

Supporting Information

Hf_xZr_{1-x}O₂ Thin Films from Chemical Vapor Deposition of Fluorinated β-Ketoenamine Precursors

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CCDC deposition numbers 2496180 (**Zr-1**) and 2496179 (**Hf-1**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk.

Table S1. Crystal data and structure refinement for **Zr-1** and **Hf-1** complexes.

	Zr-1	Hf-1
Empirical formula	ZrC ₂₄ H ₄₀ F ₆ N ₂ O ₄	HfC ₂₄ H ₄₀ F ₆ N ₂ O ₄
Formula weight	625.80	713.07
Temperature/K	100.00	100.00
Crystal system	monoclinic	monoclinic
Space group	<i>P2₁/n</i>	<i>P2₁/n</i>
a/Å	9.8124(5)	9.8037(6)
b/Å	17.2234(7)	17.2112(10)
c/Å	17.9667(8)	17.9261(12)
α/°	90	90
β/°	97.349(2)	97.076(2)
γ/°	90	90
Volume/Å ³	3011.5(2)	3001.7(3)
Z	4	4
ρ _{calc} /cm ³	1.380	1.578
μ/mm ⁻¹	0.432	3.542
F(000)	1296.0	1424.0
Crystal size/mm ³	0.05 × 0.04 × 0.02	0.13 × 0.1 × 0.07
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.506 to 56.608	4.518 to 56.598
Index ranges	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -23 ≤ l ≤ 23	-13 ≤ h ≤ 12, -22 ≤ k ≤ 22, -23 ≤ l ≤ 23
Reflections collected	83300	69998
Independent reflections	7479 [R _{int} = 0.0902, R _{sigma} = 0.0421]	7449 [R _{int} = 0.0479, R _{sigma} = 0.0238]
Data/restraints/parameters	7479/12/346	7449/0/346
Goodness-of-fit on F ²	1.053	1.085
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0497, wR ₂ = 0.1242	R ₁ = 0.0234, wR ₂ = 0.0468
Final R indexes [all data]	R ₁ = 0.0767, wR ₂ = 0.1410	R ₁ = 0.0275, wR ₂ = 0.0484
Largest diff. peak/hole / e Å ⁻³	1.65/-0.80	1.09/-0.97

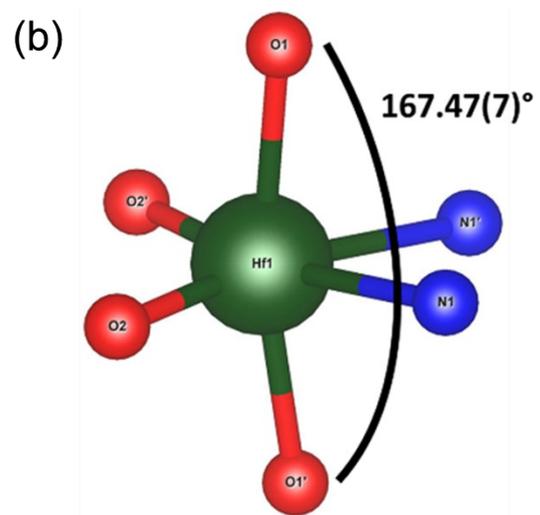
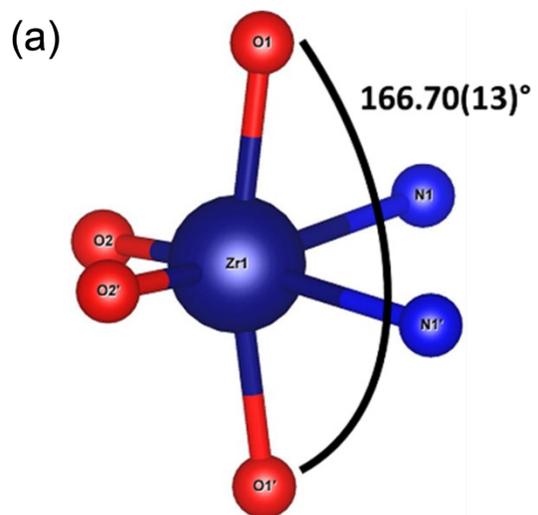


Figure S1. Coordination environments around (a) Zr center of **Zr-1** and (b) Hf center of **Hf-1**.

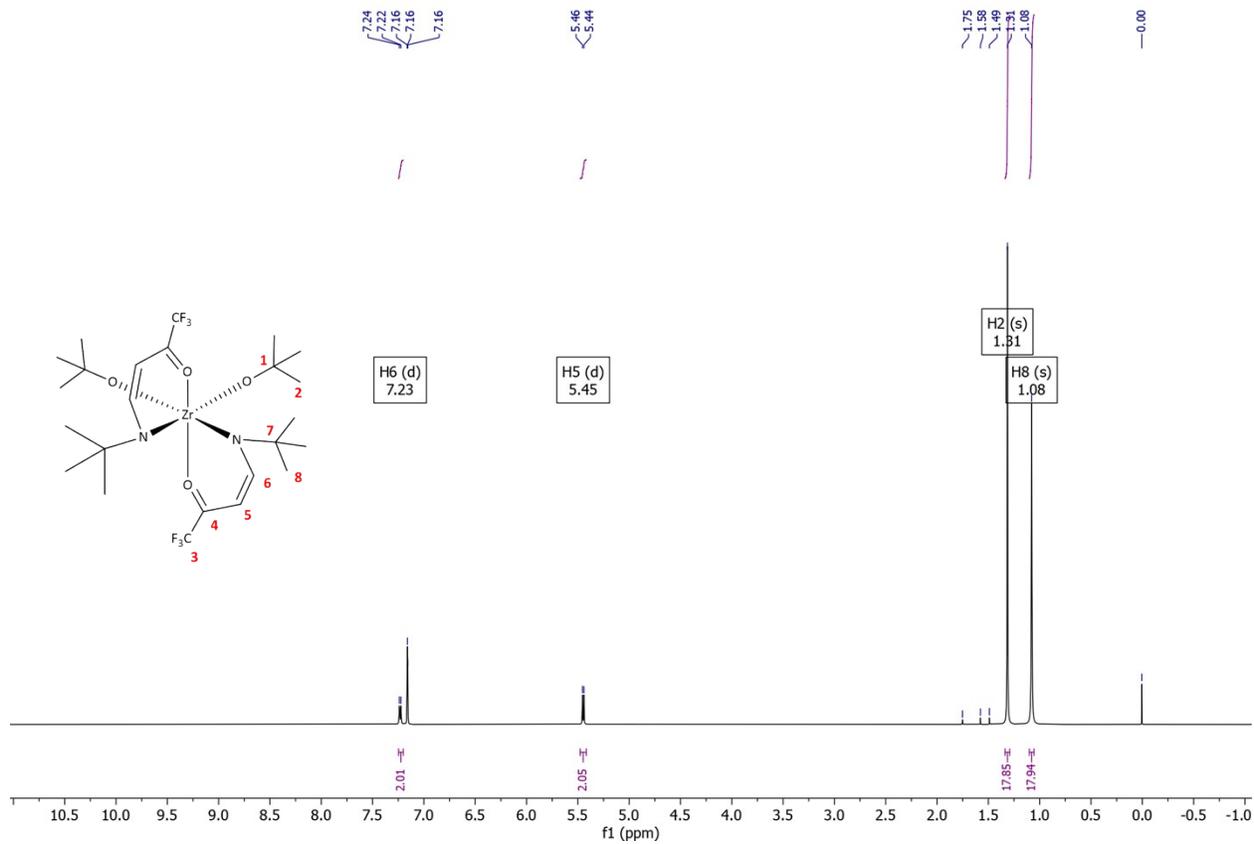


Figure S2. Room temperature ^1H NMR of **Zr-1** in benzene- d_6 on a 400 MHz *Bruker* *Avance* spectrometer.

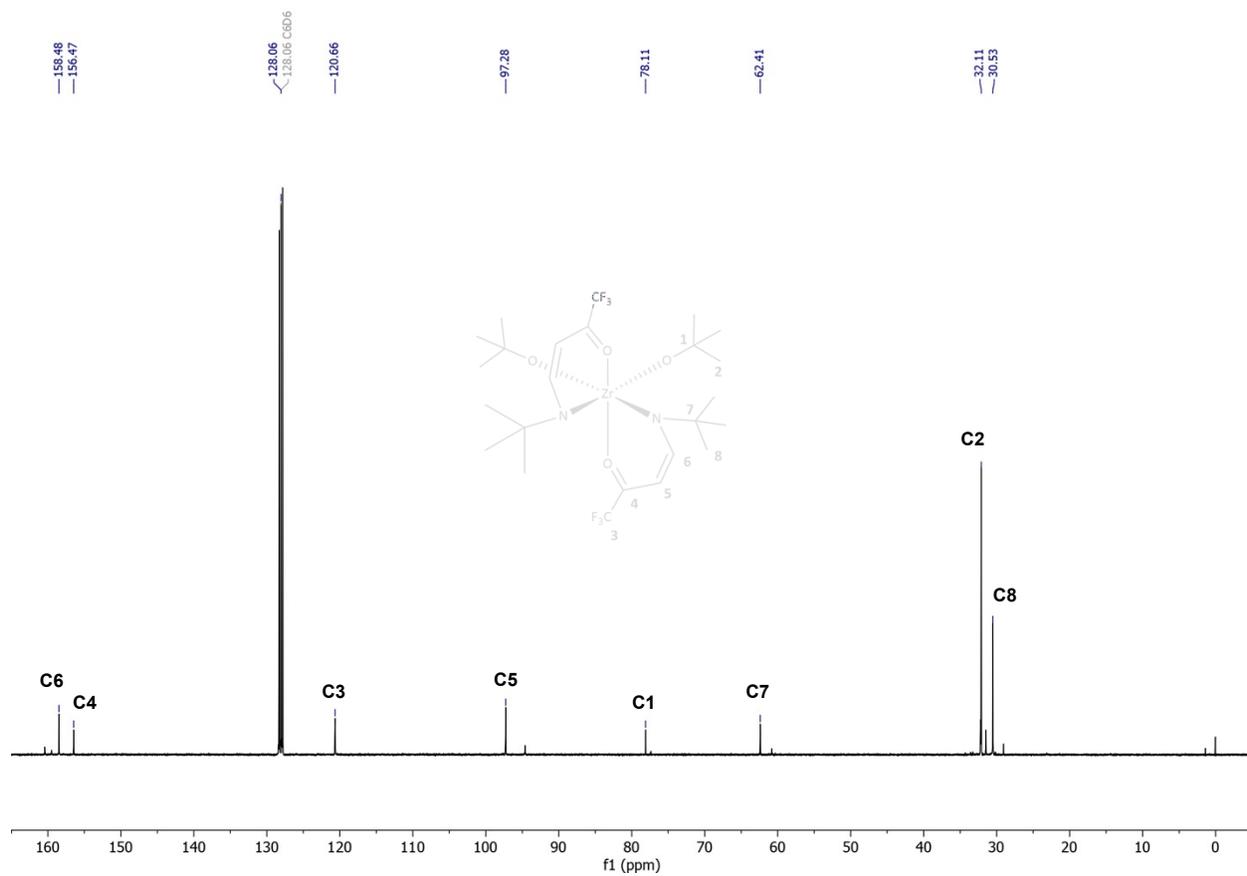


Figure S3. Room temperature $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$ NMR of **Zr-1** in benzene- d_6 on a 400 MHz *Bruker Avance* spectrometer.

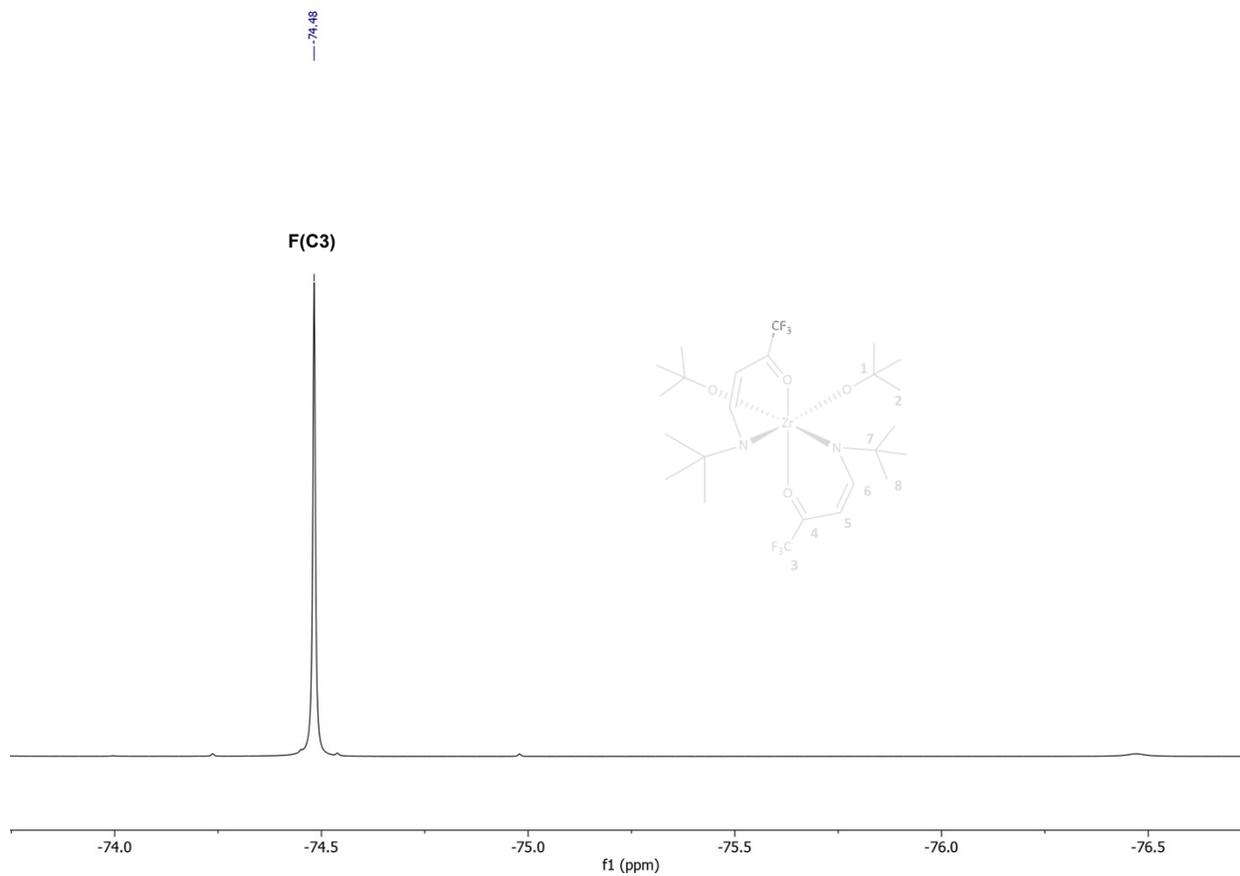


Figure S4. Room temperature ^{19}F NMR of **Zr-1** in benzene- d_6 on a 400 MHz *Bruker Avance* spectrometer.

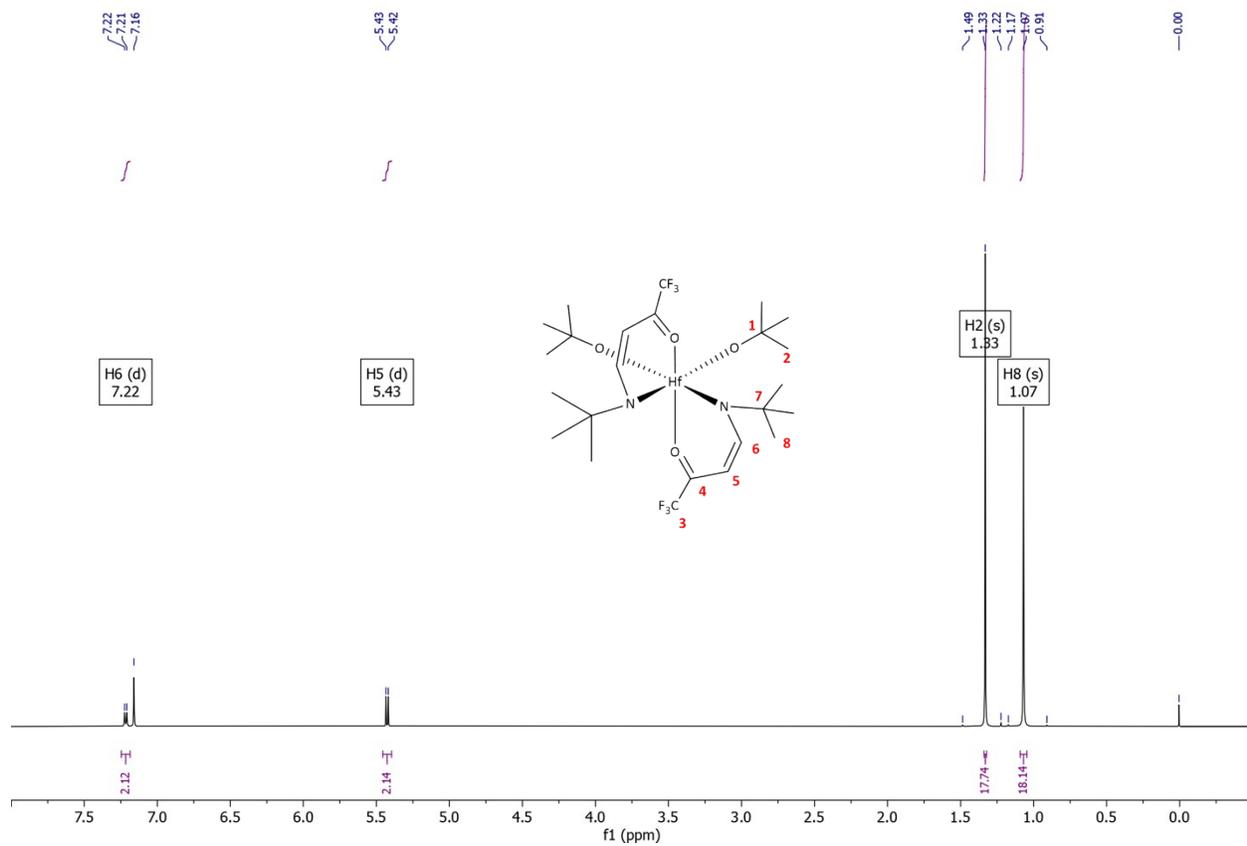


Figure S5. Room temperature ¹H NMR of **Hf-1** in benzene-*d*₆ on a 400 MHz *Bruker* *Avance* spectrometer.

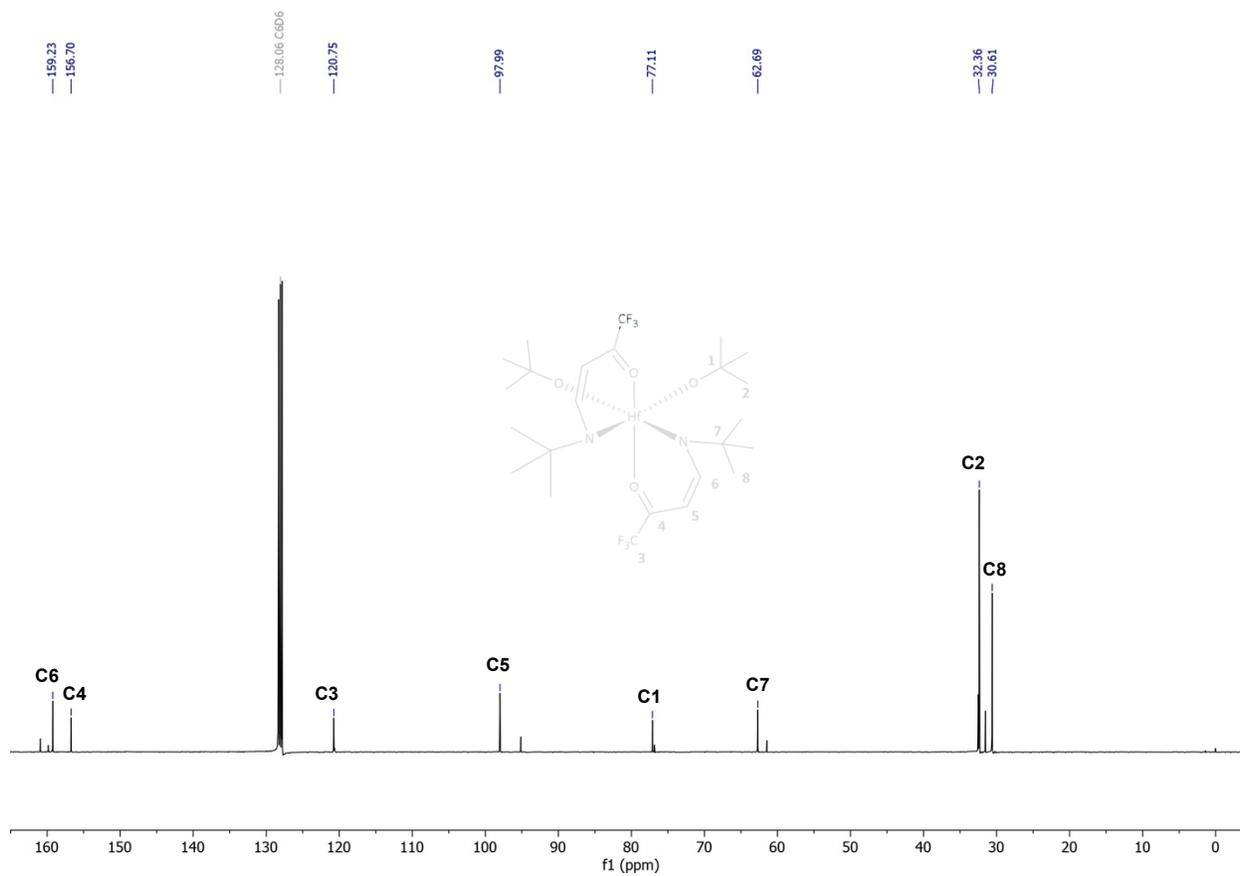


Figure S6. Room temperature $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$ NMR of **Hf-1** in benzene- d_6 on a 400 MHz *Bruker Avance* spectrometer.

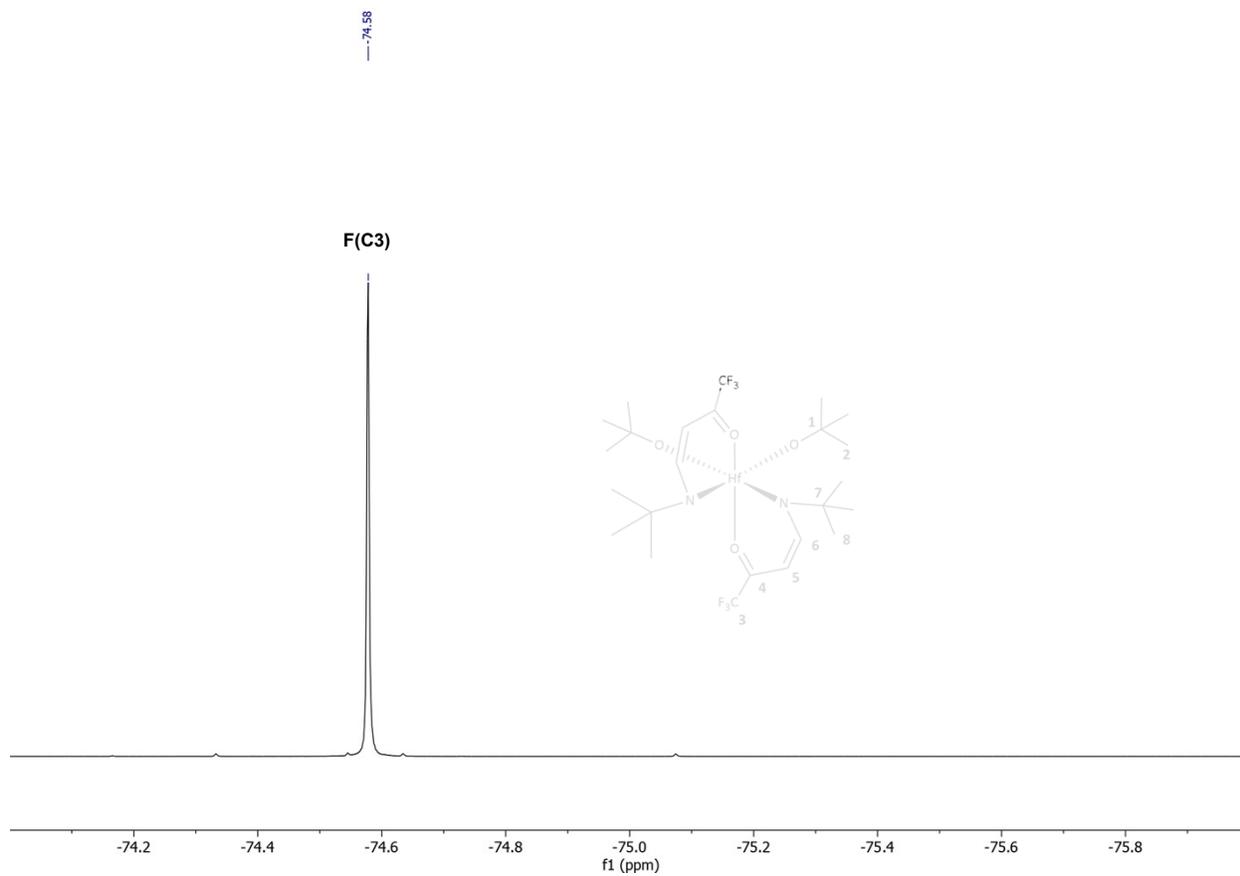


Figure S7. Room temperature ^{19}F NMR of **Hf-1** in benzene- d_6 on a 400 MHz *Bruker Avance* spectrometer.

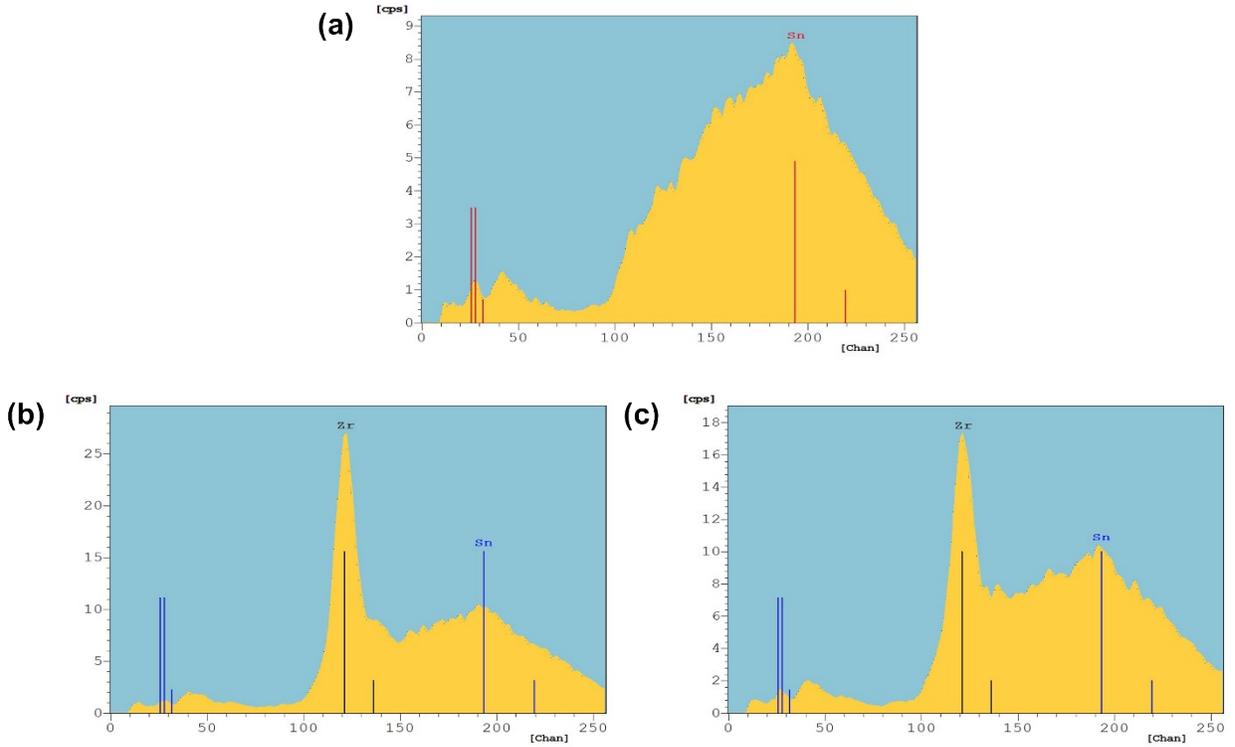


Figure S8. XRF result of (a) only FTO substrate, (b) as-deposited ZrO₂ thin films, and (c) ZrO₂ thin films after calcination in air at 600 °C for 8 hours.

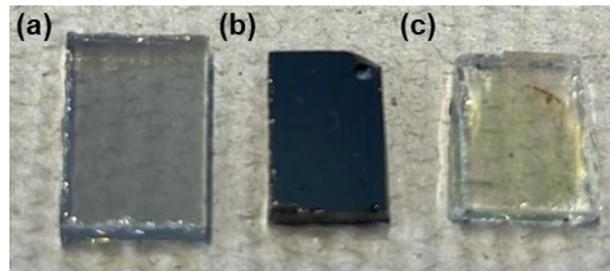


Figure S9. Surface appearance of (a) only FTO substrate, (b) as-deposited ZrO₂ thin films, and (c) ZrO₂ thin films after calcination in air at 600 °C for 8 hours.

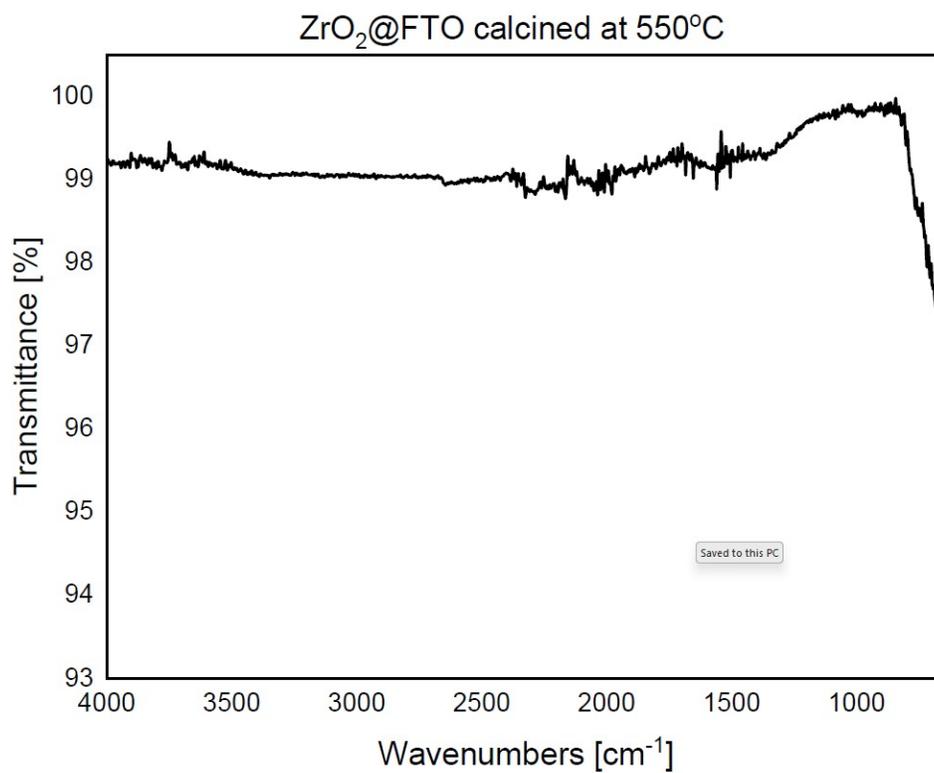


Figure S10. FTIR result of ZrO₂ thin films after calcination in air at 550 °C for 8 hours.

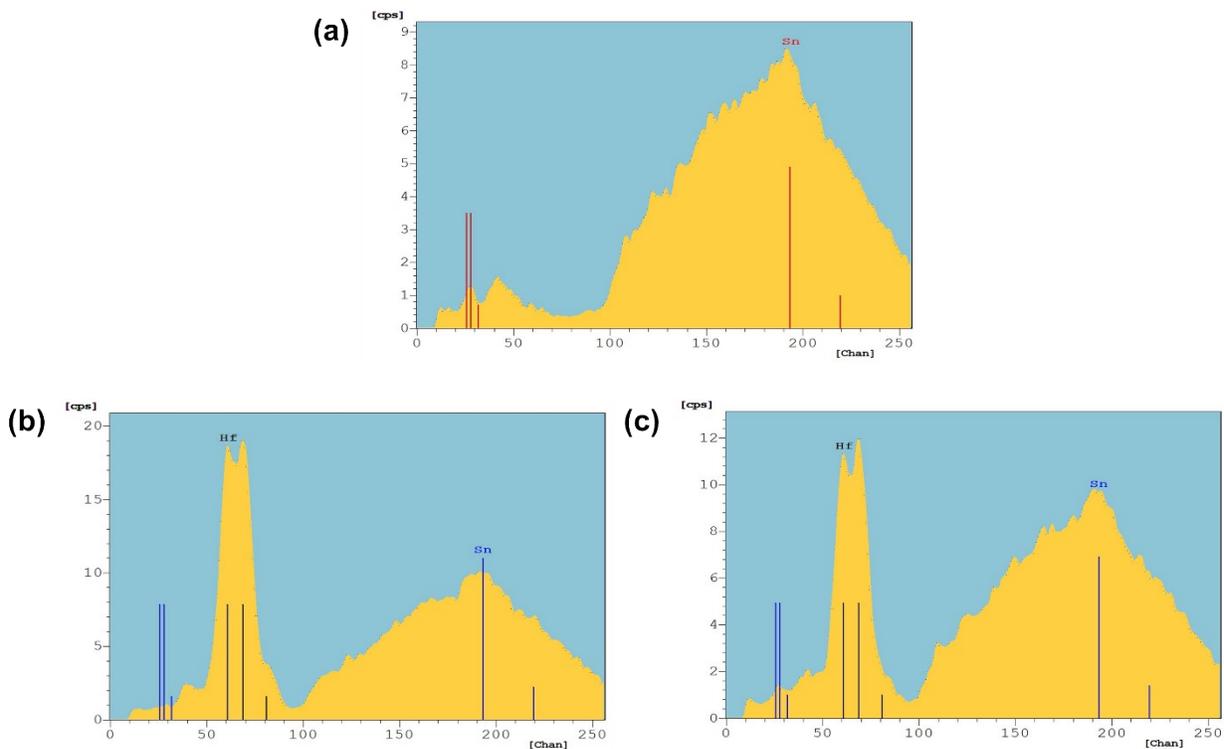


Figure S11. XRF result of (a) only FTO substrate, (b) as-deposited HfO₂ thin films, and (c) HfO₂ thin films after calcination in air at 600 °C for 8 hours.

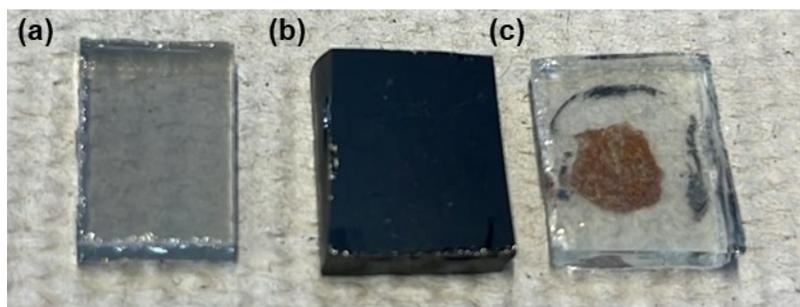


Figure S12. Surface appearance of (a) only FTO substrate, (b) as-deposited HfO₂ thin films, and (c) HfO₂ thin films after calcination in air at 600 °C for 8 hours.

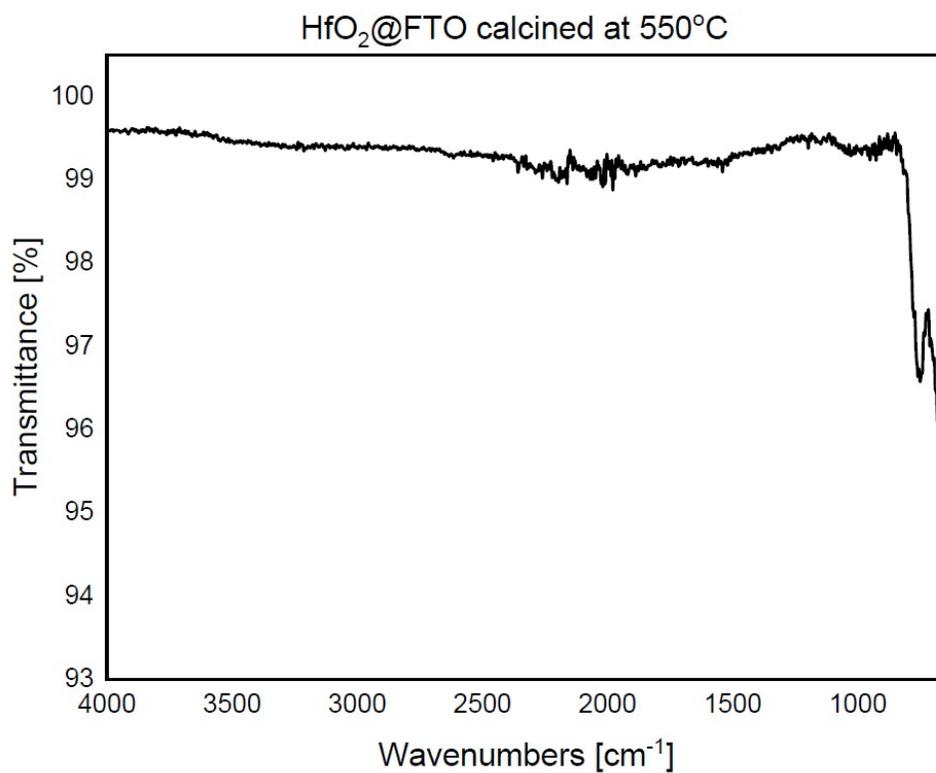


Figure S13. FTIR result of HfO₂ thin films after calcination in air at 550 °C for 8 hours.

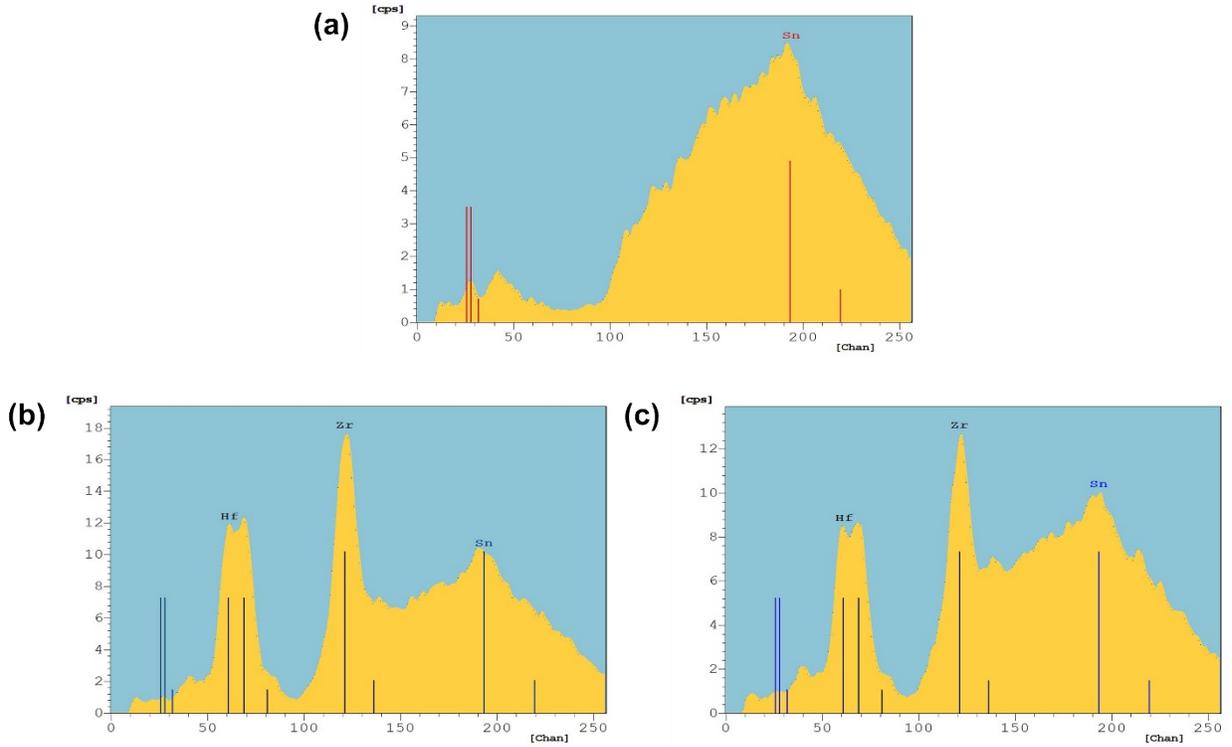


Figure S14. XRF result of (a) only FTO substrate, (b) as-deposited HZO thin films, and (c) HZO thin films after calcination in air at 600 °C for 8 hours.

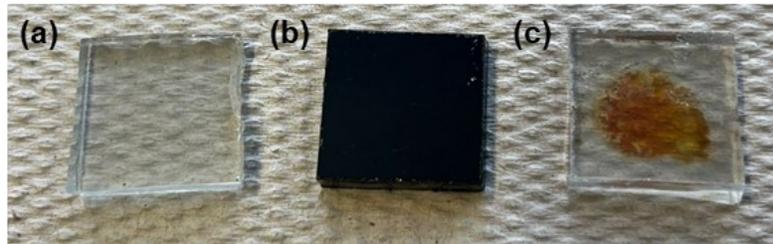


Figure S15. Surface appearance of (a) only FTO substrate, (b) as-deposited HZO thin films, and (c) HZO thin films after calcination in air at 600 °C for 8 hours.