

Synthesis and catalytic properties of *p*-acylthio(phenylacetylene)_{*n*} substituted chiral manganese salen complexes

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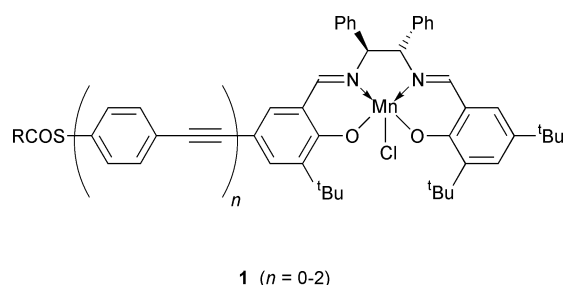
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The syntheses of three new salen ligands that are tethered to a *p*-acylthio(phenylacetylene)_{*n*} linker are described. The two key steps in the syntheses are coupling of the *p*-acylthio(phenylacetylene)_{*n*} linker (*n* = 0–2) with a 5-iodosalicylaldehyde and the subsequent condensation of the aldehyde moiety of the formed adducts with the monoimine of (*S,S*)-1,2-diphenylethylenediamine to give the salen ligands. In the catalytic asymmetric epoxidation reactions of (*Z*)-2-methylstyrene, performed using the Mn–salen complexes of these new ligands, high diastereoselectivities of up to 20 : 1 and enantioselectivities of up to 89% ee are obtained. The results are compared with the analogous reaction using Jacobsen's asymmetric epoxidation catalyst and the results are very similar. The synthesised ligands are promising candidates for the immobilisation of chiral Mn–salen complexes on gold electrodes and surfaces.

Introduction

The immobilisation of organic molecules on a conducting surface allows the study of direct electron-transfer between the immobilised molecule and the surface. Self-assembled monolayers (SAMs) of thiols on gold surfaces¹ have often been the preferred model for such studies,² due to their ease of preparation and the relatively large potential window within which such electrodes can operate.³ These systems have been applied to the development of electronic bio- and chemosensors⁴ and in molecular electronics.⁵ Jagessar and Tour have used oligo(phenylacetylene)s as conducting 'organic wires' between the gold surface and a redox-active center.⁶ In a series of papers, Lindsey *et al.* have recently described the synthesis of phenylacetylene linked porphyrin molecules.⁷

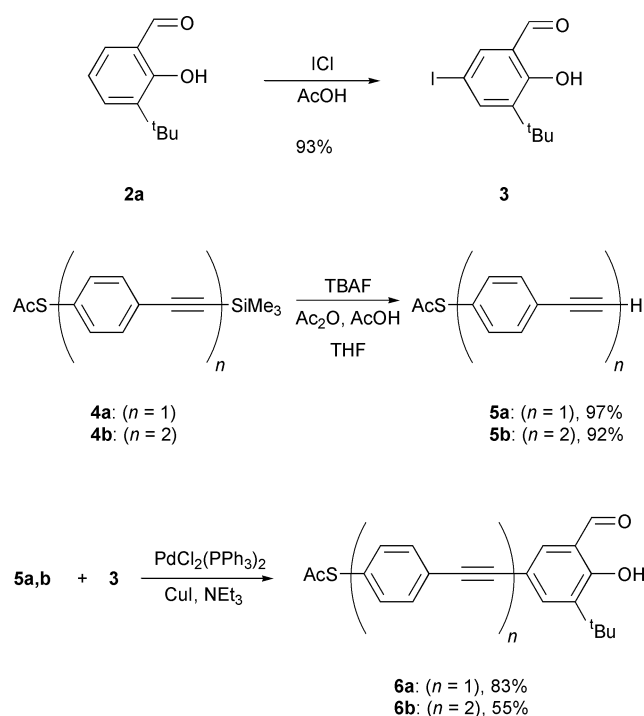
The target of the work described in this paper is to develop new ligands for asymmetric redox-catalysts that can be immobilised on an electrode *via* a conducting wire. This enables the direct monitoring of the redox processes at the catalyst center and the possible development of new electrocatalysts. We present here the syntheses and testing of catalytic properties of three new chiral manganese–salen complexes⁸ **1** that are substituted with a conducting organic wire consisting of (phenylacetylene)_{*n*} (*n* = 0, 1, 2) units. These new manganese complexes are functionalised with a terminally protected sulfur moiety, which allows immobilisation of the catalyst on gold electrodes that can be applied for studies of catalytic and electrocatalytic epoxidation reactions.^{8–10}



Results and discussion

Synthesis of the ligands

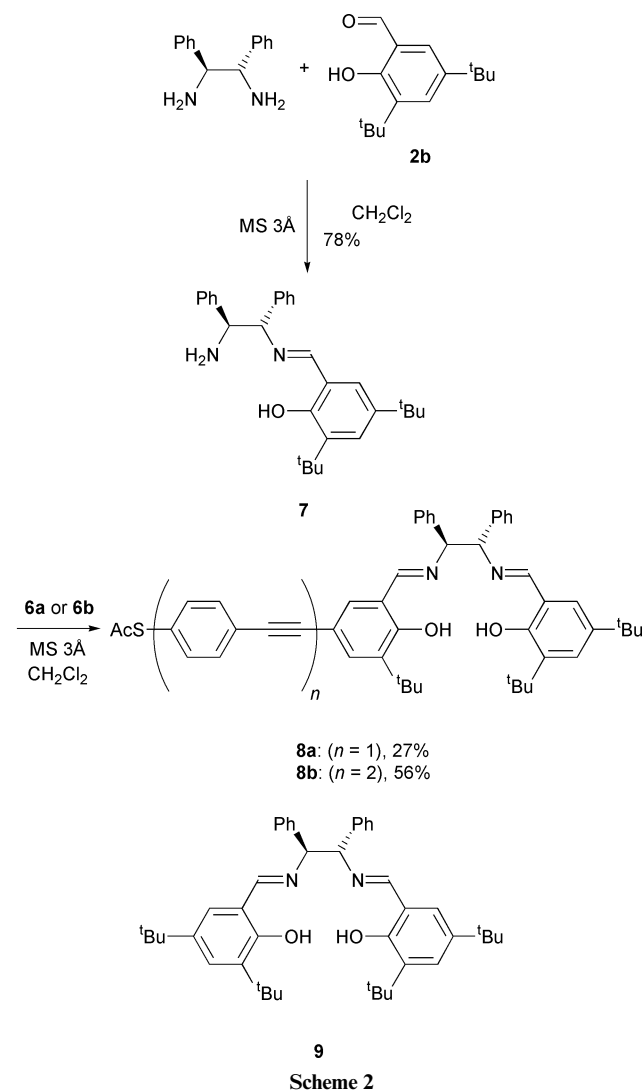
Our strategy for the synthesis of the desired ligands has been first to connect the acetylthio(phenylacetylene)_{*n*} moiety of **1** (*n* = 1, 2) with one of the salicylaldehyde groups of the desired salen moiety using a Sonogashira coupling.¹¹ The salicylaldehyde **2a**, was iodinated with ICl in acetic acid to give the 3-*tert*-butyl-5-iodosalicylaldehyde **3** in 93% yield (Scheme 1).¹² The bromination of **2a** was also performed,¹³ but the resulting 5-bromosalicylaldehyde could not be used for the following



Scheme 1

coupling reaction. The TMS protected acetylthio(phenylacetylene)_n linkers **4a, b** were synthesised according to the procedures described by Tour¹⁴ and by Sita,¹⁵ respectively, and the free terminal acetylenes **5a, b** were obtained in high yields by deprotection with TBAF.¹⁴ The coupling reaction between the linkers **5a, b** with iodosalicylaldehyde **3** was performed to give the adducts **6a** and **6b**, respectively. The catalysts for this reaction were (Ph₃P)₂PdCl₂ (7 mol%) and CuI (7 mol%) with triethylamine as the solvent. The products were obtained in 83% yield for **6a** and 55% yield for **6b**. When carried out in Hünig's base–THF, the reactions proceeded with slightly lower yields.

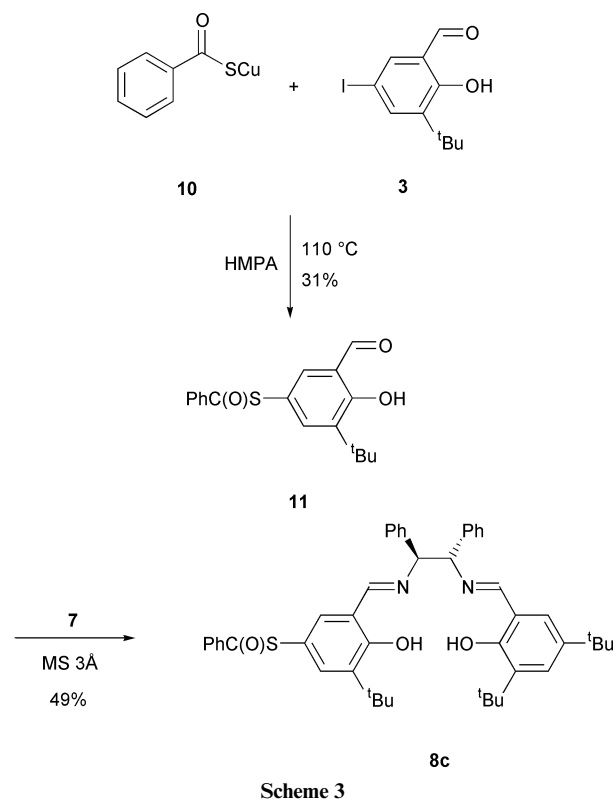
The right-hand side of the desired ligands in **1a, b** were prepared by condensation of enantiopure (1*S*,2*S*)-1,2-diphenylethylenediamine and 3,5-di-*tert*-butylsalicylaldehyde **2b** (Scheme 2). The best result, in which **7** was isolated in 78%



yield, was obtained when the reaction was performed in CH₂Cl₂ in the presence of molecular sieves (MS, 3 Å). If MgSO₄ was used as the drying agent or if MeOH was used as the solvent, the yield decreased due to an increased tendency to form the symmetric salen ligand **9** instead of the desired monoimine **7**. The syntheses of the ligands **8a** and **8b** were completed by condensation of **7** with **6a** and **6b**, respectively, using MS (3 Å) in CH₂Cl₂ as described for the synthesis of **7**. The two new salen ligands **8a** and **8b** were obtained in 27 and 56% yield, respectively. The reason for the relatively low yields obtained in these reactions is that a substantial amount of the symmetric ligand **9** was formed. This by-product was probably formed by a favoured disproportionation of the non-symmetric amines **8a**

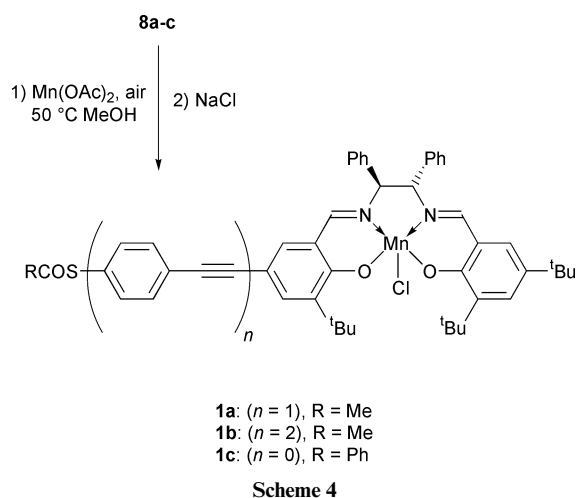
and **8b** in the presence of the free amine **7**. Thus, it was observed for these condensations that, upon prolonged reaction times, the only imine product formed was the C₂-symmetric salen ligand **9**. However, when the non-symmetric imines **8a, b** were isolated after shorter reaction times, they were stable.

The third ligand in this series, **8c**, was prepared with the sulfur handle directly attached to the salen moiety (Scheme 3).



The coupling between 3-*tert*-butyl-5-iodosalicylaldehyde **3** and Cu(I) thiobenzoate **10** was performed in HMPA to produce the benzoylthio-substituted salicylaldehyde **11** in 31% yield.^{16,17} The subsequent condensation reaction with the monoimine **7**, performed as described for the analogous reaction of **6a, b**, gave the non-symmetric salen ligand **8c** in 49% yield.

With the three new ligands **8a–c** in hand, the next step was to insert the manganese metal core in the ligands. This was performed by dissolving the ligands in a solution of Mn(OAc)₂·H₂O in methanol with stirring for 30 min under air at 50 °C (Scheme 4).¹⁸ Under these conditions Mn(II) is oxidised to



Mn(III). Subsequent exchange of the acetate ligand with chloride using NaCl, yielded the Mn–salen complexes **1a–c**.

Table 1 Comparison of the selectivities obtained in the asymmetric epoxidation of (*Z*)-2-methylstyrene in the presence of 5 mol% of the known Mn–salen complexes **12a, b** with the new catalysts **1a–c**^a

Entry	Catalyst	<i>cis</i> : <i>trans</i> ^b	Ee(<i>cis</i>) ^b (%)	Ee(<i>trans</i>) ^b (%)
1	12a	14 : 1	89	59
2	12b	20 : 1 (15 : 1) ^c	88 (88) ^c	26
3	1a	20 : 1	89	27
4	1b	15 : 1	81	14
5	1c	18 : 1	86	26

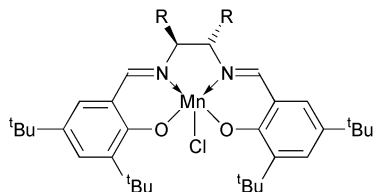
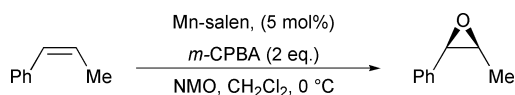
^a 0 °C, 2.5 h, NMO (5 eq.), MCPBA (2 eq.), quenched by addition of 1 M NaOH. Conversions of >90% were observed for all entries.

^b Determined by chiral GC-MS with an Astec B-DM column.

^c Selectivities obtained by Jacobsen and co-workers in a similar reaction.^{8c}

Catalytic properties

The catalytic properties of the three new phenylacetylene tethered catalysts **1a–c** were tested and compared with the Mn–salen epoxidation catalyst **12a** and the commercially available Jacobsen catalyst **12b** (Scheme 5). The test reaction of choice



12a: R = Ph

12b: R-R = (CH₂)₄

Scheme 5

was the epoxidation of (*Z*)-2-methylstyrene with MCPBA as the oxygen source and *N*-methylmorpholine *N*-oxide (NMO) as the co-oxidant. The reaction time was 2.5 h at 0 °C and the epoxidation reactions proceeded to give the epoxide with >90% conversion.

The results of these epoxidation reactions are collected in Table 1. For the two Mn–salen catalysts **12a** and **12b** the *cis*-epoxide was obtained in 89 and 88% ee, respectively (entries 1, 2). These results are very similar to those obtained by Jacobsen and co-workers, when using 2–4 mol% of catalyst **12b** at 0 °C.^{8c} The new Mn–salen catalysts **1a–c** induce diastereo- and enantioselectivities that are comparable to the known C₂-symmetric catalysts (Table 1, entries 3–5). The comparison between **1a–c** and **12a** is especially interesting because these ligands have the same diphenyl backbone in contrast to **12b**, which has a cyclohexane backbone. The highest diastereo- and enantioselectivities of the three new catalysts were obtained for **1a**, which induces 89% ee of the *cis*-epoxide, which is similar to the result obtained when using the C₂-symmetric catalysts (entries 1, 2). When applying catalyst **1b** with two phenylacetylene units the enantioselectivity decreases to 81% ee (entry 4). The catalyst ligand with the sulfur handle connected directly onto the salen core **1c** induced 86% ee for the *cis*-epoxide (entry 5). For all the catalysts **1a–c** comparable *cis*-selectivities of 15 : 1 to 20 : 1 are obtained, which is also similar to the results obtained when using **12a, b**. The selectivities obtained in the enantioselective epoxidation reaction of (*Z*)-2-methylstyrene using the three new Mn–salen complexes **1a–c** are thus similar, or slightly lower, than the selectivities obtained with the well-known catalysts **12a, b**.

In summary, we have synthesised three new sulfur functionalised (phenylacetylene)_n–Mn–salen complexes **1a–c** and we have shown that the selectivities obtained in the catalytic asymmetric epoxidation reaction are very similar to the values obtained using two well-known Mn–salen catalysts. The ligands **8a–c** are promising candidates for the immobilisation of chiral Mn–salen complexes on gold electrodes and surfaces. The ligands can also be applied for the immobilisation of other metal–salen complexes on gold for the study of their redox chemistry and for the possible development of asymmetric electrocatalysts.

Experimental

General methods

Dichloromethane and triethylamine were dried using standard methods. Pd(PPh₃)₂Cl₂, 3-*tert*-butylsalicylaldehyde and (1*S*, 2*S*)-diphenylethylenediamine were purchased from Aldrich, 3,5-di-*tert*-butylsalicylaldehyde was received from Lancaster and (*Z*)-2-methylstyrene was purchased from ICN Biomedicals. Copper(i) thiobenzoate **10**,¹⁶ 4-(acetylthio)phenylacetylene **5a**¹⁴ and 1-(4-{2-[4-(acetylthio)phenyl]ethynyl}-phenyl)-2-trimethylsilylacetylene **4b**¹⁵ were prepared according to literature procedures. Enantiomeric excesses of the products were determined by chiral GC-MS using an Astec B-DM column. High resolution mass spectral analyses were performed with a Micromass LC-TOF instrument.

3-*tert*-Butyl-5-iodosalicylaldehyde (**3**)¹²

3-*tert*-Butylsalicylaldehyde **2a** (1.63 g, 9.92 mmol) was dissolved in glacial acetic acid (10 mL) in a 100 mL round-bottomed flask equipped with a reflux condenser. Iodine monochloride (2.26 g, 13.9 mmol), dissolved in glacial acetic acid (15 mL), was added dropwise to the solution and the reaction mixture was refluxed for 4 h. The mixture was cooled to rt, stirred overnight and then poured into water (100 mL). The crude reaction mixture was extracted with CH₂Cl₂ (3 × 25 mL), the organic layers were washed with sodium thiosulfate, dried over MgSO₄ and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography (silica gel, 5% Et₂O in pentane) to yield the product **3** (2.85 g, 9.22 mmol, 93%) as a pale yellow solid after evaporation of the solvent; mp 43–44 °C; δ_H(400 MHz; CDCl₃; Me₄Si) 1.40 (s, 9 H), 7.69 (d, *J* 2.0 Hz, 1 H), 7.72 (d, *J* 2.0 Hz, 1 H), 9.80 (s, 1 H), 11.74 (s, 1 H); δ_C(100 MHz; CDCl₃; Me₄Si) 29.2, 35.3, 122.7, 140.2, 141.6, 142.8, 161.1, 164.2, 196.2; *m/z* (GC-MS) 304 (M⁺).

4-{2-[4-(Acetylthio)phenyl]ethynyl}phenylacetylene (**5b**)

The silyl protected bis(phenylacetylene) derivative **4b** (0.80 g, 2.3 mmol) was dissolved in dry THF (10 mL) in a flame dried Schlenk flask. The solution was cooled to 0 °C followed by the dropwise addition of a prepared solution of *tert*-butylammonium fluoride (11.5 mL, 1.0 M solution in THF, 11.5 mmol), acetic acid (0.69 mL, 10.0 mmol) and acetic anhydride (1.02 g, 10.0 mmol). The solution was stirred at 0 °C for 1 h, followed by stirring at rt for 1 h. The reaction mixture was poured into water (50 mL) and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were washed with brine, dried over MgSO₄ and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography (silica gel, 10% Et₂O in pentane) to yield the product **5b** (586 mg, 2.1 mmol, 92%) as a yellow oil after evaporation of the solvent; δ_H(400 MHz; CDCl₃; Me₄Si) 2.44 (s, 3 H), 3.18 (s, 1 H), 7.40 (d, *J* 8.2 Hz, 2 H), 7.48 (s, 4 H), 7.55 (d, *J* 8.2 Hz, 2 H); δ_C(100 MHz; CDCl₃; Me₄Si) 30.6, 79.3, 83.4, 90.7, 90.8, 122.4, 123.6, 124.4, 128.6, 121.8, 132.3, 132.4, 134.5, 193.7; HRMS (ES) calc. for C₁₈H₁₂OS 276.0609; found 276.0612.

5-{2-[4-(Acetylthio)phenyl]ethynyl}-3-*tert*-butylsalicylaldehyde (6a)

A mixture of (PPh₃)₂PdCl₂ (35 mg, 0.050 mmol) and CuI (9.5 mg, 0.050 mmol) was stirred for 1 h under vacuum in a flame dried Schlenk flask. 4-(Acetylthio)phenylacetylene **5a** (115 mg, 0.65 mmol), iodosalicylaldehyde **3** (200 mg, 0.65 mmol) and triethylamine (dry, 5 mL) were added and the mixture was stirred overnight at 70 °C under an argon atmosphere. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography (silica gel, 18% Et₂O in pentane) to yield **6a** (180 mg, 0.53 mmol, 83%) as a pale yellow solid after evaporation of the solvent; mp 96–97 °C; δ_H(400 MHz; CDCl₃; Me₄Si) 1.43 (s, 6 H), 1.51 (s, 3 H), 2.43 (s, 3 H), 7.39 (d, *J* 8.6 Hz, 2 H), 7.54 (d, *J* 8.6 Hz, 2 H), 7.61 (d, *J* 2.0 Hz, 1 H), 7.66 (d, *J* 8.6 Hz, 1 H), 9.87 (s, 1 H), 11.93 (s, 1 H); δ_C(100 MHz; CDCl₃; Me₄Si) 29.3, 30.6, 35.2, 87.8, 90.3, 114.2, 120.7, 124.6, 128.2, 132.3, 134.5, 135.5, 137.3, 139.2, 161.7, 193.8, 196.9; HRMS (ES) calc. for C₂₁H₂₀O₃S 352.1133; found 352.1138.

5-[2-(4-{2-[4-(Acetylthio)phenyl]ethynyl}phenyl)ethynyl]-3-*tert*-butylsalicylaldehyde (6b)

A mixture of (PPh₃)₂PdCl₂ (53 mg, 0.060 mmol) and CuI (12 mg, 0.060 mmol) was stirred for 1 h under vacuum in a flame dried Schlenk flask. Compound **5b** (205 mg, 0.74 mmol), iodosalicylaldehyde **3** (280 mg, 0.91 mmol) and dry triethylamine (6 mL) were added and the mixture was stirred overnight at 55 °C under an argon atmosphere. The reaction mixture was poured into water and extracted with CH₂Cl₂ (4 × 20 mL). The combined organic layers were washed with brine, dried over MgSO₄ and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography (silica gel, 20% Et₂O in pentane) to yield the product **6b** (186 mg, 0.41 mmol, 55%) as a yellow wax after evaporation of the solvent; δ_H(400 MHz; CDCl₃; Me₄Si) 1.44 (s, 9 H), 2.44 (s, 3 H), 7.41 (d, *J* 8.2 Hz, 2 H), 7.51 (s, 4 H), 7.56 (d, *J* 8.2 Hz, 2 H), 7.63 (d, *J* 2.0 Hz, 1 H), 7.67 (d, *J* 2.0 Hz, 1 H), 9.88 (s, 1 H), 11.95 (s, 1 H); δ_C(100 MHz; CDCl₃; Me₄Si) 29.3, 30.6, 35.2, 88.3, 90.6, 90.7, 90.9, 114.3, 120.7, 122.9, 123.5, 124.5, 128.5, 131.7, 131.9, 132.4, 134.5, 135.4, 137.3, 139.2, 161.6, 193.7, 196.9; HRMS (ES) calc. for C₂₉H₂₄O₃S 452.1446; found 452.1440.

(1*S*,2*S*)-*N*-(3,5-Di-*tert*-butylsalicylidene)-1,2-diphenylethylenediamine (7)

A Schlenk flask containing MS (3 Å, 1.5 g) and a magnetic stirring bar was dried with a flame under vacuum. 3,5-Di-*tert*-butylsalicylaldehyde **2b** (157 mg, 0.67 mmol), (1*S*,2*S*)-1,2-diphenylethylenediamine (144 mg, 0.68 mmol) and CH₂Cl₂ (dry, 5 mL) were added and the mixture was stirred for 3 h at rt under an argon atmosphere. The solids were filtered off and the volume of solvent was decreased to 0.5 mL by evaporation *in vacuo*. The residue was purified by flash chromatography (silica gel, 30% EtOAc in pentane) and, after evaporation of the solvent, **7** (226 mg, 0.53 mmol, 78%) was obtained as a yellow foam containing some minor impurities, arising from disproportionation of the product. Due to the lability of **7**, it was used directly in the next step without further purification; δ_H(400 MHz; CDCl₃; Me₄Si) 1.29 (s, 9 H), 1.48 (s, 9 H), 1.62 (s, 2 H), 4.31 (d, *J* 7.8 Hz, 1 H), 4.42 (d, *J* 7.8 Hz, 1 H), 7.08 (d, *J* 2.3 Hz, 1 H), 7.12–7.21 (m, 10 H), 7.40 (d, *J* 2.7 Hz, 1 H), 8.46 (s, 1 H), 13.59 (s, 1 H); HRMS (ES) calc. for C₂₉H₃₆N₂O 428.2828; found 428.2826.

(1*S*,2*S*)-*N*-(5-{2-[4-(Acetylthio)phenyl]ethynyl}-3-*tert*-butylsalicylidene)-*N'*-(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethylenediamine (8a)

A Schlenk flask containing MS (3 Å, 1.5 g) and a magnetic stirrer bar was dried with a flame under vacuum. Salicylaldehyde **6a** (78 mg, 0.23 mmol), amine **7** (100 mg, 0.23 mmol) and

CH₂Cl₂ (dry, 5 mL) were added and the mixture was stirred for 5 h under an argon atmosphere. The solids were filtered off and the volume of solvent was decreased to 0.5 mL by evaporation *in vacuo*. The residue was purified by flash chromatography (silica gel, 40% CH₂Cl₂ in pentane) to give **8a** (48 mg, 0.063 mmol, 27%) as a yellow solid after evaporation of the solvent; mp 114–116 °C; ν_{max} (KBr)/cm⁻¹ 3448 (OH), 2959 (CH), 2346 (C≡C), 1702 (CO), 1627 (C=N), 1441, 1273; δ_H(400 MHz; CDCl₃; Me₄Si) 1.15 (s, 9 H), 1.35 (s, 9 H), 1.37 (s, 9 H), 2.35 (s, 3 H), 4.63 (d, *J* 8.2 Hz, 1 H), 4.67 (d, *J* 8.2 Hz, 1 H), 7.11–7.19 (m, 12 H), 7.26 (d, *J* 2.3 Hz, 1 H), 7.30 (d, *J* 8.2 Hz, 2 H), 7.33 (d, *J* 2.0 Hz, 1 H), 7.43 (d, *J* 8.2 Hz, 2 H), 8.24 (s, 1 H), 8.25 (s, 1 H), 13.45 (s, 2 H); δ_C(100 MHz; CDCl₃; Me₄Si) 29.4, 29.6, 30.5, 31.6, 34.3, 35.1, 35.3, 80.2, 80.3, 86.9, 91.6, 112.3, 117.9, 118.7, 125.2, 126.4, 127.7, 127.8, 127.9, 128.2, 128.2, 128.6, 128.6, 128.7, 132.2, 133.2, 133.9, 134.4, 136.7, 138.0, 139.4, 139.7, 140.4, 158.1, 161.2, 166.5, 167.7, 193.9; HRMS (ES) calc. for C₅₀H₅₄N₂O₃S 762.3855; found 762.3901.

(1*S*,2*S*)-*N*-(5-{2-(4-{2-[4-(Acetylthio)phenyl]ethynyl}phenyl)ethynyl}-3-*tert*-butylsalicylidene)-*N'*-(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethylenediamine (8b)

A Schlenk flask containing MS (3 Å, 1.5 g) and a magnetic stirrer bar was dried with a flame under vacuum. Salicylaldehyde **6b** (48 mg, 0.106 mmol), amine **7** (60 mg, 0.14 mmol) and CDCl₃ (5 mL) were added and the mixture was stirred overnight under an argon atmosphere. Then MgSO₄ (50 mg) was added and the suspension was stirred for another 24 h. The solids were filtered off and the volume of solvent was decreased to 0.5 mL by evaporation *in vacuo*. The residue was purified by flash chromatography (silica gel, 10% Et₂O in pentane) to give **8b** (51 mg, 0.063 mmol, 56%) as a yellow solid after evaporation of the solvent; mp 118–120 °C; ν_{max} (KBr)/cm⁻¹ 3442 (OH), 2956 (CH), 2350 (C≡C), 1710 (CO), 1625 (C=N), 1441, 1384; δ_H(400 MHz; CDCl₃; Me₄Si) 1.15 (s, 9 H), 1.35 (s, 9 H), 1.38 (s, 9 H), 2.37 (s, 3 H), 4.64 (d, *J* 8.2 Hz, 1 H), 4.67 (d, *J* 8.2 Hz, 1 H), 6.87 (d, *J* 2.3 Hz, 1 H), 7.09–7.19 (m, 11 H), 7.26 (d, *J* 2.3 Hz, 1 H), 7.32–7.50 (m, 9 H), 8.26 (s, 1 H), 8.27 (s, 1 H), 13.48 (s, 2 H); δ_C(100 MHz; CDCl₃; Me₄Si) 29.3, 29.4, 29.6, 30.6, 31.6, 34.4, 35.2, 80.2, 80.3, 88.3, 90.7, 90.9, 91.1, 112.4, 117.9, 118.7, 124.1, 124.8, 125.5, 126.4, 127.8, 128.2, 128.2, 128.6, 128.7, 128.7, 130.2, 131.5, 131.5, 131.8, 132.3, 132.4, 133.1, 133.8, 134.5, 136.7, 138.0, 139.4, 139.7, 140.4, 143.6, 166.5, 167.7, 193.7. HRMS (ES) calc. for C₅₈H₅₈N₂O₃S 862.4168; found 862.4190.

5-Benzoylthio-3-*tert*-butylsalicylaldehyde (11)

The copper thiobenzoate **10** (1.75 g, 8.7 mmol) was added to a solution of iodoaldehyde **3** (1.00 g, 3.2 mmol) in HMPA (20 mL) in a flame dried Schlenk flask under an argon atmosphere. The mixture was stirred at 110 °C for 3 h and then poured into water (100 mL). The crude reaction mixture was extracted with diethyl ether (3 × 50 mL). The combined organic phases were washed with brine and water, dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, 10% Et₂O in pentane) to yield the product **11** (312 mg 0.99 mmol, 31%) as a thick brown oil after evaporation of the solvent; δ_H(400 MHz; CDCl₃; Me₄Si) 1.37 (s, 9 H), 7.43 (t, *J* 7.6 Hz, 2 H), 7.50 (s, 1 H), 7.51 (s, 1 H), 7.55 (t, *J* 6.8 Hz, 1 H), 7.95 (d, *J* 7.8 Hz, 2 H), 9.81 (s, 1 H), 11.92 (s, 1 H). δ_C(100 MHz; CDCl₃; Me₄Si) 29.6, 35.3, 117.1, 121.5, 127.7, 128.4, 129.1, 134.1, 136.5, 139.3, 140.1, 140.9, 162.5, 196.9; HRMS (ES) calc. for C₁₈H₁₈O₃S 314.0977; found 314.0972.

(1*S*,2*S*)-*N*-(5-Benzoylthio-3-*tert*-butylsalicylidene)-*N'*-(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethylenediamine (8c)

A Schlenk flask containing MS (3 Å, 1.5 g) and a magnetic stirrer bar was dried with a flame under vacuum. Salicylaldehyde

hyde **11** (53 mg, 0.17 mmol), amine **7** (72 mg, 0.17 mmol) and CDCl_3 (dry, 5 mL) were added and the mixture was stirred overnight at room temperature under an atmosphere of argon. The solids were filtered off and the volume of solvent was reduced to 0.5 mL by evaporation *in vacuo*. The residue was purified by flash chromatography (silica gel, 40% CH_2Cl_2 in pentane) to yield **8c** (60 mg 0.083 mmol, 49%) as a yellow foam after evaporation of the solvent; ν_{max} (KBr)/ cm^{-1} 3448 (OH), 2958 (CH), 2870, 1671 (CO), 1624 (C=N), 1435, 1204; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.24 (s, 9 H), 1.43 (s, 18 H), 4.74 (d, J 8.0 Hz, 1 H), 4.77 (d, J 8.0 Hz, 1 H), 6.98 (d, J 2.3 Hz, 1 H), 7.15–7.26 (m, 11 H), 7.33 (dd, J 6.2 Hz, J 2.0 Hz, 2 H), 7.46 (t, J 7.4 Hz, 2 H), 7.59 (t, J 7.4 Hz, 1 H), 7.99 (d, J 8.2 Hz, 2 H), 8.34 (s, 1 H), 8.38 (s, 1 H), 13.52 (s, 2 H); δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 29.4, 29.6, 31.6, 32.0, 34.3, 35.2, 79.9, 80.2, 114.9, 118.0, 119.6, 126.5, 127.6, 127.6, 127.8, 127.9, 128.2, 128.2, 128.6, 128.6, 128.9, 133.8, 136.6, 136.7, 136.9, 137.2, 139.0, 139.5, 139.8, 140.3, 158.2, 162.0, 166.4, 167.6, 191.3; HRMS (ES) calc. for $\text{C}_{47}\text{H}_{52}\text{N}_2\text{O}_3\text{S}$ 724.3699; found 724.3696.

General procedure for metal insertion

To a solution of the salen ligand (**8a**, **b** or **c**) (0.005 mmol) in methanol (7 mL) was added manganese(II) acetate tetrahydrate (2.5 mg, 0.010 mmol) and the solution was stirred for 30 min at 50 °C. Brine (0.5 mL) was added and the mixture was stirred for another 30 min at 50 °C. The solvent was evaporated *in vacuo* and the residue was dissolved in CH_2Cl_2 and washed with brine and H_2O . The organic phase was dried over Na_2SO_4 and evaporated *in vacuo* to give a quantitative yield of the catalysts **1a–c** as brownish solids. The catalysts were applied in the epoxidation reaction without further purification.

Epoxidation reaction

To a solution of the salen–MnCl catalyst **1a–c** (0.005 mmol), NMO (58.5 mg, 0.50 mmol) and (*Z*)-2-methylstyrene (11.8 mg, 0.10 mmol) in dry CH_2Cl_2 (5 mL) was added MCPBA (58 mg, 57–86% w/w, 0.20 mmol) in three portions at 0 °C. The solution was stirred for 2.5 h at 0 °C under an atmosphere of argon. The reaction was quenched by addition of 0.5 mL 1 M NaOH. The organic phase was separated and washed with brine and H_2O , dried over MgSO_4 and the solvent evaporated *in vacuo*. The enantiomeric excess and diastereomeric ratio were determined by chiral GC-MS using an Astec B-DM column. A 1 mM solution was injected and an initial column temperature of 70 °C was maintained for 5 minutes after which time it was increased at a rate of 5 °C min^{-1} for 15 min. The retention times were t_{R} (*cis*-epoxide) = 11.8 min (major) and 12.5 min (minor) and t_{R} (*trans*-epoxide) = 11.3 min and 11.4 min.

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