Total synthesis of (±)-9-deoxygoniopypyrone. Application of the iodocyclofunctionalization reaction of α-allenic alcohol derivatives

Richard W. Friesen and Suzanne Bissada

Abstract: The synthesis of (±)-9-deoxygoniopypyrone (**1**) from the α-allenic alcohol **5** is described. Iodocyclofunctionaliztion of the *N*-tosyl carbamate derivative of **5** using I_2 and Ag_2CO_3 provided, in a highly diastereoselective and regioselective fashion, the vinyl iodo *syn*-vicinal diol **4**. Two routes were explored in order to introduce the third stereogenic centre in the molecule. Reductive deiodination of the vinyl iodide and diastereoselective epoxidation of the derived acetonide **14** using mCPBA provided a mixture of epoxides **15** and **16** (2:1) in which the desired *threo* diastereomer predominated. Alternatively, dihydroxylation of acetonide **14** (OsO_4, NMO) yielded a mixture of diols **21** and **22** (2:3) which were separated after monosilylation (TBDMSCl) of the primary alcohol. The major silyl ether *erythro* diastereomer **24** was converted to the desired epoxide **15** by mesylation (MsCl, Et_3N) and epoxide formation (TBAF) with inversion of stereochemistry. The minor *threo* diastereomer **23** was also converted to the desired epoxide **15** (TBAF; $ArSO_2Cl$; NaOMe). Epoxide opening was effected with lithium acetylide and the resulting alkyne **27** was carbonylated (MeLi, $ClCO_2Me$) to afford the α,β-acetylenic ester **28**. Semi hydrogenation over Lindlar's catalyst followed by protecting- group removal under acidic conditions provided (±)-8-epigoniodiol **30**. Finally, conversion of **30** to (±)-9-deoxygoniopypyrone **1** was effected under basic conditions (DBU).

Key words: (±)-9-deoxygoniopypyrone, α-allenic alcohol, iodocyclofunctionalization, *syn*-diol.

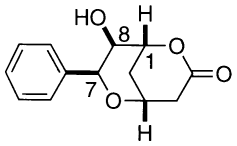
Résumé : On décrit la synthèse de la (±)-9-désoxygoniopyrone (**1**) à partir de l'alcool α-allénique **5**. L'iodocyclofonctionnalisation du dérivé *N*-tosylcarbamate du produit **5** à l'aide de I_2 et de Ag_2CO_3 a conduit au vinyl iodo diol *syn*-vicinal **4** avec une diastéréosélectivité et une régiosélectivité élevées. Dans le but d'introduire le troisième centre stéréogénique de la molécule, on a exploré deux voies. D'une part, la déiodation réductrice de l'iodure de vinyle et l'époxydation diastéréosélective du dérivé acétonide **14** à l'aide de l'acide *m*-chloroperbenzoïque (AmCPB) conduisent à un mélange d'époxydes **15** et **16** (2 : 1) dans lequel le diastéréomère *thréo* recherché prédomine. D'autre part, la dihydroxylation de l'acétonide **14** (OsO_4, NMO) fournit un mélange des diols **21** et **22** (2 : 3) qui ont pu être séparés après monosilylation («TBDMSCl») de l'alcool primaire. On a transformé l'éther silylé du diastéréomère *érythro* (**24**) prépondérant en époxyde **15** recherché en procédant à une mésylation («MsCl», Et_3N) suivie de la formation d'un époxyde («TBAF») avec inversion de stéréochimie. Le diastéréomère *thréo* (**23**) minoritaire a aussi été transformé en époxyde **15** recherché («TBAF»; $ArSO_2Cl$; NaOMe). On a effectué l'ouverture de l'époxyde à l'aide d'acétylure de lithium et on a effectué une décarbonylation de l'alcyne **27** qui en résulte (MeLi, $ClCO_2Me$) pour conduire à l'ester α,β-acétylénique **28** qui, par semihydrogénation sur du catalyseur de Lindlar suivie de l'élimination des groupes protecteurs dans des conditions acides, fournit le (±)-8-épigoniodiol **30**. Enfin, on a effectué la conversion du composé **30** en (±)-9-désoxygoniopyrone (**1**) dans des conditions basiques («DBU»).

Mots clés : (±)-9-désoxygoniopyrone, alcool α-allénique, iodocyclofonctionnalisation, *syn*-diol.

[Traduit par la rédaction]

Introduction

The cytotoxic (ED_{50} 7.4 μg/mL against HT-29 cells) bicyclic styryl lactone (+)-9-deoxygoniopypyrone (**1**) was isolated in 1990 from the stem bark of *Goniothalamus giganteus* Hook. f. & Thomas (Annonaceae) (1). (+)-9-Deoxygoniopypyrone (**1**) possesses several interesting structural features, including the novel 2,6-dioxabicyclo[3.3.1]nonan-3-one molecular scaffold, that make it attractive as a synthetic target. Within this framework, the key substructure in terms of synthesis is the triol



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moiety in which the three contiguous oxygen-bearing stereocentres (C7/C8/C1) are in a *syn*,*syn* relationship (see **2**).

We have been interested in the synthesis of natural products using our recently described method for the highly diastereoselective conversion of the *N*-tosyl carbamate derivatives of secondary α-allenic alcohols such as **5** into vinyl iodo *syn*-vicinal diols **4** (2–6). We felt that the implementation of

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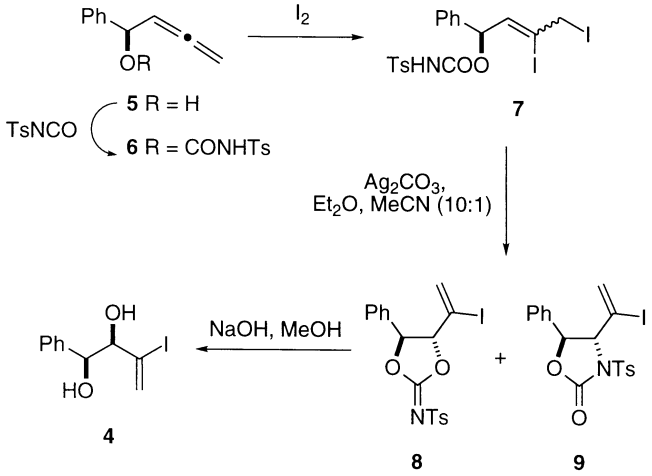
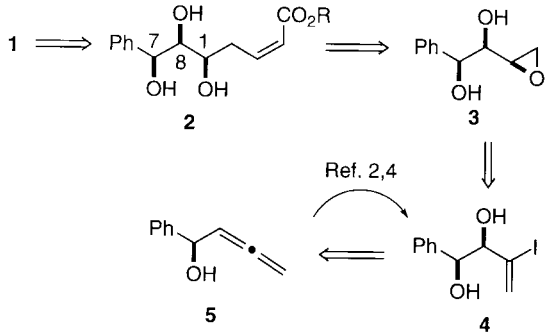
Scheme 1.



this iodocyclofunctionalization strategy would allow us to address the structurally interesting features in **1**. According to our retrosynthetic plan, the relative stereochemistry between the C7/C8 hydroxy moieties in **1** (natural product numbering used throughout) would be readily established using this method. Following reductive deiodination of the vinyl iodide moiety in **4**, diastereoselective oxidation (epoxidation or dihydroxylation) of the resulting olefin would introduce the third stereocentre and provide the epoxide **3**. Homologation of **3** would afford the α,β-unsaturated ester **2**, the immediate precursor to **1**. Herein, we describe the full details of the synthesis of (±)-**1** (Schemes 1–3) according to this strategy.[2]

Two syntheses of (+)-**1** have been reported in the literature. The first synthesis by Honda and co-workers (7), which utilized 2,3-*O*-isopropylidene-D-glyceraldehyde as the chiral



starting material, demonstrated that the absolute configuration of the natural product (+)-**1** is as depicted. Subsequent to our published synthesis of (±)-**1**,[2] Yang and Zhou described the synthesis of (+)-**1** from methyl cinnamate using Sharpless asymmetric dihydroxylation technology (8). In contrast to our synthesis, both of these groups introduced one of the three contiguous hydroxy-bearing stereocentres by the nucleophilic addition of a metalated aromatic to an α-alkoxy aldehyde.

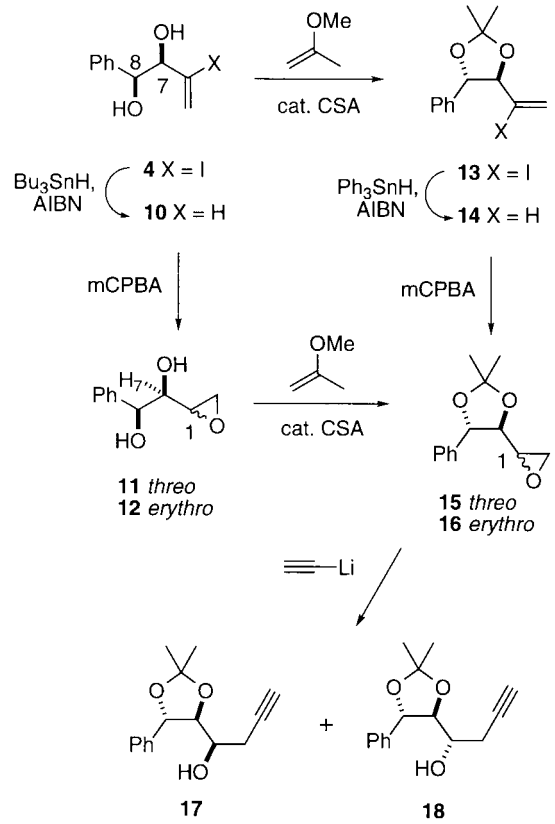
Results and discussion

The vinyl iodo *syn*-diol **4** was prepared from the racemic α-allenic alcohol **5**,[3] using our previously reported

[2] For a preliminary account of this work, see ref. 3.

[3] Although **5** is racemic, only a single enantiomer has been drawn throughout.

Scheme 2.



iodocyclofunctionalization procedure (2, 4) (Scheme 1). Thus, alcohol **5** was treated sequentially with TsNCO and I_2 to provide an *E/Z* mixture of diiodides **7** (5) that was cyclized by treatment with Ag_2CO_3 in ether–MeCN (10:1). Filtration of the silver salts and concentration of the reaction mixture provided the crude cyclization products. In accord with our earlier observations (2, 4), inspection of the ^{1}H NMR spectrum of the crude reaction mixture revealed that the imino carbonate **8** was obtained in a highly diastereoselective fashion (diastereoselectivity >50:1) together with minor amounts (<5%) of the related carbamate **9** (9). From a practical point of view, it is important to point out that it is essential to wash the solid silver salt cake extensively with ethyl acetate and methanol in order to achieve optimum recovery of the initial cyclization products. Hydrolysis of the crude mixture with methanolic sodium hydroxide yielded the desired vinyl iodo *syn*-diol **4** in 66% overall yield after chromatography. Reductive deiodination of **4** using *n*-Bu_3SnH–AIBN provided the unsaturated diol **10** in 81% yield (Scheme 2).

The strategy for the synthesis of **1** from *syn*-diol **10** required that the installation of the C1 oxygen occur with *threo* diastereoselectivity relative to the hydroxy moieties at C7 and C8. In keeping with the plan that chain extension to an intermediate such as **2** would be required, epoxidation of **10** appeared to be an obvious strategy. The directed diastereoselective epoxidation reactions of allylic and homoallylic alcohols or diols are well documented (10–15). Typically, transition metal (Ti, V) mediated epoxidations of such olefins, including monosubstituted alkenes, afford the *erythro* diastereomers with good to excellent stereoselectivity. Conversely, epoxidations of both

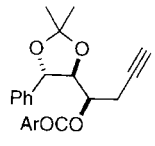
allylic and homoallylic alcohols with mCPBA are marginally diastereoselective in favour of the *threo* epoxides. For example, upon treatment of 3-buten-2-ol or 4-penten-2-ol with mCPBA, the corresponding *threo* epoxide isomers are obtained in ratios of 3:2 and 1.2:1, respectively (10–12). Not surprisingly, exposure of ene diol **10** to mCPBA at room temperature provided a mixture of epoxides **11**/**12** in a ratio of 2:1 (51%) (Scheme 2).

The stereochemical assignments of the epoxy diol diastereomers **11**/**12** are based on comparison of their ^{1}H NMR spectral data with those of structurally similar epoxy alcohols (13–15). The characteristic proton resonance in these spectra is that of H7. Typically, the resonance frequency of this proton is observed at higher field in the *threo* isomer than in the *erythro* isomer. In the case of epoxy diols **11**/**12**, the chemical shift of H7 in the major isomer (δ 3.68) is 0.25 ppm upfield relative to the corresponding resonance in the minor isomer (δ 3.93). This observation is consistent with the reported literature data (13–15) and suggests that the major isomer is in fact the *threo* epoxy diol **11**.

A variety of methods, including metal-catalyzed directed epoxidation (Ti, V) (10–12), were attempted in an effort to increase the *threo* diastereoselectivity in the epoxidation of **10** but without any improvement in selectivity. In addition, several monoprotected alcohol derivatives of **10** (MOM, TBDMS) (6) were also oxidized using mCPBA or the VO(acac)$_2$–*t*-BuOOH epoxidation system (10–12). All of these reactions were unsatisfying since they resulted in low diastereoselectivity and were also plagued by low conversion or competing side reactions such as benzylic oxidation. As far as we are aware, the general *threo* diastereoselective epoxidation of this class of monosubstituted olefinic alcohols (or diols) remains an unsolved problem in organic synthesis.[4]

We then turned our attention to the epoxidation of a protected diol, the acetonide **14** (Scheme 2). Thus, treatment of **14** with mCPBA at room temperature for 3 days provided the epoxides **15** and **16** as an inseparable 2:1 mixture in a combined isolated yield of 96%. Although in this reaction the diastereoselectivity was no better than that observed in the epoxidation of diol **10**, the yield was substantially better. Furthermore, it was anticipated that the stereocentre at C1 in isomer **16** could be inverted at a later stage in the synthesis and thus the epoxide mixture **15**/**16** was carried forward. The assignment of the relative stereochemistry in the major epoxide diastereomer **15** was only tentative and was made primarily by correlation with the products derived from the epoxidation of **10** described earlier. The epoxide mixture **11**/**12** derived from **10** was converted into the corresponding mixture of acetonides **15**/**16** (2:1) and the major isomer from this mixture was identical with the major epoxide **15** obtained upon epoxidation of **14**. The eventual conversion of **15** to **1** (vide infra) confirmed this stereochemical assignment.

The epoxide mixture **15**/**16** was treated with the dianion of propiolic acid according to the conditions of Carlson and Oyler (17). This reaction was extremely capricious and we were never able to find conditions that would bring about the epoxide opening of **15**/**16** in a reproducible fashion on a quantity of material. However, treatment of the epoxide mixture **15**/**16** with lithium acetylide – EDA complex in THF–HMPA at



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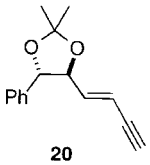

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room temperature afforded the readily separable acetylenic alcohols **17** and **18** in isolated yields of 55% and 26%, respectively. Omission of the HMPA from this reaction mixture resulted in only low (<10%) conversion. The inversion of the C1 alcohol stereocentre in **18** was attempted using Mitsunobu chemistry. The conditions described by Martin and Dodge (18) using *p*-nitrobenzoic acid and DEAD in PhMe provided predominantly the *E*-enyne **20** (76%) along with only 7% of the desired benzoate **19,** which was subsequently hydrolyzed to the alcohol **17**. Other related methods that were attempted for the inversion of the C1 stereocentre in **18**, including a two-step oxidation–reduction sequence, were also unsatisfactory.

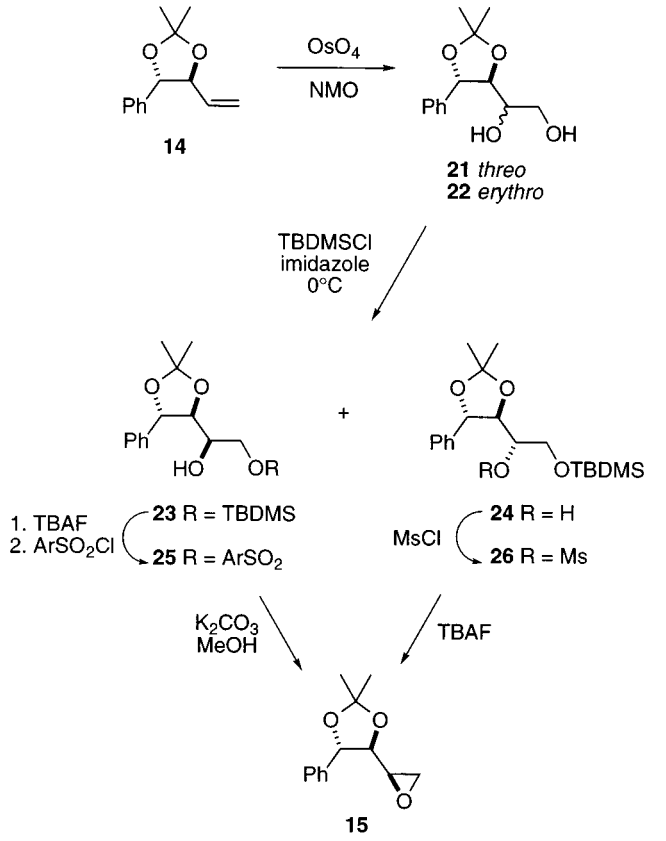
Due to our inability to invert the C1 (natural product numbering) stereocentre in the acetylenic alcohol **18**, we then considered the possibility of carrying out a dihydroxylation of olefin **14** in order to introduce the desired oxygenation pattern. It was anticipated, based on Kishi's rules (19) and additional literature precedent (20), that the bishydroxylation of monosubstituted olefin **14** would not be highly diastereoselective and that the major diastereomer would possess the undesired *erythro* relative stereochemistry at C1. However, it was expected that *both* diol diastereomers resulting from dihydroxylation could be efficiently converted into the desired epoxide **15**. Although this route would be more lengthy than direct epoxidation of the olefin, it would ultimately provide a single epoxide with the correct relative stereochemistry at C1.

In the event, olefin **14** was treated with catalytic OsO_4 and NMO to provide a 2:3 (by inspection of the integrated ^{1}H NMR spectrum) mixture of diols **21** and **22**, respectively (Scheme 3). The major diastereomer **22** was assigned the *erythro* configuration based upon literature precedent (19, 20). The crude diol mixture was silylated using TBDMSCl at 0°C and the readily separable monosilylated diols **23** and **24** were obtained in overall isolated yields of 37 and 57%, respectively, from olefin **14**. A two-step reaction sequence, involving formation of the mesylate **26** (MsCl, Et_3N, 0°C) followed by intramolecular displacement using TBAF at room temperature, effected the transformation of the major diastereomer **24** into the desired epoxide **15** in 86% overall yield. Desilylation (TBAF) of silyl ether **23** followed by conversion of the primary alcohol to the aryl sulfonate **25** using 2-mesitylenesulfonyl chloride (0°C to room temperature) was accomplished in 92% yield. Treatment of **25** with K_2CO_3 in MeOH provided epoxide **15** in 97% yield. Therefore, the overall conversion from **14** to **15** via the dihydroxylation strategy illustrated in Scheme 3 is an acceptable 82%.

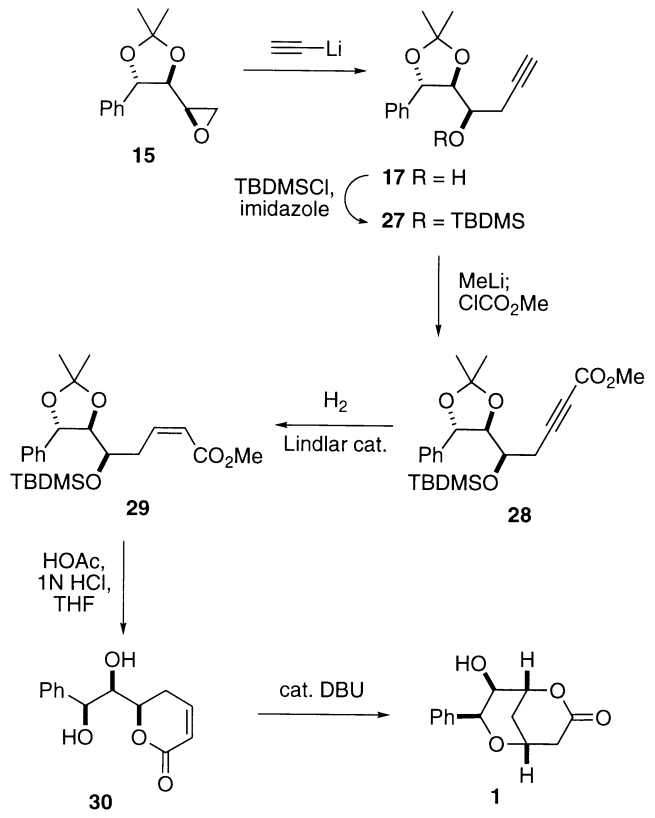
With pure epoxide **15** now in hand, alkylation with lithium

[4] Roush and Michaelides have reported that a MOM monoprotected *syn*-diol related to **10** is epoxidized with exceptionally high *threo* diastereoselectivity usingVO(acac)$_2$–*t*-BuOOH (16). However, in this literature example, the unprotected non-benzylic homoallylic alcohol is flanked by a group that is much more sterically bulky than the phenyl group of **10**.

Scheme 3.



Scheme 4.



acetylide – EDA complex in THF–HMPA at room temperature as described previously led to the acetylenic alcohol **17** (88%) (Scheme 4). Protection of the alcohol **17** (TBDMSOTf, Et_3N; 96%) followed by methoxycarbonylation (MeLi; $ClCO_2Me$; 91%) provided the α,β-acetylenic ester **28**. The three-step sequence from **15** to **28** (alkylation, silylation, methoxycarbonylation), while somewhat more lengthy than the originally anticipated reaction with propiolic acid dianion (vide supra), proceeds in excellent overall yield.

The conversion of the α,β-acetylenic ester **28** to the dihydropyran-2-one **30**, the immediate precursor to **1**, followed the strategy described by Carlson et al. for the synthesis of simple dihydropyran-2-ones (17). Thus, semi hydrogenation of the alkyne **28** over Lindlar's catalyst (5% Pd on Ca_2CO_3) cleanly provided the *Z* olefin **29**. The ^1H NMR spectrum of the crude material indicated the clean conversion of **28** to **29** without competing over-reduction or olefin *E*/*Z* isomerization. The crude reaction mixture was treated with a mixture of HOAc, 1 N HCl, and THF (1:1:1 v/v/v) at 65°C, resulting in the complete deprotection of the triol and subsequent cyclization to the lactone **30** (8-epigoniodiol) (7). Again, analysis of the crude reaction mixture (^1H NMR) revealed that a small amount of **30** had undergone cyclization to **1** under these reaction conditions. Thus, once again, the crude reaction mixture was used and the cyclization was completed using conditions that had been described by Honda and co-workers (1% DBU in THF) (7). Synthetic (±)-9-deoxygoniopypyrone (**1**) (mp 185–186°C, EtOH) was isolated in 60% yield for the three steps from **28** and exhibited spectral data (^1H and ^{13}C NMR, IR) identical to the data reported (1) for the natural product.

Experimental

General information

^1H NMR spectra were recorded at 300, 400, or 500 MHz in acetone-d_6 or $CDCl_3$ as specified. Broad-band proton-decoupled ^{13}C NMR spectra were recorded at 100 or 125 MHz in $CDCl_3$. IR spectra were recorded on neat samples unless stated otherwise. Solvents were anhydrous and were transferred via syringes under an atmosphere of argon or nitrogen. Work-up procedures involving the drying of organics were carried out with $MgSO_4$. Flash column chromatography (referred to as chromatography) was performed with 230–400 mesh silica gel, eluting with the solvents indicated (v/v). Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, N.Y., or the Laboratoire d'analyse élémentaire, Université de Montréal. Compounds for which high-resolution mass measurements are given were homogeneous by TLC analysis and gave satisfactory spectroscopic data indicative of their purity.

3,4-Dihydroxy-2-iodo-phenyl-1-butene ***4***

To a solution of 1-phenyl-2,3-butadien-1-ol **5** (10.5 g, 71.8 mmol) in ether (350 mL) at room temperature was slowly added *p*-TsNCO (12.0 mL, 1.1 equiv.). The mixture was stirred at room temperature for 30 min and then solid I_2 (18.2 g, 1.0 equiv.) was added in several portions over 1 h. Ag_2CO_3 (29.7 g, 1.5 equiv.) and MeCN (35 mL) were added sequentially and the resulting mixture was stirred at room temperature for 15 h. The reaction mixture was filtered through Celite, and the filter pad was washed extensively with ethyl acetate

(approximately 2 L) followed by methanol (approximately 500 mL). The filtrate was concentrated, the crude mixture was dissolved in methanol – 1 N NaOH (3:1 v/v, 320 mL) and stirred at room temperature for 15 h. The methanol was evaporated and the solution was neutralized to ~pH 7 by the addition of 1 N HCl. The mixture was extracted with CH_2Cl_2 (3 × 500 mL) and the combined organics were dried and concentrated. Chromatography (toluene–acetone, 6:1 to 5:1) of the residual material provided the diol **4** (13.7 g, 66%) as a white solid, mp 68.5–69.5°C. IR ($CHCl_3$): 3590, 1630, 1275 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.09 (br s, 1H), 3.23 (br s, 1H), 3.72 (br d, 1H, J = 6.0 Hz), 4.77 (d, 1H, J = 6.5 Hz), 5.80 (d, 1H, J = 1.8 Hz), 6.10 (dd, 1H, J = 1.0, 1.8 Hz), 7.26–7.39 (m, 5H); ^{13}C NMR δ: 75.8, 81.5, 111.6, 126.7, 128.2, 128.3, 128.6, 139.5. Anal. calcd. for $C_{10}H_{11}IO_2$: C 41.40, H 3.82; found: C 41.24, H 3.69.

3,4-Dihydroxy-4-phenyl-1-butene ***10***

To a solution of vinyl iodide **4** (8.0 g, 27.6 mmol) in refluxing benzene (333 mL) was added *n*-Bu_3SnH (8.2 mL, 1.1 equiv.) and AIBN (100 mg) and the solution was refluxed for 15 h. The solution was cooled to room temperature and then 10% KF (300 mL) and EtOAc (300 mL) were added. After 45 min, the white precipitate was filtered off and the filtrate was extracted with EtOAc (2×). The combined organics were washed with 10% KF and with brine, dried, and concentrated. Chromatography (hexane followed by hexane–EtOAc, 3:2) of the residue provided the diol **10** (3.66 g, 81%) as a colourless oil. IR: 3300, 1050 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.50 (br s, 2H), 4.21 (ddt, 1H, J = 5.5, 6.9, 1.5 Hz), 4.48 (d, 1H, J = 6.9 Hz), 5.13 (dt, 1H, J = 10.6, 1.5 Hz), 5.23 (dt, 1H, J = 17.3, 1.5 Hz), 5.71 (ddd, 1H, J = 5.5, 10.6, 17.3 Hz), 7.25–7.44 (m, 5H); ^{13}C NMR δ: 76.9, 77.6, 117.0, 127.0, 128.1, 128.4, 136.3, 140.2. Anal. calcd. for $C_{10}H_{12}O_2$: C 73.15, H 7.37; found: C 73.27, H 7.66.

Epoxidation of 3,4-dihydroxy-4-phenyl-1-butene ***10*** *(epoxides* ***11*** *and* ***12****)*

To a solution of diol **10** (116 mg, 0.71 mmol) in CH_2Cl_2 (3 mL) at room temperature was added mCPBA (458 mg, 3.0 equiv.) and the mixture was stirred for 16 h. Saturated sodium carbonate was added and the mixture was extracted with EtOAc (2×). The combined organics were washed with 1 N NaOH and brine, dried, and concentrated. Inspection of this crude reaction mixture by ^1H NMR spectroscopy indicated a 2:1 mixture of isomers. Chromatography (hexane–EtOAc, 1:2) of the residue provided a mixture of the epoxy diols **11** and **12** (65 mg, 51%) as a colourless oil. Major isomer **11:** ^1H NMR (500 MHz, $CDCl_3$) δ: 2.55 (dd, 1H, J = 2.8, 4.9 Hz), 2.65 (dd, 1H, J = 4.2, 4.9 Hz), 2.97 (ddd, 1H, J = 2.8, 3.8, 4.2 Hz), 3.68 (dd, 1H, J = 3.8, 7.4 Hz), 4.73 (d, 1H, J = 7.4 Hz), 7.35 (m, 5H). Minor isomer **12:** ^1H NMR (500 MHz, $CDCl_3$) δ: 2.77 (dd, 1H, J = 4.0, 5.0 Hz), 2.86 (dd, 1H, J = 2.8, 5.0 Hz), 2.94 (ddd, 1H, J = 2.8, 3.6, 4.0 Hz), 3.93 (dd, 1H, J = 3.6, 5.9 Hz), 4.70 (d, 1H, J = 5.9 Hz), 7.35 (m, 5H).

Acetonide ***13***

A solution of diol **4** (1.8 g, 6.2 mmol), 2-methoxypropene (0.9 mL, 1.5 equiv.), and camphorsulfonic acid (25 mg) in DMF (10 mL) was stirred at room temperature for 2 h. The mixture was poured into ammonium acetate buffer and extracted with ether (4×). The combined organics were washed with water and brine, dried, and concentrated. Chromatography (hexane–ether, 10:1) of the residue provided the acetonide **13** (1.89 g, 92%) as a colourless oil. IR: 1050 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.59 (s, 3H), 1.63 (s, 3H), 3.63 (dd, 1H, J = 0.8, 8.0 Hz), 4.83 (d, 1H, J = 8.0 Hz), 5.99 (d, 1H, J = 1.5 Hz), 6.28 (dd, 1H, J = 0.8, 1.5 Hz), 7.28–7.38 (m, 5H); ^{13}C NMR δ: 27.4, 27.5, 82.8, 88.0, 109.0, 110.3, 126.5, 128.36, 128.42, 130.0, 136.7. Anal. calcd. for $C_{13}H_{15}IO_2$: C 47.29, H 4.58; found: C 46.88, H 4.50.

Olefin ***14***

A mixture of vinyl iodide **13** (1.8 g, 6.2 mmol), triphenyltin hydride (2.6 g, 1.2 equiv.), and AIBN (20 mg) in benzene (40 mL) was heated at reflux for 90 min. The solution was cooled to room temperature and then 10% KF (100 mL) and EtOAc (100 mL) were added. After 15 min, the white precipitate was filtered off and the filtrate was extracted with EtOAc (2×). The combined organics were washed with 10% KF and brine, dried, and concentrated. Chromatography (hexane–ether, 15:1) of the residue provided the olefin **14** (1.09 g, 87%) as a colourless oil. IR: 2980, 1365, 1230, 1050 cm^{-1}; ^1H NMR: (300 MHz, $CDCl_3$) δ: 1.53 (s, 3H), 1.57 (s, 3H), 4.17 (app t, 1H, J = 8.4 Hz), 4.64 (d, 1H, J = 8.4 Hz), 5.20–5.27 (m, 2H), 5.87 (m, 1H), 7.26–7.58 (m, 5H); ^{13}C NMR δ: 27.0, 27.1, 82.9, 84.7, 109.3, 119.3, 126.4, 128.2, 128.4, 133.9, 137.2. Exact Mass calcd. for $C_{13}H_{17}O_2$ $(M+H)^+$: 205.1229; found: 205.1228.

Epoxidation of olefin ***14*** *(epoxides* ***15*** *and* ***16****)*

To a solution of olefin **14** (950 mg, 4.65 mmol) in dichloromethane (50 mL) at 0°C was added mCPBA (3.0 g, 3 equiv.). After 30 min, the cold bath was removed and the mixture was stirred at room temperature for 72 h. Saturated $NaHCO_3$ (100 mL) was added and the mixture was extracted with dichloromethane (2×). The combined organics were washed with saturated $NaHCO_3$ (2×), water, and brine, then dried and concentrated. Chromatography (hexane–EtOAc, 9:1) of the residue provided an inseparable mixture of the epoxides **15** and **16** (983 mg, 96%) as a colourless oil. Inspection of this mixture by ^1H NMR spectroscopy indicated a 2:1 mixture of isomers. Major isomer **15:** ^1H NMR (300 MHz, $CDCl_3$) δ: 1.50 (s, 3H), 1.55 (s, 3H), 2.48 (dd, 1H, J = 2.6, 5.3 Hz), 2.75 (dd, 1H, J = 4.2, 5.3 Hz), 3.06 (ddd, 1H, J = 2.6, 4.2, 5.0 Hz), 3.62 (dd, 1H, J = 5.0, 8.7 Hz), 4.91 (d, 1H, J = 8.7 Hz), 7.35 (m, 5H). Minor isomer **16:** ^1H NMR (300 MHz, $CDCl_3$) δ: 1.52 (s, 3H), 1.54 (s, 3H), 2.67 (dd, 1H, J = 2.6, 5.0 Hz), 2.81 (dd, 1H, J = 4.0, 5.0 Hz), 3.14 (ddd, 1H, J = 2.6, 4.0, 5.1 Hz), 3.73 (dd, 1H, J = 5.1, 8.1 Hz), 4.94 (d, 1H, J = 8.1 Hz), 7.35 (m, 5H).

Alkynes ***17*** *and* ***18***

Lithium acetylide – EDA complex (540 mg, 1.3 equiv.) was added portionwise over 2 min to a solution of the epoxide mixture **15**/**16** (887 mg, 4.03 mmol) in THF (10 mL) and HMPA (4 mL). The resulting mixture was stirred at room temperature for 15 h and then water was carefully added. The mixture was extracted with EtOAc (3×), and the combined organics were washed with 10% HCl (3×), water, and brine, then dried and concentrated. Chromatography (toluene–EtOAc, 10:1) of the residue provided the alkynes **17** and **18**. The first compound to

be eluted was the minor isomer **18** (260 mg, 26%), a colourless oil**.** IR: 3450, 3300, 2115, 1240, 1055 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.47 (s, 3H), 1.53 (s, 3H), 1.97 (t, 1H, J = 2.7 Hz), 2.15 (br s, 1H), 2.41–2.44 (m, 2H), 3.92–3.99 (m, 2H), 4.98 (AB q, 1H, J = 3.8, 11.2 Hz), 7.26–7.37 (m, 3H), 7.41–7.45 (m, 2H); ^{13}C NMR δ: 23.7, 27.0, 27.2, 70.4, 71.1, 79.9, 80.3, 84.0, 109.5, 127.4, 128.3, 128.5, 138.4. Anal. calcd. for $C_{15}H_{18}O_3$: C 73.15, H 7.37; found: C 73.27, H 7.46. Further elution provided the major isomer **17** (535 mg, 55%) as a white solid, mp 101.5–102.5°C. IR (KBr): 3460, 3300, 2120, 1240, 1060 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.51 (s, 3H), 1.56 (s, 3H), 1.95 (t, 1H, J = 2.7 Hz), 2.36 (ddd, 1H, J = 2.7, 6.5, 16.7 Hz), 2.37 (br s, 1H), 2.47 (ddd, 1H, J = 2.7, 7.3, 16.7 Hz), 3.74 (br m, 1H), 3.91 (dd, 1H, J = 2.0, 8.6 Hz), 4.91 (d, 1H, J = 8.6 Hz), 7.30–7.41 (m, 5H); ^{13}C NMR δ: 25.3, 26.9, 27.2, 67.3, 70.5, 79.1, 80.2, 83.8, 109.5, 126.8, 128.4, 128.7, 137.3. Anal. calcd. for $C_{15}H_{18}O_3$: C 73.15, H 7.37; found: C 73.19, H 7.38.

*Enyne **20** and benzoate **19***

To a solution of alcohol **18** (144 mg, 0.58 mmol) in toluene (12 mL) at room temperature was added sequentially Ph_3P (307 mg, 2 equiv.), DEAD (0.18 mL, 2 equiv.), and *p*-nitrobenzoic acid (195 mg, 2 equiv.). The resulting mixture was stirred for 2 h and then hexane (30 mL) was added. The white preciptate was filtered through Celite and to the filtrate was added EtOAc. The combined organics were washed with saturated $NaHCO_3$ (3×), dried, and concentrated. Chromatography (hexane–EtOAc, 9:1 to 4:1) of the residue first provided the enyne **20** (101 mg, 76%) as a white solid, mp 52–53°C. IR ($CHCl_3$): 3300, 1490, 1450, 1380, 1050, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.52 (s, 3H), 1.57 (s, 3H), 2.90 (d, 1H, J = 2.3 Hz), 4.20 (ddd, 1H, J = 1.3, 6.4, 8.4 Hz), 4.65 (d, 1H, J = 8.4 Hz), 5.68 (ddd, 1H, J = 1.3, 2.3, 15.9 Hz), 6.21 (ddd, 1H, J = 0.5, 6.4, 15.9 Hz), 7.27–7.37 (m, 5H); ^{13}C NMR δ: 26.9, 27.0, 78.7, 81.2, 82.8, 83.3, 109.7, 112.1, 126.4, 128.4, 128.6, 136.7, 140.0. Anal. calcd. for $C_{15}H_{16}O_2$: C 78.92, H 7.06; found: C 79.30, H 7.15. Further elution provided the benzoate **19** (17 mg, 7%), which was obtained as a white solid. Benzoate **19** was dissolved in MeOH (2 mL) and water (0.1 mL) and treated with K_2CO_3 (2 mg). After 24 h, the mixture was concentrated and subjected to chromatography (9:1 toluene–EtOAc). The alkynol **17** was obtained as a white solid (4 mg, 95%).

*Silyl ethers **23** and **24***

To a solution of alkene **14** (1.0 g, 4.9 mmol) and $NMO{\cdot}H_2O$ (1.4 g, 2.1 equiv.) in acetone (20 mL) and water (2 mL) at room temperature was added a solution of OsO_4 (1 mL of a 4% solution in water) and the mixture was stirred for 15 h. A saturated solution of Na_2SO_3 (30 mL) was added and the resulting mixture was stirred for 1 h. The mixture was extracted with EtOAc (2×) and the organics were washed successively with saturated Na_2SO_3, water, and brine and then dried and concentrated. The residual oil so obtained (analysis by ^1H NMR spectroscopy indicated it to be a 3:2 mixture of diastereomers) and imidazole (790 mg, 2.4 equiv.) were dissolved in CH_2Cl_2 (18 mL) and cooled to 0°C. TBDMSCl (875 mg, 1.2 equiv.) was added as a solid and the resulting mixture was stirred at 0°C for 2 h. Water (50 mL) was added and extracted with EtOAc (2×). The organics were washed with brine and concentrated. The residual oil was subjected to chromatography (hexane–EtOAc, 10:1). The major diastereomer, silyl ether **24** (985 mg, 57%), was eluted first and was obtained as a colourless oil. IR: 3480, 840 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 0.02 (s, 3H), 0.03 (s, 3H), 0.86 (s, 9H), 1.48 (s, 3H), 1.53 (s, 3H), 2.48 (d, 1H, J = 4.8 Hz), 3.61 (dd, 1H, J = 6.5, 10.1 Hz), 3.71 (dd, 1H, J = 3.9, 10.1 Hz), 3.83 (m, 1H), 3.92 (dd, 1H, J = 6.8, 7.7 Hz), 5.03 (d, 1H, J = 7.7 Hz), 7.26–7.47 (m, 5H); ^{13}C NMR (125 MHz) δ: –5.6, –5.5, 18.2, 25.7, 27.0, 27.1, 64.0, 72.9, 81.1, 82.3, 109.3, 127.2, 128.0, 128.3, 138.9. Anal. calcd. for $C_{19}H_{32}O_4Si$: C 64.73, H 9.15; found: C 64.89, H 9.42. Further elution provided the minor diastereomer, silyl ether **23** (648 mg, 37%), as a colourless oil. IR: 3480, 830 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: –0.04 (s, 3H), –0.01 (s, 3H), 0.81 (s, 9H), 1.51 (s, 3H), 1.55 (s, 3H), 2.45 (d, 1H, J = 7.3 Hz), 3.54 (m, 1H), 3.59–3.64 (m, 2H), 3.87 (dd, 1H, J = 1.8, 8.7 Hz), 4.99 (d, 1H, J = 8.7 Hz), 7.27–7.41 (m, 5H); ^{13}C NMR (125 MHz) δ: –5.6, –5.5, 18.1, 25.7, 26.9, 27.2, 64.7, 68.7, 79.0, 82.2, 109.3, 126.8, 128.3, 128.5, 137.5. Anal. calcd. for $C_{19}H_{32}O_4Si$: C 64.73, H 9.15; found: C 64.48, H 9.06.

*Epoxide **15** from the major silyl ether diastereomer **24***

To a solution of alcohol **24** (885 mg, 2.51 mmol) and Et_3N (1.05 mL, 3 equiv.) in CH_2Cl_2 (10 mL) at 0°C was added methanesulfonyl chloride (0.29 mL, 1.5 equiv.). After 15 min, water was added and the resulting mixture was stirred at room temperature for 15 min. The mixture was extracted with EtOAc (2×) and the organics were washed with water, dried, and concentrated. The colourless residue was dissolved in THF (10 mL) and TBAF (5.0 mL, 2 equiv.) was added. The reaction mixture was stirred at room temperature for 15 h and then water was added. The mixture was extracted with EtOAc (2×) and the organics were washed with water and brine, dried, and concentrated. Chromatography (hexane–EtOAc, 6:1) of the residual oil provided epoxide **15** (477 mg, 86%) as a colourless oil. IR: 1235 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.50 (s, 3H), 1.55 (s, 3H), 2.48 (dd, 1H, J = 2.6, 5.3 Hz), 2.75 (dd, 1H, J = 4.2, 5.3 Hz), 3.06 (ddd, 1H, J = 2.6, 4.2, 5.0 Hz), 3.62 (dd, 1H, J = 5.0, 8.7 Hz), 4.91 (d, 1H, J = 8.7 Hz), 7.35 (m, 5H); ^{13}C NMR (125 MHz) δ: 26.6, 26.9, 43.7, 50.2, 80.0, 83.2, 109.8, 126.3, 128.3, 128.6, 137.4. Anal. calcd. for $C_{13}H_{16}O_3$: C 70.89, H 7.32; found: C 70.54, H 7.34.

*Aryl sulfonate **25***

To a solution of silyl ether **23** (741 mg, 2.10 mmol) in THF (10 mL) was added TBAF (2.3 mL, 1.1 equiv.) and, after 1 h, water was added. The mixture was extracted with EtOAc (3×) and the organics were washed with water and brine, dried, and concentrated. The residual white solid was dissolved in pyridine (10 mL) and cooled to 0°C. 2-Mesitylenesulfonyl chloride (520 mg, 1.1 equiv.) was added as a solid and the resulting mixture was stirred at 0°C for 1 h and then gradually warmed to room temperature over 6 h. After stirring at room temperature for 16 h, 1 N HCl was added and the resulting mixture was extracted with EtOAc (2×). The organics were washed with 1 N HCl and brine, dried, and concentrated. Chromatography (hexane–EtOAc, 3:1) of the residual oil provided the aryl sulfonate **25** (813 mg, 92%) as a colourless glass. IR: 3500, 1380 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.47 (s, 3H), 1.51 (s, 3H), 2.28 (s, 3H), 2.43 (d, 1H, J = 8.9 Hz), 2.54 (s, 6H), 3.72 (dd, 1H, J = 1.5, 8.6 Hz), 3.77 (m, 1H), 3.94 (dd, 1H, J = 5.3, 10.4 Hz), 3.98 (dd, 1H, J = 7.1, 10.4 Hz), 4.96 (d, 1H,

J = 8.6 Hz), 6.92 (s, 2H), 7.30–7.38 (m, 5H); ^{13}C NMR (125 MHz) δ: 21.0, 22.4, 26.8, 27.1, 66.0, 70.3, 78.7, 81.9, 109.8, 126.6, 128.6, 128.7, 130.3, 131.7, 136.8, 139.9, 143.4. Anal. calcd. for $C_{22}H_{28}O_6S$: C 62.84, H 6.71; found: C 62.45, H 6.77.

*Epoxide **15** from the aryl sulfonate **25***

A mixture of aryl sulfonate **25** (761 mg, 1.81 mmol) and solid K_2CO_3 (500 mg, 2 equiv.) in MeOH (20 mL) was stirred at room temperature for 90 min and then saturated NH_4Cl was added. The mixture was extracted with EtOAc (2×) and the combined organics were washed with water and brine, dried, and concentrated. Chromatography (hexane–EtOAc, 7:1) of the residual oil provided epoxide **15** (387 mg, 97%) as a colourless oil.

*Alkyne **17***

Following the procedure described above for the alkynylation of the epoxide mixture **15**/**16**, the pure epoxide **15** (853 mg, 3.87 mmol) was converted to alkyne **17** (839 mg, 88%).

*Silyl ether **27***

To a solution of alcohol **17** (450 mg, 1.83 mmol) and Et_3N (0.6 mL, 2.4 equiv.) in dichloromethane (15 mL) at 0°C was added TBDMSOTf (0.5 mL, 1.2 equiv.). The mixture was stirred at 0°C for 30 min and then at room temperature for 2 h. Ammonium acetate buffer was added and the mixture was extracted with dichloromethane (3×). The combined organics were dried and concentrated. Chromatography (hexane–ether, 20:1) of the residue provided the silyl ether **27** (633 mg, 96%) as a white solid, mp 60.5–61.5°C. IR ($CHCl_3$): 3310, 1250, 1065, 830 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.07 (s, 3H), 0.12 (s, 3H), 0.89 (s, 9H), 1.50 (s, 3H), 1.55 (s, 3H), 1.93 (t, 1H, J = 2.7 Hz), 2.39 (ddd, 1H, J = 2.7, 6.0, 16.6 Hz), 2.58 (ddd, 1H, J = 2.7, 7.1, 16.6 Hz), 3.90 (ddd, 1H, J = 3.0, 6.0, 7.1 Hz), 4.07 (dd, 1H, J = 3.0, 8.4 Hz), 4.97 (d, 1H, J = 8.4 Hz), 7.34 (m, 5H); ^{13}C NMR δ: –4.5, –4.2, 18.1, 24.2, 25.8, 27.0, 27.4, 69.6, 70.4, 78.6, 81.1, 84.2, 109.1, 127.2, 128.2, 128.5, 138.3. Anal. calcd. for $C_{21}H_{32}O_3Si$: C 69.96, H 8.94; found: C 70.23, H 9.12.

*Ester **28***

To a solution of alkyne **27** (543 mg, 1.51 mmol) in THF (15 mL) at –78°C was added MeLi (1.6 mL of a 1.4 M solution in ether, 1.5 equiv.) and the resulting mixture was stirred at –78°C for 5 min, and at 0°C for 30 min. Methyl chloroformate (0.2 mL, 1.5 equiv.) was then added and the mixture was stirred for a further 30 min at 0°C. Ammonium acetate buffer was added and the mixture was extracted with EtOAc (3×). The combined organics were dried and concentrated. Chromatography (hexane–ether, 9:1) of the residue provided the ester **28** (576 mg, 91%) as a white solid, mp 50.5–51.5°C. IR ($CHCl_3$): 2220, 1710, 1250, 1065, 835 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.02 (s, 3H), 0.11 (s, 3H), 0.84 (s, 9H), 1.47 (s, 3H), 1.52 (s, 3H), 2.49 (dd, 1H, J = 6.2, 17.0 Hz), 2.69 (dd, 1H, J = 5.7, 17.0 Hz), 3.71 (s, 3H), 3.96–4.08 (m, 2H), 4.91 (d, 1H, J = 8.0 Hz), 7.25–7.40 (m, 5H); ^{13}C NMR δ: –4.6, 18.0, 24.3, 25.7, 26.9, 27.3, 52.4, 69.3, 74.4, 78.6, 84.3, 86.3, 109.2, 127.2, 128.3, 128.5, 138.0, 153.8. Anal. calcd. for $C_{23}H_{34}O_5Si$: C 66.00, H 8.18; found: C 66.34, H 8.40.

*Pyranone **30** ((±)-8-epigoniodiol)*

A mixture of ester **28** (330 mg, 0.79 mmol) and Lindlar's catalyst (33 mg) in THF (60 mL) was stirred under an atmosphere of hydrogen gas (1 atm (101.3 kPa)) for 1 h. The mixture was filtered through Celite, washing with EtOAc. The filtrate was concentrated and inspection by ^{1}H NMR spectroscopy indicated the absence of starting material and the presence of one olefin isomer (**29**). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.01 (s, 3H), 0.05 (s, 3H), 0.82 (s, 9H), 1.48 (s, 3H), 1.51 (s, 3H), 2.89 (m, 2H), 3.66 (s, 3H), 3.85–3.96 (m, 2H), 4.90 (d, 1H, J = 8.2 Hz), 5.74 (td, 1H, J = 1.8, 11.5 Hz), 6.30 (td, 1H, J = 7.3, 11.5 Hz), 7.25–7.40 (m, 5H). The crude mixture was stirred in a mixture of THF (2 mL), 1 N HCl (1 mL), and glacial HOAc (1 mL) at 65°C for 3 h. The solution was cooled to room temperature and then co-evaporated with toluene (3×). Ammonium acetate buffer was poured into the residue and the mixture was extracted with EtOAc (4×). The combined organics were dried and concentrated. A small portion of this material was purified by chromatography (toluene–EtOAc, 4:1) to provide the pyranone **30** as a white solid, mp 99–100°C. IR (KBr): 3400, 1710, 1250 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.11 (dddd, 1H, J = 0.7, 3.8, 6.3, 18.6 Hz), 2.81 (tdd, 1H, J = 2.4, 12.6, 18.6 Hz), 3.31 (br s, 1H), 3.44 (br s, 1H), 3.63 (br m, 1H), 4.18 (ddd, 1H, J = 2.2, 3.8, 12.6 Hz), 4.95 (d, 1H, J = 7.3 Hz), 5.92 (ddd, 1H, J = 0.7, 2.4, 9.8 Hz), 6.84 (ddd, 1H, J = 2.4, 6.3, 9.8 Hz), 7.33 (m, 5H). Exact Mass calcd. for $C_{13}H_{15}O_4$ $(M+H)^+$: 235.0971; found: 235.0970. The remainder of the material was used directly in the subsequent reaction.

*(±)-9-Deoxygoniopypyrone (**1**)*

The crude material containing the pyranone **30** was stirred in a solution of 1% DBU in THF (3 mL) at room temperature for 15 h. The mixture was concentrated and the residual material was subjected to chromatography (toluene–EtOAc, 17:3). (±)-9-Deoxygoniopypyrone (**1**) (111 mg, 60% from **28**) was obtained as a white solid, mp 183–184°C. IR (KBr): 3450, 1740, 1720, 1270 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.55 (br s, 1H), 1.83 (dd, 1H, J = 4.0, 14.1 Hz), 2.58 (d quintet, 1H, J = 14.1, 2.1 Hz), 2.85 (dd, 1H, J = 5.1, 19.3 Hz), 2.96 (dm, 1H, J = 19.3 Hz), 3.94 (m, 1H), 4.51 (m, 1H), 4.86 (app septet, 1H, J = 1.8 Hz), 4.95 (d, 1H, J = 1.6 Hz), 7.30–7.42 (m, 5H); ^{13}C NMR δ: 24.1, 36.4, 66.2, 68.4, 70.6, 74.7, 126.2, 128.4, 129.0, 136.8, 169.3. Anal. calcd. for $C_{13}H_{14}O_4$: C 66.46, H 6.02; found: C 66.20, H 6.19.

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List of abbreviations

mCPBA: *m*-chloroperoxybenzoic acid
NMO: *N*-methylmorpholine *N*-oxide
TBDMSCI: *tert*-butyldimethylsilyl chloride
TBDMSOTf: *tert*-butyldimethylsilyl trifluoromethanesulfonate
TBAF: tetrabutylammonium fluoride
DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene
AIBN: 2,2′-azobisisobutyronitrile
MOM: methoxymethyl
TBDMS: *tert*-butyldimethylsilyl
HMPA: hexamethylphosphoramide
DEAD: diethyl azodicarboxylate