Synthesis of Enantiopure 3-Azabicyclo[3.3.0]octen-7-one Derivatives via Intramolecular Pauson−Khand Cycloaddition Reaction Using Tri-*O*-acetyl-D-glucal as Starting Material

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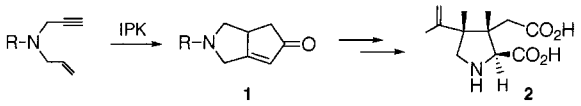
Abstract: Some *N*-substituted-3-azabicyclo[3.3.0]octen-7-one derivatives have been synthesized in an enantiomerically pure form starting from tri-*O*-acetyl-D-glucal via intramolecular Pauson−Khand (IPK) cycloaddition.

The development of convenient synthetic routes to enantiomerically pure 3-azabicyclo[3.3.0]octen-7-one derivatives **1** (Scheme 1) has attracted considerable attention because these compounds constitute advanced intermediates for the preparation of (−)-kainic acid **2**, a potent neuronal excitant[1]. A classical approach to **1** uses the intramolecular Pauson−Khand cycloaddition reaction (IPK)[2] of a suitable allylpropargylamine **3**, and after the seminal report of Pauson[3] describing this protocol, several approaches to optically pure **1** (or its saturated analogue) using different chiral auxiliary reagents have been reported.[4]

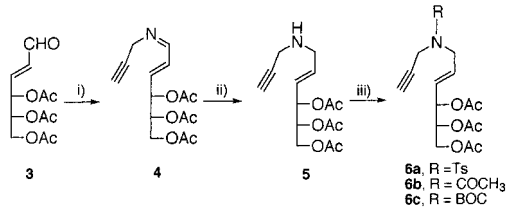
On the other hand, carbohydrates have been considered as chiral substrates for the IPK reaction.[5] However, the use of carbohydrates as chiral templates in the synthesis of enantiomerically pure N-substituted-3-azabicyclo[3.3.0]octen-7-one derivatives has not, to the best of our knowledge, been reported. In this report we account for our results in this field.

Our starting materials were the azaenynes **6a**−**c**, prepared from the aldehyde **3**, easily accessible from tri-*O*-acetyl-D-glucal in two steps and 66% overall yield.[6] (Scheme 2).

Scheme 1

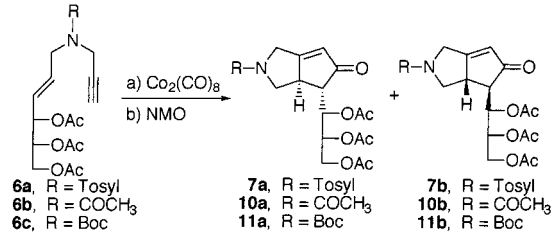


Scheme 2[a]



[a] (i) Propargylamine, molecular sieves, 87%; (ii) $NaBH_4$, MeOH, 0 °C, 72%; (iii) TsCl/Py, 63% for **6a**; Ac_2O/Py, 86% for **6b**; $(BOC)_2O$, THF, 27% for **6c**.

Scheme 3



It should be pointed out that compounds **6b** and **6c** show two groups of signals corresponding to the couple of *Z*/*E*-isomers, regarding the N−CO bond, in *Z*/*E* ratios of ∼1.0:1.5 and ∼1.0:1.0, respectively. Coalescence temperatures, T_c (DMSO), were 92 and 62 °C for **6b** and **6c**, respectively.

The reaction of compound **6a** with $Co_2(CO)_8$ in CH_2Cl_2 under an atmosphere of CO at room temperature, followed by treatment of the reaction mixture with NMO, gave an approximately 1:1 mixture of compounds **7a** and **7b** in 60% overall yield. (Scheme 3).

The separation of compounds **7a** and **7b** was achieved by column chromatography (SiO_2, hexane/ethyl acetate 1:2) followed by crystallization in hexane/ethyl acetate 1:1. The X-ray analysis[7] of **7b** confirms the proposed structures for these compounds. It should be pointed out

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(1) For some selected reviews on kainic acid and kainoids including synthetic methods, see: (a)Wood, M. E.; Fryer, A. M. Synthesis of Kainoids and Kainoid Analogues In *Advances of Nitrogen Heterocycles*; Moody, C. J., Ed; JAI Press: 1998; Vol. 3. (b) Baichi, M. D.; Melmann, A. *Pure Appl. Chem.* **1998**, *70*, 259. (c) Parsons, A. F. *Tetrahedron* **1996**, *52*, 4149. For classical reviews considering the neuronal activity of kainic acid and kainoids, see: (d) Shinozaki, H.; Konishi, S. *Brain Res.* **1970**, *24*, 368. (e) Johnston, G. A. R.; Curtis, D. R.; Davies, J.; McCulloch, R. M. *Nature* **1974**, *248*, 804. (f) McGeer, E. G.; Olney, J. W.; McGeer; P. L. *Kainic Acid as a Tool in Neurobiology*; Raven Press: New York, 1978.

(2) For recent reviews on the Pauson−Khand reaction, see: (a) Gleis, O.; Schmalz, H. G. *Angew. Chem., Int. Ed.* **1998**, *37*, 911. (b) Fletcher, A. J.; Christie, S. D. R. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1657. For other recent reviews of a more general scope, including Pauson−Khand reactions, see: (c) deMeijere, A.; Schirmer, H.; Deutsch, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964; see also 3974. (d) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591; see also 3627−3630. (e) Hartley, R. C.; Caldwell, S. T. *J. Chem. Soc., Perkin Trans. 1* **2000**, 477; see also 483−484. (f) Fletcher, A. J.; Christie, S. D. R. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1−13; see also 10−13.

(3) Brown, S. W.; Pauson, P. L. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1205.

(4) See, for instance: (a) Takano, S.; Inomata, K.; Ogasawata, K. *J. Chem. Soc. Chem. Commun.* **1992**, 169. (b) Yoo, S.; Lee, S.; Jeong, N.; Cho, I. *Tetrahedron Lett.* **1993**, *34*, 3435. (c) Yoo, S.; Lee, S. *J. Org. Chem.* **1994**, *59*, 6968. (d) Witulski, B.; Gossmann, M. *J. Chem. Soc. Chem. Commun.* **1999**, 1879. (e) Hiroi, K.; Watanabe, T. *Heterocycles* **2001**, *54*, 73. For the synthesis of *N*-tosyl-3-azabicyclo[3.3.0]octan-7-ones via catalytic IPK reaction, see: (f) Jeong, N.; Hwang, S. H.; Lee, S.; Chung, Y. K. *J. Am. Chem. Soc.* **1994**, *116*, 3159. For the "reductive" IPK reaction giving N-substituted-3-azabicyclo[3.3.0]octanones, see: (g) Becker, D. P.; Flynn, D. L. *Tetrahedron Lett.* **1993**, *34*, 2087. (h) Becker, D. P.; Flynn, D. L. *Tetrahedron* **1993**, *49*, 5047.

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(6) González, F.; Lesage, S.; Perlin, A. S. *Carbohydr. Res.* **1975**, *42*, 267.

(7) X-ray data for this structure have been deposited with the Cambridge Crystallographic Data Centre (registry number: CCDC-152005). Copies of the data may be obtained free of charge from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat. +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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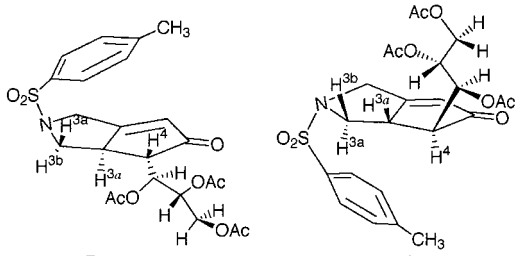
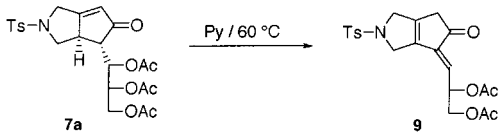


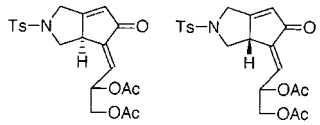
Figure 1. Conformations and chemical shifts for compounds **7a** and **7b**. Atom numbering is included for NMR assignment purposes.

Scheme 4

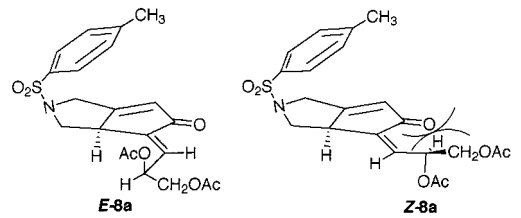


that, in the solid state, the conformation of **7b** shows the tosyl group located under the bicyclic ring (Supporting Information). The ^{1}H NMR spectrum also indicates that the solution conformation of **7b** (and **7a**) might be similar. Thus, the upfield-shifted peak for hydrogens H_{3a} and H_4 shows that both protons lie in the shielding region of the aryl group (Figure 1). Similar observations have been previously reported in related compounds.[4c]

When the reaction with NMO was prolonged by 6 h at room temperature, a 1.2:1 mixture of compounds **8a** and **8b** (11% overall yield), together with compounds **7a** and **7b** in a ratio of 1.4:1 (45% overall yield), was obtained. From the **8a**/**8b** mixture was isolated pure **8a**. The stereochemistry of **8a** at C-3*a* was tentatively established by comparison of the chemical shifts for proton H-3*a* in compounds **7a** and **7b** (3.34 and 3.09 ppm, respectively) with those for **8a** and **8b** (3.85 and 3.71 ppm, respectively). On the other hand, the stereochemistry of the exocyclic double bond in **8a** has not been determined; however, in the (*Z*)-diastereomer, an important steric hindrance



between the cyclopentenone ring system and the acetylated chain is evident. On this basis, the (*E*)-conformation of the double bond can be proposed for **8a**.



Regarding the formation of compounds **8a** and **8b**, it should be pointed out that, although hydrogenolytic[8] and reduction[9] processes have been observed in several Pauson−Khand reactions, the elimination of a leaving group in the β position of the carbonyl group has not, to the best of our knowledge, been reported yet. Apparently, deprotonation of the C positioned α to the carbonyl group followed by elimination of the acetyl leaving group could account for the observed outcome. However, treatment of **7a** with pyridine at 60 °C did not afford **8a**, and compound **9** (27%) was isolated instead (Scheme 4). Thus, the route for the formation of **8a** remains undetermined.

The IPK reactions of compounds **6b** and **6c** have been also considered. In this way, the reactions of **6b** and **6c** with $Co_2(CO)_8$ under a CO atmosphere in CH_2Cl_2 followed by treatment with NMO (1 h, rt) afford compounds **10a**,**b** and **11a**,**b** in 1:1 ratios and 56 and 47% overall yields, respectively (Scheme 3).

In the case of compounds **10**, all attempts for the isolation of pure **10a** and **10b** were unsuccessful. Careful inspection of the mixture indicates the presence of both (*E*)- and (*Z*)-isomers, regarding the N−CO bond, in *Z*/*E* ratios of ∼1:2 (T_c (DMSO) = 87 °C) for **10a** and ∼2:1 (T_c (DMSO) = 87 °C) for **10b**. Separation of **11a** and **11b** could be achieved by preparative TLC (hexane−ethyl ether 3:7). Also, for these compounds, both (*E*)- and (*Z*)-isomers were observed in ratios of ∼1:1, showing T_c (DMSO) of 72 and 37 °C for **11a** and **11b**, respectively.

In summary, in this report, a new synthesis of enantiomerically pure 3-azabicylo[3.3.0]octen-7-one derivatives has been achieved via IPK reaction and using a sugar moiety as a chiral template. Further applications of this new approach to these compounds are now in progress in our laboratory.

Experimental Section

General Methods. IPK reactions were carried out under an argon atmosphere. Anhydrous CH_2Cl_2 was distilled from sodium hydride immediately prior to use. Melting points were determined with a capillary apparatus and are uncorrected. Optical rotations were measured at 18 ± 2 °C. Analytical and preparative TLC were performed on silica gel with monitoring by UV irradiation at 254 and 360 nm or by exposure to iodine vapor. Flash chromatography[10] was performed on silica gel (230−400 mesh). In IR spectra, solid samples were run as KBr disks and liquids as thin films on NaCl plates. Details are reported as ν_{max} (cm^{-1}). ^{1}H and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively, in $CDCl_3$ (Me_4Si as the internal standard) unless otherwise specified. Elemental analyses were carried out at the Universidad de Extremadura and were also provided by the Servei de Microanàlisi del CSIC, Barcelona, Spain, and the Instituto de Investigaciones Químicas del CSIC, Seville, Spain. Only significant fragment ions are reported for mass spectra.

(2*E*)-Tri-*O*-acetyl-2,3-dideoxy-*aldehyde*-D-*erythro*-hex-2-enose Propargylimine (4). To a stirred solution of **3**[6] (6.66 g, 24.34 mmol) in dry ethyl ether (50 mL) at 0 °C were added propargylamine (1.53 mL, 22.6 mmol) and 4 Å molecular sieves. After the mixture was stirred for 1.5 h at room temperature, filtration of the molecular sieves and concentration yielded **4** as an oil (6.5 g, 87%); $[\alpha]_D$ +28.7, $[\alpha]_{578}$ +30.4, $[\alpha]_{546}$ +34.8, $[\alpha]_{436}$ +64.3 (*c* 0.5, $CHCl_3$); IR (film) 3280 m, 1745 s, 1730 s, 1660 m, 1630 m, 1240 s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dt, $J_{1,2}$ = 8.7 Hz, $J_{1,1'}$ = 1.6 Hz, H-1), 6.44 (dd, $J_{2,3}$ = 15.7 Hz, H-2), 6.15 (dd, $J_{3,4}$ = 5.9 Hz, H-3), 5.60 (t, $J_{4,5}$ = 5.5 Hz, H-4), 5.22 (ddd, H-5), 4.21 (dd, $J_{6,6'}$ = 12.0 Hz, $J_{5,6}$ = 3.6 Hz, H-6), 4.14 (dd, $J_{5,6'}$ = 6.8 Hz, H-6′), 4.36 (bs, 2H, H-1′), 2.47 (t, $J_{1',3'}$ = 2.3 Hz, H-3′), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.02 (s, 3H, OAc);

(8) See, for instance: (a) Kerr, W. J.; McLaughlin, M.; Pauson, P. L.; Robertson, S. M. *J. Chem. Soc. Chem. Commun.* **1999**, 2171. (b) Arjona, O.; García Csáky, A.; Murcia, C.; Plumet, J. *J. Org. Chem.* **1999**, *64*, 272. (c) Kerr, W. J.; McLaughlin, M.; Pauson, P. L.; Robertson, S. M. *J. Organomet. Chem.* **2001**, *630*, 104.

(9) See, for instance: Montaña, A. M.; Moyano, A.; Pericás, M. A.; Serratosa, F. *Tetrahedron* **1985**, *41*, 5995.

(10) Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.9, 169.3 (3 O*C*OCH$_3$), 161.2 (C-1), 136.6 (C-3), 132.9 (C-2), 78.3, 75.7 (C-2′, C-3′), 71.1, 71.0 (C-4, C-5), 61.5 (C-6), 46.8 (C-1′), 20.7, 20.6, 20.5 (3OCO*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-1,2,3-trideoxy-1-propargylimine-D-*erythro*-hex-2-enose (5). To a stirred solution of **4** (6.5 g, 21.01 mmol) in MeOH (35 mL) at 0 °C was added sodium borohydride (0.79 g, 21.01 mmol). The mixture was stirred for 15 min at room temperature and filtered, and the filtrate was diluted with CH_2Cl_2 (150 mL), washed successively with saturated aqueous $NaHCO_3$ (2 × 100 mL) and water (2 × 100 mL), dried with $MgSO_4$, and concentrated yielding the title product **5** as an oil (4.64 g, 71%): $[\alpha]_D$ + 32.6, $[\alpha]_{578}$ +33.0, $[\alpha]_{546}$ +37.9, $[\alpha]_{436}$ +67.4 (*c* 0.5, $CHCl_3$); IR (film) 3260 m, 1745 s, 1735 s, 1680 m, 1240 s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (dt, $J_{1,2}$ = 5.6 Hz, $J_{2,3}$ = 15.1 Hz, H-2), 5.64 (ddt, $J_{3,4}$ = 6.4 Hz, $J_{1,3}$ = 1.2 Hz, H-3), 5.47 (dd, $J_{4,5}$ = 4.5 Hz, H-4), 5.21 (ddd, H-5), 4.25 (dd, $J_{5,6}$ = 3.7 Hz, H-6), 4.15 (dd, $J_{5,6'}$ = 6.9 Hz, $J_{6,6'}$ = 12.1 Hz, H-6′), 3.41 (d, $J_{1',3'}$ = 2.4 Hz, H-1′a, H-1′b), 3.39 (bd, H-1a, H-1b), 2.24 (t, H-3′), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.0, 169.6 (3O*C*OCH$_3$), 133.8 (C-2), 125.2 (C-3), 81.6 (C-3′), 72.1 (C-4), 71.6 (C-2′), 71.4 (C-5), 61.7 (C-6), 49.1 (C-1), 37.2 (C-1′), 20.9, 20.8, 20.7 (3OCO*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-1,2,3-trideoxy-1-(*N*-propargyltosylamine)-D-*erythro*-hex-2-enose (6a). A stirred solution of **5** (8.29 g, 26.67 mmol) in pyridine (50 mL) at 0 °C was treated with tosyl chloride (15.23 g, 80.0 mmol). The mixture was kept for 48 h at 4 °C, poured into ice−water (500 mL), and extracted with Et_2O (3 × 250 mL). The combined organic layers were rinsed successively with 2 N aqueous HCl (3 × 250 mL), a saturated solution of $NaHCO_3$ (3 × 250 mL), and brine (3 × 250 mL), dried on $MgSO_4$, and filtered. Elimination of the solvent under reduced pressure afforded **6a** as an oil, which was purified by flash chromatography (hexane/ethyl acetate 2:1) (7.85 g, 63%): $[\alpha]_D$ + 23.2, $[\alpha]_{578}$ +23.6, $[\alpha]_{546}$ +26.6, $[\alpha]_{436}$ +47.8, $[\alpha]_{365}$ +79.4 (*c* 0.5, $CHCl_3$); IR (film) 3270 m, 1740 s, 1730 s, 1680 m, 1210 s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, H-2″, H-6″), 7.30 (d, H-3″, H-5″), 5.70 (dt, $J_{1a,2}$ = 5.5 Hz, $J_{1b,2}$ = 4.4 Hz, $J_{2,3}$ = 15.5 Hz, H-2), 5.68 (dd, $J_{3,4}$ = 5.4 Hz, H-3), 5.44 (t, $J_{4,5}$ = 5.2 Hz, H-4), 5.18 (ddd, $J_{5,6}$ = 3.4 Hz, $J_{5,6'}$ = 6.9 Hz, H-5), 4.22 (dd, $J_{6,6'}$ = 12.2, Hz, H-6), 4.12 (dd, H-6′), 4.06 (bs, H-1′a, H-1′b), 3.85 (dd, $J_{1a,1b}$ = 13.9 Hz, $J_{1a,2}$ = 4.0 Hz, H-1a), 3.82 (dd, $J_{1b,2}$ = 4.7 Hz, H-1b), 2.43 (s, 3H, C*H*$_3$Ar), 2.07 (s, 6H, 2OAc), 2.05 (s, 3H, OAc), 2.02 (t, $J_{1'a,3'}$ = $J_{1'b,3'}$ = 2.4 Hz, H-3′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.0, 169.5 (3O*C*OCH$_3$), 149.5 (C-3″, C-5″), 143.7 (C-1″), 135.7 (C-4″), 129.3 (C-2), 128.8 (C-3), 127.7 (C-2″, C-6″), 76.3 (C-2′), 74.0 (C-3′), 71.4 (C-4), 71.3 (C-5), 61.7 (C-6), 47.6 (C-1), 36.0 (C-1′), 21.5 (*C*H$_3$Ar), 20.8, 20.7 (3OCO*C*H$_3$); HRMS calcd for $C_{22}H_{27}NO_8S$ + H 466.1535, found 466.1533; *m*/*z* (rel intensity) 466 (M + H, 5), 222 (100), 406 (M + H − AcOH, 59), 346 (M + H − 2AcOH, 15), 310 (M − Ts, 22), 286 (M + H − 3AcOH, 10), 250 (M − Ts − AcOH, 20), 91 (C_7H_7, 55).

(2*E*)-4,5,6-Tri-*O*-acetyl-1,2,3-trideoxy-1-(*N*-propargylacetylamine)-D-*erythro*-hex-2-enose (6b). A stirred solution of **5** (4.64 g, 14.9 mmol) in pyridine (40 mL) at 0 °C was treated with acetic anhydride (40 mL) and kept in the dark for 4 h at room temperature. The mixture was then poured into ice−water (500 mL) and extracted with CH_2Cl_2 (3 × 150 mL). The combined organic layers were washed successively with 2 N HCl (2 × 150 mL), a saturated solution of $NaHCO_3$ (2 × 150 mL), and water (2 × 150 mL), dried ($MgSO_4$), and concentrated in vacuo to give an oil that was purified by flash chromatography (ethyl acetate), (4.51 g, 86%). Recrystallization from hexane/ethyl acetate gave **6b** as colorless needles: mp 52−54 °C; $[\alpha]_D$ +25.7, $[\alpha]_{578}$ +26.7, $[\alpha]_{546}$ +31.0, $[\alpha]_{436}$ +55.1, $[\alpha]_{365}$ +90.4 (*c* 0.5, $CHCl_3$); IR (KBr) 3270 m, 1740 s, 1730 s, 1640 s, 1230 s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) ((*E*)-isomer) δ 5.80 (dt, $J_{1,2}$ = 5.0 Hz, $J_{2,3}$ = 15.4 Hz, H-2), 5.63 (m, H-3), 5.49 (m, H-4), 5.20 (m, H-5), 4.24 (dd, $J_{5,6}$ = 3.4 Hz, $J_{6,6'}$ = 8.9 Hz, H-6), 4.18 (dd, $J_{5,6'}$ = 2.3 Hz, H-6′), 4.07 (d, $J_{1,2}$ = 3.9 Hz, H-1a, H-1b), 3.96 (bs, H-1′a, H-1′b), 2.31 (t, $J_{1',3'}$ = 2.4 Hz, H-3′), 2.20 (C*H*$_3$Ar), 2.10 (s, 3H, OAc), 2.09 (s, 6H, 2 OAc); ((*Z*)-isomer) δ 5.76 (dt, $J_{1,2}$ = 6.1 Hz, $J_{2,3}$ = 15.2 Hz, H-2), 5.59 (m, H-3), 5.49 (m, H-4), 5.20 (m, H-5), 4.24 (dd, $J_{5,6}$ = 3.4 Hz, $J_{6,6'}$ = 8.9 Hz, H-6), 4.18 (dd, $J_{5,6'}$ = 1.7 Hz, H-6′), 4.14 (d, $J_{1,2}$ = 3.8 Hz, H-1a, H-1b), 4.12 (bs, H-1′a, H-1′b), 2.22 (t, $J_{1',3'}$ = 2.2 Hz, H-3′), 2.15 (C*H*$_3$Ar), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$) ((*E*)-isomer) δ 170.5, 170.4, 170.2 (3O*C*OCH$_3$), 130.1 (C-2), 126.4 (C-3), 78.8 (C-2′), 72.1 (C-3′), 71.7 (C-4), 71.5 (C-5), 61.7 (C-6), 48.7 (C-1), 34.1 (C-1′), 21.3 (NCO*C*H$_3$), 20.9, 20.8, 20.7 (3 OCO*C*H$_3$); ((*Z*)-isomer) δ 170.1, 170.0, 169.6 (3O*C*OCH$_3$), 130.6 (C-2), 126.9 (C-3), 78.2 (C-2′), 72.8 (C-3′), 71.8 (C-4), 71.5 (C-5), 61.7 (C-6), 46.4 (C-1), 37.4 (C-1′), 21.5 (NCO*C*H$_3$), 20.9, 20.8, 20.7 (3OCO*C*H$_3$); HRMS calcd for $C_{17}H_{23}NO_7$ + H 354.1552, found 354.1545; *m*/*z* (rel intensity) 354 (M + H, 5), 294 (M − OAc, 100), 252 (M + H − AcOH − Ac, 4), 192 (M + H − 2AcOH − Ac, 18), 132 (M + H − 3AcOH − Ac, 13). Anal. Calcd for $C_{17}H_{23}NO_7$: C, 57.78; H, 6.56; N, 3.96. Found: C, 57.99; H, 6.63; N, 4.20.

(2*E*)-4,5,6-Tri-*O*-acetyl-1,2,3-trideoxy-1-(*N*-propargyl-*tert*-butyloxicarbonylamine)-D-*erythro*-hex-2-enose (6c). To a stirred solution of **5** (2.85 g, 9.15 mmol) in THF (10 mL) was added di-*tert*-butyl dicarbonate (1.9 g, 9.15 mmol) portionwise over a 15 min period. The resulting solution was stirred for 5 days at room temperature and then concentrated in vacuo. The residue was purified by flash chromatography (hexane/ethyl acetate 2:1) to give **6c** as an oil (949 mg, 27%): $[\alpha]_D$ + 22.5, $[\alpha]_{578}$ +23.6, $[\alpha]_{546}$ +26.5, $[\alpha]_{436}$ +47.6, $[\alpha]_{365}$ +71.8 (*c* 0.55, $CHCl_3$); IR (film) 3291 m, 1746 s, 1705 s, 1680 m, 1370 m, 1220 s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (dt, $J_{1,2}$ = 6.0 Hz, $J_{2,3}$ = 15.7 Hz, H-2), 5.53−5.65 (bm, H-3), 5.49 (dd, $J_{3,4}$ = 6.8 Hz, $J_{4,5}$ = 4.8 Hz, H-4), 5.21 (m, H-5), 4.25 (dd, $J_{5,6}$ = 3.8 Hz, $J_{6,6'}$ = 12.0 Hz, H-6), 4.16 (dd, $J_{5,6'}$ = 6.8 Hz, H-6′), 3.8−4.1 (bm, 4H, 2H-1′, 2H-1), 2.23 (t, $J_{1',3'}$ = 2.4 Hz, H-3′), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.46 (s, 9H, *t*-but); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.9, 169.4 (3O*C*OCH$_3$), 154.5 (O*C*OCH$_3$), 131.2 (C-2), 125.7 (C-3), 80.4 (2C, C-2′, C(CH$_3$)$_3$), 79.2 (C-3′), 71.8 (C-5), 71.4 (C-4), 61.7 (C-6), 47.2 b (C-1), 35.5 b (C-1′), 20.8, 20.7, 20.6 (3OCO*C*H$_3$); HRMS calcd for $C_{20}H_{29}NO_8$ + H 412.1971, found 412.1969; *m*/*z* (rel intensity) 412 (M + H, 1), 236 (M − 2AcOH − isobutylene, 100), 355 (M + H − isobutylene, 5), 296 (M + H − OAc − C(CH$_3$)$_3$, 45).

General Procedure for IPK Reactions. Synthesis of 3-Azabicyclo[3.3.0]octen-7-ones. A solution of azaenyne precursor (**6a**−**c**) in freshly distilled CH_2Cl_2 was treated with $Co_2(CO)_8$ (1.2 equiv) under a CO atmosphere, and the mixture was stirred for 45 min. Then, NMO (6 equiv) was added portionwise over a 15 min period, the reaction mixture being cooled to 0 °C before each addition and allowed to reach room temperature before a new one. The mixture was stirred for 1 h at room temperature, diluted with CH_2Cl_2, washed successively with 2 N HCl, a saturated solution of $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed to give the corresponding cyclopentenones.

(3*aR*,4*S*)-4-(Tri-*O*-acetyl-D-*erythro*-triol-1-yl)-2-tosyl-2,3,3*a*,4-tetrahydro-1*H*-cyclopenta[*c*]pyrrole-5-one (7a) and (3*aS*,4*R*)-4-(Tri-*O*-acetyl-D-*erythro*-triol-1-yl)-2-tosyl-2,3,3*a*,4-tetrahydro-1*H*-cyclopenta[*c*]pyrrole-5-one (7b). According to the general procedure, **6a** (510 mg, 1.07 mmol) was dissolved in CH_2Cl_2 (10 mL) and converted into a mixture of the cyclopentenones **7a** and **7b**. The reaction mixture was first eluted through a short column (2 cm long) of SiO_2 (2:1 hexane/ethyl acetate→ethyl acetate) to remove metal impurities, and the elution was concentrated; flash chromatography of the residue (hexane/ethyl acetate 1:1) afforded a 1.5:1 mixture (R_f 0.57, hexane/ethyl acetate 1:2) of **7a** and **7b** that was resolved by fractionated crystallization (hexane/ethyl acetate 1:1) (227 mg, 60%).

7a: mp 164 °C; $[\alpha]_D$ + 104.7, $[\alpha]_{578}$ +109.1, $[\alpha]_{546}$ +124.7, $[\alpha]_{436}$ +217.1 (*c* 0.5 $CHCl_3$); IR (KBr) 1744 s, 1707 s, 1643 m, 1600 w, 1340 s, 1160 s, 1250 s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, H-2″, H-6″), 7.38 (d, H-3″, H-5″), 6.02 (bs, H-6), 5.57 (dd, $J_{1',4}$ = 3.0 Hz, $J_{1',2'}$ = 4.6 Hz, H-1′), 5.44 (m, H-2′), 4.42 (bd, $J_{1a,1b}$ 1 = 7.0 Hz, H-1b), 4.24 (dd, $J_{2',3'b}$ = 3.9 Hz, $J_{3'a,3'b}$ = 12.0 Hz, H-3′b), 4.12 (t, $J_{3a,3b}$ = $J_{3a,3b}$ = 9.0 Hz, H-3b), 4.06 (dd, $J_{2',3'a}$ = 6.3 Hz, $J_{3'a,3'b}$ = 12.2 Hz, H-3′a), 4.04 (bd, $J_{1a,1b}$ = 16.6 Hz, H-1a), 3.34 (m, H-3*a*), 2.67 (dd, $J_{3a,3a}$ = 10.9 Hz, $J_{3a,3b}$ = 9.5 Hz, H-3a), 2.46 (s, 3H, C*H*$_3$Ar), 2.39 (t, $J_{1',4'}$ = $J_{3a,4}$ = 3.4 Hz, H-4), 2.12 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.97 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4 (C-5), 178.2 (C-6a), 170.4, 169.5, 169.1 (3O*C*OCH$_3$), 144.3 (C-1″), 133.4 (C-4″), 130.0 (C-3″, C-5″), 127.4 (C-2″, C-6″), 124.9 (C-6), 70.5 (C-2′), 68.3 (C-1′), 61.9 (C-3′), 52.3 (C-4), 52.1 (C-3), 47.7 (C-1), 46.0 (C-3*a*), 21.6 (*C*H$_3$Ar), 20.8, 20.7, 20.5 (3OCO*C*H$_3$). Anal. Calcd for $C_{23}H_{27}NO_9S$: C, 55.97; H, 5.51; N, 2.83; S, 6.49. Found: C, 56.21; H, 5.52; N, 3.08; S, 6.20.

7b: mp 110 °C; $[\alpha]_D$ −49, $[\alpha]_{578}$ −52, $[\alpha]_{546}$ −60, $[\alpha]_{436}$ −114.2 (*c* 0.5 $CHCl_3$); IR (KBr) 1750 s, 1705 s, 1649 m, 1600 w, 1350 s, 1250 s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, H-2″, H-6″), 7.36 (d, H-3″, H-5″), 5.95 (bs, H-6), 5.46 (dd, $J_{1',4}$ = 4.7 Hz, $J_{1',2'}$ = 7.4 Hz, H-1′), 5.32 (ddd, H-2′), 4.35 (dd, $J_{2',3'b}$ = 2.4 Hz, $J_{3'a,3'b}$ = 12.5 Hz, H-3′b), 4.30 (bd, $J_{1a,1b}$ = 17.0 Hz, $J_{1b,6}$ = 1.1 Hz, H-1b), 4.10 (dd, $J_{2',3'a}$ = 5.2 Hz, $J_{3'a,3'b}$ = 12.5 Hz, H-3′a), 4.08 (t, $J_{3a,3b}$ = $J_{3a,3b}$ = 9.0 Hz, H-3b), 4.00 (bd, $J_{1a,1b}$ = 17.0 Hz, $J_{1a,6}$ = 1.1 Hz, H-1a), 3.09 (m, H-3*a*), 2.66 (dd, $J_{3a,3a}$ = 10.8 Hz, $J_{3a,3b}$ = 9.0 Hz, H-3a), 2.47 (t, $J_{1',4}$ = $J_{3a,4}$ 4.7 Hz, H-4), 2.44 (s, 3H, CH_3Ar), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 1.99 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5 (C-5), 176.7 (C-6a), 170.6, 169.7, 169.6, (3 O*C*OCH$_3$), 144.3 (C-1″), 133.3 (C-4″), 130.1 (C-3″, C-5"), 127.4 (C-2″, C-6″), 125.4 (C-6), 70.2 (C-2′), 69.1 (C-1′), 61.6 (C-3′), 52.0 (C-3), 51.8 (C-4), 47.5 (C-1), 46.4 (C-3*a*), 21.5 (*C*H$_3$Ar), 20.8, 20.7 (3OCO*C*H$_3$). Anal. Calcd for $C_{23}H_{27}NO_9S$: C, 55.97; H, 5.51; N, 2.83; S, 6.49. Found: C, 56.30; H, 5.50; N, 2.82; S, 6.35.

(3*aR*,4*S*)-2-Acetyl-4-(tri-*O*-acetyl-D-*erythro*-triol-1-yl)-2,3,3*a*,4-tetrahydro-1*H*-cyclopenta[*c*]pyrrole-5-one (10a) and (3*aS*,4*R*)-2-Acetyl-4-(tri-*O*-acetyl-D-*erythro*-triol-1-yl)-2,3,3*a*,4-tetrahydro-1*H*-cyclopenta[*c*]pyrrole-5-one (10b). According to the general procedure, **6b** (555 mg, 1.56 mmol) was dissolved in CH_2Cl_2 (15 mL) and converted into a mixture of cyclopentenones **10a** and **10b** that was purified by flash chromatography, eluting first with diethyl ether/hexane 9:1, and then ethyl acetate, and finally ethyl acetate/methanol 9:1 to give a 1.5:1 mixture of **10a** and **10b** (R_f 0.31, chloroform/acetone 7:3) (290 mg, 56%). For spectral data, see Supporting Information.

(3*aR*,4*S*)-4-(Tri-*O*-acetyl-D-*erythro*-triol-1-yl)-2-(*tert*-butyloxicarbonylamine)-(2,3,3*a*,4-tetrahydro-1*H*-cyclopenta-[*c*]pyrrole-5-one (11a) and (3*aS*,4*R*)-4-(Tri-*O*-acetyl-D-*erythro*-triol-1-yl)-2-(*tert*-butyloxicarbonylamine)-(2,3,3*a*,4-tetrahydro-1*H*-cyclopenta[*c*]pyrrole-5-one (11b). According to the general procedure, **6c** (268 mg, 0.65 mmol) was dissolved in CH_2Cl_2 (10 mL) and converted into a mixture of the cyclopentenones **11a** and **11b**. The reaction mixture was purified by flash chromatography eluting first with a gradient of diethyl ether/hexane (8:2→8:1) and then with ethyl acetate to give a 1.32:1 mixture of **11b** and **11a** (R_f 0.5, hexane/ethyl acetate 1:1) that was resolved by preparative TLC (petroleum ether/ether 3:7) (113 mg, 47%).

11a: $[\alpha]_D$ +55, $[\alpha]_{578}$ +57.2, $[\alpha]_{546}$ +60.6 (*c* 0.5, $CHCl_3$); IR (film) 1755 s, 1703 s, 1384 m, 1223 s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, H-6, *Z*), 6.11 (s, H-6, *E*), 5.65 (m, H-1′), 5.42 (m, H-2′), 4.40−4.05 (m, 4H, 2 H-1, 2 H-3′), 4.18 (t, $J_{3a,3b}$ = $J_{3a,3b}$ = 10.0 Hz, H-3b), 3.39 (m, H-3*a*), 2.93 (t, $J_{3a,3a}$ = $J_{3a,3b}$ = 10.1 Hz, H-3a), 2.56 (m, H-4, *Z*), 2.52 (m, H-4, *E*), 2.12 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.49 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.3 (C-5), 180.1 (C-6a, *Z*), 179.7 (C-6a, *E*), 170.4, 169.6, 169.5, 169.2 (3O*C*OCH$_3$), 154.1 (C-1″, *Z*), 153.9 (C-1″, *E*), 124.5, 124.4 (C-6), 80.4 (C-2″), 70.8 (C-2′, *E*), 70.6 (C-2′, *Z*), 68.7 (C-1′, *Z*), 68.4 (C-1′, *E*), 61.9, 61.8 (C-3′), 52.9 (C-4, *E*), 52.8 (C-4, *Z*), 50.6, 49.9 (C-3), 46.7 (C-1, *E*), 46.3 (C-1, *Z*), 45.6, 45.2 (C-3*a*), 28.4 (C(CH$_3$)$_3$), 20.8, 20.7, 20.6 (3OCO*C*H$_3$); HRMS calcd for $C_{21}H_{30}NO_9$ + H 440.1920, found 440.1925; *m*/*z* (rel intensity) 440 (M + H, 3), 264 (M + H − isobutylene − 2AcOH, 100), 264 (M + H − isobutylene), 324 (M + H − isobutylene − AcOH, 81), 203 (M + H − isobutylene − 3AcOH, 95).

11b: $[\alpha]_D$ −98.7, $[\alpha]_{578}$ −104, $[\alpha]_{546}$ −123 (*c* 0.4, $CHCl_3$); IR (film) 1747 s, 1707 s, 1384 m, 1221 s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.04 (s, H-6, *Z*), 6.01 (s, H-6, *E*), 5.53 (m, H-1′), 5.43 (m, H-2′), 5.34 (m, H-2′), 4.40−4.10 (m, 4H, 2 H-1, 2 H-3′), 4.06 (t, $J_{3a,3b}$ = $J_{3a,3b}$ = 9.9 Hz, H-3b, *E*), 3.99 (t, $J_{3a,3b}$ = $J_{3a,3b}$ = 10.1 Hz, H-3b, *Z*), 3.20 (m, H-3*a*), 2.92 (t, $J_{3a,3a}$ = $J_{3a,3b}$ = 9.9 Hz, H-3a, *E*), 2.88 (t, $J_{3a,3a}$ = $J_{3a,3b}$ = 10.1 Hz, H-3a, *Z*), 2.58 (m, H-4), 2.09, 2.08 (s, 3H, OAc), 2.07, 2.05 (s, 3H, OAc), 2.01, 2.00 (s, 3H, OAc), 1.49 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4 (C-5), 178.7 (C-6a, *E*), 178.2 (C-6a, *Z*), 170.6, 170.0, 169.8 (3O*C*OCH$_3$), 154.0 (C-1″, *Z*), 153.8 (C-1″, *E*), 125.0 (C-6, *Z*), 124.7 (C-6, *E*), 80.4 (C-2″), 70.3 (C-2′), 69.4 (C-1′, *E*), 69.3 (C-1′, *Z*), 64.2 (C-3′, *Z*), 61.7 (C-3′, *E*), 52.3, 51.9 (C-4), 50.3 (C-3, *E*), 49.8 (C-3, *Z*), 46.5 (C-1, *E*), 46.1 (C-1, *Z*), 45.6 (C-3*a*), 30.9 (C(CH$_3$)$_3$), 20.8, 20.7, 20.6 (3OCO*C*H$_3$); HRMS calcd for $C_{21}H_{30}NO_9$ + H 440.1920, found 440.1914; *m*/*z* (rel intensity) 440 (M + H, 2), 264 (M + H − isobutylene − 2AcOH, 100), 384 (M + H − isobutylene), 324 (M + H − isobutylene − AcOH, 69), 203 (M + H − isobutylene − 3AcOH, 78).

(3*aS*,4*E*,2′*S*)-4-(2′,3′-Diacetoxypropyliden)-2-tosyl-2,3,3*a*,4-tetrahydro-1*H*-cyclopenta[*c*]pyrrole-5-one(8a)and(3*aR*,4*E*,2′*S*)-4-(2′,3′-Diacetoxypropyliden)-2-tosyl-2,3,3*a*,4-tetrahydro-1*H*-cyclopenta[*c*]pyrrole-5-one (8b). According to the general procedure, **6a** (854 mg, 1.8 mmol) was dissolved in CH_2Cl_2 (10 mL) excepting that the reaction mixture was stirred for 6 h after the addition of NMO. The residue was eluted through a short column (2 cm long) of SiO_2 (3:1 hexane/AcOEt→ethyl acetate) to remove metal impurities, and the elution was concentrated; flash chromatography of the residue (hexane/ethyl acetate 1:1) afforded a 1.5:1 mixture of **8a** and **8b** (R_f 0.76 hexane/ethyl acetate 1:2) (75 mg, 11%) and a second fraction (R_f 0.57 hexane/ethyl acetate 1:2) of a 1.2:1 mixture of **7a** and **7b** (337 mg, 45%). Cyclopentenone **8a** crystallized as a white solid from the fraction of R_f 0.76 (45 mg).

8a: $[\alpha]_D$ −31.2, $[\alpha]_{578}$ −31.2, $[\alpha]_{546}$ −37.6, $[\alpha]_{436}$ −64 (*c* 0.25 $CHCl_3$); IR (film) 1742 s, 1715 f, 1670 m, 1640 m, 1600 w, 1348 s, 1221 s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, H-2″, H-6″), 7.35 (d, H-3″, H-5″), 6.32 (dd, $J_{1',3a}$ = 1.6 Hz, $J_{1',2'}$ = 9.2 Hz, H-1′), 6.18 (bs, H-6), 5.45 (ddd, $J_{2',3'a}$ = 6.6 Hz, $J_{2',3'b}$ = 4.4 Hz, $J_{1',2'}$ = 9.2 Hz, H-2′), 4.33 (bd, $J_{1a,1b}$ = 16.0 Hz, H-1b), 4.23 (t, $J_{3a,3b}$ = 8.7 Hz, $J_{3a,3b}$ = 9.1 Hz, H-3b), 4.20 (dd, $J_{2',3'b}$ = 4.4 Hz, $J_{3'a,3'b}$ = 12.1 Hz, H-3′b), 4.12 (dd, $J_{2',3'a}$ = 6.6 Hz, $J_{3'a,3'b}$ = 11.8 Hz, H-3′a), 4.07 (bd, $J_{1a,1b}$ = 16.0 Hz, H-1a), 3.85 (t, $J_{3a,3a}$ = 9.4 Hz, $J_{3a,3b}$ 9.8 Hz, H-3*a*), 2.72 (dd, $J_{3a,3a}$ = 10.7 Hz, $J_{3a,3b}$ = 9.5 Hz, H-3a), 2.44 (s, 3H, CH_3Ar), 2.09 (s, 6H, 2OAc); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8 (C-5), 173.6 (C-6a), 170.3, 169.9 (2O*C*OCH$_3$), 144.3 (C-1″), 139.1 (C-4), 133.5 (C-4″), 130.1 (C-3″, C-5"), 127.6 (C-6), 127.4 (C-2″, C-6″), 127.3 (C-1′), 69.3 (C-2′), 64.1 (C-3′), 50.7 (C-3), 47.2 (C-1), 46.1 (C-3*a*), 21.5 (*C*H$_3$Ar), 20.8, 20.7 (2OCO*C*H$_3$); HRMS calcd for $C_{21}H_{23}NO_7S$ 433.1195, found 433.1208; *m*/*z* (rel intensity) 433 (M^+, 2), 314 (M − OAc − AcOH, 100), 374 (M − OAc, 42), 278 (M − Ts, 5), 218 (M − AcOH − Ts, 9), 158 (M − 2AcOH − Ts, 14), 91 (C_7H_7, 18).

4-(2′,3′-Diacetoxypropyliden)-2-tosyl-2,3,4,6-tetrahydro-1*H*-cyclopenta[*c*]pyrrole-5-one (9). A solution of **7a** (22 mg, 0.04 mmol) in pyridine (1 mL) was stirred for 15 h at 60 °C. Then, the reaction mixture was poured into ice−water (25 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were successively rinsed with HCl 2 N (2 × 10 mL), a saturated solution of $NaHCO_3$ (2 × 10 mL), and water (2 × 10 mL) and dried ($MgSO_4$). The solvent was removed by rotary evaporation to give **9** as an oil (11 mg, 27%): $[\alpha]_D$ +5.5, $[\alpha]_{578}$ +5.0, $[\alpha]_{546}$ +4.8 (*c* 0.5, $CHCl_3$); IR (film) 1742 s, 1630 m, 1341 m, 1163 s, 1223 s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, $J_{2'',6''}$ = 6.9 Hz, H-2″, H-6″), 7.33 (d, $J_{3'',5''}$ = 8.2 Hz, H-3″, H-5″), 5.93 (d, $J_{1',2'}$ = 9.5 Hz, H-1′), 5.46 (m, H-2′), 4.65 (m, $J_{1a,1b}$ = 13.7 Hz, H-1b), 4.52 (m, $J_{1a,1b}$ = 13.7 Hz, H-1a), 4.27 (m, H-3a, H-3b), 4.18 (dd, $J_{2',3'b}$ = 3.8 Hz, $J_{3'a,3'b}$ = 12.0 Hz, H-3′b), 2.88 (bs, 2H, H-6), 2.41 (s, 3H, CH_3Ar), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7 (C-5), 170.4, 169.9 (2O*C*OCH$_3$), 145.1 (C-3*a*), 143.9 (C-1″), 139.8 (C-6a), 136.0 (C-4), 133.9 (C-4″), 129.9 (C-3″, C-5″), 127.4 (C-2″, C-6″), 121.4 (C-1′), 69.1 (C-2′), 64.3 (C-3′), 53.0 (C-1), 52.1 (C-3), 39.5 (C-6), 21.5, 20.6 (2OCO*C*H$_3$), 20.9 (*C*H$_3$Ar); HRMS calcd for $C_{21}H_{23}NO_7S$ 433.1195, found 433.1194; *m*/*z* (rel intensity) 433 (M^+, 2), 316 (M + H − 2OAc, 100), 374 (M + H − OAc, 85), 218 (M − AcOH − Ts, 12), 91 (C_7H_7, 46).

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Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **6a**−**c**, **7a**,**b**, **8a**, **9**, **10a**,**b** (mixture), and **11a**,**b**, an ORTEP plot of **7b**, and full information concerning the X-ray structure of **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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