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Electronic Supporting Information

Pyridylamido Hafnium Complexes with Silylene Bridge

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General Information

All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware or in a nitrogen-filled Vacuum Atmospheres glove box (<1 ppm O_2). Toluene was dried and stored over 4 Å molecular sieves. 4-Methyl-1-pentene (4M1P) and 1-hexene were passed through a pad of dried alumina and stored over 4 Å molecular sieves. Toluene for polymerization experiments was distilled over sodium metal and stored over 4 Å molecular sieves. GC/MS spectra were registered with Agilent 7890A GC equipped with Agilent 5975C inert XL MSD. Gel permeation chromatograms for polyhexene samples were obtained on GPC instrument consisting of Waters 515 HPLC pump, Waters 717plus autosampler, and Polymer Laboratories PL-ELS 1000 light scattering detector using three PLGel Mixed-B columns (7.5×300 mm with 10 µm particle size). Mobile phase: THF at flow rate of 1 mL/min. Polystyrene standards produced by Polymer Standards Service GmbH were used for calibration (ReadyCal Kit Poly(styrene), M_p = 7520, 2570, 1210, 579, 246, 127, 67, 34.8, 17.8, 8.4, 3.42, and 1.62 kDa).

Characterization of 4-methyl-1-pentene-appended Ligand of 7 Residue.

Under nitrogen atmosphere in a glovebox, to a solution of **7** (600 mg, 0.803 mmol) in toluene (34 mL) in a glass vial a solution of TTB (1.48 g, 1.61 mmol, 2 equiv) in toluene (6 mL) was added at room temperature. After stirring for 5 min, 4M1P (5.1 mL, 40.2 mmol, 50 equiv) was added to the solution, which quickly became viscous with evolution of heat. The vial was taken outside the glovebox, and the reaction was quenched with excess of methanol. The precipitated polymer was collected on a frit and washed with methanol, giving white solid poly-(4M1P). The combined filtrates were evaporated to dryness, the fraction containing the insertion product was isolated by flash chromatography on silica gel (eluent: hexane/dichloromethane = 5/1) and analyzed by GC-MS (Figure S2), which revealed presence of a mixture of compounds including several peaks corresponding to 4M1P insertion products (*m/z* 239, Figure S3). The results were also compared to the GC/MS analysis of the products of decomposition of **7** with methanol: 20 mg of complex **7** were treated with 4 mL of methanol and the resulted solution was filtrated through the syringe filter (0.45 µm) and injected in the GC (Figure S1).

Characterization of 4-methyl-1-pentene-appended Ligand of 8 Residue.

Under nitrogen atmosphere in a glovebox, to a solution of **8** (400 mg, 0.502 mmol) and 4M1P (3.2 mL, 25.1 mmol, 50 equiv) in toluene (18 mL) in a glass vial with a solution of TTB (925 mg, 1.04 mmol, 2 equiv) in toluene (10 mL), was added at room temperature. After stirring for 5 min, 4M1P (3.2 mL, 25.1 mmol, 50 equiv) was added to the solution, which quickly became viscous with evolution of heat. The vial was taken outside the glovebox, and the reaction was quenched with excess of methanol. The precipitated polymer was collected on a frit and washed with methanol, giving white solid poly-(4M1P). The combined filtrates were analyzed by GC-MS (Figure S5), which revealed presence of a mixture of compounds including several peaks corresponding to 4M1P insertion products (*m/z* 289, Figure S6). The results were also compared to the GC/MS analysis of the products of decomposition of **8** with methanol: 20 mg of complex **8** were treated with 4 mL of methanol and the resulted solution was filtrated through the syringe filter (0.45 µm) and injected in the GC (Figure S4).

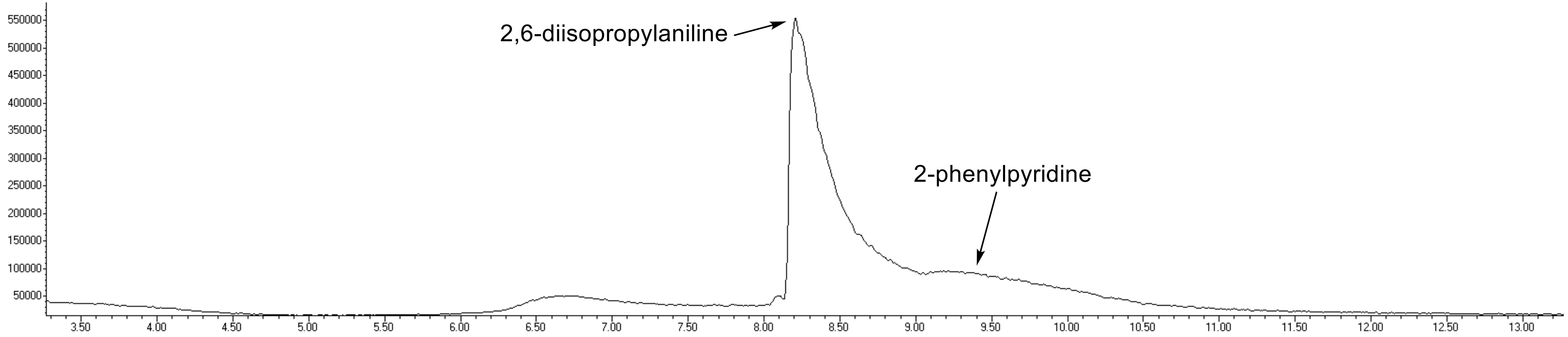

Figure S1. GC of products of decomposition of 7 with methanol.

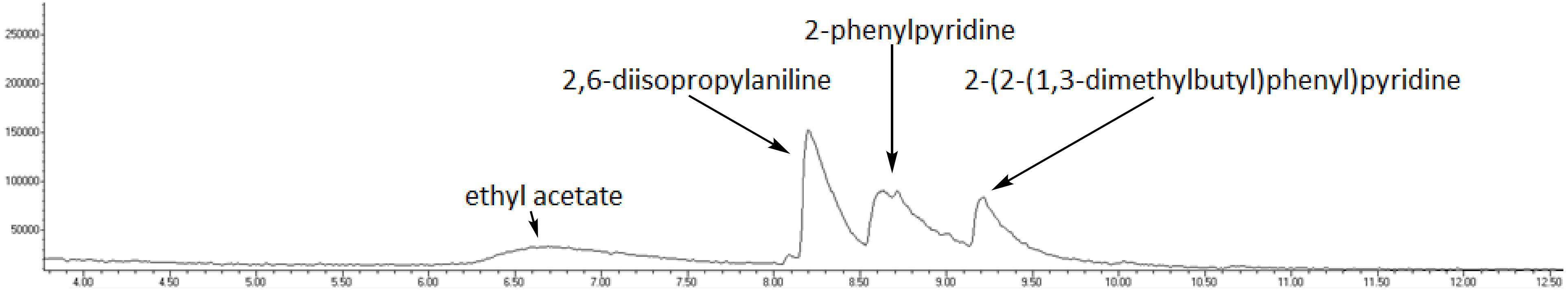

Figure S2. GC of products formed from 7 after quenching the polymerization of 4M1P on 7/TTB with methanol.

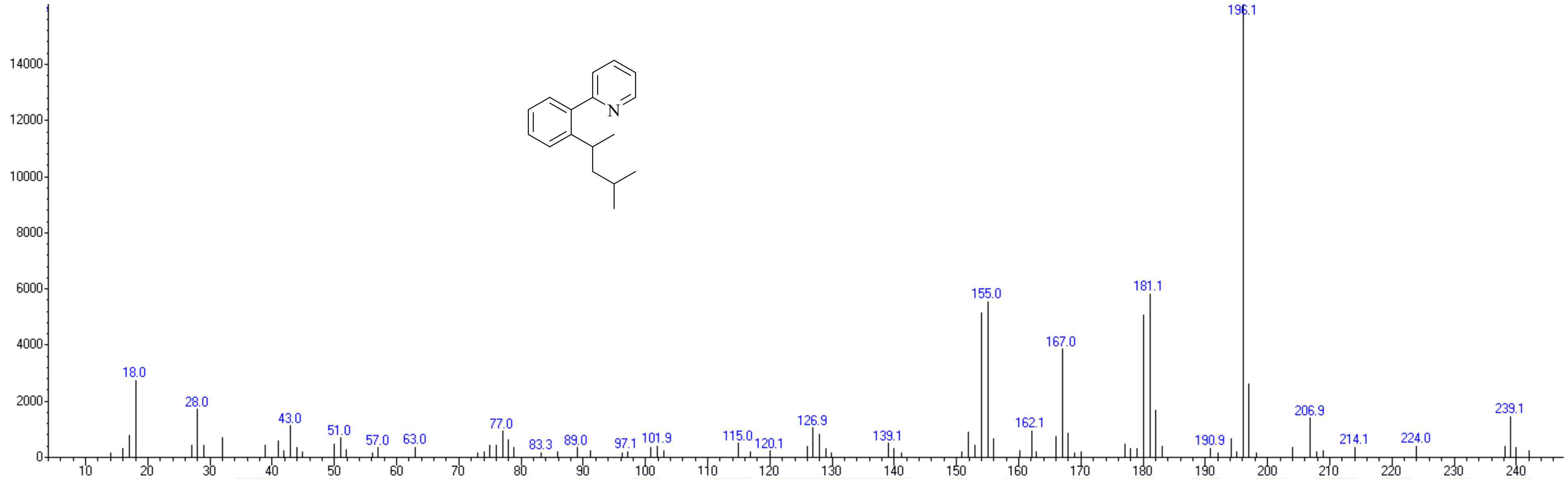

Figure S3. EI-MS spectrum of 2-(2-(1,3-dimethylbutyl)phenyl)pyridine formed during polymerization of 4M1P with 7/TTB.

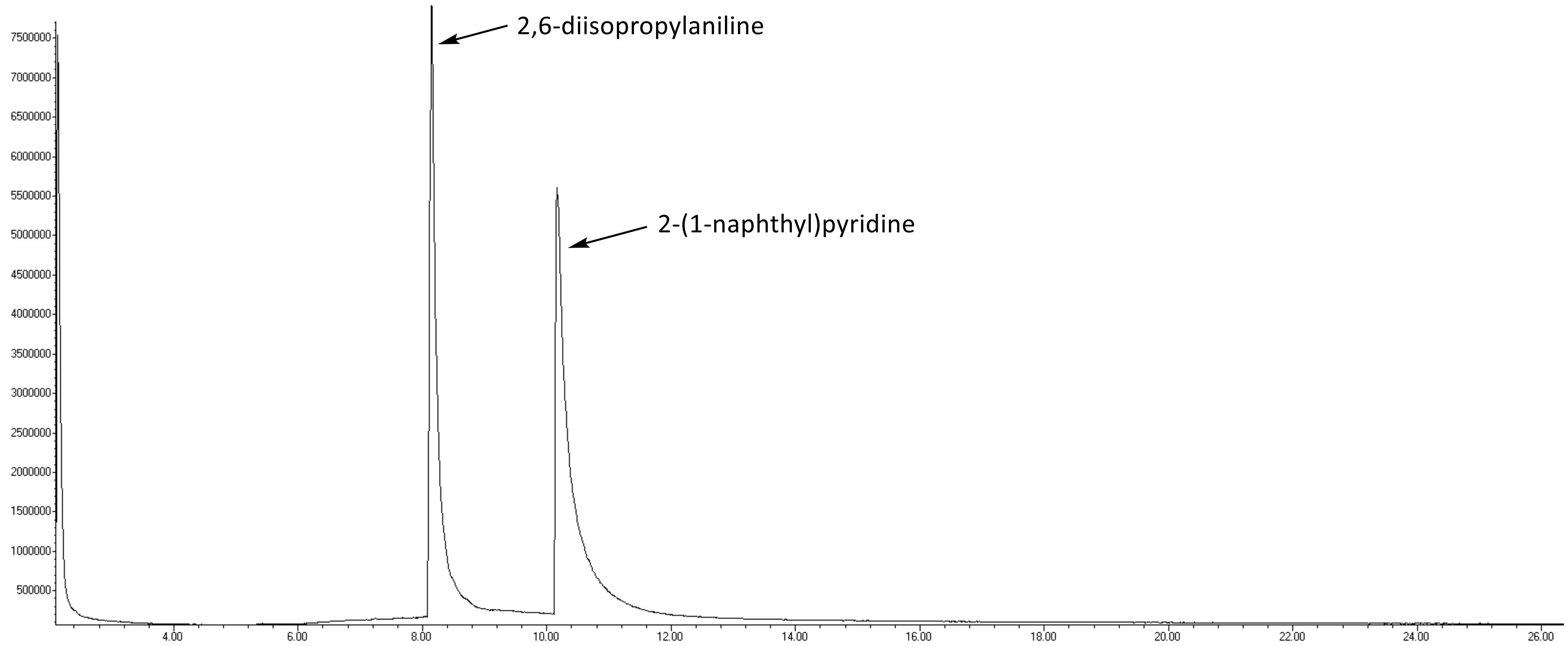

Figure S4. GC of products of decomposition of 8 with methanol.

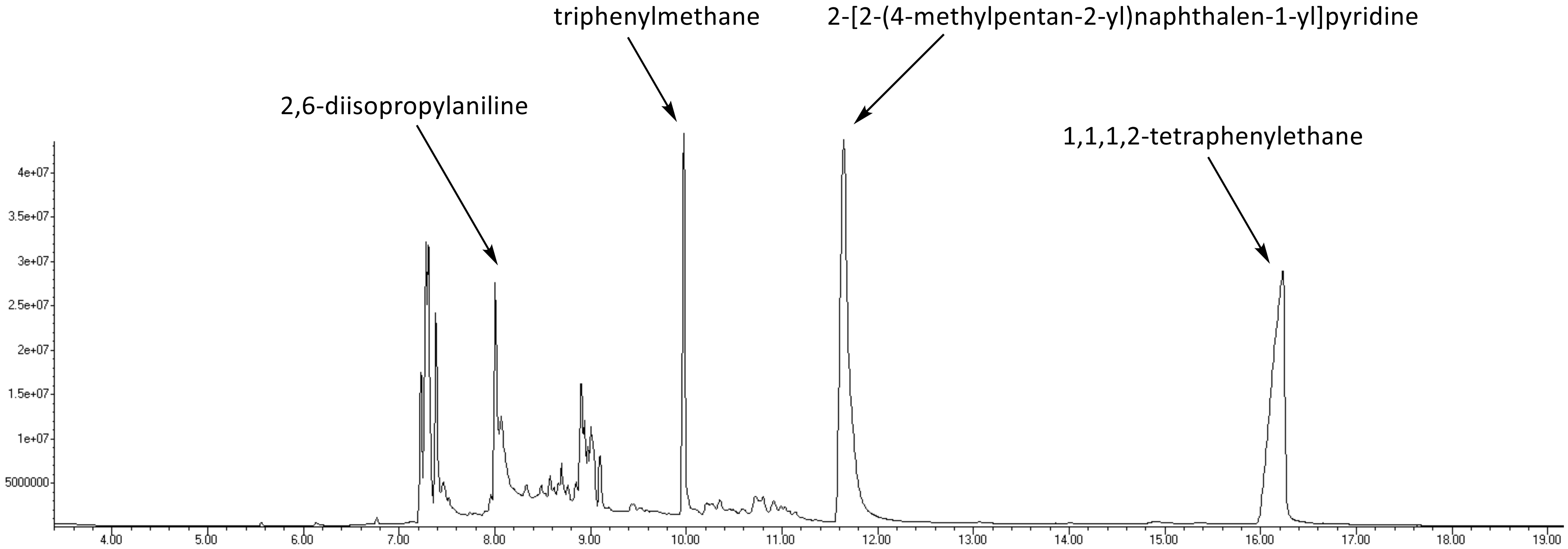

Figure S5. GC of products formed from 8 after quenching the polymerization of 4M1P on 8/TTB with methanol.

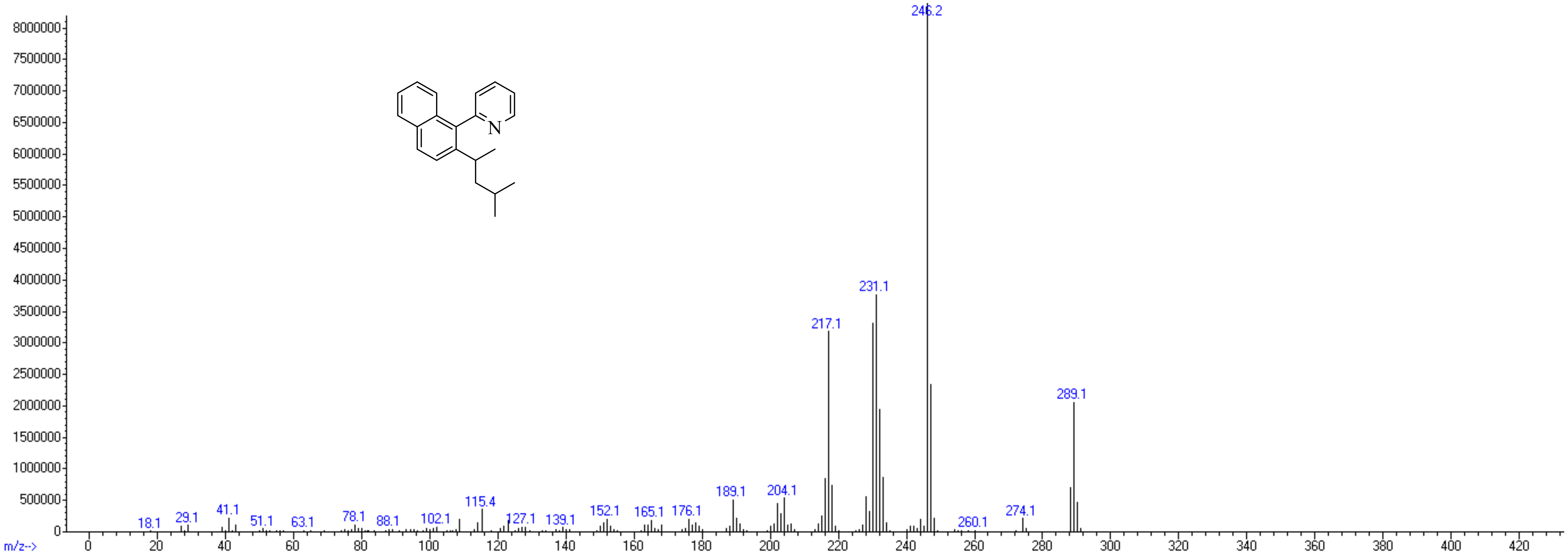

Figure S6. EI-MS spectrum of 2-(2-(4-methylpentan-2-yl)naphthalen-1-yl)pyridine formed during polymerization of 4M1P with 8/TTB.

1-Hexene Polymerization.

In a glovebox, a catalyst precursor was weighed into an oven-dried 40 mL vial. The vial was equipped with a stir bar, and the catalyst was dissolved in 5 mL of toluene. In entries 3–6 (Table 2) the vial was heated to 60 °C. To this solution was added 2 mL of 1-hexene. In a separate vial, activator was dissolved in 3 mL of toluene, this solution was added to the prepared solution of catalyst precursor and 1-hexene, and the reaction was allowed to proceed at the desired temperature with vigorous stirring for 30 min. The polymerization was quenched with 20 mL of acetone, and after completion of polymer coagulation, the polymer was isolated by decanting the supernatant and drying the residue to constant weight in vacuum at 70 °C.

Table S1. 1-Hexene polymerization data for complexes 7-12 and Ic[a]

Entry	Complex	Activator	T_{pol}, °C	Yield, mg	Conversion, %	M_n,[b] kDa	M_w,[b] kDa	Đ[b]
1	**7**	AB	25	370	27	18	48	2.6
2	**8**	AB	25	107	8	14	18	1.3
3	**7**	$B(C_6F_5)$	33	267	20	14	32	2.3[e]
4	**8**	$B(C_6F_5)$	33	1305	96	17	27	1.6
5	**Id**	$B(C_6F_5)$	33	1212	89	20	43	2.1
6	**7**	TTB	33	1267	93	9	119	14[e]
7	**8**	TTB	33	1341	99	10	17	1.7
8	**Id**	TTB	33	1145	84	10	38	3.8[e]
9	**7**	AB	60(±2)	987	73	6	8	1.4
10	**8**	AB	60(±2)	522	38	11	15	1.3
11	**7**	TTB	60(±2)	662	49	6	11	1.8[e]
12	**8**	TTB	60(±2)	865	64	7	10	1.4

[a] Polymerization conditions: **7**, **8**,or **1d**, 10 µmol, [B]/[Hf] = 1.0, 8.0 mL toluene, 2.0 mL 1-hexene, 30 min. [b] Determined using gel permeation chromatography in THF at 35 °C vs polystyrene standards. [e] Bimodal molecular weight distribution.

Propylene homopolymerization and ethylene/1-octene copolymerization – general procedure.

A pre-weighed glass vial insert and disposable stirring paddle were fitted to each reaction vessel of the reactor. The reactor was then closed and each vessel was individually heated to the desired temperature and pressurized with nitrogen to 75 psi. For ethylene/1-octene copolymerization the reactor was then purged with ethylene and pressurized with ethylene to 75 psi. Liquid monomer, such as 1-octene or liquified propylene was then injected into each reaction vessel through a valve, followed by enough isohexane to bring the total reaction volume, including the subsequent additions, to the desired volume (5 mL). The contents of the vessel were then stirred at 800 rpm. A solution of trioctylaluminum scavenger (in isohexane) was then added along with a solvent chaser. An activator solution in toluene was then injected into the reaction vessel along with a solvent chaser. Then a toluene solution of the precatalyst complex dissolved was added along with and a solvent chaser. The reaction was then allowed to proceed until either a set amount of pressure had been taken up by the polymerization or a time limit had been reached. At this point, the reaction was quenched by pressurizing the vessel with compressed air. After the polymerization reaction, the glass vial insert containing the polymer product and solvent was removed from the pressure cell and the inert atmosphere glove box, and the volatile components were removed using a Genevac HT-12 centrifuge and Genevac VC3000D vacuum evaporator operating at elevated temperature and reduced pressure. The vial was then weighed to determine the yield of the polymer product.

The resultant polymer was analyzed by Rapid GPC to determine the molecular weight. This apparatus has a series of three 30 cm x 7.5 mm linear columns, each containing PLgel 10 um, Mix B. The GPC system was calibrated using polystyrene standards ranging from 580 g/mol - 3,390,000 g/mol. The system was operated at an eluent flow rate of 2.0 mL/min and an oven temperature of 165 °C. 1,2,4-trichlorobenzene was used as the eluent. The polymer samples were dissolved in 1,2,4-trichlorobenzene at a concentration of 0.1 mg/mL - 0.9 mg/mL. 250 µL of a polymer solution was injected into the system. The concentration of the polymer in the eluent was monitored using an evaporative light scattering detector. The molecular weights presented in the examples are relative to linear polystyrene standards.

Differential Scanning Calorimetry (DSC) measurements were performed on a TA-Q100 instrument to determine the melting point of the polymers. Samples were pre-annealed at 220 °C for 15 minutes and then allowed to cool to room temperature overnight. The samples were then heated to 220 °C at a rate of 100 °C/minutes and then cooled at a rate of 50 °C/min. Melting points were collected during the heating period.

Table S2. Propylene Polymerization Data for Complexes 7-12 at 70 °C[a]

Entry	Complex	Quench Time[b], s	Yield, mg	Activity, g·mmol^{-1}·h^{-1}	M$_w$[c], kDa	M$_n$[c], kDa	Đ[c]	T$_m$[d], °C
1	**7**	461	37	7220	31	18	1.7	131
2	**8**	2701	8	270	n.d.	n.d.	n.d.	n.d.
3	**9**	819	46	5060	37	22	1.7	135
4	**10**	1696	43	2280	22	10	2.3	138
5	**11**	1310	41	2820	21	12	2.4	134
6	**12**	1193	44	3320	54	28	1.9	n.d.
7[e]	**Ib**	316	254	48200	1469	812	1.8	148

[a] Polymerization conditions: 0.04 µmol complexes; 0.044 µmol AB activator; propylene = 1 mL; total volume: 5.1 mL; 3.8 mL isohexane; 0.5 µmol of $(n\mathrm{Oct})_3\mathrm{Al}$; temperature: 70 °C; 800 rpm stirring speed. [b] Reactor quenched at 12 psig uptake (quench value, see Supporting Information for details) or at a maximum time of 45 minutes. [c] Determined using gel permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 135 °C vs polystyrene standards. [d] Determined via differential scanning calorimetry. [e] 0.06 µmol complex used.

Table S3. Ethylene/1-Octene Copolymerization Data for Complexes 7-12 at 80 °C[a]

Entry	Complex	Quench time, s	Yield[b], mg	Activity, g·mmol^{-1}·h^{-1}·bar[C_2H_4]$^{-1}$	M_w[c], kDa	M_n[c], kDa	*Đ*[c]	T_m[d], °C	Octene content, wt %
1	**7**	244	25	3580	384	110	3.5	116	7
2	**8**	1800	7	160	n.d.	n.d.	n.d.	n.d.	n.d.
3	**9**	655	19	990	87	64	1.4	120	8
4	**10**	349	24	2350	110	84	1.3	110	10
5	**11**	287	23	2770	112	80	1.4	108	12
6	**12**	1800	19	390	71	54	1.3	119	8
7[e]	**Ib**	134	60	15600	402	263	1.5	76	22

[a] Polymerization conditions: 0.04 µmol complexes; 0.04 µmol AB activator; 3.8 mL isohexane; ethylene pressure 75 psi, 0.1 mL 1-octene; 0.3 µmol of $(n\text{Oct})_3\text{Al}$; temperature: 80 °C; 800 rpm stirring speed. [b] Reactor quenched at 10 psig ethylene (quench value, see Supporting Information for details) uptake or at a maximum time limit of 30 minutes. [c] Determined using gel permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 135 °C vs polystyrene standards. [d] Determined via differential scanning calorimetry. [e] 0.02 µmol complex used.

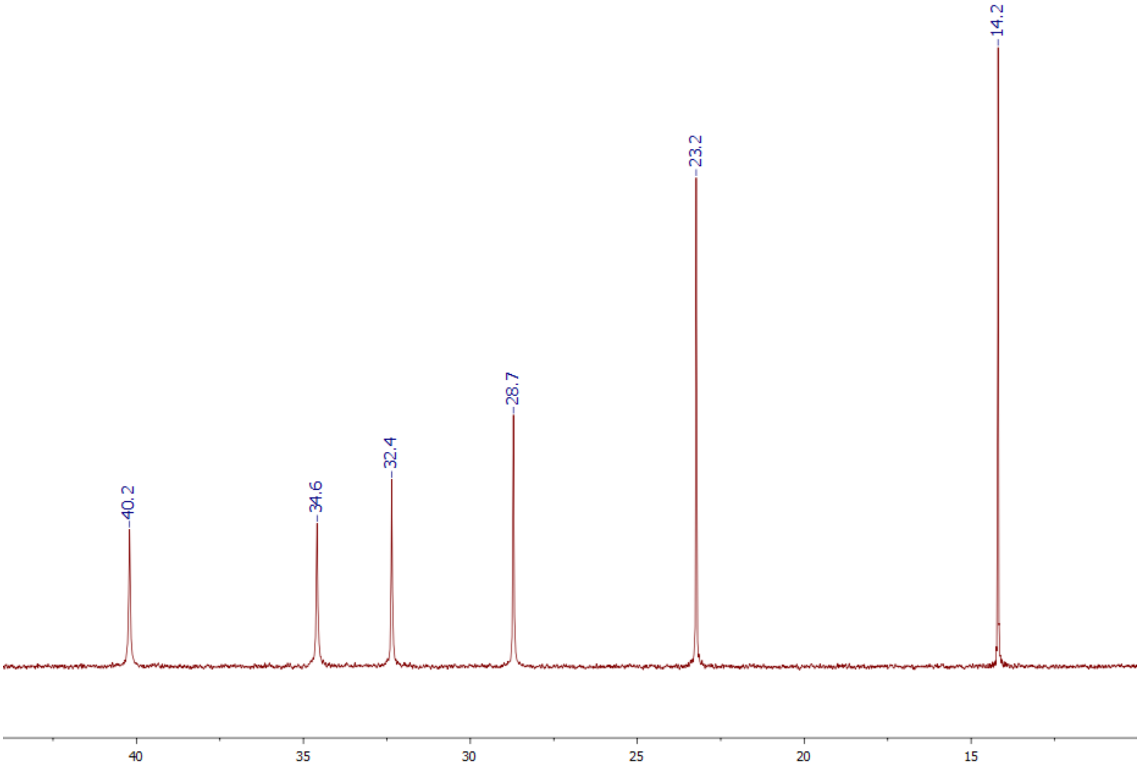

Figure S7. Fragment of ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of poly(hexene-1) obtained with 7/AB at room temperature (entry 1, Table S1).

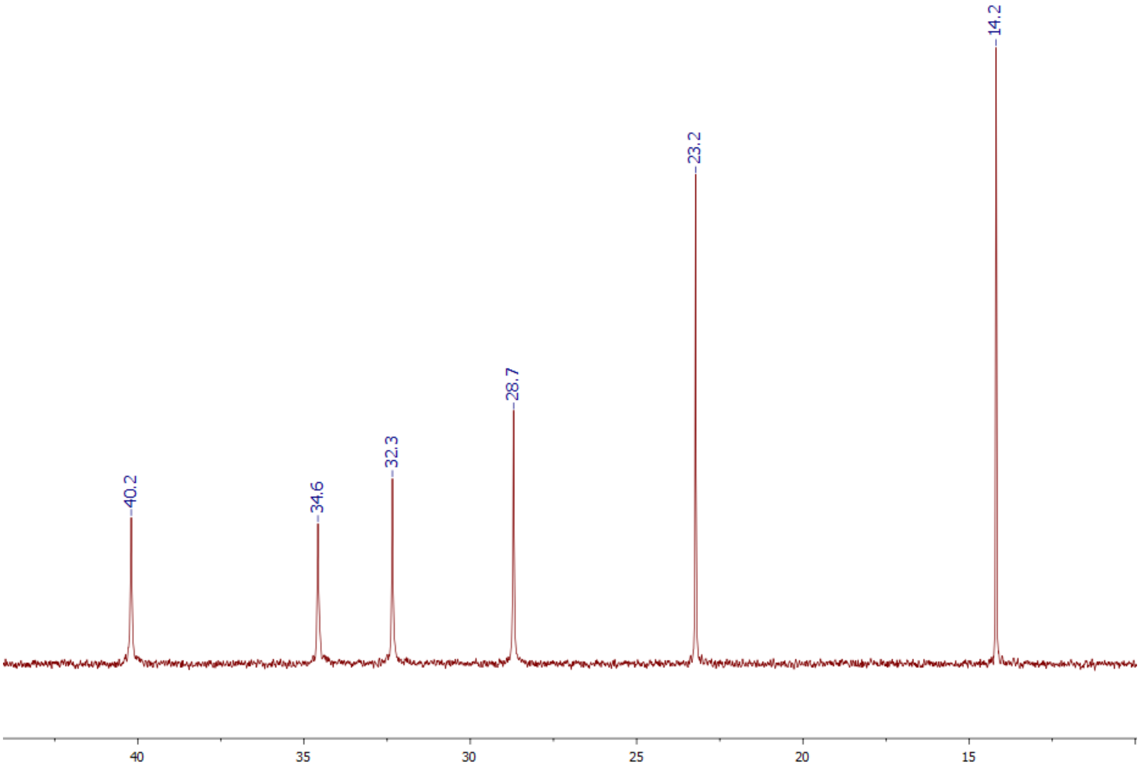

Figure S8. Fragment of ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of poly(hexene-1) obtained with 8/AB at room temperature (entry 2, Table S1).

Crystal structure determinations.

X-ray experiments were carried out using SMART 1000 CCD diffractometer (λ(Mo-$K\alpha$)=0.71073 Å, graphite monochromator, ω-scans) at 110 °K. All structures were solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. All the hydrogen atoms were placed in geometrically calculated positions and included in the refinement using riding approximation. The details of data collection and crystal structures refinement for which we used SAINT Plus,[1] SADABS[2] and SHELXTL-97[3] program packages, are summarized in Tables S4 through S7. Crystallographic data for **7**, **8**, **9**, and **11** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 1987153-1987156. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

References

[1] *SMART and SAINT, Release 5.0, Area Detector control and Integration Software*, Bruker AXS, Analytical X-Ray Instruments, Madison, Wisconsin, USA, 1998.

[2] Sheldrick, G.M. *SADABS: A Program for Exploiting the Redundancy of Area-detector X-Ray Data*, University of Göttingen, Göttingen, Germany, 1999.

[3] Sheldrick, G.M. *SHELXTL-97 Program for Solution and Refinement of Crystal Structure*, Bruker AXS Inc., Madison, WI-53719, USA, 1997.

Table S4. Crystal data and structure refinement for 7 (CCDC 1987153).

Empirical formula	$C_{39}H_{44}HfN_2Si$
Formula weight	747.34
Temperature/K	120
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.8250(9)
b/Å	11.1737(6)
c/Å	18.7813(9)
α/°	90
β/°	115.0910(10)
γ/°	90
Volume/Å^3	3387.7(3)
Z	4
ρ_{calc}g/cm^3	1.465
μ/mm^{-1}	3.144
F(000)	1512.0
Crystal size/mm^3	0.2 × 0.13 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.64 to 61.238
Index ranges	$-25 \le h \le 25$, $-15 \le k \le 16$, $-26 \le l \le 26$
Reflections collected	40379
Independent reflections	10427 [R_{int} = 0.0398, R_{sigma} = 0.0352]
Data/restraints/parameters	10427/0/394
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0243, wR_2 = 0.0567
Final R indexes [all data]	R_1 = 0.0301, wR_2 = 0.0586
Largest diff. peak/hole / e Å^{-3}	0.78/-1.19

Table S5. Crystal data and structure refinement for 8 (CCDC 1987155).

Empirical formula	$C_{43}H_{46}HfN_2Si$	
Formula weight	797.40	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 18.805(3) Å	α= 90°.
	b = 11.0536(19) Å	β= 116.015(3)°.
	c = 19.590(3) Å	γ = 90°.
Volume	3659.5(11) Å^3	
Z	4	
Density (calculated)	1.447 Mg/m^3	
Absorption coefficient	2.915 mm^{-1}	
F(000)	1616	
Crystal size	0.16 x 0.15 x 0.11 mm^3	
Theta range for data collection	2.003 to 27.000°.	
Index ranges	-24<=h<=24, -14<=k<=14, -25<=l<=25	
Reflections collected	62291	
Independent reflections	7973 [R(int) = 0.0384]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.6025	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7973 / 0 / 430	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0219, wR2 = 0.0492	
R indices (all data)	R1 = 0.0283, wR2 = 0.0526	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.741 and -0.520 e.Å $^{-3}$	

Table S6. Crystal data and structure refinement for 9 (CCDC 1987154).

Empirical formula	$C_{41}H_{44}HfN_2Si$	
Formula weight	771.36	
Temperature	120 K	
Wavelength	0.71073 E	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.6765(9) Å	α= 98.919(4)°.
	b = 11.0521(10) Å	β= 95.327(4)°.
	c = 15.8719(14) Å	γ= 106.367(4)°.
Volume	1756.7(3) E^3	
Z	2	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	3.034 mm^{-1}	
F(000)	780	
Crystal size	0.2 x 0.17 x 0.15 mm^3	
Theta range for data collection	1.956 to 26.998°.	
Index ranges	-13<=h<=13, -14<=k<=14, -20<=l<=20	
Reflections collected	24355	
Independent reflections	7673 [R(int) = 0.0307]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.5999	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7673 / 0 / 410	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0531	
R indices (all data)	R1 = 0.0281, wR2 = 0.0551	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.224 and -0.626 e. Å^{-3}	

Table S7. Crystal data and structure refinement for 11 (CCDC 1987156).

Empirical formula	$C_{40.50}H_{44}HfN_2Si$	
Formula weight	765.35	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7827(4) Å	α = 90.6290(10)°.
	b = 10.8823(5) Å	β = 92.4150(10)°.
	c = 17.9126(8) Å	γ = 111.6070(10)°.
Volume	1770.65(14) $Å^3$	
Z	2	
Density (calculated)	1.436 Mg/m^3	
Absorption coefficient	3.009 mm^{-1}	
F(000)	774	
Crystal size	0.200 x 0.180 x 0.150 mm^3	
Theta range for data collection	2.014 to 30.720°.	
Index ranges	-14<=h<=14, -15<=k<=15, -25<=l<=25	
Reflections collected	32021	
Independent reflections	10982 [R(int) = 0.0244]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2125 and 0.1659	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10982 / 1 / 428	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0228, wR2 = 0.0512	
R indices (all data)	R1 = 0.0284, wR2 = 0.0532	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.277 and -0.457 e.$Å^{-3}$	