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Conversion of 1,4-Diketones into *para*-Disubstituted Benzenes

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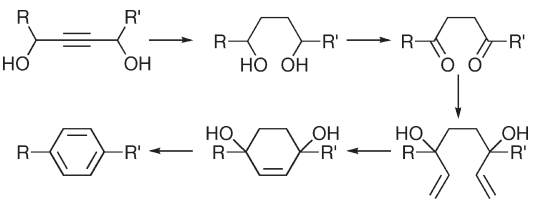
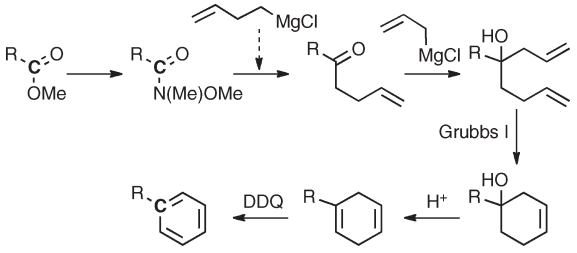


Reaction of acetylides with aldehydes to form but-2-yne-1,4-diols, followed by triple bond reduction and oxidation of the hydroxyl groups, gives 1,4-diketones; these react with vinyllithium, and the resulting diols undergo ring-closing metathesis to form 2-cyclohexene-1,4-diols. Dehydration, usually by acid treatment, then gives benzenes carrying substituents in a 1,4 relationship. Use of substituted vinyllithiums provides further substitution on the final benzene rings. The method can be applied to the synthesis of C5-aryl carbohydrates.

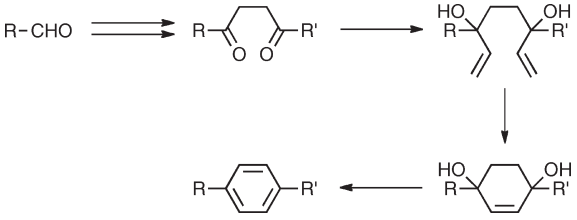
Introduction

Several years ago a need arose in this laboratory to convert a methyl ester into a benzene ring that incorporated the ester carbonyl carbon as part of the ring. Such a transformation was intended to allow, for example, conjugate addition to an α,β-unsaturated ester (or synthetic equivalent), followed by conversion of the ester into a phenyl group. The required transformation was solved[1] along the lines summarized in Scheme 1. While that method, which affords not only monosubstituted benzenes but also a limited range of polysubstituted benzenes, was being developed, a related procedure

SCHEME 1. Previous Route to Benzenes



SCHEME 2. Synthetic Plan



was also explored (Scheme 2). In this approach, 1,4-diketones were converted by reaction with vinyllithium into diols, which were then subjected to ring-closing metathesis and dehydration, producing in the simplest case *para*-disubstituted benzenes. We describe here full details of this work. Numerous methods are, of course, available for making aromatic compounds,[2,3] and a growing number of them do

(1) Clive, D. L. J.; Pham, M. P. *J. Org. Chem.* **2009**, *74*, 1685–1690.

(2) Reviews on the preparation of benzenes: (a) Bamfield, P.; Gordon, P. F. *Chem. Soc. Rev.* **1984**, *13*, 441–488. (b) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879–933. (c) Donohoe, T. J.; Orr, A. J.; Bingham, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 2664–2670. (d) Ballini, R.; Palmieri, A.; Barboni, L. *Chem. Commun.* **2008**, 2975–2985.

(3) For recent methods for the preparation of aromatic rings, see: (a) Langer, P.; Bose, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 4033–4036. (b) Park, D. Y.; Kim, S. J.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett.* **2006**, *47*, 6315–6319. (c) Grisé, C. M.; Barriault, L. *Org. Lett.* **2006**, *8*, 5905–5908. (d) Park, D. Y.; Gowrisankar, S.; Kim, J. N. *Tetrahedron Lett.* **2006**, *47*, 6641–6645. (e) Dai, M.; Sarlah, D.; Yu, M.; Danishefsky, S. J.; Jones, G. O.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 645–657. (f) Mamat, C.; Büttner, S.; Trabhardt, T.; Fischer, C.; Langer, P. *J. Org. Chem.* **2007**, *72*, 6273–6275. (g) Sher, M.; Ali, A.; Reinke, H.; Langer, P. *Tetrahedron Lett.* **2008**, *49*, 5400–5402. (h) Reim, S.; Adeel, M.; Hussain, I.; Yawer, M. A.; Ahmed, Z.; Villiger, A.; Langer, P. *Tetrahedron Lett.* **2008**, *49*, 4901–4904. (i) Reim, S.; Langer, P. *Tetrahedron Lett.* **2008**, *49*, 2329–2332. (j) Austin, W. F.; Zhang, Y.; Danheiser, R. L. *Tetrahedron* **2008**, *64*, 915–925. (k) Bunescu, A.; Reimann, S.; Lubbe, M.; Spannenberg, A.; Langer, P. *J. Org. Chem.* **2009**, *74*, 5002–5010. (l) Takahashi, H.; Yoshida, K.; Yanagisawa, A. *J. Org. Chem.* **2009**, *74*, 3632–3640.

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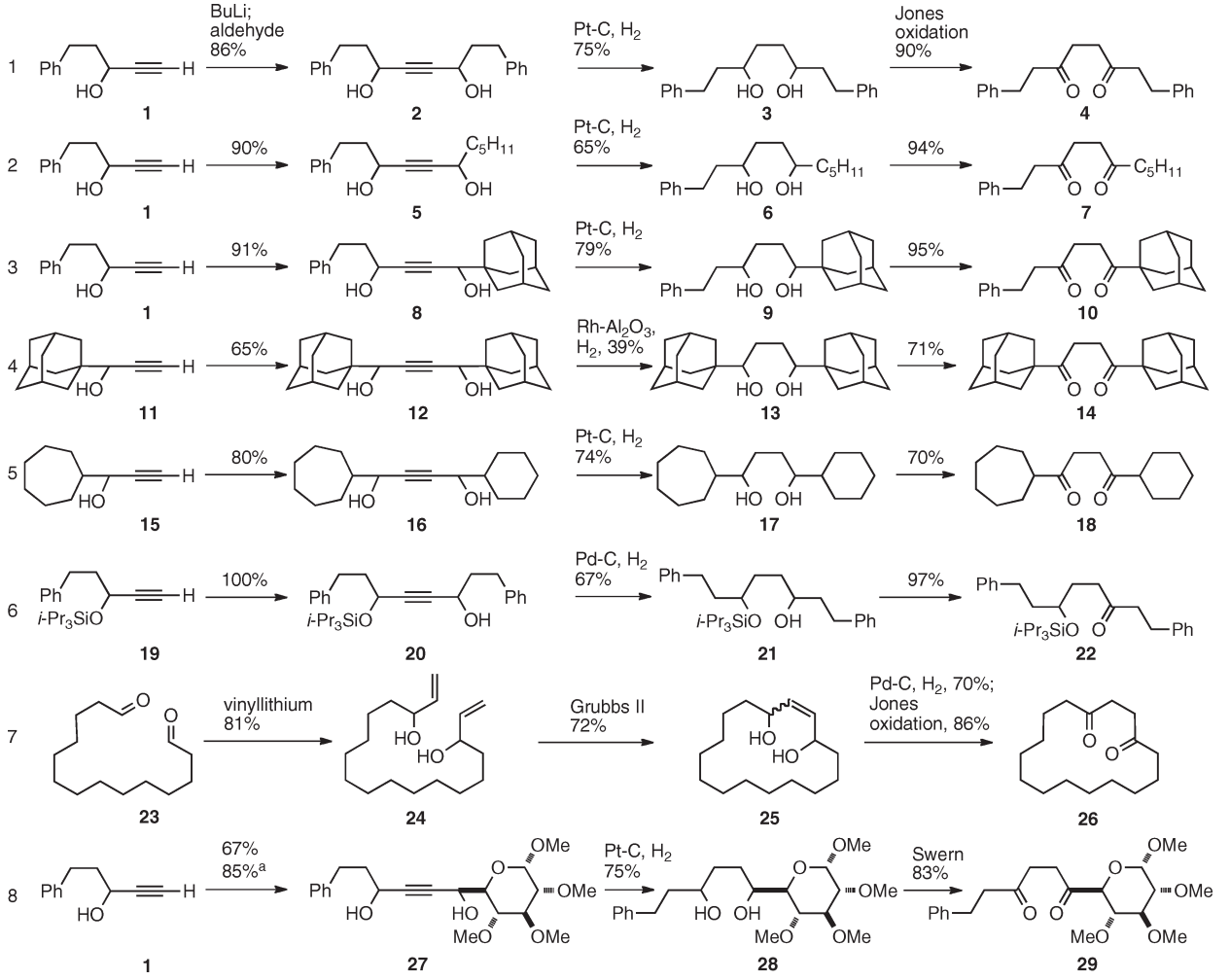
TABLE 1. Formation of Ketones

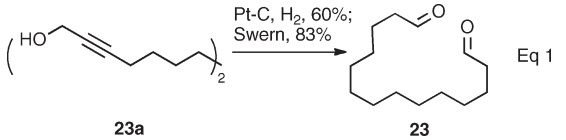


[a]Yield corrected for recovered **1**; methyl 2,3,4-tri-*O*-methyl-α-D-*gluco*-hexodialdo-1,5-pyranoside (1 equiv) and **1** (1.8 equiv) were used.

involve ring-closing metathesis.[4] The present approach differs from the others both in the manner of constructing the diene for the metathesis step and in the fact that the design specifically allows an aliphatic aldehyde to be converted into a benzene ring incorporating the original carbonyl carbon.

Results and Discussion

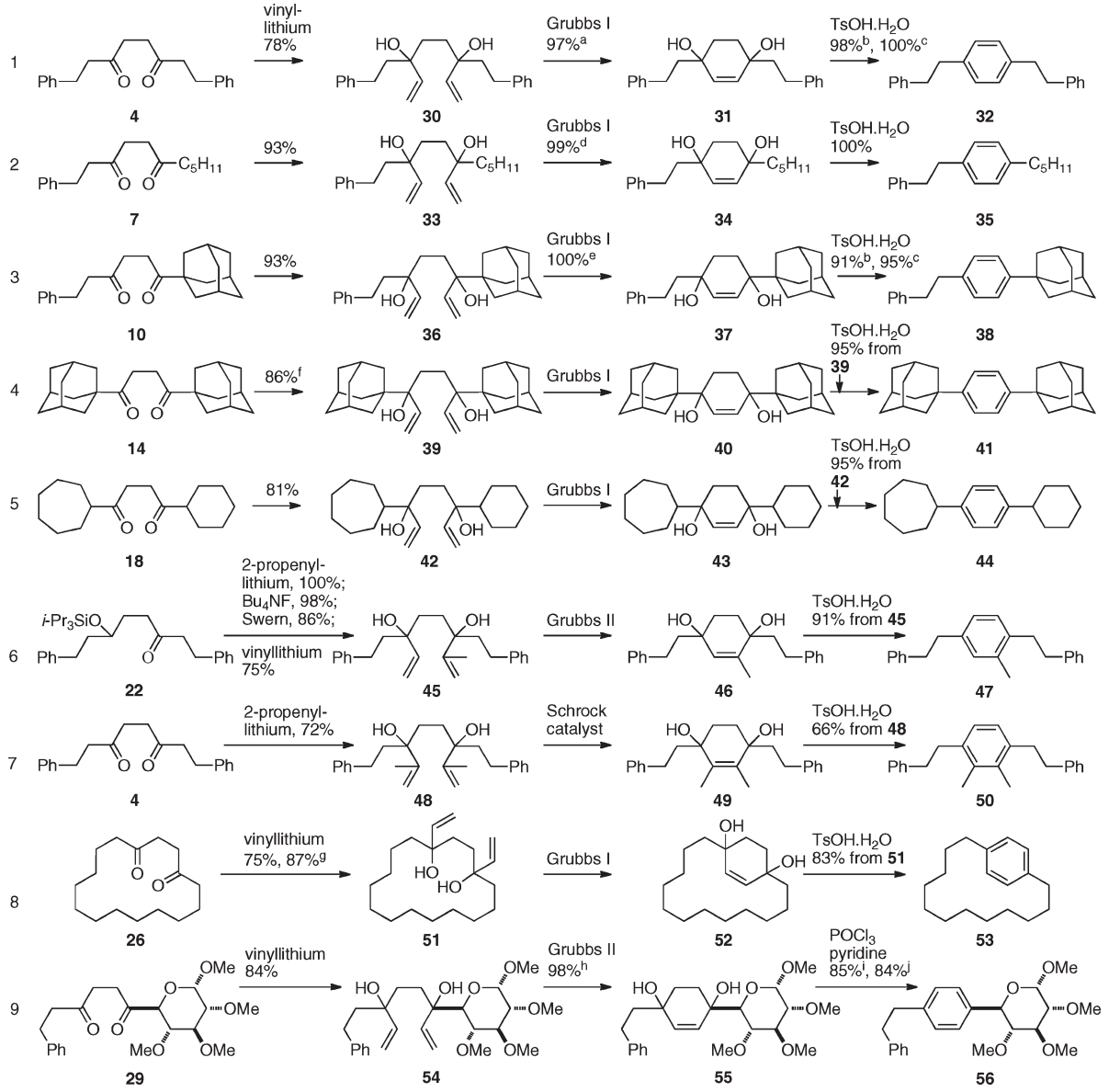
1,4-Diketones, the key intermediates for our approach, are available by a number of classical routes,[5] and we selected the use of acetylenes as representing a straightforward and versatile method that met our needs. To this end, various acetylenic alcohols (Table 1, column 1, entries 1−6, 8) were prepared by the standard process of acetylide addition to an aldehyde. We generally used trimethylsilylacetylene as a convenient acetylide synthon and then removed the silicon group with K_2CO_3 in MeOH. Small but conventional modifications of this route were applied to make acetylene **19** (entry 6). In this case, the initial adduct from dihydrocinnamaldehyde and lithium trimethylsilylacetylide was silylated with *i*-Pr_3SiCl, and after that step, removal of the Me_3Si group gave acetylene **19**. The overall sequence of entry 7 is also different from the others as it is based on an α,ω-dialdehyde that is converted into a 16-membered cyclic 1,4-diketone (**26**) by way of ring-closing metathesis under conditions of high dilution (**24** → **25**), followed by double bond hydrogenation and Jones oxidation (**25** → **26**). The starting α,ω-dialdehyde was assembled as shown in eq 1.[6]



Each of the acetylenes listed in Table 1, column 1, entries 1−6 and 8, was deprotonated and treated with an aldehyde, so as to generate the internal acetylenes shown in column 2. Hydrogenation over Pt−C or Pd−C served to saturate the triple bond, and the resulting diols for entries 1−5 were

(4) (a) Kotha, S.; Mandal, K. *Tetrahedron Lett.* **2004**, *45*, 2585–2588. (b) Yoshida, K.; Imamoto, T. *J. Am. Chem. Soc.* **2005**, *127*, 10470–10471. (c) Yoshida, K.; Kawagoe, F.; Iwadate, N.; Takahashi, H.; Imamoto, T. *Chem. Asian J.* **2006**, *1*, 611–613. (d) Yoshida, K.; Toyoshima, T.; Imamoto, T. *Chem. Commun.* **2007**, 3774–3776. (e) Yoshida, K.; Horiuchi, S.; Iwadate, N.; Kawagoe, F.; Imamoto, T. *Synlett* **2007**, 1561–1564. (f) Yoshida, K.; Shishikura, Y.; Takahashi, H.; Imamoto, T. *Org. Lett.* **2008**, *10*, 2777–2780. (g) Yoshida, K.; Takahashi, H.; Imamoto, T. *Chem.—Eur. J.* **2008**, *14*, 8246–8261.

TABLE 2. Formation of Substituted Benzenes



[a]Yield of less polar isomer 35%; yield of more polar isomer 62%. [b]Yield from more polar diol. [c]Yield from less polar diol. [d]Yield of less polar isomer 64%; yield of more polar isomer 35%. [e]Yield of less polar isomer 67%; yield of more polar isomer 33%. [f]Yield of less polar isomer 64%; yield of more polar isomer 22%. [g]Corrected for recovered starting material. [h]Yield of less polar isomer 29%; yield of more polar isomer 69%. [i]Yield from more polar isomer of **55**. [j]Yield from the less polar isomer of **55**.

oxidized to the corresponding 1,4-diketones with Jones reagent. Generally, Pt−C was used for the hydrogenation, but Pd−C was used for reduction of acetylenes **20**[7] and olefins **25**. Optimization of the triple bond reduction was made, using **2** as a test substrate, the conditions and yields with several catalysts being as follows: 10% w/w Pd−C/THF, 47%; 20% w/w $Pd(OH)_2$/MeOH, 21%; 5% w/w Rh−Al_2O_3/EtOAc, 62%; Wilkinson's catalyst/PhH, 55%; PtO_2/MeOH, 23%, and 5% w/w Pt−C, MeOH, 75%.

In the series of entry 6, the second acetylide coupling affords a monoprotected diol (**21**) after hyrogenation, so that oxidation gives a monoketone (**22**), which was processed as described below. The cyclic diketone **26** of entry 7 was prepared by ring-closing metathesis of **24**, mediated by Grubbs II catalyst[8] at high dilution; the resulting olefinic diol **25** was a mixture of stereoisomers, but this is of no consequence as

(5) For methods to prepare 1,4-diketones, see, for example: (a) Sudweeks, W. B.; Broadbent, H. S. *J. Org. Chem.* **1975**, *40*, 1131–1136. (b) Einhorn, J.; Soulier, J.-L.; Bacquet, C.; Lelandais, D. *Can. J. Chem.* **1983**, *61*, 584–587. (c) Piancatelli, G.; D'Auria, M.; D'Onofrio, F. *Synthesis* **1994**, 867–889. (d) Rio, G.; Lecas-Nawrocka, A. *Bull. Soc. Chim. France* **1976**, 317–326. (e) Nimgirawath, S.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.* **1976**, *29*, 339–356. (f) Miyakoshi, T. *Org. Prep. Proced. Int.* **1989**, *21*, 659–704. (g) Miyashita, M.; Yanami, T.; Yoshikoshi, A. *Org. Synth.* **1981**, *60*, 117–120.

(6) (a) Lemieux, R. U. U.S. Patent 2,725,392, 1955. (b) For a preparation of **23a**, see: Cao, X.; Yang, Y.; Wang, X. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2485–2489.

(7) For protection of a benzylic carbon—oxygen bond against hydrogenolysis by silylation, see: Clive, D. L. J.; Wang, J. *J. Org. Chem.* **2004**, *69*, 2773–2784.

(8) [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium.

the following steps of double bond hydrogenation and hydroxyl oxidation remove all centers of stereogenicity.

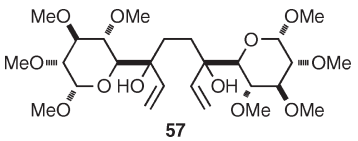
The ketones listed in Table 2 (column 1, entries 1−5, 8, and 9) were treated with an excess (8−16 mol per mol dione) of vinyllithium (made *in situ* from tetravinyltin/MeLi) to generate the expected 1,4-diols as isomer mixtures that were used without need for separation. Except for compound **54**, where we used the Grubbs II catalyst, ring-closing metathesis of these diols (Table 2, column 2, entries 1−5, 8, and 9) with the Grubbs I catalyst (loading 2−20 mol %) in CH_2Cl_2 at room temperature served to generate the required cyclohexene diols, again as isomer mixtures. In some cases (**31**, **34**, **37**) the isomers could be separated easily by flash chromatography, but this is not necessary, and the mixtures were usually carried forward by heating in PhH with $TsOH \cdot H_2O$ to generate the benzene ring. The amount of acid used was varied from 0.3 to 1.5 mol per mol diol to evaluate the robustness of the protocol. The conditions for the aromatization by double dehydration were optimized using **31** as a test substrate. The less polar and the more polar diols of structure **31** were individually treated with *p*-$TsOH \cdot H_2O$ in DMSO at 85 °C; with MsCl, Et_3N, in THF at 85 °C; with $POCl_3$, pyridine at room temperature; and with *p*-$TsOH \cdot H_2O$ (1 equiv) in refluxing PhH. The last set of conditions gave nearly quantitative yields for both isomers, whereas the other conditions never gave yields above 58%. Likewise the two individual isomers of **34** gave quantitative yields of **35** with *p*-$TsOH \cdot H_2O$ (1 equiv) in refluxing PhH. With the carbohydrate **55** our standard conditions led to an appreciable amount of an inseparable byproduct, but $POCl_3$ in ice-cold pyridine[9] was satisfactory. We noticed, in the preparation of **44**, that partial aromatization occurred in the ring-closing metathesis step.

In the sequence of Table 2, entry 6, two different vinyl units were introduced by first using 2-propenyllithium and then removing the silyl group (Bu_4NF), oxidizing the liberated hydroxyl (Jones oxidation), and treating the resulting ketone with vinyllithium. For the ring-closing metathesis in this series (**45** → **46**) we used the Grubbs II catalyst[8] (25 mol %), as prior literature suggested[10] it is more effective than the Grubbs I catalyst for construction of trisubstituted double bonds.

The example of Table 2, entry 7, illustrates formation of a tetrasubstituted double bond; consequently, after dehydration, a 1,2,3,4-tetrasubstituted benzene is produced. The metathesis step required the use of the Schrock catalyst[11] (two portions, each of 20 mol %) and a prolonged reaction time (2.5 days at 80 °C in PhH). Experiments with the Grubbs II and a Hoveda−Grubbs[12] catalyst did not work.

In most of the dehydration experiments, loss of water can in principle occur to give an endocyclic or an exocyclic double bond, and in the latter case, isomerization would afford the observed benzenoid. Using **34** as a test case, we performed the acid-mediated double dehydration with $TsOD \cdot D_2O$ and found that the disubstituted benzene produced contained some deuterium (mass spectrum), but the amount of incorporation must have been very small as the ^1H NMR spectrum of the final product failed to reveal incorporation of the isotope.

Our method for making *para*-disubstituted benzene can be used as a route to paracyclophanes, as illustrated by the preparation of [12]paracyclophane (**53**). In this connection, though, we noted a restriction on the size of the paracyclophane ring, as an attempt to make [8]paracyclophane was surprisingly thwarted at an early stage because ring closure of the appropriately olefinic alcohol (tetradeca-1,13-diene-3,12-diol) was unsuccessful, using Grubbs II catalyst (under high dilution). Similarly, we found that the diol **57** did not undergo ring-closing metathesis with Grubbs I, Grubbs II, or Schrock catalysts, and we do not know if this should be attributed to unfavorable steric or conformational factors or the presence of multiple coordination sites. In connection with the carbohydrate series (Table 2, entry 9), it should be mentioned that a number of carbohydrates bearing a C5-aryl unit have potentially important medicinal properties as examples are known that suggest use for control of diabetes[13] by inhibiting sodium-dependent glucose cotransporter 2[14] and thereby increasing urinary excretion of glucose. The present route offers an approach to the preparation of C5-aryl sugars starting from an intact sugar; conventional methods[15] usually involve early introduction of the aromatic unit followed by assembly of the pyranose ring (often by Diels−Alder reaction with a Danishefsky diene[15a−c]) or addition of a carbanion to a dialdehydofuranose, followed by ring expansion to the pyranose system.[16,17]



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Conclusion

Many methods are available for making 1,4-diketones, and the present route links those well-established procedures to the construction of substituted benzene rings. In particular, aldehydes (and their synthetic equivalents) are easily

(9) Dauben, W. G.; Boswell, G. A. *J. Am. Chem. Soc.* **1961**, *83*, 5003–5005.

(10) Cf. Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953–956.

(11) 6-Diisopropylphenylimidoneophylidene molybdenum(VI)bis(hexafluoro-*tert*-butoxide).

(12) Grela, K.; Harutyunyan, S.; Michrowska, A *Angew. Chem., Int. Ed.* **2002**, *41*, 4038–4040. We used the nitro variant (compound **9** in this reference).

(13) Goodwin, N. C.; Mabon, R.; Harrison, B. A.; Shadoan, M. K.; Almstead, Z. Y.; Xie, Y.; Healy, J.; Buhring, L. M.; DaCosta, C. M.; Bardenhagen, J.; Mseeh, F.; Liu, Q.; Amr Nouraldeen, A.; Wilson, A. G. E.; Kimball, S. D.; Powell, D. R.; Rawlins, D. B. *J. Med. Chem.* **2009**, *52*, 6201–6204.

(14) Jabbour, S. A.; Goldstein, B. J. *Int. J. Clin. Pract.* **2008**, *62*, 1279–1284.

(15) See, for example: (a) Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1986**, *108*, 7060–7067. (b) Berkowitz, D. B.; Danishefsky, S. J.; Schulte, G. K. *J. Am. Chem. Soc.* **1992**, *114*, 4518–4529. (c) Helliwell, M.; Phillips, I. M.; Pritchard, R. G.; Stoodley, R. J. *Tetrahedron Lett.* **1999**, *40*, 8651–8655. and references therein. (d) Hauser, F. M.; Ganguly, D. *J. Org. Chem.* **2000**, *65*, 1842–1849. (e) Cheng, G.; Fan, R.; Hernández-Torres, J. M.; Boulineau, F. P.; Wei, A. *Org. Lett.* **2007**, *9*, 4849–4852.

(16) (a) Harrison, B. A.; Kimball, S. D.; Mabon, R.; Rawlins, D. B. WO 2008/042688A2, 2008. (b) Goodwin, N.; Harrison, B. A.; Kimball, S. D.; Mabon, R.; Rawlins, D. B. WO 2008/109591A1, 2008. (c) Mincher, D. J.; Shaw, G. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1279–1282. (d) Inch, T. D.; Ley, R. V.; Rich, P. *J. Chem. Soc. C* **1968**, 1683–1692. (e) Bruns, R.; Wernicke, A.; Köll, P. *Tetrahedron* **1999**, *55*, 9793–9800. (f) Popsavin, V.; Benedeković, G.; Srećo, B.; Popsavin, M.; Francuz, J.; Kojić, V.; Bogdanović, G. *Org. Lett.* **2007**, *9*, 4235–4238. (g) Prakash, K. R. C.; Rao, S. P. *Synlett* **1993**, 123–124. (h) For a route via a dialdehydofuranose and a derived epoxide, see: Kilaas, L.; Anthonsen, T. *Acta Chem. Scand.* **1992**, *46*, 994–999.

(17) For a route via sugar-derived acetylenes, see: Kaliappan, K. P.; Subrahmanyam, A. V. *Org. Lett.* **2007**, *9*, 1121–1124.

converted into 1,4-diketones and so C-6 of hexoses can be incorporated into the benzene structure. Application of this approach to readily available carbohydrates may be useful in preparing medically important compounds such as inhibitors of sodium glucose cotransporter type 2 that are of interest for the treatment of diabetes.[13,14]

Experimental Section

5-Phenylpent-1-yn-3-ol (1)[18]**.** K_2CO_3 (1.459 g, 28.24 mmol) was added to a stirred and cooled (0 °C) solution of 5-phenyl-1-(trimethylsilyl)pent-1-yn-3-ol[18] (1.459 g, 6.276 mmol) in dry MeOH (60 mL). The ice bath was left in place but not recharged, and stirring was continued for 13 h. The mixture was evaporated, and the residue was partitioned between water and Et_2O. The aqueous phase was extracted with Et_2O, and the combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.8×21 cm), using 20% EtOAc−petroleum ether, gave **1** (0.9515 g, 94%) as an oil: FTIR (CH_2Cl_2, microscope) 3292, 3063, 3027, 2927, 2863, 2115, 1603, 1496 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.79−1.93 (br s, 1 H), 2.00−2.12 (m, 2 H), 2.50 (d, J = 2.2 Hz, 1 H), 2.82 (t, J = 7.9 Hz, 2 H), 4.38 (td, J = 12.5, 1.9 Hz, 1 H), 7.19−7.24 (m, 3 H), 7.28−7.33 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 31.2 (t), 39.1 (t), 61.6 (d), 73.3 (s), 84.6 (d), 126.1 (d), 128.47 (d), 128.48 (d), 141.1 (s); exact mass m/z calcd for $C_{11}H_{12}AgO$ (M + Ag) 266.9934, found 266.9933.

1,8-Diphenyloct-4-yne-3,6-diol (2)[19]**.** BuLi (2.5 M in hexane, 2.20 mL, 5.49 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **1** (0.4000 g, 2.497 mmol) in dry THF (20 mL). After 1.5 h, freshly distilled hydrocinnamaldehyde (0.43 mL, 3.25 mmol) was added dropwise. The cold bath was removed, and stirring was continued for 4 h. The mixture was cooled to 0 °C and quenched with hydrochloric acid (1.0 N, 20 mL). The organic solvent was evaporated, and the resulting aqueous mixture was extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (4 × 25 cm), using EtOAc−petroleum ether mixtures from 25% to 60% EtOAc, gave **2** (0.6376 g, 86%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR ($CHCl_3$, microscope) 3331, 3062, 3026, 2948, 2927, 2862, 1947, 1871, 1804, 1603, 1496 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.07−2.13 (m, 6 H), 2.81 (t, J = 7.9 Hz, 4 H), 4.42 (t, J = 6.8 Hz, 2 H), 7.18−7.24 (m, 6 H), 7.28−7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 31.41 (t), 31.42 (t), 39.1 (t), 61.7 (d), 86.08 (s), 86.09 (s), 126.1 (d), 128.47 (d), 128.50 (d), 141.1 (s); exact mass m/z calcd for $C_{20}H_{22}NaO_2$ (M + Na) 317.1509, found 317.1509.

1,8-Diphenyloctane-3,6-diol (3). Pt−C (5% w/w, ca. 5 mg) was added to a solution of **2** (0.0377 g, 0.128 mmol) in MeOH (5 mL), and the mixture was stirred under H_2 (doubled balloon) for 18 h and then filtered through Celite, using EtOAc as a rinse. Evaporation of the filtrate and flash chromatography of the residue over silica gel (0.7 × 16 cm), using EtOAc−petroleum ether mixtures from 20% to 50% EtOAc, gave **3** (0.0286 g, 75%) as an oil that slowly solidified: mp 83−88 °C; FTIR (CH_2Cl_2, microscope) 3323, 3243, 3022, 2937, 2913, 2861, 1942, 1495, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.50−1.61 (m, 2 H) 1.61−1.74 (m, 2 H), 1.75−1.84 (m, 4 H), 2.15−2.60 (br s, 2 H), 2.63−2.73 (m, 2 H), 2.74−2.84 (m, 2 H), 3.62−3.72 (m, 2 H), 7.17−7.23 (m, 6 H), 7.26−7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.1 (t), 33.3 (t), 34.1 (t), 39.1 (t), 71.3 (d), 71.6 (d), 125.8 (d), 128.39 (d), 128.41 (d), 142.0 (s) (two signals not observed due to overlap); exact mass m/z calcd for $C_{20}H_{26}NaO_2$ (M + Na) 321.1825, found 321.1821.

1,8-Diphenyloctane-3,6-dione (4). Jones reagent[20] (7.0 M in acetone, 0.54 mL, 3.8 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **3** (0.1620 g, 0.5428 mmol) in acetone (15 mL). After 30 min, the orange mixture was quenched with MeOH (15 mL), and stirring was continued for 30 min, by which time the mixture had become dark green. The mixture was diluted with EtOAc (30 mL), washed with water and brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (1.4 × 16 cm), using EtOAc−petroleum ether mixtures from 10% to 15% EtOAc, gave **4** (0.1448 g, 90%) as an oil: FTIR (CH_2Cl_2, cast microscope) 3062, 3027, 2925, 1711, 1603, 1496 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.68 (s, 4 H), 2.81 (apparent t, J = 7.7 Hz, 4 H), 2.91 (t, J = 7.2 Hz, 4 H), 7.17−7.22 (m, 6 H), 7.27−7.31 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.8 (t), 36.2 (t), 44.3 (t), 126.1 (d), 128.3 (d), 128.5 (d), 141.0 (s), 208.4 (s); exact mass m/z calcd for $C_{20}H_{22}O_2$ 295.1693, found 295.1696.

1-Phenylundec-4-yne-3,6-diol (5). BuLi (2.5 M in hexane, 0.87 mL, 2.2 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **1** (0.1576 g, 0.9837 mmol) in dry THF (12 mL). After 0.5 h, freshly distilled *n*-hexanal (0.23 mL, 2.0 mmol) was added dropwise. The cold bath was removed, and stirring was continued for 36 h. The mixture was cooled to 0 °C and quenched with hydrochloric acid (1.0 N, 15 mL). The organic solvent was evaporated, and the resulting aqueous mixture was extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.8 × 21 cm), using EtOAc−petroleum ether mixtures from 20% to 40% EtOAc, gave **5** (0.2321 g, 90%) as an oil: FTIR (CH_2Cl_2, cast microscope) 3322, 3027, 2953, 2931, 2860, 1943, 1873, 1803, 1745, 1604, 1496, 1455 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, J = 7.0 Hz, 3 H), 1.29−1.38 (m, 4 H), 1.41−1.51 (m, 2 H), 1.63−1.78 (m, 2 H), 1.95−2.11 (m, 2 H), 2.12−2.22 (br s, 1 H), 2.22−2.36 (br s, 1 H), 2.79 (t, J = 7.8 Hz, 2 H), 4.41 (t, J = 6.1 Hz, 2 H), 7.17−7.23 (m, 3 H), 7.27−7.32 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0 (q), 22.6 (t), 24.9 (t), 31.39 (t), 31.43 (t), 37.7 (t), 39.1 (t), 61.7 (d), 62.5 (d), 85.6 (s), 86.4 (s), 126.0 (d), 128.4 (d), 128.5 (d), 141.2 (s); exact mass m/z calcd for $C_{17}H_{24}NaO_2$ (M+Na) 283.1669, found 283.1670.

1-Phenylundecane-3,6-diol (6). Pt−C (5% w/w, ca. 3 mg) was added to a solution of **5** (0.0274 g, 0.1052 mmol) in MeOH (5 mL), and the mixture was stirred under H_2 (doubled balloon) for 1 h and then filtered through Celite, using EtOAc as a rinse. Evaporation of the filtrate and flash chromatography of the residue over silica gel (0.7 × 16 cm), using EtOAc−petroleum ether mixtures from 20% to 50% EtOAc, gave **6** (0.0182 g, 65%) as a solid that was a mixture of diastereoisomers (^{13}C NMR): mp 56−62 °C; FTIR (CH_2Cl_2, cast microscope) 3215, 3086, 3063, 3027, 2955, 2937, 2920, 2871, 2854, 1942, 1496, 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.90 (t, J = 6.7 Hz, 3 H), 1.24−1.38 (m, 6 H), 1.38−1.60 (m, 4 H), 1.63−1.74 (m, 2 H), 1.77−1.83 (m, 2 H), 1.85−2.27 (br s, 2 H), 2.69 (apparent dt, J = 13.9, 8.1 Hz, 1 H), 2.80 (dt, J = 14.2, 7.5 Hz, 1 H), 3.59−3.73 (m, 2 H), 7.17−7.24 (3 H), 7.27−7.32 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0 (q), 22.6 (t), 25.38 (t), 25.39 (t), 31.9 (t), 32.2 (t), 33.2 (t), 33.5 (t), 33.9 (t), 34.2 (t), 37.5 (t), 37.8 (t), 39.1 (t), 39.4 (t), 71.3 (d), 71.6 (d), 72.0 (d), 72.3 (d), 125.8 (d), 128.4 (d), 129.2 (d), 142.1 (s); exact mass m/z calcd for $C_{17}H_{28}NaO_2$ 287.1982, found 287.1985.

1-Phenylundecane-3,6-dione (7). Jones reagent[20] (7.0 M in acetone, 0.07 mL, 0.46 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **6** (0.0175 g, 0.0662 mmol) in

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acetone (5 mL). After 10 min, the orange mixture was quenched with MeOH (5 mL), and stirring was continued for 30 min, by which time the mixture had become dark green. The mixture was diluted with EtOAc (20 mL), washed with water and brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (0.7 × 16 cm), using EtOAc−petroleum ether mixtures from 15% to 25% EtOAc, gave **7** (0.0162 g, 94%) as an oil: FTIR (CH_2Cl_2, cast microscope) 3028, 2956, 2931, 2872, 1712, 1604, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.90 (t, J = 7.0 Hz, 3 H), 1.23−1.37 (m, 4 H), 1.59 (quintet, J = 7.6 Hz, 2 H), 2.45 (t, J = 7.4 Hz, 2 H), 2.64−2.71 (m, 4 H), 2.80 (apparent t, J = 7.9 Hz, 2 H), 2.91 (t, J = 8.0 Hz, 2 H), 7.17−7.21 (m, 3 H), 7.26−7.30 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.9 (q), 22.4 (t), 23.5 (t), 23.5 (t), 29.7 (t), 31.4 (t), 36.0 (t), 36.2 (t), 42.8 (t), 44.3 (t), 126.1 (d), 128.3 (d), 128.5 (d), 141.0 (s), 208.5 (s), 209.7 (s); exact mass m/z calcd for $C_{17}H_{24}NaO_2$ (M + Na) 283.1669, found 283.1671.

1-(1-Adamantyl)-6-phenylhex-2-yne-1,4-diol (8). BuLi (2.5 M in hexane, 0.26 mL, 0.65 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **1** (0.0472 g, 0.295 mmol) in dry THF (10 mL). After 1.5 h, 1-adamantanecarboxaldehyde (0.0414 g, 0.252 mmol) in THF (2 mL plus 2 mL as a rinse) was added dropwise, producing an orange solution. The cold bath was left in place but not recharged, and stirring was continued for 18.5 h. The mixture was cooled to 0 °C and quenched with hydrochloric acid (1.0 N, 6 mL). The organic solvent was evaporated, water (10 mL) was added, and the mixture was extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.4 × 15 cm), using EtOAc−petroleum ether mixtures from 20% to 40% EtOAc, gave **8** (0.0743 g, 91%) as a semisolid mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast microscope) 3350, 3026, 2905, 2848, 1722, 1604, 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.58−1.77 (m, 12 H), 1.99−2.11 (m, 5 H), 2.11−2.72 (br s, 2 H), 2.82 (t, J = 7.8 Hz, 2 H), 3.93 (dd, J = 5.9, 1.4 Hz, 1 H), 4.42−4.47 (m, 1 H), 7.19−7.25 (m, 3 H), 7.28−7.32 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.2 (d), 31.53 (s), 31.54 (s), 37.1 (t), 37.3 (t), 37.4 (t), 37.8 (t), 39.37 (t), 39.39 (t), 61.8 (d), 71.52 (d), 71.53 (d), 84.25 (s), 84.27 (s), 87.15 (s), 87.17 (s), 126.0 (d), 128.46 (d), 128.50 (d), 141.295 (s), 141.303 (s); exact mass m/z calcd for $C_{22}H_{28}NaO_2$ (M + Na) 347.1982, found 347.1981.

1-(1-Adamantyl)-6-phenylhexane-1,4-diol (9). Rh−Al_2O3 (5% w/w, ca. 8 mg) was added to a solution of **8** (0.023 g, 0.071 mmol) in MeOH (3 mL) and the mixture was stirred under H_2 (thick-walled balloon) for 24 h. At this point there appeared to have been no reaction (TLC, ^1H NMR) and so the mixture was filtered through Celite, using EtOAc as a rinse. The solvent was evaporated, and the residue was kept under oil pump vacuum. Pt−C (20% w/w, ca. 6.5 mg) was added to a solution of the recovered **8** in MeOH (3 mL) and the mixture was stirred under H_2 (balloon). After 30 min the mixture was filtered through Celite, using EtOAc as a rinse. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.4 × 15 cm), using EtOAc−petroleum ether mixtures from 20% to 40% EtOAc, gave **9** (0.0184 g, 79%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast) 3351, 3026, 2905, 2849, 2677, 1743, 1603, 1452 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25−1.42 (m, 2 H), 1.48−1.83 (m, 16 H), 2.00 (apparent s, 3 H), 2.00−2.42 (br s, 2 H), 2.64−2.74 (m, 1 H), 2.76−2.85 (m, 1 H), 3.04 (apparent d, J = 9 Hz, 1 H), 3.61−3.75 (m, 1 H), 7.16−7.23 (m, 3 H), 7.26−7.31 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7 (t), 26.8 (t), 28.3 (d), 32.17 (s), 32.19 (s), 35.0 (t), 35.4 (t), 37.2 (t), 37.93 (t), 37.96 (t), 39.1 (t), 39.6 (t), 71.1 (d), 71.8 (d), 80.4 (d), 80.7 (d), 125.75 (d), 125.77 (d), 128.37 (d), 128.41 (d), 142.20 (s), 142.23 (s); exact mass m/z calcd for $C_{22}H_{32}NaO_2$ (M + Na) 351.2295, found 351.2297.

1-(1-Adamantyl)-6-phenylhexane-1,4-dione (10). Jones reagent[20] (7.0 M in acetone, 0.052 mL, 0.362 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **9** (0.0170 g, 0.0518 mmol) in acetone (3 mL). After 20 min, the orange mixture was quenched with MeOH (3 mL), and stirring was continued for 30 min, by which time the mixture had become dark green. The mixture was diluted with EtOAc (20 mL), washed with water and brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (0.7 × 15 cm), using 10% EtOAc−petroleum ether, gave **10** (0.0161 g, 95%) as an oil: FTIR (CH_2Cl_2, cast) 3027, 2905, 2851, 1716, 1698, 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.68−1.79 (m, 6 H), 1.85 (d, J = 2.7 Hz, 6 H), 2.05 (apparent s, 3 H), 2.64 (apparent t, J = 6.5 Hz, 2 H), 2.75 (apparent t, J = 6.1 Hz, 2 H), 2.82 (apparent t, J = 7.9 Hz, 2 H), 2.91 (apparent t, J = 7.1 Hz, 2 H), 7.17−7.21 (m, 3 H), 7.26−7.30 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.0 (d), 29.7 (t), 30.1 (t), 36.1 (t), 36.6 (t), 38.4 (s), 44.4 (t) 46.2 (t), 126.0 (d), 128.3 (d), 128.5 (d), 141.1 (s); exact mass m/z calcd for $C_{22}H_{28}NaO_2$ (M + Na) 347.1982, found 347.1988.

1-(1-Adamantyl)prop-2-yn-1-ol (11). (a) 1-(1-Adamantyl)-3-(trimethylsilyl)prop-2-yn-1-ol (11a)[21]. BuLi (2.5 M in hexane, 0.32 mL, 0.81 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of trimethylsilylacetylene (0.12 mL, 0.81 mmol) in dry THF (8 mL). After 55 min, 1-adamantanecarboxaldehyde (0.1332 g, 0.8110 mmol) in THF (1.5 mL plus 1.5 mL as a rinse) was added dropwise by cannula. The cold bath was removed and, after 2.5 h, the mixture was recooled to 0 °C, quenched with saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.8 × 20 cm), using EtOAc−petroleum ether mixtures from 5% to 15% EtOAc, gave **11a** (0.1888 g, 88%) as an oil: FTIR (CH_2Cl_2, cast) 3390, 3309, 2906, 2849, 2676, 2658, 2170, 1718, 1452 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.98 (s, 9 H), 1.55−1.75 (m, 12 H), 1.76 (s, 1 H), 1.98−2.04 (br m, 3 H), 3.83 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.03 (q), 28.2 (d), 36.7 (s), 37.1 (t), 37.7 (t), 71.9 (d), 90.7 (s), 104.9 (s); exact mass m/z calcd for $C_{16}H_{26}NaOSi$ (M + Na) 285.1645, found 285.1648.

(b) 1-(1-Adamantyl)prop-2-yn-1-ol (11)[21]. K_2CO_3 (0.5528 g, 4.000 mmol) was added to a stirred and cooled (0 °C) solution of **11a** (0.1765 g, 0.6725 mmol) in dry MeOH (8 mL). The ice bath was left in place but not recharged, and stirring was continued for 18 h. The mixture was evaporated, and the residue was partitioned between water and Et_2O. The aqueous phase was extracted with Et_2O, and the combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.6 × 16 cm), using 10% EtOAc−petroleum ether, gave **11** (0.1167 g, 91%) as an oil: FTIR (CH_2Cl_2, cast microscope) 3278, 2902, 2848, 2674, 2656, 2111, 1449 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.56−1.76 (m, 12 H), 1.83 (s, 1 H), 1.98−2.04 (m, 3 H), 2.46 (d, J = 2.2 Hz, 1 H), 3.87 (d, J = 2.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.2 (d), 37.0 (t), 37.6 (t), 71.4 (d), 74.2 (d), 82.9 (s); the molecular ion could not be detected and a satisfactory mass spectrum could not be obtained.

1,4-Bis(1-adamantyl)but-2-yne-1,4-diol (12). BuLi (2.5 M in hexane, 0.48 mL, 1.2 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **11** (0.1071 g, 0.5401 mmol) in dry THF (10 mL). After 1 h, 1-adamantanecarboxaldehyde (0.0895 g, 0.5449 mmol) in THF (2 mL plus 2 mL as a rinse) was added dropwise. The cold bath was removed, and stirring was continued for 18 h. The mixture was cooled to 0 °C and quenched with hydrochloric acid (1.0 N, 10 mL). The organic solvent was evaporated, and the resulting aqueous mixture was extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica

(21) Cf. Bach, J.; Berenguer, R.; Garcia, J.; Loscertales, T.; Vilarrasa, J. *J. Org. Chem.* **1996**, *61*, 9021–9025.

gel (4 × 25 cm), using EtOAc−petroleum ether mixtures from 5% to 40% EtOAc, gave **12** (0.1258 g, 65%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast microscope) 3285, 2899, 2846, 2679, 2657, 1742, 1451 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.60−1.68 (m, 14 H), 1.68−1.77 (m, 12 H), 2.05 (s, 6 H), 3.93 (s, 1 H), 3.94 (s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.2 (d), 37.1 (t), 37.4 (s), 37.5 (s), 37.81 (t), 37.83 (t), 71.6 (d), 71.7 (d), 85.2 (s), 85.3 (s); exact mass m/z calcd for $C_{24}H_{34}NaO_2$ (M + Na) 377.2451, found 377.2454.

1,4-Bis(1-adamantyl)butane-1,4-diol (13). Rh−Al_2O_3 (5% w/w, 0.0100 g) was added to a solution of **12** (0.0571 g, 0.161 mmol) in MeOH (5 mL) and the mixture was stirred under H_2 (doubled balloon) for 19 h and then filtered through Celite, using EtOAc as a rinse. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.4 × 15 cm), using EtOAc−petroleum ether mixtures from 5% to 20% EtOAc, gave **13** (0.0106 g, 18%) and recovered starting material **12** (18.4 mg, 0.052 mmol). Rh−Al_2O_3 (5% w/w, 0.0050 g) was added to a solution of the recovered starting material in MeOH (3 mL) and the mixture was stirred under H_2 (balloon). After 14 h, more Rh−Al_2O_3 (5% w/w, ca. 5 mg) was added and stirring under H_2 (doubled balloon) was continued for 7 h. The mixture was filtered through Celite using EtOAc as a rinse. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.4 × 16 cm), using EtOAc−petroleum ether mixtures from 5% to 20% EtOAc, gave **13** (0.0120 g, 21%), providing a combined yield of 39%. The product was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, microscope) 3376, 2901, 2848, 2657, 1638, 1449 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36−1.48 (m, 2 H), 1.48−1.86 (m, 28 H), 2.00 (apparent s, 6 H), 3.03 (d, J = 10.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.5 (t), 27.6 (t), 28.3 (d), 36.7 (s), 36.8 (s), 37.3 (t), 37.99 (t), 38.03 (t), 80.4 (d), 80.6 (d); exact mass m/z calcd for $C_{24}H_{38}NaO_2$ (M + Na) 381.2764, found 381.2758.

1,4-Bis(1-adamantyl)butane-1,4-dione (14)[22]**.** Jones reagent[20] (7.0 M in acetone, 0.024 mL, 0.167 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **13** (0.0200 g, 0.0558 mmol) in acetone (4 mL). After 45 min, the orange mixture was quenched with MeOH (1 mL), and stirring was continued for 30 min, by which time the mixture had become dark green. The mixture was diluted with EtOAc (20 mL), washed with water and brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (1.4 × 16 cm), using EtOAc−petroleum ether mixtures from 2% to 10% EtOAc, gave **14** (0.0142 g, 71%) as an oil: FTIR (CH_2Cl_2, cast microscope) 2905, 2850, 2678, 2658, 1699, 1452 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.66−1.78 (m, 12 H), 1.85 (apparent d, J = 2.8 Hz, 12 H), 2.02−2.08 (m, 6 H), 2.71 (s, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0 (d), 29.9 (t), 36.6 (t), 38.4 (t), 46.2 (s), 214.5 (s); exact mass m/z calcd for $C_{24}H_{34}NaO_2$ (M + Na) 377.2451, found 377.2452.

1-Cycloheptylprop-2-yn-1-ol (15). (a) 1-Cycloheptyl-3-(trimethylsilyl)prop-2-yn-1-ol (15a). BuLi (2.5 M in hexane, 0.124 mL, 0.309 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of trimethylsilylacetylene (0.044 mL, 0.309 mmol) in dry THF (3 mL). After 90 min, cycloheptanecarboxaldehyde (0.039 g, 0.309 mmol) in THF (1 mL plus 1 mL as a rinse) was added dropwise. The dry ice bath was replaced by an ice bath and, after 45 min, the ice bath was removed, and stirring was continued for 14 h. The mixture was quenched with a mixture of water (5 mL) and saturated aqueous NH_4Cl (5 mL) and extracted with Et_2O. The combined organic extracts were washed with brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (1.4 × 15 cm), using EtOAc−petroleum ether mixtures from 5% to 15% EtOAc, gave **15a** (0.0569 g, 82%) as an oil: FTIR (CH_2Cl_2, microscope) 3344, 2924, 2855, 2172, 1460 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.95 (s, 9 H), 1.31−1.64 (m, 7 H), 1.68−1.79 (m, 3 H), 1.79−1.90 (m, 3 H), 2.18 (s, 1 H), 4.20 (d, J = 5.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ −0.1 (q), 26.6 (t), 26.7 (t), 28.39 (t), 28.42 (t), 29.5 (t), 45.5 (d), 67.9 (d), 89.9 (s), 106.1 (s); exact mass m/z calcd for $C_{13}H_{24}NaOSi$ (M + Na) 247.1489, found 247.1488.

(b) 1-Cycloheptylprop-2-yn-1-ol (15). K_2CO_3 (0.2697 g, 1.952 mmol) was added to a stirred and cooled (0 °C) solution of **15a** (0.0365 g, 0.1626 mmol) in dry MeOH (5 mL). The ice bath we left in place but not recharged, and stirring was continued for 13 h. The mixture was evaporated, and the residue was partitioned between water and Et_2O. The aqueous phase was extracted with Et_2O, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.7 × 7 cm), using 20% EtOAc−petroleum ether, gave **15** (0.0226 g, 91%) as an oil: FTIR (CH_2Cl_2, microscope) 3308, 2923, 2856, 2688, 2114, 1461 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30−1.65 (m, 8 H), 1.65−1.95 (m, 6 H), 2.43 (apparent d, J = 2.2 Hz, 1 H), 4.22 (dd, J = 5.4, 2.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.66 (t), 26.71 (t), 28.24 (t), 28.29 (t), 29.4 (t), 29.8 (t), 45.4 (d), 67.4 (d), 73.3 (d), 84.2 (s); exact mass m/z calcd for $C_{10}H_{16}O$ 152.1201, found 152.1203.

1-Cycloheptyl-4-cyclohexylbut-2-yne-1,4-diol (16). BuLi (2.5 M in hexane, 0.527 mL, 1.32 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **15** (0.080 g, 0.527 mmol) in dry THF (10 mL). After 1 h, cyclohexanecarboxaldehyde (0.096 mL, 0.79 mmol) in THF (2 mL plus 2 mL as a rinse) was added dropwise by cannula. Stirring at −78 °C was continued for 45 min. The cold bath was left in place but not recharged, and stirring was continued for 10.5 h. The mixture was cooled to 0 °C and quenched with hydrochloric acid (1.0 N, 10 mL). The organic solvents were evaporated, water (10 mL) was added, and the mixture was extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.4 × 19 cm), using EtOAc−petroleum ether mixtures from 5% to 40% EtOAc, gave **16** (0.1120 g, 80%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, microscope) 3327, 2924, 2853, 2673, 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.01−1.31 (m, 6 H), 1.31−1.64 (m, 8 H), 1.65−1.92 (m, 12 H), 4.20 (apparent t, J = 5.0 Hz, 1 H), 4.27 (apparent br s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.8 (t), 25.9 (t), 26.4 (t), 26.70 (t), 26.74 (t), 28.0 (t), 28.1 (t), 28.28 (t), 28.33 (t), 28.34 (t), 29.5 (t), 29.97 (t), 30.00 (t), 67.2 (t), 67.5 (t), 85.29 (s), 85.31 (s), 85.91 (s), 85.94 (s); exact mass m/z calcd for $C_{17}H_{28}NaO_2$ (M + Na) 287.1982, found 287.1982.

1-Cycloheptyl-4-cyclohexylbutane-1,4-diol (17). Pt−C (10% w/w, ca. 0.020 g) was added to a solution of **16** (0.102 g, 0.384 mmol) in MeOH (6 mL), and the mixture was stirred under H_2 (thick-walled balloon) for 12 h and then filtered through Celite, using EtOAc as a rinse. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.4 × 20 cm), using EtOAc−petroleum ether mixtures from 5% to 40% EtOAc, gave **17** (0.0761 g, 74%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, microscope) 3299, 2920, 2852, 2696, 1460, 1448 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.96−1.40 (m, 8 H), 1.40−1.63 (m, 10 H), 1.63−1.88 (m, 10 H), 2.35 (s, 2 H), 3.43−3.14 (m, 1 H), 3.45−3.58 (m, 1 H); ^{13}C NMR (acetone-d_6, 125 MHz) δ 26.97 (t), 26.99 (t), 27.1 (t), 27.3 (t), 27.67 (t), 27.69 (t), 27.97 (t), 28.00 (t), 28.70 (t), 28.72 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.6 (t), 29.7 (t), 29.8 (t), 29.9 (t), 30.0 (t), 30.2 (t), 31.15 (t), 31.20 (t), 31.9 (t), 32.0 (t), 44.7 (d), 44.9 (d), 46.2 (d), 46.3 (d), 76.0 (d), 76.1 (d), 76.7 (d), 76.8 (d); exact mass m/z calcd for $C_{17}H_{32}NaO_2$ (M + Na) 291.2295, found 291.2294.

1-Cycloheptyl-4-cyclohexylbutane-1,4-dione (18). Jones reagent[20] (7.0 M in acetone, 0.17 mL, 1.2 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **17** (0.0346 g, 0.129 mmol) in acetone (10 mL). After 1.5 h, an additional portion of Jones reagent (7.0 M in acetone, 0.10 mL, 0.70 mmol) was added, and after a further 5 min, the mixture was quenched with MeOH (15 mL). Stirring was continued for 30 min, by which

(22) Maas, G.; Fronda, A. *J. Organomet. Chem.* **1990**, *398*, 229–239.

time the mixture had become dark green. The mixture was diluted with EtOAc (25 mL), washed with water and brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (0.7 × 16 cm), using EtOAc−petroleum ether mixtures from 5% to 15% EtOAc, gave **18** (0.0239 g, 70%) as an oil: FTIR (CH_2Cl_2, microscope) 2928, 2855, 2668, 1707, 1450 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.10−1.43 (m, 6 H), 1.43−1.65 (m, 6 H), 1.65−1.83 (m, 6 H), 1.83−1.94 (m, 4 H), 2.32−2.44 (m, 1 H), 2.52−2.62 (m, 1 H), 2.66−2.75 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.7 (t), 25.9 (t), 26.7 (t), 28.3 (t), 28.5 (t), 30.0 (t), 34.1 (t), 34.2 (t), 50.8 (d), 52.4 (d), 212.8 (s), 213.1 (s); exact mass m/z calcd for $C_{17}H_{28}O_2$ 264.2089, found 264.2090.

Tris(1-methylethyl)[(5-phenylpent-1-yn-3-yl)oxy]silane (19). NaH (0.4543 g, 18.93 mmol) was added quickly to a stirred and cooled (0 °C) solution of **1a** (1.466 g, 6.310 mmol) in dry THF (50 mL). After 15 min, *i*-Pr_3SiCl (4.05 mL, 18.9 mmol) was added dropwise. The cold bath was left in place but not recharged, and stirring was continued for 12 h. The mixture was cooled to 0 °C and quenched with saturated aqueous NH_4Cl (40 mL). The aqueous phase was extracted with Et_2O, and the combined organic extracts were dried (Na_2SO_4) and evaporated. The residue (**19a**) was kept under oil pump vacuum for several hours. Oven-dried K_2CO_3 (2.617 g, 18.94 mmol) was added to a stirred and cooled (0 °C) solution of crude **19a** in dry MeOH (38 mL). The cooling bath was left in place but not recharged, and stirring was continued for 17 h. The mixture was evaporated, and the residue was partitioned between Et_2O and water. The aqueous phase was extracted with Et_2O, and the combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (5 × 22 cm), using EtOAc−petroleum mixtures from 1% to 5% EtOAc, gave **19** (1.927 g, 96% over two steps) as an oil: FTIR (CH_2Cl_2, cast microscope) 3309, 3028, 2944, 2891, 2867, 1463, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.06−1.18 (m, 21 H), 1.97−2.09 (m, 2 H), 2.44 (d, J = 2.1 Hz, 1 H), 2.76−2.89 (m, 2 H), 4.50 (ddd, J = 6.7, 5.6, 2.1 Hz, 1 H), 7.17−7.23 (m, 3 H), 7.27−7.31 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.2 (d), 18.0 (q), 31.1 (t), 40.5 (t), 62.3 (d), 72.5 (d), 85.3 (d), 125.8 (d), 128.4 (d), 128.5 (d), 141.8 (s); exact mass m/z calcd for $C_{20}H_{32}NaOSi$ (M + Na) 339.2115, found 339.2118.

6-[[Tris(1-methylethyl)silyl]oxy]-1,8-diphenyloct-4-yn-3-ol (20). BuLi (2.5 M in hexane, 1.67 mL, 4.17 mmol) was added dropwise over 3 min to a stirred and cooled (−78 °C) solution of **19** (1.0153 g, 3.207 mmol) in dry THF (50 mL). After 35 min, freshly distilled hydrocinnamaldehyde (0.68 mL, 5.1 mmol) was added dropwise over 3 min. The cold bath was left in place but not recharged, and stirring was continued for 7.5 h. The mixture was cooled to 0 °C and quenched with hydrochloric acid (1.0 N, 50 mL). The organic solvent was evaporated, and the resulting aqueous phase was extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (4×22 cm), using EtOAc−petroleum ether mixtures from 10% to 50% EtOAc, gave **20** (1.4457 g, 100%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast film) 3361, 3063, 3027, 2944, 2866, 1604, 1496, 1455 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.07−1.19 (m, 21 H), 1.64−1.72 (br s, 1 H), 1.98−2.11 (m, 4 H), 2.78−2.89 (m, 4 H), 4.42 (t, J = 6.3 Hz, 1 H), 4.58 (td, J = 5.8, 1.6 Hz, 1 H), 7.18−7.24 (m, 6 H), 7.28−7.33 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.3 (d), 18.1 (q), 31.27 (t), 31.29 (t), 31.39 (t), 31.41 (t), 39.18 (t), 39.23 (t), 40.46 (t), 40.49 (t), 61.9 (d), 62.5 (d), 85.06 (s), 85.08 (s), 86.86 (s), 86.88 (s), 125.8 (d), 126.0 (d), 128.4 (d), 128.45 (d), 128.47 (d), 128.48 (d), 141.3 (s), 141.8 (s); exact mass m/z calcd for $C_{29}H_{42}NaO_2Si$ (M + Na) 473.2846, found 473.2846.

6-[[Tris(1-methylethyl)silyl]oxy]-1,8-diphenyloctan-3-ol (21). Pd−C (5% w/w, ca. 20 mg) was added to a solution of **20** (0.1035 g, 0.2296 mmol) in EtOAc (4 mL), and the mixture was stirred under H_2 (thick-walled balloon) for 14 h and then filtered through Celite, using EtOAc as a rinse. Evaporation of the solvent and flash chromatography of the residue over silica gel (1.4×17 cm), using EtOAc−petroleum ether mixtures from 5% to 20% EtOAc, gave **21** (0.0704 g, 67%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, neat film microscope) 3370, 3086, 3063, 3027, 2943, 2891, 2866, 1941, 1869, 1801, 1604, 1496 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.06−1.08 (m, 21 H), 1.47−1.98 (m, 8 H), 2.21−2.50 (br s, 1 H), 2.55−2.73 (m, 3 H), 2.77−2.84 (m, 1 H), 3.57−3.67 (m, 1 H), 3.90−3.97 (m, 1 H), 7.16−7.23 (m, 6 H), 7.26−7.31 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.6 (d), 12.7 (d), 18.18 (q), 18.19 (q), 18.22 (q), 31.45 (t), 31.50 (t), 31.9 (t), 32.1 (t), 32.3 (t), 32.5 (t), 32.6 (t), 37.8 (t), 38.2 (t), 39.1 (t), 39.2 (t), 71.37 (d), 71.42 (d), 71.8 (d), 71.9 (d), 125.72 (d), 125.73 (d), 125.76 (d), 125.80 (d), 128.29 (d), 128.30 (d), 128.36 (d), 128.40 (d), 128.5 (d), 142.1 (s), 142.26 (s), 142.29 (s), 142.4 (s); exact mass m/z calcd for $C_{29}H_{46}NaO_2Si$ (M + Na) 477.3159, found 477.3161.

6-[[Tris(1-methylethyl)silyl]oxy]-1,8-diphenyloctan-3-one (22). Jones reagent[20] (7.0 M in acetone, 0.04 mL, 0.12 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **21** (0.0532 g, 0.117 mmol) in acetone (4 mL). After 10 min, the orange mixture was quenched with MeOH (5 mL), and stirring was continued for 30 min, by which time the mixture had become dark green. The mixture was diluted with EtOAc (15 mL), washed with water and brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (1.4×17 cm), using EtOAc−petroleum ether mixtures from 2% to 10% EtOAc, gave **22** (0.0516 g, 97%) as an oil: FTIR (CH_2Cl_2, neat film microscope) 3086, 3063, 3027, 2943, 2892, 2866, 1942, 1869, 1800, 1717, 1604, 1497 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.06 (apparent s, 21 H), 1.72−1.84 (m, 3 H), 1.85−1.93 (m, 1 H), 2.45−2.57 (m, 2 H), 2.58−2.69 (m, 2 H), 2.76 (t, J = 7.9 Hz, 2 H), 2.92 (t, J = 7.4 Hz, 2 H), 3.93 (dddd, J = 5.4, 5.4, 5.4, 5.4 Hz, 1 H), 7.16−7.22 (m, 6 H), 7.27−7.31 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.7 (d), 18.2 (q), 29.8 (t), 29.9 (t), 31.5 (t), 38.1 (t), 38.5 (t), 44.4 (t), 70.9 (d), 125.8 (d), 126.1 (d), 128.3 (d), 128.4 (d), 128.5 (d), 141.1 (s), 142.3 (s), 210.0 (s) (two signals overlap in the aromatic region); exact mass m/z calcd for $C_{29}H_{44}NaO_2Si$ (M + Na) 475.3003, found 475.3009.

Tetradecanedial (23). (a) Tetradecane-1,14-diol (23b). Pt−C (10% w/w, ca. 10 mg) was added to a solution of **23a**[6] (0.1535 g, 0.6904 mmol) in MeOH (10 mL), and the mixture was stirred under H_2 (doubled balloon) for 20 h and then filtered through Celite, using EtOAc as a rinse. Evaporation of the solvent and flash chromatography of the residue over silica gel (1.8×19 cm), using EtOAc−petroleum ether mixtures from 40% to 80% EtOAc, gave **23b** (0.0959 g, 60%) as a solid: mp 83.5−89 °C.

(b) Tetradecanedial (23)[6a]**.** $(COCl)_2$ (0.36 mL, 4.1 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of DMSO (0.5800, 8.163 mmol) in CH_2Cl_2 (5 mL). After 15 min, a solution of **23b** (0.122 mL, 0.529 mmol) in CH_2Cl_2 (3 mL) was added dropwise. After a further 45 min, Et_3N (1.474 mL, 10.57 mmol) was added dropwise, and stirring was continued for 30 min. The mixture was then stored at −20 °C (freezer) for 20 h, transferred to an ice bath, and stirred at 0 °C for 3 h. Water (6 mL) and CH_2Cl_2 (10 mL) were added, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.4×16 cm), using EtOAc−petroleum ether mixtures from 5% to 15% EtOAc, gave **23** (0.0901 g, 83%) as an oil: FTIR (CH_2Cl_2, cast) 2915, 2850, 2749, 1788, 1705, 1674, 1471 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.23−1.37 (m, 16 H), 1.63 (quintet, J = 7.2 Hz, 4 H), 2.42 (td, J = 7.4, 1.9 Hz, 4 H), 9.77 (t, J = 1.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.1 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 43.9 (t), 202.9 (d); exact mass m/z calcd for $C_{14}H_{26}NaO_2$ (M + Na) 249.1825, found 249.1828.

Octadeca-1,17-diene-3,16-diol (24). MeLi (1.6 M in Et_2O, 0.61 mL, 0.98 mmol) was added dropwise to a stirred and cooled (0 °C) solution of tetravinyltin (0.045 mL, 0.246 mmol) in dry Et_2O (6 mL). After 1 h, the mixture was cooled to −78 °C, and a solution of **23** (0.0139 g, 0.0614 mmol) in Et_2O (2 mL plus 2 mL as a rinse) was added by cannula. The cold bath was left in place but not recharged, and stirring was continued for 22 h. The mixture was cooled to 0 °C and quenched with water (10 mL), and the aqueous phase was extracted with Et_2O. The combined organic extracts were washed with brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (0.7 × 15 cm), using EtOAc−petroleum mixtures from 10% to 20% EtOAc, gave **24** (0.0141 g, 81%) as a solid: mp 49−53 °C; FTIR (CH_2Cl_2, microscope) 3312, 3092, 3015, 2986, 2914, 2849, 1857, 1646, 1465 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.24−1.44 (m, 22 H), 1.48−1.58 (m, 4 H), 4.10 (apparent qt, J = 6.1, 1.2 Hz, 2 H), 5.11 (dt, J = 10.4, 1.5 Hz, 2 H), 5.22 (dt, J = 17.2, 1.5 Hz, 2 H), 5.87 (ddd, J = 17.2, 10.4, 6.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.3 (t), 29.5 (t), 29.55 (t), 29.59 (t), 37.1 (t), 73.3 (d), 114.5 (t), 141.3 (d); exact mass m/z calcd for $C_{18}H_{34}NaO_2$ (M + Na) 305.2451, found 305.2450.

Cyclohexadec-2-ene-1,4-diol (25). A solution of **24** (0.0107 g, 0.0379 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise over 20 h to a stirred solution of Grubbs II catalyst[8] (0.0032 g, 0.0038 mmol) in CH_2Cl_2 (5 mL) (N_2 atmosphere). After 6 days, the mixture was evaporated and flash chromatography of the residue over silica gel (0.7 × 15 cm), using EtOAc−petroleum ether mixtures from 10% to 100% EtOAc, gave **25** (0.0069 g, 72%) as a semisolid that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast microscope) 3357, 2925, 2855, 2680, 1956, 1660, 1633, 1460 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.15−1.42 (m, 22 H), 1.50−1.60 (m, 2 H), 1.60−1.72 (m, 2 H), 4.10−4.15 (m, 1 H), 4.23−4.28 (m, 1 H), 5.58 (dd, J = 5.0, 2.5 Hz, 1 H), 5.71 (dd, J = 3.0, 1.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.6 (t), 24.2 (t), 25.0 (t), 25.90 (t), 25.94 (t), 27.2 (t), 27.3 (t), 27.8 (t), 28.0 (t), 36.9 (t), 37.0 (t), 72.1 (d), 73.5 (d), 133.1 (d), 135.0 (d); exact mass m/z calcd for $C_{16}H_{30}NaO_2$ (M + Na) 277.2138, found 277.2139.

Cyclohexadecane-1,4-diol. Pd−C (5% w/w, ca. 4 mg) was added to a solution of **25** (0.0252 g, 0.0991 mmol) in MeOH (1 mL), and the mixture was stirred under H_2 (doubled balloon) for 8 h and then filtered through Celite, using EtOAc as a rinse. Evaporation of the solvent and flash chromatography of the residue over silica gel (0.7 × 15 cm), using 2% MeOH−EtOAc, gave cyclohexadecane-1,4-diol (0.0179 g, 70%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast) 3392, 3313, 2921, 2850, 1644, 1469 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.18−1.43 (m, 26 H), 1.44−1.70 (m, 4 H), 3.72−3.82 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.1 (t), 23.6 (t), 26.47 (t), 26.51 (t), 26.56 (t), 26.64 (t), 26.7 (t), 26.8 (t), 26.9 (t), 27.0 (t), 29.7 (t), 30.9 (t), 31.3 (t), 31.4 (t), 35.18 (t), 35.24 (t), 70.2 (d), 71.0 (d); exact mass m/z calcd for $C_{16}H_{32}NaO_2$ (M + Na) 279.2295, found 279.2296.

Cyclohexadecane-1,4-dione (26)[23]**.** Jones reagent[20] (7.0 M in acetone, 0.025 mL, 0.176 mmol) was added dropwise to a stirred and cooled (0 °C) solution of cyclohexadecane-1,4-diol (0.0150 g, 0.0585 mmol) in acetone (4 mL). After 1.5 h, the orange mixture was quenched with MeOH (3 mL), and stirring was continued for 30 min, by which time the mixture had become dark green. The mixture was diluted with EtOAc (15 mL), washed with water and brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (0.4 × 6 cm), using 10% EtOAc−petroleum ether, gave **26** (0.0126 g, 86%) as an oil: FTIR (CH_2Cl_2, cast microscope) 2930, 2856, 1712, 1457, 1408 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.14−1.40 (m, 16 H), 1.58−1.66 (m, 4 H), 2.46−2.51 (m, 4 H), 2.69 (s, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.2 (t), 25.7 (t), 26.8 (t), 26.9 (t), 27.5 (t), 36.5 (t), 42.0 (t), 210.4 (s); exact mass m/z calcd for $C_{16}H_{28}O_2$ 252.2089, found 252.2091.

Methyl 7,8,10,11-Tetradeoxy-2,3,4-tris-*O*-methyl-11-phenyl-α-D-*gluco*-unedec-7-ynopyranoside (27). BuLi (2.5 M in hexanes, 1 mL, 2.5 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **1** (196.5 mg, 1.23 mmol) in THF (11 mL). After 1 h, a solution of freshly prepared crude methyl 2,3,4-tri-*O*-methyl-α-D-*gluco*-hexodialdo-1,5-pyranoside[24] (161.2 mg, 0.69 mmol) in THF (2 mL) was added dropwise. The cooling bath was left in place but not recharged, and stirring was continued for 23 h. The mixture was quenched with saturated aqueous NH_4Cl (8 mL) and extracted with EtOAc. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.5×15 cm), using 75% EtOAc−hexanes, gave **27** (181.2 mg, 67% or 85%, based on recovered starting material) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR ($CHCl_3$, microscope) 3423, 3085, 3062, 3026, 2934, 2836, 2248, 1604, 1496, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.94−2.12 (m, 2 H), 2.19−2.32 (m, 1 H), 2.73−2.83 (m, 3 H), 3.18−3.26 (m, 1 H), 3.31−3.73 (m, 15 H), 4.39−4.46 (m, 1 H), 4.62−4.73 (m, 1 H), 4.85 (d, J = 3.2 Hz, 1 H), 7.17−7.22 (m, 3 H), 7.26−7.31 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.58 (t), 31.66 (t), 31.69 (t), 39.3 (t), 39.4 (t), 55.4 (q), 55.5 (q), 59.3 (q), 60.9 (q), 61.1 (q), 61.2 (q), 61.5 (q), 61.6 (q), 61.8 (q), 61.9 (q), 62.8 (q), 72.21 (d), 72.26 (d), 72.30 (d), 79.5 (d), 81.3 (d), 81.4 (d), 81.99 (d), 82.04 (d), 82.5 (s), 82.6 (s), 83.6 (d), 83.8 (d), 84.3 (s), 86.2 (s), 88.0 (s), 97.7 (d), 97.9 (d), 126.30 (d), 126.31 (d), 128.71 (d), 128.72 (d), 141.34 (s), 141.36 (s); exact mass m/z calcd for $C_{21}H_{30}NaO_7$ (M + Na) 417.1884, found 417.1891.

Methyl 7,8,10,11-Tetradeoxy-2,3,4-tris-*O*-methyl-11-phenyl-α-D-*gluco*-unedecanopyranoside (28). Pt−C (5% w/w, 14 mg) was added to a solution of **27** (35.9 mg, 0.091 mmol) in MeOH (1.5 mL), and the mixture was stirred under H_2 (balloon) for 1 h and then filtered through Celite, using EtOAc as a rinse. Evaporation of the filtrate and flash chromatography of the residue over silica gel (0.6 × 8 cm), using EtOAc−hexanes from 50% EtOAc to 100% EtOAc, gave **28** (27.3 mg, 75%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR ($CHCl_3$, microscope) 3448, 3085, 3061, 3025, 2933, 2836, 1603, 1496, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.52−1.90 (m, 6 H), 2.42 (s, 1 H), 2.64−2.85 (m, 2 H), 3.14−3.20 (m, 2 H), 3.26−3.31 (m, 1 H), 3.36−3.69 (m, 15 H), 3.79 (s, 1 H), 4.78 (dd, J = 3.4, 15.4 Hz, 1 H), 7.16−7.21 (m, 3 H), 7.26−7.30 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.1 (t), 28.9 (t), 30.3 (t), 31.3 (t), 32.09 (t), 32.13 (t), 32.15 (t), 32.19 (t), 33.8 (t), 34.1 (t), 34.4 (t), 34.7 (t), 39.1 (t), 39.4 (t), 55.17 (q), 55.24 (q), 55.29 (q), 55.31 (q), 58.9 (q), 59.0 (q), 60.2 (q), 60.6 (q), 60.7 (q), 60.8 (q), 69.3 (d), 69.4 (d), 70.9 (d), 71.0 (d), 71.1 (d), 71.3 (d), 71.4 (d), 72.1 (d), 72.4 (d), 73.2 (d), 73.3 (d), 79.5 (d), 81.7 (d), 82.0 (d), 82.26 (d), 82.33 (d), 83.6 (d), 83.7 (d), 97.2 (d), 97.6 (d), 125.7 (d), 125.8 (d), 128.34 (d), 128.38 (d), 128.39 (d), 128.41 (d), 142.0 (s), 142.27 (s), 142.29 (s); exact mass m/z calcd for $C_{21}H_{34}NaO_7$ (M + Na) 421.2197, found 421.2199.

6-Phenyl-1-[(2*S*,3*S*,4*S*,5*R*,6*S*)-tetrahyro-3,4,5,6-tetramethoxypyran-2-yl]hexane-1,4-dione (29). DMSO (0.09 mL, 1.27 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise to a stirred and cooled (−78 °C) solution of $(COCl)_2$ (0.06 mL, 0.694 mmol) in CH_2Cl_2 (1 mL). After 15 min, a solution of **28** (101.6 mg, 0.255 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise, and stirring at −78 °C was continued for 35 min. Then Et_3N (0.2 mL) was added dropwise, and stirring at −78 °C was continued for 5 min. The cooling bath was removed, and stirring was continued for 25 min. Water (2 mL) was added, and the organic phase was dried

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($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.5×13 cm), using 50% EtOAc−hexanes, gave **29** (83.9 mg, 83%) as an colorless oil: $[\alpha]^{20}_D$ 79.2 (*c* 1.35, $CHCl_3$); FTIR ($CHCl_3$, cast microscope) 3062, 3027, 2933, 2836, 1716, 1604, 1497, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.60−2.68 (m, 1 H), 2.72−2.85 (m, 4 H), 2.89−3.03 (m, 3 H), 3.20−3.31 (m, 2 H), 3.45−3.63 (m, 13 H), 4.06 (dd, J = 1.6, 10 Hz, 1 H), 4.87 (dd, J = 1.6, 3.2 Hz, 1 H), 7.17−7.21 (m, 3 H), 7.26−7.30 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.0 (t), 34.7 (t), 36.0 (t), 44.5 (t), 55.9 (q), 59.4 (q), 60.8 (q), 61.2 (q), 74.0 (d), 80.9 (d), 81.5 (d), 83.7 (d), 98.1 (d), 126.3 (d), 128.5 (d), 128.7 (d), 141.2 (s), 205.8 (s), 208.2 (s); exact mass *m*/*z* calcd for $C_{21}H_{30}NaO_7$ (M + Na) 417.1884, found 417.1879.

3,6-Bis(2-phenylethyl)octa-1,7-diene-3,6-diol (30). MeLi (1.6 M in Et_2O, 3.31 mL, 5.29 mmol) was added dropwise to a stirred and cooled (0 °C) solution of tetravinyltin (0.24 mL, 1.3 mmol) in dry Et_2O (20 mL). After 35 min, the mixture was cooled to −78 °C, and a solution of **4** (0.1146 g, 0.3893 mmol) in Et_2O (3.5 mL plus 3.5 mL as a rinse) was added by cannula. The cold bath was left in place but not recharged, and stirring was continued for 12 h. The mixture was quenched with a mixture of water (50 mL) and saturated aqueous NH_4Cl (25 mL). The aqueous phase was extracted with Et_2O, and the combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.8×19 cm), using EtOAc−hexane mixtures from 15% to 30% EtOAc, gave **30** (0.1070 g, 78%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast microscope) 3416, 3085, 3062, 3026, 2946, 2863, 1945, 1867, 1744, 1642, 1603, 1497 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.55−1.70 (m, 3 H), 1.70−1.85 (m, 4 H), 1.85−1.97 (m, 3 H), 2.58−2.71 (m, 4 H), 5.18−5.24 (m, 2 H), 5.25−5.32 (m, 2 H), 5.79−5.89 (m, 2 H), 7.15−7.20 (m, 6 H), 7.25−7.30 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 30.0 (t), 34.3 (t), 34.4 (t), 42.7 (t), 43.3 (t), 75.2 (s), 75.3 (s), 113.3 (t), 113.5 (t), 125.78 (d), 125.79 (d), 128.36 (d), 128.41 (d), 142.36 (s), 142.38 (s), 143.2 (d), 143.5 (d); exact mass *m*/*z* calcd for $C_{24}H_{30}O_2$ 373.2138, found 373.2139.

1,4-Bis(2-phenylethyl)cyclohex-2-ene-1,4-diol (31). Grubbs I catalyst (0.0192 g, 0.0233 mmol) was added to a stirred solution of **30** (0.1152 g, 0.3287 mmol) in dry CH_2Cl_2 (20 mL) (N_2 atmosphere). After 24 h, the mixture was evaporated and flash chromatography of the residue over silica gel (1.3 × 11 cm), using EtOAc−petroleum ether mixtures from 10% to 100% EtOAc, gave **31** [0.0376 g, 35% less polar diastereoisomer; 0.0666 g, 62% more polar diastereoisomer (98% overall)] as semisolids: The more polar diastereoisomer: FTIR (CH_2Cl_2, cast microscope) 3377, 3061, 3025, 2933, 2858, 1945, 1870, 1663, 1496 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.56−1.65 (br s, 2 H), 1.77−1.92 (m, 8 H), 2.71 (t, J = 8.7 Hz, 4 H), 5.77 (s, 2 H), 7.17−7.23 (m, 6 H), 7.26−7.30 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.9 (t), 32.9 (t), 42.8 (t), 70.3 (s), 125.9 (d), 128.3 (d), 128.5 (d), 134.4 (d), 142.2 (s); exact mass *m*/*z* calcd for $C_{22}H_{26}NaO_2$ (M + Na) 345.1825, found 345.1824.

The less polar diastereoisomer: FTIR (CH_2Cl_2, cast microscope) 3377, 3062, 3025, 2931, 2859, 1946, 1603, 1496 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.55−1.65 (br s, 2 H), 1.77−1.94 (m, 8 H), 2.74 (t, J = 8.6 Hz, 4 H), 5.76 (s, 2 H), 7.16−7.23 (m, 6 H), 7.26−7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.9 (t), 31.8 (t), 44.0 (t), 69.5 (s), 125.9 (d), 128.3 (d), 128.4 (d), 134.2 (d), 142.1 (s); exact mass *m*/*z* calcd for $C_{22}H_{26}NaO_2$ (M + Na) 345.1825, found 345.1823.

1,4-Bis(2-phenylethyl)benzene (32)[25]. Use of More Polar Isomer of 31. $TsOH \cdot H_2O$ (0.0112 g, 0.0589 mmol) was added to a solution of the more polar diastereoisomer of **31** (0.0185 g, 0.0574 mmol) in dry PhH (2 mL), and the mixture was refluxed for 7 h, cooled to room temperature, and partitioned between water and CH_2Cl_2. The aqueous phase was extracted with hexane, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.7 × 18 cm), using EtOAc−petroleum ether mixtures from 0% to 2% EtOAc, gave **32** (0.0161 g, 98%) as a solid: mp 85−90 °C; FTIR (CH_2Cl_2, cast microscope) 3084, 3062, 3023, 2933, 2916, 2852, 1902, 1698, 1602, 1512, 1496, 1452 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.90 (s, 8 H), 7.11 (s, 4 H), 7.17−7.23 (m, 6 H), 7.26−7.31 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.5 (t), 38.0 (t), 125.9 (d), 128.3 (d), 128.38 (d), 128.44 (d), 139.3 (s), 141.9 (s); exact mass *m*/*z* calcd for $C_{22}H_{22}$ 286.1722, found 286.1723.

Use of Less Polar Isomer of 31. $TsOH \cdot H_2O$ (0.0074 g, 0.039 mmol) was added to a solution of the less polar diastereoisomer of **31** (0.0126 g, 0.0391 mmol) in dry PhH (1.5 mL), and the mixture was refluxed for 5 h, cooled to room temperature, and partitioned between water and CH_2Cl_2. The aqueous phase was extracted with hexane, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.7 × 15 cm), using EtOAc−petroleum ether mixtures from 0% to 2% EtOAc, gave **32** (0.011 g, 100%).

3-Pentyl-6-(2-phenylethyl)octa-1,7-diene-3,6-diol (33). MeLi (1.6 M in Et_2O, 1.81 mL, 2.89 mmol) was added dropwise to a stirred and cooled (0 °C) solution of tetravinyltin (0.13 mL, 0.72 mmol) in dry Et_2O (10 mL). After 45 min, the mixture was cooled to −78 °C and a solution of **7** (0.0471 g, 0.181 mmol) in Et_2O (2 mL plus 2 mL as a rinse) was added by cannula. The cooling bath was left in place but not recharged, and stirring was continued for 12 h. The mixture was quenched with a mixture of water (25 mL) and saturated aqueous NH_4Cl (25 mL). The aqueous phase was extracted with Et_2O, and the combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.4×16 cm), using EtOAc−hexane mixtures from 15% to 30% EtOAc, gave **33** (0.0533 g, 93%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast microscope) 3419, 3086, 3063, 3026, 3006, 2953, 2933, 2861, 1942, 1844, 1734, 1642, 1604, 1497, 1455 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, J = 6.7 Hz, 3 H), 1.20−1.38 (m, 6 H), 1.44−1.72 (m, 6 H), 1.72−1.98 (m, 4 H), 2.56−2.73 (m, 2 H), 5.09−5.33 (m, 4 H), 5.72−5.90 (m, 2 H), 7.15−7.20 (m, 3 H), 7.24−7.30 (2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0 (q), 22.6 (t), 23.1 (t), 30.0 (t), 32.2 (t), 34.0 (t), 34.4 (t), 34.5 (t), 41.0 (t), 41.6 (t), 42.7 (t), 43.3 (t), 75.1 (s), 75.2 (s), 112.6 (t), 112.9 (t), 113.1 (t), 113.4 (t), 125.70 (d), 125.73 (d), 128.35 (d), 128.37 (d), 142.5 (s), 143.4 (d), 143.5 (d), 143.6 (d), 143.9 (d); exact mass *m*/*z* calcd for $C_{21}H_{32}NaO_2$ (M + Na) 339.2295, found 339.2288.

1-Pentyl-4-(2-phenylethyl)cyclohex-2-ene-1,4-diol (34). Grubbs I catalyst (0.0027 g, 0.0033 mmol) was added to a stirred solution of **33** (0.0523 g, 0.165 mmol) in dry CH_2Cl_2 (7 mL) (N_2 atmosphere). After 12 h, the mixture was evaporated and flash chromatography of the residue over silica gel (1.4 × 14 cm), using EtOAc−petroleum ether mixtures from 10% to 40% EtOAc, gave **34** [0.0306 g, 64% less polar diastereoisomer; 0.0171 g, 35% more polar diastereoisomer (99% overall)] as oils. The more polar diastereoisomer: FTIR (CH_2Cl_2, neat film microscope) 3309, 3061, 3026, 2954, 2929, 2861, 1940, 1864, 1740, 1603 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.90 (t, J = 6.8 Hz, 3 H), 1.20−1.46 (m, 6 H), 1.47−1.65 (m, 4 H), 1.63−1.85 (m, 2 H), 1.81−2.17 (m, 4 H), 2.67−2.81 (m, 2 H), 5.70−5.74 (m, 2 H), 7.16−7.23 (m, 3 H), 7.28−7.32 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1 (q), 22.6 (t), 23.2 (t), 29.9 (t), 32.3 (t), 32.7 (t), 32.9 (t), 41.1 (t), 42.8 (t), 70.3 (s), 70.4 (s), 125.8 (d), 128.3 (d), 128.4 (d), 134.0 (d), 134.7 (d), 142.3 (s); exact mass *m*/*z* calcd for $C_{19}H_{28}NaO_2$ (M + Na) 311.1982, found 311.1982.

The less polar diastereoisomer: FTIR (CH_2Cl_2, neat film microscope) 3538, 3389, 3063, 3027, 2930, 2860, 1946, 1870, 1741, 1603, 1497, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.91

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(t, J = 6.9 Hz, 3 H), 1.25−1.46 (m, 6 H), 1.46−1.64 (m, 4 H), 1.66−1.81 (m, 2 H), 1.83−2.20 (m, 4 H), 2.67−2.81 (m, 2 H), 5.69−5.76 (m, 2 H), 7.17−7.23 (m, 3 H), 7.26−7.32 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1 (q), 22.6 (t), 23.2 (t), 30.0 (t), 31.7 (t), 31.9 (t), 32.3 (t), 42.2 (t), 44.0 (t), 69.5 (s), 69.6 (s), 125.8 (d), 128.3 (d), 128.4 (d), 133.8 (d), 134.7 (d), 142.2 (s); exact mass m/z calcd for $C_{19}H_{28}NaO_2$ (M + Na) 311.1982, found 311.1977.

1-Pentyl-4-(2-phenylethyl)benzene (35)[26]. Use of More Polar Isomer of 34. $TsOH \cdot H_2O$ (0.0113 g, 0.0593 mmol) was added to a solution of the more polar diastereoisomer of **34** (0.0171 g, 0.0593 mmol) in dry PhH (4 mL), and the mixture was refluxed for 1 h, cooled to room temperature, and partitioned between water and CH_2Cl_2. The aqueous phase was then extracted with hexane, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.7 × 15 cm), using EtOAc−petroleum ether mixtures from 0% to 2% EtOAc, gave **35** (0.0150 g, 100%) as an oil: FTIR (CH_2Cl_2, neat film microscope) 3026, 2955, 2928, 2857, 1604, 1514, 1496 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, J = 7.0 Hz, 3 H), 1.27−1.42 (m, 4 H), 1.63 (apparent quintet, J = 7.6 Hz, 2 H), 2.58 (dd, J = 7.7, 7.7 Hz, 2 H), 2.87−2.96 (m, 4 H), 7.14 (s, 4 H), 7.18−7.24 (m, 3 H), 7.27−7.33 (2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0 (q), 22.6 (t), 31.2 (t), 31.5 (t), 35.5 (t), 37.5 (t), 38.0 (t), 125.8 (d), 128.2 (d), 128.30 (d), 128.34 (d), 128.4 (d), 138.9 (s), 140.5 (s), 142.0 (s); exact mass m/z calcd for $C_{19}H_{24}$ 252.1878, found 252.1877.

Use of Less Polar Isomer of 34. $TsOH \cdot H_2O$ (0.0202 g, 0.106 mmol) was added to a solution of the less polar diastereoisomer of **34** (0.0306 g, 0.106 mmol) in dry PhH (4 mL), and the mixture was refluxed for 1 h, cooled to room temperature, and partitioned between water and CH_2Cl_2. The aqueous phase was then extracted with hexane, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.7 × 16 cm), using EtOAc−petroleum ether mixtures from 0% to 2% EtOAc, gave **35** (0.027 g, 100%) as an oil.

3-(1-Adamantyl)-6-(2-phenylethyl)octa-1,7-diene-3,6-diol (36). MeLi (1.6 M in Et_2O, 0.41 mL, 0.66 mmol) was added dropwise to a stirred and cooled (0 °C) solution of tetravinyltin (0.030 mL, 0.165 mmol) in dry Et_2O (3 mL). After 45 min, the mixture was cooled to −78 °C, and a solution of **10** (0.0134 g, 0.0413 mmol) in Et_2O (1 mL plus 1 mL as a rinse) was added by cannula. The cold bath was left in place but not recharged, and stirring was continued for 5 h. The mixture was cooled to 0 °C and quenched with a mixture of water (50 mL) and saturated aqueous NH_4Cl (25 mL). The aqueous phase was extracted with Et_2O, and the combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (0.7 × 15 cm), using 15% EtOAc−hexane, gave **36** (0.0146 g, 93%) as a semisolid mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast) 3433, 3085, 3025, 2905, 2849, 2679, 1742, 1667, 1497 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.44−1.53 (m, 3 H), 1.57−1.72 (m, 13 H), 1.72−1.90 (m, 3 H), 1.99 (br s, 3 H), 1.99−2.56 (br s, 1 H), 2.56−2.72 (m, 2 H), 5.12−5.32 (m, 4 H), 5.75−5.92 (m, 2 H), 7.14−7.20 (m, 3 H), 7.24−7.30 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.69 (t), 25.76 (t), 28.6 (d), 30.0 (t), 34.2 (t), 34.5 (t), 36.4 (t), 37.1 (t), 39.3 (t), 42.6 (t), 43.7 (t), 75.3 (s), 75.4 (s), 79.1 (s), 79.2 (s), 112.9 (t), 113.3 (t), 113.8 (t), 114.0 (t), 125.65 (d), 125.72 (d), 128.34 (d), 128.35 (d), 128.37 (d), 140.5 (d), 140.6 (d), 142.5 (s), 142.6 (s), 143.7 (d), 143.8 (d); exact mass m/z calcd for $C_{26}H_{36}NaO_2$ (M + Na) 403.2608, found 403.2608.

1-(Adamantyl)-4-(2-phenylethyl)cyclohex-2-ene-1,4-diol (37). Grubbs I catalyst (0.0020 g, 0.0024 mmol) was added to a stirred solution of **36** (0.0146 g, 0.0384 mmol) in dry CH_2Cl_2 (2.5 mL) (N_2 atmosphere). After 3 h, the mixture was evaporated, and flash chromatography of the residue over silica gel (0.7 × 16 cm), using EtOAc−petroleum ether mixtures from 10% to 100% EtOAc, gave **37** [0.0091 g, 67% less polar diastereoisomer; 0.0046 g, 33% more polar diastereoisomer (100% overall)] as semisolids. The less polar diastereoisomer: FTIR (CH_2Cl_2, cast) 3352, 3085, 3025, 2984, 2928, 2901, 2847, 2675, 1742, 1603, 1451 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20−1.45 (br m, 2 H), 1.54−1.82 (m, 15 H), 1.82−2.00 (m, 3 H), 2.04 (apparent s, 3 H), 2.68−2.82 (m, 2 H), 5.83 (dd, J = 10.1, 1.7 Hz, 1 H), 5.95 (dd, J = 10.3, 1.8 Hz, 1 H), 7.16−7.23 (m, 3 H), 7.26−7.31 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.3 (t), 28.5 (d), 29.9 (t), 31.1 (t), 35.8 (t), 36.4 (s), 37.1 (t), 38.4 (t), 44.3 (t), 72.7 (s), 125.8 (d), 128.32 (d), 128.37 (d), 128.39 (d), 131.3 (d), 134.9 (d), 142.3 (s); exact mass m/z calcd for $C_{24}H_{32}NaO_2$ (M + Na) 375.2295. The molecular ion could not be detected as the compound readily aromatized under all conditions tried.

The more polar diastereoisomer: FTIR (CH_2Cl_2, cast) 3397, 3085, 3062, 3026, 2904, 2849, 2677, 1742, 1603, 1452 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42−1.60 (br m, 2 H), 1.60−1.80 (m, 15 H), 1.80−1.98 (m, 3 H), 2.02 (apparent s, 3 H), 2.68−2.84 (m, 2 H), 5.81 (dd, J = 10.4, 1.5 Hz, 1 H), 5.85 (dd, J = 10.3, 1.8 Hz, 1 H), 7.16−7.23 (m, 3 H), 7.26−7.32 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.7 (t), 28.4 (d), 29.9 (t), 33.1 (t), 35.7 (s), 35.8 (t), 37.1 (t), 41.1 (t), 71.2 (s), 72.9 (s), 125.8 (d), 128.3 (d), 128.4 (d), 128.9 (d), 137.4 (d), 142.5 (s); exact mass m/z calcd for $C_{24}H_{32}NaO_2$ (M + Na) 375.2295, found 375.2295.

1-[4-(2-Phenylethyl)phenyl]adamantane (38). Use of less polar isomer of 37. $TsOH \cdot H_2O$ (0.0012 g, 0.0064 mmol) was added to a solution of the less polar diastereoisomer of **37** (0.0075 g, 0.021 mmol) in dry PhH (4 mL), and the mixture was refluxed for 2 h, cooled to room temperature, and partitioned between water and CH_2Cl_2. The aqueous phase was extracted with hexane, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.7 × 15 cm), using EtOAc−petroleum ether mixtures from 0% to 2% EtOAc, gave **38** (0.0064 g, 95%) as a solid: mp 96−99 °C; FTIR (CH_2Cl_2, cast) 3060, 3025, 2903, 2848, 2657, 1603, 1515, 1496, 1452 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.75−1.83 (m, 6 H), 1.93 (d, J = 2.7 Hz, 6 H), 2.10 (apparent s, 3 H), 2.87−2.96 (m, 4 H), 7.18 (apparent d, J = 8.4 Hz, 2 H), 7.20−7.24 (m, 3 H), 7.28−7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.0 (d), 35.9 (s), 36.8 (t), 37.5 (t), 37.9 (t), 43.3 (t), 124.8 (d), 125.9 (d), 128.1 (d), 128.3 (d), 128.4 (d), 138.9 (s), 142.1 (s), 149.0 (s); exact mass m/z calcd for $C_{24}H_{28}$ 316.2191, found 316.2192.

Use of more polar isomer of 37. $TsOH \cdot H_2O$ (0.0007 g, 0.004 mmol) was added to a solution of the more polar diastereoisomer of **37** (0.0043 g, 0.012 mmol) in dry PhH (3 mL), and the mixture was refluxed for 2 h, cooled to room temperature, and partitioned between water and CH_2Cl_2. The aqueous phase was extracted with hexane, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.7 × 15 cm), using EtOAc−petroleum ether mixtures from 0% to 2% EtOAc, gave **38** (0.0035 g, 91%) as a solid: mp 96−99 °C.

Use of a mixture of isomers of 37. Grubbs I catalyst (0.0041 g, 0.0049 mmol) was added to a stirred solution of **36** (a mixture of isomers, 0.0188 g, 0.0494 mmol) in dry CH_2Cl_2 (5 mL) (N_2 atmosphere). After 3 h, the mixture was evaporated, and the residue was stored for a few minutes under oil pump vacuum and then dissolved in PhH (5 mL). $TsOH \cdot H_2O$ (0.0028 g, 0.0148 mmol) was added to the solution of crude **37**, and the mixture was refluxed for 30 min, cooled to room temperature, and stirred for an additional 36 h. The mixture was then partitioned between water and CH_2Cl_2, and the aqueous phase was extracted with hexane. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.7 × 15 cm), using EtOAc−petroleum ether mixtures from

(26) Sundaresan, A. K.; Ramamurthy, V. *Org. Lett.* **2007**, *9*, 3575–3578.

0% to 2% EtOAc, gave **38** (0.0149 g, 95%) as a solid, identical to material obtained from the less polar isomer of **37**.

3,6-Bis(1-adamantyl)octa-1,7-diene-3,6-diol (39). MeLi (1.6 M in Et_2O, 0.50 mL, 0.80 mmol) was added dropwise to a stirred and cooled (0 °C) solution of tetravinyltin (0.037 mL, 0.201 mmol) in dry Et_2O (5 mL). After 1 h, the mixture was cooled to −78 °C, and a solution of **14** (0.0089 g, 0.025 mmol) in Et_2O (1 mL plus 1 mL as a rinse) was added by cannula. After 1.75 h the cold mixture was quenched with saturated aqueous NH_4Cl (6 mL), and the aqueous phase was extracted with Et_2O. The combined organic extracts were washed with brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (0.7 × 12 cm), using EtOAc−hexane mixtures from 2% to 10% EtOAc, gave **39** as a mixture of diastereoisomers [6.6 mg, 64% less polar diastereoisomer; 2.3 mg, 22% more polar diastereoisomer (86% overall)]. The less polar diastereoisomer: FTIR (CH_2Cl_2, microscope) 3614, 3085, 2932, 2904, 2871, 2851, 2680, 2658, 2639, 1838, 1730, 1640, 1450, 1408 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.20−1.36 (m, 4 H), 1.36−1.50 (m, 4 H), 1.51−1.72 (m, 22 H), 1.97 (s, 6 H), 5.14 (dd, J = 17.4, 1.7 Hz, 2 H), 5.21 (dd, J = 11.0, 1.7 Hz, 2 H), 5.83 (dd, J = 17.3, 11.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.9 (t), 28.6 (d), 36.4 (t), 37.1 (t), 39.4 (s), 79.4 (s), 113.5 (t), 141.0 (d); exact mass m/z calcd for $C_{28}H_{42}NaO_2$ (M + Na) 433.3077, found 433.3076.

The more polar diastereoisomer: FTIR (CH_2Cl_2, cast microscope) 3476, 2905, 2849, 1718, 1451 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.18−1.36 (m, 8 H), 1.54−1.74 (m, 22 H), 1.97 (apparent s, 6 H), 5.18 (dd, J = 17.2, 1.8 Hz, 2 H), 5.21 (dd, J = 11.0, 1.8 Hz, 2 H), 5.78 (dd, J = 17.2, 11.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.2 (t), 28.7 (d), 36.4 (t), 37.2 (t), 39.4 (s), 79.2 (s), 113.8 (t), 141.1 (d); exact mass m/z calcd for $C_{28}H_{42}NaO_2$ (M + Na) 433.3077, found 433.3079.

1,4-Bis(1-adamantyl)cyclohex-2-ene-1,4-diol (40). Grubbs I catalyst (0.0033 g, 0.0039 mmol) was added to a stirred solution of **39** (mixture of isomers, 0.008 g, 0.019 mmol) in dry CH_2Cl_2 (1 mL) (N_2 atmosphere). After 24 h, the reaction mixture was evaporated, and flash chromatography of the residue over silica gel (0.7 × 18 cm), using EtOAc−petroleum ether mixtures from 2% to 10% EtOAc, gave **40** as a mixture of two impure diastereoisomers (^{13}C NMR) (ca. 5.6 mg). We were unable to obtain satisfactory NMR data: exact mass m/z calcd for $C_{26}H_{38}NaO_2$ (M + Na) 405.2764, found 405.2768.

1-[4-(1-Adamantyl)phenyl]adamantane (41)[27]**.** TsOH·H_2O (0.0025 g, 0.013 mmol) was added to a solution of the above sample of **40** (0.0050 g, 0.013 mmol) in dry PhH (2 mL), and the mixture was refluxed for 4.5 h, cooled to room temperature, and partitioned between water and CH_2Cl_2. The aqueous phase was extracted with hexane, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel [0.5 × 6 cm (Pasteur pipet)], using EtOAc−petroleum ether mixtures from 0% to 2% EtOAc, gave **41** (0.0043 g, 95%) as a solid: sublimes at 215−227 °C; FTIR (CH_2Cl_2, microscope) 3085, 3047, 3027, 2907, 2849, 2657, 1507 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.72−1.82 (m, 12 H), 1.93 (d, J = 2.3 Hz, 12 H), 2.09 (apparent s, 6 H), 7.31 (s, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.0 (d), 35.8 (s), 36.9 (t), 43.2 (t), 124.5 (d), 148.4 (s); exact mass m/z calcd for $C_{26}H_{34}$ 346.2661, found 346.2665.

3-Cycloheptyl-6-cyclohexylocta-1,7-diene-3,6-diol (42). MeLi (1.6 M in Et_2O, 1.16 mL, 1.86 mmol) was added dropwise to a stirred and cooled (0 °C) solution of tetravinyltin (0.09 mL, 0.47 mmol) in dry Et_2O (8 mL). After 45 min, the mixture was cooled to −78 °C, and a solution of **18** (0.0150 g, 0.0567 mmol) in Et_2O (2 mL plus 2 mL as a rinse) was added by cannula. The cold bath was left in place but not recharged, and stirring was continued for 11.5 h. The mixture was quenched with saturated aqueous NH_4Cl (12 mL), and the aqueous phase was extracted with Et_2O. The combined organic extracts were washed with brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (0.7 × 17 cm), using EtOAc−hexane mixtures from 5% to 10% EtOAc, gave **42** (0.0148 g, 81%) as a semisolid that was a mixture of diastereoisomers (^{13}C NMR): FTIR ($CHCl_3$, cast microscope) 3450, 3010, 2926, 2853, 1841, 1640, 1451 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.84−1.10 (m, 2 H), 1.10−1.32 (m, 6 H), 1.32−1.62 (m, 10 H), 1.62−1.87 (m, 10 H), 1.87−2.12 (br s, 2 H), 5.10−5.24 (m, 4 H), 5.70−5.87 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.50 (t), 26.53 (t), 26.6 (t), 26.7 (t), 27.56 (t), 27.62 (t), 27.64 (t), 27.7 (t), 27.8 (t), 27.9 (t), 28.0 (t), 28.1 (t), 28.17 (t), 28.24 (t), 28.3 (t), 29.00 (t), 29.02 (t), 30.9 (t), 31.1 (t), 31.3 (t), 31.4 (t), 46.9 (d), 47.3 (d), 48.1 (d), 48.6 (d), 77.2 (s), 77.3 (s), 78.1 (s), 78.2 (s), 112.9 (t), 113.06 (t), 113.11 (t), 113.3 (t), 142.57 (d), 142.62 (d), 142.7 (d); exact mass m/z calcd for $C_{21}H_{36}NaO_2$ (M + Na) 343.2608, found 343.2609.

4-Cycloheptyl-1-cyclohexylbenzene (44). Grubbs I catalyst (0.0035 g, 0.0043 mmol) was added to a stirred solution of **42** (0.0138 g, 0.0431 mmol) in dry CH_2Cl_2 (5 mL) (N_2 atmosphere). After 18 h, the mixture was evaporated to afford a mixture of diol **43** and aromatized product **44**. The crude material was dissolved in PhH (4 mL) and TsOH·H_2O (0.0112 g, 0.0589 mmol) was added. The solution was refluxed for 1 h, cooled to room temperature, and partitioned between water and CH_2Cl_2. The aqueous phase was extracted with hexane, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.7×16 cm), using EtOAc−petroleum ether mixtures from 0% to 2% EtOAc, gave **44** (0.0105 g, 95%) as a solid: mp 75−80 °C; FTIR (CH_2Cl_2, microscope) 3050, 3010, 2923, 2850, 2668, 1899, 1785, 1647, 1515, 1447 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.20−1.34 (m, 1 H), 1.34−1.50 (m, 4 H), 1.50−1.75 (m, 8 H), 1.75−1.97 (m, 9 H), 2.44−2.51 (m, 1 H), 2.61−2.68 (m, 1 H), 7.12 (apparent s, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.2 (t), 27.0 (t), 27.2 (t), 28.0 (t), 34.5 (t), 36.8 (t), 44.1 (d), 46.6 (d), 126.5 (d), 126.6 (d), 145.1 (s), 147.3 (s); exact mass m/z calcd for $C_{19}H_{28}$ 256.2191, found 256.2184.

2-Methyl-3,6-bis(2-phenylethyl)octa-1,7-diene-3,6-diol (45). (a) 2-Methyl-6-[[tris(1-methylethyl)silyl]oxy]-8-phenyl-3-(2-phenylethyl)-oct-1-en-3-ol (45a). *t*-BuLi (1.7 M in pentane, 0.46 mL, 0.78 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of 2-bromopropene (0.035 mL, 0.390 mmol) in dry Et_2O (6 mL). After 45 min, a solution of **22** (0.0222 g, 0.0490 mmol) in Et_2O (2 mL plus 1 mL as a rinse) was added by cannula. After 15 min, the dry ice bath was replaced by an ice bath, and the mixture was quenched with saturated aqueous NH_4Cl (5 mL). The aqueous phase was extracted with CH_2Cl_2, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.7×18 cm), using EtOAc−hexane mixtures from 2% to 10% EtOAc, gave **45a** (0.0243 g, 100%) as a semisolid that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast film microscope) 3576, 3476, 3086, 3063, 3027, 2944, 2891, 2866, 1940, 1866, 1802, 1642, 1604, 1496, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.08 (apparent s, 21 H), 1.45−1.75 (m, 5 H), 1.77 (dd, J = 3.0, 0.7 Hz, 3 H), 1.80−1.97 (m, 4 H), 2.44−2.57 (m, 1 H), 2.58−2.76 (m, 3 H), 3.91 (dddd, J = 5.2, 5.2, 5.2, 5.2 Hz, 1 H), 5.01 (apparent q, J = 1.5, 1 H), 5.09 (apparent dq, J = 5.7, 0.7 Hz, 1 H), 7.16−7.22 (m, 6 H), 7.27−7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.7 (d), 18.2 (q), 19.8 (q), 29.6 (t), 29.9 (t), 31.3 (t), 31.4 (t), 34.5 (t), 34.6 (t), 38.3 (t), 38.4 (t), 41.6 (t), 41.8 (t), 71.97 (d), 72.01 (d), 111.4 (t), 111.7 (t), 125.7 (d), 128.3 (d), 128.35 (d), 128.36 (d), 128.38 (d), 142.5 (s), 142.7 (t), 147.8 (s), 147.9 (s); exact mass m/z calcd for $C_{32}H_{51}O_2Si$ 495.3653, found 495.3651; exact mass m/z calcd for $C_{32}H_{50}NaO_2Si$ (M + Na) 517.3472, found 517.3471.

(b) 2-Methyl-8-phenyl-3-(2-phenylethyl)oct-1-ene-3,6-diol (45b). Bu_4NF (1.0 M in THF, 0.163 mL, 0.163 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **45a** (0.0230 g,

(27) Bräse, S.; Waegell, B.; de Meijere, A. *Synthesis* **1998**, *2*, 148–152.

0.0465 mmol) in dry THF (6 mL). The cooling bath was left in place but not recharged, and stirring was continued for 19 h. The mixture was then quenched with water (5 mL) and extracted with EtOAc. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.4 × 15 cm), using EtOAc−petroleum ether mixtures from 20% to 100%, gave **45b** (0.0154 g, 98%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, microscope) 3381, 3085, 3062, 3026, 3001, 2943, 2861, 1946, 1870, 1805, 1707, 1643, 1604, 1584, 1496, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.35−1.74 (m, 2 H), 1.74 (dd, J = 1.5, 0.7 Hz, 1.8 H), 1.76 (dd, J = 1.5, 0.7 Hz, 1.2 H), 1.77−1.95 (m, 6 H), 2.15−2.40 (br s, 2 H), 2.46−2.56 (m, 1 H), 2.61−2.73 (m, 2 H), 2.74−2.84 (m, 1 H), 3.57−3.65 (m, 0.6 H), 3.65−3.72 (m, 0.4 H), 4.99−5.02 (m, 0.4 H), 5.02−5.04 (m, 0.6 H), 5.07−5.08 (m, 0.4 H), 5.10−5.12 (m, 0.6 H), 7.16−7.23 (m, 6 H), 7.25−7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.80 (q), 19.82 (q), 29.8 (t), 29.9 (t), 31.1 (t), 31.3 (t), 32.1 (t), 32.2 (t), 35.0 (t), 36.4 (t), 38.9 (t), 39.5 (t), 41.7 (t), 41.9 (t), 71.07 (d), 72.14 (d), 77.7 (s), 77.8 (s), 111.7 (t), 112.1 (t), 125.76 (d), 125.78 (d), 125.8 (d), 125.9 (d), 128.3 (d), 128.37 (d), 128.41 (d), 141.97 (s), 142.02 (s), 142.4 (s), 142.5 (s), 147.7 (s), 147.8 (s); exact mass m/z calcd for $C_{23}H_{30}NaO_2$ (M + Na) 361.2138, found 361.2136.

(c) 6-Hydroxy-7-methyl-1-phenyl-6-(2-phenylethyl)oct-7-en-3-one (45c). $(COCl)_2$ (0.025 mL, 0.28 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of DMSO (0.0399, 0.562 mmol) in CH_2Cl_2 (3 mL). After 10 min, a solution of **45a** (0.0123 g, 0.0363 mmol) in CH_2Cl_2 (1 mL) was added dropwise. After a further 40 min, Et_3N (0.10 mL, 0.73 mmol) was added dropwise, and stirring was continued for 10 min. The mixture was then stored at −20 °C (freezer) for 12 h and then warmed to 0 °C. Water (10 mL) was added, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (0.7 × 16 cm), using EtOAc−petroleum ether mixtures from 2% to 10% EtOAc, gave **45c** (0.0105 g, ca. 86%) as an impure oil that was used in the next step: FTIR (CH_2Cl_2, microscope) 3464, 3085, 3062, 3026, 2949, 2867, 1944, 1871, 1804, 1709, 1644, 1604, 1496, 1454 cm^{-1}; exact mass m/z calcd for $C_{23}H_{28}NaO_2$ (M + Na) 359.1982, found 359.1976.

(d) 2-Methyl-3,6-bis(2-phenylethyl)octa-1,7-diene-3,6-diol (45). MeLi (1.6 M in Et_2O, 0.24 mL, 0.39 mmol) was added dropwise to a stirred and cooled (0 °C) solution of tetravinyltin (0.018 mL, 0.096 mmol) in dry Et_2O (4 mL). After 30 min, the mixture was cooled to −78 °C, and a solution of **45c** (0.0081 g, 0.024 mmol) in Et_2O (1 mL plus 0.5 mL as a rinse) was added by cannula. The cold bath was left in place but not recharged, and stirring was continued for 12 h. The mixture was cooled to 0 °C and quenched with saturated aqueous NH_4Cl (5 mL), and the aqueous phase was extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.4 × 18 cm), using EtOAc−hexane mixtures from 2% to 20% EtOAc, gave **45** (0.0066 g, 75%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, cast microscope) 3427, 3085, 3062, 3026, 3003, 2949, 2863, 1945, 1869, 1805, 1709, 1643, 1604, 1496, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.48−1.72 (m, 4 H), 1.73 (dd, J = 1.5, 0.7 Hz, 1.1 H), 1.75 (dd, J = 1.6, 0.6 Hz, 1.9 H), 1.76−1.94 (m, 6 H), 2.45−2.53 (m, 1 H), 2.57−2.71 (m, 3 H), 4.98−5.10 (m, 2 H), 5.18−5.32 (m, 2 H), 5.78−5.90 (m, 1 H), 7.15−7.20 (m, 6 H), 7.25−7.29 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0 (q), 17.1 (q), 19.8 (t), 22.3 (t), 29.8 (t), 30.0 (t), 33.0 (t), 33.1 (t), 34.1 (t), 34.25 (t), 34.31 (t), 41.5 (t), 41.9 (t), 42.6 (t), 75.2 (s), 77.5 (s), 111.7 (t), 112.1 (t), 113.2 (t), 113.6 (t), 125.75 (d), 125.78 (d), 128.40 (d), 128.35 (d), 142.3 (s), 142.4 (s), 143.2 (s), 143.6 (s), 147.8 (s); exact mass m/z calcd for $C_{25}H_{32}NaO_2$ (M + Na) 387.2295, found 387.2293.

2-Methyl-1,4-bis(2-phenylethyl)benzene (47). Grubbs II catalyst[8] (0.0012 g, 0.0014 mmol) was added to a stirred solution of **45** (0.0020 g, 0.0055 mmol) in dry CH_2Cl_2 (2.5 mL) (N_2 atmosphere). After 15 h, the mixture was evaporated, and the residue (**46**) was dissolved in dry PhH (2 mL). $TsOH \cdot H_2O$ (0.0010 g, 0.0053 mmol) was added, and the mixture was refluxed for 30 min. Evaporation of the solvent and preparative thin layer chromatography of the residue over silica gel (plate 5 × 5 × 0.025 cm; 2% EtOAc−petroleum ether), gave **47** (0.0015 g, ca. 91%) containing minor impurities: FTIR (CH_2Cl_2, cast film) 3085, 3062, 3026, 2926, 2856, 1943, 1869, 1734, 1603, 1497, 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3 H), 2.84−2.94 (m, 8 H), 6.96−7.01 (m, 2 H), 7.06−7.11 (m, 1 H), 7.17−7.24 (6 H), 7.27−7.33 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.2 (q), 35.1 (t), 36.8 (t), 37.5 (t), 38.0 (t), 125.8 (d), 125.88 (d), 125.92 (d), 128.29 (d), 128.33 (d), 128.38 (d), 128.40 (d), 128.8 (d), 130.3 (d), 135.8 (s), 137.5 (s), 139.5 (s), 142.0 (s), 142.1 (s); exact mass m/z calcd for $C_{23}H_{24}$ 300.1878, found 300.1876.

2,7-Dimethyl-3,6-bis(2-phenylethyl)octa-1,7-diene-3,6-diol (48). Use of 2-Propenylmagnesium Bromide. Isopropenylmagnesium bromide (0.5 M in THF, 0.51 mL, 0.25 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **4** (0.0299 g, 0.102 mmol) in dry THF (5 mL). After 1 h, the dry ice bath was replaced by an ice bath, and another portion of isopropenylmagnesium bromide (0.5 M in THF, 0.51 mL, 0.25 mmol) was added dropwise. The ice bath was left in place but not recharged, and after 5 days, the mixture was cooled (0 °C) and quenched with water (10 mL). The aqueous phase was extracted with CH_2Cl_2, and the combined organic extracts were washed with brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (1.4 × 18 cm), using EtOAc−hexane mixtures from 5% to 40% EtOAc, gave **48** (0.0235 g, 61%) as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, microscope) 3435, 3085, 3062, 3026, 2929, 2855, 1942, 1870, 1804, 1727, 1643, 1604, 1496 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.52−1.58 (m, 1.5 H), 1.67−1.73 (m, 2.5 H), 1.75 (s, 2.5 H), 1.78 (s, 3.5 H), 1.81−1.97 (m, 6 H), 2.45−2.56 (m, 2 H), 2.62−2.72 (m, 2 H), 4.99−5.02 (m, 1.2 H), 5.03−5.06 (m, 0.8 H), 5.06−5.09 (m, 1.3 H), 5.12−5.14 (m, 0.7 H), 7.16−7.23 (m, 6 H), 7.26−7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.8 (q), 29.8 (t), 29.9 (t), 32.9 (t), 33.0 (t), 41.5 (t), 42.1 (t), 111.5 (s), 112.2 (s), 125.7 (d), 125.8 (d), 128.38 (d), 128.40 (d), 128.42 (d), 142.48 (s), 142.51 (s), 147.5 (t), 148.0 (t) (one signal not observed due to overlap); exact mass m/z calcd for $C_{26}H_{34}NaO_2$ (M + Na) 401.2451, found 401.2448.

Use of 2-propenyl-lithium. *t*-BuLi (1.7 M in pentane, 0.28 mL, 0.47 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of 2-bromopropene (0.021 mL, 0.237 mmol) in dry Et_2O (3 mL). After 30 min, a solution of **4** (0.0105 g, 0.0296 mmol) in Et_2O (0.5 mL plus 0.5 mL as a rinse) was added dropwise by cannula. After 3.5 h the dry ice bath was replaced by an ice bath that was left in place but not recharged, and stirring was continued for 17.5 h. The reaction mixture was cooled to 0 °C and quenched with saturated aqueous NH_4Cl (3 mL), and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (1.6 × 17 cm), using EtOAc−hexane mixtures from 2% to 10% EtOAc, gave **48** (0.0094 g, 72%) as an oil that was a mixture of diastereoisomers (^{13}C NMR).

2,3-Dimethyl-1,4-bis(2-phenylethyl)benzene (50). Schrock catalyst[11] (0.0053 g, 0.0069 mmol) and then PhH (3 mL) were added to **48** (0.0131 g, 0.0346 mmol) in a Pyrex bomb (10 mL) in a glovebox (N_2). The bomb was sealed, removed from the glovebox, and heated (ca. 80 °C) for 2.5 days. The mixture was cooled to room temperature and reintroduced into the glovebox, and a sample for TLC was removed. Little conversion to **49** had occurred. The contents of the bomb were transferred to a flask

with a reflux condenser sealed onto it, and additional Schrock catalyst (0.0053 g, 0.0069 mmol) was added. The reaction vessel was removed from the glovebox, and the mixture was refluxed (80 °C) under N_2 with frequent purging, resulting in a color change from yellow to amber after 1 h. After a further 18 h, the solution was cooled and evaporated. Flash chromatography of the residue over silica gel (1.3×11 cm), using EtOAc−petroleum ether mixtures from 5% to 100% EtOAc, gave an unidentifiable mixture (presumably containing **49**) that was dissolved in dry PhH (3 mL). $TsOH \cdot H_2O$ (0.0066 g, 0.035 mmol) was added, and the mixture was refluxed for 3 h and then evaporated. Flash chromatography of the residue over silica gel (1.4×18 cm), using EtOAc−hexane mixtures from 0% to 5% EtOAc, gave several fractions containing mostly impure **50**. The material was purified by preparative TLC (silica, 5×4.5×0.025 cm, 3 plates; 2% EtOAc−hexane) providing pure **50** (0.0072 g, 66%) as an oil: FTIR (CH_2Cl_2, microscope) 3085, 3061, 3025, 2961, 2928, 2868, 1943, 1869, 1801, 1735, 1704, 1678, 1603, 1582, 1540, 1496, 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.24 (s, 6 H), 2.91 (apparent s, 8 H), 7.11 (s, 2 H), 7.18−7.23 (m, 6 H), 7.27−7.34 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.6 (q), 37.3 (t), 37.8 (t), 125.7 (d), 128.09 (d), 128.13 (d), 128.17 (d), 128.24 (d), 131.8 (s), 139.1 (d), 141.7 (d); exact mass m/z calcd for $C_{24}H_{26}$ 314.2035, found 314.2031.

1,4-Diethenylcyclohexadecane-1,4-diol (51). MeLi (1.6 M in Et_2O, 0.97 mL, 1.6 mmol) was added dropwise to a stirred and cooled (0 °C) solution of tetravinyltin (0.070 mL, 1.32 mmol) in dry Et_2O (6 mL). After 1.5 h, the mixture was cooled to −78 °C and a solution of **26** (0.0122 g, 0.0483 mmol) in Et_2O (1.5 mL plus 1.5 mL as a rinse) was added by cannula. The cold bath was left in place but not recharged, and stirring was continued for 5 h. The mixture was quenched with saturated aqueous NH_4Cl (25 mL), and the aqueous phase was extracted with Et_2O. The combined organic extracts were washed with brine, dried (Na_2SO_4), and evaporated. Flash chromatography of the residue over silica gel (0.7 × 12 cm), using EtOAc−hexane mixtures from 20% to 30% EtOAc, gave **51** [0.0112 g, 75%; 87% corrected for recovered **26** (0.0017 g)] as an oil that was a mixture of diastereoisomers (^{13}C NMR): FTIR (CH_2Cl_2, microscope) 3339, 3089, 3010, 2981, 2928, 2856, 1846, 1641, 1457 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.28 (s, 2 H), 1.29−1.42 (m, 20 H), 1.48−1.59 (m, 8 H), 5.08 (dd, J = 10.8, 1.2 Hz, 2 H), 5.23 (dd, J = 17.4, 1.2 Hz, 2 H), 5.95 (dd, J = 17.4, 10.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.4 (t), 22.5 (t), 26.16 (t), 26.23 (t), 26.5 (t), 26.6 (t), 26.8 (t), 26.9 (t), 27.75 (t), 27.83 (t), 32.38 (t), 32.44 (t), 38.8 (t), 39.0 (t), 74.8 (s), 74.9 (s), 112.1 (t), 144.7 (d), 144.8 (d); exact mass m/z calcd for $C_{20}H_{36}NaO_2$ (M + Na) 331.2608, found 331.2610.

[12]Paracyclophane (53)[28]. Grubbs I catalyst (0.0027 g, 0.0032 mmol) was added to a stirred solution of **51** (0.0100 g, 0.0324 mmol) in dry CH_2Cl_2 (3 mL) (N_2 atmosphere). After 24 h, the reaction mixture was evaporated, and dry PhH (3 mL) was added. $TsOH \cdot H_2O$ (0.0019 g, 0.0097 mmol) was added, and the mixture was refluxed for 1 h, cooled, and partitioned between water and CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2 and hexane, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.4 × 6 cm), using EtOAc−petroleum ether mixtures from 0% to 2% EtOAc, gave **53** (0.0066 g, 83%) as an oil: FTIR (CH_2Cl_2, neat film microscope) 3006, 2926, 2855, 1898, 1510, 1460, 1444 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.75−0.82 (m, 4 H), 0.93−1.00 (m, 4 H), 1.02−1.12 (m, 8 H), 1.55−1.62 (m, 4 H), 2.60−2.63 (m, 4 H), 7.08 (s, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.4 (t), 26.6 (t), 27.4 (t), 27.5 (t), 29.8 (t), 35.2 (t), 128.8 (d), 140.0 (s); exact mass m/z calcd for $C_{18}H_{28}$ 244.2191, found 244.2188.

(28) Cram, D. J.; Allinger, N. L.; Steinberg, H. *J. Am. Chem. Soc.* **1954**, *76*, 6132–6141.

Methyl 7,8,10,11-Tetradeoxy-6,9-bis(ethenyl)-2,3,4-tris-*O*-methyl-11-phenyl-α-D-*gluco*-undecanopyranoside (54). Vinylmagnesium bromide (1.0 M in THF, 1.89 mL, 1.89 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **29** (74.3 mg, 0.189 mmol) in THF (3 mL). The cooling bath was left in place but not recharged, and stirring was continued for 7 h. The mixture was quenched with saturated aqueous NH_4Cl (3 mL) and extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.5×13 cm), using 40% EtOAc−hexanes, gave **54** (62.7 mg, 84%) as a mixture of two diastereoisomers (^{13}C NMR): FTIR ($CHCl_3$, microscope) 3453, 3086, 3061, 3025, 2931, 2837,1717, 1640, 1604, 1559, 1540, 1497, 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.56−1.92 (m, 6 H), 2.56 (s, 1 H), 2.60−2.77 (m, 2 H), 3.11−3.15 (m, 1 H), 3.25−3.29 (m, 1 H), 3.46 (s, 3 H), 3.51−3.59 (m, 8 H), 3.61 (s, 3 H), 4.47−4.63 (m, 1 H), 4.78 (d, J = 3.5 Hz, 1 H), 5.16−5.20 (m, 1 H), 5.28−5.36 (m, 2 H), 5.47−5.53 (m, 1 H), 5.78−5.95 (m, 2 H), 7.16−7.20 (m, 3 H), 7.26−7.29 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 30.07 (t), 30.09 (t), 31.3 (t), 33.4 (t), 33.5 (t), 43.2 (t), 43.7 (t), 55.7 (q), 55.8 (q), 59.0 (q), 60.03 (q), 60.05 (q), 60.7 (q), 72.0 (d), 72.6 (d), 74.6 (s), 74.8 (s), 76.9 (s), 77.0 (s), 81.7 (d), 81.8 (d), 82.1 (d), 84.0 (d), 97.37 (d), 97.44 (d), 113.0 (t), 113.2 (t), 115.0 (t), 115.5 (t), 125.55 (d), 125.63 (d), 128.29 (d), 128.34 (d), 128.39 (d), 140.0 (d), 140.4 (d), 142.8 (s), 143.0 (s), 143.8 (d), 143.9 (d); exact mass m/z calcd for $C_{25}H_{38}NaO_7$ (M + Na) 473.2510, found 473.2503.

1-(2-Phenethyl)-4-[(2*S*,3*S*,4*S*,5*R*,6*S*)-tetrahydro-3,4,5,6-tetramethoxypyran-2-yl]cyclohex-2-ene-1,4-diol (55). A solution of **54** (92.7 mg, 0.206 mmol) in CH_2Cl_2 (6 mL) was degassed for 30 min with a stream of Ar. Grubbs II catalyst[8] (26.2 mg, 0.03 mmol) was added, and the Ar stream was continued for 15 min. The mixture was stirred and refluxed for 24 h under a static pressure of Ar and then cooled and evaporated. Flash chromatography of the residue over silica gel (1.5×13 cm), using first Et_2O and then EtOAc, gave **55** as a mixture of diastereoisomers [25.1 mg, 29% less polar diastereoisomer; 60.0 mg, 69% more polar diastereoisomer (98% overall)]. The less polar diastereoisomer (small impurity signals in the ^1H and ^{13}C NMR spectra): FTIR ($CHCl_3$, microscope) 3458, 3061, 3026, 2933, 2835, 2247, 1603, 1497, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.52 (d, J = 1.0 Hz, 1 H), 1.62 (s, 1 H), 1.71−2.01 (m, 4 H), 2.15 (t, J = 13.0 Hz, 1 H), 2.28 (t, J = 13.0 Hz, 1 H), 2.78−2.90 (m, 2 H), 3.25−3.28 (m, 1 H), 3.42 (t, J = 9.2 Hz, 1 H), 3.51−3.53 (m, 4 H), 3.60−3.71 (m, 10 H), 4.90 (d, J = 2.0 Hz, 1 H), 5.93 (s, 2 H), 7.25−7.30 (m, 3 H), 7.35−7.38 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.2 (t), 30.1 (t), 31.4 (t), 44.3 (t), 55.8 (q), 59.2 (q), 60.3 (q), 61.1 (q), 69.5 (s), 70.5 (s), 73.7 (d), 80.6 (d), 82.1 (d), 84.5 (d), 97.6 (d), 126.0 (d), 128.6 (d), 128.7 (d), 131.0 (d), 135.2 (d), 142.6 (s); exact mass m/z calcd for $C_{23}H_{34}NaO_7$ (M + Na) 445.2197, found 445.2192.

The more polar diastereoisomer: FTIR ($CHCl_3$, microscope) 3441, 3061, 3026, 2934, 2835, 2248, 1603, 1497, 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.74−2.07 (m, 7 H), 2.71−2.77 (m, 2 H), 3.16 (dd, J = 3.6, 9.6 Hz, 1 H), 3.28−3.34 (m, 2 H), 3.40 (s, 3 H), 3.50−3.56 (m, 5 H), 3.59 (s, 3 H), 3.62 (s, 3 H), 4.78 (d, J = 3.6 Hz, 1 H), 5.81 (AB q, J = 10.3, $\Delta\nu_{AB}$ = 7.4 Hz, 2 H), 7.15−7.20 (m, 3 H), 7.25−7.30 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.1 (t), 30.4 (t), 32.7 (t), 42.6 (t), 55.6 (q), 59.2 (q), 60.3 (q), 61.1 (q), 70.5 (s), 71.1 (s), 73.9 (d), 80.5 (d), 82.0 (d), 84.7 (d), 97.5 (d), 126.0 (d), 128.6 (d), 128.7 (d), 131.1 (d), 135.9 (d), 142.7 (s); exact mass m/z calcd for $C_{23}H_{34}NaO_7$ (M + Na) 445.2197, found 445.2195.

Methyl (5*R*)-2,3,4-Tri-*O*-methyl-5-*C*-[4-(2-phenethyl)phenyl]-α-D-*gluco*-pyranoside (56). (a) $POCl_3$ (0.22 mL, 2.34 mmol) was added dropwise to a stirred and cooled (0 °C) solution of the less polar diastereoisomer of **55** (19.3 mg, 0.0457 mmol) in pyridine (0.86 mL), and stirring was continued for 4 h. The ice bath was left in place but not recharged, and stirring was continued for 7.5 h.

Water (0.5 mL) was added, and the mixture was extracted with Et_2O. The combined organic extracts were washed with 10% hydrochloric acid, saturated aqueous $NaHCO_3$, water and brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (0.6 × 8 cm), using 23% EtOAc−hexanes, gave **56** (15 mg, 85%) as a thick oil: $[\alpha]^{20}_D$ 92.06 (*c* 1.22, $CHCl_3$); FTIR ($CHCl_3$, microscope) 3060, 3027, 2980, 2931, 2858, 2832, 1604, 1516, 1496, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.95 (s, 4 H), 3.06 (s, 3 H), 3.12 (dd, J = 9.0, 9.8 Hz, 1 H), 3.37 (dd, J = 3.8, 9.4 Hz, 1 H), 3.45 (s, 3 H), 3.60 (s, 3 H), 3.63 (t, J = 9.2 Hz, 1 H), 3.67 (s, 3 H), 4.44 (d, J = 9.6 Hz, 1 H), 4.92 (d, J = 3.6 Hz, 1 H), 7.18−7.23 (m, 5 H), 7.26−7.31 (m, 2 H), 7.34−7.36 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.9 (t), 38.1 (t), 55.6 (q), 59.4 (q), 60.6 (q), 61.3 (q), 72.9 (d), 82.1 (d), 83.5 (d), 86.0 (d), 98.1 (d), 126.2 (d), 127.9 (d), 128.6 (d), 128.7 (d), 128.8 (d), 136.7 (s), 141.9 (s), 142.1 (s); exact mass m/z calcd for $C_{23}H_{30}NaO_5$ (M + Na) 409.1985, found 409.1984.

(b) $POCl_3$ (0.53 mL, 5.69 mmol) was added dropwise to a stirred and cooled (0 °C) solution of the more polar diastereoisomer of **55** (47 mg, 0.11 mmol) in pyridine (2 mL), and stirring was continued for 4 h. The ice bath was left in place but not recharged, and stirring was continued for 7.5 h. Water (1 mL) was added, and the mixture was extracted with Et_2O. The combined organic extracts were washed with 10% hydrochloric acid, saturated aqueous $NaHCO_3$, water, and brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1 × 8 cm), using 23% EtOAc−hexanes, gave **56** (36.1 mg, 84%) as a thick oil.

3,6-Bis[(2*S*,3*S*,4*S*,5*R*,6*S*)-tetrahydro-3,4,5,6-tetramethoxypyran-2-yl]octa-1,7-diene-3,6-diol (57). (a) Methyl 7,8-Dideoxy-2,3,4-tri-*O*-methyl-α-D-*gluco*-oct-7-ynopyranoside (57a). A solution of ethynylmagnesium bromide (0.5 M in THF, 15 mL, 7.5 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of crude 2,3,4-tri-*O*-methyl-α-D-*gluco*-hexodialdo-1,5-pyranoside[24] (540 mg, 2.31 mmol) in THF (20 mL) (Ar atmosphere). The cold bath was left in place but not recharged, and stirring was continued for 18 h. The yellow solution was then quenched with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.5 × 15 cm), using 50% EtOAc−hexanes, gave **57a** (304.8 mg, 51%) as an light yellow oil that was a mixture of two diastereoisomers (^{13}C NMR): FTIR ($CHCl_3$, microscope) 3418, 3252, 2982, 2934, 2837, 2249, 2114, 1740, 1670, 1466, 1466 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.46−2.54 (m, 1 H), 2.65 (d, J = 10.5 Hz, 1 H), 3.17−3.26 (m, 1 H), 3.33 (dd, J = 9.2, 9.7 Hz, 1 H), 3.42−3.44 (m, 3 H), 3.51−3.72 (m, 11 H), 4.56−4.67 (m, 1 H), 4.86−4.88 (m, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.1 (q), 55.3 (q), 59.1 (q), 60.6 (q), 60.8 (q), 60.9 (q), 61.3 (q), 62.4 (q), 71.8 (d), 71.9 (d), 73.1 (d), 74.8 (d), 79.3 (d), 81.0 (d), 81.8 (d), 82.7 (s), 83.4 (d), 83.6 (d), 97.55 (d), 97.59 (d); exact mass m/z calcd for $C_{12}H_{20}NaO_6$ (M + Na) 283.1152, found 283.1152.

(b) 1,4-Bis[(2*R*,3*S*,4S,5*R*,6*S*)-tetrahydro-3,4,5,6-tetramethoxypyran-2-yl]but-2-yne-1,4-diol (57b). BuLi (2.5 M in hexanes, 0.7 mL, 1.75 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **57a** (228 mg, 0.877 mmol) in THF (8 mL). After 1.5 h, freshly prepared crude methyl 2,3,4-tri-*O*-methyl-α-D-glucohexodialdo-1,5-pyranoside[24] (133.4 mg, 0.57 mmol) in THF (1 mL) was added dropwise. The cooling bath was left in place but not recharged, and stirring was continued for 40 h. The mixture was quenched with saturated aqueous NH_4Cl (8 mL) and extracted with EtOAc. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.5 × 15 cm), using 50% EtOAc−hexanes and then MeOH−EtOAc (3:100), gave **57b** (174 mg, 61% or 72%, based on recovered starting material) as a white solid that was a mixture of diastereoisomers (^{13}C NMR): FTIR ($CHCl_3$, microscope) 3433, 2934, 2836, 2249, 1466, 1446 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.63−2.75 (m, 2 H), 3.13−3.26 (m, 2 H), 3.28−3.46 (m, 8 H), 3.47−3.74 (m, 22 H), 4.59−4.69 (m, 2 H), 4.79−4.83 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.2 (q), 55.3 (q), 59.1 (q), 60.60 (q), 60.63 (q), 60.72 (q), 60.78 (q), 60.82 (q), 60.85 (q), 61.4 (q), 61.7 (q), 62.5 (q), 62.6 (q), 70.6 (d), 71.7 (d), 71.9 (d), 72.0 (d), 72.3 (d), 79.3 (d), 79.4 (d), 79.6 (d), 81.0 (d), 81.1 (d), 81.6 (d), 81.7 (d), 81.8 (d), 82.2 (s), 83.4 (d), 83.6 (d), 83.9 (s), 85.5 (s), 97.5 (d), 97.6 (d); exact mass m/z calcd for $C_{22}H_{38}NaO_{12}$ (M + Na) 517.2255, found 517.2259.

(c) 1,4-Bis[(2*R*,3*S*,4*S*,5*R*,6*S*)-tetrahydro-3,4,5,6-tetramethoxypyran-2-yl]butane-1,4-diol (57c). $Pd(OH)_2$−C (20% w/w, 23 mg) was added to a solution of **57b** (58.4 mg, 0.118 mmol) in MeOH (1.5 mL), and the mixture was stirred under H_2 (balloon) for 2 h and then filtered through Celite, using EtOAc as a rinse. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.2 × 15 cm), using EtOAc and then MeOH−EtOAc (3:50), gave **57c** (35.2 mg, 60%) as a white solid that was a mixture of diastereoisomers (^{13}C NMR): FTIR ($CHCl_3$, microscope) 3472, 2935, 2835, 2248, 1445, 1379 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.50−1.94 (m, 4 H), 2.38 (s, 1 H), 3.12−3.17 (m, 3 H), 3.26−3.31 (m, 2 H), 3.35−3.40 (m, 7 H), 3.46−3.53 (m, 9 H), 3.56−3.63 (m, 12 H), 3.80 (d, J = 3 Hz, 2 H), 4.72−4.80 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.1 (t), 30.5 (t), 32.0 (t), 55.2 (q), 55.3 (q), 58.9 (q), 59.0 (q), 60.2 (q), 60.7 (q), 60.8 (q), 69.2 (d), 69.4 (d), 71.1 (d), 71.6 (d), 72.2 (d), 72.5 (d), 73.2 (d), 79.5 (d), 81.7 (d), 82.0 (d), 82.6 (d), 83.6 (d), 83.8 (d), 97.3 (d), 97.6 (d); exact mass m/z calcd for $C_{22}H_{42}NaO_{12}$ (M + Na) 521.2568, found 521.2568.

(d) 1,4-Bis[(2*S*,3*S*,4*S*,5*R*,6*S*)tetrahydro-3,4,5,6-tetramethoxypyran-2-yl]butane-1,4-dione (57d). DMSO (0.04 mL, 0.564 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to a stirred and cooled (−78 °C) solution of $(COCl)_2$ (0.023 mL, 0.266 mmol) in CH_2Cl_2 (0.5 mL). After 15 min, a solution of **57c** (50.0 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise and stirring at −78 °C was continued for 35 min. Then Et_3N (0.08 mL) was added dropwise, and stirring was continued at −78 °C for 5 min. The cooling bath was removed, stirring was continued for 25 min, and water (2 mL) was added. The organic layer was separated, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.2 × 15 cm), using 75% EtOAc−hexanes, gave **57d** (47.6 mg, 96%) as a colorless oil: $[\alpha]_D^{20}$ 132.8 (*c* 1.32, $CHCl_3$); FTIR ($CHCl_3$, cast microscope) 2935, 2836, 1726, 1466, 1446 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.79−2.87 (m, 2 H), 2.97−3.05 (m, 2 H), 3.21 (dd, J = 3.5, 9.5 Hz, 2 H), 3.28 (dd, J = 8.5, 10.0 Hz, 2 H), 3.44 (s, 6 H), 3.51−3.56 (m, 14 H), 3.62 (s, 6 H), 4.06 (d, J = 10.0 Hz, 2 H), 4.85 (d, J = 4.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.2 (t), 55.9 (q), 59.4 (q), 60.8 (q), 61.2 (q), 74.1 (d), 81.0 (d), 81.5 (d), 83.8 (d), 98.2 (d), 205.4 (s); exact mass m/z calcd for $C_{22}H_{38}NaO_{12}$ (M + Na) 517.2255, found 517.2265.

3,6-Bis[(2*S*,3*S*,4*S*,5*R*,6*S*)-tetrahydro-3,4,5,6-tetramethoxypyran-2-yl]octa-1,7-diene-3,6-diol (57). Vinylmagnesium bromide (1.0 M in THF, 1.1 mL, 1.10 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **57d** (55.7 mg, 0.11 mmol) in THF (1 mL). The cooling bath was left in place but not recharged, and stirring was continued for 16 h. The mixture was then quenched with saturated aqueous NH_4Cl (1 mL) and extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.2 × 15 cm), using 67% EtOAc−hexanes, gave **57** (63.0 mg, ca. 100%) as a mixture of diastereoisomers (^{13}C NMR) that contained some impurities (^1H NMR). The NMR spectra were too complicated to be of diagnostic value: exact mass m/z calcd for $C_{26}H_{46}NaO_{12}$ (M + Na) 573.2881, found 573.2880.

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Supporting Information Available: General experimental techniques and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.