Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

Identification of Zr(IV)-based architectures generated from ligands incorporating the 2,2'-biphenolato unit

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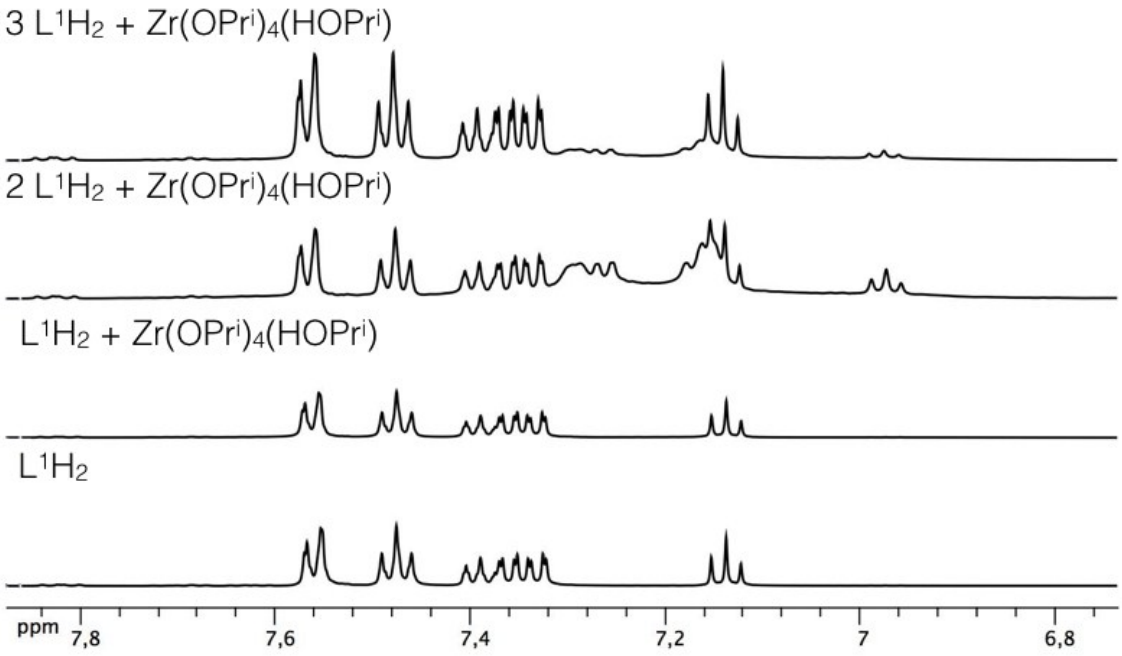

Figure 1: Aromatic region of the ^1H NMR spectra (CD_2Cl_2, 500 MHz) of the following reactions: L^1H_2, L^1H_2 + $Zr(OPr^i)_4(HOPr^i)$, 2 L^1H_2 + $Zr(OPr^i)_4(HOPr^i)$, 3 L^1H_2 + $Zr(OPr^i)_4(HOPr^i)$.

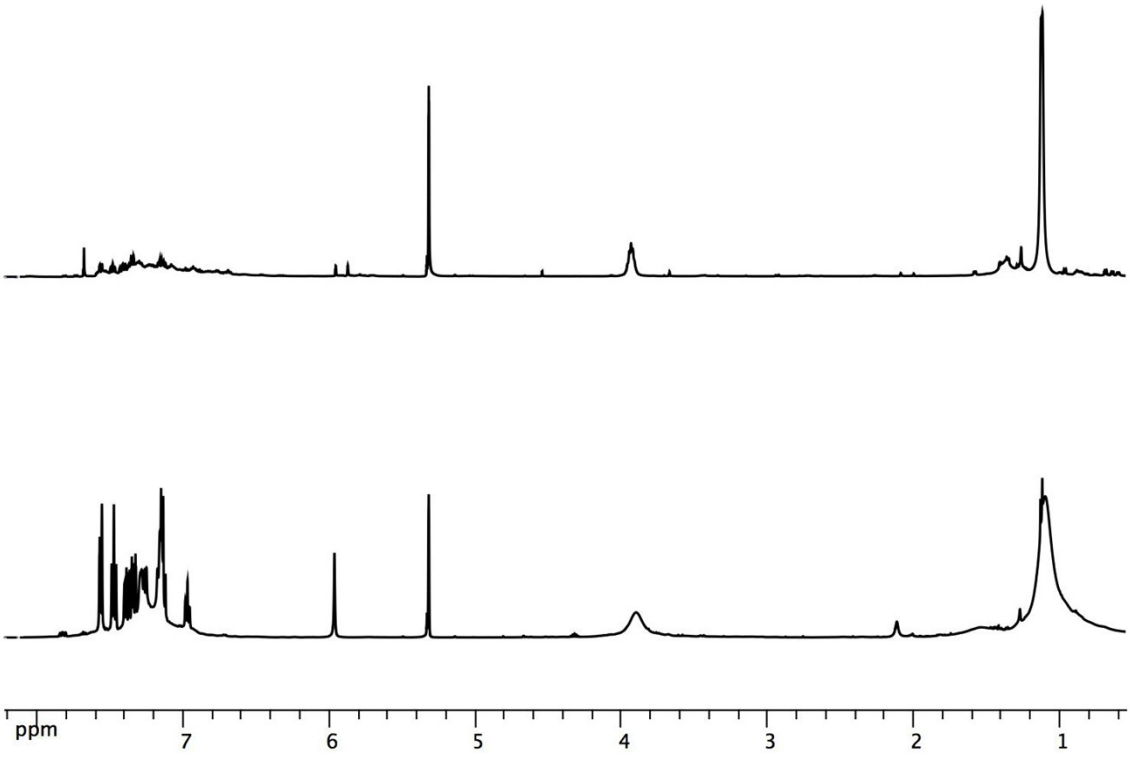

Figure 2: ^{1}H NMR spectra (500 MHz, CD_2Cl_2) of the mixture resulting from the reactions: L^2H_4 + $Zr(OPr^i)_4(HOPr^i)$ (top) and 2 L^1H_2 + $Zr(OPr^i)_4(HOPr^i)$ (down)

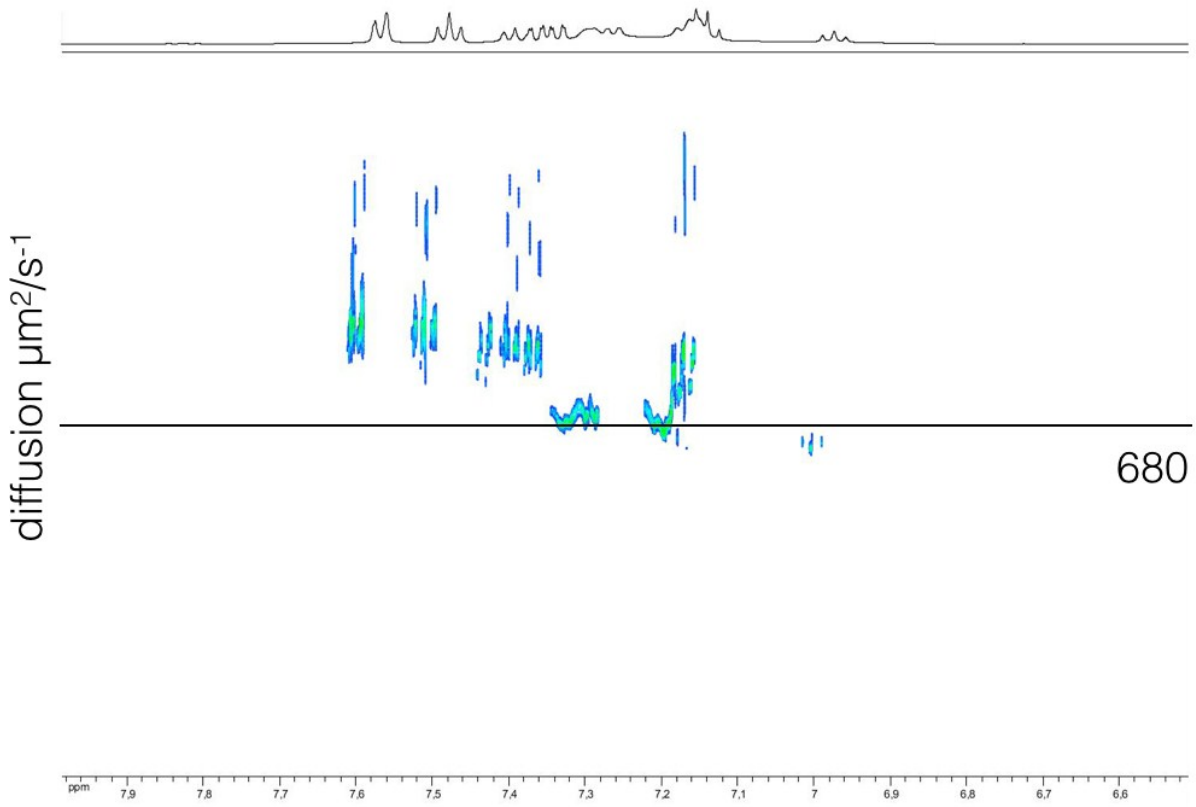

Figure 3: DOSY map of the mixture in CD_2Cl_2 resulting from the following reaction: 2 L^1H_2 + $Zr(OPr^i)_4(HOPr^i)$

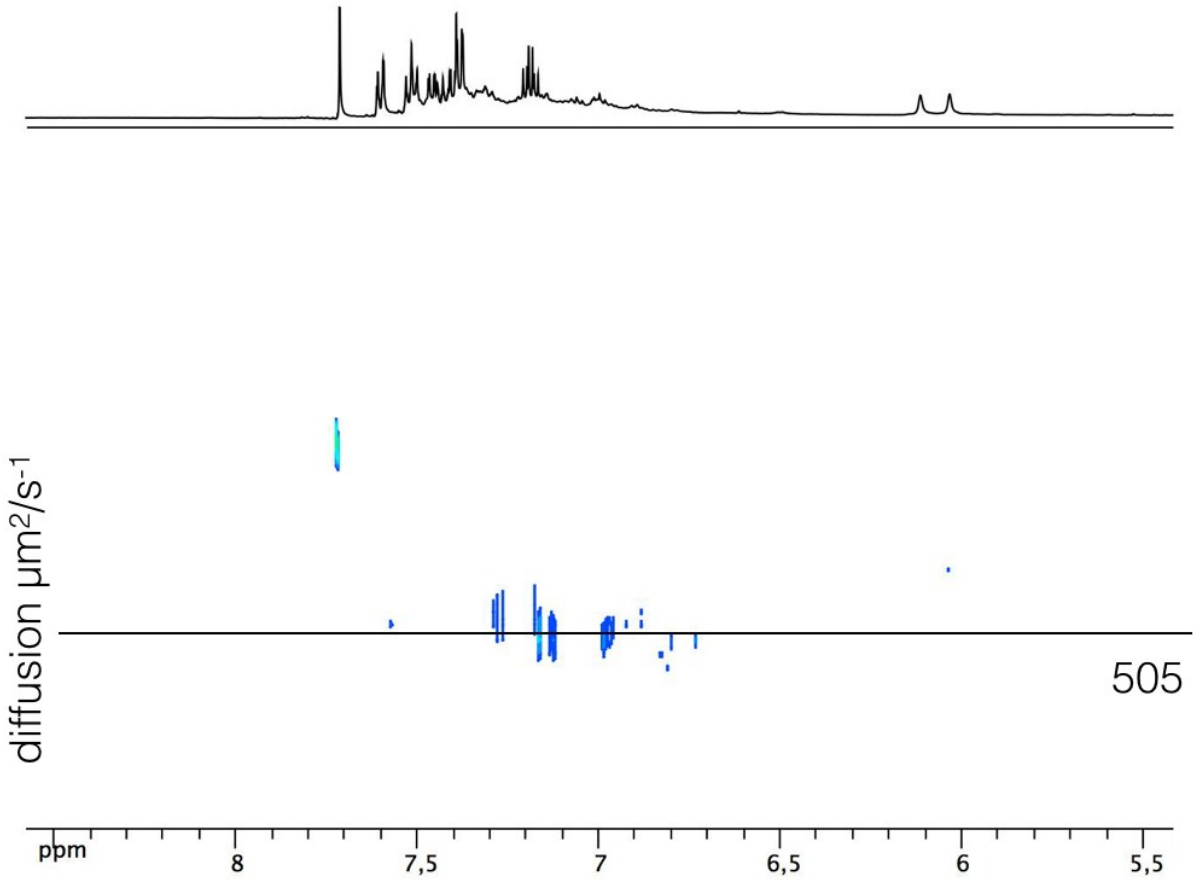

Figure 4: DOSY map of the mixture in CD_2Cl_2 resulting from the following reaction: L^2H_4 + $Zr(OPr^i)_4(HOPr^i)$.

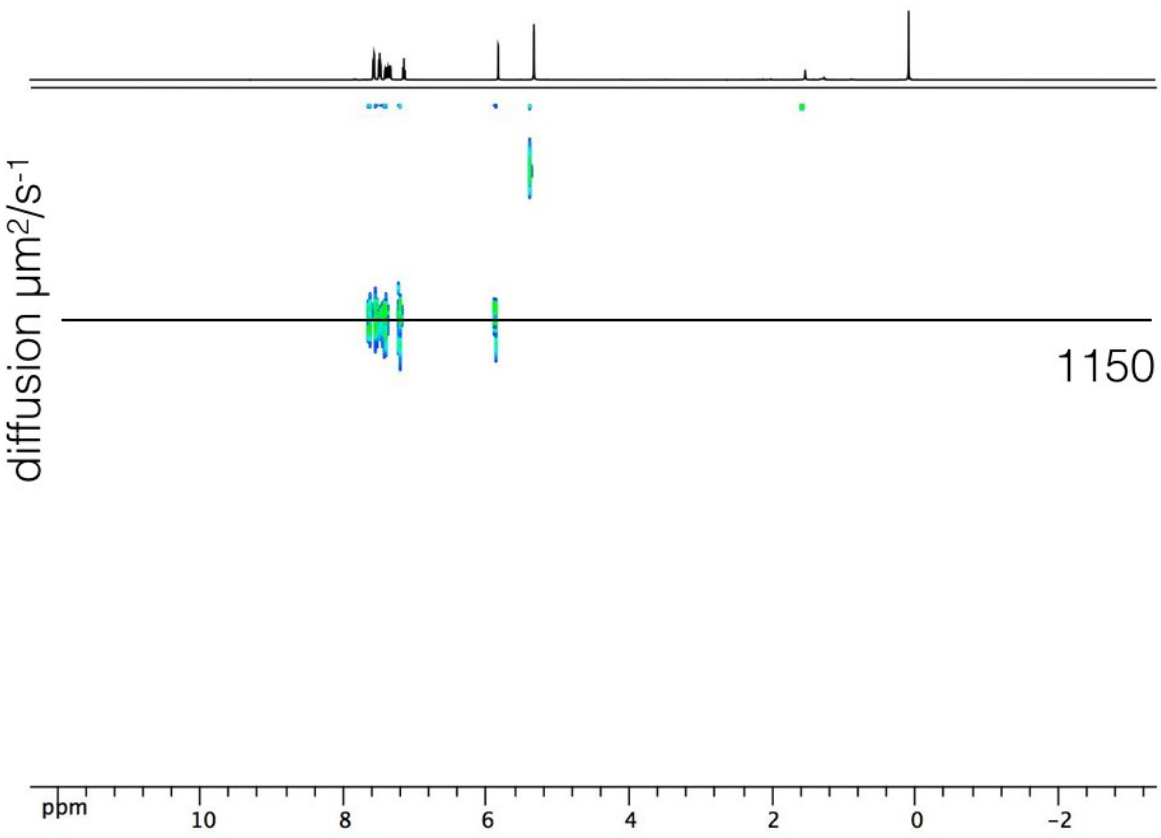

Figure 5: DOSY map of L^1H_2 in CD_2Cl_2.

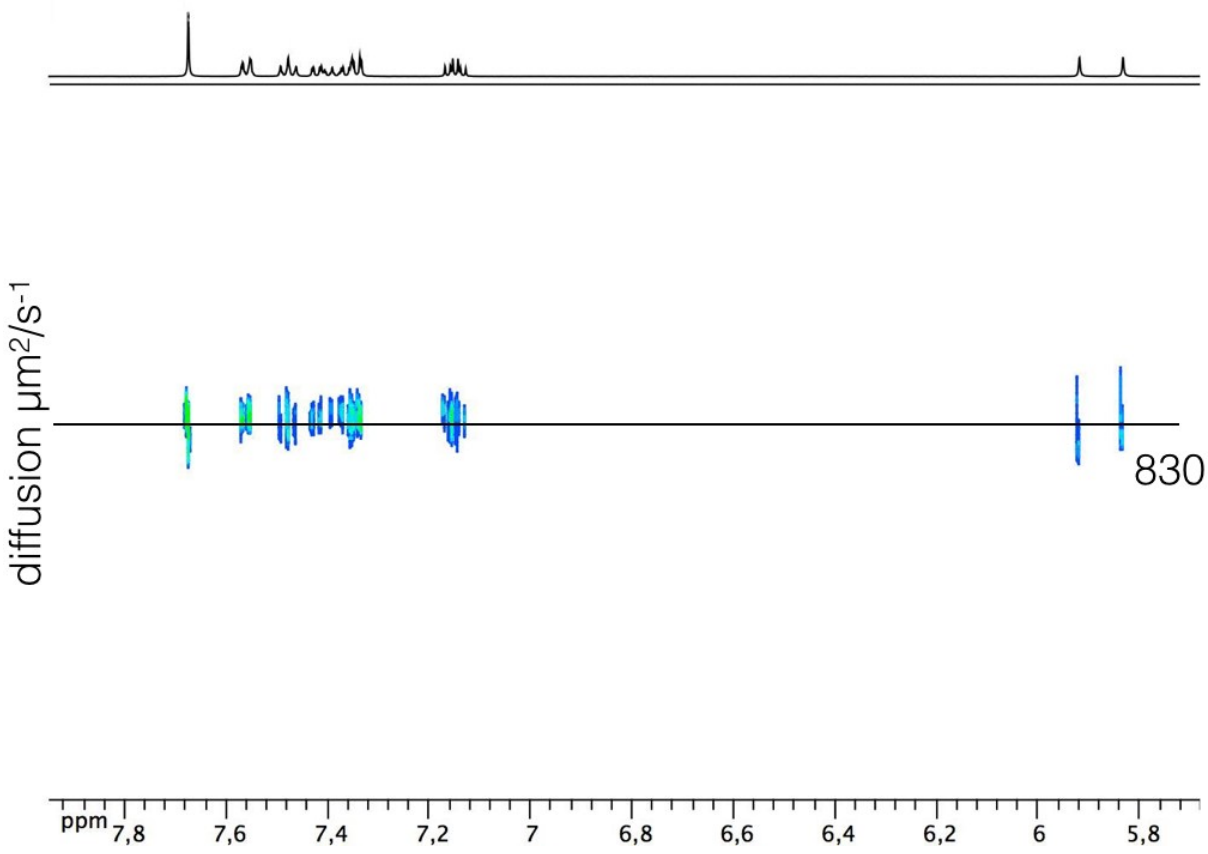

Figure 5: DOSY map of L^2H_4 in CD_2Cl_2.

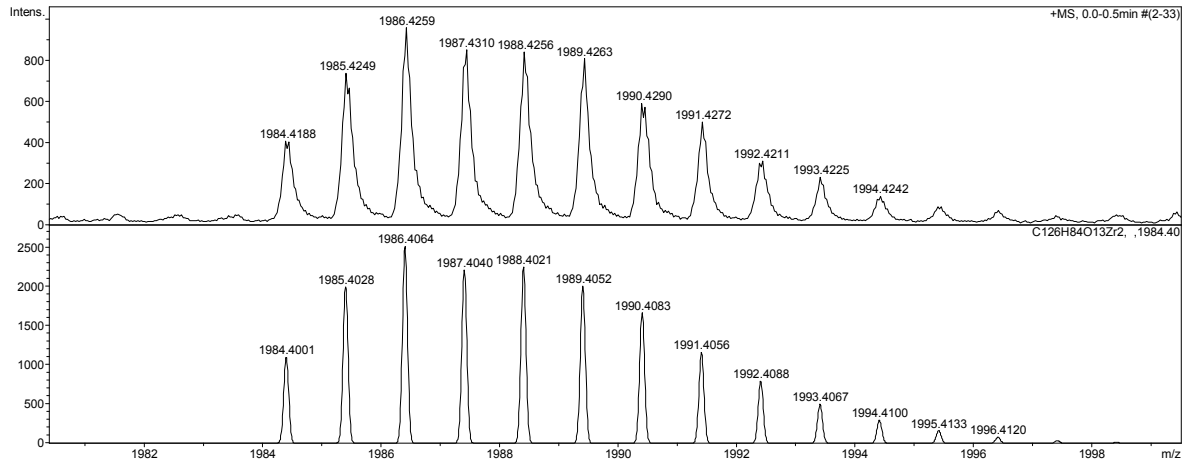

Figure 6: ESI mass spectrum of the mixture obtained after mixing two equivalents of L^2H_4 with $Zr(OPr^i)_4(HOPr^i)$. Peak at *m/z* = 1984.4188 corresponds to an assembly incorporating two Zr(IV) centres and three L^2 ligands (calcd for $[Zr_2L^2{}_3H_4(H_2O)]^+$ ($C_{126}H_{84}O_{13}Zr_2$) = 1984.40). Experimental peak (top) simulated peak (down).

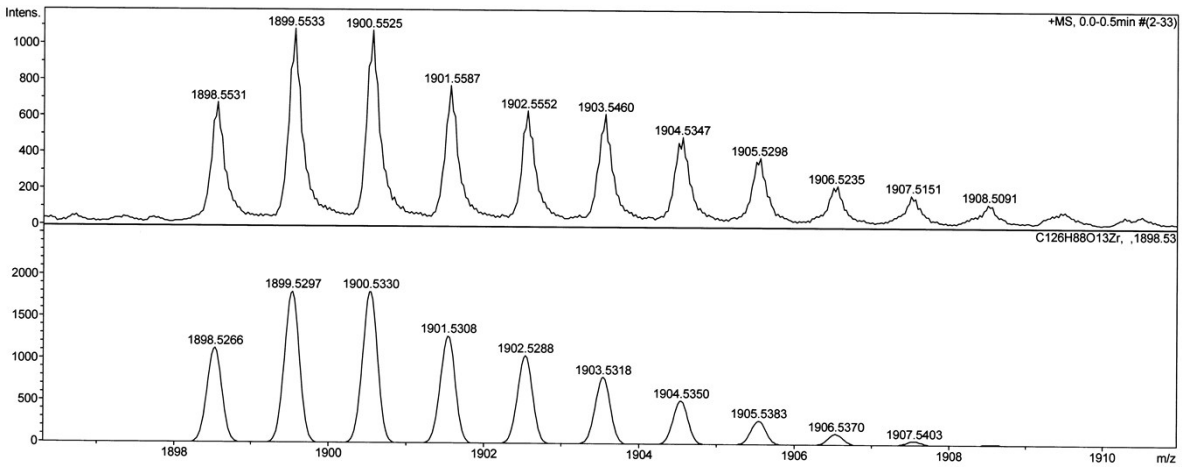

Figure 7: ESI mass spectrum of the mixture obtained after mixing two equivalents of L^2H_4 with $Zr(OPr^i)_4(HOPr^i)$. Peak at m/z = 1898.5531 is assigned to $[Zr\ L^2{}_3H_8(H_2O)]^+$ (calcd for $C_{126}H_{88}O_{13}Zr$, *m/z* = 1898.527). Experimental peak (top) simulated peak (down).

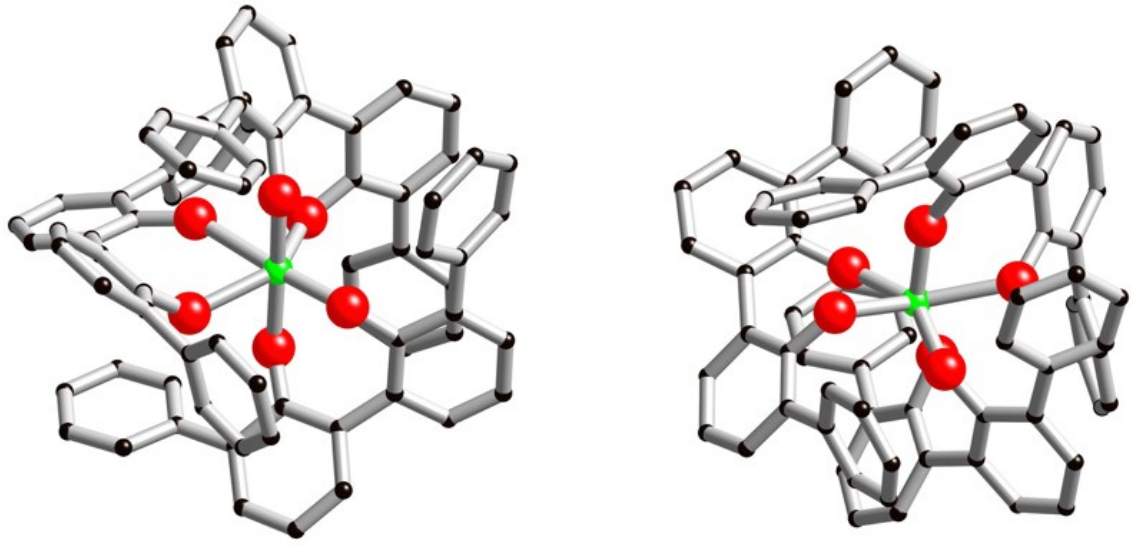

Figure 8: Computed models of Zr $L^1{}_2L^1H_2$ and *trans*-$ZrL^1(L^1H)_2$.

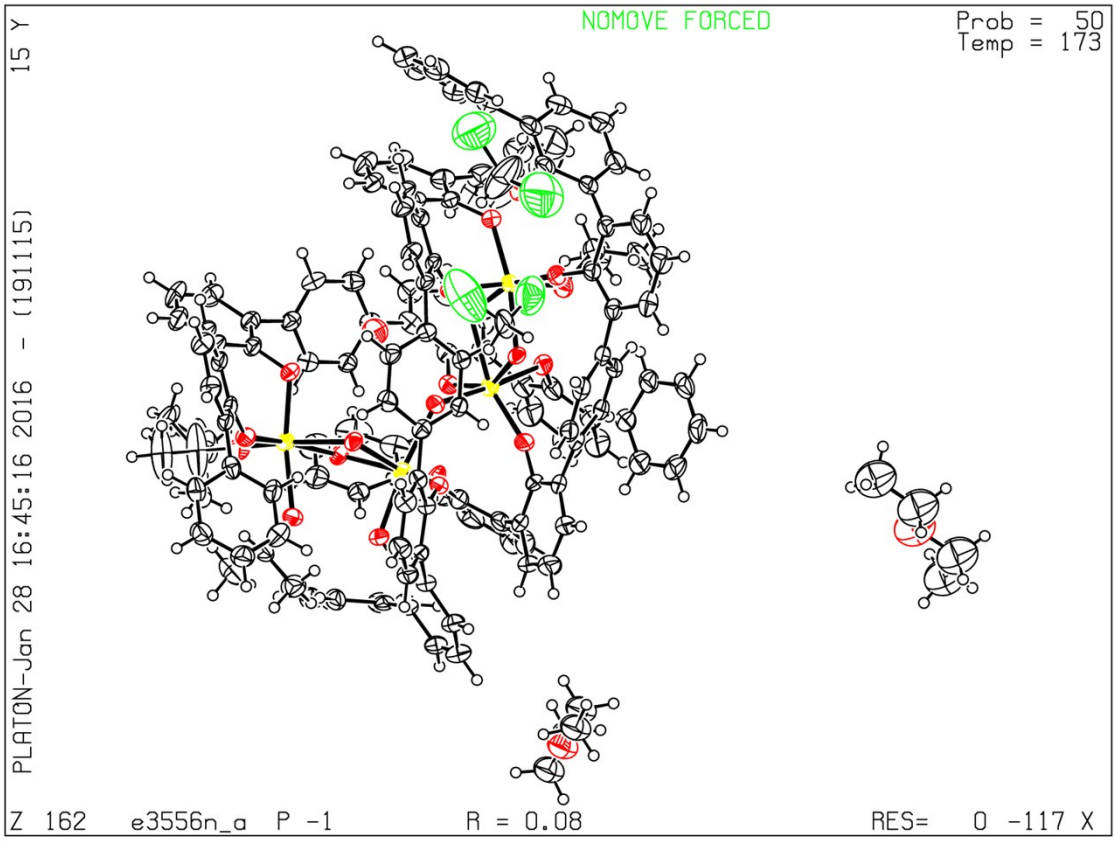

Figure 9: Thermal ellipsoids plot of $Zr_4(L^2)_2(L^2H)(\mu_2\text{-}OH)_5(HO^iPr)_3$.