Supporting Information (Revised)

Ancillary Ligand Effect on Single-Site Styrene Polymerization: Isospecificity of Group 4 Metal Bis(phenolate) Catalysts

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Experimental Procedures

General. All experiments were performed under argon with standard Schlenk techniques. Solvents were purified, dried and distilled under argon. ^{1}H and ^{13}C NMR: Bruker DRX 400, AC 200 or AM 400. Mass Spectra: Finnigan 8230. Elemental analyses: Microanalytical laboratory of this department. Polymer analysis was performed by NMR on a Bruker ARX 300 instrument using $C_2D_2Cl_4$ as a solvent. For DSC measurements a Seiko DSC 6200 was employed at a heating rate of 10 K/min. Wide angle X-ray scattering (WAXS) experiments were performed on a Siemens D500 powder diffractometer equipped with a temperature controlled sample stage. GPC-measurements were performed in 1,2,4-trichlorobenzene at 140 °C using IR detection and calibration against polystyrene.

1,4-Dithiabutanediyl-2,2'-bis(4,6-di-*tert*-butyl-phenol) (1a). To a solution of 2-mercapto-4,6-di-*tert*-butyl-phenol (1.50 g, 6.3 mmol) in 25 mL of methanol was added NaOH (0.25 g, 6.3 mmol) and the mixture was heated until all NaOH dissolved. After cooling to 0 °C, 1,2-dibromoethane (0.58 g, 3.1 mmol) was slowly added and the mixture refluxed for 1h. After evaporation of the solvent, water was added to dissolve NaBr and the organic phase separated. The aqueous phase was extracted twice with diethyl ether and the combined organic phases were dried over Na_2SO_4. The crude product was recrystallized from acetone/acetonitrile to give

colorless crystals; yield 0.84 g (55%).^{1}H NMR ($CDCl_3$, 25 °C) δ: 1.25 (s, 18 H, $C(CH_3)_3$), 1.38 (s, 18 H, $C(CH_3)_3$), 2.78 (s, 4 H, SCH_2), 7.04 (s, 2 H, OH), 7.29 (d, 2 H, J_{HH} = 2.6 Hz, 3-CH), 7.31 (d, 2 H, J_{HH} = 2.6 Hz, 5-CH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25° C) δ: 28.4 (4-C(CH_3)$_3$), 31.5 (6-C(CH_3)$_3$), 34.3 (6-*C*(CH_3)$_3$), 35.2 (4-*C*(CH_3)$_3$), 36.2 (SCH_2), 117.4 (C2), 126.1 (C3), 130.2 (C5), 135.3 (C6), 142.3 (C4), 153.2 (C1). EI MS: m/z (%) 502 (45, M^+), 265 (100, $C_{16}H_{25}OS^+$), 237 (99, $C_{14}H_{22}OS^+$), 181 (33, $C_{10}H_{14}OS^+$), 56 (76, $C_4H_8^+$). Anal. Calcd. for $C_{30}H_{46}O_2S_2$: C, 71.66; H, 9.22; S, 12.75. Found: C, 71.56; H, 9.23; S, 12.61.

1,5-Dithiapentanediyl-2,2'-bis(4,6-di-*tert*-butyl-phenol)bis(4,6-di-*tert*-butyl-phenol) (1b). This compound was prepared in 28% yield, following a procedure analogous to that to prepare **1a**. ^{1}H NMR ($CDCl_3$, 25° C) δ: 1.28 (s, 18 H, $C(CH_3)_3$), 1.41 (s, 18 H, $C(CH_3)_3$), 1.83 (quint, J_{HH} = 7.1 Hz, 2 H, CH_2), 2.78 (t, J_{HH} = 7.1 Hz, 4 H, SCH_2), 7.05 (s, 2 H, OH), 7.30 (d, J_{HH} = 2.4 Hz, 2 H, 3-CH), 7.32 (d, J_{HH} = 2.4 Hz, 2 H, 5-CH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25° C) δ: 29.3 (6-C(CH_3)$_3$), 29.4 (4-C(CH_3)$_3$), 31.5 (4-*C*(CH_3)$_3$), 34.3 (CH_2), 35.2 (6-*C*(CH_3)$_3$), 35.3 (SCH_2), 118.3 (C-2), 125.8 (C-3), 130.2 (C-5), 135.1 (C-6), 142.2 (C-4), 153.0 (C-1). EI MS: m/z (rel. int. %) 516 (100, M^+), 460 (11, $M^+ - C_4H_8$), 279 (23, $C_{17}H_{27}OS_2^+$), 279 (31, $C_{17}H_{27}OS^+$), 56 (30, $C_4H_8^+$). Anal. Calcd. for $C_{31}H_{48}O_2S_2$: C, 72.04; H, 9.36; S, 12.41. Found C, 72.09; H, 9.39; S, 12.44.

Dichloro{1,4-dithiabutanediyl-2,2'-bis(4,6-di-*tert*-butyl-phenoxy)}titanium (2a). To a solution of **1a** (0.92 g, 1.9 mmol) in 20 mL of toluene was added titanium tetrachloride (0.36 g, 1.9 mmol). The color of the solution immediately changed to red and HCl gas was evolved. The red precipitate was washed with hexane to give red-orange microcrystals; yield 1.12 g (98%). ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 1.29 (s, 18 H, $C(CH_3)_3$), 1.49 (s, 18 H, $C(CH_3)_3$), 2.65 (d, J_{HH} = 10.0 Hz, 2 H, SCH_2), 2.23 (d, J_{HH} = 10.0 Hz, 2 H, SCH_2), 7.27 (d, J_{HH} = 2.3 Hz, 2 H, 3-CH), 7.44 (d, J_{HH} = 2.3 Hz, 2 H, 5-CH). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C) δ: 29.1 (6-*C*(CH_3)$_3$), 31.1 (4-C(CH_3)$_3$),

35.2 (4-C(CH_3)$_3$), 40.7 (SCH_2), 119.5 (C-5), 126.6 (C-3), 127.0 (C-2), 136.5 (C-6), 146.2 (C-4), 166.6 (C-1). EI MS: m/z (%) 620 (100, M^+), 558 (26, $C_{26}H_{35}O_2S_2TiCl_2^+$), 264 ($C_{16}H_{24}OS^+$) 192 (19, $C_{11}H_{12}OS^+$), 92 (10, $C_6H_4O^+$). Anal. Calcd. for $C_{30}H_{44}O_2S_2TiCl_2$ (619.6): C 58.15, H 7.15, S 10.35. Found: C, 57.88; H, 7.25; S, 10.25.

Dichloro{1,5-dithiapentanediyl-2,2'-bis(4,6-di-*tert*-butyl-phenol)}titanium (2b). This compound was prepared in quantitative yield, following a procedure analogous to that to prepare **2a**. ^{1}H NMR (CD_2Cl_2, 30 °C) δ: 1.26 (br s, 18 H, C(CH_3)$_3$), 1.32 (br s, 18 H, C(CH_3)$_3$), 2.20 (br s, 2 H, CH_2), 3.49 (br s, 4 H, SCH_2), 7.10 (br s, 2 H, 3-CH), 7.23 (s, 2 H, 5-CH). ^{1}H NMR (CD_2Cl_2, –60 °C) δ: 1.23, 1.25, 1.26, 1.40 (s, 4 × 9 H, C(CH_3)$_3$), 1.89 (br quart, 1 H, CH_2), 2.65 (br d, 1 H, CH_2), 3.17 (t, J_{HH} = 12.0 Hz, 1 H, SCH_2), 3.52 (br m, 1 H, SCH_2), 3.81 (br d, 1 H, SCH_2), 3.57 (t, J_{HH} = 12.0 Hz, 1 H, SCH_2), 7.09 (s, 1 H, 3-CH), 7.16 (s, 1 H, 3-CH), 7.31 (s, 2 H, 5-CH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 22.1 (6-C(CH_3)$_3$), 29.4 (4-C(CH_3)$_3$), 31.4 (6-C(CH_3)$_3$), 35.0 (CH_2), 35.4 (SCH_2), 118.7 (C-5), 125.1 (C-3), 126.0 (C-2), 136.4 (C-6), 147.1 (C-4), 162.5 (C-1). EI MS: m/z (%) 631 (100, M^+), 616 (29, $C_{30}H_{43}O_2S_2TiCl_2^+$), 581 (15, $C_{30}H_{43}O_2S_2TiCl_2^+$), 56 (29, $C_4H_8^+$). Anal. Calcd. for $C_{31}H_{46}O_2S_2TiCl_2$: C, 58.76; H, 7.32; S, 10.12. Found: C, 59.10; H, 6.30; S, 10.26.

Di(isopropoxy){1,4-dithiabutanediyl-2,2'-bis(4,6-di-*tert*-butyl-phenoxy)}titanium (3a). To a solution of **1a** (0.92 g, 1.9 mmol) in 20 mL of toluene was added titanium tetra(isopropoxide) (0.54 g, 1.9 mmol) at room temperature. The solution became immediately yellow and the reaction mixture was stirred for 2 h. The solvent was removed in vacuo and the yellow residue was washed with hexane; yield 1.22 g (99%). ^{1}H NMR (C_6D_6, 25 °C) δ: 1.23 (s, 18 H, C(CH_3)$_3$), 1.28 (d, J_{HH} = 5.6 Hz, 12 H, CH(CH_3)$_2$), 1.72 (s, 18 H, C(CH_3)$_3$), 2.27 (d, J_{HH} = 9.7 Hz, 2 H, SCH_2), 2.55 (d, J_{HH} = 9.7 Hz, 2 H, SCH_2), 4.85 (sept, J_{HH} = 5.6 Hz, 2 H, CH(CH_3)$_2$), 7.26 (d, J_{HH} = 2.6 Hz, 2 H, 3-CH), 7.53 d, J_{HH} = 2.3 Hz, 2 H, 5-CH). ^{13}C{^{1}H} NMR (C_6D_6, 25

°C) δ: 25.9 (CH(*C*H$_3$)$_2$), 29.5 (6-C(*C*H$_3$)$_3$), 31.5 (4-C(*C*H$_3$)$_3$), 34.2 (6-*C*(CH$_3$)$_3$), 35.5 (SCH$_2$), 37.4 (4-*C*(CH$_3$)$_3$), 79.7 (*C*H(CH$_3$)$_2$), 116.9 (C-5), 126.0 (C-3), 127.2 (C-2), 136.8 (C-6), 140.9 (C-4), 167.5 (C-1). EI MS: m/z (%) 666 (100) (M^+), 608 (13, $C_{33}H_{51}O_3S_2Ti^+$), 549 (4, $C_{30}H_{44}O_2S_2Ti^+$), 503 (4, $M^+ - Ti(OC_3H_7)_3$), 333 (2, $(M/2)^+$). Anal. Calcd. for $C_{36}H_{58}O_4S_2Ti$: C, 64.84; H, 8.76; S, 9.62. Found: C, 64.26; H, 9.50; S, 9.44.

Di(isopropoxy){1,5-dithiapentanediyl-2,2'-bis(4,6-di-*tert*-butyl-phenol)}titanium (3b). This compound was prepared in quantitative yield, following a procedure analogous to that to prepare **3a**. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 1.11 (d, J_{HH} = 6.2 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.26 (s, 18 H, C(CH$_3$)$_3$), 1.44 (s, 18 H, C(CH$_3$)$_3$), 1.62 (quint, J_{HH} = 5.5 Hz, 2 H, CH$_2$), 2.76 (t, J_{HH} = 5.5 Hz, 4 H, SCH$_2$), 4.75 (sept, J_{HH} = 6.2 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.19 (d, 2 H, J_{HH} = 2.0 Hz, 3-CH), 7.23 (d, 2 H, J_{HH} = 2.0 Hz, 5-CH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): 22.7 (6-C(*C*H$_3$)$_3$), 25.7 (CH(*C*H$_3$)$_2$), 29.4 (4-C(*C*H$_3$)$_3$), 31.6 (6-*C*(CH$_3$)$_3$), 34.4 (4-*C*(CH$_3$)$_3$), 35.5 (CH$_2$), 36.5 (SCH$_2$), 79.8 (*C*H(CH$_3$)$_2$), 121.6 (C-5), 124.7 (C-3), 126.7 (C-2), 136.1 (C-6), 141.1 (C-4), 165.2 (C-1). EI MS: m/z (%) 682 (27, M^+), 623 (5, $C_{34}H_{53}O_3S_2Ti^+$), 516 (4, $C_{33}H_{46}O_2S_2^+$), 56 (29, $C_4H_8^+$). Anal. Calcd. for $C_{37}H_{60}O_4S_2Ti$: C, 65.26; H, 8.88; S, 9.42. Found. C, 64.95; H, 8.67; S, 9.37.

Dibenzyl{1,4-dithiabutanediyl-2,2'-bis(4,6-di-*tert*-butyl-phenoxy)}zirconium (4a). To a stirred solution of **1a** (2.2 g, 4.4 mmol) in 20 mL of toluene was added a solution of tetrabenzyl-zirconium (2.0 g, 4.4 mmol) in 10 mL of toluene. The color of the solution became yellow. After stirring for 2 h, the solvent was removed in vacuo and the resulting pale yellow solid washed with hexane to give pale yellow microcrystals in quantitative yield. ^{1}H NMR (C_6D_6, 25 °C) δ: 1.28 (s, 18 H, C(CH$_3$)$_3$), 1.58 (s, 18 H, C(CH$_3$)$_3$), 1.97 (d, J_{HH} = 9.2 Hz, 2 H, CH$_2$Ph), 2.07 (d, J_{HH} = 10.4 Hz 2 H, SCH$_2$), 2.38 (d, J_{HH} = 9.2 Hz, 2 H, CH$_2$Ph), 2.55 (d, J_{HH} = 10.4 Hz, 2 H, SCH$_2$), 6.94 (t, J_{HH} = 7.2 Hz, 2 H), 7.00 (d, J_{HH} = 7.0 Hz, 4 H), 7.1-7.13 (m, 6 H, C$_6$H$_5$), 7.48 (d, J_{HH} = 2.3 Hz, 2 H, 5-CH). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ: 29.7 (C(*C*H$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 34.4 (*C*(CH$_3$)$_3$), 35.4

(SCH_2), 37.9 ($C(CH_3)_3$), 59.5 (CH_2Ph), 120.3 (para $CH_2C_6H_5$), 123.1 (C-2), 126.0 (C-3), 127.8 (meta $CH_2C_6H_5$), 130.3 (ortho $CH_2C_6H_5$), 137.3 (C-4), 142.6 (C-6), 143.6 (ipso $CH_2C_6H_5$), 164.6 (C-1). Anal. Calcd. for $C_{44}H_{58}O_2S_2Zr$: C, 68.25; H, 7.55; S, 8.28. Found: C, 67.50; H, 7.89; S, 8.44.

Dibenzyl{1,4-dithiabutanediyl-2,2'-bis(4,6-di-*tert*-butyl-phenoxy)}hafnium (5a). This compound was prepared in quantitative yield, following a procedure analogous to that to prepare **4a**. ^{1}H NMR (C_6D_6, 25 °C) δ: 1.21 (s, 18 H, $C(CH_3)_3$), 1.62 (s, 18 H, $C(CH_3)_3$), 1.89 (d, J_{HH} = 10.3 Hz, 2 H, SCH_2), 2.33 (d, J_{HH} = 11.2 Hz, 2 H, CH_2Ph), 2.39 (d, J_{HH} = 10.3 Hz, 2 H, SCH_2), 2.54 (d, J_{HH} = 11.2 Hz, 2 H, CH_2Ph), 6.84 (t, J_{HH} = 7.0 Hz, 2 H, 2 H), 7.10-7.16 (m, 8 H, C_6H_5), 7.46 (d, J_{HH} = 2.3 Hz, 2 H, 5-CH). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ: 29.7 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 35.5 ($C(CH_3)_3$), 37.9 (SCH_2), 69.1 (CH_2Ph), 119.3 (C-2), 122.9 (para $CH_2C_6H_5$), 126.3 (C-5), 128.8 (ortho $CH_2C_6H_5$), 129.2 (meta $CH_2C_6H_5$), 138.6 (C-4), 142.8 (C-6), 143.1 (ipso $CH_2C_6H_5$), 164.9 (C-1). Anal. Calcd. for $C_{44}H_{58}O_2S_2Hf$: C, 61.34; H, 6.79; S, 7.44. Found: C, 60.46; H, 7.23; S, 7.74.

General Procedure for Styrene Polymerization. (a) A 100 mL glass reactor was charged sequentially with solid methylaluminoxane, toluene (11 mL), styrene (5 mL, 4.545 g, 43.6 mmol), and 0.01 μmol of catalysts precursor. After 2 h, the reaction mixture was treated with 2 mL of acidified methanol and the polymer filtered. After washing several times with methanol the polymer was dried in vacuo at 70 °C for 16 h or to constant weight. (b) A 500 mL glass reactor was charged with toluene (150 mL), styrene (100 mL, 870 mmol) and of methyl-aluminoxane solution (22.5 mL, 10wt% in toluene). The mixture was heated to 40 °C and the polymerization was started by addition of 25 μmol of catalyst precursor solution. After 2 h, reaction mixture was treated with 10 ml of isopropanol and was poured into acidified methanol (700 mL). the product was filtered off and washed several times with methanol. After drying in

vacuo for 24 h the resulting polymer was extracted with 2-butanone in a Soxhlet-apparatus to remove atactic impurities. ^{1}H NMR ($CDCl_3$, 25 °C) δ: 1.41-1.52 (m, CH_2), 2.09 (m, CH), 6.60 (m, C_6H_5), 7.07 (m, C_6H_5). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C) δ: 40.5 (CH), 42.9 (CH_2), 125.7 (C4), 127.4 (C3, C5), 128.1 (C2, C6), 146.3 (C1).

Preparation of ^{13}C-Enriched Polystyrene. After stirring a mixture of 60 mg of powdery methylaluminoxane (1 mmol), 5.0 mL of toluene, and 1.0 mL of a solution of 0.1 M $Al(CH_3)_3$ (90% ^{13}C-enriched[1]) in hexane for 15 min, a solution of **2a** (6.2 mg, 0.01 mmol) in toluene (1.0 mL) was added followed by 1.0 mL of styrene. The mixture was stirred at room temperature for further 30 min and the polymerization was terminated by adding 1.0 mL of acidified methanol. The polymer was filtered and dried in vacuum at 90° C. The ^{13}C NMR spectrum (Figure S4) was obtained on a AM 400 Bruker operating at 100 MHz in a Fourier transform mode at 298 K. Chemical shifts were referenced to isotopic impurities of deuterated solvent resonance and are reported relative to tetramethylsilane.

Crystal Structure Analysis of 2a and 5b. Relevant crystallographic data for **2b** and **5a** are summarized in Table S1. Single-crystals suitable for X-ray crystal structure analysis were obtained by cooling concentrated pentane solutions of **2b** and **5a** to –30 °C. Data collections were performed using ω scans on a Bruker AXS diffractometer with graphite-monochromated Mo-Kα radiation at 189(2) K (**2b**) and 203(2) K (**5a**). The data collection as well as the data reduction and correction for absorption was carried out using the program system SMART.[2a] The structures were solved using the program SHELXS-86.[2b] From the measured reflections, all independent reflections were used, and the parameters were refined by full-matrix least-squares against all F_o^2 data (SHELXL-97)[2c] and refined with anisotropic thermal parameters. For the graphical representation, ORTEP-III for Windows was used as implemented in the program system WINGX.[2d]

(1) Zambelli, A.; Ammendola, P.; Grassi, A.; Longo P.; Proto, A. *Macromolecules* **1986**, *19*, 2703.

(2) (a) Siemens. *ASTRO, SAINT and SADABS. Data Collection and Processing Software for the SMART System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1996. (b) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986. (c) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997. (d) Farrugia, L. J. WinGX – Version 1.64.02, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-crystal X-Ray Diffraction Data, *J. Appl. Cryst.* **1999**, *32*, 837.

Table S1. Experimental Data for the Crystal Structure Determinations of the Complexes **2b** and **5a**.

	2b	**5a**
	Crystal Data	
Formula	$C_{31}H_{46}Cl_2O_2S_2Ti \cdot C_7H_8$	$C_{44}H_{58}O_2S_2Hf \cdot 0.25\ C_5H_{12}$
Fw	725.73	879.61
cryst color	red	yellow
cryst size, mm	$0.893 \times 0.816 \times 0.473$	$0.674 \times 0.376 \times 0.099$
cryst system	orthorhombic	triclinic
space group	Pbca (no. 61)	P-1 (no. 2)
A ,Å	20.690(1)	9.4231(9)
B, Å	15.129(1)	15.756(2)
C, Å	25.412(2)	16.518(2)
α, deg	90	105.606(2)
β, deg	90	101.753(2)
γ, deg	90	102.119(2)
V, Å^3	7954.4(9)	2219.5(4)

Z	8	2
ρ_{calcd}, g cm^{-3}	1.212	1.316
μ, mm^{-1}	0.484	2.477
F(000)	3088	905
	Data collection	
$2\theta_{max}$, deg	5.38 to 56.64	5.14 to 56.68
index ranges	h, –27 to 27;	h, –11 to 12;
	k, –20 to 19;	k, –21 to 20;
	l, –33 to 33	l, –22 to 15
no. of rflns measd	70073	13853
no. of indep rflns	9865 [R_{int} = 0.1182]	10247 [R_{int} = 0.0278]
no. of obs. rflns [$I > 2\ \sigma(I)$]	6231	9258
no. of parameters	419	501
GOF	1.035	1.033
final R indices R_1, wR_2 (obsd data)	0.0475, 0.1158	0.0321, 0.0849
final R indices R_1, wR_2 (all data)	0.0947, 0.1416	0.0364, 0.0872
largest e-max, e-min,e•Å^{-3}	0.731 / –0.508	2.095 / –1.955

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ti	1530.2(2)	7149.3(3)	4810.8(2)	24.0(1)
S(1)	1428.5(3)	8371.5(4)	5527.2(3)	29.2(2)
S(2)	2187.6(3)	8361.7(5)	4339.2(3)	31.5(2)
O(1)	1054.3(9)	6640(1)	5337.9(7)	26.5(4)
O(2)	910.4(8)	7842(1)	4487.5(7)	25.9(4)
Cl(1)	1579.8(4)	6085.3(5)	4175.1(3)	37.2(2)
Cl(2)	2543.5(4)	6843.1(5)	5172.3(3)	37.1(2)
C(1)	1259(1)	7616(2)	6043(1)	27(1)
C(2)	1029(1)	6800(2)	5870(1)	25(1)
C(3)	780(1)	6185(2)	6226(1)	28(1)
C(4)	820(1)	6419(2)	6757(1)	32(1)
C(5)	1071(1)	7216(2)	6941(1)	32(1)
C(6)	1281(1)	7826(2)	6572(1)	32(1)
C(7)	469(2)	5316(2)	6039(1)	35(1)
C(8)	951(2)	4761(2)	5720(1)	45(1)
C(9)	241(2)	4743(2)	6504(1)	59(1)
C(10)	-124(2)	5544(2)	5699(1)	49(1)
C(11)	1113(2)	7432(2)	7534(1)	43(1)
C(12A)	1841(4)	7726(6)	7667(3)	51(2)
C(13A)	645(4)	8131(5)	7673(3)	49(2)
C(14A)	982(5)	6608(7)	7878(4)	66(3)
C(12B)	1770(4)	7411(6)	7724(4)	54(2)
C(13B)	728(5)	6760(7)	7868(4)	70(3)
C(14B)	842(4)	8421(6)	7630(3)	56(2)
C(15)	2191(2)	8889(2)	5691(1)	40(1)
C(16)	2385(2)	9488(2)	5233(1)	43(1)
C(17)	2702(1)	9031(2)	4765(1)	41(1)
C(18)	1521(1)	9055(2)	4186(1)	28(1)
C(19)	920(1)	8667(2)	4279(1)	25(1)
C(20)	349(1)	9125(2)	4150(1)	26(1)
C(21)	431(1)	9951(2)	3918(1)	29(1)
C(22)	1031(1)	10348(2)	3816(1)	29(1)
C(23)	1584(1)	9886(2)	3958(1)	31(1)
C(24)	-319(1)	8734(2)	4274(1)	32(1)
C(25)	-379(2)	8572(3)	4867(1)	57(1)
C(26)	-416(2)	7854(2)	3983(1)	43(1)
C(27)	-864(2)	9353(2)	4105(2)	56(1)
C(28)	1076(2)	11241(2)	3525(1)	37(1)
C(29)	519(2)	11850(3)	3667(2)	72(1)
C(30)	1706(2)	11696(3)	3625(3)	114(3)
C(31)	1023(3)	11041(3)	2934(2)	84(2)
C(32)	1804(3)	4198(4)	2559(2)	82(1)
C(33)	2271(3)	4817(3)	2425(2)	89(2)
C(34)	2606(3)	4733(5)	1980(2)	99(2)
C(35)	2482(3)	4046(4)	1650(2)	87(2)
C(36)	2020(3)	3431(5)	1767(3)	108(2)
C(37)	1670(3)	3533(4)	2229(3)	98(2)
C(38)	1472(4)	4287(5)	3059(3)	154(3)

Table S3. Bond lengths [Å] and angles [°] for **2b**.

Ti-O(1)	1.8324(18)
Ti-O(2)	1.8483(18)
Ti-Cl(1)	2.2828(8)
Ti-Cl(2)	2.3353(9)
Ti-S(2)	2.5789(8)
Ti-S(1)	2.6035(8)
S(1)-C(1)	1.774(3)
S(1)-C(15)	1.809(3)
S(2)-C(18)	1.776(3)
S(2)-C(17)	1.824(3)
O(1)-C(2)	1.374(3)
O(2)-C(19)	1.356(3)
C(1)-C(6)	1.383(4)
C(1)-C(2)	1.394(4)
C(2)-C(3)	1.396(4)
C(3)-C(4)	1.399(4)
C(3)-C(7)	1.539(4)
C(4)-C(5)	1.393(4)
C(5)-C(6)	1.387(4)
C(5)-C(11)	1.545(4)
C(7)-C(8)	1.534(4)
C(7)-C(10)	1.538(5)
C(7)-C(9)	1.540(4)
C(11)-C(12B)	1.443(10)
C(11)-C(13A)	1.476(8)
C(11)-C(13B)	1.545(11)
C(11)-C(14A)	1.546(10)
C(11)-C(12A)	1.607(9)
C(11)-C(14B)	1.615(9)
C(15)-C(16)	1.528(4)
C(16)-C(17)	1.525(5)
C(18)-C(23)	1.391(4)
C(18)-C(19)	1.395(4)
C(19)-C(20)	1.409(4)
C(20)-C(21)	1.392(4)
C(20)-C(24)	1.536(4)
C(21)-C(22)	1.403(4)
C(22)-C(23)	1.389(4)
C(22)-C(28)	1.543(4)
C(24)-C(27)	1.527(4)
C(24)-C(25)	1.531(4)
C(24)-C(26)	1.536(4)
C(28)-C(30)	1.496(5)
C(28)-C(29)	1.518(5)
C(28)-C(31)	1.535(5)
C(32)-C(37)	1.340(8)
C(32)-C(33)	1.388(7)
C(32)-C(38)	1.449(8)
C(33)-C(34)	1.331(7)
C(34)-C(35)	1.360(8)
C(35)-C(36)	1.367(9)
C(36)-C(37)	1.389(9)
O(1)-Ti-O(2)	100.97(8)
O(1)-Ti-Cl(1)	104.18(6)

Table S3. Bond lengths [Å] and angles [°] for **2b**. (continued)

O(2)-Ti-Cl(1)	96.67(6)
O(1)-Ti-Cl(2)	96.40(6)
O(2)-Ti-Cl(2)	155.52(6)
Cl(1)-Ti-Cl(2)	95.63(3)
O(1)-Ti-S(2)	157.25(6)
O(2)-Ti-S(2)	75.90(6)
Cl(1)-Ti-S(2)	98.57(3)
Cl(2)-Ti-S(2)	81.40(3)
O(1)-Ti-S(1)	75.17(6)
O(2)-Ti-S(1)	81.51(6)
Cl(1)-Ti-S(1)	177.87(3)
Cl(2)-Ti-S(1)	86.47(3)
S(2)-Ti-S(1)	82.09(3)
C(1)-S(1)-C(15)	106.36(13)
C(1)-S(1)-Ti	94.31(9)
C(15)-S(1)-Ti	113.44(11)
C(18)-S(2)-C(17)	104.80(14)
C(18)-S(2)-Ti	96.43(9)
C(17)-S(2)-Ti	115.28(10)
C(2)-O(1)-Ti	131.70(16)
C(19)-O(2)-Ti	133.23(16)
C(6)-C(1)-C(2)	121.5(2)
C(6)-C(1)-S(1)	124.3(2)
C(2)-C(1)-S(1)	113.86(19)
O(1)-C(2)-C(1)	117.0(2)
O(1)-C(2)-C(3)	122.3(2)
C(1)-C(2)-C(3)	120.7(2)
C(2)-C(3)-C(4)	115.8(3)
C(2)-C(3)-C(7)	121.6(2)
C(4)-C(3)-C(7)	122.6(2)
C(5)-C(4)-C(3)	124.4(3)
C(6)-C(5)-C(4)	117.8(2)
C(6)-C(5)-C(11)	120.1(3)
C(4)-C(5)-C(11)	122.2(3)
C(1)-C(6)-C(5)	119.7(3)
C(8)-C(7)-C(10)	110.2(3)
C(8)-C(7)-C(3)	111.0(2)
C(10)-C(7)-C(3)	108.3(2)
C(8)-C(7)-C(9)	107.2(3)
C(10)-C(7)-C(9)	108.3(3)
C(3)-C(7)-C(9)	111.8(3)
C(12B)-C(11)-C(13A)	123.7(5)
C(12B)-C(11)-C(5)	111.9(4)
C(13A)-C(11)-C(5)	110.4(4)
C(12B)-C(11)-C(13B)	106.7(6)
C(13A)-C(11)-C(13B)	90.1(6)
C(5)-C(11)-C(13B)	111.5(5)
C(12B)-C(11)-C(14A)	87.6(6)
C(13A)-C(11)-C(14A)	109.2(6)
C(5)-C(11)-C(14A)	111.7(4)
C(13B)-C(11)-C(14A)	21.4(5)
C(12B)-C(11)-C(12A)	18.6(5)
C(13A)-C(11)-C(12A)	111.5(5)
C(5)-C(11)-C(12A)	108.4(4)
C(13B)-C(11)-C(12A)	123.4(6)
C(14A)-C(11)-C(12A)	105.6(5)

Table S3. Bond lengths [A] and angles [°] for **2b**. (continued)

C(12B)-C(11)-C(14B)	107.3(5)
C(13A)-C(11)-C(14B)	22.2(4)
C(5)-C(11)-C(14B)	108.9(4)
C(13B)-C(11)-C(14B)	110.4(6)
C(14A)-C(11)-C(14B)	127.0(6)
C(12A)-C(11)-C(14B)	92.1(5)
C(16)-C(15)-S(1)	108.1(2)
C(17)-C(16)-C(15)	116.0(3)
C(16)-C(17)-S(2)	117.7(2)
C(23)-C(18)-C(19)	122.4(2)
C(23)-C(18)-S(2)	123.5(2)
C(19)-C(18)-S(2)	113.98(19)
O(2)-C(19)-C(18)	117.8(2)
O(2)-C(19)-C(20)	122.1(2)
C(18)-C(19)-C(20)	120.0(2)
C(21)-C(20)-C(19)	116.0(2)
C(21)-C(20)-C(24)	122.8(2)
C(19)-C(20)-C(24)	121.2(2)
C(20)-C(21)-C(22)	124.7(2)
C(23)-C(22)-C(21)	117.8(2)
C(23)-C(22)-C(28)	121.0(3)
C(21)-C(22)-C(28)	121.1(2)
C(22)-C(23)-C(18)	119.0(3)
C(27)-C(24)-C(25)	108.4(3)
C(27)-C(24)-C(20)	111.8(2)
C(25)-C(24)-C(20)	109.7(2)
C(27)-C(24)-C(26)	107.5(3)
C(25)-C(24)-C(26)	108.9(3)
C(20)-C(24)-C(26)	110.6(2)
C(30)-C(28)-C(29)	110.0(4)
C(30)-C(28)-C(31)	108.6(4)
C(29)-C(28)-C(31)	107.3(3)
C(30)-C(28)-C(22)	112.0(3)
C(29)-C(28)-C(22)	111.8(3)
C(31)-C(28)-C(22)	107.0(3)
C(37)-C(32)-C(33)	119.8(5)
C(37)-C(32)-C(38)	121.3(7)
C(33)-C(32)-C(38)	118.9(7)
C(34)-C(33)-C(32)	120.4(6)
C(33)-C(34)-C(35)	119.9(6)
C(34)-C(35)-C(36)	121.3(6)
C(35)-C(36)-C(37)	118.2(6)
C(32)-C(37)-C(36)	120.3(6)

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2b**. The anisotropic displacement factor exponent takes the form:$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ti	28.2(2)	19.7(2)	24.1(2)	4.8(2)	0.6(2)	-1.5(2)
S(1)	37.4(4)	18.5(3)	31.6(3)	1.9(3)	-4.6(3)	-2.7(3)
S(2)	23.4(3)	28.7(3)	42.4(4)	14.5(3)	3.1(3)	2.7(3)
O(1)	37(1)	21.7(9)	21.1(9)	1.1(7)	1.2(8)	-6.9(8)
O(2)	25.4(9)	25.5(9)	26.8(9)	6.6(8)	0.4(7)	-1.3(7)
Cl(1)	47.1(4)	31.8(4)	32.7(4)	-3.5(3)	3.0(3)	1.2(3)
Cl(2)	34.8(4)	27.1(3)	49.5(4)	9.9(3)	-8.4(3)	2.8(3)
C(1)	31(1)	24(1)	28(1)	2(1)	2(1)	0(1)
C(2)	29(1)	25(1)	21(1)	1(1)	0(1)	2(1)
C(3)	27(1)	28(1)	29(1)	3(1)	3(1)	-1(1)
C(4)	35(2)	38(2)	24(1)	6(1)	5(1)	4(1)
C(5)	34(2)	40(2)	23(1)	-3(1)	1(1)	7(1)
C(6)	36(2)	29(1)	31(1)	-6(1)	-3(1)	4(1)
C(7)	41(2)	30(2)	33(2)	4(1)	9(1)	-11(1)
C(8)	63(2)	26(2)	46(2)	1(1)	10(2)	-6(2)
C(9)	84(3)	47(2)	45(2)	8(2)	17(2)	-28(2)
C(10)	39(2)	55(2)	52(2)	-6(2)	4(2)	-19(2)
C(11)	51(2)	53(2)	24(1)	-4(1)	0(1)	10(2)
C(15)	47(2)	28(2)	45(2)	3(1)	-13(1)	-12(1)
C(16)	43(2)	25(2)	62(2)	12(1)	-15(2)	-12(1)
C(17)	26(2)	36(2)	63(2)	21(2)	-8(1)	-7(1)
C(18)	24(1)	30(1)	30(1)	8(1)	0(1)	5(1)
C(19)	31(1)	24(1)	19(1)	1(1)	1(1)	0(1)
C(20)	24(1)	26(1)	27(1)	-5(1)	0(1)	2(1)
C(21)	30(1)	25(1)	33(2)	-1(1)	-6(1)	4(1)
C(22)	35(2)	26(1)	28(1)	6(1)	-2(1)	3(1)
C(23)	27(1)	31(1)	34(2)	10(1)	0(1)	-1(1)
C(24)	26(1)	30(1)	39(2)	-7(1)	3(1)	-2(1)
C(25)	43(2)	82(3)	48(2)	-11(2)	19(2)	-15(2)
C(26)	37(2)	34(2)	59(2)	-10(2)	-6(2)	-3(1)
C(27)	26(2)	36(2)	105(3)	-3(2)	1(2)	4(1)
C(28)	38(2)	30(2)	44(2)	14(1)	-5(1)	2(1)
C(29)	91(3)	38(2)	88(3)	25(2)	27(3)	26(2)
C(30)	81(3)	54(3)	207(6)	76(4)	-71(4)	-33(2)
C(31)	148(5)	57(3)	48(2)	25(2)	18(3)	14(3)
C(32)	80(3)	88(4)	78(3)	22(3)	15(3)	25(3)
C(33)	100(4)	72(3)	95(4)	3(3)	-13(3)	-1(3)
C(34)	92(4)	113(5)	93(4)	25(4)	-11(3)	16(4)
C(35)	71(3)	112(5)	78(3)	-1(3)	-16(3)	35(3)
C(36)	97(5)	107(5)	119(5)	-22(4)	-52(4)	30(4)
C(37)	89(4)	70(3)	134(5)	11(4)	-47(4)	-3(3)
C(38)	179(8)	146(7)	137(6)	26(5)	54(5)	64(6)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **2b**.

	x	y	z	U(eq)
H(4)	670	6015	7005	39
H(6)	1436	8374	6680	38
H(8A)	1083	5085	5414	67
H(8B)	750	4218	5615	67
H(8C)	1323	4634	5934	67
H(9A)	50	4208	6373	88
H(9B)	-72	5063	6706	88
H(9C)	605	4599	6723	88
H(10A)	12	5880	5398	73
H(10B)	-423	5887	5903	73
H(10C)	-329	5009	5585	73
H(12A)	1945	8254	7474	77
H(12B)	2133	7262	7568	77
H(12C)	1880	7839	8037	77
H(13A)	695	8285	8037	73
H(13B)	213	7919	7613	73
H(13C)	721	8642	7458	73
H(14A)	1294	6159	7797	98
H(14B)	555	6388	7806	98
H(14C)	1015	6765	8243	98
H(12D)	2035	7779	7505	81
H(12E)	1928	6815	7713	81
H(12F)	1783	7625	8079	81
H(13D)	886	6175	7800	105
H(13E)	278	6793	7777	105
H(13F)	781	6896	8235	105
H(14D)	886	8572	7995	84
H(14E)	395	8447	7531	84
H(14F)	1086	8831	7420	84
H(15A)	2146	9234	6011	48
H(15B)	2519	8442	5748	48
H(16A)	2001	9793	5109	52
H(16B)	2681	9933	5366	52
H(17A)	3044	8655	4898	50
H(17B)	2904	9483	4549	50
H(21)	61	10263	3824	35
H(23)	1991	10129	3901	37
H(25A)	-324	9121	5051	86
H(25B)	-52	8162	4977	86
H(25C)	-798	8332	4943	86
H(26A)	-830	7611	4073	65
H(26B)	-82	7447	4084	65
H(26C)	-396	7953	3610	65
H(27A)	-822	9907	4286	84
H(27B)	-1273	9090	4190	84
H(27C)	-839	9452	3732	84
H(29A)	535	11983	4036	109
H(29B)	117	11564	3587	109
H(29C)	553	12387	3468	109
H(30A)	1736	11853	3990	171

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **2b**. (continued)

H(30B)	1731	12221	3413	171
H(30C)	2055	11307	3535	171
H(31A)	1009	11586	2741	127
H(31B)	635	10711	2868	127
H(31C)	1391	10702	2824	127
H(33)	2351	5293	2647	107
H(34)	2924	5143	1895	119
H(35)	2716	3995	1339	104
H(36)	1943	2956	1543	129
H(37)	1339	3139	2309	118
H(38A)	1053	4017	3035	231
H(38B)	1424	4902	3143	231
H(38C)	1719	4000	3329	231

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(2)	4684.8(9)	2965.3(5)	3775.1(5)	28.9(2)
S(1)	4392.8(9)	3058.3(5)	1694.5(6)	31.5(2)
O(2)	2472(2)	1368(1)	2502(1)	27.9(4)
O(1)	2468(2)	3862(1)	2667(1)	26.4(4)
Hf	1953.1(1)	2517.9(7)	2458.30(8)	23.94(5)
C(1)	3363(3)	4493(2)	2431(2)	24.7(6)
C(2)	4418(3)	4240(2)	1995(2)	26.4(6)
C(3)	5384(4)	4869(2)	1753(2)	30.0(6)
C(4)	5314(4)	5767(2)	1936(2)	29.9(6)
C(5)	4219(4)	6002(2)	2340(2)	29.9(6)
C(6)	3231(4)	5399(2)	2599(2)	27.6(8)
C(7)	6358(4)	6478(2)	1677(3)	37.6(8)
C(8A)	5487(11)	6717(8)	955(7)	61(3)
C(9A)	7666(13)	6156(9)	1398(10)	67(3)
C(10A)	7153(16)	7374(8)	2512(7)	85(4)
C(8B)	5897(12)	6096(9)	607(7)	71(3)
C(9B)	7955(11)	6473(9)	1974(8)	59(3)
C(10B)	6133(19)	7422(7)	1988(13)	101(6)
C(11)	2085(4)	5703(2)	3068(2)	32.0(7)
C(12)	476(4)	5067(2)	2591(3)	38.5(8)
C(13)	2552(5)	5692(3)	4008(2)	46.4(9)
C(14)	2020(5)	6673(2)	3089(3)	52(1)
C(15)	6121(4)	3077(2)	2450(3)	40.0(8)
C(16)	6220(4)	3502(2)	3399(3)	40.7(9)
C(17)	4821(3)	1819(2)	3576(2)	26.1(6)
C(18)	3618(3)	1128(2)	2931(2)	25.0(6)
C(19)	3627(3)	198(2)	2758(2)	25.3(6)
C(20)	4871(4)	33(2)	3241(2)	28.8(6)
C(21)	6073(3)	715(2)	3897(2)	27.7(6)
C(22)	6035(3)	1619(2)	4063(2)	27.9(6)
C(23)	2296(4)	-577(2)	2090(2)	33.9(7)
C(24)	882(5)	-588(3)	2419(3)	52(1)
C(25)	1989(5)	-444(3)	1195(2)	49(1)
C(26)	2600(6)	-1512(2)	1969(3)	63(1)
C(27)	7408(4)	451(2)	4387(2)	31.7(7)
C(28)	8291(4)	119(3)	3736(3)	44.2(9)
C(29)	6815(5)	-336(3)	4733(3)	52(1)
C(30)	8480(4)	1261(3)	5157(3)	45.1(9)
C(31)	689(4)	1936(2)	1033(2)	33.3(7)
C(32)	-77(4)	2568(2)	709(2)	29.0(6)
C(33)	630(4)	3185(2)	338(2)	37.5(7)
C(34)	-90(5)	3767(3)	33(3)	44.7(9)
C(35)	-1530(5)	3760(3)	87(3)	46.4(9)
C(36)	-2249(4)	3169(3)	455(2)	39.7(8)
C(37)	-1528(4)	2583(2)	762(2)	33.1(7)
C(38)	-136(4)	2307(2)	2916(2)	36.5(7)
C(39)	645(4)	2715(2)	3863(2)	34.2(7)
C(40)	1544(4)	2273(3)	4309(3)	40.9(8)
C(41)	2390(5)	2710(3)	5175(3)	55(1)

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. (continued)

	x	y	z	U(eq)
C(42)	2379(6)	3562(3)	5624(3)	62(1)
C(43)	1476(6)	4013(3)	5200(3)	57(1)
C(44)	651(4)	3599(3)	4343(3)	42.7(8)
C(45)	3168(16)	453(10)	-1077(9)	71(6)
C(46)	4247(16)	669(10)	-194(9)	48(4)
C(47)	4794(18)	-74(12)	-124(11)	35(3)
C(48)	6039(18)	6(11)	655(10)	45(3)
C(49)	6850(20)	-698(14)	740(14)	57(5)

Table S7. Bond lengths [Å] and angles [°] for **5a**.

S(2)-C(17)	1.783(3)
S(2)-C(16)	1.825(4)
S(2)-Hf	2.8260(8)
S(1)-C(2)	1.787(3)
S(1)-C(15)	1.828(4)
S(1)-Hf	2.9222(9)
O(2)-C(18)	1.347(3)
O(2)-Hf	1.989(2)
O(1)-C(1)	1.357(3)
O(1)-Hf	1.987(2)
Hf-C(38)	2.242(4)
Hf-C(31)	2.245(3)
Hf-C(39)	2.817(3)
C(1)-C(2)	1.403(4)
C(1)-C(6)	1.417(4)
C(2)-C(3)	1.398(4)
C(3)-C(4)	1.384(4)
C(4)-C(5)	1.397(5)
C(4)-C(7)	1.540(4)
C(5)-C(6)	1.401(4)
C(6)-C(11)	1.535(4)
C(7)-C(9B)	1.487(11)
C(7)-C(8A)	1.487(9)
C(7)-C(10B)	1.511(11)
C(7)-C(9A)	1.535(11)
C(7)-C(10A)	1.595(10)
C(7)-C(8B)	1.637(12)
C(11)-C(13)	1.531(5)
C(11)-C(14)	1.535(5)
C(11)-C(12)	1.541(5)
C(15)-C(16)	1.505(6)
C(17)-C(18)	1.404(4)
C(17)-C(22)	1.404(4)
C(18)-C(19)	1.418(4)
C(19)-C(20)	1.391(4)
C(19)-C(23)	1.533(4)
C(20)-C(21)	1.405(4)
C(21)-C(22)	1.385(4)
C(21)-C(27)	1.548(4)
C(23)-C(25)	1.527(5)
C(23)-C(26)	1.528(5)
C(23)-C(24)	1.536(6)
C(27)-C(30)	1.527(5)
C(27)-C(28)	1.539(5)
C(27)-C(29)	1.548(5)
C(31)-C(32)	1.493(4)
C(32)-C(37)	1.392(5)
C(32)-C(33)	1.407(5)
C(33)-C(34)	1.387(5)
C(34)-C(35)	1.377(6)
C(35)-C(36)	1.380(6)
C(36)-C(37)	1.395(5)
C(38)-C(39)	1.480(5)
C(39)-C(44)	1.404(5)

Table S7. Bond lengths [Å] and angles [°] for **5a**. (continued)

C(39)-C(40)	1.420(5)
C(40)-C(41)	1.389(6)
C(41)-C(42)	1.350(7)
C(42)-C(43)	1.414(7)
C(43)-C(44)	1.369(6)
C(45)-C(46)	1.5020
C(46)-C(47)	1.40(2)
C(47)-C(48)	1.51(2)
C(48)-C(49)	1.49(2)
C(17)-S(2)-C(16)	102.90(16)
C(17)-S(2)-Hf	96.07(10)
C(16)-S(2)-Hf	108.11(12)
C(2)-S(1)-C(15)	102.80(16)
C(2)-S(1)-Hf	94.40(11)
C(15)-S(1)-Hf	105.74(12)
C(18)-O(2)-Hf	137.67(19)
C(1)-O(1)-Hf	138.32(19)
O(1)-Hf-O(2)	153.06(9)
O(1)-Hf-C(38)	100.68(11)
O(2)-Hf-C(38)	98.94(11)
O(1)-Hf-C(31)	102.49(11)
O(2)-Hf-C(31)	94.23(10)
C(38)-Hf-C(31)	94.30(13)
O(1)-Hf-C(39)	91.22(9)
O(2)-Hf-C(39)	96.00(10)
C(38)-Hf-C(39)	31.49(11)
C(31)-Hf-C(39)	125.77(11)
O(1)-Hf-S(2)	84.13(6)
O(2)-Hf-S(2)	70.90(6)
C(38)-Hf-S(2)	114.82(9)
C(31)-Hf-S(2)	148.62(9)
C(39)-Hf-S(2)	84.12(7)
O(1)-Hf-S(1)	70.07(7)
O(2)-Hf-S(1)	92.59(7)
C(38)-Hf-S(1)	167.55(9)
C(31)-Hf-S(1)	80.07(9)
C(39)-Hf-S(1)	151.80(7)
S(2)-Hf-S(1)	73.41(3)
O(1)-C(1)-C(2)	119.5(3)
O(1)-C(1)-C(6)	121.3(3)
C(2)-C(1)-C(6)	119.2(3)
C(3)-C(2)-C(1)	121.7(3)
C(3)-C(2)-S(1)	120.9(2)
C(1)-C(2)-S(1)	117.2(2)
C(4)-C(3)-C(2)	120.3(3)
C(3)-C(4)-C(5)	117.5(3)
C(3)-C(4)-C(7)	121.7(3)
C(5)-C(4)-C(7)	120.8(3)
C(4)-C(5)-C(6)	124.4(3)
C(5)-C(6)-C(1)	116.9(3)
C(5)-C(6)-C(11)	122.2(3)
C(1)-C(6)-C(11)	120.9(3)

Table S7. Bond lengths [Å] and angles [°] for **5a**. (continued)

C(9B)-C(7)-C(8A)	134.4(6)
C(9B)-C(7)-C(10B)	113.1(9)
C(8A)-C(7)-C(10B)	67.6(9)
C(9B)-C(7)-C(9A)	34.6(6)
C(8A)-C(7)-C(9A)	108.7(7)
C(10B)-C(7)-C(9A)	132.0(7)
C(9B)-C(7)-C(4)	110.3(4)
C(8A)-C(7)-C(4)	110.7(4)
C(10B)-C(7)-C(4)	112.1(5)
C(9A)-C(7)-C(4)	113.4(5)
C(9B)-C(7)-C(10A)	73.7(8)
C(8A)-C(7)-C(10A)	110.2(7)
C(10B)-C(7)-C(10A)	44.8(8)
C(9A)-C(7)-C(10A)	104.9(8)
C(4)-C(7)-C(10A)	108.9(4)
C(9B)-C(7)-C(8B)	105.9(7)
C(8A)-C(7)-C(8B)	43.9(6)
C(10B)-C(7)-C(8B)	109.9(9)
C(9A)-C(7)-C(8B)	71.9(7)
C(4)-C(7)-C(8B)	105.1(4)
C(10A)-C(7)-C(8B)	143.7(6)
C(13)-C(11)-C(6)	108.6(3)
C(13)-C(11)-C(14)	109.0(3)
C(6)-C(11)-C(14)	111.7(3)
C(13)-C(11)-C(12)	110.4(3)
C(6)-C(11)-C(12)	111.0(3)
C(14)-C(11)-C(12)	106.2(3)
C(16)-C(15)-S(1)	113.9(2)
C(15)-C(16)-S(2)	115.6(2)
C(18)-C(17)-C(22)	122.0(3)
C(18)-C(17)-S(2)	116.3(2)
C(22)-C(17)-S(2)	121.7(2)
O(2)-C(18)-C(17)	118.8(3)
O(2)-C(18)-C(19)	121.8(3)
C(17)-C(18)-C(19)	119.4(3)
C(20)-C(19)-C(18)	116.7(3)
C(20)-C(19)-C(23)	122.6(3)
C(18)-C(19)-C(23)	120.7(3)
C(19)-C(20)-C(21)	124.6(3)
C(22)-C(21)-C(20)	117.8(3)
C(22)-C(21)-C(27)	122.0(3)
C(20)-C(21)-C(27)	120.2(3)
C(21)-C(22)-C(17)	119.5(3)
C(25)-C(23)-C(26)	107.4(3)
C(25)-C(23)-C(19)	111.4(3)
C(26)-C(23)-C(19)	111.5(3)
C(25)-C(23)-C(24)	109.1(3)
C(26)-C(23)-C(24)	108.6(3)
C(19)-C(23)-C(24)	108.8(3)
C(30)-C(27)-C(28)	108.7(3)
C(30)-C(27)-C(29)	108.5(3)
C(28)-C(27)-C(29)	109.0(3)
C(30)-C(27)-C(21)	112.2(3)
C(28)-C(27)-C(21)	108.0(3)
C(29)-C(27)-C(21)	110.3(3)

Table S7. Bond lengths [Å] and angles [°] for **5a**. (continued)

C(32)-C(31)-Hf	113.6(2)
C(37)-C(32)-C(33)	116.3(3)
C(37)-C(32)-C(31)	121.8(3)
C(33)-C(32)-C(31)	121.9(3)
C(34)-C(33)-C(32)	121.7(3)
C(35)-C(34)-C(33)	120.7(3)
C(34)-C(35)-C(36)	119.0(3)
C(35)-C(36)-C(37)	120.4(3)
C(32)-C(37)-C(36)	121.9(3)
C(39)-C(38)-Hf	96.2(2)
C(44)-C(39)-C(40)	116.6(3)
C(44)-C(39)-C(38)	121.3(3)
C(40)-C(39)-C(38)	121.8(3)
C(44)-C(39)-Hf	118.5(2)
C(40)-C(39)-Hf	95.4(2)
C(38)-C(39)-Hf	52.30(17)
C(41)-C(40)-C(39)	120.7(4)
C(42)-C(41)-C(40)	121.6(4)
C(41)-C(42)-C(43)	118.8(4)
C(44)-C(43)-C(42)	120.5(4)
C(43)-C(44)-C(39)	121.7(4)
C(47)-C(46)-C(45)	111.8(8)
C(46)-C(47)-C(48)	122.1(14)
C(49)-C(48)-C(47)	126.3(15)

Table S8. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **5a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
S(2)	26.8(4)	16.6(3)	36.6(4)	4.9(3)	-1.2(3)	6.8(3)
S(1)	33.7(4)	20.5(3)	42.1(4)	7.4(3)	13.5(3)	12.3(3)
O(2)	25(1)	17.7(9)	36(1)	5.7(9)	0.4(9)	6.6(8)
O(1)	27(1)	17.5(9)	36(1)	7.9(9)	8.2(9)	8.2(8)
Hf	21.20(7)	16.13(7)	32.49(8)	7.09(5)	2.62(5)	6.86(5)
C(1)	25(1)	19(1)	28(1)	7(1)	3(1)	8(1)
C(2)	29(2)	18(1)	33(2)	7(1)	7(1)	11(1)
C(3)	30(2)	28(2)	37(2)	14(1)	12(1)	13(1)
C(4)	32(2)	25(2)	35(2)	14(1)	8(1)	8(1)
C(5)	33(2)	20(1)	39(2)	12(1)	9(1)	10(1)
C(6)	30(2)	18(1)	28(2)	5(1)	7(1)	9(1)
C(7)	38(2)	33(2)	53(2)	24(2)	18(2)	12(1)
C(8A)	55(5)	70(6)	75(7)	54(6)	14(5)	14(5)
C(9A)	52(6)	70(8)	117(10)	65(8)	49(8)	28(6)
C(10A)	100(10)	53(6)	67(7)	5(5)	29(7)	-40(7)
C(8B)	57(6)	103(9)	78(7)	65(7)	31(5)	19(6)
C(9B)	33(4)	73(8)	81(7)	50(7)	14(5)	1(4)
C(10B)	125(12)	36(5)	199(17)	62(9)	125(13)	32(7)
C(11)	36(2)	20(1)	39(2)	4(1)	14(1)	11(1)
C(12)	33(2)	31(2)	50(2)	7(2)	10(2)	15(1)
C(13)	47(2)	47(2)	38(2)	3(2)	14(2)	10(2)
C(14)	58(3)	23(2)	85(3)	14(2)	40(2)	20(2)
C(15)	28(2)	35(2)	72(3)	28(2)	21(2)	18(1)
C(16)	25(2)	25(2)	67(2)	20(2)	-1(2)	2(1)
C(17)	26(2)	20(1)	34(2)	9(1)	6(1)	11(1)
C(18)	26(1)	18(1)	31(2)	8(1)	5(1)	9(1)
C(19)	29(2)	18(1)	30(2)	7(1)	9(1)	9(1)
C(20)	36(2)	22(1)	35(2)	12(1)	12(1)	14(1)
C(21)	27(2)	30(2)	33(2)	14(1)	9(1)	15(1)
C(22)	25(2)	24(1)	34(2)	10(1)	5(1)	9(1)
C(23)	39(2)	18(1)	38(2)	5(1)	3(1)	6(1)
C(24)	37(2)	48(2)	60(3)	15(2)	12(2)	-3(2)
C(25)	65(3)	35(2)	35(2)	2(2)	6(2)	12(2)
C(26)	70(3)	19(2)	75(3)	2(2)	-15(2)	11(2)
C(27)	30(2)	34(2)	39(2)	18(1)	9(1)	18(1)
C(28)	39(2)	49(2)	56(2)	21(2)	19(2)	26(2)
C(29)	43(2)	64(3)	73(3)	49(2)	19(2)	28(2)
C(30)	40(2)	48(2)	45(2)	13(2)	-1(2)	24(2)
C(31)	34(2)	29(2)	34(2)	5(1)	7(1)	11(1)
C(32)	31(2)	24(1)	25(2)	2(1)	1(1)	6(1)
C(33)	32(2)	39(2)	39(2)	13(2)	7(1)	7(1)
C(34)	48(2)	36(2)	50(2)	20(2)	11(2)	8(2)
C(35)	56(2)	34(2)	50(2)	16(2)	5(2)	22(2)
C(36)	35(2)	41(2)	43(2)	9(2)	8(2)	18(2)
C(37)	33(2)	29(2)	34(2)	8(1)	6(1)	7(1)
C(38)	31(2)	34(2)	42(2)	10(2)	7(1)	9(1)
C(39)	24(2)	36(2)	46(2)	17(2)	14(1)	6(1)
C(40)	40(2)	40(2)	47(2)	20(2)	13(2)	12(2)
C(41)	50(2)	62(3)	53(2)	30(2)	3(2)	10(2)
C(42)	64(3)	59(3)	45(2)	16(2)	-1(2)	-5(2)
C(43)	65(3)	40(2)	53(3)	4(2)	16(2)	5(2)
C(44)	36(2)	38(2)	52(2)	14(2)	10(2)	9(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **5a**.

	x	y	z	U(eq)
H(3)	6076	4683	1468	36
H(5)	4142	6598	2443	36
H(8A1)	4714	6965	1140	92
H(8A2)	5031	6176	453	92
H(8A3)	6154	7165	808	92
H(9A1)	7267	5605	902	100
H(9A2)	8275	6037	1873	100
H(9A3)	8273	6626	1244	100
H(10A)	6405	7661	2678	128
H(10B)	7883	7796	2374	128
H(10C)	7649	7205	2988	128
H(8B1)	4906	6144	378	106
H(8B2)	5900	5465	413	106
H(8B3)	6613	6454	404	106
H(9B1)	8039	5864	1738	89
H(9B2)	8273	6664	2601	89
H(9B3)	8585	6887	1774	89
H(10D)	6746	7832	1776	151
H(10E)	6420	7646	2616	151
H(10F)	5089	7386	1769	151
H(12A)	446	4451	2581	58
H(12B)	200	5079	2002	58
H(12C)	-221	5274	2892	58
H(13A)	2560	5081	4001	70
H(13B)	1845	5882	4311	70
H(13C)	3543	6104	4303	70
H(14A)	1245	6824	3350	78
H(14B)	1797	6696	2503	78
H(14C)	2977	7106	3426	78
H(15A)	6183	2452	2351	48
H(15B)	6983	3415	2320	48
H(16A)	6251	4143	3505	49
H(16B)	7165	3483	3750	49
H(20)	4909	-572	3121	35
H(22)	6809	2089	4494	33
H(24A)	1068	-674	2980	78
H(24B)	47	-1081	2012	78
H(24C)	648	-15	2469	78
H(25A)	1166	-945	788	73
H(25B)	2876	-424	992	73
H(25C)	1730	122	1243	73
H(26A)	2791	-1619	2521	94
H(26B)	3463	-1522	1746	94
H(26C)	1735	-1984	1562	94
H(28A)	8666	604	3519	66
H(28B)	7635	-403	3256	66
H(28C)	9124	-52	4025	66
H(29A)	6182	-862	4251	77
H(29B)	6242	-139	5129	77
H(29C)	7653	-494	5033	77
H(30A)	9283	1067	5445	68

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **5a**. (continued)

H(30B)	7936	1482	5563	68
H(30C)	8895	1744	4949	68
H(31A)	1389	1793	696	40
H(31B)	-63	1367	934	40
H(33)	1605	3204	297	45
H(34)	407	4166	-211	54
H(35)	-2012	4148	-121	56
H(36)	-3220	3160	499	48
H(37)	-2030	2191	1010	40
H(38A)	-811	2643	2718	44
H(38B)	-678	1663	2752	44
H(40)	1568	1684	4019	49
H(41)	2977	2409	5453	66
H(42)	2957	3847	6203	75
H(43)	1442	4594	5505	68
H(44)	80	3913	4073	51
H(45A)	3850	764	-1400	107
H(45B)	2960	-195	-1355	107
H(45C)	2277	686	-1024	107
H(46A)	5089	1194	-98	58
H(46B)	3737	832	255	58
H(47A)	5135	-284	-639	42
H(47B)	3936	-563	-164	42
H(48A)	6817	563	750	54
H(48B)	5624	125	1152	54
H(49A)	6926	-771	1227	86
H(49B)	5735	-1302	311	86
H(49C)	7713	-697	492	86

Figure S1. ORTEP diagram of the dichloro titanium complex **2b**. Hydrogen atoms and methyl groups of the *tert*-butyl groups have been omitted for clarity, thermal ellipsoids drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Ti-O1 1.832 (2), Ti-O2 1.848(2), Ti-Cl1 2.2828(8), Ti-Cl2 2.3353(9), Ti-S1 2.6035(8), Ti-S2 2.5789(8), O1-Ti-O2 100.97(8), O1-Ti-Cl1 104.18(6), O2-Ti-Cl1 96.67(6), O1-Ti-Cl2 96.40(6), Cl1-Ti-S1 177.87(3), O1-Ti-S2 157.25(6), O2-Ti-Cl2 155.52(6).

Figure S2. ORTEP diagram of the dibenzyl hafnium complex **5a**. Hydrogen atoms and methyl groups of the *tert*-butyl groups have been omitted for clarity, thermal ellipsoids drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Hf-S1 2.9222(9), Hf-S2 2.8260(8), Hf-O1 1.987(2), Hf-O2 1.989(2), Hf-C38 2.242(4), Hf-C31 2.245(3), Hf-C39 2.817(3), Hf-C31-C32 113.6(2), Hf-C38-C39 96.2(2), C31-Hf-C38 94.3(1), O1-Hf-O2 153.06(9), S1-Hf-S2 73.41(3).

Figure S3. ^{1}H and ^{13}C NMR spectra of polystyrenes obtained by MAO-activated titanium complexes **2a** and **2b**.

Figure S4. (a) ^{13}C NMR spectrum of a isotactic polystyrene obtained using ^{13}C-enriched trimethylaluminum in CD_2Cl_2. Insert shows 16 fold expansion. (b) Sample prepared without ^{13}C-enriched trimethylaluminum in CD_2Cl_2.

Figure S5. DSC curves of polystyrenes obtained by MAO-activated titanium complexes **2a** and **2b**.

Figure S6. WAXS of isotactic polystyrene obtained by MAO-activated titanium complex **2a**.

Figure S7. GPC-curves of polystyrenes obtained by MAO-activated titanium complexes **2a** and **2b**.

Figure S1

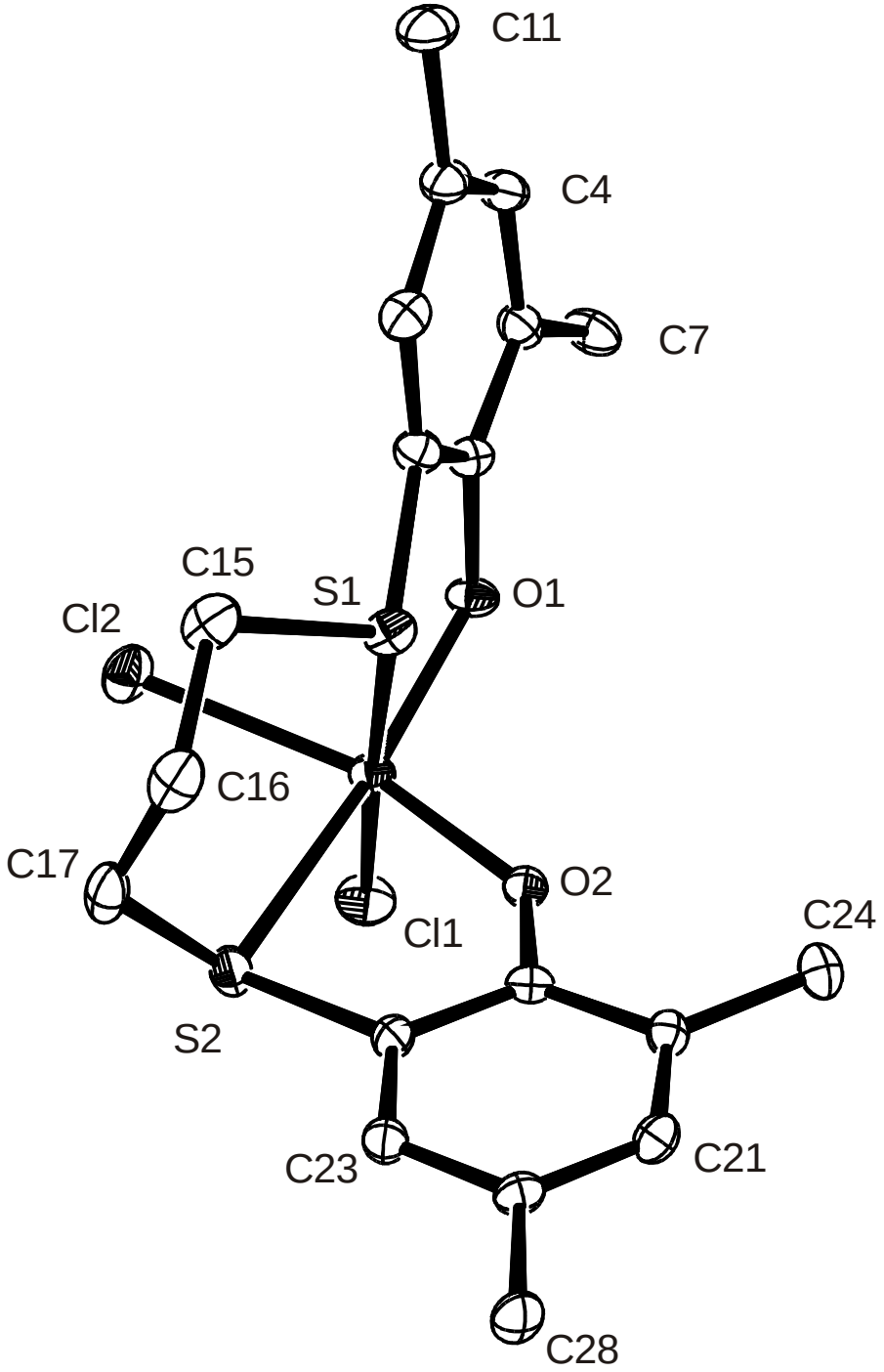


Figure S2

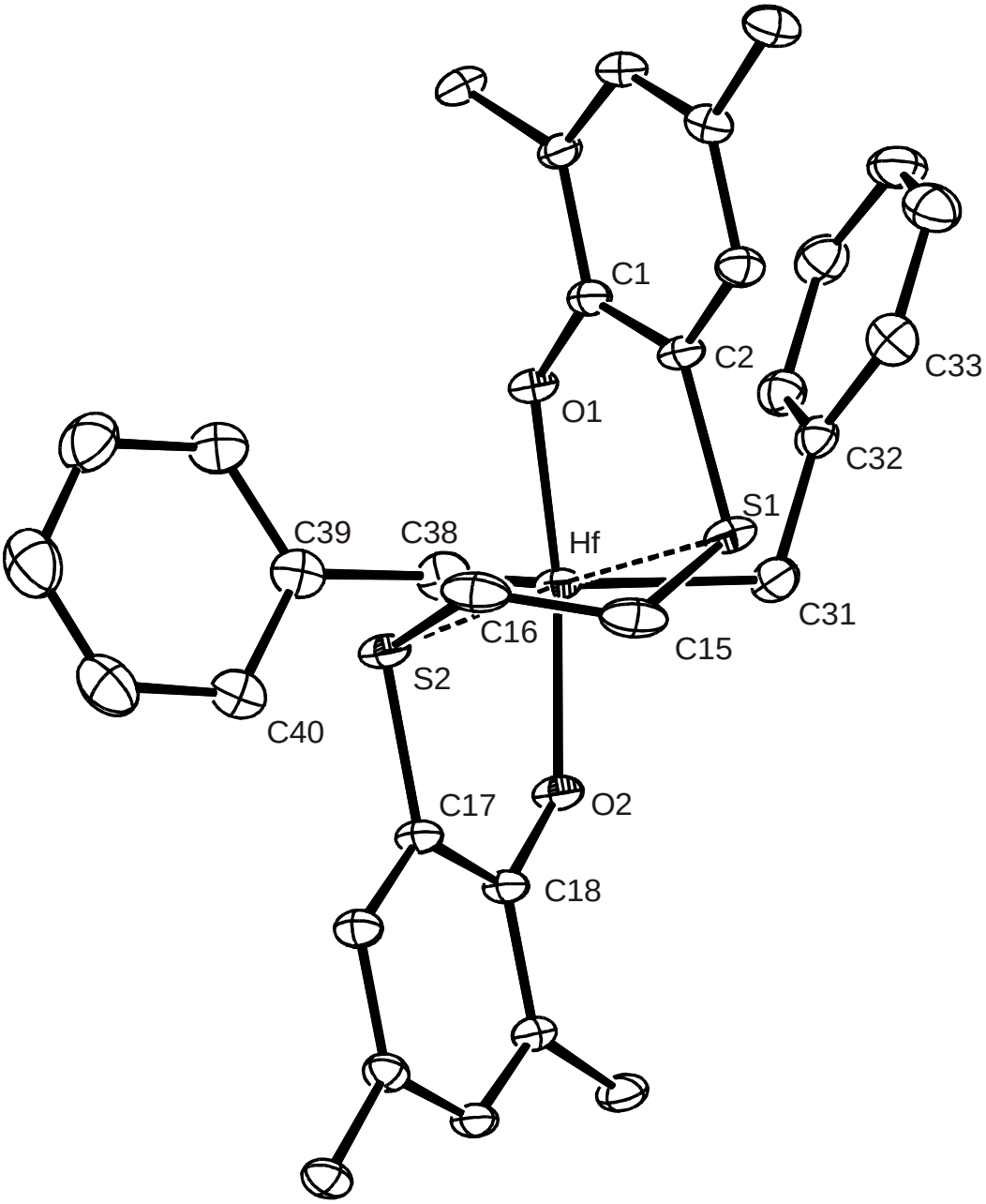
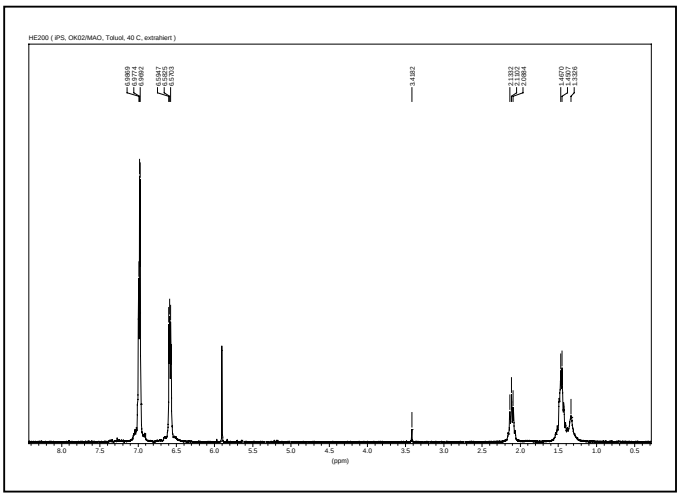
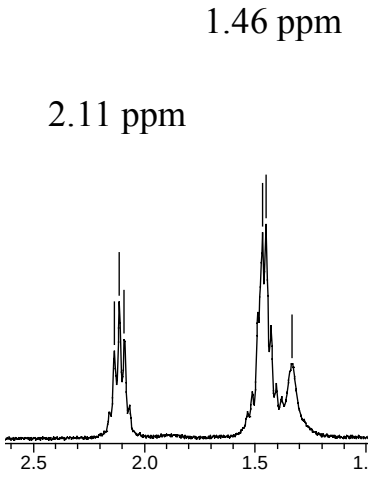


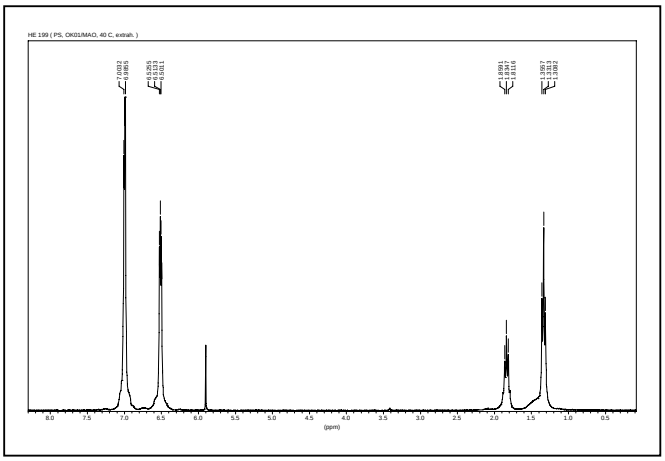
Figure S3



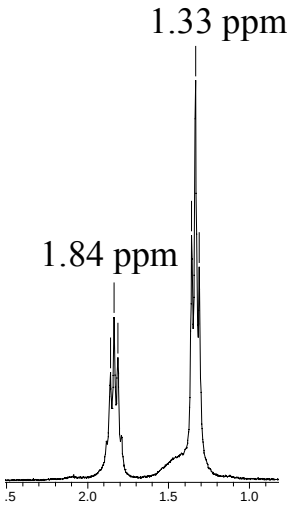
iPS (2a/MAO)



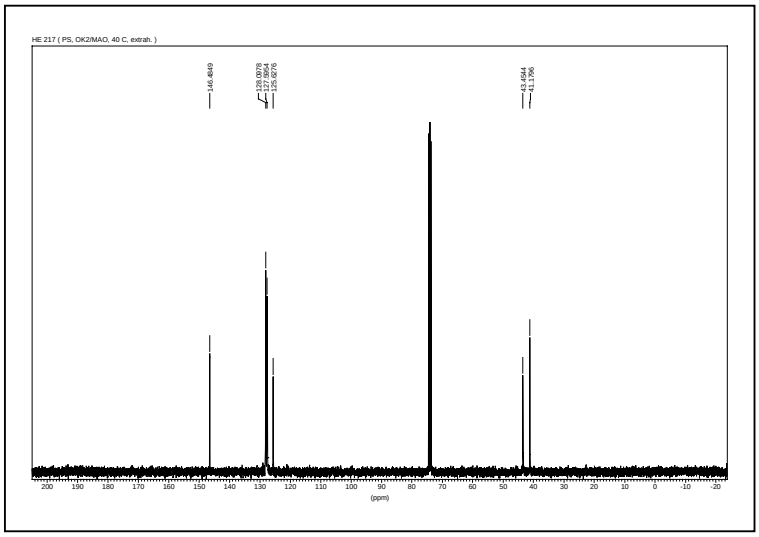
iPS (2a/MAO)



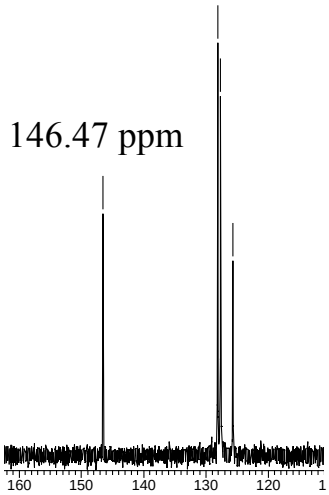
sPS (2b/MAO)



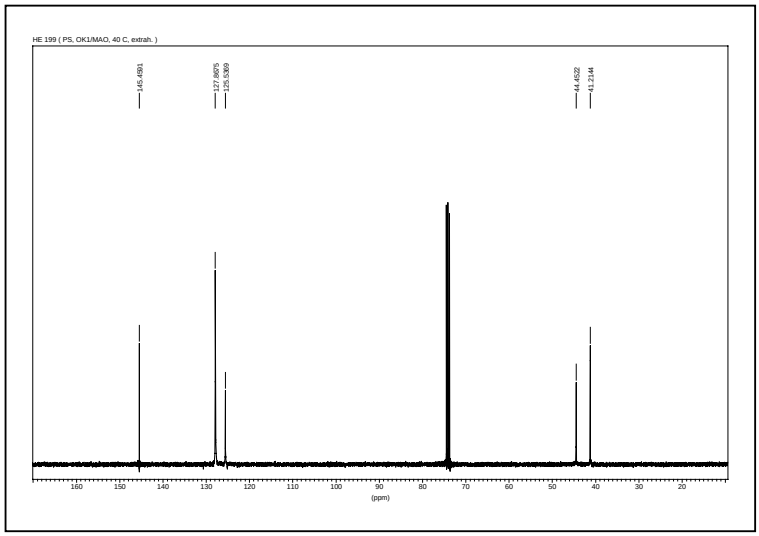
sPS (2b/MAO)



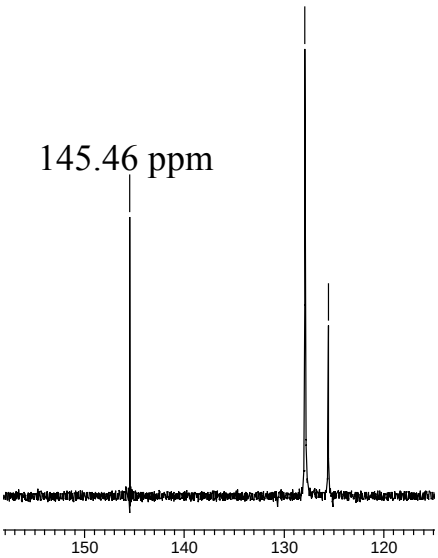
iPS (2a/MAO)



iPS (2a/MAO)



sPS (2b/MAO)



sPS (2b/MAO)

Figure S4

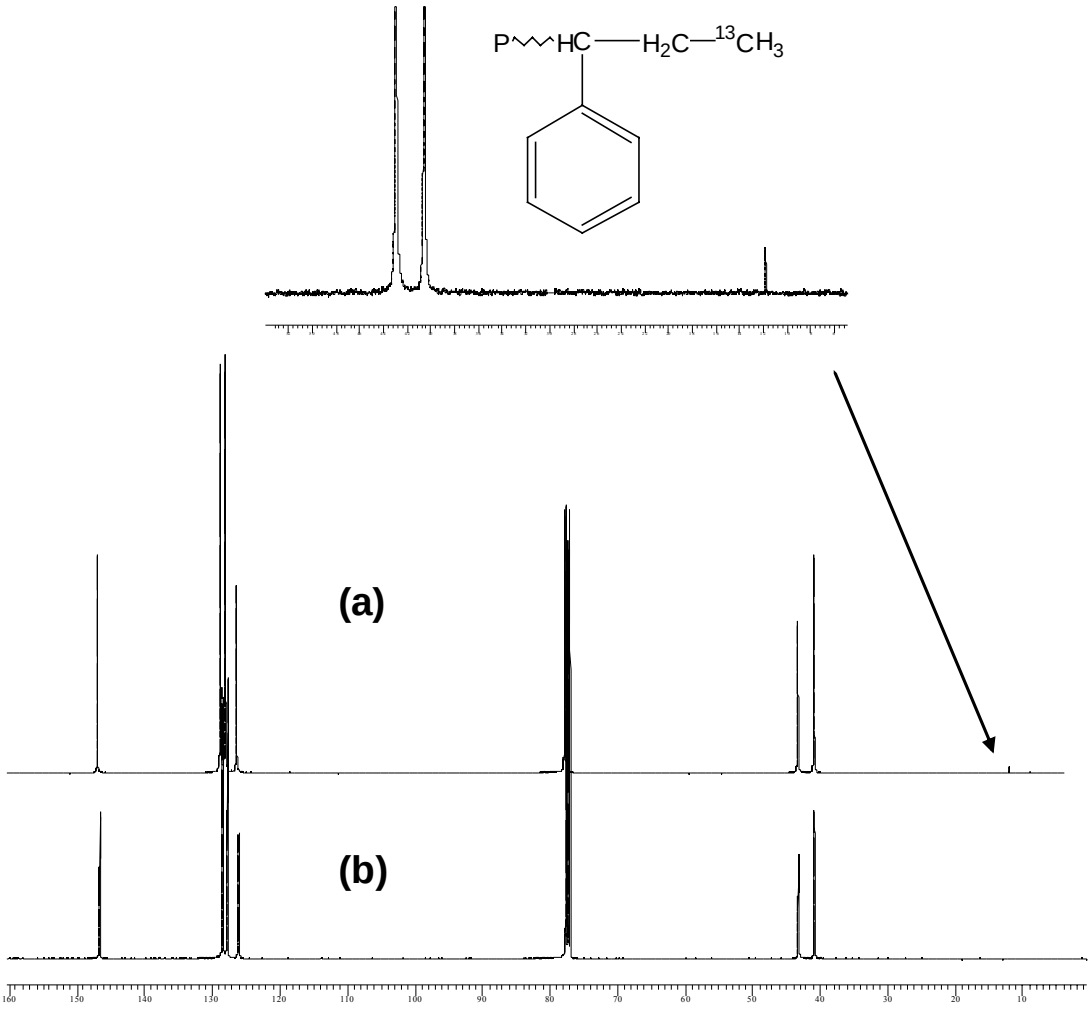

P HC H2C 13CH3
(a)
(b)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

Figure S5

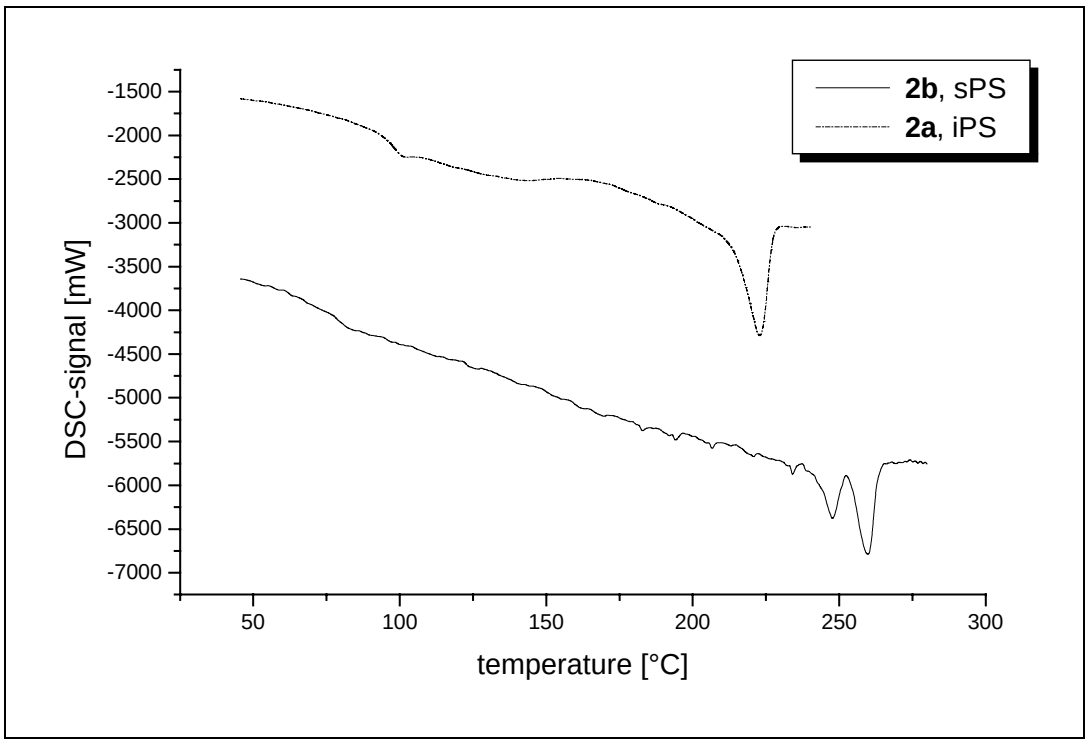

2b, sPS
2a, iPS
DSC-signal [mW]
-1500
-2000
-2500
-3000
-3500
-4000
-4500
-5000
-5500
-6000
-6500
-7000
50
100
150
200
250
300
temperature [°C]

Figure S6

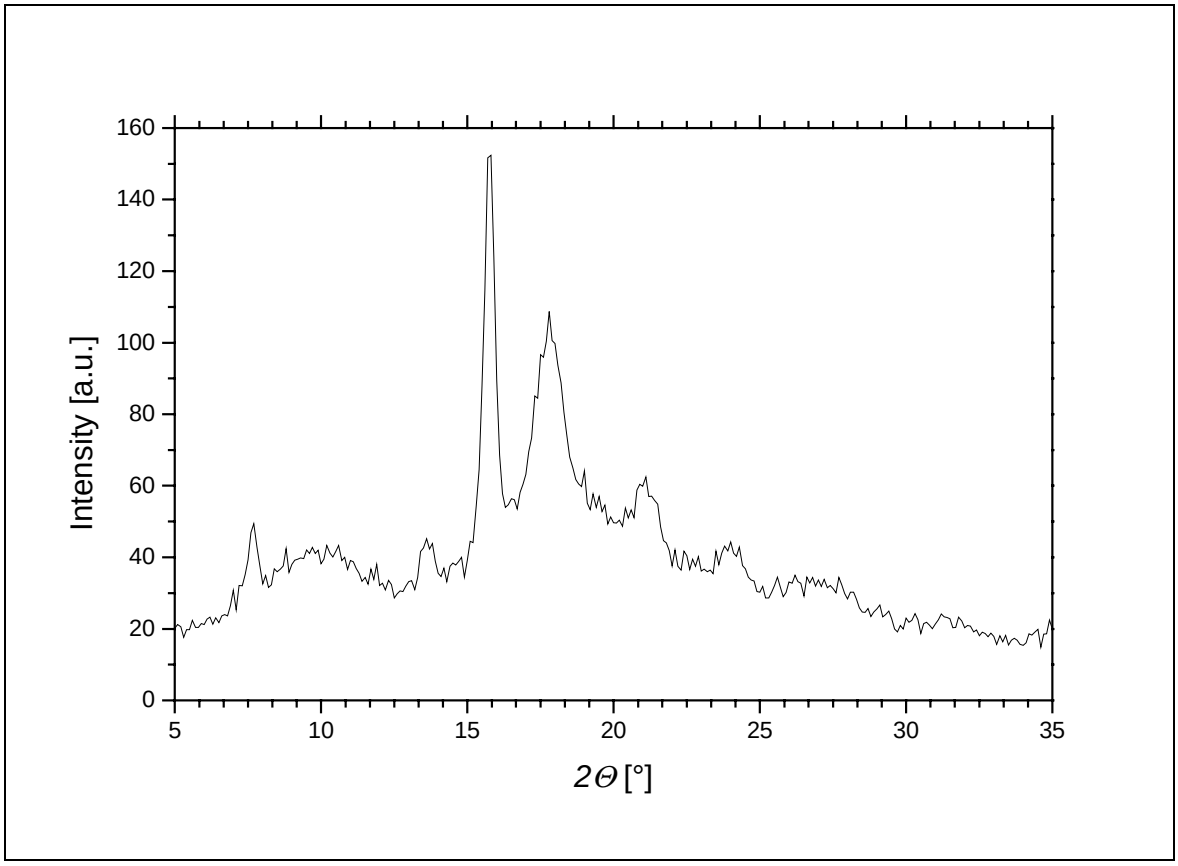
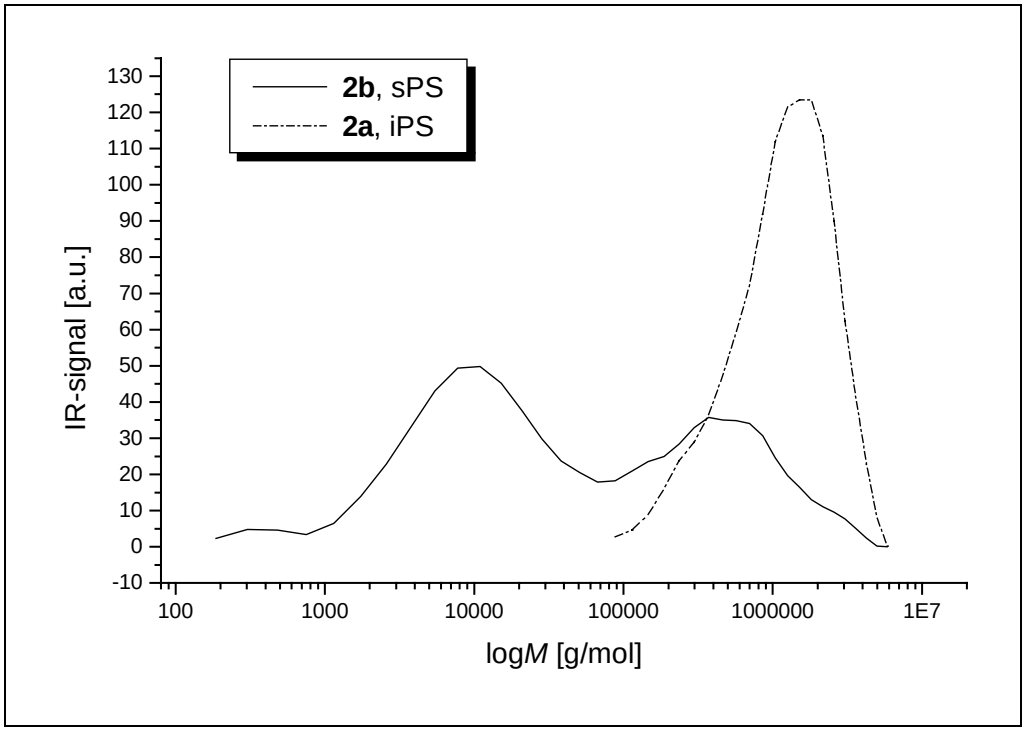


Figure S7


2b, sPS
2a, iPS
IR-signal [a.u.]
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
100
1000
10000
100000
1000000
1E7
logM [g/mol]