

Supporting Information for

Cp* as Removable Protecting Group: Low Valent Zn(I) Compounds by Reductive Elimination, Protolytic and Oxidative Cleavage of Zn-Cp*

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Materials and Methods

Spectroscopy NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer (^1H , 250.1 MHz; ^{13}C , 62.9 MHz) in CD_2Cl_2 at 298 K unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the residual solvent peak as internal standards. Chemical shifts are reported in parts per million, downfield shifted from TMS, and are consecutively reported as position (δ_{H} or δ_{C}), relative integral, multiplicity (s = singlet, d = doublet, sept = septet, m = multiplet), coupling constant (J in Hz) and assignment. IR spectra were recorded on a Bruker Alpha-P Fourier transform spectrometer. FT-IR spectra were measured in an ATR setup with a Bruker Alpha FTIR spectrometer under an inert gas atmosphere in a glove-box.

Spectrometry Mass spectrometry was measured with a Waters LCT; Ionisation method: liquid injection field desorption ionization (LIFDI; special ionization cell obtained from Linden CMS GmbH, Leeste, Germany; <http://www.linden-cms.de>), solvent: toluene.

X-ray crystallography The X-ray diffraction intensities of compound **1** were collected on an Oxford XcaliburTM2 diffractometer with a Sapphire2 CCD, whereas the reflections of compound **2** were measured on an Oxford SuperNova diffractometer with an Atlas CCD detector. The crystals were coated with a perfluoropolyether, picked up with a glass fiber, and immediately mounted in the nitrogen cold gas stream of the diffractometer. The crystal structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97. CCDC 928866 (**1**) and CCDC 928867 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[\text{Zn}_4\text{Cp}^*_3(\text{Et}_2\text{O})_3][\text{BAr}_4^{\text{F}}]$ (**1**)

To a mixture of 100 mg $[\text{Zn}_2\text{Cp}^*_2]$ (0.249 mmol) and 126 mg $[\text{H}(\text{Et}_2\text{O})_2][\text{BAr}_4^{\text{F}}]$ (0.125 mmol) 3 ml F-Benzene were added at $-25\text{ }^\circ\text{C}$ whereas a colour change from orange to yellow and back to orange could be observed. The solution was stirred for 30 min at $-25\text{ }^\circ\text{C}$. Afterwards, the product was precipitated by the addition of 16 ml hexane at $-25\text{ }^\circ\text{C}$. The colourless powder with a yield of 70 % was isolated, washed with 4 ml of hexane three times and dried in vacuum. Colourless crystals, suitable for single crystal X-ray diffraction could be obtained by layering the F-Benzene solution at $-25\text{ }^\circ\text{C}$ with 9 ml hexane and storage at $-30\text{ }^\circ\text{C}$ after six days.

Synthesis of $[\text{Cp}^*\text{Zn}_2(\text{Et}_2\text{O})_3][\text{BAr}_4^{\text{F}}]$ (**2**)

100 mg $[\text{Zn}_2\text{Cp}^*_2]$ (0.249 mmol) and 261 mg $[\text{FeCp}_2][\text{BAr}_4^{\text{F}}]$ (0.249 mmol) were dissolved in 5 ml Et_2O at room temperature and stirred for 15 min, whereupon the initial blue solution immediately turned orange. The solvent was removed in vacuo and the residue was washed with *n*-hexane (4 x 2 ml) to give 240 mg (71 %) of the product as a gray powder. Recrystallization by slow diffusion of *n*-hexane into a F-benzene solution of $[\text{Cp}^*\text{Zn}_2(\text{Et}_2\text{O})_3][\text{BAr}_4^{\text{F}}]$ at $-30\text{ }^\circ\text{C}$ gave suitable colorless crystals for single crystal X-ray diffraction.

Synthesis of $[\text{Zn}_2\text{Cp}^*_2]$

A mixture of ZnCp^*_2 (1.507 g, 0.00449 mol) and ZnH_2 (0.119 g, 0.0018 mol) was taken in 10 ml of THF and stirred at room temperature for 4 h. It was filtered and the remaining precipitate was extracted with 20 ml of THF. The combined filtrates were vacuum dried and the white residue was suspended in 20 ml of *n*-hexane. The suspension was stored at $-30\text{ }^\circ\text{C}$ overnight and filtered to afford analytically pure white crystalline product of $[\text{Zn}_2\text{Cp}^*_2]$ in 64 % yield (772 mg).

Table S1. Crystallographic data and refinement details for **1** and **2**.

	1 · 2(C ₆ H ₅ F)	2
Empirical formula	C ₈₂ H ₈₇ BF ₂₆ Zn ₄	C ₅₄ H ₅₇ BF ₂₄ O ₃ Zn ₂
<i>M_r</i>	1870.81	1351.55
<i>T</i> (K)	110(2)	100(2)
λ (Å)	0.71073	1.54178
Crystal size (mm ³)	0.34 × 0.25 × 0.22	0.09 × 0.11 × 0.06
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 21/ <i>c</i>	<i>Pbca</i>
<i>a</i> (Å)	14.0958(2)	18.6723(4)
<i>b</i> (Å)	23.3198(3)	24.9419(7)
<i>c</i> (Å)	26.1788(4)	25.4726(5)

α (°)	90.00	90.00
β (°)	92.926(2)	90.00
γ (°)	90.00	90.00
V (Å ³)	8594.0(2)	11863.2(5)
Z	4	8
$\rho_{\text{calc.}}$ (g cm ⁻³)	1.446	1.513
μ (mm ⁻¹)	1.203	2.049
$F(000)$	3816	5488
$2\theta_{\text{max}}$ (°)	50	148.24
Reflexions collected	15097	32253
Reflexions unique	10706	11818
R_{int}	0.1132	0.0311
Reflexions observed [$I > 2\sigma(I)$]	10706	8393
Parameters / restraints	420 / 0	262 / 915
Goodness-of-fit on F^2	1.062	1.025
R_1 [$I > 2\sigma(I)$]	0.0763	0.0631
wR_2 (all data)	0.1893	0.2000
Residuals (e Å ⁻³)	0.773 / -0.559	0.867 / -0.462

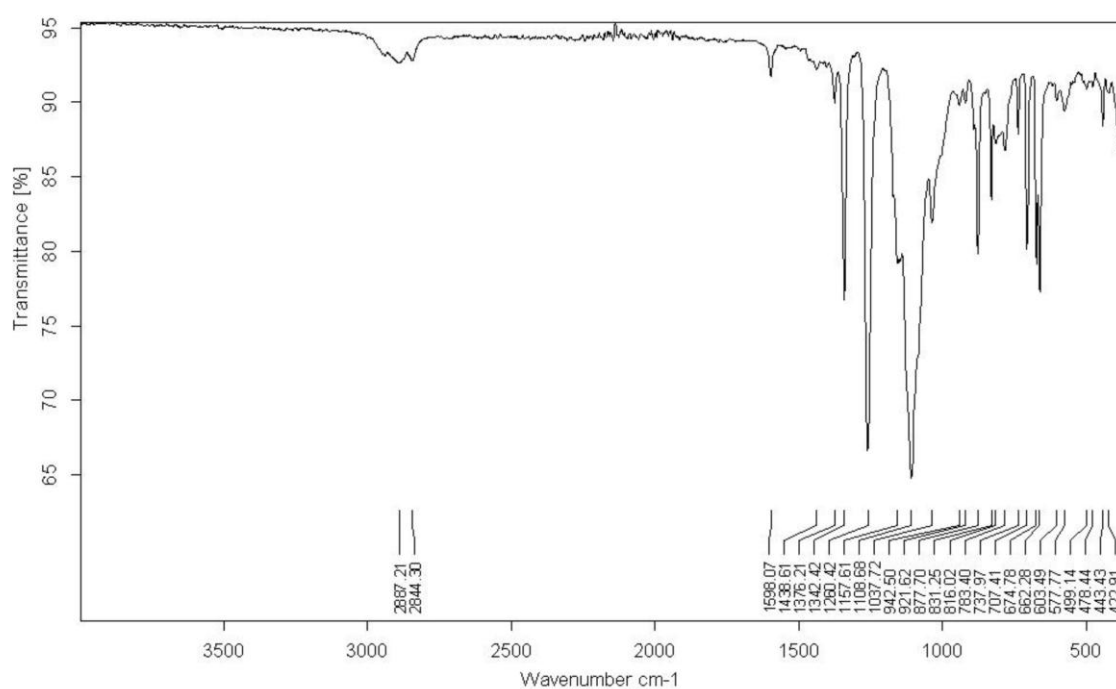


Figure S1. IR Spectrum of **1**.

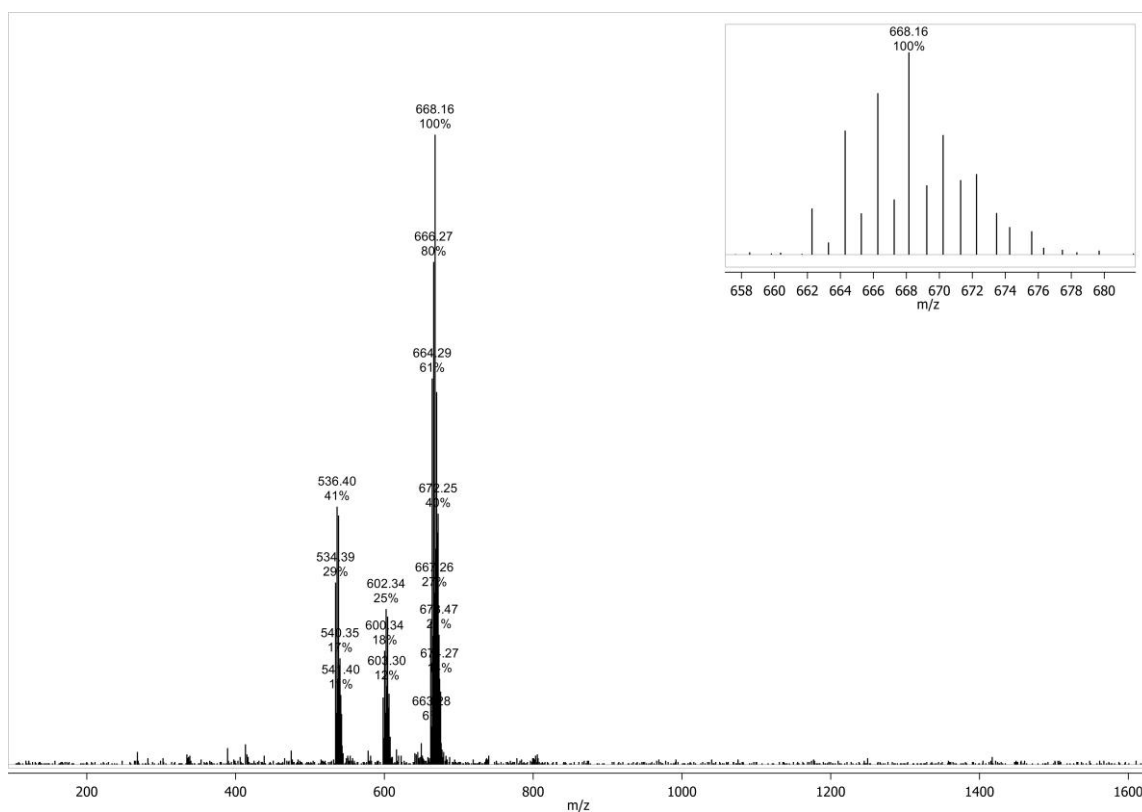


Figure S2. LIFDI-MS Spectrum of **1** including a depiction of the isotopic pattern of the [M-2(Et₂O)]⁺ peak.

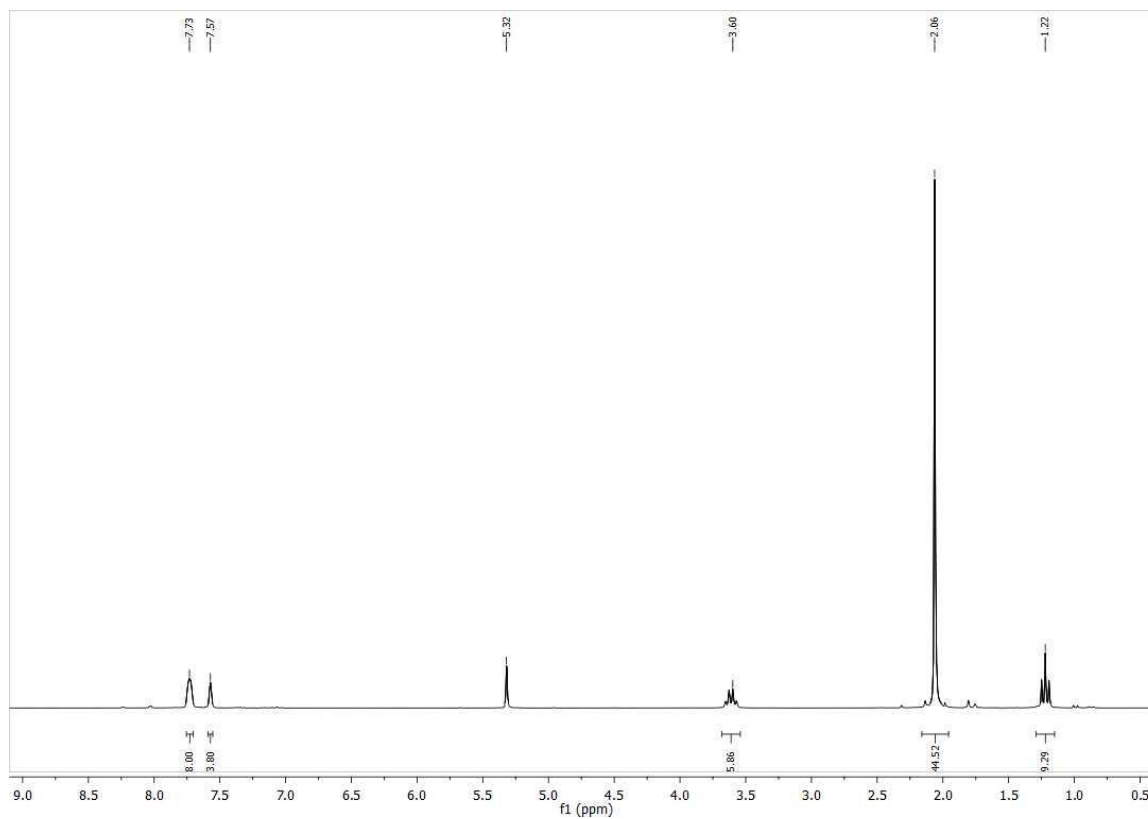


Figure S3. ^1H -NMR spectrum of **1**, recorded at room temperature in CD_2Cl_2 .

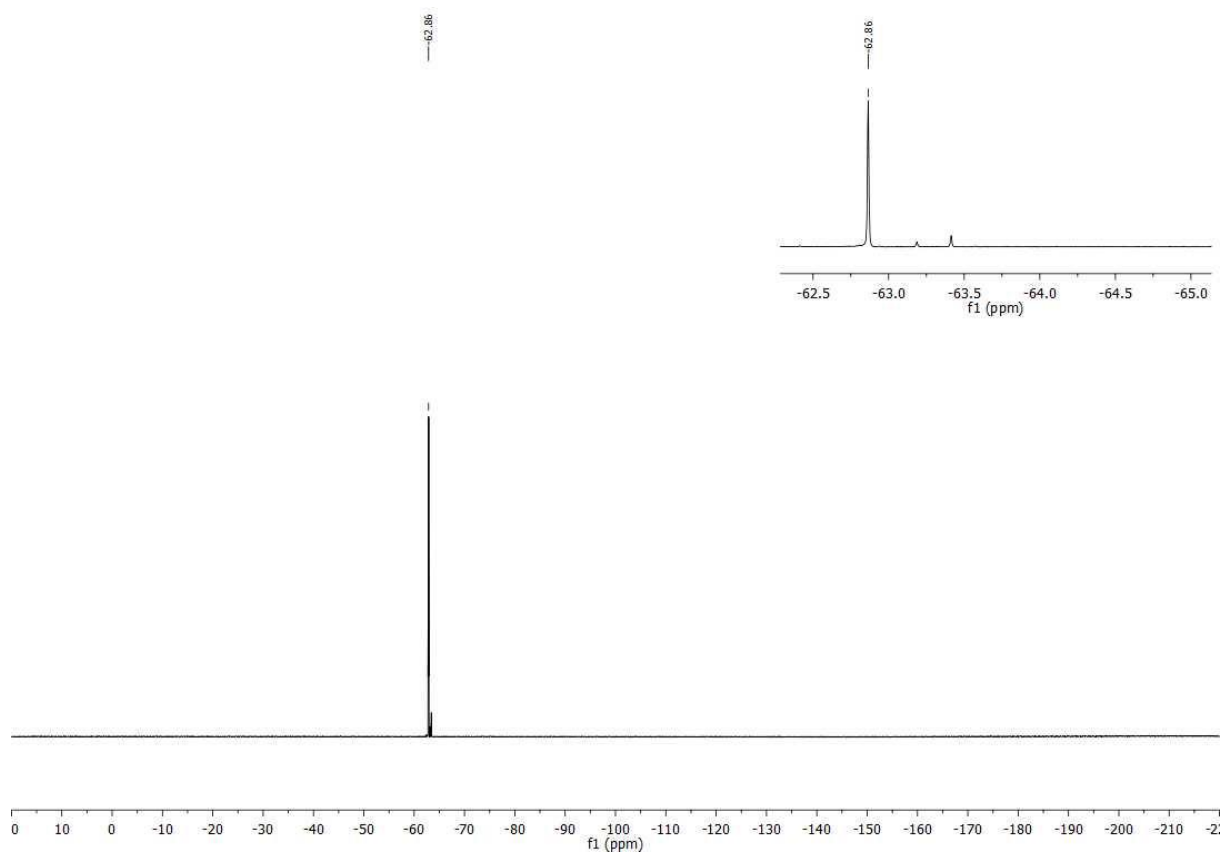


Figure S4. ^{19}F -NMR spectrum of **1** recorded at room temperature in CD_2Cl_2 .

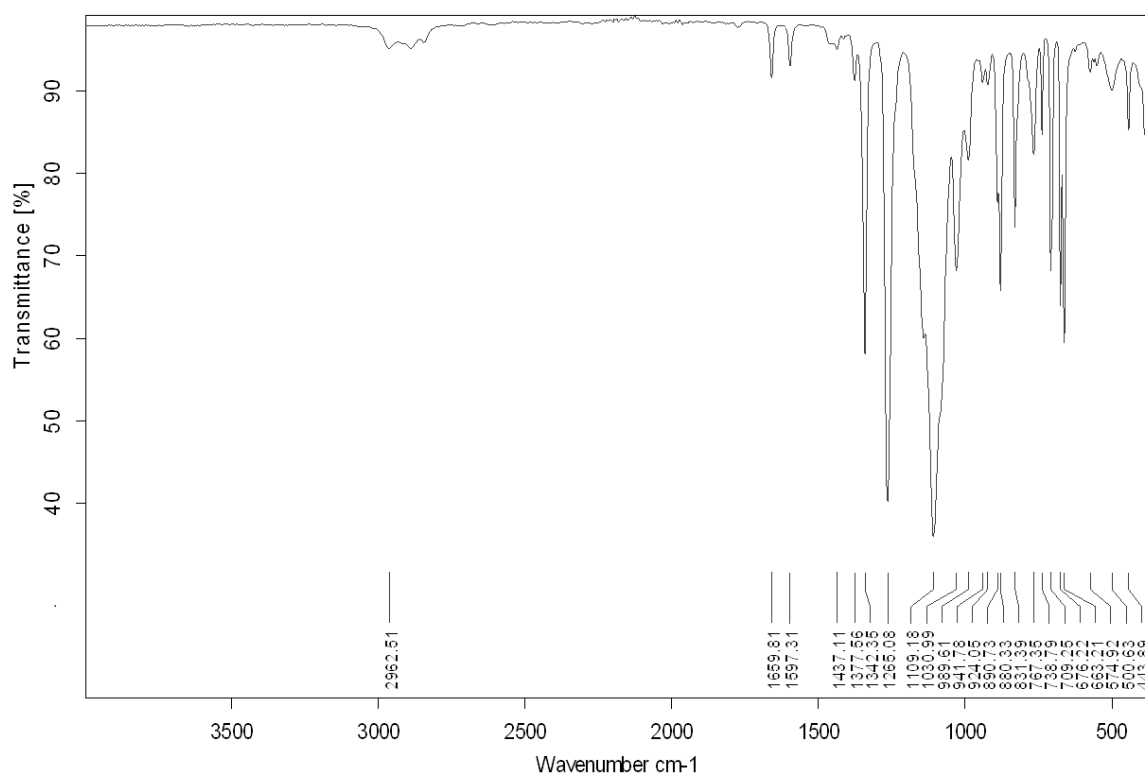


Figure S5. IR Spectrum of **2**.

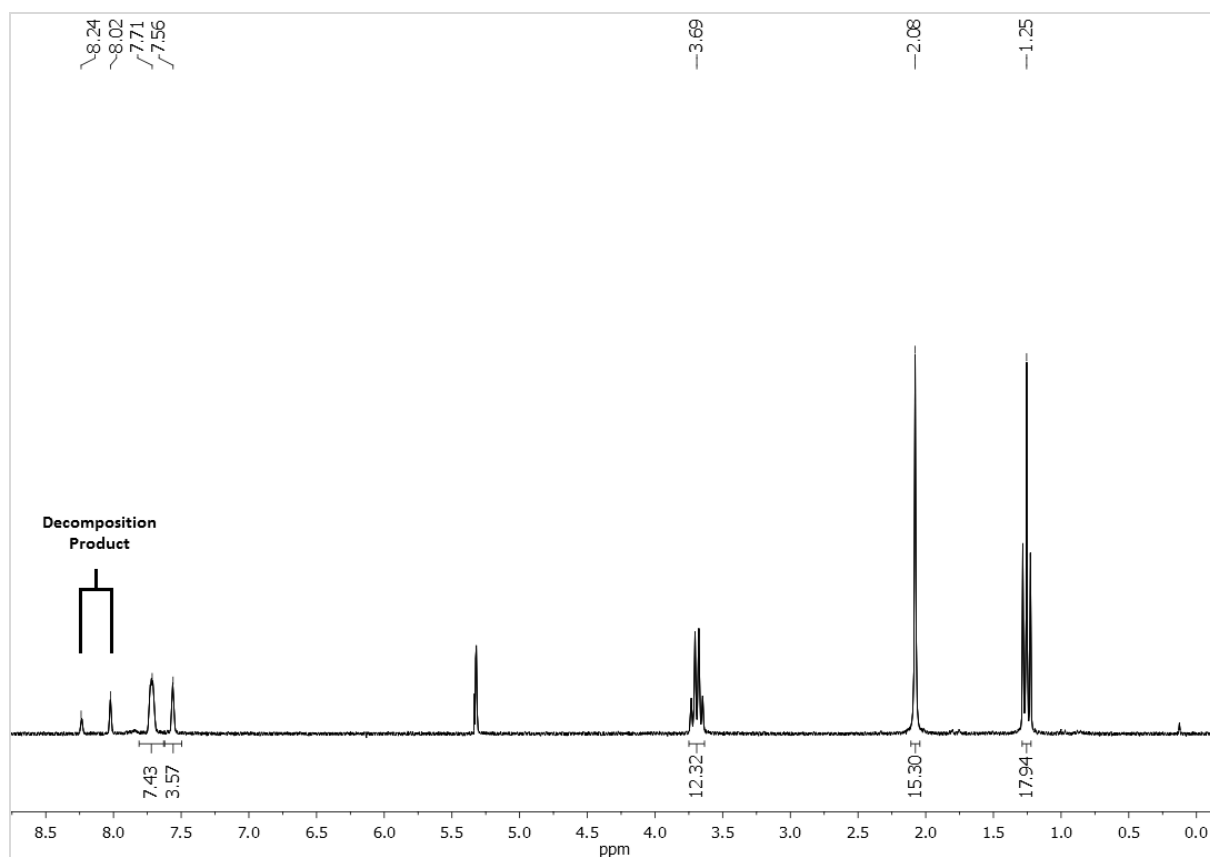


Figure S6. ¹H NMR spectrum of **2** in CD₂Cl₂ at room temperature.

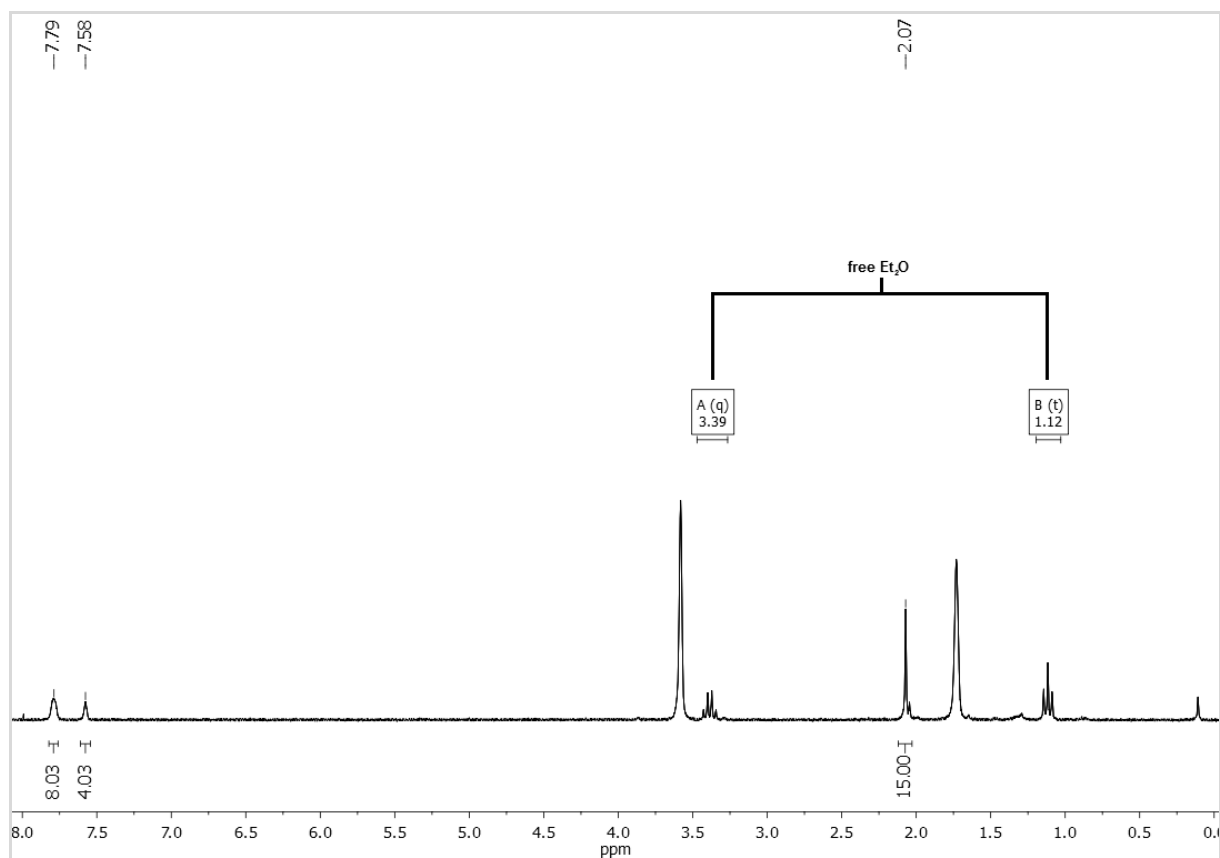


Figure S7. ¹H NMR spectrum of **2** in thf-*d*₈ at room temperature.

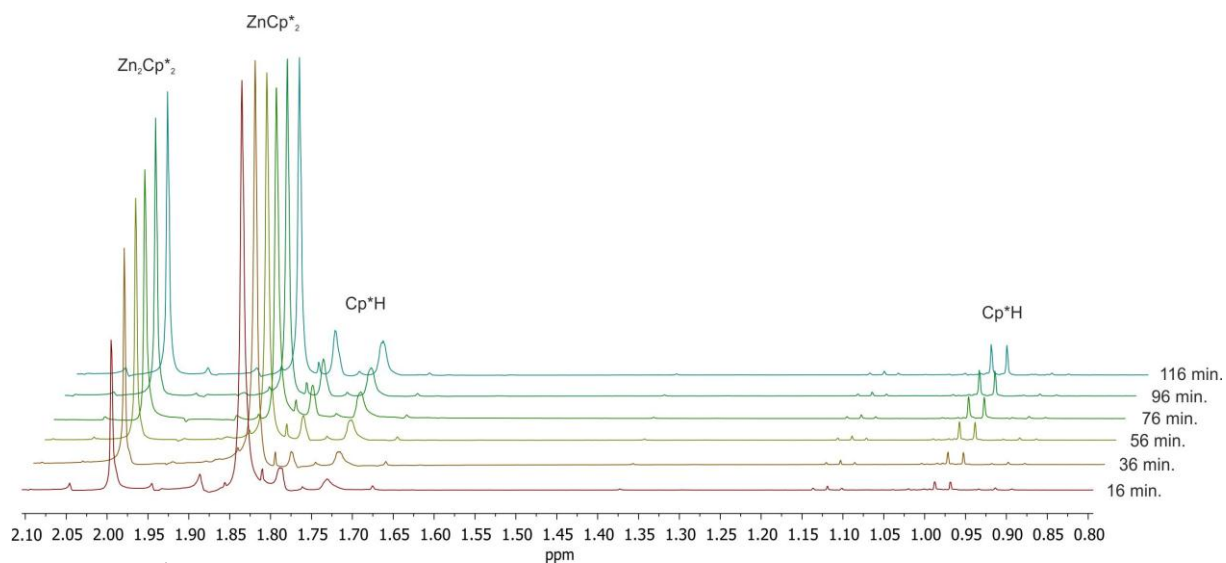


Figure S8. ¹H NMR spectra from the NMR reaction, showing the gradual formation of [Zn₂Cp*₂] from ZnH₂ and [ZnCp*₂], recorded in thf-*d*₈ at room temperature.

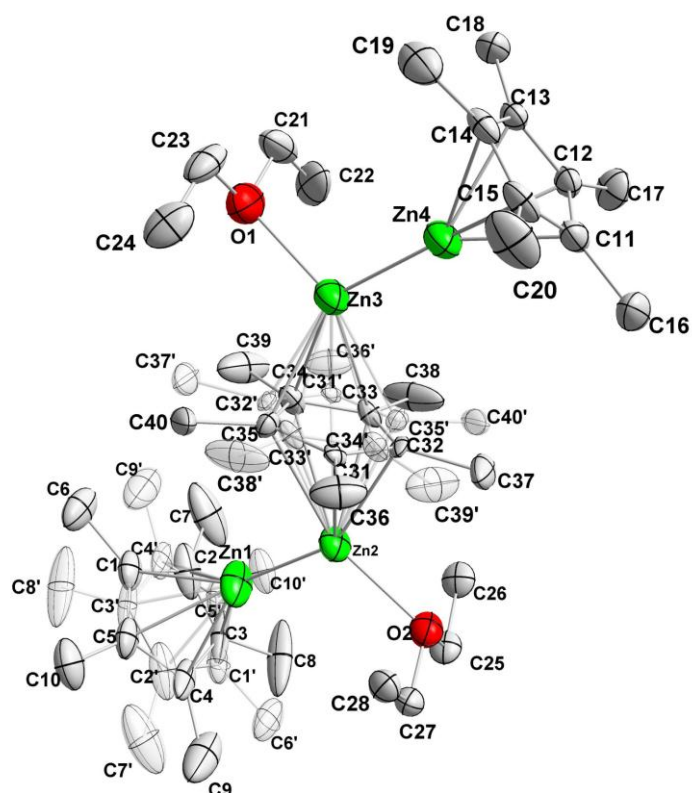


Figure S9: Molecular structure of the cation [Zn₄Cp*₃(Et₂O)₂]⁺ in the crystal of **1**·2C₆H₅F. Displacement ellipsoids are drawn at the 30 % probability level. Disorder is shown in form of the transparent lower occupied part. Hydrogen atoms are omitted for clarity.

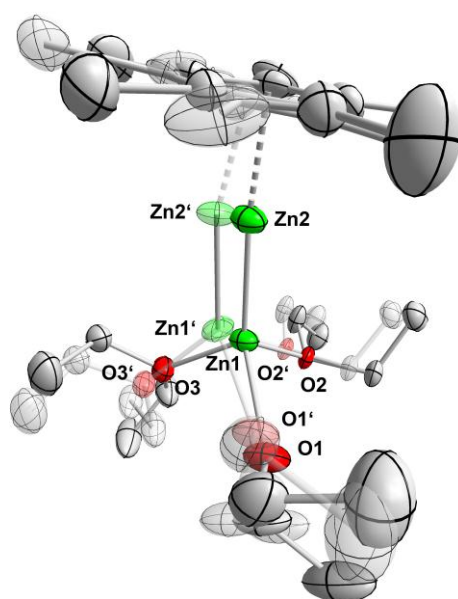


Figure S9: Molecular structure of the cation $[\text{Cp}^*\text{Zn}_2(\text{OEt}_2)_3]^+$ in the crystal of **2**. Displacement ellipsoids are shown at the 30 % probability level. Disorder is shown in form of the transparent lower occupied part. Hydrogen atoms are omitted for clarity.