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Catalytic Diastereo- and Enantioconvergent Synthesis of Vicinal Diamines from Diols through Borrowing Hydrogen

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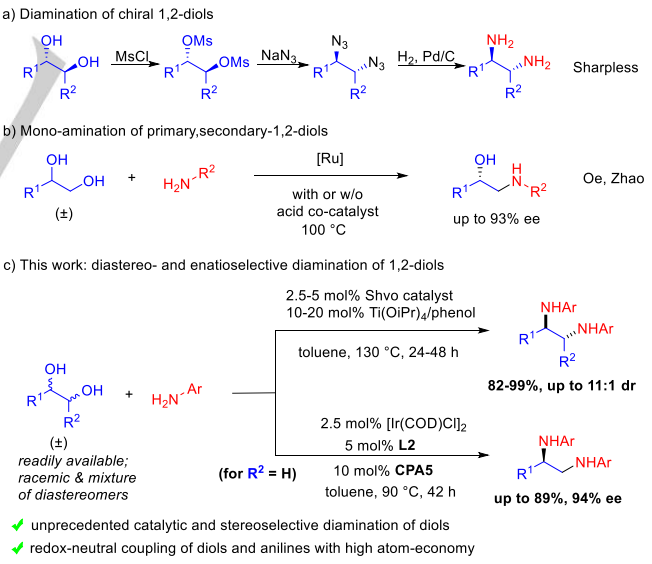
Abstract: We present herein an unprecedented diastereoconvergent synthesis of vicinal diamines from diols through an economical, redox-neutral process. Under cooperative ruthenium and Lewis acid catalysis, readily available anilines and 1,2-diols (as a mixture of diastereomers) couple to forge two C-N bonds in an efficient and diastereoselective fashion. By identifying an effective chiral iridium/phosphoric acid co-catalyzed procedure, the first enantioconvergent double amination of racemic 1,2-diols has also been achieved, resulting in a practical access to highly valuable enantioenriched vicinal diamines.

Chiral vicinal diamines are a key structural motif in numerous pharmaceuticals and biologically active entities.[1] They also find extensive use in asymmetric synthesis as chiral catalysts/ligands or precursors to them.[2] Accordingly, the preparation of various chiral vicinal diamines, especially in an enantiopure form, remains a significant topic in synthetic chemistry.[3] While classical methods that rely on resolution or diastereoselective reactions using stoichiometric chiral reagents still find wide use,[4] extensive and continuous efforts have been devoted to the development of catalytic enantioselective diamine synthesis. Notably, many catalytic methods have focused on the enantioselective functionalization of amine-containing substrates that include Mannich reaction of α-amino carbonyls,[5] aziridine ring opening by amine-based nucleophiles,[6] hydroamination of allylamines,[7] etc. In contrast, the construction of C-N bond directly from simple feedstock substrates, especially diamination of alkenes,[8] provides great advantage for practical access to chiral diamines. Significant advancement has been made for this topic of research in recent years. The available methods, however, either require a tethering amino alkene substrate or specially-substituted/protected amines to proceed in high efficiency and selectivity. The identification of alternative readily available substrates for stereoselective diamine synthesis is still of tremendous interest.

Compared to diamines, vicinal diols are much more abundant and readily available from feedstock chemicals. The conversion of diols to diamines, however, typically requires a multi-step procedure involving leaving group introduction and nucleophilic substitution. As these reactions proceed with retention of stereochemistry, the diol substrates need to be in an enantioenriched form to produce chiral diamines in the same fashion (as exemplified in **Scheme 1a**).[9] Undoubtedly, a one-pot, stereoconvergent double amination of simple racemic diols using minimal reagents will be much more desirable for diamine synthesis.



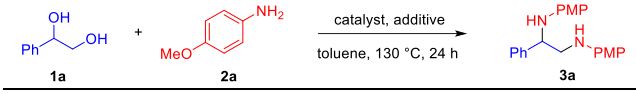
Scheme 1. Efforts towards stereoselective amination of 1,2-diols.

We envisioned that such an unprecedented stereoconvergent synthesis of diamines from diols could be achieved through a catalytic borrowing hydrogen process.[10] The high atom- and step-economy of this redox-neutral strategy has been widely recognized by the chemical industry.[11] Amination of mono-alcohols using this catalytic mechanism has been realized using various transition metal catalysts. Enantioconvergent variant of this reaction has also been reported by our group and others.[12-14] It is worth noting that amination of vicinal diols via catalytic

borrowing hydrogen has been attempted; however, only mono-amination was achieved producing enantioenriched amino alcohols by the Oe group[14b] and our group (**Scheme 1b**).[12c] A catalytic amination of diols using simple amines leading to flexible acyclic vicinal diamines still remains elusive, let alone stereoselective variants. Importantly, even mono-amination of alcohols requires high temperature to drive this three-step one-pot transformation to high conversion; a double amination reaction that includes multiple redox cycles and condensation steps is without doubt even more challenging to achieve.

Herein, we present our development of a cooperative catalytic system using Shvo's catalyst[15] and titanium-based Lewis acid that promotes highly efficient and diastereoselective synthesis of diamines from a wide range of readily available vicinal diols using simple anilines (**Scheme 1c top**). For the subclass of secondary-primary diols, we have also achieved the first enantioconvergent double amination, in which commercially available diols and anilines undergo C-N coupling, in the absence of any other stoichiometric reagent, to produce vicinal diamines in high level of enantioselectivity (**Scheme 1c bottom**).

Table 1. Optimization of double amination of **1a**[a]

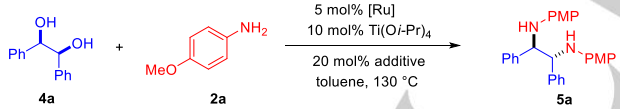


1a **2a** **3a**

Entry	Catalyst (mol%)	Additives (mol%)	Yield(%)[b]
1	$[IrCp^*Cl_2]_2$ (5)	K_2CO_3 (20)	<2
2	$[RuCl_2(p\text{-cymene})]_2$ (5)	dppf (10)	10
3	$Ru_3(CO)_{12}$ (5)	*rac*-BINAP (15)	<2
4	$Cu(OTf)_2$ (5)	K_2CO_3 (20)	<2
5	**Ru-1** (2.5)	\	15
6	**Ru-1** (2.5)	Ti(O*i*-Pr)$_4$ (5)	81
7	**Ru-1** (2.5)	Ti(O*i*-Pr)$_4$ (5) & PhOH (20)	99
8	\	Ti(O*i*-Pr)$_4$ (10)	<2

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), catalyst and additive in toluene (1.0 mL) at 130 ℃ under N_2 for 24 h. [b] Yield determined by crude ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.

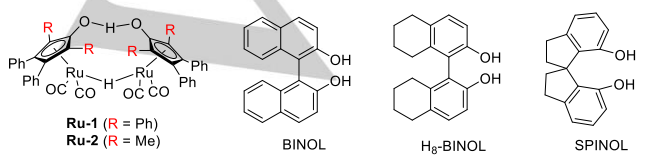
Table 2. Optimization of diastereoselective double amination of **4a**[a]



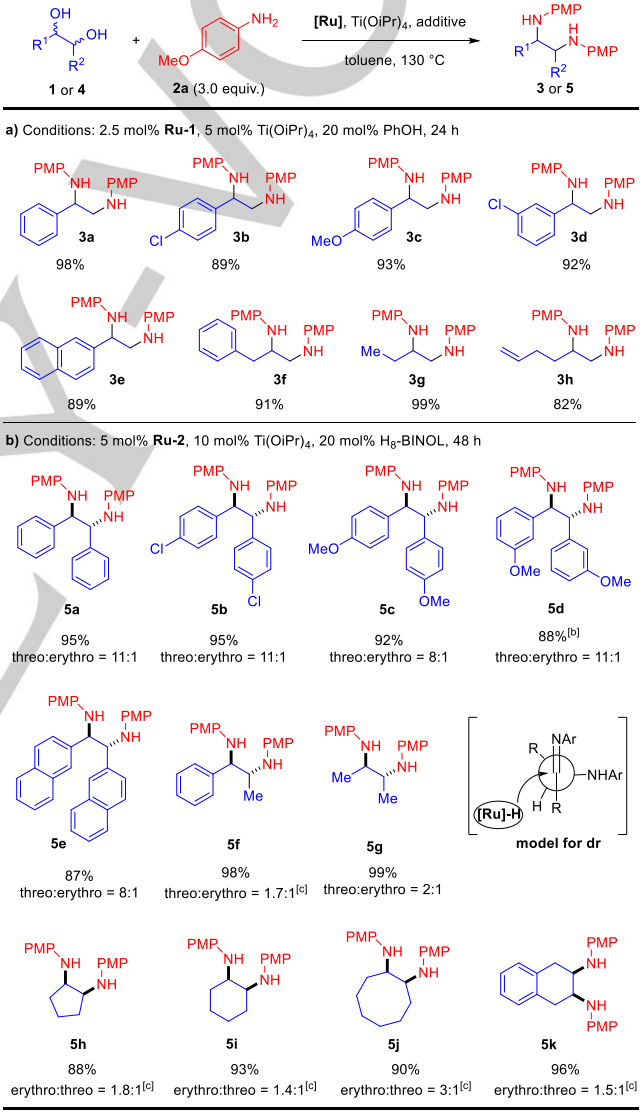
4a **2a** **5a**

Entry	Catalyst	Additive	Time (h)	Yield (%)[b]	dr[b]
1	**Ru-1**	PhOH	90	62%	4:1
2	**Ru-1**	BINOL	66	99%	5:1
3	**Ru-1**	BINAP	48	25%	4:1
4	**Ru-1**	PPh_3	48	<2%	\
5	**Ru-2**	BINOL	48	95	8:1
6	**Ru-2**	SPINOL	48	95%	9:1
7	**Ru-2**	H_8-BINOL	48	**90%**	**11:1**

[a] Reaction conditions: **4a** (0.1 mmol), **2a** (0.3 mmol), catalyst and additive in toluene (1.0 mL) at 130 ℃ under N_2. [b] Yield and dr (threo:erythro) determined by crude ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.



We initiated our investigation with **1a** and **2a** as our model substrates by testing a wide range of established catalytic systems for borrowing hydrogen process (**Table 1**). As exemplified by entries 1-5, different iridium, ruthenium and copper-based catalytic systems under basic and neutral conditions led to no or low conversion to the desired product **3a**, with Shvo's catalyst **Ru-1** giving the most promising 15% yield (entry 5). Different co-catalysts, and especially acids were examined at this point. The use of Ti(O*i*-Pr)$_4$ proved to be the optimal choice (entry 6); further modification using phenol then resulted in a quantitative formation of **3a** (entry 7). To rule out a simple Lewis acid-catalyzed diamine formation, the reaction was carried out only in the presence of Ti(O*i*-Pr)$_4$ (without **Ru-1**), under which no formation of **3a** was observed at all (entry 8).



[a]The reactions were carried out at 0.2 mmol scale in the diol substrates and all yields were isolated. The dr of the products was determined by crude ^{1}H NMR. [b]Reaction time 72 h. [c]The diastereomers were separated and characterized in pure form.

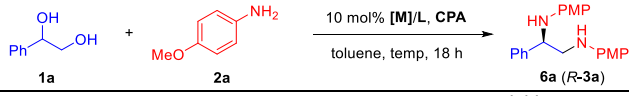
Scheme 2. Scope of Ru-catalyzed double amination of vicinal diols[a]

With the proof-of-principle reaction achieved for **1a**, our efforts then turned to double amination of secondary diols such as **4a** to achieve the preparation of vicinal diamines bearing two stereocenters. As illustrated in **Table 2**, the optimal conditions

from **Table 1** produced **5a** with moderate yield and 4:1 dr (entry 1). Further screening of various types of ligands for the Lewis acid including BINOL and phosphines led to no improvement (entries 2-4). Variations on the Shvo's catalyst structure were probed, from which **Ru-2** turned out to be beneficial for **5a** formation (95% yield & 8:1 dr; entry 5). Further fine tuning of ligand for titanium complex showed H_8-BINOL as the optimal choice. Under the optimal conditions, **5a** was produced in a high yield (90%) with 11:1 dr (entry 7).

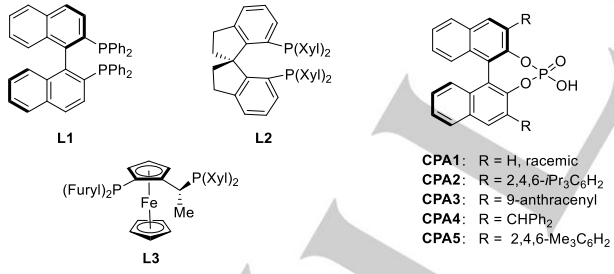
The scope of this Ru/Ti-catalyzed double amination of vicinal diols was probed as summarized in **Scheme 2**. By the use of the first set of optimal conditions from **Table 1**, a wide range of secondary-primary diols underwent amination smoothly to produce **3a**-**3h** bearing various aryl and alkyl substituents in high yields. Notably, the alkene functionality was well-tolerated in **3h**.

Table 3. Optimization of enantioselective double amination of **1a**[a]



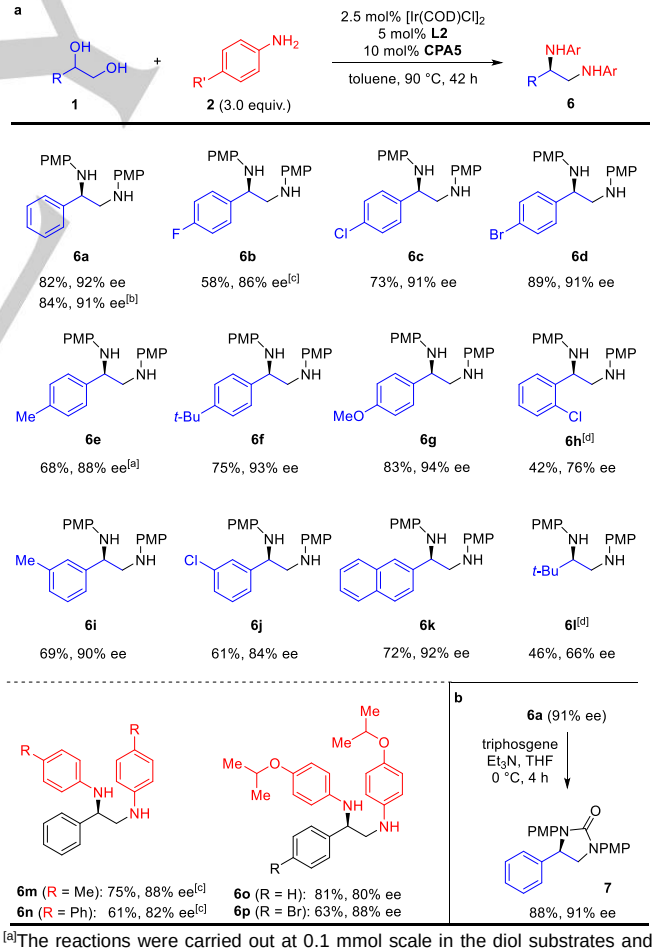
Entry	[M]	L	Acid	Temp (°C)	Yield (%)[b]	ee (%)[c]
1	**Ru-1**	\	Ti/BINOL	130	\	<2
2	$[Ir(COD)OMe]_2$	**L1**	**CPA1**	130	51	18
3	$[Ir(COD)OMe]_2$	**L2**	**CPA1**	130	62	65
4	$[Ir(COD)OMe]_2$	**L3**	**CPA1**	130	12	14
5	$[Ir(COD)Cl]_2$	**L2**	**CPA1**	130	70	65
6	$[Ir(COD)Cl]_2$	**L2**	**CPA1**	90	72	73
7	$[Ir(COD)Cl]_2$	**L2**	**CPA2**	90	64	79
8	$[Ir(COD)Cl]_2$	**L2**	*ent*-**CPA2**	90	54	60
9	$[Ir(COD)Cl]_2$	**L2**	**CPA3**	90	70	50
10	$[Ir(COD)Cl]_2$	**L2**	**CPA4**	90	64	41
11	$[Ir(COD)Cl]_2$	**L2**	**CPA5**	90	70	92
12[d]	$[Ir(COD)Cl]_2$	**L2**	**CPA5**	90	94	92

[a]General conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), 10 mol% [Ir]/ligand, 10 mol% **CPA** and 4 Å MS (20 mg) were mixed in toluene (1.0 mL) and allowed to react at the indicated temp for 18 h. [b]NMR yield using 1,3,5-trimethoxybenzene as the internal standard. [c]Determined by HPLC on a chiral stationary phase. [d]The optimized conditions used a lower 5 mol% [Ir] and **L2** in 0.5 mL toluene for a reaction time of 42 h.



Alternatively, amination of secondary-secondary diols were carried out using the catalytic conditions from Table 2. Firstly, various biaryl-substituted diamines **5a**-**5e** were obtained in high yields and good dr (8:1 to 11:1). For acyclic substrates bearing small alkyl substituents, however, the dr dropped significantly to ~2:1 favoring the same major isomer (for **5f** & **5g**). Considering the model for stereoselectivity, we propose that the proper choice of catalyst enhances the inherent selectivity in the final imine reduction step, as illustrated by the Felkin-Ann model. In contrast, while amination of cyclic diols proceeded smoothly to yield the diamine products, the opposite *erythro*-diastereomer was formed as the major (albeit with low 1.4:1 to 3:1 dr). In these cases, the catalyst control likely goes against the inherent substrate control, in which the *erythro*-isomer is preferred based on the cyclic structure. Overall, this catalytic double amination proceeded with high efficiency and synthetically useful level of diastereoselectivity to yield vicinal diamines in a highly atom- and step-economical fashion.

With double amination of diols achieved, we then focused on achieving enantioselectivity for this process. All our efforts on modifying the Ru/Ti system by developing a planar chiral Ru-complex or the use of chiral Lewis acid proved futile (exemplified by entry 1, **Table 3**), which prompted us to reinvestigate a new catalytic system with the reaction of **1a** and **2a** as the model. After extensive screening of different systems, we were delighted to observe the formation of **6a** (i.e., *R*-**3a**) with moderate yield at 130 ℃ with a noticeable 18% ee by the use of a commercial iridium methoxide complex, BINAP in combination with chiral phosphoric acid (entry 2). Examination on the chiral phosphine ligands identified **L2** as the most promising choice (entry 3 vs. entries 2 & 4). Further variation on the iridium precursor showed the chloride complex worked better under this set of conditions (entries 5 & 6), and produced **6a** with up to 73% ee at a lower temperature of 90 ℃. At this stage, various chiral phosphoric acids were systematically screened (entries 7-11), which identified **CPA5** as the optimal choice (92% ee for **6a**). Finally, efforts to lower the catalyst loading worked out nicely with an extended reaction time (entry 12). This set of conditions was then adopted for exploring the scope of this catalytic enantioconvergent double amination of diols.



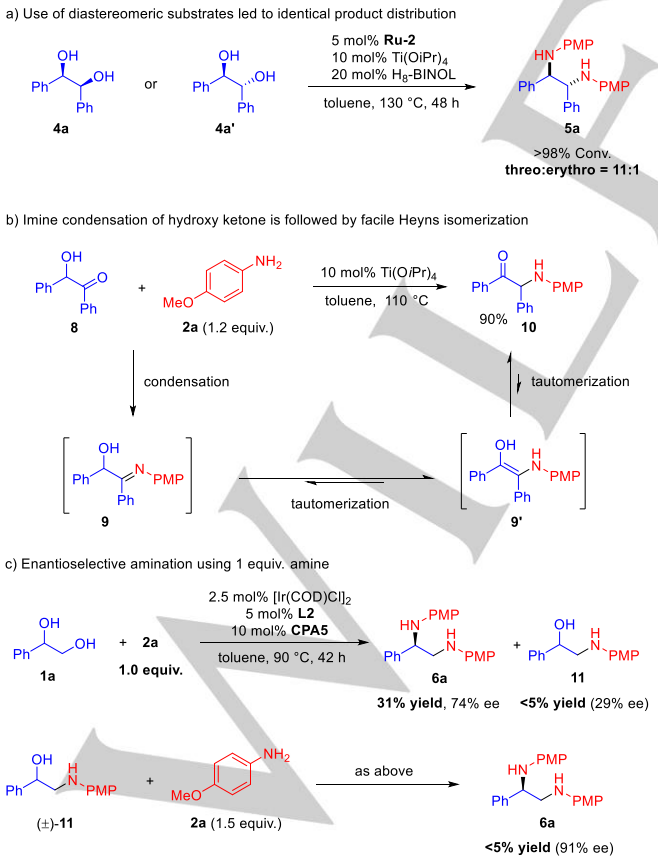
[a]The reactions were carried out at 0.1 mmol scale in the diol substrates and all yields were isolated. [b]Results of a 1.0 mmol reaction. [c]66 h reaction time. [d]10 mol% [Ir]/ligand was used instead.

Scheme 3. Scope of enantioselective double amination of diols[a]

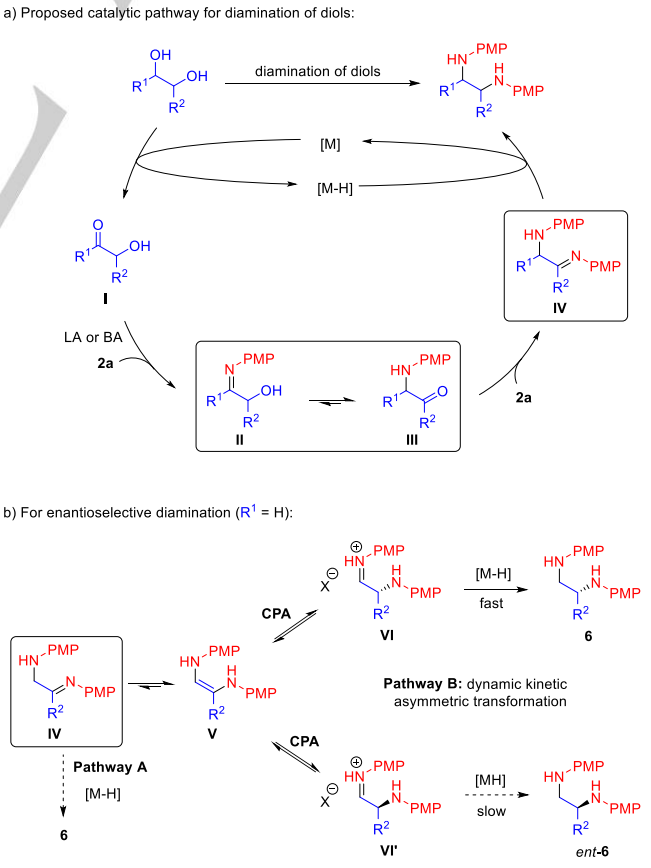
As summarized in **Scheme 3a**, a wide range of secondary-primary diols bearing an aryl substituent could participate in this amination with high efficiency and good to excellent enantioselectivity. Vicinal diamines **6a**-**6j** bearing electron-withdrawing, donating or neutral substituents on the phenyl ring were formed in 76-94% ee with up to 89% isolated yield. Naphthyl-substituted **6k** was also formed in high yield and ee. When alkyl-containing substrates were examined, however, the level of enantioselectivity dropped significantly; diamine **6l** was formed in a moderate 66% ee. In addition, variations on the aniline reagent could also be well-tolerated; chiral diamines **6m**-**6p** were accessed in good to high yields and ee. The absolute configuration of this series of enantioenriched vicinal diamines was established by an alternative multi-step asymmetric synthesis of *ent*-**6a** (see SI for details). Unfortunately, this chiral iridium/phosphoric acid co-catalyzed procedure failed to deliver chiral diamines bearing two stereocenters due to lack of reactivity for secondary-secondary diol substrates. The identification of a more reactive catalytic system is still required to deliver chiral diamines with both diastereo- and enantiocontrol. These catalytic reactions could be smoothly scaled up; a 1.0 mmol reaction of **6a** formation resulted in the same efficiency and selectivity. These chiral anilines are valuable compounds themselves, removal of the PMP groups to access the free diamines were also attempted. Notably effective deprotection of diamines **5a**, **5i**, etc. were reported.[16] When a similar procedure was followed for deprotection of **6a**, cyclic **7** could be accessed smoothly (**Scheme 3b**), reaction of which with various oxidants (CAN, $PhI(OAc)_2$, etc.), however, only led to decomposition. Efforts are now focused on for identifying effective enantioselective diamine synthesis using other amine sources.

With the amination of diols achieved, we turned to some key control experiments to shed light on the operating mechanism of this transformation. Firstly, the amination was confirmed to be a diastereoconvergent process by the use of either *meso* **4a** or racemic **4a'** as the substrate; both diastereomers of the substrate led to the same outcome for the diamine **5a** (**Scheme 4a**). Secondly, during our efforts to individually synthesize the presumed intermediates in our cascade reaction, we were intrigued to observe that the imine condensation product of α-hydroxyketone **8** and **2a** (the presumed **9**) could not be isolated at all. Instead, it underwent a facile double tautomerization to produce α-aminoketone **10** through enol **9'** (**Scheme 4b**), which has been known as the Heyns Rearrangement that mainly finds wide application in carbohydrate chemistry.[17] This provided a key clue for our reaction mechanism: the double amination does not take place via two individual amination by borrowing hydrogen, but involves a Heyns Rearrangement instead. The proposed amino alcohol intermediate (such as **11**) is likely not a productive intermediate.

To provide further support for this alternative mechanistic pathway, the amination of diol **1a** using only 1 equiv. of **2a** was performed under the standard conditions (**Scheme 4c**). Amino alcohol **11** was only observed with <5% yield with a low 29% ee. Instead, diamine **6a** was formed in a moderate 31% yield (consuming >60% of the aniline) with a moderate 74% ee. When racemic **11** was prepared and subjected to the same reaction conditions with 1.5 equiv. **2a**, diamine **6a** was only formed in <5% yield, further supporting that **11** is not a productive intermediate in our catalytic double amination. It is important to note that the high 91% ee of **6a** was consistent of the enantioconvergent nature of our catalytic reaction.



Scheme 4. Mechanistic studies on double amination of diols



Scheme 5. Proposed catalytic pathway for double amination of diols

With these information, we propose a reasonable catalytic pathway as illustrated in **Scheme 5a**. Mono-oxidation of diol and imine condensation (leading to **II**) is followed by a facile Heyns Rearrangement to yield **III**. A second imine condensation yields the key amino imine **IV**, which undergoes reduction by the metal hydride to deliver the desired diamine with regeneration of catalyst. Overall, one redox cycle is coupled with two condensation and one isomerization to realize an efficient double amination of diols. For the enantioselective variant, we propose that the reaction likely proceeds through a dynamic kinetic asymmetric transformation similar to our previous reported examples (**Scheme 5b**).[12b-c] Although a direct enantioselective reduction of ketimine **IV** to produce **6** (**Pathway A**) cannot be completely ruled out, we believe it is relatively sluggish compared to the tautomerization to enamine **V** and then **VI/VI'**. In that case, a catalyst-controlled selective reduction of **VI** in preference over **VI'** then lead to enantioenriched vicinal diamine synthesis through a dynamic kinetic asymmetric transformation (**Pathway B**).

In conclusion, we have achieved an unprecedented diastereo- and enantioconvergent synthesis of diamines from simple diols using anilines. These transformations proceed through a redox-neutral process with high atom- and step-econony, employ simple Ru- or Ir-based catalysts in combination with Lewis or Bronsted acid co-catalyst, and deliver highly valuable enantioenriched vicinal diamines. Further investigation will be focused on the development more efficient catalytic borrowing hydrogen systems to address simultaneous control of contiguous stereocenters for the access to a wider range of enantiopure vicinal diamines and other valuable poly-functionalized compounds.

Acknowledgements

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Keywords: chiral diamines • redox-neutral • double amination of diols • cooperative catalysis • enantioselectivity

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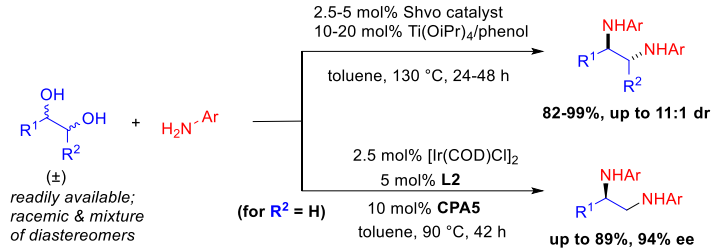

We present herein an unprecedented diastereoconvergent synthesis of vicinal diamines from diols through an economical, redox-neutral process. Under cooperative ruthenium and Lewis acid catalysis, readily available anilines and 1,2-diols (as a mixture of diastereomers) couple to forge two C-N bonds in an efficient and diastereoselective fashion. By identifying an effective chiral iridium/phosphoric acid co-catalyzed procedure, the first enantioconvergent double amination of racemic 1,2-diols has also been achieved, resulting in a practical access to highly valuable enantioenriched vicinal diamines.