

## Supporting Information

# Probing Secondary Coordination Sphere Influence on the Oxygenation of Zinc Alkyls: A Unique Formation of a Zinc Peroxide Species

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## I. Synthetic procedure and characterization

**Synthesis of 1:** A solution of o-phenylphenol (1 g, 5.87 mmol) in toluene (10 mL) was cooled to 0°C and afterwards a 1 M solution of ZnEt<sub>2</sub> (5.87 mL, 5.87 mmol) in hexane was added dropwise. Following solvent removal afforded crystalline material which <sup>1</sup>H NMR spectroscopy revealed to incorporate aryloxide and ethylzinc moieties in a 1:1 ratio, EtZn(OAr) (**1**). Attempts to isolate single crystals of **1** from the toluene solution were unsuccessful. <sup>1</sup>H NMR (500 MHz, C<sub>7</sub>D<sub>8</sub>, concentration 10% w/w): δ 7.60 - 6.65 (m, ArH, OAr), 2.09 (qn, toluene), 1.02 (t, ZnCH<sub>2</sub>CH<sub>3</sub>), 0.02 (q, *J* = 8.0 Hz, ZnCH<sub>2</sub>CH<sub>3</sub>).

**Synthesis of 2:** A solution of o-phenylphenol (2 g, 11.75 mmol) in toluene (20 mL) was cooled to 0°C and afterwards a 1 M solution of ZnEt<sub>2</sub> (8.82 mL, 8.81 mmol) in hexane was added dropwise. The solution was warmed to room temperature, and the volume was reduced and followed by addition of hexane. Compound **2** was obtained as colourless crystals after crystallization from hexane/toluene at 25°C; isolated yield ca. 2.35g (86 %). Elemental analysis (%) calcd for C<sub>52</sub>H<sub>46</sub>O<sub>4</sub>Zn<sub>3</sub>: C 67.07, H 4.98; found: C 67.90, H 5.12. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.60 - 6.71 (m, ArH, OAr), 0.96 (t, *J* = 8.0 Hz, ZnCH<sub>2</sub>CH<sub>3</sub>), 0.70 (t, *J* = 8.0 Hz, ZnCH<sub>2</sub>CH<sub>3</sub>), -0.18 (t, *J* = 8.0 Hz, ZnCH<sub>2</sub>CH<sub>3</sub>), -0.67 (q, *J* = 8.0 Hz, ZnCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>CNMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ 157.1, 157, 156.4, 139.8, 139.1, 131.6, 131.3, 130.1, 129.8, 129.6, 129.4, 129.1, 127.5, 121, 120.8, 120.6 (ArH, OAr), 12.1 (ZnCH<sub>2</sub>CH<sub>3</sub>), 12 (ZnCH<sub>2</sub>CH<sub>3</sub>), -1.2 (ZnCH<sub>2</sub>CH<sub>3</sub>), -1.7 (ZnCH<sub>2</sub>CH<sub>3</sub>).

**Synthesis of 3:** The solution containing **2** (1 g, 1.08 mmol) and two equivalents of o-phenylphenol in toluene (20 mL) was exposed to an excess of dry oxygen for 2 minutes at 0°C and stirred for 12h, during which the colorless solution slowly turned to a dark blue solution. Then the excess O<sub>2</sub> was removed and the system was purged with nitrogen using a vacuum-nitrogen line. The volume was reduced to 5 mL, and the gray precipitate was filtered off,

washed with hexane (10 x 5 mL) and dried under vacuum. Compound **3** was obtained as colorless crystals after crystallization from dichloromethane at 25°C; isolated yield ca. 0.69 g (72 % based on zinc). Elemental analysis (%) calcd for  $C_{96}H_{78}O_{16}Zn_8 \cdot 2(C_{12}H_{10}O)$ : C 61.30, H 4.20; found: C 62.92, H 4.53.  $^1H$  NMR (500 MHz,  $C_6D_6$ ):  $\delta$  7.30 - 6.82 (m, ArH, OAr), 4.73 (s, OH).  $^{13}C$  NMR (125 MHz,  $C_6D_6$ ):  $\delta$  153.2 - 153.1, 137.9, 130.6, 129.4, 129.3, 129.2, 121, 116.3 (ArH, OAr).

We note that in the oxygenation reactions of other ethylzinc derivatives being under investigation in our laboratory we observed no hydroxides formation although we used the same batches of solvents. This observation does not only conclusively rules out hydrolysis as the most likely event leading to hydroxide species but also substantiates the assumed role of the suitably positioned aromatic functionalities close to the metal center on the course of oxygenation reactions. Nevertheless, as it is stated in the main text, the mechanism by which the aggregate **3** is formed is not known on this stage of our investigations.

## II. X-ray structure determination

Crystal data for **2**, C<sub>52</sub>H<sub>46</sub>O<sub>4</sub>Zn<sub>3</sub>:  $M_r = 931$ , crystal dimensions  $0.1 \times 0.05 \times 0.04 \text{ mm}^3$ , triclinic, space group  $P\bar{1}$  (no. 2),  $a = 10.018(2) \text{ \AA}$ ,  $b = 14.641(4) \text{ \AA}$ ,  $c = 15.057(5) \text{ \AA}$ ,  $\alpha = 78.61(2)^\circ$ ,  $\beta = 77.69(2)^\circ$ ,  $\gamma = 83.52(3)^\circ$ ,  $V = 2109.4(10) \text{ \AA}^3$ ,  $Z = 2$ ,  $F_{000} = 960$ ,  $D_c = 1.466 \text{ Mg m}^{-3}$ ,  $T = 100(2) \text{ K}$ ,  $\mu(\text{Mo-K}\alpha) = 1.74 \text{ mm}^{-1}$ , KUMA KM4 CCD  $\kappa$ -geometry diffractometer,  $\theta_{max} = 30.0^\circ$ , 10950 unique reflections. The structure was solved by direct methods using SHELXS97<sup>[1]</sup> and refined by the full-matrix least-squares method on all  $F^2$  data using SHELXL97<sup>[2]</sup>. All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were positioned geometrically and treated as riding atoms, with C–H = 0.95 – 0.99  $\text{ \AA}$ , and with  $U_{iso}(\text{H}) = 1.2U_{eq}(\text{C}_{aromatic}, \text{C}_{methylene})$  or  $1.5U_{eq}(\text{C}_{methyl})$ . Refinement converged at  $R1 = 0.0608$ ,  $wR2 = 0.0727$  for all data and 552 parameters ( $R1 = 0.0345$ ,  $wR2 = 0.0687$  for 7540 reflections with  $I_o > 2\sigma(I_o)$ ). The goodness-of-fit on  $F^2$  was equal 0.871. A weighting scheme  $w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$  was used in the final stage of refinement. The residual electron density =  $+0.66/-0.36 \text{ e\AA}^{-3}$ . One of the ethyl groups is disordered in two positions, with site-occupancy factors, from refinement of 0.826(11) and 0.174(11). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-955216. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **3**,  $C_{96}H_{78}O_{16}Zn_8 \cdot 2(C_{12}H_{10}O) \cdot 2.42(CH_2Cl_2)$ :  $M_r = 2556.32$ , crystal dimensions  $0.54 \times 0.36 \times 0.15$  mm, triclinic, space group  $P\bar{1}$  (no. 2),  $a = 17.903(3)$  Å,  $b = 22.986(4)$  Å,  $c = 39.788(5)$  Å,  $\alpha = 91.26(2)^\circ$ ,  $\beta = 91.15(3)^\circ$ ,  $\gamma = 94.10(3)^\circ$ ,  $V = 16324(4)$  Å<sup>3</sup>,  $Z = 6$ ,  $F_{000} = 7821.5$ ,  $D_c = 1.560$  Mg m<sup>-3</sup>,  $T = 100(2)$  K,  $\mu(Mo-K\alpha) = 1.92$  mm<sup>-1</sup>, KUMA KM4 CCD  $\kappa$ -geometry diffractometer,  $\theta_{max} = 30.0^\circ$ , 91751 unique reflections. The structure was solved by direct methods using SHELXS97<sup>[Błąd! Nie zdefiniowano zakładek.]</sup> and refined by the full-matrix least-squares method on all  $F^2$  data using SHELXL97<sup>[2]</sup>. All non-hydrogen atoms, excluding seven dichloromethane molecules were refined with anisotropic displacement parameters. The hydrogen atoms of bridging hydroxyl groups were found in difference Fourier maps and refined using DFIX instructions, with  $U_{iso}(H) = 1.5U_{eq}(O)$ . The remaining H atoms were positioned geometrically and treated as riding atoms, with O–H = 0.84 Å, C–H = 0.95 – 0.99 Å, and with  $U_{iso}(H) = 1.5U_{eq}(O)$  or  $1.2U_{eq}(C)$ . Refinement converged at  $R1 = 0.1402$ ,  $wR2 = 0.1858$  for all data and 4255 parameters ( $R1 = 0.0635$ ,  $wR2 = 0.1592$  for 45332 reflections with  $I_o > 2\sigma(I_o)$ ). The goodness-of-fit on  $F^2$  was equal 1.031. A weighting scheme  $w = 1/[\sigma^2(F_o^2) + (0.0886P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$  was used in the final stage of refinement. The residual electron density = +2.65/–1.49 eÅ<sup>-3</sup>. The refinement of the disordered orthophenylphenolate were made anisotropically using PART restrictions with occupation factors in the ratio 0.64(3)/0.36(3), 0.670(4)/0.330(4), 0.580(4)/0.420(4) and 0.563(5)/0.437(5), respectively. Moreover, the  $U^{ij}$  components of disordered ligands were restrained using EADP instructions. The site occupation factors of the partially occupied dichloromethane molecules were equal to 0.877(5), 0.618(6), 0.211(5), 0.483(5), 0.418(7), 0.462(7), 0.277(7), 0.330(4) and 0.580(4). One of the solvent molecules is disordered in three positions, with site-occupancy factors, from refinement of 0.265(7)/0.368(8)/0.367(6), their sum can be restrained to unity by the use of a SUMP restraint. Additionally, the SAME commands were used to improve the geometry of six dichloromethane molecules. For more

details related to the refinement and a list of restraints used see `_refine_special_details` and `_iucr_refine_instructions_details` in CIF. Crystallographic data (including structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-955217. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

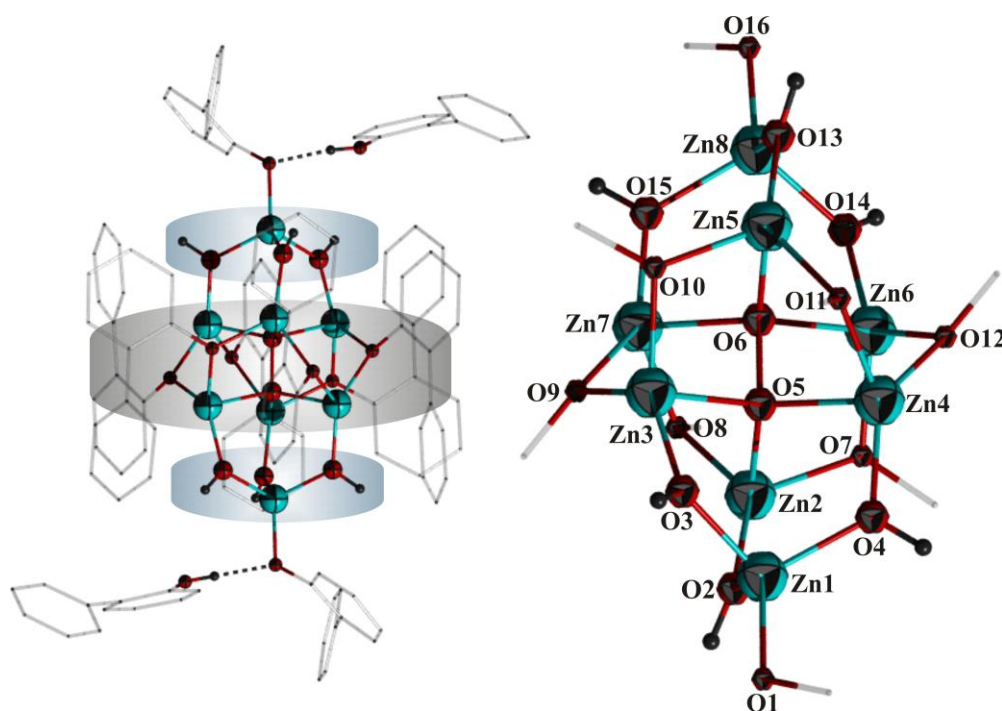


Figure 1S. Molecular structure of  $3 \cdot 2\text{ArOH}$  with thermal ellipsoids set at 50% probability; H-atoms and minor disorder omitted. Selected bond lengths (Å): Zn1–O1 1.901(3), Zn1–O2 1.946(3), Zn1–O3 1.948(3), Zn1–O4 1.932(3), Zn2–O2 1.895(3), Zn2–O5 2.130(3), Zn2–O7 1.962(3), Zn2–O8 1.973(3), Zn3–O3 1.875(3), Zn3–O5 2.146(3), Zn3–O9 1.976(3), Zn3–O10 1.974(3), Zn4–O4 1.885(4), Zn4–O5 2.126(3), Zn4–O11 1.973(3), Zn4–O12 1.959(3), Zn5–O6 2.109(3), Zn5–O10 1.970(3), Zn5–O11 1.975(3), Zn5–O13 1.879(3), Zn6–O6 2.141(3), Zn6–O7 1.977(3), Zn6–O12 1.968(3), Zn6–O14 1.864(3), Zn7–O6 2.101(3), Zn7–O8 1.981(3), Zn7–O9 1.963(3), Zn7–O15 1.880(3), Zn8–O13 1.942(3), Zn8–O14 1.958(3), Zn8–O15 1.951(3), Zn8–O16 1.899(3), O5–O6 1.527(4).

### III. Diffusivity measurement

Application of Diffusion Ordered Spectroscopy (DOSY), which has happened to become a very routine NMR technique lately, provided us with a reliable evidence of approximate size of the species existing in the solution. As already discussed in antecedent works<sup>[3,4]</sup> molecular weight can be straightforwardly obtained by combining Stokes-Einstein equation ( $D = (kT) / (6\pi\eta r_H)$ ) and the relationship between molecular weight  $M$  and molar radius, which reads  $M = (4\pi r_M^3 \rho N_A) / 3$ , where  $r_H$  and  $r_M$  are hydrodynamic and molar radii respectively,  $\eta$  is viscosity and  $\rho$  is density of the liquid. It has also been shown that these quantities are much alike for small molecules, which is the case in our system. DOSY measurement was performed in dry and degassed [D8]toluene or [D8]THF as we exploited the fact that the physical properties of the diluted solution, namely density and viscosity, deviate only slightly from properties of the pure solvent.<sup>[3]</sup> Pulsed field gradient double stimulated echo convection-compensated (PFGSTE) sequence with total of 15 diffusion encoding gradients (ranging from 3 to 45 G/cm, sine shaped, equal steps in gradient squared) was used and the total width of the gradient pulse was optimised to achieve attenuation of about 90% of the initial intensity of the signals. Overall, the key acquisition parameters were as follows: total length of gradient encoding pulses gradient - 2ms, diffusion delay - 50ms, gradient recovery delay - 1ms, relaxation delay - 2s. Steady-state scans in number of 16 were performed prior to acquisition of the data. The sample was allowed to equilibrate in the set temperature (298 K or 273 K), controlled by VT module. Spinner was turned off. Raw data was processed with powerful DOSY Toolbox which is extensively described in its author's paper<sup>[5]</sup>

Since **1** was generated *in situ* only, product of the reaction could not be isolated (as it would be necessary for a cryometry). Thus, DOSY measurement was the only way to identify its aggregation state. However, it proved unsuccessful in the room temperature due to the dynamics of the system causing the signals to broaden severely when using the PFGSTE

sequence. As a consequence, the measurement was performed in 273 K, a temperature at which the dynamics is considerably slowed down. Since molecular mass of **1** is 279,64 g/mol, its aggregation state by DOSY is 2,5 which indicates that it most likely exists as a dimer, trimer or a mixture thereof, depending on a temperature, hence the dynamics observed on the spectra.

Table 1S. Diffusion coefficient of **1**, its estimated hydrodynamic radius and molecular weight.

	D · 10 <sup>10</sup> m <sup>2</sup> /s	r / Å	MW / Da
<b>1</b>	3.76	6.88	711

Trinuclear nature of **2** was verified using DOSY which simultaneously exposed an issue potentially arising with the relatively widely used simplified approach. We applied a typical procedure involving the Stokes-Einstein equation, assuming sphericity of the molecule (which is, however, often not the case) and then calculated the corresponding molecular weights using another well-established method mentioned previously (Table 1). Clearly, there is a major discrepancy, regarding the molecular mass of **2** being 931 g/mol. This deflection of about 23 % from the values calculated using diffusion coefficients corresponds to only 8% deviation in molecular radii which is, apparently, due to rather bulky biphenyl ligands. The relative position of the aromatic systems renders the existence of two isomeric forms possible with a very high interchange energy (as discussed in the paper). Reversely, calculating the radius for the relevant 931 Da gives the result of 7,48 Å, exactly on the average of the two under- and overestimated values.

Table 2S. Diffusion coefficient of **2a** and **2b** species, their estimated hydrodynamic radii and molecular weights.

	D · 10 <sup>10</sup> m <sup>2</sup> /s	r / Å	MW / Da
isomer <b>2a</b>	5.80	6.90	712
isomer <b>2b</b>	4.95	8.15	1146



#### IV. $^1\text{H}$ NMR spectra for the oxygenation reactions

We performed the oxygenation of  $\text{EtZn(OAr)}$  (**1**) in  $[\text{D}8]\text{toluene}$  monitored by  $^1\text{H}$  NMR using two slightly different samples. In the case shown in the Figure 2S a pure **1** was oxygenated while in the Figure 3S we present the spectra for the oxygenation of **1** with traces of trinuclear product **2**. According to the latter we were able to conclude that the reaction of **1** with molecular oxygen is faster than the similar reaction of **2**. It is expressed by the fact that the signals corresponding to the alkyl groups of **1** disappear significantly faster than those originating from **2**.

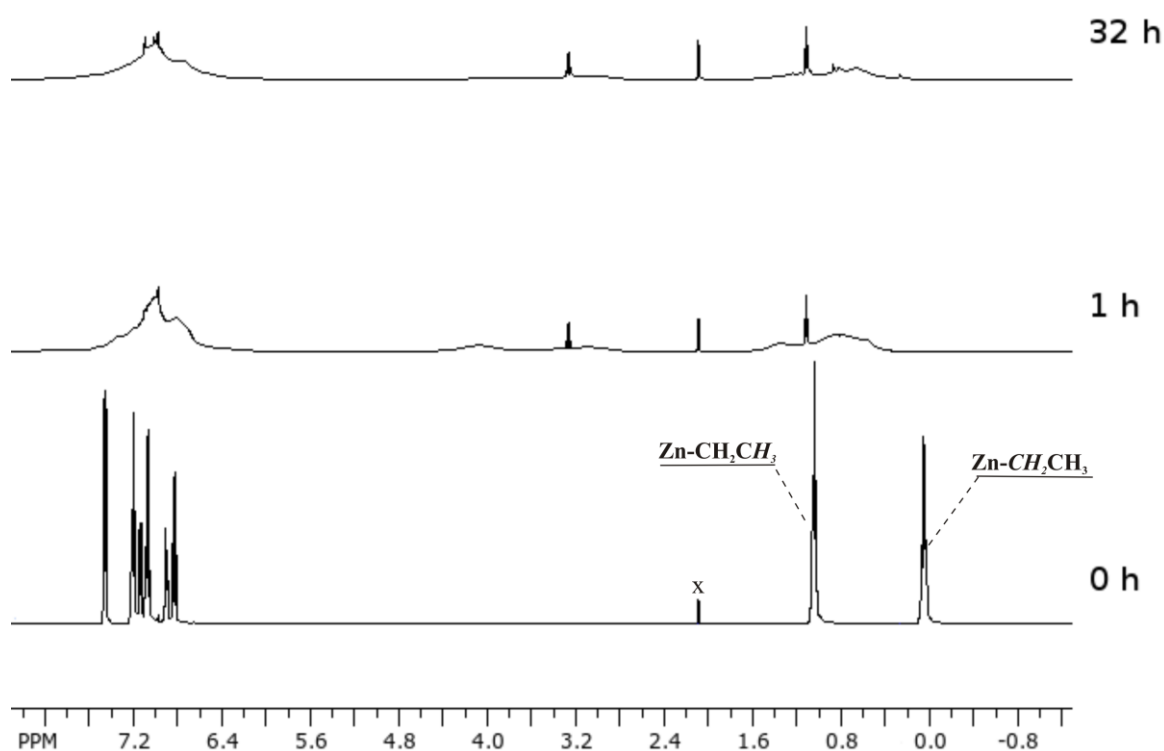


Figure 2S.  $^1\text{H}$  NMR spectra for the oxygenation of  $\text{EtZn(OAr)}$  (**1**) at  $25^\circ\text{C}$  ( $[\text{D}8]\text{toluene}$ ): before introduction of  $\text{O}_2$  (initial); during the reaction with  $\text{O}_2$ : after 1 and 32 hours. The “x” symbol indicates residual signal of  $[\text{D}8]\text{toluene}$  (2.09 ppm, as reference).

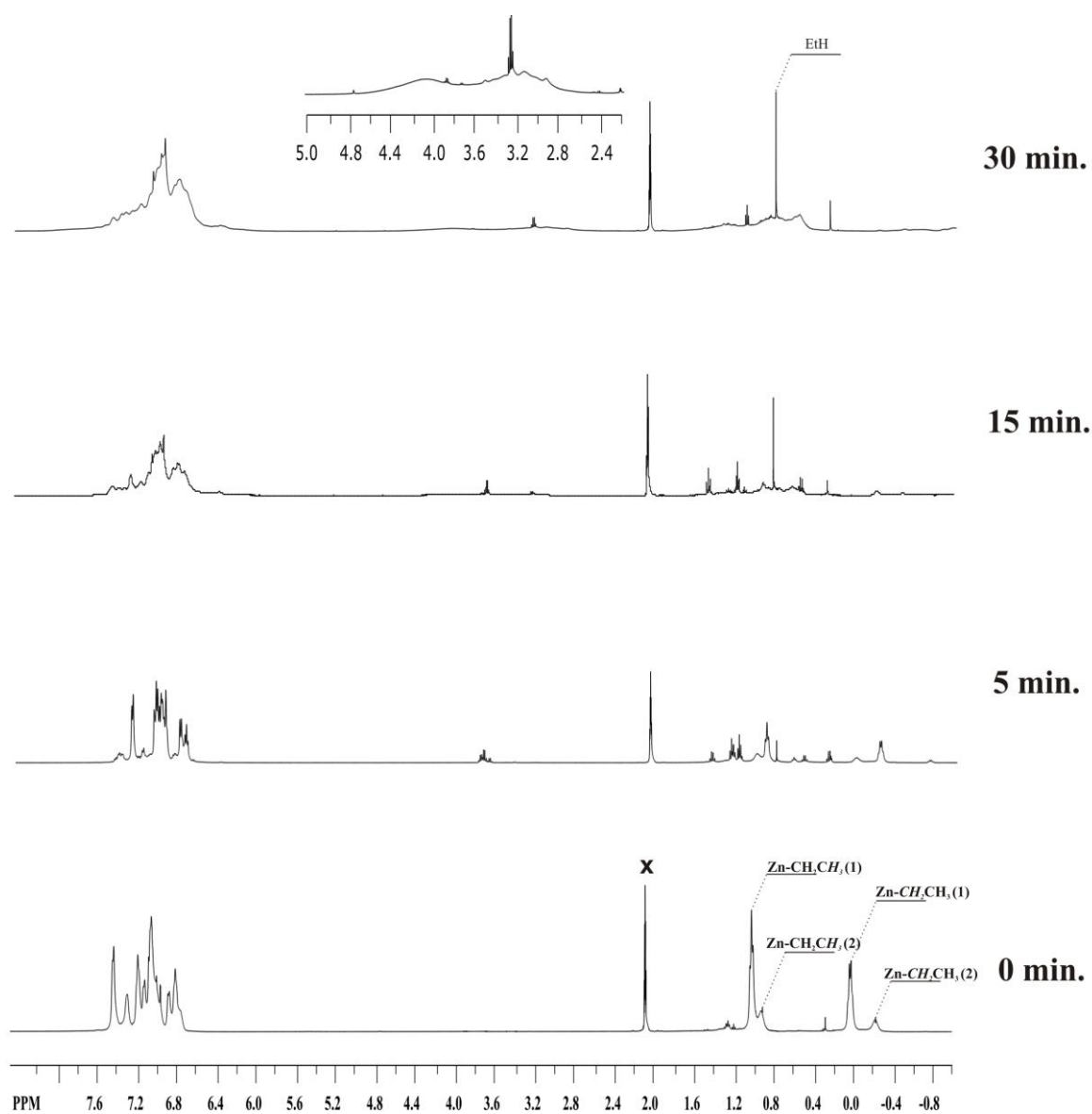


Figure 3S.  $^1\text{H}$  NMR spectra for the oxygenation of  $\text{EtZn(OAr)}$  (**1**) with traces of **2** at  $25^\circ\text{C}$  ( $[\text{D}8]\text{toluene}$ ): before introduction of  $\text{O}_2$  (initial); during the reaction with  $\text{O}_2$ : after 5, 15 and 30 minutes. The “x” symbol indicates residual signal of  $[\text{D}8]\text{toluene}$  (2.09 ppm, as reference).

## V. Workup procedure on the post-oxygenation reaction mixtures

A standard workup procedure for the post-reaction mixtures derived from the oxygenation of **1** and **2** was performed. After the oxygenation reaction the solvent was removed by vacuum transfer and the residue was treated with 10% hydrochloric acid (10 mL). The organic products were extracted with diethyl ether (3 × 20 mL) and the organic fraction was dried over anhydrous magnesium sulphate. The products were analysed by GCMS and ESI-MS<sup>-</sup> technique without further purification.

**Table 3S.** GCMS and ESI-MS analysis of organic products formed in the oxygenation of **1** and **2**.

COMPOUND	M-H m/z (GCMS)	M <sup>-</sup> m/z (ESI-MS <sup>-</sup> )
ethanol	46.1	—
diethyl toluene	148.2	—
biphenyl	154.1	—
ArOH	170.1	169.1
bibenzyl	182.2	—
<i>ArOH derivatives of variously substituted by R, R' and R''</i>		
R = OH	186.1	185.1
R = Et	198.2	197.1
R = Et, R' = OH or R = OEt	—	213.1
R = PhCH <sub>2</sub>	260.2	
bis(ArOH)	—	337.1
<i>bis(ArOH) derivatives of variously substituted by R, R' and R''</i>		
R = OH	—	353.2
R = Et	366.2	365.2
2 x R = OH	—	369.1
R = Et, R' = OH or R = OEt	—	381.2
R = Et, 2 x R' = OH or R = OEt, R' = OH	—	397.2
2 x R = Et, R' = OH or R = Et, R' = OEt	—	409.2
2 x R = Et, 2 x R' = OH or R = Et, R' = OEt, R'' = OH or 2 x R = OEt	—	425.2
2 x R = Et, 3 x R = OH or R = Et, R' = OEt, 2 x R'' = OH; or 2 x R = OEt, R' = OH	—	441.2
3 x R = Et, 2 x R' = OH or 2 x R = Et, R' = OEt, R'' = OH; or R = Et, 2 x R' = OEt	—	453.2
3 x R = Et, 3 x R' = OH or 2 x R = Et, R' = OEt, 2 x R'' = OH; or R = Et, 2 x R' = OEt, R'' = OH or 3 x R = OEt	—	469.2

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