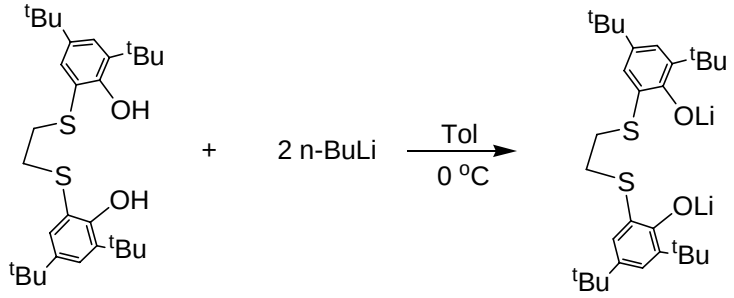
Experimental Section

1 General Procedures

All experiments were carried out under purified argon using standard Schlenk techniques or a glove box (<1 ppm O_2, 1 ppm H_2O). Toluene, *n*-hexane, and THF were distilled under argon from sodium/benzophenone ketyl prior to use. *n*-Pentane was purified by distillation from sodium/triglyme benzophenone ketyl. Chlorinated solvents were distilled from calcium hydride. Deuterated solvents were purchased from Aldrich and purified before use. Complexes (**edtbp**)Ti(CH_2Ph)$_2$ (**2**),[Si] (**edtbp**)Zr(CH_2Ph)$_2$ (**3**),[Sii] (**edtbp**)Hf(CH_2Ph)$_2$ (**4**),[Sii] **edtbp**H_2,[Sii] and 1-^{13}C-labled 1-hexene[Siii] were synthesized according to literature methods. All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on Bruker DRX 400 (^{1}H, 400 MHz; ^{13}C, 101 MHz) and Varian 200 spectrometers in Teflon-valved NMR tubes at 25 °C otherwise stated. ^{1}H and ^{13}C NMR chemical shifts were determined using residual solvent resonances and are reported vs. $SiMe_4$. Assignment of signals was made from ^{1}H-^{13}C HMQC and ^{1}H-^{13}C HMBC 2D NMR experiments. Coupling constants are given in Hertz. Elemental analyses (C, H) were performed by the Microanalytical Laboratory of this department. Molecular weights of Oligomers were determined by gel permeation chromatography (GPC) at room temperature in THF and calibrated with respect to polystyrene standards. The microstructure of oligomer was determined by ^{1}H NMR in $CDCl_3$. GC analyses were carried out on a Shimadzu GC-2010A (FID) with a DB-1 column (60 m, J&W Scientific) and hydrogen carrier gas.

2 Synthesis of Neutral Complex (edtbp)TiMe$_2$ (1a).

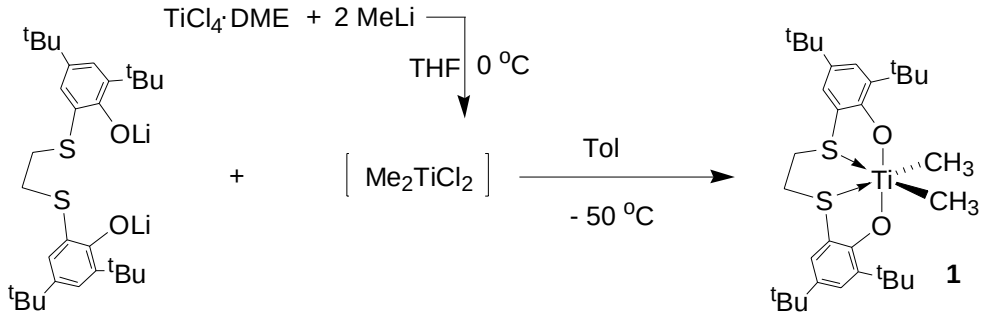
2.1 Synthesis of edtbpLi$_2$



To a solution of ligand 1,4-dithiabutanediyl-bis(4,6-di-*tert*-butylphenol) (**edtbp**H_2) (1.60 g, 3.18 mmol) in toluene (50 mL) was slowly added n-BuLi (2.6 mL, 2.5 M in hexane, 6.4 mmol) at 0 °C. The reaction mixture was warmed to room temperature and further stirred for 5 h. After evaporation of volatile under vacuum, the residue was washed with 40 mL of pentane to give a white powder as **edtbp**Li_2 (1.45 g, 89%). ^{1}H NMR (C_6D_6): δ 7.49 (d, $^4J_{HH}$ = 2.6 Hz, 2 H, Ph-5-*H*), 7.38 (d, $^4J_{HH}$ = 2.6 Hz, 2 H, Ph-3-*H*), 2.76 (d, $^2J_{HH}$ = 10.1 Hz, 2H, SCH_2), 2.34 (d, $^2J_{HH}$ = 10.1 Hz, 2H, SCH_2), 1.44 (s, 18H, C(CH_3)$_3$), 1.31 (s, 18H, C(CH_3)$_3$). ^{1}H NMR ($CDCl_3$): δ 7.17 (d, $^4J_{HH}$ = 2.6 Hz, 2 H, Ph-5-*H*), 7.14 (d, $^4J_{HH}$ = 2.6 Hz, 2 H, Ph-3-*H*), 3.19 (d, $^2J_{HH}$ = 10.0 Hz, 2H, SCH_2), 2.43 (d, $^2J_{HH}$ = 10.0 Hz, 2H, SCH_2), 1.26 (s, 18H, C(CH_3)$_3$), 1.25 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 164.65 (Ph-*C*1), 138.72 (Ph-*C*6), 138.04 (Ph-*C*4), 130.39 (Ph-*C*5), 125.55 (Ph-*C*3), 116.32 (Ph-*C*2), 34.87

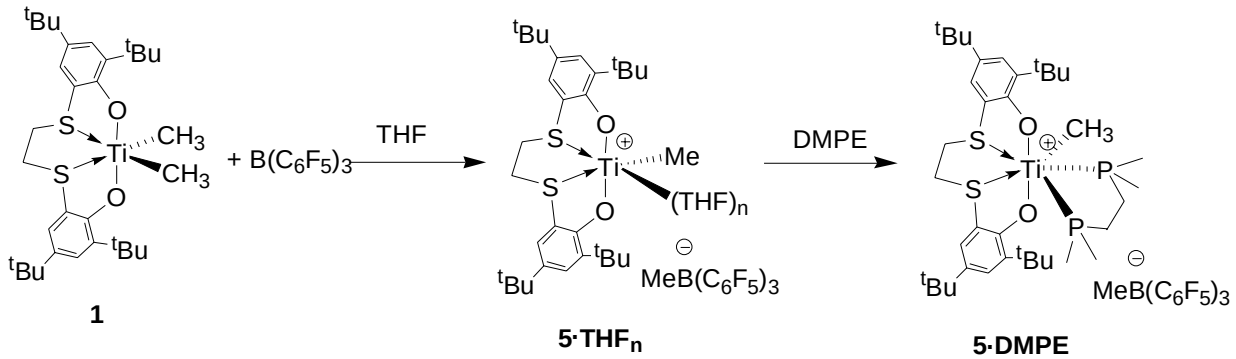
($C(CH_3)_3$), 34.04 ($C(CH_3)_3$), 31.73 ($C(CH_3)_3$), 31.10 (SCH_2), 30.75 ($C(CH_3)_3$). Anal. Calcd for $C_{30}H_{44}Li_2O_2S_2$ (514.68): C, 70.01; H, 8.62. Found: C, 70.54; H, 8.15.

2.2 Synthesis of (edtbp)$TiMe_2$ (1a)



To a 100 mL Schlenk-tube containing a solution of $TiCl_4$·DME (707 mg, 2.52 mmol, DME = 1,2-dimethoxyethane) in THF (30 mL), was added dropwise a solution of MeLi (3.16 mL, 1.6 M in Et_2O, 5.05 mmol) at 0 °C. This orange reaction solution was further stirred for 20 min at 0 °C. Then a solution of **edtbp**Li_2 (1.3 g, 2.52 mmol) in toluene (30 mL) was added dropwise to the orange solution at –50 °C. The reaction mixture was warmed to room temperature and further stirred for 5 h yielding a dark brown solution. The solvent was removed under vacuum, leaving an oily brown residue that was recrystallized with pentane giving brown crystals of (**edtbp)**$TiMe_2$ (**1a**) (1.06 g, 73%). A suitable crystal of (**edtbp)**$TiMe_2$ was selected for X-ray diffraction analysis. ^{1}H NMR ($CDCl_3$): δ 7.38 (d, $^4J_{HH}$ = 2.5 Hz, 2 H, Ph-5-*H*), 7.14 (d, $^4J_{HH}$ = 2.5 Hz, 2 H, Ph-3-*H*), 3.02 (d, $^2J_{HH}$ = 10.1 Hz, 2H, SCH_2), 2.10 (d, $^2J_{HH}$ = 10.1 Hz, 2H, SCH_2), 1.69 (s, 18H, $C(CH_3)_3$), 1.27 (s, 18H, $C(CH_3)_3$), 1.21 (s, 6H, $Ti(CH_3)_2$). ^{1}H NMR (C_6D_6): δ 7.59 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, Ph-5-*H*), 7.16 (2 H, Ph-3-*H*, overlapped with C_6D_6 solvent residue peak), 2.45 (d, $^2J_{HH}$ = 10.0 Hz, 2H, SCH_2), 1.92 (d, $^2J_{HH}$ = 10.0 Hz, 2H, SCH_2), 1.87 (s, 18H, $C(CH_3)_3$), 1.75 (s, 6H, $Ti(CH_3)_2$), 1.23 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.36 (Ph-*C*1), 143.03 (Ph-*C*6), 136.90 (Ph-*C*4), 127.04 (Ph-*C*5), 125.89 (Ph-*C*3), 119.12 (Ph-*C*2), 65.78 ($Ti(CH_3)_2$, $^1J_{CH}$ = 124 Hz), 37.33 (SCH_2), 35.68 ($C(CH_3)_3$), 34.52 ($C(CH_3)_3$), 31.60 ($C(CH_3)_3$), 29.62 ($C(CH_3)_3$). Anal. Calcd for $C_{32}H_{50}O_2S_2Ti$ (578.74): C, 66.41; H, 8.71. Found: C, 66.07; H, 8.62.

3 Synthesis of Cationic Complex [(edtbp)TiMe(L)]$^+$[$MeB(C_6F_5)_3$]$^-$ (L=THF, DMPE) (5·L)



3.1 Generation of Cationic Species [(edtbp)TiMe(THF-d_8)$_2$]$^+$[MeB(C_6F_5)$_3$]$^-$ (5·(THF-d_8)$_2$)

In the glovebox, a Teflon-valved NMR tube was charged with complex (**edtbp**)$TiMe_2$ (20 mg, 0.034 mmol) and $B(C_6F_5)_3$ (17.7 mg, 0.034 mmol), and THF-d_8 was vacuum transferred or CD_2Cl_2 was vacuum transferred in the presence of one drop of THF-d_8 (THF free cationic species was found not stable in CD_2Cl_2 at room temperature). The tube was sealed and NMR spectroscopy was recorded, which revealed quantitative formation of cationic species [(**edtbp**)TiMe(THF-d_8)$_2$]$^+$-[$MeB(C_6F_5)_3$]$^-$ (**5·(THF-d_8)$_2$**). ^{1}H NMR (CD_2Cl_2): δ 7.55 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, Ph-5-*H*), 7.28 (d, $^4J_{HH}$ = 2.5 Hz, 2 H, Ph-3-*H*), 3.36 (d, $^2J_{HH}$ = 10.0 Hz, 2H, SCH_2), 2.51 (d, $^2J_{HH}$ = 10.0 Hz, 2H, SCH_2), 2.15 (s, 3H, TiCH_3), 1.60 (s, 18H, C(CH_3)$_3$), 1.30 (s, 18H, C(CH_3)$_3$). ^{1}H NMR (THF-d_8): δ 7.57 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, Ph-5-*H*), 7.47 (d, $^4J_{HH}$ = 2.5 Hz, 2 H, Ph-3-*H*), 2.12 (s, 3H, TiCH_3), 1.62 (s, 18H, C(CH_3)$_3$), 1.60 (2H, SCH_2, overlapped with C(CH_3)$_3$ peaks), 1.50 (d, $^2J_{HH}$ = 10.0 Hz, 2H, SCH_2), 1.30 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 164.77 (Ph-*C*1), 148.33 (Ph-*C*6), 137.57 (Ph-*C*4), 128.31 (Ph-*C*5), 127.82 (Ph-*C*3), 120.45 (Ph-*C*2), 88.67 (Ti*C*H$_3$), 40.20 (S*C*H$_2$), 35.85 (*C*(CH$_3$)$_3$), 35.21 (*C*(CH$_3$)$_3$), 31.39 (C(*C*H$_3$)$_3$), 29.82 (C(*C*H$_3$)$_3$). NMR data for the free anion $MeB(C_6F_5)_3^-$: ^{1}H NMR (CD_2Cl_2): δ 0.46 (br s, 3H, BCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 148.61 (dm, $^1J_{CF}$ = 231 Hz, *o*-C_6F_5), 137.90 (dm, $^1J_{CF}$ = 231 Hz, *p*-C_6F_5), 136.63 (dm, $^1J_{CF}$ = 250 Hz, *m*-C_6F_5), 130.52 (C_{ipso}), 10.07 (br, B*C*H$_3$). ^{11}B NMR (CD_2Cl_2): δ –14.9 (s, *B*CH$_3$). ^{19}F NMR (CD_2Cl_2): δ –133.1 (d, $^3J_{FF}$ = 19 Hz, 6F, *o*-F), –165.3 (t, $^3J_{FF}$ = 19 Hz, 3F, *p*-F), –167.9 (m, $^3J_{FF}$ = 19 Hz, 6F, *m*-F).

3.2 Generation of Cationic Species [(edtbp)TiMe(THF)$_2$]$^+$[MeB(C_6F_5)$_3$]$^-$ (5·(THF)$_2$)

The same procedure was followed as mentioned above, using THF instead of THF-d_8. ^{1}H NMR (CD_2Cl_2): δ 7.53 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, Ph-5-*H*), 7.26 (d, $^4J_{HH}$ = 2.5 Hz, 2 H, Ph-3-*H*), 4.10 (m, 8H, O(CH_2CH$_2$)$_2$), 3.35 (d, $^2J_{HH}$ = 10.0 Hz, 2H, SCH_2), 2.50 (d, $^2J_{HH}$ = 10.0 Hz, 2H, SCH_2), 2.14 (s, 3H, TiCH_3), 1.98 (m, 8H, O(CH$_2$CH_2)$_2$), 1.58 (s, 18H, C(CH_3)$_3$), 1.29 (s, 18H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 164.79 (Ph-*C*1), 148.36 (Ph-*C*6), 137.59 (Ph-*C*4), 128.33 (Ph-*C*5), 127.84 (Ph-*C*3), 120.47 (Ph-*C*2), 88.80 (Ti*C*H$_3$, J_{CH} = 128 Hz), 72.32 (O(*C*H$_2$CH$_2$)$_2$), 41.36 (S*C*H$_2$), 35.87 (*C*(CH$_3$)$_3$), 35.23 (*C*(CH$_3$)$_3$), 31.41 (C(*C*H$_3$)$_3$), 29.85 (C(*C*H$_3$)$_3$), 26.02 (O(CH$_2$*C*H$_2$)$_2$). NMR spectroscopic data for the anion $MeB(C_6F_5)_3^-$ was the same as those described above.

3.3 Generation of Cationic Species [(edtbp)TiMe(THF)]$^+$[MeB(C_6F_5)$_3$]$^-$ (5·THF)

In the glovebox, a Teflon-valved NMR tube was charged with complex (**edtbp**)$TiMe_2$ (**1**) (20 mg, 0.034 mmol) and $B(C_6F_5)_3$·THF (20.2 mg, 0.034 mmol), and CD_2Cl_2 was vacuum transferred. The tube was sealed and NMR spectroscopy was recorded, which revealed quantitative formation of the ion pair [(**edtbp**)TiMe(THF)]$^+$[$MeB(C_6F_5)_3$]$^-$ (**5·THF**). ^{1}H NMR (CD_2Cl_2): δ 7.54 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, Ph-5-*H*), 7.27 (d, $^4J_{HH}$ = 2.5 Hz, 2 H, Ph-3-*H*), 4.60 (m, 4H, O(CH_2CH$_2$)$_2$), 3.37 (br s, 2H, SCH_2), 2.50 (br s, 2H, SCH_2), 2.22 (m, 4H, O(CH$_2$CH_2)$_2$), 2.19 (s, 3H, TiCH_3), 1.60 (s, 18H, C(CH_3)$_3$), 1.30 (s, 18H,

C(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 164.57 (Ph-*C*1), 148.16 (Ph-*C*6), 137.37 (Ph-*C*4), 128.02 (Ph-*C*5), 127.53 (Ph-*C*3), 120.32 (Ph-*C*2), 88.75 (Ti*C*H$_3$), 78.71 (O(*C*H$_2$CH$_2$)$_2$), 35.38 (S*C*H$_2$), 35.23 (*C*(CH$_3$)$_3$), 34.75 (*C*(CH$_3$)$_3$), 30.92 (C(*C*H$_3$)$_3$), 29.38 (C(*C*H$_3$)$_3$), 25.62 (O(CH$_2$*C*H$_2$)$_2$). NMR spectroscopic data for the free anion MeB(C$_6$F$_5$)$_3^-$ were the same as those described above.

3.4 Synthesis of [(edtbp)TiMe(DMPE)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (DMPE: Me$_2$PCH$_2$CH$_2$PMe$_2$) (5·DMPE)

DMPE (5.1 mg, 0.034 mmol) was added by a microsyringe to a solution of [(**edtbp**)TiMe(THF)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (**5·THF**) in CD_2Cl_2 in an NMR tube. An analytically pure sample [(**edtbp**)TiMe(DMPE)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (**5·DMPE**) was obtained by recrystallization from CH_2Cl_2/pentane; yield 38 mg (90%). ^{1}H NMR (CD_2Cl_2): δ 7.38 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5-*H*), 7.36 (d, $^4J_{HH}$ = 2.5 Hz, 1 H, Ph-5´-*H*), 7.34 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3-*H*), 7.30 (d, $^4J_{HH}$ = 2.5 Hz, 1 H, Ph-3´-*H*), 3.78 (d, $^2J_{HH}$ = 10.0 Hz, 1H, SCH_2), 3.49 (d, $^2J_{HH}$ = 10.0 Hz, 1H, SCH_2), 2.68 (d, $^2J_{HH}$ = 10.0 Hz, 2H, SCH_2), 1.84 (d, $^2J_{PH}$ = 12 Hz, 3H, P(CH_3)$_2$), 1.68 (d, $^2J_{PH}$ = 12 Hz, 3H, P(CH_3)$_2$), 1.63 (d, $^2J_{PH}$ = 12 Hz, 3H, P(CH_3)$_2$), 1.32 (s, 3H, TiCH_3), 1.30 (s, 18H, C(CH_3)$_3$), 1.29 (s, 18H, C(CH_3)$_3$), 1.13 (m, 4H, Me$_2$PCH_2CH_2PMe$_2$), 1.01 (d, $^2J_{PH}$ = 12 Hz, 3 H, P(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 164.21 (Ph-*C*1), 164.12 (Ph-*C*1´), 146.25 (Ph-*C*6), 145.51 (Ph-*C*6´), 136.40 (Ph-*C*4), 136.27 (Ph-*C*4´), 128.49 (Ph-*C*5), 127.38 (Ph-*C*5´), 127.16 (Ph-*C*3), 126.78 (Ph-*C*3´), 121.64 (Ph-*C*2), 120.39 (Ph-*C*2´), 88.62 (Ti*C*H$_3$), 43.72(P*C*H$_2$), 43.38(P*C*H$_2$), 41.14 (S*C*H$_2$), 39.34 (S*C*H$_2$), 35.69 (*C*(CH$_3$)$_3$), 35.51 (*C*(CH$_3$)$_3$), 34.89 (*C*(CH$_3$)$_3$), 34.50 (*C*(CH$_3$)$_3$), 31.50 (C(*C*H$_3$)$_3$), 31.47 (C(*C*H$_3$)$_3$), 30.37 (C(*C*H$_3$)$_3$), 29.58 (C(*C*H$_3$)$_3$), 12.07 (P*C*H$_3$), 11.78 (P*C*H$_3$), 11.65 (P*C*H$_3$), 10.81 (P*C*H$_3$). ^{31}P NMR (CD_2Cl_2): δ 32.78 (s), 19.79 (s). NMR spectroscopic data for the anion MeB(C$_6$F$_5$)$_3^-$ were the same as those described above. Anal. Calcd for $C_{56}H_{66}BF_{15}O_2P_2S_2Ti$ (1240.85): C, 54.20; H, 5.36. Found: C, 54.26; H, 5.02.

4. Typical Oligomerization Procedure

1-Hexene: To a 10 mL flask equipped with a magnetic stirrer, was added the catalyst (0.02 mmol) and 1.5 g 1-hexane, then kept at the desired polymerization temperature. Activator B(C$_6$F$_5$)$_3$ (0.02 mmol) in 1.5 g 1-hexene was rapidly added by syringe. The polymerization was carried out for the specified time period. The reaction was then quenched by addition of acidified methanol (3% HCl, 1 mL). The reaction mixture was dried under vacuum. Oligo(1-hexene)s were purified by passing their hexane solution through a pipette containig silica gel. GC MS analysis of the dimer fraction showed at least 6 isomers, the major product appears to be 4- or 5-dodecene.

Using 1-^{13}C labeled 1-hexene the ^{13}C NMR spectra showed the following labelled peaks (assignment according to Table 3 in ref.[S3]). Mixture obtained from (edtbp)TiMe$_2$ (**1a**) / B(C$_6$F$_5$)$_3$ (Figure 7a): 19.52, 26.55 (^{n}PrCH=CH*C*H$_2$R), 29.86 (^{n}BuCH=CH*C*H$_2$R), 33.57 (^{n}PrCH=CHCH$_2$*C*H$_2$R', $^1J_{CC}$ = 37.1 Hz), 37.50 (^{n}BuCH=CH*C*H$_2$R'), 128.44 (*Z*-^{n}BuCH=*C*HCH$_2$R $^1J_{CC}$ = 43.0 Hz), 130.60 (*E*-^{n}BuCH=*C*HCH$_2$R, $^1J_{CC}$ = 43.0 Hz). Mixture obtained from (edtbp)Zr(CH$_2$Ph)$_2$ (**3**)/ B(C$_6$F$_5$)$_3$ (Figure 7b): 33.48, 36.11, 41.32 (H$_2$C=C(^{n}Bu)(*C*H$_2$R)), 108.3, 110.01 (H$_2$*C*=C(^{n}Bu)(R')).

References

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