Communication

Vanadium(V) Complex-Catalyzed One-Pot Synthesis of Phenanthridines via a Pictet-Spengler-Dehydrogenative Aromatization Sequence

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Abstract: Phenanthridine and its derivatives are important structural motifs that exist in natural products, biologically active compounds, and functional materials. Here, we report a mild, one-pot synthesis of 6-arylphenanthridine derivatives by a sequential cascade Pictet-Spengler-dehydrogenative aromatization reaction mediated by oxovanadium(V) complexes under aerobic conditions. The reaction of 2-(3,5-dimethoxyphenyl)aniline with a range of commercially available aryl aldehydes provided the desired phenanthridine derivatives in up to 96% yield. The ability of vanadium(V) complexes to function as efficient redox and Lewis acid catalysts enables the sequential reaction to occur under mild conditions.

Keywords: phenanthridines; catalysis; Pictet-Spengler; Lewis acid; heteroarenes; dehydrogenative aromatization; vanadium(V); domino reaction

1. Introduction

Phenanthridine and its structurally related compounds play essential roles in a variety of chemical fields due to their existence in a broad range of natural products, bioactive compounds, and functional materials (Figure 1) [1–5]. Phenanthridine was first synthesized from the reaction between benzaldehyde and aniline in 1889 [6], and a number of preparative methods have been reported to date [1,7–9]. However, since most protocols necessitate harsh reaction conditions and/or multi-step reaction sequences from commercially available starting materials [10,11], concise and mild preparation procedures for this important class of compounds are still in high demand [12–15].

Organometallic vanadium(V) complexes have been employed in the development of a wide range of organic reactions [16–23]. Their high valency and ability to exist in multiple oxidation states enable vanadium complexes to act as Lewis acid and/or redox catalysts. We theorized that these functionalities can be used to perform domino reaction sequences in a single operation. Furthermore, there are a few reports on the cooperative effect of vanadium(V) complexes in synthesis [24–28].

Figure 1. Examples of phenanthridine derivatives.

Recently, we developed chiral oxovanadium complexes [29] that act as redox and/or Lewis acid catalysts for the enantioselective oxidative coupling of arenols [30–33], Friedel–Crafts-type reactions [34], and a sequential cascade reaction that affords oxahelicenes [28]. As part of our ongoing research, we envisioned a one-pot synthesis of phenanthridine derivatives **5** using vanadium(V) complexes **6** as Lewis acid/oxidation catalysts (Scheme 1). Thus, Lewis acidic vanadium(V) complex **6** would promote a Pictet–Spengler reaction of imine intermediate **3** formed by the condensation of aniline **1** and benzaldehyde **2** to afford tetrahydroisoquinoline **4**. A subsequent dehydrogenative aromatization of **4**, assisted by the same vanadium(V) complex, now operating as a one-electron oxidant, would yield the desired phenanthridine product **5** [28,35].

Scheme 1. This work: synthesis of phenanthridines derivatives by a vanadium(V)-catalyzed Pictet–Spengler-dehydrogenative aromatization reaction sequence.

2. Results and Discussion

Our initial investigations focused on the reaction between 2-(3,5-dimethoxyphenyl)aniline (**1a**) and benzaldehyde (**2a**) (1.2 equivalents) using vanadium(V) catalyst *rac*-**6a** (10 mol%) in various solvents at 50 °C (Table 1). The reaction in tetrahydrofuran (THF) afforded the desired product **5a** in 31% yield (Entry 1), however, the reaction cascade performed markedly better in dichloromethane, toluene, and acetonitrile (Entries 2–4). Of the solvents tested, acetonitrile (MeCN) gave the best outcome, affording **5a** in 95% yield (Entry 4). Next, we turned our attention to the vanadium(V) catalyst complex. Catalysts (*S*)-**6b** and (*S*)-**6c** bearing an *iso*-propyl and *tert*-butyl group, respectively, showed comparable catalytic activities to *rac*-**6a** (Figure 2), which contains a benzyl group on the amino acid moiety (Entries 5 and 6). The bulkier di-*tert*-butyl-substituted catalyst (*S*)-**6d** and naphthalene-based catalyst (*S*)-**6e** resulted in lower yields of **5a**, 68% and 85%, respectively (Entries 7 and 8). The optimum temperature

for the reaction was 50 °C. A significantly diminished yield of product **5a** was observed at 40 °C, which may be attributed to suppression of the Pictet–Spengler-dehydrogenative aromatization cascade (Entry 9), whereas the marginally lower yields recorded at 60 °C and 70 °C (Entries 10 and 11) may be due to partial decomposition of the vanadium complex. Only a trace amount of phenanthridine **5a** was obtained in the absence of the catalyst (Entry 12). The commercially available vanadium(V) and vanadium(IV) catalysts, V_2O_5 and $VOSO_4$ respectively, displayed poor activity; less than 15% yield of **5a** observed after 72 h at 50 °C in both cases (Entry 13). Finally, we decided on the optimal reaction conditions of 10 mol% of catalyst (*S*)-**6b** in MeCN (0.2 M) at 50 °C, shown in Entry 4, to continue with our studies; due to the lower cost of (*S*)-valine than that of the racemic amino acids and other optically pure amino acids, chiral vanadium complex (*S*)-**6b** with the high activity was selected as an appropriate catalyst for this reaction.

Table 1. Screening of reaction conditions.

Entry	V cat (10 mol%)	Solvent	Temp. (°C)	Yield of 5a (%) ¹
1	<i>rac</i> - 6a	THF	50	31 ²
2	<i>rac</i> - 6a	CH ₂ Cl ₂	reflux	86
3	<i>rac</i> - 6a	Toluene	50	89
4	<i>rac</i> - 6a	MeCN	50	95
5	(<i>S</i>)- 6b	MeCN	50	95
6	(<i>S</i>)- 6c	MeCN	50	91
7	(<i>S</i>)- 6d	MeCN	50	68 ²
8	(<i>S</i>)- 6e	MeCN	50	85
9	(<i>S</i>)- 6b	MeCN	40	35 ²
10	(<i>S</i>)- 6b	MeCN	60	87
11	(<i>S</i>)- 6b	MeCN	70	75
12	-	MeCN	50	Trace
13	V_2O_5 or $VOSO_4$	MeCN	50	<15 ²

¹ Determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. ² Imine **3a** and tetrahydroisoquinoline **4a** were observed by ¹H NMR.

Figure 2. Structures of vanadium(V) complexes and observed intermediates.

Under the optimal reaction conditions, we conducted the one-pot reaction sequence on a range of aryl aldehydes (**2a–y** Table 2). Benzaldehydes **2a–q**, containing electron-donating and electron-withdrawing groups in the *para*-, *meta*-, or *ortho*-positions, underwent smooth transformations to give the corresponding 6-arylphenanthridines **5a–q** in 72–96% yields. Notably, the reaction exhibited high functional group tolerance as evident by the presence of phenolic (**5c**), cyano (**5e**), halide (**5f–h**, **5k–o**), and nitro (**5j** and **5q**) substituents. The reaction of di- and penta-substituted benzaldehydes **2r** and **2s** afforded the products **5t** and **5u** in 78% and 85% yields, respectively. When 2-naphthaldehydes (**5t** and **5u**) and 1-naphthaldehydes (**5e–x**) were employed, the desired products **5t–x** were also obtained in moderate to good yields. We were also pleased to observe that bipyridine derivative **5y** was synthesized in 83% yield using 2-formylpyridine.

Table 2. Substrate scope.

1 + **2** (1.2 equiv)

(S)-**6b** (10 mol %)

MeCN, air
50 °C, 72 h

5

(S)-**6b**

5a-j

5	R	yield
5a	H	92%
5b	Et	79%
5c	OH	79%
5d	OBn	86%

5e-g

5	R	yield
5e	CN	86%
5f	F	95%
5g	Cl	96%

5h-j

5	R	yield
5h	Br	92%
5i	CF ₃	72%
5j	NO ₂	92%

5k-l

5	R	yield
5k	F	90%
5l	Br	92%

5m-q

5	R	yield
5m	F	89%
5n	Cl	82%
5o	Br	91%

5p-q

5	R	yield
5p	CF ₃	86%
5q	NO ₂	79%

5r, 78%

5s, 85%

5t, 69%

5u, 69%

5v, 89%

5w, 78%

5x, 95%

5y, 83%

A plausible catalytic cycle for the vanadium(V)-catalyzed cascade reaction of aniline **1a** with benzaldehyde **2a** is shown in Figure 3. In the first step, condensation of **1a** with **2a** occurs to give imine **3a**. Subsequently, the vanadium(V) complex (*S*)-**6b** promotes the intramolecular cyclization of the imine via complex **A**; this key carbon-carbon bond forming step completes construction of the phenanthridine core and affords the intermediate **B** [34]. Intermediate **C** is generated after re-aromatization of **B**. At this stage in the cycle, the addition of water to **C** might yield tetrahydroisoquinoline **4a**, which was observed by proton nuclear magnetic resonance (^1H NMR) analysis (vide supra), and (*S*)-**6b**. Dehydrogenative aromatization of **4a** proceeds via intermediate **C** and a single-electron transfer from the electron-rich nitrogen center to vanadium(V) forms the intermediate **D**, which undergoes the dehydrogenative aromatization to give the desired product **5a** [35]; when (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) (1.0 equivalent) was added to the optimal conditions, no desired product **5a** was obtained at all. Under degassed N_2 instead of air, the sequential reaction proceeded to give **5a**, probably due to easily auto-oxidation of **4a** during analysis. Finally, oxidation of vanadium(IV) by molecular oxygen regenerates the vanadium(V) complex (*S*)-**6b**.

Figure 3. A plausible catalytic cycle for the vanadium(V)-catalyzed Pictet-Spengler-dehydrogenative aromatization cascade reaction of aniline **1a** and benzaldehyde **2a**.

In order to realize an enantioselective vanadium(V)-catalyzed domino cascade reaction, we turned our attention to the construction of trimethoxyphenanthridine derivative **5w** (Scheme 2), which contains an axis of chirality and potentially has a role as a chiral reagent such as 6-(2'-diphenylphosphino-1'-naphthyl)phenanthridine (PHENAP) ligand in Figure 1. In a preliminary study, treatment of aniline **1a** and 2-methoxy-1-naphthaldehyde (**2w**) with binaphthol vanadium(V) complex (*R_a,S*)-**6f** in chloroform (CHCl_3) at 20°C successfully afforded **5w** in moderate yield and 65% ee. X-ray crystallographic analysis of optically pure **5w** (The Cambridge crystallographic data centre number: CCDC 2005061) was performed after the optical resolution of the mixture involving the major product **5w** by using preparative chiral high-performance liquid chromatography (chiral HPLC) (CHIRALPAK IC, *n*-hexane/*i*-PrOH = 2/1, $v = 10\text{ mL min}^{-1}$, $\lambda = 231\text{ nm}$). The absolute configuration of **5w** with catalyst (*R_a,S*)-**6f** was determined to be *S* based on the Flack parameter (0.02(6)). The tetrahydroisoquinoline intermediate **4w** readily underwent auto-dehydrogenative aromatization, which implies that the enantioenrichment step may be the carbon-carbon bond-forming step of the Pictet-Spengler reaction, i.e., intermediate **A** to intermediate **B** (Figure 3); we clarified a possibility of kinetic resolution of

rac-**4b** [36] using catalyst (*R_a,S*)-**6f** under the reaction conditions as shown in Scheme 2 because isolation of **4w** was difficult due to its stability. After 3 h, 70% of **4b** was converted to **5b** and the optical purity of the recovered **4b** was 8% ee. Additional investigation of the enantioselective reaction mechanism from both experimental and theoretical perspectives is now in progress.

Scheme 2. Enantioselective domino reaction towards axially chiral phenanthridine derivative **5w**.

3. Materials and Methods

^1H -, ^{13}C -, and ^{19}F -NMR were recorded with JEOL JMN ECS400 FT NMR, JNM ECA600 FT NMR (JEOL, Tokyo, Japan) or Bruker AVANCE II (BRUKER, Billerica, MA, USA) (^1H -NMR 400, 600, or 700 MHz, ^{13}C -NMR 100, 150, or 175 MHz, ^{19}F -NMR 376 MHz.) ^1H -NMR spectra (see Supplementary Materials) are reported as follows: chemical shift in ppm relative to the chemical shift of tetramethylsilane (TMS) at 0 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). ^{13}C -NMR spectra reported in ppm relative to the central line of triplet for CDCl_3 at 77.0 ppm. $\text{CF}_3\text{CO}_2\text{H}$ used as external standards for ^{19}F -NMR. FT-MS spectra were obtained with LTQ Orbitrap XL (Thermo Fisher Scientific, Waltham, MA, USA). ESI-MS spectra were obtained with JMS-T100LC (JEOL, Tokyo, Japan). FT-IR spectra were recorded on a JASCO FT-IR system (FT/IR4100) (JASCO, Tokyo, Japan). Column chromatography on SiO_2 was performed with Kanto Silica Gel 60 (63–210 μm). Commercially available organic and inorganic compounds were used without further purification.

3.1. Vanadium(V) Complex-Catalyzed Pictet-Spengler Reaction and Dehydrogenative Aromatization Sequence

In a test tube, to a solution of a 2-(3,5-dimethoxyphenyl)aniline (**1a**) in acetonitrile (0.2 M) a benzaldehyde derivative **2** (1.2 eq) and a mononuclear vanadium catalyst (*S*)-**6b** (10 mol%) were added. The reaction was stirred at 50 °C for 72 h under air atmosphere. After the reaction, the reaction mixture was concentrated in vacuo and purified by silica column chromatography using hexane/acetone as eluent to afford the phenanthridine derivatives **5**.

3.2. Enantioselective Reaction

In a test tube, to a solution of **1a** in chloroform (0.1 M), 2-methoxy-1-naphthaldehyde **2w** (1.2 equivalent), and a mononuclear vanadium catalyst (*R_a,S*)-**6f** (10 mol%) were added. The reaction was stirred at 20 °C under air atmosphere. After 99 h, the reaction mixture was concentrated in vacuo and purified by preparative thin-layer chromatography using hexane/dichloromethane/ethyl acetate (5/5/1) as eluent to afford (*S*)-7,9-dimethoxy-6-(2-methoxynaphthalen-1-yl)phenanthridine **5w** in 51% yield with 65% ee.

4. Conclusions

Vanadium(V)-catalyzed domino reactions for the efficient synthesis of phenanthridines have been achieved. Vanadium(V) complexes promote a Pictet-Spengler-dehydrogenative aromatization cascade due to their ability to mediate Lewis acid and oxidative catalysis under mild reaction conditions. The vanadium catalysis exhibited high functional group tolerance using various aryl aldehydes. Furthermore, a chiral vanadium(V) complex was applied to the enantioselective synthesis of an axially chiral phenanthridine derivative. Further applications of the reaction to other aniline derivatives are ongoing in our laboratory.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/8/860/s1>. SI-1: Compound Data, SI-2: NMR Spectra, SI-3: HPLC Chromatograms, SI-4: X-ray Crystallographic Analysis of (S)-5w.

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