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Asymmetric Synthesis of Tetracyclic Benzo[*a*]quinolizidine Targets

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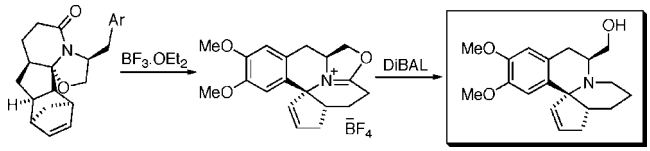
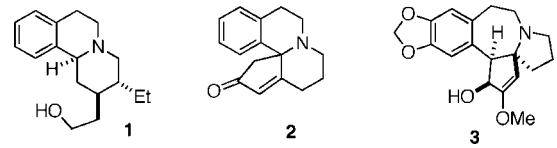


We report a novel, facile, and asymmetric approach for the synthesis of polycyclic benzo[*a*]quinolizidine targets. In the formation of more functionalized derivatives, we have observed the generation of an iminium ether salt intermediate, formed during an unprecedented retro-Diels−Alder/*N*-acyliminium cyclization cascade. The iminium ether intermediate was isolated in good yield, characterized by X-ray crystallography, and subsequently applied as a synthetic building block.

Benzo[*a*]quinolizidines are of significance since this ring system is found within a wide range of biologically active alkaloids, including protoemetinol **1**,[1] psychotrine,[2] and alganine.[3] Fusion of additional rings to this parent heterocycle brings additional interest; indeed, derivatives such as **2** have recently been applied as synthetic building blocks in a new approach to the antileukemic *Cephalotaxus* alkaloids, such as **3**, by Li and co-workers,[4] through a transannular reductive rearrangement strategy from substrate **2**.

Indeed, it was the recent work of Li that inspired us to investigate the possible application of the stereoselective *N*-acyliminium cyclization of "Meyers-type" chiral lactams[5] as a new asymmetric approach to nonracemic tetracyclic benzo[*a*]quinolizidine ring systems, such as the heterocyclic core found within **2**. Such targets contain a quaternary benzylic stereocenter as an added challenge to their synthesis. Other research groups have also been engaged in the successful development of alternative stereoselective *N*-acyliminium cyclization reactions to access similar heterocycles.[6]



Our own approach to the target system was similar to that previously adopted by us in our route to the *Erythrina* alkaloids,[7] in which cyclocondensation of an enantiomerically pure amino alcohol with a racemic ketoacid substrate would generate a tricyclic lactam intermediate, which in turn would function as an appropriate *N*-acyliminium ion precursor, thus promoting cyclization of the pendent aromatic nucleus from the original amino acid substrate. The racemic keto acid **4** required for the cyclocondensation step was synthesized by application of the method of Stork.[8] Subsequent condensation of this keto acid with the appropriate *R*-amino alcohol under Dean−Stark conditions in toluene for 48 h generated the desired tricyclic lactam **5** as a single diastereoisomer in 71% yield, as illustrated in Scheme 1. The application of racemic, but enolizable, keto acids in chiral lactam chemistry is now well established.[9]

The stereochemistry of the cyclopentane moiety within **5** is represented by analogy to our work in the homologous series,[7] with the ring junction fused cis with respect to the aromatic substituent, and also from the result of the cyclization reaction, detailed below, to yield **7**, the structure of which has been determined by X-ray crystallography. Treatment of tricyclic lactam **5** with titanium tetrachloride in dichloromethane at −78 °C generated, presumably, the reactive *N*-acyliminium ion intermediate **6**, which then underwent a stereoselective cyclization to afford exclusively the tetracyclic benzo[*a*]quinolizidine

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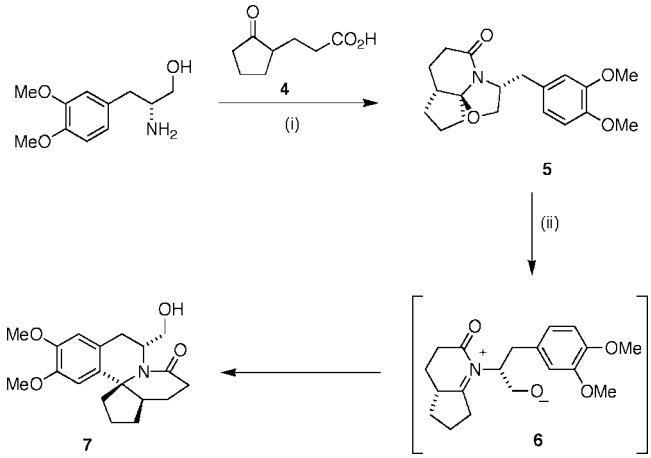
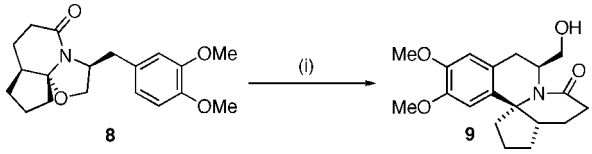
SCHEME 1[a]



[a] Key: (i) toluene, Δ, 48 h (71%); (ii) $TiCl_4$, −78 °C, 48 h, DCM (73%).

SCHEME 2[a]



[a] Key: (i) $TiCl_4$, −78 °C, 48 h, DCM (68%).

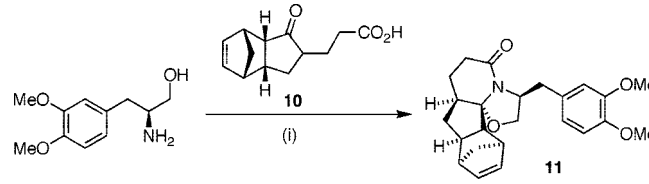
derivative **7** in 73% yield, and as a single diastereoisomer. The absolute stereochemistry of target **7** was confirmed by single-crystal X-ray analysis. The relative stereochemistry of **7** was identical to that seen in the homologous series in our work on the *Erythrina* alkaloids,[7] with the cyclopentane ring fused *anti* to the hydroxymethyl group.

Clearly, the availability of enantiomeric amino alcohol reagents is a significant strength of this approach and allows for the corresponding synthesis of the enantiomeric series of cyclized products. Hence, condensation of the corresponding *S*-amino alcohol with keto acid **4** in toluene for 48 h under Dean−Stark conditions generated tricyclic lactam **8** as a single diastereoisomer, in 76% yield. Treatment of the tricyclic lactam **8** with the Lewis acid afforded the tetracyclic target **9** in 68% yield and as a single diastereoisomer. The absolute stereochemistry of **9** was confirmed by single-crystal X-ray analysis (Scheme 2).

We were pleased to observe that the stereochemical outcome of these cyclizations could be rationalized using the same conformational models previously proposed by us to explain all related cyclizations.[5]

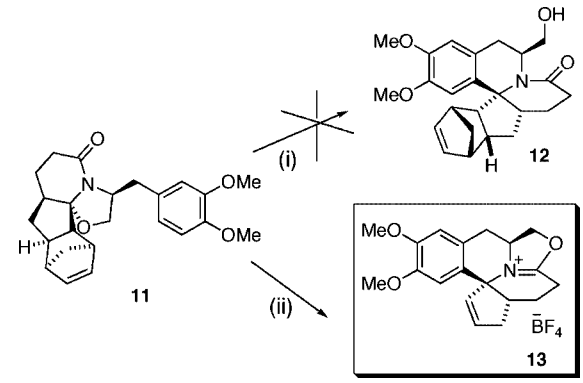
With the success of the *N*-acyliminium methodology demonstrated with the preparation of model systems **7** and **9**, we focused our attention on the preparation of a more functionalized tetracyclic target. Our attention turned to work by Lete and co-workers describing a synthesis of functionalized polycyclic lactam derivatives, in which a masked olefin moiety was introduced in the form of a Diels−Alder adduct.[10] With this approach in mind, the highly functionalized polycyclic lactam **11** was then successfully prepared in 45% yield, as a single diastereoisomer, by cyclocondensation of the racemic keto acid **10** and an enantiomerically pure amino alcohol under Dean−Stark conditions (Scheme 3).

SCHEME 3[a]



[a] Key: (i) toluene, Δ, 48 h (45%).

SCHEME 4[a]



[a] Key: (i) $TiCl_4$, − 78 °C, DCM; (ii) $BF_3 \cdot OEt_2$, DCM, Δ (91%).

With lactam **11** in hand, we had visualized an asymmetric *N*-acyliminium ion cyclization upon treatment with a Lewis acid at low temperature to form target **12**, containing a masked olefin unit, that could be realized at a later stage through a retro-Diels−Alder reaction (Scheme 4).

Unfortunately, treatment of the *N*-acyliminium ion precursor **11** with titanium tetrachloride at −78 °C failed to produce the desired product **12** and resulted only in the degradation of the starting material. Attempts to generate the *N*-acyliminium intermediate and encourage the desired cyclization using an alternative Lewis acid, boron trifluoride etherate, was also unsuccessful at low temperatures with only starting materials being recovered. In a final attempt to drive this cyclization, the temperature of the reaction was elevated to refluxing dichloromethane. After 24 h under these revised conditions, we were delighted to observe, and isolate in good yield, the unexpected iminium ether salt **13**, shown in Scheme 4, as a single diastereoisomer. A preference for boron trifluoride etherate over titanium tetrachloride in the cyclization of L-DOPA-derived acyliminium precursors has previously been noted by Lete and co-workers.[11] The structure of iminium salt **13** was unequivocally determined by single-crystal X-ray crystallography (Figure 1), also confirming that the relative stereochemistry of this densely functionalized product followed the same stereochemical trends observed in the model tetracyclic systems and thus confirming the relative stereochemistry of **11** by analogy. Clearly, in the presence of excess boron trifluoride etherate, and at moderately elevated temperatures, an unexpected reaction cascade is occurring, although it is not clear at what point in the sequence the retro-Diels−Alder reaction is occurring.

The intermediacy of iminium ethers in chiral lactam chemistry has previously been proposed by Ennis,[12] and more recently, a range of bicyclic iminium ether salts were prepared and applied

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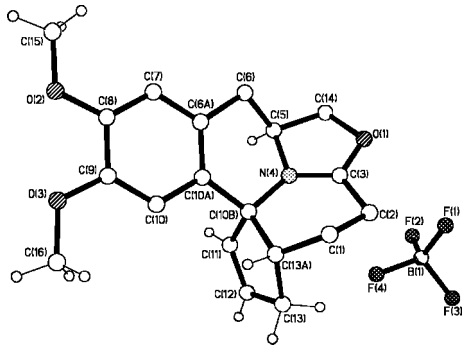
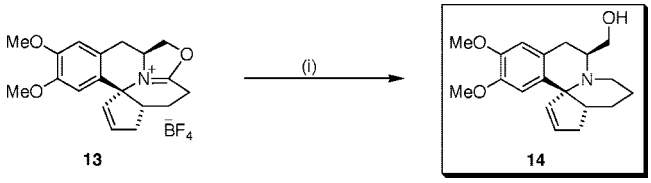


FIGURE 1. Single-crystal X-ray structure of iminium ether salt **13**.

SCHEME 5[a]



[a] Key: (i) DiBAL (2.5 equiv), DCM, 0 °C, then Δ, 5 h (65%).

as synthetic building blocks by Aube and co-workers, since these compounds can display a range of useful reactivities.[13] In our hands, reductive ring-opening of the pentacyclic iminium ether **13** was achieved using diisobutylaluminium hydride to furnish the enantiomerically pure target amine **14** in 65% yield (Scheme 5). It is noteworthy that the intermediacy of this iminium ether effectively acts to remove the lactam carbonyl group from the template through reductive ring opening. Although not subsequently performed in this current study, removal of the pendent hydroxymethyl auxiliary group from similar heterocyclic templates has now been well established and documented by our research group.[14]

In summary, we report a facile new asymmetric route to access novel functionalized tetracyclic benzo[*a*]quiolizidine targets. We have observed the generation of a pentacyclic iminium ether intermediate, formed during an unprecedented retro-Diels−Alder/*N*-acyliminium cyclization cascade sequence. The iminium ether intermediate was isolated and characterized by X-ray crystallography and further applied as a synthetic building block. Current work in our group is focused on applying nonracemic cyclopentene-containing building blocks, such as **14**, in an approach to natural products.

Experimental Section

(3*R*,6a*R*,10a*S*)-3-(3,4-Dimethoxybenzyl)hexahydro-1-oxa-3a-azacyclopenta[*d*]inden-5-one, 5. (2*R*)-2-Amino-3-(3,4-dimethyloxy)-phenyl)propan-1-ol (584 mg, 2.77 mmol) and 3-(2-oxocyclopentyl)propionic acid **4** (518 mg, 3.32 mmol) were dissolved in toluene (60 mL) and refluxed under Dean−Stark conditions for 48 h. The reaction was allowed to cool to room temperature and the solvent removed by rotary evaporation. The crude product was adsorbed onto silica and chromatographed using 3% methanol in dichloromethane as eluent to produce a yellow oil (652 mg, 71%): $[\alpha]_D$ −86.3 (c = 1.05 in CH_2Cl_2); IR ν_{max} (thin film, CH_2Cl_2)/cm^{-1} 1651 (NCO) and 2950 (aliphatic CH); HMR δ_H (400 MHz, $CDCl_3$) 1.37−1.46 (2H, m), 1.60−1.66 (2H, m), 1.73−1.80 (2H, m), 1.87−1.91 (1H, m), 2.01−2.16 (2H), 2.34−2.37 (2H, m), 2.67 (1H, dd, *J* 10.0, 13.4), 3.31 (1H, dd, *J* 3.6, 13.3), 3.70 (1H, dd, *J* 8.0, 9.1), 3.86 (3H, s), 3.88 (3H, s), 3.96 (1H, dd, *J* 7.8, 9.2), 4.39−4.48 (1H, m), 6.74−6.81 (3H, m); NMR δ_C (100 MHz, $CDCl_3$) 21.9, 25.0, 29.4, 30.6, 36.1, 38.8, 42.1, 56.0, 55.9, 56.2, 67.3, 102.0, 111.2, 112.5, 121.3, 129.7, 147.7, 148.9, 169.8; MS (EI) *m*/*z* 331 [M$^+$, 28.5] (M$^+$, 331.1782; $C_{19}H_{25}NO_4$ requires 331.1784).

(5*R*,10b*R*,13a*R*)-5-Hydroxymethyl-8,9-dimethoxy-1,2,5,6,11,12,-13,13a-octahydrocyclopenta[2,3]pyrido[2,1-*a*]isoquinolin-3-one, 7. (3*R*,7a*R*,10a*S*)-3-(3,4-Dimethoxybenzyl)hexahydro-1-oxa-3a-azacyclopenta[*d*]inden-5-one **5** (426 mg, 1.29 mmol) was dissolved in dry dichloromethane (25 mL) under nitrogen. The mixture was cooled to −78 °C, and titanium tetrachloride (732 mg, 0.43 mL, 3.86 mmol) was added dropwise. After being stirred at −78 °C for 10 min, the reaction was allowed to warm to room temperature and stirred for 48 h. The reaction mixture was quenched with saturated aqueous ammonium chloride (50 mL), extracted with dichloromethane (3 × 50 mL), and dried over anhydrous magnesium sulfate. The product was filtered and the solvent removed by rotary evaporation to yield the target compound, a single diastereoisomer, which was purified by column chromatography over silica gel with ethyl acetate as eluent to yield a colorless solid (310 mg, 73%): mp 138−141 °C; $[\alpha]_D$ + 141.2 (c = 1.01 in CH_2Cl_2); IR ν_{max} (thin film, CH_2Cl_2)/cm^{-1} 1621, 2947, 3379; NMR δ_H (400 MHz, $CDCl_3$) 1.70−1.82 (5H, m), 1.95−2.02 (1H, m), 2.14−2.25 (2H, m), 2.29−2.36 (1H, m), 2.52−2.57 (1H, m), 2.69−2.80 (2H, m), 3.24 (1H, dd, *J* 9.4, 16.2), 3.71−3.75 (2H, m), 3.87 (3H, s), 3.88 (3H, s), 4.07−4.13 (1H, m), 6.64 (1H, s), 6.69 (1H, s); NMR δ_C (100 MHz, $CDCl_3$) 22.7, 23.9, 30.1, 30.2, 30.4, 43.1, 43.9, 55.9, 56.3, 56.5, 63.7, 72.0, 108.5, 112.0, 127.9, 134.0, 147.2, 147.9, 173.1; MS (EI) *m*/*z* 331 [M$^+$, 46.5] (M$^+$, 331.1784; $C_{19}H_{25}NO_4$ requires 331.1784). The product was recrystallized from dichloromethane/hexane by vapor diffusion to produce clear, colorless crystals. The relative stereochemistry was confirmed by single-crystal X-ray analysis.

(3*S*,6a*S*,10a*R*)-3-(3,4-Dimethoxybenzyl)hexahydro-1-oxa-3a-azacyclopenta[*d*]inden-5-one, 8. (2*S*)-2-Amino-3-(3,4-dimethyloxy)phenyl)propan-1-ol (900 mg, 4.26 mmol) and 3-(2-oxocyclopentyl)-propionic acid **4** (798 mg, 5.11 mmol) were dissolved in toluene (60 mL) and refluxed under Dean−Stark conditions for 48 h. The reaction was allowed to cool to room temperature and the solvent removed by rotary evaporation. The crude product was adsorbed onto silica and chromatographed over silica gel using 3% methanol/dichloromethane as eluent to produce the target compound as a yellow oil (1.07 g, 76%): $[\alpha]_D$ +80.8 (c = 1.00 in CH_2Cl_2); IR ν_{max} (thin film, CH_2Cl_2)/cm^{-1} 1648, 2950; NMR δ_H (400 MHz, $CDCl_3$) 1.37−1.46 (2H, m), 1.59−1.66 (2H, m), 1.74−1.81 (2H, m), 1.87−1.90 (1H, m), 2.01−2.15 (2H, m), 2.34−2.37 (2H, m), 2.66 (1H, dd, *J* 10.0, 13.4), 3.32 (1H, dd, *J* 3.6, 13.3), 3.69 (1H, dd, *J* 8.0, 9.1), 3.86 (3H, s), 3.88 (3 H, s), 3.96 (1H, dd, *J* 7.8, 9.2), 4.39−4.47 (1H, m), 6.73−6.80 (3 H, m); NMR δ_C (100 MHz, $CDCl_3$) 21.8, 24.9, 29.3, 30.6, 36.0, 38.8, 42.1, 55.9, 55.9, 56.1, 67.2, 102.0, 111.1, 112.4, 121.3, 129.7, 147.7, 148.9, 169.6; MS (EI) *m*/*z* 331 [M$^+$, 28.5] (M$^+$, 331.1782; $C_{19}H_{25}NO_4$ requires 331.1784).

(5*S*,10b*S*,13a*S*)-5-Hydroxymethyl-8,9-dimethoxy-1,2,5,6,11,-12,13,13a-octahydro-cyclopenta[2,3]pyrido[2,1-*a*]isoquinolin-3-one, 9. (3*S*,7a*S*,10a*R*)-3-(3,4-Dimethoxybenzyl)hexahydro-1-oxa-3a-azacyclopenta[*d*]inden-5-one **8** (438 mg, 1.32 mmol) was dissolved in anhydrous dichloromethane (25 mL) under nitrogen. The mixture was cooled to −78 °C, and titanium tetrachloride (752 mg, 0.43 mL, 3.97 mmol) was added dropwise. After being stirred at −78 °C for 10 min, the reaction was allowed to warm to room temperature and stirred for 48 h. The reaction mixture was quenched with saturated ammonium chloride (50 mL), extracted with dichloromethane (3 × 50 mL), and dried over anhydrous magnesium sulfate. The product was filtered and the solvent removed by rotary

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(14) Allin, S. M.; Gaskell, S. N.; Elsegood, M. R. J.; Martin, W. P. *Tetrahedron Lett.* **2007**, *48*, 5669. Allin, S. M.; Gaskell, S. N.; Towler, J. M. R.; Page, P. C. B.; Saha, B.; McKenzie, M. J.; Martin, W. P. *J. Org. Chem.* **2007**, *72*, 8972.

evaporation to yield the target compound as a single diastereoisomer, which was purified by column chromatography using silica gel and ethyl acetate as eluent to yield a colorless solid (300 mg, 68%): mp 138−141 °C; $[\alpha]_D$ −136.8 (c = 5.00 in CH_2Cl_2); IR ν_{max} (thin film, CH_2Cl_2)/cm^{-1} 1620, 2947, 3376; NMR δ_H (400 MHz, $CDCl_3$) 1.70−1.82 (5H, m), 1.95−2.02 (1H, m), 2.14−2.25 (2H, m), 2.29−2.36 (1H, m), 2.52−2.57 (1H, m), 2.69−2.80 (2 H, m), 3.24 (1H, dd, J 9.4, 16.2), 3.71−3.75 (2 H, m), 3.87 (3 H, s), 3.88 (3 H, s), 4.07−4.13 (1 H, m), 4.72 (1 H, br, s), 6.64 (1 H, s), 6.69 (1 H, s); NMR δ_C (100 MHz, $CDCl_3$) 22.7, 23.9, 30.1, 30.2, 30.4, 43.1, 43.9, 55.9, 56.3, 56.5, 63.7, 72.0, 108.5, 112.0, 127.9, 134.0, 147.2, 147.9 and 173.1; MS (EI) m/z 331 [M$^+$, 46.5] (M$^+$, 331.1782; $C_{19}H_{25}NO_4$ requires 331.1784). The product was recrystallized from dichloromethane/hexane via vapor diffusion to produce clear, colorless crystals. The relative stereochemistry was confirmed by single-crystal X-ray analysis.

(3*S*,6a*R*,10a*S*)-3-(3,4-Dimethoxybenzyl)octahydro-1-oxa-3a-azacyclopenta[*d*]inden-4-one-8,9-bicyclo[2.2.1]hept-2-ene, 11. (2*S*)-2-Amino-3-(3,4-dimethyloxy)phenyl)propan-1-ol (1.88 g, 8.91 mmol) and 3-(1-oxo-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-methanoinden-2-yl)-propionic acid **10** (1.96 g, 8.91 mmol) were dissolved in toluene (50 mL) and refluxed under Dean−Stark conditions for 48 h. The reaction was allowed to cool to room temperature and the solvent removed by rotary evaporation. The crude product was adsorbed onto silica and chromatographed over silica gel using 3:2 ethyl acetate/light petroleum as eluent to produce the target compound as a yellow oil (1.59 g, 45%): $[\alpha]_D$ −34.1 (c 1.08, $CHCl_3$); IR ν_{max} (thin film)/cm^{-1} 1650, 2956; NMR δ_H (400 MHz, $CDCl_3$) 1.38−1.46 (2H, m), 1.56−1.73 (3H, m), 1.77−1.85 (1H, m), 2.05−2.09 (1H, m), 2.28−2.37 (1H, m), 2.54 (1H, dt, J 5.6, 18.0), 2.68−2.77 (3H, m), 2.98−3.05 (2H, m), 3.41 (1H, dd, J 4.0, 13.2), 3.75 (1H, dd, J 7.6, 8.8), 3.83−3.88 (4H, m), 3.90 (3H, s), 4.56−4.60 (1H, m), 6.12 (1H, dd, J 3.2, 6.0), 6.23 (1H, dd, J 2.8, 5.6), 6.81 (2H, s), 6.84 (1H, s); NMR δ_C (100 MHz, $CDCl_3$) 24.1, 30.3, 31.8, 39.5, 44.8, 45.2, 46.7, 47.2, 53.8, 55.9, 55.9, 56.1, 57.1, 67.6, 101.3, 111.2, 112.2, 121.1, 130.0, 133.7, 137.0, 147.9, 149.1, 170.1; MS (FAB) m/z 396 [MH$^+$, 0.4] (MH$^+$, 396.2181; $C_{24}H_{29}NO_4$ requires 396.2175).

(5*S*,10b*R*,13a*R*)-(8,9-Dimethoxy-1,2,5,6,13,13a-hexahydrocyclopenta[*e*]oxazolo[3,2-*a*]pyrido[2,1-*a*]isoquinolinylium Tetrafluoroborate, 13. To a stirred solution of (3*S*,6a*R*,10a*S*)-3-(3,4-dimethoxybenzyl)octahydro-1-oxa-3a-azacyclopenta[*d*]inden-4-one-8,9-bicyclo[2.2.1]hept-2-ene **11** (723 mg, 1.83 mmol) in anhydrous dichloromethane (15 mL) was added boron trifluoride diethyl etherate (778 mg, 0.68 mL, 5.48 mmol) dropwise at room temperature, and the resultant solution was heated under reflux. After 15 h, the reaction was cooled to room temperature and quenched with a saturated aqueous solution of ammonium chloride (15 mL). The product was then extracted with dichloromethane (3 × 20 mL), dried over anhydrous magnesium sulfate, and evaporated to yield the crude product, which was recrystallized from dichloromethane/hexane to yield a colorless crystalline solid (664 mg, 91%): mp 206−207 °C; $[\alpha]_D$ −286.3 (c 1.01, CH_2Cl_2); IR ν_{max} (thin film, CH_2Cl_2)/cm^{-1} 1652, 2942; NMR δ_H (400 MHz, $CDCl_3$) 2.01−2.13 (2H, m), 2.55−2.62 (1H, m), 2.81−2.88 (2H, m), 2.98 (1H, ddt, J 2.4, 9.2, 18.0), 3.17−3.23 (3H, m), 3.84 (3H, s), 3.86 (3H, s), 4.78−4.87 (1H, m), 4.95 (1H, dd, J 4.4, 9.6), 5.30 (1H, dd, J 6.0, 9.2), 5.87−5.90 (1H, m), 6.15−6.17 (1H, m), 6.53 (1H, s), 6.61 (1 H, s); NMR δ_C (100 MHz, $CDCl_3$) 20.1, 22.1, 33.8, 37.3, 42.9, 56.1, 56.1, 56.2, 74.1, 77.7, 108.3, 111.6, 122.9, 128.3, 132.9, 135.2, 148.9, 149.1, 175.2; MS (EI) m/z 312 [M$^+$, 3.4] (M$^+$, 312.1595; $C_{19}H_{22}NO_3$ requires 312.1600). The product was recrystallized from dichloromethane/hexane via vapor diffusion to produce clear, colorless crystals. The relative stereochemistry was confirmed by single-crystal X-ray analysis.

(5*S*,10b*R*,13a*R*)-(8,9-Dimethoxy-2,3,5,6,13,13a-hexahydro-1*H*-cyclopenta[2,3]pyrido[2,1-*a*]isoquinolin-5-yl)methanol, 14. (5*S*,10b*R*,13a*R*)-(8,9-Dimethoxy-1,2,5,6,13,13a hexahydrocyclopenta[*e*]oxazolo[3,2-*a*]pyrido[2,1-*a*]isoquinolinylium tetrafluoroborate **13** (612 mg, 1.53 mmol) was dissolved in anhydrous dichloromethane (5 mL) under nitrogen and cooled to 0 °C in an ice bath. A 1 M solution of diisobutylaluminium hydride in hexane (3.83 mL, 3.83 mmol) was added dropwise at 0 °C, and the reaction was heated under reflux for 5 h. The reaction was then cooled to 0 °C, and methanol (5 mL) followed by saturated ammonium chloride (10 mL) were added carefully. The organics were washed with water (5 mL), dried over magnesium sulfate, and concentrated to give an oily residue, which was purified by column chromatography on silica gel and 3:2 ethyl acetate/light petroleum as eluent to yield a yellow oil (315 mg, 65%): $[\alpha]_D$ −177.5 (c 1.02, CH_2Cl_2); IR ν_{max} (thin film, CH_2Cl_2)/cm^{-1} 2930, 3389; NMR δ_H (400 MHz, $CDCl_3$) 1.42−1.54 (2H, m), 1.70−1.77 (2H, m), 2.14−2.20 (1H, m), 3.32−2.43 (2H, m), 2.64−2.71 (3H, m), 2.75−2.82 (1H, m), 3.40−3.46 (1H, m), 3.52−3.63 (2H, m), 3.85 (3H, s), 3.86 (3H, s), 5.89−5.91 (1H, m), 5.94−5.98 (1H, m), 6.58 (1H, s) and 6.76 (1H, s); NMR δ_C (100 MHz, $CDCl_3$) 21.3, 24.0, 25.5, 35.7, 38.0, 44.0, 54.9, 55.8, 56.0, 60.8, 70.6, 109.7, 111.7, 126.6, 131.0, 132.7, 139.9, 147.4, 147.7; MS (FAB) m/z 316 (MH$^+$, 316.1920; $C_{19}H_{25}NO_3$ requires 316.1913).

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra of representative compounds **5**, **7**−**9**, **11**, **13**, and **14**. Crystallographic data for compounds **7**, **9**, and **13**. Experimental procedures for the synthesis of compounds **4** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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