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# Stereospecific synthesis of a DL-*gala*-aminoquercitol derivative

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ABSTRACT

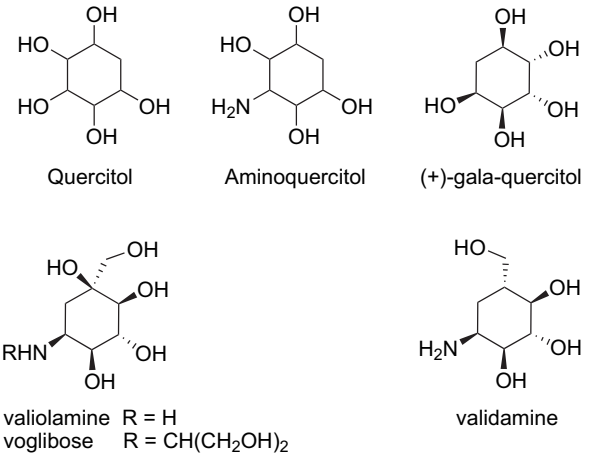
A new aminoquercitol derivative was synthesized starting from 1,4-cyclohexadiene. Photooxygenation of cyclohexa-1,4-diene afforded *anti*-2,3-dioxabicyclo[2.2.2]oct-7-en-5-yl hydroperoxide as the main product. The formed hydroperoxy endoperoxide was reduced with $LiAlH_4$ to produce *anti*-2,3-dioxabicyclo[2.2.2]oct-7-en-5-ol. Protection of alcohol with acetyl chloride followed by reduction of the endoperoxide with thiourea, and then palladium-catalyzed ionization/cyclization reaction gave an oxazolidinone derivative. Hydrolysis of the oxazolidinone ring and acetylation gave an amino compound. Oxidation of the double bond in the amino compound with $OsO_4$ followed by acetylation gave the amino tetraacetate and removal of the acetate groups furnished the desired aminoquercitol whose exact configuration was determined by X-ray diffraction analysis.



## 1. Introduction

The cyclitols, polyhydroxy cyclic compounds have long been of interest to those concerned with carbohydrates.[1] The first known cyclohexanepentol was dextrorotary cyclitol obtained from the acorns of *Quercus* species (Oaks)[2] hence the name (+)-*proto* quercitol. Due to their biological activities against glycosidases, their syntheses have been attracting a great deal of interest to the synthetic community.[3] Quercitol has 10 possible diastereomers, in its family, *proto*-,[4] *allo*-,[5] *epi*-,[6] *vibo*-,[7] *talo*-,[4,7] *gala*-,[7,8] *scyllo*-,[9] *neo*-,[5] *cis*-,[10] and *muco*-[11] quercitols. They have been synthesized by different approaches to provide either their racemic or enantiomerically enriched forms. Recently, we described a highly efficient enantioselective syntheses of (+) and (−)-*proto* quercitols where we applied, for the first time, a biotransformation reaction to an alcohol containing endoperoxide functionality.[12]

In particular, cyclic polyhydroxylated amines, also known as aminocyclitols such as valiolamine, validamine were shown to possess a wide variety of biological activities.[13] The antibiotics containing an aminocyclitol unit have attracted much interest, because they were not only considered as glycosidase inhibitors, but also constituted a key segment of aminoglycosidase antibiotics.[14]




There have been a few cases reported on the synthesis of these quercitol-like aminocyclitols. Notable among them are reports by Ogawa et al.[15] who synthesized optically active aminoquercitol derivatives from (−)-*vibo*-quercitol.

Here we describe an approach toward DL-*gala*-aminoquercitol derivative **18**, starting from commercially available 1,4-cyclohexadiene where we used ene and [4+2] cycloaddition reactions of singlet oxygen,[16] followed by a key step including palladium-catalyzed ionization/cyclization reaction.[17]

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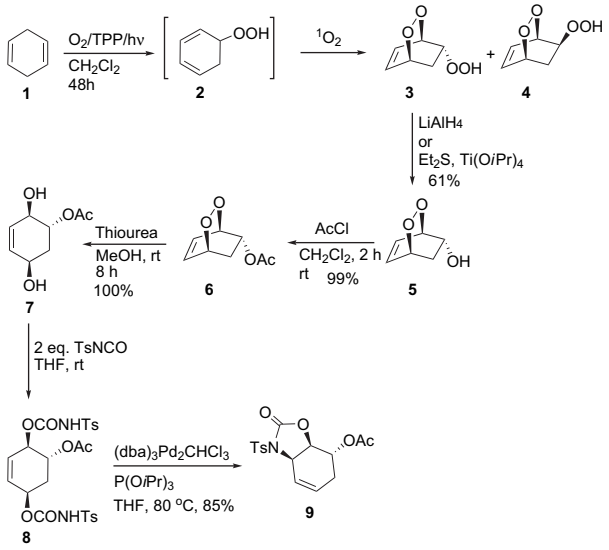
## 2. Results and discussion

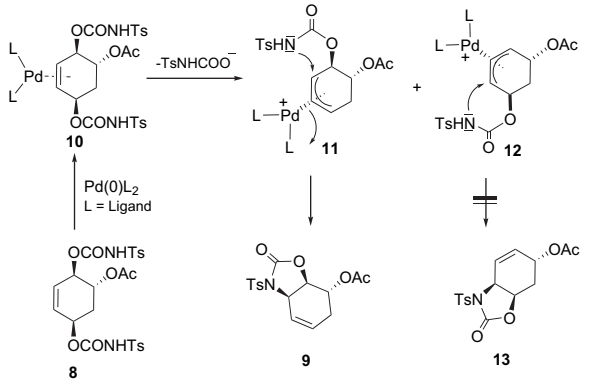
In order to reach the target compound **16**, we selected **7** as a key compound for the palladium-catalyzed ionization/cyclization reaction since the two hydroxy and one acetate functionalities are regiomerically properly located in the six-membered ring. The key compound monoacetate **7** was conveniently prepared from 1,4-cyclohexadiene (**1**) beginning with photooxygenation followed by key steps including selective reduction of hydroperoxide functionality, protection and reduction of an O–O bond (Scheme 1). Tetraphenylporphine (TPP)-sensitized photooxygenation of 1,4-cyclohexadiene (**1**) at room temperature in DCM gave the two known endoperoxides **3** and **4** in a ratio of 88:12.[7,18,19] The major isomer **3** was obtained in 63% yield after column chromatography on silica gel. Since the endoperoxide **3** possesses both endoperoxide and hydroperoxide linkages, a selective reduction was required for the preservation of the endoperoxide functionality. This selective reduction was achieved by either employing diethyl sulfide in the presence of titanium tetraisopropoxide or $LiAlH_4$ as reductant, which gave the desired hydroxy endoperoxide **5**.[18] The hydroxy endoperoxide **5** was converted to the corresponding acetate **6**[12] by treatment with acetyl chloride at room temperature. The structure assignment of the acetate endoperoxide **6** is based on its analytical and spectroscopic data. The HRMS analysis revealed the empirical formula $C_8H_{10}O_4$, while the $^{13}C$ NMR spectrum displayed the expected eight carbon resonances. The IR band at 1746 $cm^{-1}$ indicates the presence of the carbonyl group.




**Scheme 1.** Synthesis of oxazolidinone **9**.

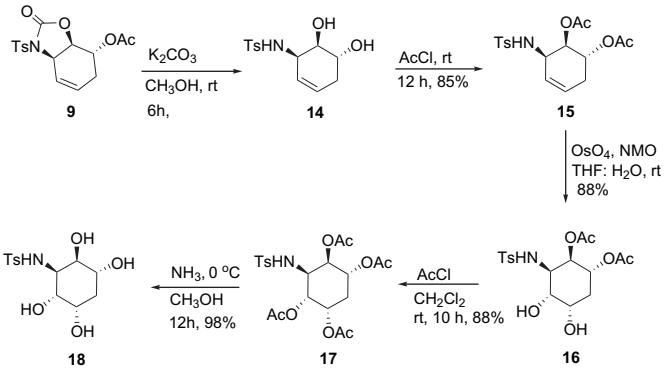
After the successful isolation and characterization of the bicyclic endoperoxide acetate **6**, the peroxide linkage in **6** was reduced with thiourea[20] to give the desired key compound **7**,[12] which possesses diol and acetate functionalities. Since only the oxygen–oxygen bond in **6** cleaved in this reaction, the configurations of the carbon atoms were preserved. Oxazolidinone **9** was synthesized by two consecutive reactions including in situ generation of **8** and subsequent a regio- and stereospecific Pd(0) catalyzed cyclization.[17] To this end, The in situ generated biscarbamate **8** by the reaction of **7** with TsNCO was mixed with a solution of 5 mol% of palladium catalyst, prepared by stirring a mixture of tris(dibenzylideneacetone)dipalladium–chloroform complex and triisopropylphosphite in THF. After the reaction was complete, the mixture was purified by chromatography on a silica gel column eluting with hexane/DCM (70:30) to give oxazolidinone **9** in 98% yield. The structure of oxazolidinone **9** was determined from its $^1H$ and $^{13}C$ NMR spectroscopic data as well as later from the X-ray crystallographic analysis of DL-*gala*-aminoquercitol (**18**).

The observed regio- and stereoselectivity were remarkable. The basic catalytic cycle for this transformation consists of metal–olefin complexation followed by ionization, substitution, and decomplexation. Metal–olefin complexation is potential source of stereoselectivity. Since only palladium–olefin complexation *anti* to the leaving group will lead to oxazolidinone **9**,[21] the metal will approach the double bond in biscarbamate **8** from the back-face of the urethane functionalities (Scheme 2). Since the double bond is not symmetrically disubstituted, palladium can theoretically form two different complexes **11** and **12** after ionization. From the structure of the product **9**, it could be concluded that the metal-complex **11** is preferentially produced. We assume that the acetoxy group can hinder the removal of the neighboring urethane unit due to the electron with-drawing ability. Furthermore, the acetoxy group may also retard the formation of complex **12** because of the possible steric interaction between the acetoxy group and palladium unit.




**Scheme 2.** Mechanism of formation of oxazolidinone **9**.

After successful characterization of the oxazolidinone **9**, we turned our attention to cleavage of oxazolidinone ring. For this purpose, the oxazolidinone **9** was mixed with $K_2CO_3$ in methanol to give compound **14**, which was characterized as its diacetate derivative **15** by treatment with acetyl chloride at room temperature (Scheme 3).




**Scheme 3.** Synthesis of aminoquercitol **18**.

cis-Dihydroxylation of compound **15** with a catalytic amount of $OsO_4$ in the presence of NMO as cooxidant in a mixture of THF/$H_2O$ (1:1) at room temperature gave the corresponding diol **16**; subsequent acetylation with AcCl yielded the tetraacetate **17** as a single isomer. Hydrolysis of tetraacetate groups in **17** was performed with ammonia or $K_2CO_3$ in MeOH under very mild conditions to give DL-*gala*-aminoquercitol **18** in 98% yield.

The spectroscopic data allowed the assignment of the structure **18**. In order to confirm the structure we conducted single crystal X-ray analysis studies on the product **18** (Fig. 1).

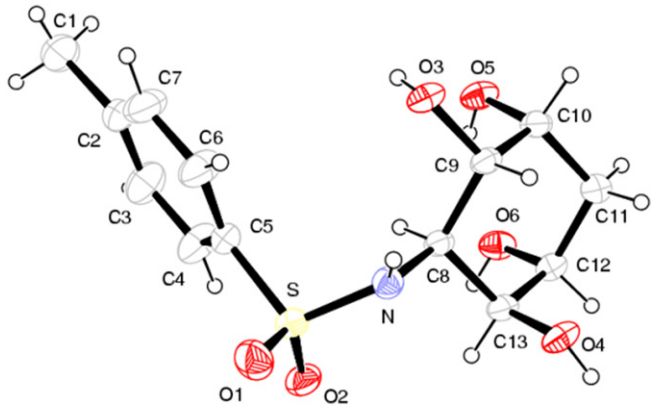



**Figure 1.** Single crystal X-ray diffraction analysis of **18**. The ORTEP drawing depicts thermal ellipsoids at a 40% probability level.

The results of this study confirmed unambiguously the proposed structure (Fig. 1). The compound crystallizes in the triclinic space group *P*-1, with two molecules in the unit cell (Fig. 2). The cyclohexane ring is in the chair conformation. C–$O_{hydx}$ bond lengths are within the expected range [1.425(3)–1.436(3) Å]. Furthermore, the crystal structure of the title compound consists of a 2D-network of hydrogen bonded chains running along the *a* and *b* axis (Fig. 2b). Referring to Table 1, O3–H···O5 and O5–H···O6 are the intramolecular hydrogen bonds detected in the structure.

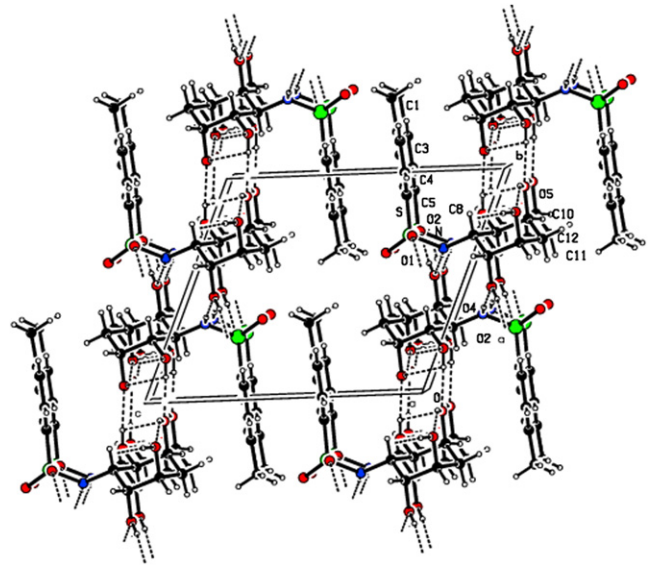


**Figure 2.** Packing diagram along the *a*-axis.

**Table 1**
Hydrogen bonds for **18** [Å, °]

| D–H···A | *d*(H···A) | *d*(D···A) | <(DHA) |
|---|---|---|---|
| O(4)–H···O(2)[a] | 1.95 | 2.762(3) | 173 |
| O(3)–H···O(5) | 2.47 | 2.841(3) | 109 |
| O(3)–H···O(5)[b] | 2.01 | 2.714(3) | 143 |
| O(5)–H···O(6) | 2.02 | 2.726(3) | 144 |
| O(6)–H···O(3)[c] | 1.96 | 2.784(3) | 176 |
| N–H···O(4)[d] | 2.00 | 2.865(3) | 170 |

Symmetry transformations used to generate equivalent atoms: [a]1−*x*,1−*y*,−*z*; [b]−*x*,2−*y*,−*z*; [c]1+*x*,*y*,*z*; [d]−*x*,1−*y*,−*z*.

In summary, we have described the stereospecific synthesis of DL-*gala*-aminoquercitol derivative **18** in eight steps starting from commercially available 1,4-cyclohexadiene and introduced the complex stereochemistry in a very simple way.

## 3. Experimental section

### 3.1. General

Melting points were determined on a Buchi 539 capillary melting apparatus and are uncorrected. Infrared spectra were obtained from KBr pellets on a Mattson 1000 FT-IR spectrophotometer. The $^{1}H$ and $^{13}C$ NMR were recorded on 200(50) and 400(100) MHz Varian spectrometers. Elemental analyses were carried out on a Leco-932 model CHNS analyzer. Column chromatography was performed on silica gel (60-mesh, Merck).

### 3.2. *rel*-(1*R*,4*R*,7*R*)-7-Hydroperoxy-2,3-dioxabicyclo[2.2.2]oct-5-ene (4)

The hydroperoxy endoperoxide was synthesized as described in the literature.[18]

### 3.3. *rel*-(1*R*,4*R*,5*R*)-2,3-Dioxabicyclo[2.2.2]oct-7-en-5-ol (5)[18]

*3.3.1. Method A.* See Ref. 18b for the reduction of **3** with diethyl sulfide in the presence of Ti(O*i*-Pr)$_4$.

*3.3.2. Method B.* To a stirred solution of the hydroperoxide **3** (3.0 g, 21.0 mmol) in dry THF (60 mL), $LiAlH_4$ (0.38 g 10.0 mmol) was added portion wise at −30 °C until the release of hydrogen gas ceased. After stirring at the same temperature for 2 h the mixture was warmed to 0 °C and hydrolyzed by addition of THF/$H_2O$ (1:1). The mixture was filtered (inorganic salts) and the solid was washed with THF. After the solvent was removed under reduced pressure, the hydroxy endoperoxide **5** was recrystallized from ether/hexane to give a white powder (1.60 g, 61%), mp 104–105 °C (106–107 °C[18b]); $\nu_{max}$ (KBr) 3412, 3080, 2978, 2953, 1446, 1395, 1293, 910 cm$^{-1}$; $\delta_H$ (200 MHz, $CDCl_3$) 6.71 (ddd, *J*=8.2, 6.1, 1.8 Hz, 1H), 6.48–6.42(m, 1H), 4.64–4.55 (m, 2H), 4.28–4.20 (m, 1H), 2.50 (ddd, *J*=14.0, 7.9, 3.6 Hz, 1H), 1.75 (br d, 1H), 1.24 (dm, *J*=14.0 Hz, 1H); $\delta_C$ (50 MHz, $CDCl_3$) 134.8, 129.0, 73.0, 70.8, 62.5, 35.0.

### 3.4. *rel*-(1*R*,4*R*,5*R*)-2,3-Dioxabicyclo[2.2.2]oct-7-en-5-yl acetate (6)[12]

To a precooled solution of hydroxy endoperoxide **5** (1.64 g 12.8 mmol) in 50 mL of $CH_2Cl_2$, AcCl (1.09 g 14.0 mmol) was added dropwise over 2 h and the resulting solution was stirred additionally 1 h. After removal of the solvent and unreacted AcCl under reduced pressure, compound **6** was recrystallized from a mixture of ether/pentane (1:1) to give colorless crystals (2.15 g, 99%), mp 79–80 °C; $\nu_{max}$ (KBr) 2993, 2945, 1746, 1495, 1267, 1075, 931 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 6.78 (ddd, A part of an AB system, *J*=8.1, 6.2, 1.6 Hz, 1H), 6.49 (ddd, *J*=8.1, 6.1, 1.5 Hz, 1H), 5.20 (ddd, *J*=7.5, 4.5, 2.3 Hz, 1H), 4.70 (m, 1H), 4.60 (m, 1H), 2.65 (ddd, *J*=14.2, 8.1, 3.8 Hz, 1H), 1.24 (s, 3H), 1.40 (dt, *J*=14.2, 2.1 Hz, 1H); $\delta_C$ (100 MHz, $CDCl_3$) $\delta$ 172.1, 136.4, 130.7, 72.5, 72.0, 66.8, 34.1, 22.8; HRMS (EI): $(M+Na)^+$, found 193.0477. $C_8H_{10}O_4$ requires 193.0476.

### 3.5. *rel*-(1*R*,4*R*,5*R*)-2,5-dihydroxycyclohex-3-enyl acetate (7)[12]

To magnetically stirred slurry of thiourea (0.95 g 12.5 mmol) in methanol (20 mL) was added a solution of (2.15 g 12.5 mmol) endoperoxide acetate **6** in 50 mL of a mixture of $CH_2Cl_2$/$CH_3OH$ (1:9)

at room temperature. After the completion of addition (ca. 10 min), the mixture was stirred for 5 h and the solid was removed by filtration. The evaporation of the solvent gave diol **7** (2.15 g, 100%) as colorless crystals, mp 77–78 °C. Found: C, 55.69; H, 6.99. $C_8H_{12}O_4$ requires C, 55.81; H, 7.02; $\nu_{max}$ (KBr) 3350, 2920, 1440, 1190 $cm^{-1}$; $\delta_H$ (200 MHz, $D_2O$) 5.81 (br dd, $J$=10.1, 3.0 Hz, 1H), 5.74 (dd, $J$=10.1, 2.2 Hz, 1H), 4.92 (ddd, $J$=11.9, 7.2, 4.6 Hz, 1H), 4.74 (s, 2H (HOD)), 4.32 (dt, $J$=6.0, 3.8 Hz, 1H), 4.19–4.16 (m, 1H), 2.07 (s, 3H), 1.98–1.80 (m, 2H); $\delta_C$ (50 MHz, $D_2O$) 178.3, 134.7, 134.5, 77.1, 73.0, 68.4, 37.5, 25.2.

### 3.6. *rel*-(3a*R*,7*R*,7a*R*)-2-oxo-3-tosyl-2,3,3a,6,7,7a-hexahydrobenzol[*d*]oxazol-7-yl acetate (9)

*3.6.1. Preparation of palladium complex.* To a flask containing tris(dibenzylidenacetone)dipalladium–chloroform complex (0.382 g, 370 μmol) in anhydrous THF (25 mL) under nitrogen was added triisopropylphosphite (0.745 mL, 2.95 mmol). The mixture was stirred at room temperature for 30 min until a clear yellow solution was obtained.

*3.6.2. Cyclization of* ***7****.* To a stirred solution of diol **7** (4.3 g 25 mmol) in anhydrous THF (50 mL) under a nitrogen atmosphere at room temperature was added *p*-toluenesulfonyl isocyanate (7.65 mL, 50 mmol) dropwise. The final reaction mixture was stirred at room temperature for 5 h, heated to 80 °C, stirred for 60 min, and cooled to room temperature. During vigorous stirring, a solution of palladium complex prepared as described above in THF (25 mL) was added to the reaction mixture and heated to 80 °C, and kept for 4 h. After the removal of the solvent under reduced pressure, the residue was dissolved in $CH_2Cl_2$ (100 mL) and the organic phase was washed with saturated $NaHCO_3$ solution (2×50 mL), water (1×50 mL), and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by means of column chromatography on silica gel (120 g) by eluting with $CH_2Cl_2$/hexane (30:70) to afford oxazolidin-2-one monoacetate **9** (7.37 g, 84%) as white crystals, mp 110–111 °C. Found: C, 54.48; H, 4.66;N, 3.69; S, 8.88. $C_{16}H_{17}NO_6S$ requires C, 54.69; H, 4.88; N, 3.99; S, 9.13%; $\nu_{max}$ (KBr) 3133, 1794, 1602, 1243, 979 $cm^{-1}$; $\delta_H$ (200 MHz, $CDCl_3$) 7.92 (br d, A part of AA′BB′ system, $J$=8.4 Hz, 2H), 7.35 (br d, B part of AA′BB′ system, $J$=8.4 Hz, 2H), 6.10 (br d, A part of AB system, $J$=10.3 Hz, 1H), 5.91 (dt, B part of AB system, $J$=10.3, 3.9 Hz, 1H), 5.18 (dt, $J$=5.1, 4.7 Hz, 1H), 4.94 (br dd, A part of AB system, $J$=7.3, 1.7 Hz, 1H), 4.66 (dd, B part of AB system, $J$=7.3, 5.6 Hz, 1H), 2.53 (br d, $J$=18.3, 1H), 2.43 (s, 3H), 2.26 (dt, $J$=18.3, 4.1 Hz, 1H), 2.05 (s, 3H); $\delta_C$ (50 MHz, $CDCl_3$) 171.7, 153.0, 147.7, 136.9, 131.8, 130.5, 130.2, 124.4, 74.7, 68.8, 56.5, 27.5, 23.7, 22.9.

### 3.7. *rel*-(1*R*,2*R*,3*R*)-3-(4-Methylphenylsulfonamido)cyclohex-4-ene-1,2-diyl acetate (15)

A solution of oxazolidinone **9** (1 g, 2.85 mmol) in 50 mL of $CH_3OH$ was mixed with $K_2CO_3$ (0.466 g, 4.3 mmol). Upon completion of the reaction (TLC monitoring), the mixture was filtered and $CH_3OH$ was removed under reduced pressure to give **14**. The crude mixture was treated with excess of AcCl (15 mL) and stirred overnight at room temperature. The excess acetyl chloride was evaporated under reduced pressure and the residue was recrystallized from ethyl acetate/hexane (1:3) to give **15** (0.89 g, 85%) as white crystals, mp 149–150 °C. Found: C, 55.26; H, 5.94; N, 4.04; S, 8.56. $C_{17}H_{21}NO_6$ requires C, 55.57; H, 5.76; N, 3.81; S, 8.73%; $\nu_{max}$ (KBr) 3566, 3276, 3048, 2954, 1745, 1394, 1249 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.74 (br d, A part of AA′BB′ system, $J$=8.4 Hz, 2H), 7.29 (br d, B part of AA′BB′ system, $J$=8.4 Hz, 2H), 5.64 (ddt, $J$=9.9, 3.7, 1.5 Hz, 1H), 5.37–5.28 (m, 2H), 5.13 (dt, $J$=8.5, 6.1 Hz, 1H), 4.87 (dd, $J$=8.7, 4.7 Hz, 1H), 4.22–4.15 (m, 1H), 2.59–2.44 (m, 1H), 2.42 (s, 3H), 2.1–2.0 (m, 1H), 2.03 (s, 3H), 1.98 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 172.2, 172.1, 145.4, 140.3, 131.7, 129.1, 128.0, 126.2, 71.8, 68.7, 51.6, 31.2, 23.5, 23.1, 22.8.

### 3.8. *rel*-(1*R*,2*R*,3*R*,4*R*,5*S*)-3-(4-Methylphenylsulfonamido)-cyclohexane-1,2,4,5-tetrayl tetraacetate (17)

To a solution of *N*-methylmorpholine *N*-oxide (502 mg, 4.3 mmol) in water (5 mL) was added a solution of **15** (1.0 g, 2.72 mmol) in THF (20 mL). Then, the mixture was cooled to −5 °C, $OsO_4$ (3.0 mg, 0.0118 mmol) was added under a nitrogen atmosphere and continued stirring for 20 h. After the completion of the reaction, the mixture was treated with $NaHSO_3$ (750 mg), water (6 mL), and stirred for 3 h. Then, Celite (4 g) was added and slurry was stirred for 1 h. The mixture was filtered and the solid was washed with acetone (2×30 mL). The organic layers were combined and solvents were removed under vacuum. The crude mixture was dissolved in $CH_2Cl_2$ and acetyl chloride (6 mL) and stirred at room temperature for 10 h. After the solvent was evaporated, the tetraacetate **17** was recrystallized from ethyl acetate/hexane (1:3) to give white crystals (1.17 g, 88%), mp 150–151 °C. Found C, 51.74; H, 5.81; N, 3.25; S, 6.29. $C_{21}H_{27}NO_{10}S$ requires C, 51.95; H, 5.61; N, 2.88; S, 6.60%; $\nu_{max}$ (KBr) 3564, 3276, 2945, 1745, 1394, 1249 $cm^{-1}$; $\delta_H$ (200 MHz $CDCl_3$) 7.71 (d, A part of AA′BB′ system, $J$=8.2 Hz, 2H), 7.27 (d, B part of AA′BB′ system, $J$=8.2 Hz, 2H), 5.96 (br s, 1H), 5.32–5.25 (m, 1H), 5.13 (dd, $J$=8.0, 3.1 Hz, 1H), 5.04–4.92 (m, 2H), 4.02 (dt, $J$=8.4, 3.3 Hz, 1H), 2.39 (s, 3H), 2.13–1.92 (m, 2H), 2.03 (s, 3H), 2.00 (s, 3H), 1.94 (s, 3H), 1.92 (s, 3H); $\delta_C$ (50 MHz, $CDCl_3$) 172.2, 171.9, 171.8, 171.5, 145.5, 139.8, 131.7, 129.1, 72.9, 71.4, 69.5, 69.0, 53.1, 30.3, 23.4, 22.9, 22.8, 22.6.

### 3.9. *rel*-(1*R*,2*R*,3*R*,5*S*,6*R*)-(4-Methyl-*N*-2,3,5,6-tetrahydroxycyclohexyl)benzenesulfonamide (18)

*3.9.1. Method A.* Dry $NH_3$ was passed through a solution tetraacetate **17** (1.0 g, 2.06 mmol) in absolute methanol (50 mL) at 0 °C for 12 h. After removal of methanol and the acetamide, DL-*gala*-aminoquercitol **18** was obtained as a white powder (0.65 g, 98%, recrystallized from ethanol to give white powder, mp 192–193 °C). Found: C, 48.90; H, 6.07; N, 4.65; S, 9.84. $C_{13}H_{19}NO_6S$ requires C, 49.20; H, 6.03; N, 4.41; S, 10.10%; $\nu_{max}$ (KBr) 3480, 1431, 1309, 1286, 1160, 1110 $cm^{-1}$; $\delta_H$ (400 MHz, $CD_3OD$) 7.79 (d, A part of AA′BB′ system, $J$=8.1 Hz, 2H), 7.35 (d, B part of AA′BB′ system, $J$=8.1 Hz, 2H), 3.96 (m, 1H), 3.78 (br s, 1H), 3.64 (br s, 2H), 3.52 (br s, 1H), 2.41 (s, 3H), 1.90–1.78 (m, 2H); $\delta_C$ (100 MHz, $CD_3OD$) 145.1, 136.3, 130.0, 127.2, 70.7, 70.4, 68.7, 67.4, 55.8, 32.4, 20.7.

*3.9.2. Method B.* A solution of tetraacetate **17** (1.0 g, 2.06 mmol) in methanol (50 mL) was mixed with $K_2CO_3$ (28 mg, 0.21 mmol) and stirred at room temperature for 10 h. The reaction mixture was filtered and the solvent removed under reduced pressure to give DL-*gala*-aminoquercitol **18** in 95% yield.

Crystallographic data (excluding structure factors) for the structure **18** in this paper was deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 734309. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax:+44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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## Supplementary data

$^{1}H$ and $^{13}C$ NMR spectra for all new compounds (18 pages) and crystallographic data for compound **18** are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.03.028.

## References and notes


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