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Diastereoselective Synthesis of *C*-Glycosylnorbornenones

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Abstract: Thermal reaction of (*E*)-3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-*C*-nitro-D-*galacto*- (**1a**) and -D-*manno*-hept-1-enitol (**1b**) with 2-methyl-3,4-diaryl-5-phenylcyclopentadienones (**2a-c**) afforded diastereoselectively 1-methyl-2,3-diaryl-4-phenyl-(5*S*,6*R*)-5-*exo*-(D-*galacto*- (**3a-c**) and -(5*R*,6*S*)-5-*exo*-(D-*manno*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-ones (**6a-c**) and variable amounts of the 1-phenyl-4-methyl regioisomers **4a-c** and **7a-c**, depending upon the *p*-substituent in the aryl moiety. 1-*C*-Arylalditols **5**, **8-9** are also obtained in refluxing xylene.

INTRODUCTION

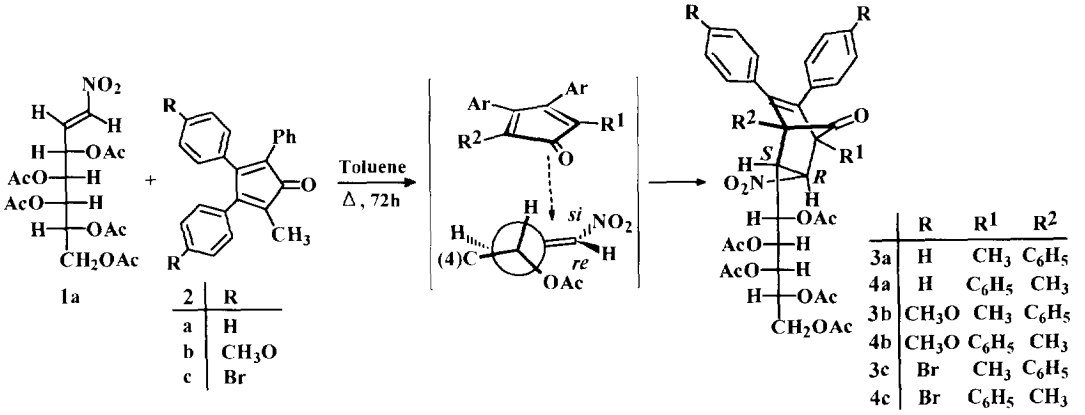
C-Glycosides[1] are important as new drugs as well as organic synthetic tools. Some examples of both naturally occurring and synthetic *C*-glycosyl derivatives, specially those bearing arylic aglycones,[2] have shown potent antitumor activity.[3] Moreover, their use as chiral synthons allow the synthesis of enantiomerically pure intermediates useful in synthesis.[4] In this field, sugar-derived alkenes have been employed as dienophiles in stereocontrolled Diels-Alder cycloadditions.[5-9] Specifically, uncatalysed reactions of acyclic sugar dienophiles to cyclopentadienes give in general moderate levels of asymmetric induction,[5-7] but the diastereoselectivity is high in a few cases, specially when Lewis-acid catalyzed conditions are employed[5] or in the reactions of substituted butadienes to acyclic sugar dienophiles.[8]

We have previously reported that 1-nitroalkenyl sugar dienophiles react with 1,3-dipoles affording glycosyl pyrazoles and pyrroles,[9] and react with tetracyclones to give the corresponding arylalditols in one step.[10] In this paper we now report on thermal cycloadditions of (*E*)-3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-*C*-nitro-D-*galacto*-hept-1-enitol (**1a**) and (*E*)-3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-*C*-nitro-D-*manno*-hept-1-enitol (**1b**) to 2-methyl-3,4-diaryl-5-phenylcyclopentadienones (**2a-c**) which afford diastereoselectively new polysubstituted 5-*C*-glycosylbicyclo[2.2.1]hept-2-en-7-ones (**3a-c**, **4a-c**, **6a-c**, and **7a-c**). Some of these compounds are converted by pyrolysis into new 1-*C*-arylalditols (**5**, **8-9**), that can be obtained as well in one step from **1a-b** and **2a** in refluxing xylene.

RESULTS AND DISCUSSION

The reaction of (*E*)-D-*galacto*-3,4,5,6,7-pentaacetoxy-1-nitrohept-1-ene (**1a**) and 2-methyl-3,4,5-triphenylcyclopentadienone (**2a**) in boiling toluene for 72 h afforded, after column chromatography of the reaction mixture, a colorless crystalline solid **3a** as the main product, and a colorless amorphous solid **4a** as by-product. Unreacted **1a** and **2a** were also recovered. MS, IR and analytical data showed that **3a** and **4a** were

isomers. In addition, ^{1}H and ^{13}C NMR spectra showed, besides a similar number of signals for both **3a** and **4a**, different but related signals for each proton and carbon atom of **3a** and **4a**, thus confirming that both compounds were Diels-Alder cycloadducts. Differences between chemical shifts in ^{1}H NMR spectra of protons originally belonging to the dienophilic double bond in **1a** permitted to make evident that **3a** and **4a** were regioisomers, having a CH_3-C-CH(6)-NO_2 group [δ 5.55($J_{5,6}$=3.5Hz) for H-6], and a C_6H_5-C-CH(5)-sugar-chain [δ 3.45 for H-5] in **3a**, and a C_6H_5-C-CH(6)-NO_2 group [δ 6.51 ($J_{5,6}$=2.5Hz) for H-6] besides a CH_3-C-CH(5)-sugar-chain [δ 3.05 for H-5] in **4a**. Because the reaction of **1a** and **2a** may afford up to eight possible structures for the reaction products, the existence of two regioisomers as the only reaction products can be explained by considering a unique transition state for the reaction. In this way, an attack of **2a** on the less hindered C-1 *si* face of **1a**, in its presumably most stable conformer,[8b] can be postulated. Because both faces of the cyclopentadienone are diastereotopic, methyl and phenyl groups (R^1 and R^2) from cyclopentadienone **2a** can be interchanged in the transition state of the reaction, thus affording regioisomers **3a**, obtained in 55% yield, and **4a**, obtained in 29% yield, as is shown in Scheme 1.



Scheme 1

The reaction was accelerated by sonication, but yields and ratio between products remained unchanged. Therefore, the reaction is partially regioselective, affording a 1.9:1 ratio between products **3a** and **4a**. This is probably due to electronic rather than steric factors,[11] which favor **3a** over the less hindered **4a**.

When 3,4-bis(*p*-substitutedphenyl)cyclopentadienones (**2b,c**) were used instead of **2a**, the corresponding reactions with **1a** afforded, in each case, two regioisomers which were obtained as the only reaction products, but regioselectivity changed according to the nature of aryl substituents. The reaction of **1a** and 3,4-di(*p*-methoxyphenyl)substituted cyclopentadienone **2a** showed no regioselectivity [1:1.1 ratio for products **3b** (36% yield) and **4b** (40% yield)], but improved regioselectivity [2.5:1 ratio for products **3c** (45% yield) and **4c** (18% yield)] was obtained when **1a** reacted to 3,4-bis(*p*-bromophenyl) derivative **2c**, as is shown in Scheme 1.

Single crystal X-Ray diffractometry of **3a** afforded the absolute stereochemistry of (5*S*,6*R*)-1-methyl-2,3,4-triphenyl-5-*exo*-(D-*galacto*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one(**3a**), being the second product the corresponding regioisomer (5*S*,6*R*)-1,2,3-triphenyl-4-methyl-5-*exo*-(D-*galacto*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (**4a**). The X-ray analysis of compound **3a** confirmed our hypothesis regarding the positions of the linkage of the nitro-group and of the sugar chain. The sugar chain in **3a** is disposed in all-trans conformation, as showed by the dihedral angles C5-C27-C30-C33, C27-C30-C33-C36, and C30-C33-C36-C39, which have values of 179(1), -179(1), and 176(1)°

respectively. Figure 1 shows the ORTEP view of the molecular structure[12] of **3a**.

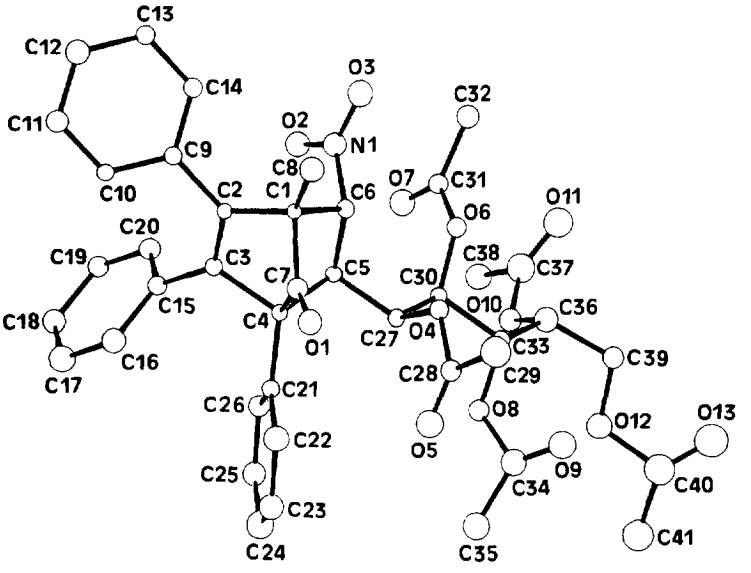
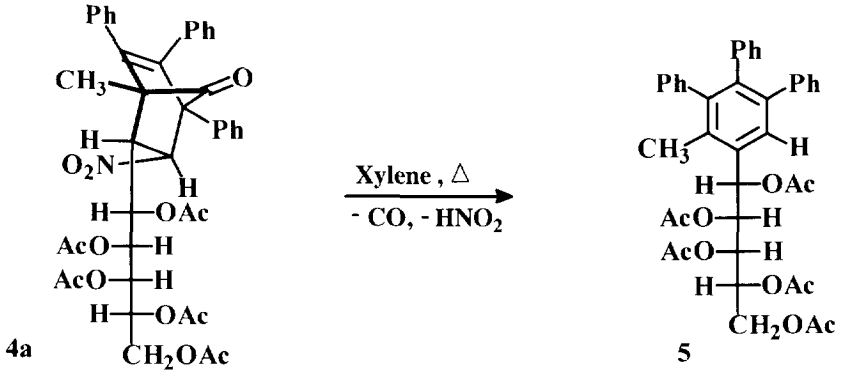


Figure 1

When the reaction of nitroalkenyl sugar **1a** and cyclopentadienone **2a** was conducted in refluxing xylene for 72 h, product **3a** was obtained in lower yield (42%) but instead of **4a**, that was not obtained, a new product **5** was obtained. The ^{1}H and ^{13}C NMR spectra of **5** only showed signals corresponding to the sugar chain and the aromatic moiety. IR, MS and analytical data confirmed, besides the loss of CO, the elimination of HNO_2 from **4a**, thus affording 1-*C*-(2-methyl-3,4,5-triphenylphenyl)-D-*galacto*-penta-*O*-acetylpentitol (**5**), obtained in 27% yield. Compound **5** is obtained quantitatively by refluxing **4a** in xylene for 5 h, as is seen in Scheme 2. On the contrary, **3a** showed remarkable thermal stability until its melting point (198°C), in which it decomposed. Unfortunately, when reactions of formation of products **3b-c** and **4b-c** were conducted in boiling xylene for 72 h (also by refluxing **3b-c** or **4b-c** in xylene), only decomposition was observed in each case.

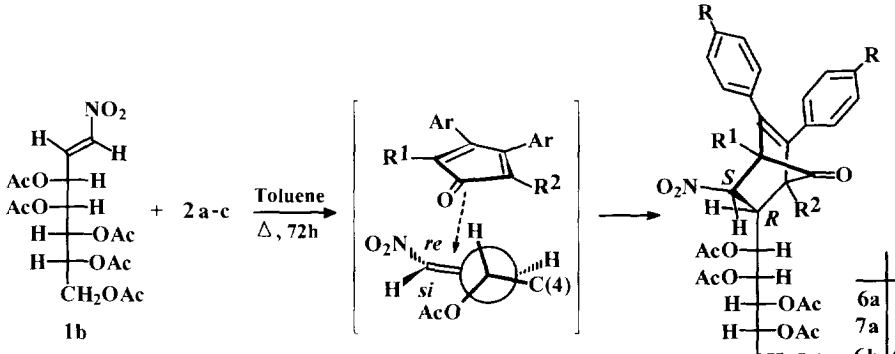


Scheme 2

The geometry of the obtained products **3a-c**, **4a-c** matched with the predictions made by Franck[13] for simpler Diels-Alder cycloadditions. With the aim to expand the possibilities offered by these findings, the (*E*)-

3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-*C*-nitro-D-*manno*-hept-1-enitol (**1b**), whose configuration of the allylic chiral center is the opposite to **1a**, was subjected to reaction. Thus, when **1b** was allowed to react with cyclopentadienone **2a**, a colorless crystalline solid **6a** was obtained as the main product, and a colorless amorphous solid **7a** as by-product. As in the former case, spectral and analytical data showed that **6a** and **7a** were regioisomers obtained from the Diels-Alder cycloaddition. In each case, differences between chemical shifts in ^{1}H NMR spectra of protons originally belonging to the dienophilic double bond in **1b** were conclusive for the assignation of structures. For instance, a CH_3-C-CH(6)-NO_2 group [δ 5.32($J_{5,6}$=4.6Hz) for H-6] and a C_6H_5-C-CH(5)-sugar-chain [δ 3.52 for H-5] in **6a**, besides a C_6H_5-C-CH(6)-NO_2 group [δ 6.24($J_{5,6}$=3.7Hz) for H-6] and a CH_3-C-CH(5)-sugar-chain [δ 3.14 for H-5] in **7a** could be settled for the obtained *C*-glycosylnorbornenones **6a**, obtained in 51% yield, and **7a**, obtained in 45% yield [1.1:1 ratio for **6a**:**7a**]. As in the case of **1a**, we have considered a unique transition state for the reaction to explain the obtention of regioisomers **6a** and **7a**. In this manner, an attack of **2a** on the less hindered C-1 *re* face of **1b**, in its presumably most stable conformer,[8b] is postulated. Both diastereotopic faces of **2a** may attack, therefore methyl and phenyl groups (R^1 and R^2) from cyclopentadienone **2a** can be interchanged in the transition state of the reaction, which afford regioisomers **6a** and **7a**, as is shown in Scheme 3. Although in this case the overall yield was the highest obtained in these reactions, regioselectivity was very poor, probably because steric restrictions equilibrated electronic factors, making disappear regioselectivity. Yield and ratio between products were not modified by sonication of the reaction.

Analogously, when **1b** was treated with 3,4-bis(*p*-substitutedphenyl)cyclopentadienones (**2b,c**), the corresponding reactions afforded, in each case, two regioisomers. The reaction of **1b** and 3,4-bis(*p*-methoxyphenyl)substituted cyclopentadienone **2a** afforded products **6b** (38% yield) and **7b** (37% yield) [1:1 ratio]. The corresponding reaction of **1b** and 3,4-bis(*p*-bromophenyl) derivative **2c** afforded products **6c** (23% yield) and **7c** (19% yield) [1.2:1 ratio] as is shown in Scheme 3.



	R	R^1	R^2
6a	H	CH_3	C_6H_5
7a	H	C_6H_5	CH_3
6b	CH_3O	CH_3	C_6H_5
7b	CH_3O	C_6H_5	CH_3
6c	Br	CH_3	C_6H_5
7c	Br	C_6H_5	CH_3

Scheme 3

Single crystal X-Ray diffractometry of **6a** afforded the absolute stereochemistry of (5*R*,6*S*)-1-methyl-2,3,4-triphenyl-5-*exo*-(D-*manno*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (**6a**), being the second product the corresponding regioisomer (5*R*,6*S*)-1,2,3-triphenyl-4-methyl-5-*exo*-(D-*manno*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (**7a**). The X-ray analysis of compound

6a confirmed our hypothesis regarding the positions of the linkage of the nitro-group and of the sugar chain. Figure 2 shows the ORTEP view of the molecular structure[12] of **3a**.

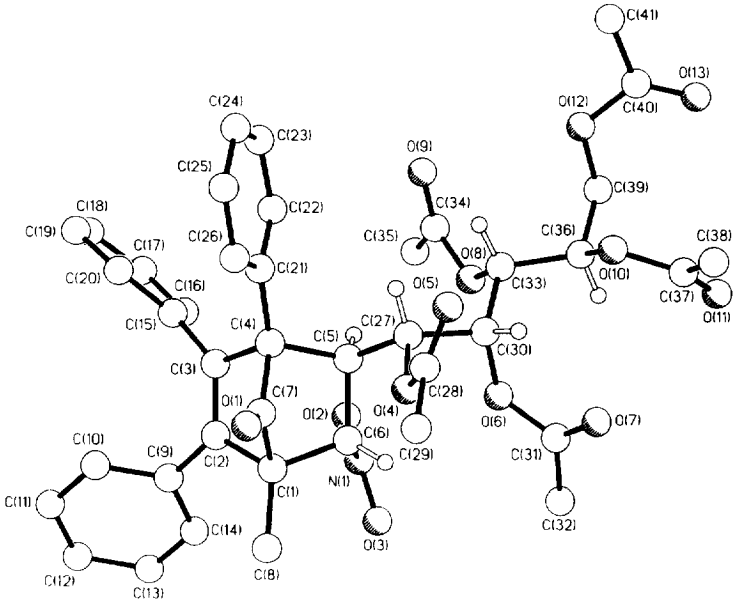


Figure 2

There is evidence for a fairly strong intramolecular C-H···O interaction between the C6 methine proton and the oxygen atom O4 of the adjacent acetate group. The C6···O4 and H6···O4 distances are 2.68 and 2.23Å respectively; the C-H···O angle is 108°. There is an accompanying increase from a normal gauche relationship of the H27-C27-C5-H5 torsion angle to a value of 79°. Figure 3 shows the ORTEP view of a partial structure of **6a** that corresponds to the atoms involved in the explained interaction.

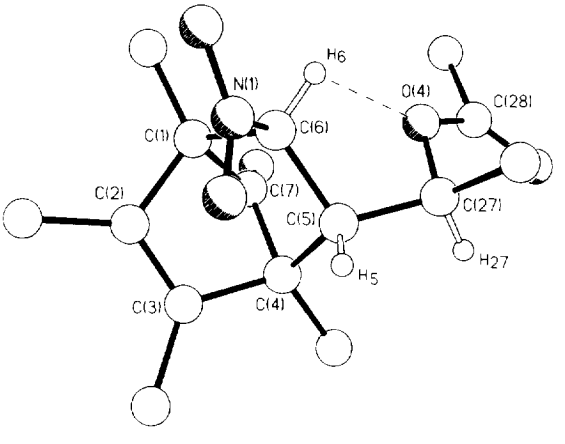
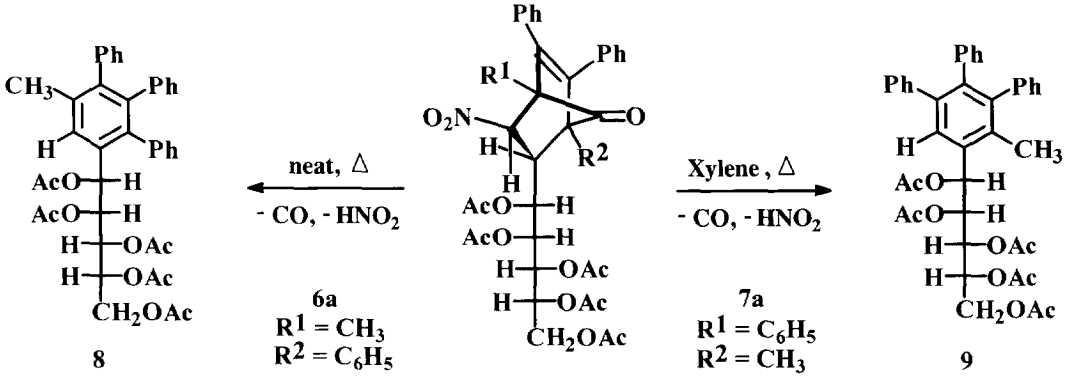


Figure 3

When the reaction of nitroalkenyl sugar **1b** and cyclopentadienone **2a** was conducted in refluxing xylene for 72 h, product **6a** was obtained in only 16% yield. Instead of **7a**, that was not obtained, two new products **8** and **9** were obtained. The ^{1}H and ^{13}C NMR spectra of **8** and **9** showed, in each case, signals corresponding

to the sugar chain and the aromatic moieties. IR, MS and analytical data confirmed, besides the loss of CO, the elimination of HNO_2 in both compounds, that were regioisomers. Compound **8** was obtained quantitatively from **6a**, by heating the neat compound in an oil bath or by refluxing a solution of **6a** in xylene for 20h. Thus the structure 1-*C*-(2,3,4-triphenyl-5-methylphenyl)-D-*manno*-penta-*O*-acetylpentitol was assigned to **8**, obtained from **1b** in 39% yield. Compound **9** was obtained quantitatively by refluxing **7a** in xylene for 5 h, therefore the structure 1-*C*-(2-methyl-3,4,5-triphenylphenyl)-D-*manno*-penta-*O*-acetylpentitol was assigned to **9**, obtained from **1b** in 34% yield. Scheme 4 shows both pyrolysis reactions. Unfortunately, when reactions of formation of products **6b-c** and **7b-c** were conducted in boiling xylene for 72 h (also by refluxing **6b-c** or **7b-c** in xylene), only decomposition was observed in each case.



Scheme 4

Evidence for all the assigned structures was provided by spectroscopic and analytical data. The assignment of the ^1H and ^{13}C NMR signals corresponding to the sugar moiety in all new compounds has been made as described in ref.[14]. The assignments are in agreement with those found in the bibliography for other 1-*C*-substituted alditols.[15] Chemical shifts and coupling constants in the ^1H NMR spectra of all new compounds are compiled in Tables 1, 2 and 4 and ^{13}C NMR data of the same compounds in Tables 3 and 5. In all of the cases studied, the electron-releasing and -withdrawing effects of *p*-methoxy and *p*-bromo groups in the cyclopentadienones **2b-c** give rise to a decrease in the yields of these reactions.

In all the reactions conducted in toluene that we have studied, the observed stereoselectivity differs from the described in literature for reactions of **1a-b** and cyclopentadiene[6-7] (where mixtures of 5-*exo*- and 5-*endo*-nitro compounds are obtained, the latter being favored) and the described for reactions of (*E*)-2,3-unsaturated sugar carboxylates and cyclopentadiene[5] (where *exo*-carboxylate products are favored as a result of an opposite facial selectivity). Furthermore, the geometric and facial selectivities obtained in our reactions are similar to those described for reactions of **1a-b** and substituted butadienes[8] (where geometry of products depend on the configuration of the allylic carbon of dienophile) or in Lewis-acid catalyzed cycloadditions of arabinose-derived dienophiles and cyclopentadiene[5] (where *endo*-carboxylate products are obtained). We have found modest to poor regioselectivity in the reported reactions, but, on the other side, the total diastereoselectivity found in these reactions is really uncommon for uncatalysed Diels-Alder reactions of open chain sugar dienophiles, and can be employed with synthetic purposes. These reactions extend the current methodology for the preparation of open chain *C*-glycosides by opening a straightforward route to new and potentially useful *C*-glycosylnorbornenones and 1-*C*-arylalditols.

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EXPERIMENTAL

Melting points were determined with a Gallenkamp MFB-595 apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 MC polarimeter at 18±2°C. IR spectra were measured with Perkin-Elmer 399 and 1310 spectrophotometers. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC200-E spectrometer; chemical shifts are reported in ppm relative to tetramethylsilane as internal standard, coupling constants in Hz. Methyl, methylene and methine groups, as well as quaternary carbon atoms, were discriminated in the ^{13}C-NMR spectra by DEPT experiments. Mass spectral data were taken at the Service of Spectroscopy, Imperial College of Science, Technology and Medicine, London (U.K.), at 70 eV. Elemental analyses were performed with a Perkin Elmer 240-B apparatus. Sonication of reactions was performed with a Vibra Cell 375 Watt sonicator, with a 13 mm probe at high intensity.

General Procedure for the Synthesis of 2-methyl-3,4-diaryl-5-phenylcyclopentadienones 2a-c: 2-Methyl-3,4,5-triphenylcyclopentadienone **2a** (5.5 g, 70%) was prepared from benzil (5g, 24 mmol) and 1-phenyl-2-butanone (6 ml, 41 mmol), following the method of Allen and Van Allan.[16] The same procedure was used for the preparation of **2b-c**. Thus, reaction of bis(*p*-methoxy)benzil (5 g, 18.5 mmol) and 1-phenyl-2-butanone (5.5 ml, 37 mmol) afforded **2b** (6.15 g, 87%) and reaction of bis(*p*-bromo)benzil (3 g, 8.1 mmol) and the latter ketone, 1-phenyl-2-butanone (1.21 g, 8.2 mmol), afforded **2c** (3.05 g, 78%).

2-Methyl-3,4-bis(*p*-methoxyphenyl)-5-phenylcyclopentadienone (2b): Red needles from ethanol, mp 149-150°C; IR ν_{max} 1700 (C=O) and 1600 cm^{-1} (C=C); ^{1}H NMR δ ($CDCl_3$) 1.91(s, 3H, CH_3), 7.20(s, 5H, C_6H_5), 6.65-6.94(m, 8H, 2xC_6H_4), 3.75(s, 3H, OCH_3), 3.80(s, 3H, OCH_3); ^{13}C NMR δ ($CDCl_3$) 8.8(CH_3), 55.1(OCH_3), 55.2(OCH_3), 113.1, 113.2, 126.9, 127.9, 129.8, 130.5, 131.0 ($CH_{aromatic}$), 123.1, 124.7, 125.5, 131.5, 152.6, 154.1, 159.4, 159.6 (*quaternary* C), 201.8(C=O); MS (EI, 75 eV) m/z (%) 382 (100, $M^{+\cdot}$), 367 (6, M-CH_3), 354 (32, M-CO), 238 (25), 208 (80, *p*-$CH_3OC_6H_4C{\equiv}CC_6H_5$), 28 (47). Anal. Calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C 81.59; H 5.92.

2-Methyl-3,4-bis(*p*-bromophenyl)-5-phenylcyclopentadienone (2c): Red needles from ethanol, mp 199-200°C; IR ν_{max} 1710 (C=O) and 1580 cm^{-1} (C=C); ^{1}H NMR δ ($CDCl_3$) 1.89(s, 3H, CH_3), 7.21(m, 5H, C_6H_5), 6.74-7.45(m, 8H, 2xC_6H_4); ^{13}C NMR δ ($CDCl_3$) 8.75(CH_3), 127.6, 128.1, 129.7, 130.4, 130.5, 130.8, 131.2, 131.4 ($CH_{aromatic}$), 122.7, 123.0, 124.6, 126.1, 131.7, 131.8, 151.6, 152.5 (*quaternary* C), 201.0(C=O); MS (EI, 75 eV) m/z (%) 480 (100, $M^{+\cdot}$), 465 (2, M-CH_3), 452 (40, M-CO), 336 (32), 258 and 256 (85, *p*-$BrC_6H_4C{\equiv}CC_6H_5$), 176 (52). Anal. Calcd for $C_{24}H_{16}OBr_2$: C, 60.03; H, 3.36. Found: C 59.96; H 3.39.

General Procedure for the Synthesis of 5-*C*-glycosylnorbornenones 3a-c, 4a-c, 6a-c, and 7a-c: Nitroalkenyl sugar **1a** or **1b** (1.75 g, 4.04 mmol), prepared from D-galactose[17] or D-mannose[18], and the corresponding cyclopentadienone **2a-c** (4.66 mmol), were dissolved in toluene (150 ml) at room temp. The resulting solution was refluxed for 72 h. Then the mixture was evaporated to dryness. The products were separated by column chromatography (length 120 cm, diameter 5 cm), silica gel type 60 (Merck) with benzene/ethyl acetate (7:1) as the eluent.

(5*S*,6*R*)-1-Methyl-2,3,4-triphenyl-5-*exo*-(D-*galacto*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]-hept-2-en-7-one (3a): Colorless prisms from ethanol (1.68g, 55%), mp 196-198°C; $[\alpha]_D$ -8; $[\alpha]_{578}$ -9; $[\alpha]_{546}$ -10; $[\alpha]_{436}$ -20 (c 1.7, $CHCl_3$); IR (KBr) ν_{max} 1753 (C=O), 1552 (NO_2), 1220 and 1035 (C-O-C), 703 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 755 (1, $M^{+\cdot}$), 680 (4), 398(9), 331 (100), 322(46). Anal. Calcd for $C_{41}H_{41}O_{13}N$: C, 65.16; H, 5.47; N, 1.85. Found: C 65.19; H 5.51; N, 1.80.

(5*S*,6*R*)-1,2,3-Triphenyl-4-methyl-5-*exo*-(D-*galacto*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]-hept-2-en-7-one (4a): Sticky solid (0.88g, 29%); $[\alpha]_D$ -18; $[\alpha]_{578}$ -19; $[\alpha]_{546}$ -22; $[\alpha]_{436}$ -36 (c 4.0, $CHCl_3$); IR (neat) ν_{max} 1753 (C=O), 1552 (NO_2), 1212 and 1035 (C-O-C), 703 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 680 (10, M-[CO+HNO_2]), 398(28), 349 (100). Anal. Calcd for $C_{41}H_{41}O_{13}N$: C, 65.16; H, 5.47; N, 1.85. Found: C 65.23; H 5.53; N, 1.79.

(5*S*,6*R*)-1-Methyl-2,3-bis(4-methoxyphenyl)-4-phenyl-5-*exo*-(D-*galacto*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (3b): Sticky solid (1.18g, 36%); $[\alpha]_D$ -20; $[\alpha]_{578}$ -21; $[\alpha]_{546}$ -24; $[\alpha]_{436}$ -64 (c 2.0, $CHCl_3$); IR (neat) ν_{max} 1753 (C=O), 1552 (NO_2), 1259 and 1020 (C-O-C), 803 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 727 (10), 686 (12), 477(63), 413 (100), 393(95). Anal. Calcd for $C_{43}H_{45}O_{15}N$: C, 63.31; H, 5.56; N, 1.72. Found: C 63.23; H 5.61; N, 1.67.

(5*S*,6*R*)-1-Phenyl-2,3-bis(4-methoxyphenyl)-4-methyl-5-*exo*-(D-*galacto*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (4b): Sticky solid (1.32g, 40%); $[\alpha]_D$ -37; $[\alpha]_{578}$ -41; $[\alpha]_{546}$ -53; $[\alpha]_{436}$ -97 (c 2.0, $CHCl_3$); IR (neat) ν_{max} 1753 (C=O), 1552 (NO_2), 1212 and 1027 (C-O-C), 734 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 477(16), 416 (53), 385(100). Anal. Calcd for $C_{43}H_{45}O_{15}N$: C, 63.31; H, 5.56; N, 1.72. Found: C 63.19; H 5.64; N, 1.62.

(5*S*,6*R*)-1-Methyl-2,3-bis(4-bromophenyl)-4-phenyl-5-*exo*-(D-*galacto*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (3c): Sticky solid (1.66g, 45%); $[\alpha]_D$ -11; $[\alpha]_{578}$ -12; $[\alpha]_{546}$ -14; $[\alpha]_{436}$ -19 (c 0.5, $CHCl_3$); IR (neat) ν_{max} 1753 (C=O), 1552 (NO_2), 1212 and 1035 (C-O-C), 734 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 633 (15), 543(37), 515 (100). Anal. Calcd for $C_{41}H_{39}O_{13}NBr_2$: C, 53.90; H, 4.30; N, 1.53. Found: C 53.78; H 4.22; N, 1.55.

(5*S*,6*R*)-1-Phenyl-2,3-bis(4-bromophenyl)-4-methyl-5-*exo*-(D-*galacto*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (4c): Sticky solid (0.66g, 18%); $[\alpha]_D$ -38; $[\alpha]_{578}$ -39; $[\alpha]_{546}$ -41; $[\alpha]_{436}$ -48 (c 2.0, $CHCl_3$); IR (neat) ν_{max} 1807 and 1753 (C=O), 1552 (NO_2), 1212 and 1033 (C-O-C), 803 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 772 (23), 635 (63), 586(29), 549 (100). Anal. Calcd for $C_{41}H_{39}O_{13}NBr_2$: C, 53.90; H, 4.30; N, 1.53. Found: C 53.68; H 4.20; N, 1.57.

(5*R*,6*S*)-1-Methyl-2,3,4-triphenyl-5-*exo*-(D-*manno*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]-hept-2-en-7-one (6a): Colorless prisms from ethanol (1.55g, 51%), mp 113-115°C; $[\alpha]_D$ +65; $[\alpha]_{578}$ +69; $[\alpha]_{546}$ +78; $[\alpha]_{436}$ +103 (c 2.5, $CHCl_3$); IR (KBr) ν_{max} 1753 and 1683 (C=O), 1552 (NO_2), 1212 and 1050 (C-O-C), 703 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 680 (1, M-[CO+HNO_2]), 398(9), 331 (36), 43 (100). Anal. Calcd for $C_{41}H_{41}O_{13}N$: C, 65.16; H, 5.47; N, 1.85. Found: C 65.09; H 5.53; N, 1.81.

(5*R*,6*S*)-1,2,3-Triphenyl-4-methyl-5-*exo*-(D-*manno*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]-hept-2-en-7-one (7a): Sticky solid (1.37g, 45%); $[\alpha]_D$ +130; $[\alpha]_{578}$ +136; $[\alpha]_{546}$ +154; $[\alpha]_{436}$ +240 (c 3.5, $CHCl_3$); IR (neat) ν_{max} 1753 (C=O), 1552 (NO_2), 1228 and 1073 (C-O-C), 703 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 755 (1, $M^{+\cdot}$), 680 (1), 322(70), 170 (80), 43 (100). Anal. Calcd for $C_{41}H_{41}O_{13}N$: C, 65.16; H, 5.47; N, 1.85. Found: C 65.05; H 5.42; N, 1.88.

(5*R*,6*S*)-1-Methyl-2,3-bis(4-methoxyphenyl)-4-phenyl-5-*exo*-(D-*manno*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (6b): Sticky solid (1.25g, 38%); $[\alpha]_D$ +195; $[\alpha]_{578}$ +202; $[\alpha]_{546}$ +228; $[\alpha]_{436}$ +335 (c 1.0, $CHCl_3$) IR (neat) ν_{max} 1750 (C=O), 1550 (NO_2), 1220 and 1020 (C-O-C), 740 cm^{-1} (Ar). Anal. Calcd for $C_{43}H_{45}O_{15}N$: C, 63.31; H, 5.56; N, 1.72. Found: C 63.22; H 5.63; N, 1.62.

(5*R*,6*S*)-1-Phenyl-2,3-bis(4-methoxyphenyl)-4-methyl-5-*exo*-(D-*manno*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (7b): Sticky solid (1.22g, 37%); $[\alpha]_D$ +168; $[\alpha]_{578}$ +174; $[\alpha]_{546}$ +197; $[\alpha]_{436}$ +288 (c 1.0, $CHCl_3$); IR (neat) ν_{max} 1750 (C=O), 1555 (NO_2), 1225 and 1050 (C-O-C), 740 cm^{-1} (Ar). Anal. Calcd for $C_{43}H_{45}O_{15}N$: C, 63.31; H, 5.56; N, 1.72. Found: C 63.20; H 5.42; N, 1.61.

(5*R*,6*S*)-1-Methyl-2,3-bis(4-bromophenyl)-4-phenyl-5-*exo*-(D-*manno*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (6c): Sticky solid (0.85g, 23%); $[\alpha]_D$ +54; $[\alpha]_{578}$ +57; $[\alpha]_{546}$ 65°; $[\alpha]_{436}$ 108 (c 1.0, $CHCl_3$); IR (neat) ν_{max} 1779 (C=O), 1552 (NO_2), 1212 and 1050 (C-O-C), 734 cm^{-1} (Ar). Anal. Calcd for $C_{41}H_{39}O_{13}NBr_2$: C, 53.90; H, 4.30; N, 1.53. Found: C 53.70; H 4.38; N, 1.48.

(5*R*,6*S*)-1-Phenyl-2,3-bis(4-bromophenyl)-4-methyl-5-*exo*-(D-*manno*-penta-*O*-acetylpentitol-1-yl)-6-*endo*-nitrobicyclo[2.2.1]hept-2-en-7-one (7c): Sticky solid (0.70g, 19%); $[\alpha]_D$ +85; $[\alpha]_{578}$ +89; $[\alpha]_{546}$ +101°; $[\alpha]_{436}$ +159 (c 1.0, $CHCl_3$); IR (neat) ν_{max} 1753 (C=O), 1552 (NO_2), 1212 and 1050 (C-O-C), 734 cm^{-1} (Ar). Anal. Calcd for $C_{41}H_{39}O_{13}NBr_2$: C, 53.90; H, 4.30; N, 1.53. Found: C 53.71; H 4.41; N, 1.53.

Synthesis of 1-*C*-arylalditols 5, 8, and 9: Nitroalkenyl sugar **1a** or **1b** (1.75 g, 4.04 mmol) and the corresponding cyclopentadienone **2a-c** (4.66 mmol), were dissolved in xylene (150 ml) at room temp. The resulting solution was refluxed for 72 h. Then the mixture was evaporated to dryness. The products were separated by column chromatography (length 120 cm, diameter 5 cm), silica gel type 60 (Merck) with benzene-/ethyl acetate (7:1) as the eluent.

1-*C*-(2-Methyl-3,4,5-triphenylphenyl)-D-*galacto*-penta-*O*-acetylpentitol (5): Colorless prisms from ethanol (0.74g, 27%), mp 160°C; $[\alpha]_D$ +122; $[\alpha]_{578}$ +128; $[\alpha]_{546}$ +149; $[\alpha]_{436}$ +286 (c 4.5, $CHCl_3$); IR (KBr) ν_{max} 1745 (C=O), 1220 and 1035 (C-O-C), 703 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 680 (1, $M^{+\cdot}$), 398(3), 349 (38), 43(100). Anal. Calcd for $C_{40}H_{40}O_{10}$: C, 70.57; H, 5.92. Found: C 70.49; H 5.86.

1-*C*-(2,3,4-Triphenyl-5-methylphenyl)-D-*manno*-penta-*O*-acetylpentitol (8): Colorless prisms from ethanol (1.07g, 39%), mp 164°C; $[\alpha]_D$ +54; $[\alpha]_{578}$ +57; $[\alpha]_{546}$ +66; $[\alpha]_{436}$ +121 (c 3.0, $CHCl_3$); IR (KBr) ν_{max} 1745 (C=O), 1212 and 1035 (C-O-C), 703 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 680 (1, $M^{+\cdot}$), 398(4), 349 (42), 43(100). Anal. Calcd for $C_{40}H_{40}O_{10}$: C, 70.57; H, 5.92. Found: C 70.64; H 5.97.

1-*C*-(2-Methyl-3,4,5-triphenylphenyl)-D-*manno*-penta-*O*-acetylpentitol (9): Sticky solid (0.93g, 34%); $[\alpha]_D$ +33; $[\alpha]_{578}$ +35; $[\alpha]_{546}$ +41; $[\alpha]_{436}$ +76 (c 3.0, $CHCl_3$); IR (neat) ν_{max} 1745 (C=O), 1212 and 1035 (C-O-C), 703 cm^{-1} (Ar); MS (EI, 75 eV) m/z (%) 680 (1, $M^{+\cdot}$), 398(3), 331 (85), 43(100). Anal. Calcd for $C_{40}H_{40}O_{10}$: C, 70.57; H, 5.92. Found: C 70.38; H 5.83.

Table 1: ^{1}H NMR data for compounds **3a-c** and **4a-c** (in $CDCl_3$).

Comp	CH_3C_q*	CH_3CO	CH_3O	H-5	H-6	H-1'	H-2'	H-3'	H-4'	H-5'	H-5''	H-Ar
3a	1.57 (s,3H)	1.82(s,3H) 1.94(s,3H) 1.97(s,3H) 2.04(s,6H)		3.44 (d,1H) $J_{5,6}$=3.6	5.54 (d,1H)	5.38 (d,1H) $J_{1',2'}$= 3.0	5.24 (dd,1H) $J_{2',3'}$=9.2	4.98 (dd,1H) $J_{3',4'}$=1.8	5.13 (m,1H) $J_{4',5'}$= 4.6	4.21 (dd,1H) $J_{5',5''}$= -11.8	3.70 (dd,1H) $J_{4',5''}$=7.3	6.5-7.4 (m,15H)
4a	1.36 (s,3H)	1.84(s,3H) 1.96(s,3H) 1.99(s,3H) 2.05(s,3H) 2.09(s,3H)		3.04 (d,1H) $J_{5,6}$=3.5	6.51 (d,1H)	5.41 (s,1H)	5.27 (m,3H)	5.27 (m,3H)	5.27 (m,3H) $J_{4',5'}$= 5.2	4.24 (dd,1H) $J_{5',5''}$= -11.6	3.63 (dd,1H) $J_{4',5''}$=7.1	6.5-7.3 (m,15H)
3b	1.48 (s,3H)	1.71(s,3H) 1.85(s,3H) 1.89(s,3H) 1.93(s,6H)	3.57 (s,3H) 3.59 (s,3H)	3.41 (d,1H) $J_{5,6}$=3.6	5.44 (d,1H)	5.29 (d,1H) $J_{1',2'}$= 3.3	5.15 (dd,1H) $J_{2',3'}$=9.2	4.89 (dd,1H) $J_{3',4'}$=1.9	5.03 (m,1H) $J_{4',5'}$= 4.6	4.13 (dd,1H) $J_{5',5''}$= -11.7	3.62 (dd,1H) $J_{4',5''}$=7.1	6.3-7.3 (m,13H)
4b	1.34 (s,3H)	1.82(s,3H) 1.97(s,3H) 1.98(s,3H) 2.04(s,3H) 2.08(s,3H)	3.55 (s,3H) 3.77 (s,3H)	3.01 (d,1H) $J_{5,6}$=3.5	6.50 (d,1H)	5.41 (s,1H)	5.23 (m,3H)	5.23 (m,3H)	5.23 (m,3H) $J_{4',5'}$= 5.1	4.24 (dd,1H) $J_{5',5''}$= -11.5	3.81 (dd,1H) $J_{4',5''}$=7.1	6.4-7.3 (m,13H)
3c	1.47 (s,3H)	1.73(s,3H) 1.86(s,3H) 1.90(s,3H) 1.96(s,6H)		3.32 (d,1H) $J_{5,6}$=3.2	5.46 (d,1H)	5.31 (d,1H) $J_{1',2'}$= 3.1	5.17 (dd,1H) $J_{2',3'}$=9.2	4.88 (dd,1H) $J_{3',4'}$=1.8	5.05 (m,1H) $J_{4',5'}$= 3.8	4.14 (dd,1H) $J_{5',5''}$= -11.6	3.62 (dd,1H) $J_{4',5''}$=7.3	6.3-7.2 (m,13H)
4c	1.36 (s,3H)	1.83(s,3H) 1.99(s,3H) 2.00(s,3H) 2.05(s,3H) 2.08(s,3H)		2.96 (d,1H) $J_{5,6}$=3.4	6.50 (d,1H)	5.43 (s,1H)	5.31 (m,3H)	5.31 (m,3H)	5.31 (m,3H) $J_{4',5'}$= 4.9	4.25 (dd,1H) $J_{5',5''}$= -11.6	3.81 (dd,1H) $J_{4',5''}$=7.0	6.5-7.5 (m,13H)

*C_q ≡ *Quaternary Carbon atom*

Table 2: ^{1}H NMR data for compounds **6a-c** and **7a-c** (in $CDCl_3$).

Comp	CH_3C_q*	CH_3CO	CH_3O	H-5	H-6	H-1'	H-2'	H-3'	H-4'	H-5'	H-5''	H-Ar
6a	1.55 (s,3H)	1.90(s,3H) 1.96(s,3H) 1.99(s,3H) 2.12(s,3H) 2.16(s,3H)		3.52 (d,1H) $J_{5,6}$=4.6	5.32 (d,1H)	5.37 (m,1H) $J_{1',5}$= 1.3	4.90 (m,2H) $J_{2',3'}$=3.1	5.23 (dd,1H) $J_{3',4'}$=8.3	4.90 (m,2H) $J_{4',5'}$= 3.0	4.08 (dd,1H) $J_{5',5''}$= -12.6	4.05 (dd,1H) $J_{4',5''}$=4.6	6.5-7.5 (m,15H)
7a	1.31 (s,3H)	1.81(s,3H) 1.92(s,3H) 1.96(s,3H) 1.99(s,3H) 2.21(s,3H)		3.14 (d,1H) $J_{5,6}$=3.7	6.24 (d,1H)	5.58 (s,1H)	5.36 (m,2H) $J_{2',3'}$=2.5	5.36 (m,2H) $J_{3',4'}$=7.5	4.98 (m,1H) $J_{4',5'}$= 2.5	4.13 (dd,1H) $J_{5',5''}$= -12.5	4.06 (dd,1H) $J_{4',5''}$=4.1	6.5-7.4 (m,15H)
6b	1.54 (s,3H)	1.86(s,3H) 1.97(s,3H) 1.99(s,3H) 2.11(s,3H) 2.15(s,3H)	3.71 (s,6H)	3.46 (d,1H) $J_{5,6}$=4.5	5.29 (d,1H)	5.37 (t,1H) $J_{1',5}$= 1.2	4.90 (m,2H) $J_{2',3'}$=3.0	5.23 (dd,1H) $J_{3',4'}$=8.1	4.90 (m,2H) $J_{4',5'}$= 3.1	4.09 (dd,1H) $J_{5',5''}$= -12.5	4.03 (dd,1H) $J_{4',5''}$=4.6	6.4-7.5 (m,13H)
7b	1.28 (s,3H)	1.86(s,3H) 1.95(s,3H) 2.03(s,3H) 2.05(s,3H) 2.23(s,3H)	3.62 (s,3H) 3.82 (s,3H)	3.06 (d,1H) $J_{5,6}$=3.8	6.17 (d,1H)	5.55 (m,1H)	5.36 (m,1H) $J_{2',3'}$=2.5	5.23 (dd,1H) $J_{3',4'}$=7.6	4.97 (m,1H) $J_{4',5'}$= 2.8	4.16 (dd,1H) $J_{5',5''}$= -12.7	4.11 (dd,1H) $J_{4',5''}$=4.2	6.4-7.4 (m,13H)
6c	1.52 (s,3H)	1.89(s,3H) 1.99(s,3H) 2.02(s,3H) 2.12(s,3H) 2.15(s,3H)		3.50 (d,1H) $J_{5,6}$=4.5	5.31 (d,1H)	5.33 (m,1H) $J_{1',5}$= 1.1	4.90 (m,2H) $J_{2',3'}$=3.5	5.21 (dd,1H) $J_{3',4'}$=7.8	4.90 (m,2H)	4.09 (d,1H)	4.07 (d,1H) $J_{4',5''}$=4.4	6.4-7.4 (m,13H)
7c	1.30 (s,3H)	1.86(s,3H) 1.98(s,3H) 1.98(s,3H) 2.04(s,3H) 2.22(s,3H)		3.06 (d,1H) $J_{5,6}$=3.6	6.18 (d,1H)	5.53 (m,1H)	5.28 (d,1H) $J_{2',3'}$=3.1	5.33 (dd,1H) $J_{3',4'}$=7.9	4.99 (m,1H) $J_{4',5'}$= 2.3	4.20 (dd,1H) $J_{5',5''}$= -12.7	4.10 (dd,1H) $J_{4',5''}$=4.3	6.3-7.5 (m,13H)

*C_q ≡ *Quaternary Carbon atom*

Table 3. ^{13}C NMR data for compounds **3a-c**, **4a-c**, **6a-c** and **7a-c** (in $CDCl_3$).

Comp	CH_3C_q	CH_3CO	C-1'-4'	C-5'	CH_3O	C-1	C-2,3	C-4	C-5	C-6	O=C-7	$CH_{aromatic}$	*quat*C_{arom}	CO_{acetyl}
3a	10.7	19.9 20.3 20.4 20.5 20.6	66.5 67.5 68.5 70.0	62.3		61.9	138.2 144.7		48.7	87.3	196.0	127.5, 127.6 127.7, 127.8 128.0, 128.3 129.0, 129.1 129.9	132.1 132.7 133.1	168.0 169.7 169.7 170.2 170.3
4a	9.6	20.1 20.4 20.5 20.5 20.6	67.2 67.7 69.1 69.2	61.9			138.8 143.6	55.3	48.9	83.4	197.3	127.4, 127.5 127.6, 128.2 128.3, 128.7 128.9, 129.3 129.7	130.3 131.6 133.5	169.1 169.8 169.8 170.2 170.4
3b	10.7	19.9 20.3 20.3 20.5 20.6	66.5 67.5 68.5 70.0	62.2	54.8 54.9	62.0	137.3 143.2		48.6	87.4	196.2	113.1, 113.4 127.6, 128.2 129.1, 130.3 131.3	124.6 125.2 133.0 158.8 158.7	167.9 169.6 169.6 170.1 170.3
4b	9.6	20.0 20.3 20.4 20.4 21.3	67.0 67.6 69.1 69.2	61.7	54.7 55.0		138.0 141.7	56.0	48.7	83.3	197.5	112.9, 114.1 127.5, 128.1 128.9, 130.5 131.0	124.1 125.7 158.4 159.3	169.0 169.7 170.0 170.1 170.2
3c	10.6	19.9 20.4 20.4 20.5 20.6	66.3 67.5 68.5 70.2	62.4		61.9	137.9 144.1		48.5	87.2	195.4	128.2, 128.6 129.1, 130.5 131.1, 131.5 131.7	122.4 122.5 130.7 132.1	167.9 169.7 170.0 170.2 170.3
4c	9.6	20.1 20.4 20.6 21.0 22.7	66.9 67.6 68.4 69.1	61.9			138.5 143.0	56.3	48.7	83.3	197.7	128.3, 128.5 128.9, 130.8 131.1, 131.3 132.2	122.2 123.0 129.8 134.0	169.1 169.8 170.1 170.4 170.4
6a	10.5	19.7 19.9 20.2 20.3 20.4	67.8 68.2 69.3 69.8	61.0		61.7	138.0 144.2	60.8	47.1	87.2	196.0	127.6, 127.8 128.0, 128.3 129.0, 130.1	132.3 133.0	168.0 169.7 169.7 170.2 170.3
7a	9.2	19.6 19.8 20.2 20.4 20.6	67.9 68.4 69.1 70.1	60.8			138.4 143.0	61.2	46.5	83.2	199.6	127.6, 128.1 128.3, 128.7 129.5, 130.0	130.5 131.7 133.2	168.0 169.7 169.7 170.2 170.3

Table 3. Continues ^{13}C NMR data for compounds **3a-c**, **4a-c**, **6a-c** and **7a-c** (in $CDCl_3$).

Comp	CH_3C_q	CH_3CO	C-1'-4'	C-5'	CH_3O	C-1	C-2,3	C-4	C-5	C-6	O=C-7	$CH_{aromatic}$	*quat*C_{arom}	CO_{acetyl}
6b	10.8	20.0 20.2 20.3 20.5 20.6	68.2 68.4 69.3 70.0	61.1	55.0 55.2	62.1	137.8 143.1		47.6	87.6	196.6	128.3, 129.0 130.4, 130.8 131.2, 131.5	113.2 113.5 125.6 158.9	168.5 169.6 169.9 170.0 170.5
7b	9.6	20.0 20.2 20.4 20.5 20.6	68.1 68.7 69.7 70.4	61.1	54.9 55.2		137.9 141.3	55.9	46.8	83.4	197.4	112.9, 114.0 128.3, 128.9 130.6, 131.0	124.3 125.5 158.4 159.3	169.6 169.8 169.8 170.0 170.4
6c	10.6	19.9 20.3 20.6 20.6 20.7	68.1 68.5 69.3 70.1	61.0		61.9	137.9 143.9	61.0	47.3	87.3	195.5	128.2, 128.6 128.9, 130.5 131.1, 131.5 131.6	122.5 130.9 131.8	168.3 169.6 169.8 169.8 170.4
7c	9.4	19.7 20.2 20.4 20.6 20.7	68.3 68.6 69.0 70.3	61.1		69.2	138.2 142.6	56.1	46.7	83.3	196.5	128.3, 128.4 128.8, 130.8 131.0, 131.3 132.0	122.1 123.0 130.1 130.6	169.4 169.7 169.8 169.8 170.4

Table 4: ^1H NMR data for compounds **5**, **8** and **9** (in $CDCl_3$).

Comp	CH_3-Ar	CH_3CO	H-1	H-2	H-3	H-4	H-5	H-5'	H-Ar
5	1.87 (s,3H)	2.02(s,3H) 2.06(s,3H) 2.13(s,3H) 2.17(s,3H) 2.19(s,3H)	6.30 (d,1H) J_{1-2}=2.4	5.52 (dd,1H) J_{2-3}=9.8	5.60 (dd,1H) J_{3-4}=1.7	5.36 (m,1H) J_{4-5}=5.0	4.31 (dd,1H) $J_{5-5'}$=-11.6	3.89 (dd,1H) $J_{4-5'}$=7.5	7.35 (s,1H) 6.71-7.22 (m,15H)
8	1.60 (s,3H)	1.82(s,3H) 1.93(s,3H) 1.99(s,3H) 2.00(s,3H) 2.06(s,3H)	5.52 (s,2H)	5.52 (s,2H)	5.37 (d,1H) J_{3-4}=9.5	4.96 (m,1H) J_{4-5}=2.5	4.11 (dd,1H) $J_{5-5'}$=-12.5	3.95 (dd,1H) $J_{4-5'}$=5.0	7.36 (s,1H) 6.50-7.33 (m,15H)
9	1.81 (s,3H)	2.02(s,3H) 2.05(s,6H) 2.12(s,3H) 2.23(s,3H)	6.13 (d,1H) J_{1-2}=9.6	5.74 (dd,1H) J_{2-3}=2.1	5.70 (dd,1H) J_{3-4}=8.7	5.18 (m,1H) J_{4-5}=2.5	4.26 (dd,1H) $J_{5-5'}$=-12.5	4.13 (dd,1H) $J_{4-5'}$=4.9	7.49 (s,1H) 6.72-7.30 (m,15H)

Table 5. ^{13}C NMR data for compounds **5**, **8** and **9** (in $CDCl_3$).

Comp	CH_3Ar	CH_3CO	C-1-4	C-5	$CH_{aromatic}$	*quat*$C_{aromatic}$	CO
5	16.7	20.3	67.9	62.1	125.4, 126.0	132.4, 133.3	168.9
		20.4	68.4		126.7, 127.2	138.7, 139.7	169.6
		20.5	68.5		127.4, 127.5	139.9, 140.5	169.8
		20.6	69.3		129.5, 130.0	141.7, 142.3	170.0
		20.9			130.5, 131.0		170.4
8	20.0	20.4	67.3	62.0	125.1, 126.0	132.6, 135.4	168.9
		20.6	67.8		126.1, 126.3	138.5, 139.4	169.3
		20.9	69.4		126.5, 126.7	139.9, 140.1	169.5
		21.0	70.9		127.0, 127.3	140.9, 141.7	169.9
		21.1			127.4, 127.8		170.5
					128.1, 129.9		
					130.7, 130.9		
					131.2		
9	16.5	19.7	67.4	61.8	125.4, 125.9	133.7, 133.9	168.6
		20.1	69.9		126.6, 127.3	138.9, 139.6	169.5
		20.3	68.4		127.9, 128.3	140.1, 140.6	169.6
		20.4	71.1		129.6, 130.3	141.5, 141.8	169.7
		20.7			130.8, 131.0		170.4

Crystal Structure Determination of 3a: A single crystal of **3a** of appropriate size (0.7 x 0.6 x 0.4 mm) was mounted on a Enraf-Nonius CAD4 automatic diffractometer. Determination of the cell parameters was performed by least-squares refinement of 25 reflections. The compound crystallizes in the monoclinic system, space group $P2_1$, with a = 10.149(2), b = 8.289(6), c = 23.348(7) Å, ß = 100.27(2)°; Z = 2, U = 1933(2) Å^3; μ = 0.91 cm^{-1}; D_c = 1.30 g cm^{-3}. 3743 Reflections were collected in the range $5 < 2\Theta < 50°$, using Mo-Kα radiation (λ = 0.7107 Å), Θ-2Θ scan mode. The structure was solved by direct methods of SIR88[19] and refined by full-matrix least-squares to R = 0.072 and R_w = 0.051 ($w = 1/\sigma(F_o)^2$), by using the 1083 observed reflections having $|F_o| > 3\sigma(|F_o|)$ for 184 parameters refined. The phenyl groups were refined in idealized geometry as rigid groups. The temperature factors for all atoms were refined isotropically; the hydrogen atoms were introduced in calculated positions, with an overall temperature factor U of 0.05 Å^2. The fractional atomic coordinates and the temperature factors for non-hydrogen atoms of **3a** are reported in Table 6, whereas selected distances and angles for **3a** are reported in Tables 7 and 8.

Crystal Data of 6a: Single crystal, size 0.33 x 0.36 x 0.50 mm. Monoclinic, a = 22.466(7), b = 8.902(2), c = 20.945(7) Å, ß = 107.24(2)°, U = 4001(2)Å^3, space group $C2$, Z = 4, D_c = 1.26 gcm^{-3}, μ = 7.8 cm^{-1}. 2902 Independent reflections ($\Theta > 58°$) were measured on a Siemens P3/PC diffractometer with Cu-K_α radiation (graphite monocromator) using ω-scans. Of these 2767 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; no absorption correction was applied. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. The phenyl groups were refined as idealised rigid bodies. The positions of the hydrogen atoms were idealised C-H = 0.96 Å, assigned isotropic thermal parameters U(H) = 1.2U_{eq}(C), and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to R = 0.037, R_w = 0.041 ($w^{-1} = \sigma^2(F) + 0.0005F^2$). The absolute stereochemistry was determined by internal reference. Computations were carried out on a 486 PC using the SHELXTL-PC program system. The fractional atomic coordinates and the temperature factors for non-hydrogen atoms of **6a** are reported in Table 9, whereas selected distances and angles for **6a** are reported in Tables 10 and 11.

Table 6. Atomic Coordinates ($x10^4$) and Thermal Parameters ($x10^3$) with Their Standard Deviations, for Compound **3a**.

Atom	x/a	y/b	z/c	*U*(Å)
O(1)	-6842(10)	-5285	-6725(4)	57(4)
O(2)	-3021(11)	-1938(21)	-7563(5)	60(4)
O(3)	-3234(11)	-4144(20)	-8074(5)	62(4)
O(4)	-7606(9)	-3175(19)	-7999(4)	34(3)
O(5)	-9387(11)	-2797(21)	-7541(5)	73(4)
O(6)	-6009(9)	-1229(19)	-8606(4)	38(3)
O(7)	-4603(11)	878(20)	-8437(5)	64(4)
O(8)	-9050(10)	520(19)	-8276(4)	42(3)
O(9)	-10809(11)	-906(20)	-8697(5)	74(4)
O(10)	-7500(10)	2282(21)	-9007(5)	49(4)
O(11)	-6369(11)	2136(22)	-9733(5)	82(5)
O(12)	-10294(11)	2137(21)	-9323(5)	62(4)
O(13)	-11743(12)	1999(22)	-10148(6)	106(6)
N(1)	-3648(13)	-3108(23)	-7763(7)	53(5)
C(1)	-4662(14)	-4697(23)	-7049(6)	22(4)
C(2)	-3762(13)	-3929(23)	-6552(6)	22(4)
C(3)	-4365(14)	-2652(24)	-6374(6)	30(5)
C(4)	-5822(14)	-2491(24)	-6750(7)	24(4)
C(5)	-5660(14)	-2038(24)	-7371(6)	25(5)
C(6)	-4941(15)	-3516(23)	-7580(7)	31(5)
C(7)	-5969(17)	-4394(25)	-6821(7)	46(5)
C(8)	-4466(15)	-6442(26)	-7200(7)	61(6)
C(10)	-1942(9)	-4466(18)	-5695(4)	28(5)
C(11)	-645(9)	-4968(18)	-5462(4)	47(5)
C(12)	220(9)	-5455(18)	-5831(4)	55(6)
C(13)	-211(9)	-5440(18)	-6433(4)	35(5)
C(14)	-1507(9)	-4938(18)	-6666(4)	34(5)
C(9)	-2373(9)	-4451(18)	-6297(4)	30(5)
C(16)	-4267(9)	-1099(19)	-5434(5)	55(6)
C(17)	-3783(9)	184(19)	-5071(5)	63(6)
C(18)	-2870(9)	1267(19)	-5238(5)	50(6)
C(19)	-2441(9)	1067(19)	-5769(5)	41(5)
C(20)	-2925(9)	-217(19)	-6132(5)	44(5)
C(15)	-3838(9)	-1300(19)	-5965(5)	36(5)
C(22)	-7897(11)	-2243(16)	-6286(4)	64(7)
C(23)	-8837(11)	-1291(16)	-6074(4)	61(6)
C(24)	-8703(11)	384(16)	-6062(4)	72(7)
C(25)	-7630(11)	1107(16)	-6263(4)	51(6)
C(26)	-6691(11)	155(16)	-6475(4)	45(5)
C(21)	-6825(11)	-1521(16)	-6487(4)	31(5)
C(27)	-6999(14)	-1648(24)	-7752(6)	28(5)
C(28)	-8829(16)	-3551(26)	-7842(7)	42(6)
C(29)	-9282(17)	-5073(25)	-8144(7)	89(7)
C(30)	-6871(13)	-577(24)	-8268(6)	28(5)
C(31)	-4898(15)	-320(26)	-8695(7)	37(5)
C(32)	-4207(14)	-1133(23)	-9118(6)	51(6)
C(33)	-8215(13)	-233(24)	-8647(6)	31(5)
C(34)	-10416(18)	8(27)	-8321(8)	66(7)
C(35)	-10972(15)	776(26)	-7847(7)	68(6)
C(36)	-8158(16)	800(27)	-9173(8)	55(6)
C(37)	-6616(21)	2880(28)	-9336(10)	81(8)
C(38)	-6032(15)	4387(25)	-9087(7)	65(6)
C(39)	-9450(15)	1086(25)	-9592(6)	43(5)
C(40)	-11613(21)	2452(32)	-9669(10)	86(8)
C(41)	-12334(16)	3424(26)	-9337(8)	89(8)

Table 7. Selected Bond Distances (Å) for **3a**

O1 - C7	1.20(2)	C1 - C7	1.54(2)
O2 - N1	1.21(2)	C1 - C8	1.51(3)
O3 - N1	1.24(2)	C2 - C3	1.33(3)
O4 - C27	1.48(2)	C2 - C9	1.49(2)
O4 - C28	1.39(2)	C3 - C4	1.58(2)
O5 - C28	1.16(2)	C3 - C15	1.51(2)
O6 - C30	1.39(2)	C4 - C5	1.53(2)
O6 - C31	1.40(2)	C4 - C7	1.59(3)
O7 - C31	1.17(3)	C4 - C21	1.51(2)
O8 - C33	1.45(2)	C5 - C6	1.55(3)
O8 - C34	1.44(2)	C5 - C27	1.52(2)
O9 - C34	1.17(2)	C27 - C30	1.52(2)
O10 - C36	1.42(3)	C28 - C29	1.48(3)
O10 - C37	1.37(3)	C30 - C33	1.51(2)
O11 - C37	1.18(3)	C31 - C32	1.47(2)
O12 - C39	1.44(2)	C33 - C36	1.51(3)
O12 - C40	1.46(2)	C34 - C35	1.47(3)
O13 - C40	1.16(3)	C36 - C39	1.51(2)
N1 - C6	1.49(2)	C37 - C38	1.46(3)
C1 - C2	1.49(2)	C40 - C41	1.41(3)
C1 - C6	1.57(2)		

Table 8. Selected Bond Angles (degree) for **3a**

C27 - O4 - C28	115(1)	C2 - C9 - C14	119(1)
C30 - O6 - C31	119(1)	C2 - C9 - C10	121(1)
C33 - O8 - C34	119(1)	C3 - C15 - C20	119(1)
C36 - O10 - C37	119(2)	C3 - C15 - C16	121(1)
C39 - O12 - C40	115(1)	C4 - C21 - C26	118(1)
O2 - N1 - O3	125(1)	C4 - C21 - C22	122(1)
O3 - N1 - C6	115(2)	O4 - C27 - C5	108(1)
O2 - N1 - C6	120(1)	C5 - C27 - C30	113(1)
C7 - C1 - C8	113(1)	O4 - C27 - C30	106(1)
C6 - C1 - C8	115(1)	O4 - C28 - O5	126(2)
C6 - C1 - C7	97(1)	O5 - C28 - C29	127(2)
C2 - C1 - C8	120(1)	O4 - C28 - C29	106(1)
C2 - C1 - C7	96(1)	O6 - C30 - C27	112(1)
C2 - C1 - C6	110(1)	C27 - C30 - C33	112(1)
C1 - C2 - C9	126(1)	O6 - C30 - C33	110(1)
C1 - C2 - C3	109(1)	O6 - C31 - O7	121(1)
C3 - C2 - C9	124(1)	O7 - C31 - C32	129(2)
C2 - C3 - C15	131(1)	O6 - C31 - C32	110(1)
C2 - C3 - C4	109(1)	O8 - C33 - C30	107(1)
C4 - C3 - C15	119(1)	C30 - C33 - C36	115(1)
C3 - C4 - C21	117(1)	O8 - C33 - C36	111(1)
C3 - C4 - C7	92(1)	O8 - C34 - O9	116(2)
C3 - C4 - C5	107(1)	O9 - C34 - C35	136(2)
C7 - C4 - C21	121(1)	O8 - C34 - C35	108(1)
C5 - C4 - C21	117(1)	O10 - C36 - C33	111(1)
C5 - C4 - C7	100(1)	C33 - C36 - C39	118(1)
C4 - C5 - C27	112(1)	O10 - C36 - C39	111(2)
C4 - C5 - C6	104(1)	O10 - C37 - 011	120(2)
C6 - C5 - C27	114(1)	O11 - C37 - C38	129(2)
C1 - C6 - C5	106(1)	O10 - C37 - C38	110(2)
N1 - C6 - C5	114(1)	O12 - C39 - C36	109(1)
N1 - C6 - C1	109(1)	O12 - C40 - O13	114(2)
C1 - C7 - C4	97(1)	O13 - C40 - C41	137(2)
O1 - C7 - C4	130(1)	O12 - C40 - C41	108(2)
O1 - C7 - C1	132(2)		

Table 9. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2x10^3$) for **6a**.

Atom	x	y	z	$U(eq)^*$
O(1)	2880(1)	3442	971(1)	50(1)
O(2)	2340(1)	997(5)	3100(1)	71(1)
O(3)	2488(1)	3316(5)	3374(1)	78(1)
O(4)	3928(1)	2595(4)	2193(1)	47(1)
O(5)	4734(2)	1770(6)	1907(3)	153(3)
O(6)	3996(1)	1693(4)	3556(1)	51(1)
O(7)	4916(2)	2822(5)	3968(2)	105(2)
O(8)	3733(1)	-1220(4)	3502(1)	56(1)
O(9)	3611(2)	-3395(5)	2940(2)	98(2)
O(10)	5371(1)	-515(4)	3777(1)	60(1)
O(11)	5828(2)	19(6)	4858(2)	107(2)
O(12)	5127(2)	-3536(5)	3664(2)	87(1)
O(13)	6055(2)	-3931(9)	4386(3)	160(3)
N(1)	2544(1)	2234(5)	3044(1)	53(1)
C(1)	2393(1)	3210(5)	1878(2)	41(1)
C(2)	1837(1)	2151(5)	1642(1)	40(1)
C(3)	2036(1)	855(5)	1439(1)	37(1)
C(4)	2735(1)	990(4)	1504(1)	36(1)
C(5)	3099(1)	1047(5)	2275(1)	38(1)
C(6)	2857(1)	2495(5)	2514(2)	42(1)
C(7)	2720(1)	2689(5)	1364(2)	39(1)
C(8)	2283(2)	4880(5)	1895(2)	56(1)
C(9)	1193(1)	2553(5)	1612(2)	42(1)
C(10)	713(2)	2292(5)	1036(2)	55(1)
C(11)	106(2)	2673(6)	992(2)	66(1)
C(12)	-28(2)	3345(6)	1522(2)	65(2)
C(13)	440(2)	3605(6)	2099(2)	68(2)
C(14)	1047(2)	3220(5)	2142(2)	56(1)
C(15)	1650(1)	-507(4)	1222(2)	42(1)
C(16)	1385(2)	-1180(5)	1676(2)	57(1)
C(17)	982(2)	-2383(6)	1481(3)	77(2)
C(18)	835(2)	-2909(6)	852(3)	86(2)
C(19)	1095(2)	-2271(6)	395(3)	76(2)
C(20)	1510(2)	-1083(5)	584(2)	53(1)
C(21)	2980(1)	-125(5)	1104(2)	37(1)
C(22)	3009(2)	-1628(5)	1277(2)	46(1)
C(23)	3199(2)	-2688(5)	899(2)	53(1)
C(24)	3377(2)	-2271(5)	360(2)	53(1)
C(25)	3355(2)	-781(5)	186(2)	57(1)
C(26)	3150(2)	290(5)	548(2)	45(1)
C(27)	3808(1)	1094(5)	2393(2)	40(1)
C(28)	4399(2)	2777(6)	1926(3)	76(2)
C(29)	4447(2)	4343(7)	1710(3)	104(3)
C(30)	4221(1)	813(5)	3100(2)	45(1)
C(31)	4385(2)	2687(5)	3966(2)	63(1)
C(32)	4077(2)	3496(6)	4386(2)	87(2)
C(33)	4280(2)	-813(5)	3317(2)	47(1)
C(34)	3453(2)	-2548(6)	3301(2)	68(2)
C(35)	2931(3)	-2762(7)	3589(3)	103(3)
C(36)	4833(2)	-1088(5)	3936(2)	58(1)
C(37)	5841(2)	24(7)	4295(3)	82(2)
C(38)	6377(2)	527(10)	4067(3)	122(3)
C(39)	4940(2)	-2693(6)	4148(2)	78(2)
C(40)	5712(3)	-4115(8)	3856(4)	99(3)
C(41)	5839(3)	-4960(9)	3311(4)	122(3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 10. Bond Lengths (Å) for **6a**

O(1)-C(7)	1.196 (4)	O(2)-N(1)	1.211 (6)
O(3)-N(1)	1.214 (6)	O(4)-C(27)	1.450 (5)
O(4)-C(28)	1.346 (6)	O(5)-C(28)	1.179 (7)
O(6)-C(30)	1.438 (5)	O(6)-C(31)	1.356 (5)
O(7)-C(31)	1.198 (6)	O(8)-C(33)	1.441 (5)
O(8)-C(34)	1.346 (6)	O(9)-C(34)	1.194 (7)
O(10)-C(36)	1.437 (5)	O(10)-C(37)	1.358 (5)
O(11)-C(37)	1.189 (7)	O(12)-C(39)	1.422 (7)
O(12)-C(40)	1.357 (7)	O(13)-C(40)	1.159 (8)
N(1)-C(6)	1.499 (5)	C(1)-C(2)	1.525 (5)
C(1)-C(6)	1.563 (4)	C(1)-C(7)	1.544 (5)
C(1)-C(8)	1.509 (6)	C(2)-C(3)	1.351 (6)
C(2)-C(9)	1.475 (5)	C(3)-C(4)	1.539 (4)
C(3)-C(15)	1.481 (5)	C(4)-C(5)	1.579 (4)
C(4)-C(7)	1.538 (6)	C(4)-C(21)	1.505 (5)
C(5)-C(6)	1.539 (6)	C(5)-C(27)	1.538 (4)
C(9)-C(10)	1.378 (4)	C(9)-C(14)	1.382 (6)
C(10)-C(11)	1.382 (5)	C(11)-C(12)	1.370 (7)
C(12)-C(13)	1.367 (5)	C(13)-C(14)	1.383 (6)
C(15)-C(16)	1.396 (6)	C(15)-C(20)	1.378 (5)
C(16)-C(17)	1.385 (6)	C(17)-C(18)	1.343 (9)
C(18)-C(19)	1.384 (9)	C(19)-C(20)	1.387 (6)
C(21)-C(22)	1.383 (6)	C(21)-C(26)	1.380 (5)
C(22)-C(23)	1.379 (6)	C(23)-C(24)	1.355 (6)
C(24)-C(25)	1.374 (7)	C(25)-C(26)	1.380 (6)
C(27)-C(30)	1.516 (4)	C(28)-C(29)	1.480 (8)
C(30)-C(33)	1.511 (6)	C(31)-C(32)	1.461 (8)
C(33)-C(36)	1.526 (4)	C(34)-C(35)	1.482 (8)
C(36)-C(39)	1.495 (7)	C(37)-C(38)	1.490 (9)
C(40)-C(41)	1.465(11)		

Table 11. Bond Angles (°) for **6a**

C(27)-O(4)-C(28)	118.0(3)	C(30)-O(6)-C(31)	119.2(3)
C(33)-O(8)-C(34)	119.6(4)	C(36)-O(10)-C(37)	116.7(3)
C(39)-O(12)-C(40)	116.9(4)	O(2)-N(1)-O(3)	124.2(4)
O(2)-N(1)-C(6)	119.0(4)	O(3)-N(1)-C(6)	116.7(4)
C(2)-C(1)-C(6)	107.5(3)	C(2)-C(1)-C(7)	95.8(3)
C(6)-C(1)-C(7)	97.8(3)	C(2)-C(1)-C(8)	119.5(3)
C(6)-C(1)-C(8)	117.0(3)	C(7)-C(1)-C(8)	115.3(3)
C(1)-C(2)-C(3)	108.4(3)	C(1)-C(2)-C(9)	124.2(3)
C(3)-C(2)-C(9)	127.3(3)	C(2)-C(3)-C(4)	109.2(3)
C(2)-C(3)-C(15)	125.2(3)	C(4)-C(3)-C(15)	125.5(3)
C(3)-C(4)-C(5)	107.4(3)	C(3)-C(4)-C(7)	95.6(3)
C(5)-C(4)-C(7)	97.9(3)	C(3)-C(4)-C(21)	115.5(3)
C(5)-C(4)-C(21)	115.2(3)	C(7)-C(4)-C(21)	122.2(3)
C(4)-C(5)-C(6)	103.5(3)	C(4)-C(5)-C(27)	111.3(3)
C(6)-C(5)-C(27)	111.9(3)	N(1)-C(6)-C(1)	110.7(3)
N(1)-C(6)-C(5)	113.6(3)	C(1)-C(6)-C(5)	105.9(3)
O(1)-C(7)-C(1)	127.8(4)	O(1)-C(7)-C(4)	133.5(3)
C(1)-C(7)-C(4)	98.6(3)	C(2)-C(9)-C(1O)	120.0(3)
C(2)-C(9)-C(14)	122.2(3)	C(10)-C(9)-C(14)	117.8(3)
C(9)-C(10)-C(11)	121.1(4)	C(10)-C(11)-C(12)	120.2(3)
C(11)-C(12)-C(13)	119.6(4)	C(12)-C(13)-C(14)	120.1(4)
C(9)-C(14)-C(13)	121.2(3)	C(3)-C(15)-C(16)	118.1(3)
C(3)-C(15)-C(20)	123.1(3)	C(16)-C(15)-C(20)	118.6(3)
C(15)-C(16)-C(17)	120.4(4)	C(16)-C(17)-C(18)	120.5(5)
C(17)-C(18)-C(19)	120.3(5)	C(18)-C(19)-C(20)	120.0(5)
C(15)-C(20)-C(19)	120.2(4)	C(4)-C(21)-C(22)	119.3(3)

Table 11. Continues Bond Angles (°) for **6a**

C(4)-C(21)-C(26)	122.1(4)	C(22)-C(21)-C(26)	118.5(4)
C(21)-C(22)-C(23)	120.7(4)	C(22)-C(23)-C(24)	120.6(4)
C(23)-C(24)-C(25)	119.3(4)	C(24)-C(25)-C(26)	120.8(4)
C(21)-C(26)-C(25)	120.0(4)	O(4)-C(27)-C(5)	104.5(3)
O(4)-C(27)-C(30)	108.7(3)	C(5)-C(27)-C(30)	117.3(3)
O(4)-C(28)-0(5)	120.7(6)	O(4)-C(28)-C(29)	112.3(5)
O(5)-C(28)-C(29)	126.9(6)	O(6)-C(30)-C(27)	109.0(3)
O(6)-C(30)-C(33)	109.8(3)	C(27)-C(30)-C(33)	115.2(3)
O(6)-C(31)-0(7)	121.5(4)	O(6)-C(31)-C(32)	111.8(4)
O(7)-C(31)-C(32)	126.7(4)	O(8)-C(33)-C(30)	108.4(3)
O(8)-C(33)-C(36)	106.0(3)	C(30)-C(33)-C(36)	112.7(3)
O(8)-C(34)-O(9)	123.6(5)	O(8)-C(34)-C(35)	109.8(4)
O(9)-C(34)-C(35)	126.6(5)	O(10)-C(36)-C(33)	106.0(3)
O(10)-C(36)-C(39)	109.6(4)	C(33)-C(36)-C(39)	115.1(4)
O(10)-C(37)-O(11)	123.3(5)	O(10)-C(37)-C(38)	111.2(5)
O(11)-C(37)-C(38)	125.4(4)	O(12)-C(39)-C(36)	110.3(4)
O(12)-C(40)-O(13)	122.8(7)	O(12)-C(40)-C(41)	111.0(5)
O(13)-C(40)-C(41)	126.2(6)		

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