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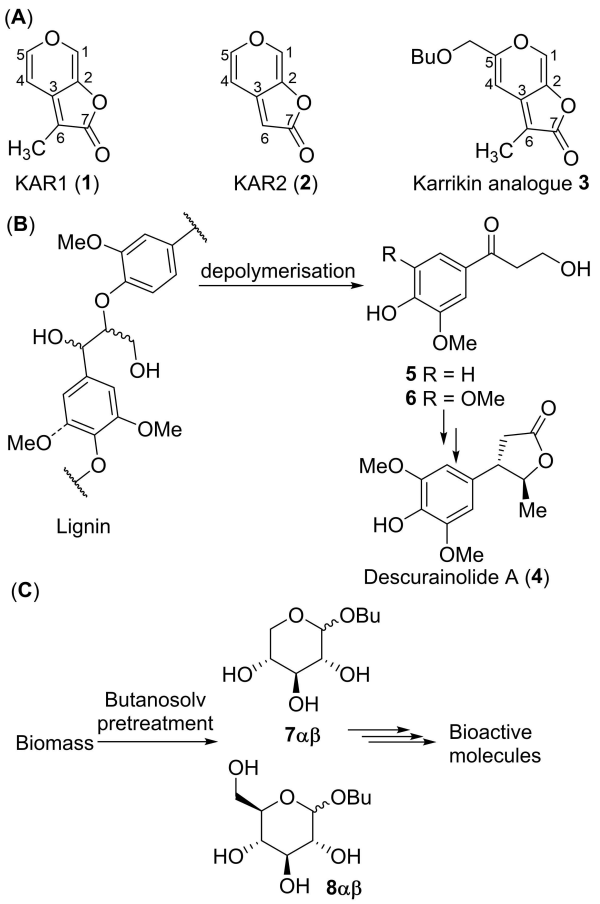
From Biomass to the Karrikins *via* Selective Catalytic Oxidation of Hemicellulose-Derived Butyl Xylosides and Glucosides

Ganyuan Xiao,[a] Gerard Su,[a] Alexandra M. Z. Slawin,[a] and Nicholas Westwood*[a]

Members of the karrikin family of bioactive small molecules are known to promote germination of a range of plants following large scale fires. As a result, they are relevant and interesting compounds. This report describes their synthesis from a biomass-derived product stream. During work to fractionate biomass with the goal of obtaining high quality lignins, an interesting co-product stream derived from the hemicellulose in the biomass, was obtained. Whilst many applications of this co-product stream can be proposed, in this case the major monosaccharides have been converted to relevant karrikins in short reaction sequences. Key results include a highly selective catalytic oxidation reaction, conversion of the resulting ketone to a butenolide by two alternative approaches, a selective acetal reductive opening reaction, X-ray crystallographic analysis of two compounds and detailed comparison of the final products with previous literature reports. Only through successful use of all the components generated during biomass refining, can economic sustainability be potentially achieved.

Introduction

The dramatic impact of forest fires is increasingly visible with frequent reports appearing in the media.[1–2] An under-discussed component of these dramatic events is how the forest recovers once the fire is out. The most frequent response to fire involves the rapid germination of a wide variety of plants often referred to as "fire-followers".[3] The seeds of these plants lie dormant in the soil for many years and their germination post-fire is triggered by specific compounds that are present in the smoke generated during the fire. One example of this is the karrikin family of compounds represented by karrikins 1 (KAR1, **1**) and 2 (KAR2, **2**, Scheme 1A). Potential applications of the karrikins include promoting the germination of garden or horticultural seeds, revegetation of degraded land and in landscape restoration projects.[3] It has been shown that the presence of KAR1 **1** at concentrations in aqueous solutions as low as 10^{-9} M can trigger germination of the seeds of fire-follower plants.[4] Since their discovery in fire smoke water, there has been significant interest in the mode of action of karrikins and rapid progress is being made.[5–8] One contributing factor to the improved understanding has been the synthesis of authentic samples of the karrikins and of novel karrikin analogues. Several elegant routes[9–15] to KAR1 **1** have been published and structure activity relationship studies[16–18] have started to define the key



Scheme 1. (A) The chemical structures of KAR1 (**1**), KAR2 (**2**) and Karrikin analogue **3**; (B) The depolymerisation of lignin to give keto-alcohols **5** and **6**,[23] and the synthesis of natural product **4** from **6**;[22] (C) Conversion of the hemicellulose derived-monosaccharides αβ-butoxylated xylose/glucose **7αβ**/**8αβ** to important bioactive molecules.

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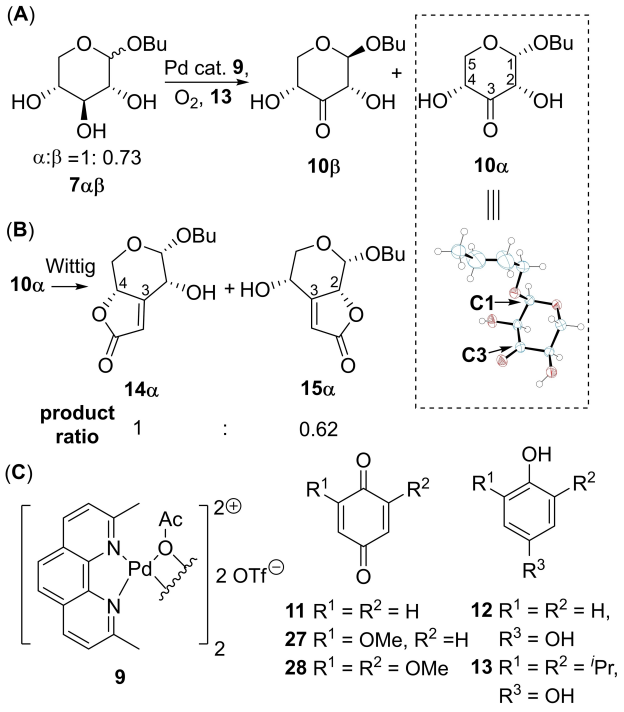
chemical features in the karrikins that trigger their important biological impact. For example, a recent report[18] described the potent seed germination activity of karrikin analogue **3** demonstrating the tolerance to substituents at the C5-position (Scheme 1A).

In recent years, interested has grown in the synthesis of bioactive molecules from renewable starting materials.[19–21] For example, we have reported the synthesis of the natural product descurainolide A **4** (Scheme 1B) and cyclic peptides from the biopolymer lignin-derived compounds **5** and **6**.[22,23] Lignin is a very heterogeneous material that is abundant in biomass and is one of the few biopolymers that contains a large numbers of aryl rings. These types of studies are relevant as it may not always be possible to start synthetic routes from the currently pervasive oil-derived aromatic building blocks. One factor that influences the production of lignin-derived starting compounds such as **5** and **6** is the quality of the starting lignin that is isolated from the biomass. Whilst many options are available for obtaining lignin, including very well-established industrial processes,[24] one focus of recent studies has been the use of organic solvents in what are referred to as organosolv pretreatment protocols.[25] Whilst the use of ethanol dominates,[26–27] there is interest in using butanol as the organic solvent and studies have shown that the resulting butanosolv lignin can be depolymerised to aromatic units or further modified.[28–33] A variety of different biomass sources, including soft- and hardwoods,[34] nut shells,[34] rice husks[30] and draff[35] (waste from the whisky industry) have been used to date.

In addition to the lignin fraction, butanosolv processing of biomass leads to another fraction derived from the hemicellulose polymer (the **H**emicellulose-**D**erived **F**raction, HDF). The constituents of the HDF vary depending on the biomass used, but butanosolv HDF always includes a large percentage of butoxylated monosaccharides. For example, the HDF from the rice husks used in this study has butoxylated xylose **7αβ** and butoxylated glucose **8αβ** as the two main components (Scheme 1C). Numerous possible applications of these important monosaccharides in the synthesis of bioactive molecules can be envisaged. Here one application is used to illustrate the potential of this HDF. We report the conversion of **7αβ** to the germination inducer KAR1 **1** and **8αβ** to compound **3**, a highly bioactive analogue of KAR1 **1**. Both synthetic sequences initially rely on a highly selective palladium-catalysed oxidation reaction.[36–42]



Scheme 2. (A) The synthesis of **10αβ** and the X-ray crystal structure of **10α** confirmed that selective oxidation at the C3 position had occurred (ORTEP representation 50% ellipsoid probability, CCDC 2117933); Pd. pre-catalyst **9** (2.0 mol%), 2,6-diisopropylphenol (**13**, 30 mol%), oxygen, MeCN/H_2O (10:1), 60 °C, overnight; **10α** = 40%; **10β** = 10%; (B) Wittig reaction to form butenolides **14α** and **15α**; $Ph_3P{=}CHCO_2Et$ (1.5 eq.), MeCN, 75 °C, 72 h; **14α** = 55%; **15α** = 32%; (C) Structure of **9**, the benzoquinones used in this study, the reduction product dihydrobenzoquinone (**12**) and 2,6-diisopropylphenol (**13**).

Results and Discussion

This study began with the conversion of αβ-butoxylated xylose **7αβ** to KAR1 **1**. Preparation of the palladium pre-catalyst **9** and **7αβ** was achieved using reported protocols (Scheme 2 and Scheme S1).[30,43] Initial attempts to convert **7αβ** selectively to the corresponding 3-ketose derivative **10αβ** using **9** (2 mol%) under modified Minnard conditions[36] with benzoquinone (**11**, BQ) were successful with full conversion of **7αβ** to **10αβ** (65% NMR yield, Table S1, Figures S1–S5). However, this protocol was not applicable at increased scale due to challenges in removing the large amounts of the dihydrobenzoquinone (**12**) that is formed (Figure S5). Instead, catalytic oxidation of **7αβ** with **9** (2.0 mol%) using O_2 in the presence of the additive 2,6-diisopropylphenol (**13**, 30 mol%), according to the optimized protocol of Waymouth[43] led to **10αβ** in an isolated yield of 64% on a 6 g scale (Scheme 2A and Table S1). During purification of **10αβ**, it was found out that the α- and β-anomers of **10αβ** could be separated giving pure samples of the α- and β-anomer in 40% and 10% isolated yield respectively (Scheme 2A and Figure S6). The β-anomer **10β** was unstable and partially decomposed during chromatography accounting for its low isolated yield (Figure S7). Initially, HMBC NMR analysis of **10α** was used to confirm the regioselectivity of the oxidation reaction (Figure S8) with X-ray crystallographic analysis of **10α** further supporting this conclusion (Scheme 2).

Whilst ketoses **10αβ** should be viewed as important synthetic intermediates for a wide range of potential applications, the next step in the route to KAR1 **1** involved a Wittig reaction of **10αβ** using conditions reported by Rauter and Calhorda *et al.*[44] In the first trial, the relatively abundant α-anomer **10α** was reacted with $Ph_3P{=}CHCO_2Et$ (1.5 equiv.) in MeCN at 75 °C for 72 h to give the isomeric cyclized products **14α** and **15α** in 55% and 32% isolated yields respectively (Scheme 2B and Figures S9 and S10). Subsequent attempts to

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eliminate BuOH from **15α** were made using DBU as reported by Takei *et al.*[45] in an analogous system. This led to a complicated and inseparable reaction mixture.

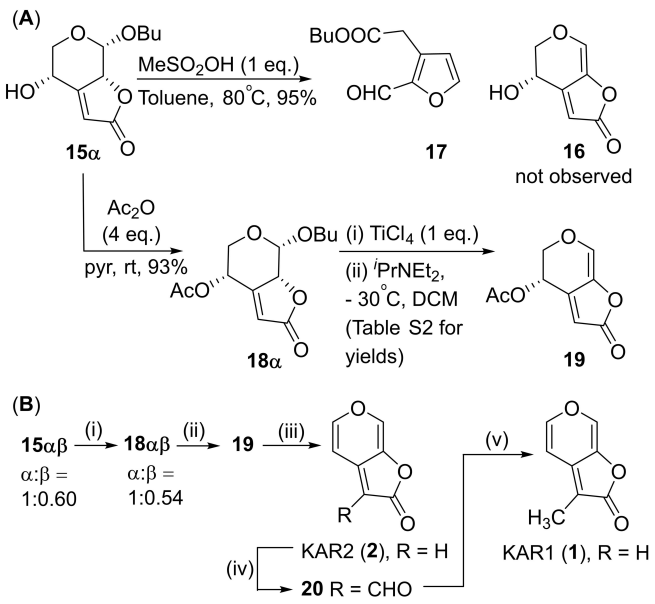
Whilst Bronsted acid catalysis[45,46] of this type of reaction has been reported, treatment of **15α** with methanesulfonic acid (MsOH) did not give the expected product **16** but instead led to the formation of an unexpected product **17** in excellent yield (Scheme 3A and Scheme S2). More encouragingly, initial treatment of **18α**, formed by acetylation of **15α**, with $TiCl_4$ and Hünig's base at − 30 °C gave **19** (Scheme 3A). ^{1}H NMR analysis of the crude reaction mixture (Figure S11) showed that, whilst conversion was low (21%), **19** was produced in a clean transformation with the only other major compound present being unreacted **18α**. Further attempts to optimise this reaction proved challenging (Table S2, entries B–F). However, this chemistry was sufficiently robust to enable the rapid conversion of a diastereomeric mixture of **18αβ** [α:β 1:0.54, generated from **10αβ** via **15αβ**] to produce **19** with any unreacted starting material **18αβ** being recovered. The synthesis of KAR1 **1** from **19** was completed using the method reported by *Stick et al.*[9] (Scheme 3B). In brief, palladium catalysed elimination of acetic acid from **19** gave KAR2 **2** (Table S3 for comparison with previously reported NMR data[9]). A subsequent Vilsmeier reaction of KAR2 **2** gave aldehyde **20** and reductive deoxygenation of **20** gave the natural product KAR1 **1**. Comparison of analytical data with those reported by Meijler *et al.*[47] confirmed the structure of KAR1 **1** which was prepared in an as yet unoptimized 6-step route from **7αβ** (Table S4 and Figures S12–S15).

In addition to the availability of the xylose-derived **7αβ** from rice husks, a glucose-derived product **8αβ** (Scheme 1C) can also be obtained.[30] A retrosynthetic analysis of karrikin analogue **3** starting from **8αβ** was therefore proposed (Scheme 4). This started with the selective C3-oxidation of **8αβ** to **21αβ**. The incorporation of a 4,6-*O*-butylidene group in **22αβ** would not only control the regioselectivity of butenolide ring formation in **23αβ** but also provide all the carbons required for the C6-*O*-butyl group in **3**, as long as regioselective reductive opening of the acetal could be achieved. Formation of the 4,6-*O*-butylidene group in **22αβ** could occur through the use of butanal (available from bio-butanol[48] and a recurring reagent in this strategy).

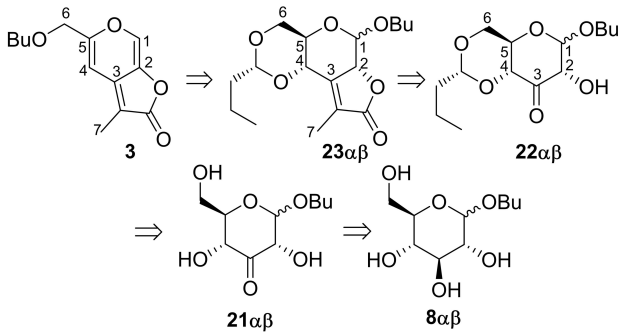
A repeat of the reported[39] oxidation of α-methoxy-glucose **24α** using pre-catalyst **9** (3 mol%) with BQ (**11**, 1.5 equivs.) at 50 °C in MeCN/water (10:1) was achieved to give **25α** in excellent yield (using NMR analysis, Scheme 5, Table 1, entry 1). Analogous transformation of **24α** to **25α** using a modified version of Minnard's protocol[36] was also achieved (entry 2).

Application of these protocols to the diastereomeric mixture of butoxylated glucose **8αβ** proceeded to give **21αβ** with good conversion but decreased NMR yields compared to **24α** (entries 3 and 4). Oxidation of **8αβ** to **21αβ** was also achieved using O_2 and **13** (30 mol%) giving the desired products in good isolated yield on up to a 6 gram scale (Table 1, entries 5 and 6). When these reaction conditions were used, chromatographic purification was straightforward although the α- and β-anomers of **21αβ** were inseparable in contrast to the xylose-derived compounds **10α** and **10β** (Scheme 2).

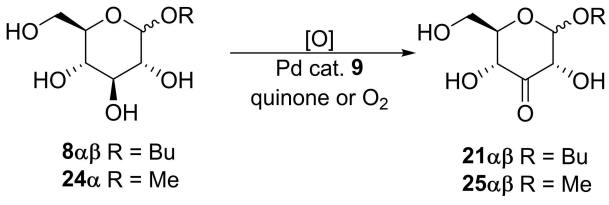
In an attempt to expand the range of quinones that can be used in this oxidation method, it was decided to test whether



Scheme 3. (A) The treatment of **15α** with MsOH led to the formation of unexpected product **17**; $TiCl_4$-^{i}Pr$_2$NEt treatment of **18α** gave the required **19**; (B) Completion of the synthesis of KAR1 **1** from **15αβ** inspired by the previous report of Meijler *et al.*[47] *Reagents & conditions:* (i) Ac_2O (4 eq.), C_5H_5N, rt., 30 min; **18αβ** = 95%; (ii) 1 M $TiCl_4$ in DCM (1.0 eq.), ^{i}Pr$_2$NEt (1.0 eq.), −30 °C, 30 min; **19** = 10% (unreacted starting material was recovered after purification); (iii) $(Ph_3P)_4Pd$ (50 mol%), 1,4-dioxane, 100 °C, 72 h, **2** = 77%; (iv) $POCl_3$ (15 eq.), DMF, 50 °C, 2 h, **20** = 79%; (v) $AlCl_3$ (3 eq.), *t*-$BuNH_2 \cdot BH_3$ (7 eq.), DCM, reflux, 10 min, **1** = 76%.



Scheme 4. Retrosynthetic analysis of **3**.



Scheme 5. Oxidation of glucose units into their corresponding C3 ketose.

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Table 1. Selective oxidation of glucose-derived monosaccharides.

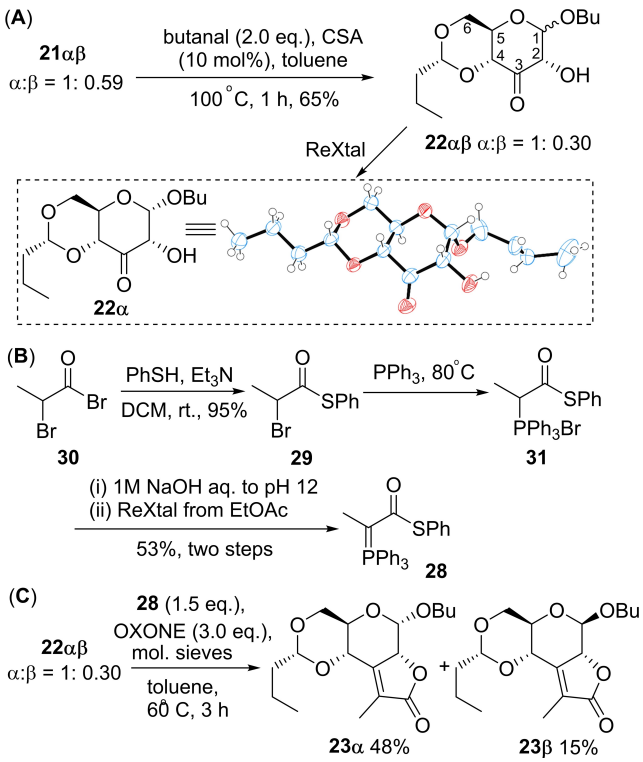
Entry	Substrate (α:β ratio)	Oxidant (eq.), Cat. **9**, [mol%]	T [°C], t [h], Conc. (M)	Conversion; NMR Yield
1[a]	**24α**	BQ **11** (1.5 eq.), 3	50, 0.5, 0.15	>99; 86% [88][39]
2[a]	**24α**	BQ **11** (1.5 eq.), 3	rt, 3, 0.36	>99; 94% [96][35]
3[a]	**8αβ** (1.3:1)	BQ **11** (1.5 eq.), 3	50, 0.5, 0.15	>99; 65% α:β = 1:1.3
4[a]	**8αβ** (1.2:1)	BQ **11** (1.5 eq.), 3	rt, 3, 0.36	>76; 72% α:β = 1:1
5[d]	**8αβ** (1.6:1)	O_2, **13**[c], 3	60, o.n.	>99; α:β = 1.6:1 Isolated 80%
6[e]	**8αβ** (1.5:1)	O_2, **13**[c], 3	60, o.n.	>99; α:β = 1.5:1 Isolated 69%
7[a,b]	**8αβ** (1.2:1)	MeOBQ **26** (2.5 eq.), 2.1	rt, 3, 0.36	56; n.d.
8[a,b]	**8αβ** (1.2:1)	MeOBQ **26** (2.5 eq.), 2.1	40, 3, 0.36	>99; 70% α:β = 1.1:1
9[a,b]	**8αβ** (1.2:1)	diMeOBQ **27** (2.5 eq.), 2.1	rt, 3, 0.36	42; n.d.
10[a,b]	**8αβ** (1.2:1)	diMeOBQ **27** (2.5 eq.), 2.1	40, 3, 0.36	68; n.d.

[a] Performed in deuterated solvents. [b] Quinones **26** and **27** were not fully dissolved; [c] additive used in 30 mol%; [d] carried out on 50 mg scale; [e] carried out on 6 g scale. See Figures S16–S23 for more detail.

methoxy-**26** or dimethoxy-**27** benzoquinone could replace BQ **11** (see Table S5 and Figures S24-S26 for analogous experiments with **26** or **27** in the xylose series). Quinones **26** and **27** were selected as they have both been prepared by depolymerisation of lignin.[49] In brief, both **26** and **27** functioned as the co-oxidant under modified Minnard conditions with the conversion of **8αβ** to **21αβ** using **26** proving particularly effective (entries 7 and 8). The poor solubility of the dimethoxybenzoquinone **27** in acetonitrile/water likely resulted in the lower conversion to product (entries 9 and 10).

Reaction of **21αβ** with butanal catalysed by (1*R*)-10-camphorsulfonic acid (CSA) gave the required **22αβ**, with recrystallisation of the anomeric mixture affording the pure α-anomer **22α**. X-ray crystallographic analysis of **22α** confirmed the stereochemistry (Scheme 6A, CCDC 2117934). A report by Shindo *et al.*[50] during their synthesis of KAR1 **1** involved a Cu(II)-catalysed transesterification-Wittig reaction. Application of this methodology to **22αβ** required the initial synthesis of the phosphorous ylide thiol ester **28**. This was achieved using a modified literature procedure, with thiol ester **29** formed on treatment of 2-bromopropionyl bromide (**30**) with thiophenol and Et_3N. Reaction of **29** with triphenylphosphine afforded the phosphonium salt **31** which was converted to **28** (Scheme 6B). Reaction of **22αβ** with **28** (1.5 equiv.), $Cu(OAc)_2$ (10 mol%) and Oxone® (3.0 equiv.) gave the desired C7-methyl butenolide **23αβ** with pure samples of the α- and β-anomers obtained following chromatographic purification (Scheme 6C).

Inspired by a report by Lemaire *et al.*,[51] reaction of **23α** or **23β** with a TMDS-$AlCl_3$ reducing system, gave **32α** or **32β** in isolated yields of 60% and 55% respectively (Scheme 7). Evidence in support of the assigned structure of **32α** came from HMBC analysis, with a correlation between H9 and C6 being observed (Figure S27).



Scheme 6. (A) The synthesis of 4,6-*O*-alkylidene acetal **22αβ** and the ORTEP representation of the crystal structure of **22α** (50% ellipsoid probability, CCDC 2117934); (B) The synthesis of the phosphorous ylide thiol ester **28**; (C) Installation of the butenolide ring to give **23α** and **23β**.

Completion of the synthesis of **3** required formation of the double bonds at the C1–C2 and C4–C5 positions. The diastereomeric mixture **32αβ** (obtained on combination of **32α** and **32β**) was converted to **33αβ** in a three step, one pot protocol. This involved initial reaction with $(CF_3SO_2)_2O$ in DCM/pyridine (10/1)

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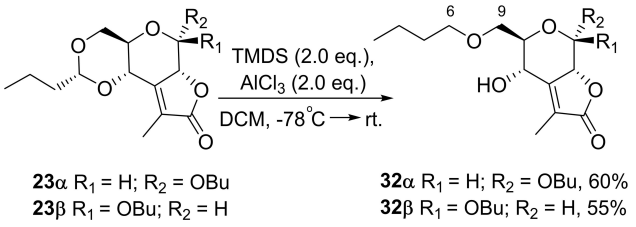
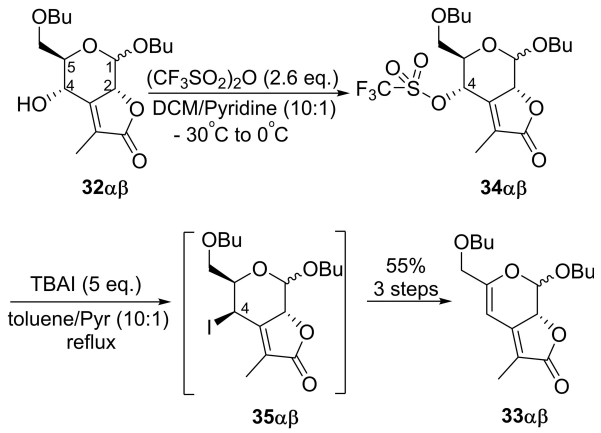


Scheme 7. Reductive opening of the 4,6-*O*-acetal ring in **23α and 23β** to form the required C6-OBu-containing **32α** and **32β** respectively using the TMDS-$AlCl_3$ system.[51]



Scheme 8. The three-step one pot reaction to convert **32αβ** to **33αβ**.

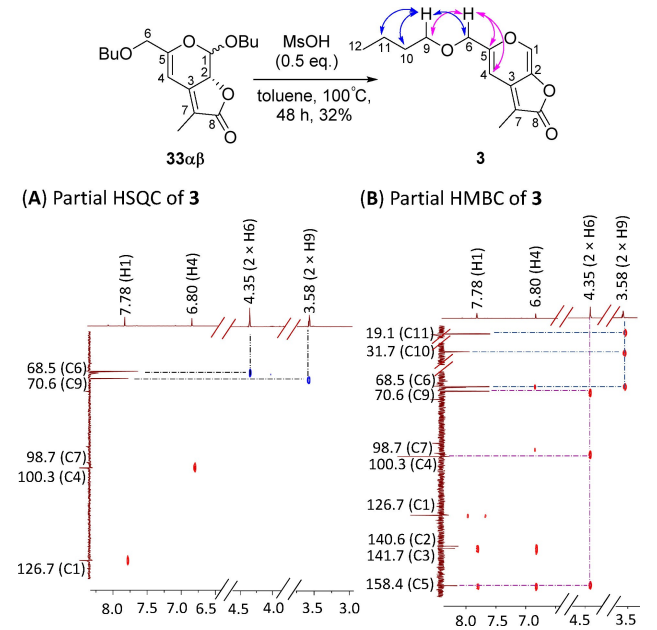


Figure 1. Acid conversion of **33αβ** to karrikin analogue **3**. (A) and (B) Regions of the HSQC and HMBC analysis of **3**: H6 shows correlations to C4, C5 and C9; while H9 shows correlations to C6, C10 and C11.

followed by removal of the solvent and subsequent treatment with TBAI in toluene/pyridine (10/1) at reflux overnight to give **33αβ** in 55% yield after purification (Scheme 8). This reaction is proposed to occur via initial formation of triflate **34αβ** with retention of configuration at C4, followed by conversion to the corresponding iodide **35αβ** (with inversion) and then elimination (Scheme S3).

Treatment of **33αβ** with a catalytic amount of MsOH (0.5 equiv.) in toluene gave the target molecule **3** with an isolated yield of 32% (Figure 1). NMR analysis of the prepared sample of **3** (Table S6) was consistent with the literature assignments of Flematti *et al.*[18] However reassignment of the signals in the ^{13}C NMR spectrum at 68.5 ppm (originally assigned to C9[18]) and 70.6 ppm (originally assigned to C6[18]) to 68.5 ppm (C6) and 70.6 ppm (C9) respectively was carried out based on detailed 2D NMR analysis (Figure 1A and Figure 1B, Figures S28–S30 and Table S6 for comparison with the literature and clarification regarding the more standard karrikin numbering system[18]). Overall, the Karrikin analogue **3** was prepared in an unoptimized 6 steps from glucose derivative **8αβ**.

Having identified relatively short reaction sequences to converted both xylose- and glucose-based starting materials to known bioactive compounds, it was decided to revisit the preparation of **7αβ** and **8αβ** from rice husks in an attempt to avoid the use of chromatography techniques in the early stages of the sequence. This was readily achieved in the case of the xylose-derived product **7αβ** which could be obtained in almost pure form as a mixture of diastereomers using solvent partitioning methods alone (Figure S31). Full conversion of the almost pure sample of **7αβ** from rice husks (no chromatography) to **10αβ** was achieved although additional aliquots of **9** were added after 2 and 4 hours (Figure S32). Obtaining a pure sample of **8αβ** direct from biomass proved more challenging with the only current solution of use on releatively large scale involving the use of dry column vacuum chromatography (DCVC). Work is ongoing to solve this challenging problem.

Conclusion

The elegant selective catalytic oxidation of monosaccharides report by Waymouth[35] and Minnaard[39] has been applied to substrates that are available as co-products from butanosolv processing of biomass (rice husks). Whilst the rapid access to these complex and highly useful synthetic intermediates opens up a wide range of applications, here subsequent modification of the resulting C3-ketone has enabled the synthesis of bioactive karrikins (KAR1 (**1**), KAR2 (**2**) and **3**). The reaction sequences presented are comparable or shorter in length to those reported in the literature[9–15,18] but several of the steps will require further optimisation if this approach is to be used in the synthesis of large quantities of these karrikins. X-ray crystallographic analysis and detailed NMR comparison with the reported chemicals shifts has confirmed the structures of the prepared compounds. As researchers continue to develop effective biorefinery strategies it is essential that applications for all of the possible product streams are consider. In this case, a possible use for a hemicellulose-derived fraction is identified

that compliments current thinking on the potential uses of butanosolv lignin.[29–35]

Experimental Section

General Experimental

All reagents were purchased from commercial sources and used without further purification unless otherwise stated. Anhydrous solvents (DCM, THF, toluene) were obtained from the Solvent Purification System MB SPS-800. ^{1}H NMR and ^{13}C NMR analysis was performed on a Bruker Avance II 400 MHz, a Bruker Avance III 500 MHz spectrometer equipped with a nitrogen cooled (Prodigy) BBO probe or a Bruker Avance III 700 MHz spectrometer equipped with a nitrogen cooled (Prodigy) TCI probe with the solvent peak used as the internal standard. Multiplicities are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet and the *J* couplings are reported in Hz. NMR spectra were processed using TopSpin 3.1 (PC version) or MestReNova. NMR peak assignments were confirmed using COSY (2D ^{1}H-^{1}H correlated spectroscopy), HMBC (2D ^{1}H-^{13}C heteronuclear multiple-bond correlation spectroscopy), and HSQC (2D ^{1}H-^{13}C heteronuclear single quantum coherence) if necessary. Column chromatography was performed using Davisil® silica (40–63 μm, 230–400 mesh). Thin layer chromatography was performed on pre-coated glass plates (Silica Gel 60A, Fluorochem) and visualised under UV light (254 nm) or by staining with $KMnO_4$. Differences in α anomer:β anomer ratios are noted after column purification. IR spectra were obtained on a Shimadzu IRAffinity-1 Fourier transform IR spectrophotometer as thin films. Analysis was carried out using Shimadzu IR solution v1.50 and only characteristic peaks are recorded. Mass spectrometry data were acquired by Mrs Caroline Horsburgh in the University of St Andrews School of Chemistry mass spectrometry service.

General Procedures

General procedure A for preparation of **10α/β** and **21αβ**: αβ-Butoxylated xylose or αβ-butoxylated glucose (**7αβ** or **8αβ**, 1.0 eq.) was dissolved in acetonitrile/water (10:1). The palladium pre-catalyst **9** (2.0 mol%) and 2,6-diisopropylphenol (**13**, 0.3 eq.) were then added and the reaction mixture was stirred vigorously at 60 °C under an oxygen balloon overnight. After cooling to room temperature, the solvent was removed *in vacuo*.

General procedure B for preparation of **15α/β**: Butoxylated 3-keto xylose **10α/β** (1.0 eq.) was dissolved in acetonitrile. Ethyl (triphenylphosphoranylidene)acetate (1.5 eq.) was then added, and the reaction mixture was heated at 75 °C for 72 h. After cooling to room temperature, the solvent was removed *in vacuo*.

General procedure C for preparation of **18α/β**: Acetic anhydride (4.0 eq.) was added to butenolide **15α/β** (1.0 eq.) in pyridine and the reaction mixture was stirred at room temperature for 30 mins. Methanol was then added, and the solution was stirred for 10 mins further. The solvent was removed *in vacuo*.

General procedure D for preparation of **32α/β**: To a solution of 4,6-O-butylidene acetal **23α/β** (1.0 eq.) in DCM was added $AlCl_3$ (2.0 eq.) and TMDS (2.0 eq.) at −78 °C. The reaction was then stirred at room temperature for 24 hours and the crude reaction mixture was washed with 3 M HCl and extracted with EtOAc (3 times). The combined organic layers were washed with brine, dried (Na_2SO_4) and then concentrated *in vacuo*.

General procedure E for preparation of **33α/β**: **32α/β** (1.0 eq.) was dissolved in anhydrous DCM/pyridine (10/1), and the solution was cooled to − 30 °C. Triflic anhydride (2.6 eq.) was added to the solution dropwise and the mixture was then stirred under N_2 with the reaction temperature kept under 0 °C. After 40 mins, the solvent was removed quickly *in vacuo*. The crude triflate **34α/β** was dissolved in anhydrous toluene/pyridine (10/1) and *tetra*-butylammonium iodide (5 eq.) was added. The mixture was heated at 100 °C for 4 h after which the solution was concentrated *in vacuo*, diluted with Et_2O, washed with sat. $Na_2S_2O_4$ solution (once), water (once), dried (Na_2SO_4), filtered and concentrated *in vacuo*.

Synthesis of Kar1 (1) and Kar2 (2)

Synthesis of **10α** and **10β**: General procedure A was used with **7αβ** (6.0 g, 29.00 mmol, 1.0 eq., α/β = 1/0.73), Pd. pre-catalyst **9** (434.0 mg, 0.58 mmol, 2.0 mol%) and 2,6-diisopropylphenol (**13**, 1.6 g, 8.73 mmol, 0.3 eq.) in MeCN/H_2O (50 mL/5 mL). Purification was achieved by column chromatography eluting with DCM/methanol (70/1). The pure α-anomer **10α** was obtained as a light yellow solid (2.4 g, 11.60 mmol, 40%) and the pure β-anomer **10β** was obtained as a light yellow oil (590.0 mg, 2.90 mmol, 10%). Recrystallisation of the pure α-anomer **10α** by slow evaporation from hexane/EtOAc/Acetone (8/1/1) produced crystals which were subjected to X-ray crystallographic analysis (CCDC 2117933).

10α: m.p: 85–86 °C. $[\alpha]_D^{20} = +102.30$ (*c* = 1.04 in $CHCl_3$); IR (FTIR) ν_{max} 3327, 2911, 1734, 1070 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_9H_{16}O_5Na$ 227.0895, $[M+Na]^+$ found 227.0887; ^{1}H NMR (700 MHz, MeOD) δ 5.12 (d, *J* = 4.2 Hz, 1H, H1), 4.41–4.39 (m, 1H, H2), 4.39–4.36 (m, 1H, H4), 4.02 (dd, *J* = 10.3, 7.9 Hz, 1H, H5), 3.75–3.68 (m, 1H, 1×H6), 3.64 (t, *J* = 10.4 Hz, 1H, 1×H5), 3.49–3.46 (m, 1H, 1×H6), 1.67–1.51 (m, 2H, 2×H7), 1.47–1.35 (m, 2H, 2×H8), 0.94 (t, *J* = 7.4 Hz, 3H, 3×H9). ^{13}C NMR (175 MHz, MeOD) δ 205.3 (C3), 101.9 (C1), 74.9 (C2), 71.8 (C4), 67.8 (C6), 64.0 (C5), 31.2 (C7), 18.9 (C8), 12.8 (C9).

10β: $[\alpha]_D^{20} = -32.30$ (*c* = 1.01 in $CHCl_3$); IR (FTIR) ν_{max} 3429, 2902, 1732, 1051 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_9H_{16}O_5Na$ 227.0895, $[M+Na]^+$ found 227.0886; ^{1}H NMR (700 MHz, MeOD) δ 4.40–4.35 (m, 1H, H4), 4.31 (d, *J* = 7.7 Hz, 1H, H1), 4.22 (dd, *J* = 11.1, 7.6 Hz, 1H, 1×H5), 4.12 (dd, *J* = 7.7, 1.7 Hz, 1H, H2), 3.90 (dt, *J* = 9.6, 6.6 Hz, 1H, 1×H6), 3.62 (dt, *J* = 9.6, 6.6 Hz, 1H, 1×H6), 3.28 (t, *J* = 10.9 Hz, 1H, 1×H5), 1.68–1.58 (m, 2H, 2×H7), 1.49–1.41 (m, 2H, 2×H8), 0.96 (t, *J* = 7.3 Hz, 3×H9). ^{13}C NMR (175 MHz, MeOD) δ 205.2 (C3), 105.5 (C1), 77.0 (C2), 72.0 (C4), 69.4 (C6), 65.7 (C5), 31.5 (C7), 18.8 (C8), 12.8 (C9).

Synthesis of **14** and **15**: General procedure B was used with **10α** (2.0 g, 9.80 mmol, 1.0 eq.) and $Ph_3P{=}CHCOOEt$ (5.1 g, 14.7 mmol, 1.5 eq.) in MeCN (25 mL). Purification was achieved by column chromatography eluting in petroleum/ether acetate (3/1 to 2/1) to give **14α** (1.2 g, 5.40 mmol, 55%) as a light yellow wax and **15α** (1.1 g, 9.00 mmol, 32%) as a colorless oil.

14α: $[\alpha]_D^{20} = -43.10$ (*c* = 1.34 in $CHCl_3$); IR (FTIR) ν_{max} 3466, 2957, 1760, 1120, 1040 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{11}H_{16}O_5Na$ 251.0895, $[M+Na]^+$ found 251.0888; ^{1}H NMR (500 MHz, MeOD) δ 6.02 (t, *J* = 1.9, 1H, H6), 5.03 (d, *J* = 9 Hz, 1H, H1), 4.63 (dd, *J* = 9, 1.4 Hz, 1H, H2), 4.23–4.15 (m, 1H, 1×H5), 3.69 (dt, *J* = 9.8, 6.9 Hz, 1H, 1×H8), 3.51 (dt, *J* = 9.8, 6.9 Hz, 1H, 1×H8), 3.45–3.34 (m, 1H, 1×H5), 1.69–1.53 (m, 2H, 2×H9), 1.46–1.35 (m, 2H, 2×H10), 0.95 (t, *J* = 7.4 Hz, 3H, 3×H11). ^{13}C NMR (175 MHz, MeOD) δ 173.4 (C7), 171.5 (C3), 111.8 (C6), 99.0 (C1), 76.7 (C4), 69.1 (C2), 68.1 (C8), 62.4 (C5), 31.1 (C9), 19.0 (C10), 12.8 (C11).

15α: $[\alpha]_D^{20} = +191.00$ (*c* = 0.83 in $CHCl_3$); IR (FTIR) ν_{max} 3368, 2933, 1753, 1238, 1030 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{11}H_{16}O_5Na$

251.0895, $[M+Na]^+$ found 251.0887; ^{1}H NMR (700 MHz, MeOD) δ 5.95 (t, J=1.9 Hz, 1H, H6), 5.23 (d, J=4.4 Hz, 1H, H1), 5.01 (dd, J=7, 1.5 Hz, 1H, H2), 4.64 (dd, J=9.9, 7.5 Hz, 1H, H4), 3.99–3.86 (m, 1H, 1×H5), 3.70 (dt, J=9.7, 6.4 Hz, 1H, 1×H8), 3.48 (dt, J=9.7, 6.4 Hz, 1H, 1×H8), 3.43 (t, J=10.1 Hz, 1H, 1×H5), 1.58–1.51 (m, 2H, 2×H9), 1.41–1.34 (m, 2H, 2×H10), 0.93 (t, J=7.4 Hz, 3H, 2×H11). ^{13}C NMR (175 MHz, MeOD) δ 174.2 (C7), 169.8 (C3), 111.0 (C6), 96.6 (C1), 78.7 (C2), 67.8 (C8), 65.7 (C4), 63.3 (C5), 31.1 (C9), 18.9 (C10), 12.7 (C11).

General procedure B was used with **10β** (523.0 mg, 2.56 mmol, 1.0 eq.) and Ph_3P=CHCOOEt (1.3 g, 3.84 mmol, 1.5 eq.) in MeCN (6 mL) were used. Purification was achieved by column chromatography eluting in petroleum/ether acetate (3/1 to 2/1) to give **14β** (251.0 mg, 1.10 mmol, 43%) as a light yellow oil and **15β** (234.0 mg, 1.02 mmol, 40%) as a light yellow oil.

14β: $[\alpha]_D^{20}=-281.90$ (c=0.37 in $CHCl_3$); IR (FTIR) ν_{max} 3454, 2958, 1730, 1138, 1058 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{11}H_{16}O_5Na$ 251.0895, $[M+Na]^+$ found 251.0886; ^{1}H NMR (500 MHz, MeOD) δ 6.04 (t, J=1.9 Hz, 1H, H6), 5.02 (dd, J=10.4, 6.9 Hz, 1H, H4), (dd, J=10.4, 6.9 Hz, 1H, 1×H5), 4.33 (dd, J=7.0, 1.8 Hz, 1H, H2), 4.16 (d, J=7.0 Hz, 1H, H1), 3.89 (dt, J=9.6, 6.7 Hz, 1H, 1×H8), 3.61 (dt, J=9.6, 6.5 Hz, 1H, 1×H8), 3.12 (t, J=10.2 Hz, 1H, 1×H5), 1.73–1.55 (m, 2H, 2×H9), 1.48–1.42 (m, 2H, 2×H10), 0.96 (t, J=7.4 Hz, 3H, 3×H11); ^{13}C NMR (125 MHz, MeOD) δ 173.4 (C7), 172.2 (C3), 112.0 (C6), 106.4 (C1), 77.0 (C4), 70.9 (C2), 69.7 (C8), 66.9 (C5), 31.5 (C9), 18.8 (C10), 12.8 (C11).

15β: $[\alpha]_D^{20}=-16.00$ (c=0.40 in $CHCl_3$); IR (FTIR) ν_{max} 3393, 2959, 1736, 1143, 1058 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{11}H_{16}O_5Na$ 251.0895, $[M+Na]^+$ found 251.0887; ^{1}H NMR (700 MHz, MeOD) δ 6.00 (t, J=1.9 Hz, 1H, H6), 4.70 (dd, J=7.2, 1.7 Hz, 1H, H2), 4.67–4.58 (m, 1H, H4), 4.27–4.16 (m, 2H, H1 and 1×H5), 3.89 (dt, J=9.6, 6.5 Hz, 1H, 1×H8), 3.60 (dt, J=9.6, 6.5 Hz, 1H, 1×H8), 3.14 (t, J=10.3 Hz, 1H, 1×H5), 1.66–1.57 (m, 2H, 2×H9), 1.48–1.42 (m, 2H, 2×H10), 0.96 (t, J=7.4 Hz, 3H, 3×H11). ^{13}C NMR (175 MHz, MeOD) δ 173.4 (C7), 171.2 (C3), 111.5 (C6), 105.2 (C1), 81.2 (C2), 69.2 (C8), 68.9 (C5), 66.2 (C4), 31.4 (C9), 18.8 (C10), 12.7 (C11).

Synthesis of **18**: General procedure C was used with **15α** (1.0 g, 4.40 mmol, 1.0 eq.) and acetic anhydride (1.66 mL, 17.50 mmol, 4.0 eq.) in pyridine (15.0 mL). Purification was achieved by column chromatography eluting in petroleum/ether acetate (3/1 to 2/1) to give **18α** (1.1 g, 4.05 mmol, 92%) as a white wax.

18α: $[\alpha]_D^{20}=+230.30$ (c=0.35 in $CHCl_3$); IR (FTIR) ν_{max} 3406, 2954, 1739, 1163, 1026 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{13}H_{18}O_6Na$ 293.1001, $[M+Na]^+$ found 293.0985; ^{1}H NMR (500 MHz, MeOD) δ 6.00 (t, J=1.7 Hz, 1H, H6), 5.79–5.64 (m, 1H, H4), 5.29 (d, J=4.4 Hz, 1H, H1), 5.11 (dd, J=4.4, 1.8 Hz, 1H, H2), 4.06 (dd, J=10.3, 7.4 Hz, 1H, 1×H5), 3.71 (dt, J=9.7, 6.4 Hz, 1H, 1×H8), 3.60–3.42 (m, 2H, 1×H5 and 1×H8), 2.18 (s, 3H, 3×H13), 1.68–1.49 (m, 2H, 2×H9), 1.43–1.30 (m, 2H, 2×H10), 0.93 (t, J=7.39 Hz, 3H, 3×H11). ^{13}C NMR (125 MHz, MeOD) δ 173.3 (C7), 169.7 (C12), 164.0 (C3), 112.0 (C6), 96.6 (C1), 78.5 (C2), 68.1 (C8), 66.7 (C4), 60.1 (C5), 31.1 (C9), 19.1 (C10), 18.9 (C13), 12.8 (C11).

General procedure C was used with **15β** (100.0 mg, 0.44 mmol, 1.0 eq.) and acetic anhydride (0.17 mL, 1.75 mmol, 4.0 eq.) in pyridine (2 mL). Purification was achieved by column chromatography eluting with petroleum/ether acetate (3/1 to 2/1) to give **18β** (113.0 mg, 0.42 mmol, 95%) as a colorless oil.

18β: $[\alpha]_D^{20}=+5.80$ (c=0.43 in $CHCl_3$); IR (FTIR) ν_{max} 3410, 2935, 1738, 1159, 1059 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{13}H_{18}O_6Na$ 293.1001, $[M+Na]^+$ found 293.0991; ^{1}H NMR (400 MHz, MeOD) δ 6.07 (t, J=1.9 Hz, 1H, H6), 5.72–5.66 (m, 1H, H4), 4.80 (dd, J=7.1, 1.8 Hz, 1H, H2), 4.37 (dd, J=10.6, 7.0 Hz, 1H, 1×H5), 4.30 (d, J=7.2 Hz, 1H, H1), 3.90 (dt, J=9.6, 6.5 Hz, 1H, 1×H8), 3.62 (dt, J=9.6, 6.5 Hz, 1H, 1×H8), 3.36–3.25 (m, H, 1×H5), 2.18 (s, 3H, 3×H13), 1.70–1.56 (m, 2H, 2×H9), 1.51–1.39 (m, 2H, 2×H10), 0.97 (t, J=7.4 Hz, 3H, 3×H11). ^{13}C NMR (125 MHz, MeOD) δ 172.6 (C7), 169.6 (C12), 165.4 (C3), 112.5 (C6), 105.0 (C1), 81.0 (C2), 69.3 (C8), 67.2 (C4), 65.7 (C5), 31.4 (C9), 19.0 (C10), 18.8 (C13), 12.7 (C11).

Synthesis of **19**: $TiCl_4$ (3.14 mmol, 3.14 mL of 1 M solution in DCM) was added dropwise to a solution of **18αβ** (850.0 mg, 3.14 mmol, 1.0 eq., α/β=1/0.54) in dry DCM (40 mL) at–30 °C. The solution was stirred for 30 min followed by the addition of ^{i}Pr$_2$NEt (0.52 mL, 3.14 mmol, 1.0 eq.). The reaction was then stirred for an additional 30 mins and quenched by addition of saturated $NaHCO_3$ solution (20 mL). The reaction was partitioned, and the aqueous layer was extracted with DCM (3×20 mL). The combined organic layers were dried (Na_2SO_4), and solvent was removed under reduced pressure. Purification was achieved by column chromatography eluting with petroleum/ether acetate (5/1 to 4/1) to give **19** (58.0 mg, 0.31 mmol, 10%) as a yellow oil. $[\alpha]_D^{20}=+3.0$ (c=0.52 in $CHCl_3$); IR (FTIR) ν_{max} 1716, 1225, 933 cm^{-1}; HRMS (ESI$^+$) *m/z* clacd for $C_9H_9O_5$ 197.0450, $[M+H]^+$ found 197.0749; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J=1.8 Hz, 1H, H1), 5.95 (dd, J=1.9, 0.8 Hz, 1H, H6), 5.86 (t, J=4.0, Hz, 1H, H4), 4.36 (dd, J=12.6, 4.1 Hz, 1H, H5), 4.22 (dd, J=12.6, 3.5 Hz, 1H, H5), 2.16 (s, 3H, 3×H9). Spectral data were consistent with those previously reported.[9]

Synthesis of KAR2 (**2**): $(Ph_3P)_4Pd$ (161.0 mg, 0.14 mmol, 50 mol%) was added to **19** (55.0 mg, 0.28 mmol) in 1,4-dioxane (3 mL) and the resulting solution was heated at 100 °C for 72 h under argon. The reaction mixture was concentrated under reduced pressure and purification was achieved by column chromatography eluting with petroleum/ether acetate (1/3) to give **2** (30.0 mg, 0.22 mmol, 77%) as a tan solid. m.p: 109–111 °C (lit.[9] 109–110 °C); IR (FTIR) ν_{max} 2910, 1780, 1590, 810 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_7H_4O_3Na$ 159.0058, $[M+Na]^+$ found 159.0049; ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.95 (d, J=1.4 Hz, 1H, H1), 7.77 (d, J=5.4 Hz, 1H, H5), 6.93 (d, J=5.4 Hz, 1H, H4), 5.42 (d, J=1.4 Hz, 1H, H6). ^{13}C NMR (125 MHz, Acetone-d_6) δ170.0 (C7), 150.2 (C5), 145.7 (C3), 143.1 (C2), 128.5 (C1), 104.6 (C4), 89.8 (C6). Spectral data and melting point were consistent with those previously reported (see Table S3).[9]

Synthesis of **20**: $POCl_3$ (0.25 mL, 2.76 mmol, 15 eq.) was added dropwise to **2** (25.0 mg, 0.18 mmol, 1.0 eq.) in dry DMF (2 mL) and the solution was stirred at 50 °C for 2 hours. The reaction mixture was diluted with DCM (5 mL) and poured into a solution of saturated aqueous $NaHCO_3$ (5 mL). The reaction mixture was partitioned and the aqueous layer was extracted with DCM (3×10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification was achieved by column chromatography eluting with petroleum/ether acetate (3/1 to 2/1) to give **20** (24.0 mg, 0.14 mmol, 79%) as a tan solid. m.p: 208–210 °C. (lit.[9] 216–217.5 °C); IR (FTIR) ν_{max} 3109, 1771, 1755, 1660, 1225, 978 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_8H_4O_4Na$ 187.0007, $[M+Na]^+$ found 186.9997; ^{1}H NMR (500 MHz, Acetone-d_6) δ 9.83 (s, 1H, C<u>H</u>O), 8.63 (d, J=0.6 Hz, 1H, H1), 8.43 (d, J=5.1 Hz, 1H, H5), 7.75 (dd, J=5.1, 0.6 Hz, 1H, H4). ^{13}C NMR (125 MHz, Acetone-d_6) δ 184.2 (<u>C</u>HO), 167.8 (C7), 155.8 (C5), 146.9 (C3), 142.8 (C2), 135.1 (C1), 107.2 (C4), 99.5 (C6). Spectral data were consistent with those previously reported.[9]

Synthesis of KAR1 (**1**): $AlCl_3$ (49.0 mg, 0.36 mmol, 3.0 eq.) and tBuNH$_2$·BH$_3$ (73.0 mg, 0.84 mmol, 7.0 eq.) were added to a solution of **20** (20.0 mg, 0.12 mmol, 1.0 eq.) in dry DCM (2 mL) and the reaction mixture was refluxed for 10 mins. The reaction mixture was concentrated under reduced pressure. Purification was achieved by column chromatography eluting with petroleum/ether acetate (5/1) to give **1** (14.0 mg, 0.09 mmol, 76%) as a white solid. m.p: 117–121 °C (lit.[9] 118–120 °C); IR (FTIR) ν_{max} 3084, 1732, 1666, 1226, 981 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_8H_6O_3Na$ 173.0215, [M+

Na]$^+$ found 173.0207; ^{1}H NMR (700 MHz, Acetone-*d6*) δ 7.77 (s, 1H, H1), 7.62 (dt, *J* = 5.6, 1.5 Hz, 1H, H5), 6.79 (dt, *J* = 5.5, 2.0 Hz, 1H, H4), 1.86 (s, 3H, C$\underline{H}_3$). ^{13}C NMR (125 MHz, Acetone-*d6*) δ 170.3 (C7), 148.9 (C5), 142.2 (C2), 139.7 (C3), 127.2 (C1), 103.2 (C4), 99.1 (C6), 6.7 ($\underline{C}H_3$). Spectral data were consistent with those previously reported by Meijler *et. Al* (see Table S4).[47]

Synthesis of Karrikin analogue 3

Synthesis of **21 αβ**: General procedure A was used with **8 αβ** (6.0 g, 25.4 mol, 1.0 eq., α:β = 1.5:1) Pd. pre-catalyst **9** (379 mg, 0.51 mmol, 2.0 mol%) and 2,6-diisopropylphenol (**13** 1.36 g, 7.6 mmol, 0.3 eq.). Purification was achieved by column chromatography eluting with DCM/methanol (30/1) to give **21 αβ** as an anomeric mixture as a red oil (4.1 g, 17.5 mmol, 69%, α:β = 1.5:1). IR (FTIR) ν_{max} 3207, 1730, 1020 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{10}H_{18}O_6Na$ 257.1001, [M + Na]$^+$ found 257.0990; Major α-anomer: ^{1}H NMR (500 MHz, MeOD) δ 5.16 (d, *J* = 4.3 Hz, 1H, H1), 4.42 (dd, *J* = 4.4, 1.5 Hz, 1H, H2), 4.25 (d, *J* = 9.8 Hz, 1H, H4), 3.90–3.86 (m, 1H, 1×H6), 3.84–3.79 (m, 1H, 1×H6), 3.75 (dt, *J* = 9.7, 6.8 Hz, 1H, 1×H7), 3.73–3.68 (m, 1H, H5), 3.49 (dt, *J* = 9.7, 6.3 Hz, 1H, 1×H7), 1.73–1.53 (m, 2H, 2×H8), 1.51–1.32 (m, 2H, 2×H9), 0.95 (t, J = 7.4 Hz, 3H, 3×H10). ^{13}C NMR (125 MHz, MeOD) δ 205.7 (C3), 101.3 (C1), 75.4 (C5), 74.7 (C2), 72.0 (C4), 67.7 (C7), 61.1 (C6), 32.0 (C8), 18.8 (C9), 12.8 (C10). Minor β-anomer: ^{1}H NMR (500 MHz, MeOD) 4.37 (d, *J* = 7.9 Hz, 1H, H1), 4.25 (d, *J* = 9.8 Hz, 1H, H4), 4.14 (d, *J* = 7.9 Hz, 1H, H2), 4.02–3.93 (m, 3H, 1×H7 and 2×H6), 3.62 (dt, *J* = 9.6, 6.7 Hz, 1H, 1×H7), 3.35–3.31 (m, 1H, H5), 1.73–1.53 (m, 2H, 2×H8), 1.51–1.32 (m, 2H, 2×H9), 0.95 (t, *J* = 7.4 Hz, 3H, 3×H10). ^{13}C NMR (125 MHz, MeOD) δ 205.7 (C3), 104.4 (C1), 76.9 (C5), 76.8 (C2), 72.3 (C4), 69.4 (C7), 61.1 (C6), 32.0 (C8), 18.8 (C9), 12.8 (C10).

Synthesis of **22 αβ**: **21 αβ** (2.0 g, 8.50 mmol, 1.0 eq., α/β = 1/0.59), butyraldehyde (1.2 g, 17.00 mmol, 2.0 eq.) and (1*R*)-10-camphorsulfonic acid (394.0 mg, 1.70 mmol, 10 mol%) were dissolved in toluene (50 mL) in a sealed tube. The reaction mixture was heated at 100 °C for 1 hour. The solvent was concentrated *in vacuo*, and toluene (50 mL) and butyraldehyde (0.6 g, 8.50 mmol, 1.0 eq.) were added. The solution was again heated at 100 °C for 1 hour. The volatiles were evaporated. Purification was achieved by column chromatography eluting in petroleum/ether acetate (4/1 to 3/1) to give an anomeric mixture of **22 αβ** (1.6 g, 5.50 mmol, 65%, α/β = 1/0.30) as a white solid. Anomeric mixture **22 αβ** was recrystallised in hexane/ether acetate (50/1) to give pure α anomer **22 α** as a white solid. Recrystallisation of pure α anomer **22 α** from slow evaporation in Hexane/EtOAc/Acetone (8/1/1) produced crystals which were subjected to X-ray crystallographic analysis (CCDC 2117934).

22 α: IR (FTIR) ν_{max} 2962, 1741, 1070, 993 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{14}H_{24}O_6Na$, 311.1470, found 311.1456; Major α anomer: ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.21 (d, *J* = 4.4 Hz, 1H, H1), 4.64–4.60 (m, 1H, H7), 4.37–4.33 (m, 1H, H2), 4.25 (dd, *J* = 10.4, 9 Hz, 1H, 1×H6), 4.13 (dd, *J* = 9.7, 1.6 Hz, 1H, H4), 3.96–3.90 (m, 1H, H5), 3.75–3.69 (m, 2H, 2×H11), 3.49 (dt, *J* = 9.6, 6.5 Hz, 1H, 1×H6), 1.81–1.64 (m, 2H, 2×H8), 1.62–1.54 (m, 2H, 2×H12), 1.51–1.41 (m, 2H, 2×H9), 1.39–1.32 (m, 2H, 2×H13), 1.01–0.87 (m, 6H, 3×H14, 3×H10). ^{13}C NMR (175 MHz, $CDCl_3$) δ198.9 (C3), 102.8 (C7), 102.4 (C1), 82.0 (C4), 75.0 (C2), 69.1 (C11), 68.8 (C6), 66.2 (C5), 36.0 (C8), 31.3 (C12), 19.2 (C9), 17.4 (C13), 13.8 (C14), 13.8 (C10).

22 β: ^{1}H NMR (700 MHz, $CDCl_3$) δ 4.64–4.60 (m, 1H, H7), 4.44 (d, *J* = 7.4 Hz, H1), 4.37–4.33 (m, 1H, H11), 4.21 (dd, *J* = 9.8, 2.0 Hz, 1H, H4), 4.16 (dd, *J* = 7.4, 1.9 Hz, 1H, H2), 3.96–3.90 (m, 1H, 1×H6), 3.75–3.69 (m, 1H, H11), 3.66 (dt, *J* = 9.4, 6.7 Hz, 1H, 1×H6), 3.43 (td, *J* = 9.9, 4.9 Hz, 1H, H5), 1.81–1.64 (m, 4H, 2×H8, 2×H12), 1.51–1.41 (m, 2H, 2×H9), 1.39–1.32 (m, 2H, 2×H13), 1.01–0.87 (m, 6H, 3×H14, 3×H10). ^{13}C NMR (175 MHz, $CDCl_3$) δ 199.2 (C3), 106.1 (C7), 102.8 (C1), 81.4 (C4), 77.3 (C2), 70.7 (C6), 68.8 (C11), 67.2 (C5), 36.0 (C8), 31.6 (C12), 19.1 (C9), 17.4 (C13), 13.8 (C14), 13.8 (C10).

Synthesis of **23 α** and **23 β**: To a solution of **22 αβ** (1.5 g, 5.20 mmol, 1.0 eq., α/β = 1/0.30) in toluene (20 mL) was added $Cu(OAc)_2$ (89.0 mg, 0.52 mmol, 10 mol%), phosphorous ylide (**28**, 3.3 g, 7.80 mmol, 1.5 eq., see SI for procedures) and Oxone® (4.8 g, 15.60 mmol, 3.0 eq.). The mixture was heated at 60 °C under air for 3 hours. The resulting mixture was filtered through celite, and the solvent was evaporated under reduced pressure. Purification was achieved by column chromatography eluting in petroleum ether/ethyl acetate (15/1 to 10/1) to give pure α anomer **23 α** (815.0 mg, 2.50 mmol, 48%) as a yellow oil and pure β anomer **23 β** (254.0 mg, 0.78 mmol, 15%) as a yellow oil.

23 α: $[\alpha]_D^{20} = +113.8$ (*c* = 0.55 in $CHCl_3$); IR (FTIR) ν_{max} 3030, 1740, 1049 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{17}H_{26}O_6Na$ 349.1627, [M + Na]$^+$, found 349.1611; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.19 (dd, *J* = 7, 0.5 Hz, 1H, H1), 4.93–4.60 (m, 2H, H2 and H9), 4.28–4.23 (m, 1H, H4), 4.20 (dd, *J* = 10.1, 4.4 Hz, 1H, H6), 3.79–3.71 (m, 1H, H5), 3.71–3.62 (m, 2H, 2×H13), 3.48 (dt, *J* = 9.7, 6.6 Hz, 1H, H6), 2.02 (t, *J* = 1.8 Hz, 3H, C$\underline{H}_3$), 1.75–1.65 (m, 2H, 2×H10), 1.56 (ddt, *J* = 8.9, 7.8, 6.4 Hz, 2H, 2×H14), 1.52–1.42 (m, 2H, 2×H11), 1.40–1.29 (m, 2H, 2×H15), 0.98 (t, *J* = 7.4 Hz, 3H, 3×H12), 0.91 (t, *J* = 7.4 Hz, 3H, 3×H16). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4 (C8), 150.3 (C3), 121.3 (C7), 102.9 (C9), 98.0 (C1), 78.3 (C4), 76.5 (C2), 69.1 (C6), 68.9 (C13), 65.2 (C5), 36.2 (C10), 31.3 (C14), 19.2 (C15), 17.4 (C11), 14.0 (C12), 14.0 (C16), 8.8 ($\underline{C}H_3$).

23 β: $[\alpha]_D^{20} = -3.80$ (*c* = 0.42 in $CHCl_3$); IR (FTIR) ν_{max} 3046, 1796, 1051 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{17}H_{26}O_6Na$ 349.1627, [M + Na]$^+$, found 349.1619; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.55 (s, 1H, H1), 5.06 (dq, *J* = 9.2, 2.0 Hz, 1H, H2), 4.57 (t, *J* = 5.2 Hz, 1H, H9), 4.20 (dd, *J* = 10.5, 5.0 Hz, 1H, H6), 3.89 (dt, *J* = 9.8, 4.9 Hz, 1H, H5), 3.80 (dt, *J* = 9.5, 6.8 Hz, 1H, H13), 3.61–3.48 (m, 2H, H13 and H6), 3.30 (t, *J* = 9.3 Hz, 1H, H4), 1.93 (d, *J* = 2.0 Hz, 3H, C$\underline{H}_3$), 1.72–1.60 (m, 4H, 2×H14 and 2×H10), 1.52–1.35 (m, 4H, 2×H15 and 2×H11), 1.00–0.92 (m, 6H, 3×H16 and 3×H12). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5 (C8), 151.2 (C3), 124.0 (C7), 102.4 (C9), 94.0 (C1), 83.7 (C4), 78.3 (C2), 68.2 (C6), 68.2 (C13), 62.2 (C5), 36.1 (C10), 31.5 (C14), 19.3 (C11), 17.4 (C15), 13.9 (C12), 13.8 (C16), 8.9 ($\underline{C}H_3$).

Synthesis of **32**: General procedure D was used with **23 α** (800.0 mg, 2.50 mmol, 1.0 eq.), $AlCl_3$ (654.0 mg, 5.00 mol, 2.0 eq.), TMDS (660.0 mg, 5.00 mol, 2.0 eq.) in 20.0 mL DCM. Purification was achieved by column chromatography eluting in petroleum/ether acetate (6/1 to 4/1) to give **32 α** (483.0 mg, 1.50 mmol, 60%) as a colorless oil.

32 α: $[\alpha]_D^{20} = +90.6$ (*c* = 0.53 in $CHCl_3$); IR (FTIR) ν_{max} 2930, 1736, 1682, 1277, 1047 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{17}H_{28}O_6Na$ 351.1783, [M + Na]$^+$, found 351.1772; ^{1}H NMR (500 MHz, MeOD) δ 5.20 (d, *J* = 4.4 Hz, 1H, H1), 4.82 (ddd, *J* = 4.4, 1.8, 0.7 Hz, 1H, H2), 4.56 (dq, *J* = 9.2, 1.9 Hz, 1H, H4), 3.78–3.75 (m, 2H, 2×H6), 3.74–3.68 (m, 2H, H5, H13), 3.60–3.52 (m, 2H, 2×H9), 3.49 (dt, *J* = 9.7, 6.4 Hz, 1H, H13), 2.02 (t, *J* = 1.8 Hz, 3H, CH_3), 1.65–1.50 (m, 4H, 2×H10 and 2×H14), 1.48–1.27 (m, 4H, 2×H11 and 2×H15), 0.98–0.91 (m, 6H, 2×H16 and 2×H12). ^{13}C NMR (125 MHz, MeOD) δ 175.9 (C8), 157.3 (C3), 121.1 (C7), 96.6 (C1), 77.4 (C2), 73.4 (C5), 71.1 (C9), 69.2 (C6), 67.81 (C13), 67.3 (C4), 31.5 (C14), 31.1 (C10), 19.0 (C15), 19.0 (C11), 12.9 (C16), 12.9 (C12), 7.5 ($\underline{C}H_3$).

General procedure D was used with **23 β** (200.0 mg, 0.63 mmol, 1.0 eq.), $AlCl_3$ (163.0 mg, 1.26 mol, 2.0 eq.), TMDS (169.0 mg, 1.26 mol, 2.0 eq.) in 8.0 mL DCM. Purification was achieved by column chromatography eluting in petroleum/ether acetate (6/1 to 4/1) to give **32 β** (113.0 mg, 0.35 mmol, 55%) as a colorless oil.

32β: $[\alpha]_D^{20} = -43.60$ ($c = 0.44$ in $CHCl_3$); IR (FTIR) ν_{max} 2931, 1756, 1680, 1251, 1018 cm^{-1}; HRMS (ESI^+) *m/z* calculated for $C_{17}H_{28}O_6Na$ 351.1783, $[M+Na]^+$, found 351.1773; ^1H NMR (500 MHz, $CDCl_3$) δ 5.57 (s, 1H, H1), 4.97 (dd, $J = 8.5$, 2.1 Hz, 1H, H2), 3.93 (dt, $J = 9.7$, 4.2 Hz, 1H, H4), 3.85–3.77 (m, 2H, H6 and H13), 3.70 (dd, $J = 10.4$, 4.2 Hz, 1H, H6), 3.64 (dd, $J = 9.7$, 8.5 Hz, 1H, H5), 3.56 (dt, $J = 9.5$, 6.5 Hz, 2H, H13 and H9), 3.49 (dt, $J = 9.4$, 6.7 Hz, 1H, H9), 1.91 (d, $J = 2.0$ Hz, 3H, $C\underline{H}_3$), 1.70–1.54 (m, 4H, 2×H14 and 2×H10), 1.48–1.34 (m, 4H, 2×H15 and 2×H11), 0.98–0.91 (m, 6H, 3×H12 and 3×H16). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7 (C8), 151.5 (C3), 122.7 (C7), 93.2 (C1), 81.9 (C2), 75.6 (C5), 71.9 (C9), 69.7 (C6), 69.0 (C4), 67.9 (C13), 31.5 (C14), 31.5 (C10), 19.3 (C15), 19.3 (C11), 13.8 (C16), 13.8 (C12), 8.9 ($\underline{C}H_3$).

Synthesis of **33**: General procedure E was used with **32α** (100.0 mg, 0.30 mmol, 1.0 eq.) in DCM/pyridine (2.5 mL/0.25 mL), triflic anhydride (0.13 mL, 0.79 mmol, 2.6 eq.), tetrabutylammonium iodide (526.0 mg, 1.50 mmol, 5.0 eq.) in toluene/pyridine (2.5 mL/0.25 mL) were used. Purification was achieved by column chromatography eluting in petroleum/ether acetate (8/1 to 6/1) to give **33α** (50.0 mg, 0.16 mmol, 53%) as a yellow wax.

33α: $[\alpha]_D^{20} = -4.00$ ($c = 0.35$ in $CHCl_3$); IR (FTIR) ν_{max} 2931, 1750, 1680, 1251, 989 cm^{-1}; HRMS (ESI^+) *m/z* calculated for $C_{17}H_{26}O_5Na$ 333.1678, $[M+Na]^+$, found 333.1665; ^1H NMR (700 MHz, $CDCl_3$) δ 5.91 (s, 1H, H4), 5.44 (d, $J = 3.7$ Hz, 1H, H1), 5.01 (dq, $J = 3.8$, 1.8 Hz, 1H, H2), 4.04–3.95 (m, 2H, 2×H6), 3.75 (dt, $J = 9.8$, 6.6 Hz, 1H, H13), 3.61 (dt, $J = 9.8$, 6.6 Hz, 1H, H13), 3.58–3.48 (m, 2H, 2×H9), 1.90 (d, $J = 1.7$ Hz, 3H, $C\underline{H}_3$), 1.67–1.59 (m, 2H, 2×H10), 1.57–1.49 (m, 2H, 2×H14), 1.43 (dq, $J = 14.9$, 7.4 Hz, 2H, 2×H11), 1.31 (h, $J = 7.4$ Hz, 2H, 2×H15), 0.96 (t, $J = 7.4$ Hz, 3H, 3×H12), 0.89 (t, $J = 7.4$ Hz, 3H, 3×H16). ^{13}C NMR (175 MHz, $CDCl_3$) δ 175.0 (C8), 156.2 (C5), 148.7 (C3), 116.2 (C7), 98.9 (C1), 97 (C4), 79 (C2), 71.2 (C9), 69.9 (C13), 69.5 (C6), 31.7 (C10), 31.4 (C14), 19.3 (C11), 19.0 (C15), 13.9 (C12), 13.7 (C16), 8.6 ($\underline{C}H_3$).

General procedure E was used with **32β** (22.0 mg, 0.07 mmol, 1.0 eq.) in DCM/pyridine (1.0 mL/0.10 mL), triflic anhydride (20.0 µl, 0.17 mmol, 2.6 eq.), tetrabutylammonium iodide (124.0 mg, 0.35 mmol, 5.0 eq.) in toluene/pyridine (1.0 mL/0.10 mL) were used. Purification was achieved by column chromatography eluting in petroleum/ether acetate (15/1 to 10/1) gave **33β** (12.0 mg, 0.04 mmol, 50%) as a yellow oil.

33β: $[\alpha]_D^{20} = -1.30$ ($c = 0.45$ in $CHCl_3$); IR (FTIR) ν_{max} 2922, 1753, 1670, 1247, 999 cm^{-1}; HRMS (ESI^+) *m/z* calculated for $C_{17}H_{26}O_5Na$ 333.1678, $[M+Na]^+$, found 333.1665; ^1H NMR (700 MHz, $CDCl_3$) δ 5.78 (d, $J = 2.0$ Hz, 1H, H1), 5.76 (s, 1H, H4), 4.74 (t, $J = 5.5$ Hz, 1H, H2), 3.91 (dt, $J = 9.7$, 6.6 Hz, 1H, H6), 3.71–3.64 (m, 2H, H13 and H6), 3.58 (dd, $J = 10.1$, 5.3 Hz, 1H, H13), 3.53 (t, $J = 6.7$ Hz, 2H, 2×H9), 1.97 (s, 3H, CH_3), 1.69–1.56 (m, 4H, 2×H14 and 2×H10), 1.47–1.33 (m, 4H, 2×H15 and 2×H11), 0.98–0.93 (m, 6H, 3×H16 and 3×H12). ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.3 (C8), 146.1 (C5), 141.9 (C3), 121.6 (C7), 106.1 (C1), 93.0 (C4), 72.4 (C13), 71.7 (C9), 68.7 (C6), 67.6 (C2), 31.6 (C14), 31.6 (C10),19.3 (C15), 19.3 (C11),13.9 (C16), 13.9 (C12), 8.6 (CH_3).

Karrikin analogue 3: To a solution of **33αβ** (25.0 mg, 0.08 mmol, 1.0 eq., α/β = 1/0.15) in toluene (2.0 mL) was added methanesulfonic acid (2.5 µl, 0.04 mmol, 50 mol%). The reaction mixture was then heated at 100 °C for 48 h. The reaction mixture was concentrated *in vacuo* after reaction. Purification was achieved by column chromatography eluting in petroleum/ether acetate (8/1) to give **3** (6.0 mg, 0.03 mmol, 32%) as a yellow wax. IR (FTIR) ν_{max} 2943, 1767, 1673, 1221, 975 cm^{-1}; HRMS (ESI^+) *m/z* clacd. for $C_{13}H_{16}O_4Na$ 259.0946, $[M+Na]^+$, found 259.0936; ^1H NMR (700 MHz, Acetone-d_6) δ 7.78 (s, 1H, H1), 6.80 (s, 1H, H4), 4.35 (s, 2H, H6), 3.58 (t, $J = 6.49$ Hz, 2H, 2×H9), 1.89 (s, 3H, $C\underline{H}_3$), 1.63–1.57 (m, 2H, 2×H10), 1.45–1.39 (m, 2H, 2×H11), 0.93 (t, $J = 7.41$, 3H, 3×H12). ^{13}C NMR (175 MHz, Acetone-d_6) δ 170.4 (C8), 158.4 (C5), 141.7 (C3), 140.6 (C2), 126.7 (C1), 100.3 (C4), 98.7 (C7), 70.6 (C9), 68.5 (C6), 31.7 (C10), 19.1 (C11), 13.2 (C12), 6.7 ($\underline{C}H_3$). Spectral data were consistent with those previously reported.[18]

Deposition 2117933 (for **10α**) and 2117934 (for **22α**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in Figshare at https://figshare.com/10.6084/m9.figshare.16886437, reference number 16886437.

Keywords: Acetal reductive opening · Biomass · Karrikins · Natural products · Oxidation

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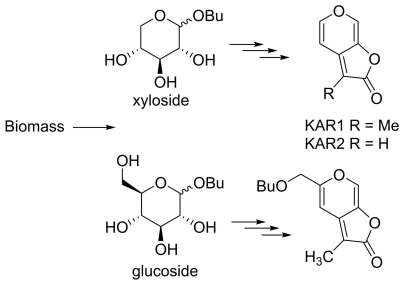
RESEARCH ARTICLE

The selective catalytic oxidation of monosaccharides was applied to butyl xylosides and butyl glucosides leading to the formation of bioactive karrikins, molecules that are important in the response to catastrophic fires. Butanosolv processing of biomass provides a co-product stream that contains these starting materials providing relevance to this work in the biorefinery context.



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