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The Stereocontrolled Synthesis of Methyl 2,6-*N,N*-Diacetyl-D-purpurosaminide C

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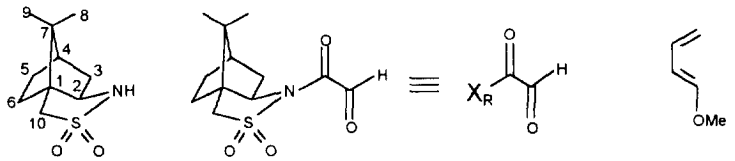
Abstract: Methyl 2,6-*N,N*-diacetyl-D-purpurosaminide **4** (methyl 2,6-diacetamido-2,3,4,6-tetradeoxy-α-D-erythrohexopyranoside) was synthesized from *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **2** and 1-methoxybuta-1,3-diene **3** in an 11-step reaction sequence with 6.5% of the overall yield.

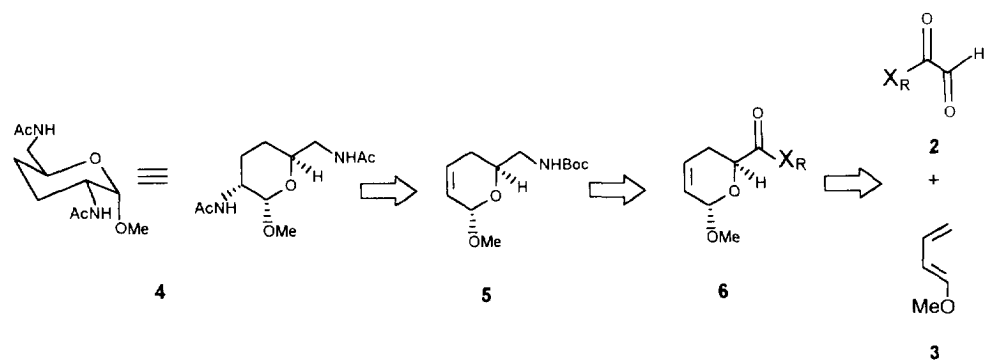
2,6-Diamino-2,3,4,6-tetradeoxy-D-erythrohexopyranose, commonly called purpurosamine C, is one of the two sugar components of the aminoglycosidic antibiotic gentamicin C_{1a}.[1,2] Several syntheses of this diaminotetradeoxyhexose have been reported.[3-9] We have also published [10] the total synthesis of racemic purpurosamine C, using the high-pressure hetero-Diels-Alder reaction of *N-tert*-butoxycarbonyloaminoethanal with 1-methoxybuta-1,3-diene **3**. In general, [4+2] cycloadditions of diene **3** to α-amino aldehydes offer an easy access to the 5,6-dihydro-2*H*-pyran system with amino functionality attached to the C-6 carbon atom. Besides racemic purpurosamine C, this approach has been applied to the syntheses of purpurosamine B[11] and *6-epi*-B[12] in enantiomerically pure form. Subsequent stereoselective functionalization of the C-2 carbon atom (sugar numbering) of the respective [4+2] cycloadduct gives a direct route to the corresponding purpurosamine.

Recently, we have described an efficient method of the large-scale preparation of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **2**,[13] starting from (2*R*)-bornane-10,2-sultam **1**, introduced by Oppolzer *et al.*,[14] and its successful application to the hetero-Diels-Alder reaction with diene **3**.[15,16] The aim of this work is the highly stereoselective total synthesis of methyl 2,6-*N,N*-diacetyl-D-purpurosaminide C, starting from diene **3** and heterodienophile **2**.



1 X_RH **2** **3**

Our approach to this synthesis, according to the simple retrosynthetic analysis (Scheme 1), is based on our well elaborated [15,16] [4+2] cycloaddition of diene **3** to heterodienophile **2**, affording the [4+2] cycloadduct **6**. Further transformation of **6** into compound **5**, followed by stereoselective functionalization of the C-3 carbon atom (pyran numbering) should give a direct route to the desired derivative **4** of purpurosamine C.



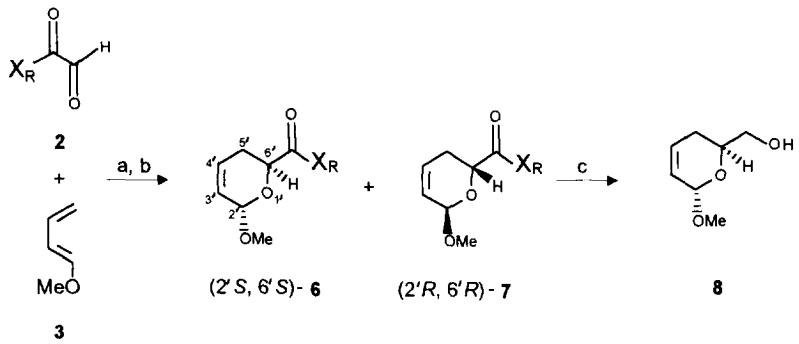
4 **5** **6** **2** + **3**

Scheme 1

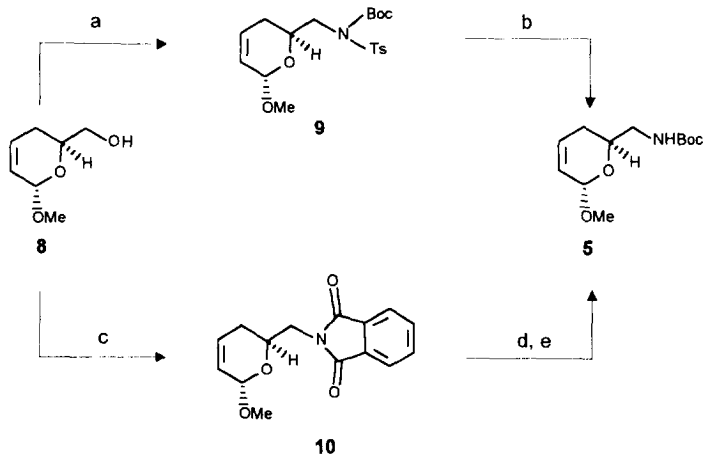
In this work, we applied the $Eu(fod)_3$-mediated [4+2] cycloaddition of **3** to **2**, carried out in methylene chloride under ambient conditions,[16] followed by chromatographic separation and lithium aluminum hydride (LAH) reduction of diastereoisomerically pure (2'*S*, 6'*S*)-**6** (Scheme 2).

The resulting alcohol **8** was transformed into the desired compound **5** in two independent ways (Scheme 3). The first comprises the Mitsunobu reaction of **8** with *N-tert*-butoxycarbonyl-*p*-toluenesulfonamide, leading to the crystalline diprotected amine **9** in 83% yield, and subsequent partial deprotection of **9** affording the compound **5** in 53% yield. The second comprises also the Mitsunobu reaction of **8** with phthalimide, leading to the crystalline compound **10** in 96% yield, its deprotection to the corresponding free amine, and the final protection of the amine with $(Boc)_2O$, affording the compound **5** in 45% overall yield.

Hydroboration of the compound **5** using thexylborane,[10] followed by oxidative workup, afforded alcohol **11** in 60% yield. The next step of the synthesis consisted of oxidation of the chromatographically pure alcohol **11** using pyridinium chlorochromate (PCC) in the presence of 4A molecular sieves[17] (Scheme 4).



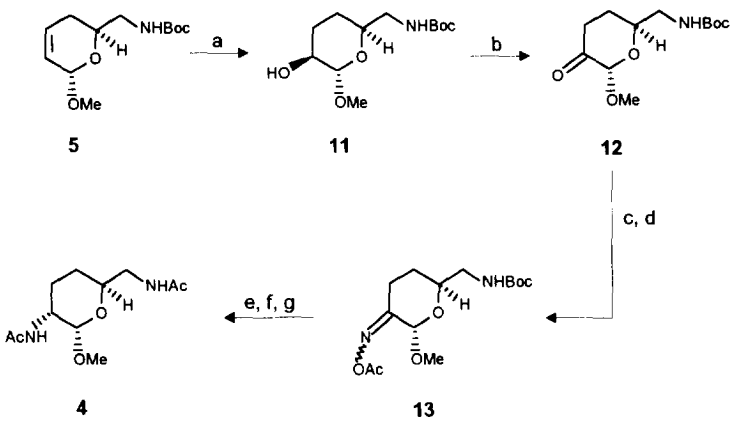
Scheme 2. Reagents and reaction conditions: (a) 2% $Eu(fod)_3$, CH_2Cl_2, 20°C, 3 h; (b) PPTS, MeOH, RT, 15 h; (c) LAH, Et_2O, 0°C→RT, 2 h.



Scheme 3. Reagents and reaction conditions: (a) TsNHBoc, TPP, DEAD, THF, RT, 20 h; (b) naphthalene sodium, DME, -5°C, 10 min; (c) PhtNH, TPP, DEAD, THF, RT, 4 h; (d) $MeNH_2$, MeOH, RT, 12 h; (e) $(Boc)_2O$, AcOEt, sat. Na_2CO_3, RT, 6 h.

Direct displacement at the C-3 carbon atom failed, giving exclusively the elimination product **5**.[10-12] Ketone **12** was transformed into an oxime which was then acetylated affording a 1:1 *syn-anti*

mixture of oxime acetates **13** in 65% yield. This mixture was reduced with a BH_3·THF complex to give a 6:1 *cis-trans* mixture of corresponding amines.[10] The stereochemical course of the reduction of the acetyloxyimino functionality is strongly controlled by the anomeric substituent.[18-20] Finally, deprotection of the second amino functionality, followed by acetylation, afforded methyl *N,N*-diacetyl-D-purpurosaminide C **4** in 6.5% overall yield (based on the Diels-Alder adduct **6**).



Scheme 4. Reagents and reaction conditions: (a) ThxBH$_2$·DMS (3 eq), Et_2O, -25°C, 3 h; (b) PCC, 4A molecular sieves , CH_2Cl_2, RT, 15 h; (c) NH_2OH·HCl, K_2CO_3, MeOH, RT, 16 h; (d) Ac_2O, Et_3N, DMAP (cat.), CH_2Cl_2, RT, 1 h; (e) BH_3, THF , -50°C→RT, 24 h; (f) TFA, RT, 1 h; (g) Ac_2O, Et_3N, CH_2Cl_2, RT, 1 h.

The synthetic sequence detailed herein shows the great utility of [4+2] cycloaddition of 1-methoxybuta-1,3-diene **3** to *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **2**. The presented total synthesis proves to be a practical alternative to known procedures[3-9] using mainly monosaccharides as starting materials.

EXPERIMENTAL

General. Melting points were determined using a Kofler hot stage apparatus and are not corrected. Rotations were recorded using a JASCO DIP-360 polarimeter with a thermally jacketed 10 cm cell. IR spectra were obtained with a Perkin-Elmer 1640 FTIR spectrometer in films (for liquids) or KBr pellets (for solids). ^{1}H NMR spectra were recorded using a Varian Gemini (200 MHz) spectrometer, and ^{13}C NMR spectra were recorded with DEPT editing as necessary, using also a Varian Gemini (50 MHz) spectrometer. All chemical shifts are quoted in parts per milion relative to tetramethylsilane (δ, 0.00 ppm) and coupling constants (J) are measured in Hertz. Mass spectra were recorded on an AMD-604 Intectra

instrument using the electron impact (EI) technique. Flash chromatography was performed according to Still *et al.*[21] on silica gel (Kieselgel-60, Merck, 200-400 mesh). (2'*S*)-Methoxy-(6'*S*)-[(2*R*)-bornane-10,2-sultam]-carbonyl-5',6'-dihydro-2*H*-pyran (**6**) was prepared according to our own methodology.[16]

Preparation of (2*S*)-methoxy-(6*S*)-hydroxymethyl-5,6-dihydro-2*H*-pyran **8**. To the solution of compound **6** (8.2 g, 22.8 mmol) in Et_2O (50 mL) lithium aluminum hydride (0.95 g) was added portionwise at 0°C. After stirring at room temperature over a period of 2 h, the reaction mixture was treated with an aqueous solution of sodium potassium tartrate (50 mL) and stirring was continued for additional 2 h. The post-reaction mixture was transferred into a separatory funnel and the aqueous layer was extracted with Et_2O (3 x100 mL). The organic layers were combined, dried ($MgSO_4$), and evaporated in vacuo. The oily residue was treated with a mixture of Et_2O and *n*-hexane to give crystalline (2*R*)-bornane-10,2-sultam (**1**) in 90% yield. The mother liquor was evaporated and the oily residue was chromatographed (*n*-hexane - Et_2O, 9:1) to afford the product **8** (2.0 g, 60%) as an oil: $[\alpha]_D^{20}$=-79.2 (*c* 1.5, C_6H_6), lit.[22] $[\alpha]_D^{20}$=-79.9 (*c* 1.55, C_6H_6); δ_H (200 MHz, $CDCl_3$) 6.09-5.98(m, 1H), 5.81-5.70(m, 1H), 4.90(d, J=2.0, 1H), 4.01(m, 1H), 3.82-3.69(m, 1H), 3.69-3.54(m, 1H), 3.44(s, 3H), 2.29(bs, 1H), 2.25-2.06(m, 1H), 1.99-1.81(m, 1H); δ_C (50 MHz, $CDCl_3$) 128.6, 125.3, 95.7, 67.0, 65.2, 55.3, 26.0.

Preparation of (2*S*)-methoxy-(6*S*)-(*N*-*tert*-butoxycarbonyl)-aminomethyl-5,6-dihydro-2*H*-pyran **5**. **Method A.** To a solution of the alcohol **8** (1.19 g, 8.3 mmol) in dry THF (50 mL) *N*-Boc-*p*-toluenesulfonamide (3.39 g, 12.5 mmol) and triphenylphosphine (TPP, 6.53 g, 24.9 mmol) were added. Then diethyl azadicarboxylate (DEAD, 3.2 mL, 20.8 mmol) was slowly added, the mixture stirred at room temperature over a period of 4 h, and evaporated in vacuo. Flash chromatography (hexanes-ethyl acetate, 8:2→6:4) of the residue afforded the crystalline diprotected amine **9** (2.74 g, 83.5%): mp 108-110°C (from isopropanol); $[\alpha]_D^{20}$=-27.3 (*c* 6.2, CH_2Cl_2); ν_{max} (KBr)/cm^{-1} 3046, 2981, 2931, 2827, 1732, 1598, 1394, 1348, 1257, 964, 806, 721, 675); δ_H (200 MHz, $CDCl_3$) 7.85(d, J=8.2, 2H), 7.29(d, J=8.2, 2H), 5.99(dt, J_1=10.0, J_2=3.9, 1H), 5.73(dq, J_1=10.0, J_2=4.7, J_3=2.4, 1H), 4.83(d, J=2.1, 1H), 4.29-4.09(m, 1H), 4.12(dd, J_1=13.7, J_2=8.8, 1H), 3.86(dd, J_1=13.7, J_2=2.9, 1H) 3.17(s, 3H), 2.42(s, 3H), 2.09-1.95(m, 2H), 1.35(s, 9H), δ_C (50 MHz, $CDCl_3$) 151.5, 144.5, 137.9, 129.5, 128.9, 128.6, 125.1, 96.0, 84.7, 65.6, 55.5, 50.4, 28.4, 28.3, 22.0; m/z (EI) 366 $(M\text{-}OCH_3)^+$ (4%), 341 $(M\text{-}C_4H_9)^+$ (4%), 310 $(M\text{-}OCH_3\text{-}C_4H_9)^+$ (7%), 266 (9%), 184(65%), 155(75%), 126(100%), 113(88%); m/z (EIHR) calculated for $C_{18}H_{24}NO_5S$ $(M\text{-}OCH_3)^+$ 366.1375, found 366.1376; calculated for $C_{15}H_{18}NO_6S$ $(M\text{-}C_4H_9)^+$ 341.0933, found 341.0930; calculated for $C_{14}H_{15}NO_5S$ $(M\text{-}OCH_3\text{-}C_4H_9)^+$ 310.0749, found 310.0747. To a solution of naphthalene (2.25 g, 17.6 mmol) in 1,2-dimethoxyethane (DME, 15 mL) was added sodium metal (0.39 g, 17 mmol) under argon.[23] After stirring at room temperature over a period of 2 h, the mixture was cooled to -5°C and precooled solution of the compound **9** (0.7 g, 1.76 mmol) in DME (2 mL) was added slowly. Stirring was continued for additional 10 min, and the reaction was quenched with water (one drop). The product

was extracted with Et_2O (3 x 50 mL), the organic layers were combined, washed with saturated *aq.* $NaHCO_3$ (30 mL), dried ($MgSO_4$), and evaporated in vacuo. Flash chromatography (hexanes-ethyl acetate 8:2→6:4) of the residue afforded the oily *N*-Boc-amine **5** (0.227 g, 53%): $[\alpha]_D^{20}$=+2.0 (*c* 1.41, CH_2Cl_2); ν_{max} (film)/cm^{-1} 3350, 1720, 1175, 1050; δ_H (200 MHz, $CDCl_3$) 6.06-5.93(m, 1H), 5.79-5.66(m, 1H), 4.88(m, 1H), 4.85(d, J=2.5, 1H), 3.95(dddd, J_1=14.5, J_2=13.6, J_3=10.6, J_4=3.5, 1H), 3.89-3.50(m, 1H), 3.42(s, 3H), 3.25-3.05(m, 1H), 2.09-1.91(m, 2H), 1.44(s, 9H); δ_C (50 MHz, $CDCl_3$) 150.1, 128.5, 125.3, 112.3, 95.7, 65.7, 55.1, 44.5, 28.4, 27.4; elemental analysis: found C, 58.3; H, 9.0; N, 5.4; $C_{12}H_{21}NO_4$ requires C, 58.7; H,8.6; N, 5.7%.

Method B. To a solution of the alcohol **8** (0.8 g, 5.55 mmol) in dry THF (40 mL) phthalimide (1.22 g, 8.33 mmol) and TPP (2.18 g, 8.33 mmol) were added. Then DEAD (0.94 mL, 6.1 mmol) was slowly added, the mixture was stirred at room temperature over a period of 4 h, and evaporated in vacuo. Flash chromatography (hexanes-ethyl acetate, 8:2→6:4) of the residue afforded the crystalline compound **10** (1.45 g, 96%): mp 120-121°C (from MeOH); $[\alpha]_D^{20}$=+29.6 (*c* 1.11, CH_2Cl_2); ν_{max} (KBr)/cm^{-1} 3038, 2981, 2931, 2827, 1703, 1443, 1407, 1337, 1226, 966, 908, 874, 798, 727; δ_H (200 MHz, $CDCl_3$) 7.92-7.85(m, 2H), 7.77-7.70(m, 2H), 6.05-5.93(m, 1H), 5.77-5.66(m, 1H), 4.85(d, J=2.8, 1H), 4.22(ddt, J_1=8.0, J_2=5.0, J_3=J_4=4.2, 1H), 3.95(dd, J_1=13.8, J_2=8.0, 1H), 3.78(dd, J_1=13.8, J_2=4.2, 1H), 3.18(s, 3H), 2.15-2.04(m, 2H); δ_C (500 MHz, $CDCl_3$) 168.1, 133.9, 131.8, 127.9, 125.3, 123.2, 95.4,64.4, 54.7, 41.7, 28.6; m/z (EI) 273 $(M)^+$ (3%), 255 (10%). 242 (34%), 224 (7%), 160 (100%), 148 (3%), 133 (15%), 130 (25%), 126 (47%), 113 (95%); m/z (EIHR) calculated for $C_{15}H_{15}NO_4$ $(M)^+$ 273.1001, found 273.1000. To a solution of the compound **10** (0.4 g, 2.77 mmol) in MeOH (40 mL) the 5*N* solution of $MeNH_2$ in MeOH (15 mL) was added and the mixture was stirred at room temperature over a period of 16 h.[24] After evaporation of solvents, the residue was dissolved in saturated *aq.* $NaHCO_3$ (40 mL), and a solution of $(Boc)_2O$ (0.67 g, 3.05 mmol) in ethyl acetate (40 mL) was added. The mixture was stirred at room temperature over a period of 6 h, then it was transferred into a separatory funnel and the organic layer was washed with water (40 mL), brine (40 mL), and dried ($MgSO_4$). After evaporation in vacuo, the residue was chromatographed (hexanes-ethyl acetate 8:2→6:4) to afford the *N*-Boc-amine **5** (0.16 g, 45.0%).

Preparation of methyl 2,6-*N*,*N*-diacetyl-D-purpurosaminide C **4**. To a solution of 2,3-dimethylbutene-2 (0.7 mL, 6 mmol) in Et_2O (20 mL) a BH_3·Me_2S complex (BMS, 0.58 mL, 5.8 mmol) was added at -5°C. The mixture was stirred at 0°C over a period of 3 h, then it was cooled to -25°C, and the compound **5** (0.47 g, 1.9 mmol) dissolved in Et_2O (5 mL) was added. The reaction mixture was kept at -25°C over a period of 3 h, and excess of borane was decomposed with MeOH (1 mL), followed by addition of a mixture of 30% H_2O_2 and 30% *aq.* NaOH (2 mL, 1:1, v/v). Temperature was raised to 20°C, and stirring was continued for additional 2h. The reaction mixture was extracted with ethyl acetate (3 x 20 mL), the combined extracts were washed with water (2 x 50 mL), dried $MgSO_4$ and evaporated in

vacuo. Flash chromatography (hexanes-ethyl acetate 1:1→4:6) afforded the product **11** as an oil (0.25 g, 60.0%), which was characterized by ^{1}H and ^{13}C NMR: δ_H (200 MHz, $CDCl_3$) 4.94(bs, 1H), 4.55(s, 1H), 3.83(ddt, J_1=11.1, J_2=8.0, J_3=J_4=3.5, 1H), 3.65(s, 1H), 3.45-3.23(m, 1H), 3.38(s, 3H), 3.05(ddd, J_1=13.9, J_2=7.8, J_3=5.0, 1H), 2.10(bs, 1H), 2.01(ddd, J_1=13.7, J_2=4.9, J_3=2.8, 1H), 1.87(ddd, J_1=13.7, J_2=4.9, J_3=2.8, 1H), 1.82-1.55(m, 2H), 1.45(s, 9H); δ_C (50 MHz, $CDCl_3$) 156.1, 120.3, 100.8, 67.7, 65.6, 54.7, 45.0, 28.4, 25.0, 22.1. To a solution of alcohol **11** (0.153 g, 0.59 mmol) in CH_2Cl_2 (5 mL) were added pyridinium chlorochromate (PCC, 0.647 g, 3 mmol) and freshly dried 4A molecular sieves (1 g). The heterogeneous mixture was stirred at room temperature over a period of 1.5 h, then Et_2O (30 mL) was added, and the mixture was filtered through a short silica gel pad. The filtrate was evaporated and the residue was dissolved in dry MeOH (5 mL). Solid hydroxylamine hydrochloride (0.082 g, 1,17 mmol) and solid K_2CO_3 (0.163 g, 1.17 mmol) were added in one portion, and the whole mixture was stirred at room temperature over a period of 16 h. Then MeOH was evaporated and the residue was dissolved in CH_2Cl_2 (1.5 mL). To this solution were added Et_3N (162 μL, 1.17 mmol), Ac_2O (92 μL, 0.97 mmol), and a crystal of DMAP, and the reaction mixture was stirred over a period of 1 h. After evaporation of solvents, the oily residue was dissolved in THF (2 mL) and the solution was cooled to -50°C. The BH_3·THF complex (0.9 mL of 1M solution, 0.9 mmol) was added, the reaction mixture was stirred at -50°C over a period of 8 h, and then at room temperature for additional 16 h. An excess of borane was decomposed with MeOH (1 mL), solvents were evaporated and the residue was dissolved in trifluoroacetic acid (TFA, 0.5 mL). The solution was stirred at room temperature over a period of 1 h. Then TFA was evaporated and to the residue, dissolved in CH_2Cl_2 (1.5 mL), were added Et_3N (176 μL, 1.28 mmol) and Ac_2O (100μL, 1.06 mmol). The reaction mixture was stirred at room temperature over a period of 1 h, and after evaporation of solvents, the crude product was subjected to flash chromatography ($CHCl_3$-MeOH, 99:1) to afford, after recrystallization from acetone, the title compound **4** (0.102 g, 26%): mp 200-202°C; Lit.[1] mp 200-208°C; Lit.[25] mp 195-197°C; $[\alpha]_D^{20}$=+164.9 (*c* 0.4, MeOH); Lit.[1] $[\alpha]_D^{20}$=+161 (*c* 0.9, MeOH); Lit.[25] $[\alpha]_D^{20}$=+166 (*c* 0.8, MeOH); ν_{max} (KBr)/cm^{-1} 3308, 1644, 1554; δ_H (200 MHz, $CDCl_3$); 5.81(m, 1H), 5.64(d, J=8.6, 1H), 4.56(d, J=3.2, 1H), 4.02(ddd, J_1=9.2, J_2=5.6, J_3=3.6, 1H), 3.82-3.65(m, 1H), 3.50(ddd, J_1=13.9, J_2=6.5, J_3=3.3, 1H), 3.34(s, 3H), 3.11(ddd, J_1=13.9, J_2=7.3, J_3=5.5, 1H), 1.98(s, 3H), 1.95(s, 3H), 1.82-1.39(m, 4H); δ_C (50 MHz, $CDCl_3$) 170.1, 169.5, 98.1, 67.1, 54.7, 47.6, 43.2, 27.3, 24.3, 23.5, 23.3; m/z (EI) 245 $(M+H)^+$ (0.8%), 213 $(M-OCH_3)^+$ (5%), 185 (33%), 172 (10%), 153 (9%), 141 (13%), 125 (91%), 112 (46%), 100 (100%); m/z (EIHR) calculated for $C_{11}H_{21}N_2O_4$ $(M+H)^+$ 245.1502, found 245.1509; calculated for $C_{10}H_{17}N_2O_3$ $(M-OCH_3)^+$ 213.1231, found 213.1230.

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