Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION
For

The Synthesis and Structure of $[Zn(TEMPO)_2]_2$ and $[Zn(\mu\text{-}H)(\mu^2\text{-}\eta^1{:}\eta^1\text{--}TEMPO)]_6$

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General Considerations All manipulations were performed under an atmosphere of dry, oxygen-free N_2 by means of standard Schlenk or glovebox techniques (MBraun glovebox equipped with a –40 ºC freezer) unless otherwise noted. C_6D_6 and [D_8]toluene were dried over Na/benzophenone ketyl, D_5Pyridine was dried over CaH_2 and vacuum transferred before use. Other solvents were purified using an Innovative Technologies solvent purification system. [$ZnCp^*_2$][18] was prepared according to published protocols. TEMPO (Aldrich) and Carbenes I*t*Bu (TCI), IDipp (Aldrich) and IMes (Aldrich) were used as received. NMR spectra were recorded on Bruker Avance 400 MHz, an Agilent DD2 500, or an Agilent DD2 600Hz spectrometer. Chemical shifts were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. X-ray crystallography (Bruker Kappa Apex II), FTIR (KBr, Perkin-Elmer Spectrum One) and elemental analysis (Perkin-Elmer CHN Analyzer) were performed in house.

$Zn(TEMPO)_2$. A vial was charged with ZnCp*2 (52 mg, 0.155 mmol) and TEMPO (0.333 mmol) and Et2O (2 mL) was added. All solids dissolved to give a pale yellow solution from which the product crystallizes within minutes. To complete crystallization the mixture was kept in a freezer over night. The colorless crystals were isolated by decantation, washed with pentane and dried in vacuo (53 mg, 0.140 mmol, 90%). ^{1}H-NMR (400 MHz, [D_5]Pyridine, 25 °C): δ= 1.63 (br s, 8H, β-CH_2), 1.45 (br s, 28H, γ-CH_2 and Me); ^{13}C-NMR (100 MHz, [D_5]Pyridine, 25 °C): δ= 59.3 (C), 41.4 (β-CH_2), 34.0 (br, Me), 18.9 (γ-CH_2); elemental analysis calcd for $C_{18}H_{36}N_2O_2Zn$: C 57.21, H 9.60, N 7.41; found: C 56.83, H 8.91, N 7.43.

[Zn(μ-H)(μ^2-η^1-η^1-TEMPO)]$_6$. A suspension of $Zn(TEMPO)_2$ (24 mg, 0.64 mmol) in benzene (4 mL) was exposed to H_2 (100 atm) for 72 h. The resulting colorless crystals were separated from the faint red solution by decantation, washed with pentane and dried in vacuo (13 mg, 0.058 mmol, 91%). ^{1}H-NMR (400 MHz, C_6D_6, 25°C): δ= 3.63 (ZnH), 1.41 (m, 4H, β-CH_2), 1.31 (br, 2H, γ-CH_2), 1.15 (s, 12H, Me); ^{13}C-NMR (100 MHz, C_6D_6, 25 °C): δ= 58.5 (C), 39.8 (β-CH_2), 25.5 (br, Me), 17.4 (γ-CH_2), repeated attempts to obtain EA were unsuccessful presumably due to the sensitivity of this species

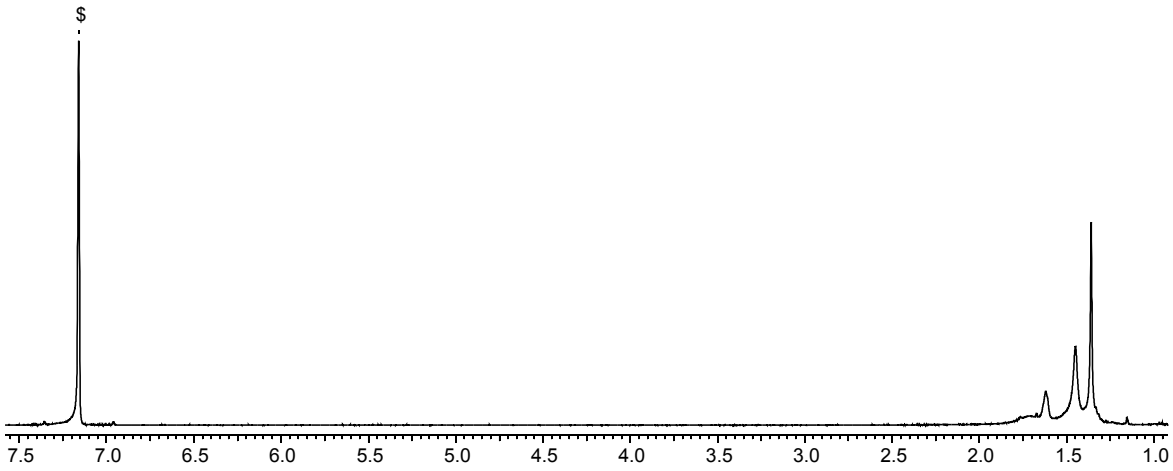

Figure 1. ^{1}H NMR spectrum of Zn(TEMPO)$_2$ in C_6D_5 ($) at 25 °C.

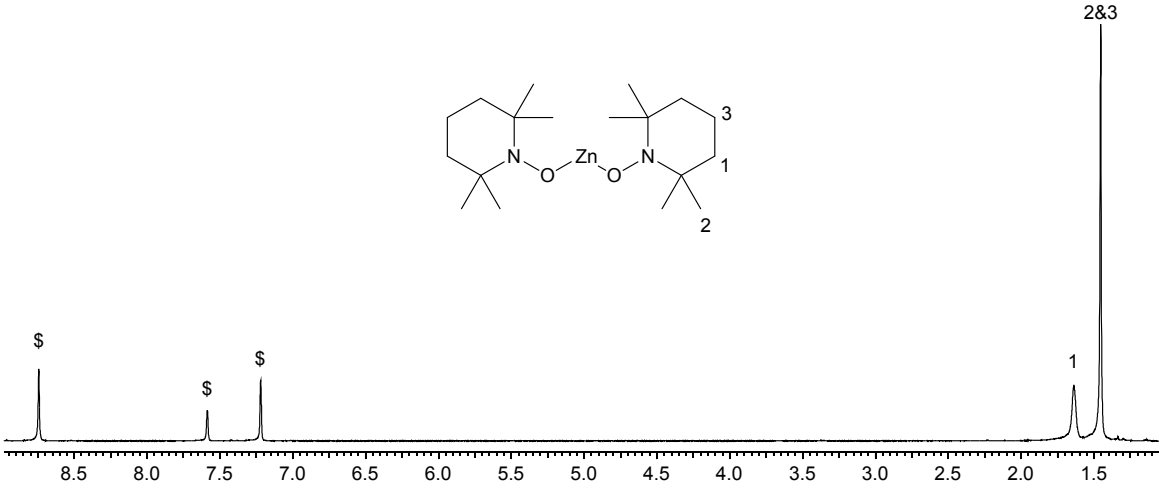

Figure 2. ^{1}H NMR spectrum of Zn(TEMPO)$_2$ in [D_5]pyridine ($) at 25 °C.

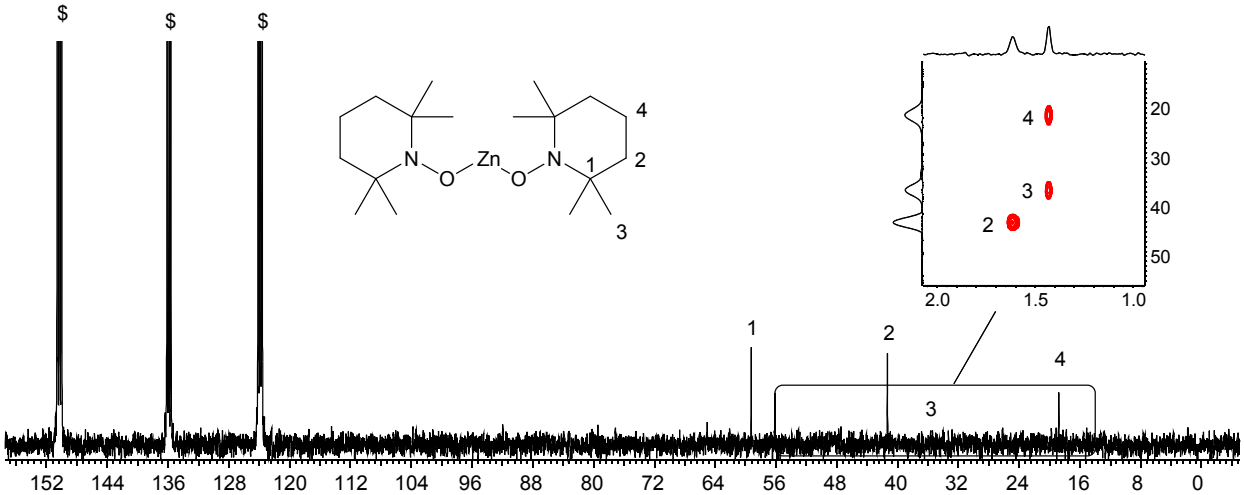

Figure 3. ^{13}C NMR spectrum of Zn(TEMPO)$_2$ in [D_5]pyridine ($) at 25 °C. Partial HSQC spectrum depicted for assignment of methyl groups.

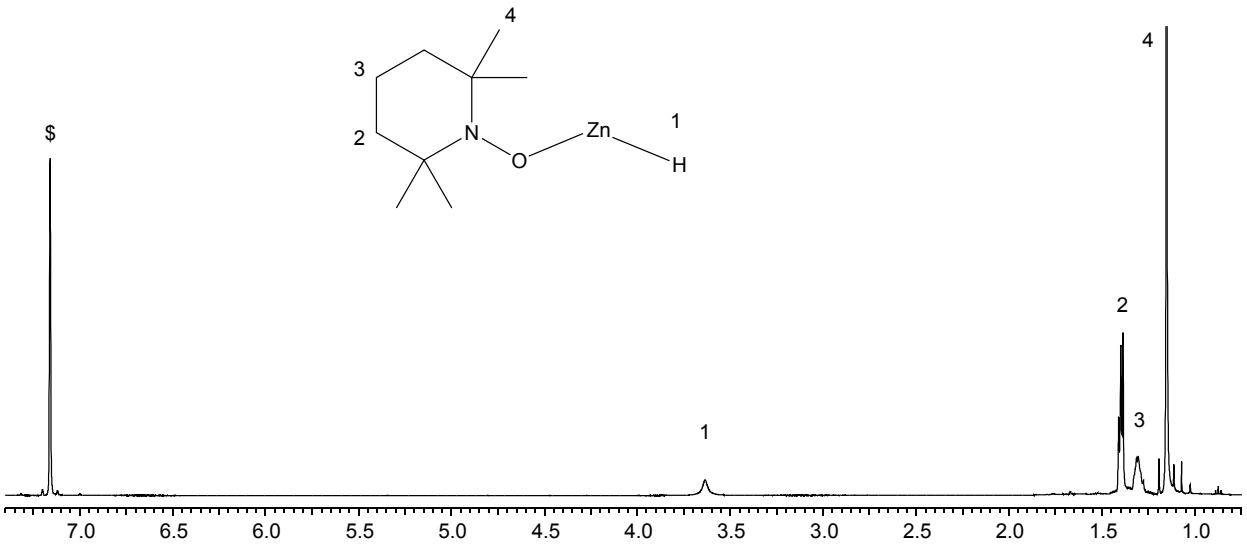

Figure 4. ^{1}H NMR spectrum of HZn(TEMPO) in C_6D_5 ($) at 25 °C.

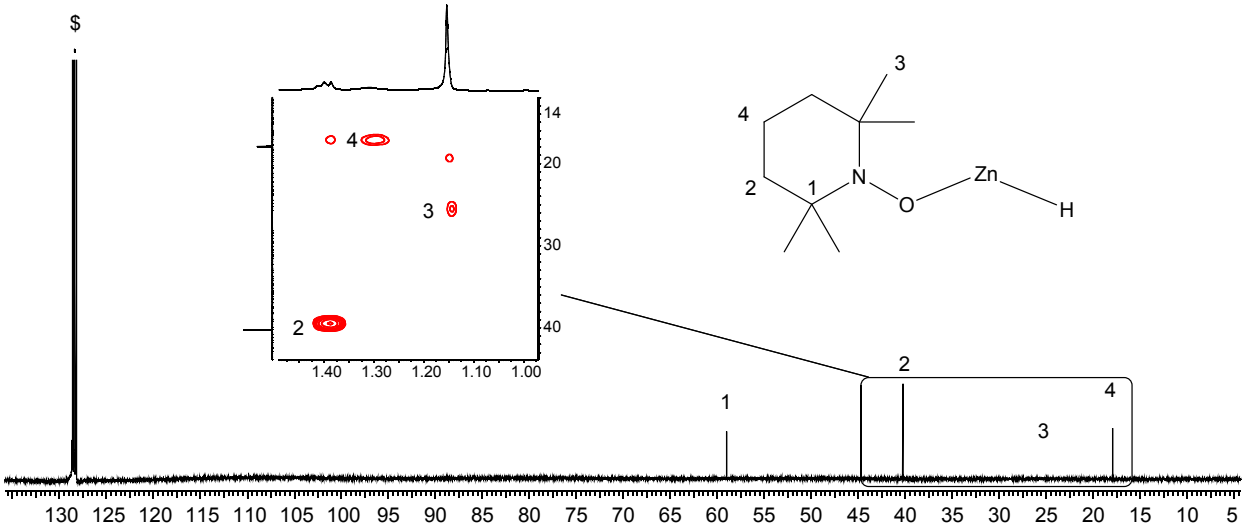

Figure 5. ^{13}C NMR spectrum of HZn(TEMPO) in C_6D_5 ($) at 25 °C. Partial HSQC spectrum depicted for assignment of methyl groups.

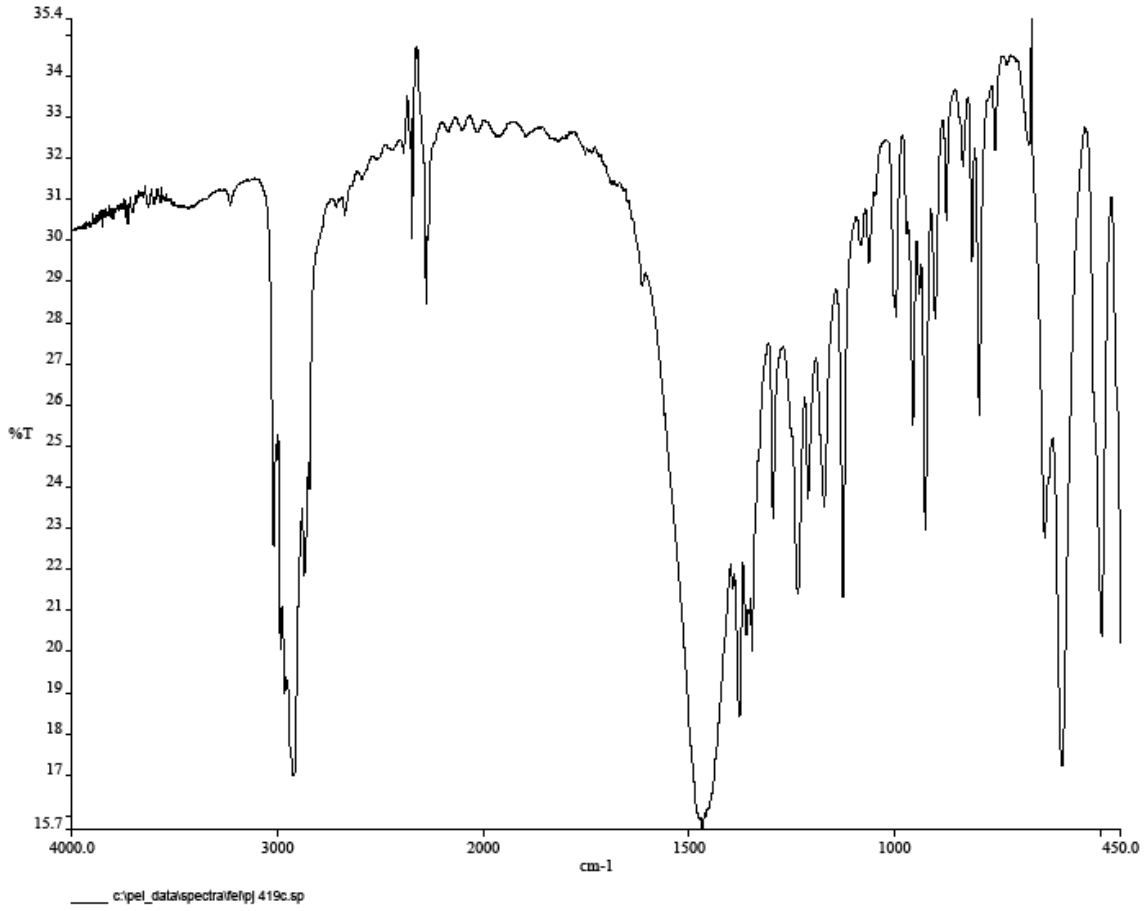

Figure 5. FTIR spectrum of HZn(TEMPO) (KBr disc).