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Manganese(I)-catalyzed access to 1,2-bisphosphine ligands†

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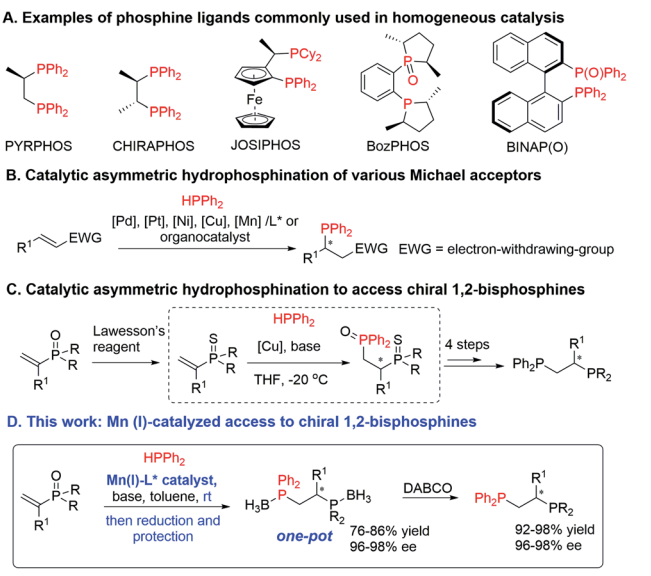
Chiral bisphosphine ligands are of key importance in transition-metal-catalyzed asymmetric synthesis of optically active products. However, the transition metals typically used are scarce and expensive noble metals, while the synthetic routes to access chiral phosphine ligands are cumbersome and lengthy. To make homogeneous catalysis more sustainable, progress must be made on both fronts. Herein, we present the first catalytic asymmetric hydrophosphination of α,β-unsaturated phosphine oxides in the presence of a chiral complex of earth-abundant manganese(I). This catalytic system offers a short two-step, one-pot synthetic sequence to easily accessible and structurally tunable chiral 1,2-bisphosphines in high yields and enantiomeric excess. The resulting bidentate phosphine ligands were successfully used in asymmetric catalysis as part of earth-abundant metal based organometallic catalysts.

The vast majority of important catalytic transformations make use of very effective catalysts based on scarce, expensive and toxic noble transition metals and phosphine containing ligands that, especially when chiral, are often as expensive as the noble metals themselves due to their cumbersome synthetic accessibility.[1] The past decade has witnessed significant progress towards the development of competitive catalysts that contain earth-abundant transition metals instead. These catalysts, however, still frequently rely on the use of chiral phosphine ligands. Bisphosphine ligands (Scheme 1A) for instance Pyrphos,[2a] Chiraphos,[2b] as well as Josiphos[2c] are among the most successful chiral ligands used in homogeneous catalysis. In recent years, bis(phosphine) monoxide compounds such as Bozphos,[2d] and Binap(o)[2e] have been shown to be powerful ligands in asymmetric catalysis as well. Unfortunately, the synthesis of these frequently and successfully used chiral phosphine-based ligands often requires stoichiometric amounts of chiral auxiliaries, enantiopure substrates, or separation by resolution to obtain them enantiomerically pure.[1b–f]

Catalytic asymmetric hydrophosphination is one of the most straightforward approaches for generating optically active P-chiral or C-chiral phosphines, from which chiral ligands can be derived.[3] The potential of hydrophosphination reactions to access enantioenriched chiral phosphines catalytically was demonstrated for the first time by Glueck and coworkers in 2001 using a catalytic system based on Pt and the chiral bisphosphine ligand Me-DuPhos.[4] Following the publication of this initial work, precious noble metal complexes such as chiral Pd or Pt catalysts have been widely used in the field of asymmetric hydrophosphination (Scheme 1B).[5] Only few examples utilizing earth-abundant metals such as Ni,[6] Cu[7] and very recently Mn[8] have been reported to date for catalytic asymmetric hydrophosphination. Apart from metal based catalytic systems, examples of asymmetric organocatalytic hydrophosphination reactions were also presented in the literature.[9] So far, all successful methods that rely on the addition of phosphines to



Scheme 1 (A) Examples of phosphine ligands commonly used in homogeneous catalysis. (B) Catalytic asymmetric hydrophosphination of various Michael acceptors. (C) This work: Mn (I)-catalyzed access to chiral 1,2-bisphosphines.

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α,β-unsaturated conjugated systems provide chiral monophosphines.[3] Interestingly, the only reported example of catalytic hydrophosphination that allows access to chiral 1,2-bisphosphine ligands utilizes a Michael acceptor with a P-containing electron-withdrawing group.[7b]

While α,β-unsaturated phosphine oxides are bench stable and readily available Michael acceptors, their application is less common when compared to conventional carbonyl based Michael acceptors, which is in part due to their lower reactivity.[10] Yin and co-workers found an elegant solution to this problem by transforming α,β-unsaturated phosphine oxides into phosphine sulphides. This allows a 'soft–soft' interaction to be established between the Cu(I) atom of the chiral Cu(I)-catalyst and the S atom of the phosphine sulphide, enabling catalytic hydrophosphination towards the synthesis of chiral bisphosphines.[7b] While successful in applying this strategy for catalytic synthesis of variety of chiral bisphosphines, nevertheless it requires 6-steps synthetic sequence starting from α,β-unsaturated phosphine oxides (Scheme 1C).[7b]

Herein, we present a highly efficient, short and scalable catalytic protocol for the synthesis of chiral 1,2-bisphosphines from readily available, bench stable α,β-unsaturated phosphine oxides employing Mn(I)-catalyzed hydrophosphination as its core transformation (Scheme 1D).

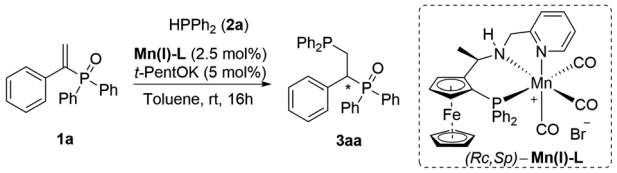
The last five years witnessed remarkable success of Mn(I)-complexes as catalysts for reductive transformations of carbonyl compounds including asymmetric variants.[11–13] Next to these reports, we have recently demonstrated that such complexes are capable of catalytic H–P bond activation of diarylphosphines.[8] Based on these findings we hypothesised that Mn(I)-complexes should be able to bring the phosphine oxide and the phosphine reagents into closer proximity thus allowing the hydrophosphination reaction to take place directly with α,β-unsaturated phosphine oxides. This approach would avoid the additional synthetic steps and purifications procedures necessitated by the installation and removal of the sulphur atom that are intrinsic to the method utilising phosphine sulphides.

At the outset of this work, bench-stable α-substituted α,β-unsaturated phosphine oxide **1a** was chosen as the model substrate in the reaction with $HPPh_2$ (Table 1). Chiral Mn(I)-complex, **Mn(I)-L**, developed by Clark and co-workers[13a,d] for hydrogenation and transfer hydrogenation of carbonyl compounds, was selected as the chiral catalyst. After extensive optimization, the reaction with 5 mol% *t*-PentOK, 2.5 mol% **Mn(I)-L**, 1.05 equiv. of $HPPh_2$ in toluene at room temperature for 16 hours was found to be optimal. Under these conditions, the product **3aa** was obtained with 96% isolated yield and over 99% ee (entry 1).

In the absence of both the base and the catalyst, as well as in the presence of only **Mn(I)-L**, no reaction occurs at room temperature (entries 2 and 3). In the presence of only the base (5 mol% of *t*-PentOK), however, 99% conversion towards the phosphine product **3aa** was observed (entry 4).[14]

The screening of various solvents (entries 5–8) revealed excellent yields and enantiomeric ratios when using any of the following solvents: toluene, THF, and 1,4-dioxane. Given that the stereocenter in this reaction is generated upon formal

Table 1 Optimization of the reaction conditions[a]



Entry	Deviation standard conditions	Conv.[b] (%)	Ee[c] (%)
1	None	>99 (96)[d]	>99
2	Without **Mn(I)-L** and *t*-PentOK	0	—
3	Without *t*-PentOK	0	—
4	Without **Mn(I)-L**	99	—
5	THF instead of toluene	99	96
6	1,4-Dioxane instead of toluene	98	97
7	i-PrOH instead of toluene	75	95
8	MeOH instead of toluene	90	52
9	*t*-BuOK instead of *t*-PentOK	99	97
10	Barton's base instead of *t*-PentOK	98	98
11	*t*-PentOK (2.5 mmol%)	56	99
12	*t*-PentOK (7.5 mmol%)	99	95

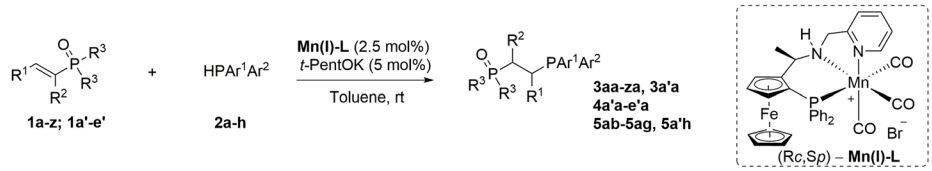
[a] General conditions: **1a** (0.1 mol), Mn(I) (2.5 mol%), *t*-PentOK (5 mol%), **2a** (0.105 mol) in toluene (1.0 ml) at rt for 16 h. [b] Determined by ^{1}H NMR of reaction crude. [c] Determined by HPLC on a chiral stationary phase. [d] Isolated yield.

stereospecific protonation, it was surprising that only a slight decrease in enantiomeric purity of the final product was observed in protic solvents, such as i-PrOH. On the other hand, running the reaction in MeOH led to a significant decrease in both substrate conversion and product ee.

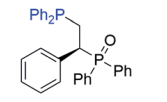
As for the nature of the base we discovered that alkoxides and Barton's base provide the best results regarding the product yield and enantiopurity. The optimal performance of the base in the Mn(I)-catalyzed reaction is achieved with between 1.5 and 2 equivalents of the base with respect to the catalyst. A higher or lower amount of the base results in lower enantioselectivity or lower yield, respectively (compare entries 1, 11 and 12).

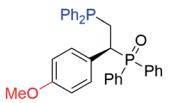
With the optimized conditions in hand, we moved to explore the scope of this methodology, first concentrating on the R^2 substituent on the phosphine oxide. Various substitutions with aryl or alkyl groups led to excellent results in all cases (Scheme 2). Substrates with either an electron-donating group (**3ba** and **3ca**) or an electron-withdrawing group (**3da**, **3ea**, and **3fa**) at the *para*-position of the phenyl ring led to the corresponding products with over 98% ee. The phenyl and ester functional groups at the *para*-position were also well tolerated, providing products **3ga** and **3ha** with high yields and enantiopurities. Similar results were obtained for substrates containing methyl- (**3ia**), chloro- (**3ja**) or methoxy- (**3ka**) substituents at the *meta*-position of the phenyl ring.

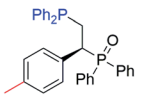
α,β-Unsaturated phosphine oxides containing a heteroaryl moiety, such as 2-naphthyl (**3ma**), 3-thienyl (**3na**), and 3-pyridinyl (**3oa**), were well applicable in our catalytic system. We were pleased to see that substrate **3pa**, bearing a ferrocenyl substituent – an essential structural component for many

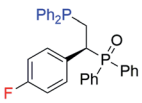


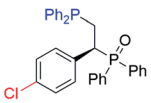
α-substituted α,β-unsaturated phosphine oxides

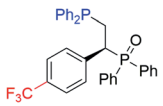

3aa
96% yield, >99% ee

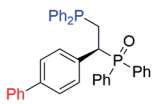

3ba
90% yield, 98% ee

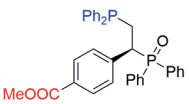

3ca
88% yield, 98% ee

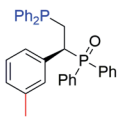

3da
98% yield, 98% ee

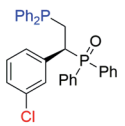

3ea
93% yield, 99% ee

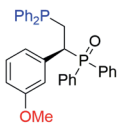

3fa
79% yield, 98% ee

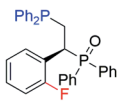

3ga
95% yield, 94% ee

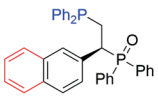

3ha
91% yield, 96% ee


3ia
81% yield, >99% ee

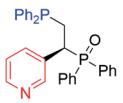

3ja
90% yield, 97% ee

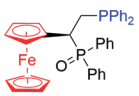

3ka
82% yield, 97% ee[b]

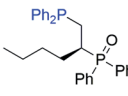

3la
94% yield, 93% ee

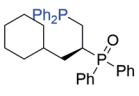

3ma
80% yield, 99% ee[b]

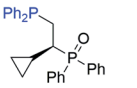

3na
97% yield, 97% ee

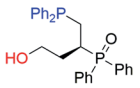

3oa
80% yield, 94% ee

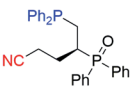

3pa
92% yield, 98% ee

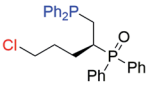

3qa
95% yield, >99% ee[c]

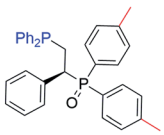

3ra
80% yield, 90% ee[c]

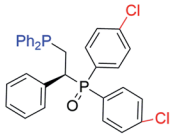

3sa
90% yield, >99% ee[c]

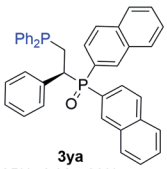

3ta
61% yield, 82% ee[d]


3ua
93% yield, >99% ee[c]

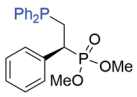

3va
88% yield, 93% ee[c]

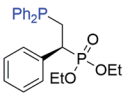

3wa
87% yield, 98% ee

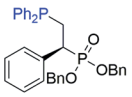

3xa
90% yield, 98% ee


3ya
95% yield, >99% ee

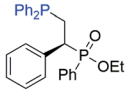
α-substituted α,β-unsaturated phosphinates and phosphonates


4a'a
88% yield, 90% ee

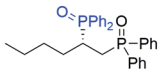

4b'a
79% yield, 89% ee

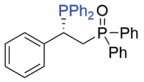

4c'a
78% yield, 91% ee


4d'a
98% yield, 95% ee

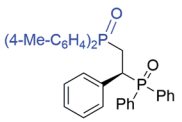

4e'a
88% yield, 1:1 dr
99% (80%) ee

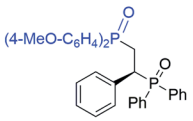
β-substituted α,β-unsaturated phosphine oxides


3za
82% yield, 87% ee[e,f,g]

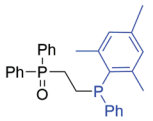

3a'a
no conversion

R_2PH or Ar^1Ar^2PH


5ab
82% yield, 96% ee[f]


5ac
76% yield, 42% ee[b,f]


5ag
no conversion


5a'h
86% yield, 0% ee[c]

Scheme 2 Product scope of Mn(I)-catalyzed asymmetric hydrophosphination of α,β-unsaturated phosphine oxides[a].[a]Reaction conditions: 0.1 M of **1** in toluene, **Mn(I)-L** (2.5 mol%), *t*-PentOK (5 mol%), $HP(Ar)_2$ (1.05 equiv) at rt. Isolated yields reported. For products **3aa** and **3za** the absolute configurations were determined by transforming them into the corresponding known compounds **6aa** and **6da** and for the remainder of the products by analogy (for details see ESI†); [b]5 mol% Barton's base used; [c]5 mol% **Mn(I)-L**,10 mol% *t*-PentOK used and reaction was carried out at rt for 72 h; [d]5 mol% **Mn(I)-L**,10 mol% *t*-PentOK used and reaction was carried out at rt for 5 days; [e]5 mol% **Mn(I)-L**,10 mol% *t*-PentOK used and reaction carried out at 60 °C; [f]the reaction quenched with H_2O_2; [g]for the absolute configuration of **3za**, see the ESI.†

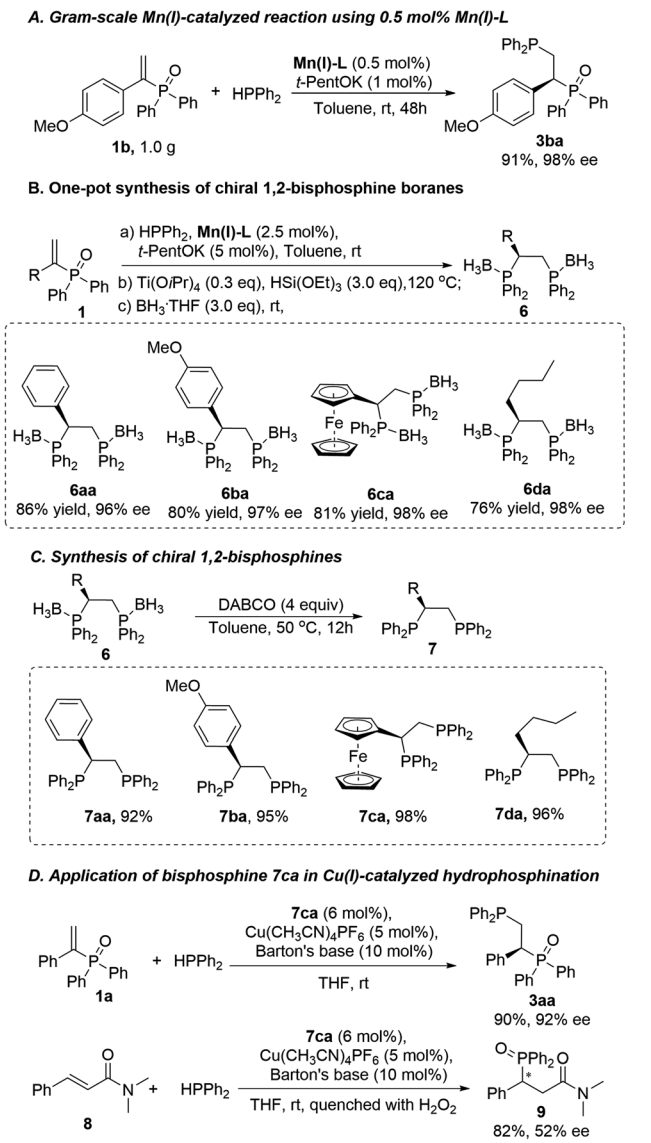
successful chiral ligands – can also be hydrophosphinated with excellent results. Next, α-alkyl substituted substrates were evaluated. The enantioselectivities observed for substrates with linear (**3qa**) and branched aliphatic substituents (**3ra** and **3sa**) were in line with the results obtained for their aromatic counterparts. Substrates bearing functional groups amenable to further transformations, namely hydroxyl- (**3ta**), cyano- (**3ua**) or chloro-substituents provided the corresponding phosphine products with equally good results. We then move to study the effect of varying the substituents at the phosphorus atom. Various unsaturated diaryl phosphine oxides are compatible with this catalytic system and afford the corresponding products **3wa**, **3xa**, and **3ya** with excellent enantiomeric excess and high isolated yield.

The relatively less reactive β-butyl-substituted α,β-unsaturated phosphine oxide is well tolerated as well, providing the corresponding enantioenriched oxide product **3za** with 87% ee. On the other hand, no conversion to the product **3a′a** was observed with β-phenyl-substituted α,β-unsaturated phosphine oxide. Interestingly, this catalytic system also supports α,β-unsaturated phosphonates, generating the corresponding final products (**4a′a**, **4b′a**, **4c′a**, and **4d′a**) with enantiomeric excesses in the range of 89–95%. The catalytic protocol was also applied to a phosphinate substrate, allowing access to the product **4e′a** with two chiral centers (dr 1 : 1) with high ee. Finally, screening of various phosphine reagents revealed some limitations of the protocol. Hydrophopshination with $(p\text{-Me-C}_6\text{H}_4)_2\text{PH}$ and $(p\text{-MeO-C}_6\text{H}_4)_2\text{PH}$ led to the corresponding products **5ab** and **5ac** with good yields and good to excellent enantioselectivities. However, no conversion was obtained with the sterically more demanding $(o\text{-Me-C}_6\text{H}_4)_2\text{PH}$, $(3,5\text{-CF}_3\text{-C}_6\text{H}_3)_2\text{PH}$, nor with Cy_2PH and $(p\text{-CF}_3\text{-C}_6\text{H}_4)_2\text{PH}$. Attempts to access P-chiral phosphine product *via* addition of racemic diarylphosphine to α, β-unsaturated phosphine oxides led to the racemic P-chiral phosphine **5a′h**.

To demonstrate the potential application of our catalytic protocol in chiral phosphine ligand synthesis, we performed a gram-scale reaction between **1b** and **2a** (Scheme 3A). To our delight, the catalyst loading could be decreased to 0.5 mol%, leading to the product **3ba** without deterioration of the yield (91%) or the enantioselectivity (98%).

Building on these results, we then developed a highly efficient one-pot method for the synthesis of four different chiral phosphine boranes (**6aa–6da**) (Scheme 3B) that yield the corresponding chiral 1,2-bisphosphine ligands (**7aa–7da**) in a single deprotection step (Scheme 3C). As is typical of any phosphines, the 1,2-bisphosphines **7** prepared in this study can easily oxidize during chromatographic purifications.[7b]

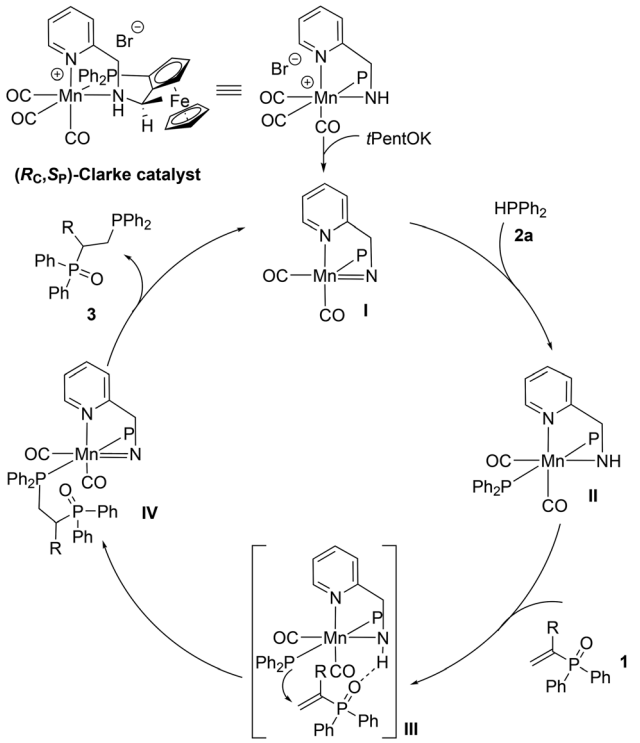
Therefore, to minimise chromatographic purification, as well as to facilitate product separation, degassed water was used to wash the reaction mixture, followed by the removal of volatiles under high vacuum. The free ligands **7** were obtained in good yields and high purity. Importantly, the 1,2-bisphosphine **7aa** is a known, efficient chiral ligand for Rh-catalyzed asymmetric hydrogenation of α-amino-α,β-unsaturated esters.[7b] We also examined our bisphosphine ligand **7ca** in the Cu-catalyzed hydrophosphination of α,β-unsaturated phosphine oxide **1a**



Scheme 3 (A) Gram-scale Mn(I)-catalyzed reaction using 0.5 mol% **Mn(I)-L**. (B) One-pot synthesis of chiral 1,2-bisphosphine boranes. (C) Synthesis of chiral 1,2-bisphosphines. (D) Application of bisphosphine **7ca** in Cu(I)-catalyzed hydrophosphination.

(Scheme 3D), obtaining the desired product **3aa** in good yield (90%) and high enantioselectivity (92%). Similarly, α,β-unsaturated carboxamide **8** was investigated,[7c] providing the corresponding product **9** in good yield (82%) and moderate ee (52%).

From a mechanistic point of view, we wondered whether our base activated Mn-catalyst **I** is involved in the activation of the phosphine reagent **2a** *via* ligand–metal cooperation, as proposed in our previous work on α,β-unsaturated nitriles,[8] or whether it also plays a role in the activation of the phosphine oxide substrate **1**. Preliminary NMR spectroscopic studies did not reveal any interaction between **I** and **1** (see ESI†) leading us to hypothesise that the current transformation might follow a mechanistic path that primarily involves phosphine activation, as depicted in Scheme 4. Additional interaction between the NH and P═O moieties of the catalyst and phosphine oxide



Scheme 4 Hypothetical catalytic cycle.

respectively is also possible and cannot be excluded at this stage. Detailed mechanistic studies are currently underway.

In summary, we have developed the first manganese(I) catalyzed enantioselective strategy for the hydrophosphination of α, β-unsaturated phosphine oxides. This methodology allows a high-yielding, catalytic, two-step sequence for the synthesis of enantiopure chiral 1,2-bisphosphine ligands, that were successfully applied in asymmetric catalysis. Since manganese is the third most abundant transition metal in the Earth's crust, a general catalytic method to access chiral bisphosphine ligands using this metal is further step towards more sustainable homogeneous catalysis. Further work is currently underway in order to unravel the mechanism of this transformation.

Data availability

Detailed synthetic procedures, complete characterization data for all new compounds can be found in the ESI.†

Author contributions

L. G conducted all experiments and characterized the novel compounds. L. G and S. R. H designed the experiments and wrote the manuscript. S. R. H directed the research.

Conflicts of interest

The authors declare no conflict of interest.

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