Notes

Synthesis of *C*-Aryl Furanosides by the "Reverse Polarity" Strategy

Kathlyn A. Parker*,[1] and Dai-Shi Su[2]

Department of Chemistry, Brown University, Providence, Rhode Island 02912

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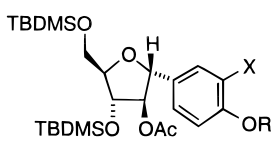
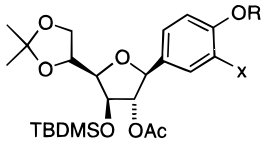
The *C*-aryl glycoside antitumor antibiotics have served as the inspiration for the recent development of synthetic methods which connect the polyketide "aglycone" and the carbohydrate appendage.[3] One of these methods, developed in our labs, is based on a novel application of the umpolung concept. It uses the addition of a lithio glycal to a quinol ketal or quinone and the reductive or nonreductive aromatization of the adduct as the key steps.[4]

To date, these methods have been applied only in the context of the preparation of *C*-aryl *pyrano*sides. We are now pleased to report the extension of this strategy to the synthesis of *C*-aryl *furano*sides with the efficient preparation of model compounds **1** and **2**.



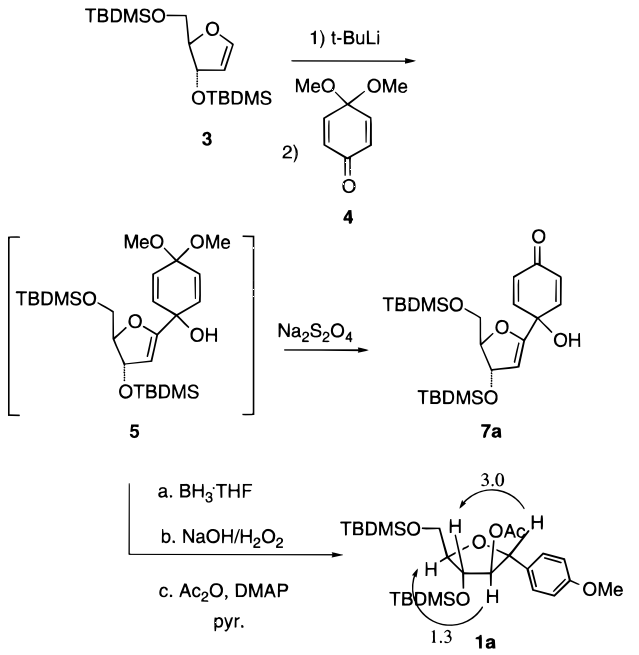
1 a X = H, R = Me
b X = H. R = Ac
c X = Br, R = Ac



2 a X=H, R = Me
b X=H, R = Ac
c X = Br, R = Ac

Elaboration of a Trans-Disubstituted Furanoid Glycal. Synthesis of C-1 Aryl Arabinofuranosides 1. The known trans-disubstituted furanoid glycal **3** was prepared from D-ribose according to Ireland's method.[5] Lithiation of this compound and addition of the resulting reagent to quinone ketal **4** gave quinol ketal **5**, contaminated with significant amounts of the starting material **4**. The components of this mixture could not be separated. Therefore the crude product was used in subsequent reactions, and byproducts were removed at a later stage. The attempted reduction of crude adduct **5** with sodium dithionite afforded none of the *C*-aryl glycal. Instead quinol **7a**, the hydrolysis product, was obtained in 53% yield.

Scheme 1



On the other hand, both reductive aromatization and anti-Markovnikov hydration could be effected in one procedure by treatment of crude **5** with 5 mol equiv of borane−THF followed by stirring with basic hydrogen peroxide. The resulting *C*-aryl glycoside was isolated and characterized as the 2′-acetate **1a**, obtained in an overall 40% yield from glycal **3**. The stereochemistry of this product was determined by an NOE difference experiment. The NOE enhancements are shown on the structure in Scheme 1.

The four-step procedure described above was convenient and gave an acceptable overall yield. However, we imagined that we might have use for derivatives in which the phenolic hydroxyl group was free or protected by an easily removable group. We needed then to be able to effect the reductive aromatization of quinol glycal **7a**. Substrate **7a** was most conveniently obtained (Scheme 2) by the addition of the lithio reagent derived from glycal **3** to benzoquinone (**6a**).

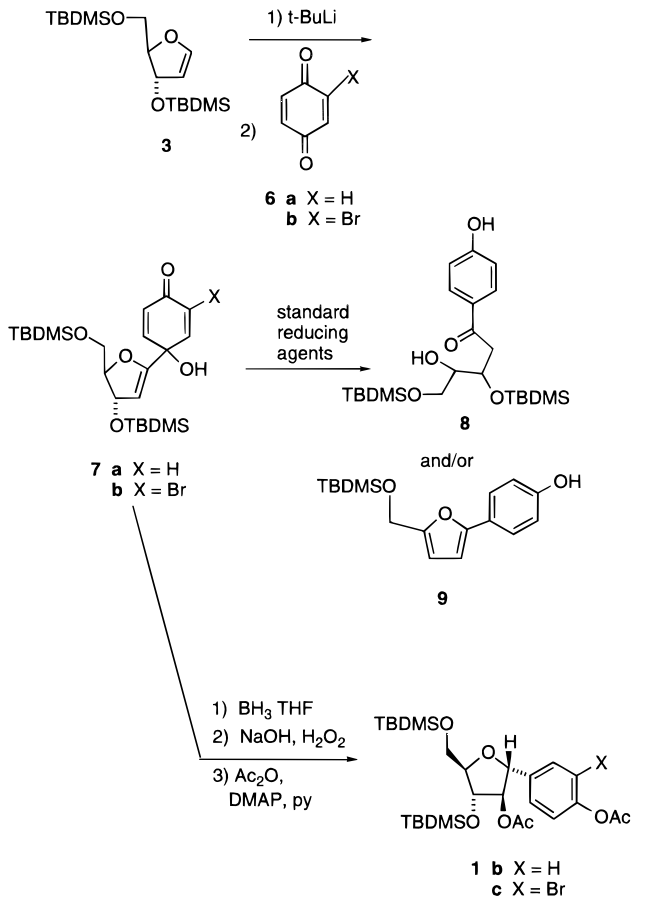
Attempts to apply literature methods for reductive aromatization of quinols to the glycal-substituted quinol **7a** resulted in recovery of starting material (with $NaBH_4$[6])[4b] or hydrolytic ring opening and dehydration (with $Na_2S_2O_4$,[4b] Al/Hg,[7] Li/NH_3 to afford ketone **8** and furan **9**). Similarly, treatment with Li(O*t*-Bu)$_3$AlH or Red-Al resulted in the recovery of starting material **7a**, and treatment with $LiAlH_4$ or DIBAL-H gave the dehydration product **9**.

On the other hand, under controlled conditions (0 °C to room temperature), treatment with BH_3·THF (5 equiv) followed by stirring with basic hydrogen peroxide converted quinol **7a** to the desired aryl glycoside. The BH_3·THF reagent gave better yields than the BH_3·SMe_2

(1) Recipient of an NSF Career Advancement Award, 1992−1993.
(2) Government Assistance in Areas of National Needs Fellow, 1993−95.
(3) For excellent reviews, see: (a) Postema, M. H. D. *Tetrahedron* **1992**, 48, 8545. (b) Suzuki, K.; Matsumoto, T. In *Recent Progress in the Chemical Synthesis of Antibiotics and Related Microbial Products*; Lukacs, G., Ed.; Springer Verlag: Berlin, 1993; Vol. 2, pp 352−403. (c) Jaramillo, C.; Knapp, S. *Synthesis* **1994**, 1. (d) Postema, M. H. D. In *C-Glycoside Synthesis*; Rees, C. W., Ed.; CRC Press: Boca Raton, FL, 1995.
(4) (a) Parker, K. A.; Coburn, C. A. *J. Am. Chem. Soc.* **1991**, *113*, 8516. (b) Parker, K. A.; Coburn, C. A. *J. Org. Chem.* **1992**, *57*, 5547. (c) Parker, K. A.; Koh, Y.-h. *J. Am. Chem. Soc.* **1994**, *116*, 11149−11150. (d) Parker, K. A.; Coburn, C. A.; Koh, Y.-h. *J. Org. Chem.* **1995**, *60*, 2938.
(5) (a) Ireland, R. E.; Thaisrivongs, S.; Vanier, N.; Wilcox, C. S. *J. Org. Chem.* **1980**, *45*, 48. (b) Ireland, R. E.; Norbeck, D. W.; Mandel, G. S.; Mandel, N. S. *J. Am. Chem. Soc.* **1985**, *107*, 3285.
(6) Manning, M. J.; Henton, D. R.; Swenton, J. S. *Tetrahedron Lett.* **1977**, 1679.
(7) Stahly, G. P.; Bell, D. R. *J. Org. Chem.* **1989**, *54*, 2873.

0022-3263/96/1961-2191$12.00/0

Scheme 2



(BMS) reagent. Without purification, the crude product was protected as the corresponding diacetate **1b**, which was obtained in an overall yield of 68%. A similar sequence converted quinol **7b** to *C*-aryl furanoside **1c** in 71% yield.

Elaboration of a Cis-Disubstituted Furanoid Glycal. Synthesis of C-1 Aryl Glucofuranosides 2. In order to determine the generality of the chemistry described above, the reductive aromatization schemes were examined in a furanoglycal system in which the 3- and 5-substituents were cis (Scheme 3). We chose to work with substrates derived from the known furanoid glycal **10** (prepared by the literature procedure from D-mannose).[8]

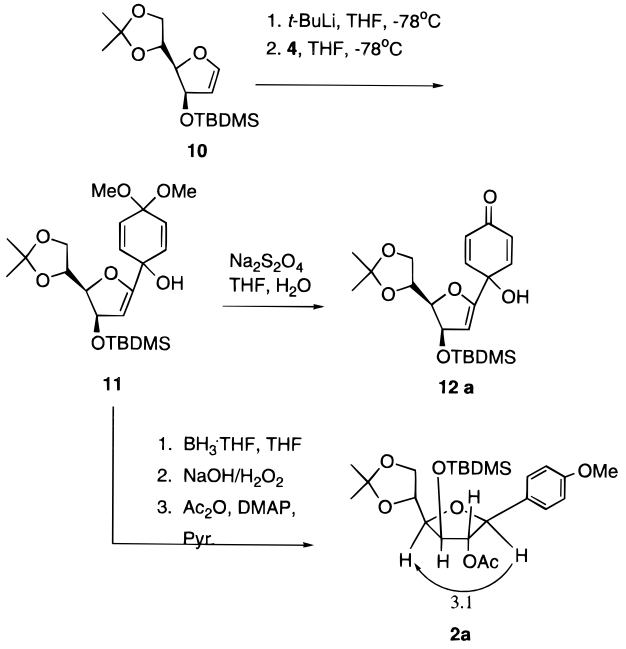
Lithiation of glycal **10** gave a reagent which added to quinol ketal **4**, affording adduct **11**. The attempted reduction of **11** with sodium dithionite gave the hydrolysis product, quinol **12a,** in 90% yield.

Reductive aromatization proceeded, however, when the borane protocol (−15 °C, 4 h) was applied to quinol acetal **11**. As expected, borane added to the glycal double bond on the side opposite the substituents. After acylation, a 70% overall yield of C-glycoside **2a** was obtained. The stereochemistry of this reductive aromatization/hydroboration product was verified by an NOE difference experiment. The enhancement is shown on the structure in Scheme 3.

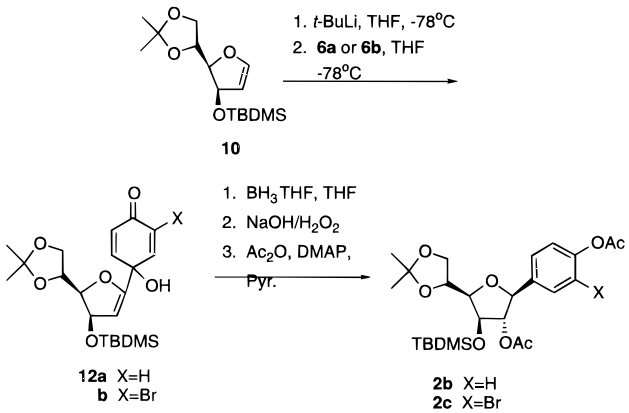
Reductive aromatization of quinol substrates was also examined with the quinol substrates **12a** and **12b**, prepared by addition of lithiated glycal **10** to quinones

(8) Ghosh, A. K.; McKee, S. P.; Thompson, W. J. *J. Org. Chem.* **1991**, *56*, 6500.

Scheme 3



Scheme 4



6a and **6b** respectively (Scheme 4). Treatment of quinol **12a** with BH_3·THF (−15 °C, 4 h) followed by stirring with $NaOH/H_2O_2$ and acylation gave *C*-aryl furanoside **2b** in an overall yield of 54%. Likewise, quinol **12b** was converted to *C*-aryl furanoside **2c** in 43% overall yield. The cis-disubstituted dihydrofurans **12a** and **12b** were reduced by BH_3·THF at lower temperature and in shorter reaction times than the trans-disubstituted substrates **7a** and **7b**.

Conclusions

The reverse polarity strategy provides an alternative to conventional C-glycosylation methods for the preparation of *C*-aryl furanosides with some stereochemical patterns. These procedures are simple and good yields are obtained. We are continuing to examine applications of this methodology in the context of natural product synthesis.

Experimental Section

Solvents were dried and purified by standard methods before use. Ether refers to diethyl ether. Flash chromatography was performed with silical gel (0.035−0.07 mm). Bromobenzo-

quinone (**6b**) was prepared according to the procedure of Carlson and Miller and used without purification.[9]

Quinol Glycal 7a from 3 and 6a. To a solution of 202 mg (0.586 mmol) of glycal **3**[5] in 4 mL of THF at −78 °C was added 1.1 mL (1.87 mmol) of *t*-BuLi (1.7 M in pentane). The solution was stirred at −78 °C for 1 h and then added dropwise by cannula to a solution of 86 mg (0.796 mmol) of *p*-benzoquinone **6a** in 20 mL of THF at −78 °C . The dark reaction mixture was stirred for 4 h, quenched with 25 mL of H_2O, and extracted with CH_2Cl_2 (3 × 40 mL). The combined organic solution was dried with Na_2SO_4, filtered, and concentrated. Chromatography (3:1 hexanes/EtOAc) gave 229 mg (86%) of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.90 (ddd, J = 10.4, 3.2, 2.1 Hz, 2H), 6.19 (ddd, J = 10.2, 3.4, 1.9 Hz, 2H), 5.01 (d, J = 2.6 Hz, 1H), 4.93 (t, J = 2.9 Hz, 1H), 4.36 (dd, J = 5.3, 2.2 Hz, 1H), 3.69 (dd, J = 9.9, 5.1 Hz, 1H), 3.57 (dd, J = 9.8, 5.5 Hz, 1H), 0.88 ("s", 18H), 0.06 ("s", 12H); ^{13}C NMR ($CDCl_3$) δ 185.0, 158.5, 147.0, 128.8, 128.6, 100.6, 90.2, 66.9, 62.6, 25.8, 18.1, −4.28, −4.44, −5.40, −5.45; IR (neat) 3381, 1673, 1651 cm^{-1}; HRMS (FAB, NaI) calcd 475.2312, found 475.2318 (M + Na).

Quinol Glycal 7a from Quinol Ketal 5. To a solution of 31 mg (*ca.* 0.062 mmol) of crude quinol ketal **5** in 1 mL of THF/H_2O (3:1) was added 54 mg (0.31 mmol) of sodium dithionite. The solution was stirred at rt for 8.5 h. The reaction mixture was quenched with H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated. Preparative TLC (3:1 hexanes/EtOAc with 1% Et_3N) afforded 18 mg (53% from glycal **3**) of a yellow oil.

Bromoquinol Glycal 7b. To a solution of 90 mg (0.261 mmol) of glycal **3**[5] in 2 mL of THF at −78 °C was added 0.5 mL (0.85 mmol) of *t*-BuLi (1.7 M in pentane). The solution was stirred at this temperature for 1 h and then added dropwise by cannula to a solution of 44 mg (0.235 mmol) of bromobenzoquinone (**6b**)[9] in 10 mL of THF at −78 °C. The dark reaction mixture was stirred for 9 h and then quenched with 20 mL of H_2O and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic solution was dried with Na_2SO_4, filtered, and concentrated. Chromatography (3:1 hexanes/EtOAc) gave 121 mg (87%) of a yellow oil: ^{1}H NMR (CD_2Cl_2) δ 7.34 (dd, J = 2.8, 1.0 Hz, 1H), 6.9 (dd, J = 10.0, 3.0 Hz, 1H), 6.3 (dd, J = 10.0, 1.0 Hz, 1H), 5.09 (t, J = 2.3 Hz, 1H), 4.94 (t, J = 2.3 Hz, 1H), 4.33 (m, 1H), 3.79 (dd J = 11.0, 4.9 Hz, 1H), 3.61 (dd, J = 11.1, 5.1 Hz, 1H), 2.97 (s, 1H), 0.88 (s, 18H), 0.05 (s, 12H); ^{13}C NMR (CD_2Cl_2) δ 178.0, 158.0, 147.7, 147.6, 133.2, 127.7, 101.6, 90.9, 76.6, 69.8, 63.1, 25.9, 18.5, −4.4, −5.3; FTIR (neat) 3406, 1673, 1605, 1257 cm^{-1}; HRMS (FAB, NaI) calcd 555.1397, found 555.1390 (M + Na, ^{81}Br).

Monoacetate 1a. To a solution of 168 mg (0.49 mmol) of glycal **3**[4] in 5 mL of THF at −78 °C was added 0.9 mL (1.53 mmol) of *t*-BuLi (1.7 M in pentane). The resulting solution was stirred at −78 °C for 30 min and then added dropwise by cannula to a solution of 65 mL (0.47 mmol) of 4,4-dimethoxy-2,5-cyclohexadien-1-one (**4**) in 5 mL of THF at −78 °C. The yellow reaction mixture was stirred at −78 °C for 5 h and 45 min, quenched with 50 mL of H_2O, and extracted with EtOAc (4 × 30 mL). The combined EtOAc solution was washed with brine (2 × 100 mL), dried with Na_2SO_4, filtered, and concentrated to give 241 mg of crude product **5**. To a solution of 39 mg of this material in 1 mL of THF at 0 °C was added 0.4 mL (0.4 mmol) of BH_3·THF (1 M solution in THF) dropwise over 5 min. The resulting solution was stirred at 0 °C for 3 h and quenched with 1 mL of MeOH and 2 mL of 3 N NaOH/H_2O_2 (1/1) solution. The resulting mixture was stirred at rt for 3.5 h and then partitioned between brine (15 mL) and EtOAc (4 × 20 mL). The combined organic solution was washed with brine (2 × 20 mL), dried with Na_2SO_4, and concentrated. To a solution of the crude product in 1 mL of pyridine were added a catalytic amount of DMAP and 0.5 mL of Ac_2O. The reaction mixture was stirred at rt overnight, quenched with 20 mL of H_2O, and extracted with CH_2Cl_2 (4 × 20 mL). The combined organic solution was dried over Na_2SO_4, filtered, and concentrated. Chromatography (one column with CH_2Cl_2 and then one with 3:1 hexanes/EtOAc) gave 10 mg (40% overall) of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.34 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 5.11 (t, J = 4.0 Hz, 1H), 4.87 (d, J = 4.1 Hz, 1H), 4.41 (t, J = 3.5 Hz, 1H), 4.09 (m, 1H), 3.77 (m, 5H), 2.05 (s, 3H), 0.93 ("s", 18H), 0.12 ("s", 12H); ^{13}C NMR ($CDCl_3$) δ 170.2, 159.6, 132.7, 128.0, 114.3, 113.9, 86.6, 85.8, 84.6, 77.3, 63.0, 55.6, 26.1, 26.0, 25.7, 21.2, −4.8, −5.3; FTIR (neat) 1747, 1233 cm^{-1}; HRMS (FAB) calcd 451.2670, found 451.2678 (M − OAc).

Diacetate 1b. To a solution of 54 mg (0.13 mmol) of quinol glycal **7a** in 1 mL of THF at 0 °C was added 0.65 mL (0.65 mmol) of BH_3·THF (1 M solution in THF). The reaction mixture was gradually warmed up to rt overnight and then quenched with 2 mL of MeOH and 3 mL of 3 N NaOH/H_2O_2 (1/1) solution. The resulting mixture was stirred at rt for 8.5 h and then extracted with ether (3 × 20 mL). The combined organic solution was washed with H_2O (1 × 30 mL), dried with Na_2SO_4, and concentrated. To a solution of the crude product in 1 mL of pyridine were added a catalytic amount of DMAP and 0.6 mL of Ac_2O. The resulting solution was stirred at rt for 11 h, quenched with 5 mL of H_2O, and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic solution was dried with Na_2SO_4, filtered, concentrated, and subjected to chromatography (9:1 hexanes/EtOAc) to give 48 mg (68% overall) of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.44 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2 H), 5.1 (t, J = 2.8 Hz, 1H), 4.97 (d, J = 3.3 Hz, 1H), 4.41 (t, J = 3.0 Hz, 1 H), 4.15 (m, 1H), 3.77 (m, 1H), 2.27 (s, 3H), 2.1 (s, 3H), 0.9 ("s", 18H), 0.1 ("s", 12H); ^{13}C NMR (CD_2Cl_2) δ 170.2, 169.7, 138.4, 127.7, 127.6 87.2, 86.0, 84.7, 77.4, 63.0, 26.1, 25.9, 25.6, 21.2, 18.6, −4.9, −5.3; FTIR (neat) 1745, 1370, 1196 cm^{-1}; HRMS (FAB), calcd 539.2860, found 539.2868 (M + H).

Diacetate 1c. To a solution of 34 mg (0.071 mmol) of quinol glycal **7b** in 1 mL of THF at 0 °C was added 0.4 mL (0.4 mmol) of BH_3·THF (1 M solution in THF). The reaction mixture was gradually warmed up to rt overnight and then quenched with 2 mL of MeOH and 3 mL of 3 N NaOH/H_2O_2 (1/1). The resulting mixture was stirred at rt for 8.5 h and extracted with ether (3 × 20 mL) The combined ether solution was washed with H_2O (1 × 30 mL), dried with Na_2SO_4, and concentrated. The crude product was dissolved in 1 mL of pyridine and to this solution was added a catalytic amount of DMAP and 0.6 mL of Ac_2O. The resulting solution was stirred at rt for 11 h, quenched with 5 mL of H_2O, and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic solution was dried with Na_2SO_4, filtered, and concentrated. Chromatography (9:1 hexanes/EtOAc) gave 31 mg (71% overall) of a yellow oil: ^{1}H NMR (CD_2Cl_2) δ 7.73 (s, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 5.05 (t, J = 2.5 Hz, 1H), 4.98 (d, J = 2.6 Hz, 1H), 4.40 (t, J = 2.4 Hz, 1H), 4.2 (m, 1H), 3.75 (m, 2H), 2.32 (s, 3H), 2.1 (s, 3H), 0.9 ("s", 18H), 0.1 ("s", 12H); ^{13}C NMR (CD_2Cl_2) δ 170.3, 168.8, 140.7, 131.3, 126.7, 124.2, 123.7, 87.9, 86.0, 84.5, 77.5, 63.0, 29.1, 26.1, 25.6, 21.2, 21.0, −4.9, −5.2; FTIR (neat) 1771, 1748, 1232 cm^{-1}; HRMS (FAB) calcd 617.1965, found 617.1959 (M + H, ^{79}Br).

Quinol Ketal Glycal 11. The procedure used for the preparation of quinol ketal glycal **5** was applied to lithiation of 149 mg (0.49 mmol) of glycal **10**[8] with 1 mL of *t*-BuLi (1.7M solution in pentane) and addition to quinone ketal **4** (68 mL, 0.49 mmol) to give 120 mg (78%) of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.17 (d, J = 10.2 Hz, 2H), 5.94 (d, J = 10.5 Hz, 2H), 4.93 (m, 2H), 4.45 (m, 2H), 4.08 (m, J = 9.5, 6.4 Hz, 1H), 3.90 (dd, J = 9.5, 5.9 Hz, 1H), 3.28 (s, 1H), 3.20 (s, 1H), 2.44 (s, 1H), 1.41 (s, 3H), 1.33 (s, 3H), 0.86 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 161.6, 133.7, 133.6, 128.2, 128.0, 108.6, 100.2, 93.5, 85.6, 73.9, 73.4, 65.9, 65.7, 50.4, 50.2, 26.5, 25.7, 25.1, −4.6, −5.0; FTIR (neat) 3382, 1672, 1066 cm^{-1}; HRMS (FAB, NaI); calcd 477.2284, found 477.2288 (M + Na).

Quinol Glycal 12a from 10 and 6a. A 50-mg sample (0.167 mmol) of glycal **10**[8] was lithiated (*t*-BuLi, 1.7 M solution in pentane, 0.5 mL) and coupled with **6a** (24 mg, 0.222 mmol) in a procedure resembling that for preparing **7a** to give 52 mg (76%) of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.88 (dd, J = 10.1, 1.7 Hz, 2H), 6.22 (dd, J = 10.0, 2.3Hz, 2H), 5.04 (d, J = 3.6 Hz, 1H), 4.96 (dd, J = 2.5, 7.0 Hz, 1H), 4.46 (m, 2H), 4.04 (dd, J = 9.8, 6.6 Hz, 1H), 3.88 (dd, J = 9.7, 6.7 Hz, 1H), 3.07 (s, 1H), 1.39 (s, 1H), 1.32 (s, 3H), 0.84 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 185.1, 159.8, 147.2, 129.1, 109.0, 101.8, 86.3, 74.2. 73.8, 67.3, 65.9, 26.6, 25.9, 25.3, 18.4, −4.5, −4.9; FTIR (neat) 3348 1673, 1066 cm^{-1}; HRMS (EI) calcd 333.1522, found 333.1526 (M − $C_3H_7O_2$).

Quinol Glycal 12a from Quinol Ketal 11. To a solution of 112 mg (0.247 mmol) of quinol ketal **11** in 2 mL of THF/H_2O

(9) Carlson, B. W.; Miller, L. L. *J. Am. Chem. Soc.* **1985**, *107*, 479.

(3:1) was added 165 mg (0.948 mmol) of sodium dithionite. The solution was stirred at rt for 4.5 h. The reaction mixture was quenched with H_2O (10 mL) and extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated. Preparative TLC (3:1 hexanes/EtOAc) afforded 91 mg (90%) of a yellow oil.

Bromoquinol Glycal 12b. The procedure used for the preparation of bromoquinol glycal **7b** was applied with 41 mg (0.14 mmol) of glycal **10**,[8] 0.4 mL *t*-BuLi (1.7 M solution in pentane), and *ca.* 25 mg of bromobenzoquinone **6b**[9] to give 52 mg (83%) of a yellow oil: ^{1}H NMR (CD_2Cl_2) δ 7.34 (d, J = 2.9 Hz, 1H), 6.92 (dd, J = 10.0, 2.9 Hz, 1H), 6.32 (dd, J = 10.0, 1.0 Hz, 1H), 5.15 (dd, J = 6.5, 2.5 Hz, 1H), 5.00 (m, 1H), 4.47 (m, 2H), 4.05 (m, 1H), 3.90 (m, 1H), 3.22 (s, 1H), 1.40 (s, 3H), 1.30 (s, 3H), 0.87 (s, 9H), 0.07 ("s", 6H); ^{13}C NMR (CD_2Cl_2) δ 177.9, 157.7, 147.5, 147.2, 132.8, 127.7, 109.1, 102.2, 86.4, 74.1, 73.6, 69.7, 65.8, 26.6, 25.9, 25.2, 18.3, −4.6, −4.9; FTIR (neat) 3388, 1674, 1066 cm^{-1}; HRMS (FAB) calcd 485.0995, found 485.0990 (M − H).

Monoacetate 2a. A 10-mg sample (0.022 mmol) of quinol ketal glycal **11** was treated with 0.11 mL of BH_3·THF (1 M solution in THF) in a procedure similiar to that for preparing compound **1a** (except temperature and time of reaction, see text) to give 7 mg (70%) of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.34 (d, J = 7.1 Hz, 2H), 6.80 (d, J = 7.0 Hz, 2H), 4.46 (d, J = 1.7 Hz, 1H), 4.81 (d, J = 1.6 Hz, 1H), 4.41 (m, 1H), 4.19 (m, 1H), 4.0 (dd, J = 8.4, 2.0 Hz), 3.91 (dd, J = 8.3, 2.8 Hz, 1H), 3.76 (m, 3H), 2.10 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H), 0.78 (s, 9H), 0.07 (s, 3H), −0.03 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.0, 159.1, 132.0, 127.9, 113.5, 109.0, 86.1, 85.7, 84.0, 76.4, 72.3, 68.1, 55.3, 26.8, 25.6, 25.4, 21.1, 18.0, −5.0, −5.5; FTIR (neat) 1754, 1221, 1069 cm^{-1}; HRMS (FAB) calcd 467.2465, found 467.2458 (M + H).

Diacetate 2b. An 11-mg sample (0.027 mmol) of quinol glycal **12a** was treated with 0.13 mL of BH_3·THF (1 M solution in THF) in a procedure resembling that for making compound **2b** (except temperature and time of reaction, see text) to yield 7 mg (54%) of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.43 (d, J = 6.8 Hz, 2H), 7.00 (d, J = 6.6 Hz, 2H), 4.89 (dd, J = 2.2, 1.4 Hz, 2H), 4.42 (m, 1H), 4.20 (m, 2H), 4.0 (dd, J = 9.4, 6.3 Hz, 1H), 3.95 (dd, J = 9.3, 5.7 Hz, 1H), 2.26 (s, 3H), 2.12 (s, 3H), 1.33 (s, 3H), 1.23 (s, 3H), 0.75 (s, 9H), 0.06 (s, 3H), −0.06 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.3, 169.5, 127.2, 122.0, 109.1, 108.9, 99.6, 82.9, 79.9, 75.5, 73.1, 71.6, 67.8, 30.1, 26.8, 26.0, 25.8, 25.4, 18.3, −4.9, −5.2; FTIR (neat) 1748, 1234, 1069 cm^{-1}; HRMS (FAB) calcd 435.2203, found 435.2199 (M − $C_4H_3O_2$).

Diacetate 2c. A 24-mg sample (0.049 mmol) of bromoquinol glycal **12b** was treated with 0.25 mL of BH_3·THF (1 M solution in THF) in a procedure similiar to that for preparing **2c** (except temperature and time of reaction) to give (after double elution of a prep TLC plate with hexanes/EtOAc 3:1) 12 mg (43%) of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.81 (d, J = 2.0 Hz, 1H), 7.53 (dd, J = 1.9, 8.3 Hz, 1H), 7.10 (d, J = 8.8 Hz, 1H), 4.95 (d, J = 3.9 Hz, 1H), 4.14 (m, 3H), 3.85 (m, 3H), 2.34 (s, 3H), 2.06 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H), 0.88 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.3, 168.7, 157.0, 130.8, 130.2, 126.2, 124.0, 116.6, 109.0, 100.8, 85.9, 79.9, 74.6, 73.7, 66.4, 26.8, 26.0, 25.8, 25.4, 20.9, 18.4, −4.4, −4.8; FTIR (neat) 1772, 1191, 1069 cm^{-1}; HRMS (FAB, NaI) calcd 597.1318, found 597.1314 (M + Na, ^{81}Br).

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Supporting Information Available: ^{1}H and ^{13}C NMR and infrared spectra for compounds **1**, **2**, **7**, **11**, and **12** (33 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, see any current masthead page for ordering information.

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