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Model studies towards the synthesis of gilvocarcin M

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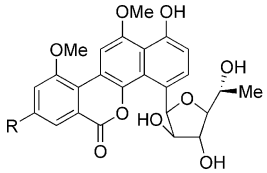
In model studies towards the synthesis of gilvocarcin M, a convergent, xanthate-based free-radical strategy was tested in order to construct the key aromatic ring attached to the sugar unit.

Introduction

C-Aryl glycosides, or glycosylarenes, represent an important class of natural products in which carbohydrates are directly bound to an aromatic moiety through a C–C bond, and which have been shown to be especially resistant to enzymatic and acidic hydrolysis.[1] These compounds constitute interesting synthetic targets in the light of their biological activities and unique structures. The anticancer gilvocarcins[2] (**1a–c**) are metabolites of certain *Streptomyces* species and belong to one of four classes of naturally occurring *C*-aryl glycosides, in which the sugar is located *para* to a phenolic hydroxyl group (Fig. 1).



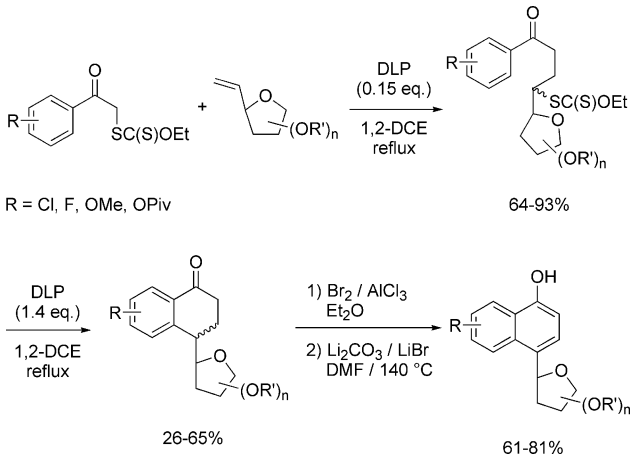
Gilvocarcin M, R = CH_3 (**1a**)
Gilvocarcin V, R = $CH{=}CH_2$ (**1b**)
Gilvocarcin E, R = CH_2CH_3 (**1c**)

Fig. 1 Gilvocarcin class *C*-aryl glycosides.

Owing to their biological and synthetic utility, efficient synthetic routes to *C*-aryl glycosides from sugar precursors have been reported, based either on the regiocontrolled construction of the *C*-naphthyl glycosidic linkage using various glycosyl donors[1,3] or on the elaboration of the naphthyl appendage *via* transformation of a *C*-alkyl or a *C*-furanyl glycoside.[1,4] Amongst these methods, the *O*→*C* glycoside rearrangement reported by Suzuki *et al.*[5] is probably the most useful because it has several advantages in terms of regio- and stereoselectivity. This method was successfully applied to the total synthesis of the gilvocarcins and their analogues.[2] However, because this is a Lewis acid-promoted process, the aromatic moieties that take part in the reaction have to be electron-rich and the carbohydrate unit solidly protected.

Recently, we reported a new acces to group I *C*-aryl glycosides using a xanthate-mediated free-radical addition–cyclisation sequence followed by an efficient aromatisation protocol.[6] This process allows the synthesis of a wide variety of substituted glycosylarenes under mild conditions (Scheme 1).

Furthermore, because this approach allows the use of a great variety of substituents (including electron-withdrawing groups) on the aromatic ring and on the sugar moiety, it should be useful for the expedient preparation of a broad variety of analogues of the natural products. Because of our continuing interest in the synthetic applications of xanthate-based free-radical chemistry, we decided to pursue the synthesis of gilvocarcin M using this approach.



Scheme 1 Xanthate-based approach to *C*-aryl glycosides.

Retrosynthetic analysis and strategy

The general features of our route are outlined in Scheme 2. Gilvocarcin M (**1a**) would be prepared from protected tetralone **2** by simple aromatisation of the A ring. In the key step of the synthesis, tetralone **2** would be obtained in a convergent manner from an acetophenone xanthate (**3**) and the appropriate olefin (**4**), the latter serving as an effective radical trap.

The required complex xanthate **3** would be obtained by Friedel–Crafts type acylation of tricyclic lactone **5**. On the basis of the the synthesis of the gilvocarcin aglycon by Martin *et al.*,[7] it was projected that the carbon–carbon bond joining rings B and D would be constructed through a palladium-mediated cyclisation and an esterification reaction between the known acid chloride **6**[8] and commercially available *p*-methoxyphenol (**7**).

In parallel, olefin **4** would be obtained by vinylation of the known D-fucose derivative **8**. Thus, in the synthetic direction, reaction of lactol **8** with an organometallic compound (*e.g.* vinylmagnesium bromide) would produce a diol intermediate that could be cyclised stereoselectively to afford the desired radical trap **4**.

Results and discussion

Our synthesis starts with the preparation of the desired xanthate **3**. The first step in this sequence was the esterification of commercially available *p*-methoxyphenol with acid chloride **6** under standard conditions to afford ester **9** in 95% yield (Scheme 3). With an appropiately placed iodine atom, intermediate **9** was used to test the Pd-mediated cyclisation reaction. Thus, treatment of **9** with a catalytic amount (26 mol%) of $Pd(PPh_3)_2Cl_2$ and sodium acetate in *N*,*N*-dimethylacetamide (DMA) at 130 °C simultaneously created the desired B–D bond and completed the annulation of ring C in a single operation, affording tricylic system **5** in 85% yield.

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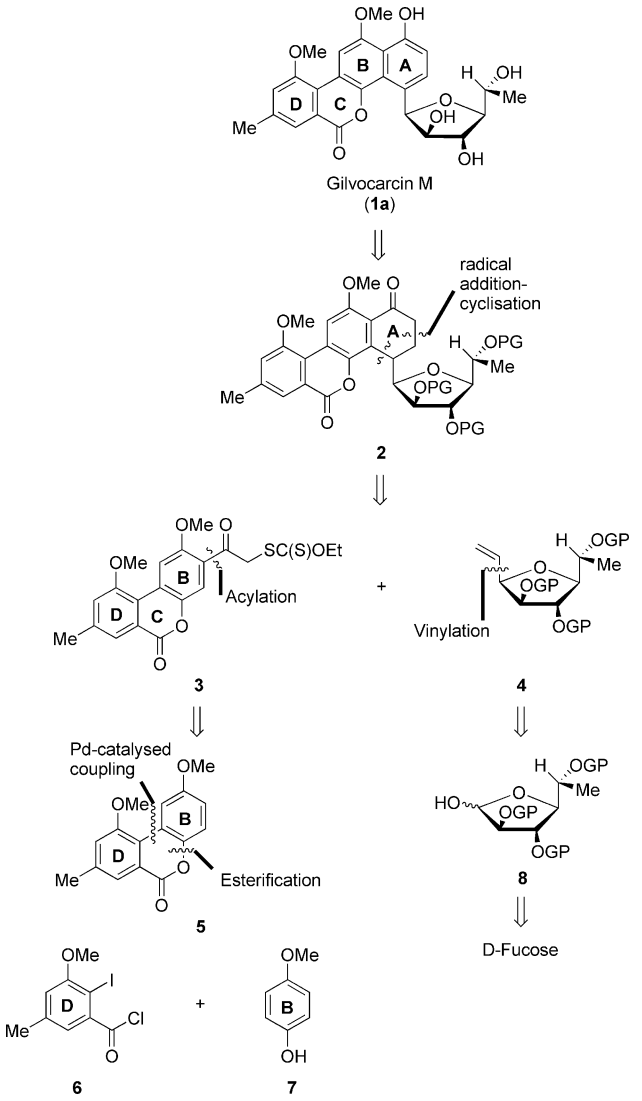
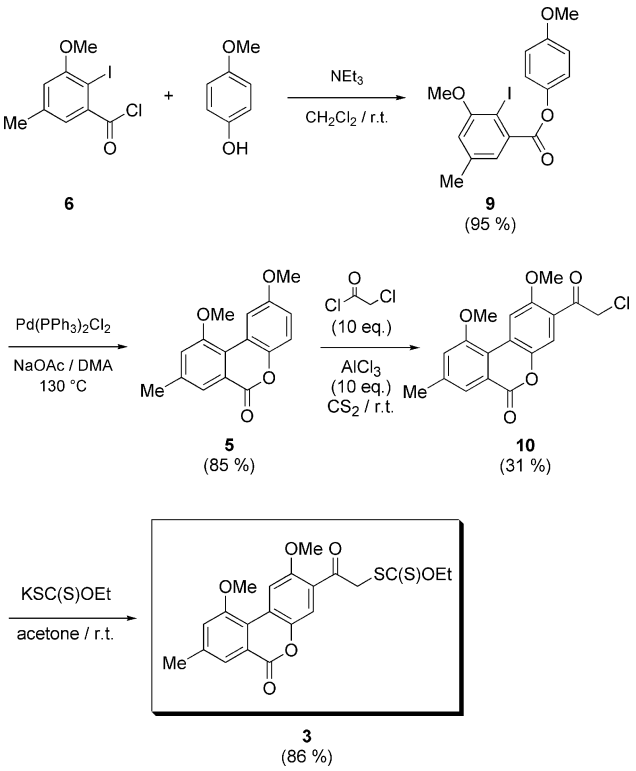


Scheme 2 Retrosynthetic analysis of gilvocarcin M (**1a**).

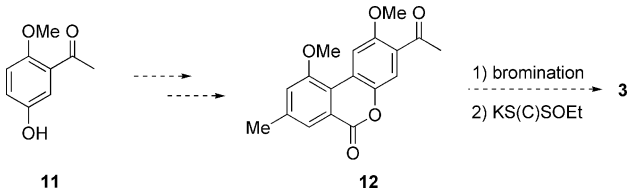
The next step required the introduction of the chloroacetyl group at the C-2 position of tricycle **5**. However, the Friedel–Crafts-type acylation, an apparently simple transformation, was the most challenging step in the preparation of the key xanthate. After several unsuccesful attempts, we found that treatement of **5** with a large excess of chloroacetyl chloride (10 equiv.) and $AlCl_3$ (10 equiv.) in CS_2 at room temperature furnished the desired compound (**10**), albeit in low yield (31%) together with several side products. Finally, treatment of the latter with potassium ethyl xanthate in acetone at room temperature afforded the desired radical precursor **3** in 86% yield.

The unexpectedly low yield for the acylation step forced us to explore an alternative synthetic route for the preparation of compound **10**. We envisaged that the use of a phenolic acetophenone would provide a derivative **11** that would already possess the required ketone moiety, and which could be used as starting material for the synthesis of **10** *via* a chlorination (or bromination) protocol (Scheme 4).

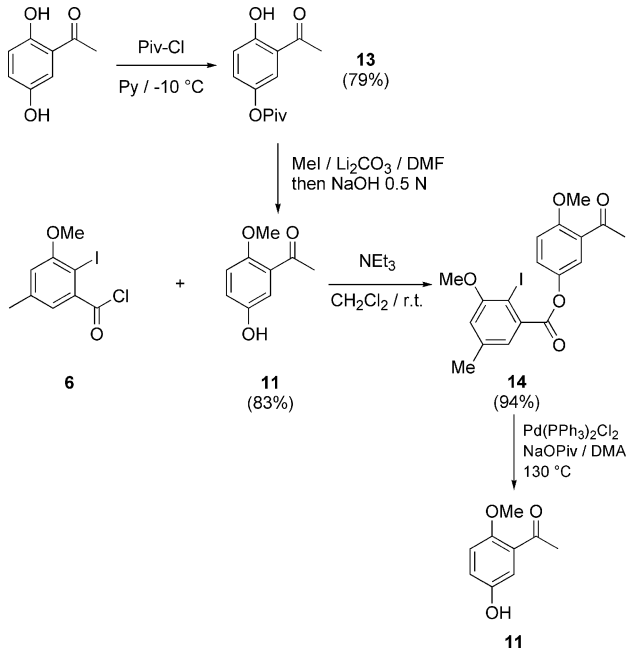
In order to test this route, we first prepared the required acetophenone **11** in good overall yield by using the sequence shown in Scheme 5. Esterification with acid chloride **6** under standard conditions furnished compound **14** in 94% yield. However, when this compound was subjected to the typical reaction conditions for the Pd-catalysed cyclisation, only acetophenone **11** (derived from the acyl exchange by attack of an acetate anion at the ester carbonyl of **14**), was recovered from the reaction mixture.



Scheme 3 Synthesis of the radical precursor (**3**).



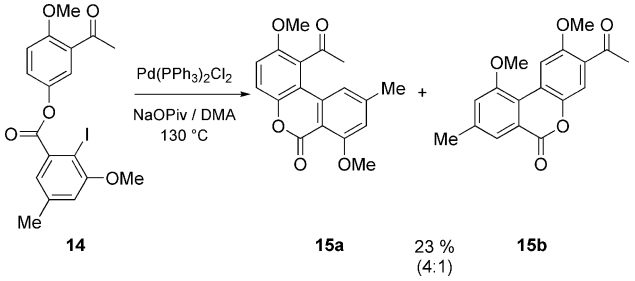
Scheme 4 Proposed route to intermediate **3**.



Scheme 5 Alternative route to intermediate **3**.

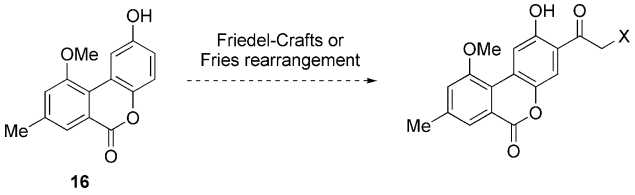
This problem had already been observed by Suzuki *et al.*[2] during the total synthesis of the gilvocarcins. In fact, when electron-poor aromatics are used for this coupling reaction (as in the case of **14** due to the presence of the ketone), the ester moiety becames highly electrophilic, thus favouring the

attack of a nucleophile, and furnishing mostly the hydrolysis product (*e.g.* **11**). To circumvent this problem, Suzuki employed a sterically hindered base (sodium pivalate), wich suppressed this side reaction. When we applied this modification to intermediate **14**, the expected coupling product was observed, unfortunately as an inseparable 4 : 1 mixture of **15a** and **15b** in favour of the undesired regioisomer **15a** (Scheme 6).



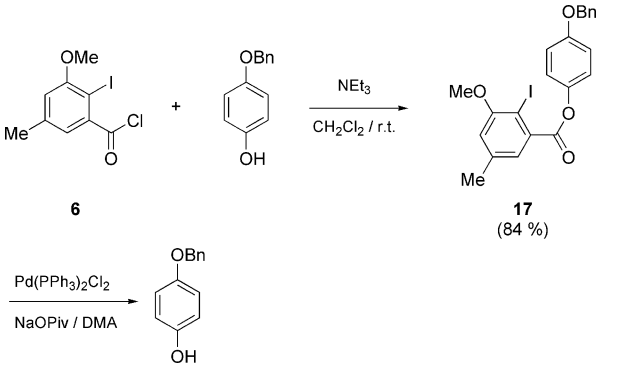
Scheme 6 Use of a hindered base for the Pd-catalysed cyclisation.

We next turned our attention to the directed Friedel–Crafts acylation and to the Fries rearrangement. We expected that a phenol like **16** could be prepared in order to perform the acylation step under milder conditions and consequently with a better yield (Scheme 7).



Scheme 7 Alternative route.

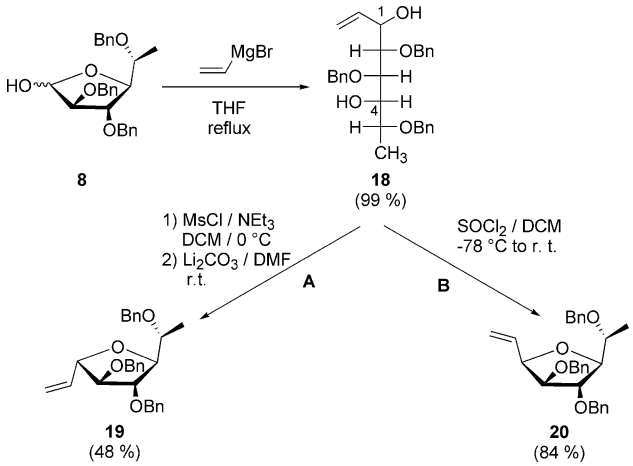
For this purpose, we envisaged that a benzyl protection in the initial phenol moiety would not change the electronic nature of the aromatic moiety and could be selectively removed after the Pd-catalysed step, thus providing the desired alcohol **16**. The required ester (**17**) for the cyclisation step was prepared as shown in Scheme 8. Unfortunately, when this compound was treated with a catalytic amount of the palladium complex and either sodium acetate or sodium pivalate, *p*-benzyloxyphenol was observed as the only product.



Scheme 8 Use of benzyl protection.

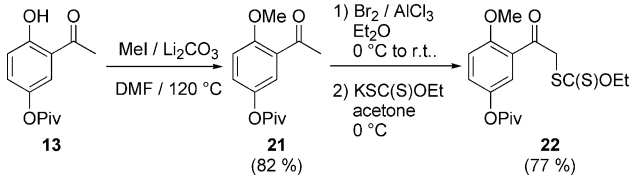
Because of these unexpected difficulties, we decided that the original approach (see Scheme 3) was the best way to access to radical precursor **3**, even if optimisation of the acylation step must eventually be performed.

The elaboration of the carbohydrate moiety of gilvocarcin M required a stereoselective coupling of D-fucose derivative **8**[9] with a suitable synthetic equivalent for the vinyl anion (see Scheme 2). Treatement of **8** with an excess of vinylmagnesium bromide in refluxing THF resulted in the formation of diol **18** as an inseparable 12 : 1 mixture of distereoisomers in almost quantitative yield (99%) (Scheme 9). Because at this stage it was not possible to determine the stereochemistry of C-1, diol **18** was cyclised by different methods. When the allylic alcohol (C-1) in **18** was mesylated and the resulting sulfonyl derivative treated in basic media, olefin **19** was obtained in 48% yield as an inseparable mixture of diastereoisomers (ratio $\alpha/\beta = 1 : 5$) by inversion of configuration at the allylic position (path A). Alternatively, when $SOCl_2$ was added to a cold (−78 °C) solution of **18** in CH_2Cl_2, the expected isomer (α) was formed in 84% yield by a double inversion of configuration (global retention, path B).[10]



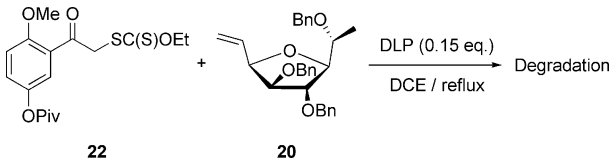
Scheme 9 Synthesis of olefin **20**.

Before testing the radical sequence between olefin **20** and xanthate **3**, we decided to perform a model study in order to evaluate the compatibility of the benzyl protections on sugar **20** with the radical process. Thus, xanthate **22**, which possesses a similar substitution pattern on the aromatic ring (a methoxy group and an ester), and which can be easily prepared on a multigram scale, was first synthesised from acetophenone **13** in good overall yield (Scheme 10).



Scheme 10 Preparation of model xanthate **22**.

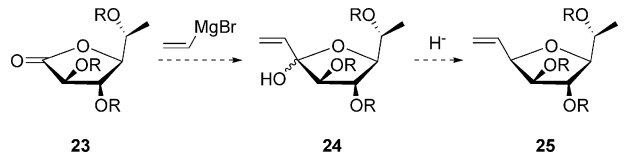
With model xanthate **22** in hand, we proceeded with the radial sequence on olefin **20**. When these two compounds were allowed to react in a refluxing solution of 1,2-dichloroethane (DCE) using dilauroyl peroxide (DLP) as initiator, the expected adduct was not observed, but a complex mixture of degradation products instead (Scheme 11).



Scheme 11 Model study.

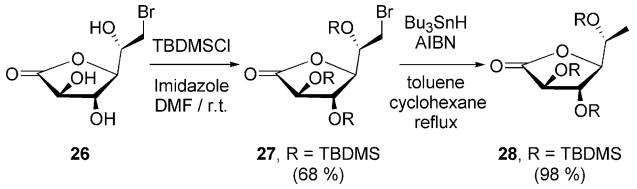
The reasons for the failure of this reaction are still unclear. It is possible that intramolecular hydrogen abstraction, probably from a benzylic position, followed by an uncontrolled sequence competed successfully with the desired ring-closure to the tetralone.

Since the supposed reason for this failure was the presence of the benzylic protections in the sugar moiety, we decided to replace these protective groups. According to this, and in an effort to simplify our route to the radical trap, we decided to prepare lactone **23**, which could be used as starting material for a sequence involving nucleophilic addition and stereoselective lactol reduction to furnish the desired olefin **25** (Scheme 12).[3f,11]



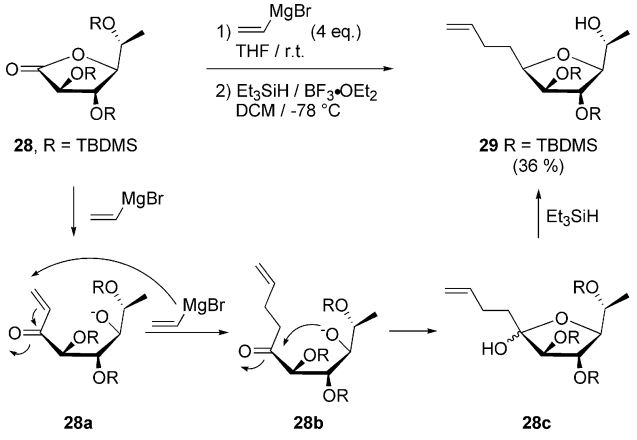
Scheme 12 Lactone strategy.

We started our route by the synthesis of the requisite lactone in three steps from known bromo derivative **26**,[12] prepared in one step from commercially available D-galactono-1,4-lactone (Scheme 13). Protection of the hydroxyl groups in the form of *tert*-butyldimethylsilyl ethers followed by radical reduction of the bromine atom afforded lactone **28** in an excellent overall yield (67%), in only three steps and on a multigram scale.



Scheme 13 Preparation of lactone **28**.

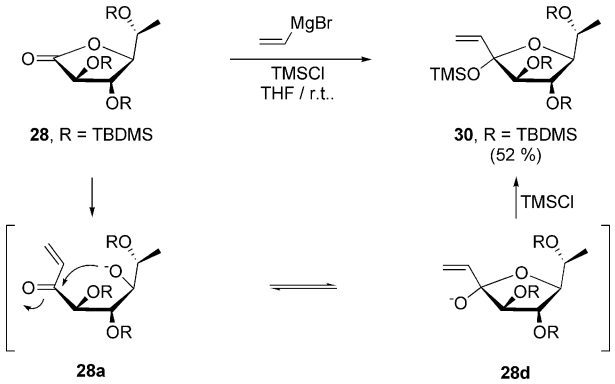
The addition of vinylmagnesium bromide to lactone **28** was then tested. Treatement of the latter with excess vinylmagnesium bromide followed by reduction of the lactol intermediate with Et_3SiH and $BF_3{\cdot}OEt_2$ unexpectedly gave compound **29** in 36% yield as a single isomer[13] (Scheme 14).



Scheme 14 Unexpected formation of compound **29**.

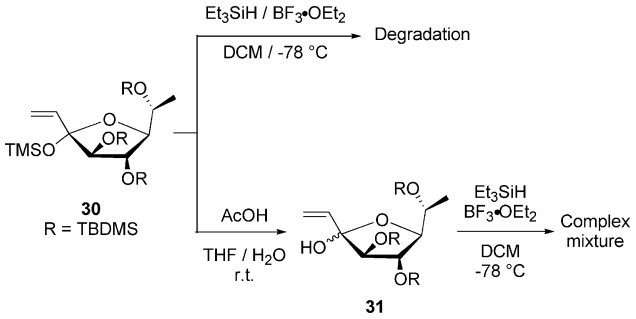
In fact, formation of hemiketal **28c** results from double addition of vinylmagnesium bromide to lactone **28**. This problem had already been observed by Xie *et al.*,[14] but could not be completely circumvented in order to provide the single addition product. In order to solve this problem, we reasoned that a highly oxophilic reagent such as trimethylsilyl chloride (TMSCl) could trap the corresponding alcoholate after the addition of one equivalent of vinylmagnesium bromide and formation of the hemiketal (**28c**).[15] Gratifyingly, when the Grignard reaction was performed in the presence of 2 equivalents of TMSCl, silyl ether **30** was isolated in 52% yield as the only product (Scheme 15).

Although we were pleased to find that the Grignard addition had been successful, attempts to reduce the lactol function in



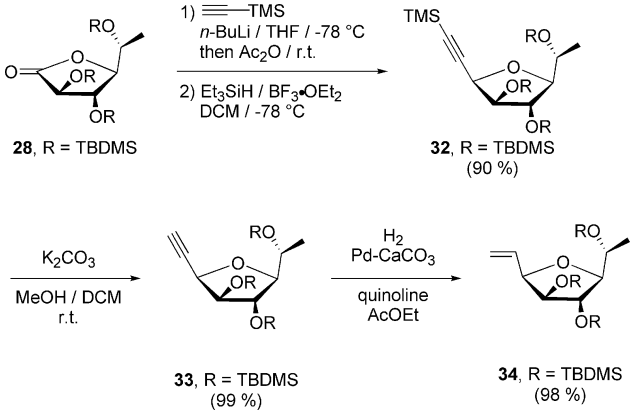
Scheme 15 Trapping of the single addition product.

compound **30**, or the unstable deprotected hemiketal **31**, led only to a complex mixture of degradation products (Scheme 16).



Scheme 16 Attempts to reduce hemiketal **30**.

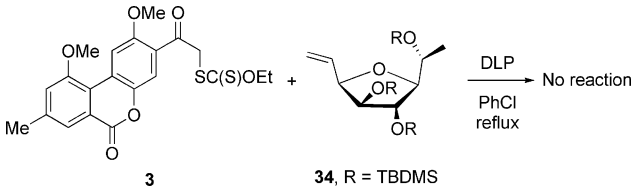
The introduction of the vinyl substituent was finally achieved using TMS-acetylene as a vinyl equivalent. When a cold (−78 °C) solution of lactone **28** in dry THF was treated with a slight excess of lithium TMS-acetylene and the resulting acetate reduced under standard conditions ($Et_3SiH/BF_3{\cdot}OEt_2$), alkyne **32** was obtained in excellent overall yield (90% over 2 steps) and as a single isomer (α) (Scheme 17). With precursor **32** in hand, completion of the synthesis of the desired olefin **34** became straightforward. Thus, deprotection of the TMS group in a basic medium afforded terminal alkyne **33** in almost quantitative yield (99%). Finally, hydrogenation over Lindlar catalyst completed the sequence. In this way, olefin **34** was isolated in excellent yield (98%).



Scheme 17 Synthesis of olefin **34**.

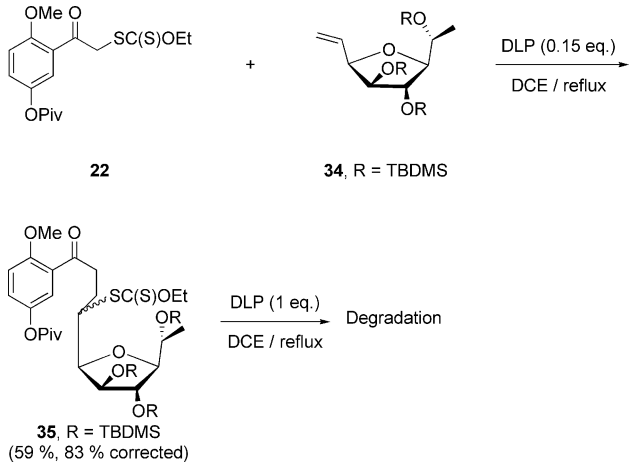
With both building blocks required for the radical step now in hand, we attempted the crucial reaction between xanthate **3** and olefin **34**. Unfortunately, the insolubility of compound **3** in the solvent typically used for this reaction (1,2-dichloroethane) forced us to change the reaction conditions. When a diluted (0.1 M) solution of xanthate **3** and olefin **34** were refluxed

in chlorobenzene (PhCl) using dilauroyl peroxide (DLP) as initiator, only starting materials together with some degradation products were isolated from the reaction mixture (Scheme 18).



Scheme 18 Attempt at the key radical reaction.

Because of this setback, we examined the radical reaction with xanthate **22**, since the coupling product could also be used in the total synthesis of gilvocarcins. Thus, when compounds **22** and **34** were allowed to react under the standard reaction conditions (refluxing 1,2-dichloroethane and DLP), adduct **35** was obtained in 59% yield (83% yield based on recovered starting material). However, when this compound was subjected to the conditions for the radical cyclisation, a complex mixture of degradation products was observed (Scheme 19).



Scheme 19 Model study.

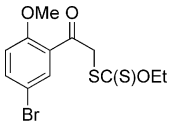
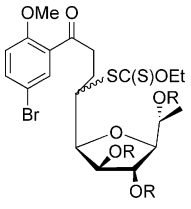
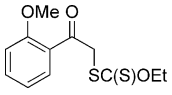
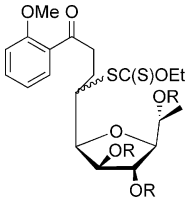
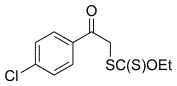
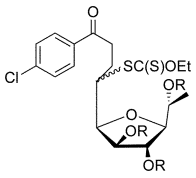
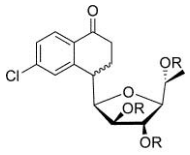
In order to understand the behaviour of olefin **34**, we carried out a series of experiments with diverse acetophenone xanthates possessing electron-donating and electron-withdrawing groups. The results for these reactions are summarised in Table 1.

As can be seen, the addition reaction succeeded for the three starting xanthates, affording adducts **39–41** in good to moderate yields. Neverthless, only compound **41** led to the formation of the expected tetralone (**42**) after treatment with 1.2 equivalents of DLP.

Our hopes for constructing ring A have thus been temporarily frustrated. The factors underlying the failure of the cyclisation step are not clear, but are probably due to steric constraints disfavouring the desired transition state. Earlier model studies[6] on other sugar olefins were quite encouraging. In the present case, the closure to form the aromatic ring is probably slower than possible competing side reactions such as hydrogen abstraction (probably from C-5 and/or C-6 on the sugar moiety). These side reactions could be at the beginning of an uncontrolled sequence of steps that lead to the decomposition of the starting material. When the aromatic ring bears only a *para* substituent (**41**), cyclisation of the nucleophilic radical is faster than the side reactions, and allows the formation of the expected tetralone (**42**). Unfortunately, this compound does not bear the substituents on the aromatic ring required for the total synthesis of gilvocarcin M.

Neverthless, these preliminary results have shown that the use of a free-radical strategy could be used for the construction of the A ring of gilvocarcins if the appropiate substituents are present in the aromatic ring. Although we have not been able to achieve the total synthesis of gilvocarcin M so far, the successful synthesis of building blocks **3** and **34** is particularly relevant in this context. Furthermore, because this approach allows the use of a great variety of substituents (including electron-withdrawing groups) on the aromatic ring and on the sugar moiety, it should be useful for the expedient preparation of a broad variety of analogues of the natural product.

Table 1 Radical reactions between olefin **34** and xanthates **36–38**

Xanthate	Adduct (% yield)[a]	Tetralone (% yield)
 **36**	 **39**, R = TBDMS (45 %, 64% corrected)	Degradation
 **37**[6]	 **40**, R = TBDMS (35 %, 59% corrected)	Degradation
 **38**[16]	 **41**, R = TBDMS (72%)	 **42**, R = TBDMS (54%)

[a] Reaction conditions: refluxing 1,2-dichloroethane (1 M concentration) using DLP as radical initiatior (0.15 to 0.2 equiv.). [b] Reaction conditions: refluxing 1,2-dichloroethane (0.1 M concentration) using DLP as initiator and oxidant (1 to 1.4 equiv.).

Experimental

All reactions were carried under an inert atmosphere. Commercial reagents were used as received without further purification. All products were purified by using silica gel SDS 60 C. C. 40–63 or by crystallisation. NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard at room temperature on a Bruker AMX400 spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C. Infrared absorption spectra were recorded as solutions in CCl_4 with a Perkin–Elmer 1600 Fourier transform spectrophotometer. Some mass spectra were determined at 70 eV with an AutoSpec Micromass spectrometer, and the others were recorded with an HP 5989B mass spectrometer using ammonia as the reagent gas. Melting points were determined by a Reichert microscope apparatus and are uncorrected.

2-Iodo-3-methoxy-5-methylbenzoic acid 4-methoxyphenyl ester (9)

A solution of 2-iodo-3-methoxy-5-methylbenzoyl chloride (2.26 g, 7.73 mmol) in CH_2Cl_2 (15 mL) was added dropwise to

an ice-cooled solution of *p*-methoxyphenol (0.8 g, 6.44 mmol) and triethylamine (3.6 mL, 2.61 g, 25.77 mmol) in CH_2Cl_2 (64 mL). The mixture was stirred at room temperature for 1 h, basified with saturated aqueous $NaHCO_3$, extracted with dichloromethane, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 95 : 5 to 8 : 2) and recrystallised with dichloromethane–petroleum ether to give ester **9** (95% yield) as white needles (mp 101–103 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 (s, 1H, C*H* arom.), 7.22 (d, 2H, C*H* arom., J = 8.0 Hz), 6.95 (d, 2H, C*H* arom., J = 8.0 Hz), 6.81 (s, 1H, C*H* arom.), 3.92 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5 (O-*C*O), 158.6 (*C*-OMe), 157.5 (*C*-OMe), 144.3 (*C*-O-CO), 140.0 (*C*–CO), 137.7 (*C*-Me), 123.5 (*C*H arom.), 122.4 (3C, *C*H arom.), 114.5 (*C*H arom.), 82.9 (*C*-I), 56.8 (O*C*H$_3$), 56.9 (O*C*H$_3$), 21.4 (*C*H$_3$); MS (CI + NH_3) m/z: 419 (MH^+ + NH_3), 417 (MH^+ + NH_3), 399 (MH^+), 397 (MH^+); IR (cm^{-1}, CCl_4): 1751 (O–C=O); HRMS calcd for $C_{16}H_{15}O_4I$ 398.00154; found 398.00139.

2,10-Dimethoxy-8-methylbenzo[*c*]chromen-6-one (5)

A degassed, yellow suspension of ester **9** (1.9 g, 4.77 mmol), $Pd(PPh_3)_2Cl_2$ (0.87 g, 1.24 mmol, 26 mol%) and NaOAc (1.17 g, 14.31 mmol) in *N*,*N*-dimethylacetamide (430 mL) was heated at 125 °C for 5 h. After the solution was cooled to room temperature, the resulting dark brown suspension was diluted with Et_2O, and the mixture was washed with water, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 9 : 1 to 7:3) and recrystallised with dichloromethane–petroleum ether to give lactone **5** (85% yield) as white needles (mp 155–157 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, 1H, C*H* arom., J = 2.8), 7.81 (s, 1H, C*H* arom.), 7.22 (d, 1H, C*H* arom., J = 8.8 Hz), 7.06 (s, 1H, C*H* arom.), 6.95 (dd, 1H, C*H* arom., J = 9.0, 3.0 Hz), 4.0 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 2.44 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 181.0 (O-*C*O), 157.1 (*C*-OMe), 155.6 (*C*-OMe), 144.7 (*C*-O-CO), 139.8 (*C*-CO), 122.7 (*C*-Ar), 122.7 (*C*H arom.), 121.1 (Ar-*C*), 118.3 (*C*-Me), 117.8 (*C*H arom.), 117.7 (*C*H arom.), 117.4 (*C*H arom.), 115.1 (*C*H arom.), 55.9 (O*C*H$_3$), 55.7 (O*C*H$_3$), 21.7 (*C*H$_3$); MS (CI + NH_3) m/z: 288 (MH^+ + NH_3), 271 (MH^+); IR (cm^{-1}, CCl_4): 1732 (O–C=O); HRMS calcd for $C_{16}H_{14}O_4$ 270.08921; found 270.08953.

3-(2-Chloroacetyl)-2,10-dimethoxy-8-methylbenzo[*c*]chromen-6-one (10)

To a well-stirred suspension of $AlCl_3$ (0.25 g, 1.87 mmol) and chloroacetyl chloride (0.15 mL, 0.21 g, 1.87 mmol) in CS_2 (0.9 mL) at room temperature were added, portionwise, 0.05 g (0.18 mmol) of lactone **5**. After standing at room temperature for 2 h, the residue was hydrolysed by careful addition of water at 0 °C. Extraction with ether yielded compound **10** (31% yield) after flash column chromatography (silica gel, petroleum ether–AcOEt, 4 : 1) and recrystallisation with dichloromethane–petroleum ether (white needles, mp 227–227 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (s, 1H, C*H* arom.), 7.86 (s, 1H, C*H* arom.), 7.76 (s, 1H, C*H* arom.), 7.16 (s, 1H, C*H* arom.), 4.77 (s, 2H, CH_2-Cl), 4.10 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 2.50 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.7 (*C*O), 183.9 (O-*C*O), 158.4 (*C*-OMe), 157.6 (*C*-OMe), 154.8 (*C*-O-CO), 124.4 (*C*-CO), 123.7 (*C*-Ar), 123.5 (*C*-COO), 123.3 (*C*H arom.), 119.9 (Ar-*C*), 119.0 (*C*H arom.), 118.2 (*C*H arom.), 115.6 (*C*-CH$_3$), 110.6 (*C*H arom.), 56.4 (O*C*H$_3$), 56.1 (O*C*H$_3$), 51.3 (*C*H$_2$-Cl), 21.7 (Ar-*C*H$_3$); MS (CI + NH_3) m/z: 349 (MH^+), 347 (MH^+); IR (cm^{-1}, CCl_4): 1729 (O–*C*=*O*), 1684 (C=O), 1264 (*O*–*C*=O).

Dithiocarbonic acid *S*-[2-(2,10-dimethoxy-8-methyl-6-oxo-6*H*-benzo[*c*]chromen-3-yl)-2-oxoethyl] ester *O*-ethyl ester (3)

To a solution of **10** (0.018 g, 0.05 mmol) in acetone (0.06 mL) at 0 °C was added potassium *O*-ethyl xanthate (0.01 g, 0.06 mmol) and the reaction mixture was stirred for 2 h at 0 °C. After consumption of all the starting material, acetone was evaporated and the resulting mixture was diluted with water, extracted with ethyl acetate, dried and concentrated. The residue was purified by crystallisation with CH_2Cl_2–petroleum ether to afford **3** (86%) as a yellow solid (mp 188–191 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.53 (s, 1H, C*H* arom.), 7.88 (s, 1H, C*H* arom.), 7.71 (s, 1H, C*H* arom.), 7.17 (s, 1H, C*H* arom.), 4.62 (q, 2H, O-CH_2, J = 7.1 Hz), 4.61 (s, 2H, CH_2-S), 4.10 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 2.51 (s, 3H, Ar-CH_3), 1.41 (t, 3H, CH_3, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 213.6 (*C*S), 192.5 (*C*O), 161.0 (*C*-OMe), 157.5 (*C*-OMe), 154.6 (*C*-O-CO), 126.0 (*C*-CO), 123.5 (*C*-Ar), 123.5 (*C*-COO), 123.2 (*C*H arom.), 122.8 (Ar-*C*), 120.0 (*C*-CH$_3$), 118.7 (*C*H arom.), 118.1 (*C*H arom.), 110.6 (*C*H arom.), 70.6 (O-*C*H$_2$), 56.4 (O*C*H$_3$), 56.0 (O*C*H$_3$), 47.7 (*C*H$_2$-S), 21.7 (Ar-*C*H$_3$), 13.8 (*C*H$_3$); MS (CI + NH_3) m/z: 433 (MH^+); IR (cm^{-1}, CCl_4): 1740 (O-*C*=*O*), 1686 (C=O), 1260 (*O*–*C*=O); HRMS calcd for $C_{21}H_{20}O_6S$ 432.07014; found 432.07097.

2,2-Dimethylpropionic acid 3-acetyl-4-hydroxyphenyl ester (13). Trimetylacetyl chloride (0.89 mL, 0.87 g, 7.22 mmol) was added dropwise to a stirred solution of 2′,5′-dihydroxyacetophenone (1 g, 6.57 mmol) in pyridine (2 mL) at room temperature and the reaction mixture was stirred for 1 h at room temperature. The solution was then extracted with CH_2Cl_2, the combined organic layers were dried, filtered and concentrated *in vacuo*. The excess of pyridine was co-evaporated with toluene under reduced pressure and the residue was purified by flash chromatography (silica gel, petroleum ether–ethyl acetate, 98 : 2 to 8 : 2) to yield **13** (79% yield) as a colourless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 12.16 (s, 1H, O*H*), 7.4 (d, 1H, C*H* arom., J = 2.8), 7.17 (dd, 1H, C*H* arom., J = 9.0, 2.6 Hz), 6.98 (d, 1H, C*H* arom., J = 9.6 Hz), 2.63 (s, 3H, COCH_3), 1.37 (s, 9H, (CH_3)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 204.0 (*C*O), 177.4 (O-*C*O), 160.0 (2C, *C*-OH and *C*-OPiv), 142.4 (*C*-CO), 130.2 (*C*H arom.), 122.6 (*C*H arom.), 119.3 (*C*H arom.), 39.1 (*C*(CH$_3$)$_3$), 27.2 ((*C*H$_3$)$_3$), 26.8 (CO*C*H$_3$); MS (CI + NH_3) m/z: 254 (MH^+ + NH_3), 237 (MH^+); IR (cm^{-1}, CCl_4): 3486 (OH), 1752 (O–C=O), 1650 (C=O).

1-(5-Hydroxy-2-methoxyphenyl)ethanone (11). A solution of phenol **13** (1.1 g, 4.65 mmol), Li_2CO_3 (1.03 g, 73.89 mmol) and MeI (0.87 mL, 1.98 g, 13.96 mmol) in DMF (12 mL) was heated at 100 °C for 26 h. After the solution was cooled to room temperature, 5 mL of a 2 M NaOH aqueous solution were added to the reaction mixture and the resulting solution was heated at 100 °C for further 12 h. The resulting mixture was then cooled at room temperature, neutralised with 2 N HCl solution, extracted with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 4 : 1 to 2 : 1) to give compound **11** (83% yield) as a yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (d, 1H, C*H* arom., J = 2.8 Hz), 7.30 (s, 1H, O*H*), 7.05 (dd, 1H, C*H* arom., J = 8.8, 2.8 Hz), 6.86 (d, 1H, C*H* arom., J = 8.8 Hz), 3.85 (OCH_3), 2.64 (s, 3H, COCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.1 (*C*O), 153.8 (*C*-OMe), 149.9 (*C*-OH), 127.8 (*C*-CO), 121.6 (*C*H arom.), 116.6 (*C*H arom.), 113.3 (*C*H arom.), 56.0 (O*C*H$_3$), 32.0 (CO*C*H$_3$).

2-Iodo-3-methoxy-5-methylbenzoic acid 3-acetyl-4-methoxyphenyl ester (14)

A solution of 2-iodo-3-methoxy-5-methylbenzoyl chloride (0.18 g, 0.60 mmol) in CH_2Cl_2 (1 mL) was added dropwise to an ice-cooled solution of acetophenone **11** (0.05 g, 0.30 mmol) and triethylamine (0.17 mL, 0.12 g, 1.20 mmol), in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for

1 h, basified with saturated aqueous $NaHCO_3$, extracted with dichloromethane, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 4 : 1) and recrystallised with dichloromethane–petroleum ether to give ester **14** (94% yield) as white needles (mp 114–115 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, 1H, C*H* arom., $J = 2.8$ Hz), 7.41 (dd, 1H, C*H* arom., $J = 8.8$, 2.8 Hz), 7.26 (s, 1H, C*H* arom.), 7.02 (d, 1H, C*H* arom., $J = 8.8$ Hz), 6.8 (s, 1H, C*H* arom.), 3.93 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 2.64 (COCH_3), 2.39 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.6 (*C*O), 166.3 (O-*C*O), 158.6 (*C*-OMe), 156.9 (*C*-OMe), 144.0 (*C*-O-CO), 140.1 (*C*-CO), 137.1 (*C*-CO_2Ar), 128.6 (*C*-Me), 126.8 (*C*H arom.), 123.6 (*C*H arom.), 123.2 (*C*H arom.), 114.8 (*C*H arom.), 112.6 (*C*H arom.), 82.9 (*C*-I), 56.8 (OCH_3), 56.0 (OCH_3), 31.9 (COCH_3), 21.3 (CH_3); MS (CI + NH_3) *m/z*: 458 ($MH^+ + NH_3$), 441 (MH^+); IR (cm^{-1}, CCl_4): 1754 (O–*C*=*O*), 1682 (C=O), 1270 (*O*–*C*=O); HRMS calcd for $C_{18}H_{17}O_5I$ 440.01210; found 440.01187.

2-Iodo-3-methoxy-5-methylbenzoic acid 4-benzyloxyphenyl ester (17)

A solution of 2-iodo-3-methoxy-5-methylbenzoyl chloride (0.29 g, 0.99 mmol) in CH_2Cl_2 (2 mL) was added dropwise to an ice-cooled solution of *p*-benzyloxyphenol (0.10 g, 0.50 mmol) and triethylamine (0.28 mL, 0.20 g, 1.99 mmol), in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 1 h, basified with saturated aqueous $NaHCO_3$, extracted with dichloromethane, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 9 : 1 to 8 : 2) and recrystallised with dichloromethane–petroleum ether to give ester **18** (84% yield) as white needles (mp 93–94 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47–7.35 (m, 5H, C*H* arom.), 7.28 (s, 1H, C*H* arom.), 7.26 (d, 2H, C*H* arom., $J = 8.0$ Hz), 7.04 (d, 2H, C*H* arom., $J = 8.0$ Hz), 6.81 (s, 1H, C*H* arom.), 5.09 (s, 2H, CH_2-Ph), 3.93 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 2.41 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5 (O-*C*O), 158.6 (*C*-OMe), 156.7 (*C*-OBn), 144.5 (*C*-O-CO), 140.0 (*C*-CO), 137.6 (*C*-CH_2), 136.8 (*C*-Me), 128.7 (*C*H arom.), 128.1 (*C*H arom.), 127.6 (*C*H arom.), 123.6 (*C*H arom.), 122.4 (3C, *C*H arom.), 115.6 (2C, *C*H arom.), 114.6 (*C*H arom.), 114.7 (*C*H arom.), 82.9 (*C*-I), 70.5 (*C*H_2-Ph), 56.8 (OCH_3), 21.4 (CH_3); MS (CI + NH_3) *m/z*: 492 ($MH^+ + NH_3$), 475 (MH^+); IR (cm^{-1}, CCl_4): 1753 (O–*C*=*O*), 1185 (*O*–*C*=O).

2,2-Dimethylpropionic acid 3-acetyl-4-methoxyphenyl ester (21)

A solution of phenol **13** (0.61 g, 2.58 mmol), Li_2CO_3 (0.57 g, 7.76 mmol) and MeI (0.48 mL, 1.10 g, 7.76 mmol) in DMF (6.5 mL) was heated at 120 °C for 4 h. The resulting mixture was then cooled at room temperature, neutralised with saturated citric acid solution, extracted with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 9 : 1 to 8 : 2) to give compound **21** (82% yield) as a colourless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 (d, 1H, C*H* arom., $J = 2.8$ Hz), 7.16 (dd, 1H, C*H* arom., $J = 8.8$, 2.8 Hz), 6.95 (d, 1H, C*H* arom., $J = 8.8$ Hz), 3.90 (OCH_3), 2.61 (s, 3H, COCH_3), 1.34 (s, 9H, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.7 (*C*O), 177.3 (O-*C*O), 156.6 (*C*-OMe), 144.3 (*C*-OPiv), 128.5 (*C*-CO), 126.8 (*C*H arom.), 123.2 (*C*H arom.), 112.4 (*C*H arom.), 55.9 (OCH_3), 39.1 (COCH_3), 31.9 (*C*(CH_3)$_3$), 27.2 (3C, *C*(CH_3)$_3$); MS (CI + NH_3) *m/z*: 268 ($MH^+ + NH_3$), 251 (MH^+); IR (cm^{-1}, CCl_4): 1753 (O–C=O), 1682 (C=O).

2,2-Dimethylpropionic acid 3-(2-(ethoxythiocarbonylsulfanyl)-acetyl)-4-methoxyphenyl ester (22)

To a stirred solution of acetophenone **21** (0.53 g, 2.12 mmol) and $AlCl_3$ (0.03 g, 0.21 mmol) in ether (3.5 mL) at 0 °C was added dropwise Br_2 (0.11 mL, 0.34 g, 2.12 mmol). The cooling bath was then removed and the mixture was stirred at room temperature for 2 h. When starting material was completely consumed, the solvent was removed under reduced pressure, the resulting mass decolourised with a 1 : 1 mixture of CH_2Cl_2–water, and extracted with CH_2Cl_2. The combined organic extracts were dried and evaporated, the residue dissolved in 4.2 mL of acetone, and 0.37 g (2.33 mmol) of potassium *O*-ethylxanthate added. The reaction mixture was stirred at room temperature for a further 1 h, the solvent was evaporated and the resulting mixture partitioned between water and CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2, the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by recrystallisation with CH_2Cl_2–petroleum ether to give xanthate **22** (77% overall yield from **21**) as white crystals (mp 63–65 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (d, 1H, C*H* arom., $J = 3.0$ Hz), 7.23 (dd, 1H, C*H* arom., $J = 8.9$, 3.0 Hz), 7.0 (d, 1H, C*H* arom., $J = 9.0$ Hz), 4.61 (q, 2H, OCH_2, $J = 7.1$ Hz), 4.61 (s, 2H, CH_2-S), 3.96 (OCH_3), 1.39 (t, 3H, CH_3, $J = 7.1$ Hz), 1.34 (s, 9H, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 213.6 (*C*S), 192.8 (*C*O), 177.2 (O-*C*O), 156.4 (*C*-OMe), 144.7 (*C*-OPiv), 127.7 (*C*H arom.), 126.7 (*C*-CO), 123.7 (*C*H arom.), 112.5 (*C*H arom.), 70.5 (O*C*H_2), 56.3 (OCH_3), 47.6 (*C*H_2-S), 39.1 (*C*(CH_3)$_3$), 27.2 (3C, C(*C*H_3)$_3$), 13.8 (*C*H_3); MS (CI + NH_3) *m/z*: 388 ($MH^+ + NH_3$), 371 (MH^+); IR (cm^{-1}, CCl_4): 1754 (O–*C*=*O*), 1679 (C=O), 1221 (S–*C*=*S*), 1056 (*O*–*C*=S).

Dithiocarbonic acid *S*-[2-(5-bromo-2-methoxyphenyl)-2-oxoethyl] ester *O*-ethyl ester (37)

A solution of 2′-hydroxy-5′-bromoacetophenone (2.0 g, 9.30 mmol), K_2CO_3 (2.6 g, 19.0 mmol) and MeI (0.72 mL, 0.91 g, 12.1 mmol) in acetone (20 mL) was refluxed for 3 h. After the solution was cooled to room temperature, acetone was evaporated and the resulting mixture was then extracted with Et_2O, washed with saturated aqueous NaCl solution, dried (Na_2SO_4), and concentrated under reduced pressure. To a stirred solution of the residue and $AlCl_3$ (0.12 g, 0.93 mmol) in ether (93 mL) at 0 °C was added dropwise Br_2 (0.48 mL, 1.49 g, 9.3 mmol). The cooling bath was then removed and the mixture was stirred at room temperature for 1 h. When starting material was completely consumed, the solvent was removed under reduced pressure and the resulting mass decolourised with a 1 : 1 mixture of CH_2Cl_2/water and extracted with CH_2Cl_2. The combined organic extracts were dried and evaporated, the residue dissolved in 19 mL of acetone, and 1.64 g (10.23 mmol) of potassium *O*-ethylxanthate added. The reaction mixture was stirred at room temperature for a further 1 h, the solvent was evaporated and the resulting mixture partitioned between water and CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2, the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 95 : 5 to 8 : 2) and recrystallised with dichloromethane–petroleum ether to give xanthate **37** (94% overall yield) as a white powder (mp 63 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, 1H, C*H* arom., $J = 2.6$ Hz), 7.60 (dd, 1H, C*H* arom., $J = 8.8$, 2.6 Hz), 6.90 (d, 1H, C*H* arom., $J = 8.9$ Hz), 4.61 (q, 2H, O-CH_2, $J = 7.1$ Hz), 4.56 (s, 2H, *C*H_2-S), 3.95 (s, 3H, OCH_3), 1.40 (t, 3H, CH_3, $J = 7.1$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 213.4 (*C*S), 192.7 (*C*O), 157.7 (*C*-OMe), 136.8 (*C*H arom.), 133.5 (*C*H arom.), 127.9 (*C*-CO), 113.6 (*C*H arom.), 113.5 (*C*-Br), 70.6 (O-*C*H_2), 561 (O-*C*H_3), 47.4 (CO*C*H_2), 13.8 (*C*H_3); MS (CI + NH_3) *m/z*: 351 (MH^+), 349 (MH^+); IR (cm^{-1}, CCl_4): 1692 (C=O), 1227 (S–*C*=*S*), 1054 (*O*–*C*=S).

1-Vinyl-2,3,5-tri-*O*-benzyl-D-fucocitol (18)

A solution of 2,3,5-tri-*O*-benzyl-D-fucose **8** (0.2 g, 0.46 mmol) in dry THF (4.6 mL) was slowly added to a refluxing solution

of vinylmagnesium bromide in THF (1.84 mL of a 1 M solution, 1.84 mmol). The reaction mixture was refluxed for further 30 min, cooled to room temperature and quenched with saturated aqueous NH_4Cl solution. Extraction with ethyl acetate yielded compound **18** (yellow oil, 99% yield) after flash column chromatography (silica gel, petroleum ether–AcOEt, 4 : 1) as an inseparable 12 : 1 mixture of distereoisomers (only the major disatereoisomer is described): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.23 (m, 15H, C*H* arom.), 5.40 (ddd, 1H, *H*-1′, J = 17.2, 10.5, 5.6 Hz), 5.40 (dd, 1H, *H*-2′, J = 17.2, 1.5 Hz), 5.24 (dd, 1H, *H*-2′, J = 10.5, 1.4 Hz), 4.79 (d, 1H, CH_2-Ph, J = 11.3 Hz), 4.69 (d, 2H, CH_2-Ph, J = 11.4 Hz), 4.58 (d, 1H, CH_2-Ph, J = 11.3 Hz), 4.49–4.44 (m, 1H, *H*-1), 4.36 (d, 1H, CH_2-Ph, J = 11.6 Hz), 4.35 (d, 1H, CH_2-Ph, J = 11.2 Hz), 3.94–3.86 (m, 1H, *H*-5), 3.79–3.74 (m, 2H, *H*-2 and *H*-3), 3.72–3.78 (m, 1H, *H*-4), 3.19 (br, 1H, O*H*), 2.78 (br, 1H, O*H*), 1.36 (d, 3H, *H*-6, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.6 (*C*-1′), 138.4 (*C*-CH_2), 138.1 (*C*-CH_2), 138.0 (*C*-CH_2), 128.5 (*C*H arom.), 128.2 (*C*H arom.), 128.1 (*C*H arom.), 127.9 (*C*H arom.), 127.8 (*C*H arom.), 116.1 (*C*-2′), 81.9 (*C*-2), 78.1 (*C*-3), 75.3 (*C*-4), 74.7 (*C*H_2-Ph), 73.4 (*C*H_2-Ph), 72.9 (*C*-5), 72.2 (*C*-1), 70.4 (*C*H_2-Ph), 16.0 (*C*-6); MS (CI + NH_3) m/z: 480 (MH^+ + NH_3), 463 (MH^+); $[\alpha]_D^{25} = -37.5$ (c = 1, $CHCl_3$).

1-Vinyl-2,3,5-tri-*O*-benzyl-α-D-fucofuranose (19)

Methanesulfonyl chloride (0.016 mL, 0.025 g, 0.22 mmol) was added dropwise to a stirred solution of diol **18** (0.05 g, 0.11 mmol) in CH_2Cl_2 (1 mL) at 0 °C, and the reaction mixture was stirred for further 30 min at 0 °C. The solution was then extracted with ethyl acetate, the combined organic layers were dried, filtered and concentrated *in vacuo*. The residue was then dissolved in 1 mL of DMF and 0.024 g (0.32 mmol) of Li_2CO_3 were added to the reaction mixture. The solution was stirred for 1 h at room temperature, neutralised with saturated aqueous citric acid solution, extracted with diethyl ether and the combined organic extracts were dried and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 98 : 2) to give compound **19** (48% yield) as a colourless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.25 (m, 15H, C*H* arom.), 5.95 (ddd, 1H, *H*-1′, J = 17.2, 10.3, 7.0 Hz), 5.37 (dd, 1H, *H*-2′, J = 17.1, 1.4 Hz), 5.22 (dd, 1H, *H*-2′, J = 10.3, 1.3 Hz), 4.66 (d, 1H, CH_2-Ph, J = 12.0 Hz), 4.61 (d, 1H, CH_2-Ph, J = 12.0 Hz), 4.53 (d, 1H, CH_2-Ph, J = 10.8 Hz), 4.50 (d, 1H, CH_2-Ph, J = 11.9 Hz), 4.47 (d, 1H, CH_2-Ph, J = 11.1 Hz), 4.46 (dd, 1H, *H*-1, J = 1.22 Hz), 4.44 (d, 1H, CH_2-Ph, J = 11.6 Hz), 4.13 (s, 1H, *H*-3), 3.99–3.94 (m, 2H, *H*-2 and *H*-4), 3.65 (dq, 1H, *H*-5, J = 6.4, 4.7 Hz), 1.23 (d, 3H, *H*-6, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.7 (*C*-CH_2), 138.0 (*C*-CH_2), 137.9 (*C*-CH_2), 136.9 (*C*-1′), 128.5 (*C*H arom.), 128.5 (*C*H arom.), 128.4 (*C*H arom.), 128.3 (*C*H arom.), 128.0 (*C*H arom.), 127.9 (*C*H arom.), 127.9 (*C*H arom.), 127.8 (*C*H arom.), 127.6 (*C*H arom.), 127.6 (*C*H arom.), 127.5 (*C*H arom.), 117.5 (*C*-2′), 88.3 (*C*-2), 84.9 (*C*-4), 84.5 (*C*-3), 83.3 (*C*-1), 74.2 (*C*-5), 72.1 (2C, *C*H_2-Ph), 71.2 (*C*H_2-Ph), 15.9 (*C*-6); MS (CI + NH_3) m/z: 462 (MH^+ + NH_3), 445 (MH^+).

1-Vinyl-2,3,5-tri-*O*-benzyl-β-D-fucofuranose (20)

A solution of $SOCl_2$ (0.03 mL, 0.05 mmol) in CH_2Cl_2 (4 mL) was added dropwise to a stirred solution of diol **18** (0.18 g, 0.39 mmol) in CH_2Cl_2 (8 mL) at −78 °C. The reaction mixture was warmed to room temperature over 2 h, neutralised with saturated $NaHCO_3$ solution, and extracted with dichloromethane. The combined organic layers were dried, filtered and concentrated. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 98 : 2 to 95 : 5) to afford olefin **20** (84% yield) as a colourless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33–7.12 (m, 15H, C*H* arom.), 5.98 (ddd, 1H, *H*-1′, J = 17.2, 10.4, 6.8 Hz), 5.39 (d, 1H, *H*-2′, J = 17.1 Hz), 5.3–5.27 (m, 2H, *H*-1 and *H*-2′), 4.87 (dd, 1H, *H*-4, J = 8.4, 2.4 Hz), 4.62–4.68 (m, 3H, CH_2-Ph), 4.36 (d, 1H, CH_2-Ph, J = 12.0 Hz), 4.28 (d, 1H, CH_2-Ph, J = 12.0 Hz), 4.13 (d, 1H, CH_2-Ph, J = 11.6 Hz), 4.02 (dd, 1H, *H*-3, J = 8.4, 3.6 Hz), 3.94 (dd, 1H, *H*-5, J = 6.4, 2.4 Hz), 3.69 (d, 1H, *H*-2, J = 2.4 Hz), 1.25 (d, 3H, *H*-6, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.2 (*C*-CH_2), 137.7 (*C*-CH_2), 137.6 (*C*-CH_2), 134.1 (*C*-1′), 128.6 (*C*H arom.), 128.5 (*C*H arom.), 128.3 (*C*H arom.), 128.2 (*C*H arom.), 128.1 (*C*H arom.), 128.0 (*C*H arom.), 127.8 (*C*H arom.), 127.7 (*C*H arom.), 119.3 (*C*-2′), 81.8 (*C*-2), 77.6 (*C*-3), 73.5 (*C*-4), 73.0 (*C*H_2-Ph), 72.9 (*C*-1), 72.8 (*C*H_2-Ph), 72.0 (*C*-5), 70.6 (*C*H_2-Ph), 15.6 (*C*-6); MS (CI + NH_3) m/z: 462 (MH^+ + NH_3), 445 (MH^+).

2,3,5-Tri-*O*-*tert*-butyldimethylsilyl-6-bromo-6-deoxy-D-galactono-1,4-lactone (27)

Tert-butyldimethylsilyl chloride (19.2 g, 127.4 mmol) was added to a stirred solution of 6-bromo-6-deoxy-D-galactono-1,4-lactone (**26**) (5.12 g, 21.24 mmol) and imidazole (11.57 g, 169.93 mmol) in DMF (85 mL) at room temperature, and the reaction mixture was stirred for 48 h. The solution was then extracted with ethyl ether, the combined organic layers were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, petroleum ether–AcOEt, 95 : 5 to 9 : 1) to yield **27** (68% yield) as a colourless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.51 (t, 1H, *H*-4, J = 1.8 Hz), 4.35 (m, 2H, *H*-2 and *H*-3), 4.02 (ddd, 1H, *H*-5, J = 9.3, 4.3, 1.7 Hz), 3.51 (t, 1H, *H*-6, J = 9.8 Hz), 3.37 (dd, 1H, *H*-6′, J = 10.2, 4.1 Hz), 0.92 (s, 9H, Si-C(CH_3)$_3$), 0.91 (s, 9H, Si-C(CH_3)$_3$), 0.89 (s, 9H, Si-C(CH_3)$_3$), 0.21 (s, 3H, Si-CH_3), 0.16 (s, 3H, Si-CH_3), 0.15 (s, 3H, Si-CH_3), 0.14 (s, 3H, Si-CH_3), 0.13 (s, 6H, Si-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.3 (*C*-1), 81.8 (*C*-4), 76.9 (*C*-2), 75.9 (*C*-3), 71.3 (*C*-5), 31.6 (*C*-6), 25.9 (Si-C(*C*H_3)$_3$), 25.8 (Si-C(*C*H_3)$_3$), 25.7 (Si-C(*C*H_3)$_3$), 18.3 (Si–*C*(CH$_3$)$_3$), 18.2 (Si–*C*(CH$_3$)$_3$), 17.9 (Si-*C*(CH$_3$)$_3$), −3.3 (Si-*C*H$_3$), −3.9 (Si-*C*H$_3$), −4.0 (Si-*C*H$_3$), −4.1 (Si-*C*H$_3$), −4.3 (Si-*C*H$_3$), −4.7 (Si-*C*H$_3$); MS (CI + NH_3) m/z: 602 (MH^+ + NH_3), 600 (MH^+ + NH_3), 585 (MH^+), 583 (MH^+); IR (cm^{-1}, CCl_4): 1804 (O–*C*=*O*), 1255 (*O*–*C*=O); $[\alpha]_D^{25} = -3.2$ (c = 1, $CHCl_3$).

2,3,5-Tri-*O*-*tert*-butyldimethylsilyl-D-fucono-1,4-lactone (28)

A solution of **27** (7.5 g, 12.85 mmol), Bu_3SnH (5.18 mL, 5.61 g, 19.27 mmol) and AIBN (0.02 g, 0.13 mmol) in a 1 : 1 toluene–cyclohexane mixture (40 mL) was heated at 80–90 °C for 30 min. When the starting material was totally consumed, the crude mixture was cooled to room temperature, concentrated under reduced pressure and purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 99 : 1) to give lactone **28** (98% yield) as a white solid (mp 38–39 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.34 (t, 1H, *H*-3, J = 5.0 Hz), 4.29 (d, 1H, *H*-2, J = 5.2 Hz), 4.07 (dd, 1H, *H*-5, J = 6.4, 3.6 Hz), 3.99 (t, 1H, *H*-4, J = 4.0 Hz), 1.33 (d, 3H, *H*-6, J = 6.4 Hz), 0.96 (s, 9H, Si-C(CH_3)$_3$), 0.94 (s, 9H, Si-C(CH_3)$_3$), 0.93 (s, 9H, Si-C(CH_3)$_3$), 0.25 (s, 3H, Si-CH_3), 0.20 (s, 3H, Si-CH_3), 0.17 (s, 3H, Si-CH_3), 0.16 (s, 3H, Si-CH_3), 0.14 (s, 3H, Si-CH_3), 0.13 (s, 3H, Si-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.8 (*C*-1), 87.6 (*C*-4), 76.7 (*C*-2), 75.8 (*C*-3), 67.2 (*C*-5), 25.9 (Si-C(*C*H_3)$_3$), 25.9 (Si-C(*C*H_3)$_3$), 25.8 (Si-C(*C*H_3)$_3$), 20.3 (*C*-6), 18.3 (Si-*C*(CH$_3$)$_3$), 18.2 (Si-*C*(CH$_3$)$_3$), 17.9 (Si-*C*(CH$_3$)$_3$), −3.5 (Si-*C*H$_3$), −4.0 (Si-*C*H$_3$), −4.1 (Si-*C*H$_3$), −4.3 (Si-*C*H$_3$), −4.4 (Si-*C*H$_3$), −4.7 (Si-*C*H$_3$); MS (CI + NH_3) m/z: 522 (MH^+ + NH_3), 505 (MH^+); IR (cm^{-1}, CCl_4): 1799 (O–*C*=*O*) 1253 (*O*–*C*=O); HRMS calcd for $C_{24}H_{52}O_5Si_3$ 504.31226; found 504.31258; $[\alpha]_D^{25} = -2.8$ (c = 1, $CHCl_3$).

1-(3′-Butenyl)-2,3-di-*O*-*tert*-butyldimethylsilyl-β-D-fucofuranose (29)

A solution of lactone **28** (0.05 g, 0.10 mmol) in dry THF (1 mL) was slowly added to a stirred solution of vinylmagnesium

bromide in THF (0.40 mL of a 1 M solution, 0.40 mmol) at r.t. The solution was then stirred at room temperature for 1 h, diluted with saturated NH_4Cl solution, and extracted with dichloromethane. The combined organic layers were dried, filtered and concentrated. The residue was then dissolved in 2 mL of CH_2Cl_2 and cooled to −78 °C. To this solution was added Et_3SiH (0.06 mL, 0.05 g, 0.40 mmol) followed by $BF_3{\cdot}OEt_2$ (0.05 mL, 0.06 g, 0.40 mmol). When starting material was completely consumed, the reaction was neutralised with triethylamine and extracted with dichloromethane. The combined organic layers were dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 95 : 5) to afford olefin **29** (36% overall yield from **28**) as a colourless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.84 (tdd, 1H, *H*-3′, J = 16.9, 10.2, 6.5 Hz), 5.04 (dd, 1H, *H*-4′, J = 17.1, 1.6 Hz), 4.98 (dd, 1H, *H*-4′, J = 10.2, 1.6 Hz), 3.98–3.88 (m, 4H, *H*-1, *H*-2, *H*-3 and *H*-5), 3.72 (dd, 1H, *H*-4, J = 5.5 and 1.3 Hz), 2.93 (bs, 1H, O*H*), 2.25–2.16 (m, 1H, *H*-2′), 2.14–2.05 (m, 1H, *H*-2′), 1.86–1.76 (m, 1H, *H*-1′), 1.71–1.62 (m, 1H, *H*-1′), 1.22 (d, 3H, *H*-6, J = 6.3 Hz), 0.89 (s, 18H, Si-C(CH_3)$_3$), 0.10 (s, 3H, Si-CH_3), 0.09 (s, 3H, Si-CH_3), 0.08 (s, 3H, Si-CH_3), 0.08 (s, 3H, Si-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.3 (*C*-3′), 114.8 (*C*-4′), 91.4 (*C*-4), 87.1 (*C*-1), 82.8 (*C*-2), 81.5 (*C*-3), 67.4 (*C*-5), 32.1 (*C*-2′), 30.4 (*C*-1′), 25.8 (Si-C(*C*H$_3$)$_3$), 25.7 (Si-C(*C*H$_3$)$_3$), 19.7 (*C*-6), 18.0 (Si-*C*(CH$_3$)$_3$), 17.9 (Si-*C*(CH$_3$)$_3$), −4.5 (Si-*C*H$_3$), −4.5 (Si-*C*H$_3$), −4.5 (Si-*C*H$_3$), −4.6 (Si-*C*H$_3$).

1-Trimethylsilyloxy-1-vinyl-2,3,5-tri-*O*-*tert*-butyldimethylsilyl-α-D-fucofuranoside (30)

Vinylmagnesium bromide (1.18 mL of a 1 M solution in THF, 1.18 mmol) was slowly added to a stirred solution of lactone **28** (0.3 g, 0.59 mmol) and TMSCl (0.15 mL, 0.13 g, 1.18 mmol) in dry THF (6 mL) at 0 °C. The solution was then stirred at room temperature for 1 h, diluted with a saturated NH_4Cl solution, and extracted with dichloromethane. The combined organic layers were dried, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 99 : 1) to afford olefin **30** (52% yield) as a colourless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.91 (dd, 1H, *H*-1′, J = 17.4, 10.6 Hz), 5.34 (dd, 1H, *H*-2′, J = 17.4, 1.4 Hz), 5.17 (dd, 1H, *H*-2′, J = 10.8, 1.6 Hz), 3.88–3.79 (m, 4H, *H*-2, *H*-3, *H*-4 and *H*-5), 1.16 (d, 3H, *H*-6, J = 5.2 Hz), 0.91 (s, 18H, Si-C(CH_3)$_3$), 0.86 (s, 9H, Si-C(CH_3)$_3$), 0.12 (s, 9H, O-Si(CH_3)$_3$), 0.11 (s, 3H, Si-CH_3), 0.09 (s, 6H, Si-CH_3), 0.08 (s, 3H, Si-CH_3), 0.06 (s, 3H, Si-CH_3), 0.03 (s, 3H, Si-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.6 (*C*-1′), 116.5 (*C*-2′), 107.7 (*C*-1), 91.9 (*C*-4), 86.1 (*C*-2), 80.3 (*C*-3), 69.7 (*C*-5), 26.2 (Si-C(*C*H$_3$)$_3$), 25.9 (Si-C(*C*H$_3$)$_3$), 25.9 (Si-C(*C*H$_3$)$_3$), 20.4 (*C*-6), 18.5 (Si-*C*(CH$_3$)$_3$), 18.1 (Si-*C*(CH$_3$)$_3$), 18.0 (Si-*C*(CH$_3$)$_3$), 1.9 (O-Si(*C*H$_3$)$_3$), −4.1 (2C, Si-*C*H$_3$), −4.1 (Si-*C*H$_3$), −4.2 (Si-*C*H$_3$), −4.3 (Si-*C*H$_3$), −4.4 (Si-*C*H$_3$); MS (CI + NH_3) m/z: 532 (MH^+ − TMSOH + NH_3), 515 (MH^+ − TMSOH).

1-Trimethylsilylethynyl-2,3,5-tri-*O*-*tert*-butyldimethylsilyl-β-D-fucofuranose (32)

To a solution of TMS-acetylene (0.73 mL, 0.51 g, 5.15 mmol) in THF (10 mL) was added under nitrogen at −10 °C *n*-BuLi (4.27 mL, 5.54 mmol, 1.3 mol L^{-1}). The reaction mixture was allowed to warm up to room temperature for 15 min and was then cooled to −78 °C. A solution of lactone **28** (2 g, 3.96 mmol) in THF (10 mL) was added dropwise, the reaction mixture was allowed to warm up to room temperature over 2 h and quenched with Ac_2O (4 mL). The resulting mixture was extracted with CH_2Cl_2. The combined extracts were dried and concentrated *in vacuo*. To a cooled (−78 °C) solution of the residue and triethylsilane (2.53 mL, 1.84 g, 15.84 mmol) in anhydrous CH_2Cl_2 (80 mL) was added dropwise $BF_3{\cdot}OEt_2$ (2 mL, 2.25 g, 15.84 mmol). When the starting material was completely consumed, the reaction was neutralised with triethylamine and extracted with dichloromethane. The combined organic layers were dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 99 : 1) and recrystallised with methanol to give compound **32** (90% overall yield from **28**) as white needles (mp 91–92 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.71 (d, 1H, *H*-1, J = 2.7 Hz), 4.01 (dq, 1H, *H*-5, J = 8.0, 6.2 Hz), 3.87 (s, 1H, *H*-3), 3.84 (dd, 1H, *H*-2, J = 2.7, 0.9 Hz), 3.59 (d, 1H, *H*-4, J = 8.2 Hz), 1.14 (d, 3H, *H*-6, J = 6.3 Hz), 0.92 (s, 9H, Si-C(CH_3)$_3$), 0.90 (s, 9H, Si-C(CH_3)$_3$), 0.85 (s, 9H, Si-C(CH_3)$_3$), 0.16 (s, 12H, Si-(CH_3)$_3$ and Si-CH_3), 0.12 (s, 6H, Si-CH_3), 0.11 (s, 3H, Si-CH_3), 0.07 (s, 3H, Si-CH_3), 0.07 (s, 3H, Si-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 101.7 (*C*-1′), 92.3 (*C*-1), 91.9 (*C*-2′), 79.9 (*C*-4), 79.2 (*C*-5), 73.0 (*C*-2), 69.1 (*C*-3), 26.2 (Si-C(*C*H$_3$)$_3$), 25.9 (Si-C(*C*H$_3$)$_3$), 25.7 (Si-C(*C*H$_3$)$_3$), 20.6 (*C*-6), 18.5 (Si-*C*(CH$_3$)$_3$), 18.3 (Si-*C*(CH$_3$)$_3$), 17.8 (Si-*C*(CH$_3$)$_3$), −0.1 (Si-(*C*H$_3$)$_3$), −4.1 (Si-*C*H$_3$), −4.4 (Si-*C*H$_3$), −4.4 (Si-*C*H$_3$), −4.5 (Si-*C*H$_3$), −4.7 (Si-*C*H$_3$), −4.8 (Si-*C*H$_3$); MS (CI + NH_3) m/z: 604 (MH^+ + NH_3), 587 (MH^+); IR (cm^{-1}, CCl_4): 2183 (TMS–C≡C); $[\alpha]_D^{25} = -7.2$ (c = 1, $CHCl_3$).

1-Ethynyl-2,3,5-tri-*O*-*tert*-butyldimethylsilyl-β-D-fucofuranose (33)

Potassium carbonate (1.9 g, 13.79 mmol) was added to a stirred solution of compound **32** (1.62 g, 2.76 mmol) in a 1 : 1 mixture of methanol–CH_2Cl_2 (30 mL) at room temperature, and the reaction mixture was stirred for 4 h. The methanol was then evaporated, the solution extracted with dichloromethane, and the combined organic layers dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, petroleum ether–AcOEt, 98 : 2 to 95 : 5) and recrystallised with methanol to yield **33** (99% yield) as a white solid (mp 56–59 °C): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.68 (t, 1H, *H*-1, J = 2.5 Hz), 4.01 (dq, 1H, *H*-5, J = 12.5, 6.3 Hz), 3.90 (s, 1H, *H*-3), 3.87 (dd, 1H, *H*-2, J = 2.8, 0.9 Hz), 3.61 (dd, 1H, *H*-4, J = 7.9, 0.7 Hz), 2.41 (d, 1H, *H*-2′, J = 2.2 Hz), 1.15 (d, 3H, *H*-6, J = 6.3 Hz), 0.92 (s, 9H, Si-C(CH_3)$_3$), 0.90 (s, 9H, Si-C(CH_3)$_3$), 0.87 (s, 9H, Si-C(CH_3)$_3$), 0.14 (s, 3H, Si-CH_3), 0.12 (s, 3H, Si-CH_3), 0.11 (s, 3H, Si-CH_3), 0.10 (s, 3H, Si-CH_3), 0.09 (s, 3H, Si-CH_3), 0.08 (s, 3H, Si-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 92.4 (*C*-1′), 80.0 (*C*-1), 79.0 (*C*-5), 79.0 (*C*-3), 75.2 (*C*-2′), 72.3 (*C*-2), 69.1 (*C*-4), 26.2 (Si-C(*C*H$_3$)$_3$), 25.9 (Si-C(*C*H$_3$)$_3$), 25.7 (Si-C(*C*H$_3$)$_3$), 20.5 (*C*-6), 18.5 (Si-*C*(CH$_3$)$_3$), 18.3 (Si-*C*(CH$_3$)$_3$), 17.9 (Si-*C*(CH$_3$)$_3$), −4.1 (Si-*C*H$_3$), −4.3 (Si-*C*H$_3$), −4.4 (Si-*C*H$_3$), −4.5 (Si-*C*H$_3$), −4.7 (Si-*C*H$_3$), −4.8 (Si-*C*H$_3$); MS (CI + NH_3) m/z: 532 (MH^+ + NH_3), 515 (MH^+); IR (cm^{-1}, CCl_4): 3312 (C≡C–H). $[\alpha]_D^{25} = -9.5$ (c = 1, $CHCl_3$).

1-Vinyl-2,3,5-tri-*O*-*tert*-butyldimethylsilyl-β-D-fucofuranose (34)

A mixture of compound **33** (0.84 g, 1.63 mmol), 20% Pd/$CaCO_3$ (0.17 g) and 10% quinoline (0.08 g) in ethyl acetate (8 mL) was hydrogenated at 1 atm at room temperature. The catalyst was filtered off (over Celite) and the resulting solution evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, petroleum ether–AcOEt, 99 : 1) to yield olefin **34** (98% yield) as a colourless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.93 (ddd, 1H, *H*-1′, J = 17.5, 10,3, 7.7 Hz), 5.34 (ddd, 1H, *H*-2′, J = 17.4, 1,8, 0.9 Hz), 5.22 (ddd, 1H, *H*-2′, J = 10.4, 1,9, 0.6 Hz), 4.41 (dd, 1H, *H*-1, J = 7.8, 2.7 Hz), 3.97 (dq, 1H, *H*-5, J = 7.7, 6.3 Hz), 3.90 (s, 1H, *H*-3), 3.77 (dd, 1H, *H*-2, J = 2.7, 0.8 Hz), 3.65 (dd, 1H, *H*-4, J = 7.8, 0.9 Hz), 1.15 (d, 3H, *H*-6, J = 6.4 Hz), 0.90 (s, 18H, Si-C(CH_3)$_3$), 0.88 (s, 9H, Si-C(CH_3)$_3$), 0.10 (s, 3H, Si-CH_3), 0.09 (s, 3H, Si-CH_3), 0.08 (s, 3H, Si-CH_3), 0.08 (s, 3H, Si-CH_3), 0.07 (s, 3H, Si-CH_3), 0.04 (s, 3H, Si-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.0 (*C*-1′), 118.2 (*C*-2′), 92.5 (*C*-4), 83.3 (*C*-1), 80.9 (*C*-2), 79.9 (*C*-3), 69.5 (*C*-5), 26.2 (Si-C(*C*H$_3$)$_3$), 25.9 (Si-C(*C*H$_3$)$_3$), 25.8 (Si-C(*C*H$_3$)$_3$), 20.6 (*C*-6), 18.5 (Si-*C*(CH$_3$)$_3$), 18.2 (Si-*C*(CH$_3$)$_3$), 17.9 (Si-*C*(CH$_3$)$_3$), −4.0 (Si-*C*H$_3$), −4.3 (Si-*C*H$_3$), −4.4 (Si-*C*H$_3$), −4.5 (Si-*C*H$_3$),

−4.6 (Si-CH_3), −4.7 (Si-CH_3); MS (CI + NH_3) *m/z*: 534 (MH^+ + NH_3), 517 (MH^+); $[\alpha]_D^{25} = -19.9$ (*c* = 1, $CHCl_3$); HRMS calcd for $C_{26}H_{56}O_4Si_3$ 516.34865; found 516.34916.

(±)-*S*-[4-(2-Methoxy-5-trimethylacetylphenyl)-1-(2,3,5-tri-*O*-*tert*-butyldimethylsilyl-β-D-fucofuranosyl)-4-oxobutyl]-*O*-ethyldithiocarbonate (35)

A solution of xanthate **22** (0.05 g, 0.13 mmol) and olefin **34** (0.14 g, 0.27 mmol) in 0.14 mL of 1,2-dichloroethane (DCE) was refluxed for 15 min under argon. Lauroyl peroxide (DLP) was then added (5 mol%) to the refluxing solution, followed by additional portions (5 mol% every 90 min). When the starting material was completely consumed (after addition of 15 mol% of DLP), the mixture was cooled to room temperature, concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 95 : 5 to 9 : 1) to give adduct **35** (yellow oil, 59% yield, 83% based on recovered starting material) as an inseparable 2 : 1 mixture of diastereoisomers (labelled ***a*** and ***b***): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 (d, 0.3H, *H*-10′***b***, *J* = 2.9 Hz), 7.37 (d, 0.7H, *H*-10′***a***, *J* = 2.9 Hz), 7.18–7.14 (m, 1H, *H*-8′***a*** and *H*-8′***b***), 6.95 (d, 0.3H, *H*-7′***b***, *J* = 8.9 Hz), 6.93 (d, 0.7H, *H*-7′***a***, *J* = 8.9 Hz), 4.68–4.52 (m, 2H, *H*-12′***a*** and *H*-12′***b***), 4.24 (td, 0.3H, *H*-1′***b***, *J* = 9.9, 3.1 Hz), 4.06 (m, 1.7H, *H*-1***a***, *H*-1***b*** and *H*-1′***a***), 3.93–3.87 (m, 3H, *H*-2***a***, *H*-2***b***, *H*-3***a***, *H*-3***b***, *H*-5***a*** and *H*-5***b***), 3.88 (s, 3H, OCH_3***a*** and OCH_3***b***), 3.62 (t, 1H, *H*-4***a*** and *H*-4***b***, *J* = 8.0 Hz), 3.34–3.10 (m, 2H, *H*-3′***a*** and *H*-3′***b***), 2.47–2.40 (m, 0.7H, *H*-2′***a***), 2.32–2.24 (m, 0.7H, *H*-2′***a***), 2.21–2.15 (m, 0.3H, *H*-2′***b***), 1.98–1.88 (m, 0.3H, *H*-2′***b***), 1.41 (t, 2.1H, *H*-13′***a***, *J* = 7.1 Hz), 1.41 (t, 0.9H, *H*-13′***b***, *J* = 7.0 Hz), 1.14 (d, 3H, *H*-6***a*** and *H*-6***b***, *J* = 6.2 Hz), 0.95 (s, 2,7H, Si-C(CH_3)$_3$***a***), 0.90 (s, 6,3H, Si-C(CH_3)$_3$***b***), 0.88 (s, 11,7H, Si-C(CH_3)$_3$***a***, Si-C(CH_3)$_3$***b***, and Si-C(CH_3)$_3$***b***), 0.87 (s, 6.3H, Si-C(CH_3)$_3$***a***), 0.18 (s, 0.9H, Si-CH_3***b***), 0.15 (s, 0.9H, Si-CH_3***b***), 0.12 (s, 2.1H, Si-CH_3***a***), 0.10 (s, 5.1H, Si-CH_3***a***, Si-CH_3***a*** and Si-CH_3***b***), 0.09 (s, 3H, Si-CH_3***a*** and Si-CH_3***b***), 0.08 (s, 2,1H, Si-CH_3***a***), 0.07 (s, 2,1H, Si-CH_3***a***), 0.06 (s, 0,9H, Si-CH_3***b***), 0.04 (s, 0,9H, Si-CH_3***b***); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 213.9 (*C*-11′***b***), 212.4 (*C*-11′***a***), 200.7 (*C*-4′***a***), 200.0 (*C*-4′***b***), 177.3 (O-*C*O***a***), 177.2 (O-*C*O***b***), 156.5 (*C*-6′***b***), 156.1 (*C*-6′***a***), 144.3 (*C*-9′***a*** and *C*-9′***b***), 128.7 (*C*-5′***a*** and *C*-5′***b***), 126.6 (*C*-10′***b***), 126.2 (*C*-10′***a***), 123.1 (*C*-8′***b***), 123.0 (*C*-8′***a***), 112.4 (*C*-7′***b***), 112.2 (*C*-7′***a***), 92.9 (*C*-4***a***), 92.5 (*C*-4***b***), 81.2 (*C*-1***b***), 80.2 (*C*-1***a***), 79.2 (*C*-2***b***), 79.1 (*C*-2***a***), 78.4 (*C*-3***a***), 78.3 (*C*-3***b***), 69.9 (*C*-12′***a***), 69.7 (*C*-12′***b***), 69.5 (*C*-5***b***), 69.4 (*C*-5***a***), 56.0 (O*C*H$_3$***b***), 55.9 (O*C*H$_3$***a***), 49.9 (*C*-1′***b***), 47.6 (*C*-1′***a***), 40.7 (*C*-3′***b***), 40.2 (*C*-3′***a***), 39.1 (*C*(CH$_3$)$_3$***a*** and *C*(CH$_3$)$_3$***b***), 27.2 (C(*C*H$_3$)$_3$***a*** and C(*C*H$_3$)$_3$***b***), 26.4 (*C*-2′***b***), 26.4 (*C*-2′***a***), 26.1 (Si-C(*C*H$_3$)$_3$***b***), 26.0 (Si-C(*C*H$_3$)$_3$***a***), 25.9 (Si-C(*C*H$_3$)$_3$***a***), 25.9 (Si-C(*C*H$_3$)$_3$***b***), 25.7 (Si-C(*C*H$_3$)$_3$***a*** and Si-C(*C*H$_3$)$_3$***b***), 20.7 (*C*-6***a***), 20.6 (*C*-6***a***), 18.4 (Si-*C*(CH$_3$)$_3$***a***), 18.3 (Si-*C*(CH$_3$)$_3$***b***), 18.1 (Si-*C*(CH$_3$)$_3$***b***), 18.0 (Si-*C*(CH$_3$)$_3$***a***), 17.9 (Si-*C*(CH$_3$)$_3$***a*** and Si-*C*(CH$_3$)$_3$***b***), 13.9 (*C*-13′***b***), 13.7 (*C*-13′***a***), −3.4 (Si-*C*H$_3$***b***), −3.9 (Si-*C*H$_3$***a***), −4.1 (Si-*C*H$_3$***b***), −4.2 (Si-*C*H$_3$***a***), −4.3 (Si-*C*H$_3$***a***), −4.3 (Si-*C*H$_3$***a***), −4.4 (Si-*C*H$_3$***b***), −4.4 (Si-*C*H$_3$***b***), −4.7 (Si-*C*H$_3$***a***), −4.8 (Si-*C*H$_3$***b***), −5.1 (Si-*C*H$_3$***a***), −5.3 (Si-*C*H$_3$***b***); MS (CI + NH_3) *m/z*: 887 (MH^+); IR (cm^{-1}, CCl_4): 1741 (O–*C*=*O*), 1680 (C=O), 1255 (S–*C*=*S*), 1109 (*O*–*C*=O), 1048 (*O*–*C*=S).

(±)-*S*-[4-(2-Methoxy-5-bromophenyl)-1-(2,3,5-tri-*O*-*tert*-butyldimethylsilyl-β-D-fucofuranosyl)-4-oxobutyl]-*O*-ethyldithiocarbonate (39)

Using the same procedure as **35**, xanthate **36** (0.05 g, 0.14 mmol) and olefin **34** (0.15 g, 0.28 mmol) gave the adduct **39** (yellow oil, 45% yield, 64% yield based on recovered starting material) as an inseparable 2 : 1 mixture of diastereoisomers (labelled ***a*** and ***b***): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, 0.3H, *H*-10′***b***, *J* = 2.6 Hz), 7.76 (d, 0.7H, *H*-10′***a***, *J* = 2.6 Hz), 7.53 (dd, 0.3H, *H*-8′***b***, *J* = 9.2, 2.1 Hz), 7.51 (dd, 0.7H, *H*-8′***a***, *J* = 8.8, 2.5 Hz), 6.85 (d, 0.3H, *H*-7′***b***, *J* = 8.8 Hz), 6.83 (d, 0.7H, *H*-7′***a***, *J* = 8.8 Hz), 4.69–4.50 (m, 2H, *H*-12′***a*** and *H*-12′***b***), 4.23 (td, 0.3H, *H*-1′***b***, *J* = 9.9 and 3.3 Hz), 4.02–3.99 (m, 1.7H, *H*-1***a***, *H*-1***b*** and *H*-1′***a***), 3.91–3.86 (m, 3H, *H*-2***a***, *H*-2***b***, *H*-3***a***, *H*-3***b***, *H*-5***a*** and *H*-5***b***), 3.86 (s, 3H, OCH_3***a*** and OCH_3***b***), 3.61 (t, 1H, *H*-4***a*** and *H*-4***b***, *J* = 9.1 Hz), 3.30–3.08 (m, 2H, *H*-3′***a*** and *H*-3′***b***), 2.47–2.39 (m, 0.7H, *H*-2′***a***), 2.32–2.24 (m, 0.7H, *H*-2′***a***), 2.19–2.13 (m, 0.3H, *H*-2′***b***), 1.98–1.89 (m, 0.3H, *H*-2′***b***), 1.41 (t, 2.1H, *H*-13′***a***, *J* = 7.1 Hz), 1.40 (t, 0.9H, *H*-13′***b***, *J* = 7.1 Hz), 1.14 (d, 3H, *H*-6***a*** and *H*-6***b***, *J* = 6.2 Hz), 0.94 (s, 2.7H, Si-C(CH_3)$_3$***a***), 0.90 (s, 6.3H, Si-C(CH_3)$_3$***b***), 0.87 (s, 11.7H, Si-C(CH_3)$_3$***a***, Si-C(CH_3)$_3$***b*** and Si-C(CH_3)$_3$***b***), 0.86 (s, 6.3H, Si-C(CH_3)$_3$***a***), 0.17 (s, 0.9H, Si-CH_3***b***), 0.15 (s, 0.9H, Si-CH_3***b***), 0.12 (s, 2.1H, Si-CH_3***a***), 0.11 (s, 0.9H, Si-CH_3***b***), 0.10 (s, 5.1H, Si-CH_3***a***, Si-CH_3***a*** and Si-CH_3***b***), 0.09 (s, 2.1H, Si-CH_3***a***), 0.07 (s, 2.1H, Si-CH_3***a***), 0.05 (s, 3H, Si-CH_3***a*** and Si-CH_3***b***), 0.03 (s, 0.9H, Si-CH_3***b***); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 213.9 (*C*-11′***b***), 212.4 (*C*-11′***a***), 200.6 (*C*-4′***a***), 200.0 (*C*-4′***b***), 157.8 (*C*-6′***b***), 157.5 (*C*-6′***a***), 136.0 (*C*-10′***b***), 135.7 (*C*-10′***a***), 132.9 (*C*-8′***a*** and *C*-8′***b***), 129.9 (*C*-5′***a***), 129.4 (*C*-5′***b***), 113.6 (*C*-7′***b***), 113.5 (*C*-7′***a***), 113.2 (*C*-9′***b***), 113.2 (*C*-9′***a***), 92.9 (*C*-4***a***), 92.5 (*C*-4***b***), 81.1 (*C*-1***b***), 80.2 (*C*-1***a***), 79.1 (*C*-2***a*** and *C*-2***b***), 78.3 (*C*-3***a*** and *C*-3***b***), 69.9 (*C*-12′***a***), 69.7 (*C*-12′***b***), 69.5 (*C*-5***b***), 69.4 (*C*-5***a***), 55.9 (O*C*H$_3$***b***), 55.8 (O*C*H$_3$***a***), 49.9 (*C*-1′***b***), 47.5 (*C*-1′***a***), 40.6 (*C*-3′***b***), 40.2 (*C*-3′***a***), 26.3 (*C*-2′***a***), 26.3 (*C*-2′***b***), 26.1 (Si-C(*C*H$_3$)$_3$***b***), 25.9 (Si-C(*C*H$_3$)$_3$***a***), 25.9 (Si-C(*C*H$_3$)$_3$***a***), 25.8 (Si-C(*C*H$_3$)$_3$***b***), 25.7 (Si-C(*C*H$_3$)$_3$***a*** and Si-C(*C*H$_3$)$_3$***b***), 20.8 (*C*-6***a***), 20.6 (*C*-6***b***), 18.4 (Si-*C*(CH$_3$)$_3$***a***), 18.3 (Si-*C*(CH$_3$)$_3$***b***), 18.1 (Si-*C*(CH$_3$)$_3$***b***), 18.0 (Si-*C*(CH$_3$)$_3$***a***), 17.8 (Si-*C*(CH$_3$)$_3$***a*** and Si-*C*(CH$_3$)$_3$***b***), 13.9 (*C*-13′***b***), 13.8 (*C*-13′***a***), −3.4 (Si-*C*H$_3$***b***), −3.9 (Si-*C*H$_3$***a***), −4.1 (Si-*C*H$_3$***b***), −4.2 (Si-*C*H$_3$***a***), −4.3 (Si-*C*H$_3$***a*** and Si-*C*H$_3$***a***), −4.3 (Si-*C*H$_3$***b***), −4.4 (Si-*C*H$_3$***b***), −4.7 (Si-*C*H$_3$***a***), −4.8 (Si-*C*H$_3$***b***), −5.2 (Si-*C*H$_3$***a***), −5.3 (Si-*C*H$_3$***b***); MS (CI + NH_3) *m/z*: 884 (MH^+ + NH_3), 882 (MH^+ + NH_3), 867 (MH^+), 865 (MH^+); IR (cm^{-1}, CCl_4): 1683 (C=O), 1252 (S–*C*=*S*), 1049 (*O*–*C*=S).

(±)-*S*-[4-(2-Methoxyphenyl)-1-(2,3,5-tri-*O*-*tert*-butyldimethylsilyl-β-D-fucofuranosyl)-4-oxobutyl]-*O*-ethyldithiocarbonate (40)

Using the same procedure as **35**, xanthate **37**[6] (0.05 g, 0.18 mmol) and olefin **34** (0.19 g, 0.37 mmol) gave the adduct **40** (yellow oil, 35% yield, 59% yield based on recovered starting material) as an inseparable 2 : 1 mixture of diastereoisomers: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (dd, 0.3H, *H*-8′***b***, *J* = 7.7, 1.7 Hz), 7.66 (dd, 0.7H, *H*-8′***a***, *J* = 7.7, 1.7 Hz), 7.48–7.41 (m, 1H, *H*-10′***a*** and *H*-10′***b***), 7.00–6.93 (m, 2H, *H*-7′***a***, *H*-7′***b***, *H*-9′***a*** and *H*-9′***b***), 4.68–4.50 (m, 2H, *H*-12′***a*** and *H*-12′***b***), 4.24 (td, 0.3H, *H*-1′***b***, *J* = 10.1, 3.2 Hz), 4.06–3.99 (m, 1.7H, *H*-1***a***, *H*-1***b*** and *H*-1′***a***), 3.93–3.86 (m, 3H, *H*-2***a***, *H*-2***b***, *H*-3***a***, *H*-3***b***, *H*-5***a*** and *H*-5***b***), 3.87 (s, 3H, OCH_3***a*** and OCH_3***b***), 3.62 (t, 1H, *H*-4***a*** and *H*-4***b***, *J* = 9.1 Hz), 3.32–3.10 (m, 2H, *H*-3′***a*** and *H*-3′***b***), 2.49–2.39 (m, 0.7H, *H*-2′***a***), 2.33–2.25 (m, 0.7H, *H*-2′***a***), 2.23–2.17 (m, 0.3H, *H*-2′***b***), 2.00–1.90 (m, 0.3H, *H*-2′***b***), 1.41 (t, 2.1H, *H*-13′***a***, *J* = 7.1 Hz), 1.40 (t, 0.9H, *H*-13′***b***, *J* = 7.1 Hz), 1.14 (d, 3H, *H*-6***a*** and *H*-6***b***, *J* = 6.2 Hz), 0.94 (s, 6.3H, Si-C(CH_3)$_3$***a***), 0.90 (s, 2.7H, Si-C(CH_3)$_3$***b***), 0.87 (s, 11.7H, Si-C(CH_3)$_3$***a***, Si-C(CH_3)$_3$***b*** and Si-C(CH_3)$_3$***b***), 0.86 (s, 6.3H, Si-C(CH_3)$_3$***a***), 0.18 (s, 0.9H, Si-CH_3***b***), 0.15 (s, 0.9H, Si-CH_3***b***), 0.12 (s, 2.1H, Si-CH_3***a***), 0.10 (s, 6H, Si-CH_3***a***, Si-CH_3***a***, Si-CH_3***b*** and Si-CH_3***b***), 0.09 (s, 2.1H, Si-CH_3***a***), 0.07 (s, 2.1H, Si-CH_3***a***), 0.06 (s, 3H, Si-CH_3***a*** and Si-CH_3***b***), 0.04 (s, 0.9H, Si-CH_3***b***); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 214.0 (*C*-11′***b***), 212.5 (*C*-11′***a***), 202.2 (*C*-4′***a***), 201.5 (*C*-4′***b***), 158.8 (*C*-6′***b***), 158.5 (*C*-6′***a***), 133.6 (*C*-10′***b***), 133.3 (*C*-10′***a***), 130.4 (*C*-7′***a*** and *C*-7′***b***), 128.6 (*C*-5′***a***), 128.1 (*C*-5′***b***), 120.7 (*C*-9′***a*** et *C*-9′***b***), 111.6 (*C*-8′***b***), 111.5 (*C*-8′***a***), 92.9 (*C*-4***a***), 92.5 (*C*-4***b***), 81.2 (*C*-1***b***), 80.2 (*C*-1***a***), 79.2 (*C*-2***a*** and *C*-2***b***), 78.3 (*C*-3***a*** and *C*-3***b***), 69.9 (*C*-12′***a***), 69.6 (*C*-12′***b***), 69.5 (*C*-5***b***), 69.4 (*C*-5***a***), 55.6 (O*C*H$_3$***b***), 55.5 (O*C*H$_3$***a***), 50.0 (*C*-1′***b***), 47.6 (*C*-1′***a***), 40.7 (*C*-3′***b***), 40.3 (*C*-3′***a***), 26.5 (*C*-2′***a*** and *C*-2′***b***), 26.1 (Si-C(*C*H$_3$)$_3$***b***), 25.9 (Si-C(*C*H$_3$)$_3$***a***), 25.9 (Si-C(*C*H$_3$)$_3$***a***), 25.7

(Si-C(CH_3)$_3$***a***, Si-C(CH_3)$_3$***b*** and Si-C(CH_3)$_3$***b***), 20.8 (*C*-6***a***), 20.6 (*C*-6***b***), 18.4 (Si-*C*(CH_3)$_3$***a***), 18.3 (Si-*C*(CH_3)$_3$***b***), 18.1 (Si-*C*(CH_3)$_3$***b***), 18.0 (Si-*C*(CH_3)$_3$***a***), 17.9 (Si-*C*(CH_3)$_3$***a*** and Si-*C*(CH_3)$_3$***b***), 13.9 (*C*-13′***b***), 13.7 (*C*-13′***a***), −3.4 (Si-*C*H_3***b***), −3.9 (Si-*C*H_3***a***), −4.1 (Si-*C*H_3***b***), −4.2 (Si-*C*H_3***a***), −4.3 (Si-*C*H_3***a*** and Si-*C*H_3***a***), −4.4 (Si-*C*H_3***b***), −4.4 (Si-*C*H_3***b***), −4.7 (Si-*C*H_3***a***), −4.8 (Si-*C*H_3***b***), −5.1 (Si-*C*H_3***a***), −5.3 (Si-*C*H_3***b***); MS (CI + NH_3) *m*/*z*: 804 (MH^+ + NH_3), 787 (MH^+); IR (cm^{-1}, CCl_4): 1678 (C=O), 1252 (S–*C*=*S*), 1049 (*S*–*C*=S).

(±)-*S*-[4-(4-Chlorophenyl)-1-(2,3,5-tri-*O*-*tert*-butyldimethylsilyl-β-D-fucofuranosyl)-4-oxobutyl]-*O*-ethyldithiocarbonate (41)

Using the same procedure as **35**, xanthate **38** (0.04 g, 0.15 mmol) and olefin **34** (0.15 g, 0.29 mmol) gave the adduct **41**[15] (yellow oil, 72% yield) as an inseparable 2 : 1 mixture of diastereoisomers: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 1.4H, *H*-6′***a***, J = 8.6 Hz), 7.88 (d, 0.6H, *H*-6′***b***, J = 8.6 Hz), 7.43 (d, 0.6H, *H*-7′***b***, J = 8.6 Hz), 7.43 (d, 1.4H, *H*-7′***a***, J = 8.6 Hz), 4.69–4.52 (m, 2H, *H*-10′***a*** and *H*-10′***b***), 4.25 (td, 0.3H, *H*-1′***b***, J = 10.0, 3.2 Hz), 4.05–4.01 (m, 1.7H, *H*-1***a***, *H*-1***b*** and *H*-1′***a***), 3.92–3.60 (m, 3H, *H*-2***a***, *H*-2***b***, *H*-3***a***, *H*-3***b***, *H*-5***a*** and *H*-5***b***), 3.65–3.61 (m, 1H, *H*-4***a*** and *H*-4***b***), 3.35–3.12 (m, 2H, *H*-3′***a*** and *H*-3′***b***), 2.48–2.39 (m, 0.7H, *H*-2′***a***), 2.33–2.25 (m, 0.7H, *H*-2′***a***), 2.24–2.19 (m, 0.3H, *H*-2′***b***), 2.05–1.88 (m, 0.3H, *H*-2′***b***), 1.42 (t, 2.1H, *H*-11′***a***, J = 7.1 Hz), 1.41 (t, 0.9H, *H*-11′***b***, J = 7.1 Hz), 1.14 (d, 2.1H, *H*-6***a***, J = 6.2 Hz), 1.14 (d, 0.9H, *H*-6***b***, J = 6.3 Hz), 0.94 (s, 2.7H, Si-C(CH_3)$_3$***b***), 0.90 (s, 6.3H, Si-C(CH_3)$_3$***a***), 0.89 (s, 6.3H, Si-C(CH_3)$_3$***a***), 0.88 (s, 2.7H, Si-C(CH_3)$_3$***b***), 0.86 (s, 9H, Si-C(CH_3)$_3$***a*** and Si-C(CH_3)$_3$***b***), 0.16 (s, 0.9H, Si-CH_3***b***), 0.15 (s, 0.9H, Si-CH_3***b***), 0.13 (s, 2.1H, Si-CH_3***a***), 0.11 (s, 3H, Si-CH_3***a*** and Si-CH_3***b***), 0.10 (s, 2.1H, Si-CH_3***a***), 0.09 (s, 2.1H, Si-CH_3***a***), 0.09 (s, 0.9H, Si-CH_3***b***), 0.07 (s, 2.1H, Si-CH_3***a***), 0.06 (s, 0.9H, Si-CH_3***b***), 0.05 (s, 2.1H, Si-CH_3***a***), 0.04 (s, 0.9H, Si-CH_3***b***); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 214.1 (*C*-9′***b***), 212.2 (*C*-9′***a***), 198.6 (*C*-4′***a***), 198.2 (*C*-4′***b***), 139.7 (*C*-5′***b***), 139.3 (*C*-5′***a***), 135.4 (*C*-8′***a***), 135.1 (*C*-8′***b***), 129.7 (*C*-6′***a***), 129.6 (*C*-6′***b***), 129.0 (*C*-7′***b***), 128.9 (*C*-7′***a***), 92.9 (*C*-4***a***), 92.5 (*C*-4***b***), 81.2 (*C*-1***b***), 80.1 (*C*-1***a***), 79.2 (*C*-2***a***), 79.1 (*C*-2***b***), 78.5 (*C*-3***b***), 78.4 (*C*-3***a***), 70.1 (*C*-10′***a***), 69.9 (*C*-10′***b***), 69.4 (*C*-5***b***), 69.3 (*C*-5***a***), 50.1 (*C*-1′***b***), 47.5 (*C*-1′***a***), 35.4 (*C*-3′***b***), 35.1 (*C*-3′***a***), 26.3 (*C*-2′***a***), 26.1 (*C*-2′***b***), 26.1 (Si-C(*C*H_3)$_3$***b***), 25.9 (Si-C(*C*H_3)$_3$***a***), 25.9 (Si-C(*C*H_3)$_3$***a***), 25.8 (Si-C(*C*H_3)$_3$***b***), 25.7 (Si-C(*C*H_3)$_3$***a***), 25.7 (Si-C(*C*H_3)$_3$***b***), 20.8 (*C*-6***a***), 20.6 (*C*-6***b***), 18.4 (Si-*C*(CH_3)$_3$***a***), 18.3 (Si-*C*(CH_3)$_3$***b***), 18.1 (Si-*C*(CH_3)$_3$***b***), 18,0 (Si-*C*(CH_3)$_3$***a***), 17.9 (Si-*C*(CH_3)$_3$***a***), 17.8 (Si-*C*(CH_3)$_3$***b***), 13.9 (*C*-11′***b***), 13.8 (*C*-11′***a***), −3.,4 (Si-*C*H_3***b***), −3.8 (Si-*C*H_3***a***), −4.1 (Si-*C*H_3***b***), −4.2 (Si-*C*H_3***a***), −4.3 (Si-*C*H_3***a***), −4.3 (Si-*C*H_3***a***), −4.3 (Si-*C*H_3***a***), −4.4 (Si-*C*H_3***b***), −4.6 (Si-*C*H_3***b***), −4.7 (Si-*C*H_3***a***), −5.1 (Si-*C*H_3***b***), −5.2 (Si-*C*H_3***b***); MS (CI + NH_3) *m*/*z*: 810 (MH^+ + NH_3), 808 (MH^+ + NH_3), 793 (MH^+), 791 (MH^+); IR (cm^{-1}, CCl_4): 1691 (C=O), 1255 (S–*C*=*S*), 1051 (*O*–*C*=S).

(±)-6-Chloro-4-(2,3,5-*O*-*tert*-butyldimethylsilyl-β-D-fucofuranosyl)-3,4-dihydro-2*H*-naphthalen-1-one (42)

A solution of **41** (0.03 g, 0.04 mmol) in 1,2-dichloroethane (0.4 mL) was refluxed for 15 min under argon. Lauroyl peroxide (DLP) was then added portionwise (20 mol% h^{-1}) to the refluxing solution. When starting material was completely consumed (after addition of 1.2 equiv. of DLP), the crude mixture was cooled to room temperature, concentrated under reduced pressure and purified by flash column chromatography (silica gel, petroleum ether–AcOEt, 99 : 1) to give tetralone **42** (57% yield) as a separable mixture of diastereoisomers. Diastereoisomer I (colourless oil): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, 1H, *H*-6′, J = 8.4 Hz), 7.39 (d, 1H, *H*-9′, J = 2.0 Hz), 7.33 (dd, 1H, *H*-7′, J = 8.4, 2.0 Hz), 3.98 (dd, 1H, *H*-1, J = 10.6, 2.5 Hz), 3.96 (s, 1H, *H*-3), 3.91 (td, 1H, *H*-5, J = 14.6, 6.2 Hz), 3.69 (d, 1H, *H*-2, J = 1.7 Hz), 3.59 (dd, 1H, *H*-4, J = 8.5, 0.8 Hz), 3.44 (td, 1H, *H*-1′, J = 10.1, 3.5 Hz), 2.95–2.84 (m, 2H, *H*-3′), 2.64–2.54 (m, 1H, *H*-2′), 2.20–2.11 (m, 1H, *H*-2′), 1.18 (d, 3H, *H*-6, J = 6.2 Hz), 0.92 (s, 9H, Si-C(CH_3)$_3$), 0.89 (s, 9H, Si-C(CH_3)$_3$), 0.87 (s, 9H, Si-C(CH_3)$_3$), 0.26 (s, 3H, Si-CH_3), 0.20 (s, 3H, Si-CH_3), 0.12 (s, 3H, Si-CH_3), 0.11 (s, 3H, Si-CH_3), 0.06(s, 3H, Si-CH_3), 0.01 (s, 3H, Si-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.9 (*C*-4′), 146.9 (*C*-8′), 139.5 (*C*-5′), 131.1 (*C*-10′), 129.5 (*C*-6′), 128.5 (*C*-7′), 127.8 (*C*-9′), 92.4 (*C*-4), 81.9 (*C*-1), 79.0 (*C*-2), 78.3 (*C*-3), 69.5 (*C*-5), 32.0 (*C*-1′), 34.5 (*C*-3′), 26.3 (Si-C(*C*H_3)$_3$), 26.0 (Si-C(*C*H_3)$_3$), 25.7 (Si-C(*C*H_3)$_3$), 25.2 (*C*-2′), 20.8 (*C*-6), 18.5 (Si-*C*(CH_3)$_3$), 18.4 (Si-*C*(CH_3)$_3$), 17.8 (Si-*C*(CH_3)$_3$), −2.1 (Si-CH_3), −4.0 (Si-CH_3), −4.2 (Si-CH_3), −4.3 (Si-CH_3), −4.6 (Si-CH_3), −5.2 (Si-CH_3); MS (CI + NH_3) *m*/*z*: 688 (MH^+ + NH_3), 686 (MH^+ + NH_3), 671 (MH^+), 669 (MH^+); IR (cm^{-1}, CCl_4): 1692 (C=O); $[a]_D^{25}$ = − 13.0 (c = 1, $CHCl_3$). Diastereoisomer II (colourless oil): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, 1H, *H*-6′, J = 8.4 Hz), 7.92 (d, 1H, *H*-9′, J = 1.8 Hz), 7.31 (dd, 1H, *H*-7′, J = 8.4, 2.0 Hz), 4.08 (dd, 1H, *H*-1, J = 10.0, 2.0 Hz), 3.93 (m, 3H, *H*-2, *H*-3 and *H*-5), 3.65 (d, 1H, *H*-4, J = 8.3 Hz), 3.28–3.23 (m, 1H, *H*-1′), 2.72–2.57 (m, 2H, *H*-3′), 2.21–2.13 (m, 1H, *H*-2′), 2.00–1.92 (m, 1H, *H*-2′), 1.20 (d, 3H, *H*-6, J = 6.4 Hz), 0.95 (s, 9H, Si-C(CH_3)$_3$), 0.91 (s, 9H, Si-C(CH_3)$_3$), 0.86 (s, 9H, Si-C(CH_3)$_3$), 0.19 (s, 3H, Si-CH_3), 0.17 (s, 3H, Si-CH_3), 0.12 (s, 3H, Si-CH_3), 0.11 (s, 3H, Si-CH_3), 0.10 (s, 3H, Si-CH_3), 0.09 (s, 3H, Si-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.1 (*C*-4′), 148.0 (*C*-8′), 139.9 (*C*-5′), 130.7 (*C*-10′), 130.3 (*C*-6′), 128.8 (*C*-7′), 127.6 (*C*-9′), 92.8 (*C*-4), 82.9 (*C*-1), 78.9 (*C*-2), 78.5 (*C*-3), 69.4 (*C*-5), 38.0 (*C*-1′), 36.2 (*C*-3′), 26.1 (Si-C(*C*H_3)$_3$), 25.9 (Si-C(*C*H_3)$_3$), 25.7 (2C, Si-C(*C*H_3)$_3$ and *C*-2′), 20.7 (*C*-6), 18.3 (Si-*C*(CH_3)$_3$), 18.2 (Si-*C*(CH_3)$_3$), 17.9 (Si-*C*(CH_3)$_3$), −3.0 (Si-CH_3), −3.9 (Si-CH_3), −4.1 (Si-CH_3), −4.3 (Si-CH_3), −4.5 (Si-CH_3), −5.3 (Si-CH_3); MS (CI + NH_3) *m*/*z*: 688 (MH^+ + NH_3), 686 (MH^+ + NH_3), 671 (MH^+), 669 (MH^+); IR (cm^{-1}, CCl_4): 1691 (C=O); $[a]_D^{25}$ = + 2.6 (c = 1, $CHCl_3$).

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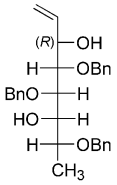
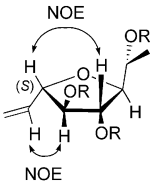
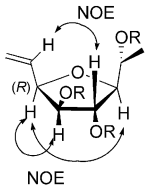


18



19, R = Bn
(inversion)



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