Electronic Supplementary Material (ESI) for Dalton Transactions.


**Supplementary Information**

# Fluorescent phenoxy benzoxazole complexes of zirconium and hafnium: synthesis, structure and photo-physical behaviour

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# Table of contents

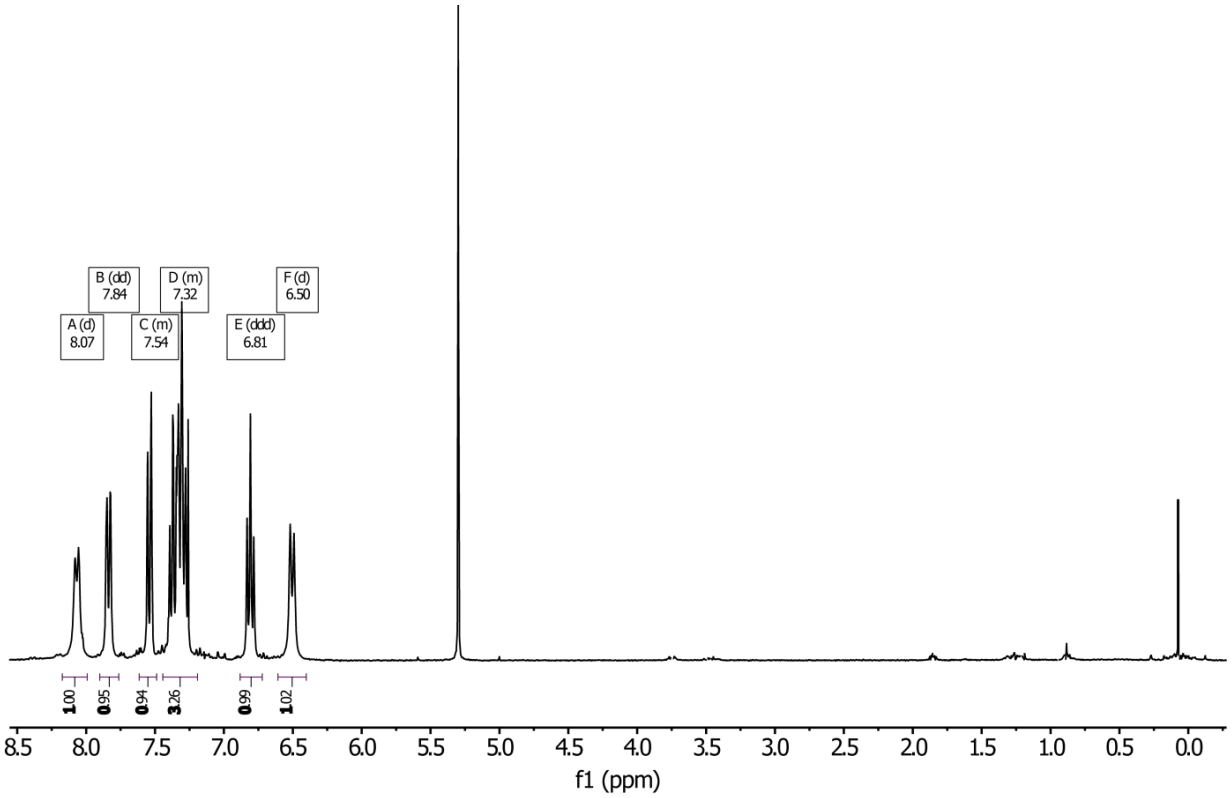


**Figure S1.** $^{1}H$ NMR spectrum of a solution of complex **1** in $CDCl_3$ measured at rt.

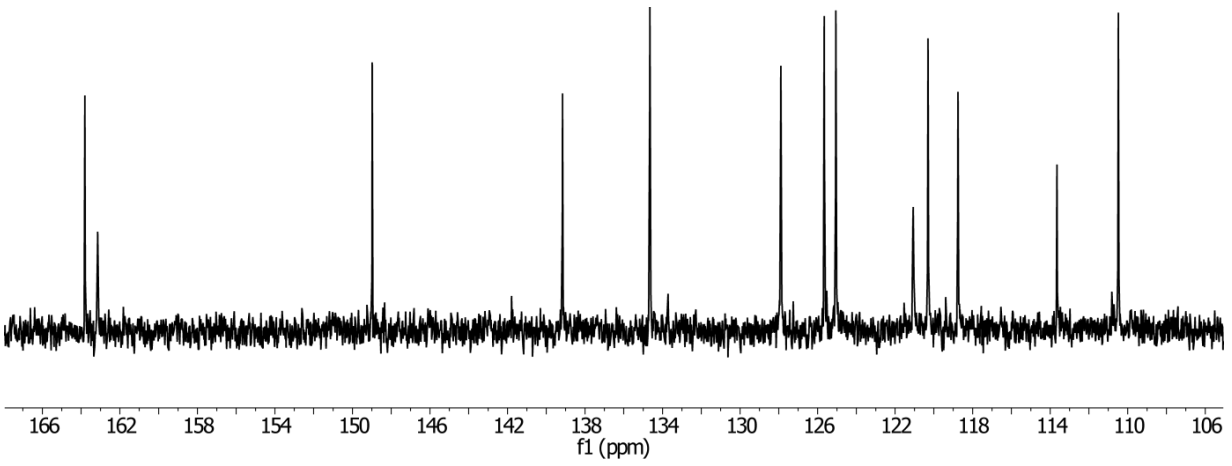


**Figure S2.** $^{13}C\{^{1}H\}$ NMR spectrum of a solution of complex **1** in $CDCl_3$ measured at rt.

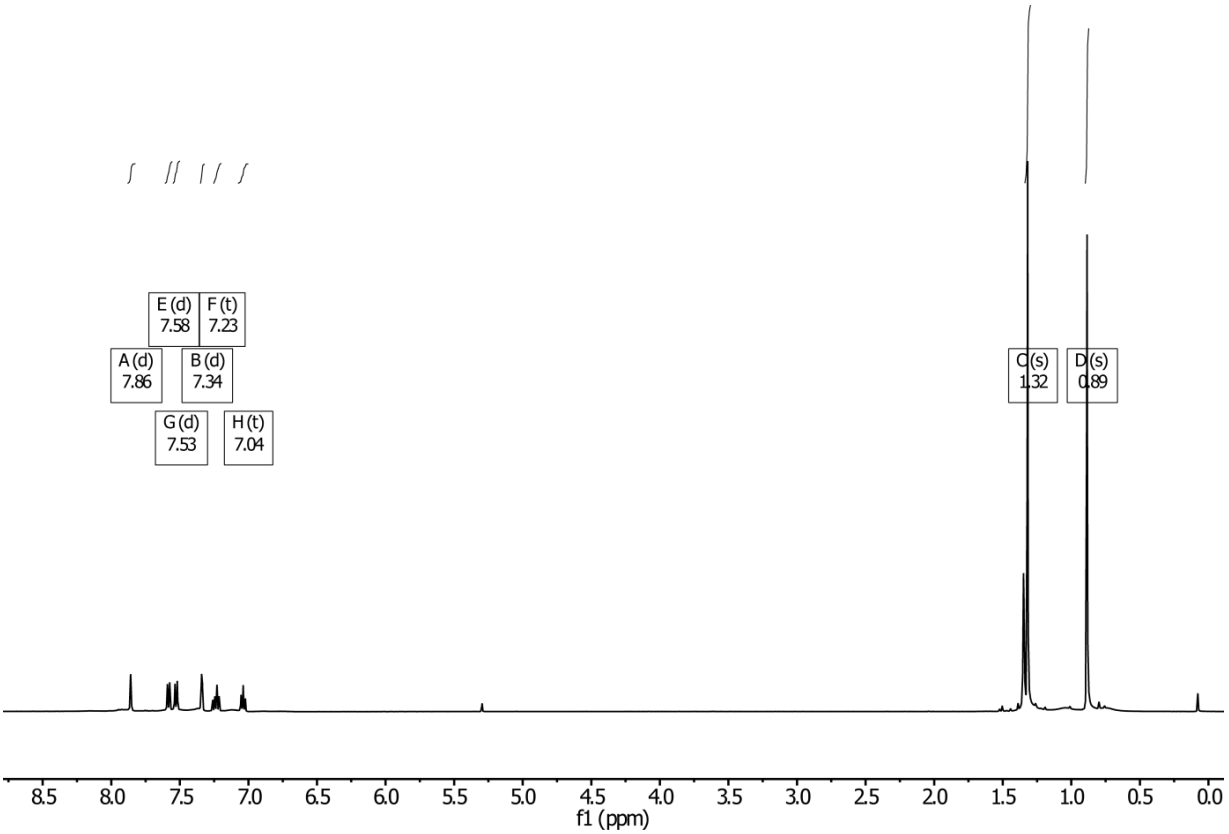


**Figure S3.** $^{1}H$ NMR spectrum of a solution of complex **2** in $CDCl_3$ measured at rt.

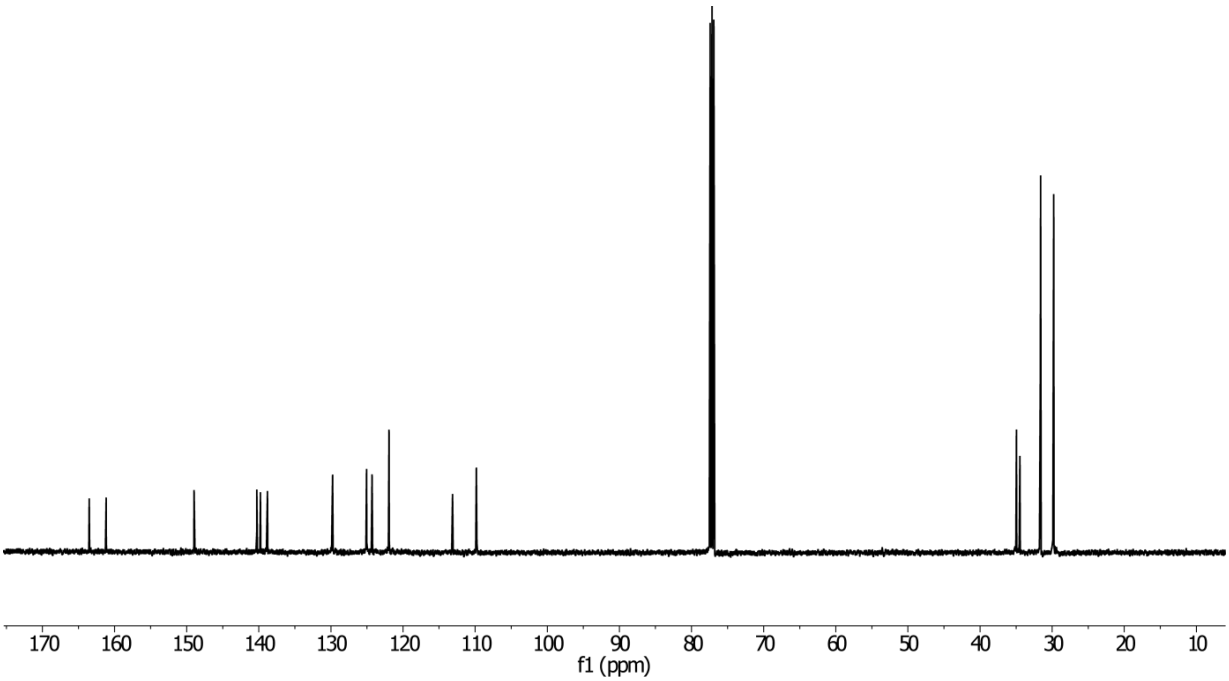


**Figure S4.** $^{13}C\{^{1}H\}$ NMR spectrum of a solution of complex **2** in $CDCl_3$ measured at rt.

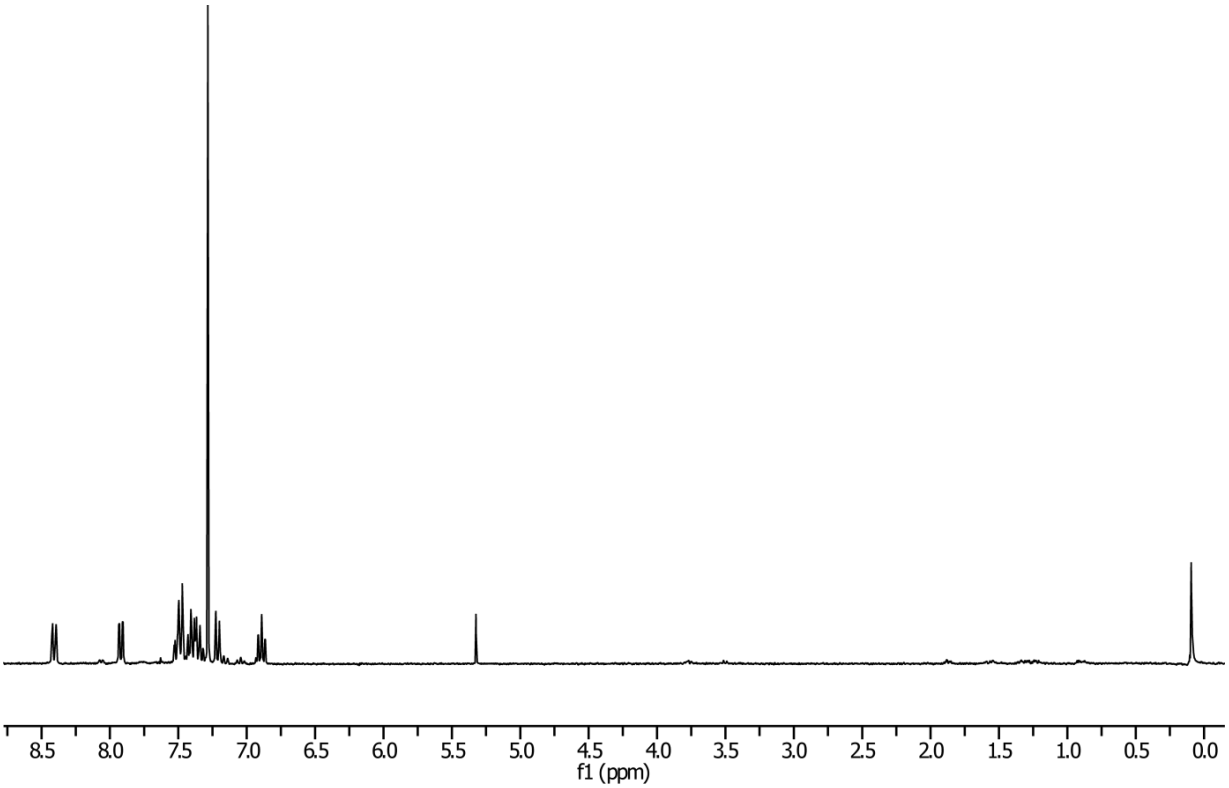


**Figure S5.** $^{1}$H NMR spectrum of a solution of complex **3** in $CDCl_3$ measured at rt.

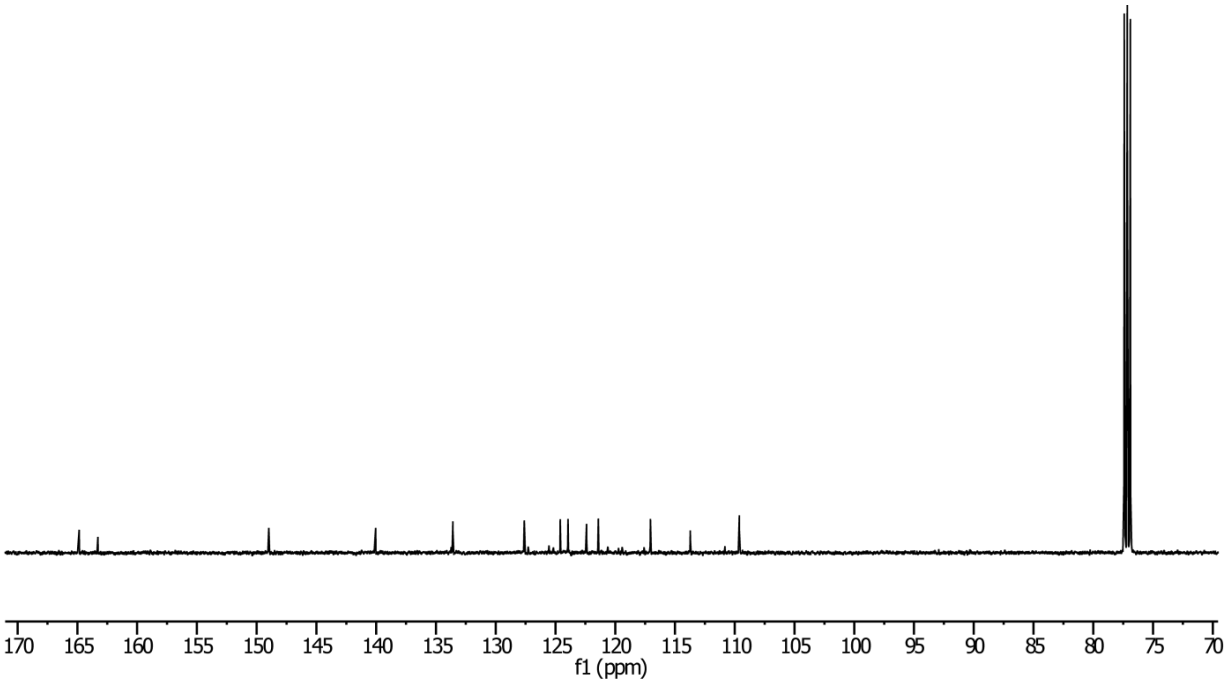


**Figure S6.** $^{13}C\{^{1}H\}$ NMR spectrum of a solution of complex **3** in $CDCl_3$ measured at rt.

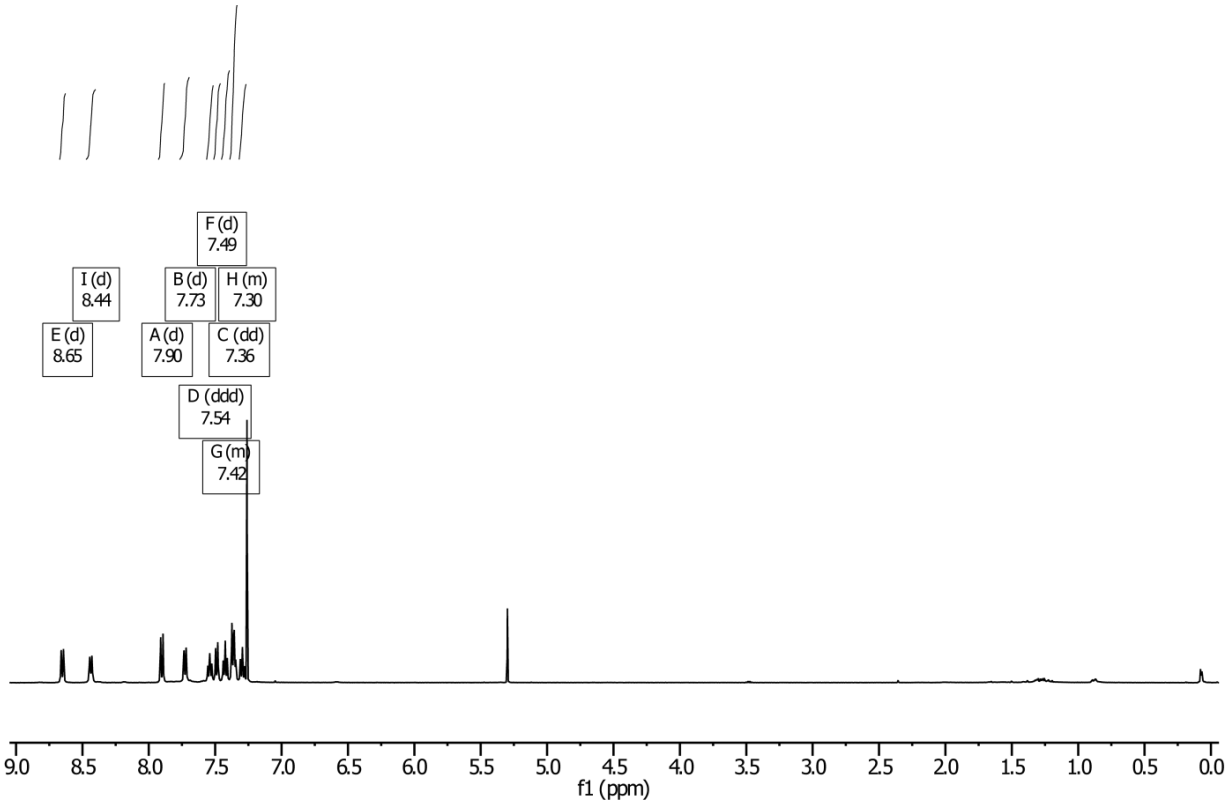


**Figure S7.** $^{1}H$ NMR spectrum of a solution of complex **4** in $CDCl_3$ measured at rt.

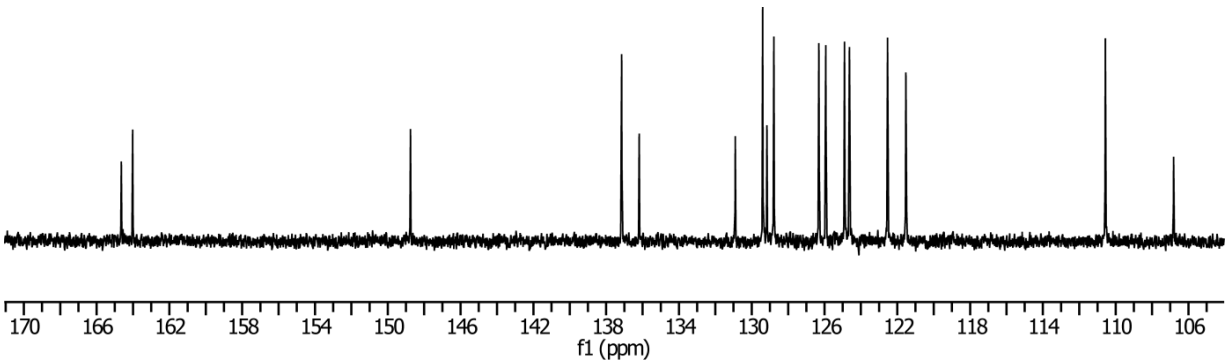


**Figure S8.** $^{13}C\{^{1}H\}$ NMR spectrum of a solution of complex **4** in $CDCl_3$ measured at rt.

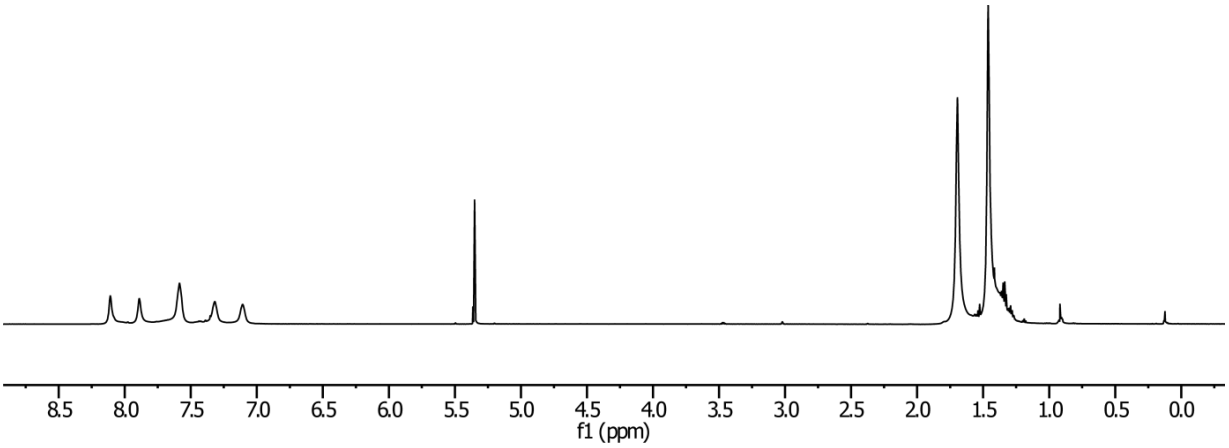


**Figure S9.** $^{1}H$ NMR spectrum of a solution of complex **5** in $CDCl_3$ measured at rt.

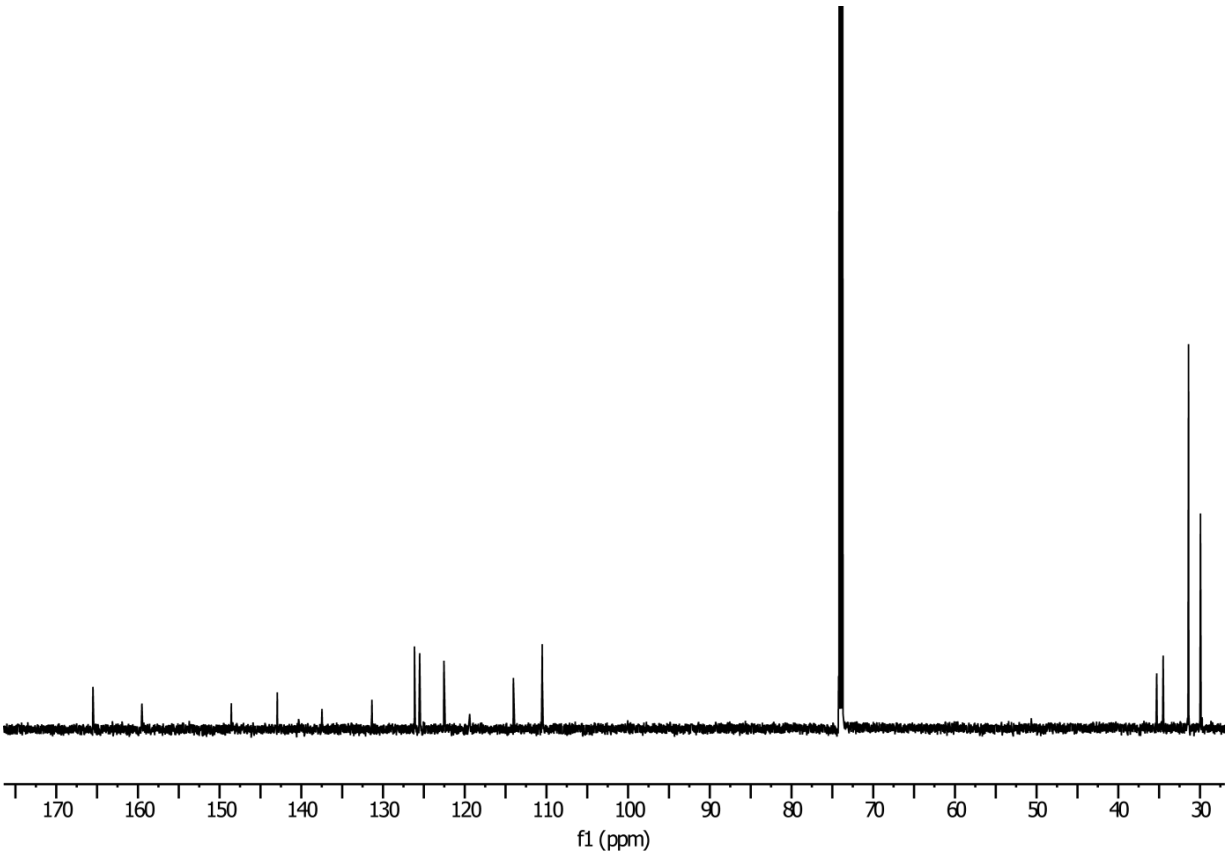


**Figure S10.** $^{13}C\{^{1}H\}$ NMR spectrum of a solution of complex **5** in $CDCl_3$ measured at 373 K.

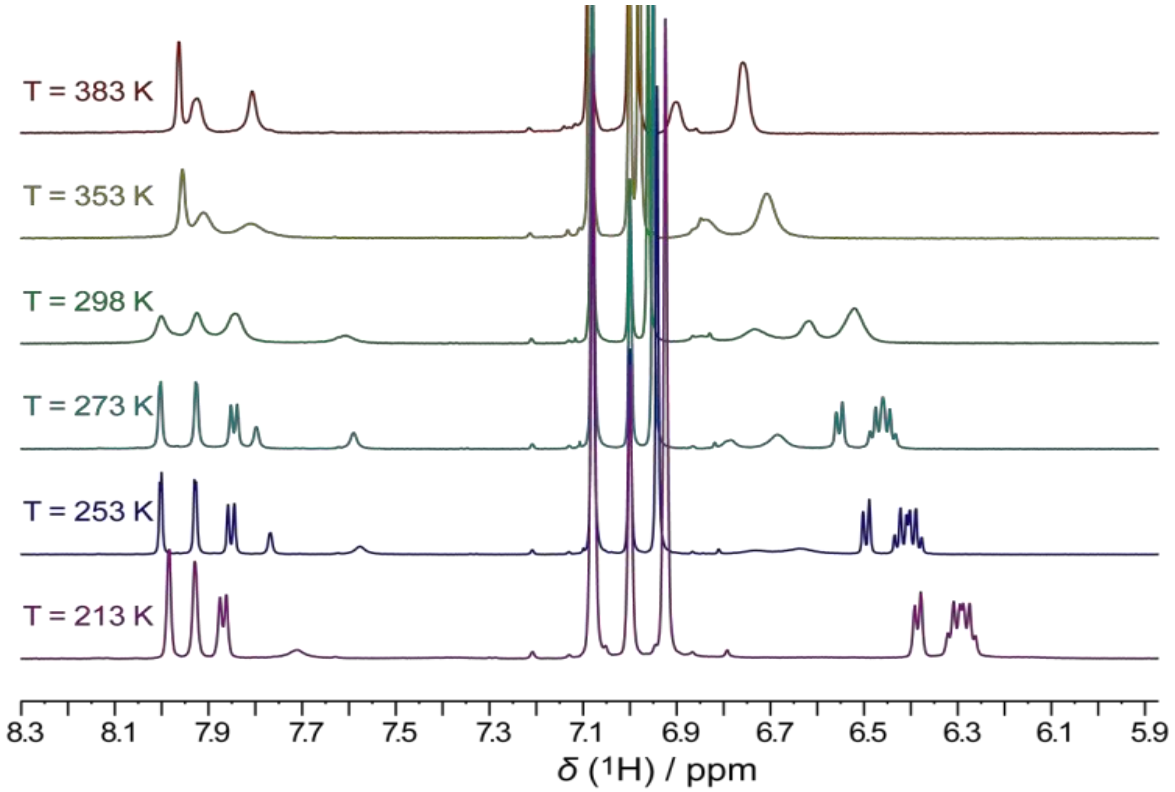


**Figure S11.** Temperature dependent $^{1}$H NMR spectra of compound **5** in toluene-d8.

**Table S1.** Crystallographic data of compounds **1** – **5**.

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| Empirical formula | $C_{47}H_{40}ClN_3O_8Zr$ | $C_{63}H_{72}ClN_3O_6Zr$ | $C_{26}H_{16}Cl_2HfN_2O_4$ | $C_{38}H_{28}Cl_2HfN_2O_5$ | $C_{42}H_{48}N_2O_4Cl_2Hf$ |
| $M_r$ | 901.49 | 1093.90 | 669.80 | 842.01 | 894.21 |
| Crystal system | monoclinic | monoclinic | orthorhombic | orthorhombic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $Pna2_1$ | $Pna2_1$ | $P2_1/n$ |
| $a$ [Å] | 14.90366(12) | 16.4267(2) | 17.0405(2) | 16.80102(10) | 9.72013(6) |
| $b$ [Å] | 19.19921(17) | 9.93661(12) | 11.75814(13) | 13.26904(8) | 17.14975(8) |
| $c$ [Å] | 14.99834(15) | 34.2635(3) | 11.48058(13) | 14.54335(10) | 24.24585(13) |
| $\beta$ [°] | 111.6376(10) | 96.5453(11) | 90 | 90 | 98.7930(5) |
| $V$ [Å$^3$] | 3989.19(7) | 5556.22(12) | 2300.30(5) | 3242.20(3) | 3994.23(4) |
| $Z$ | 4 | 4 | 4 | 4 | 4 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.501 | 1.308 | 1.934 | 1.725 | 1.487 |
| $\mu$ [mm$^{-1}$] | 3.383 | 2.490 | 10.849 | 3.431 | 2.788 |
| $F$(000) | 1856 | 2304 | 1296 | 1664 | 1808 |
| Radiation used | Cu-Kα | Cu-Kα | Cu-Kα | Mo-Kα | Mo-Kα |
| 2$\theta$ range [°] | 6.4-144.0 | 5.4-144.0 | 12.0-152.3 | 4.2-60.2 | 3.4-60.2 |
| Index range $h$ | − 18 – 18 | −20 – 18 | −19 – 21 | −23 – 23 | −13 – 13 |
| Index range $k$ | −22 – 23 | −12 – 12 | −14 – 11 | −18 – 18 | −24 – 24 |
| Index range $l$ | −18 – 18 | −42 – 42 | −14 – 13 | −20 – 20 | −34 – 34 |
| Refl. collect. | 72509 | 112191 | 9686 | 128732 | 231858 |
| Indep. refl. | 7843 | 10923 | 4272 | 9535 | 11737 |
| $R_{int}$ | 0.0391 | 0.0607 | 0.0192 | 0.0344 | 0.0372 |
| Data/restraints | 7843/0 | 10923/0 | 4272/1 | 9535/1 | 11737/0 |
| Parameters | 545 | 692 | 317 | 434 | 472 |
| $R_1$/w$R_2$ [$I$>2$\sigma$($I$)] | 0.026/0.063 | 0.032/0.076 | 0.017/0.045 | 0.014/0.035 | 0.021/0.055 |
| $R_2$ (all data)/w$R_2$ | 0.029/0.065 | 0.039/0.080 | 0.017/0.046 | 0.015/0.035 | 0.023/0.057 |
| GoF on $F^2$ | 1.025 | 1.026 | 1.092 | 1.039 | 1.111 |
| $\rho_{fin}$ (max/min) [$e$ $^{-3}$] | 0.57/−0.52 | 1.08/−0.55 | 0.36/−0.49 | 0.33/−0.58 | 1.05/−0.92 |
| Flack parameter | | | -0.025(7) | 0.333(5)[a] | |
| CCDC no. | 1817378 | 1817379 | 1817380 | 1817381 | 1817382 |
| Empirical formula | $C_{47}H_{40}ClN_3O_8Zr$ | $C_{63}H_{72}ClN_3O_6Zr$ | $C_{26}H_{16}Cl_2HfN_2O_4$ | $C_{38}H_{28}Cl_2HfN_2O_5$ | $C_{42}H_{48}N_2O_4Cl_2Hf$ |
| $M_r$ | 901.49 | 1093.90 | 669.80 | 842.01 | 894.21 |