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PREPARATION OF (*R*)-(+)-3-PHENYL-2,3,5,6,7,8-HEXAHYDRO-OXAZOLO[3,2-*a*]PYRIDIN-4-YLIUM BROMIDE: SYNTHESIS OF (*S*)-(+)-CONIINE, (*R*)-(-)-CONICEINE AND (*R*)-(+)-ANABASINE

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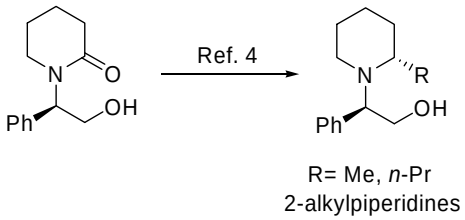
Abstract – We describe the transformation of (*R*)-(-)-1-(2'-hydroxy-1'-phenylethyl)piperidin-2-one **1** into (*R*)-(-)-3-phenyl-2,3,5,6,7,8-hexahydro-oxazolo[3,2-*a*]pyridin-4-ylium bromide **2** using $POBr_3$. Reduction of **2** with Red-Al at -78 ºC gave (3*R*,8*aR*)-(-)-3-phenylhexahydro-2*H*-oxazolo[3,8-*a*]-pyridine **3** as a single diastereoisomer. The synthetic potential of these transformation is illustrated by the enantiopure synthesis of (*S*)-(+)-coniine, (*R*)-(-)-coniceine and (*R*)-(+)-anabasine.

INTRODUCTION

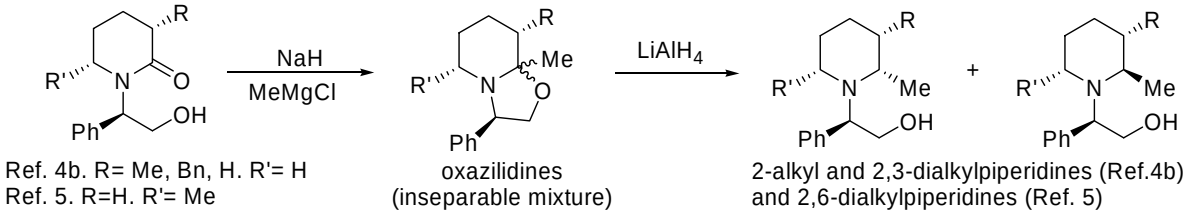
A large number of piperidine-containing compounds, either natural or synthetic, are biologically and medicinally interesting.[1,2] As a consequence, the development of new methods for the enantioselective synthesis of piperidine derivatives by stereoselective introduction of substituents at the carbon positions of the heterocycle constitutes an area of current interest.[3] In this context, (*R*)-(-)-1-(2'-hydroxy-1'-phenylethyl)piperidin-2-one **1** is a versatile synthetic building block which has been used in asymmetric synthesis of 2-alkylsubstituted piperidine derivatives[4] (Scheme 1).



Scheme 1

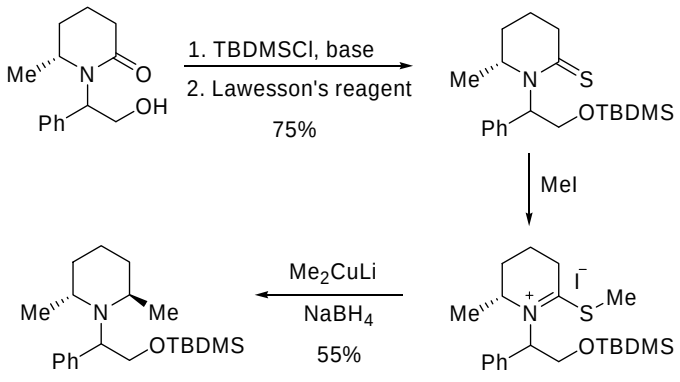
In particular, there are two general methods to carry out the diastereoselective alkylation at C-2 of piperidin-2-ones derived from (*R*)-(-)-2-phenylglycinol.

The first one involve the treatment of the corresponding piperidin-2-one with the corresponding Grignard reagents in presence of sodium hydride.[4,5] In this conditions, a inseparable mixture of oxazolidines is obtained (d.e. 60-85%, yield 44-87%), then reduction of this mixture generates the corresponding alkylated product at C-2 in moderate to good diastereoisomeric excesses (64-84%) and good yields (80-88%). However, the overall yield of this synthesis is low (Scheme 2).



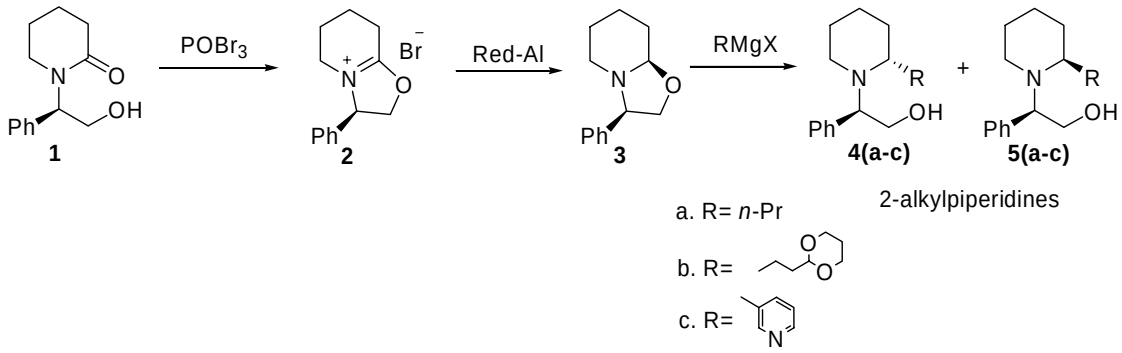
Scheme 2

On the other hand, the second methodology involve the transformation of piperidin-2-ones derived from (*R*)-2-phenylglycinol into thiolactams, which can be alkylated at C-2 easier than corresponding piperidin-2-ones since thiolactams can form with methyl iodide iminium salts which are more reactive towards nucleophiles.[6,7] But the conversion of piperidin-2-ones into thiolactams involve more steps and therefore decrease in overall yield[6] (Scheme 3).



Scheme 3

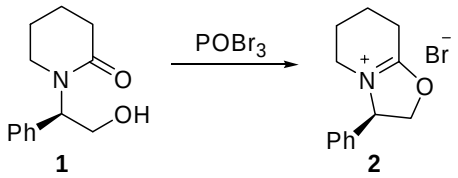
We now describe our findings that piperidin-2-one 1 can be transformed, in one step, to oxazoliminium bromide **2** using $POBr_3$. Then, reduction of iminium moiety of compound **2** using Red-Al® at -78 ºC afforded quantitatively the corresponding oxazolopiperidine **3**. These transformations led us to carry out the diastereoselective alkylation at C-2 of pyridine ring in high overall yield (Scheme 4).



Scheme 4

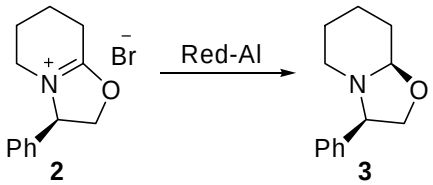
RESULTS AND DISCUSSION

The transformation of piperidin-2-one **1** into oxazoliminium bromide **2** was achieved using 1.2 eq. of phosphorus oxybromide in refluxing chloroform for 75 min. The reaction crude was purified by flash chromatography to give oxazoliminium bromide **2** in quantitative yield (Scheme 5).



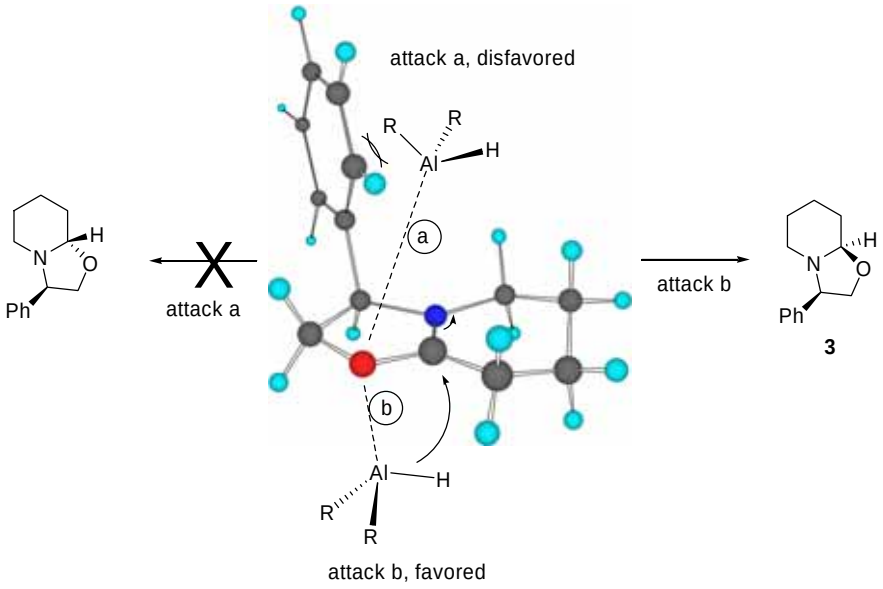
Scheme 5

Initial attempt to reduce **2** with L-Selectride® in THF at 0 ºC[7] resulted in recovered starting material and the desired oxazolopiperidine **3** in only 70% yield. This result was attributed to the poor solubility of compound **2** in THF.[8] However, when the reduction was carried out with Red-Al® in dichloromethane at -78 ºC, the oxazolopiperidine **3** was isolated in quantitative yield as an only diastereoisomer detectable by NMR. Compound **3** is identical to the product described by François *et al*.[9] (Scheme 6).



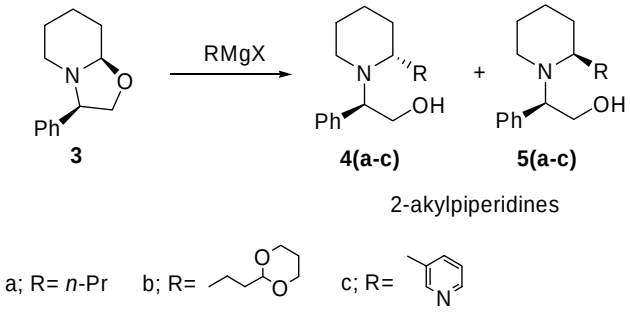
Scheme 6

The excellent diastereoselectivity observed in the reduction of **2** can be explained by coordination of $HAlR_2$ to oxygen of the oxazolidine ring **2** from the less hindered side. Subsequent delivery of hydride from the oxygen-aluminium hydride face provides the observed product[10] (Scheme 7).



Scheme 7

Next we turned our attention to the alkylation of compound **3**, which took place with diverse bulky Grignard reagents to furnish the diastereoisomeric mixture of 2-alkylpiperidines **4+5** in different ratios (Scheme 8: Table 1).



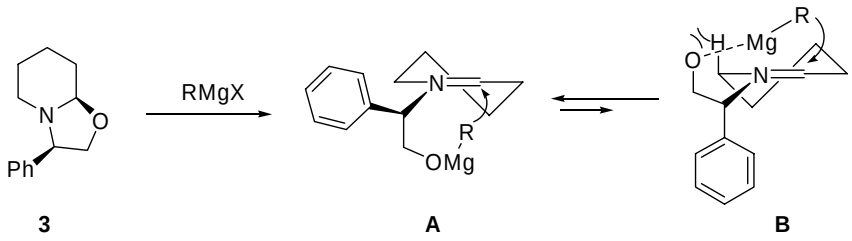
Scheme 8

Table 1. Diastereoisomeric ratio of 2-alkylpiperidines **4+5**.

Entry	R	**4**+**5** ratio	Yield [%]
1	*n*-propyl	65 + 35	90
2	2-[1,3]dioxan-2-yl-ethyl	75 + 25	93
3	3-pyridyl	98 + 2	96

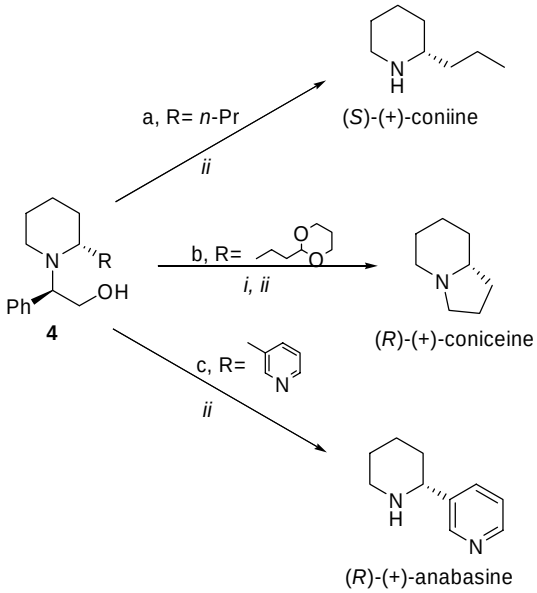
Diastereoisomeric mixture was determined by NMR ^{1}H and ^{13}C from crude reactions.

The diastereoselectivity observed in this process can be explained by axial attack of the Grignard reagent[11] to the iminium intermediate[12] in a half-chair conformation **A** or **B**. In conformation **B** axial hydrogen at C-6 hinders the axial attack of the Grignard reagent, and prefers the less sterically hindered conformation **A** (Scheme 9).



Scheme 9

The above discussion is according with our results. When we realized the alkylation of **3** with bulkier Grignard reagents, the ratio of compounds **4(a-c)** is increased due to a stronger steric hindrance between the attacking Grignard reagent and the axial hydrogen at C-6 demonstrated by the high diastereoselectivity observed in entry 3. Finally, hydrogenolysis of compound **4a** and **4c** furnished (*S*)-(+)-coniine and (*R*)-(+)-anabasine, in 95% and 96% yield, respectively, while compound **4b** was converted to the corresponding aldehyde, which was directly hydrogenated over 10% Pd/C affording (*R*)-(-)-coniceine in 60% yield (Scheme 10).



Scheme 10. *Reagents and conditions*; (*i*) HCl, THF, reflux, 96 h.[10] (*ii*) H_2, 10% Pd/C, MeOH-HCl

CONCLUSION

We have developed a simple and concise procedure for the diastereoselective alkylation at C-2 starting from piperidin-2-one **1**.

Furthermore, a route to oxazolopiperidine **3** has been achieved in higher yield than the synthesis previously reported by other authors.[13]

EXPERIMENTAL

General

^{1}H-NMR spectra were recorded at 400 MHz, and ^{13}C-NMR spectra at 100 MHz (tetramethylsilane as internal reference). IR spectra were obtained with a Nicolet FT-IR Magna 750 spectrometer. Optical rotations were determined at room temperature with a Perkin-Elmer 341 polarimeter, using a 1dm cell with a total volume of 1 mL and are referenced to the D-line of sodium. Mass spectra were recorded with a JEOL JEM-AX505HA instrument at a voltage of 70 eV.

Dehydration of compound 1.

To a solution of **1** (0.150 g, 0.684 mmol) in $CHCl_3$ (5 mL) was added drop wise a solution of $POBr_3$ (0.234 g, 0.820 mmol) in $CHCl_3$ (5 mL). The mixture reaction was refluxed for 1 h. After, the reaction was evaporated under reduced pressure to afford **2** in quantitative yield after purification by flash chromatography (SiO_2, CH_2Cl_2:MeOH= 95:5).

(*R*)-(-)-3-Phenyl-2,3,5,6,7,8-hexahydro-oxazolo[3,2-*a*]pyridin-4-ylium bromide 2.

Yellow solid $[\alpha]_D^{20}$ -11.41 (*c* 1.5, CH_2Cl_2). IR (KBr) 1663 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm, *J* Hz): 1.85-2.23 (m, 4H), 2.90-3.24 (m, 3H), 3.81 (m, 1H), 4.79 (t, *J*=8.8; Hz, 1H), 5.60 (dd, *J*=10.8, 9.2 Hz, 1H), 5.93 (dd, *J*=10.8, 8.8 Hz, 1H), 7.42-7.57 (m, 5H). ^{13}C NMR ($CDCl_3$): 17.90, 20.93, 24.76, 44.81, 66.53, 78.45, 128.35, 129.93, 130.40, 132.96, 176.41. HRMS (FAB): *Anal*. Calcd for $C_{13}H_{16}BrNO$: C, 55.33; H, 5.72; Br, 28.32; N, 4.96; O, 5.67. Found: C, 55.27; H, 5.70; N, 4.91.

Reduction of compound 2.

To a solution of **2** (0.100 g, 0.354 mmol) in anhydrous CH_2Cl_2 (8 mL) under nitrogen atmosphere at -78 ºC was added dropwise Red-Al® (1.016 mmol, 65% in toluene) and stirred for 15 min. Then the mixture reaction was quenched with saturated aqueous NH_4Cl (1.0 mL). After, the reaction was filtered and dried with Na_2SO_4. Finally, the solvent was evaporated under reduced pressure to afford **3** in quantitative yield after purification of flash chromatography (SiO_2, CH_2Cl_2).

(3*R*,8*aR*)-(-)-3-Phenylhexahydro-2*H*-oxazolo[3,8-*a*]pyridine 3.

Colorless oil. $[\alpha]_D^{20}$ -103 (*c* 1.0, $CHCl_3$), lit.,[13] $[\alpha]^{20}_D$-103 (*c* 1, $CHCl_3$). IR (KBr) 1663 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm, *J* Hz): 1.30-1.45 (m, 1H), 1.46-1.59 (m, 3H), 1.85 (m, 1H), 1.99-2.04 (m, 2H), 2.82 (m, 1H), 3.52 (t, *J*=8 Hz, 1H), 3.64-3.71 (m, 2H), 4.16 (t, *J*=7.2 Hz, 1H), 7.25-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$): 22.52, 24.80, 30.38, 47.86, 67.16, 72.98, 94.69, 127.64, 127.78, 128.48, 138.96.

Alkylation of compound 3.

General Procedure. To a stirred solution of **3** (0.150g, 0.738 mmol) in anhydrous THF (10 mL) under nitrogen atmosphere at 0ºC was added dropwise propylmagnesium chloride (2.0 M in THF, 1.107 mmol).

The mixture was stirred for 12 h at 0 ºC. Then, the mixture was quenched with saturated aqueous of NH_4Cl (1 mL), extracted with Et_2O (3 x 20 mL), dried with Na_2SO_4 and concentrated under reduced pressure. Mixture of compounds **4a + 5a** was inseparable at this stage, but benzoylation of the two alcohol mixture with DCC and DMAP in $CHCl_3$ furnished products that were readily purified to a single diastereomer by silica gel chromatography. Removal of benzoyl moiety gave piperidine **4a** in 60% yield.

(2*R*,2'*S*)-(-)-2-Phenyl-2-(2'-propylpiperidin-1'-yl)ethanol 4a.
Colorless oil. $[\alpha]_D^{20}$ -31.45 (*c* 1.1, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm, *J* Hz): 0.86 (t, *J*=7.2 Hz, 3H), 1.16-1.24 (m, 3H), 1.40-1.55 (m-6H), 1.64 (m, 1H), 2.54 (m, 1H), 2.61 (m, 1H), 2.89 (m, 1H), 3.64-3.77 (m, 2H), 3.84 (t, *J*=6.2 Hz, 1H), 7.25-7.36 (m, 5H). ^{13}C NMR ($CDCl_3$): 14.33, 19.63, 20.31, 25.69, 28.09, 28.42, 43.10, 57.29, 61.98, 67.37, 127.47, 128.33, 128.66, 136.43. HRMS (FAB): *Anal*. Calcd for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66; O, 6.47. Found: C, 77.63; H, 10.11; N, 5.62.

The mixture **4b + 5b** was achieved by alkylation of **3** with commercially available (1,3-dioxan-2-ylethyl)magnesium bromide (0.5 M in THF). Purification of this mixture by flash chromatography (Si_2O_2, CH_2Cl_2:Petroleum ether = 50:50, CH_2Cl_2: petroleum ether= 70:30) gave **4b** in 66% yield.
(2*R*,2'*S*)-(+)-2-[2'-(2-[1,3]Dioxan-2-yl-ethyl)piperidin-1-yl]-2-phenylethanol 4b.
Colorless oil. $[\alpha]_D^{20}$ -30.55 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm, *J* Hz):1.29-1.35 (m, 1H), 1.46-1.62 (m, 10H), 1.98-2.14 (m, 1H), 2.48-2.62 (m, 2H), 2.89 (m, 1H), 3.68-3.77 (m, 4H), 3.85 (t, *J*=5.85 Hz, 1H), 4.07 (dd, *J*=5.1, 1.2 Hz, 1H), 7.25-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$): 19.61, 20.49, 25.27, 25.79, 27.64, 30.30, 32.51, 43.01, 56.57, 62.23, 66.85, 102.31, 127.38, 128.33, 128.64, 140.81. HRMS (FAB): *Anal*. Calcd for $C_{19}H_{29}NO_3$: C, 71.44; H, 9.15; N, 4.38; O, 15.03. Found: C, 71.39; H, 9.11; N, 4.33.

Alkylation of compound 3 with pyridine-3-magnesium bromide. To a stirred solution of 3-bromopyridine (0.171g, 1.086 mmol) in anhydrous THF (10 mL) at rt was added isopropylmagnesium chloride (2.0M in THF, 1.086 mmol). After 1 h compound **3** (0.36 mmol) was added in anhydrous THF (5 mL) at 0 ºC. The mixture was stirred for 18 h and quenched with a saturated aqueous of NH_4Cl (2 mL), extracted with Et_2O (3 x 20 mL), dried with Na_2SO_4 and concentrated under reduced pressure. Purification of this mixture by flash chromatography (Si_2O_2, CH_2Cl_2: petroleum ether 50:50, CH_2Cl_2:Petroleum ether 70:30) gave **4c** in 90% yield.
(2*R*,2'*R*)-(-)-2-Phenyl-2-[2'-(pyridin-3-yl)piperidin-1-yl]ethanol 4c. Colorless oil. $[\alpha]_D^{20}$ -22.2 (*c* 1.0, $CHCl_3$), lit.,[14] $[\alpha]^{20}_D$-22.7 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm, *J* Hz): 1.40-1.85 (m, 6H), 2.56 (td, *J*=11.4, 2.7 Hz, 1H), 2.92 (m, 1H), 3.78 (t, *J*=6.9 Hz, 1H), 3.89 (dd, *J*=10.2, 2.7 Hz, 1H), 4.05 (t,

J=6 Hz, 1H), 4.11 (t, *J*=6 Hz, 1H), 7.19-7.35 (m, 5H), 7.42 (dt, *J*=8.1, 1.8 Hz, 1H), 7.75 (dt, *J*=7.8, 1.8 Hz, 1H), 8.40 (dd, *J*=4.5, 1.8 Hz, 1H), 8.56 (d, *J*=1.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): 24.78, 26.15, 36.87, 47.31, 60.05, 62.89, 63.08, 123.62, 126.85, 127.93, 128.20, 135.24, 139.91, 140.35, 148.37, 149.40. HRMS (FAB): *Anal*. Calcd for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92; O, 5.67. Found: C, 76.51; H, 7.82; N, 9.89.

Catalytic hydrogenation of compound 4a.

General Procedure. To a solution of **4a HCl** (0.050 g, 0.202 mmol) in MeOH (5 mL) under hydrogen atmosphere was added 10% Pd/C, (0.015 g) and the mixture reaction was stirred for 96 h at rt. After, the reaction was filtered and the solvent was evaporated under reduced pressure to afford (*S*)-(+)-coniine hydrochloride salt in 95% yield.

(*S*)-(+)-Coniine Hydrochloride.

Yellow solid. Mp 185-186ºC. $[\alpha]_D^{20}$ +9.50 (*c* 0.5, EtOH); lit.,[10] $[\alpha]_D^{20}$ +9.37 (*c* 0.32, EtOH). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm, *J* Hz): 0.91 (t, *J*=6.7 Hz, 3H), 1.24-1.54 (m, 5H), 1.53-2.10 (m-7H), 2.72-2.99 (m, 2H), 3.36-3.49 (m, 1H), 9.22 (br, 1H), 9.52 (br, 1H). ^{13}C NMR ($CDCl_3$): 13.78, 18.61, 22.22, 22.46, 28.16, 35.39, 44.79, 57.18.

(*R*)-(+)-Anabasine.

Following the above procedure, and finally the mixture reaction was washing with a solution of NaOH and extracted with Et_2O (3x20 mL) we achieved pure (*R*)-(+)-anabasine in 96 % yield from piperidine **4c** (0.070g, 0.247 mmol).

Transparent Oil. $[\alpha]_D^{20}$ +79.56 (*c* 0.9, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm, *J* Hz): 1.50-2.0 (m, 6H), 2.80 (td, *J*=11.4, 3.0 Hz, 1H), 3.20 (dm, *J*=11.4 Hz, 1H), 3.64 (dd, *J*= 10.2, 2.7 Hz, 1H) 7.24 (dd, *J*=7.8, 4.8 Hz, 1H), 7.72 (dt, *J*=7.8, 1.5 Hz, 1H), 8.48 (dd, *J*=4.8, 1.5 Hz, 1H), 8.56 (d, *J*=1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$): 25.23, 25.71, 34.65, 47.59, 59.78, 123.41, 134.11, 140.37, 148.49, 148.56.

Hydrolysis of compound 4b.

A solution of **4b** (0.25 g, 0.783 mmol) in THF (20 mL) was treated with a solution of HCl (5 mL, 15 %) and refluxed for 96 h. The solvent was removed under reduced pressure to give the corresponding aldehyde, which was directly hydrogenated following the procedure described above. After, the mixture reaction was washing with a solution of NaOH and extracted with Et_2O (3x20 mL) giving the pure (*R*)-(+)-coniceine in 60% yield from piperidine **4b**.

Finally, the alkaloid was dissolved in EtOH and treated with excess of picric acid. (*R*)-(+)-coniceine was characterized as its picrate.

(*R*)-(-)-Coniceine.

Yellow solid. Mp 228-230ºC. (lit.,[10]: 227-228ºC). $[\alpha]_D^{20}$ -2.10 (*c* 0.5, EtOH); lit.,[10] $[\alpha]_D^{20}$ -2.0 (*c* 0.35, EtOH). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm, *J* Hz): 1.40-2.31 (m, 10H), 2.64-2.91 (m, 2H), 3.11-3.92 (m, 3H), 8.85 (s, 2H), 10.12 (s, 1H), 10.77 (s, 1H). ^{13}C NMR ($CDCl_3$): 19.23, 22.34, 22.60, 26.76, 26.87, 27.54, 52.80, 53.01, 67.91, 126.11, 141.23, 161.81.

ACKNOWLEDGEMENTS

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