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Diastereoselective Michael Initiated Ring Closure on Vinyl Sulfone-Modified Carbohydrates: A Stereospecific and General Route to α-Substituted Cyclopropanes

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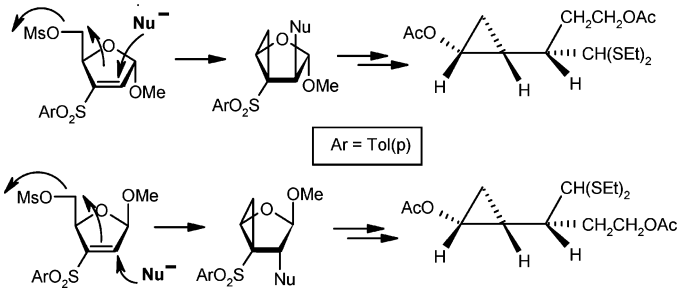


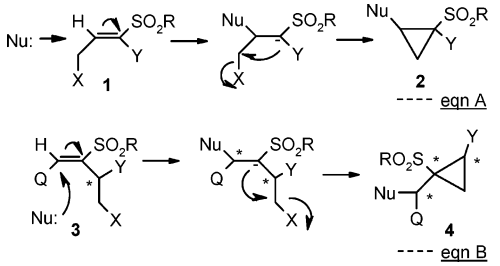
Suitably designed vinyl sulfone-modified furanosides act as substrates for Michael initiated ring closure reactions yielding cyclopropanated carbohydrates. The strategy is general in nature and gives access to cyclopropanes with predefined chiralities on three consecutive carbons with varying substitutions at the α-position.

Introduction

Integration of cyclopropanes and carbohydrates has been identified as an important area of research in cyclopropane related synthetic chemistry.[1] This particular combination provides access to a class of strained and reactive cyclopropanes embedded in chiral appendages like carbohydrates. Although study related to cyclopropanated carbohydrates is an emerging area, chemists have long been fascinated by the cyclopropane subunit as such because of its presence in a wide range of natural products as well as the usefulness of this strained cycloalkane in other areas of research.[2] While unactivated cyclopropanes have been directly utilized to a limited extent in chemical synthesis, activated cyclopropanes, such as cyclopropanes substituted with electron withdrawing or electron donating groups, have been used extensively as precursors in several chemical syntheses.[2b]

Michael initiated ring closure (MIRC) is one of the most important strategies for the construction of cyclopropane rings.[2a] A simple method of cyclopropane formation reported almost three decades back[3] involved the attack of a nucleophile on the electron deficient double bond of 3-halo-1-alkenylsulfones **1** (Scheme 1; eq A; Y = H)).[4] However, desulfonylation of **2** led to a cyclopropane derivative with only one functionalized center. Since cyclopropanations via the MIRC reactions of acyclic olefins are usually non-stereospecific,[2a,4] we argued that a

SCHEME 1. Michael Initiated Ring Closures with Vinyl Sulfones



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(1) (a) Cousins, G. S.; Hoberg, J. O. *Chem. Soc. Rev.* **2000**, *29*, 165. (b) Yu, M.; Pagenkopf, B. L. *Tetrahedron* **2005**, *61*, 321.

(2) (a) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977. (b) Reissig, H.-U.; Zimmer, R. *Chem. Rev.* **2003**, *103*, 1151. (c) Kulinkovich, O. G. *Chem. Rev.* **2003**, *103*, 2597.

(3) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3277.

(4) This type of reaction using 3-halo-1-alkenylsulfones was rarely studied, see: (a) Ogura, K.; Iihama, T.; Takahashi, K.; Iida, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3347. (c) Zindel, J.; de Meijere, A. *Synthesis* **1994**, *2*, 190.

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suitably designed vinyl sulfone, such as **3**, with a predesigned chiral center (C*−Y) would generate cyclopropanes **4** with three consecutive chiral centers provided that the first attack of the nucleophile to **3** is stereoselective in nature (Scheme 1; eq B). However, this hitherto unknown cyclopropanation using vinyl sulfones would be possible only if the sulfonyl and the alkyl chain carrying the leaving group were connected to the same carbon of the olefin as in **3**. Desulfonylation of **4** would also generate another set of cyclopropanes with defined chiral centers.

Results and Discussion

The diastereoselectivity of the addition of carbon and amino nucleophiles at C-2 of vinyl sulfone-modified pent-2-enofuranosides was controlled by the anomeric configuration to a great extent:[5] especially carbon nucleophiles added to the C-2 position from a direction opposite to that of the disposition of the anomeric methoxy group (Figure 1).[5b] Since the first step of eq

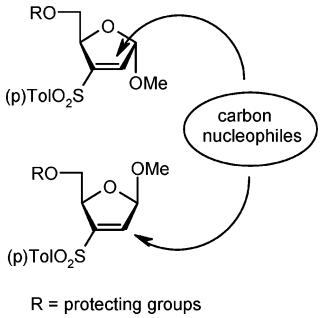
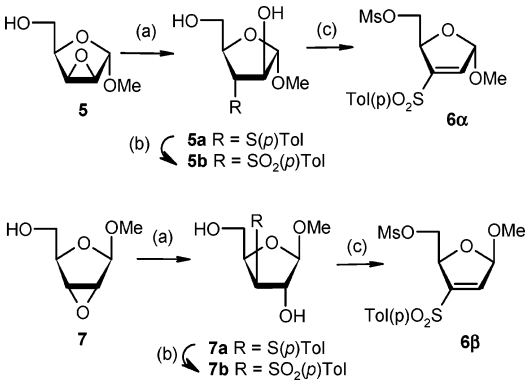


FIGURE 1. Attack of carbon nucleophiles to C-2 of vinyl sulfone-modified pent-2-enofuranosides.

B (Scheme 1) (i.e. the diastereoselective addition of nucleophiles to vinyl sulfones)[3] could be achieved using a vinyl sulfone-modified pent-2-enofuranoside, we decided to construct the vinyl sulfone group on a carbohydrate framework having a leaving group at the C-5 position. Therefore, vinyl sulfone-modified carbohydrates **6**α and **6**β were synthesized in large scale from easily accessible epoxides **5**[6a] and **7**,[6b] respectively (Scheme 2).

SCHEME 2. Synthesis of Vinyl Sulfone-Modified Carbohydrates[a]

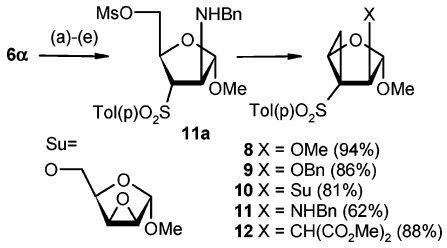


[a] Reagents and conditions: (a) *p*-thiocresol, NaOMe, DMF, 100 °C, 4 h, 80−90%; (b) MMPP, MeOH, rt, 6 h; and (c) MsCl, py, 0−4 °C, 24 h, 86−88%.

Thus, α-anomeric epoxide **5** was reacted with sodium tolylthiolate to obtain **5a** in high yield. Oxidation of **5a** with magnesium monoperoxyphthalate hexahydrate (MMPP) produced **5b**. Mesylation of sulfone **5b** followed by concomitant elimination of the mesyl group afforded the vinyl sulfone **6**α in 88% yield. The β-anomeric epoxide **7** under similar reaction conditions produced the vinyl sulfone **6**β in 86% yield through intermediates **7a** and **7b**.

The vinyl sulfone-modified carbohydrate **6**α was reacted with NaOMe or NaOBn to obtain the cyclopropanated carbohydrates **8** and **9**, respectively, in excellent yields. A bulky, sugar-derived nucleophile, methyl-2,3-anhydro-lyxofuranoside, in the presence of NaH easily produced disaccharide **10** in high yield (Scheme 3). Interestingly, reactions of benzylamine and the sodium salt

SCHEME 3. Cyclopropanation of α-Anomeric Vinyl Sulfone[a]



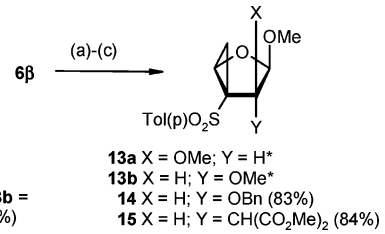
[a] Reagents and conditions: (a) NaOMe, MeOH, rt, 14 h; (b) NaH, $PhCH_2OH$, DMF, rt, 23 h; (c) NaH, methyl 2,3-anhydro-α-D-lyxofuranoside, DMF, rt, 24 h; (d) (i) $PhCH_2NH_2$ (neat), rt, 1 h and (ii) K_2CO_3, MeOH, rt, 24 h; and (e) (i) NaH, $CH_2(CO_2Me)_2$, DMF, rt, 10 h and (ii) NaH, DMF, rt, 10 h.

of dimethylmalonate with **6**α did not produce any cyclopropane derivative but generated only addition products instead. However, these intermediates on treatment with K_2CO_3/MeOH or NaH yielded cyclopropanes **11** and **12**. The benzylamino intermediate was isolated and identified as the addition product **11a**. We concluded that the C-3 proton of **11a** was abstracted by K_2CO_3/MeOH and that the carbanion thus generated intramolecularly attacked C-5 to produce **11**. The amino derivative **11a** did not undergo intramolecular attack by NHBn to C-5 to produce any five-membered ring containing a bicyclic compound; probably the steric bulk around the *N*-nucleophile in **11a** increased the feasibility of formation of the cyclopropanated carbohydrate **11** in a selective fashion. Similarly, compound **12** was also produced from the addition product of **6**α and the sodium salt of dimethylmalonate (Scheme 3). In the case of **8**−**10**, the anions of the alcohols used were sufficiently basic to abstract the C-3 protons, and the concomitant cyclopropane ring formation took place. The role of the substituent at C-2 of intermediates such as **11a**, if any, remains unclear at the moment. The other vinyl sulfone **6**β, under similar conditions, produced cyclopropanated carbohydrates **13a**/**13b** (1:1), **14**, and **15** (Scheme 4). Mg in MeOH desulfonylated **9** and **14** to cyclopropane ethers **16** and **18**, respectively, in high yields. The aminocyclopropane **11** was desulfonylated to **17** with Mg−$NiBr_2$−MeOH at 60 °C in good yield (Scheme 5).[5c]

(5) (a) Ravindran, B.; Sakthivel, K.; Suresh, C. G.; Pathak, T. *J. Org. Chem.* **2000**, *65*, 2637. (b) Sanki, A. K.; Suresh, C. G.; Falgune, U. D.; Pathak, T. *Org. Lett.* **2003**, *5*, 1285. (c) Das, I.; Pathak, T. *Org. Lett.* **2006**, *8*, 1303.

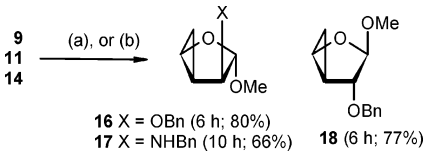
(6) (a) Baker, B. R.; Schaub, R. E.; Williams, J. H. *J. Am. Chem. Soc.* **1955**, *77*, 7. (b) Anderson, C. D.; Goodman, L.; Baker, B. R. *J. Am. Chem. Soc.* **1958**, *80*, 5247.

SCHEME 4. Cyclopropanation of *β*-Anomeric Vinyl Sulfone[a]



[a] Reagents and conditions: (a) NaOMe, MeOH, rt, 12 h; (b) NaH, $PhCH_2OH$, DMF, rt, 21 h; (c) (i) NaH, $CH_2(CO_2Me)_2$, DMF, rt, 10 h and (ii) NaH, DMF, rt, 10 h.

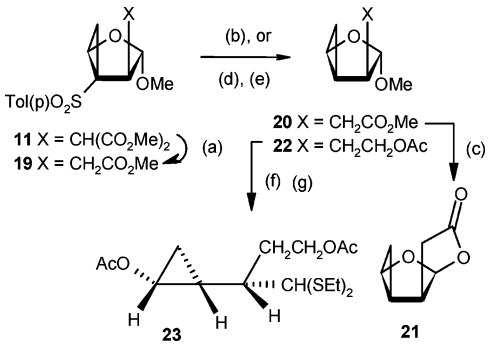
SCHEME 5. Desulfonylation of Cyclopropanated Carbohydrates[a]



[a] Reagents and conditions: (a) Mg, MeOH, rt and (b) Mg, $NiBr_2$, MeOH, 60 °C.

Although the cyclopropanated sugars would be useful for the synthesis of a host of branched-chain sugars using the reported methods,[1] we also decided to establish a new strategy for the conversion of cyclopropanated sugars to functionalized cyclopropanols **23** and **26**. The synthesis of the diastereomerically pure cyclopropanes was initiated by converting **11** to the monoester **19** (Scheme 6). Desulfonylation of **19** by Mg in MeOH easily afforded **20**.

SCHEME 6. Derivatization of α-Anomeric Cyclopropanated Furanosides[a]

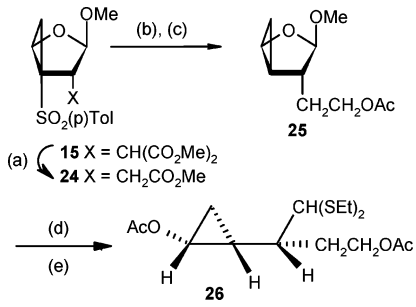


[a] Reagents and conditions: (a) NaCl, DMSO-H_2O (10:1), 120 °C, 72 h, 81%; (b) Mg, MeOH, rt, 5 h, 77%; (c) TFA-H_2O (9:1), rt, 2 h, 69%; (d) $LiAlH_4$, THF, rt, 20 h; (e) Ac_2O, DMAP, rt, 10 h, 75%; (f) EtSH, $AlCl_3$, rt, 8 h; and (g) Ac_2O, DMAP, rt, 10 h, 71%.

Monoester **20** under acidic conditions yielded lactone **21**. To explain the formation of **21**, we presumed that the acid hydrolysis of **20** resulted in the formation of a free anomeric hydroxyl group that intramolecularly attacked the CO_2Me group to produce the cyclopropane-based lactone; alternatively, the oxygen of the ester carbonyl group intramolecularly attacked the oxonium ion intermediate during hydrolysis. On the other hand, compound **19** was reduced and desulfonylated in one step, and the product was isolated as the acetate **22**. $AlCl_3$ mediated dithioacetal formation opened the sugar ring of **22**; acetylation of the product afforded the α-substituted cyclopropanol **23** (Scheme 6).

In the *β*-series, compound **15** was converted to a monoester **24** that under reductive desulfonylation conditions afforded easily a branched-chain sugar **25**. In this case also, it was also possible to convert **24** to another cyclopropanol **26** following the route described for **23** (Scheme 7).

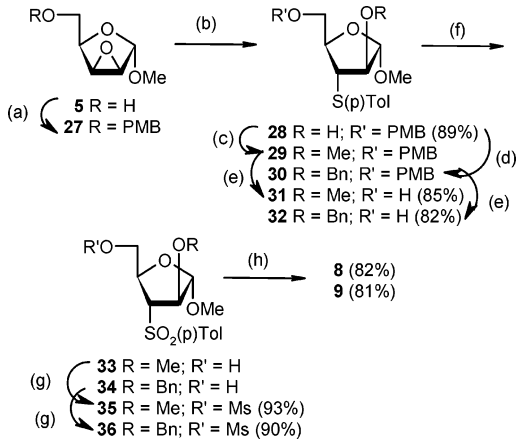
SCHEME 7. Derivatization of *β*-Anomeric Cyclopropanated Furanosides[a]



[a] Reagents and conditions: (a) NaCl, DMSO-H_2O (10:1), 100 °C, 24 h, 83%; (b) $LiAlH_4$, THF, rt, 20 h; (c) Ac_2O, DMAP, rt, 10 h, 71%; (d) EtSH, $AlCl_3$, rt, 8 h; and (e) Ac_2O, DMAP, rt, 12 h, 68%.

Structural Elucidation. Compounds **11**, **12**, **21**, and **24** were characterized by X-ray diffraction of the single crystals. The identities of compounds **8** and **9** were established unambiguously by synthesizing them through alternative routes. Thus, the *p*-methoxybenzyl (PMB) protected epoxide **27**, obtained from **5**, was reacted with *p*-thiocresol to afford **28**. Methylation and benzylation of **28** produced **29** and **30**, respectively. Removal of the PMB group from **29** and **30** by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) produced alcohols **31** and **32**. Compounds **31** and **32** were oxidized with MMPP to generate sulfones **33** and **34**, respectively. Mesylation of **33** and **34** afforded **35** and **36**, respectively. Mesylates **35** and **36**, on treatment with NaOMe in MeOH, afforded cyclopropanated carbohydrates **8** and **9** (mixed ^1H NMR), respectively (Scheme 8). The identity of compound **10** was established as follows. It

SCHEME 8. Alternative Synthesis of Cyclopropanated Carbohydrates 8 and 9[a]

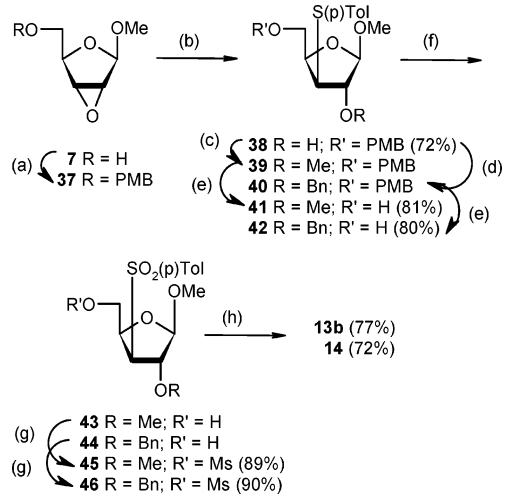


[a] Reagents and Conditions: (a) *p*-methoxybenzyl chloride, NaH, DMF, rt, 2.5 h; (b) *p*-thiocresol, NaOMe, DMF, 120 °C, 4 h; (c) CH_3I, NaH, DMF, rt, 2 h; (d) $PhCH_2Br$, NaH, DMF, rt, 2.5 h; (e) DDQ, DCM-H_2O (20:1), rt, 16 h; (f) MMPP, MeOH, 6 h, rt; (g) MsCl, py, 0−4 °C, 24 h; and (h) NaOMe, MeOH, rt, 22 h.

is well-documented in the literature[7] that the $J_{1,2}$ values of authentic methyl α-D-arabinofuranosides range between 0.0 and 3.0 Hz. The $J_{1,2}$ values for authentic methyl α-D-ribofuranosides range between 4.0 and 4.9 Hz, and for methyl α-D-xylofuranosides, these values always range between 4.0 and 4.7 Hz. Excluding the possibility of any lyxo derivative formation, the coupling constant ($J_{1,2}$) value of H-1 and H-2 protons of compound **10** was 0.0 Hz, indicating the presence of an arabino configuration in this molecule. Futhermore, by compairing the $J_{1,2}$ values of compound **10** (0.0 Hz) with those of our synthesized compounds **8** (0.0 Hz), **9** (0.0 Hz), **11** (0.0 Hz), and **12** (1.1 Hz), a trans relationship between H-1 and H-2 in the cyclopropanated sugar component of compound **10** was concluded.[7]

Compounds **13b** and **14** were also identified through alternative syntheses. In this case, the lyxo epoxide **7** was protected with the *p*-methoxybenzyl group to obtain **37**, which with reaction with *p*-thiocresol afforded the sulfide **38**. Methylation and benzylation of the alcohol **38** produced **39** and **40**, respectively. Removal of the PMB group from **39** and **40** by DDQ produced alcohols **41** and **42**, respectively. Oxidation of **41** and **42** with MMPP produced sulfones **43** and **44**, respectively. Mesylation of **43** and **44** afforded **45** and **46**. Mesylates **45** and **46**, on treatment with NaOMe in MeOH, afforded cyclopropanes **13b** and **14** (mixed ^{1}H NMR), respectively (Scheme 9).

SCHEME 9. Alternative Synthesis of Cyclopropanated Carbohydrates 13b and 14[a]



[a] Reagents and conditions: (a) *p*-methoxybenzyl chloride, NaH, DMF, rt, 2.5 h; (b) *p*-thiocresol, NaOMe, DMF, 120 °C, 4 h; (c) CH_3I, NaH, DMF, rt, 2 h; (d) $PhCH_2Br$, NaH, DMF, rt, 2.5 h; (e) DDQ, DCM-H_2O (20:1), rt, 18 h; (f) MMPP, MeOH, 6 h, rt; (g) MsCl, py, 0−4 °C, 24 h; and (h) NaOMe, MeOH, rt, 24 h.

The overwhelming majority of donor−acceptor cyclopropanes derived from carbohydrates was constructed on the C1−C2 bond of the pyranosides because glycals are the only class of starting materials useful for cyclopropanation reactions.[1] On the other hand, there are only scant reports on cyclopropanes built on furanose rings.[1,8] The present work reports for the first time the hitherto unknown combination of cyclopropanes, carbohydrates, and an electron withdrawing group such as sulfone (**8**−**15**/**19**/**24**).[9] The desulfonylated analogues **16**−**18**/**20**−**22**/**25**, on the other hand, represent another distinct class of cyclopropanes built on furanose appendages. The strategy also gives easy access to cyclopropane derivatives (**23** and **26**) with predefined chiralities on three consecutive carbons with varying substitutions at the α-position. The scopes and limitations of these new chiral synthons are currently under study.

Experimental Section

General Procedure for the Synthesis of 6α and 6β. To a well-stirred solution of **5** or **7** in dry DMF (4 mL/mmol) were added *p*-thiocresol (5 equiv/mmol) and NaOMe (2.5 equiv/mmol). The mixture was heated at 100 °C with stirring for 4 h under N_2. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of $NaHCO_3$, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over a silica gel column to afford compound **5a** or **7a**. To a solution of compound **5a** or **7a** in dry MeOH (10 mL/mmol) was added magnesium monoperoxyphthalate hexahydrate (2.5 equiv/mmol), and the mixture was stirred for 6 h at ambient temperature under N_2. After completion of the reaction (TLC), MeOH was evaporated to dryness under reduced pressure, and the residue was dissolved in saturated $NaHCO_3$. The product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to afford compound **5b** or **7b**. To a solution of compound **5b** or **7b** in dry pyridine (5 mL/mmol) was added methanesulfonyl chloride (8 equiv/mmol) in dry pyridine (1 mL/mmol of MsCl) dropwise at 0 °C under N_2. The reaction mixture was left at +4 °C. After 24 h (TLC), the reaction mixture was poured into an ice-cold saturated solution of $NaHCO_3$, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over a silica gel column to afford **6**α or **6**β.

General Procedure for the Synthesis of 8, 13a, and 13b. To a well-stirred solution of **6**α or **6**β in MeOH was added sodium methoxide (2 equiv/mmol), and the mixture was stirred at ambient temperature for 12−14 h. After completion of the reaction (TLC), MeOH was evaporated to dryness under reduced pressure, and the residue was poured into a saturated solution of NH_4Cl. The product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The resulting residue was purified over a silica gel column to afford compound **8**, **13a**, or **13b**.

(7) (a) Casini, G.; Goodman, L. *J. Am. Chem. Soc*. **1964**, *86*, 1427. (b) Montgomery, J. N.; Thorpe, M. C.; Clayton, S. D.; Thomas, H. J. *Carbohydr. Res*. **1974**, *32*, 404. (c) Bock, K.; Pedersen, C.; Thiem, J. *Carbohydr. Res*. **1979**, *73*, 85. (d) Liptak, A.; Neszmelyi, A.; Kovac, P.; Hirsch, J. *Tetrahedron* **1981**, *37*, 2379. (e) Su, T.-L.; Klein, R. S.; Fox, J. J. *J. Org. Chem*. **1981**, *46*, 1790. (f) Kawana, M.; Kuzuhara, H.; Emoto, S. *Bull. Chem. Soc. Jpn*. **1981**, *54*, 1492. (g) Kawana, M.; Koresawa, T.; Kuzuhara, H. *Bull. Chem. Soc. Jpn*. **1983**, *56*, 1095.

(8) (a) Brimacombe, J. S.; Evans, M. E.; Forbes, E. J.; Foster, A. B.; Webber, J. M. *Carbohydr. Res*. **1967**, *4*, 239. (b) Sasaki, T.; Minamoto, K.; Suzuki, H. *J. Org. Chem*. **1973**, *38*, 598. (c) Kawana, M.; Kuzuhara, H. *Synthesis* **1995**, *5*, 544. (d) Gagneron, J.; Gosselin, G.; Mathe, C. *J. Org. Chem*. **2005**, *70*, 6891. (e) Testero, S. A.; Spanevello, R. A. *Carbohydr. Res*. **2006**, *341*, 1057. (f) Besada, P.; Shin, D. H.; Costanzi, S.; Ko, H.; Mathe, C.; Gagneron, J.; Gosselin, G.; Maddileti, S.; Harden, T. K.; Jacobson, K. A. *J. Med. Chem*. **2006**, *49*, 5532. (g) Nowak, I.; Cannon, J. F.; Robins, M. J. *J. Org. Chem*. **2007**, *72*, 532.

(9) Schemes 8 and 9 represent a non-Michael addition approach to the synthesis of cyclopropanated carbohydrates containing an electron withdrawing group at C-3 of pentofuranosides. This strategy may be explored when the introduction of a group at C-2 is less efficient through Michael addition to vinyl sulfone-modified carbohydrates.

General Procedure for the Synthesis of 9, 10, and 14. To a well-stirred solution of **6**α or **6**β in DMF was added sodium salt of benzyl oxide or methyl-2,3-anhydro-α-D-lyxofuranosyl oxide (2 equiv/mmol), and the mixture was stirred at ambient temperature for 21−24 h. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of NH_4Cl, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The resulting residue was purified over a silica gel column to afford compound **9**, **10**, or **14**.

General Procedure for the Synthesis of 12 and 15. To a well-stirred solution of **6**α or **6**β in dry DMF (10 mL/mmol) was added sodium salt of dimethyl malonate (2 equiv/mmol), and the mixture was stirred at room temperature for 10 h. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of NH_4Cl, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The resulting residue was purified over a silica gel column [eluent: EtOAc/petroleum ether (1:2)] to afford a residue. The residue was stirred at ambient temperature with NaH and dry DMF for 10 h under Ar. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of NH_4Cl, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The resulting residue was purified over a silica gel column to afford compound **12** or **15**.

General Procedure for the Synthesis of 16, 18, and 20. To a well-stirred solution of **9**, **14**, or **19** in dry MeOH (10 mL) was added Mg turnings (15 mmol) under Ar. The mixture was stirred at ambient temperature. After 3 h, another portion of Mg turnings (15 mmol) and dry MeOH (5 mL) were added. The mixture was stirred for an additional 2−3 h. The reaction mixture was filtered through Celite. The residue was washed thoroughly with MeOH. The filtrates were pooled together, and the liquid was concentrated under reduced pressure. The resulting residue was dissolved in EtOAc and was washed with saturated NH_4Cl solution, dried over anhydrous Na_2SO_4, and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over a silica gel column to afford compound **16**, **18**, or **20**.

General Procedure for the Synthesis of 19 and 24. A well-stirred solution of **11** or **15** in a mixture of DMSO (10 mL) and water (1 mL) containing NaCl (5 equiv/mmol) was heated at 100−120 °C for 24−72 h. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of NaCl, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over a silica gel column to afford **19** or **24**.

General Procedure for the Synthesis of 22 and 25. To a well-stirred solution of **19** or **24** in dry THF (10 mL) was added LAH (5 equiv/mmol) at 0 °C under Ar, and the mixture was stirred at ambient temperature for 20 h. After completion of the reaction (TLC), a saturated NH_4Cl solution was added, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The resulting residue was purified over a silica gel column to afford a residue. The residue was acetylated with acetic anhydride (1 mL) and DMAP (catalytic) at room temperature for 10 h. After completion of the reaction (TLC), a saturated $NaHCO_3$ solution was added, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The resulting residue was purified over a silica gel column to afford **22** or **25**.

General Procedure for the Synthesis of 23 and 26. To a well-stirred solution of **22** or **25** was added EtSH and $AlCl_3$, and the mixture was stirred at room temperature for 8 h. After completion of the reaction (TLC), a saturated NH_4Cl solution was added, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The resulting residue was purified over silica gel column to afford a residue. The product, thus obtained, was acetylated with acetic anhydride (1 mL) and DMAP (catalytic) at ambient temperature for 10−12 h. After completion of the reaction (TLC), a saturated $NaHCO_3$ solution was added, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The resulting residue was purified over a silica gel column to afford **23** or **26**.

General Procedure for the Synthesis of 27 and 37. To a well-stirred solution of **5** or **7** (1 equiv/mmol) in DMF (8 mL/mmol) were added *p*-methoxybenzyl chloride (1.3 equiv/mmol) and NaH (1.3 equiv/mmol). The mixture was stirred at ambient temperature for 2.5 h under N_2. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of NH_4Cl, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over a silica gel column to afford **27** or **37**.

General Procedure for the Synthesis of 28 and 38. To a well-stirred solution of **27** or **37** in DMF (4 mL/mmol) were added *p*-thiocresol (5 equiv/mmol) and NaOMe (2.5 equiv/mmol). The mixture was heated at 120 °C with stirring for 4 h under N_2. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of $NaHCO_3$, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a gummy residue. The residue was purified over a silica gel column to afford sulfides **28** or **38**.

General Procedure for the Synthesis of 29 and 39. Compound **28** or **38** (1 equiv/mmol) was stirred at 0 °C with NaH (1.2 equiv/mmol) and MeI (2 equiv/mmol) in DMF (8 mL/mmol). Then, the mixture was stirred at ambient temperature under N_2. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of NH_4Cl, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over a silica gel column to afford **29** or **39**.

General Procedure for the Synthesis of 30 and 40. Compound **28** or **38** (1 equiv/mmol) was stirred at 0 °C with NaH (1.2 equiv/mmol) and BnBr (1.2 equiv/mmol) in DMF (8 mL/mmol). Then, the mixture was stirred at ambient temperature under N_2. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of NH_4Cl, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over a silica gel column to afford **30** or **40**.

General Procedure for the Synthesis of 31, 32, 41, and 42. To a well-stirred solution of **29**, **30**, **39**, or **40** in DCM−H_2O (20:1) was added DDQ (1.2 equiv/mmol), and the mixture was stirred at ambient temperature for 16−18 h. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of $NaHCO_3$, and the mixture was extracted with DCM (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The resulting residue was purified over a silica gel column to afford **31**, **32**, **41**, or **42**.

General Procedure for the Synthesis of 33, 34, 43, and 44. To a well-stirred solution of **31**, **32**, **41**, or **42** in dry MeOH (10 mL/mmol) was added magnesium monoperoxyphthalate hexahydrate (2.5 equiv/mmol), and the mixture was stirred for 6 h under N_2. After completion of the reaction (TLC), MeOH was evaporated to dryness under reduced pressure, and the residue was dissolved in saturated $NaHCO_3$. The aqueous portion was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over a silica gel column to obtain **33**, **34**, **43**, or **44**.

General Procedure for the Synthesis of 35, 36, 45, and 46. To a well-stirred solution of **33**, **34**, **43**, or **44** in dry pyridine (5 mL/mmol) was added methanesulfonyl chloride (4 equiv/mmol) in pyridine (1 mL/mmol of MsCl) dropwise at 0 °C under N_2. After completion of the addition, the reaction mixture was kept at +4 °C. After 24 h (TLC), the reaction mixture was poured into an ice-cold saturated solution of $NaHCO_3$, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over a silica gel column to afford **35**, **36**, **45**, or **46**.

General Procedure for the Synthesis of 8, 9, 13b, and 14 (from 35, 36, 45, and 46). To a well-stirred solution of **35**, **36**, **45**, or **46** in dry MeOH (10 mL/mmol) was added NaOMe (2.5 equiv/mmol), and the mixture was stirred for 22−24 h at ambient temperature under N_2. After completion of the reaction (TLC), MeOH was evaporated to dryness under reduced pressure, and the residue was dissolved in saturated NH_4Cl. The product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over silica gel column to obtain **8**, **9**, **13b**, or **14**.

Methyl 3-Deoxy-3-*S*-(4-methylphenyl)-3-thio-α-D-arabinofuranoside (5a). Compound **5** (1.2 g, 8.2 mmol) was converted to **5a** following the general procedure (2.0 g, 90%). Eluent: EtOAc/petroleum ether (1:6). Yellow gum. $[\alpha]^{27}_D$ (+) 131.6 (*c* 7.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H), 3.39 (s, 3H), 3.43 (m, 1H), 3.58 (m, 1H), 3.88 (m, 1H), 4.12−4.18 (m, 2H), 4.91 (s, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.9, 52.4, 54.9, 61.7 (CH_2), 81.3, 84.1, 109.6, 129.8, 131.0, 131.4, 137.2. Anal. calcd for $C_{13}H_{18}O_4S$: C, 57.76; H, 6.71. Found: C, 57.75; H, 6.48.

Methyl 2,3-Dideoxy-5-*O*-mesyl-3-(4-methylphenyl)sulfonyl-α-D-*erythro*-pent-2-enofuranoside (6α). Compound **5a** (2.0 g, 7.4 mmol) was converted to **6**α via **5b** following the general procedure (2.4 g, 88%). Eluent: EtOAc/petroleum ether (1:1). Yellow gum. $[\alpha]^{27}_D$ (−) 4.5 (*c* 10.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 3H), 3.04 (s, 3H), 3.37 (s, 3H), 4.35 (dd, J = 3.8, 11.5 Hz, 1H), 4.60 (dd, J = 2.2, 11.2 Hz, 1H), 5.13 (m, 1H), 5.86 (d, J = 4.4 Hz, 1H), 6.54 (m, 1H), 7.39 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.5, 37.4, 55.0, 68.9 (CH_2), 81.1, 107.4, 128.0, 130.2, 135.3, 137.6, 145.0, 145.8. Anal. calcd for $C_{14}H_{18}O_7S_2$: C, 46.40; H, 5.01. Found: C, 46.58; H, 4.90.

Methyl 3-Deoxy-3-*S*-(4-methylphenyl)-3-thio-β-D-xylofuranoside (7a). Compound **7** (0.84 g, 5.75 mmol) was converted to **7a** following the general procedure (1.2 g, 80%). Eluent: EtOAc/petroleum ether (1:6). White crystalline solid. Solvent of crystallization: DCM and petroleum ether. Mp: 73 °C. $[\alpha]^{27}_D$ (−) 36.4 (*c* 1.22, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H), 3.46 (s, 3H), 3.65−3.84 (m, 3H), 4.33 (m, 1H), 4.46 (m, 1H), 4.88 (d, J = 2.5 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.9, 55.2, 56.1, 63.1 (CH_2), 81.6, 82.1, 109.7, 129.9, 130.7, 131.6, 137.0. Anal. calcd for $C_{13}H_{18}O_4S$: C, 57.76; H, 6.71. Found: C, 58.02; H, 6.48.

Methyl 2,3-Dideoxy-5-*O*-mesyl-3-(4-methylphenyl)sulfonyl-β-D-*erythro*-pent-2-enofuranoside (6β). Compound **7a** (1.2 g, 4.44 mmol) was converted to **6**β via **7b** following the general procedure (1.4 g, 86%). Eluent: EtOAc/petroleum ether (1:1). Yellow crystalline solid. Solvent of crystallization: EtOAc and petroleum ether. Mp: 70 °C. $[\alpha]^{27}_D$ (−) 47.2 (*c* 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 3H), 3.03 (s, 3H), 3.45 (s, 3H), 4.25 (dd, J = 6.0, 11.4 Hz, 1H), 4.60 (dd, J = 2.3, 15.4 Hz, 1H), 4.95 (m, 1H), 5.67 (m, 1H), 6.60 (m, 1H), 7.39 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.6, 37.4, 56.0, 70.2 (CH_2), 80.9, 107.5, 128.1, 130.3, 135.3, 137.3, 145.5, 145.9. Anal. calcd for $C_{14}H_{18}O_7S_2$: C, 46.40; H, 5.01. Found: C, 46.20; H, 5.33.

Methyl 3,5-Cyclo-3,5-dideoxy-2-*O*-methyl-3-(4-methylphenyl-)sulfonyl-α-D-arabinofuranoside (8). Compound **6**α (0.53 g, 1.46 mmol) was converted to **8** following the general procedure (0.41 g, 94%). Eluent: EtOAc/petroleum ether (1:3). White crystalline solid. Solvent of crystallization: EtOAc and petroleum ether. $[\alpha]^{27}_D$ (+) 125.9 (*c* 0.6, $CHCl_3$). Mp: 60 °C. ^{1}H NMR ($CDCl_3$): δ 1.77 (dd, J = 3.3, 6.4 Hz, 1H), 1.94 (t, J = 6.3 Hz, 1H), 2.45 (s, 3H), 3.12 (s, 3H), 3.13 (s, 3H), 4.26 (s, 1H), 4.56 (m, 1H), 4.66 (s, 1H), 7.35 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.5, 22.2 (CH_2), 51.3, 54.3, 56.7, 66.5, 84.7, 115.2, 128.5, 129.6, 135.9, 144.7. Anal. calcd for $C_{14}H_{18}O_5S$: C, 56.36; H, 6.08. Found: C, 56.76; H, 5.85.

Methyl 2-*O*-Benzyl-3,5-cyclo-3,5-dideoxy-3-(4-methylphenyl)-sulfonyl-α-D-arabinofuranoside (9). Compound **6**α (0.28 g, 0.77 mmol) was converted to **9** following the general procedure (0.25 g, 86%). Eluent: EtOAc/petroleum ether (1:5). White amorphous solid. $[\alpha]^{27}_D$ (+) 63.9 (*c* 0.6, $CHCl_3$). Mp: 70 °C. ^{1}H NMR ($CDCl_3$): δ 1.92 (dd, J = 3.3, 6.6 Hz, 1H), 1.99 (t, J = 5.9 Hz, 1H), 2.44 (s, 3H), 3.10 (s, 3H), 4.33−4.46 (m, 3H), 4.57 (m, 1H), 4.72 (s, 1H), 7.19−7.34 (m, 7H), 7.74 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.5, 22.2 (CH_2), 51.7, 54.3, 66.6, 70.9 (CH_2), 82.7, 115.1, 127.7, 127.8, 128.3, 128.6, 129.6, 135.8, 136.9, 144.7. Anal. calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.92. Found: C, 64.19; H, 5.78.

Methyl 3,5-Cyclo-3,5-dideoxy-2-*O*-(methyl 2,3-anhydro-α-D-lyxofuranos-5-yl)-3-(4-methylphenyl)sulfonyl-α-D-arabinofuranoside (10). Compound **6**α (0.34 g, 0.94 mmol) was converted to **10** following the general procedure (0.31 g, 81%). Eluent: EtOAc/petroleum ether (1:3). White crystalline solid. Solvent of crystallization: $CHCl_3$ and petroleum ether. Mp: 115 °C. $[\alpha]^{27}_D$ (+) 88.7 (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.85 (dd, J = 3.3, 6.5 Hz, 1H), 1.95 (t, J = 6.2 Hz, 1H), 2.45 (s, 3H), 3.13 (s, 3H), 3.37 (s, 3H), 3.41−3.53 (m, 2H), 3.61 (s, 2H), 4.00 (m, 1H), 4.43 (s, 1H), 4.56 (m, 1H), 4.71 (s, 1H), 4.90 (s, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.3, 22.0 (CH_2), 51.3, 53.7, 54.2, 55.3, 55.8, 66.3, 67.2 (CH_2), 74.0, 83.5, 102.0, 114.8, 128.3, 129.4, 135.7, 144.6. Anal. calcd for $C_{19}H_{24}O_8S$: C, 55.33; H, 5.87. Found: C, 55.0; H, 5.77.

Methyl 2-*N*-Benzylamino-2,3-dideoxy-5-*O*-mesyl-3-(4-methylphenyl)sulfonyl-α-D-arabinofuranoside (11a). A mixture of compound **6**α (0.33 g, 0.91 mmol) and neat benzylamine (2 equiv/mmol) was stirred at room temperature for 1 h. After completion of the reaction (TLC), the reaction mixture was poured into a saturated solution of NH_4Cl, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over silica gel column to afford **11a** (0.39 g, 92%). Eluent: EtOAc/petroleum ether (1:1). White amorphous solid. $[\alpha]^{25}_D$ (+) 24.2 (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.45 (s, 3H), 3.04 (s, 3H), 3.26 (s, 3H), 3.46−3.74 (m, 4H), 4.29 (m, 1H), 4.52−4.60 (m, 2H), 4.82 (s, 1H), 7.10−7.34 (m, 7H), 7.67 (d, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.6, 37.7, 51.6 (CH_2), 55.1, 65.8, 69.0 (CH_2), 69.1, 74.8, 108.4, 127.2, 128.2, 128.4, 128.8, 130.1, 134.3, 138.8, 145.5. Anal. calcd for $C_{21}H_{27}NO_7S_2$: C, 53.71; H, 5.80; N, 2.98. Found: C, 53.41; H, 6.09; N, 3.30.

Methyl 2-*N*-Benzylamino-3,5-cyclo-3-(4-methylphenyl)sulfonyl-2,3,5-trideoxy-α-D-arabinofuranoside (11). Compound **11a** (0.36 g, 0.77 mmol) was stirred at room temperature with K_2CO_3 and MeOH for 24 h. After completion of the reaction (TLC), MeOH

was evaporated to dryness under reduced pressure. The reaction mixture was poured into a saturated solution of NH_4Cl, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The resulting residue was purified over a silica gel column to afford **11** (0.18 g, 62%). Eluent: EtOAc/petroleum ether (1:3). Yellow crystalline solid. Solvent of crystallization: DCM and petroleum ether. $[\alpha]^{27}_D$ (+) 14.0 (*c* 0.7, $CHCl_3$). Mp: 140 °C. ^{1}H NMR ($CDCl_3$): δ 1.80 (dd, J = 3.0, 6.7 Hz, 1H), 1.92 (t, J = 6.4 Hz, 1H), 2.44 (s, 3H), 3.15 (s, 3H), 3.52−3.72 (m, 3H), 4.50 (m, 1H), 4.56 (s, 1H), 7.20−7.38 (m, 7H), 7.62 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.1 (CH_2), 21.4, 50.7, 51.3 (CH_2), 54.7, 63.8, 64.4, 115.3, 127.0, 128.0, 128.2, 128.4, 129.6, 135.3, 139.2, 144.5. Anal. calcd for $C_{20}H_{23}NO_4S$: C, 64.32; H, 6.21; N, 3.75. Found: C, 64.66; H, 5.98; N, 4.03.

Methyl 3,5-Cyclo-2-bis(methoxycarbonylmethyl)-3-(4-methylphenyl)sulfonyl-2,3,5-trideoxy-α-D-arabinofuranoside (12). Compound **6**α (0.98 g, 2.7 mmol) was converted to **12** following the general procedure (0.95 g, 88%). Eluent: EtOAc/petroleum ether (1:3). White crystalline solid. Solvent of crystallization: EtOAc and petroleum ether. Mp: 90 °C. $[\alpha]^{27}_D$ (+) 47.5 (*c* 1.8, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.71 (dd, J = 2.9, 7.6 Hz, 1H), 2.11 (t, J = 6.5 Hz, 1H), 2.46 (s, 3H), 3.04 (s, 3H), 3.26 (m, 1H), 3.43 (m, 1H), 3.71 (s, 3H), 3.77 (s, 3H), 4.34 (m, 1H), 4.67 (d, J = 1.1 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.5, 22.2 (CH_2), 46.8, 48.5, 50.5, 52.7, 52.9, 54.7, 64.5, 113.5, 129.1, 129.6, 134.4, 144.8, 166.9, 167.9. IR (KBr): 1105, 1305, 1329, 1435, 1732, 1756 cm^{-1}. Anal. calcd for $C_{18}H_{22}O_8S$: C, 54.26; H, 5.57. Found: C, 54.58; H, 5.39.

Methyl 3,5-Cyclo-3,5-dideoxy-2-*O*-methyl-3-(4-methylphenyl-)sulfonyl-β-D-arabinofuranoside (13a) and Methyl 3,5-Cyclo-3,5-dideoxy-2-*O*-methyl-3-(4-methylphenyl)sulfonyl-β-D-ribofuranoside (13b). Compound **6**β (0.42 g, 1.2 mmol) was converted to **13a**/**13b** (1:1) following the general procedure (0.31 g, 90%), which was separated by column chromatography. Compound **13a**: eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27}_D$ (−) 120.6 (*c* 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.64 (m, 1H), 2.07 (dd, J = 3.1, 6.9 Hz, 1H), 2.43 (s, 3H), 3.21 (s, 3H), 3.38 (s, 3H), 4.50 (m, 1H), 4.63 (m, 1H), 5.00 (d, J = 5.1 Hz, 1H), 7.33 (d, J = 7.9 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 19.9 (CH_2), 21.5, 48.6, 56.3, 58.2, 61.9, 80.7, 105.1, 128.0, 129.6, 136.3, 144.6. Anal. calcd for $C_{14}H_{18}O_5S$: C, 56.36; H, 6.08. Found: C, 56.73; H, 5.98. Compound **13b**: eluent: EtOAc/petroleum ether (1:3). White crystalline solid. Solvent of crystallization: DCM and petroleum ether. Mp: 114 °C. $[\alpha]^{27}_D$ (−) 75.8 (*c* 0.46, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.70 (dd, J = 3.1, 7.2 Hz, 1H), 2.01 (t, J = 6.8 Hz, 1H), 2.43 (s, 3H), 3.28 (s, 6H), 3.76 (s, 1H), 4.53 (m, 1H), 4.88 (s, 1H), 7.31 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 19.2 (CH_2), 21.5, 47.8, 55.1, 57.8, 63.9, 85.7, 110.1, 128.2, 129.2, 138.5, 144.0. Anal. calcd for $C_{14}H_{18}O_5S$: C, 56.36; H, 6.08. Found: C, 56.40; H, 6.00.

Methyl 2-*O*-Benzyl-3,5-cyclo-3,5-dideoxy-3-(4-methylphenyl)-sulfonyl-β-D-ribofuranoside (14). Compound **6**β (0.22 g, 0.6 mmol) was converted to **14** following the general procedure (0.19 g, 83%). Eluent: EtOAc/petroleum ether (1:5). White amorphous solid. Mp: 172 °C. $[\alpha]^{27}_D$ (−) 49.5 (*c* 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.72 (dd, J = 3.3, 7.2 Hz, 1H), 2.04 (t, J = 6.9 Hz, 1H), 2.35 (s, 3H), 3.20 (s, 3H), 4.07 (s, 1H), 4.50−4.55 (m, 3H), 4.82 (s, 1H), 7.08 (d, J = 7.9 Hz, 2H), 7.18−7.35 (m, 5H), 7.64 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 19.2 (CH_2), 21.4, 47.7, 55.2, 64.4, 72.9 (CH_2), 84.1, 110.8, 127.8, 128.1, 128.2, 129.1, 136.5, 138.4, 143.7. Anal. calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.92. Found: C, 64.48; H, 5.77.

Methyl 3,5-Cyclo-2-bis(methoxycarbonylmethyl)-3-(4-methylphenyl)sulfonyl-2,3,5-trideoxy-β-D-ribofuranoside (15). Compound **6**β (0.88 g, 2.4 mmol) was converted to **15** following the general procedure (0.81 g, 84%). Eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27}_D$ (−) 57.3 (*c* 1.64, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.66−1.73 (m, 2H), 2.45 (s, 3H), 2.66 (m, 1H), 3.27 (s, 3H), 3.73 (s, 3H), 3.80 (s, 3H), 4.36 (d, J = 3.6 Hz, 1H), 4.81 (m, 1H), 5.35 (d, J = 1.3 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.2, 22.9 (CH_2), 45.7, 48.0, 50.0, 52.1, 52.5, 55.1, 66.8, 110.9, 127.1, 129.8, 136.9, 144.4, 166.9, 168.5. IR (KBr): 1084, 1144, 1304, 1735 cm^{-1}. Anal. calcd for $C_{18}H_{22}O_8S$: C, 54.26; H, 5.57. Found: C, 54.45; H, 5.55.

Methyl 2-*O*-Benzyl-3,5-cyclo-3,5-dideoxy-α-D-arabinofuranoside (16). Compound **9** (0.38 g, 1.01 mmol) was desulfonylated to **16** following the general procedure (0.18 g, 80%). Eluent: EtOAc/petroleum ether (1:12). Yellow oil. $[\alpha]^{27}_D$ (+) 258.7 (*c* 2.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.73 (m, 1H), 1.14 (m, 1H), 1.80 (m, 1H), 3.33 (s, 3H), 4.15−4.27 (m, 2H), 4.41 (d, J = 11.5 Hz, 1H), 4.63 (d, J = 11.5 Hz, 1H), 4.73 (d, J = 0.8 Hz, 1H), 7.28−7.37 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 13.8 (CH_2), 18.0, 54.6, 61.5, 70.3 (CH_2), 84.0, 114.2, 127.5, 127.7, 128.2, 137.6. Anal. calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.53; H, 7.46.

Methyl 2-*N*-Benzylamino-3,5-cyclo-2,3,5-trideoxy-α-D-arabinofuranoside (17). To a well-stirred solution of **11** (0.25 g, 0.66 mmol) in dry MeOH (10 mL) was added Mg turnings (15 mmol) and $NiBr_2$ (10 mol %) under Ar. The mixture was heated at 60 °C. After 5 h, another portion of Mg turnings (15 mmol) and dry MeOH (5 mL) were added. The mixture was stirred for an additional 5 h at 60 °C. The reaction mixture was filtered through Celite. The residue was washed thoroughly with MeOH. The filtrates were pooled together, and the liquid was evaporated under reduced pressure. The resulting residue was dissolved in EtOAc. The solution was washed with saturated NH_4Cl solution, dried over anhydrous Na_2SO_4, and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over a silica gel column to afford **17** (0.1 g, 66%). Eluent: EtOAc/petroleum ether (1:3). Yellow oil. $[\alpha]^{27}_D$ (+) 201.4 (*c* 0.44, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.62 (m, 1H), 0.94 (m, 1H), 1.75 (m, 1H), 3.33 (s, 3H), 3.55 (m, 1H), 3.72 (d, J = 12.9 Hz, 1H), 3.86 (d, J = 12.9 Hz, 1H), 4.10 (m, 1H), 4.52 (s, 1H), 7.27−7.35 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 13.0 (CH_2), 18.9, 52.1 (CH_2), 55.1, 60.1, 64.9, 115.0, 127.1, 128.2, 128.4, 139.9. Anal. calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.47; H, 8.22; N, 6.42. HRMS [ES$^+$, $(M + H)^+$]; for $C_{13}H_{18}NO_2$: calcd 220.1338, obsd 220.1341.

Methyl 2-*O*-Benzyl-3,5-cyclo-3,5-dideoxy-β-D-ribofuranoside (18). Compound **14** (0.32 g, 0.85 mmol) was desulfonylated to **18** following the general procedure (0.15 g, 77%). Eluent: EtOAc/petroleum ether (1:12). Yellow oil. $[\alpha]^{27}_D$ (−) 30.5 (*c* 1.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.56 (m, 1H), 0.87 (m, 1H), 1.63 (m, 1H), 3.29 (s, 3H), 3.92 (s, 1H), 4.15 (m, 1H), 4.59 (s, 2H), 5.04 (d, J = 0.9 Hz, 1H), 7.28−7.37 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 10.6 (CH_2), 18.5, 55.0, 59.7, 71.5 (CH_2), 84.7, 111.2, 127.8, 128.4, 137.8. Anal. calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.0; H, 7.47.

Methyl 3,5-Cyclo-2-(methoxycarbonylmethyl)-3-(4-methylphenyl)sulfonyl-2,3,5-trideoxy-α-D-arabinofuranoside (19). Compound **11** (0.6 g, 1.51 mmol) was converted to **19** following the general procedure (0.41 g, 81%). Eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27}_D$ (+) 59.7 (*c* 3.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.37 (dd, J = 2.8, 7.2 Hz, 1H), 1.91 (m, 1H), 2.27−2.39 (m, 2H), 2.46 (s, 3H), 3.11 (m, 1H), 3.17 (s, 3H), 3.66 (s, 3H), 4.45 (m, 1H), 4.59 (d, J = 2.6 Hz, 1H), 7.37 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.0 (CH_2), 21.6, 33.6 (CH_2), 43.5, 49.3, 51.9, 55.2, 63.2, 113.9, 128.6, 129.8, 135.2, 144.9, 171.1. IR (KBr): 1139, 1166, 1303, 1316, 1736 cm^{-1}. Anal. calcd for $C_{16}H_{20}O_6S$: C, 56.46; H, 5.92. Found: C, 56.79; H, 5.80.

Methyl 3,5-Cyclo-2-(methoxycarbonylmethyl)-2,3,5-trideoxy-α-D-arabinofuranoside (20). Compound **19** (0.42 g, 1.23 mmol) was desulfonylated to **20** following the general procedure (0.18 g, 77%). Eluent: EtOAc/petroleum ether (1:8). Yellow oil. $[\alpha]^{27}_D$ (+) 210.3 (*c* 1.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.44−0.58 (m, 2H), 1.73 (m, 1H), 2.38−2.46 (m, 2H), 2.81 (m, 1H), 3.35 (s, 3H), 3.69 (s, 3H), 4.05 (m, 1H), 4.45 (d, J = 2.9 Hz, 1H). ^{13}C NMR

($CDCl_3$): δ 12.6 (CH_2), 18.3, 34.4 (CH_2), 43.2, 51.6, 55.4, 58.5, 113.1, 172.4. IR (KBr): 1083, 1105, 1169, 1260, 1736 cm^{-1}. Anal. calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.35; H, 7.29.

(3a*S*, 3b*R*, 4a*R*, 5a*S*)-Tetrahydro-3b*H*-cyclopropa[*b*]furo[3,2-*d*]furan-2(3*H*)-one (21). Compound **20** (0.25 g, 1.34 mmol) was stirred at room temperature with 90% trifluoroacetic acid (10 mL) for 2 h. After completion of the reaction (TLC), the solvent was evaporated to dryness under reduced pressure to obtain a residue. The residue was purified over a silica gel column to obtain compound **21** (0.13 g, 69%). Eluent: EtOAc/petroleum ether (1:2). White crystalline solid. Solvent of crystallization: DCM and petroleum ether. Mp: 99 °C. $[\alpha]^{27}_D$ (+) 242.4 (*c* 0.2, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.65 (m, 1H), 0.81 (m, 1H), 1.85 (m, 1H), 2.62−2.85 (m, 2H), 3.36 (m, 1H), 4.27 (m, 1H), 6.13 (d, J = 6.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 12.1 (CH_2), 20.2, 32.9 (CH_2), 40.7, 63.2, 111.4, 174.8. IR (KBr): 1006, 1129, 1189, 1364, 1764, 1781 cm^{-1}. Anal. calcd for $C_7H_8O_3$: C, 60.0; H, 5.75. Found: C, 59.77; H, 5.56.

Methyl 3,5-Cyclo-2-(acetyloxyethyl)-2,3,5-trideoxy-α-D-arabinofuranoside (22). Compound **19** (0.49 g, 1.44 mmol) was converted to **22** following the general procedure (0.22 g, 75%). Eluent: EtOAc/petroleum ether (1:5). Yellow oil. $[\alpha]^{27}_D$ (+) 202.6 (*c* 0.76, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.44−0.57 (m, 2H), 1.57−1.98 (m, 3H), 2.05 (s, 3H), 2.46 (m, 1H), 3.34 (s, 3H), 4.03−4.19 (m, 3H), 4.41 (d, J = 3.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 12.1 (CH_2), 17.6, 20.7, 28.5 (CH_2), 43.5, 55.3, 58.4, 62.8 (CH_2), 113.8, 170.8. IR (KBr): 1093, 1243, 1366, 1740 cm^{-1}. Anal. calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.20; H, 8.39.

(1*R*,2*R*)-2-{(1*S*)-3-(Acetyloxy)-1-[bis(ethylthio)methyl]propyl}-cyclopropyl Acetate (23). Compound **22** (0.17 g, 0.85 mmol) was converted to **23** following the general procedure (0.2 g, 71%). Eluent: EtOAc/petroleum ether (1:6). Yellow oil. $[\alpha]^{27}_D$ (+) 11.7 (*c* 0.56, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.50 (m, 1H), 1.05−1.15 (m, 2H), 1.18−1.31 (m, 6H), 1.77−1.82 (m, 2H), 2.03 (s, 3H), 2.05 (s, 3H), 2.15 (m, 1H), 2.62−2.70 (m, 4H), 3.99 (d, J = 2.4 Hz, 1H), 4.10−4.35 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 11.2 (CH_2), 14.5, 14.6, 19.9, 20.8, 20.9, 26.3 (CH_2), 26.7 (CH_2), 30.5 (CH_2), 39.8, 52.4, 57.0, 62.8 (CH_2), 170.8, 171.3. IR (KBr): 1037, 1241, 1371, 1732, 1732, 1747 cm^{-1}. Anal. calcd for $C_{15}H_{26}O_4S_2$: C, 53.86; H, 7.83. Found: C, 53.55; H, 7.56.

Methyl 3,5-Cyclo-2-(methoxycarbonylmethyl)-3-(4-methylphenyl)sulfonyl-2,3,5-trideoxy-β-D-ribofuranoside (24). Compound **15** (0.52 g, 1.3 mmol) was converted to **24** following the general procedure (0.37 g, 83%). Eluent: EtOAc/petroleum ether (1:4). White crystalline solid. Solvent of crystallization: acetone and petroleum ether. $[\alpha]^{27}_D$ (−) 41.6 (*c* 0.76, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.76 (t, J = 6.6 Hz, 1H), 1.91 (dd, J = 3.2, 6.6 Hz, 1H), 2.44 (s, 3H), 2.48−2.59 (m, 2H), 3.16 (m, 1H), 3.27 (s, 3H), 3.67 (s, 3H), 4.74 (m, 1H), 4.83 (s, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.3, 22.1 (CH_2), 34.1 (CH_2), 44.5, 46.4, 51.5, 54.9, 64.7, 112.4, 127.1, 129.8, 137.2, 144.4, 171.7. IR (KBr): 1086, 1303, 1312, 1737 cm^{-1}. Anal. calcd for $C_{16}H_{20}O_6S$: C, 56.46; H, 5.92. Found: C, 56.56; H, 6.03.

Methyl 3,5-Cyclo-2-(acetyloxyethyl)-2,3,5-trideoxy-β-D-ribofuranoside (25). Compound **24** (0.24 g, 0.7 mmol) was desulfonylated to **25** following the general procedure (0.1 g, 71%). Eluent: EtOAc/petroleum ether (1:5). Yellow oil. $[\alpha]^{27}_D$ (−) 47.2 (*c* 0.7, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.52 (m, 1H), 0.93 (m, 1H), 1.28 (m, 1H), 1.64−1.81 (m, 2H), 2.05 (s, 3H), 2.18 (m, 1H), 3.27 (s, 3H), 4.00 (m, 1H), 4.14 (t, J = 6.7 Hz, 2H), 4.81 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 12.7 (CH_2), 18.6, 20.8, 31.7 (CH_2), 45.0, 54.5, 59.3, 62.3 (CH_2), 112.0, 170.9. IR (KBr): 772, 1086, 1245, 1741 cm^{-1}. Anal. calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.20; H, 8.13.

(1*R*,2*R*)-2-{(1*R*)-3-(Acetyloxy)-1-[bis(ethylthio)methyl]propyl}-cyclopropyl Acetate (26). Compound **25** (0.08 g, 0.4 mmol) was converted to **26** following the general procedure (0.09 g, 68%). Eluent: EtOAc/petroleum ether (1:7). Yellow oil. $[\alpha]^{27}_D$ (−) 63.8 (*c* 0.56, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.51 (m, 1H), 1.03−1.14 (m, 2H), 1.15−1.35 (m, 6H), 1.78−1.86 (m, 2H), 2.05 (s, 3H), 2.06 (s, 3H), 2.27 (m, 1H), 2.51−2.73 (m, 4H), 3.96 (d, J = 2.3 Hz, 1H), 4.14−4.26 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 11.7 (CH_2), 14.6, 14.7, 19.0, 20.9, 21.0, 26.1 (CH_2), 26.8 (CH_2), 29.5 (CH_2), 40.4, 51.4, 56.0, 63.0 (CH_2), 171.0, 171.5. IR (KBr): 1036, 1230, 1369, 1742 cm^{-1}. Anal. calcd for $C_{15}H_{26}O_4S_2$: C, 53.86; H, 7.83. Found: C, 53.66; H, 8.03.

Methyl 3-Deoxy-5-*O*-*p*-methoxybenzyl-3-*S*-(4-methylphenyl)-3-thio-α-D-arabinofuranoside (28). Compound **5** (1.4 g, 9.6 mmol) was converted to **28** following the general procedure (3.3 g, 89%). Eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27}_D$ (+) 121.9 (*c* 2.1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 2.31 (s, 3H), 3.39 (s, 3H), 3.45−3.73 (m, 3H), 3.80 (s, 3H), 4.12 (m, 1H), 4.26 (m, 1H), 4.50 (q, J = 11.5, 11.5 Hz, 2H), 4.92 (s, 1H), 6.87 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.20−7.26 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 20.9, 52.9, 54.9, 55.1, 69.2 (CH_2), 73.1 (CH_2), 80.6, 83.7, 110.0, 113.8, 129.0, 129.4, 129.7, 130.8, 131.6, 136.8, 159.3. Anal. calcd for $C_{21}H_{26}O_5S$: C, 64.59; H, 6.71. Found: C, 64.48; H, 6.73.

Methyl 3-Deoxy-2-*O*-methyl-3-*S*-(4-methylphenyl)-3-thio-α-D-arabinofuranoside (31). Compound **28** (0.66 g, 1.7 mmol) was converted to **31** following the general procedure (0.41 g, 85%). Eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27}_D$ (+) 158.4 (*c* 3.34, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 2.32 (S, 3H), 3.27 (s, 3H), 3.37 (s, 3H), 3.42 (m, 1H), 3.76−3.78 (m, 2H), 4.05 (m, 1H), 4.92 (s, 1H), 5.30 (s, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.9, 50.3, 54.6, 57.4, 61.7 (CH_2), 83.5, 91.6, 107.2, 129.7, 130.3, 132.3, 137.5. Anal. calcd for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09. Found: C, 58.73; H, 7.36.

Methyl 2-*O*-Benzyl-3-deoxy-3-*S*-(4-methylphenyl)-3-thio-α-D-arabinofuranoside (32). Compound **28** (0.72 g, 1.8 mmol) was converted to **32** following the general procedure (0.55 g, 82%). Eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27}_D$ (+) 102.6 (*c* 0.9, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 2.33 (s, 3H), 3.35 (s, 3H), 3.47−3.66 (m, 2H), 3.83 (m, 1H), 3.99−4.10 (m, 2H), 4.42 (q, J = 11.7, 11.7 Hz, 2H), 4.94 (s, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.19−7.37 (m, 7H). ^{13}C NMR ($CDCl_3$): δ 21.0, 51.0, 54.8, 61.9 (CH_2), 71.8 (CH_2), 83.3, 89.6, 107.7, 127.7, 127.8, 128.3, 129.9, 130.2, 132.6, 137.2, 137.7. Anal. calcd for $C_{20}H_{24}O_4S$: C, 66.64; H, 6.71. Found: C, 66.70; H, 6.86.

Methyl 3-Deoxy-5-*O*-mesyl-2-*O*-methyl-3-(4-methylphenyl)-sulfonyl-α-D-arabinofuranoside (35). Compound **31** (0.44 g, 1.55 mmol) was converted to **35** following the general procedure (0.57 g, 93%). Eluent: EtOAc/petroleum ether (1:3). White crystalline solid. Solvent of crystallization: DCM and petroleum ether. Mp: 98 °C. $[\alpha]^{27}_D$ (+) 81.4 (*c* 2.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 2.47 (s, 3H), 3.05 (s, 3H), 3.14 (s, 3H), 3.30 (s, 3H), 3.58 (dd, J = 3.4, 8.6 Hz, 1H), 4.11−4.24 (m, 2H), 4.49−4.65 (m, 2H), 4.88 (s, 1H), 7.40 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.6, 37.7, 54.8, 57.6, 68.7 (CH_2), 69.0, 75.3, 86.6, 107.0, 128.6, 130.0, 134.7, 145.7. Anal. calcd for $C_{15}H_{22}O_8S_2$: C, 45.67; H, 5.62. Found: C, 45.78; H, 5.40.

Methyl 2-*O*-Benzyl-3-deoxy-5-*O*-mesyl-3-(4-methylphenyl)-sulfonyl-α-D-arabinofuranoside (36). Compound **32** (0.27 g, 0.75 mmol) was converted to **36** following the general procedure (0.31 g, 90%). Eluent: EtOAc/petroleum ether (1:3). White crystalline solid. Solvent of crystallization: DCM and petroleum ether. Mp: 105 °C. $[\alpha]^{27}_D$ (+) 37.9 (*c* 2.6, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 2.45 (s, 3H), 3.02 (s, 3H), 3.27 (s, 3H), 3.71 (dd, J = 3.7, 8.6 Hz, 1H), 4.22−4.32 (m, 4H), 4.53−4.62 (m, 2H), 4.90 (s, 1H), 7.05−7.10 (m, 2H), 7.26−7.38 (m, 5H), 7.77 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.5, 37.6, 54.8, 68.7 (CH_2), 69.2, 72.0 (CH_2), 75.0, 84.7, 107.1, 127.7, 127.9, 128.2, 130.0, 134.6, 136.3, 145.5. Anal. calcd for $C_{21}H_{26}O_8S_2$: C, 53.60; H, 5.57. Found: C, 53.70; H, 5.54.

Methyl 3,5-Cyclo-3,5-dideoxy-2-*O*-methyl-3-(4-methylphenyl)-sulfonyl-α-D-arabinofuranoside (8). Compound **35** (0.14 g, 0.35 mmol) was converted to **8** following the general procedure (0.09 g, 82%). Eluent: EtOAc/petroleum ether (1:3). White crystalline solid.

Methyl 2-*O*-Benzyl-3,5-cyclo-3,5-dideoxy-3-(4-methylphenyl)-sulfonyl-α-D-arabinofuranoside (9). Compound **36** (0.2 g, 0.42 mmol) was converted to **9** following the general procedure (0.13 g, 81%). Eluent: EtOAc/petroleum ether (1:5). White amorphous solid.

Methyl 3-Deoxy-5-*O*-*p*-methoxybenzyl-3-*S*-(4-methylphenyl)-3-thio-*β*-D-xylofuranoside (38). Compound **7** (0.44 g, 3.0 mmol) was converted to **38** following the general procedure (0.85 g, 72%). Eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27}_D$ (+) 22.4 (*c* 4.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 3H), 3.41 (s, 3H), 3.60−3.75 (m, 3H), 3.80 (s, 3H), 4.28 (m, 1H), 4.51 (s, 2H), 4.59 (m, 1H), 4.84 (d, J = 2.2 Hz, 1H), 6.86 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 7.24−7.32 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 20.7, 54.8, 55.0, 55.3, 70.8 (CH_2), 72.7 (CH_2), 79.8, 81.2, 109.3, 113.5, 129.2, 129.6, 130.0, 130.4, 132.0, 136.5, 158.9. Anal. calcd for $C_{21}H_{26}O_5S$: C, 64.59; H, 6.71. Found: C, 64.78; H, 7.01.

Methyl 3-Deoxy-2-*O*-methyl-3-*S*-(4-methylphenyl)-3-thio-*β*-D-xylofuranoside (41). Compound **38** (0.4 g, 1.02 mmol) was converted to **41** following the general procedure (0.24 g, 81%). Eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27}_D$ (−) 49.7 (*c* 1.08, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H), 3.40 (s, 3H), 3.46 (s, 3H), 3.65−3.93 (m, 4H), 4.45 (m, 1H), 4.88 (d, J = 2.1 Hz, 1H), 7.10 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.9, 53.3, 55.8, 58.3, 63.1 (CH_2), 82.6, 91.2, 108.5, 129.2, 129.8, 130.9, 131.9, 137.0. Anal. calcd for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09. Found: C, 59.34; H, 7.19.

Methyl 2-*O*-Benzyl-3-deoxy-3-*S*-(4-methylphenyl)-3-thio-*β*-D-xylofuranoside (42). Compound **38** (0.33 g, 0.84 mmol) was converted to **42** following the general procedure (0.24 g, 80%). Eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27}_D$ (−) 61.9 (*c* 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H), 3.41 (s, 3H), 3.75−3.89 (m, 3H), 4.15 (dd, J = 1.9, 6.6 Hz, 1H), 4.44−4.59 (m, 3H), 4.91 (d, J = 2.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.23−7.36 (m, 7H). ^{13}C NMR ($CDCl_3$): δ 20.9, 53.7, 55.8, 63.2 (CH_2), 72.7 (CH_2), 82.6, 89.7, 108.8, 127.7, 128.3, 129.8, 131.0, 131.9, 137.0, 137.4. Anal. calcd for $C_{20}H_{24}O_4S$: C, 66.64; H, 6.71. Found: C, 66.33; H, 6.69.

Methyl 3-Deoxy-5-*O*-mesyl-2-*O*-methyl-3-(4-methylphenyl)-sulfonyl-*β*-D-xylofuranoside (45). Compound **41** (0.2 g, 0.7 mmol) was converted to **45** following the general procedure (0.25 g, 89%). Eluent: EtOAc/petroleum ether (1:3). White crystalline solid. Solvent of crystallization: EtOAc and petroleum ether. Mp: 108 °C. $[\alpha]^{27}_D$ (−) 25.2 (*c* 0.76, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 3H), 3.06 (s, 3H), 3.08 (s, 3H), 3.45 (s, 3H), 3.85 (m, 1H), 4.13 (dd, J = 1.9, 6.6 Hz, 1H), 4.64−4.88 (m, 4H), 7.38 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.6, 37.4, 55.9, 58.0, 69.5 (CH_2), 70.1, 77.0, 86.6, 109.2, 128.3, 129.9, 135.9, 145.5. Anal. calcd for $C_{15}H_{22}O_8S_2$: C, 45.67; H, 5.62. Found: C, 45.29; H, 5.47.

Methyl 2-*O*-Benzyl-3-deoxy-5-*O*-mesyl-3-(4-methylphenyl)-sulfonyl-*β*-D-xylofuranoside (46). Compound **42** (0.15 g, 0.42 mmol) was converted to **46** following the general procedure (0.18 g, 90%). Eluent: EtOAc/petroleum ether (1:3). White crystalline solid. Solvent of crystallization: DCM and petroleum ether. Mp: 134 °C. $[\alpha]^{27}_D$ (+) 5.1 (*c* 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 3H), 3.09 (s, 3H), 3.41 (s, 3H), 4.00 (m, 1H), 4.12−4.39 (m, 3H), 4.67 (m, 1H), 4.81−4.90 (m, 3H), 6.85−6.89 (m, 2H), 7.23−7.33 (m, 5H), 7.77 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.5, 37.3, 55.9, 69.5 (CH_2), 70.2, 72.7 (CH_2), 76.9, 85.2, 109.3, 127.5, 127.8, 128.1, 128.2, 129.9, 135.8, 136.2, 145.4. Anal. calcd for $C_{21}H_{26}O_8S_2$: C, 53.60; H, 5.57. Found: C, 53.71; H, 5.37.

Methyl 3,5-Cyclo-3,5-dideoxy-2-*O*-methyl-3-(4-methylphenyl-)sulfonyl-*β*-D-ribofuranoside (13b). Compound **45** (0.12 g, 0.3 mmol) was converted to **13b** following the general procedure (0.07 g, 77%). Eluent: EtOAc/petroleum ether (1:3). White crystalline solid.

Methyl 2-*O*-Benzyl-3,5-cyclo-3,5-dideoxy-3-(4-methylphenyl)-sulfonyl-*β*-D-ribofuranoside (14). Compound **46** (0.1 g, 0.21 mmol) was converted to **14** following the general procedure (0.06 g, 72%). Eluent: EtOAc/petroleum ether (1:5). White amorphous solid.

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Supporting Information Available: General experimental methods, ORTEP diagrams, and crystallographic information files for **11**, **12**, **21**, and **24** and spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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