Electronic supplementary information

Zirconium and Hafnium Complexes Containing *N*-alkyl Substituted Amine Biphenolate Ligands: Coordination Chemistry and Living Ring-opening Polymerization Catalysis

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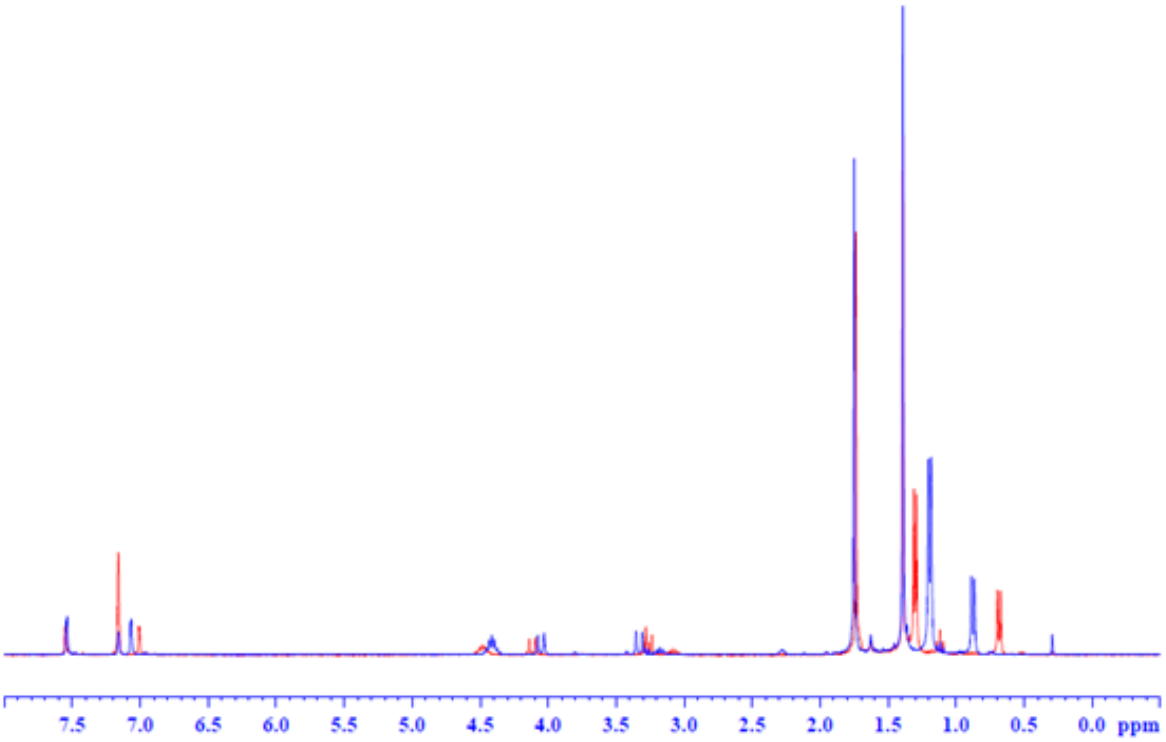

Figure S1. The ^{1}H NMR spectra (300 MHz) of [**1b**]Zr(O*i*Pr)$_2$(HO*i*Pr) (**2b**·HO*i*Pr, blue) and [**1b**]Zr(O*i*Pr)$_2$ (**2b**, red) in C_6D_6 at room temperature.

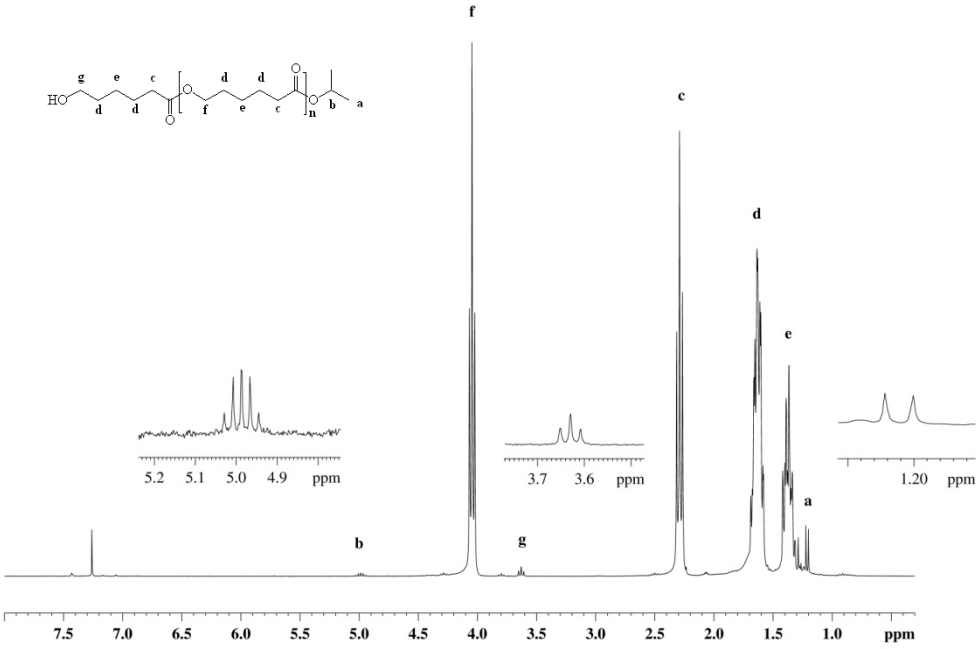

Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of PCLs prepared by **3c**·MeCN catalyzed ROP of ε-CL ($[\varepsilon\text{-CL}]_0/[\mathbf{3c}\cdot\text{MeCN}]_0 = 100$).

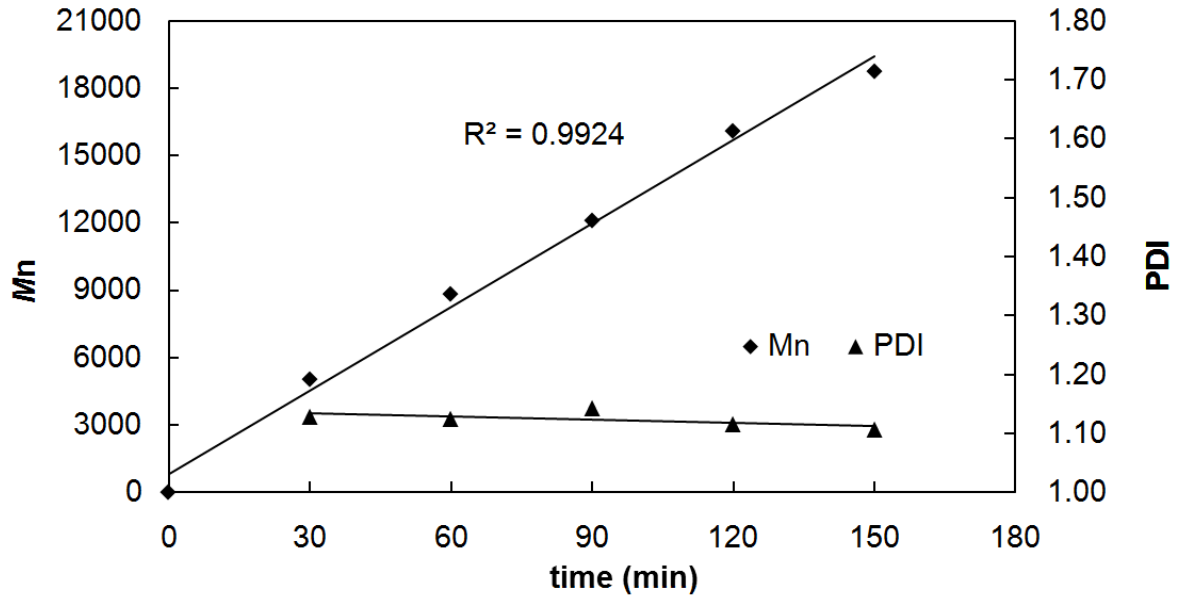

Figure S3. Linear plot of *M*n of PCLs prepared by **3b** versus polymerization time. Conditions: $[\varepsilon\text{-CL}]_0/[\mathbf{3b}]_0 = 250$, toluene, 25 ºC.

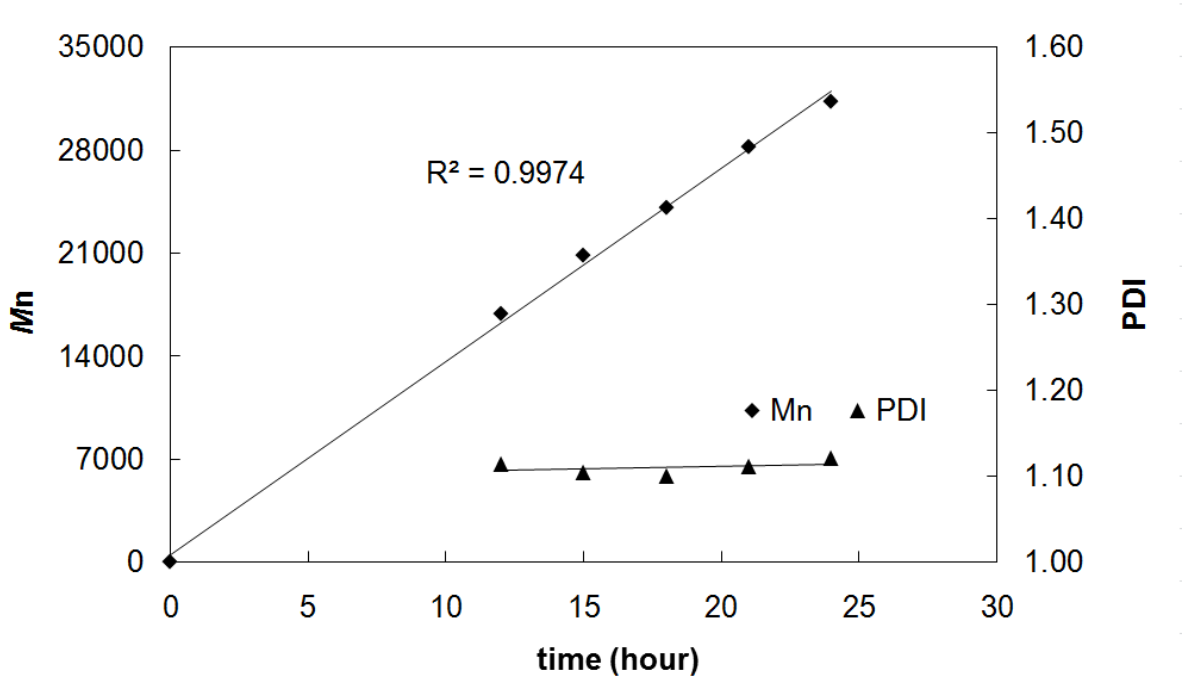

Figure S4. Linear plot of *M*n of PCLs prepared by **3c**·MeCN versus polymerization time. Conditions: $[\varepsilon\text{-CL}]_0/[\mathbf{3c}\cdot\text{MeCN}]_0 = 400$, toluene, 25 ºC.

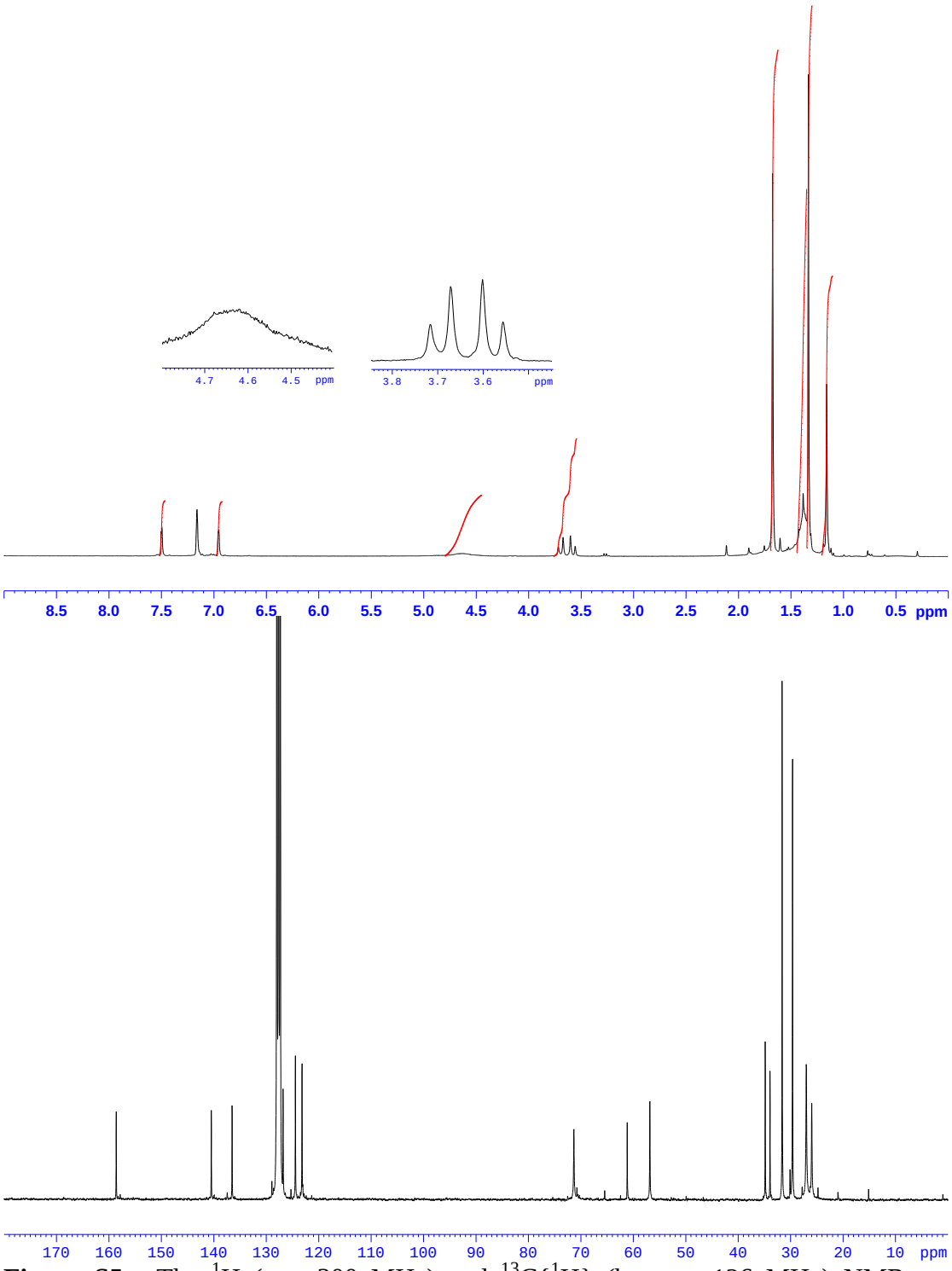

Figure S5. The ^{1}H (top, 300 MHz) and $^{13}C\{^{1}H\}$ (bottom, 126 MHz) NMR spectra of **[1a]Hf(O*i*Pr)$_2$ (3a)** in C_6D_6 at room temperature.

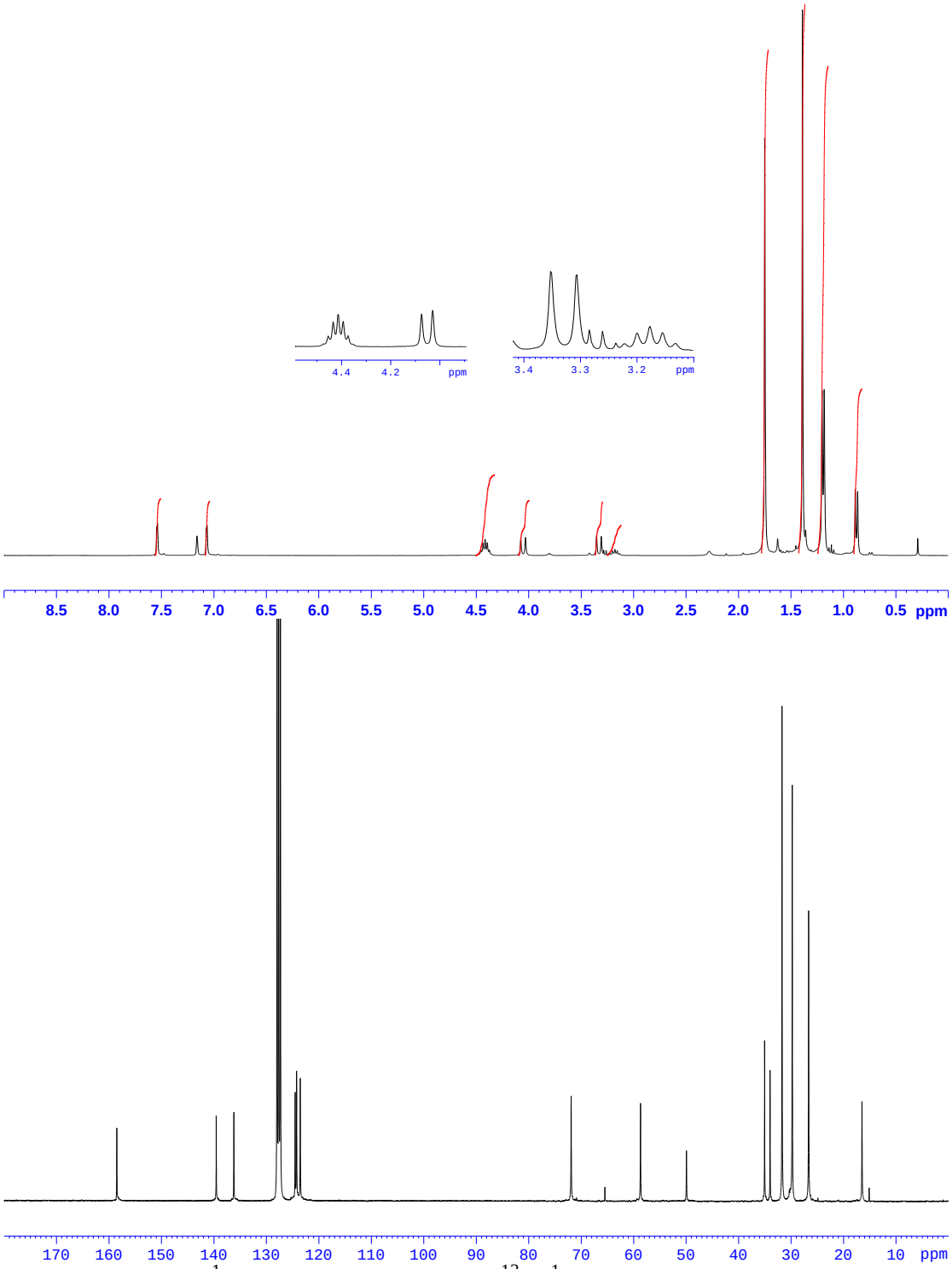

Figure S6. The ^{1}H (top, 300 MHz) and $^{13}C\{^{1}H\}$ (bottom, 126 MHz) NMR spectra of **[1b]Zr(O*i*Pr)$_2$ (2b)** in C_6D_6 at room temperature.

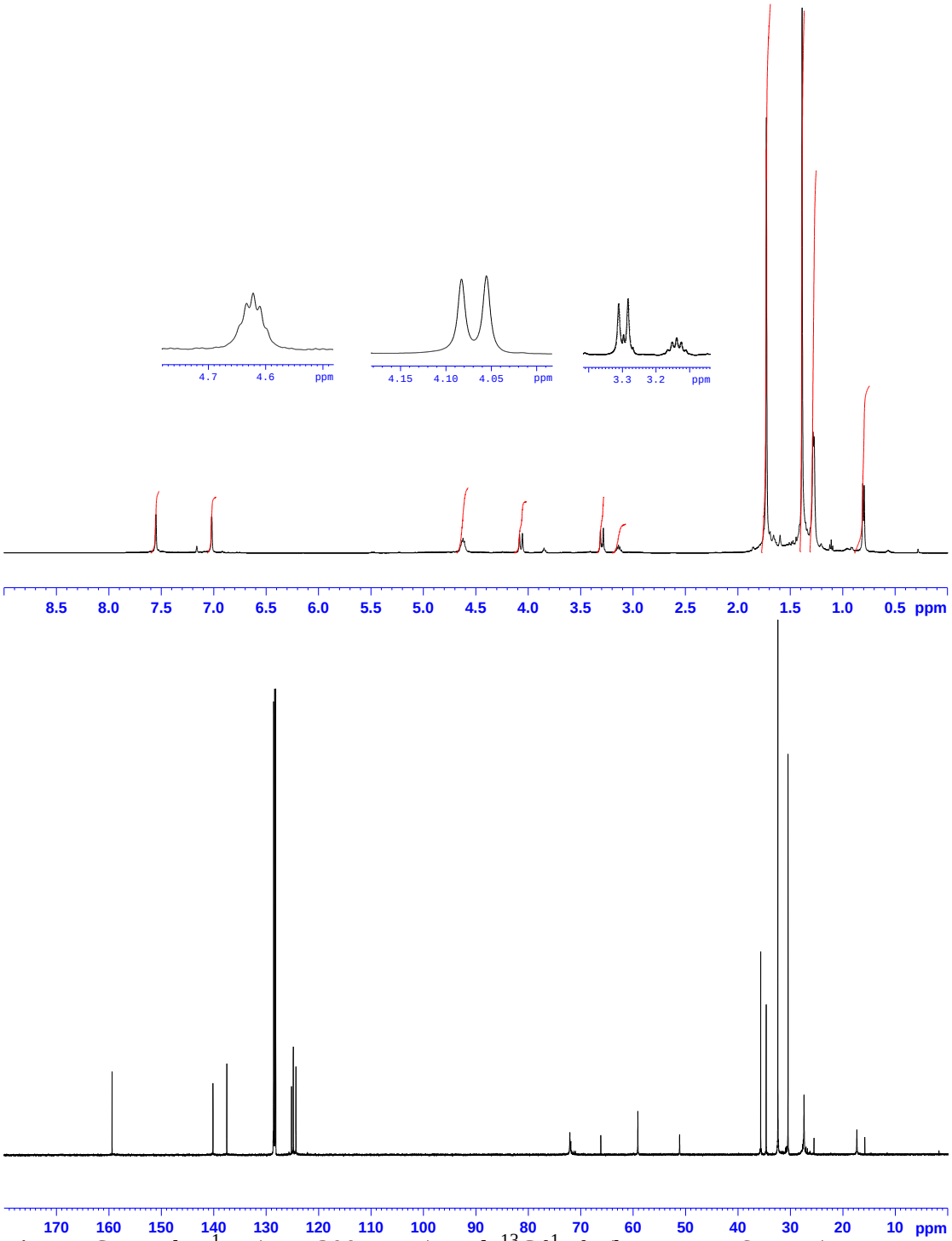

Figure S7. The ^{1}H (top, 300 MHz) and $^{13}C\{^{1}H\}$ (bottom, 126 MHz) NMR spectra of **[1b]Hf(O*i*Pr)$_2$ (3b)** in C_6D_6 at room temperature.

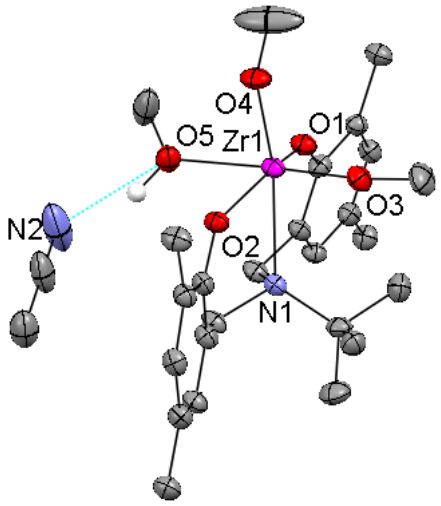

Figure S8. Molecular structure of (**2a**·HO*i*Pr)(MeCN) with thermal ellipsoids drawn at the 35% probability level, highlighting the intermolecular hydrogen bonding with co-crystallized acetonitrile. All methyl groups except those in *N*-bound *tert*-butyl or acetonitrile are omitted for clarity.

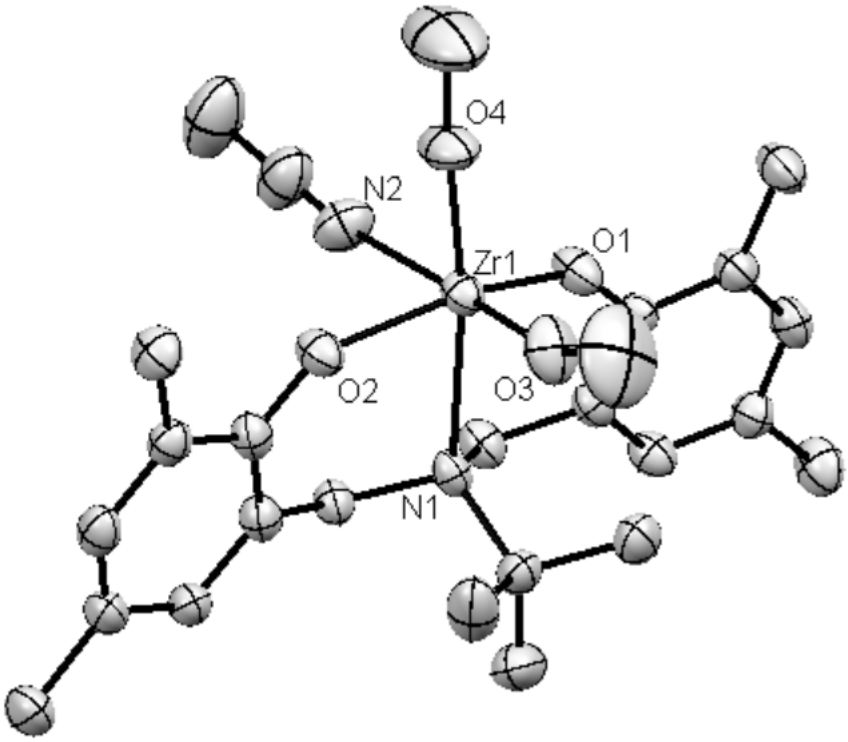

Figure S9. Molecular structure of **2a**·MeCN with thermal ellipsoids drawn at the 35% probability level. All methyl groups except those in *N*-bound *tert*-butyl and coordinated acetonitrile are omitted for clarity.

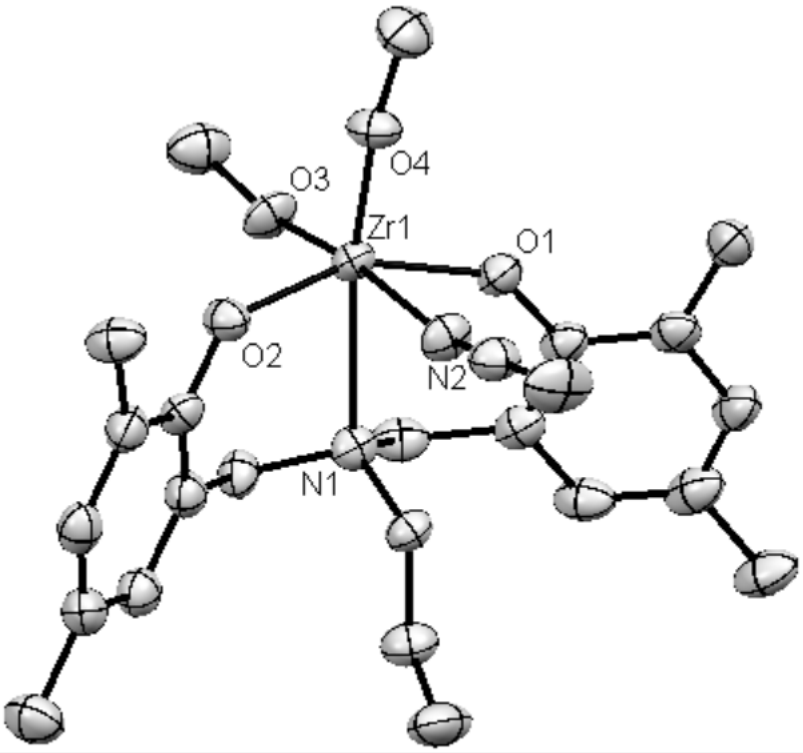

Figure S10. Molecular structure of **2c**·MeCN with thermal ellipsoids drawn at the 35% probability level. All methyl groups except those in *N*-bound *n*-propyl and coordinated acetonitrile are omitted for clarity.

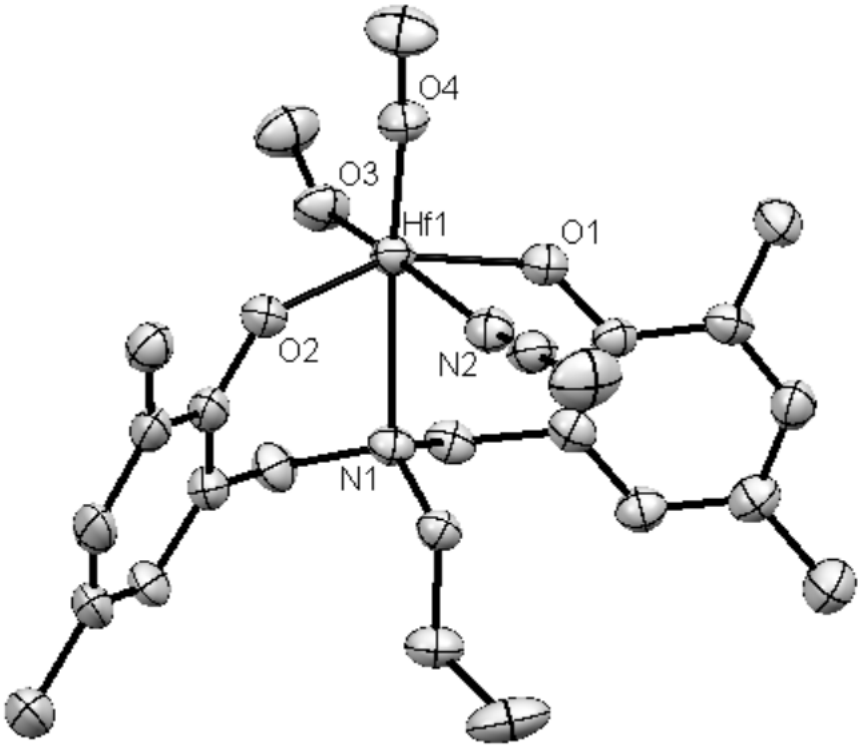

Figure S11. Molecular structure of **3c**·MeCN with thermal ellipsoids drawn at the 35% probability level. All methyl groups except those in *N*-bound *n*-propyl and coordinated acetonitrile are omitted for clarity.

Table S1. Crystal data and structure refinement for [**1a**]Zr(O*i*Pr)$_2$(HO*i*Pr) (**2a**·HO*i*Pr).

Identification code	a12717	
Empirical formula	C45 H78 N2 O5 Zr	
Formula weight	818.31	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.4727(11) Å	α= 90°.
	b = 21.469(2) Å	β= 92.473(3)°.
	c = 21.279(2) Å	γ = 90°.
Volume	4780.0(8) Å^3	
Z	4	
Density (calculated)	1.137 Mg/m^3	
Absorption coefficient	0.271 mm^{-1}	
F(000)	1768	
Crystal size	0.44 x 0.11 x 0.06 mm^3	
Theta range for data collection	2.13 to 25.02°.	
Index ranges	-12<=h<=12, -25<=k<=24, -25<=l<=24	
Reflections collected	30282	
Independent reflections	8373 [R(int) = 0.0511]	
Completeness to theta = 25.02°	99.1 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9839 and 0.8901	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8373 / 4 / 475	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1199	
R indices (all data)	R1 = 0.0834, wR2 = 0.1347	
Largest diff. peak and hole	0.702 and -0.567 e.Å^{-3}	

Table S2. Crystal data and structure refinement for [**1a**]Zr(O*i*Pr)$_2$(MeCN) (**2a**·MeCN).

Identification code	a12795	
Empirical formula	C44 H73 N3 O4 Zr	
Formula weight	799.27	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 44.5839(13) Å	α= 90°.
	b = 11.9319(4) Å	β= 109.2300(10)°.
	c = 20.2471(5) Å	γ = 90°.
Volume	10169.9(5) Å^3	
Z	8	
Density (calculated)	1.044 Mg/m^3	
Absorption coefficient	0.253 mm^{-1}	
F(000)	3440	
Crystal size	0.46 x 0.38 x 0.22 mm^3	
Theta range for data collection	7.77 to 25.00°.	
Index ranges	-51<=h<=52, -13<=k<=14, -20<=l<=24	
Reflections collected	18127	
Independent reflections	8393 [R(int) = 0.0281]	
Completeness to theta = 25.08°	93.7 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9465 and 0.8927	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8393 / 6 / 489	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1461	
R indices (all data)	R1 = 0.0618, wR2 = 0.1785	
Largest diff. peak and hole	0.608 and -0.801 e.Å^{-3}	

Table S3. Crystal data and structure refinement for [**1c**]Zr(O*i*Pr)$_2$(HO*i*Pr) (**2c**·HO*i*Pr).

Identification code	a12645	
Empirical formula	C42 H73 N O5 Zr	
Formula weight	763.23	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.6470(16) Å	α= 90°.
	b = 20.835(3) Å	β= 96.473(2)°.
	c = 22.341(4) Å	γ = 90°.
Volume	4461.8(13) Å^3	
Z	4	
Density (calculated)	1.136 Mg/m^3	
Absorption coefficient	0.285 mm^{-1}	
F(000)	1648	
Crystal size	0.39 x 0.27 x 0.13 mm^3	
Theta range for data collection	1.83 to 25.05°.	
Index ranges	-11<=h<=11, -24<=k<=24, -13<=l<=26	
Reflections collected	27658	
Independent reflections	7839 [R(int) = 0.0401]	
Completeness to theta = 25.05°	99.1 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9639 and 0.8969	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7839 / 6 / 438	
Goodness-of-fit on F^2	0.996	
Final R indices [I>2sigma(I)]	R1 = 0.0599, wR2 = 0.1620	
R indices (all data)	R1 = 0.0867, wR2 = 0.1890	
Largest diff. peak and hole	0.809 and -0.810 e.Å^{-3}	

Table S4. Crystal data and structure refinement for [**1c**]Zr(O*i*Pr)$_2$(MeCN) (**2c**·MeCN).

Identification code	a12523	
Empirical formula	C41 H68 N2 O4 Zr	
Formula weight	744.19	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 14.2006(14) Å	α= 90°.
	b = 15.6501(16) Å	β= 90°.
	c = 19.191(2) Å	γ = 90°.
Volume	4264.9(8) Å^3	
Z	4	
Density (calculated)	1.159 Mg/m^3	
Absorption coefficient	0.296 mm^{-1}	
F(000)	1600	
Crystal size	0.78 x 0.56 x 0.34 mm^3	
Theta range for data collection	1.94 to 25.02°.	
Index ranges	-14<=h<=16, -16<=k<=18, -22<=l<=19	
Reflections collected	25025	
Independent reflections	7390 [R(int) = 0.0545]	
Completeness to theta = 25.02°	99.6 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9061 and 0.8021	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7390 / 12 / 428	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1353	
R indices (all data)	R1 = 0.0552, wR2 = 0.1430	
Absolute structure parameter	0.02(5)	
Largest diff. peak and hole	0.564 and -1.311 e.Å^{-3}	

Table S5. Crystal data and structure refinement for [**1c**]Hf(O*i*Pr)$_2$(MeCN) (**3c**·MeCN).

Identification code	a12511	
Empirical formula	C41 H68 Hf N2 O4	
Formula weight	831.46	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 14.3071(6) Å	α= 90°.
	b = 15.6544(5) Å	β= 90°.
	c = 19.1151(7) Å	γ = 90°.
Volume	4281.2(3) Å^3	
Z	4	
Density (calculated)	1.290 Mg/m^3	
Absorption coefficient	2.474 mm^{-1}	
F(000)	1728	
Crystal size	0.57 x 0.48 x 0.20 mm^3	
Theta range for data collection	1.68 to 25.03°.	
Index ranges	-15<=h<=16, -18<=k<=18, -22<=l<=22	
Reflections collected	23245	
Independent reflections	7475 [R(int) = 0.0282]	
Completeness to theta = 25.03°	99.3 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.6374 and 0.3328	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7475 /12 / 428	
Goodness-of-fit on F^2	1.091	
Final R indices [I>2sigma(I)]	R1 = 0.0234, wR2 = 0.0564	
R indices (all data)	R1 = 0.0271, wR2 = 0.0657	
Absolute structure parameter	-0.004(8)	
Largest diff. peak and hole	0.600 and -0.851 e.Å^{-3}	