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Graphical Abstract

In-situ generated chiral iron complex as efficient catalyst for enantioselective sulfoxidation using aqueous H_2O_2 as an oxidant

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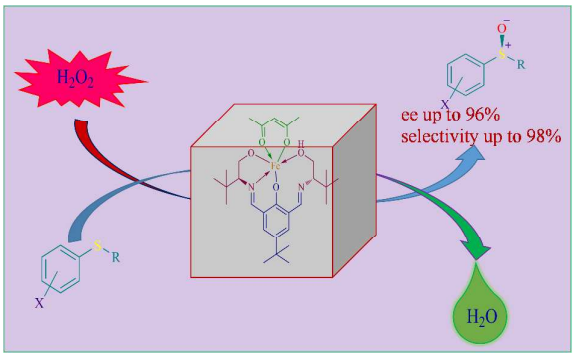

This study represents the rare combination of non-toxic Fe based catalyst/H_2O_2 as an efficient catalytic protocol for asymmetric sulfoxidation reaction.

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A series of amino alcohol derived Schiff base ligands **L1**-**L4** were synthesised and characterized. Iron complexes of these ligands [Fe**L1**(acac)], [Fe**L2**(acac)], [Fe**L3**(acac)] and [Fe**L4**(acac)] were generated *in situ* to catalyze the asymmetric oxidation of prochiral sulfides using aqueous H_2O_2 as a terminal oxidant. One of these complexes [Fe**L1**(acac)] was identified as very efficient catalyst for the enantioselective oxidation of a series of alkyl aryl sulfides with excellent enantioselectivity (75% to 96% ee), conversion (up to 92%) and chemo selectivity (up to 98%). During the optimization process, a series of electron donating benzoic acid derivatives were found to favour both conversion and enantioselectivity.

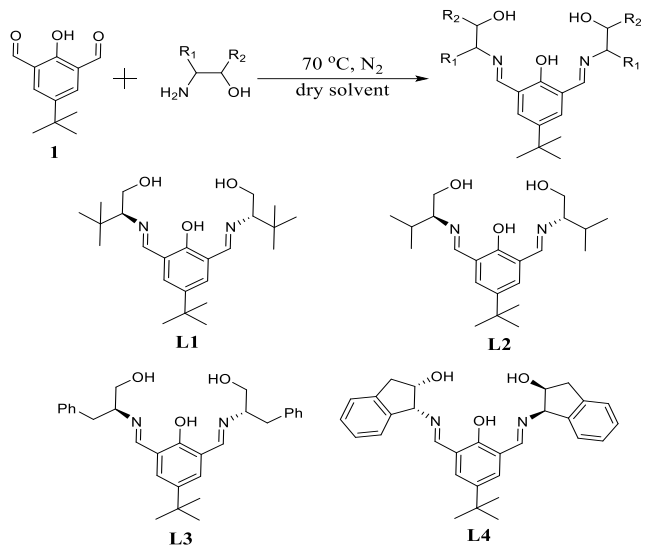
Introduction

Chiral sulfoxides are valuable compounds for their application as chiral auxiliaries,[1] ligands,[2] organo-catalysts[3] and in pharmaceutical industries.[4] The direct and most efficient synthetic route to synthesize chiral sulfoxides was developed simultaneously by Kagan *et al.*[5] and Modena *et al.*[6] adapting modified Sharpless epoxidation catalytic system. Since then there were spurt of activities in this area of research and in the course of period various organocatalysts[7] and metal based catalysts have been developed[8] including titanium,[9] vanadium,[10] manganese,[11] iron,[12] aluminum,[13] copper[14] and polyoxometalate.[15] Though metal based catalysts efficiently promote asymmetric sulfoxidation reaction, the contamination of toxic metal in the product is a serious issue especially in the synthesis of biologically active intermediates and products. In this context iron being an essential bio element, its use in various organic transformations was widely encouraged[16] because of its low cost, abundance in nature and environmental friendly aspects. Recently Benjamin List *et al.* reported a novel concept of an asymmetric counter-anion directed catalysis (ACDC)[12t] in asymmetric sulfoxidation reaction using iron complex. This catalytic protocol provided an excellent enantioselectivity for few substrates using PhIO as an oxidant. Among the asymmetric sulfoxidation protocol utilizing iron based catalysts with hydrogen peroxide is attractive for environment and economic reasons but at the same time has inherent disadvantage as iron is known to decompose H_2O_2, thereby cause catalyst destruction *via* hydroxyl radical generation.[12r] Yet Fontecave and co-worker's[12i-12k] dinuclear iron-(–)-4,5-pinene-2,2'-bipyridine complex and Bolm *et al*'s[12l] iron-amino alcohol derived Schiff base complexes had set the stage for the iron-H_2O_2 combination. Although the yield and enantioselectivity were low to moderate with this protocol, a quantum improvement in the catalytic performance was observed when a catalytic amount of Li/Na salt of 4-methoxy benzoic acid was used as an additive.[12m, 12n] Later on Katsuki *et al.* has also reported the use of iron-salan complex with H_2O_2[12p] in water medium for the sulfoxidation reaction with high yield and enantioselectivity. Still, Fe-H_2O_2 combination is under-represented for this reaction, except for couple of reports e.g., Simonneaux *et al.* in 2011[12r] reported an iron-porphyrin catalyst (maximum sulfoxide ee 87%) and Tsogoeva *et al.*[12s] in 2012 using *in situ* generated iron complex of primary amine-derived non-symmetrical Schiff base (with $FeCl_3$ as iron source) but with lower enantioselectivity (highest ee being 36%). Our conviction for Fe-H_2O_2 based catalytic system is that a suitable modification in promising salen and salan ligands in combination with an appropriate iron source may provide excellent results. With this view we have prepared a series of pentadentate salen ligands **L1**-**L4** and used their *in situ* generated iron complexes as catalyst in enantioselective sulfoxidation of prochiral sulfides. Among these, the ligand **L1** with [Fe(acac)$_3$] as iron source

proved to be an efficient catalytic system by providing excellent enantioselectivity up to 98% ee in the presence of 4-MeO-C_6H_4COOH as an additive.

Results and discussion

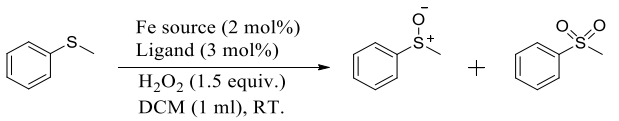
A series of pentadentate salen ligands **L1**-**L4** were synthesized by simple condensation of commercially available bis-aldehyde (**1**) with different chiral amino alcohols as shown in scheme 1. Treating these ligands with $Fe(acac)_3$ with appropriate M:L ratio in CH_2Cl_2, a series of Fe complexes [Fe**L1**(acac)] to [Fe**L4**(acac)] were generated *in situ*.



Scheme 1 Synthesis and structure of ligands (**L1**-**L4**).

The *in situ* generated iron complexes Fe**L1**(acac), Fe**L2**(acac), Fe**L3**(acac) and Fe**L4**(acac), were applied as catalyst in asymmetric sulfoxidation reaction using methyl phenyl sulfide as a model substrate and aqueous H_2O_2 (30%) as an oxidant in CH_2Cl_2 at room temperature (25 °C ± 2). The respective data are given in Table 1. Since free iron salt itself can catalyze the oxidation of sulfide in a non-enantioselective manner (Table 1, entry 1), the ligand was taken in slight excess (1.5 equiv.) to ensure complete consumption of $Fe(acac)_3$. All these ligands gave moderate to high conversions and excellent selectivity (Table 1, entries 2-5), which clearly indicates that there is no beneficial oxidative kinetic resolution taking place under this reaction condition (see supporting information for detail). However among these ligands, the ligand **L1** (Table 1, entry 2) was found better in terms of both enantioselectivity (ee, 73%) and yield (82%). Other ligands (**L2, L3** and **L4**) with varied amino alcohols resulted in significant drop in enantioselectivity (Table 1, entries 3-5). To further investigate the effect of iron source with the optimized ligand **L1**, attempts were made with [Fe(III)(dphpd)$_3$] (dphpd = 1,3-diphenyl-1,3-propanedionate) and $FeCl_3$ (Table 1, entries 6 and 7) and observed that none of these sources were better than $Fe(acac)_3$ in terms of conversion and enantioselectivity.

Table 1 Screening of ligands and iron source for asymmetric sulfoxidation of methyl phenyl sulfide[a]

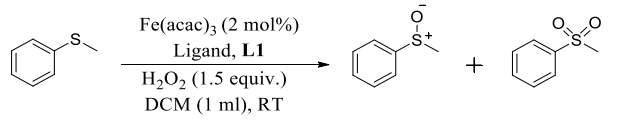


Entry	Ligand	Iron source	Conversion[b] (%)	Selectivity[b] (%)	ee[c] (%)
1	-	$Fe(acac)_3$	21	-	-
2	**L1**	$Fe(acac)_3$	82	95	73
3	**L2**	$Fe(acac)_3$	75	90	40
4	**L3**	$Fe(acac)_3$	67	98	18
5	**L4**	$Fe(acac)_3$	55	98	20
6	**L1**	$Fe(dphpd)_3$	29	99	27
7	**L1**	$FeCl_3$	22	99	5

[a] Reaction condition: methyl phenyl sulfide (0.25 mmol), Fe source (2 mol%), Ligand (3 mol%), aqueous H_2O_2 (30%, 1.2 equiv.), in CH_2Cl_2 (1 ml) at RT for 12 h. [b] Conversion and selectivity were calculated by ^1H NMR analysis. [c] Enantiomeric excess were determined by HPLC analysis on a chiral phase Daicel Chiralcel OD column.

Based on these experimental results, the ligand **L1** and $Fe(acac)_3$ was selected as preferred combination and was taken forward to optimize the catalyst loading and metal to ligand ratio as shown in Table 2. We have observed a considerable decrease in the enantioselectivity, when the catalyst loading (by keeping metal to ligand ratio 1:1.5) was decreased to 1 mol% (entry 1; conversion 70%; ee 59%) from 2 mol% (entry 2; conversion 82%; ee 73%) taken in the beginning. At the same time an increase in the catalyst loading to 4 mol% was of no consequence particularly in improving enantioselectivity (entry 3; conversion 93%; ee 72%), although there was an increase in conversion, but product selectivity dropped significantly (Table 2, entries 1-3).

Table 2 Optimization of catalyst loading and metal to ligand ratio with **L1**/$Fe(acac)_3$[a]

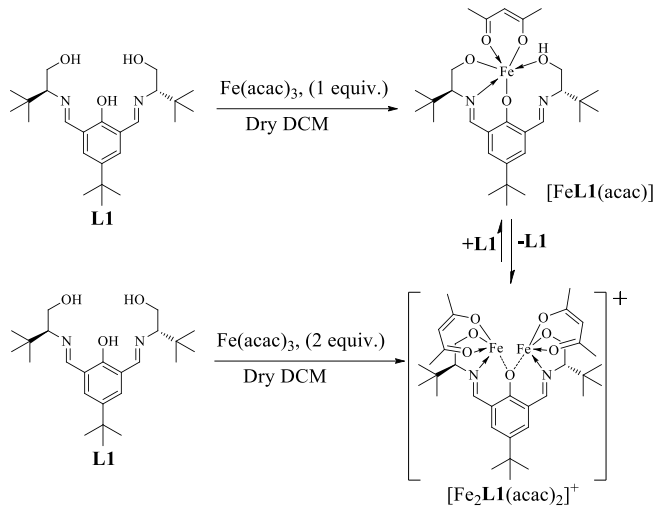


Entry	Catalyst loading (mol%)	Metal:Ligand	Conversion[b] (%)	Selectivity[b] (%)	ee[c] (%)
1	1	1:1.5	70	94	59
2	2	1:1.5	82	95	73
3	4	1:1.5	93	85	72
4	2	1:0.5	67	94	55
5	2	1:1.0	73	96	64
6	2	1:2.0	76	96	68
7[d]	2	1:1.5	81	95	65

[a] Reaction condition: methyl phenyl sulfide (0.25 mmol), $Fe(acac)_3$, **L1**, aqueous H_2O_2 (30%, 1.2 equiv.), in CH_2Cl_2 (1 ml) at RT for 12 h. [b] Conversion and selectivity were calculated by ^1H NMR analysis. [c] Enantiomeric excess were determined by HPLC analysis on a chiral phase Daicel Chiralcel OD column. [d] H_2O_2 was added at once.

Considering the structure and the number of the donor atoms in the ligand, the formation of bimetallic complex cannot be ruled out (Scheme 2). Hence to address this issue, UV-vis and ESI-MS

spectra were recorded for the *in situ* generated complexes of $Fe(acac)_3$ and ligand **L1** in 1:1 and 2:1 ratios. The UV-vis spectra (Fig. 1) recorded for 1:1 metal to ligand ratio revealed peaks at 332, 340 and 430 nm, while the 2:1 ratio showed peaks at 359, 388 and 432 nm, which clearly indicates the formation of different predominant complexes.



Scheme 2 Plausible structures of the *in situ* generated monomeric [Fe**L1**(acac)] and dimeric [Fe_2**L1**$(acac)_2$] complex.

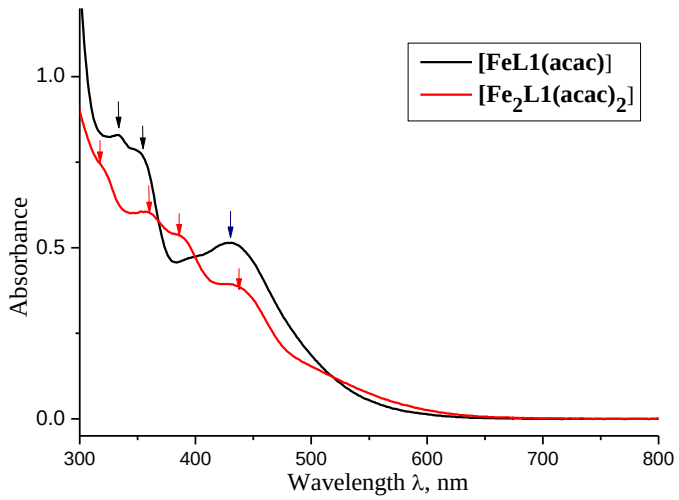


Fig. 1 UV vis. spectra of *in situ* generated complex with metal to ligand ratio of 1:1 and 2:1.

The ESI-MS spectra (see supporting information) recorded for 1:1 ratio (Figure S1) showed predominant peak at m/z = 558.39 attributed to monoprotonated mononuclear species [Fe**L1**(acac)+H^+] which matches with the calculated value 558.28 and a trace of binuclear monopositive molecular ion *i.e.*, [Fe_2**L1**$(acac)_2$]$^+$ at 711.41. On the other hand for 2:1 ratio, a significant amount of binuclear species was detected in the ESI-MS spectra (Figure S2) along with the mononuclear complex. These mononuclear and binuclear complexes were further analyzed by the HRMS. The obtained m/z for mononuclear complex [Fe**L1**(acac)] and binuclear complex ion [Fe_2**L1**$(acac)_2$]$^+$ are 557.2666 (calculated value 557.278) and 711.2378 (calculated value 711.2395) respectively support our assumption (Figure S3 and S4). Interestingly, the complex prepared with 1:1 ratio of metal and ligand in CH_2Cl_2 or $CHCl_3$ on aging (>2 days) partially crystallize out **L1** and the supernatant liquid showed m/z peaks arising out of both bimetallic and monometallic species. Due to this behavior it was prudent to optimize the M:L ratio. It is noteworthy to mentioned that in the 2:1 metal:ligand ratio, a significant drop in both conversion and enantioselectivity (Table 2, entry 4, conversion 67%, ee 55%) was observed, while with 1:1 ratio the conversion was almost comparable (Table 2, entry 5: conversion 73%, ee 64%). Further the ee value was little less than what was obtained with 1:1.5 ratio. An increase in the metal to ligand ratio beyond 1:1.5 like in the case of 1:2 (conversion 76%, ee 68%) was counterproductive. These experimental results (Table 2, entries 4-6) and spectral studies discussed above clearly indicate that the monometallic complex is more reactive and enantioselective than the bimetallic complex.

In continuation of optimization of the reaction parameters, the effect of oxidants such as urea hydrogen peroxide (UHP) and *tert* butyl hydrogen peroxide (TBHP), were also tested besides 30% aqueous H_2O_2 and the respective date are depicted in Figure 2. The conversion and enantioselectivity obtained for UHP were moderate, whereas TBHP as an oxidant fared poorly with this catalytic system, nevertheless the catalyst retained the high selectivity for the desired product.

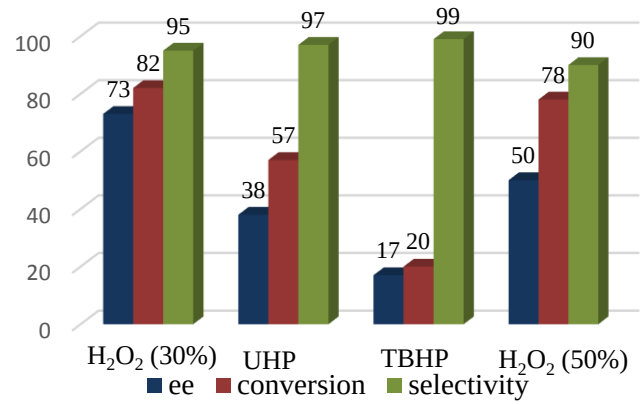
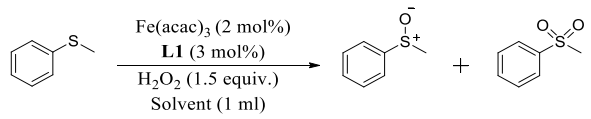


Fig. 2 Effect of oxidant on the enantioselective oxidation of methyl phenyl sulfide, catalyzed by *in situ* generated [Fe**L1**(acac)] complex in CH_2Cl_2 at RT.

Next, effect of solvent using CH_2Cl_2, $CHCl_3$, CH_3OH, THF, toluene, dimethyl carbonate (DMC) and diethyl carbonate (DEC) were screened adapting above optimized reaction conditions (Table 3). The results in CH_2Cl_2 and $CHCl_3$ (Table 3, entries 1 and 2) were at par, but other solvents caused significant drop in the ee (Table 3, entries 3-5). A trial to replace the chlorinated solvent by green solvents like DMC and DEC (Table 3, entries 6-7) was failed as these solvents gave very poor conversion and ee. Furthermore a little increase in the enantioselectivity was observed on reducing the temperature from RT to 15 °C, but

caused lowering the conversion (Table 3, entries 8 and 9) below 15 °C.

Table 3 Variation of solvents for the asymmetric oxidation of methyl phenyl sulfide with **L1**/Fe(acac)$_3$ system[a]



Entry	Solvent	Conversion[b] (%)	Selectivity[b] (%)	ee[c] (%)
1	CH_2Cl_2	82	95	73
2	$CHCl_3$	75	96	70
3	CH_3OH	67	98	14
4	THF	60	98	55
5	$PhCH_3$	85	96	40
6	DMC	20	97	10
7	DEC	25	96	26
8[d]	CH_2Cl_2	79	95	80
9[e]	CH_2Cl_2	71	98	81

[a] Reaction condition: methyl phenyl sulfide (0.25 mmol), Fe(acac)$_3$ (2 mol%), **L1** (3 mol%), aqueous H_2O_2 (30%, 1.2 equiv.), in organic solvent (1 ml) at RT for 12 h. [b] Conversion and selectivity were calculated by ^{1}H NMR analysis. [c] Enantiomeric excess were determined by HPLC analysis on a chiral phase Daicel Chiralcel columns. [d] The reaction was carried out at 15 °C. [e] The reaction was carried out at 5 °C.

Taking a clue from the results published by Bolm *et al.*[12m, 12n] we further tried to increase the enantioselectivity of the present system by using sub-stoichiometric amounts of electron rich benzoic acid derivatives as additive. The use of *p*-OMeC$_6$H$_4$COOH (2 mol%) as an additive revealed its beneficial effect on the conversion and enantioselectivity (conversion 91%, ee 88%) (Fig. 3). But the same additive at higher loadings beyond 2 mol% caused lowering the enantioselectivity significantly. Furthermore, several other electron rich benzoic acid derivatives and sodium salt of *p*-OMeC$_6$H$_4$COOH were also checked (Table S1). Among these, the *p*-OMeC$_6$H$_4$COOH was found to be ideal for better conversion (91%), selectivity (95%) and ee (88%).

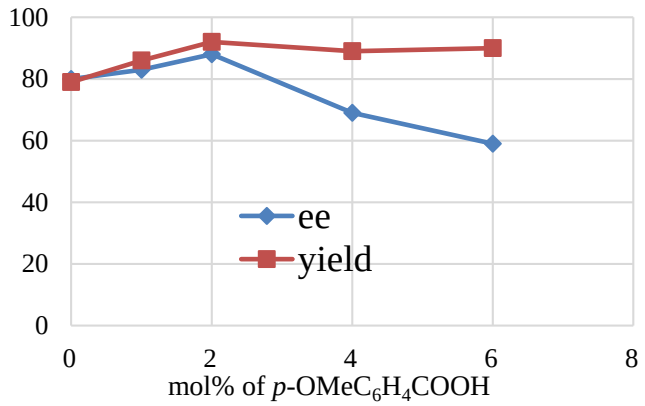
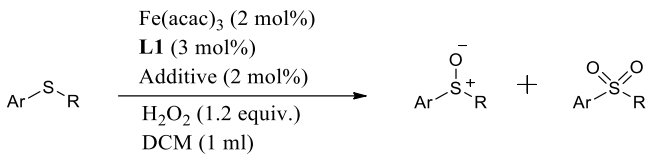
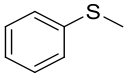
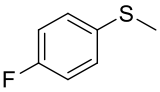
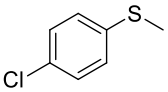
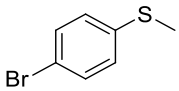
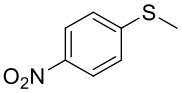
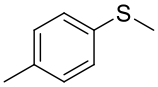
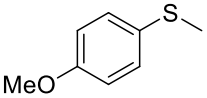
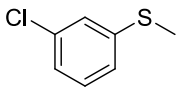
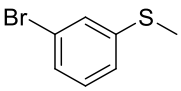
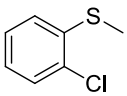
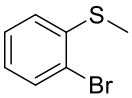
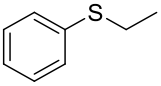
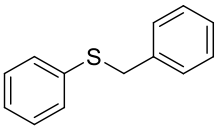
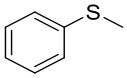


Fig. 3 Effect of the concentration of *p*-OMeC$_6$H$_4$COOH as additive on enantioselective oxidation of methyl phenyl sulfide catalyzed by *in situ* generated **[**Fe**L1**(acac)] complex at 15 °C.

Finally adapting 2 mol% of Fe(acac)$_3$, 3 mol% of ligand **L1**, 2 mol% *p*-OMeC$_6$H$_4$COOH and 1.2 equiv. of aqueous H_2O_2 in CH_2Cl_2 at 15 °C as optimum reaction condition, we applied this catalytic protocol for the asymmetric oxidation of various prochiral alkyl aryl sulfides (Table 4). Alkyl aryl sulfides with electron withdrawing F, Cl, Br substituent at *para* position

Table 4 Enantioselective oxidation of various prochiral sulfides with *in situ* generated Fe**L1**(acac)$_3$ complex[a]



Entry	Sulfide	Conversion[b] (%) (Yield)	Selectivity[b] (%)	ee[c] (%)
1		91 (86)	95	88
2		78 (76)	98	95
3		82 (80)	98	95
4		81 (79)	97	94
5		72 (69)	96	96
6		90 (86)	96	87
7		92 (86)	93	85
8		79 (77)	98	96
9		80 (78)	97	94
10		80 (76)	95	91
11		78 (73)	94	90
12		89 (87)	98	85
13		88 (85)	97	75
14[d]		90 (85)	94	89

[a] Reaction condition: Sulfide (0.25 mmol), $Fe(acac)_3$ (2 mol%), **L1** (3 mol%), *p*-$OMeC_6H_4COOH$ (2 mol%), additive (1 mol%), aqueous H_2O_2 (30%, 1.2 equiv.), in CH_2Cl_2 (1 ml) at 15 °C for 12 h. [b] Conversion and selectivity were calculated by ^1H NMR analysis and the values in the parentheses refer to calculated yield. [c] Enantiomeric excess were determined by HPLC analysis on a chiral phase Daicel Chiralcel columns. [d]Reaction was carried out in 0.75 mmol scale.

(Table 4, entries 2-5), *meta* position (Table 4, entry 8-9) and *ortho* position of aromatic ring (Table 4, entries 10 and 11) behaves almost similar and gave high selectivity (up to 98%) and excellent ee (91% to 96%) but provided little low conversions with respect to unsubstituted methyl phenyl sulfide (Table 4, entry 1). Replacing electron withdrawing substituent at the *para* position by electron donating Me and OMe group (Table 4, entries 6, 7) retains both conversion and ee as obtained for representative substrate, but we noticed a little lowering of the selectivity (93%).

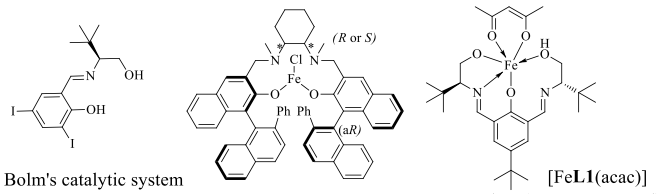


Fig. 4 Structural correlation of present catalyst with previously reported iron based catalytic systems.

For most of the alkyl aryl sulfides the enantioselectivity is comparable with the previously reported Fe/H_2O_2 based Bolm's[12n] and Katsuki's[12p] catalytic system (Fig. 4), however we observed a significant improvement in the yield of the sulfoxide and in case of *ortho* substituted substrate both yield and enantioselectivity are higher when compared to the Bolm's system. But, in case of substrates with electron donating group, slight inferior results were obtained compared to the Katsuki's catalytic system. Finally we have used ethyl phenyl sulfide (Table 4, entry 12) and benzyl phenyl sulfide (Table 4, entry 13) as variant for the methyl group and obtained comparable enantioselectivity as reported by Bolm *et al*. and Katsuki *et al*. The little drop in enantioselectivity in case of ethyl phenyl sulfide (conversion 89%, ee 85%) and benzyl phenyl sulfide (conversion 88%, ee 75%) having bulkier ethyl and benzyl group may be attributed to the steric effect in comparison with the methyl group. This catalytic system retained the activity even with 0.75 mmol scale (Table 4, entry 14).

Experimental

General

All the solvents were dried using standard procedures, distilled and stored under nitrogen. NMR spectra were obtained with a Bruker-Avance-DPX-200 (200 MHz) or 500 MHz spectrometer at ambient temperature using tetramethylsilane (TMS) as internal standard. Electronic spectra were recorded in chloroform on a Varian Cary 500 Scan UV–vis.–NIR spectrophotometer and TOFF mass of the catalysts and ligands were determined on a Micromass Q-TOF-micro instrument. Microanalysis of the ligands were carried out on a Perkin Elmer 2400 CHNS analyser. Enantiomeric excess (ee) values were determined by Shimadzu-HPLC with SPD-M10A-VP and SPD-M20A UV detector and PDR-Chiral Lnc. advanced Laser Polarimeter (PDR-CLALP), using chiral Daicel Chiralcel columns with 2-propanol/hexane mixture as eluent of the crude products.

Typical experimental procedure for the enantioselective sulfoxidation reaction

A mixture of **1** (0.0075 mmol) and $Fe(acac)_3$ (0.005 mmol) in dry CH_2Cl_2 (1 ml), was stirred for 3 h at room temperature. After the formation of the complex, *p*-$OMeC_6H_4COOH$ (0.005 mmol) was added to the reaction mixture and the stirring was continued for another 20 min. Following this an appropriate sulfide (0.25 mmol) was added to the reaction mixture, which was allowed to stir for another 20 min. Finally the reaction mixture was cooled to 15 °C and 1.2 equiv. of aqueous hydrogen peroxide (30%; 34 µl, 0.3 mmol) was added in 6 fraction over 40 min. and the reaction mixture was allowed to stir for 12 h. Then the reaction was quenched by washing the organic layer with water (1 ml x 3), sample of the crude reaction mixture was taken for the HPLC and NMR analysis to determine enantioselectivity, conversion and selectivity.

General methods for the synthesis of ligands (L1- L4):

General methods for the synthesis of ligands

Chiral ligands were synthesized by the condensation reaction of readily available 4-*tert*-butyl-2,6-diformylphenol **with chiral** 2-aminoethanol derivatives by the modified procedure. The solvent for the condensation was taken depending on the solubility of the product.

Synthesis of ligand L1: To a stirring solution of 4-*tert*-butyl-2,6-diformylphenol (1 mmol) in dry toluene (10 ml) under nitrogen atmosphere, was added (*S*)-(+)-*tert*-Leucinol (1.2 mmol) solution in 2 ml dry toluene at room temperature under N_2 atm. After the addition of (*S*)-(+)-*tert*-Leucinol, yellow precipitate of the ligand appeared to form. The reaction mixture was then heated to 70 °C and allowed to stir for 36 h. After the complete consumption of the bis-aldehyde, yellow precipitate was filtered and washed three times with cold toluene to remove the excess (*S*)-(+)-*tert*-Leucinol and dried under vacuum. yield: 88 %; m.p.: 247-249 °C; ^1H NMR (500 MHz, DMSO-D_6): δ = 14.65 (s, 1H), 8.53 (s, 2H), 7.80 (s, 2H), 4.49 (s, 2H), 3.78 (d, *J* = 10.5 Hz, 2H), 2.86, (d, *J* = 8.5 Hz, 2H), 1.29 (s, 9H), 0.92 (s, 18H); ^{13}C NMR (50 MHz, DMSO-D_6): δ = 159.15, 139.73, 128.11, 120.64, 80.51, 60.45, 33.65, 32.76, 31.07; Anal. Calcd. for $C_{24}H_{40}N_2O_3$ C, 71.25; H, 9.97; N, 6.92%; Found C, 71.31; H, 9.89; N, 6.97%; TOF-MS (ESI^+): m/z Calcd. for $[C_{24}H_{40}N_2O_3]$ 404.30, Found 405.31 $[M]+H^+$.

Synthesis of ligand L2, L3 and L4: To a stirring solution of 4-*tert*-butyl-2,6-diformylphenol (1 mmol) in dry methanol (2 ml), was added (*S*)-(+)-Valinol (1.2 mmol)/(*S*)-(-)-phenylalaninol (1.2 mmol)/ (1*R*,2*S*)-(+)-cis-1-Amino-2-indanol (1.2 mmol) in methanol (0.5 ml). After the addition of amino alcohol, the color of the reaction mixture changed from yellow to deep yellow, which was followed by the formation of a precipitate. The reaction mixture was then allowed to stir for 24 h. After the complete consumption of 4-*tert*-butyl-2, 6-diformylphenol (checked in TLC), the precipitate was filtered off, washed with cold hexane and finally dried in vacuum.

Ligand L2: Yellow solid; yield: 88 %; m.p.: 197-199 °C; ^{1}H NMR (500 MHz, DMSO-D$_6$): δ = 14.57 (s, 1H), 8.56 (s, 2H), 7.77 (s, 2H), 4.66 (s, 2H), 3.65 (d, *J* = 10 Hz, 2H), 3.00 (s, 2H), 1.90 (m, 2H), 1.27, (s, 9H), 0.86, (d, *J* = 7 Hz, 12H); ^{13}C NMR (125 MHz, DMSO-d6): δ = 159.48, 139.64, 128.42, 120.67, 76.96, 62.74, 33.67, 31.09, 29.21, 19.89, 18.00; Anal. Calcd. for $C_{22}H_{36}N_2O_3$ C, 70.18; H, 9.64; N, 7.44%; Found C, 70.24; H, 9.59; N, 7.48%; TOF-MS (ESI$^+$): m/z Calcd. for [$C_{22}H_{36}N_2O_3$] 376.27, Found 377.28 [M]+H$^+$.

Ligand L3: Yellow solid; yield: 88 %; m.p.: 136-138 °C; ^{1}H NMR (500 MHz, DMSO-D$_6$): δ = 14.25 (s, 1H), 8.38 (s, 2H), 7.68 (s, 2H), 7.26-7.23 (m, 4H), 7.19-7.14 (m, 6H), 4.83 (s, 2H), 3.61 (m, 2H), 3.48 (d, *J* = 3.5, 2H), 2.97 (dd, *J* = 13.5 Hz, *J* = 3.5 Hz, 2H), 2.79 (dd, *J* = 13.5 Hz, *J* = 8 Hz, 2H), 1.25 (s, 9H); ^{13}C NMR (125 MHz, DMSO-D$_6$): 159.19, 139.84, 138.90, 129.35, 128.13, 125.96, 120.45, 73.01, 64.24, 38.47, 33.74, 31.13; Anal. Calcd. for $C_{30}H_{36}N_2O_3$ C, 76.24; H, 7.68; N, 5.93%; Found C, 76.19; H, 7.74; N, 5.87%; TOF-MS (ESI$^+$): m/z Calcd. for [$C_{30}H_{36}N_2O_3$] 472.27, Found 473.28 [M]+H$^+$.

Ligand L4: Yellow solid; yield: 88 %; m.p.: 195-197 °C; ^{1}H NMR (500 MHz, DMSO-D$_6$): δ = 14.18 (br, 1H), 8.81 (s, 1H), 8.68 (s, 1H), 7.82 (s, 1H), 7.53 (d, *J* = 2.5 Hz, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.35-7.34 (m, 1H), 7.31-7.27 (m, 2H), 7.23-7.21 (m, 3H), 7.14-7.12 (m, 1H), 5.04 (br, 2H), 4.77-4.70 (m, 2H), 4.53 (q, *J* = 5 Hz, 2H), 3.17-307 (m, 2H), 2.99-2.89 (m, 2H), 1.27 (s, 9H); ^{13}C NMR (125 MHz, DMSO-D$_6$): δ = 166.43, 161.38, 158.84, 142.39, 142.07, 141.81, 141.63, 141.17, 140.98, 139.17, 139.06, 128.52, 128.48, 127.99, 127.78, 126.69, 126.57, 126.46, 125.58, 124.99, 124.62, 124.62, 124.55, 124.43, 117.35, 87.28, 78.48, 74.05, 73.77, 73.20, 68.35, 33.72, 31.12; Anal. Calcd. for $C_{30}H_{32}N_2O_3$ C, 76.90; H, 6.88; N, 5.98%; Found C, 76.84; H, 6.93; N, 6.07%; TOF-MS (ESI$^+$): m/z Calcd. for [$C_{30}H_{32}N_2O_3$] 468.24, Found 469.25 [M]+H$^+$.

Conclusions

In conclusion, highly efficient iron-H_2O_2 based catalytic protocol was developed for asymmetric sulfoxidation. The simplicity of the procedure and reaction condition makes it attractive over other metal catalyzed catalytic systems. This catalyst not only showed high enantioselectivity (up to 96%) for sterically and electronically diverse type of sulfides, but it also provides excellent chemo selectivity (up to 98%) with good conversion (up to 92%). Substrates containing electron withdrawing substituents seem to be less reactive as those gave comparatively low conversion, but provide slightly higher enantioselectivity and chemo selectivity even for *ortho* substituted sulfides.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Characterization data of products, ^{1}H, ^{13}C NMR spectra of products and ligands and HPLC chromatograms of products are described herein]. See DOI: 10.1039/b000000x/

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