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Total synthesis of gabosines via an iron-catalyzed intramolecular tandem aldol process

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ABSTRACT

Several gabosines, belonging to polyhydroxy-cyclohexenone and cyclohexanone class of natural products, are synthesized in various stereoforms using an intramolecular iron-catalyzed tandem aldol process. The reaction, which starts from vinylic pyranoses, is compatible with two different OH protecting groups (acetyl and benzyl). Further, like the Ferrier carbocyclisation, it is not sensitive to the stereochemistry of sugar molecules used as precursors: six different gabosine-type molecules have been prepared by this route starting from D-Glucose, D-Mannose, and D-Galactose derivatives.

1. Introduction

The synthesis of polyhydroxycyclohexane derivatives from natural sugars, popularly called 'carbohydrates to carbocycles' is a powerful tool in natural product synthesis. These carbocycles, especially in the cyclohexane form, have attracted wider attention owing to their broad range of biological activities. The hexose sugars have been the natural choice for construction of this type of molecules. Excellent reviews have appeared in the literature describing the methods of synthesis of carbasugars and their applications.[1]

Gabosines belong to this set of natural products and over 14 gabosines have been isolated to date from *Streptomyces* strains. The first of this class, gabosine C, was isolated way back in 1974,[2] and some members (gabosines L, N, and O) very recently.[3] These secondary metabolites have been shown to display some interesting antibiotic, anticancer, and weak DNA binding properties (Fig. 1).

Several groups have reported elegant syntheses of various gabosines. Most of these syntheses have used the carbohydrates as chiral pool, as expected for the preparation of this class of molecules. They employ different methodologies for building the target molecules: intramolecular Nozaki–Kishi reaction,[4] aldol-type condensations,[5] Horner–Wadsworth–Emmons reactions,[6] ring-closing metathesis,[7] intramolecular cycloadditions,[8] and Ferrier carbocyclisation,[9] *inter alia*. Other chiral pool approaches involved quinic acid[10] or [(*p*-tolylsulfinyl)methyl]-*p*-quinols[11] as starting materials. The other strategies include the utilisation of norbornene,[12] asymmetric Diels–Alder reactions,[13] masked *p*-benzoquinones,[14] chemoenzymatic approaches,[15] *inter alia*…

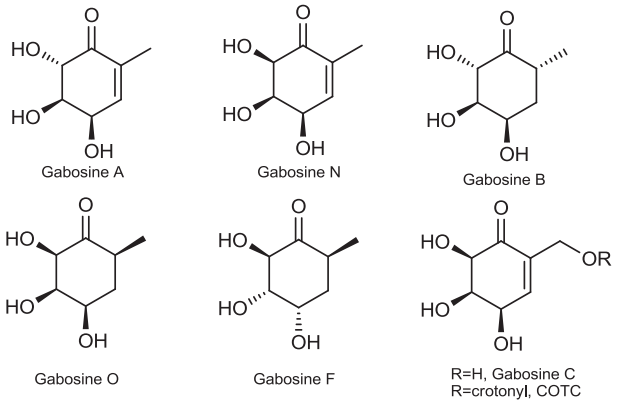

Fig. 1. Selected members from the gabosine family.

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Recently we have demonstrated first potentialities of a transition metal-mediated tandem isomerization–aldolisation reaction.[16] In an intramolecular fashion and starting from vinyl lactols, it allows efficient construction of cyclopentanoids and cyclohexenones.[17] The precursors for this process are either the vinyl furanoses or vinyl pyranoses, respectively. The utility of this procedure was also demonstrated by us in the synthesis of 4-epigabosine A and the dihydro-analogue 4-epigabosine B starting from D-Glucose.[18]

Herein, in this full article, we wish to report the consolidated results pertaining to this intramolecular aldolisation process starting from three different sugars namely D-Glucose, D-Mannose, and D-Galactose. The vinyl lactols derived from these sugars have been converted to six different derivatives: gabosine A, 4-epigabosine N, 4-epigabosine A, 6-epigabosine O, as well as 4-epigabosine B and 4-*epi*-6-epigabosine B.

The strategy we have adapted is shown in Fig. 2: from the vinylic pyranose **A**, by using the tandem isomerization–aldolisation reaction with $Fe(CO)_5$ as catalyst, we can get directly the cyclohexanols **B**, which give the cyclohexenones **C** by simple dehydratation. In order to obtain **D**- and **E**-type cyclohexanone members, deprotection and hydrogenation steps have to be employed. Clearly in this strategy, the role of the R protecting group should be considered.

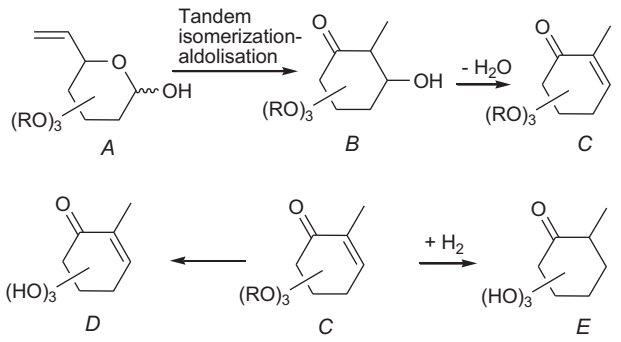
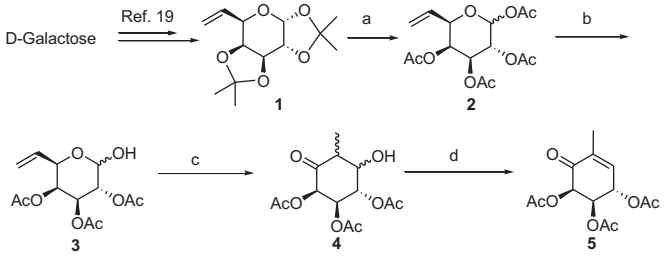


Fig. 2. Strategy for the synthesis of selected members of the gabosine family.

2. Results and discussion

Based on the strategy shown in Fig. 2, the initial objective was to synthesize vinyl pyranoses with different protective and stereomeric hydroxyl groups. In this endeavor, we prepared the vinyl pyranoses of D-Glucose, D-Mannose, and D-Galactose with acetate and benzyl as protecting groups for application in the tandem isomerization–aldolisation process.

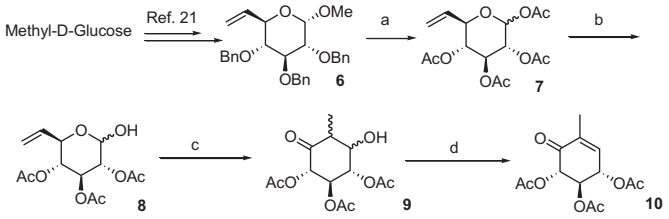
From D-Galactose, the vinyl pyranose **1** was synthetized as described in literature.[19] The conversion of protecting groups gave tetraacetate **2**,[20] which was deprotected selectively by hydrazine acetate to afford the vinylic lactol **3** with a fair yield (Scheme 1).



Scheme 1. Synthesis of cyclohexenone **5**. Reagents and conditions: (a) AcOH 70% then Ac_2O, Py, DMAP, 91% for two steps, (b) Hydrazine acetate, DMF, 50 °C, 66%, (c) $Fe(CO)_5$, *hν*, THF, (d) MsCl, Et_3N, CH_2Cl_2, 32% from **3**.

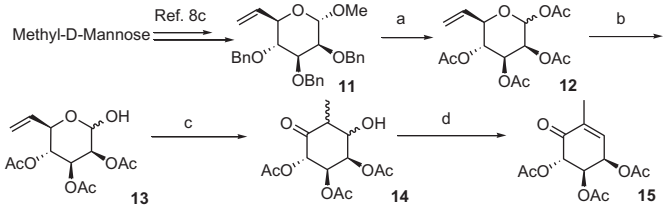
With this lactol in hand, we performed the isomerization–aldolisation process using $Fe(CO)_5$ as catalyst and under irradiation. The aldol product **4** (as a stereoisomeric mixture) was immediately used in a dehydration reaction to give 4-epigabosine N, under acetate protected form **5**, in moderate yield.

Using protocol developed as above, from methyl α-D-glucopyranoside, intermediate **6** was prepared easily as described in literature.[21] After two steps of transprotection of benzyl groups by acetates by the method of Stubbs,[22] then deprotection selectively in anomeric position,[23] the lactol **8** was ready for tandem aldol process (Scheme 2). The conversion of this vinyl pyranose to cyclohexanols, followed by the dehydratation with $MsCl/Et_3N$ gave the desired product **10** in moderate yield.



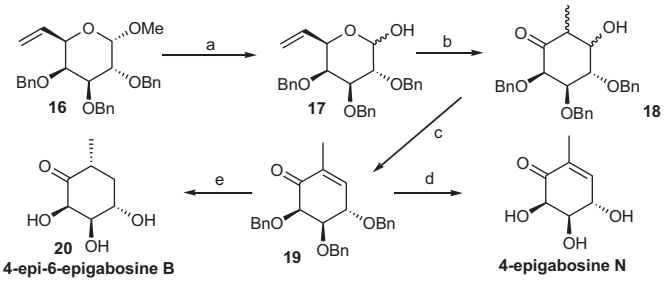
Scheme 2. Synthesis of cyclohexenone **10**. Reagents and conditions: (a) Ac_2O, TMSOTf, 56%, (b) Hydrazine acetate, DMF, 50 °C, 76%, (c) $Fe(CO)_5$, *hν*, THF, (d) MsCl, Et_3N, CH_2Cl_2, 35% from **8**.

Scheme 3 summarizes the synthetic steps from α-D-mannopyranoside to the tri-acetate protected gabosine A **15**. The synthesis of compound **11** was achieved from commercially available methyl-α-D-Mannose as reported in literature.[8c] The benzyl group and anomeric methyl ether functionality were converted to tetracetate **12** by using Ac_2O/TMSOTf. The precursor for tandem reaction, **13**, was obtained by selective hydrolysis and anomeric acetoxy group deprotection by hydrazine hydrate. Once again, this tandem process allowed us to prepare the cyclohexenone **15**, via intermediates **14**. These three targets (**5**, **10**, and **15**) were characterized from extensive NMR studies.



Scheme 3. Synthesis of cyclohexenone **15**. Reagents and conditions: (a) Ac_2O/TMSOTf, 59%, (b) Hydrazine acetate, DMF, 50 °C, 68%, (c) $Fe(CO)_5$, *hν*, THF, (d) MsCl, Et_3N, CH_2Cl_2, 40% from **13**.

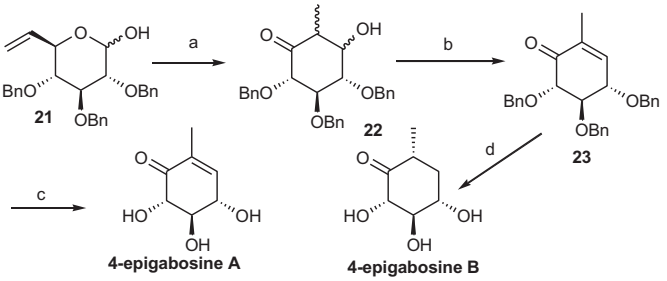
By performing this tandem process with three sugar derivatives, we have demonstrated the capacities of this reaction on the different substrates. However, the yields in the tandem aldol process were only moderate. Therefore it was of interest to check the possibility of using another, more robust, protective group. Toward this goal, benzyl protection appeared the best choice and the reactions were performed starting from similar vinyl lactols but with benzyl protected alcohols. This strategy allowed us to prepare 4-epigabosine N and 4-6-diepigabosine B starting from D-Galactose (Scheme 4). The lactol **17** was obtained from vinyl pyranose **16** by demethylation using a 70% AcOH solution, in good yield. The substrate **17**, now ready for the tandem isomerization–aldolisation, was subjected to catalytic reaction by using $Fe(CO)_5$ at 10 mol % to provide the cyclohexanol derivative **18** in almost quantitative yield and as a diastereomeric mixture. This crude mixture was exposed to MsCl and triethylamine to realize the cyclohexanone **19** in 54% overall yield for two steps.



Scheme 4. Synthesis of 4-*epi* 6-epigabosine B and 4-epigabosine N. Reagents and conditions: (a) AcOH 70%, H_2SO_4 cat. 75%, (b) (i) $Fe(CO)_5$ 10%, THF, *hν*, (c) TMsCl, Et_3N, CH_2Cl_2, 54% for two steps, (d) $FeCl_3$, CH_2Cl_2, 0 °C, 15 min 50%, (e): Pd/C, EtOH, 3 days, 80%.

The debenzylation was achieved by using $FeCl_3$ in CH_2Cl_2,[24] to furnish the 4-epigabosine N in 55% yield. The isolated compound had spectroscopical data fully matching with literature.[14a] On the other hand by using Pd/C in ethanol, a completely stereoselective hydrogenation of **19** occurs together with tri-debenzylation, affording the diastereoisomer **20** of gabosine B, in a one-pot 80% yield reaction. The stereochemistry of this compound was unambiguously established by extensive NMR experiments. Particularly relevant for the axial position of the C*H*Me proton were the two J_3 coupling constants (13.3 and 6.0 Hz) with the vicinal CH_2 protons.

The 4-epigabosine A and 4-epigabosine B were similarly synthesized from D-Glucose as depicted in Scheme 5. The intermediate **6** was converted to vinyl lactol pyranose **21** by using a known protocol.[21] This compound, under the usual conditions, underwent the tandem isomerization–aldolisation, followed by the dehydration to give a benzyl protected gabosine derivative **23**.

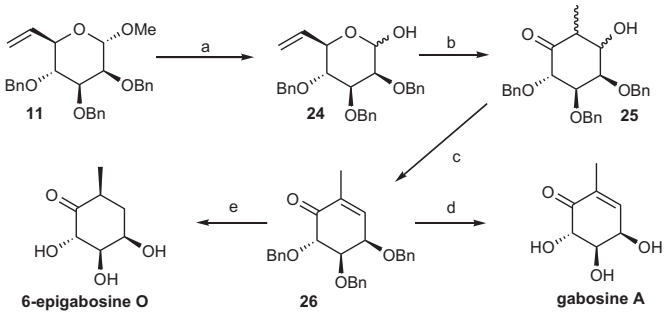


Scheme 5. Synthesis of 4-epigabosine A and 4-epigabosine B. Reagents and conditions: (a) $Fe(CO)_5$ 10%, THF, *hν*, (b) TMSCl, Et_3N, CH_2Cl_2, 65% for two steps (c) $FeCl_3$, CH_2Cl_2, 55%, (d): Pd/C, EtOH, 3 days, 90%.

The deprotection of benzyl group by $FeCl_3$ gave the 4-epigabosine A in 55% yield. This compound had spectral data in good agreement with the literature.[11] Hydrogenation, followed by complete debenzylation, afforded the 4-epigabosine B in 90% yield.

To complete the research on this reaction a third sugar, namely the methyl mannoside **11**, was converted to the vinyl pyranoside **24**, followed by catalytic aldolisation yielding **26**. A simple debenzylation furnished in 50% yield gabosine A whose spectral data and optical rotation were in good agreement with literature.[7b,9,15] On the other hand, hydrogenation of double bond and deprotection of all benzyl groups by using methanol as solvent finally gave 6-epigabosine O in moderate yield. The structure of this compound was also confirmed by extensive NMR studies. Particularly relevant for the axial position of the C*H*Me proton were the two J_3 coupling constants (12.8 and 6.1 Hz) with the vicinal CH_2 protons (Scheme 6).

It is worthy of note that hydrogenation of the double bond in **26**, like for **18** and **23**, occurred exclusively from the face *anti* to allylic OBn groups.



Scheme 6. Synthesis of gabosine A and 6-epigabosine O. Reagents and conditions: (a) AcOH 70%, H_2SO_4 cat, 65%, (b) $Fe(CO)_5$ 10%, THF, *hν*, (c) TMSCl, Et_3N, CH_2Cl_2, 75% for two steps, (d) $FeCl_3$, CH_2Cl_2. 50%, (e): Pd/C, MeOH, 3 days, 60%.

3. Conclusion

In conclusion, we have demonstrated that the intramolecular tandem isomerization–aldolisation reaction starting from vinyl pyranoses allows a short synthesis of natural product gabosine A as well as 4-epigabosine A, 4-epigabosine B, 4-epigabosine N, 6-epigabosine O, and 4-*epi*-6-epigabosine B. This process is not sensitive to the stereochemistry of the starting sugar molecule and further was developed with two different protective groups for the alcohol functions. However, for these syntheses the benzyl group proved to be more appropriate.

4. Experimental section

4.1. General information

All reactions were carried out under argon or nitrogen atmosphere. TLC spots were examined under UV light and revealed by sulfuric acid–anisaldehyde, $KMnO_4$ solution or phosphomolybdic acid. Dichloromethane was distilled from calcium hydride, tetrahydrofuran and diethylether were distilled from sodium/benzophenone, methanol was distilled over magnesium. NMR spectra were obtained at 300 MHz or 500 MHz for ^1H and 75 MHz or 125 MHz for ^{13}C with BRUCKER AVANCE 300 or 500 spectrometers. Chemical shifts are given in parts per million (δ) relative to chloroform (7.26 ppm) or benzene (7.16) residual peaks. Assignments of ^1H and ^{13}C resonances for complex structures were confirmed by extensive 2D experiments (COSY, HMQC, and HMBC). Mass spectral analyses have been performed at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO) in Rennes (France). *Caution*: all reactions involving $Fe(CO)_5$ have to be carried out under a well ventilated hood. These iron carbonyl-mediated reactions have been performed in usual Pyrex glassware equipment.

4.2. Synthesis

*4.2.1. General procedure A for the tandem aldolisation reaction, followed by dehydration. Representative example: preparation of cyclohexenone **23**.* A solution of vinylic lactol **21** (890 mg, 2 mmol) and $Fe(CO)_5$ (26 μl, 10% mol) in anhydrous THF (20 mL) was irradiated with a Philips HPK125 W during 1 h. After being cooled to room temperature and concentrated, the residue was diluted in ether, filtered on a short pad of silica gel, and concentrated under vacuum to afford aldol products as a mixture of diastereoisomers: (45/50/5 by ^1H NMR). This mixture was purified by column chromatography on silica gel with pentane/AcOEt: 7/3 as eluent to afford **22** (845 mg, 95%). To an ice-cold solution of previous aldol products **22** (700 mg, 1.57 mmol) and Et_3N (1.1 mL, 5 equiv) in anhydrous CH_2Cl_2 (15 mL), was added MsCl (303 μl, 2.5 equiv) at 0 °C. After being stirred at room temperature during 24 h, the mixture was diluted with CH_2Cl_2 and H_2O. The organic phase was separated

and the aqueous phase was extracted with CH_2Cl_2 (3×20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under vacuum to afford a residue, which was purified by chromatography on silica gel with pentane/AcOEt (90/10; R_f: 0.3) as eluent to afford cyclohexenone **23** as a white solid 464 mg (69% yield), mp: 64–66 °C.

4.2.2. General procedure B for the debenzylation. Representative example: synthesis of 4-epigabosine N. To a solution of cyclohexenone **19** (80 mg, 0.18 mmol) in anhydrous CH_2Cl_2 was added under argon at 0 °C anhydrous $FeCl_3$ (86 mg, 3 equiv). After 15 min, reaction was complete, as indicated by TLC analysis, and the reaction mixture was quenched with H_2O (5 mL). It was stirred for 1 min and then extracted with AcOEt (3×30 mL). The organic layers were dried over Na_2SO_4, filtered, and the solvents were removed under reduced pressure. This crude reaction mixture was purified by flash silica gel column chromatography (AcOEt as eluent) to afford 4-*epi*-Gabosine N as a colorless viscous oil: 14 mg (50% yield).

4.2.3. General procedure C for the hydrogenation. Representative example: synthesis of 4-epi-6-epigabosine N. To a solution of **19** (30 mg, 0.07 mmol) in absolute ethanol (2.5 mL) was added palladium on activated carbon (5 mg). The flask was flushed with hydrogen three times. When analytical TLC showed the disappearance of starting material, the reaction mixture was filtered through a pad of silica gel. The filtrate was concentrated under vacuum to afford desired 4-*epi*-6-*epi*-gabosine N: 9 mg (80% yield).

*4.2.4. 1,2,3,4-Tetra-O-acetyl-6,7-dideoxy-D-galacto-hept-6-enopyranose **2**.* A solution of **1** (1.8 g, 7 mmol) in 70% acetic acid (42 mL) was reflux at 80 °C for 7 h. The solvent was co-evaporated with toluene under reduced pressure to give crude product as viscous oil. This crude product was then dissolved in anhydrous pyridine (30 mL). To this solution, DMAP (50 mg) and acetic anhydride (20 mL) were added successively at 0 °C under nitrogen, then the mixture was kept under stirring for 24 h at room temperature. After addition of water, the aqueous phase was extracted with CH_2Cl_2 (3×50 mL) and the combined organic phases were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford compound **2** as a colorless oil: 2.2 g (yield: 91% for two steps) (it was obtained as a mixture of two isomers in a 75/25 ratio by ^1H NMR) (eluent pentane/ether: 6/4; R_f: 0.3); ^1H NMR (300 MHz, $CDCl_3$): δ=2.00 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 2.05 (s, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 2.14 (s, 3H), 2.15 (s, 3H), 2.16 (s, 3H), 4.32 (dd, *J*=1.2, 5.1 Hz, 1H), 4.65 (dd, *J*=1.2, 5.1 Hz, 1H), 5.10 (d, *J*=3.5 Hz, 1H), 5.15 (d, *J*=3.4 Hz, 1H), 5.24–5.48 (m, 4H), 5.67 (ddd, *J*=5.0, 10.6, 15.6 Hz, 1H), 5.73 (s, 1H), 5.76 (s, 1H), 6.44 (d, *J*=2.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.5, 20.58, 20.62, 20.8, 66.5, 67.6, 67.9, 69.2, 69.8, 71.0, 71.7, 74.6, 89.8, 92.1, 118.4, 118.9, 131.1, 131.6, 169.0, 169.3, 169.9, 170.2.

*4.2.5. 2,3,4-Tri-O-acetyl-6,7-dideoxy-D-galacto-hept-6-enopyranose **3**.* To a solution of **2** (600 mg, 1.74 mmol) in anhydrous DMF (20 mL) was added under nitrogen at 50 °C hydrazine acetate (204 mg) in one portion. The reaction mixture was stirred at this temperature for another 30 min. When TLC indicates complete consumption of starting material, the mixture was diluted with ethyl acetate (30 mL). The organic phase was washed with H_2O (3×30 mL) and brine (20 mL). The organic phase was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford compound **3** as a colorless viscous oil (347 mg, 66%) (eluent pentane/ether: 7/3; R_f=0.2); ^1H NMR (300 MHz, $CDCl_3$): δ=1.98 (s, 3H), 1.99 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.10 (s, 3H), 2.16 (s, 3H), 3.46 (br s, OH), 3.82 (br s, OH), 4.22 (dd, *J*=1.4, 5.0 Hz, 1H), 4.71 (br s, 1H), 4.76 (d, *J*=5.3 Hz, 1H), 5.09 (d, *J*=5.2 Hz, 1H), 5.18 (dd, *J*=1.6, 3.6 Hz, 1H), 5.22 (dd, *J*=1.3, 10.7 Hz, 1H), 5.25 (dd, *J*=1.4, 10.7 Hz, 1H), 5.34 (dd, *J*=1.4, 17.3 Hz, 1H), 5.35 (dd, *J*=1.3, 17.3 Hz, 1H), 5.40 (br s, 1H), 5.54 (br s, 1H), 5.7 (ddd, *J*=5.9, 10.8, 17.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.56, 20.58, 20.7, 20.8, 67.4, 68.3, 69.1, 70.4, 70.6, 71.0, 73.9, 90.6, 95.8, 118.1, 118.5, 131.7, 132.4, 170.1, 170.4, 170.5, 171.2; HRMS *m/z* calculated for $[M+Na]^+$ ($C_{13}H_{18}O_8Na$): 325.0899, found 325.0890.

*4.2.6. (4S,5R,6R)-4,5,6-Tris(acetoxy)-2-methylcyclohex-2-enone **5**.* The reaction was realized following the general procedure A with: lactol **3** (300 mg, 1 mmol), $Fe(CO)_5$ (26 μl, 20% mol) to give cyclohexenone **5** as a viscous oil (90 mg: 32% for two steps) (pentane/AcOEt: 9/1; R_f: 0.3); ^1H NMR (300 MHz, $CDCl_3$): δ=1.86 (s, 3H), 2.03 (s, 3H), 2.10 (s, 3H), 2.14 (s, 3H), 5.69 (m, 1H), 5.48 (m, 1H), 5.79 (d, *J*=3.0 Hz, 1H), 6.54 (dq, *J*=1.4, 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=15.6, 20.5, 20.69, 20.72, 66.9, 71.4, 135.1, 138.5, 139.4, 169.5, 169.8, 190.8; HRMS *m/z* calculated for $[M+Na]^+$ ($C_{13}H_{16}O_7Na$): 307.2517, found 307.2520; $[\alpha]_D^{20}$ +158.7 (*c* 0.6, MeOH).

*4.2.7. 1,2,3,4-Tetra-O-acetyl-6,7-dideoxy-D-gluco-hept-6-enopyranose **7**.* To a solution of the vinyl glucopyranose **6** (3.4 g, 7.9 mmol) in acetic anhydride (20 mL), was added dropwise with vigorous stirring under nitrogen at room temperature trimethylsilyl trifluoromethanesulfonate (0.452 mL, 2.35 mmol). The reaction mixture was stirred for an additional 10 h. After cooling to 0 °C, the dark solution was diluted with AcOEt (50 mL) and poured in a cold saturated $NaHCO_3$ solution (50 mL). The organic phase was separated and washed with a saturated $NaHCO_3$ solution (3×50 mL), brine (100 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford compound **7** as a yellowish liquid (1.52 g, 56%) (hexane/ethyl acetate, 9/1 R_f: 0.7); ^1H NMR (300 MHz, $CDCl_3$) δ=1.94 (s, 6H), 1.96 (s, 3H), 2.11 (s, 3H), 4.20 (dd, *J*=7.2, 9.9 Hz, 1H), 4.88 (dd, *J*=9.8 Hz, 1H), 5.03 (dd, *J*=3.7, 10.3 Hz, 1H), 5.20–5.45 (m, 4H), 5.68 (d, *J*=6.2 Hz, 1H), 5.69 (ddd, *J*=4.9, 10.4, 17.3 Hz, 1H), 6.2 (d, *J*=3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=20.6, 20.7, 20.8, 68.2, 68.4, 68.4, 74.1, 90.4, 120.1, 132.8, 168.1, 169.5, 169.7, 169.9.

*4.2.8. 1-Hydroxy-2,3,4-tetra-O-acetyl-6,7-dideoxy-D-gluco-hept-6-enopyranose **8**.* To a solution of **7** (1.2 g, 3.485 mmol) in anhydrous DMF (20 mL) was added under nitrogen at 50 °C, hydrazine acetate (204 mg). The reaction mixture was stirred at this temperature for another 30 min. When the TLC analysis indicates the complete consumption of starting material, the mixture was diluted with ethyl acetate (30 mL). The organic phases were washed with H_2O (3×30 mL) and brine (20 mL). The organic phases were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford compound **8** as colorless viscous oil (800 mg, 76%) (eluent pentane/ether: 7/3; R_f: 0.2); ^1H NMR (300 MHz, $CDCl_3$) δ=2.00 (s, 3H), 2.02 (s, 3H), 2.04 (s, 3H), 2.86 (d, *J*=3.3 Hz, 1H), 4.46 (dd, *J*=7.5, 9.9 Hz, 1H), 4.48–4.94 (m, 2H), 5.20–5.33 (m, 2H), 5.47 (t, *J*=3.3 Hz, 1H), 5.58 (t, *J*=9.8 Hz, 1H), 5.69–5.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=20.7, 69.5, 70.6, 71.6, 90.1, 95.4, 119.9, 120.0, 120.8, 124.1, 132.6, 133.3, 169.6, 170.1, 178.1; HRMS *m/z* calculated for $[M+Na]^+$ ($C_{13}H_{18}O_8Na$): 325.0899, found 325.0890.

*4.2.9. (4S,5R,6S)-4,5,6-Tris (acetoxy)-2-methylcyclohex-2-enone **10**.* The reaction was realized following the general procedure A with: lactol **8** (500 mg, 1.66 mmol), $Fe(CO)_5$ (44 μl, 20 mol %) to give in two steps cyclohexenone **10** as a viscous oil (165 mg: 35% for two steps) (pentane/AcOEt: 9/1; R_f: 0.3); ^1H NMR (300 MHz, $CDCl_3$)

δ=1.80 (s, 3H), 2.0 (s, 3H), 2.04 (s, 3H), 2.10 (s, 3H), 5.34 (d, J=11.5 Hz, 1H), 5.50 (dd, J=8.4, 11.5 Hz, 1H), 5.70 (ddd, J=2.2, 8.5, 12.9 Hz, 1H), 6.44 (d, J=1.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=15.2, 20.4, 20.6, 20.7, 70.5, 71.9, 74.3, 136.3, 140.3, 169.8, 170.11, 190.3, 191.6; HRMS *m/z* calculated for $[M+Na]^+$ ($C_{13}H_{16}O_7Na$): 307.2517, found 307.2520; $[\alpha]_D^{20}$ −18.7 (*c* 0.2, MeOH).

4.2.10. 1,2,3,4-Tetra-O-acetyl-6,7-dideoxy-D-manno-hept-6-enopyranose ***12***. To a solution of vinyl glucopyranose **11** (1.5 g, 3.4 mmol) in acetic anhydride (20 mL), was added dropwise with vigorous stirring under nitrogen at room temperature trimethylsilyl trifluoromethanesulfonate (0.253 mL, 1.395 mmol). The solution was stirred for an additional 10 h. After cooling to 0 °C, the dark solution was diluted with AcOEt (50 mL) and poured in a cold saturated $NaHCO_3$ solution (50 mL). The organic phases were separated and washed with a saturated $NaHCO_3$ solution (3×50 mL), brine (100 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford compound **12** as a yellowish liquid (700 mg, 59%) (hexane/ethyl acetate, 9/1, R_f: 0.7); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.99 (s, 3H), 2.15 (s, 3H), 2.16 (s, 3H), 4.21 (dd, J=1.1, 9.2 Hz, 1H), 5.20 (t, J=9.9 Hz, 1H), 5.26 (dd, J=7.4, 10.9 Hz, 2H), 5.32 (t, J=3.5 Hz, 1H), 5.37 (d, J=3.2 Hz, 1H), 5.71–5.82 (m, 1H), 6.07 (d, J=1.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=20.6, 20.7, 20.8, 68.2, 68.4, 68.4, 74.1, 90.4, 120.1, 132.8, 168.1, 169.5, 169.7, 169.9.

4.2.11. 1-Hydroxy-2,3,4-tetra-O-acetyl-6,7-dideoxy-D-manno-hept-6-enopyranose ***13***. To a solution of **12** (500 mg, 1.45 mmol) in anhydrous DMF (20 mL) was added under nitrogen at 50 °C hydrazine acetate (170 mg, 1.88 mmol) in one portion. The reaction mixture was stirred at this temperature for another 30 min. When the TLC shows the complete consumption of starting material, the mixture was diluted with ether (30 mL). The organic phases were washed with H_2O (3×30 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford compound **13** as colorless viscous oil (300 mg, 68%) (eluent pentane/ether: 7/3; R_f: 0.2); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.93 (s, 3H), 1.94 (s, 3H), 2.09 (s, 3H), 2.99 (d, J=3.9 Hz, 1H), 4.36 (dd, J=7.6, 17.1 Hz, 1H), 5.10 (d, J=11.5 Hz, 1H), 5.17 (d, J=11.5 Hz, 1H), 5.23 (dd, J=1.9, 3.3 Hz, 1H), 5.24 (d, J=1.3 Hz, 1H), 5.36 (dd, J=3.4, 10.1 Hz, 1H), 5.69–5.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=20.9, 21.0, 21.0, 68.6, 69.0, 70.1,7 2.32, 92.4, 120.0, 133.8, 170.0, 170.1, 170.3; HRMS *m/z* calculated for $[M+Na]^+$ ($C_{13}H_{18}O_8Na$): 325.0899, found 325.0890.

4.2.12. (4R,5R,6S)-4,5,6-Tris(acetoxy)-2-methylcyclohex-2-enone ***15***. The reaction was realized following the general procedure A with: lactol **13** (240 mg, 0.78 mmol), $Fe(CO)_5$ (21 μl, 20 mol %) to give cyclohexenone **15** as a viscous oil (87 mg: 40% for two steps) (pentane/AcOEt: 9/1; R_f: 0.3); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.82 (s, 3H), 1.99 (s, 3H), 2.06 (s, 3H), 2.1 (s, 3H), 5.33 (dd, J=3.8, 11.3 Hz, 1H), 5.67 (d, J=4.2 Hz, 1H), 5.70 (dd, J=2.6, 5.8 Hz, 1H), 6.62 (dd, J=1.4, 6.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=15.5, 20.5, 20.6, 20.7, 65.4, 68.6, 72.0, 135.9, 139.8, 169.6, 170.1, 190.1, 191.3; HRMS *m/z* calculated for $[M+Na]^+$ ($C_{13}H_{16}O_7Na$): 307.2517, found 307.2520; $[\alpha]_D^{20}$ −47.0 (*c* 0.1, MeOH).

4.2.13. (3R,4S,5S,6R)-3,4,5-Tris(benzyloxy)-6-vinyl-tetrahydro-2H-pyran-2-ol ***17***. To a solution of **16** (500 mg, 1.09 mmol) in 70% acetic acid (20 mL) was added dropwise concentrated sulfuric acid (1 mL) at room temperature. The mixture was heated at 80 °C for 24 h, and the solvent was evaporated with toluene under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and the organic phase was washed with water (50 mL), a saturated $NaHCO_3$ solution then dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford lactol **17** as colorless viscous oil (363 mg, 75%, 70/30 mixture of α/β anomers, pentane/EtOAc: 8/2 R_f=0.2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.86 (dd, J=1.3, 2.7 Hz, 1H), 3.98 (d, J=2.8 Hz, 1H), 4.07 (d, J=3.6 Hz, 1H), 4.47 (d, J=6.9 Hz, 1H), 4.70–4.94 (m, 6H), 5.19 (dd, J=1.4, 10.6 Hz, 1H), 5.33 (dd, J=1.5, 17.3 Hz, 1H), 5.36 (m, 1H), 5.89 (ddd, J=6.1, 10.5, 17.2 Hz, 1H), 7.29–7.41 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=71.9, 72.9, 73.6, 74.7, 76.4, 77.5, 78.6, 80.6, 82.0, 91.9, 97.8, 117.1, 127.5, 127.6, 127.8, 128.0, 128.2, 128.3, 128.4, 128.44, 134.6, 134.9, 137.8, 138.1, 138.2, 138.4.

4.2.14. (4S,5R,6R)-4,5,6-Tris(benzyloxy)-2-methylcyclohex-2-enone ***19***. The reaction was realized following the general procedure A with: lactol **17** (350 mg, 0.78 mmol), $Fe(CO)_5$ (11 μl, 10 mol %) to give in two steps cyclohexenone **19** as a colorless viscous liquid (180 mg, 54% for two steps) (pentane/AcOEt: 9/1; R_f: 0.3). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.83 (t, J=1.5 Hz, 3H), 3.98 (dd, J=2.5, 5.5 Hz, 1H), 4.30 (d, J=2.0 Hz, 1H), 4.42 (br s, 1H), 4.59 (d, J=12.2 Hz, 1H), 4.66 (d, J=12.1 Hz, 1H), 4.68 (d, J=11.5 Hz, 1H), 4.74 (d, J=11.5 Hz, 1H), 4.75 (d, J=12.1 Hz, 1H), 4.86 (d, J=12.2 Hz, 1H), 6.59 (m, 1H), 7.32–7.45 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=15.3, 72.4, 72.6, 72.9, 75.1, 78.9, 127.71, 127.73, 127.84, 127.86, 127.9, 128.29, 128.32, 128.4, 137.6, 137.8, 137.9, 196.4; HRMS *m/z* calculated for $[M+Na]^+$ ($C_{28}H_{28}O_4Na$): 451.1885, found 451.1876; $[\alpha]_D^{20}$ +167.1 (*c* 0.7, MeOH).

4.2.15. Synthesis of 4-epigabosine N. The reaction was realized following the general procedure B with cyclohexenone **19** (80 mg, 0.18 mmol), $FeCl_3$ (86 mg, 3 equiv) to afford 4-*epi*-Gabosine N as a colorless viscous oil, 14 mg (50% yield) [R_f: 0.2; AcOEt/MeOH: 8/2]; ^{1}H NMR (300 MHz, CD_3COCD_3): δ=1.77 (t, J=1.3 Hz, 3H), 4.07 (d, J=4.0 Hz, 1H), 4.13 (m, 1H), 4.28 (J=3.6 Hz, 1H), 4.37 (m, 1H), 4.51 (dd, J=2.9, 4.0 Hz, 1H), 4.59 (d, J=5.4 Hz, 1H), 6.57 (qd, J=1.7, 4.7 Hz, 1H); ^{13}C NMR (75 MHz, CD_3COCD_3): δ=16.2, 69.7, 74.6, 76.8, 135.2, 142.7, 200.6; HRMS *m/z* calculated for $[M+Na]^+$ ($C_7H_{10}O_4Na$): 181.0471, found 181.0474; $[\alpha]_D^{20}$ +223.7 (*c* 0.08, MeOH).

4.2.16. Synthesis of 4-epi-6-epigabosine B. The reaction was realized following the general procedure C to afford desired 4-*epi*-6-*epi*-gabosine B, 9 mg (80%); ^{1}H NMR (300 MHz, MeOD): δ=0.98 (d, J=6.6 Hz, 3H), 1.83 (ddd, J=2.7, 13.0, 13.7 Hz, 1H), 1.96 (ddd, J=2.7, 6.1, 13.7 Hz, 1H), 2.82 (ddq, J=13.0, 6.1, 6.6 Hz, 1H), 3.94 (dd, J=2.7, 6.3 Hz, 1H), 4.17 (ddd, J=1.7, 3.4, 3.4 Hz, 1H), 4.50 (d, J=3.4 Hz, 1H); ^{13}C NMR (75 MHz, MeOD): δ=13.9, 38.8, 38.9, 70.0, 75.9, 79.1, 213.1; HRMS *m/z* calculated for $[M]^+$ $C_7H_{12}O_4$: 160.0735, found 160.0743; $[\alpha]_D^{20}$ −23.3 (*c* 0.06, MeOH).

4.2.17. (3R,4S,5R,6R)-3,4,5-Tris(benzyloxy)-6-vinyl-tetrahydro-2H-pyran-2-ol ***21***. Starting from **6**, similar synthetic procedure as adopted for compound **17** was followed to obtain **21**. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.85 (d, J=2.4 Hz, 1H), 3.10 (d, J=5.1 Hz, 1H), 3.19 (d, J=9.4 Hz, 1H), 3.32 (dd, J=7.7, 9.3 Hz, 1H), 3.50 (d, J=9.4 Hz, 1H), 3.59 (d, J=9.1 Hz, 1H), 3.76 (dd, J=6.4, 9.7 Hz, 1H), 3.90 (d, J=9.3 Hz, 1H), 4.30 (dd, J=6.5, 9.7 Hz, 1H), 4.53–4.89 (m, 7H), 5.16 (t, J=3.0 Hz, 1H), 5.21 (dt, J=1.3, 10.6 Hz, 1H), 5.35 (dt, J=1.4, 17.2 Hz, 1H), 5.83 (ddd, J=6.5, 10.5, 17.0 Hz, 1H), 7.18–7.30 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=71.7, 74.8, 75.1, 75.8, 76.0, 77.2, 80.0, 81.3, 82.1, 82.2,83.1, 84.2, 91.2, 97.3, 99.1, 118.3, 118.4, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.37,128.40, 128.5, 34.6, 135.1, 137.8, 137.9, 138.1, 138.3, 138.5, 138.7.

4.2.18. (4S,5R,6S)-4,5,6-Tris(benzyloxy)-2-methylcyclohex-2-enone ***23***. The reaction was realized following the general procedure A as indicated above; **23** was obtained in 65% overall yield (two steps) as a white solid, mp: 64–66 °C: ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.75 (t, J=1.8 Hz, 3H), 3.87 (dd, J=7.8, 10.7 Hz, 1H), 3.95 (d, J=10.7 Hz, 1H), 4.24 (dt, J=2.1, 7.8 Hz, 1H), 4.67 (d, J=11.5 Hz, 1H), 4.73 (d, J=10.9 Hz,

1H), 4.76 (d, J=11.6 Hz, 1H), 4.89 (d, J=10.9 Hz, 1H), 5.03 (d, J=10.3 Hz, 1H), 6.52 (t, J=1.8 Hz, 1H), 7.23–7.39 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.3, 73.5, 74.6, 75.6, 78.5, 83.9, 84.7, 127.78, 127.8, 127.91, 127.98, 128.2, 128.3, 128.38, 128.41, 128.6, 135.0, 137.8, 137.9, 138.3, 143.0, 197.6; HRMS m/z calculated for $[M+Na]^+$ ($C_{28}H_{28}O_4Na$): 451.1885, found 451.1876; $[\alpha]_D^{20}$ −3.6 (c 0.19, MeOH).

4.2.19. (4S,5R,6S)-4,5,6-Trihydroxy-2-methylcyclohex-2-enone (4-epigabosine A). The reaction was realized following the general procedure B with cyclohexenone **23** (142 mg, 0.33 mmol), $FeCl_3$ (162 mg, 3 equiv) in anhydrous CH_2Cl_2 to afford 4-*epi*-gabosine A (32 mg, 55%) (AcOEt as eluent) R_f: 0.2 (AcOEt/MeOH: 8/2); ^{1}H NMR (300 MHz, MeOD): δ=1.82 (t, J=1.8 Hz, 1H), 3.32 (m, 3H), 3.54 (dd, J=8.2, 10.9 Hz, 1H), 4.00 (d, J=10.9 Hz, 1H), 4.30 (td, J=2.1, 8.2 Hz, 1H), 6.67 (t, J=1.6 Hz, 1H); ^{13}C NMR (75 MHz, MeOD): δ=13.8, 71.1, 76.6, 78.6, 133.3, 146.4, 198.7; HRMS m/z calculated for $[M+Na]^+$ $C_7H_{10}O_4Na$: 181.0471, found 181.0474; $[\alpha]_D^{20}$ +47.3 (c 0.3, MeOH).

4.2.20. (2S,3R,4S,6R)-2,3,4-Trihydroxy-6-methylcyclohexanone (4-epi-gabosine B). The reaction was realized following the general procedure C with **23** (200 mg, 0.467 mmol), absolute ethanol (2.5 mL), and palladium on activated carbon (7 mg) to afford 4-*epi*-gabosine B (67 mg, 90%), mp: 108−110 °C; ^{1}H NMR (300 MHz, MeOD): δ=0.96 (d, J=6.5 Hz, 3H), 1.18 (dt, J=13.2, 11.5 Hz, 1H), 2.07 (dt, J=13.0, 5.0 Hz, 1H), 2.56 (ddq, J=5.5, 10.3, 6.5 Hz, 1H), 3.15 (dd, J=9.3, 9.7 Hz, 1H), 3.79 (ddd, J=4.7, 9.0, 11.5 Hz, 1H), 3.98 (dd, J=10.0, 1.4 Hz). ^{13}C NMR (75 MHz, MeOD): δ=13.9, 39.0, 40.2, 71.8, 79.4, 81.4, 210.3; HRMS m/z calculated for $[M]^+$ $C_7H_{12}O_4$: 160.0735, found 160.0743. $[\alpha]_D^{20}$ −107.8 (c 0.4, $CHCl_3$).

*4.2.21. (3S,4S,5R,6R)-3,4,5-Tris(benzyloxy)-6-vinyl-tetrahydro-2H-pyran-2-ol **24**.* Similar synthetic procedure as adopted for compound **17** was followed to obtain **24**. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.67 (d, J=3.4 Hz, 1H), 3.62–3.85 (m, 3H), 3.97 (dd, J=3.0, 9.4 Hz, 1H), 4.21 (dd, J=6.8, 9.1 Hz, 1H), 4.61–4.86 (m, 6H), 5.11 (d, J=11.6 Hz, 1H), 5.29 (dd, J=1.6, 10.5 Hz, 1H), 5.46 (dd, J=1.7, 17.2 Hz, 1H), 6.02 (ddd, J=6.7, 10.4, 17.2 Hz, 1H), 7.27–7.39 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=72.6, 72.9, 73.15, 73.17, 74.8, 74.9, 75.13, 76.3, 76.5, 77,2, 78.4, 78.8, 79.2, 82.6, 93.0, 93.4118.3, 118.4, 127.5, 127.6, 127.6, 127.7, 127.9, 128.0, 128.1, 128.3, 128.33, 128.34, 128.5, 128.6, 128.9, 134.5, 135.5, 137.9, 138.05, 138.07, 138.2, 138.4, 138.5.

*4.2.22. (4R,5R,6S)-4,5,6-Tris(benzyloxy)-2-methylcyclohex-2-enone **26**.* The reaction was realized following the general procedure A with lactol **24** (150 mg, 0.35 mmol), $Fe(CO)_5$ (5 μl, 10 mol %) to give cyclohexenone **26** as a colorless viscous liquid (104 mg, 75% for two steps) (pentane/AcOEt: 9/1; R_f: 0.7); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.80 (t, J=1.3, 3 Hz), 3.95 (dd, J=3.2, 8.0 Hz, 1H), 4.34 (d, J=8.1 Hz, 1H), 4.35–4.37 (m, 1H), 4.65 (d, J=10.5 Hz, 1H), 4.67 (d, J=11.5 Hz, 1H), 4.68 (d, J=10.7 Hz, 1H), 4.78 (d, J=12.0 Hz, 1H), 4.80 (d, J=12.2 Hz, 1H), 4.90 (d, J=11.5 Hz, 1H), 6.59 (dq, J=1.5, 3.0 Hz, 1H), 7.28–7.39 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.6, 72.5, 73.2, 73.9, 78.6, 80.1, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 136.1, 137.8, 138.1, 140.4, 197.1; HRMS m/z calculated for $[M+Na]^+$ ($C_{28}H_{28}O_4Na$): 451.1885, found 451.1876; $[\alpha]_D^{20}$ −114.3 (c 0.14, MeOH).

4.2.23. Synthesis of gabosine A. The reaction was realized following the general procedure B with cyclohexenone **26** (80 mg, 0.18 mmol), CH_2Cl_2, and anhydrous $FeCl_3$ (86 mg, 3 equiv) to afford gabosine A as a colorless viscous liquid (14 mg, 50% yield) [R_f: 0.2; AcOEt/MeOH: 8/2]; ^{1}H NMR (300 MHz, CD_3COCD_3): δ=1.77 (t, J=1 Hz, 3H), 3.76 (dd, J=4.2, 5.7 Hz, 1H), 4.28 (s, 3H), 4.38 (d, J=4.8 Hz, 1H), 4.44 (q, J=4.3 Hz, 1H), 6.73 (dq, J=1.5, 5.4 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OCD_3): δ=16.5, 67.8, 74.7, 75.9, 136.6, 143.9, 200.4; HRMS m/z calculated for $[M+Na]^+$ $C_7H_{10}O_4Na$: 181.0471, found 181.0474; $[\alpha]_D^{20}$ −216.5 (c 0.133, MeOH).

4.2.24. Synthesis of 6-epigabosine O. The reaction was realized following the general procedure C with **26** (30 mg, 0.07 mmol), methanol (2.5 mL), and palladium on activated carbon (5 mg) to afford 6-epigabosine O as a white solid (6.7 mg, 60%), mp: 90–92 °C; ^{1}H NMR (500 MHz, MeOD): δ=1.07 (d, J=6.8 Hz, 3H), 1.80 (dt, J=10.3, 12.8 Hz, 1H), 1.94 (dddd, J=1.5, 4.6, 6.1, 10.3 Hz, 1H), 2.91 (ddq, J=6.1, 12.8, 6.8 Hz, 1H), 3.82 (ddd, J=1.5, 2.7, 4.3 Hz, 1H), 3.97 (d, J=5.4 Hz, 1H), 4.33 (ddd, J=2.7, 4.4, 9.9 Hz, 1H); ^{13}C NMR (75 MHz, MeOD): δ=15.6, 36.9, 39.3, 68.6, 77.0, 77.8; $[\alpha]_D^{20}$ −82.5 (c 0.04, MeOH); HRMS m/z calculated for $[M]^+$ $C_7H_{12}O_4$: 160.0735, found 160.0743.

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