

Covalently functionalized carbon nanoparticles by a chiral Mn-Salen: a new nanocatalyst for enantioselective epoxidation of alkenes

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General Experimental Methods

The NMR experiments were carried out at 27 °C on a Varian UNITY Inova 500 MHz spectrometer (¹H at 499.88 MHz, ¹³C-NMR at 125.7 MHz) equipped with pulse field gradient module (Z axis) and a tunable 5 mm Varian inverse detection probe (ID-PFG). ESI mass spectra were acquired on a API 2000TM AB Sciex using MeOH (positive ion mode). All chemicals were reagent grade and were used without further purification. Enantiomeric excesses were determined by GC analysis with a Perkin Elmer Capillary (Perkin Elmer, Waltham, MA, USA) using helium as carrier (flow 1 mL/min.), dimethylpentyl-beta (DIMEPEBETA-086) chiral column (25 m × 0.25 mm ID, 0.25 μm film) for 6-cyano-2,2-dimethylchromene (oven conditions: 120 °C for 0 min., ramp 2 °C/min. to 200 °C for 20 min.), DiAcTBuSiliBETA-ov-1701 chiral column (25 m × 0.25 mm ID, 0.25 μm film) for *cis*-β-ethylstyrene (oven conditions: 50 °C for 0 min., ramp 5 °C/min. to 180 °C) and dimethyl-pentyl-beta (DMePeBETACDX) chiral column (25 m × 0.25 mm ID, 0.25 μm film) for 1,2-dihydronaphthalene (oven conditions: 100 °C for 5 min., ramp 5 °C/min. to 180 °C for 10 min.). The injector and detector temperatures were maintained at 250 °C for all columns, *n*-dodecane was used as an internal standard throughout. The absolute configuration of the obtained epoxides were determined by measuring the optical rotation with a polarimeter. Absolute configurations were assigned by comparison of the measured $[\alpha]_D^{20}$ values with those reported in the literature.¹ Characterization of compounds **1**, **2** are in tune with the literature.² Enantiomeric excesses were calculated by using the formula:

$$\frac{[R] - [S]}{[R] + [S]} \times 100$$

Synthesis of aldehyde 1. Aqueous formaldehyde (3.6 mL, 43 mmol) and HCl conc. (50 mL) were added to salicylaldehyde (5.73 g, 47 mmol). The mixture was refluxed for 16 h. The precipitate was filtered, washed with water, redissolved in diethyl ether, and dried over MgSO₄. After evaporation of the solvent, compound **1** was recrystallized from *n*-hexane to afford white crystals (85%). ¹H NMR (500 MHz, CDCl₃): δ = 11.06 (s, 1H), 9.90 (s, 1H), 7.59 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 4.59 ppm (s, 2H); ESI-MS: *m/z*: 171.0 [M+H]⁺; Elemental analysis calcd (%) for C₈H₇ClO₂: C 56.33, H 4.14, Cl 20.78; found: C 56.27, H 4.11, Cl 20.74.

Synthesis of aldehyde 2. Aldehyde **1** (850 mg, 5 mmol) and CuSO₄ (795 mg, 5 mmol) were dissolved in 10 mL of a mixture H₂O/DMSO (1/2). The mixture was stirred at 110 °C for 2 h, then cooled to room temperature, and diluted with water. Extraction with diethyl ether, followed by evaporation of the solvent, affords to compound **2** (87 %). ¹H NMR (500 MHz, CDCl₃): δ = 10.99 (s, 1H), 9.91 (s, 1H), 7.58 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 4.69 ppm (s, 2H); ESI-MS: *m/z*: 153.0 [M+H]⁺; Elemental analysis calcd (%) for C₈H₈O₃: C 63.15, H 5.30; found: C 63.07, H 5.22.

Synthesis of Salen 4. 66.1 mg (0.435 mmol) of aldehyde **2** and 202 mg (0.435 mmol) of (*1R,2R*)-diphenyl-ethylendiamino-monochloride derivative **3** were dissolved into 10 mL of absolute ethanol. Then, 250 μL (1.80 mmol) of triethylamine were added and reaction was stirred at room temperature overnight. The reaction was monitored by TLC (*n*-hexane/EtOAc 80:20) to follow the disappearing of the starting aldehyde **2** and then quenched by evaporation of the solvent under vacuum. Salen **4** (65%) was purified by flash chromatography (*n*-hexane/EtOAc 90:10). ¹H NMR (500 MHz, CDCl₃): δ = 13.53 (s, 1H), 13.28 (s, 1H), 8.40 (s, 1H), 8.31 (s, 1H), 7.31 (d, *J* = 2.5 Hz, 1H), 7.14-7.22 (m, 12H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 4.74 (d, *J* = 8.5 Hz, 1H), 4.67 (d, *J* = 8.5 Hz, 1H), 4.52 (s, 2H), 1.43 (s, 9H), 1.22 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ = 167.4, 166.0, 160.5, 157.8, 140.1, 139.4, 136.4, 131.6, 131.2, 130.7, 128.4, 128.3, 127.8, 127.5, 127.4, 127.2, 126.3, 118.5, 117.7, 117.0, 80.5, 80.1, 79.8, 31.4, 29.3. ESI-MS: *m/z*: 585.3 [M+Na]⁺; Elemental analysis calcd (%) for C₃₇H₄₂N₂O₃: C, 78.97; H, 7.52; N, 4.98; found: C, 78.91; H, 7.45; N, 4.95.

Synthesis of Mn-Salen-OH. 0.159 mg (0.282 mmol) of salen **4** were dissolved in 10 mL of absolute ethanol. Then, 80 mg (0.3 mmol) of manganese (III) acetate dihydrate were added. Mixture was stirred at room temperature overnight. Then, solvent was removed under reduced pressure, crude product was dissolved in CH₂Cl₂ and filtered to remove the excess of manganese (III) acetate. Evaporation of solvent leads to **Mn-Salen-OH** (yield 95%). ESI-MS m/z 615.7 [M]⁺. Anal. Calcd. For C₃₇H₄₀MnN₂O₃: C, 72.18; H, 6.55; N, 4.55. Found: C, 72.10; H, 6.49; N, 4.51.

Functionalization of CNPs. In a round bottom flask containing 5 mg of native CNPs were introduced 220 mg of pentafluorophenol (1.20 mmol) and 85 mg of EDAC x HCl (0.44 mmol). The mixture was heated at 50°C, in order to melt the pentafluorophenol which act also as solvent. Reaction was stirred under nitrogen for 16h, then mixture was poured into CH₂Cl₂ and washed with water to remove the unreacted CNPs. The residue was dried under vacuum at 100°C overnight, obtaining **CNPs-PFF**. Subsequently, after solubilization in dry CH₂Cl₂, **Mn-Salen-OH** (20 mg, 0.03 mmol) and DIPEA (*N,N*-Diisopropylethylamine, 300 μL) were added. Mixture was stirred under nitrogen at room temperature for 3 days. Then, solvent was removed under reduced pressure and the crude was purified by SEC chromatography (Sephadex LH-20), using organic non polar solvent as phase mobile, thus obtaining **CNPs-Mn-Salen**.

XPS measurements. X-ray photoelectron spectra (XPS) were measured at 45° take-off angle relative to the surface plane with a PHI 5600 Multi Technique System (base pressure of the main chamber 1×10^{-8} Pa).^{3,4} Samples, deposited on clean SiO₂ substrates, were excited with Al K α X-ray radiation using a pass energy of 5.85 eV. Structures due to the K α satellite radiations were subtracted from the spectra prior to data processing. The XPS peak intensities were obtained after Shirley background removal.^{3,4} The atomic concentration analysis was performed by taking into account the relevant atomic sensitivity factors. The instrumental energy resolution was ≤ 0.5 eV. Spectra calibration was achieved by fixing the main C 1s signal at 285.0 eV.

Recycling tests. **CNPs-Mn-Salen** were recovered from the reaction media by extraction with 1 mL of CH₂Cl₂ (three times), then the solvent was removed under reduced pressure. The residue **CNPs-Mn-Salen** have been put at 100 °C under vacuum for two hours with a rotary pump, thus obtaining the nanocatalyst ready for the next cycle.

SEM analysis. Scanning electron microscopy was performed by Supra 55VP Field Emission Microscope (FE-SEM). Working acceleration voltage was 15 kV and high efficiency In-lens detector was used.

TEM analysis have been performed with a probe Cs-corrected JEOL JEM-ARM200F microscope, operated at 200KeV. Images have been acquired in Bright Filed mode (BF) and low e⁻ dose in order to reduce the beam damage. HR-TEM reported in S11 b-c, have been obtained by staking 30 images acquired at 80ms, after applying drift correction. This allowed us to have images with good SNR and no specimen modification under the e⁻ beam. The measured distance between the crystal fringes is of 3.2Å, compatible with crystalline carbon .

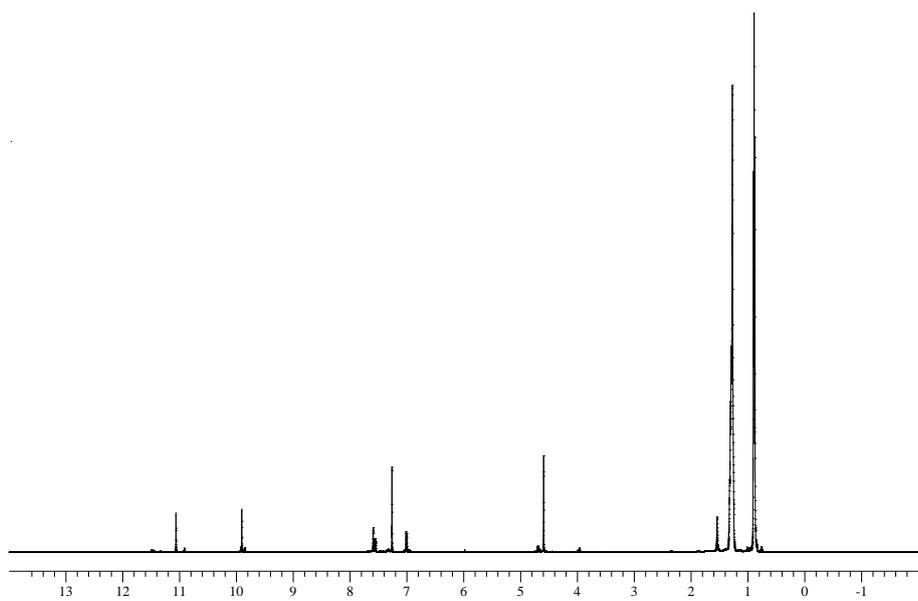


Figure S1. ^1H NMR spectrum of **1** in CDCl_3

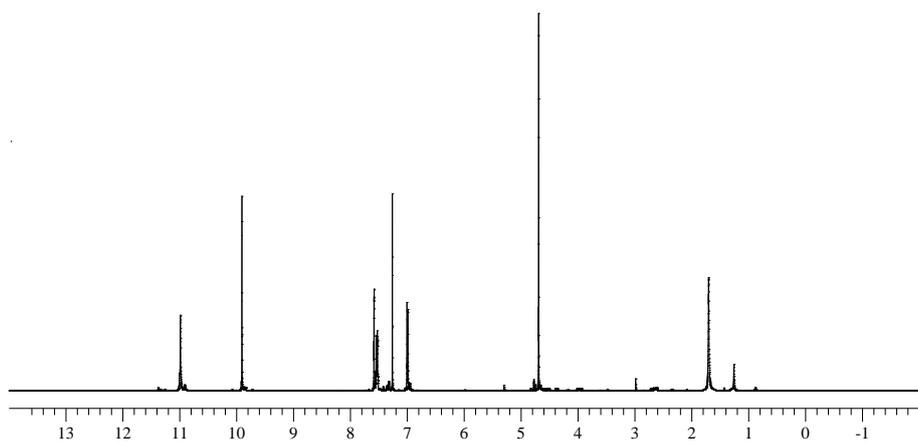


Figure S2. ^1H NMR spectrum of **2** in CDCl_3

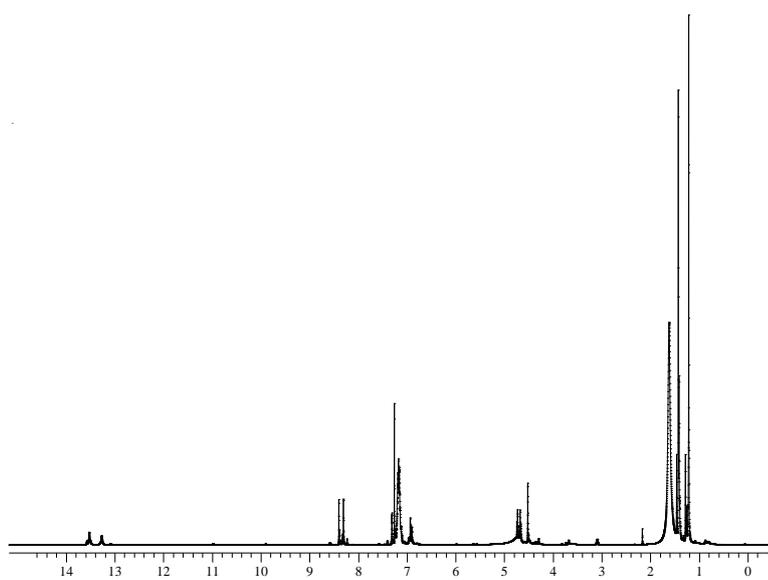


Figure S3. ^1H NMR spectrum of **4** in CDCl_3

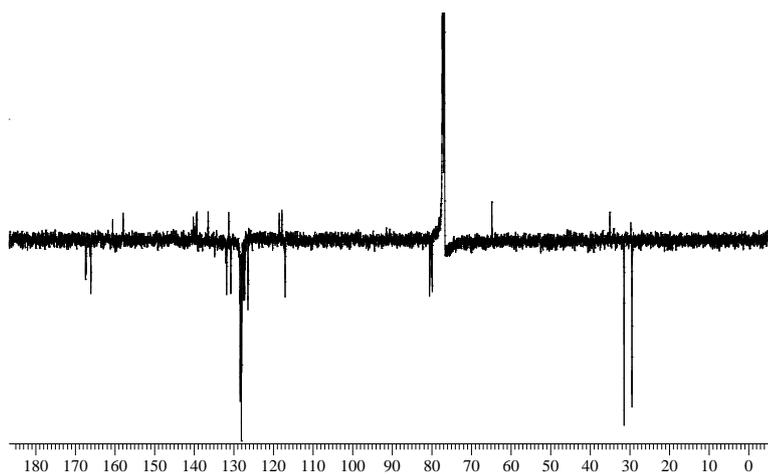


Figure S4. APT spectrum of **4** in CDCl_3

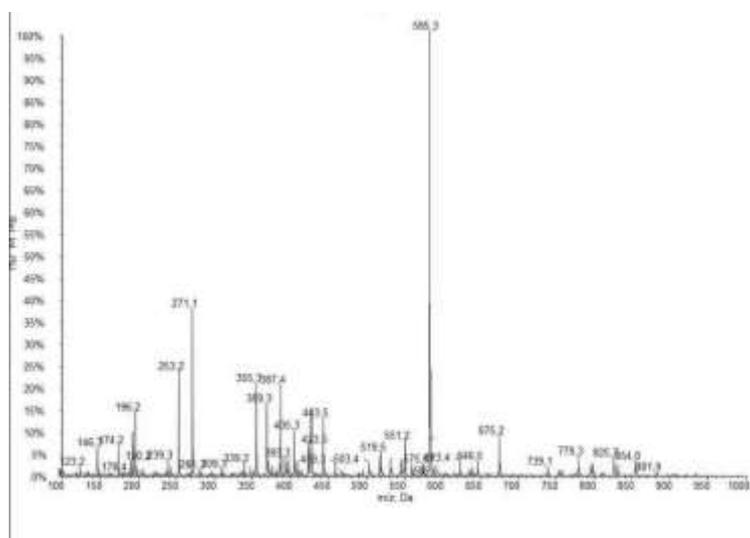


Figure S5. ESI-MS spectrum of **4**

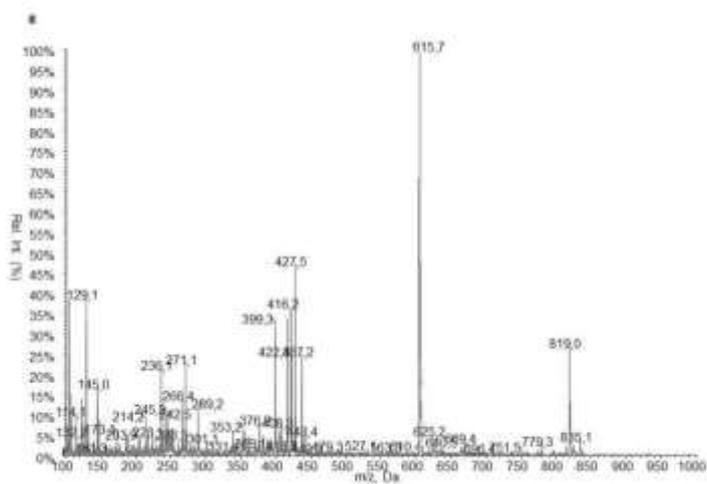


Figure S6. ESI-MS spectrum of **Mn-Salen-OH**

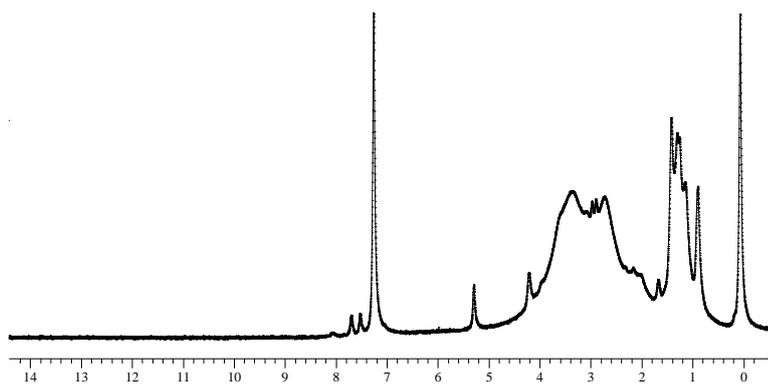


Figure S7. ^1H NMR spectrum of **CNPs-Mn-Salen** in CDCl_3

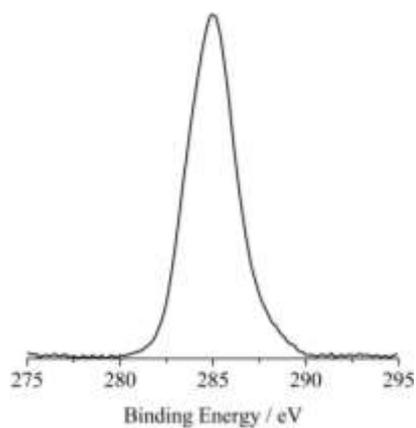


Figure S8. $\text{Al K}\alpha$ excited XPS of the CNPs sample, measured in the C 1s binding energy region. Structure due to satellite radiations has been subtracted from the spectra.

XPS results

Sample	C 1s	O 1s	N 1s	Mn 2p
CDs-Mn-Salen	78.4	19.0	2.2	0.4

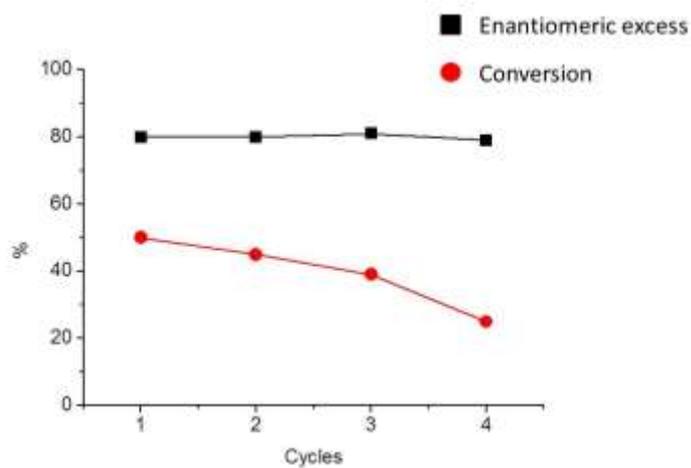


Figure S9. Variations in e.e. and conv. values after reusing **CNPs-Mn-Salen** in the epoxidation of 1,2-dihydronaphthalene for 24 h.

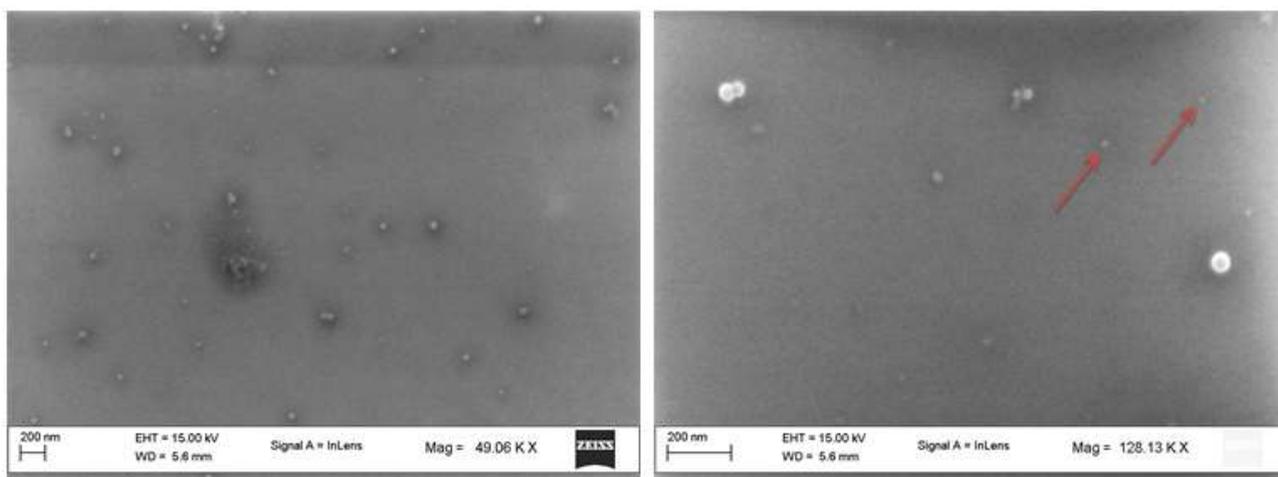


Figure S10. SEM image of **CNPs-Mn-Salen**

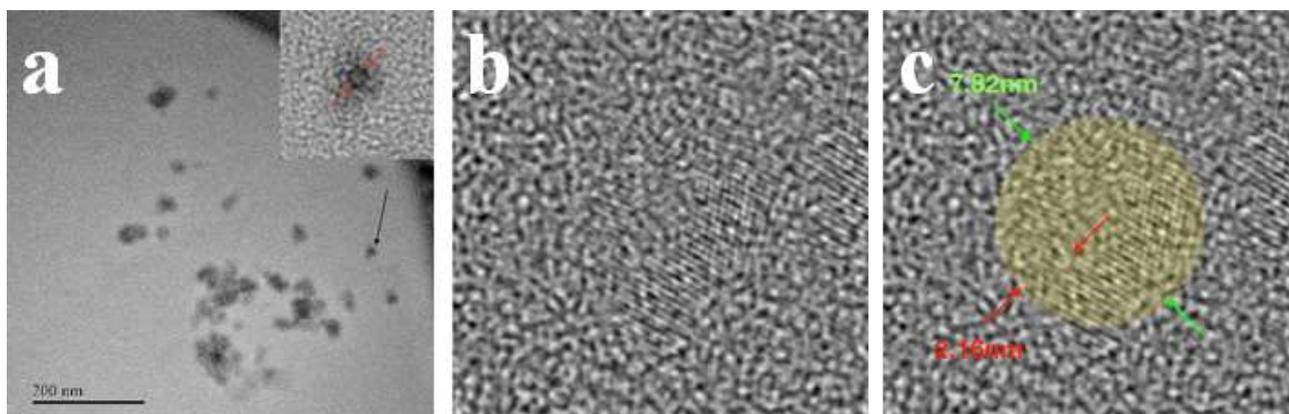


Figure S11. TEM images of **CNPs-Mn-Salen**. Low mag BF-TEM (a), HR-TEM of a **CNP-Mn-Salen** (b), same image as (b) with yellow disc as guide for the eye on a **CNP-Mn-Salen**.

References

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