Supplementary Material

Synthesis and Characterisation of Trigonal C_2-Chiral di- and tetra-substituted Bis(Oxazoline) Alkyl Zinc Complexes and Their Reactivity Towards Protic Reagents

Erwan Le Roux,* Nicolas Merle, Karl W. Törnroos

Department of Chemistry, University of Bergen, Allégaten 41, N-5007, Bergen, Norway. Fax: +47 555 89490; Tel: +47 555 89854; E-mail: Erwan.LeRoux@kj.uib.no

X-ray Crystallography and Crystal Structure Determination. *Crystal data:* for **1b**: from toluene. $C_{21}H_{22}N_2O_2Zn$, M = 399.78, orthorhombic, space group $P2_12_12_1$, a = 5.4113(7), b = 21.983(3), c = 31.330(4) Å, V = 3726.9(8) Å^3, Z = 8, ρ_{calc} = 1.425 g.cm^{-3}, F(000) = 1664, μ(Mo-K$_\alpha$) = 1.335 mm^{-1}, λ = 0.71073 Å, T = 103(2) K. The 42494 reflections measured on a *Bruker* APEXII Ultra CCD area detector yielded 6679 unique data (θmax = 25.15°, R_{int} = 0.0715) [6227 observed reflections ($I > 2\sigma(I)$]. $R1$ = 0.0376, $wR2$ = 0.0908. Flack parameter: 0.003(10). CCDC reference number 791883. for **2b**: from toluene. $C_{38}H_{34}N_4O_4Zn$, M = 676.06, orthorhombic, space group $C222_1$, a = 10.3033(7), b = 16.6104(11), c = 75.385(5) Å, V = 12901.5(15) Å^3, Z = 16, ρ_{calc} = 1.392 g.cm^{-3}, F(000) = 5632, μ(Mo-K$_\alpha$) = 0.809 mm^{-1}, λ = 0.71073 Å, T = 100(2) K. The 110073 reflections measured on a *Bruker* APEXII Ultra CCD area detector yielded 19733 unique data (θmax = 30.59°, R_{int} = 0.0422) [19509 observed reflections ($I > 2\sigma(I)$]. $R1$ = 0.0673, $wR2$ = 0.1484. Flack parameter: 0.088(10). CCDC reference number 791885.

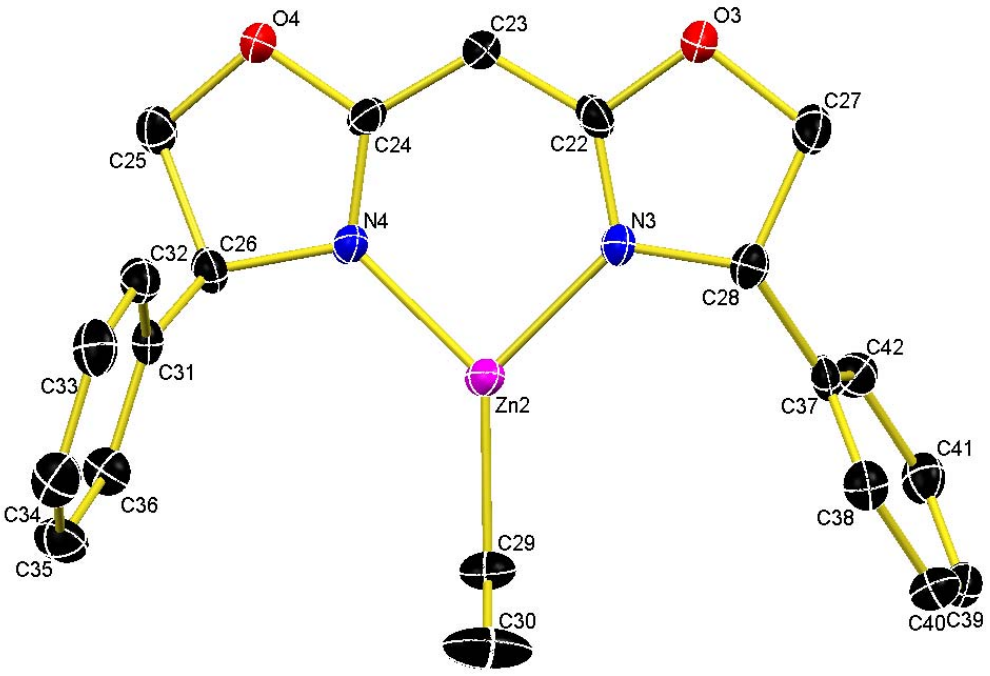

Figure S1 Molecular structure of (^{Ph,H}BOX)ZnEt (**1b**). Selected bond lengths (Å) and angles (°) for the 2nd conformer of **1b**: Zn(2)-C(29) 1.961(3), Zn(2)-N(3) 1.967(3), Zn(2)-N(4) 1.971(2), N(3)-C(22) 1.323(4), N(4)-C(24) 1.316(4), C(22)-C(23) 1.386(5), C(24)-C(23) 1.394(5), N(3)-Zn(2)-N(4) 94.00(10), N(4)-Zn(2)-C(29) 132.22(13), N(3)-Zn(2)-C(29) 133.57(13), C(22)-C(23)-C(24) 121.9(3), C(23)-Zn(1)-C(29) 176.99(13).

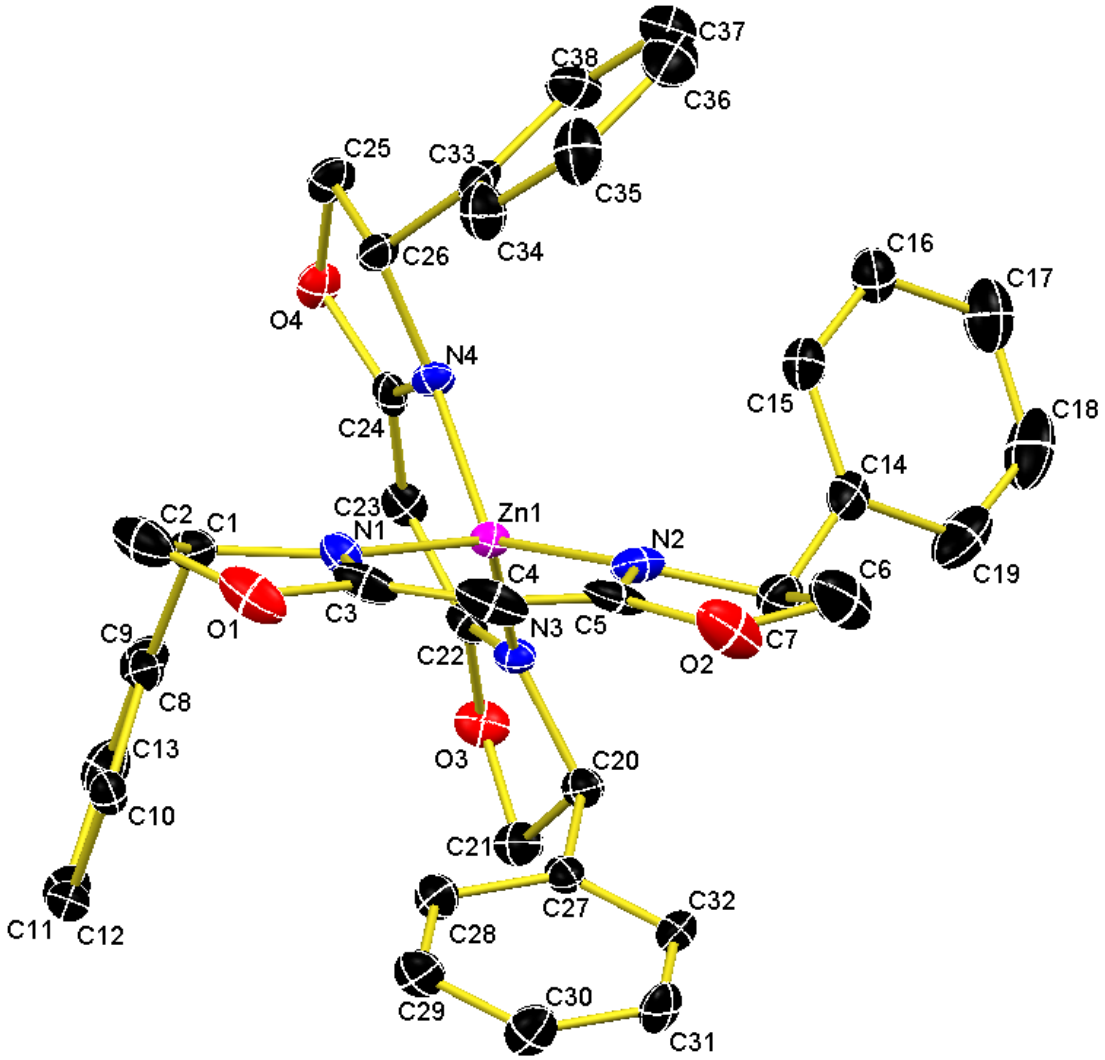

Figure S2 Molecular structure of (^{Ph,H}BOX)$_2$Zn (**2b**). Hydrogen atoms and toluene molecule are omitted for clarity.Selected bond lengths (Å) and angles (°) for the 1st conformer of **2b**: Zn(1)-N(1) 1.998(3), Zn(1)-N(2) 1.964(3), Zn(1)-N(3) 1.972(3), Zn(1)-N(4) 1.1.988(3), N(1)-C(3) 1.312(5), N(2)-C(5) 1.317(5), N(3)-C(22) 1.318(5), N(4)-C(24) 1.317(5), C(3)-C(4) 1.400(7), C(4)-C(5) 1.390(7), C(22)-C(23) 1.401(5), C(23)-C(24) 1.392(6), N(1)-Zn(1)-N(2) 95.39(14), N(3)-Zn(1)-N(4) 94.00(13), N(1)-Zn(1)-N(4) 102.56(14), N(1)-Zn(1)-N(3) 126.30(13), N(2)-Zn(1)-N(3) 110.59(14), N(2)-Zn(1)-N(4) 131.71(14), C(3)-C(4)-C(5) 123.9(4), C(22)-C(23)-C(24) 121.7(3).

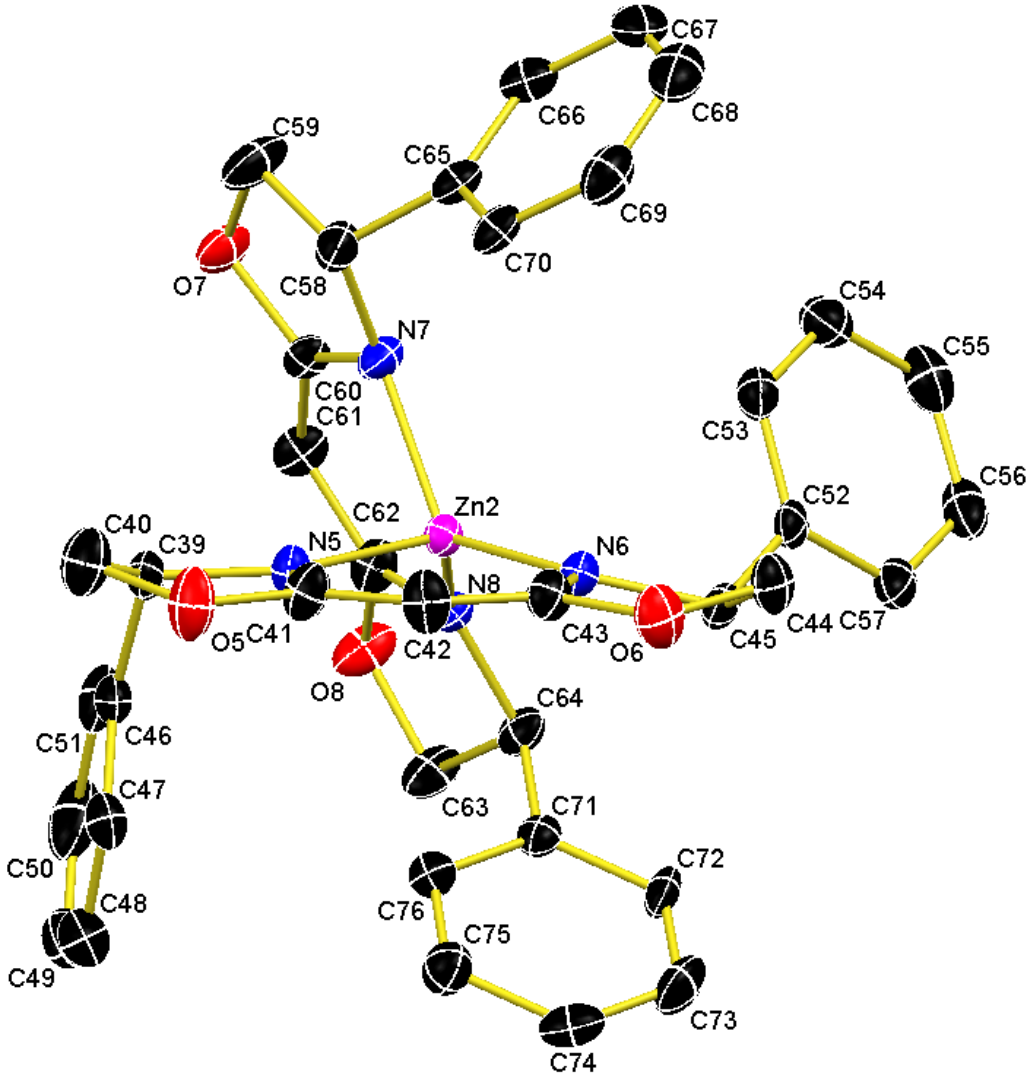

Figure S3 Molecular structure of (^{Ph,H}BOX)$_2$Zn (**2b**). Hydrogen atoms and the toluene molecule are omitted for clarity.Selected bond lengths (Å) and angles (°) for the 2nd conformer of **2b**: Zn(2)-N(5) 2.006(3), Zn(2)-N(6) 1.953(3), Zn(2)-N(7) 2.017(4), Zn(2)-N(8) 1.966(3), N(5)-C(41) 1.297(5), N(6)-C(43) 1.325(5), N(7)-C(60) 1.318(5), N(8)-C(62) 1.373(5), C(41)-C(42) 1.412(6), C(42)-C(43) 1.392(6), C(60)-C(61) 1.397(6), C(61)-C(62) 1.388(6), N(5)-Zn(2)-N(6) 94.22(14), N(7)-Zn(2)-N(8) 92.43(14), N(5)-Zn(1)-N(7) 97.45(15), N(5)-Zn(1)-N(8) 122.56(14), N(6)-Zn(2)-N(7) 129.27(14), N(6)-Zn(2)-N(8) 121.35(14), C(41)-C(42)-C(43) 121.1(4), C(60)-C(61)-C(62) 121.4(4).

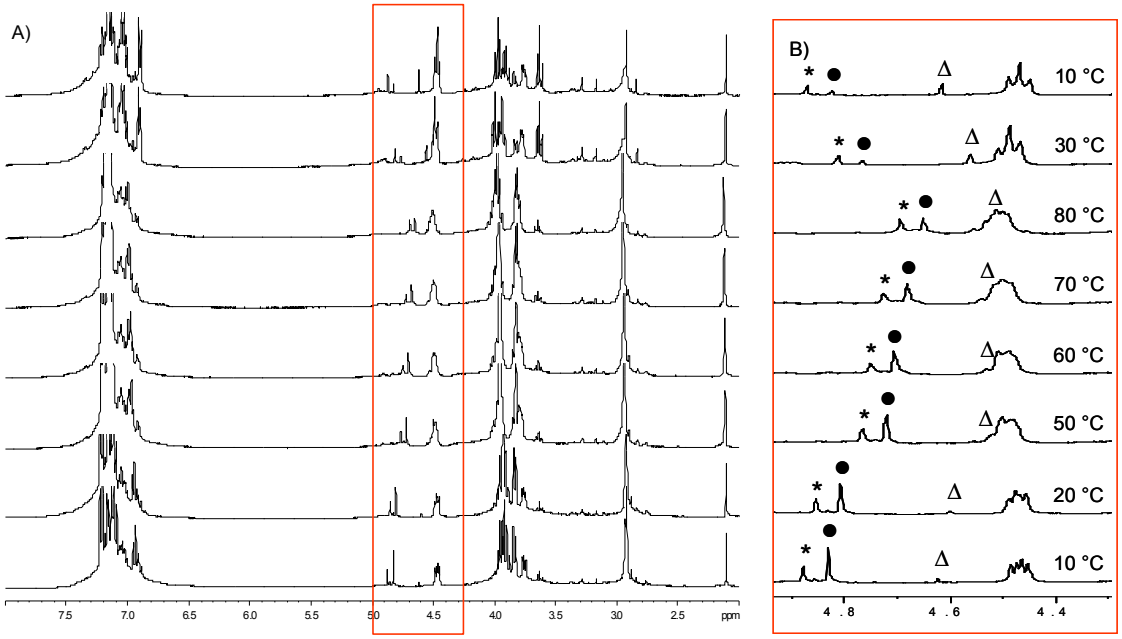

Figure S4 A) Variable temperature ^{1}H NMR spectra (400.13 MHz, in benzene-d_6) of monometallic (^{Ph,H}BOX)Zn(OMe) **4b** (*), bimetallic [(^{Ph,H}BOX)Zn(μ-OMe)]$_2$ **4b'** (●) and (^{Ph,H}BOX)$_2$Zn **2b** (Δ) species. B) Zoom in the methylenic (*H*C$_1$) area [5.0-4.3 ppm].

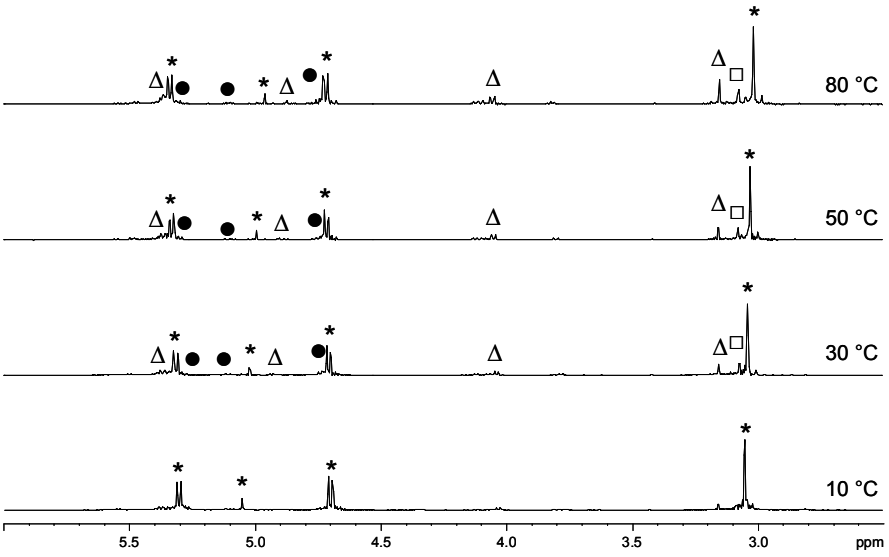

Figure S5 Variable temperature ^{1}H NMR spectra of (400.13 MHz, in benzene-d_6) monometallic (^{PhPh}BOX)Zn(OMe) **4c** (*) and formation of side products increasing with temperature: (^{PhPh}BOX)$_2$Zn **2c** (●), [Zn(OMe)$_2$]*n* (□) and (^{Ph,Ph}BOX)Zn(OMe) aggregates (Δ).

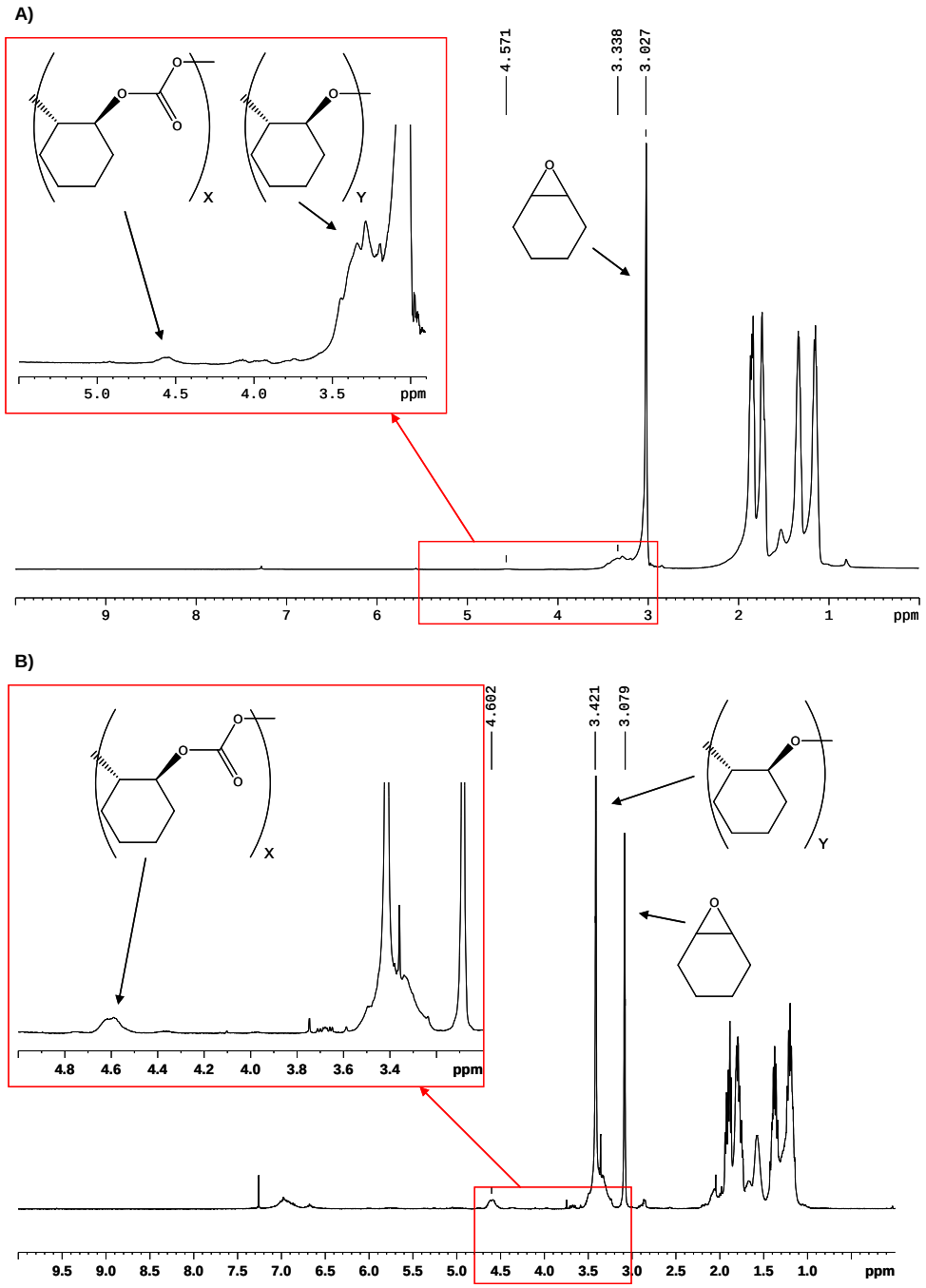

Figure S6 ^{1}H NMR spectra (in $CDCl_3$) of the polymers produced after 24 h at 50 °C for the copolymerization of CO_2/CHO by [(^{Ph,Ph}BOX)Zn(μ-η^2-OAc)]$_2$ **3c'**and **2c**. A) ^{1}H NMR spectrum of the aliquot taken from the crude material. B) ^{1}H NMR spectrum after quenching with MeOH and dried *in vacuo*.