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Recent advances in the oxovanadium mediated biaryl coupling and modified Mannich-type reaction

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Dedicated to Professor Chun-Chen Liao on the occasion of his 60th birthday

Contents

Abstract

Vanadium induced organic synthesis has gained significant importance in recent years. In this proceeding, we have discussed the recent advances in vanadium mediated biaryl coupling and some C–C bond formation reactions. Efficacy of the vanadium in various oxidative coupling reactions of phenols, naphthols, their methyl ethers and in the asymmetric synthesis of chiral BINOLs is discussed in this review. Vanadium catalysed modified Mannich reaction is also discussed.

Keywords: Oxovanadium; Biaryls; C–C bond formation; Oxidative coupling; Modified Mannich reaction

1. Introduction

The design of novel reactions that proceed with high atom economy and enable multiple transformations through a shorter reaction sequence is an integral part of modern day organic synthesis. Over the past two decades vanadium chemistry has been developed into an important component of organic synthesis addressing the aforementioned goals in an elegant manner. Vanadium complexes exhibit a rich redox chemistry providing potential tools in organic synthesis [1]. The utility of oxo-vanadium compounds in C–C bond formation is amply demonstrated in a myriad of organic transformations. For example, oxovanadium compounds such as $VOCl_3$ and VOF_3 promoted oxidative biaryl coupling [2]. Low valent vanadium species such as $CpV(CO)_4$ and Cp_2VCl_2 in combination with Zn and R_3SiCl bring about efficient pinacolic coupling of aliphatic and aromatic aldehydes, ketones and aldimines in a highly selective manner [3]. This methodology was subsequently utilised in the synthesis of some interesting bioactive molecules [4]. Vanadium salen catalysed asymmetric silylcyanation of aldehydes has become a novel entry to the synthesis of chiral cyanohydrins [5]. The oxovanadium compound $VO(OEt)Cl_2$ has been

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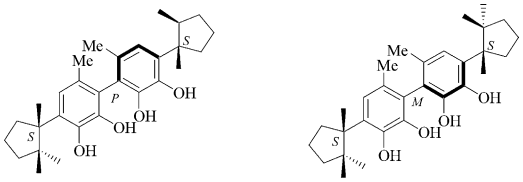
explored extensively in the oxidation of main group organometallics such as organoboranes [6a], organolithium and organomagnesium [6b], organoaluminium [6c], organozinc [6d,6e,6f] and organozirconate [6g] compounds. Vanadium catalysed asymmetric epoxidation is an important reaction in organic synthesis [7]. Aldol type additions could also be carried out in the presence of vanadium [8]. Chiral vanadium(IV) bis(1,3-diketonato) complexes catalysed asymmetric hetero Diels–Alder reactions [9]. The pioneering work from the Hirao group [3,6] in vanadium chemistry has encouraged many others to venture to the area of organic synthesis using vanadium compounds.

In the present article, we wish to discuss recent advances made in vanadium mediated C–C bond formation in biaryl coupling reactions. Some other relevant vanadium induced reactions carried out in our laboratories are also discussed. These reactions are categorised into four parts, viz.

i) Oxidative coupling of phenols, naphthols and arenes
ii) Oxidation of hydroquinones into quinones
iii) Asymmetric synthesis of BINOLs
iv) Modified Mannich-type reaction

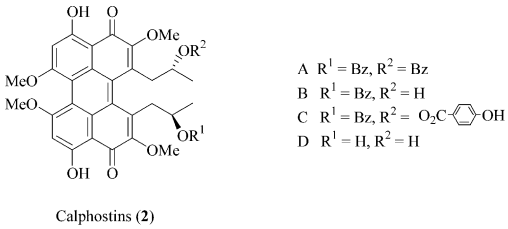
2. Oxidative coupling of phenols, naphthols and arenes

The biaryl moiety is the core structural component of many important natural products such as mastigophorenes (**1**) [10], calphostins (**2**) [11], vancomycin (**3**) [2a], colchicine (**4**) [12], korupensamines (**5**) [13] etc. The oxidative biaryl coupling of phenols has received considerable attention owing both to its utility as a synthetic reaction and its proposed involvement in the biosynthesis of many natural products containing the biaryl segment [14].

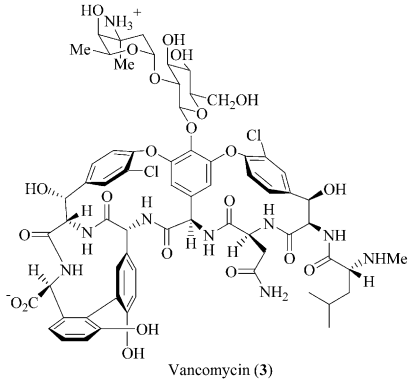


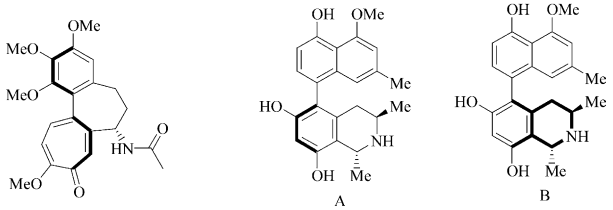
Mastigophorenes (**1**)

Oxovanadium compounds such as $VOCl_3$ and VOF_3 are capable of mediating the oxidative coupling of various phenols and aromatic ethers. This coupling is well utilised in the synthesis of many natural products. For example, the oxidative coupling of laudauosine (**6**) in the presence of VOF_3/trifluoroacetic acid furnished glaucine (**7**) [15] (Eq. (1)). The conversion of septicine (**8**) into phenanthroindolizidine alkaloid tylophorine (**9**)



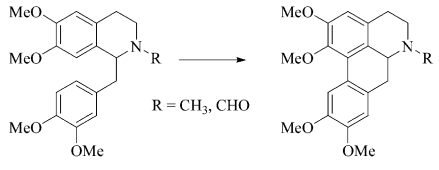
Calphostins (**2**)


Vancomycin (**3**)

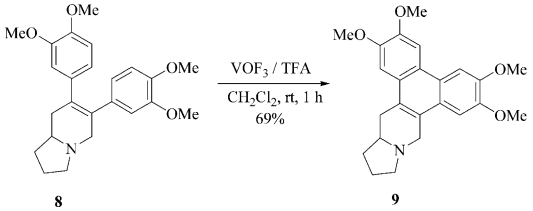


Colchicine (**4**) Korupensamines (**5**)

[16] by VOF_3 (Eq. (2)) and the synthesis of glycopeptide antibiotics, vancomycin [2a] through VOF_3 induced biaryl coupling are some other examples illustrating the applicability of oxovanadium species in the synthesis of some prominent bioactive natural products.



6 **7** (1)

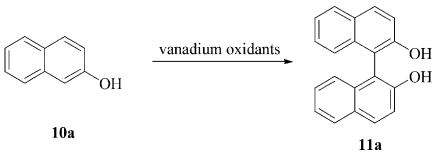


8 **9** (2)

Documented methods for the oxidative coupling of 2-naphthols made use of various transitional metal species as oxidants both in stoichiometric and catalytic

amounts. For example, Fe(III) [17], Mn(III) [18] and Cu(II)-amine [19] were used in stoichiometric amount to mediate the coupling. Whereas $CuCl_2$-amine/AgCl [19c], CuCl(OH)tmeda/O_2 [20], $CuSO_4$ (Al_2O_3)/O_2 [21] and $FeCl_3$ in the presence of ultra-sound irradiation [17a] were employed as catalytic systems to assist the oxidative coupling. However, most of these methods have their own limitations either involving tedious procedures as in the case of the preparation of aforementioned copper complexes or requiring harsh reaction conditions when an oxidant such as $FeCl_3$ was used in combination with ultra-sound irradiation.

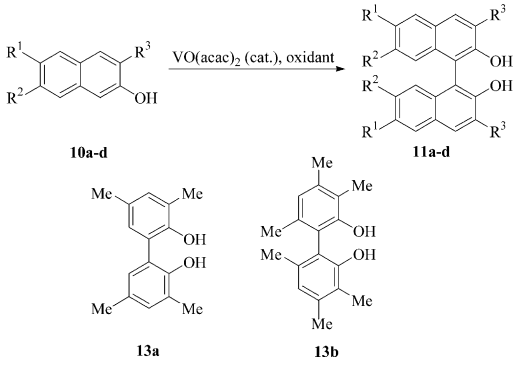
In the light of these observations, we have initially studied the ability of various oxovanadium compounds such as $VOCl_3$, V_2O_5, VO(salen)ClO_4·(H_2O) and $VO(acac)_2$ in the oxidative coupling of 2-naphthol (**10a**) in the absence of any external oxidant (Eq. (3)) [22]. The results are shown in Table 1. Oxidation of 2-naphthol using stoichiometric amount of $VOCl_3$ in dichloromethane at 0 °C for 0.5 h yielded the BINOL (**11a**) in 74% yield. However, similar results were observed when the amount of $VOCl_3$ was lowered to 0.5 equivalents. Coupling was very sluggish when V_2O_5 was used, yielding the BINOL in only 53% yield even after 72 h, presumably due to its poor solubility in dichloromethane. Increasing the amount of V_2O_5 to 3 equivalents and raising the temperature led to significant enhancement in the yield of product. Vanadium pentoxide failed to react in protic solvents such as H_2O or methanol. Sterically hindered oxovanadium salen complex, VO(salen)ClO_4·(H_2O) was prepared by a two step procedure starting from salen and was used in 0.5 equivalents to promote the coupling. The reaction did not proceed in dichloromethane, whereas in 1,2-dichloroethane at 80 °C, BINOL was obtained in 64% yield. Another vanadium species, $VO(acac)_2$ was not useful in inducing the coupling. Obviously, V(IV) species could not mediate the oxidative coupling in these reactions. The fact that similar yields were obtained irrespective of the number of equivalents of $VOCl_3$ may be attributed to the conversion of V(V) to V(III) during the course of the reaction.



10a **11a** (3)

Thus, while the yields were moderate with $VOCl_3$, other vanadium species either did not react or required harsh reaction conditions to accomplish oxidative coupling.

Obviously, the catalytic cycle in the vanadium mediated coupling of naphthols requires an oxidant which will selectively oxidise V(IV) to V(V) without interfering with the coupling process. Accordingly, we have used $VO(acac)_2$ as a precatalyst in combination with molecular oxygen to mediate the oxidative coupling in naphthols and phenols [23]. Oxidants such as H_2O_2, ^{t}BuOOH and oxone were not found to be very rewarding in conjunction with 10 mol% $VO(acac)_2$. Gratifyingly, molecular oxygen served as a gainful oxidant in this catalytic coupling of 2-naphthols **10a**–**d** conducted in dichloromethane at room temperature, and the corresponding 1,1′-bi-2-naphthols **11a**–**d** were furnished in high yields (Table 2). Though phenol could not be coupled under these reaction conditions, substituted phenols such as 2,4-dimethylphenol (**12a**) and 2,3,5-trimethylphenol (**12b**) afforded the corresponding *ortho*–*ortho* coupled products **13** in moderate yields (Eq. (4)).



10a-d **11a-d** (4)

13a **13b**

Recently, two other research groups have carried out biaryl coupling using oxovanadium compounds. Hazra et al. have reported the oxidative dimerisation of

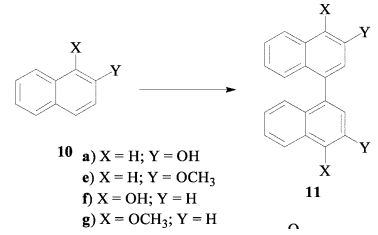
Table 1
Oxidation of 2-naphthol (**10a**) into BINOL (**11a**) by vanadium oxidants

Entry	Oxidant (equivalent)	Solvent	Temperature (°C)	Time (h)	Yield (%)
1	$VOCl_3$ (1)	CH_2Cl_2	0	0.5	74
2	$VOCl_3$ (0.5)	CH_2Cl_2	0	0.5	68
3	V_2O_5 (1)	CH_2Cl_2	25	72	53
4	V_2O_5 (3)	CH_2Cl_2	Reflux	3	80
5	V_2O_5 (1)	MeOH	Reflux	24	0
6	V_2O_5 (1)	H_2O	Reflux	24	0
7	VO(salen)ClO_4(H_2O) (0.5)	$ClCH_2CH_2Cl$	80	24	64
8	$VO(acac)_2$ (1)	CH_2Cl_2	Reflux	24	Trace

Table 2
Oxidative coupling of 2-naphthols **10a**–**d** and phenols **12a**,**b** catalysed by $VO(acac)_2$

ArOH	R^1	R^2	R^3	Time (h)	Product	Yield (%)
10a	H	H	H	24	**11a**	92
10b	Br	H	H	24	**11b**	90
10c	H	OMe	H	9	**11c**	76
10d	H	H	CO_2Me	120	**11d**	35
12a				120	**13a**	66
12b				48	**13b**	62

naphthols and their derivatives **10** into the corresponding 1,1′-dimers **11** using ammonium metavanadate in combination with dilute perchloric acid [24]. Their interest in diospyrin, a bioactive bisnaphthoquinanoid natural product [25], prompted them to study this oxidative dimerisation reaction as a general method to synthesise bisnaphthalene derivatives. 2-Naphthol (**10a**) and its methyl ether **10e** afforded the corresponding dimers in 95% yield. While, 1-naphthol (**10f**) gave a mixture of products, its methyl ether **10g** could be dimerised in quantitative yields under these reaction conditions. Naphthols were found to be more reactive than their methyl ethers in these dimerisation processes. This vanadium induced C–C bond formation methodology was also applied in the dimerisation of 2-hydroxy-1,4-naphthaquinone (lawsone, **14a**) and its methyl ether **14b** and interestingly both the compounds gave the same bisnaphthaquinone derivative **15**, the dimer of lawsone (Eqs. (5) and (6)).



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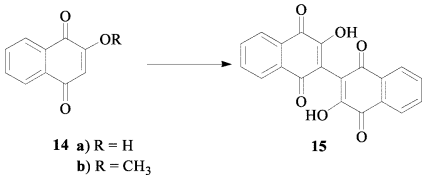
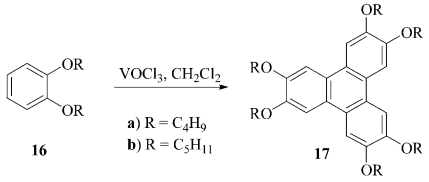


(6)

The oxidative trimerisation of 1,2-dialkoxybenzenes **16** to hexaalkoxytriphenylenes **17** was achieved in the presence of $VOCl_3$ in dichloromethane under mild conditions in good yields (Eq. (7)) [26]. The reaction was carried out with or with out using acid catalyst, H_2SO_4 (Table 3). This vanadium induced coupling could also be utilised in the synthesis of unsymmetrical triphenylenes (**20**) from the reaction of 3,3′,4,4′-tetrapentyloxybiphenyl **18** and appropriate 1,2-dialkoxybenzenes **19** under similar experimental conditions (Eq. (8)).

However, monoalkoxy phenol reacted very slowly in these coupling reactions.



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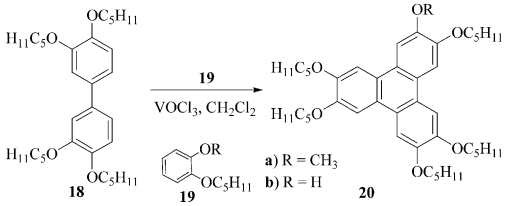


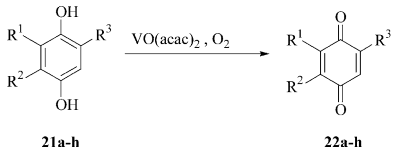
(8)

3. Oxidation of hydroquinones into quinones

Vanadyl acetylacetonate catalysed aerobic oxidation of phenols was tested with *ortho*- and *para*-hydroquinones to provide the corresponding quinones **22a**–**h** [27]. Oxidation of various hydroquinone derivatives **21** using catalytic amount of tetravalent vanadium species, $VO(acac)_2$ in the presence of molecular oxygen furnished the corresponding quinones **22** as sole products in good to excellent yields (Table 4) thus providing a new facile entry to quinones (Eq. (9)).

Table 3
Preparation of triphenylene derivatives using $VOCl_3$ in CH_2Cl_2 solution

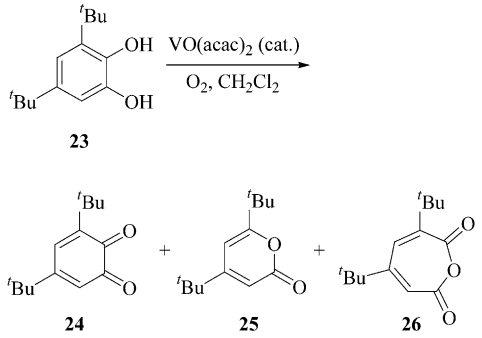
Starting material(s)	% of H_2SO_4	Product	Yield (%)
16a	0	**17a**	86
16a	0.2–0.4	**17a**	79
16b	0	**17b**	85
16b	0.2–0.4	**17b**	83
18+**19a**	0.0	**20a**	68
18+**19a**	0.2–0.4	**20a**	71
18+**19b**	0	**20b**	30
18+**19b**	0.2–0.4	**20b**	35



21a-h 22a-h (9)

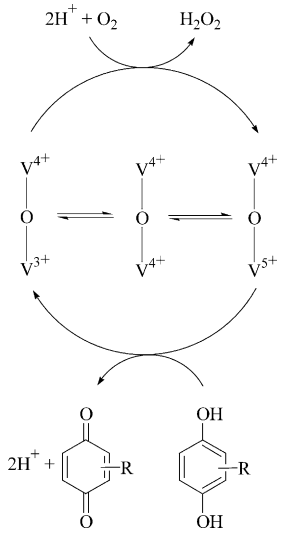
Trimethylhydroquinone (**21d**) afforded the corresponding **22d** quinone in near quantitative yield. Phenyl and *tert*-butyl substituted hydroquinones (**21e**,**f**) underwent facile oxidation under these reaction conditions. Even phenylthiohydroquinone (**21h**) tolerated this catalytic system to afford the corresponding quinone (**22h**) as the sole product without undergoing any side reaction (formation of sulphoxide or sulphone). Polar solvents such as methanol, ethanol and acetonitrile inhibited the oxidation.

Aerobic oxidation of 3,5-di-*tert*-butylpyrocatechol (**23**) in the presence of $VO(acac)_2$ yielded orthoquinone **24** in 15% yield along with two other compounds, lactone **25** and anhydride **26** (Eq. (10)) [28].



(10)

The disproportionation of oxovanadium(IV) complex to the V(V) [29] and V(III) and subsequent molecular oxygen oxidation of V(III) to V(V) [30] constitutes the catalytic cycle in this oxidation reaction (Scheme 1).



Scheme 1.

4. Asymmetric synthesis of chiral BINOLs

Homochiral 1,1′-binaphthalene derivatives have been extensively utilised as chiral inducers in asymmetric synthesis in view of their axial dissymetry and molecular flexibility [31]. Immense research activity has been witnessed in the past decade in the asymmetric synthesis of chiral 1,1′-binaphthalene derivatives especially binaphthols [32] and attention was focussed on asymmetric coupling of naphthols. Though stoichiometric use of chiral ligands led to good selectivities, catalytic enantioselective oxidative couplings are relatively few [33]. Kozlowski's and Nakajima's chiral copper complexes 34a34b and Katsuki's chiral ruthenium complex 34c are excellent recent contributions to the catalysed enantioselective biaryl coupling reactions.

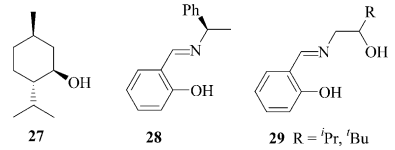
Vanadium complex mediated enantioselective syntheses are not well explored. Asymmetric oxidation of sulphides [35], epoxidation of allylic alcohols [7] asymmetric silylcyanation [5] are a few such vanadium induced reactions reported so far. We have explored the enantioselective synthesis of chiral BINOLs by employing chiral vanadium complexes [36].

In this context, we have synthesised various chiral vanadium complexes making use of monodentate, bidentate and tridentate chiral ligands and used them in the in situ asymmetric oxidative coupling of 2-naphthol. While menthol (**27**) served as monodentate ligand, bidentate ligand **28** was prepared from the condensation of (*R*)-(+)-α-methylphenylamine and sal-

Table 4
Oxidation of hydroquinones **21a**–**h**

Hydroquinone	R^1	R^2	R^3	Time (h)	Product	Yield (%)
21a	H	H	H	10	**22a**	75
21b	Me	H	H	14	**22b**	76
21c	Me	Me	H	15	**22c**	76
21d	Me	Me	Me	14	**22d**	97
21e	^{t}Bu	H	H	10	**22e**	92
21f	Ph	H	H	20	**22f**	88
21g	Br	H	H	25	**22g**	72
21h	SPh	H	H	12	**22h**	85

icylaldehyde. Tridentate ligands **29** were obtained by known procedures [37] from the condensation of chiral α-amino alcohols and salicylaldehyde.

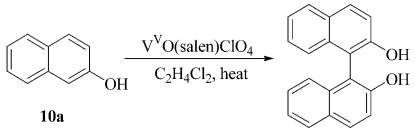


27 **28** **29** R = ^{i}Pr, ^{t}Bu

Deprotonation of the ligand with butyl lithium followed by addition of $VOCl_3$ and subsequent reaction with lithium salt of 2-naphthol led to the formation of BINOL (**11a**) (Scheme 2), albeit with poor enantioselectivity.

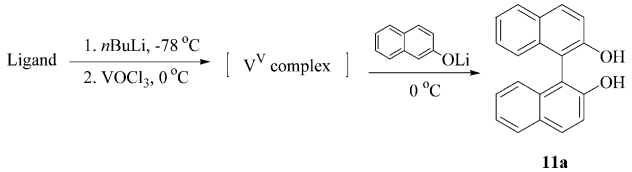
Then we focussed our attention on chiral $V^{V}O$(salen) whose ability in promoting asymmetric synthesis was reported subsequently in other cases [5]. In order to study the coupling reactions using chiral $V^{V}O$(salen), we synthesised five chiral salens **32** from the condensation of different chiral diamines **30** with salicylaldehyde derivatives **31**. These chiral salens were converted into chiral vanadium complexes **33** by reacting with $VO(acac)_2$ in ethanol. Oxidation of the resulted V(IV) complexes **33** with ceric ammonium nitrate (CAN) and subsequent treatment with perchloric acid afforded the required vanadium species **34** (Scheme 3) [35b].

Oxidative coupling of 2-naphthol was carried out in 1,2-dichloroethane using $V^{V}O$(salen) perchlorate salts (Eq. (11)). Though this vanadium species could induce the oxidative coupling, the results were similar to those from in situ experiments (Table 5).



10a **11a** (11)

As the results were not encouraging from the stoichiometric reactions of chiral salen, we have focussed our attention on catalytic asymmetric coupling. As we could conduct the aerobic oxidative coupling of 2-naphthols using a catalytic amount of $VO(acac)_2$, we have carried out the asymmetric oxidative coupling of naphthol using chiral $VO(hfc)_2$ complexes but the yields and selectivity remained poor under these catalytic conditions. Usage

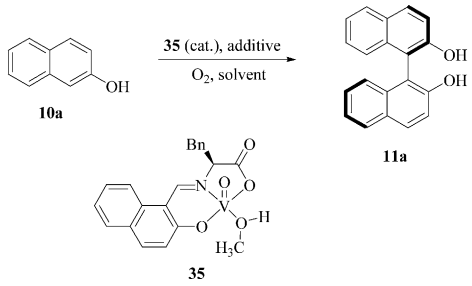


11a

Scheme 2.

of chiral $V^{IV}O$(salen) as the catalyst in the presence of strong acid in these reactions also led to similar results.

Finally, chiral oxovanadium complexes prepared from aldehyde, a chiral amino acid and vanadyl sulphate served as highly useful chiral catalysts in the asymmetric synthesis of BINOLs [38]. Thus we have synthesised the chiral BINOLs by the enantioselective oxidative coupling of 2-naphthol (Eq. (12)) using 2 mol% of chiral oxovanadium complex **35** prepared from



10a **11a** **35** (12)

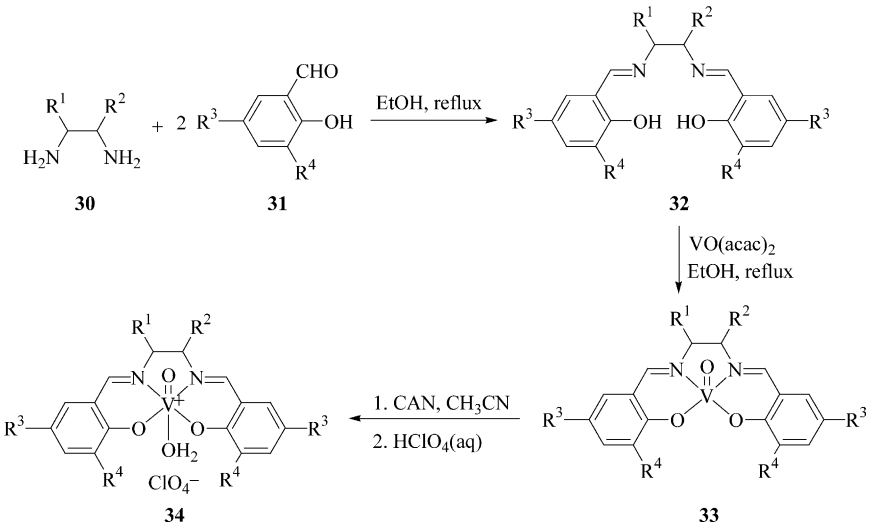
aldehyde, chiral amino acids such as (*S*)-valine or (*S*)-phenylleucine and vanadyl sulphate [39].

Among the chiral vanadium species tested, complex **35** induced better selectivity (Table 6). Complexes prepared from bulkier amino acids such as (*S*)-*tert*-leucine or (*S*)-phenylglycine did not provide significant enantioselectivity.

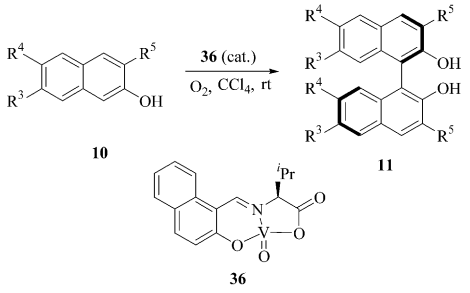
Decrease in the concentration of complexes from 10 to 2 mol% led to a marked enhancement in enantioselectivity. Additives such as TMSOTf, TFAA, $HClO_4$, TMSCl, TESCl, TBDPSCl, TMSBr and TfOH were used to study the promoter effect. TMSCl was found to be a better promoter in terms of yield and selectivity when compared to the other additives. Greater enantioselectivity was observed in polar chloro solvents such as dichloromethane, chloroform and 1,2-dichloroethane.

Though similar selectivity was observed with other substituted 2-naphthols, yield of the BINOL increased with the electron donating capacity of the substituent (Table 7).

Chen and co-workers have independently carried out similar work using oxovanadium complexes [40]. They have employed chiral oxovanadium(IV) complexes derived from tridentate *N*-3,5-substituted and *N*-5,6-benzosalicylidene-α-amino acids in the enantioselective synthesis of chiral BINOLs from 3-, 6-, and 7-substituted 2-naphthols (Eq. (13)). The catalytic profiles of vanadium complexes prepared from different natural and unnatural α-amino acids were studied. Phenylalanine, valine, and *tert*-leucine were found to produce the more useful catalysts. Good enantioselectivity and high chemical yield were obtained with the complex **36** prepared from 5,6-benzosalicylaldehyde and valine.

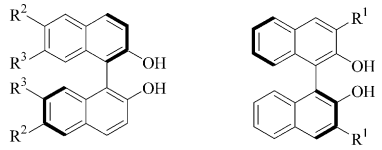


Scheme 3.



(13)

The effect of the substituents on the enantioselectivity was studied by conducting the reaction with various substituted 2-naphthols. Relatively better selectivity was observed in the formation of parent BINOL and 3,3′-dibenzyloxy BINOL (Table 8).

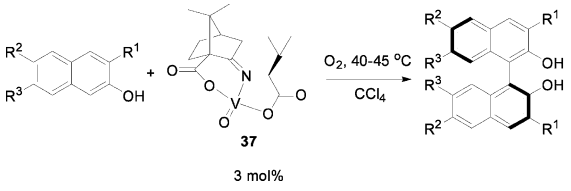


(*R*)-**11a**: $R^2 = R^3 = H$
(*R*)-**11b**: $R^2 = Br$, $R^3 = H$

(*S*)-**11h**: $R^1 = OBn$

The authors have extended this methodology to the cross coupling between the 2-naphthol and 2-aminonaphthalene for accessing the scalemic BINOL derivative in 74% yield, albeit with low enantioselectivity (33%). Oxidative coupling of 2-aminonaphthalene under this set of conditions suffered from low chemical yield and poor enantioselectivity.

Subsequently, the same authors have recently described the catalytic utility of oxovanadium(IV) complexes derived from tridentate *N*-ketopinidene-α-amino acids in the enantioselective oxidative coupling of 2-naphthols [41]. The asymmetric coupling was conducted at 40–45 °C under a stream of oxygen and chiral BINOLs were obtained in 61–99% yields with 42–87% ee (Eq. (14)).



(14)

A maximum selectivity of 87% was observed when the vanadyl complex **37** prepared from L-*tert*-leucine was employed as the catalyst. Among the substituted-2-naphthols, 7-methoxy- and 7-benzyloxy-2-naphthols afforded the corresponding BINOLS with better selectivity though reaction needed 8 days to complete (Table 9, entries 5 and 6). The presence of an electron withdrawing substituent such as bromine in the substrate led to poor selectivity (entry 2).

Table 5
Oxidative coupling of 2-naphthol by V^VO(salen) perchlorate salts

Salen perchlorate	R^1	R^2	R^3	R^4	Temperature (°C)	Time (h)	Yield (%)	ee (%)
34a	H	H	H	H	Reflux	3	59	–
34b	$-(CH_2)_4-$		H	H	73	50	42	11
34c	$-(CH_2)_4-$		H	^{t}Bu	80	10	36	7
34d	$-(CH_2)_4-$		^{t}Bu	^{t}Bu	88	13	55	13
34e	$-(CH_2)_4-$		NO_2	^{t}Bu	80	45	59	26

Table 6
Enantioselective oxidative coupling of 2-naphthol (**10a**)

Entry	Catalyst [c]	Additive	Time (h)	Yield (%)	ee (%)
1	**35**	TfOH	12	56	27 [a]
2	**35**	TMSOTf	12	94	23 [a]
3	**35**	TMSOTf	12	87	31 [b]
4	**35**	TMSOTf	24	80	42 [b]

[a] Concentration of the substrate is 0.1 M.
[b] Concentration of the substrate is 0.5 M.

Table 7
Enantioselective oxidative coupling of 2-naphthol derivatives into BINOLs

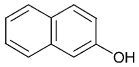
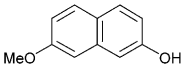
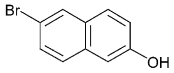
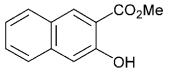
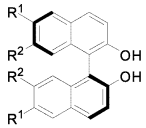
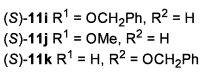
Entry	Naphthol	Time(h)	Yield(%)	ee(%)
1		24	82	51
2		24	91	51
3		24	50	51
4		69	trace	--

Table 8
Effects of substituents on catalytic asymmetric coupling mediated by **36**

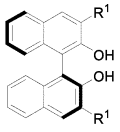
Catalyst	Time (days)	Product	Yield (%)	ee (%)
36	9	**11a**	94	62
36	7	**11b**	97	52
36	8	**11h**	91	68



(*S*)-**11a** $R^1 = R^2 = H$
(*S*)-**11b** R^1= Br, $R^2 = H$
(*S*)-**11c** $R^1 = H$, R^2= OMe

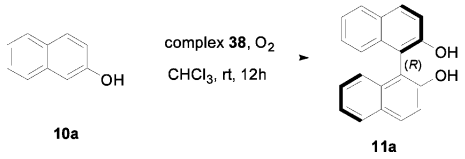


(*S*)-**11i** $R^1 = OCH_2Ph$, $R^2 = H$
(*S*)-**11j** R^1 = OMe, $R^2 = H$
(*S*)-**11k** $R^1 = H$, $R^2 = OCH_2Ph$

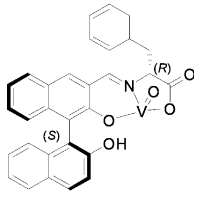


(*S*)-**11l** $R^1 = CPh_2(OH)$

Recently, we have synthesised BINOL based chiral oxovanadium complexes and tested them as catalysts in the asymmetric synthesis of BINOL [42]. Various chiral oxovanadium complexes were prepared from the condensation of BINOL monoaldehyde with chiral amino acids and vanadyl sulphate. Complex **38** provided better selectivity. Oxidative coupling of 2-naphthol in the presence of catalyst **38** and molecular oxygen furnished BINOL in good yield with moderate selectivity (Eq. (15)).



10a **11a** (15)



38

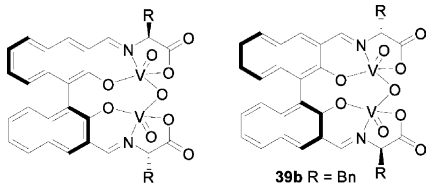
Oxidative coupling of 2-naphthol was investigated by varying the concentration of the substrate as well as mol% of the catalyst (Table 10). For the same concentration of the substrate (entries 1–3) decrease in the amount of the catalyst led to diminished yields though there was no significant effect on the selectivity. Variation of the concentration of the substrate (entries 1, 4 and 5) also did not affect the selectivity. This BINOL based chiral vanadium catalyst **38** was found to be superior to our earlier catalyst **35** in terms of reactivity.

More recently, Gong and co-workers reported the enantioselective oxidative coupling reactions of 2-naphthols using chiral oxovanadium(IV) complexes [43]. They have prepared oxovanadium(IV) complexes **39a**–**e** having chiral centers in both aminoacid and binaphthyl unit by the condensation of chiral 3,3-diformyl-2,2′-dihydroxy-1,1′-bi-2-naphthol with (*S*)-

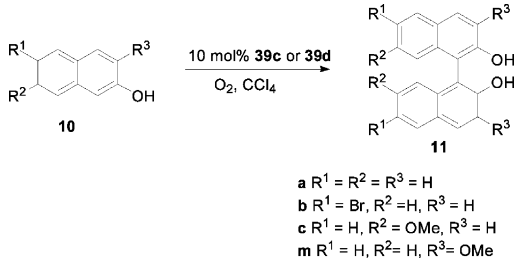
Table 9
Effect of substituents on the catalytic asymmetric coupling mediated by **37**

Entry	Time (days)	Product	Yield (%)	ee (%)
1	7	**11a**	99	84
2	8	**11b**	86	42
3	8	**11j**	99	64
4	10	**11i**	95	59
5	8	**11c**	99	85
6	7	**11k**	96	87
7	10	**11l**	61	76

amino acids and vanadyl sulphate.



Catalysts **39c** and **39d** provided good selectivities. Coupling products were obtained in 86–99% yields and with 83–99% ee when 2-naphthols were submitted to oxidative coupling in the presence of 10 mol% of either catalyst **39c** or **39d** and oxygen in CCl_4 (Table 11). While 7,7′-dimethoxy-BINOL (**11c**) was formed with highest enantioselectivity (entry 4), 3,3′-dimethoxy-BINOL (**11e**) could not be obtained by this oxidative coupling (entries 7 and 8).



5. Modified Mannich-type reaction

Mannich reaction [44] is an important C–C bond formation reaction widely used in the synthesis of secondary and tertiary amine derivatives and applied as a key step in the synthesis of many bioactive molecules and complex natural products [45]. This reaction basically involves the addition of a carbon-nucleophile to an iminium ion resulting in a secondary or tertiary amine derivative depending on the nature of the substrate used. The required iminium ion is often prepared by Polonovsky or modified Polonovsky reaction [46] in which a tertiary amine oxide is treated with a promoter [47]. However, these promoter reagents are either expensive, difficult to handle or required in more than stoichiometric amount. Though the vanadium catalysed oxidation of amine to amine oxide was reported earlier [48], vanadium mediated generation of the iminium ion from amine oxide was hitherto unreported. During the course of our studies towards finding an ideal combination of vanadium oxidant and external co-oxidant to promote the homo-coupling of phenols and naphthols, we have conducted an equimolar reaction of *N*-methylmorpholine *N*-oxide (NMO) and 2-naphthol in the presence of 10 mol% of V_2O_5 in dichloromethane under refluxing conditions [49]. To our pleasant surprise, the corresponding Mannich adduct was obtained as the product in good yield in this reaction (Scheme 4). The yield of the product could be further upgraded by increasing the amount of NMO to 3 equivalents. We have developed this vanadium catalysed reaction into an expedient general method for the in situ generation of iminium ions from tertiary amine oxides for their subsequent application in a modified Mannich-type reaction.

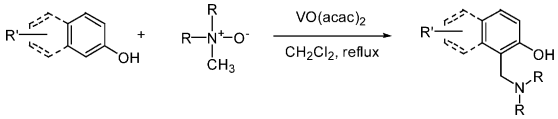
Table 10
Oxidative coupling of 2-naphthol (**10a**) using vanadium catalyst **38**

Entry	Concentration of substrate (M)	Mol% of catalyst	Yield [a] (%)	ee (%)
1	0.1	10	72	52
2	0.1	5	51	51
3	0.1	2	44	53
4	0.2	5	74	54
5	0.5	2	72	46

[a] Reaction time 12 h.

The ability of other V(IV) and V(V) species such as $VO(acac)_2$, $VO(O^iPr)_3$ and $VOSO_4{\cdot}2H_2O$ to promote the Mannich reaction was examined. Among these oxovanadium species, $VO(acac)_2$ with its greater solubility in dichloromethane has efficiently brought about the reaction to provide the Mannich base in excellent yield (92%) in a relatively shorter reaction time. Moderate yields of Mannich base in $VOSO_4{\cdot}H_2O$ catalysed reaction may be attributed to the poor solubility of this vanadium species in dichloromethane (Table 12).

Various naphthol and phenolic nucleophiles were reacted with NMO and trimethylamine *N*-oxide (TMNO) under these optimised reaction conditions (Eq. (16)). Mannich products were obtained in excellent yields in case of 2-naphthol, bromo and methoxy substituted 2-naphthols. The yield is moderate when an ester substituent is present in 2-naphthol. 1-Naphthol and phenol derivatives also yielded the ortho directed Mannich products albeit in low yields (Table 13).

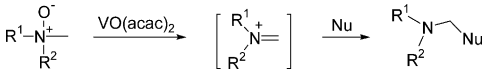


(16)

This $VO(acac)_2$ catalysed methodology could be successfully applied for the conversion of trimethylamine oxide into iminium salt which is equivalent to an Eschenmoser salt. Our procedure was found to be more convenient when compared to the earlier reported methods [50] for the generation of these unstable Eschenmoser salts.

Table 11
Coupling reaction of 2-naphthol and derivatives using catalysts **39c** and **39d**

Entry	Catalyst	Product	Time (days)	Yield (%)	ee (%)
1	**39c**	**11a**	8	86	81
2	**39d**	**11a**	6	95	83
3	**39c**	**11c**	5	85	97
4	**39d**	**11c**	5	88	98
5	**39c**	**11b**	5	98	87
6	**39d**	**11b**	5	99	88
7	**39c**	**11m**	7	Trace	ND
8	**39d**	**11m**	7	Trace	ND



Scheme 4.

The possible role of the vanadium catalyst in this modified Mannich-type reaction is illustrated in Scheme 5 by taking the reaction of 2-naphthol and *N*-oxide as a representative example. Complexation of the catalyst and *N*-oxide followed by an intramolecular elimination through six-membered transition structure **A** leads to iminium ion **B**. The resulted vanadium species abstracts an acidic proton from 2-naphthol to produce naphtholate, which adds on to the iminium ion **B** to provide the Mannich base. Finally, the oxovanadium catalyst is regenerated by the elimination of water molecule from the protonated vanadium species **C**.

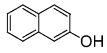
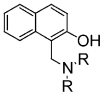
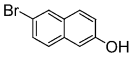
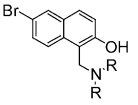
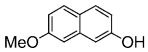
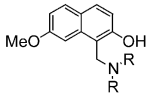
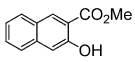
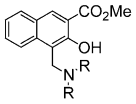
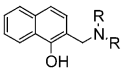
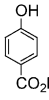
When *N*-methylpyrrolidine *N*-oxide was used as source of iminium ion in the Mannich reaction with 2-naphthol, C–C bond formation has taken place from *endo* position. On the other hand, *exo* addition characterised the reaction when *N*-substituted morpholines were employed as amine oxides. Reaction with allyl morpholine resulted in semi-ketal product through initial 1,4-addition of iminium ion and subsequent hydrolysis. When 1,3-diketone derivatives were used as nucleophiles, product was formed through the double alkylation of imine carbon (Table 14).

Table 12
Preparation of the Mannich base from 2-naphthol and NMO using vanadium catalysts

Entry	Catalyst	Time (h)	Yield [a] (%)
1	V_2O_5	30	78
2	$VO(O^iPr)_3$	16	78
3	$VO(acac)_2$	8	92
4	$VOSO_4 \cdot 2H_2O$	24	52
5	VO(salen)	24	22

[a] Reaction conditions: catalyst (10 mol%), CH_2Cl_2, reflux.

Table 13
Reactions of naphthols and phenols with amine *N*-oxide catalysed by $VO(acac)_2$

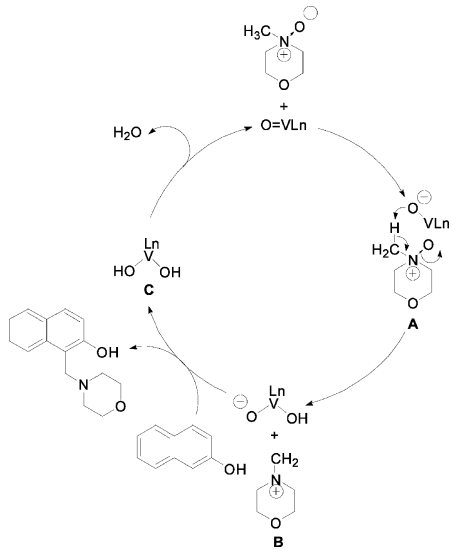
Entry	ArOH	Amine *N*-oxide	Time (h)	Product[a]	Yield (%)
1		NMO	8		92
2		TMNO	24		78
3		NMO	8		84
4		NMO	8		81
5		NMO	72		61
6		NMO	8		58
7		NMO	48		37
8		TMNO	24		82
9		NMO	48		33
10		NMO	120		43

[a] For entries 2, and 8: R = CH_3; For the remaining entries: R,R = -($CH_2CH_2OCH_2CH_2$)-

NMO = *N*-methylmorphorline *N*-oxide
TMNO = trimethylamine *N*-oxide

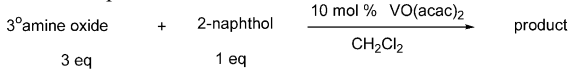
6. Conclusions

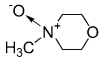
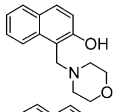
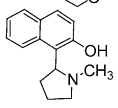
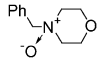
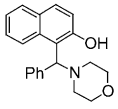
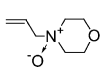
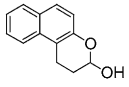
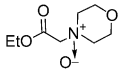
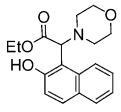
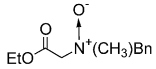
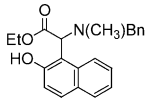
Vanadium mediated C–C bond formation has ushered a new era in the domain of organic synthesis. In this article we have described a new dimension of the chemistry of vanadium induced biaryl coupling and a modified Mannich-type reaction. The immense research activity in this area has led to some new findings on the



Scheme 5.

Table 14
$VO(acac)_2$ catalysed modified Mannich-type reactions of 3° amine oxides with naphthols



Entry	3°amine oxide	Temp. (°C)	Time (h)	Product	Yield (%)
1		reflux	8		92
2		reflux	48		64
3		reflux	48		63
4		reflux	48		52
5		25	4		81
6		25	12		70

application of the known vanadium species and the development of new complexes. A few reports have been devoted to the vanadium catalysed asymmetric synthesis of BINOLs and this version is in its infancy. Several aspects such as the promoter effect on the asymmetric coupling of naphthols remain unclear and need further investigation. Our $VO(acac)_2$ catalysed in situ generation of iminium ions from amine *N*-oxides presents scope to access a variety of Mannich bases.

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