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 $^1$H NMR spectra (CD$_2$Cl$_2$, 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 $L^1H_2 + Zr(OPr^i)_4(HOPr^i)$.

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Figure 2: $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$) of the mixture resulting from the reactions: L$^2$H$_4$ + Zr(OPr$i$)$_4$(HOPr$i$) (top) and 2 L$^1$H$_2$ + Zr(OPr$i$)$_4$(HOPr$i$) (down)
Figure 3: DOSY map of the mixture in CD$_2$Cl$_2$ resulting from the following reaction: $2 \text{LiH}_2^+ + \text{Zr(OPr$^i$)}_4(\text{HOPr$^i$})$
Figure 4: DOSY map of the mixture in CD$_2$Cl$_2$ resulting from the following reaction: L$_2$H$_4$ + Zr(OPr$^i$)$_4$(HOPr$^i$).
Figure 5: DOSY map of L$^1$H$_2$ in CD$_2$Cl$_2$. 
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^t)_4(HOPr^t). Peak at m/z = 1984.4188 corresponds to an assembly incorporating two Zr(IV) centres and three L^2 ligands (calcd for [Zr_2L^2H_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^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 ZrL^1_2L^1H_2 and trans-ZrL^1(L^1H)_2.
Figure 9: Thermal ellipsoids plot of $\text{Zr}_4(L^2)\text{L}_2\text{H}(\mu_2\text{-OH})_5(\text{HO}^+\text{Pr})_3$. 