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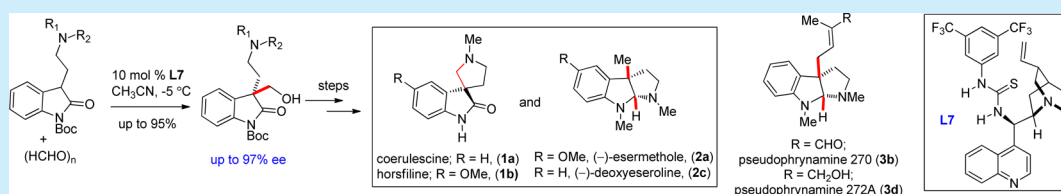
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Unified Approach to the Spiro(pyrrolidinyl-oxindole) and Hexahydropyrrolo[2,3-*b*]indole Alkaloids: Total Syntheses of Pseudophrynamines 270 and 272A

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S Supporting Information



ABSTRACT: The first enantioselective total syntheses of architecturally interesting prenylated pyrroloindole alkaloids, (–)-pseudophrynamines 272A (**3d**) and 270 (**3b**), have been achieved starting from enantioenriched 2-oxindoles having all-carbon quaternary stereocenters. A common strategy involving a thio-urea catalyzed aldol reaction is employed for the total synthesis of both spiro(pyrrolidinyl-oxindole) and hexahydropyrrolo[2,3-*b*]indole alkaloids.

Architecturally intriguing spiro(pyrrolidinyl-oxindole) alkaloids such as coerulescine (**1a**, Figure 1) and horsfieldine (**1b**),

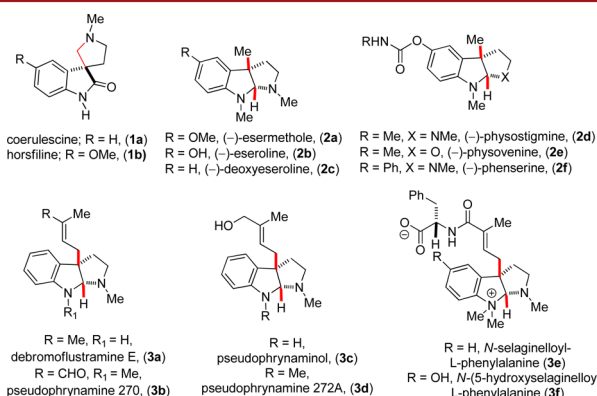


Figure 1. Selected pyrroloindole and spiro-pyrroloindole alkaloids.

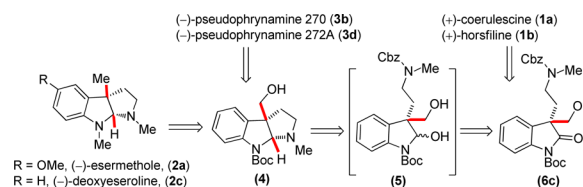
owing to the presence of the all-carbon quaternary stereocenters,¹ pose a great synthetic challenge. They were isolated from *Pharalis coerulescens*² in 1998 and *Horsfieldia superba*³ in 1991, respectively, and since then, a number of efficient strategies for the construction of such quaternary stereogenic centers were developed.⁴ The hexahydropyrrolo[2,3-*b*]indole alkaloids (2–3, Figure 1), on the other hand, are frequently found in a range of natural alkaloids,⁵ numerous marketed drugs, and drug candidates.⁶ One of the congeners of this family, physostigmine (**2d**), isolated from the African Calabar bean seeds,⁷ *Physostigma venenosum*,⁸ displays huge biological activities. In fact, its therapeutic properties for the treatment of Alzheimer's disease, glaucoma, and myasthenia gravis^{7,9} account for numerous

synthetic reports for the synthesis of esermethole (**2a**) and physostigmine (**2d**).¹⁰

Hexahydropyrrolo[2,3-*b*]indole alkaloids (**3a–3f**, Figure 1) having a prenyl moiety adjacent to the pseudobenzyl 3a-site, viz. flustramines,¹¹ pseudophrynamines,¹² and sellaginellin acid,¹³ have gained considerable attention owing to their potential biological activities. Biosynthetically, these alkaloids are believed to be originated from L-tryptophan.¹² Although there are a few reports on diastereoselective approaches to access these moieties,¹⁴ efficient enantioselective approaches to these targets still need to be addressed.¹⁵

Intrigued by their challenging structural arrays and impressive biological activities, we envisioned a unified approach to these targets in an asymmetric fashion. Retrosynthetically, we imagined that enantioenriched compound **6c** could serve as an advanced intermediate for the total syntheses of spiro(pyrrolidinyl-oxindole) alkaloids, coerulescine (**1a**) and horsfieldine (**1b**), and hexahydropyrrolo[2,3-*b*]indole alkaloids, (–)-esermethole (**2a**) and (–)-deoxyeseroline (**2c**) (Scheme 1). Additionally, total syntheses of C-3a prenylated alkaloids,

Scheme 1. Our Retrosynthetic Analysis



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(-)-pseudophrynamines 270 (3b) and 272A (3d), could easily be achieved from a pyrroloindoline intermediate 4 (Scheme 1). We thought to access enantioenriched 6c from 3-substituted 2-oxindole 8c following a Dynamic Kinetic Asymmetric Transformation (DYKAT)¹⁶ involving a hydroxymethylation reaction using paraformaldehyde as the C1 unit,¹⁷ in the presence of a suitable bifunctional thio-urea ligand.

At the outset, enantioselective organocatalytic hydroxymethylations of 2-oxindoles 7a and 7b were carried out using paraformaldehyde in the presence of ligand L1 (Figure 2).

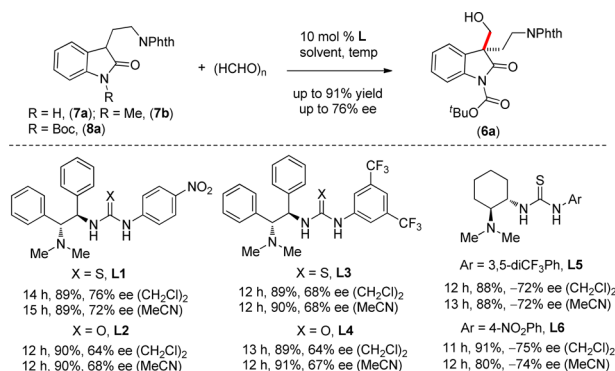


Figure 2. Optimization of aldol reaction of (±)-8a in the presence of TU-catalysts.

However, the reaction was not successful, and we imagined that the pH of the methine proton in 7a–b might be responsible for this failure. To circumvent this, we changed the protecting group to an electron-withdrawing Boc-group which may enhance the acidity of the methine proton^{10i,18} sufficiently by allowing a facile enolization of compound 8a. We then carried out the reaction with 8a using paraformaldehyde and in the presence of ligands L1–L6 (Figure 2). The reactions were performed in dichloroethane and acetonitrile as solvent at room temperature. The product was formed in a maximum 76% enantioselectivity when 10 mol % of thio-urea L1 was used as catalyst (Figure 2). Among other ligands used, L5¹⁹ and L6 were also found to be promising in affording product 6a in the range 72–75% ee.

We then attempted the hydroxymethylation of 8a in the presence of other ligands L7²⁰ and L8 at 25 °C in the presence of dichloroethane and acetonitrile (Table 1). The reaction afforded 78% ee (entry 1) in dichloroethane using L7, whereas using L8 afforded product in just 46% ee (entry 3). Solvent screening showed acetonitrile to be the best solvent, furnishing the product in up to 81% ee at 25 °C (entry 2). However, other solvents such as dichloromethane, chloroform, acetone, ethyl acetate, and tetrahydrofuran were not good for this reaction, affording products in the 35–71% ee range (entries 5–9). Ligand loading of 5 mol % yielded the product in 77% ee (entry 10).

Hydroxymethylation of 8a was further studied in the presence of L7 at different temperatures, and it was found that lower temperatures led to higher enantioselection with a maximum of 91% ee at -5 °C (Table 1, entry 15). Bifunctional thio-urea ligands L9–L11 in acetonitrile at -5 °C afforded enantioenriched product 6a in 85% ee, -87% ee, and -83% ee, respectively (Figure 3). Exhaustive optimization studies eventually led us to choose 10 mol % of L7 in acetonitrile for asymmetric hydroxymethylation of 8a with paraformaldehyde in acetonitrile at -5 °C.

We then looked for a substrate scope with a wide range of 2-oxindoles 8a–h. All these substrates underwent a smooth

Table 1. Optimization of Aldol Reaction of (±)-8a

Reaction scheme: $(\pm)\text{-}8\text{a} + (\text{HCHO})_n \xrightarrow{10 \text{ mol } \% \text{ L7, solvent, temp}}$ up to 92% yield, up to 91% ee \rightarrow 6a

Ligand structures and conditions:

- Ar = 3,5-diCF₃Ph, L7:** 10 h, 89%, 78% ee (CH_2Cl_2); 10 h, 92%, 81% ee (CH_3CN)
- Ar = 4-NO₂Ph, L8:** 11 h, 90%, 46% ee (CH_2Cl_2); 12 h, 92%, 76% ee (CH_3CN)
- Ar = 3,5-diCF₃Ph, L5:** 10 h, 91%, 68% ee (CH_2Cl_2); 10 h, 90%, 35% ee (CHCl_3)
- Ar = 4-NO₂Ph, L6:** 20 h, 86%, 70% ee (acetone); 22 h, 81%, 66% ee (EtOAc)
- Ar = 3,5-diCF₃Ph, L5:** 20 h, 82%, 71% ee (THF)
- Ar = 4-NO₂Ph, L6:** 18 h, 65%, 77% ee (CH_3CN)
- Ar = 3,5-diCF₃Ph, L5:** 20 h, 90%, 85% ee (CH_3CN)
- Ar = 4-NO₂Ph, L6:** 22 h, 81%, 54% ee (acetone)
- Ar = 3,5-diCF₃Ph, L5:** 20 h, 90%, 73% ee (CH_2Cl_2)
- Ar = 4-NO₂Ph, L6:** 20 h, 89%, 71% ee ($(\text{CH}_2)_2\text{Cl}_2$)
- Ar = 3,5-diCF₃Ph, L5:** 30 h, 88%, 91% ee (CH_3CN)

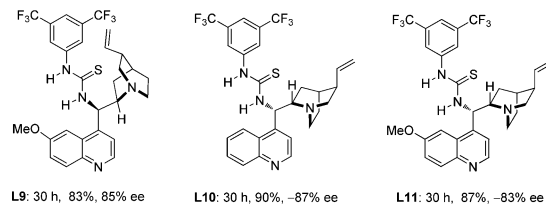


Figure 3. Optimization of aldol reaction of (±)-8a in the presence of TU-catalysts.

reaction to afford a variety of products 6a–h in excellent yields with up to 97% ee (in the case of 6h) (Figure 4). Interestingly, the TBS-protected hydroxyethyl group at the 3-position of 2-oxindoles (8i and 8l) was also found to be a good aldol donor, furnishing products having an all-carbon quaternary stereocenters 6i and 6l in excellent yields and up to 95% ee. Also, an

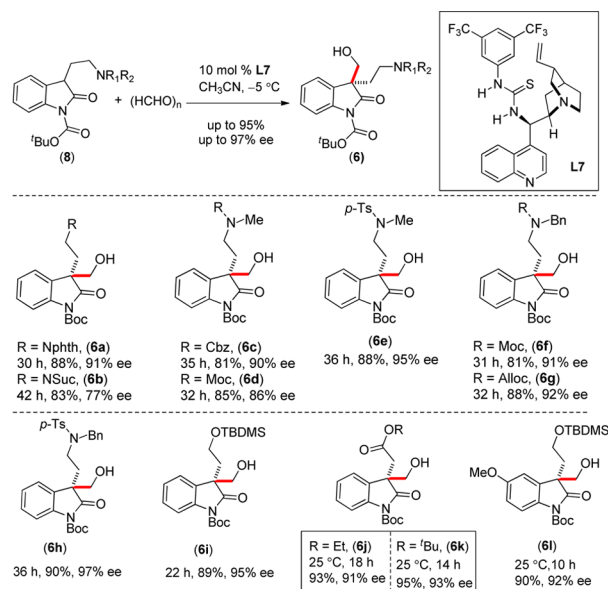
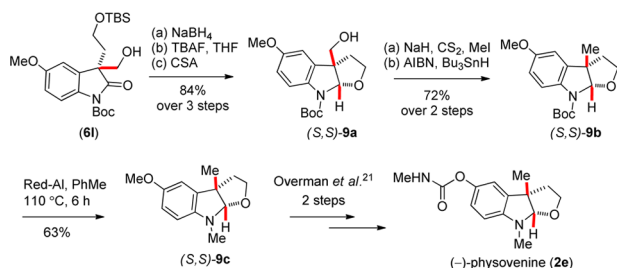


Figure 4. Substrates scope of TU-catalyzed hydroxymethylation.

alkyl acetate group at the 3-position of 2-oxindoles (**8j** and **8k**) also proved to be good aldol donors, to afford products **6j** and **6k** in excellent yields in up to 93% ee (Figure 4).

Starting from the enantioenriched compound **6l**, we carried out the formal total synthesis of (–)-physovenine **2e** in a few steps (Scheme 2). First, we converted compound **6l** to advanced

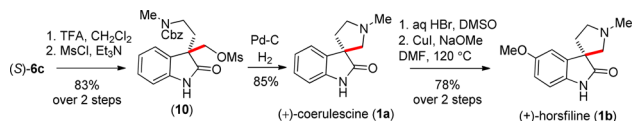
Scheme 2. Formal Synthesis of (–)-Physovenine (2e)



intermediate [6,5,5]-tricyclic core **9a** in 3 steps, which on subsequent deoxygenation afforded furoindoline intermediate **9b** (Scheme 2). The latter was then reduced in refluxing toluene to afford **9c** from where the synthesis of physovenine (**2e**) was already reported;²¹ thus, our efforts led to the formal total synthesis of this alkaloid (Scheme 2).

Further, starting from compound **6c** as potential intermediate, we then turned our attention toward the total syntheses of alkaloids, (+)-coerulescine (**1a**) and (+)-horsfiline (**1b**). Compound **6c** was treated with trifluoroacetic acid to get oxindole which was further reacted with methanesulfonyl chloride to afford mesylate (+)-**10** in 83% yield over 2 steps (Scheme 3). The latter was then converted to naturally occurring

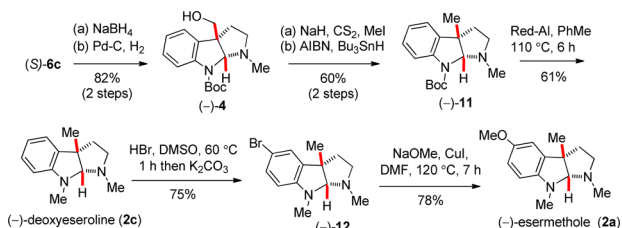
Scheme 3. Total Syntheses of (+)-Coerulescine (1a) and (+)-Horsfiline (1b)



(+)-coerulescine (**1a**) in 85% yield when subjected to catalytic Pd–C in ethanol (1 atm of H₂). Further, (+)-**1a** was treated with aqueous HBr in DMSO to furnish 5-bromo coerulescine in 93% yield (see Supporting Information for details), which was further treated with NaOMe in the presence of catalytic CuI to complete the total synthesis of (+)-horsfiline (**1b**) in 84% yield (78% over 2 steps from **1a**) (Scheme 3).

We further elaborated **6c** for the total synthesis of hexahydropyrrolo[2,3-*b*]indole alkaloids, deoxyeseroline (**2c**) as well (Scheme 4). 2-Oxindole **6c** was treated with NaBH₄ followed

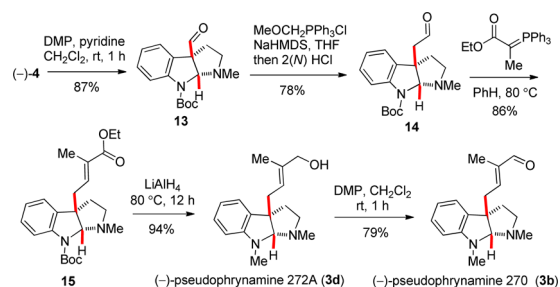
Scheme 4. Total Syntheses of (–)-Deoxyeseroline (2c) and (–)-Esermethole (2a)



by hydrogenolysis in the presence of catalytic Pd–C in ethanol (1 atm of H₂) to furnish [6,5,5]-tricyclic core (–)-**4** (Scheme 4). The latter on deoxygenation afforded pyrroloindoline intermediate (–)-**11** in 60% overall yield in 2 steps. (–)-**11** was further reduced with Red-Al in refluxing toluene to complete the total synthesis of (–)-deoxyeseroline (**2c**) in 61% yield (Scheme 4). Further, (–)-**2c** was treated with aqueous HBr (in DMSO) in ethyl acetate to afford 5-bromo compound (–)-**12** in 75% yield, which on subsequent treatment with NaOMe in the presence of catalytic CuI completed the total synthesis of (–)-esermethole (**2a**) in 78% yield (Scheme 4). This completed the formal total syntheses of pyrroloindoline alkaloids, physostigmine (**2d**)^{10f,i} and phenserine (**2f**),^{10k} from **2a** (Scheme 4).

Further, we were interested for the total syntheses of C-3a prenylated hexahydropyrrolo[2,3-*b*]indole alkaloids, (–)-pseudophrynamines **270** (**3b**) and **272A** (**3d**). For this, a Dess-Martin periodinane (DMP) oxidation of compound (–)-**4** (Scheme 5)

Scheme 5. Total Syntheses of (–)-Pseudophrynamines 272A (3d) and 270 (3b)



afforded aldehyde **13**, which on subsequent homologation furnished advanced key intermediate **14** in 68% overall yield in 2 steps (Scheme 5). Next, the aldehyde **14** was treated with stabilized Wittig reagent to afford α,β -unsaturated ester **15** in 86% yield, which on subsequent treatment with LiAlH₄ simply completed the first total synthesis of (–)-pseudophrynamine **272A** (**3d**) without event. Alkaloid (–)-**3d** was further oxidized with DMP to complete the first total synthesis of (–)-pseudophrynamine **270** (**3b**) as well (Scheme 5).

The stereochemical rationale for our hypothesized catalytic aldol process following a DYKAT phenomenon in the presence of thio-urea ligand **L7** is shown in Figure 5. It has been proposed

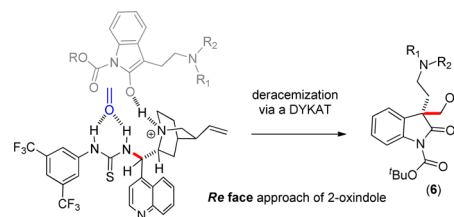


Figure 5. Stereochemical rationale.

that if the enolate of **8** can establish H-bonding with ligand **L7** and activate the nucleophile, **8**, and electrophile (formaldehyde), favorable stereoselectivity could be obtained *via* the *Re*-face approach of 2-oxindole leading to the formation of enantioenriched hydroxyl methylated product **6** (Figure 5).

In conclusion, we achieved the total syntheses of spiro-(pyrrolidinyl-oxindole) alkaloids, (+)-coerulescine (**1a**) and (+)-horsfiline (**1b**), and hexahydropyrrolo[2,3-*b*]indole alkaloids, (–)-deoxyeseroline (**2c**) and (–)-esermethole (**2a**),

sharing an all-carbon quaternary stereocenter in a highly efficient manner applying a unified enantioselective approach. In addition, the aforementioned strategy was also utilized for the first total syntheses of (–)-pseudophrynamines 272A (**3d**) and 270 (**3b**).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03082.

General experimental procedures and analytical data (PDF)

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Notes

The authors declare no competing financial interest.

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