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# Total synthesis of (+)-taberdicatine B and (+)-tabernabovine B

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ABSTRACT

The first total synthesis of (+)-taberdicatine B and (+)-tabernabovine B has been accomplished in 10 steps with 26.9% overall yield and 15 steps with 7.3% overall yield, respectively. The prominent features of this efficient synthetic strategy include the following: (1) (+)-Taberdicatine B and (+)-tabernabovine B were accessed from common advanced intermediates by varying the substituents; (2) A one-pot asymmetric bromocyclization/hydrolysis was explored to assemble HPI skeleton; (3) Dieckmann condensation to form $\beta$-keto ester for the assembly of seven-membered ring; (4) An ester reduction/amide semireduction/cyclization sequence was applied to form the cage-like framework.



Plants of genus *Tabernaemontana*, widely distributed species of Apocynaceae family, are often used as traditional folk medicine due to their abundant bioactivities, such as antitumor, hypotensive, and analgesic activities [1–5]. The broad bioactivities are related to the structurally diverse monoterpenoid indole alkaloids (MIAs) that are common secondary metabolites. These MIAs have emerged as attractive targets for synthesis owing to the diverse biological properties as well as unique and structurally complex molecular architectures [6–9]. There has been tremendous interest in the synthesis of monoterpene indole alkaloid natural products isolated from *Tabernaemontana* species. Recently, two MIA-type natural products have been isolated from plants of genus *Tabernaemontana*. Taberdicatine B (**1**) [10], a bridged molecule isolated from *Tabernaemontana divaricata*, consists 3a-hydroxyhexahydropyrrolo[2,3-*b*]indole (3-OH–HPI) [11–13] skeleton and a highly rigid 6/5/5/6/6-fused pentacyclic framework, bearing 4 stereogenic centers with 3 quanternary chiral centers. 3-OH–HPIs are privileged scaffolds in some representative MIAs such as Alsmaphorazine D [14], Leuconodine E [15], and Hunteracine [16] illustrated in Fig. 1. Tabernabovine B (**2**) [17], isolated from *Tabernaemontana bovina*, is a type of rare rigid cage-shaped MIA natural product with similar 3-OH–HPI moiety, complicated by multi-substituted hexacyclic ring system featuring 6 stereogenic centers, 3 of which are quanternary chiral centers, all of which posed challenges to the total synthesis. We anticipated that the characteristic structural features of **1** and **2** present significant synthetic challenges, including rigid and cage-like framework as well as multiple quaternary stereogenic centers. The intriguing structures of **1** and **2** have rendered them appealing synthetic molecules. Since these two natural products have the same HPI skeletons and similar diazabicyclic core structures, we sought to develop a unified synthetic strategy involving first construction of 3-OH–HPI skeleton, and assembly of diazabicycles through different cyclization methods from different side chains. Herein, we reported the first total synthesis of (+)-taberdicatine B (**1**) and (+)-tabernabovine B (**2**).

We embarked on expeditious total synthesis of (+)-taberdicatine B (**1**) and (+)-tabernabovine B (**2**), and speculated that **1** and **2** might be accessed from common advanced intermediates by varying the substituent types. With this design, the retrosynthetic analysis of **1** and **2** is shown in Scheme 1. We anticipated that the synthesis of **1** could be realized from reductive cyanation of **3**, tracking back to **4** through deprotection/reductive amination. We rationalized that **2** might be synthesized from **6** through reductive cyclization to furnish the rigid cage-like framework. In turn, **6** was assumed to be prepared from Dieckmann condensation of **7**. Specifically, the retrosynthetic analysis revealed that tetracyclic compound **5** could be a versatile and advanced precursor. Further disconnection of **4** and **7** led to intermediate **5** with slight difference of substituents. The access to enantiopure **5** could be achieved through asymmetric dearomatization of **8** [18,19], and vicinal quaternary stereogenic centers were constructed in one-pot manner. **8** could be accessible from C–H activation of tryptamine **9** [20,21]. When the $R^1$ is hydrogen and $R^2$ is Cbz group in **5**, acylation/alkylation of intermediate **5** gave

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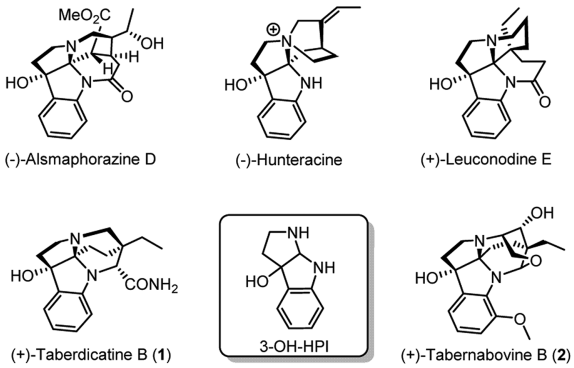
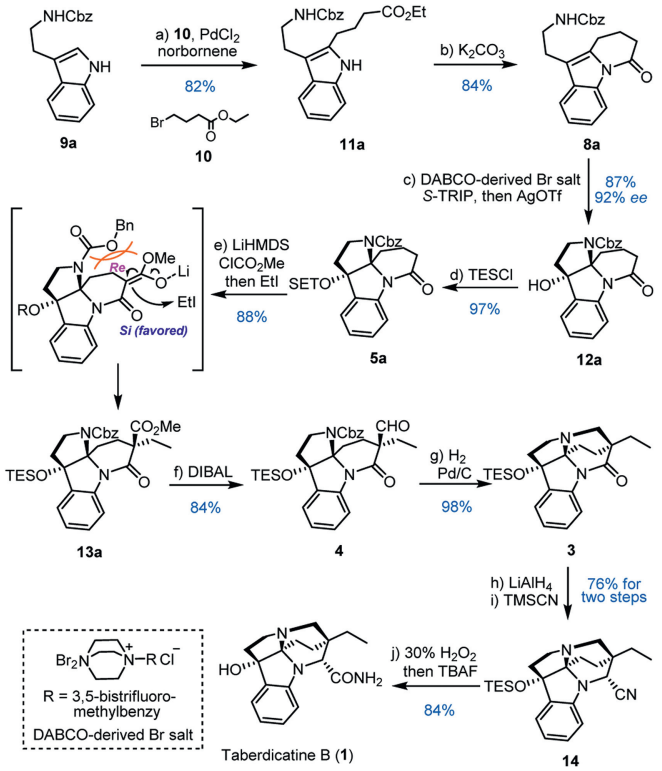



**Fig. 1.** Representative natural products containing 3-OH–HPI skeleton.

compound **4**. When the $R^1$ is methoxy group and $R^2$ is Boc group in **5**, acylation/alkylation of intermediate **5** would give compound **7**. As such, two parallel synthetic pathways leading to similar intermediates can be envisaged.

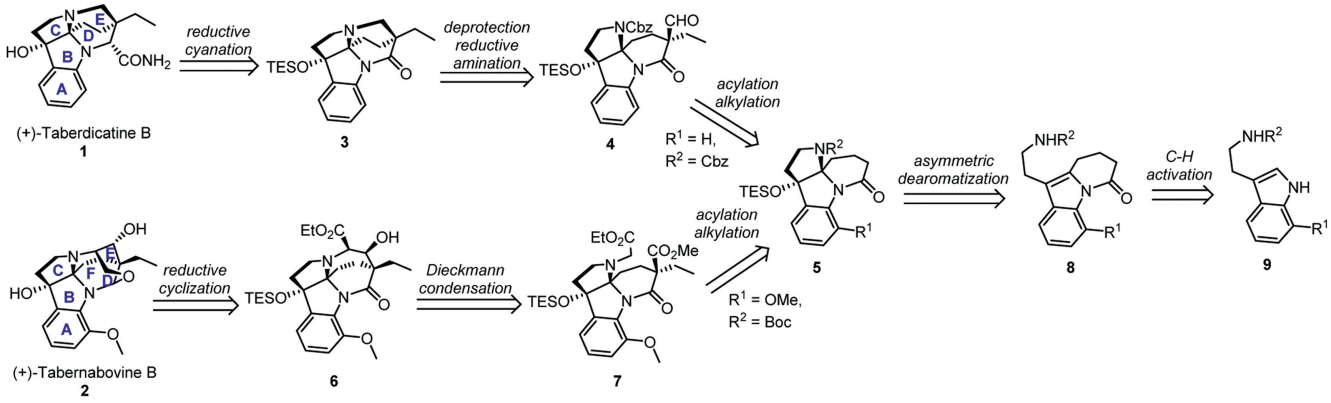
As depicted in Scheme 2, our synthesis of (+)-taberdicatine B (**1**) commenced with the construction of D ring through the 2-alkylation of tryptamine with 4-bromobutanoate to provide functionalized 2,3-disubstituted indole. A palladium-catalyzed norbornene-mediated cascade C–H activation was successfully applied to **9a**, delivering 2-substituted tryptamine **11a** in 82% yield [20,21]. Treatment of compound **11a** with $K_2CO_3$ afforded lactam **8a** in 84% yield [22,23]. Chiral phosphoric acid *S*-TRIP catalyzed asymmetric dearomatization of tryptamine derivative **8a** was conducted to construct HPI skeleton through asymmetric bromocyclization by using readily available DABCO-derived bromine salt, and the one-pot direct hydrolysis of the bromide group occurred smoothly, affording tertiary alcohol **12a** in 87% yield with 92% *ee* [18,19]. With enantioriched **12a** in hand, a subsequent TES protection of the hydroxy group in **12a** worked well, delivering **5a** in 97% yield. It is noteworthy that the above-mentioned routes allowed multigram-scale reactions, which is beneficial for rapid accumulation of advanced intermediate **5a**.

Next, our attention was turned to the construction of final E ring. To this end, the introduction of the crucial quaternary stereocenter next to the carbonyl of lactam of **5a** was first executed. One-pot installation of an ester group followed by alkylation of the resulting 1,3-dicarbonyl derivative with ethyl iodide, gave **13a** as single diastereoisomer in 88% yield. The diastereoselectivity during the formation of the quaternary stereogenic center could be attributed to the steric hindrance. Since the *Re* face was blocked by the *N*-protecting group, ethyl iodide attack from *Si* face was favored, therefore furnishing **13a** as single diastereoisomer. Selective

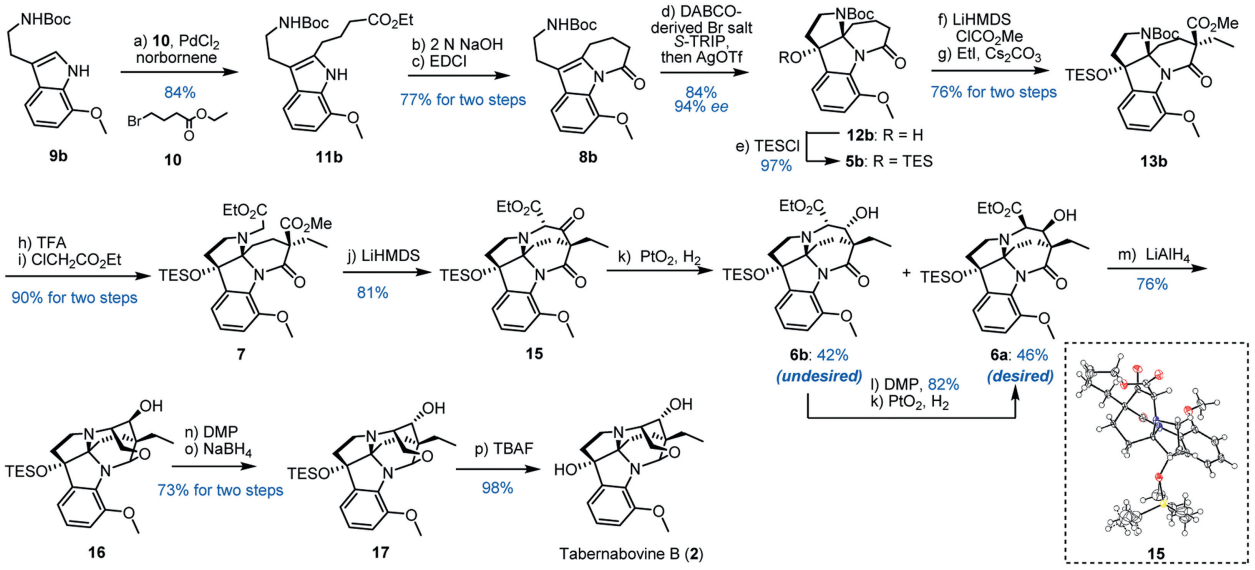



**Scheme 2.** Total synthesis of (+)-taberdicatine B (**1**). Reagents and conditions: (a) **10**, $PdCl_2$ (10 mol%), norbornene, $K_2CO_3$, DMF/DMSO (9:1), $H_2O$, 70 °C, air, 82%; (b) $K_2CO_3$, MeCN, reflux, 84%; (c) Br salt, *S*-TRIP, $Na_2CO_3$, toluene, 0 °C, then AgOTf, $H_2O$, 25 °C, 87%, 92% *ee*; (d) TESCl, DMAP, imidazole, DCM, 25 °C, 97%; (e) LiHMDS, $ClCO_2Me$, THF, −78 °C, then EtI, −20 °C, 88%; (f) DIBAL, DCM, −78 °C, 84%; (g) Pd/C, $H_2$ (1 atm), MeOH, 25 °C, 98%; (h) $LiAlH_4$, THF, 25 °C; (i) TMSCN, $BF_3{\cdot}Et_2O$, DCM, −30 °C, 76% for two steps; (j) $K_2CO_3$, 30% $H_2O_2$ DMSO; then TBAF, 25 °C, 84%. DMSO = dimethyl sulfoxide, DMAP = 4-dimethylaminopyridine, TBAF = tetrabutylammonium fluoride.

and partial reduction of the ester group with DIBAL at −78 °C led to the corresponding aldehyde **4** in 84% yield [24]. **4** was then subjected to *N*–Cbz deprotection/reductive amination sequence under the treatment of Pd/C, affording **3** in 98% yield [25,26]. To our delight, the final six-membered E ring was successfully formed and the main skeleton of (+)-taberdicatine B (**1**) was constructed. Then, LAH reduction of the lactam of **3** gave the corresponding labile hemiaminal intermediate, which was employed immediately in the next step without purification. Subsequent cyanation of hemiaminal with TMSCN and boron trifluoride diethyl etherate provided nitrile **14** as single diastereoisomer in 76% overall yield from **3**




**Scheme 1.** Retrosynthetic analysis of **1** and **2**.



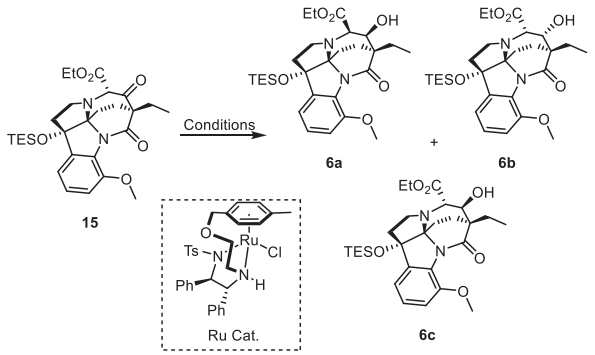

**Scheme 3.** Total synthesis of (+)-tabernabovine B (**2**). Reagents and conditions: (a) **10**, $PdCl_2$ (10 mol%), norbornene, $K_2CO_3$, DMF/DMSO (9:1), $H_2O$, 70 °C, air, 84%; (b) 2 mol/L NaOH, MeOH/$H_2O$, 25 °C; (c) EDCI, DMAP, DCM, 25 °C, 77% for two steps; (d) Br salt, *S*-TRIP, $Na_2CO_3$, toluene, 0 °C, then AgOTf, $H_2O$, 25 °C, 84%, 94% *ee*; (e) TESCl, DMAP, imidazole, DCM, 25 °C, 97%; (f) LiHMDS, $ClCO_2Me$, THF, −30 °C; (g) $Cs_2CO_3$, EtI, MeCN, 25 °C, 76% for two steps; (h) TFA, DCM, 25 °C; (i) $ClCH_2CO_2Et$, KI, $K_2CO_3$, MeCN, 70 °C, 90% for two steps; (j) LiHMDS, THF, 15 °C, 81%; (k) $PtO_2$, $H_2$ (1 atm), EtOH, 25 °C; (l) DMP, DCM, 25 °C, 82%; (m) $LiAlH_4$, THF, 15 °C, 76%; (n) DMP, DCM, 25 °C; (o) $NaBH_4$, MeOH, 25 °C, 73% for two steps; (p) TBAF, THF, 0 °C, 98%. EDCI = 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide.

[27–29]. Finally, the total synthesis of **1** was completed by treating **14** with $K_2CO_3$ and $H_2O_2$ [30,31], followed by one-pot desilylation of TES group, and **1** was obtained in 84% yield. Synthetic **1** exhibited identical $^1H$ and $^{13}C$ NMR data to those reported for natural product (+)-taberdicatine B.

As summarized in Scheme 3, total synthesis of (+)-tabernabovine B (**2**) commenced with the elaboration of **5b**, which could be prepared on a multigram scale from tryptamine **9b**. The synthetic route began with 2-alkylation of the indole ring of tryptamine, delivering **11b** in 84% yield. Due to the steric hindrance of 7–methoxy substitution on the indole ring in comparison to **11a**, the reactivity of **11b** is weaker than that of **11a**, therefore the synthetic route for D ring in **2** was different from the previous route explored in **1**. Thus, we converted the ester group in **11b** to carboxyl group first, which is more reactive in the presence of condenser to proceed lactamisation. As we expected, the acid intermediate obtained from the hydrolysis of the ester group was smoothly converted to **8b** in the presence of the condenser EDCI. After conversion of **11b** into **8b** [32], *S*-TRIP catalyzed asymmetric dearomatization, bromide hydrolysis, and TES protection proceeded well to give **5b** with excellent enantioselectivity and efficiency. Next, the same one-pot acylation/alkylation conditions were used in **5b** to get **13b**, however poor diastereoselectivity was obtained. Then, various bases were screened, and it was found that the alkylation step needs the use of extra base. When $Cs_2CO_3$ was used as base in the alkylation step, the quaternary stereocenter was formed with exclusive diastereoselectivity in 76% yields over two steps. It is reasonable to assume that due to the steric hindrance of methoxy group in comparison to **5a**, the reactivity of **5b** is different from that of **5a**. Removal of Boc group of **13b** by TFA, followed by *N*-alkylation of the resulting free amine with ethyl chloroacetate afforded **7** in 90% yield for two steps. Dieckmann condensation of **7** with LiHMDS gave $\beta$-keto ester **15** in 81% yield [33,34], and the relative configuration of **15** was determined by X-ray analysis. Thus, the assembly of seven-membered E ring was accomplished.

With **15** in hand, the subsequent construction of caged F ring was investigated. We first screened reduction conditions for the formation of $\beta$–hydroxy ester (Table 1). In the presence of $NaBH_4$ (Table 1, entry 1), a pair of diastereomers **6a** (desired, 24% yield) and **6b** (57% yield) were mainly obtained with trace amount of **6c**. The relative configurations of **6a**-**6c** were elucidated separately through demethoy-**6a** (CCDC 2255376), demethoxy-**6b** derivative (CCDC 2255374) and demethoy-**6c** (CCDC 2255375) by X-ray crystallographic analysis. Since the stereochemistry of the carbon chiral center adjacent to ester functionality is essential for the following reductive cyclization to assemble the caged ring, more productive condition was needed. When $NaBH_4$ reduction with $NH_4Cl$ as buffering reagent [35–37] was carried out, the diastereoselectivity did not increase (Table 1, entry 2). An attempted addition of

**Table 1**
Screening of conditions for reduction of $\beta$-keto ester **15**.




| Entry | Conditions | Result (%) |
|---|---|---|
| 1 | $NaBH_4$, MeOH, 25 °C | **6a** (24) + **6b** (57) + **6c** (5) |
| 2 | $NaBH_4$, $NH_4Cl$, MeOH, 25 °C | **6a** (16) + **6b** (61) + **6c** (8) |
| 3 | $NaBH_4$, $MgCl_2$, MeOH, 25 °C | **6a** (20) + **6b** (62) + **6c** (trace) |
| 4 | $Me_4NBH(OAc)_3$, AcOH, MeCN, 70 °C | No reaction |
| 5 | $^nBu_4NBH_4$, MeOH, 25 °C | **6a** (19) + **6b** (56) + **6c** (trace) |
| 6 | L-Selectride, THF, −70 °C | **6b**[a] |
| 7 | $LiAl(O^tBu)_3H$, THF, 25 °C | **6b**[a] |
| 8 | Ru Cat., HCOOH, TEA, EA, 60 °C | TES deprotection |
| 9 | Crabtree's cat. DCM, 25 °C | No reaction |
| 10 | $H_2$, $PtO_2$, EtOH, 25 °C | **6a** (46) + **6b** (42) + **6c** (trace) |

[a] Complex reaction mixture, and trace amount of **6b** was obtained.

metal salt such as $MgCl_2$ as chelating reagent [38] did not improve the selectivity (Table 1, entry 3). When $Me_4NBH(OAc)_3$ [39] was used as reductant, no reaction occurred and **15** was recovered (Table 1, entry 4). $^nBu_4NBH_4$ reduction [40] also did not give better result (Table 1, entry 5). When the reaction was perfomed in the presence of bulky reductants such as L-selectride [41–43] and $LiAl(O^tBu)_3H$ [44], the reactions were complicated, and only undesired **6b** was obtained (Table 1, entries 6 and 7). Ru-catalyzed transfer hydrogenation (Table 1, entry 8) [45–49] and Crabtree's catalyst (Table 1, entry 9) [50,51] failed to give the desired $\beta$–hydroxy ester. After much experimentation on selective hydride reduction, an acceptable and reliable hydrogenation reaction condition was found. Hydrogenation of the $\beta$-keto ester **15** using $H_2$ over $PtO_2$ under mild condition allowed the generation of two diastereomers $\alpha$–hydroxy esters **6a** in 46% yield and **6b** in 42% yield (Table 1, entry 10) [52,53]. One of the resulting diastereomer **6b** can be further transferred to **6a** through hydroxy oxidation and ketone reduction, which implied that $\beta$-keto ester **15** underwent enolization when the hydrogenation occurred. We also conducted an extensive evaluation of reaction conditions to promote epimerization of **6b** to the desired stereo-configuration by the enolization/kinetic protonation sequence. Despite screening for bases, reaction times, and temperatures, we were unable to achieve the epimerization of **6b**. In almost all cases, **6b** was recovered, and no other products were generated. By treating **6b** with KHMDS and then quenching with $D_2O$, it was found by NMR that the $\alpha$-H of the ester group was partially deuterated. We assumed that the enolization of the ester could occur under the reaction condition, but the proton was still subsequently attacked from the side with relatively small steric hindrance, affording configuration-preserving starting materials. The failure of enolization of **6b** under strongly basic conditions by the kinetic protonation prompted us to evaluate thermodynamic conditions for the epimerization. A wide range of bases were examined, such as DBU, $^t$BuOK and NaOEt, however all conditions lead to decomposition or unreacted starting material. Since **6b** can be transferred to **6a**, the condition using $H_2$ over $PtO_2$ (Table 1, entry 10) was applied to synthesize **6a**. Reductive cyclization of **6a** with LAH afforded cage-like skeleton **16** in 76% yield [54,55]. As a result, the crucial caged F ring was successfully formed *via* ester reduction/amide semireduction/cyclization sequence. We also investigated reduction of **15** with LAH to get **16** *via* ketone reduction/ester reduction/amide semireduction/cyclization sequence directly, however complex reaction mixture was obtained along with 10% yield of desired **16**. Since the stereochemistry of the carbon chiral center adjacent to hydroxy functionality of **16** was opposite to the natural product, we planned to invert the stereochemistry by DMP oxidation and $NaBH_4$ reduction. The expected epimerization occurred and afforded **17** in 73% yield over two steps. The total synthesis was wrapped up with desilylation of TES group with TBAF, and thereby (+)-tabernabovine B (**2**) was obtained in 98% yield. The $^1$H and $^{13}$C NMR data of synthetic **2** was in agreement with those reported for natural product (+)-tabernabovine B.

In conclusion, we have developed efficient approaches for the first total synthesis of (+)-taberdicatine B (10 steps, 26.9% overall yield) and (+)-tabernabovine B (15 steps, 7.3% overall yield) from tryptamine derivatives. The key steps involved one-pot asymmetric bromocyclization/hydrolysis for the assembly of HPI skeleton, Dieckmann condensation to form $\beta$-keto ester for the assembly of seven-membered ring, and an ester reduction/amide semireduction/cyclization sequence for the formation of the cage-like framework. The prominent feature of this synthetic strategy is that (+)-taberdicatine B and (+)-tabernabovine B were accessed from common advanced intermediates by varying the substituents. Thus, the strategy could be applied to the synthesis of natural product analogues for medicinal investigation to explore potential biological activities, and is expected to be shown in total syntheses of other MIAs containing 3-OH–HPI skeleton.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.109816.

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