Synthesis, characterization, and structures of oxovanadium(v) complexes of Schiff bases of β-amino alcohols as tunable catalysts for the asymmetric oxidation of organic sulfides and asymmetric alkynylation of aldehydes

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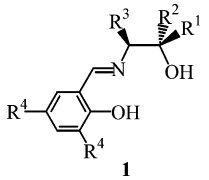
Oxovanadium(v) complexes **3a–3k** and **4a–4d** with general formula $VO(L_3^*)(OR^5)$ were prepared in quantitative yields in alcohol (R^5OH) from reactions of $VO(O\text{-}i\text{-}Pr)_3$ and tridentate Schiff bases of β-amino alcohols having one or two stereogenic centers, $(HO)C^*(R^1)(R^2)C^*H(R^3)N{=}CH(2\text{-}OH\text{-}3,5\text{-}R^4{}_2\text{–}C_6H_2)$ ($H_2L_3^*$). The alkoxy OR^5 ligand exchanges readily with the alcoholic molecule in the solvent. Crystal structures of **3b**, **3f**, **3i**, and **4a** were determined to be five-coordinate square pyramidal monomers. However, ^{1}H NMR spectra of the complexes reveal two sets of signals, indicating the presence of two isomers in solution. The two isomers are suggested to be the *endo*/*exo* pair or the monomer/dimer pair. Asymmetric oxidations of methyl phenyl sulfide catalyzed by catalyst precursors **3** were demonstrated to afford the chiral sulfoxide in yields and ee values similar to those obtained from the *in situ*-formed catalytic systems of $VO(acac)_2$ and corresponding Schiff base ligands. Complexes **3** and **4** are also good catalysts for asymmetric alkynyl additions to aldehydes. Structural differences between the oxovanadium complexes, for inducing high stereoselectivities in the asymmetric oxidation of organic sulfides and the asymmetric alkynyl addition to aldehydes, are rationalized.

Introduction

Ever since the vanadium metal center was recognized at the active site in biological systems of nitrogenase[1] and bromoperoxidase,[2] many vanadium complexes with ligands bearing oxygen and nitrogen donors have been developed for mimicking biological activity in natural systems.[3] Structurally, both monomeric and dimeric oxovanadium complexes having five-coordinate[4] or six-coordinate[5] geometries were documented. Meanwhile, oxovanadium complexes were illustrated to be catalysts[6] in a variety of asymmetric reactions such as the cyanation reaction,[7] the epoxidation of allyl alcohols,[6a,8] the oxidative coupling of 2-naphthol,[9] the oxidation of organic sulfides,[6a,10] alkynyl addition to aldehydes,[11] and others.[12] The asymmetric oxidation of organic sulfides catalyzed by oxovanadium complexes of Schiff bases of chiral β-amino alcohols **1** is the reaction which has attracted the most attention since the catalytic system is highly effective with a catalyst loading of ≤1 mol% for achieving chiral sulfoxides in good yields and good to excellent enantioselectivities. Despite extensive studies, only two papers[13,14] report crystal structures of oxovanadium(v) complexes of Schiff bases of chiral amino alcohols. The complexes reported by Ellman *et al.* were shown to be catalyst precursors in asymmetric oxidations of organic disulfides[13] and complexes prepared by Hartung and coworkers successfully catalyze oxidation of bis(homoallylic) alcohols to afford functionalized tetrahydrofurans.[14]



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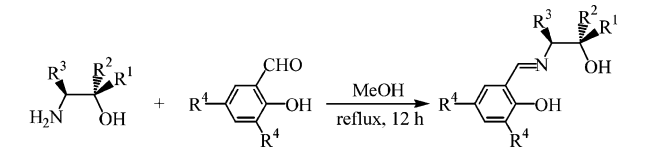
To continue exploring structural and electronic effects of chiral metal complexes applied to asymmetric catalysis,[15] we report here the synthesis of a series of oxovanadium(v) complexes $VO(L_3^*)(OR)$ (**3a–3k**, **4a–4d**) from reactions of $VO(O\text{-}i\text{-}Pr)_3$ with Schiff bases **1** ($H_2L_3^*$). Solid-state structures of **3b**, **3f**, **3i**, and **4a** were determined to be five-coordinate square pyramidal monomers. However, two isomers are observed in solution according to ^{1}H NMR spectroscopy and solution structures of the complexes are discussed. Complexes **3** and **4** are catalyst precursors or catalysts for asymmetric oxidations of methyl phenyl sulfide and asymmetric alkynyl additions to aldehydes. Structural differences between the catalysts for these two asymmetric reactions are rationalized.

Results and discussion

Synthesis of tridentate Schiff bases of β-amino alcohols and their V(v) complexes

Eleven tridentate Schiff bases **1a–1k** were prepared in quantitative yields in methanol according to standard synthetic procedures from reactions of β-amino alcohols **2a–2g** with 2-hydroxy arylaldehydes in the presence of Na_2SO_4 under reflux conditions for 12 h (Scheme 1). The Schiff bases synthesized include species having one stereogenic center with $R^1 = R^2 =$ Ph groups (**1a** and **1b**) or with $R^1 = R^2 =$ H (**1c–1g**) and species with two stereogenic centers (**1h–1k**).

According to synthetic procedures by Hartung *et al.*,[14] oxovanadium(v) complexes **3a–3k** were prepared in quantitative yields



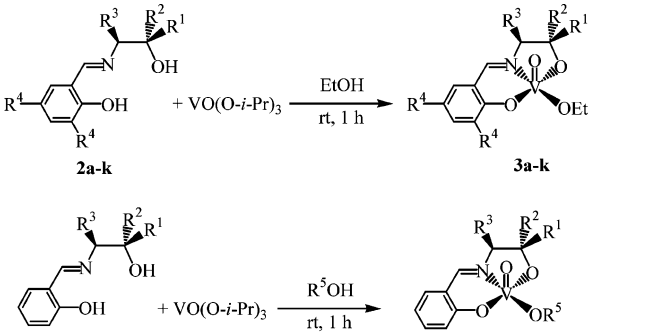
2a: $R^1 = R^2 = Ph$, $R^3 = Bn$
2b: $R^1 = R^2 = H$, $R^3 = Bn$
2c: $R^1 = R^2 = H$, $R^3 = Ph$
2d: $R^1 = R^2 = H$, $R^3 = i$-Bu
2e: $R^1 = R^2 = H$, $R^3 = t$-Bu
2f: $R^1 = Ph$, $R^2 = H$, $R^3 = Bn$
2g: $R^1 = t$-Bu, $R^2 = H$, $R^3 = Bn$

$R^4 = H$, t-Bu, I

1a: $R^1 = R^2 = Ph$, $R^3 = Bn$, $R^4 = H$
1b: $R^1 = R^2 = Ph$, $R^3 = Bn$, $R^4 = t$-Bu
1c: $R^1 = R^2 = H$, $R^3 = Bn$, $R^4 = H$
1d: $R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = H$
1e: $R^1 = R^2 = H$, $R^3 = i$-Bu, $R^4 = H$
1f: $R^1 = R^2 = H$, $R^3 = t$-Bu, $R^4 = H$
1g: $R^1 = R^2 = H$, $R^3 = t$-Bu, $R^4 = I$
1h: $R^1 = Ph$, $R^2 = H$, $R^3 = Bn$, $R^4 = H$
1i: $R^1 = Ph$, $R^2 = H$, $R^3 = Bn$, $R^4 = t$-Bu
1j: $R^1 = t$-Bu, $R^2 = H$, $R^3 = Bn$, $R^4 = H$
1k: $R^1 = t$-Bu, $R^2 = H$, $R^3 = Bn$, $R^4 = t$-Bu

Scheme 1 Synthesis of tridentate Schiff bases of amino alcohols **1a–1k**.

in a reaction time of 1 h from reactions of **1a–1k** and 1 molar equiv. of $VO(O\text{-}i\text{-}Pr)_3$ in ethanol and, similarly, complexes **4a–4d** were prepared in 2-propanol, *i*-butanol, or *t*-butanol (Scheme 2). Elemental analyses reveal that the complexes have a 1 : 1 composition ratio of the vanadium metal relative to the Schiff base ligand. The alkoxy OR^5 ligand in complexes readily exchanges with the alcoholic solvent molecule. For example, recrystallization of the ethoxy complex **3a** in 2-propanol affords a crystalline material of 2-propoxy complex **4a** and *vice versa*. These oxovanadium complexes are considerably stable and can be stored under a nitrogen atmosphere for months.



4a: $R^1 = R^2 = Ph$, $R^3 = Bn$, $R^5 = i$-Pr
4b: $R^1 = t$-Bu, $R^2 = H$, $R^3 = Bn$, $R^5 = i$-Bu
4c: $R^1 = t$-Bu, $R^2 = H$, $R^3 = Bn$, $R^5 = i$-Pr
4d: $R^1 = t$-Bu, $R^2 = H$, $R^3 = Bn$, $R^5 = t$-Bu

Scheme 2 Synthesis of oxovanadium(v) complexes of Schiff bases of β-amino alcohols.

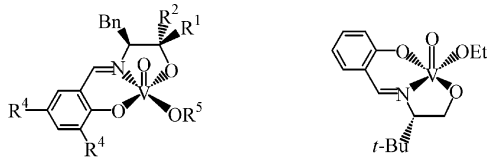
Solid state structures of 3b, 3f, 3i, and 4a

Suitable crystals of **3b**, **3f**, **3i**, and **4a** were subjected to X-ray diffraction analyses. Selected bond lengths and bond angles are listed in Table 1 and molecular structures are shown in Fig. 1. In the solid state, all four structures are square pyramidal monomers. The V–O(oxo) bonds are strong with short bond lengths ranged from 1.576(2) to 1.595(3) Å which are shorter than the terminal V–O(Et or *i*-Pr) bond distances by ~0.2 Å. In comparison with the chelating V–OR* and the V–OAr bonds, the V–O(oxo) bond lengths are shorter by ~0.25 Å. The strong V–O(oxo) bonding causes the coordination site *trans* to it to be rather labile[16] or even unfavorable for coordination. For oxovanadium complexes

Table 1 Crystallographic data for **3b**, **3f**, **3i**, and **4a**

Complex	3b	3f	3i	4a
Bond lengths/Å				
V–O	1.586(3)	1.595(3)	1.584(2)	1.576(2)
V–OEt (*i*-Pr)	1.788(3)	1.763(3)	1.777(2)	1.775(2)
V–OR*	1.846(2)	1.839(3)	1.826(2)	1.833(2)
V–OAr	1.843(2)	1.844(2)	1.889(2)	1.865(2)
V–N	2.134(3)	2.117(3)	2.117(2)	2.118(2)
V–basal	0.486	0.469	0.471	0.484
Bond angles/°				
O–V–OEt(*i*-Pr)	103.55(15)	102.09(16)	105.70(9)	105.08(10)
O–V–OR	111.67(14)	112.84(13)	107.21(8)	107.20(9)
O–V–OAr	109.60(14)	110.13(13)	106.27(8)	106.66(11)
O–V–N	94.68(13)	92.71(12)	97.92(8)	100.33(10)

of Schiff bases of amino acids, both five-coordinate square pyramidal structure and six-coordinate octahedral structure were reported and two diastereomeric structures, *i.e.*, the *exo*-[17] and the *endo*-structures[18] are observed. In contrast, for oxovanadium(v) complexes of Schiff bases of amino alcohols[13,14] including the four structures reported in this work, only the five-coordinate square pyramidal geometry is observed. The solid state structures of **3b**, **3i**, and **4a** with $R^3 = Bn$ adopt the *endo*-structure, in which the Bn group and the oxo ligand are on the same side of the basal plane defined by the donor atoms of the Schiff base ligand and the terminal alkoxy ligand. However, the complex **3f** adopts the *exo*-structure with the *t*-butyl R^3 group *trans* to the oxo ligand. The *exo*-structure is also observed for the complex with $R^3 = i$-Pr.[14]



endo-structure

3b: $R^1 = R^2 = Ph$, $R^4 = t$-Bu, $R^5 = Et$
3i: $R^1 = Ph$, $R^2 = H$, $R^4 = H$, $R^5 = Et$
4a: $R^1 = R^2 = Ph$, $R^4 = H$, $R^5 = i$-Pr

exo-structure

3f

For either the *exo*-structure **3f** or the *endo*-structures **3b**, **3i**, and **4a**, the basal donor atoms are bent away from the oxo ligand. Variations of the distance from the vanadium metal center to the basal plane are minimal from 0.469 to 0.486 Å. However, larger variations in the O(oxo)–V–L angles are observed and differences in the O(oxo)–V–N angles are up to ~8° between **3f** at 92.71(12)° and **4a** at 100.33(10)°.

NMR study of complexes 3a–3k and 4a–4d

Complexes **3a–3k** and **4a–4d** were characterized by ^1H and ^{13}C NMR spectroscopy and the ^1H NMR spectra clearly reveal two sets of signals, suggesting the presence of two isomers in solution. Since the co-existence of both the *endo*- and the *exo*-structures in solid state oxovanadium complexes of Schiff bases of amino acids have been observed previously,[17a] the two isomers in solution can be rationalized as the *endo*/*exo* pair. However, in the study of the $VO(cyclo\text{-}C_5H_9O)_3$ complex, a monomer/dimer equilibrium was suggested based on the concentration-difference ^{51}V NMR study.[19] In addition, six-coordinate dimeric oxovanadium complexes bridging through the alkoxy or the oxo donors are known.[20]

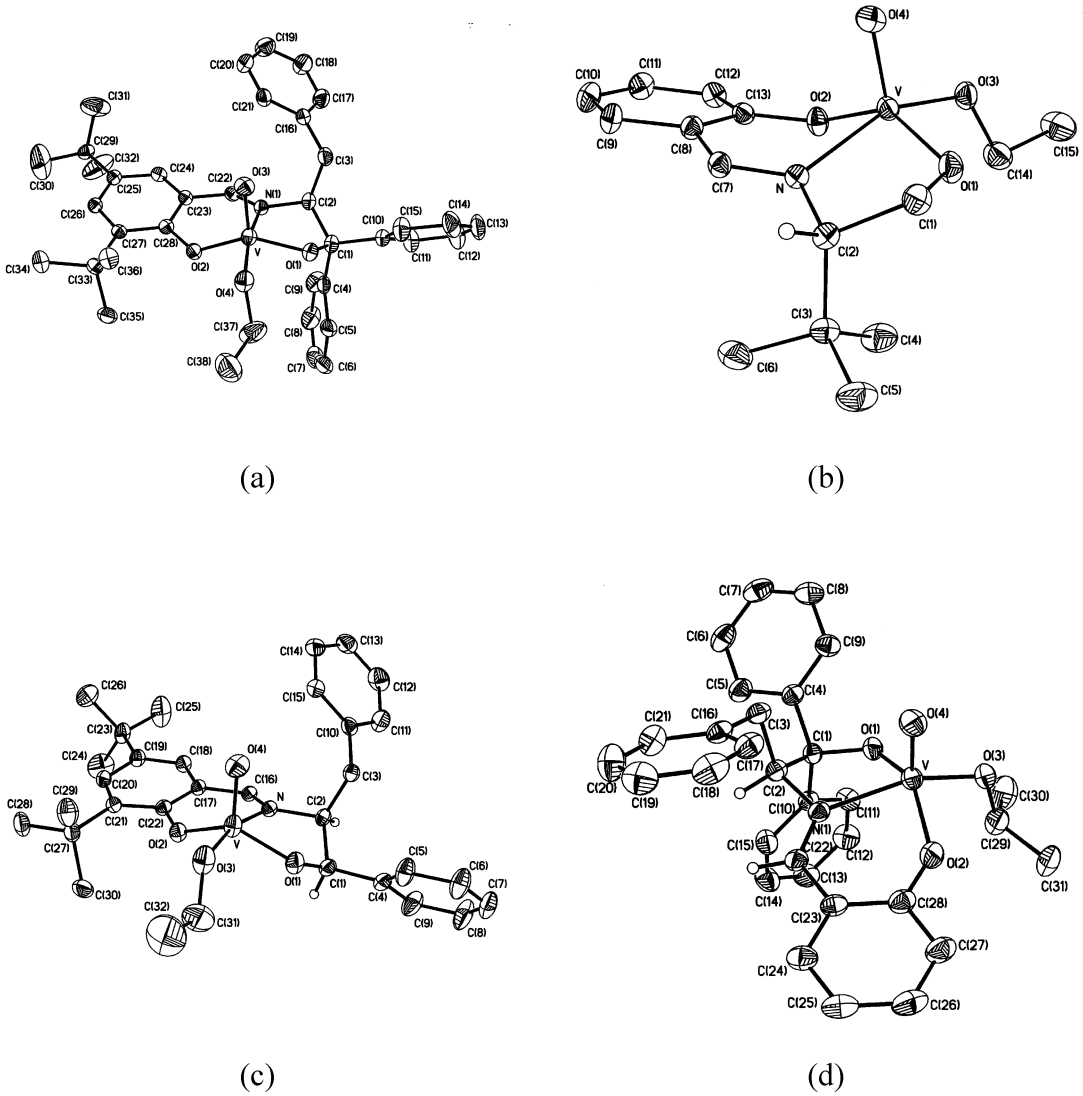
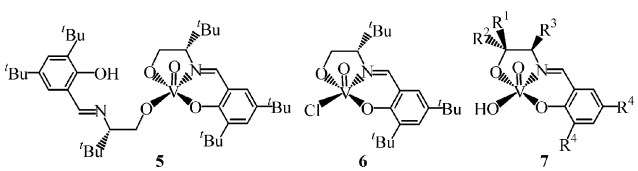


Fig. 1 Molecular structures of (a) **3b** ($R^1 = R^2 = Ph$, $R^3 = Bn$, $R^4 = t$-Bu, $R^5 = Et$), (b) **3f** ($R^1 = R^2 = H$, $R^3 = t$-Bu, $R^4 = H$, $R^5 = Et$), (c) **3i** ($R^1 = Ph$, $R^2 = H$, $R^3 = Bn$, $R^4 = t$-Bu, $R^5 = Et$), and (d) **4a** ($R^1 = R^2 = Ph$, $R^3 = Bn$, $R^4 = H$, $R^5 = i$-Pr). Ellipsoids of the atoms are 20% probability.

It seems that the possibility of the monomer/dimer pair can not be ruled out completely. In this study, concentration-difference ^{1}H NMR experiments in $CDCl_3$ were conducted. For **3c** at 6.04×10^{-2} M and 21.9×10^{-2} M, the major : minor ratios vary from 1.78 to 1.33 : 1 and, for **3f** at 1.51×10^{-2} M and 6.04×10^{-2} M, the ratios increase about 10% from 3.55 to 4.00 : 1. For **4b** with the Schiff base ligand bearing two stereogenic centers, the ratios change from 2.44 (6.04×10^{-2} M) to 2.22 : 1 (17.8×10^{-2} M). Due to small changes in the ratios of the two sets of signals, results from concentration-difference ^{1}H NMR experiments do not fully support the argument of the monomer/dimer pair in solution. It is worth noting that additional minor signals are observed for complexes **3g–3j** and **4a–4d**. Yet, it is not clear whether these additional signals are due to isomers in solution or are just minor impurities.

Asymmetric oxidation of methyl phenyl sulfide by catalyst precursors 3a–3g

Asymmetric oxidations of organic sulfides by the H_2O_2 oxidant employing catalytic systems of $VO(acac)_2$ and Schiff bases of β-amino alcohols have been extensively studied.[10] Although the oxovanadium(IV) species $VO(acac)_2$ is used as the metallic reagent, the active oxovanadium(V) catalytic species have been illustrated using evidence from ^{51}V NMR studies. Further evidence to support the active oxovanadium(V) catalytic species is from the work by Ellman and coworkers. In their work, oxovanadium(V) complexes **5** and **6** were demonstrated to be catalyst precursors for asymmetric oxidation of organic disulfides.[13] In addition, the hydroxyl oxovanadium(V) complexes **7** also catalyze the asymmetric oxidation of methyl phenyl sulfide.[21]



5 **6** **7**

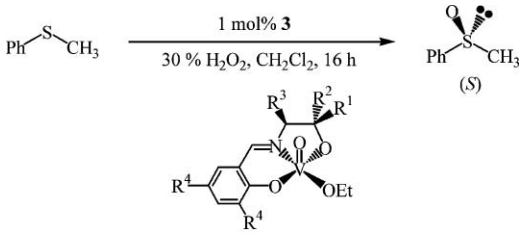
In this study, asymmetric oxidations of methyl phenyl sulfide were conducted employing 1 mol% catalyst precursors

Table 2 Asymmetric oxidation of methyl phenyl sulfide with H_2O_2 catalyzed by vanadium(V) complexes of Schiff bases[a]

Entry	Complex	R	T/°C	Yield (%)	ee (%) (*S*)
1	**3a**	$R^1 = R^2 = Ph$, $R^3 = Bn$, $R^4 = H$	rt	70	*rac*
2	**3b**	$R^1 = R^2 = Ph$, $R^3 = Bn$, $R^4 = t$-Bu	rt	67	*rac*
3	**3c**	$R^1 = R^2 = H$, $R^3 = Bn$, $R^4 = H$	rt	72	56
4	**3d**	$R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = H$	rt	76	26
5	**3e**	$R^1 = R^2 = H$, $R^3 = i$-Bu, $R^4 = H$	rt	62	58
6	**3f**	$R^1 = R^2 = H$, $R^3 = t$-Bu, $R^4 = H$	rt	74	60
7	**3g**	$R^1 = R^2 = H$, $R^3 = t$-Bu, $R^4 = I$	rt	79	83
8	**3g**	$R^1 = R^2 = H$, $R^3 = t$-Bu, $R^4 = I$	0	80	87
9	**3g**	$R^1 = R^2 = H$, $R^3 = t$-Bu, $R^4 = I$	−20	75	90
10[b]	**3g**	$R^1 = R^2 = H$, $R^3 = t$-Bu, $R^4 = I$	−20	61	98

[a] Methyl phenyl sulfide : 30% H_2O_2 : catalyst precursor = 1.0 mmol : 1.1 mmol : 0.010 mmol; solvent: CH_2Cl_2 (2 mL); reaction time, 16 h. [b] Solvent, toluene–CH_2Cl_2 = 2 : 1, 2 mL.

3a–3g (eqn (1))

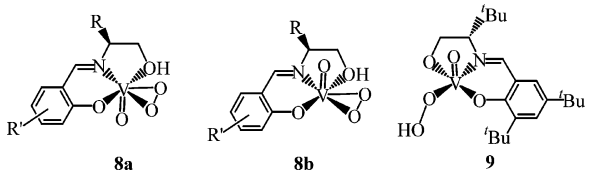


(1)

3

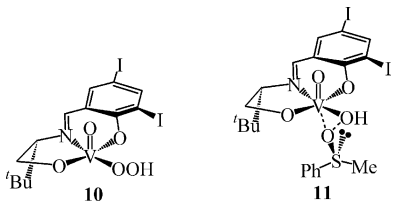
and results are listed in Table 2. For **3a** or **3b** having $R^1 = R^2 = Ph$ and $R^3 = Bn$, the reactions gave the racemic sulfoxide in 70 and 67% yield (entries 1 and 2), respectively. For **3c** of both R^1 and R^2 of the smaller H substituent and R^3 also Bn, the enantioselectivity of the product improves dramatically to 56% ee (entry 3). For **3d** with $R^3 = Ph$, the product was obtained in a lower enantioselectivity of 26% ee (entry 4). For **3e** of $R^3 = i$-Bu or **3f** of $R^3 = t$-Bu, enantioselectivities of the product in 58% and 60% ee (entries 5 and 6) were obtained. When the catalyst precursor **3g** (having an iodo group as R^4) was used, the enantioselectivity improves significantly to 83% ee (entry 7). With the reaction carried out at 0 or at −20 °C, enantioselectivities further increase to 87 and 90% ee (entries 8 and 9), respectively. Yet, the best enantioselectivity of 98% ee (entry 10) was obtained with the reaction conducted in 1 : 1 mixed solvents of toluene–CH_2Cl_2.

Results obtained in this work are comparable to those obtained by employing the *in situ*-formed catalytic systems of $VO(acac)_2$ and corresponding Schiff bases, indicating that the same active species is involved for both catalytic systems. For the *in situ*-formed catalytic system, Bolm and Bienewald proposed possible active V(V) complex species of either *exo*-$VO(HL_3^*)(OO)$ (**8a**) or *endo*-$VO(HL_3^*)(OO)$ (**8b**).[22] A recent computational study by Maseras *et al.*[23] using the structural data of complexes **5** and **6** suggests an active catalytic species of complex **9**.



8a **8b** **9**

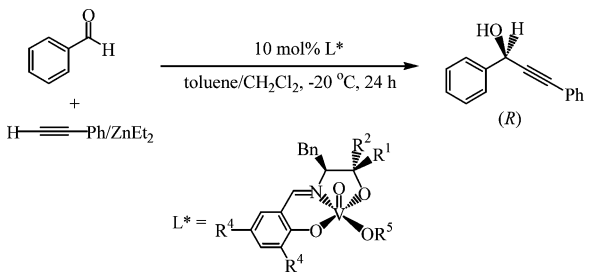
In this study, the best performing catalyst precursor **3g** is reacted with H_2O_2 to afford the active species **10** having a structure similar to **9**. In order to achieve the chiral sulfoxide in the observed *S*-configuration, the methyl phenyl sulfide should attach to the peroxy oxygen in an orientation with the phenyl group pointing away from the *ortho* iodo substituent to afford an intermediate or a transition state **11**. Detachment of the sulfoxide product from **11** affords the hydroxyl complex having a structure similar to **7** for next cycle of asymmetric reaction.



10 **11**

Asymmetric alkynyl additions to aldehydes catalyzed by complexes 3 and 4

Our recent paper demonstrates that oxovanadium complexes of Schiff bases of amino alcohol also catalyze asymmetric alkynyl additions to aldehydes (eqn (2))



(2)

and extracted results are listed in Table 3.[11] This study shows that, for catalysts bearing both R^1 and $R^2 = Ph$, a racemic mixture of propargyl alcohol is obtained (entry 1). For catalysts with $R^1 = R^2 = H$, the product is obtained with a low enantioselectivity of 12% ee (entry 2). However, the enantioselectivity improves to 43% ee for catalyst **3h** ($R^1 = Ph$, entry 3) having the Schiff base ligand with two stereogenic centers and to 75% ee for catalyst **3j** ($R^1 = t$-Bu, entry 4). However, the enantioselectivity drops to 32% ee for catalyst **3k** having R^4 of a bulkier *t*-Bu substituent (entry 5). This study also demonstrates that enantioselectivities of the product are sensitive to variations of the terminal alkoxy OR^5 ligand. For catalyst **4b** with R^5 of *i*-Bu instead of Et as in **3j**, a 20% increase

Table 3 Asymmetric alkynylation of benzaldehyde catalyzed by oxovanadium(v) complexes of Schiff bases of β-amino alcohols[a,b]

Entry	Complex	R^1	R^2	R^4	R^5	Yield[c] (%)	ee[d] (%)
1	**3a**	Ph	Ph	H	Et	100	*rac*
2	**3c**	H	H	H	Et	100	12
3	**3h**	Ph	H	H	Et	100	43
4	**3j**	*t*-Bu	H	H	Et	95	75
5	**3k**	*t*-Bu	H	*t*-Bu	Et	78	32
6	**4b**	*t*-Bu	H	H	*i*-Bu	98	96
7	**4c**	*t*-Bu	H	H	*i*-Pr	100	84
8	**4d**	*t*-Bu	H	H	*t*-Bu	100	69

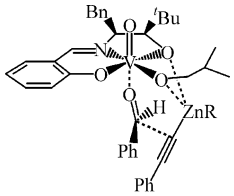
[a] Benzaldehyde–$ZnEt_2$–phenylacetylene–catalyst = 0.5 : 1.5 : 1.5 : 0.05 mmol; toluene, 5 ml; CH_2Cl_2, 2.5 mL. [b] $ZnEt_2$ and phenylacetylene were refluxed in toluene for 6 h and the resulting solution cooled to room temperature. The resulting mixture was transferred to the solution of catalyst in CH_2Cl_2 at −20 °C followed by addition of benzaldehyde. [c] Yields were calculated based on ^{1}H NMR spectra. [d] ee values were determined by HPLC using an OD column from Daicel.

in enantioselectivity to 96% ee is obtained (entry 6). However, increasing steric size of R^5 to *i*-Pr (**4c**) or to *t*-Bu (**4d**) results in decreasing enantioselectivities of 84% and 69% ee (entries 7 and 8), respectively. For comparison, alkynyl additions to aromatic aldehydes catalyzed by the best performing oxovanadium complex **4b** afford products in comparable enantioselectivities to products obtained by zinc-,[24] titanium-,[25] or indium-catalytic systems.[26]

Structural requirements of oxovanadium complexes for asymmetric oxidations of organic sulfides and for asymmetric alkynyl additions to aldehydes

Though oxovanadium(v) complexes of Schiff bases of amino alcohols are catalyst precursors for asymmetric oxidations of organic sulfides or catalysts for asymmetric alkynyl additions to aldehydes, structural requirements to induce high stereoselectivities are quite different for the two reactions. In asymmetric oxidations of organic sulfides, the Schiff base ligands with one stereogenic center having small $R^1 = R^2 = H$ substituents and large $R^4 = I$ or *t*-Bu are essential for directing organic sulfides in the best orientation for achieving good stereoselectivities. The terminal alkoxy OR^5 ligand plays no role in the oxidation reaction since, under the catalytic reaction conditions, the alkoxy ligand is replaced by the peroxy O_2H group to afford the active peroxy catalytic species.

In contrast, catalysts having Schiff base ligands with two stereogenic centers, *i.e.* having R^1 other than the H atom and both R^2 and R^4 of H substituents provide good stereoselectivities for the asymmetric alkynyl additions to aldehydes. In this reaction, the OR^5 ligand plays a key role in stereoselectivities probably due to the size of the OR^5 ligand which strongly affects the orientation of the aldehyde substrate and the alkynyl reagent accessing the vanadium metal center from the open site *trans* to the strong oxo ligand. To achieve the desired (*R*)-propargyl alcohol, the aldehyde attaches to the catalyst from the empty site *trans* to the oxo ligand with the larger Ph group oriented under the open edge defined by the phenoxy and the terminal alkoxy. Then, the zinc alkynyl reagent accesses the complex through weak interactions of the zinc metal and the two alkoxy oxygen donors to afford a likely intermediate or transition state **12**. After transferring the alkynyl group to the aldehyde ligand, the resulting product detaches from the vanadium metal center as the zinc alkoxide ZnR(OR*) for regenerating the catalyst for the next cycle of the catalytic reaction.



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Conclusions

A series of oxovanadium(V) complexes **3** and **4** of Schiff bases of amino alcohols were prepared easily in quantitative yields. The complex with R^3 of *t*-Bu has the *exo*-structure and the complexes having R^3 = Bn adopt the *endo* structures. ^{1}H NMR studies of the complexes reveal two isomers in solution and the two isomers are suggested to be either the *endo*/*exo* pair or the monomer/dimer pair. The complexes **3** were demonstrated to be catalyst precursors for the asymmetric oxidation of organic sulfides. For asymmetric oxidations of organic sulfides and disulfides, catalyst precursors with smaller $R^1 = R^2 = H$ and larger $R^4 = I$ or *t*-Bu induce higher enantioselectivities for the sulfoxide products. In contrast, vanadium catalysts having R^1 of a group other than the H atom and R^2 and R^4 of small H substituents afford better stereocontrol for asymmetric alkynyl addition reactions to aldehydes. Our studies demonstrate that oxovanadium(v) complexes of Schiff bases of amino alcohols are highly tunable catalytic systems through adjustments of R^1, R^2, R^3, and R^4 substituents of the Schiff base ligands and also through adjustment of the terminal alkoxy OR^5 ligand. Further studies of the oxovanadium complexes in asymmetric catalysis are currently underway.

Experimental

Reagents and general techniques

β-Amino alcohols with one stereogenic centre were prepared according to standard synthetic procedures and (1*R*,2*S*)-β-amino alcohols were synthesized based on modified procedures reported by Reetz *et al.*[27] 2-Hydroxy arylaldehydes and $VO(O\text{-}i\text{-}Pr)_3$ (Aldrich) were used without further purification. H_2O_2 (30%) was used directly. Methanol, absolute ethanol, and 2-propanol were dried over CaH_2 and were freshly distilled prior to use. Other solvents were dried by refluxing for at least 24 h over P_2O_5 (dichloromethane) or sodium–benzophenone (*n*-hexane or toluene) and were freshly distilled prior to use. Deuterated solvents were dried over molecular sieves. All syntheses and manipulations were carried out under a dry nitrogen atmosphere.

Physical measurements

^{1}H NMR spectra were obtained with a Varian Mercury-400 (400 MHz) spectrometer and chemical shifts were measured relative to tetramethylsilane as the internal reference. ^{13}C NMR spectra were recorded with the Varian Mercury-400 (100 MHz) spectrometer and chemical shifts are relative to TMS as the internal reference. Elemental analyses were performed using a Heraeus CHN-OS-RAPID instrument.

General procedures for the synthesis of Schiff bases of amino alcohols

2-Hydroxy arylaldehyde (3.0 mmol) was added to a solution of an amino alcohol (3.0 mmol) and sodium sulfate (1.28 g, 9.00 mmol) in 50 mL methanol at room temperature. The mixture was refluxed for 12 h and was filtered. The solvent was removed under reduced pressure to furnish a quantitative yield of product.

2-Hydroxy-benzaldehyde 2*S*-(1,1,3-triphenylpropanol) imine (1a). Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.66–6.85 (m, 19H), 4.35 (d, $J = 9.2$ Hz, C*H*N), 3.04 (d, $J = 13.6$ Hz, 1H, PhCH_AH_B), 2.95 (br, 1H, OH), 2.84 (dd, $J = 10.4$, 13.6 Hz, 1H, PhCH_AH_B) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.40, 160.52, 145.15, 144.06, 138.80, 132.27, 131.37, 129.61, 128.30, 128.22, 128.10, 126.97, 126.81, 126.21, 126.16, 126.00, 118.47, 118.22, 116.68, 79.69, 78.62, 37.35 ppm. Anal. calcd. $C_{28}H_{25}NO_2$: C, 82.53; H, 6.18; N, 3.44%. Found: C, 82.84; H, 5.86; N, 3.77%.

2-Hydroxy-3,5-di-*tert*-butyl-benzaldehyde 2*S*-(1,1,3-triphenyl-propanol) imine (1b). Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.67–6.67 (m, 19H), 4.36 (dd, $J = 2.0$, 9.6 Hz, 1H, C*H*N), 3.05 (d, $J = 13.2$ Hz, 1H, PhCH_AH_B), 2.86 (dd, $J = 10.4$, 13.6 Hz, 1H, PhCH_AH_B), 1.40 (s, 9H, *t*-Bu), 1.22 (s, 9H, *t*-Bu) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 167.71, 157.53, 145.55, 144.23, 139.88, 139.13, 136.28, 129.72, 128.65, 128.37, 128.28, 128.21, 127.07, 126.94, 126.79, 126.25, 126.16, 126.09, 126.01, 117.57, 79.82, 78.39, 37.52, 34.92, 33.97, 31.38, 29.39 ppm. Anal. calcd. $C_{36}H_{41}NO_2$: C, 83.20; H, 7.95; N, 2.70%. Found: C, 83.20; H, 8.18; N, 2.72%.

2-Hydroxy-3,5-di-*tert*-butyl-benzaldehyde 2*S*-(1,3-diphenyl-propanol) imine (1i). Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.82 (s, 1H, C*H*=N), 7.40–6.82 (m, 12H, Ar*H*), 4.93–4.91 (m, 1H, C*H*O), 3.63 (m, 1H, C*H*N), 3.14 (dd, $J = 3.2$, 13.6 Hz, 1H, PhCH_AH_B), 2.86 (dd, $J = 9.6$, 13.8 Hz, 1H, PhCH_AH_B), 2.21 (br, 1H, OH), 1.44 (s, 9H, *t*-Bu), 1.24 (s, 9H, *t*-Bu) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.79, 158.03, 140.80, 139.73, 138.52, 136.45, 129.62, 128.27, 128.23, 127.90, 127.07, 126.95, 126.15, 126.05, 117.60, 76.78, 76.78, 38.26, 34.98, 34.01, 31.42, 29.39 ppm. Anal. calcd. $C_{30}H_{37}NO_2$: C, 81.22; H, 8.41; N, 3.16%. Found: C, 81.15; H, 8.57; N, 3.35%.

2-Hydroxy-benzaldehyde 2*S*-(1-*tert*-butyl-3-phenylpropanol) imine (1j). Yellow solid. ^{1}H NMR(400 MHz, $CDCl_3$): δ 7.58 (s, 1H, C*H*=N), 7.30–6.77 (m, 9H, Ar*H*), 3.59 (d, $J = 5.6$ Hz, 1H, C*H*O), 3.49–3.44 (m, 1H, C*H*N), 3.40 (dd, $J = 2.4$, 13.6 Hz, 1H, CH_AH_BPh), 2.82 (dd, $J = 10.4$, 13.6 Hz, 1H, CH_AH_BPh), 1.01 (s, 9H, *t*-Bu) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.16, 161.05, 138.85, 132.18, 131.27, 129.90, 128.24, 126.18, 118.48, 116.91, 81.36, 74.06, 39.13, 35.77, 26.84 ppm. Anal. calcd. $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09; N, 4.50%. Found: C, 77.25; H, 8.23; N, 4.39%.

2-Hydroxy-3,5-di-*tert*-butyl-benzaldehyde 2*S*-(1-*tert*-butyl-3-phenylpropanol) imine (1k). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H, C*H*=N), 7.38–6.76 (m, 7H, Ar*H*), 3.56 (d, $J = 4.4$ Hz, 1H, C*H*O), 3.51–3.44 (m, 1H, C*H*N), 3.33 (dd, $J = 2.4$, 13.6 Hz, 1H, CH_AH_BPh), 2.88 (dd, $J = 10.0$, 13.6 Hz, 1H, CH_AH_BPh), 1.94 (br, 1H, O*H*), 1.45 (s, 9H, *t*-Bu), 1.25 (s, 9H, *t*-Bu), 1.02 (s, 9H, *t*-Bu) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.10, 158.14, 139.58, 139.04, 136.36, 129.80, 128.14, 126.73, 125.97, 125.79, 117.57, 81.39, 73.70, 38.93, 35.96, 35.64, 35.03, 34.91, 33.92, 31.51, 31.43, 29.48, 26.95 ppm. Anal. calcd. $C_{28}H_{41}NO_2$: C, 79.39; H, 9.76; N, 3.31%. Found: C, 79.58; H, 9.57; N, 3.12%.

General procedures for synthesis of oxovanadium(v) complexes of Schiff bases

To a solution of a Schiff base (1.00 mmol) in 10 mL alcohol, VO(O-*i*-Pr)$_3$ (0.24 mL, 1.0 mmol) was added at room temperature. The mixture was stirred for 1 h and the solvent was removed under reduced pressure to give a quantitative yield of the product. Analytically pure samples and crystals for X-ray structural determination were recrystallized from the alcohol solvent. ^{1}H NMR spectra in $CDCl_3$ were measured to suggest the presence of two isomers in solution. Chemical shifts for the two isomers are listed separately and designated as major and minor. Resonances of minor aromatic hydrogens are included in the major resonances due to overlapping of these signals. In a few complexes, extra minor peaks are observed. NMR and elemental analysis data of **3h** and **4b** have already been reported.[11]

Ethoxo[2-oxobenzaldehyde 2*S*-(1,1,3-triphenylpropoxo) imine]-oxovanadium(v) (3a). Yellowish-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): **major** (95%): δ 7.90–6.74 (m), 5.30–5.22 (m, OCH_2), 4.88 (dd, $J = 2.4$, 11.2 Hz, C*H*N), 3.71 (dd, $J = 11.6$, 13.2 Hz, CH_AH_BPh), 2.86 (dd, $J = 2.4$, 13.2 Hz, CH_AH_BPh), 1.58 (t, $J = 6.8$ Hz, 3H, CH_3) ppm; **minor** (5%): δ 5.43–5.38 (m, OCH_2), 5.10–5.03 (m, C*H*N), 3.98–3.88 (m, CH_AH_BPh), 3.14–3.06 (m, CH_AH_BPh), 2.68–2.60 (m, CH_AH_BPh), 2.50–2.42 (m, CH_AH_BPh), 1.73 (t, $J = 6.8$ Hz, CH_3), 1.24 (t, $J = 6.8$ Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.86, 162.87, 147.39, 144.88, 138.15, 135.63, 132.20, 130.35, 130.26, 128.62, 128.49, 128.42, 128.35, 128.16, 126.99, 126.87, 126.80, 126.73, 126.63, 126.55, 126.23, 125.91, 119.61, 119.26, 118.60, 96.13, 86.13, 77.97, 38.08, 17.69 ppm. Anal. calcd. $C_{30}H_{28}NO_4V$: C, 69.63; H, 5.45; N, 2.71%. Found: C, 69.55; H, 4.97; N, 2.73%.

Ethoxo[2-oxo-3,5-di-*tert*-butylbenzaldehyde 2*S*-(1,1,3-triphenyl-propoxo) imine]oxovanadium(v) (3b). Green solid. ^{1}H NMR (400 MHz, $CDCl_3$): **major** (87%): δ 7.90–6.58 (m), 5.23–5.11 (m, OCH_2), 4.85 (dd, $J = 2.0$, 8.8 Hz, C*H*N), 3.66 (dd, $J = 11.6$, 13.6 Hz, CH_AH_BPh), 2.81 (dd, $J = 2.0$, 13.6 Hz, CH_AH_BPh), 1.48 (t, $J = 11.2$ Hz, CH_3), 1.41 (s, *t*-Bu), 1.23 (s, *t*-Bu) ppm; **minor** (13%): δ 5.50–5.30 (m, OCH_2), 5.06–4.94 (m, C*H*N), 3.80–3.72 (m, CH_AH_BPh), 3.00–2.92 (m, CH_AH_BPh), 2.64 (dd, $J = 2.0$, 10.4 Hz, CH_AH_BPh), 2.50–2.40 (m, CH_AH_BPh), 1.68 (t, $J = 6.8$ Hz, CH_3), 1.51 (s, *t*-Bu), 1.46 (s, *t*-Bu), 1.33 (s, *t*-Bu) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.46, 161.31, 147.88, 145.45, 141.74, 138.48, 137.99, 130.49, 130.39, 130.19, 128.47, 128.41, 128.05, 126.83, 126.73, 126.58, 126.54, 126.50, 126.36, 126.29, 126.05, 126.02, 125.85, 119.32, 95.84, 85.46, 76.18, 38.07, 35.26, 35.17, 34.11, 34.08, 31.25, 29.71, 29.58, 19.13, 18.17 ppm. Anal. calcd. $C_{38}H_{44}NO_4V$: C, 72.48; H, 7.04; N, 2.22%. Found: C, 72.33; H, 7.43; N, 2.21%.

Ethoxo[2-oxo-benzaldehyde 2*S*-(3-phenylpropoxo) imine]oxo-vanadium(v) (3c). Red solid. ^{1}H NMR (400 MHz, $CDCl_3$): **major** (57%): δ 7.55 (s, C*H*=N), 7.54–6.82 (m), 5.28 (q, $J = 6.8$ Hz, OCH_2), 5.17 (dd, $J = 4.8$, 9.2 Hz, CH_AH_BO), 4.77 (d, br, CH_AH_BO), 4.12 (m, C*H*N), 3.87 (dd, $J = 10.0$, 14.0 Hz, CH_AH_BPh), 3.33 (dd, $J = 4.8$, 13.2 Hz, CH_AH_BPh), 1.55

(t, J = 6.8 Hz, CH_3) ppm; **minor** (43%): δ 7.80 (s, CH=N), 5.35 (q, J = 6.8 Hz, OCH_2), 4.63 (br, C$H_A H_B$O), 4.50 (m, 1H, C$H_A H_B$O), 3.05 (dd, J = 6.4, 13.2 Hz, C$H_A H_B$Ph), 2.87 (dd, J = 4.8, 13.2 Hz, C$H_A H_B$Ph), 1.65, (t, J = 6.8 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.02, 163.77, 163.26, 162.83, 137.30, 136.80, 135.71, 135.54, 132.46, 132.34, 129.88, 129.83, 128.64, 128.58, 126.92, 126.85, 119.99, 119.58, 119.39, 119.21, 118.73, 81.89, 79.16, 78.77, 78.17, 78.09, 77.21, 75.58, 41.59, 40.87, 17.97, 17.65 ppm. Anal. calcd. $C_{18}H_{20}NO_4V$: C, 59.18; H, 5.52; N, 3.83%. Found: C, 58.95; H, 5.76; N, 4.23%.

Ethoxo[2-oxo-benzaldehyde 2*S*-(2-phenyethoxo) imine]oxovanadium(v) (3d). Dark brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): **major** (60%): δ 8.28 (s, CH=N), 7.54–6.84 (m), 5.48–5.39 (m, CHN), 5.39–5.26 (m, OCH_2), 5.02–4.88 (m, CH_2O), 1.63 (t, J = 7.2 Hz, CH_3) ppm; **minor** (40%): δ 8.20 (s, CH=N), 5.86–5.78 (m, CHN), 1.59 (t, J = 6.8 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.57, 164.25, 163.83. 138.43, 138.22, 135.90, 135.77, 132.87, 132.83, 129.26, 129.16, 128.95. 128.76, 128.71, 128.13, 120.14, 119.56, 119.36, 118.81, 82.68, 82.41, 78.58, 77.87, 17.85, 17.78 ppm. Anal. calcd. $C_{17}H_{18}NO_4V$: C, 58.13; H, 5.16; N, 3.99%. Found: C, 57.85; H, 5.31; N, 4.11%.

Ethoxo[2-oxo-benzaldehyde 2*S*-(2-isobutylethoxo) imine]oxovanadium(v) (3e). Black solid. ^{1}H NMR (600 MHz, $CDCl_3$): **major** (53%): δ 8.44 (s, CH=N), 7.56–7.36 (m, 4H), 7.10–6.90 (m), 5.25 (q, J = 6.6 Hz, OCH_2), 4.62–4.44 (m), 4.16–4.06 (m, CHN), 1.80–1.76 (m, C$H_A H_B$), 1.64–1.58 (m, CH_3), 1.50–1.40 (m), 1.03 (d, J = 10.8 Hz, CH(CH_3)$_2$), 0.99 (d, J = 10.8 Hz, CH(CH_3)$_2$) ppm; **minor** (47%): δ 8.51 (s, CH=N), 5.36–5.26 (m, OCH_2), 5.08–4.90 (m, OC$H_A H_B$), 4.74 (dd, J = 3.6, 8.0 Hz), 2.20–2.02 (m, CH_AH$_B$), 1.56–1.51 (m), 1.36–1.18 (m), 0.97 (d, J = 6.6, Hz, CH(CH_3)$_2$), 0.96 (d, J = 6.6 Hz, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.66, 163.60, 162.52. 162.44, 162.21, 135.95, 135.63, 135.47, 132.76, 132.63, 120.26, 119.55, 119.48, 119.39, 118.65, 117.92, 81.54, 78.37, 78.23, 77.67, 74.59, 72.39, 43.99, 43.39, 43.20, 24.73, 24.61, 23.02, 22.76, 22.41, 21.89, 17.86, 17.62 ppm. Anal. calcd. $C_{15}H_{22}NO_4V$: C, 54.38; H, 6.69; N, 4.23%. Found: C, 54.54; H, 6.40; N, 4.54%.

Ethoxo[2-oxo-benzaldehyde 2*S*-(2-*tert*-butylethoxo) imine]oxovanadium(v) (3f). Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): **major** (75%): δ 8.53 (s, CH=N), 7.58–7.38 (m), 7.12–6.90 (m), 5.27 (q, J = 6.8 Hz, OCH_2), 5.23 (m, 1H, C$H_A H_B$O), 4.92–4.82 (m, br, C$H_A H_B$O), 3.99 (d, J = 5.6 Hz, CHN), 1.62 (t, J = 6.8 Hz, CH_3), 0.93 (s, *t*-Bu) ppm; **minor** (25%): δ 8.45 (s, 1H, CH=N), 5.26–5.18 (m. OCH_2), 5.14–5.04 (m, C$H_A H_B$O), 3.88–3.82 (m, CHN), 1.51 (t, J = 6.8 Hz, CH_3), 1.18 (s, *t*-Bu) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.21, 165.83, 164.05, 135.99, 135.87, 132.91, 132.71, 120.50, 119.46, 119.36, 118.76, 85.85, 83.89, 78.23, 75.69, 36.19, 35.56, 27.16, 27.00, 17.92, 17.71 ppm. Anal. calcd. $C_{15}H_{22}NO_4V$: C, 54.38; H, 6.69; N, 4.23%. Found: C, 54.01; H, 6.39; N, 4.28%.

Ethoxo[2-oxo-3,5-diiodo-benzaldehyde 2*S*-(2-*tert*-butylethoxo)-imine]oxovanadium(v) (3g). Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): **major** (76%): δ 8.39 (s, CH=N), 8.27 (d, J = 2.4 Hz), 7.70 (d, J = 2.4 Hz), 5.54–5.38 (m, OCH_2), 5.31 (dd, J = 6.0, 7.2 Hz, C$H_A H_B$O), 4.87 (br, C$H_A H_B$O), 4.02 (d, J = 5.6 Hz, CHN), 1.69 (t, J = 6.8 Hz, CH_3), 0.93 (s, *t*-Bu) ppm; **minor** (24%): δ 8.31 (s, CH=N), 8.12–8.02 (m), 7.86–7.78 (m), 7.63 (d, J = 2.0 Hz), 7.46 (d, J = 2.0 Hz), 5.17 (dd, J = 2.8, 10.8 Hz, C$H_A H_B$O), 5.12–5.00 (m), 3.90–3.82 (m, CHN), 3.73 (br), 1.63 (d, J = 6.4 Hz), 1.59 (t, J = 6.8 Hz, CH_3), 1.49 (br), 1.28 (s), 1.16 (s, *t*-Bu), 0.84 (d, J = 10.4 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.61, 163.99, 163.03, 151.38, 151.30, 141.28, 141.05, 121.66, 120.39, 91.77, 85.77, 84.11, 83.84, 79.82, 79.70, 79.66, 79.57, 79.45, 78.48, 77.20, 75.91, 75.71, 36.34, 35.62, 27.27, 27.10, 26.96, 25.52, 25.10, 24.97, 19.08, 18.45, 18.27 ppm. Anal. calcd. $C_{15}H_{20}NO_4I_2V$: C, 30.90; H, 3.46; N, 2.40%. Found: C, 30.82; H, 3.59; N, 2.14%.

Ethoxo[2-oxo-3,5-di-*tert*-butylbenzaldehyde 2*S*-(1*R*,3-diphenylpropoxo) imine]oxovanadium(v) (3i). Red solid. ^{1}H NMR (400 MHz, $CDCl_3$): **major** (80%): δ 7.56–6.64 (m), 6.38 (d, J = 4.4 Hz, CHO), 5.34–5.20 (m, OCH_2), 4.18–4.10 (m, CHN), 3.62–3.50 (m, C$H_A H_B$Ph), 2.60 (dd, J = 2.8, 13.6 Hz, C$H_A H_B$Ph), 1.51 (t, J = 6.8 Hz, CH_3), 1.49 (s, *t*-Bu), 1.25 (s, *t*-Bu) ppm; **minor** (20%): δ 6.54 (d, J = 4.8 Hz, 1H, CHO), 5.37 (q, J = 7.2 Hz, OCH_2), 4.58–4.50 (m, CHN), 3.76–3.58 (m, C$H_A H_B$Ph), 2.54–2.42 (m, C$H_A H_B$Ph), 1.69 (br), 1.63 (t, J = 7.2 Hz, CH_3), 1.53 (s, *t*-Bu) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.53, 163.29, 162.17, 161.05, 141.85, 141.34, 141.05, 140.41, 138.11, 138.07, 137.86, 137.33, 130.55, 130.38, 130.14, 130.06, 128.44, 128.36, 128.32, 127.37, 127.22, 126.68, 126.44, 126.36, 126.06, 125.91, 119.62, 119.16, 90.73, 86.75, 83.90, 78.89, 77.25, 76.93, 36.45, 35.91, 35.27, 35.21, 34.10, 31.27, 31.24, 29.59, 18.33, 18.20 ppm. Anal. calcd. $C_{32}H_{40}NO_4V$: C, 69.43; H, 7.28; N, 2.53%. Found: C, 69.28; H, 7.28; N, 2.57%.

Ethoxo[2-oxo-benzaldehyde 2*S*-(1*R*-*tert*-butyl-3-phenylpropoxo) imine]oxovanadium(v) (3j). Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): **major** (66%): δ 7.48–6.72 (m), 5.16–5.00 (m, OCH_2), 4.93 (d, J = 4.0 Hz, CHO), 4.18–4.00 (m, CHN), 3.82 (dd, J = 12.4, 12.4 Hz, C$H_A H_B$Ph), 3.44 (dd, J = 3.2, 13.2 Hz, C$H_A H_B$Ph), 1.49 (t, J = 7.2 Hz, CH$_2$CH_3), 1.19 (s, *t*-Bu) ppm; **minor** (34%): δ 5.34–5.20 (m, OCH_2, CHO), 4.38–4.30 (m, CHN), 3.76–3.66 (m), 3.28 (dd, J = 3.2, 13.2 Hz, C$H_A H_B$Ph), 2.63 (dd, J = 13.2, 13.6 Hz), 1.66 (t, J = 7.2 Hz, CH$_2$CH_3), 1.22 (s, *t*-Bu), 1.09 (s), 1.06 (s) ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 165.13, 163.73, 162.00, 161.92, 137.92, 137.14, 135.45, 135.14, 132.28, 132.19, 130.20, 130.03, 128.46, 128.40, 126.69, 126.63, 119.95, 119.39, 119.06, 118.98, 118.60, 118.51, 98.17, 94.79, 83.47, 78.24, 77.92, 76.40, 36.76, 36.33, 35.85, 27.56, 27.13, 17.91, 17.48 ppm. Anal. calcd. $C_{22}H_{28}NO_4V$: C, 62.70; H, 6.70; N, 3.32%. Found: C, 62.21; H, 6.40; N, 3.11%.

Ethoxo[2-oxo-3,5-di-*tert*-butyl-benzaldehyde 2*S*-(1*R*-*tert*-butyl-3-phenylpropoxo) imine]oxovanadium(v) (3k). Greenish-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): too complicated for assignment. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.69, 162.58, 161.06, 141.59, 140.91, 138.38, 138.09, 137.62, 130.28, 129.93, 128.50, 126.64, 126.47, 126.32, 119.07, 98.12, 94.18, 82.94, 77.75, 75.20, 37.04, 36.74, 36.31, 35.90, 35.26, 35.21, 34.11, 31.31, 31.28, 30.01, 29.78, 29.63, 29.59, 27.66, 27.24, 27.11, 19.10, 18.34, 18.06 ppm. Anal. calcd. $C_{30}H_{44}NO_4V$: C, 67.52; H, 8.31; N, 2.62%. Found C, 67.56; H, 7.95; N, 2.43%.

2-Propoxo[2-oxo-3,5-di-*tert*-butylbenzaldehyde 2*S*-(1,1,3-triphenylpropoxo) imine]oxovanadium(v) (4a). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): **major** (90%): δ 7.92–6.66 (m), 5.61 (sept, OCH), 4.87 (dd, J = 2.0, 9.6 Hz, CHN), 3.71 (dd, J = 12.0, 13.4 Hz, C$H_A H_B$Ph), 2.87 (dd, J = 2.4, 13.6 Hz, C$H_A H_B$Ph), 1.60 (d, J = 6.4 Hz, CH(CH_3)$_2$), 1.57 (d, J = 6.4 Hz, CH(CH_3)$_2$)

ppm; **minor** (10%): δ 5.71 (sept, OC*H*), 5.47 (m), 5.14 (dd, J = 2.8, 8.8 Hz, C*H*N), 5.06 (dd, J = 2.0, 9.6 Hz), 3.93 (dd, J = 12.4, 13.6 Hz, CH_AH_BPh), 3.09 (dd, J = 2.0, 9.6 Hz, CH_AH_BPh), 2.62 (dd, J = 2.4, 13.6 Hz), 2.46 (dd, J = 11.2, 13.6 Hz), 1.72 (d, J = 6.4 Hz, CH(CH_3)$_2$), 1.69 (d, J = 6.4 Hz, CH(CH_3)$_2$), 1.42 (d, J = 6.0 Hz, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 162.69, 162.58, 161.06, 141.59, 140.91, 138.38, 138.09, 137.62, 130.28, 129.93, 128.50, 126.64, 126.47, 126.32, 119.07, 98.12, 94.18, 82.94, 77.75, 75.20, 37.04, 36.74, 36.31, 35.90, 35.26, 35.21, 34.11, 31.31, 31.28, 30.01, 29.78, 29.63, 29.59, 27.66, 27.24, 27.11, 19.10, 18.34, 18.06 ppm. Anal. calcd. $C_{31}H_{30}NO_4V$:. C, 70.05; H, 5.69; N, 2.64%. Found: C, 69.95; H, 5.77; N, 2.73%.

2-Propoxo[2-oxo-benzaldehyde 2*S*-(1*R*-*tert*-butyl-3-phenylpropoxo) imine]oxovanadium(v) (4c). Brown solid. ^{1}H NMR(400 MHz, $CDCl_3$): **major** (58%): δ 7.46–6.70 (m), 5.43 (sept, OC*H*(CH$_3$)$_2$), 4.86 (d, J = 2.8 Hz, C*H*O), 4.10–4.00 (m, C*H*N), 3.82 (dd, J = 12.8, 12.8 Hz, CH_AH_BPh), 3.43 (d, J = 12.4 Hz, CH_AH_BPh), 1.47 (d, J = 6.0 Hz, CH(CH_3)$_2$), 1.45 (d, J = 6.0 Hz, CH(CH_3)$_2$), 1.17 (s, *t*-Bu) ppm; **minor** (42%): δ 5.56 (sept, OC*H*(CH$_3$)$_2$), 5.22 (d, J = 3.6 Hz, C*H*O), 5.33 (br), 5.17 (br), 5.08 (br), 4.97 (br), 4.38–4.26 (m, C*H*N), 3.27 (d, J = 12.8 Hz, CH_BH_APh), 2.62 (dd, J = 12.0, 12.0 Hz, CH_AH_BPh), 1.64 (d, J = 6.0 Hz, CH(CH_3)$_2$), 1.61 (d, J = 6.4 Hz, CH(CH_3)$_2$), 1.42 (d, J = 6.0 Hz, CH(CH_3)$_2$), 1.37 (s), 1.21 (s, *t*-Bu), 1.10 (d, J = 6.0 Hz), 1.07 (s), 1.01 (s) ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 165.34, 163.95, 162.04, 161.87, 138.18, 137.43, 135.64, 135.40, 135.06, 132.29, 132.18, 130.35, 130.17, 129.98, 128.70, 128.66, 128.53, 128.48, 126.90, 126.73, 126.68, 120.09, 119.27, 119.07, 118.94, 118.77, 97.79, 94.58, 84.20, 83.31, 82.96, 78.06, 77.20, 36.84, 36.49, 36.01, 27.66, 27.26, 25.66, 25.55, 25.36, 24.69, 24.63, 24.08, 24.01 ppm. Anal. calcd. $C_{23}H_{30}NO_4V$: C, 63.44; H, 6.94; N, 3.22%. Found: C, 63.46; H, 6.58; N, 3.09%.

***tert*-Butoxo[2-oxo-benzaldehyde 2*S*-(1*R*-*tert*-butyl-3-phenylpropoxo) imine]oxovanadium(v) (4d).** Brown solid. ^{1}H NMR(400 MHz, $CDCl_3$): **major** (56%): δ 7.44–6.70 (m), 5.26 (m, OC*H*), 4.78 (d, J = 4.0 Hz, C*H*O), 4.08–4.00 (m, C*H*N), 3.82 (dd, J = 13.6, 13.6 Hz, CH_AH_BPh), 3.43 (dd, J = 2.8, 13.0 Hz, CH_AH_BPh), 1.59 (s, *t*-Bu), 1.17 (s, *t*-Bu) ppm; **minor** (44%): δ 5.33 (d, J = 4.0 Hz), 5.19 (d, J = 4.0 Hz, C*H*O), 5.08 (d, J = 3.6 Hz), 4.34–4.24 (m, C*H*N), 4.16–4.08 (m), 3.25 (dd, J = 2.8, 13.2 Hz, CH_AH_BPh), 2.63 (t, J = 13.2, 13.2 Hz, CH_AH_BPh), 1.69 (s, *t*-Bu), 1.47 (s), 1.28 (s), 1.20 (s, *t*-Bu), 1.09 (s), 1.07 (s) ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 165.47, 162.00, 161.82, 138.33, 137.55, 135.25, 134.90, 132.25, 132.15, 130.38, 130.21, 128.50, 128.46, 126.69, 126.63, 120.12, 118.96, 118.84, 118.73, 96.81, 94.25, 83.14, 77.94, 36.82, 36.63, 36.04, 31.25, 30.65, 30.22, 26.67, 27.32 ppm. Anal. calcd. $C_{24}H_{32}NO_4V$: C, 64.13; H, 7.18; N, 3.12%. Found C, 64.18; H, 7.36; N, 3.06%.

General procedures for asymmetric oxidation of methyl phenyl sulfide

To a solution of complex **3** (0.010 mmol) in 2.0 mL CH_2Cl_2, methyl phenyl sulfide (1.0 mmol, 0.12 mL) was added at room temperature. 30% H_2O_2 (1.1 mmol, 0.13 mL) was added over 2 h using a syringe pump and the resulting mixture was stirred for 16 h. The reaction was quenched with 2.0 mL H_2O and the solution was extracted with ethyl acetate (3 × 10 mL). The organic phase was dried with anhydrous $MgSO_4$ and concentrated to give a colorless oil. The product was separated by column chromatography with an eluent of EtOAc. Enantioselectivities were determined by HPLC

Table 4 Crystal and structure refinement data

	3b	**3f**	**3i**	**4a**
Empirical formula	$C_{38}H_{44}NO_4V$	$C_{15}H_{22}NO_4V$	$C_{32}H_{40}NO_4V$	$C_{31}H_{30}NO_4V$
M/g mol^{-1}	629.68	331.28	553.69	531.50
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	9.8460(8)	8.2505(7)	6.3509(4)	10.9280(8)
b/Å	11.2520(9)	11.0013(10)	19.3947(12)	12.6932(10)
c/Å	31.761(3)	9.4013(8)	25.8562(16)	19.5875(15)
α/°	90	90	90	90
β/°	90	109.720(2)	90	90
γ/°	90	90	90	90
V/Å^3	3518.8(5)	803.28(12)	3184.8(3)	2717.0(4)
Z	4	2	4	4
D_{calc}/g cm^{-3}	1.189	1.370	1.155	1.299
μ(Mo-Kα)/mm^{-1}	0.320	0.631	0.344	0.401
F(000)	1336	348	1176	1112
Reflections collected	19900	4478	18010	15500
Independent reflections	6877	3054	6243	5334
Observed reflections [$I > 2\sigma(I)$]	5504	2973	4547	3483
R_{int}	0.0354	0.0143	0.0353	0.0373
Parameter refined	397	190	343	334
R_1	0.0556	0.0265	0.0530	0.0369
wR_2	0.1556	0.0733	0.1367	0.0807
S	1.059	1.025	1.018	0.920
Absolute structure parameter	−0.01(3)	0.053(17)	−0.01(3)	0.07(3)
$\Delta\rho_{min}$/e Å^{-3}	−0.411	−0.175	−0.475	−0.263
$\Delta\rho_{max}$/e Å^{-3}	0.789	0.266	0.819	0.163

using chiral OD column (*i*-PrOH–hexane = 10 : 90, flow rate = 0.5 mL min^{-1}) from Diacel.

Crystal structure determinations

A green crystal of **3b** of size 0.68 × 0.46 × 0.25 mm, a red crystal of **3f** of size 0.80 × 0.26 × 0.24 mm, a brown crystal of **3i** of size 0.60 × 0.44 × 0.32 mm, and a dark red crystal of **4a** of size 0.63 × 0.60 × 0.39 mm in sealed capillaries under nitrogen atmosphere were used for X-ray diffraction studies. Diffraction intensities were collected on a Bruker CCD Smart-1000 diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All refinements and calculations were carried out with the Bruker AXS SHELXTL software package on a P4 2.4 GHz computer. Positions of heavy atoms were determined by direct methods and remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Refinements were carried out using full-matrix least-squares techniques. All non-hydrogen atoms were refined as individual anisotropic atoms. Hydrogen atoms were considered as the riding atoms on carbon atoms with a C–H bond length of 0.96 Å and hydrogen atom temperature factors were fixed at 0.08 Å. Crystal and structure refinement data are listed in Table 4.

CCDC reference numbers 620539–620542.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613212j

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