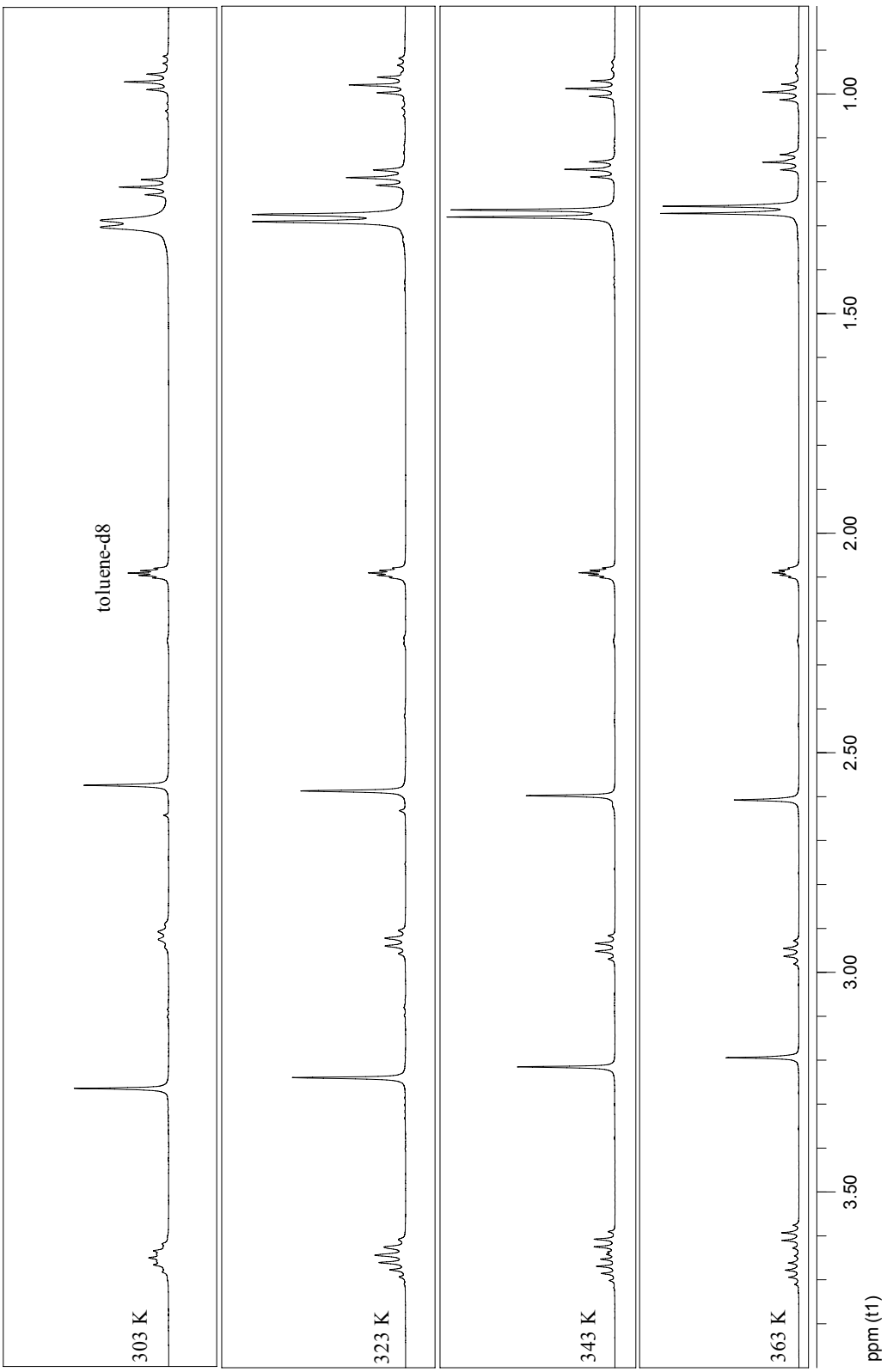
Electronic Supplementary Information for Dalton Transactions

SUPPORTING INFORMATION

The room temperature ^{1}H-NMR spectrum of [Zr(NEtMe)$_2$(guanid)$_2$] complex shows some complexity. The broad resonance centered at 0.94 ppm and a multiplet centered at 3.6 ppm had to be assigned based on variable temperature NMR studies (Fig. 1 supplementary data). The broad resonance centered at 1.24 ppm resolves itself into a sharp doublet at 363 K and is assigned to isopropyl (methyl) groups of the guanidinate ligand. The multiplet observed at 3.6 ppm was separated into a septet and a quartet at 363 K. The septet was assigned to isopropyl (methyne) groups and quartet was assigned to methylene group of the amide moiety directly attached to the metal center. This behavior was anticipated as a result of interaction of ethylmethylamido groups and the guanidinate ligands.[22] These groups display non-equivalent behavior on the NMR time scale. The spectroscopic equivalence for the ^{i}Pr groups (both CH and CH_3) bonded to N(11) and N(13) with those on N(21) and N(23) as well as the appearance of a singlet for the amide-methyl protons attached to Zr center (C33 and C43) indicates that the guanidinato ligands in [Zr(NEtMe)$_2$(guanid)$_2$] are fluxional in solution. The monomeric structure of the complex revealed from ^{1}H NMR spectroscopic data were consistent with the structural assignment postulated from the X-ray diffraction data.



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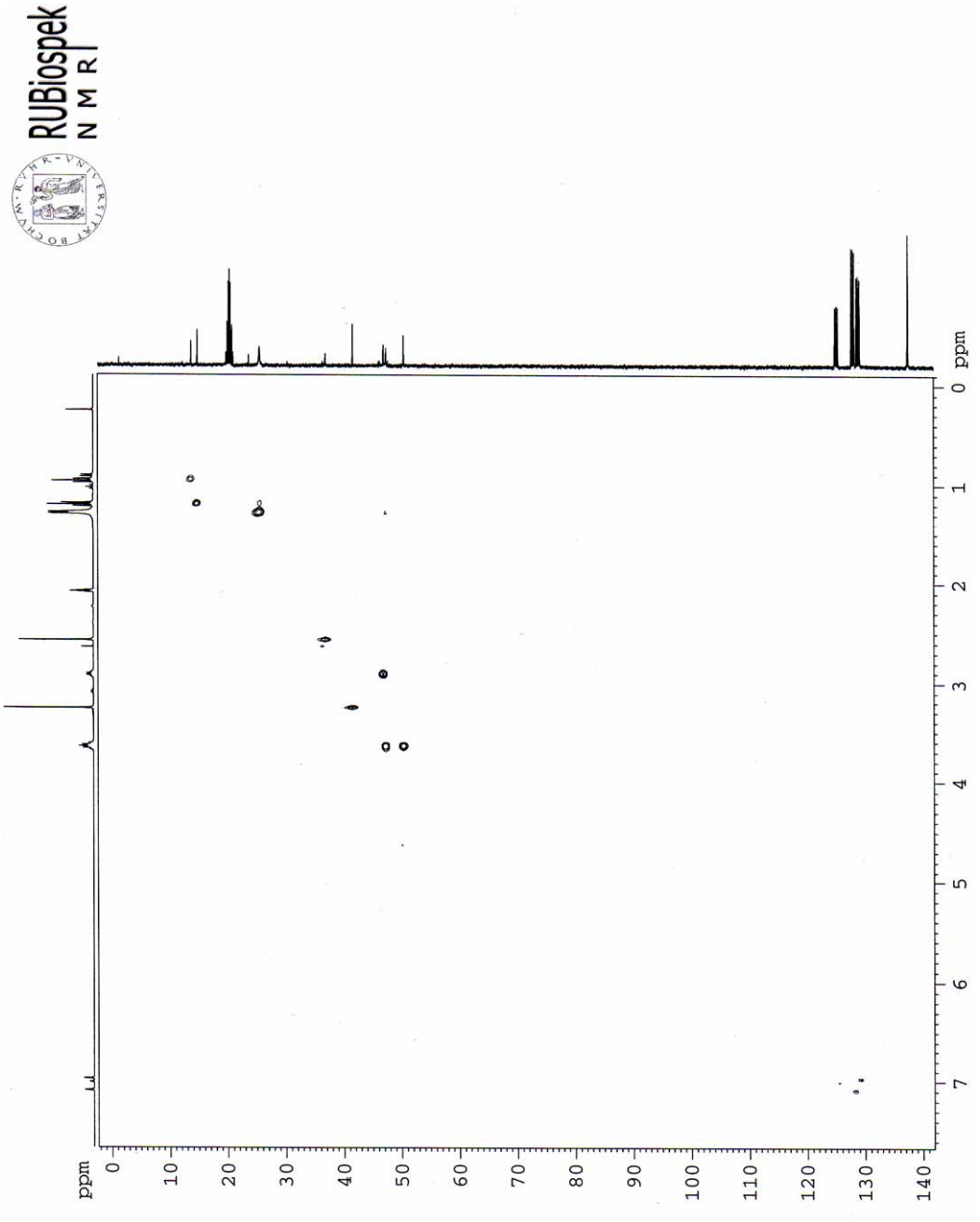
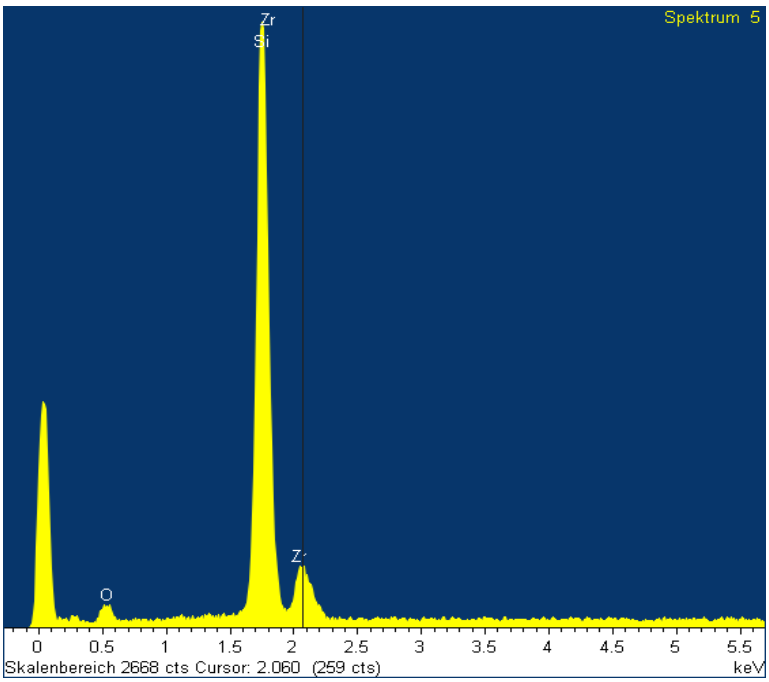
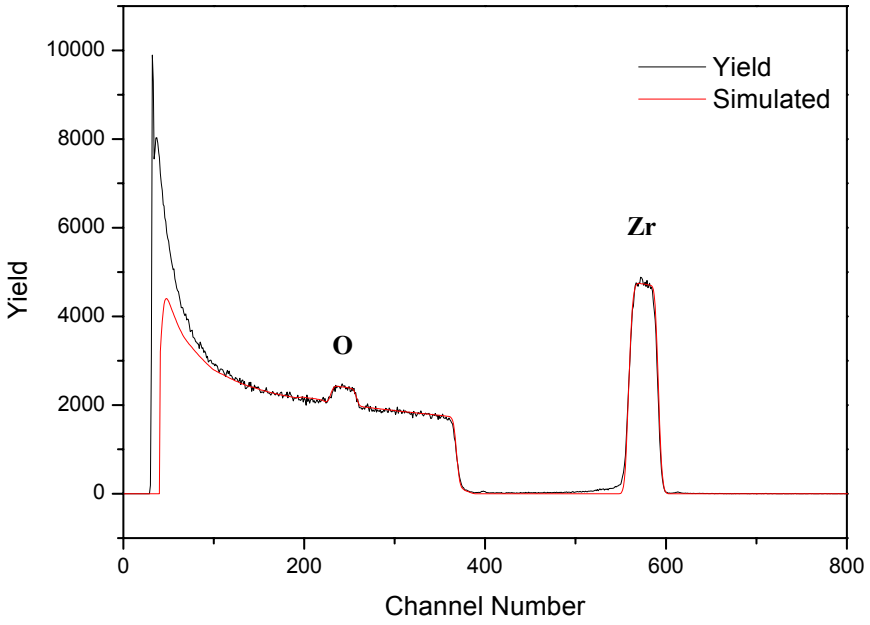
Supplementary Fig. 1. Variable temperature ^{1}H-NMR for [Zr(NEtMe)$_2$(guanid)$_2$] complex with toluene-d^8 as solvent.



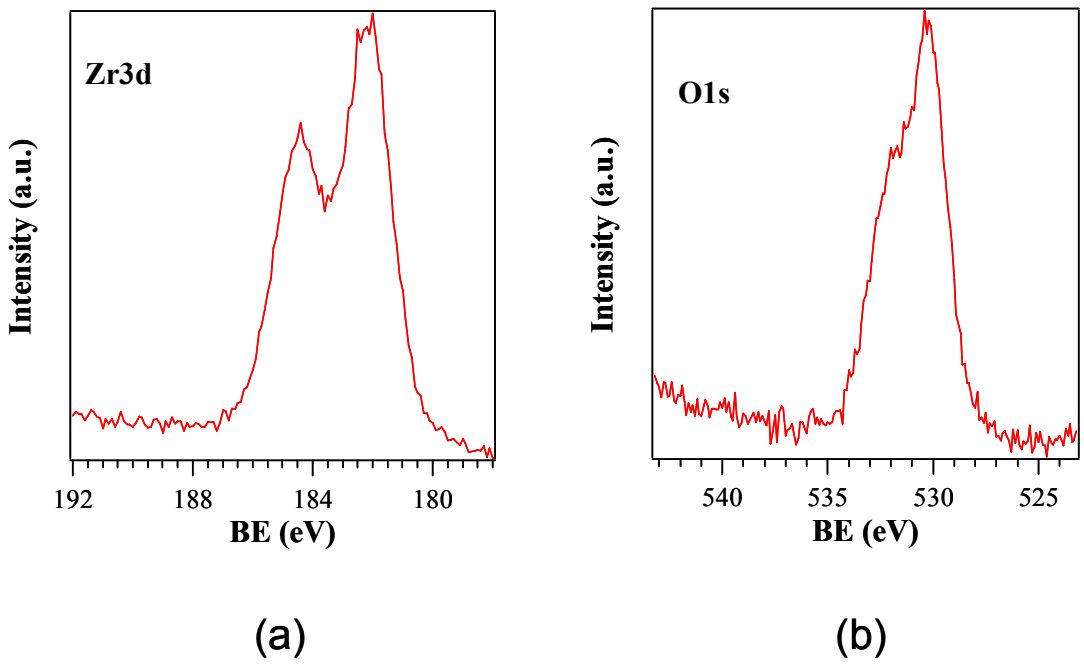
Supplementary Fig. 2. HMQC spectrum of $[Zr(NEtMe)_2(guanid)_2]$ complex at room temperature with toluene-d^8 as solvent.



Supplementary Fig. 3. EDX spectrum of a ZrO_2 film grown from $[Zr(NEtMe)_2(guanid)_2]$ at 500°C.



Supplementary Fig. 4: RBS analysis of a ZrO_2 film grown from $[Zr(NEtMe)_2(guanid)_2]$ at 500°C.



Supplementary Fig. 5: XPS analysis (a) Zr 3d region and (b) oxygen 1S region of a ZrO_2 thin film grown from $[Zr(NEtMe)_2(guanid)_2]$ at 500°C.