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Synthesis of (*S*)-(−)- and (*R*)-(+)-*O*-methylbharatamine using a diastereoselective Pomeranz–Fritsch–Bobbitt methodology

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Abstract—Laterally lithiated (*S*)-(−)- and (*R*)-(+)-*o*-toluamides **6** with a chiral auxiliary derived from (*S*)- and (*R*)-phenylalaninol, respectively, were used as the building blocks and chirality inductors in the asymmetric modification of the Pomeranz–Fritsch–Bobbitt synthesis of isoquinoline alkaloids. Their addition to imine **2** proceeded with partial cyclization, giving isoquinolones (+)-**7** and (−)-**7** along with acyclic products, (−)-**8** and (+)-**8**, respectively. LAH-reduction of (+)-**7** and (−)-**7**, followed by cyclization, afforded both enantiomers of the alkaloid, (*S*)-(−)- and (*R*)-(+)-*O*-methylbharatamine **5**, in 32% and 40% overall yield and with 88% and 73% ees, respectively.

1. Introduction

The crucial step in the classic Pomeranz–Fritsch–Bobbitt synthesis of isoquinoline alkaloids,[1] the construction of the tetrahydroisoquinoline ring system, involves acid catalyzed cyclization/hydrogenolysis of *N*-benzylaminoacetaldehyde acetal of type **1**.[2,3] In the stereoselective modification,[4] chiral non-racemic 1-substituted *N*-benzylaminoacetaldehyde acetals **1** have been used as key intermediates, and further transformed into isoquinoline alkaloids of different types. In most cases intermediates **1** were prepared by substitution of benzylic oxygen into the corresponding chiral alcohols[5] or epoxides[6–8] with nitrogen nucleophiles[5–8] or by addition of carbon nucleophiles to benzalamines, prochiral **2**[9,10] or chiral **3**[11,12] (Fig. 1).

Several reports concerning the synthesis of chiral non-racemic benzylamines of type **1**, performed by the addition of organometallic reagents to imines, **2** or **3**, realized in both enantio- and diastereoselective manner, have been published.[9–12]

Enantioselective addition of organolithium reagents to prochiral 'Pomeranz–Fritsch imine' **2** was conducted in the presence of chiral oxazolines **4** (R = H, SCH_3 and R^1, R^2 = alkyl, aryl),[9,10] used as external controllers of stereochemistry as well as catalysts (Fig. 1). Addition

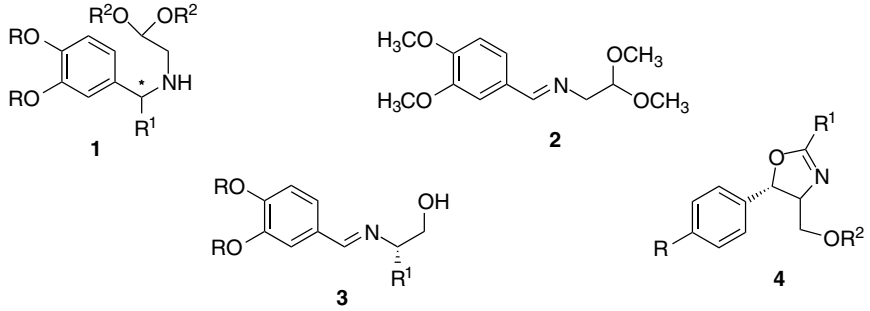

Figure 1.

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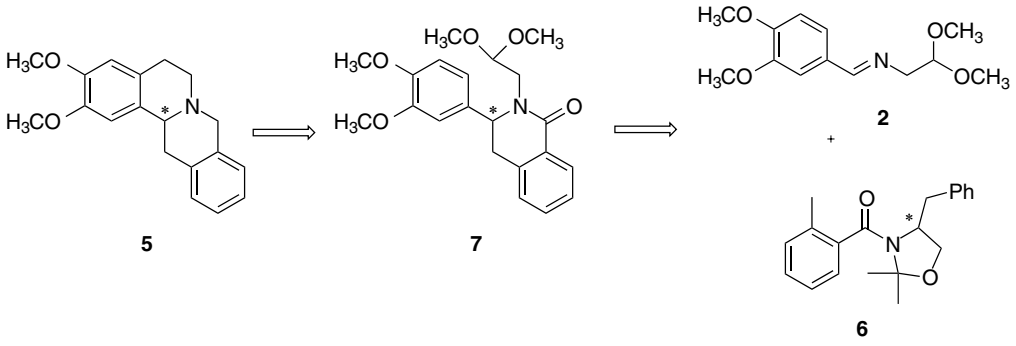


Scheme 1.

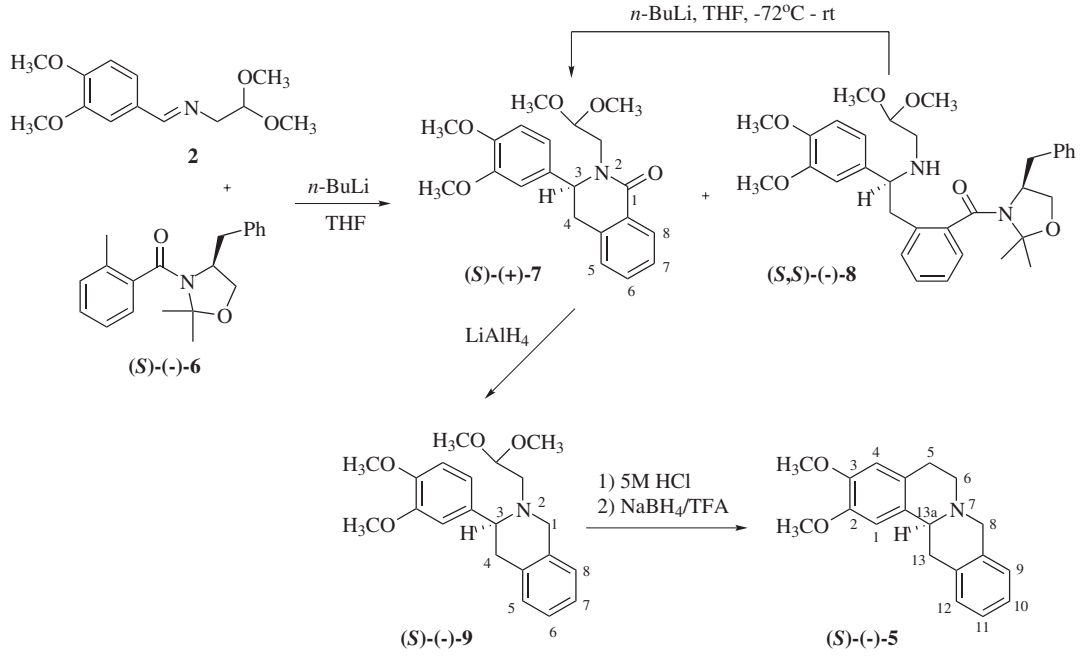
product **1** ($R = R^1 = R^2 = CH_3$) obtained with an ee up to 76%,[10] was then converted into alkaloids, (−)-salsolidine and (−)-carnegine.[9]

In diastereoselective synthesis,[11,12] chiral imines **3** (R = H, OH, OCH_3; $R + R = OCH_2O$ and $R^1 = C_6H_5$, *i*-C_3H_7), derived from aromatic aldehydes and chiral β-aminoalcohols, were treated with Grignard reagents. Using this method, isopavines, (−)-*O*-methylthalisopavine and (−)-amurensinine,[12] aporphine and (*S*)-(+)-glaucine,[11] were synthesized with high enantiomeric purity.

Herein, we report the results of our work on another version of the diastereoselective synthesis of the Pomeranz–Fritsch–Bobbitt cyclization, in which two enantiomers of protoberberine alkaloid, (*S*)-(−)- and (*R*)-(+)-*O*-methylbharatamine **5** have been synthesized. In this approach, a chiral auxiliary was introduced into the carbon nucleophile. As such, both enantiomers of (*S*)-(−)- and (*R*)-(+)-*o*-toluamide **6**,[13] derived from (*S*)- and (*R*)-phenylalaninol, respectively, incorporating an oxazolidine moiety, were prepared and added to imine **2**, using the lateral metallation methodology.[13–15] As a result, a new stereogenic centre was created with high diastereoselectivity. The retrosynthetic analysis is shown in Scheme 1.

2. Results and discussion

In continuation of our study on the stereoselective modification of the Pomeranz–Fritsch–Bobbitt synthesis of isoquinoline alkaloids,[9,10] and the application of chiral *o*-toluamides **6** in the synthesis of isoquinoline alkaloids,[13] we became interested in extending this approach to the addition of **6** to acyclic imine **2**. At first, the reaction of imine **2** with a carbanion, generated from (*S*)-(−)-**6** under the action of 1.1 equiv of *n*-butyllithium at −72 °C, was carried out. This resulted in the formation of two compounds: the addition–partial cyclization product, isoquinolone **7** and the acyclic addition product **8** (Scheme 2). After chromatographic separation, pure isoquinolone (+)-**7** in 56% yield, $[\alpha]_D = +36.3$ (*c* 0.465, $CHCl_3$), and (−)-**8** in 20% yield with 97% dr (HPLC), $[\alpha]_D = -5.3$ (*c* 0.33, $CHCl_3$), were obtained.



Scheme 2.

Compound (−)-**8** was easily converted into isoquinolone (+)-**7** in 71% yield, upon treatment with 1 equiv of *n*-butyllithium in THF at −72 °C, providing an additional 14% of (+)-**7**.

The (*S*)-configuration of the newly created stereocentre in (*S*)-(+)-**7** and (*S*)-(−)-**8** was established in the final stage of the synthesis, in which (*S*)-(−)-*O*-methylbharatamine **5** of known stereochemistry[13] was formed. The stereoselectivity of the addition step was determined for (−)-**8** by HPLC (97% dr), while for **7**, analytical separation of the enantiomers using standard techniques (chiral HPLC, NMR with various shift reagents) failed.

To complete the synthesis, cyclization to the tetrahydroisoquinoline ring system and reduction of the lactam carbonyl were needed. Unfortunately, isoquinolone **7** turned out to be very difficult to cyclize. When hydrogenated in 5 M aqueous hydrochloric acid (the Bobbitt et al. modification[2]) or reduced with $NaBH_4/CF_3COOH$[11] in refluxing dioxane, it was transformed either into a tetrahydroisoquinoline in very poor yield or into a mixture of products. Reduction of the carbonyl group in **7** prior to the cyclization was then undertaken. LAH reduced the dextrorotatory isoquinolone (+)-**7** to the levorotatory tetrahydroisoquinoline (−)-**9**, in 84% yield, $[\alpha]_D = -43.6$ (*c* 0.49, $CHCl_3$). This cyclization occurred after stirring in 5 M aqueous hydrochloric acid for 18 h at room temperature, followed by reduction with sodium borohydride in trifluoroacetic acid, without isolation of the intermediate products. From the crude reaction mixture, after purification by column chromatography, (*S*)-(−)-*O*-methylbharatamine **5** was isolated in 54% yield with 88% ee, as estimated by HPLC.

Following the same reaction sequence, the synthesis of the opposite enantiomer, (*R*)-(+)-*O*-methylbharatamine **5** was performed starting with imine **2** and (*R*)-(+)-*o*-toluamide **6**. The addition step also afforded two products: isoquinolone (−)-**7**, in 57% yield, $[\alpha]_D = -39.2$ (*c* 0.665, $CHCl_3$) and the addition product, (+)-**8**, in 28% yield, $[\alpha]_D = +5.4$ (*c* 0.22, $CHCl_3$), which could easily be cyclized to (−)-**7** in 74% yield. Further transformation, involving LAH-reduction of (−)-**7** to give (+)-**9** {80% yield, $[\alpha]_D = +49.1$ (*c* 0.375, $CHCl_3$)} and cyclization–hydrogenolysis, resulted in formation of the alkaloid, (*R*)-(+)-**5**, in 65% yield, with 73% ee (HPLC).

The absolute configuration and enantiomeric excess of the final products, (*S*)-(−)-**5** and (*R*)-(+)-**5**, were established by comparison with samples of enantiomerically pure alkaloids, (*S*)-(−)- and (*R*)-(+)-*O*-methylbharatamine **5** synthesized in our laboratory, whose absolute configuration was known.[13]

3. Conclusion

In summary, we have developed a convenient, synthetically useful procedure for the preparation of protoberberine alkaloids with reasonable enantiomeric purity, using stereoselective Pomeranz–Fritsch–Bobbitt cyclization as the synthetic strategy and chiral *o*-toluamides as the building blocks as well as inductors of chirality. The key step of the synthesis, in which a new stereogenic centre was formed, involved the addition of the 'Pomeranz–Fritsch imine' to benzylic carbanion, generated by the lateral metallation methodology from enantiopure *o*-toluamide. Reduction of the addition product, followed by a Bobbitt cyclization furnished the synthesis. In this way both enantiomers of *O*-methylbharatamine **5** were prepared in satisfactory overall yield and with high enantiomeric excess.

4. Experimental

4.1. General

IR spectra: Bruker FT-IR IFS 113V. NMR spectra: Varian Gemini 300 with TMS as the internal standard. Mass spectra (EI): instrument AMD 402. Optical rotations: Perkin–Elmer polarimeter 242B, at 20 °C. Merck Kieselgel 60 (70–230 mesh) and Merck aluminium oxide 90 active neutral (70–230 mesh) were used for column chromatography; Merck DC-Alufolien Kieselgel 60_{254} for TLC. Analytical HPLC: Waters HPLC system with Mallinkrodt–Baker Chiralcel OD-H column.

THF and diethyl ether were freshly distilled from $LiAlH_4$. Imine **2**[16] and *o*-toluamides **6**[13] were prepared as previously described.

4.2. General procedure for addition reaction of *o*-toluamide 6 to imine 2

o-Toluamide **6** (309 mg, 1 mmol) was dissolved in dry THF (6 mL) under an argon atmosphere and the solution cooled to −72 °C. *n*-BuLi (1.6 M solution in hexanes, 0.7 mL) was added and the carbanion generated for 30 min at −72 °C. A solution of imine **2** (253 mg, 1 mmol) in dry THF (6 mL) was introduced dropwise and the mixture allowed to warm-up to +10 °C, then treated at this temperature with 20% aqueous NH_4Cl (7 mL). When the temperatue of the reaction mixture reached room temperature, the phases were separated and the aqueous one extracted with diethyl ether (3×10 mL). The combined organic extracts were dried and the solvents removed under reduced pressure. The resulting oil was dissolved in diethyl ether (20 mL) and extracted with 5% aqueous HCl (3×2 mL). The organic phase was dried and evaporated, yielding isoquinolone **7**, purified by column chromatography (dichloromethane/methanol, 200:1).

The acidic aqueous phase was rendered alkaline with KOH pellets, re-extracted with diethyl ether (3×10 mL), dried and evaporated to give addition product **8** as an oil, which was further purified by column chromatography (dichloromethane/methanol, 100:1).

4.2.1. (3*S*)-(+)-*N*-(2,2-Dimethoxyethyl)-3-(3,4-dimethoxyphenyl)-3,4-dihydro-1-(2*H*)-isoquinolone 7. Yield 56%, solidifying oil, $[\alpha]_D = +36.3$ (*c* 0.465, $CHCl_3$); IR (KBr) *v*: 2937, 2834, 1649 (C=O), 1516, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) *δ*: 2.81 (dd, $J = 7.7$, 13.7 Hz, 1H,

NCH_2), 2.98 (dd, $J = 1.9$, 15.6 Hz, 1H, H-4), 3.43 (s, 3H, $CHOCH_3$), 3.48 (s, 3H, $CHOCH_3$), 3.68 (dd, $J = 6.6$, 15.6 Hz, 1H, H-4), 3.69 (s, 3H, $ArOCH_3$), 3.79 (s, 3H, $ArOCH_3$), 4.31 (dd, $J = 3.3$, 13.7 Hz, 1H, NCH_2), 4.67 (dd, $J = 3.3$, 7.7 Hz, 1H, $CHOCH_3$), 4.99 (dd, $J = 1.9$, 6.6 Hz, 1H, H-3), 6.52 (d, $J = 1.9$ Hz, 1H, ArH), 6.58 (dd, $J = 1.9$, 8.2 Hz, 1H, ArH), 6.68 (d, $J = 8.2$ Hz, 1H, ArH), 7.02 (dd, $J = 2.2$, 6.5 Hz, 1H, ArH), 7.31–7.39 (m, 2H, ArH), 8.11 (dd, $J = 2.2$, 6.0 Hz, 1H, H-8); ^{13}C NMR and DEPT and ^{1}H–^{13}C COSY ($CDCl_3$) δ: 35.8 (C-4), 48.5 (NCH_2), 54.5 ($CHOCH_3$), 55.6 ($ArOCH_3$), 55.7 ($ArOCH_3$), 56.1 ($CHOCH_3$), 60.3 (C-3), 103.7 ($CH(OCH_3)_2$), 109.3 (CH), 110.8 (CH), 118.6 (CH), 127.1 (CH), 127.4 (C-8), 127.7 (CH), 129.2 (C-4a), 132.0 (CH), 132.4 (C), 135.5 (C-8a), 148.3, 148.9 (C-3, C-4), 164.9 (C-1); MS m/z (%): 371 (M^+, 9), 340 (11), 284 (14), 283 (42), 267 (16), 151 (28), 133 (23), 75 (100); HRMS calcd for $C_{21}H_{25}NO_5$: 371.17328. Found: 371.17274.

4.2.2. (3*R*)-(−)-*N*-(2,2-Dimethoxyethyl)-3-(3,4-dimethoxyphenyl)-3,4-dihydro-1-(2*H*)-isoquinolone 7. Yield 57%; solidifying oil, $[\alpha]_D = -39.2$ (c 0.665, $CHCl_3$).

4.2.3. Addition product (*S*,*S*)-(−)-8. Yield 20%, solidifying oil, 97% dr by HPLC [hexane/propan-2-ol = 4:1, 0.5 mL/min; t_R 15.8 min, t_R 17.4 min (major)]; $[\alpha]_D = -5.3$ (c 0.33, $CHCl_3$); IR (KBr) ν: 3014, 2936, 2834, 1636, 1510, 1402, 1257, 750 cm^{-1}; ^{1}H NMR (DMSO-d_6 at 50 °C) δ: 1.65 (s, 3H, $C(CH_3)_2$), 1.73 (s, 3H, $C(CH_3)_2$), 1.86 (s, broad, 1H, NH), 2.34 (t, $J = 4.9$, 2H), 2.56–2.59 (m, 1H), 2.73–2.91 (m, 2H), 3.07 (d, $J = 4.5$ Hz, 1H), 3.12 (s, 3H, $CHOCH_3$), 3.13 (s, 3H, $CHOCH_3$), 3.58–3.62 (m, 2H), 3.65 (s, 3H, $ArOCH_3$), 3.67 (s, 3H, $ArOCH_3$), 3.69–3.79 (m, 1H), 3.80–3.94 (m, 1H), 4.23 (t, $J = 5.3$ Hz, 1H), 6.47–6.50 (m, 2H, ArH), 6.77–6.80 (m, 2H, ArH), 6.83–6.89 (m, 1H, ArH), 7.10–7.12 (m, 3H, ArH), 7.28–7.39 (m, 4H, ArH); ^{13}C NMR and DEPT and ^{1}H–^{13}C COSY ($CDCl_3$) δ: 22.9 ($C(CH_3)_2$), 26.9 ($C(CH_3)_2$), 40.2 (CH_2Ph), 43.0 ($ArCH_2CH(NH)Ar$), 48.7 ($NHCH_2CH(OCH_3)_2$), 53.4 ($CHOCH_3$), 53.7 ($CHOCH_3$), 55.7 ($ArOCH_3$), 55.8 ($ArOCH_3$), 61.0 ($NCHCH_2O$), 63.3 ($ArCH_2CH(NH)Ar$), 66.1 (OCH_2), 95.3 ($C(CH_3)_2$), 103.4 ($CHO(CH_3)_2$), 109.9 (CH) 110.8 (CH), 119.2 (CH), 126.2 (C), 126.5 (CH), 126.6 (2CH), 128.6 (3CH), 128.9 (3CH), 130.8 (C), 137.4 (C), 138.0 (C), 147.0 (C), 148.8 (C), 167.7 (C=O); MS m/z (%): 563 (M^++1, 0.8), 400 (19), 255 (17), 254 (100), 222 (36), 91 (13), 75 (22); HRMS calcd for $C_{33}H_{43}N_2O_6$: 563.31213. Found: 563.31148.

4.2.4. Addition product (*R*,*R*)-(+)-8. Yield 28%, solidifying oil, $[\alpha]_D = +5.4$ (c 0.22, $CHCl_3$). For this compound only one peak was observed on HPLC chromatogram [hexane/propan-2-ol = 9:1, 0.5 mL/min; t_R 28.7 min].

4.3. General procedure for the cyclization of 8

To a solution of compound **8** (372 mg, 0.66 mmol) in dry THF (10 mL), *n*-BuLi (1.6 M solution in hexanes, 0.46 mL) was added at −72 °C under an argon atmosphere. The reaction mixture was allowed to warm-up to ambient temperature and quenched by the addition of 20% aqueous NH_4Cl (5 mL). The aqueous phase was extracted with diethyl ether (3 × 10 mL) washed with 5% aqueous HCl (4 × 2 mL) and the organic phase was dried and evaporated, to yield isoquinolone **7.**

4.3.1. Isoquinolone (*S*)-(+)-7. Yield 71%, solidifying oil, $[\alpha]_D = +35.4$ (c 0.48, $CHCl_3$).

4.3.2. Isoquinolone (*R*)-(−)-7. Yield 74%, solidifying oil, $[\alpha]_D = -37.0$ (c 0.54, $CHCl_3$).

4.4. General procedure for reduction of isoquinolone 7

To a solution of isoquinolone **7** (108 mg, 0.29 mmol), in dry THF (15 mL), $LiAlH_4$ (108 mg) was added portionwise with stirring. The mixture was heated under reflux for 2 h and left to reach ambient temperature. The excess of the reducing agent was decomposed with water (2.5 mL) and 20% aqueous NaOH (0.8 mL) and extracted with diethyl ether (15 mL). The organic solution was dried, the solvent evaporated to give an oil, which after column chromatography on aluminium oxide (dichloromethane), gave pure tetrahydroisoquinoline **9**.

4.4.1. (*S*)-(−)-*N*-(2,2-Dimethoxyethyl)-3-(3,4-dimethoxyphenyl)-1,2,3,4-tetrahydroisoquinoline 9. Yield 84%, solidifying oil, $[\alpha]_D = -43.6$ (c 0.49, $CHCl_3$); IR (KBr) ν: 2933, 2832, 1510, 1261 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.31 (dd, $J = 5.4$, 13.5 Hz, 1H, NCH_2), 2.76 (dd, $J = 5.4$, 13.5 Hz, 1H, NCH_2), 2.97–3.01 (m, 1H, H-4), 3.09–3.19 (m, 1H, H-4), 3.23 (s, 3H, $CHOCH_3$), 3.30 (s, 3H, $CHOCH_3$), 3.67 (dd, $J = 4.7$, 9.6 Hz, 1H, H-3), 3.71–3.80 (m, 1H, H-1), 3.86 (s, 3H, $ArOCH_3$), 3.88 (s, 3H, $ArOCH_3$), 4.22 (d, $J = 15.9$ Hz, 1H, H-1), 4.50 (t, $J = 5.4$ Hz, 1H, $CHOCH_3$), 6.81 (d, $J = 8.1$ Hz, 1H, ArH), 6.87 (d, $J = 8.1$ Hz, 1H, ArH), 6.98 (d, $J = 2.1$ Hz, 1H, ArH), 7.07–7.10 (m, 2H, ArH), 7.12–7.16 (m, 2H, ArH); ^{13}C NMR and DEPT and ^{1}H–^{13}C COSY ($CDCl_3$) δ: 36.9 (C-4), 52.9 ($CHOCH_3$), 53.8 ($CHOCH_3$), 55.3 (C-1), 55.7 ($ArOCH_3$), 55.8 ($ArOCH_3$), 55.8 (NCH_2), 64.1 (C-3), 103.6 ($CH(OCH_3)_2$), 110.5 (CH), 110.6 (CH), 120.1 (CH), 125.7 (CH), 126.1 (CH), 126.2 (CH), 128.0 (CH), 134.1 (C), 134.3 (C), 135.1 (C), 148.1, 149.0 (C-3, C-4); MS m/z (%): 357 (M^+, 7), 283 (20), 282 (100), 254 (13), 253 (52), 252 (13), 223 (10), 222 (11), 151 (16), 115 (19), 75 (14); HRMS calcd for $C_{21}H_{27}NO_4$: 357.19400. Found: 357.19253.

4.4.2. (*R*)-(+)-*N*-(2,2-Dimethoxyethyl)-3-(3,4-dimethoxyphenyl)-1,2,3,4-tetrahydroisoquinoline 9. Yield 80%, solidifying oil, $[\alpha]_D = +49.1$ (c 0.375, $CHCl_3$).

4.5. General procedure for cyclization of tetrahydroisoquinoline 9

A solution of tetrahydroisoquinoline **9** (131 mg, 0.37 mmol) and 5 M aqueous HCl (3.7 mL) was stirred overnight at rt. The mixture was basified with 20% aqueous NaOH (4 mL) and extracted with dichloromethane (3 × 15 mL). The combined organic extracts were dried and the solvent evaporated under reduced pressure. The resulting oil was dissolved in dichloromethane

(15 mL) and treated with a mixture of $NaBH_4$ (165 mg, 4 mmol) and TFA (2.7 mL, 35 mmol) in dichloromethane (6 mL), 0 °C. The reaction mixture was stirred at rt for 6 h, and then the solvent and TFA were removed under reduced pressure. The resulting slurry was dissolved in water (10 mL), basified with 20% aqueous NaOH (4 mL) and extracted with dichloromethane (3×10 mL). The organic extracts were dried and evaporated to yield *O*-methylbharatamine **5**, which was purified by column chromatography (dichloromethane).

4.5.1. (*S*)-(−)-2,2-Dimethoxy-5,8,13,13a-tetrahydro-6*H*-dibenzo[*a*,*g*]quinolizine (*O*-methylbharatamine) 5. Yield 54%, solidifying oil, 88% ee by HPLC [hexane/propan-2-ol = 9:1, 0.5 mL/min; t_R 23.9 min (major), t_R 49.1 min]. The product obtained was identical to (*S*)-(−)-*O*-methylbharatamine in terms of spectral data as well as TLC and HPLC comparisons.[13]

4.5.2. (*R*)-(+)-2,2-Dimethoxy-5,8,13,13a-tetrahydro-6*H*-dibenzo[*a*,*g*]quinolizine (*O*-methylbharatamine) 5. Yield 65%, solidifying oil, 73% ee by HPLC [hexane/propan-2-ol = 9:1, 0.5 mL/min; t_R 24.1 min, t_R 46.5 min (major)]. The product obtained was identical to (*R*)-(+)-*O*-methylbharatamine in terms of TLC and HPLC comparisons.[13]

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