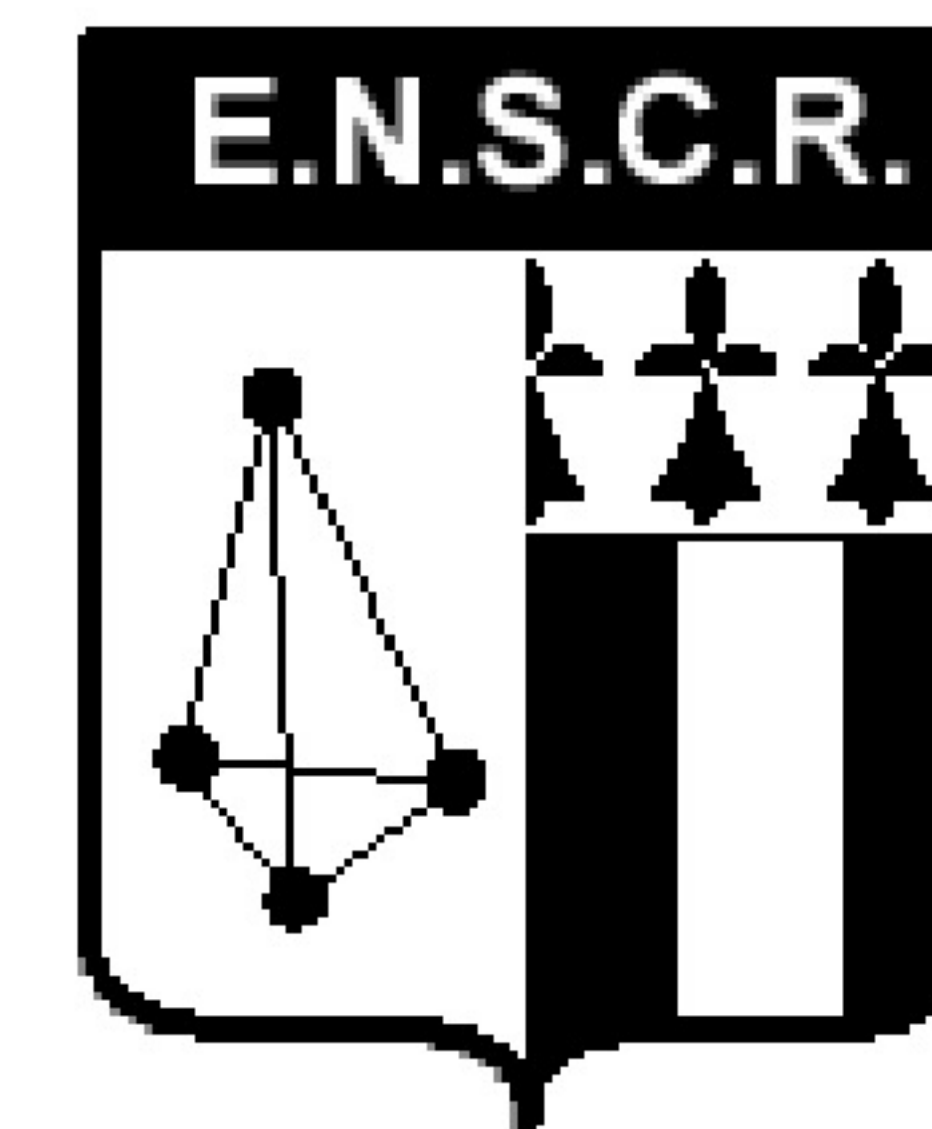




# Transition Metal Complexes for the Enantioselective Epoxidation of Olefines



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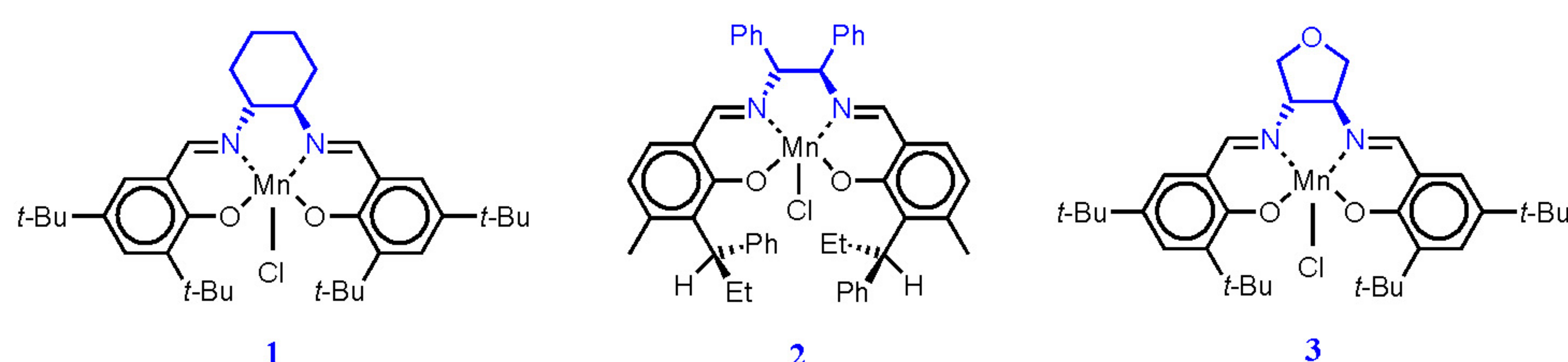
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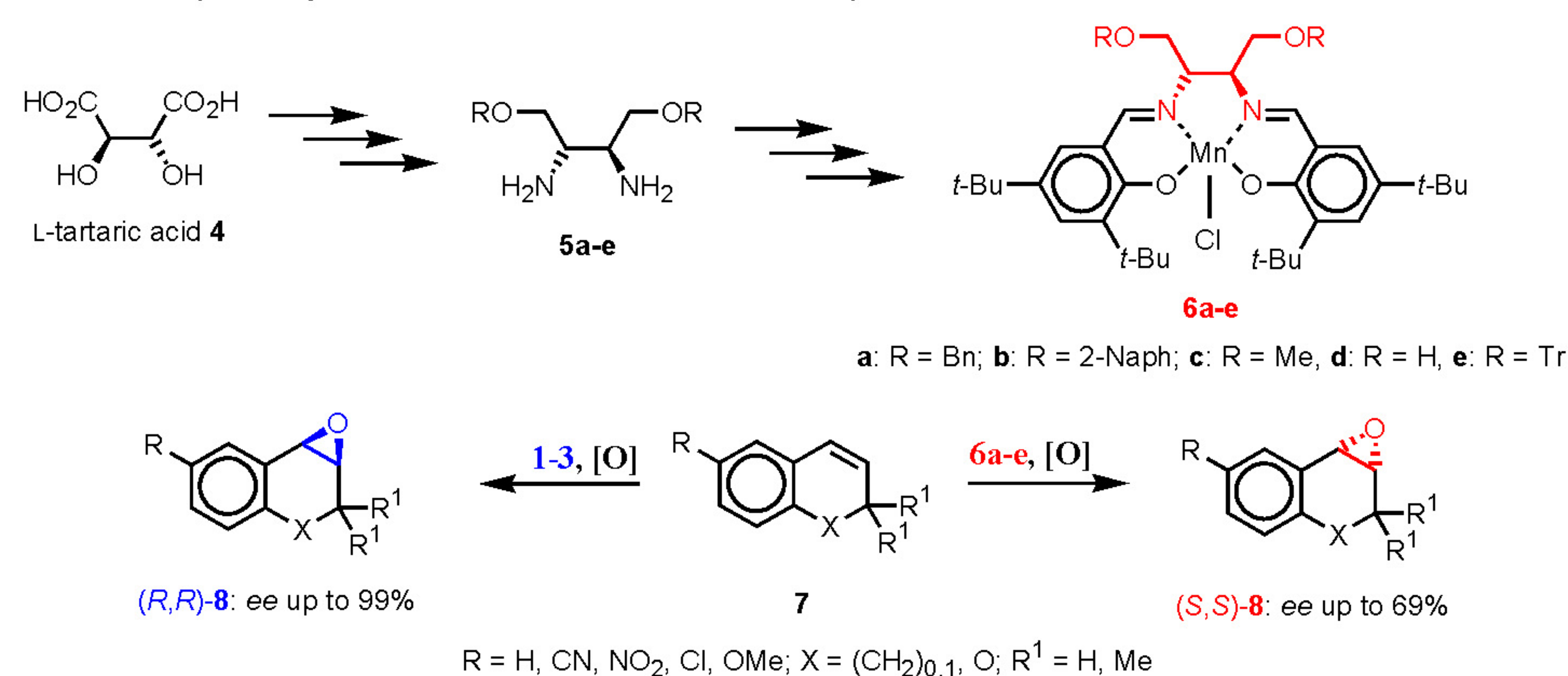
## Introduction

The asymmetric epoxidation of alkenes catalysed by chiral salen Mn(III) complexes **1-3** (Jacobsen, Katsuki, and Bell)<sup>[1-3]</sup> is extensively studied in organic chemistry, since optically active epoxides are useful intermediates for the synthesis of many natural products.



## Results

Starting from L-tartaric acid **4**, a series of new salen Mn(III)Cl complexes **6a-e** were prepared *via* diamines **5a-e**<sup>[4,5]</sup> and studied as catalysts for the enantioselective epoxidation of unfunctionalised Z-alkenes (ee up to 69% were obtained).<sup>[6,7]</sup>



Compared to the literature catalysts **1-3**, stereochemically identical **6a-e** furnished epoxides with opposite configuration [(*S,S*)-**8**]. This unusual reversal of asymmetric induction is likely due to the co-ordination of the oxygen functionality in the diimine moiety to the metal centre. There is further evidence for an ether-metal interaction shown by <sup>1</sup>H NMR spectroscopy of **10** and the calculated model compound **11** (Figure 1).<sup>[8,9]</sup>

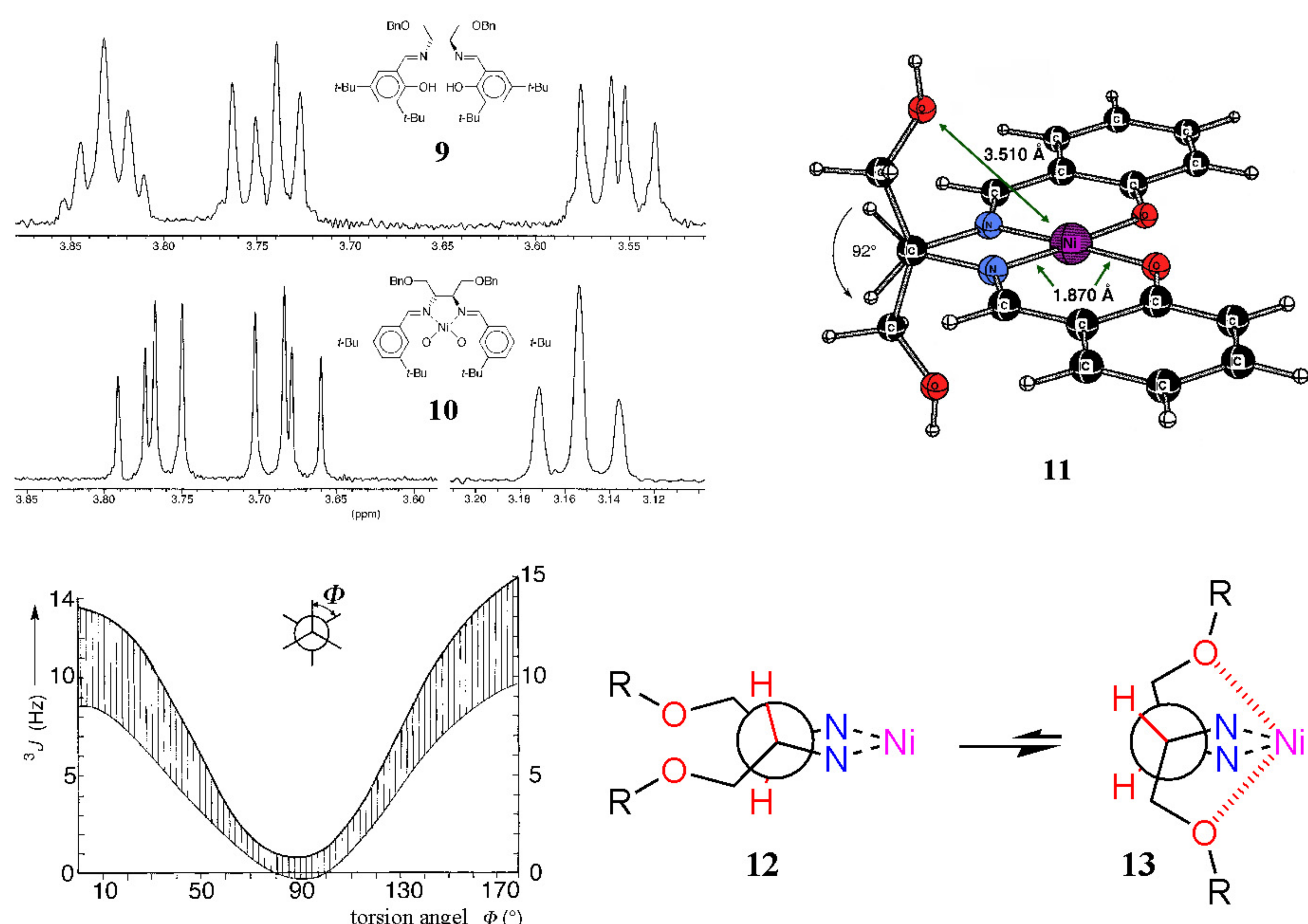
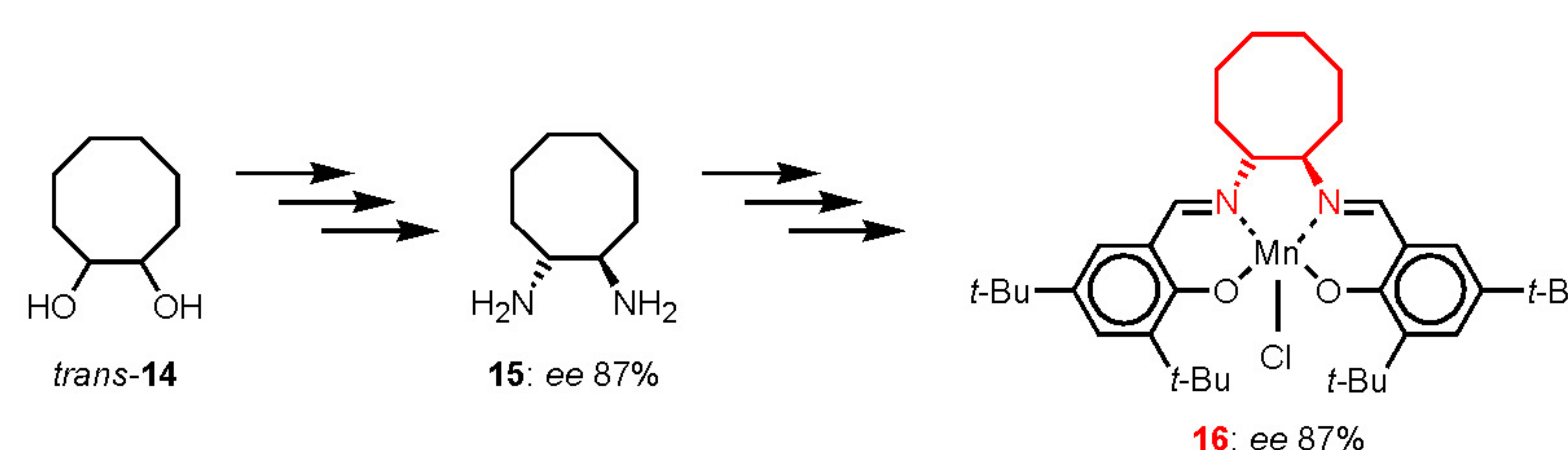


Fig. 1: <sup>1</sup>H NMR spectra of **9** and **10**, calculated structure **11**, Karplus-curve, and the possible Newman projections **12,13** for salen Ni(II) complex **10**.

For the salen Ni(II) complex **10**, the <sup>1</sup>H NMR spectrum showed an AA'BB'CC'-spin system with a vicinal coupling constant <sup>3</sup>J<sub>CC'</sub> ≈ 0 Hz (ligand **9**: <sup>3</sup>J<sub>CC'</sub> = 4.3 Hz). Therefore, following the Karplus-curve, a dihedral angle  $\phi$  of about 90° between the vicinal hydrogens in the backbone of **10** is expected. This is in good accordance with the proposed Newman projection **13** and the calculated structure of model compound **11** ( $\phi$  = 92°).

Compared to **1** and **3**, the influence of a larger carbocyclic substituent in the chiral unit was studied. Starting from *trans*-1,2-cyclooctanediol **14**, the new salen Mn(III)Cl complex **16** was generated *via* diamine **15** (resolution with L-tartaric acid afforded **15** with ee 87%).<sup>[10]</sup> The enantioselective epoxidation catalysed by **16** of chromenederivatives **7** led to epoxides **8** with low optical yield (ee ≤ 25%).



In Figure 2 the calculated model compound<sup>[9,11]</sup> and the crystal structure of **16** are represented. The eight-membered ring in the backbone of **16** is twisted towards the molecular plane which led probably to the poorer enantioselection.

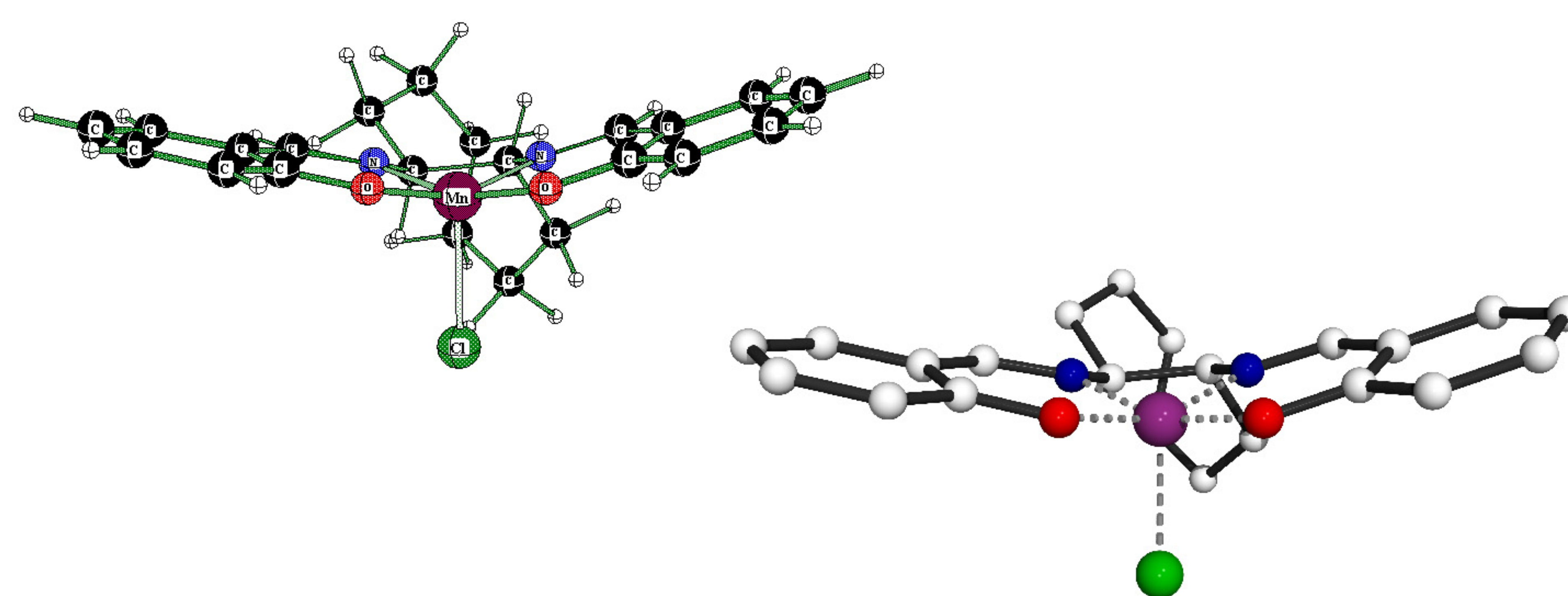


Fig. 2: Calculated structure of model compound (left) and crystal structure of **16** (right).

## Conclusion

The oxygen functionality of the diimine moiety in complexes **6a-e** co-ordinates to the metal centre. This leads to a *pseudo*-enantiomeric conformation of **6a-e** which causes the inversed enantioselection. The introduction of a eight-membered ring in **16** does not support the enantioselectivity.

## Literature

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