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# Facile and Highly Stereoselective Synthesis of the Tetracyclic Erythrinane Core

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**Abstract:** A highly stereoselective synthesis of the tetracyclic core of the *Erythrina* alkaloids is reported through the application of a Meyers bicyclic lactam template.

The genus *Erythrina* is common in tropical and subtropical regions, and the alkaloids have been used in indigenous medicine.[1] Members of the *Erythrina* family, as exemplified in Figure 1, display curare-like and hypnotic activity, and a variety of pharmacological effects are associated with the erythrinane skeleton including sedative, hypotensive, neuromuscular blocking, and CNS activity.[2]

There has been much interest in the synthesis of *Erythrina* alkaloids and their derivatives (including pyrroloisoquinoline precursors) over recent years,[2,3] with many approaches involving *N*-acyliminium cyclization as a key ring-forming step, several of which have sought to address the question of stereocontrol in the cyclization. In this paper we report a novel approach to construct the tetracyclic core of the erythrinane ring system in a highly diastereoselective manner.

On the basis of our novel stereoselective approach to the isoindoloisoquinoline[4] and pyrroloisoquinoline ring systems,[5] we reasoned that a suitably substituted *N*-acyliminium precursor could allow a facile approach to the tetracyclic core of the target erythrinane ring system. Although the bicyclic lactams of Meyers have been widely utilized in asymmetric synthesis,[6] to the best of our knowledge the present application, as a precursor in an intramolecular *N*-acyliminium mediated cyclization reaction leading to erythrinane-like targets, represents a novel application of this popular chiral template.

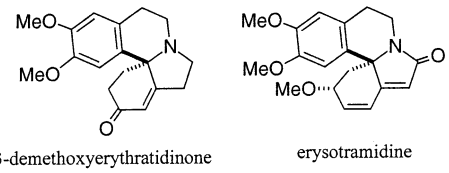
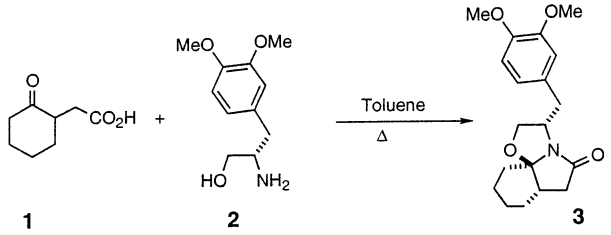
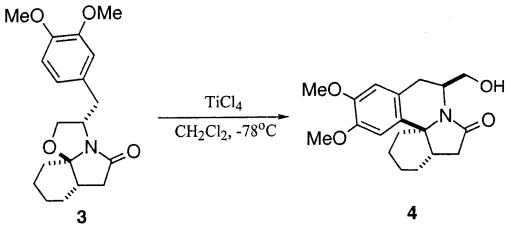



**FIGURE 1.** Examples of *Erythrina* alkaloids.

**SCHEME 1**




**SCHEME 2**




Our synthesis of the required tricyclic lactam substrate **3** followed similar methodology previously described by Ragan using racemic keto acids such as **1**, (Scheme 1).[7] The required $\beta$-amino alcohol **2** was prepared in quantitative yield by reducing the commercially available amino acid, 3-(3,4-dimethoxyphenyl)-L-alanine, with $LiBH_4$ in the presence of $Me_3SiCl$ in THF for 24 h at room temperature. Condensation of the substrates under Dean–Stark conditions in toluene for 144 h gave a 58% yield of the desired lactam **3** as a single diastereoisomer. The formation of a single product diastereoisomer of lactam **3** from a racemic keto acid requires the epimerization of the stereogenic center adjacent to the ketone during the reaction, and this fact has been noted by others in the preparation of polycyclic lactams for use as *N*-acyliminium precursors.[7]

With **3** in hand, we turned to the proposed asymmetric *N*-acyliminium cyclization study (Scheme 2.) On treating lactam **3** with 3 equiv of $TiCl_4$ as Lewis acid activator at

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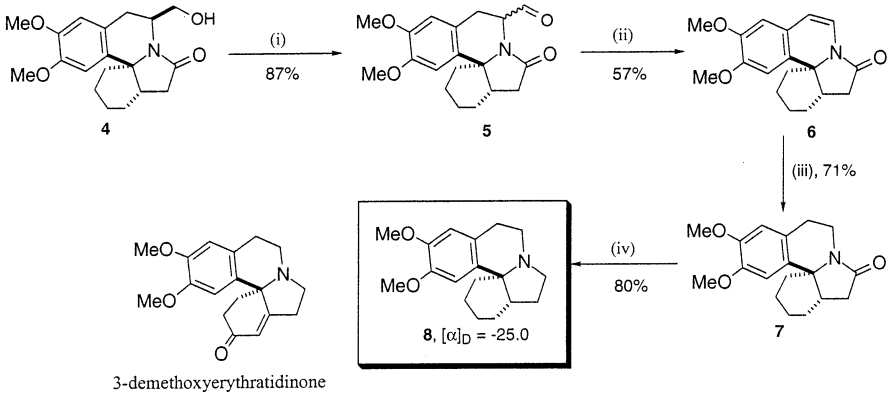
**SCHEME 3**[a]




[a] (i) Dess−Martin periodinane, $CH_2Cl_2$; (ii) $Rh(PPh_3)_2(CO)Cl$, dppp, xylene, Δ, 8 days; (iii) $H_2$/10% Pd-C, EtOH; (iv) $[(MeOCH_2CH_2O)_2AlH_2]Na$, toluene.

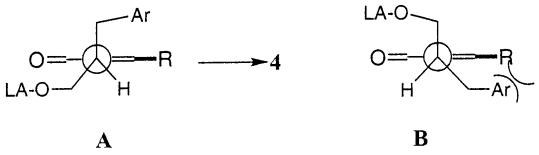



**FIGURE 2.** Conformational models for acyliminium cyclization.

low temperature in dichloromethane for 20 h we were pleased to isolate the desired tetracyclic product **4** in an excellent 98% yield. $^1$H NMR analysis of the crude product mixture revealed the formation of a 10:1 mixture of product diastereoisomers. The major diastereoisomer **4** was isolated by column chromatography, and the relative stereochemistry was determined by X-ray crystallography.

We were pleased to note that the stereochemical outcome of this cyclization reaction could be rationalized using the conformational model previously proposed by our group for other related cyclizations.[5] As highlighted in Figure 2, we believe that activation of the tricyclic lactam substrate by the Lewis acid leads to the formation of a formal *N*-acyliminium species.

The steric influence provided by the angular alkyl substituent, R, at the iminium carbon atom favors the proposed conformational model **A** that leads to the observed major product diastereoisomer **4** with overall retention of stereochemistry.

One can envisage steric interactions between this same angular alkyl group and the benzyl substituent that might disfavor the alternative conformation **B**, which in turn would lead to the minor diastereoisomer. One also cannot rule out the possible influence of chelation control with a Lewis acid such as $TiCl_4$. The presence of an asymmetric center next to the iminium carbon may also act to influence the formation of the new chiral center on cyclization. If this were to be a contributing factor, one can appreciate that the aromatic ring accordingly approaches the planar acyliminium intermediate from the direction of least steric hindrance.

Removal of the pendant hydroxymethyl substituent (auxiliary) from the tetracyclic product **4** was achieved by application of a three-step procedure (Scheme 3) previously demonstrated for other product types in our laboratory.[5] Dess−Martin periodinane oxidation of the primary alcohol proceeded in 87% yield to provide aldehyde **5**. This transformation was accompanied by racemization of the amino aldehyde stereocenter; however, this was of little consequence since the aldehyde substituent was then removed completely in the next step of the sequence.

We employed a Rh-catalyzed decarbonylation to access enamide **6** in 57% yield. Interestingly this decarbonylation reaction was now found to require 8 days at reflux rather than the 20 h reaction time noted with simpler systems.[5] Our decarbonylation sequence was completed by catalytic hydrogenation of **6** to furnish the desired compound **7** in 71% yield. Further elaboration of the product structure by reduction of the lactam carbonyl group gave the amine derivative **8** in 80% yield.

We report a facile and highly stereoselective synthesis of the tetracyclic erythrinane skeleton, assembled as a single diastereoisomer in only two steps from readily available reagents (condensation to the bicyclic lactam and Lewis acid promoted cyclization). The hydroxymethyl auxiliary group is conveniently removed by an established three-step procedure. Further work is underway to access more functionalized targets.

## Experimental Section

**General.** All solvents were dried and stored over 4Å molecular sieves prior to use, where necessary. Reagent chemicals were purchased from commercial sources and were used as supplied. Analytical thin-layer chromatography was carried out using aluminum-backed plates coated with 0.2 mm silica. Plates were visualized under UV light (at 254 nm) or by staining with either potassium permanganate solution or iodine. Flash column chromatography was carried out using 70−230 mesh silica gel; samples were applied as saturated solutions in an appropriate solvent or preadsorbed onto the minimum quantity of silica. Hand bellows were used to apply pressure when required at the column. Fourier transform infra red spectroscopy (FTIR) spectra were recorded in the range 4000−600 $cm^{-1}$; solid samples were run as a Nujol mull and liquids as thin films.

Nuclear magnetic resonance (NMR) spectra ($^1$H and $^{13}$C) were recorded using either 250 or 400 MHz instruments. Multiplicities were recorded as broad peaks (br. s), singlets (s), doublets (d), triplets (t), double doublets (dd), and multiplets (m). All NMR samples were prepared in deuterated chloroform with all values quoted in ppm relative to tetramethylsilane as internal reference. Coupling constants (*J* values) are reported in Hertz (Hz).

Diastereoisomeric ratios were calculated from the integration of suitable peaks in the proton NMR spectrum.

**2-(2-Oxocyclohexyl)ethanoic Acid (1).** Ethyl-2-cyclohexanone acetate (0.50 g, 2.71 mmol) was dissolved in a mixture of THF (18 mL) and water (8 mL). Lithium hydroxide (0.17 g, 4.07 mmol) was added, and the mixture was stirred at room temperature for 20 h. The reaction mixture was concentrated, resuspended in water (30 mL), and acidified with 1 M HCl. The aqueous layer was then extracted into ethyl acetate, dried over anhydrous magnesium sulfate, and evaporated to dryness, giving a colorless oil (0.42 g, 100%) that required no further purification: FTIR (thin film, $\nu$, $cm^{-1}$) 3200, 1702; $^1H$ NMR ($CDCl_3$, 250 MHz, $\delta$, ppm) 1.30−3.00 (m, 11H), 9.10−9.90 (br. s, 1H); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 25.2, 27.8, 33.8, 34.3, 41.8, 46.9, 178.2, 211.4; MS (EI) $m/z$ 156 [$M^+$, 37.33%]; HRMS calcd for $C_8H_{12}O_3$ 156.0786, found $M^+$ 156.0786.

**(2*S*)-2-Amino-3-[3,4-di(methoxy)phenyl]propan-1-ol (2).** A solution of chlorotrimethylsilane (4.50 mL, 35.52 mmol) in THF (10 mL) was added under nitrogen to a solution of lithium borohydride (8.88 mL of a 2.0 M solution in THF, 17.76 mmol) over the course of 2 min. 3-(3,4-Dimethoxyphenyl)-L-alanine (2.00 g, 8.88 mmol) was added portion-wise to the mixture over 5 min, and this mixture was then left to stir at room temperature for 24 h. Methanol (20 mL) was slowly added to the resulting blue solution, and the solvents were removed by rotary evaporation. The residue was treated with excess 20% aqueous potassium hydroxide solution and extracted with dichloromethane (3 × 20 mL). The organic phases were combined and dried over anhydrous sodium sulfate, and the solvent was removed by evaporation to yield white crystals in quantitative yield (1.87 g, 100%) that required no further purification: mp 82−83 °C (lit.[8] mp 79−80 °C); $[\alpha]_D = -21.6$ ($c$ 0.45, EtOH), lit.[8] $[\alpha]_D = -21.5$ ($c$ 8, EtOH). Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.29; H, 8.02; N, 6.53. FTIR (thin film, DCM, $\nu$, $cm^{-1}$) 3356; $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$, ppm) 2.48 (dd, $J$ = 13.6, 8.4, 1H), 2.69−2.76 (br. s, 3H), 2.74 (dd, $J$ = 13.6, 5.2, 1H), 3.08−3.13 (m, 1H), 3.42 (dd, $J$ = 10.6, 6.9, 1H), 3.64 (dd, $J$ = 10.6, 3.7, 1H), 3.86 (s, 3H), 6.71−6.74 (m, 2H), 6.78−6.80 (m, 1H); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 40.2, 54.3, 55.9 (2), 66.1, 111.4, 112.4, 121.2, 131.3, 147.7, 149.2; MS (EI) $m/z$ 211 [$M^+$, 6.51%]; HRMS calcd for $C_{11}H_{17}NO_3$ 211.1208, found $M^+$ 211.1210.

**(3*S*,6a*S*,10a*R*)-3-{[3,4-Di(methoxy)phenyl]methyl}perhydro[1,3]oxazolo[2,3-1]indol-5-one (3).** (2*S*)-2-Amino-3-[3,4-di(methoxy)phenyl]propan-1-ol (1.60 g, 7.58 mmol) and ethyl-2-cyclohexanoneacetate (1.18 g, 7.58 mmol) were dissolved in toluene (100 mL) and refluxed under Dean−Stark conditions for 144 h. After this time the solution was allowed to cool, and the solvent was removed by rotary evaporation. The resulting yellow oil was purified by flash column chromatography using a 1:1 mixture of ethyl acetate and hexanes as eluent. Evaporation of the desired fractions under reduced pressure afforded the target compound as a yellow oil (1.45 g, 58%): $[\alpha]_D = +26.9$ ($c$ 0.34, $CHCl_3$); FTIR (thin film, $\nu$, $cm^{-1}$) 1702; $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$, ppm) 1.37−1.90 (m, 8H), 2.30−2.41 (m, 2H), 2.57−2.65 (m, 1H), 2.69 (dd, $J$ = 13.8, 9.2, 1H), 3.04 (dd, $J$ = 13.8, 5.2, 1H), 3.85 (s, 3H), 3.87 (s, 3H), 3.93 (dd, $J$ = 8.8, 5.6, 1H), 4.02 (dd, $J$ = 8.8, 6.8, 1H), 4.23−4.27 (m, 1H), 6.72−6.81 (m, 3H); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 19.8, 20.9, 25.1, 32.8, 39.2, 39.6, 40.8, 55.3, 55.9, 56.0, 71.7, 99.6, 111.3, 112.5, 121.3, 129.7, 147.9, 149.0, 176.2; MS (EI) $m/z$ 331 [$M^+$, 41.22%]; HRMS calcd for $C_{19}H_{25}NO_4$ 331.1783, found $M^+$ 331.1786.

**(4*S*,9b*S*,13a*S*)-4-(Hydroxymethyl)-7,8-di(methoxy)-1,4,5,-10,11,12,13,13a-octahydro-2*H*-indolo[7a,1-*a*]isoquinolin-2-one (4).** (3*S*,6a*S*,10a*R*)-3-{[3,4-Di(methoxy)phenyl]methyl}-perhydro[1,3]oxazolo[2,3-1]indol-5-one (1.20 g, 3.63 mmol) was dissolved in dry dichloromethane (50 mL) under a nitrogen atmosphere. The mixture was cooled to −78 °C, and 3 equiv of $TiCl_4$ (1.19 mL, 10.88 mmol) was added dropwise via syringe. After stirring at this temperature for 10 min, the mixture was allowed to reach room temperature and left to stir for a further 20 h. The reaction mixture was quenched with saturated aqueous ammonium chloride solution (50 mL), extracted with dichloromethane (3 × 50 mL), and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, and the diastereoselectivity of the reaction was determined by $^1H$ NMR spectroscopy on the crude reaction mixture. The yellow oil was purified by flash column chromatography using 100% ethyl acetate as eluent, yielding the target compound as a white solid (1.18 g, 98%), a portion of which was recrystallized from ethyl acetate to give colorless crystals: mp 191−192 °C; $[\alpha]_D = -79.1$ ($c$ 0.53, $CHCl_3$); FTIR (thin film, DCM, $\nu$, $cm^{-1}$) 3383, 1655; $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$, ppm) 1.35−1.45 (m, 1H), 1.46−1.55 (m, 1H), 1.60−1.70 (m, 2H), 1.74−1.83 (m, 1H), 1.85−1.95 (m, 2H), 2.00−2.09 (m, 1H), 2.31−2.44 (m, 2H), 2.61−2.67 (m, 1H), 2.82 (dd, $J$ = 16.0, 5.2, 1H), 3.13 (dd, $J$ = 16.0, 7.6, 1H), 3.70−3.76 (m, 1H), 3.80−3.85 (m, 1H), 3.86 (s, 3H), 3.89 (s, 3H), 3.88−3.94 (m, 1H), 4.63 (dd, $J$ = 7.2, 6.0, 1H), 6.65 (s, 1H), 6.88 (s, 1H); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 20.8, 21.1, 27.5, 29.9, 36.2, 36.8, 38.1, 52.6, 55.9, 56.3, 64.0, 65.2, 108.4, 112.3, 126.0, 134.0, 147.4, 148.0, 176.0; MS (EI) $m/z$ 331 [$M^+$, 29.89%]; HRMS calcd for $C_{19}H_{25}NO_4$ 331.1783, found $M^+$ 331.1779.

**(9b*S*,13a*S*)-7,8-Di(methoxy)-2-oxo-1,4,5,10,11,12,13,13a-octahydro-2*H*-indolo[7a,1-*a*]isoquinolin-4-carbaldehyde (5).** A solution of (4*S*,9b*S*,13a*S*)-4-(hydroxymethyl)-7,8-di(methoxy)-1,4,5,10,11,12,13,13a-octahydro-2*H*-indolo[7a,1-*a*]isoquinolin-2-one (1.18 g, 3.56 mmol) in dichloromethane (25 mL) was added to a solution of Dess−Martin periodinane (11.08 mL of a 15 wt % solution in dichloromethane, 3.92 mmol) in dichloromethane (25 mL) with stirring. After 20 h, excess dichloromethane was removed, and the yellow oil was loaded directly on to silica. Purification by flash column chromatography using a 2:1 mixture of ethyl acetate and hexanes as eluent yielded a 1:1 mixture of inseparable aldehyde diastereoisomers as a colorless oil (1.02 g, 87%): FTIR (thin film, $\nu$, $cm^{-1}$) 1733, 1683; $^1H$ NMR (both isomers, $CDCl_3$, 250 MHz, $\delta$, ppm) 1.21−3.16 (m, 26H), 3.80−3.85 (m, 12H), 4.20 (m, 1H), 4.50 (m, 1H), 6.60 (s, 1H), 6.68 (s, 1H), 6.84 (s, 1H), 6.92 (s, 1H), 9.53 (s, 1H), 9.66 (s, 1H); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 20.8 and 20.9, 21.2 and 21.6, 26.1 and 27.5, 27.7 and 28.1, 35.6 and 36.0, 36.8 and 37.2, 38.1 and 38.6, 55.9 and 56.0, 56.3 and 56.4, 57.1 and 57.2, 62.7 and 63.7, 108.2 and 108.4, 112.08 and 112.13, 124.0 and 124.4, 134.3 and 134.4, 147.7 and 147.8, 148.15 and 148.19, 174.4 and 176.0, 199.7 (2); MS (EI) $m/z$ 329 [$M^+$, 32.07%]; HRMS calcd for $C_{19}H_{23}NO_4$ 329.1627, found $M^+$ 329.1627.

**(9b*S*,13a*S*)-7,8-Di(methoxy)-1,10,11,12,13,13a-hexahydro-2*H*-indolo[7a,1-*a*]isoquinolin-2-one (6).** [Bis(triphenylphosphine)]rhodium(I) carbonyl chloride (88 mg, 0.12 mmol) was added to anhydrous xylene (20 mL) under a nitrogen atmosphere. The mixture was stirred at 80 °C for 15 min. 1,3-Bis-(diphenyl phosphino)propane (0.12 g, 0.30 mmol) was added, and the mixture was heated at 80 °C for 30 min until formation of a yellow precipitate. (9b*S*,13a*S*)-7,8-Di(methoxy)-2-oxo-1,4,5,10,-11,12,13,13a-octahydro-2*H*-indolo[7a,1-*a*]isoquinolin-4-carbaldehyde (0.81 g, 2.47 mmol) in anhydrous xylene (20 mL) was added, and the mixture was heated at reflux for 192 h. The solvent was removed by rotary evaporation giving a thick green oil. Purification by flash column chromatography using a mixture of 1:1 ethyl acetate and hexanes as eluent gave the product as white crystals (0.42 g, 57%), a portion of which was recrystallized from ethyl acetate to give colorless crystals: mp 175−177 °C; $[\alpha]_D = -238.7$ ($c$ 0.45, $CHCl_3$); FTIR (thin film, DCM, $\nu$, $cm^{-1}$) 1696, 730; $^1H$ NMR ($CDCl_3$, 250 MHz, $\delta$, ppm) 1.14−1.61 (m, 4H), 1.72−1.89 (m, 1H); 1.96−2.24 (m, 3H), 2.48 (dd, $J$ = 17.1, 9.3, 1H), 2.60 (dd, $J$ = 17.1, 11.7, 1H), 2.80−2.97 (m, 1H), 3.89 (s, 3H), 3.92 (s, 3H), 5.94 (d, $J$ = 7.4, 1H), 6.67 (s, 1H), 6.85 (d, $J$ = 7.6, 1H), 6.97 (s, 1H); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 20.0, 20.8, 27.0, 35.1, 35.3, 37.9, 56.0, 56.4, 61.9, 108.9, 109.2, 111.2, 119.5, 124.1, 130.2, 147.9, 148.2, 170.7; MS (EI) $m/z$ 299 [$M^+$, 30.63%]; HRMS calcd for $C_{18}H_{21}NO_3$ 299.1521, found $M^+$ 299.1526.

**(9b*S*,13a*S*)-7,8-Di(methoxy)-1,4,5,10,11,12,13,13a-octahydro-2*H*-indolo[7a,1-*a*]isoquinolin-2-one (7).** (9b*S*,13a*S*)-7,8-Di(methoxy)-1,10,11,12,13,13a-hexahydro-2*H* indolo[7a,1-*a*] isoquinolin-2-one (0.14 g, 0.47 mmol) was dissolved in absolute ethanol (15 mL) in a Schlenk tube. The reaction mixture was

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purged with nitrogen. A catalytic amount of 10% palladium-charcoal was added to the mixture, a balloon filled with hydrogen was fitted, and the system was purged with hydrogen, the mixture was then stirred for a further 20 h. The mixture was filtered through Celite, the organic filtrate was collected and dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation to give a yellow oil. Purification by flash column chromatography using a 4:1 mixture of ethyl acetate and hexanes as eluent gave the target compound as a colorless oil (0.10 g, 71%): $[\alpha]_D = -96.4$ (*c* 0.25, $CHCl_3$); FTIR (thin film, *v*, $cm^{-1}$) 1683; $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$, ppm) 1.48−1.56 (m, 2H), 1.62−1.75 (m, 3H), 1.83 (dd, $J$ = 14.3, 6.0, 1H), 1.90 (dd, $J$ = 14.3, 6.2, 1H), 2.00−2.08 (m, 1H), 2.32 (dd, $J$ = 16.8, 7.6, 1H), 2.37 (dd, $J$ = 16.8, 8.0, 1H), 2.54−2.60 (m, 1H), 2.68 (ddd, $J$ = 16.2, 5.4, 3.0, 1H), 2.94−3.02 (m, 1H), 3.22 (ddd, $J$ = 13.2, 10.4, 5.6, 1H), 3.85 (s, 3H), 3.89 (s, 3H), 4.11 (ddd, $J$ = 13.2, 7.2, 2.8, 1H), 6.59 (s, 1H), 6.88 (s, 1H); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 20.4, 20.8, 27.18, 27.21, 34.9, 35.9, 36.6, 37.7, 55.9, 56.2, 62.3, 108.3, 112.0, 125.8, 134.9, 147.4, 147.9, 174.2; MS (EI) *m*/*z* 301 [$M^+$, 23.13%]; HRMS calcd for $C_{18}H_{23}NO_3$ 301.1677, found $M^+$ 301.1683.

**(9b*S*,13a*S*)-7,8-Di(methoxy)-1,4,5,10,11,12,13,13a-octahydro-2*H*-indolo[7a,1-*a*]isoquinoline (8).** A solution of (9b*S*,-13a*S*)-7,8-di(methoxy)-1,4,5,10,11,12,13,13a-octahydro-2*H*-indolo-[7a,1-*a*]isoquinolin-2-one (0.100 g, 0.33 mmol) in dry toluene (10 mL) was stirred at 25 °C, under nitrogen, with sodium bis-(methoxyethoxy)aluminum hydride (65+ wt % solution in toluene, 0.33 mL) for 16 h. The reaction mixture was quenched by careful addition of saturated Rochelle's salt (10 mL). The organic layer was separated, and the salt solution was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were dried over aqueous sodium sulfate, and the solvent was removed to yield a yellow oil. Further purification by flash column chromatography using a 9:1 mixture of dichloromethane and methanol as eluent gave the product as a colorless oil (76 mg, 80%): $[\alpha]_D = -25.0$ (*c* 0.38, $CHCl_3$); FTIR (thin film, *v*, $cm^{-1}$) 2929, 2848, 1123, 1104; $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$, ppm) 1.23−1.77 (m, 9H), 1.89−2.00 (m, 1H), 2.22−2.32 (m, 2H), 2.86 (dt, $J$ = 10.4, 2.4, 1H), 3.04−3.22 (m, 4H), 3.83 (s, 3H), 3.87 (s, 3H), 6.50 (s, 1H), 6.70 (s, 1H); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 21.3, 21.5, 25.1, 28.6, 29.0, 35.7, 40.4, 43.6, 46.2, 55.7, 56.0, 64.5, 108.8, 111.1, 126.9, 136.0, 146.9, 147.2; MS (EI) *m*/*z* 287 [$M^+$, 24.31%]; HRMS calcd for $C_{18}H_{25}NO_2$ 287.1885, found $M^+$ 287.1885.

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**Supporting Information Available:** $^1H$ NMR and $^{13}C$ NMR spectra for compounds **3**−**8** and X-ray crystal structure (ORTEP) and crystallographic data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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