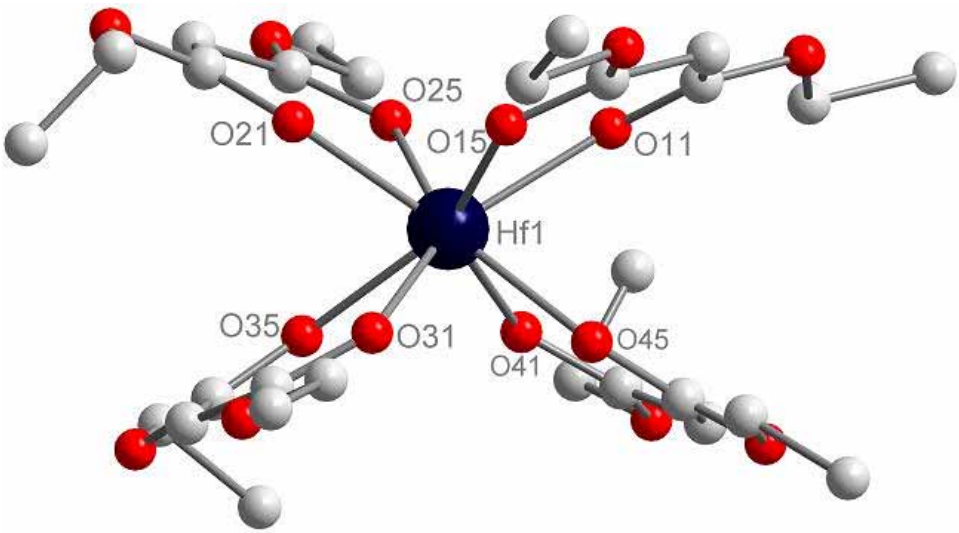
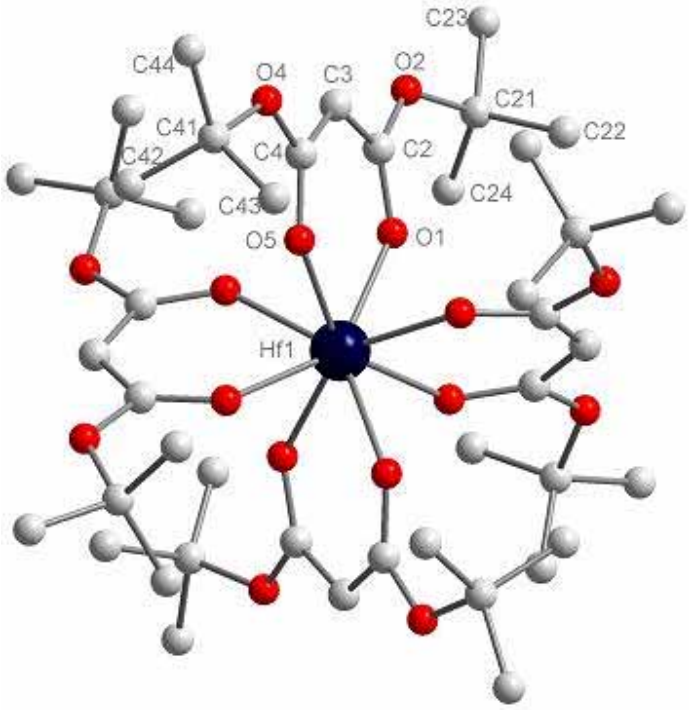
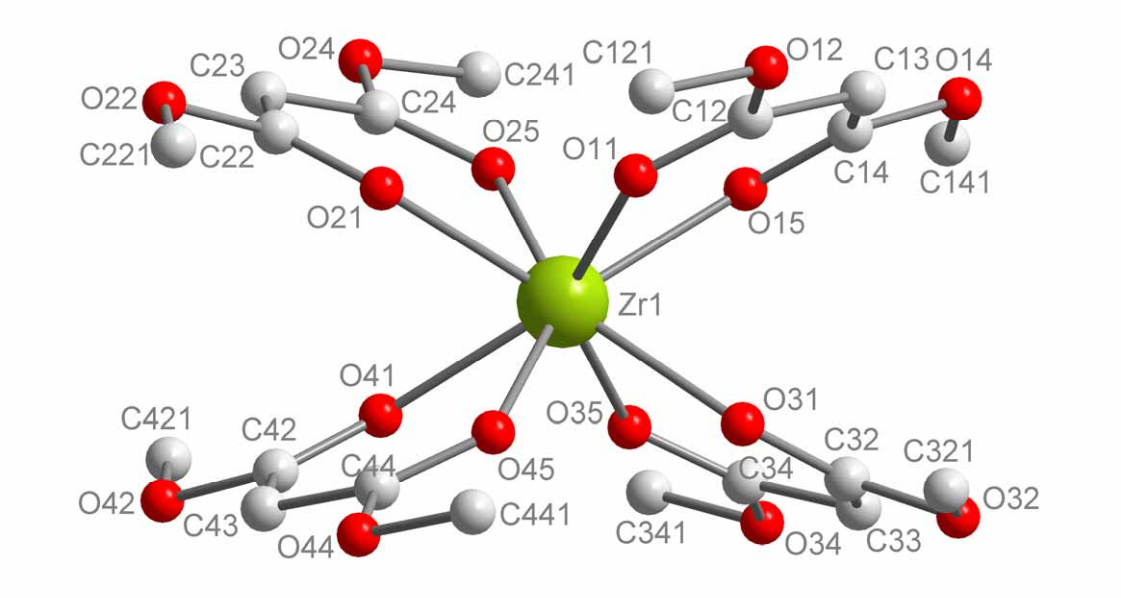
Supplementary Data:



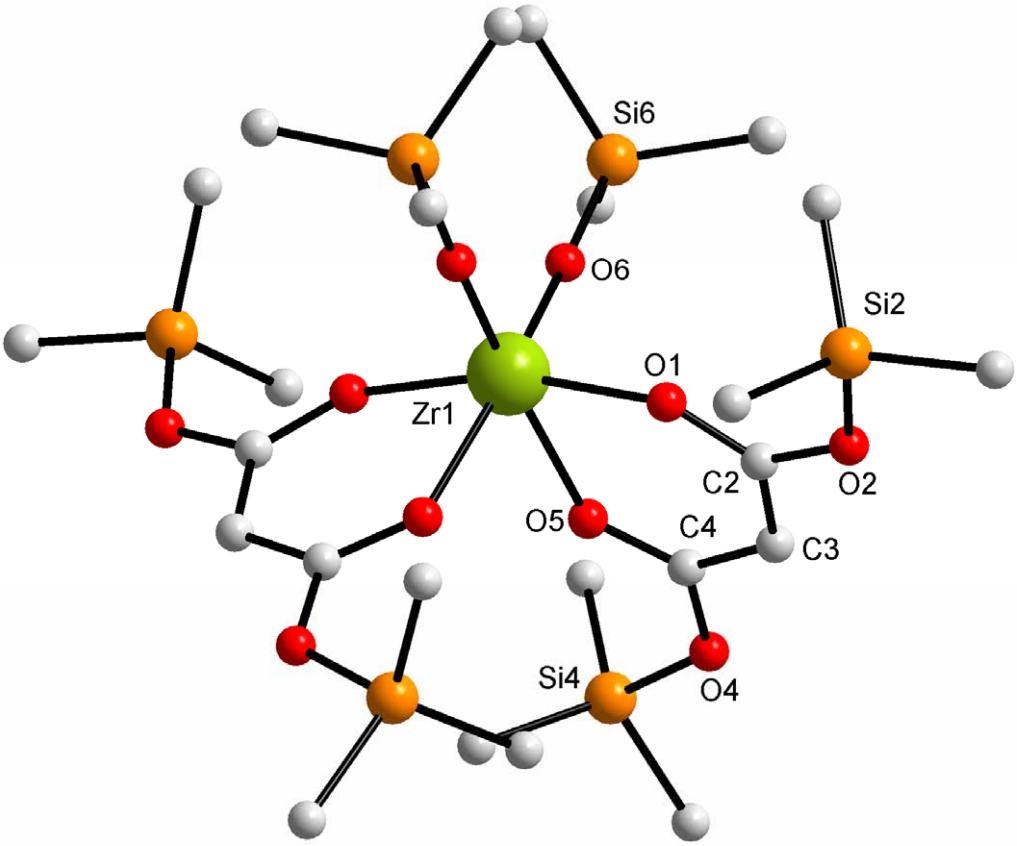
Suppl. Fig. 1: Molecular structure of **2**.



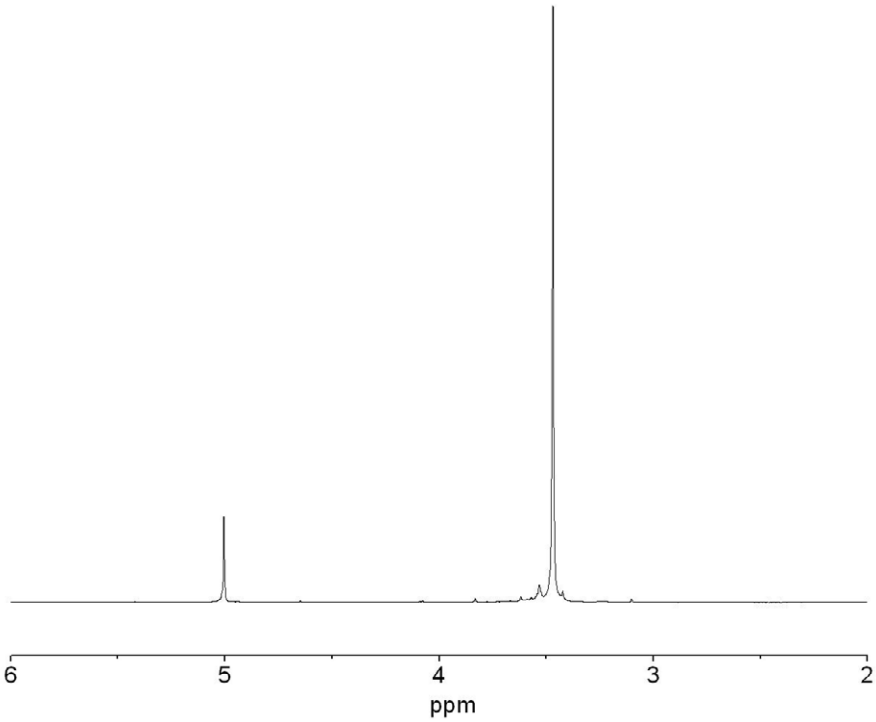
Suppl. Fig. 2: Molecular structure of **3**.



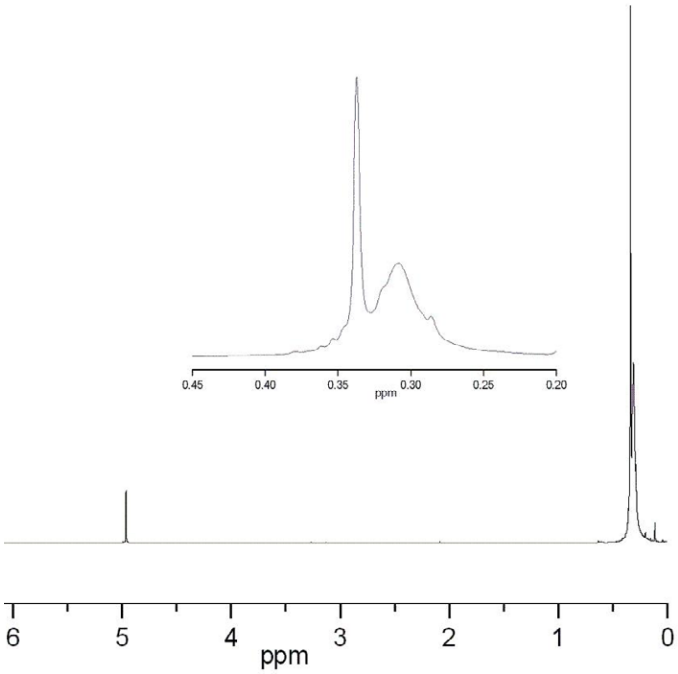
Suppl. Fig. 3: Molecular structure of **5**.



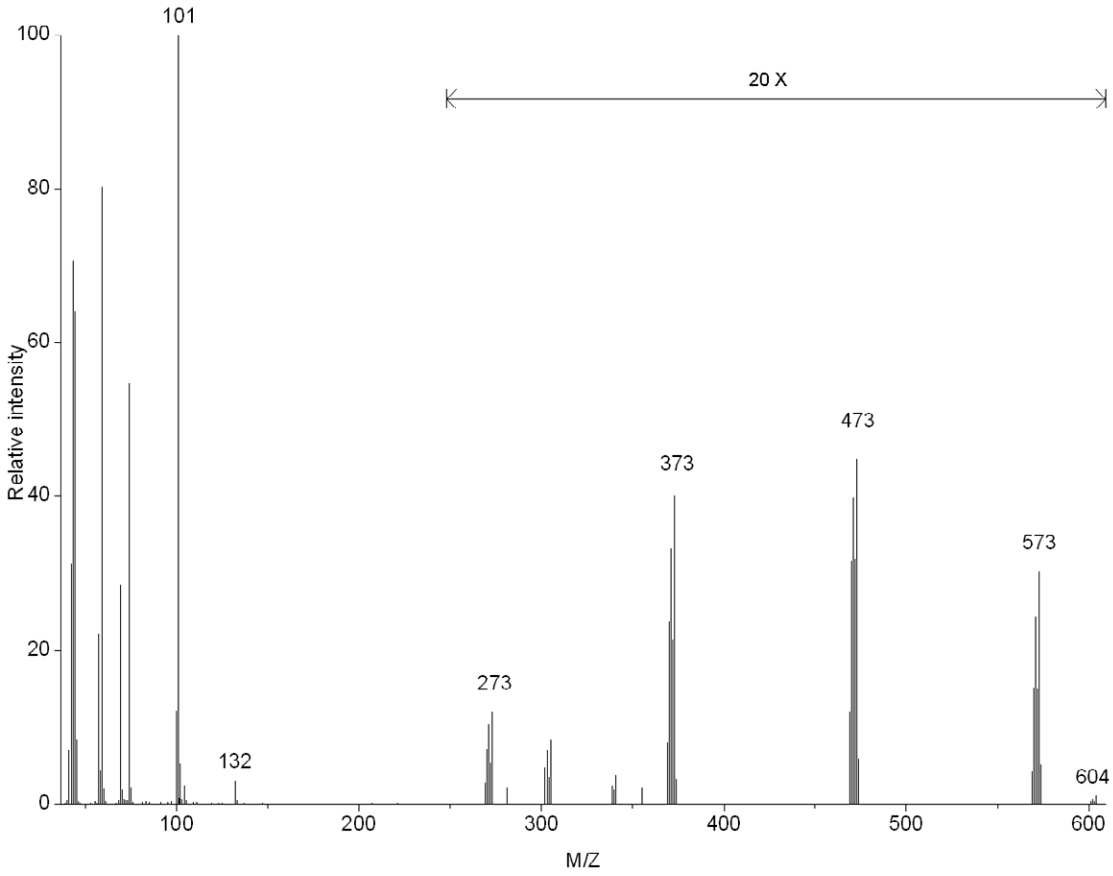
Suppl. Fig. 4: Molecular structure of **8**.



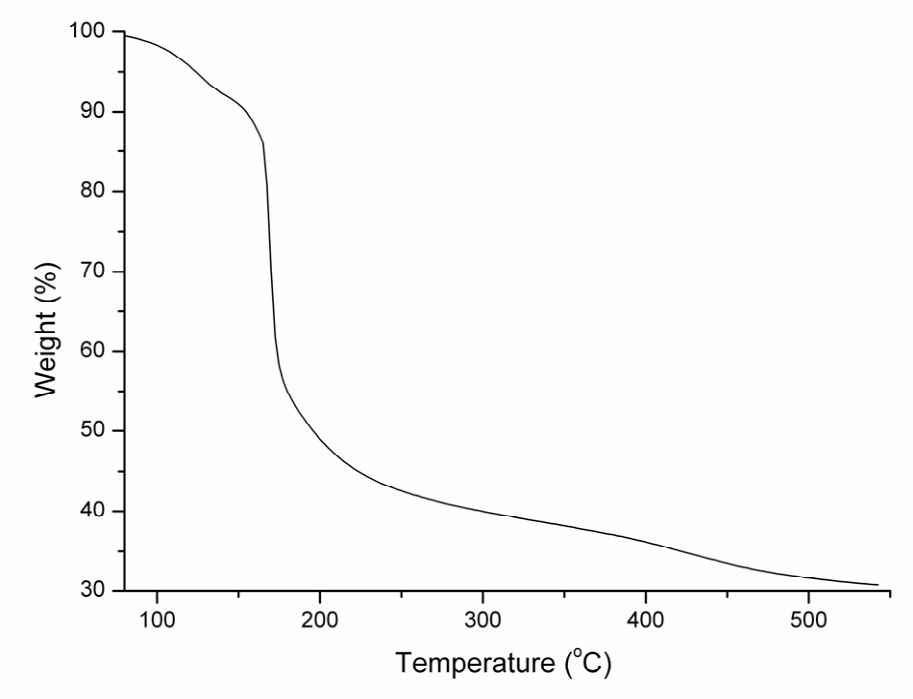
Suppl. Fig. 5: ^{1}H NMR spectrum of [Zr(dmml)$_4$] (**5**).



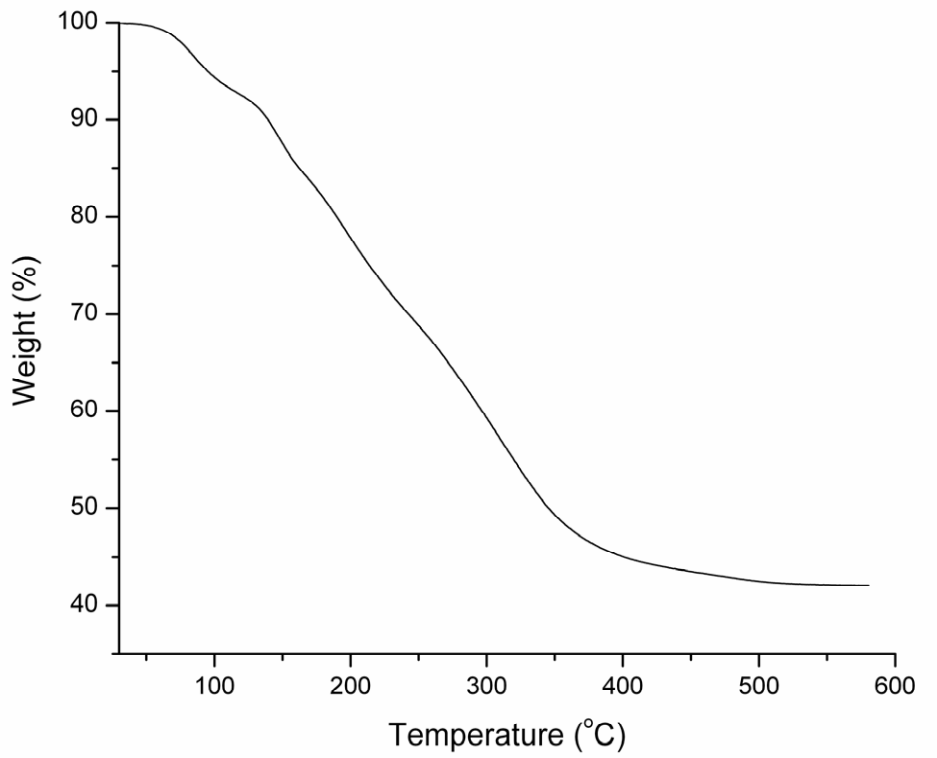
Supp. Fig. 6: ^{1}H NMR spectrum of [Zr(bsml)$_2$(OSiMe$_3$)$_2$] (**8**)



Supp. Fig. 7 EI Mass spectrum of [Hf(dmml)$_4$] (**1**)



Supp. Fig. 8 TG curve of $[Hf(bsml)_4]$ (**4**)



Supp. Fig. 9 TG curve of $[Zr(bsml)_2(OSiMe_3)_2]$ (**8**)

Comments on Crystallographic data

For CCDC Numbers 692630, 692631, 692632 and 692635:

The ratio of maximum to minimum residual density is high due the poor crystal quality and disorder in the solvent, which could not be refined satisfyingly.

For CCDC Numbers 692634, 692635 and 692636:

The GOF is below 0.8 due to the weak data in 692634 and twinned crystals in 692635 and 692636.

Suppl. Table 1: Crystal and data collection parameter for compounds **1-8**

Identification code	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Emp. formula	$C_{27}H_{36}HfO_{16}$	$C_{35}H_{52}HfO_{16}$	$C_{44}H_{76}HfO_{16}$	$C_{36}H_{76}Hf\,O_{16}Si_8$	$C_{27}H_{36}O_{16}Zr$	$C_{35}H_{52}O_{16}Zr$	$C_{120}H_{224}O_{40}Zr_4$	$C_{24}H_{56}O_{10}Si_6Zr$
Form. Wt.	795.05	907.26	1039.54	1168.18	707.78	819.99	2671.87	764.45
Temp., K	113(2)	113(2)	103(2)	115(2)	113(2)	105(2)	105(2)	104(2)
W. length , Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Cryst. system	Monoclinic	Monoclinic	Tetragonal	Tetragonal	Monoclinic	Monoclinic	Triclinic	Monoclinic
space group	P2(1)/c	P2(1)/c	P4/ncc	I4(1)/a	P2(1)/c	P2(1)/c	P-1	C2/c
a, Å	10.9049(3)	15.3042(7)	14.7752(3)	20.2381(6)	10.9113(3)	15.2848(7)	13.8318(5)	20.198(1)
b, Å	13.6935(5)	18.4262(8)	14.7752(3)	20.2381(6)	13.6640(6)	18.3600(7)	16.0899(5)	12.197(1)
c, Å	21.4560(8)	15.8807(7)	23.5966(13)	14.2483(6)	21.4648(8)	15.8340(8)	16.8531(5)	20.232(1)
α (deg)	90	90	90	90	90	90	84.441(3)	90
β (deg)	97.425(3)	117.421(4)	90	90	97.516(3)	117.278(6)	89.034(3)	106.847(7)
γ (deg)	90	90	90	90	90	90	84.501(3)	90
Volume, $Å^3$	3177.1(2)	3975.2(3)	5151.3(3)	5835.8(3)	3172.7(2)	3949.3(3)	3715.8(2)	4770.3(6)
Z	4	4	4	4	4	4	1	4
Absorption coefficient (mm^{-1})	3.356	2.692	2.087	2.006	0.419	0.347	0.342	0.416
Crystal size (mm)	0.48 x 0.44 x 0.32	0.52 x 0.33 x 0.31	0.34 x 0.10 x 0.06	0.26 x 0.19 x 0.11	0.50 x 0.22 x 0.20	0.31 x 0.21 x 0.18	0.25 x 0.15 x 0.07	0.30 x 0.25 x 0.20
Reflections collected / unique	18215 / 7258 [R(int) = 0.0176]	32128 / 6982 [R(int) = 0.0342]	11329 / 2188 [R(int) = 0.0931]	13188 / 2553 [R(int) = 0.0479]	18409 / 5561 [R(int) = 0.0345]	19872 / 6934 [R(int) = 0.0545]	59810 / 13039 [R(int) = 0.0675]	19257 / 4168 [R(int) = 0.1059]
Data / restraints / parameters	7258 / 0 / 397	6982 / 0 / 469	2188 / 0 / 139	2553 / 0 / 144	5561 / 0 / 397	6934 / 0 / 478	13039 / 12 / 737	4168 / 0 / 195
Goodness-of-fit on F^2	1.121	1.078	0.675	1.024	1.043	0.793	1.026	0.745
R indices (all data)	R1 = 0.0390, wR2 = 0.0555	R1 = 0.0510, wR2 = 0.0723	R1 = 0.0731, wR2 = 0.0380	R1 = 0.0361, wR2 = 0.0622	R1 = 0.0440, wR2 = 0.0786	R1 = 0.0716, wR2 = 0.0738	R1 = 0.0778, wR2 = 0.1368	R1 = 0.0971, wR2 = 0.0974