A One-Pot Deprotection and Intramolecular Oxa-Michael Addition to Access Angular Trioxatriquinanes

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Abstract: An efficient one-pot deprotection–oxa-Michael addition strategy has been used to synthesize a few trioxatriquinanes starting from commercially available sugars.

Key words: triquinane, RCM, allylic oxidation, deprotection

The triquinanes,[1] a unique substructural class of a family of sesquiterpenoid natural products, are endowed with three five-membered fused rings and can be classified into three broad categories: linear **1**, angular **2**, and modephane **3** depending upon the mode of their ring fusion (Figure 1). The synthesis of triquinanes has been a vibrant area of organic synthesis ever since the structural elucidation of a carbocyclic linear triquinane, hirsutic acid (**4**).

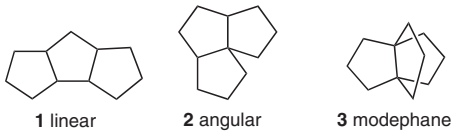

Figure 1 Classification of triquinanes

The enticing molecular architecture of triquinanes coupled with their wide spectrum of biological properties has made them attractive synthetic targets. Several methods, especially cascade radical methods,[2] transannulation reactions,[3] alkene-arene and photocycloaddition reactions[4] have been developed to synthesize the core framework as well as several natural products belonging to this category. The diversity of carbocyclic triquinanes extends to their hetero analogues, namely the azatriquinanes[5] and oxatriquinanes.[6] However, these hetero variants of the triquinanes have received much less attention than their carbon analogues, which is evident from the limited reports appearing in the literature. The activity of a natural product can often be attributed to the presence of a heterocycle. For example, the biological activity of merrilactone A (**8**), isolated from *Illicium merrillianum*,[7] is attributed to the presence of the oxygenated pentacyclic architecture. In addition, there are steroid-based hybrid natural products, such as isogenine (**9**)[8] and *C*-norcardanolide (**10**),[9] and hirundigenin (**11**)[10] having dioxatriquinane and trioxatriquinane subunits with interesting biological profiles (Figure 2).

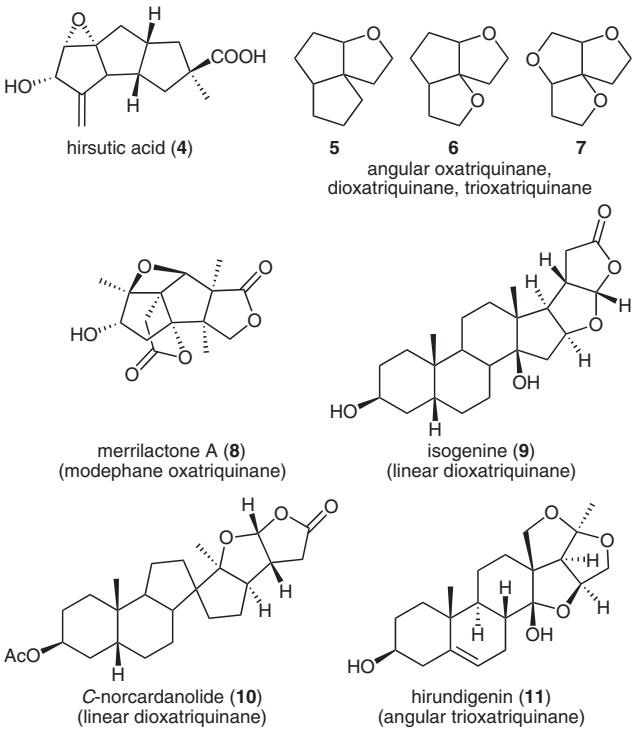

Figure 2

The total synthesis of (±)-hirsutene reported by Fukumoto[11] and co-workers particularly drew our attention to our current objective of synthesizing angular trioxatriquinane frameworks, as some of the synthetic intermediates possessing oxa-triquinane systems were proven to exhibit potent in vitro cytotoxic activity.

In continuation[12] of our interest in exploring these aesthetically pleasing molecules, we developed interest in designing the angular trioxatriquinane framework **7** from commercially available carbohydrate precursors. Our target, the angular trioxatriquinane framework **12** can be considered as a template of the syringolides[13] 1 (**13**) and 2 (**14**) produced by *Pseudomonas syringae* pv. *tomato*, which elicit a hypersensitive defense response (HR) in specific soybean cultivars (Figure 3). Herein, we describe the synthesis of an angular trioxatriquinane framework using one-pot deprotection and intramolecular oxa-Michael addition as key steps, starting from sugars such as D-xylose, L-xylose, and D-glucose.

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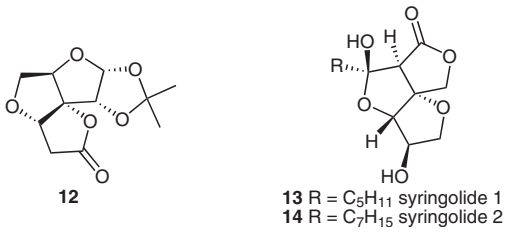
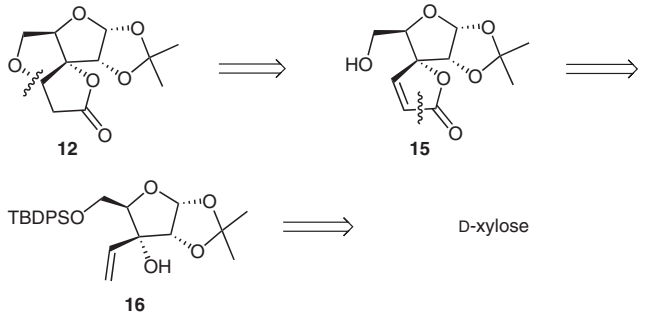


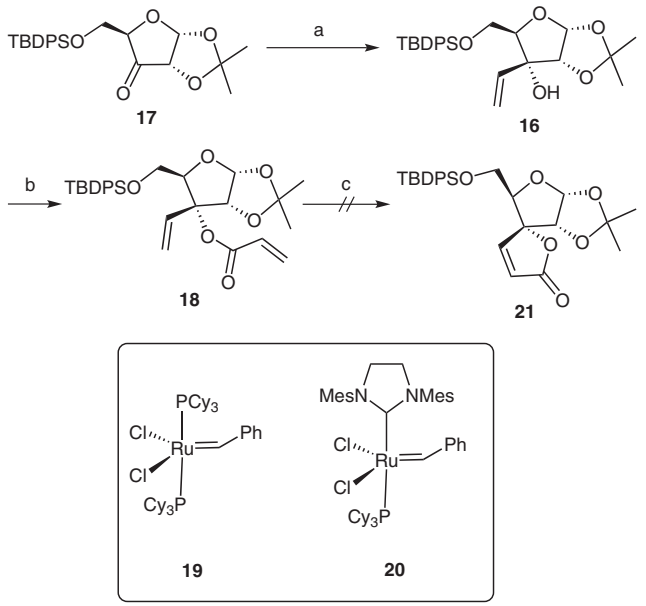
Figure 3

As outlined in Scheme 1, we envisaged that angular trioxatriquinane **12** could be obtained from the hydroxyspirolactone **15** by an intramolecular oxa-Michael addition, which, in turn, could be accessed from allyl alcohol **16**. This allyl alcohol could be easily obtained from D-xylose in a few steps.



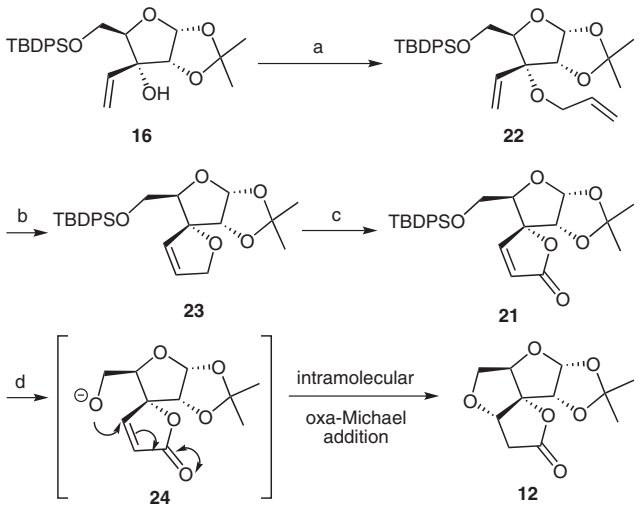
Scheme 1 Retrosynthetic analysis of angular trioxatriquinane

Thus, our synthesis embarked with the TBDPS-protected ketone **17**, readily available from D-xylose by a three-step protocol.[14] Addition of vinyl magnesium bromide to ketone **17** afforded the alcohol **16** stereoselectively which, upon treatment with acryloyl chloride and NaH, gave the ring-closing metathesis precursor diene **18**. However, all attempts to accomplish the key ring-closing metathesis (RCM)[15] of diene **18** with both Grubbs first- and second-generation catalysts (**19** and **20**) resulted mainly in recovery of the starting material even after prolonged periods of refluxing in CH_2Cl_2–toluene. Then, prompted by literature reports[16] and based on our own experience,[17] we performed the RCM of diene **18** by employing 10 mol% of Grubbs first-generation catalyst with 15 mol% of Ti(O*i*-Pr)$_4$ in dichloromethane. Much to our disappointment, this modification did not have significant impact on the outcome with only trace amounts of cyclized product **21** being obtained now (Scheme 2).

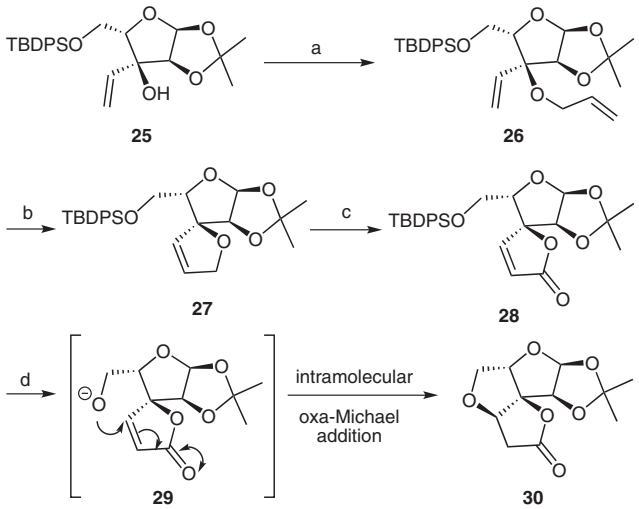


Scheme 2 *Reagents and conditions*: (a) vinyl magnesium bromide, THF, –10 °C to r.t., 3 h, 85%; (b) NaH, acryloyl chloride, THF, r.t., 2 h, 89%; (c) various conditions.

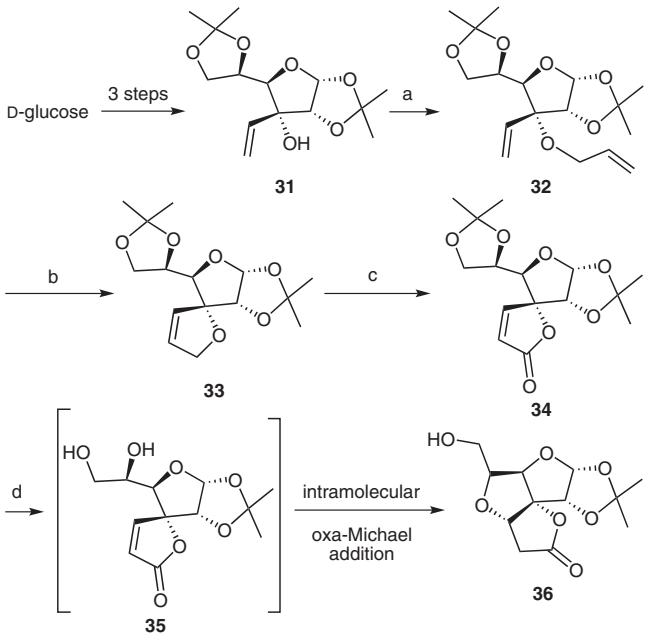
In view of this unexpected difficulty, we next focused on synthesizing the spirolactone **21** by subjecting diene **22** to RCM followed by allylic oxidation (Scheme 3). Accordingly, diene **22**[18] was obtained by allylation of alcohol **16** using NaH and allyl bromide. Now, diene **22** underwent



Scheme 3 *Reagents and conditions*: (a) NaH, allyl bromide, THF, 0 °C to reflux, 4 h, 76%; (b) Grubbs I (**19**), CH_2Cl_2, reflux, 12 h, 91%; (c) PDC, Celite, *t*-BuOOH, PhH, 8 h, 75%; (d) TBAF, 0 °C, 1 h, 60%.



Scheme 4 *Reagents and conditions*: (a) NaH, allyl bromide, THF, 0 °C to reflux, 4 h, 76%; (b) Grubbs I (**19**), CH_2Cl_2, reflux, 12 h, 91%; (c) PDC, Celite, *t*-BuOOH, PhH, 8 h, 75%; (d) TBAF, 0 °C, 1 h, 60%.



Scheme 5 *Reagents and conditions*: (a) NaH, allyl bromide, THF, 0 °C to reflux, 6 h, 90%; (b) Grubbs I (**19**), CH_2Cl_2, reflux, 12 h, 89%; (c) PDC, Celite, *t*-BuOOH, PhH, 18 h, 70%; (d) 60% aq AcOH, r.t., 16 h, 74%.

RCM reaction smoothly, unlike diene **18**, leading to the formation of the spiro ether **23** in 91% yield with 5 mol% of Grubbs first-generation catalyst.[19] It is important to note that the spiro ether was quite unstable, and further transformations needed to be carried out immediately. Thus, allylic oxidation[20] of **23** with pyridinium dichromate (PDC) and *tert*-butylhydroperoxide (TBHP) was carried out to furnish the required spiro lactone **21** in 85% yield.[21] Having compound **21** in hand, the stage was then set for the deprotection of the TBDPS group by treating with tetra-*n*-butylammonium fluoride (TBAF) at 0 °C for one hour.

Gratifylingly, this resulted in the direct formation of trioxatriquinane **12** in 60% yield via deprotection of the silyl group with concomitant intramolecular oxa-Michael addition in a single step.[22] It should be noted that attempts to accomplish a similar kind of intramolecular oxa-Michael addition in the synthesis of secosyrins by Mukai[23] and coworkers under several acidic and basic conditions were futile.

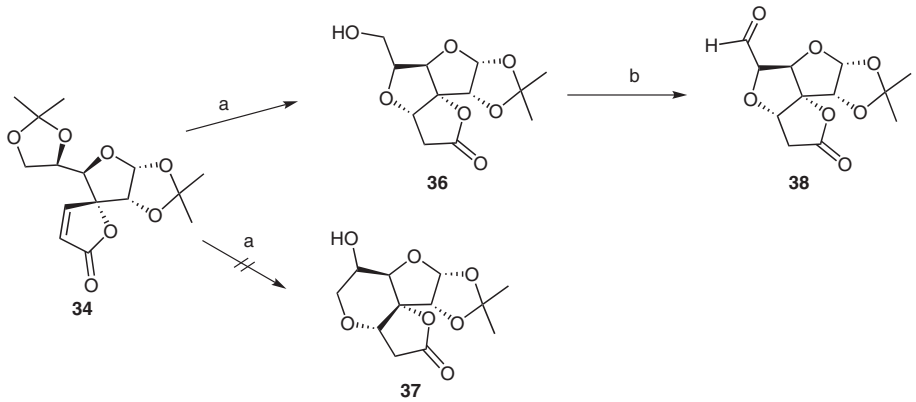
Having optimized the reaction conditions with D-xylose, the same series of transformations was carried out on L-xylose-derived alcohol **25** to synthesize the trioxatriquinane **30**, as shown in Scheme 4.

As D-glucose diacetonide has a similar stereochemical relationship to D-xylose monoacetonide, it seemed logical to this sequence. Accordingly, the known alcohol **31**,[24] readily available from D-glucose diacetonide, was converted into the RCM precursor **32** by a base-mediated alkylation with allyl bromide.

The key RCM of diene **32** with 5 mol% of Grubbs first-generation catalyst furnished the spiro ether **33** in 90% yield. This spiro ether was relatively stable, unlike the spiro ethers derived from D- and L-xylose. Allylic oxidation of **33** under PDC and Celite conditions furnished the spiro lactone **34** in 70% yield. Finally, selective deprotection of the more exposed acetonide group of **34**, with 60% AcOH, directly furnished the anticipated cyclized product **36** (Scheme 5).

The formation of the five-membered cyclized product **36** over the other possible six-membered cyclized product **37** was confirmed by carrying out the oxidation of the free hydroxyl group. Interestingly, oxidation of compound **36** with *O*-iodoxybenzoic acid (IBX) furnished aldehyde **38**, which was unambiguously characterized from its ^1H NMR spectroscopic data. We attributed this outcome to the stability of the five-five-five-membered ring fusion over the five-six-five-membered ring fusion (Scheme 6).

In summary, we have synthesized a few angular trioxatriquinanes from readily available carbohydrate starting materials. The key steps involved in this strategy are RCM followed by allylic oxidation to construct the spiro lactone and formation of trioxatriquinane in a single step by desilylation with concomitant intramolecular oxa-Michael addition. Our efforts in the application of this method to construct azadioxatriquinane and tetraoxatetraquinane frameworks are underway.



Scheme 6 *Reagents and conditions*: (a) 60% aq AcOH, r.t., 16 h, 74%; (b) IBX, EtOAc, reflux, 6 h.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(18) A 60% oil dispersion of NaH (75 mg, 1.84 mmol, 3 equiv), after washing with anhyd hexanes (3 × 5 mL), was suspended in anhyd THF (5 mL), and the reaction mixture was cooled to 0 °C. To this, a solution of compound **16** (280 mg, 0.61 mmol, 1 equiv) in anhyd THF (5 mL) was added dropwise and allowed to stir at r.t. for 1 h. Allyl bromide (0.1 mL, 1.23 mmol, 2 equiv) and TBAI (cat.) were added to the mixture at 0 °C, which was further stirred for 1 h at r.t. followed by heating to reflux for 4 h. The mixture was quenched by the careful addition of sat. aq NH_4Cl and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo to give the crude product. Silica gel column chromatography of the residue, eluting with 4% EtOAc in hexanes provided **22** (230 mg, 76%) as a colorless syrup. R_f = 0.45 (10% EtOAc in hexanes); $[\alpha]_D^{20}$ 28.9 (*c* 1.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 4 H), 7.42–7.33 (m, 6 H), 5.94–5.85 (m, 1 H), 5.81 (d, *J* = 3.6 Hz, 1 H), 5.58 (dd, *J* = 17.8, 11.3 Hz, 1 H), 5.25 (dd, *J* = 11.3, 0.9 Hz, 1 H), 5.23 (dq, *J* = 17.2, 1.8 Hz, 1 H), 5.16 (dd, *J* = 17.8, 0.9 Hz, 1 H), 5.11 (dq, *J* = 10.4, 1.5 Hz, 1 H), 4.45 (d, *J* = 3.6 Hz, 1 H), 4.33 (dd, *J* = 7.1, 3.5 Hz, 1 H), 4.10 (ddt, *J* = 12.4, 5.1, 1.6 Hz, 1 H), 3.98 (ddt, *J* = 12.4, 5.3, 1.6 Hz, 1 H), 3.78 (dd, *J* = 11.4, 3.5 Hz, 1 H), 3.70 (dd, *J* = 11.4, 7.2 Hz, 1 H), 1.61 (s, 3 H), 1.36 (s, 3 H), 1.03 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9, 135.8, 135.1, 134.6, 133.8, 133.7, 129.7, 129.6, 127.8, 127.7, 117.9, 116.0, 112.9, 104.5, 84.9, 82.8, 81.8, 66.3, 63.5, 27.2, 27.0, 26.9, 19.4. IR (neat): ν = 3072, 2932, 2858, 1646, 1462, 1428, 1383, 1217, 1121, 1042, 927, 878, 823, 758, 704, 612, 548, 505 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{29}H_{38}O_5SiNa$ $[M + Na]^+$: 517.2386; found: 517.2380.

(19) To a solution of diene **22** (210 mg, 0.42 mmol, 1 equiv) in argon-purged CH_2Cl_2 was added Grubbs first-generation catalyst (5 mol%), and the mixture was refluxed for 12 h. DMSO (2–3 drops) was added and the mixture stirred for 6 h to remove metal impurities. The mixture was then concentrated in vacuo to give a residue which, upon purification by silica gel column chromatography with 14% EtOAc in hexane, afforded compound **23** (180 mg, 91%) as a colorless syrup. R_f = 0.26 (16% EtOAc in hexanes); $[\alpha]_D^{20}$ +27.6 (*c* 1.56, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.65 (m, 4 H), 7.43–7.34 (m, 6 H), 5.98 (dt, *J* = 6.2, 1.3 Hz, 1 H), 5.80 (d, *J* = 3.6 Hz, 1 H), 5.67 (dt, *J* = 6.2, 1.5 Hz, 1 H), 4.69 (ddd, *J* = 13.4, 2.5, 1.7 Hz, 1 H) 4.57 (ddd, *J* = 13.4, 2.4, 1.7 Hz, 1 H), 4.32 (t, *J* = 4.5 Hz, 1 H), 4.22 (d, *J* = 3.7 Hz, 1 H), 3.68, 3.64 (ABq, J_{AB} = 11.4 Hz, 1 H), 3.66, 3.63 (ABq, J_{AB} = 11.4 Hz, 1 H), 1.63 (s, 3 H), 1.36 (s, 3 H), 1.03 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9, 135.8, 133.6, 133.5, 129.8, 129.6, 127.8, 125.6, 113.2, 103.5, 95.8, 83.0, 80.4, 75.9, 63.0, 27.0, 26.9, 26.6, 19.3. IR (neat): ν = 3019, 2930, 2857, 1597, 1216, 1113, 1082, 1042, 758,

668 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{27}H_{34}O_5SiNa$ $[M + Na]^+$: 489.2073; found: 489.2081.

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(21) To a solution of spiroether **23** (260 mg, 0.56 mmol, 1 equiv) in benzene (20 mL) was added Celite (1.2 g/mmol) at r.t. and the mixture cooled to 0–10 °C. To this reaction mixture was added PDC (1.06 g, 2.8 mmol, 5 equiv), followed by *t*-BuOOH (0.39 mL, 2.8 mmol, 5 equiv), and the whole was stirred for 8 h at r.t. The reaction mixture was filtered through a pad of Celite and washed with EtOAc, the filtrate was concentrated in vacuo to furnish the crude product as a yellow syrup. Silica gel column chromatography, eluting with 20% EtOAc in hexanes afforded the spirolactone **21** (230 mg) as a colorless syrup in 85% yield. R_f = 0.39 (40% EtOAc in hexanes); $[\alpha]_D^{20}$ +52.2 (*c* 1.41, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.59 (m, 4 H), 7.53 (d, *J* = 5.7 Hz, 1 H), 7.46–7.36 (m, 6 H), 6.14 (d, *J* = 5.7 Hz, 1 H), 5.98 (d, *J* = 3.7 Hz, 1 H), 4.52 (t, *J* = 3.7 Hz, 1 H), 4.49 (d, *J* = 3.7 Hz, 1 H), 3.73 (dd, *J* = 11.9, 4.1 Hz, 1 H), 3.61 (dd, *J* = 11.9, 3.6 Hz, 1 H), 1.63 (s, 3 H), 1.36 (s, 3 H), 1.03 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 153.8, 135.7, 135.6, 132.7, 132.6, 130.1, 130.0, 128.0, 127.9, 121.3, 114.3, 103.5, 91.4, 81.6, 79.2, 61.0, 26.9, 26.8, 26.7, 19.3. IR (neat): ν = 3021, 2933, 2860, 1774, 1601, 1216, 1166, 1106, 1013, 759, 670 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{27}H_{32}O_6SiNa$ $[M + Na]^+$: 503.1866; found: 503.1879.

(22) To a solution of spirolactone **21** (270 mg, 0.56 mmol, 1 equiv) in anhyd THF (6 mL) was added TBAF solution in THF (1 M, 1.12 mL, 2 equiv) at 0 °C, and the mixture was stirred at the same temperature for 1 h. The reaction mixture was diluted with EtOAc, and solvents were removed in vacuo to obtain the crude product, which was purified by silica gel chromatography, eluting with 32% EtOAc in hexanes to afford the trioxatriquinane **12** (80 mg) as a white low-melting solid in 60% yield. R_f = 0.19 (40% EtOAc in hexanes); $[\alpha]_D^{20}$ +27.8 (*c* 1.29, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.99 (d, *J* = 3.6 Hz, 1 H), 4.82 (d, *J* = 2.9 Hz, 1 H), 4.59 (d, *J* = 3.6 Hz, 1 H), 4.55 (dd, *J* = 6.7, 1.3 Hz, 1 H), 4.13 (d, *J* = 11.0 Hz, 1 H), 4.03 (dd, *J* = 11.0, 2.9 Hz, 1 H), 2.88 (dd, *J* = 19.0, 6.7 Hz, 1 H), 2.74 (dd, *J* = 19.0, 1.3 Hz, 1 H), 1.63 (s, 3 H), 1.39 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.6, 114.6, 105.9, 97.7, 83.0, 79.6, 79.2, 72.3, 35.5, 27.2, 27.0. IR (neat): ν = 3021, 2937, 1799, 1731, 1376, 1217, 1106, 1012, 909, 870, 758, 712, 669 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{11}H_{14}O_6Na$ $[M + Na]^+$: 265.0688; found: 265.0682.

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