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Asymmetric sulfoxidation of prochiral sulfides using aminoalcohol derived chiral C_3-symmetric trinuclear vanadium Schiff base complexes

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Abstract—A series of trimeric variants of the efficient and well known Bolm's chiral vanadium salen catalysts are reported. These C_3-symmetric trinuclear chiral Schiff bases were synthesized by condensing a variety of trialdehydes with optically active aminoalcohols. The catalytic activity of the chiral vanadium complexes of these ligands was investigated for the enantioselective oxidation of prochiral sulfides using hydrogen peroxide as an oxidant. The procedure afforded the corresponding sulfoxide in good yield and the enantioselectivities were comparable to those obtained with the mononuclear complexes.

1. Introduction

Enantiomerically pure sulfoxides are widely used as drug intermediates in pharmaceutical industries,[1] and also chiral sulfinyl groups have been used as auxiliaries in a variety of highly diastereoselective carbon–carbon bond forming reactions, including the synthesis of α-branched amines, α- and β-amino acids, aziridines, and amino phosphonic acids.[2]

Enantioselective sulfide oxidations catalyzed by chiral complexes of transition metals such as titanium, manganese, iron, and vanadium have produced interesting results in the synthesis of optically active sulfoxides.[3] Fujita et al. have introduced the use of alkyl peroxide as the oxidant for vanadium catalyzed asymmetric sulfoxidation.[4] Subsequently, Bolm et al.[5] have employed a highly selective and promising aminoalcohol based mononuclear chiral Schiff base vanadium complexes (Fig. 1). These catalyst systems gave high enantioselectivity with very low catalyst loading in the presence of an environmentally benign, nontoxic, and inexpensive stoichiometric oxidant. Various modifications of Bolm's vanadium Schiff base complexes have been synthesized and explored. Polymer supported modification[6] of these vanadium Schiff base complex has also been reported in recent years; however, it gave moderate yield and enantioselectivity. Herein we report the first synthesis of a series of chiral trinuclear aminoalcohol based vanadium Schiff base complexes, which when applied for asymmetric sulfide oxidation gave higher yields with moderate to good enantioselectivities of the sulfoxides.

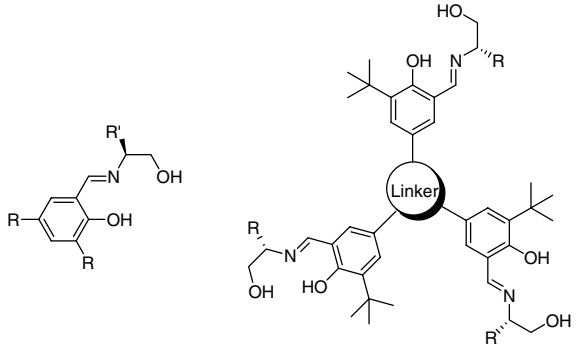

Figure 1.

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2. Results and discussion

2.1. Synthesis and characterization of the ligands

In asymmetric catalysis, chiral ligands with a C_3-axis of symmetry showed higher level of asymmetric induction.[7] Similarly, multi-metallic complexes were generally found to induce higher enantioselectivity in many asymmetric transformations.[8] Although the effect of additional chirality in the Bolm type catalyst had been explored, multinuclear Bolm type catalysts have not been explored so far. A series of trinuclear chiral vanadium Schiff base complexes were synthesized and explored for the enantioselective oxidation of prochiral sulfides for the first time. Trialdehydes with different architectures namely (i) trialdehydes with all the formyl groups in the same aromatic moieties; and (ii) trialdehydes with formyl groups in different aromatic moieties separated by tethers. Different chiral aminoalcohols were also employed for this purpose. C_3-Symmetric tris(hydroxyaldehyde) without a spacer **1** was synthesized by Duff formylation of phloroglucinol.[9]

Structurally related triketones were synthesized for a comparative study. Accordingly, 1,1′,1″-(2,4,6-trihydroxybenzene-1,3,5-triyl)triethanone **2** and (2,4,6-trihydroxybenzene-1,3,5-triyl)tris(phenylmethanone) **3** were synthesized by Fries rearrangement of the corresponding benzene-1,3,5-triyl triacetate and benzene-1,3,5-triyl tribenzoate (Fig. 2). Trialdehydes possessing tunable tethers (more than one atom) were synthesized from 3-*tert*-butyl-2,5-dihydroxybenzaldehyde. The EDCI coupling of 3-*tert*-butyl-2,5-dihydroxybenzaldehyde with benzene-1,3,5-tricarboxylic acid in the presence of a catalytic amount of DMAP and anhydrous CH_2Cl_2 afforded the corresponding tris(hydroxyaldehydes) **4** in 74% yield according to Scheme 1.

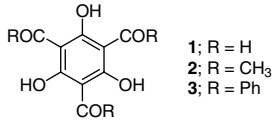


Figure 2.

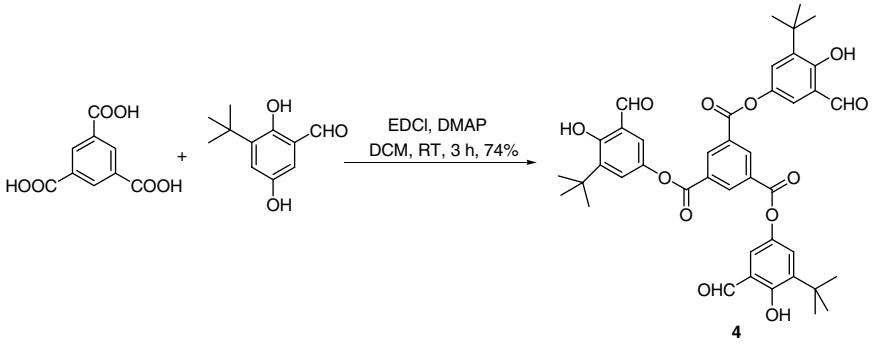
Apart from ligands with ester based tethers, the conjugated acetylene tethered tris(hydroxyaldehyde) ligand with an acetylene backbone was synthesized. The trialdehyde, 5,5′,5″-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(3-*tert*-butyl-2-hydroxybenzaldehyde) was synthesized from 1,3,5-tribromobenzene according to Scheme 2. Accordingly, 1,3,5-tris((trimethylsilyl)ethynyl)benzene was synthesized via a Pd-catalyzed Sonogashira–Hagihara cross-coupling of ethynyltrimethylsilane with 1,3,5-tribromobenzene. Deprotection of the TMS group gave 1,3,5-triethynylbenzene in 97% yield. Compound 1,3,5-triethynylbenzene was unstable under normal conditions. However, under the second Sonogashira–Hagihara cross-coupling with 3-*tert*-butyl-2-hydroxy-5-iodobenzaldehyde, the trialdehyde was formed in 52% yield (Scheme 3).[10]

The chiral aminoalcohols for the ligand synthesis were synthesized from the corresponding amino acids. (*S*)-Amino-acids were converted to the corresponding methyl ester hydrochloride and then reduced using sodium borohydride to afford aminoalcohols in good yields.

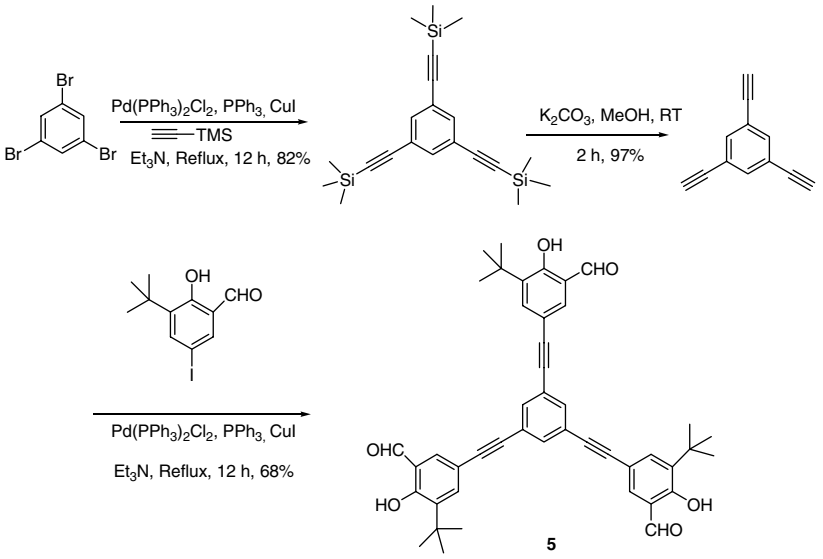
Microwave irradiation (5 min) of a mixture of trialdehydes and chiral aminoalcohols in the presence of potassium carbonate afforded chiral trinuclear Schiff bases in good yields (89–96%) (Scheme 3). The condensation does not require any anhydrous condition and in many cases the products were purified by column chromatography over silica gel. The yields of the chiral ligands formed are given in Table 1.

Trinuclear Schiff base ligands derived from structurally related triketones were also attempted in a similar way. Accordingly, a mixture of triketone 1,1′,1″-(2,4,6-trihydroxybenzene-1,3,5-triyl)triethanone and (*S*)-2-amino-3-phenylpropan-1-ol was subjected to microwave irradiation, the reaction however did not produce any trinuclear ligand as observed by NMR and MS. On the other hand, the reaction afforded only the mono condensed product (Scheme 4), which did not undergo any further condensation with higher equivalents of the aminoalcohol and also upon further irradiation.

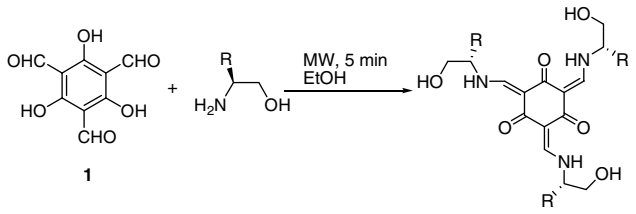
Proton NMR spectra of chiral ligands **L7** and **L8** showed a single set of proton NMR signals indicating a highly symmetrical structure, and also indicating that the ligands were perfectly C_3-symmetric in nature. The proton NMR spectra of C_3-symmetric chiral ligands **L1**–**L6** were surprisingly complicated. In these cases, the ^{1}H NMR spectra showed a



Scheme 1.



Scheme 2.



Scheme 3.

doublet around 8.0–8.5 ppm and doublet of doublet around 11.5–12.5 ppm in $CDCl_3$ instead of the expected singlets around 8.0 ppm (imine NH) and ~12 ppm (phenolic OH). Similarly, ^{13}C NMR showed the carbonyl resonance of the central ring at ca. 185 ppm, characteristic of the keto isomer.

Both the spectral data indicated that the compound did not exist in an imine form, but as the corresponding keto-enamine isomers. Plausible isomeric structures of compound **L4** are shown in Figure 3 as compounds (A)–(C). ^1H NMR and ^{13}C NMR spectra of compound **L4** shown in Figure 4a and b, respectively, confirmed the presence of symmetric isomers of a keto-enamine (B) in $CDCl_3$. The single crystal X-ray crystallographic structure of **L2** also supported this hypothesis.[11]

2.2. Asymmetric sulfoxidation studies catalyzed by chiral vanadium Schiff base complexes

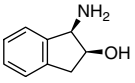
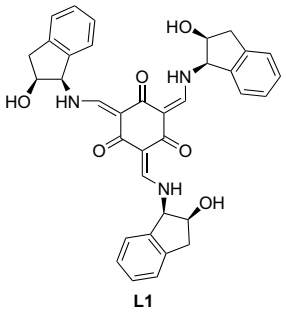
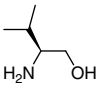
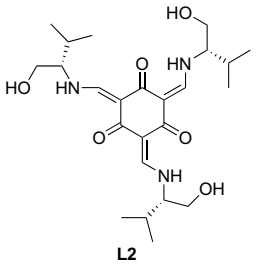
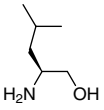
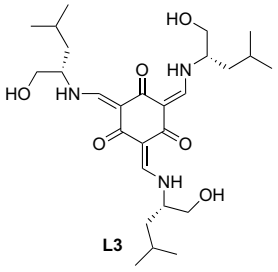
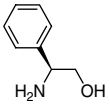
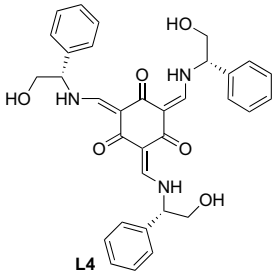
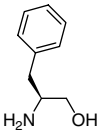
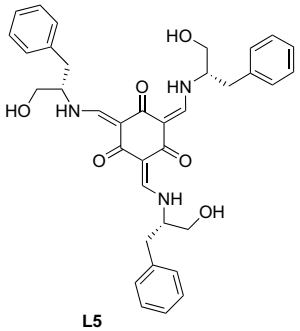
2.2.1. Asymmetric sulfoxidation of methyl phenyl sulfide using C_3-symmetric chiral trinuclear vanadium Schiff's base complexes. The catalytic efficiency of the trinuclear vanadium complexes was evaluated for the enantioselective oxidation of prochiral sulfides. The well established Bolm's protocol was followed for the oxidation of thioanisole, in which the catalytic system was formed in situ from the reaction of $VO(acac)_2$ and a C_3-symmetric chiral ligand (Scheme 5). The environmentally benign hydrogen peroxide was used as an oxidant and the reaction was carried out at room temperature with dichloromethane as solvent. The procedure afforded the chiral sulfoxide in good yields, however, the enantioselectivities were moderate compared to those reported with a monomeric chiral vanadium Schiff base catalyst system.

2.2.2. Effect of the substituents of the chiral aminoalcohol of the ligand on thioanisole oxidation. A series of functionalized trinuclear Schiff base ligands as shown in Table 2 were used to explore the steric effect of the R group on the chiral carbon of the aminoalcohol moiety toward the enantioselectivity of sulfide oxidation.

All the ligands displayed poor enantioselectivity in combination with $VO(acac)_2$. The poor selectivity could be either due to the existence of the ligands as keto-enamine isomer in comparison to the usual ONO imine environment observed with other Schiff bases or due to steric crowding of metal centers with respect to one another.

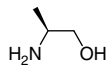
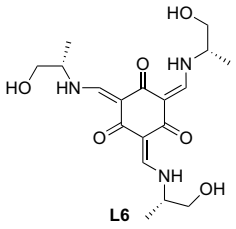
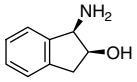
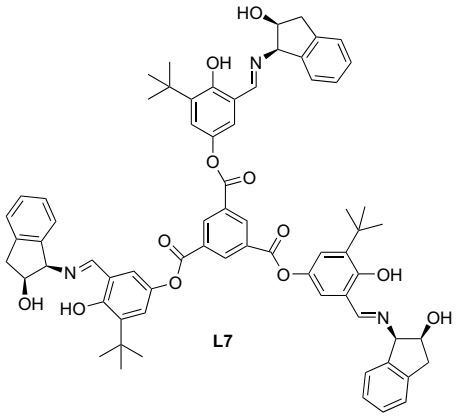
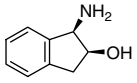
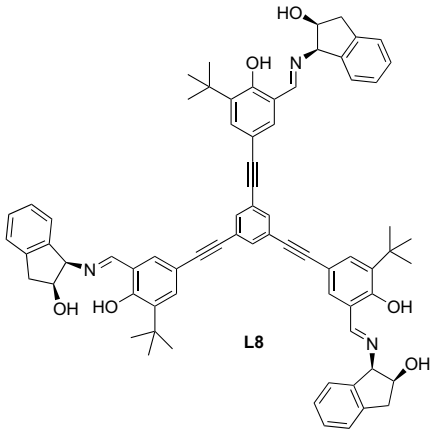
2.2.3. Asymmetric oxidation of aryl methyl sulfide catalyzed by $VO(acac)_2$/trinuclear Schiff bases possessing tethers. The lower activity of ligands **L1**–**L5** toward the enantioselective oxidation of thioanisole was overcome by employing trinuclear ligands possessing tethers. Ligands **L7** and **L8** were used for this purpose. The use of tethers in the ligand keeps all three catalytic centers far apart. The ONO coordinating system possessing a *tert*-butyl group resembles the Bolm's ligand and behaved as three individual moieties under the experimental conditions exhibiting good reactivity and enantioselectivity. Both the ligands with the ester and acetylene based tethers exhibited similar reactivity during the oxidation of aryl methyl sulfides affording sulfoxides in 81–98% yield and 54–89% ee depending on the electronic effect of the substituent on the *para*-position of the benzene ring of the substrate (Table 3).

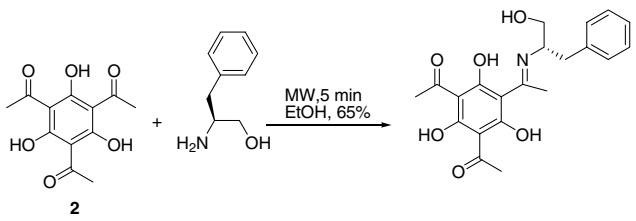
Table 1.

Trialdehyde	Aminoalcohol	C_3-Symmetric ligand	Yield (%)
1		 **L1**	96
1		 **L2**	86
1		 **L3**	74
1		 **L4**	93
1		 **L5**	96

(*continued on next page*)

Table 1 (*continued*)

Trialdehyde	Aminoalcohol	C_3-Symmetric ligand	Yield (%)
1		 **L6**	92
4		 **L7**	93
5		 **L8**	98



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Scheme 4.

The catalytic oxidation reaction of benzyl phenyl sulfide provided high yields (92–98%) and remarkable enantioselectivity (86–89%) (Table 3, entry 6), whereas the electron-deficient sulfide bearing a nitro group on the *para*-position of the aryl group resulted in moderate enantioselectivity (50–54%) though in good yields (Table 3, entry 4). As the nitro group is replaced by an electron donating methyl or methoxy group, the ee values increased to 80–82% (Table 3, entry 3).

3. Conclusion

An efficient and facile method for the synthesis of trinuclear Schiff base ligands derived from chiral aminoalcohols in good yields has been described. All the ligands in combination with $VO(acac)_2$ resemble the most efficient Bolm's catalyst which forms a multi-metallic catalyst system for an asymmetric sulfoxidation reaction. The vanadium complex with all the three salen moieties in the same aryl moiety displayed poor enantioselectivity toward the

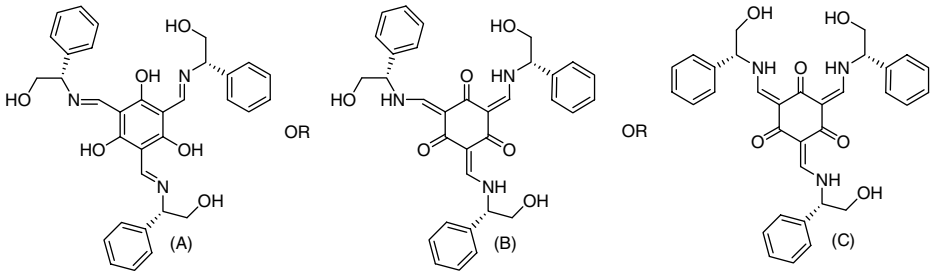


Figure 3.

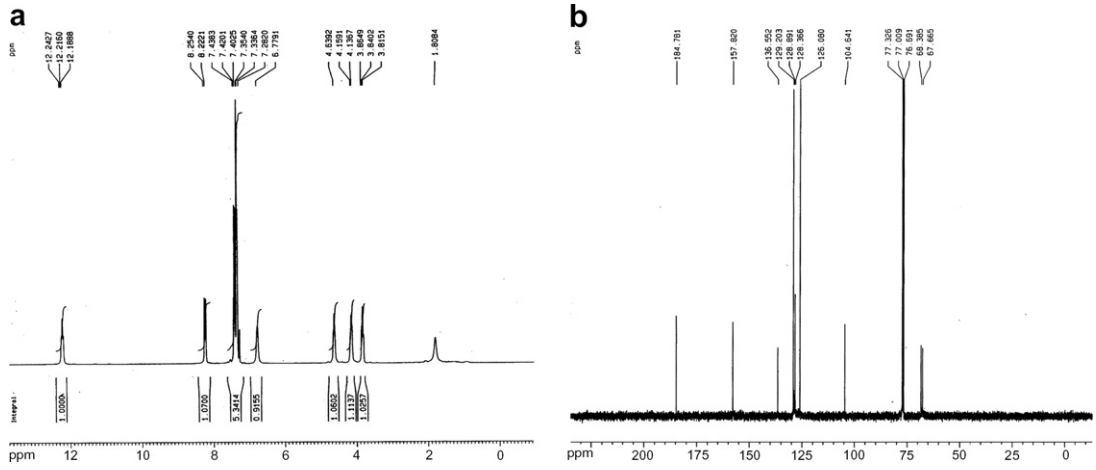
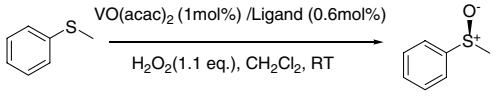


Figure 4.



Scheme 5.

Table 2. Asymmetric oxidation of thioanisole catalyzed by different $VO(acac)_2$/trinuclear Schiff base ligands derived from various chiral aminoalcohols

Entry	Ligands screened	Yield (%)	ee (%)	Configuration
1	**L1**	91	12	(*R*)
2	**L2**	89	8	(*S*)
3	**L3**	87	6	(*S*)
4	**L4**	93	5	(*S*)
5	**L5**	90	4	(*S*)

asymmetric oxidation of aryl methyl sulfides. However, catalysts derived from ligands with the three salen moieties separated from one another by a tether displayed high enantioselectivities. The salen moieties of these complexes behaved as individual units and both the ligands with a flexible (ester) and rigid (acetylene) tether showed similar reactivities and enantioselectivities. A more detailed mechanistic investigation of the presented catalyst systems as well as broad catalytic studies is currently under way.

Table 3. Asymmetric oxidation of aryl methyl sulfides catalyzed by $VO(acac)_2$/**L7** or **L8**

Entry	Thioethers	Ligands employed	Yield (%)	ee (%)
1	$PhSCH_3$	**L7**	92	70
		L8	88	72
2	*p*-CH_3PhSCH_3	**L7**	95	83
		L8	94	78
3	*p*-OCH_3PhSCH_3	**L7**	90	80
		L8	90	82
4	*p*-$BrPhSCH_3$	**L7**	87	62
		L8	87	67
5	*p*-NO_2PhSCH_3	**L7**	82	54
		L8	81	58
6	$PhSCH_2Ph$	**L7**	98	86
		L8	92	89

4. Experimental

4.1. General information

^1H NMR spectra were recorded on 400 MHz Bruker AVANCE 400 spectrometer and ^{13}C NMR spectra were recorded on 100 MHz Bruker AVANCE 400 spectrometer, respectively, using TMS as an internal standard. IR spectra were recorded on a Perkin–Elmer FT/IR 100 spectrometer. Mass spectra were recorded on MALDI TOF mass spectrometer. Optical rotations were measured by a Rudolph Autopol V polarimeter. All reactions were monitored by

thin layer chromatography (TLC). TLC was performed on F254, 0.25 mm silica gel plates (Merck). Plates were eluted with appropriate solvent systems, and then stained with either alkali $KMnO_4$ or Ceric ammonium molybdate solutions prepared in the laboratory. The developed plates were first analyzed under UV 254 nm then stained with the appropriate reagent. Column chromatography was performed using silica gel with particle size 100–200 mesh. High-performance liquid chromatograph with Daicel Chiracel OD-H (25 cm × 0.46 cm i.d.) and Daicel Chiracel OB-H (25 cm × 0.46 cm i.d.) chiral columns were used for the measurements.

4.2. General procedure for the synthesis of chiral C_3-symmetric aminoalcohol based Schiff's base ligands

To a solution of trialdehyde (1 mmol) in ethanol (1 mL) was added a solution of corresponding equivalent of chiral aminoalcohol in ethanol (1 mL). The homogeneous mixture was irradiated in an unmodified domestic microwave oven at a low power setting for 5 min. The reaction mixture was then cooled to room temperature and ethanol was removed under reduced pressure to afford the crude product which was purified by column chromatography over silica gel using EtOAc–hexane to give pure C_3-symmetric aminoalcohol based Schiff's base ligands as yellow solids (86–98% yield).

4.2.1. Spectral data for L1. Yellow solid; yield 96%; $[\alpha]_D^{25} = +28.5$ (c 0.6, $CHCl_3$); IR (KBr): 3338, 3050, 2975, 1619, 1547, 1448, 858, 841, 738 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.82 (br s, 1H), 2.87–3.04 (m, 2H), 4.42–4.56 (m, 2H), 7.21–7.43 (m, 5H), 7.91 (s, 1H), 11.25 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 39.9, 67.6, 73.6, 105.2, 125.2, 127.2, 128.8, 139.4, 141.0, 157.1, 184.5; mp slow decomposition >156 °C; HRMS (ESI) calcd for $C_{36}H_{33}N_3O_6$ $[M+H]^+$: Calcd: 604.7317; Obsd: 604.7320.

4.2.2. Spectral data for L2. Yellow solid; yield 96%; $[\alpha]_D^{25} = -274.8$ (c 0.35, $CHCl_3$); IR (KBr): 3322, 3054, 2965, 1613, 1546, 1458, 1377, 1307, 1265, 1074, 858, 841, 738 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.04–1.06 (d, $J = 4.9$ Hz, 6H), 1.93–1.95 (m, 1H), 3.26 (m, 1H), 3.60–3.66 (t, $J = 12$ Hz, 1H), 3.94–3.97 (d, $J = 12$ Hz, 1H), 6.43 (br s, 1H) 8.01–8.04 (d, $J = 12$ Hz, 1H), 11.57–11.63 (dd, $J = 12$ Hz and 12 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 17.9, 19.3, 29.3, 64.4, 70.4, 104.1, 158.5, 184.5; mp slow decomposition >135 °C; HRMS (ESI) calcd for $C_{24}H_{40}N_3O_6$ $[M+H]^+$: Calcd: 466.2917; Obsd: 466.2940.

4.2.3. Spectral data for L3. Orange syrup; yield 91%; $[\alpha]_D^{25} = -172.6$ (c 0.85, $CHCl_3$); IR (KBr): 3401, 2959, 1612, 1546, 1461, 1378, 1320, 1265, 1153, 1069, 836, 739 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.83 (s, 6H), 1.21–1.59 (m, 2H), 1.91–1.92 (m, 1H), 1.91–2.00 (dd, $J = 16$ Hz and 4 Hz, 1H), 3.36–3.38 (t, $J = 12$ Hz, 1H), 3.76–3.79 (d, $J = 12$ Hz, 1H), 6.32 (br s, 1H) 7.86–7.89 (d, $J = 12$ Hz, 1H), 11.13–11.19 (dd, $J = 12$ Hz and 12 Hz 1H); ^{13}C NMR ($CDCl_3$): δ 22.6, 23.2, 24.8, 39.7, 62.8, 66.6, 104.0, 157.9, 184.4; HRMS (ESI) calcd for $C_{27}H_{46}N_3O_6$ $[M+H]^+$: Calcd: 508.3342; Obsd: 508.3360.

4.2.4. Spectral data for L4. Orange solid; yield 94%; $[\alpha]_D^{25} = +181.2$ (c 0.5, $CHCl_3$); IR (KBr): 3304, 2923, 2862, 1605, 1546, 1452, 1376, 1313, 1230, 1071, 832, 758 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.81–3.87 (t, $J = 9.6$ Hz, 1H), 4.13–4.15 (d, $J = 9.6$ Hz, 1H), 4.63 (m, 1H), 6.77 (br s, 1H) 7.33–7.43 (m 5H), 8.22–8.25 (d, $J = 12$ Hz, 1H), 12.18–12.24 (dd, $J = 12$ Hz and 12 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 67.6, 68.3, 104.6, 126.0, 128.3, 129.2, 136.5, 157.8, 184.7; mp slow decomposition >65 °C; HRMS (ESI) calcd for $C_{27}H_{46}N_3O_6$ $[M+H]^+$: Calcd: 568.2448; Obsd: 568.2464.

4.2.5. Spectral data for L5. Yellow solid; yield 95%; $[\alpha]_D^{25} = -329.9$ (c 0.48, CH_2Cl_2); IR (KBr): 3342, 3054, 2930, 1609, 1546, 1456, 1381, 1266, 1053, 835, 735, 701 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.78–2.82 (m 2H), 2.84–2.92 (dd, $J = 8$ Hz and 1H), 3.55–3.6 (m, 1H), 3.69–3.72 (d, $J = 12$ Hz, 1H), 6.26 (br s, 1H), 7.11–7.37 (m 5H), 7.76–7.79 (d, $J = 12$ Hz 1H), 11.18–11.23, (dd, $J = 12$ Hz and 12 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 59.4, 68.9, 69.6, 105.7, 127.8, 129.6, 130.4, 137.6, 157.8, 184.7; mp 149–150 °C; HRMS (ESI) calcd for $C_{36}H_{40}N_3O_6$ $[M+H]^+$: Calcd: 610.2917; Obsd: 610.2907.

4.2.6. Spectral data for L6. Orange syrup; yield 89%; $[\alpha]_D^{25} = -154.2$ (c 0.62, $CHCl_3$); IR (KBr): 3338, 3021, 2932, 1612, 1552, 1454, 1391, 1256, 1049, 837, 729 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.15–1.16 (d, $J = 6.5$ Hz, 3H), 3.32–3.57 (m, 2H), 3.71–3.73 (d, $J = 10$ Hz, 1H), 5.24 (br s, 1H), 7.81–7.84 (d, $J = 12$ Hz, 1H), 11.04–11.09 (dd, $J = 12$ Hz and 12 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 17.3, 60.1, 67.8, 104.6, 158.2, 185.1; HRMS (ESI) calcd for $C_{18}H_{28}N_3O_6$ $[M+H]^+$: Calcd: 382.1916; Obsd: 382.1931.

4.2.7. Spectral data for L7. Yellow solid; yield 93%; $[\alpha]_D^{25} = 32.3$ (c 1.04, $CHCl_3$); IR (KBr): 2957, 1740, 1630, 1434, 1213, 1096, 734, 597 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.42 (s, 6H), 3.19 (m, 3H), 4.60–4.73 (m, 2H), 7.13–7.30 (m, 6H), 8.20 (s, 1H), 9.09 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 29.2, 33.9, 35.1, 39.3, 75.1, 118.1, 122.5, 123.6, 124.8, 125.5, 127.1, 128.6, 131.2, 135.6, 139.7, 140.6, 140.8, 141.3, 159.4, 164.0, 166.0. ESI-MS $[M+H]^+$: 1131.

4.2.8. Spectral data for L8. Yellow solid; yield 93%; $[\alpha]_D^{25} = -153.4$ (c 0.94, $CHCl_3$); IR (KBr): 3361, 2950, 2207, 1624, 1574, 1267, 1126, 735, 501 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.42 (s, 6H), 3.12–3.14 (d, $J = 5.4$ Hz, 1H), 3.21–3.22 (d, $J = 5.0$ Hz, 1H), 4.68–4.69 (d, $J = 5.0$ Hz, 1H), 4.75–4.77 (d, $J = 5.0$ Hz, 1H), 7.16–7.35 (m, 5H), 7.51 (s, 1H), 7.60 (s, 1H), 8.47 (s, 1H), 14.2 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 29.3, 34.9, 39.5, 72.9, 75.1, 86.4, 90.6, 112.1, 118.5, 124.9, 125.4, 125.6, 126.9, 127.9, 128.7, 133.8, 138.5, 140.5, 140.8, 143.7, 161.9, 166.6. ESI-MS $[M+H]^+$: 1073.

4.3. General procedure for the preparation of chiral sulfoxides

Vanadyl acetylacetonate (0.01 mmol) and the ligand (0.006 mmol) were dissolved in dichloromethane (2 mL), and the solution was stirred for 5 min at room temperature. To this reaction mixture was added the corresponding sul-

fide (1 mmol) followed by the dropwise addition of 30% hydrogen peroxide (1.1 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for a further 16 h at ambient temperature. After the completion of the reaction, the aqueous layer was extracted with dichloromethane (2 × 2 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and evaporated under vacuum to afford the crude product which was purified by column chromatography over silica gel.

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