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Sulfonyl-Stabilized Oxiranyllithium-Based Approach to Polycyclic Ethers. Convergent Synthesis of the ABCDEF-Ring System of Yessotoxin and Adriatoxin

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Convergent synthesis of the ABCDEF-ring system of yessotoxin and adriatoxin, marine polycyclic ether toxins causative of diarrheic shellfish poisoning, has been accomplished. The A-ring fragment was constructed by coupling of an appropriately functionalized sulfonyl-stabilized oxiranyl anion and a triflate prepared from an erythritol derivative. An iterative protocol of the oxiranyl anion strategy was also applied for the construction of the DEF-ring fragment. The triflate derivatives of the A-ring and the DEF-ring fragments were connected with lithium acetylide. The resulting acetylene derivative was further transformed into the hexacyclic ABCDEF fragment via oxidation of the acetylene unit to 1,2-diketone, double methyl acetal formation, and reductive etherification.

Introduction

Yessotoxin (**1**, YTX) is a unique polycyclic ether isolated as one of the causative toxins of diarrheic shellfish poisoning from the digestive glands of scallops, *Patinopecten yessoensis*, infested by toxic dinoflagellates in Japan,[1] and *Protoceratium reticulatum* was identified as the biogenetic origin of YTX.[2] The relative stereochemistry was assigned by extensive NOE studies[3] and the absolute configuration was determined by an NMR method, using a chiral anisotropic reagent.[4] Recently, adriatoxin (**2**, ATX), a new analogue of YTX, was isolated from the mussels, *Mytilus galloprovincialis*, which caused diarrheic shellfish poisoning in Italy.[5] Structurally, YTX bears a triene side chain and two sulfate ester groups on a trans-fused undecacyclic ether ring system. The polycyclic skeleton of ATX is identical with that of the A−J ring system of YTX but lacks the K-ring with a side chain containing three olefinic bonds. The occurrence of a wide variety of yessotoxin analogues, such as 45-hydroxy-YTX,[6] 45,46,47-trinorYTX,[7] homoYTX,[8] 1-desulfoYTX,[9] and carboxyYTX,[10] has also been confirmed from scallops and mussels. As these toxins showed potent mouse lethality,[11] contamination of bivalves by YTXs and ATX poses a problem worldwide to human health,[12] as well as to the shellfish industry.

Their impressive molecular architectures and biological activities have made them challenging synthetic targets, and efforts toward the synthesis of polycyclic ether frameworks of YTX and ATX have been reported by us[13] and by Nakata.[14] Recently, we have demonstrated an iterative linear synthesis of the ABCDEF-ring system by repeated coupling of sulfonyl-substituted oxiranes as building blocks.[15] Although the synthesis is conceptually very simple and efficient, the lengthy approach prompted us to pursue an alternative convergent approach to the ABCDEF-ring system. In this paper, we describe full details of a convergent synthesis of the ABCDEF fragment **3** of YTX and ATX, taking advantage of the rapid assembly of two stereochemically advanced fragments.

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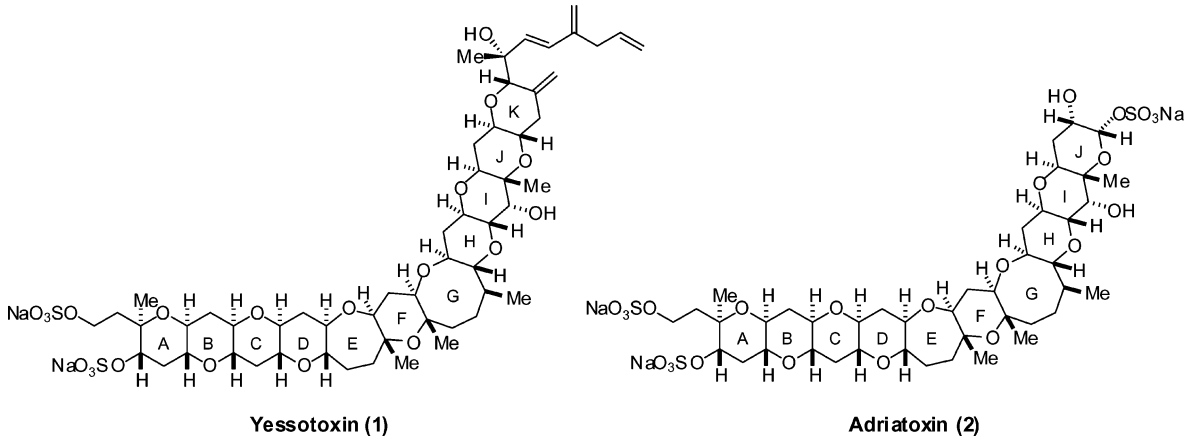

FIGURE 1. Structures of yessotoxin and adriatoxin.

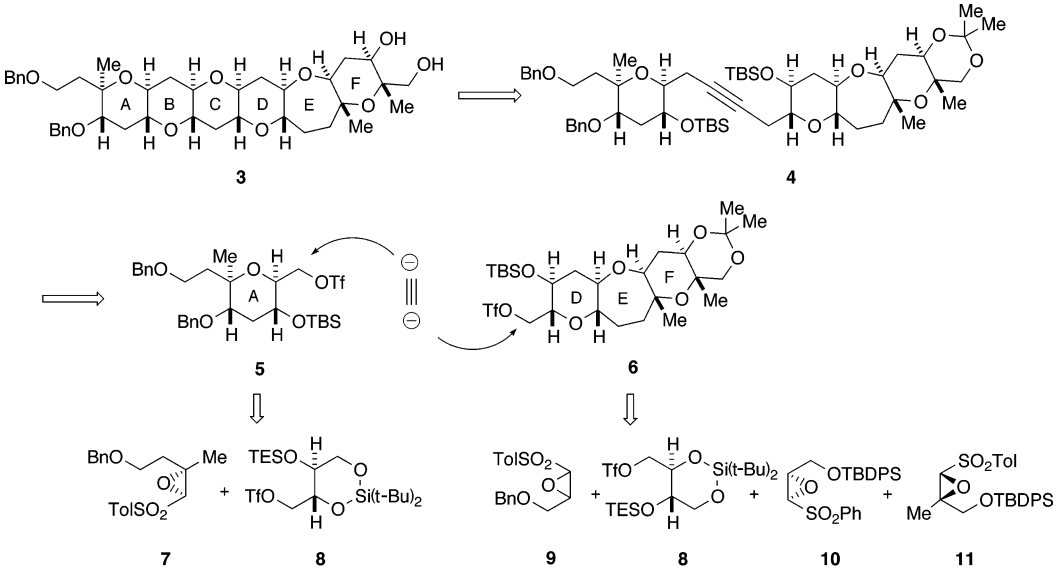

FIGURE 2. Retrosynthetic analysis of the ABCDEF-ring fragment of yessotoxin and adriatoxin.

The strategy for the synthesis of **3** is shown in Figure 2, which involves the assembling of the A-ring fragment **5** and the DEF-ring fragment **6** with acetylene to alkyne **4**. The conversion of **4** to **3** requires (i) oxidation of a triple bond to a 1,2-diketone, (ii) double acetal-ring formation, and (iii) reductive etherification of the acetal rings. This idea of a convergent approach has been reported independently by three groups, including our laboratory, at almost the same time.[16−18] In turn, fragments **5** and **6** could be prepared by an oxirany anion strategy developed in our laboratory[19] with use of appropriately functionalized epoxy sulfones **7**, **9**, **10**, and **11** and triflate **8**, in which alkylation of a sulfonyl-stabilized oxiranyl anion and the subsequent 6-endo cyclization of a hydroxy epoxide are employed as key reactions.

Results and Discussion

Synthesis of the A-Ring Fragment. Synthesis of the A-ring started from the coupling reaction of the oxiranyl anion generated from epoxy sulfone **7** and triflate **8** (Scheme 1). The chiral trisubstituted epoxy sulfone **7** was synthesized from (*R*)-(−)-1-chloromethyl *p*-tolyl sulfoxide and 4-benzyloxybutan-2-one according to the reported procedure,[20] and triflate **8** was prepared from the 1,3-*O*-di-*tert*-butylsilylene-D-erythritol derivative.[21] Alkylation of the oxiranyl anion generated from **7** with **8** was carried out by an internal quenching method to prevent decomposition of the unstable oxiranyl anion.[22] Thus, treatment of a mixture of **7** and **8** with *n*-BuLi in THF in the presence of HMPA at −100 °C gave epoxy sulfone **12** in 81% yield. Cyclization proceeded smoothly when **12** was

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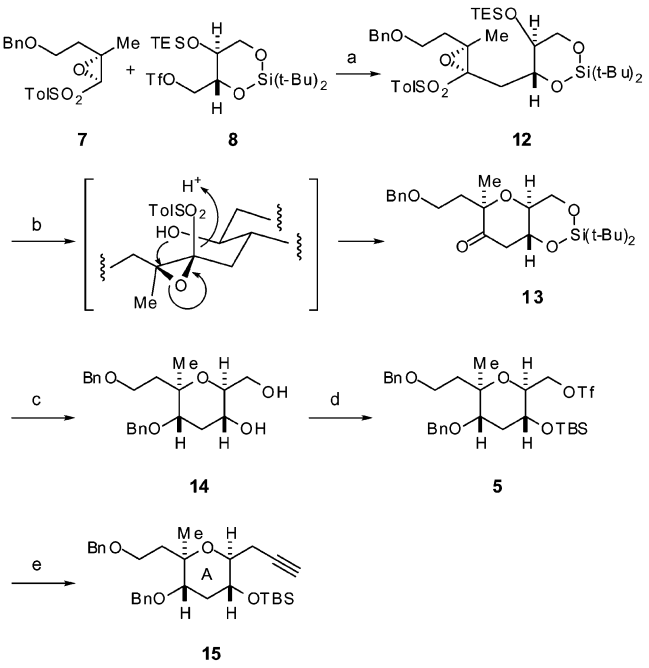
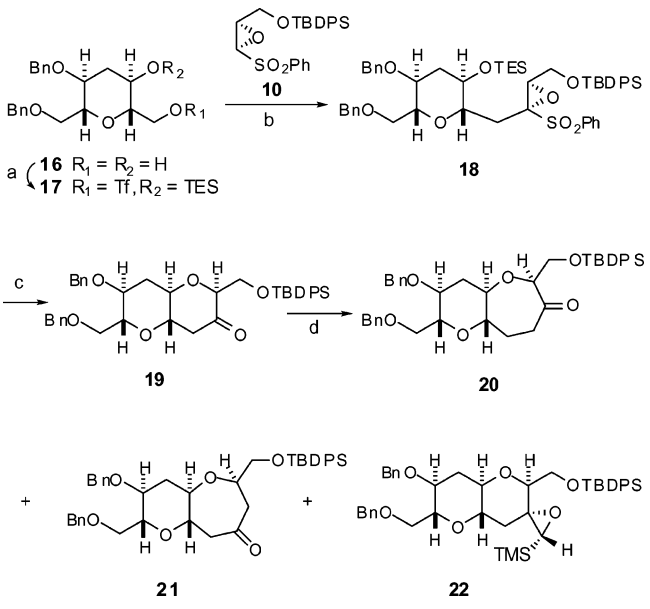
SCHEME 1[a]



[a] Conditions: (a) *n*-BuLi, THF, HMPA, −100 °C, 81%; (b) TsOH·H_2O, $CHCl_3$, 0 °C, 93%; (c) (i) $NaBH_4$, MeOH−CH_2Cl_2, −78 °C, 99%; (ii) KHMDS, BnBr, THF, rt, 100%; (iii) TBAF, THF, rt, 100%; (d) Tf_2O, 2,6-lutidine, CH_2Cl_2, −78 °C, 30 min, then TBSOTf, 88%; (e) (i) TMS−acetylene, *n*-BuLi, THF, HMPA, −78 °C, 95%, (ii) K_2CO_3, MeOH, rt, 96%.

SCHEME 2[a]



[a] Conditions: (a) Tf_2O, 2,6-lutidine, THF, −78 °C, 30 min, then TESOTf, 82%; (b) *n*-BuLi, THF, HMPA, −100 °C, 89%; (c) TsOH·H_2O, $CHCl_3$, 55 °C, 82%; (d) (i) Me_3SiCHN_2, BF_3·OEt_2, CH_2Cl_2, −78 °C; (ii) PPTS, MeOH, rt, 60% for **20**, 3% for **21**, 18% for **22**.

exposed to TsOH·H_2O in $CHCl_3$ at 0 °C. Under these conditions, detriethylsilylation and the subsequent stereospecific 6-endo cyclization of the resulting 4,5-epoxy alcohol led to the formation of ketone **13** in 93% yield. The reaction temperature of the 6-endo cyclization of **12** was critical because elevated temperatures induced a 1,2-sulfonyl shift of the epoxy sulfone moiety,[23] rather than 6-endo cyclization, to give the corresponding α-sulfonyl ketone as a byproduct. The stereochemistry of **13** was established by NOE experiments as shown in Figure 3. Stereoselective reduction with $NaBH_4$ at −78 °C gave an equatorial alcohol as the sole product, and the subsequent *O*-benzylation with benzyl bromide and KHMDS in THF and deprotection of the silylene group with TBAF gave the A-ring diol **14**. A one-pot double protection of **14** was effected by selective triflation of the primary alcohol with 1 equiv of triflic anhydride followed by silylation of the secondary alcohol with TBSOTf, affording **5** in 88% yield. Reaction of triflate **5** with lithium trimethylsilylacetylide in THF at −78 °C in the presence of HMPA and removal of the TMS group with K_2CO_3 in MeOH provided the A-ring acetylene **15** in 91% overall yield.

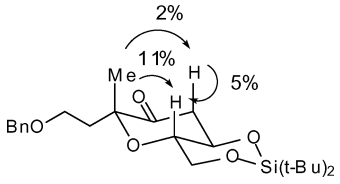


FIGURE 3. NOE correlation of **13**.

Synthesis of the DEF-Ring Fragment. Synthesis of the other coupling partner **6** started from the readily available diol **16**[21] as shown in Scheme 2. Diol **16** was transformed into triflate **17** by regioselective *O*-triflation and *O*-silylation by a one-pot procedure. The coupling reaction of triflate **17** and the oxiranyllithium generated from **10**[24] in THF−HMPA at −100 °C by an in situ quenching method afforded epoxy sulfone **18** in 89% yield. Deprotection of the triethylsilyl group of **18** and 6-endo cyclization of the resulting epoxy alcohol were carried out by heating **18** with TsOH·H_2O in $CHCl_3$ at 55 °C to give ketone **19** in 82% yield. In contrast to the case of **12**, heating was necessary to induce 6-endo cyclization because the oxirane ring of **18** is less reactive than that of **12**, which is activated by the presence of a methyl group.[25] Fortunately, the 1,2-migration of the sulfonyl group was not observed in this case. The oxepane formation was accomplished by one-carbon homologation of a keto tetrahydropyran. Thus, **19** was treated with trimethylsilyldiazomethane[24,26] in the presence of BF_3·OEt_2 at −78 °C and the resulting β-keto silane was subjected to protonolysis with PPTS in MeOH, affording the seven-membered ketone **20** in 60% yield along with its regioisomeric ketone **21** in 3% yield and epoxide **22** in 18% yield. The stereochemistry of the spiro-epoxide **22** was established by NOE experiments (Figure 4).

To construct a tertiary alcohol on the E-ring, direct methylation of **20** with MeMgBr, MeLi, and Me_3Al was first examined. However, the major product was a

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(24) Mori, Y.; Yaegashi, K.; Furukawa, H. *Tetrahedron* **1997**, *53*, 12917−12932. Epoxy sulfone **10** was prepared from (*R*)-*O*-isopropylideneglyceraldehyde.

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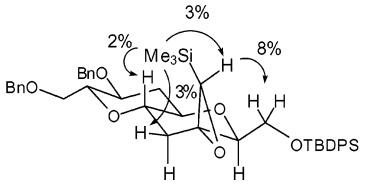
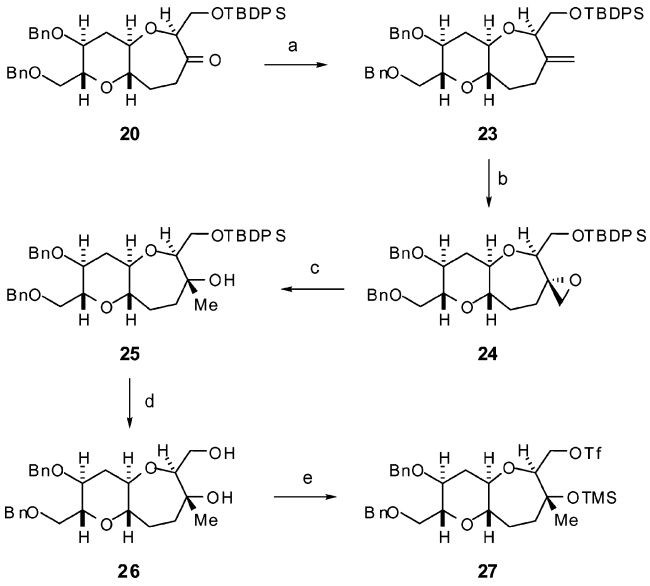


FIGURE 4. NOE correlation of **22**.

compound methylated undesirably from the less-hindered α-side. Then, stereocontrolled installation of a methyl group in this seven-membered ketone was accomplished via a spiro-epoxide intermediate in a stepwise manner (Scheme 3). Olefination of **20** with methylenetriphenylphosphorane in THF gave olefin **23**. Epoxidation with *m*-CPBA in toluene resulted in the formation of a 3:1 mixture of diastereomers and the desired α-epoxide **24** was obtained as a major product in 65% yield. To improve the diastereoselectivity, epoxidation with dioxiranes[27] was then examined. The dioxirane-mediated epoxidation is known to proceed through a spiro transition state[28] and, therefore, is more sensitive to the steric environment than other epoxidizing reagents such as *m*-CPBA. In the event, substantial improvement of the diastereomeric ratio was observed when the epoxidation was carried out with the phenyl(trifluoromethyl)dioxirane generated in situ from trifluoroacetophenone−Oxone[29] in MeCN−CH_2Cl_2−H_2O. This procedure gave a 9:1 mixture of products, but the desired α-epoxide **24** was isolated only in 52% yield. The moderate yield was due to an unexpected partial cleavage of the benzyl group of the primary or secondary alcohol (35% combined yield). Subsequent reduction of the epoxide with lithium triethylborohydride gave a tertiary alcohol **25** with the correct stereochemistry. Removal of the TBDPS group with TBAF produced diol **26**, which was converted into triflate **27** by *O*-triflation and *O*-silylation in one pot.

Construction of the F-ring is a challenging synthetic issue because it contains sterically congested 1,3-diaxial methyl groups adjacent to the ring oxygen, and requires the assembly of **27** and the methyl-substituted epoxy sulfone **11** (Scheme 4). This chiral epoxy sulfone was prepared from 1-*tert*-butyldiphenylsilyloxy-propan-2-one and (*S*)-(+)-1-chloromethyl *p*-tolyl sulfoxide according to the reported procedure.[20] The coupling reaction was performed by adding *n*-BuLi to a solution of triflate **27** and epoxy sulfone **11** in THF−HMPA at −100 °C, providing **28** in 90% yield. Stereocontrolled 6-endo cyclization was successfully achieved with the method previously reported from our laboratory.[25] Treatment of **28** with BF_3·OEt_2 at room temperature effected the F-ring formation to afford the tricyclic ketone **29** in 90% yield as a single isomer. Reduction of the ketone with $NaBH_4$ in methanol−dichloromethane gave alcohol **30** as the sole product. The stereochemistry of the diaxial methyl groups

SCHEME 3[a]



[a] Conditions: (a) $Ph_3P^+CH_3Br^-$, KHMDS, THF, −78 to 0 °C, 91%; (b) *m*-CPBA, $NaHCO_3$, toluene, 65%; (c) $LiBHEt_3$, THF, 0 °C, 96%; (d) TBAF, THF, rt, 100%; (e) Tf_2O, 2,6-lutidine, THF, −78 °C, 30 min, then TMSOTf, 99%.

of **30** was confirmed at this stage by NOE experiments, in which 6% of NOE was observed between the two methyl groups. The TBDPS ether in **30** was cleaved with TBAF and the resulting diol was protected with 2,2-dimethoxypropane to form acetonide **31**. For the synthesis of key fragment **6**, the two benzyl groups were removed by hydrogenolysis with $Pd(OH)_2$/C in THF to give diol **32**, which was then converted into the TBS-protected triflate **6** by regioselective *O*-triflation of the primary alcohol and *O*-*tert*-butyldimethylsilylation of the secondary alcohol with TBSOTf in one pot.

Synthesis of the ABCDEF-Ring. Convergent synthesis of the target molecule **3** is shown in Scheme 5. Treatment of a mixture of triflate **6** and acetylene **15** in THF at −78 °C with *n*-BuLi afforded the disubstituted acetylene **4** in 80% yield. Direct oxidation of the acetylene to the corresponding 1,2-diketone was achieved according to the reported procedure.[30] Thus, treatment of **4** with RuO_2−$NaIO_4$ provided a yellow diketone **33** in 80% yield. Heating of the diketone with CSA in methanol and trimethyl orthoformate at 80 °C led to desilylation, intramolecular double acetalization, and removal of the acetonide group, giving the hexacyclic diol **34** as a major product along with two other stereoisomers of the methoxy groups in 87% yield (8:1:1 ratio). Finally, reduction of the acetal mixture with Et_3SiH in the presence of TMSOTf at 0 °C completed the synthesis of the ABCDEF fragment **3** in 70% yield, which was identical with the sample synthesized by the iterative linear route[15] by ^1H NMR, ^{13}C NMR, and IR analysis.

Conclusion

In summary, a rapid entry to the construction of the ABCDEF-ring of yessotoxin and adriatoxin has been

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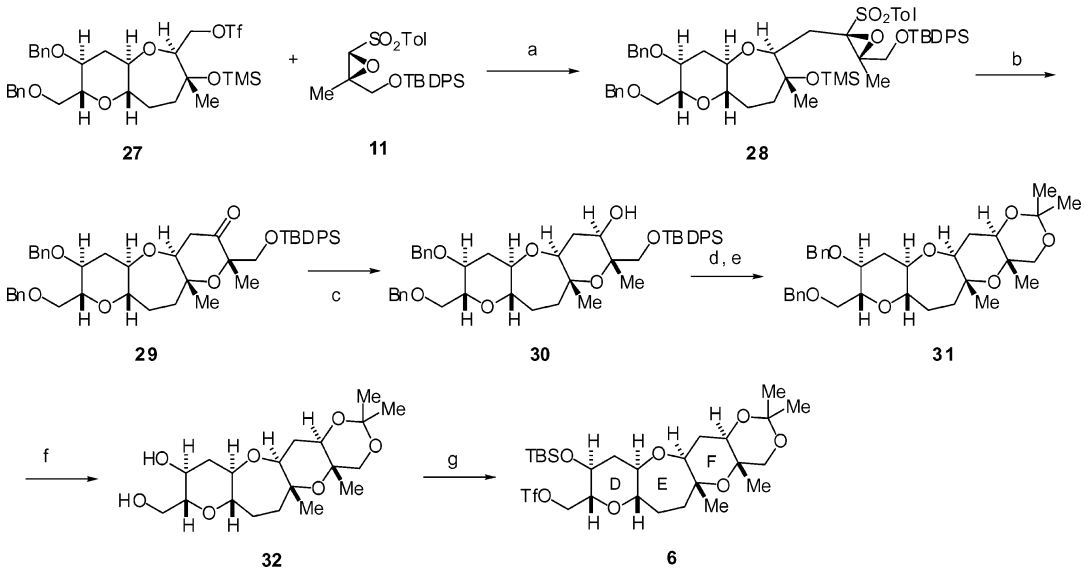
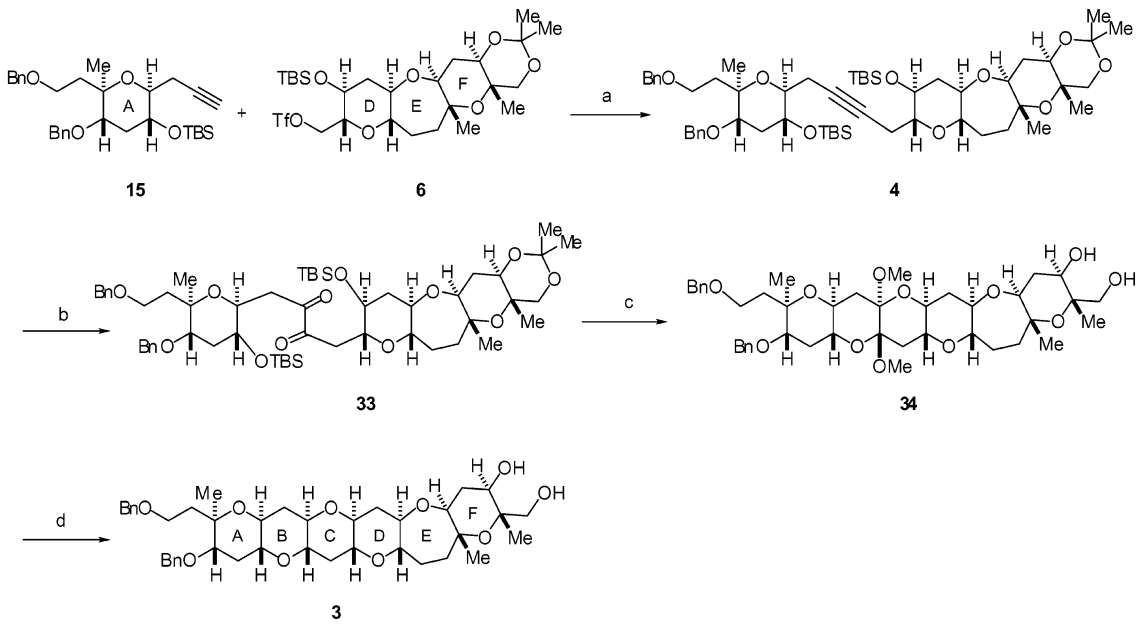
SCHEME 4[a]



[a] Conditions: (a) *n*-BuLi, THF, HMPA, −100 °C, 90%; (b) BF_3·OEt_2, CH_2Cl_2, rt, 90%; (c) $NaBH_4$, MeOH−CH_2Cl_2, 0 °C, 98%; (d) TBAF, THF, rt, 100%; (e) $Me_2C(OMe)_2$, PPTS, THF, reflux, 98%; (f) H_2, $Pd(OH)_2$/C, THF, rt, 97%; (g) Tf_2O, 2,6-lutidine, THF, −78 °C, 30 min, then TBSOTf, 96%.

SCHEME 5[a]



[a] Conditions: (a) *n*-BuLi, THF, HMPA, −78 °C, 80%; (b) RuO_2·H_2O, $NaIO_4$, CCl_4−MeCN−H_2O, rt, 80%; (c) CSA, MeOH, $CH(OMe)_3$, 80 °C, 87% (**34** + two isomers); (d) Et_3SiH, TMSOTf, CH_2Cl_2, 0 °C, 70%.

achieved through the connection of two fragments, prepared by the oxiranyl anion strategy, by an acetylene unit and a subsequent oxidation−double acetalization protocol. The convergent synthesis of **3** features 21 steps of the longest linear sequence from **16**, which was prepared from 1,3-*O*-di-*tert*-butylsilylene-L-erythritol in eight steps, whereas the iterative linear approach of **3** from 1,3-*O*-di-*tert*-butylsilylene-D-erythritol required 35 steps.[15] The present study constitutes an important contribution to the development of efficient and scalable approaches to yessotoxin and its analogues. Further studies are ongoing in our laboratory to synthesize natural toxins.

Experimental Section

(2*S*,3*R*)-2-(2-Benzyloxyethyl)-2-methyl-3-(toluene-4-sulfonyl)-oxirane (7). Compound **7** was prepared from (−)-(*R*)-1-chloromethyl *p*-tolyl sulfoxide and 4-benzyloxybutan-2-one according to the reported procedure.[20] Colorless oil: $[\alpha]^{25}_D$ +96.4 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1495, 1454, 1221, 1211, 1088 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (3H, s), 2.46 (3H, s), 2.50 (2H, t, J = 6.3 Hz), 3.76 (1H, s), 3.78 (2H, ddd, J = 6.3, 6.3, 2.0 Hz), 4.56 (2H, s), 7.26−7.84 (9H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 23.5, 31.9, 66.7, 72.9, 74.5, 127.6, 127.7, 128.3, 128.4, 130.0, 145.4; FABMS *m*/*z* 347 (MH^+).

(4*R*,5*S*)-4-[(2*S*,3*R*)-3-(2-Benzyloxyethyl)-3-methyl-2-(toluene-4-sulfonyl)-oxiranylmethyl]-2,2-di-*tert*-butyl-5-(tri-

ethylsilyloxy)-[1,3,2]dioxasilinane (12). To a stirred solution of epoxy sulfone **7** (5.13 g, 14.852 mmol) and triflate **8** (5.03 g, 9.902 mmol) in HMPA (5.17 mL, 29.705 mmol) and THF (66 mL) at −100 °C was added *n*-BuLi (9.52 mL of a 1.56 M solution in hexane, 14.852 mmol) dropwise. After the solution was stirred at −100 °C for 30 min, the reaction was quenched with saturated aqueous NH_4Cl. The reaction mixture was warmed to room temperature and extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (7→10% EtOAc in hexane) gave **12** (5.63 g, 81%) as a colorless oil. $[\alpha]^{24}_D$ +70.5 (*c* 0.96, $CHCl_3$); IR ($CHCl_3$) 1599, 1473, 1304, 1103 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.62 (6H, q, J = 7.8 Hz), 0.92 (9H, s), 0.95 (9H, s), 0.98 (9H, t, J = 7.8 Hz), 1.53 (3H, s), 2.02 (1H, dd, J = 15.6, 9.8 Hz), 2.42 (3H, s), 2.56 (1H, ddd, J = 14.2, 6.8, 6.8 Hz), 2.62 (1H, ddd, J = 14.2, 6.3, 6.3 Hz), 2.74 (1H, d, J = 15.6 Hz), 3.23 (1H, t, J = 8.3 Hz), 3.28 (1H, ddd, J = 9.8, 9.8, 3.9 Hz), 3.34 (1H, t, J = 9.8 Hz), 3.74 (1H, ddd, J = 9.8, 6.3, 6.3 Hz), 3.80 (1H, ddd, J = 9.8, 6.3, 6.3 Hz), 3.87 (1H, dd, J = 9.8, 3.9 Hz), 4.54 (2H, s), 7.26−7.79 (9H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.9 (3 × C), 6.8 (3 × C), 19.7, 21.6, 22.1, 22.6, 26.9 (3 × C), 27.4 (3 × C), 31.3, 33.4, 67.7, 68.4, 69.4, 70.9, 72.8, 75.7, 80.1, 127.4, 127.6, 128.3, 129.5, 129.6, 135.9, 138.6, 144.5; HRFABMS calcd for $C_{37}H_{61}O_7SSi_2$ (MH^+) 705.3673, found 705.3689.

(4a*S*,6*R*,8a*R*)-6-(2-Benzyloxyethyl)-2,2-di-*tert*-butyl-6-methyl-decahydro-1,3,5-trioxa-2-sila-naphthalen-7-one (13). A solution of **12** (5.63 g, 7.997 mmol) and $TsOH\cdot H_2O$ (2.28 g, 12.00 mmol) in $CHCl_3$ (80 mL) was stirred at 0 °C for 23 h. The reaction mixture was diluted with EtOAc and washed successively with saturated aqueous $NaHCO_3$, water, and brine. The organic layer was dried and concentrated in vacuo. Purification by flash chromatography (12% Et_2O in hexane) gave ketone **13** (3.22 g, 93%) as a colorless oil. $[\alpha]^{25}_D$ −69.2 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1716, 1473, 1365, 1097, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (9H, s), 1.03 (9H, s), 1.32 (3H, s), 1.71 (1H, ddd, J = 14.2, 5.4, 3.4 Hz), 2.31 (1H, dd, J = 18.1, 10.7 Hz), 2.43 (1H, ddd, J = 14.2, 9.3, 6.3 Hz), 2.83 (1H, dd, J = 18.1, 6.3 Hz), 3.44 (1H, ddd, J = 9.3, 6.3, 3.4 Hz), 3.61 (1H, ddd, J = 9.3, 9.3, 5.4 Hz), 3.66 (1H, ddd, J = 9.8, 9.8, 4.9 Hz), 3.86 (1H, t, J = 10.3 Hz), 4.02 (1H, ddd, J = 10.7, 9.8, 6.3 Hz), 4.16 (1H, dd, J = 10.3, 4.9 Hz), 4.34 and 4.44 (each 1H, d, J = 11.7 Hz), 7.24−7.35 (5H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 22.6, 22.9, 27.0 (3 × C), 27.4 (3 × C), 38.6, 45.6, 65.2, 67.2, 70.1, 71.8, 72.7, 81.7, 127.5, 127.5, 128.3, 138.1, 209.3; HRFABMS calcd for $C_{24}H_{39}O_5Si$ (MH^+) 435.2564, found 435.2582.

(2*S*,3*R*,5*S*,6*R*)-5-Benzyloxy-6-(2-benzyloxyethyl)-2-hydroxymethyl-6-methyl-tetrahydropyran-3-ol (14). (i) To a stirred solution of **13** (3.22 g, 7.419 mmol) in CH_2Cl_2 (18 mL) and MeOH (18 mL) at −78 °C was added $NaBH_4$ (418 mg, 11.060 mmol), and the reaction mixture was stirred at −78 °C for 1 h. The reaction mixture was poured into water and extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated. Purification by flash chromatography (14% EtOAc in hexane) gave an alcohol (3.21 g, 99%) as a colorless oil. $[\alpha]^{25}_D$ −6.75 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$) 3390, 1473, 1363, 1078, 824 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (9H, s), 1.04 (9H, s), 1.20 (3H, s), 1.59 (1H, q, J = 11.2 Hz), 1.78 (1H, ddd, J = 15.1, 4.4, 4.4 Hz), 1.87 (1H, ddd, J = 15.1, 6.3, 6.3 Hz), 2.20 (1H, ddd, J = 12.2, 4.9, 4.9 Hz), 3.48 (1H, ddd, J = 9.6, 9.6, 4.9 Hz), 3.56 (1H, ddd, J = 12.2, 4.4, 4.4 Hz), 3.59 (2H, dd, J = 6.3, 4.4 Hz), 3.69 (1H, ddd, J = 11.2, 9.3, 4.4 Hz), 3.73 (1H, t, J = 10.3 Hz), 3.95 (1H, d, J = 3.4 Hz, OH), 4.01 (1H, dd, J = 10.3, 4.9 Hz), 4.51 and 4.54 (each 1H, d, J = 11.7 Hz), 7.28−7.38 (5H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 19.9, 22.6, 27.1 (3 × C), 27.5 (3 × C), 36.3, 41.8, 60.1, 67.8, 70.0, 70.8, 73.4, 73.6, 77.6, 127.9, 128.6, 137.1; HRFABMS calcd for $C_{24}H_{41}O_5Si$ (MH^+) 437.2721, found 437.2724.

(ii) To a stirred solution of the alcohol (2.26 g, 6.101 mmol) in THF (30 mL) at 0 °C was added KHMDS (18.2 mL of a 0.67 M solution in toluene, 12.202 mmol), and the reaction mixture was stirred for 5 min. Benzyl bromide (1.09 mL, 9.151 mmol) was then added and the mixture was stirred at 0 °C for 30 min. The reaction was quenched with aqueous saturated NH_4Cl and the mixture was extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated. Purification by flash chromatography (8% Et_2O in hexane) gave a dibenzyl ether (3.20 g, 100%) as a colorless oil. $[\alpha]^{25}_D$ +29.6 (*c* 0.82, $CHCl_3$); IR ($CHCl_3$) 1473, 1365, 1090, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (9H, s), 1.04 (9H, s), 1.24 (3H, s), 1.60 (1H, q, J = 11.7 Hz), 1.88 (1H, ddd, J = 14.2, 6.8, 6.8 Hz), 2.00 (1H, ddd, J = 14.2, 7.3, 7.3 Hz), 2.43 (1H, ddd, J = 12.2, 4.4, 4.4 Hz), 3.39 (1H, dd, J = 12.7, 4.9 Hz), 3.48 (1H, ddd, J = 9.8, 9.8, 4.9 Hz), 3.56 (2H, t, J = 6.8 Hz), 3.64 (1H, ddd, J = 11.2, 9.8, 4.4 Hz), 3.71 (1H, t, J = 9.8 Hz), 4.00 (1H, dd, J = 9.8, 4.4 Hz), 4.41 and 4.61 (each 1H, d, J = 11.7 Hz), 4.43 and 4.46 (each 1H, d, J = 12.2 Hz), 7.27−7.35 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 19.9, 27.1 (3 × C), 27.5 (3 × C), 33.6, 39.6, 62.8, 67.7, 70.0, 70.9, 72.9, 73.2, 78.0, 127.4, 127.5, 127.6, 128.30, 138.34, 138.4; HRFABMS calcd for $C_{31}H_{47}O_5Si_2$ (MH^+) 527.3190, found 527.3184.

(iii) To a stirred solution of the dibenzyl ether (3.55 g, 6.749 mmol) in THF (44 mL) was added TBAF (16.9 mL of a 1.0 M solution in THF, 16.90 mmol), and the mixture was stirred at room temperature for 18 h. The reaction mixture was concentrated in vacuo and the residue was purified by flash chromatography (80% EtOAc in hexane) to give diol **14** (2.61 g, 100%) as a colorless oil. $[\alpha]^{25}_D$ +17.7 (*c* 0.89, $CHCl_3$); IR ($CHCl_3$) 3597, 3423, 1496, 1367, 1111, 1051 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, s), 1.57 (1H, q, J = 11.7 Hz), 1.59 (1H, br, OH), 1.89 (1H, ddd, J = 13.9, 7.1, 7.1 Hz), 2.03 (1H, ddd, J = 13.9, 6.8, 6.8 Hz), 2.04 (1H, br, OH), 2.32 (1H, ddd, J = 12.0, 4.9, 4.9 Hz), 3.35 (1H, dd, J = 11.7, 4.4 Hz), 3.37 (1H, ddd, J = 10.5, 10.5, 4.4 Hz), 3.52 (1H, ddd, J = 11.5, 10.5, 4.9 Hz), 3.56 (1H, t, J = 6.8 Hz), 3.68 (1H, dd, J = 11.2, 4.9 Hz), 3.73 (1H, dd, J = 11.2, 4.2 Hz), 4.43 and 4.59 (each 1H, d, J = 11.7 Hz), 4.45 (2H, s), 7.27−7.34 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2, 33.4, 39.5, 63.4, 65.8, 67.0, 71.0, 71.1, 77.7, 127.5, 127.6, 127.7, 128.33, 138.34, 138.4; HRFABMS calcd for $C_{23}H_{31}O_5$ (MH^+) 387.2169, found 387.2166.

Trifluoromethanesulfonic Acid (2*S*,3*R*,5*S*,6*R*)-5-Benzyloxy-6-(2-benzyloxyethyl)-3-(*tert*-butyldimethylsilyloxy)-6-methyl-tetrahydropyran-2-ylmethyl Ester (5). To a stirred solution of **14** (1.28 g, 3.316 mmol) in CH_2Cl_2 (17 mL) and 2,6-lutidine (1.53 mL, 13.264 mmol) at −78 °C was added Tf_2O (0.57 mL, 3.382 mmol). After the solution was stirred at −78 °C for 30 min, TBSOTf (1.14 mL, 4.749 mmol) was added and the reaction mixture was stirred for 45 min. The reaction was quenched with saturated aqueous $NaHCO_3$ and the mixture was extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (6% EtOAc in hexane) gave triflate **5** (1.84 g, 88%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.88 (9H, s), 1.24 (3H, s), 1.56 (1H, q, J = 11.7 Hz), 1.96 (1H, ddd, J = 13.9, 13.9, 6.6 Hz), 2.03 (1H, ddd, J = 13.9, 7.8, 5.9 Hz), 2.13 (1H, ddd, J = 12.1, 4.8, 4.8 Hz), 3.39 (1H, dd, J = 11.7, 4.8 Hz), 3.44 (1H, ddd, J = 11.0, 9.5, 4.8 Hz), 3.54 (1H, ddd, J = 9.5, 4.8, 2.2 Hz), 3.62 (1H, ddd, J = 9.5, 7.7, 5.9 Hz), 3.66 (1H, ddd, J = 9.5, 7.7, 6.6 Hz), 4.47 and 4.50 (each 1H, d, J = 11.7 Hz), 4.50 (1H, t, J = 10.6 Hz), 4.51 and 4.55 (each 1H, d, J = 11.7 Hz), 4.63 (1H, dd, J = 10.6, 1.8 Hz), 7.25−7.36 (10H, Ar); FABMS *m*/*z* 633 (MH^+).

(2*S*,3*R*,5*S*,6*R*)-5-Benzyloxy-6-(2-benzyloxyethyl)-3-*tert*-butyldimethylsilyloxy-6-methyl-2-(prop-2-ynyl)-tetrahydropyran (15). (i) To a stirred solution of trimethylsilylacetylene (1.19 mL, 8.402 mmol) in THF (9 mL) at 0 °C was added *n*-BuLi (5.39 mL of a 1.56 M solution in hexane, 8.402 mmol). After being stirred at 0 °C for 30 min, the solution was cooled to −78 °C and a solution of **5** (1.77 g, 2.801 mmol) in HMPA (1.46 mL, 8.402 mmol) and THF (3 mL) was added. After the solution was stirred at −78 °C for 45 min, the reaction was quenched with saturated aqueous NH_4Cl and the mixture was

extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (5% EtOAc in hexane) gave TMS−acetylene (1.546 g, 95%) as a colorless oil. $[\alpha]^{25}_D$ −22.4 (*c* 0.96, $CHCl_3$); IR ($CHCl_3$) 2175, 1463, 1362, 1250, 1091 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (3H, s), 0.07 (3H, s), 0.15 (9H, s), 0.86 (9H, s), 1.21 (3H, s), 1.52 (1H, q, J = 11.7 Hz), 1.94 (1H, ddd, J = 14.2, 8.3, 6.4 Hz), 2.02 (1H, ddd, J = 14.2, 8.3, 5.9 Hz), 2.10 (1H, ddd, J = 12.2, 4.4, 4.4 Hz), 2.38 (1H, dd, J = 17.1, 5.9 Hz), 2.54 (1H, dd, J = 17.1, 2.9 Hz), 3.32−3.44 (3H, m), 3.68 (2H, m), 4.46 and 4.55 (each 1H, d, J = 11.7 Hz), 4.47 (2H, s), 7.25−7.34 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.8, −4.2, 0.2 (3 × C), 16.5, 17.9, 23.4, 25.8 (3 × C), 34.5, 39.3, 66.1, 69.3, 71.3, 72.6, 72.9, 75.4, 77.9, 85.7, 104.2, 127.4, 127.50, 127.53, 127.6, 128.3, 138.6, 138.7; HRFABMS calcd for $C_{34}H_{53}O_4Si_2$ (MH^+) 581.3479, found 581.3487.

(ii) A mixture of the TMS−acetylene (1.53 g, 2.638 mmol) and K_2CO_3 (364 mg, 2.638 mmol) in MeOH (26 mL) was stirred at room temperature for 19 h. The reaction mixture was extracted with EtOAc and the extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (8% EtOAc in hexane) gave acetylene **15** (1.29 g, 96%) as a colorless oil. $[\alpha]^{25}_D$ −22.1 (*c* 1.04, $CHCl_3$); IR ($CHCl_3$) 3308, 1454, 1362, 1091 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (3H, s), 0.07 (3H, s), 0.87 (9H, s), 1.22 (3H, s), 1.52 (1H, q, J = 11.7 Hz), 1.89 (1H, t, J = 2.4 Hz), 1.91−2.05 (2H, m), 2.10 (1H, ddd, J = 12.2, 4.4, 4.4 Hz), 2.34 (1H, ddd, J = 16.6, 5.4, 2.4 Hz), 2.51 (1H, ddd, J = 16.6, 2.4, 2.4 Hz), 3.33−3.43 (3H, m), 3.59−3.72 (2H, m), 4.46 and 4.49 (each 1H, d, J = 11.7 Hz), 4.47 and 4.55 (each 1H, d, J = 11.7 Hz), 7.24−7.36 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.8, −4.1, 16.4, 17.9, 22.1, 25.7 (3 × C), 34.4, 39.7, 66.0, 69.3, 69.3, 71.3, 72.4, 72.9, 75.4, 77.8, 81.3, 127.4, 127.52, 127.55, 127.6, 127.7, 128.3, 138.7, 138.7; HREIMS calcd for $C_{31}H_{44}O_4Si$ (M^+) 508.3006, found 508.3028.

(2*S*,3*R*,5*S*,6*R*)-5-Benzyloxy-6-benzyloxymethyl-2-hydroxymethyl-tetrahydropyran-3-ol (16). To a stirred solution of (1*R*,6*S*,8*R*,9*S*)-8-benzyloxymethyl-3,3-di-*tert*-butyl-2,4,7-trioxa-3-silabicyclo[4.4.0]decan-9-ol,[21] $[\alpha]^{25}_D$ +6.17 (*c* 1.0, $CHCl_3$) (1.49 g, 3.652 mmol), and benzyl bromide (0.52 mL, 4.382 mmol) in THF (18 mL) was added excess KH (suspension in mineral oil) at 0 °C. The reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with careful addition of MeOH, and the mixture was extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (8% Et_2O in hexane) gave a dibenzyl ether (1.58 g, 87%) as a colorless oil: $[\alpha]^{20}_D$ +52.5 (*c* 0.43, $CHCl_3$). To a stirred solution of the dibenzyl ether obtained above in THF (16 mL) was added TBAF (7.56 mL of a 1 M solution in THF, 7.566 mmol). The reaction mixture was stirred at room temperature for 17 h and then concentrated in vacuo. Purification by flash chromatography (EtOAc) gave diol **16** (993 mg, 88%) as a crystalline solid, mp 43−45 °C. $[\alpha]^{25}_D$ +42.5 (*c* 0.28, $CHCl_3$); IR ($CHCl_3$) 3586, 3438, 1454, 1211, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (1H, q, J = 11.9 Hz), 2.56 (1H, ddd, J = 11.9, 4.4, 4.4 Hz), 3.23 (1H, ddd, J = 14.0, 4.9, 3.9 Hz), 3.43 (1H, ddd, J = 9.3, 4.4, 1.9 Hz), 3.47 (1H, ddd, J = 11.2, 9.3, 4.4 Hz), 3.63 (1H, ddd, J = 14.0, 11.9, 4.4 Hz), 3.66 (1H, dd, J = 13.2, 4.4 Hz), 3.76 (1H, dd, J = 13.2, 1.9 Hz), 3.79 (1H, dd, J = 11.7, 4.9 Hz), 3.86 (1H, dd, J = 11.7, 3.9 Hz), 4.41 and 4.59 (each 1H, d, J = 11.2 Hz), 4.52 and 4.58 (each 1H, d, J = 11.7 Hz), 7.22−7.33 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.2, 63.0, 66.3, 69.3, 71.1, 72.1, 73.5, 79.8, 81.2, 127.72, 127.76, 127.79, 127.9, 128.37, 128.42, 138.15, 138.18; FABMS *m*/*z* 359 (MH^+). Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.11; H, 7.45.

(2*S*,3*R*,5*S*,6*R*)-2-[(2*S*,3*R*)2-Benzenesulfonyl-3-(*tert*-butyldiphenylsilyloxymethyl)-oxiranylmethyl]-5-benzyloxy-6-benzyloxymethyl-3-triethylsilyloxy-tetrahydropyran (18). The procedure for compound **5** was employed with diol **16** (1.79 g, 4.988 mmol), Tf_2O (0.86 mL, 5.088 mmol), TESOTf (1.66 mL, 7.480 mmol), and 2,6-lutidine (2.3 mL, 19.952 mmol) in CH_2Cl_2 (18 mL). Purification by flash chromatography (7% EtOAc in hexane) gave triflate **17** (2.47 g, 82%) as a pale yellow oil. A solution of triflate **17** (2.47 g, 4.093 mmol) and epoxy sulfone **10** (2.77 g, 6.139 mmol) in HMPA (2.14 mL, 12.280 mmol) and THF (41 mL) was cooled to −100 °C, and *n*-BuLi (3.89 mL of a 1.58 M solution in hexane, 6.146 mmol) was added dropwise. After the solution was stirred at −100 °C for 45 min, the reaction was quenched with saturated aqueous NH_4Cl. The reaction mixture was warmed to room temperature and extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (20% EtOAc in hexane) gave **18** (3.29 g, 89%) as a colorless oil. $[\alpha]^{20}_D$ −26.5 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1324, 1114, 1083 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.36 (6H, m), 0.79 (9H, t, J = 7.8 Hz), 1.07 (9H, s), 1.34 (1H, q, J = 11.2 Hz), 2.10 (1H, dd, J = 15.1, 1.5 Hz), 2.21 (1H, dd, J = 15.1, 9.8 Hz), 2.29 (1H, ddd, J = 12.0, 4.4, 4.4 Hz), 2.83 (1H, ddd, J = 9.8, 9.8, 1.5 Hz), 3.19 (2H, m), 3.52 (1H, ddd, J = 11.2, 9.8, 4.4 Hz), 3.56 (1H, dd, J = 10.2, 1.5 Hz), 3.66 (1H, dd, J = 10.2, 3.4 Hz), 3.82 (1H, dd, J = 5.8, 1.9 Hz), 4.41 and 4.99 (each 1H, d, J = 11.7 Hz), 4.44 and 4.61 (each 1H, d, J = 12.7 Hz), 7.19−7.84 (25H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.9 (3 × C), 6.8 (3 × C), 19.3, 26.8 (3 × C), 30.4, 39.6, 61.6, 66.6, 68.5, 69.1, 71.4, 71.6, 73.4, 75.2, 76.9, 79.8, 126.0, 127.6, 127.70, 127.73, 127.79, 128.3, 129.0, 129.1, 129.7, 133.5, 133.9, 135.0, 135.1, 135.6, 137.4, 138.2; HRFABMS calcd for $C_{52}H_{67}O_8SSi_2$ (MH^+) 907.4091, found 907.4067.

(2*S*,4a*S*,6*R*,7*S*,8a*R*)-7-Benzyloxy-6-benzyloxymethyl-2-(*tert*-butyldiphenylsilyloxymethyl)-octahydropyrano-[3,2-*b*]pyran-3-one (19). A solution of **18** (971 mg, 1.072 mmol) and $TsOH\cdot H_2O$ (245 mg, 1.286 mmol) in $CHCl_3$ (22 mL) was heated at 55 °C for 4 h. The reaction mixture was extracted with EtOAc and the extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (18→30% EtOAc in hexane) gave **19** (574 mg, 82%) as a colorless oil. $[\alpha]^{24}_D$ +24.3 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1724, 1454, 1112 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (9H, s), 1.57 (1H, q, J = 11.2 Hz), 2.46 (1H, dd, J = 17.1, 9.1 Hz), 2.62 (1H, ddd, J = 11.7, 4.4, 4.4 Hz), 2.99 (1H, dd, J = 17.1, 5.8 Hz), 3.33 (1H, ddd, J = 11.2, 9.3, 4.4 Hz), 3.45−3.52 (2H, m), 3.61 (1H, ddd, J = 10.7, 9.3, 4.4 Hz), 3.69 (1H, dd, J = 10.3, 4.4 Hz), 3.76 (1H, dd, J = 10.7, 2.0 Hz), 3.93 (1H, dd, J = 6.4, 2.9 Hz), 3.98 (2H, m), 4.44 and 4.61 (each 1H, d, J = 11.7 Hz), 4.55 and 4.62 (each 1H, d, J = 12.7 Hz), 7.24−7.71 (20H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 26.7 (3 × C), 35.1, 44.9, 63.3, 69.0, 71.2, 72.0, 73.5, 74.0, 75.6, 79.9, 83.6, 127.6, 127.78, 127.8, 127.9, 128.3, 128.4, 129.59, 129.62, 133.3, 133.4, 135.6, 135.7, 137.9, 138.1, 205.3; HRFABMS calcd for $C_{40}H_{47}O_6Si$ (MH^+) 651.3139, found 651.3148.

(2*R*,3*S*,4a*R*,6*S*,9a*S*)-3-Benzyloxy-2-benzyloxymethyl-6-(*tert*-butyldiphenylsilyloxymethyl)-hexahydro-1,5-dioxabenzocycloheptan-7-one (20), (2*R*,3*S*,4a*R*,6*S*,9a*S*)-3-Benzyloxy-2-benzyloxymethyl-6-(*tert*-butyldiphenylsilyloxymethyl)-hexahydro-1,5-dioxabenzocycloheptan-8-one (21), and Spiro-Epoxide 22. To a stirred mixture of ketone **19** (540 mg, 0.831 mmol) and 3A MS (2.70 g) in CH_2Cl_2 (16.6 mL) at −78 °C were added $BF_3\cdot OEt_2$ (0.41 mL, 3.332 mmol) and trimethylsilyldiazomethane (0.5 mL of a 2.0 M solution in hexane, 1.00 mmol), and the reaction mixture was stirred for 40 min. The reaction was quenched with saturated aqueous $NaHCO_3$ and the mixture was extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (3.0 mL) and MeOH (3.0 mL), and PPTS (42 mg) was added to the solution. After the mixture was stirred at room temperature for 3 h, the reaction was quenched with triethylamine (0.2 mL) and the mixture was concentrated in vacuo. Purification by flash chromatography (14→20% EtOAc in hexane) gave epoxide **22** (112 mg, 18%), ketone **20** (333 mg, 60%), and ketone **21** (17 mg, 3%) in this order. Ketone **20**: $[\alpha]^{25}_D$ −26.7 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1715, 1454, 1428, 1112 cm^{-1}; ^1H NMR (400

MHz, $CDCl_3$) δ 1.02 (9H, s), 1.57 (1H, m), 1.64 (1H, q, J = 11.7 Hz), 2.23 (1H, m), 2.45 (1H, ddd, J = 12.2, 7.3, 1.5 Hz), 2.57 (1H, ddd, J = 12.2, 12.2, 4.4 Hz), 2.98 (1H, ddd, J = 12.2, 12.2, 2.0 Hz), 3.06 (1H, ddd, J = 12.2, 9.3, 4.4 Hz), 3.39 (1H, ddd, J = 10.7, 8.8, 4.4 Hz), 3.46 (1H, m), 3.65 (1H, dd, J = 10.7, 4.4 Hz), 3.76 (1H, dd, J = 10.7, 1.5 Hz), 3.86−3.90 (2H, m), 3.94 (1H, dd, J = 10.7, 4.4 Hz), 4.41 and 4.58 (each 1H, d, J = 11.7 Hz), 4.54 and 4.61 (each 1H, d, J = 12.2 Hz), 7.22−7.73 (20H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 26.7 (3 × C), 29.1, 37.0, 38.2, 66.1, 69.2, 71.1, 72.3, 73.5, 80.0, 80.2, 80.8, 87.8, 127.6, 127.66, 127.73, 127.76, 127.8, 128.3, 128.4, 129.7, 133.7, 135.6, 135.7, 138.0, 138.2, 214.9; HRFABMS calcd for $C_{41}H_{49}O_6Si$ (MH^+) 665.3296, found 665.3273.

Ketone **21**: $[\alpha]^{25}_D$ +50.6 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1708, 1428, 1113 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (9H, s), 1.47 (1H, q, J = 11.2 Hz), 2.46 (1H, dd, J = 18.1, 11.2 Hz), 2.50 (1H, m), 2.70 (1H, dd, J = 18.1, 2.4 Hz), 2.84 (1H, dd, J = 12.7, 2.4 Hz), 3.02 (1H, t, J = 12.7 Hz), 3.19 (1H, ddd, J = 12.7, 8.8, 2.4 Hz), 3.35 (2H, m), 3.52 (1H, dd, J = 10.3, 5.4 Hz), 3.54 (1H, m), 3.63−3.74 (3H, m), 4.38 and 4.53 (each 1H, d, J = 11.7 Hz), 4.52 and 4.63 (each 1H, d, J = 12.2 Hz), 4.53 (1H, m), 7.19−7.71 (20H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 26.8 (3 × C), 36.4, 47.8, 50.1, 66.4, 68.9, 71.1, 71.9, 73.5, 77.9, 80.3, 81.4, 91.3, 127.6, 127.70, 127.73, 127.76, 127.8, 128.3, 128.4, 129.77, 129.82, 133.4, 135.56, 135.63, 207.1; HRFABMS calcd for $C_{41}H_{49}O_6Si$ (MH^+) 665.3296, found 665.3259.

Spiro-epoxide **22**: $[\alpha]^{25}_D$ +14.5 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) 1605, 1454, 1428, 1112 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 0.13 (9H, s), 1.04 (9H, s), 1.42 (1H, q, J = 11.7 Hz), 1.83 (1H, dd, J = 12.2, 4.4 Hz), 1.97 (1H, ddd, J = 12.2, 12.2, 1.5 Hz), 2.41 (1H, d, J = 1.0 Hz), 2.51 (1H, ddd, J = 11.2, 11.2, 4.4 Hz), 3.14 (1H, ddd, J = 11.7, 8.8, 4.4 Hz), 3.24 (1H, ddd, J = 11.2, 8.8, 4.4 Hz), 3.45 (1H, ddd, J = 9.8, 4.9, 2.0 Hz), 3.60 (1H, ddd, J = 10.7, 8.3, 4.4 Hz), 3.63 (1H, dd, J = 11.2, 5.9 Hz), 3.67 (1H, dd, J = 11.2, 2.4 Hz), 3.69 (1H, dd, J = 10.7, 4.9 Hz), 3.78 (1H, dd, J = 10.7, 1.5 Hz), 3.82 (1H, dd, J = 5.9, 2.4 Hz), 4.52 and 4.57 (each 1H, d, J = 12.2 Hz), 4.53 and 4.68 (each 1H, d, J = 11.7 Hz), 7.27−7.76 (20H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.7 (3 × C), 19.3, 26.8 (3 × C), 35.1, 36.8, 55.3, 59.7, 61.9, 69.1, 71.2, 72.3, 73.5, 75.7, 77.2, 80.3, 81.7, 127.5, 127.6, 127.7, 127.9, 128.32, 128.39, 129.46, 129.54, 133.6, 133.9, 135.7, 135.8, 138.1, 138.2; HRFABMS calcd for $C_{44}H_{57}O_6Si_2$ (MH^+) 737.3690, found 737.3673.

(2*R*,3*S*,4a*R*,6*R*,9a*S*)-3-Benzyloxy-2-benzyloxymethyl-6-(*tert*-butyldiphenylsilyloxymethyl)-7-methylene-hexahydro-1,5-dioxabenzocycloheptane (23). To a stirred suspension of methyltriphenylphosphonium bromide (717 mg, 2.006 mmol) in THF (5.0 mL) was added KHMDS (2.24 mL of a 0.67 M solution in toluene, 1.501 mmol) at 0 °C, and the reaction mixture was stirred for 30 min. The mixture was then cooled to −78 °C and a solution of the ketone **20** (333 mg, 0.502 mmol) in THF (5.0 mL) was added. After the solution was stiired at −78 °C for 0.5 h, the reaction mixture was warmed to 0 °C and stirred for another 30 min. The reaction was quenched with saturated aqueous NH_4Cl and the mixture was extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (14% EtOAc in hexane) gave **23** (303 mg, 91%) as a colorless oil. $[\alpha]^{24}_D$ −9.08 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) 1498, 1453, 1112 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (9H, s), 1.34 (1H, m), 1.49 (1H, q, J = 11.2 Hz), 2.12 (2H, m), 2.18 (1H, m), 2.49 (1H, ddd, J = 12.2, 4.4, 4.4 Hz), 3.14 (2H, m), 3.35 (1H, ddd, J = 9.3, 4.9, 2.0 Hz), 3.40 (1H, ddd, J = 9.3, 9.3, 4.4 Hz), 3.52 (1H, dd, J = 10.7, 5.4 Hz), 3.61 (1H, dd, J = 10.7, 4.9 Hz), 3.69 (1H, dd, J = 10.7, 6.4 Hz), 3.73 (1H, dd, J = 10.7, 1.5 Hz), 4.16 (1H, t, J = 5.8 Hz), 4.38 and 4.57 (each 1H, d, J = 11.7 Hz), 4.54 and 4.60 (each 1H, d, J = 12.2 Hz), 4.75 (1H, s), 4.97 (1H, s), 7.20−7.72 (20H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 26.8 (3 × C), 27.6, 35.8, 37.0, 66.9, 69.3, 70.9, 72.4, 73.4, 75.6, 79.6, 80.6, 83.9, 113.2, 127.5, 127.6, 127.7, 127.8, 128.3, 128.4, 129.5, 133.7, 133.8, 135.7, 138.2, 138.4, 150.3; HRFABMS calcd for $C_{42}H_{51}O_5Si$ (MH^+) 663.3503, found 663.3538.

(2*R*,3*S*,4a*R*,6*S*,7*S*,9a*S*)-3-Benzyloxy-2-benzyloxymethyl-6-(*tert*-butyldiphenylsilyloxymethyl)-hexahydro-1,5-dioxabenzocycloheptane-7-sipro-2′-oxirane (24). A solution of **23** (460 mg, 0.695 mmol), *m*-CPBA (600 mg, 3.474 mmol), and $NaHCO_3$ (292 mg, 3.474 mmol) in toluene (14 mL) was stirred at room temperature for 3 h. The reaction quenched with saturated aqueous $Na_2S_2O_3$, the mixture was extracted with EtOAc, and the extract was washed with saturated aqueous $NaHCO_3$, water, and brine, dried, and concentrated in vacuo. Purification by flash chromatography (15% EtOAc in hexane) gave epoxide **24** (306 mg, 65%) as a colorless oil. $[\alpha]^{24}_D$ −0.72 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1601, 1453, 1112 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (9H, s), 1.23 (1H, ddd, J = 13.6, 5.9, 3.4 Hz), 1.45 (1H, q, J = 11.2 Hz), 1.77 (1H, m), 1.97 (1H, m), 2.08 (1H, ddd, J = 13.6, 13.6, 2.4 Hz), 2.49 (1H, ddd, J = 12.2, 4.4, 4.4 Hz), 2.67 and 2.82 (each 1H, d, J = 4.9 Hz), 3.16 (1H, ddd, J = 10.7, 9.3, 5.4 Hz), 3.31 (1H, t, J = 5.4 Hz), 3.39 (1H, m), 3.42 (1H, ddd, J = 9.8, 9.8, 4.4 Hz), 3.47 (1H, ddd, J = 11.2, 8.8, 4.9 Hz), 3.61 (1H, dd, J = 10.7, 4.8 Hz), 3.64 (1H, dd, J = 10.7, 5.4 Hz), 3.66 (1H, dd, J = 10.7, 5.4 Hz), 3.76 (1H, dd, J = 10.7, 1.5 Hz), 4.39 and 4.56 (each 1H, d, J = 11.2 Hz), 4.55 and 4.61 (each 1H, d, J = 12.2 Hz), 7.22−7.65 (20H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 25.5, 26.8 (3 × C), 29.1, 37.0, 52.1, 60.3, 65.2, 69.5, 71.0, 72.4, 73.4, 74.9, 79.7, 80.4, 83.6, 127.5, 127.66, 127.76, 127.8, 128.3, 128.4, 129.8, 133.2. 135.6, 138.1, 138.4; HRFABMS calcd for $C_{42}H_{51}O_6Si$ (MH^+) 679.3452, found 679.3486.

(2*R*,3*S*,4a*R*,6*S*,7*R*,9a*S*)-3-Benzyloxy-2-benzyloxymethyl-6-(*tert*-butyldiphenylsilyloxymethyl)-7-methyl-hexahydro-1,5-dioxa-benzocycloheptan-7-ol (25). To a stirred solution of **24** (680 mg, 1.003 mmol) in dry THF (10 mL) at 0 °C was added lithium triethylborohydride (3.0 mL of a 1.0 M solution in THF, 3.00 mmol), and the reaction mixture was stirred at 0 °C for 40 min. The reaction was quenched with water and the mixture was extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated. Purification by flash chromatography (30% EtOAc in hexane) gave **25** (657 mg, 96%) as a colorless oil. $[\alpha]^{24}_D$ −38.5 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3505, 1455, 1114 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (9H, s), 1.22 (3H, s), 1.41 (1H, q, J = 11.7 Hz), 1.64 (1H, m), 1.91 (2H, m), 1.96 (1H, m), 2.45 (1H, ddd, J = 11.7, 4.4, 4.4 Hz), 2.98 (1H, ddd, J = 9.8, 9.8, 2.9 Hz), 3.04 (1H, s, OH), 3.14 (1H, ddd, J = 11.7, 9.3, 3.9 Hz), 3.35 (1H, ddd, J = 9.3, 4.9, 2.0 Hz), 3.46 (1H, ddd, J = 9.8, 9.8, 4.9 Hz), 3.63 (2H, m), 3.37 (3H, m), 4.32 and 4.50 (each 1H, d, J = 11.2 Hz), 4.54 and 4.61 (each 1H, d, J = 12.7 Hz), 7.22−7.70 (20H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 24.3, 26.8 (3 × C), 27.1, 36.8, 38.6, 64.1, 69.3, 70.9, 72.6, 73.4, 80.3, 82.0, 83.9, 84.7, 127.6, 127.7, 127.9, 128.3, 130.1, 132.4, 135.58, 135.6, 138.0; HRFABMS calcd for $C_{42}H_{53}O_6Si$ (MH^+) 681.3608, found 681.3587.

(2*R*,3*S*,4a*R*,6*S*,7*R*,9a*S*)-3-Benzyloxy-2-benzyloxymethyl-6-hydroxymethyl-7-methyl-octahydro-1,5-dioxa-benzocyclohepten-7-ol (26). To a solution of **25** (657 mg, 0.967 mmol) in THF (10 mL) was added TBAF (1.45 mL of a 1.0 M solution in THF, 1.45 mmol), and the reaction mixture was stirred at room temperature for 1.5 h. The reaction mixture was concentrated in vacuo. Purification of the residue by flash chromatography (EtOAc) gave diol **26** (426 mg, 100%) as a colorless oil. $[\alpha]^{24}_D$ +25.3 (*c* 0.72, $CHCl_3$); IR ($CHCl_3$) 3599, 3477, 1501, 1454, 1074 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, s), 1.51 (1H, q, J = 11.2 Hz), 1.75 (1H, m), 1.85 (2H, m, including OH), 1.92 (1H, m), 2.05 (1H, br s, OH), 2.56 (1H, ddd, J = 11.2, 4.4, 4.4 Hz), 3.05 (1H, m), 3.24 (1H, ddd, J = 11.2, 9.3, 3.9 Hz), 3.39 (1H, ddd, J = 9.3, 4.9, 2.0 Hz), 3.50 (1H, ddd, J = 10.7, 10.7, 4.4 Hz), 3.53 (1H, dd, J = 7.8, 5.4 Hz), 3.62 (1H, dd, J = 10.7, 5.4 Hz), 3.65 (1H, m), 3.74 (1H, dd, J = 10.7, 2.0 Hz), 3.75 (1H, m), 4.38 and 4.57 (each 1H, d, J = 11.2 Hz), 4.54 and 4.61 (each 1H, d, J = 12.2 Hz), 7.19−

7.35 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 27.1, 36.9, 39.2, 62.4, 69.3, 71.0, 72.7, 73.4, 74.4, 80.3, 81.8, 83.3, 86.9, 127.6, 127.7, 127.9, 128.3, 128.4, 138.0, 138.2; HRFABMS calcd for $C_{26}H_{35}O_6$ (MH^+) 443.2431, found 443.2436.

Trifluoromethanesulfonic Acid (2*R*,3*S*,4a*R*,6*S*,7*R*,-9a*S*)-3-Benzyloxy-2-benzyloxymethyl-7-methyl-7-(trimethylsilyloxy)-octahydro-1,5-dioxa-benzocyclohepten-6-ylmethyl Ester (27). The procedure for compound **5** was employed with diol **26** (916 mg, 2.071 mmol), Tf_2O (0.358 mL, 2.113 mmol), TMSOTf (0.496 mL, 2.279 mmol), and 2,6-lutidine (0.720 mL, 6.214 mmol) in CH_2Cl_2 (10 mL). Purification by flash chromatography (12% EtOAc in hexane) gave triflate **27** (1.32 g, 99%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (9H, s), 1.13 (3H, s), 1.49 (1H, q, J = 11.2 Hz), 1.68 (1H, m), 1.88 (2H, m), 1.92 (1H, m), 1.97 (1H, m), 2.64 (1H, ddd, J = 11.2, 4.4, 4.4 Hz), 3.04 (1H, ddd, J = 8.8, 8.8, 4.4 Hz), 3.17 (1H, ddd, J = 11.7, 9.3, 3.9 Hz), 3.39 (1H, ddd, J = 9.8, 5.4, 2.0 Hz), 3.49 (1H, ddd, J = 10.7, 10.7, 4.9 Hz), 3.60 (1H, dd, J = 10.7, 4.9 Hz), 3.68 (1H, dd, J = 9.3, 1.9 Hz), 3.74 (1H, dd, J = 10.7, 1.9 Hz), 4.37 and 4.59 (each 1H, d, J = 11.2 Hz), 4.45 (1H, t, J = 9.8 Hz), 4.53 and 4.60 (each 1H, d, J = 12.2 Hz), 4.63 (1H, dd, J = 9.8, 2.0 Hz), 7.19−7.35 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.3 (3 × C), 24.6, 27.1, 36.3, 38.2, 69.4, 71.0, 72.7, 73.5, 76.5, 77.2, 80.4, 82.5, 83.2, 86.1, 127.6, 127.7, 127.8, 127.9, 128.3, 128.4, 137.9, 138.2; FABMS m/z 647 (MH^+).

(2*R*,3*S*,4a*R*,6*S*,7*R*,9a*S*)-3-Benzyloxy-2-benzyloxymethyl-6-[(2*S*,3*R*)-3-(*tert*-butyldiphenylsilyloxymethyl)-3-methyl-2-(toluene-4-sulfonyl)-oxiranylmethyl]-7-methyl-7-(trimethylsilyloxy)-octahydro-1,5-dioxa-benzocycloheptene (28). The procedure for compound **12** was employed with triflate **27** (1.32 g, 2.049 mmol), epoxy sulfone **11** (1.47 g, 3.074 mmol), *n*-BuLi (1.97 mL of a 1.56 M solution in hexane, 3.074 mmol), and HMPA (1.06 mL, 6.149 mmol) in THF (13 mL). Purification by flash chromatography (20% EtOAc in hexane) gave **28** (1.80 g, 90%) as a colorless oil. $[\alpha]^{20}_D$ −17.8 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1597, 1453, 1319, 1154 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (9H, s), 1.05 (3H, s), 1.10 (9H, s), 1.33 (1H, q, J = 11.2 Hz), 1.56 (3H, s), 1.58 (1H, m), 1.70 (1H, m), 1.77 (1H, m), 1.92 (1H, dd, J = 14.4, 7.8 Hz), 2.08 (1H, dd, J = 15.6, 10.3 Hz), 2.35 (1H, d, J = 15.6 Hz), 2.38 (3H, s), 2.78 (1H, ddd, J = 11.2, 3.9, 3.9 Hz), 2.92 (1H, ddd, J = 9.3, 9.3, 3.4 Hz), 3.02 (1H, ddd, J = 11.7, 11.7, 3.9 Hz), 3.37 (2H, m), 3.45 (1H, ddd, J = 10.7, 10.7, 4.9 Hz), 3.59 (1H, dd, J = 10.7, 5.4 Hz), 3.73 (1H, dd, J = 10.7, 1.5 Hz), 4.30 and 4.34 (each 1H, d, J = 11.2 Hz), 4.32 and 4.58 (each 1H, d, J = 9.8 Hz), 4.54 and 4.60 (each 1H, d, J = 12.2 Hz), 7.15−7.76 (25H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.5 (3 × C), 17.2, 19.4, 21.7, 24.4, 26.8, 26.9 (3xC), 28.7, 36.1, 38.2, 64.8, 69.6, 70.0, 70.9, 73.1, 73.4, 77.8, 80.4, 81.1, 81.9, 83.9, 84.8, 127.5, 127.68, 127.73, 127.9, 128.27, 128.30, 129.2, 129.5, 129.7, 129.8, 133.2, 133.3, 135.7, 138.2, 138.3, 144.5; HRFABMS calcd for $C_{56}H_{73}O_9SSi_2$ (MH^+) 977.4483, found 977.4451.

(2*S*,4a*S*,5a*R*,7*S*,8*R*,9a*S*,11a*R*)-7-Benzyloxy-8-benzyloxymethyl-2-(*tert*-butyldiphenylsilyloxymethyl)-2,11a-dimethyl-decahydro-1,5,9-trioxa-dibenzo[*a*,*d*]cyclohepten-3-one (29). To a solution of **28** (1.80 g, 1.844 mmol) in CH_2Cl_2 (37 mL) was added $BF_3{\cdot}OEt_2$ (1.13 mL, 9.221 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 1.5 h. The reaction was quenched with saturated aqueous $NaHCO_3$ and the mixture was extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (20% EtOAc in hexane) gave ketone **29** (1.24 g, 90%) as a colorless oil. $[\alpha]^{20}_D$ +2.75 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1716, 1455, 1114, 1089 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (9H, s), 1.14 (6H, s), 1,43 (1H, q, J = 11.2 Hz), 1.80 (1H, ddd, J = 15.1, 9.3, 3.4 Hz), 1.98 (2H, m), 2.22 (1H, ddd, J = 15.1, 8.3, 3.4 Hz), 2.39 (1H, dd, J = 19.0, 10.7 Hz), 2.48 (1H, ddd, J = 11.7, 3.9, 3.9 Hz), 2.83 (1H, dd, J = 19.0, 6.9 Hz), 2.98 (1H, ddd, J = 11.2, 9.3, 3.9 Hz), 3.07 (1H, ddd, J = 8.3, 8.3, 4.9 Hz), 3.36 (2H, m), 3.56 and 3.65 (each 1H, d, J = 9.8 Hz), 3.60 (1H, dd, J = 10.7, 4.9 Hz), 3.74 (1H, dd, J = 10.7, 1.5 Hz), 4.19 (1H, dd, J = 10.7, 6.8 Hz), 4.39 and 4.58 (each 1H, d, J = 11.2 Hz), 4.54 and 4.59 (each 1H, d, J = 12.2 Hz), 7.20−7.70 (20H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 20.5, 23.4, 26.9 (3 × C), 28.2, 36.9, 38.4, 42.1, 69.4, 70.9, 72.5, 73.4, 78.3, 79.3, 80.2, 82.7, 83.4, 127.7, 127.8, 127.8, 128.3, 128.4, 129.9, 132.5, 133.1, 135.5, 135.6, 138.0, 138.3, 213.0; HRFABMS calcd for $C_{46}H_{57}O_7Si$ (MH^+) 749.3870, found 749.3887.

(2*S*,3*R*,4a*S*,5a*R*,7*S*,8*R*,9a*S*,11a*R*)-7-Benzyloxy-8-benzyloxymethyl-2-(*tert*-butyldiphenylsilyloxymethyl)-2,11a-dimethyl-dodecahydro-1,5,9-trioxa-dibenzo[*a*,*d*]cyclohepten-3-ol (30). To a stirred solution of **29** (1.236 g, 1.652 mmol) in CH_2Cl_2 (6.5 mL) and MeOH (6.5 mL) at 0 °C was added $NaBH_4$ (94 mg, 2.478 mmol), and the reaction mixture was stirred at 0 °C for 30 min. The reaction mixture was poured into water and extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated. Purification by flash chromatography (14% EtOAc in hexane) gave alcohol **30** (1.21 g, 98%) as a colorless oil. $[\alpha]^{20}_D$ +1.75 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3521, 1475, 1457, 1067 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (9H, s), 1.25 (3H, s), 1.32 (3H, s), 1.46 (1H, q, J = 11.2 Hz), 1.68−1.78 (2H, m), 1.81 (1H, q, J = 11.7 Hz), 1.83 (1H, m), 1.99 (2H, m), 2.58 (1H, ddd, J = 11.7, 4.4, 4.4 Hz), 3.13−3.26 (3H, m), 3.32 (1H, ddd, J = 9.3, 4.9, 1.5 Hz), 3.37 (1H, dd, J = 11.7, 3.9 Hz), 3.46 (3H, m), 3.59 (1H, dd, J = 10.7, 3.4 Hz), 3.72 (1H, dd, J = 10.7, 2.0 Hz), 3.86 (1H, ddd, J = 11.7, 4.4, 1.5 Hz), 4.37 and 4.57 (each 1H, d, J = 11.2 Hz), 4.53 and 4.60 (each 1H, d, J = 12.2 Hz), 7.20−7.66 (20H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 19.1, 23.2, 26.9 (3 × C), 29.2, 31.5, 37.0, 39.6, 69.3, 70.8, 72.3, 73.4, 73.5, 73.7, 75.2, 77.5, 79.3, 79.9, 80.4, 80.7, 127.5, 127.66, 127.71, 127.8, 128.29, 128.34, 129.9, 130.0, 132.2, 135.5, 135.7, 138.1, 138.3; HRFABMS calcd for $C_{46}H_{59}O_7Si$ (MH^+) 751.4027, found 751.4059.

(2*R*,3*S*,4a*R*,5a*S*,6a*R*,10a*S*,11a*R*,13a*S*)-3-Benzyloxy-2-benzyloxymethyl-8,8,10a,11a-tetramethyl-dodecahydro-1,5,7,9,11-pentaoxa-benzo[4,5]cyclohepta[1,2-*b*]naphthalene (31). (i) To a solution of **30** (1.21 g, 1.613 mmol) in THF (13 mL) was added TBAF (1.93 mL of a 1 M solution in THF, 1.930 mmol), and the reaction mixture was stirred at room temperature for 70 min. The reaction mixture was concentrated in vacuo. Purification of the residue by flash chromatography (90% EtOAc in hexane) gave a diol (827 mg, 100%) as a colorless oil. $[\alpha]^{20}_D$ +22.6 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3599, 3442, 1497, 1454, 1065 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (3H, s), 1.28 (3H, s), 1.46 (1H, q, J = 11.2 Hz), 1.79−1.89 (4H, m), 1.96−2.15 (4H, m), 2.57 (1H, ddd, J = 11.7, 4.4, 4.4 Hz), 3.21 (2H, m), 3.35 (2H, m), 3.36 and 3.43 (each 1H, d, J = 10.7 Hz), 3.46 (1H, ddd, J = 10.7, 9.3, 4.4 Hz), 3.60 (1H, dd, J = 10.7, 5.4 Hz), 3.73 (1H, dd, J = 10.7, 1.5 Hz), 3.91 (1H, dd, J = 12.2, 4.4 Hz), 4.38 and 4.57 (each 1H, d, J = 11.7 Hz), 4.54 and 4.60 (each 1H, d, J = 12.2 Hz), 7.19−7.34 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 22.9, 29.1, 32.2, 37.0, 39.6, 68.1, 68.2, 69.3, 70.9, 72.3, 73.4, 76.5, 77.7, 79.3, 79.9, 80.6, 80.8, 127.5, 127.68, 127.71, 127.8, 128.3, 128.4, 138.0, 138.2; HRFABMS calcd for $C_{30}H_{41}O_7$ (MH^+) 512.2772, found 512.2758.

(ii) A solution of the diol (827 mg, 1.616 mmol), PPTS (20 mg, 0.081 mol), and 2,2-dimethoxypropane (4 mL) in THF (16 mL) was refluxed for 45 min. After the solution was cooled to room temperature, the reaction was quenched with triethylamine (0.2 mL) and the mixture was concentrated in vacuo. Purification of the residue by flash chromatography (25% EtOAc in hexane) gave acetonide **31** (875 mg, 98%) as a colorless oil. $[\alpha]^{20}_D$ +7.93 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1455, 1383, 1073 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (3H, s), 1.37 (3H, s), 1.41 (3H, s), 1.48 (3H, s), 1.47 (1H, q, J = 11.2 Hz), 1.84 (1H, q, J = 11.2 Hz), 1.86 (2H, m), 2.02 (1H, m), 2.57 (1H, ddd, J = 11.7, 3.9, 3.9 Hz), 3.21 (2H, m), 3.33 (1H, ddd, J = 9.8, 5.4, 2.0 Hz), 3.43 and 3.50 (each 1H, d, J = 10.3 Hz), 3.47 (1H, m), 3.55 (1H, dd, J = 10.7, 4.9 Hz), 3.57−3.63 (2H, m), 3.73 (1H, dd, J = 10.7, 2.0 Hz), 4.38 and 4.58 (each 1H, d, J = 11.7 Hz), 4.54 and 4.60 (each 1H, d, J = 12.2 Hz), 7.20−7.34

(10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 19.3, 25.5, 29.2, 29.5, 29.5, 36.9, 39.8, 69.3, 69.8, 70.8, 71.1, 72.3, 73.0, 73.4, 79.0, 79.9, 79.9, 80.0, 81.0, 99.9, 127.5, 127.66, 127.70, 127.8, 128.29, 128.34, 138.1, 138.3; HRFABMS calcd for $C_{33}H_{45}O_7$ (MH^+) 553.3163, found 553.3177.

(2*R*,3*S*,4a*R*,5a*S*,6a*R*,10a*S*,11a*R*,13a*S*)-2-Hydroxymethyl-8,8,10a,11a-tetramethyl-dodecahydro-1,5,7,9,11-pentaoxabenzo[4,5]cyclohepta[1,2-*b*]naphthalen-3-ol (32). A suspension of dibenzyl ether **31** (775 mg, 1.404 mmol) and 10% $Pd(OH)_2$−C (232 mg) in THF (9.4 mL) was stirred under hydrogen at room temperature for 1 h. The reaction mixture was filtered through a short pad of Celite, and the filtrate was concentrated in vacuo to give diol **32** (506 mg, 97%) as a white solid, mp 209−210 °C. $[\alpha]^{23}_D$ −23.3 (*c* 0.27, $CHCl_3$); IR ($CHCl_3$) 3599, 3451, 1462, 1383, 1118, 1072 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (3H, s), 1.38 (3H, s), 1.41 (3H, s), 1.48 (3H, s), 1.50 (1H, q, *J* = 11.7 Hz), 1.60 (1H, br s, OH), 1.79−1.91 (5H, m), 1.92−2.03 (2H, m, including OH), 2.41 (1H, ddd, *J* = 11.7, 4.4, 4.4 Hz), 3.14 (1H, ddd, *J* = 9.3, 4.9, 4.9 Hz), 3.23 (2H, m), 3.44 and 3.50 (each 1H, d, *J* = 10.3 Hz), 3.55 (1H, dd, *J* = 10.7, 4.9 Hz), 3.60 (1H, dd, *J* = 11.2, 4.4 Hz), 3.64 (1H, ddd, *J* = 11.2, 9.3, 4.9 Hz), 3.75 (1H, dd, *J* = 11.2, 4.9 Hz), 3.84 (1H, dd, *J* = 11.2, 4.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 19.3, 25.4, 29.2, 29.5 (2 × C), 39.7, 40.1, 36.2, 66.9, 69.8, 71.1, 73.1, 78.9, 79.8, 79.9, 80.8, 81.3, 100.0; HRFABMS calcd for $C_{197}H_{33}O_7$ (MH^+) 373.2224, found 373.2238.

Trifluoromethanesulfonic Acid (2*R*,3*S*,4a*R*,5a*S*,6a*R*,-10a*S*,11a*R*,13a*S*)-3-(*tert*-Butyldimethylsilyloxy)-8,8,10a,-11a-tetramethyl-dodecahydro-1,5,7,9,11-pentaoxa-benzo-[4,5]cyclohepta[1,2-*b*]naphthalen-2-ylmethyl Ester (6). The procedure for compound **5** was employed with diol **32** (506 mg, 1.360 mmol), Tf_2O (0.235 mL, 1.387 mmol), TBSOTf (0.468 mL, 2.040 mmol), and 2,6-lutidine (0.730 mL, 6.800 mmol) in THF (13.6 mL). Purification by flash chromatography (5% acetone in hexane) gave triflate **6** (805 mg, 96%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (3H, s), 0.10 (3H, s), 0.87 (9H, s), 1.32 (3H, s), 1.38 (3H, s), 1.41 (3H, s), 1.48 (3H, s), 1.53 (1H, q, *J* = 12.2 Hz), 1.78−1.90 (5H, m), 2.01 (1H, m), 2.35 (1H, ddd, *J* = 12.2, 4.4, 4.4 Hz), 3.18−3.27 (2H, m), 3.33 (1H, ddd, *J* = 9.3, 5.4, 2.0 Hz), 3.44 and 3.50 (each 1H, d, *J* = 10.3 Hz), 3.53 (1H, dd, *J* = 9.8, 4.7 Hz), 3.56 (1H, m), 3.60 (1H, dd, *J* = 11.7, 3.9 Hz), 4.49 (1H, dd, *J* = 10.7, 5.4 Hz), 4.69 (1H, dd, *J* = 10.7, 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.1, −4.0, 17.8, 18.4, 19.3, 25.4, 25.6 (3 × C), 29.1, 29.2, 29.5, 39.6, 40.5, 65.9, 69.8, 71.1, 73.0, 75.3, 78.8, 78.9, 79.4, 80.0, 81.3, 100.0; FABMS *m*/*z* 619 (MH^+).

(2*R*,3*S*,4a*R*,5a*S*,6a*R*,10a*S*,11a*R*,13a*S*)-2-{4-[(2*S*,3*R*,5*S*,-6*R*)-5-Benzyloxy-6-(2-benzyloxyethyl)-3-(*tert*-butyldimethylsilyloxy)-6-methyl-tetrahydropyran-2-yl]-but-2-ynyl}-3-(*tert*-butyldimethylsilyloxy)-8,8,10a,11a-tetramethyl-dodecahydro-1,5,7,9,11-pentaoxa-benzo[4,5]cyclohepta[1,2-*b*]-naphthalene (4). To a stirred solution of acetylene **15** (347 mg, 0.683 mmol) and triflate **6** (141 mg, 0.227 mmol) in THF (2.3 mL) and HMPA (0.2 mL, 1.138 mmol) was added *n*-BuLi (0.390 mL of a 1.58 M solution in hexane) at −78 °C, and the reaction mixture was stirred for 30 min. The reaction was quenched with saturated aqueous NH_4Cl and the mixture was extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (10→25% Et_2O in hexane) gave **4** (178 mg, 80%) as a colorless oil. $[\alpha]^{24}_D$ −3.91 (*c* 0.65, $CHCl_3$); IR ($CHCl_3$) 1463, 1383, 1259, 1074 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (3H, s), 0.07 (3H, s), 0.08 (6H, s), 0.87 (18H, s), 1.21 (3H, s), 1.31 (3H, s), 1.37 (3H, s), 1.41 (3H, s), 1.47 (3H, s), 1.48 (1H, q, *J* = 11.2 Hz), 1.52 (1H, q, *J* = 12.2 Hz), 1.78−1.91 (4H, m), 1.92−2.04 (4H, m), 2.10 (1H, ddd, *J* = 12.2, 4.4, 4.4 Hz), 2.24−2.32 (3H, m), 2.50 (1H, dd, *J* = 17.0, 2.4 Hz), 2.58 (1H, dd, *J* = 17.1, 2.4 Hz), 3.08 (1H, ddd, *J* = 8.8, 6.8, 2.9 Hz), 3.15−3.24 (2H, m), 3.30−3.41 (3H, m), 3.43 (1H, d, *J* = 10.3 Hz), 3.48 (1H, m), 3.50 (1H, d, *J* = 10.3 Hz), 3.54 (1H, dd, *J* = 11.2, 4.9 Hz), 3.59 (1H, dd, *J* = 11.7, 3.9 Hz), 3.61−3.73 (2H, m), 4.45 and 4.55 (each 1H, d, *J* = 11.7 Hz), 4.46 (2H, s), 7.25−7.34 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.7 (2 × C), −4.2, −4.1, 16.5, 17.9, 18.4, 19.3, 22.2, 22.6, 25.6, 25.7 (3 × C), 25.8 (3 × C), 29.2, 29.5, 29.6, 34.5, 39.7, 39.8, 40.7, 66.1, 69.1, 69.4, 69.8, 71.1, 71.3, 72.9, 72.9, 73.1, 75.3, 77.5, 77.9, 78.1, 79.0, 80.0, 80.1, 80.4, 80.9, 99.9, 127.4, 127.5, 127.7, 128.3, 138.7, 138.7; HRFABMS calcd for $C_{56}H_{89}O_{10}Si_2$ (MH^+) 977.1408, found 977.1452.

1-[(2*S*,3*R*,5*S*,6*R*)-5-Benzyloxy-6-(2-benzyloxyethyl)-3-(*tert*-butyldimethylsilyloxy)-6-methyl-tetrahydropy-ran-2-yl]-4-[(2*R*,3*S*,4a*R*,5a*S*,6a*R*,10a*S*,11a*R*,13a*S*)-3-(*tert*-butyldimethylsilyloxy)-8,8,10a,11a-tetramethyl-dodecahydro-1,5,7,9,11-pentaoxabenzo[4,5]cyclohepta[1,2-*b*]naphthalen-2-yl]-butane-2,3-dione (33). To a suspension of **4** (85 mg, 0.0871 mmol) in CCl_4 (0.4 mL), MeCN (0.4 mL), and water (0.6 mL) were added $NaIO_4$ (46.5 mg, 0.2177 mmol) and RuO_2·H_2O (0.6 mg), and the reaction mixture was stirred vigorously at room temperature for 1 h. The reaction mixture was extracted with EtOAc and the extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (8% acetone in hexane) gave **33** (70.3 mg, 80%) as a yellow oil. $[\alpha]^{24}_D$ −7.32 (*c* 0.43, $CHCl_3$); IR ($CHCl_3$) 1716, 1463, 1383, 1074 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (6H, s), 0.07 (3H, s), 0.08 (3H, s), 0.85 (9H, s), 0.86 (9H, s), 1.19 (3H, s), 1.30 (3H, s), 1.36 (3H, s), 1.41 (3H, s), 1.47 (3H, s), 1.46−1.58 (2H, m), 1.75−1.95 (8H, m), 2.10 (1H, ddd, *J* = 12.2, 4.4, 4.4 Hz), 2.27 (1H, ddd, *J* = 12.2, 4.4, 4.4 Hz), 2.68 (1H, dd, *J* = 16.1, 9.3 Hz), 2.82 (1H, dd, *J* = 16.1, 9.3 Hz), 2.98 (2H, dd, *J* = 16.1, 2.9 Hz), 3.12 (1H, ddd, *J* = 11.7, 11.7, 4.4 Hz), 3.17 (1H, m), 3.23 (1H, ddd, *J* = 11.2, 9.3, 4.9 Hz), 3.31 (1H, dd, *J* = 11.7, 4.4 Hz), 3.39 (1H, ddd, *J* = 10.7, 9.3, 4.9 Hz), 3.43 (1H, d, *J* = 10.2 Hz), 3.47−3.53 (5H, m), 3.57 (1H, dd, *J* = 11.7, 3.9 Hz), 3.83 (1H, ddd, *J* = 9.3, 9.3, 2.9 Hz), 4.41 and 4.44 (each 1H, d, *J* = 13.2 Hz), 4.45 and 4.54 (each 1H, d, *J* = 11.7 Hz), 7.24−7.35 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.7, −4.1, −4.0 (2 × C), 16.2, 17.9, 18.4, 19.3, 25.6, 25.6 (3 × C), 25.7 (3 × C), 29.2, 29.3, 29.4, 29.5, 29.7, 34.7, 38.6, 39.55, 39.65, 40.7, 65.9, 69.8, 70.2, 70.78, 70.80, 71.1, 71.3, 72.9, 73.0, 75.7, 77.7, 77.9, 79.0, 79.9, 80.0, 80.9, 99.9, 127.4, 127.6, 128.3, 128.4, 129.6, 138.5, 138.7, 197.7, 197.9; HRFABMS calcd for $C_{56}H_{89}O_{12}Si_2$ (MH^+) 1009.5887, found 1009.5851.

ABCDEF-Ring Fragment (3). To a solution of diketone **33** (338 mg, 0.3350 mmol) in MeOH (3.4 mL) and trimethyl orthoformate (3.4 mL) was added CSA (156 mg, 0.670 mmol). The reaction mixture was stirred at room temperature for 1.5 h and then heated at 80 °C for 12 h. After the solution was cooled to room temperature, reaction was quenched with triethylamine (0.5 mL) and the mixture was concentrated in vacuo. Purification by flash chromatography (8% acetone in hexane) gave a mixture of **34** and its isomers (223 mg, 87%). To a solution of the mixture (223 mg, 0.290 mmol) and triethylsilane (0.465 mL, 2.909 mmol) in CH_2Cl_2 (2.9 mL) was added TMSOTf (0.116 mL, 0.640 mmol) at 0 °C, and the reaction mixture was stirred at 0 °C for 90 min. The reaction was quenched with saturated aqueous $NaHCO_3$ and the mixture was extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated in vacuo. Purification by flash chromatography (20→30% EtOAc in Et_2O) gave the ABCDEF fragment **3** (144 mg, 70%) as a crystalline solid, mp 159−160 °C. $[\alpha]^{25}_D$ +0.95 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3674, 3462, 1455, 1066 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.11 (3H, s), 1.21 (3H, s), 1.26 (3H, s), 1.31 (1H, q, *J* = 11.7 Hz), 1.36 (1H, q, *J* = 11.7 Hz), 1.40 (1H, q, *J* = 11.7 Hz), 1.48 (1H, q, *J* = 11.7 Hz), 1.73−1.82 (2H, m), 1.80 (1H, q, *J* = 11.7 Hz), 1.87−1.96 (5H, m), 2.10 (1H, ddd, *J* = 11.7, 3.7, 3.7 Hz), 2.20 (1H, ddd, *J* = 11.7, 3.7, 3.7 Hz), 2.33 (1H, ddd, *J* = 11.7, 4.4, 4.4 Hz), 2.93 (1H, ddd, *J* = 11.7, 9.5, 4.4 Hz), 3.00 (1H, ddd, *J* = 11.7, 8.8, 3.7 Hz), 3.02 (1H, ddd, *J* = 11.7, 11.0, 3.7 Hz), 3.07 (1H, ddd, *J* = 11.7, 9.5, 4.4 Hz), 3.11 (1H, ddd, *J* = 11.7, 8.8, 4.4 Hz), 3.17−3.22 (2H, m), 3.24−3.36 (4H, m), 3.42 (1H, dd, *J* = 11.7, 3.7 Hz), 3.52 (1H, dd, *J* = 11.7, 4.4 Hz), 3.56−3.63 (2H, m), 3.87 (1H, m), 3.90 (1H, br d, *J* = 4.4 Hz,

OH), 4.44 and 4.46 (each 1H, d, J = 12.5 Hz), 4.49 and 4.65 (each 1H, d, J = 11.7 Hz), 7.25−7.34 (10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 19.0, 23.5, 31.2, 33.2, 33.3, 36.1, 36.5, 37.9, 40.3, 40.6, 66.4, 68.8, 69.3, 70.1, 71.4, 73.2, 76.6, 77.1, 77.6, 77.7, 77.80, 77.81, 78.0, 78.2, 79.0, 80.5, 81.67, 81.71, 128.0, 128.2, 128.3, 128.5, 128.9, 129.0, 139.9, 140.0; HR-FABMS calcd for $C_{41}H_{57}O_{10}$ (MH^+) 709.3948, found 709.3932.

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Supporting Information Available: ^{1}H NMR spectra for compounds **3**−**6**, **12**−**15**, and **18**−**34**. This material is available free of charge via the Internet at http://pubs.acs.org.

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