Supporting Information
for the
Article Entitled

N-Substituted Iminocaprolactams as Versatile and Low Cost Ligands in Group 4 Metal Initiators for the Living Coordinative Chain Transfer Polymerization of α-Olefins

Authored by

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Supporting NMR spectra for **1**, **2**, and **3** and polypropylene products. Crystallographic information regarding X-ray analyses, including tables of bond length and angles, for **1**, **2**, and **3**.

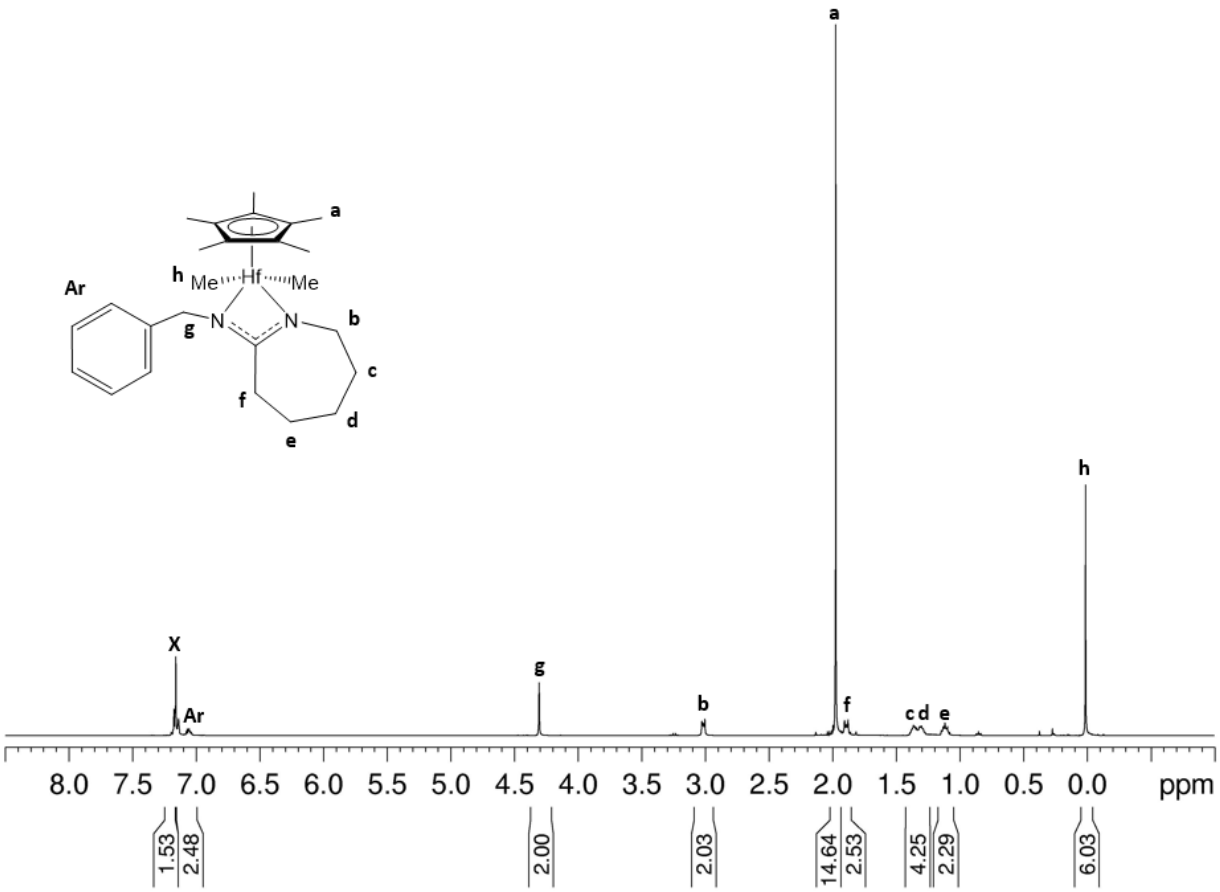

Figure S1: ^{1}H NMR (400 MHz, C_6D_6, 25 °C) spectrum of **1**; **X** denotes benzene-d_6 solvent.

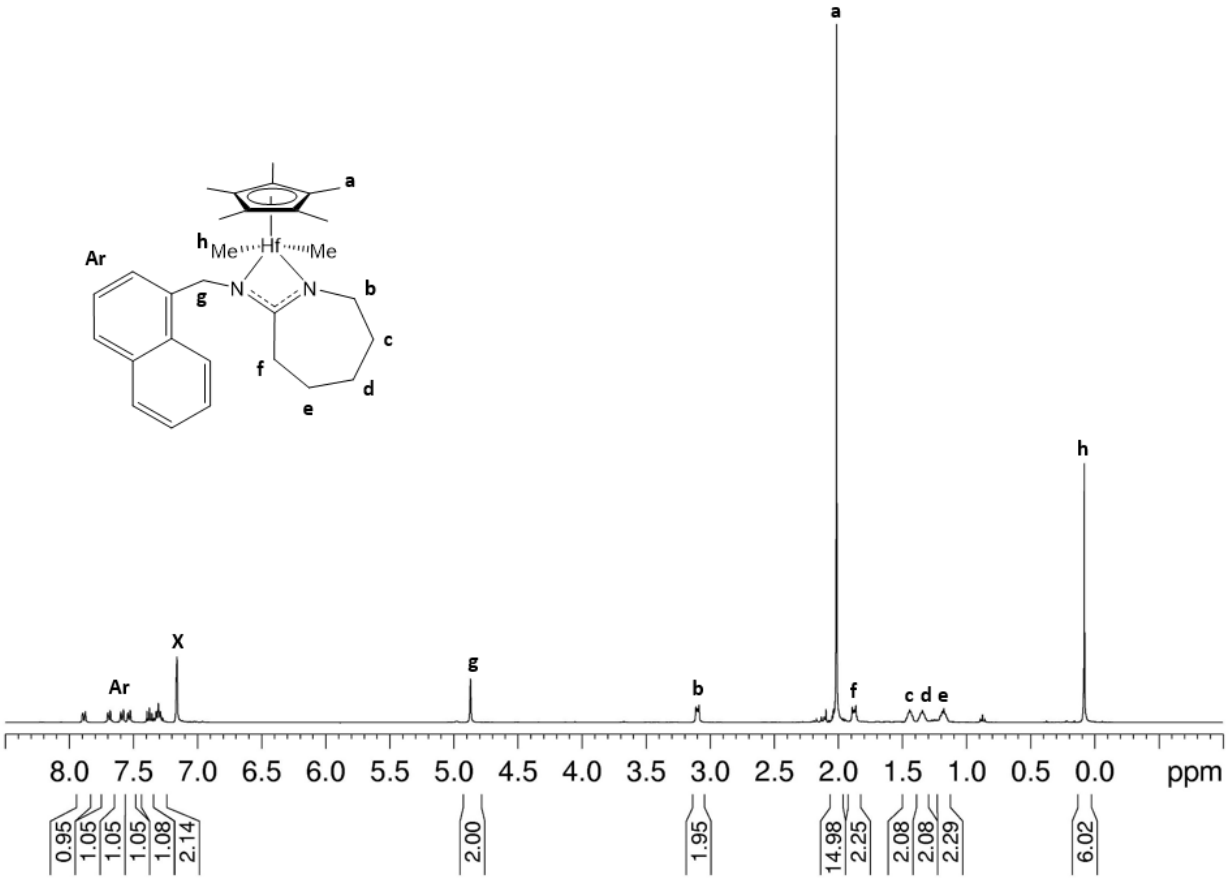

Figure S2: ^{1}H NMR (400 MHz, C_6D_6, 25 °C) spectrum of **2**; **X** denotes benzene-d_6 solvent.

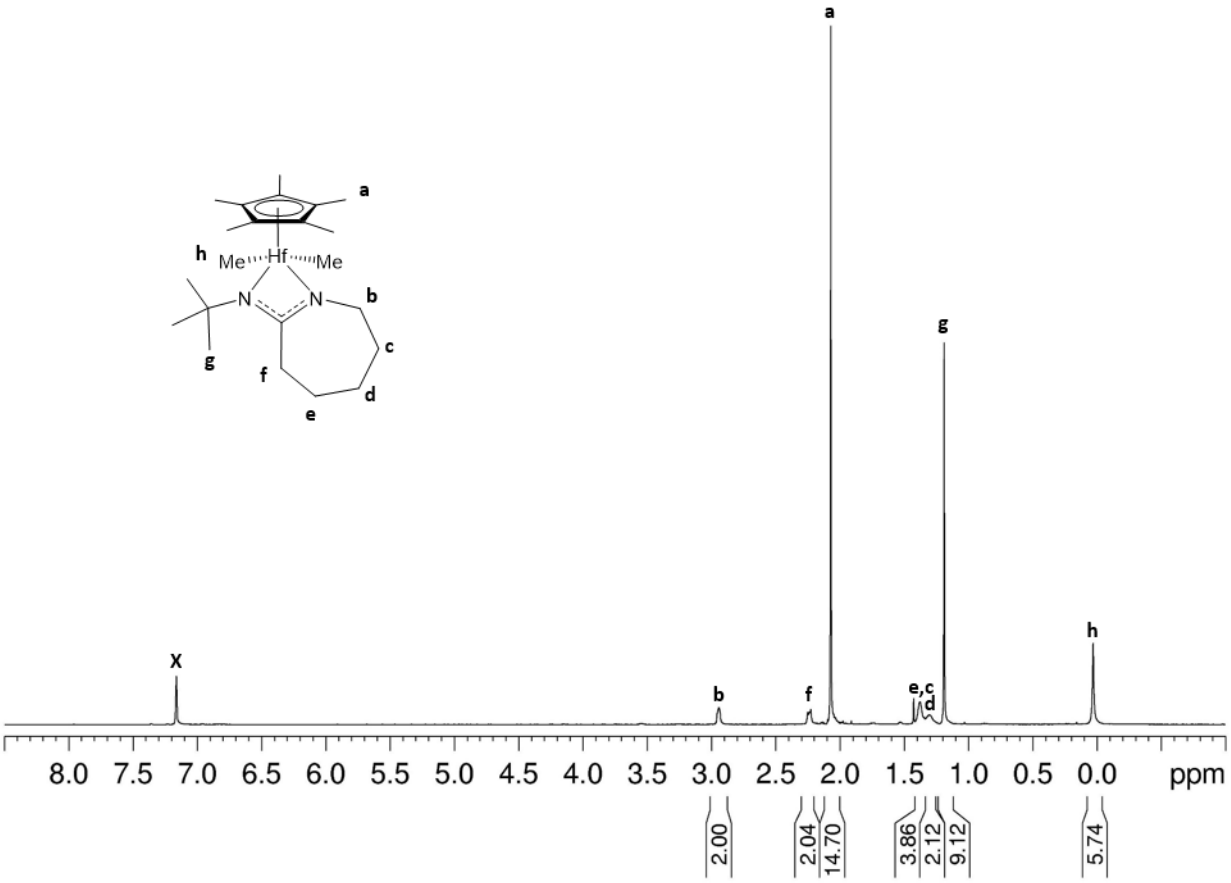

Figure S3: ^{1}H NMR (400 MHz, C_6D_6, 25 °C) spectrum of **3**; **X** denotes benzene-d_6 solvent.

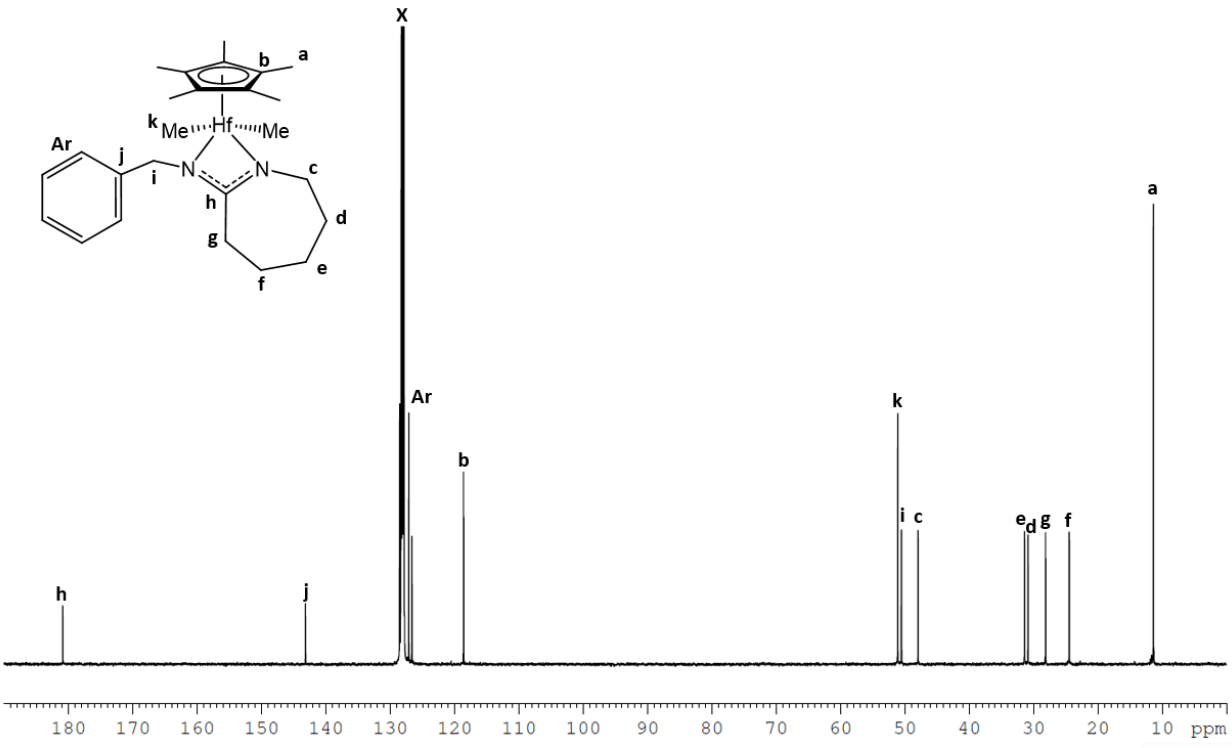

Figure S4: ^{13}C NMR (125MHz, C_6D_6, 25 °C) spectrum of **1**; **X** denotes benzene-d_6 solvent.

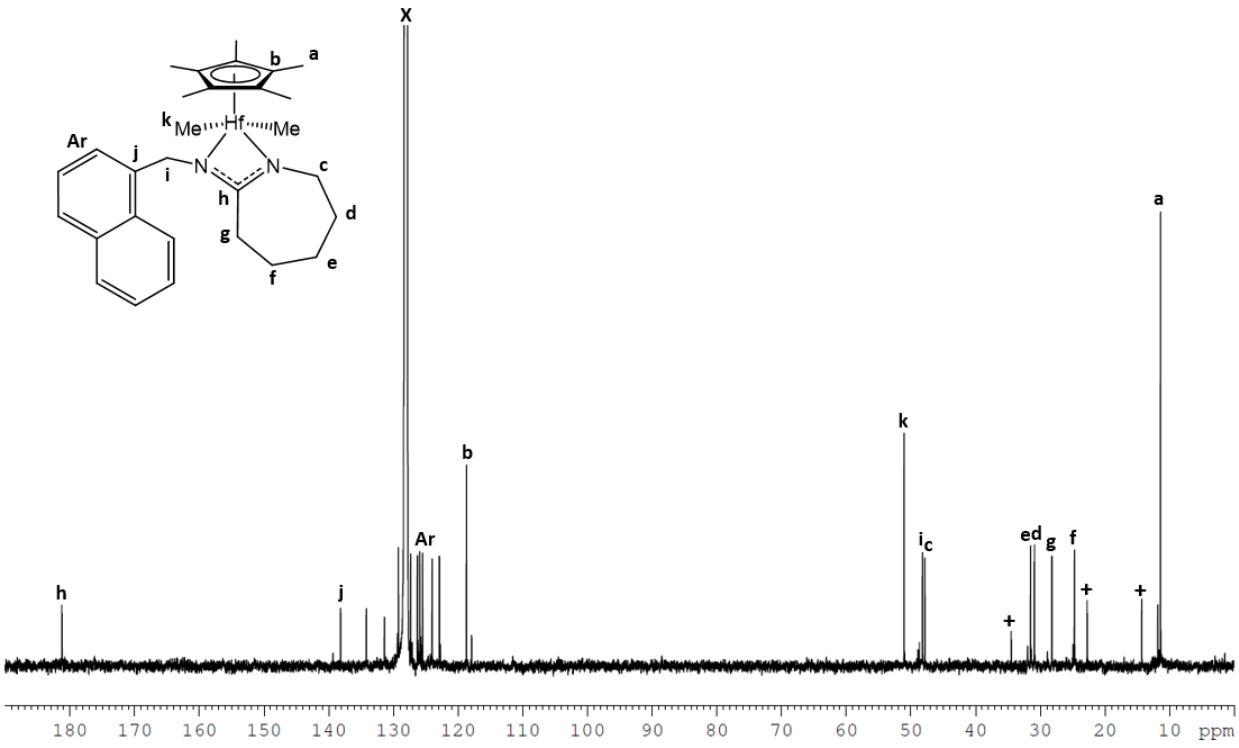

Figure S5: ^{13}C NMR (125 MHz, C_6D_6, 25 °C) spectrum of **2**; **+** denotes pentane solvent impurity, **X** denotes benzene-d_6 solvent.

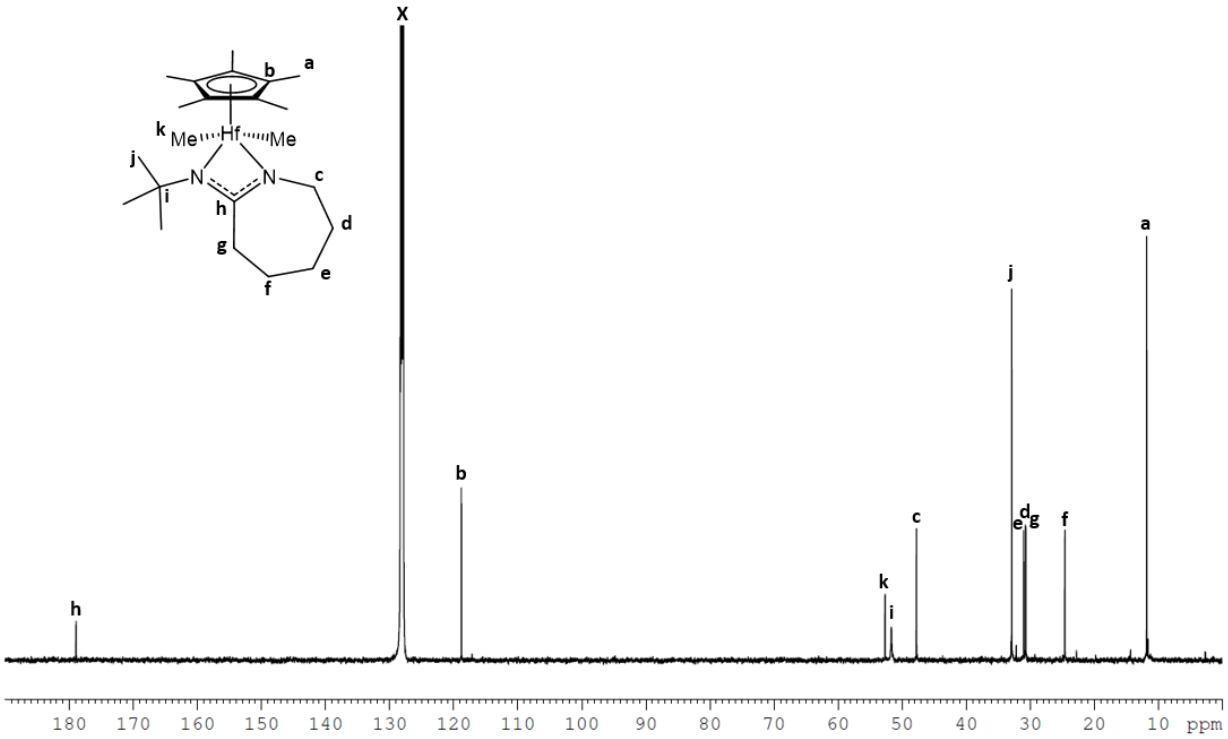

Figure S6: ^{13}C NMR (125 MHz, C_6D_6, 25 °C) spectrum of **3**; **X** denotes benzene-d_6 solvent.

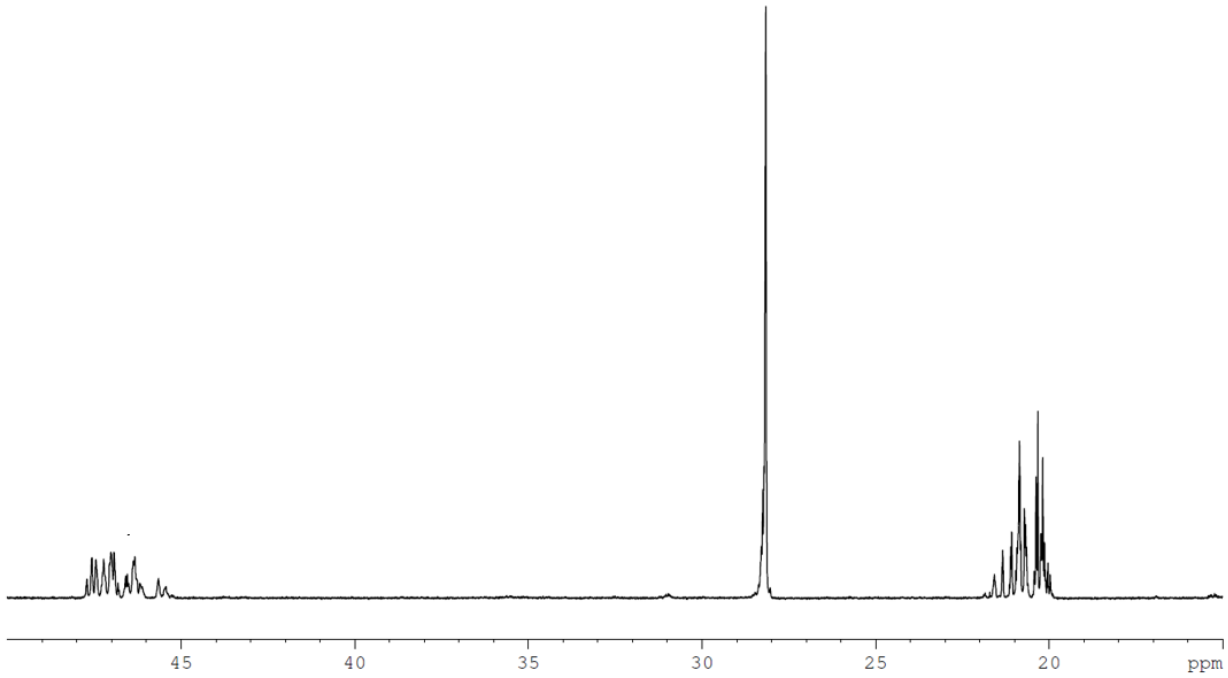

Figure S7: ^{13}C NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 90 °C) spectrum of polypropylene obtained by LCP using **1** (see Figure 3 for expanded methyl region).

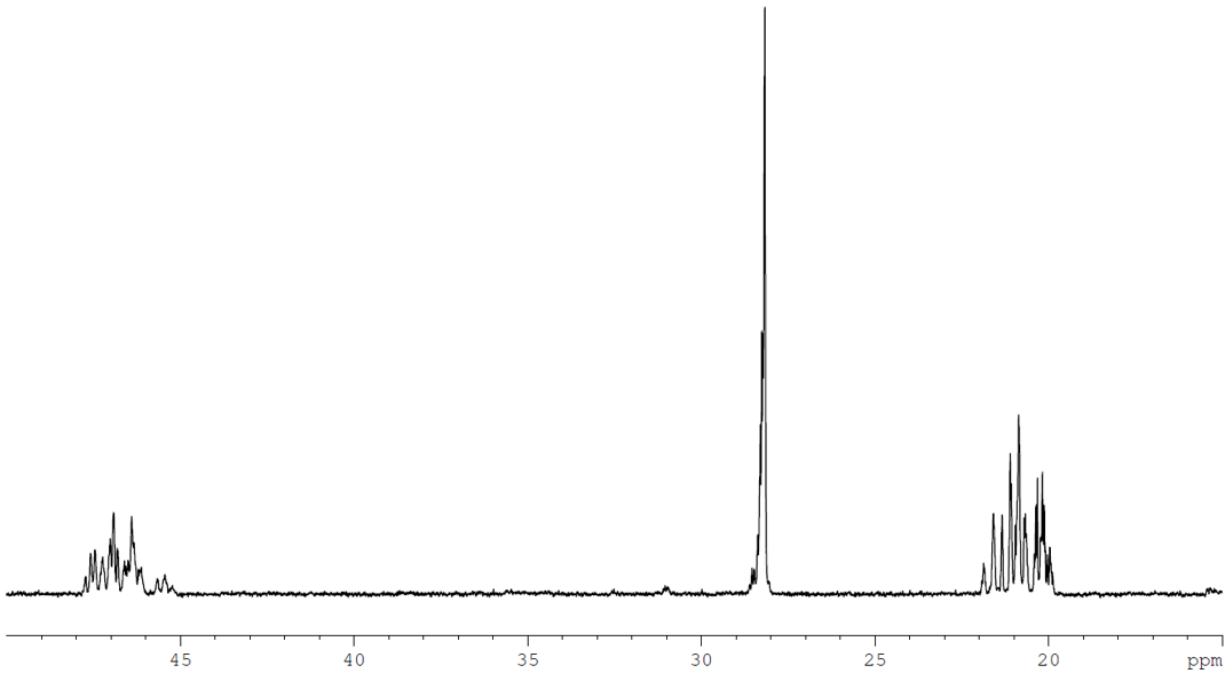

Figure S8: ^{13}C NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 90 °C) spectrum of polypropylene obtained by LCP using **2** (see Figure 3 for expanded methyl region).

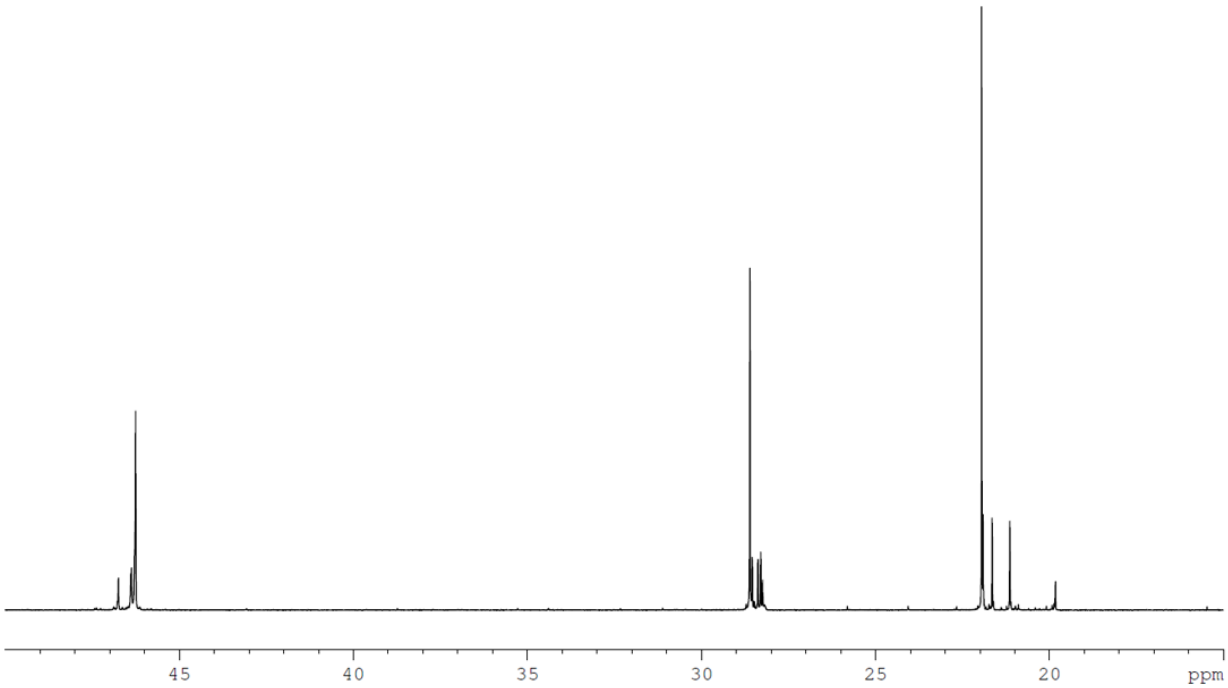

Figure S9: ^{13}C NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 90 °C) spectrum of polypropylene obtained by LCP using **3** (see Figure 3 for expanded methyl region).

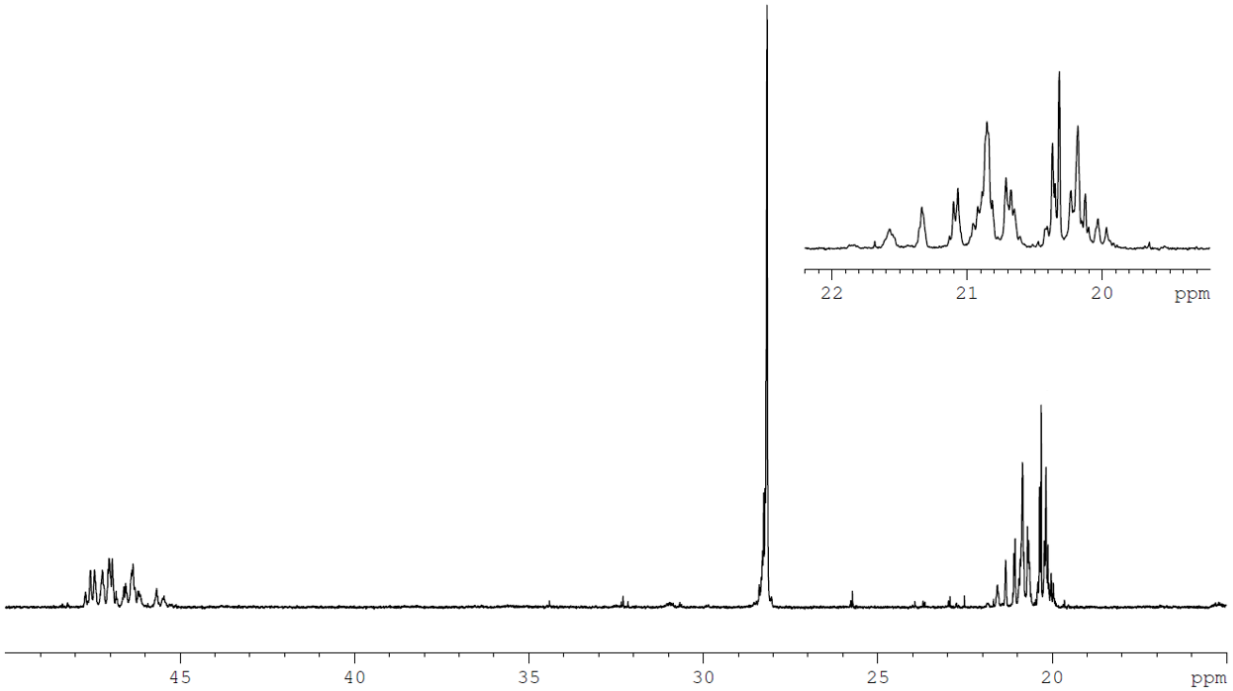

Figure S10: ^{13}C NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 90 °C) spectrum of polypropylene obtained by LCCPT using **1** with expanded methyl region.

Cp*Hf[(*N*-$CH_2C_6H_5$)(N^{imcap}N](Me)$_2$ (1)

See Figure 1a for Structure.

Crystal Structure Collection, Structure Solution and Refinement Data for 1.

A colorless prism-like specimen of $C_{25}H_{38}HfN_2$, approximate dimensions 0.12 mm × 0.21 mm × 0.40 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoKα sealed tube (λ = 0.71073 Å). Data collection temperature was 150 K.

The total exposure time was 7.58 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 28709 reflections to a maximum θ angle of 30.00° (0.71 Å resolution), of which 6990 were independent (average redundancy 4.107, completeness = 100.0%, R_{int} = 2.02%) and 6176 (88.35%) were greater than 2σ(F^2). The final cell constants of *a* = 15.7236(7) Å, *b* = 8.6027(4) Å, *c* = 19.2275(8) Å, β = 112.7457(5)°, *V* = 2398.55(18) Å^3, are based upon the refinement of the XYZ-centroids of 9998 reflections above 20 σ(I) with 5.263° < 2θ < 61.24°. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4360 and 0.5930.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2(1)/n, with Z = 4 for the formula unit, $C_{25}H_{38}HfN_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 298 variables converged at R_1 = 1.86%, for the observed data and wR_2 = 3.90% for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 1.072 e^-/Å^3 and the largest hole was -1.081 e^-/Å^3 with an RMS deviation of 0.071 e^-/Å^3. On the basis of the final model, the calculated density was 1.509 g/cm^3 and F(000), 1096 e^-.

Table S1. Sample and crystal data for 1.

Chemical formula	$C_{25}H_{38}HfN_2$
Formula weight	545.06
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal size	0.12 × 0.21 × 0.40 mm
Crystal habit	colorless prism
Crystal system	monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 15.7236(7) Å α = 90°

	b = 8.6027(4) Å	β = 112.7457(5)°
	c = 19.2275(8) Å	γ = 90°
Volume	2398.55(18) $Å^3$	
Z	4	
Density (calculated)	1.509 Mg/cm^3	
Absorption coefficient	4.361 mm^{-1}	
F(000)	1096	

Table S2. Data collection and structure refinement for 1.

Diffractometer	Bruker APEX-II CCD	
Radiation source	sealed tube, MoKα	
Theta range for data collection	2.13 to 30.00°	
Index ranges	$-22 \le h \le 22$, $-12 \le k \le 12$, $-26 \le l \le 27$	
Reflections collected	28709	
Independent reflections	6990 [R(int) = 0.0202]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.5930 and 0.4360	
Structure solution technique	direct methods	
Structure solution program	ShelXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	ShelXL-2012 (Sheldrick, 2012)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6990 / 0 / 298	
Goodness-of-fit on F^2	1.000	
Δ/σ_{max}	0.001	
Final R indices	6176 data; I>2σ(I)	R_1 = 0.0186, wR_2 = 0.0374
	all data	R_1 = 0.0233, wR_2 = 0.0390
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0100P)^2+2.5000P]$, $P=(F_o^2+2F_c^2)/3$	

Largest diff. peak and hole	1.072 and -1.081 eÅ^{-3}
R.M.S. deviation from mean	0.071 eÅ^{-3}

$R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})| / \Sigma[F_o^2]$
$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$
$\text{GOOF} = S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

Table S3. Bond lengths (Å) for 1.

Hf1-N2	2.2219(16)	Hf1-N1	2.2390(16)
Hf1-C2	2.256(2)	Hf1-C1	2.257(2)
Hf1-C30	2.4924(19)	Hf1-C34	2.499(2)
Hf1-C31	2.5008(19)	Hf1-C33	2.502(2)
Hf1-C32	2.509(2)	Hf1-C10	2.6894(18)
C1-H1A	0.98	C1-H1B	0.98
C1-H1C	0.98	C2-H2A	0.98
C2-H2B	0.98	C2-H2C	0.98
N1-C10	1.328(2)	N1-C15	1.457(2)
C10-N2	1.335(2)	C10-C11	1.506(2)
C11-C12	1.532(3)	C11-H11A	0.99
C11-H11B	0.99	C12-C13	1.524(3)
C12-H12A	0.99	C12-H12B	0.99
C13-C14	1.521(3)	C13-H13A	0.99
C13-H13B	0.99	C14-C15	1.524(3)
C14-H14A	0.99	C14-H14B	0.99
C15-H15A	0.99	C15-H15B	0.99
N2-C20	1.451(2)	C20-C21	1.521(3)
C20-H20A	0.99	C20-H20B	0.99
C21-C22	1.384(3)	C21-C26	1.388(3)
C22-C23	1.395(3)	C22-H22	0.95
C23-C24	1.368(3)	C23-H23	0.95
C24-C25	1.370(4)	C24-H24	0.95
C25-C26	1.400(4)	C25-H25	0.95
C26-H26	0.95	C30-C31	1.405(3)
C30-C34	1.416(3)	C30-C35	1.507(3)

C31-C32	1.408(3)	C31-C36	1.509(3)
C32-C33	1.401(4)	C32-C37	1.506(3)
C33-C34	1.403(4)	C33-C38	1.515(4)
C34-C39	1.512(4)	C35-H35A	0.98
C35-H35B	0.98	C35-H35C	0.98
C36-H36A	0.98	C36-H36B	0.98
C36-H36C	0.98	C37-H37A	0.98
C37-H37B	0.98	C37-H37C	0.98
C38-H38A	0.98	C38-H38B	0.98
C38-H38C	0.98	C39-H39A	0.98
C39-H39B	0.98	C39-H39C	0.98

Table S4. Bond angles (°) for 1.

N2-Hf1-N1	58.97(6)	N2-Hf1-C2	87.63(9)
N1-Hf1-C2	128.45(8)	N2-Hf1-C1	130.06(8)
N1-Hf1-C1	84.61(8)	C2-Hf1-C1	90.88(11)
N2-Hf1-C30	86.72(6)	N1-Hf1-C30	95.43(7)
C2-Hf1-C30	122.72(9)	C1-Hf1-C30	133.14(8)
N2-Hf1-C34	95.82(8)	N1-Hf1-C34	126.93(8)
C2-Hf1-C34	91.49(9)	C1-Hf1-C34	134.12(9)
C30-Hf1-C34	32.96(8)	N2-Hf1-C31	111.27(6)
N1-Hf1-C31	89.87(6)	C2-Hf1-C31	141.07(8)
C1-Hf1-C31	100.59(8)	C30-Hf1-C31	32.69(6)
C34-Hf1-C31	54.22(7)	N2-Hf1-C33	127.88(8)
N1-Hf1-C33	143.82(7)	C2-Hf1-C33	87.37(8)
C1-Hf1-C33	101.86(9)	C30-Hf1-C33	54.24(7)
C34-Hf1-C33	32.60(9)	C31-Hf1-C33	53.98(7)
N2-Hf1-C32	140.82(7)	N1-Hf1-C32	115.95(7)
C2-Hf1-C32	114.49(9)	C1-Hf1-C32	83.69(8)
C30-Hf1-C32	54.22(7)	C34-Hf1-C32	54.06(8)
C31-Hf1-C32	32.65(7)	C33-Hf1-C32	32.46(9)
N2-Hf1-C10	29.64(5)	N1-Hf1-C10	29.50(5)
C2-Hf1-C10	107.89(8)	C1-Hf1-C10	106.91(7)
C30-Hf1-C10	93.54(6)	C34-Hf1-C10	115.76(8)
C31-Hf1-C10	104.08(6)	C33-Hf1-C10	146.92(7)
C32-Hf1-C10	136.15(7)	Hf1-C1-H1A	109.5

Hf1-C1-H1B	109.5	H1A-C1-H1B	109.5
Hf1-C1-H1C	109.5	H1A-C1-H1C	109.5
H1B-C1-H1C	109.5	Hf1-C2-H2A	109.5
Hf1-C2-H2B	109.5	H2A-C2-H2B	109.5
Hf1-C2-H2C	109.5	H2A-C2-H2C	109.5
H2B-C2-H2C	109.5	C10-N1-C15	122.68(17)
C10-N1-Hf1	94.39(11)	C15-N1-Hf1	140.20(13)
N1-C10-N2	111.07(16)	N1-C10-C11	124.40(17)
N2-C10-C11	124.52(17)	N1-C10-Hf1	56.11(9)
N2-C10-Hf1	55.39(9)	C11-C10-Hf1	173.22(13)
C10-C11-C12	114.31(17)	C10-C11-H11A	108.7
C12-C11-H11A	108.7	C10-C11-H11B	108.7
C12-C11-H11B	108.7	H11A-C11-H11B	107.6
C13-C12-C11	114.86(19)	C13-C12-H12A	108.6
C11-C12-H12A	108.6	C13-C12-H12B	108.6
C11-C12-H12B	108.6	H12A-C12-H12B	107.5
C14-C13-C12	114.80(18)	C14-C13-H13A	108.6
C12-C13-H13A	108.6	C14-C13-H13B	108.6
C12-C13-H13B	108.6	H13A-C13-H13B	107.5
C13-C14-C15	114.00(18)	C13-C14-H14A	108.8
C15-C14-H14A	108.8	C13-C14-H14B	108.8
C15-C14-H14B	108.8	H14A-C14-H14B	107.6
N1-C15-C14	115.06(17)	N1-C15-H15A	108.5
C14-C15-H15A	108.5	N1-C15-H15B	108.5
C14-C15-H15B	108.5	H15A-C15-H15B	107.5
C10-N2-C20	123.13(17)	C10-N2-Hf1	94.97(11)
C20-N2-Hf1	141.85(13)	N2-C20-C21	116.78(17)
N2-C20-H20A	108.1	C21-C20-H20A	108.1
N2-C20-H20B	108.1	C21-C20-H20B	108.1
H20A-C20-H20B	107.3	C22-C21-C26	118.5(2)
C22-C21-C20	122.62(18)	C26-C21-C20	118.9(2)
C21-C22-C23	120.8(2)	C21-C22-H22	119.6
C23-C22-H22	119.6	C24-C23-C22	120.4(3)
C24-C23-H23	119.8	C22-C23-H23	119.8
C23-C24-C25	119.4(2)	C23-C24-H24	120.3
C25-C24-H24	120.3	C24-C25-C26	120.9(2)

C24-C25-H25	119.6	C26-C25-H25	119.6
C21-C26-C25	120.0(2)	C21-C26-H26	120.0
C25-C26-H26	120.0	C31-C30-C34	107.71(19)
C31-C30-C35	126.3(2)	C34-C30-C35	125.9(2)
C31-C30-Hf1	73.98(11)	C34-C30-Hf1	73.77(12)
C35-C30-Hf1	120.13(15)	C30-C31-C32	108.21(19)
C30-C31-C36	125.0(2)	C32-C31-C36	126.7(2)
C30-C31-Hf1	73.32(11)	C32-C31-Hf1	74.00(12)
C36-C31-Hf1	121.23(14)	C33-C32-C31	107.8(2)
C33-C32-C37	126.4(3)	C31-C32-C37	125.4(3)
C33-C32-Hf1	73.49(13)	C31-C32-Hf1	73.35(11)
C37-C32-Hf1	123.69(17)	C32-C33-C34	108.5(2)
C32-C33-C38	125.5(3)	C34-C33-C38	125.8(3)
C32-C33-Hf1	74.04(12)	C34-C33-Hf1	73.57(12)
C38-C33-Hf1	122.09(18)	C33-C34-C30	107.7(2)
C33-C34-C39	126.4(3)	C30-C34-C39	125.8(3)
C33-C34-Hf1	73.83(14)	C30-C34-Hf1	73.27(11)
C39-C34-Hf1	120.85(17)	C30-C35-H35A	109.5
C30-C35-H35B	109.5	H35A-C35-H35B	109.5
C30-C35-H35C	109.5	H35A-C35-H35C	109.5
H35B-C35-H35C	109.5	C31-C36-H36A	109.5
C31-C36-H36B	109.5	H36A-C36-H36B	109.5
C31-C36-H36C	109.5	H36A-C36-H36C	109.5
H36B-C36-H36C	109.5	C32-C37-H37A	109.5
C32-C37-H37B	109.5	H37A-C37-H37B	109.5
C32-C37-H37C	109.5	H37A-C37-H37C	109.5
H37B-C37-H37C	109.5	C33-C38-H38A	109.5
C33-C38-H38B	109.5	H38A-C38-H38B	109.5
C33-C38-H38C	109.5	H38A-C38-H38C	109.5
H38B-C38-H38C	109.5	C34-C39-H39A	109.5
C34-C39-H39B	109.5	H39A-C39-H39B	109.5
C34-C39-H39C	109.5	H39A-C39-H39C	109.5
H39B-C39-H39C	109.5		

Cp*Hf[(*N*-CH_2(1-$C_{10}H_7$))(N^{imcap}N](Me)$_2$ (2)

See Figure 1b for Structure.

Crystal Structure Collection, Structure Solution and Refinement Data for 2.

A colorless prism of $C_{29}H_{40}N_2Hf$, approximate dimensions 0.100 x 0.220 x 0.315 mm^3, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 100(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073 Å) . The detector was placed at a distance of 5.0000 cm from the crystal.

A total of 3030 frames were collected with a scan width of -0.30° an exposure time of 15 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 17.7 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 40302 reflections to a maximum θ angle of 29.99°, of which 7589 were independent (completeness = 99.8%, R_{int} = 2.00%, R_{sig} = 1.36%) and 7086 were greater than 2σ(I). The final cell dimensions of *a* = 12.4154(11) Å, *b* = 14.4484(12) Å, *c* = 14.7104(13) Å, α = 90°, β = 99.4140(10)°, γ = 90°, *V* = 2603.3(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 29590 reflections with 2.2 < θ < 32.4° using Apex2 software. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.354 and 0.669.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group $P2_1/n$ with *Z* = 4 for the formula unit $C_{29}H_{40}N_2Hf$. The final anisotropic full-matrix least-squares refinement on F^2 with 316 variables converged at R_1 = 1.47 % for the observed data and wR_2 = 3.42 % for all data. The goodness-of-fit was 1.003. The largest peak on the final difference map was 1.149 $e^-/Å^3$ and the largest hole was -0.411 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.518 g/cm^3 and F(000), 1200e^-.

Table S5. Crystal data and structure refinement for 2.

Empirical formula	C29 H40 Hf N2
Formula weight	595.12
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.315x0.220x0.100 mm^3
Crystal habit	colorless prism
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	*a* = 12.4154(11) Å α = 90°
	b = 14.4484(12) Å β = 99.4140(10)°
	c = 14.7104(13) Å γ = 90°
Volume	2603.3(4) $Å^3$
Z	4
Density, ρ_{calc}	1.518 g/cm^3
Absorption coefficient, m	4.025 mm^{-1}
F(000)	1200e^-

Diffractometer		Bruker Smart Apex II CCD area detector
Radiation source		fine-focus sealed tube, MoKa
Detector distance		5.0000 cm
Data collection method		ω and ϕ scans
Total frames		3030
Frame size		512 pixels
Frame width		-0.30°
Exposure per frame		15 sec
Total measurement time		17.7 hours
θ range for data collection		1.99 to 29.99°
Index ranges		$-17 \leq h \leq 17$, $-20 \leq k \leq 20$, $-20 \leq l \leq 20$
Reflections collected		40302
Independent reflections		7589
Observed reflection, I>2σ(I)		7086
Coverage of independent reflections		99.8 %
Variation in check reflections		0 %
Absorption correction		Semi-empirical from equivalents SADABS (Sheldrick, 1996)
Max. and min. transmission		0.669 and 0.354
Structure solution technique		direct
Structure solution program		SHELXS-97 (Sheldrick, 1990)
Refinement technique		Full-matrix least-squares on F^2
Refinement program		SHELXL-97 (Sheldrick, 1997)
Function minimized		$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters		7589 / 0 / 316
Goodness-of-fit on F^2		1.003
Δ/σ_{max}		0.006
Final R indices:	R_1, I>2σ(I)	0.0147
	wR_2, all data	0.0342
	R_{int}	0.0200
	R_{sig}	0.0136
Weighting scheme		$w = 1/[\sigma^2(F_o^2)+ (0.01P)^2 + 2.8P]$, $P = [\max(F_o^2 ,0) + 2F_o^2]/3$
Largest diff. peak and hole		1.149 and -0.411e^-/Å^3

Table S6. Bond lengths (Å) and angles (°) for 2.

Hf1-N2	2.2083(13)	Hf1-N1	2.2444(12)	Hf1-C2	2.2598(15)
Hf1-C1	2.2683(16)	Hf1-C31	2.4796(15)	Hf1-C32	2.4840(15)
Hf1-C30	2.5036(15)	Hf1-C33	2.5113(15)	Hf1-C34	2.5169(15)
N1-C21	1.3385(18)	N1-C10	1.4562(18)	C10-C11	1.521(2)
C11-C12	1.371(2)	C11-C20	1.4346(19)	C12-C13	1.420(2)
C13-C14	1.367(2)	C14-C15	1.420(2)	C15-C16	1.421(2)
C15-C20	1.427(2)	C16-C17	1.365(3)	C17-C18	1.409(2)
C18-C19	1.377(2)	C19-C20	1.422(2)	N2-C21	1.3332(18)
N2-C26	1.4599(18)	C21-C22	1.501(2)	C22-C23	1.540(2)
C23-C24	1.529(2)	C24-C25	1.524(2)	C25-C26	1.527(2)
C30-C31	1.420(2)	C30-C34	1.422(2)	C30-C35	1.506(2)
C31-C32	1.425(2)	C31-C36	1.503(2)	C32-C33	1.423(2)
C32-C37	1.499(2)	C33-C34	1.414(2)	C33-C38	1.502(2)

C34-C39	1.502(2)				
N2-Hf1-N1	59.41(4)	N2-Hf1-C2	85.51(5)	N1-Hf1-C2	128.22(5)
N2-Hf1-C1	130.19(6)	N1-Hf1-C1	84.69(5)	C2-Hf1-C1	92.84(6)
N2-Hf1-C31	118.33(5)	N1-Hf1-C31	94.01(5)	C2-Hf1-C31	137.54(6)
C1-Hf1-C31	95.71(6)	N2-Hf1-C32	142.08(5)	N1-Hf1-C32	124.69(5)
C2-Hf1-C32	106.57(6)	C1-Hf1-C32	85.89(6)	C31-Hf1-C32	33.37(5)
N2-Hf1-C30	88.82(5)	N1-Hf1-C30	91.59(5)	C2-Hf1-C30	127.07(6)
C1-Hf1-C30	128.41(6)	C31-Hf1-C30	33.10(5)	C32-Hf1-C30	54.94(5)
N2-Hf1-C33	118.75(5)	N1-Hf1-C33	145.55(5)	C2-Hf1-C33	83.17(6)
C1-Hf1-C33	110.39(6)	C31-Hf1-C33	54.90(5)	C32-Hf1-C33	33.10(5)
C30-Hf1-C33	54.51(5)	N2-Hf1-C34	89.30(5)	N1-Hf1-C34	119.55(5)
C2-Hf1-C34	94.35(6)	C1-Hf1-C34	140.31(6)	C31-Hf1-C34	54.77(5)
C32-Hf1-C34	54.68(5)	C30-Hf1-C34	32.91(5)	C33-Hf1-C34	32.65(5)
C21-N1-C10	122.13(13)	C21-N1-Hf1	91.73(9)	C10-N1-Hf1	138.56(10)
N1-C10-C11	114.86(12)	C12-C11-C20	119.05(13)	C12-C11-C10	121.29(13)
C20-C11-C10	119.64(13)	C11-C12-C13	121.71(14)	C14-C13-C12	120.13(15)
C13-C14-C15	120.34(14)	C14-C15-C16	121.17(14)	C14-C15-C20	119.54(14)
C16-C15-C20	119.25(14)	C17-C16-C15	121.08(15)	C16-C17-C18	120.04(15)
C19-C18-C17	120.49(15)	C18-C19-C20	120.98(14)	C19-C20-C15	118.13(13)
C19-C20-C11	122.64(13)	C15-C20-C11	119.21(14)	C21-N2-C26	122.33(13)
C21-N2-Hf1	93.46(9)	C26-N2-Hf1	136.72(10)	N2-C21-N1	111.37(13)
N2-C21-C22	122.97(13)	N1-C21-C22	125.66(13)	C21-C22-C23	112.64(12)
C24-C23-C22	114.84(13)	C25-C24-C23	115.42(13)	C24-C25-C26	113.66(13)
N2-C26-C25	113.83(12)	C31-C30-C34	107.94(13)	C31-C30-C35	127.35(14)
C34-C30-C35	124.62(14)	C31-C30-Hf1	72.52(8)	C34-C30-Hf1	74.06(8)
C35-C30-Hf1	121.83(10)	C30-C31-C32	107.94(13)	C30-C31-C36	126.19(14)
C32-C31-C36	125.82(15)	C30-C31-Hf1	74.38(8)	C32-C31-Hf1	73.48(8)
C36-C31-Hf1	119.83(11)	C33-C32-C31	107.78(14)	C33-C32-C37	124.56(14)
C31-C32-C37	127.38(14)	C33-C32-Hf1	74.51(9)	C31-C32-Hf1	73.15(8)
C37-C32-Hf1	122.91(11)	C34-C33-C32	108.15(13)	C34-C33-C38	126.49(14)
C32-C33-C38	125.03(15)	C34-C33-Hf1	73.89(9)	C32-C33-Hf1	72.39(8)
C38-C33-Hf1	124.75(11)	C33-C34-C30	108.19(13)	C33-C34-C39	126.71(14)
C30-C34-C39	125.05(15)	C33-C34-Hf1	73.46(9)	C30-C34-Hf1	73.03(8)
C39-C34-Hf1	121.46(11)				

Cp*Hf[(*N*-C(CH$_3$)$_3$)(N^{imcap}N](Me)$_2$ (3)

See Figure 1c for Structure.

Crystal Structure Collection, Structure Solution and Refinement Data for 1c.

A colorless prism-like specimen of $C_{22}H_{40}HfN_2$, approximate dimensions 0.03 mm × 0.21 mm × 0.24 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoKα sealed tube (λ = 0.71073 Å). Data collection temperature was 150 K.

The total exposure time was 22.72 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 7802 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 7802 were independent (average redundancy 1.000, completeness = 99.9%) and 5245 (67.23%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.3014(19) Å, b = 16.1418(19) Å, c = 8.5713(10) Å, β = 92.463(2)°, V = 2253.3(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 3276 reflections above 20 σ(I) with 5.385° < 2θ < 48.68°. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4400 and 0.8910.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Pc, with Z = 4 for the formula unit, $C_{22}H_{40}HfN_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 430 variables converged at R_1 = 4.94%, for the observed data and wR_2 = 13.26% for all data. The goodness-of-fit was 1.025. The largest peak in the final difference electron density synthesis was 1.148 $e^-/Å^3$ and the largest hole was -1.256 $e^-/Å^3$ with an RMS deviation of 0.139 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.506 g/cm^3 and F(000), 1032 e^-.

Table S7. Sample and crystal data for 3.

Chemical formula	$C_{22}H_{40}HfN_2$	
Formula weight	511.05	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	0.03 × 0.21 × 0.24 mm	
Crystal habit	colorless prism	
Crystal system	monoclinic	
Space group	Pc	
Unit cell dimensions	a = 16.3014(19) Å	α = 90°
	b = 16.1418(19) Å	β = 92.463(2)°
	c = 8.5713(10) Å	γ = 90°
Volume	2253.3(5) $Å^3$	
Z	4	
Density (calculated)	1.506 Mg/cm^3	

Absorption coefficient	4.636 mm^{-1}
F(000)	1032

Table S8. Data collection and structure refinement for 3.

Diffractometer	Bruker APEX-II CCD	
Radiation source	sealed tube, MoKα	
Theta range for data collection	2.50 to 25.00°	
Index ranges	$-19 \le h \le 19$, $-19 \le k \le 19$, $-10 \le l \le 10$	
Reflections collected	7802	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8910 and 0.4400	
Structure solution technique	direct methods	
Structure solution program	ShelXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	ShelXL-2012 (Sheldrick, 2012)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7802 / 714 / 430	
Goodness-of-fit on F^2	1.025	
Final R indices	5245 data; $I>2\sigma(I)$	$R_1 = 0.0494$, $wR_2 = 0.1125$
	all data	$R_1 = 0.0807$, $wR_2 = 0.1326$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0200P)^2+22.0000P]$, $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.0(0)	
Largest diff. peak and hole	1.148 and -1.256 eÅ^{-3}	
R.M.S. deviation from mean	0.139 eÅ^{-3}	

$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

GOOF = S = $\{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

Table S9. Bond lengths (Å) for 3.

Hf1-N1	2.20(2)	Hf1-N2	2.245(19)
Hf1-C1	2.25(4)	Hf1-C2	2.35(4)
Hf1-C20	2.49(2)	Hf1-C24	2.49(2)
Hf1-C21	2.529(19)	Hf1-C23	2.53(2)
Hf1-C22	2.56(2)	C1-H1A	0.98
C1-H1B	0.98	C1-H1C	0.98
C2-H2A	0.98	C2-H2B	0.98
C2-H2C	0.98	N1-C10	1.32(2)
N1-C15	1.53(2)	C10-N2	1.36(2)
C10-C11	1.60(2)	C11-C12	1.50(2)
C11-H11A	0.99	C11-H11B	0.99
C12-C13	1.54(2)	C12-H12A	0.99
C12-H12B	0.99	C13-C14	1.59(2)
C13-H13A	0.99	C13-H13B	0.99
C14-C15	1.49(2)	C14-H14A	0.99
C14-H14B	0.99	C15-H15A	0.99
C15-H15B	0.99	N2-C16	1.465(19)
C16-C17	1.47(2)	C16-C18	1.52(2)
C16-C19	1.53(2)	C17-H17A	0.98
C17-H17B	0.98	C17-H17C	0.98
C18-H18A	0.98	C18-H18B	0.98
C18-H18C	0.98	C19-H19A	0.98
C19-H19B	0.98	C19-H19C	0.98
C20-C21	1.42	C20-C24	1.42
C20-C25	1.504(15)	C21-C22	1.42
C21-C26	1.512(14)	C22-C23	1.42
C22-C27	1.507(15)	C23-C24	1.42
C23-C28	1.511(14)	C24-C29	1.519(15)
C25-H25A	0.98	C25-H25B	0.98
C25-H25C	0.98	C26-H26A	0.98
C26-H26B	0.98	C26-H26C	0.98
C27-H27A	0.98	C27-H27B	0.98
C27-H27C	0.98	C28-H28A	0.98

C28-H28B	0.98	C28-H28C	0.98
C29-H29A	0.98	C29-H29B	0.98
C29-H29C	0.98	Hf2-N3	2.21(2)
Hf2-C4	2.22(5)	Hf2-N4	2.25(2)
Hf2-C3	2.28(4)	Hf2-C41	2.44(2)
Hf2-C42	2.45(2)	Hf2-C40	2.52(2)
Hf2-C43	2.54(2)	Hf2-C44	2.58(2)
Hf2-C30	2.73(3)	C3-H3A	0.98
C3-H3B	0.98	C3-H3C	0.98
C4-H4A	0.98	C4-H4B	0.98
C4-H4C	0.98	N3-C30	1.34(2)
N3-C35	1.53(3)	C30-N4	1.36(2)
C30-C31	1.59(2)	C31-C32	1.510(19)
C31-H31A	0.99	C31-H31B	0.99
C32-C33	1.541(18)	C32-H32A	0.99
C32-H32B	0.99	C33-C34	1.580(19)
C33-H33A	0.99	C33-H33B	0.99
C34-C35	1.500(19)	C34-H34A	0.99
C34-H34B	0.99	C35-H35A	0.99
C35-H35B	0.99	N4-C36	1.463(19)
C36-C37	1.47(2)	C36-C38	1.52(2)
C36-C39	1.53(2)	C37-H37A	0.98
C37-H37B	0.98	C37-H37C	0.98
C38-H38A	0.98	C38-H38B	0.98
C38-H38C	0.98	C39-H39A	0.98
C39-H39B	0.98	C39-H39C	0.98
C40-C41	1.42	C40-C44	1.42
C40-C45	1.507(15)	C41-C42	1.42
C41-C46	1.510(15)	C42-C43	1.42
C42-C47	1.496(15)	C43-C44	1.42
C43-C48	1.512(14)	C44-C49	1.509(15)
C45-H45A	0.98	C45-H45B	0.98
C45-H45C	0.98	C46-H46A	0.98
C46-H46B	0.98	C46-H46C	0.98
C47-H47A	0.98	C47-H47B	0.98
C47-H47C	0.98	C48-H48A	0.98

C48-H48B	0.98	C48-H48C	0.98
C49-H49A	0.98	C49-H49B	0.98
C49-H49C	0.98		

Table S10. Bond angles (°) for 3.

N1-Hf1-N2	59.1(6)	N1-Hf1-C1	81.1(16)
N2-Hf1-C1	125.3(15)	N1-Hf1-C2	134.3(13)
N2-Hf1-C2	87.7(12)	C1-Hf1-C2	96.9(18)
N1-Hf1-C20	134.7(9)	N2-Hf1-C20	141.3(7)
C1-Hf1-C20	93.2(14)	C2-Hf1-C20	91.0(12)
N1-Hf1-C24	132.0(10)	N2-Hf1-C24	108.3(7)
C1-Hf1-C24	126.4(14)	C2-Hf1-C24	85.6(12)
C20-Hf1-C24	33.2(3)	N1-Hf1-C21	102.3(8)
N2-Hf1-C21	139.0(8)	C1-Hf1-C21	81.3(14)
C2-Hf1-C21	122.7(12)	C20-Hf1-C21	32.9(2)
C24-Hf1-C21	54.5(3)	N1-Hf1-C23	99.3(10)
N2-Hf1-C23	90.8(8)	C1-Hf1-C23	134.5(14)
C2-Hf1-C23	112.8(12)	C20-Hf1-C23	54.5(3)
C24-Hf1-C23	32.8(3)	C21-Hf1-C23	54.0(2)
N1-Hf1-C22	83.5(9)	N2-Hf1-C22	106.6(8)
C1-Hf1-C22	104.2(14)	C2-Hf1-C22	139.5(12)
C20-Hf1-C22	54.2(3)	C24-Hf1-C22	54.1(3)
C21-Hf1-C22	32.4(2)	C23-Hf1-C22	32.4(2)
Hf1-C1-H1A	109.5	Hf1-C1-H1B	109.5
H1A-C1-H1B	109.5	Hf1-C1-H1C	109.5
H1A-C1-H1C	109.5	H1B-C1-H1C	109.5
Hf1-C2-H2A	109.5	Hf1-C2-H2B	109.5
H2A-C2-H2B	109.5	Hf1-C2-H2C	109.5
H2A-C2-H2C	109.5	H2B-C2-H2C	109.5
C10-N1-C15	119.(2)	C10-N1-Hf1	96.2(13)
C15-N1-Hf1	129.0(18)	N1-C10-N2	109.5(16)
N1-C10-C11	117.(2)	N2-C10-C11	125.(2)
C12-C11-C10	104.(2)	C12-C11-H11A	111.0
C10-C11-H11A	111.0	C12-C11-H11B	111.0
C10-C11-H11B	111.0	H11A-C11-H11B	109.0

C11-C12-C13	107.(2)	C11-C12-H12A	110.3
C13-C12-H12A	110.3	C11-C12-H12B	110.3
C13-C12-H12B	110.3	H12A-C12-H12B	108.6
C12-C13-C14	116.5(19)	C12-C13-H13A	108.2
C14-C13-H13A	108.2	C12-C13-H13B	108.2
C14-C13-H13B	108.2	H13A-C13-H13B	107.3
C15-C14-C13	106.(2)	C15-C14-H14A	110.6
C13-C14-H14A	110.6	C15-C14-H14B	110.6
C13-C14-H14B	110.6	H14A-C14-H14B	108.7
C14-C15-N1	106.(2)	C14-C15-H15A	110.6
N1-C15-H15A	110.6	C14-C15-H15B	110.6
N1-C15-H15B	110.6	H15A-C15-H15B	108.7
C10-N2-C16	122.1(15)	C10-N2-Hf1	93.1(11)
C16-N2-Hf1	144.4(13)	N2-C16-C17	106.7(16)
N2-C16-C18	111.9(17)	C17-C16-C18	109.(2)
N2-C16-C19	113.9(17)	C17-C16-C19	105.7(19)
C18-C16-C19	109.7(19)	C16-C17-H17A	109.5
C16-C17-H17B	109.5	H17A-C17-H17B	109.5
C16-C17-H17C	109.5	H17A-C17-H17C	109.5
H17B-C17-H17C	109.5	C16-C18-H18A	109.5
C16-C18-H18B	109.5	H18A-C18-H18B	109.5
C16-C18-H18C	109.5	H18A-C18-H18C	109.5
H18B-C18-H18C	109.5	C16-C19-H19A	109.5
C16-C19-H19B	109.5	H19A-C19-H19B	109.5
C16-C19-H19C	109.5	H19A-C19-H19C	109.5
H19B-C19-H19C	109.5	C21-C20-C24	108.0
C21-C20-C25	125.9(8)	C24-C20-C25	125.9(8)
C21-C20-Hf1	75.2(9)	C24-C20-Hf1	73.5(8)
C25-C20-Hf1	121.(2)	C22-C21-C20	108.0
C22-C21-C26	125.2(8)	C20-C21-C26	126.3(8)
C22-C21-Hf1	75.0(8)	C20-C21-Hf1	71.9(9)
C26-C21-Hf1	125.1(16)	C23-C22-C21	108.0
C23-C22-C27	125.1(8)	C21-C22-C27	126.7(8)
C23-C22-Hf1	72.9(8)	C21-C22-Hf1	72.6(8)
C27-C22-Hf1	123.7(19)	C22-C23-C24	108.0
C22-C23-C28	126.3(8)	C24-C23-C28	125.5(8)

C22-C23-Hf1	74.8(8)	C24-C23-Hf1	71.8(9)
C28-C23-Hf1	124.(2)	C20-C24-C23	108.0
C20-C24-C29	125.3(8)	C23-C24-C29	125.4(9)
C20-C24-Hf1	73.3(8)	C23-C24-Hf1	75.4(9)
C29-C24-Hf1	128.(2)	C20-C25-H25A	109.5
C20-C25-H25B	109.5	H25A-C25-H25B	109.5
C20-C25-H25C	109.5	H25A-C25-H25C	109.5
H25B-C25-H25C	109.5	C21-C26-H26A	109.5
C21-C26-H26B	109.5	H26A-C26-H26B	109.5
C21-C26-H26C	109.5	H26A-C26-H26C	109.5
H26B-C26-H26C	109.5	C22-C27-H27A	109.5
C22-C27-H27B	109.5	H27A-C27-H27B	109.5
C22-C27-H27C	109.5	H27A-C27-H27C	109.5
H27B-C27-H27C	109.5	C23-C28-H28A	109.5
C23-C28-H28B	109.5	H28A-C28-H28B	109.5
C23-C28-H28C	109.5	H28A-C28-H28C	109.5
H28B-C28-H28C	109.5	C24-C29-H29A	109.5
C24-C29-H29B	109.5	H29A-C29-H29B	109.5
C24-C29-H29C	109.5	H29A-C29-H29C	109.5
H29B-C29-H29C	109.5	N3-Hf2-C4	129.9(18)
N3-Hf2-N4	58.6(7)	C4-Hf2-N4	92.0(16)
N3-Hf2-C3	87.1(14)	C4-Hf2-C3	78.3(19)
N4-Hf2-C3	125.2(13)	N3-Hf2-C41	91.4(9)
C4-Hf2-C41	138.0(17)	N4-Hf2-C41	120.5(9)
C3-Hf2-C41	99.7(14)	N3-Hf2-C42	97.1(11)
C4-Hf2-C42	127.6(17)	N4-Hf2-C42	95.4(8)
C3-Hf2-C42	133.1(13)	C41-Hf2-C42	33.8(3)
N3-Hf2-C40	118.2(8)	C4-Hf2-C40	106.8(16)
N4-Hf2-C40	150.4(8)	C3-Hf2-C40	81.8(13)
C41-Hf2-C40	33.2(3)	C42-Hf2-C40	55.1(3)
N3-Hf2-C43	128.6(12)	C4-Hf2-C43	94.8(17)
N4-Hf2-C43	102.8(7)	C3-Hf2-C43	131.5(12)
C41-Hf2-C43	55.0(3)	C42-Hf2-C43	33.0(3)
C40-Hf2-C43	54.0(3)	N3-Hf2-C44	145.7(10)
C4-Hf2-C44	84.3(17)	N4-Hf2-C44	133.5(7)
C3-Hf2-C44	99.5(12)	C41-Hf2-C44	54.4(3)

C42-Hf2-C44	54.3(3)	C40-Hf2-C44	32.3(3)
C43-Hf2-C44	32.2(3)	N3-Hf2-C30	28.9(6)
C4-Hf2-C30	111.7(17)	N4-Hf2-C30	29.8(5)
C3-Hf2-C30	105.9(13)	C41-Hf2-C30	109.1(9)
C42-Hf2-C30	99.0(10)	C40-Hf2-C30	141.4(9)
C43-Hf2-C30	120.8(9)	C44-Hf2-C30	152.1(10)
Hf2-C3-H3A	109.5	Hf2-C3-H3B	109.5
H3A-C3-H3B	109.5	Hf2-C3-H3C	109.5
H3A-C3-H3C	109.5	H3B-C3-H3C	109.5
Hf2-C4-H4A	109.5	Hf2-C4-H4B	109.5
H4A-C4-H4B	109.5	Hf2-C4-H4C	109.5
H4A-C4-H4C	109.5	H4B-C4-H4C	109.5
C30-N3-C35	121.(2)	C30-N3-Hf2	98.0(14)
C35-N3-Hf2	138.9(16)	N3-C30-N4	108.1(17)
N3-C30-C31	116.(2)	N4-C30-C31	123.(2)
N3-C30-Hf2	53.1(12)	N4-C30-Hf2	55.2(11)
C31-C30-Hf2	142.(2)	C32-C31-C30	102.(2)
C32-C31-H31A	111.4	C30-C31-H31A	111.4
C32-C31-H31B	111.4	C30-C31-H31B	111.4
H31A-C31-H31B	109.3	C31-C32-C33	109.(2)
C31-C32-H32A	109.9	C33-C32-H32A	109.9
C31-C32-H32B	109.9	C33-C32-H32B	109.9
H32A-C32-H32B	108.3	C32-C33-C34	118.(2)
C32-C33-H33A	107.8	C34-C33-H33A	107.8
C32-C33-H33B	107.8	C34-C33-H33B	107.8
H33A-C33-H33B	107.1	C35-C34-C33	105.(2)
C35-C34-H34A	110.7	C33-C34-H34A	110.7
C35-C34-H34B	110.7	C33-C34-H34B	110.7
H34A-C34-H34B	108.8	C34-C35-N3	107.(2)
C34-C35-H35A	110.2	N3-C35-H35A	110.2
C34-C35-H35B	110.2	N3-C35-H35B	110.2
H35A-C35-H35B	108.5	C30-N4-C36	124.1(17)
C30-N4-Hf2	95.0(13)	C36-N4-Hf2	139.7(14)
N4-C36-C37	106.7(16)	N4-C36-C38	112.8(17)
C37-C36-C38	108.0(19)	N4-C36-C39	113.2(17)
C37-C36-C39	104.8(19)	C38-C36-C39	110.8(18)

C36-C37-H37A	109.5	C36-C37-H37B	109.5
H37A-C37-H37B	109.5	C36-C37-H37C	109.5
H37A-C37-H37C	109.5	H37B-C37-H37C	109.5
C36-C38-H38A	109.5	C36-C38-H38B	109.5
H38A-C38-H38B	109.5	C36-C38-H38C	109.5
H38A-C38-H38C	109.5	H38B-C38-H38C	109.5
C36-C39-H39A	109.5	C36-C39-H39B	109.5
H39A-C39-H39B	109.5	C36-C39-H39C	109.5
H39A-C39-H39C	109.5	H39B-C39-H39C	109.5
C41-C40-C44	108.0	C41-C40-C45	126.0(8)
C44-C40-C45	126.0(8)	C41-C40-Hf2	70.0(10)
C44-C40-Hf2	76.3(10)	C45-C40-Hf2	119.(2)
C40-C41-C42	108.0	C40-C41-C46	125.7(8)
C42-C41-C46	126.3(8)	C40-C41-Hf2	76.7(10)
C42-C41-Hf2	73.5(10)	C46-C41-Hf2	119.(2)
C43-C42-C41	108.0	C43-C42-C47	125.9(8)
C41-C42-C47	126.0(8)	C43-C42-Hf2	77.1(10)
C41-C42-Hf2	72.7(10)	C47-C42-Hf2	114.(2)
C42-C43-C44	108.0	C42-C43-C48	126.5(8)
C44-C43-C48	125.2(8)	C42-C43-Hf2	69.9(10)
C44-C43-Hf2	75.7(9)	C48-C43-Hf2	124.7(19)
C43-C44-C40	108.0	C43-C44-C49	126.2(8)
C40-C44-C49	125.7(8)	C43-C44-Hf2	72.1(9)
C40-C44-Hf2	71.5(10)	C49-C44-Hf2	124.(2)
C40-C45-H45A	109.5	C40-C45-H45B	109.5
H45A-C45-H45B	109.5	C40-C45-H45C	109.5
H45A-C45-H45C	109.5	H45B-C45-H45C	109.5
C41-C46-H46A	109.5	C41-C46-H46B	109.5
H46A-C46-H46B	109.5	C41-C46-H46C	109.5
H46A-C46-H46C	109.5	H46B-C46-H46C	109.5
C42-C47-H47A	109.5	C42-C47-H47B	109.5
H47A-C47-H47B	109.5	C42-C47-H47C	109.5
H47A-C47-H47C	109.5	H47B-C47-H47C	109.5
C43-C48-H48A	109.5	C43-C48-H48B	109.5
H48A-C48-H48B	109.5	C43-C48-H48C	109.5
H48A-C48-H48C	109.5	H48B-C48-H48C	109.5

C44-C49-H49A	109.5	C44-C49-H49B	109.5
H49A-C49-H49B	109.5	C44-C49-H49C	109.5
H49A-C49-H49C	109.5	H49B-C49-H49C	109.5